Supporting Information

Iodine-Photoredox Dual Catalysis Unlock Bifunctional Reactivity of α-Diazoesters in Radical Cascade Cyclization Reaction via Remote C–I Bond Dissociation

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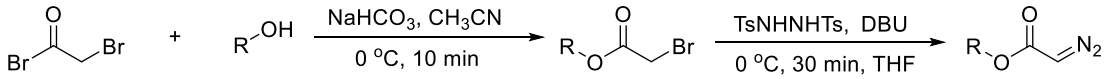
1. General

All substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). ^{1}H, ^{13}C spectra were recorded in $CDCl_3$ on Bruker 400 MHz NMR (AVANCE III HD 400 and AVANCE NEO 400) spectrometers and chemical shifts of ^{1}H NMR are reported in ppm, relative to the internal standard of tetramethylsilane (TMS, δ = 0.00 ppm). Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$, δ = 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C spectra were recorded in $CDCl_3$ on 100 MHz NMR spectrometers and resonances (δ) are given in ppm. The high resolution mass spectrometers were obtained on a Waters Synapt G2-Si HDMS or German Thermo Fisher Q Exactive equipped with an electrospray source. The *X-ray* crystal-structure determinations of **3b** were obtained on a Bruker D8 VENTURE Mo/Cu system. Melting points were determined using XT-4 apparatus and not corrected.

2. General procedure for the synthesis of 1[1]

The diazo compounds **1** were synthesized according to literature procedure.[1] (Caution! Diazo compounds are presumed to be toxic and potentially explosive and therefore should be handled with caution in a fume hood.)



A reaction mixture of alcohol (5.0 mmol), $NaHCO_3$ (15.0 mmol) in CH_3CN (50 mL) and then 2-bromoacetyl bromide (7.5 mmol) was added slowly at 0 °C. After stirring for 10 min, the water was then added to the mixture and the organic layer was extracted with DCM three times. The product was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue without purified for next reaction. The bromoacetate thus obtained and TsNHNHTs (10 mmol) were dissolved in THF (50 mL) and cooled to 0 °C. DBU (25 mmol) was dropwise and stirred at 0 °C for 30 min. Brine (100 mL) was then added to the mixture. The organic layer was separated and the aqueous layer was extracted with EtOAc (50 mL × 3). The product was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product **1**.

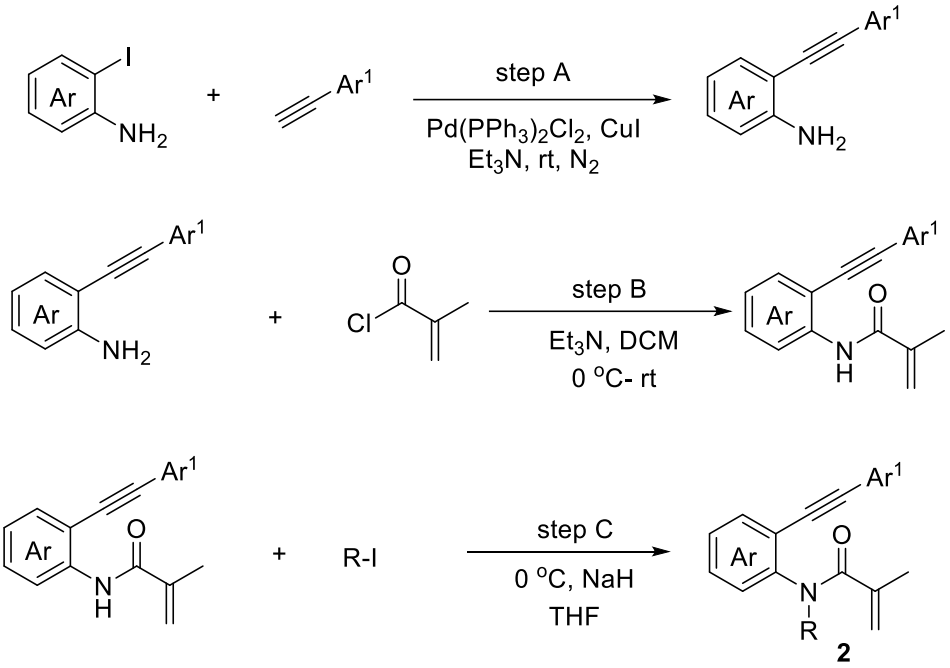
3. General procedure for the synthesis of 2[2]

Step A: to a 50-mL flask was charged with iodoaniline (10 mmol), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol) and CuI (76 mg, 0.4 mmol) in Et_3N (25 mL) at room temperature under argon. After stirring for 5 minutes, phenylacetylene (15 mmol) was added dropwise to the reaction mixture. After the reaction was complete (monitored by TLC), the reaction mixture was filtered through a pad of celite, eluting with EtOAc (3 × 20 mL). The combined organics were sequentially washed with H_2O (2 × 20 mL) and brine (1× 20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was used in the next step without purification.

Step B: the above-obtained compound was dissolved in DCM (20 mL). Et_3N (2.02 g, 20 mmol) was added. Methacryloyl chloride (1.56 g, 15 mmol) was added dropwise to the reaction mixture at 0 °C. The reaction was stirred at room temperature for 6-12 h. Then the reaction was quenched by

adding saturated $NaHCO_3$ solution, and the mixture was extracted with DCM (3 × 30 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography.

Step C: to a suspension of NaH (60%, 480 mg, 12 mmol) in THF (30 mL) at 0 ℃ was added a solution of above-obtained compound (6 mmol) in THF (10 mL) dropwise and the mixture was stirred for 5 min. Alkyl iodide compound (18 mmol) was added at 0 ℃. The reaction was stirred at room temperature and was monitored by TLC. The reaction was quenched by adding water. The mixture was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to afford compound **2**.



4. General procedure for the synthesis of 3 (3a as an example)

4.1 In 0.2 mmol scale

A sealed tube was charged with ethyl diazoacetate (**1a**) (1.0 mmol, 114 mg), 1,7-enyne (**2a)** (0.2 mmol, 55 mg), I_2 (0.03 mmol, 8 mg), *fac*-Ir(ppy)$_3$ (0.004 mmol, 3 mg), CH_3CN (3 mL). The reactions exposed to blue LEDs irradiation at room temperature in Ar with stirring for 24 h till almost completed conversion of the substrates by TLC analysis. After completion of the reaction, the mixture was diluted with water and extracted with ethyl acetate, the organic layer was combined, dried over by anhydrous Na_2SO_4, and filtered, then concentrated to yield the crude product, which was further purified by flash chromatography (petroleum ether/ethyl acetate = 15:1, V/V) to give the product **3a** (59 mg) in 82% yield.

Photoreactor: The photoreactors used in this work were purchased from Taobao website. All visible light-induced reactions were conducted in borosilicate glass tubes with Teflon-coated magnetic stirring bars in Ar atmosphere and placed 5 cm from two commercial blue LEDs. (Figure S1: 18 w blue LEDs, λ = 460−462 nm, manufacturer: Qin Tao Trading Co., model: SSG11701)

Figure S1. Photoreactor used in this research

4.2 In 10 mmol scale

A sealed tube was charged with ethyl diazoacetate (**1a**) (50 mmol, 5.7 g), 1,7-enyne (**2a)** (10 mmol, 2.75 g), I_2 (1.5 mmol, 380 mg), *fac*-Ir(ppy)$_3$ (0.2 mmol, 131 mg), CH_3CN (30 mL). The reactions exposed to blue LEDs irradiation at room temperature in Ar with stirring for 24 h till almost completed conversion of the substrates by TLC analysis. After completion of the reaction, the mixture was diluted with water and saturated sodium thiosulfate solution, extracted with ethyl acetate, the organic layer was combined, dried over by anhydrous Na_2SO_4, and filtered, then concentrated to yield the crude product, which was further purified by flash chromatography (petroleum ether/ethyl acetate = 15:1, V/V) to give the product **3a** (2.88 g) in 80% yield.

Photoreactor: The photoreactors used in this work were purchased from Taobao website. All visible light-induced reactions were conducted in borosilicate glass tubes with Teflon-coated magnetic stirring bars in Ar atmosphere and placed 5 cm from two commercial blue LEDs. (Figure S2: 18 w blue LEDs, λ = 460−462 nm, manufacturer: Qin Tao Trading Co., model: SSG11701)

Figure S2. Photoreactor used in this research

References:

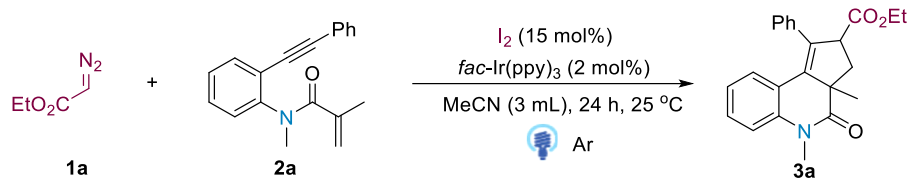
1**.** Zhao, P.; Liu, Y.; Zhang, Y.; Wang, L.; Ma, Y. *Org. Lett.* **2024**, *26*, 2511-2516.

2. Wu, C.; Liao, J.; Ge, S. *Angew Chem Int Ed,* **2019**, *58*, 8882-8886.

5. Optimization of the reaction conditions

We commenced with the reaction of ethyl diazoacetate (EDA) **1a** and 1,7-enyne **2a** in the presence of 2 mol% *fac*-Ir(ppy)$_3$ and 15 mol% iodine in MeCN at room temperature under blue LEDs for 24 h. The desired cascade annulation product **3a** was afforded in 82% yield (Table S1, entry 1). We then investigated different photocatalysts, including Ru(bpy)$_2$Cl$_3$·6H$_2$O, 4CzIPN, and Ir(dtbbpy)(ppy)$_2$PF$_6$ (Table S1, entries 2-4), with 4CzIPN gave a comparable yield (Table S1, entry 3). Screening of solvents (Table S1, entries 5-7) confirmed that acetonitrile was optimal.Various bases (e.g., DABCO, NaOAc and K_2HPO_4) were also screened, none of which significantly affected the outcome (Table 1, entries 8-10). Further optimization of the iodine loading revealed that increasing the amount of iodine did not improve the reaction yield. In contrast, reducing the iodine loading to 10 mol% led to a decreased yield of 69% (Table S1, entries 11-13). Notably, in absence of iodine, this reaction did not proceed (Table S1, entry 14); instead, a cyclopropanation product was detected, suggesting the possible generation of triplet carbene species under these conditions. Finally, a series of control experiments demonstrated that light, and photocatalyst are all essential for this transformation (Table S1, entries 15-16). As a result, the initial reaction conditions (with the highest yield, 82%) were adopted as the standard conditions for subsequent studies.

Table S1 Screening the reaction conditions[a]



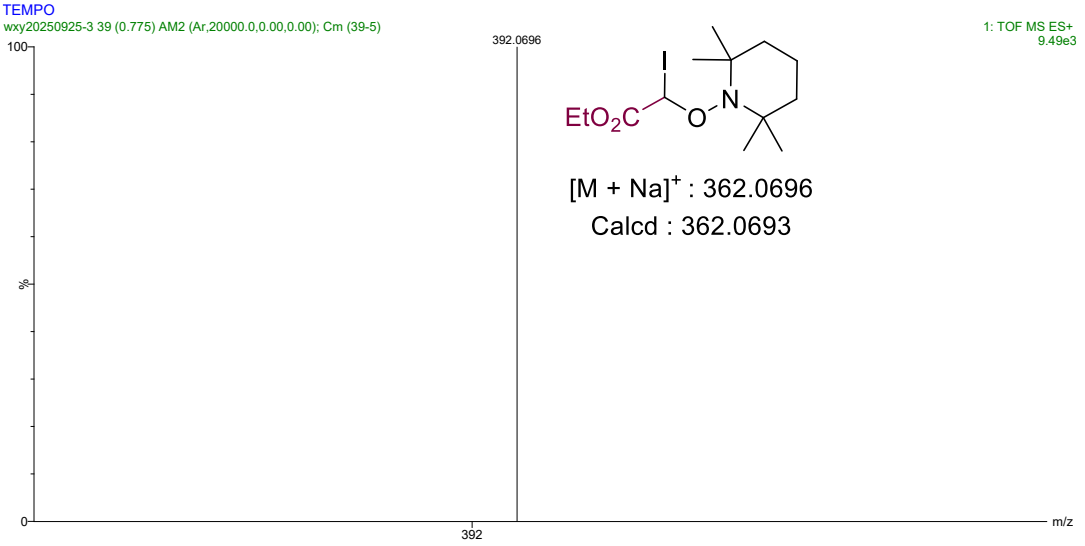
Entry	Variation from 'standard conditions'	Yield of **3a** (%)[b]
1	none	82
2	Ru(bpy)$_2$Cl$_3$·6H$_2$O as photocatalyst	60
3	4CzIPN as photocatalyst	74
4	Ir(dtbbpy)(ppy)$_2$PF$_6$ as photocatalyst	53
5	DCM as solvent	58
6	NMP as solvent	72
7	THF as solvent	29
8	DABCO as additive	76
9	NaOAc as additive	77
10	K_2HPO_4 as additive	70
11	50 mol% I$_2$	82
12	30 mol% I$_2$	82
13	10 mol% I$_2$	69
14	Without I$_2$	ND
15	In dark	ND
16	Without PC	ND

[a] Reaction conditions: 2 mol% *fac*-Ir(ppy)$_3$ and 15 mol% I$_2$ were added to MeCN (3 mL) solution containing **2a** (0.2 mmol) and **1a** (1.0 mmol), and the reaction was kept under Ar and 18 W blue LEDs for 24 h at 25 °C. [b]Isolated yield.

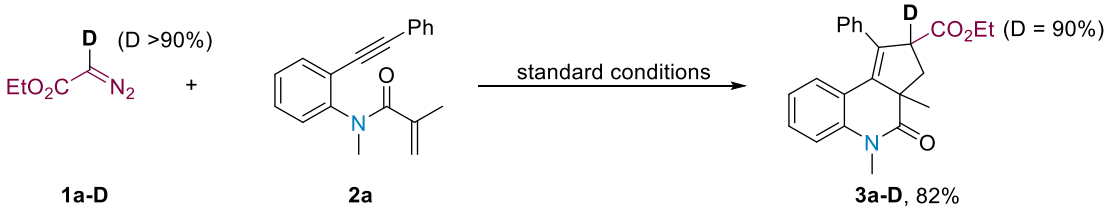
6. Mechanism studies

The reaction was performed in the presence of 2.5 eq radical quenchers 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO), showing that the desired product **3a** could not be generated. The captured iodinated alkyl radical was detected by high-resolution mass spectrometry.

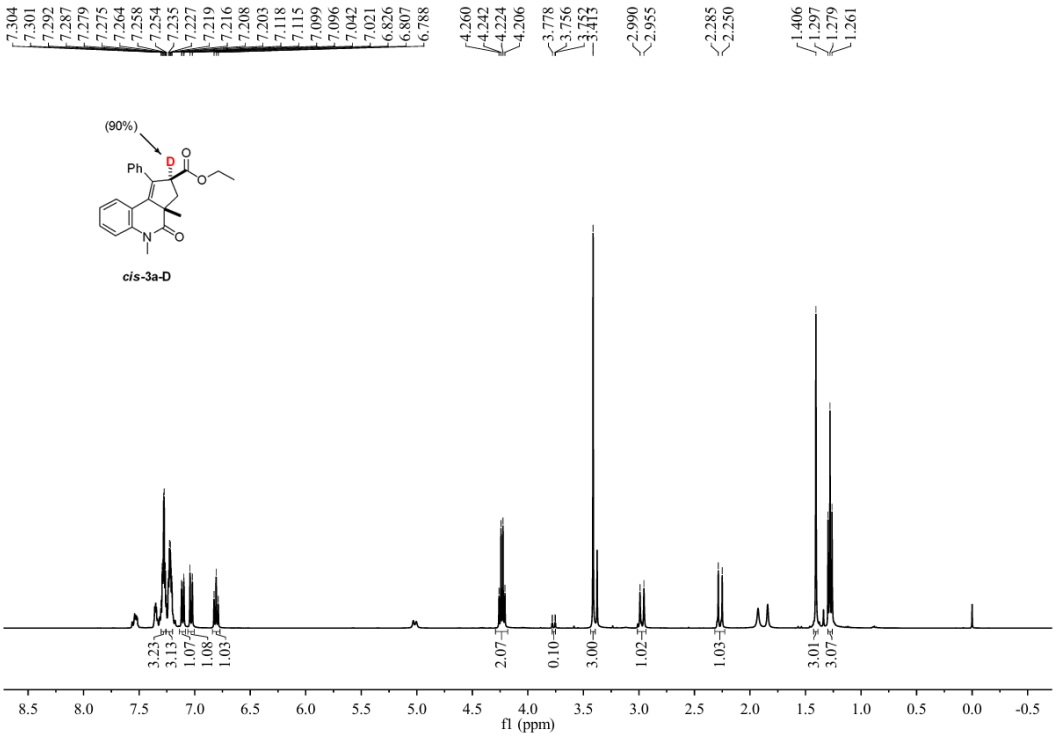
1a **2a** **3a**, 0%



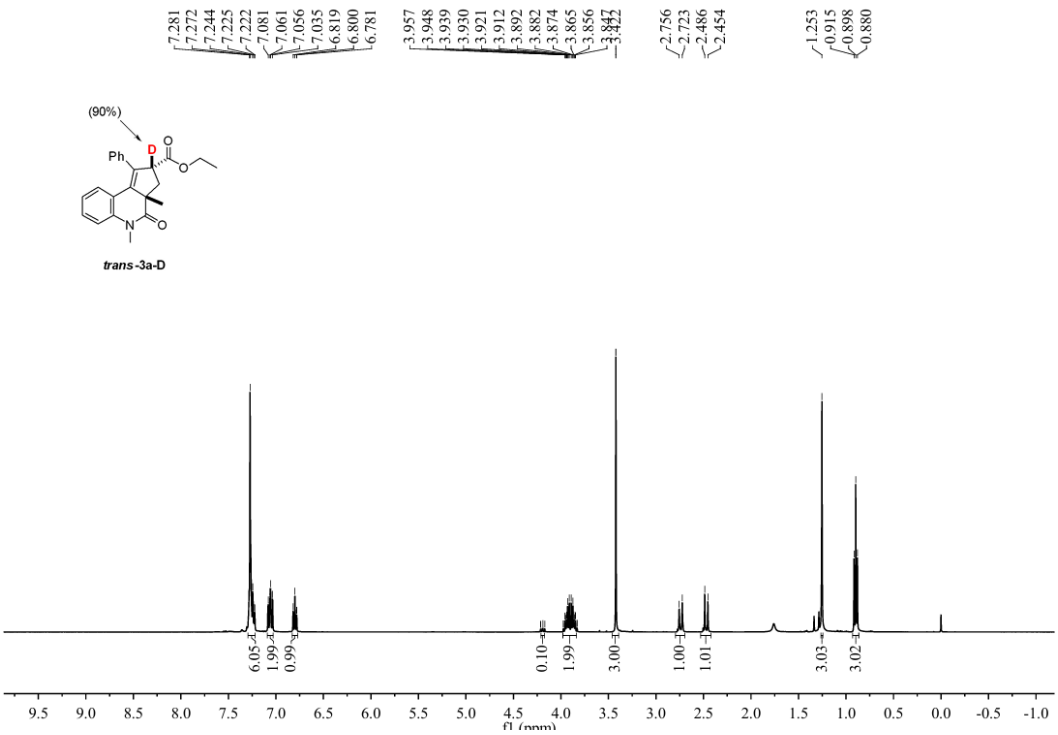
Then, the prepared deuterated EDA **1a-D** was reacted with **2a** under standard conditions, affording the deuterated product **3a-D** in 82% yield. These results indicated that the 1,5-HAT process was inhibited in this reaction.



1a-D **2a** **3a-D**, 82%



^{1}H NMR Spectrum of Compound ***cis*-3a-D** (400 MHz, $CDCl_3$)

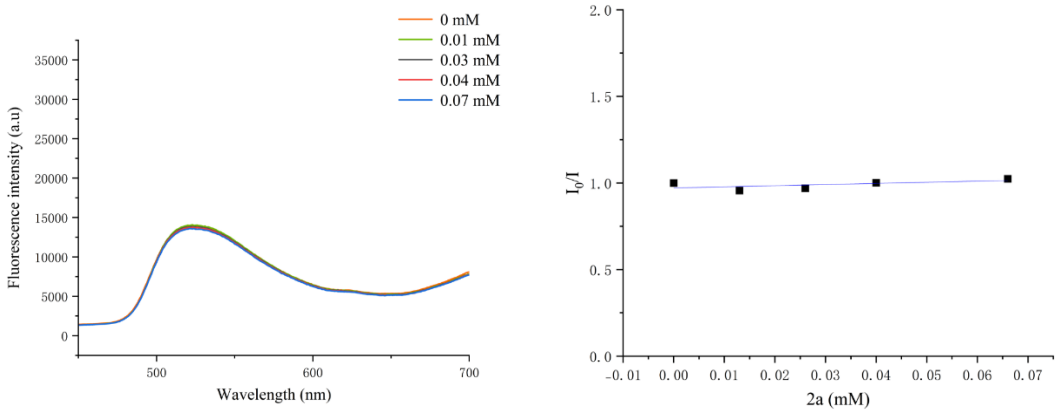


^{1}H NMR Spectrum of Compound ***trans*-3a-D** (400 MHz, $CDCl_3$)

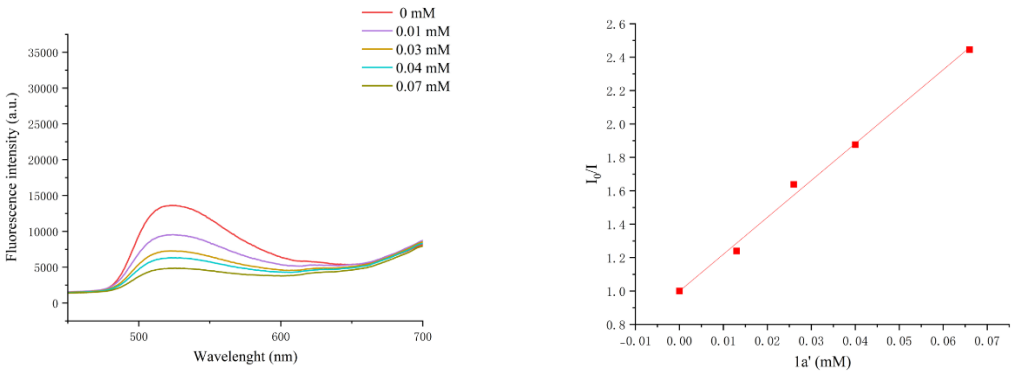
Stern−Volmer Luminescence Quenching Studies

Visible light luminescence intensities were recorded using a Shimadzu UV-Vis (UV-2600i) spectrofluorometer. All luminescence measurements were recorded using a screw-top quartz cuvette (Hellma fluorescence quartz cuvette, 10 × 10 mm, 3.5 mL). The Stern−Volmer analysis was

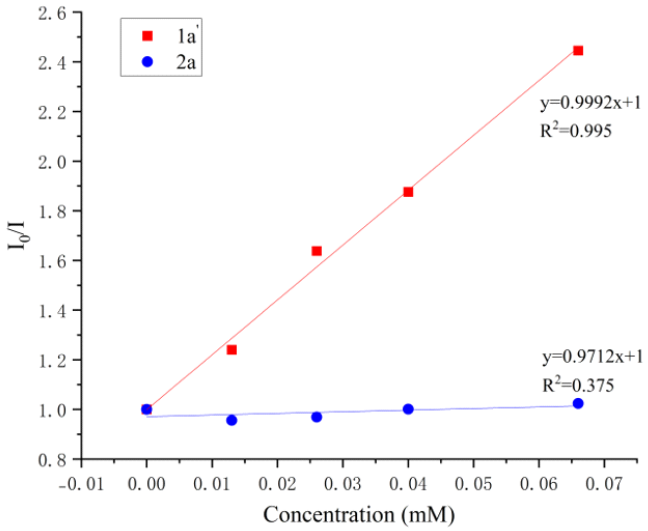
conducted according to the following relationship: $\mathbf{I_0/I = 1 + K_{SV}[Q]}$ Where, $\mathbf{I_0}$ is the luminescence intensity of the catalyst solution without the quencher, and **I** is the intensity in presence of the quencher. [**Q**] is concentration of quencher and **Ksv** is quenching rate constant.



- **Emission spectra for *fac-Ir*(ppy)$_3$ luminescence quenching by 2a as additive (left) and Stern-Volmer plot (right).**

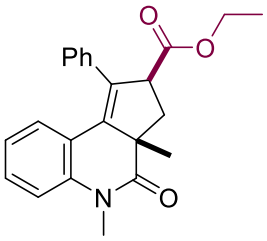


- **Emission spectra for *fac-Ir*(ppy)$_3$ luminescence quenching by 1a' as additive (left) and Stern-Volmer plot (right).**



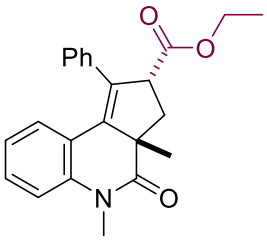
- **Stern−Volmer fluorescence quenching plot of *fac*-Ir(ppy)$_3$ with various quenchers.**

7. Characterization data



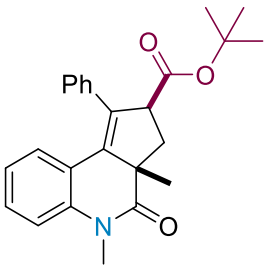
Ethyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3a):

Yield 33%; 24 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 3H), 7.25–7.20 (m, 3H), 7.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.81 (td, *J* = 7.6, 0.8 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.76 (dt, *J* = 8.8, 4.4 Hz, 1H), 3.42 (s, 3H), 2.98 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.28 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.40 (s, 3H), 1.28 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 175.2, 140.0, 137.9, 136.4, 136.1, 128.9, 128.42, 128.41, 128.1, 127.7, 122.4, 121.0, 114.9, 61.0, 55.1, 54.4, 38.1, 29.9, 25.1, 14.2. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO_3^+$ $(M+H)^+$ 362.1751, found: 362.1748.



Ethyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3a):

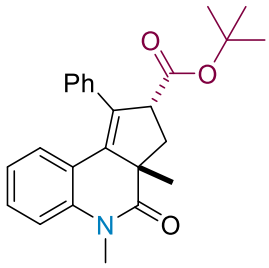
Yield 49%; 35 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.21 (m, 6H), 7.10–7.01 (m, 2H), 6.80 (t, *J* = 7.6 Hz, 1H), 4.19 (dd, *J* = 10.0, 7.6 Hz, 1H), 3.90 (dd, *J* = 15.6, 7.2 Hz, 2H), 3.42 (s, 3H), 2.74 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.48 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.25 (s, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 173.2, 140.2, 136.5, 136.3, 135.4, 128.9, 128.3, 128.1, 127.7, 127.5, 122.3, 120.5, 115.2, 60.5, 53.4, 52.8, 38.6, 29.8, 23.1, 13.8. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO_3^+$ $(M+H)^+$ 362.1751, found: 362.1749.



Tert-butyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3b):

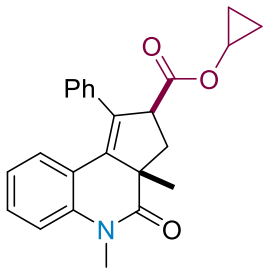
Yield 44%; 34 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.22 (m, 6H), 7.16 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.81 (td, *J* = 7.6, 0.8 Hz, 1H), 3.67 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.41 (s, 3H), 2.95 (dd, *J* = 14.0, 10.8 Hz,

1H), 2.25 (dd, J = 14.0, 2.0 Hz, 1H), 1.49 (s, 9H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 174.4, 140.0, 137.4, (136.6, 136.5), 128.8, 128.5, 128.3, 128.1, 127.6, 122.4, 121.2, 114.9, 81.0, 56.2, 54.3, 38.3, 29.9, 28.0, 25.1. HRMS (ESI) m/z calcd for $C_{25}H_{28}NO_3^+$ $(M+H)^+$ 390.2064, found: 390.2062.



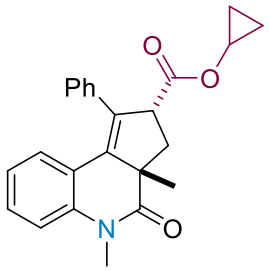
Tert-butyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3b):

Yield 46%; 36 mg; yellow solid; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.24 (m, 6H), 7.09–7.03 (m, 2H), 6.80 (t, J = 7.6 Hz, 1H), 4.07 (dd, J = 9.6, 7.6 Hz, 1H), 3.42 (s, 3H), 2.71 (dd, J = 12.8, 10.0 Hz, 1H), 2.45 (dd, J = 13.2, 7.6 Hz, 1H), 1.24 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 172.3, 140.2, 137.2, (135.77, 135.70), 128.8, 128.33, 128.28, 127.6, 122.3, 120.7, 115.2, 80.6, 53.9, 53.3, 38.6, 29.9, 27.5, 23.1. HRMS (ESI) m/z calcd for $C_{25}H_{28}NO_3^+$ $(M+H)^+$ 390.2064, found: 390.2062.



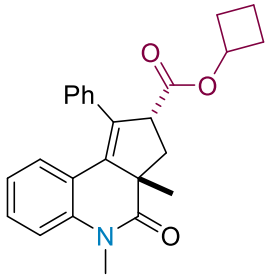
Cyclopropyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3c):

Yield 40%; 30 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.27 (m, 3H), 7.25–7.18 (m, 3H), 7.10 (dd, J = 7.6, 1.6 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.81 (td, J = 7.6, 0.8 Hz, 1H), 4.26–4.21 (m, 1H), 3.73 (dd, J = 10.8, 2.0 Hz, 1H), 3.41 (s, 3H), 2.96 (dd, J = 14.4, 10.8 Hz, 1H), 2.24 (dd, J = 14.4, 2.0 Hz, 1H), 1.39 (s, 3H), 0.78–0.71 (m, 2H), 0.71–0.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 175.2, 140.0, 138.0, 136.3, 135.9, 128.9, (128.44, 128.40), 128.1, 127.8, 122.5, 120.9, 115.0, 54.9, 54.4, 49.4, 38.0, 29.9, 25.2, (5.1, 5.0). HRMS (ESI) m/z calcd for $C_{24}H_{24}NO_3^+$ $(M+H)^+$ 374.1751, found: 374.1749.



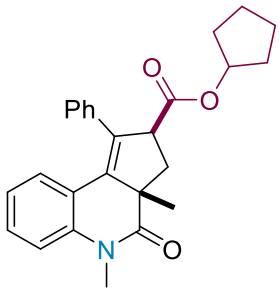
Cyclopropyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3c):

Yield 51%; 37 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m,3H), 7.2–7.21 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 5.12–5.04 (m, 1H), 3.74 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.41 (s, 3H), 2.97 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.43–2.33 (m, 2H), 2.27 (dd, *J* = 14.0, 1.6 Hz, 1H), 2.11–2.02 (m, 2H), 1.81 (q, *J* = 10.4 Hz, 1H), 1.69–1.64 (m 1H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 174.6, 140.0, 137.9, 136.4, 136.1, 128.9, (128.43, 128.41), 128.1, 127.7, 122.5, 121.0, 115.0, 69.3, 55.0, 54.4, 38.1, (30.2, 30.1), 29.9, 25.1, 13.6. HRMS (ESI) m/z calcd for $C_{24}H_{24}NO_3^+$ $(M+H)^+$ 374.1751, found: 374.1750.



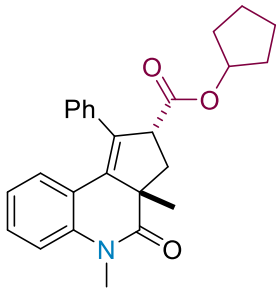
Cyclobutyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3d):

Yield 52%, trans : cis > 20:1; 40 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.2, 3.6 Hz, 3H), 7.25–7.19 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 5.08 (p, *J* = 7.5 Hz, 1H), 3.74 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.41 (s, 3H), 2.97 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.43–2.33 (m, 2H), 2.27 (dd, *J* = 14.0, 1.6 Hz, 1H), 2.11–2.02 (m, 2H), 1.81 (q, *J* = 10.4 Hz, 1H), 1.67 (dd, *J* = 14.4, 6.4 Hz, 1H), 1.40 (s, 3H). HRMS (ESI) m/z calcd for $C_{25}H_{26}NO_3^+$ $(M+H)^+$ 388.1907, found: 388.1907.



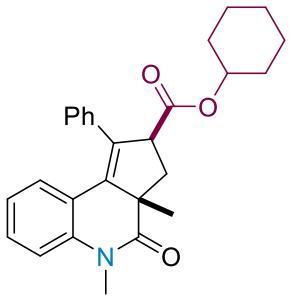
Cyclopentyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3e):

Yield 38%; 30 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.22 (m, 6H), 7.16–7.11 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 5.28–5.24 (m, 1H), 3.73 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.41 (s, 3H), 2.96 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.26 (dd, *J* = 14.0, 1.6 Hz, 1H), 1.94–1.81 (m, 2H), 1.74–1.64 (m, 4H), 1.63–1.54 (m, 2H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (175.3, 174.9), 140.0, 137.7, (136.4, 136.2), 128.9, (128.45, 128.36), 128.1, 127.7, 122.4, 121.1, 114.9, 77.8, 55.3, 54.4, 38.1, (32.6, 32.5), 29.9, 25.1, 23.6. HRMS (ESI) m/z calcd for $C_{26}H_{28}NO_3^+$ $(M+H)^+$ 402.2064, found: 402.2067.



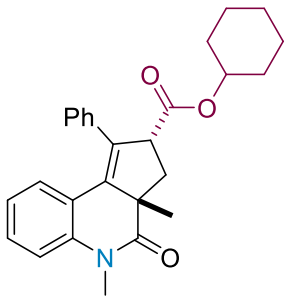
Cyclopentyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3e):

Yield 44%; 35 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.16 (m, 6H), 6.99 (t, *J* = 8.4 Hz, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 4.89–4.83 (m, 1H), 4.08 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.36 (s, 3H), 2.64 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.39 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.58–1.44 (m, 4H), 1.36–1.29 (m , 4H), 1.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 173.0, 140.2, 136.7, 136.1, 135.5, 128.9, 128.4, 128.1, 127.7, 127.5, 122.3, 120.6, 115.2, 53.3, 53.0, 38.7, (32.3, 32.2), 29.9, (23.6, 23.5), 23.1. HRMS (ESI) m/z calcd for $C_{26}H_{28}NO_3^+$ $(M+H)^+$ 402.2064, found: 402.2065.



Cyclohexyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3f):

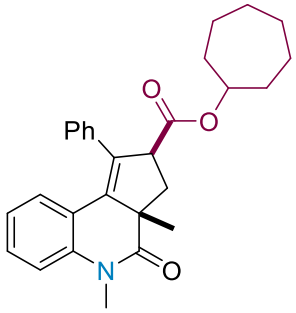
Yield 43%; 36 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.24 (m, 6H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.82 (t, *J* = 7.6 Hz, 1H), 4.89–4.83 (m, 1H), 3.75 (d, *J* = 9.2 Hz, 1H), 3.41 (s, 3H), 2.98 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.27 (dd, *J* = 14.0, 1.6 Hz, 1H), 1.89 (t, *J* = 12.4 Hz, 2H), 1.72 (t, *J* = 10.4 Hz, 2H), 1.65–1.42 (m, 3H), 1.40 (s, 3H), 1.38–1.28 (m, 2H), 1.27–1.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 174.6, 140.0, 137.7, 136.4, 136.3, 128.9, 128.5, 128.4, 128.1, 127.7, 122.4, 121.1, 114.9, 73.4, 55.4, 54.4, 38.3, 31.5, 29.9, 25.3, 25.1, 23.7. HRMS (ESI) m/z calcd for $C_{27}H_{30}NO_3^+$ $(M+H)^+$ 416.2220, found: 416.2222.



Cyclohexyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-

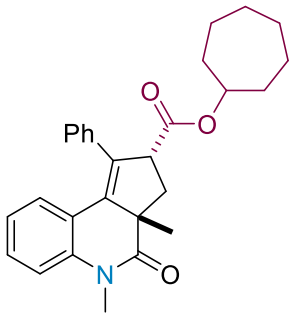
cyclopenta[c]quinoline-2-carboxylate (*trans*-3f):

Yield 42%; 35 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 3.2 Hz, 4H), 7.25–7.22 (m, 2H), 7.09–7.04 (m, 2H), 6.80 (t, *J* = 7.6 Hz, 1H), 4.57–4.49 (m, 1H), 4.17 (dd, *J* = 10.0, 7.6 Hz, 1H), 3.43 (s, 3H), 2.72 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.48 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.61–1.38 (m, 6H), 1.25 (s, 3H), 1.18–1.05 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 172.7, 140.3, 136.8, 136.1, 135.5, 128.9, 128.4, 128.2, 127.7, 127.5, 122.3, 120.7, 115.2, 72.8, 53.3, 53.1, 38.8, 31.1, 29.9, 25.3, 23.6, 23.1. HRMS (ESI) m/z calcd for $C_{27}H_{30}NO_3^+$ $(M+H)^+$ 416.2220, found: 416.2222.



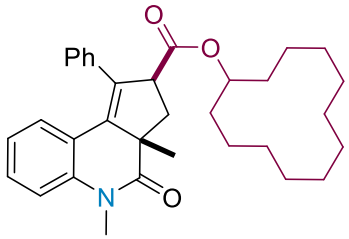
Cycloheptyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3g):

Yield 15%; 12 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.18 (m , 5H), 7.17–7.15 (m, 1H), 7.07 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.78–6.71 (m, 1H), 4.98–4.92 (m, 1H), 3.67 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.34 (s, 3H), 2.90 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.19 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.93–1.79 (m, 2H), 1.63–1.54 (m, 3H), 1.49 (d, *J* = 3.6 Hz, 3H), 1.38–1.35 (m, 1H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 174.5, 140.0, 137.7, (136.4, 136.3), 128.9, 128.5, 128.4, 128.1, 127.7, 122.4, 121.1, 114.9, 75.9, 55.4, 54.4, 38.3, (33.72, 33.70), 29.9, 28.2, 25.1, (22.82, 22.80). HRMS (ESI) m/z calcd for $C_{28}H_{32}NO_3^+$ $(M+H)^+$ 430.2377, found: 430.2382.



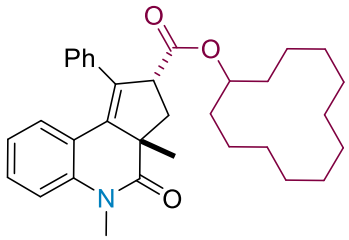
Cycloheptyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3g):

Yield 20%; 17 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 10.0 Hz, 6H), 7.06 (dd, *J* = 12.4, 7.6 Hz, 2H), 6.80 (t, *J* = 7.6 Hz, 1H), 4.73–4.66 (m, 1H), 4.16 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.43 (s, 3H), 2.71 (dd, *J* = 12.8, 10.0 Hz, 1H), 2.47 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.63–1.57 (m, 1H), 1.43 (d, *J* = 2.0 Hz, 5H), 1.38–1.26 (m, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 174.5, 140.0, 137.7, (136.4, 136.3), 128.9, (128.5, 128.4), 128.1, 127.7, 122.4, 121.1, 114.9, 75.9, 55.4, 54.4, 38.3, (33.72, 33.70), 29.9, 28.2, 25.1,(22.82, 22.80). HRMS (ESI) m/z calcd for $C_{28}H_{32}NO_3^+$ $(M+H)^+$ 430.2377, found: 430.2380.



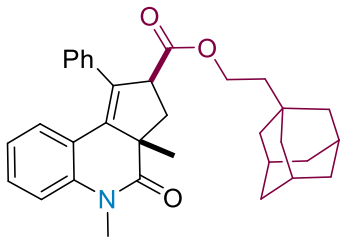
Cyclododecyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3h):

Yield 15%; 15 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 5H), 7.24–7.22 (m, 1H), 7.14 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.83–6.79 (m,1H), 5.14–5.07 (m, 1H), 3.74 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.41 (s, 3H), 2.97 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.25 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.76–1.65 (m, 3H), 1.56–1.51 (m, 2H), 1.49–1.44 (m, 2H), 1.40 (s, 7H), 1.34 (d, *J* = 4.8 Hz, 11H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 174.9, 140.0, 137.7, 136.4, 136.2, 128.8, 128.4, 128.3, 128.1, 127.7, 122.4, 121.1, 114.9, 73.0, 55.3, 54.4, 38.3, 29.9, (29.07, 29.05), 25.1, (24.01, 23.97), 23.8, 23.4, 23.2, (21.0, 20.9). HRMS (ESI) m/z calcd for $C_{33}H_{42}NO_3^+$ $(M+H)^+$ 500.3159, found: 500.3161.



Cyclododecyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3h):

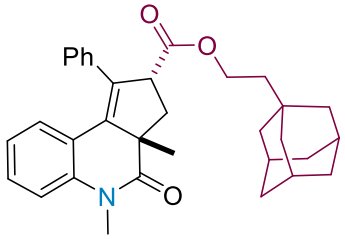
Yield 26%; 26 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.26 (m, 4H), 7.26–7.22 (m, 2H), 7.10–7.03 (m, 2H), 6.80 (t, *J* = 7.6 Hz, 1H), 4.78–4.75 (m, 1H), 4.17 (dd, *J* = 10.0, 7.6 Hz, 1H), 3.42 (s, 3H), 2.71 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.47 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.43–1.34 (m, 3H), 1.29–1.20 (m, 20H), 1.12–1.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 173.9, 141.3, 137.8, 137.1, 136.5, 129.9, 129.4, 129.2, 128.7, 128.6, 123.3, 121.7, 116.2, 78.4, 78.0, 77.7, 73.7, (54.44, 54.37), 54.2, 39.9, 30.9, 29.8, 29.6, 25.0, 24.8, 24.4, 24.3, 24.2, (24.11, 24.07), 21.7, 21.6. HRMS (ESI) m/z calcd for $C_{33}H_{42}NO_3^+$ $(M+H)^+$ 500.3159, found: 500.3159.



2-((3S,5S,7S)-adamantan-1-yl)ethyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3i):

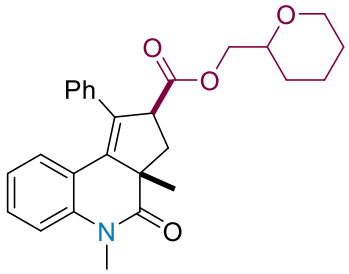
Yield 30%; 32 mg; yellow oil; column chromatography, dr > 20:1; silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.26 (m, 3H), 7.25–7.20 (m, 3H), 7.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.81 (dd, *J* = 10.8, 4.4 Hz, 1H), 4.27–4.17 (m, 2H), 3.75 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.41 (s, 3H), 2.97 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.27 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.93 (s, 3H),

1.69 (d, J = 12.0 Hz, 3H), 1.60 (d, J = 10.8 Hz, 4H), 1.51 (d, J = 2.0 Hz, 6H), 1.43 (d, J = 7.2 Hz, 1H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 140.0, 137.8, 136.4, 136.1, 128.9, 128.43, 128.41, 128.1, 127.7, 122.4, 121.1, 115.0, 61.6, 55.2, 54.4, 42.5, 42.3, 38.1, 37.0, 31.8, 29.9, 28.5, 25.1. HRMS (ESI) m/z calcd for $C_{33}H_{38}NO_3^+$ $(M+H)^+$ 496.2846, found: 496.2845.



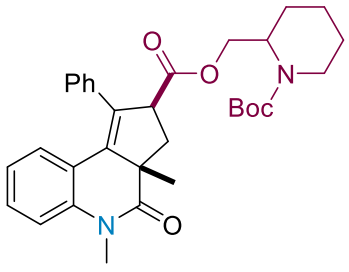
2-((3R,5R,7R)-adamantan-1-yl)ethyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3i):

Yield 35%; 35 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.24 (m, 6H), 7.10–7.01 (m, 2H), 6.81 (t, J = 7.6 Hz, 1H), 4.18 (dd, J = 9.6, 7.6 Hz, 1H), 3.97–3.82 (m, 2H), 3.42 (s, 3H), 2.74 (dd, J = 13.2, 10.0 Hz, 1H), 2.47 (dd, J = 13.2, 7.6 Hz, 1H), 1.88 (s, 3H), 1.66 (d, J = 12.0 Hz, 3H), 1.55 (s, 3H), 1.36 (d, J = 2.0 Hz, 6H), 1.25 (s, 3H), 1.06 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 173.4, 140.3, 136.6, 136.3, 135.4, 129.0, 128.4, 128.2, 127.8, 127.6, 125.6, 122.3, 120.7, 115.2, 61.1, 53.5, 53.0, 42.3, 42.0, 38.7, 37.0, 31.6, 29.9, 28.5, 23.3. HRMS (ESI) m/z calcd for $C_{33}H_{38}NO_3^+$ $(M+H)^+$ 496.2846, found: 496.2847.



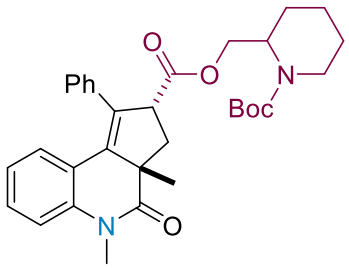
(tetrahydro-2H-pyran-2-yl)methyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3j):

Yield 80%; cis : trans > 20:1; 69 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.17 (m, 6H), 7.04 (dd, J = 7.6, 1.6 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.74 (t, J = 7.6 Hz, 1H), 4.010–4.08 (m, 2H), 3.94–3.92 (m, 1H), 3.76 (dd, J = 10.8, 1.6 Hz, 1H), 3.50–3.45 (m, 1H), 3.37–3.32 (m, 4H), 2.91 (dd, J = 14.0, 10.8 Hz, 1H), 2.22 (dd, J = 14.4, 1.6 Hz, 1H), 1.84–1.74 (m, 1H), 1.49–1.41 (m, 3H), 1.33 (s, 3H), 1.31–1.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 175.24, 175.21, 140.0, 138.02, 137.99, 136.4, 136.1, 136.0, 128.9, 128.52, 128.48, 128.4, 128.2, 127.7, 122.4, 121.05, 121.04, 114.9, 75.5, 75.4, 68.4, 68.3, 67.81,67.78, 54.92, 54.85, 54.4, 38.3, 29.9, 27.81, 27.79, 25.7, 25.0, 24.9, 23.0. HRMS (ESI) m/z calcd for $C_{27}H_{30}NO_4^+$ $(M+H)^+$ 432.2169, found: 432.2172.



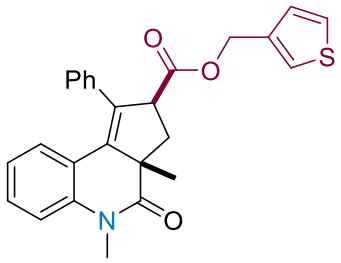
(1-(tert-butoxycarbonyl)piperidin-2-yl)methyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3k):

Yield 34%; 36 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 3H), 7.25–7.19 (m, 3H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.82 (t, *J* = 7.6 Hz, 1H), 4.52 (s, 1H), 4.39–4.32 (m, 1H), 4.29–4.17 (m, 2H), 4.02 (d, *J* = 10.4 Hz, 1H), 3.81–3.77 (m,, 1H), 3.43 (s, 3H), 2.98 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.81 (t, *J* = 10.8 Hz, 1H), 2.34–2.26 (m, 1H), 1.68–1.57 (m, 5H), 1.45 (d, *J* = 8.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 175.13, 175.06, 164.9, 155.0, 154.92,154.90, 139.97, 139.96, 138.1, 136.30, 136.26, 135.9, 135.8, 128.9, 128.5, 128.42, 128.37, 128.3, 128.08, 128.05, 127.7, 122.4, 120.93, 120.90, 114.9, 79.7, 79.6, 79.5, 62.52, 62.49, 62.2, 62.1, 55.0, 54.8, 54.4, 38.1, 38.0, 29.9, 28.4, 25.2, 25.13, 25.09, 25.05, 19.2, 19.1. HRMS (ESI) m/z calcd for $C_{32}H_{39}N_2O_5^+$ $(M+H)^+$ 531.2853, found: 531.2853.



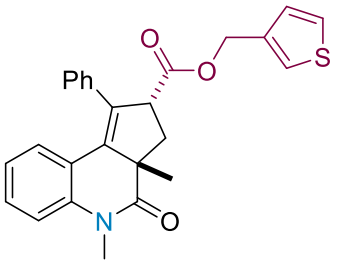
(1-(tert-butoxycarbonyl)piperidin-2-yl)methyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3k):

Yield 44%; 47 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 2.8 Hz, 5H), 7.26–7.23 (m, 1H), 7.10–7.04 (m, 2H), 6.8–6.81 (m, 1H), 4.24 (dd, *J* = 9.6, 7.6 Hz, 2H), 4.00 (d, *J* = 8.8 Hz, 1H), 3.93–3.84 (m, 3H), 3.44 (d, *J* = 2.8 Hz, 3H), 2.77–2.72 (m, 1H), 2.56–2.48 (m, 3H), 1.46 (d, *J* = 13.2 Hz, 12H), 1.26 (d, *J* = 1.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 174.4, 173.30, 173.26, 154.9, 154.8, 140.30, 140.25, 136.6, 136.5, 136.1, 135.24, 135.23, 129.1, 129.0, 128.54, 128.51, 128.1, 128.0, 127.8, 127.52, 127.50, 122.3, 120.50, 120.46, 115.23, 115.17, 79.55, 79.48, 61.9, 61.8, 53.4, 52.6, 38.9, 38.8, 29.9, 29.7, 28.43, 28.37, 25.0, 24.8, 24.7, 23.2, 23.0, 19.0, 18.9. HRMS (ESI) m/z calcd for $C_{32}H_{39}N_2O_5^+$ $(M+H)^+$ 531.2853, found: 531.2850.



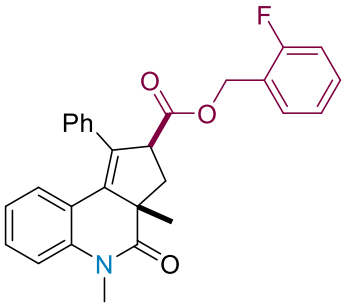
Thiophen-3-ylmethyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3l):

Yield 18%; 15 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.23 (m, 2H), 7.19–7.15 (m, 4H), 7.06–6.99 (m, 4H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 5.18–5.11 (m, 2H), 3.72 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.33 (s, 3H), 2.89 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.18 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.29 (s, 3H). HRMS (ESI) m/z calcd for $C_{26}H_{24}NO_3^+$ $(M+H)^+$ 430.1471, found: 430.1476.



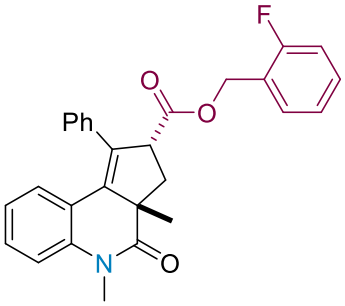
Thiophen-3-ylmethyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3l):

Yield 17%; 15 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 2H), 7.18 (s, 4H), 7.10 (dd, *J* = 4.8, 3.2 Hz, 1H), 6.98 (dd, *J* = 11.2, 4.8 Hz, 2H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.65 (dd, *J* = 4.8, 0.8 Hz, 1H), 4.87 (d, *J* = 12.4 Hz, 1H), 4.76 (d, *J* = 12.4 Hz, 1H), 4.17 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.34 (s, 3H), 2.69 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.42 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 173.2, 140.3, 136.6, 136.4, 136.1, 135.3, 129.0, 128.5, 128.0, 127.8, 127.5, 127.4, 125.8, 124.1, 122.3, 120.5, 115.2, 61.5, 53.4, 52.7, 38.8, 29.9, 23.2. HRMS (ESI) m/z calcd for $C_{26}H_{24}NO_3^+$ $(M+H)^+$ 430.1471, found: 430.1477.



2-fluorobenzyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3m):

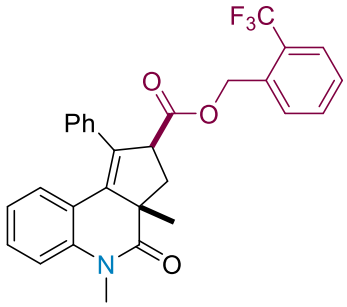
Yield 30%; 26 mg; yellow solid; column chromatography, silica gel (PE/EA, 15:1); mp 87.5–89.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m,2H), 7.26 (s, 1H), 7.23 (d, *J* = 7.2 Hz, 3H), 7.15 (dd, *J* = 7.6, 2.0 Hz, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 5.28 (s, 2H), 3.81 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.41 (s, 3H), 2.97 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.28 (dd, *J* = 14.4, 1.6 Hz, 1H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 174.9, 140.0, 138.2, 136.1 (d, *J*= 37 Hz), 130.9 (d, *J*= 4.0 Hz), 130.4 (d, *J*= 8.0 Hz), 130.37, 129.0, 128.5, 128.4, 128.2, 127.7, 124.2 (d, *J*= 4.0 Hz), 122.5, 121.0, 115.5 (d, *J*= 21 Hz), 115.0, 60.8 (d, *J*= 5.0 Hz), 54.9, 54.5, 38.1, 30.0, 25.0. HRMS (ESI) m/z calcd for $C_{28}H_{25}FNO_3^+$ $(M+H)^+$ 442.1813, found: 442.1815.



2-fluorobenzyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-

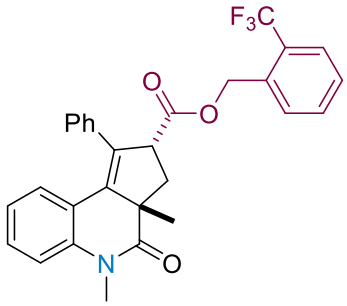
cyclopenta[c]quinoline-2-carboxylate (*trans*-3m):

Yield: 41%; 36 mg; yellow solid; column chromatography, silica gel (PE/EA, 15:1); mp 58.1–59.7 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 7H), 7.07–7.03 (m, 2H), 6.97 (t, *J* = 8.4 Hz, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 4.96 (dd, *J* = 43.6, 12.4 Hz, 2H), 4.26 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.41 (s, 3H), 2.77 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.50 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 173.1, 160.7 (d, *J*= 247 Hz), 140.3, 136.6, 136.1, 135.2, 130.5 (d, *J*= 4.0 Hz), 130.0 (d, *J*= 9.0 Hz), 129.1, 128.5, 128.0, 127.8, 127.5, 124.0 (d, *J*= 4.0 Hz), 122.8 (d, *J*= 15 Hz), 122.3, 120.6, 115.27 (d, *J*= 21 Hz), 115.25, 60.2 (d, *J*= 4.0 Hz), 53.5, 52.7, 38.8, 29.9, 23.2. HRMS (ESI) m/z calcd for $C_{28}H_{25}FNO_3^+$ $(M+H)^+$ 442.1813, found: 442.1815.



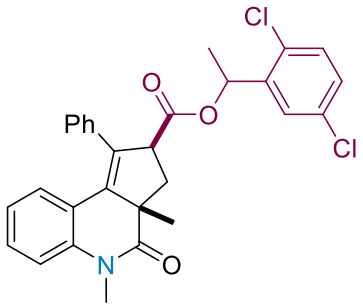
2-(trifluoromethyl)benzyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3n):

Yield 12%; 12 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.0 Hz, 2H), 7.55–7.48 (m, 2H), 7.28–7.23 (m, 4H), 7.17–7.12 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 5.30–5.23 (m, 2H), 3.87 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.43 (s, 3H), 3.03 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.30 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 174.8, 139.9, 138.2, 136.6, 136.1, 135.7, 131.6, 131.5–130.5 (m), 129.1, 129.0, 128.4, 128.3, 128.0, 127.8, 125.2–125.0 (m), 122.5, 120.8, 115.0, 65.9, 54.9, 54.5, 37.9, 29.9, 25.1. HRMS (ESI) m/z calcd for $C_{29}H_{25}FNO_3^+$ $(M+H)^+$ 492.1781, found: 492.1778.



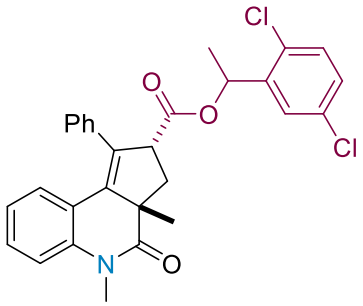
2-(trifluoromethyl)benzyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3n):

Yield 12%; 12 mg; yellow solid; column chromatography, silica gel (PE/EA, 15:1); mp 76.6–78.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.27–7.24 (m, 2H), 7.19–7.14 (m, 7H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.98–6.96 (m,2H), 6.72 (t, *J* = 7.6 Hz, 1H), 4.89 (d, *J* = 12.4 Hz, 1H), 4.77 (d, *J* = 12.4 Hz, 1H), 4.20 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.34 (s, 3H), 2.71 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.43 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 173.1, 140.2, 136.7, 136.4, 135.9, 135.1, 131.5, 131.1–130.2 (m), 129.1, 128.9, 128.5, 127.9, 127.8, 127.5, 125.2–122.5 (m), 122.3, 120.5, 115.2, 65.7, 53.5, 52.7, 38.6, 29.9, 23.2. HRMS (ESI) m/z calcd for $C_{29}H_{25}FNO_3^+$ $(M+H)^+$ 492.1781, found: 492.1778.



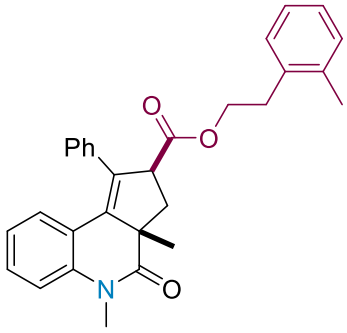
1-(2,5-dichlorophenyl)ethyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3o):

Yield 21%; 21 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.18 (m, 4H), 7.16–7.10 (m, 5H), 7.06–7.03 (m, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.74 (q, J = 7.6 Hz, 1H), 6.19–6.13 (m, 1H), 3.78 (d, J = 10.4 Hz, 1H), 3.34 (s, 3H), 2.98–2.90 (m, 1H), 2.24 (d, J = 14.4 Hz, 1H), 1.45 (dd, J = 24.0, 6.4 Hz, 3H), 1.29 (d, J = 10.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.18, 175.12, 174.2, 173.8, 141.0, 140.97, 140.0, 138.2, 138.1, 136.2, 136.0, 135.7, 135.6, 133.13, 133.07, 130.76, 130.71, 130.11, 130.07, 129.03, 129.0, 128.9, 128.5, 128.43, 128.41, 128.2, 128.14, 128.07, 127.81, 127.77, 126.9, 126.7, 122.51, 122.50, 120.93, 120.90, 115.0, 69.56, 69.54, 55.0, 54.8, 54.44, 54.43, 38.2, 37.8, 29.95, 29.94, 29.7, 25.0, 24.96, 21.0, 20.8. HRMS (ESI) m/z calcd for $C_{29}H_{26}Cl_2NO_3^+$ $(M+H)^+$ 506.1284, found: 506.1285.



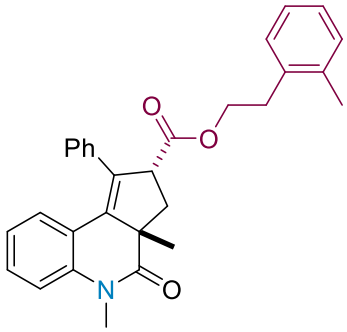
1-(2,5-dichlorophenyl)ethyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3o):

Yield 34%; 34 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.15 (m, 6H), 7.14–7.11 (m, 1H), 7.10–7.07 (m, 1H), 7.06–7.03 (m, 1H), 7.01–6.99 (m, 1H), 6.98–6.96 (m, 1H), 6.76–6.72 (m, 1H), 5.90–5.80 (m, 1H), 4.23–4.17 (m, 1H), 3.36 (d, J = 2.0 Hz, 3H), 2.76–2.65 (m, 1H), 2.48–2.38 (m, 1H), 1.19 (s, 3H), 1.06 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.49,174.48, 172.02, 171.98, 140.81, 140.77, 140.3, 136.7, 136.6, 136.0, 135.34, 135.29, 132.90, 132.86, 130.60, 130.56, 130.1, 130.0, 129.10, 129.06, 128.8, 128.6, 128.5, 128.2, 128.0, 127.8, 127.6, 126.9, 126.8, 122.4, 120.6, 115.3, 69.2, 53.49, 53.46, 52.9, 52.8, 38.7, 38.4, 29.9, 23.5, 23.2, 20.5, 20.4. HRMS (ESI) m/z calcd for $C_{29}H_{26}Cl_2NO_3^+$ $(M+H)^+$ 506.1284, found: 506.1284.



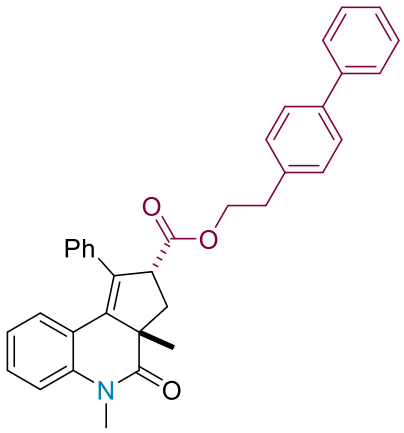
2-methylphenethyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3p):

Yield 20%; 18 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.15 (m, 4H), 7.10–7.02 (m, 7H), 6.95 (d, J = 8.0 Hz, 1H), 6.74 (t, J = 7.6 Hz, 1H), 4.36–4.23 (m, 2H), 3.69 (dd, J = 10.8, 1.6 Hz, 1H), 3.33 (s, 3H), 2.92–2.84 (m, 3H), 2.26 (s, 3H), 2.16 (dd, J = 14.4, 2.0 Hz, 1H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 175.1, 139.9, 137.9, (136.4, 136.3), 136.0, 135.5, 130.3, 129.5, 128.9, 128.4, 128.3, 128.1, 127.7, 126.8, 126.1, 122.4, 120.9, 114.9, 64.5, 55.0, 54.4, 38.0, 32.3, 29.9, 25.1, 19.4. HRMS (ESI) m/z calcd for $C_{30}H_{30}NO_3^+$ $(M+H)^+$ 452.2220, found: 452.2224.



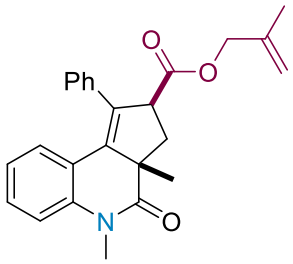
2-methylphenethyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3p):

Yield 33%; 30 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.14 (m 6H), 7.03–6.97 (m, 5H), 6.91 (d, J = 6.4 Hz, 1H), 6.73 (t, J = 7.6 Hz, 1H), 4.13 (dd, J = 9.6, 7.6 Hz, 1H), 3.96–3.88 (m,2H), 3.36 (s, 3H), 2.69 (dd, J = 13.2, 10.0 Hz, 1H), 2.49–2.37 (m, 3H), 2.13 (s, 3H), 1.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 173.2, 140.2, 136.4, 135.5, 135.3, 130.2, 129.3, 129.0, 128.4, 128.1, 127.7, 127.5, 126.6, 125.9, 122.3, 120.5, 115.2, 64.0, 53.5, 52.9, 38.6, 31.9, 29.9, 23.3, 19.2. HRMS (ESI) m/z calcd for $C_{30}H_{30}NO_3^+$ $(M+H)^+$ 452.2220, found: 452.2221.



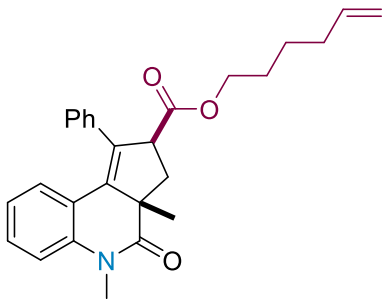
2-([1,1'-biphenyl]-4-yl)ethyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3q):

Yield 50%; trans: cis > 20:1; 51 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.21 (s, 1H), 7.19 (s, 2H), 7.17–7.16 (m, 4H), 7.08–7.02 (m, 3H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 4.42–4.32 (m, 2H), 3.70 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.33 (s, 3H), 2.95–2.87 (m, 3H), 2.16 (dd, *J* = 14.4, 1.6 Hz, 1H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 175.1, 140.9, 140.0, 139.6, 138.0, 136.7, 136.3, 136.0, 129.3, 129.0, 128.8, 128.45, 128.39, 128.1, 127.7, 127.3, 127.2, 127.0, 122.5, 121.0, 115.0, 65.5, 55.1, 54.4, 38.1, 34.7, 30.0, 25.0. HRMS (ESI) m/z calcd for $C_{35}H_{32}NO_3^+$ $(M+H)^+$ 514.2377, found: 514.2381.



2-methylallyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3r):

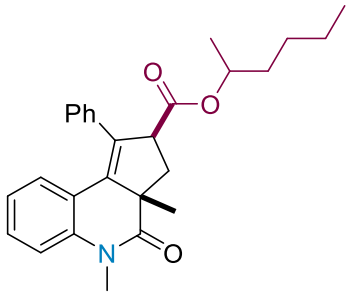
Yield 19%; cis: trans > 20:1; 15 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.26 (m,3H), 7.24 – 7.21 (m, 3H), 7.12 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.81 (t, *J* = 7.5 Hz, 1H), 4.96 (d, *J* = 19.9 Hz, 2H), 4.65 – 4.55 (m, 2H), 3.82 (dd, *J* = 10.6, 1.7 Hz, 1H), 3.42 (s, 3H), 3.00 (dd, *J* = 14.1, 10.6 Hz, 1H), 2.30 (dd, *J* = 14.2, 1.8 Hz, 1H), 1.74 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 174.9, 140.0, 139.6, 138.1, 136.3, 136.0, 128.9, 128.45, 128.42, 128.1, 127.7, 122.5, 121.0, 115.0, 113.6, 68.4, 55.0, 54.4, 38.2, 30.0, 25.1, 19.6. HRMS (ESI) m/z calcd for $C_{25}H_{26}NO_3^+$ $(M+H)^+$ 388.1907, found: 388.1909.



Hex-5-en-1-yl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3s):

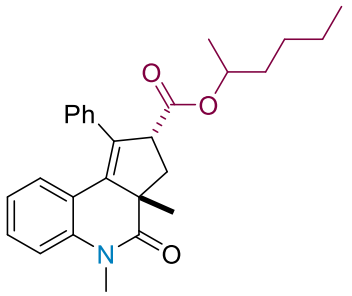
Yield 20%; cis: trans > 20:1; 17 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.19 (m, 3H), 7.17–7.13 (m, 3H), 7.04 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.74 (td, *J* = 7.6, 0.8 Hz, 1H), 5.75–5.65 (m, 1H), 4.96–4.87 (m, 2H), 4.10 (t, *J* = 6.8 Hz, 2H), 3.70 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.34 (s, 3H), 2.91 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.20 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.00 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.60 (d, *J* = 6.8 Hz, 1H), 1.57 (s, 1H), 1.37 (dd, *J* = 15.2, 8.0 Hz, 2H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.30, 175.25, 140.0, 138.2, 137.9, 136.4, 136.1, 128.9, (128.42, 128.39), 128.1, 127.7, 122.5, 121.0, (114.95,

114.88), 65.0, 55.1, 54.4, 38.1, 33.2, 29.9, 28.0, (25.12, 25.10). HRMS (ESI) m/z calcd for $C_{27}H_{30}NO_3^+$ $(M+H)^+$ 416.2220, found: 416.2225.



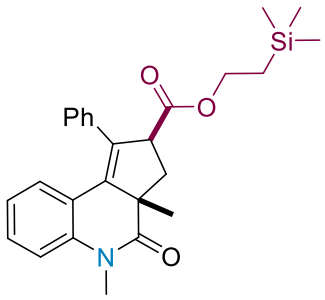
Hexan-2-yl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3t):

Yield 33%; 28 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.22 (m, 6H), 7.16–7.13 (m, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 5.04–4.96 (m, 1H), 3.76–3.73 (m, 1H), 3.41 (s, 3H), 3.01–2.95 (m, 1H), 2.28–2.23 (m, 1H), 1.61–1.44 (m, 2H), 1.40 (s, 3H), 1.33–1.28 (m,3H), 1.27–1.25 (m, 3H), 1.23 (d, J = 6.4 Hz, 1H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 174.90, 174.89, 140.0, 137.8, (136.47,136.44), (136.26,136.24), 128.9, (128.50,128.48), (128.41, 128.38), 128.1, 127.7, 122.5, 121.1, 115.0, 71.9, 71.8, 55.4, 55.3, 54.4, 38.3, 35.6, 35.5, 30.0, 27.5, 25.1, 25.0, 22.54, 22.50, 19.92, 19.87, 14.0. HRMS (ESI) m/z calcd for $C_{27}H_{32}NO_3^+$ $(M+H)^+$ 418.2377, found: 418.2382.



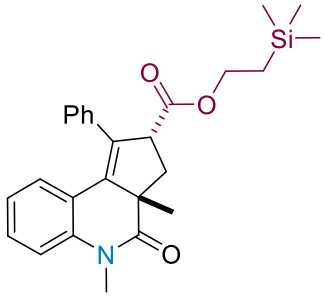
Hexan-2-yl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3t):

Yield 33%; 28 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.23 (m, 6H), 7.10–7.04 (m, 2H), 6.80 (t, J = 7.6 Hz, 1H), 4.70–4.64 (m, 1H), 4.20–4.15 (m, 1H), 3.43 (s, 3H), 2.71 (dd, J = 12.8, 10.4 Hz, 1H), 2.53–2.44 (m, 1H), 1.34–1.27 (m, 1H), 1.25 (s, 3H), 1.21–1.02 (m, 4H), 0.95–0.88 (m, 3H), 0.81 (dd, J = 14.0, 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 174.6, 172.90, 172.88, 140.3, 136.7, 136.6, 136.12, 136.09, 135.5, 135.4, 128.9, 128.4, 128.14, 128.13, 127.70, 127.67, 127.5, 122.3, 120.63, 120.60, 115.2, 71.40, 71.36, 53.34, 53.32, 53.1, 53.0, 38.9, 38.8, 35.3, 29.9, 27.3, 27.1, 23.07, 23.04, 22.4, 19.5, 19.3, 13.9, 13.8. HRMS (ESI) m/z calcd for $C_{27}H_{32}NO_3^+$ $(M+H)^+$ 418.2377, found: 418.2381.



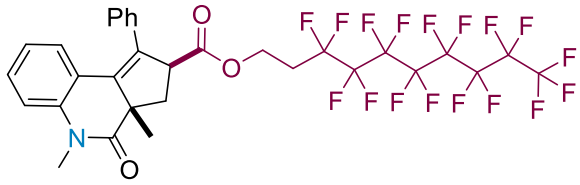
2-(trimethylsilyl)ethyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3u):

Yield 40%; 35 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.17 (m, 6H), 7.07 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 4.25–4.17 (m, 2H), 3.70 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.37 (s, 3H), 2.93 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.22 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.36 (s, 3H), 1.01–0.91 (m, 2H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (176.87, 176.84), 141.5, 139.4, 138.0, 137.7, 130.4, 129.9, 129.6, 129.2, 123.9, 122.5, 116.5, 78.8, 78.5, 78.2, 64.9, 56.7, 55.9, 39.6, 31.5, 26.7, 18.8, -0.00. HRMS (ESI) m/z calcd for $C_{26}H_{32}NO_3Si^+$ $(M+H)^+$ 434.2146, found: 434.2151.



2-(trimethylsilyl)ethyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-3u):

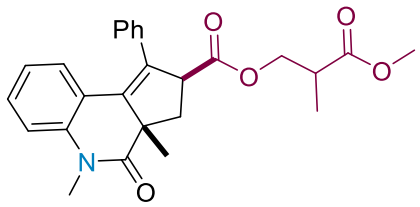
Yield 49%; 42 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.31 (m, 6H), 7.14–7.09 (m, 2H), 6.86 (t, *J* = 7.6 Hz, 1H), 4.24 (dd, *J* = 9.6, 7.6 Hz, 1H), 4.01–3.94 (m, 2H), 3.48 (s, 3H), 2.80 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.54 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.31 (s, 3H), 0.73–0.64 (m, 2H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 173.4, 140.3, 136.5, 136.3, 135.4, 128.9, 128.4, 128.1, 127.7, 127.5, 122.3, 120.6, 115.2, 62.8, 53.4, 53.0, 38.7, 29.9, 23.3, 17.0, -1.64. HRMS (ESI) m/z calcd for $C_{26}H_{32}NO_3Si^+$ $(M+H)^+$ 434.2146, found: 434.2151.



3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3v):

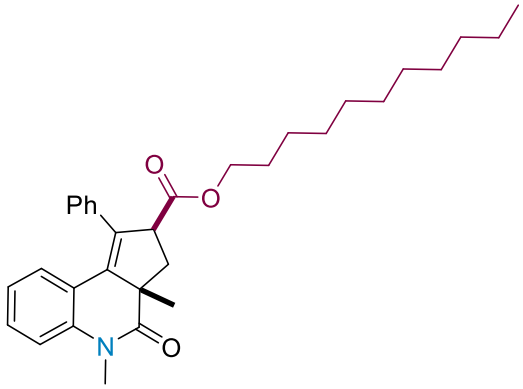
Yield 20%; cis: trans > 20:1; 31 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.19 (m, 4H), 7.14–7.12 (m, 2H), 7.05 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 4.39 (t, *J* = 6.4 Hz, 2H), 3.73 (dd, *J* = 10.8, 1.6

Hz, 1H), 3.35 (s, 3H), 2.93 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.47–2.34 (m, 2H), 2.20 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 174.8, 140.0, 138.3, 136.2, 135.5, 129.1, 128.5, 128.3, 128.0, 127.8, 122.5, 120.8, 115.0, 56.9, 54.8, 54.5, 37.8, 30.0, 25.2. HRMS (ESI) m/z calcd for $C_{31}H_{23}F_{17}NO_3^+$ $(M+H)^+$ 780.1401, found: 780.1396.



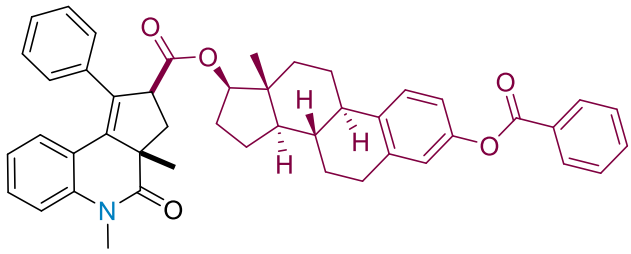
3-methoxy-2-methyl-3-oxopropyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3w):

Yield 79%; cis: trans > 20:1; 68 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.17 (m, 4H), 7.15–7.12 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 4.33–4.13 (m, 2H), 3.7 (dd, *J* = 10.4, 1.6 Hz 1H), 3.58 (d, *J* = 3.6 Hz, 3H), 3.34 (s, 3H), 2.90 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.76 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.20–2.15 (m, 1H), 1.30 (s, 3H), 1.12 (dd, *J* = 7.2, 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 174.90, 174.86, 174.1, 140.0, 138.1, 136.2, 135.7, 129.0, 128.4, 128.3, 128.1, 127.7, 122.5, 120.9, 115.0, 66.2, 60.4, 54.84, 54.80, 54.4, 51.9, 38.9, 38.1, 29.9, 24.9, 21.0, 14.2, 13.84, 13.82. HRMS (ESI) m/z calcd for $C_{26}H_{28}NO_5^+$ $(M+H)^+$ 434.1962, found: 434.1969.



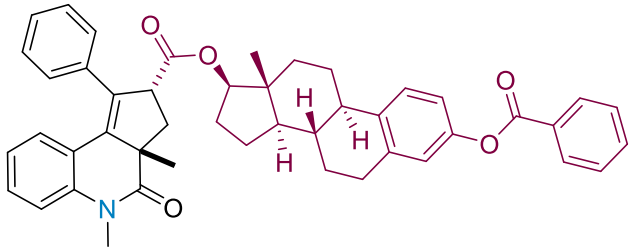
Undecyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-3x):

Yield 18%; cis : trans >20:1; 18 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.19 (m, 3H), 7.17–7.13 (m, 3H), 7.04 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 4.09 (t, *J* = 6.8 Hz, 2H), 3.70 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.34 (s, 3H), 2.91 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.20 (dd, *J* = 14.0, 1.6 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 1H), 1.55 (s, 2H), 1.33 (s, 3H), 1.26–1.21 (m, 5H), 1.18 (s, 10H), 0.81 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.32, 175.28, 140.0, 137.8, 136.4, 136.1, 128.9, 128.41, 128.1, 127.7, 122.5, 121.0, 115.0, 65.2, 55.1, 54.4, 38.1, 31.9, 29.9, 29.6, 29.54, 29.50, 29.3, 29.2, 28.6, 25.9, 25.1, 22.7, 14.1; HRMS (ESI) m/z calcd for $C_{32}H_{42}NO_3^+$ $(M+H)^+$ 488.3159, found: 488.3157.



(8S,9R,13R,14R,17R)-3-(benzoyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4a)

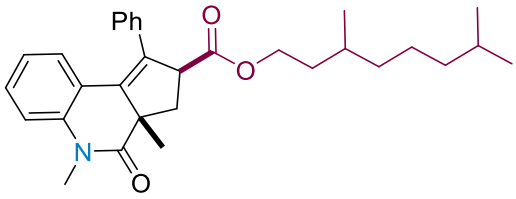
Yield 40%; 55 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 3.2 Hz, 5H), 7.20–7.17 (m, 1H), 7.04 (d, J = 8.4 Hz, 1H), 6.98 (dd, J = 8.4, 2.0 Hz, 1H), 6.93 (d, J = 2.0 Hz, 1H), 6.83 (td, J = 7.6, 2.4 Hz, 1H), 4.80 (dt, J = 26.8, 8.4 Hz, 1H), 3.81 (dt, J = 10.8, 2.0 Hz, 1H), 3.42 (s, 3H), 3.05–2.97 (m,1H), 2.94–2.84 (m, 2H), 2.35–2.30 (m, 2H), 2.28 (dd, J = 4.4, 1.6 Hz, 1H), 1.98–1.75 (m, 3H), 1.66–1.47 (m, 5H), 1.42 (d, J = 4.0 Hz, 4H), 1.38–1.30 (m, 2H), 0.79 (d, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.35, 175.27, 165.4, 148.7, 140.0, 139.9, 138.20, 138.18, 137.80, 137.77, 136.3, 136.2, 136.1, 133.4, 130.1, 129.7, 128.9, 128.5, 128.4, 128.3, 128.1, 128.0, 127.7, 126.45, 126.43, 122.5, 122.49, 121.6, 121.12, 121.10, 118.7, 114.98, 114.97, 83.6, 83.3, 55.3, 55.1, 54.44, 54.38, 49.8, 44.0, 43.1, 42.9, 38.5, 38.3, 38.1, 37.0, 36.9, 30.0, 29.5, 27.6, 27.4, 27.0, 26.1, 26.0, 25.1, 24.9, 23.29, 23.26, 12.13, 12.05; HRMS (ESI) m/z calcd for $C_{46}H_{46}NO_5^+$ $(M+H)^+$ 692.3371, found: 692.3369.



(8S,9R,13R,14R,17R)-3-(benzoyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4a):

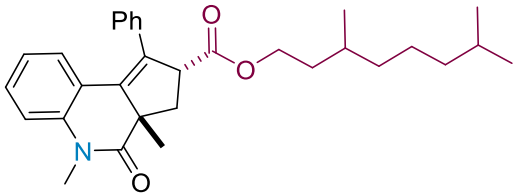
Yield 32%; 44 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.31–7.26 (m, 6H), 7.23 (s, 1H), 7.08 (dd, J = 19.2, 8.4 Hz, 2H), 6.98–6.93 (m, 1H), 6.90 (s, 1H), 6.81 (t, J = 7.6 Hz, 1H), 4.46 (q, J = 8.4 Hz, 1H), 4.28–4.18 (m, 1H), 3.43 (s, 3H), 2.89–2.82 (m, 2H), 2.76 (dt, J = 12.8, 9.6 Hz, 1H), 2.54–2.46 (m, 1H), 2.25–2.11 (m, 2H), 1.99–1.87 (m, 1H), 1.82 (d, J = 11.6 Hz, 1H), 1.69–1.57 (m, 2H), 1.39 (dd, J = 20.8, 8.0 Hz, 3H), 1.25 (s, 3H), 1.13 (dd, J = 16.4, 4.8 Hz, 3H), 0.89 (dd, J = 26.0, 22.0 Hz, 1H), 0.60 (d, J = 10.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.62, 174.58, 173.4, 173.2, 165.4, 148.6, 140.27,140.24, 138.2, 137.9, 136.7, 136.4, 136.3, 136.2, 135.5, 135.3, 133.4, 130.1, 129.7, 128.96, 128.94, 128.5, 128.4, 128.3, 128.2, 127.73, 127.68, 127.53, 127.51, 126.46, 126.43, 122.3, 121.5, 120.7, 120.6, 118.6, 115.21, 115.18, 82.87, 82.86, 53.5, 53.4, 53.3, 53.0, 49.64, 49.59, 43.9, 42.7,

42.6, 39.1, 38.7, 38.1, 36.3, 36.2, 29.9, 29.5, 26.94, 26.91, 25.9, 23.2, 23.14, 23.11, 14.2, 11.9, 11.8. HRMS (ESI) m/z calcd for $C_{46}H46NO_5^+$ $(M+H)^+$ 692.3371, found: 692.3366.



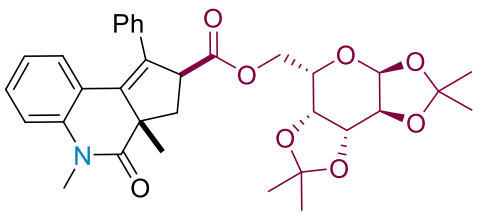
3,7-dimethyloctyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4b):

Yield 38%; 36 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.20 (m, 6H), 7.11 (d, J = 7.6 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.81 (t, J = 7.6 Hz, 1H), 4.28–4.14 (m, 2H), 3.77 (d, J = 10.4 Hz, 1H), 3.41 (s, 3H), 2.98 (dd, J = 14.0, 10.8 Hz, 1H), 2.27 (d, J = 14.4 Hz, 1H), 1.71–1.63 (m,1H), 1.56–1.44 (m, 3H), 1.40 (d, J = 1.6 Hz, 3H), 1.29–1.24 (m, 3H), 1.15–1.11 (m, 3H), 0.89 (dd, J = 6.4, 2.4 Hz, 3H), 0.85 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.27, 175.25, 140.0, 137.8, 136.4, 136.12, 136.09, 128.9, 128.4, 128.1, 127.7, 122.4, 121.0, 114.9, 63.60, 63.57, 55.13, 55.08, 54.41, 54.38, 39.2, 39.1, 38.14, 38.08, 37.11, 37.07, 35.5, 29.9, 29.73, 29.66, 27.9, 25.1, 25.0, 24.6, 22.65, 22.55, 19.41, 19.38. HRMS (ESI) m/z calcd for $C_{31}H_{40}NO_3^+$ $(M+H)^+$ 474.3003, found: 474.3005.



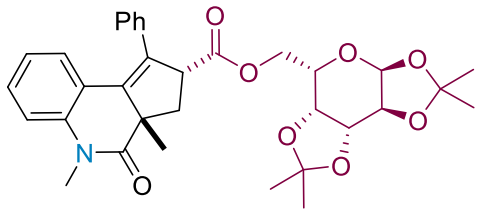
3,7-dimethyloctyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4b):

Yield 39%; 37 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 5H), 7.23 (d, J = 8.0 Hz, 1H), 7.08–7.03 (m 2H), 6.80 (t, J = 7.6 Hz, 1H), 4.23–4.16 (m, 1H), 3.94–3.89 (m, 1H), 3.88–3.80 (m, 1H), 3.42 (s, 3H), 2.77–2.71 (m, 1H), 2.50–2.45 (m, 1H), 1.63–1.42 (m, 2H), 1.34–1.29 (m, 1H), 1.25 (s, 3H), 1.18–1.04 (m, 6H), 1.03–0.95 (m, 1H), 0.86 (d, J = 6.8 Hz, 6H), 0.75–0.69 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 173.4, 140.3, 136.48, 136.45, 136.34, 136.30, 135.4, 129.0, 128.4, 128.1, 127.7, 127.5, 122.3, 120.6, 115.2, 63.2, 53.4, 52.9, 39.2, 38.78, 38.74, 37.03, 36.99, 35.2, 29.9, 29.4, 27.9, 24.4, 23.2, 23.1, 22.7, 22.6, 19.34, 19.26. HRMS (ESI) m/z calcd for $C_{31}H_{40}NO_3^+$ $(M+H)^+$ 474.3003, found: 474.3006.



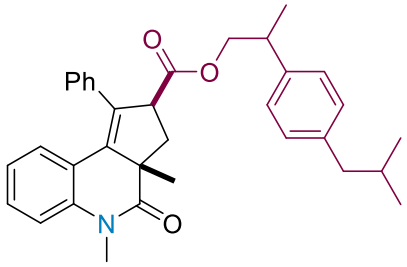
((3aS,5S,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4c):

Yield 45%; 52 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.22 (m, 6H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 5.54 (dd, *J* = 4.8, 2.0 Hz, 1H), 4.66–4.57 (m, 1H), 4.42–4.28 (m, 3H), 4.17 (ddd, *J* = 52.0, 8.0, 2.0 Hz, 1H), 4.09–4.03 (m, 1H), 3.85–3.80 (m, 1H), 3.41 (s, 3H), 3.03–2.93 (m, 1H), 2.37–2.24 (m, 1H), 1.46 (dd, *J* = 12.4, 6.8 Hz, 6H), 1.40 (s, 3H), 1.33 (dd, *J* = 7.2, 4.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.32, 175.27, 175.02, 175.00, 140.0, 138.1, 136.3, 135.85, 135.81, 128.92, 128.89, 128.5, 128.4, 128.2, 128.1, 127.7, 127.6, 122.4, 121.00, 120.97, 114.9, 109.6, 109.5, 108.73, 108.70, 96.3, 96.2, 71.0, 70.8, 70.7, 70.6, 70.4, 70.3, 65.9, 65.6, 64.0, 63.6, 54.9, 54.5, 54.4, 38.3, 38.1, 29.9, 26.1, 26.0, 25.95, 25.91, 25.1, 24.9, 24.5, 24.4. HRMS (ESI) m/z calcd for $C_{33}H_{38}NO_8^+$ $(M+H)^+$ 576.2592, found: 576.2593.



((3aS,5S,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4c):

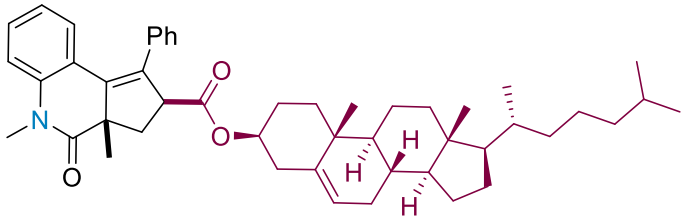
Yield 40%; dr: 1.1:1; 46 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.22 (m, 6H), 7.10–6.99 (m, 2H), 6.82–6.76 (m, 1H), 5.46 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.48 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.41 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.32–4.22 (m, 2H), 4.11 (m, 1H), 4.03–3.91 (m, 1H), 3.75 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.41 (d, *J* = 2.8 Hz, 3H), 2.81–2.68 (m, 1H), 2.53–2.46 (m, 1H), 1.48 (d, *J* = 8.0 Hz, 3H), 1.39 (d, *J* = 7.2 Hz, 3H), 1.32 (s, 3H), 1.29 (s, 2H), 1.27–1.22 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 173.4, 140.3, 136.5, 136.4, 136.34, 136.30, 135.4, 129.0, 128.4, 128.1, 127.7, 127.5, 122.3, 120.6, 115.2, 63.2, 53.4, 52.9, 39.2, 38.8, 38.7, 37.03, 36.99, 35.2, 29.9, 29.4, 27.9, 24.4, 23.2, 23.1, 22.7, 22.6, 19.34, 19.26. HRMS (ESI) m/z calcd for $C_{33}H_{38}NO_8^+$ $(M+H)^+$ 576.2592, found: 576.2592.



2-(4-isobutylphenyl)propyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4d):

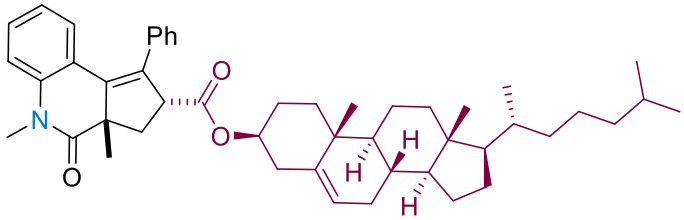
Yield 25%; cis: trans > 20:1; 25 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.15 (m, 4H), 7.10–7.09 (m, *J* = 6.4, 3.2 Hz, 1H), 7.05–6.94 (m, 7H), 6.76–6.72 (m 1H), 4.30–4.19 (m, 1H), 4.12–4.02 (m, 1H), 3.68–3.65 (m, 1H), 3.33 (s, 3H), 3.03–2.98 (m, 1H), 2.90–2.83 (m, 1H), 2.35 (d, *J* = 7.2 Hz, 2H), 2.15–2.07 (m, 1H), 1.78–1.71 (m, 1H), 1.21 (d, *J* = 4.4 Hz, 6H), 0.80 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.26, 175.24, 175.1, 175.0, 140.2, 140.1, 140.0, 137.9, 137.8, 136.3, 136.0, 135.9, 129.2, 128.91, 128.89, 128.40, 128.38, 128.1, 127.7, 127.6, 127.0, 126.9,

122.43, 122.40, 121.1, 121.0, 114.94, 114.91, 70.2, 70.1, 60.4, 55.1, 55.0, 54.39, 54.36, 45.0, 38.5, 38.1, 38.0, 30.1, 29.9, 29.7, 24.9, 24.8, 22.4, 18.24, 18.20, 14.2. HRMS (ESI) m/z calcd for $C_{34}H_{38}NO_3^+$ $(M+H)^+$ 508.2846, found: 508.2849.



(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4e):

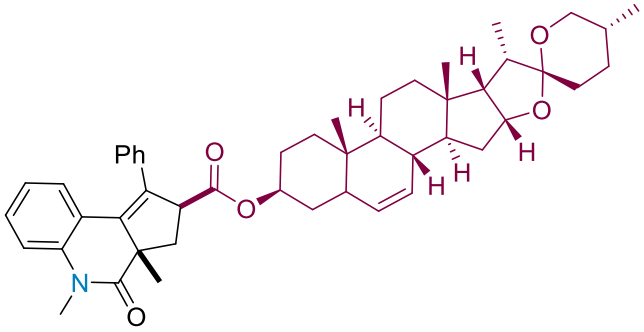
Yield 25%; 35 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.27 (m, 3H), 7.25–7.22 (m, 3H), 7.15–7.11 (m, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.81 (t, J = 7.6 Hz, 1H), 5.40 (d, J = 4.8 Hz, 1H), 4.76–4.65 (m, 1H), 3.74 (dd, J = 10.4, 1.6 Hz, 1H), 3.41 (s, 3H), 2.97 (dd, J = 14.0, 10.8 Hz, 1H), 2.39–2.25 (m, 3H), 2.07–1.99 (m, 2H), 1.90–1.84 (m, 2H), 1.62–1.48 (m, 7H), 1.40 (s, 3H), 1.33 (s, 3H), 1.26 (s, 5H), 1.12 (dd, J = 18.8, 12.8 Hz, 7H), 1.01 (s, 3H), 0.92 (d, J = 6.4 Hz, 3H), 0.87 (d, J = 1.6 Hz, 3H), 0.86 (d, J = 1.6 Hz, 3H), 0.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 174.60, 174.57, 140.0, 139.6, 139.4, 137.80, 137.78, 136.5, 136.3, 128.9, 128.5, 128.4, 128.1, 127.7, 122.9, 122.8, 122.5, 121.1, 115.0, 74.7, 56.7, 56.1, 55.4, 54.4, 50.0, 42.3, 39.7, 39.5, 38.3, 38.0, 37.0, 36.6, 36.2, 35.8, 31.92, 31.86, 31.4, 30.20, 30.17, 30.0, 29.7, 28.3, 28.0, 27.7, 25.2, 24.3, 23.8, 22.8, 22.6, 19.3, 18.7, 11.9; HRMS (ESI) m/z calcd for $C_{48}H_{64}NO_3^+$ $(M+H)^+$ 702.4884, found: 702.4873.



(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4e):

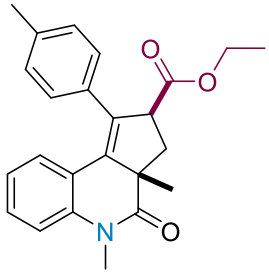
Yield 28%; 39 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.29 (m, 6H), 7.12–7.06 (m, 2H), 6.82 (t, J = 7.6 Hz, 1H), 5.23 (s, 1H), 4.44–4.34 (m, 1H), 4.18 (t, J = 8.8 Hz, 1H), 3.45 (s, 3H), 2.80–2.70 (m, 1H), 2.52–2.47 (m, 1H), 2.05–1.93 (m, 3H), 1.92–1.78 (m, 3H), 1.76–1.69 (m, 2H), 1.61–1.49 (m, 3H), 1.46–1.40 (m, 3H), 1.40–1.32 (m, 5H), 1.27 (s, 4H), 1.18–1.09 (m, 5H), 1.07–1.03 (m, 2H), 1.0–0.96 (m, 2H), 0.93 (s, 4H), 0.91 (s, 1H), 0.89 (d, J = 2.0 Hz, 3H), 0.87 (d, J = 2.0 Hz, 3H), 0.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 172.6, 172.5, 140.3, 139.6, 136.7, 136.1, 135.5, 128.9, 128.4, 128.24, 128.22, 127.7, 127.6, 122.4, 122.3, 120.6, 115.2, 74.1, 56.6, 56.1, 53.3, 53.0, 49.9, 42.3, 39.7, 39.5, 38.8, 38.7, 37.5, 36.8, 36.4, 36.1, 35.8, 31.8, 29.9, 28.2, 28.0, 24.2, 23.8, 23.2, 23.1, 22.8, 22.5, 20.9, 19.2, 18.7, 11.8. HRMS (ESI) m/z calcd for $C_{48}H_{64}NO_3^+$ $(M+H)^+$

702.4884, found: 702.4875.



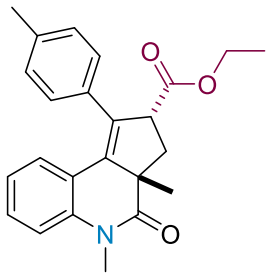
(4S,5'R,6aS,6bS,8aS,8bS,9S,10R,11aR,12aS,12bR)-5',6a,8a,9-tetramethyl-2a,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl(2S,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4f):

Yield 43%; cis: trans > 20:1; 62 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); the dr value cannot be obtained from the ^{1}H NMR; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 3H), 7.23 (dd, *J* = 7.6, 2.0 Hz, 3H), 7.15–7.10 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 5.36 (dd, *J* = 14.8, 10.4 Hz, 2H), 4.78–4.63 (m, 1H), 4.41 (d, *J* = 7.6 Hz, 1H), 3.74 (d, *J* = 9.2 Hz, 1H), 3.47 (d, *J* = 10.0 Hz, 1H), 3.41 (s, 3H), 2.97 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.38–2.21 (m, 3H), 2.06–1.97 (m, 3H), 1.92–1.82 (m, 3H), 1.81–1.69 (m, 3H), 1.64–1.60 (m, 7H), 1.40 (s, 3H), 1.26 (s, 6H), 1.03 (s, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 1H), 0.79 (d, *J* = 4.0 Hz, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 174.6, 156.8, 140.0, 139.6, 139.5, 137.8, 136.4, 136.2, 128.9, 128.5, 128.4, 128.1, 127.7, 122.6, 122.5, 121.0, 115.0, 109.3, 80.8, 74.6, 66.8, 62.0, 56.4, 55.3, 54.4, 49.9, 41.6, 40.2, 39.7, 38.3, 38.0, 36.9, 36.7, 32.0, 31.8, 31.4, 30.3, 29.9, 29.3, 28.8, 27.6, 27.2, 25.2, 22.6, 20.8, 20.4, 19.3, 18.8, 17.1, 16.3, 14.5, 14.1. HRMS (ESI) m/z calcd for $C_{48}H_{60}NO_5^+$ $(M+H)^+$ 730.4466, found: 730.4460.



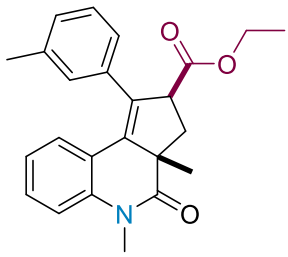
Ethyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-(p-tolyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4g):

Yield 40%; 30 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.21 (m, 1H), 7.15 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.12–7.07 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.84–6.80 (m, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.73 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.41 (s, 3H), 2.96 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.33 (s, 3H), 2.25 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.39 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.35, 175.26, 139.9, 137.4, 137.3, 136.1, 133.3, 129.1, 128.8, 128.2, 128.1, 122.4, 121.2, 114.9, 61.0, 55.1, 54.3, 38.1, 29.9, 25.0, 21.2, 14.2. HRMS (ESI) m/z calcd for $C_{24}H_{26}NO_3^+$ $(M+H)^+$ 376.1907, found: 376.1910.



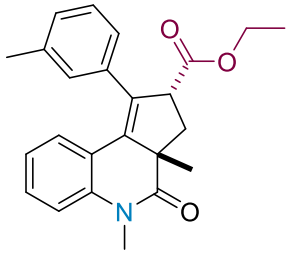
ethyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-(p-tolyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4g):

Yield 33%; 25 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.21 (m, 1H), 7.17–7.11 (m, 3H), 7.09–7.03 (m, 3H), 6.83–6.79 (m, 1H), 4.17 (dd, *J* = 10.0, 7.6 Hz, 1H), 3.97–3.86 (m, 2H), 3.41 (s, 3H), 2.72 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.46 (dd, *J* = 13.2, 7.6 Hz, 1H), 2.33 (s, 3H), 1.23 (s, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 173.4, 140.2, 137.4, 136.6, 135.6, 132.3, 129.1, 128.8, 127.9, 127.5, 122.3, 120.8, 115.2, 60.5, 53.3, 52.8, 38.7, 29.9, 23.1, 21.3, 13.8. HRMS (ESI) m/z calcd for $C_{24}H_{26}NO_3^+$ $(M+H)^+$ 376.1907, found: 376.1907.



Ethyl(2S,3aS)-3a,5-dimethyl-4-oxo-1-(m-tolyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4h):

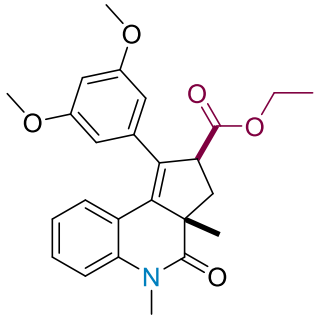
Yield 33%; 25 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.21 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.13–7.08 (m, 2H), 7.04–6.99 (m 3H), 6.81 (td, *J* = 7.6, 0.8 Hz, 1H), 4.27–4.19 (m, 2H), 3.75 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.41 (s, 3H), 2.96 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.29 (s, 3H), 1.40 (s, 3H), 1.28 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 175.2, 139.9, 138.0, 137.6, 136.33, 136.32, 128.85, 128.81, 128.4, 128.3, 128.1, 125.5, 122.4, 121.0, 114.9, 60.9, 55.2, 54.4, 38.0, 29.9, 25.2, 21.4, 14.2. HRMS (ESI) m/z calcd for $C_{24}H_{26}NO_3^+$ $(M+H)^+$ 376.1907, found: 376.1907.



Ethyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-(m-tolyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4h):

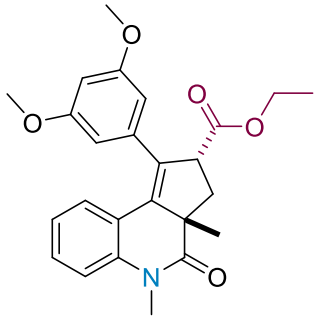
Yield 32%; 24 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.22 (m, 1H), 7.18–7.14 (m, 1H), 7.10–7.03 (m,5H), 6.80 (t, *J* = 7.6 Hz, 1H), 4.17 (dd, *J* = 10.0, 7.6 Hz, 1H), 3.96–3.86 (m, 2H), 3.42 (s, 3H), 2.72 (dd, *J* = 13.2, 10.0 Hz, 1H),

2.46 (dd, J = 13.2, 7.6 Hz, 1H), 2.28 (s, 3H), 1.24 (s, 3H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 173.3, 140.2, 137.9, 136.7, 136.0, 135.3, 128.9, 128.5, 128.4, 128.3, 127.6, 125.2, 122.3, 120.7, 115.2, 60.5, 53.3, 52.8, 38.7, 29.9, 23.2, 21.3, 13.8. HRMS (ESI) m/z calcd for $C_{24}H_{26}NO_3^+$ $(M+H)^+$ 376.1907, found: 376.1907.



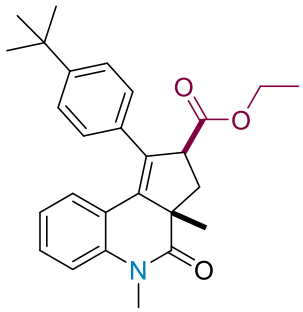
Ethyl(2S,3aS)-1-(3,5-dimethoxyphenyl)-3a,5-dimethyl-4-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4i):

Yield 20%; 17 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.12 (m, 2H), 6.95 (d, J = 8.0 Hz, 1H), 6.78 (t, J = 7.2 Hz, 1H), 6.31–6.30 (m, 3H), 4.16 (q, J = 7.2 Hz, 2H), 3.68 (dd, J = 10.8, 1.6 Hz, 1H), 3.63 (s, 6H), 3.34 (s, 3H), 2.89 (dd, J = 14.0, 10.8 Hz, 1H), 2.18 (dd, J = 14.0, 1.6 Hz, 1H), 1.33 (s, 3H), 1.23 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 175.2, 160.7, 139.9, 138.3, 138.1, 135.9, 129.0, 128.3, 122.5, 120.8, 114.9, 106.4, 100.0, 61.0, 55.3, 55.1, 54.4, 38.1, 29.9, 25.2, 14.2. HRMS (ESI) m/z calcd for $C_{25}H_{28}NO_5^+$ $(M+H)^+$ 422.1962, found: 422.1960.



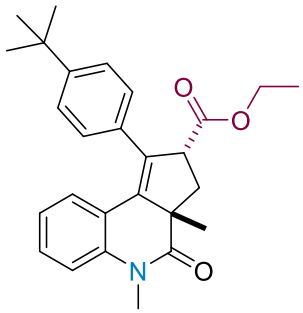
Ethyl(2R,3aS)-1-(3,5-dimethoxyphenyl)-3a,5-dimethyl-4-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4i):

Yield 20%; 17 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.19 (m,2H), 7.03 (d, J = 8.4 Hz, 1H), 6.84 (t, J = 7.6 Hz, 1H), 6.43 (d, J = 2.4 Hz, 2H), 6.36 (t, J = 2.4 Hz, 1H), 4.15 (dd, J = 10.0, 7.6 Hz, 1H), 4.01–3.92 (m, 2H), 3.69 (s, 6H), 3.41 (s, 3H), 2.70 (dd, J = 13.2, 10.0 Hz, 1H), 2.47 (dd, J = 13.2, 7.6 Hz, 1H), 1.24 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 173.3, 160.7, 140.2, 137.2, 136.7, 136.2, 129.1, 127.9, 122.2, 120.4, 115.2, 105.9, 100.4, 60.6, 55.3, 53.4, 52.8, 38.8, 29.9, 23.2, 13.9. HRMS (ESI) m/z calcd for $C_{25}H_{28}NO_5^+$ $(M+H)^+$ 422.1962, found: 422.1964.



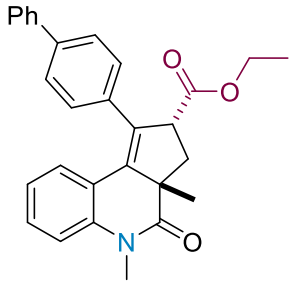
Ethyl(2S,3aS)-1-(4-(tert-butyl)phenyl)-3a,5-dimethyl-4-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4j):

Yield 49%; 41 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.19 (m, 3H), 7.17–7.12 (m, 2H), 7.10 (s, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.79–6.75 (m, 1H), 4.19–4.14 (m, 2H), 3.68 (dd, J = 10.8, 1.6 Hz, 1H), 3.34 (s, 3H), 2.88 (dd, J = 14.0, 10.8 Hz, 1H), 2.18 (dd, J = 14.0, 2.0 Hz, 1H), 1.31 (s, 3H), 1.23 (s, 9H), 1.20 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 175.3, 150.7, 140.0, 137.3, 136.0, 133.2, 128.8, 128.2, 128.0, 125.2, 122.4, 121.3, 114.9, 61.0, 55.0, 54.4, 38.1, 34.5, 31.3, 29.9, 24.9, 14.2. HRMS (ESI) m/z calcd for $C_{27}H_{32}NO_3^+$ $(M+H)^+$ 418.2377, found: 418.2379.



Ethyl(2R,3aS)-1-(4-(tert-butyl)phenyl)-3a,5-dimethyl-4-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4j):

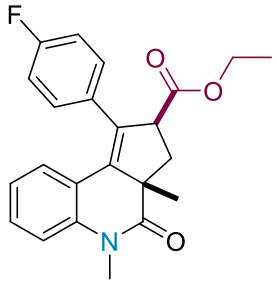
Yield 40%; 33 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.17 (m, 3H), 7.13–7.08 (m, 3H), 6.97 (d, J = 8.0 Hz, 1H), 6.77–6.73 (m, 1H), 4.10 (dd, J = 10.0, 7.6 Hz, 1H), 3.89–3.76 (m, 2H), 3.35 (s, 3H), 2.66 (dd, J = 13.2, 10.0 Hz, 1H), 2.38 (dd, J = 13.2, 7.6 Hz, 1H), 1.23 (s, 9H), 0.76 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 173.4, 150.7, 140.2, 136.6, 135.6, 132.2, 128.8, 127.7, 127.5, 125.2, 122.3, 120.8, 115.1, 60.4, 53.4, 53.0, 38.6, 34.6, 31.3, 29.9, 23.2, 13.7. HRMS (ESI) m/z calcd for $C_{27}H_{32}NO_3^+$ $(M+H)^+$ 418.2377, found: 418.2379.



Ethyl(2S,3aS)-1-([1,1'-biphenyl]-4-yl)-3a,5-dimethyl-4-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4k):

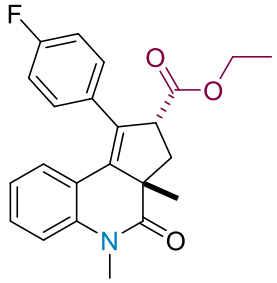
Yield 78%; tans : cis > 20:1; 68 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 3H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 4.15 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.91–3.80 (m, 2H), 3.36 (s, 3H), 2.68 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.42 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.19 (s, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 173.3, 140.4, 140.3, 136.5, 136.1, 134.4, 129.0, 128.8, 128.5, 127.6, 127.4, 126.9, 126.8, 122.3, 120.6, 115.2, 60.6, 53.5, 52.8, 38.7, 29.9, 23.2, 13.8. HRMS (ESI) m/z calcd for $C_{29}H28NO_3^+$ $(M+H)^+$ 438.2064, found: 438.2068.



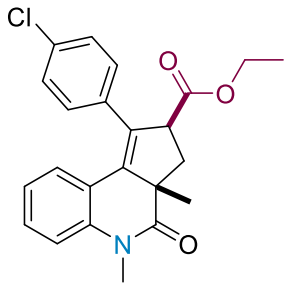
Ethyl(2S,3aS)-1-(4-fluorophenyl)-3a,5-dimethyl-4-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4l):

Yield 38%; 29 mg; yellow solid; column chromatography, silica gel (PE/EA, 15:1); mp 109.5℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.11 (m, 3H), 7.01–6.96 (m, 2H), 6.93–6.89 (m, 2H), 6.76 (t, *J* = 7.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.66 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.34 (s, 3H), 2.90 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.20 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.31 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 175.1, 162.2 (d, *J* = 245 Hz), 140.0, 138.3, 134.9, 133.6 (d, *J* = 8.0 Hz), 132.7 (d, *J* = 4.0 Hz), 130.2 (d, *J* = 8.0 Hz), 129.0, 128.0, 122.5, 120.7, 115.8 (d, *J* = 22Hz), 115.5, 115.3, 115.0, 61.1, 55.0, 54.3, 38.1, 29.9, 25.0, 14.2. HRMS (ESI) m/z calcd for $C_{23}H_{23}FNO_3^+$ $(M+H)^+$ 380.1656, found: 380.1653.



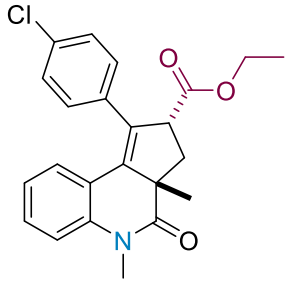
Ethyl(2R,3aS)-1-(4-fluorophenyl)-3a,5-dimethyl-4-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4l):

Yield 38%; 29 mg; yellow solid; column chromatography, silica gel (PE/EA, 15:1); mp 85.7℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.16 (m, 3H), 6.99–6.89 (m, 4H), 6.77–6.73 (m, 1H), 4.09 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.92–3.78 (m, 2H), 3.35 (s, 3H), 2.67 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.40 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.17 (s, 3H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 173.1, 162.2 (d, *J* = 246 Hz),140.3, 136.7, 135.3, 131.3 (d, *J* = 3.0 Hz), 129.9 (d, *J* = 8.0 Hz), 129.1, 127.3, 122.4, 120.3, 115.6, 115.3 (d, *J* = 5.0 Hz), 60.6, 53.3, 52.8, 38.7, 29.9, 23.2, 13.8. HRMS (ESI) m/z calcd for $C_{23}H_{23}FNO_3^+$ $(M+H)^+$ 380.1656, found: 380.1655.



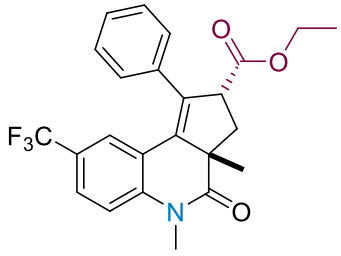
Ethyl(2S,3aS)-1-(4-chlorophenyl)-3a,5-dimethyl-4-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4m):

Yield 30%; 23 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.33 (m, 1H), 7.29–7.27 (m, 2H), 7.20–7.17 (m, 2H), 7.11–7.04 (m, 2H), 6.85 (t, *J* = 7.6 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.74 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.42 (s, 3H), 2.98 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.29 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.39 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.03, 174.98, 140.0, 138.7, 134.9, 134.6, 132.8, 129.8, 129.2, 128.8, 128.7, 128.0, 122.5, 115.0, 61.1, 54.8, 54.4, 38.1, 29.9, 25.0, 14.1. HRMS (ESI) m/z calcd for $C_{23}H_{23}ClNO_3^+$ $(M+H)^+$ 396.1361, found: 396.1361.



Ethyl(2R,3aS)-1-(4-chlorophenyl)-3a,5-dimethyl-4-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4m):

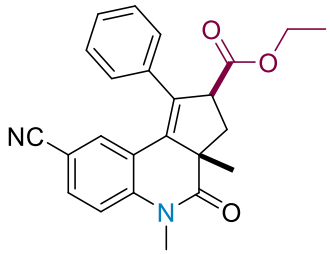
Yield 40%; 32 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.28 (m, 3H), 7.25–7.23 (m, 2H), 7.09–7.06 (m, 2H), 6.88–6.84 (m, 1H), 4.18 (dd, *J* = 10.0, 7.6 Hz, 1H), 4.00–3.90 (m, 2H), 3.44 (s, 3H), 2.75 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.50 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.27 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 173.0, 140.3, 137.3, 135.0, 133.9, 133.5, 129.5, 129.3, 128.7, 127.4, 122.4, 120.2, 115.3, 60.7, 53.5, 52.6, 38.7, 29.9, 23.2, 13.9. HRMS (ESI) m/z calcd for $C_{23}H_{23}ClNO_3^+$ $(M+H)^+$ 396.1361, found: 396.1361.



Ethyl(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-8-(trifluoromethyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4n):

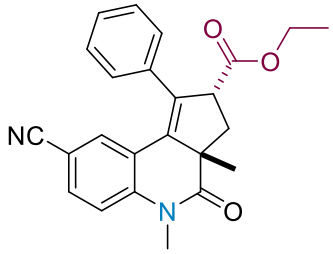
Yield 70%; trans : cis > 20:1; 60 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.33–7.31 (m, 4H), 7.27–7.25 (m,2H), 7.14 (d, *J* = 8.8 Hz, 1H), 4.24 (dd, *J* = 9.6, 7.6 Hz, 1H), 4.02–3.87 (m, 2H), 3.47 (s, 3H), 2.80 (dd,

J = 13.2, 10.0 Hz, 1H), 2.52 (dd, J = 13.2, 7.6 Hz, 1H), 1.29 (s, 3H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 172.9, 142.8, 138.7, 134.7, 134.4, 128.6, 128.3, 127.8, 125.7 (q , J = 4.0 Hz), 124.7 (q, J = 4.0 Hz), 124.5–122.3(m), 120.8, 115.2, 60.7, 53.2, 52.8, 38.6, 30.0, 23.4, 13.8. HRMS (ESI) m/z calcd for $C_{24}H_{23}F_3NO_3^+$ $(M+H)^+$ 430.1625, found: 430.1624.



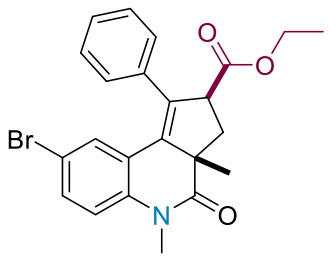
ethyl(2R,3aS)-8-cyano-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4o):

Yield 33%; 25 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 8.4, 1.6 Hz, 1H), 7.27–7.26 (m, 4H), 7.11–7.08 (m, 2H), 7.03 (d, J = 8.8 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.72 (dd, J = 10.4, 1.6 Hz, 1H), 3.35 (s, 3H), 2.91 (dd, J = 14.4, 10.8 Hz, 1H), 2.23 (dd, J = 14.4, 1.6 Hz, 1H), 1.33 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 174.5, 143.3, 139.3, 135.3, 135.2, 132.7, 131.6, 128.8, 128.6, 128.1, 121.8, 118.4, 115.5, 105.8, 61.2, 55.2, 54.1, 38.0, 30.1, 25.2, 14.1. HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2O_3^+$ $(M+H)^+$ 387.1703, found: 387.1702.



Ethyl(2R,3aS)-8-cyano-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4o):

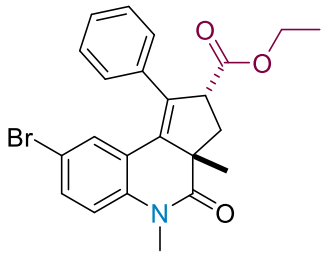
Yield 34%; 26 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 8.8, 1.6 Hz, 1H), 7.36–7.33 (m, 4H), 7.25–7.22 (m, 2H), 7.13 (d, J = 8.8 Hz, 1H), 4.25–4.21 (m, 1H), 3.98–3.88 (m, 2H), 3.46 (s, 3H), 2.79 (dd, J = 13.2, 9.6 Hz, 1H), 2.51 (dd, J = 13.2, 7.6 Hz, 1H), 1.27 (s, 3H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 172.7, 143.6, 139.6, 134.1, 133.7, 132.7, 131.1, 128.8, 128.6, 127.8, 121.4, 118.4, 115.7, 105.7, 60.7, 53.1, 53.0, 38.5, 30.1, 23.4, 13.8. HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2O_3^+$ $(M+H)^+$ 387.1703, found: 387.1703.



Ethyl(2S,3aS)-8-bromo-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-

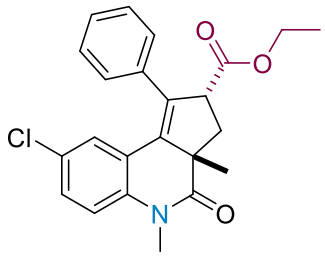
cyclopenta[c]quinoline-2-carboxylate (*cis*-4p):

Yield 30%; 26 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.24 (m, 4H), 7.14–7.12 (m, 3H), 6.82 (d, *J* = 8.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.70 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.31 (s, 3H), 2.89 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.20 (dd, *J* = 14.4, 1.6 Hz, 1H), 1.32 (s, 3H), 1.22 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 174.8, 139.1, 137.8, 136.5, 135.6, 131.6, 130.6, 128.6, 128.22, 128.15, 122.8, 116.5, 115.2, 61.1, 55.1, 54.2, 38.0, 30.0, 25.1, 14.2. HRMS (ESI) m/z calcd for $C_{23}H_{23}BrNO_3^+$ $(M+H)^+$ 440.0856, found: 440.0856.



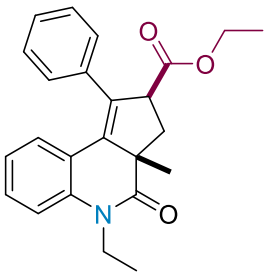
Ethyl(2R,3aS)-8-bromo-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4p):

Yield 33%; 29 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.23 (m, 3H), 7.22–7.17 (m, 3H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 4.13 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.89–3.79 (m , 2H), 3.32 (s, 3H), 2.67 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.40 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.18 (s, 3H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 173.0, 139.3, 138.2, 134.9, 134.6, 131.6, 130.1, 128.6, 128.2, 127.9, 122.5, 116.8, 115.2, 60.6, 53.2, 52.8, 38.6, 30.0, 23.3, 13.8. HRMS (ESI) m/z calcd for $C_{23}H_{23}BrNO_3^+$ $(M+H)^+$ 440.0856, found: 440.0856.



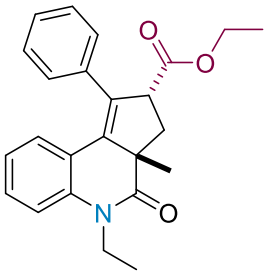
Ethyl(2R,3aS)-8-chloro-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4q):

Yield 62%; trans: cis >20:1; 49 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.22 (m,3H), 7.20–7.18 (m, 2H), 7.13 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.94–6.89 (m, 2H), 4.12 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.89–3.79 (m, 2H), 3.33 (s, 3H), 2.66 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.40 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.18 (s, 3H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 173.0, 138.8, 138.1, 135.0, 134.6, 128.7, 128.6, 128.2, 127.9, 127.7, 127.1, 122.1, 116.5, 60.6, 53.2, 52.8, 38.6, 30.0, 23.2, 13.8. HRMS (ESI) m/z calcd for $C_{23}H_{23}ClNO_3^+$ $(M+H)^+$ 396.1361, found: 396.1364.



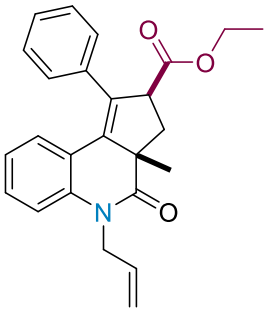
Ethyl(2S,3aS)-5-ethyl-3a-methyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4r):

Yield 26%; 20 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.19 (m, 3H), 7.18–7.13 (m, 3H), 7.04 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 4.19–4.07 (m, 3H), 3.84–3.75 (m, 1H), 3.69 (dd, *J* = 10.8, 2.0 Hz, 1H), 2.92 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.17 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.32 (s, 3H), 1.23–1.21 (m, 3H), 1.20–1.18 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 174.7, 138.9, 138.0, 136.4, 135.8, 128.9, 128.4, 127.7, 122.2, 121.1, 114.7, 61.0, 55.0, 54.2, 37.9, 37.6, 25.0, 14.2, 12.6. HRMS (ESI) m/z calcd for $C_{24}H_{26}NO_3^+$ $(M+H)^+$ 376.1907, found: 376.1907.



Ethyl(2R,3aS)-5-ethyl-3a-methyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4r):

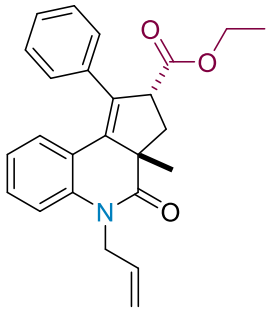
Yield 30%; 23 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.14 (m, 6H), 6.99 (t, *J* = 8.0 Hz, 2H), 6.71 (t, *J* = 7.6 Hz, 1H), 4.16–4.09 (m, 2H), 3.89–3.77 (m, 3H), 2.67 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.39 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.22–1.18 (m, 6H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 173.3, 139.2, 136.4, 136.3, 135.4, 129.0, 128.4, 128.1, 127.8, 127.7, 122.1, 120.7, 115.0, 60.5, 53.2, 52.8, 38.5, 37.6, 29.7, 23.0, 13.8, 12.6. HRMS (ESI) m/z calcd for $C_{24}H_{26}NO_3^+$ $(M+H)^+$ 376.1907, found: 376.1906.



Ethyl(2S,3aS)-5-allyl-3a-methyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4s):

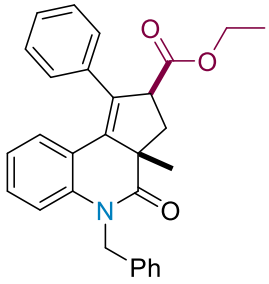
Yield 10%; 8 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.19 (m, 3H), 7.16–7.10 (m, 3H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 5.89–5.80 (m, 1H), 5.11 (t, *J* = 15.2 Hz, 2H), 4.89–4.84 (m, 1H), 4.20–4.14

(m, 3H), 3.70 (dd, *J* = 10.4, 1.6 Hz, 1H), 2.94 (dd, *J* = 14.0, 10.8 Hz, 1H), 2.19 (dd, *J* = 14.4, 1.6 Hz, 1H), 1.38 (s, 3H), 1.20 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 174.9, 139.3, 137.9, 136.4, 136.2, 132.4, 128.8, 128.43, 128.40, 128.2, 127.7, 122.5, 121.1, 116.0, 115.6, 61.0, 55.1, 54.4, 45.2, 37.9, 25.2, 14.2. HRMS (ESI) m/z calcd for $C_{25}H_{26}NO_3^+$ $(M+H)^+$ 388.1907, found: 388.1905.



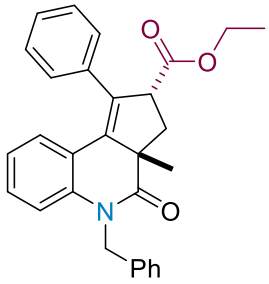
Ethyl(2R,3aS)-5-allyl-3a-methyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4s):

Yield 10%; 8 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.19 (m, 5H), 7.15–7.10 (m, 1H), 7.01–6.94 (m, 2H), 6.71 (t, *J* = 7.6 Hz, 1H), 5.91–5.82 (m, 1H), 5.16–5.08 (m, 2H), 4.94–4.88 (m, 1H), 4.18–4.11 (m, 2H), 3.89–3.78 (m, 2H), 2.70 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.40 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.23 (s, 3H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 173.2, 139.6, 136.6, 136.2, 135.4, 132.5, 128.9, 128.4, 128.1, 127.7, 127.6, 122.3, 120.6, 116.0, 115.8, 60.5, 53.4, 52.9, 45.2, 38.4, 23.3, 13.8. HRMS (ESI) m/z calcd for $C_{25}H_{26}NO_3^+$ $(M+H)^+$ 388.1907, found: 388.1906.



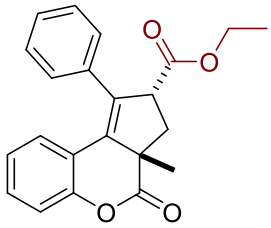
Ethyl(2S,3aS)-5-benzyl-3a-methyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*cis*-4t):

Yield 17%; 15 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.30 (m, 5H), 7.29 –7.25 (m, 5H), 7.15–7.09 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.82–6.76 (m, 1H), 5.66 (d, *J* = 16.4 Hz, 1H), 4.81 (d, *J* = 16.4 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.84 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.10 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.34 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.58 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 175.2, 139.4, 137.8, 137.1, 136.4, 136.3, 128.9, 128.8, 128.45, 128.40, 128.2, 127.8, 127.1, 126.1, 122.6, 121.1, 115.8, 61.0, 55.1, 54.5, 46.6, 37.9, 25.3, 14.2. HRMS (ESI) m/z calcd for $C_{29}H_{28}NO_3^+$ $(M+H)^+$ 438.2064, found: 438.2068.



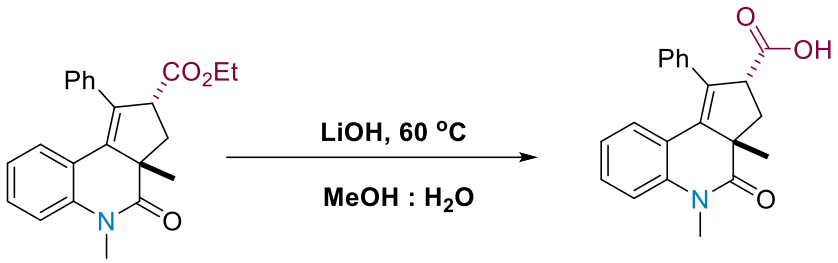
Ethyl(2R,3aS)-5-benzyl-3a-methyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (*trans*-4t):

Yield 18%; 16 mg; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 6H), 7.29–7.26 (m, 4H), 7.12–7.09 (m, 2H), 6.94 (d, J = 8.0 Hz, 1H), 6.79–6.76 (m,1H), 5.71 (d, J = 16.4 Hz, 1H), 4.78 (d, J = 16.4 Hz, 1H), 4.26 (dd, J = 9.6, 8.0 Hz, 1H), 4.00–3.90 (m, 2H), 2.87 (dd, J = 13.2, 9.6 Hz, 1H), 2.55 (dd, J = 13.2, 7.6 Hz, 1H), 1.42 (s, 3H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 173.3, 139.7, 137.2, 136.8, 136.2, 135.4, 129.0, 128.8, 128.5, 128.2, 127.8, 127.6, 127.1, 126.2, 122.5, 120.8, 116.1, 60.6, 53.6, 53.0, 46.6, 38.5, 23.5, 13.9. HRMS (ESI) m/z calcd for $C_{29}H_{28}NO_3^+$ $(M+H)^+$ 438.2064, found: 438.2070.



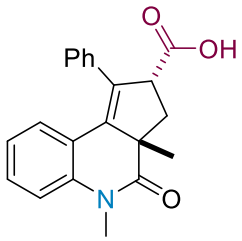
Ethyl (2R,3aS)-3a-methyl-4-oxo-1-phenyl-2,3,3a,4-tetrahydrocyclopenta[c]chromene-2-carboxylate (*trans*-4u):

Yield 27%; 19 mg; trans: cis >20:1; yellow oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.27 (m, 6H), 7.14–7.05 (m, 2H), 6.89 (t, J = 7.6 Hz, 1H), 4.20 (dd, J = 9.6, 8.0 Hz, 1H), 3.99–3.82 (m, 2H), 2.84 (dd, J = 13.2, 10.0 Hz, 1H), 2.51 (dd, J = 13.2, 7.6 Hz, 1H), 1.37 (s, 3H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 172.3, 151.6, 138.0, 134.6, 133.0, 129.9, 128.6, 128.2, 127.9, 127.0, 124.0, 118.3, 117.0, 60.8, 52.9, 52.3, 37.8, 23.3, 13.8. HRMS (ESI) m/z calcd for $C_{22}H_{20}O_4Na^+$ $(M+Na)^+$ 371.1254, found: 371.1258.



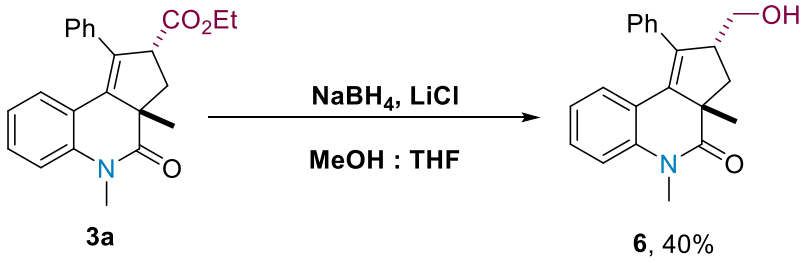
3a **5**, 79%

A reaction mixture of **3a** (1.0 mmol, 361 mg), LiOH (5.0 mmol, 120 mg) in MeOH/H_2O (5 mL, v: v = 1:1) stirring at 60 °C for 6 h. After the reaction is completed, the water was then added to the mixture and adjusted the pH to 1-2 by 1M HCl. The organic layer was extracted with DCM three times. The product was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product **5** in 79% yield.



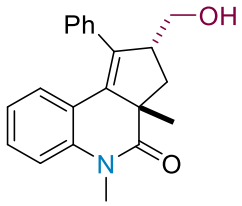
(2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylic acid (5):

Yield 79 %; 263 mg; white oil; column chromatography, silica gel (DCM/MeOH, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.16 (d, *J* = 13.2 Hz, 6H), 6.96 (t, *J* = 6.8 Hz, 2H), 6.72 (t, *J* = 7.6 Hz, 1H), 4.07 (t, *J* = 8.8 Hz, 1H), 3.30 (s, 3H), 2.66–2.54 (m, 1H), 2.33 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 174.7, 140.0, 136.6, 135.9, 134.9, 129.0, 128.5, 127.9, 127.8, 127.4, 122.4, 120.5, 115.3, 53.4, 52.4, 38.6, 29.9, 23.1. HRMS (ESI) m/z calcd for $C_{21}H_{20}NO_3^+$ $(M+H)^+$ 334.1438, found: 334.1445.



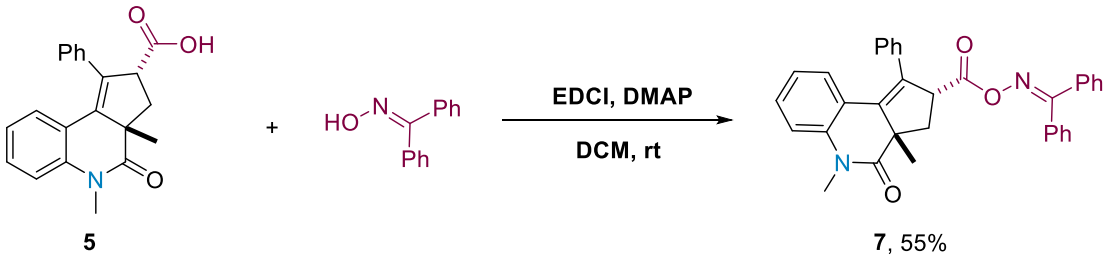
3a **6**, 40%

A reaction mixture of **3a** (1.0 mmol, 361 mg), $NaBH_4$ (10.0 mmol, 380 mg) and LiCl (2.0 mmol, 84 mg) in MeOH/THF (5 mL, v:v = 1:1) stirring at rt for 24 h. After the reaction is completed, the water was then added to the mixture, and the organic layer was extracted with DCM three times. The product was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product **6** in 40% yield.

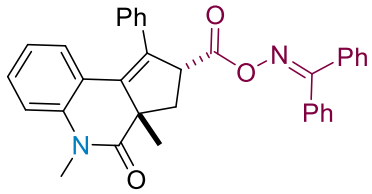


(2R,3aS)-2-(hydroxymethyl)-3a,5-dimethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[c]quinolin-4-one (6):

Yield 40 %; 128 mg; white solid; column chromatography, silica gel (PE/EA, 2:1); mp 137–139°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.31 (m, 3H), 7.24 (dd, *J* = 14.8, 7.2 Hz, 3H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 3.67–3.60 (m, 1H), 3.59–3.50 (m, 2H), 3.43 (s, 3H), 2.45 (dd, *J* = 13.2, 8.8 Hz, 1H), 2.35 (dd, *J* = 13.2, 7.2 Hz, 1H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 140.1, 139.0, 136.1, 135.7, 128.8, 128.4, 128.1, 127.6, 127.5, 122.2, 121.0, 115.1, 64.0, 52.6, 49.0, 37.2, 29.9, 23.7. HRMS (ESI) m/z calcd for $C_{21}H_{22}NO_2^+$ $(M+H)^+$ 320.1645, found: 320.1647.

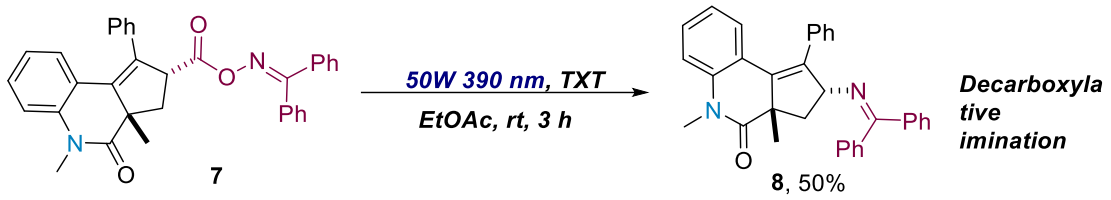


A reaction mixture of **5** (0.2 mmol, 37 mg), EDCI (0.5 mmol, 96 mg), DMAP (0.04 mmol, 5 mg), diphenylmethanone oxime (0.2 mmol, 40 mg) in dry DCM (2 mL) stirring at rt for 24 h. After the reaction is completed, the residue concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product **7** in 55% yield.

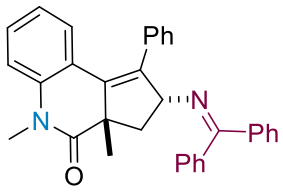


(2R,3aS)-2-((((diphenylmethylene)amino)oxy)carbonyl)-3a,5-dimethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[c]quinolin-4-one (7):

Yield 55 %; 56 mg; Notable: this compound is extremely difficult to dissolve; white solid; column chromatography, silica gel (PE/EA, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$+CF_3CO_2D) δ 7.57–7.44 (m, 4H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.36–7.27 (m, 6H), 7.19 (t, *J* = 7.6 Hz, 3H), 7.13–7.08 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 4.31–4.20 (m, 1H), 3.51 (s, 3H), 2.76–2.66 (m, 1H), 2.52 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.27 (s, 3H). ^{13}C NMR $CDCl_3$+CF_3CO_2D) δ 161.8–160.5 (m), 138.8–138.7 (m), 136.2–135.2 (m), 133.9–133.79 (m), 133.4–133.1(m), 132.0–131.6 (m), 130.4–130.2 (m), 129.7, 129.4, 129.2, 128.5, 127.9, 127.6, 127.3, 124.3–124.2(m), 120.7–120.6 (m), 118.53–118.5 (m), 115.71–115.68 (m), 112.8, 111.0, 53.8, 51.8, 38.52–38.2 (m), 23.0–22.6 (m) HRMS (ESI) m/z calcd for $C_{34}H_{28}N_2NaO_3^+$ $(M+Na)^+$ 535.1992, found: 535.1996.

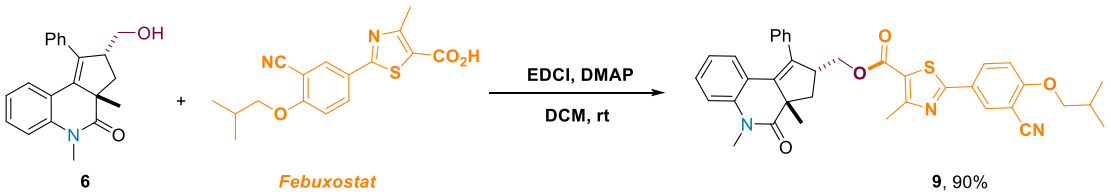


A sealed tube was charged with **7** (0.1 mmol, 51 mg), TXT (0.01 mmol, 2 mg), EtOAc (2 mL). The reactions exposed to 50W 390 nm kessil LED irradiation at room temperature in N_2 with stirring for 3 h till almost completed conversion of the substrates by TLC analysis. After completion of the reaction, the mixture was extracted with ethyl acetate, the organic layer was combined concentrated to yield the crude product, which was further purified by flash chromatography (petroleum ether/ethyl acetate = 15:1, V/V) to give the product **8** in 50% yield.

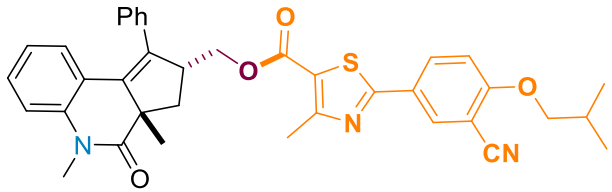


(2R,3aS)-2-((diphenylmethylene)amino)-3a,5-dimethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[c]quinolin-4-one (8):

Yield 50%; 24 mg; white oil; column chromatography, silica gel (PE/EA, 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 6.8 Hz, 3H), 7.29–7.09 (m, 14H), 7.06 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 5.01 (t, J = 7.6 Hz, 1H), 3.43 (s, 3H), 2.81–2.71 (m, 1H), 2.42 (dd, J = 13.2, 7.2 Hz, 1H), 1.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 168.5, 141.3, 140.0, 137.03, 136.99, 136.97, 136.4, 136.0, 135.8, 134.6, 129.8, 128.6, 128.5, 128.2, 128.0, 127.8, 127.4, 127.2, 122.2, 115.1, 67.9, 52.7, 42.9, 29.8, 24.4. HRMS (ESI) m/z calcd for $C_{33}H_{29}N_2O^+$ $(M+H)^+$ 469.2274, found: 469.2281.



A reaction mixture of **6** (0.1 mmol, 32 mg), EDCI (0.25 mmol, 50 mg), DMAP (0.04 mmol, 5 mg), Febuxostat (0.1 mmol, 32 mg) in dry DCM (2 mL) stirring at rt for 24 h. After the reaction is completed, the residue concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product **9** in 90% yield.

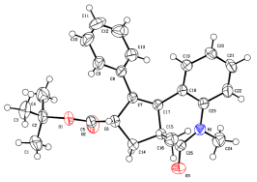


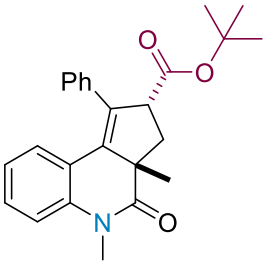
((2R,3aS)-3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinolin-2-yl)methyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (9):

Yield 90%; 56 mg; white oil; column chromatography, silica gel (PE/EA, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 2.0 Hz, 1H), 8.00 (dd, J = 8.8, 2.0 Hz, 1H), 7.25–7.13 (m, 6H), 6.99 (d, J =

8.4 Hz, 1H), 6.94 (d, J = 8.8 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.72 (t, J = 7.6 Hz, 1H), 4.32 (dd, J = 10.8, 4.0 Hz, 1H), 3.94 (dd, J = 10.8, 6.8 Hz, 1H), 3.83 (d, J = 6.4 Hz, 2H), 3.70 (s, 1H), 3.36 (s, 3H), 2.60 (s, 3H), 2.39 (dd, J = 7.6, 6.4 Hz, 2H), 2.20–2.07 (m, 1H), 1.21 (s, 3H), 1.02 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 167.2, 162.4, 161.7, 161.0, 140.0, 138.1, 135.8, 135.4, 132.5, 132.0, 128.8, 128.7, 128.1, 127.7, 127.5, 125.9, 122.3, 121.8, 120.8, 115.3, 115.1, 112.5, 102.8, 75.6, 66.8, 52.9, 45.9, 37.9, 29.9, 28.1, 24.0, 19.0, 17.4. HRMS (ESI) m/z calcd for $C_{37}H_{36}N_3O_4S^+$ $(M+H)^+$ 618.2421, found: 618.2419.

8. Crystallographic data and molecular structure of 3b





***trans*-3b**

Figure S3. X-ray crystal structure of **3b**, thermal ellipsoids shown at 50% probability level. Sample preparation: 20 mg of **3b** was dissolved in 5 mL DCM at room temperature for slow evaporation about a week. The crystals were mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker D8 VENTURE diffractometer with Mo Kα radiation (1.54178 Å) at room temperature. Crystal Data for Compound **3b**: CCDC: 2520249 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic.

Datablock: 1

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Bond precision:   C-C = 0.0022 A          Wavelength=1.54178

Cell:             a=10.3209(2)     b=11.6795(2)       c=17.3932(3)
                  alpha=90         beta=97.822(1)     gamma=90
Temperature:      273 K

                 Calculated                Reported
Volume           2077.12(7)                2077.12(6)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2yn
Moiety formula   C25 H27 N O3              C25 H27 N O3
Sum formula      C25 H27 N O3              C25 H27 N O3
Mr               389.48                    389.47
Dx,g cm-3        1.245                     1.245
Z                4                         4
Mu (mm-1)        0.645                     0.645
F000             832.0                     832.0
F000'            834.41
h,k,lmax         12,14,20                  12,14,20
Nref             3822                      3740
Tmin,Tmax        0.862,0.873               0.365,0.753
Tmin'            0.862

Correction method= # Reported T Limits: Tmin=0.365 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.979           Theta(max)= 68.421

R(reflections)= 0.0562( 3467)                wR2(reflections)=
                                             0.1464( 3740)
S = 1.063                 Npar= 267
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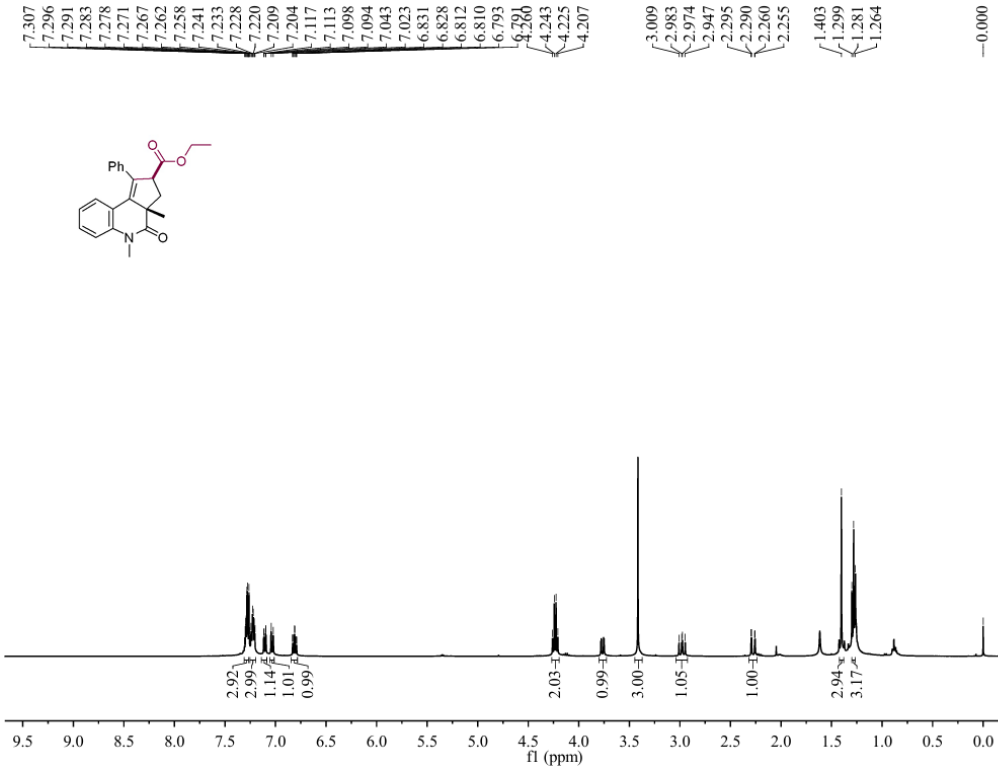
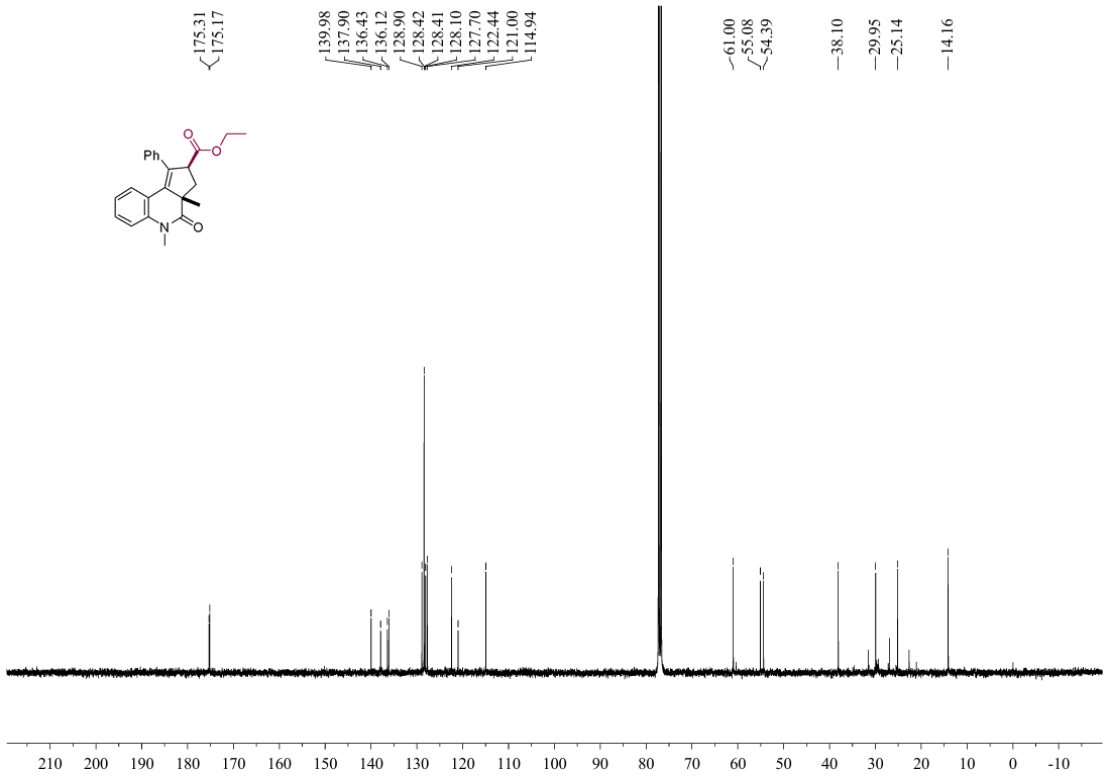
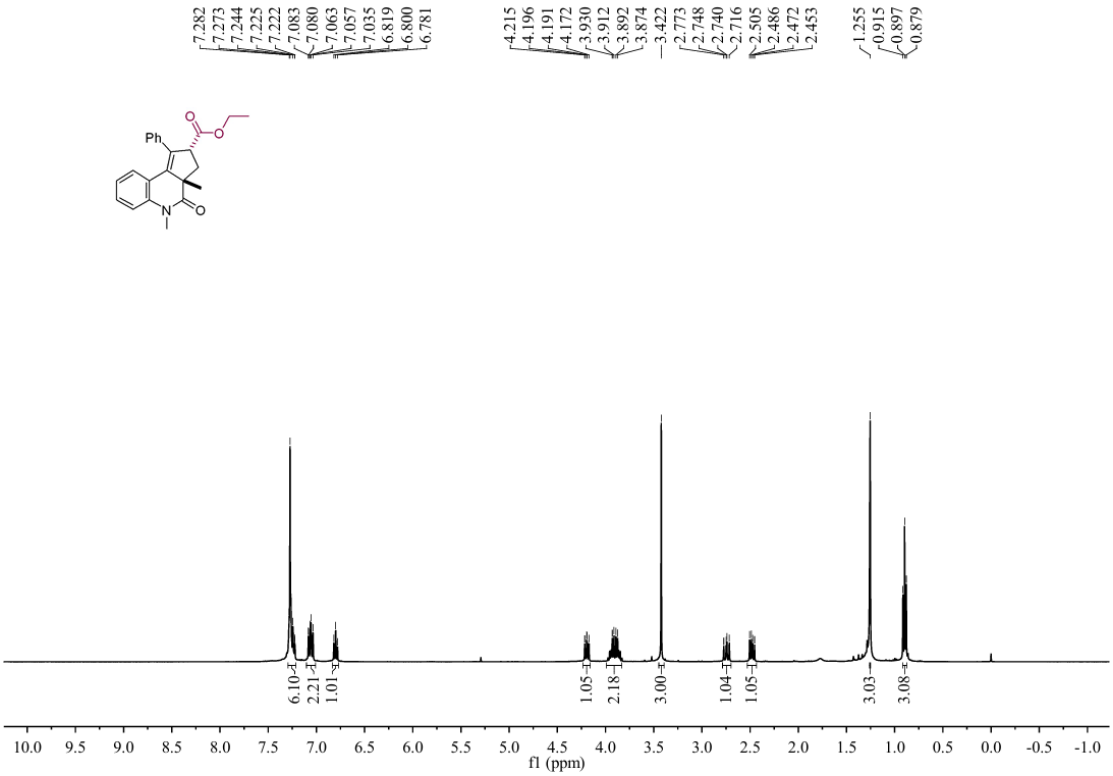
9. ^{1}H, ^{13}C NMR spectra of compounds



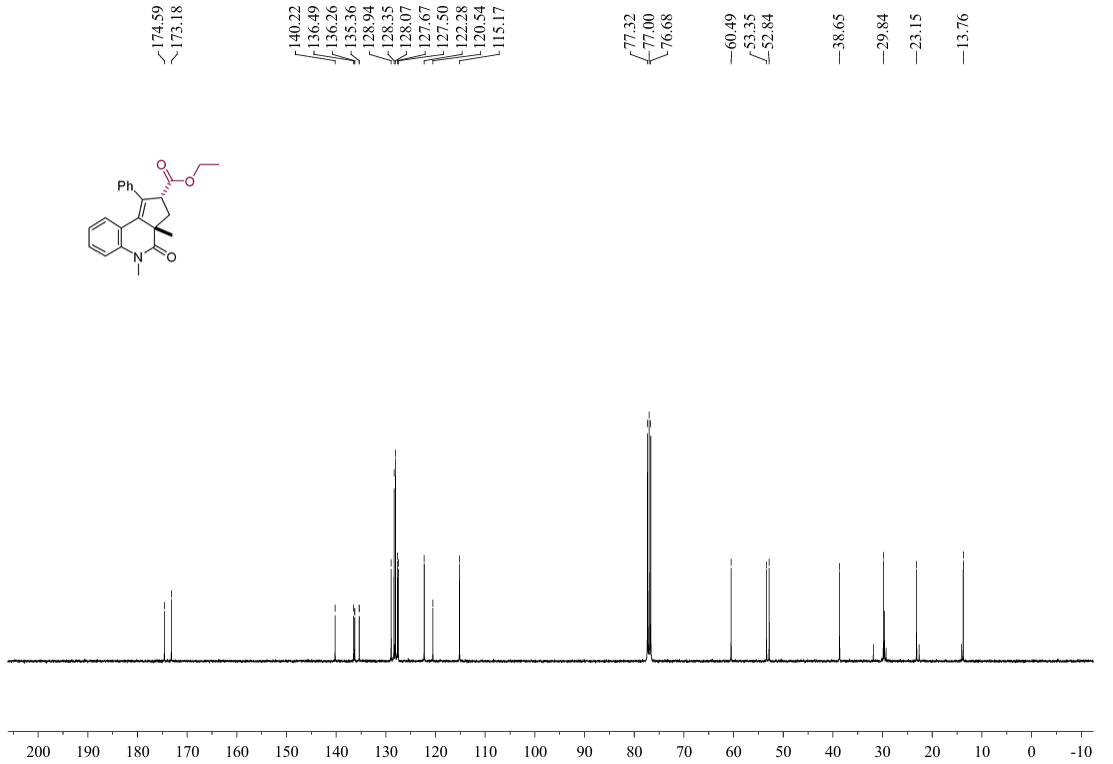
^{1}H NMR Spectrum of Compound ***cis*-3a** (400 MHz, $CDCl_3$)



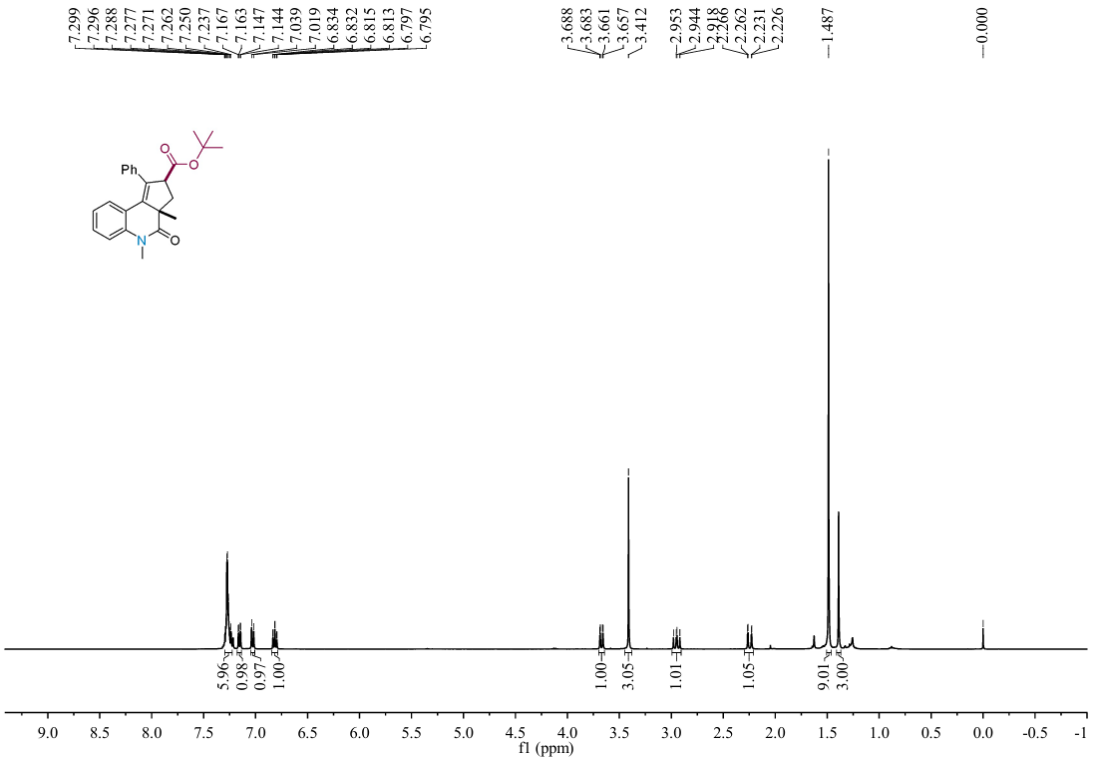
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-3a** (100 MHz, $CDCl_3$)



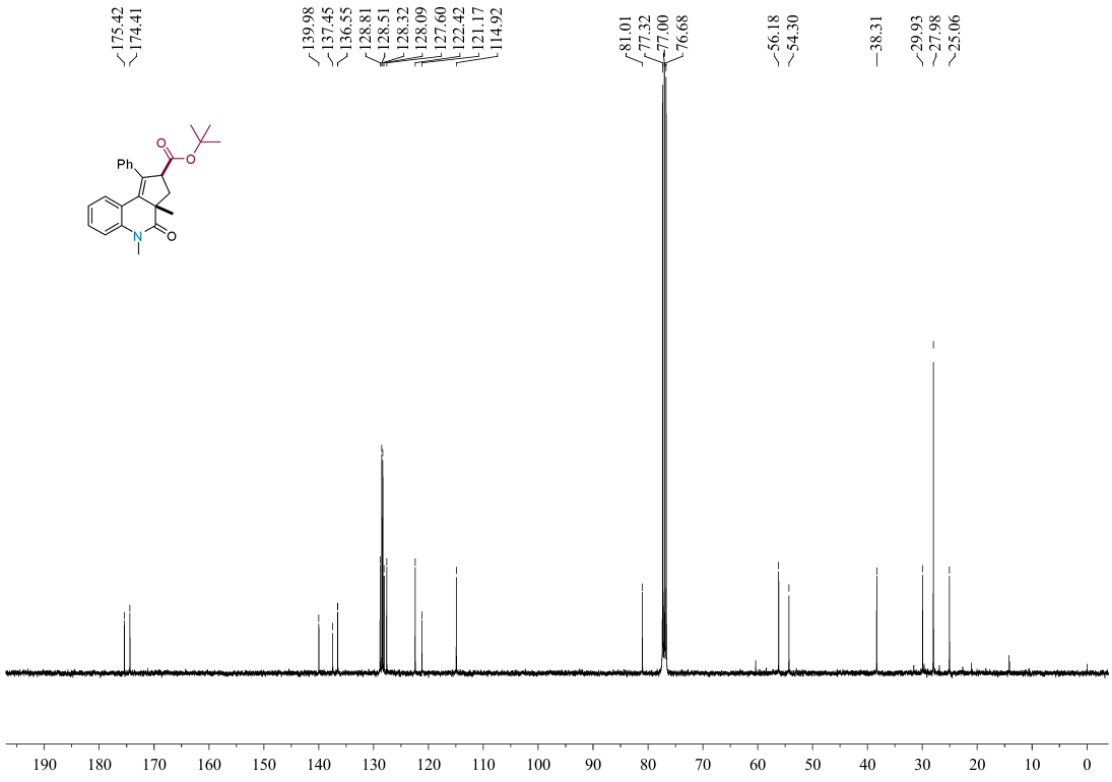
^{1}H NMR Spectrum of Compound ***trans*-3a** (400 MHz, $CDCl_3$)



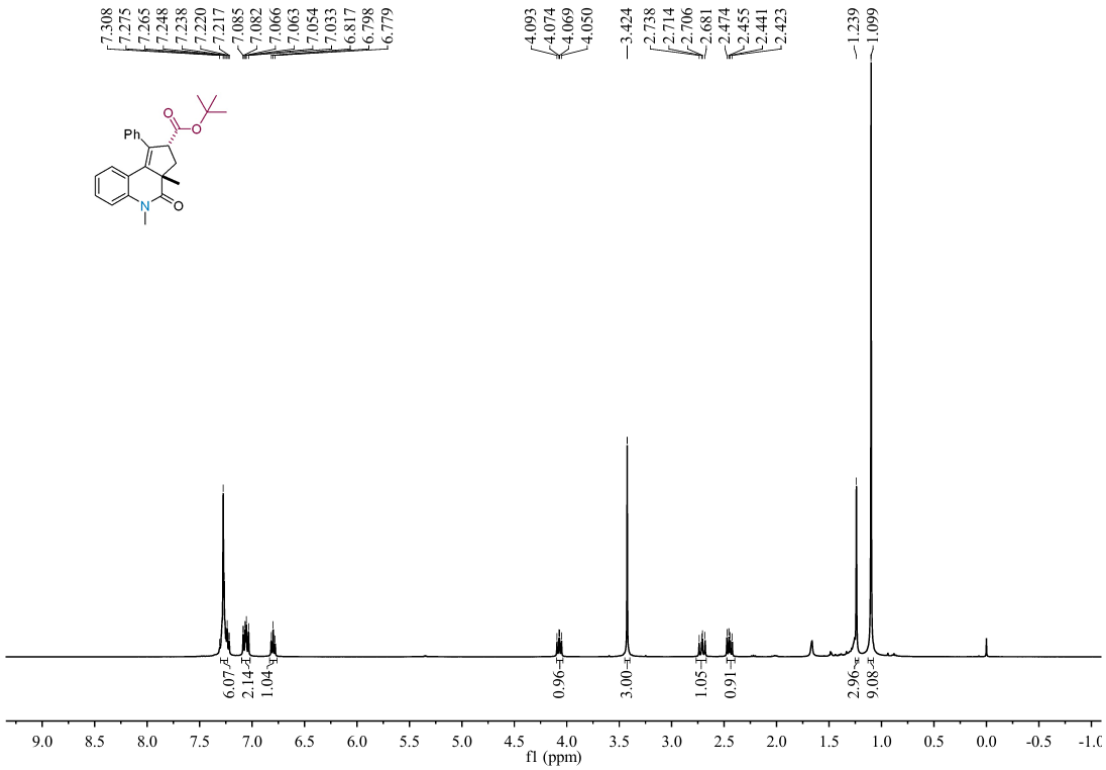
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3a** (100 MHz, $CDCl_3$)



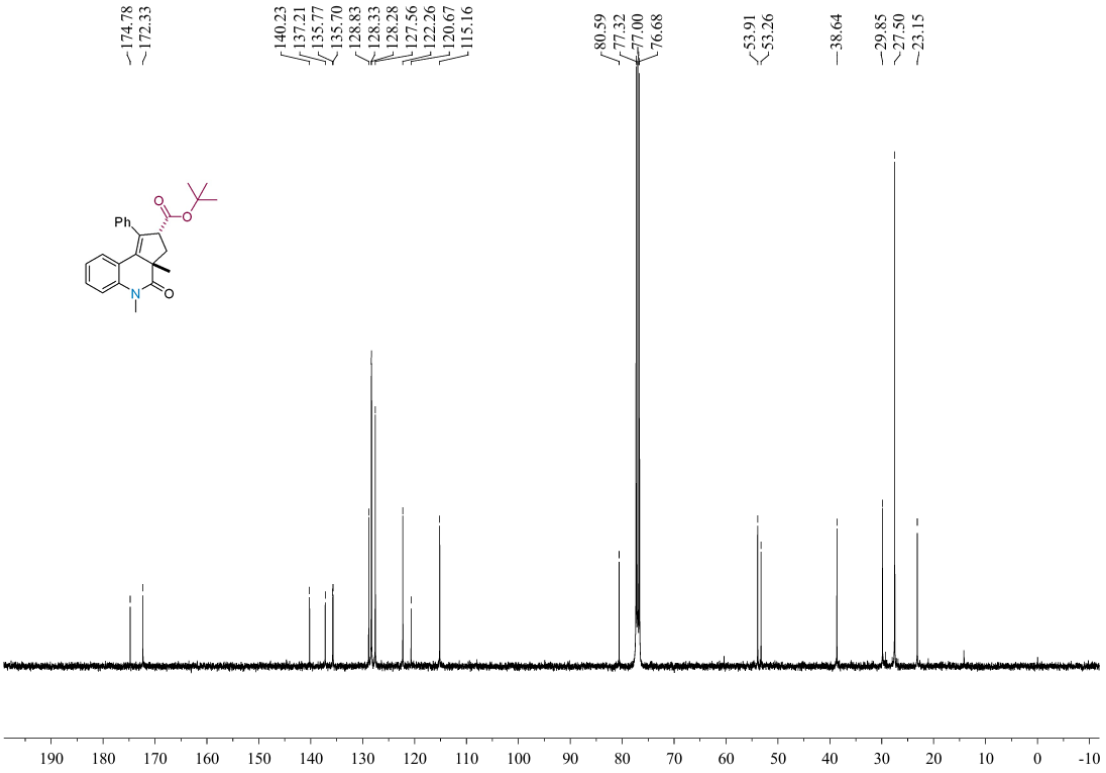
^{1}H NMR Spectrum of Compound ***cis*-3b** (400 MHz, $CDCl_3$)



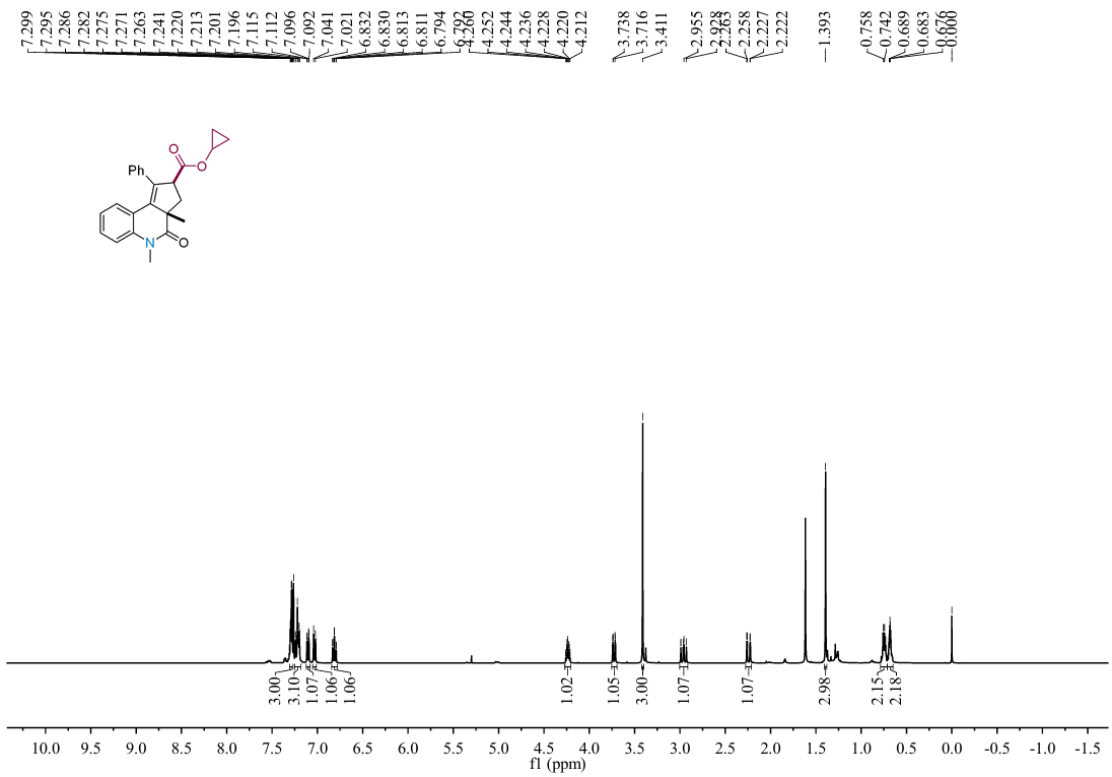
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3b** (100 MHz, $CDCl_3$)



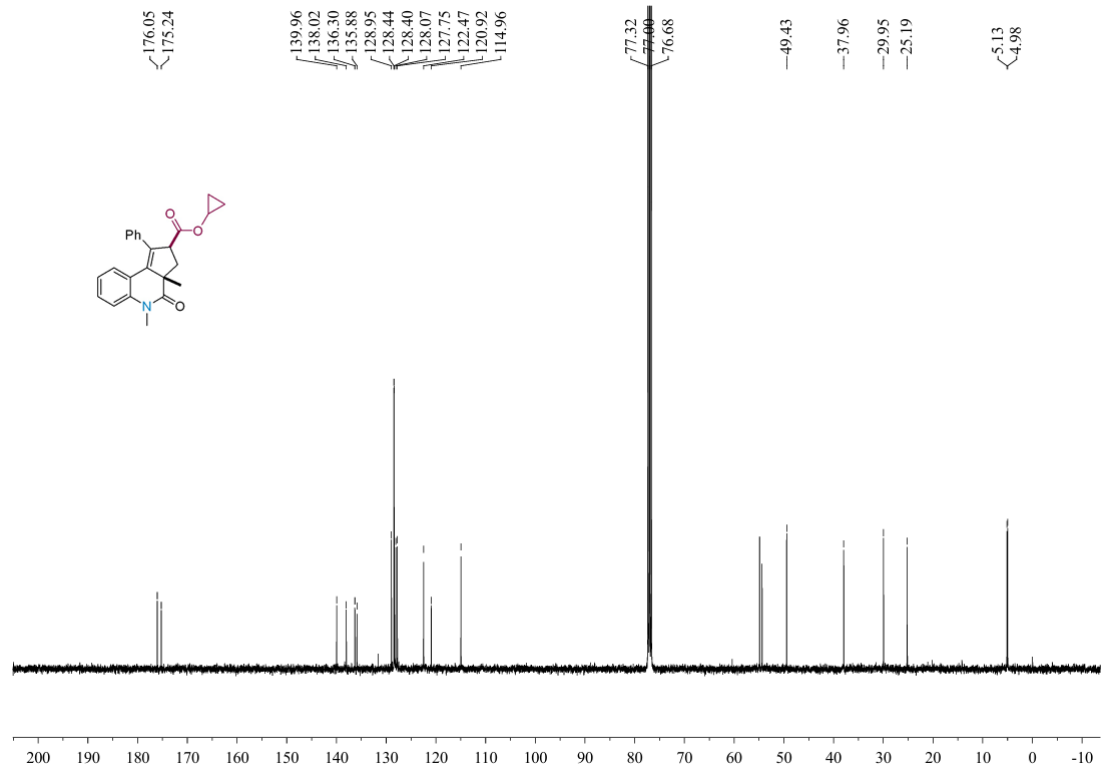
^{1}H NMR Spectrum of Compound ***trans*-3b** (400 MHz, $CDCl_3$)



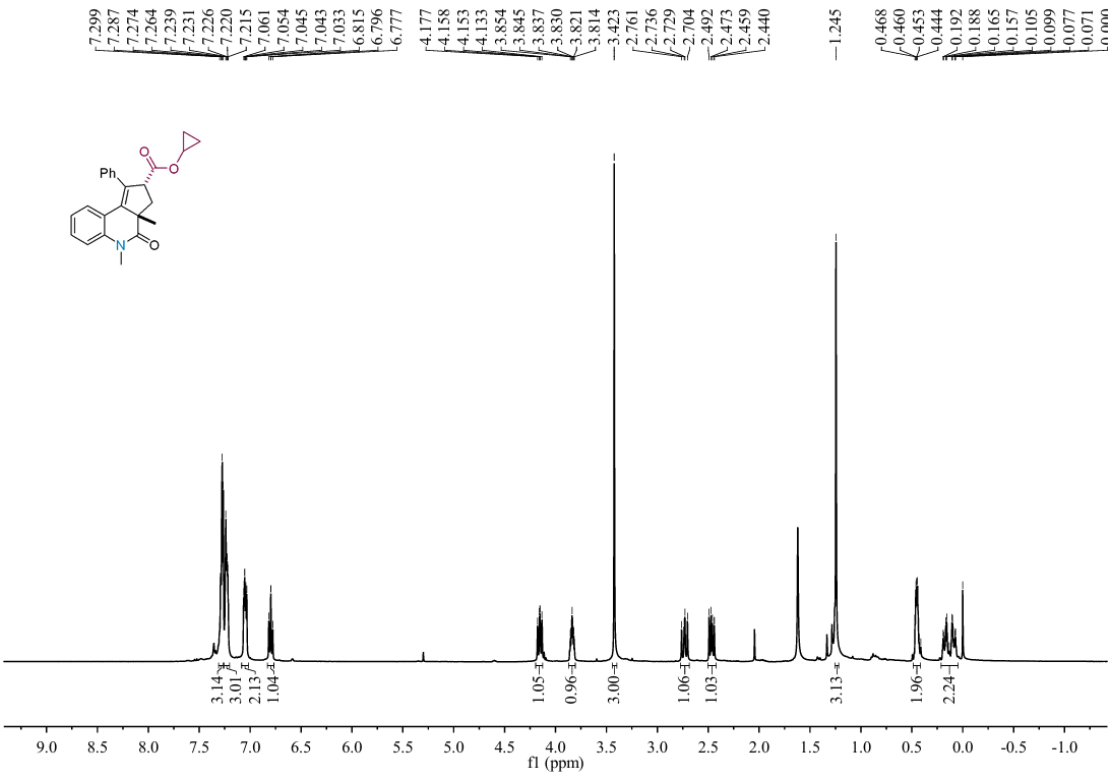
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3b** (100 MHz, $CDCl_3$)



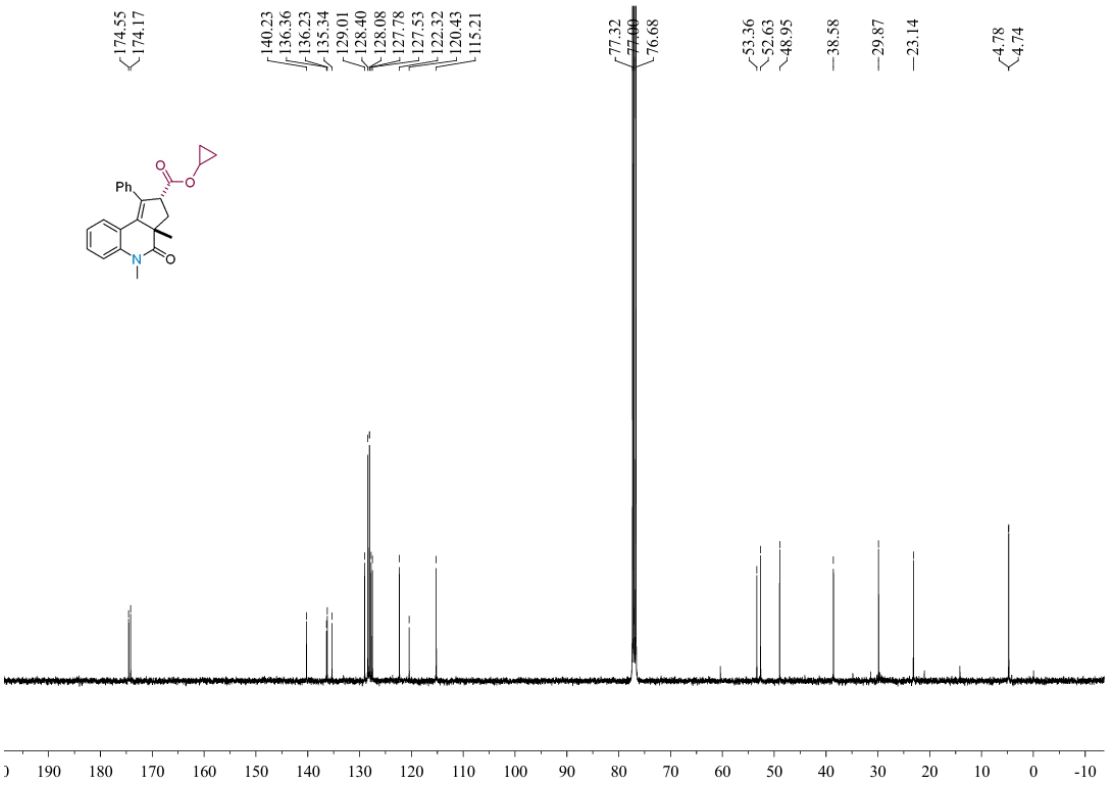
^{1}H NMR Spectrum of Compound ***cis*-3c** (400 MHz, $CDCl_3$)



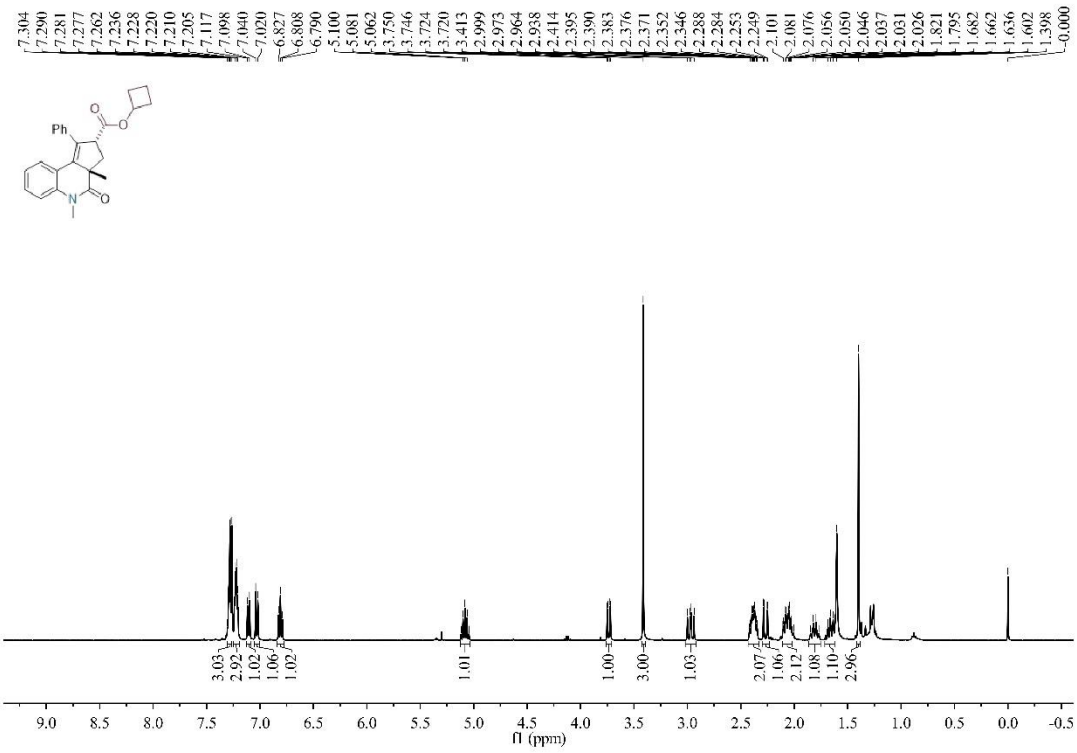
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3c** (100 MHz, $CDCl_3$)



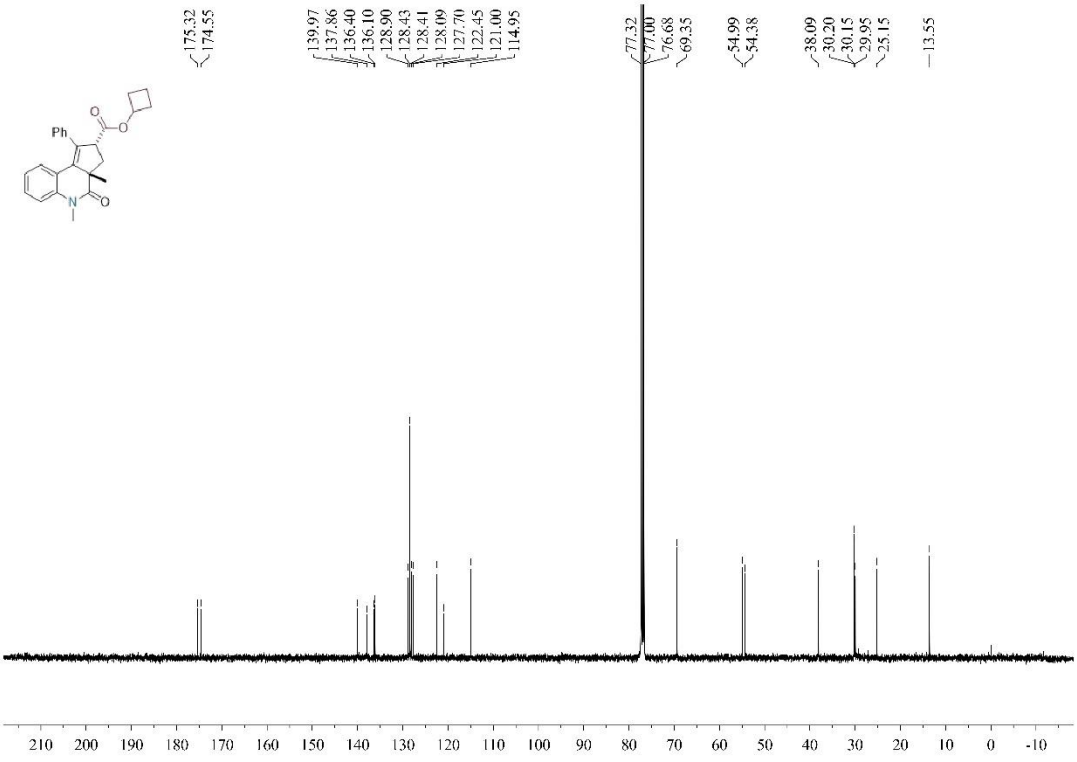
^{1}H NMR Spectrum of Compound ***trans*-3c** (400 MHz, $CDCl_3$)



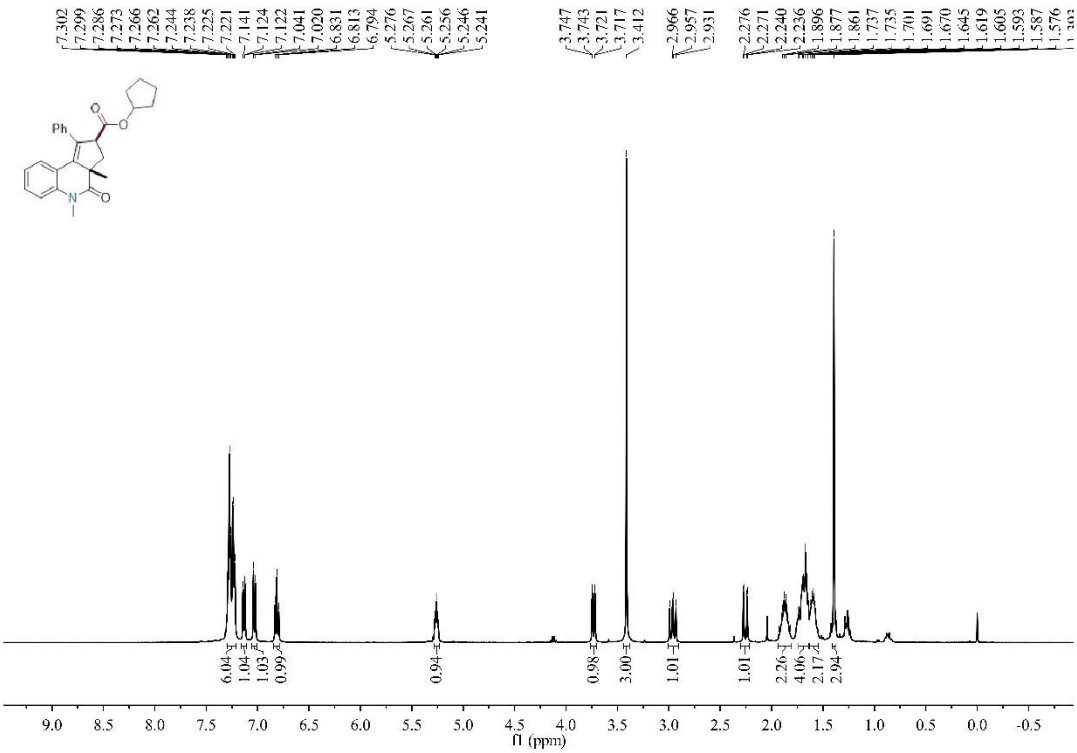
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3c** (100 MHz, $CDCl_3$)



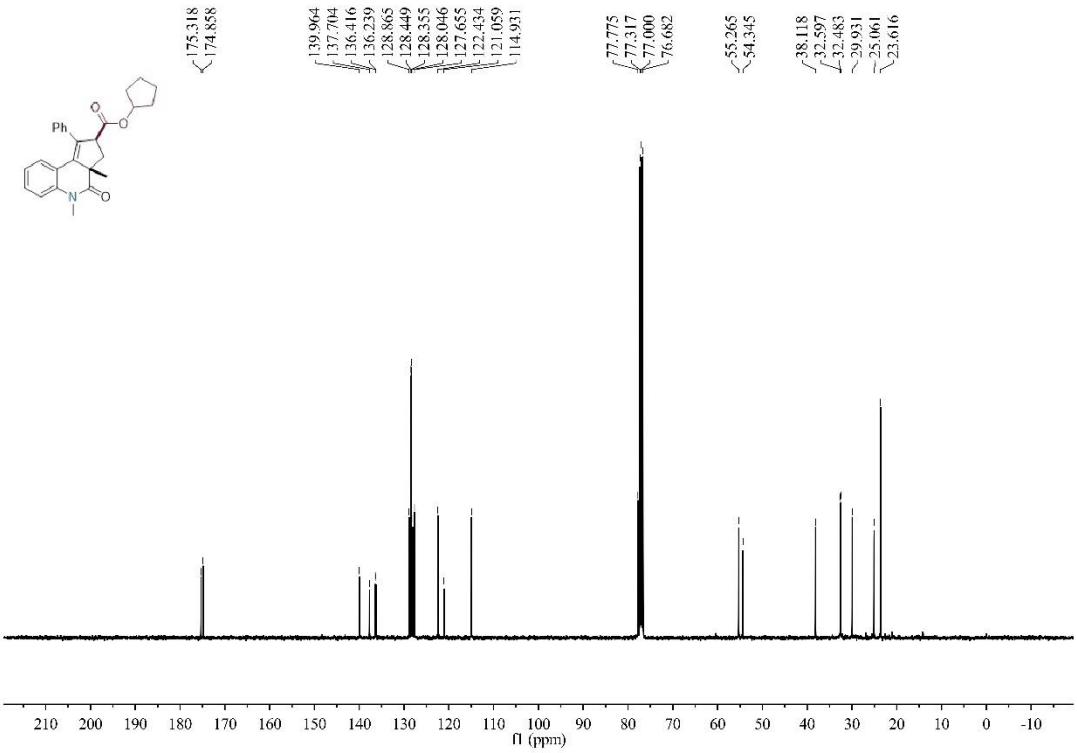
^{1}H NMR Spectrum of Compound ***trans*-3d** (400 MHz, $CDCl_3$)



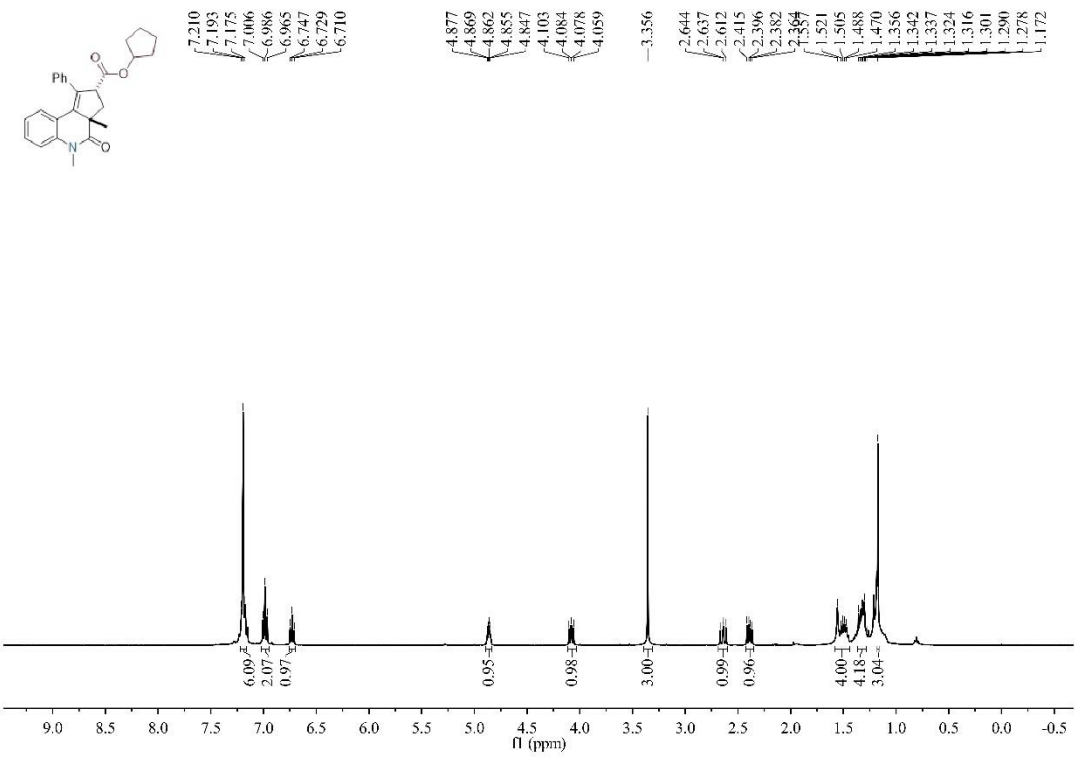
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3d** (100 MHz, $CDCl_3$)



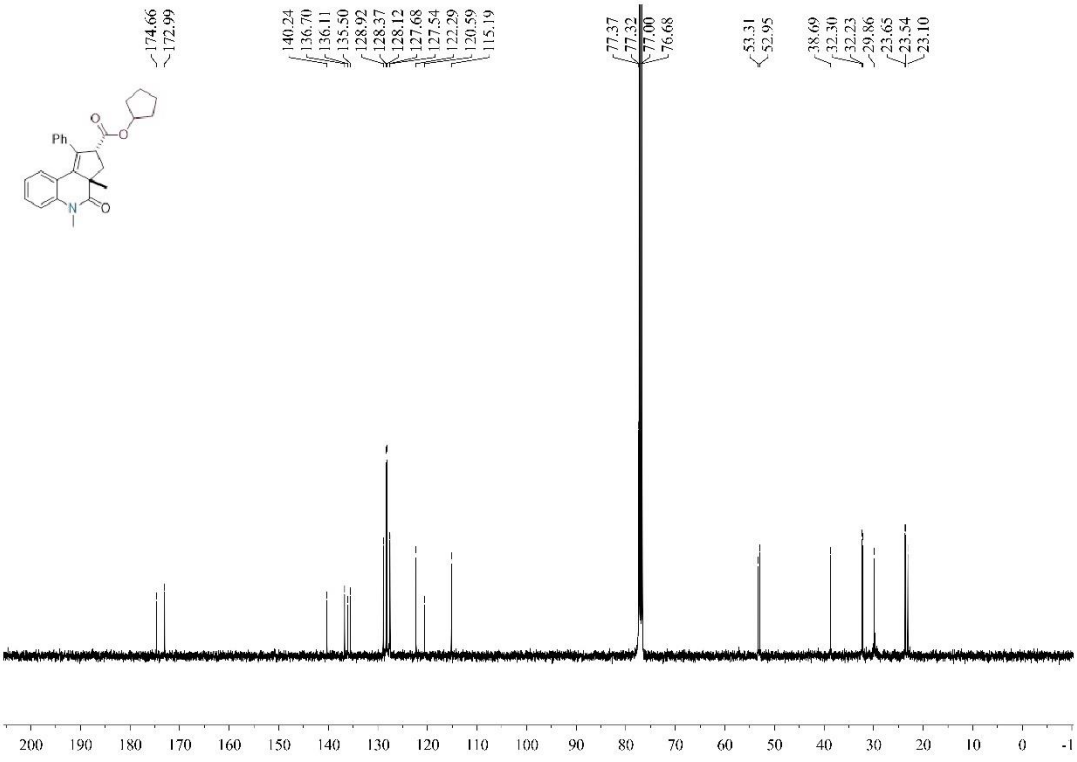
^{1}H NMR Spectrum of Compound ***cis*-3e** (400 MHz, $CDCl_3$)



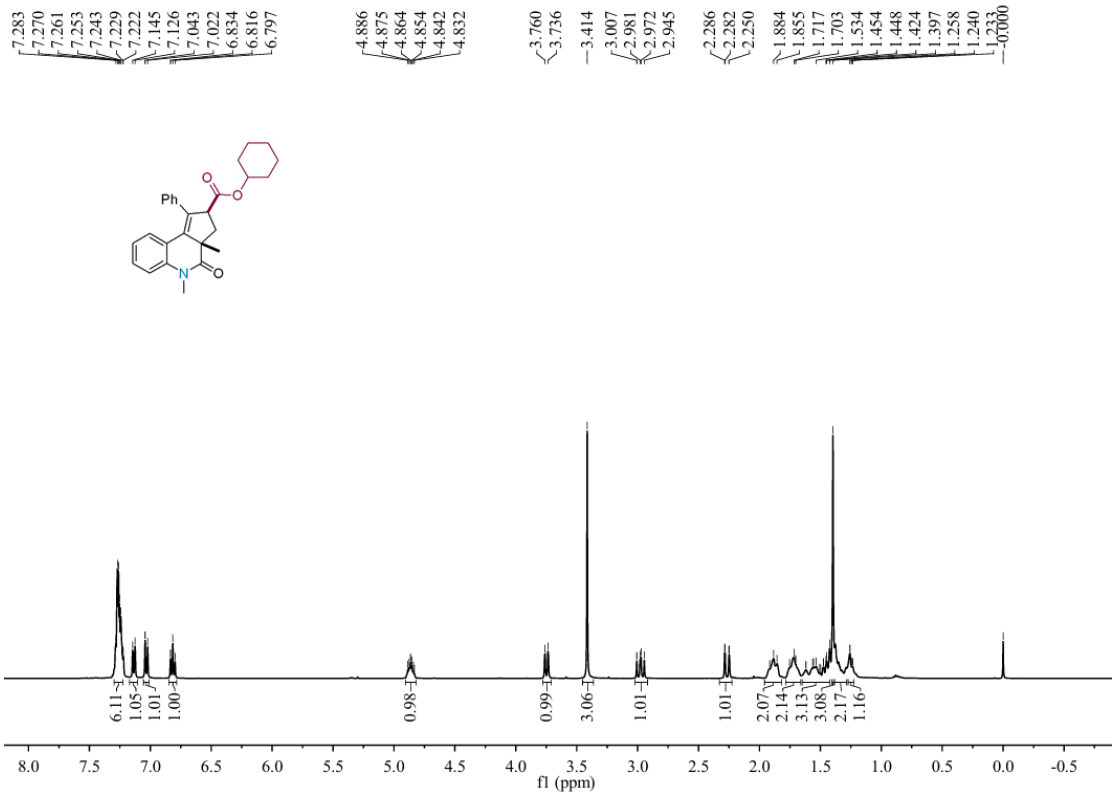
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-3e** (100 MHz, $CDCl_3$)



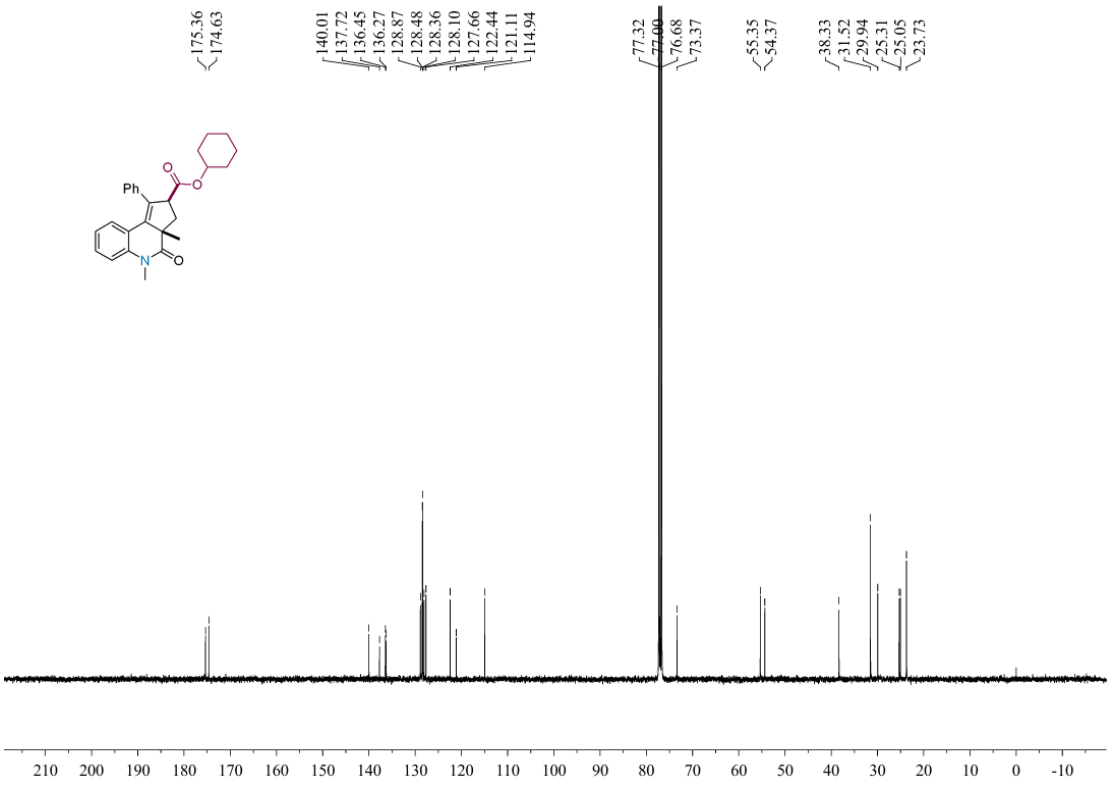
^{1}H NMR Spectrum of Compound ***trans*-3e** (400 MHz, $CDCl_3$)



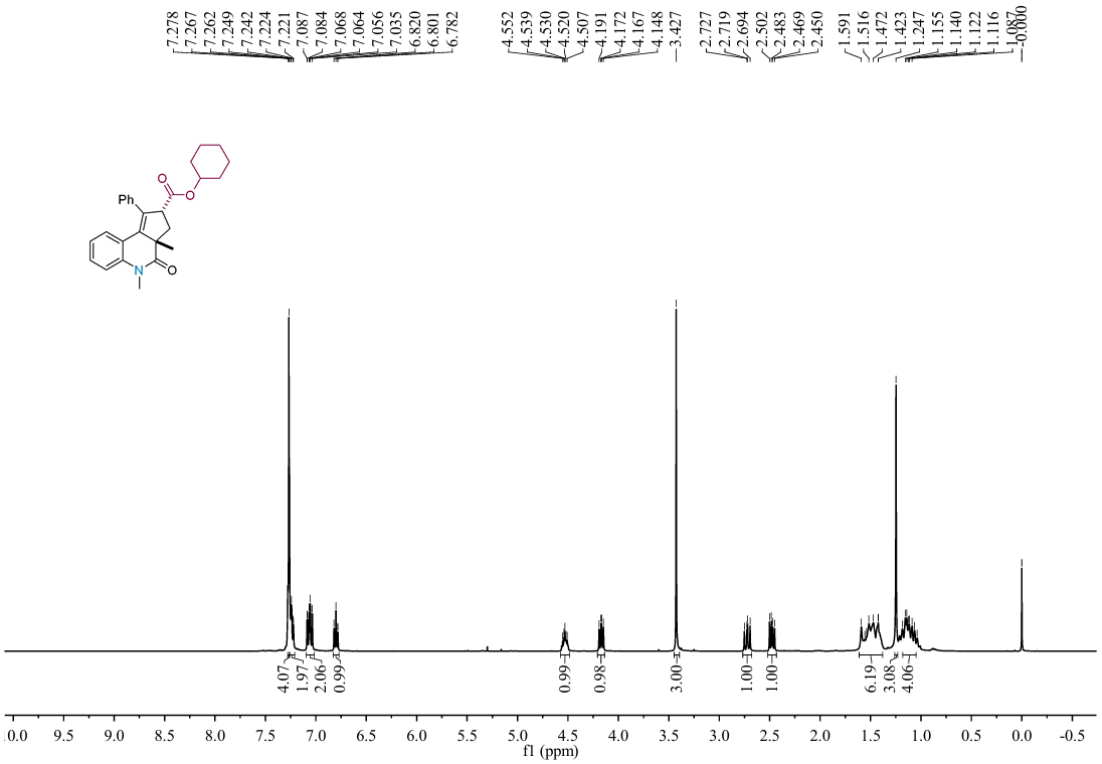
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3e** (100 MHz, $CDCl_3$)



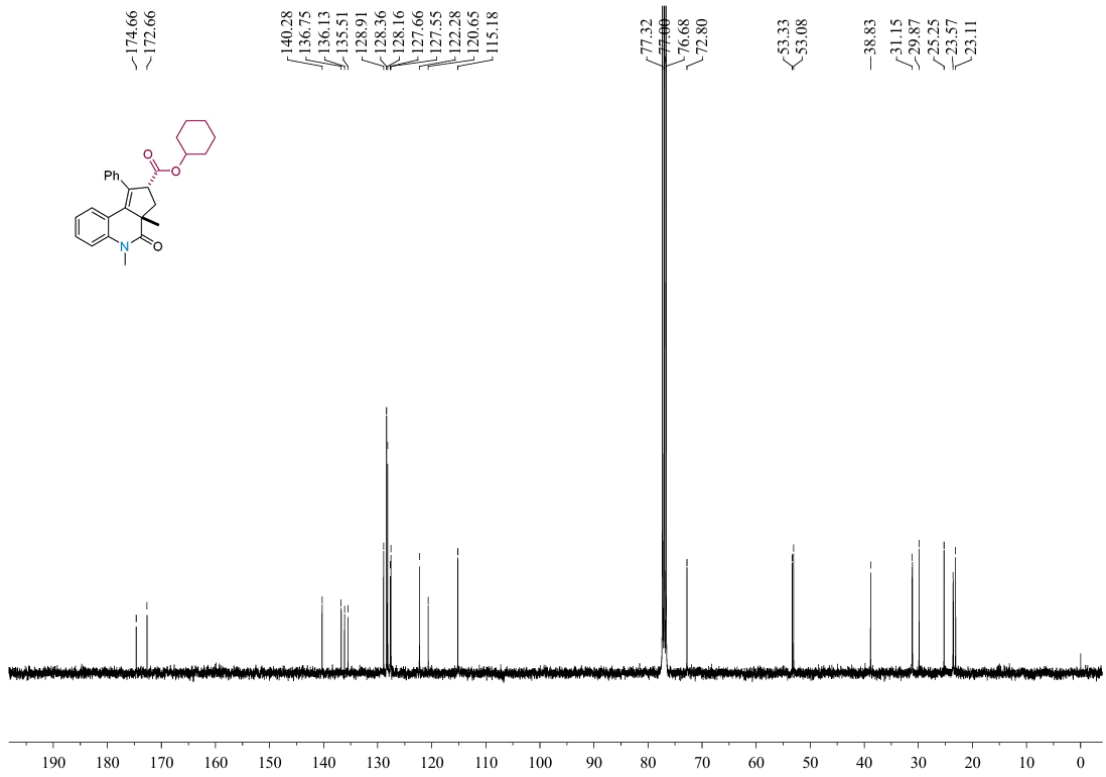
^{1}H NMR Spectrum of Compound ***cis*-3f** (400 MHz, $CDCl_3$)



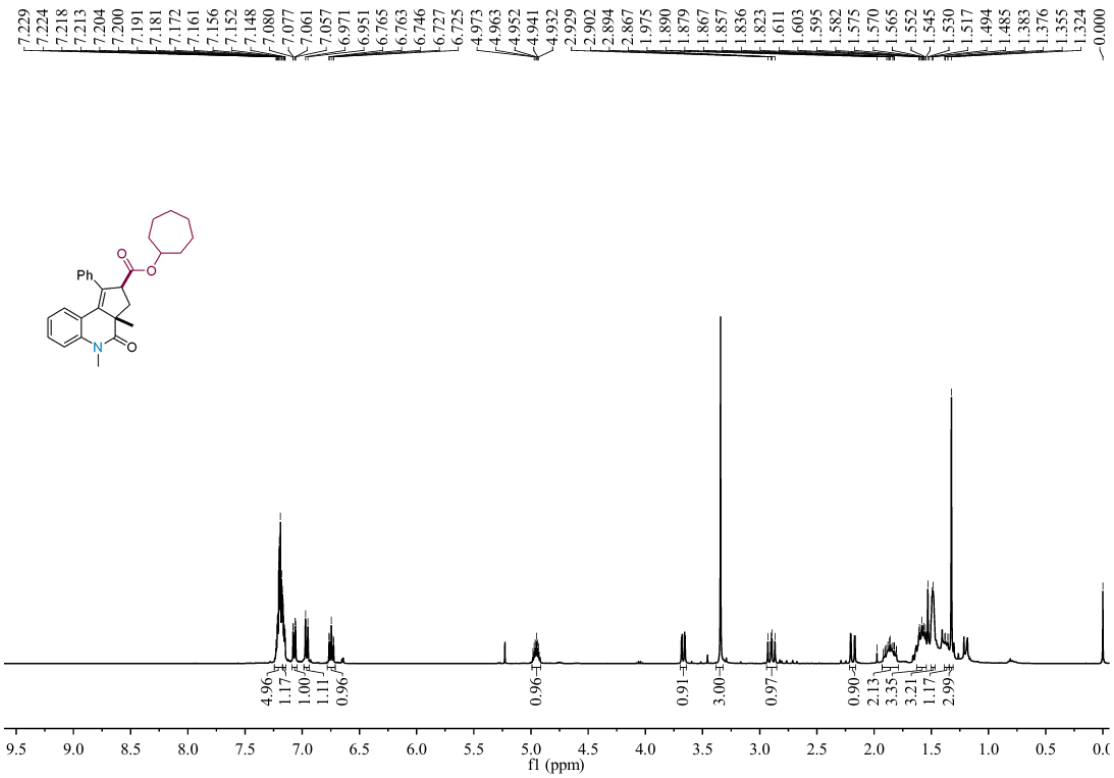
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3f** (100 MHz, $CDCl_3$)



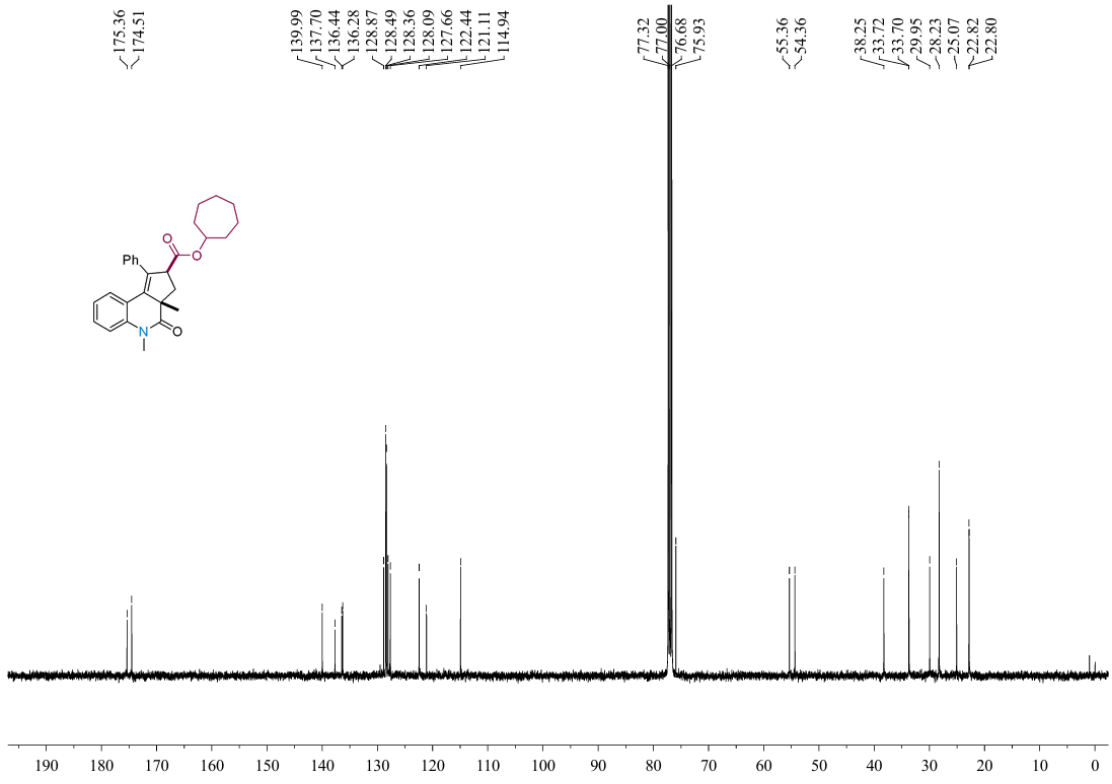
^{1}H NMR Spectrum of Compound ***trans*-3f** (400 MHz, $CDCl_3$)



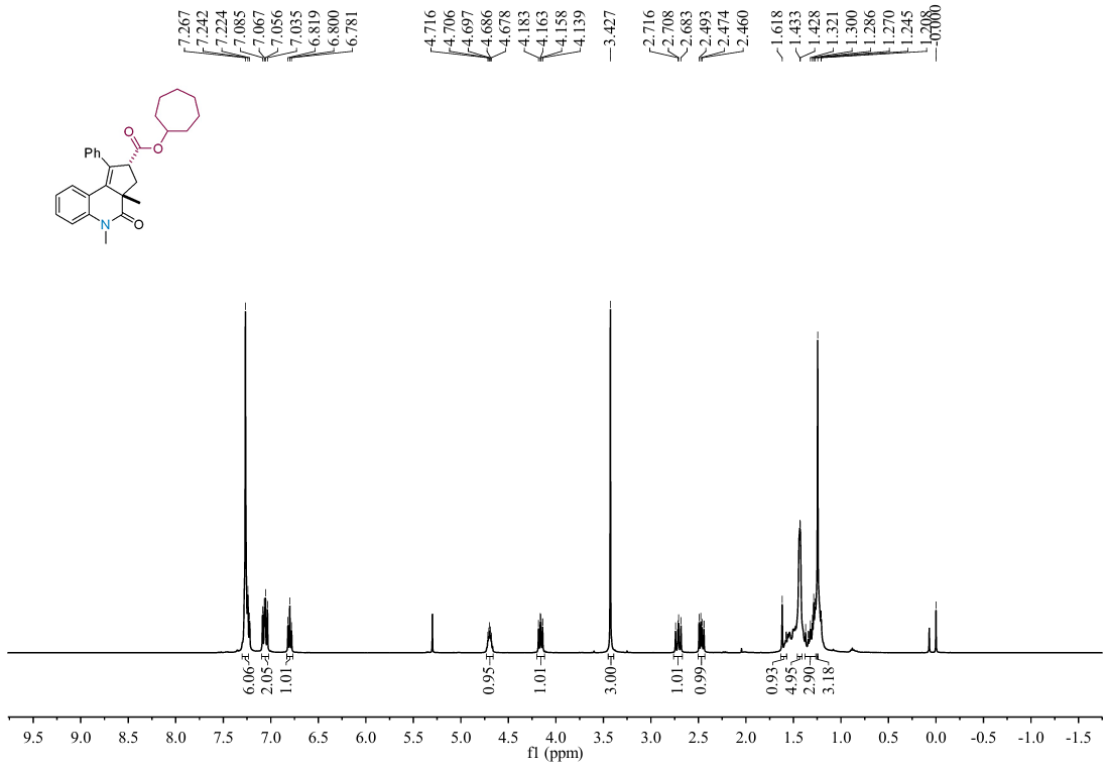
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3f** (100 MHz, $CDCl_3$)



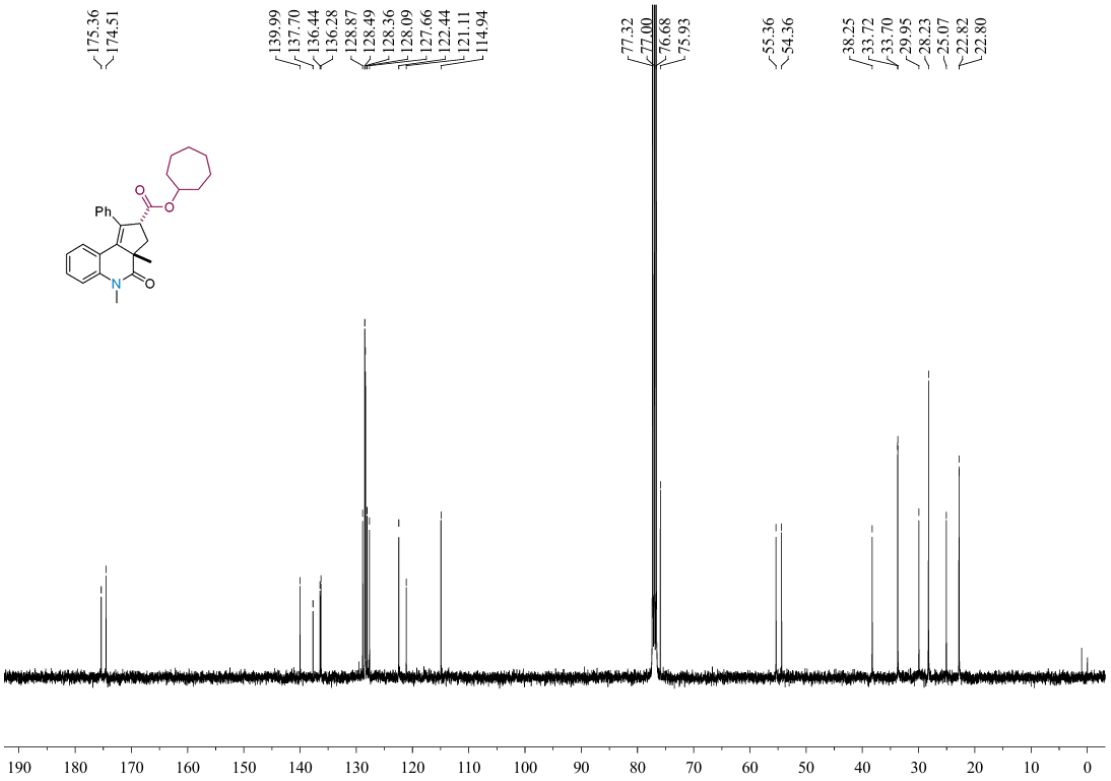
^{1}H NMR Spectrum of Compound ***cis*-3g** (400 MHz, $CDCl_3$)



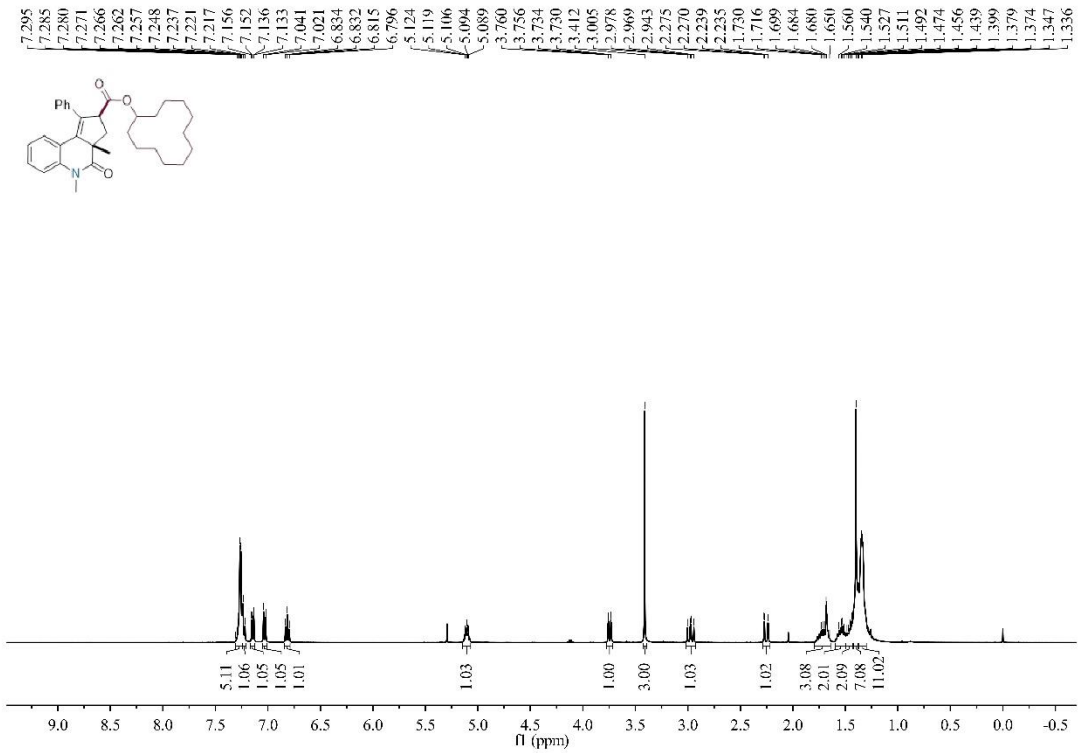
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3g** (100 MHz, $CDCl_3$)



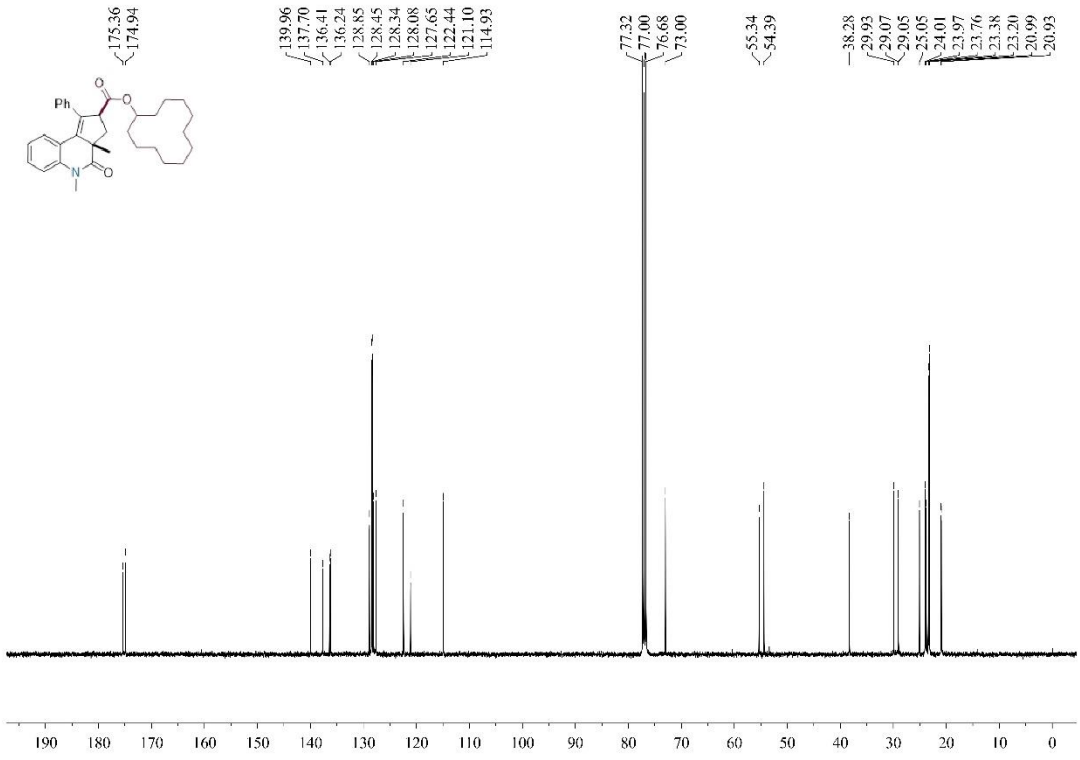
^{1}H NMR Spectrum of Compound ***trans*-3g** (400 MHz, $CDCl_3$)



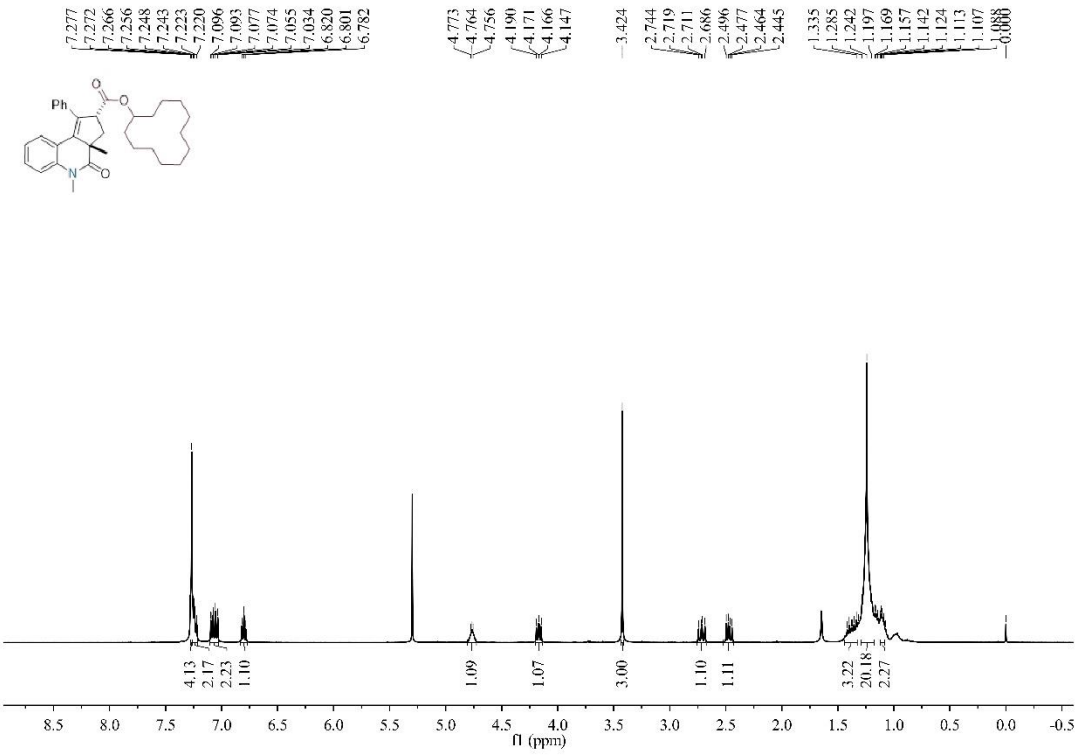
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3g** (100 MHz, $CDCl_3$)



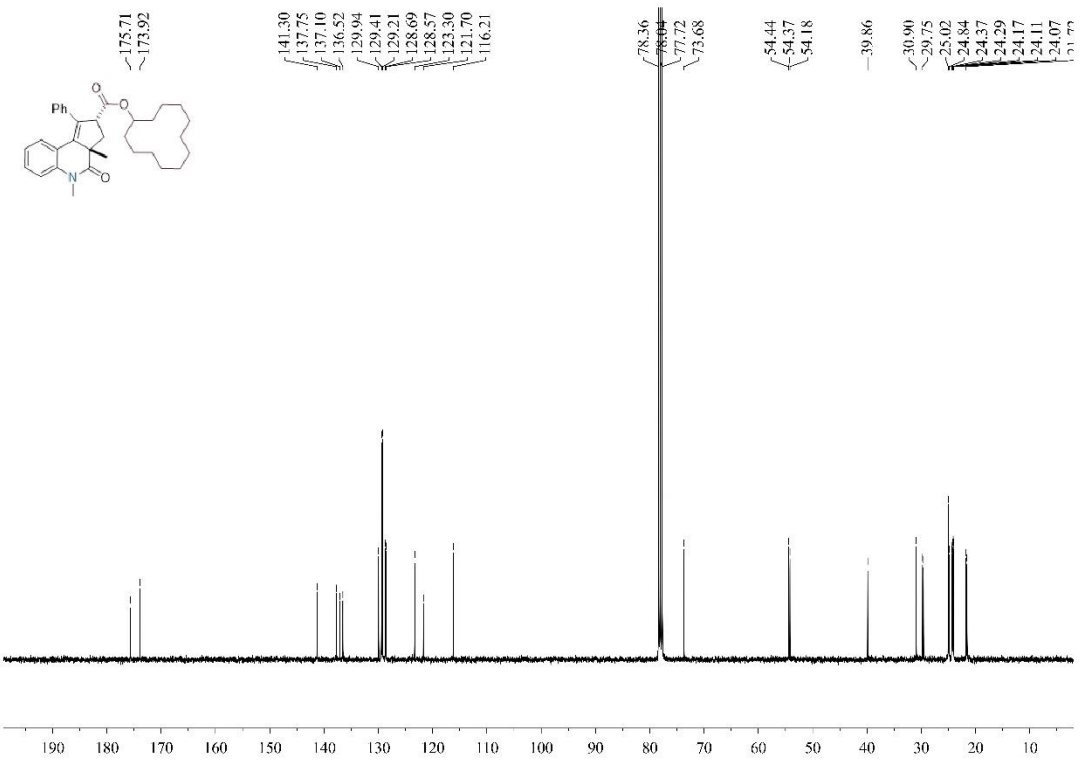
^{1}H NMR Spectrum of Compound ***cis*-3h** (400 MHz, $CDCl_3$)



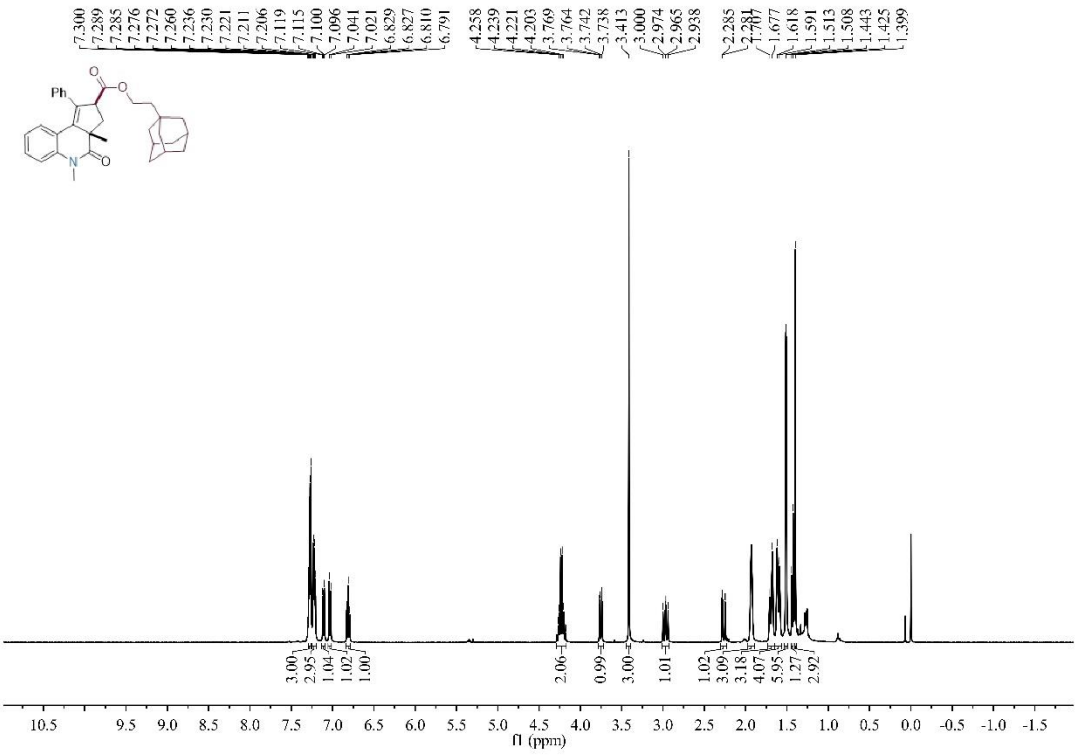
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3h** (100 MHz, $CDCl_3$)



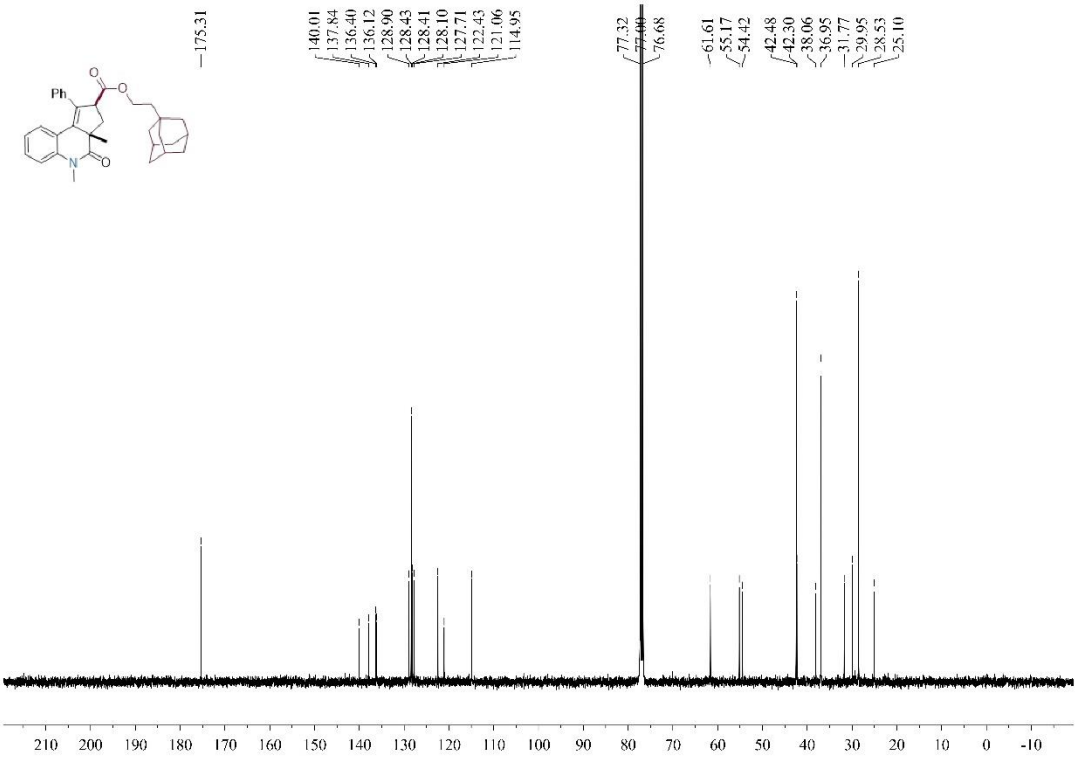
^{1}H NMR Spectrum of Compound ***trans*-3h** (400 MHz, $CDCl_3$)



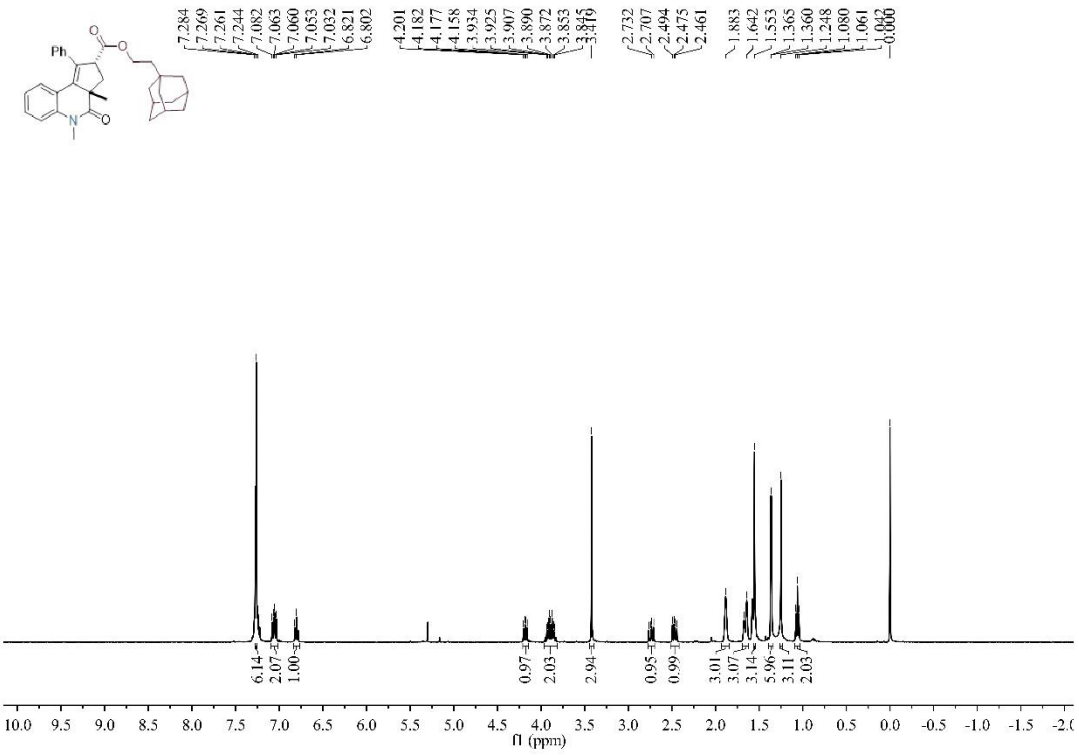
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3h** (100 MHz, $CDCl_3$)



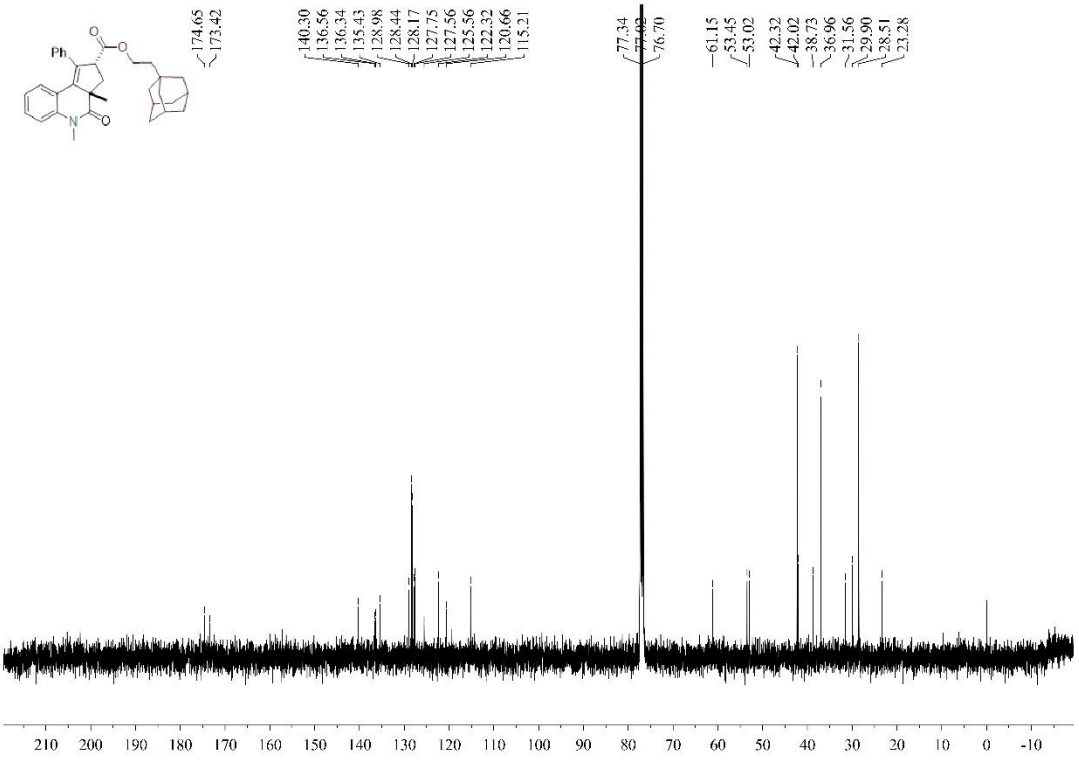
^{1}H NMR Spectrum of Compound ***cis*-3i** (400 MHz, $CDCl_3$)



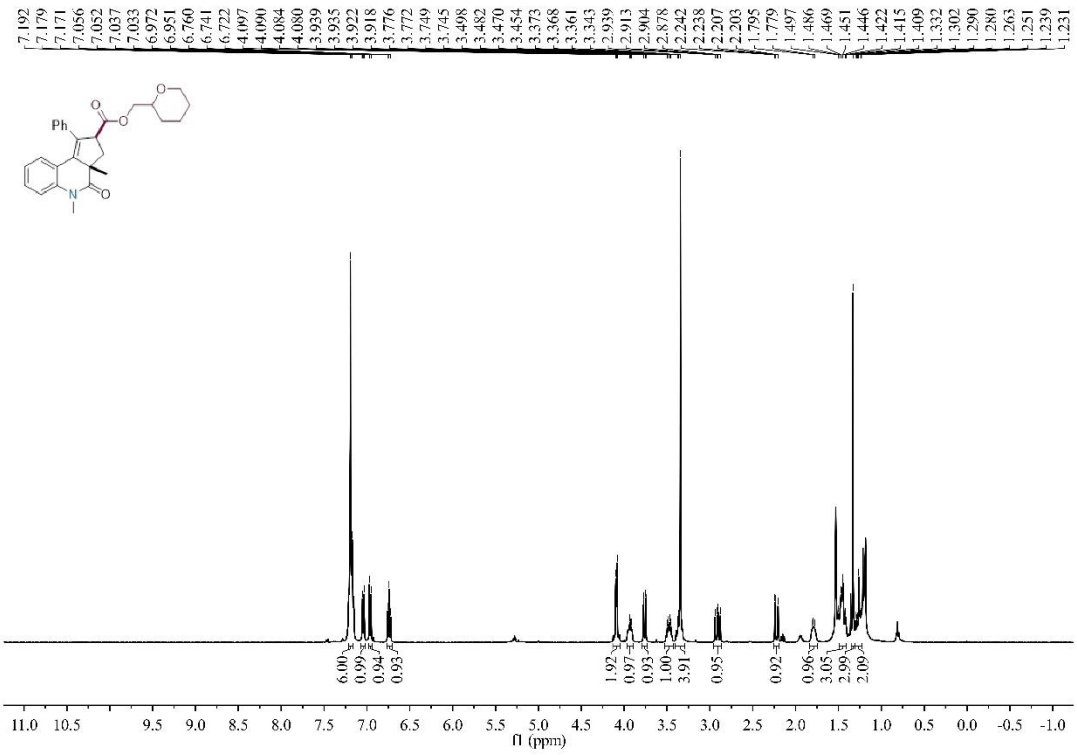
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-3i** (100 MHz, $CDCl_3$)



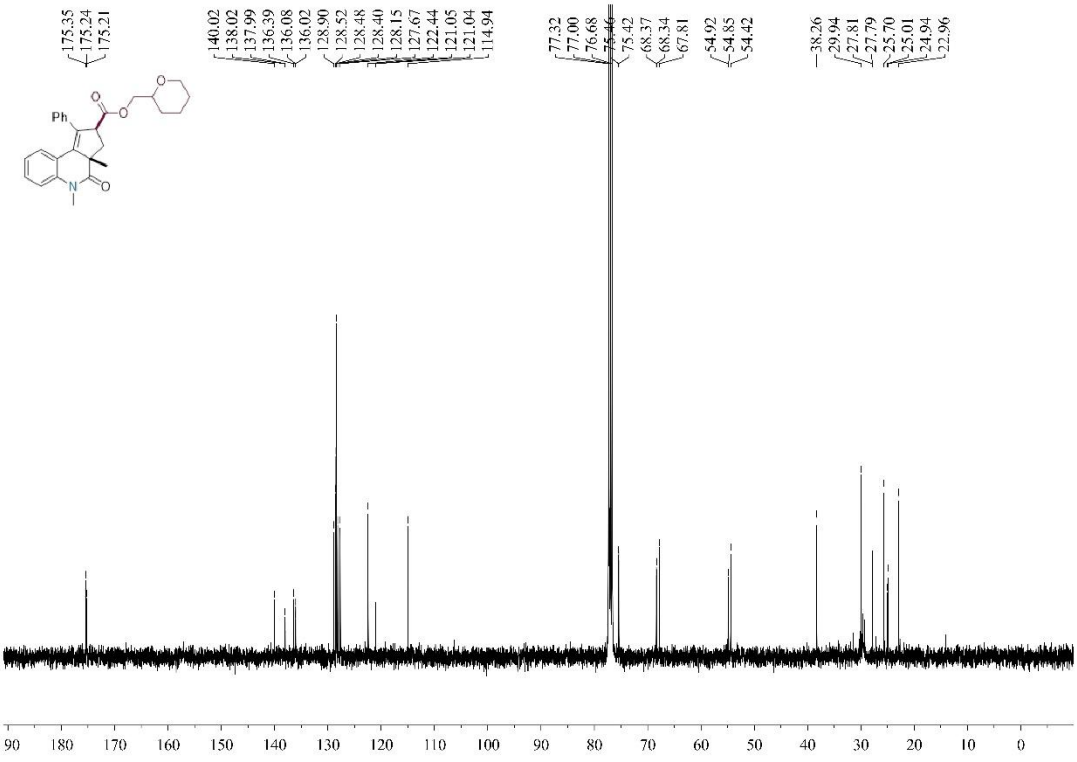
^{1}H NMR Spectrum of Compound ***trans*-3i** (400 MHz, $CDCl_3$)



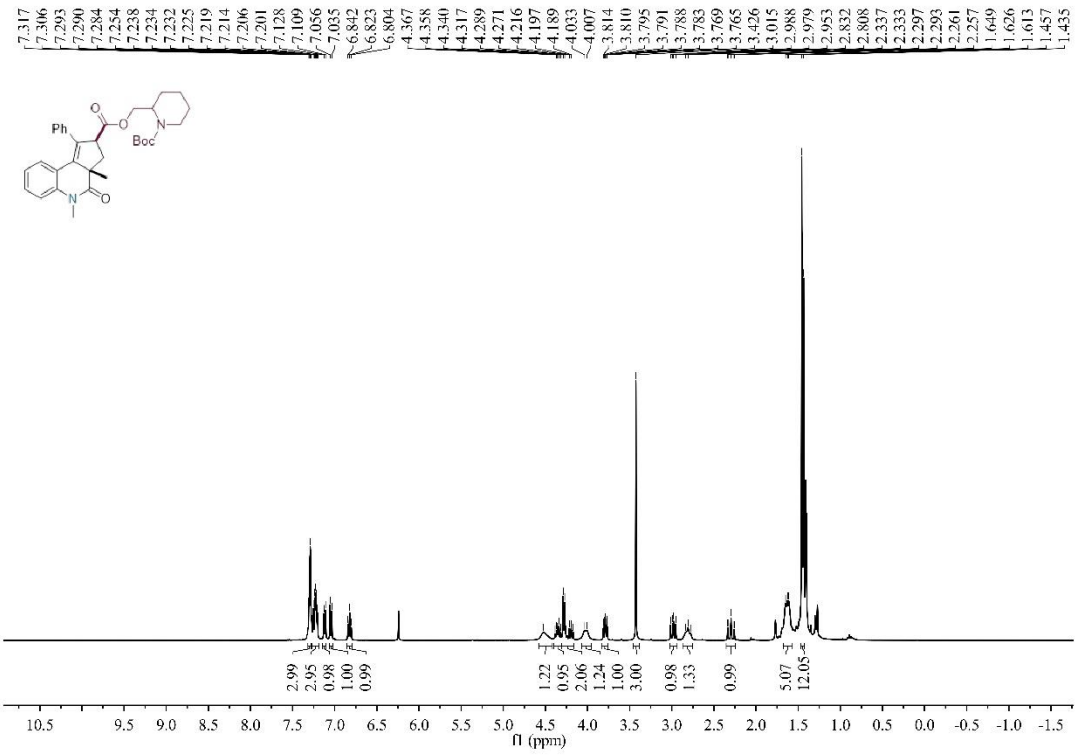
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***trans*-3i** (100 MHz, $CDCl_3$)



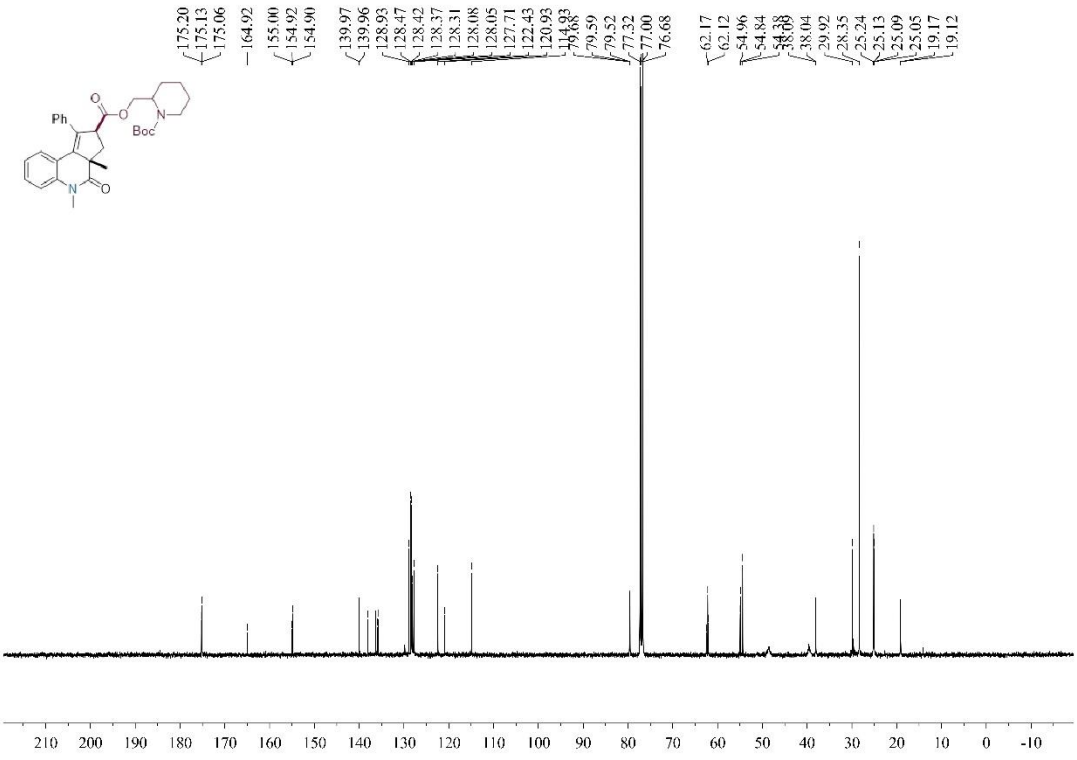
^{1}H NMR Spectrum of Compound ***cis*-3j** (400 MHz, $CDCl_3$)



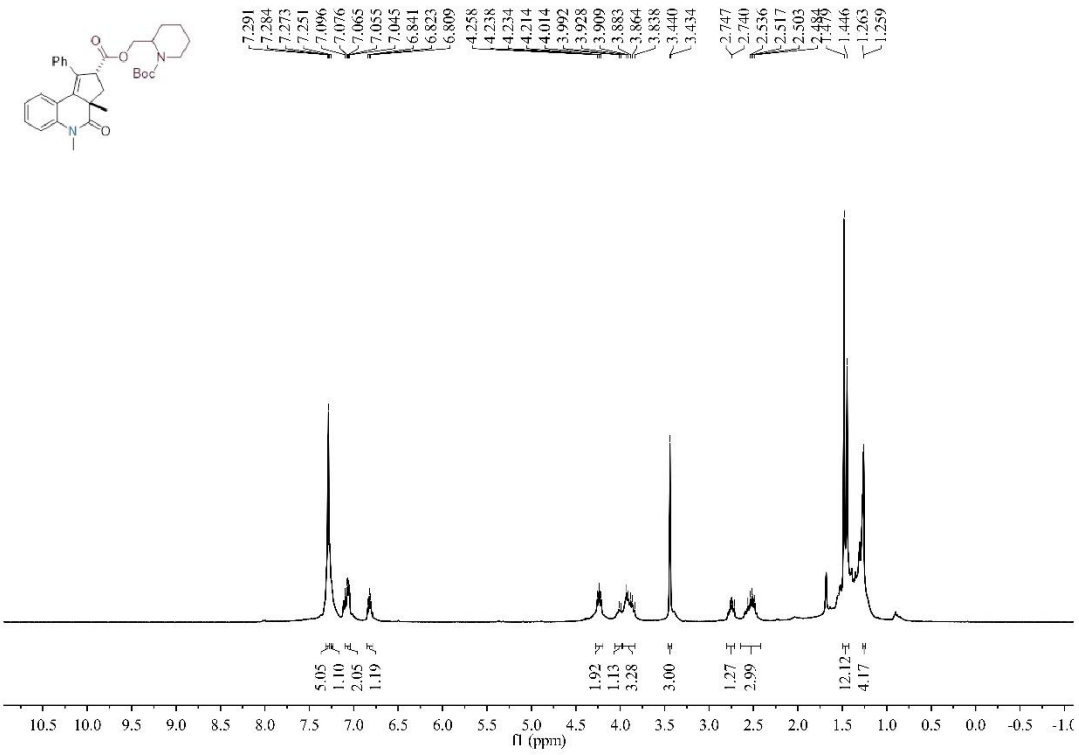
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3j** (100 MHz, $CDCl_3$)



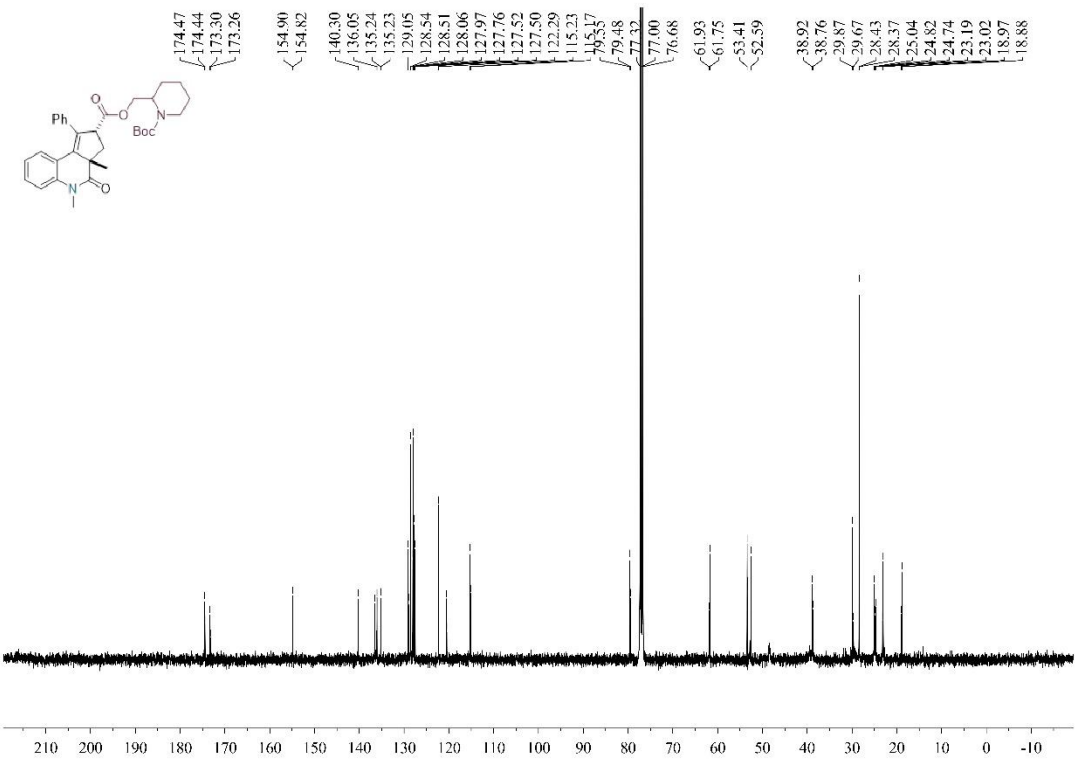
^{1}H NMR Spectrum of Compound ***cis*-3k** (400 MHz, $CDCl_3$)



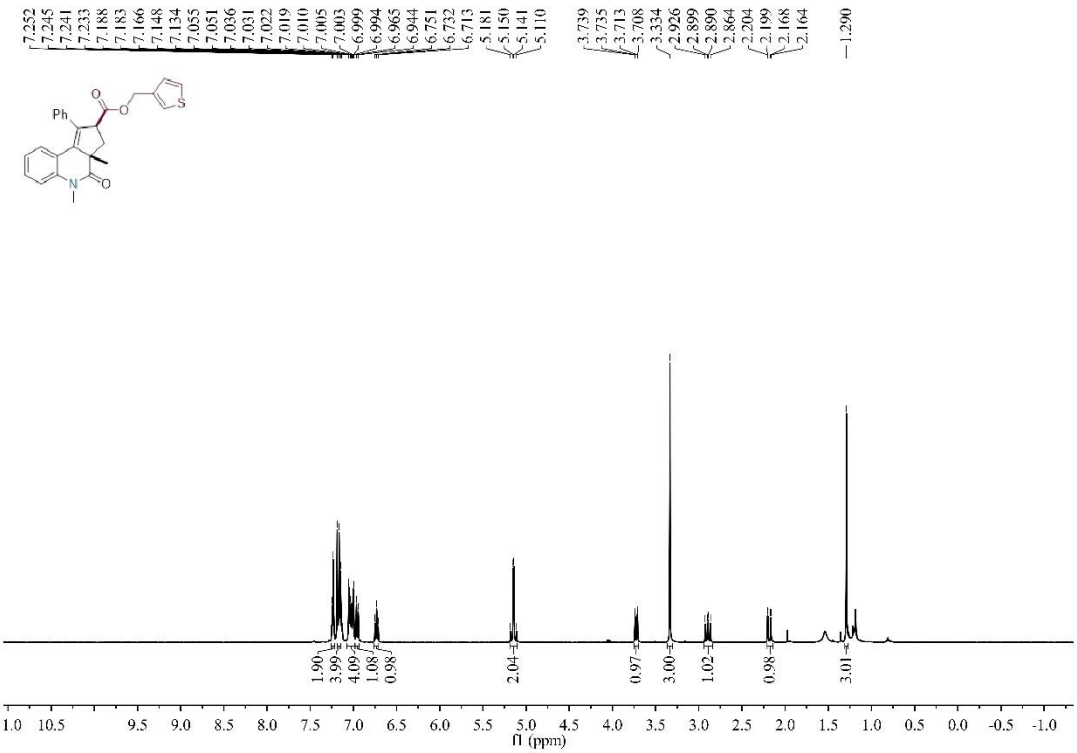
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3k** (100 MHz, $CDCl_3$)



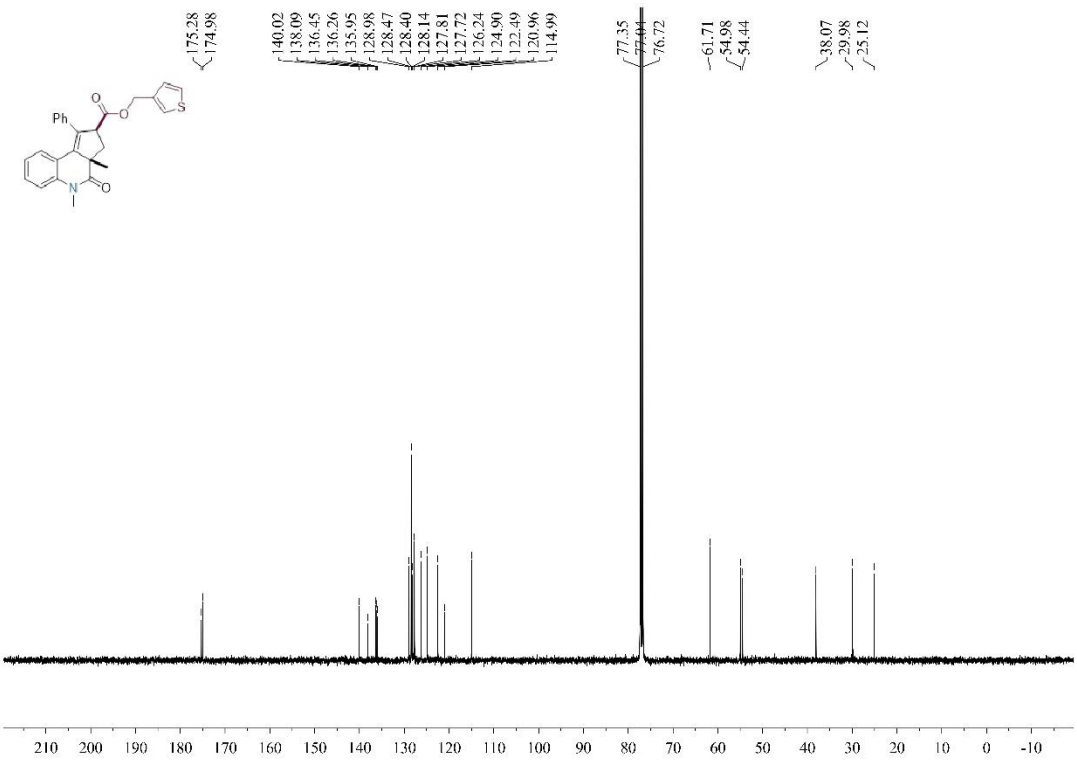
^{1}H NMR Spectrum of Compound ***trans*-3k** (400 MHz, $CDCl_3$)



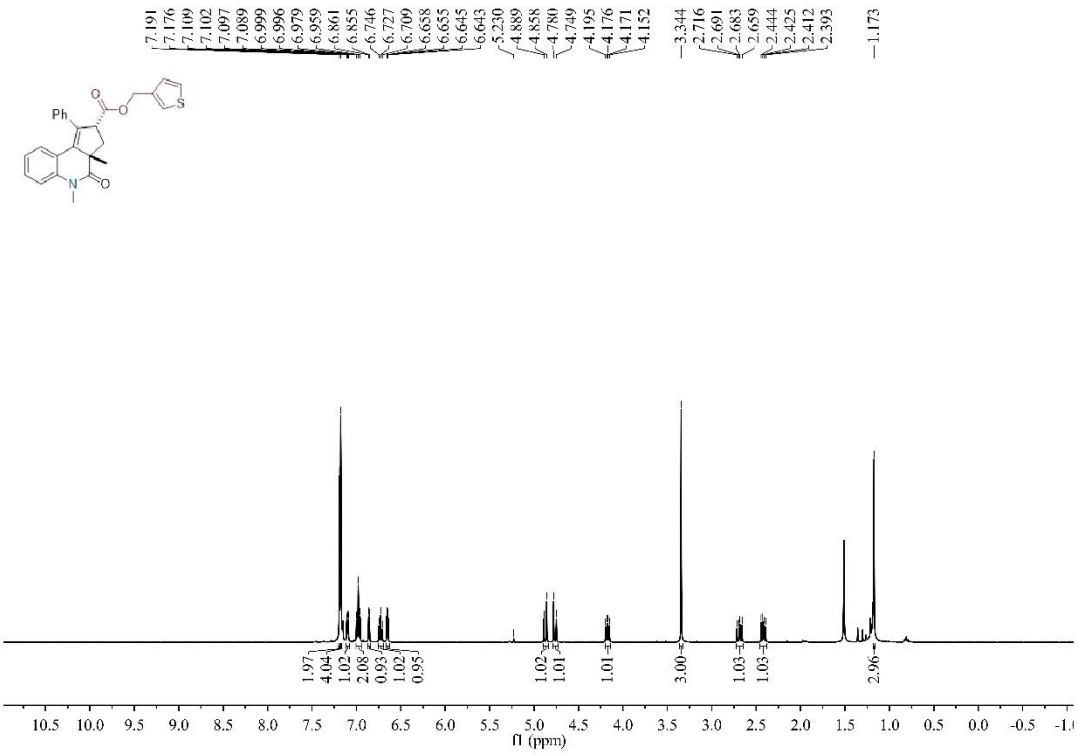
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3k** (100 MHz, $CDCl_3$)



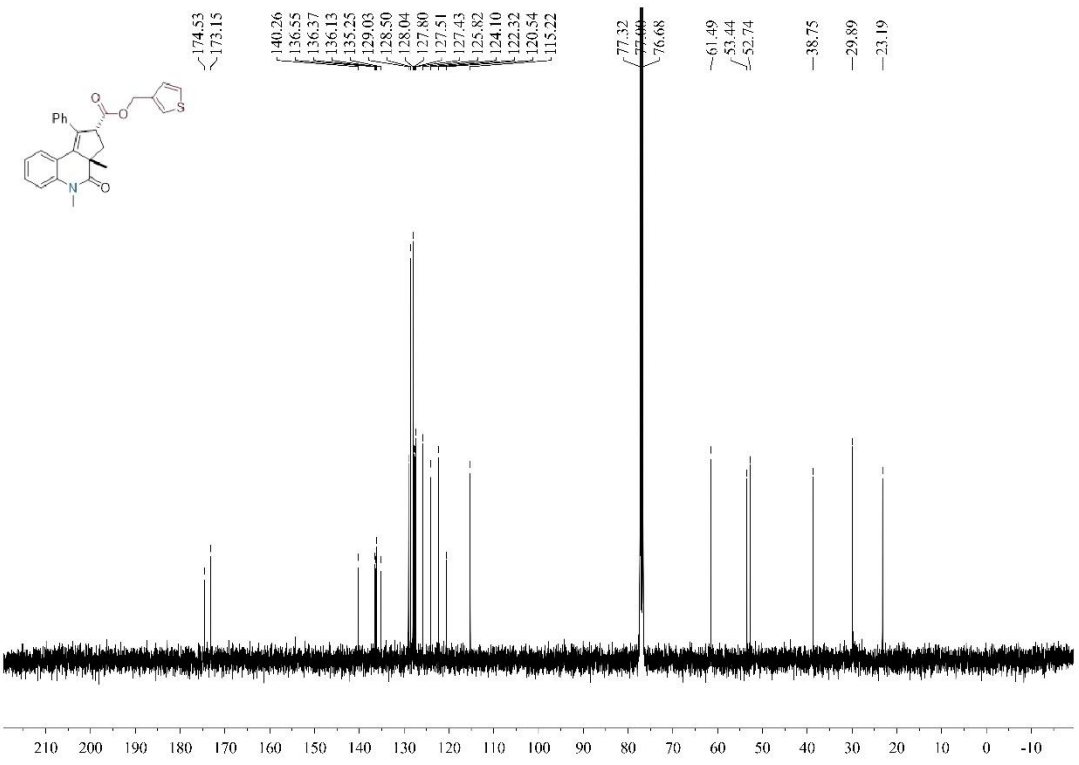
^{1}H NMR Spectrum of Compound ***cis*-3l** (400 MHz, $CDCl_3$)



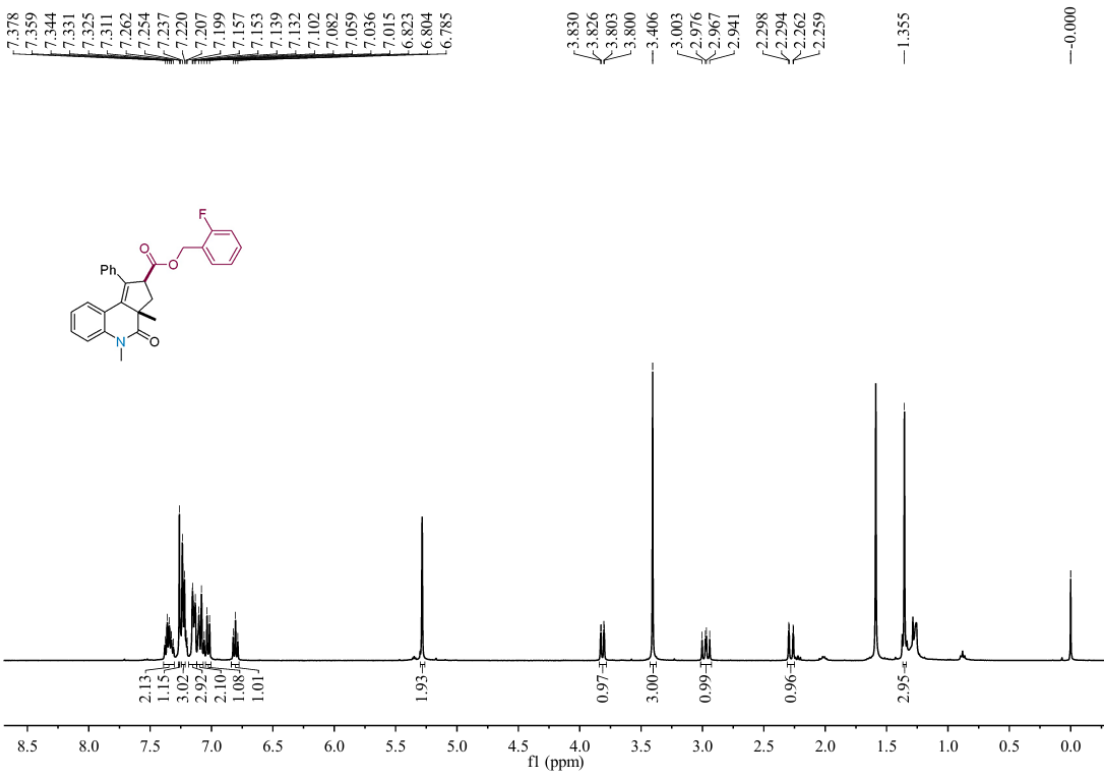
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3l** (100 MHz, $CDCl_3$)



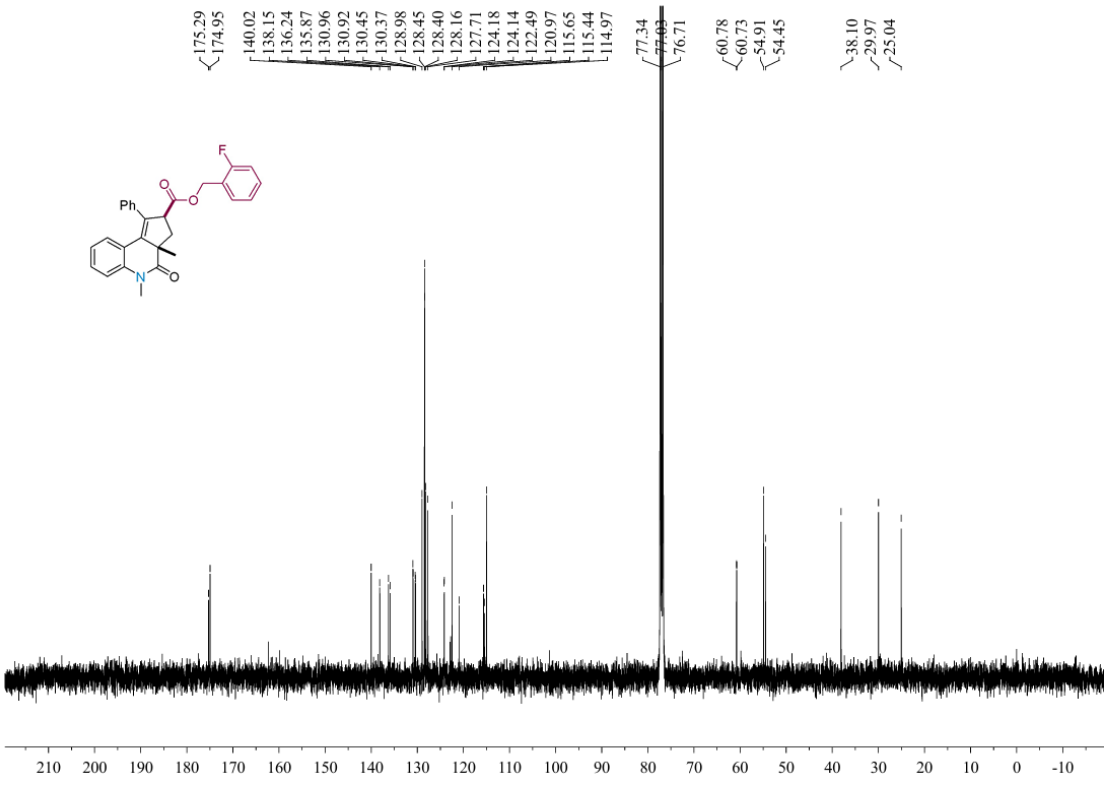
^{1}H NMR Spectrum of Compound ***trans*-3l** (400 MHz, $CDCl_3$)



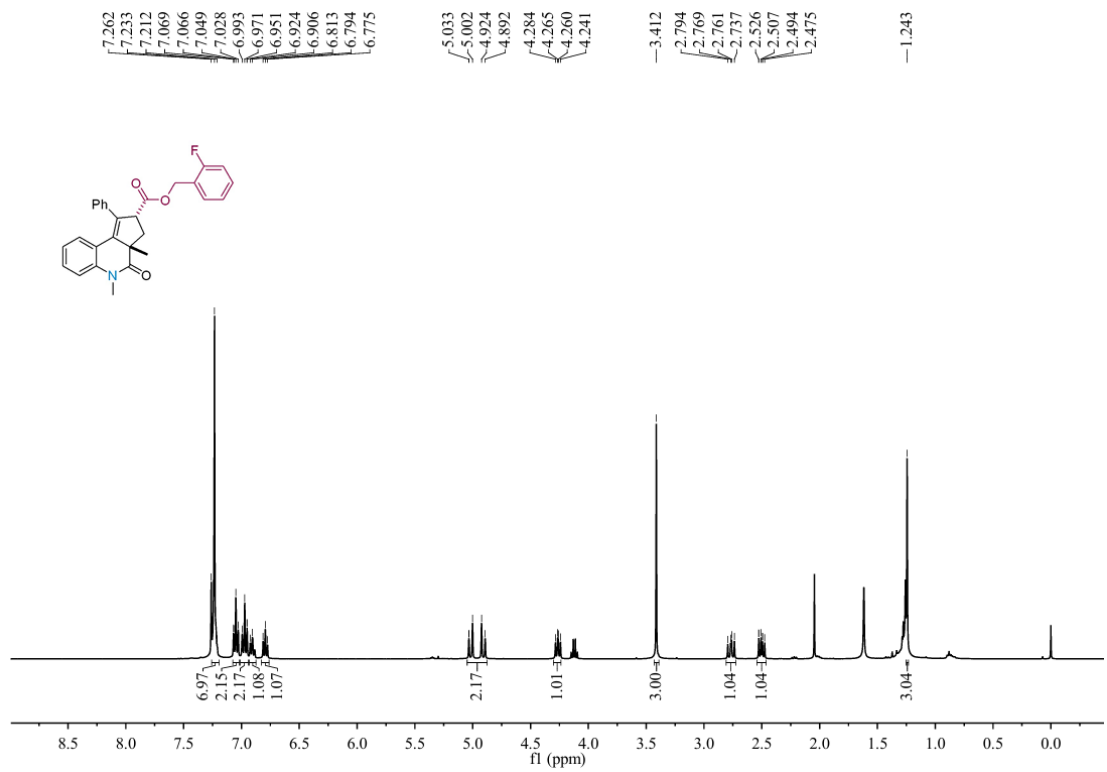
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3l** (100 MHz, $CDCl_3$)



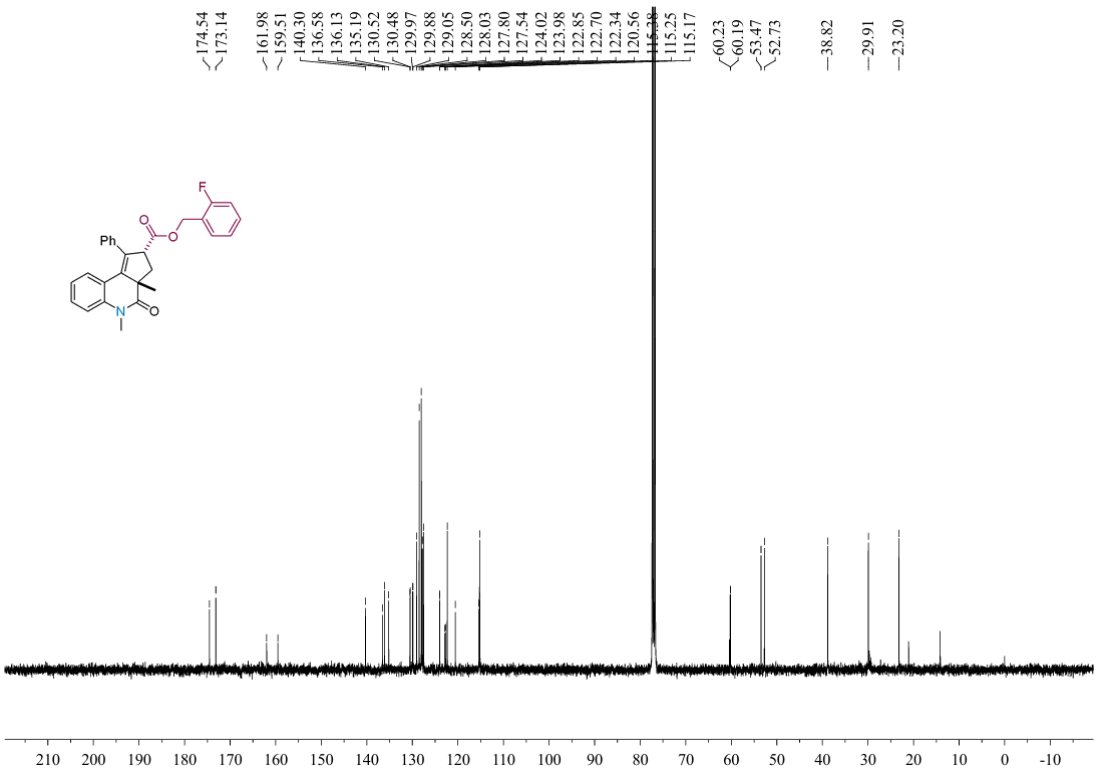
^{1}H NMR Spectrum of Compound ***cis*-3m** (400 MHz, $CDCl_3$)



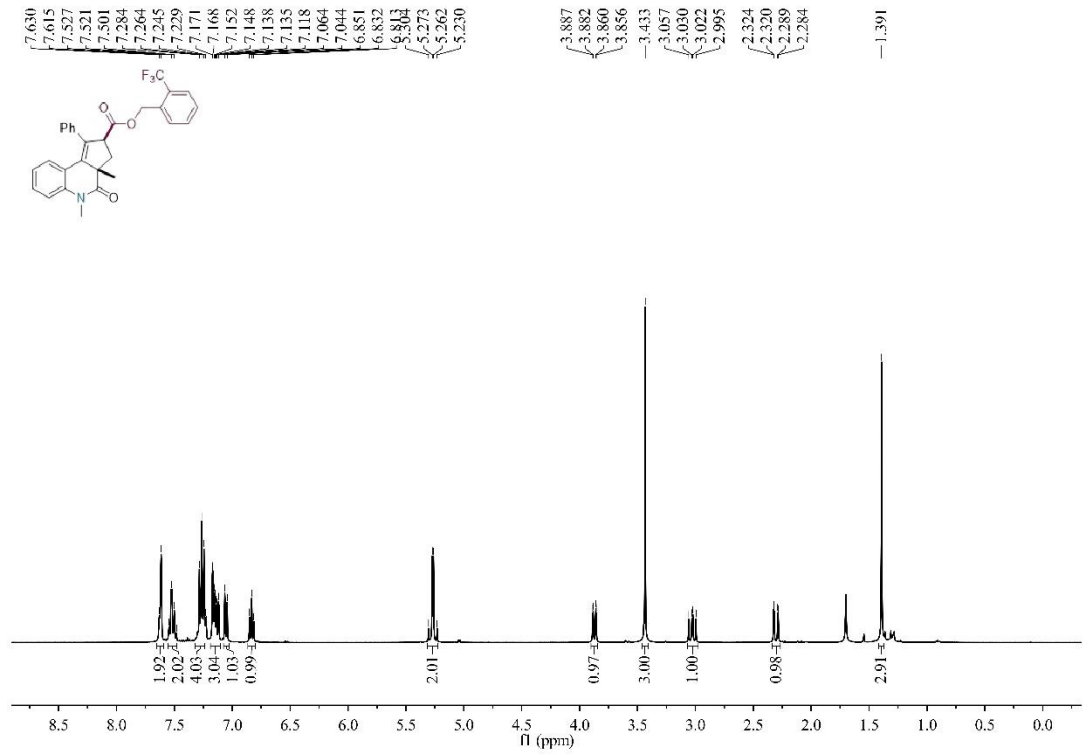
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3m** (100 MHz, $CDCl_3$)



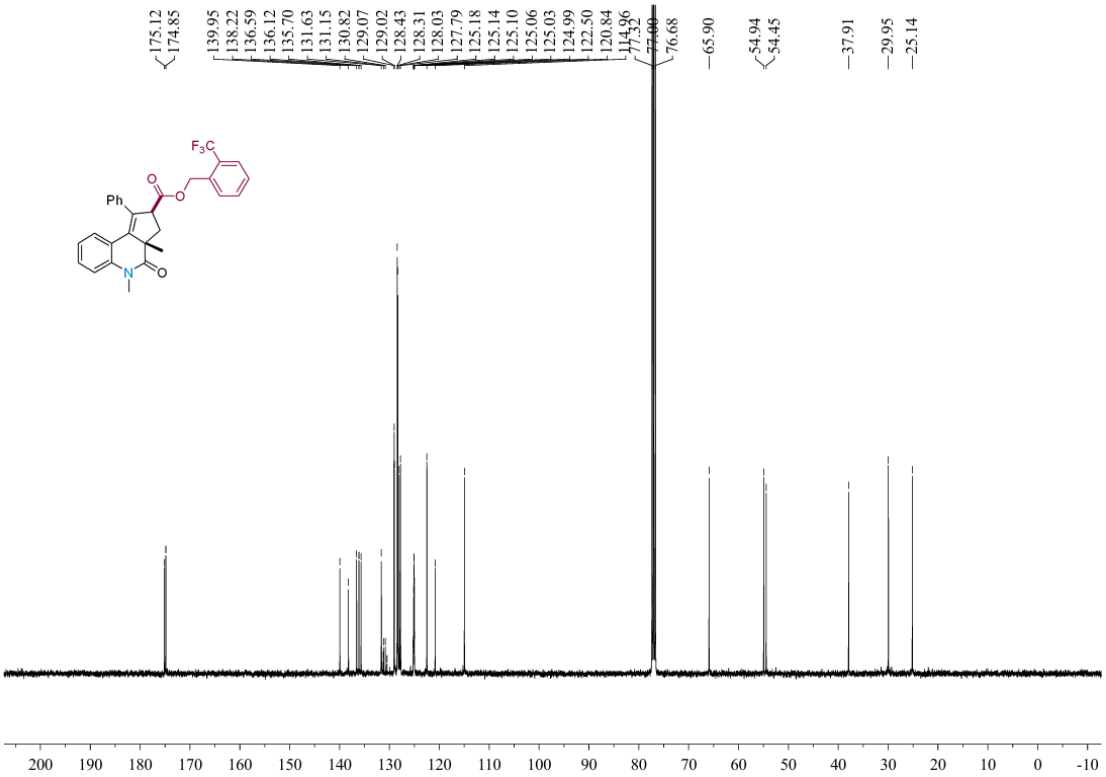
^{1}H NMR Spectrum of Compound ***trans*-3m** (400 MHz, $CDCl_3$)



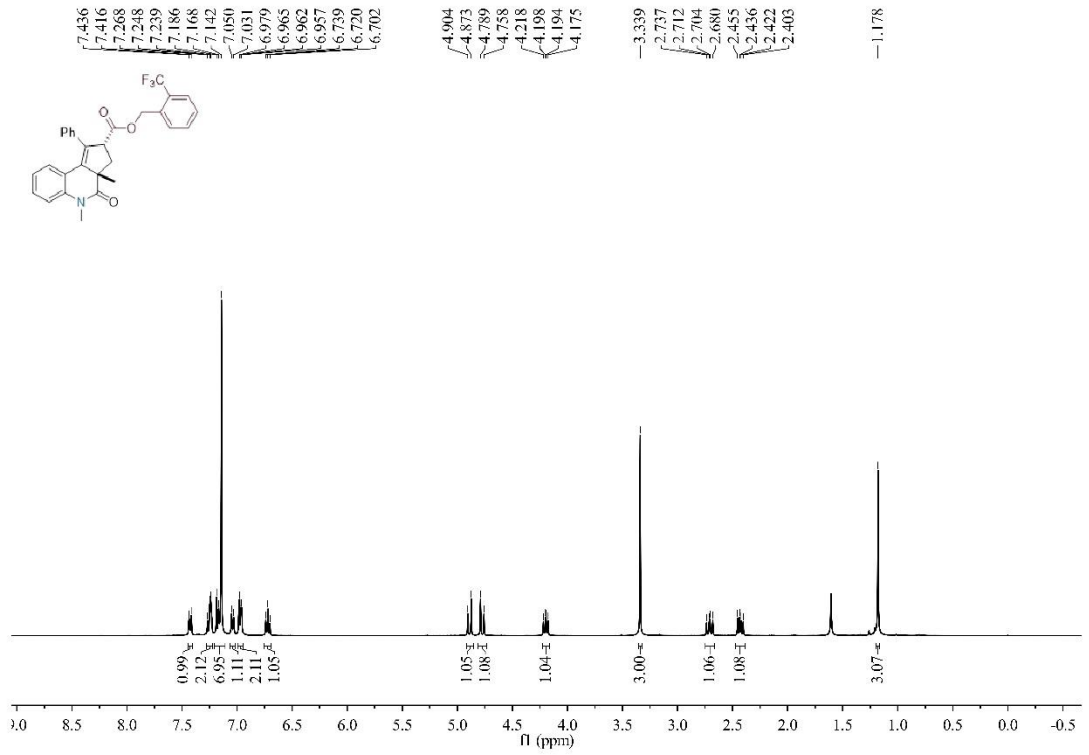
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3m** (100 MHz, $CDCl_3$)



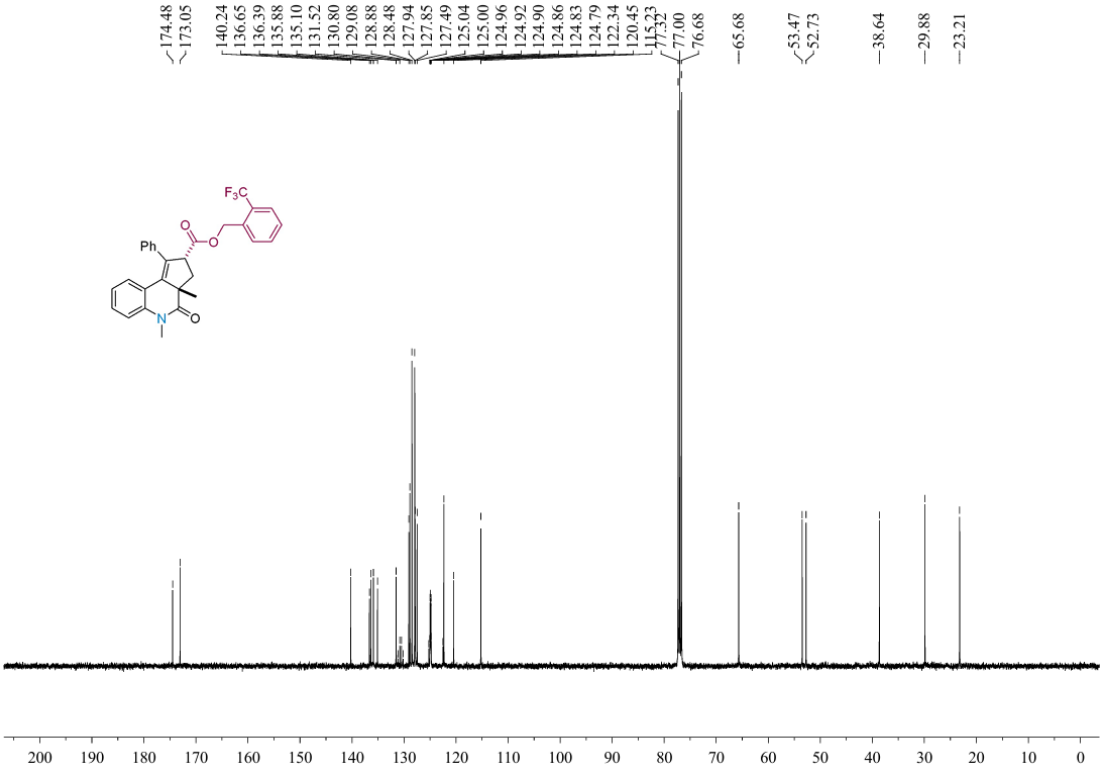
^{1}H NMR Spectrum of Compound ***cis*-3n** (400 MHz, $CDCl_3$)



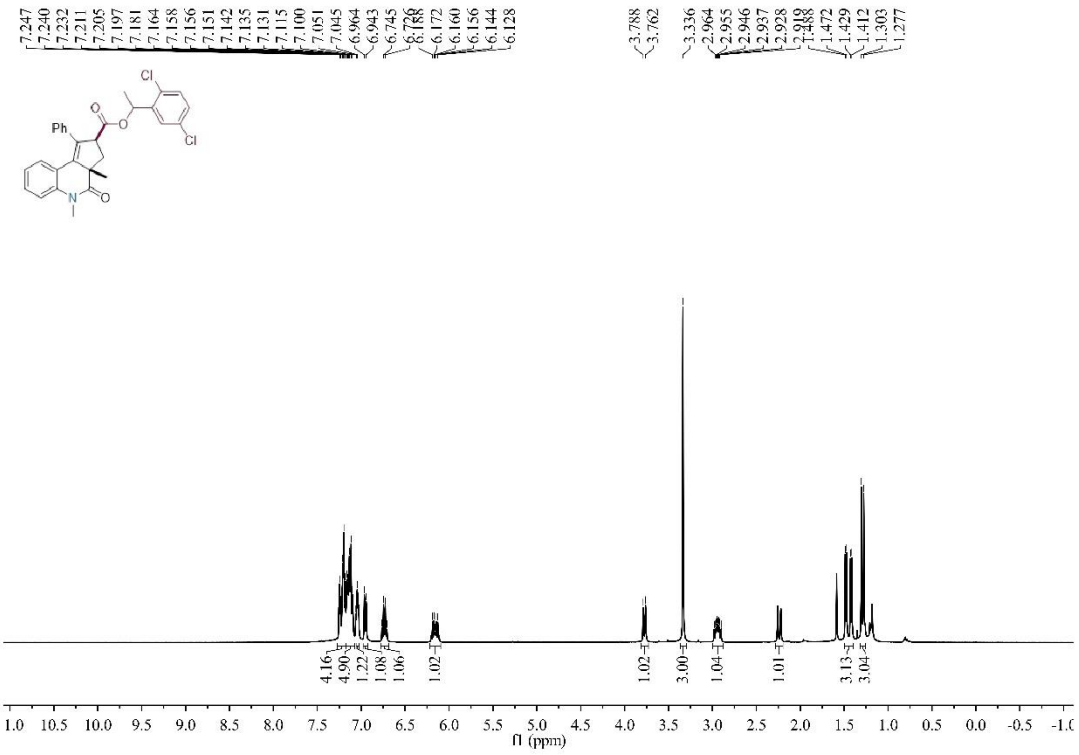
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3n** (100 MHz, $CDCl_3$)



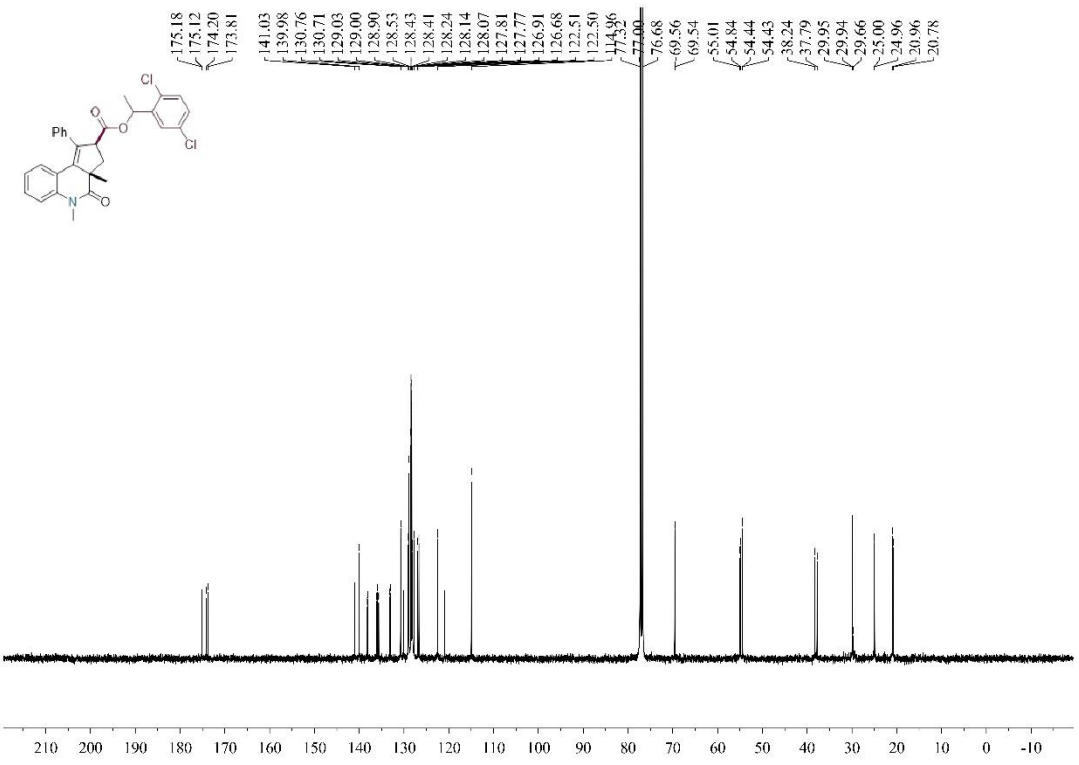
^{1}H NMR Spectrum of Compound ***trans*-3n** (400 MHz, $CDCl_3$)



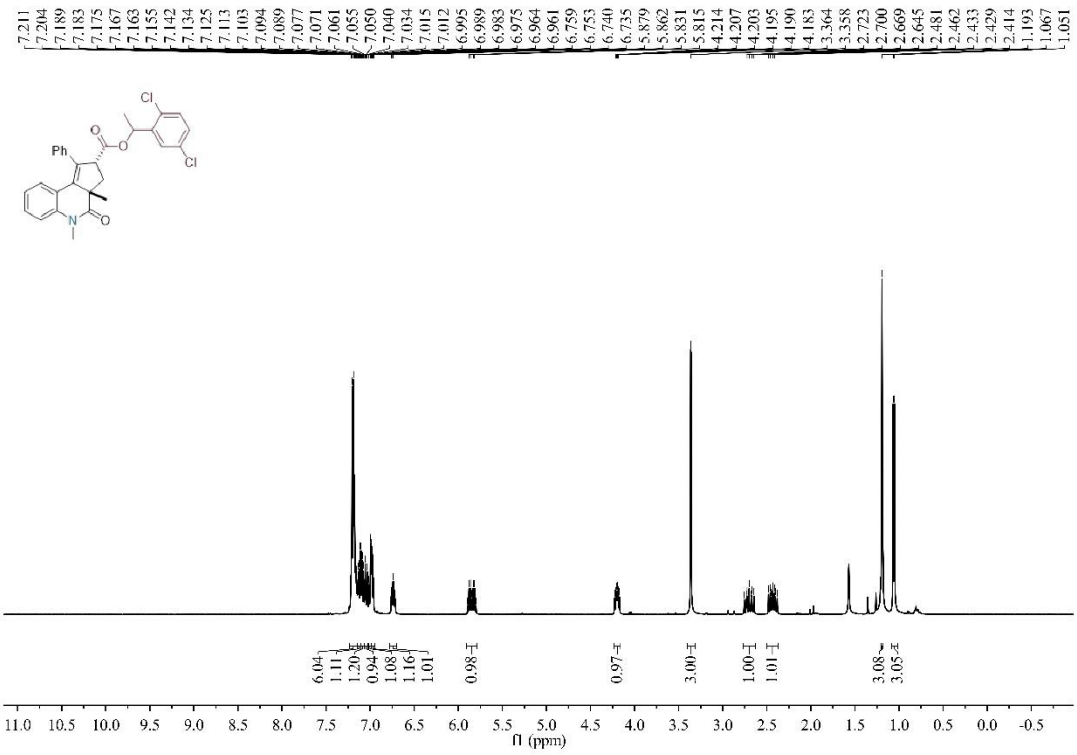
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3n** (100 MHz, $CDCl_3$)



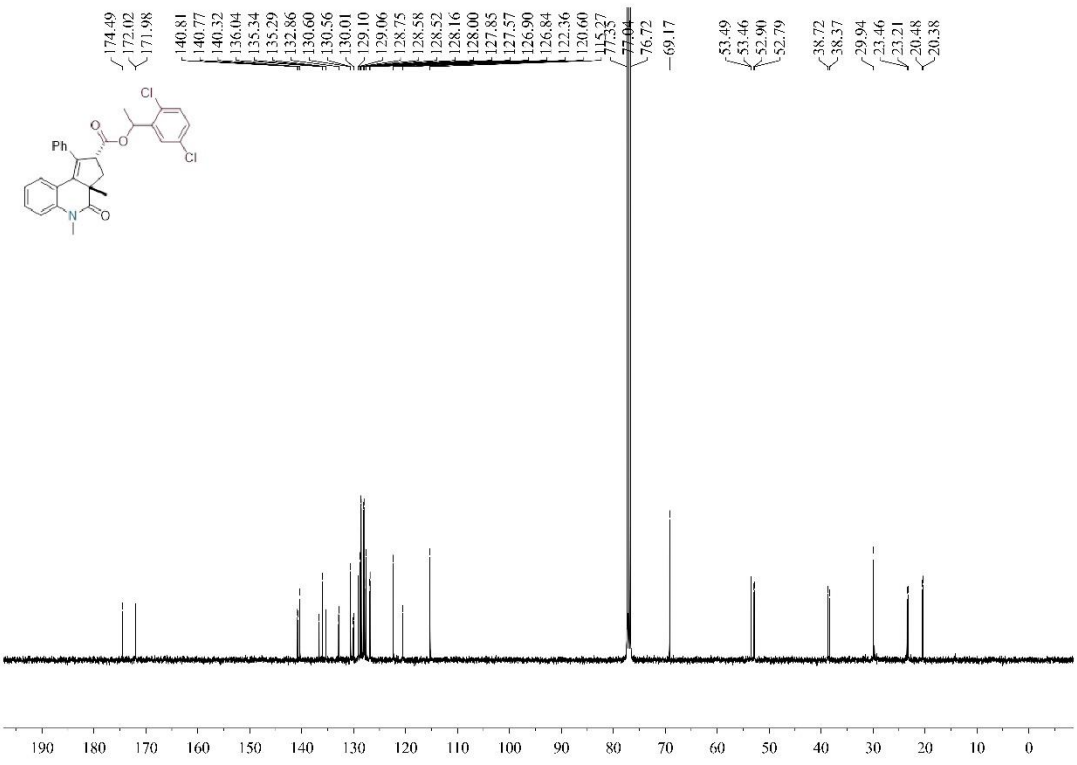
^{1}H NMR Spectrum of Compound ***cis*-3o** (400 MHz, $CDCl_3$)



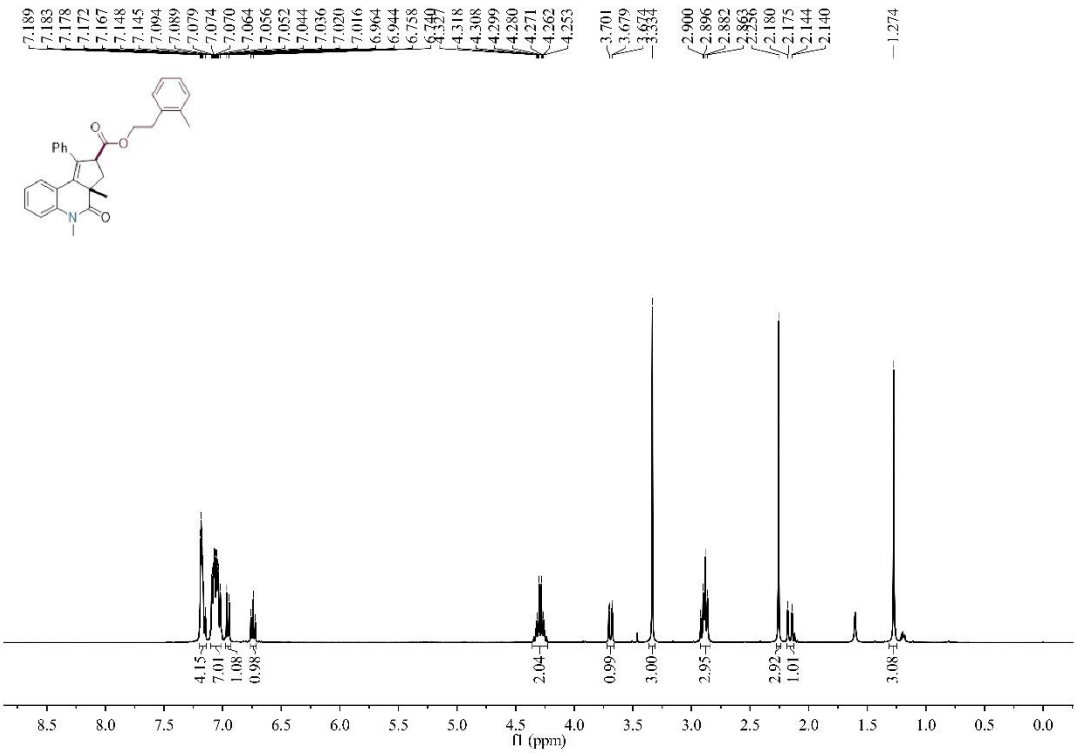
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-3o** (100 MHz, $CDCl_3$)



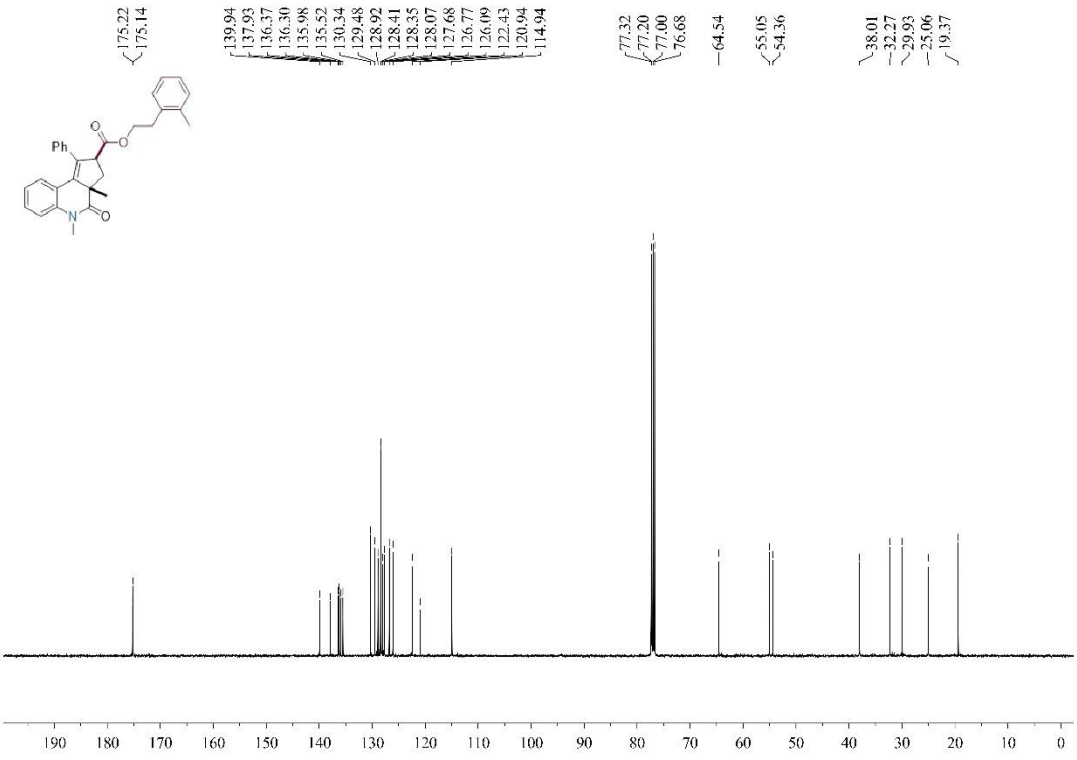
^{1}H NMR Spectrum of Compound ***trans*-3o** (400 MHz, $CDCl_3$)



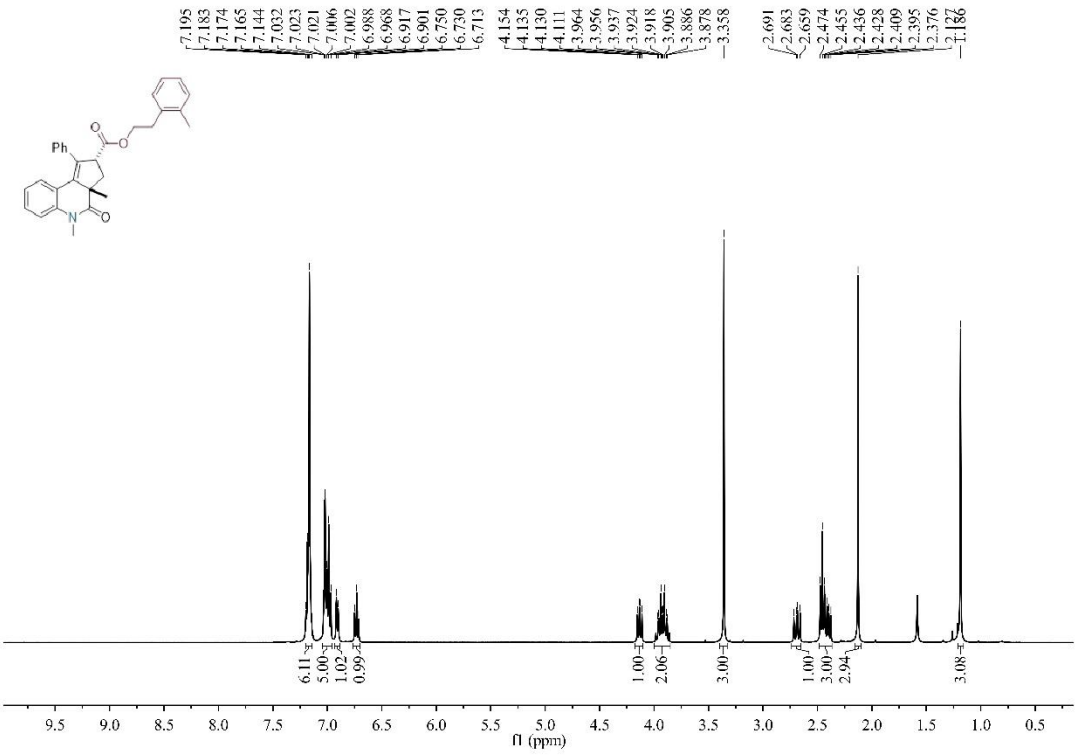
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3o** (100 MHz, $CDCl_3$)



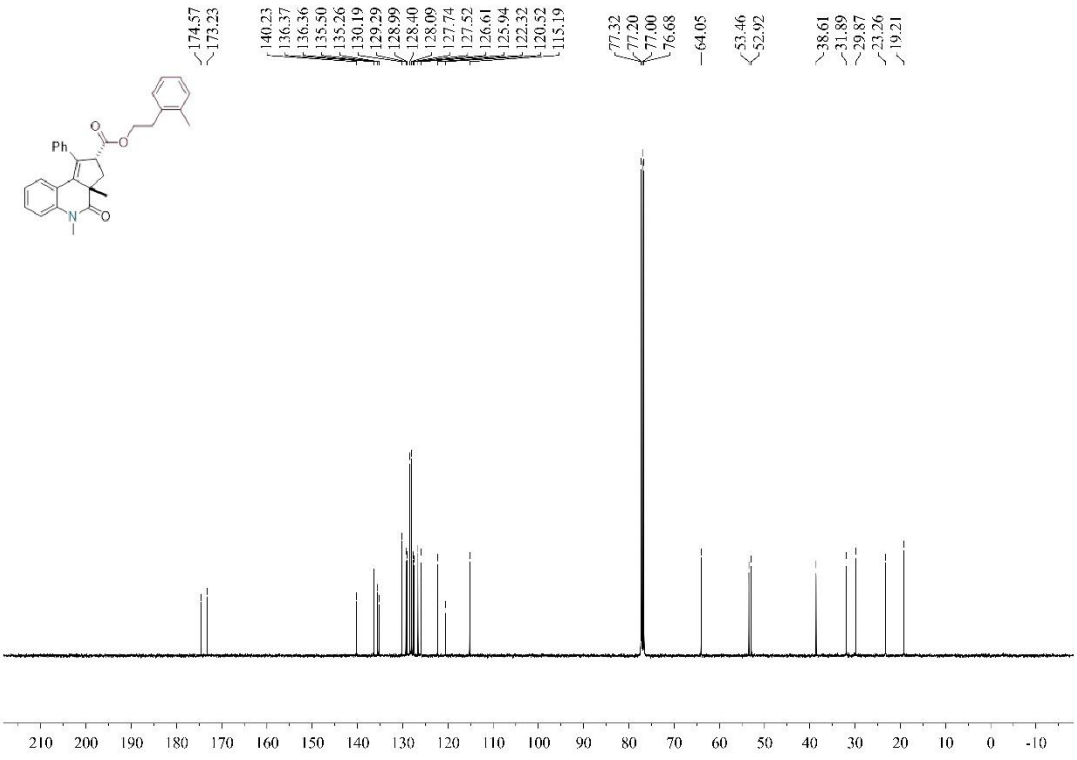
^{1}H NMR Spectrum of Compound ***cis*-3p** (400 MHz, $CDCl_3$)



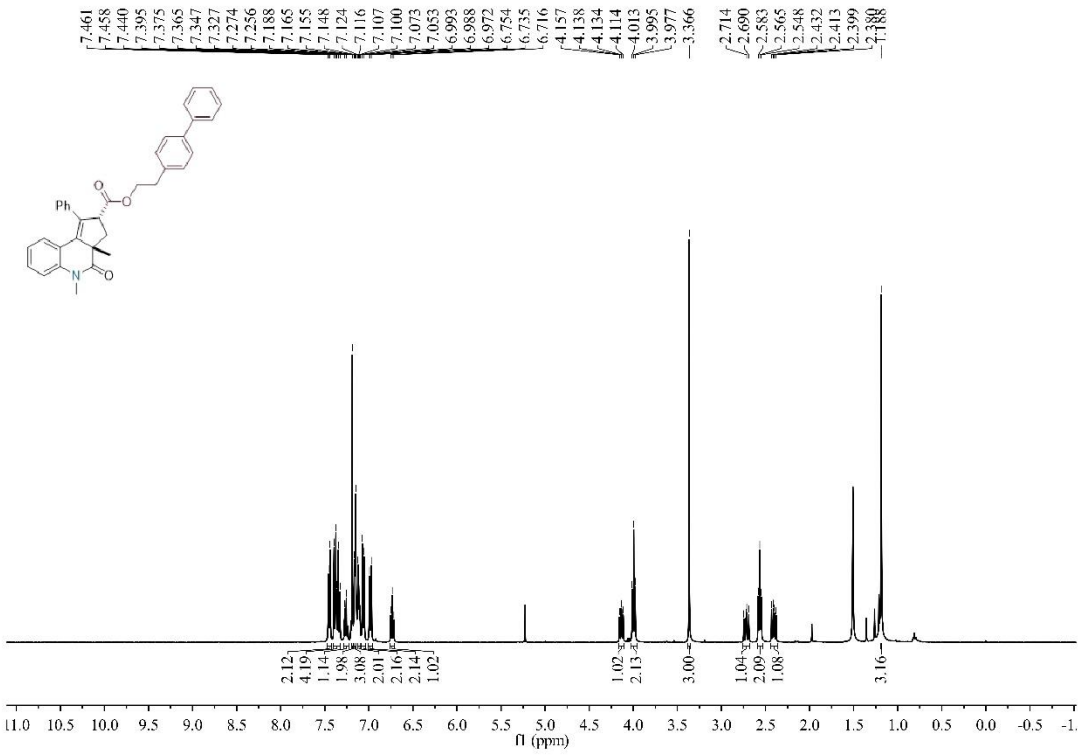
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3p** (100 MHz, $CDCl_3$)



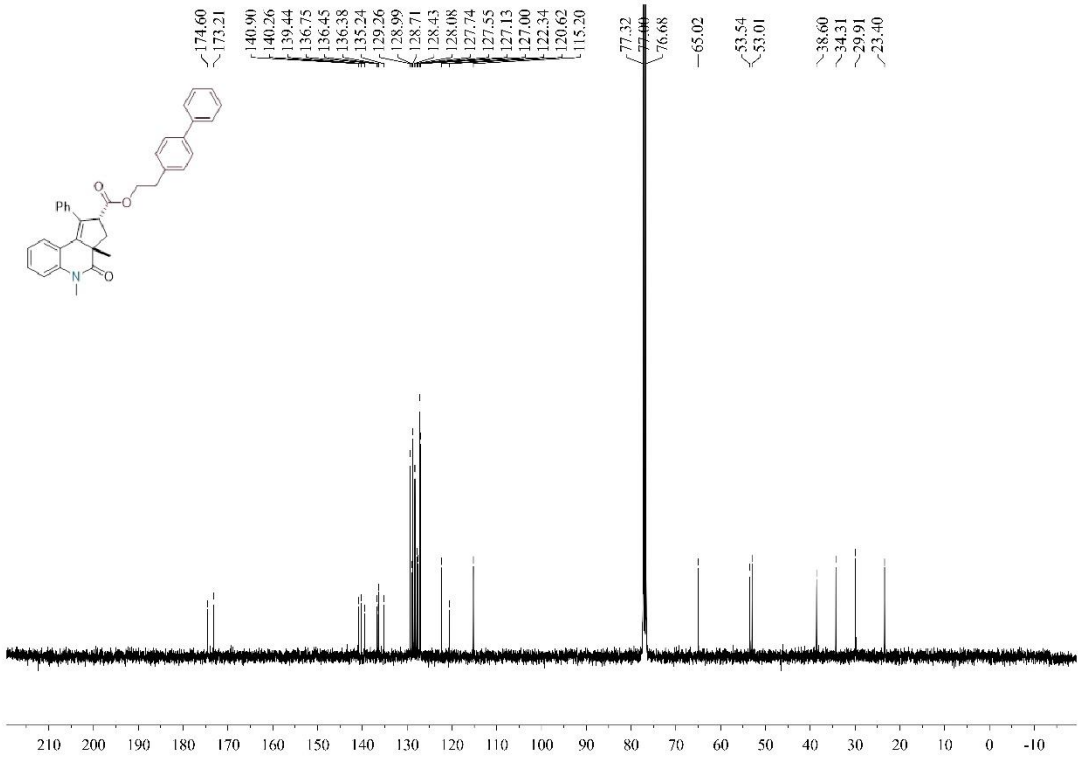
^{1}H NMR Spectrum of Compound ***trans*-3p** (400 MHz, $CDCl_3$)



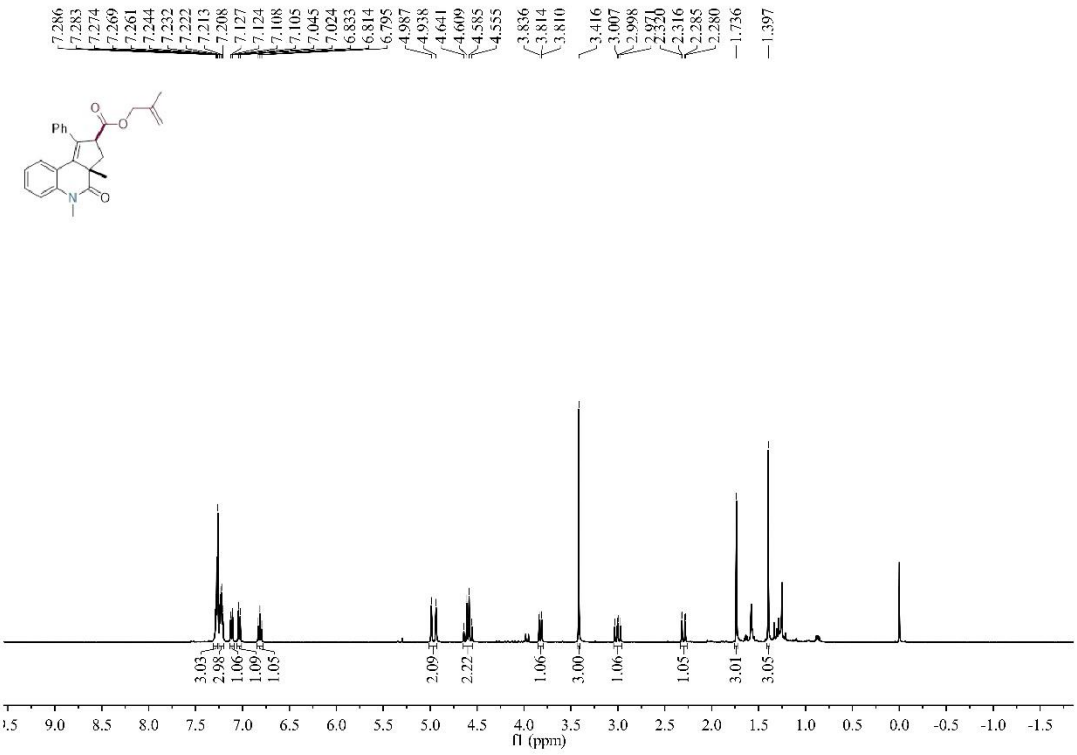
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3p** (100 MHz, $CDCl_3$)



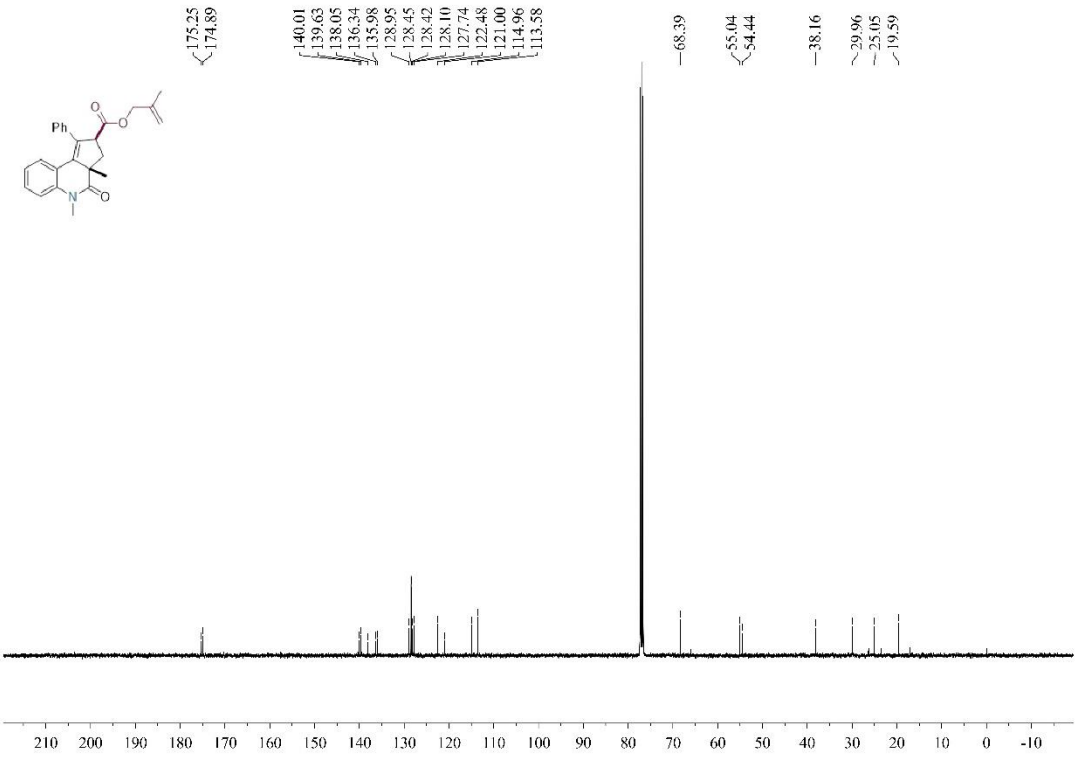
^{1}H NMR Spectrum of Compound ***trans*-3q** (400 MHz, $CDCl_3$)



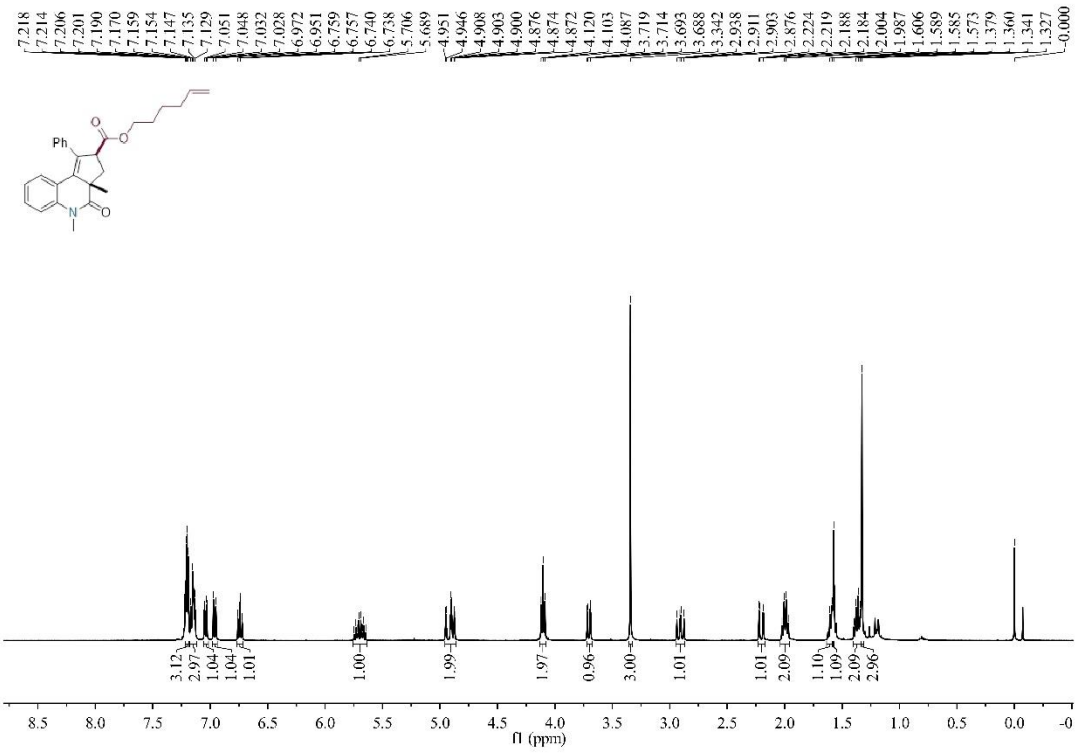
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3q** (100 MHz, $CDCl_3$)



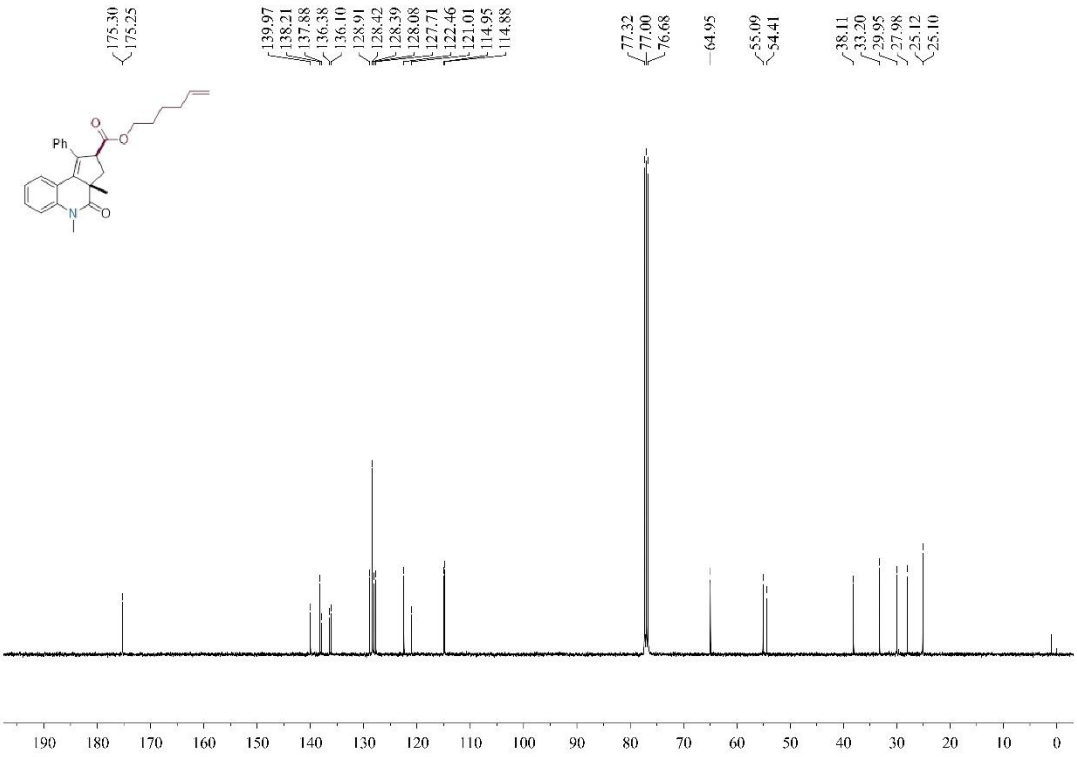
^{1}H NMR Spectrum of Compound ***cis*-3r** (400 MHz, $CDCl_3$)



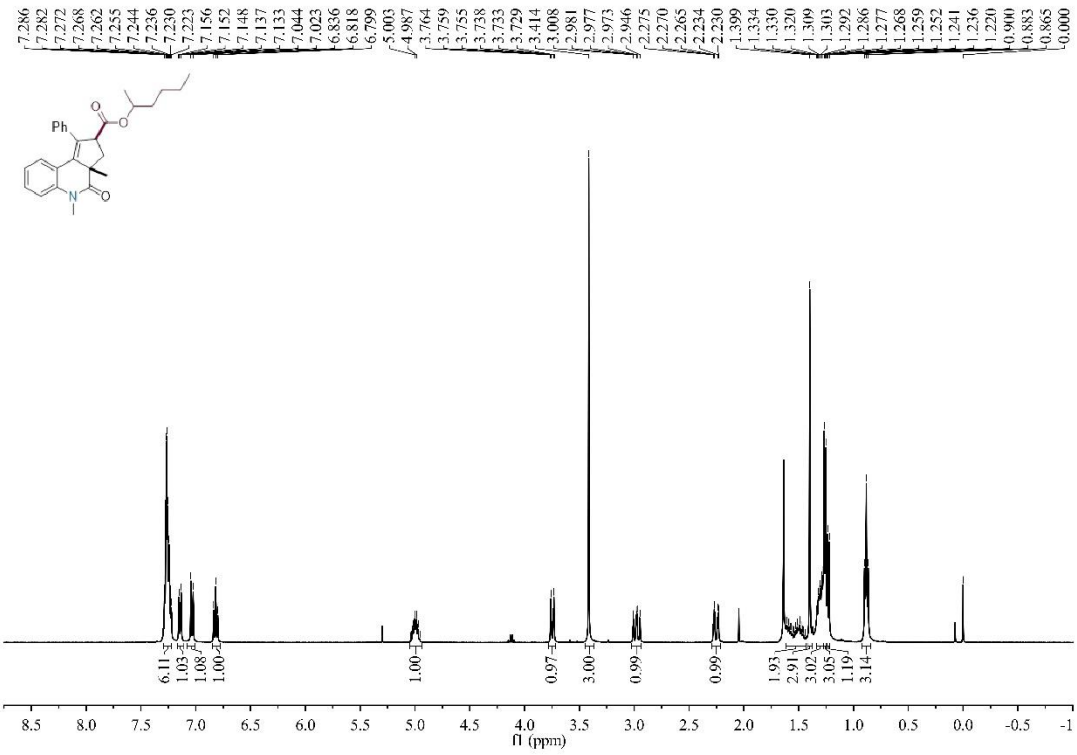
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3r** (100 MHz, $CDCl_3$)



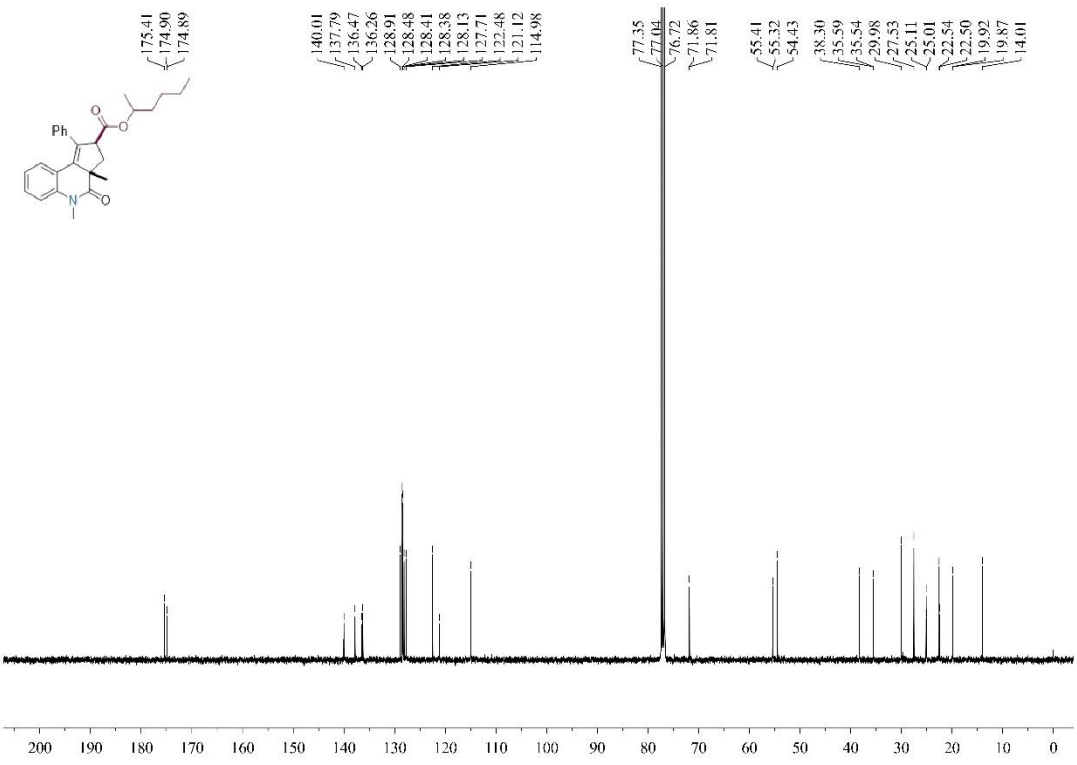
^{1}H NMR Spectrum of Compound ***cis*-3s** (400 MHz, $CDCl_3$)



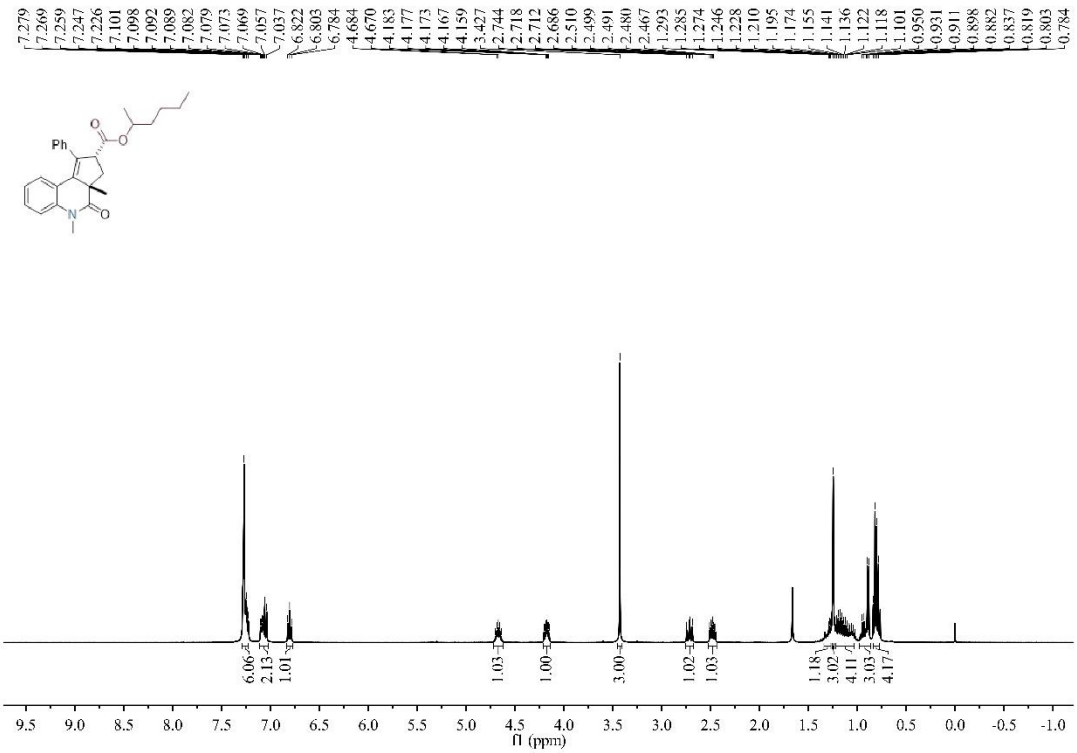
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3s** (100 MHz, $CDCl_3$)



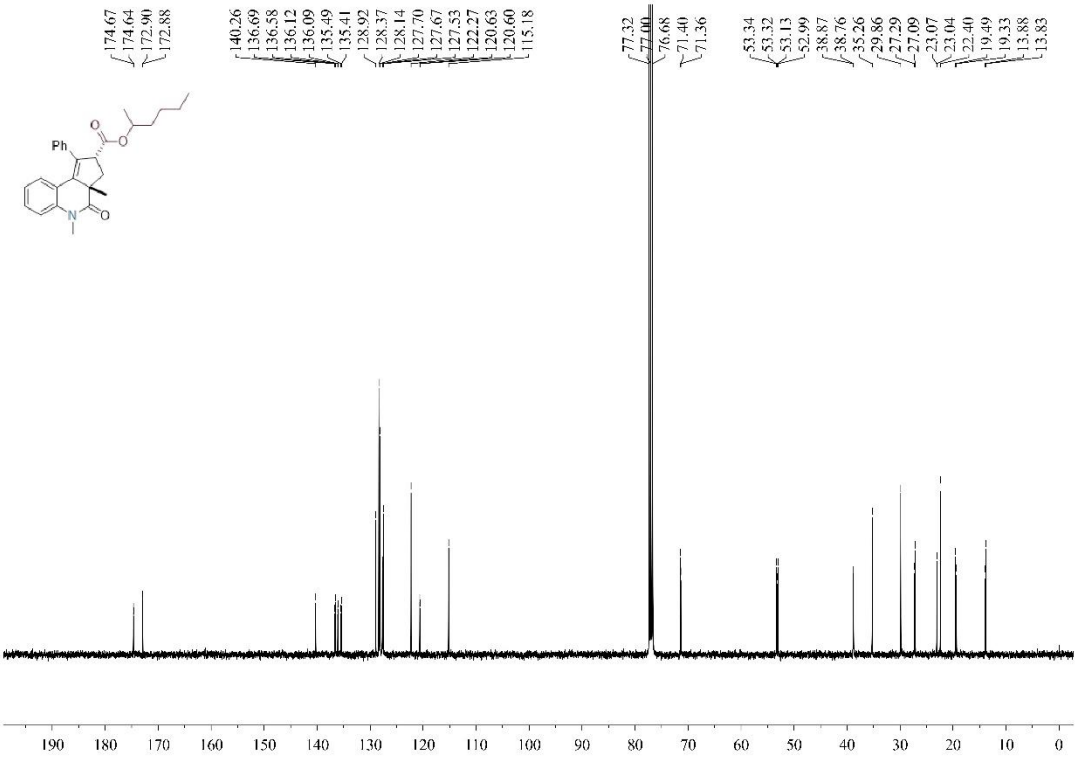
^{1}H NMR Spectrum of Compound ***cis*-3t** (400 MHz, $CDCl_3$)



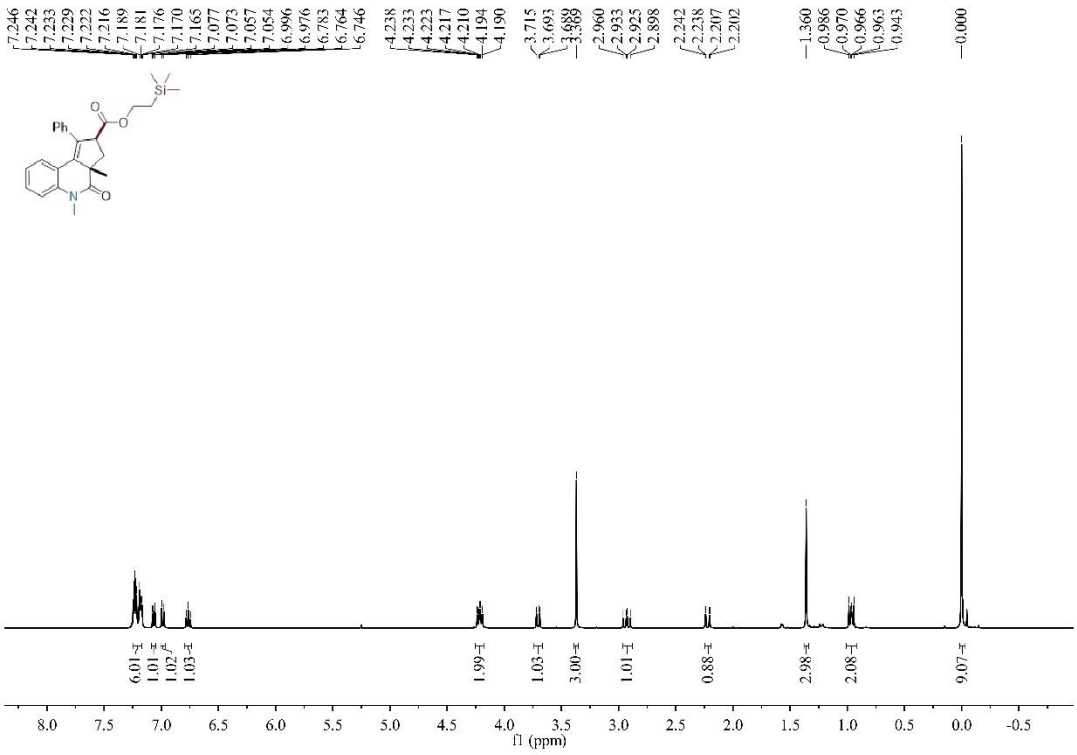
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-3t** (100 MHz, $CDCl_3$)



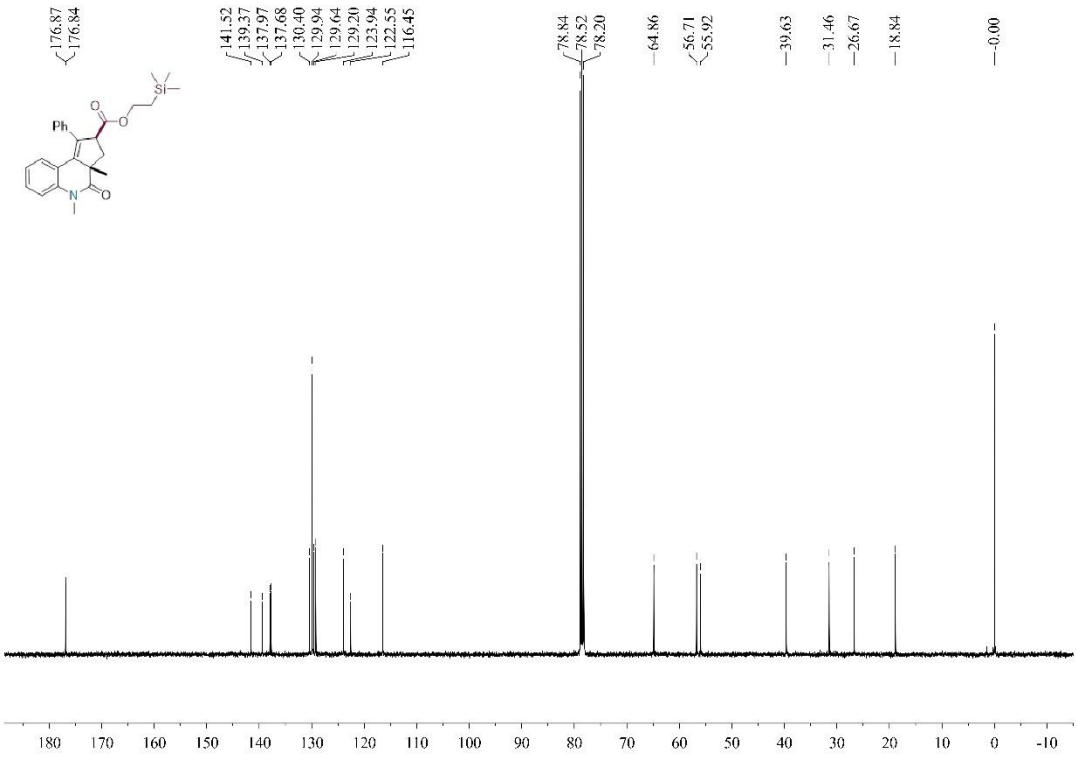
^{1}H NMR Spectrum of Compound ***trans*-3t** (400 MHz, $CDCl_3$)



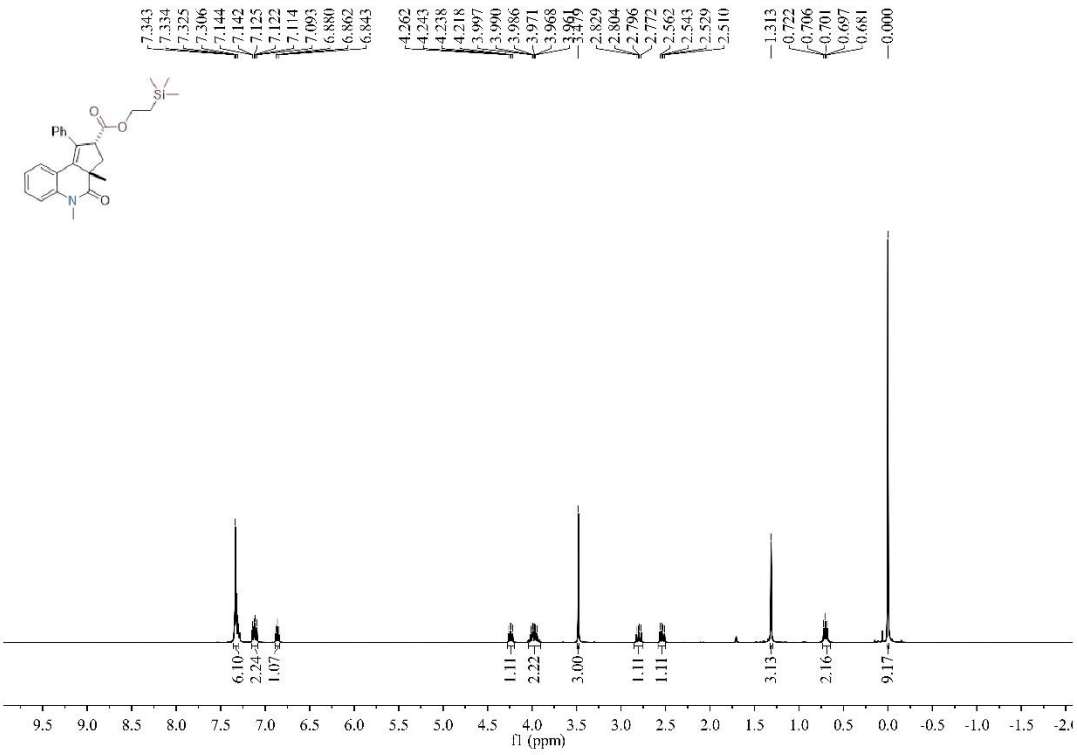
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3t** (100 MHz, $CDCl_3$)



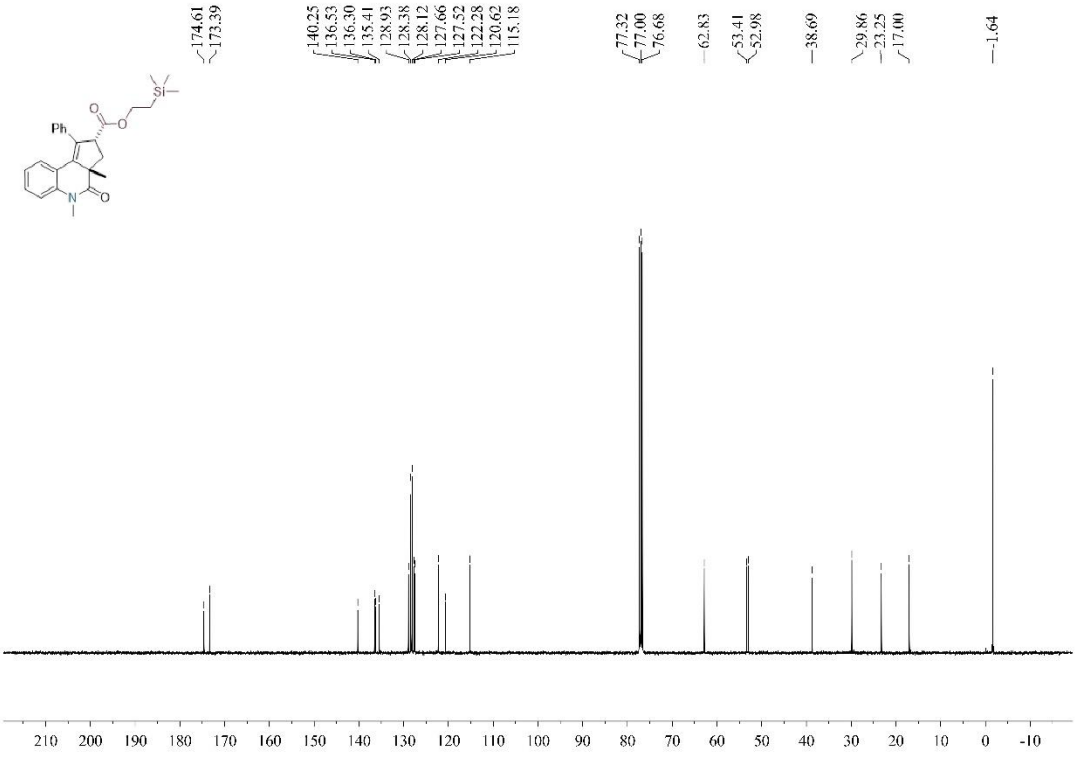
1H NMR Spectrum of Compound ***cis*-3u** (400 MHz, CDCl3)



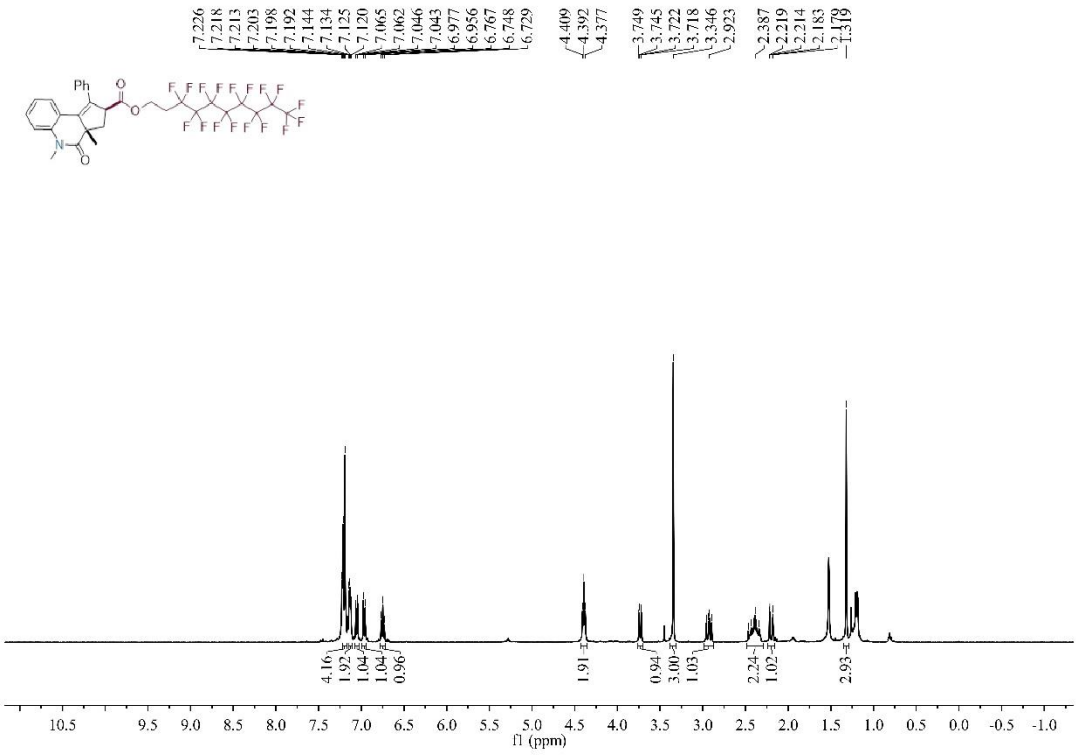
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-3u** (100 MHz, $CDCl_3$)



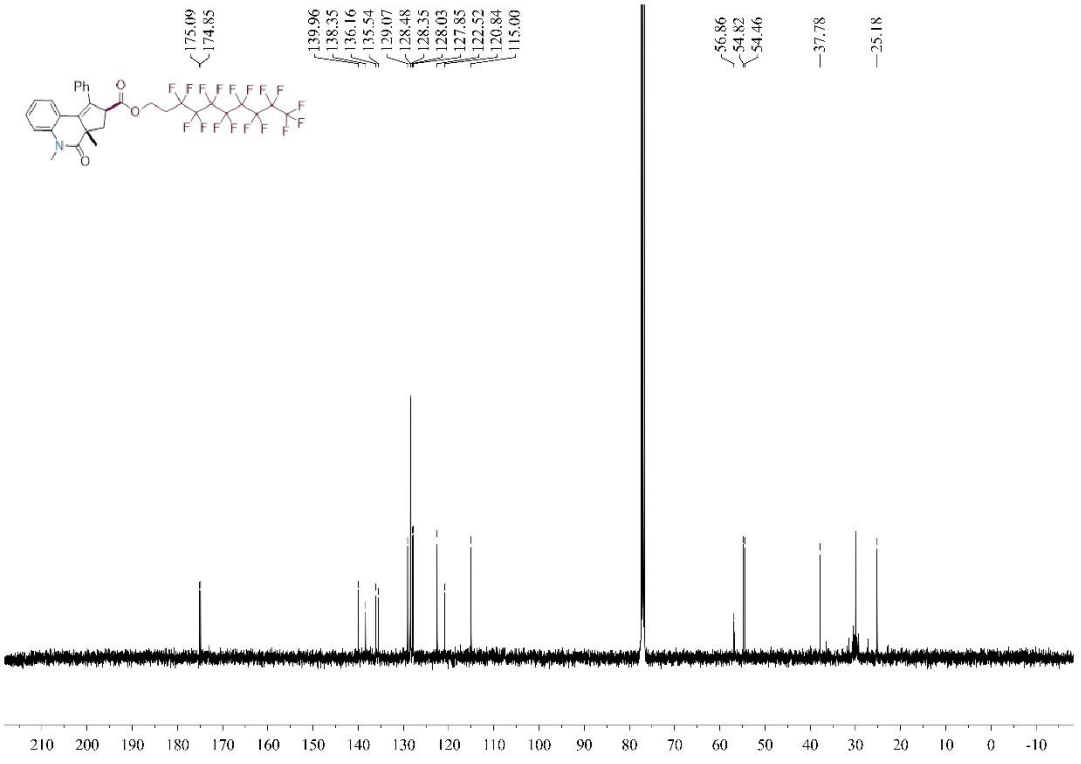
^{1}H NMR Spectrum of Compound ***trans*-3u** (400 MHz, $CDCl_3$)



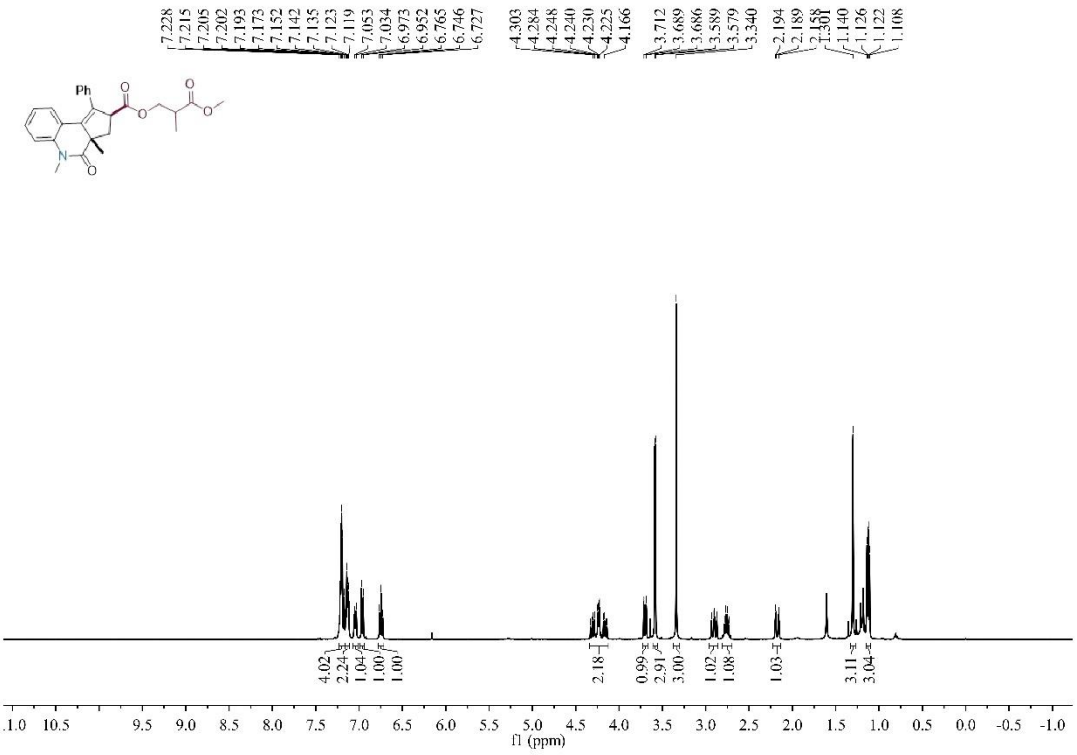
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-3u** (100 MHz, $CDCl_3$)



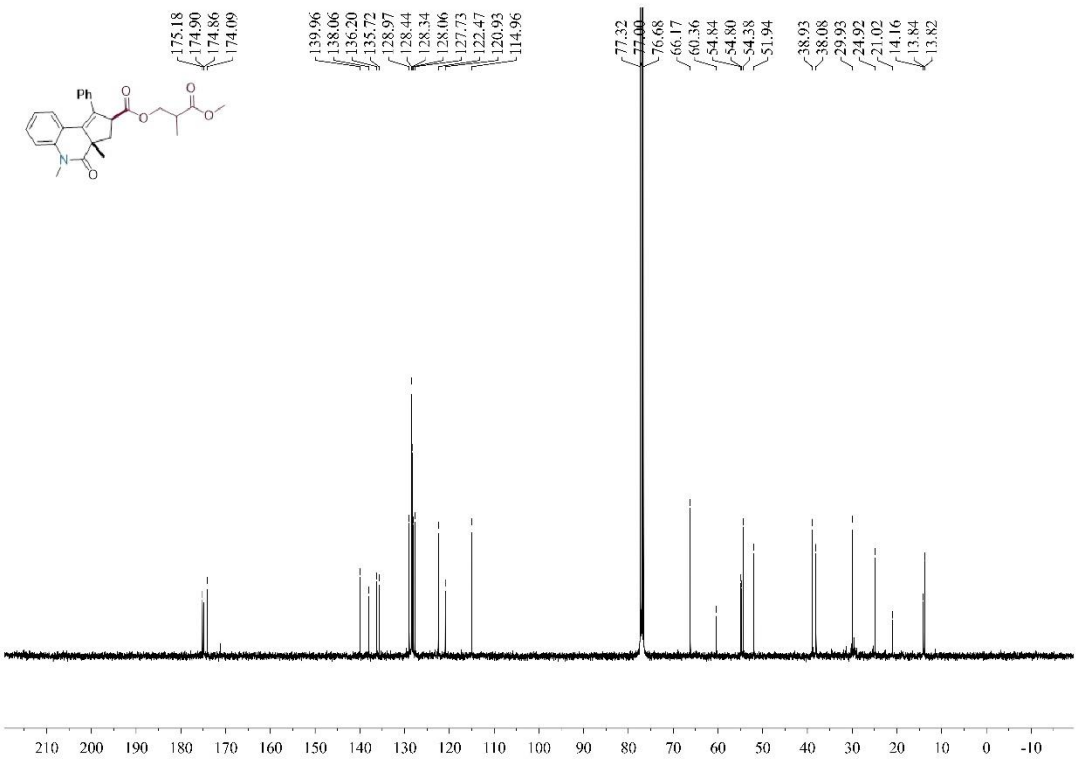
^{1}H NMR Spectrum of Compound ***cis*-3v** (400 MHz, $CDCl_3$)



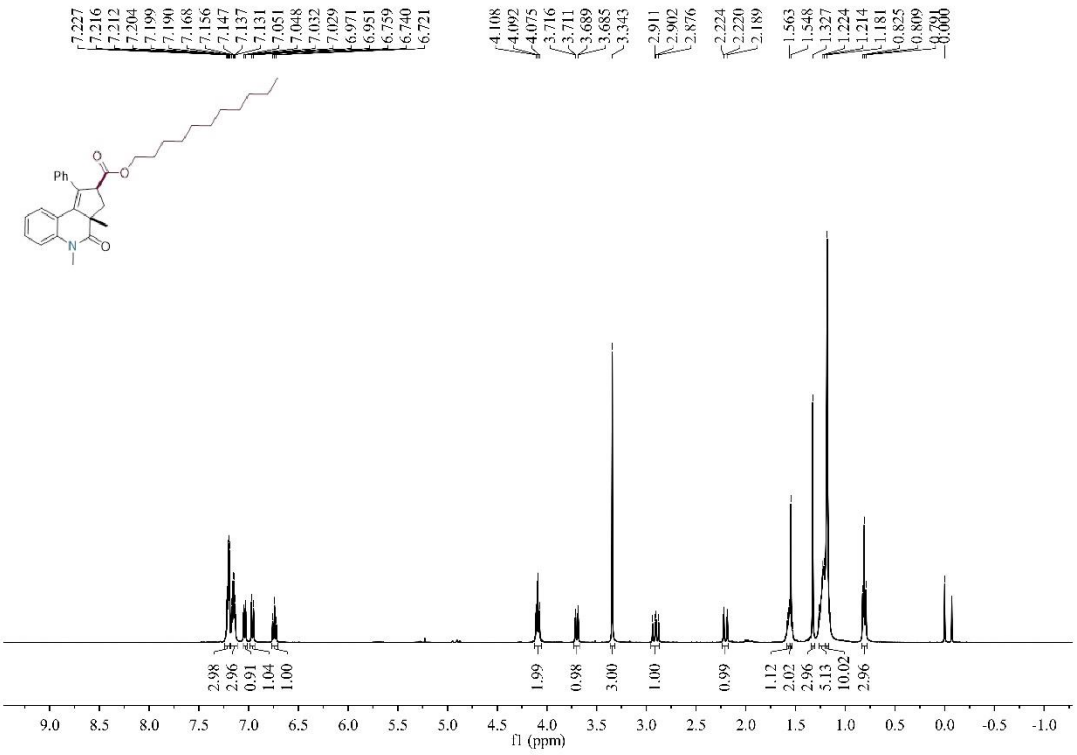
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3v** (100 MHz, $CDCl_3$)



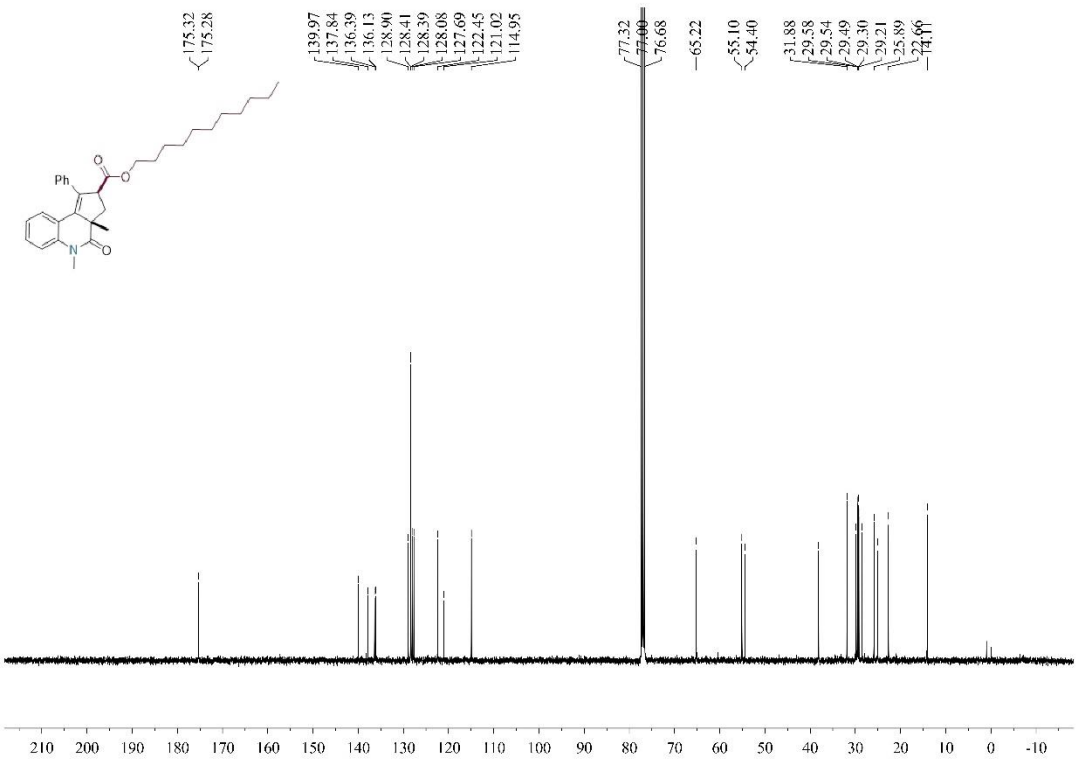
^{1}H NMR Spectrum of Compound ***cis*-3w** (400 MHz, $CDCl_3$)



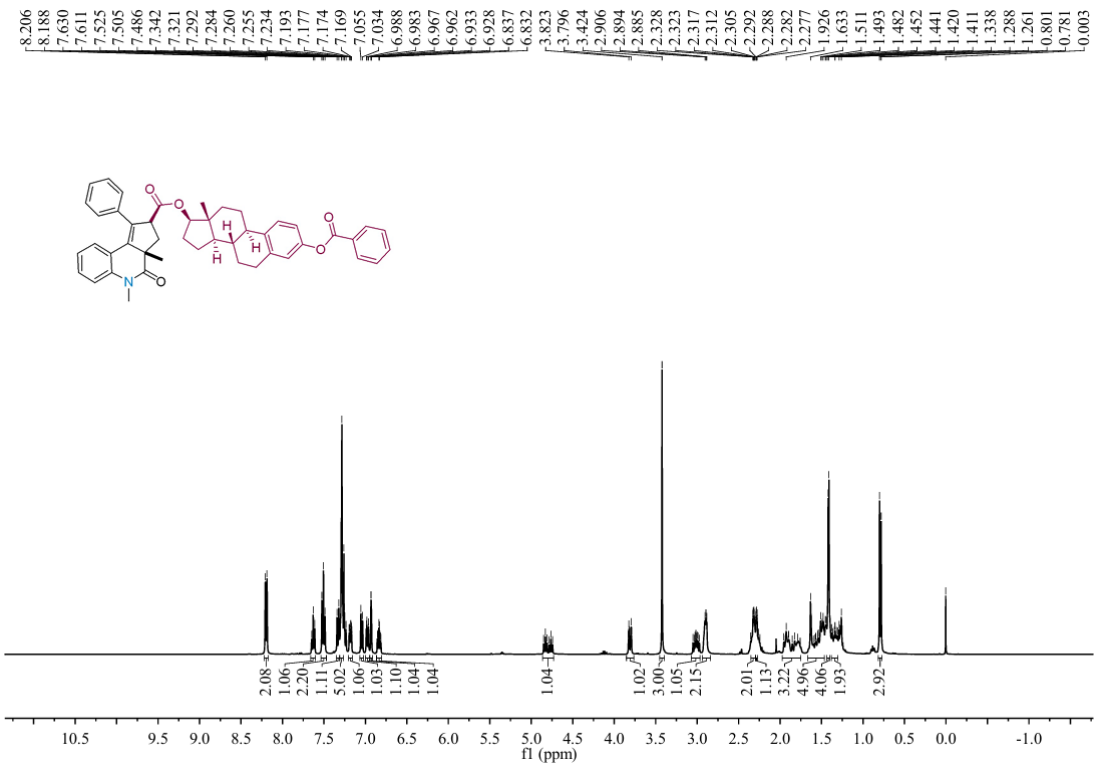
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3w** (100 MHz, $CDCl_3$)



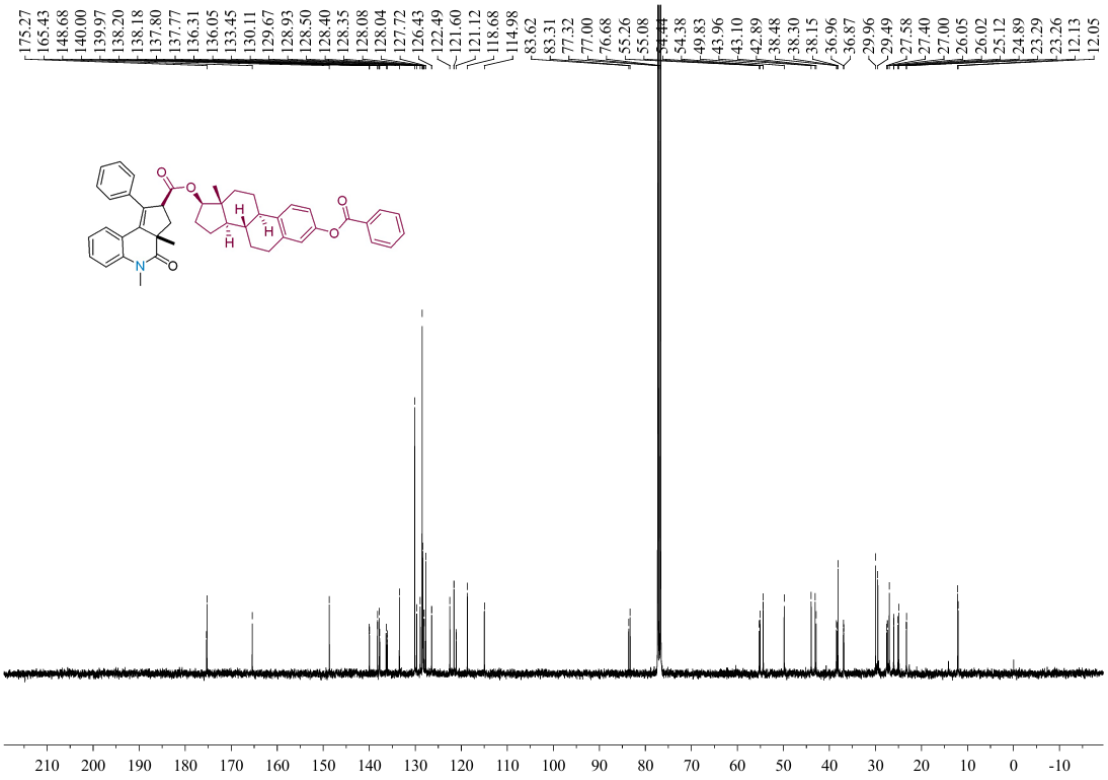
^{1}H NMR Spectrum of Compound ***cis*-3x** (400 MHz, $CDCl_3$)



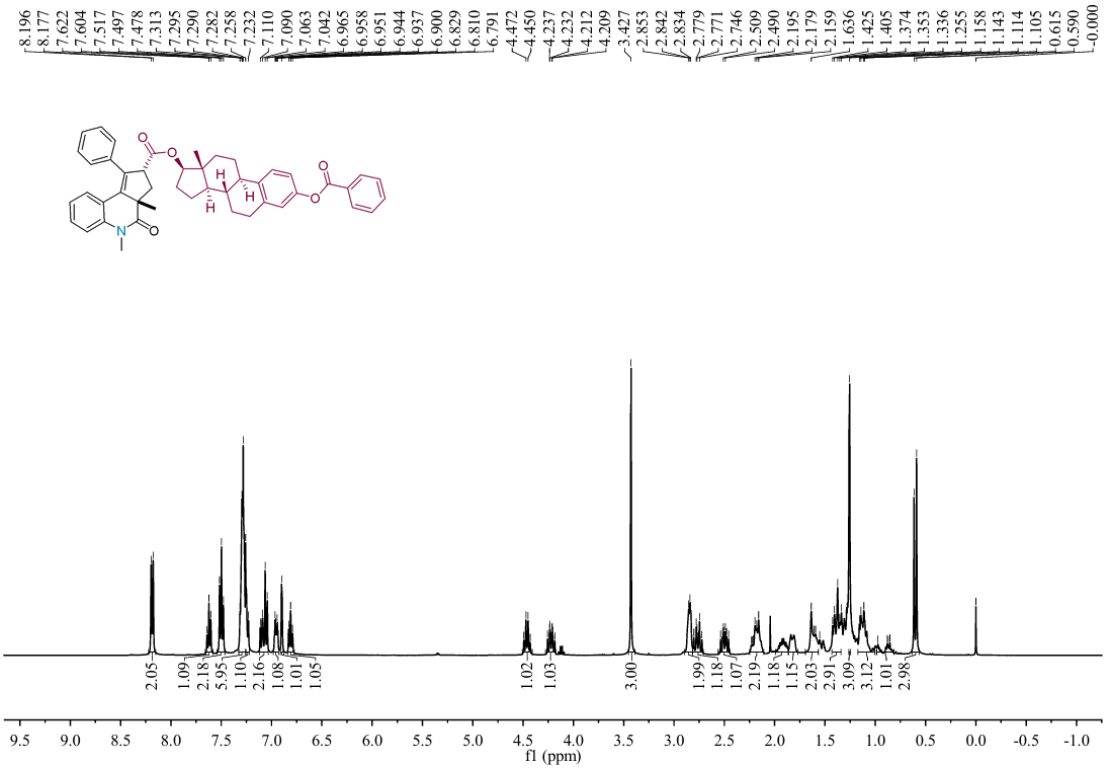
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-3x** (100 MHz, $CDCl_3$)



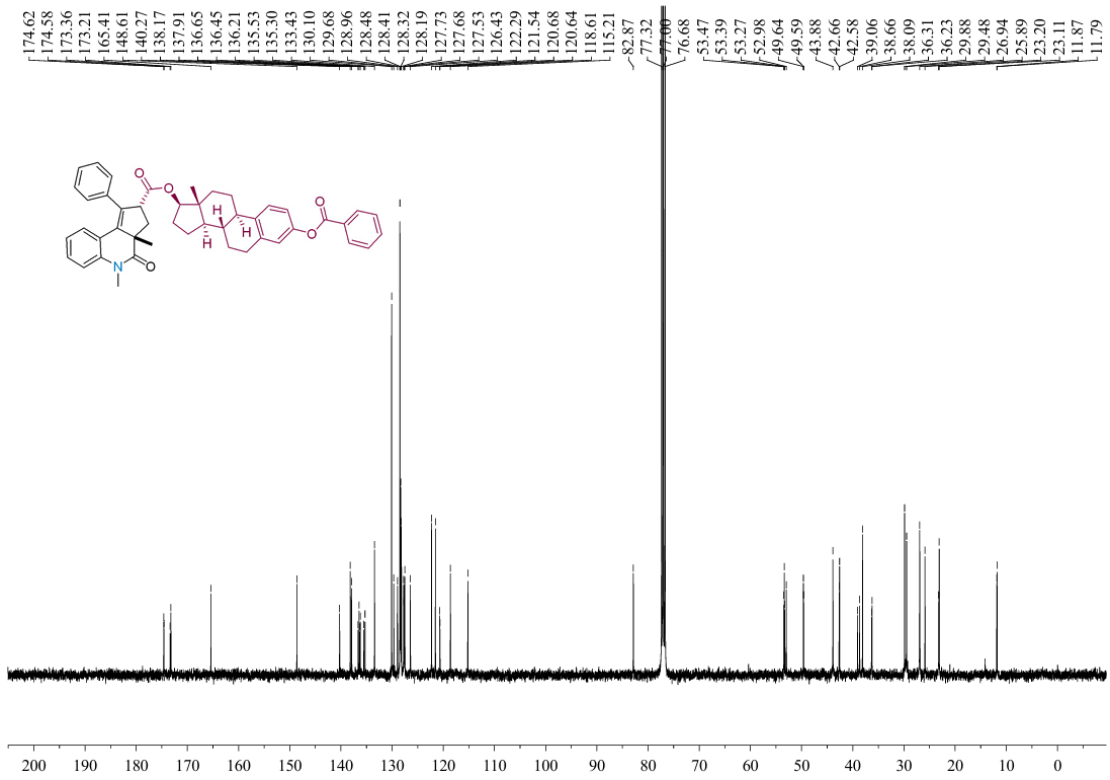
^{1}H NMR Spectrum of Compound ***cis*-4a** (400 MHz, $CDCl_3$)



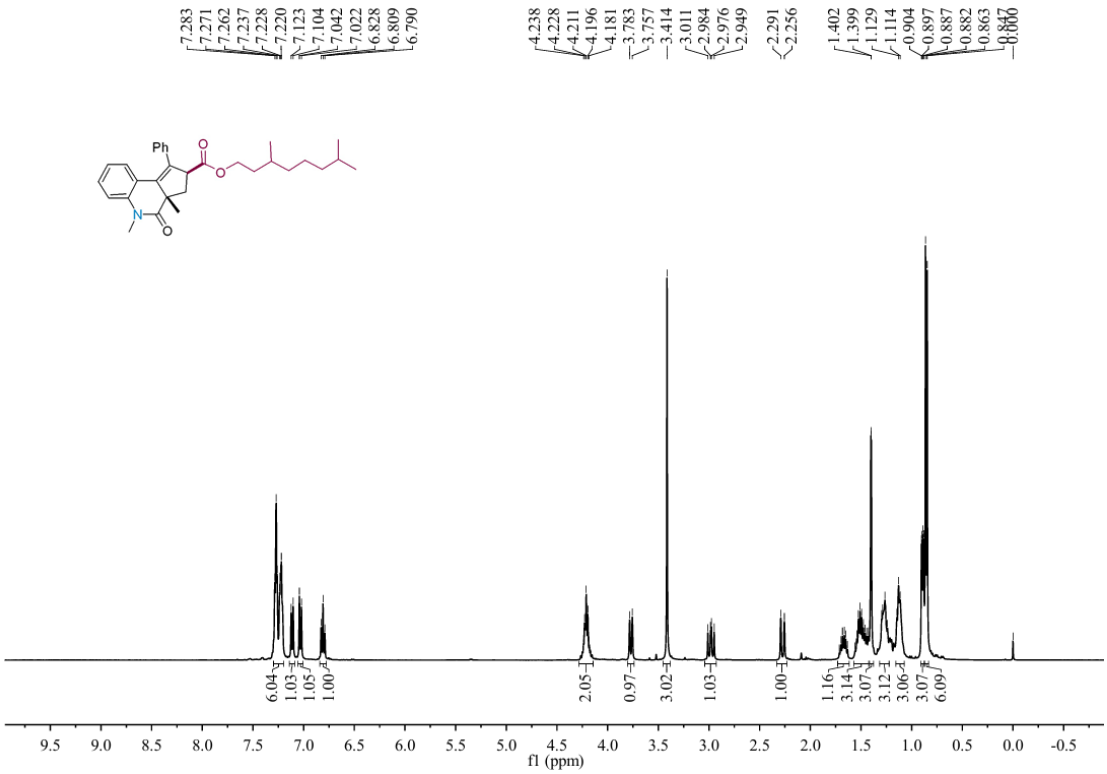
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-4a** (100 MHz, $CDCl_3$)



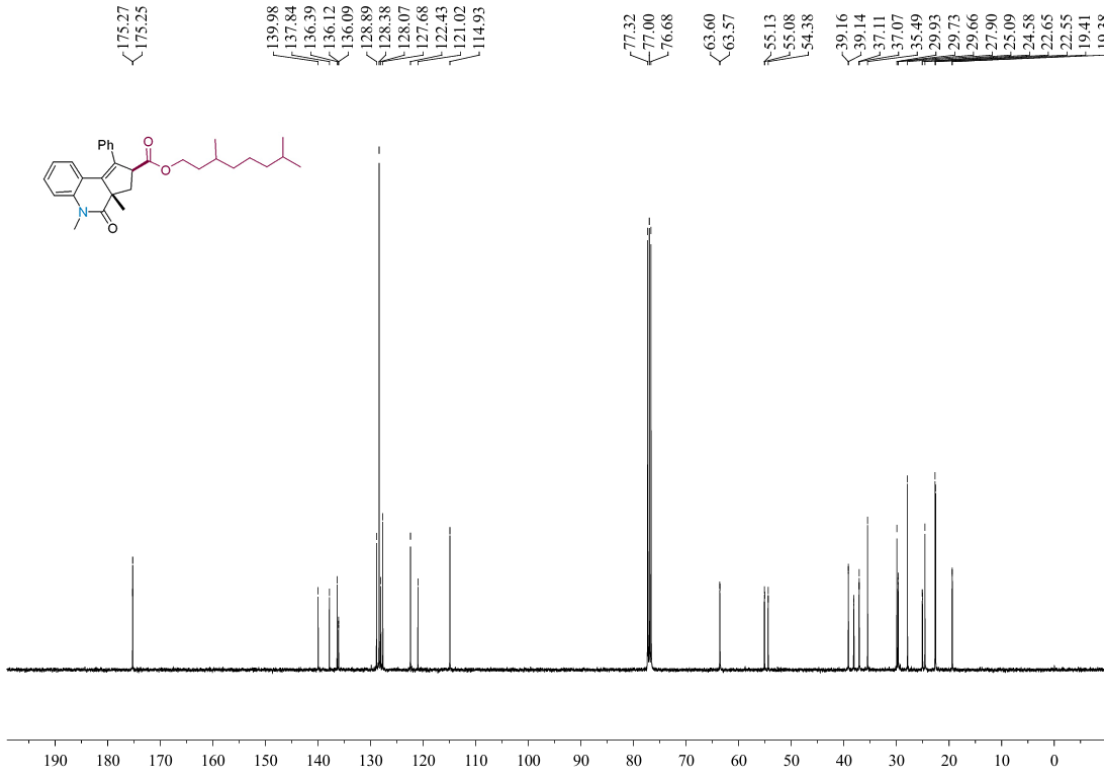
^{1}H NMR Spectrum of Compound ***trans*-4a** (400 MHz, $CDCl_3$)



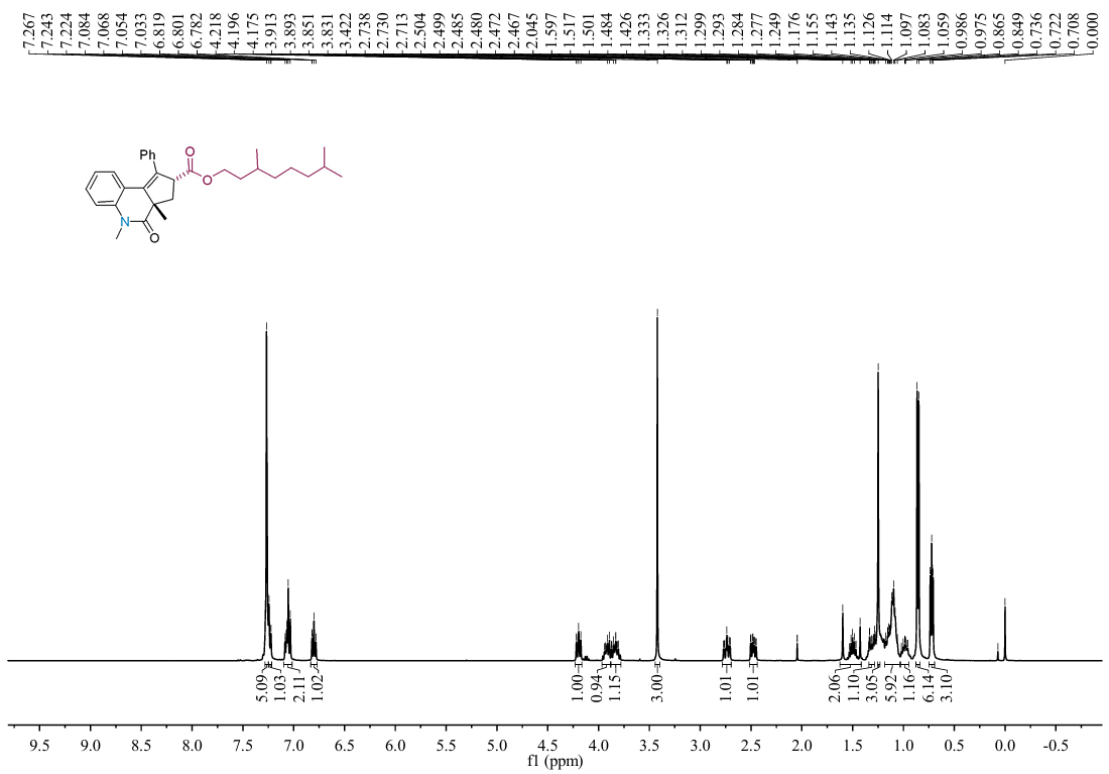
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4a** (100 MHz, $CDCl_3$)



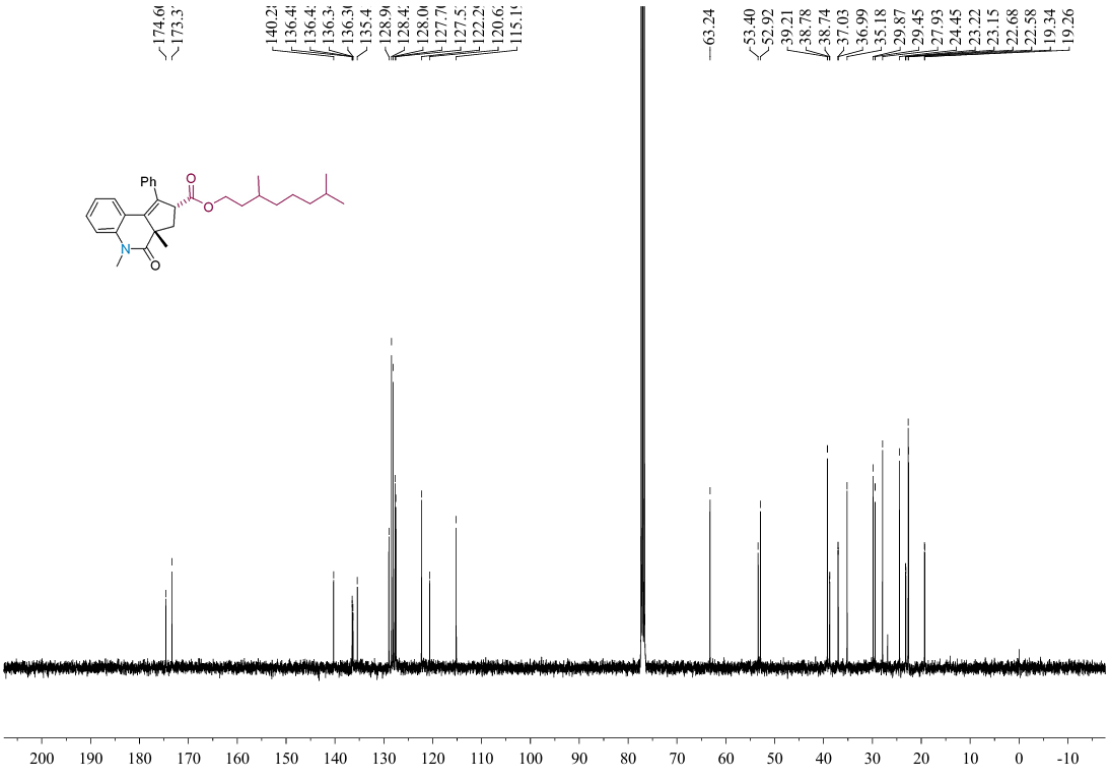
^{1}H NMR Spectrum of Compound ***cis*-4b** (400 MHz, $CDCl_3$)



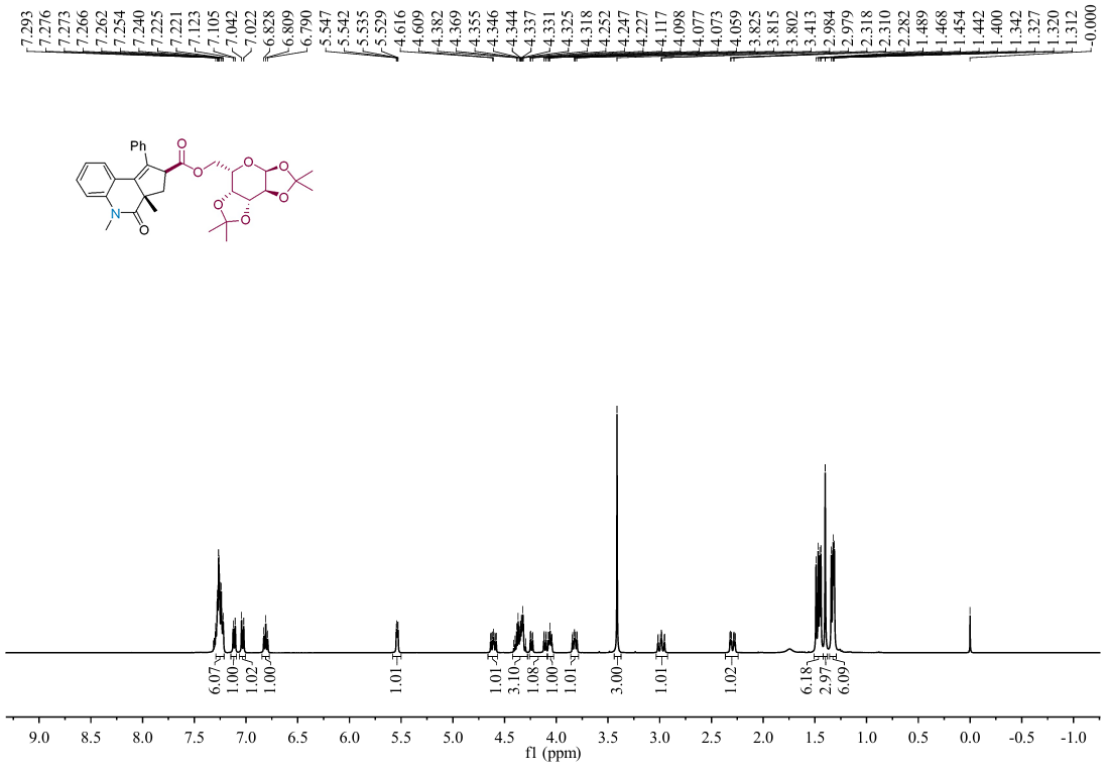
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-4b** (100 MHz, $CDCl_3$)



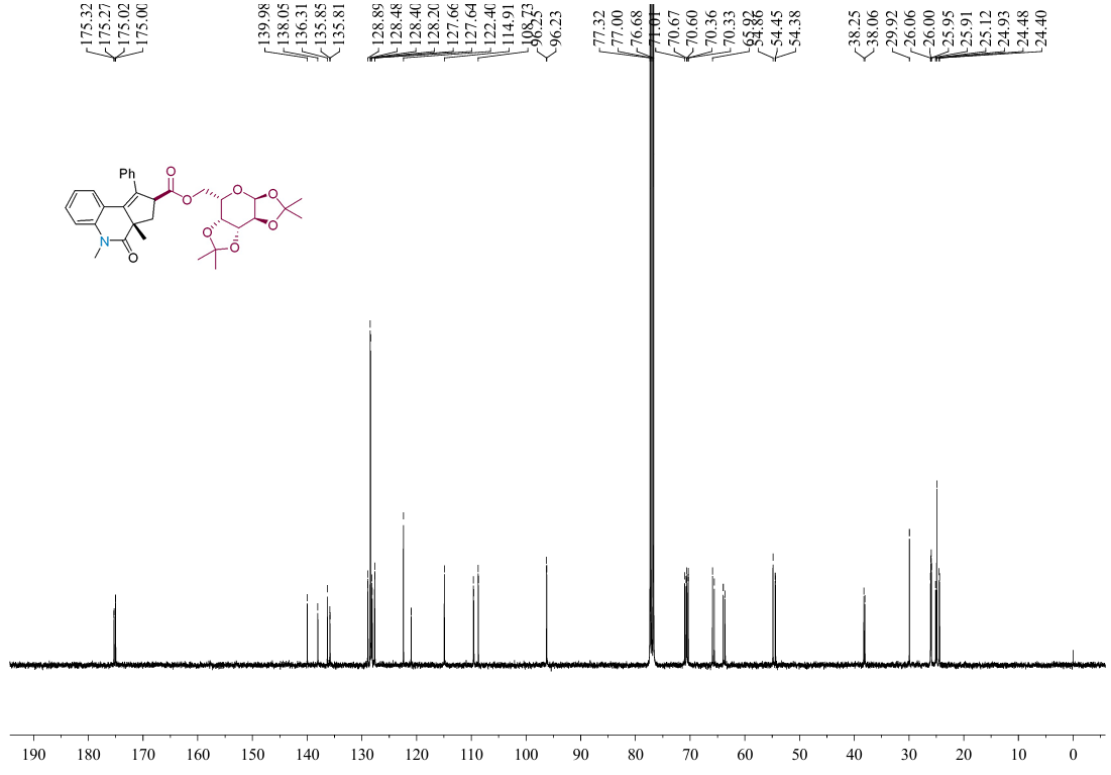
^{1}H NMR Spectrum of Compound ***trans*-4b** (400 MHz, $CDCl_3$)



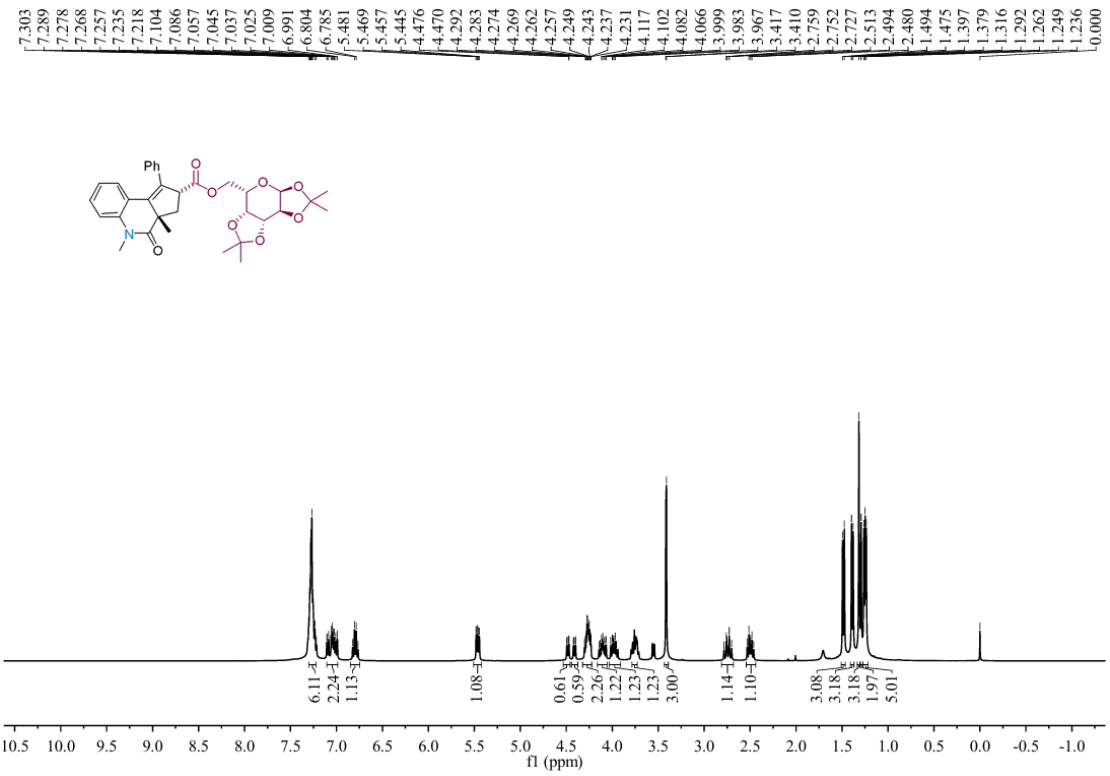
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4b** (100 MHz, $CDCl_3$)



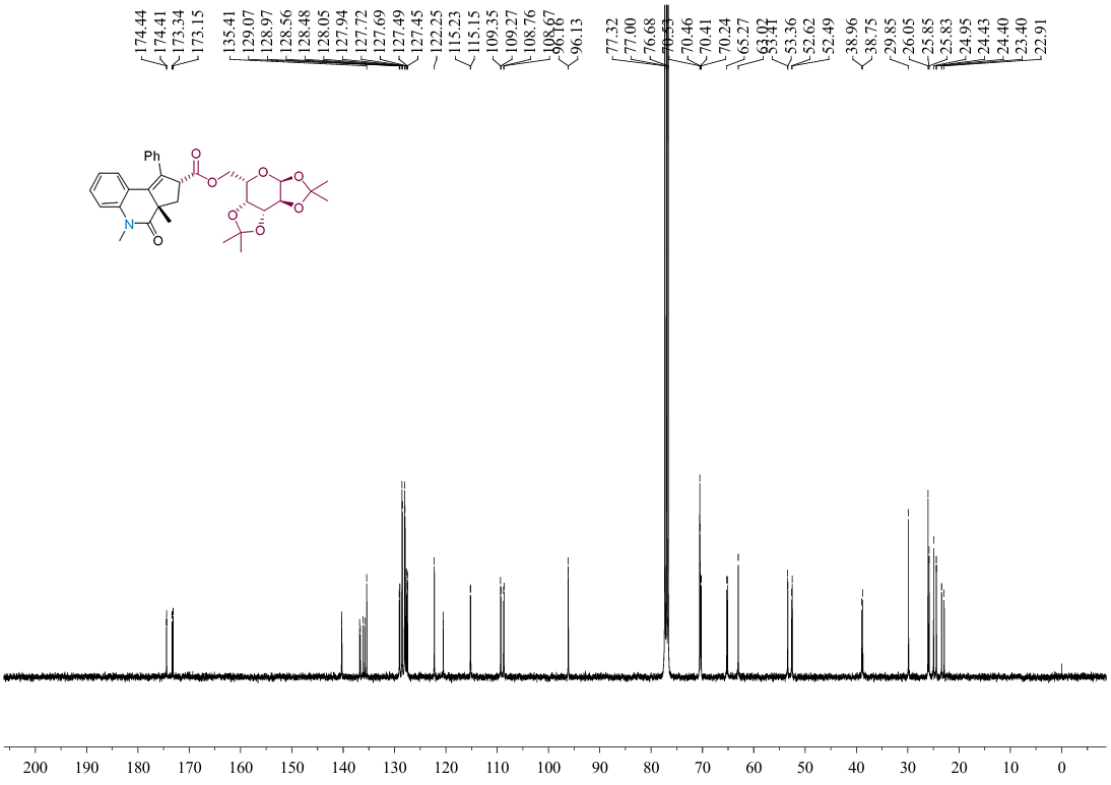
^{1}H NMR Spectrum of Compound ***cis*-4c** (400 MHz, $CDCl_3$)



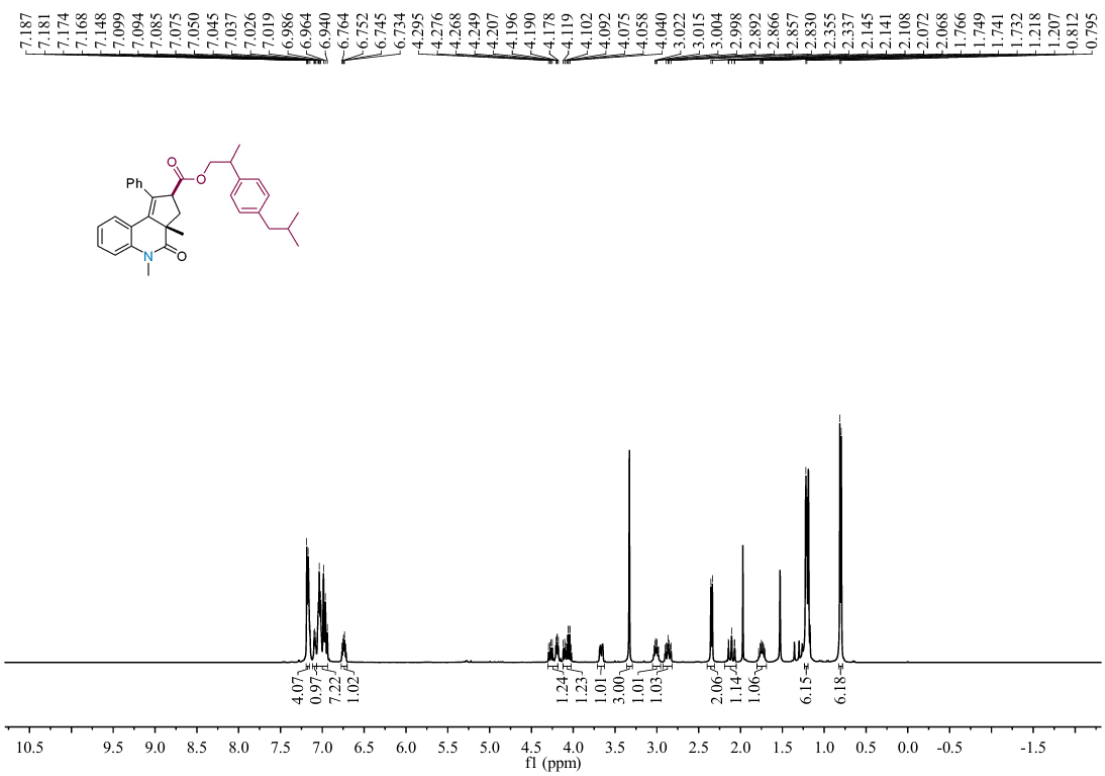
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-4c** (100 MHz, $CDCl_3$)



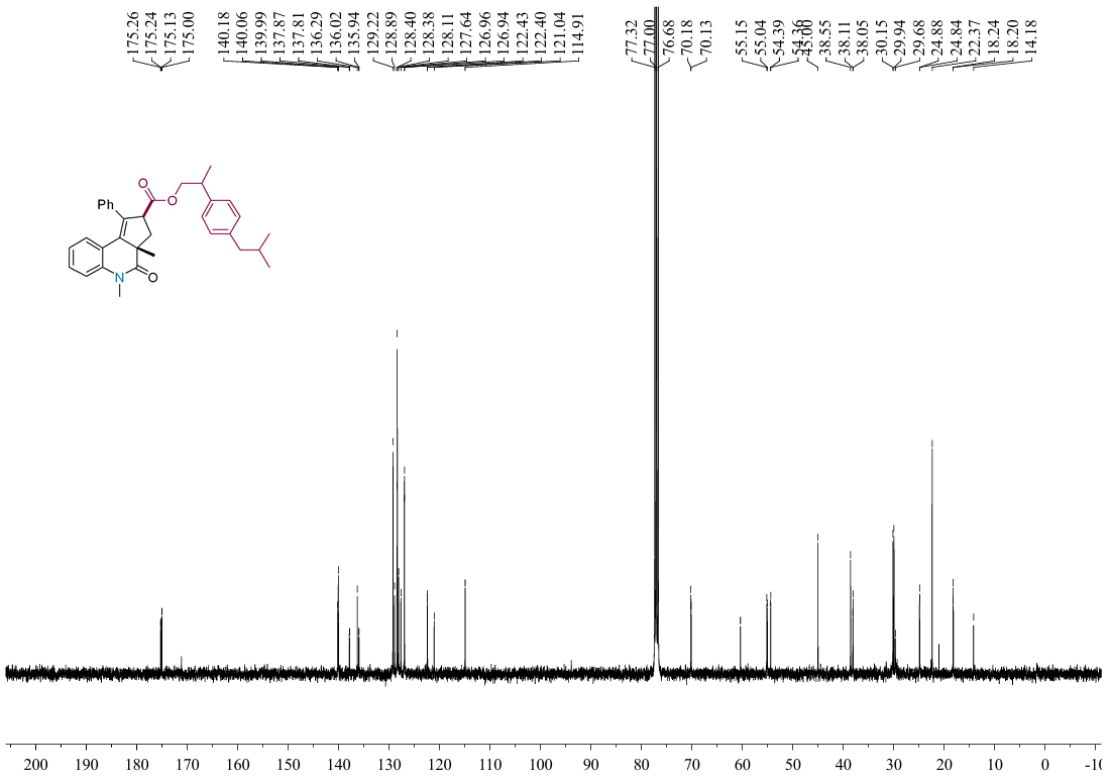
^{1}H NMR Spectrum of Compound ***trans*-4c** (400 MHz, $CDCl_3$)



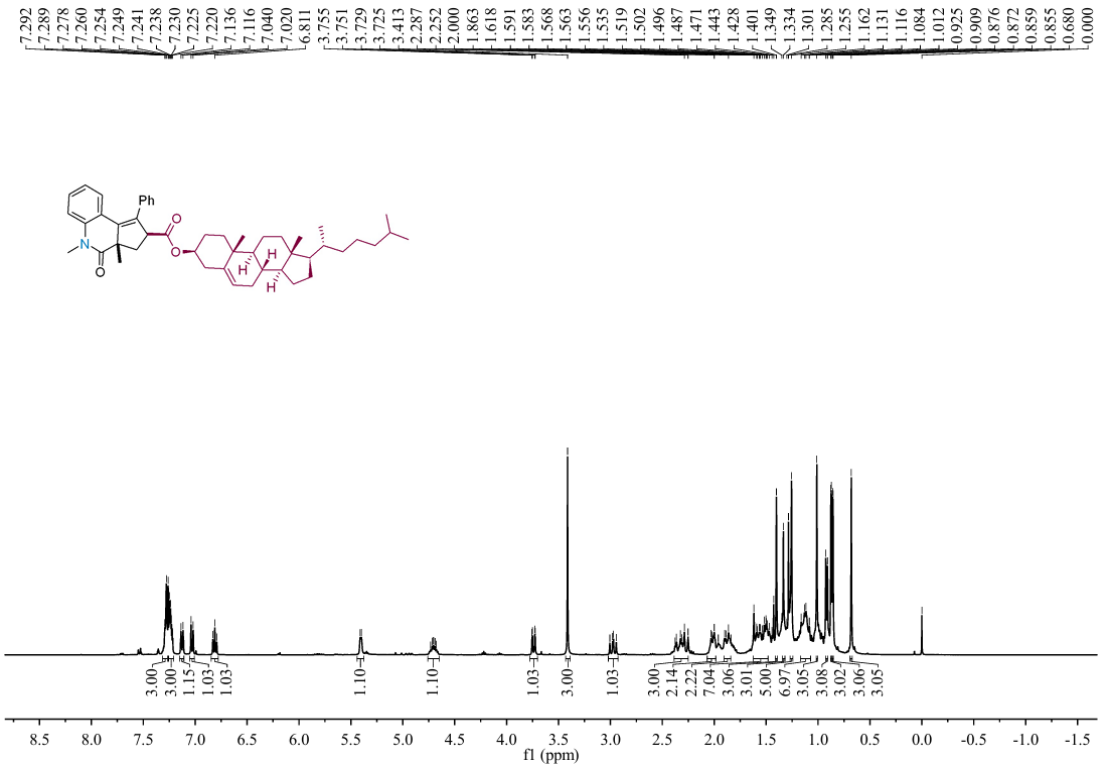
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4c** (100 MHz, $CDCl_3$)



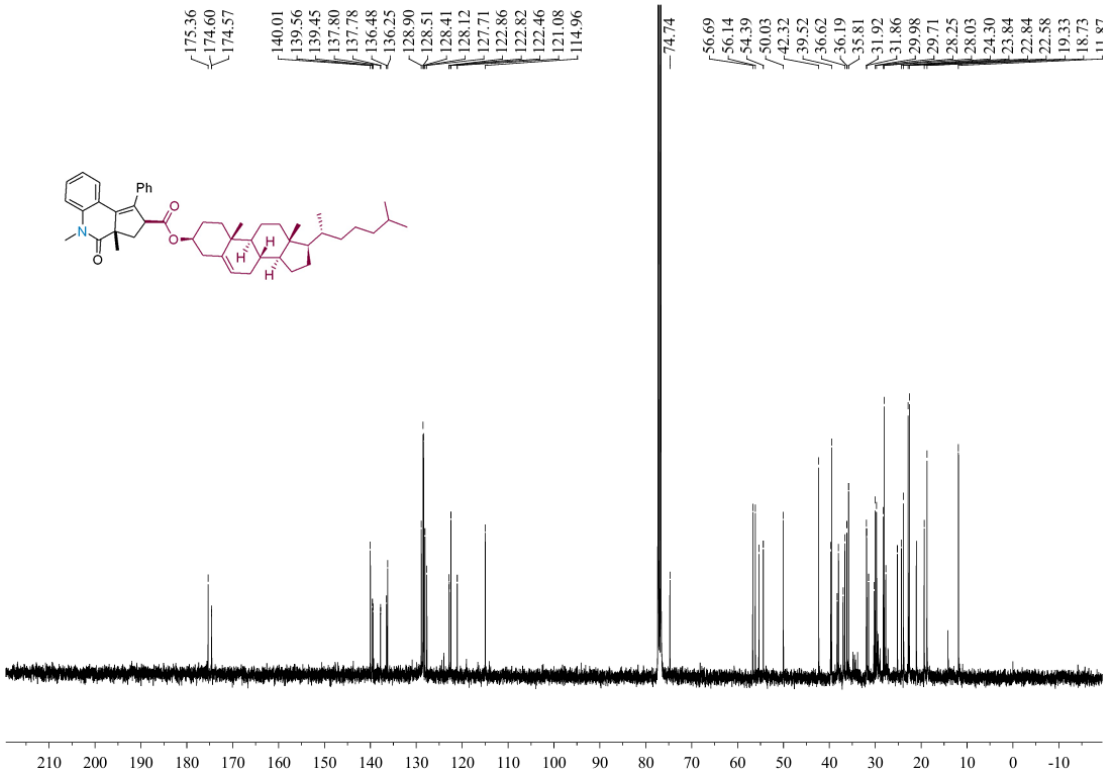
^{1}H NMR Spectrum of Compound ***cis*-4d** (400 MHz, $CDCl_3$)



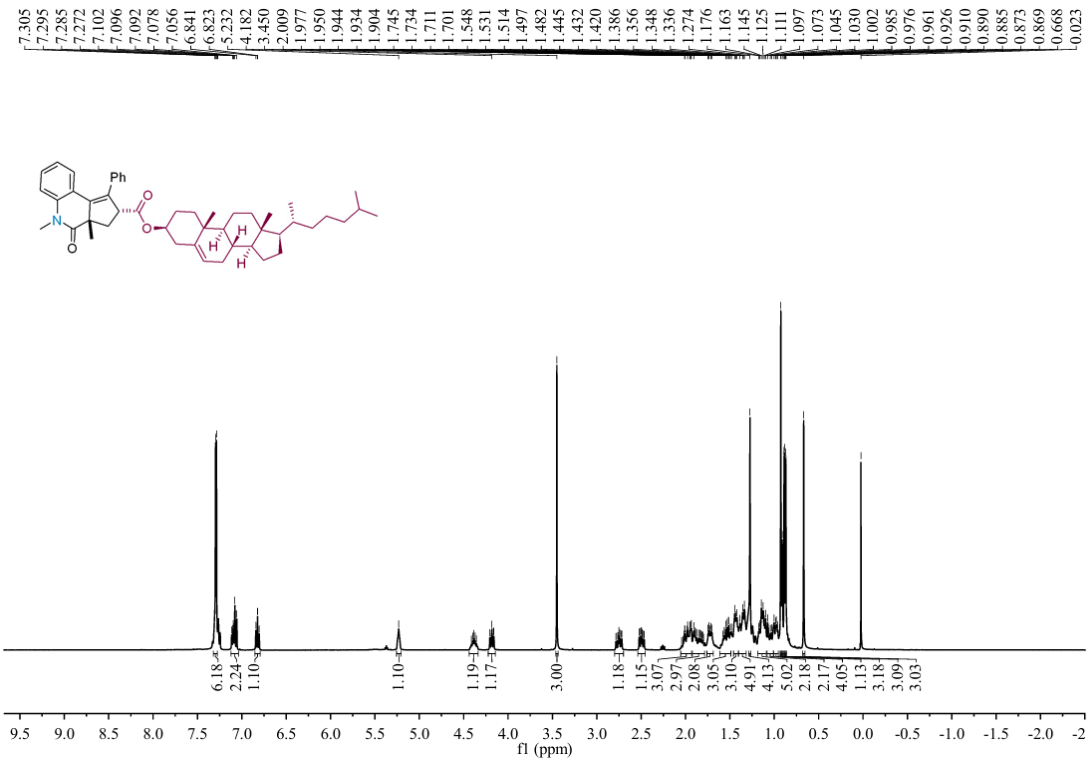
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-4d** (100 MHz, $CDCl_3$)



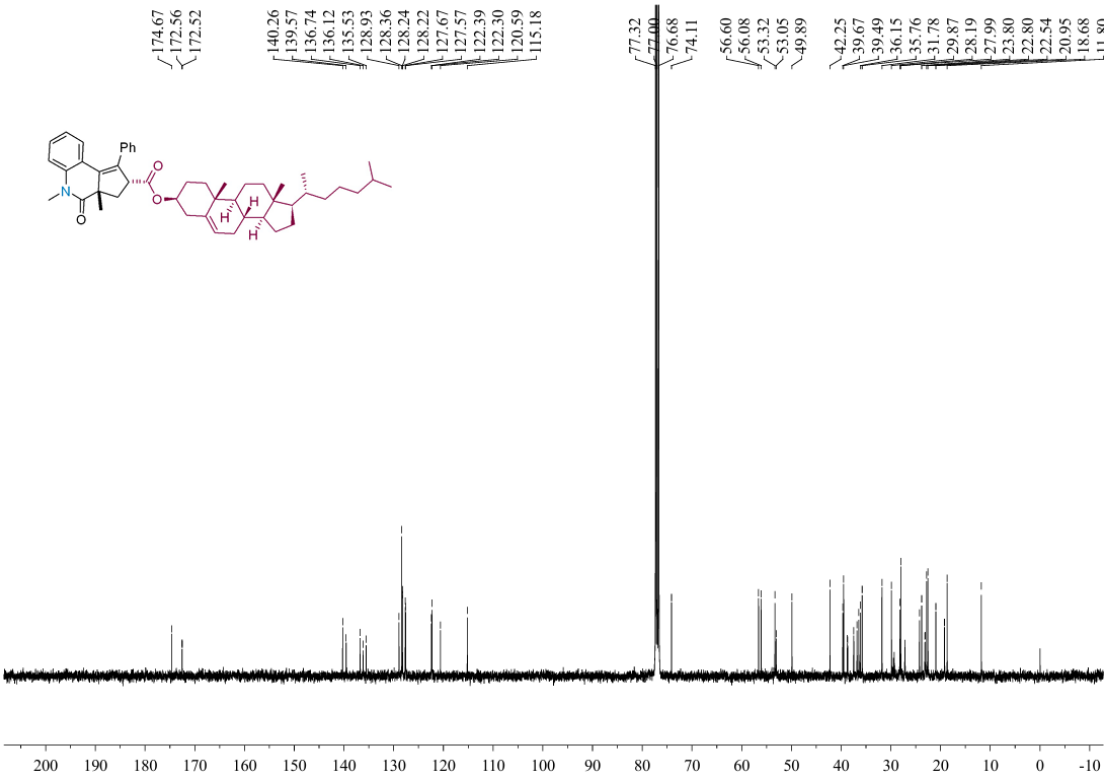
^{1}H NMR Spectrum of Compound ***cis*-4e** (400 MHz, $CDCl_3$)



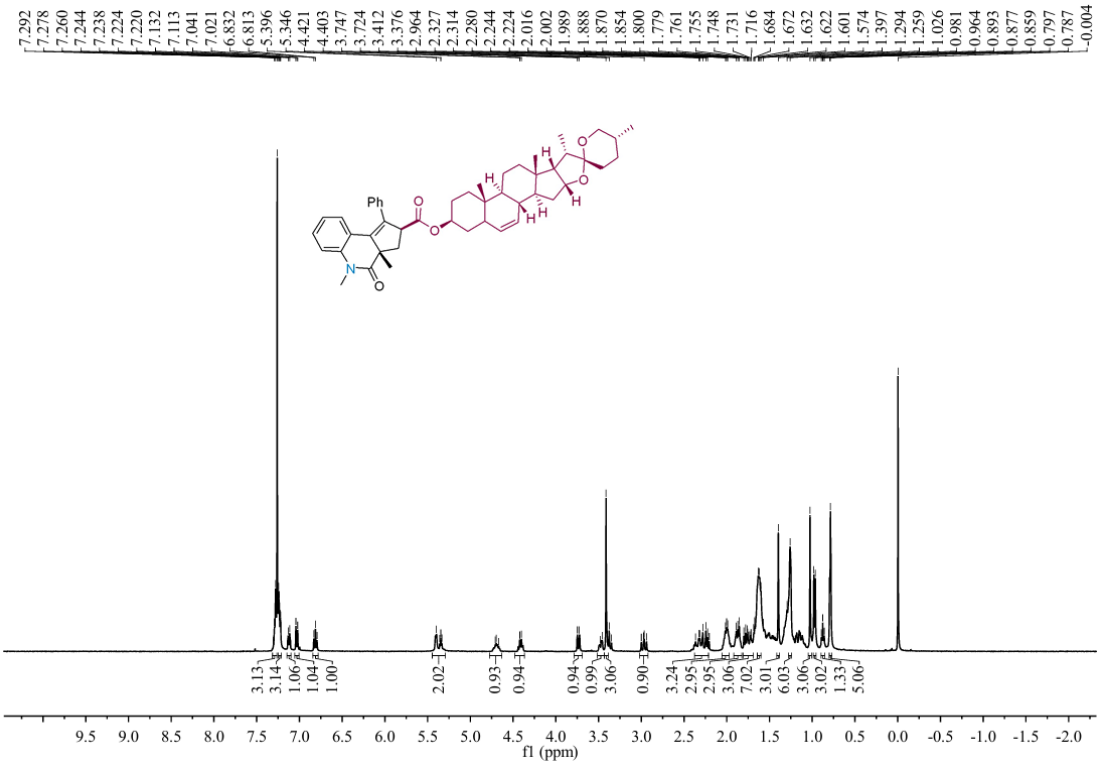
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-4e** (100 MHz, $CDCl_3$)



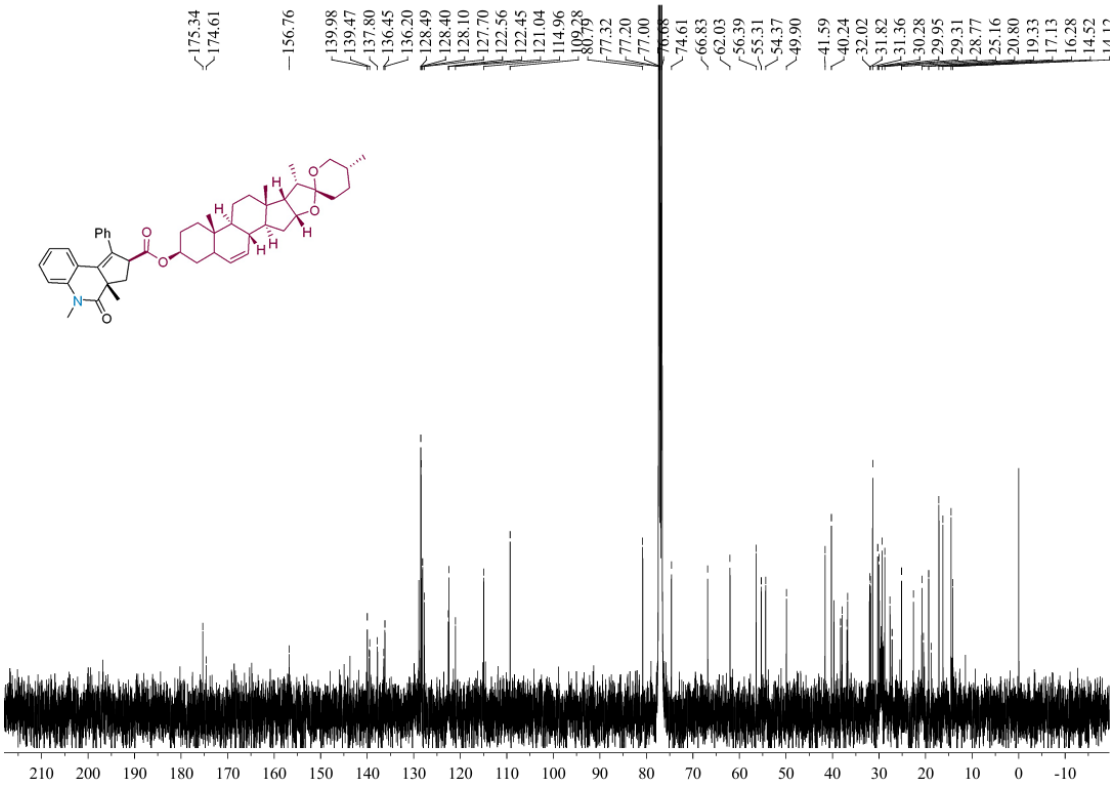
^{1}H NMR Spectrum of Compound ***trans*-4e** (400 MHz, $CDCl_3$)



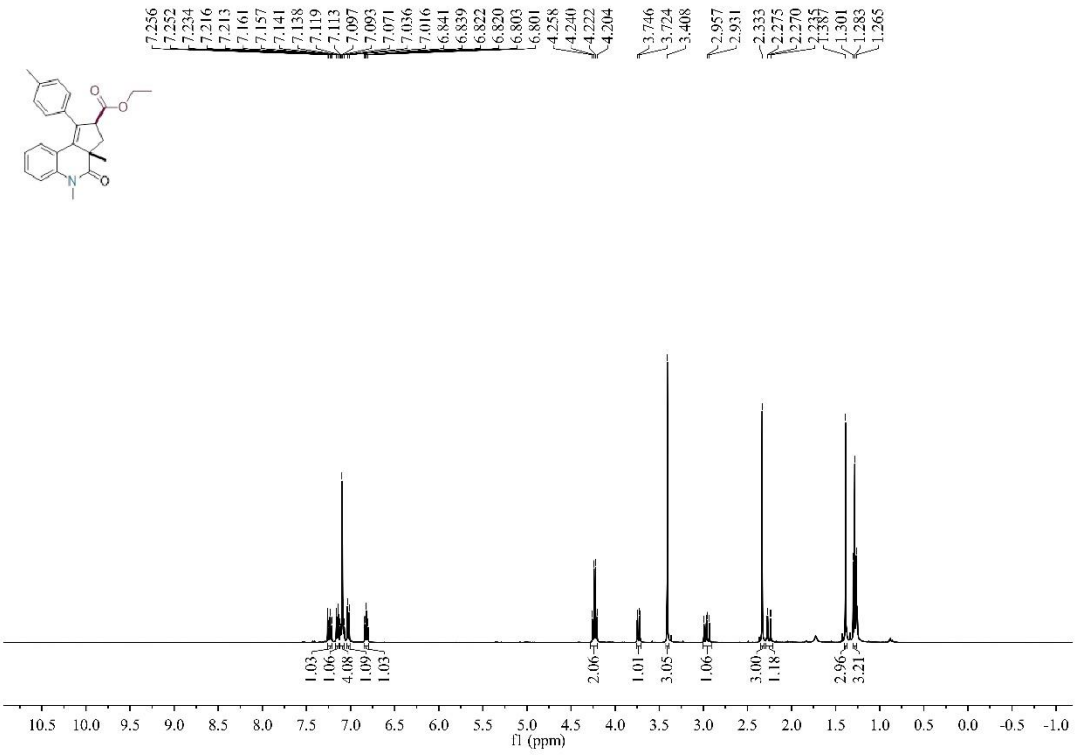
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4e** (100 MHz, $CDCl_3$)



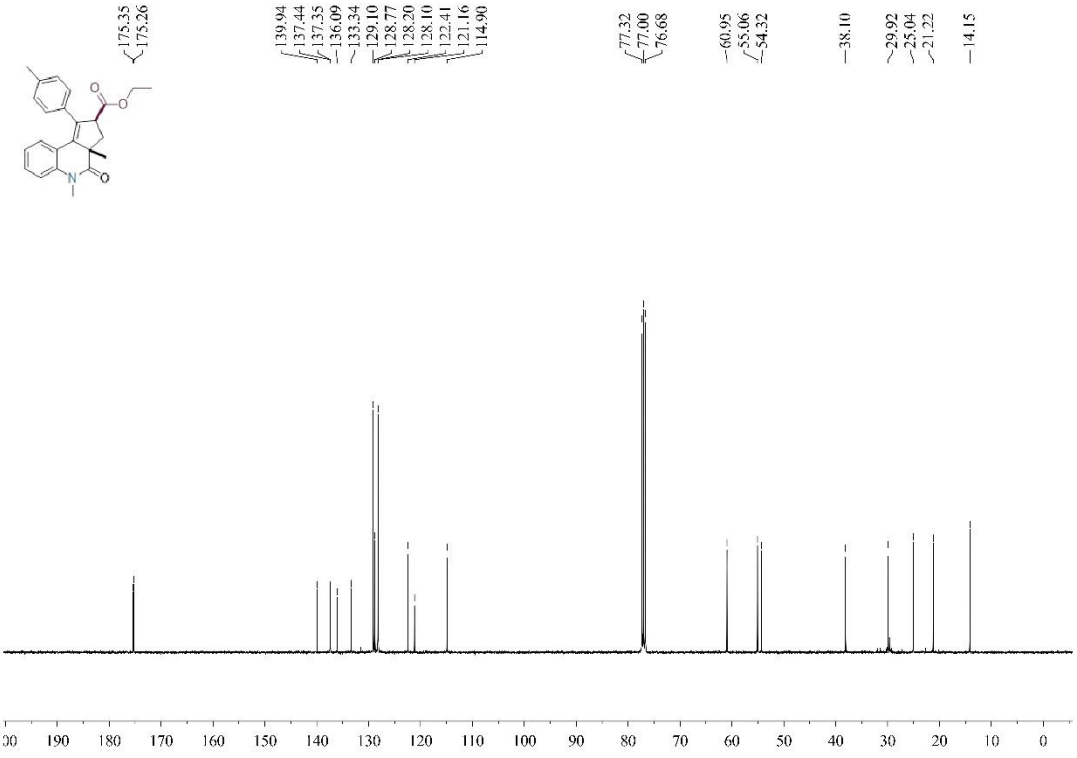
^{1}H NMR Spectrum of Compound ***cis*-4f** (400 MHz, $CDCl_3$)



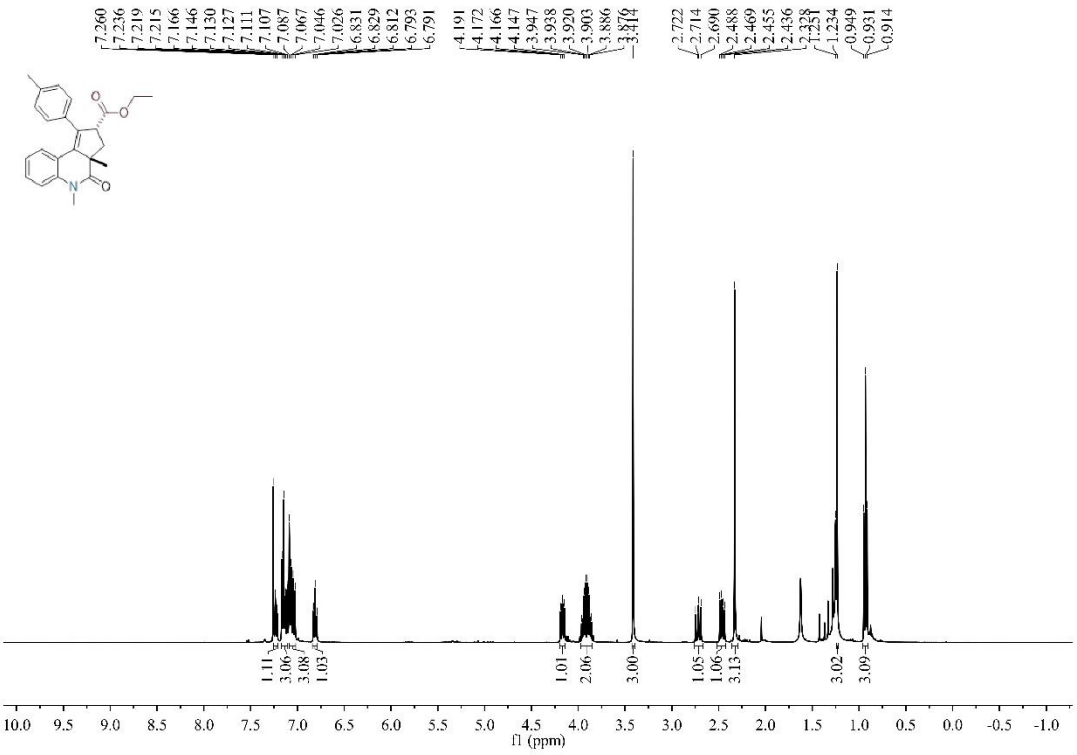
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-4f** (100 MHz, $CDCl_3$)



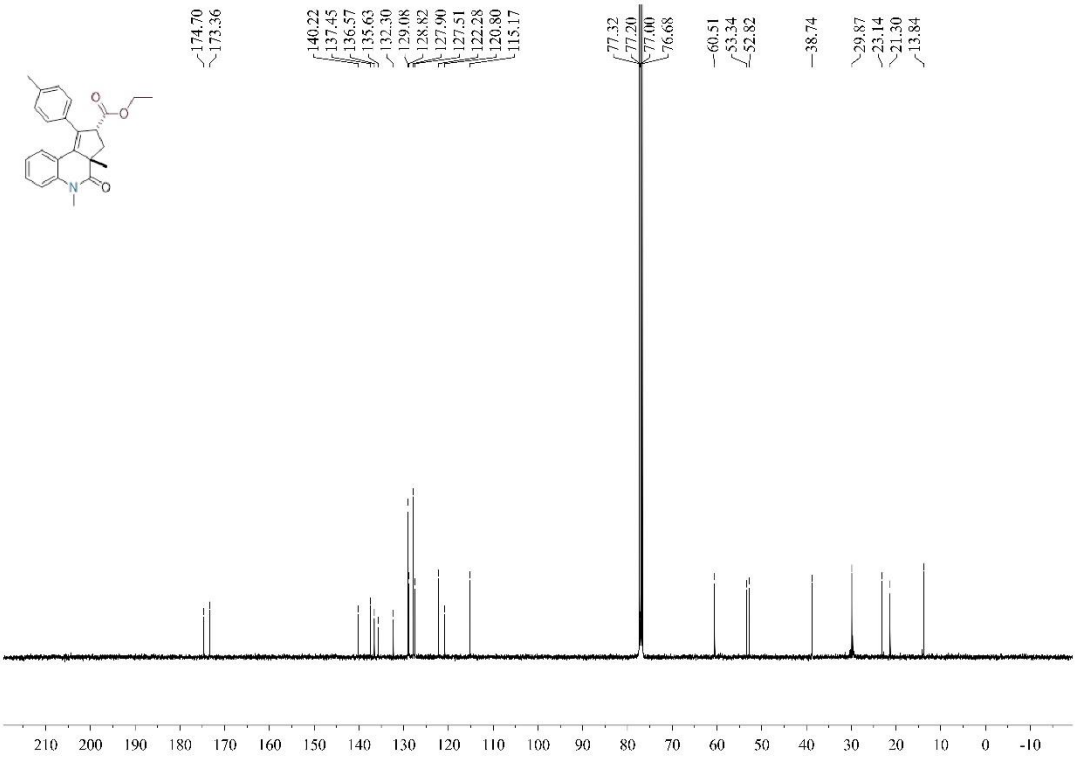
^{1}H NMR Spectrum of Compound ***cis*-4g** (400 MHz, $CDCl_3$)



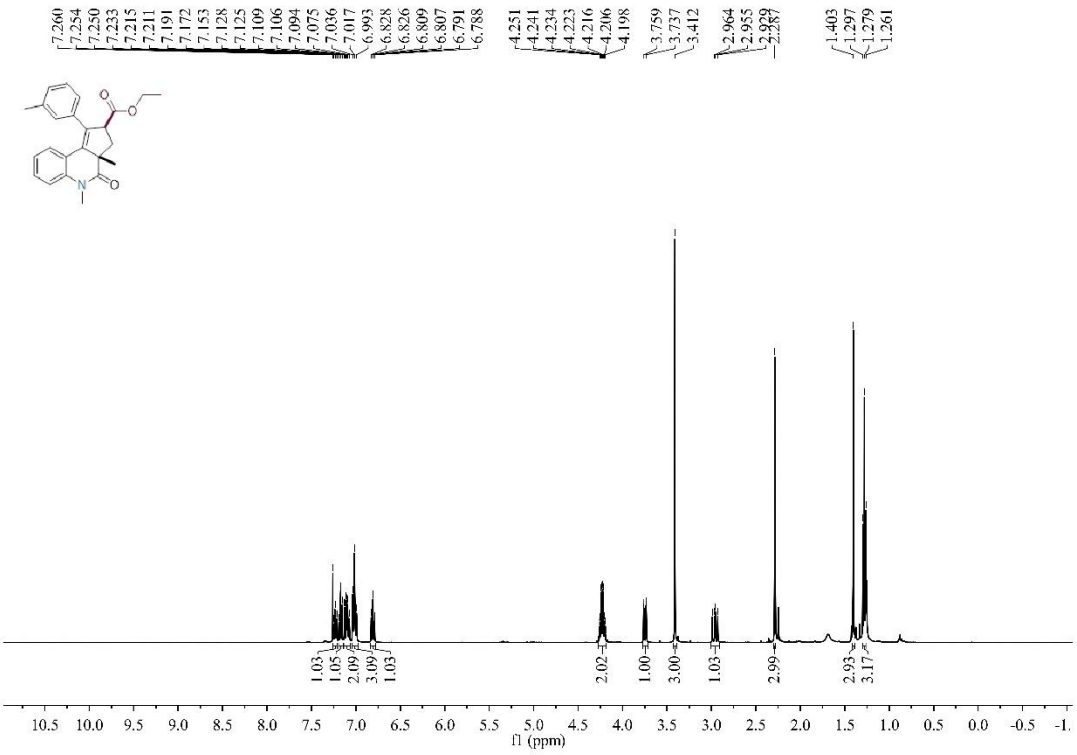
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-4g** (100 MHz, $CDCl_3$)



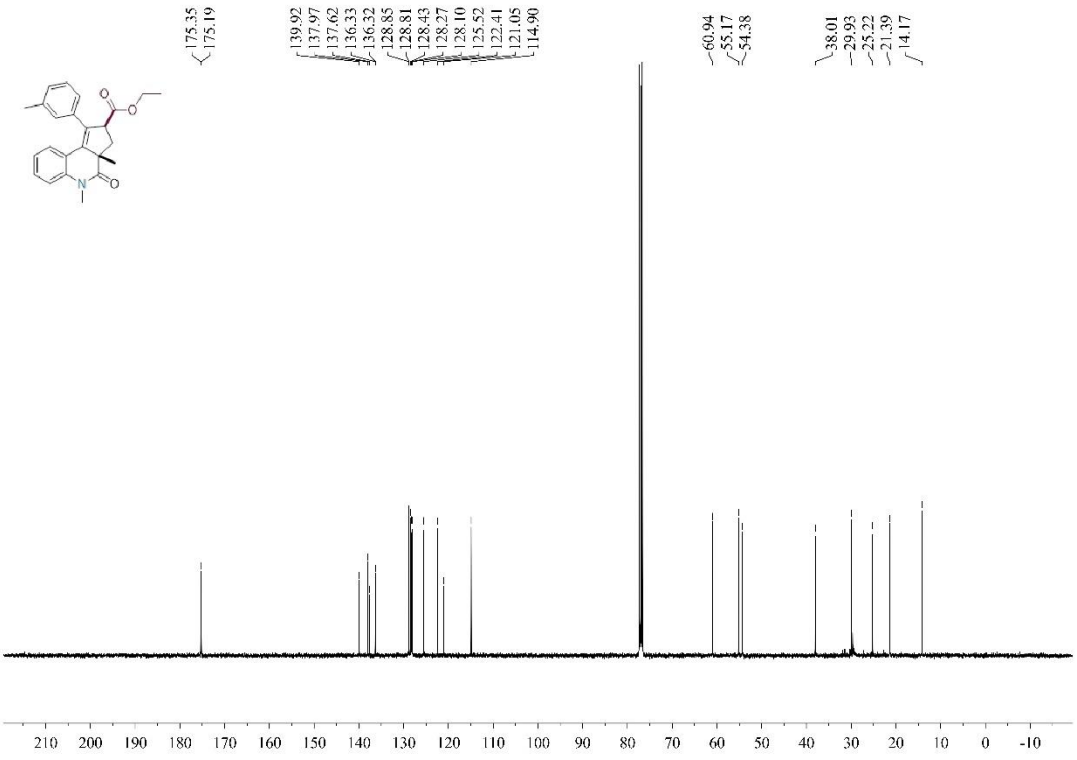
^{1}H NMR Spectrum of Compound ***trans*-4g** (400 MHz, $CDCl_3$)



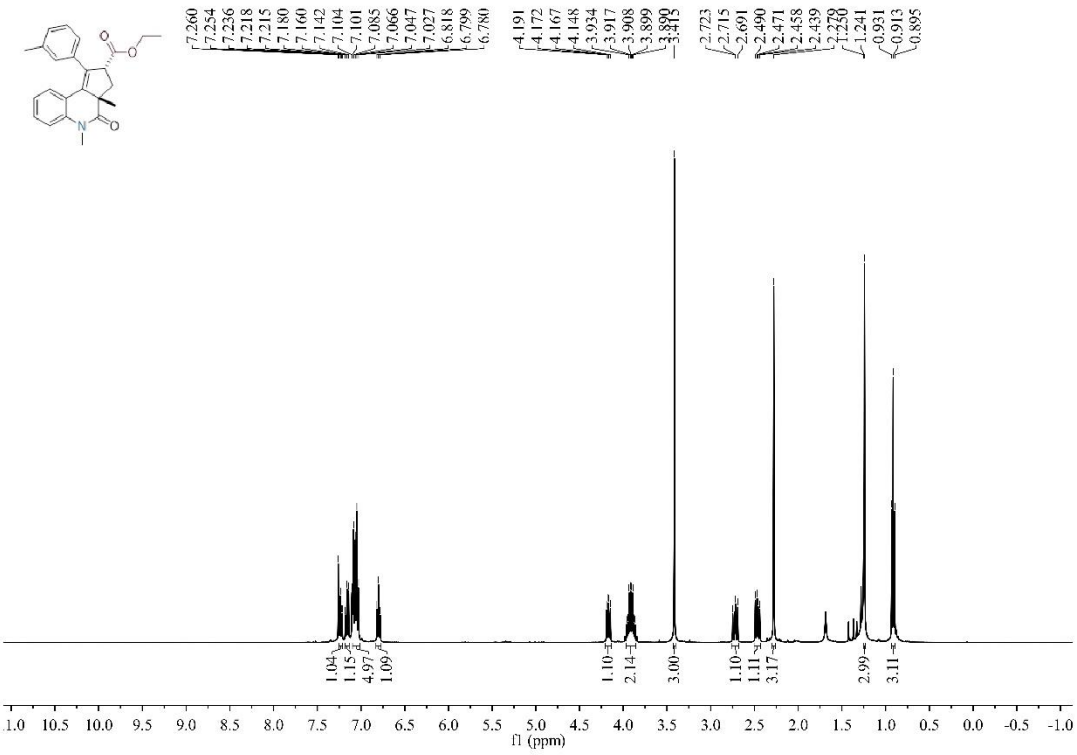
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***trans*-4g** (100 MHz, $CDCl_3$)



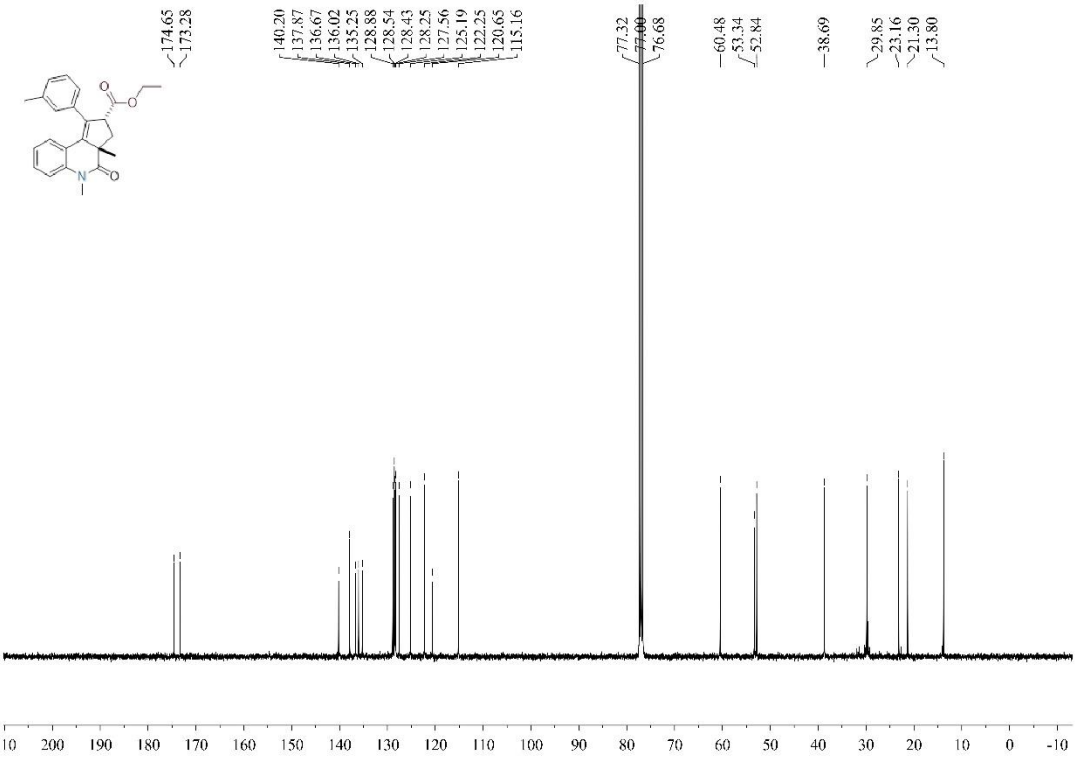
^{1}H NMR Spectrum of Compound ***cis*-4h** (400 MHz, $CDCl_3$)



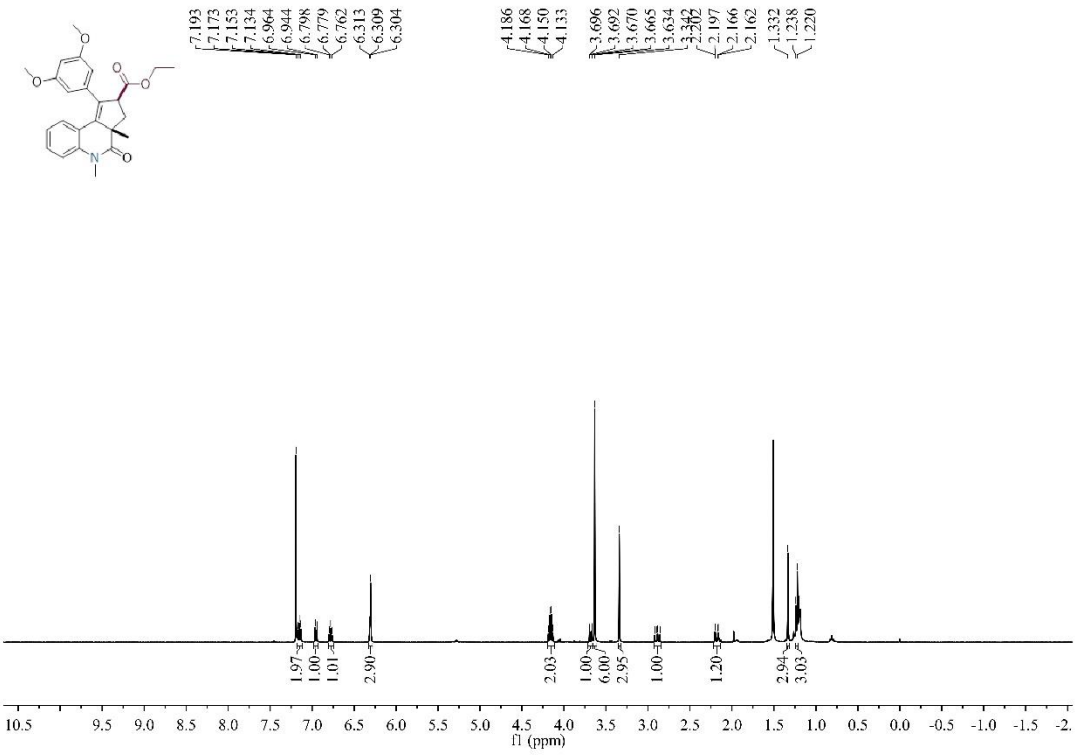
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-4h** (100 MHz, $CDCl_3$)



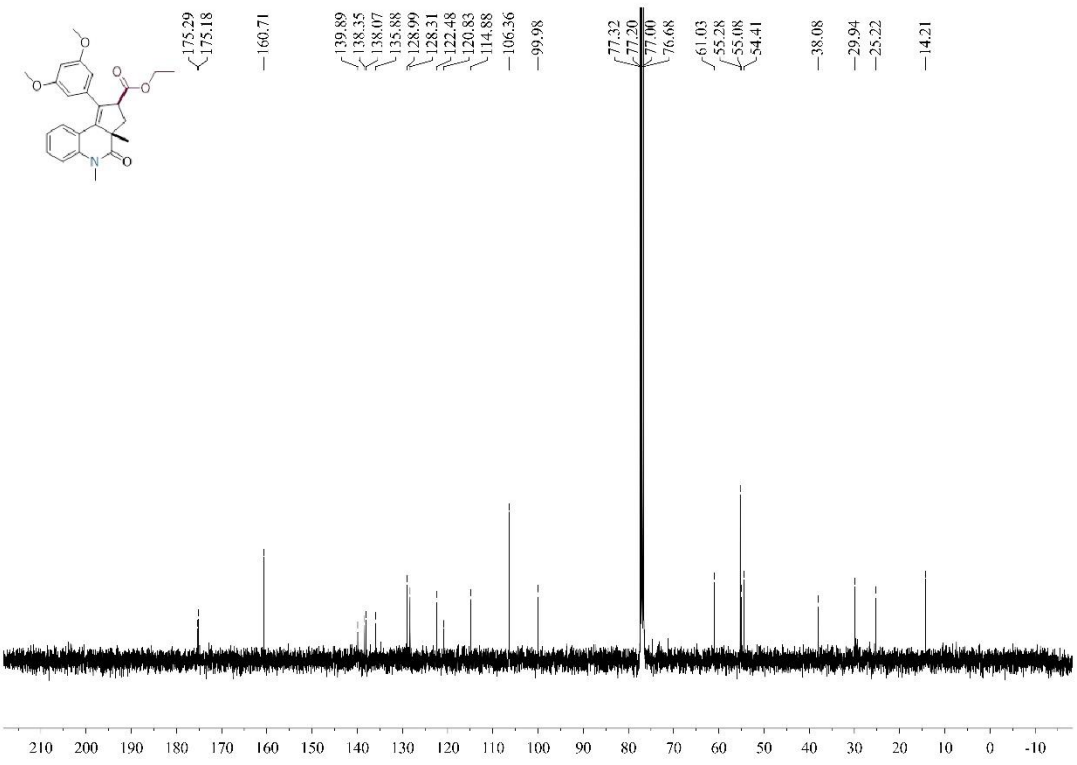
^{1}H NMR Spectrum of Compound ***trans*-4h** (400 MHz, $CDCl_3$)



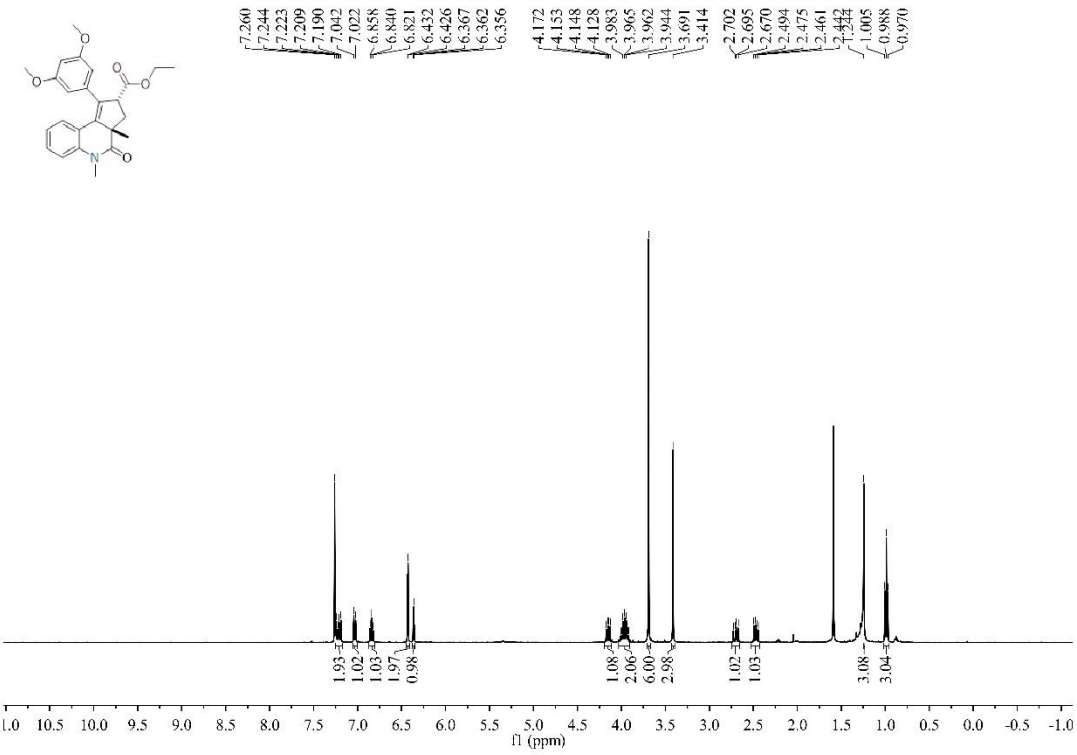
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4h** (100 MHz, $CDCl_3$)



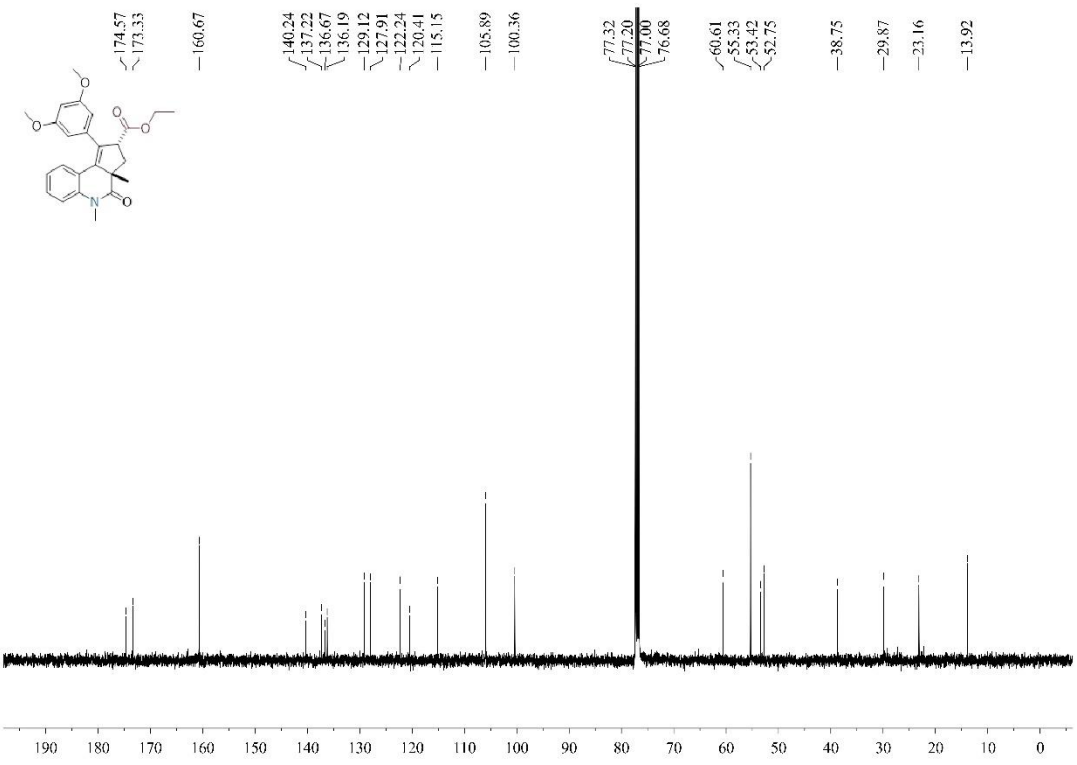
^{1}H NMR Spectrum of Compound ***cis*-4i** (400 MHz, $CDCl_3$)



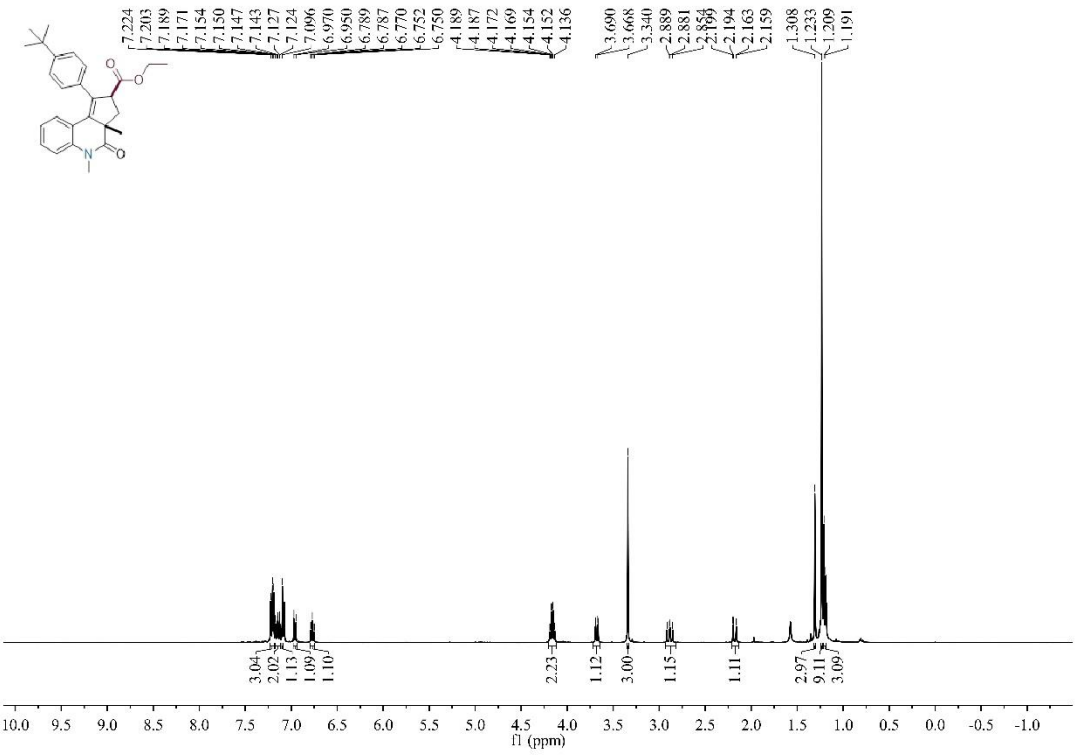
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-4i** (100 MHz, $CDCl_3$)



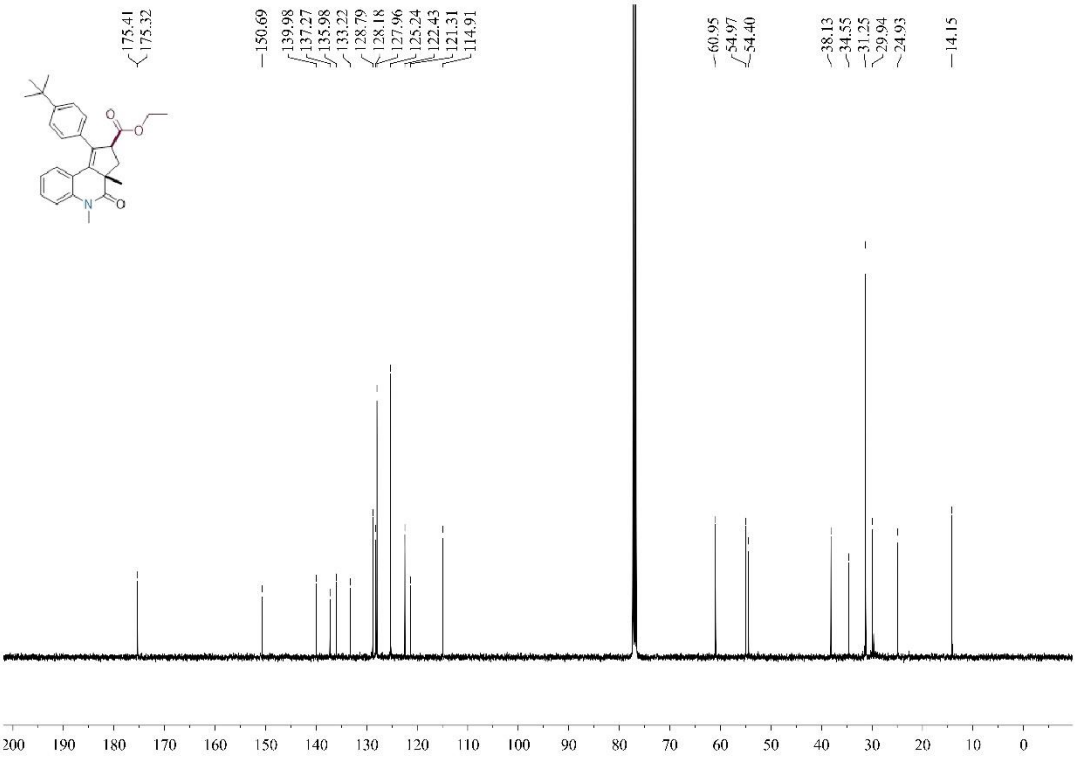
^{1}H NMR Spectrum of Compound ***trans*-4i** (400 MHz, $CDCl_3$)



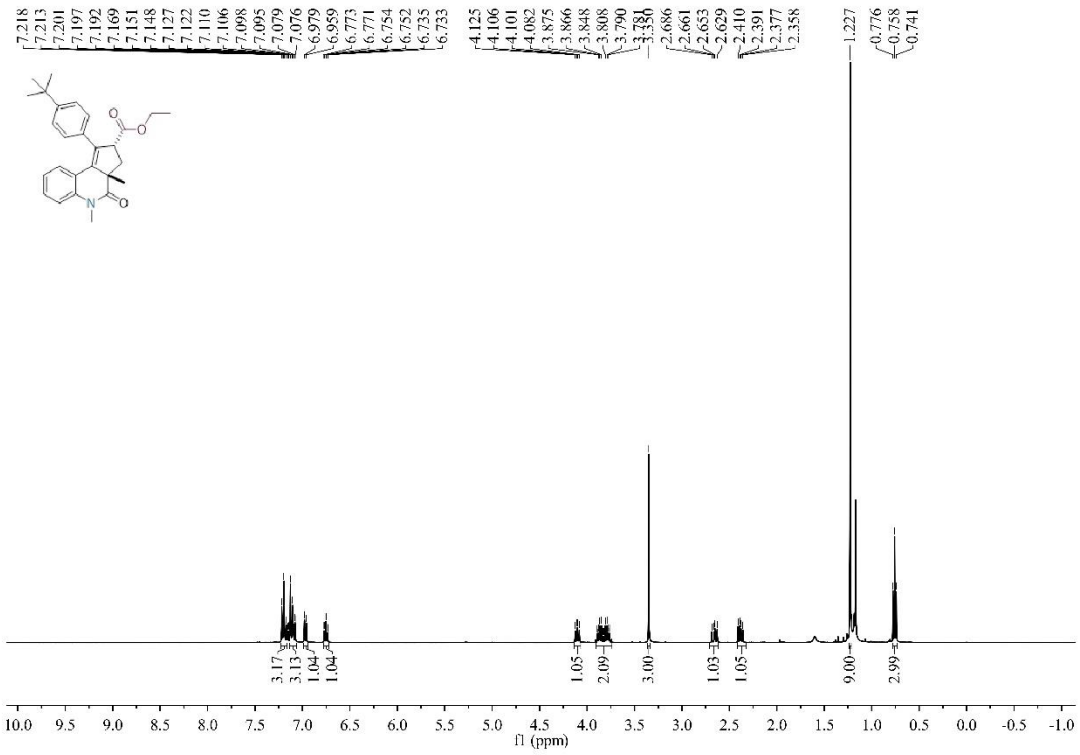
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4i** (100 MHz, $CDCl_3$)



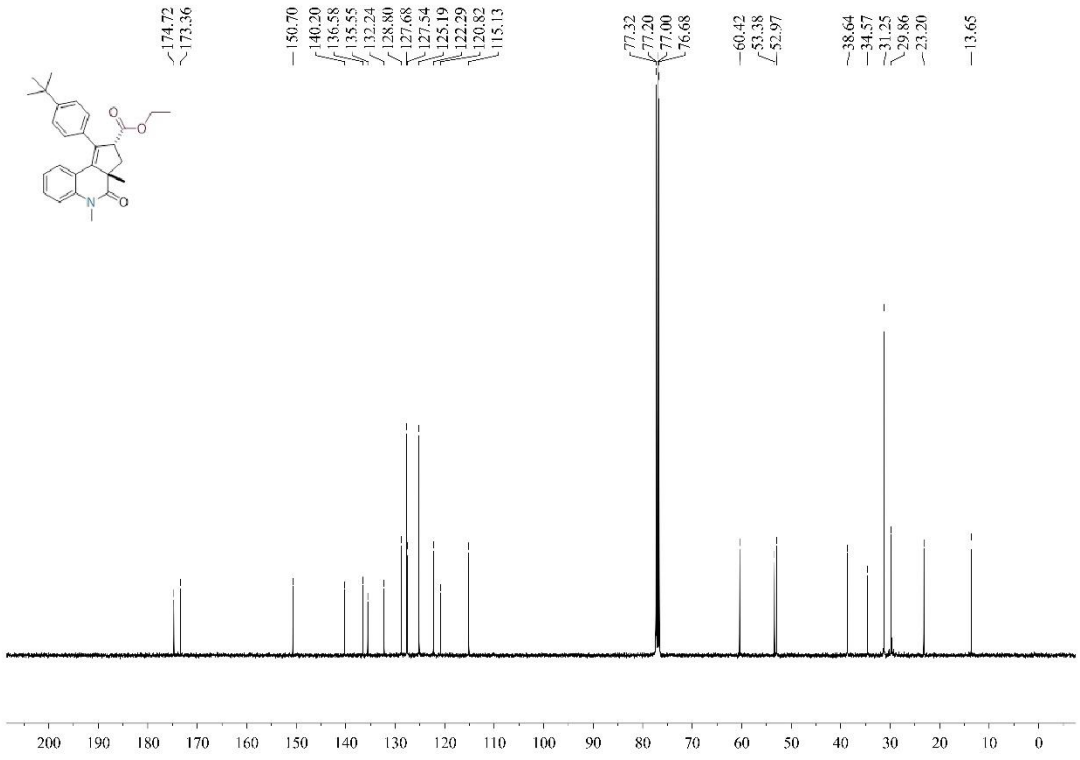
^{1}H NMR Spectrum of Compound ***cis*-4j** (400 MHz, $CDCl_3$)



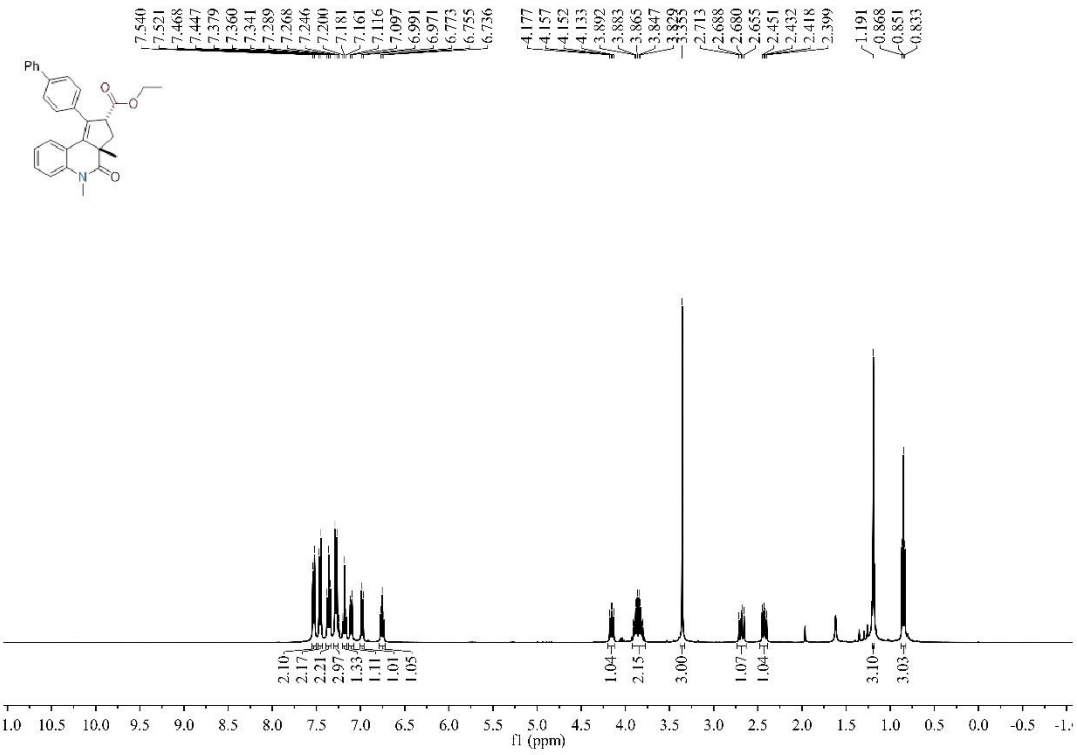
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-4j** (100 MHz, $CDCl_3$)



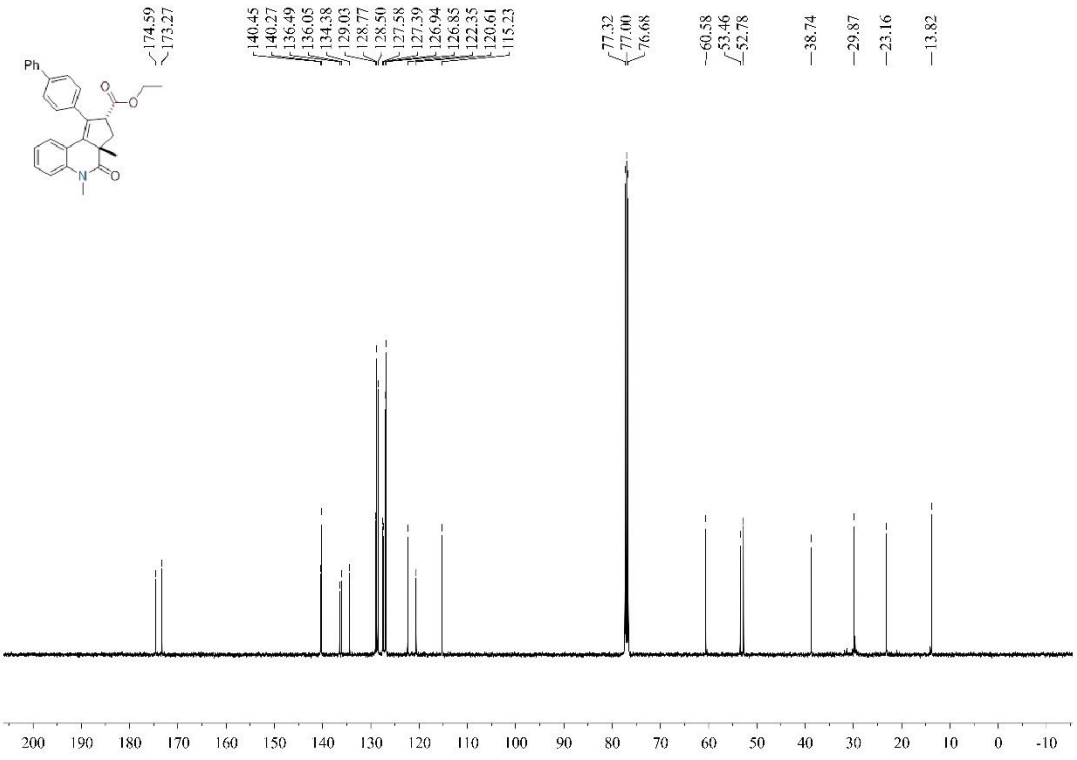
^{1}H NMR Spectrum of Compound ***trans*-4j** (400 MHz, $CDCl_3$)



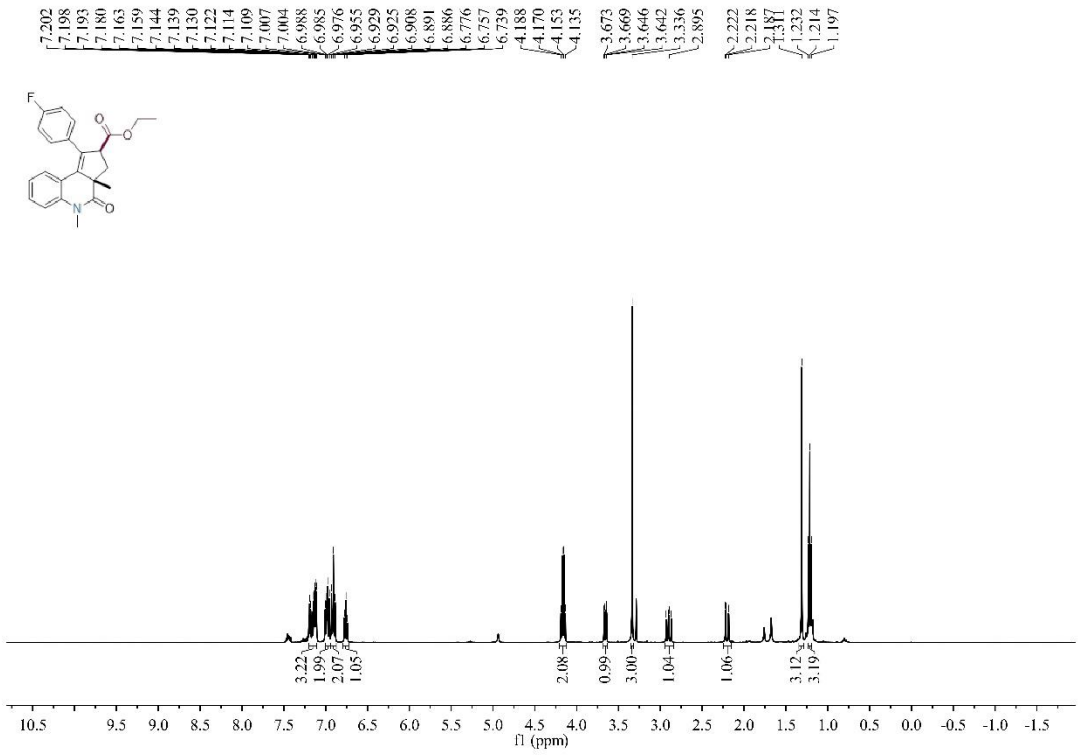
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***trans*-4j** (100 MHz, $CDCl_3$)



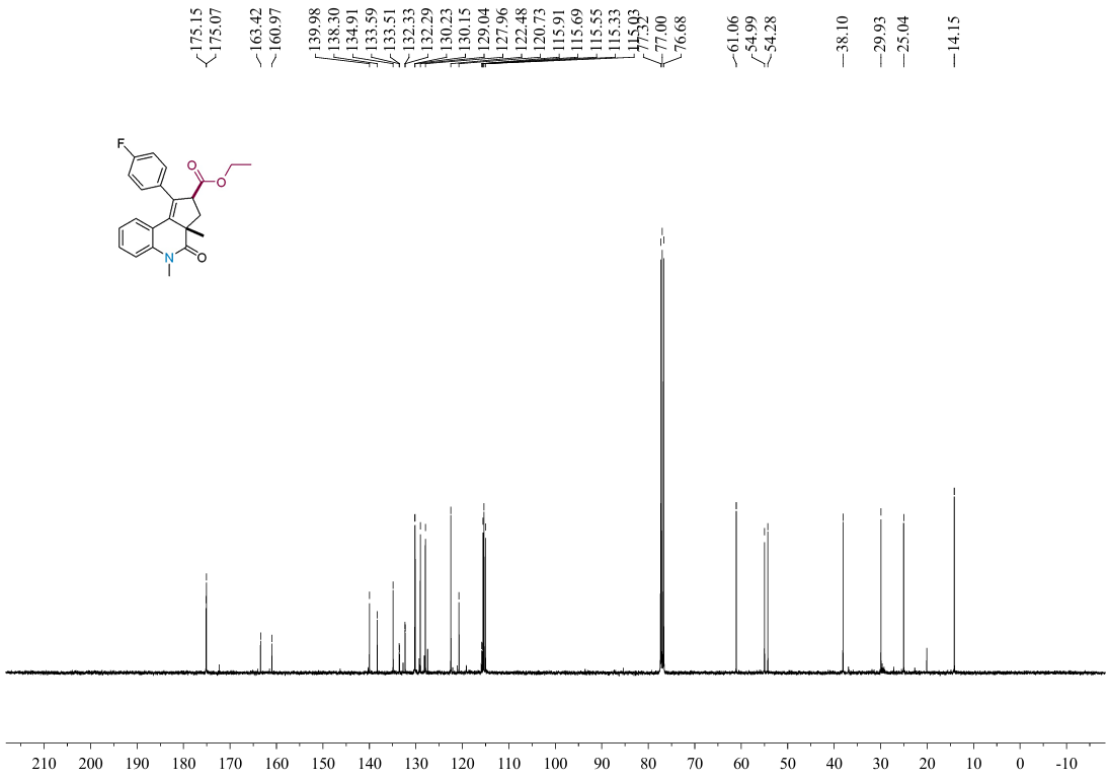
^{1}H NMR Spectrum of Compound ***trans*-4k** (400 MHz, $CDCl_3$)



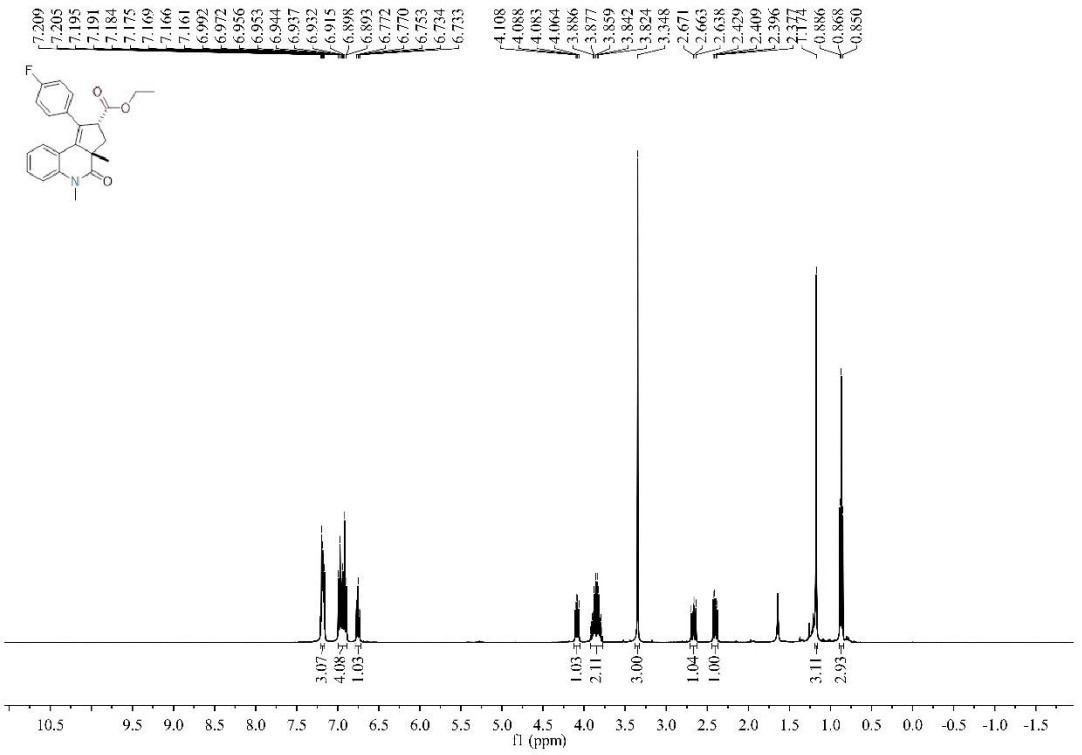
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4k** (100 MHz, $CDCl_3$)



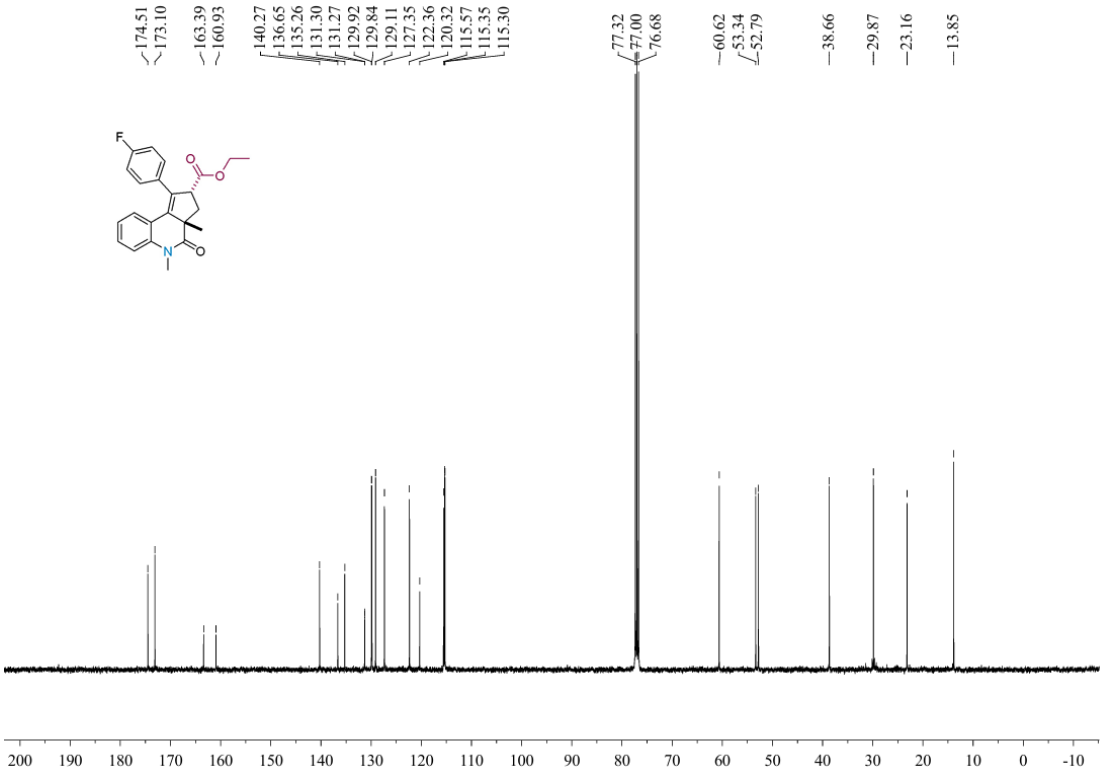
^{1}H NMR Spectrum of Compound ***cis*-4l** (400 MHz, $CDCl_3$)



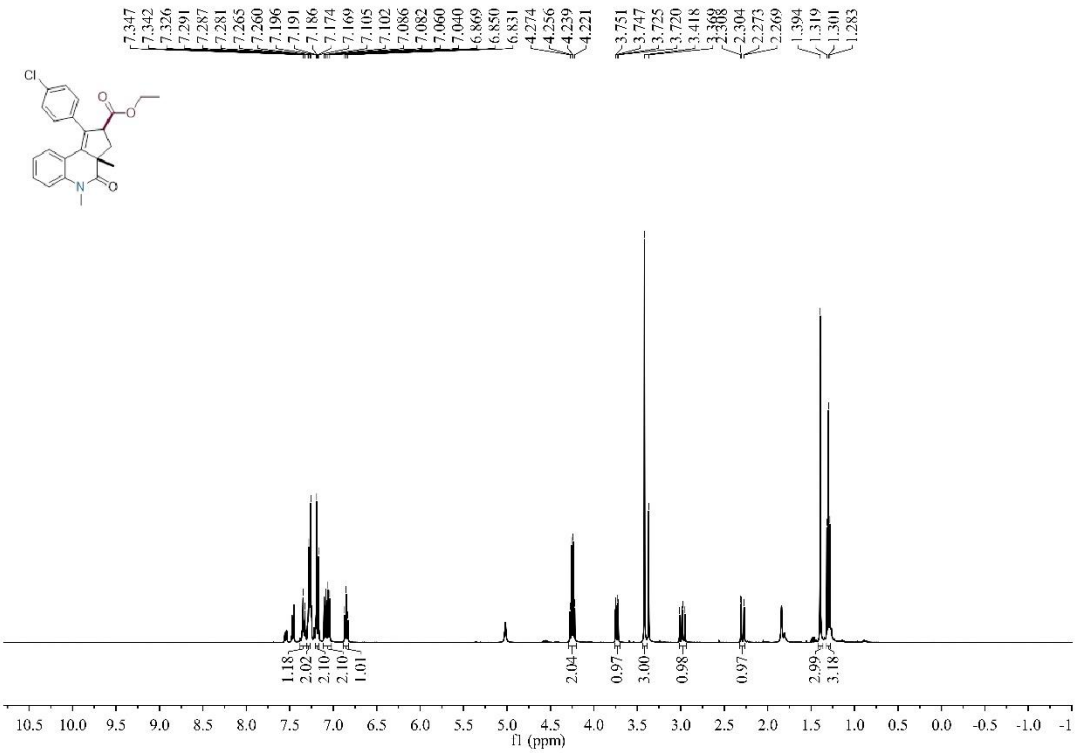
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-4l** (100 MHz, $CDCl_3$)



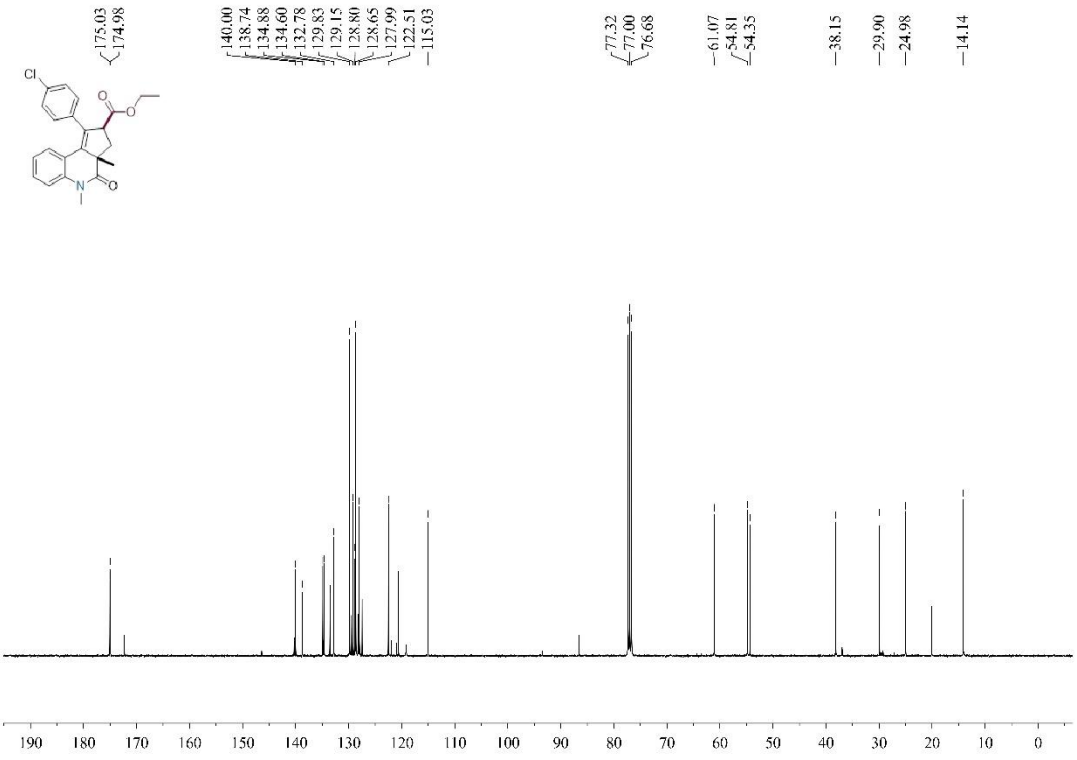
^{1}H NMR Spectrum of Compound ***trans*-4l** (400 MHz, $CDCl_3$)



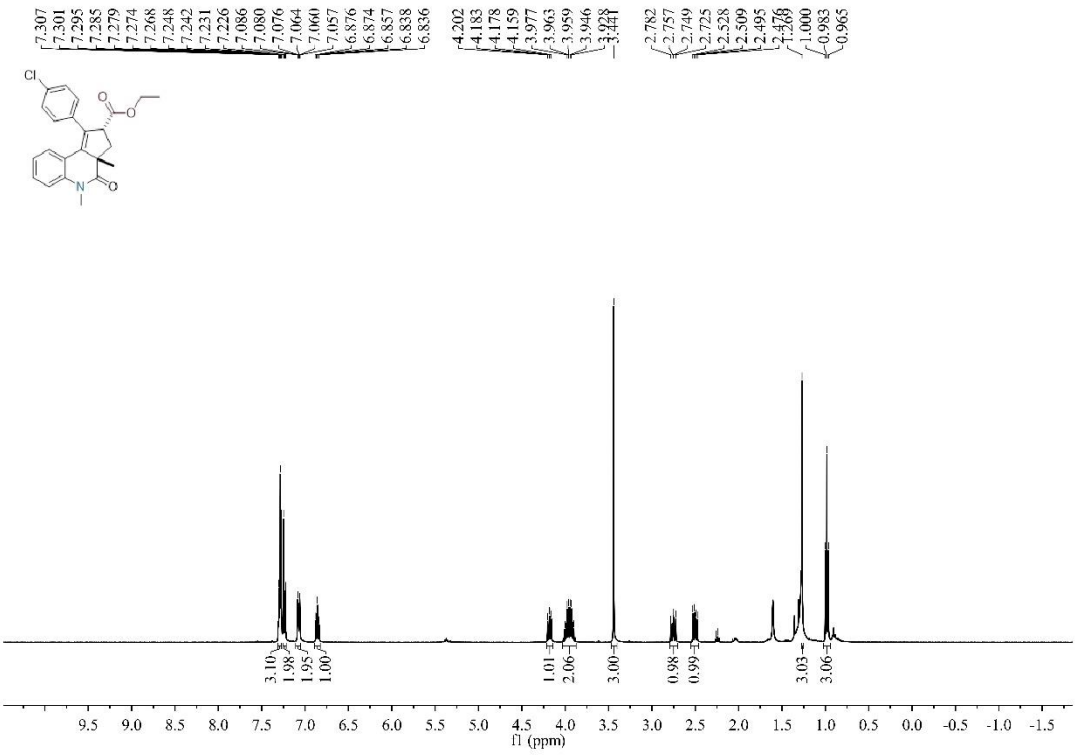
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4l** (100 MHz, $CDCl_3$)



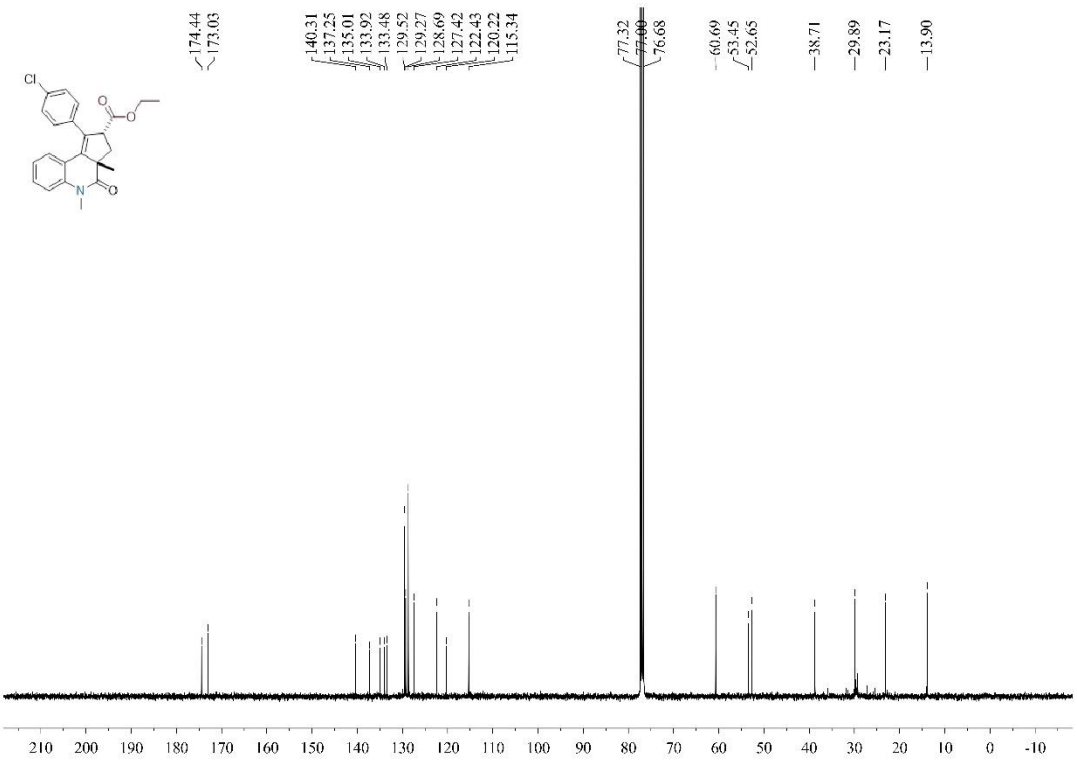
^{1}H NMR Spectrum of Compound ***cis*-4m** (400 MHz, $CDCl_3$)



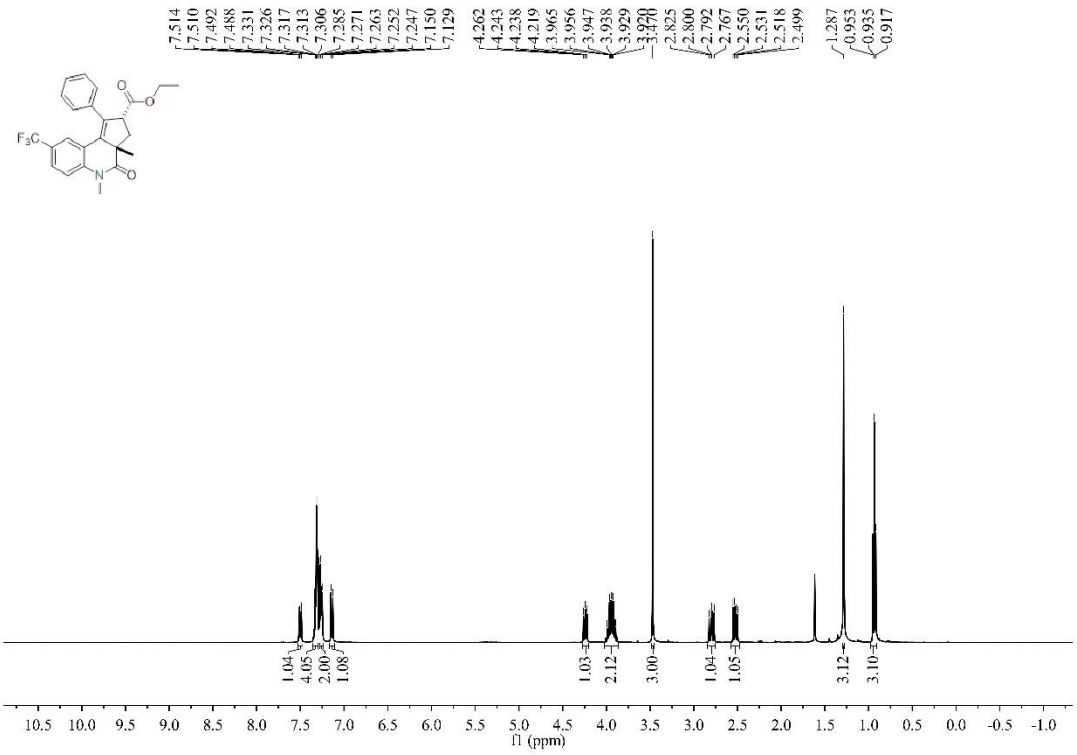
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-4m** (100 MHz, $CDCl_3$)



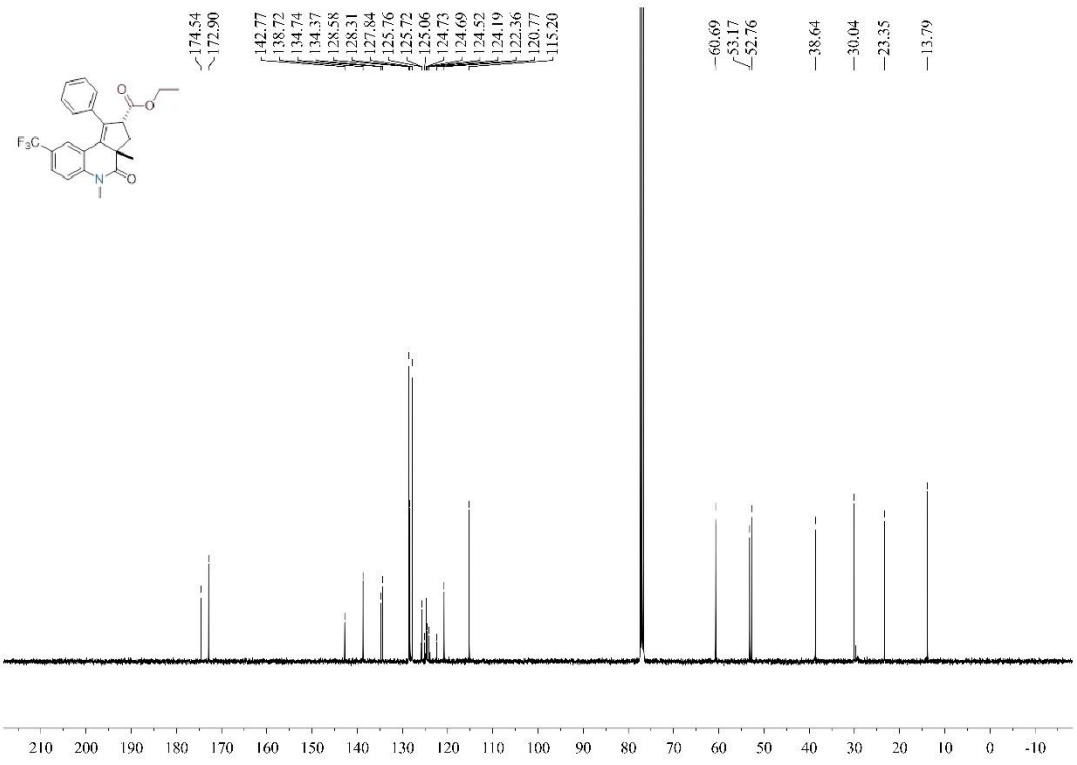
^{1}H NMR Spectrum of Compound ***trans*-4m** (400 MHz, $CDCl_3$)



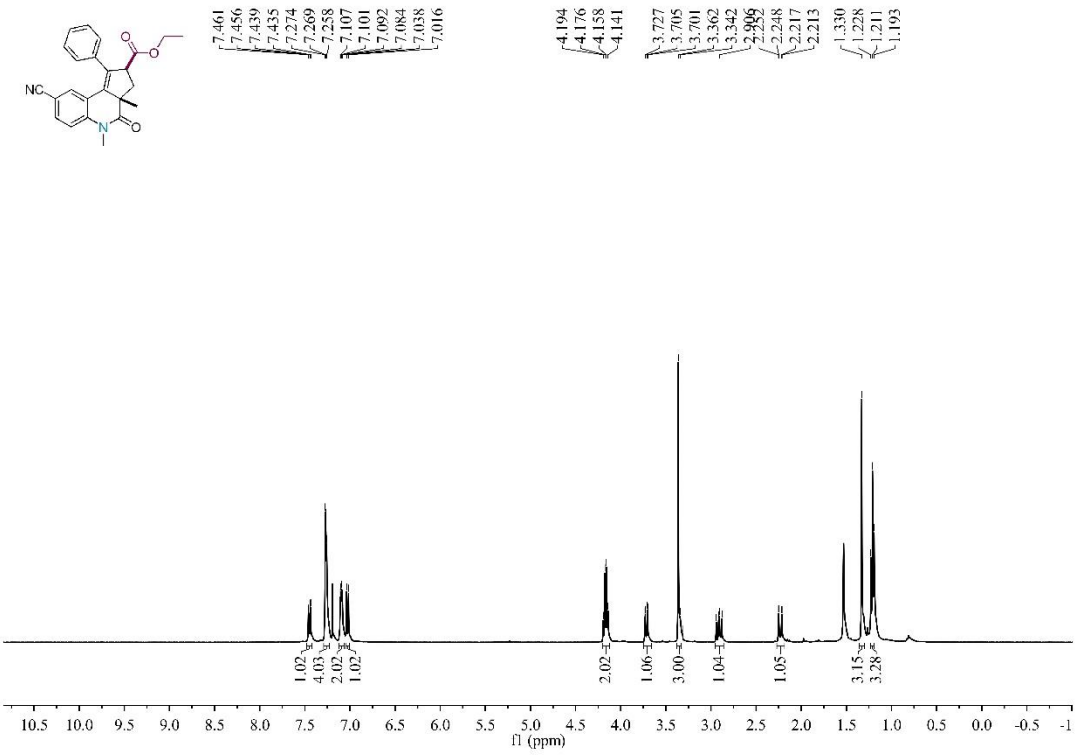
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4m** (100 MHz, $CDCl_3$)



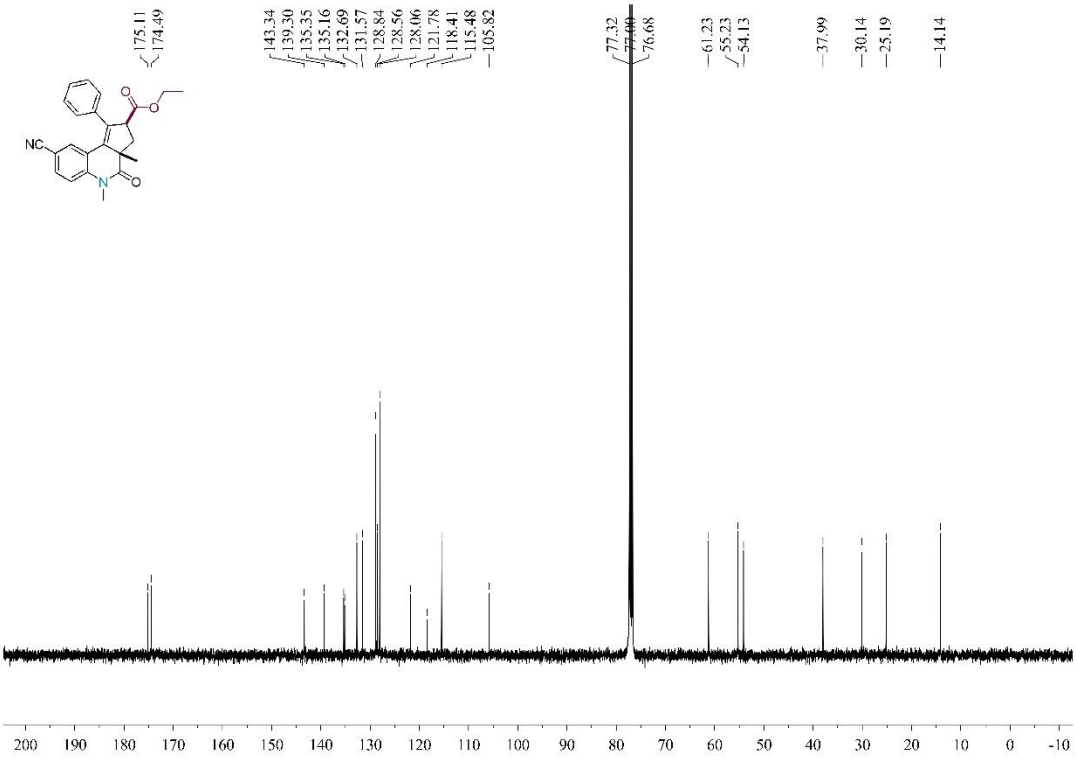
^{1}H NMR Spectrum of Compound ***trans*-4n** (400 MHz, $CDCl_3$)



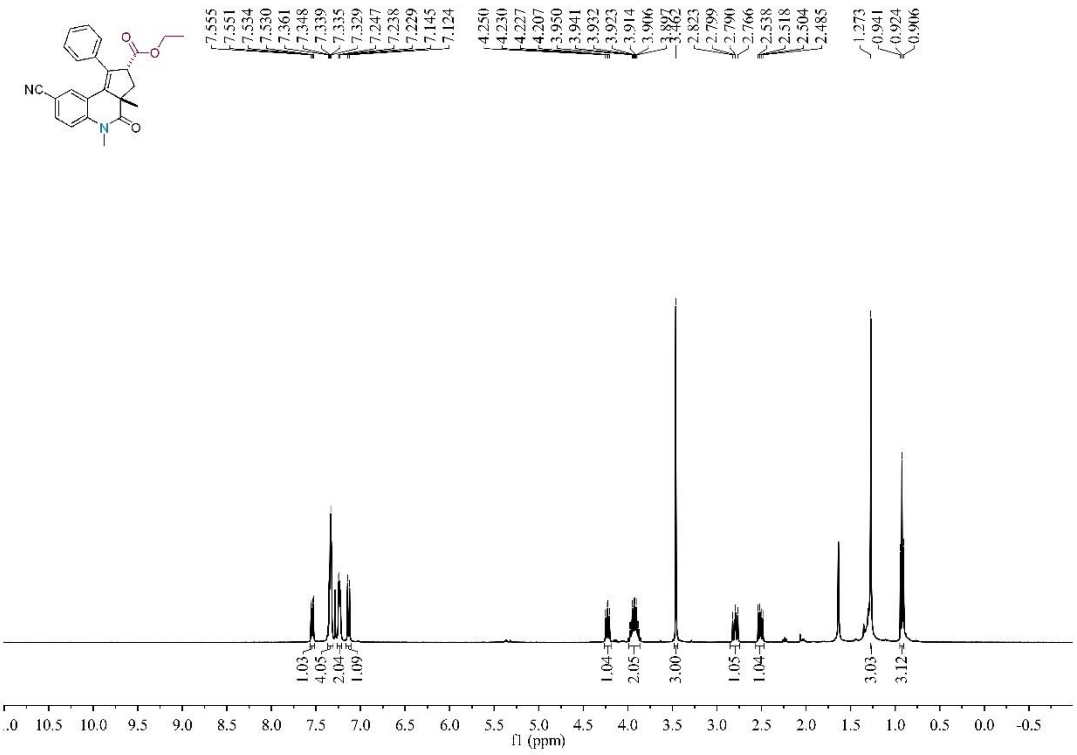
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***trans*-4n** (100 MHz, $CDCl_3$)



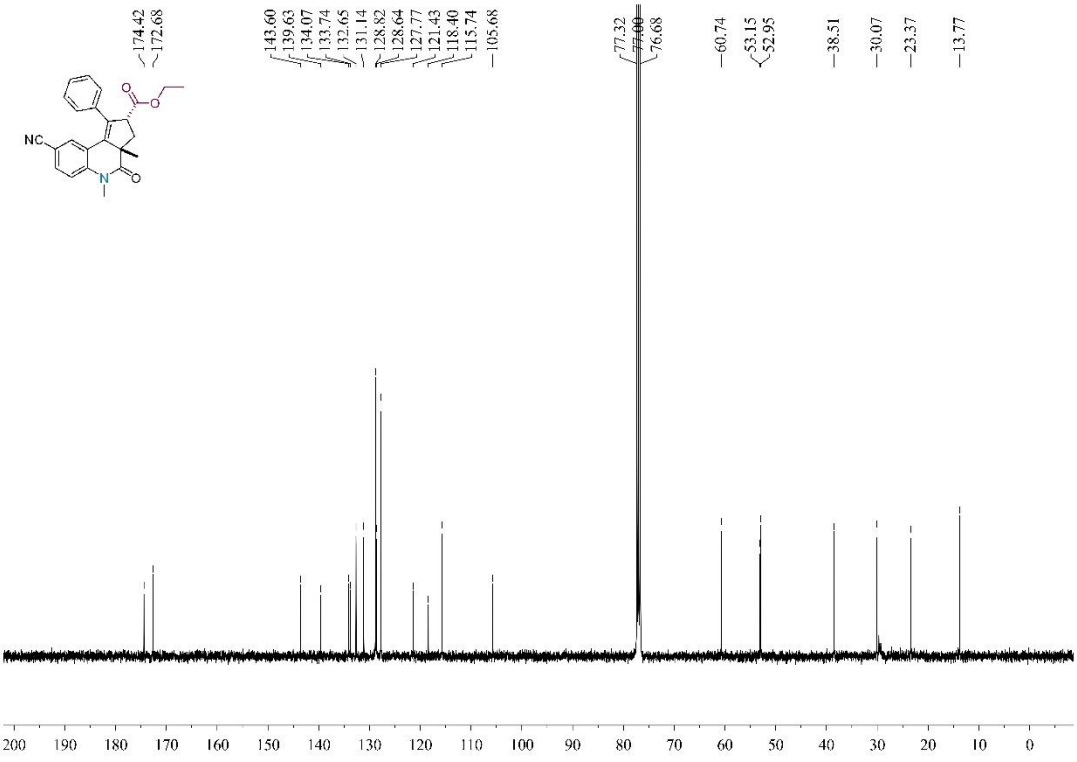
^{1}H NMR Spectrum of Compound ***cis*-4o** (400 MHz, $CDCl_3$)



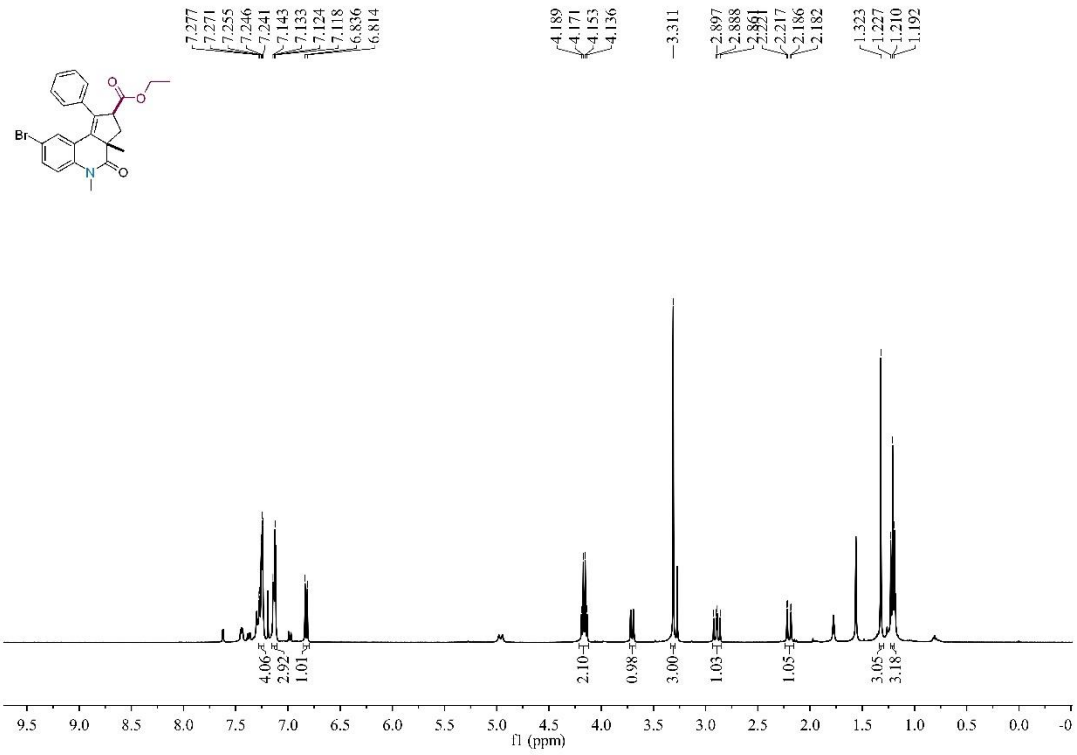
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-4o** (100 MHz, $CDCl_3$)



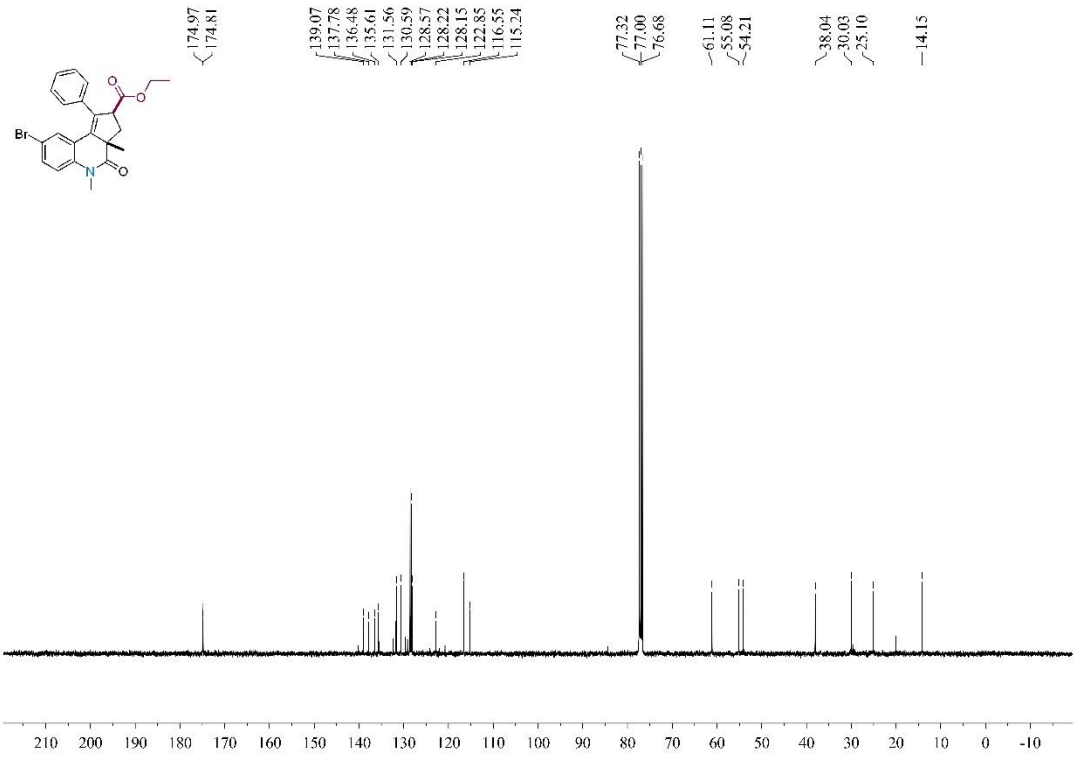
^{1}H NMR Spectrum of Compound ***trans*-4o** (400 MHz, $CDCl_3$)



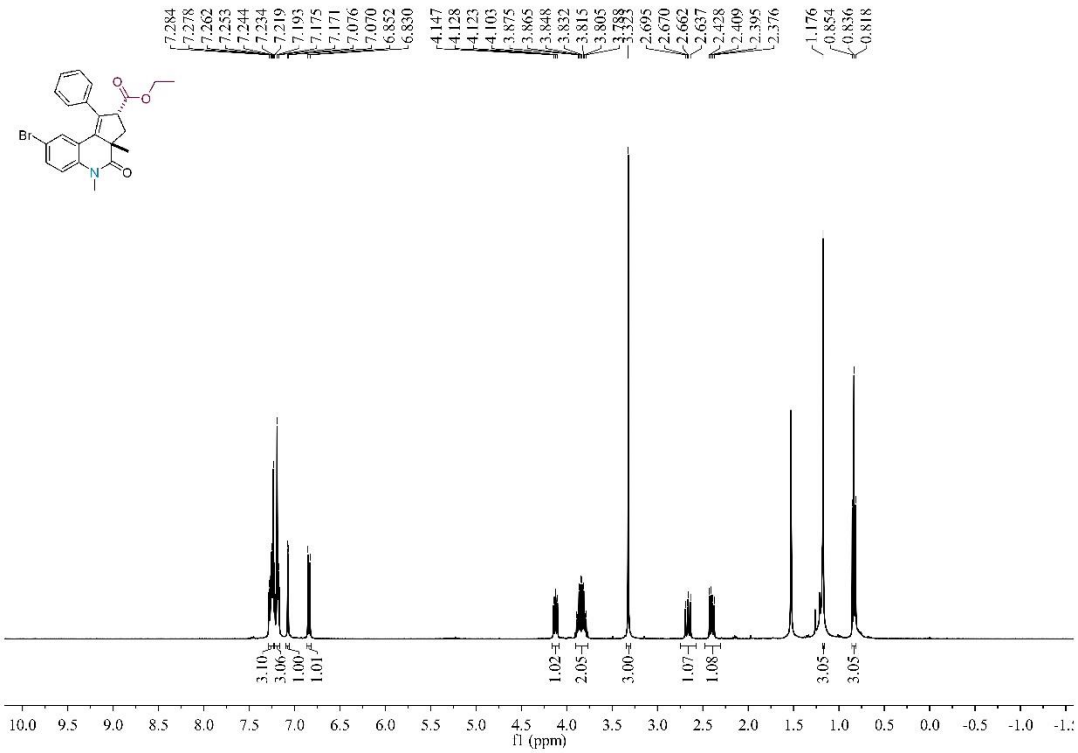
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4o** (100 MHz, $CDCl_3$)



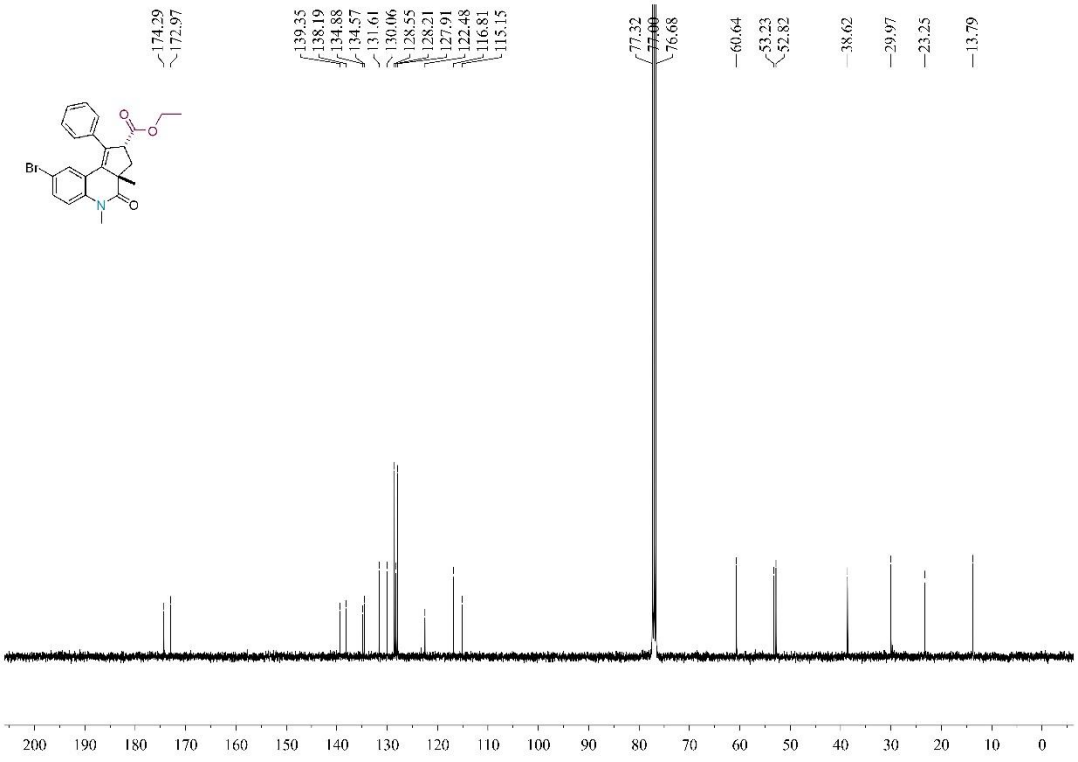
^{1}H NMR Spectrum of Compound ***cis*-4p** (400 MHz, $CDCl_3$)



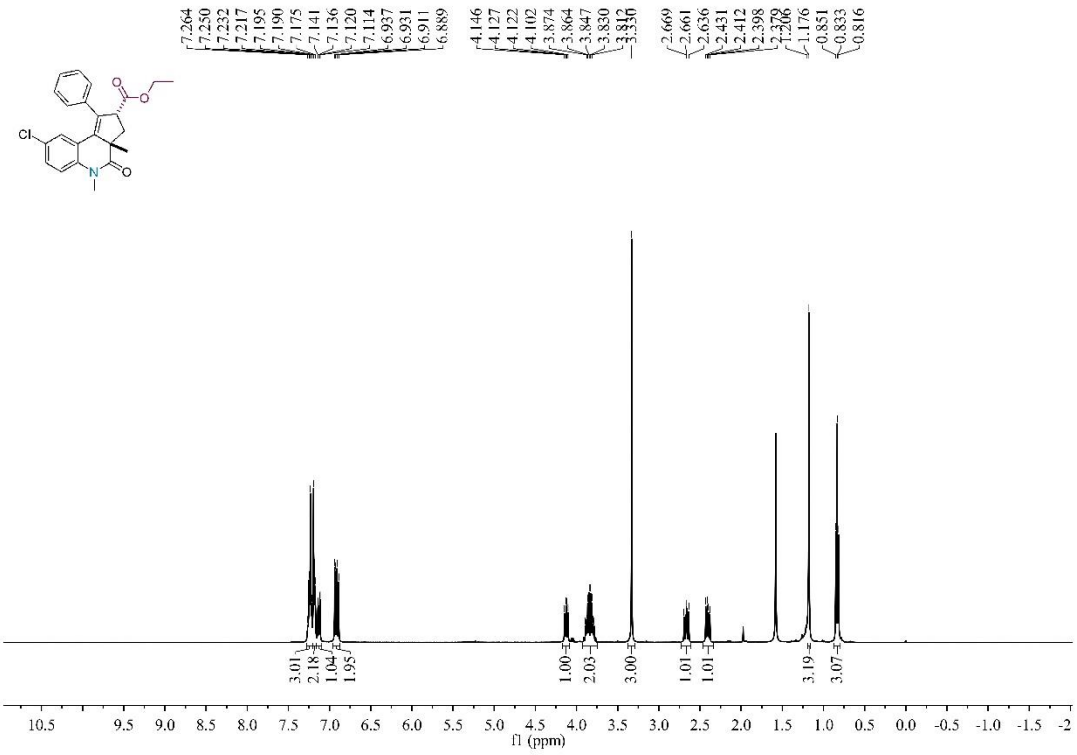
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-4p** (100 MHz, $CDCl_3$)



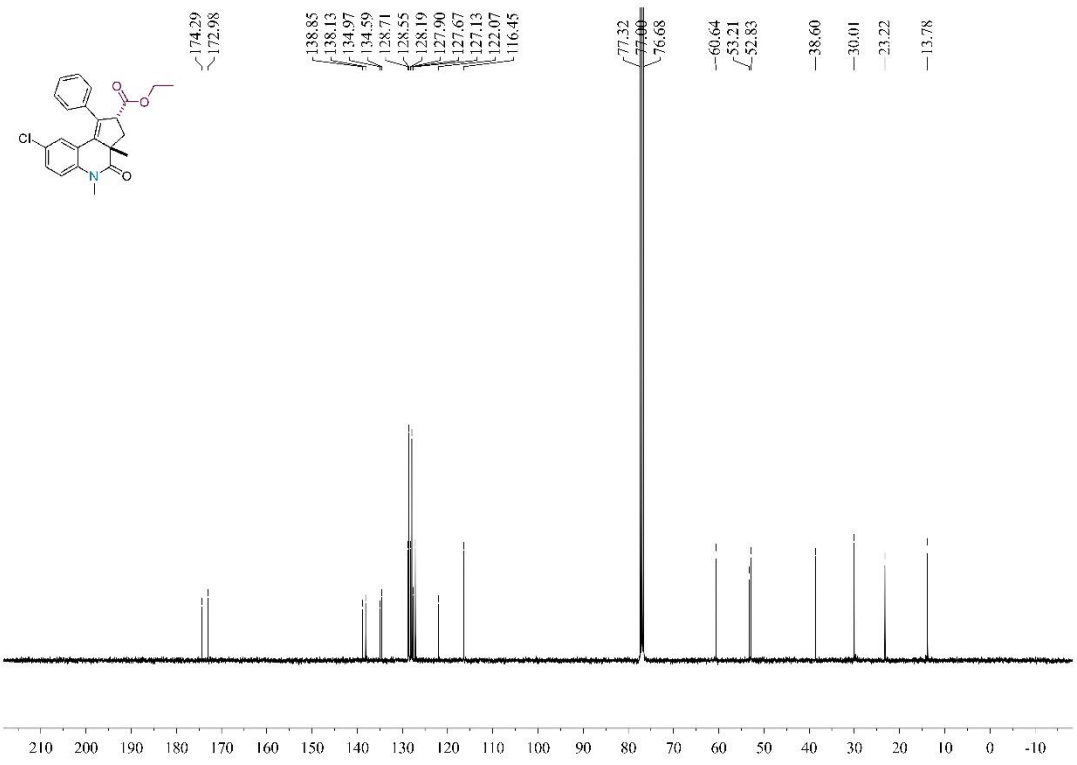
^{1}H NMR Spectrum of Compound ***trans*-4p** (400 MHz, $CDCl_3$)



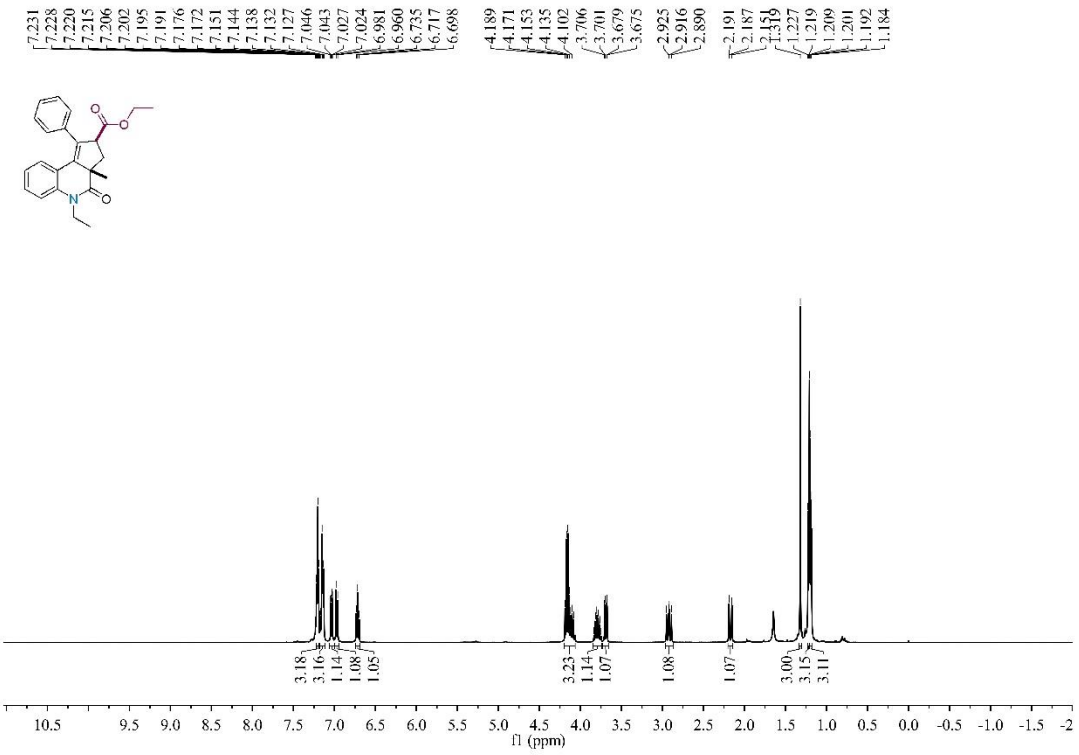
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***trans*-4p** (100 MHz, $CDCl_3$)



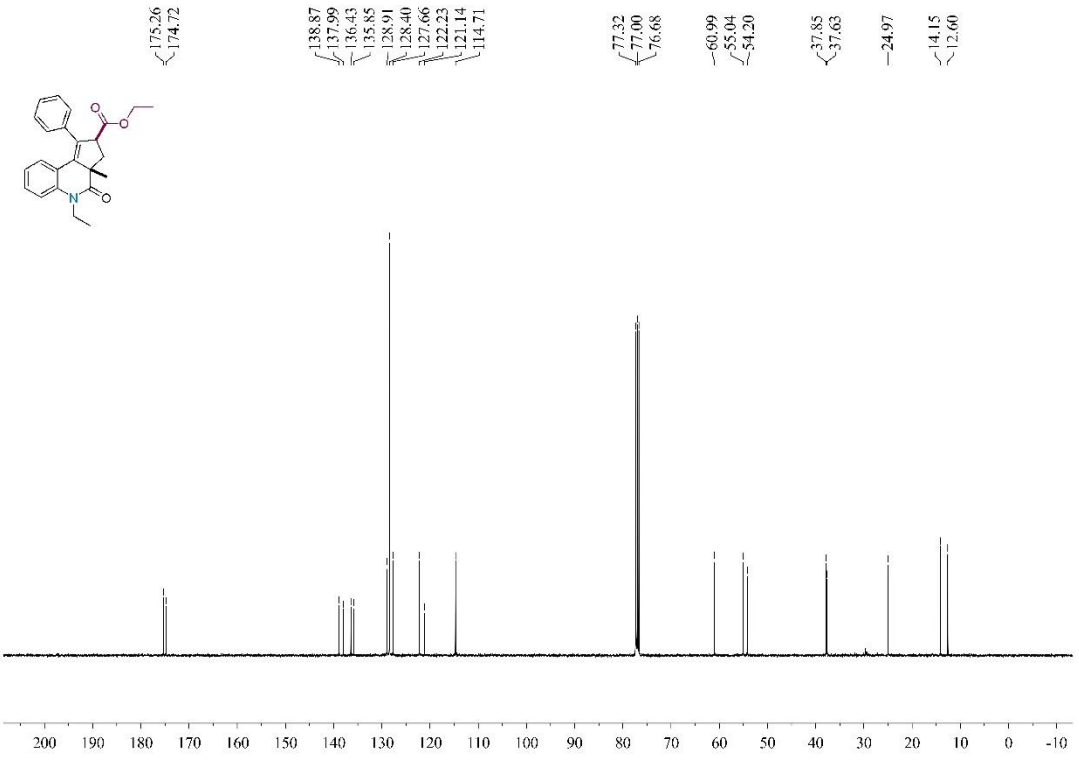
^{1}H NMR Spectrum of Compound ***trans*-4q** (400 MHz, $CDCl_3$)



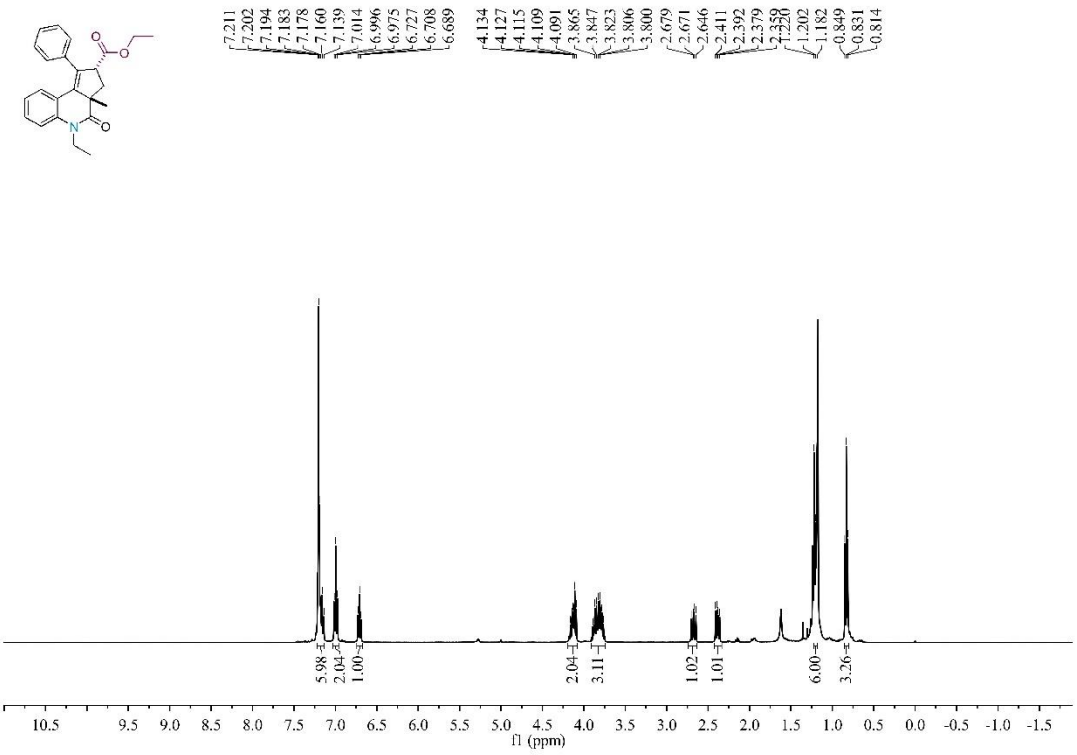
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4q** (100 MHz, $CDCl_3$)



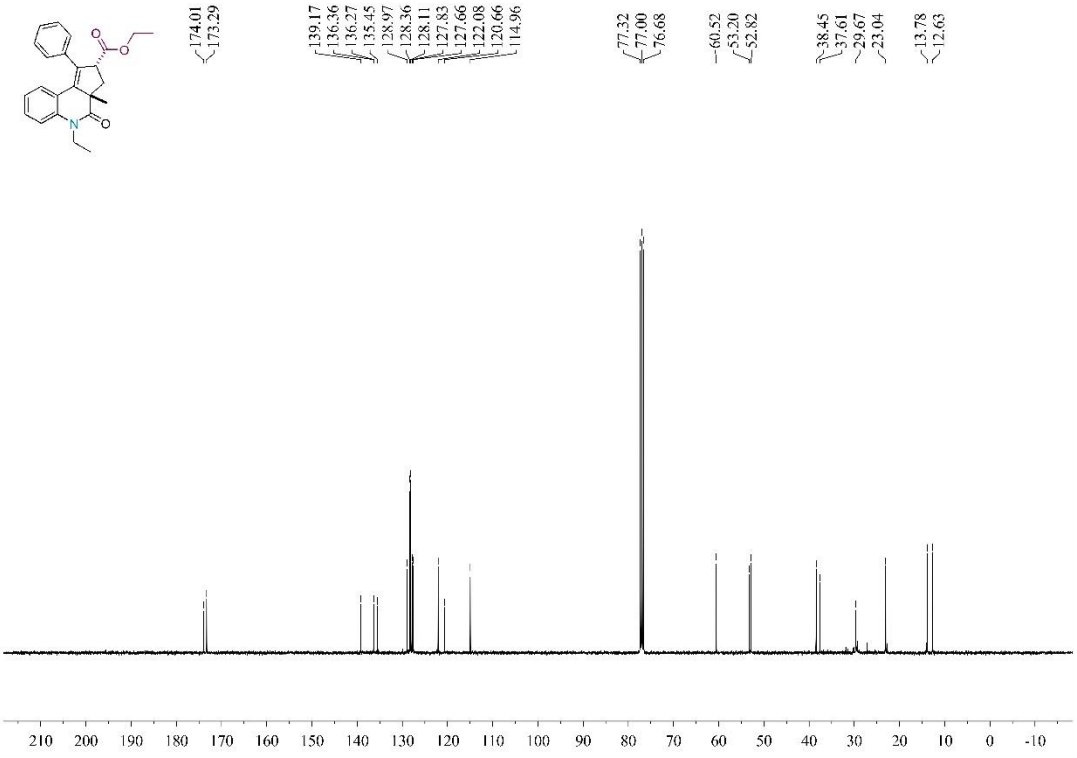
^{1}H NMR Spectrum of Compound ***cis*-4r** (400 MHz, $CDCl_3$)



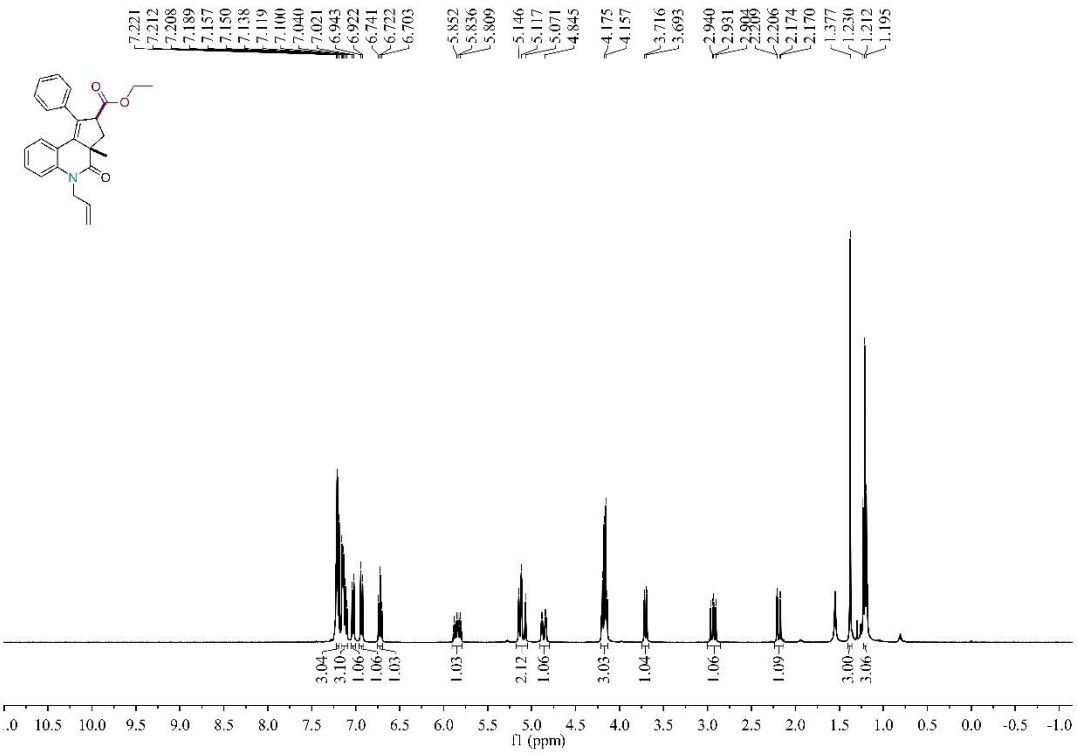
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-4r** (100 MHz, $CDCl_3$)



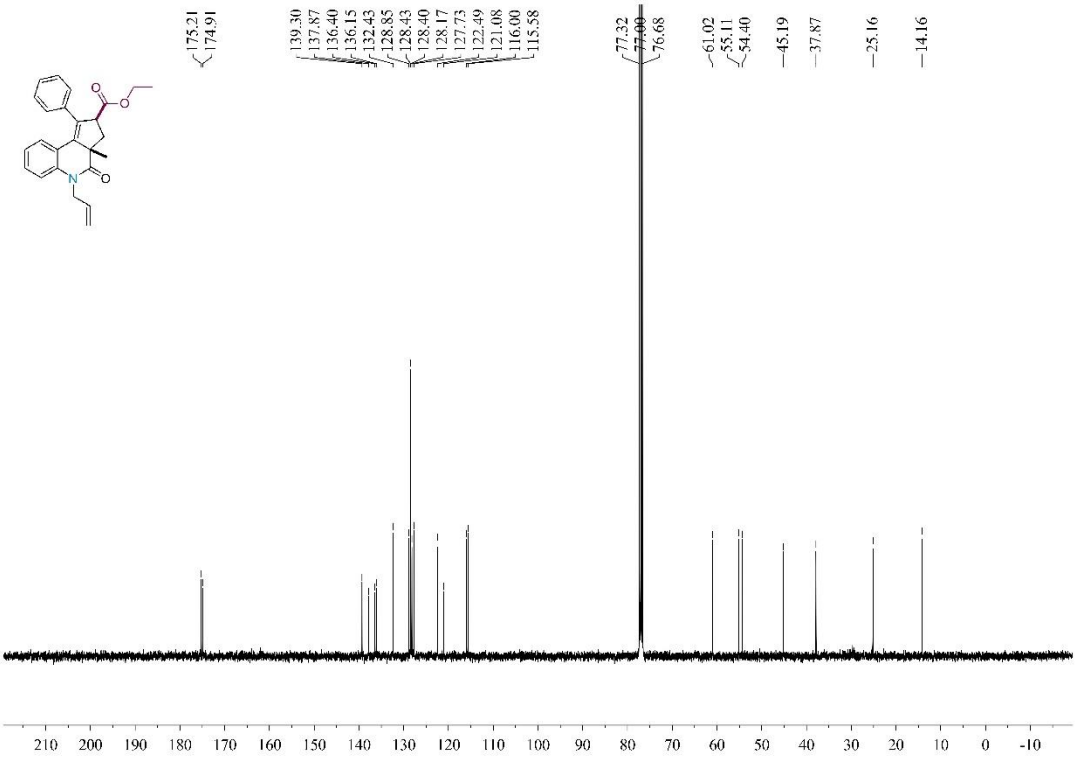
^{1}H NMR Spectrum of Compound ***trans*-4r** (400 MHz, $CDCl_3$)



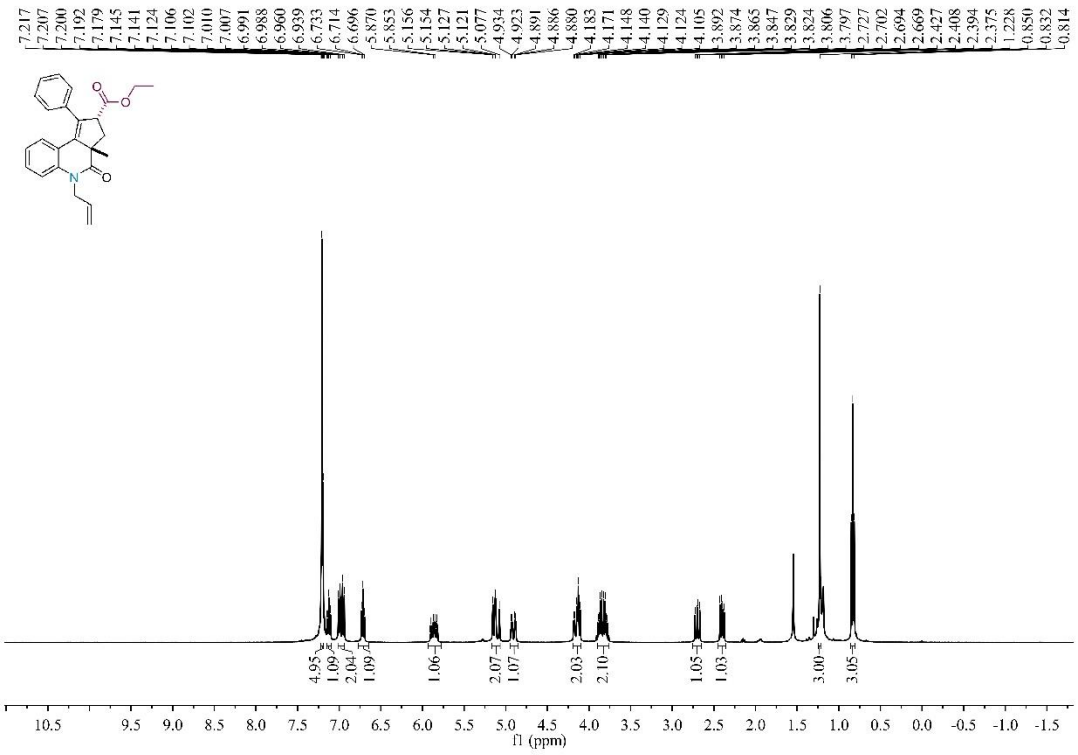
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4r** (100 MHz, $CDCl_3$)



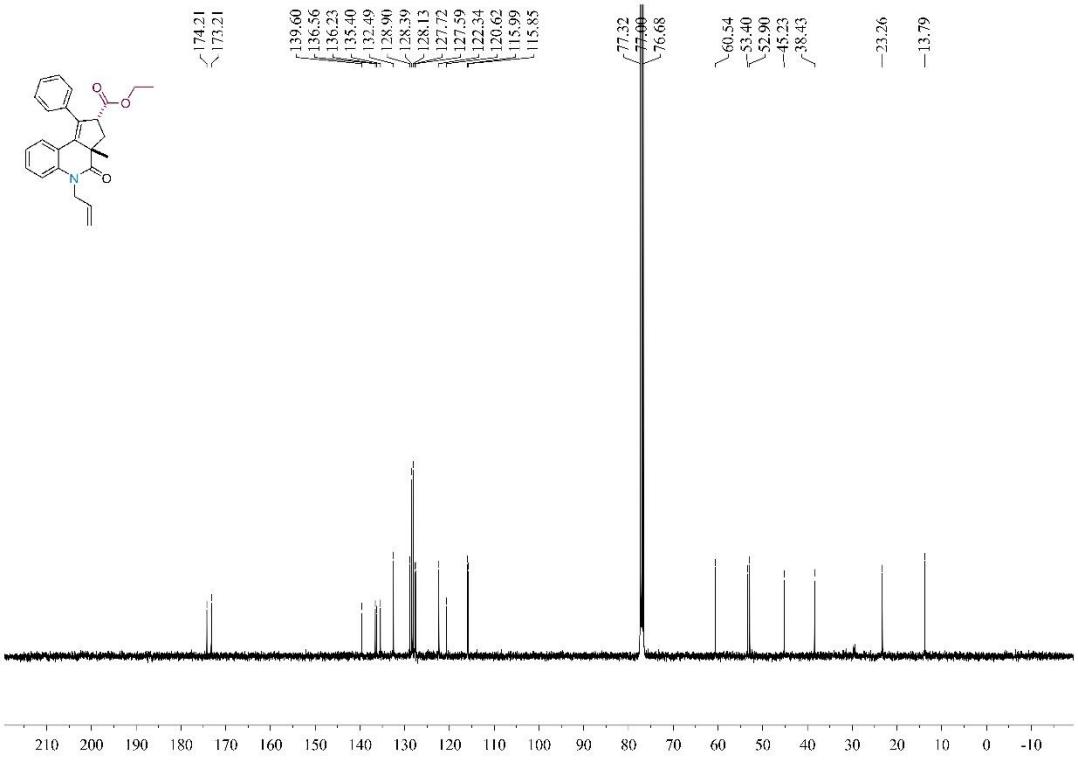
^{1}H NMR Spectrum of Compound ***cis*-4s** (400 MHz, $CDCl_3$)



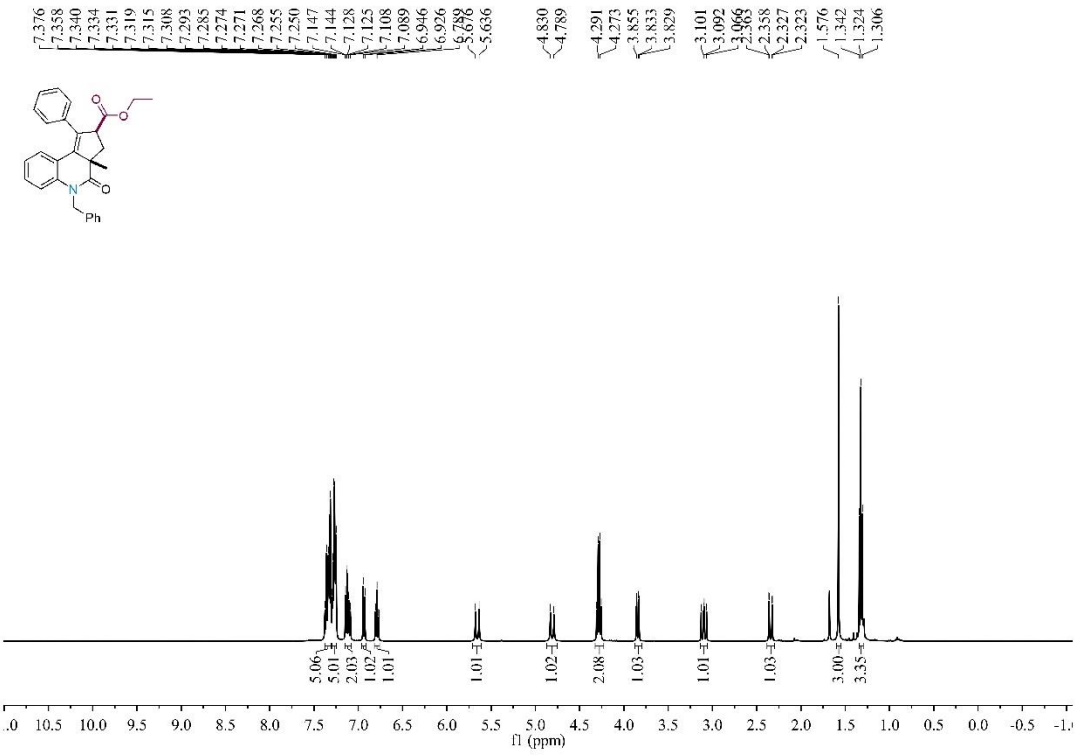
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***cis*-4s** (100 MHz, $CDCl_3$)



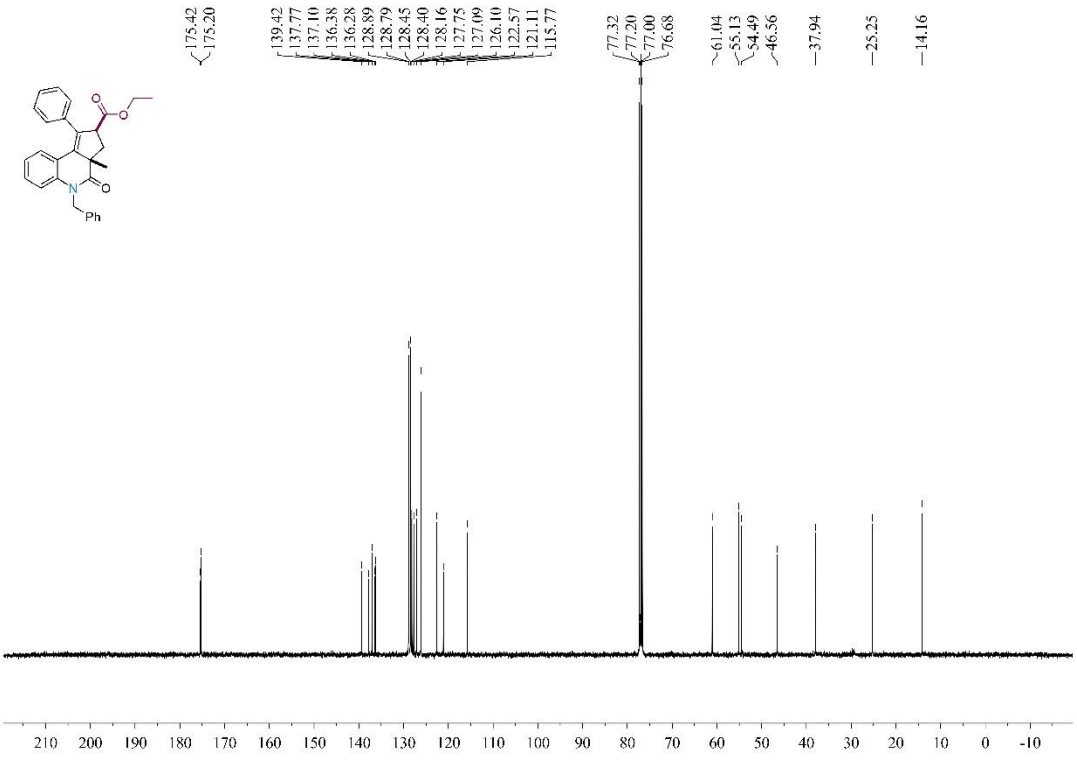
^{1}H NMR Spectrum of Compound ***trans*-4s** (400 MHz, $CDCl_3$)



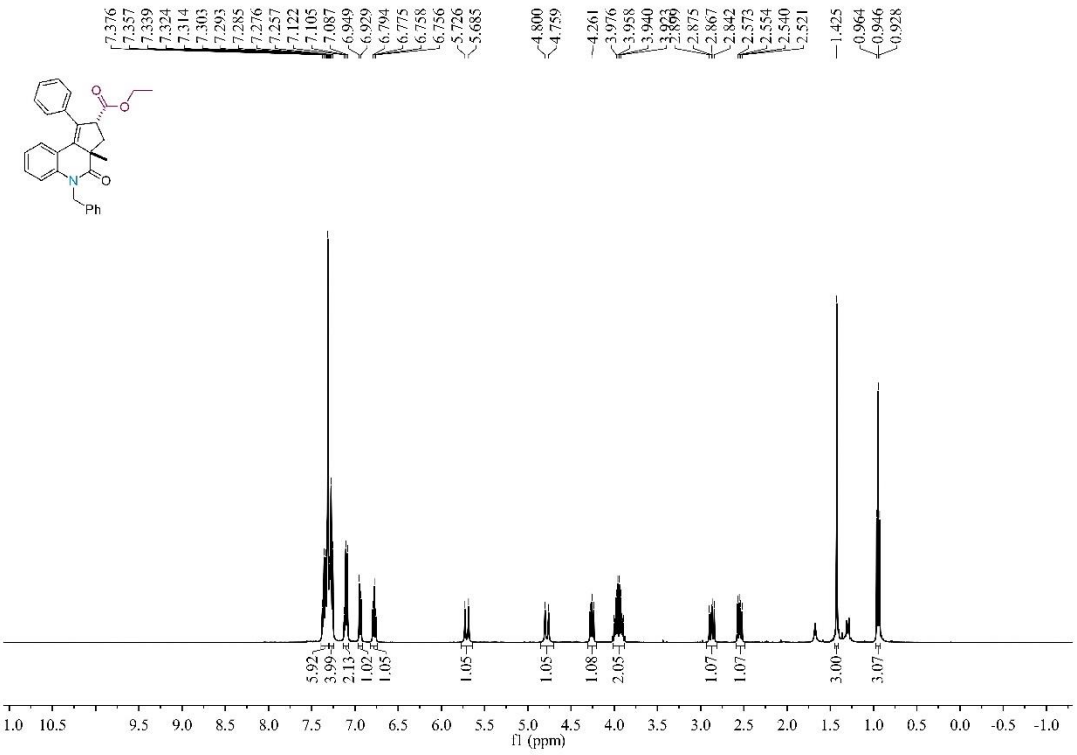
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound ***trans*-4s** (100 MHz, $CDCl_3$)



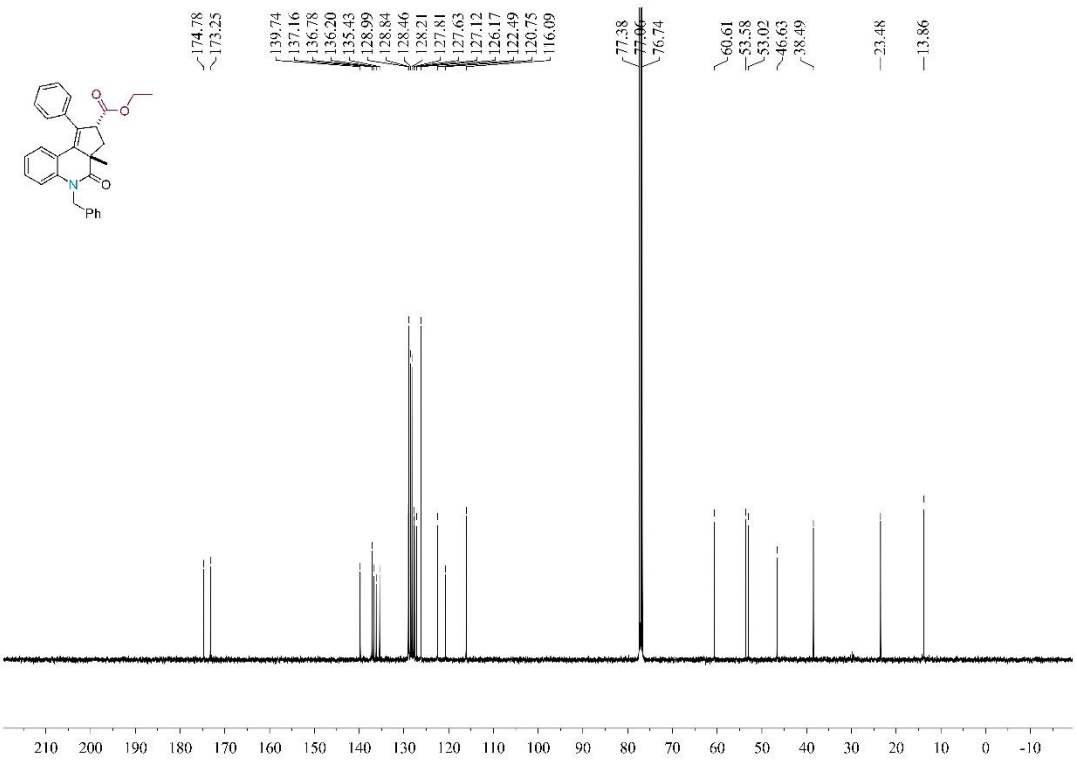
^{1}H NMR Spectrum of Compound ***cis*-4t** (400 MHz, $CDCl_3$)



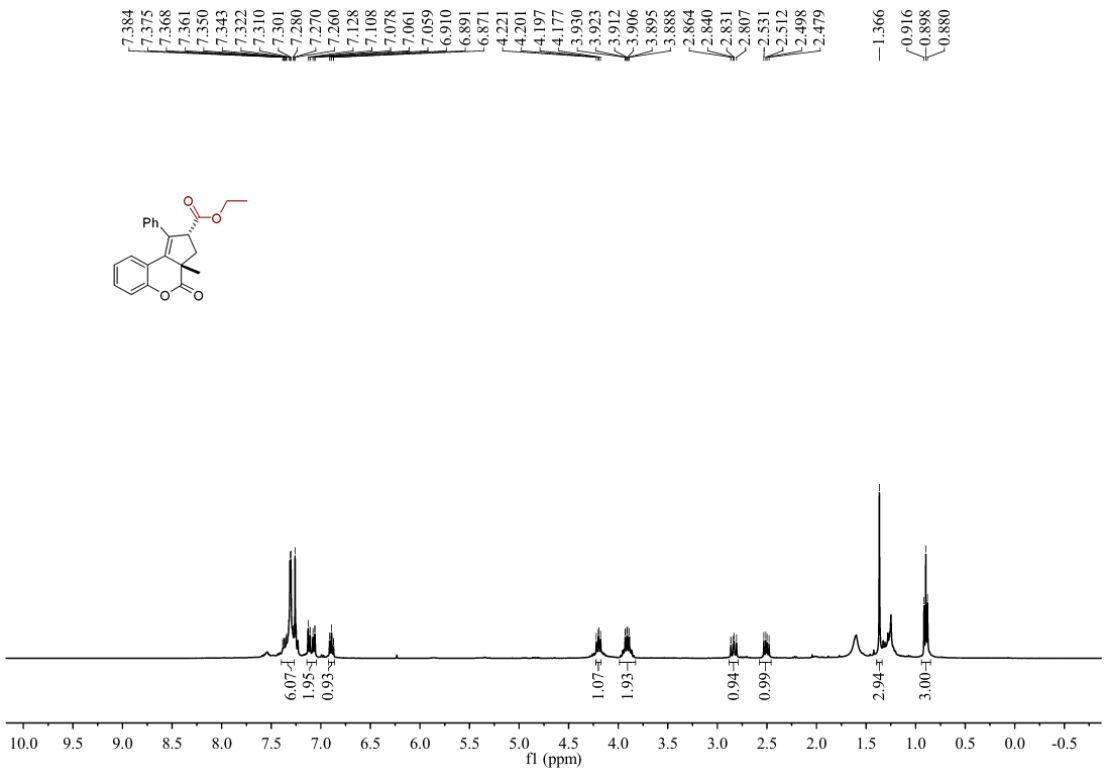
^{13}C{^{1}H} NMR Spectrum of Compound ***cis*-4t** (100 MHz, $CDCl_3$)



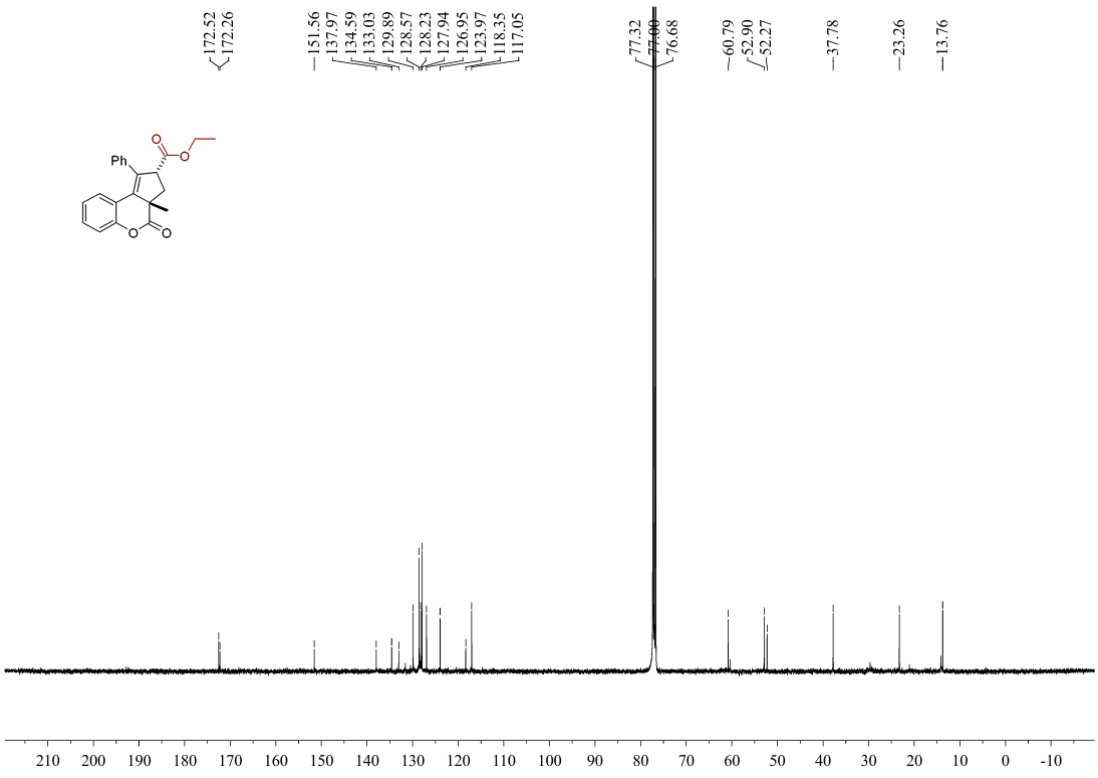
^{1}H NMR Spectrum of Compound ***trans*-4t** (400 MHz, $CDCl_3$)



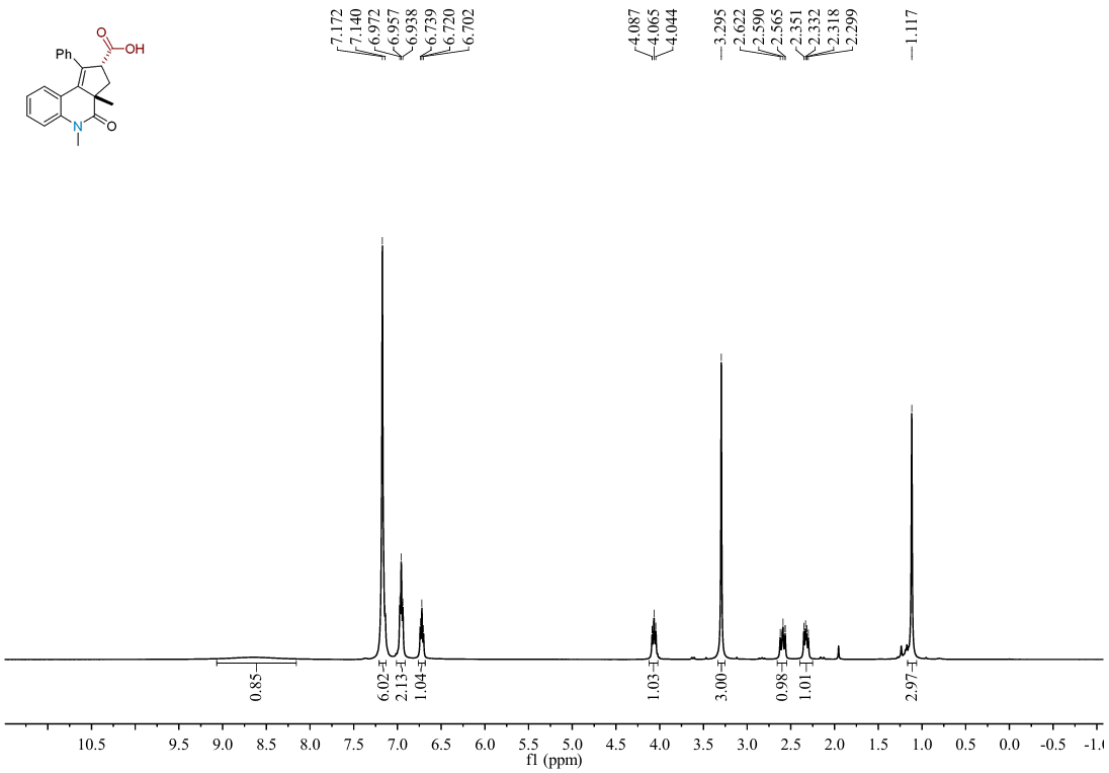
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4t** (100 MHz, $CDCl_3$)



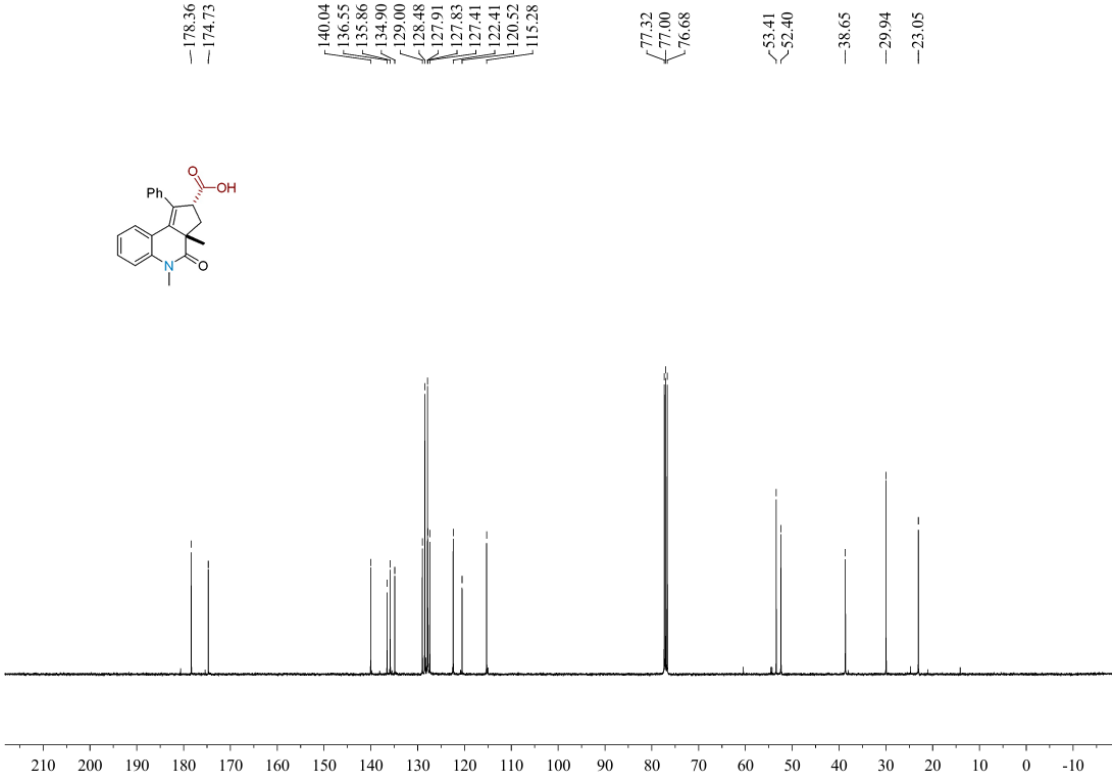
^{1}H NMR Spectrum of Compound ***trans*-4u** (400 MHz, $CDCl_3$)



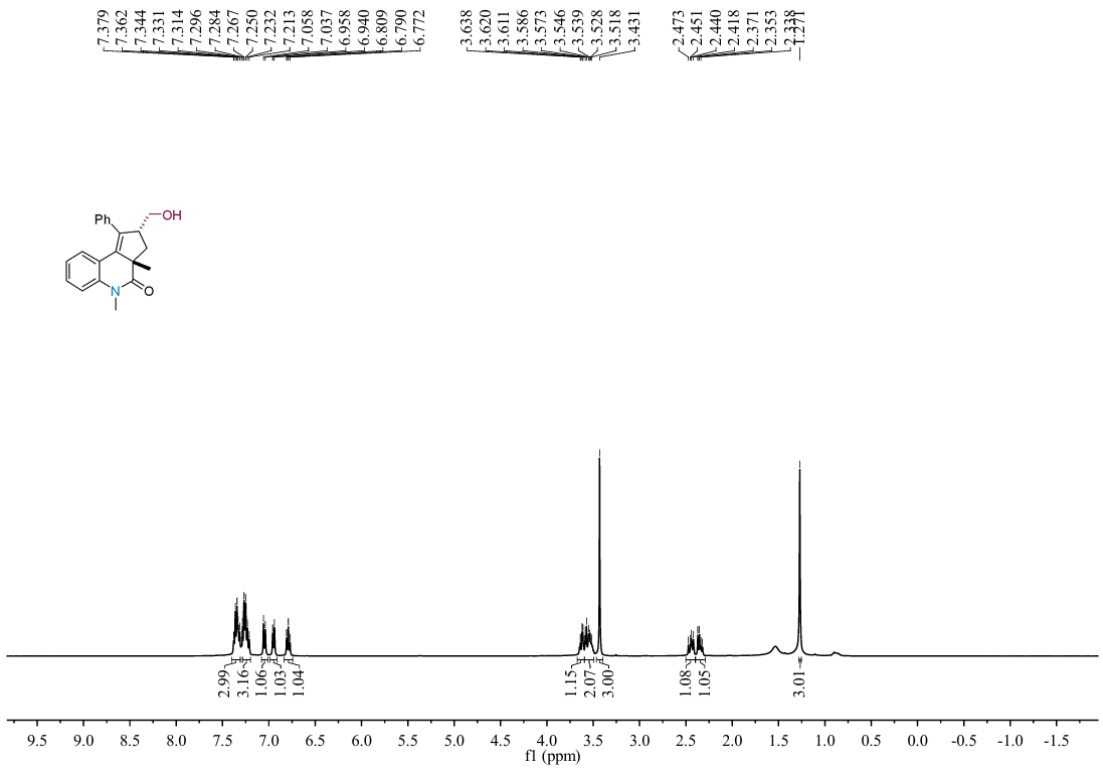
^{13}C{^{1}H} NMR Spectrum of Compound ***trans*-4u** (100 MHz, $CDCl_3$)



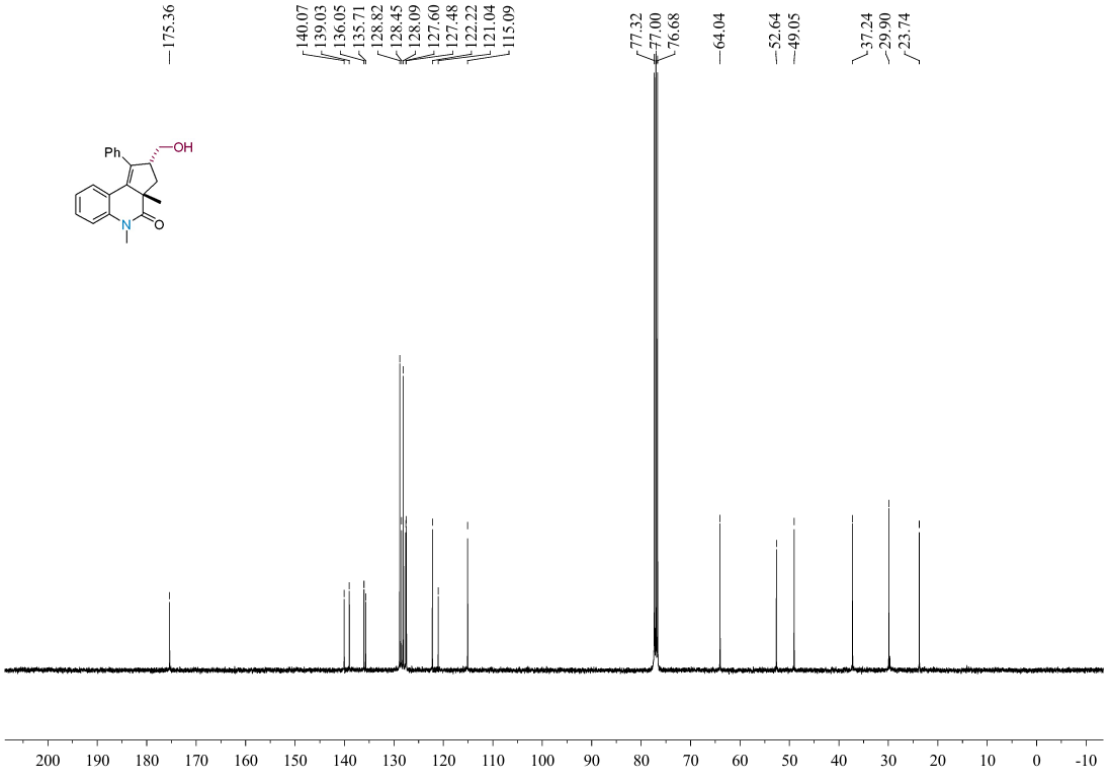
^{1}H NMR Spectrum of Compound **5** (400 MHz, $CDCl_3$)



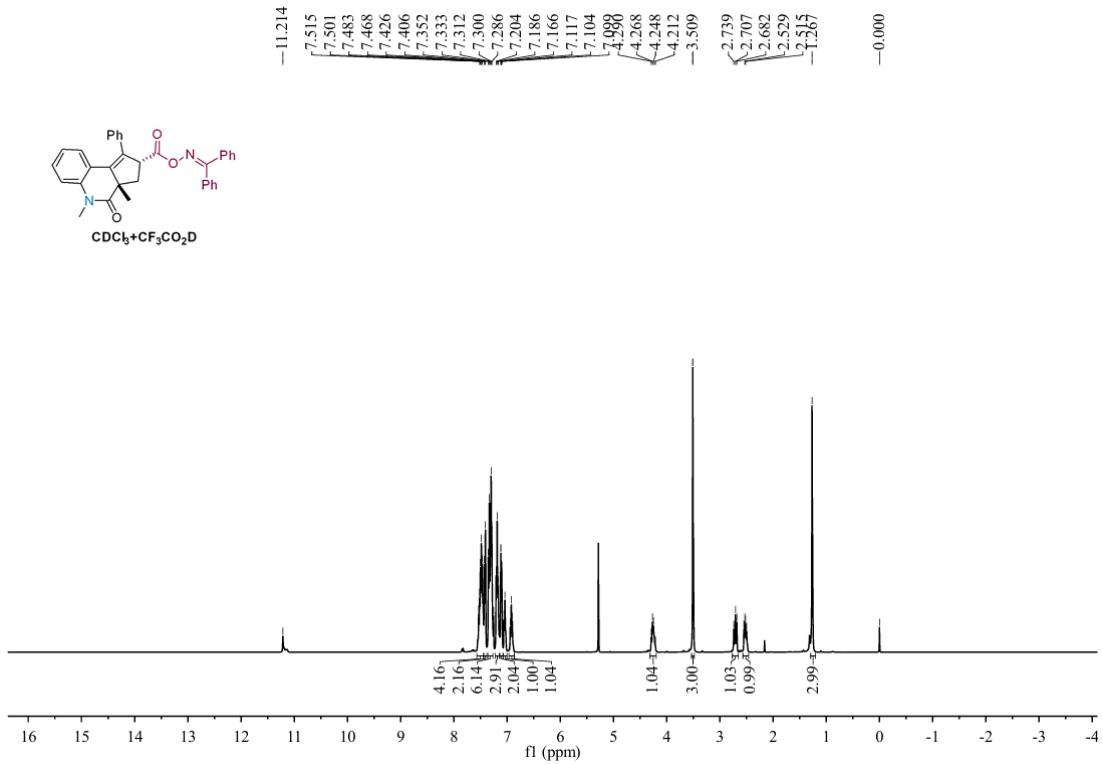
^{13}C{^{1}H} NMR Spectrum of Compound **5** (100 MHz, $CDCl_3$)



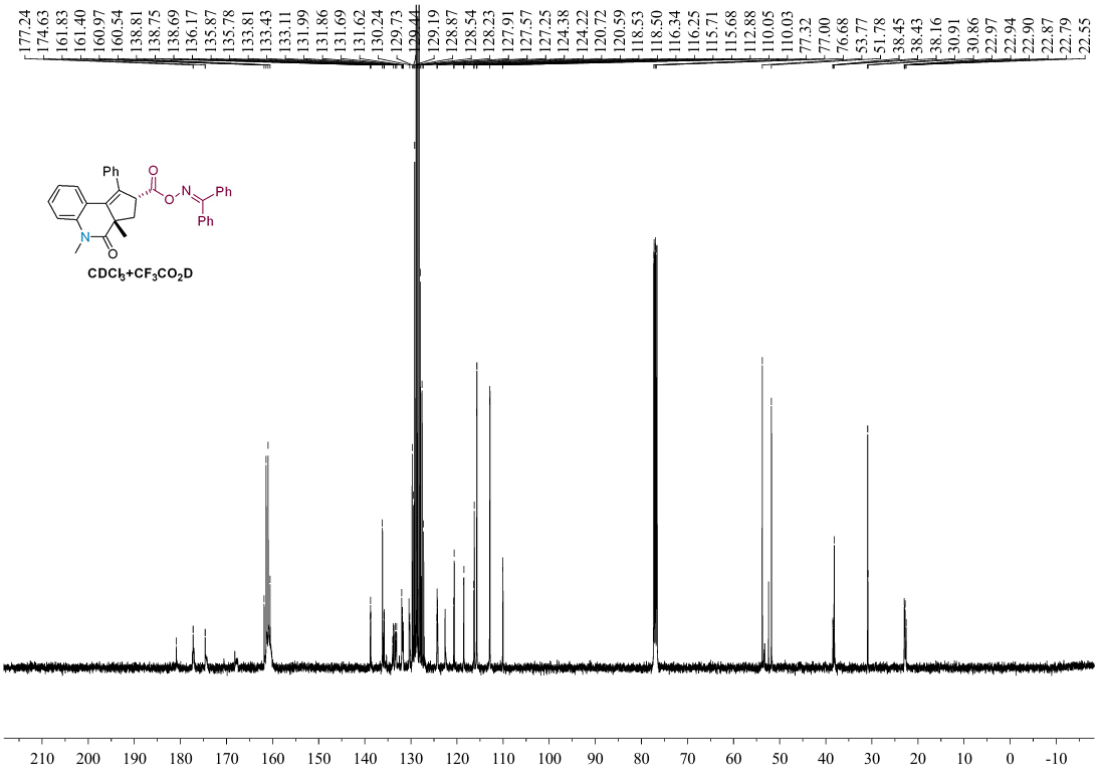
^{1}H NMR Spectrum of Compound **6** (400 MHz, $CDCl_3$)



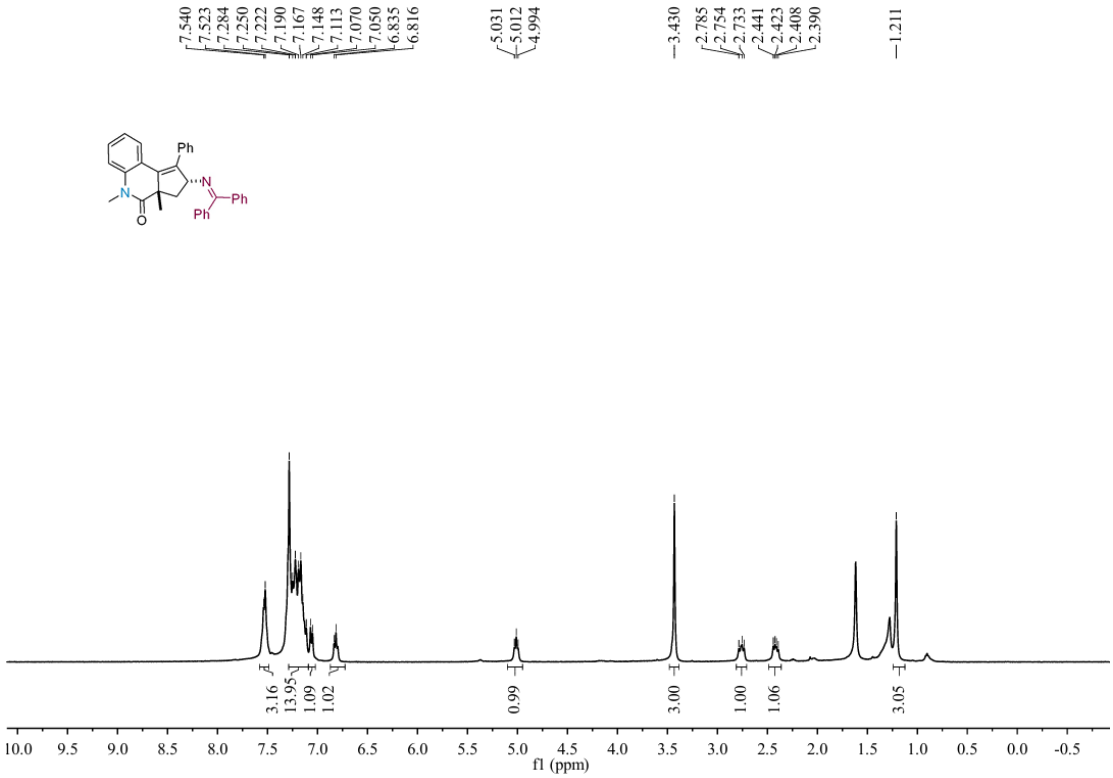
^{13}C{^{1}H} NMR Spectrum of Compound **6** (100 MHz, $CDCl_3$)



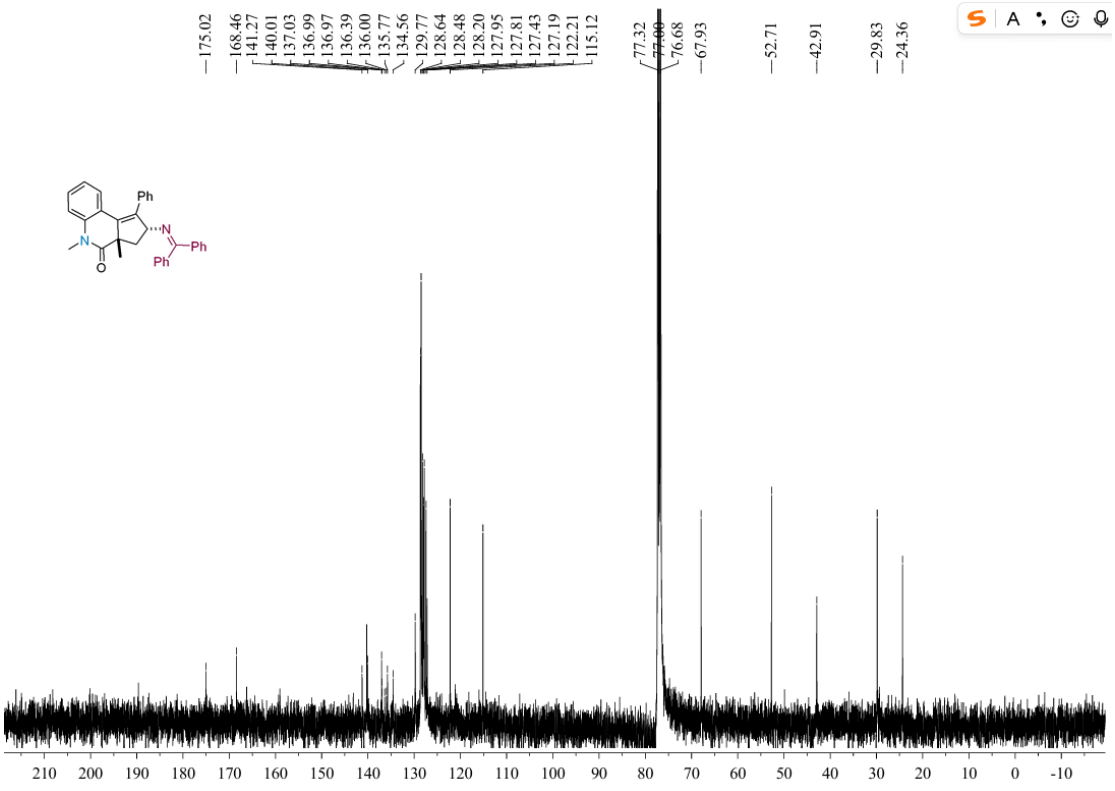
^{1}H NMR Spectrum of Compound **7** (400 MHz, $CDCl_3$ + CF_3CO_2D)



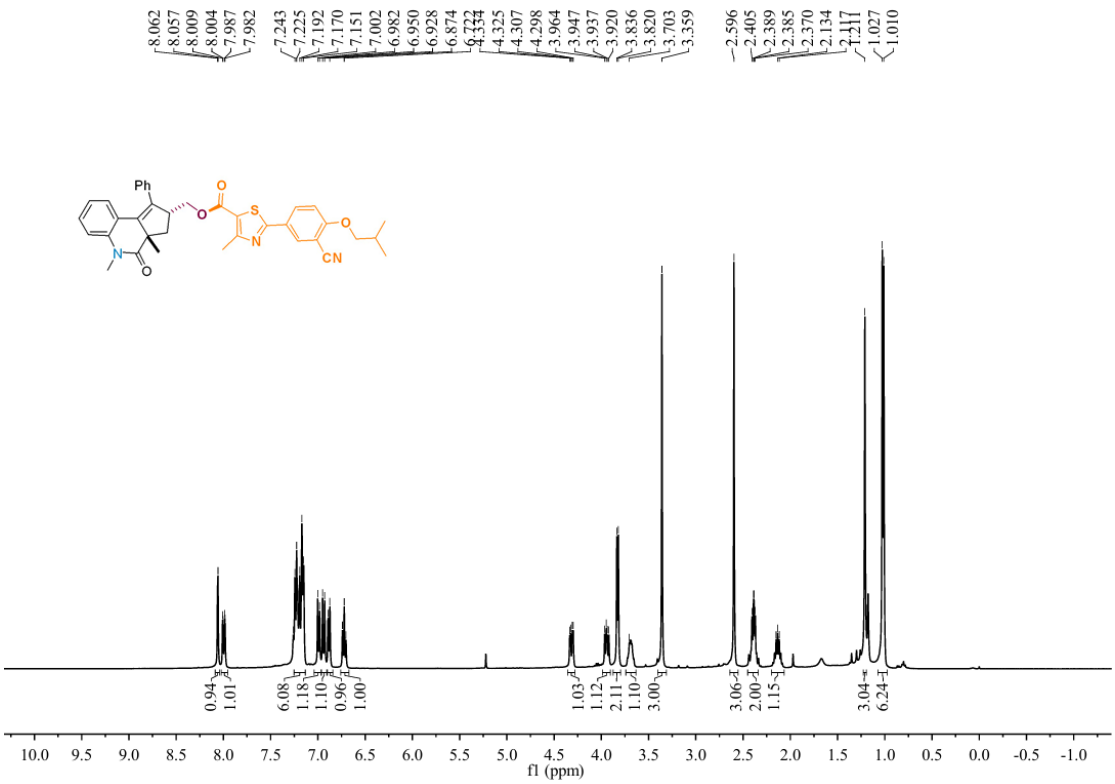
^{13}C{^{1}H} NMR Spectrum of Compound **7** (100 MHz, $CDCl_3$ + CF_3CO_2D)



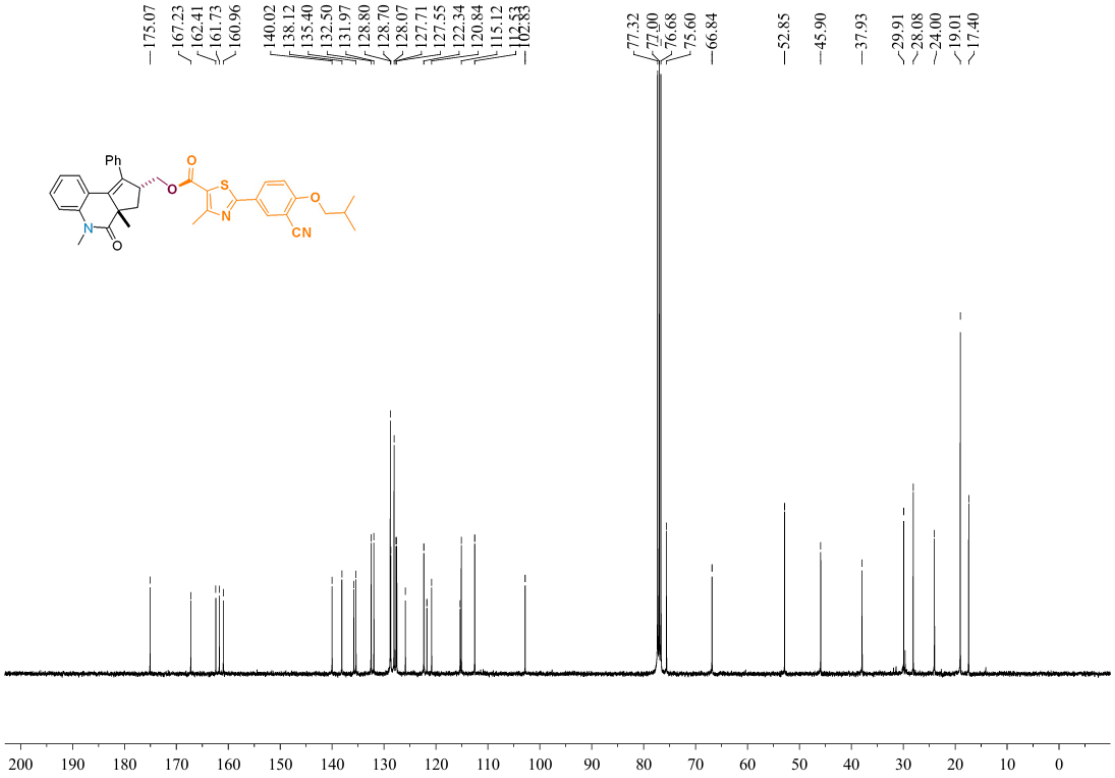
^{1}H NMR Spectrum of Compound **8** (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR Spectrum of Compound **8** (100 MHz, $CDCl_3$)



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



^{13}C{^{1}H} NMR Spectrum of Compound **9** (100 MHz, $CDCl_3$)