Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Skeletal rearrangement through photocatalytic denitrogenation: An access to C-3 aminoquinolin-2(1*H*)-ones

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1. General information

Commercial grade reagents, solvents, and starting materials were purchased of pure analytical grades and used as purchased without further purification unless otherwise stated. Commercially available 7 mL screw cap vials fitted with PTFE/silicone septa were purchased from Sigma-Aldrich for performing the reaction. Chromatographic purification of products was undertaken on silica gel (230-400 mesh) using a proper eluent system. For thin-layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used and visualized with UV light and developed using an ethanol solution of phosphomolybdic acid or basic aqueous potassium permanganate ($KMnO_4$) stain solutions. Organic solutions were concentrated under vacuum pressure using a rotary evaporator. The ^{1}H (400 MHz and 500 MHz) and ^{13}C (101 MHz and 126 MHz) nuclear magnetic resonance spectra were recorded on 400 MHz and 500 MHz spectrometers. Chemical shifts (δ) for ^{1}H and ^{13}C are reported in parts per million (ppm) relative to internal standard tetramethylsilane (tetramethylsilane @ 0 ppm) and residual solvent peak in the NMR solvent (for ^{1}H NMR (DMSO @ 2.50 ppm and $CHCl_3$ @ 7.26 ppm), for ^{13}C NMR (DMSO @ 39.52 ppm and $CHCl_3$ @ 77.16 ppm). Coupling constants are given in Hertz (Hz). The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; p, pentet; sept, septet; m, multiplet; br, broad signal. Ultraviolet-visible experiments were recorded on a SHIMADZU-UV-1900i instrument using HPLC grade acetonitrile (EtOAc). The fluorescence emission spectra were carried out on a model Fluoromax-4 (Horiba Scientific) spectrofluorometer using HPLC grade acetonitrile. High-resolution mass spectra (HRMS) were recorded on a Mass Spectrometry Unit using electrospray ionization-time of flight (ESI-TOF) reflectron experiments.

2. General procedure for the synthesis of 3-ylideneoxindoles derivatives

The 3-ylideneoxindoles were synthesized according to previously reported literature.[1] An aqueous solution of NaOH (1.0 M, 100mL) was added to the solution of alkylphosphonium salt (28.0 mmol) in DCM (100 mL) in a 500 mL round bottom flask with a magnetic stirring bead and the reaction was stirred at room temperature for 15 minute. Then, the reaction mixture was extracted with EtOAc (three times). Then, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in rotary evaporation to get the crude ylide which was further dissolved in toluene in round bottom flask with magnetic bead. Then, isatin (25.4 mmol) was added and stirred at room temperature for 12 h. Then, solvent was removed in rotary evaporation and the purification of resultant residues was achieved by column chromatography to get the desired 3-ylideneoxindoles derivatives. For the alkylation of 3-ylideneoxindoles, a solution of 3-ylideneoxindoles (1.0 mmol, 1.0 equiv.) and potassium carbonate (1.2 equiv.) in DMSO (0.25 M) was added to a 50 mL round-bottomed flask followed by the addition of the corresponding alkyl halides (1.6 equiv.). The resultant solution was stirred overnight at room temperature. After completion, the reaction mixture was extracted with saturated brine solution and EtOAc (three times). Then, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in rotary evaporation. The purification of resultant residues was achieved by column chromatography to get the desired *N*-alkylation of 3-ylideneoxindoles derivatives.

3. Reaction Set-up:

The light setup for the photochemical reaction is shown in Figure S-01. The photochemical reactions were carried out using irradiation from blue LED (455 nm, 3 W) placed underneath of a custom-made six-vial aluminium photoreactor. In order to maintain the ambient temperature, this photochemical reactor was also coupled to a continuous passive liquid cooling system. The 3-Watt blue LED was placed around 4 mm from the bottom of the glass vial. 25 °C was the recorded temperature in this reaction set-up.

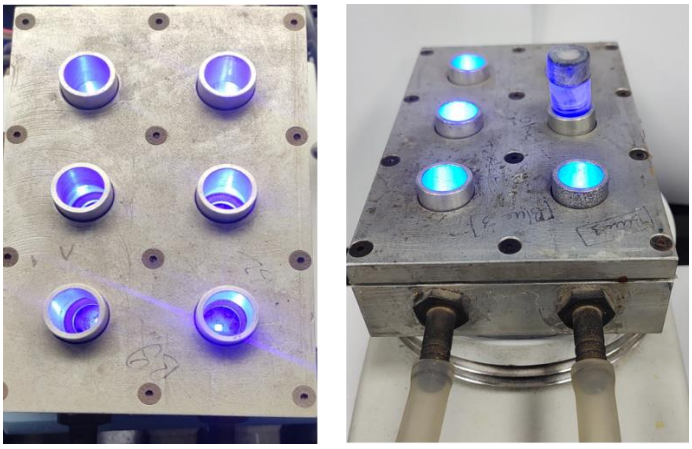
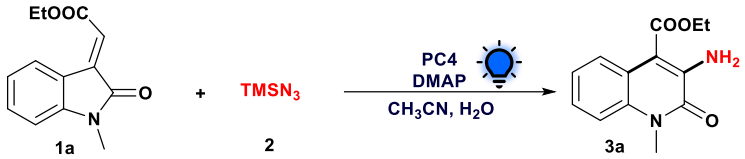


Figure S-01: Light set-up.

4. General procedure for photochemical amination:

In a 7 mL glass vial having a septum cap with a magnetic stirring bead, 3-ylideneoxindoles (0.2 mmol), DMAP (0.24 mmol), and PC4 (2 mol%) were added and then 1.6 mL of acetonitrile and 40 µL of water as solvent was added. Then, azidotrimethylsilane (0.4 mmol) was added to the solution. The reaction mixtures were irradiated with a temperature (25 ºC) controlled 3W blue LED reactor and stirred for 24 hours under an argon atmosphere. After the completion, the reaction mixture was quenched and extracted with EtOAc. Then, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in rotary evaporation. The resultant residue was purified by column chromatography using hexane/EtOAc to achieve the desired aminated quinolin-2(1*H*)-one products.

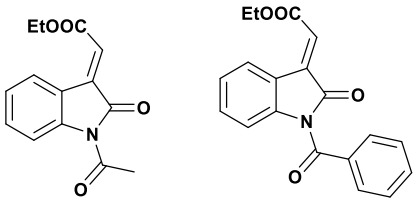
5. Optimization studies for the photochemical amination:



Entry	Photocatalyst	Solvent	Additive	Yield (%)[b]
1	PC1	MeCN	DMAP	40
2	PC2	MeCN	DMAP	n.r.
3	PC3	MeCN	DMAP	n.r.
4[a]	**PC4**	**MeCN**	**DMAP**	**82**
5	PC4	MeCN	DABCO	33
6	PC4	MeCN	DIPEA	63
7	PC4	MeCN	K_2CO_3	34
8	PC4	DCE	DMAP	41
9	PC4	^{t}BuOH	DMAP	42
10	-	MeCN without H_2O	DMAP	53
11	-	MeCN	DMAP	trace
12	PC4	MeCN	-	n.r.
13[c]	PC4	MeCN	DMAP	n.r.
14[d]	PC4	MeCN	DMAP	n.r.

[a]Reaction conditions: Unless otherwise specified, 3-ylideneoxindoles (**1a**) (0.2 mmol), **2** (0.4 mmol), **DMAP** (0.24 mmol) and **PC4** (2 mol%) in 40 µL of water in 1.6 mL solvent irradiated with blue LED (455 nm) for 24 h under argon atmosphere. [b]yields determined by NMR using trichloroethylene as a standard. [c]Under dark conditions. [d]Using NaN_3 instead of $TMSN_3$.

6. Unsuccessful Reactions:



7. Reaction setup and procedure for scale-up reaction:

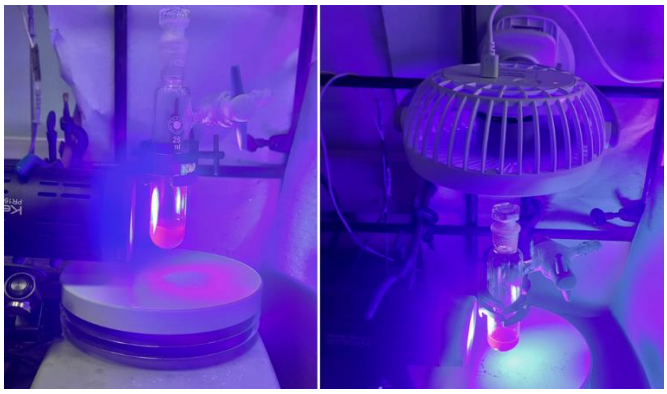


Figure S-02: Kessil lamp setup with equipped fan for scale-up reaction.

7.1. Scaled up synthesis for 3a

In a 25 mL Schlenk tube having a glass cap with a magnetic stirring bead, 3-ylideneoxindoles (1 mmol), DMAP (1.2 mmol, 1.2 equiv.), and PC4 (10 mol%) were added and, then 5 mL of acetonitrile and 200 µL of water solvent was added. Then, azidotrimethylsilane (2 mmol) was added to the solution. The reaction mixtures were irradiated with a Kessil® PR160-456 nm lamp (Figure S-02) with a cooling fan at a distance of 2 cm and stirred for 24 hours under an argon atmosphere. After the completion, the reaction mixture was quenched and extracted with EtOAc. Then, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in rotary evaporation. The resultant residue was purified by column chromatography using hexane/EtOAc to achieve the desired aminated quinolin-2(*1H*)-ones (75% yield, 0.19g).

8. Radical inhibition experiments

In a 7 mL glass vial having a septum cap with a magnetic stirring bead, 3-ylideneoxindoles (0.1 mmol), DMAP (0.12 mmol), and PC4 (1 mol%) were added and, then 0.8 mL of acetonitrile and 20 µL of water solvent was added. Then, azidotrimethylsilane (0.2 mmol) was added to the solution. The reaction mixtures were irradiated with a temperature (25 ºC) controlled 3W blue LED reactor and stirred for 24 hours under an argon atmosphere. After completion of the reaction, an aliquot portion of the reaction mixture was subjected to HRMS (Figure S-03). We were able to detect radical-BHT adduct (**4**). The HRMS data of BHT-adduct of radical intermediate was given below (Figure S-03).

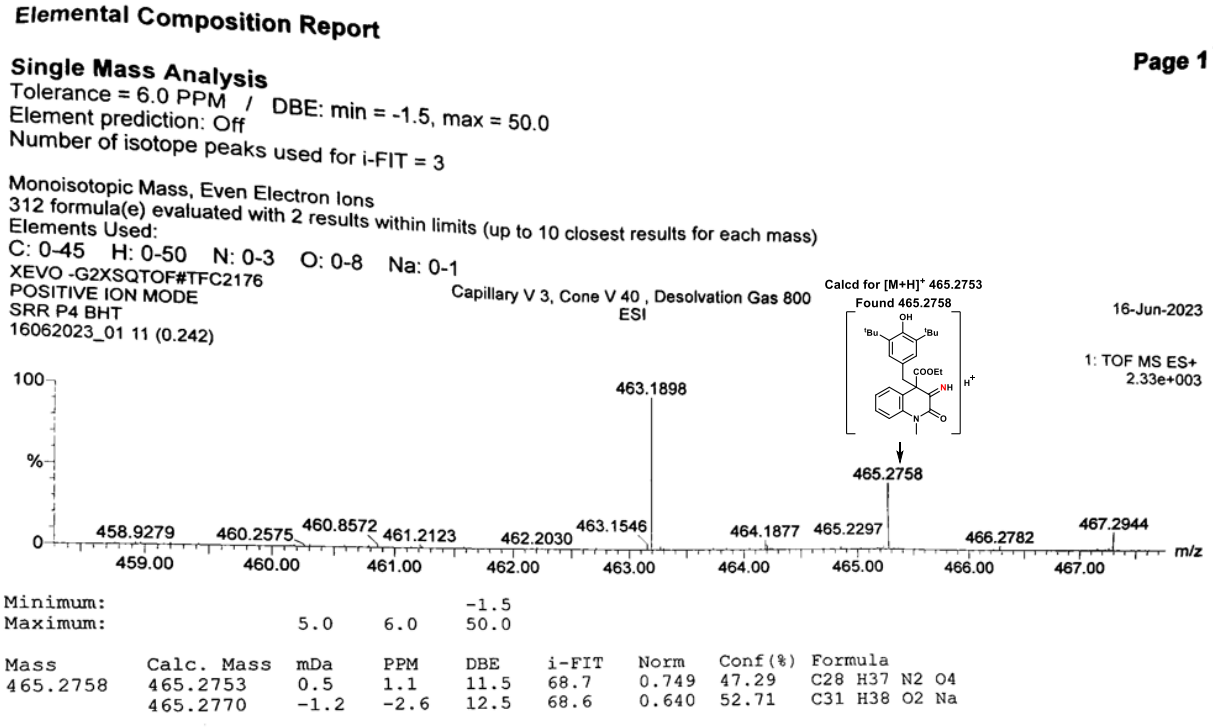


Figure S-03: HRMS data of BHT-adduct radical (**4**).

9. Radical trapping experiments

In a 7 mL glass vial having a septum cap with a magnetic stirring bead, 1,1-diphenylethylene (0.2 mmol), DMAP (0.12 mmol), and PC4 (1 mol%) were added and, then 0.8 mL of acetonitrile and 20 µL of water solvent was added. Then, azidotrimethylsilane (0.2 mmol) was added to the solution. The reaction mixtures were irradiated with a temperature (25 ºC) controlled 3W blue LED reactor and stirred for 24 hours under an argon atmosphere. After completion of the reaction, an aliquot

portion of the reaction mixture was subjected to HRMS (Figure S-04). The HRMS data of radical adduct (**5**) is given below (Figure S-04).

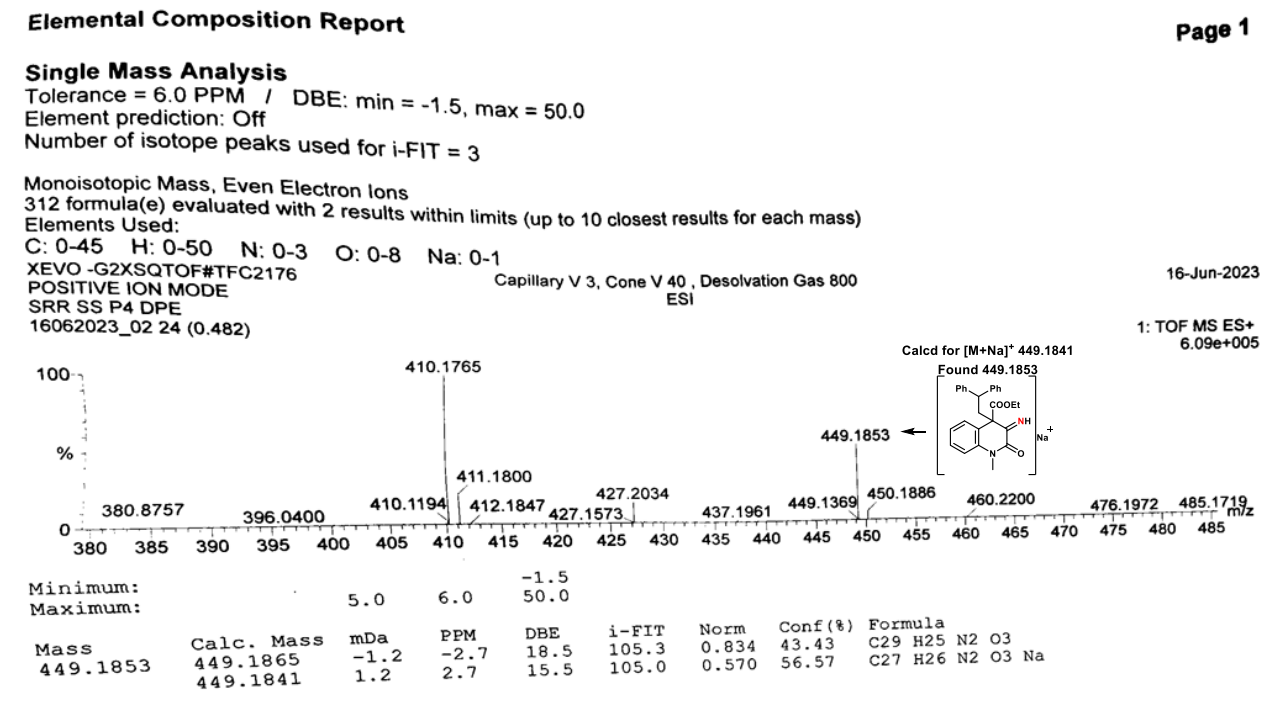


Figure S-04: HRMS data of radical intermediate adduct (**5**).

10. Switch on/off experiment

In six different glass vials (**A-F**) having a septum cap with a magnetic stirring bead, 3-ylideneoxindoles (0.1 mmol), DMAP (0.12 mmol), and PC4 (1 mol%) were added, and then 0.8 mL of acetonitrile and 20 µL of water solvent was added. Then, azidotrimethylsilane (0.2 mmol) was added to the solution. All six reaction vials were irradiated with a temperature (25 ºC) controlled 3W blue LED reactor and stirred under an argon atmosphere. After the 6-hour vial-A was removed, and for the remaining vials (**B-F**) light source was switched off with continuous stirring for the next 6 hours. The vial-**A** reaction mixture was quenched and extracted with EtOAc. Then, the crude ^{1}H NMR of the resultant residue was taken using the trichloroethylene as an internal standard to obtain the yield of aminated product. After 6 hours in dark conditions, the vial-**B** was removed, and the remaining vials (**C-F**) were subjected to 6 hours of light. The vial-**B** reaction mixture was quenched and extracted with EtOAc, and crude ^{1}H NMR of resultant residue was taken using trichloroethylene

as an internal standard to obtain the yield of aminated product. This ON-OFF cycle was repeated with the remaining four vials (**C**-**F**), as represented in Figure S-05a. The yield of **3a** of all the six sets of reaction (Vial **A**-**F**) was plotted with respect to time as shown in the adjoining figure (Figure S-05b).

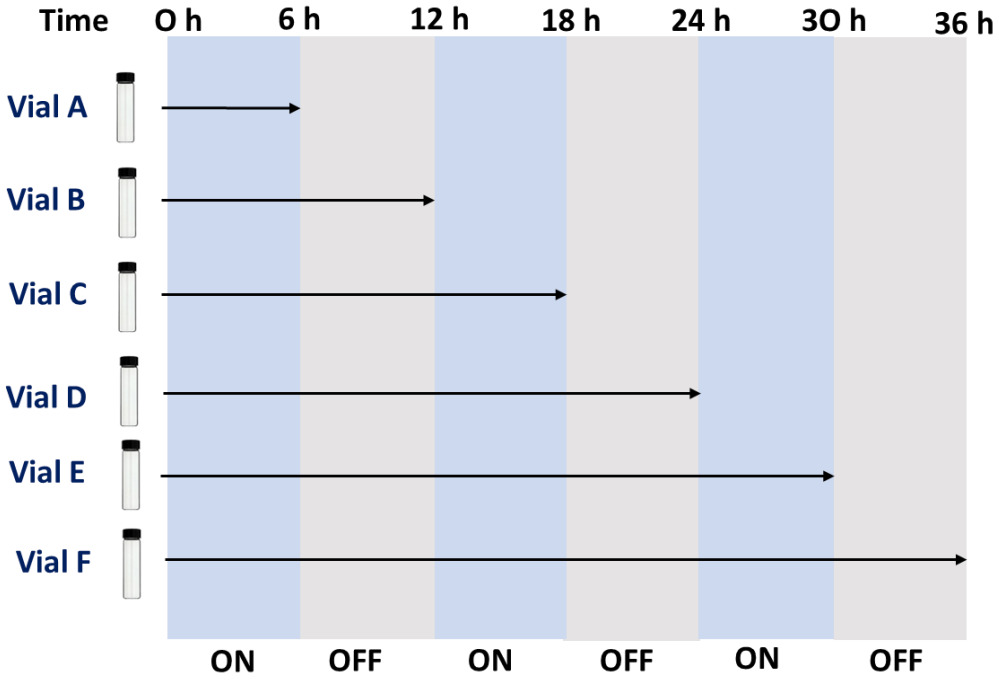


Figure S-05a: Graphical representation of ON-OFF experiments

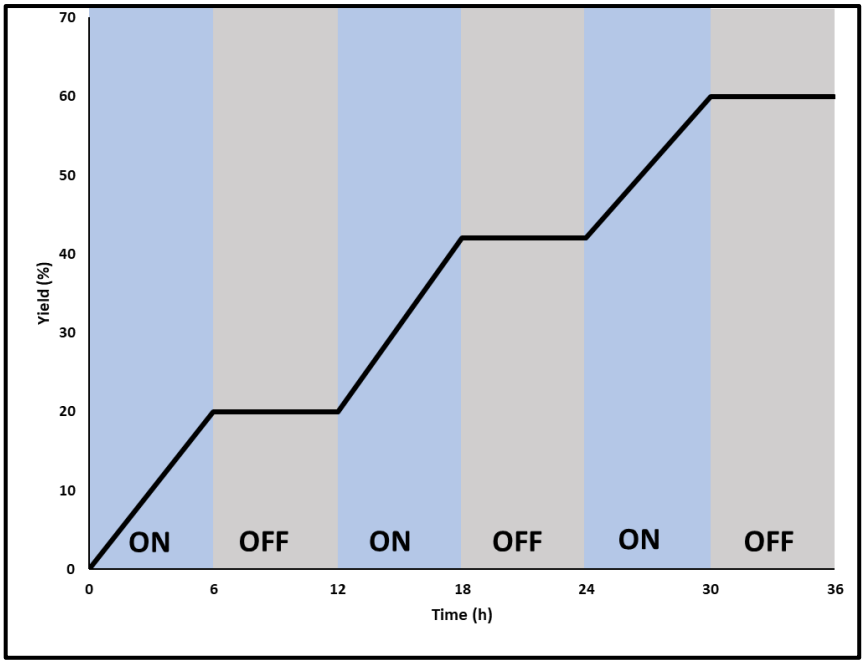


Figure S-05b: Switch on/off experiment

11. UV-Vis absorption studies

The UV-Vis measurements were performed using a UV-Vis spectrophotometer (SHIMADZU-UV-1900i) using a quartz cuvette equipped with a Teflon® septum (1 cm path length). The UV-Vis spectra were collected in the 300-550 nm range. The absorption spectra of ethyl (*E*)-2-(1-methyl-2-oxoindolin)-3-ylideneacetate) (**1a**,3.3 mM), DMAP (3.3 mM), azido trimethylsilane (3.3 mM), and triazoline intermediate (**6**, 3.3 mM) were recorded in acetonitrile as shown in figure S-06. In figure S-07 absorbance of solution of **PC4** with ethyl (*E*)-2-(1-methyl-2-oxoindolin)-3-ylideneacetate) (**1a**,3.3 mM), DMAP (3.3 mM), azido trimethylsilane (3.3 mM), and triazoline intermediate (**6**, 3.3 mM) separately were recorded.

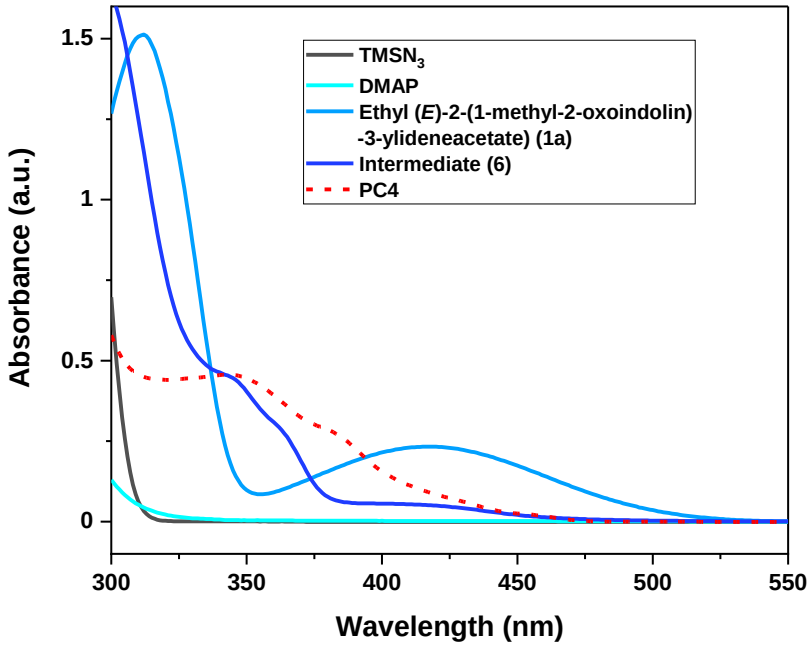


Figure S-06: UV-Vis spectra of solution of $TMSN_3$ (3.3 mM), DMAP (3.3 mM), ethyl (E)-2-(1-methyl-2-oxoindolin)-3-ylideneacetate) (**1a**, 3.3 Mm), Intermediate (**6**, 3.3 mM), and **PC4** (0.33 mM).

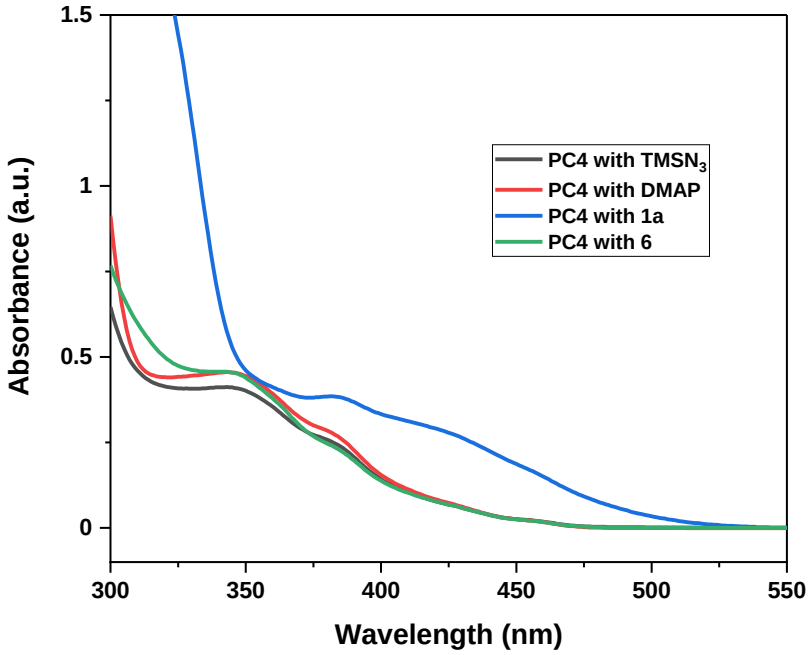


Figure S-07: UV-Vis spectra of solution of $TMSN_3$ (3.3 mM), DMAP (3.3 mM), ethyl (E)-2-(1-methyl-2-oxoindolin)-3-ylideneacetate) (**1a**, 3.3 Mm) and Intermediate (**6**, 3.3 mM) with **PC4** (0.33 mM).

12. Fluorescence Quenching Experiment and Stern-Volmer Studies:

Fluorescence quenching experiments were carried out on a model Fluoromax-4 spectrofluorometer using a quartz cuvette with 1 cm path length equipped with a Teflon® septum. A 0.02 M solution of **PC4** in acetonitrile was prepared and taken in a 3 mL fluorescence cuvette. For collection of data, the excitation and emission slit widths were fixed at 2 and 4 nm, respectively. Fluorescence emission spectra of **PC4** were recorded from 425 nm to 600 nm with an excitation wavelength of 410 nm. λ_{max}(emission) of **PC4** was observed at 500 nm. For each fluorescence quenching experiment, a 10 µL of 0.2 M solution of the $TMSN_3$ (**2**), DMAP, triazoline intermediate **6** and **1a** (prepared in MeCN) was added individually to **PC4** solution (0.02 M) taken in a fluorescence cuvette, and emission spectra were recorded after each sequential addition. Figure S08a shows a decrease in emission intensity after each addition of $TMSN_3$ (0.2 M) and respective Stern-Volmer plot are shown in Figure S08b.

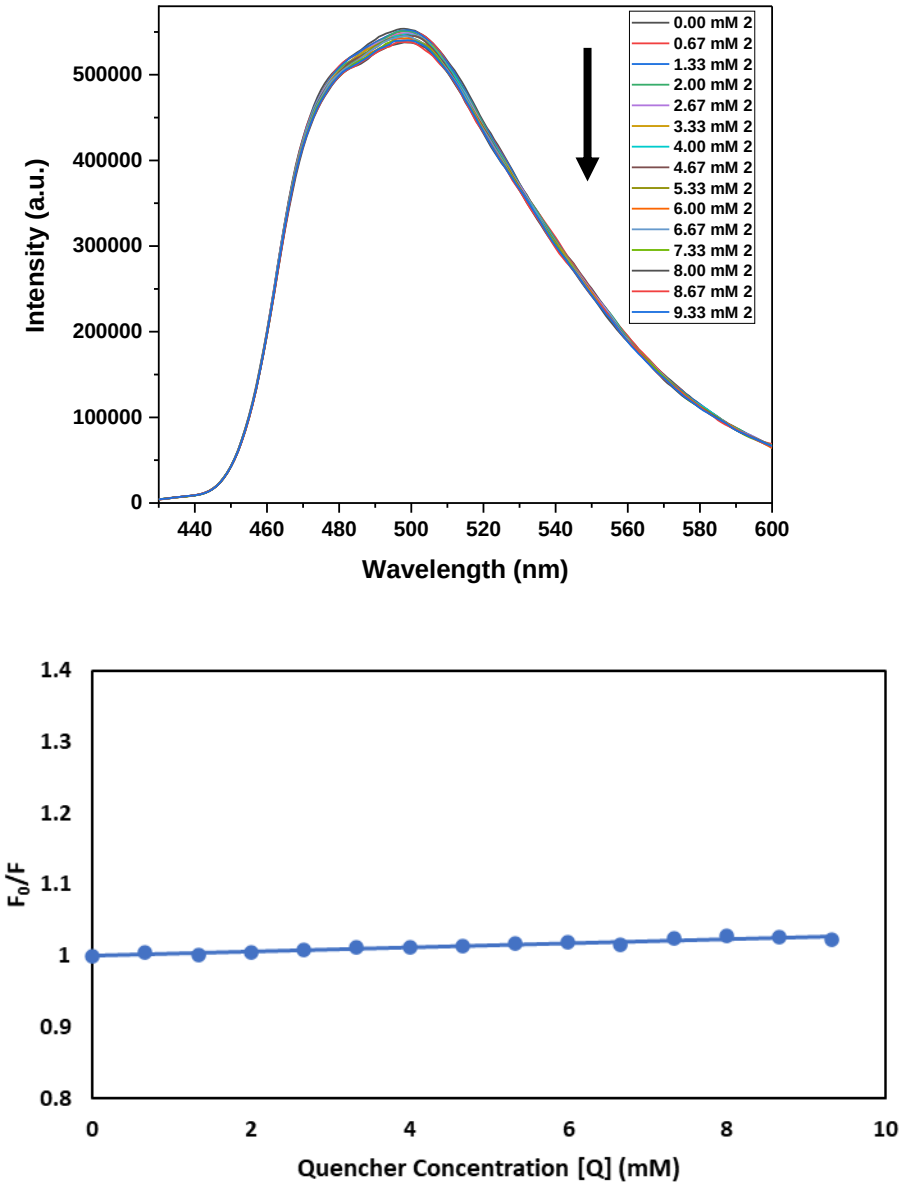


Figure S-08: (a) Fluorescence quenching spectra **(b)** Stern-Volmer plot of solution of **PC4** (0.02 M) in acetonitrile with **2** (0.2 M) as the quencher.

In a similar fashion fluorescence quenching experiment of **PC4** (0.02 M) was performed with DMAP (0.2 M). The collective emission spectra and the Stern Volmer plot shown in Figure S09a-b.

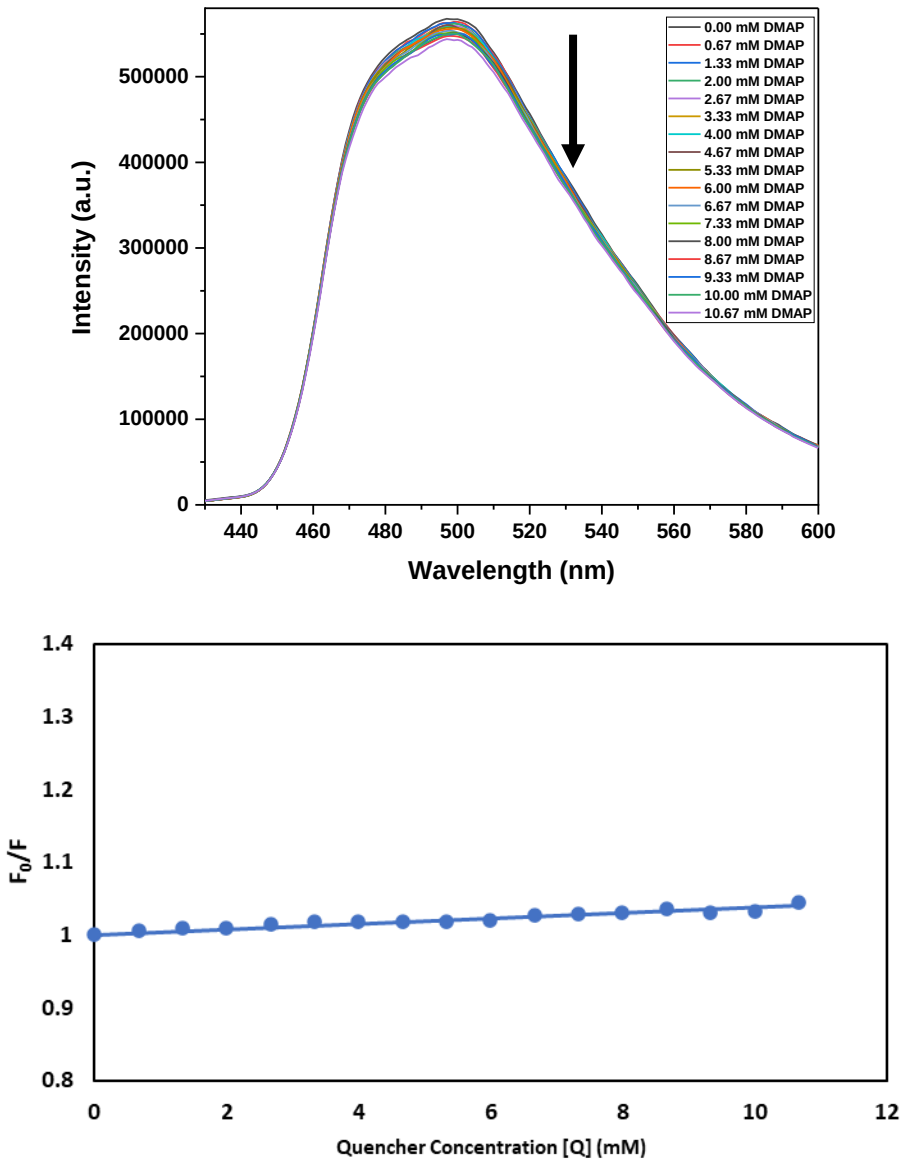


Figure S-09: (a) Fluorescence quenching spectra **(b)** Stern-Volmer plot of solution of **PC4** (0.02 M) in acetonitrile with DMAP (0.2 M) as the quencher.

Similarly, fluorescence quenching experiment of **PC4** (0.02 M) was performed with triazoline intermediate **6** (0.2 M). The collective emission spectra and the Stern Volmer plot shown in Figure S10a-b.

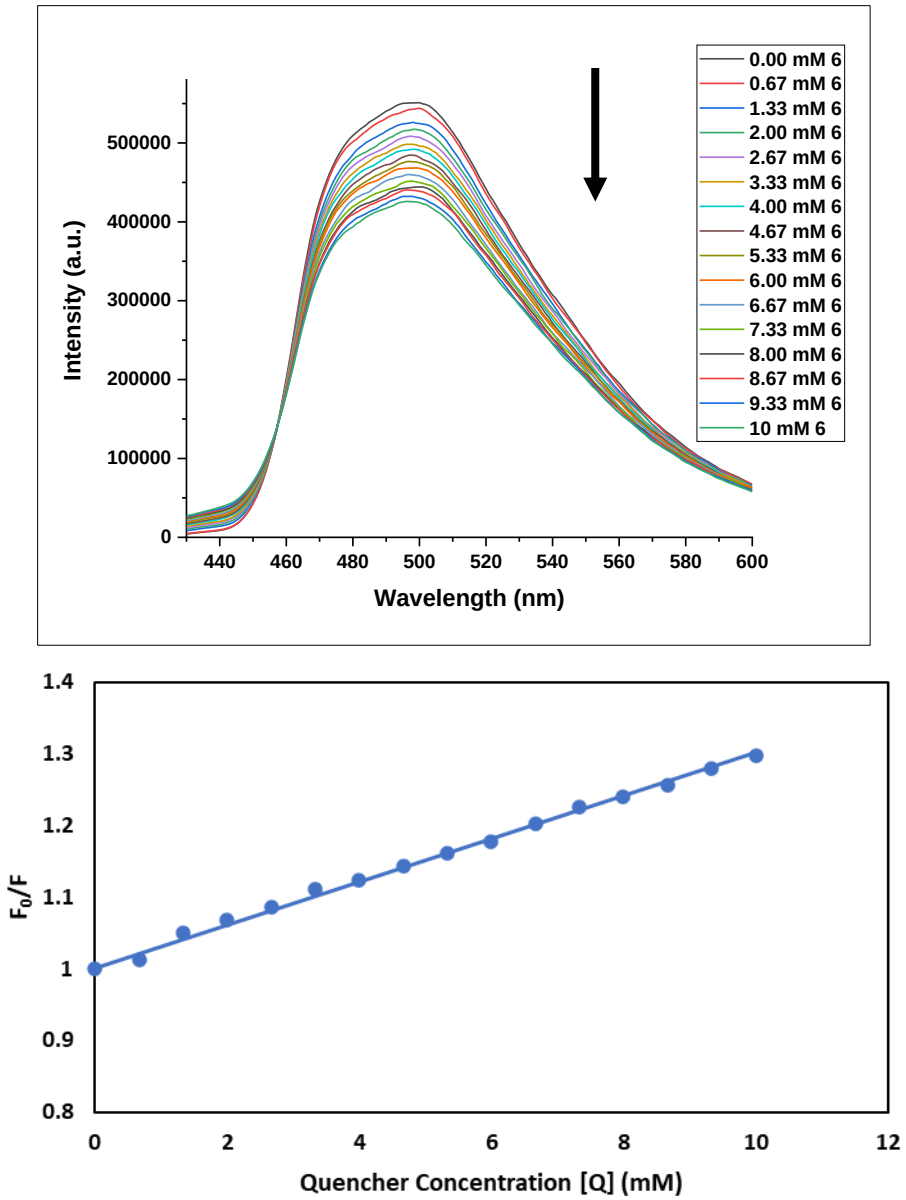


Figure S-10: (a) Fluorescence quenching spectra **(b)** Stern-Volmer plot of solution of **PC4** (0.02 M) in acetonitrile with Triazoline Intermediate **6** (0.2 M) as the quencher.

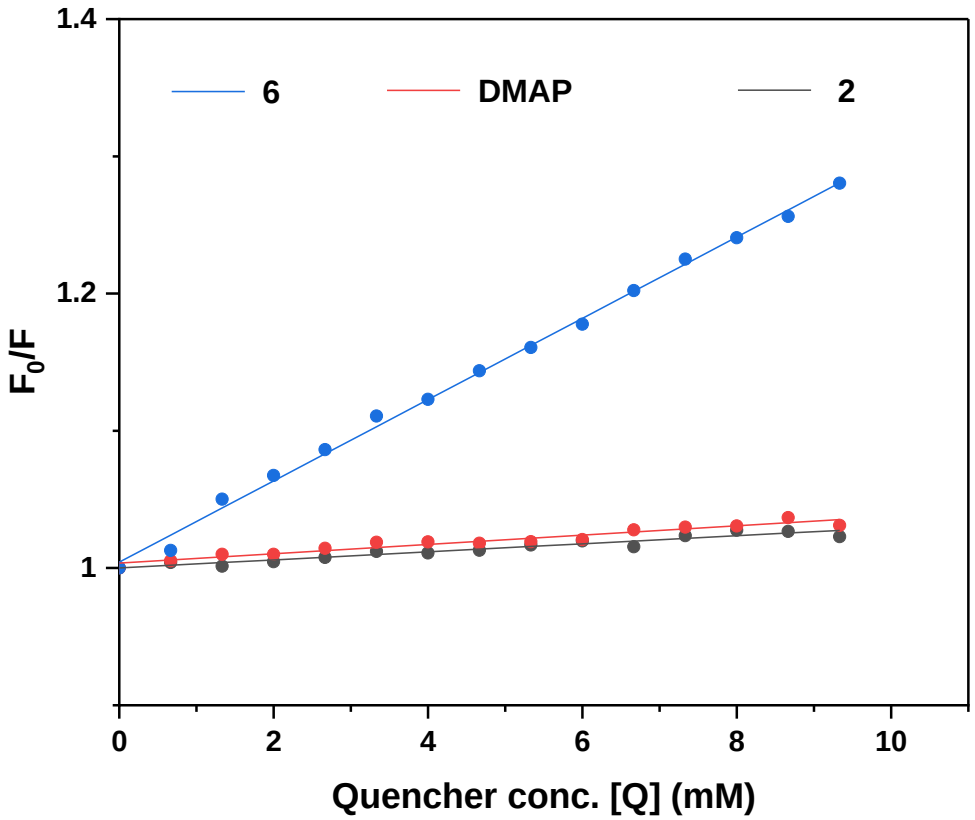


Figure S-11: Combined Stern-Volmer plot of solution of **PC4** (0.02 M) in acetonitrile with intermediate **6** (Blue line), DMAP (Red line) and azidotrimethylsilane (Black line) as the quencher.

Similarly, fluorescence quenching experiment of **PC4** (0.02 M) was performed with **1a** (0.2 M). The fluorescence emission spectra are shown in Figure S12.

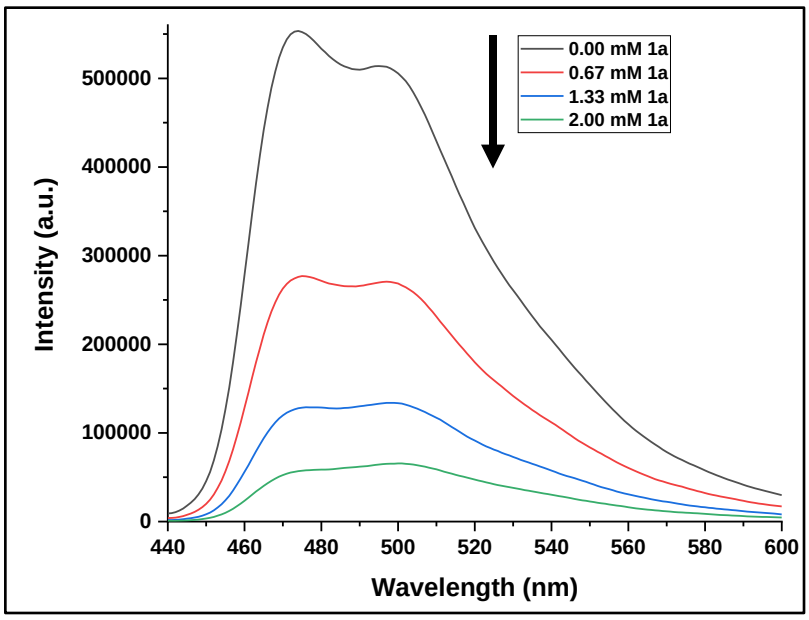


Figure S-12: Fluorescence quenching spectra of **PC4** (0.02 M) in acetonitrile with **1a** (0.2 M) as the quencher.

13. Reaction monitoring using in situ FTIR ReactIR configuration.:

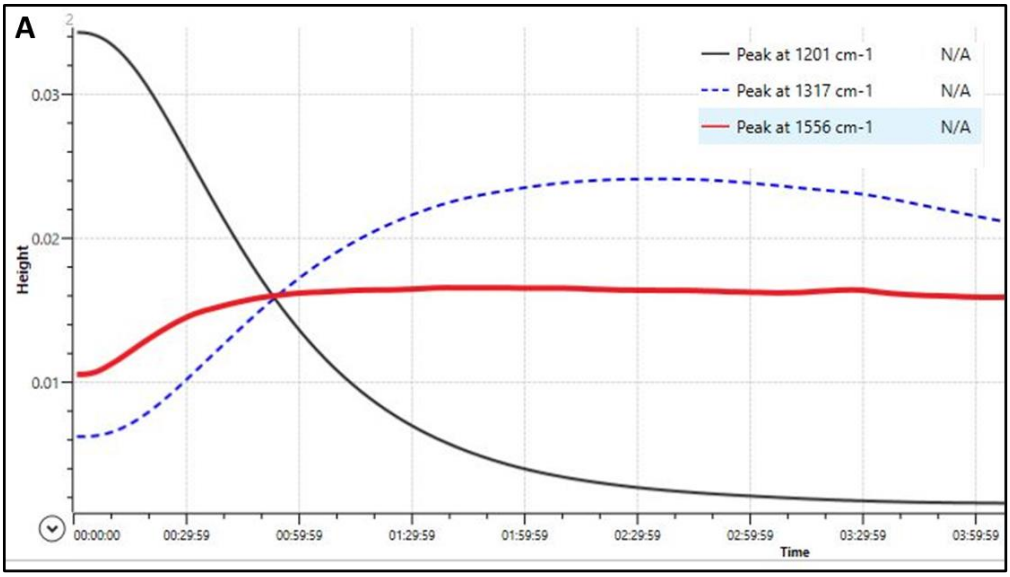
Data was collected using a Mettler-Toledo ReactIR 700 (SN: C049640472) equipped with a TEMCT detector, DiComp (Dimond) probe, with a 9.5mm x 2m AgX fiber interface. Data was using the spectral window of 2000 to 650 cm^{-1} with 8 cm^{-1} resolution.

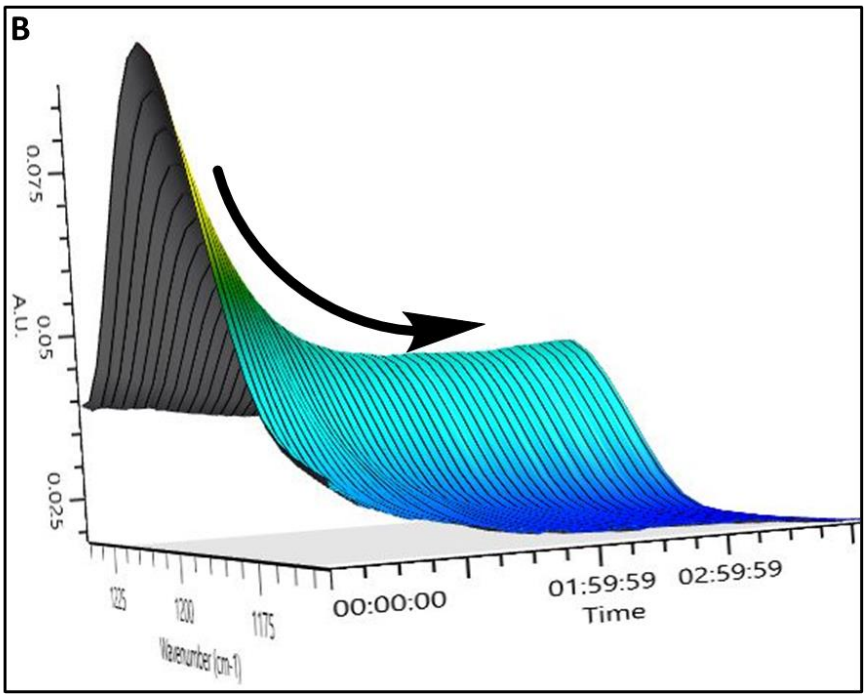
Representative procedure for in situ FTIR experiments: Prior to carrying out the experiment, the solvent background of MeCN was collected. In a 7 mL glass vial with a magnetic stirring bead, 3-ylideneoxindoles (0.1 mmol), DMAP (0.12 mmol), and PC4 (1 mol%) were added and, then 0.8 mL of acetonitrile and 20 µL of water solvent was added. Then, azidotrimethylsilane (0.2 mmol) was added to the solution. The reaction mixture was set to stir, and the ReactIR probe was immersed in the solution and attached at an appropriate height just above the solution with the help of parafilm tape. This was then subjected to irradiation of a 3 W blue LED. Data acquisition was then commenced using iC IR (React IR software) in the 'rapid collect' mode.

8.2. Monitoring Reaction profile using ReactIR: The ReactIR enables the monitoring of the consumption of starting materials and the formation of products throughout the reaction. Herein, we have exploited the in situ FTIR methodology to study the reaction, thereby monitoring the time-dependent changes that occur during the course of the reaction (Figure S13). The reaction was set up according to the representative procedure for in situ FTIR experiments. The reaction progress data is displayed by characteristic signals of

starting material **1a** (Black line, ṽ: 1201 cm^{-1}), intermediate **6** (Blue dotted line, ṽ: 1317 cm^{-1}), and product (Red line, ṽ: 1556 cm^{-1}) in Figure S12A.

NOTE: *The peaks which were not merging/interfering between starting materials, product and intermediate were monitored during the course of the reaction for the in-situ FTIR studies.*





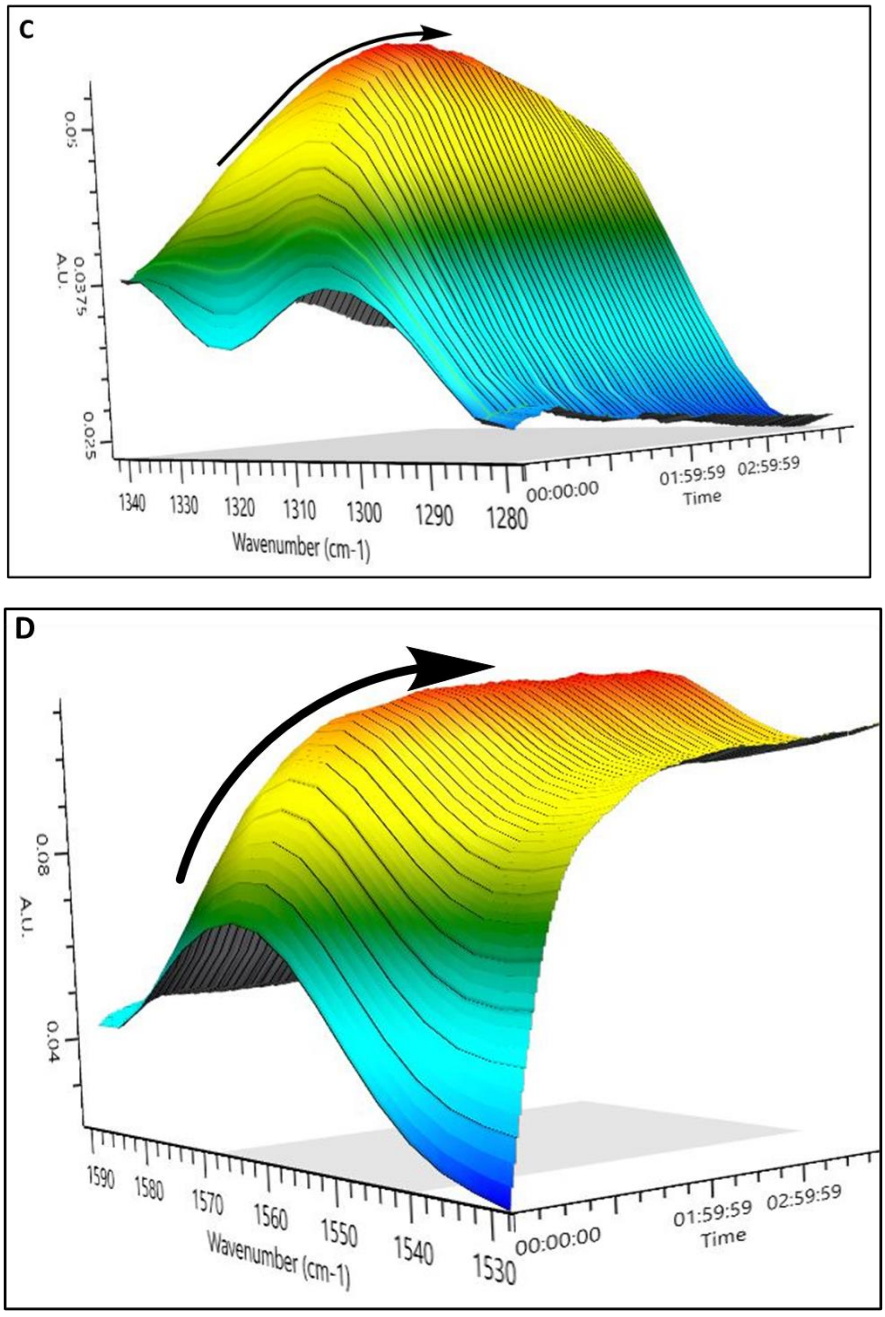


Figure S-13. (A) ReactIR full reaction progress data. Surface spectral changes in the ReactIR reaction profile for **(B) 1a** decreasing (characteristic signal 1201 cm^{-1}). **(D)** Triazoline-intermediate **6** increasing then decreasing (characteristic signal 1317 cm^{-1}) **(C)** 3a increasing (characteristic signal 1556 cm^{-1}).

14. Crystallographic Data:

Sample preparation: For single-crystal X-ray diffraction studies, crystallisation of compound **3a** was carried out at room temperature using EtOAc/Heptane as a solvent system.

Molecular structure determination of compounds 3a: Single crystal X-ray diffraction data of crystals for compound **3a** were collected using a Bruker APEX-II CCD diffractometer equipped with a 3-axis goniometer. The crystals were covered with Paratone–N oil and mounted a glass capillary. The data were collected at room temperature using Mo Kα radiation (λ = 0.71073). The measured intensities were reduced to F^2 and corrected for absorption with SAINT. Structure solutions were accomplished by direct methods and refined by full matrix least-square on F^2 using OLEX2. Non-hydrogen atoms were refined anisotropically. All non-hydrogen atoms were refined anisotropically. The position of hydrogen atoms were fixed according to a riding model and was refined isotropically. Images were created with the program Mercury. The crystal structure has been deposited to Cambridge Crystallographic Data Centre and allocated deposition number (**3a**: CCDC 2251989).

1. **Crystal data and structure refinement for SSP41_0m_a.**

Identification code	SSP41_0m_a
Empirical formula	$C_{13}H_{14}N_2O_3$
Formula weight	246.26
Temperature/K	298 (2)
Crystal system	triclinic
Space group	P -1
a/Å	7.7425(15)
b/Å	8.7545(18)
c/Å	18.745(4)
α/°	101.445(7)
β/°	91.780(6)
γ/°	93.333(6)
Volume/Å^3	1242.0(4)
Z	25
ρ_{calc}g/cm^3	1.317
μ/mm^{-1}	0.095
F(000)	520
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.219 to 28.320

Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -24 ≤ l ≤ 24
Reflections collected	6162
Data/restraints/parameters	2726/0/330
Goodness-of-fit on F^2	1.023
R (reflections)	0.0630 (2726)
wR2 (reflections)	0.2106 (6162)
S	1.023
Npar	330

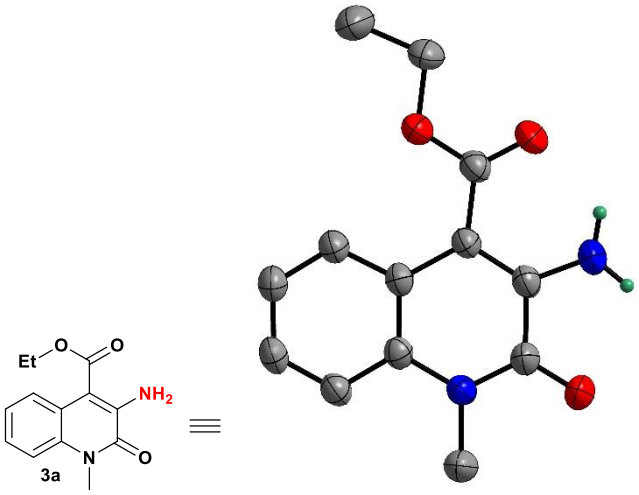
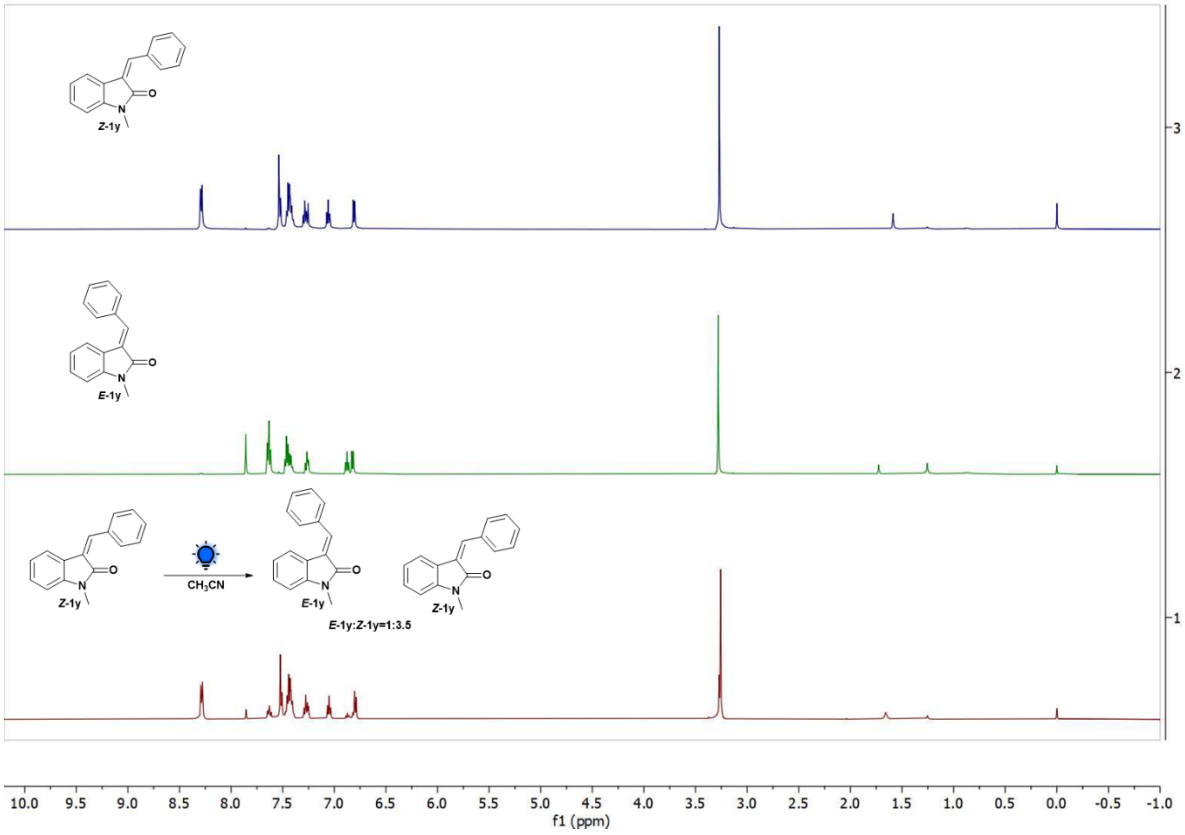


Figure S14: Crystal structure of compound **3a**. Thermal ellipsoids are shown at the 35% level

15. Photoisomerization of starting material 1y and 1z:

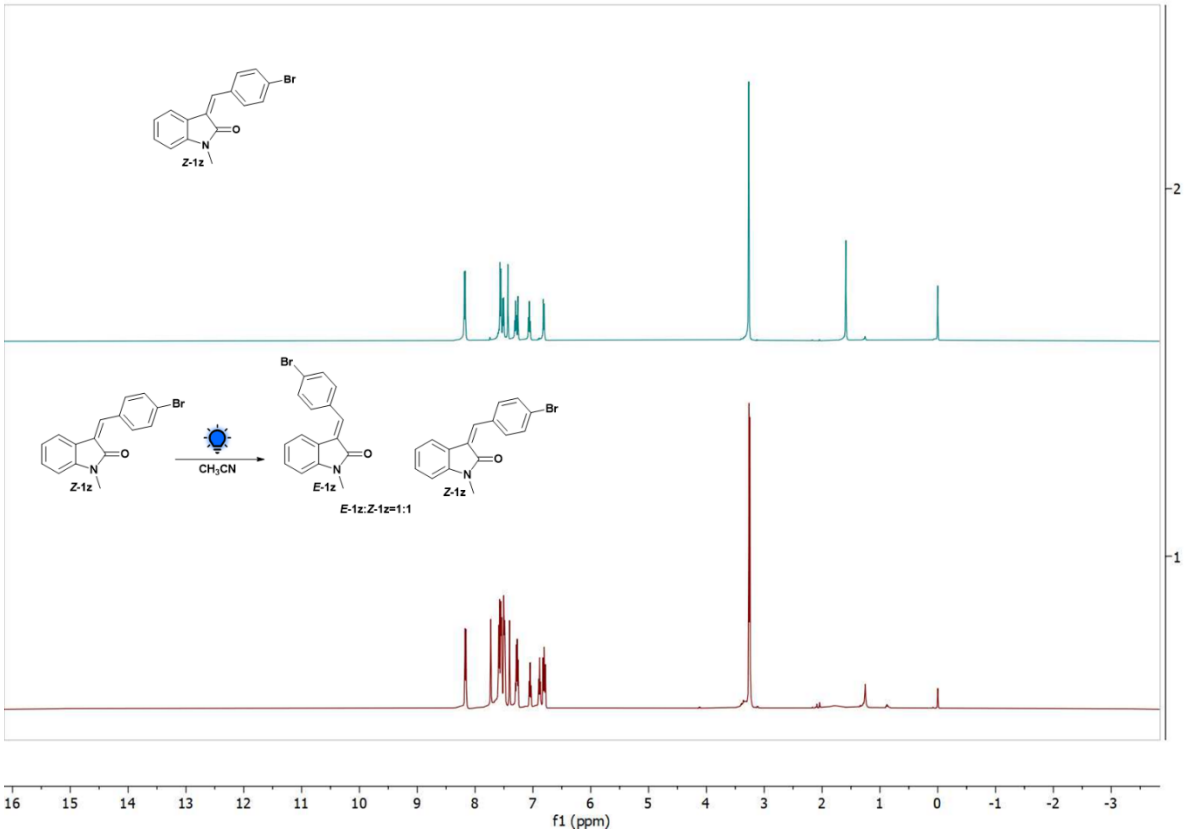
(*Z*)-3-benzylidene-1-methylindolin-2-one (*Z*-1y):[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.0 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.46-7.40 (m, 3H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 3.27 (s, 3H).

(*E*)-3-benzylidene-1-methylindolin-2-one (*E*-1y):[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.65-7.62 (m, 3H), 7.48-7.42 (m, 3H), 7.27 (t, *J* = 7.7 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 3.28 (s, 3H).



(*Z*)-3-(4-bromobenzylidene)-1-methylindolin-2-one(*Z*-1z):[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.43 (s, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 3.27 (s, 3H).

(*E*)-3-(4-bromobenzylidene)-1-methylindolin-2-one(*E*-1z):[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.61-7.55 (m, 3H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 6.89 (t, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 3.28 (s, 3H).



16. Characterization data of the synthesized compounds:

Ethyl 3-amino-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3a): yield 82% (40.4 mg); Light brown solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.2 Hz, 1H), 7.31-7.30 (m, 2H), 7.24 (dt, *J* = 8.2, 5.8 Hz, 1H), 6.85 (s, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.4, 158.0, 141.7, 132.7, 125.5, 125.3, 123.3, 119.9, 114.3, 102.4, 61.2, 31.0, 14.6. **HRMS-ESI:** calcd for $C_{13}H_{15}N_2O_3$ $[M+H]^+$ 247.1083, found 247.1087. **m.p:** 75 °C.

Ethyl 3-amino-1-isopropyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3b): yield 77% (42.2 mg); White solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.76 (s, 2H), 5.36 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.68 (s, 3H), 1.66 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 13C NMR (126 MHz, CDCl3) δ 168.4, 158.2, 142.1, 132.0, 125.7, 124.7, 122.9, 120.8, 115.0, 102.5, 61.2, 19.8, 14.6. **HRMS-ESI:** calcd for $C_{15}H_{19}N_2O_3$ $[M+H]^+$ 275.1396, found 275.1394. **m.p:** 110 °C.

Ethyl 3-amino-1-benzyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3c): yield 83% (53.5 mg); White solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.31-7.29 (m, 2H), 7.26-7.22 (m, 2H), 7.20-7.16 (m, 4H), 6.85 (s, 2H), 5.62 (s, 2H), 4.51 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.4, 158.3, 141.4, 135.9, 132.0, 129.0, 127.5, 126.6, 125.5, 125.4, 123.3, 120.1, 115.3, 103.1, 61.4, 47.5, 14.6. **HRMS-ESI:** calcd for $C_{19}H_{19}N_2O_3$ $[M+H]^+$ 323.1396, found 323.1387. **m.p:** 158 °C.

Ethyl 3-amino-1-(cyclopropylmethyl)-2-oxo-1,2-dihydroquinoline-4-carboxylate (3d): yield 78% (44.7 mg); Colourless liquid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.34-7.30 (m, 1H), 7.25-7.22 (m, 1H), 6.78 (s, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.33 (d, *J* = 6.9 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.35-1.29 (m, 1H), 0.57-0.53 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.4, 158.0, 141.7, 132.1, 125.6, 125.2, 123.1, 120.1, 114.7, 102.8, 61.2, 47.4, 14.6, 9.9, 4.2. **HRMS-ESI:** calcd for $C_{16}H_{19}N_2O_3$ $[M+H]^+$ 287.1396, found 287.1385.

ethyl 3-amino-2-oxo-1,2-dihydroquinoline-4-carboxylate (3e): yield 85% (39.5 mg); Light White solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, DMSO) δ 12.15 (s, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.20-7.17 (m, 1H), 7.14-7.11 (m, 1H), 6.99 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 167.5, 157.0, 141.8, 130.8,

124.5, 124.0, 122.6, 118.6, 115.4, 101.6, 60.7, 14.2. **HRMS-ESI:** calcd for $C_{12}H_{13}N_2O_3$ $[M+H]^+$ 233.0926, found 233.0916. **m.p:** 98 °C.

Ethyl 1-allyl-3-amino-2-oxo-1,2-dihydroquinoline-4-carboxylate (3f): yield 74% (40.3 mg); Colourless solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.2 Hz, 1H), 7.28-7.26 (m, 2H), 7.24-7.22 (m, 1H), 6.81 (s, 2H), 6.01-5.93 (m, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 5.12 (d, *J* = 17.3 Hz, 1H), 5.01 (d, *J* = 2.9 Hz, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.3, 157.6, 141.4, 131.8, 131.3, 125.5, 125.2, 123.2, 120.0, 117.5, 114.9, 102.8, 61.3, 46.1, 14.5. **HRMS-ESI:** calcd for $C_{15}H_{17}N_2O_3$ $[M+H]^+$ 273.1239, found 273.1227. **m.p:** 102 °C.

Ethyl 3-amino-2-oxo-1-(prop-2-yn-1-yl)-1,2-dihydroquinoline-4-carboxylate (3g): yield 68% (36.8 mg); White solid, Hexane/EtOAc = 97/3, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.3 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.37-7.34 (m, 1H), 7.28-7.25 (m, 1H), 6.80 (s, 2H), 5.16 (s, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 1H), 1.47 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.3, 157.4, 141.3, 131.2, 125.7, 125.4, 123.6, 120.2, 114.8, 103.0, 77.5, 73.0, 61.4, 33.3, 14.6. **HRMS-ESI:** calcd for $C_{15}H_{14}N_2NaO_3$ $[M+Na]^+$ 293.0902, found 293.0910. **m.p:** 100 °C.

Ethyl 3-amino-1-(2-ethoxy-2-oxoethyl)-2-oxo-1,2-dihydroquinoline-4-carboxylate (3h): yield 72% (45.8 mg); Colourless solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.1 Hz, 1H), 7.28-7.24 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.80 (s, 2H), 5.14 (s, 2H), 4.50 (q, *J* = 7.0 Hz, 2H), 4.24 (q, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.3, 167.8, 158.1, 141.2, 131.9, 125.8, 125.5, 123.6, 120.0, 113.7, 103.2, 62.0, 61.4, 45.3, 14.6, 14.3. **HRMS-ESI:** calcd for $C_{16}H_{18}N_2NaO_5$ $[M+Na]^+$ 341.1113, found 341.1122. **m.p:** 104 °C.

Ethyl 3-amino-2-oxo-1-phenyl-1,2-dihydroquinoline-4-carboxylate (3i): yield 65% (40.1 mg); Yellow solid, Hexane/EtOAc = 94/6, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.3 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.28-7.26 (m, 2H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.86 (s, 2H), 6.60 (d, *J* = 8.4 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.4, 158.0, 142.0, 137.9, 133.9, 130.4, 129.3, 128.6, 125.2, 124.9, 123.4, 119.8, 116.4, 103.0, 61.4, 29.8, 14.6. **HRMS-ESI:** calcd for $C_{18}H_{16}N_2NaO_3$ $[M+Na]^+$ 331.1059, found 331.1049. **m.p:** 165 °C.

Ethyl 3-amino-1,6-dimethyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3k): yield 85% (44.2 mg); Brown solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.20 (d, *J*

= 8.5 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.79 (s, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 2.41 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.4, 157.7, 141.6, 132.6, 130.7, 126.3, 125.5, 119.8, 114.2, 102.4, 61.2, 31.0, 21.4, 14.5. **HRMS-ESI:** calcd for $C_{14}H_{16}N_2NaO_3$ $[M+Na]^+$ 283.1059, found 283.1064. **m.p:** 94 °C.

Ethyl 3-amino-6-methoxy-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3l): yield 88% (48.6 mg); White solid, Hexane/EtOAc = 94/6, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.7 Hz, 1H), 7.24 (d, *J* = 9.1 Hz, 1H), 7.00 (s, 2H), 6.92 (dd, *J* = 9.1, 2.8 Hz, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.5, 157.3, 155.6, 142.6, 127.1, 121.0, 115.3, 112.9, 108.8, 101.6, 61.2, 55.6, 31.1, 14.6. **HRMS-ESI:** calcd for $C_{24}H_{16}N_2NaO_4$ $[M+Na]^+$ 299.1008, found 299.1013. **m.p:** 106 °C.

Ethyl 3-amino-1-methyl-2-oxo-6-(trifluoromethoxy)-1,2-dihydroquinoline-4-carboxylate (3m): yield 73% (48.2 mg); Yellow solid, Hexane/EtOAc = 94/6, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43-8.42 (m, 1H), 7.30 (d, J=9.1 Hz,1H), 7.17-7.14 (m, 3H), 4.48 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -58.0. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 157.7, 145.0 (q, *J* = 2.3 Hz), 143.1, 130.9, 121.1, 117.9 (q, *J* = 1.3 Hz), 117.8 (q, *J* = 0.5 Hz), 115.4, 100.7, 61.6, 31.3, 14.3. **HRMS-ESI:** calcd for $C_{14}H_{14}N_2O_4F_3$ $[M+H]^+$ 331.0906, found 331.0901.**m.p:** 116 °C.

Ethyl 3-amino-6-fluoro-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3n): yield 81% (42.8 mg); White solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 12.0 Hz, 1H), 7.26-7.23 (m, 1H), 7.10 (s, 2H), 7.02 (t, *J* = 6.9 Hz, 1H), 4.49 (q, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -119.2. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.2, 159.0 (d, *J* = 238.6 Hz), 158.0, 143.0 (d, *J* = 13.2 Hz), 129.0, 121.4 (d, *J* = 9.9 Hz), 115.5 (d, *J* = 8.9 Hz), 112.3 (d, *J* = 16.4 Hz), 111.5 (d, *J* = 26.9 Hz), 101.0, 61.4, 31.3, 14.5. **HRMS-ESI:** calcd for $C_{13}H_{14}N_2O_3F$ $[M+H]^+$ 265.0988, found 265.0978. **m.p:** 103 °C.

Ethyl 3-amino-6-chloro-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3o): yield 83% (46.6 mg); White solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 1.7 Hz, 1H), 7.28-7.23 (m, 2H), 7.07 (s, 2H), 4.51 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 1.51 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.1, 157.6, 142.7, 131.1, 129.0, 125.1, 125, 121.3, 115.5, 100.8, 61.5, 31.2, 14.5. **HRMS-ESI:** calcd for $C_{13}H_{14}N_2O_3Cl$ $[M+H]^+$ 281.0693, found 281.0687. **m.p:** 106 °C.

Ethyl 3-amino-5-chloro-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3p): yield 74% (41.5 mg); White solid, Hexane/EtOAc = 94/6, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 -7.24 (m, 3H), 5.79 (s, 2H), 4.38 (s, 2H), 3.77 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.3, 157.7, 138.7, 134.9, 130.0, 125.7, 125.5, 118.2, 113.1, 61.8, 31.2, 14.2. **HRMS-ESI:** calcd for $C_{13}H_{14}N_2O_3Cl$ $[M+H]^+$ 281.0693, found 281.0687. **m.p:** 108 °C.

Ethyl 3-amino-8-bromo-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3q): yield 72% (46.8 mg); White solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.04 (t, *J* = 8.1 Hz, 1H), 6.76 (s, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 160.3, 141.5, 132.6, 132.2, 124.5, 124.4, 124.4, 109.6, 102.2, 61.4, 40.4, 14.6.**HRMS-ESI:** calcd for $C_{13}H_{14}N_2O_3Br$ $[M+H]^+$ 325.0188, found 325.0183. **m.p:** 110 °C.

Methyl 3-amino-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3r): yield 87% (40.4 mg); White solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 3.7 Hz, 2H), 7.26 -7.23 (m, 1H), 6.89 (s, 2H), 4.00 (s, 3H), 3.80 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 157.9, 141.9, 132.6, 125.5, 125.3, 123.4, 119.8, 114.3, 102.0, 52.0, 31.0. **HRMS-ESI:** calcd for $C_{12}H_{13}N_2O_3$ $[M+H]^+$ 233.0926, found 233.0937. **m.p:** 105 °C.

***tert*-Butyl 3-amino-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3s):** yield 81% (44.4 mg); Off-white solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 3.5 Hz, 2H), 7.24-7.22 (m, 1H), 6.66 (s, 2H), 3.79 (s, 3H), 1.67 (s, 9H)**^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.6, 158.1, 140.8, 132.7, 125.4, 125.2, 123.1, 120.1, 114.2, 104.4, 82.7, 30.9, 28.7.**HRMS-ESI:** calcd for $C_{15}H_{18}N_2NaO_3$ $[M+Na]^+$ 297.1215, found 297.1216. **m.p:** 106 °C.

Benzyl 3-amino-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3t): yield 82% (50.6 mg); White solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$ δ 8.41 (d, *J* = 8.3 Hz, 1H), 7.48 (d, *J* = 7.3 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.30 (d, *J* = 5.1 Hz, 2H), 7.22 – 7.18 (m, 1H), 6.88 (s, 2H), 5.47 (s, 2H), 3.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.2, 157.9, 142.0, 135.8, 132.6, 128.9, 128.6, 128.4, 125.5, 125.3, 123.4, 119.8, 114.3, 101.9, 67.0, 31.0.**HRMS-ESI:** calcd for $C_{18}H_{17}N_2O_3$ $[M+H]^+$ 309.1239, found 309.1230. **m.p:** 105 °C.

Phenyl 3-amino-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3u): yield 71% (41.8 mg); White solid, Hexane/EtOAc = 94/6, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1H NMR (500 MHz, CDCl3) δ 8.56 (d, *J* = 8.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.26 (d, *J* = 5.7 Hz, 3H), 7.12 (s, 2H), 3.84 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.4,

157.7, 150.4, 143.3, 132.7, 129.8, 126.4, 125.6, 125.5, 123.6, 122.1, 119.7, 114.5, 100.7, 31.2. **HRMS-ESI:** calcd for $C_{17}H_{15}N_2O_3$ $[M+H]^+$ 295.1083, found 295.1093. **m.p:** 112 °C.

3-Amino-4-benzoyl-1-methylquinolin-2(1H)-one (3v): yield 69% (38.4 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 5.72 (s, 2H), 3.86 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.0, 158.3, 138.3, 137.0, 133.6, 133.1, 129.7, 129.0, 125.7, 125.7, 122.7, 120.5, 114.4, 113.6, 30.8. **HRMS-ESI:** calcd for $C_{17}H_{15}N_2O_2$ $[M+H]^+$ 279.1134, found 279.1117. **m.p:** 136 °C.

3-Amino-4-(4-methylbenzoyl)-1-methylquinolin-2(1H)-one (3w): yield 73% (42.7 mg); Yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.29-7.26 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.11 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.01-6.98 (m, 1H), 5.50 (s, 2H), 3.84 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.4, 158.3, 144.7, 136.2, 135.4, 133.1, 129.9, 129.6, 125.6, 125.4, 122.7, 120.5, 114.4, 114.3, 30.7, 21.8. **HRMS-ESI:** calcd for $C_{18}H_{17}N_2O_2$ $[M+H]^+$ 293.1303, found 293.1290.

3-Amino-4-(4-methoxybenzoyl)-1-methylquinolin-2(1H)-one (3x): yield 62% (38.2 mg); Yellow solid, Hexane/EtOAc = 94/6, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 2H), 5.29 (s, 2H), 3.86 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.2, 164.4, 158.4, 135.5, 133.3, 132.3, 130.5, 125.8, 125.3, 122.8, 120.6, 115.2, 114.3, 114.3, 55.7, 30.7. **HRMS-ESI:** calcd for $C_{18}H_{17}N_2O_3$ $[M+H]^+$ 309.1225, found 309.1239.

3-Amino-1-methyl-4-phenylquinolin-2(1H)-one (3y): yield 85% (42.6 mg); Light yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (t, *J* = 7.5 Hz, 2H), 7.46 (dd, *J* = 10.7, 4.3 Hz, 1H), 7.38-7.32 (m, 4H), 7.11 – 7.07 (m, 2H), 4.34 (s, 2H), 3.87 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.3, 135.1, 134.0, 133.3, 130.0, 129.6, 128.3, 125.6, 124.7, 122.8, 122.5, 120.2, 114.0, 30.2. **HRMS-ESI:** calcd for $C_{16}H_{14}N_2NaO$ $[M+Na]^+$ 273.1004, found 273.1013. **m.p:** 134 °C.

3-Amino-4-(4-bromophenyl)-1-methylquinolin-2(1H)-one (3z): yield 76% (50.0 mg); Light yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.37-7.32 (m, 2H), 7.24 (d, *J* = 7.1 Hz, 2H), 7.11-7.04 (m, 2H), 4.35 (s, 2H), 3.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.1, 134.1, 134.0, 133.4, 132.9, 131.9, 125.8, 124.4, 122.7, 122.5, 122.4, 118.7, 114.1, 30.3. **HRMS-ESI:** calcd for $C_{16}H_{14}N_2OBr$ $[M+H]^+$ 329.0290, found 329.0280. **m.p:** 120 °C.

Ethyl 1-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-[1,2,3]triazole]-5'-carboxylate (6): yield 96% (52.7 mg); yellow liqid, Hexane/EtOAc = 92/8, **^{1}H NMR** (500 MHz, $CDCl_3$) 1H NMR (500 MHz, CDCl3) δ 7.40 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 4.06-4.03 (m, 2H), 3.24 (s, 3H), 1.95 (s, 2H), 1.12 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.8, 165.1, 143.5, 130.8, 130.1, 123.9, 123.3, 108.6, 60.9, 56.7, 26.7, 14.3. **HRMS-ESI:** calcd for $C_{13}H_{14}N_4O_3Na$ $[M+Na]^+$ 297.0964, found 297.0953.

Diethyl 1,1''-dimethyl-2,2''-dioxodispiro[indoline-3,1'-cyclobutane-3',3''-indoline]-2',4'-dicarboxylate (7): yield 91% (84.2 mg); Light yellow solid, Hexane/EtOAc = 95/5, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.29-7.27 (m, 4H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.72 (d, *J* = 7.8 Hz, 2H), 4.54 (s, 2H), 3.92 (dq, *J* = 14.3, 7.0 Hz, 2H), 3.81 (dq, *J* = 14.5, 7.1 Hz, 2H), 3.02 (s, 6H), 0.75 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.9, 168.9, 143.7, 129.4, 128.5, 123.4, 121.4, 107.7, 60.9, 54.4, 44.2, 26.7, 13.8. **HRMS-ESI:** calcd for $C_{26}H_{27}N_2O_6$ $[M+H]^+$ 463.1869, found 463.1852.

3-Amino-1-methylquinolin-2(1H)-one (8): yield 92% (32.1 mg); White solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.35-7.28 (m, 2H), 7.18 (ddd, *J* = 8.0, 6.7, 1.7 Hz, 1H), 6.82 (s, 1H), 4.42 (s, 2H), 3.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.8, 136.2, 134.5, 125.9, 125.7, 122.7, 122.4, 113.9, 109.2, 30.2.

Ethyl 3-benzamido-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (9): yield 77% (53.4 mg); White solid, Hexane/EtOAc = 95/5, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.10 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.98-7.96 (m, 2H), 7.60-7.48 (m, 4H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.33 (ddd, *J* = 8.2, 7.3, 1.0 Hz, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.7, 165.2, 158.7, 136.0, 133.8, 132.6, 129.6, 128.9, 127.7, 126.7, 125.4, 125.3, 123.7, 118.0, 114.4, 61.8, 31.0, 14.3.

Ethyl 3-amino-6-bromo-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate (3za): yield 79% (51.4 mg); Light yellow solid, Hexane/EtOAc = 96/4, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.17 (d, *J* = 8.9 Hz, 1H), 7.04 (s, 2H), 4.49 (q, *J* = 6.8 Hz, 2H), 3.77 (s, 3H), 1.49 (t, *J* = 6.8 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.0, 157.6, 142.6, 131.5, 128.1, 127.8, 121.7, 116.8, 115.8, 100.8, 61.5, 31.2, 14.5. **HRMS-ESI:** calcd for $C_{13}H_{14}N_2O_3Br$ $[M+H]^+$ 325.0188, found 325.0183. **m.p:** 123 °C.

***N*-(6-bromo-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)-4-methoxybenzamide (10):** yield 71% (55.0 mg); White solid, Hexane/EtOAc = 94/6, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.78

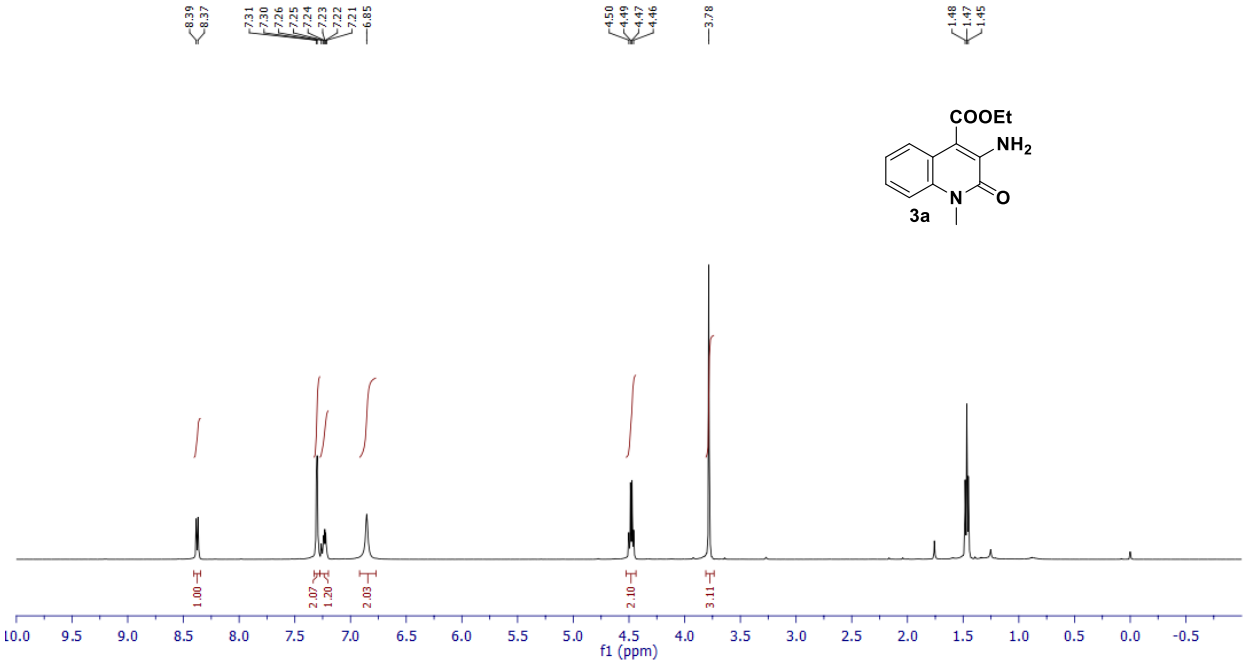
(s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 8.9 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H), 3.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.6, 163.0, 158.1, 134.6, 131.3, 130.7, 129.3, 129.0, 126.4, 123.1, 118.8, 116.2, 115.7, 114.2, 55.6, 30.6.

17. References:

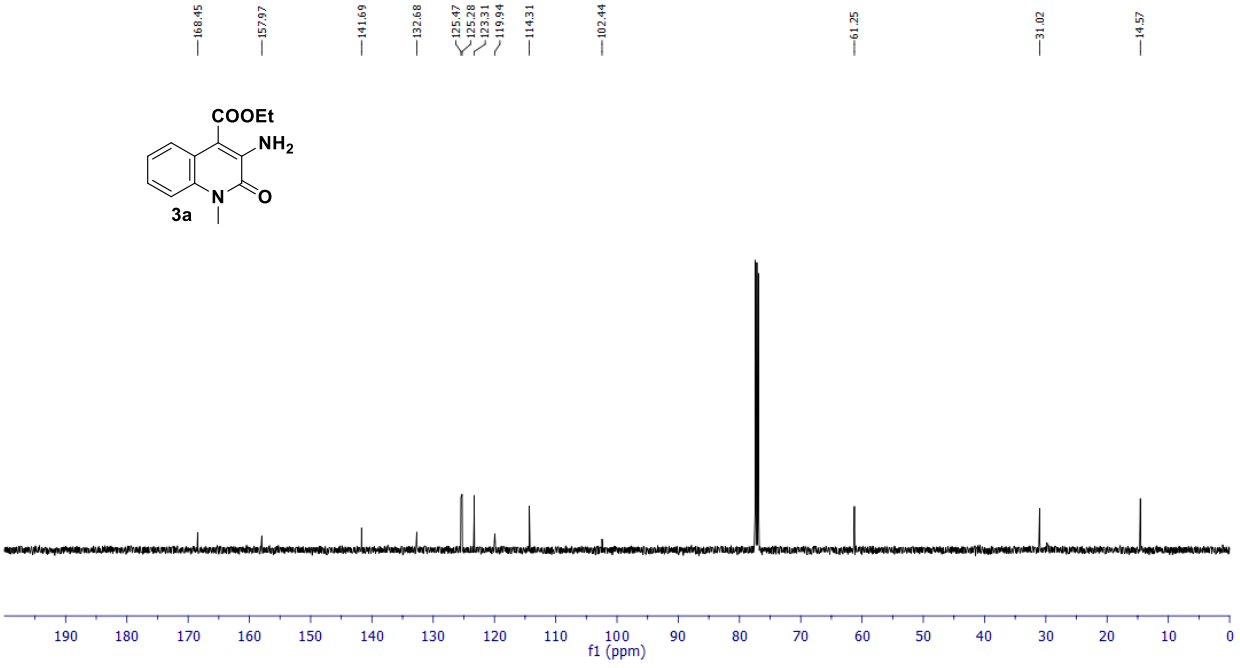
1. (a) F. Manoni and S. J. Connon, *Angew. Chem. Int. Ed.*, 2014, **53**, 2628–2632. (b) W.-K. Yuan, T. Cui, W. Liu, L.-R. Wen and M. Li, *Org. Lett.*, 2018, **20**, 1513–1516.
2. X.-H. Yang, K. Li, R.-J. Song and J.-H. Li, *European J. Org. Chem.*, 2014, **2014**, 616–623.

18. ^{1}H and ^{13}C NMR Spectra:

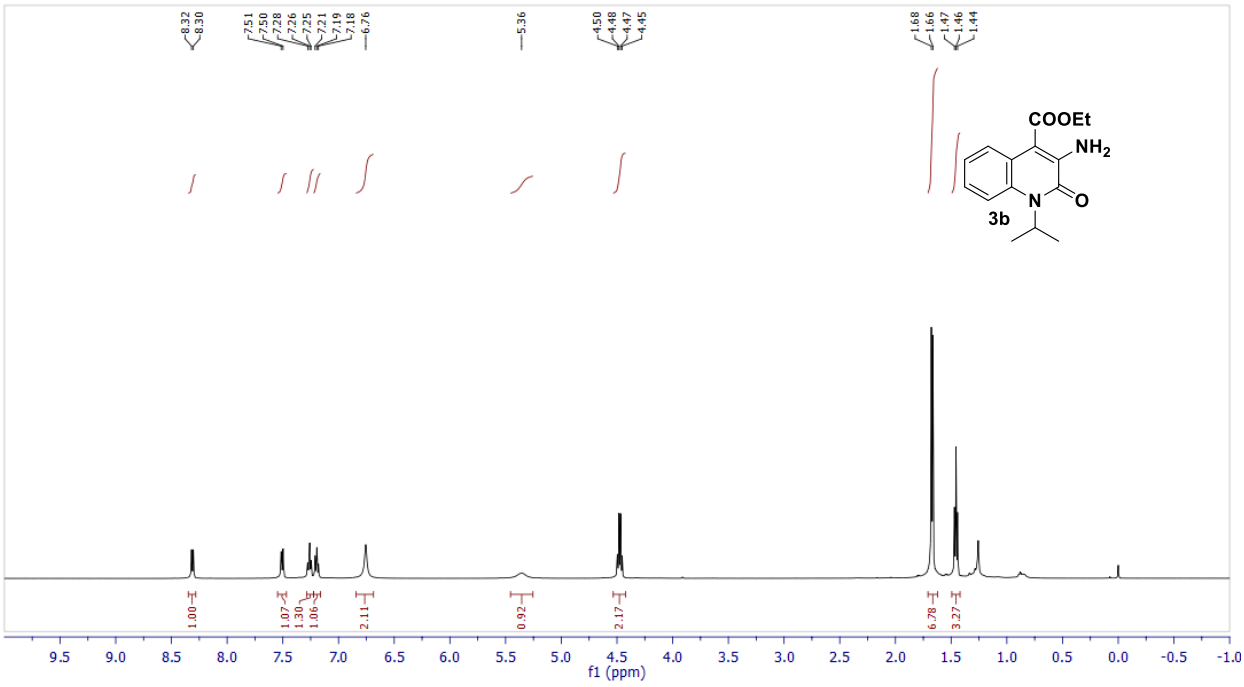
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3a**



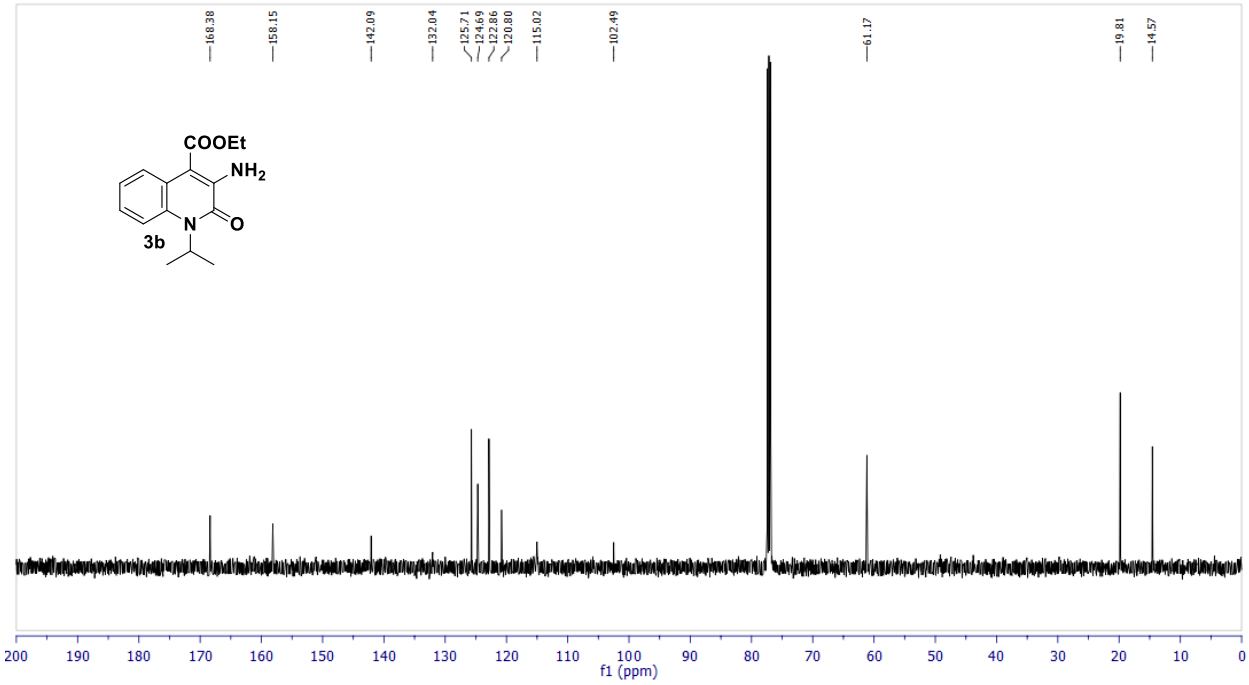
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3a**



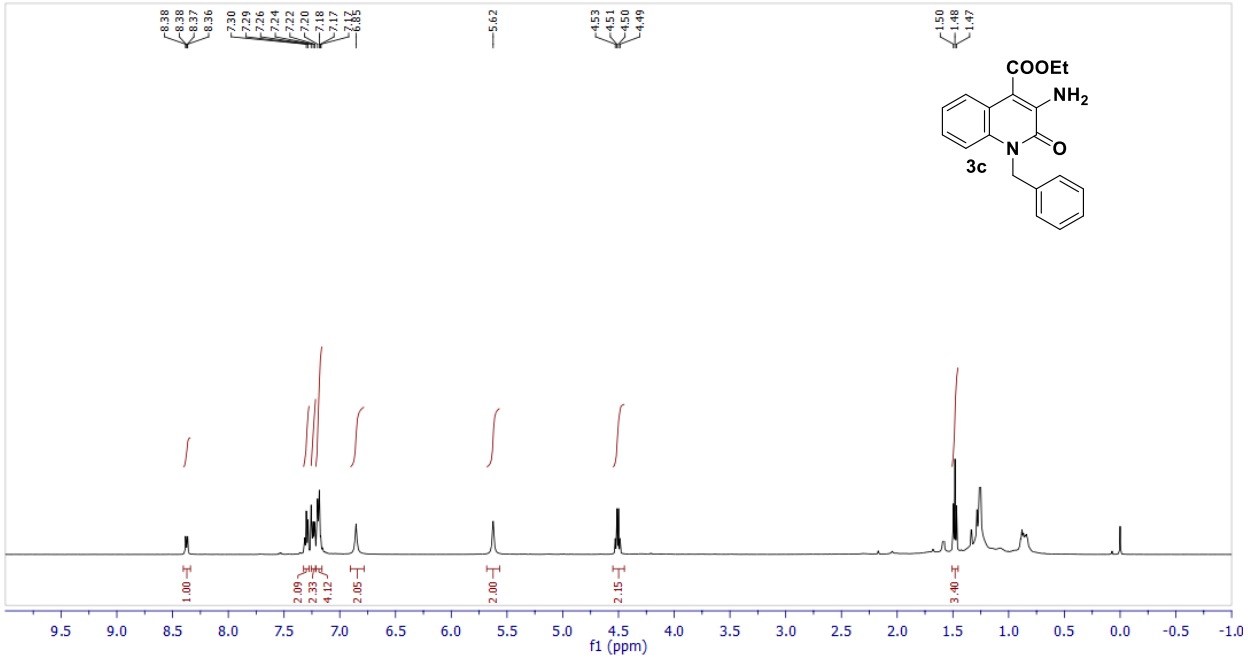
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3b**



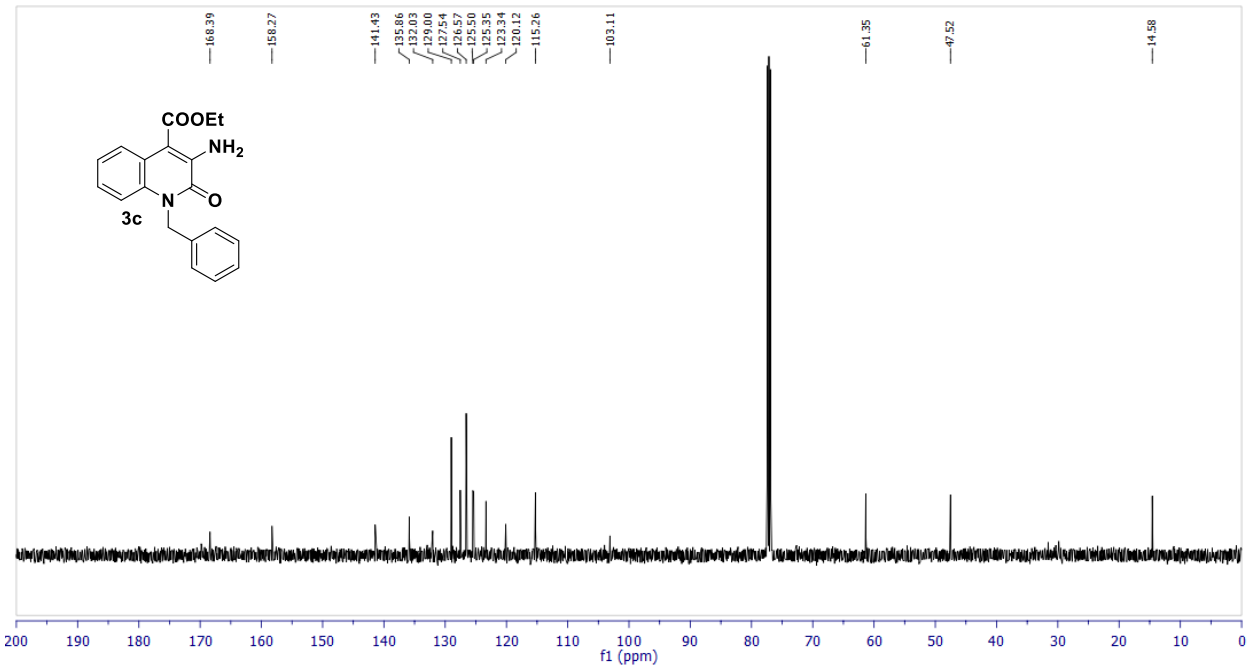
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3b**



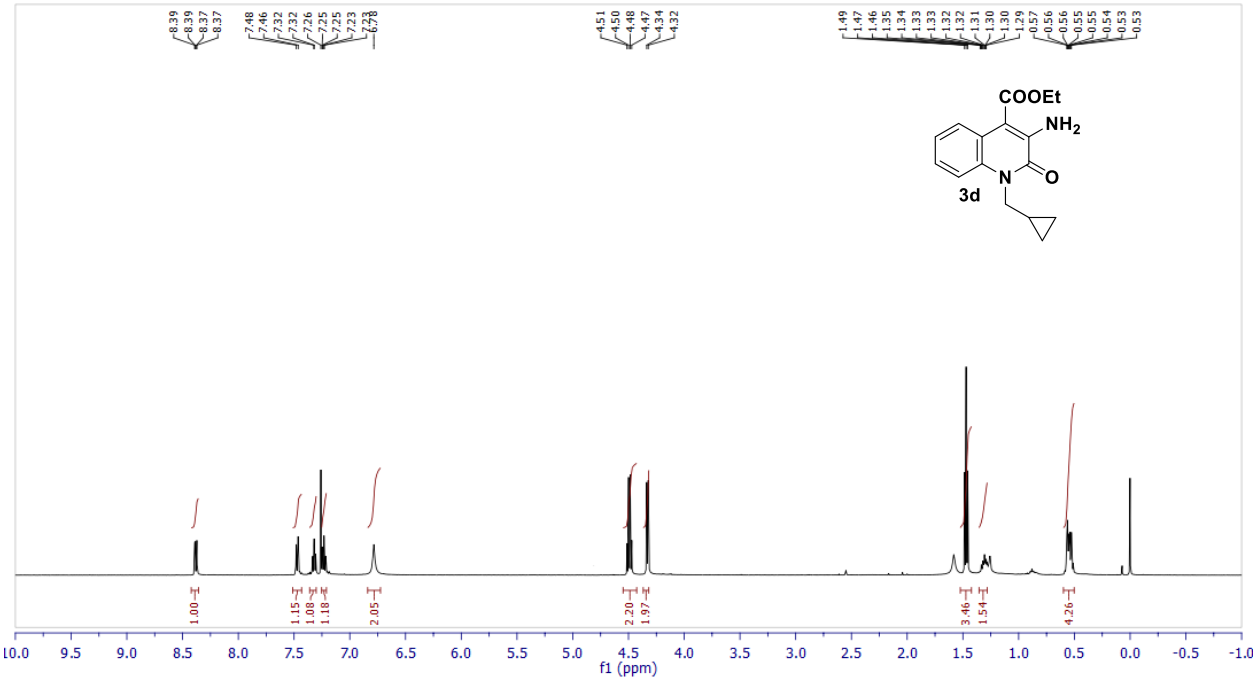
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3c**



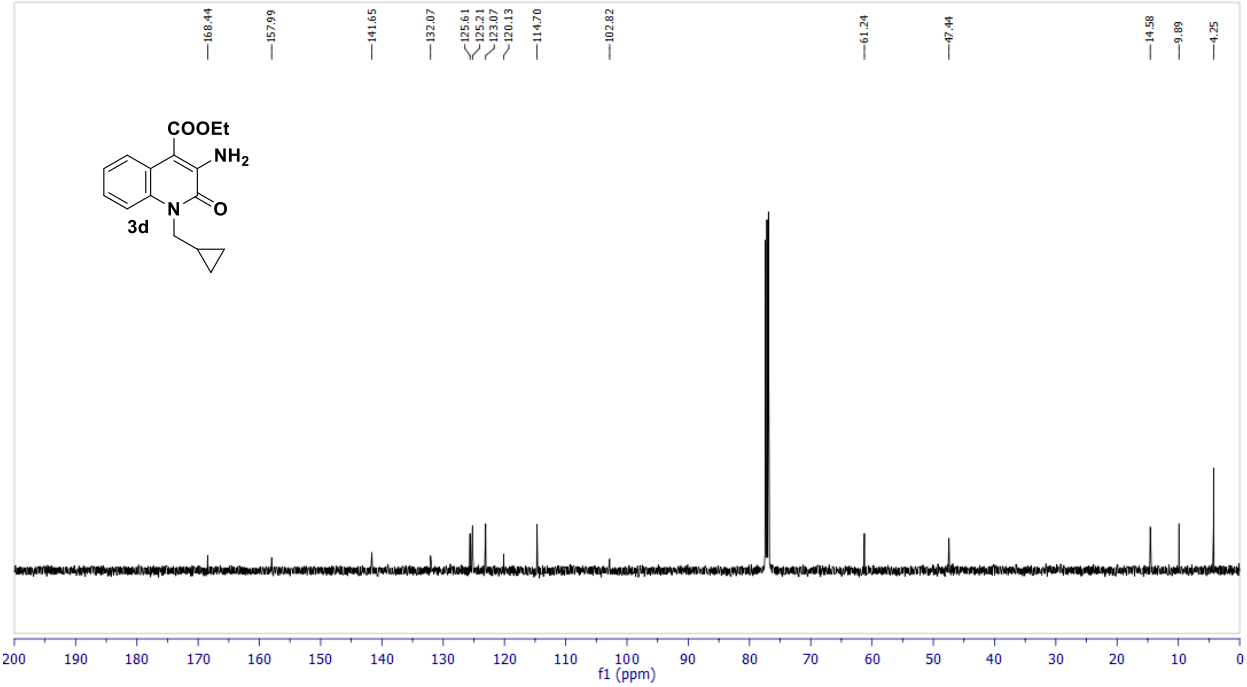
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3c**



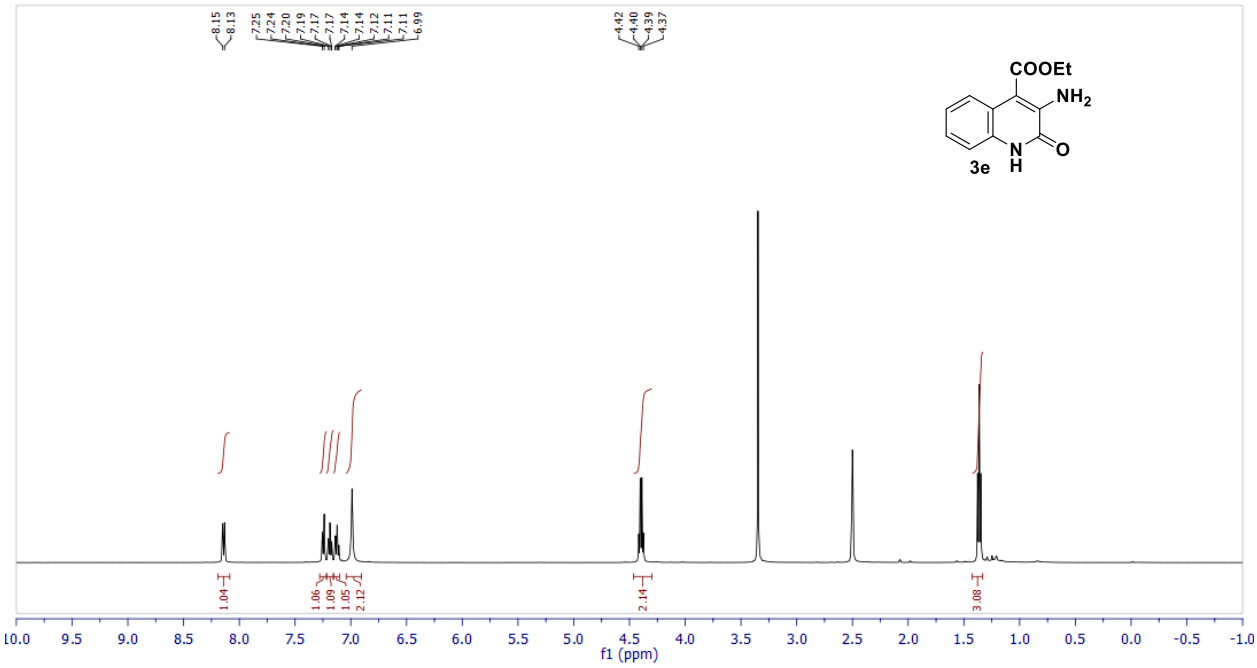
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3d**



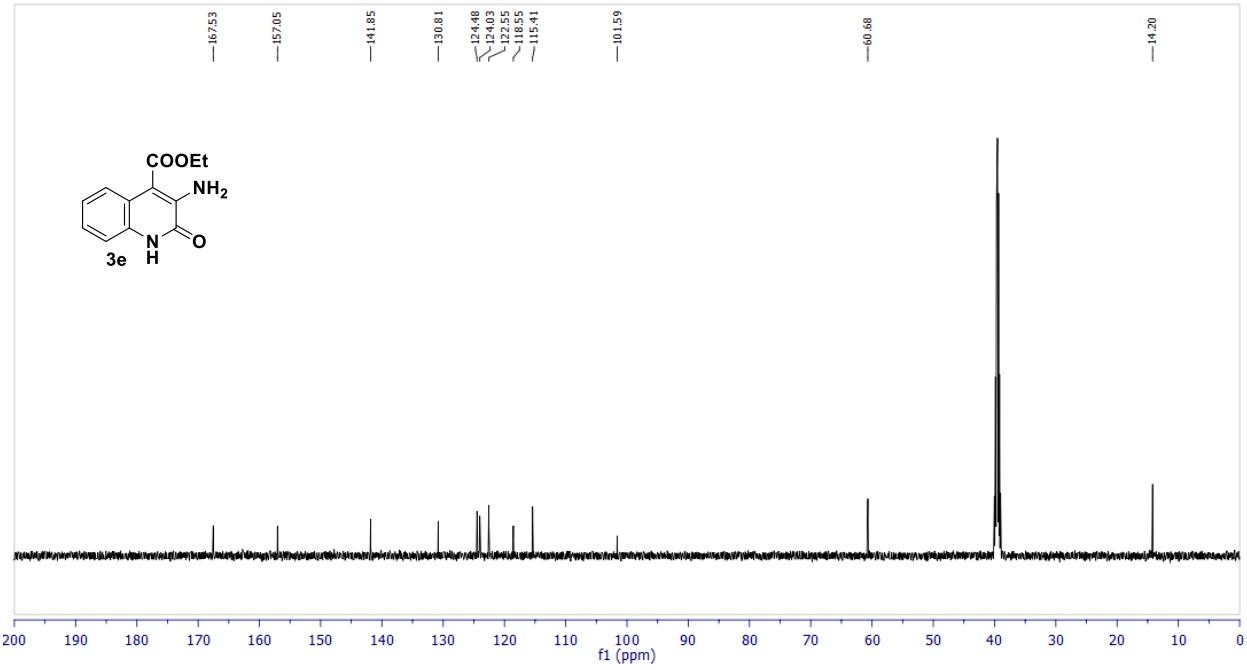
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3d**



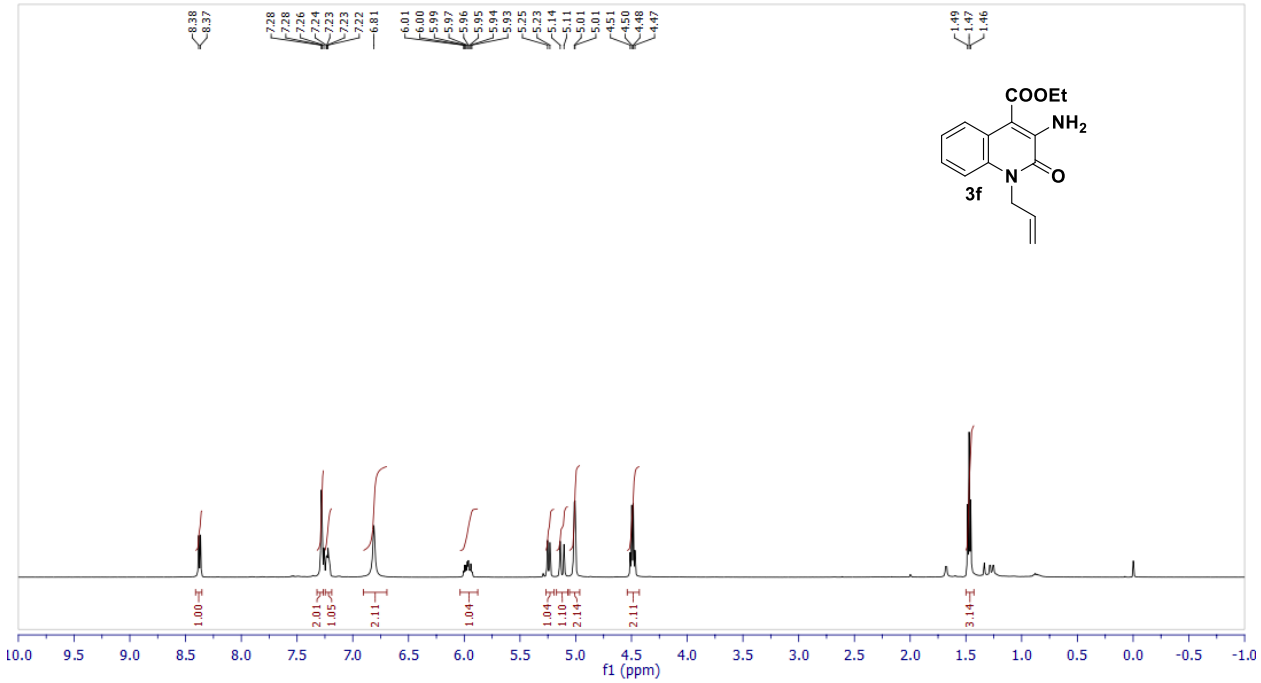
^{1}H NMR (500 MHz, DMSO) of compound **3e**



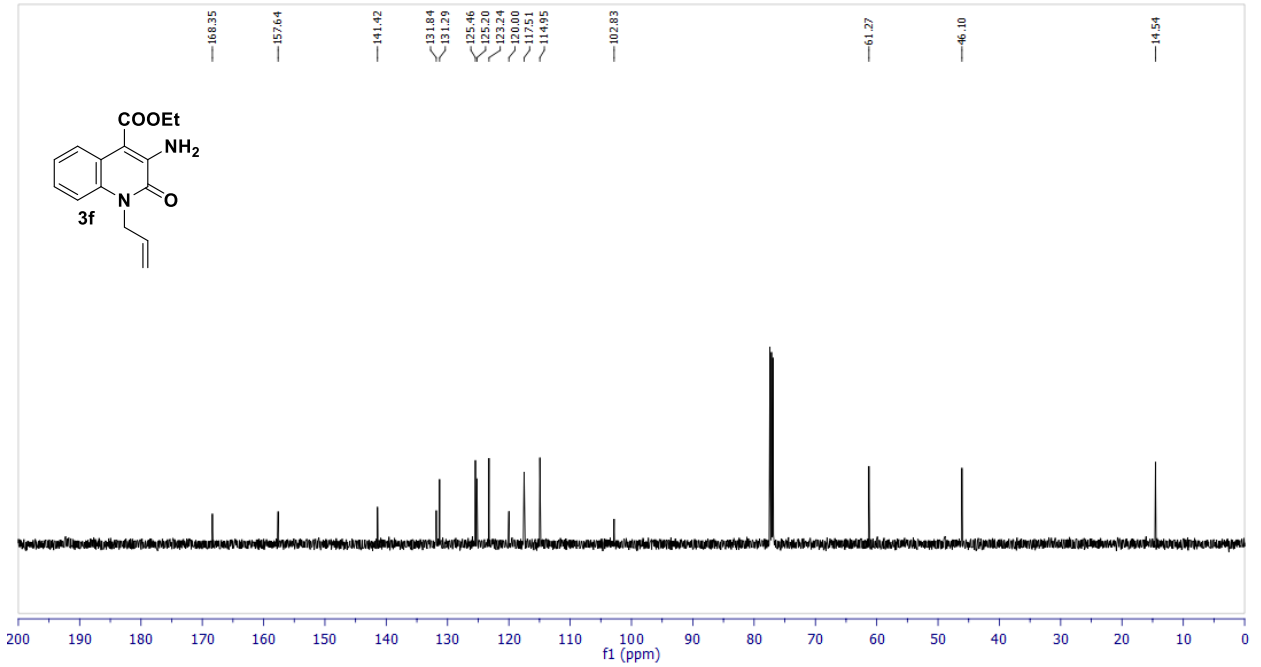
^{13}C NMR (126 MHz, DMSO) of compound **3e**



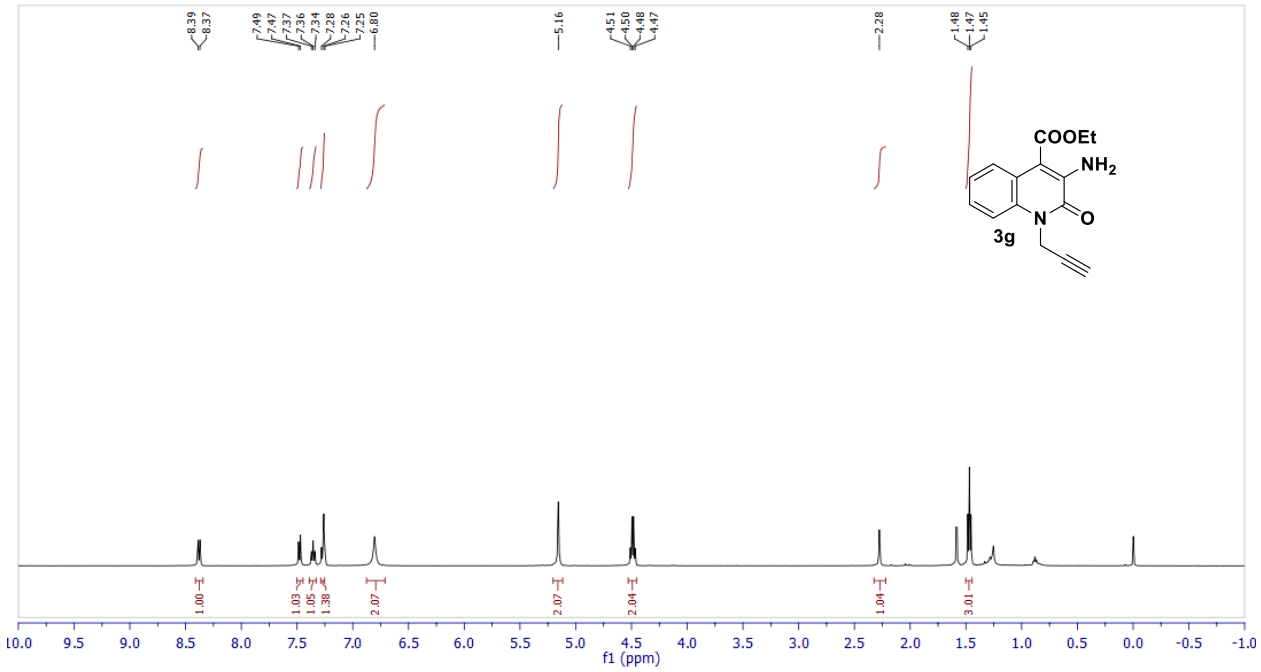
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3f**



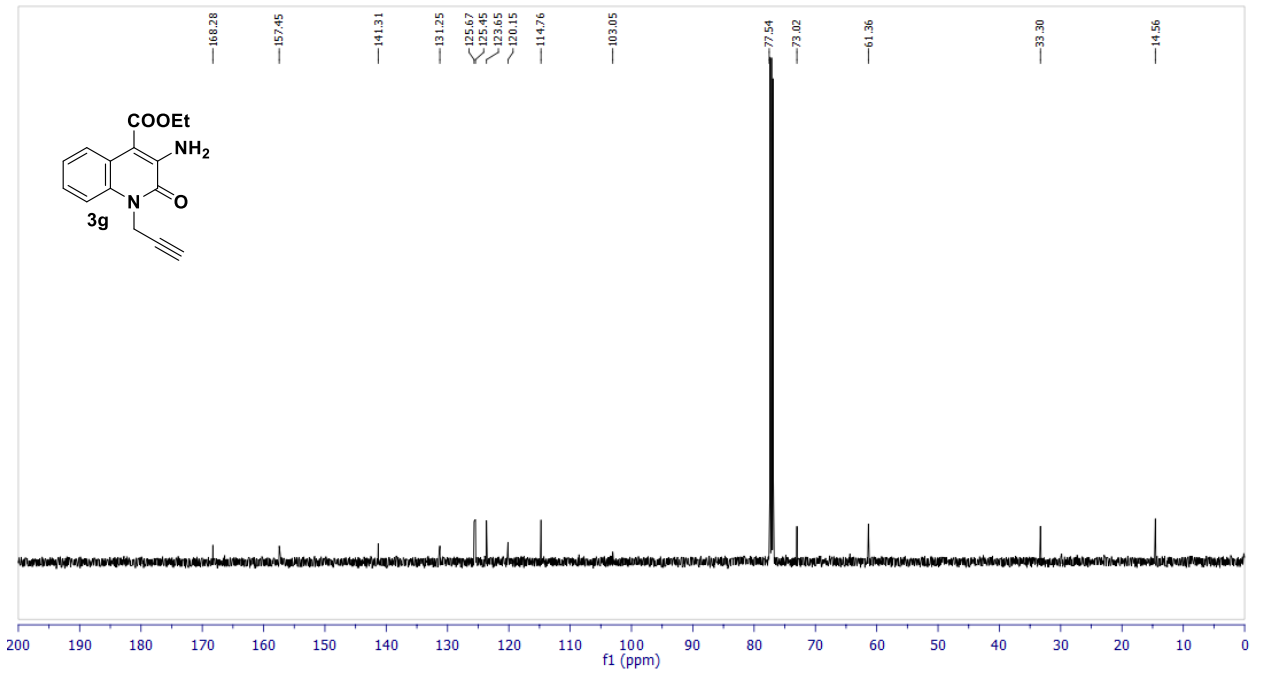
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3f**



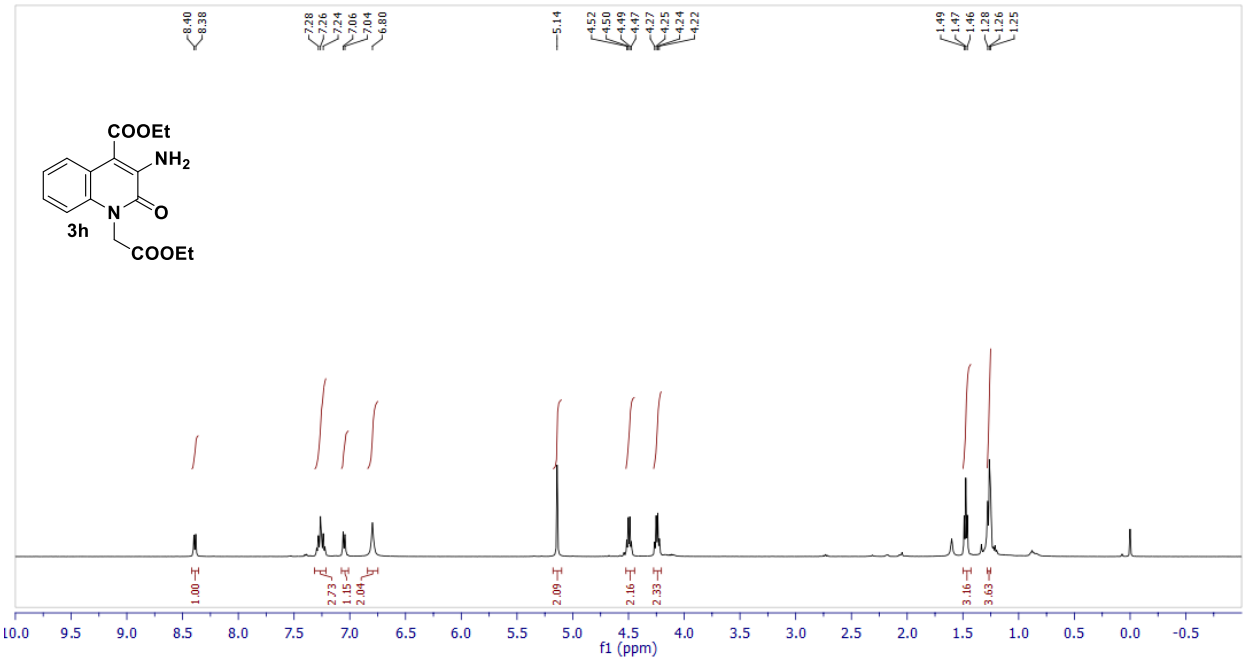
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3g**



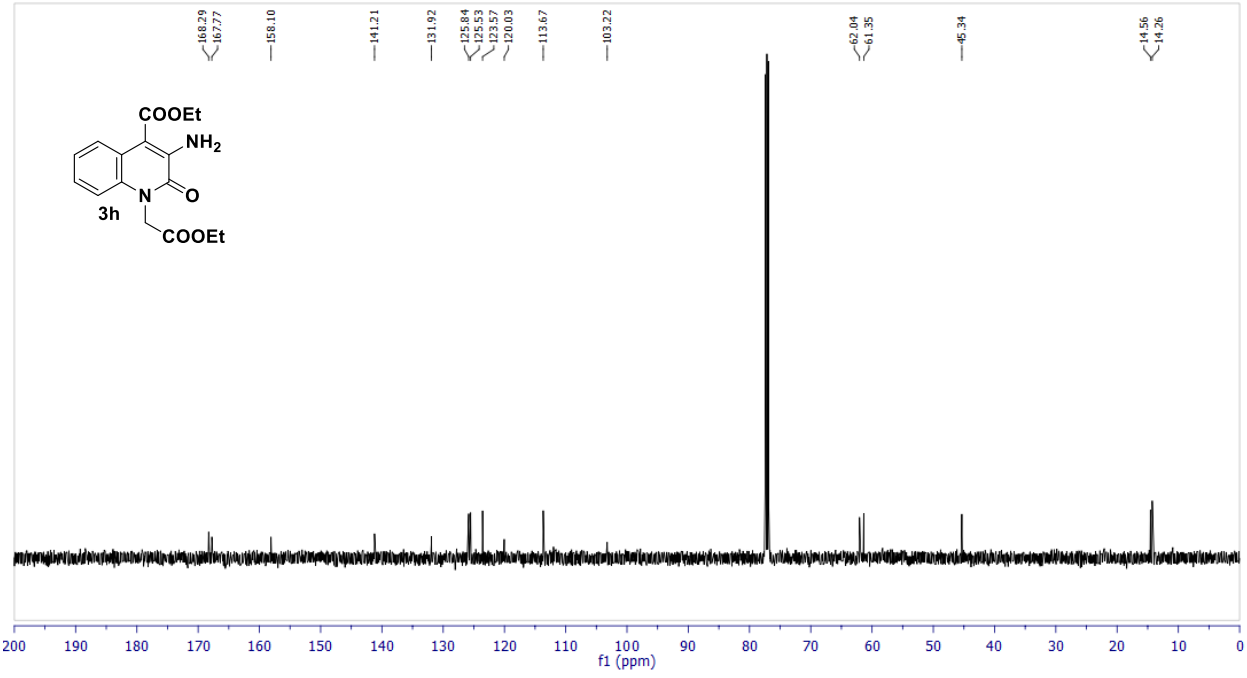
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3g**



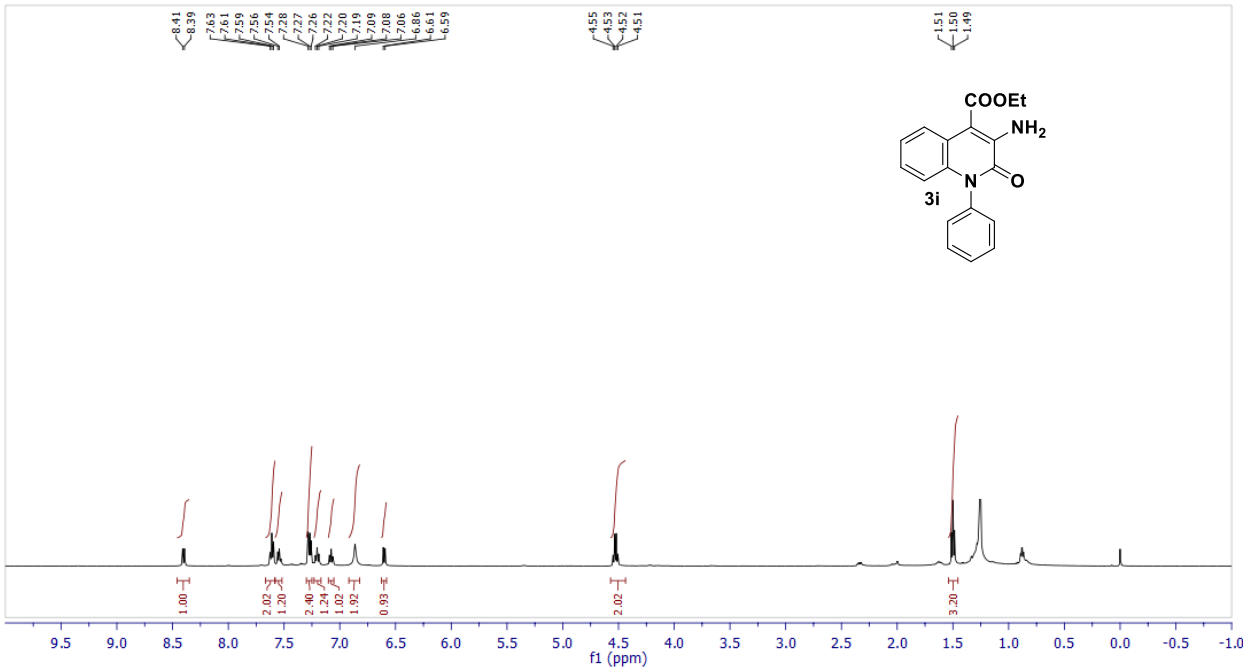
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3h**



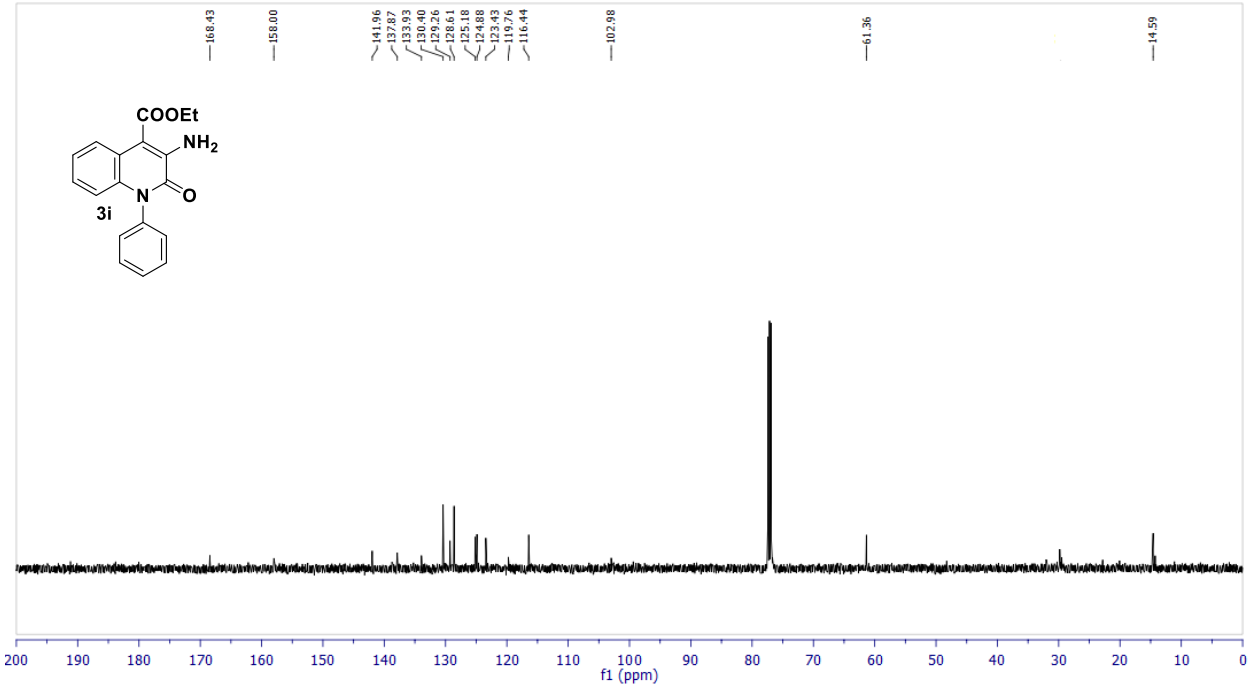
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3h**



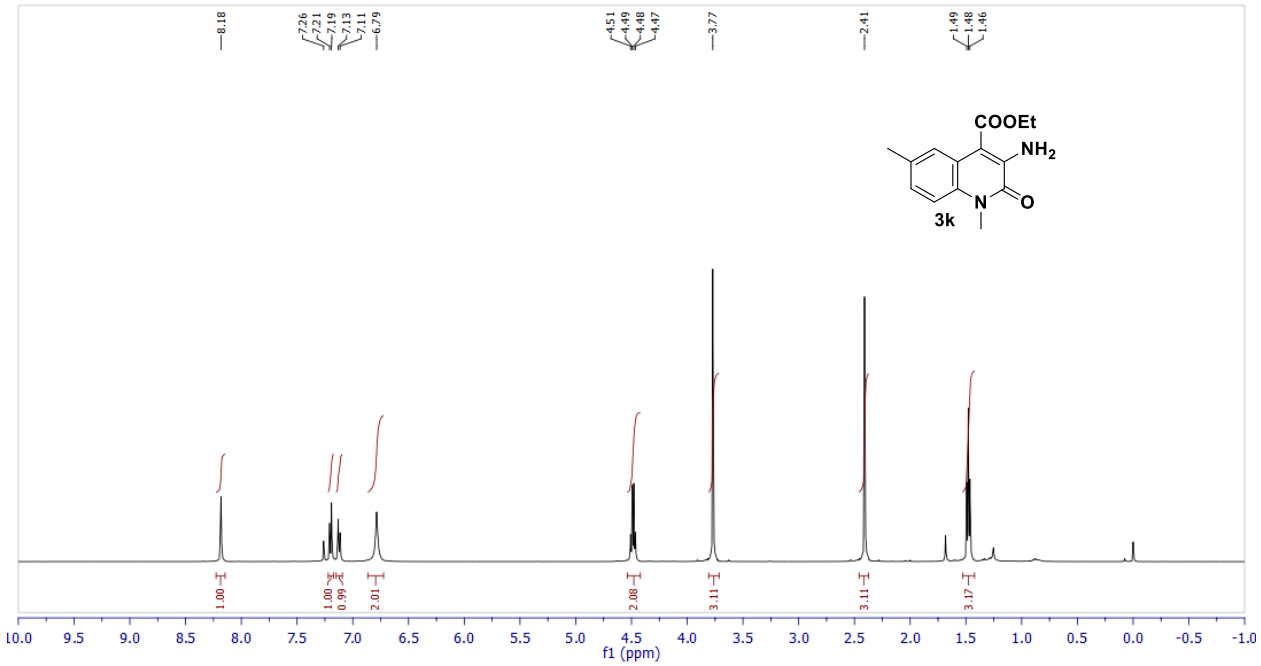
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3i**



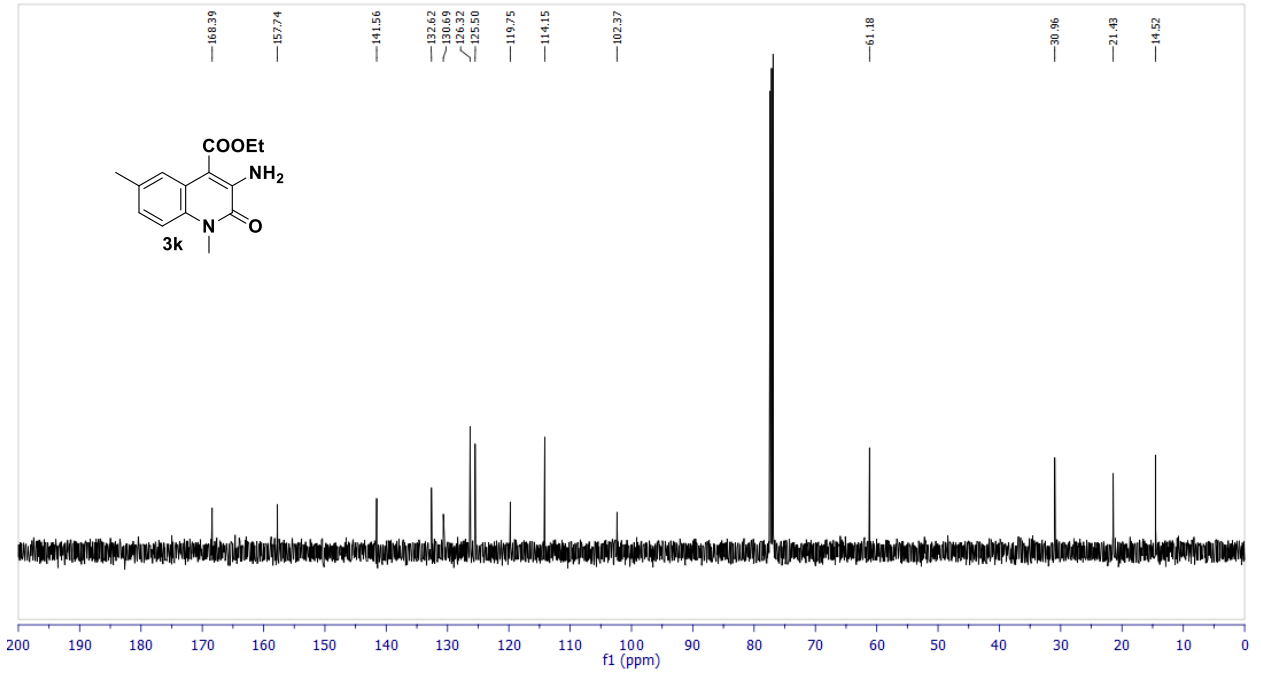
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3i**



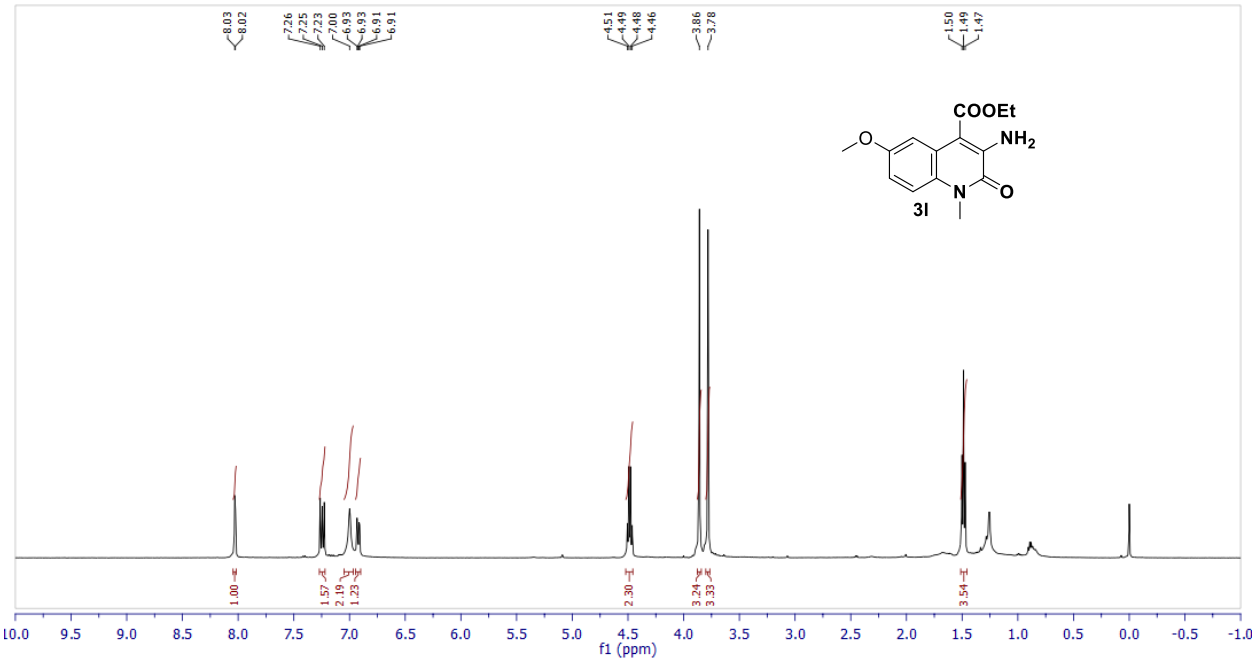
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3k**



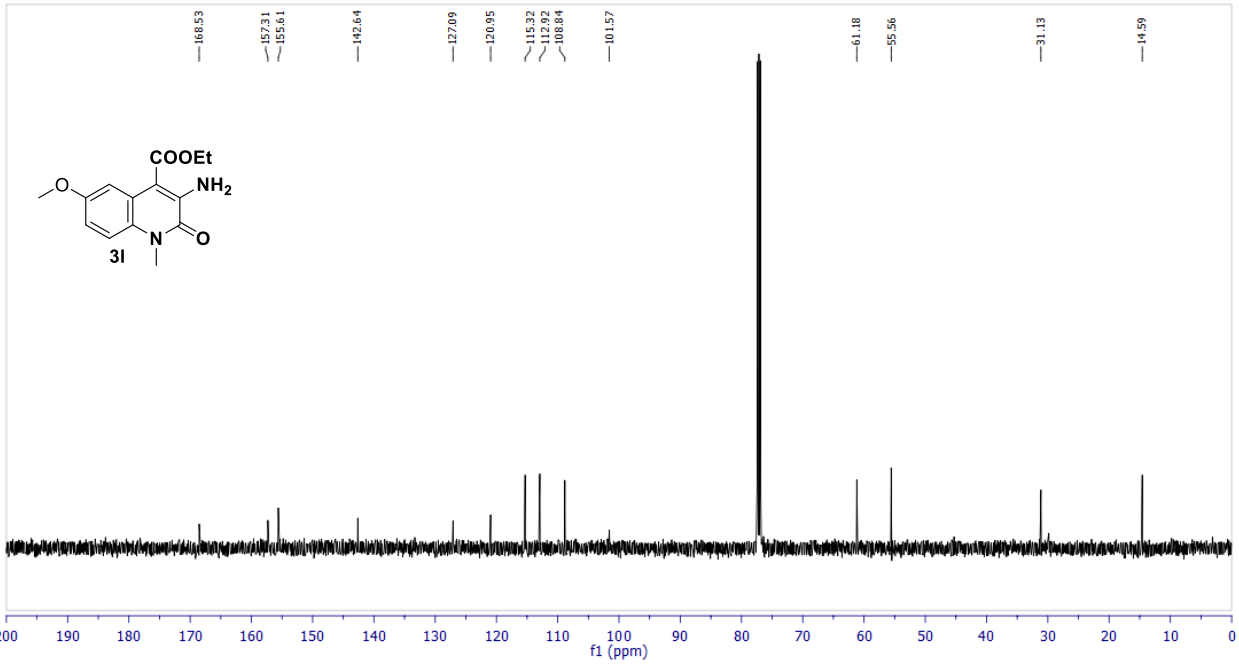
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3k**



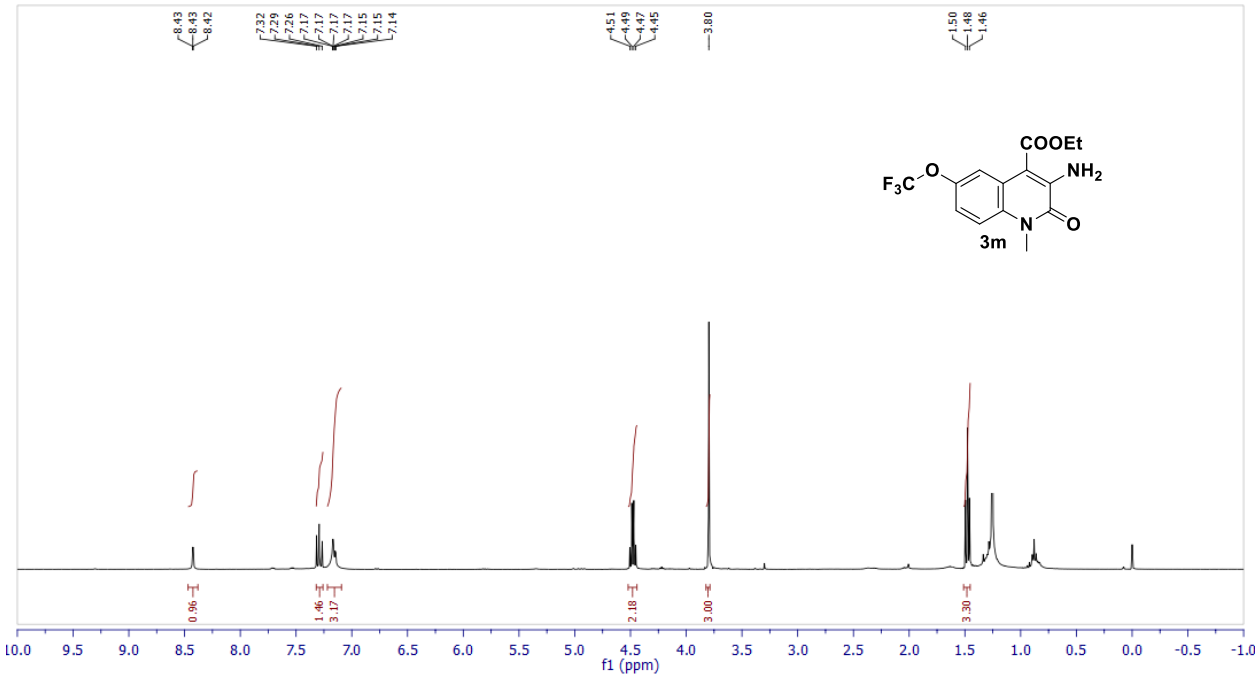
H NMR (500 MHz, $CDCl_3$) of compound **3l**



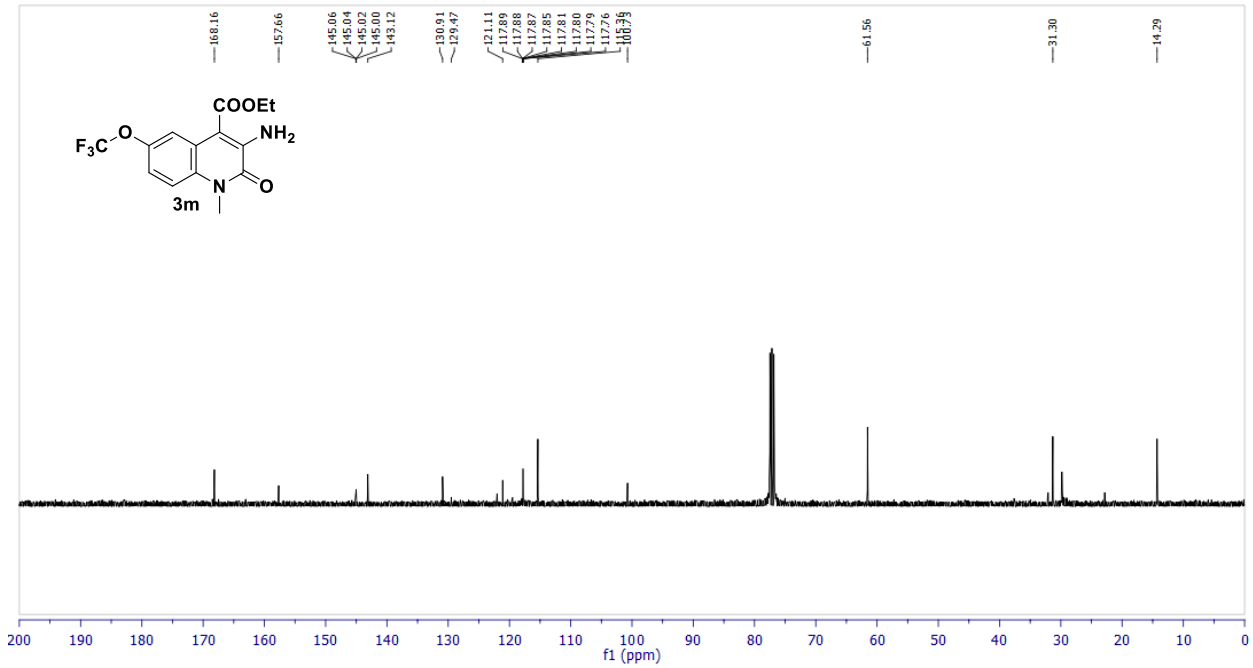
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3l**



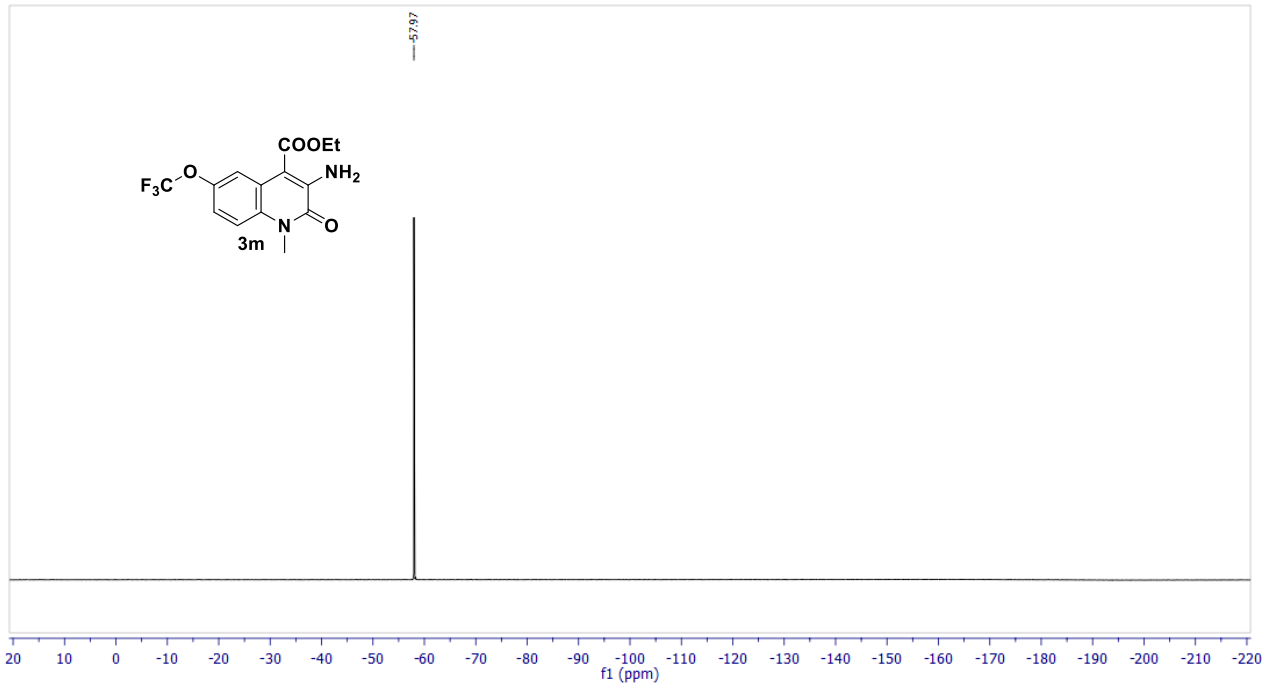
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3m**



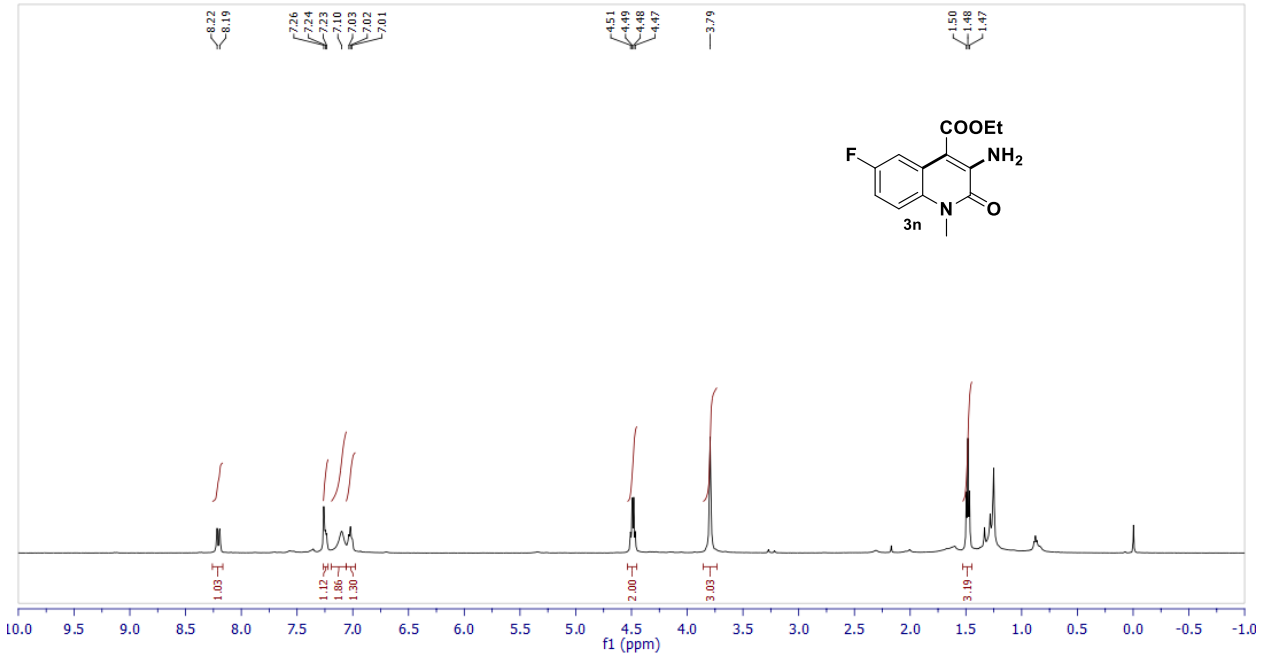
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3m**



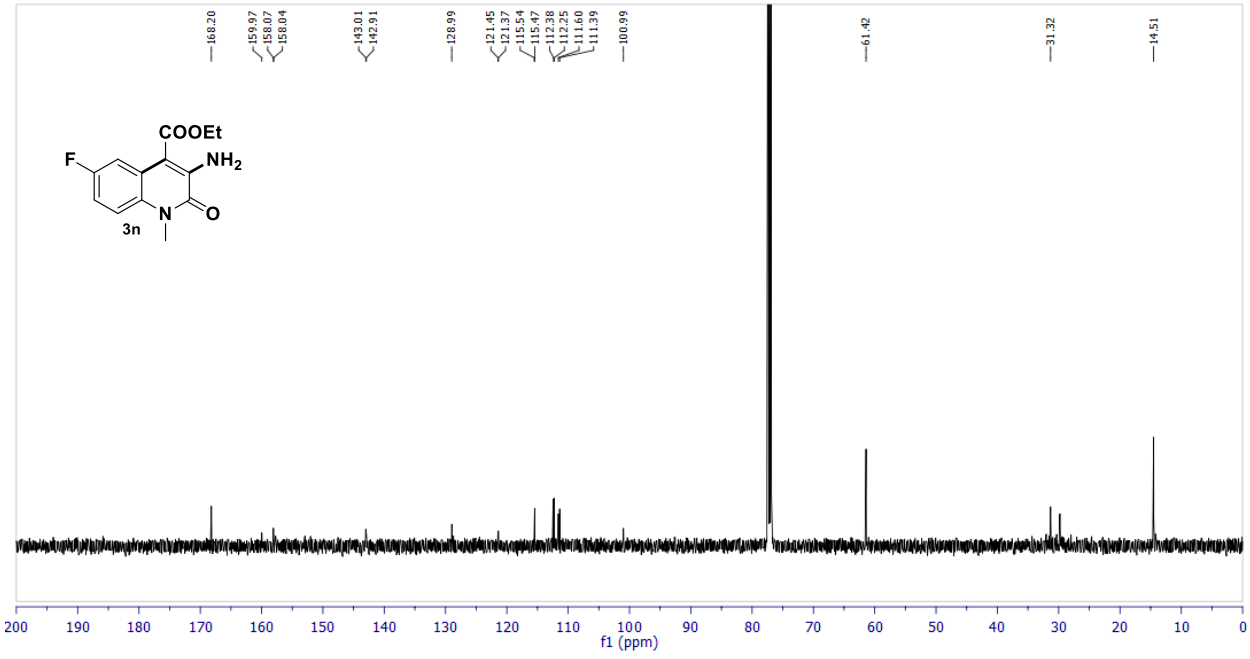
^{19}F NMR (471 MHz, $CDCl_3$) of compound **3m**



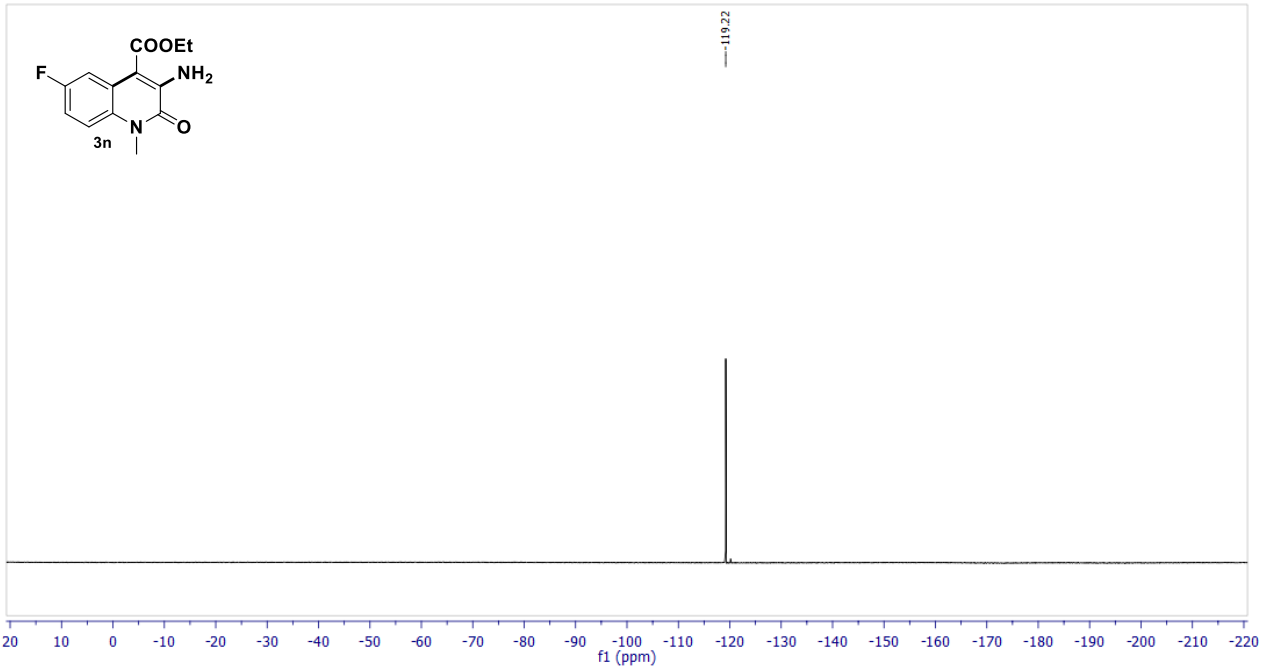
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3n**



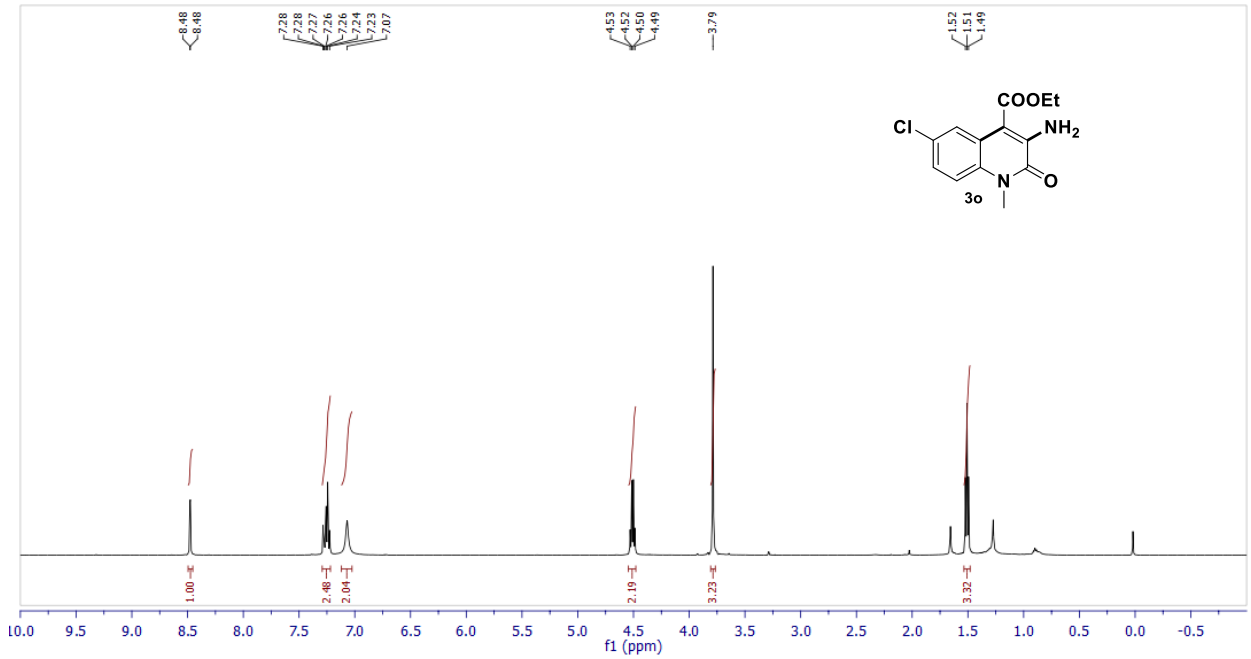
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3n**



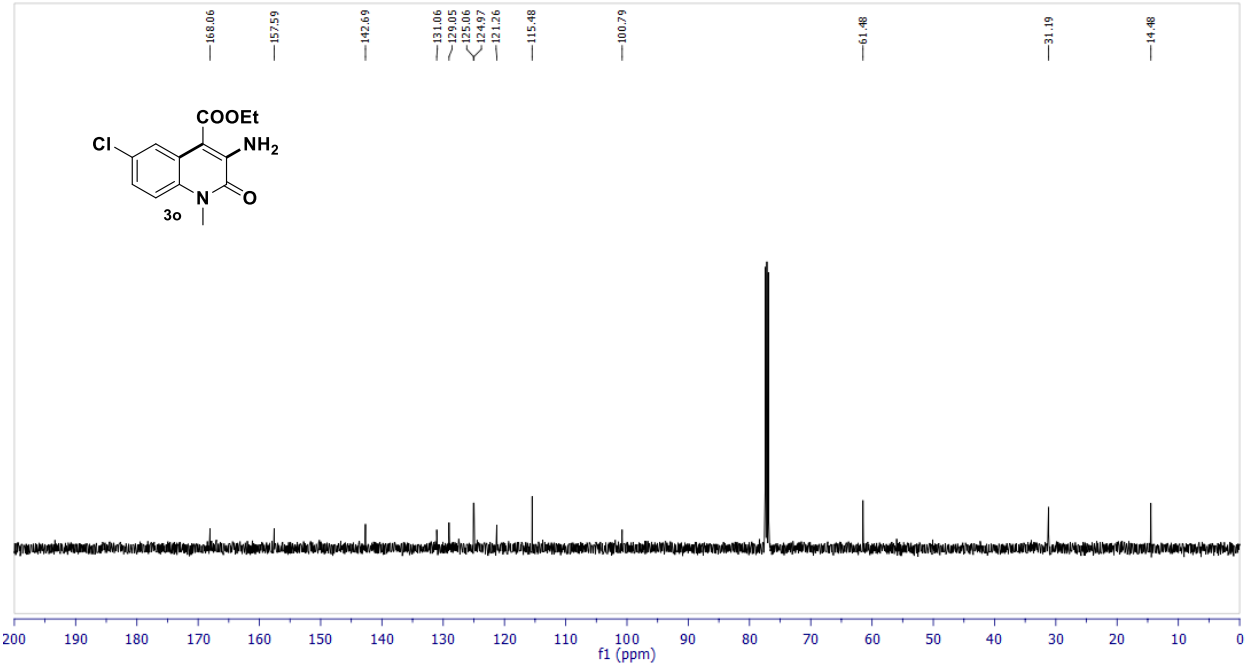
^{19}F NMR (471 MHz, $CDCl_3$) of compound **3n**



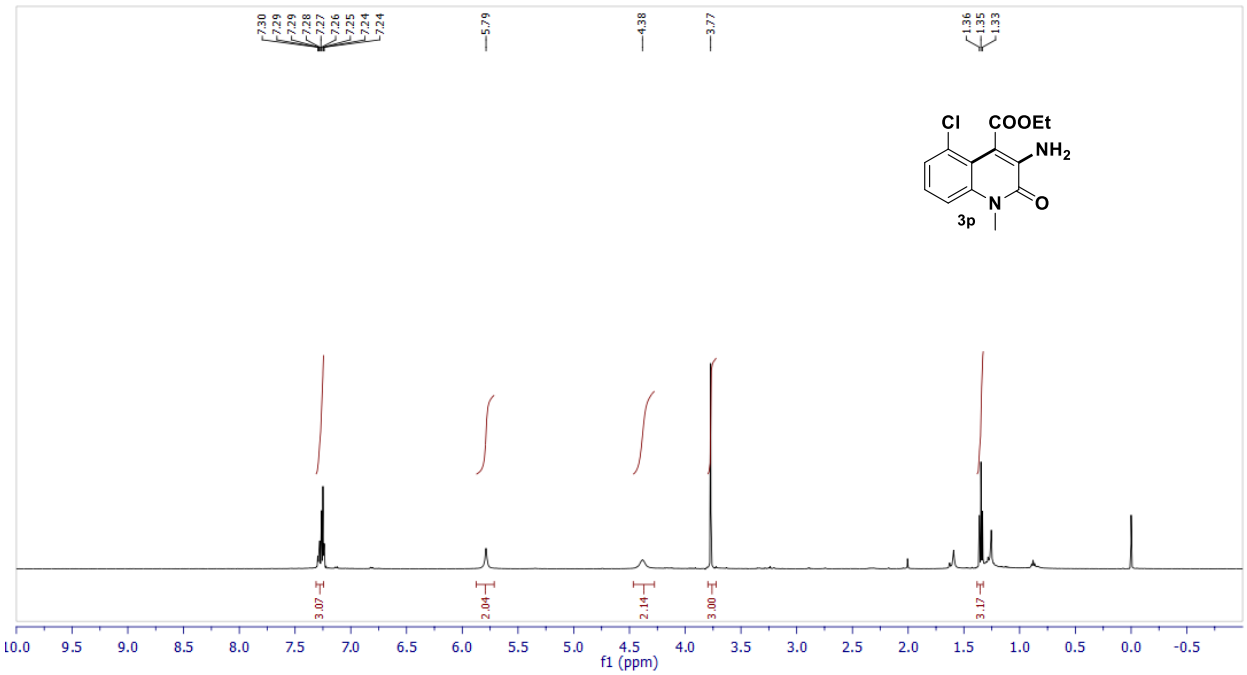
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3o**



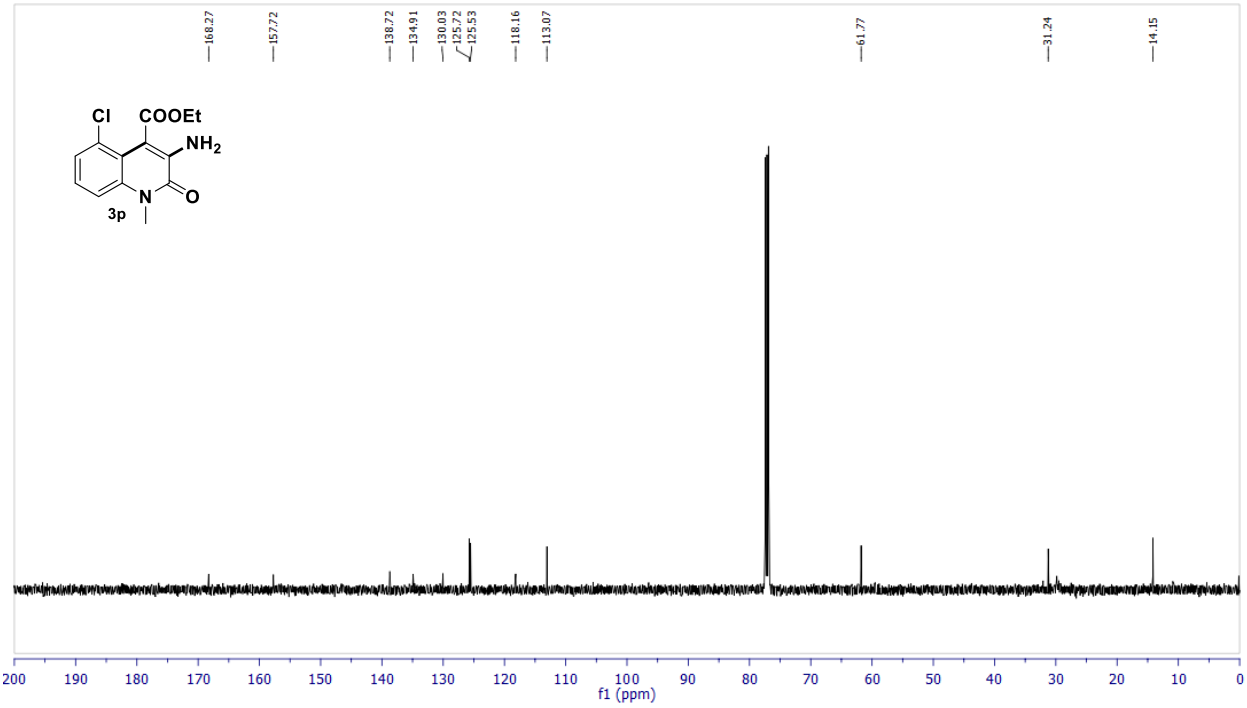
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3o**



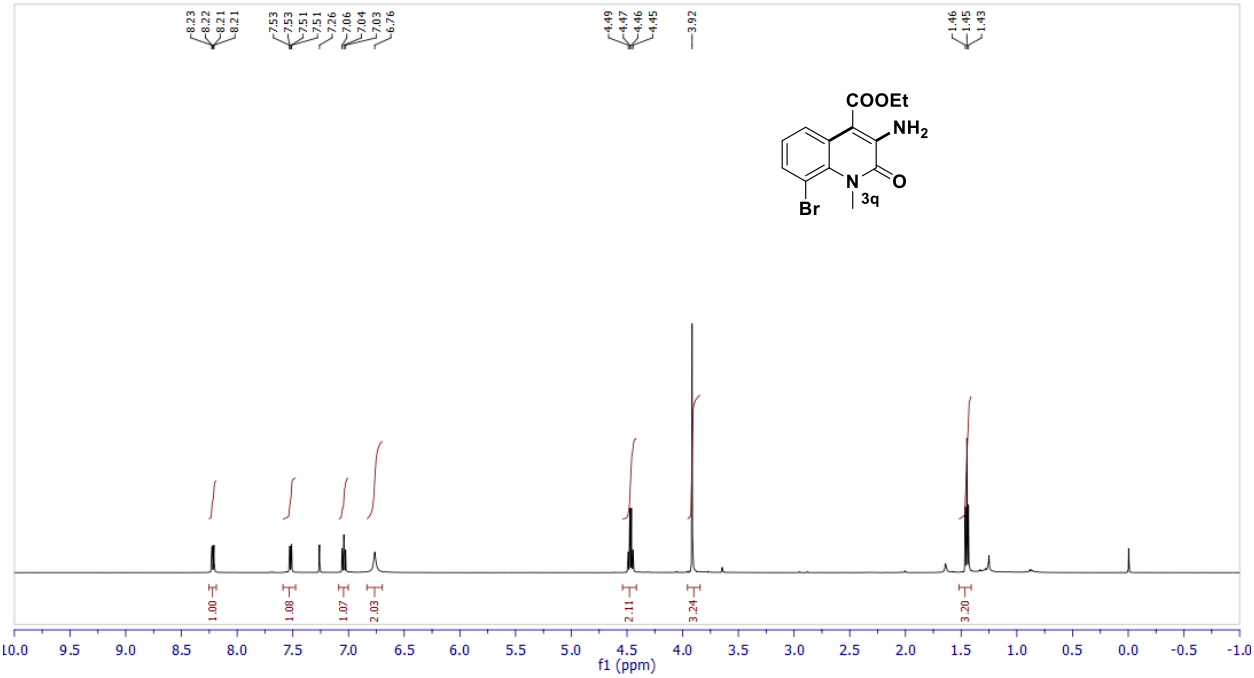
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3p**



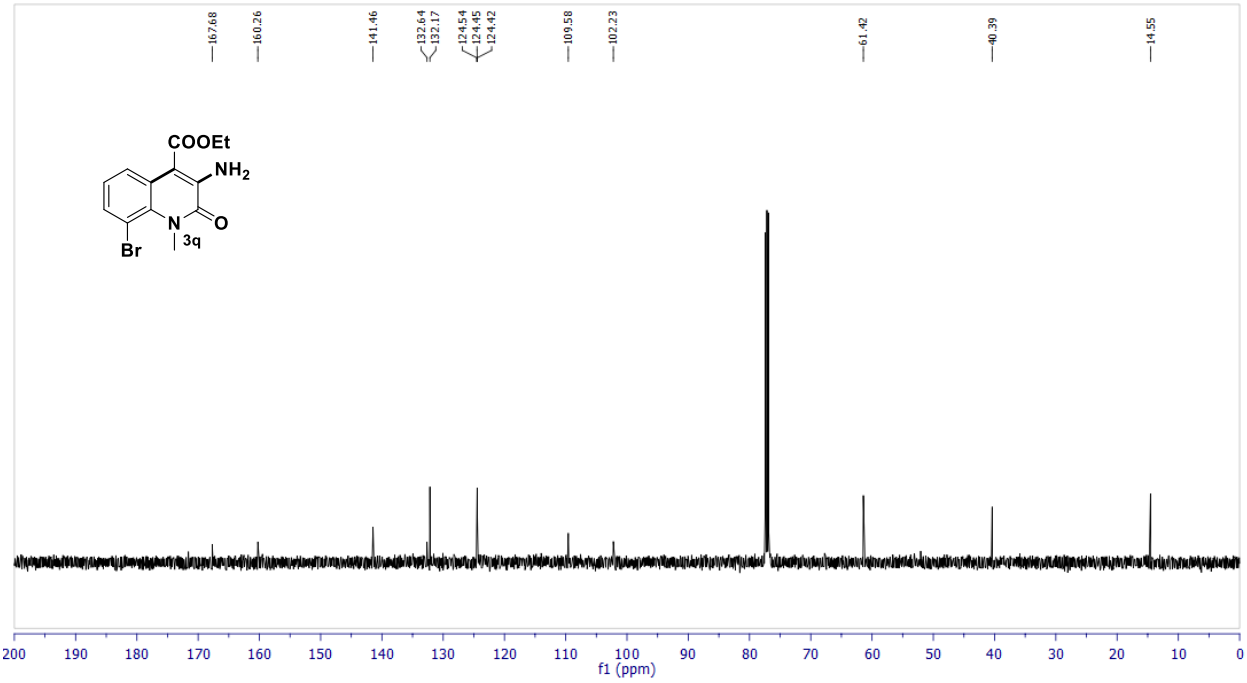
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3p**



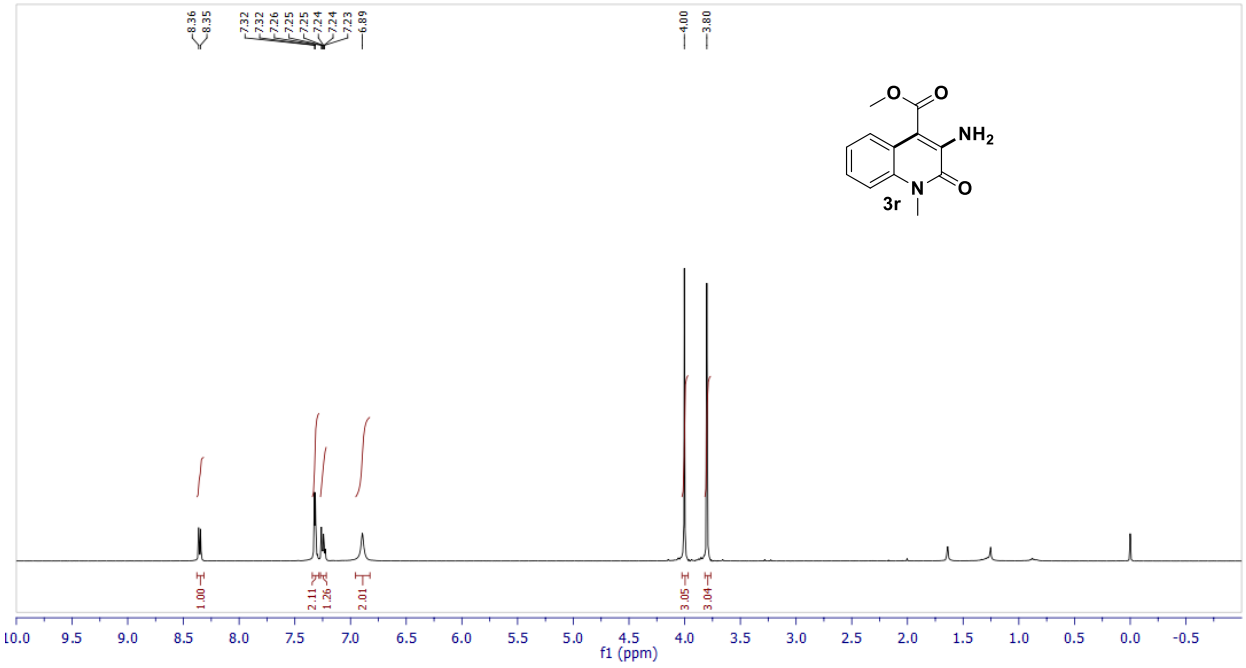
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3q**



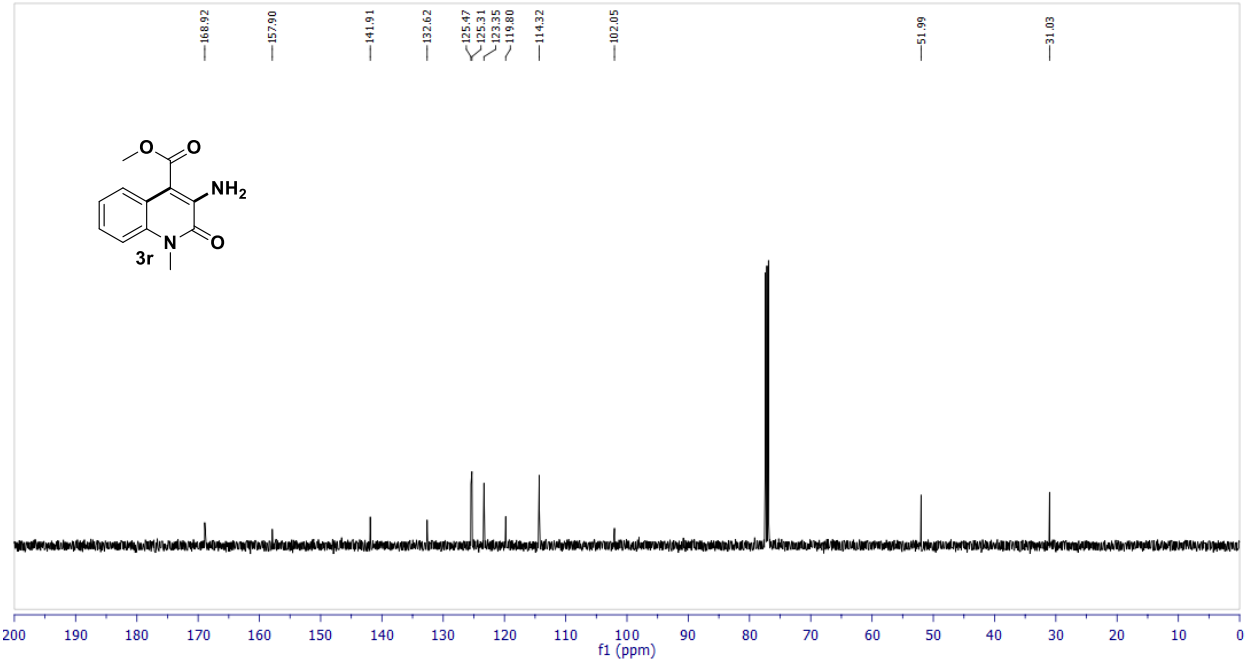
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3q**



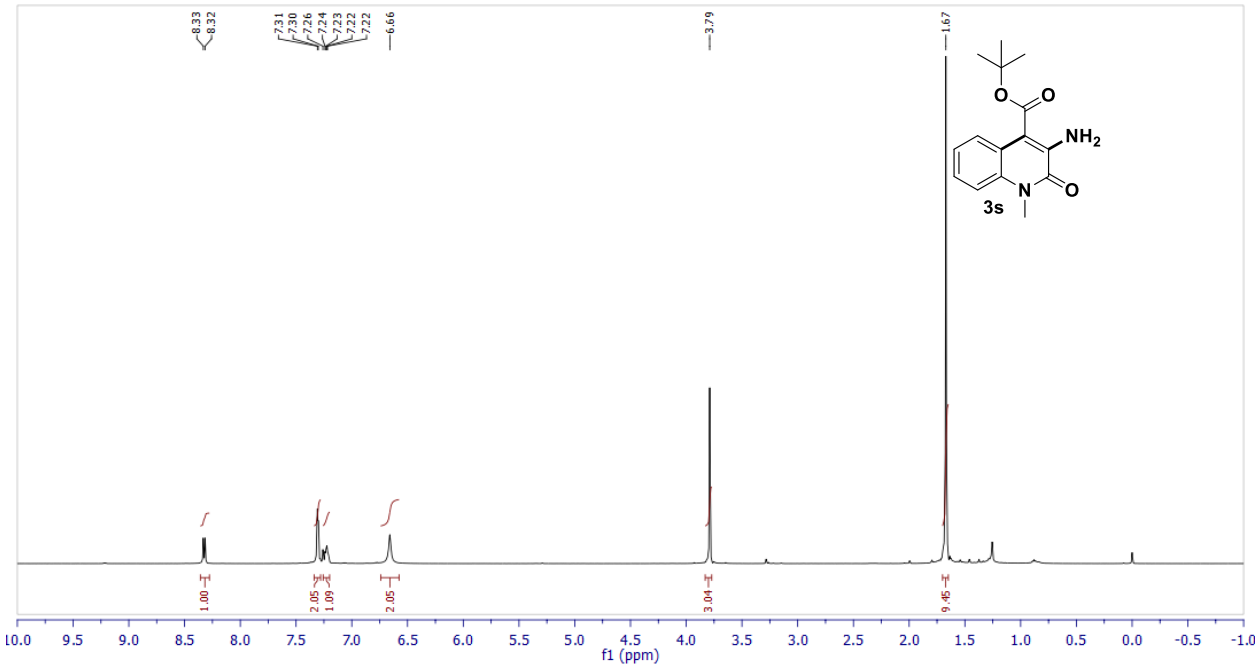
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3r**



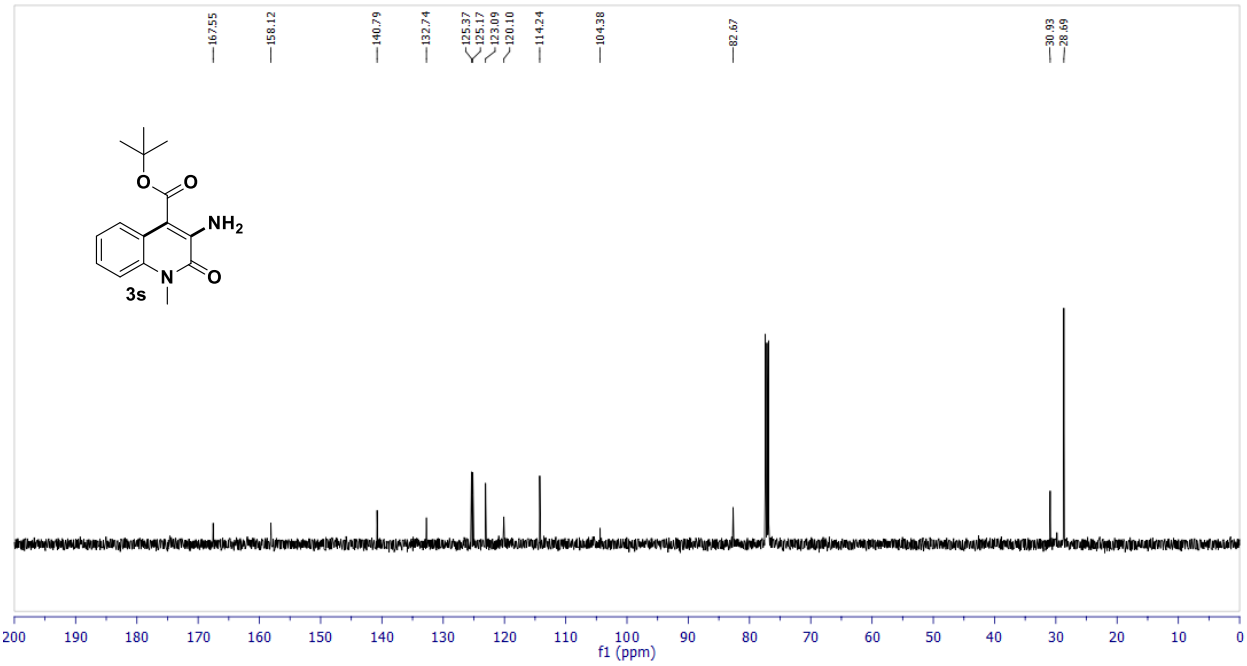
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3r**



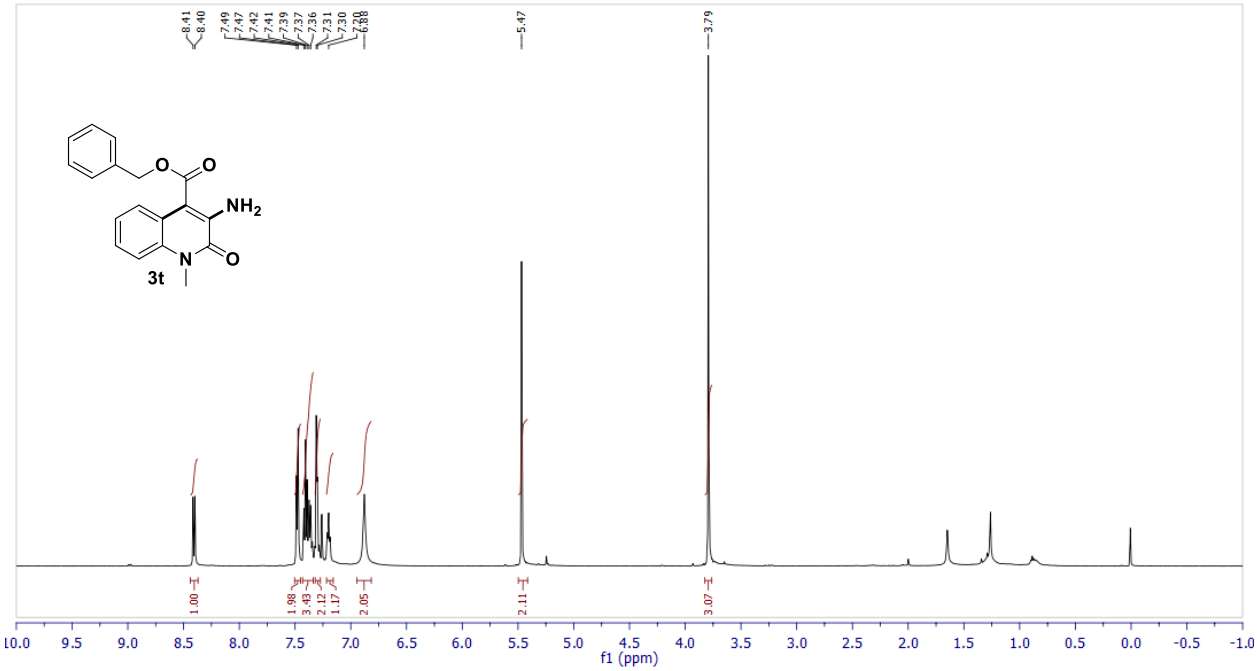
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3s**



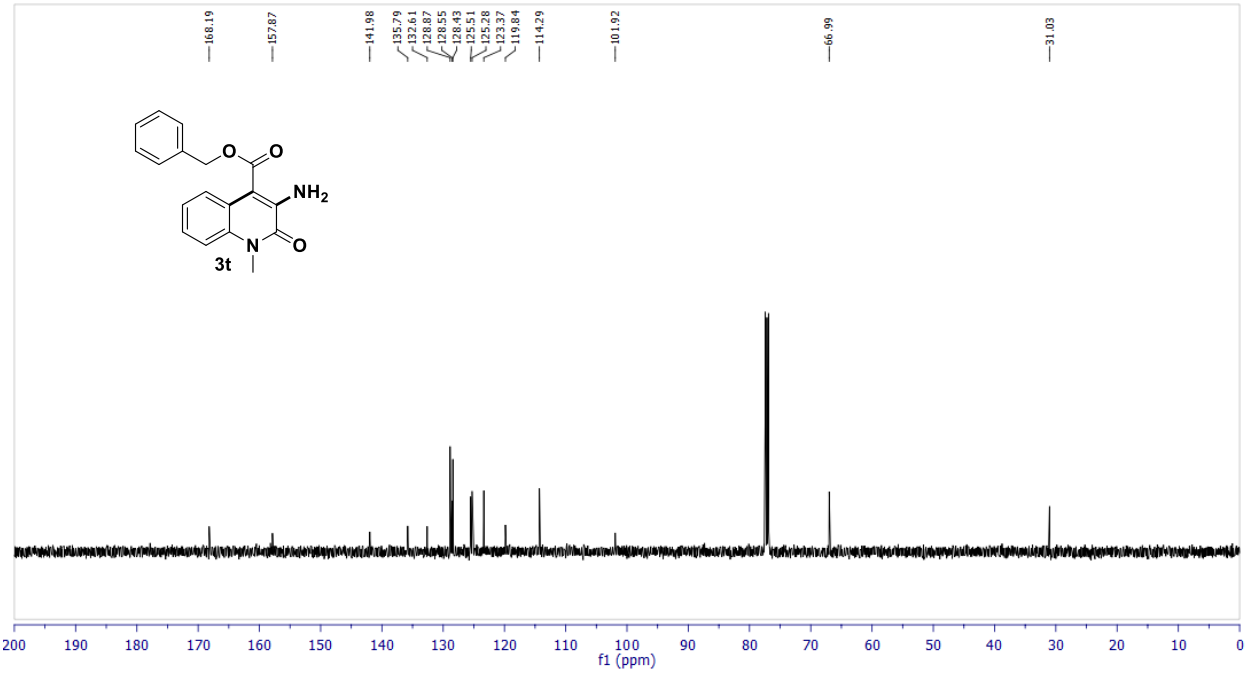
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3s**



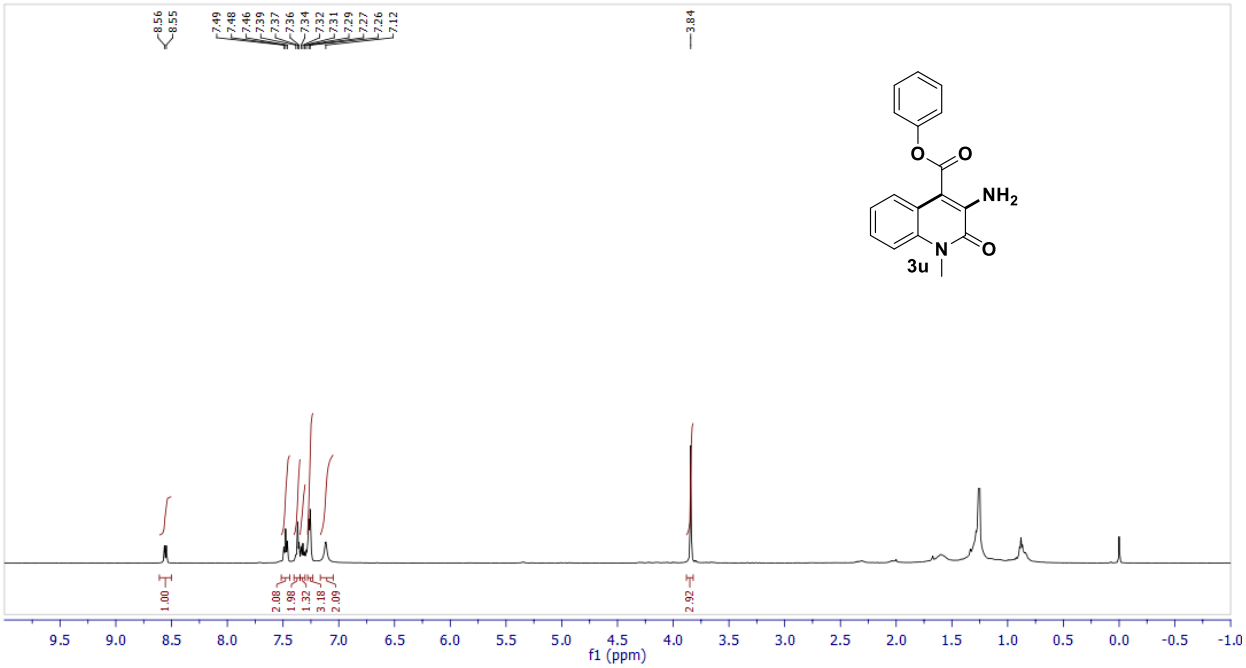
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3t**



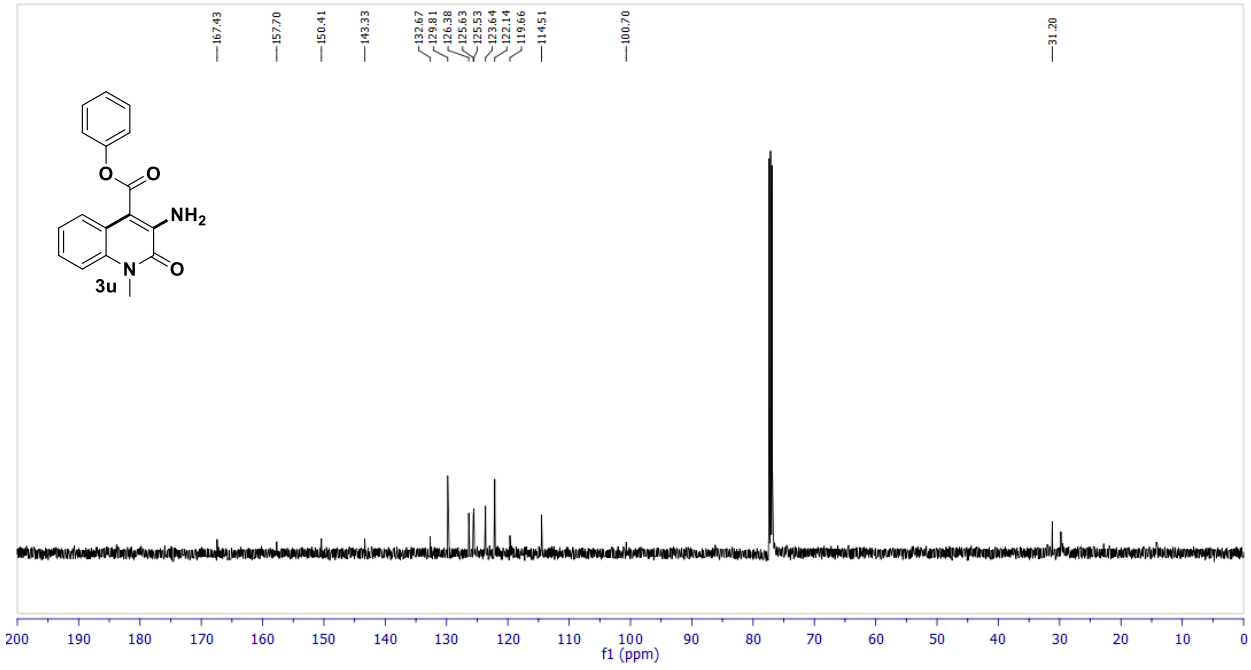
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3t**



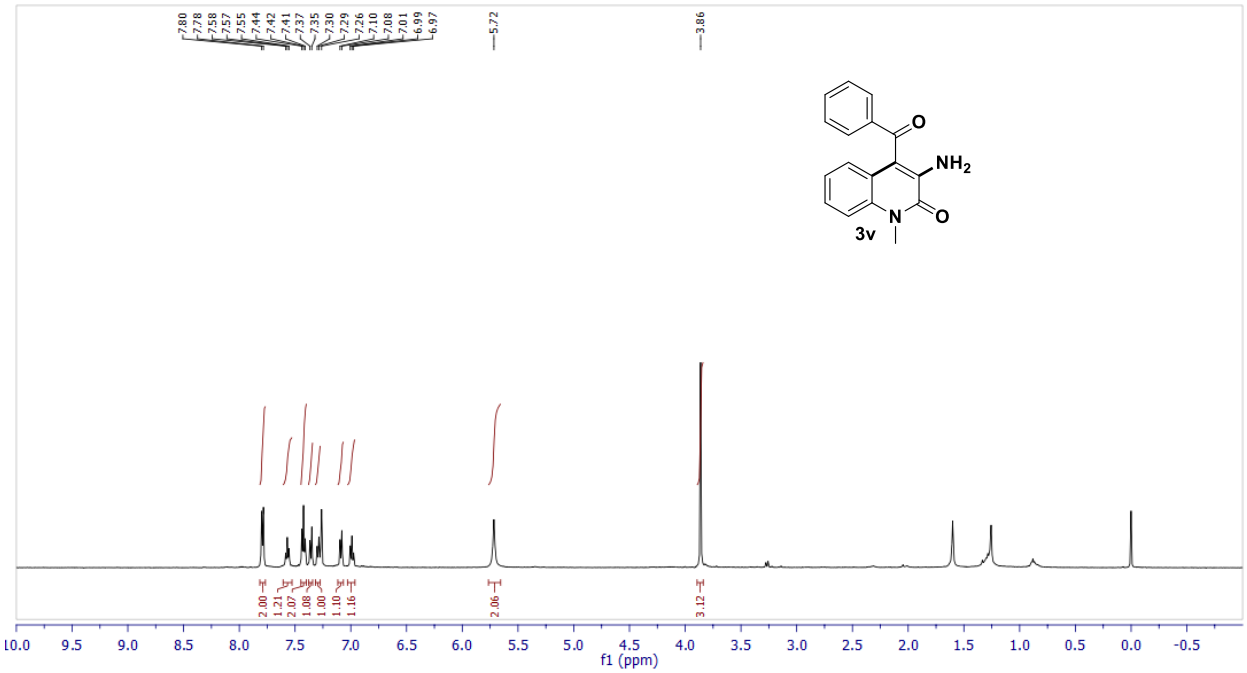
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3u**



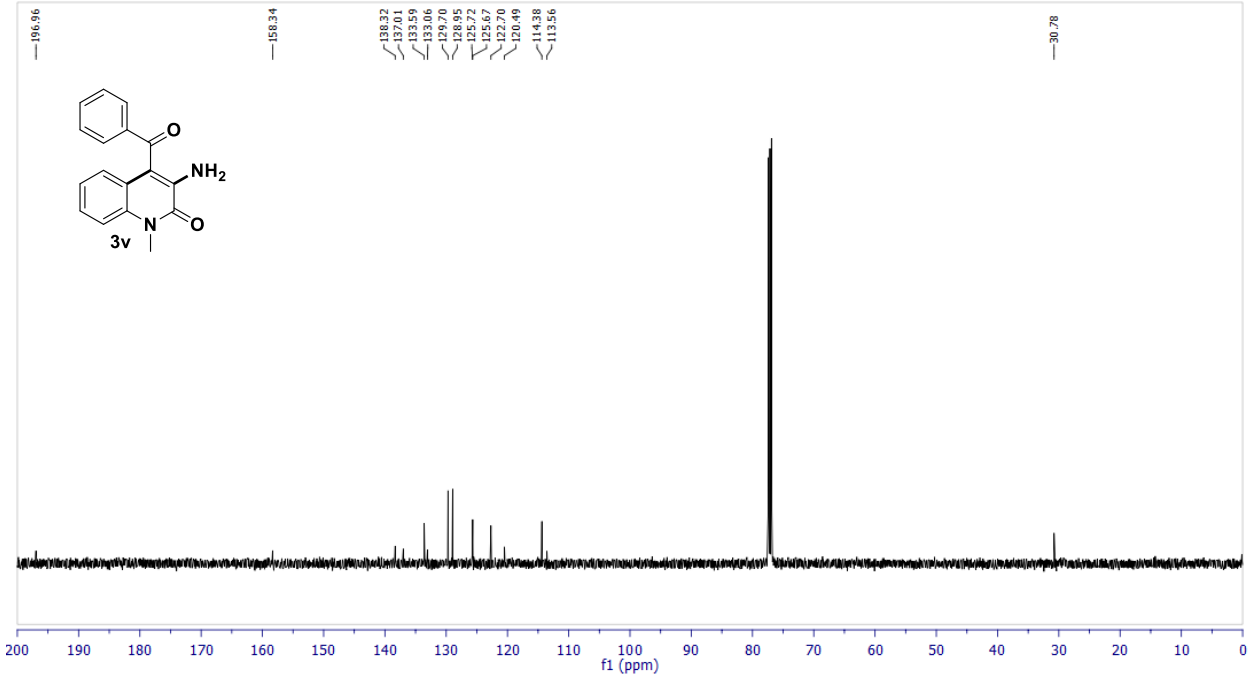
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3u**



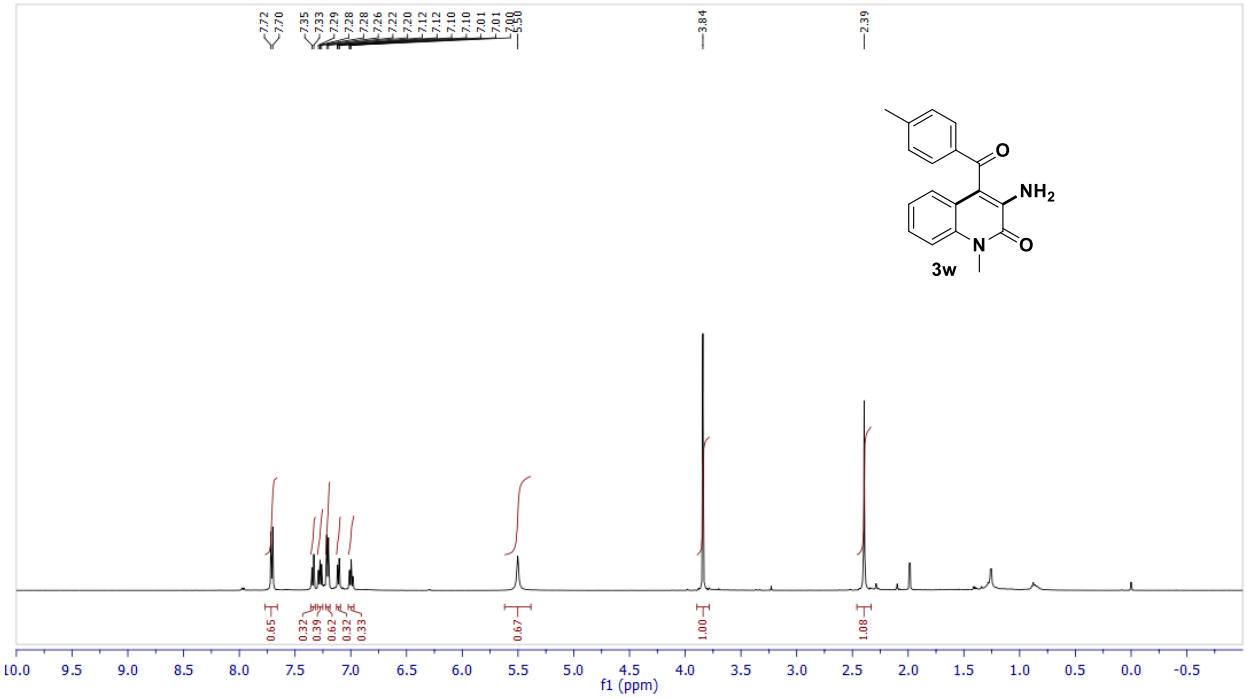
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3v**



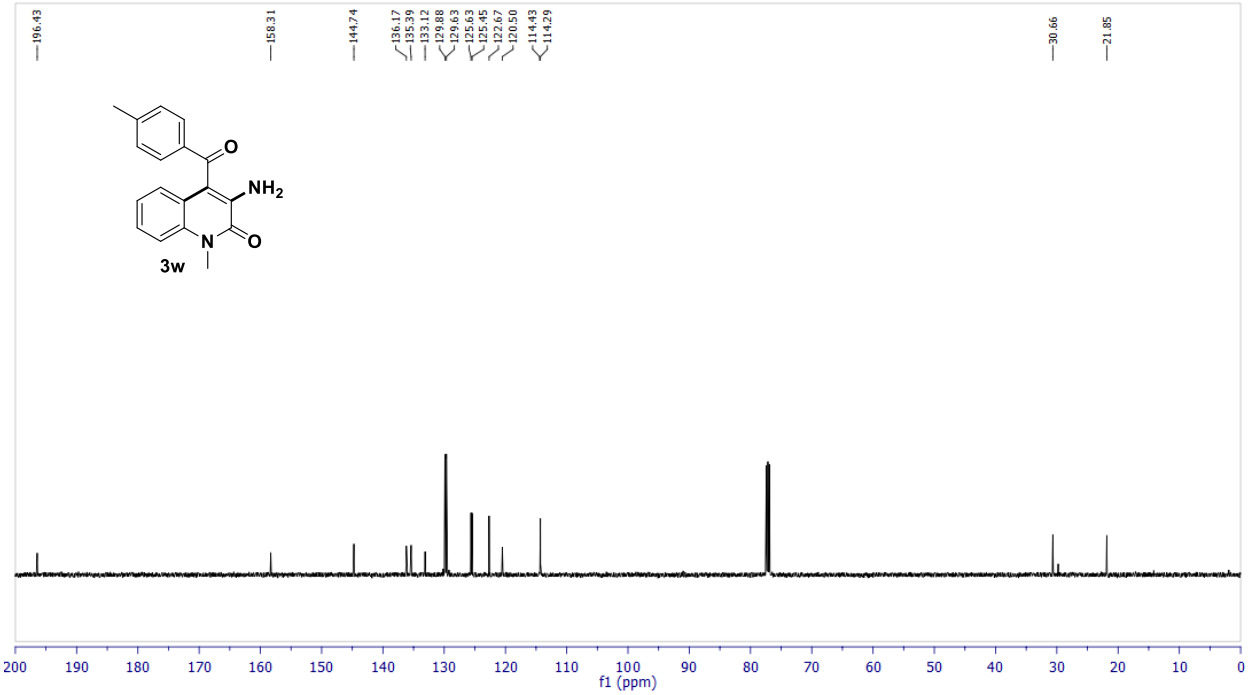
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3v**



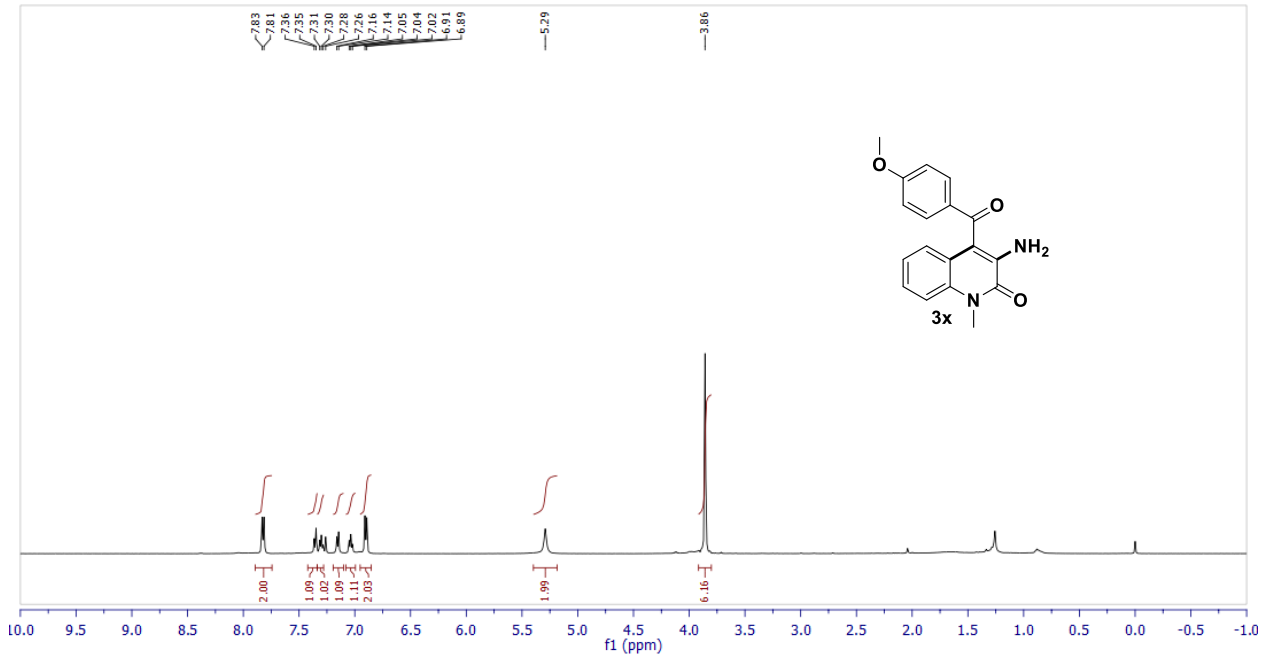
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3w**



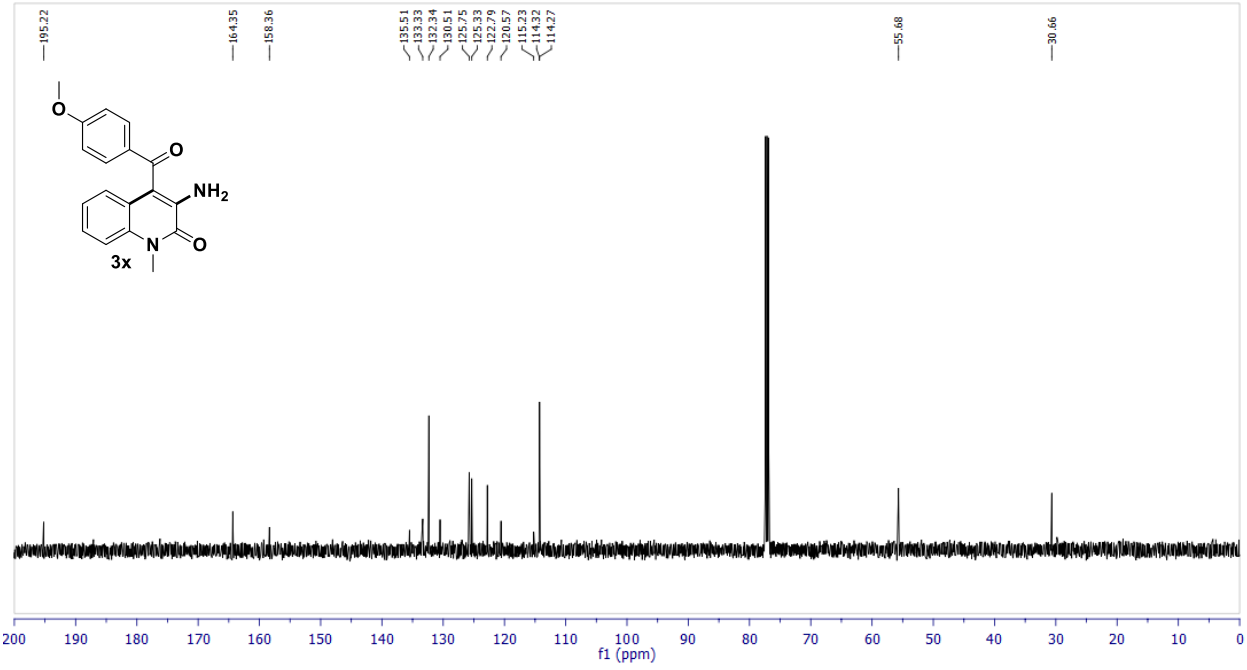
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3w**



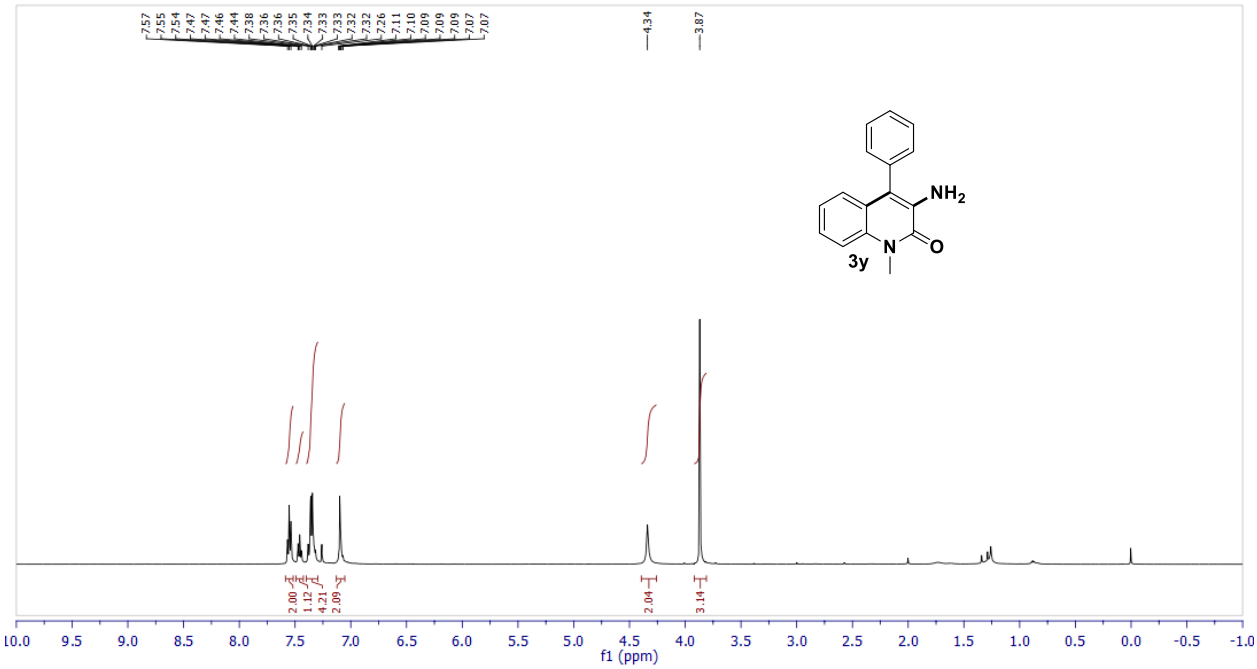
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3x**



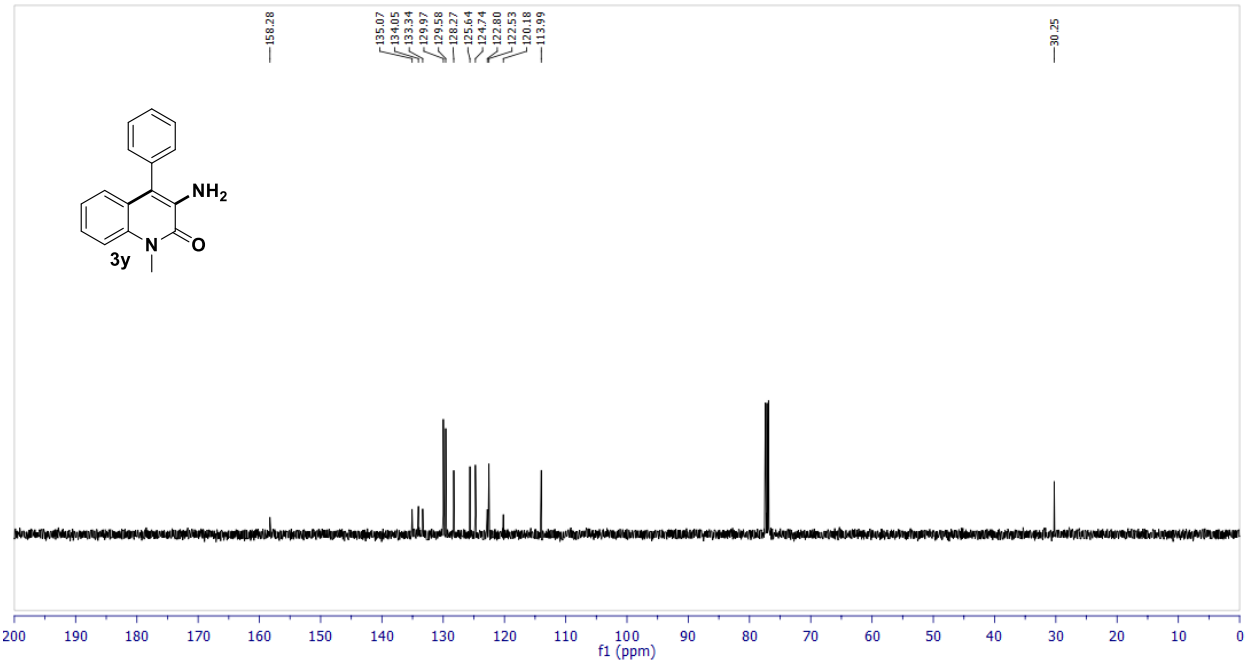
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3x**



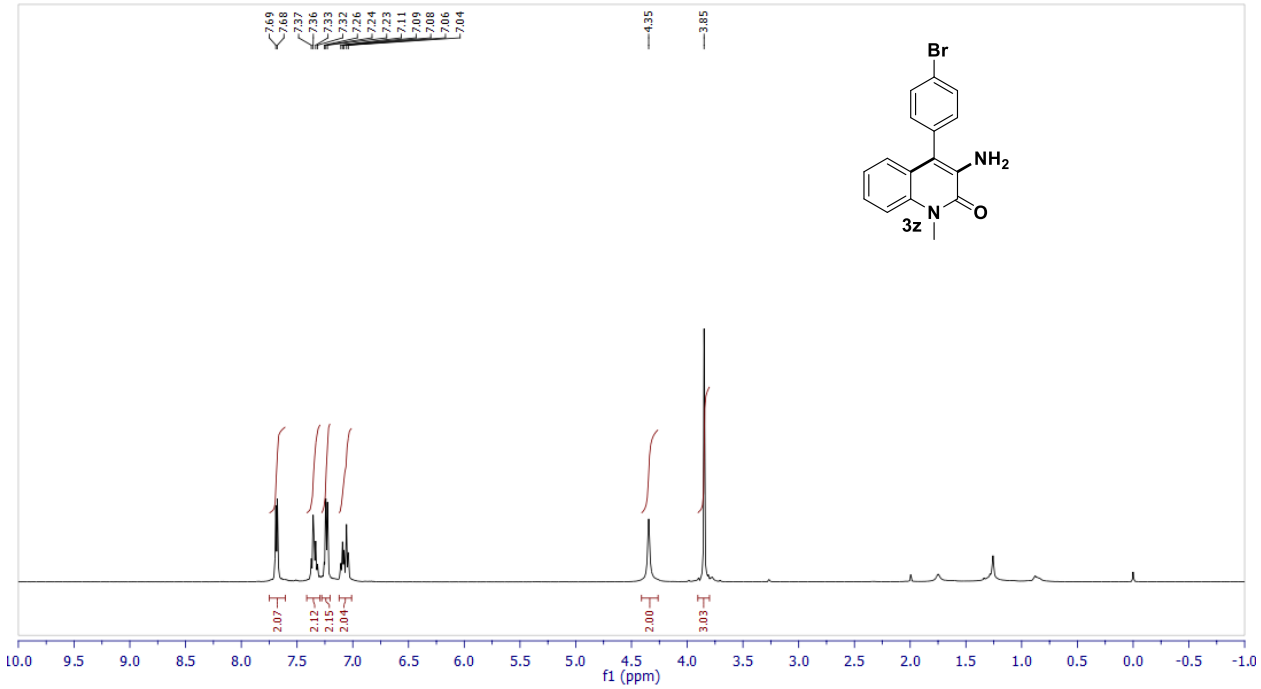
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3y**



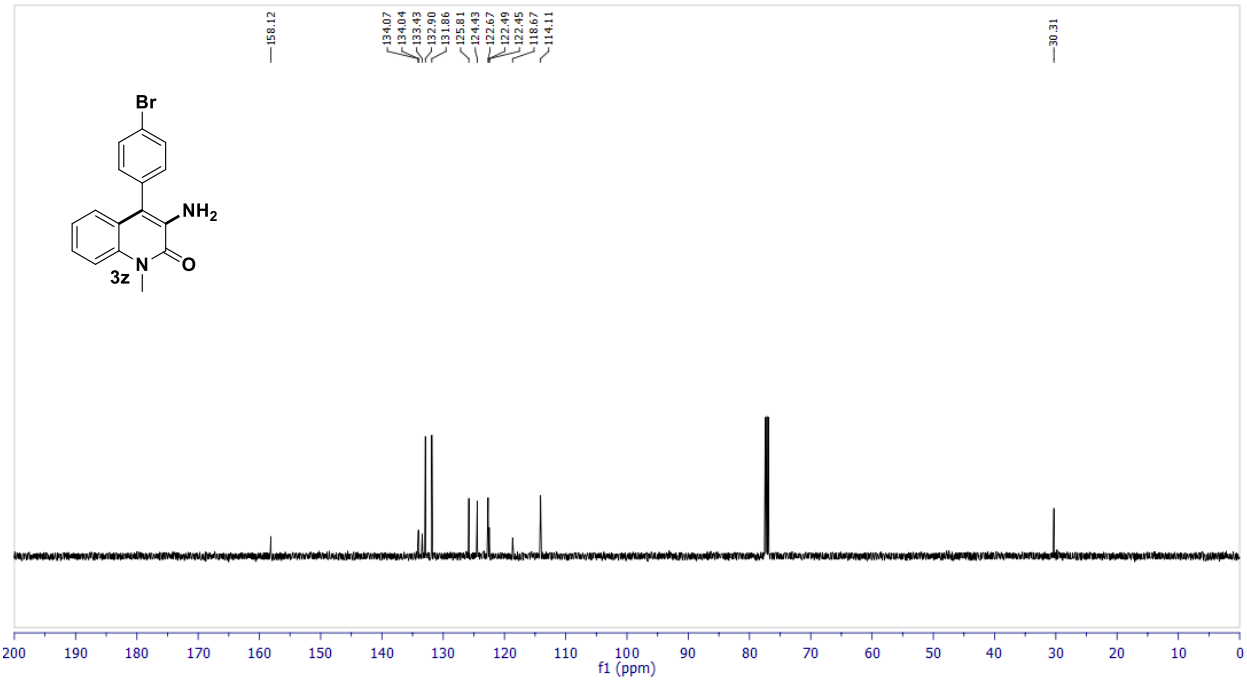
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3y**



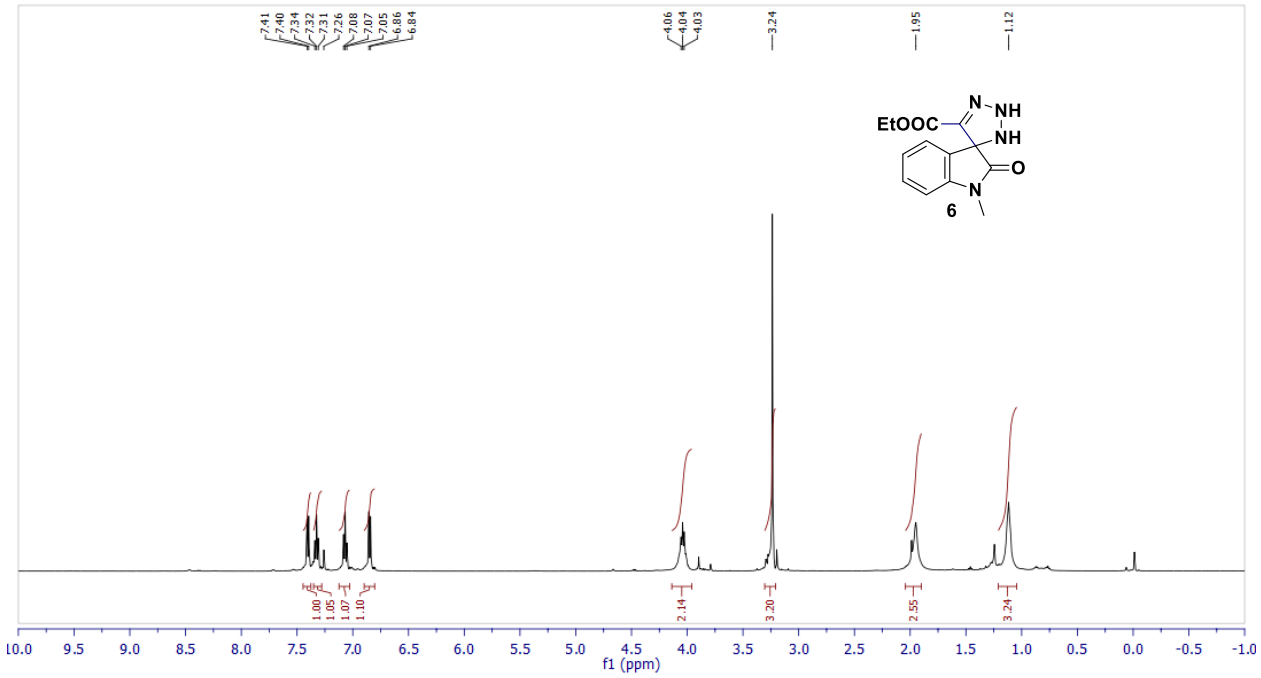
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3z**



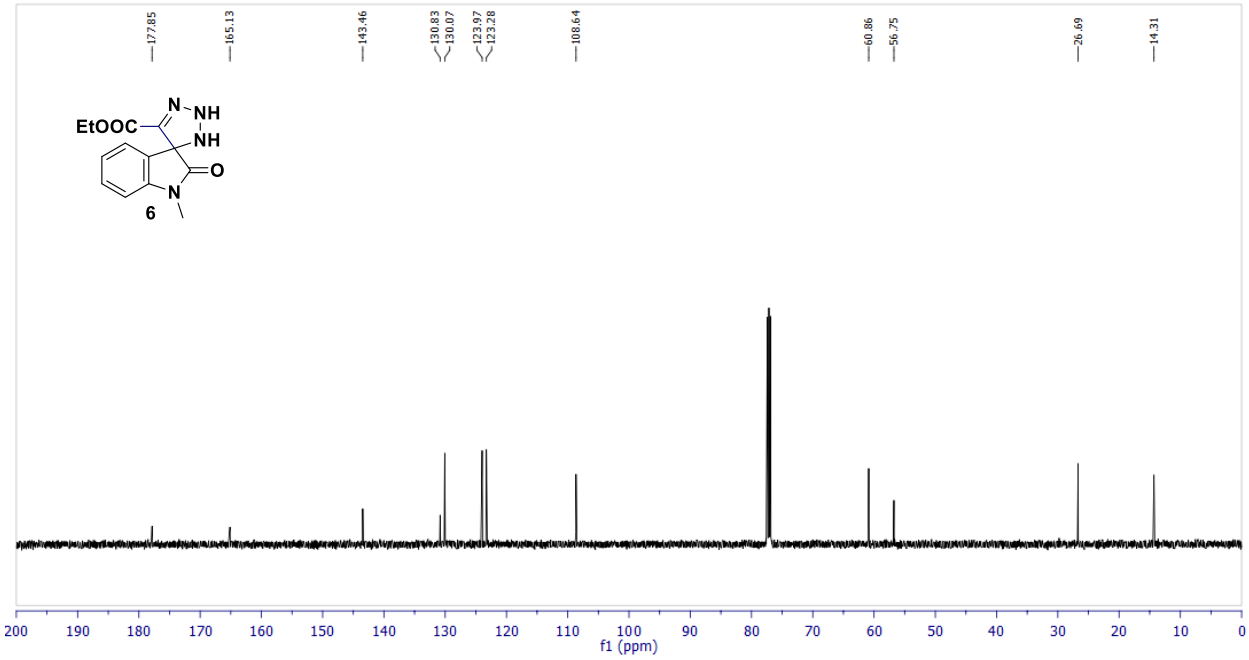
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3z**



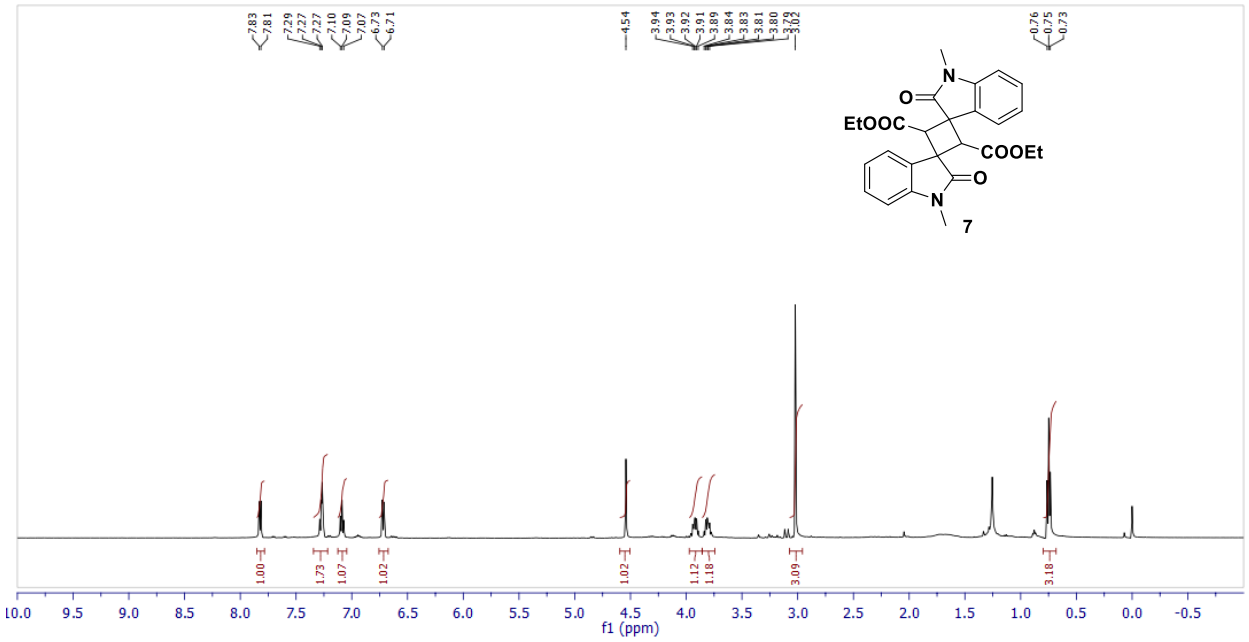
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**



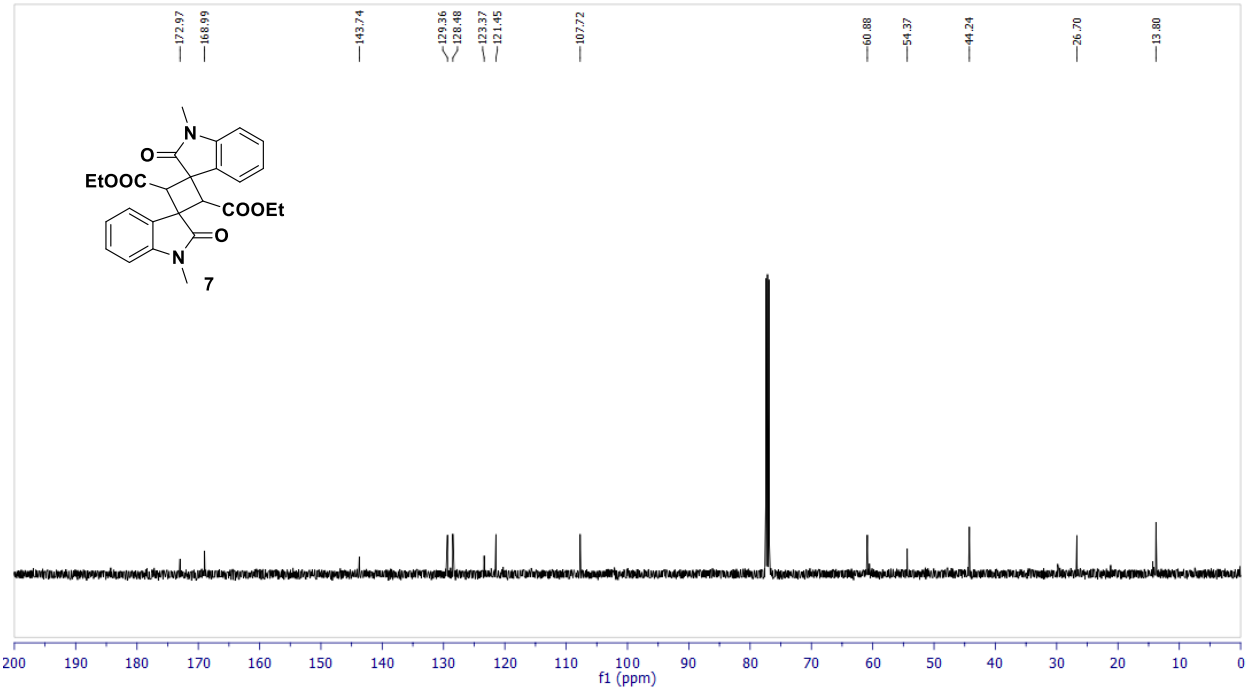
^{13}C NMR (126 MHz, $CDCl_3$) of compound **6**



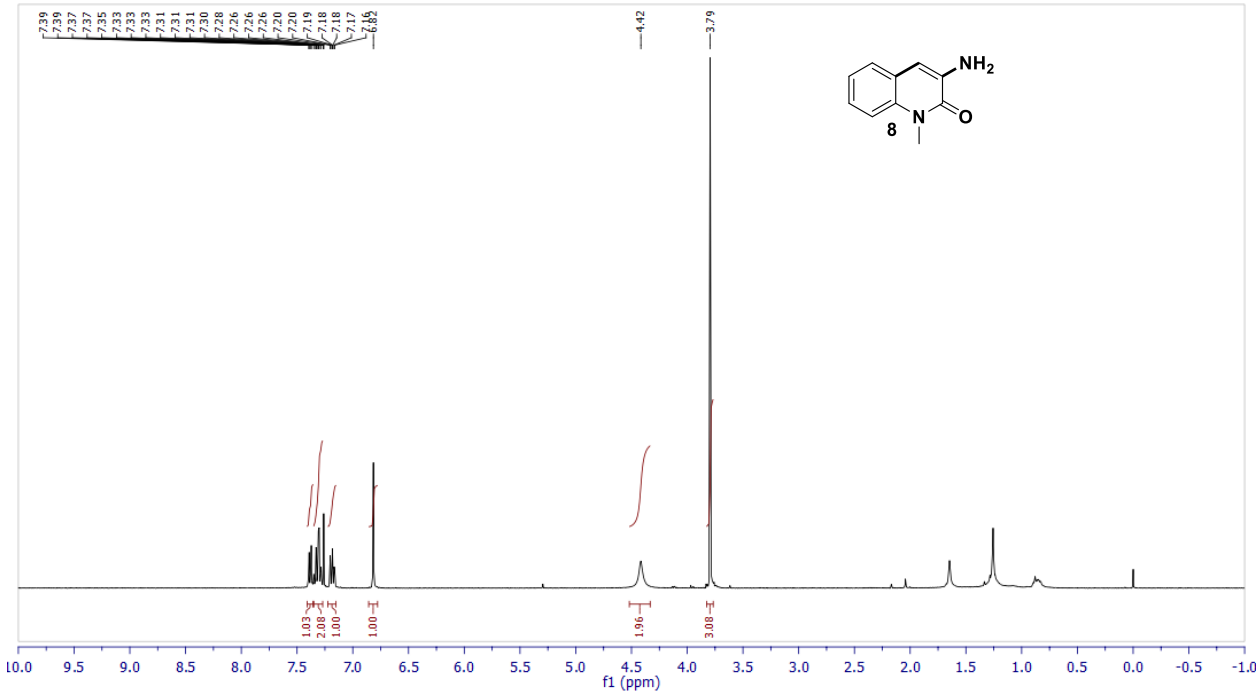
^{1}H NMR (500 MHz, $CDCl_3$) of compound **7**



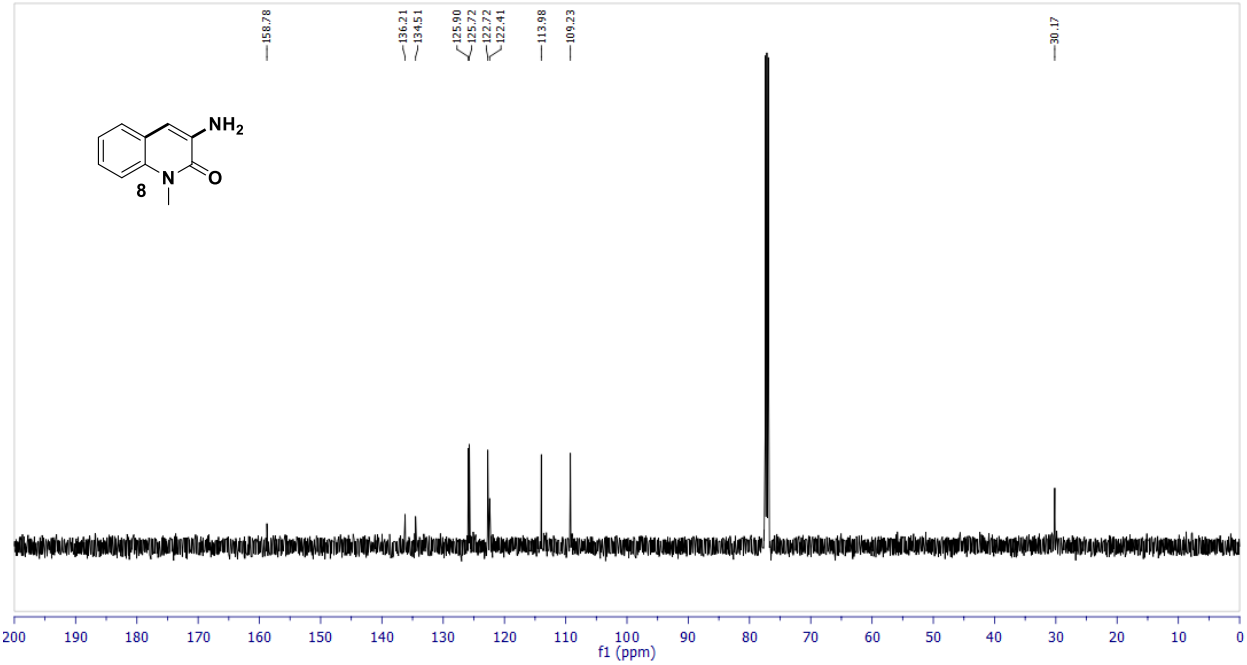
^{13}C NMR (126 MHz, $CDCl_3$) of compound **7**



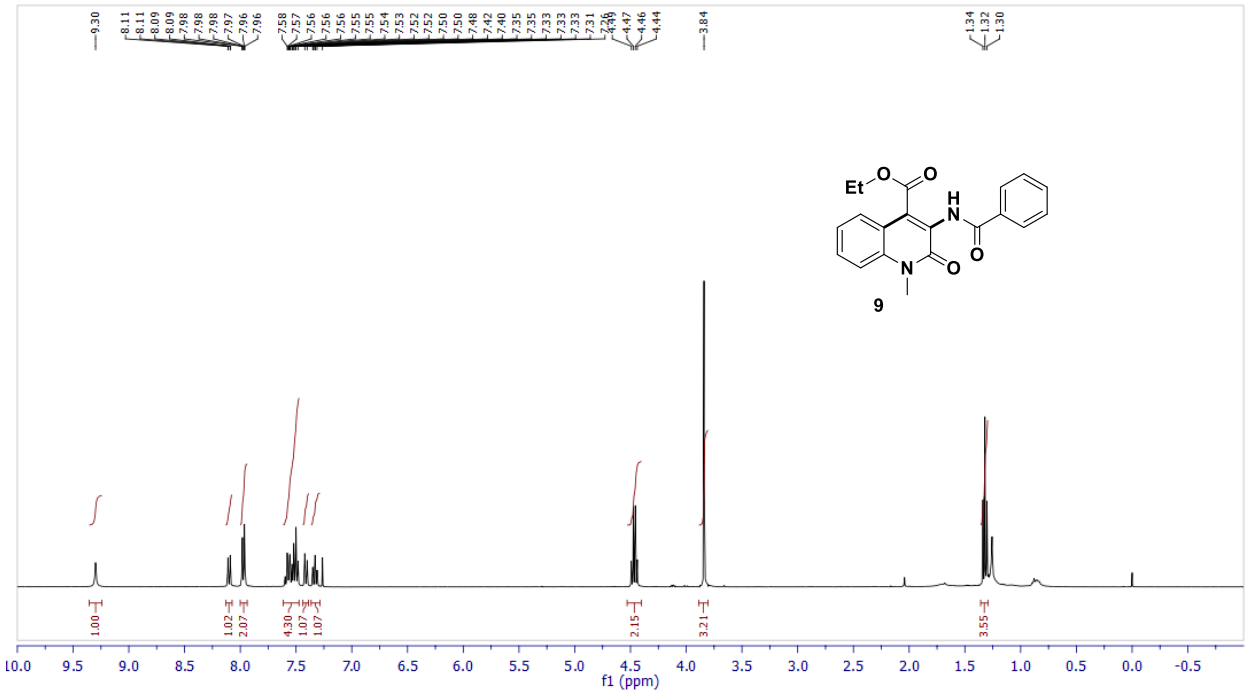
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8**



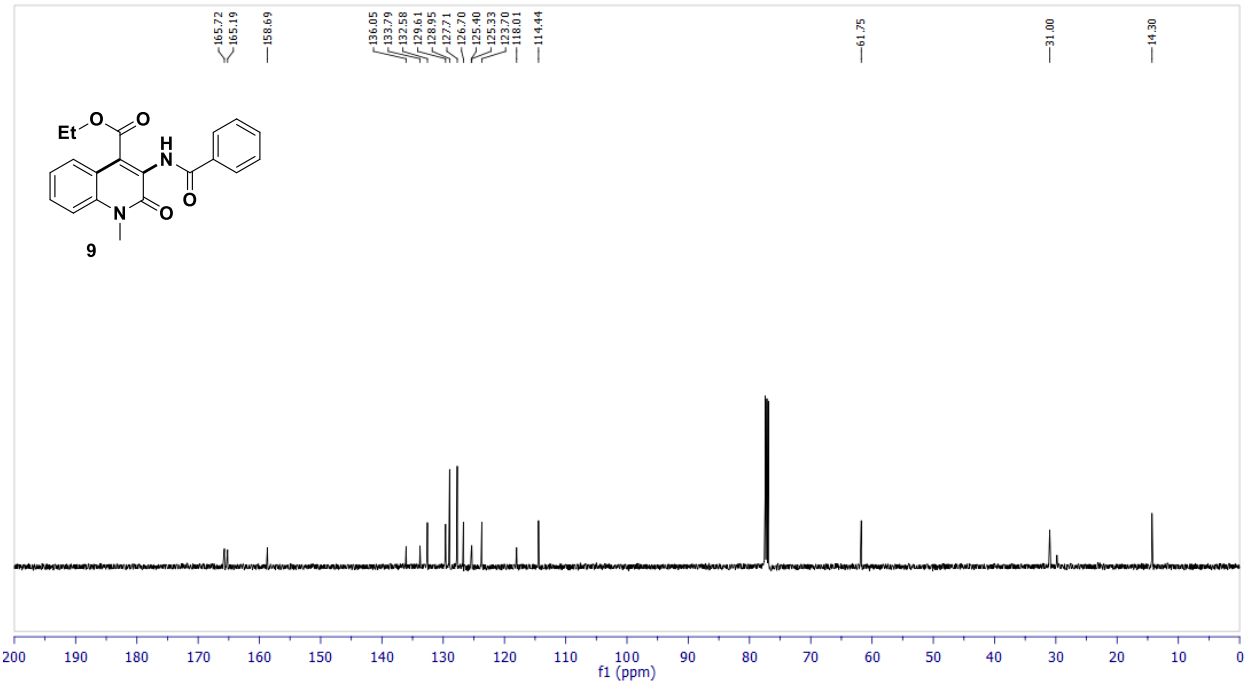
^{13}C NMR (126 MHz, $CDCl_3$) of compound **8**



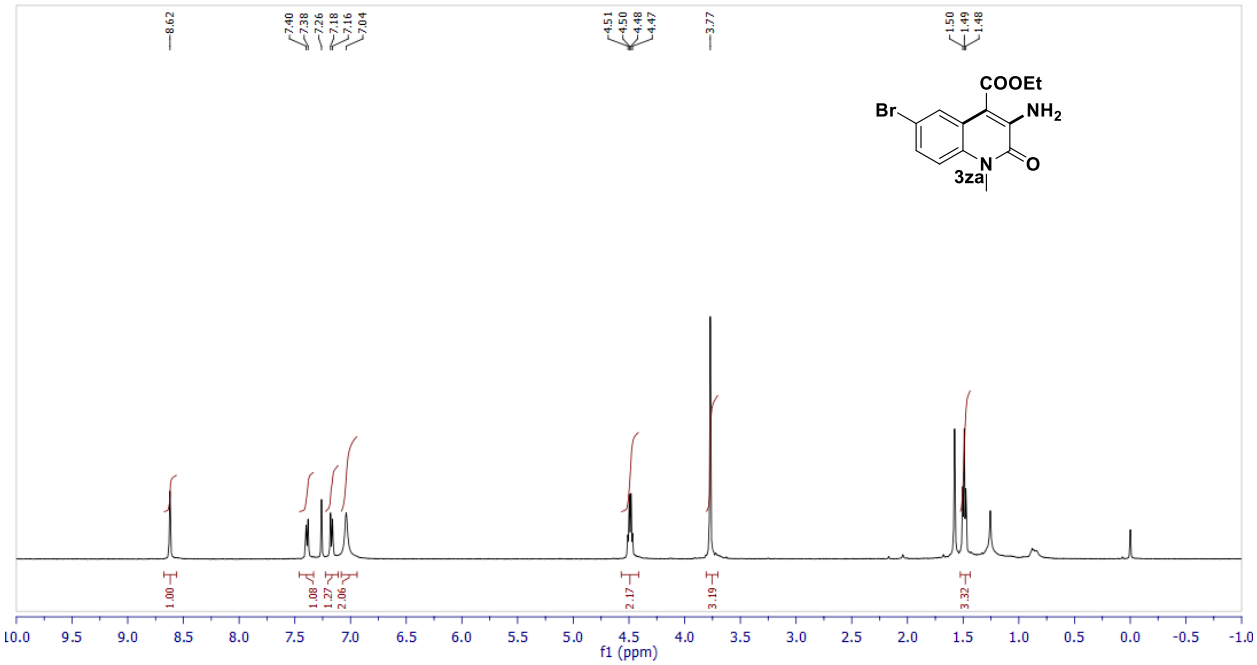
^{1}H NMR (400 MHz, $CDCl_3$) of compound **9**



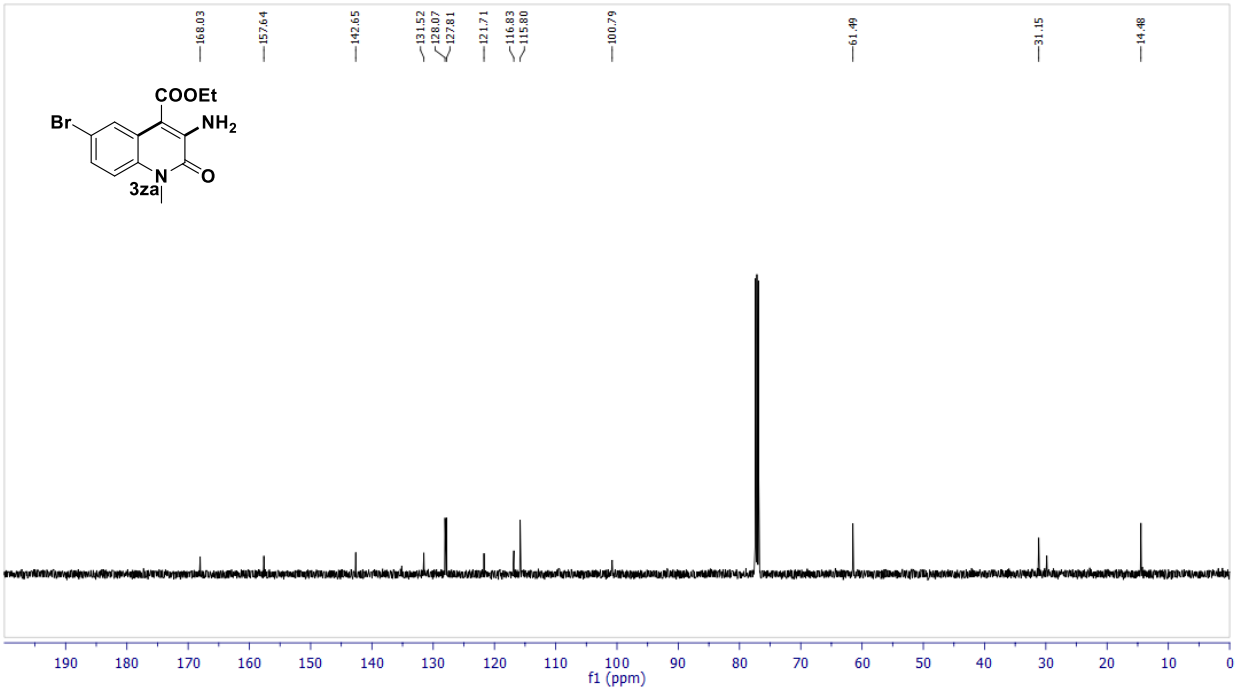
^{13}C NMR (126 MHz, $CDCl_3$) of compound **9**



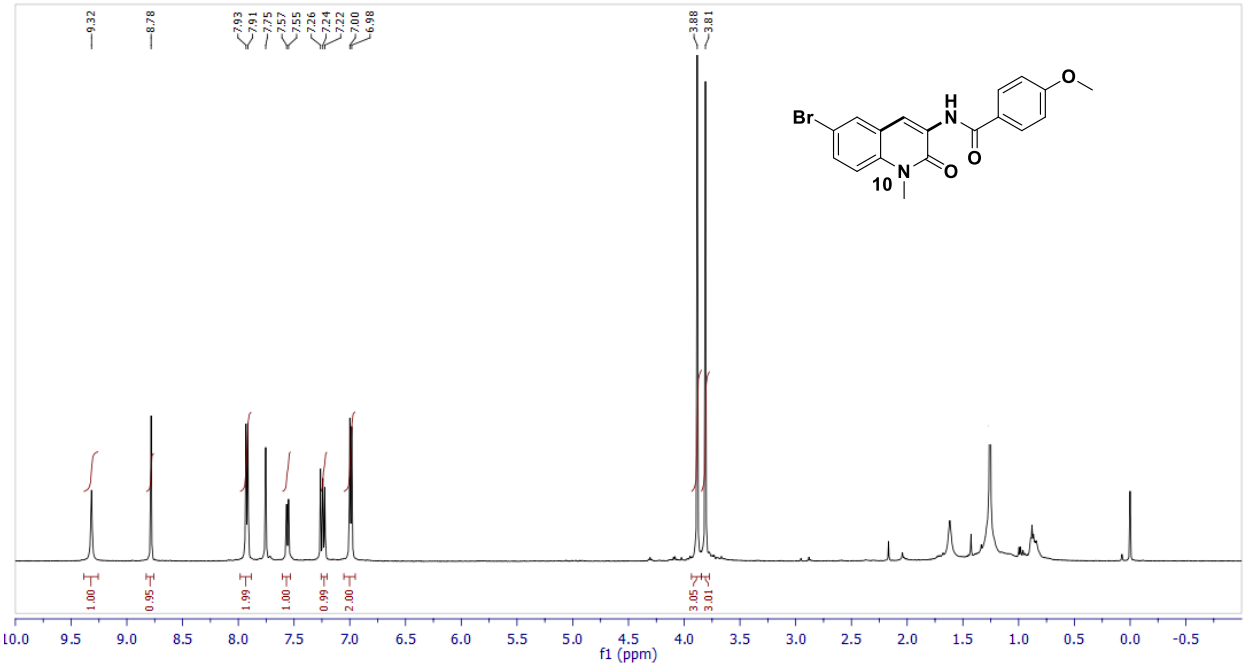
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3za**



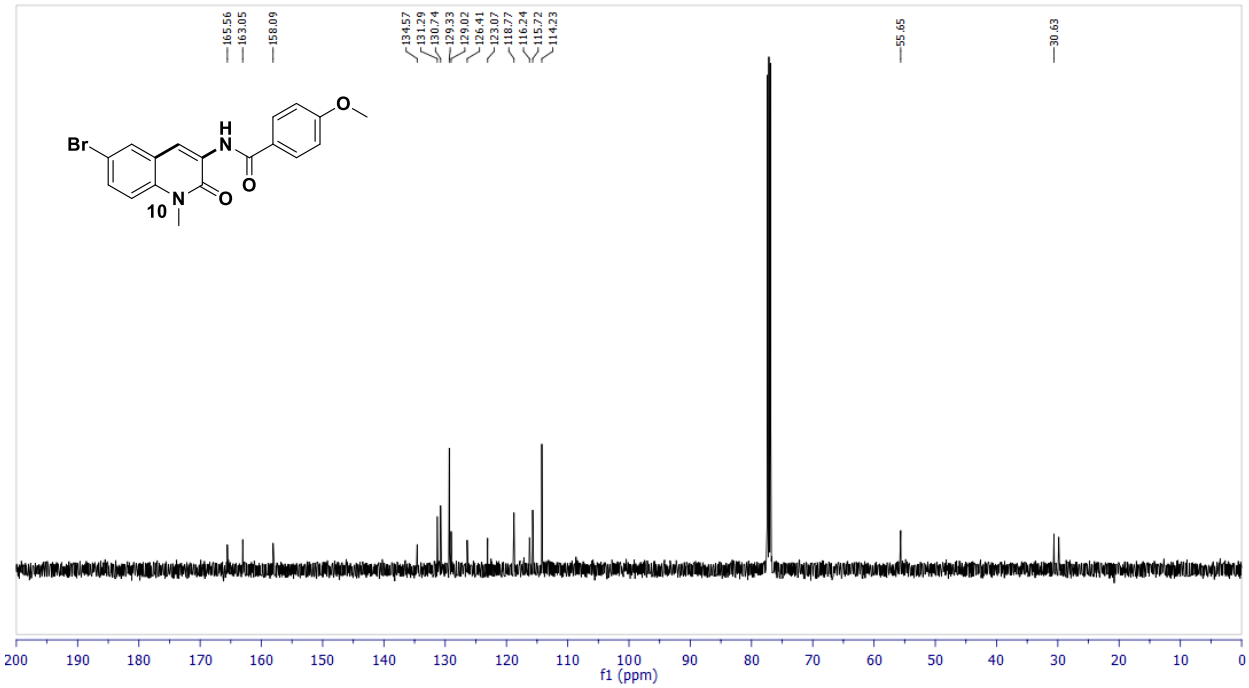
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3za**



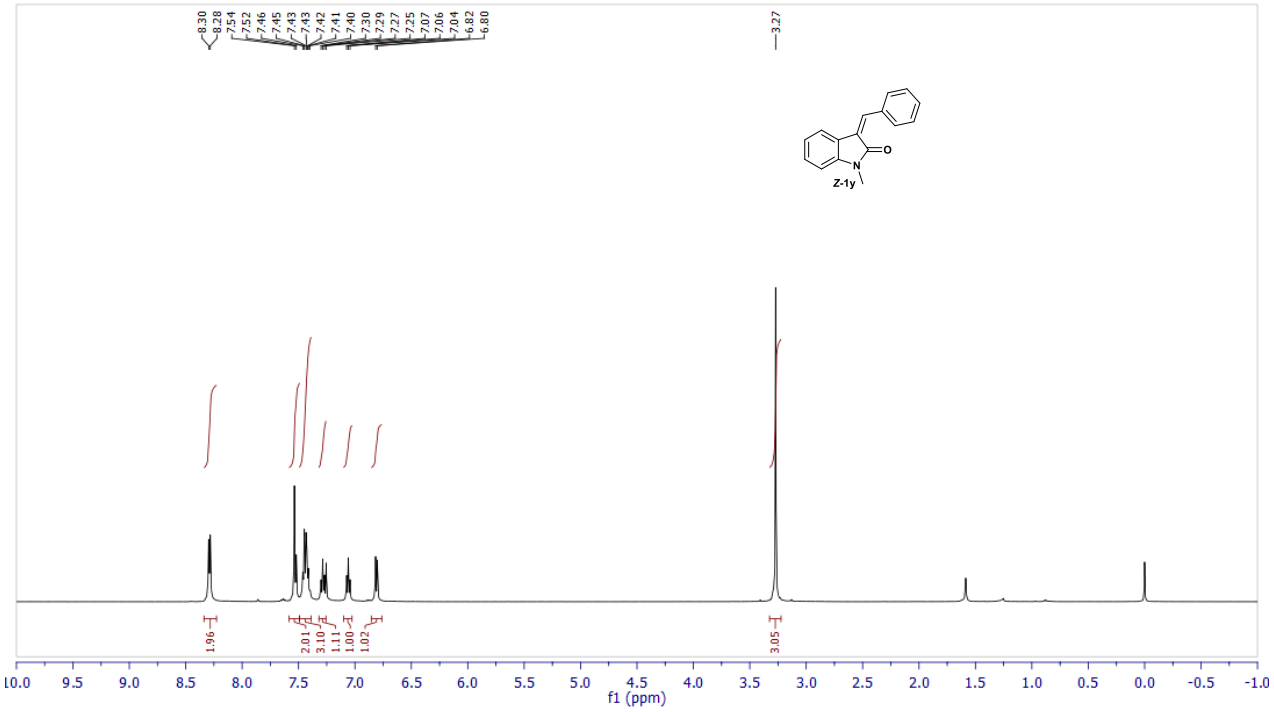
^{1}H NMR (500 MHz, $CDCl_3$) of compound **10**



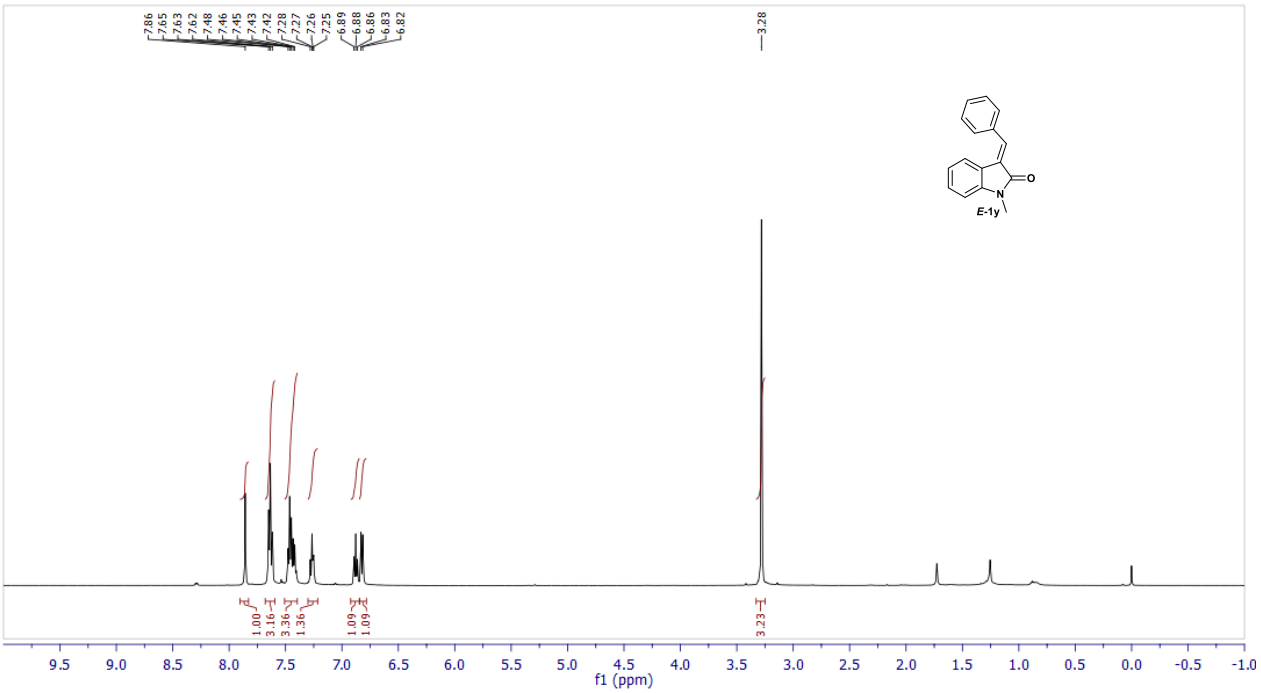
^{13}C NMR (126 MHz, $CDCl_3$) of compound **10**



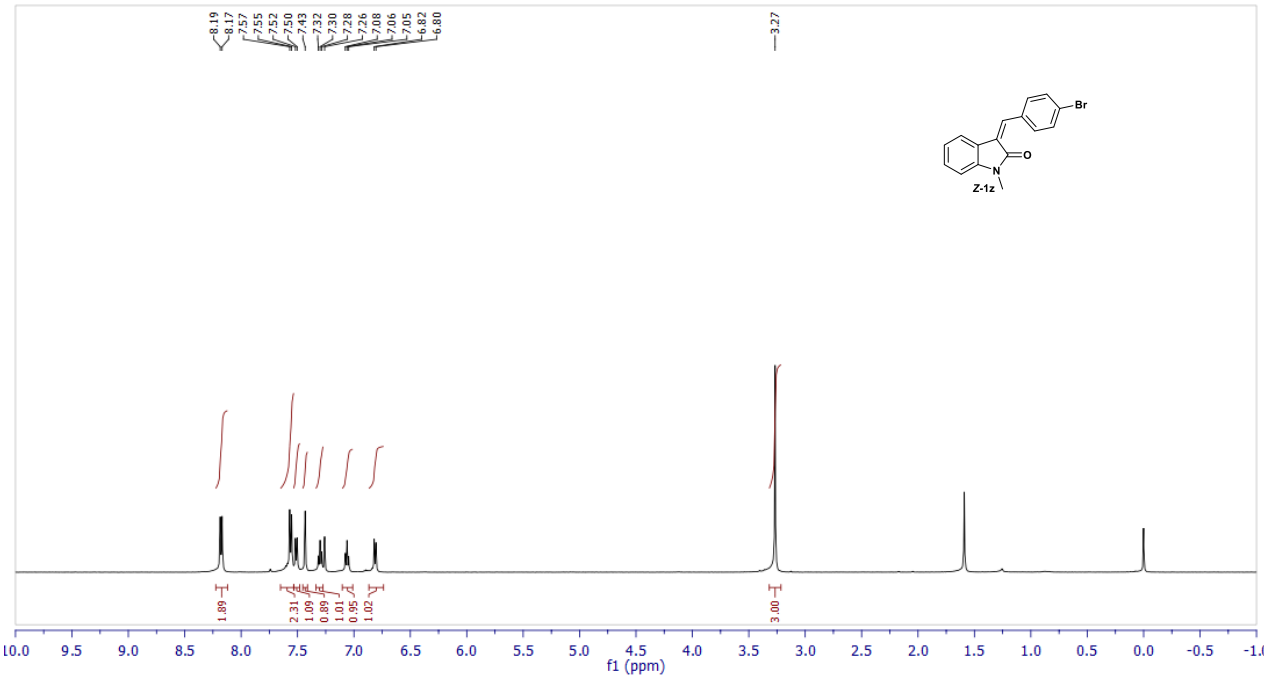
^{1}H NMR (500 MHz, $CDCl_3$) of compound ***Z*-1y**



^{1}H NMR (500 MHz, $CDCl_3$) of compound ***E*-1y**



^{1}H NMR (500 MHz, $CDCl_3$) of compound ***Z*-1z**



^{1}H NMR (500 MHz, $CDCl_3$) of compound ***E*-1z**