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Supporting Information

$^1O_2$ mediated synthesis of carbonyl substituted quinoline-2,4(1*H*,3*H*)-diones in visible light: 4CzIPN as a reusable photocatalyst

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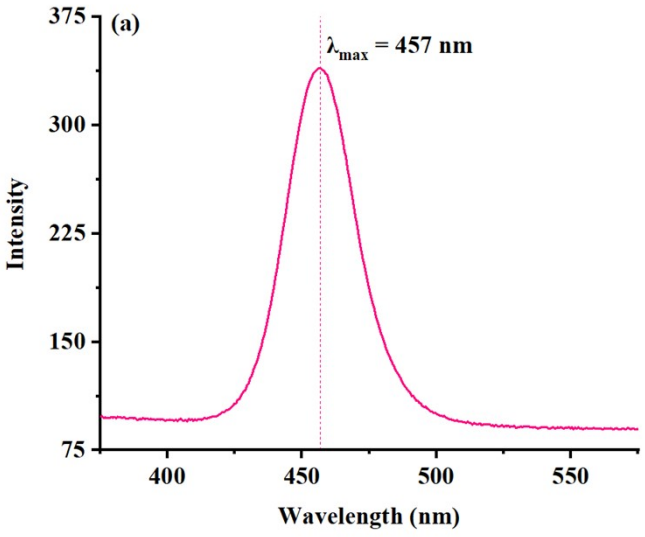
1. General information:

All the commercially available analytical grade reagents were used directly without any further purification. Dry solvents were used for the reaction and column chromatography. The progress of the reactions was monitored using thin-layer chromatography carried out on 0.25 mm Merck silica plates (60F-254). UV light (λ_{max} = 254 nm) was used as a visualizing agent, and iodine vapor as a staining agent. Merck silica gel with particle sizes of 60−120 and 100-200 mesh was used as a stationary phase, while an appropriate amount of petroleum ether and ethyl acetate was used as eluent (mobile phase) in column chromatography. The ^{1}H NMR spectra were recorded at 400 or 500 MHz, and the ^{13}C NMR spectra at 100 or 125 MHz using $CDCl_3$ or DMSO-d6 as the solvent. The splitting pattern of the peaks in ^{1}H NMR is mentioned as singlet (s), doublet (d), triplet (t), broad singlet (bs), and multiplet (m). The chemical shifts and coupling constants are reported as parts per million (ppm) and hertz (Hz), respectively, in ^{1}H NMR. The high-resolution mass spectra were recorded on a mass spectrometer using electrospray ionization time-of-flight (ESI-TOF) reflection experiments. Data collection was carried out, and the refinement single-crystal X-ray data of compounds were collected on a Bruker APEX-IICCD diffractometer using graphite-mono chromated MoKα radiation (λ = 0.71073Å). EPR spectra were obtained using a Bruker A300-9.5/12/S/W instrument.

2. LED emission spectra and reaction setup:

The measurement was recorded using an Open Spectrophotometer Ava Light-DH-S-BAL Avantes. The light source used for illuminating the reaction vessel is 10 W Blue LED (λ_{max} = 457 nm).



(b)

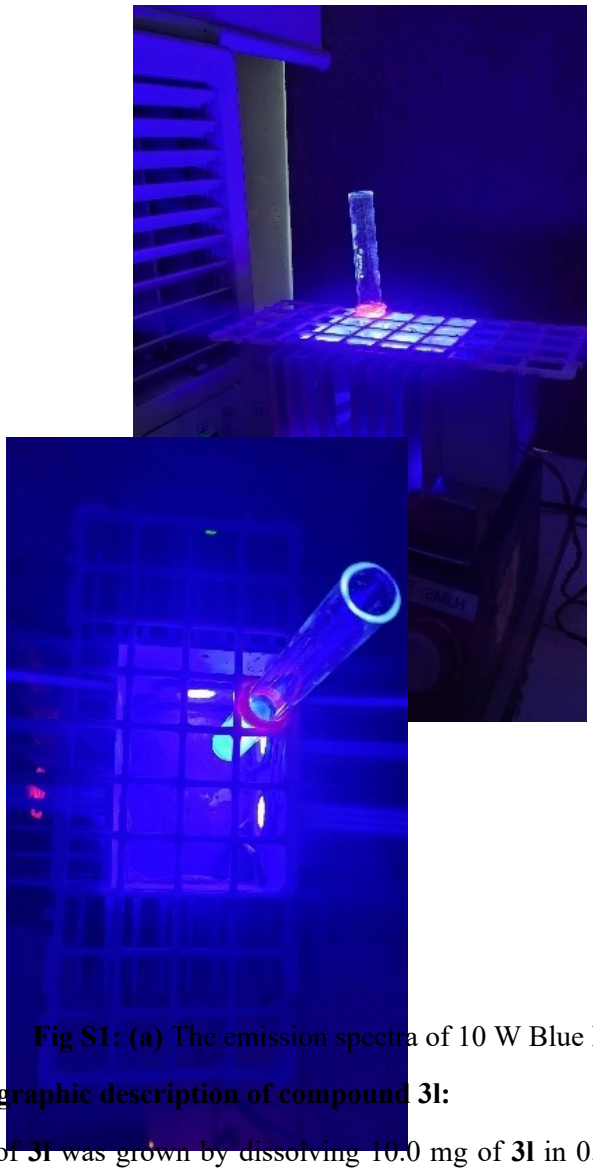
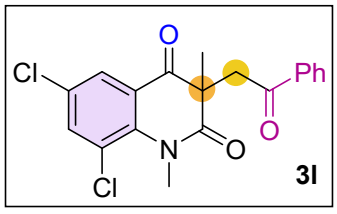


Fig S1: (a) The emission spectra of 10 W Blue LED **(b)** Reaction setup

3. Crystallographic description of compound 3l:

The crystal of **3l** was grown by dissolving 10.0 mg of **3l** in 0.5 mL of chloroform while heating the solution at 40-50 ℃. Then, the clear solution was covered and kept at room temperature for 48 h.



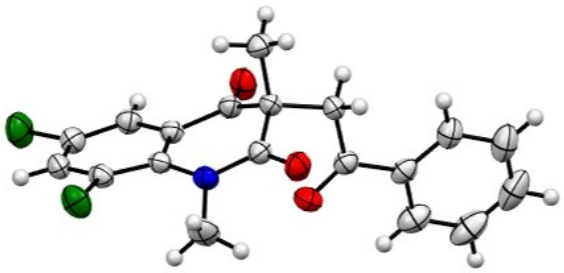


Fig. S2: ORTEP diagram of compound **3l** (with 40% probability ellipsoids)

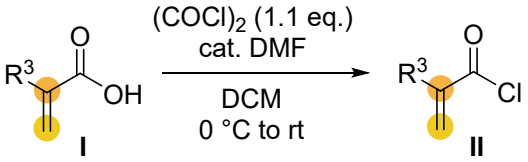
Identification code	hd777c_0ma_a
Empirical formula	$C_{19}H_{15}Cl_2NO_3$
Formula weight	376.22
Temperature	300 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 21/c 1

Unit cell dimensions	a = 16.1234(10) Å	α = 90°
	b = 11.9822(7) Å	β = 94.945° (2)
	c = 8.9939(6) Å	γ = 90°
Volume	1731.10(19) $Å^3$	
Z	4	
Density (calculated)	1.444 g/cm^3	
Absorption coefficient	0.393	
F(000)	776.0	
Crystal size	0.014 x 0.012 x 0.011	
Theta range for data collection	2.54 to 24.74°	
Index ranges	-19<=h<=19, -14<=k<=14, -10<=l<=10	
Reflections collected	3187	
Independent reflections	30352 [R_{int} = 0.0667]	
Completeness to theta = 25.00°	99.90%	
Absorption correction	-	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	30352 / 0 / 228	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R_1 = 0.0390, WR_2 = 0.1021	
R indices (all data)	R_1 = 0.0491, WR_2 = 0.1091	
CCDC	2310779	

4. Synthesis of starting materials, photocatalyst, and products:

4a) General procedure for the synthesis of *N*-methyl acrylamides (1):[1a, 1b]

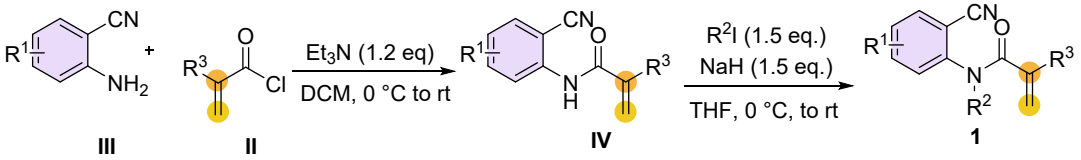
Step 1**:** Acrylic acid (**I**) (1.0 equiv., 8.0 mmol) was dissolved in DCM (10.0 mL) and charged with nitrogen. At 0 ℃, oxalyl chloride (0.8 mL, 1.1 equiv., 8.8 mmol) was added dropwise along with a catalytic amount of dry DMF (2 drops). Then, the reaction was allowed to stir at room temperature for 3 h, and the reaction mixture was concentrated under reduced pressure to afford the corresponding acid chloride (**II**) and used directly for step 2. Methacryloyl chloride was commercially available.



Scheme S1: Conversion of acid (**S1**) to acid chloride (**S2**)

Step 2: To a solution of anthranilonitrile (**III**) (1.0 equiv., 8.0 mmol) and triethylamine (1.3 mL, 1.2 equiv., 9.6 mmol) in 20.0 mL of anhydrous DCM, acryloyl chloride (**II**) (1.1 equiv., 8.8 mmol) was added at 0 °C. The mixture was allowed to stir at room temperature. Upon completion of the reaction as observed by TLC, it was quenched by adding a saturated $NaHCO_3$ solution, then extracted with DCM, followed by brine. The organic phase was dried over Na_2SO_4, concentrated via reduced pressure, formed the corresponding amides (**IV**), and used further without additional purification.

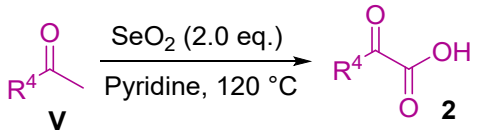
Step 3: To a solution containing amides (**IV**) (1.0 equiv., 5.0 mmol) in 20.0 mL of anhydrous THF, NaH (55-60% in oil) (298.8 mg, 1.5 equiv., 7.5 mmol) was added at 0 °C under N_2 atmosphere. The mixture was allowed to stir at room temperature for 1 h. Subsequently, alkyl iodide (1.5 equiv., 7.5 mmol) was added dropwise into the reaction mixture at 0 °C. The reaction mixture was then allowed to warm to room temperature. Upon the completion of the reaction, observed by TLC, it was cooled to 0 °C and quenched with water, followed by extraction with diethyl ether. The resulting extract was subjected to a brine and dried over Na_2SO_4. Concentrated under reduced pressure, purified by column chromatography, yielded *N*-methyl amides **1**. **1a-1q** NMR were in accordance with the literature.[1b-e]



Scheme S2: Conversion of anthranilonitriles **S3** to *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1**

4b) General procedure for the synthesis of *α*-oxo carboxylic acids (2):[2a]

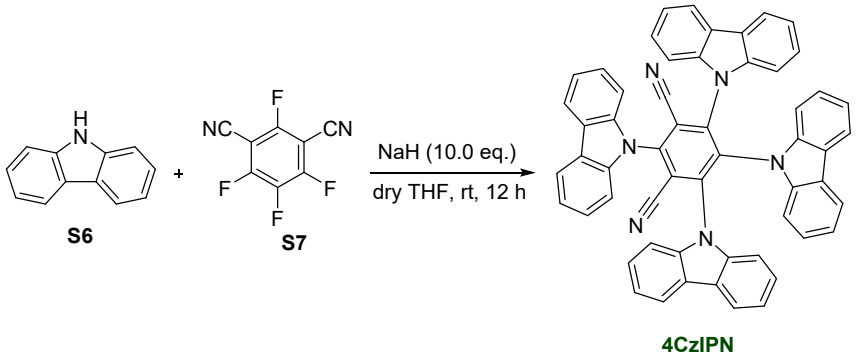
A mixture containing acetophenone derivatives (**V**) (1.0 equiv., 8.0 mmol) and selenium dioxide (1.78 g, 2.0 equiv., 16.0 mmol) dissolved in 5.0 mL of anhydrous pyridine was stirred under nitrogen atmosphere at 120 °C for 18 h. The mixture was filtered upon the disappearance of acetophenones, as monitored by TLC, and the organic phase was collected. The solvent was removed under reduced pressure. A 2.0 M aqueous NaOH solution was introduced to the residue, and the resulting mixture was extracted with ethyl acetate (3 x 15 mL). The aqueous phase was isolated and conc. HCl was cautiously added dropwise until the pH reached a range of 1-2. The mixture was then filtered, yielding the desired product **2**. **2a-2h** NMR were in accordance with the literature.[1c, 2a-2d]



Scheme S3: To prepare the *α*-oxo carboxylic acids (**2**)

4c) Preparation of 4CzIPN photocatalyst:[3]

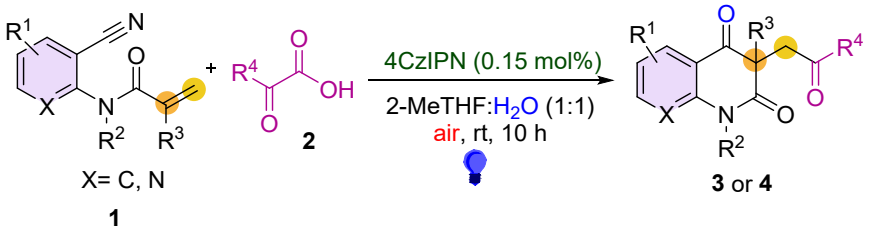
NaH (55-60% in oil) (995.8 mg, 10.0 equiv., 25.0 mmol) was added to the solution of carbazole (**S6**) (2.1 g, 5.0 quiv., 12.5 mmol) in dry THF and stirred for 30 minutes. Then, tetrafluoroisophthalonitrile (**S7**) (500 mg, 1.0 equiv., 2.5 mmol) was added to the reaction mixture and stirred again for 12 h. After completion of the reaction, the reaction mixture was quenched with H_2O, filtered, and further purified by column chromatography, giving 4CzIPN as a bright yellow solid. The NMR spectroscopic data was in accordance with the literature.[3]



Scheme S4: Preparation of 4CzIPN photocatalyst

4d) General procedure for the synthesis of 3 and 4:

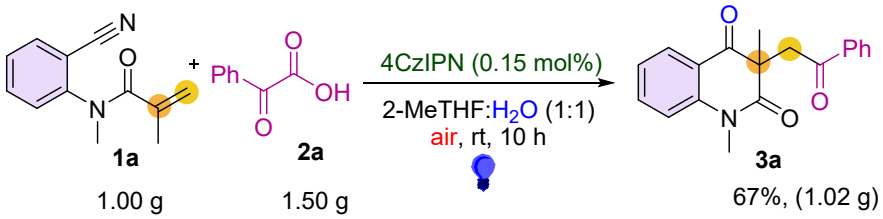
To an oven-dried reaction tube, *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (100.0 mg, 1.0 equiv., 0.5 mmol), phenylglyoxylic acid **2a** (150.0 mg, 2.0 equiv., 1.0 mmol), and 4CzIPN (0.6 mg, 0.15 mol%) were mixed in 2-MeTHF:H_2O (1:1) (1.0 mL) and irradiated under 10 W Blue LED at room temperature for 10 h. Upon completion of the reaction, as confirmed by TLC, the reaction was quenched by adding aqueous $NaHCO_3$ to the reaction mixture and was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo; the residue was purified by column chromatography on the silica gel with hexane/EtOAc as the eluent to afford the desired products **3** and **4**.



Scheme S5: General procedure of Compounds **3** and **4**

5. Procedure for gram-scale synthesis of 3a and recyclability and reusability of 4CzIPN photocatalyst:

N-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (1.00 g, 1.0 equiv., 5.0 mmol), phenylglyoxylic acid **2a** (1.50 g, 10.0 mmol), 4CzIPN (6.0 mg, 0.15 mol%), were dissolved in 2-MeTHF:H_2O (1:1) (20.0 mL) and taken in an oven-dried 100 mL round bottom flask equipped with a magnetic stirring bar. The contents were irradiated using 10 W Blue LED at room temperature for 10 h under air. After completion of the reaction as monitored by TLC, the reaction was quenched with a saturated solution of $NaHCO_3$, and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography to give the desired product **3a** in 67% (1.02 g) yield. The catalyst was recovered by column chromatography, and the recovered catalyst was used for the next reaction. Again, the catalyst was recovered by column chromatography and used sequentially for the next five consecutive cycles. Very negligible loss in activity and reactivity of the photocatalyst was observed in each cycle.



Scheme S6: Gram Scale synthesis of **3a**

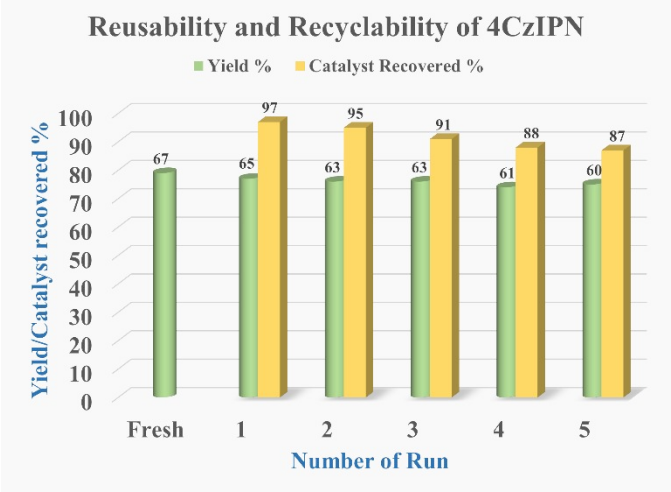
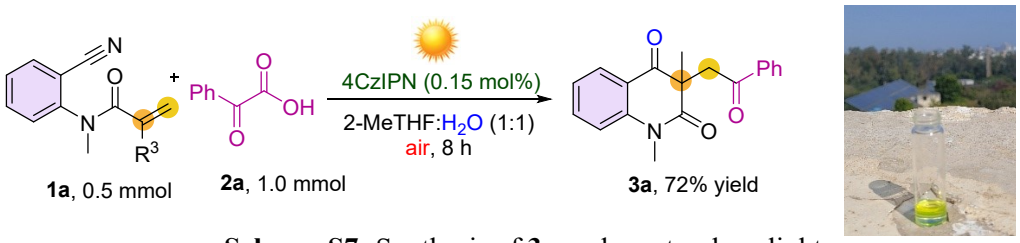


Fig. S3: Recyclability and reusability of 4CzIPN photocatalyst

6. Irradiation with natural sunlight:

To an oven-dried reaction vial, *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (100.0 mg, 1.0 equiv., 0.5 mmol), phenylglyoxylic acid **2a** (150.0 mg, 2.0 equiv., 1.0 mmol), and 4CzIPN (0.6 mg, 0.15 mol%) were mixed in 2-MeTHF:H_2O (1:1) (1.0 mL). The contents were kept in sunlight in an open atmosphere

for 8 h (from 9:00 to 17:00, 2024/01/29 in IIT Delhi, India. Temperature: 18 °C - 21 °C) without stirring. The reaction was then quenched with saturated $NaHCO_3$, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography to give the desired product **3a** in 72% (110.6 mg) yield.

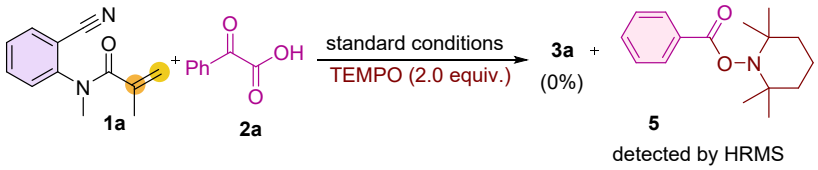


Scheme S7: Synthesis of **3a** under natural sunlight

7. Mechanistic Studies:

7a) Free radical-trapping experiment:

To an oven-dried reaction tube, *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (100.0 mg, 1.0 equiv., 0.5 mmol), phenylglyoxylic acid **2a** (150.0 mg, 2.0 equiv., 1.0 mmol), TEMPO (156.3 mg, 2.0 equiv., 1.0 mmol) and 4CzIPN (0.6 mg, 0.15 mol%) were mixed in 2-MeTHF:H_2O (1:1) (1.0 mL) and irradiated under 10 W Blue LED at room temperature for 10 h. The reaction was quenched completely, as observed by TLC, and benzoyl-TEMPO adduct **5** was detected by HRMS, which confirms the presence of free radical during the progress of the reaction.



Scheme S8: Control study to check free radical pathway.

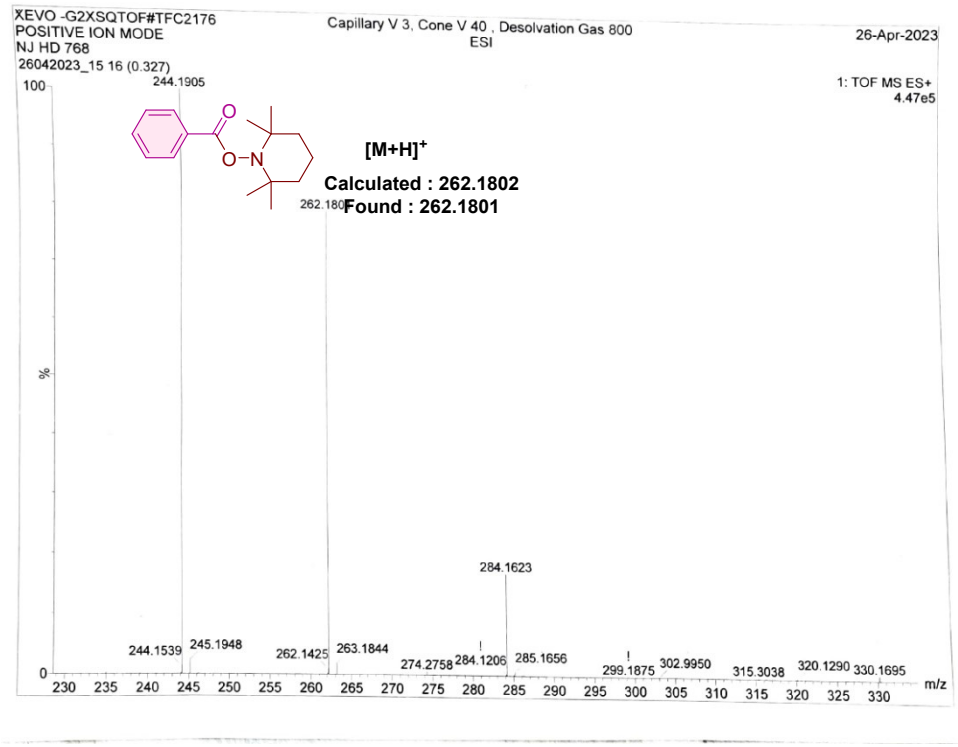
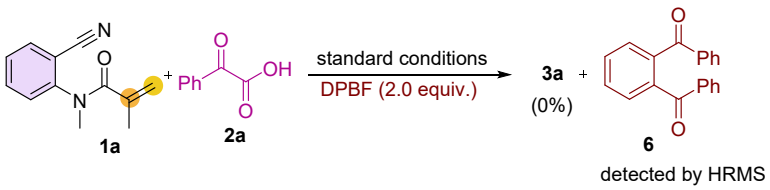


Fig S4: HRMS of the reaction mixture.

7b) Singlet oxygen quencher experiment:

To an oven-dried reaction tube, *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (100.0 mg, 1.0 equiv., 0.5 mmol), phenylglyoxylic acid **2a** (150.0 mg, 2.0 equiv., 1.0 mmol), DPBF (270.3 mg, 2.0 equiv., 1.0 mmol) and 4CzIPN (0.6 mg, 0.15 mol%) were mixed in 2-MeTHF:H_2O (1:1) (1.0 mL) and irradiated under 10 W Blue LED at room temperature for 10 h. The reaction was quenched completely, as observed by TLC, and adduct **6** was obtained (detected by HRMS), which confirms the presence of singlet oxygen during the progress of a reaction.



Scheme S9: Control study to confirm the singlet oxygen formation

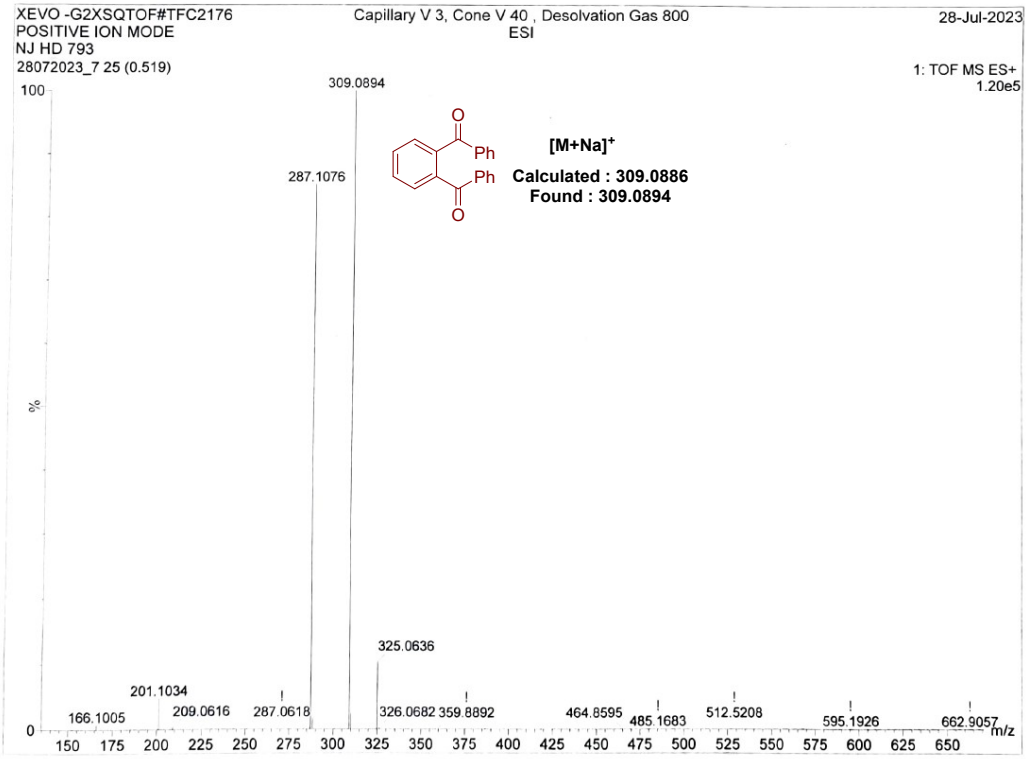
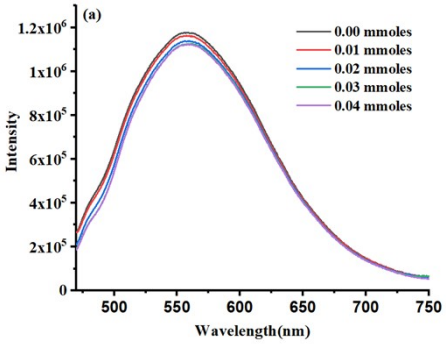
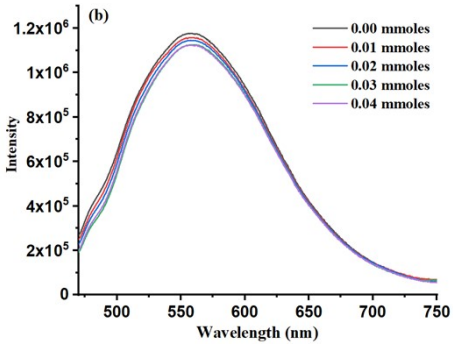


Fig S5: HRMS of the reaction mixture.

7c) Fluorescence Quenching Experiments:

Fluorescence quenching studies were performed using the Horiba-Jobin-Yvon Fluorescence Spectrophotometer. A 1.67 × 10^{-5} M solution of 4CzIPN in 2-MeTHF:H_2O in 1:1 (3.0 mL) was prepared, and 0.01 mM of quencher **2a** and **1a** were added successively to the measured N_2-saturated solution of 2-MeTHF:H_2O in a quartz cuvette and emission spectrum was observed. All the solutions were excited at 457 nm, and emission intensity was collected at 558 nm.





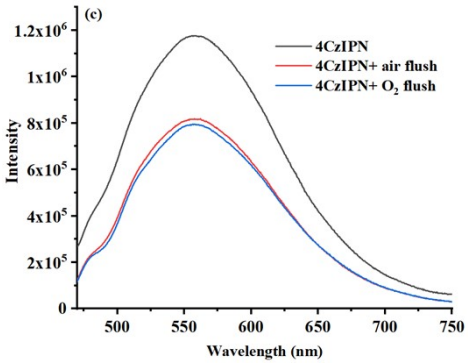


Fig. S6: (a) and **(b)** Fluorescence quenching experiment of 4CzIPN with a gradual increment of **1a** and **2a** in N_2-saturated solution of 2-MeTHF and H_2O in 1:1, respectively. **(c)** Fluorescence quenching experiment of air and oxygen-saturated solution of THF and H_2O in 1:1, respectively.

7d) ESR studies

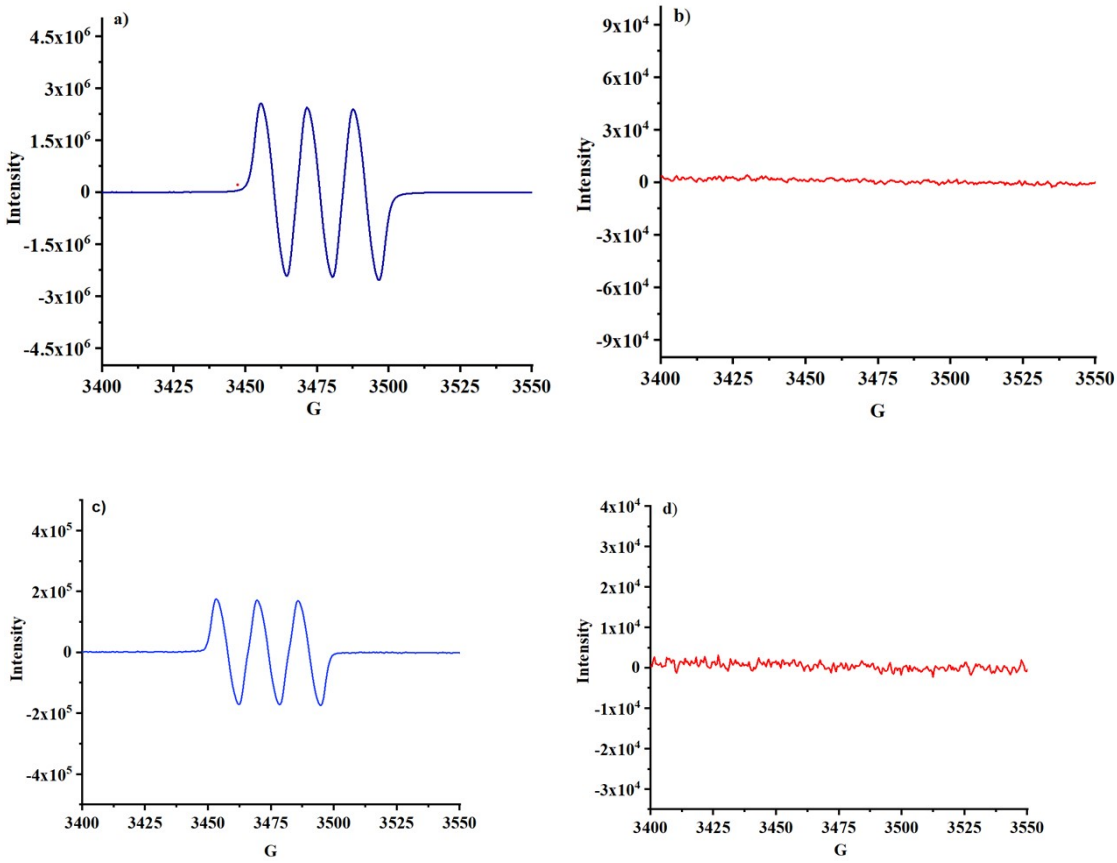


Fig. S7: ESR spectrum of air-saturated 2-MeTHF:H_2O solution of **a)** 4CzIPN (0.05 mM) and TEMP (0.05 mM) upon irradiation of Blue LED for 120 s; **b) 2a** (50.0 mM), 4CzIPN (0.05 mM), and TEMP (0.05 mM) upon irradiation of Blue LED for 120 s; **c) 1a** (50.0 mM), 4CzIPN (0.05 mM), and TEMP (0.05 mM) upon irradiation of Blue LED for 120 s; **d)** 4CzIPN (0.05 mM) and DMPO (0.05 mM) upon irradiation of Blue LED for 120 s.

7e) *In-situ* FTIR experiments for the detection of CO_2 evolution:[4]

To detect the evolution of CO_2 in the reaction, an *in-situ* FTIR experiment was conducted using a Mettler-Toledo React IR 700 (SN: C049640472) equipped with a TEMCT detector, DiComp (Dimond) probe, with a 9.5mm x 2m AgX fiber interface. Data was collected using the 2500 to 650 cm-1 spectral window with 8 cm^{-1} resolution and sampled in 60 second intervals. In a glass vial, 4CzIPN (0.6 mg, 0.15 mol%), phenylglyoxylic acid **2a** (150.0 mg, 2.0 equiv., 1.0 mmol) and *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (100.0 mg, 1.0 equiv., 0.5 mmol) with a magnetic stirring bead was taken and 1.0 mL of 2-MeTHF:H_2O (1:1) solvent was added. Then, a diamond probe was inserted in a solution containing a vial, and *in-situ* FTIR spectra were recorded for 6 hr at 60 second intervals. As depicted in Figure S8 (side view and top view), the signal intensity at 2357 cm^{-1} (corresponding to asymmetric stretching of CO_2) gradually increases with the progression of the reaction.

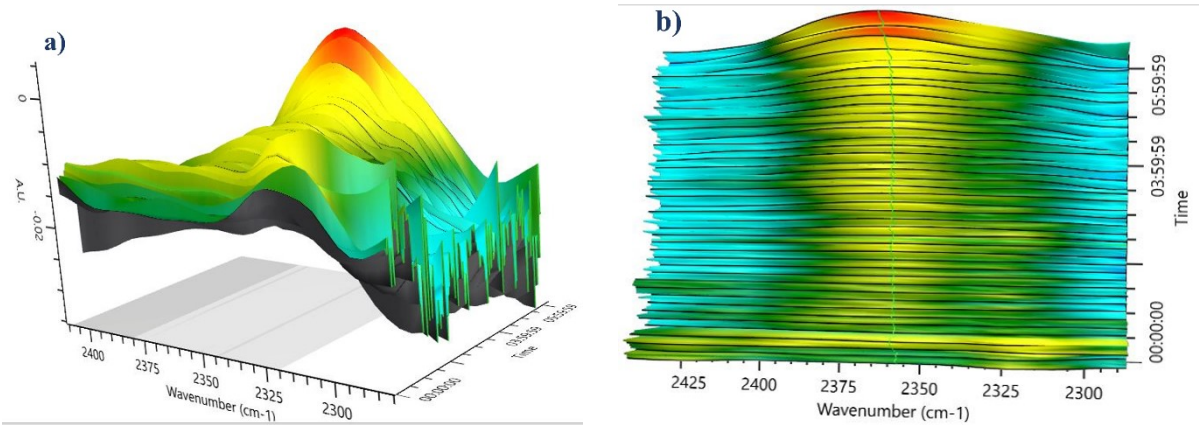
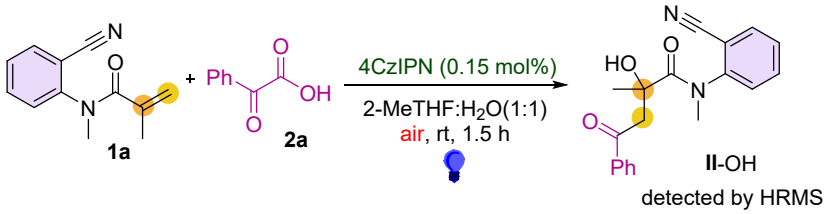


Fig. S8: *In-situ* FTIR graph for CO_2 detection with the progress of the reaction **a**) Side view **b**) Top view

7f) Detection of intermediate (II):

To an oven-dried reaction tube, *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (100.0 mg, 1.0 equiv., 0.5 mmol), phenylglyoxylic acid **2a** (150.0 mg, 2.0 equiv., 1.0 mmol), and 4CzIPN (0.6 mg, 0.15 mol%) were mixed in 2-MeTHF:H_2O (1:1) (1.0 mL) and irradiated under 10 W Blue LED at room temperature for 1.5 h. After that, the reaction mixture was subjected to HRMS, and hydroxy adduct of radical intermediate **II** was detected as **II**-OH in HRMS.



Scheme S10: Control study for the detection of intermediate **II**.

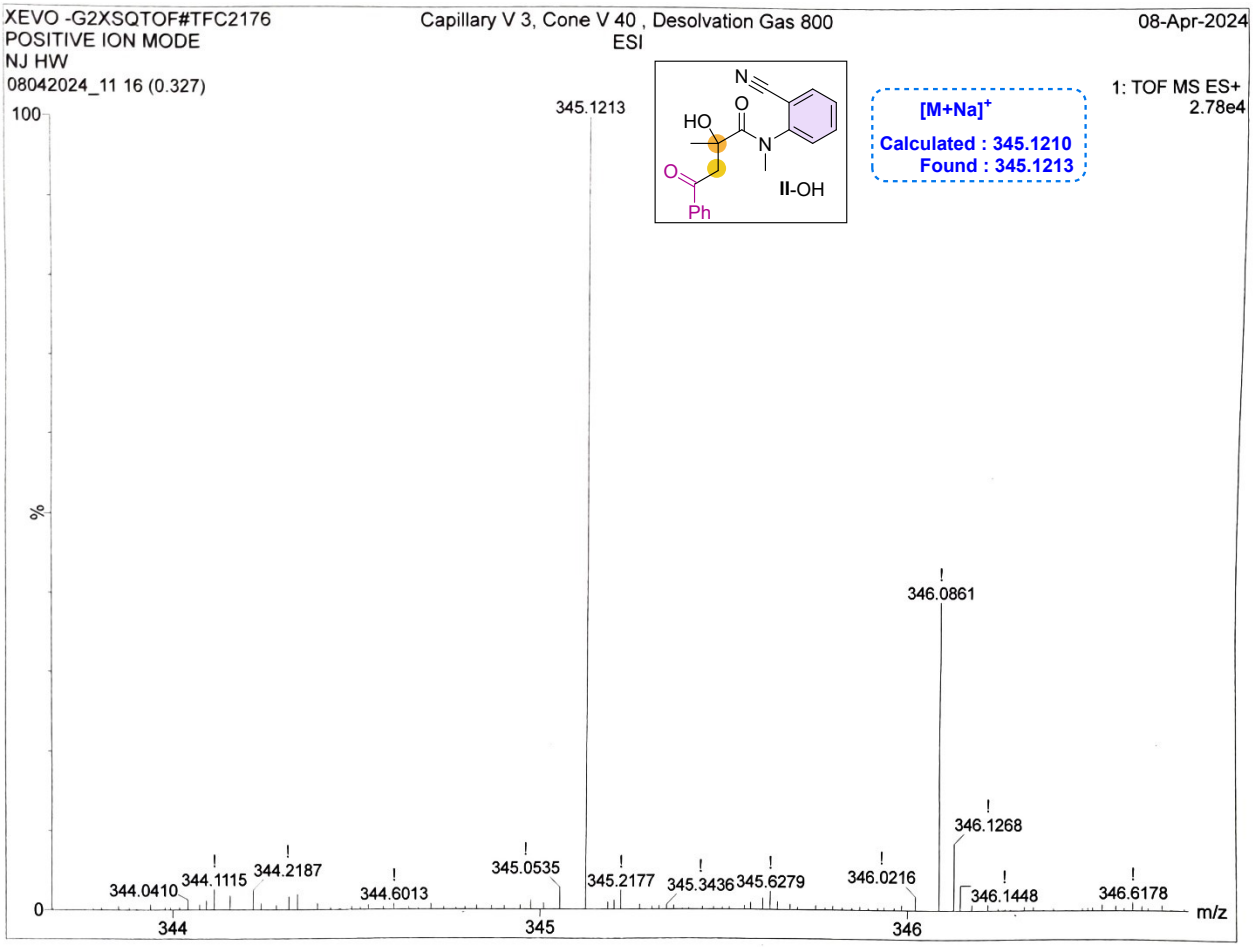
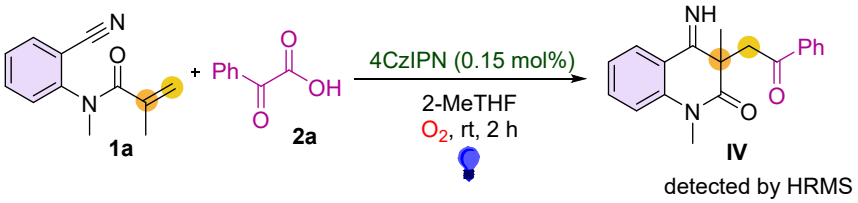


Fig. S9: HRMS of the reaction mixture for the detection of intermediate **II**

7g) Detection of imine intermediate (IV):

To an oven-dried reaction tube, *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (100.0 mg, 1.0 equiv., 0.5 mmol), phenylglyoxylic acid **2a** (150.0 mg, 2.0 equiv., 1.0 mmol) and 4CzIPN (0.6 mg, 0.15 mol%) were mixed in 2-MeTHF (1.0 mL). The resulting mixture was degassed using three freeze-pump-thaw cycles, and the tube was finally backfilled with argon. The reaction mixture was allowed to stir at room temperature under 10 W Blue LED for 2 h under an oxygen atmosphere. After that, the reaction mixture was subjected to HRMS.



Scheme S11: Control study for the detection of imine intermediate IV.

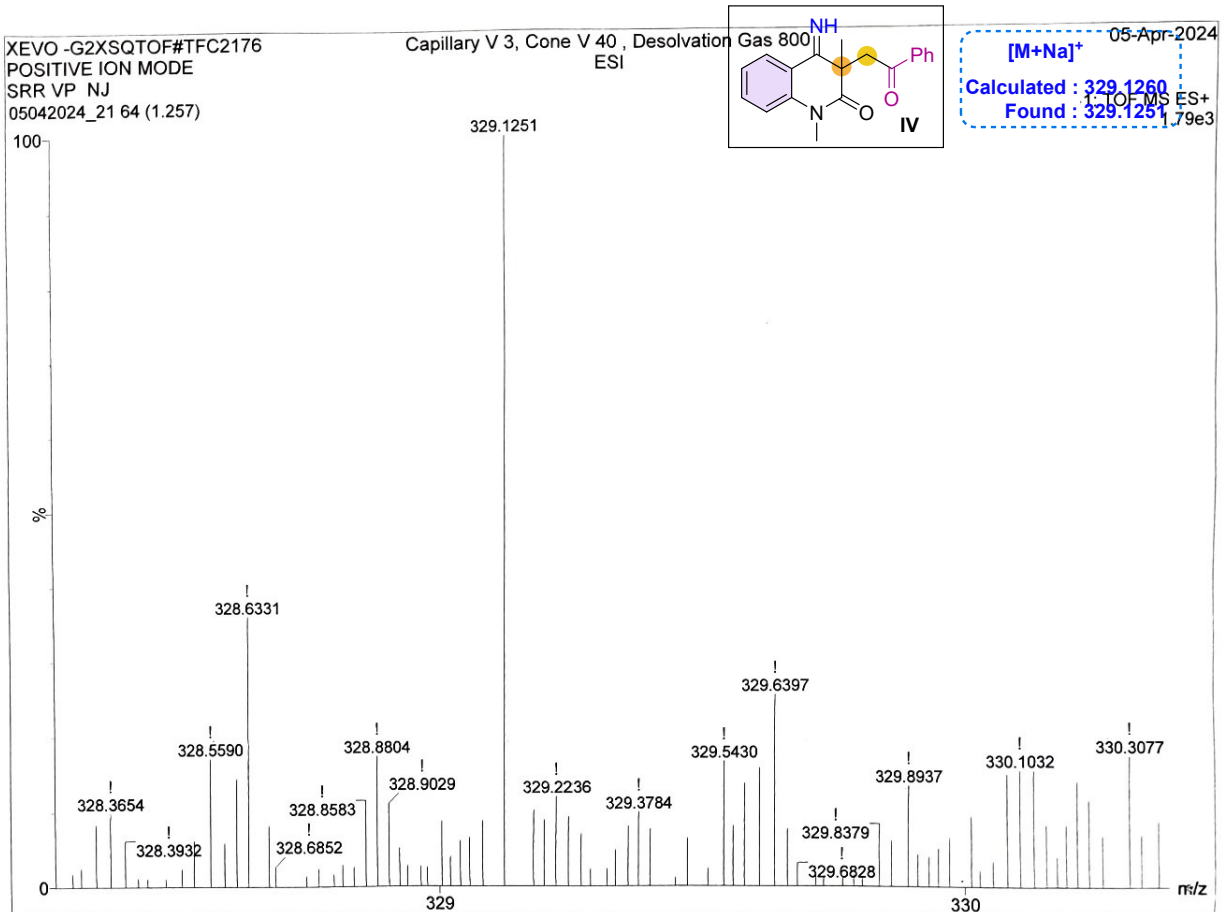
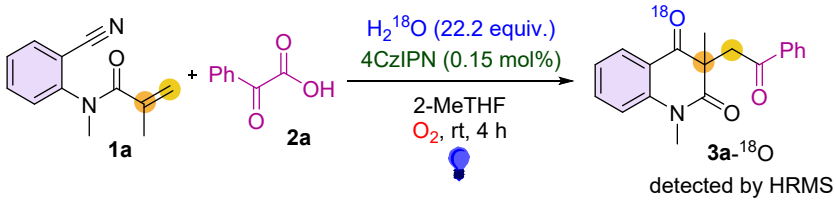


Fig. S10: HRMS of the reaction mixture for the detection of imine intermediate **IV**

7h) $H_2{}^{18}O$ labelled experiment:

To an oven-dried reaction tube, *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (10.0 mg, 1.0 equiv., 0.05 mmol), phenylglyoxylic acid **2a** (15.0 mg, 2.0 equiv., 0.1 mmol), and 4CzIPN (0.06 mg, 0.15 mol%) were mixed in 2-MeTHF (80 µL) and $H_2{}^{18}O$ (20 µL, 22.2 equiv., 1.11 mmol) and irradiated

under 10 W Blue LED at room temperature under oxygen atmosphere for 4 h. After that, the reaction mixture was subjected to HRMS, and **3a**-^{18}O was detected by HRMS.



Scheme S12: $H_2{}^{18}O$ labelled experiment to confirm the source of oxygen.

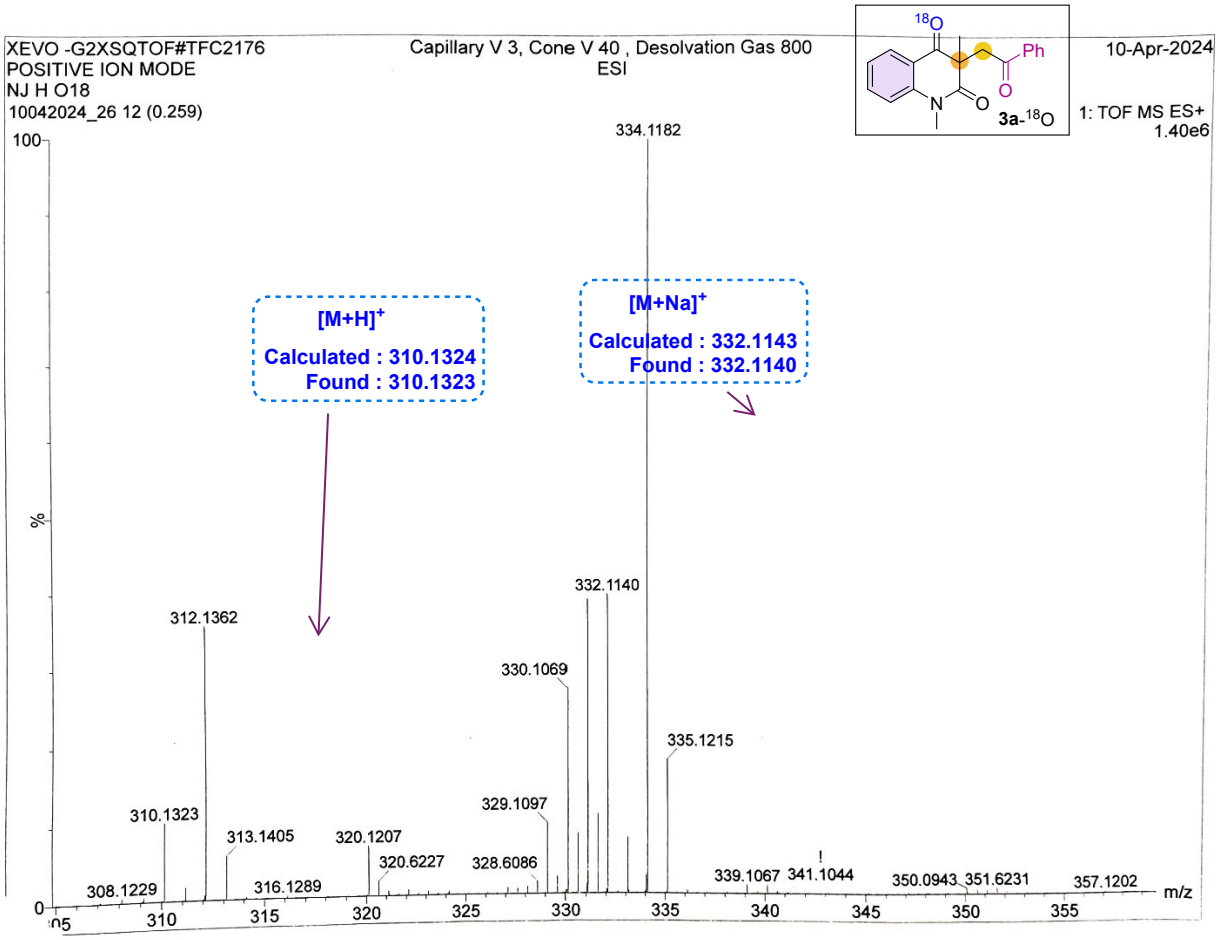
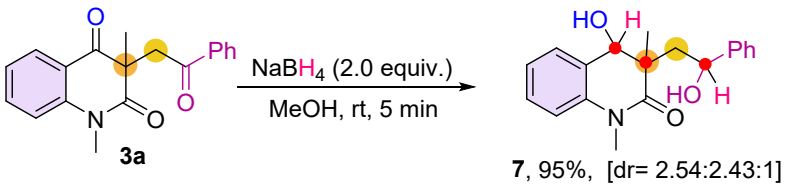


Fig. S11: HRMS of the reaction mixture for the detection of **3a**-^{18}O.

8. Post synthetic modification of 3a and 4f:

8a) Synthesis of 4-hydroxy-3-(2-hydroxy-2-phenylethyl)-1,3-dimethyl-3,4-dihydroquinolin-2(1H)-one (7):[5a]

The photocatalytic reaction was performed according to the general procedure for the synthesis of **3a**, using *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (200.1 mg, 1.0 mmol, 1.0 equiv.) and phenylglyoxylic acid **2a** (300.1 mg, 2.0 equiv., 2.0 mmol). After the reaction was complete as observed by TLC, the solvent was removed under reduced pressure, and the resulting crude mixture **3a** was taken in MeOH (10.0 mL) to which 2 drops of ACN were added to dissolve **3a**. To this solution, $NaBH_4$ (75.7 mg, 2.0 equiv., 2.0 mmol) was added portion wise at room temperature, and the mixture was stirred for 5 min. After completion of the reaction, as observed by TLC, the reaction was quenched with H_2O and the resulting mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over Na_2SO_4, the solvent was removed in vacuo, and the crude product was purified by column chromatography to yield the reduced product **7** as a mixture of three diastereomers in 95% overall yield with dr= 2.54:2.43:1.



Scheme S13: Procedure for the synthesis of compound **7**.

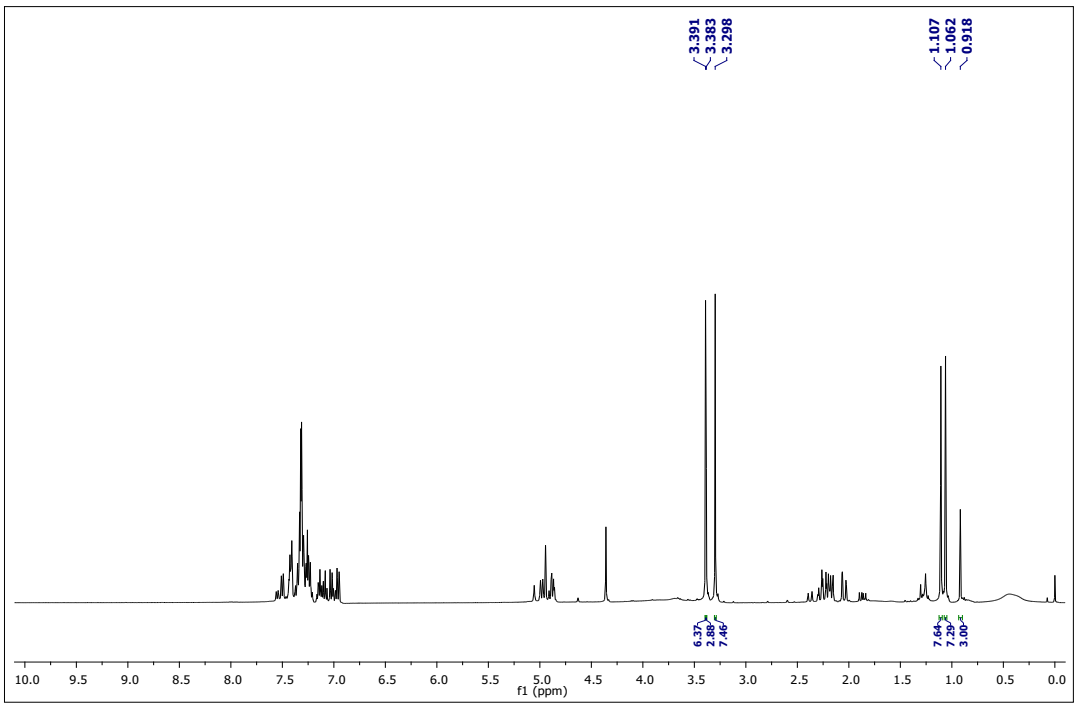
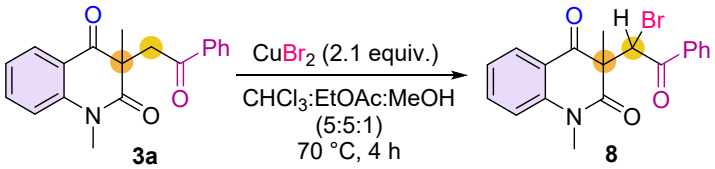


Fig. S12: ^{1}H NMR of reaction mixture.

8b) Synthesis of 3-(1-bromo-2-oxo-2-phenylethyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (8):[5b]

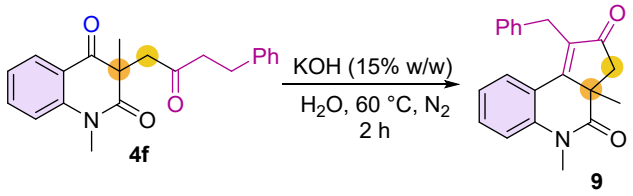
The crude **3a** was generated by the photocatalytic reaction based on the general procedure for the synthesis of **3a**, using *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (200.1 mg, 1.0 equiv., 1.0 mmol) and phenylglyoxylic acid **2a** (300.1 mg, 2.0 equiv., 2.0 mmol). After the removal of solvent in vacuo, the resulting residue was dissolved in a mixed solvent of $CHCl_3$/ethyl acetate/MeOH (5:5:1). Copper (II) bromide ($CuBr_2$) (469.1 mg, 2.1 equiv., 2.1 mmol) was added in this solution, and the reaction mixture was heated to reflux (70 °C) overnight. After the completion of the reaction as monitored by TLC, the reaction mixture was filtered and concentrated under reduced pressure. The resulting residue was re-dissolved in ethyl acetate and washed three times with brine. The combined organic layer was dried over anhydrous $MgSO_4$, filtrated, concentrated under reduced pressure, and purified by column chromatography to give the desired product **8** in 75% yield with dr = 1.20:1.



Scheme S14: Procedure for the synthesis of compound (**8**)

8c) Synthesis of 1-benzyl-3a,5-dimethyl-3,3a-dihydro-2H-cyclopenta[c]quinoline-2,4(5H)-dione (9):[5c]

After the photocatalytic reaction between *N*-(2-cyanophenyl)-*N*-methylmethacrylamide (**1a**) (200.1 mg, 1.0 equiv., 1.0 mmol) and 2-oxo-4-phenylbutanoic acid (**2f**) using the general procedure for the synthesis of **3a**, the solution was concentrated in vacuo to provide the crude product **4f**, which was then re-dissolved in H_2O (5.0 mL), and under a nitrogen atmosphere, aqueous KOH (15% w/w, 8.0 mL) was added to the mixture dropwise over a period of 15 min. Then, the mixture was stirred at 60 °C for 2 h; after completion of the reaction, as observed by TLC, the reaction mixture was cooled to room temperature and extracted with DCM (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, the solvent was removed in vacuo, and the crude product was purified by column chromatography to yield the desired product **9** in 91%.

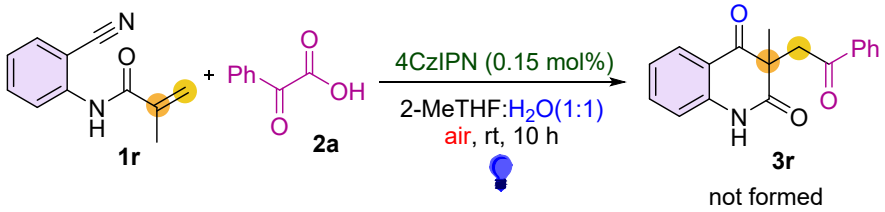


Scheme S15: Procedure for the synthesis of compound (**9**).

9) Unsuccessful attempt for synthesis of secondary amide (3r):

To an oven-dried reaction tube, *N*-(2-cyanophenyl)methacrylamide **1r** (93.0 mg, 1.0 equiv., 0.5 mmol), phenylglyoxylic acid **2a** (150.0 mg, 2.0 equiv., 1.0 mmol), and 4CzIPN (0.6 mg, 0.15 mol%) were mixed in 2-MeTHF:H_2O (1:1) (1.0 mL) and irradiated under 10 W Blue LED at room temperature for

10 h. HRMS of the reaction mixture after 10 h did not show any peak corresponding to the mass of secondary amide **3r**.



Scheme S16: Preparation of secondary amide (**3r**).

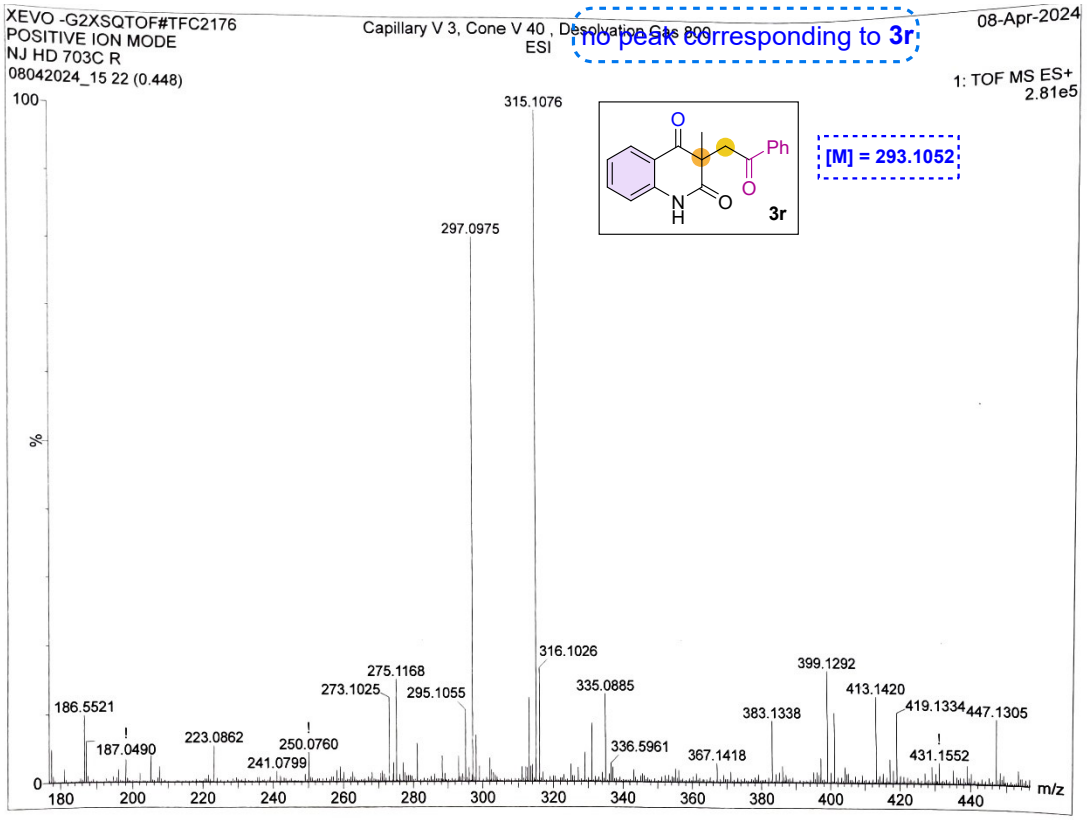
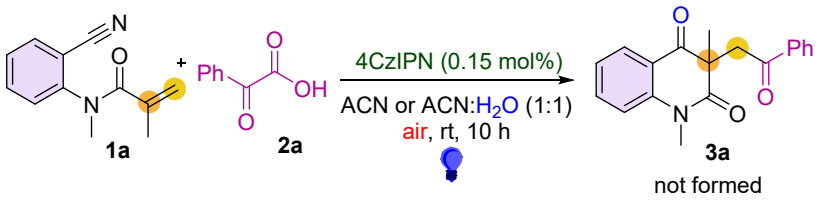


Fig. S13: HRMS of the crude reaction mixture of **3r**.

10) Reaction in ACN and ACN:H_2O (1:1):

Two separate reactions were performed using *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **1a** (100.0 mg, 1.0 equiv., 0.5 mmol), phenylglyoxylic acid **2a** (150.0 mg, 2.0 equiv., 1.0 mmol), and 4CzIPN (0.6

mg, 0.15 mol%) in ACN (1.0 mL) and ACN:H_2O (1:1) (1.0 mL) respectively, and irradiated under 10 W Blue LED at room temperature for 10 h. The desired product **3a** did not form in either case. The TLC profile showed several unidentified side products in ACN while the starting material (**1a**) remained unreacted in ACN:H_2O (1:1).



Scheme **S17**: Reaction in ACN and ACN:H_2O (1:1)

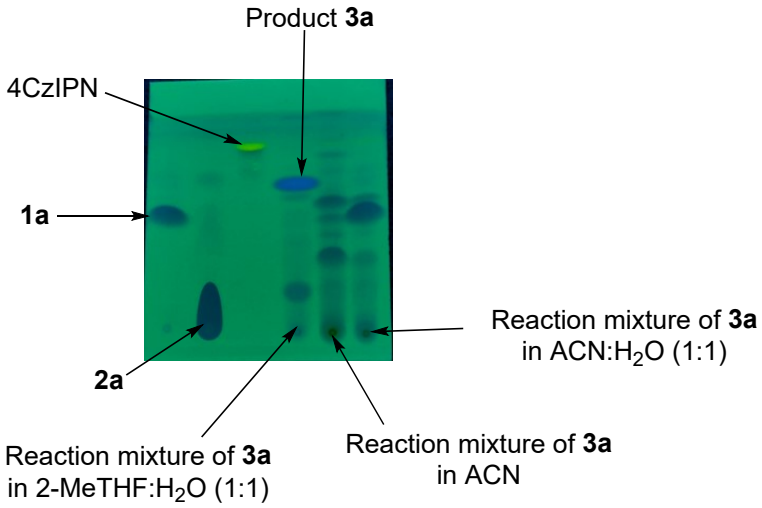
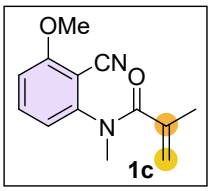


Fig S14: TLC profile of the reaction mixture in 2-MeTHF:H_2O (1:1), ACN and ACN:H_2O (1:1).

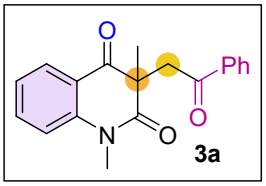
11. Compound Characterization data:

***N*-(2-cyano-3-methoxyphenyl)-*N*-methylmethacrylamide (1c):**



Brown viscous liquid, (782.0 mg, 68% yield), hexane/EtOAc (95/5); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 (t, J = 8.4 Hz, 1H), 6.91 (d, J = 8.8 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 5.10 (s, 1H), 5.04 (s, 1H), 3.95 (s, 3H), 3.35 (s, 3H), 1.88 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 171.8, 162.5, 149.0, 140.1, 134.7, 120.4, 119.7, 113.9, 110.2, 101.5, 56.6, 37.6, 20.2 ppm; HRMS (ESI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}N_2O_2$, 231.1128; found, 231.1135.

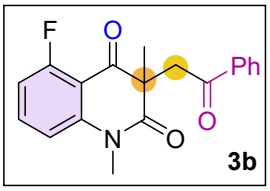
1,3-Dimethyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3a):[6]



White solid, (124.5 mg, 81% yield), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.08 (d, J = 7.5 Hz, 1H), 7.96 (d, J = 7.5 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.27 (s, 1H), 7.22 (t, J = 7.5 Hz, 1H), 4.14-4.05 (m, 2H), 3.54 (s, 3H), 1.48 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 198.0, 196.7, 174.1, 143.5, 136.1, 135.8,

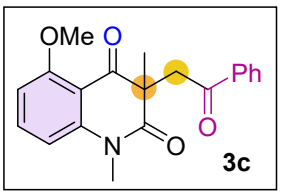
133.7, 128.7, 128.5, 128.5, 123.1, 119.7, 115.1, 53.6, 47.1, 30.0, 24.7 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{19}H_{17}NNaO_3$, 330.1101; found, 330.1113.

5-Fluoro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3b):[6]



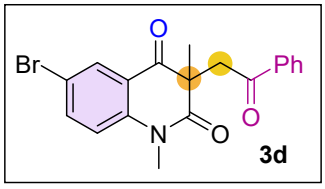
White solid, (109.0 mg, 67% yield), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.94 (d, J = 8.0 Hz, 2H), 7.60-7.54 (m, 2H), 7.43 (t, J = 8.0 Hz, 2H), 7.05 (d, J = 8.5 Hz, 1H), 6.88 (t, J = 8.5 Hz, 1H), 4.08-3.99 (m, 2H), 3.51 (s, 3H), 1.48 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 198.0, 193.9, 173.6, 162.9 (d, $^1J_{C\text{-}F}$ = 264.5 Hz), 144.7, 136.2 (d, $^2J_{C\text{-}F}$ = 11.6 Hz), 135.9, 133.7, 128.7, 128.5, 111.2 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 110.9 (d, $^3J_{C\text{-}F}$ = 3.5 Hz), 109.5 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 54.5, 46.4, 30.9, 24.4 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{19}H_{16}FNNaO_3$, 348.1006; found, 348.1021.

5-Methoxy-1,3-dimethyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3c):



White solid, (111.5 mg, 66% yield), hexane/EtOAc (90/10), mp = 155-160 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.94 (d, J = 7.0 Hz, 2H), 7.56-7.53 (m, 2H), 7.43-7.41 (m, 2H), 6.86 (d, J = 8.5 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 4.07-3.95 (m, 2H), 3.92 (s, 3H), 3.51 (s, 3H), 1.46 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 198.0, 194.9, 173.9, 161.7, 145.4, 136.3, 135.9, 133.4, 128.6, 128.5, 109.8, 107.6, 106.5, 56.4, 54.6, 46.1, 30.9, 24.7 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{20}H_{19}NNaO_4$, 360.1206; found, 360.1213.

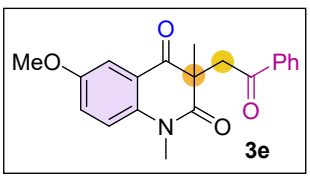
6-Bromo-1,3-dimethyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3d):[6]



White solid, (136.5 mg, 71% yield), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.16 (d, J = 2.0 Hz, 1H), 7.93 (d, J = 7.5 Hz, 2H), 7.74 (dd, J = 9.0, 2.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.14 (d, J = 8.5 Hz, 1H), 4.13-40.03 (m, 2H), 3.49 (s, 3H), 1.46 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 198.0, 195.5, 173.8, 142.5, 138.5, 135.7, 133.8, 131.0, 128.7, 128.5, 121.1, 117.1, 116.1, 53.6, 47.4, 30.2, 24.5 ppm HRMS (ESI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{19}H_{17}BrNO_3$, 386.0386; found, 386.0391.

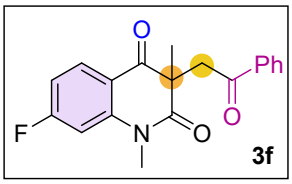
6-Methoxy-1,3-dimethyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3e):

White solid, (126.4 mg, 75% yield), hexane/EtOAc (90/10), mp = 118-122 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.94 (d, J = 7.5 Hz, 2H), 7.54-7.52 (m, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.24 (dd, J = 9.0, 2.5 Hz, 1H), 7.18 (d, J = 9.0 Hz, 1H), 4.13-4.01 (m, 2H), 3.84 (s, 3H), 3.49 (s, 3H), 1.45 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 198.1, 196.8, 173.6, 155.5, 137.7, 135.9, 133.6, 128.7, 128.5,



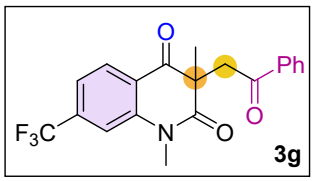
124.1, 120.4, 116.7, 110.2, 55.9, 53.4, 47.2, 30.1, 24.8 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{20}H_{19}NNaO_4$, 360.1206; found, 360.1213.

7-Fluoro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3f):[6]



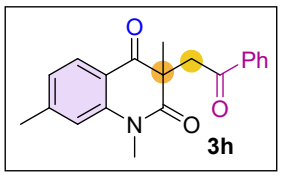
White solid, (128.4 mg, 79% yield)), hexane/EtOAc (90/10); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.10-8.07 (m, 1H), 7.93 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 6.95-6.87 (m, 2H), 4.11-4.03 (m, 2H), 3.49 (s, 3H), 1.46 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 198.0, 195.2, 174.2, 167.6 (d, $^1J_{C\text{-}F}$ = 253.6 Hz), 145.7 (d, $^3J_{C\text{-}F}$ = 11.6 Hz), 135.7, 133.7, 131.4 (d, $^3J_{C\text{-}F}$ = 11.0 Hz), 128.7, 128.5, 116.4, 110.4 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 102.6 (d, $^2J_{C\text{-}F}$ = 25.7 Hz), 53.5, 47.2, 30.2, 24.7 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{19}H_{16}FNNaO_3$, 348.1006; found, 348.1027.

1,3-Dimethyl-3-(2-oxo-2-phenylethyl)-7-(trifluoromethyl)quinoline-2,4(1*H*,3*H*)-dione (3g):



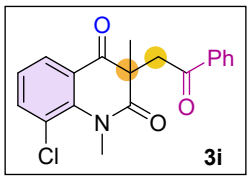
White solid, (163.1 mg, 87% yield)), hexane/EtOAc (90/10), mp = 132-136 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.18 (d, J = 8.0 Hz, 1H), 7.94-7.92 (m, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.48 (s, 1H), 7.44 (t, J = 7.5 Hz, 3H), 4.17-4.05 (m, 2H), 3.56 (s, 3H), 1.48 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 197.9, 195.7, 173.7, 143.7, 137.0 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 135.5, 133.7, 129.3, 128.6, 128.4, 123.3 (q, $^1J_{C\text{-}F}$ = 271.5 Hz), 121.68, 119.3 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 112.1 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 53.7, 47.4, 30.1, 24.2 ppm; HRMS (ESI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}F_3NO_3$, 376.1155; found, 376.1162.

1,3,7-Trimethyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3h):[6]



White solid, (118.8 mg, 74% yield), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.94 (t, J = 8.5 Hz, 3H), 7.54 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.04 (s, 1H), 7.01 (d, J = 7.5 Hz, 1H), 4.10-4.02 (m, 2H), 3.50 (s, 3H), 2.47 (s, 3H), 1.45 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 198.0, 196.4, 174.4, 147.4, 143.6, 136.0, 133.6, 128.7, 128.6, 128.5, 124.1, 117.7, 115.6, 53.5, 47.1, 30.0, 24.8, 22.6 ppm; HRMS (ESI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{20}H_{20}NO_3$, 322.1438; found, 322.1438.

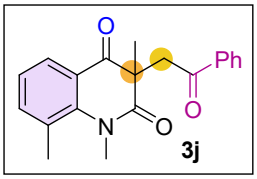
8-Chloro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3i):



White solid, (126.2 mg, 74% yield)), hexane/EtOAc (95/5), mp = 119-123 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.97-7.95 (m, 2H), 7.90 (dd, J = 8.0, 1.5 Hz, 1H), 7.66 (dd, J = 8.0, 1.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H), 4.10-3.95 (m, 2H), 3.64 (s, 3H), 1.43 (s, 3H) ppm;

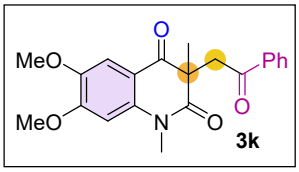
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 197.8, 196.4, 174.8, 142.5, 138.4, 136.0, 133.7, 128.8, 128.6, 127.1, 124.8, 124.2, 122.9, 53.9, 46.9, 38.1, 23.5 ppm; HRMS (ESI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{19}H_{17}ClNO_3$, 342.0891; found, 342.0897.

1,3,8-Trimethyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3j):



White solid, (115.6 mg, 72% yield), hexane/EtOAc (93/7), mp = 127-130 °C; **^1H NMR** (500 MHz, $CDCl_3$): *δ* 7.97 – 7.96 (m, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 3H), 7.13 (t, *J* = 8.0 Hz, 1H), 4.08-3.94 (m, 2H), 3.50 (s, 3H), 2.53 (s, 3H), 1.41 (s, 3H) ppm; **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ 197.6, 197.3, 175.2, 144.4, 139.3, 136.0, 133.3, 128.4, 128.3, 126.9, 126.0, 123.9, 122.6, 53.5, 46.4, 37.8, 23.4, 22.0 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{20}H_{19}NNaO_3$, 344.1257; found, 344.1262.

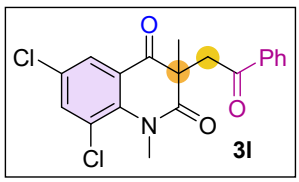
6,7-Dimethoxy-1,3-dimethyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3k):[6]



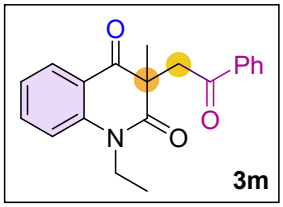
White solid, (106.5 mg, 58% yield), hexane/EtOAc (80/20); **^1H NMR** (500 MHz, $CDCl_3$): *δ* 7.94 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.56-7.53 (m, 1H), 7.52 (s, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 6.70 (s, 1H), 4.06 (s, 2H), 4.04 (s, 3H), 3.92 (s, 3H), 3.53 (s, 3H), 1.46 (s, 3H) ppm; **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ 198.2, 195.6, 174.6, 155.8, 145.4, 139.7, 136.0, 133.6, 128.7, 128.6, 112.6, 109.5, 98.6, 56.5, 56.4, 53.2, 47.3, 30.1, 25.2 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{21}H_{21}NNaO_5$, 390.1312; found, 390.1313.

6,8-Dichloro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3l):[6]

White solid, (138.8 mg, 74% yield), hexane/EtOAc (95/5); **^1H NMR** (500 MHz, $CDCl_3$): *δ* 7.95-7.94 (m, 2H), 7.86 (d, *J* = 2.5 Hz, 1H), 7.65 (d, *J* = 2.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 4.12-3.95 (m, 2H), 3.62 (s, 3H), 1.43 (s, 3H) ppm; **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ 197.7, 195.3, 174.5, 141.2, 137.5, 135.8, 133.8, 129.9, 128.8, 128.5, 126.8, 124.7, 123.7, 53.8, 47.2, 38.0, 23.3 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{19}H_{15}Cl_2NNaO_3$, 398.0321; found, 398.0316.



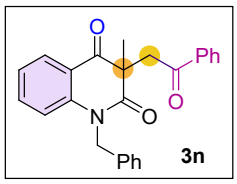
1-Ethyl-3-methyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3m):



White solid, (136.4 mg, 85% yield)), hexane/EtOAc (95/5), mp = 150-153 °C; **^1H NMR** (500 MHz, $CDCl_3$): *δ* 8.09 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 7.0 Hz, 2H), 7.67 (t, *J* = 7.0 Hz, 1H), 7.57 (t, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.28 (s, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 4.23-4.13 (m, 2H), 4.11-4.04 (m, 2H), 1.47 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H) ppm; **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ 197.9, 196.8, 173.6, 142.4, 136.0, 136.0, 133.6, 128.9, 128.7, 128.5, 122.8, 120.0, 115.0,

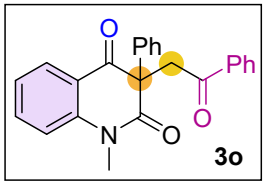
53.5, 47.0, 37.5, 24.6, 12.4 ppm; HRMS (ESI/TOF-Q) m/z: [M + Na]$^+$ calcd for $C_{20}H_{19}NNaO_3$, 344.1257; found, 344.1268.

1-Benzyl-3-methyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3n):[6]



White solid, (143.6 mg, 75% yield)), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.07 (dd, J = 7.5, 1.5 Hz, 1H), 8.00-7.97 (m, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.50-7.47 (m, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.36-7.31 (m, 4H), 7.25-7.24 (m, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.5 Hz, 1H), 5.35 (s, 2H), 4.19-4.10 (m, 2H), 1.57 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 198.0, 196.5, 174.5, 142.6, 136.3, 136.0, 135.93, 133.7, 129.1, 128.7, 128.7, 128.5, 127.4, 126.4, 123.1, 120.0, 116.1, 53.8, 47.2, 46.2, 24.8 ppm; HRMS (ESI/TOF-Q) m/z: [M + Na]$^+$ calcd for $C_{25}H_{21}NNaO_3$, 406.1414; found, 406.1412.

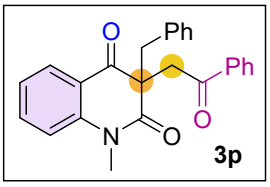
1-Methyl-3-(2-oxo-2-phenylethyl)-3-phenylquinoline-2,4(1*H*,3*H*)-dione (3o):[6]



White solid, (114.4 mg, 62% yield)), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.03 (d, J = 7.5 Hz, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.61-7.54 (m, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.35-7.26 (m, 5H), 7.19 (d, J = 8.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 4.40-4.33 (m, 2H), 3.59 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 198.0, 194.2, 171.8, 143.2, 136.0, 135.9, 135.7, 133.7, 129.3, 128.7, 128.6, 128.6, 128.4, 127.2, 123.2, 121.2, 115.1, 62.9, 48.7, 30.4 ppm; HRMS (ESI/TOF-Q) m/z: [M + Na]$^+$ calcd for $C_{24}H_{19}NNaO_3$, 392.1257; found, 392.1263.

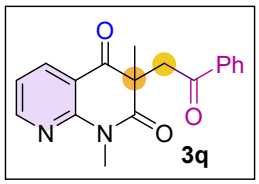
3-Benzyl-1-methyl-3-(2-oxo-2-phenylethyl)quinoline-2,4(1*H*,3*H*)-dione (3p):[6]

White solid, (136.0 mg, 71% yield), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.94 (d, J =



7.5 Hz, 3H), 7.55 (t, J = 7.5 Hz, 1H), 7.44-7.42 (m, 3H), 7.04 (t, J = 7.5 Hz, 1H), 7.00-6.99 (m, 3H), 6.91 (s, 2H), 6.83 (d, J = 8.0 Hz, 1H), 4.23-4.16 (m, 2H), 3.31 (s, 3H), 3.22-3.14 (m, 2H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 197.9, 196.7, 172.8, 143.1, 135.9, 135.6, 133.9, 133.7, 129.7, 128.7, 128.5, 127.6, 127.4, 122.7, 121.7, 114.6, 58.8, 48.0, 46.4, 29.5 ppm; HRMS (ESI/TOF-Q) m/z: [M + Na]$^+$ calcd for $C_{25}H_{21}NNaO_3$, 406.1414; found, 406.1416.

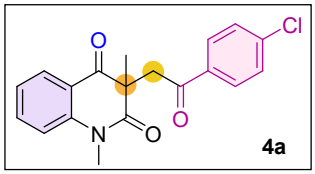
1,3-Dimethyl-3-(2-oxo-2-phenylethyl)-1,8-naphthyridine-2,4(1*H*,3*H*)-dione (3q):[6]



White solid, (112.4 mg, 73% yield), hexane/EtOAc (90/10); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.64 (dd, J = 4.5, 2.0 Hz, 1H), 8.29 (dd, J = 8.0, 2.0 Hz, 1H), 7.92 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.14 (dd, J = 7.5, 5.0 Hz, 1H), 4.16-4.02 (m, 2H), 3.63 (s, 3H), 1.48 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 198.0, 196.2, 174.6, 154.5, 154.2, 136.9,

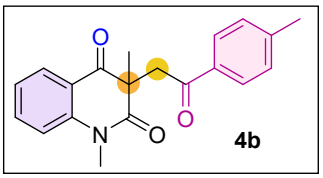
135.6, 133.8, 128.7, 128.4, 118.8, 115.0, 53.7, 47.4, 28.9, 24.4 ppm; HRMS (ESI/TOF-Q) m/z: [M + Na]$^+$ calcd for $C_{18}H_{16}N_2NaO_3$, 331.1053; found, 331.1047.

3-(2-(4-Chlorophenyl)-2-oxoethyl)-1,3-dimethylquinoline-2,4(1*H*,3*H*)-dione (4a):[6]



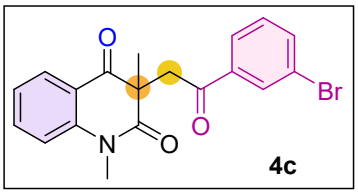
White solid, (150.0 mg, 88% yield), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.08 (dd, J = 8.0, 1.5 Hz, 1H), 7.91-7.90 (m, 2H), 7.70-7.67 (m, 1H), 7.44-7.41 (m, 2H), 7.28 (s, 1H), 7.24-7.20 (m, 1H), 4.09-4.00 (m, 2H), 3.53 (s, 3H), 1.48 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 196.8, 196.5, 173.9, 143.4, 140.1, 136.1, 134.2, 129.9, 129.0, 128.5, 123.1, 119.7, 115.1, 53.7, 46.8, 30.0, 24.7 ppm HRMS (ESI/TOF-Q) m/z: [M + Na]$^+$ calcd for $C_{19}H_{16}ClNNaO_3$, 364.0711; found, 364.0710.

1,3-Dimethyl-3-(2-oxo-2-(p-tolyl)ethyl)quinoline-2,4(1*H*,3*H*)-dione (4b):[6]



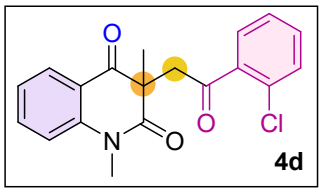
White solid, (153.5 mg, 90% yield), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.07 (dd, J = 7.5, 1.5 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.68-7.64 (m, 1H), 7.26-7.18 (m, 4H), 4.10-4.01 (m, 2H), 3.52 (s, 3H), 2.39 (s, 3H), 1.46 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 197.6, 196.7, 174.1, 144.5, 143.5, 136.0, 133.4, 130.3, 129.3, 129.3, 128.6, 128.5, 123.0, 119.8, 115.1, 53.6, 47.1, 30.0, 24.6, 21.8 ppm; HRMS (ESI/TOF-Q) m/z: [M + Na]$^+$ calcd for $C_{20}H_{19}NNaO_3$, 344.1257; found, 344.1266.

3-(2-(3-Bromophenyl)-2-oxoethyl)-1,3-dimethylquinoline-2,4(1*H*,3*H*)-dione (4c):[6]



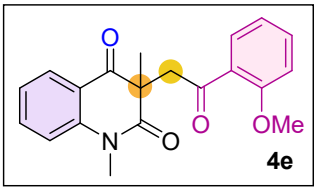
White solid, (109.7 mg, 57% yield)), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.07 (dd, J = 7.5, 1.5 Hz, 2H), 7.89-7.87 (m, 1H), 7.70-7.67 (m, 2H), 7.33 (t, J = 8.0 Hz, 1H), 7.28 (s, 1H), 7.22 (t, J = 7.5 Hz, 1H), 4.08-4.00 (m, 2H), 3.53 (s, 3H), 1.48 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 196.8, 196.5, 173.9, 143.5, 137.6, 136.5, 136.1, 131.6, 130.3, 128.6, 127.0, 123.1, 123.0, 119.7, 115.1, 53.7, 46.9, 30.1, 24.7 ppm; HRMS (ESI/TOF-Q) m/z: [M + Na]$^+$ calcd for $C_{19}H_{16}BrNNaO_3$, 408.0206; found, 408.0213.

3-(2-(2-Chlorophenyl)-2-oxoethyl)-1,3-dimethylquinoline-2,4(1*H*,3*H*)-dione (4d):[1c]



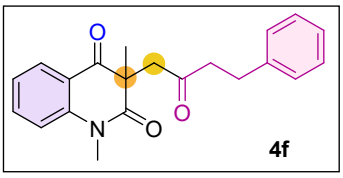
White solid, (88.7 mg, 52% yield)), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.07 (dd, J = 7.5, 1.5 Hz, 1H), 7.70-7.63 (m, 2H), 7.42-7.37 (m, 2H), 7.33-7.29 (m, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 4.10-4.02 (m, 2H), 3.52 (s, 3H), 1.44 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 200.0, 196.5, 173.8, 143.5, 137.2, 136.1, 132.5, 132.0, 131.0, 130.2, 128.6, 127.0, 123.1, 119.8, 115.1, 54.3, 50.4, 30.1, 24.8 ppm; HRMS (ESI/TOF-Q) m/z: [M + Na]$^+$ calcd for $C_{19}H_{16}ClNNaO_3$, 364.0711; found, 364.0719.

3-(2-(2-Methoxyphenyl)-2-oxoethyl)-1,3-dimethylquinoline-2,4(1*H*,3*H*)-dione (4e):[6]



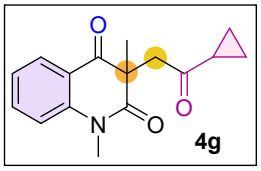
White solid, (91.1 mg, 54% yield)), hexane/EtOAc (95/5); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (dd, J = 8, 1.6 Hz, 1H), 7.73 (dd, J = 8, 1.6 Hz, 1H), 7.65-7.61 (m, 1H), 7.46-7.42 (m, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.19-7.15 (m, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.93-6.89 (m, 1H), 4.15-4.05 (m, 2H), 3.95 (s, 3H), 3.50 (s, 3H), 1.42 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 198.4, 196.9, 174.3, 159.8, 143.5, 135.8, 134.6, 131.2, 128.5, 125.9, 122.8, 120.6, 119.9, 115.0, 111.7, 55.7, 53.8, 52.6, 29.9, 24.6 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{20}H_{19}NNaO_4$, 360.1206; found, 360.1202.

1,3-Dimethyl-3-(2-oxo-4-phenylbutyl)quinoline-2,4(1*H*,3*H*)-dione (4f):[6]



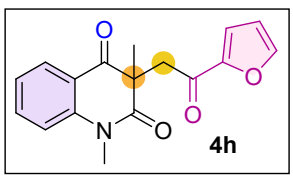
White solid, (97.7 mg, 58% yield)), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.04 (dd, J = 7.5, 1.5 Hz, 1H), 7.67-7.63 (m, 1H), 7.28-7.25 (m, 2H), 7.23-7.17 (m, 3H), 7.13 (d, J = 7.5 Hz, 2H), 3.52 (s, 2H), 3.50 (s, 3H), 2.84-2.80 (m, 2H), 2.77-2.74 (m, 2H), 1.35 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 208.0, 196.7, 174.0, 143.4, 140.9, 136.1, 128.6, 128.5, 128.4, 126.3, 123.1, 119.7, 115.1, 53.5, 50.3, 43.6, 30.0, 29.6, 24.6 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{21}H_{21}NNaO_3$, 358.1414; found, 358.1411.

3-(2-Cyclopropyl-2-oxoethyl)-1,3-dimethylquinoline-2,4(1*H*,3*H*)-dione (4g):[6]



White solid, (70.5 mg, 52% yield), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.02 (d, J = 7.5 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.20-7.15 (m, 2H), 3.66 (s, 2H), 3.47 (s, 3H), 1.97-1.96 (m, 1H), 1.35 (s, 3H), 0.95-0.86 (m, 4H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 208.8, 196.6, 173.9, 143.4, 136.0, 128.5, 122.9, 119.7, 115.0, 53.4, 50.9, 30.0, 24.5, 20.1, 11.2, 11.1 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{16}H_{17}NNaO_3$, 294.1101; found, 294.1108.

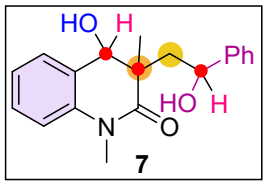
3-(2-(Furan-2-yl)-2-oxoethyl)-1,3-dimethylquinoline-2,4(1*H*,3*H*)-dione (4h):



colourless viscous liquid, (47.5 mg, 32% yield), hexane/EtOAc (95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.06 (dd, J = 8.0, Hz, 1.5 Hz, 1H), 7.65 (td, J = 7.5, 1.5 Hz, 1H), 7.57-7.56 (m, 1H), 7.24-7.15 (m, 3H), 6.51-6.50 (m, 1H), 3.98-3.90 (m, 2H), 3.50 (s, 3H), 1.45 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 196.6, 187.0, 174.0, 152.3, 146.6, 143.5, 136.1, 128.6, 123.1, 119.8, 117.6, 115.1, 112.5, 53.3, 46.6, 30.0, 24.8 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{17}H_{15}NNaO_4$, 320.0893; found, 320.0899.

4-hydroxy-3-(2-hydroxy-2-phenylethyl)-1,3-dimethyl-3,4-dihydroquinolin-2(1H)-one (7) (mixture of two diastereomers):

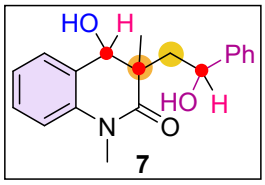
Colourless viscous liquid, (255.1 mg, 82% yield), hexane/EtOAc (80/20); **^{1}H NMR** (500 MHz, $CDCl_3$):



major isomer: δ 7.47-7.46 (m, 1H), 7.35-7.31 (m, 2H, peaks of two isomers overlapped), 7.31-7.27 (m, 3H, peaks of two isomers overlapped),7.24-7.23 (m, 1H, peaks of two isomers overlapped), 7.11 (td, J = 7.5, 1.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 4.85-4.82 (m, 1H), 4.31 (s, 1H), 3.27 (s, 3H), 2.15-2.12 (m, 1H, peaks of two isomers overlapped), 2.04-2.01 (m, 1H), 1.02 (s, 3H) ppm; **minor isomer:** δ 7.40-7.39 (m, 2H), 7.31-7.27 (m, 3H, peaks of two isomers overlapped), 7.24-7.23 (m, 1H, peaks of two isomers overlapped), 7.22-7.20 (m, 1H, peaks of two isomers overlapped), 7.06 (td, J = 7.5, 1.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 4.96-4.94 (m, 1H), 4.89 (s, 1H), 3.36 (s, 3H), 2.27-2.23 (m, 1H), 2.18-2.15 (m, 1H, peaks of two isomers overlapped), 1.07 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): **major isomer:** δ 174.8, 145.9, 138.6, 129.6, 128.5, 127.6, 126.0, 125.8, 123.8, 114.9, 76.0, 70.7, 46.7, 44.3, 30.2, 16.47 ppm; **minor isomer:** 174.7, 145.2, 137.6, 128.6, 128.2, 127.3, 126.8, 125.8, 123.6, 114.1, 70.9, 70.4, 47.0, 45.6, 30.5, 21.1 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{19}H_{21}NNaO_3$, 334.1414; found, 334.1424.

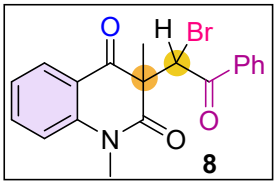
4-hydroxy-3-(2-hydroxy-2-phenylethyl)-1,3-dimethyl-3,4-dihydroquinolin-2(1H)-one (7) (single diastereomer):

brown liquid, (40.4 mg, 13% yield), hexane/EtOAc (84/16); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57-7.55



(m, 1H), 7.45-7.43 (m, 2H), 7.36-7.30 (m, 3H), 7.28-7.23 (m, 1H), 7.15 (td, J = 7.2, 0.8 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 5.10 (s, 1H), 4.95-4.93 (m, 1H), 3.39 (s, 3H), 2.41-2.37 (m, 1H), 1.92-1.86 (m, 1H), 0.93 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 174.5, 145.6, 137.8, 128.7, 128.5, 128.2, 127.6, 125.5, 125.4, 123.7, 114.1, 72.3, 69.8, 47.3, 43.8, 30.3, 16.9 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{19}H_{21}NNaO_3$, 334.1414; found, 334.1415.

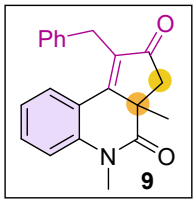
3-(1-bromo-2-oxo-2-phenylethyl)-1,3-dimethylquinoline-2,4(1*H*,3*H*)-dione (8):



Light brown solid, (288.8 mg, 75% yield), hexane/EtOAc (90/10), mp = 92-96 °C, dr = 1.20:1, **^{1}H NMR** (500 MHz, $CDCl_3$): **major isomer:** δ 8.12 (d, 8.0, 1.5 Hz, 1H), 7.56-7.53 (m, 2H), 7.45-7.42 (m, 4H), 7.25-7.22 (m, 1H, peaks of two isomers overlapped), 7.17 (d, J = 8.5 Hz, 1H), 6.28 (s, 1H), 3.41 (s, 3H), 1.73 (s, 3H) ppm; **minor isomer:** δ 7.98-7.96 (m, 4H), 7.94 (dd, J = 8.0, 1.5 Hz, 1H), 7.66-7.62 (m, 2H), 7.25-7.22 (m, 1H, peaks of two isomers overlapped) 7.14-7.11 (m, 1H), 6.23 (s, 1H), 3.53 (s, 3H), 1.71 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): **major isomer:** δ 195.1, 193.8, 171.9, 142.0, 135.8, 134.0, 133.9, 129.4, 128.6, 128.5, 123.7, 120.4, 114.9, 54.3, 52.3, 30.2, 24.2 ppm; **minor isomer:** δ 193.8, 193.8, 171.6, 143.5, 136.7, 134.2, 133.9, 129.4, 128.5, 128.5,

122.9, 118.5, 115.1, 55.0, 52.1, 29.7, 24.6 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{19}H_{16}BrNNaO_3$, 408.0206; found, 408.0215.

1-benzyl-3a,5-dimethyl-3,3a-dihydro-2H-cyclopenta[c]quinoline-2,4(5*H*)-dione (9):



Off-white solid, (288.6 mg, 91% yield), hexane/EtOAc (96/4), mp = 112-117 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.52 (d, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 8.0 Hz, 3H), 7.16 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 4.00-3.97 (m, 1H), 3.62-3.59 (m, 1H), 3.43 (s, 3H), 3.22-3.18 (m, 1H), 2.60-2.57 (m, 1H), 1.39 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 205.7, 172.7, 165.3, 139.8, 138.6, 136.9, 132.0, 128.9, 128.3, 128.2, 126.6, 123.4, 120.0, 115.6, 48.7, 44.9, 30.4, 29.1, 27.5 ppm; HRMS (ESI/TOF-Q) m/z: $[M + Na]^+$ calcd for $C_{21}H_{19}NNaO_2$, 340.1308; found, 340.1320.

12. References

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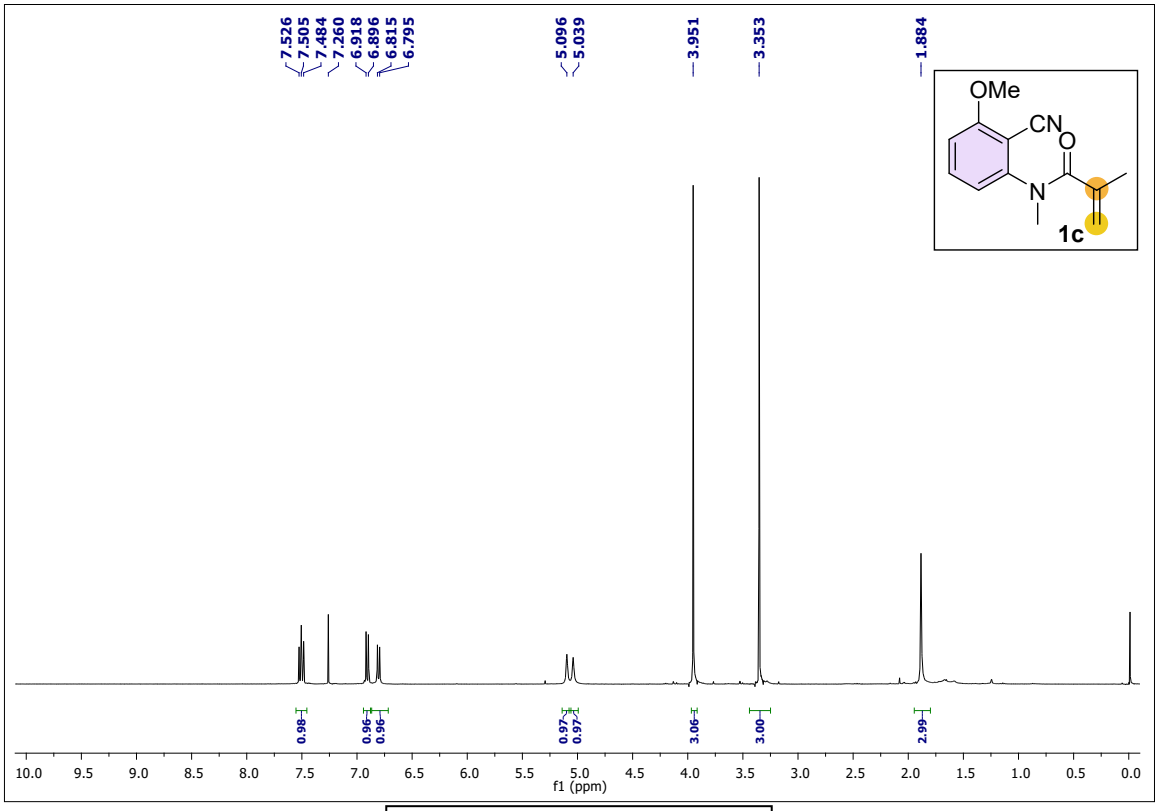
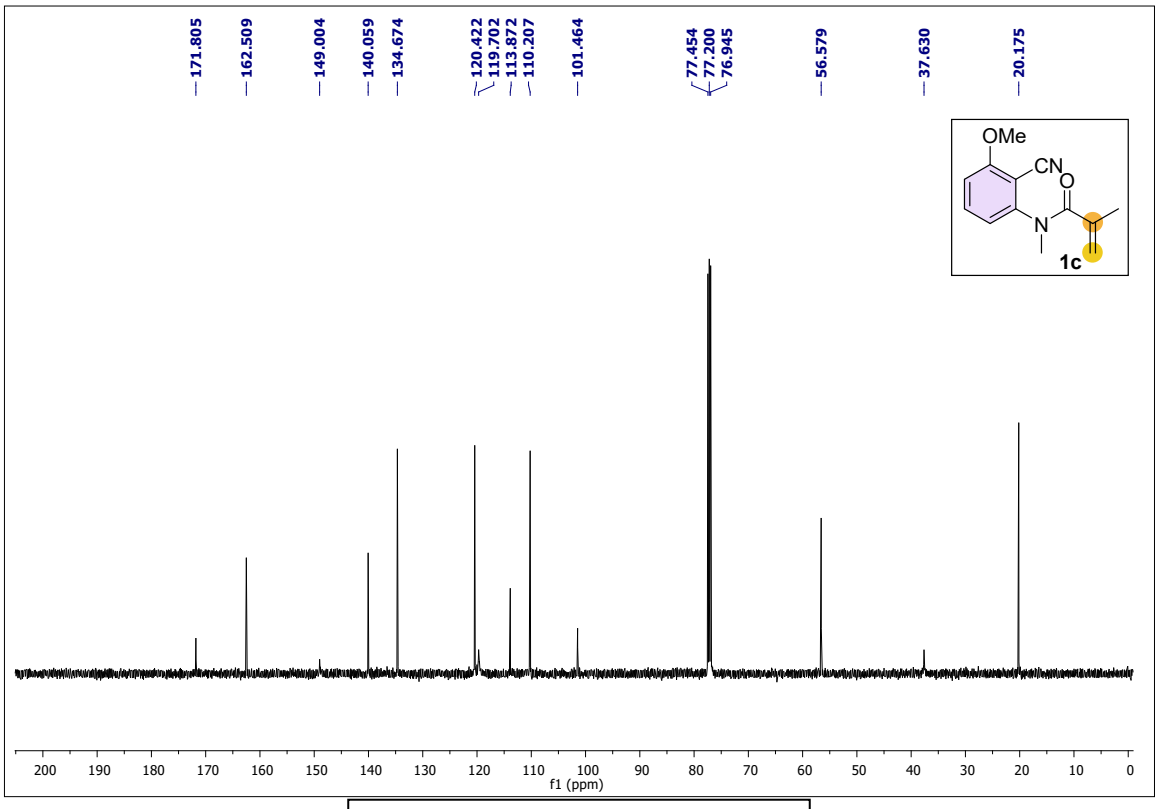
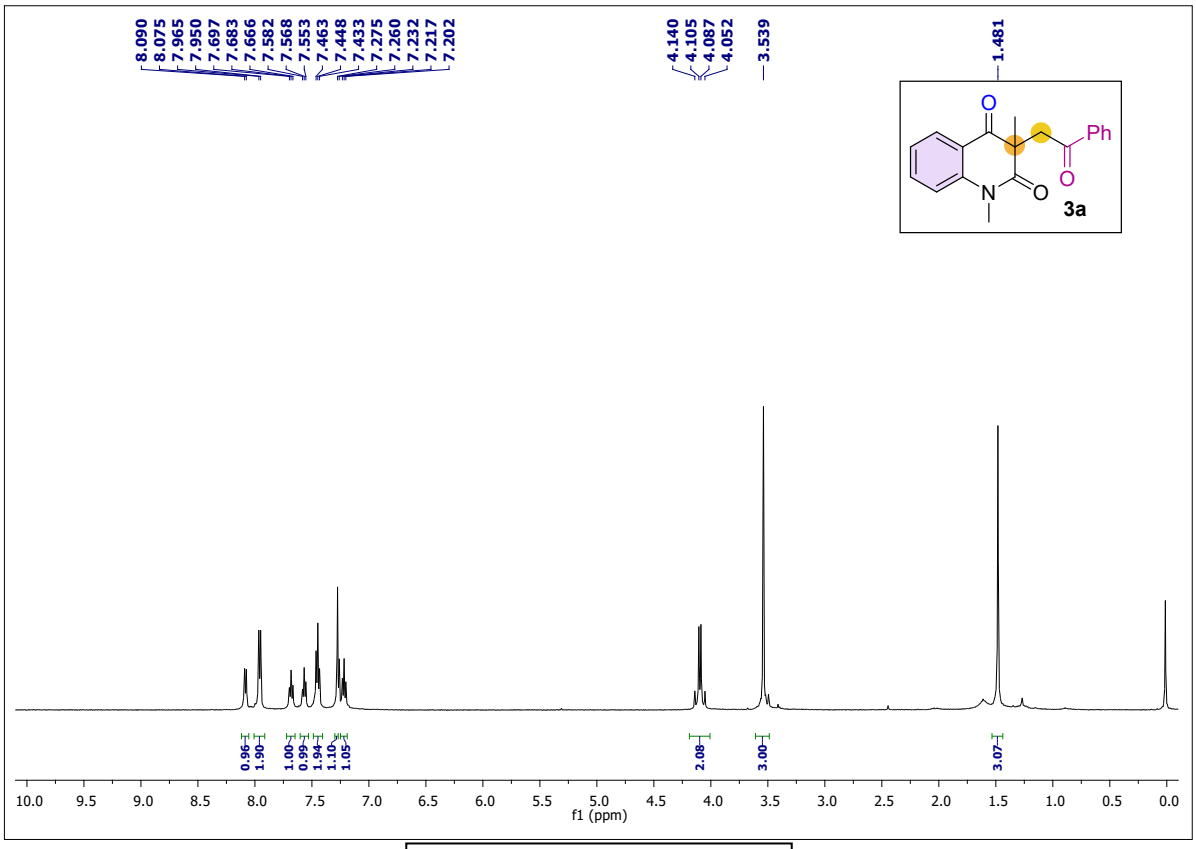
13. Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of synthesized compounds



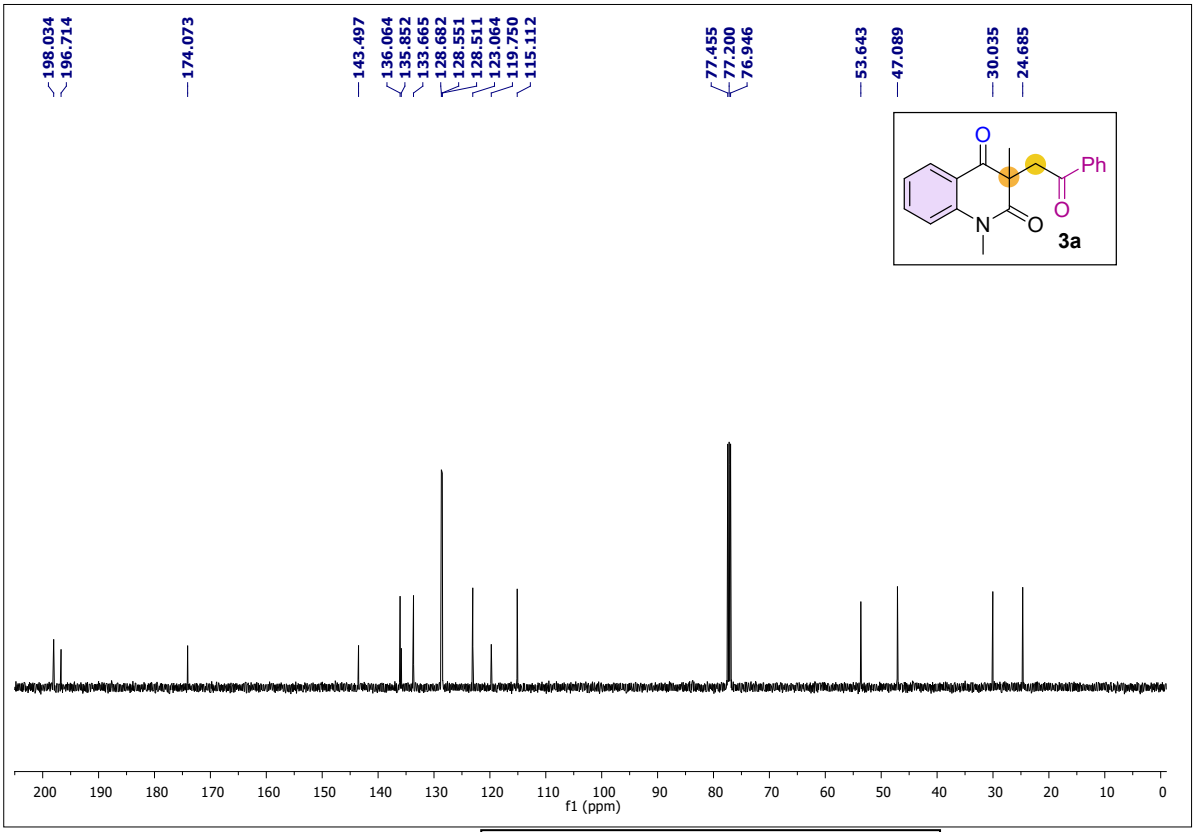
^{1}H NMR (400 MHz, $CDCl_3$)



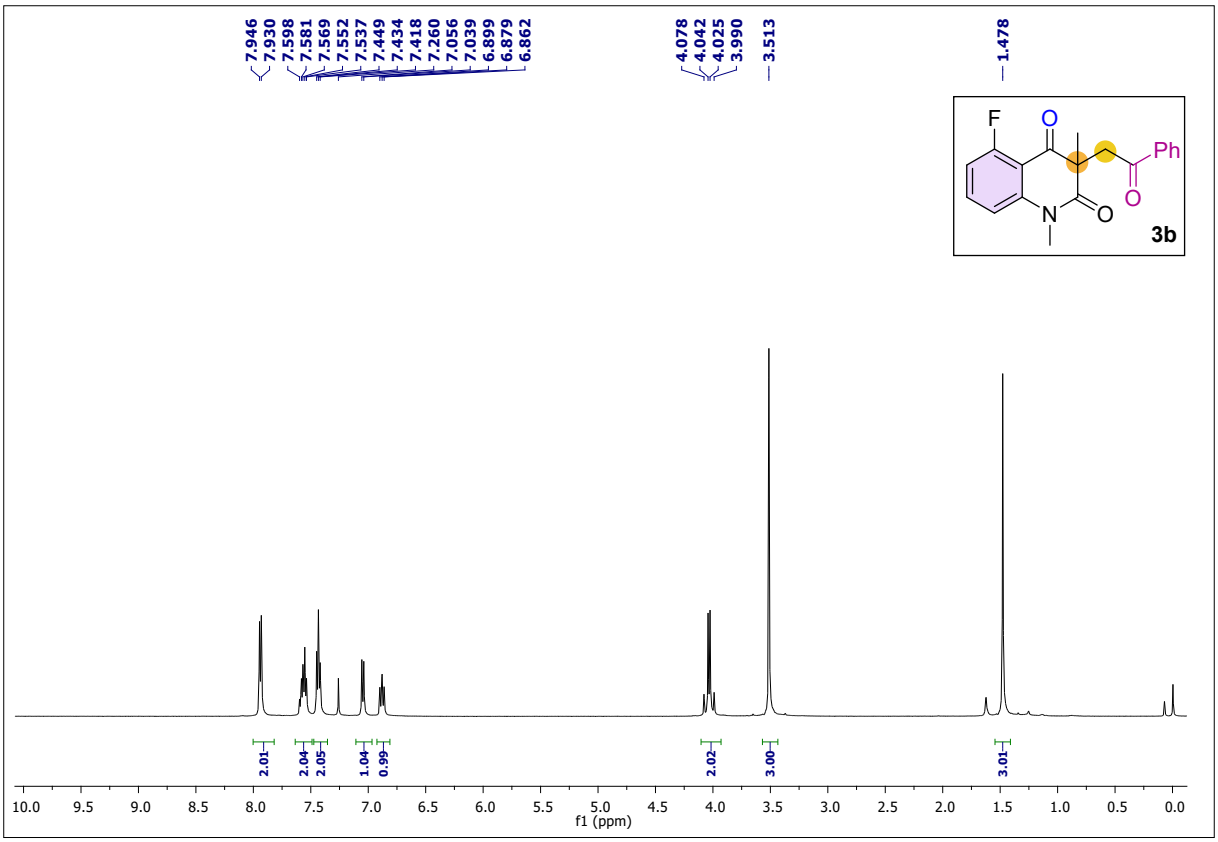
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



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



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



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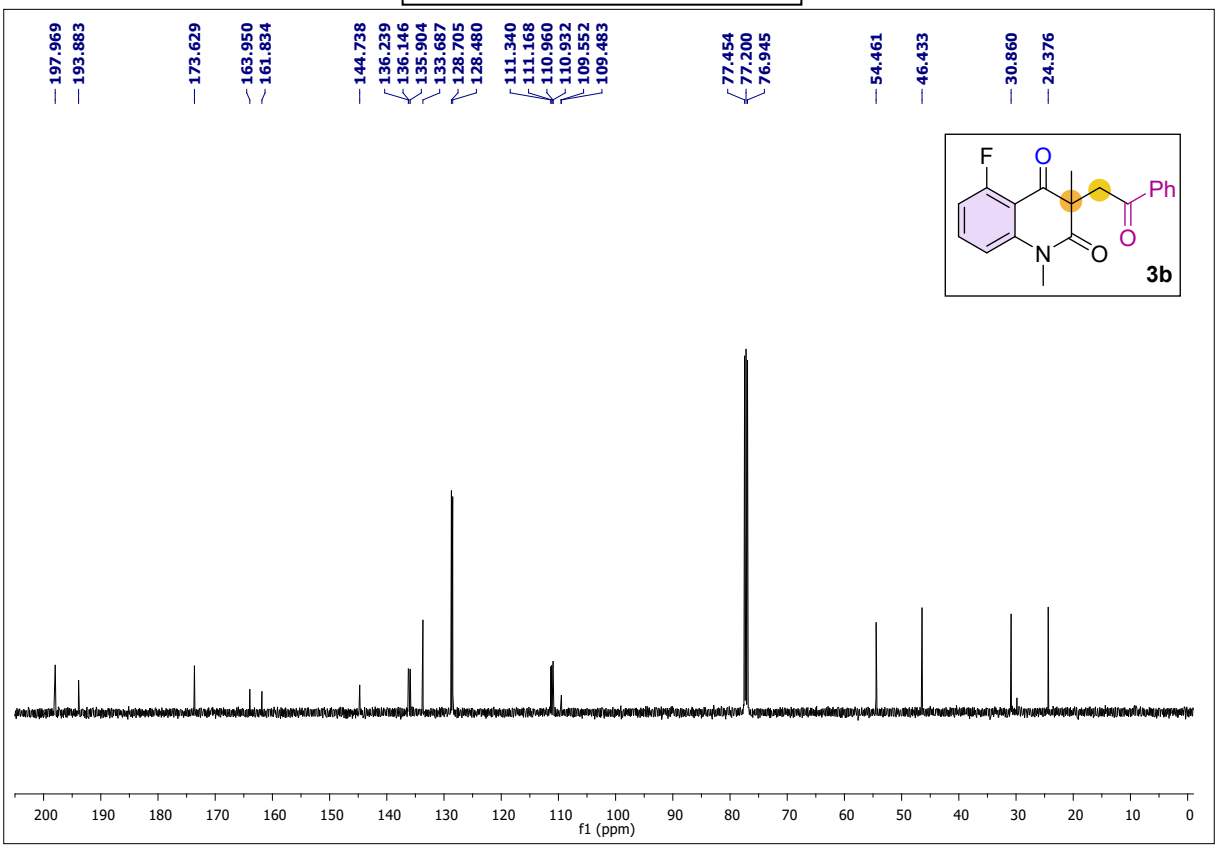

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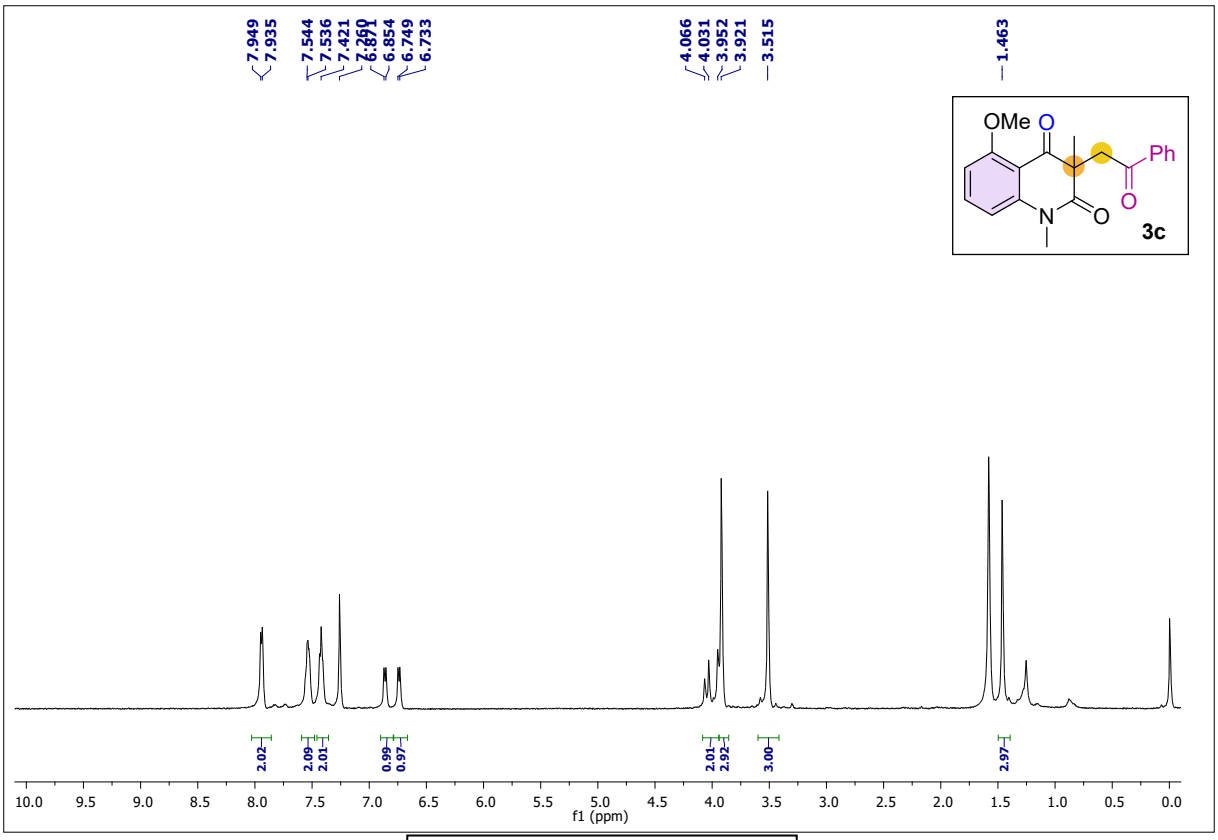

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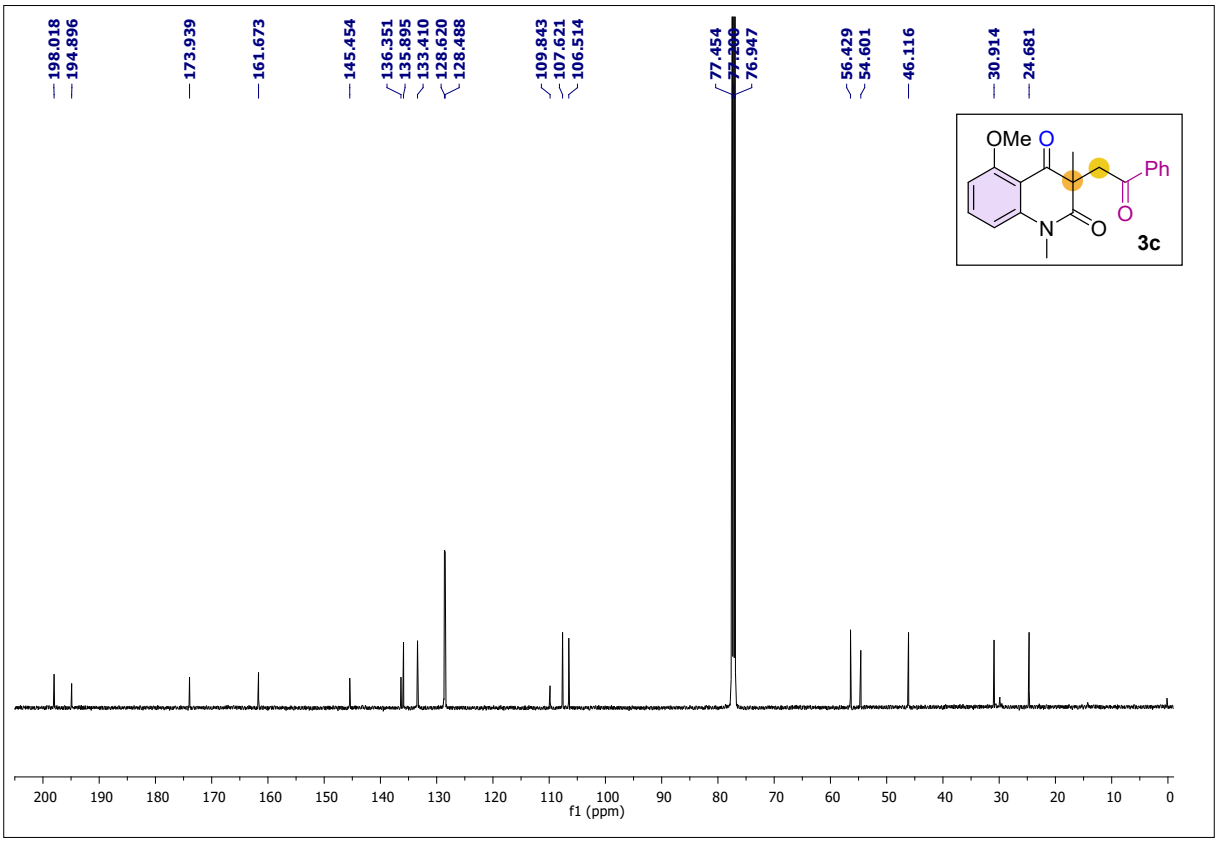

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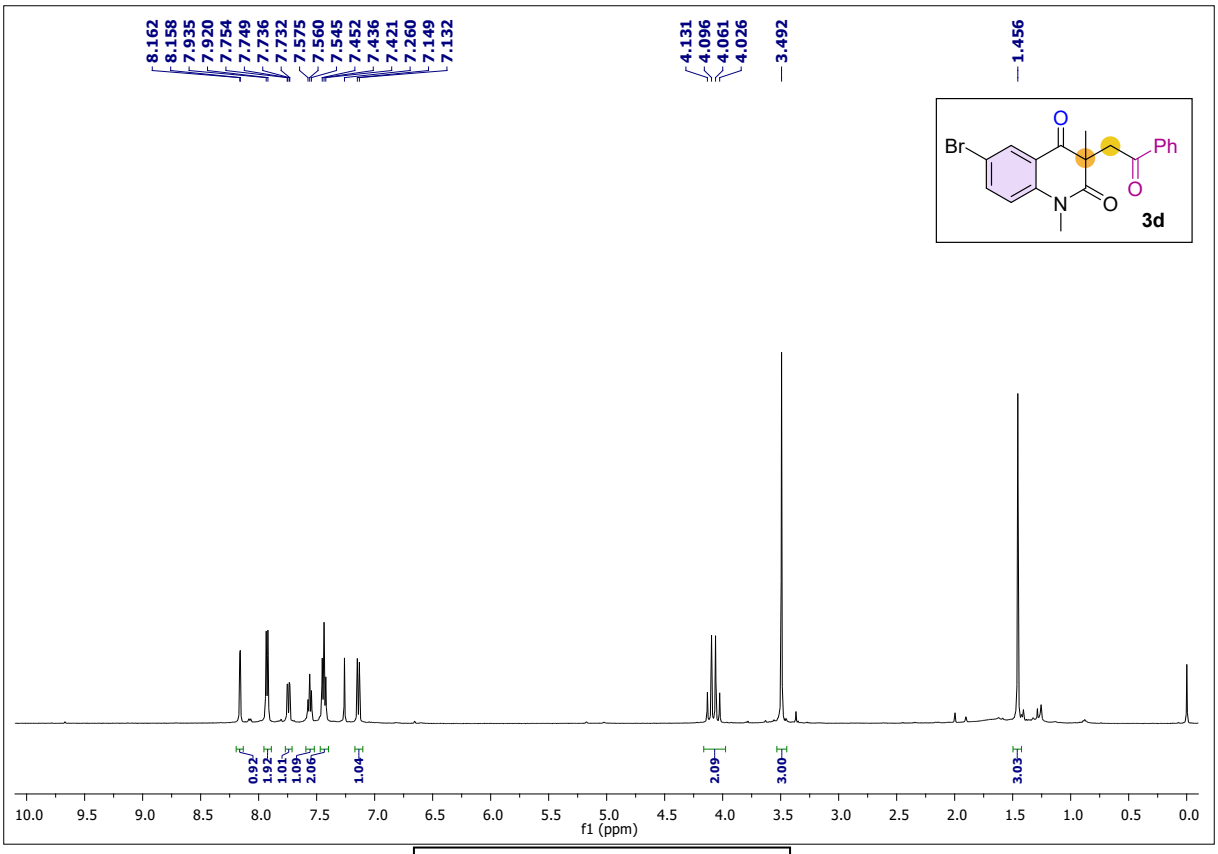

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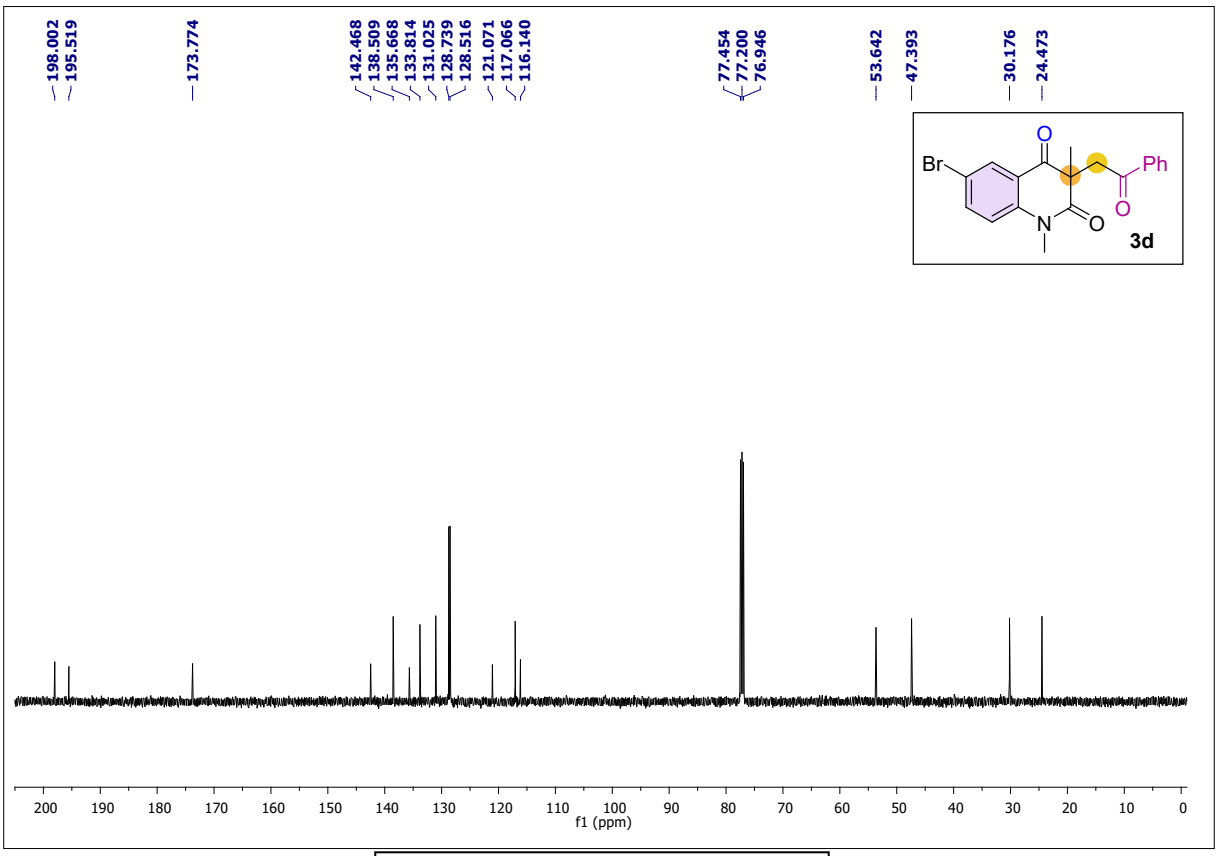

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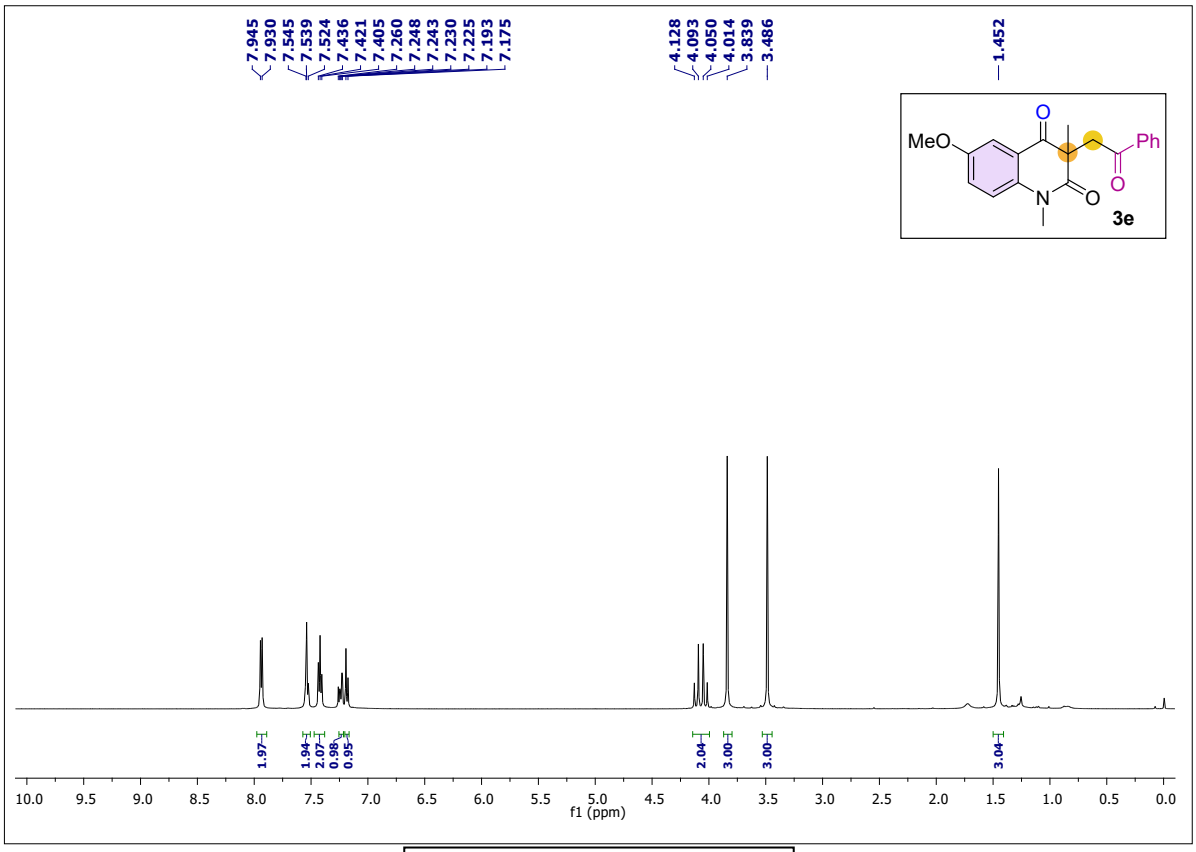

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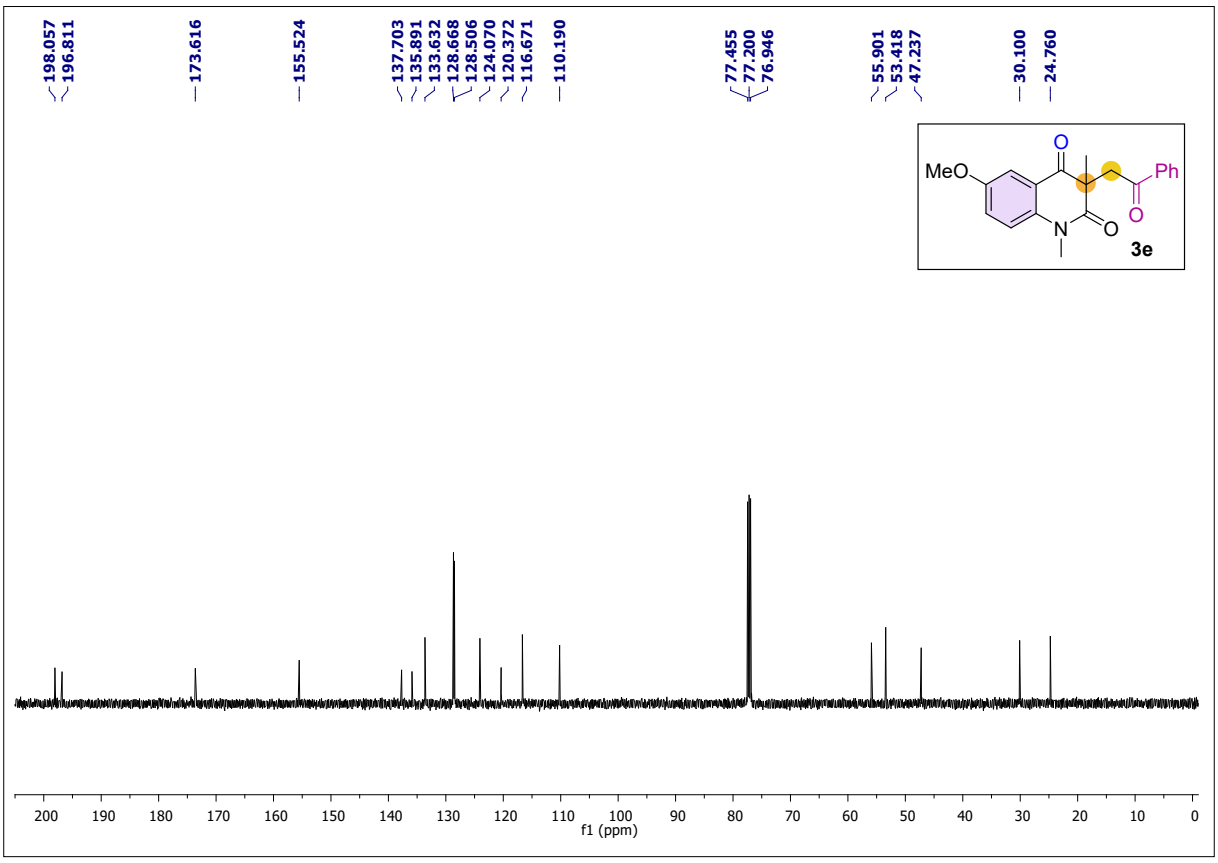

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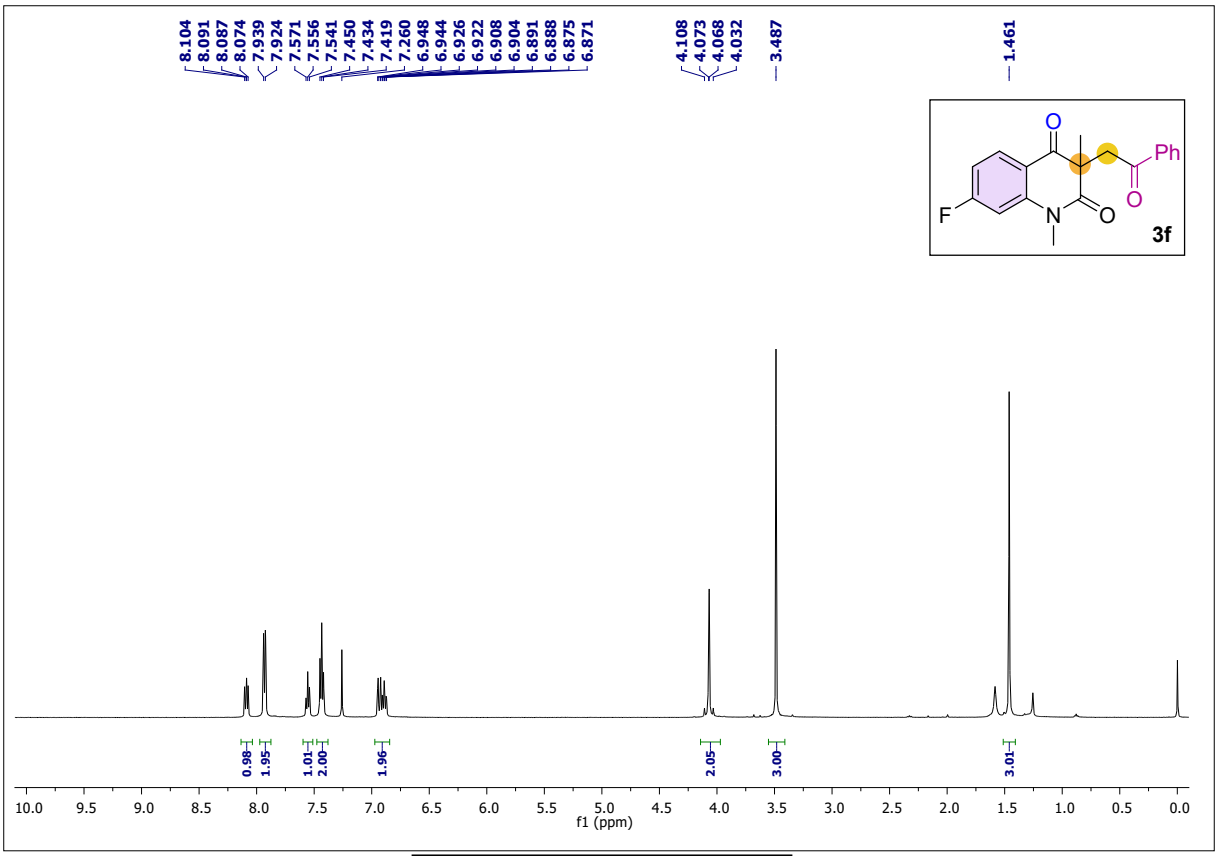

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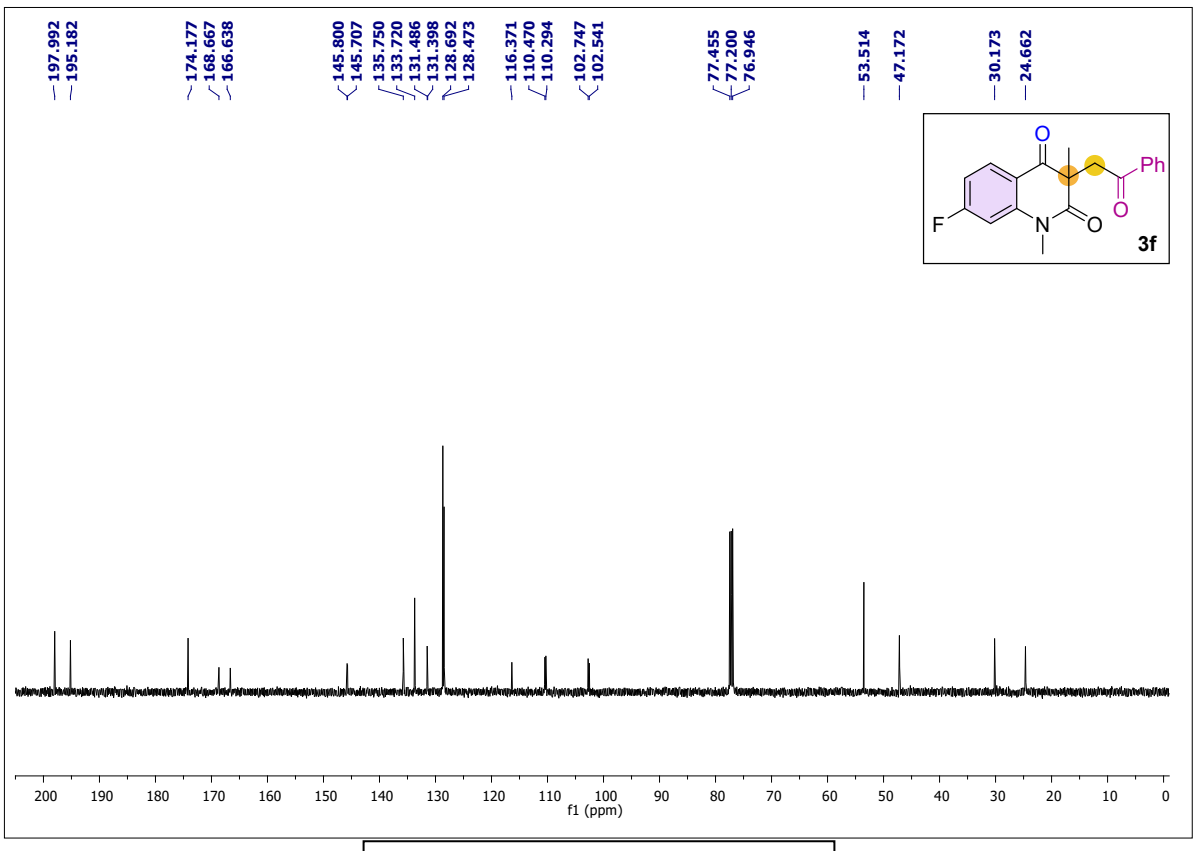

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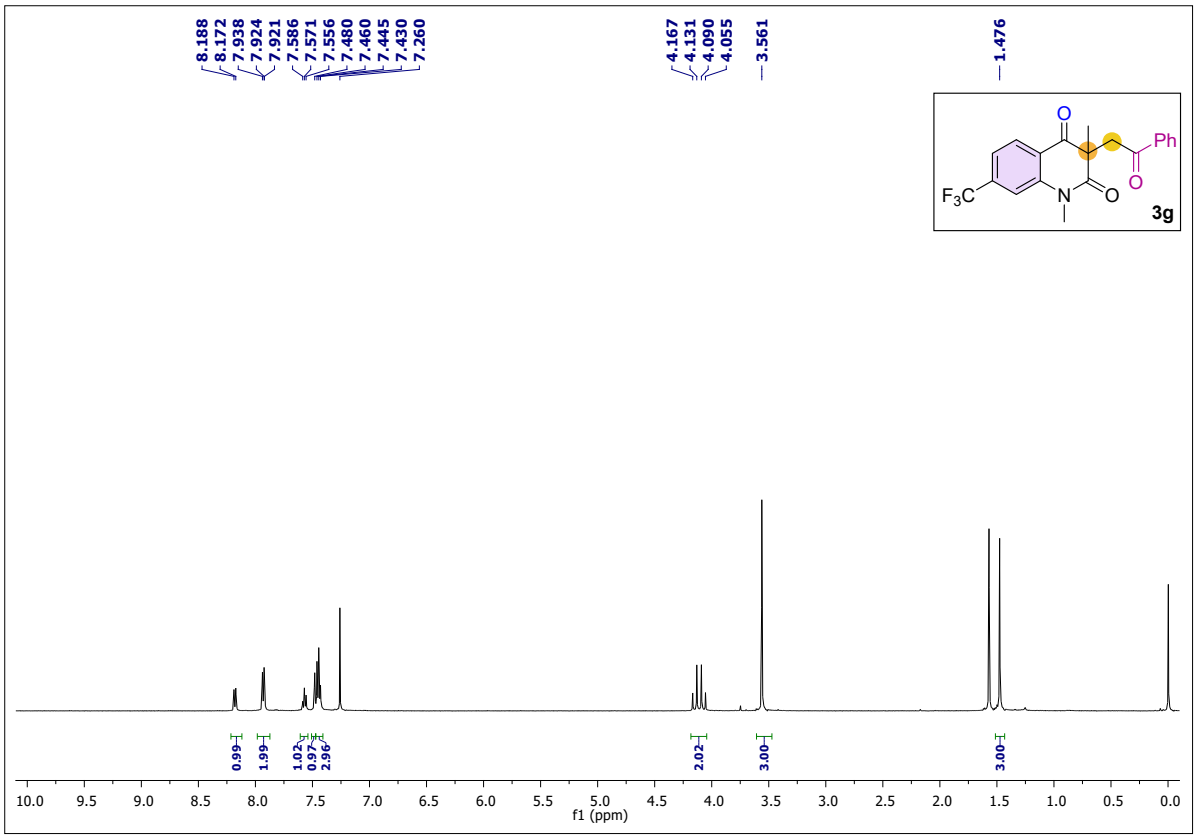

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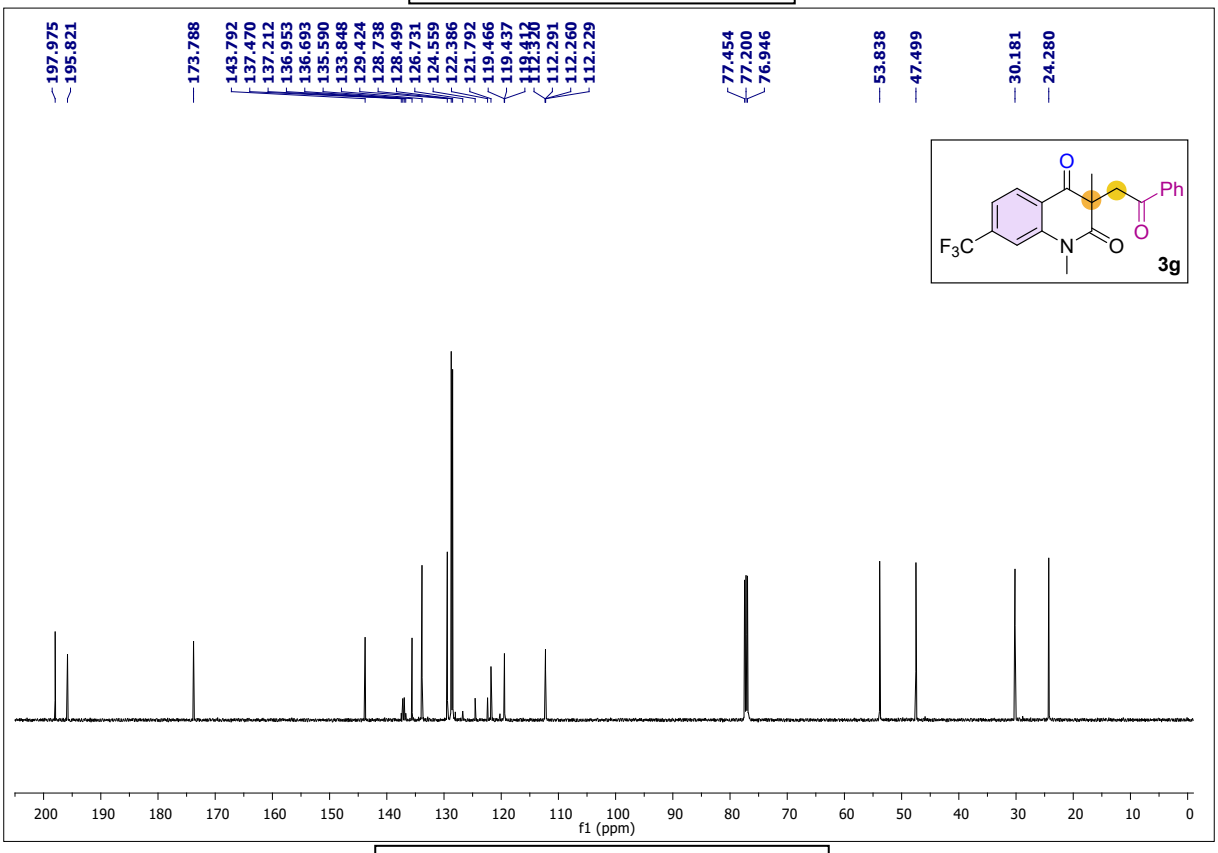

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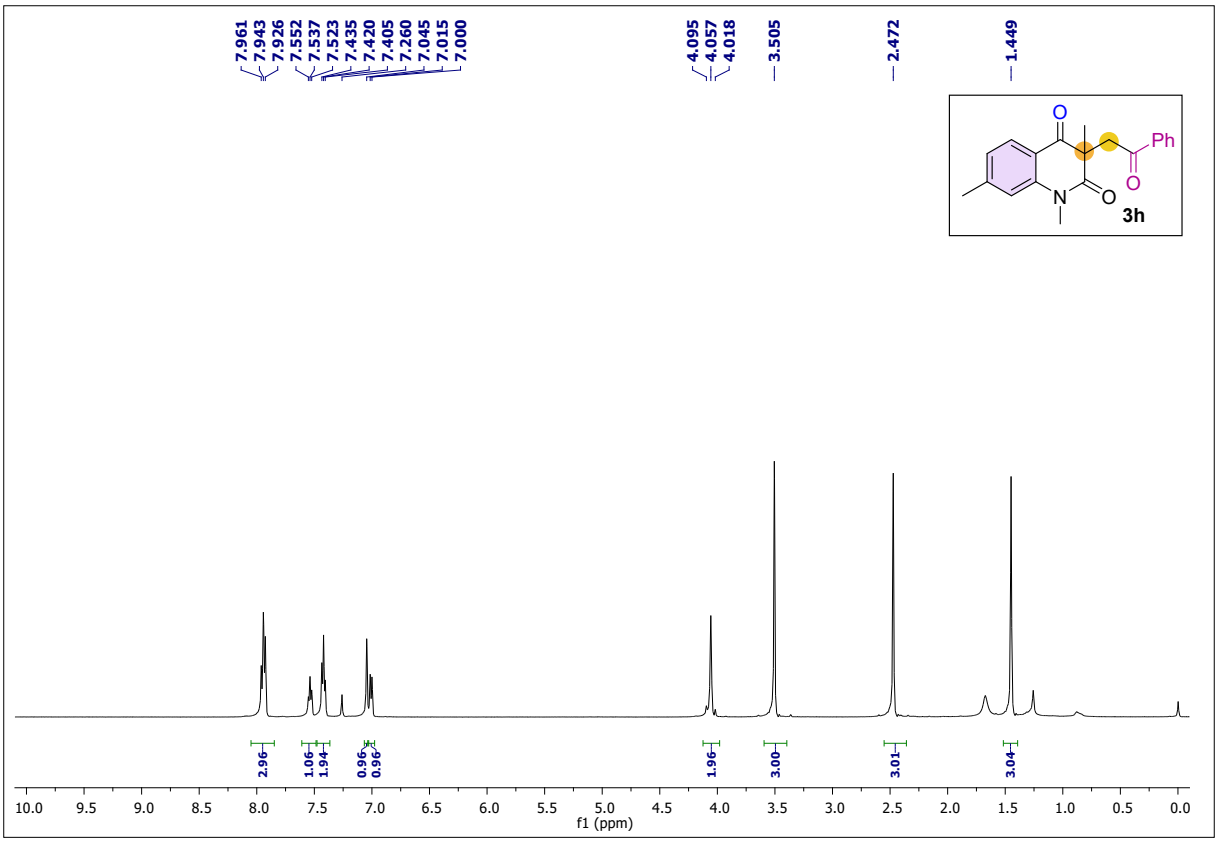

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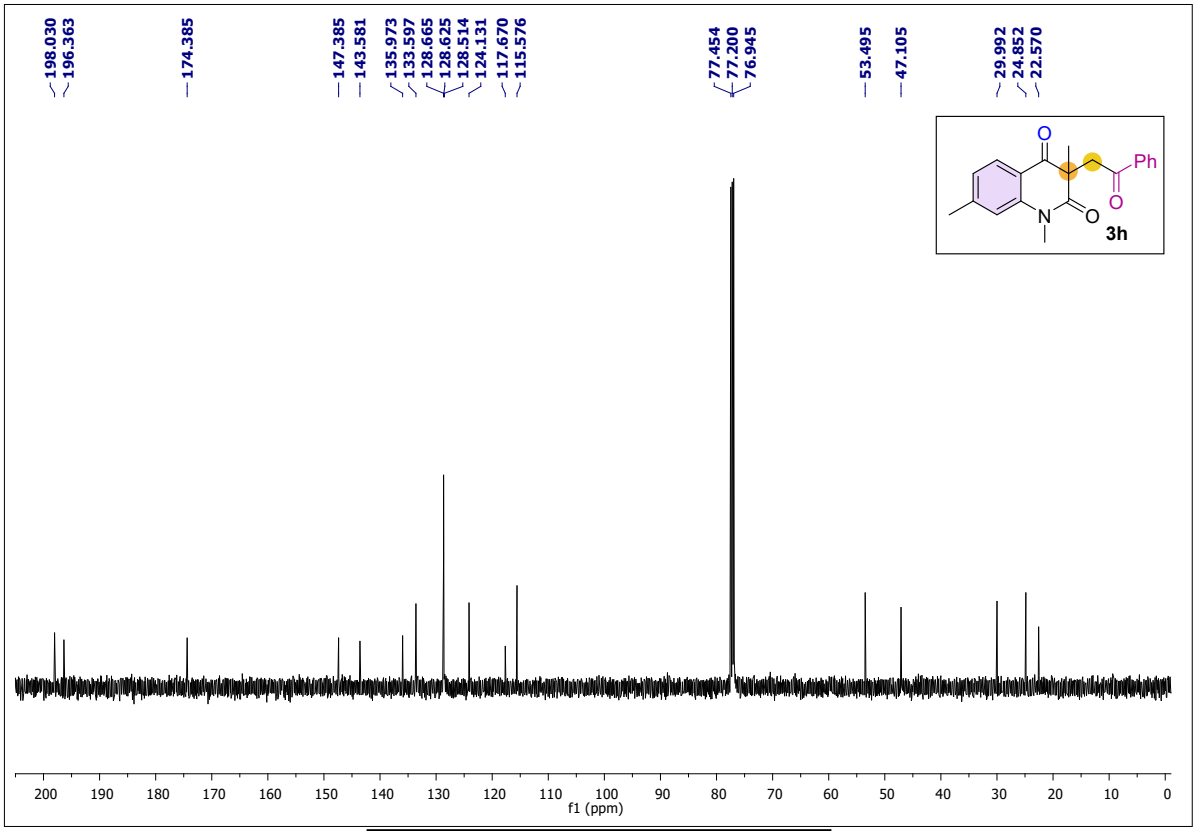

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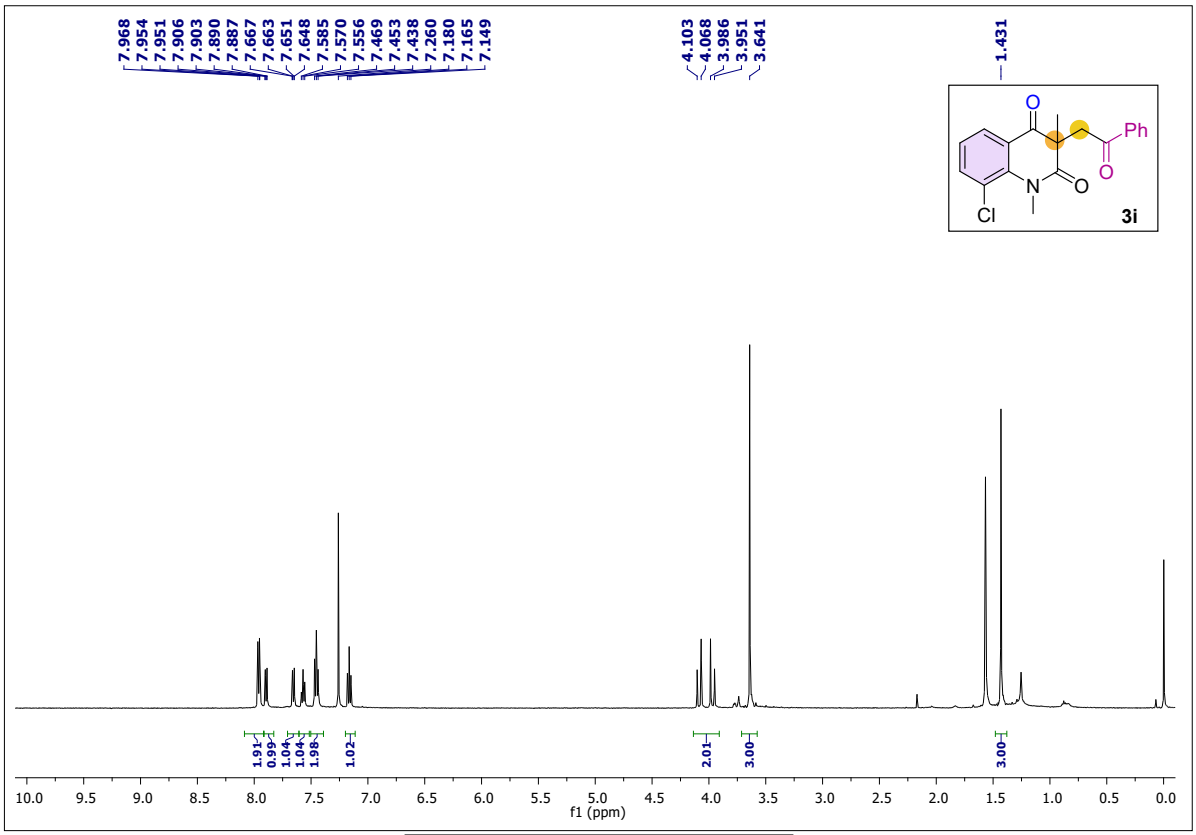

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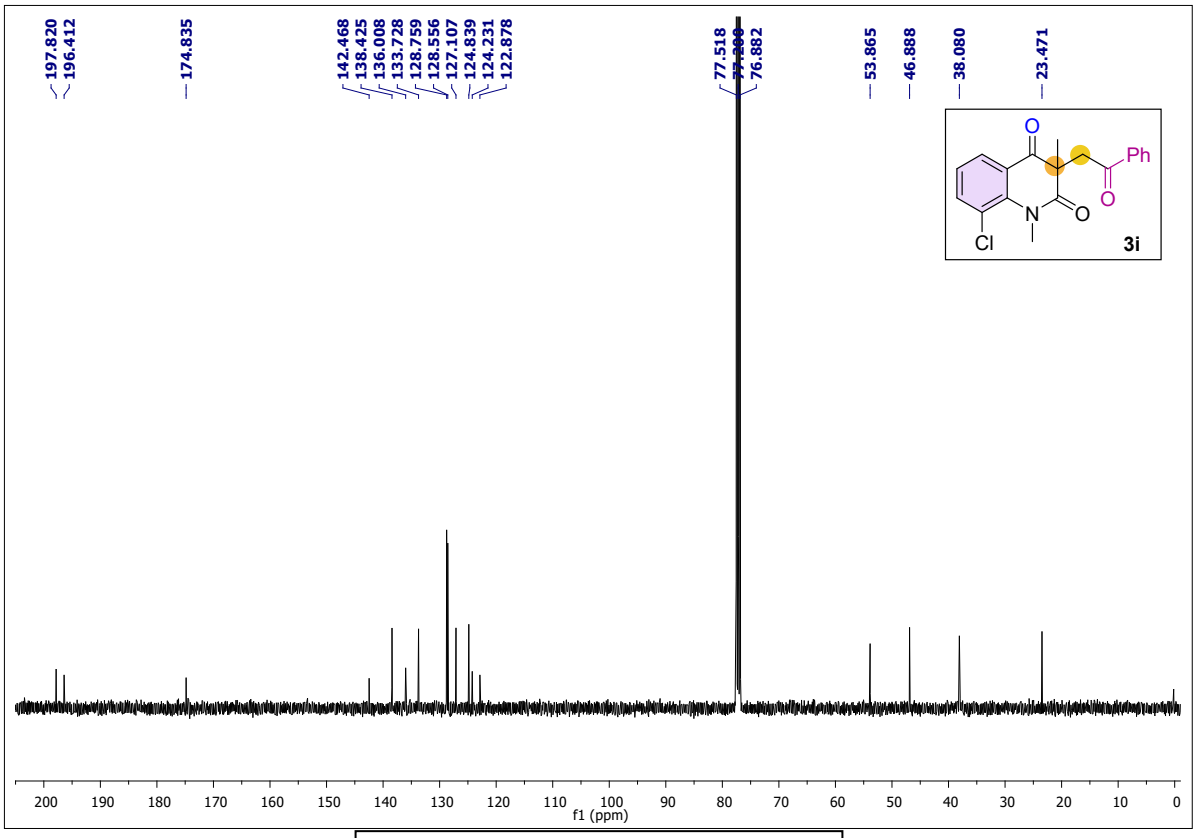

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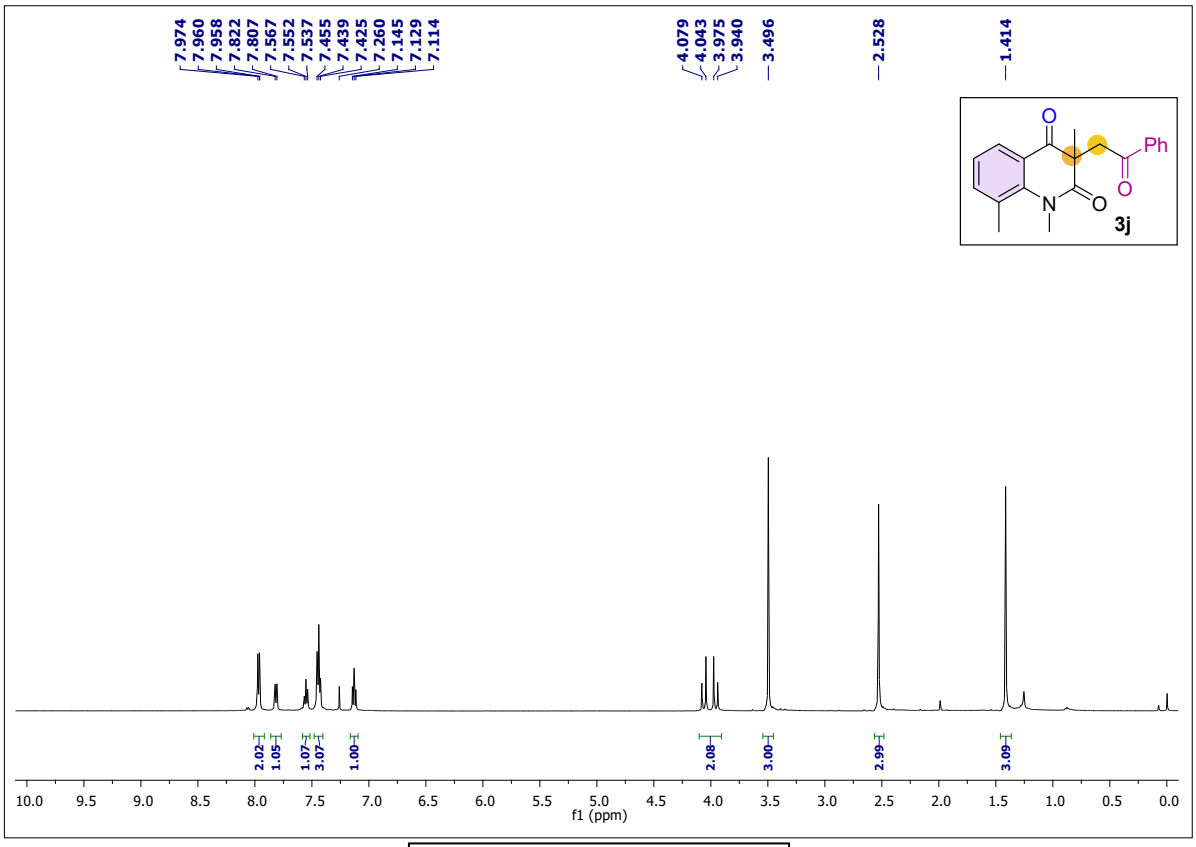
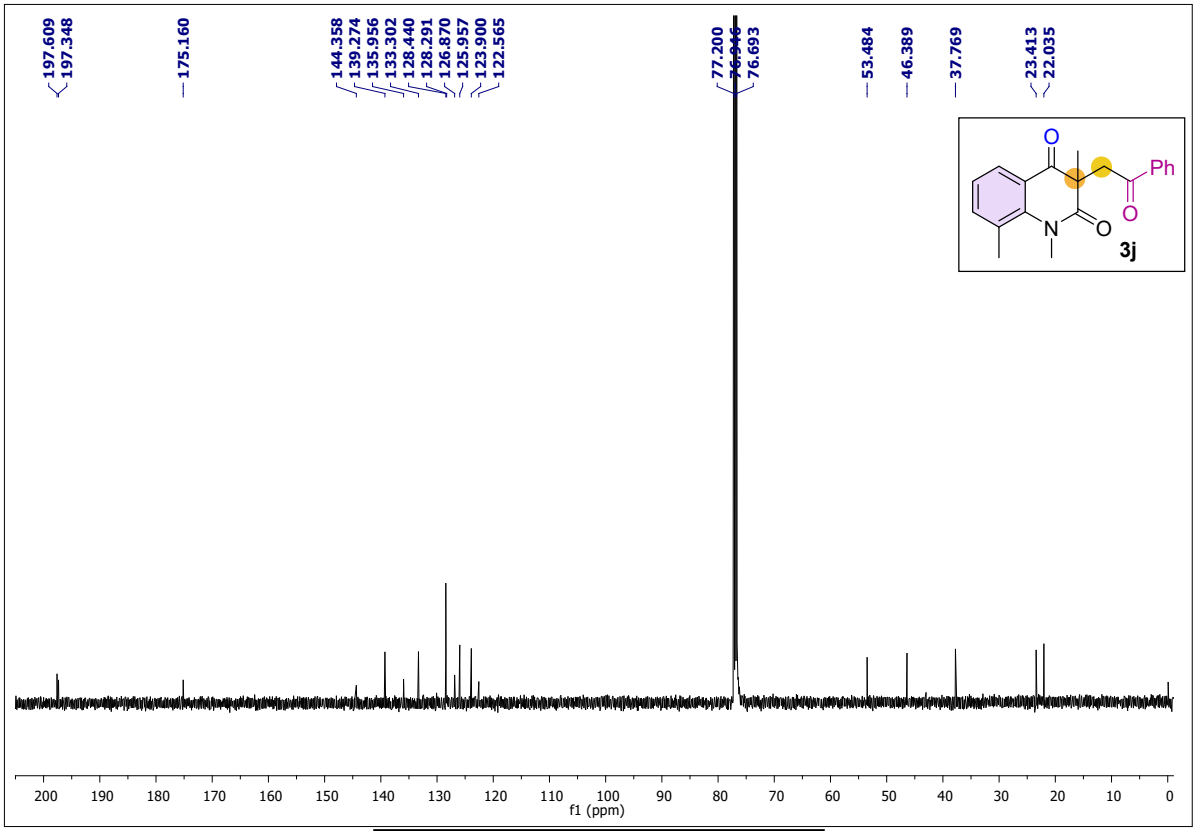


^{1}H NMR (500 MHz, $CDCl_3$)



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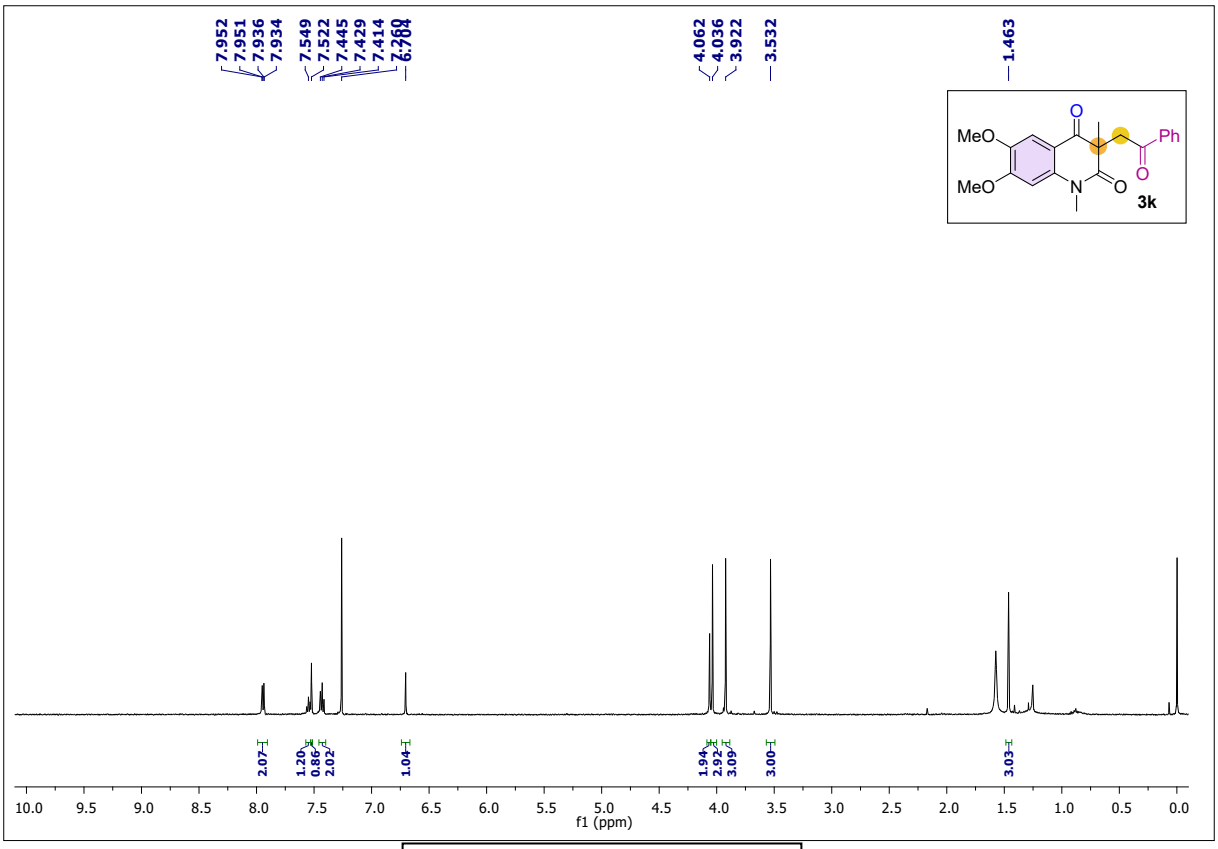

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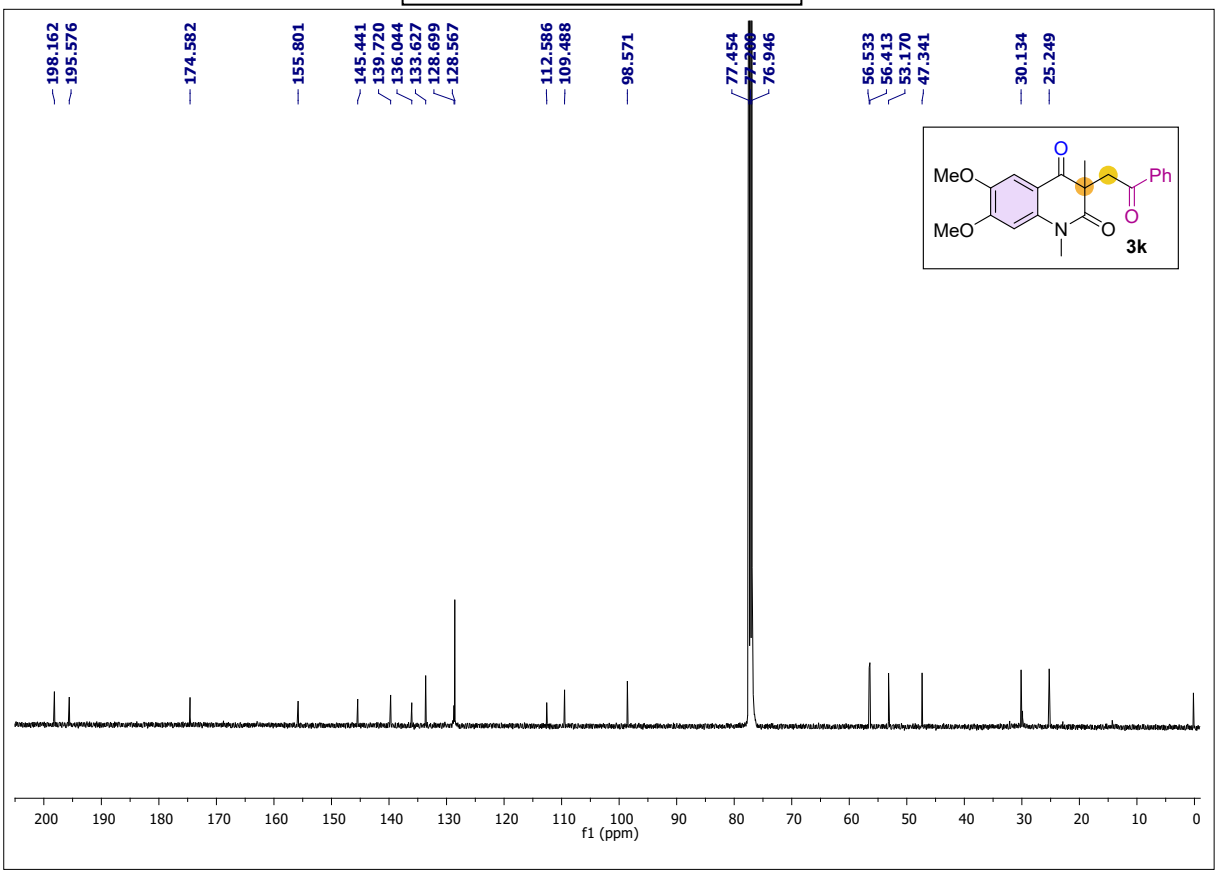
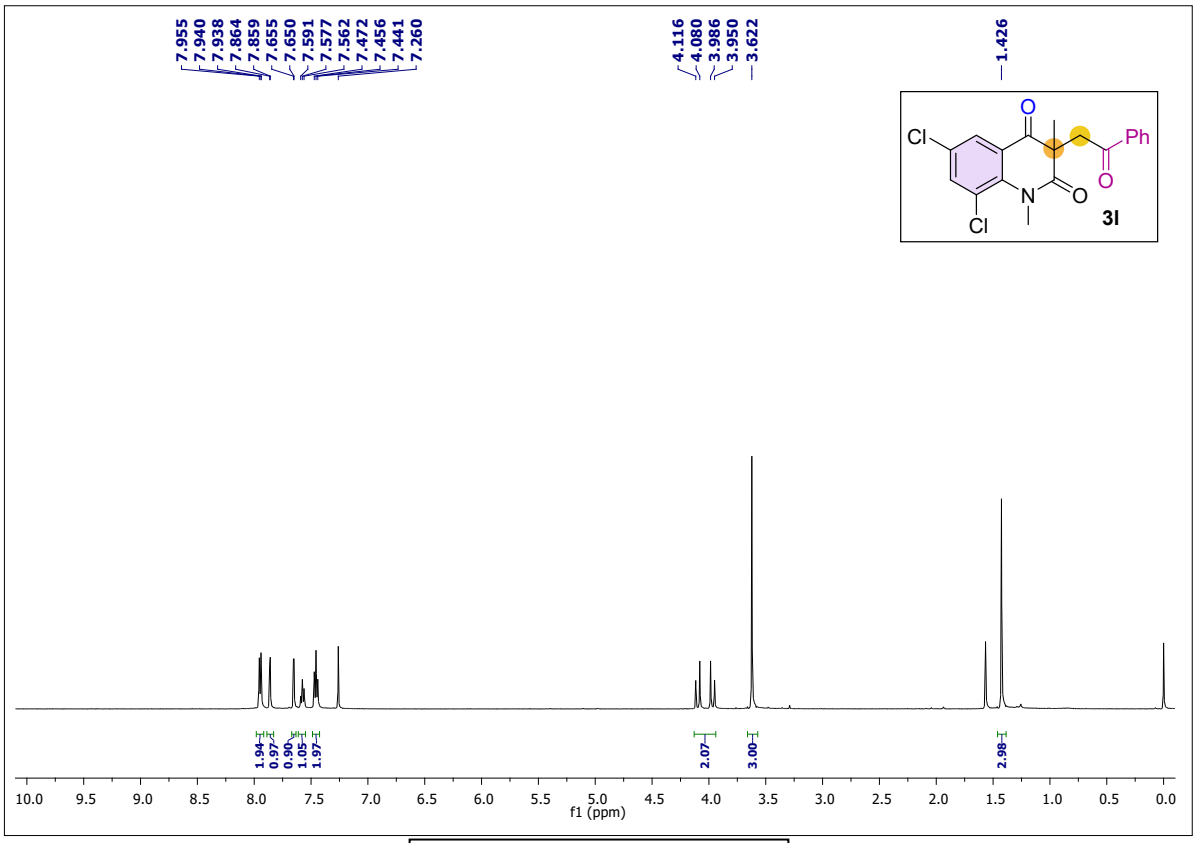


$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



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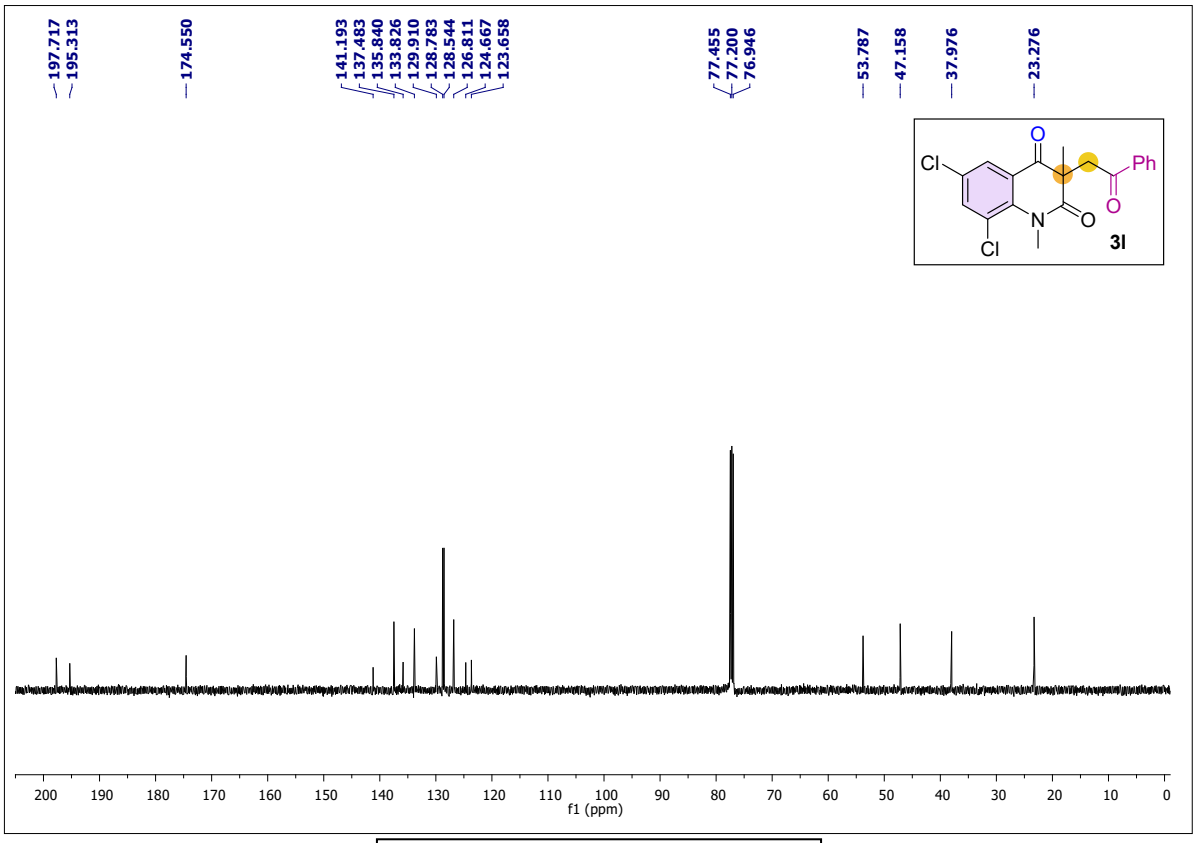

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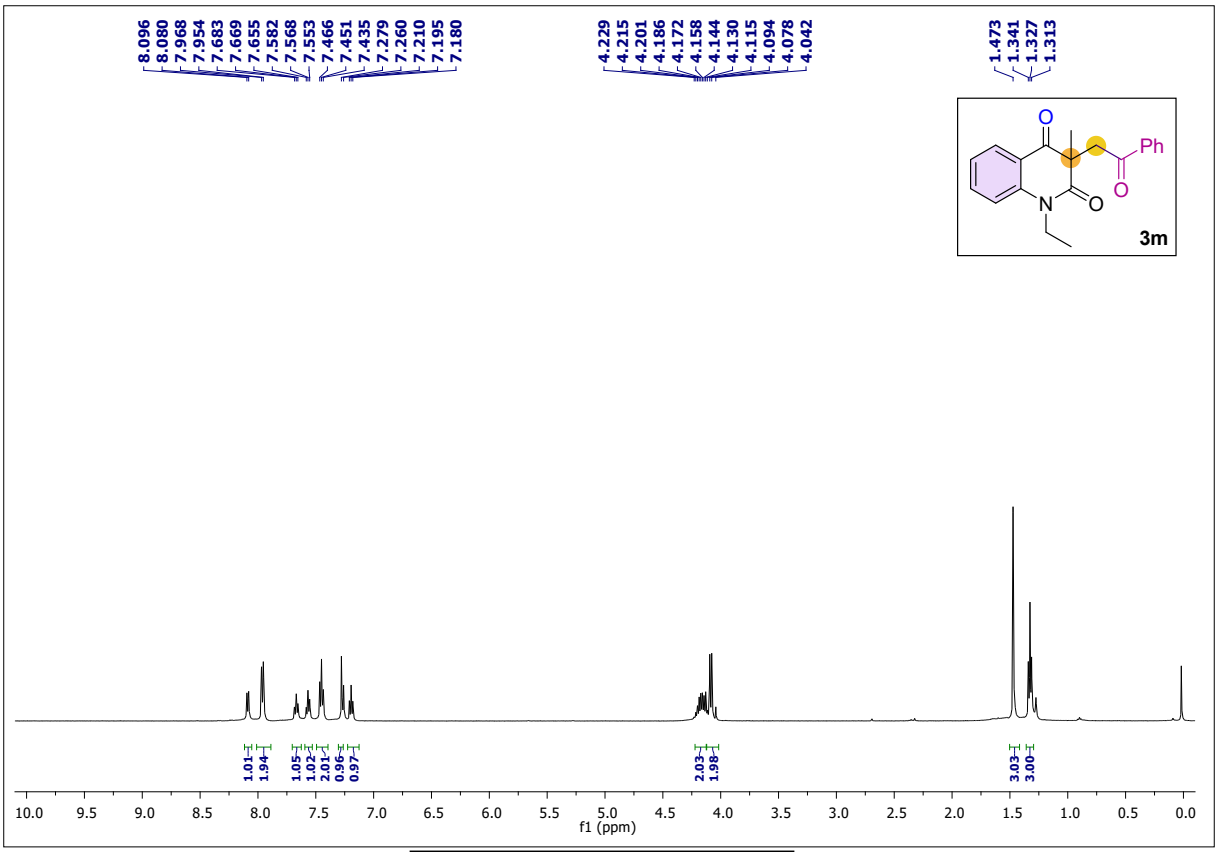
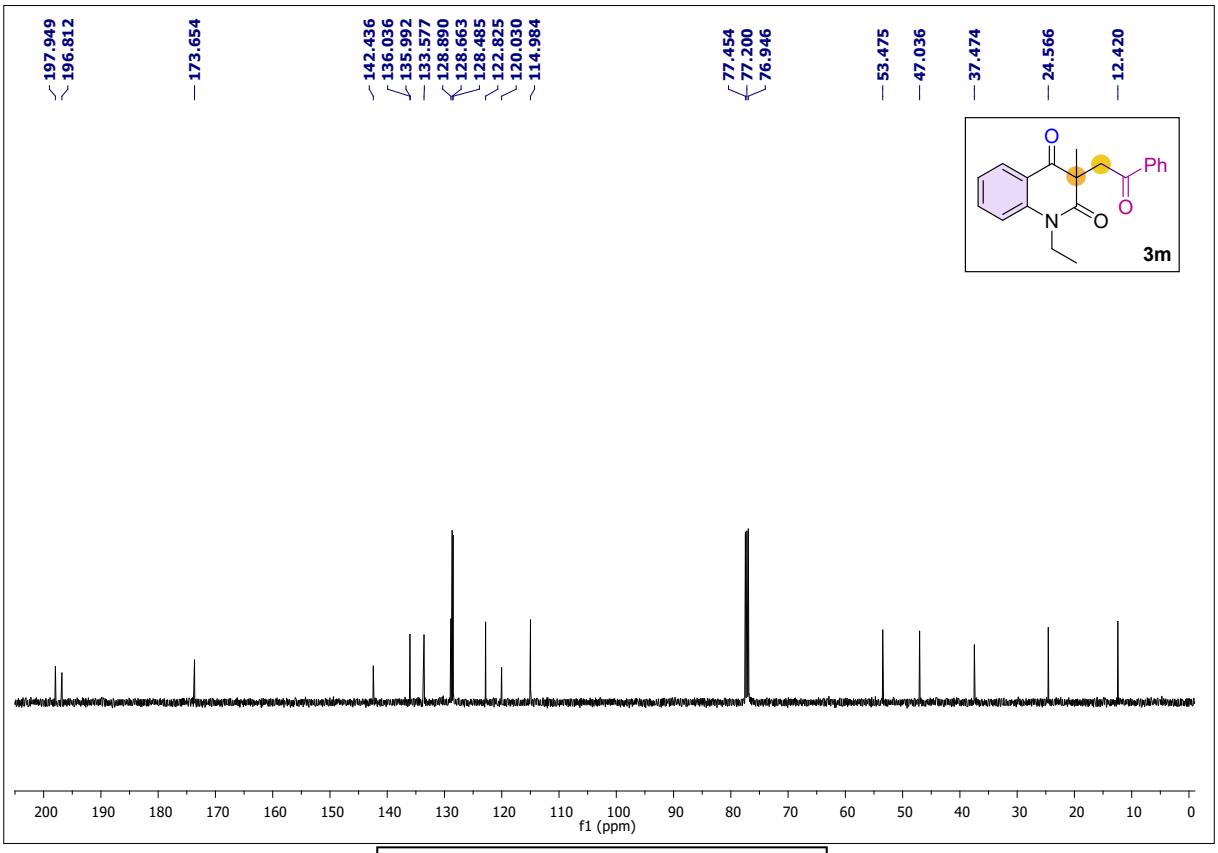
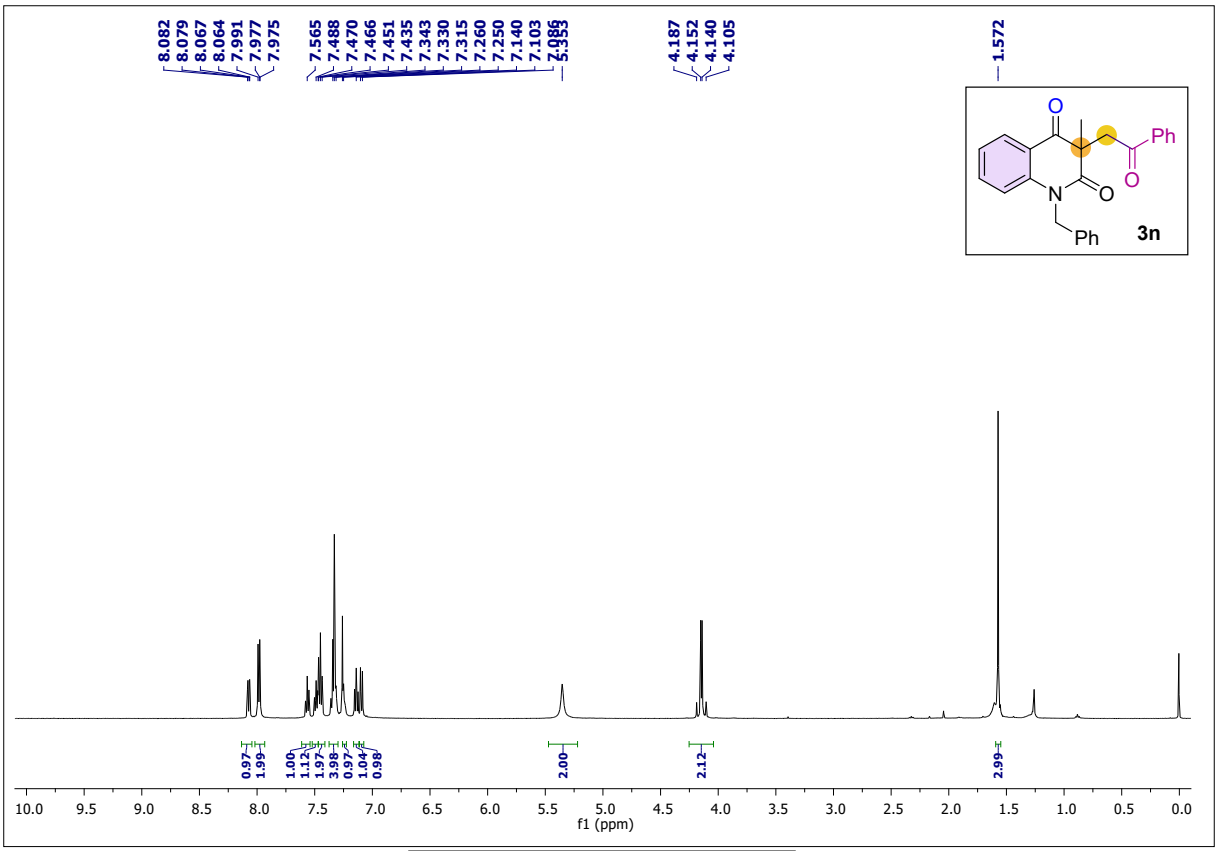


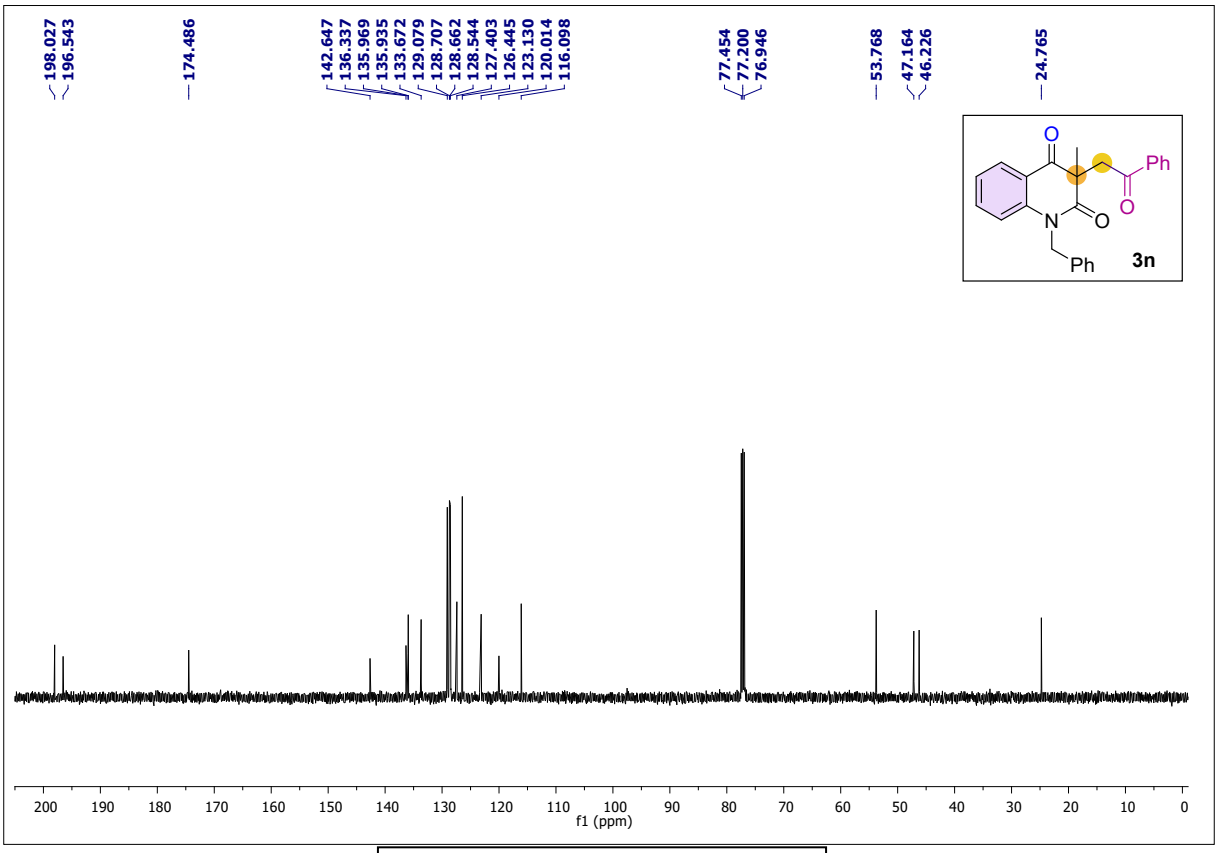
^{1}H NMR (500 MHz, $CDCl_3$)



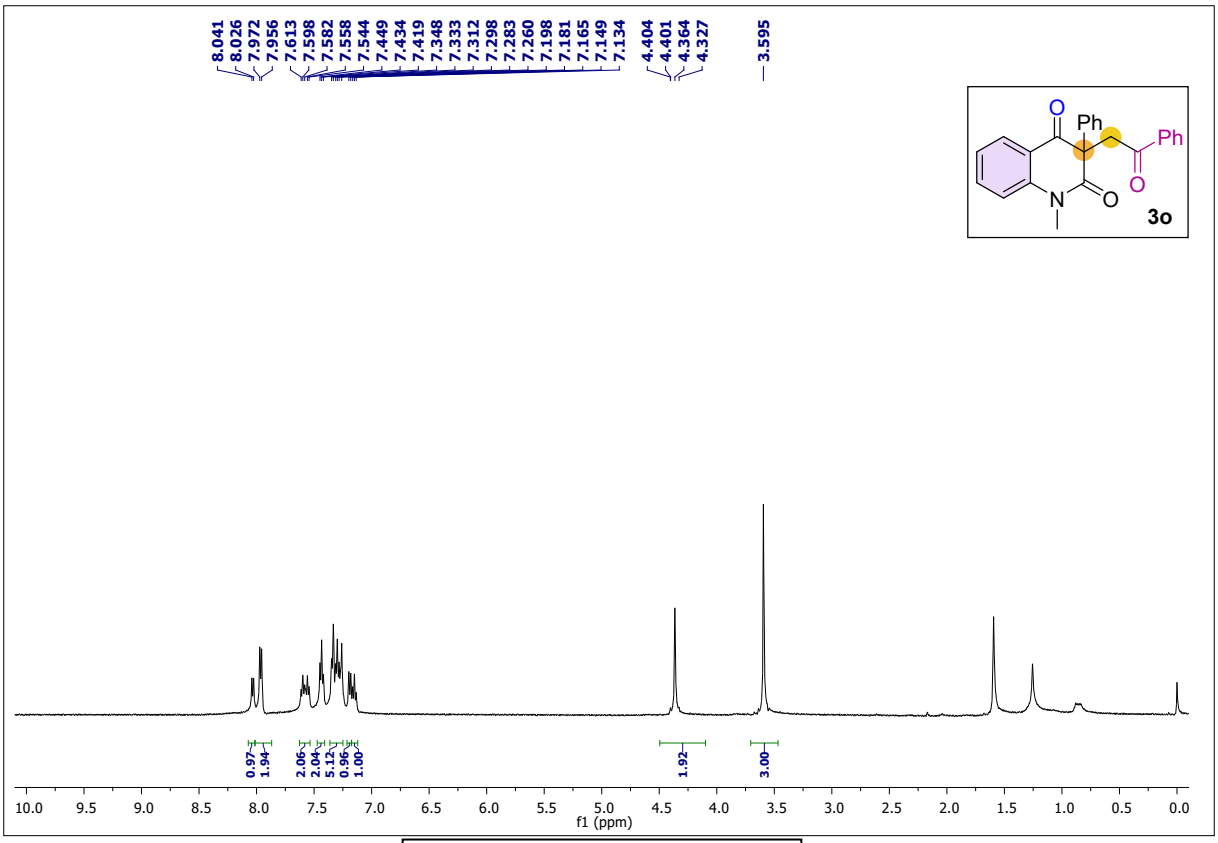
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



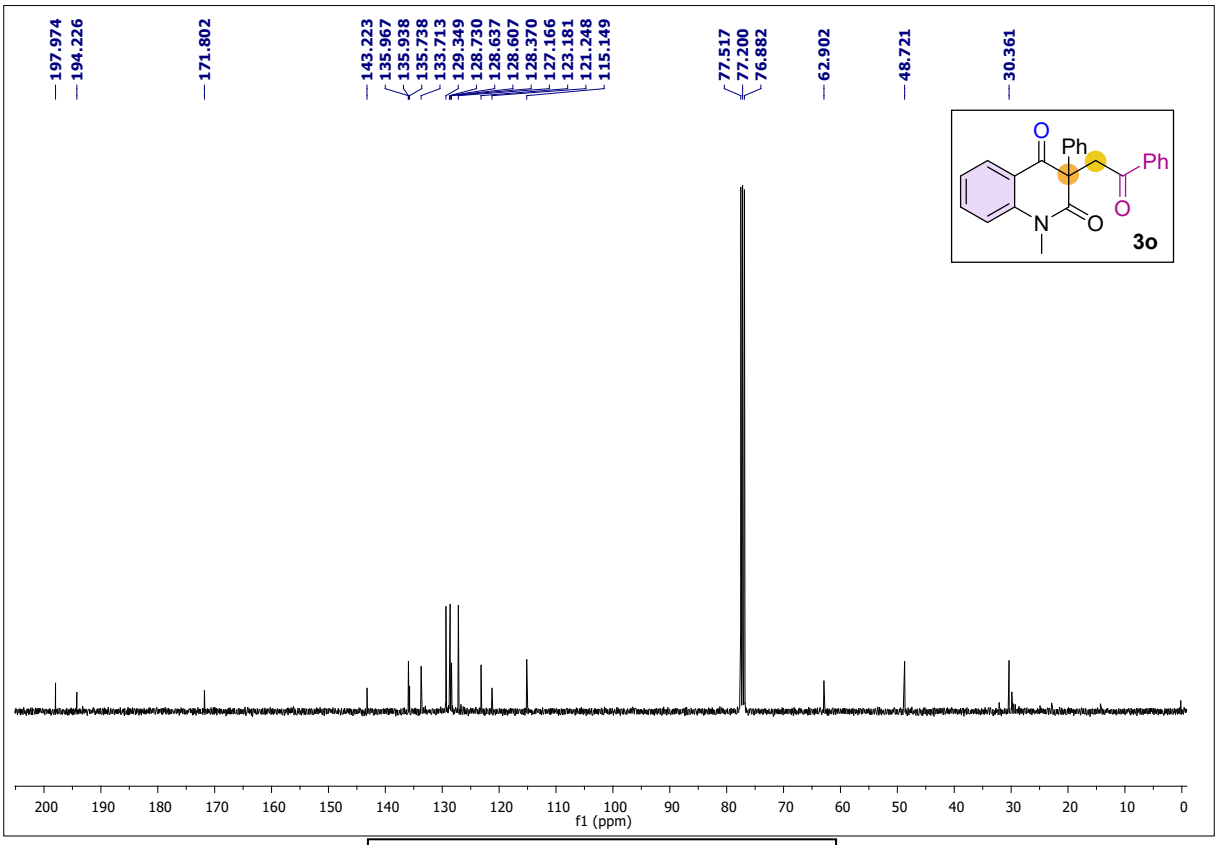
^{1}H NMR (500 MHz, $CDCl_3$)



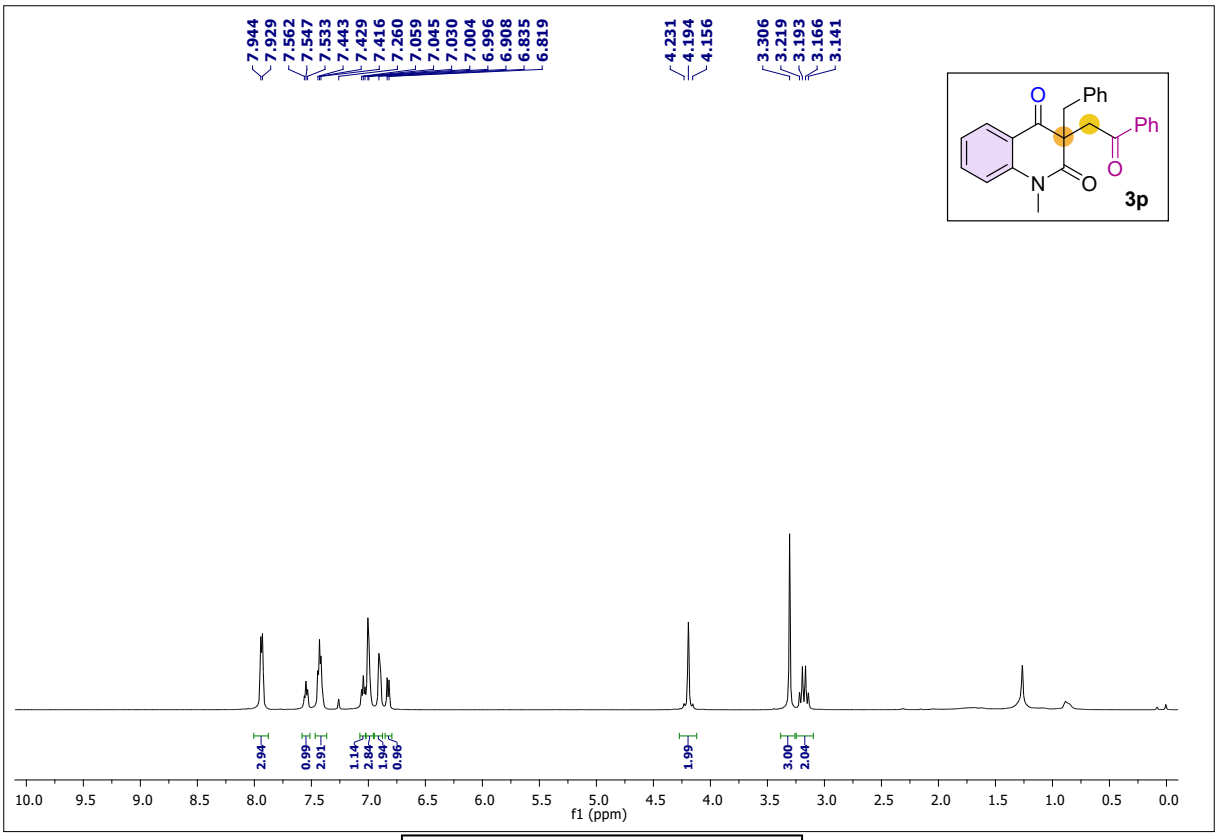
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



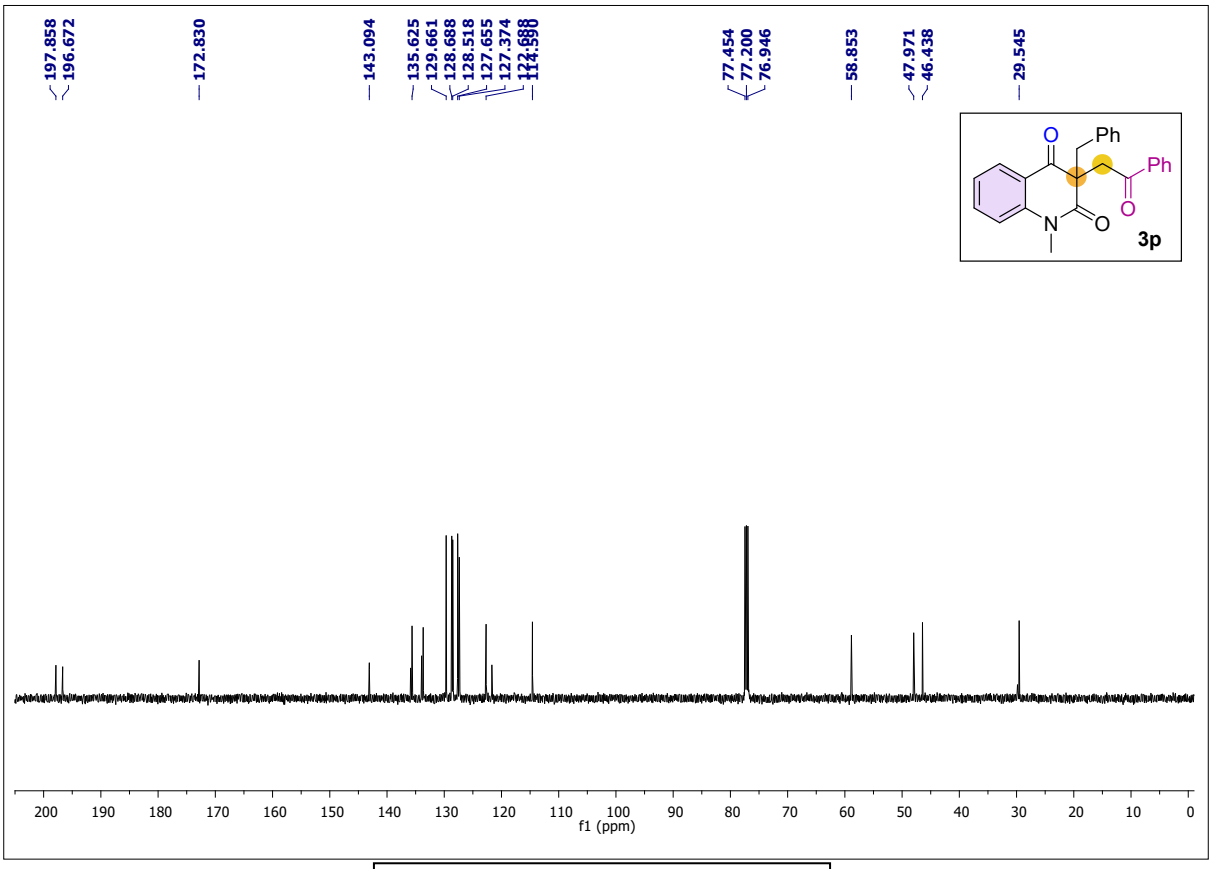
^{1}H NMR (500 MHz, $CDCl_3$)



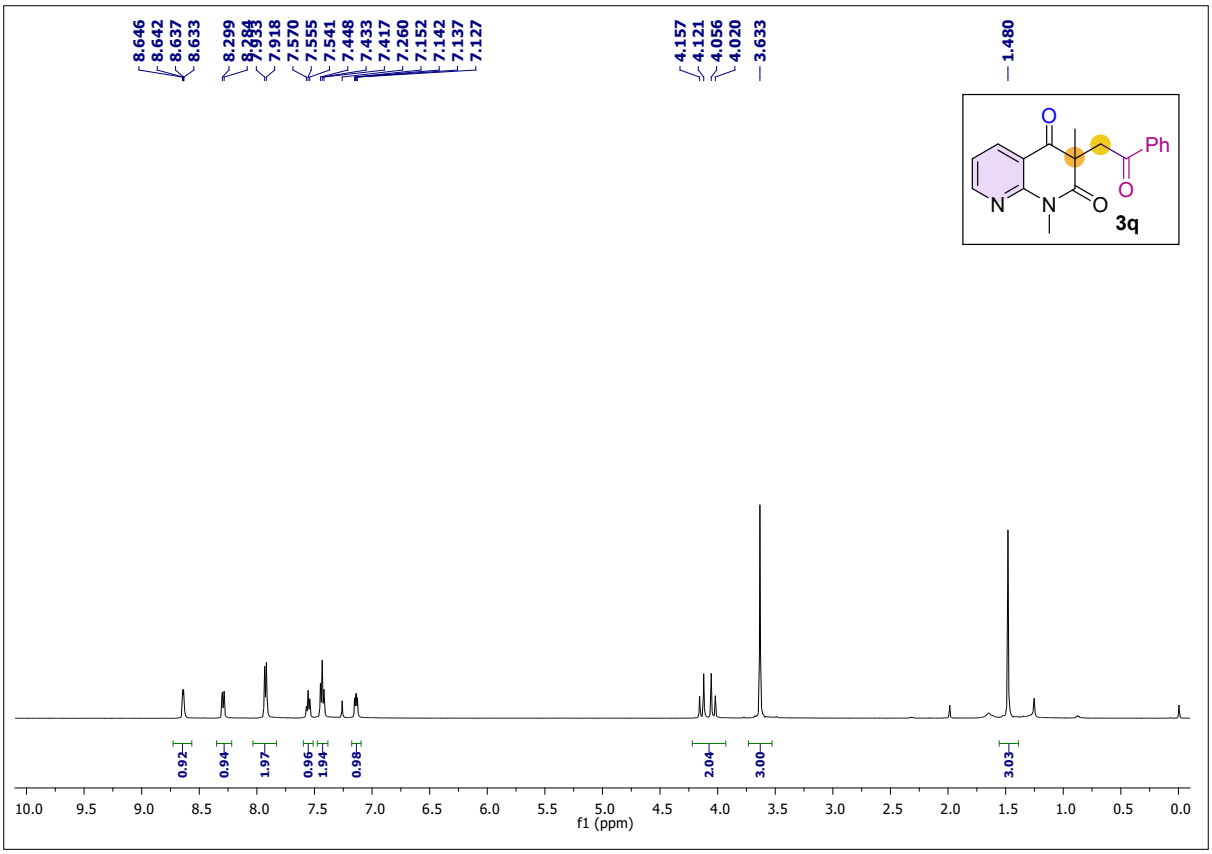
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



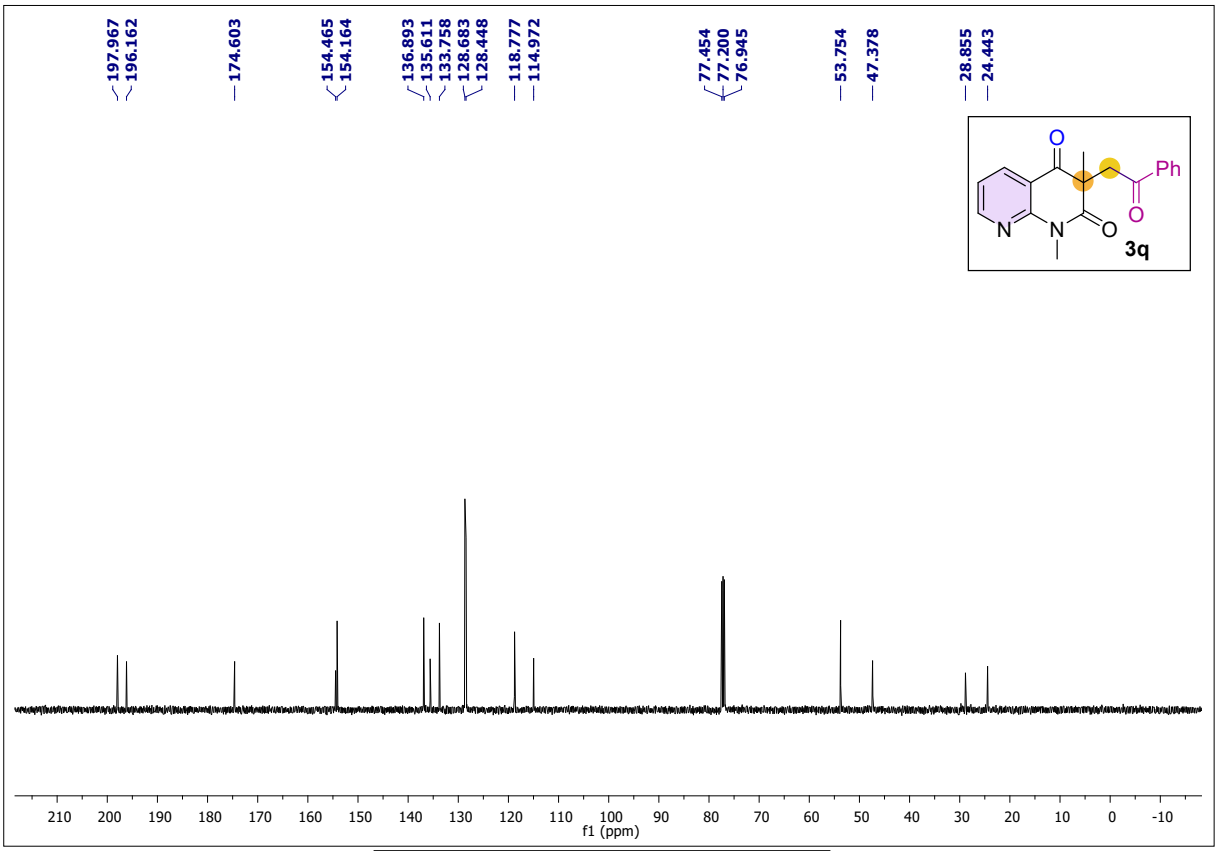
^{1}H NMR (500 MHz, $CDCl_3$)



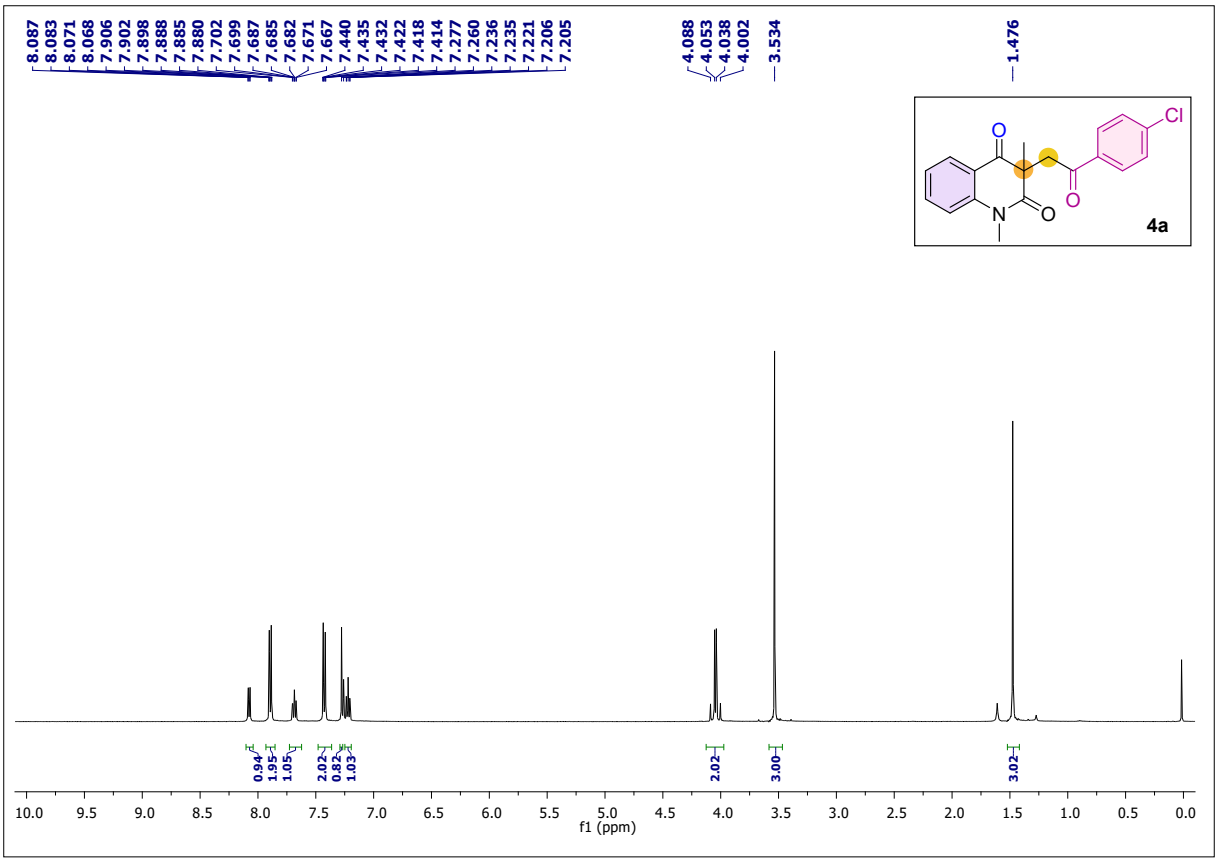
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



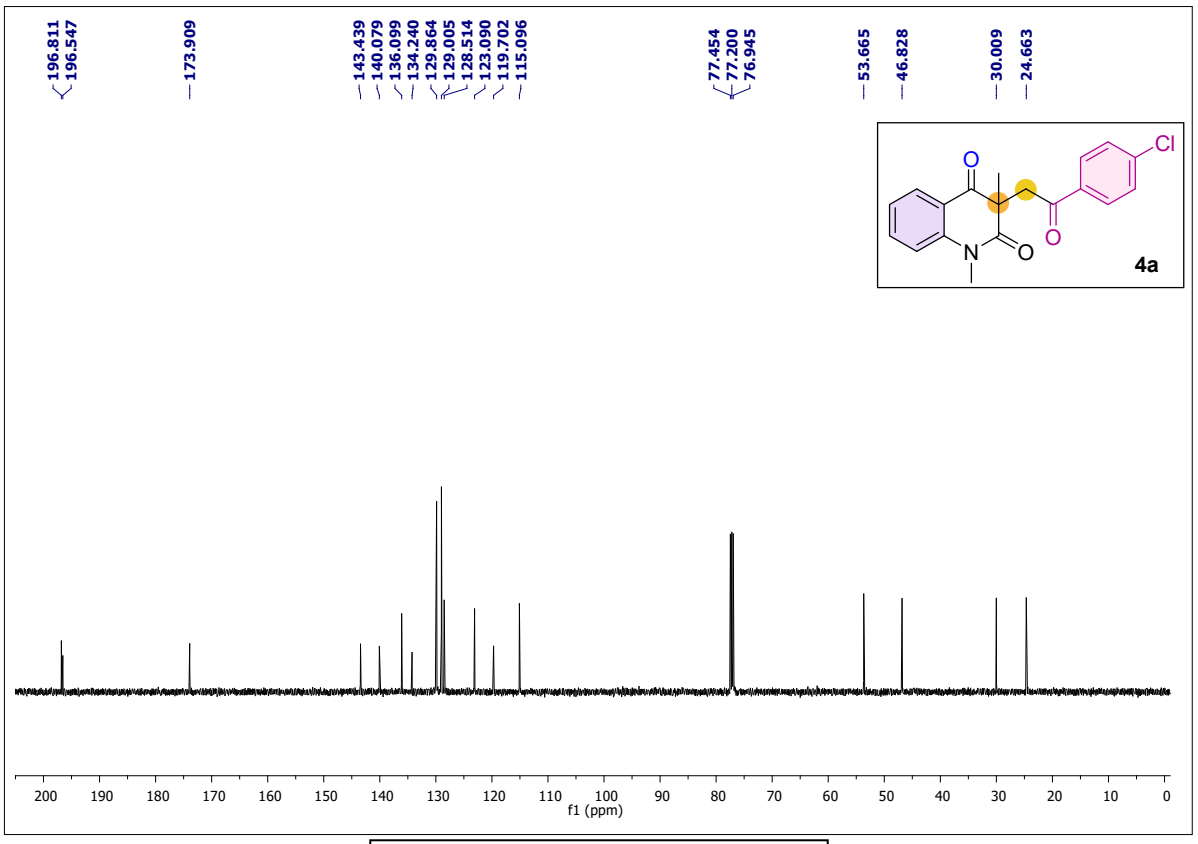
^{1}H NMR (500 MHz, $CDCl_3$)



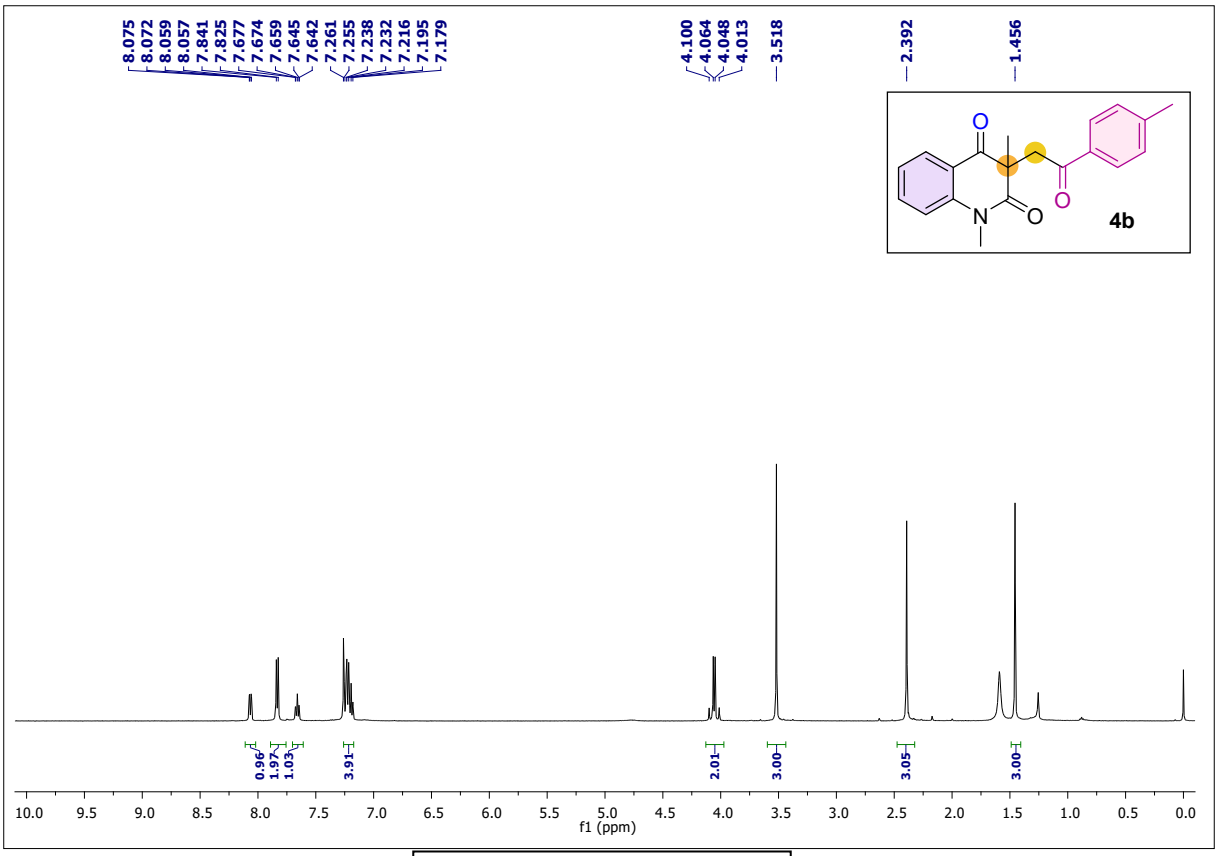
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



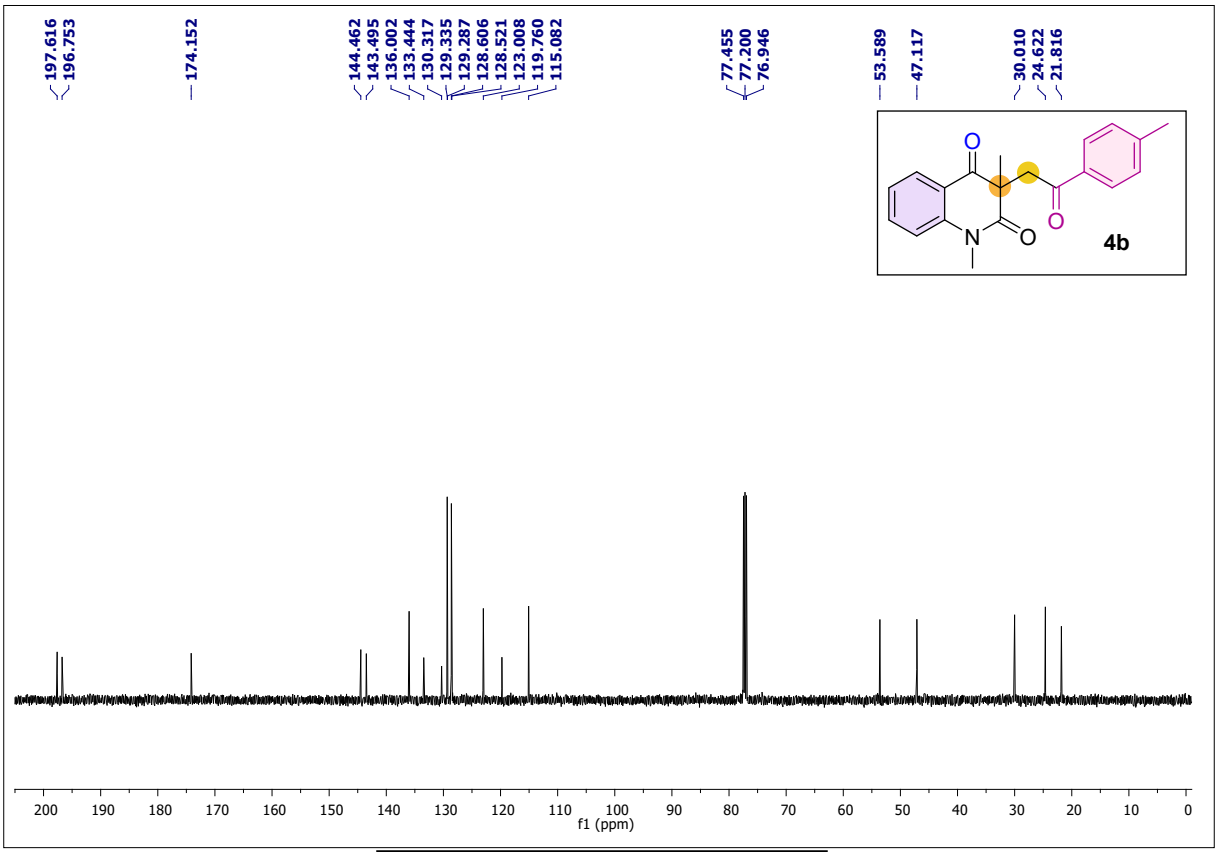
^{1}H NMR (500 MHz, $CDCl_3$)



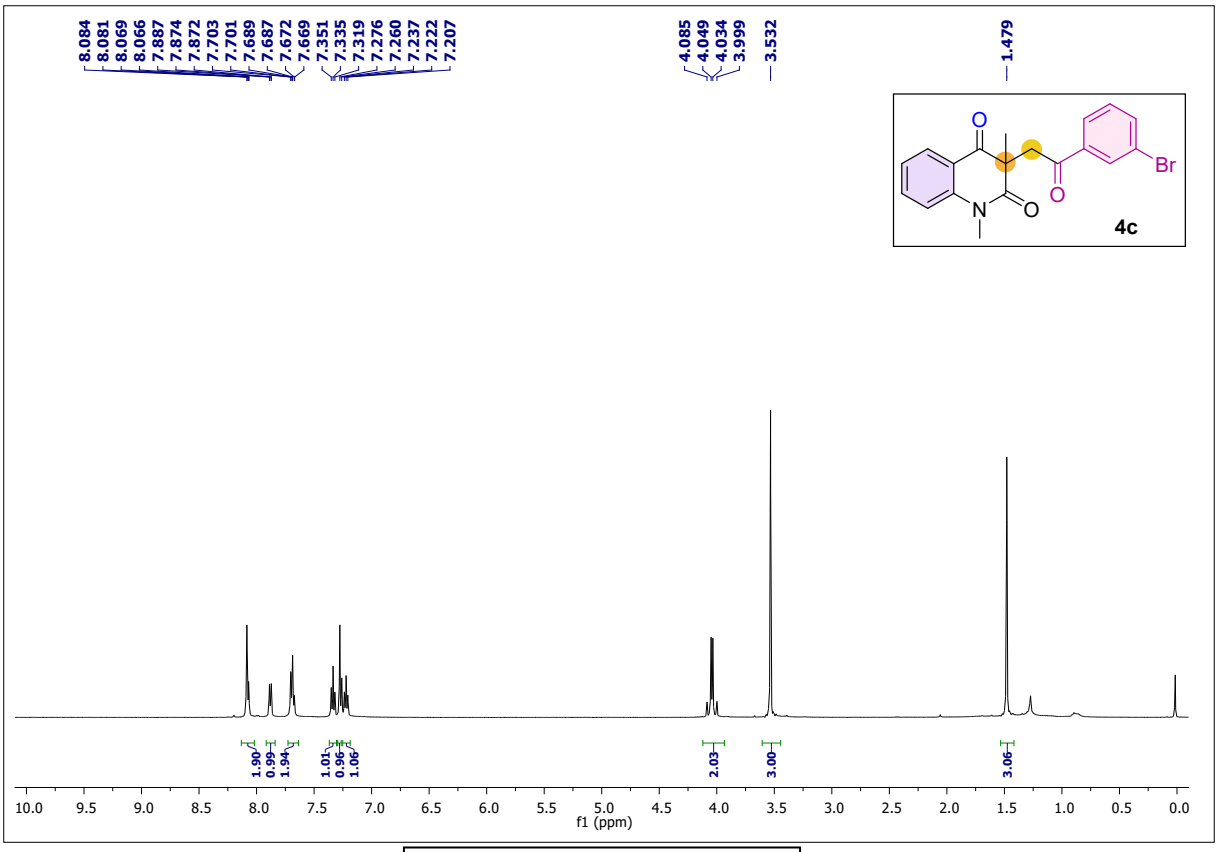
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



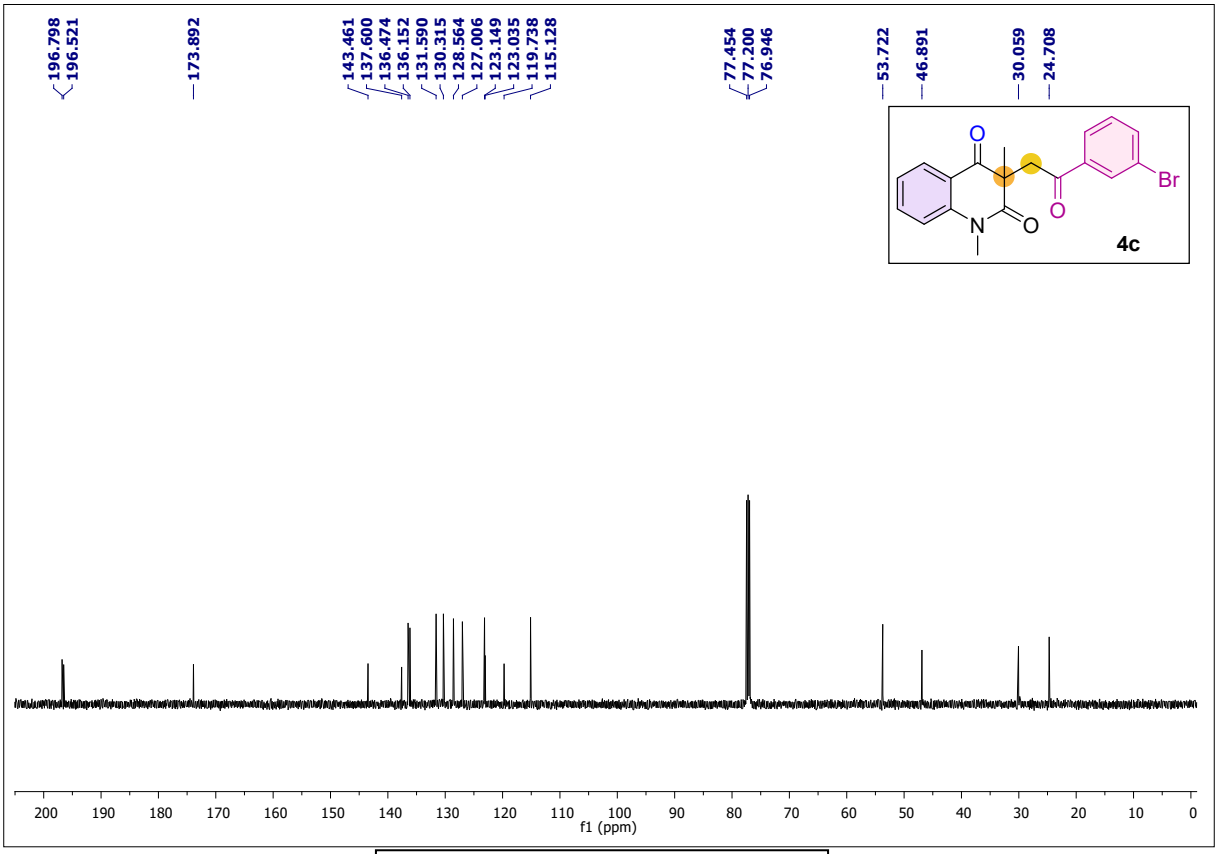
^{1}H NMR (500 MHz, $CDCl_3$)



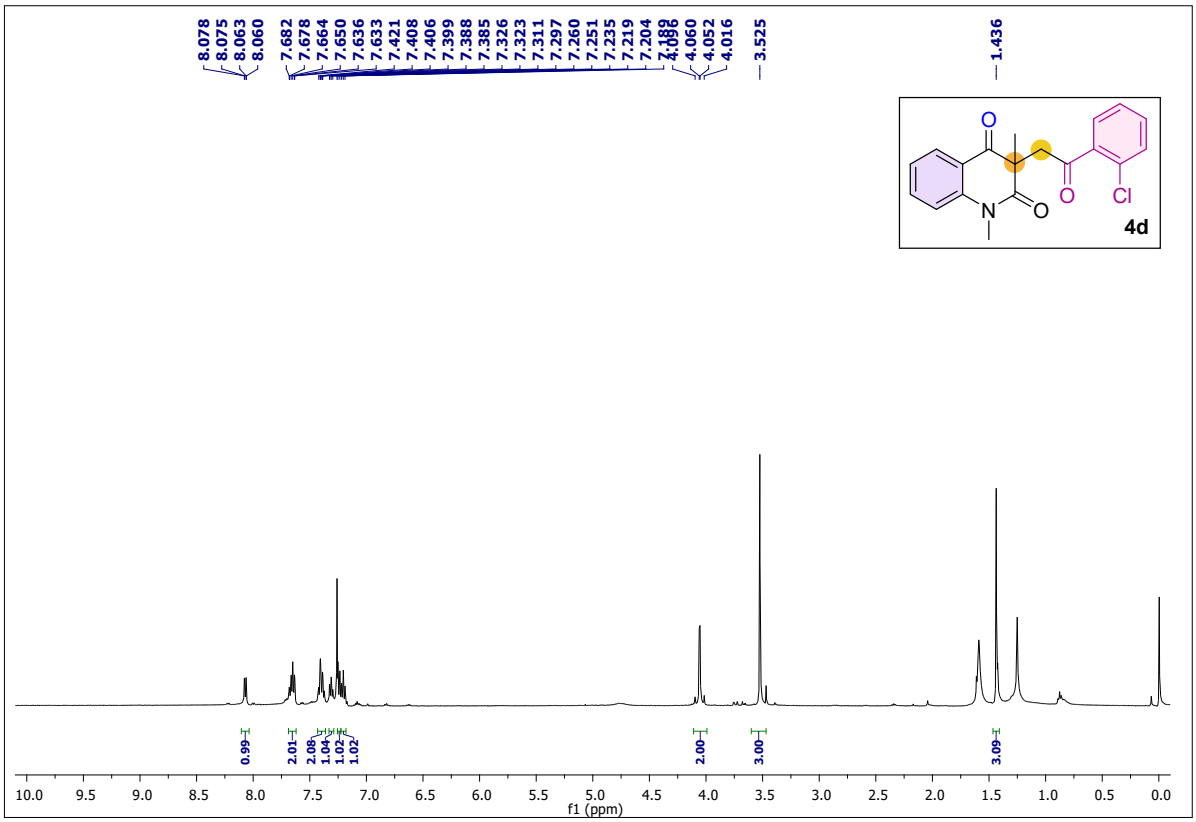
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



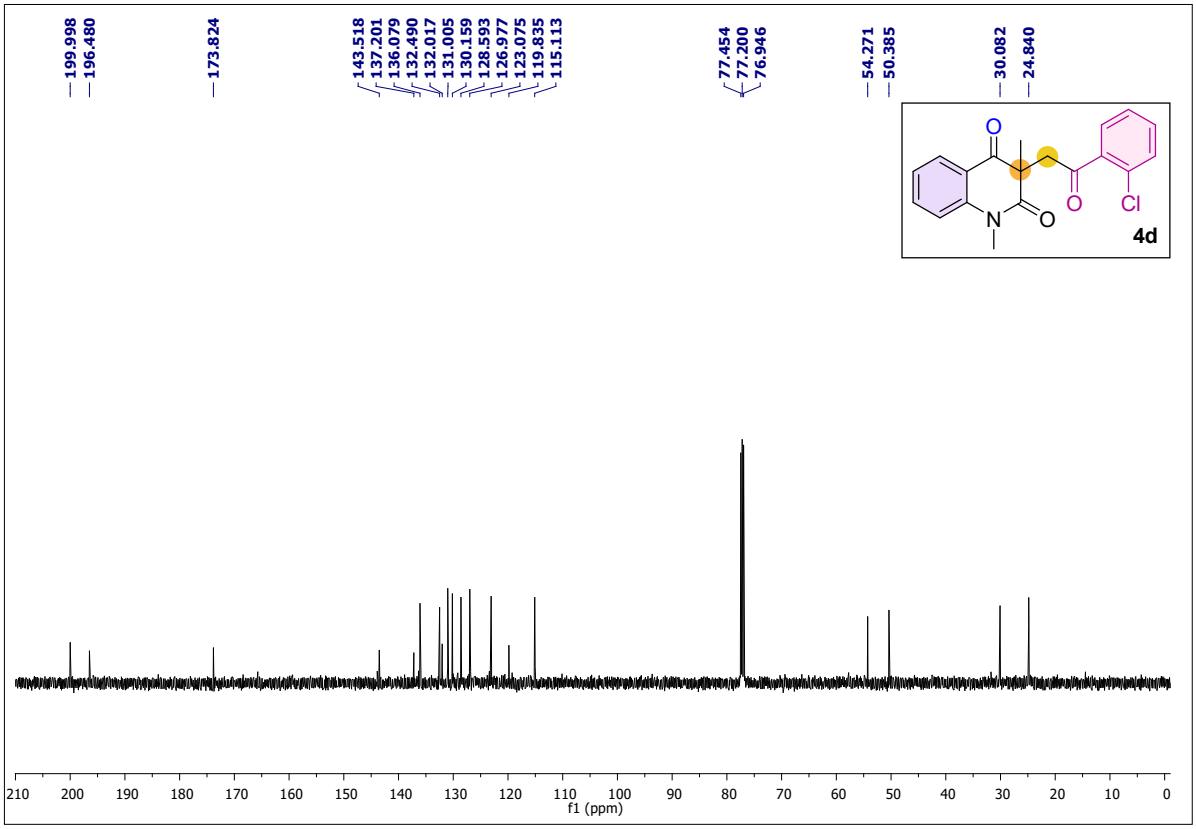
^{1}H NMR (500 MHz, $CDCl_3$)



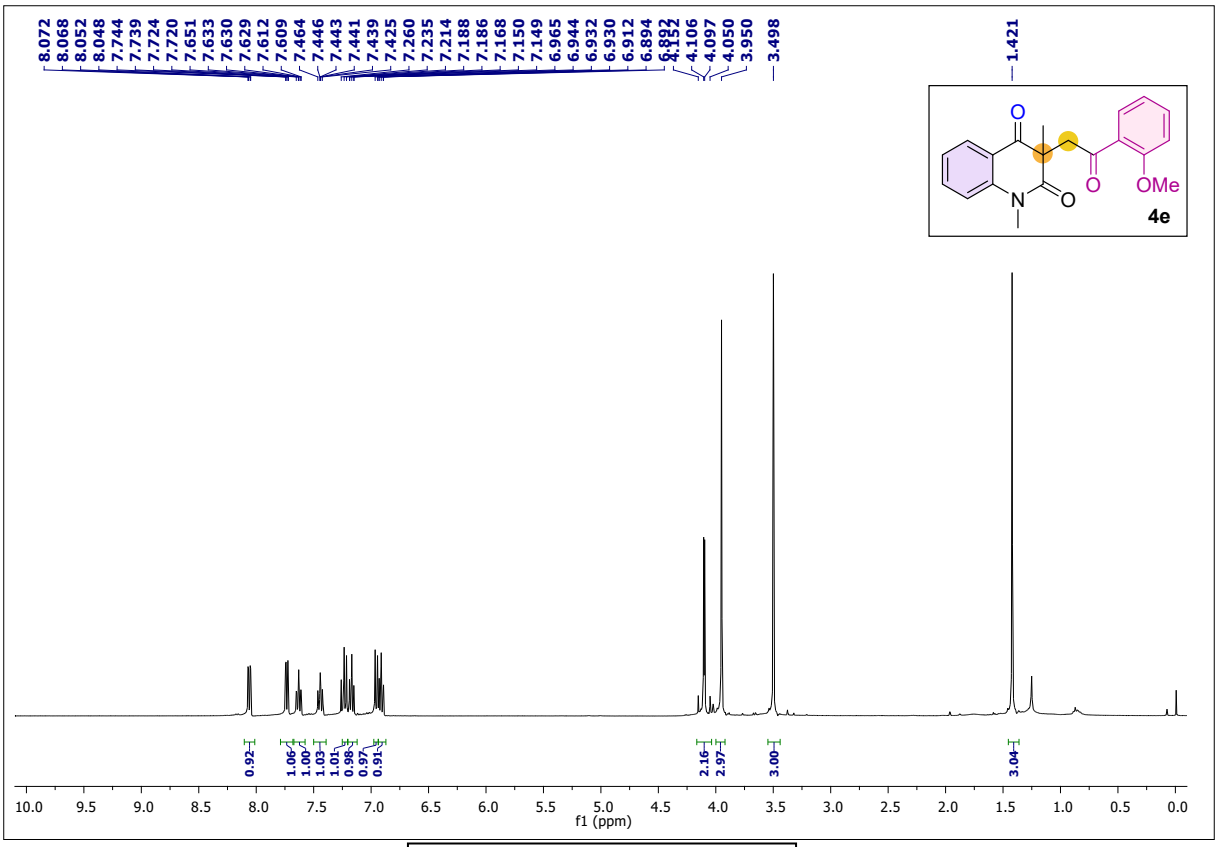
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



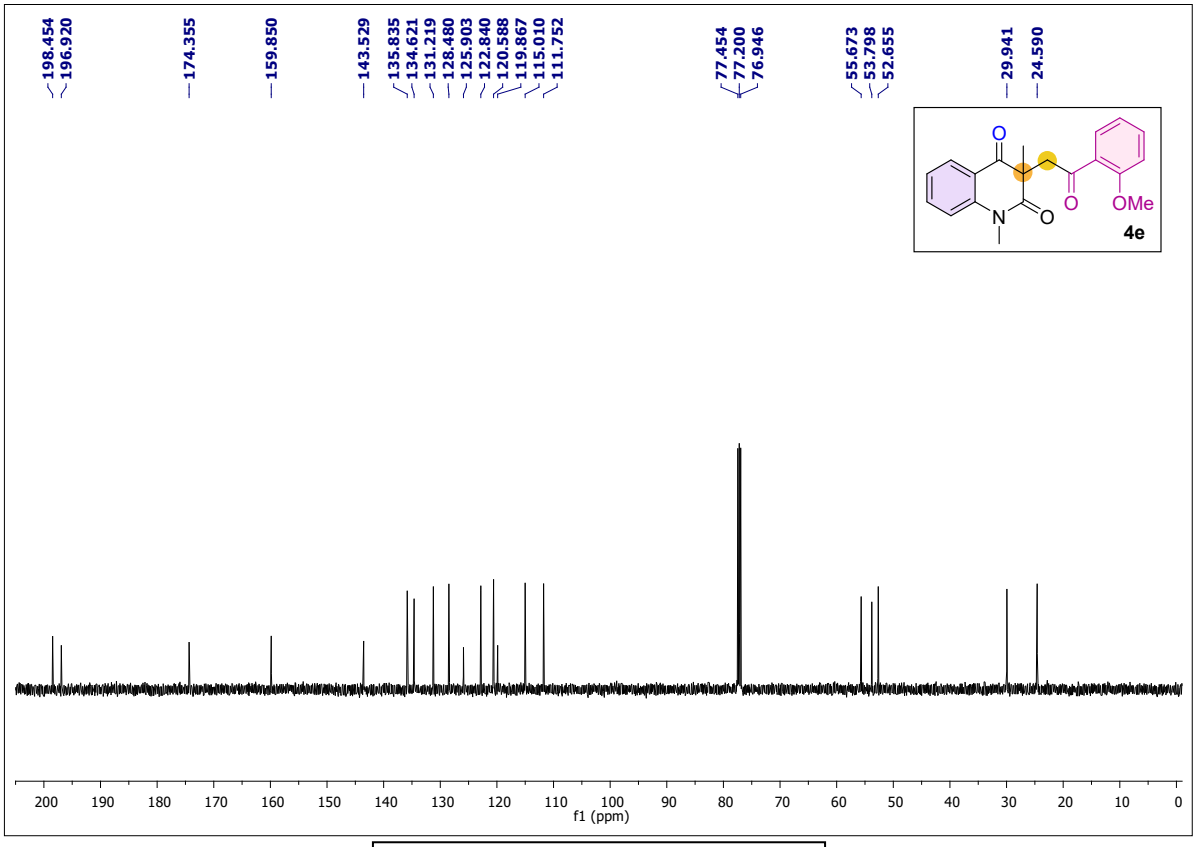
^{1}H NMR (500 MHz, $CDCl_3$)



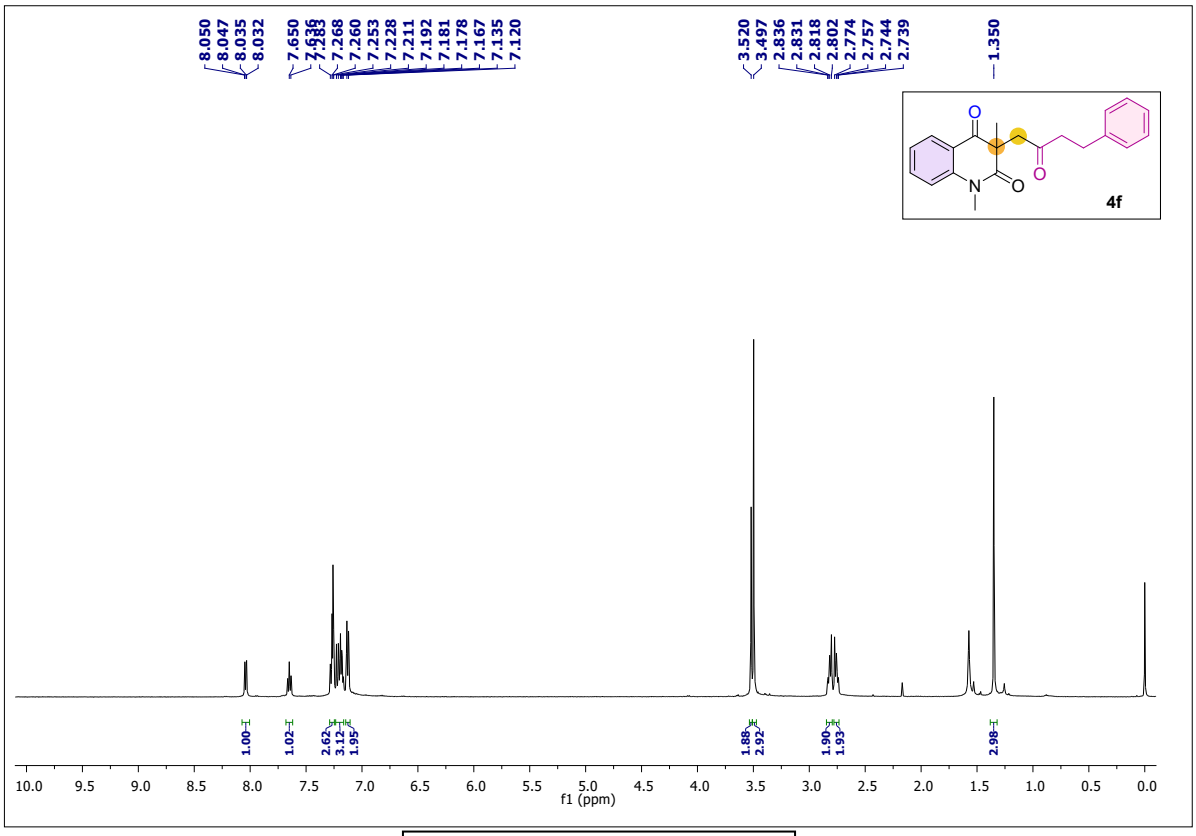
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



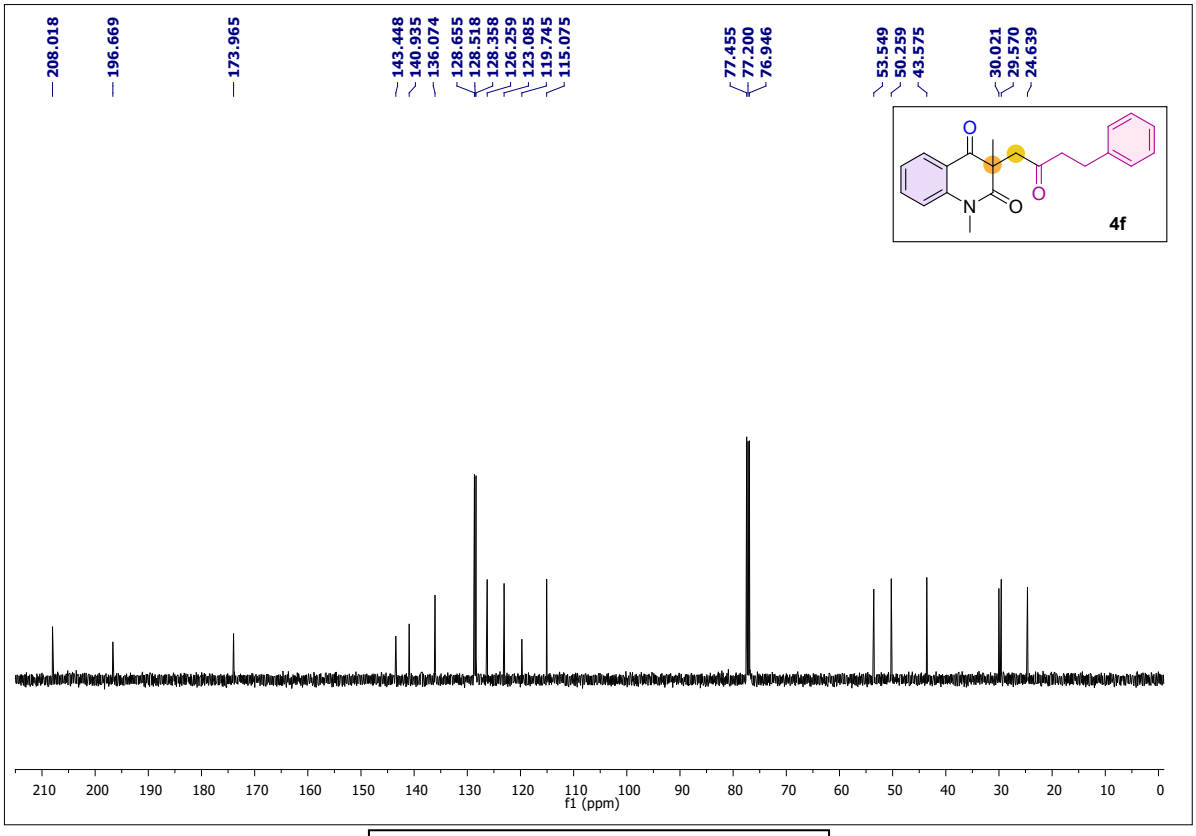
^{1}H NMR (400 MHz, $CDCl_3$)



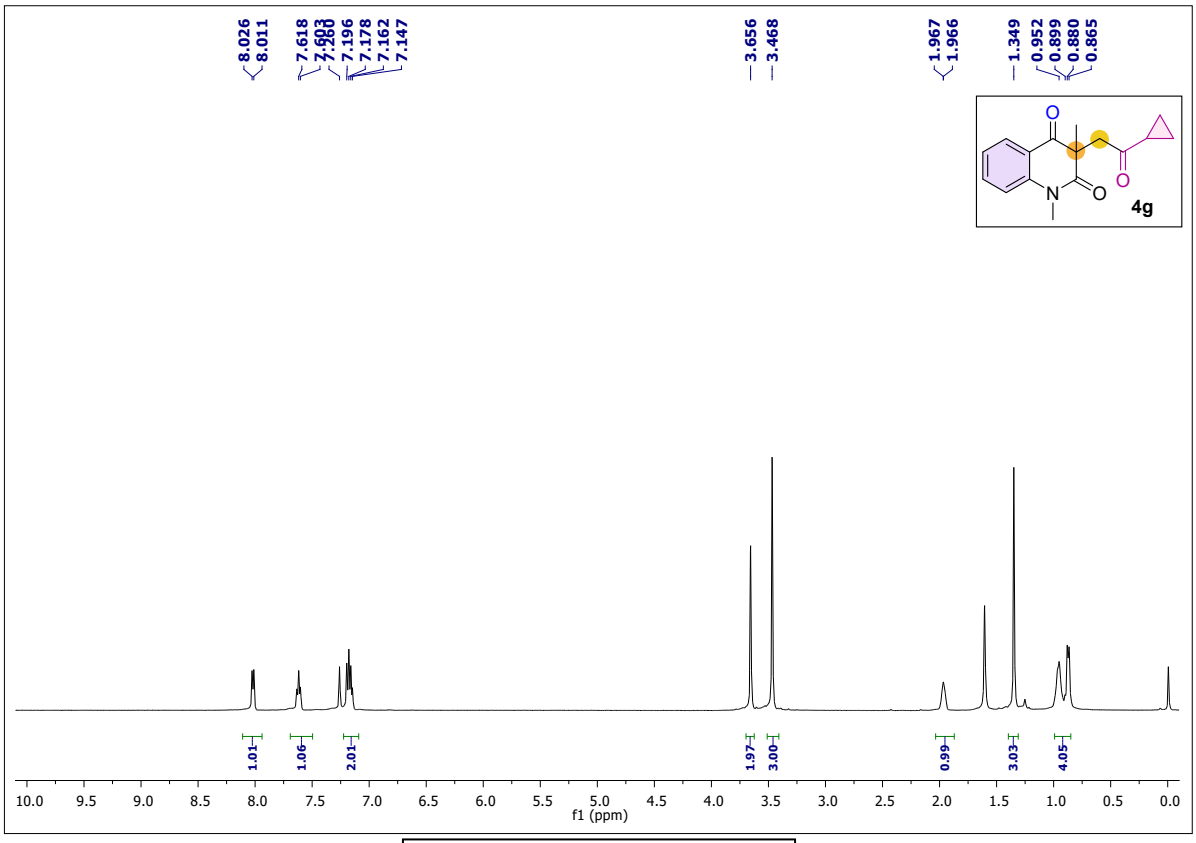
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



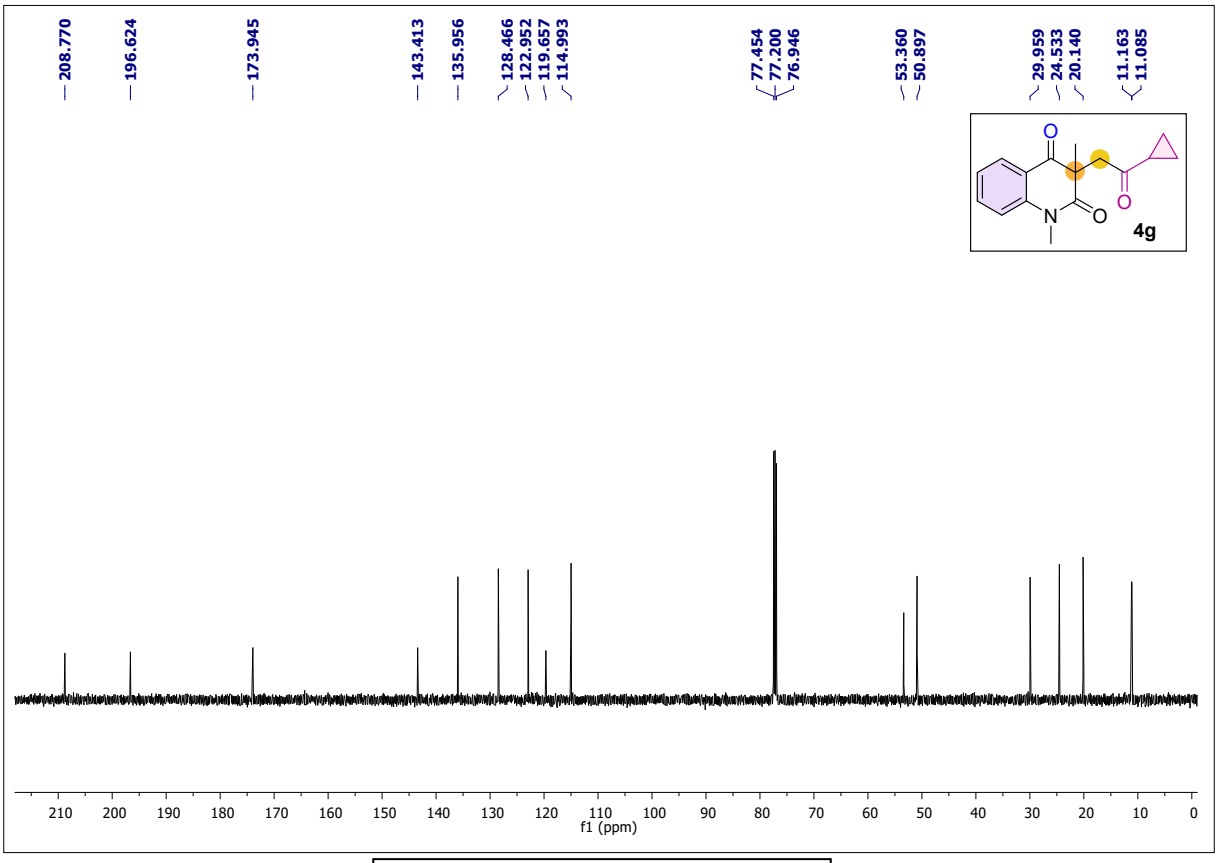
^{1}H NMR (500 MHz, $CDCl_3$)



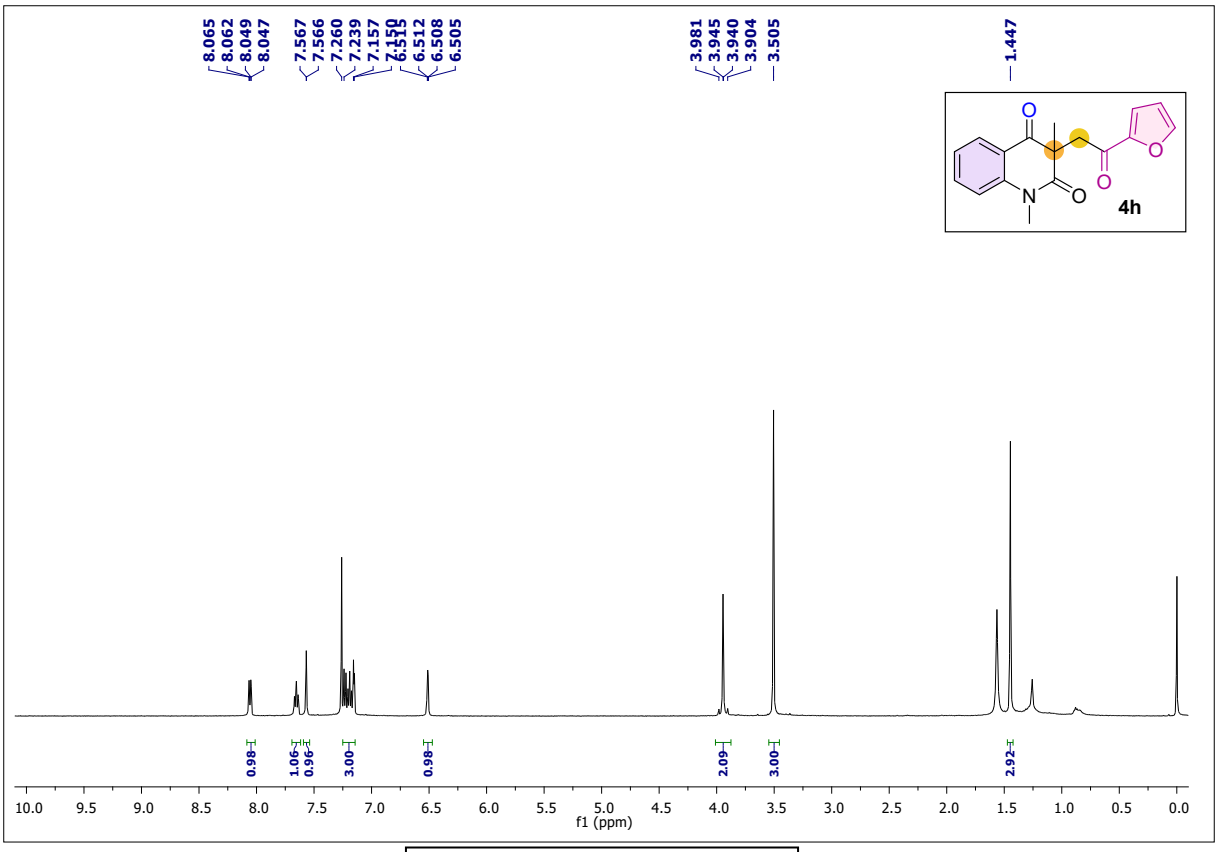
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



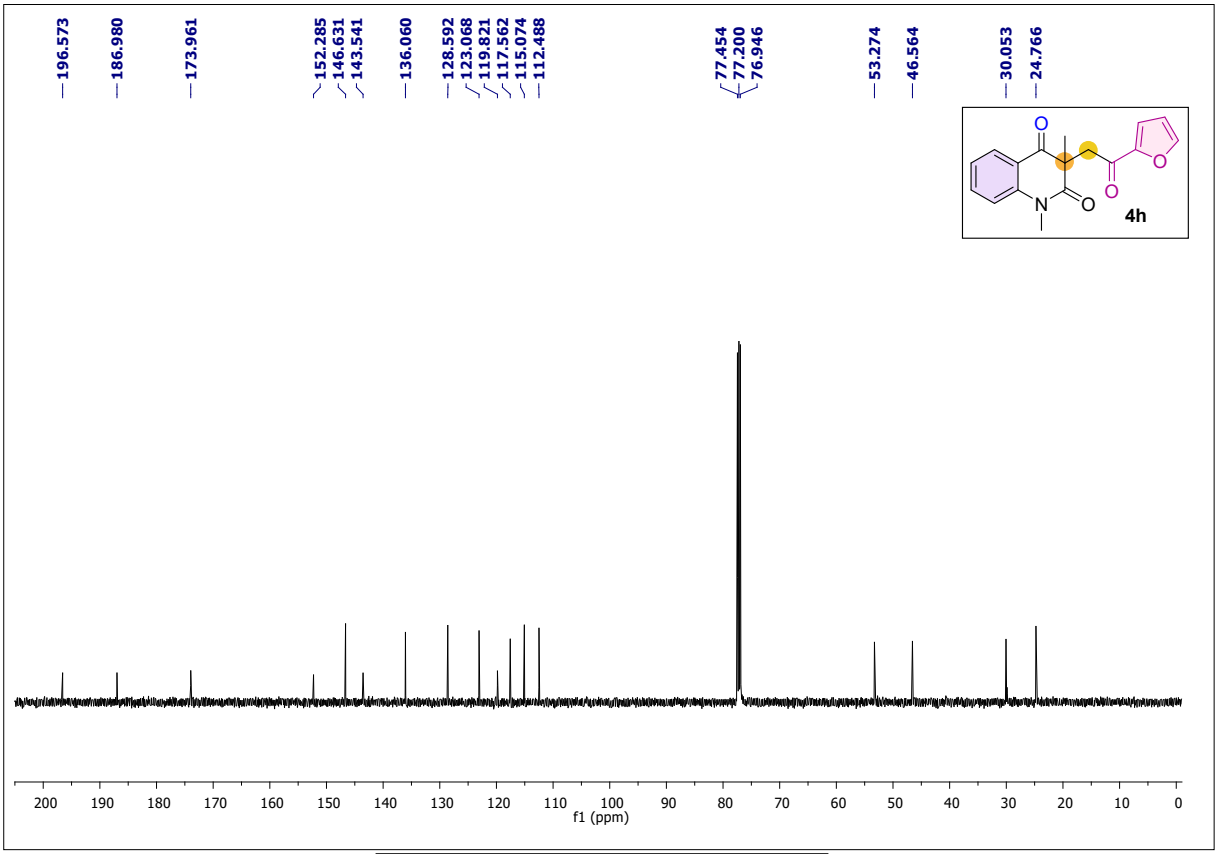
^{1}H NMR (500 MHz, $CDCl_3$)



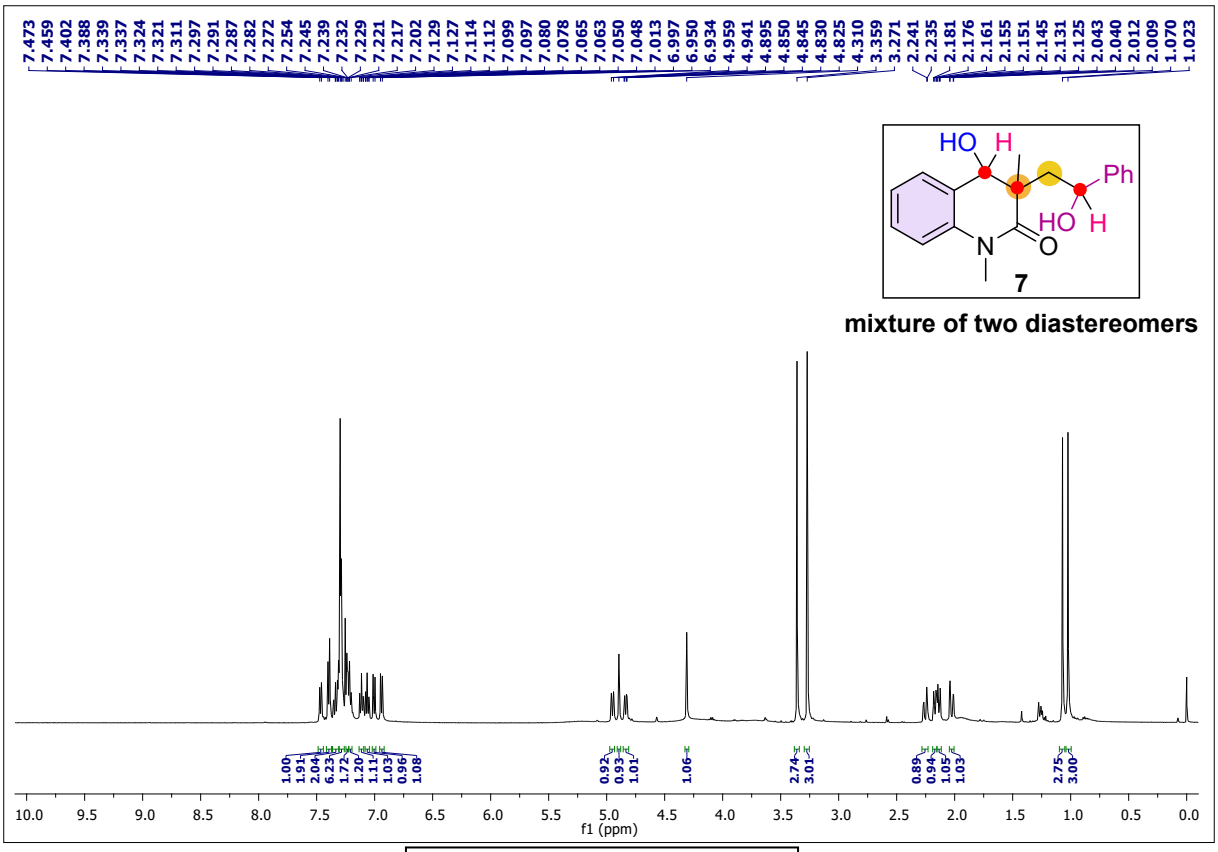
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



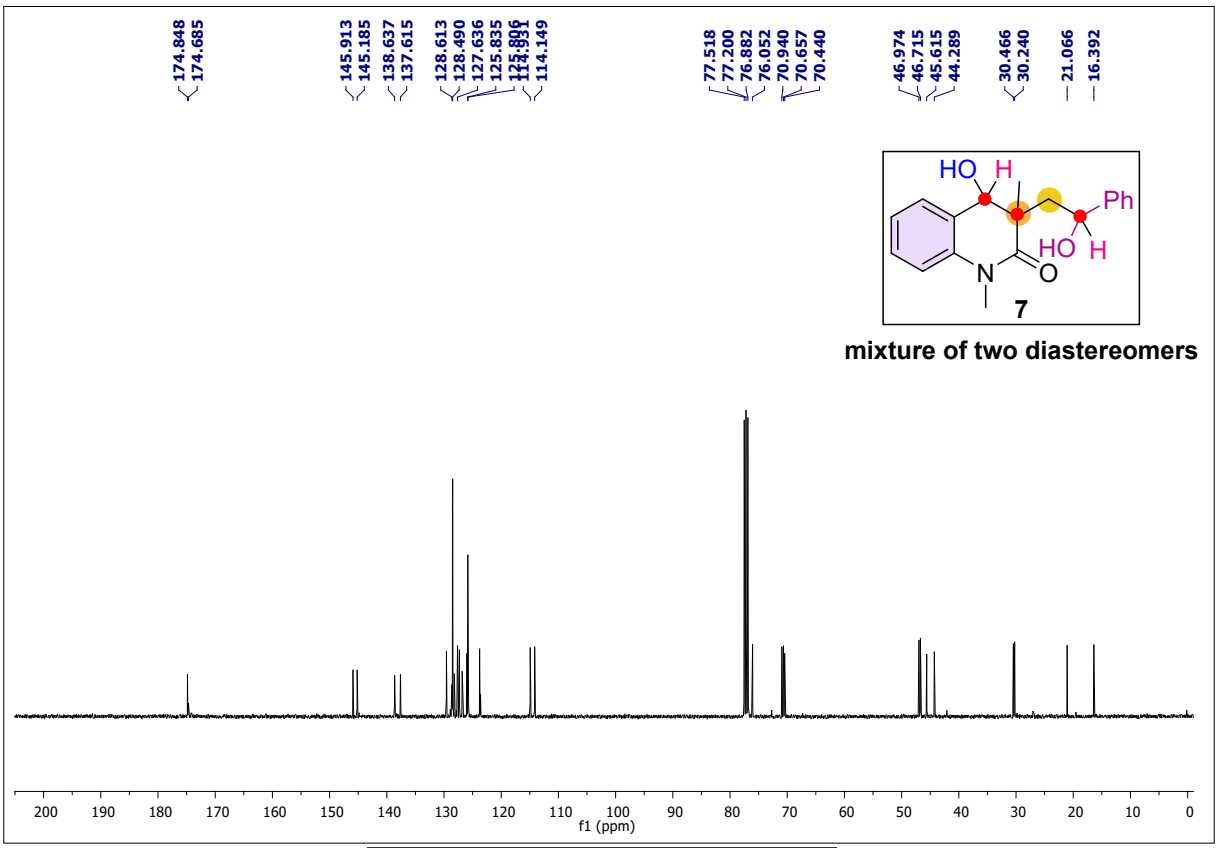
^{1}H NMR (500 MHz, $CDCl_3$)



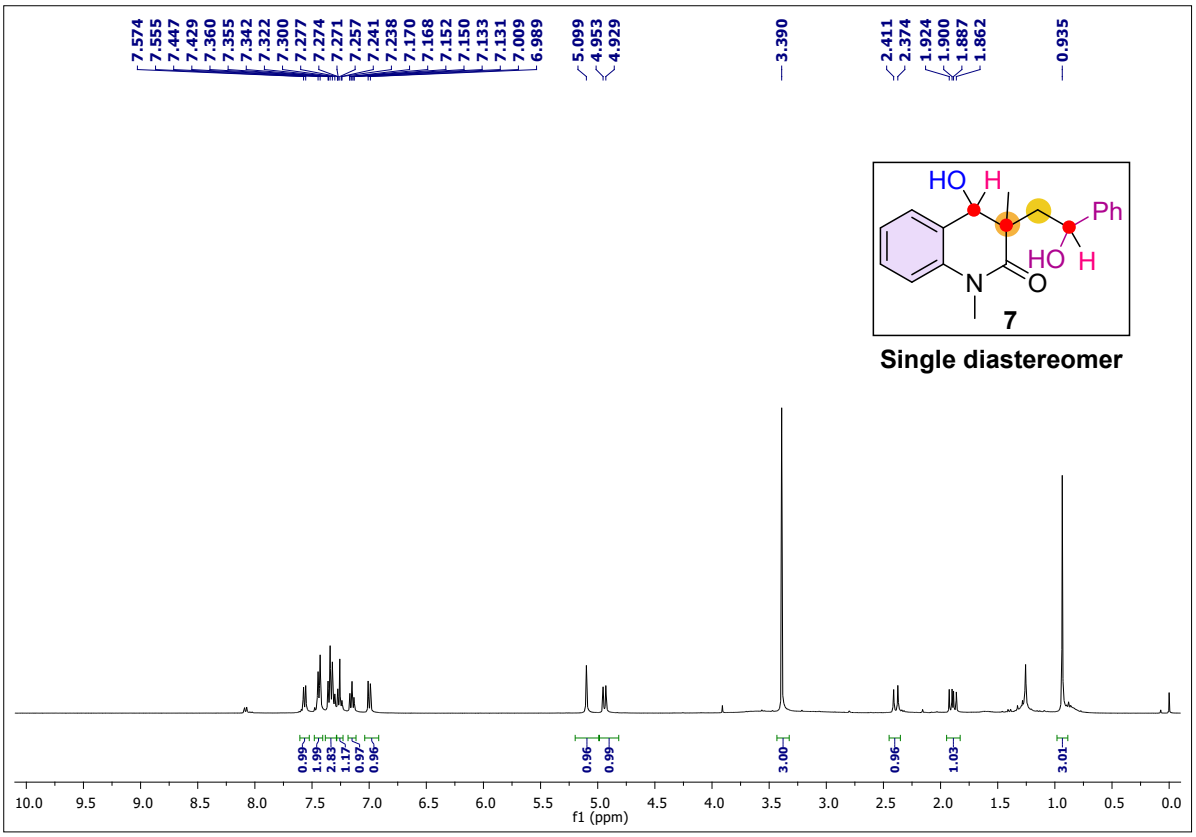
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



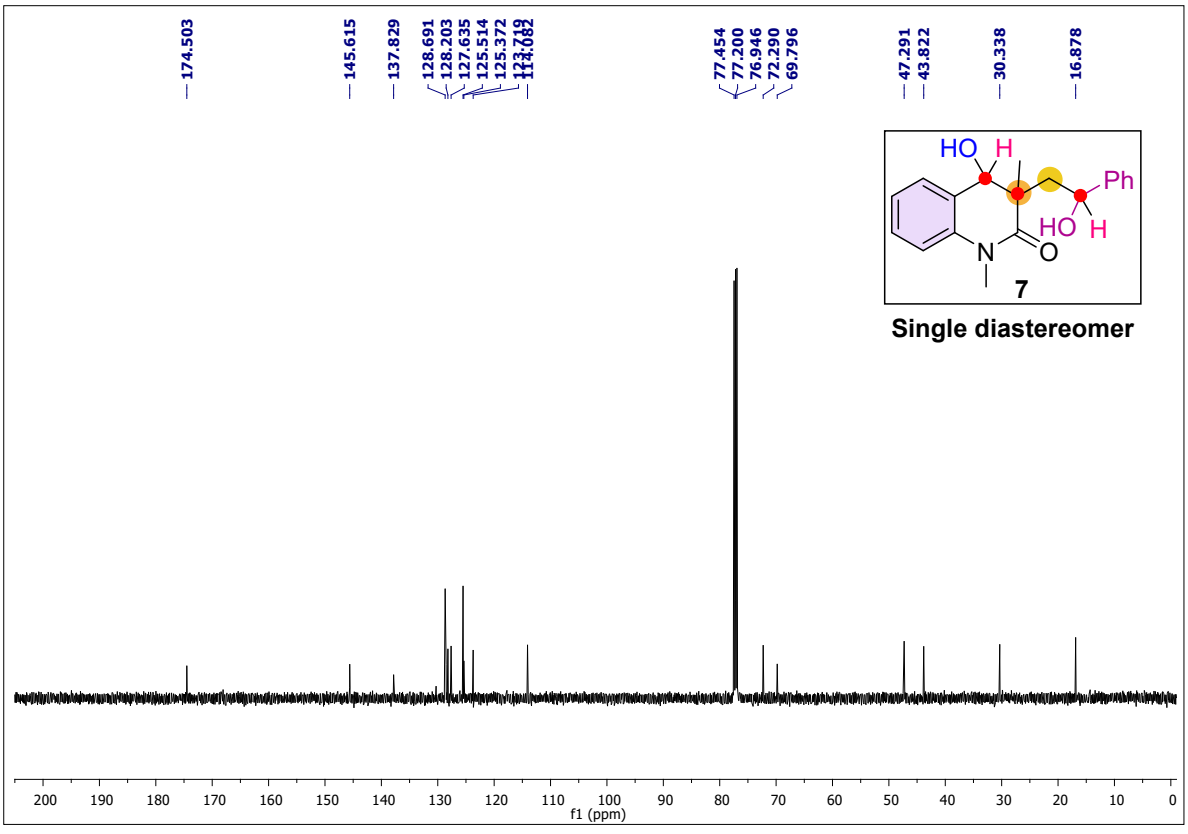
^{1}H NMR (500 MHz, $CDCl_3$)



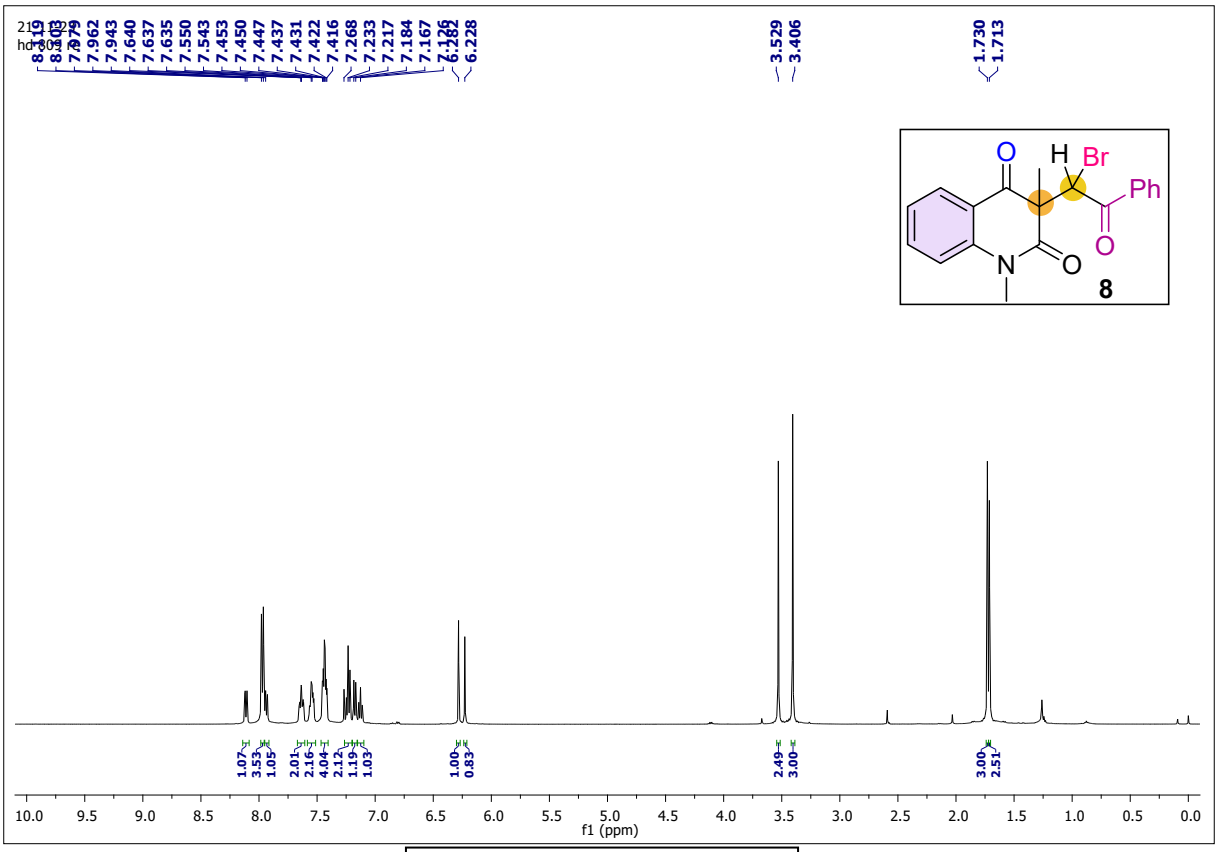
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



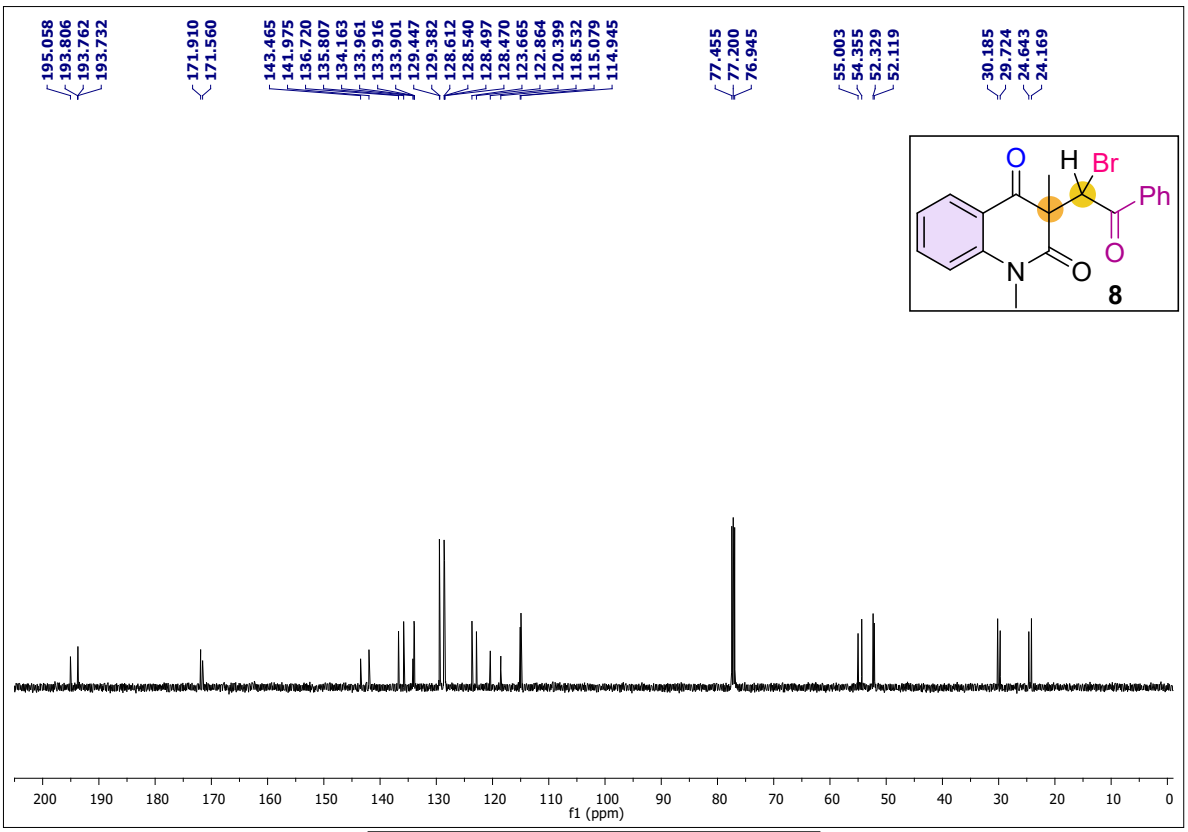
^{1}H NMR (400 MHz, $CDCl_3$)



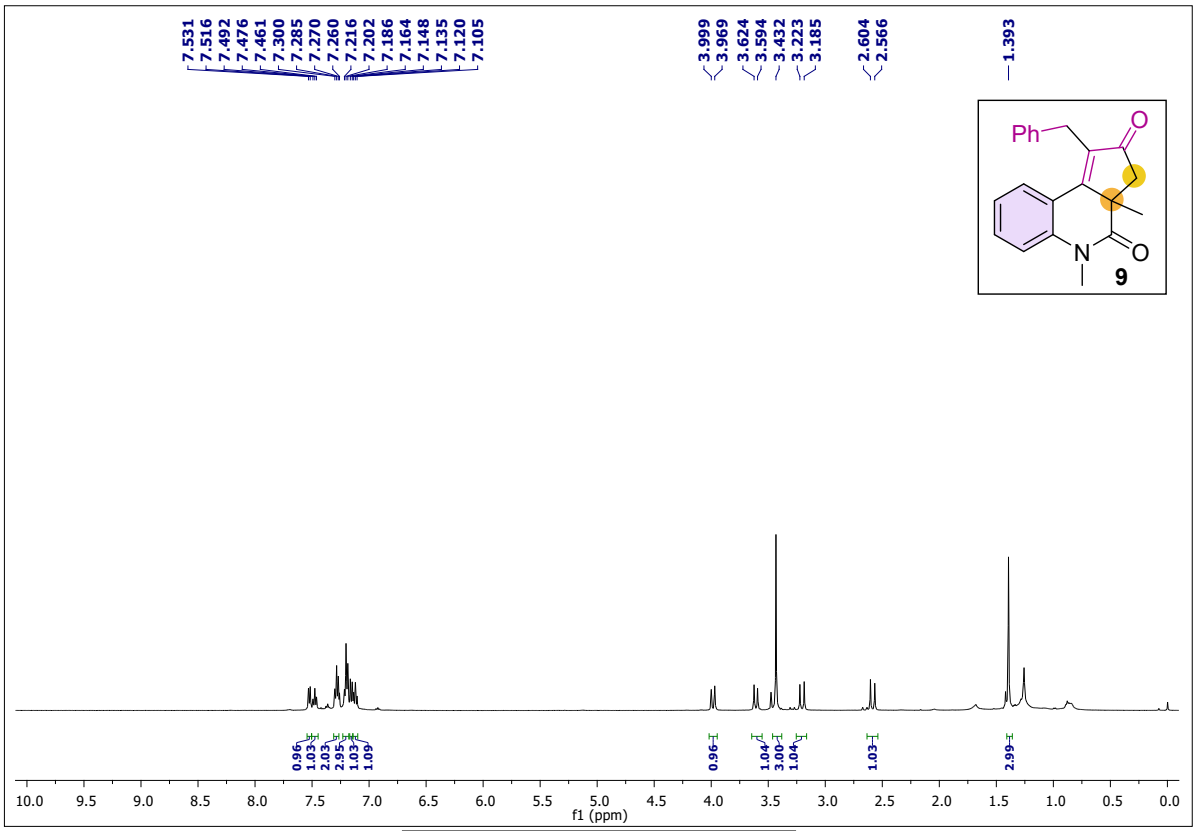
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



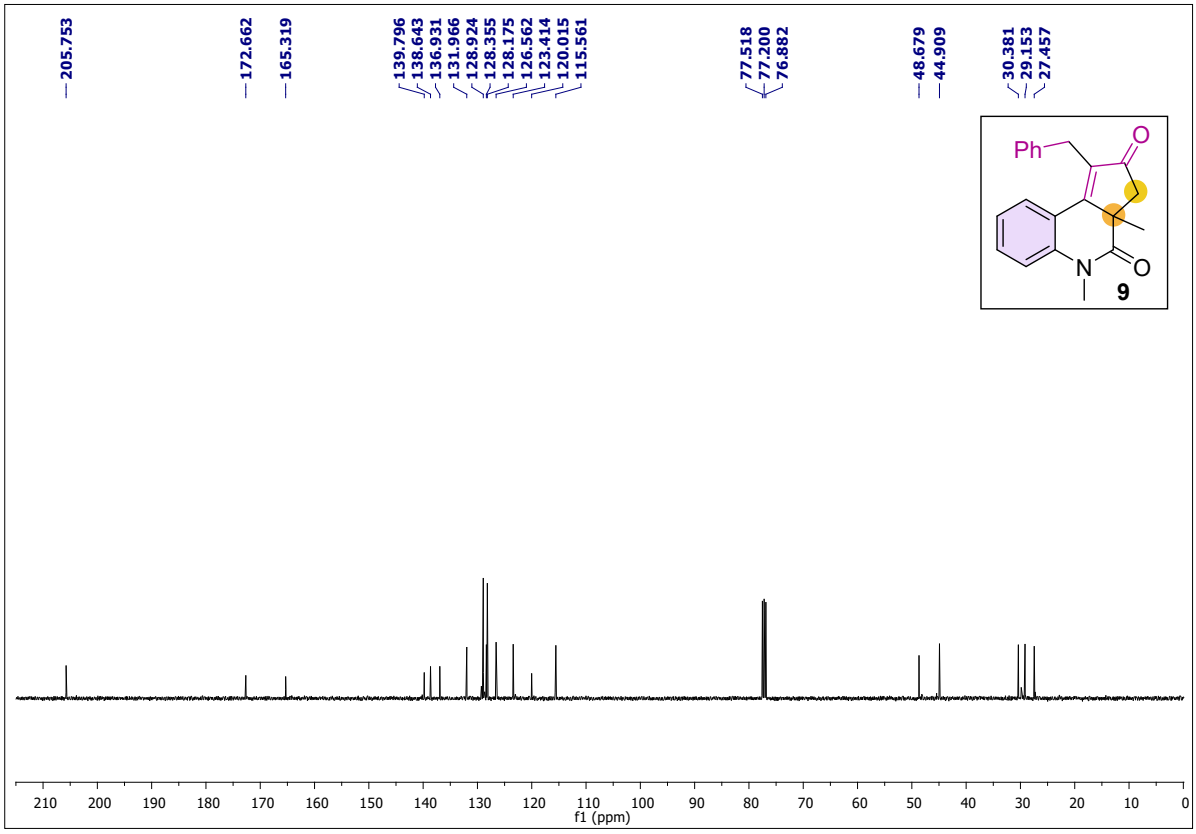
^{1}H NMR (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



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



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)