

## Supporting Information

### Visible-Light-Promoted Acyl Radical Cascade Reaction for Accessing Acylated Isoquinoline-1,3(2*H*,4*H*)-dione Derivatives

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## 1. Synthesis of the Starting Materials

*N*-Arylacrylbenzamides **1** were prepared according to the literatures.<sup>1</sup>

$\alpha$ -Keto acids **2** were prepared according to the literatures.<sup>2</sup>

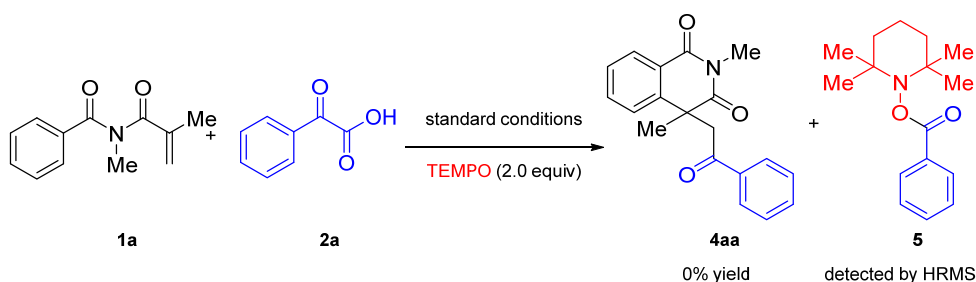
### General procedure for the synthesis of *N*-methyl benzamide:

A 100-mL round bottom flask was charged with methylamine hydrochloride (15 mmol), K<sub>2</sub>CO<sub>3</sub> (20 mmol) in Ethyl acetate (20 mL) and H<sub>2</sub>O (10 mL). Then, benzoyl chloride (10mmol) was added slowly to the reaction mixture at 0 °C. After that, the residue was stirred at room temperature for 4-6 h. The reaction was completed by TLC monitoring, the organic phase was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The resulting residue was purified by flash silica gel column chromatography (eluent: hexane/EtOAc, v/v = 1/1) to give the desired product in 95% yield.

### General procedure for the synthesis of *N*-methacryloyl-*N*-methyl-benzamide:

A 100-mL round bottom flask was charged with *N*-methyl benzamide (10 mmol), DMAP (1 mmol), triethylamine (20 mmol) in dichloromethane (20 mL). Then, methacryloyl chloride (15 mmol) was added slowly to the reaction mixture at 0 °C. After that, the residue was stirred at room temperature for 4-6 h. The reaction was completed by TLC monitoring, the organic phase was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The resulting residue was purified by flash silica gel column chromatography (eluent: hexane/EtOAc, v/v = 10/1) to give the desired product in 75% yield.

## 2. Control Experiments.

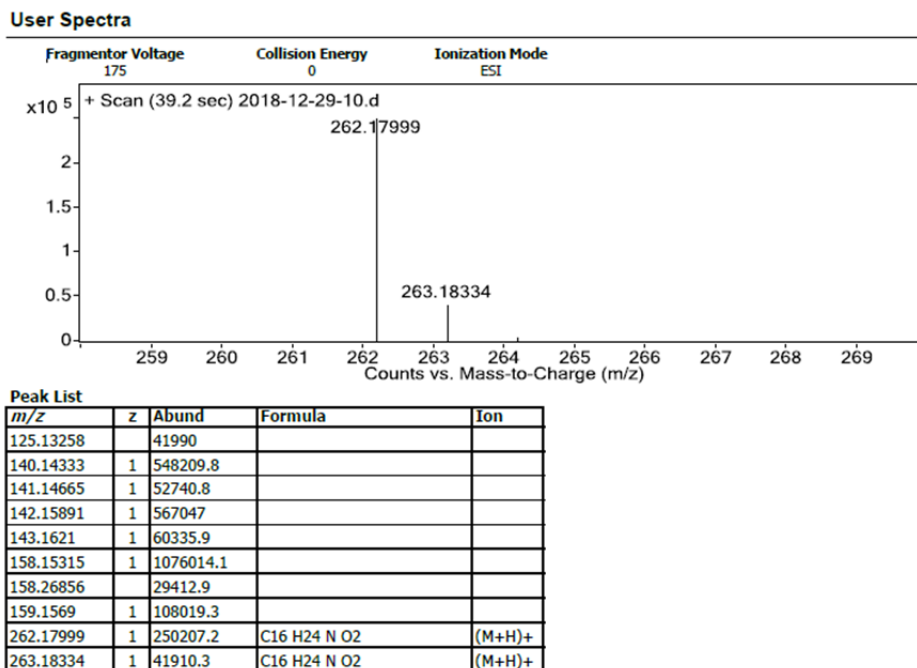


HRMS (ESI): calcd for C<sub>16</sub>H<sub>24</sub>NO<sub>2</sub> [M + H]<sup>+</sup> 262.18016; found 262.17999.

<sup>1</sup> (a) Y.-q., Yuan; P. S., Kumar; C.-n., Zhang; M.-h., Yang; S.-r., Guo *Org. Biomol. Chem.* 2017, **15**, 7330; (b) C., Liu; W., Zhao; Y., Huang; H., Wang; B., Zhang *Tetrahedron* 2015, **71**, 4344.

<sup>2</sup> (a) A., Hossian; M. K., Manna; K., Manna; R., Jana *Org. Biomol. Chem.* 2017, **15**, 6592; (b) J., Zhuang; C., Wang; F., Xie; W., Zhang *Tetrahedron* 2009, **65**, 9797.

An oven-dried Schlenk tube (20 mL) was equipped with a magnetic stir bar, *N*-methacryloyl-*N*-methylbenzamide **1a** (0.3 mmol), 2-oxo-2-phenylacetic acid **2a** (3.0 equiv) TEMPO (2.0 equiv), eosin B (4.0 mg, 0.02 equiv), (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.5 equiv) and DMSO (3.0 mL). The tube was placed at a distance (app. 2 cm) 2 × 3 W blue LEDs, and the resulting red solution was stirred at ambient temperature under the visible-blue light irradiation. The mixture was stirred at r.t. for 12 h. TLC shows that the product **4aa** was not formed and adduct **5** was detected by HRMS.



### 3. General procedures for the synthesis of isoquinoline-1,3(2*H*,4*H*)-diones **4**

*N*-arylacrylbenzamides **1** (0.30 mmol),  $\alpha$ -keto acids **2** (0.90 mmol), eosin B (0.006 mmol, 2.0 mol%) and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.75 mmol) were dissolved in DMSO (3.0 mL). Then, the solution was stirred at room temperature under 2 × 3 W blue LEDs irradiation for 24 hrs-72 hrs. After the reaction was completed by TLC monitoring, the reaction mixture was diluted by adding NaHCO<sub>3</sub> and brine. The aqueous layer was extracted with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 5:1 as the eluant) on silica gel to give the desired isoquinoline-1,3(2*H*,4*H*)-diones **4**.

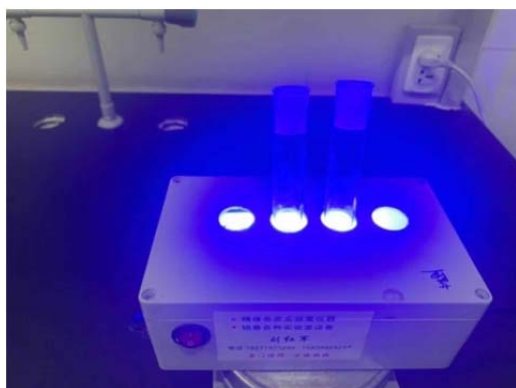
#### 4. Photoreaction device diagram<sup>3</sup>



I



II



III



IV

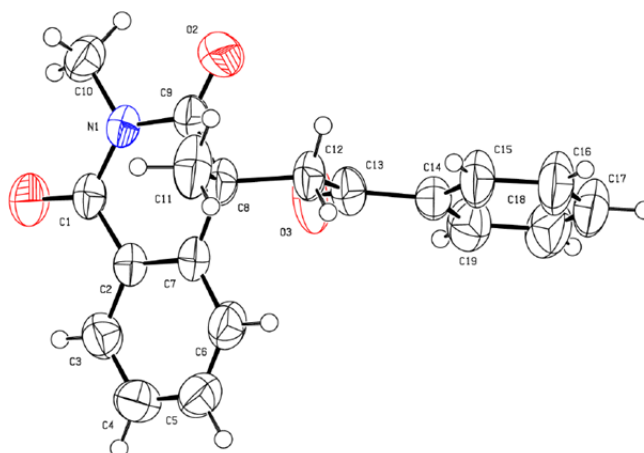
Figure SI Photoreactor used in this research

The photoreactors were bought from Wuhan Jiushang Technology Co. , Ltd (Blue LEDs, 1 W for every LED bead; 3 LED beads on one chip; 8 LED chips in the photoreactor box; every reaction tube was irradiated by 2 LED chips (6 LED beads) from two sides;  $\lambda_{\max} = 460 \text{ nm}$ )

#### 5. Crystallographic Data of the Compound 4aa:

Thermal ellipsoids are set at a 50% probability level

<sup>3</sup> J. Chen, P.-Z. Wang, B. Lu, D. Liang, X.-Y. Yu, W.-J. Xiao and J.-R. Chen, *Org. Lett.*, 2019, **21**, 9763-9768.



Procedure for recrystallization of compounds **4aa**: the hexane was slowly added into the solution of target products in dichloromethane (with different concentration), then the dichloromethane was evaporated from the mixed solvent system at room temperature and the crystals were obtained after a few days.

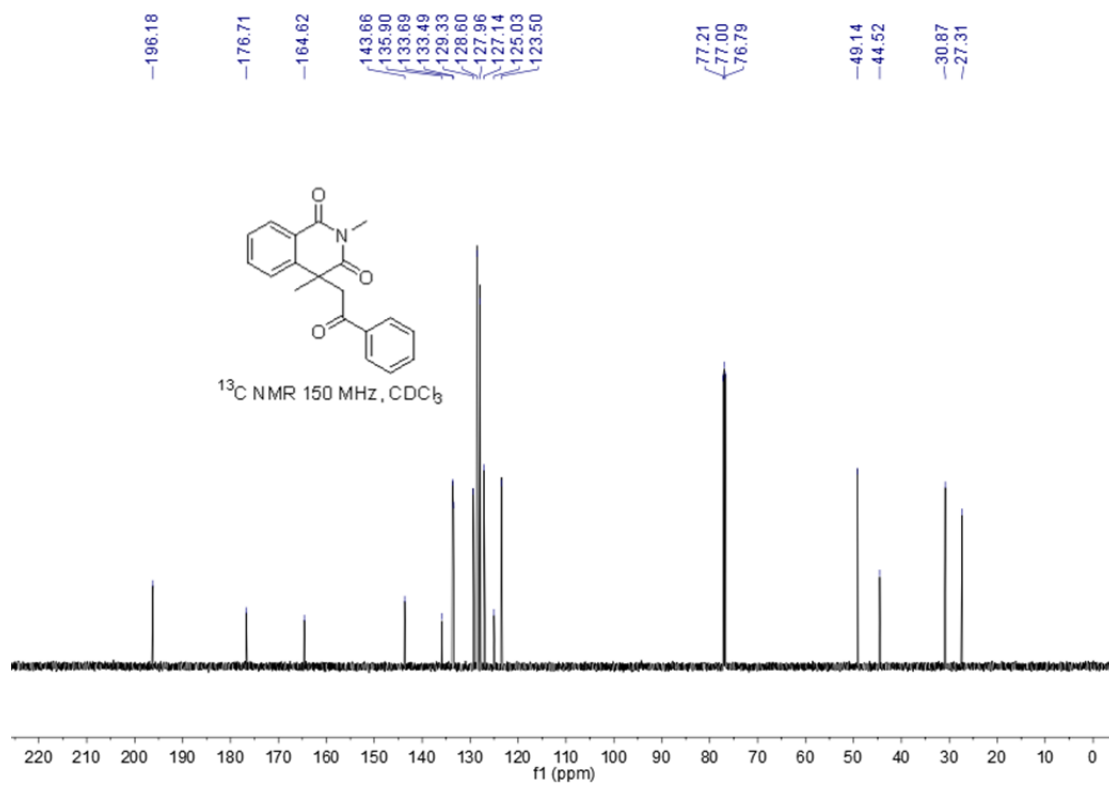
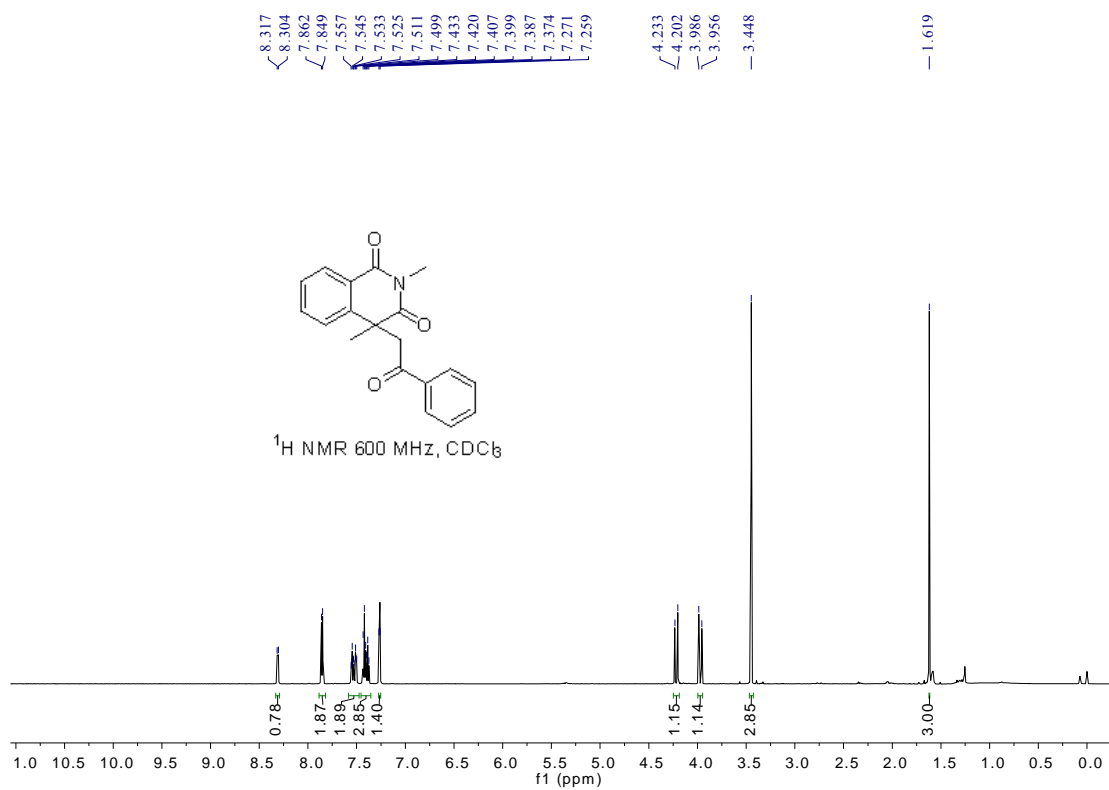
**Table S1 Crystallographic Data of 4aa**

CCDC number	1937084
Bond precision	C.C = 0.0027 Å Wavelength = 0.71073
Cell	a = 9.0158(2) b = 10.7244(3) c = 32.8321(9) alpha = 90 beta = 90 gamma = 90
Temperature/K	291
Volume	3174.50(14)
Space group	pbca
Sum formula	C <sub>19</sub> H <sub>17</sub> NO <sub>3</sub>
Mr	307.33
Dx, g cm <sup>-3</sup>	1.286
Z	8
Mu (mm <sup>-1</sup> )	0.087
F000	1296.0
h, k, lmax	11,13,40

Nref	3116
Correction method	Not given
Data completeness	0.999
Theta(max)	25.994
R(reflections)	0.0572(2454)
wR2(reflections)	0.1810(3116)
S	1.082
Npar	211

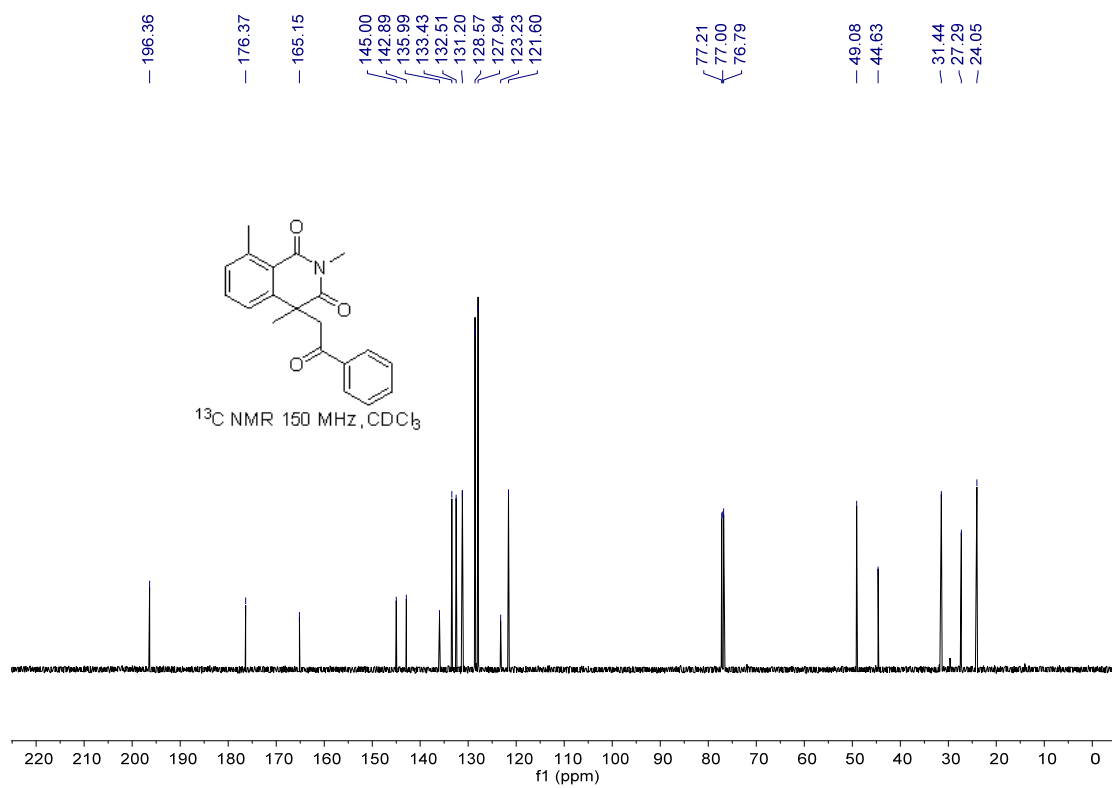
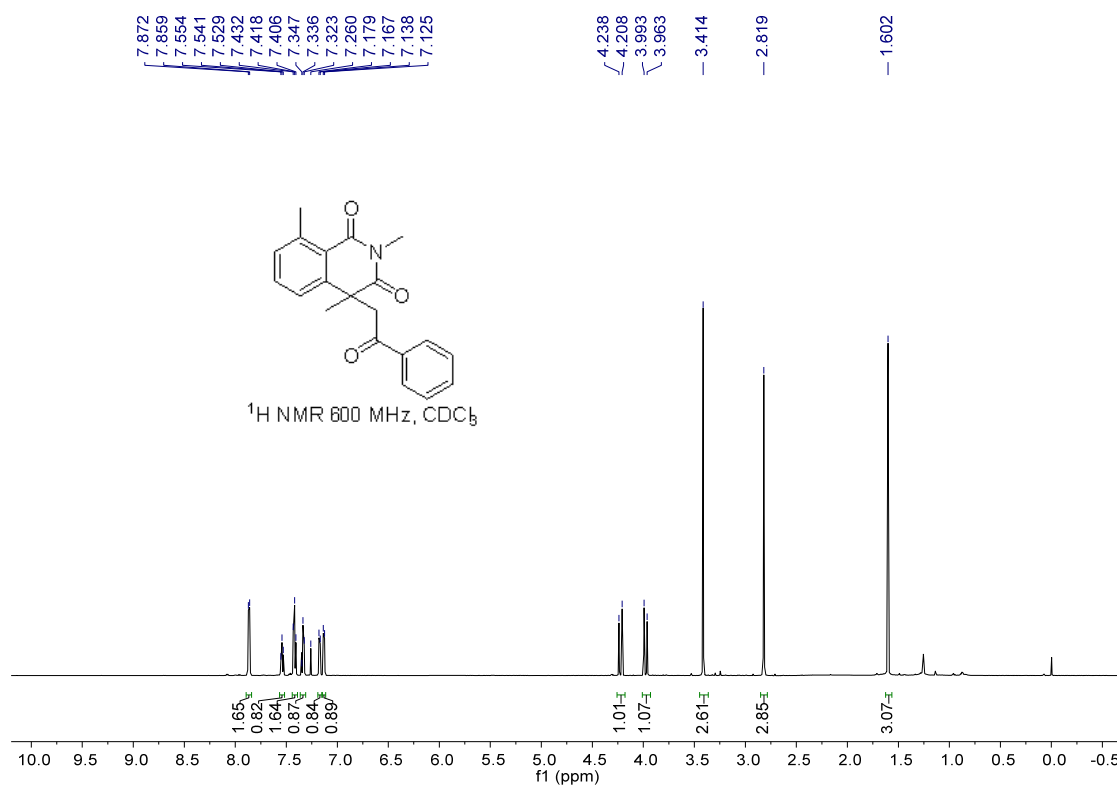
## 6. NMR copies

NMR copies of compound **4aa**:

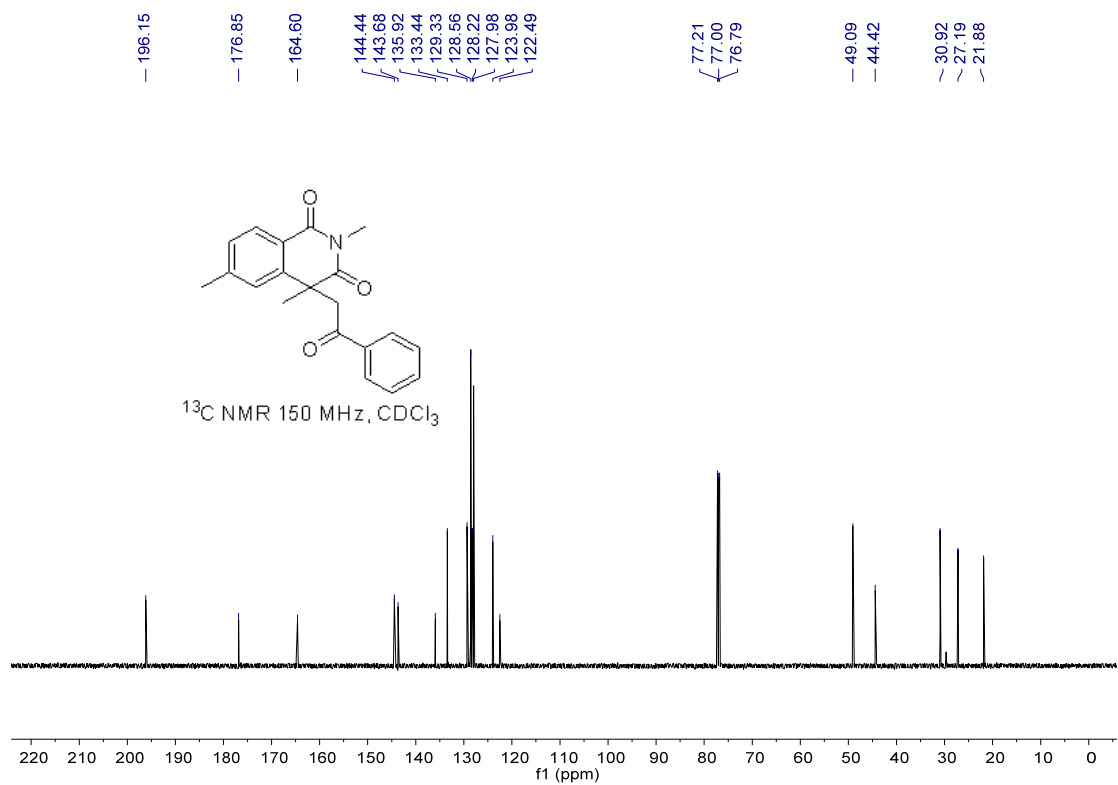
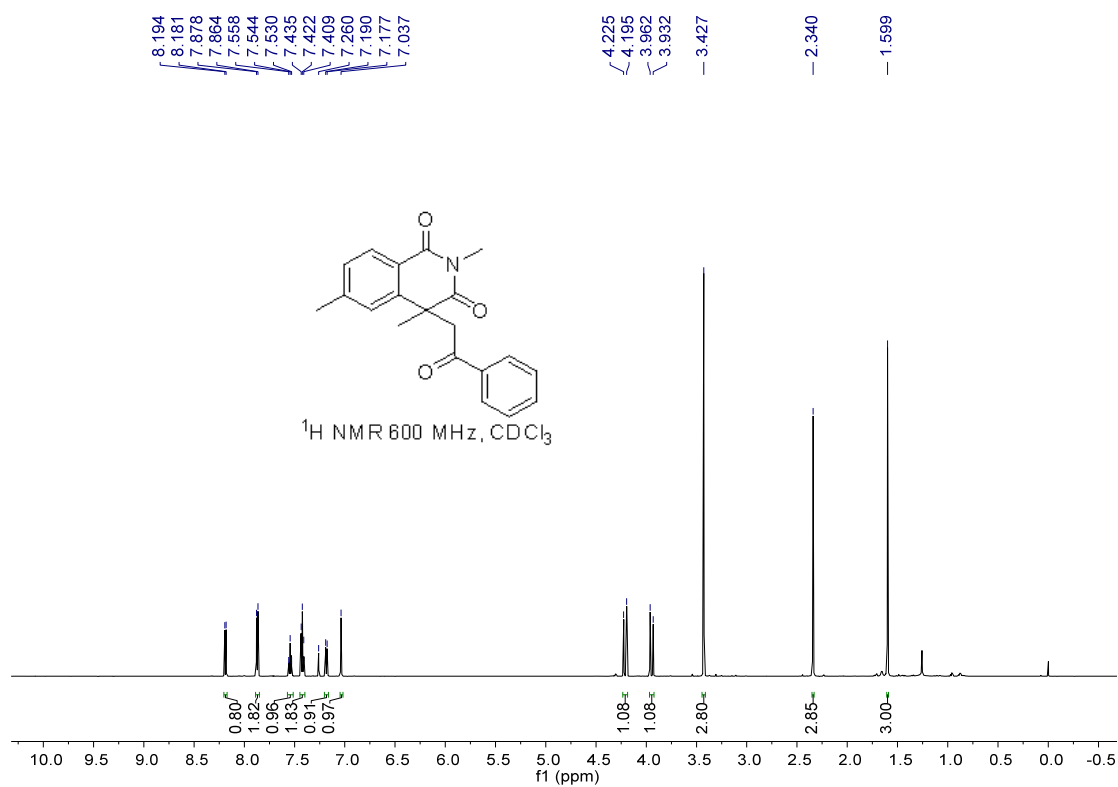




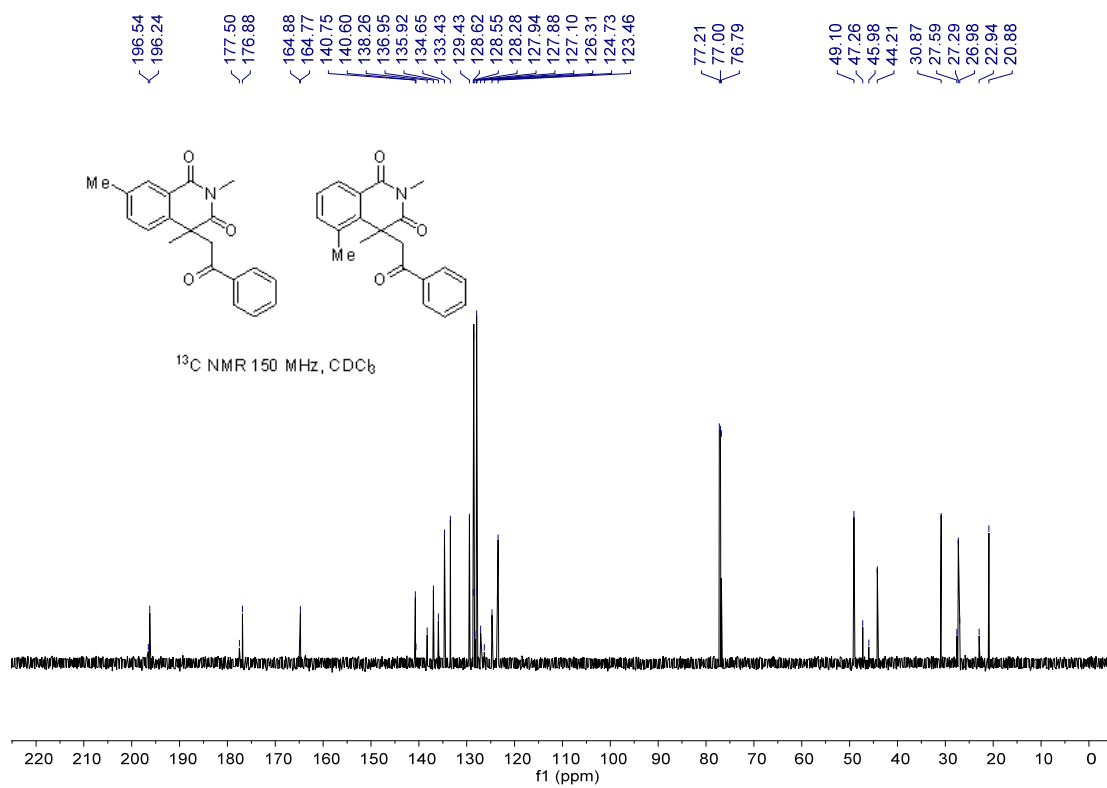
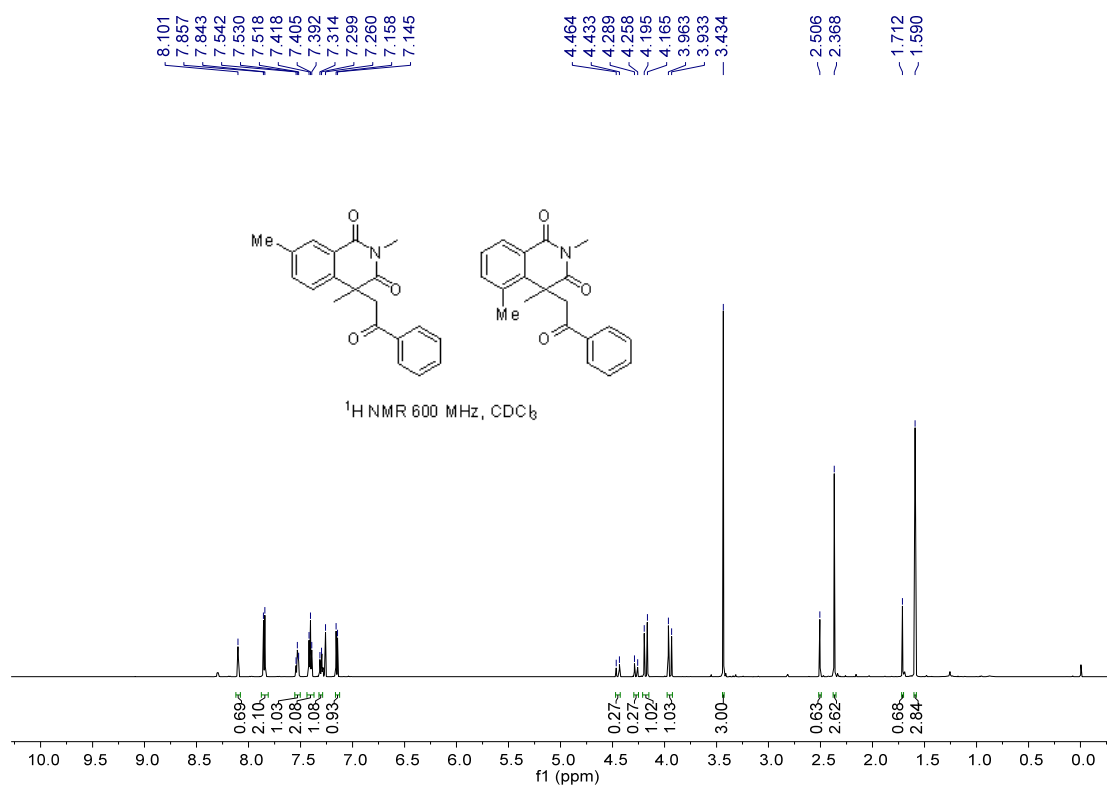
NMR copies of compound **4ba**:



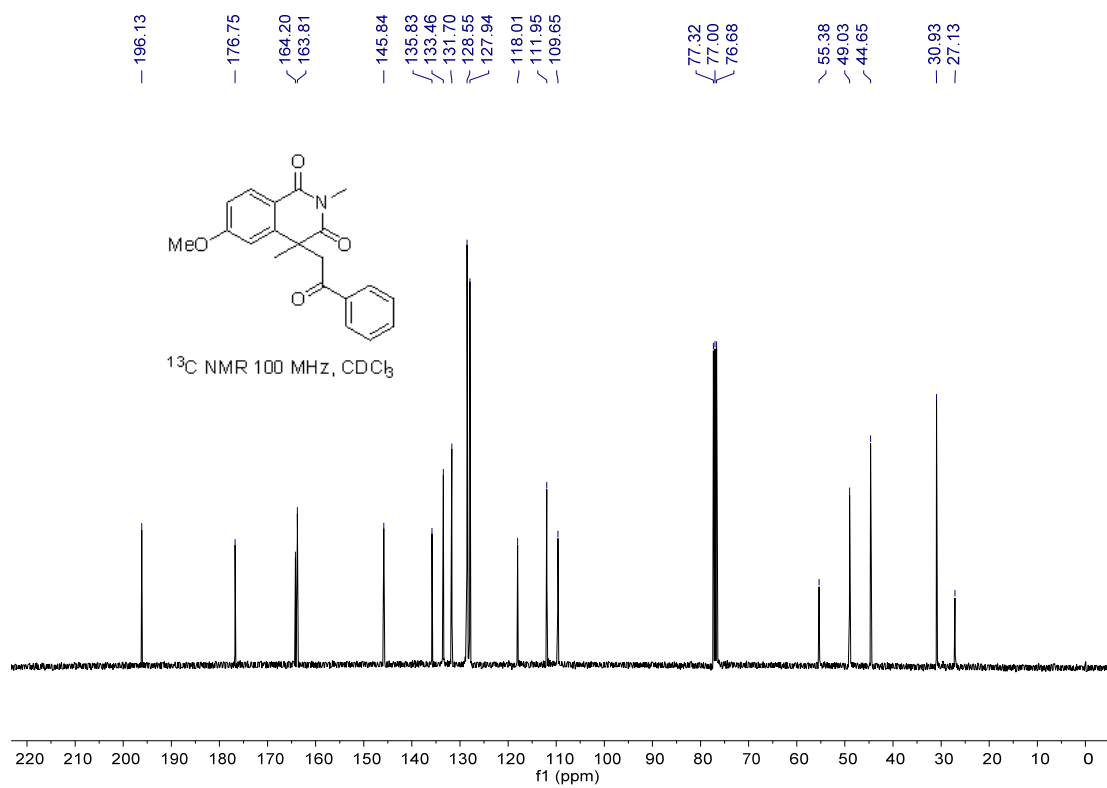
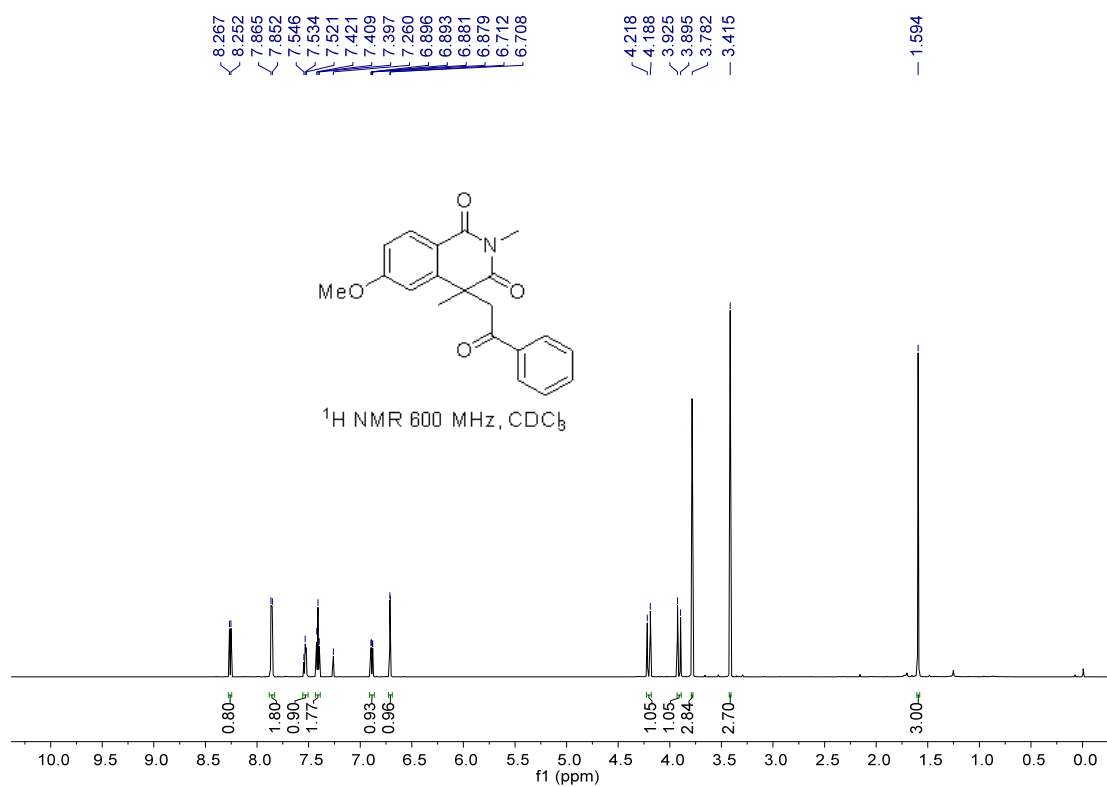
NMR copies of compound **4ca**:



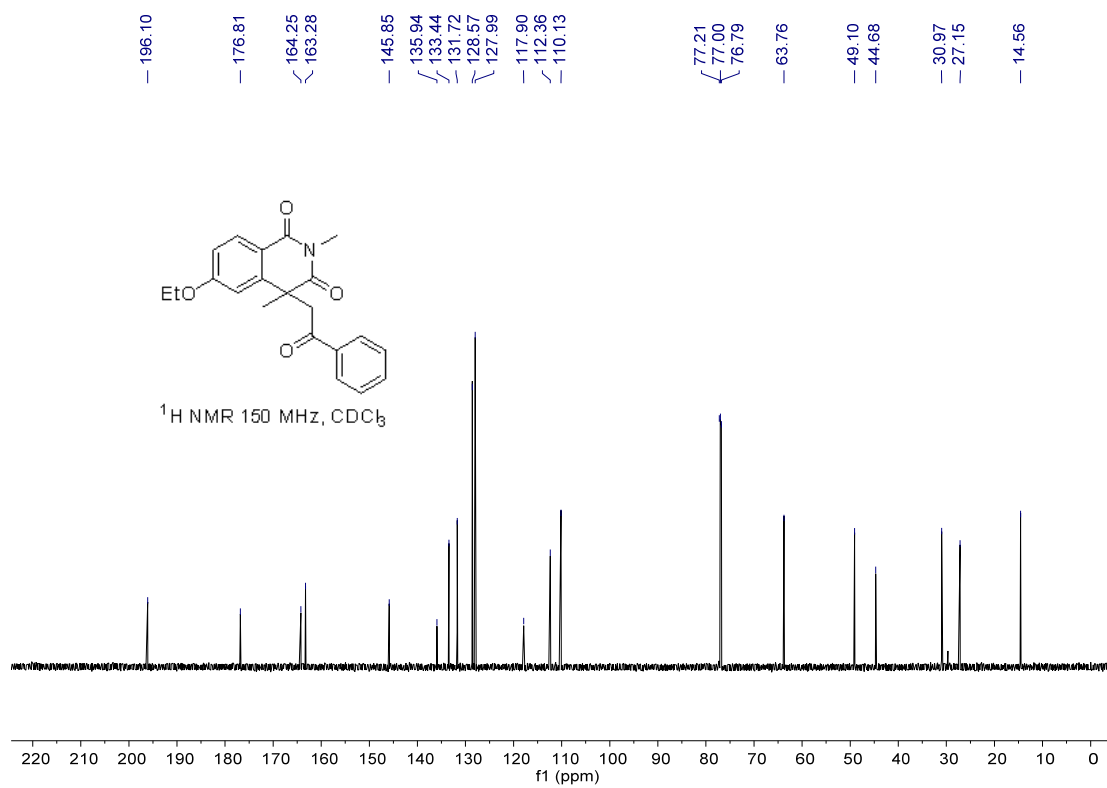
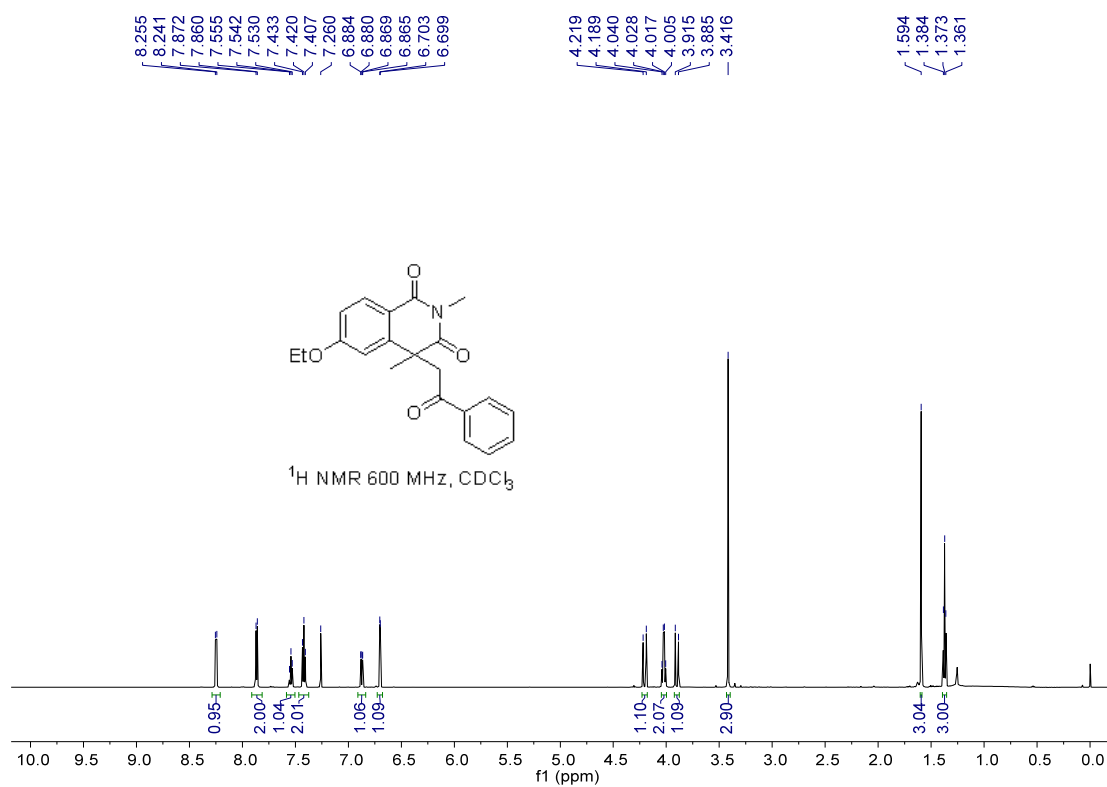
NMR copies of compound **4da** and **4da'**:



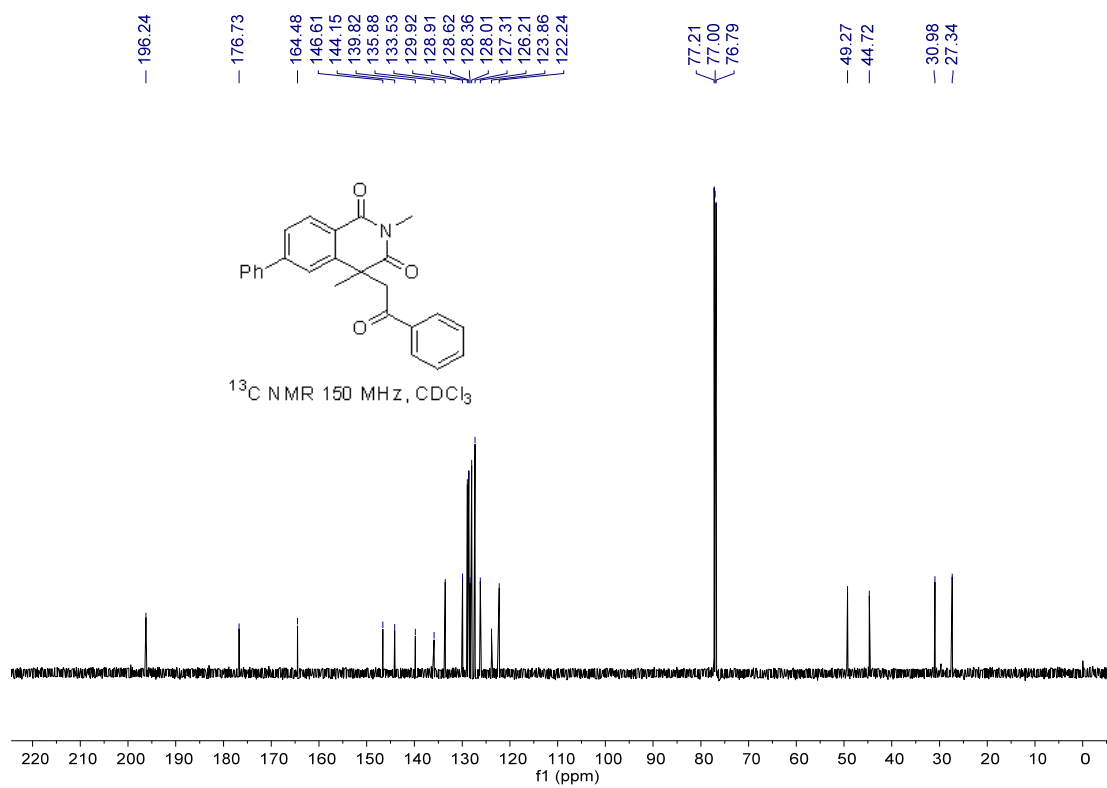
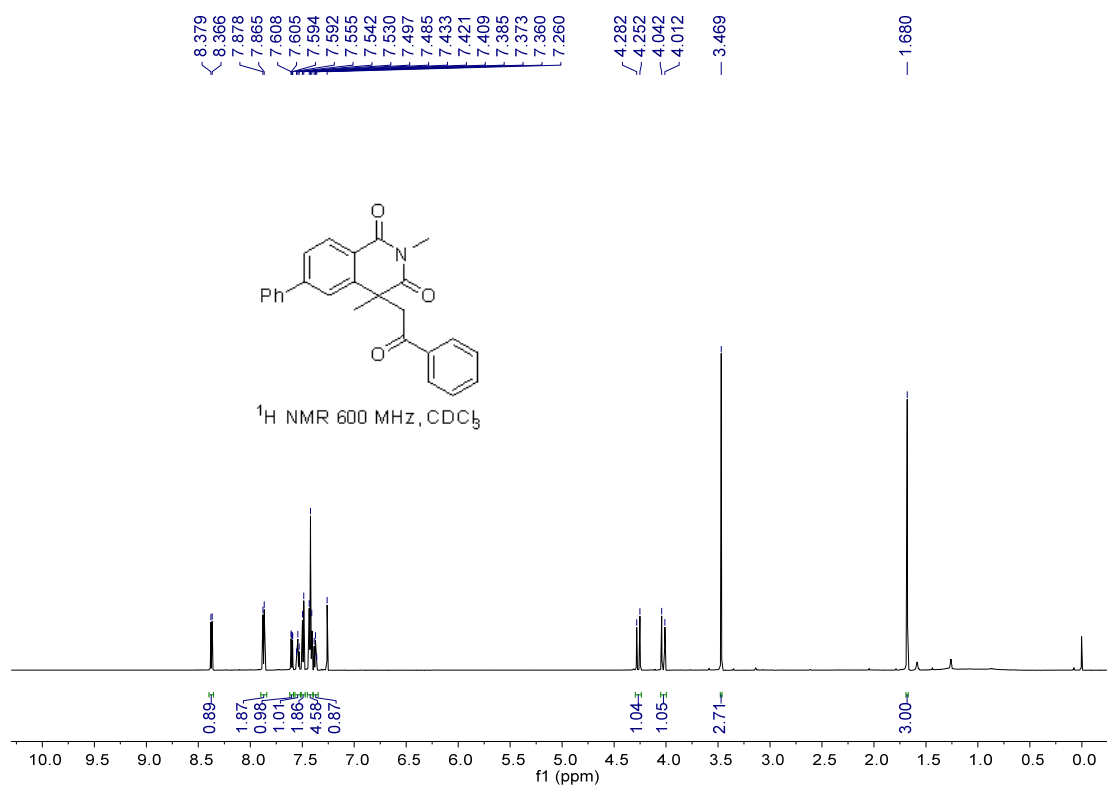
NMR copies of compound **4ea**:



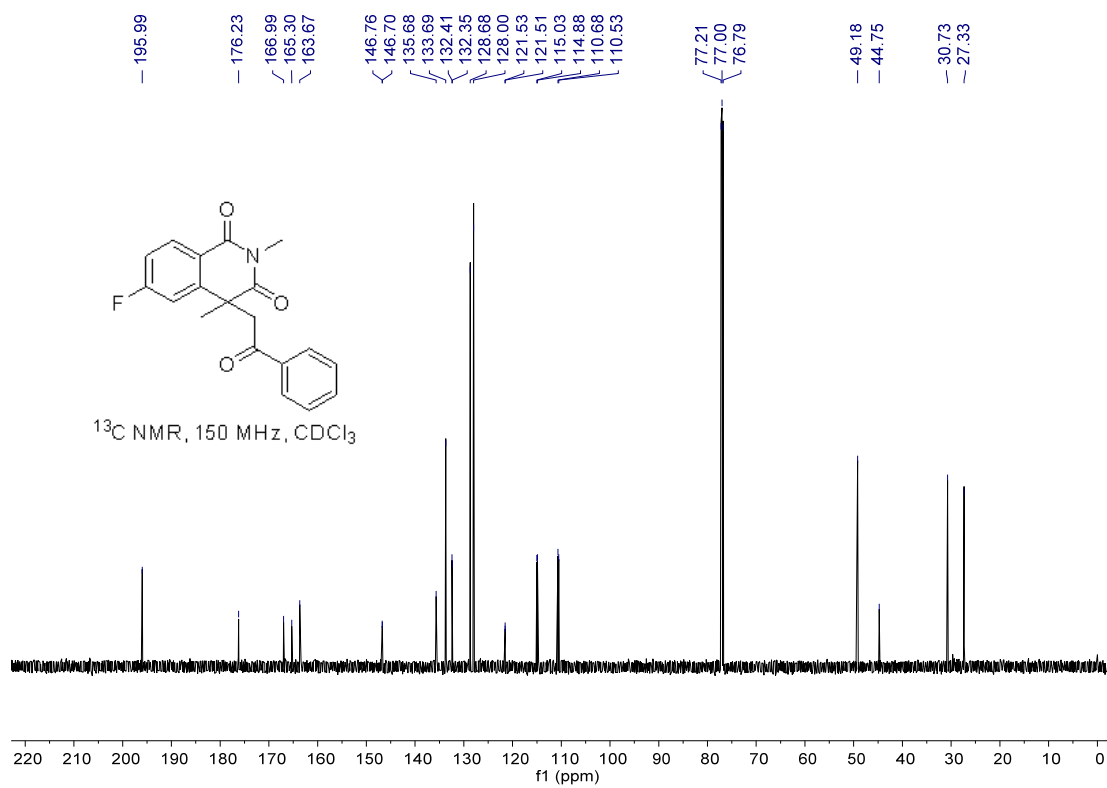
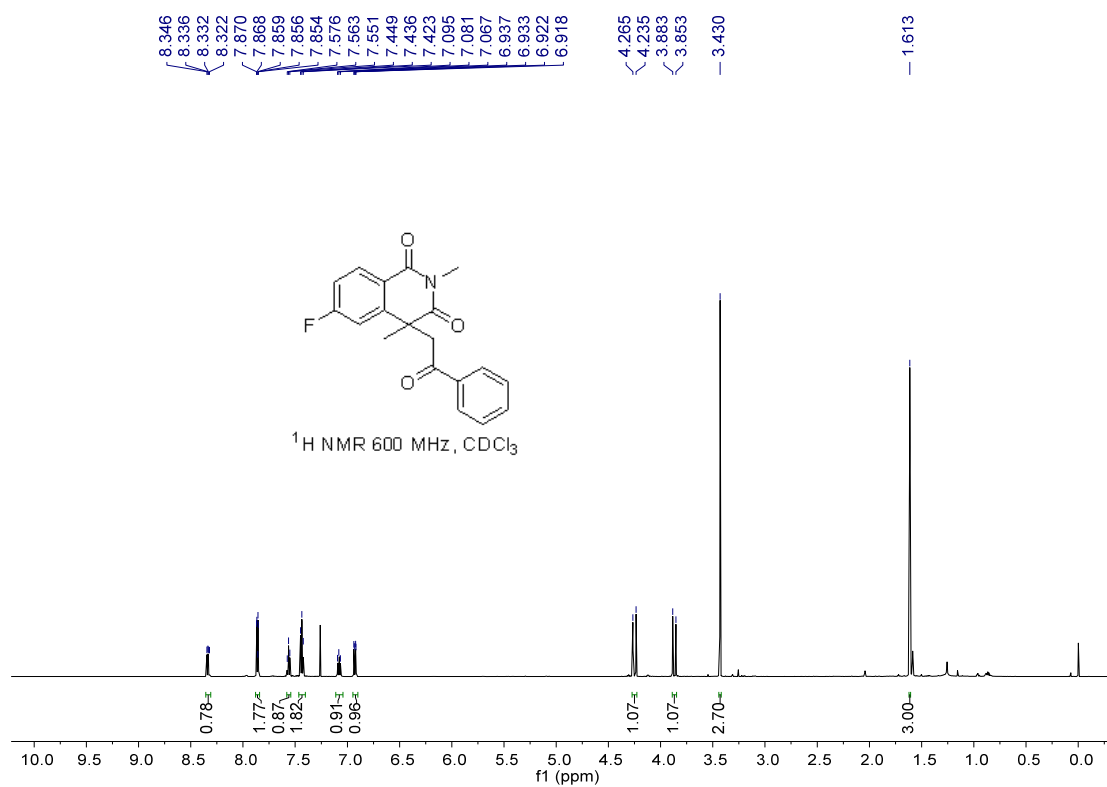
NMR copies of compound **4fa**:



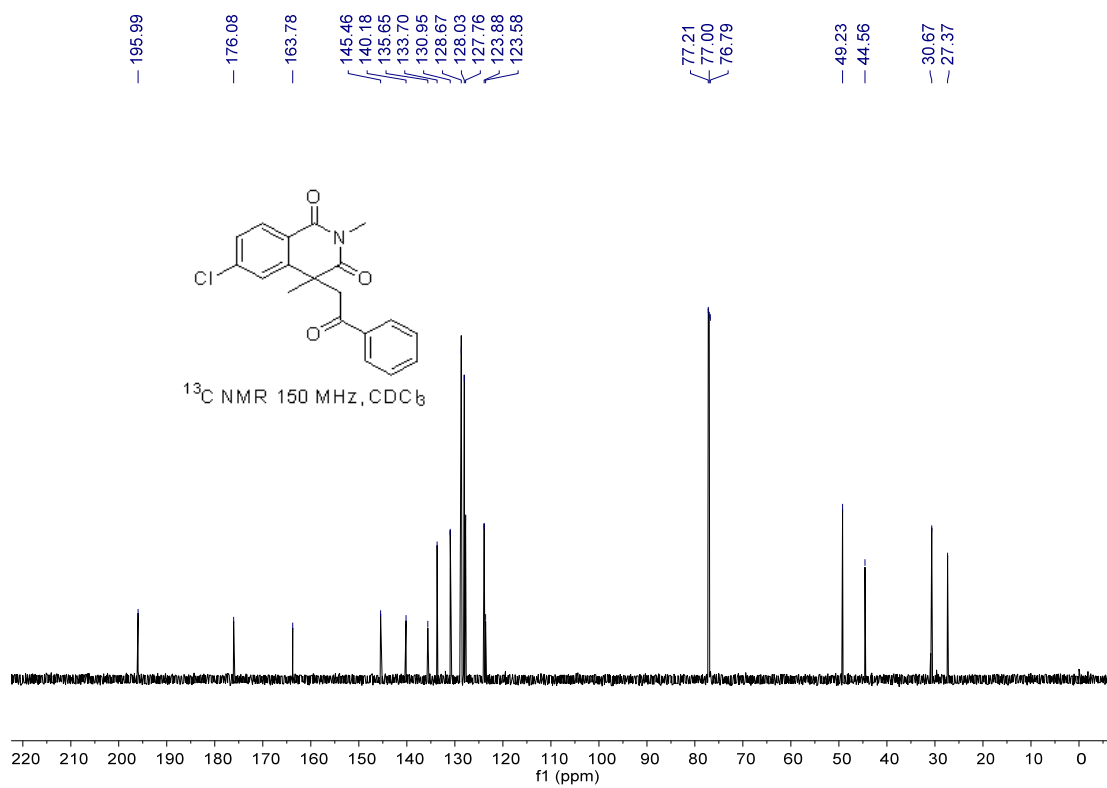
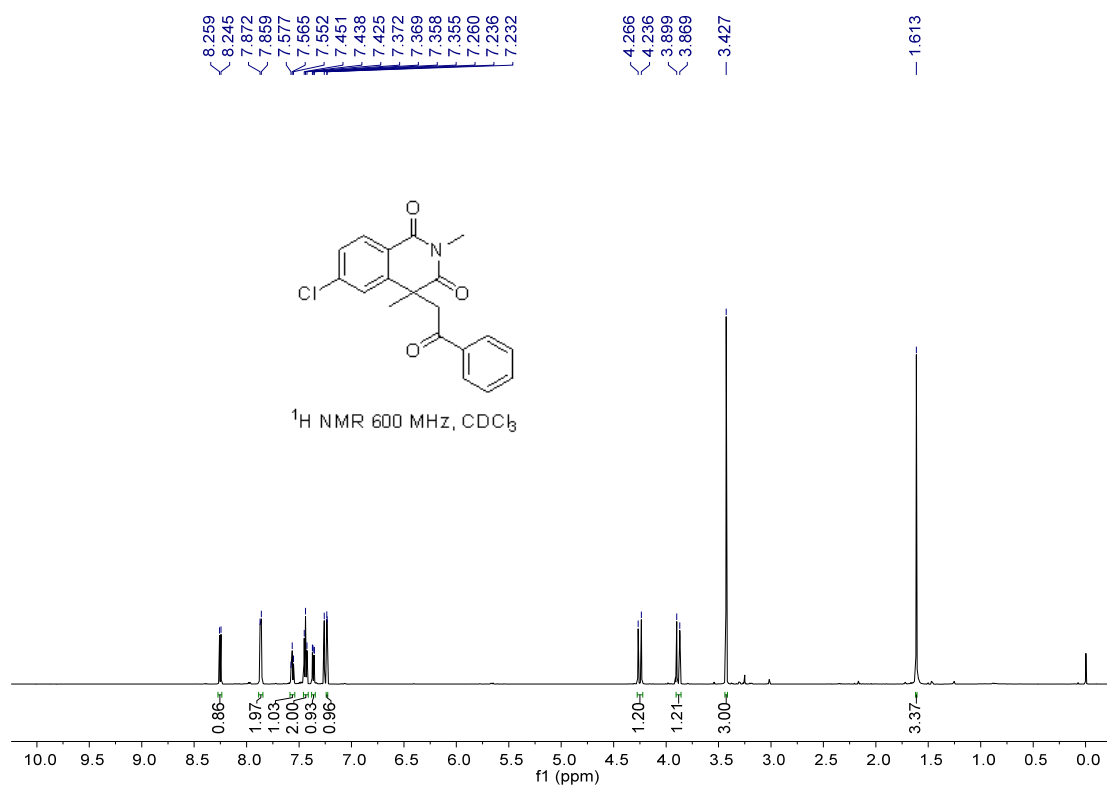
NMR copies of compound **4ga**:



NMR copies of compound **4ha**:

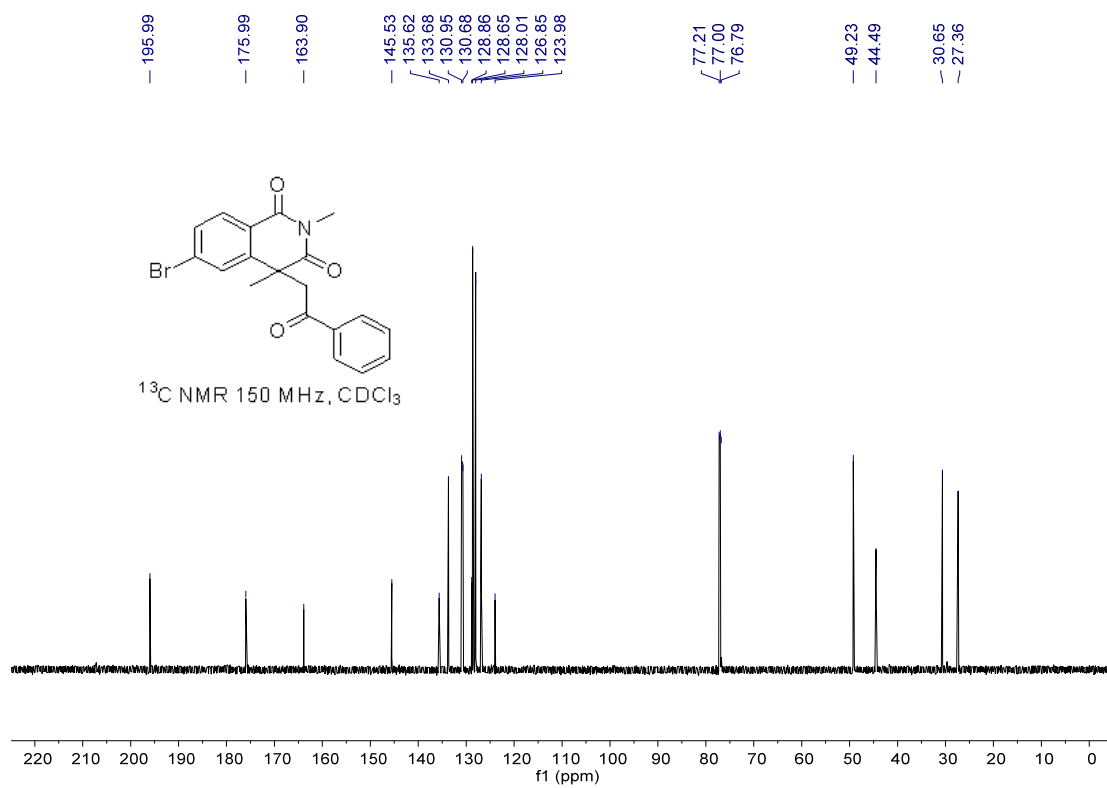
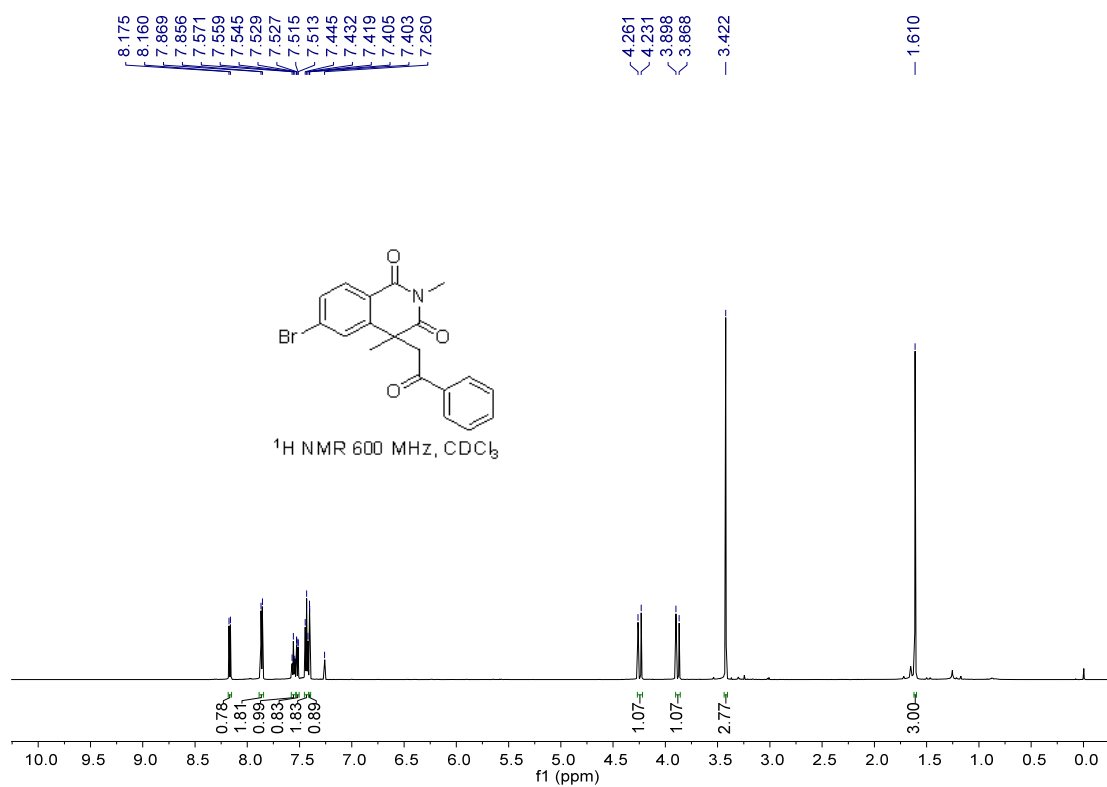


NMR copies of compound **4ia**:

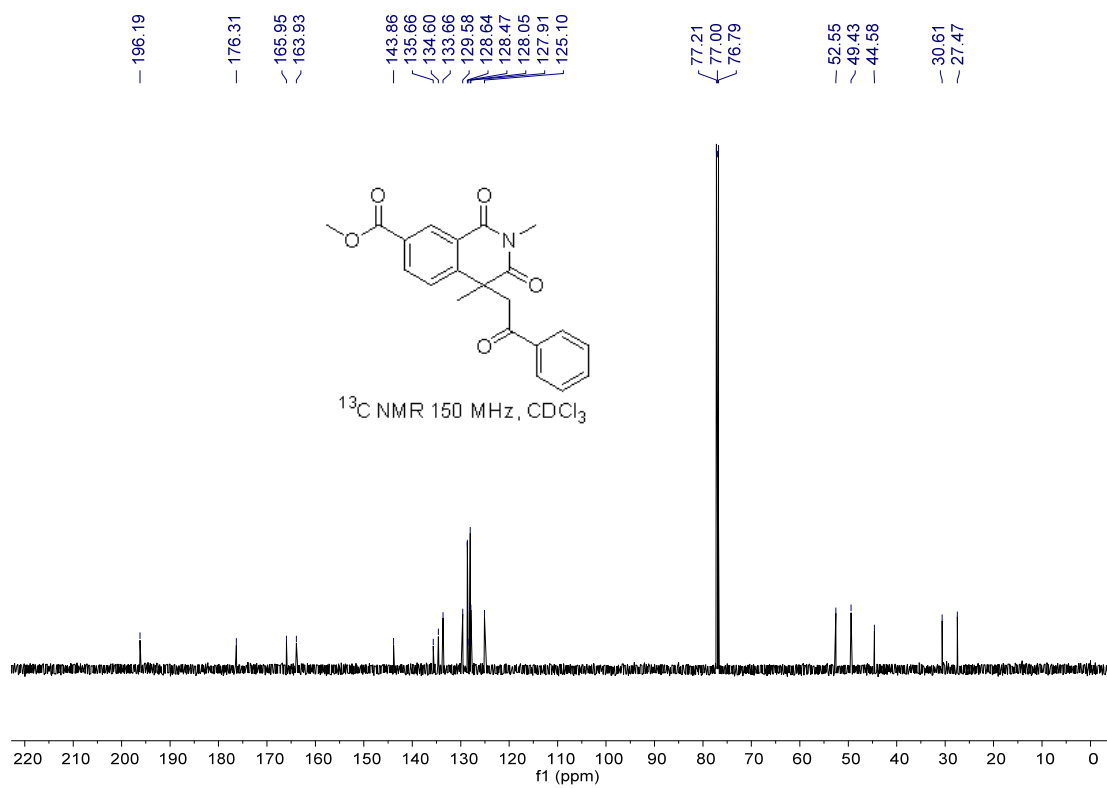
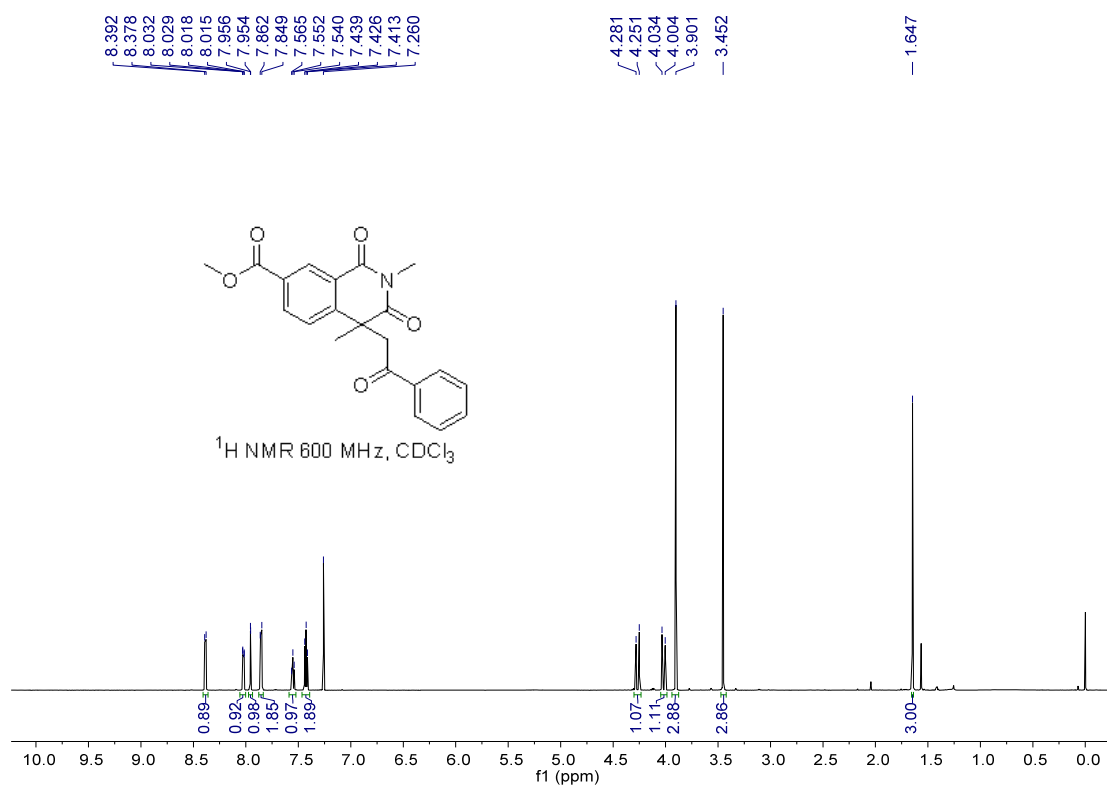




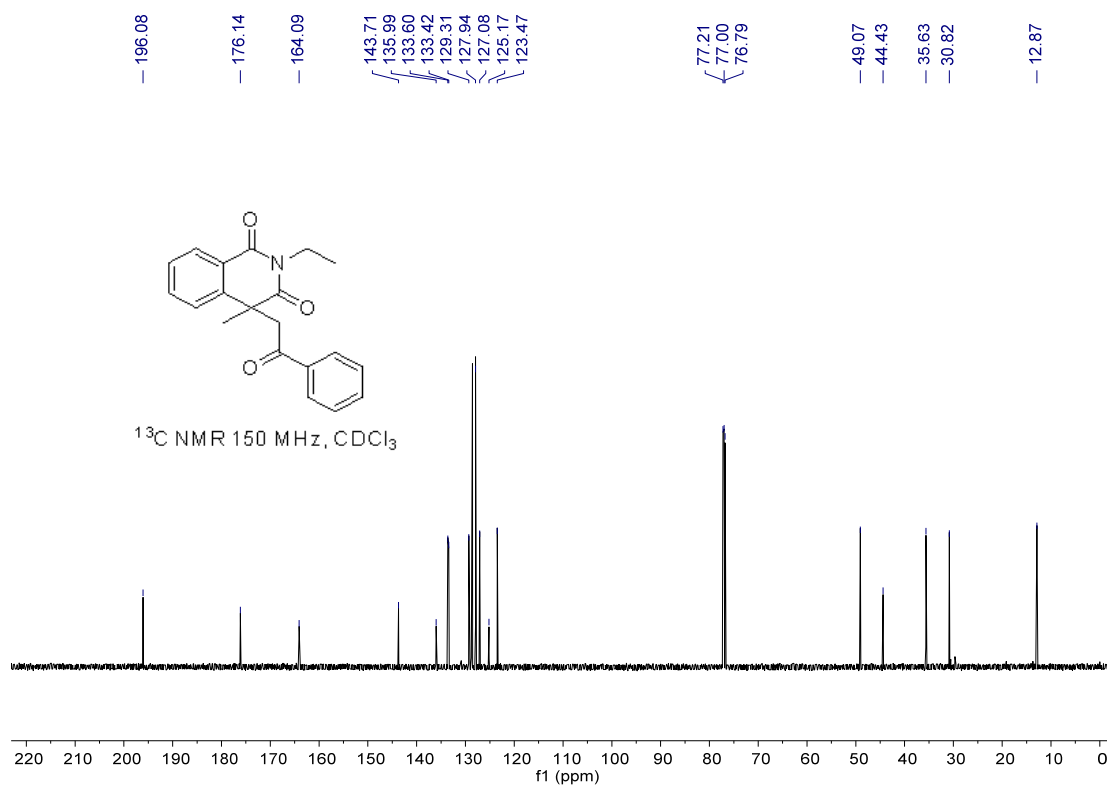
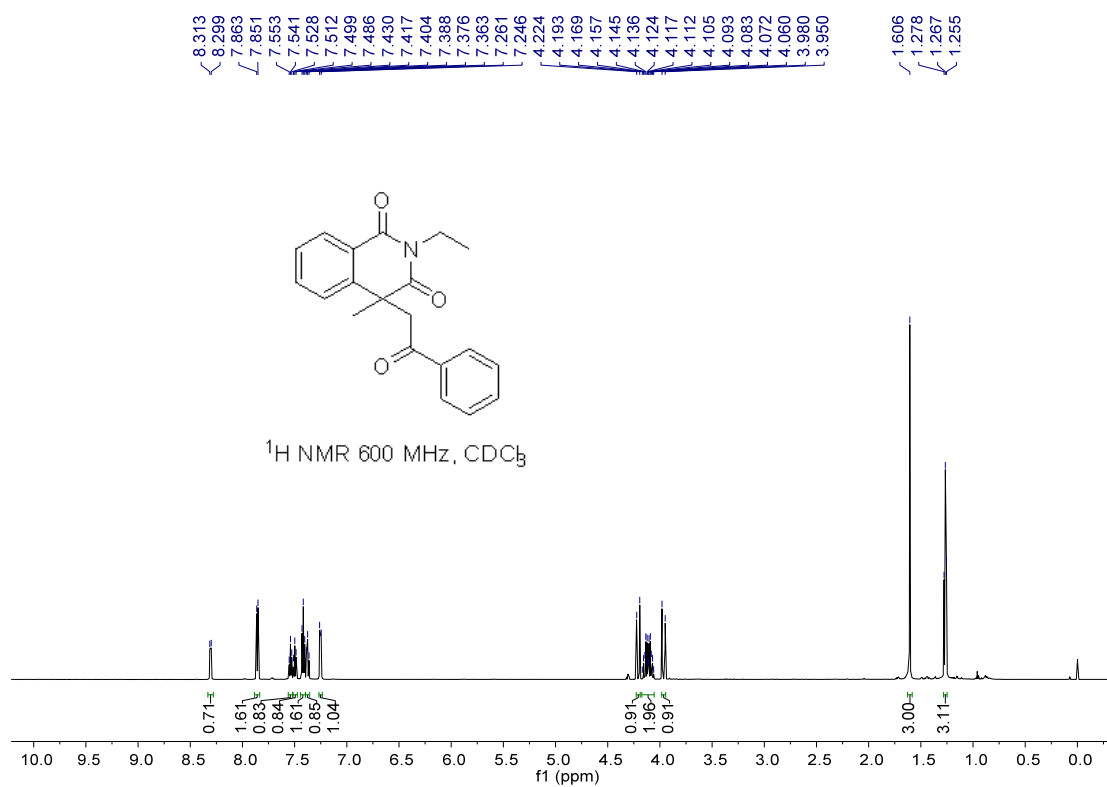
NMR copies of compound **4ja**:



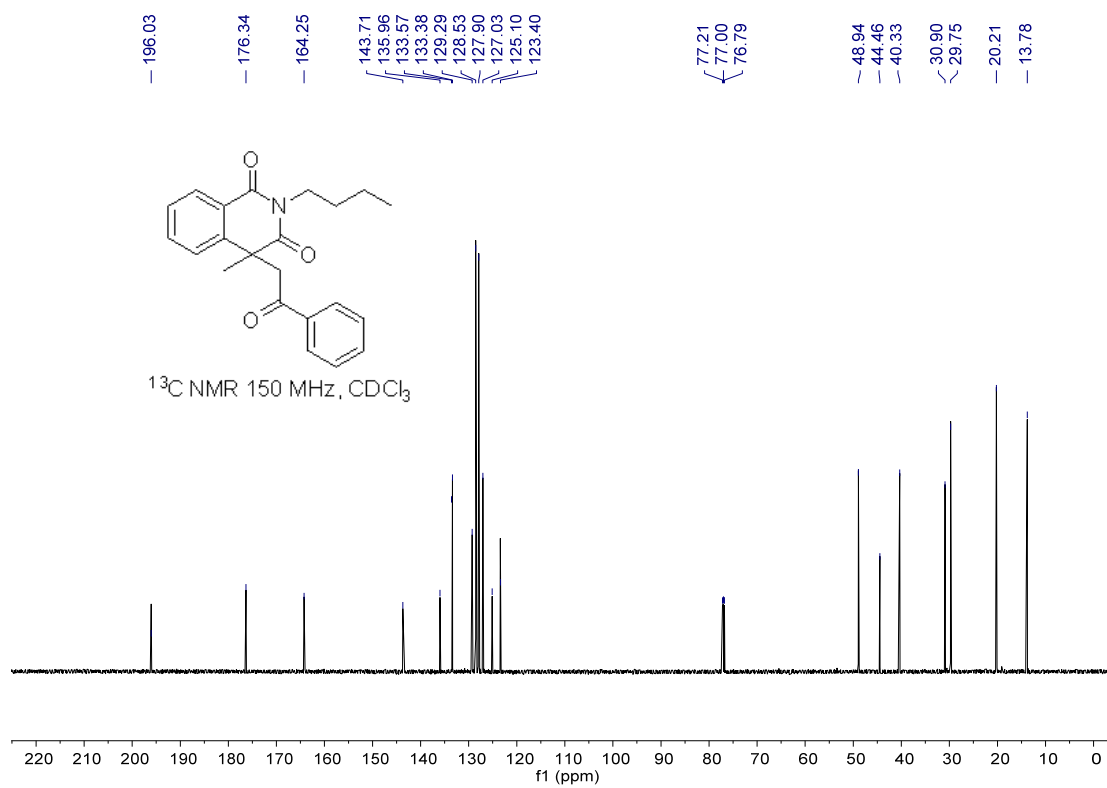
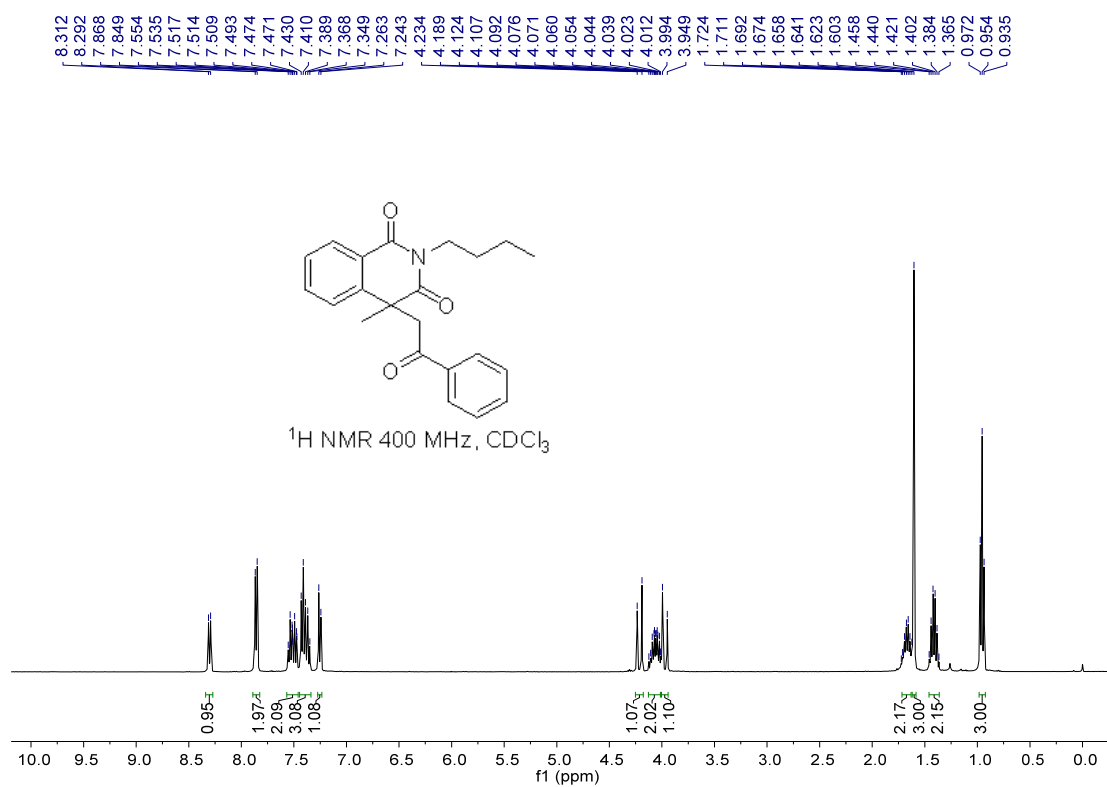
NMR copies of compound **4ka**:



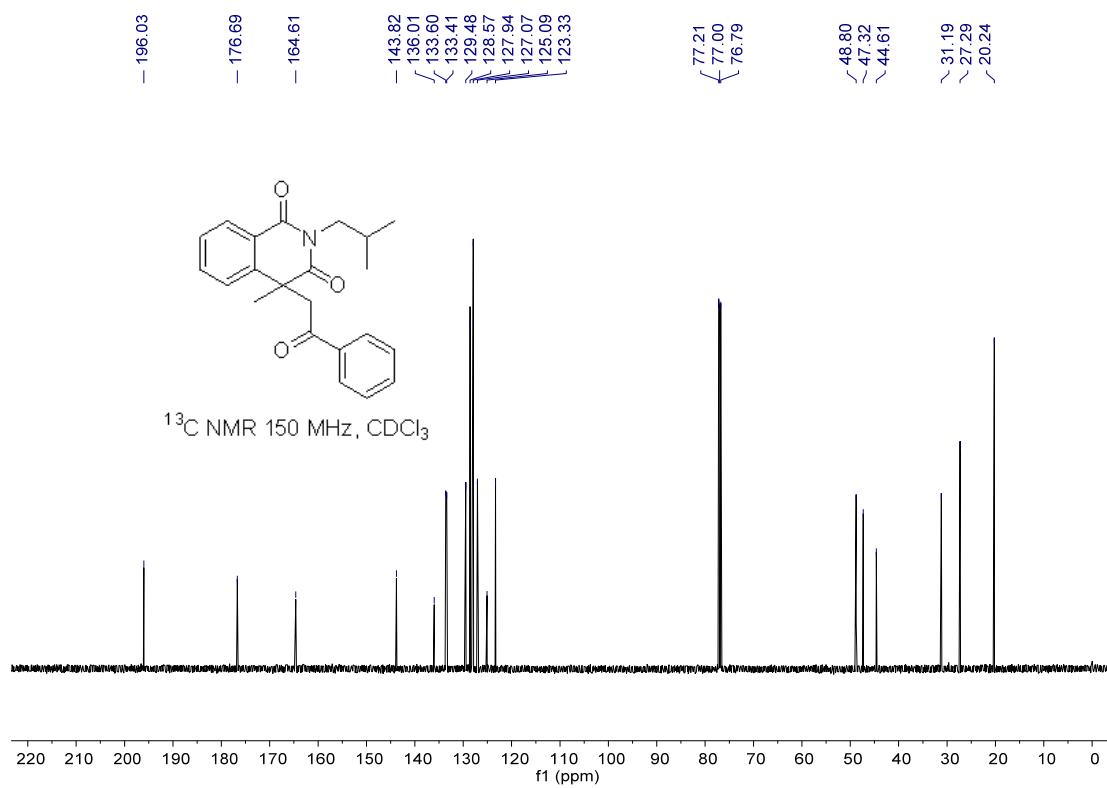
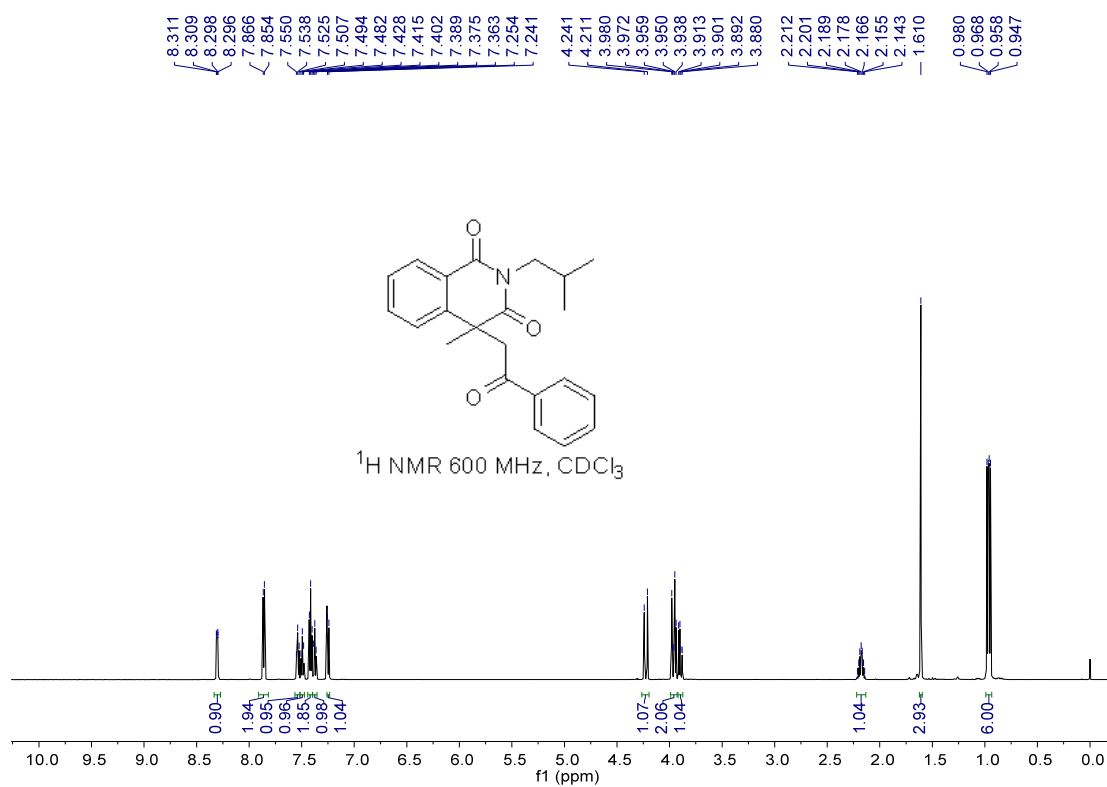
NMR copies of compound **41a**:



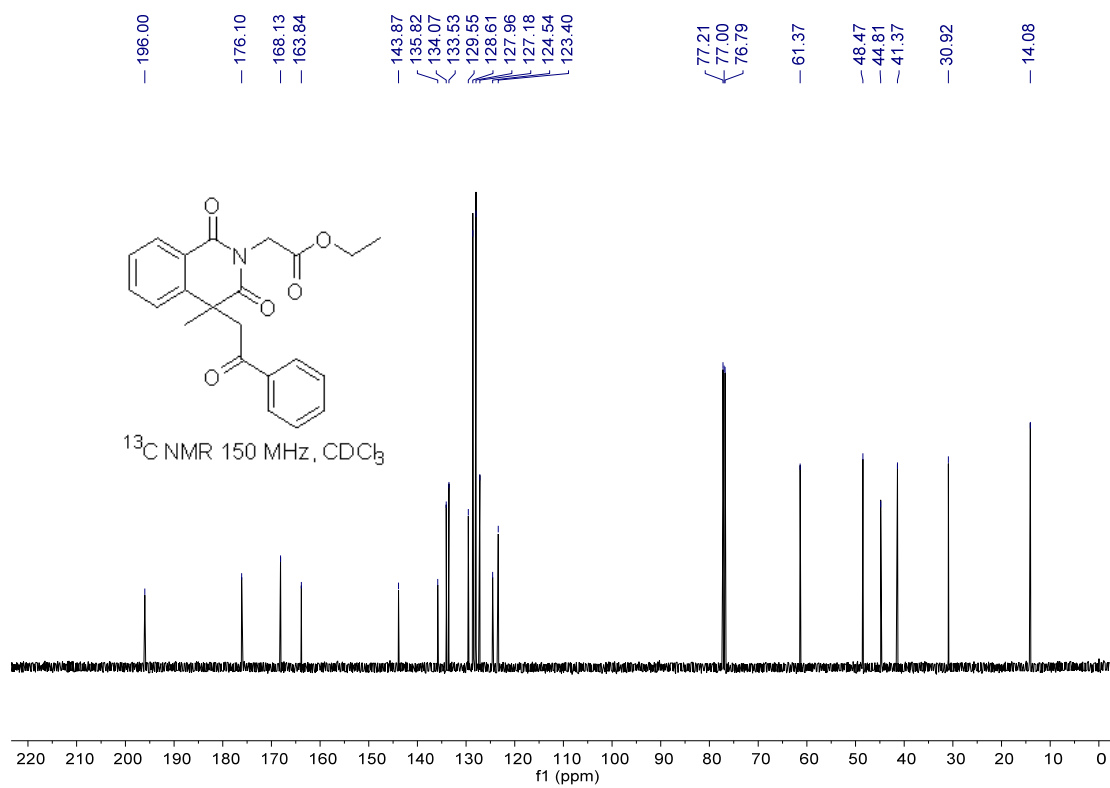
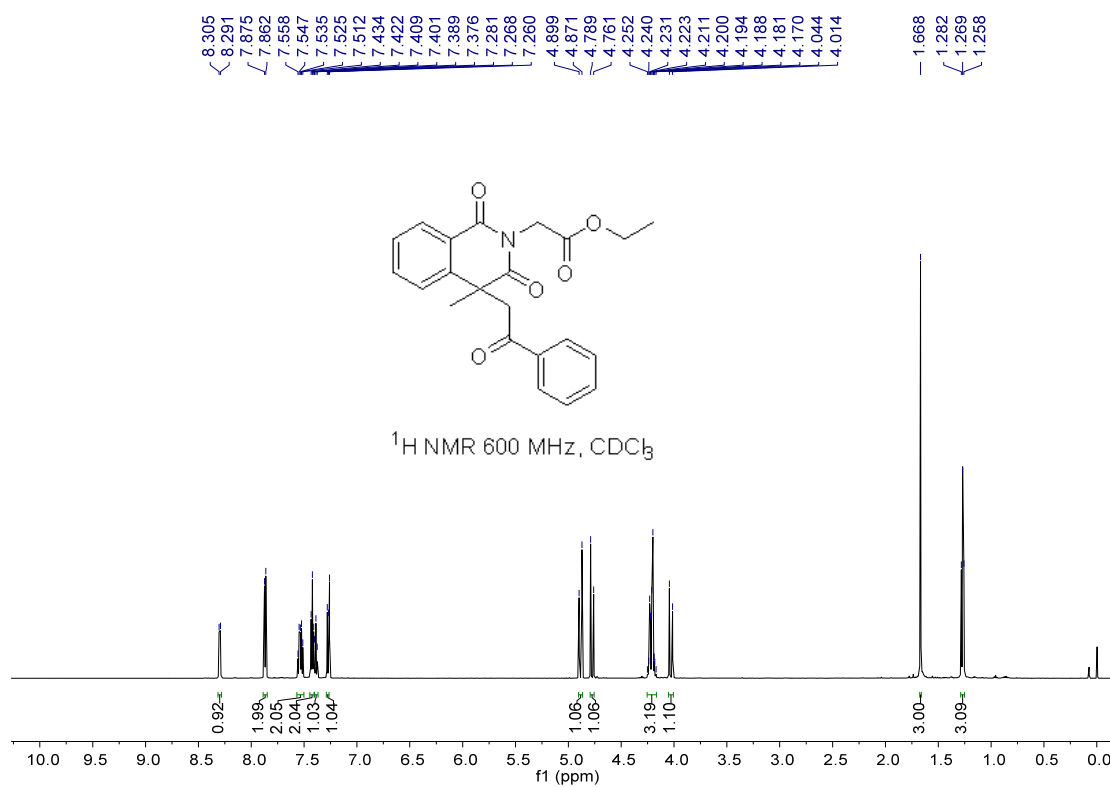
NMR copies of compound **4ma**:



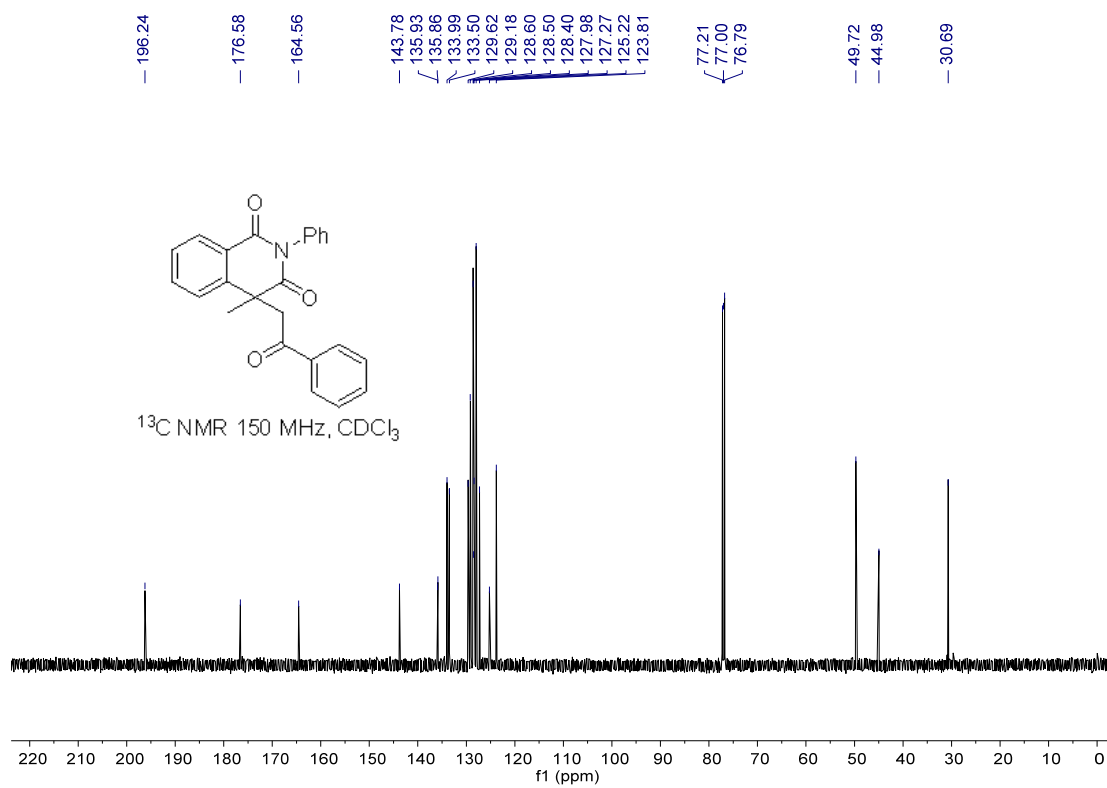
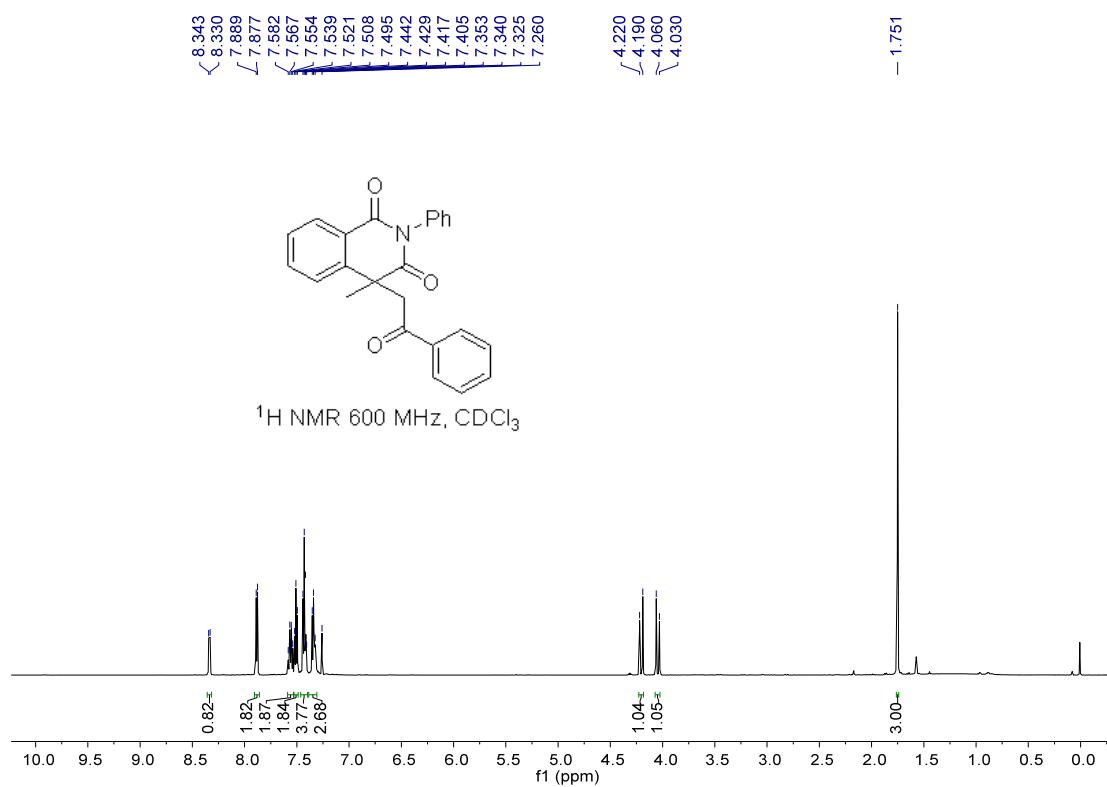
NMR copies of compound **4na**:



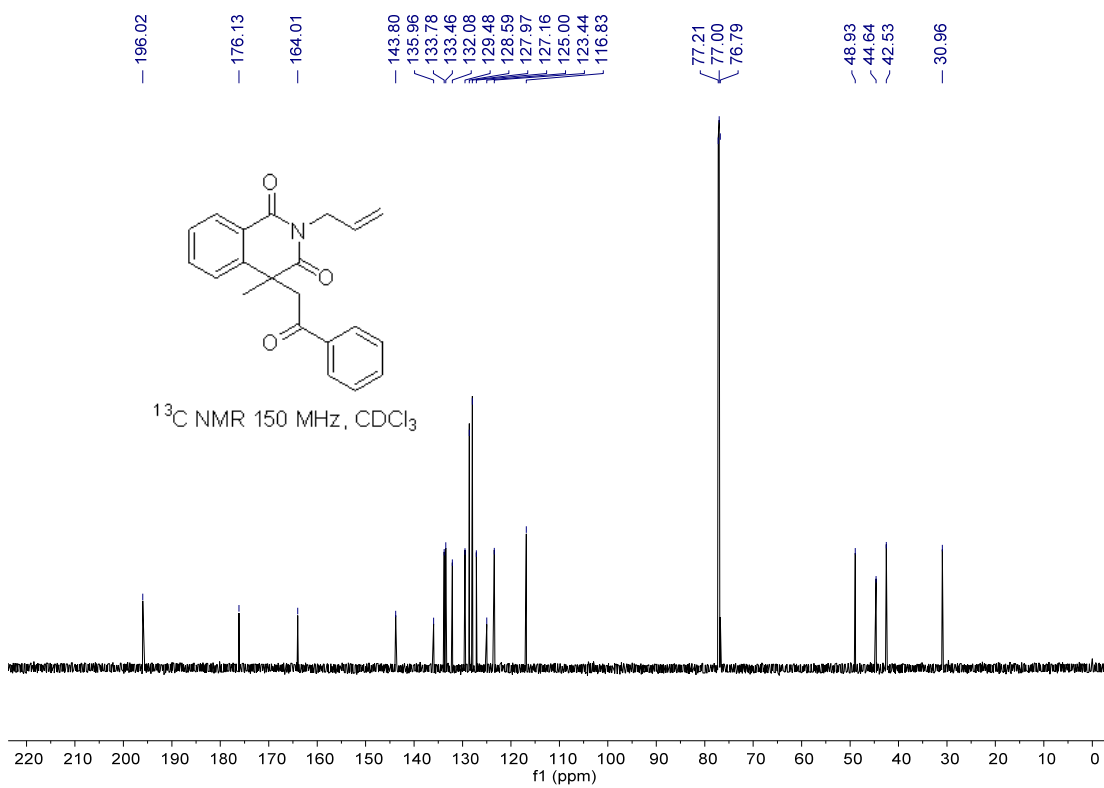
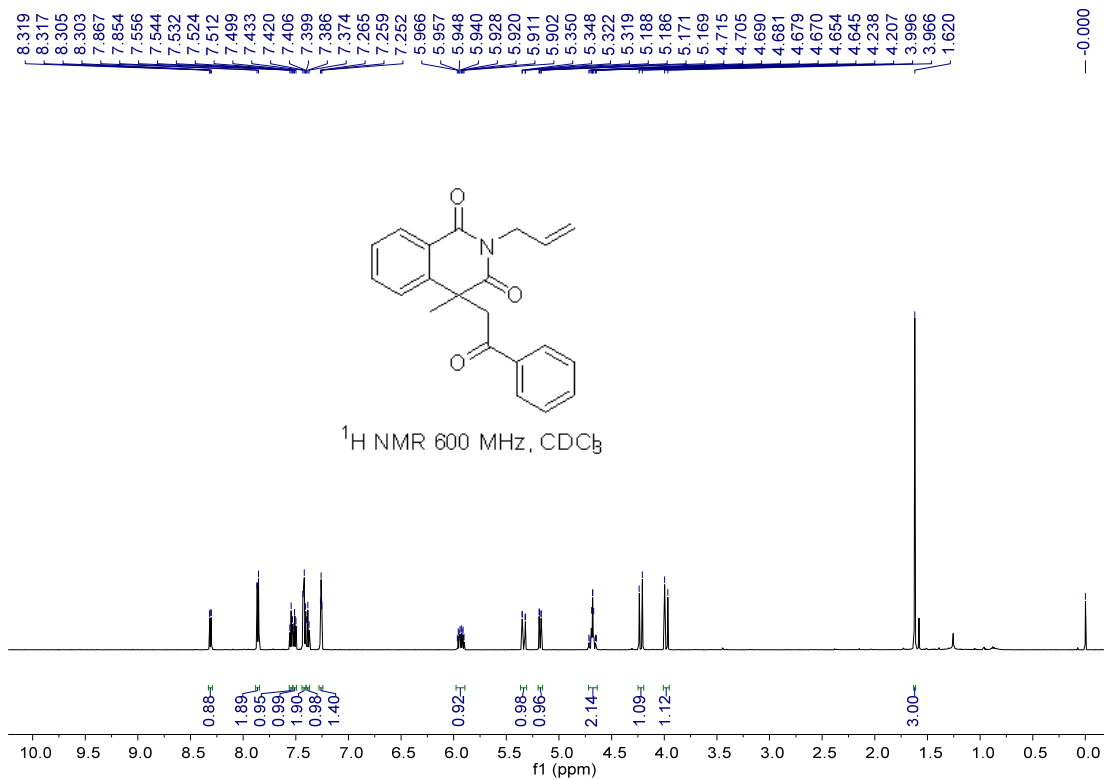
NMR copies of compound **40a**:



NMR copies of compound **4pa**:

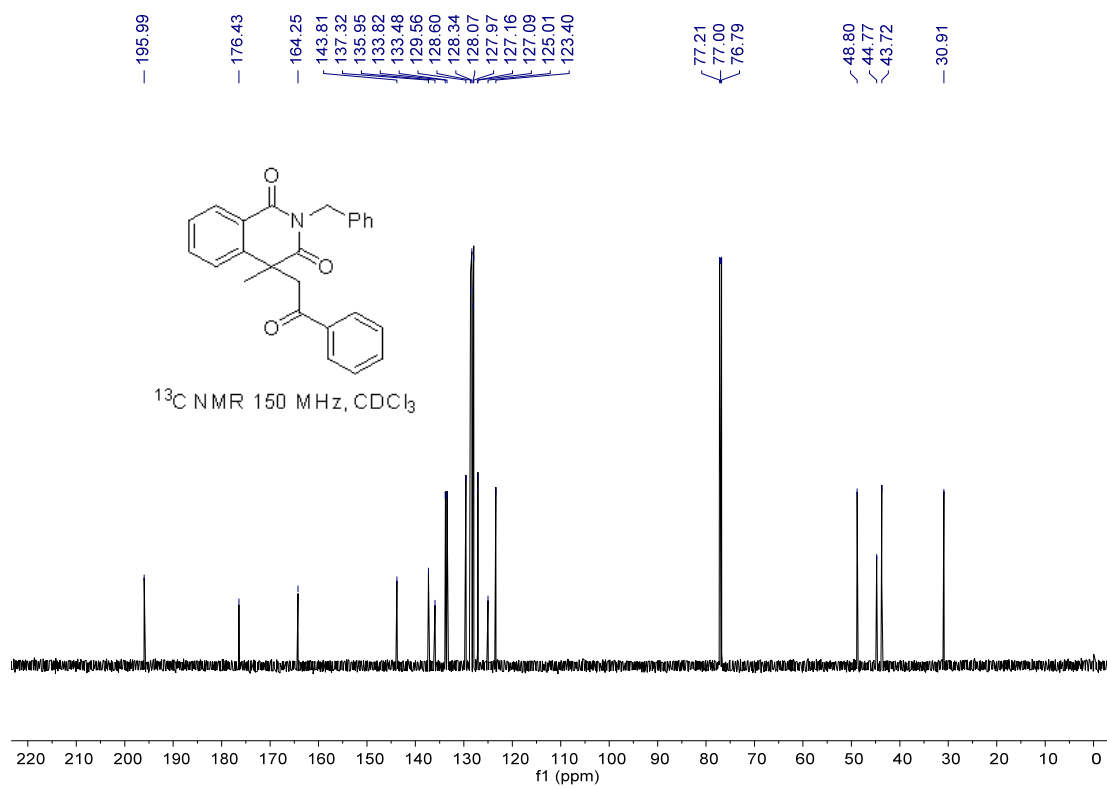
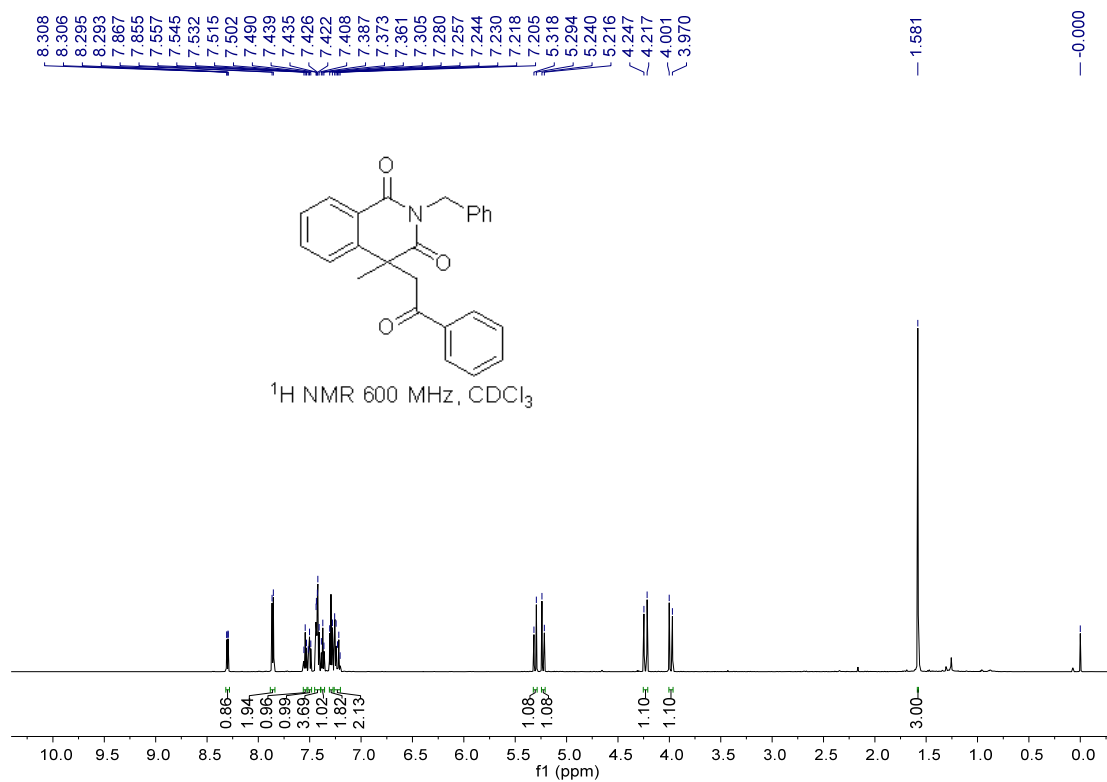


NMR copies of compound **4qa**:

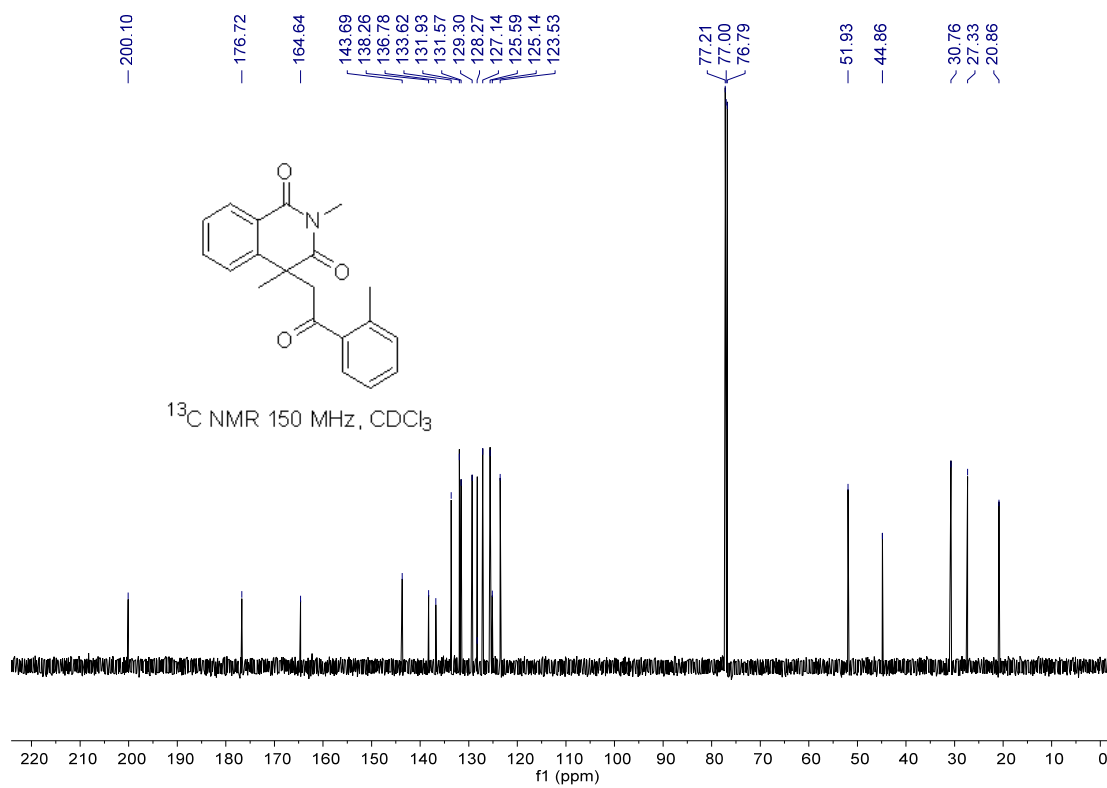
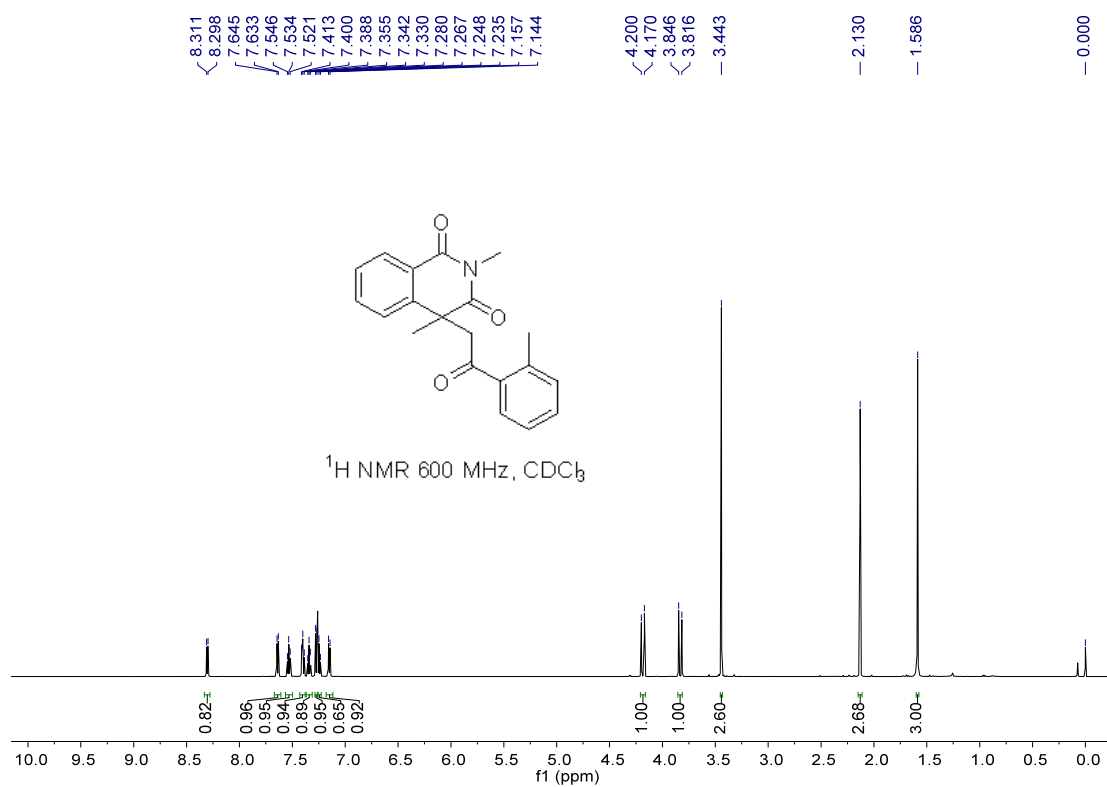




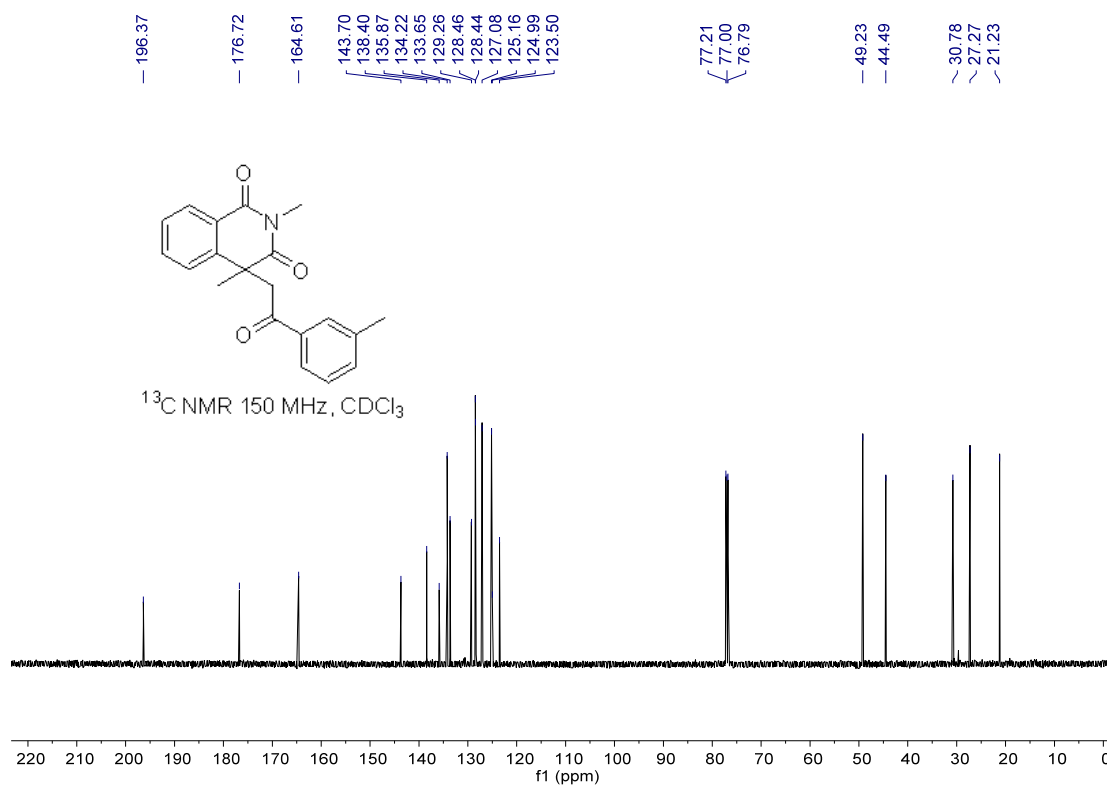
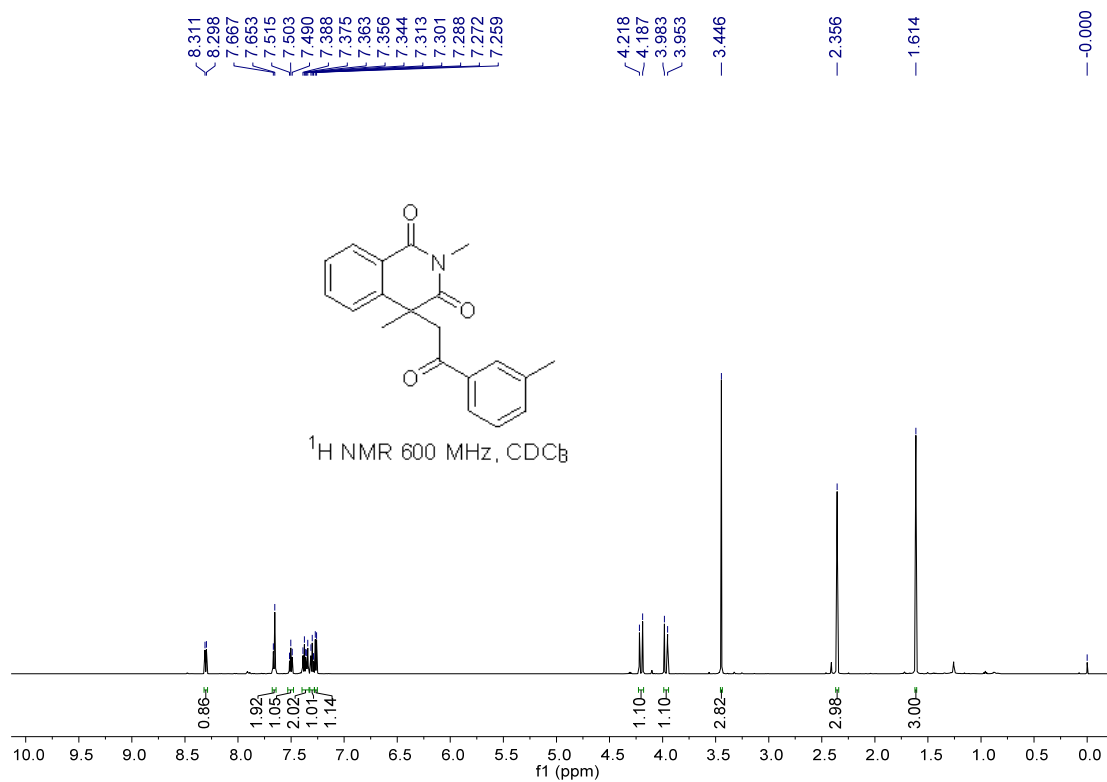
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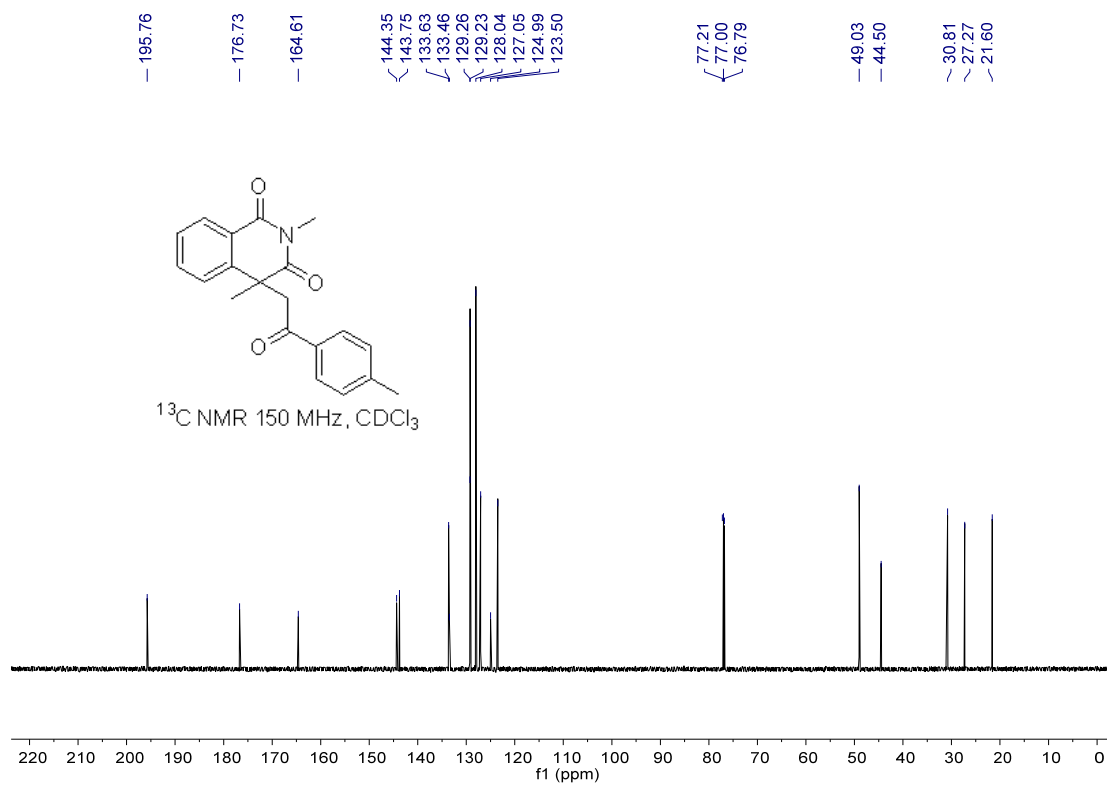
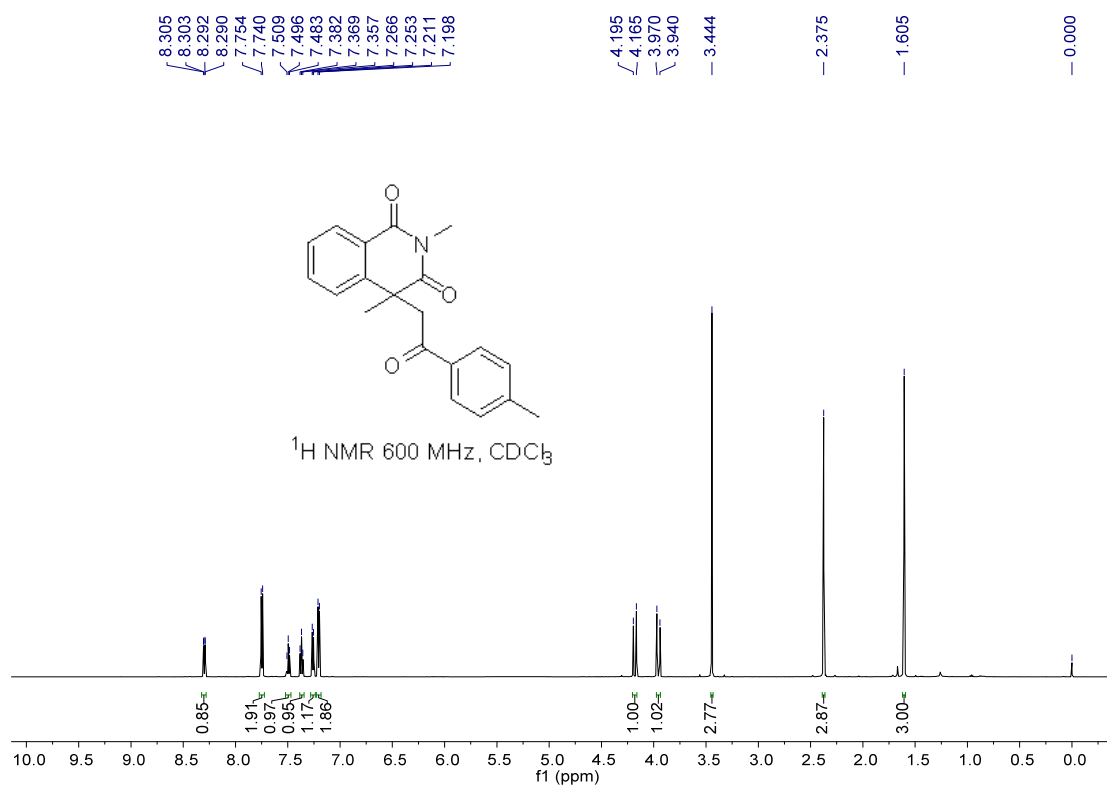
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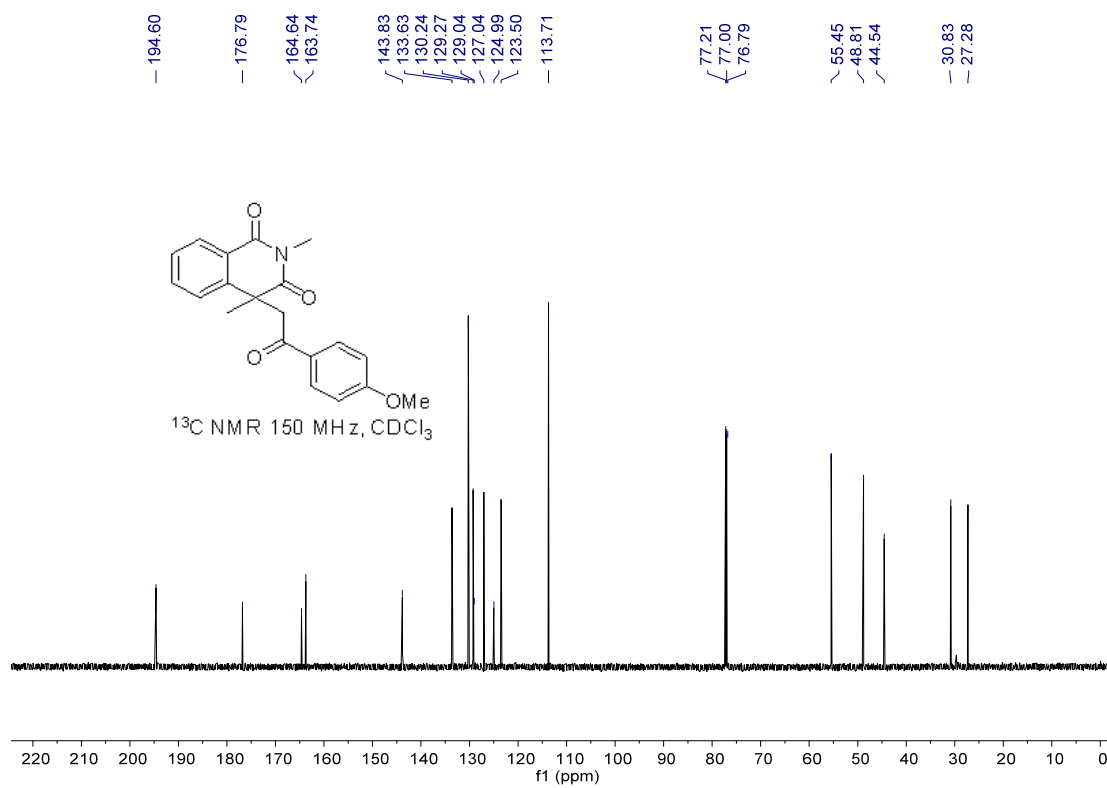
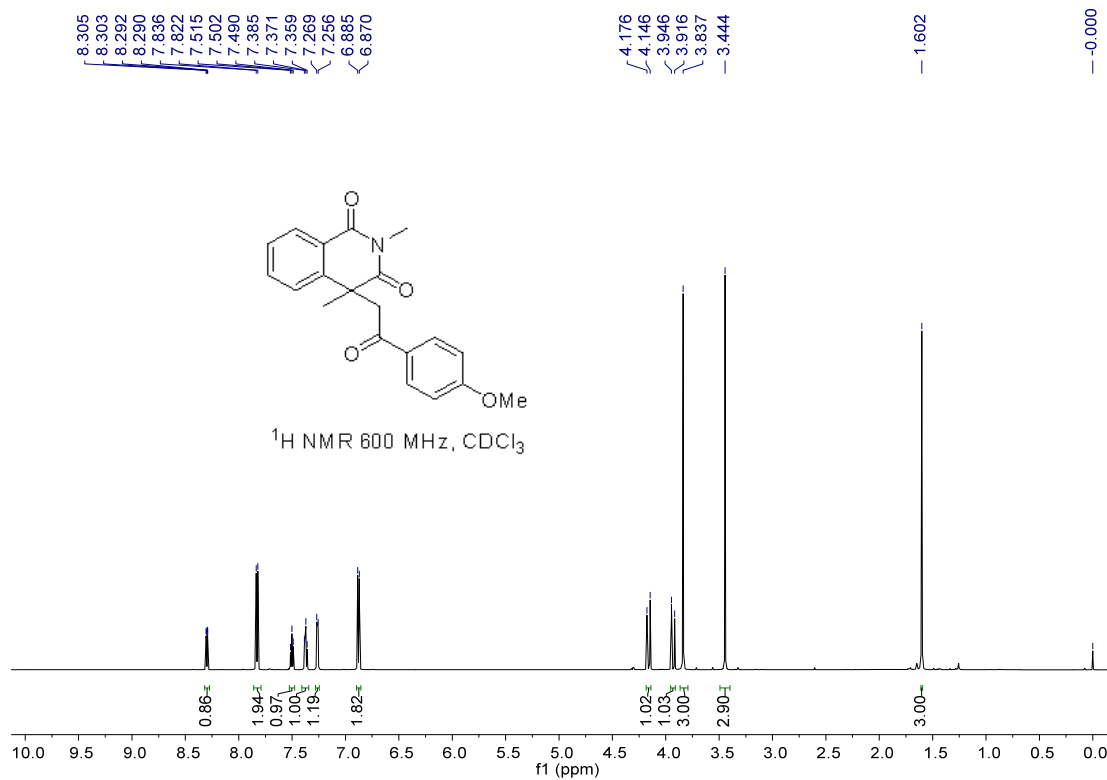
NMR copies of compound **4ac**:



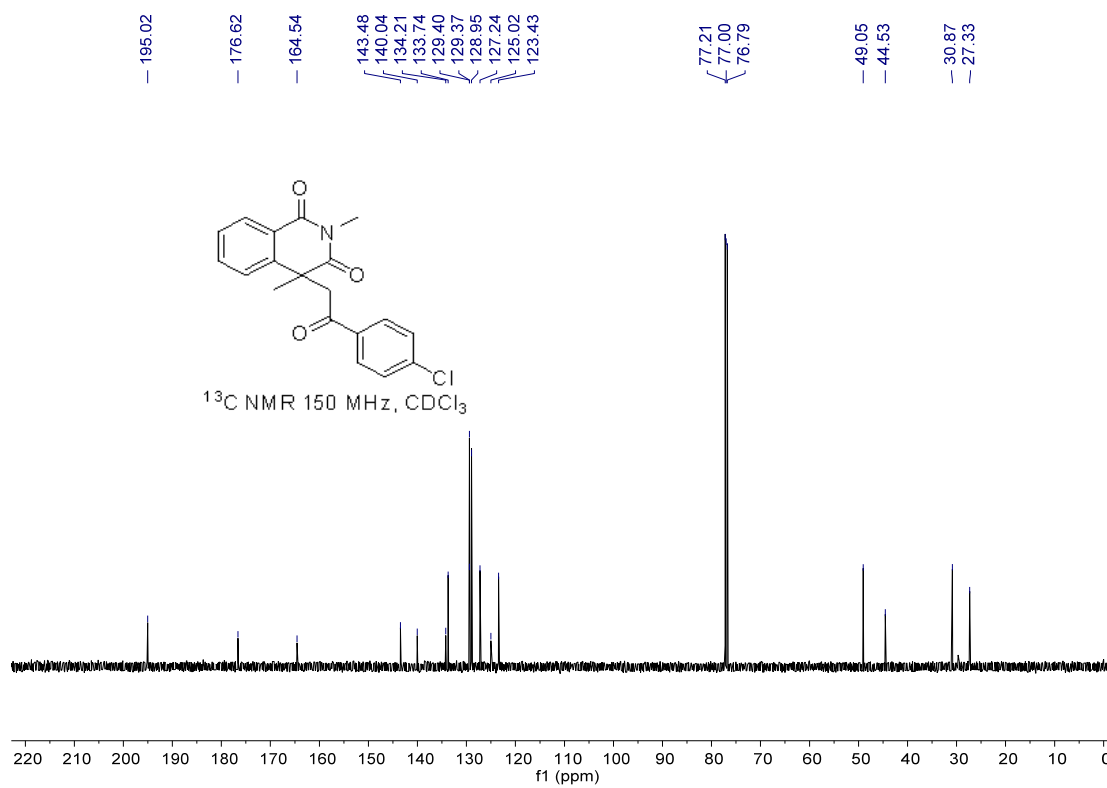
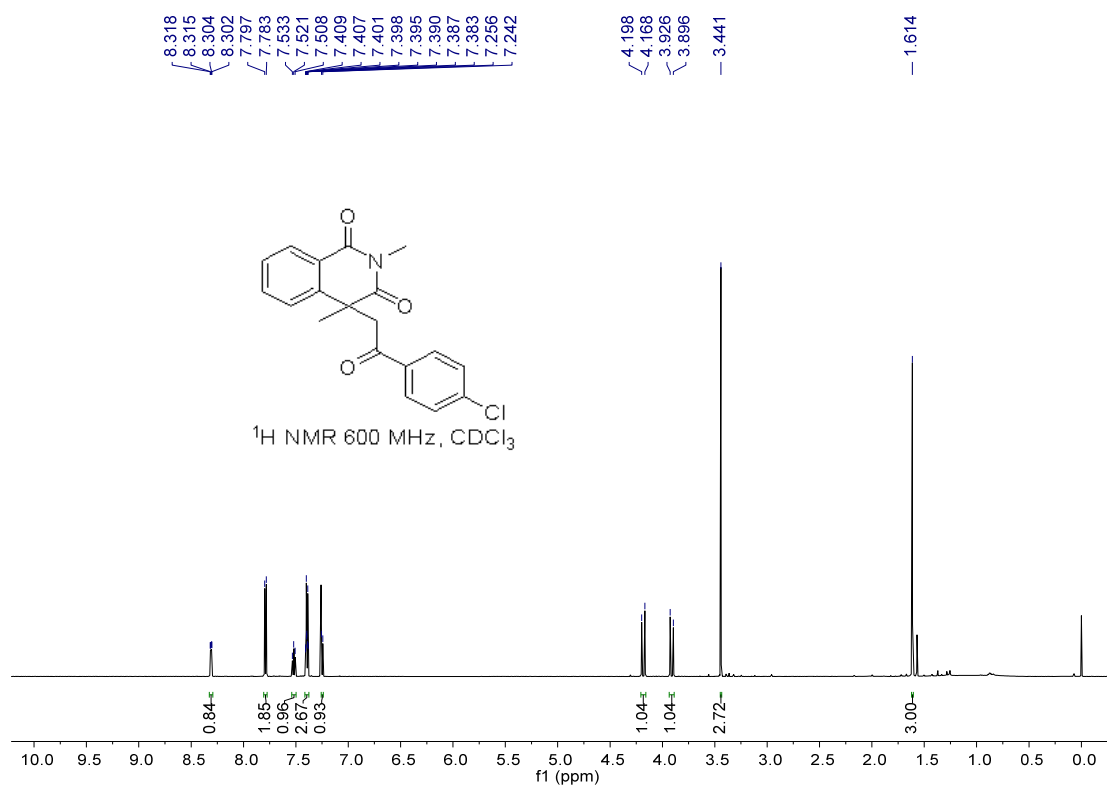
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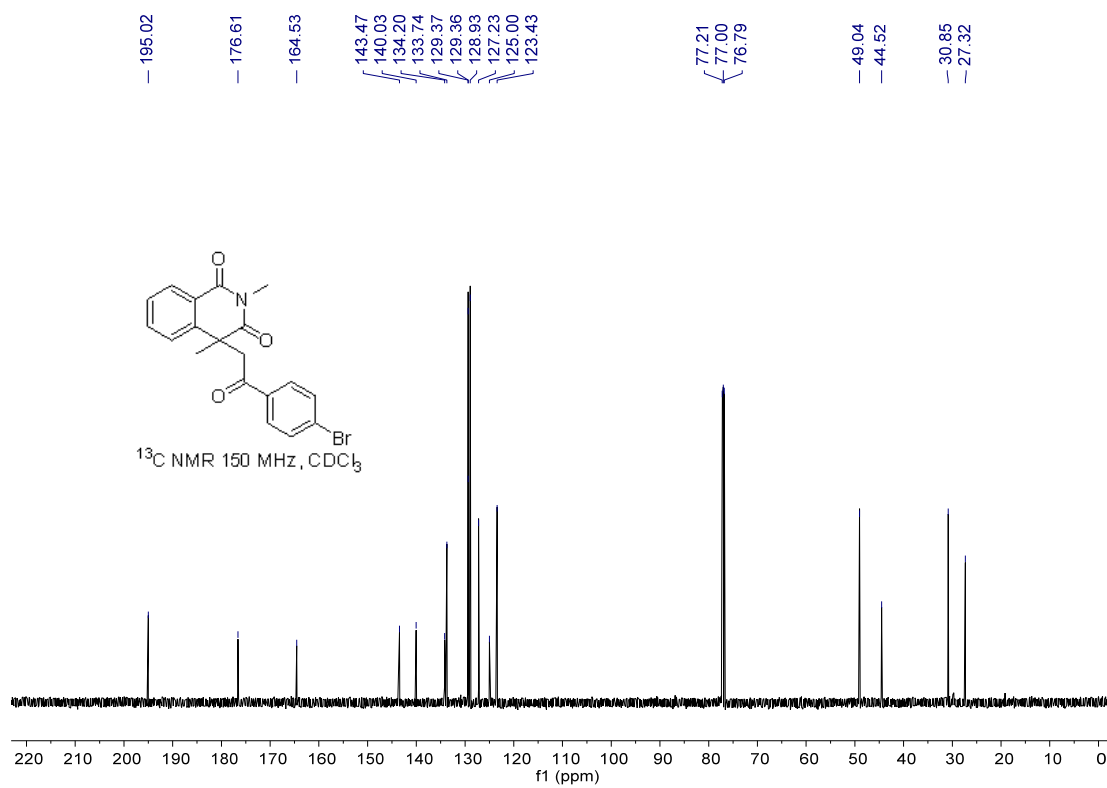
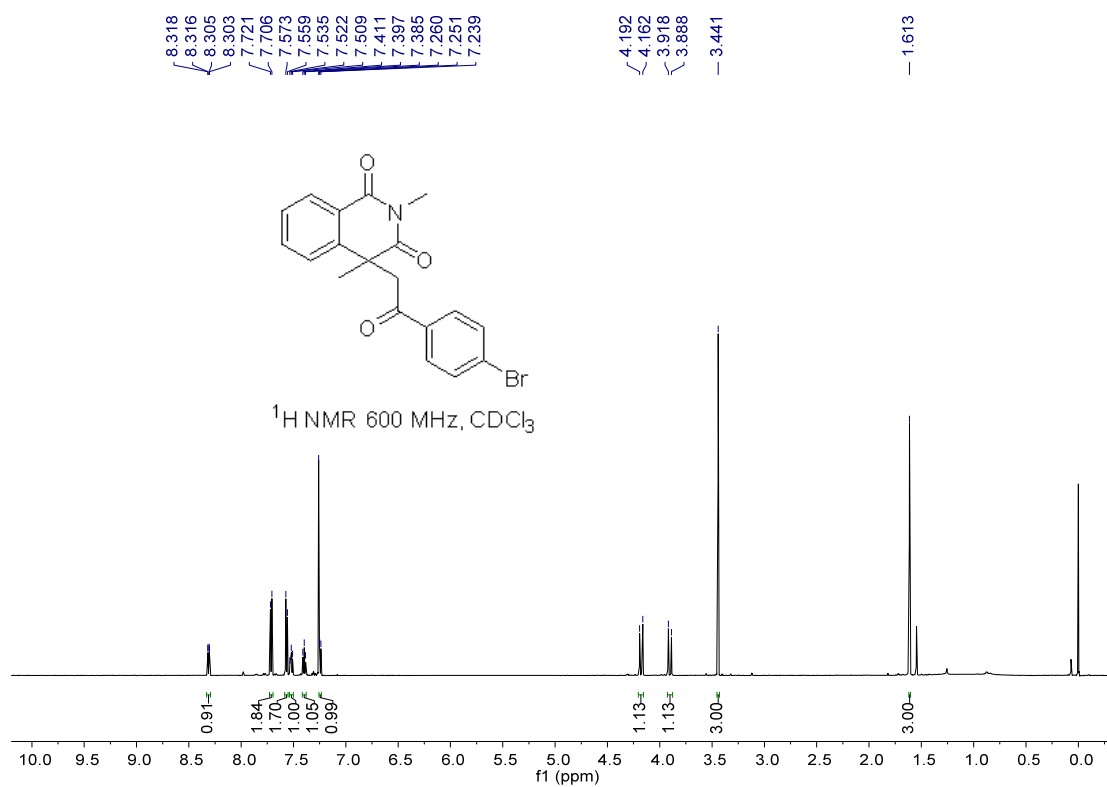
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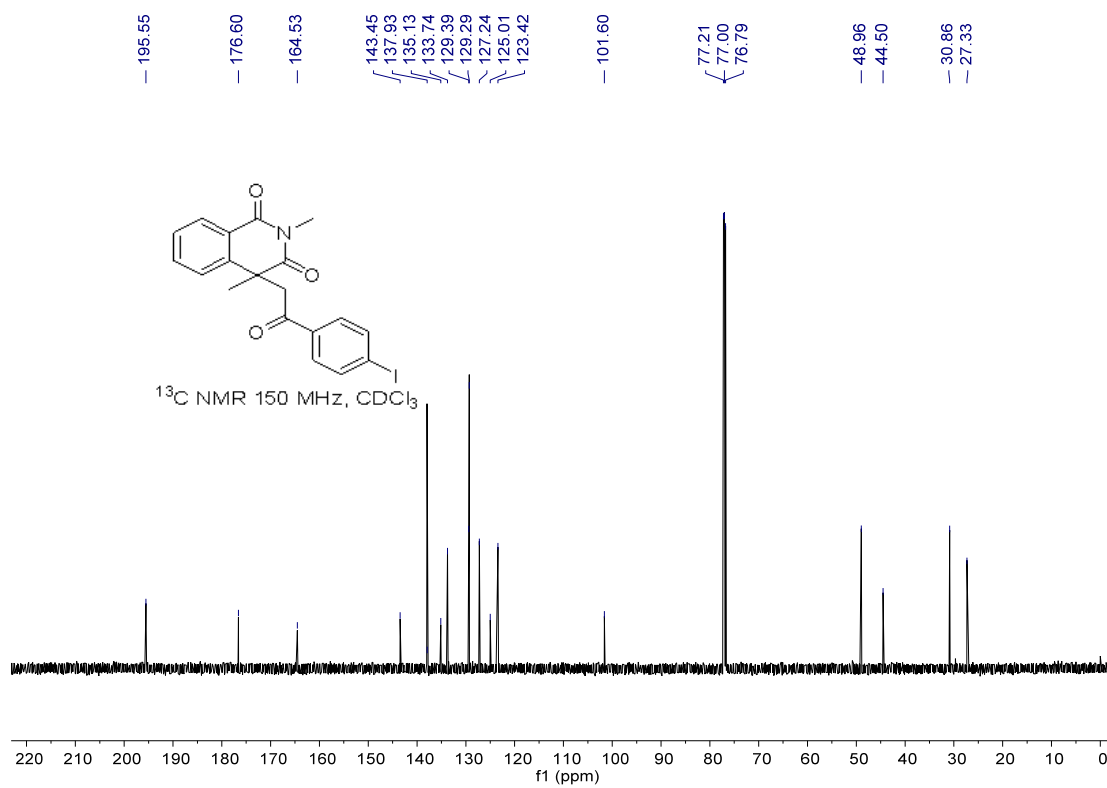
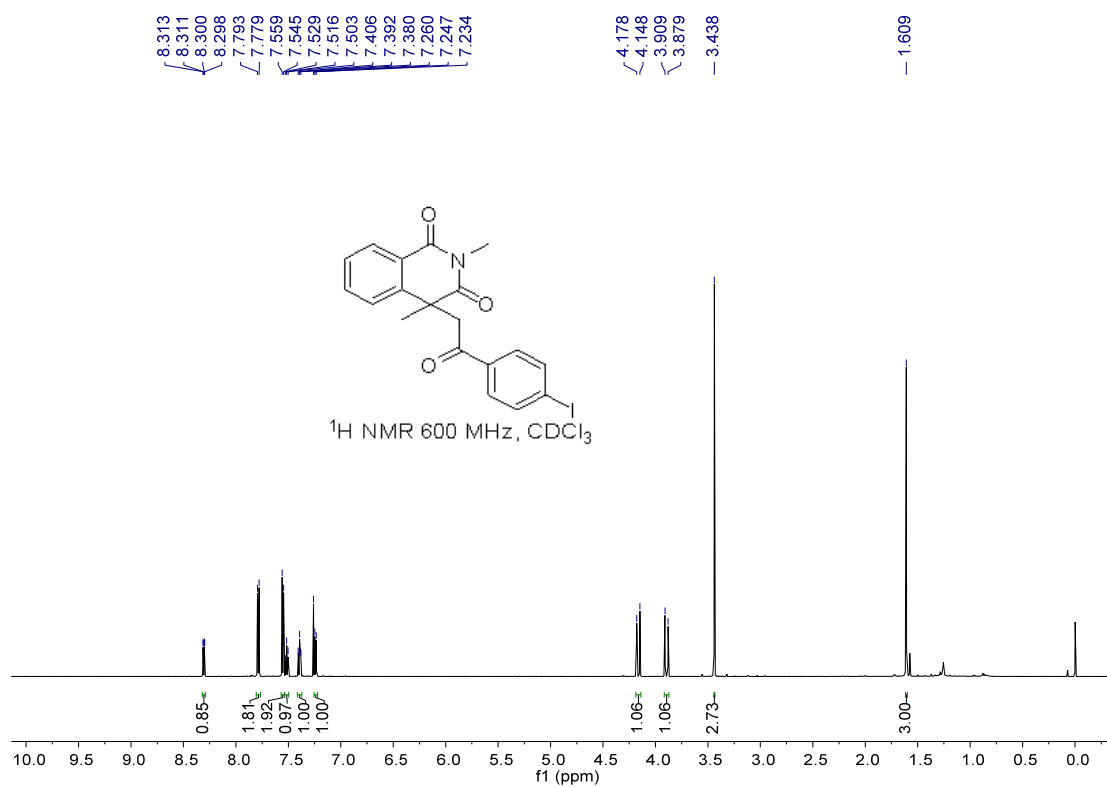
NMR copies of compound **4af**:



NMR copies of compound **4ag**:

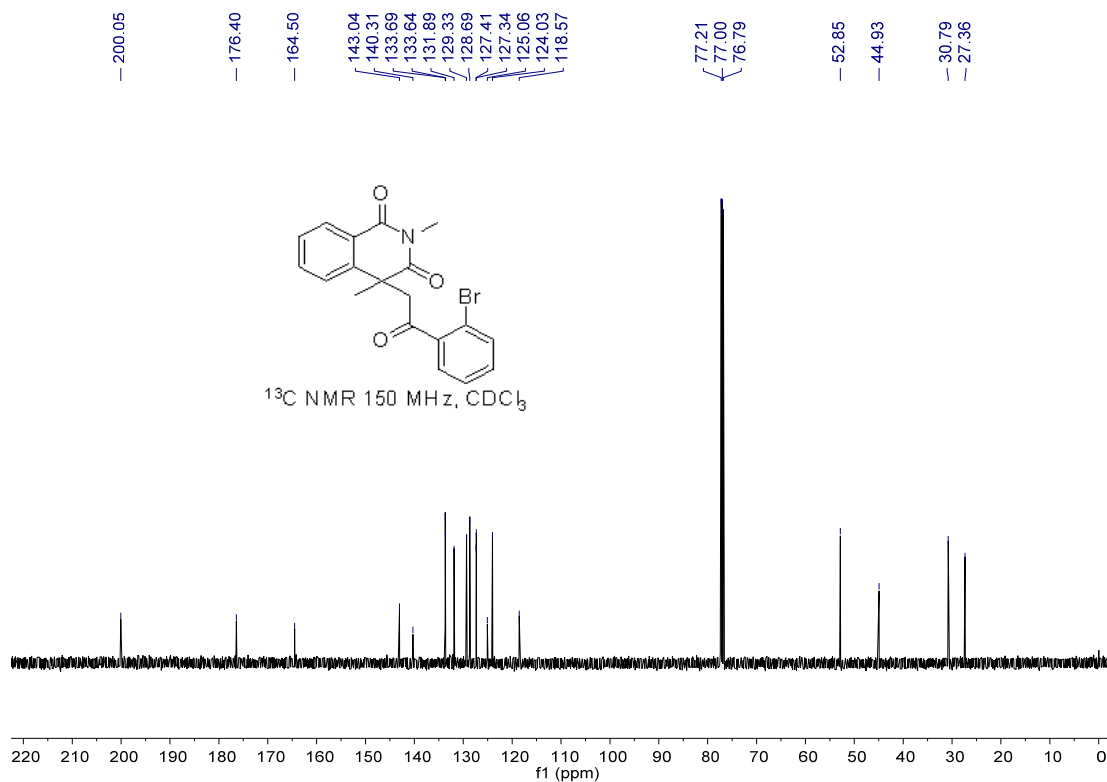
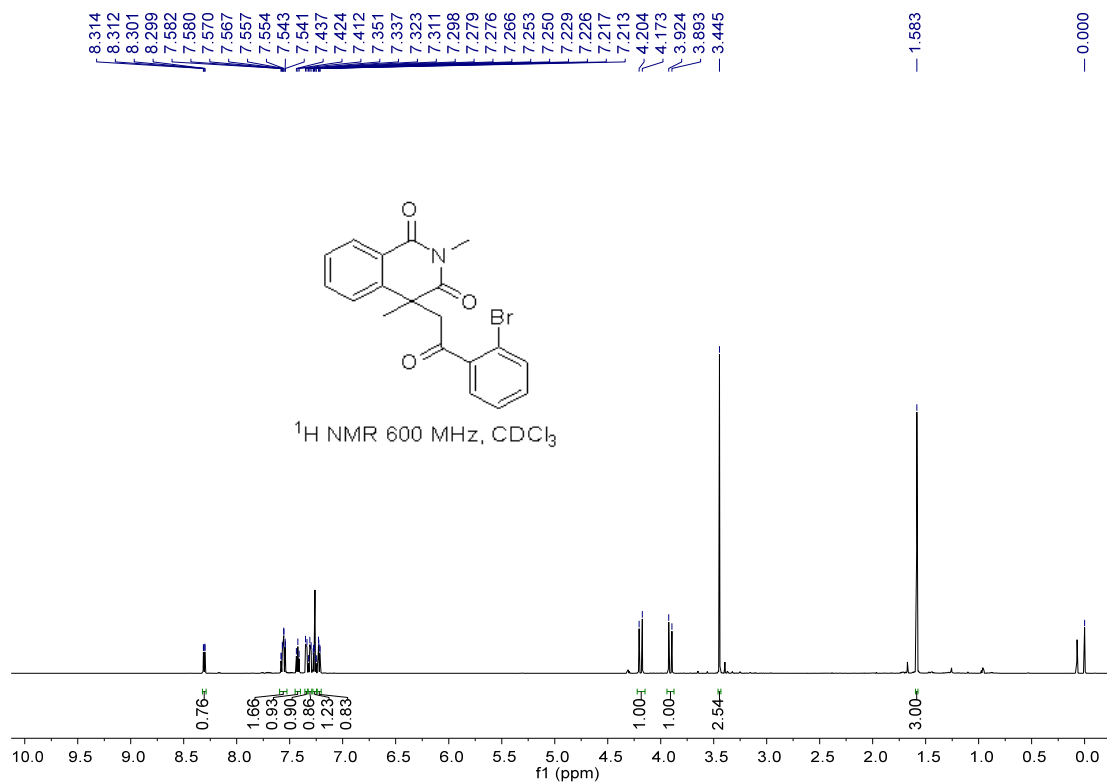


NMR copies of compound **4ah**:

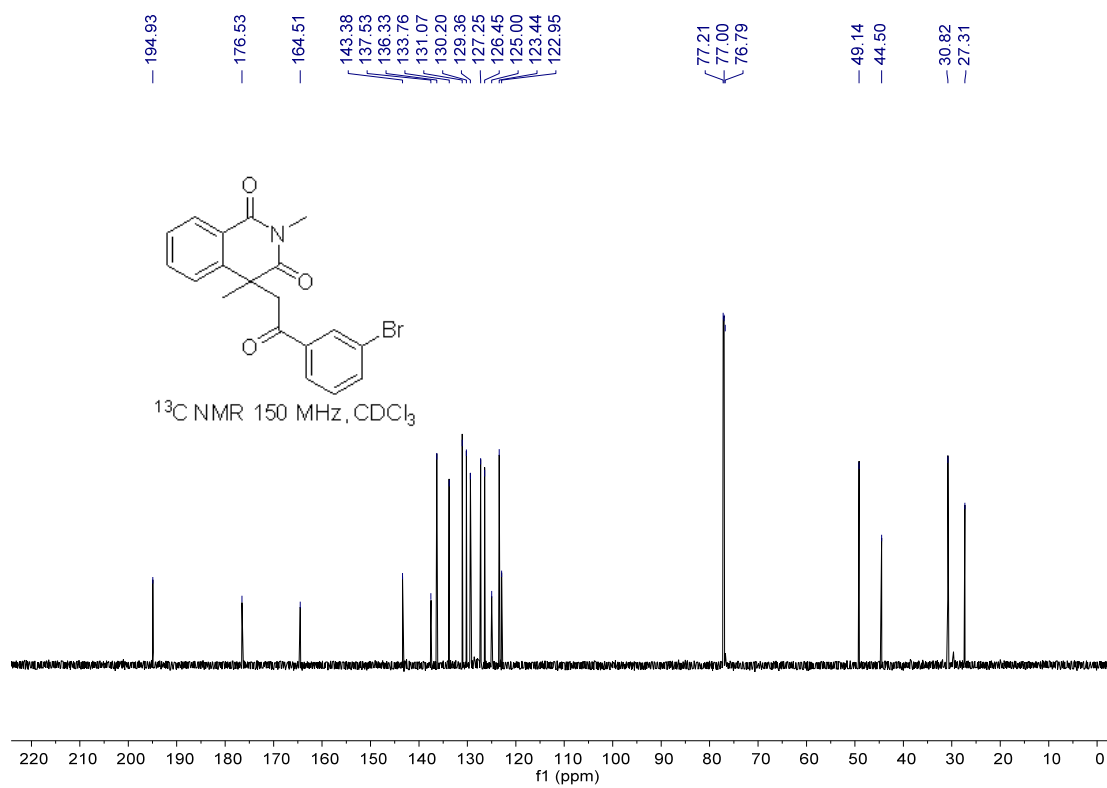
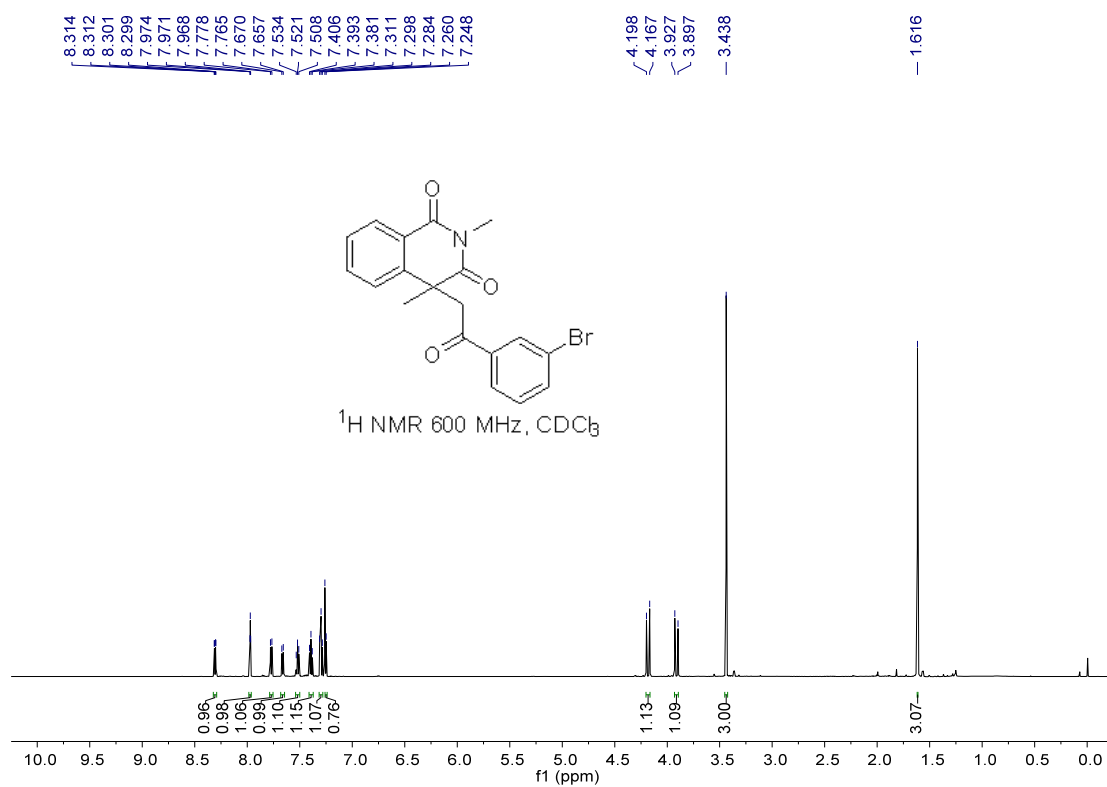




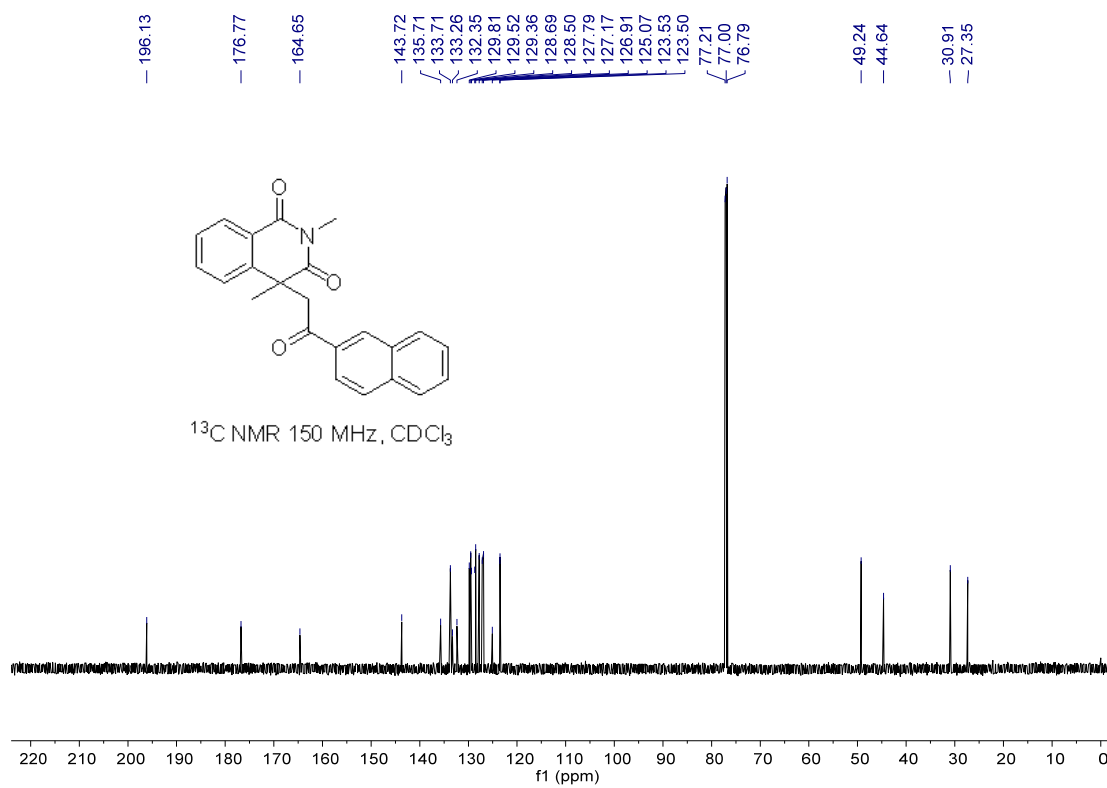
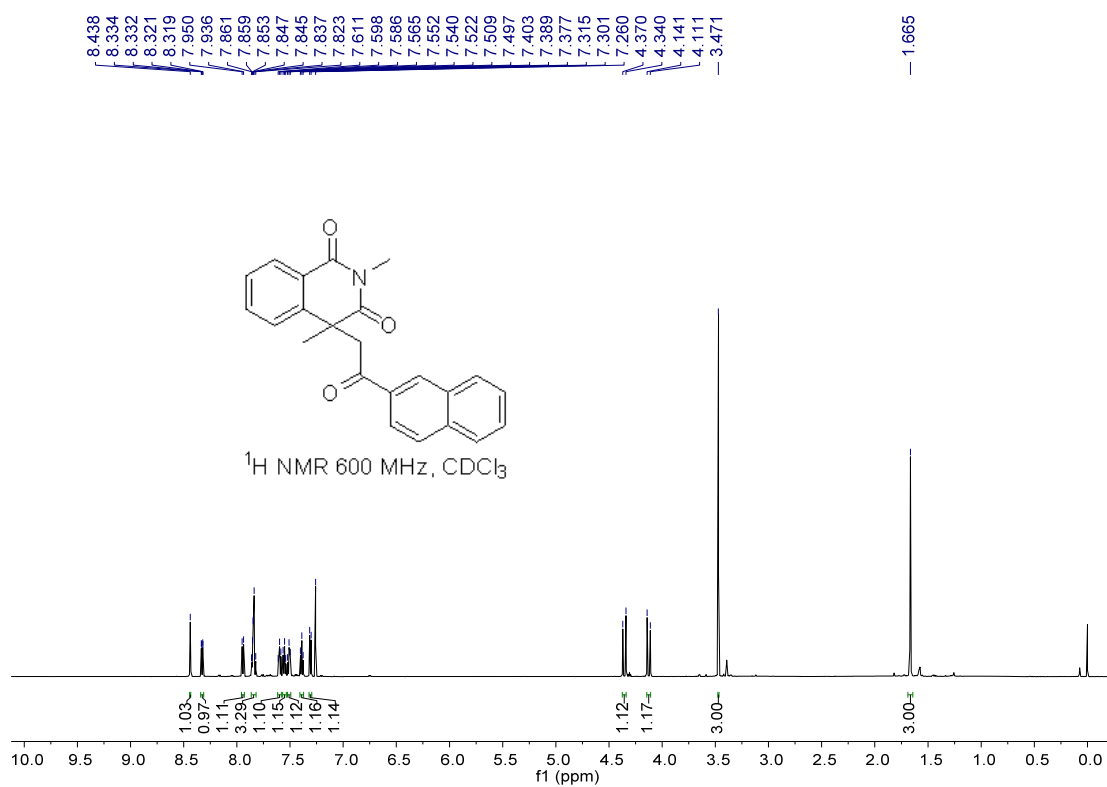
NMR copies of compound **4ai**:



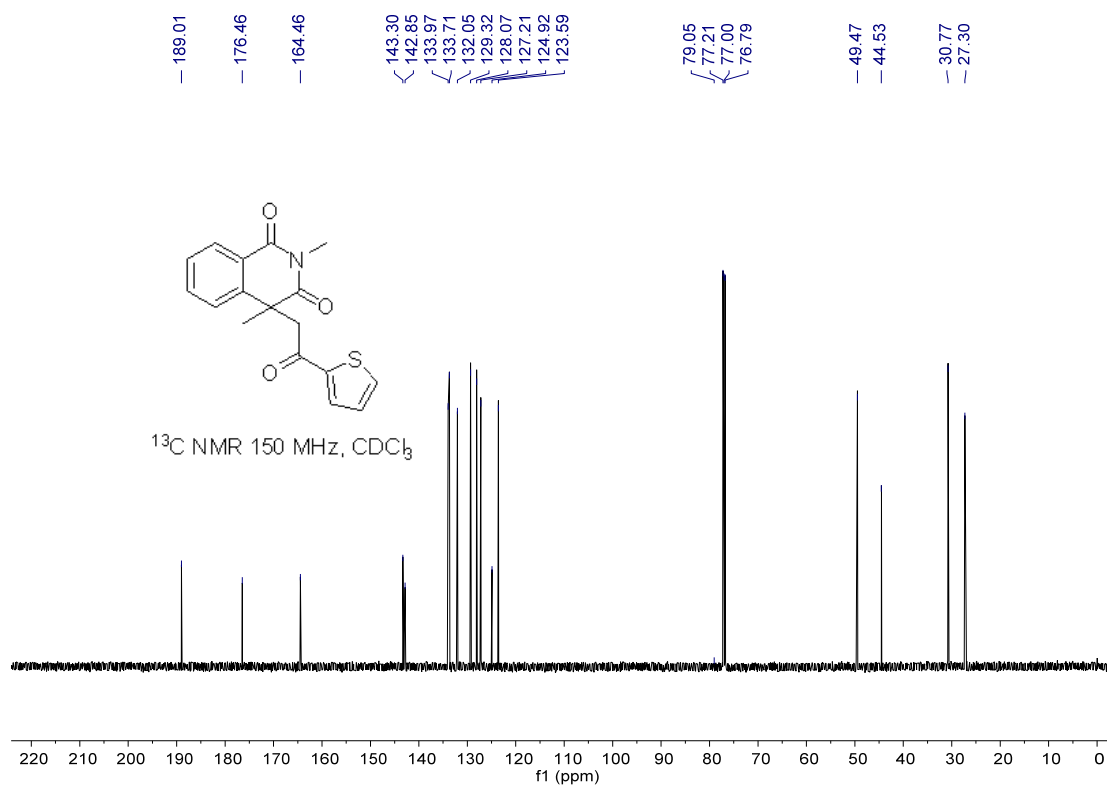
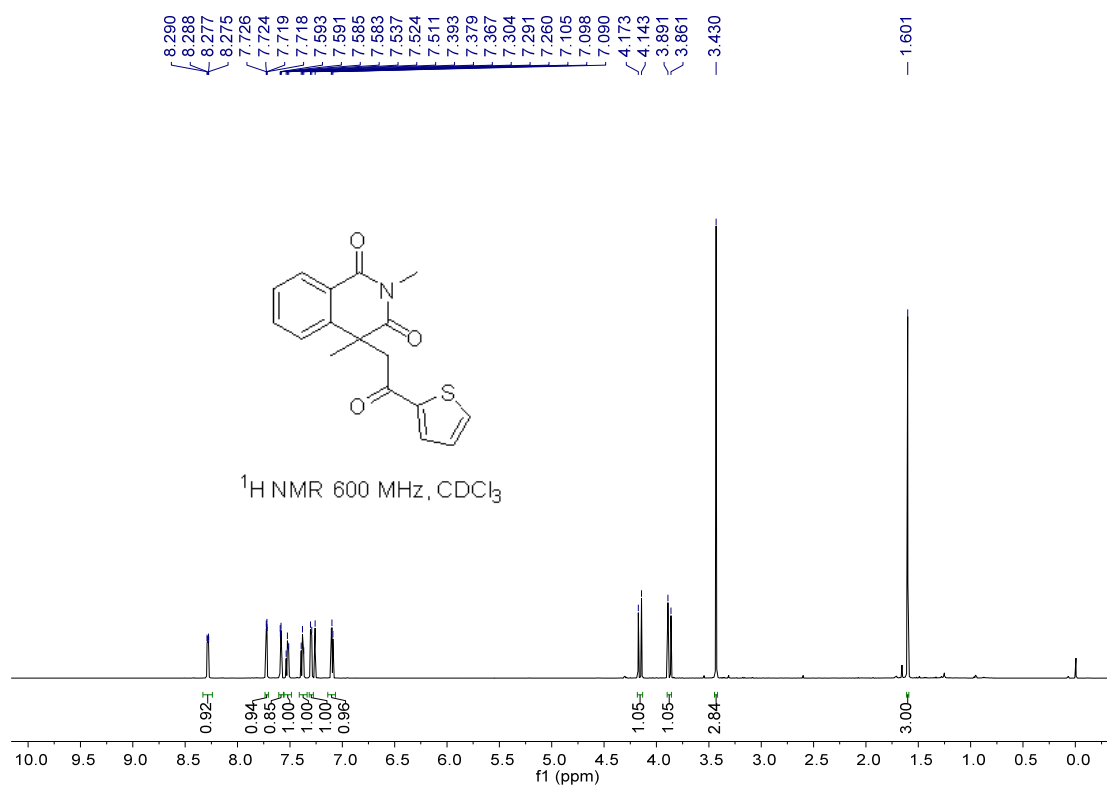
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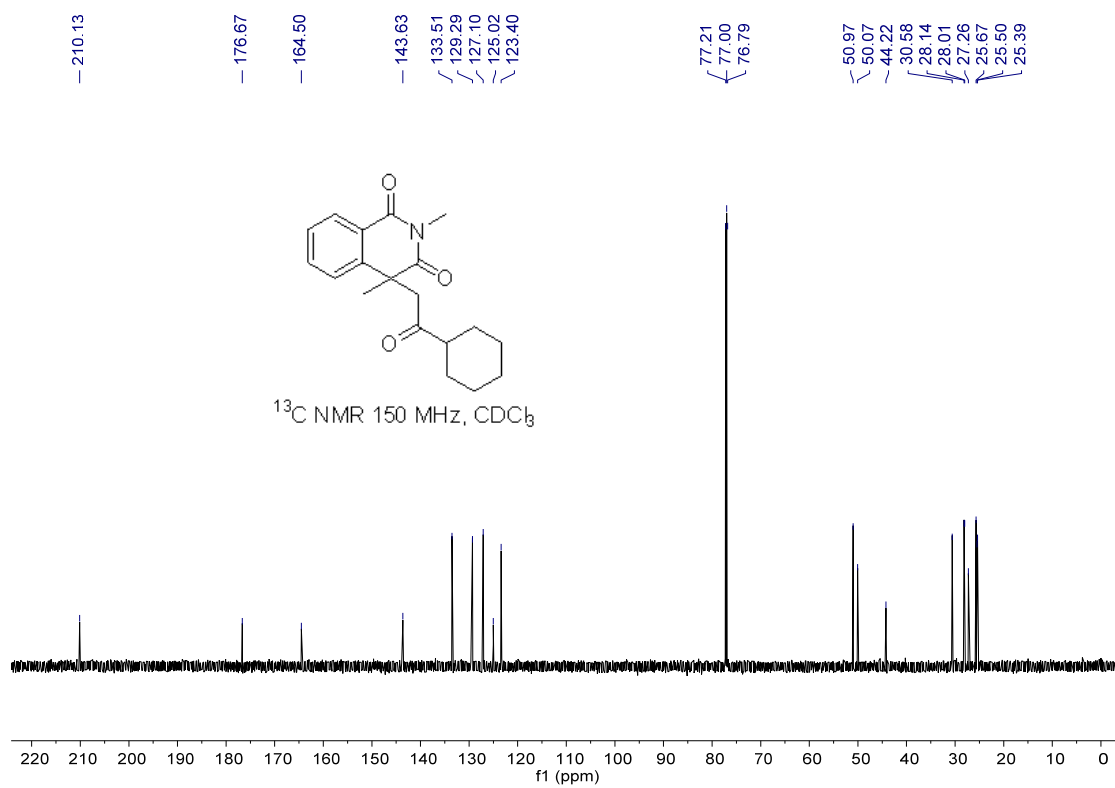
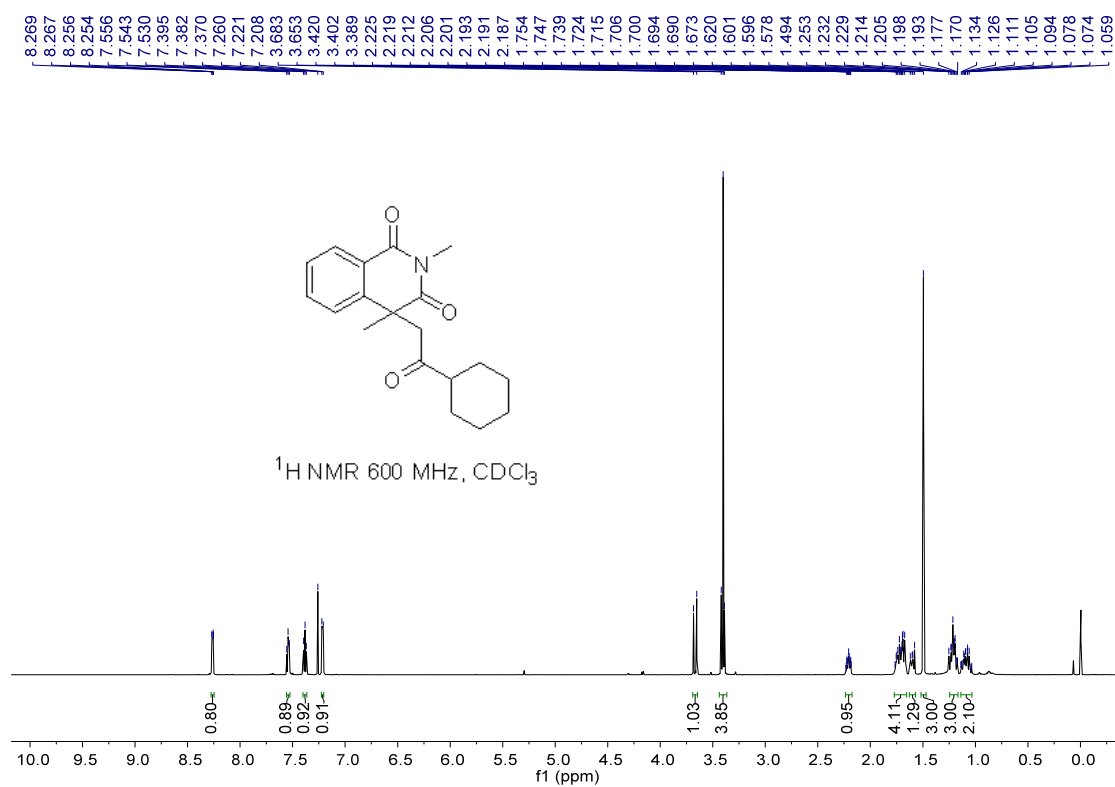
NMR copies of compound **4ak**:



NMR copies of compound **4al**:



NMR copies of compound **4am**:



NMR copies of compound **4an**:

