# Supporting Information

## Chlorophyll-Catalyzed Visible-Light-Mediated Synthesis of Tetrahydroquinolines from N,N-Dimethylanilines and Maleimides

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## 1 Materials

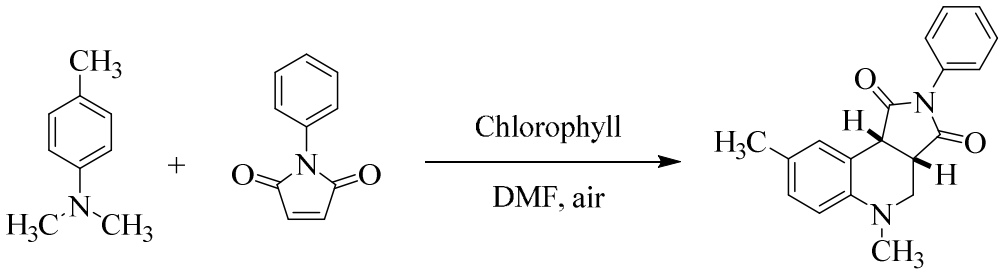
The natural pigment chlorophyll we used was purchased from Tokyo Chemical Industry (TCI, Product No. C0780). This is a mixture powder of chlorophyll, lactose and dry gum arabic (according to the product description the additives lactose and dry gum arabic are added to improve the dispersion of chlorophyll in water if a solution is prepared). In this chlorophyll reagent, the mass percentage of total chlorophyll from plants is ca. 0.5% (according to the product description). We determined the total chlorophyll content in this reagent, and found that it is 0.52% (mass percentage) by measuring the absorbance of chlorophyll at 663 nm and 645 nm in 80% acetone solution.[1] The brand of fluorescent lamp is Philips. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification.

## 2 Analytical Methods

Reactions were monitored by thin-layer chromatography (TLC) using UV light and vanillic aldehyde as visualizing agents. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. $^{1}$H NMR and $^{13}$C NMR spectra were recorded on 600 MHz NMR. Chemical shifts were reported in ppm from TMS with the solvent resonance as the internal standard. Data were reported as follows: chemical shifts (δ) in ppm, coupling constants (*J*) in Hz, and solvent ($CDCl_3$ and DMSO-$d_6$). Light absorbance was determined by UV-VIS spectrophotometer. High-resolution mass spectra were obtained on mass spectrometer by using ESI-TOF. Melting points were taken on a melting point apparatus and were uncorrected.

## 3 Extra information for optimization of reaction conditions

**Table S1. Screening of molar ratio, solvent volume and wattage of lamp and time-course investigation**[a]




**1a** **2a** **3a**

| Entry | Molar ratio (**1a**:**2a**) | DMF (mL) | Wattage of lamp (W) | Time (h) | Yield (**3a**) % [b] |
|---|---|---|---|---|---|
| 1 | 1:1 | 1.0 | 23 | 36 | 51 |
| 2 | 1.5:1 | 1.0 | 23 | 36 | 66 |
| **3** | **2:1** | **1.0** | **23** | **36** | **80** |
| 4 | 2.5:1 | 1.0 | 23 | 36 | 67 |
| 5 | 1:1.5 | 1.0 | 23 | 36 | 57 |
| 6 | 1:2 | 1.0 | 23 | 36 | 59 |
| 7 | 2:1 | 0.5 | 23 | 36 | 47 |
| 8 | 2:1 | 1.5 | 23 | 36 | 82 |
| **9** | **2:1** | **2.0** | **23** | **36** | **89** |
| 10 | 2:1 | 2.5 | 23 | 36 | 79 |
| 11 | 2:1 | 2.0 | 5 | 36 | 55 |
| 12 | 2:1 | 2.0 | 12 | 36 | 78 |
| 13 | 2:1 | 2.0 | 32 | 36 | 66 |
| 14 | 2:1 | 2.0 | 45 | 36 | 69 |
| 15 | 2:1 | 2.0 | 23 | 4 | 5 |
| 16 | 2:1 | 2.0 | 23 | 8 | 10 |
| 17 | 2:1 | 2.0 | 23 | 12 | 47 |
| 18 | 2:1 | 2.0 | 23 | 18 | 58 |
| 19 | 2:1 | 2.0 | 23 | 24 | 70 |
| 20 | 2:1 | 2.0 | 23 | 48 | 97 |

[a] Reaction conditions: A mixture of **1a** (0.25-0.63 mmol), **2a** (0.25-0.50 mmol), 0.16 mg of chlorophyll (30 mg of chlorophyll powder preparation, in which total chlorophyll content is 0.52%) in DMF (0.5-2.5 mL) was irradiated with a fluorescent lamp (5 W-45 W) for 4-48 h.

[b] Yield of the isolated product after silica gel chromatography.

**4 UV-visible absorption of chlorophyll, gum arabic and lactose**

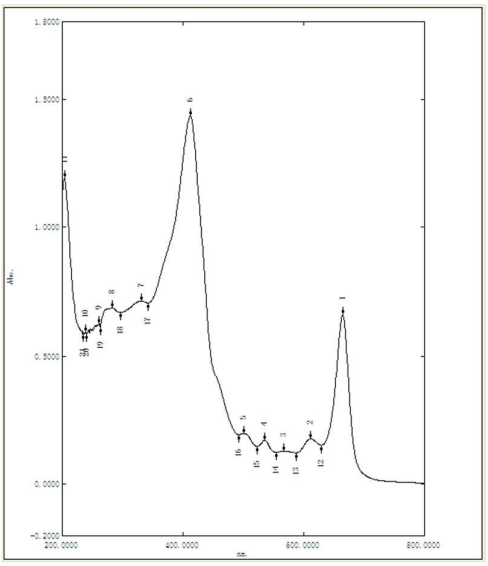


**Figure S1.** UV-visible absorption of chlorophyll

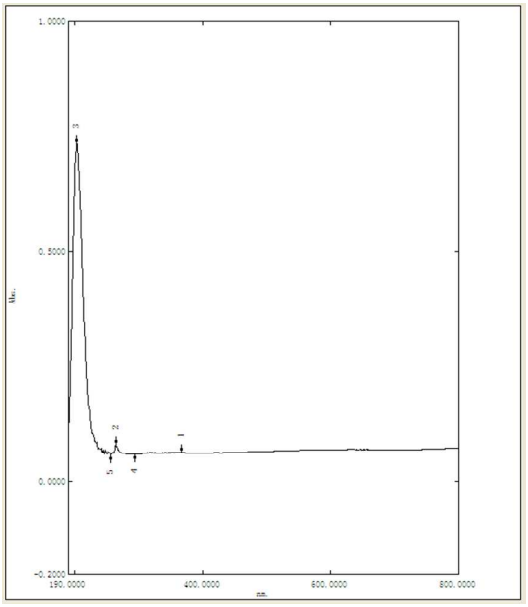


**Figure S2.** UV-visible absorption of gum arabic

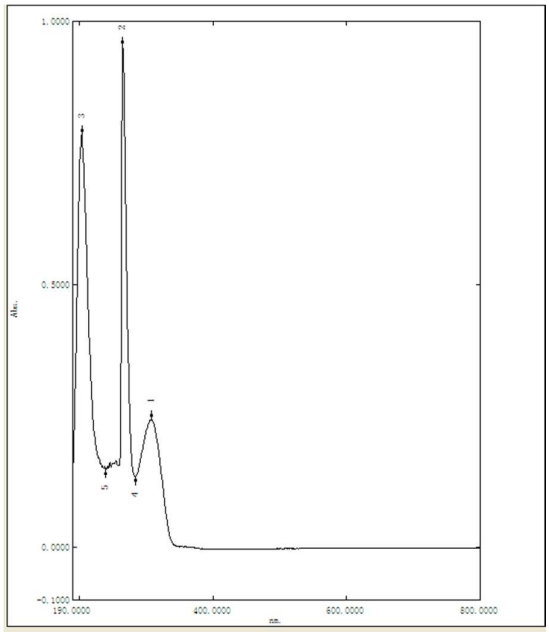
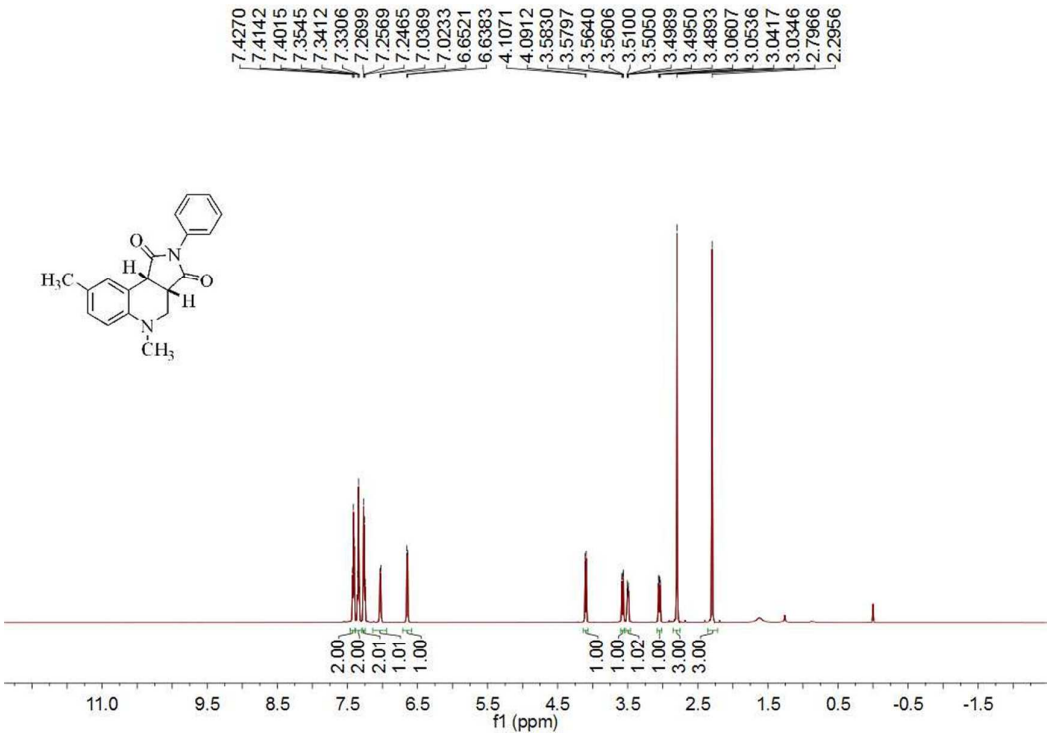


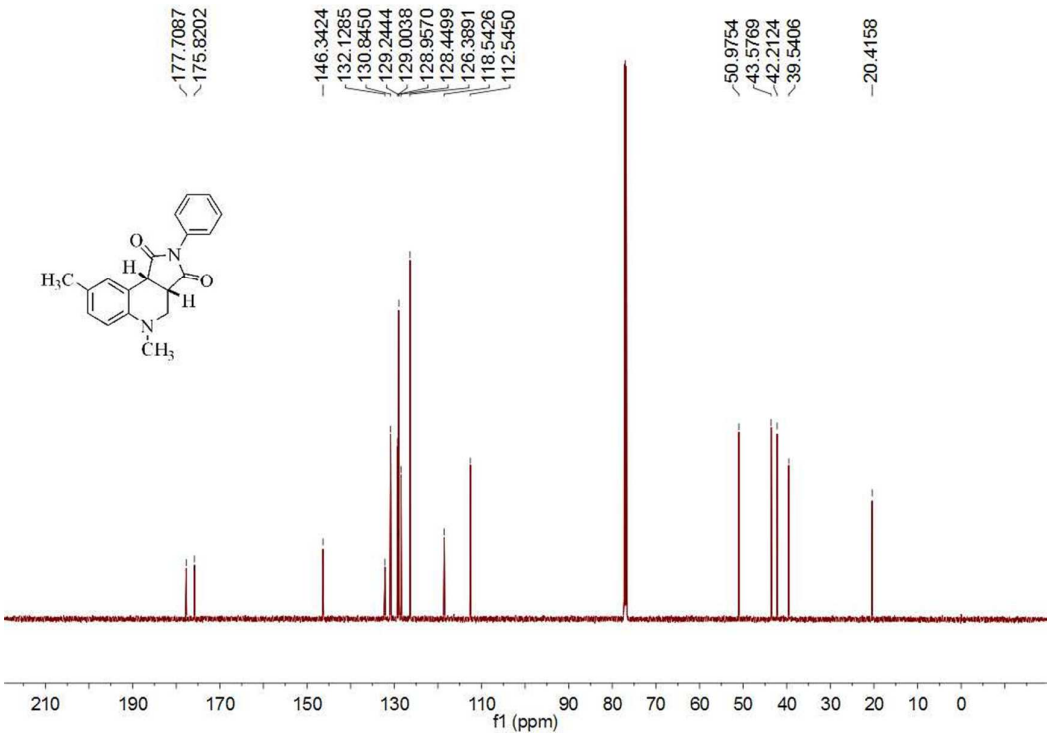

**Figure S3.** UV-visible absorption of lactose

## 5 $^{1}$H NMR, $^{13}$C NMR, and HRMS spectra of the products

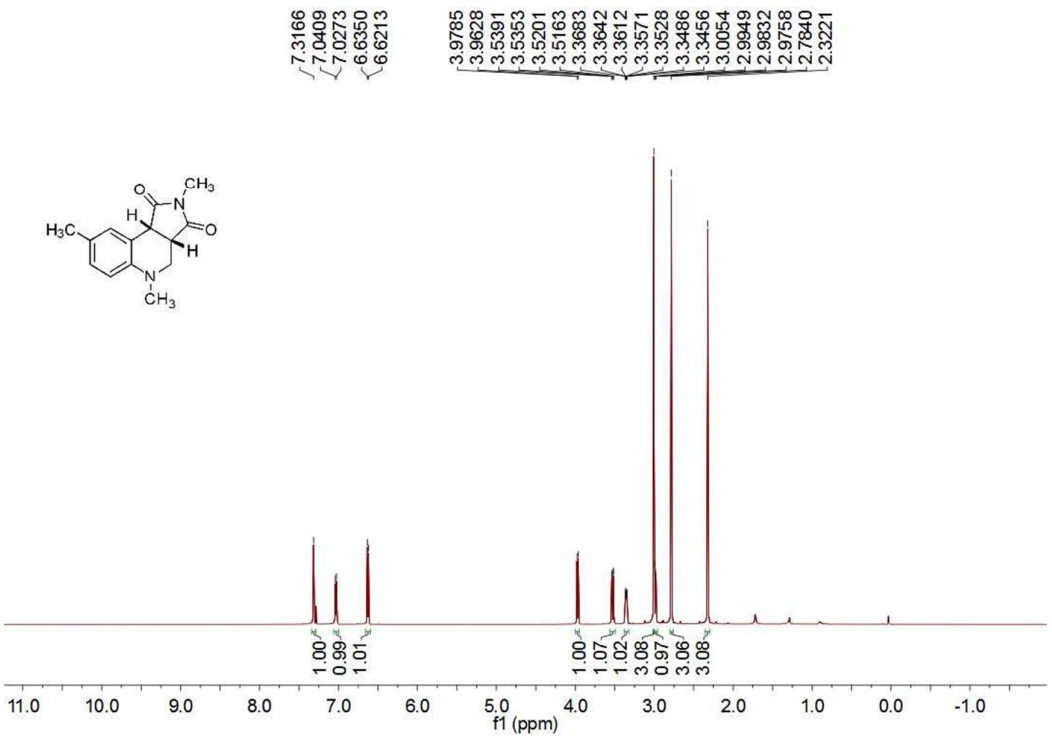
### 3a-$^{1}$H NMR




### 3a-$^{13}$C NMR



**3b-$^{1}$H NMR**

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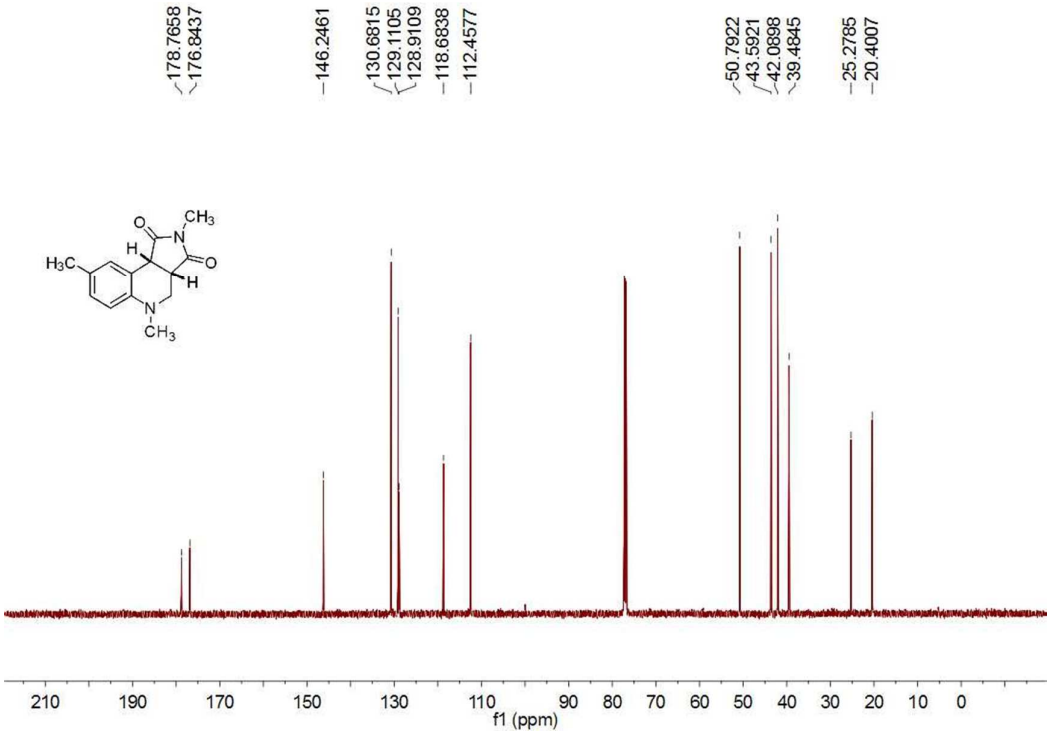

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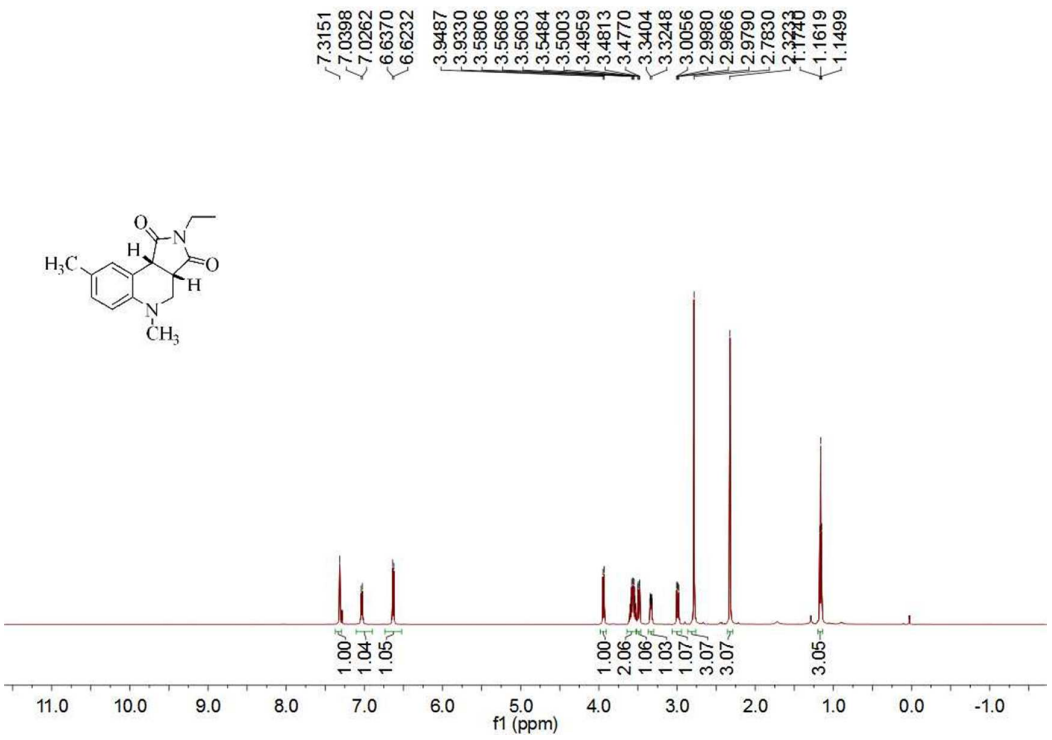


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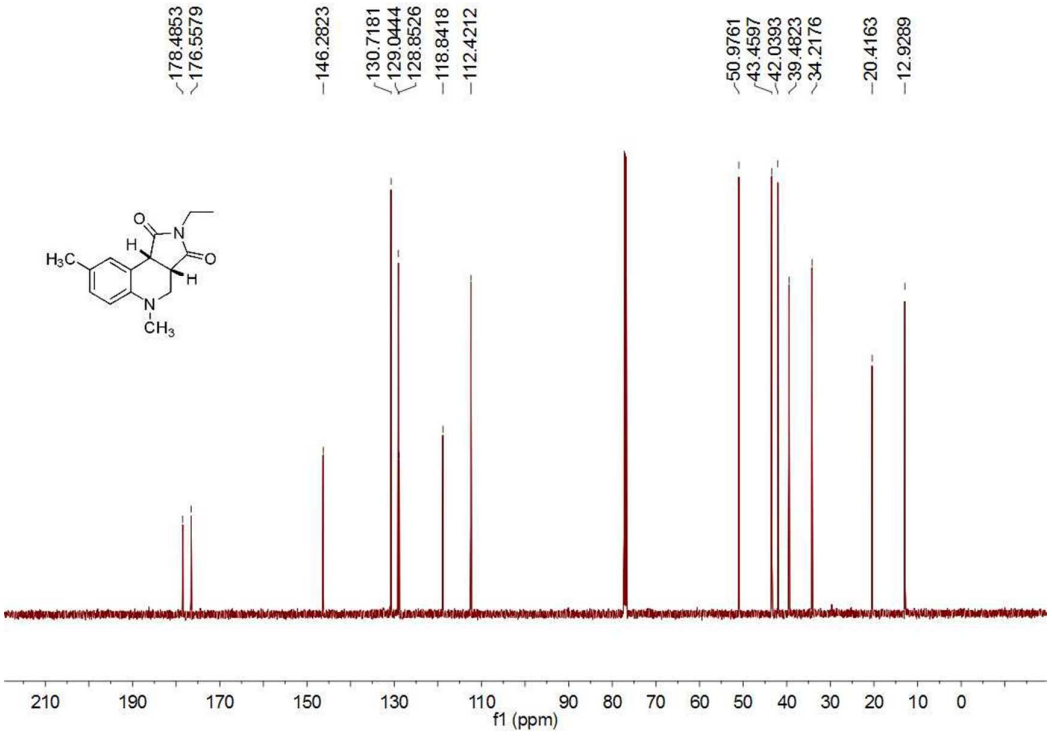

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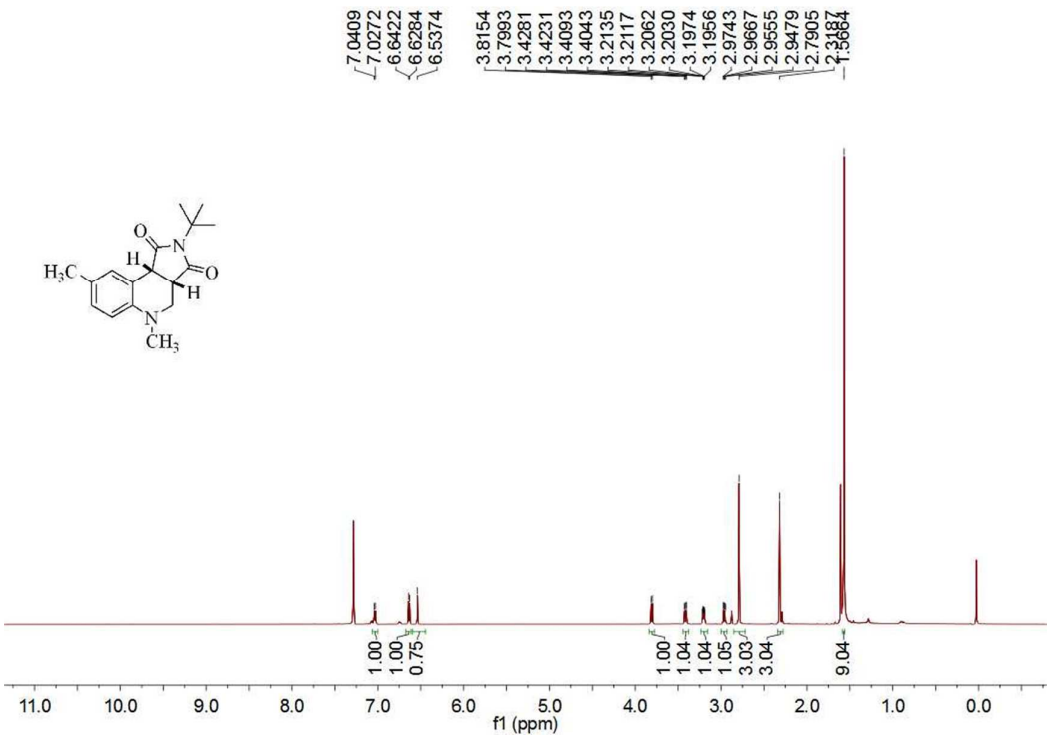


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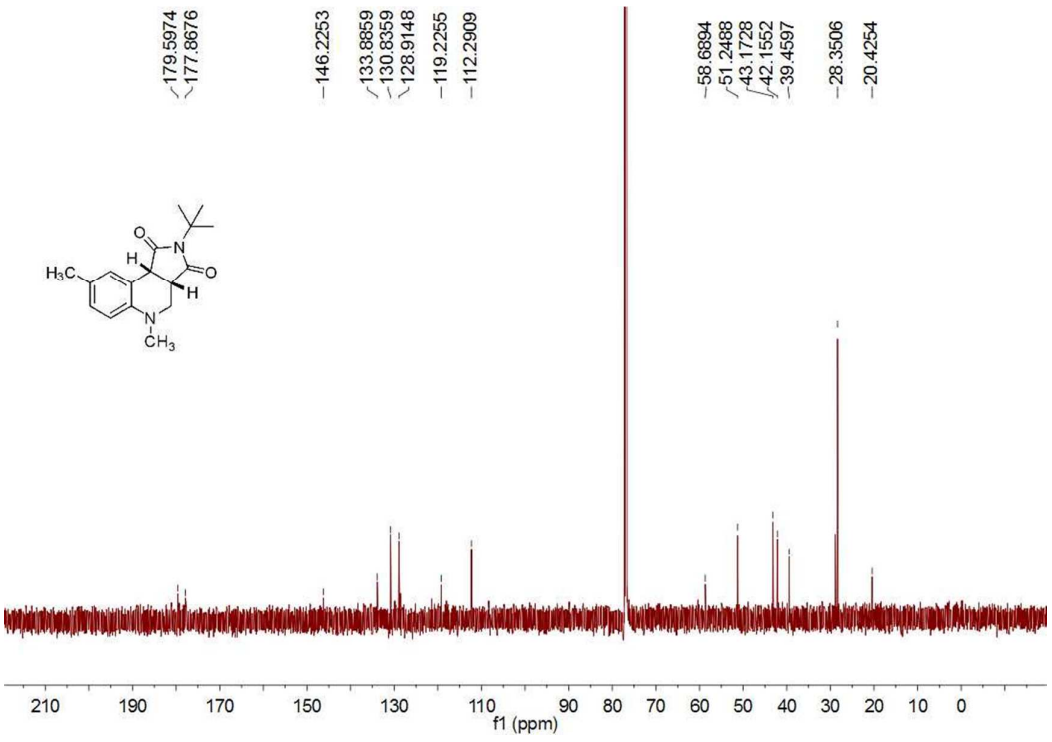
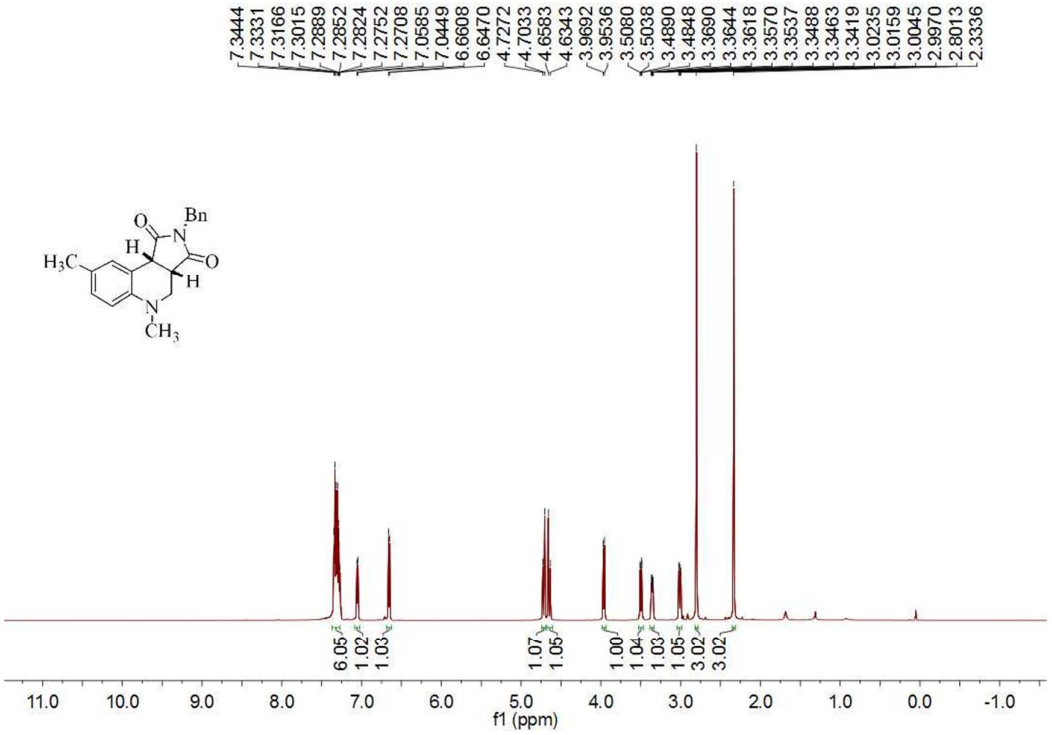


**3e-$^{1}$H NMR**

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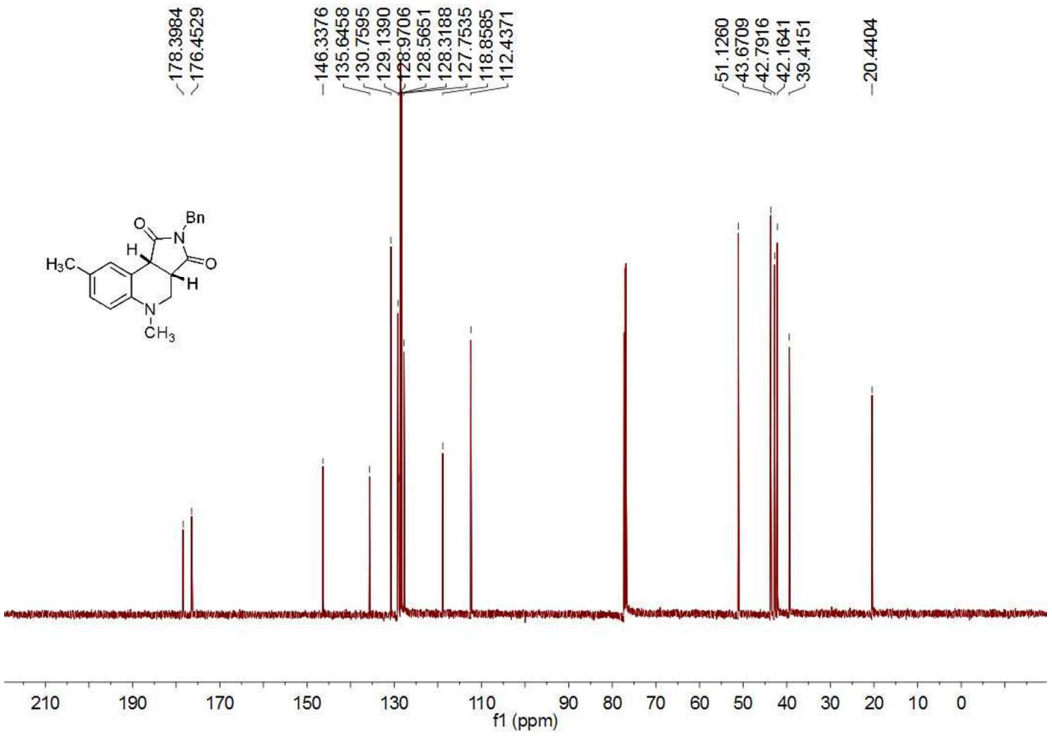

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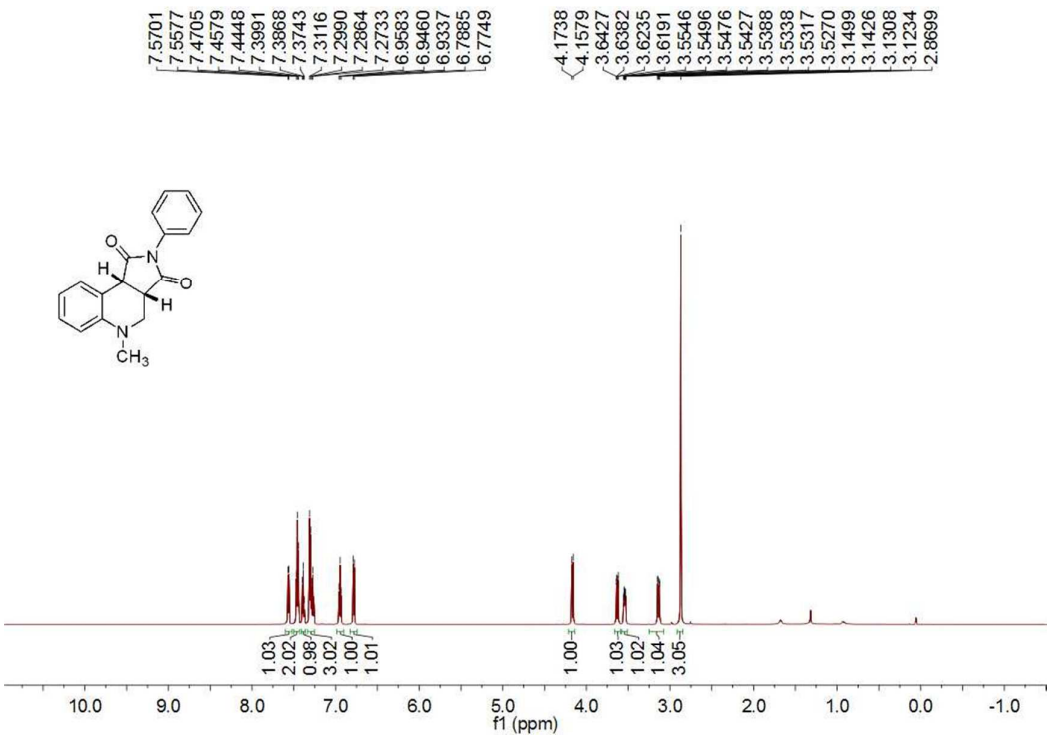
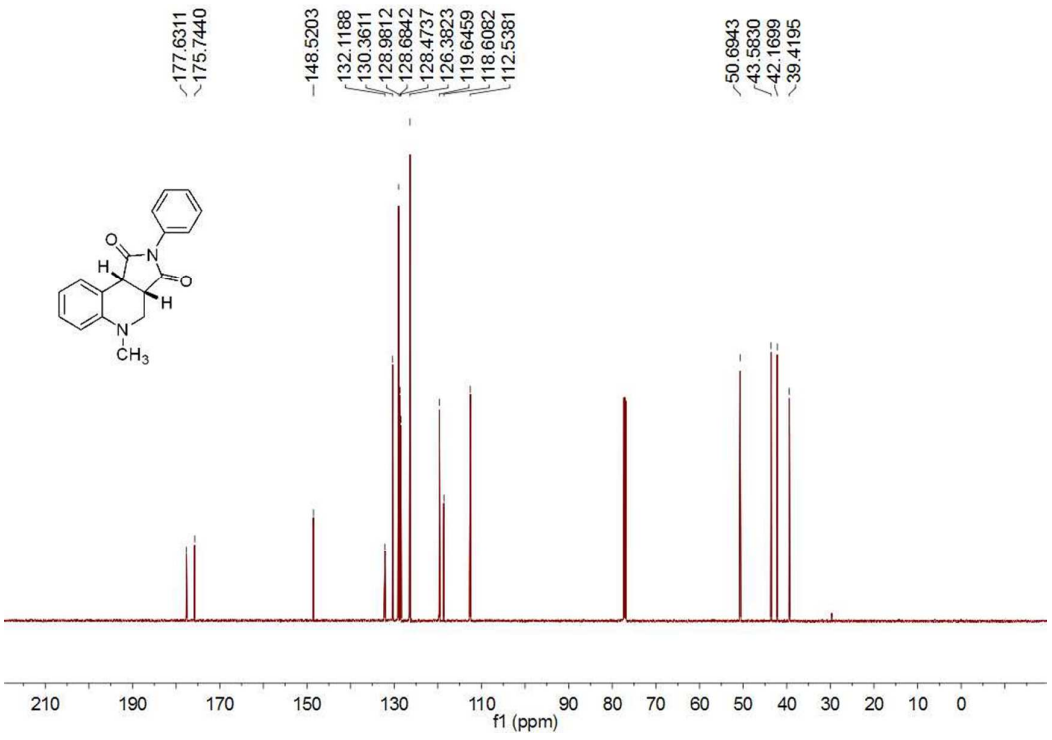



**3f-$^{13}$C NMR**



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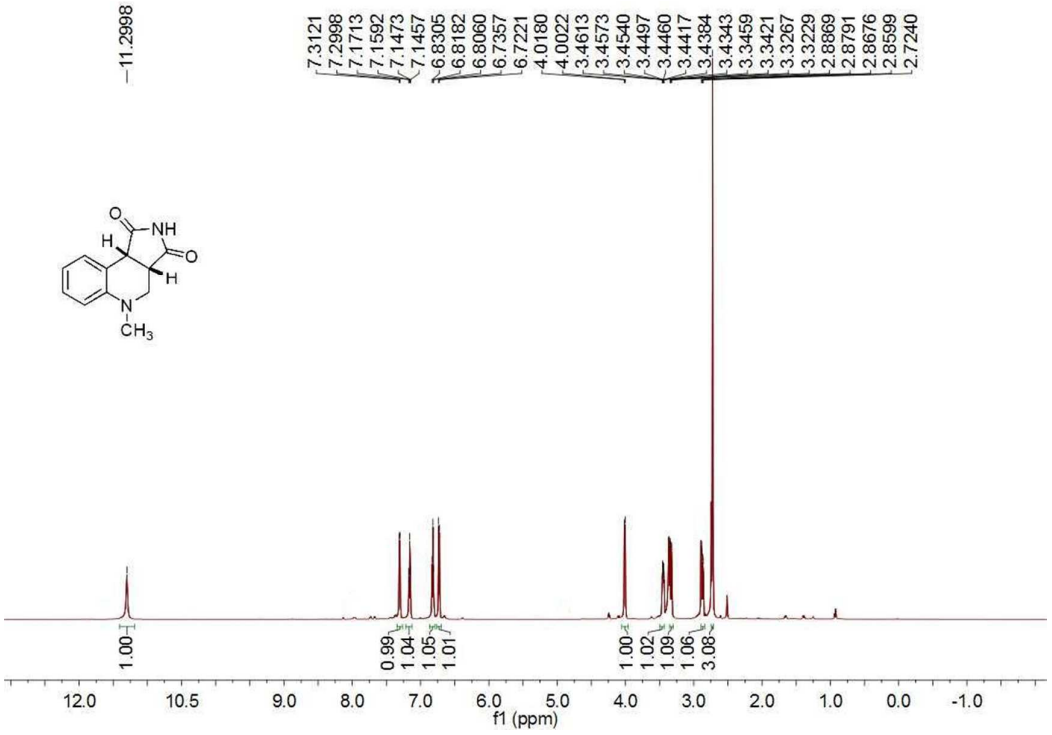
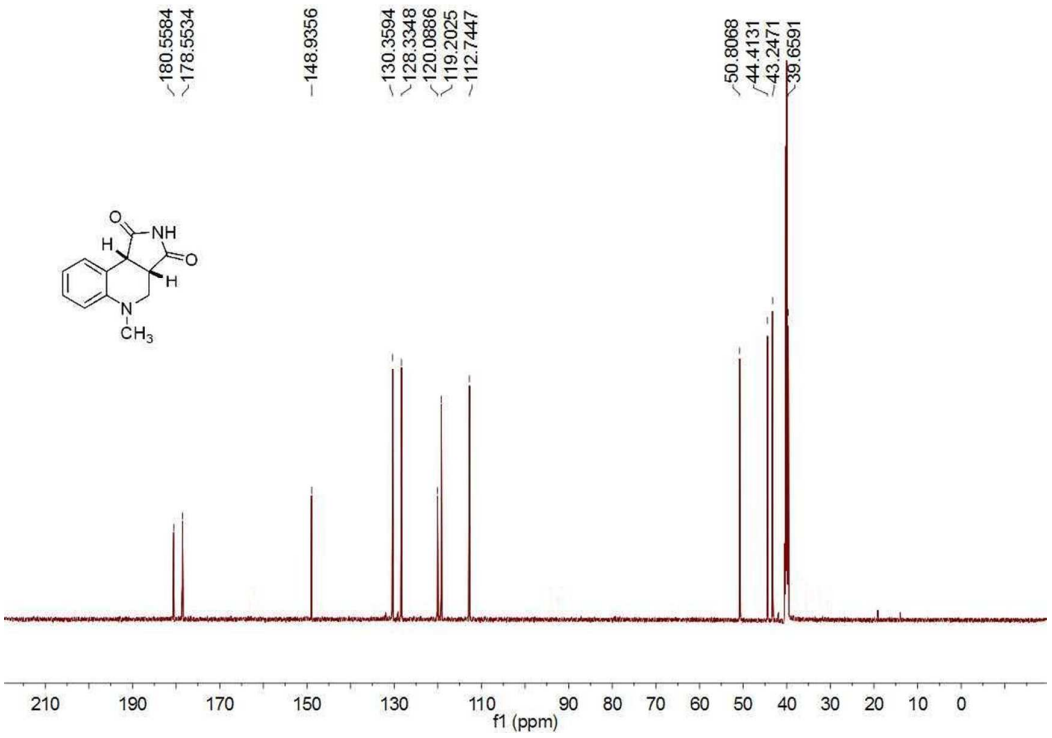



**3g-$^{13}$C NMR**



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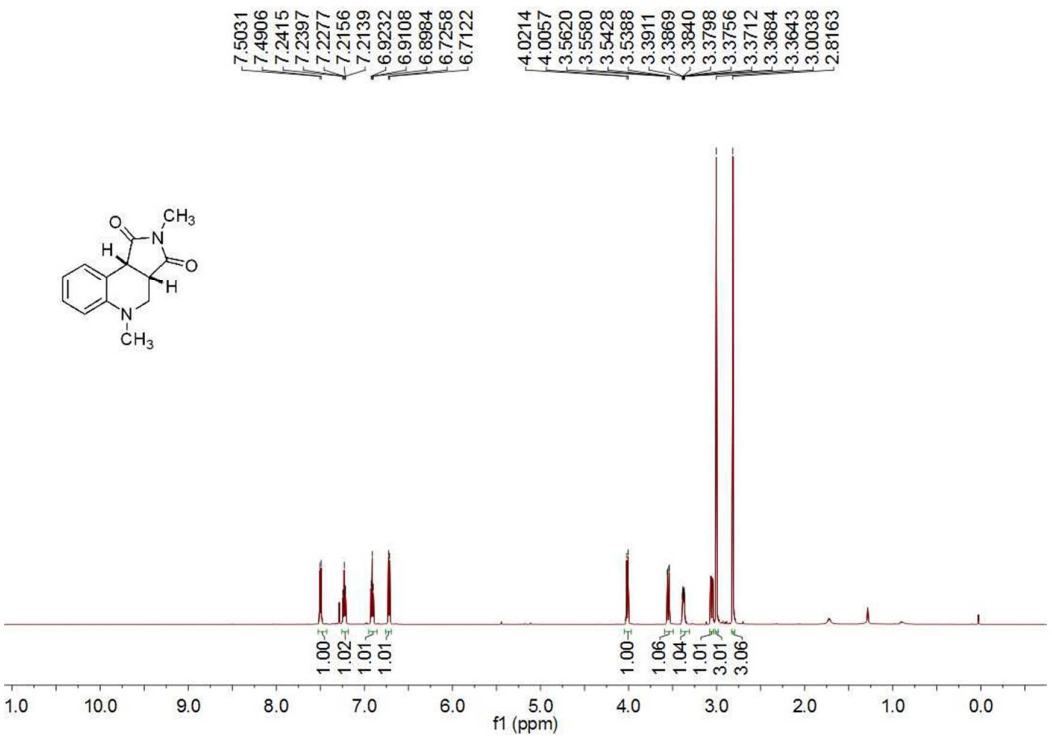


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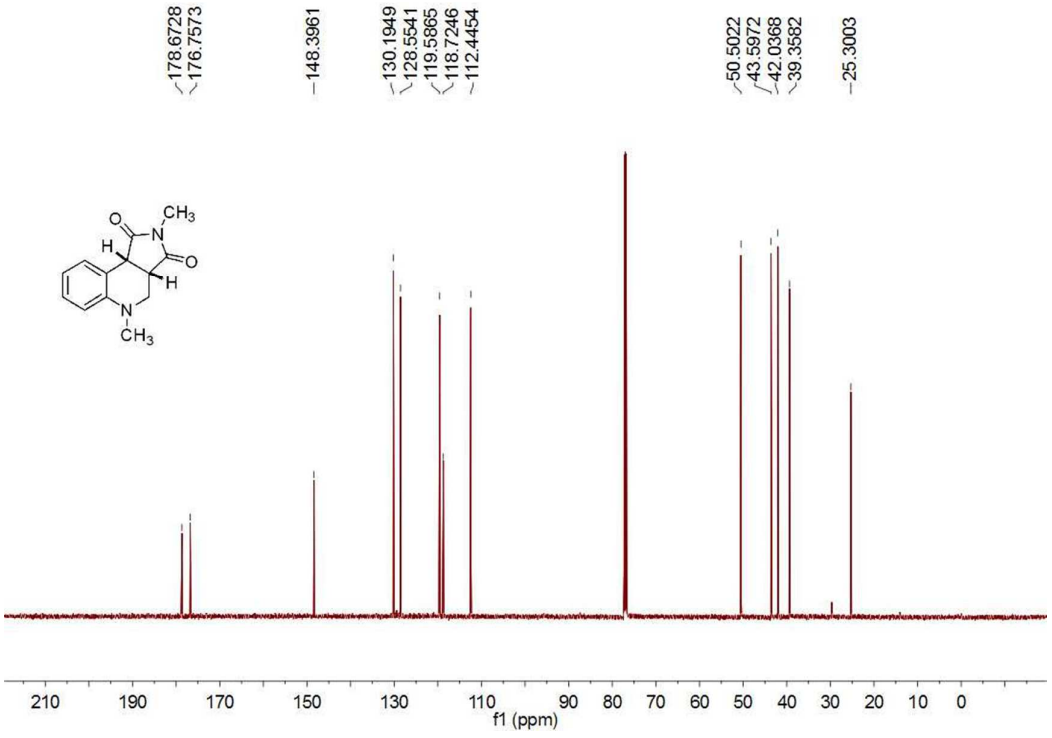

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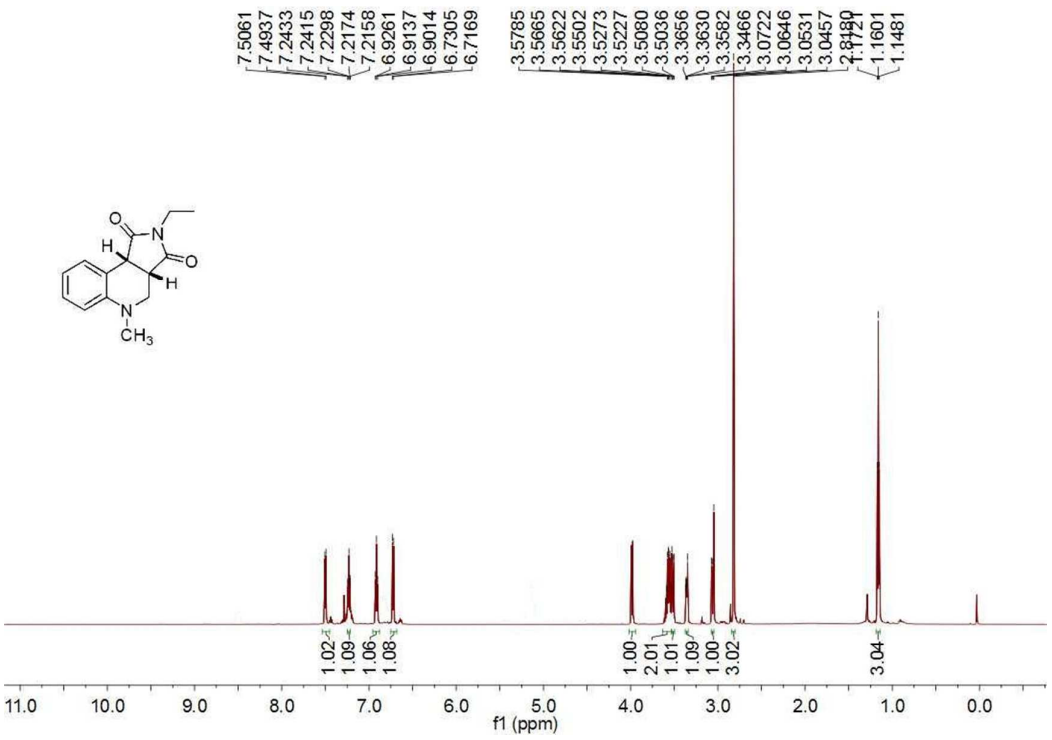


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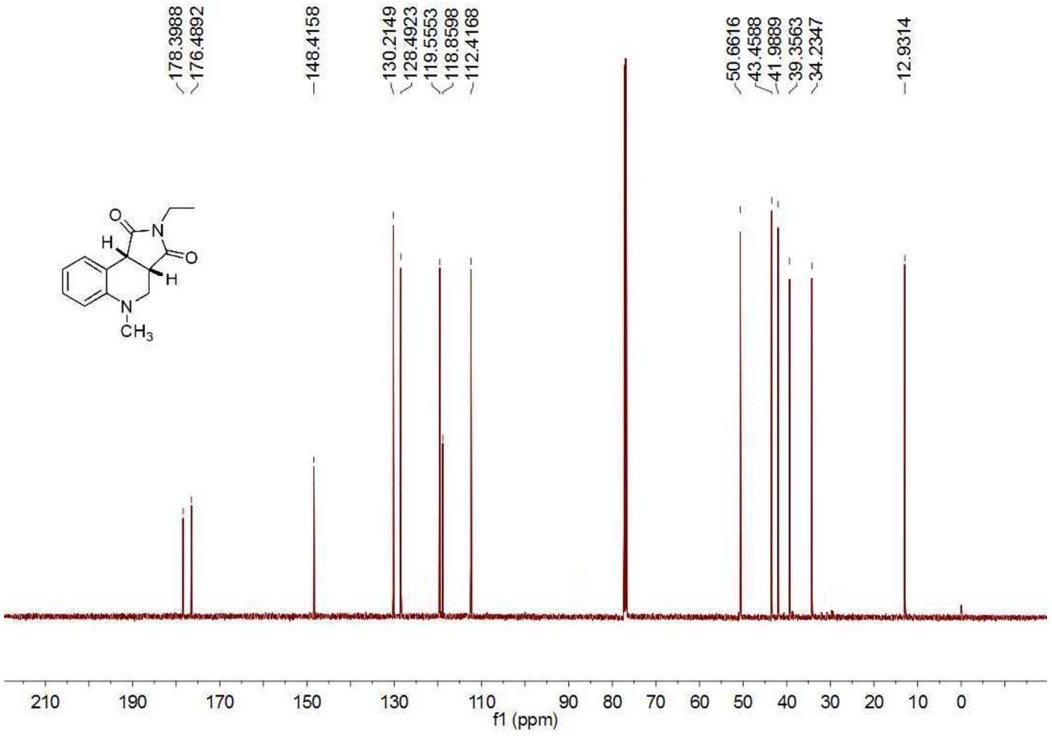

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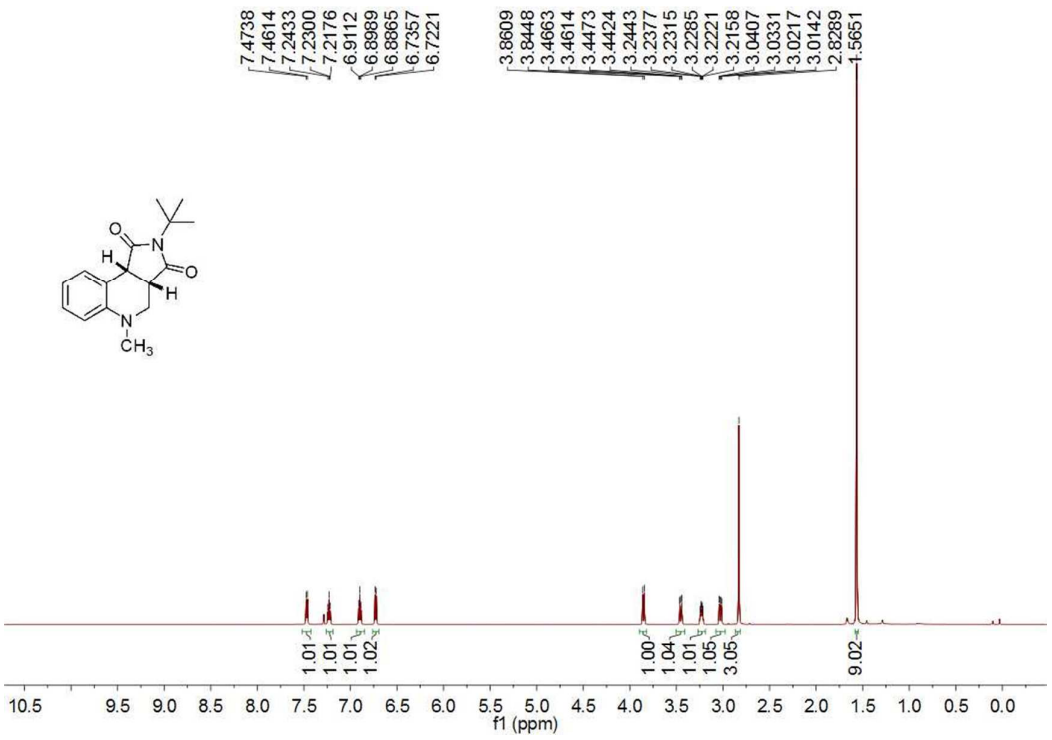


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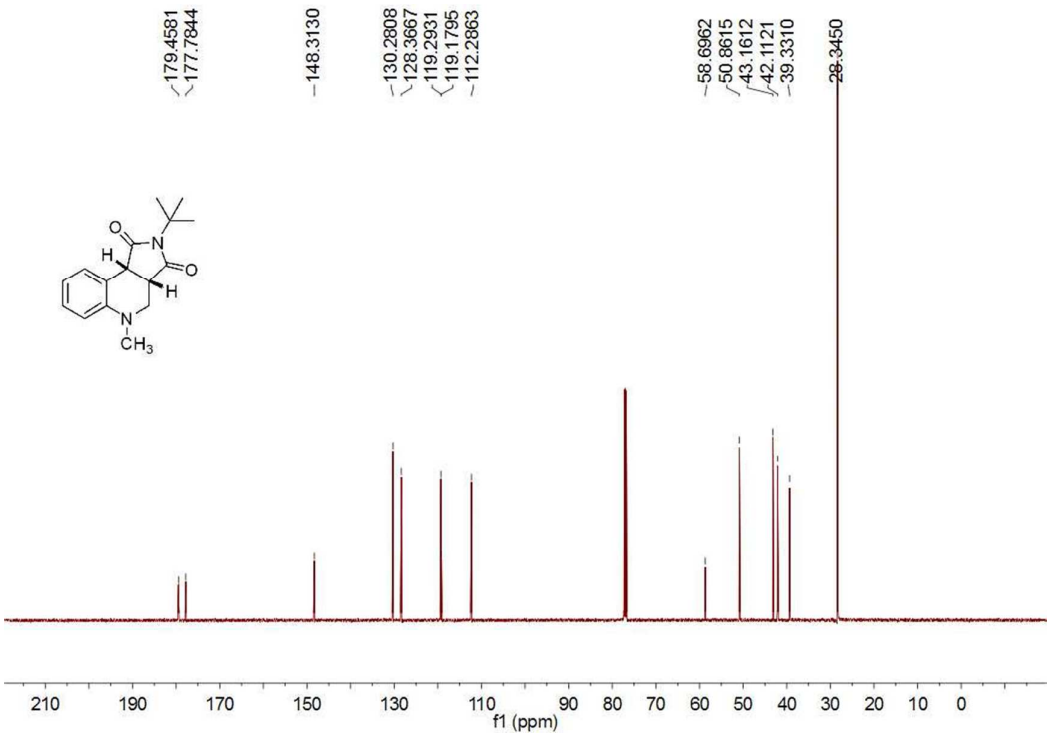
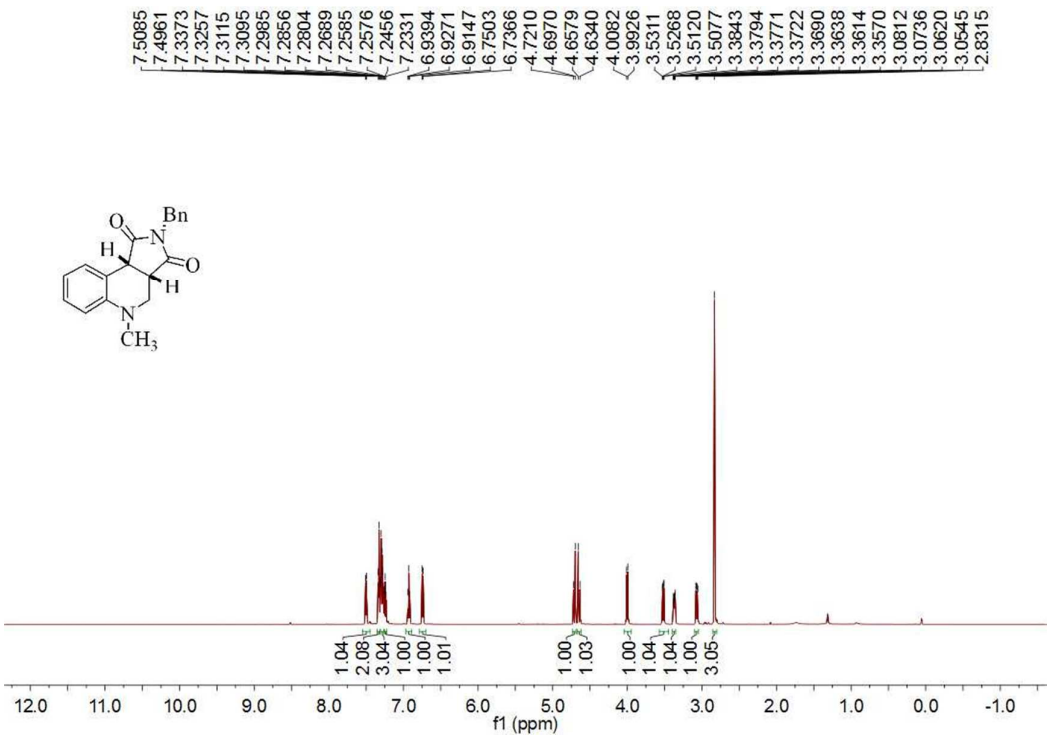


**3k-$^{1}$H NMR**

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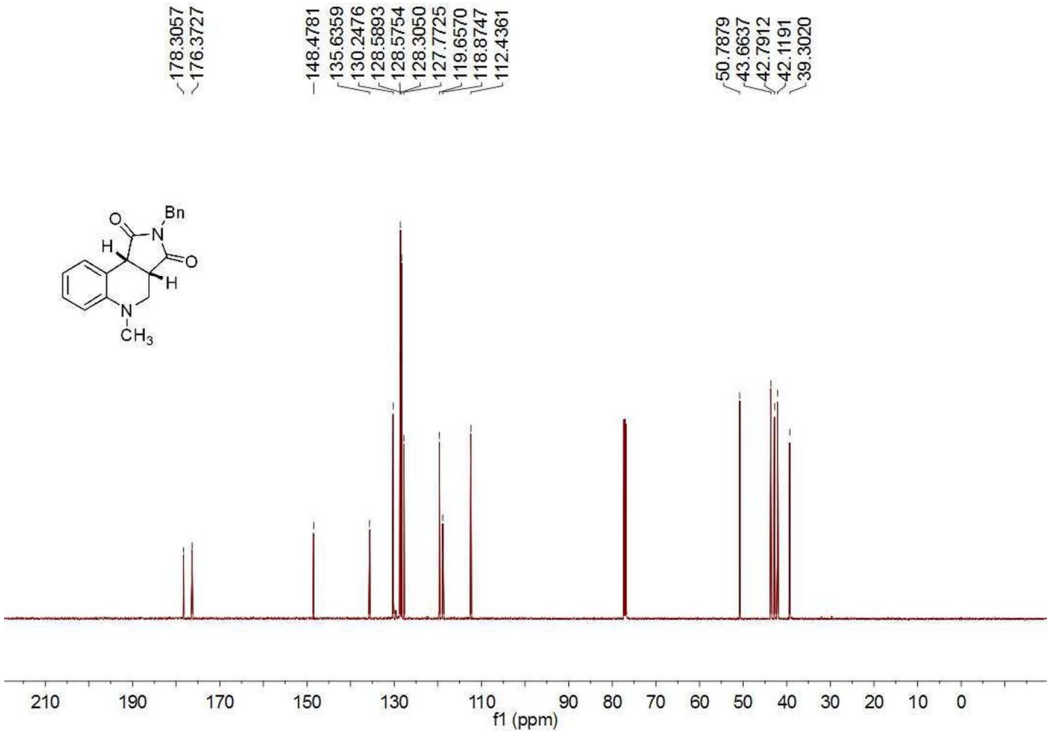
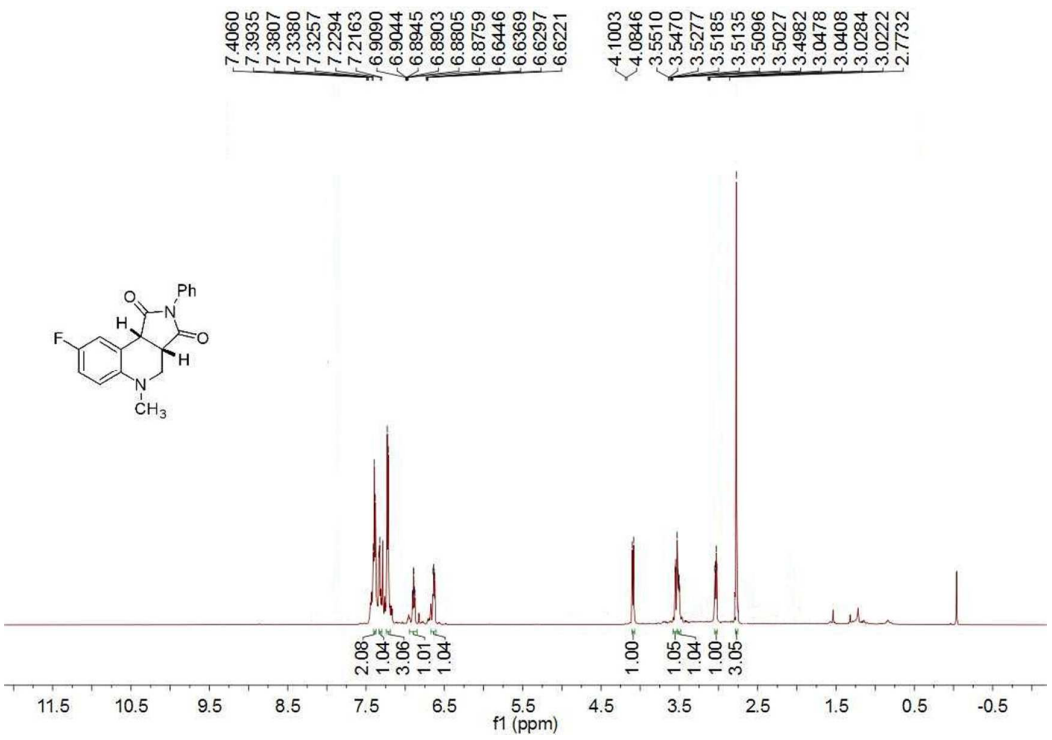


**3l-$^{1}$H NMR**

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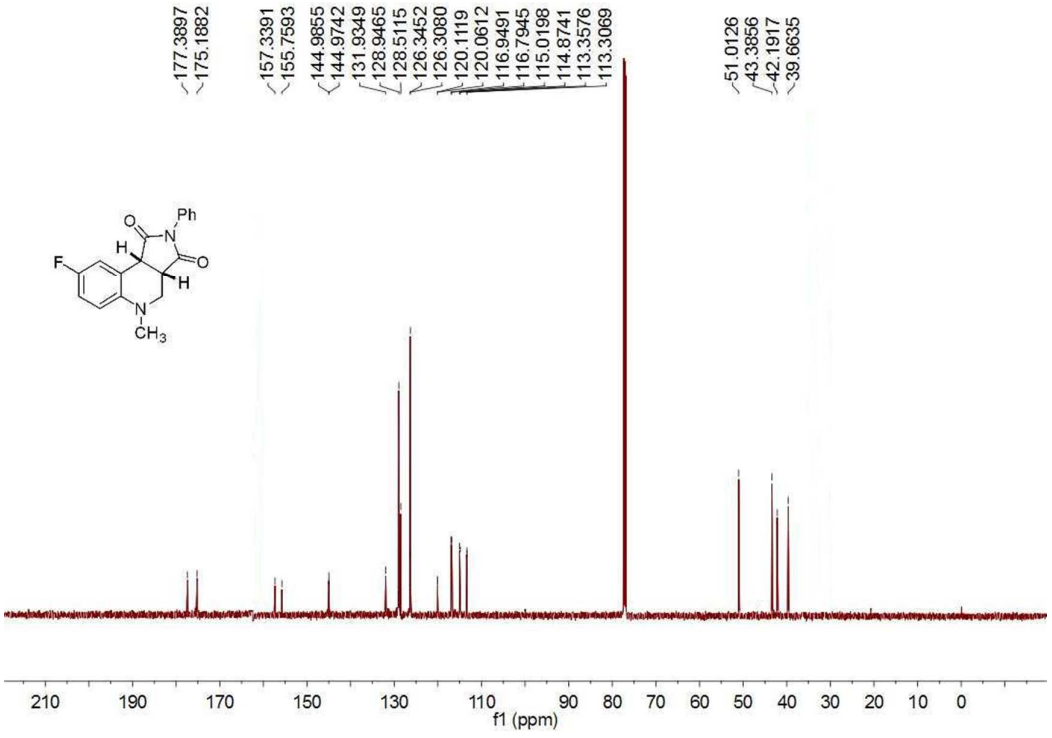

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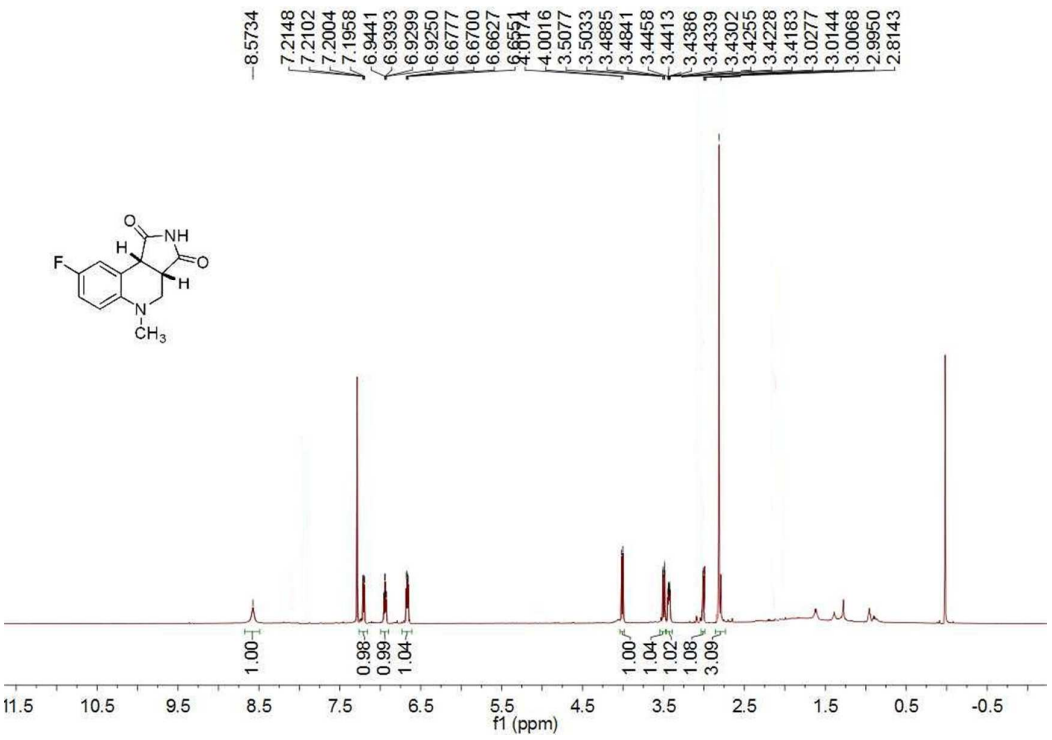


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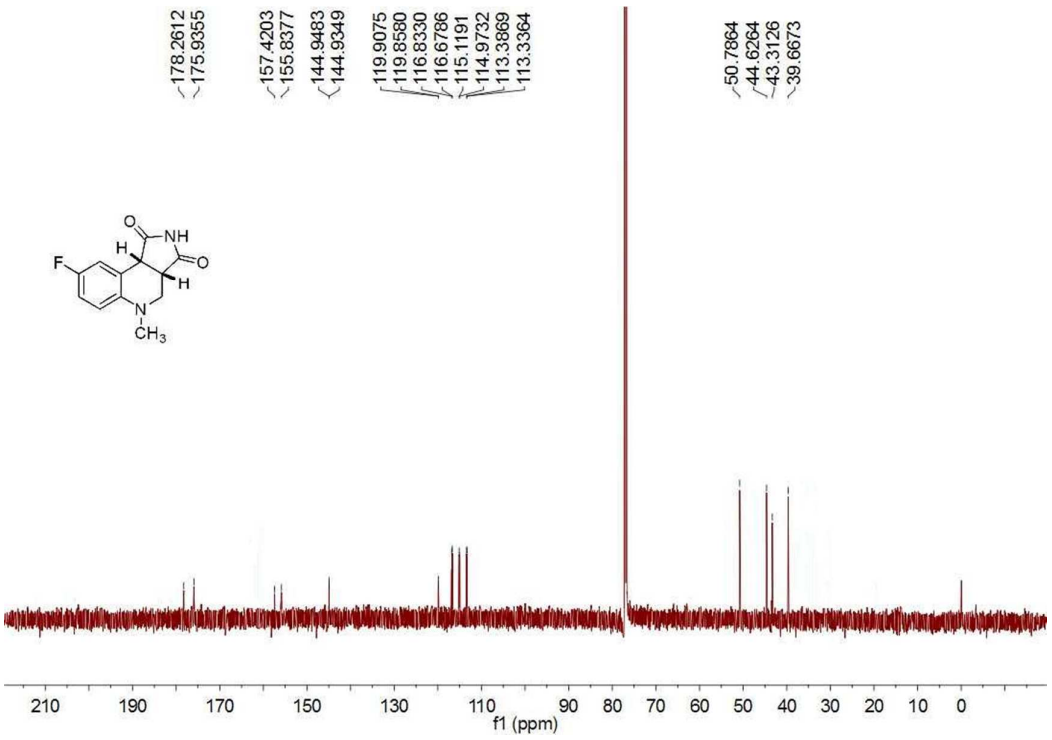

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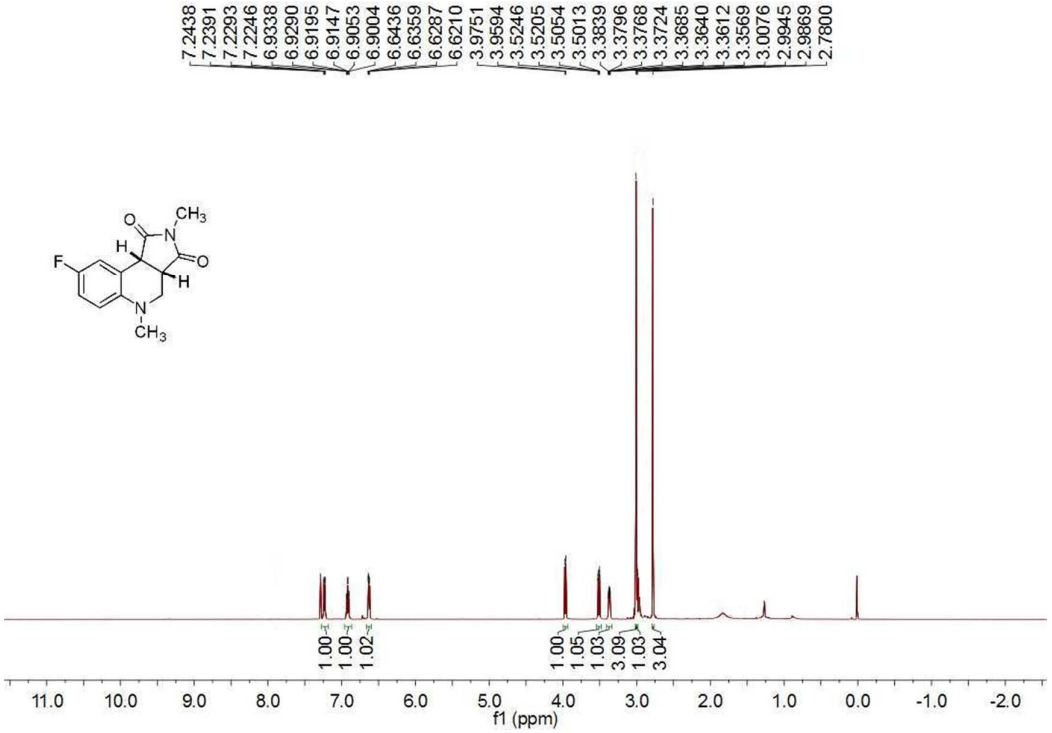


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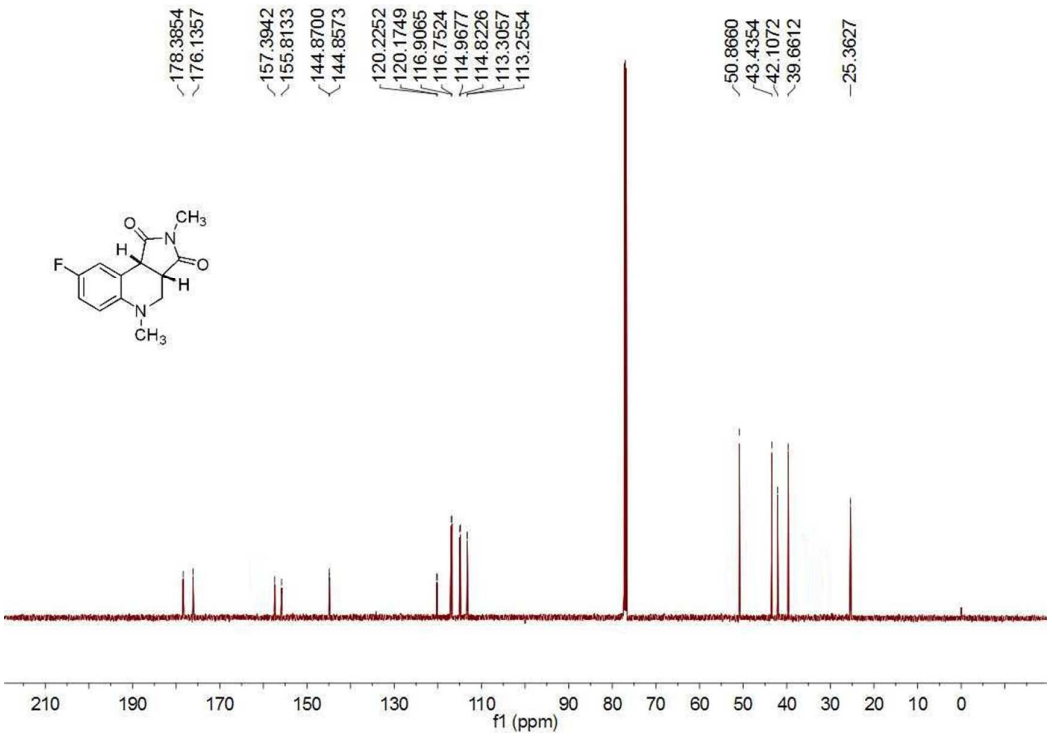

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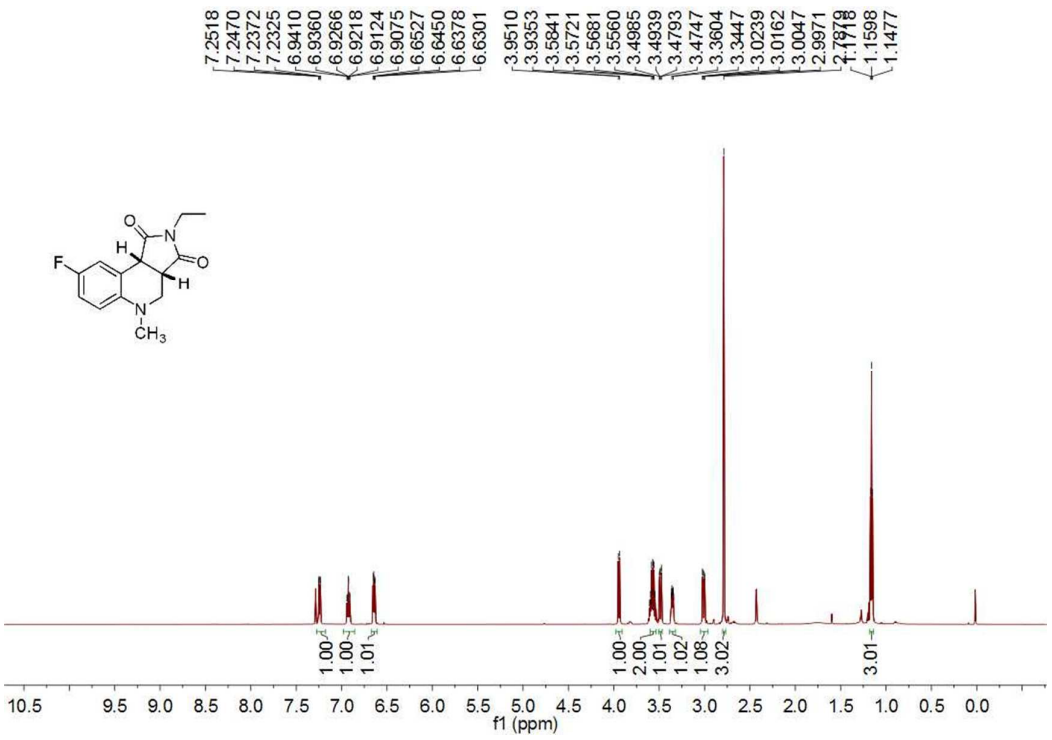


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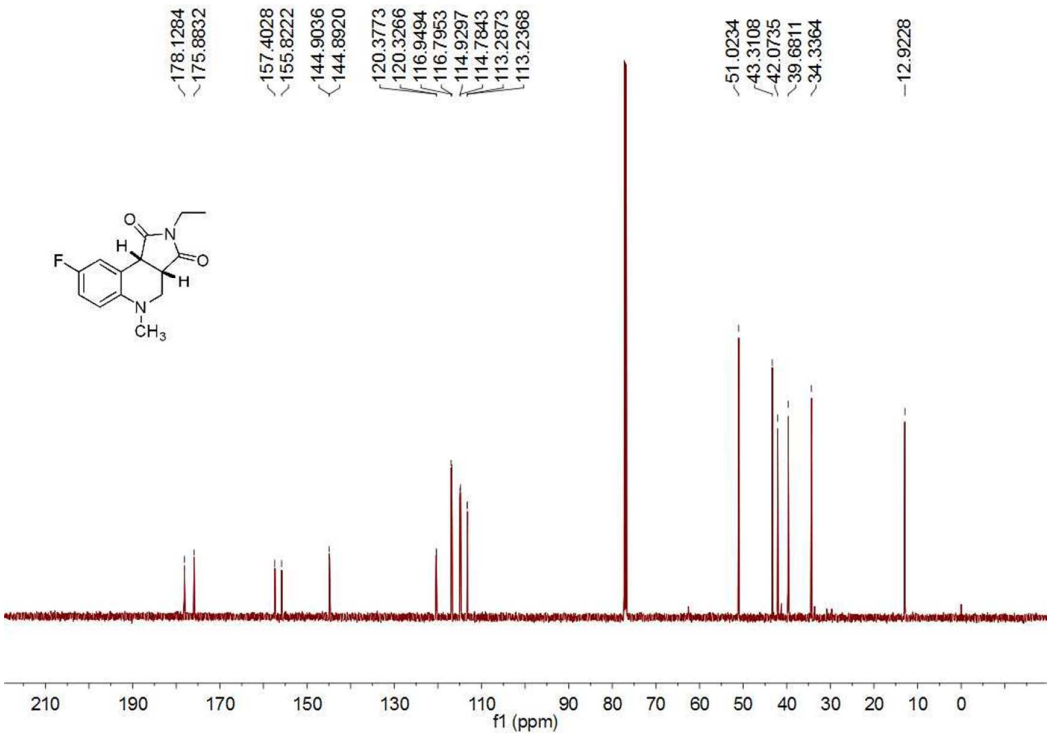

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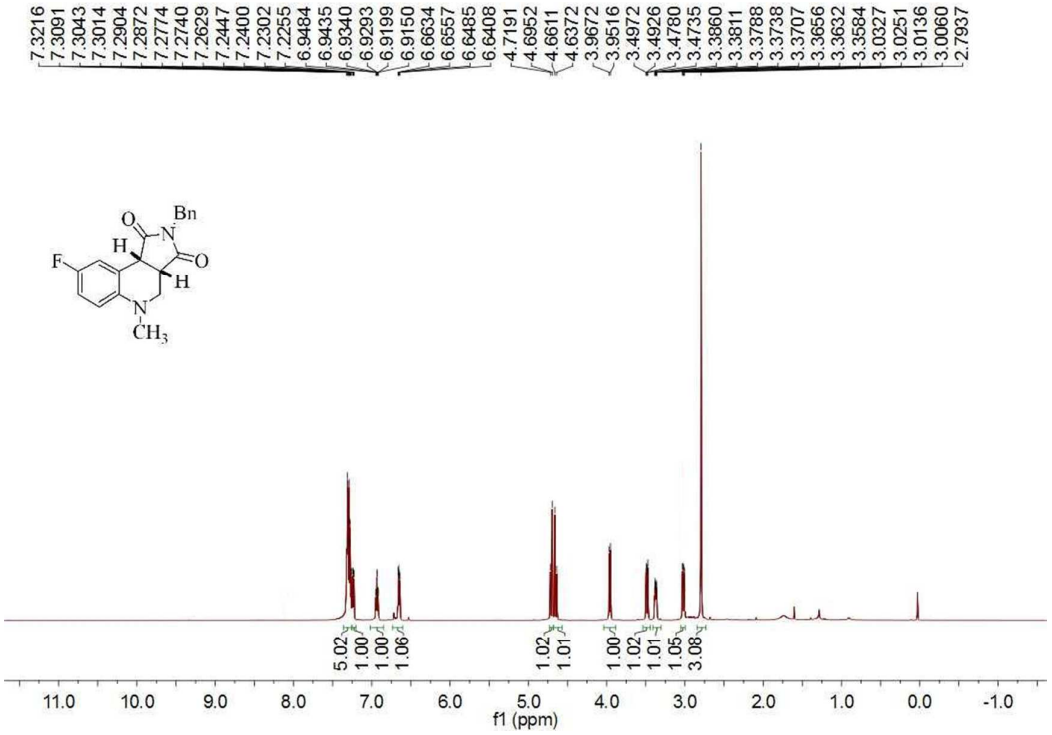


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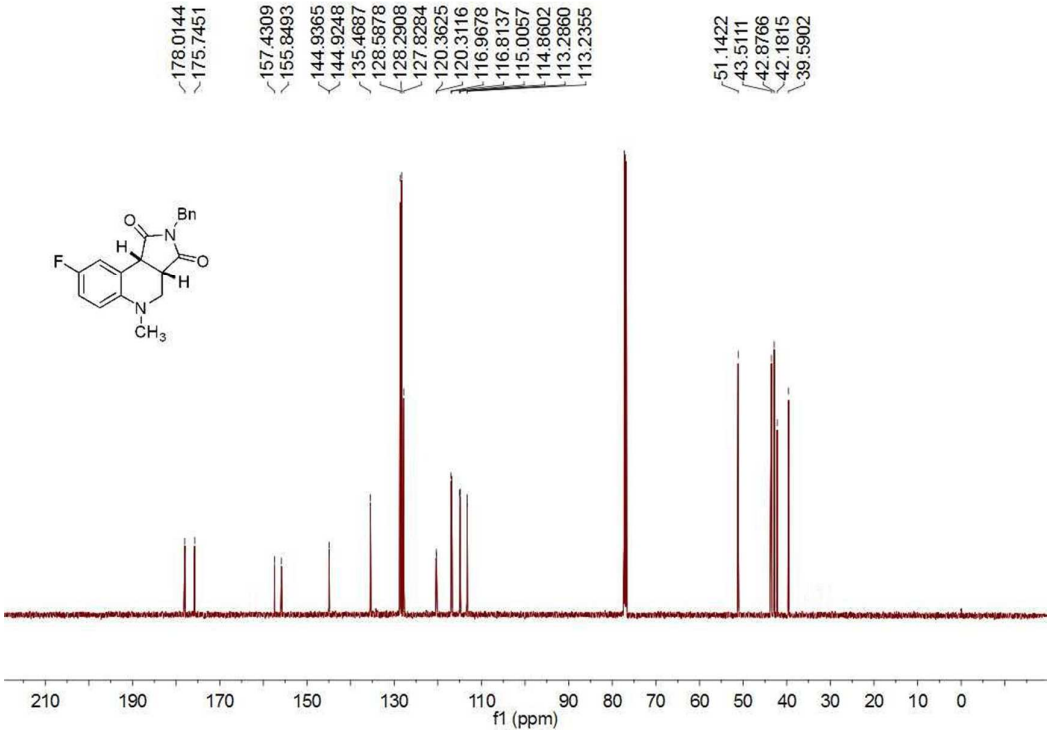

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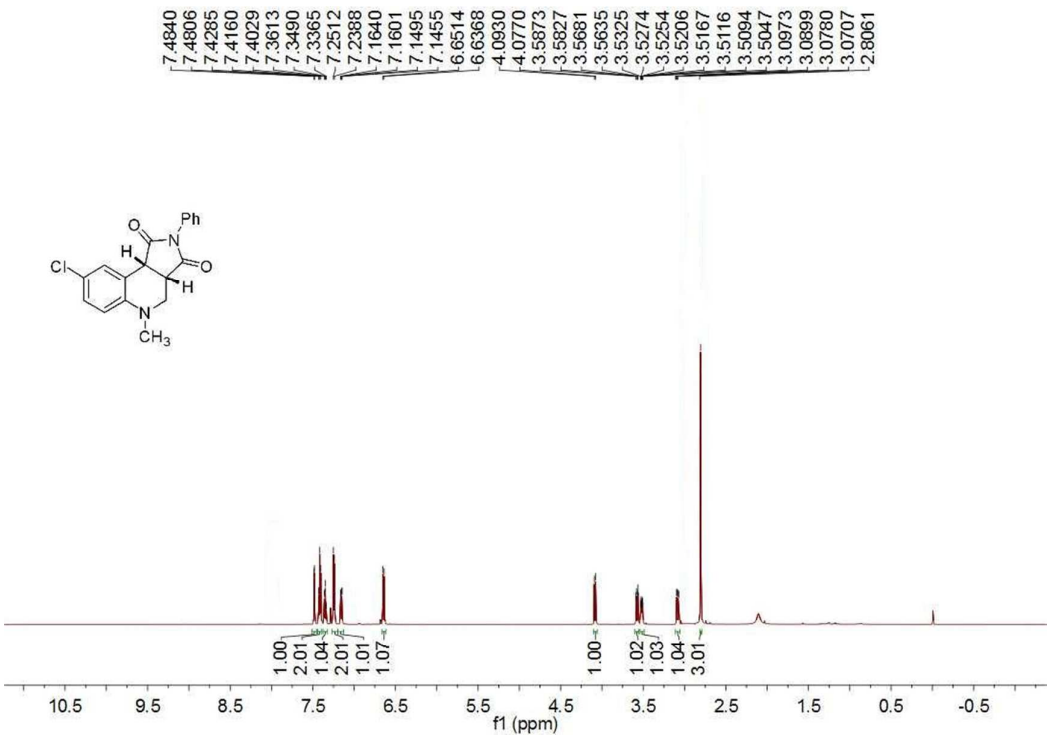
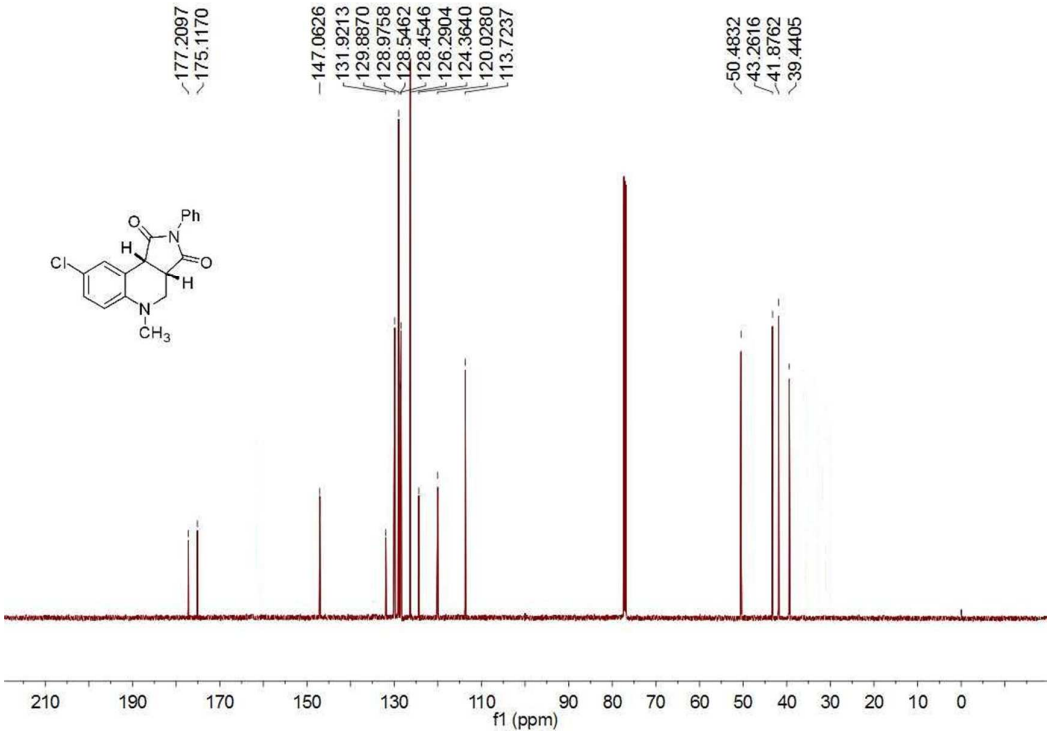



**3q-$^{13}$C NMR**



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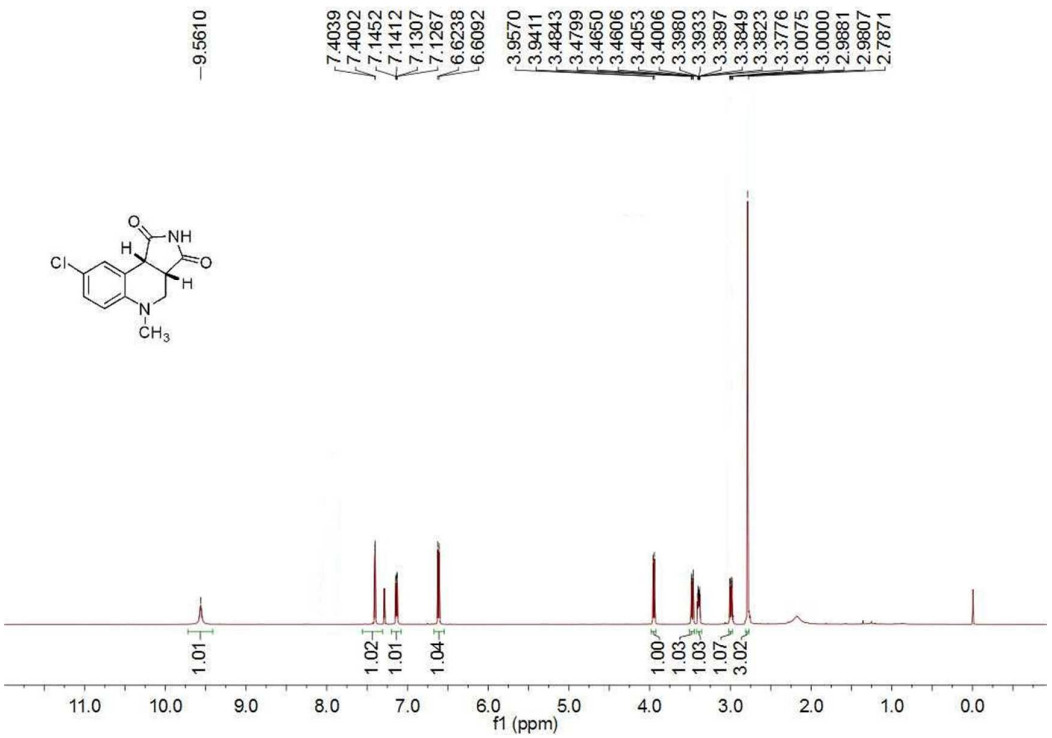
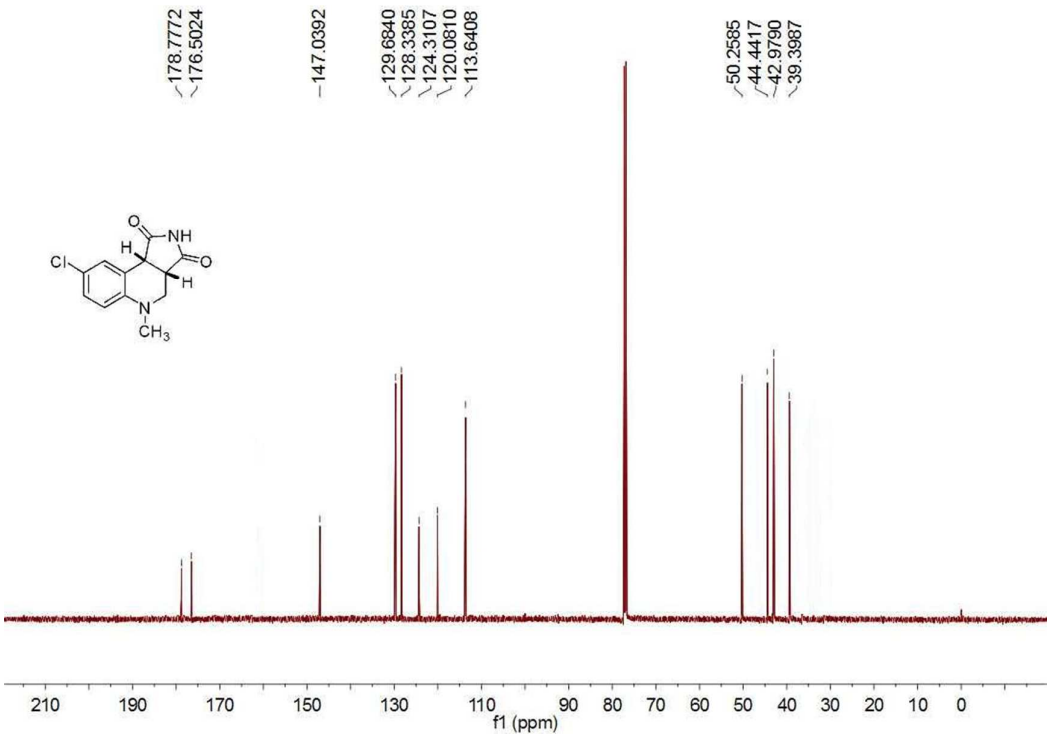



**3r-$^{13}$C NMR**



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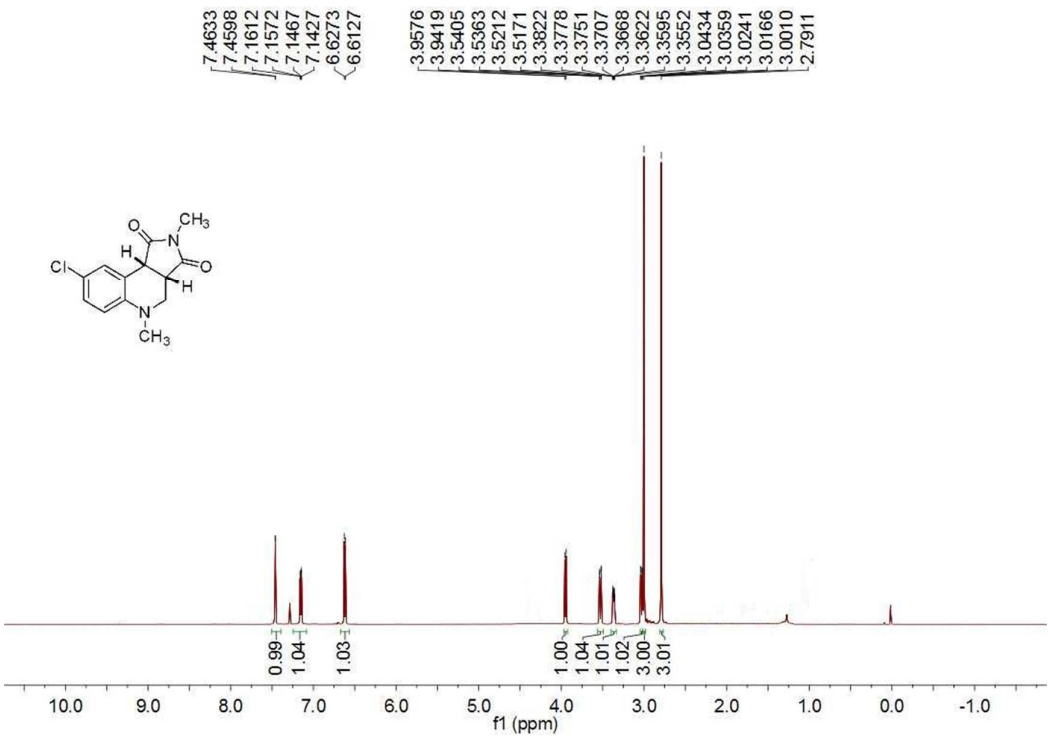
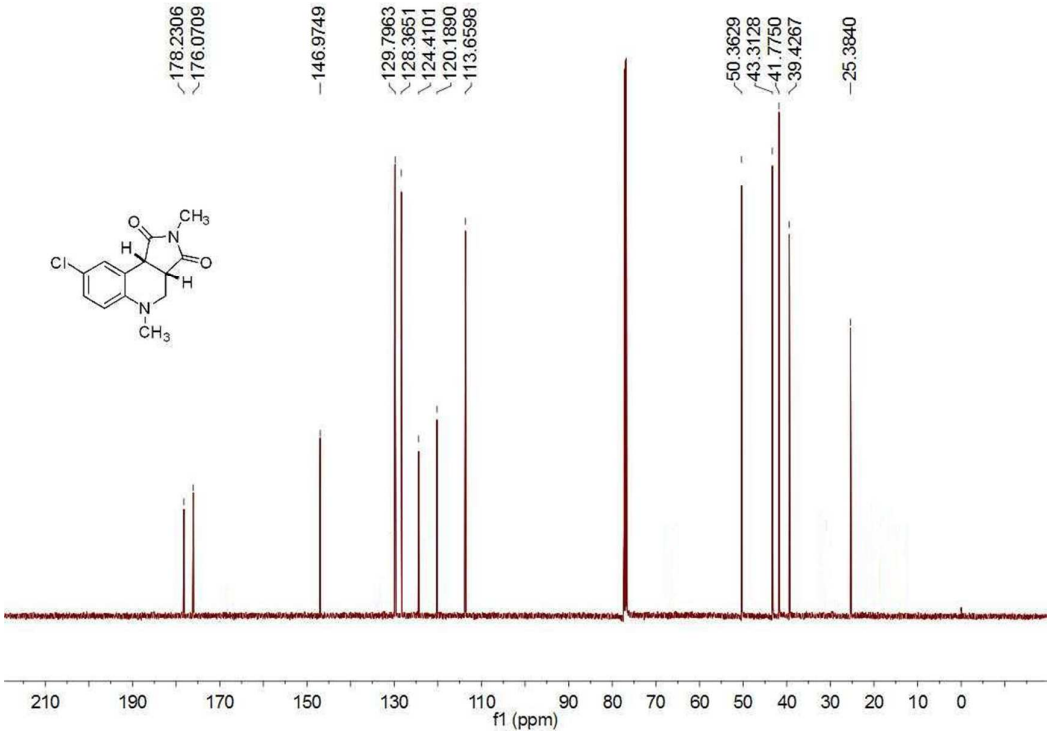



**3s-$^{13}$C NMR**



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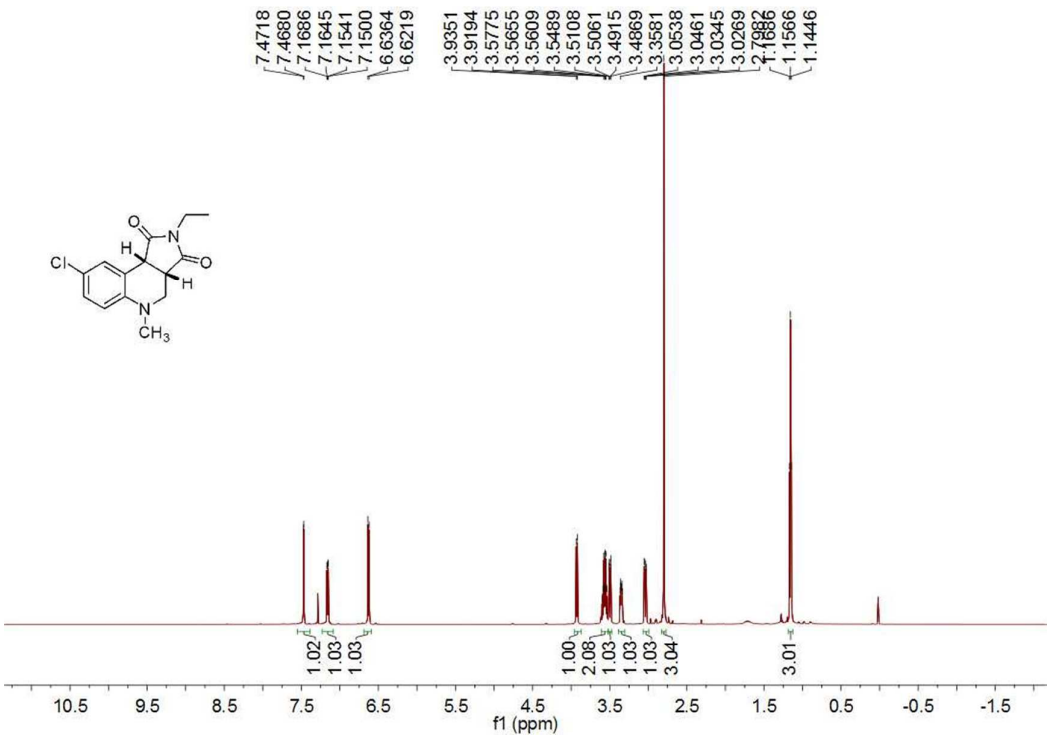


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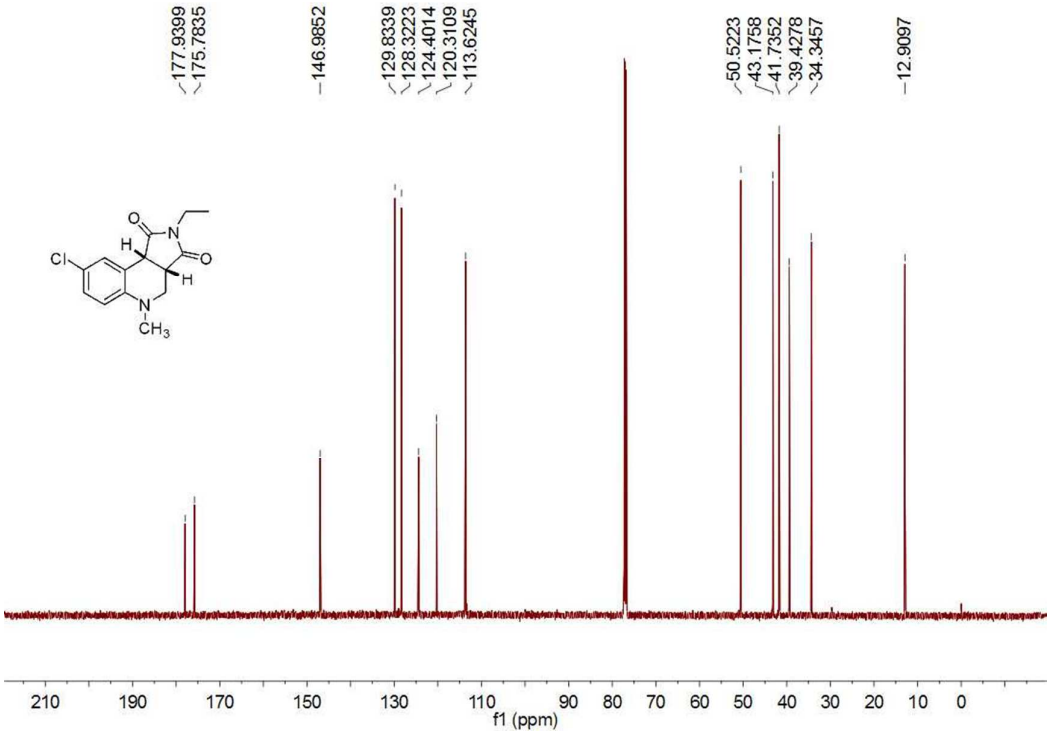

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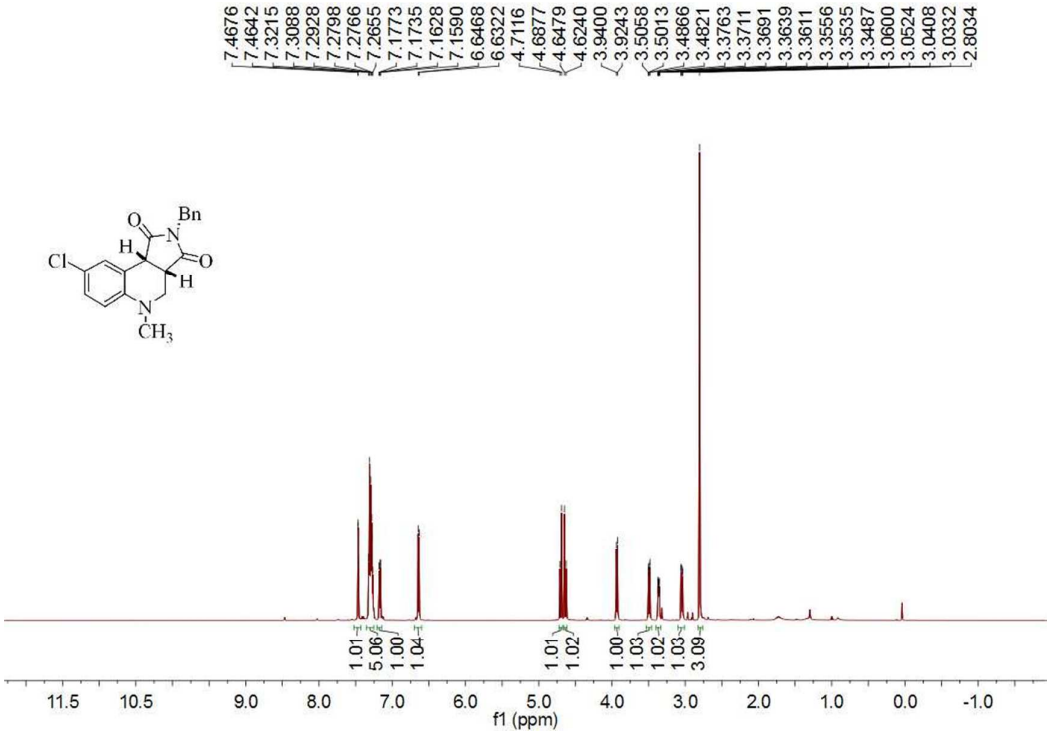


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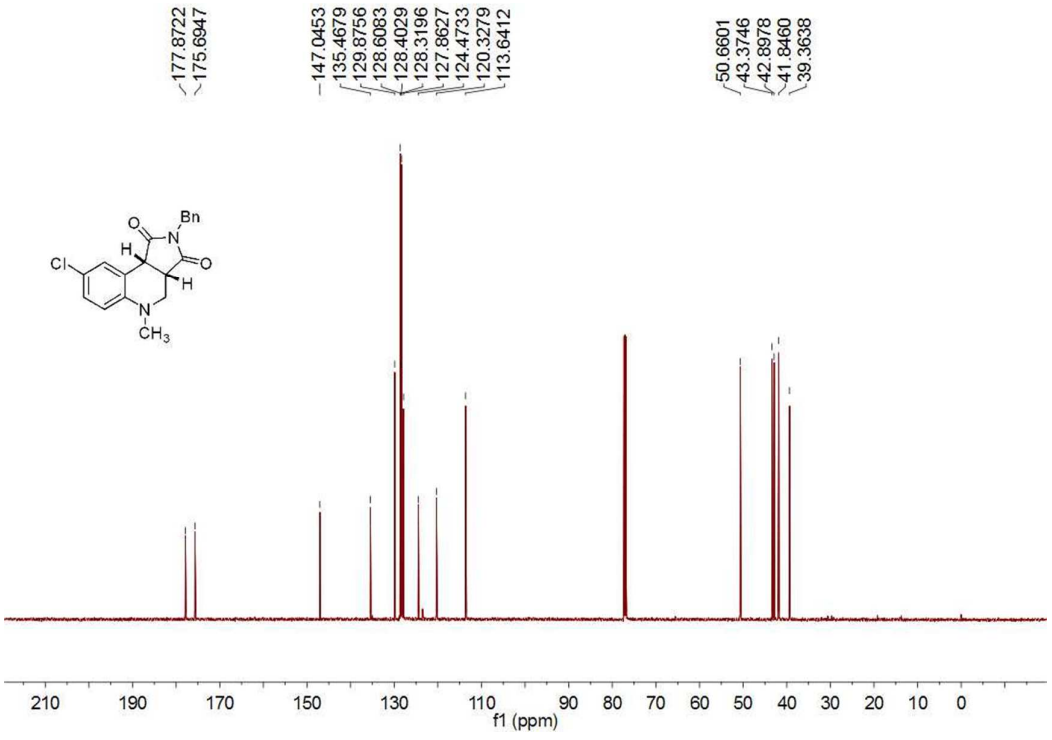
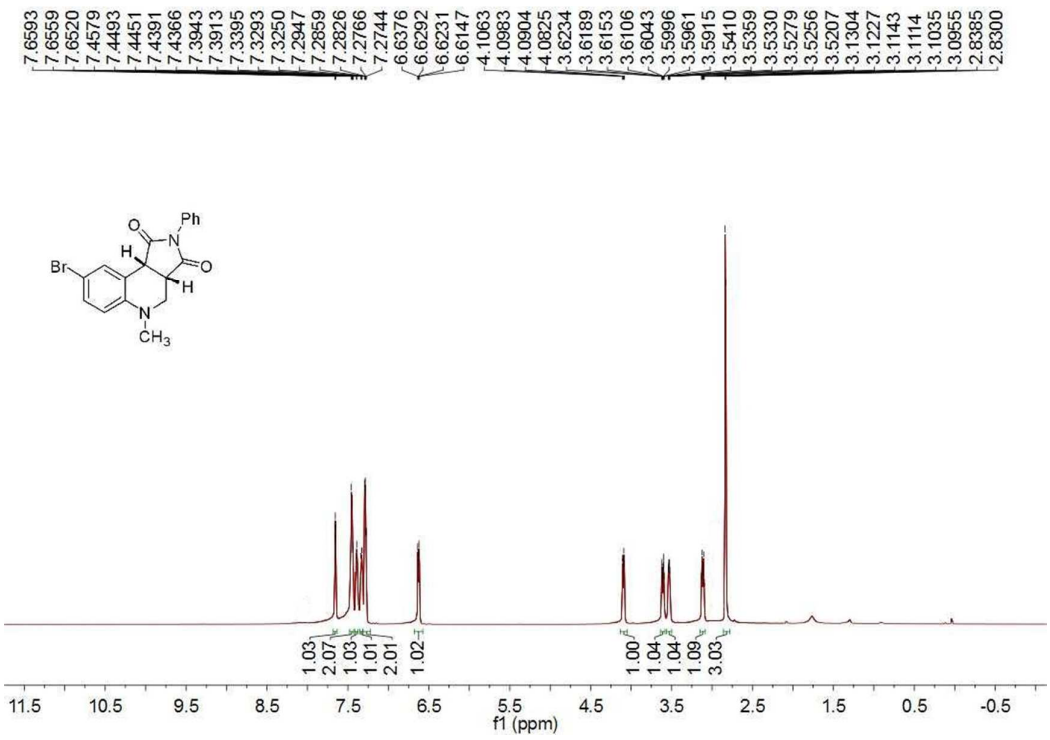
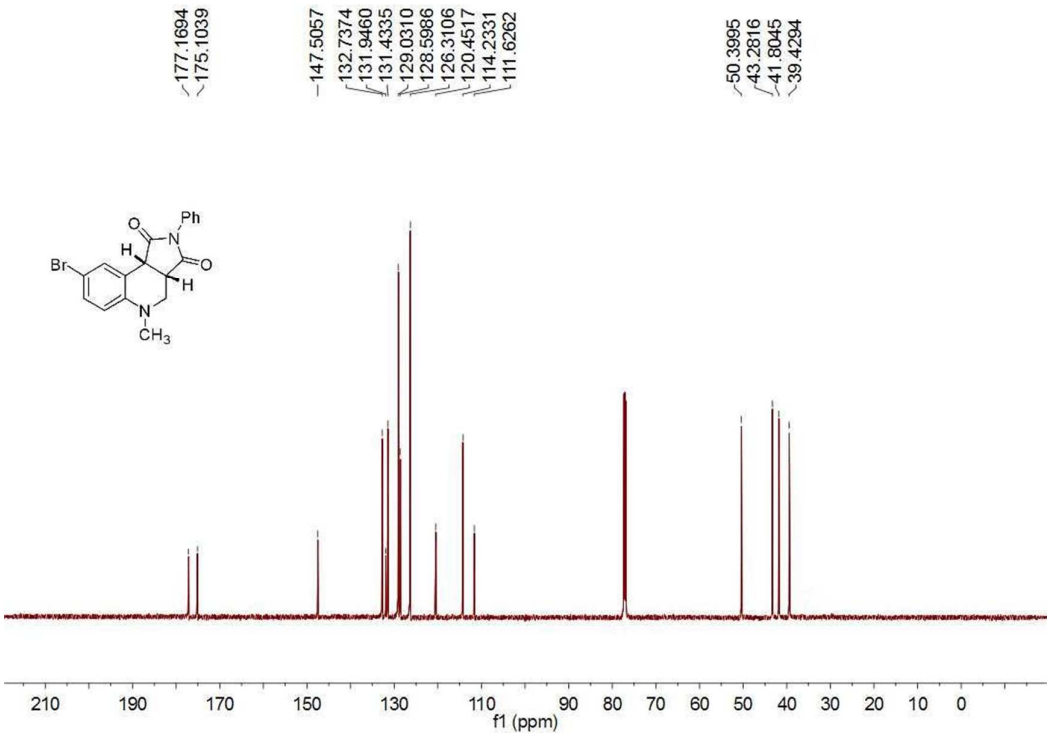


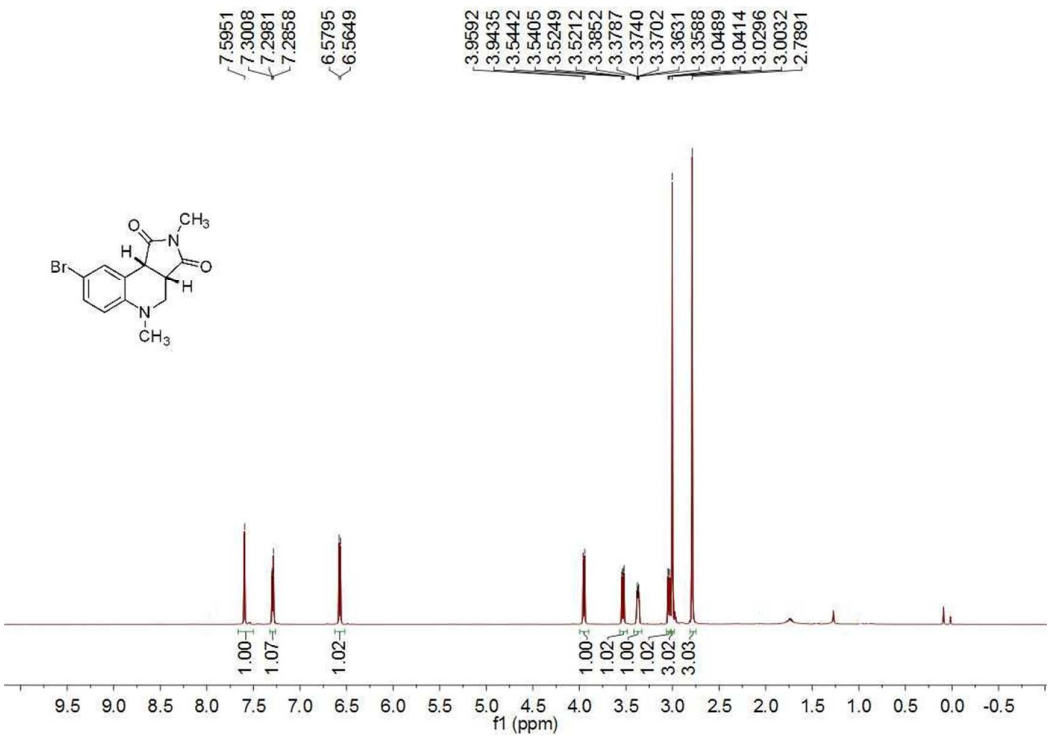
**3v-$^{1}$H NMR**



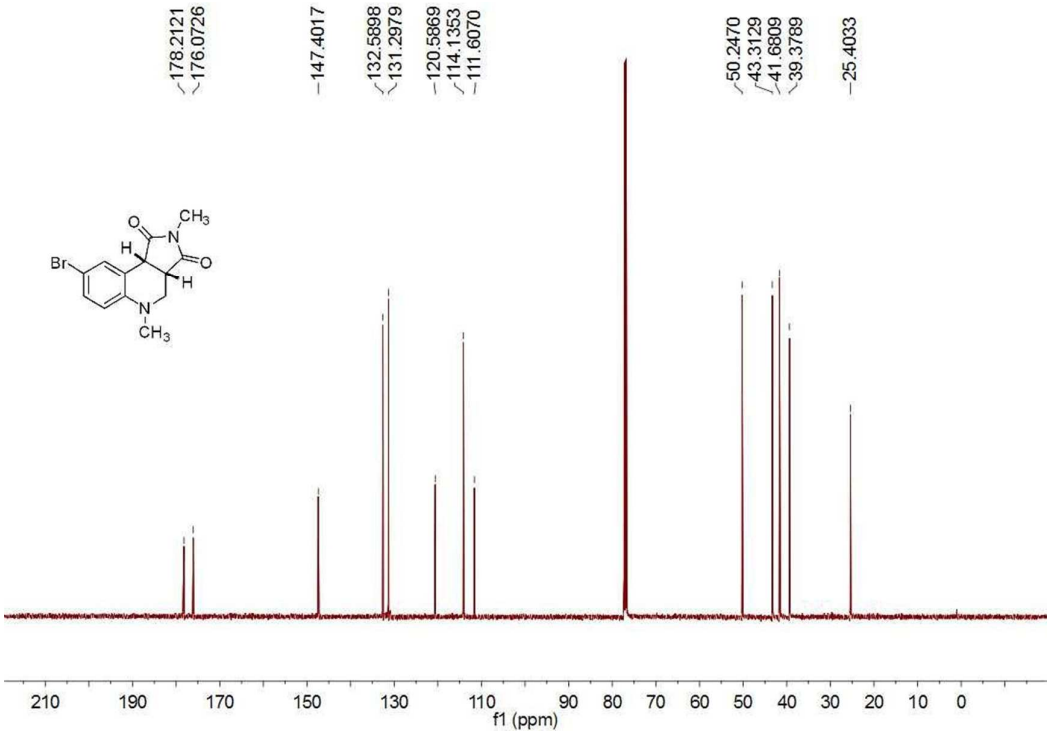

**3v-$^{13}$C NMR**



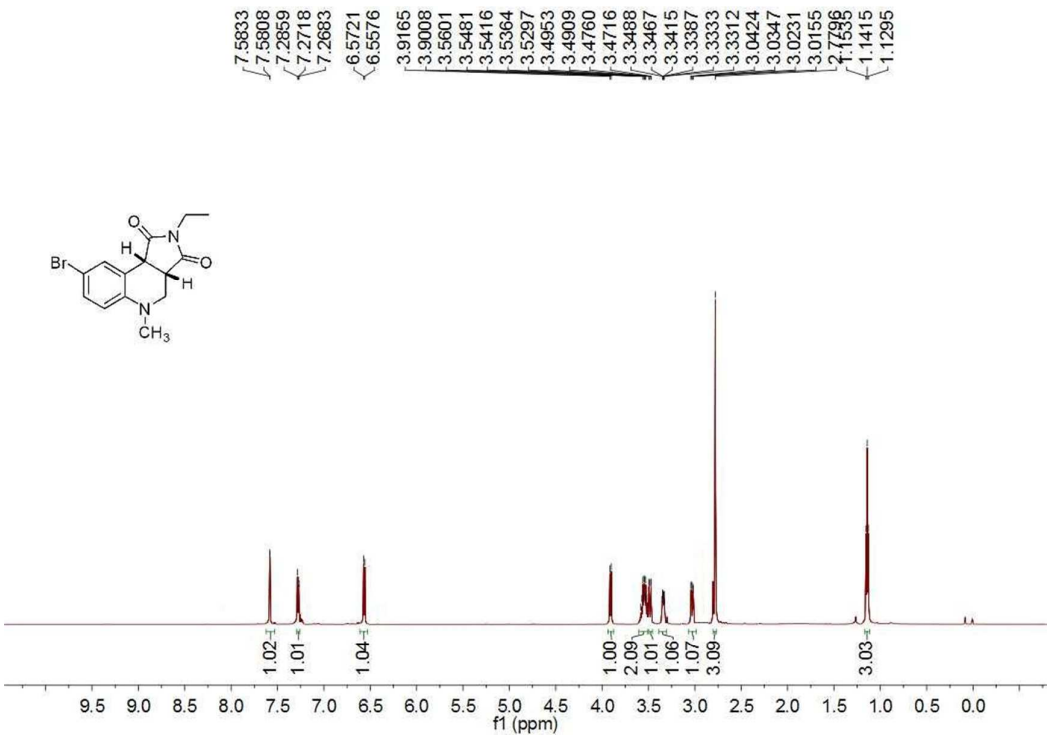
**3w-$^{1}$H NMR**



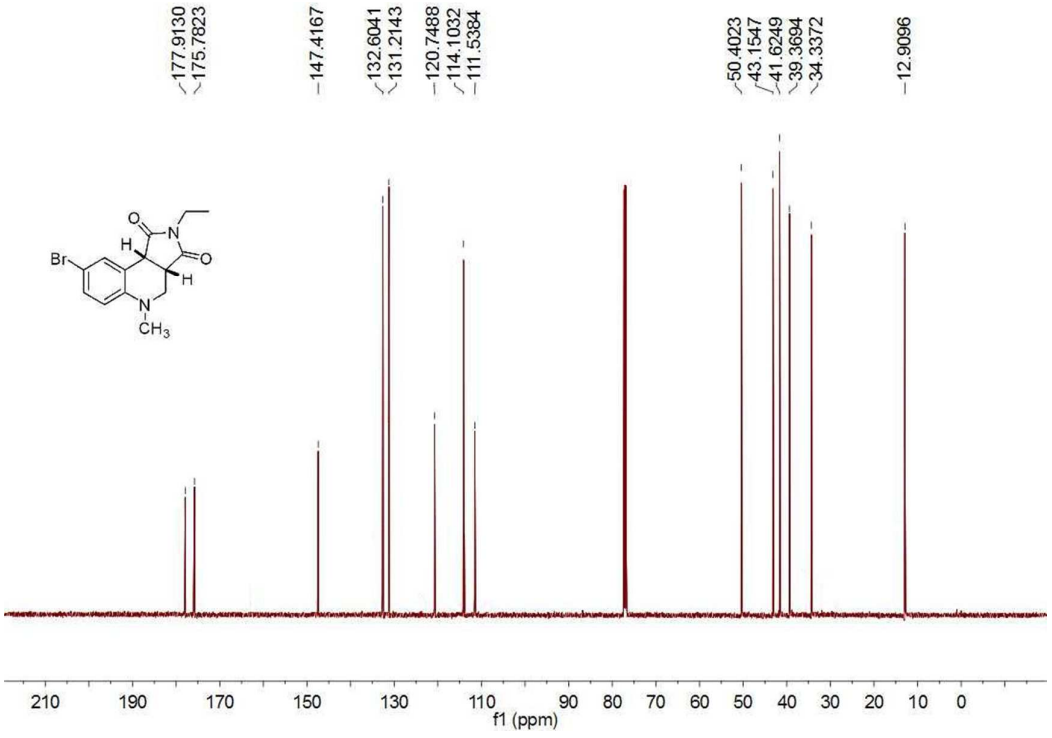

**3w-$^{13}$C NMR**



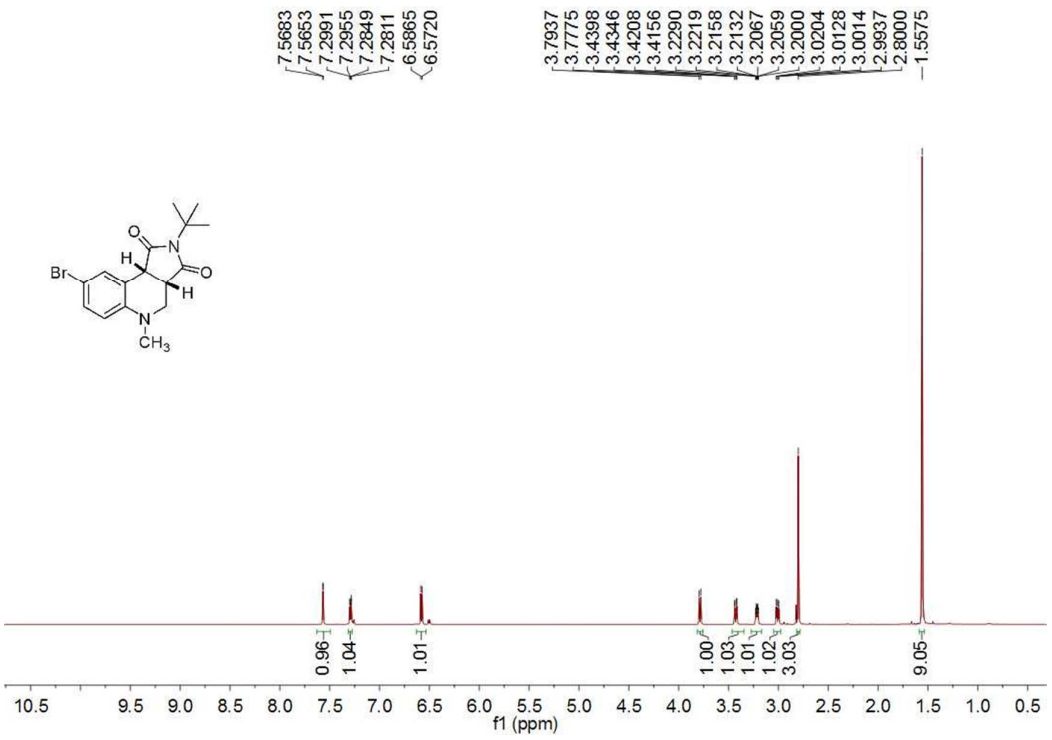
**3x-$^{1}$H NMR**



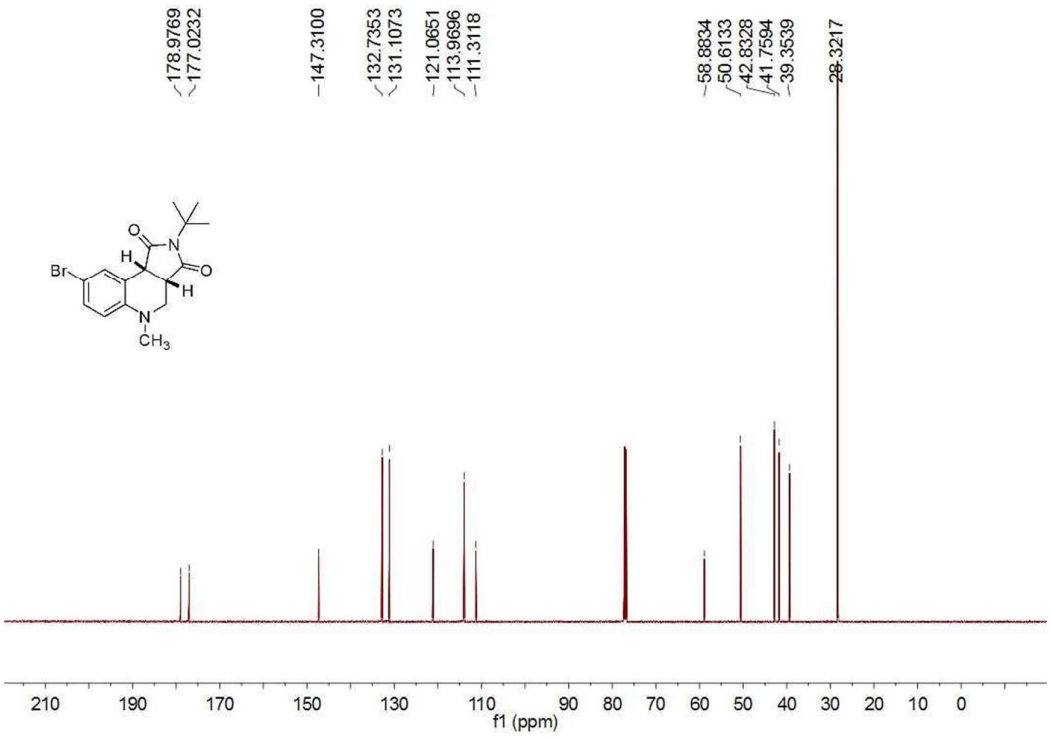

**3x-$^{13}$C NMR**



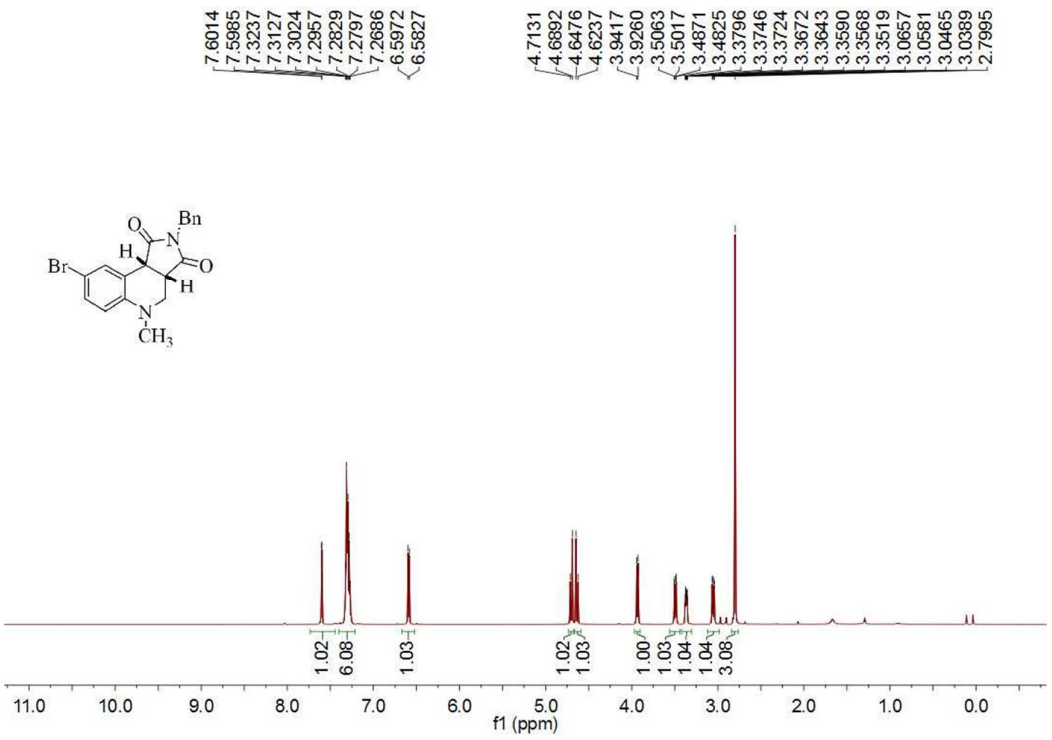
**3y-$^{1}$H NMR**



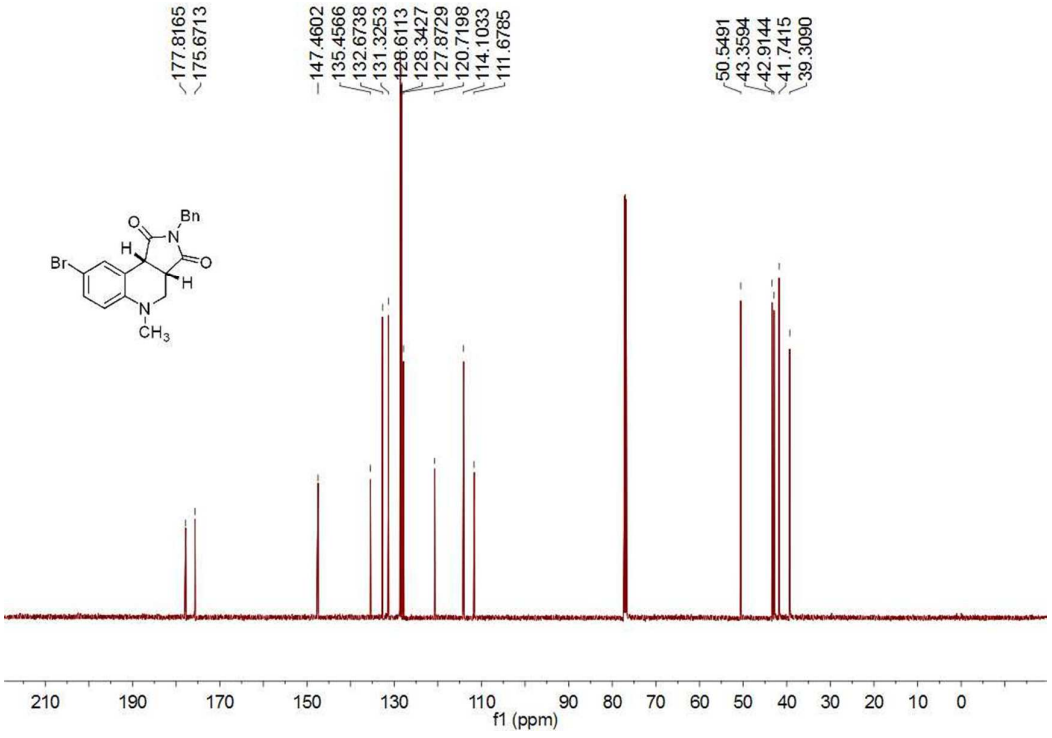

**3y-$^{13}$C NMR**



**3z-$^{1}$H NMR**

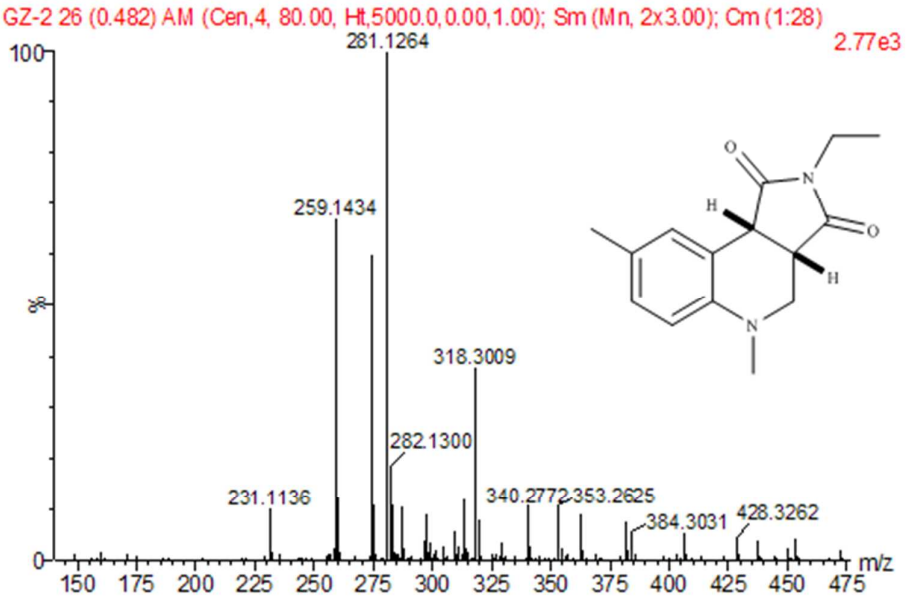



**3z-$^{13}$C NMR**

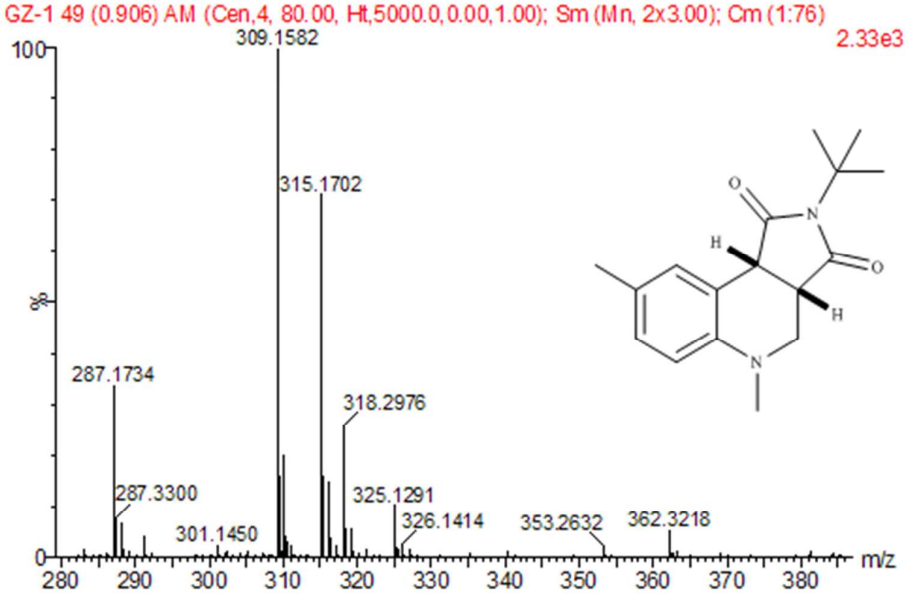


## HRMS of new compounds

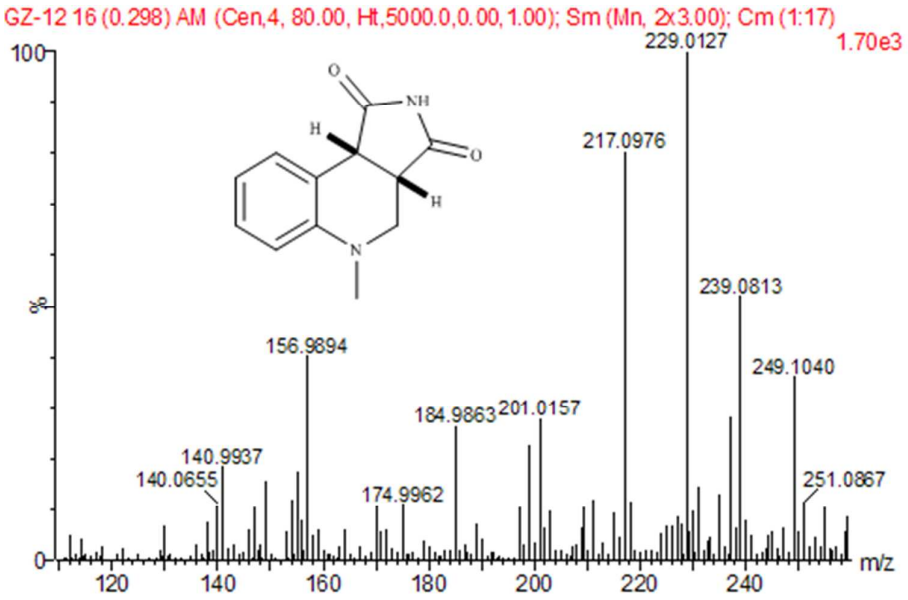
HRMS-**3c**



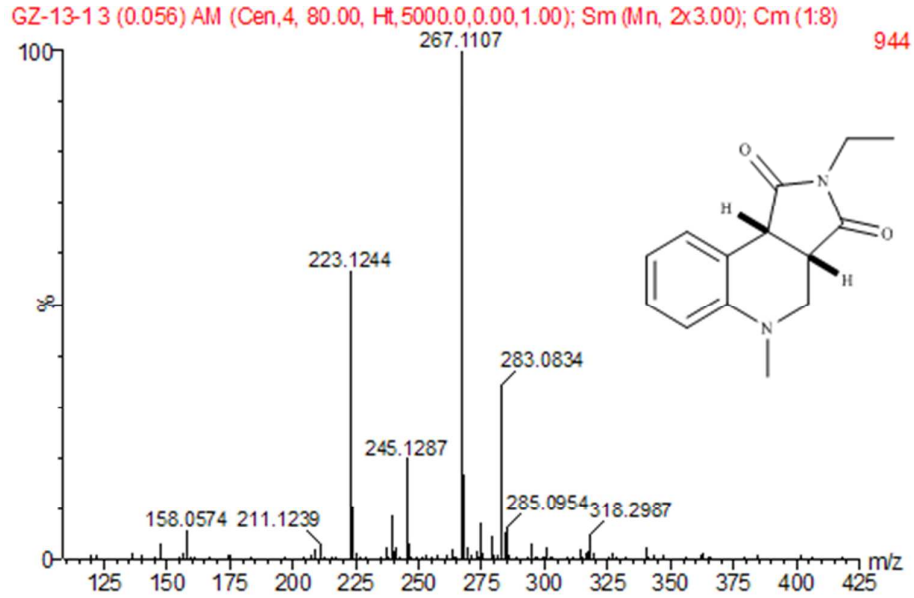

HRMS-**3d**



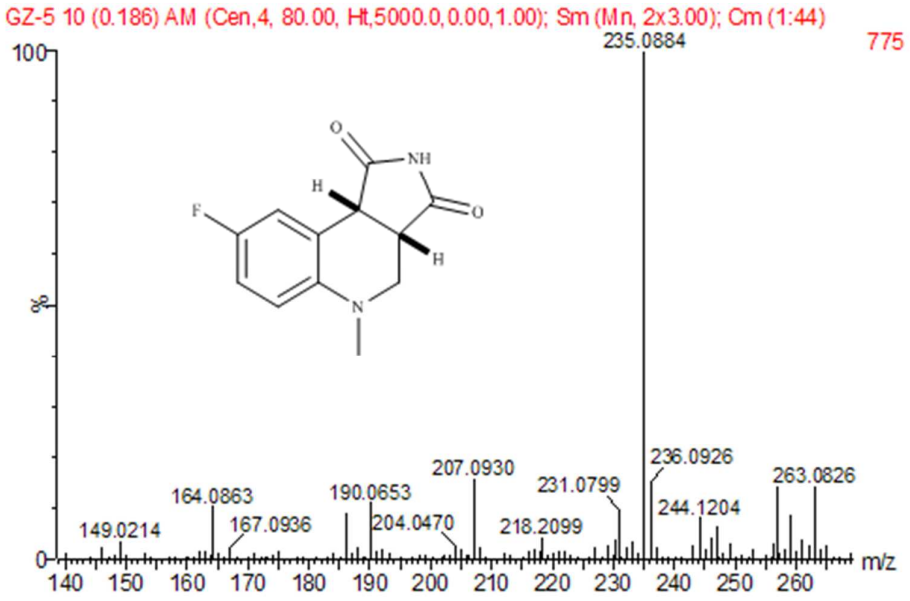
HRMS-**3g**



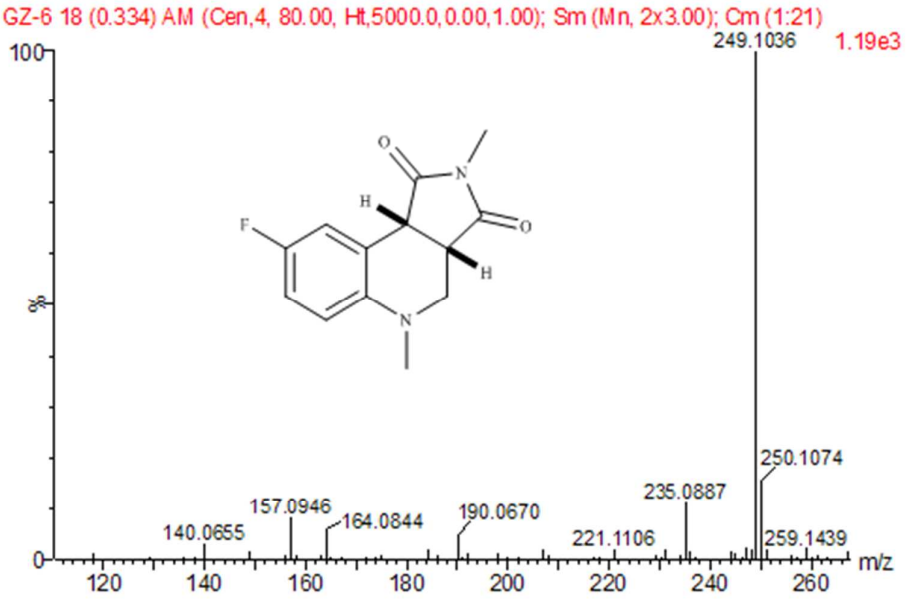

HRMS-**3i**



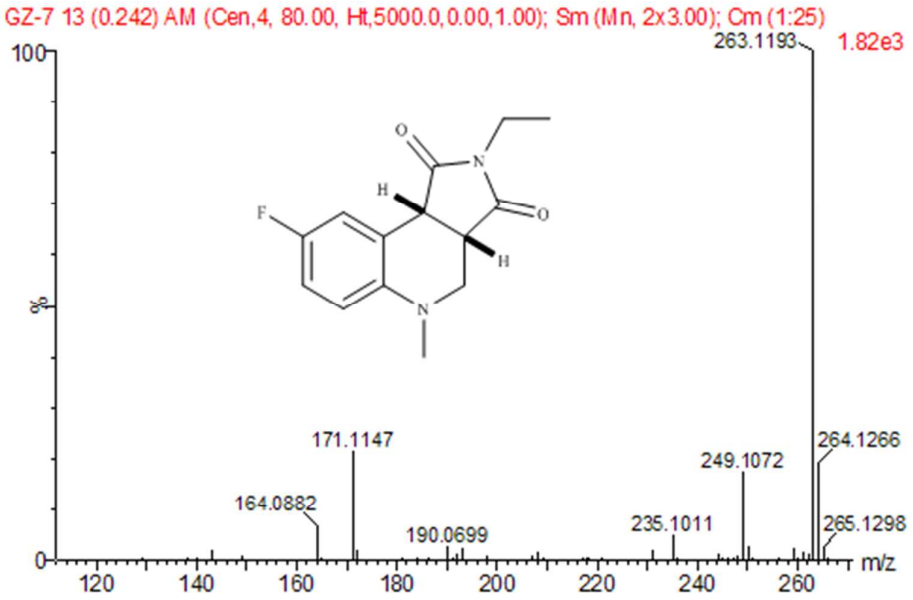
HRMS-**3m**



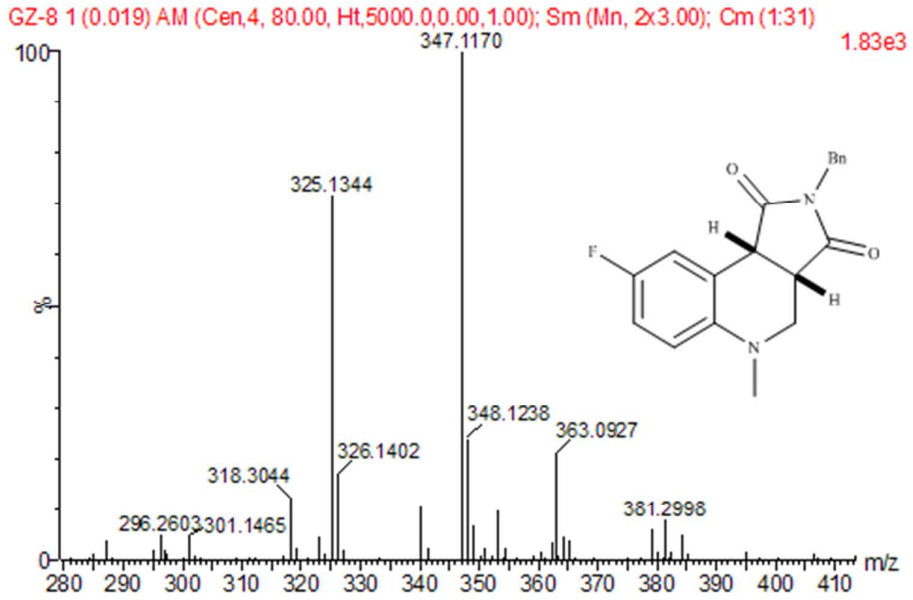

HRMS-**3n**



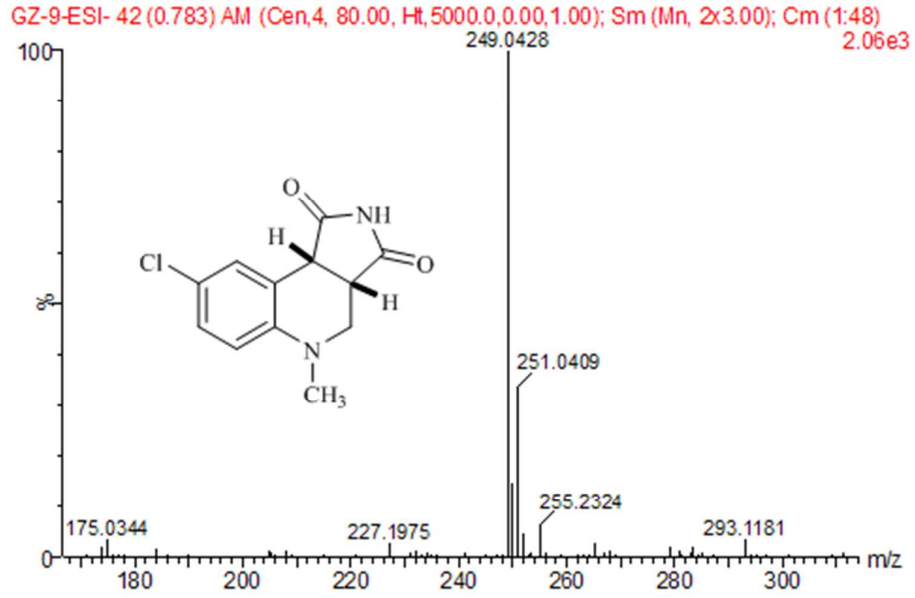
HRMS-**3o**



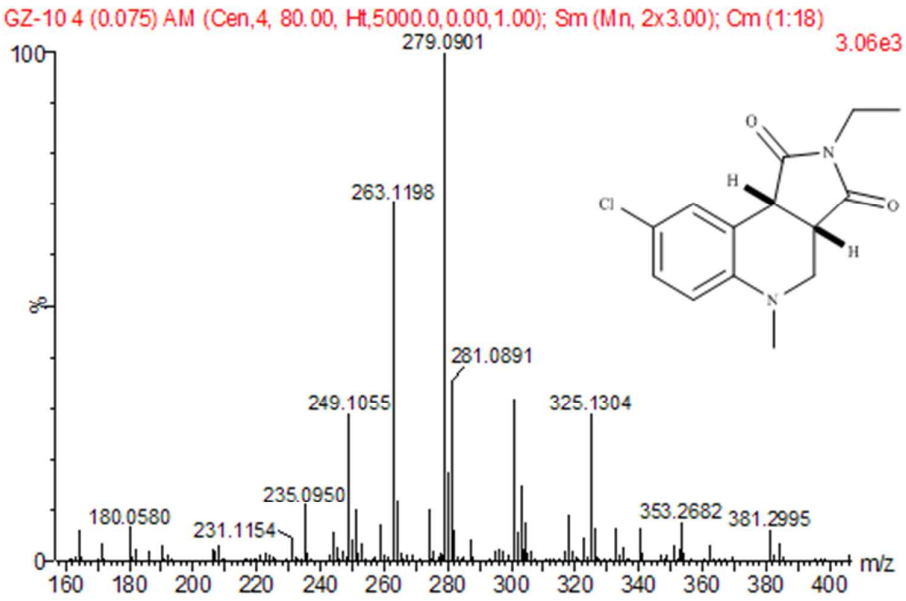

HRMS-**3p**



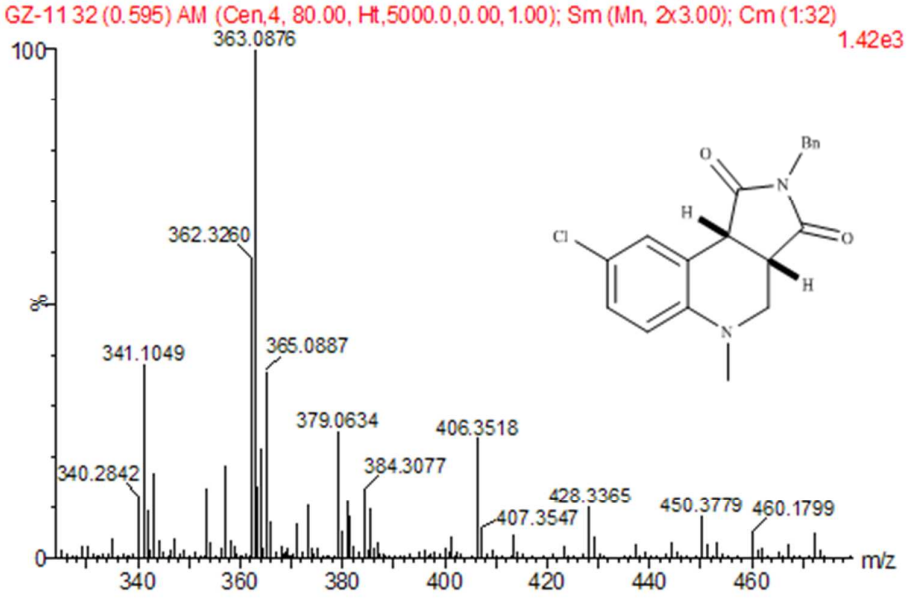
HRMS-**3r**



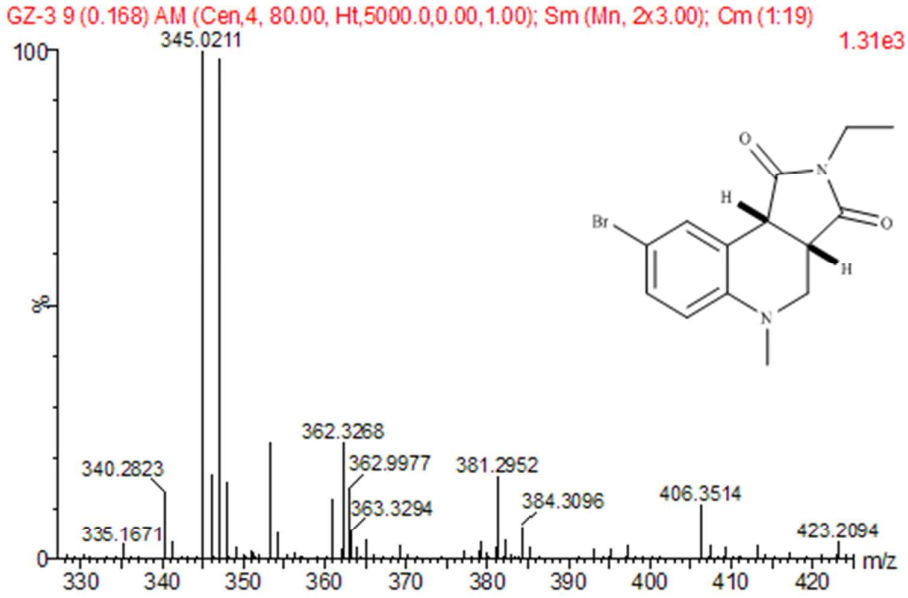

HRMS-**3t**



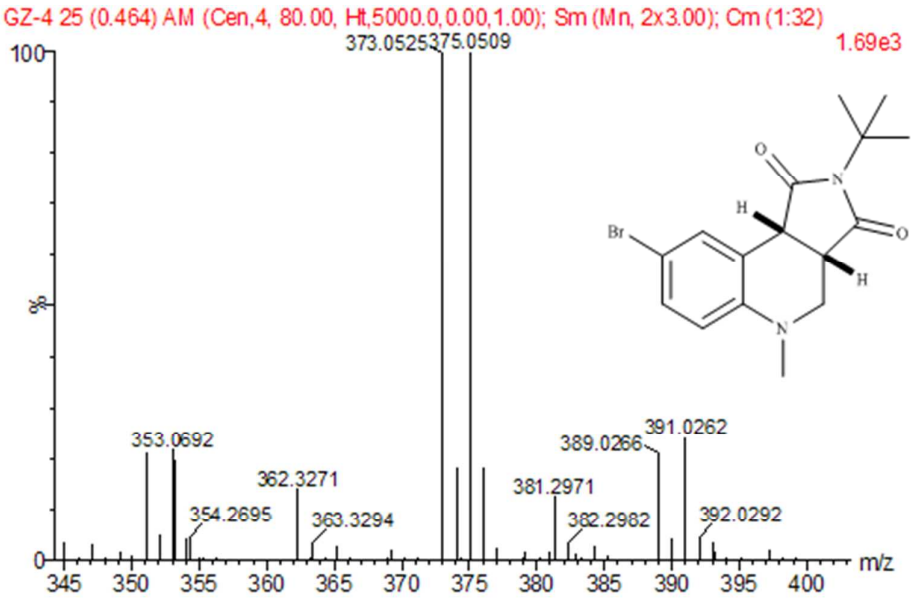
HRMS-**3u**




HRMS-**3x**



HRMS-**3y**




## 6 References

1 Aliu, S; Rusinovci, I; Fetahu, S; Gashi, B; Simeonovska, E; Rozman, L. *Acta Agriculturae Slovenica*. **2015**, *105*(1), 85-94.