

**Ruthenium-Catalyzed Cyclization of *N*-Carbamoyl Indolines with Alkynes: An Efficient Route to Pyrroloquinolinones**

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**Electronic Supplementary Information (ESI)**

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## Experimental section

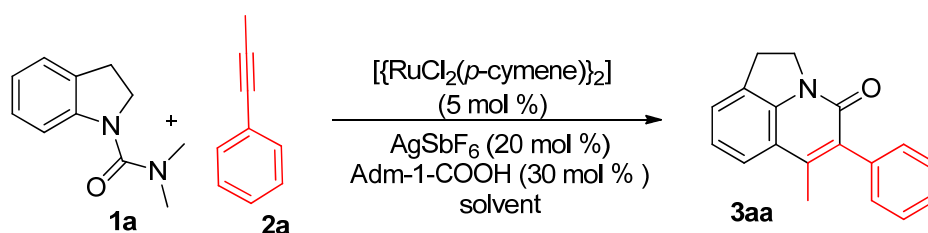
### General Procedure for the Preparation of Pyrroloquinolinones Catalyzed by Ruthenium Complex.

A 15-mL pressure tube with septum containing [ $\{\text{RuCl}_2(p\text{-cymene})\}_2$ ] (5.0 mol %), *N*-carbamoyl indolines **1** (100 mg), Adm-1-COOH (30 mol %), alkyne **2** (1.2 equiv) (if alkyne is solid) and  $\text{AgSbF}_6$  (20 mol %) was evacuated and purged with nitrogen gas three times ( $\text{AgSbF}_6$  was taken inside the glove box). To the tube were then added *tert*-amyl alcohol (3 ml) via syringe after that the reaction mixture was evacuated and purged with nitrogen gas three times (liquid alkynes were added at this stage via syringe). After that, the septum was taken out and immediately a screw cap was used to cover the tube under the nitrogen atmosphere and the reaction mixture stirred at room temperature for 5 minutes. Then, the reaction mixture was allowed to stir at 130 °C for 24 h. After cooling to ambient temperature, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , filtered through Celite and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure product **3**.

### General Procedure for the Aromatization of Pyrroloquinolinones.

A 15-mL pressure tube with septum containing pyrroloquinolinone **3aa** or **3ah** (50 mg) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (5.0 equiv) was evacuated and purged with nitrogen gas three times. To the tube was then added 1,4-dioxane (2.0 mL) via syringe after that the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube under the nitrogen atmosphere and the reaction mixture was stirred at room temperature for 5 minutes. Then, the reaction mixture was allowed to stir at 100 °C for 12 h. After cooling to ambient temperature, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , and concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure aromatized product **4a** or **4b**.

### Solvent Optimization.

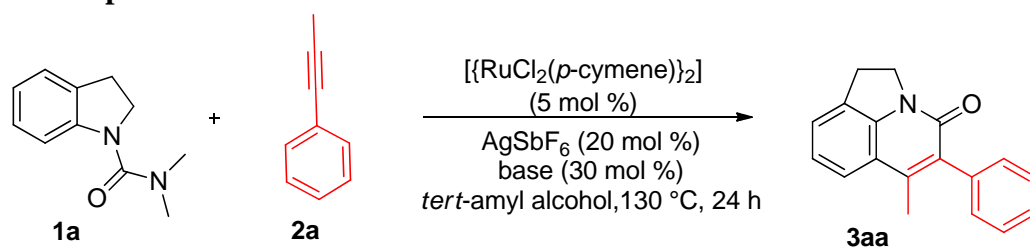


S. No	Solvent	Base (30 mol %)	Additive (20 mol %)	Yield (%) <sup>b</sup>
1	DCE	Adm-1-COOH	$AgSbF_6$	58
2	1,4-dioxane	Adm-1-COOH	$AgSbF_6$	27
3	<i>iso</i> -PrOH	Adm-1-COOH	$AgSbF_6$	20
4	<i>tert</i> -amyl alcohol	Adm-1-COOH	$AgSbF_6$	79
5	1,2-dimethoxyethane	Adm-1-COOH	$AgSbF_6$	32
6	THF	Adm-1-COOH	$AgSbF_6$	15
7	<i>t</i> -BuOH	Adm-1-COOH	$AgSbF_6$	17
8	Toluene	Adm-1-COOH	$AgSbF_6$	NR
9	Acetonitrile	Adm-1-COOH	$AgSbF_6$	NR
10	DMSO	Adm-1-COOH	$AgSbF_6$	NR
11	DMF	Adm-1-COOH	$AgSbF_6$	NR
12	<i>tert</i> -amyl alcohol	Adm-1-COOH	$AgSbF_6$	45 <sup>c</sup>

<sup>a</sup>All reactions were carried out using **1** (100 mg), alkynes **2a** (1.2 equiv),  $\{[RuCl_2(p\text{-cymene})]_2\}$  (5 mol %),  $AgSbF_6$  (20 mol %) and solvent (3.0 mL) at 130°C for 24 h. <sup>b</sup>GC yield. <sup>c</sup> at 110°C for 24 h

**Note:**

1. The catalytic reaction was tried without  $[\{\text{RuCl}_2(p\text{-cymene})\}_2]$ . No product **3aa** was observed.
2. The catalytic reaction was tried without  $\text{AgSbF}_6$ . No product **3aa** was observed.

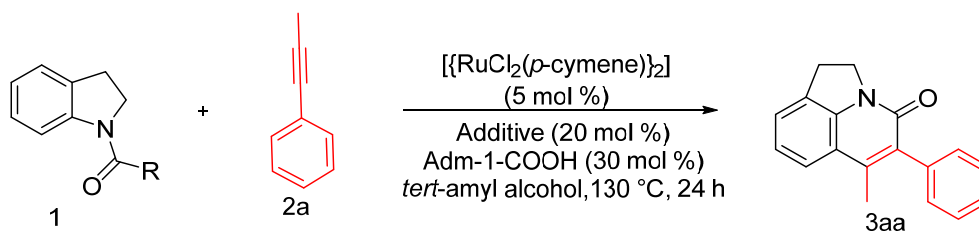
**Base Optimization:**

S. No	Solvent	Base ( 30 mol % )	Additive (20 mol % )	Yield (%) <sup>a</sup>
1	<i>tert</i> -amyl alcohol	NaOAc	$\text{AgSbF}_6$	25
2	<i>tert</i> -amyl alcohol	LiOAc	$\text{AgSbF}_6$	-
3	<i>tert</i> -amyl alcohol	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	$\text{AgSbF}_6$	37
4	<i>tert</i> -amyl alcohol	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	$\text{AgSbF}_6$	39 <sup>b</sup>
5	<i>tert</i> -amyl alcohol	AgOAc	$\text{AgSbF}_6$	29
6	<i>tert</i> -amyl alcohol	$\text{Ag}_2\text{CO}_3$	$\text{AgSbF}_6$	0
7	<i>tert</i> -amyl alcohol	AcOH	$\text{AgSbF}_6$	-
8	<i>tert</i> -amyl alcohol	Mesitylinic acid	$\text{AgSbF}_6$	47
<b>9</b>	<b><i>tert</i>-amyl alcohol</b>	<b>Adm-1-COOH</b>	<b><math>\text{AgSbF}_6</math></b>	<b>79 (73)<sup>c</sup></b>
10	<i>tert</i> -amyl alcohol	$\text{CF}_3\text{COOH}$	$\text{AgSbF}_6$	-
11	<i>tert</i> -amyl alcohol	PivOH	$\text{AgSbF}_6$	51
12	<i>tert</i> -amyl alcohol	CsOPiv	$\text{AgSbF}_6$	0
13	<i>tert</i> -amyl alcohol	CsOAc	$\text{AgSbF}_6$	0
14	<i>tert</i> -amyl alcohol	Adm-1-COOH	$\text{AgSbF}_6$	81 <sup>d</sup>

<sup>a</sup>GC Yield. <sup>b</sup>Under air. <sup>c</sup>Yield in the paranthesis is isolated yield. <sup>d</sup>100 mol % of Adm-1-

COOH was used.

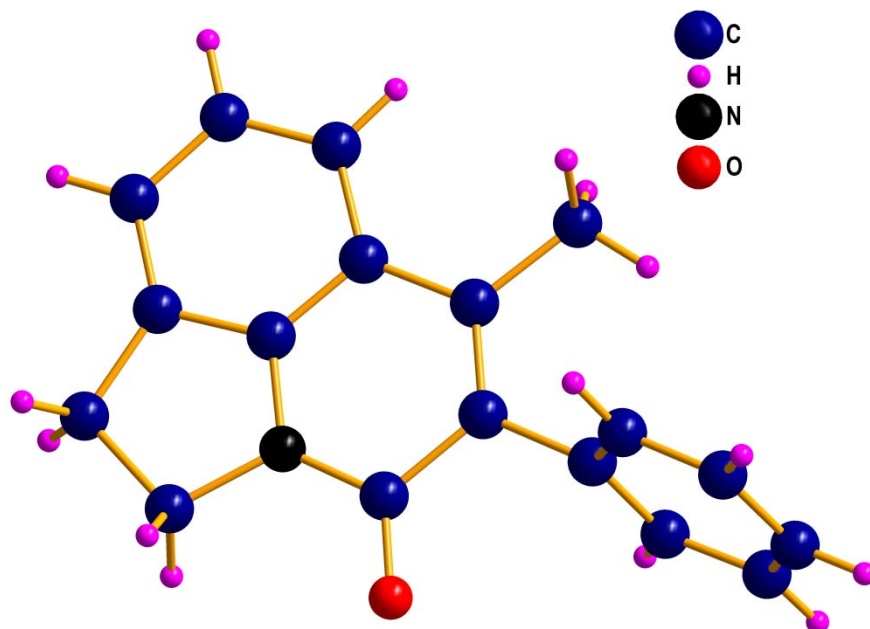
### Additive Optimization:



Entry	Solvent	Base ( 30 mol % )	Additive ( 20 mol % )	Yield (%) <sup>a</sup>
1	<i>tert</i> -amyl alcohol	Adm-1-COOH	AgSbF <sub>6</sub>	79
2	<i>tert</i> -amyl alcohol	Adm-1-COOH	AgBF <sub>4</sub>	41
3	<i>tert</i> -amyl alcohol	Adm-1-COOH	AgOTf	0
4	<i>tert</i> -amyl alcohol	Adm-1-COOH	KPF <sub>6</sub>	0

<sup>a</sup>GC Yield.

## Crystal structure of Compound 3aa.

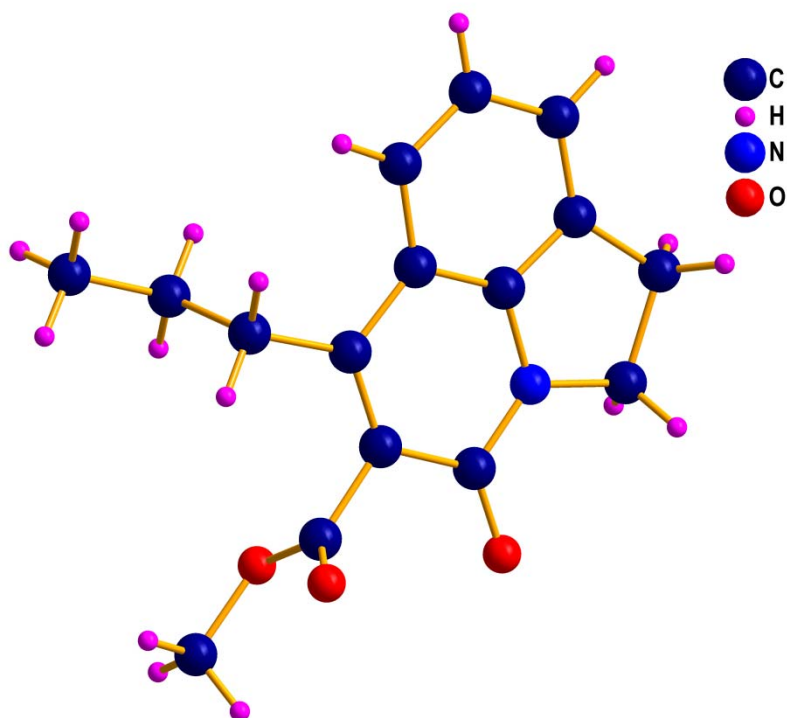


### Crystal data and structure refinement for 3aa.

Identification code	NRM 323	
Empirical formula	$C_{18}H_{15}NO$	
Formula weight	261.31	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	$a = 7.6266(8)$ Å	$\alpha = 90^\circ$ .
	$b = 18.5193(18)$ Å	$\beta = 108.801(5)^\circ$ .
	$c = 10.0793(10)$ Å	$\gamma = 90^\circ$ .
Volume	$1347.6(2)$ Å <sup>3</sup>	
Z	4	
Density (calculated)	1.288 Mg/m <sup>3</sup>	
Absorption coefficient	0.625 mm <sup>-1</sup>	
F(000)	594	
Crystal size	?x ?x ? mm <sup>3</sup>	
Theta range for data collection	4.776 to 68.371°.	

Index ranges	-9<=h<=9, -22<=k<=22, -10<=l<=12
Reflections collected	16428
Independent reflections	2475 [R(int) = 0.0426]
Completeness to theta = 67.679°	100.0 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2475 / 0 / 182
Goodness-of-fit on F <sup>2</sup>	0.882
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.1216
R indices (all data)	R1 = 0.0540, wR2 = 0.1389
Extinction coefficient	n/a
Largest diff. peak and hole	0.190 and -0.115 e.Å <sup>-3</sup>

## Crystal structure of Compound 3af.



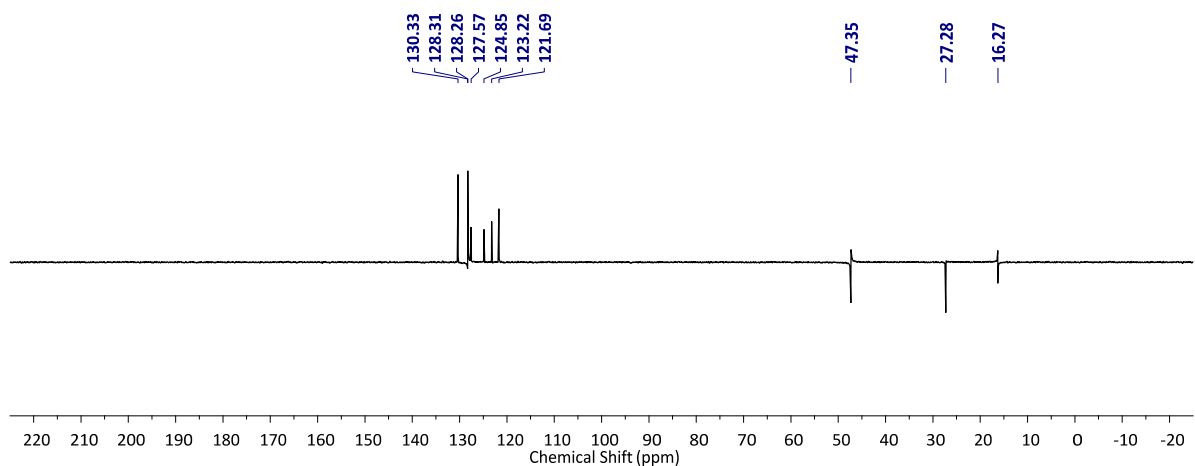
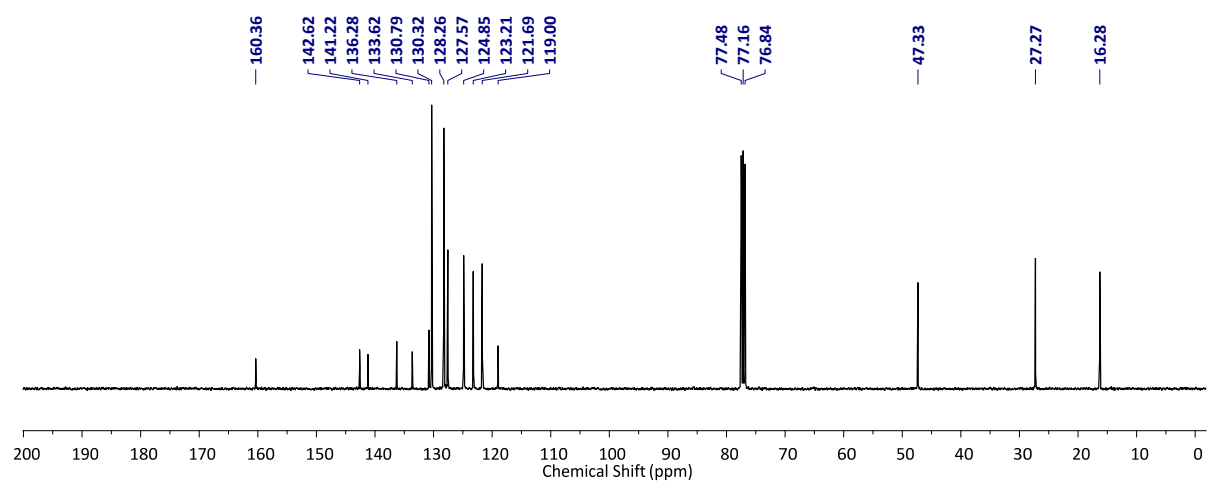
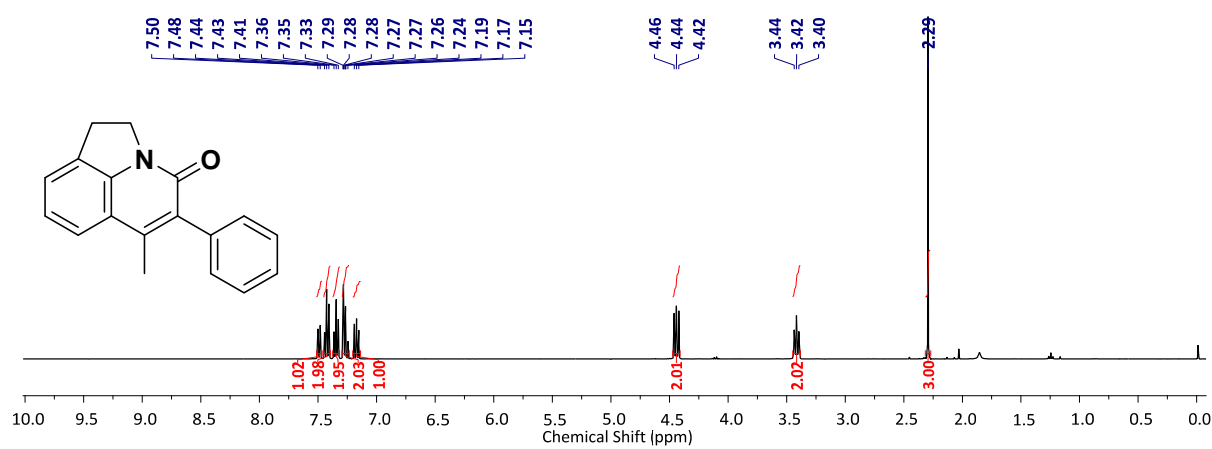
Identification code	NRM 22	
Empirical formula	$C_{16}H_{17}NO_3$	
Formula weight	271.31	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 8.1792(3)$ Å	$\alpha = 91.062(2)^\circ$ .
	$b = 8.2361(3)$ Å	$\beta = 95.422(2)^\circ$ .
	$c = 11.9209(4)$ Å	$\gamma = 119.402(2)^\circ$ .
Volume	$694.53(4)$ Å <sup>3</sup>	
Z	2	
Density (calculated)	1.297 Mg/m <sup>3</sup>	
Absorption coefficient	0.730 mm <sup>-1</sup>	
F(000)	308	
Crystal size	0.230 x 0.100 x 0.050 mm <sup>3</sup>	
Theta range for data collection	3.735 to 68.392°.	
Index ranges	$-9 \leq h \leq 9$ , $-9 \leq k \leq 9$ , $-13 \leq l \leq 14$	
Reflections collected	7560	
Independent reflections	2525 [R(int) = 0.0259]	



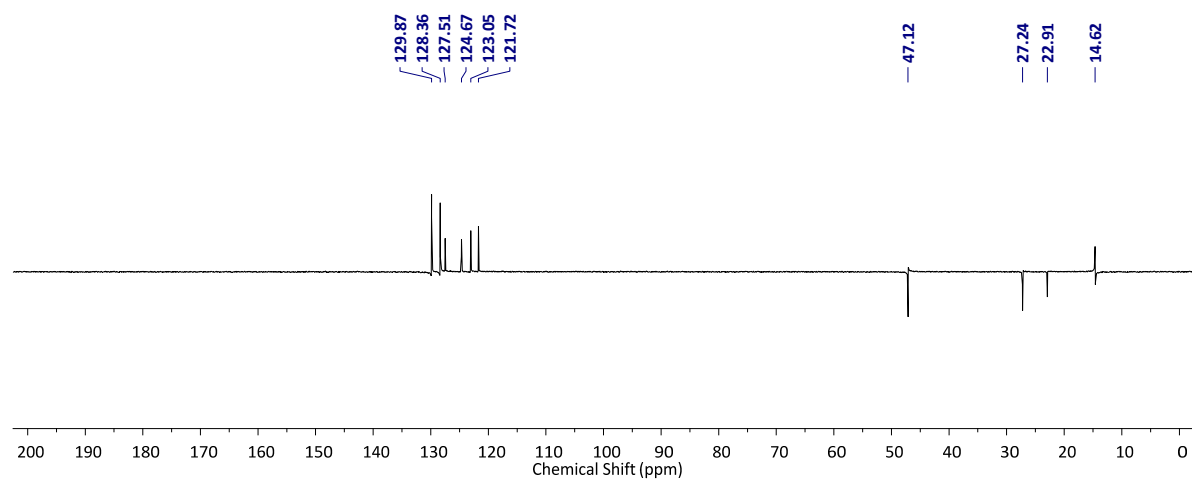
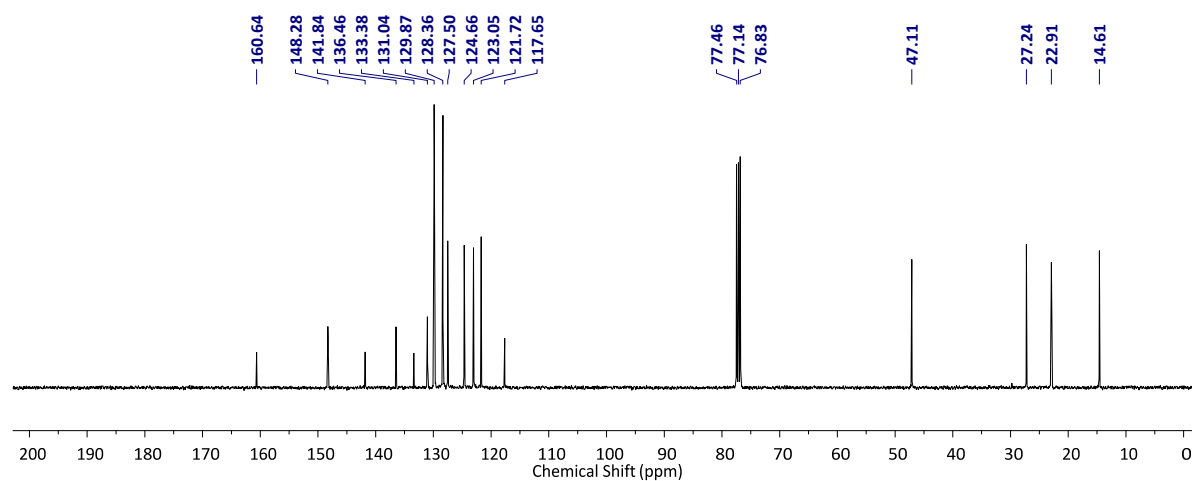
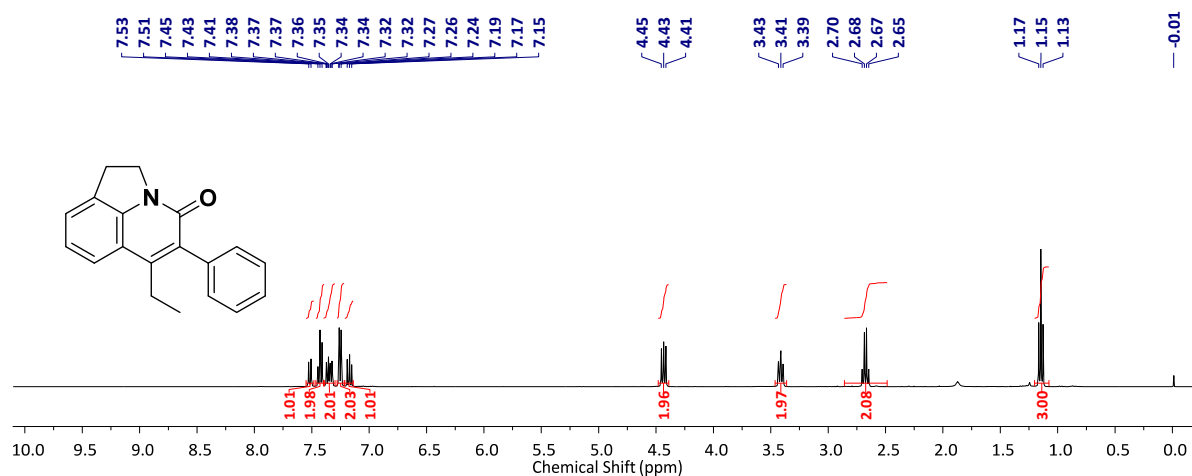
Completeness to theta = 67.679°	99.4 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2525 / 0 / 183
Goodness-of-fit on F <sup>2</sup>	0.639
Final R indices [I>2sigma(I)]	R1 = 0.0445, wR2 = 0.1168
R indices (all data)	R1 = 0.0551, wR2 = 0.1311
Extinction coefficient	n/a
Largest diff. peak and hole	0.297 and -0.247 e.Å <sup>-3</sup>

## Spectral Data of Compounds

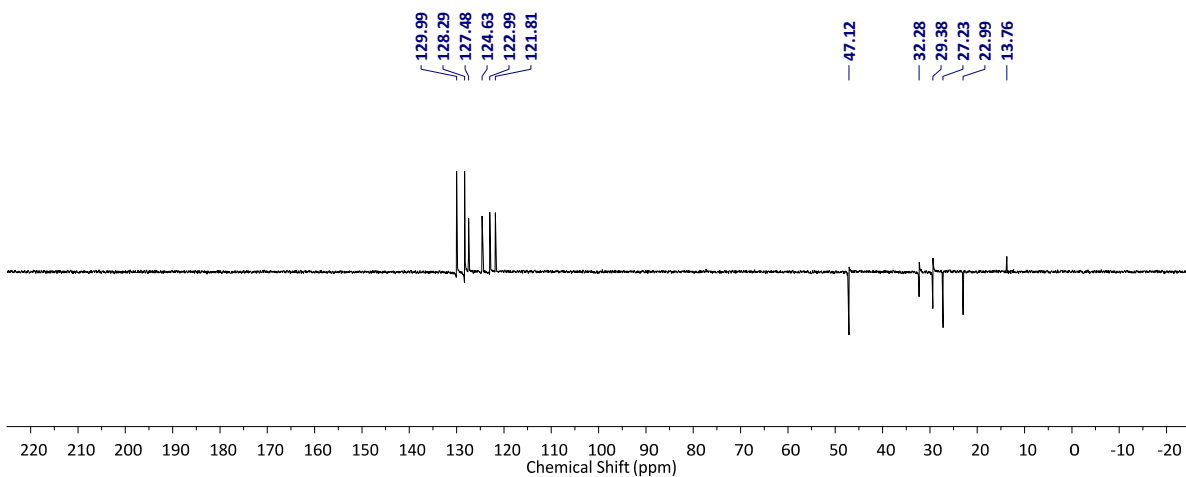
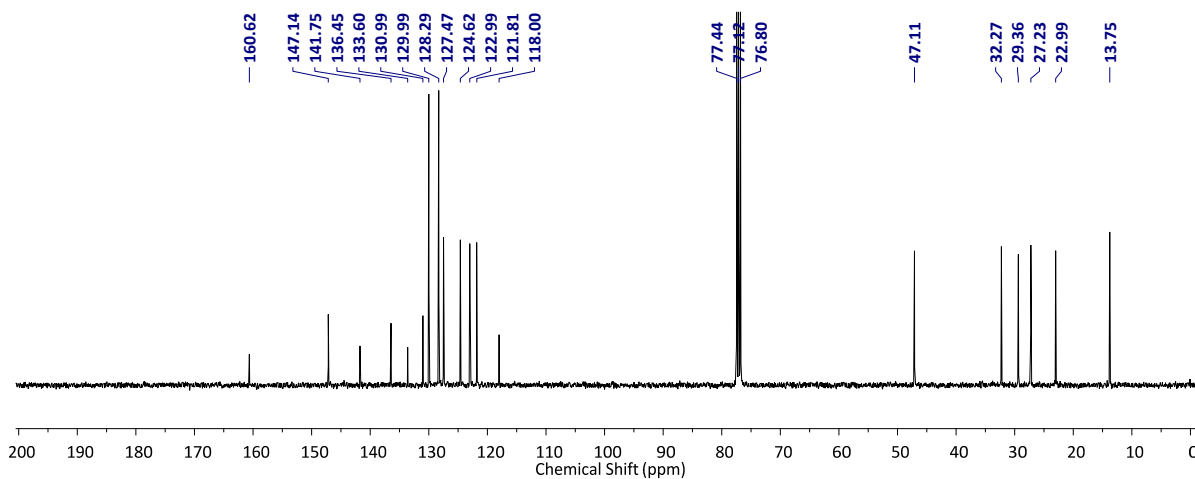
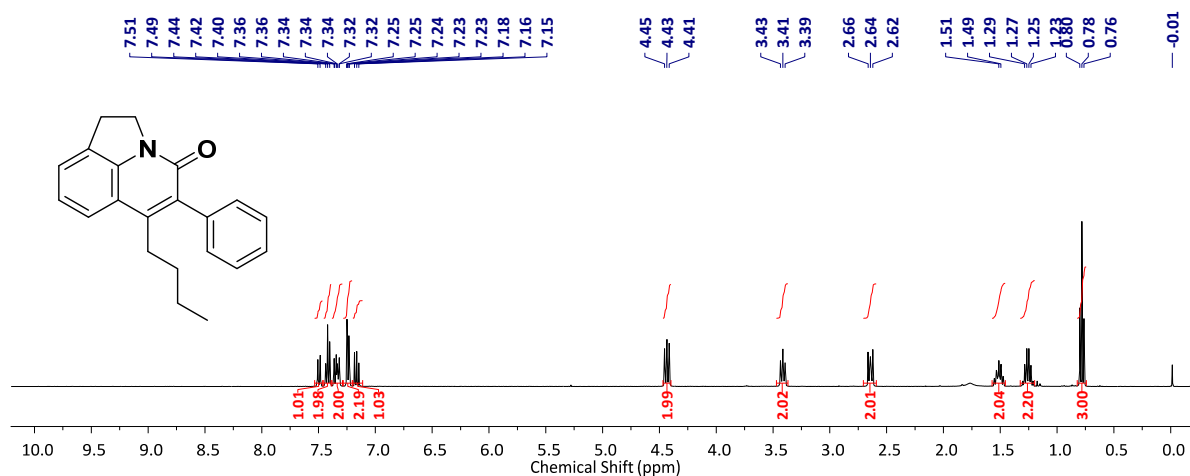
### $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 3aa.



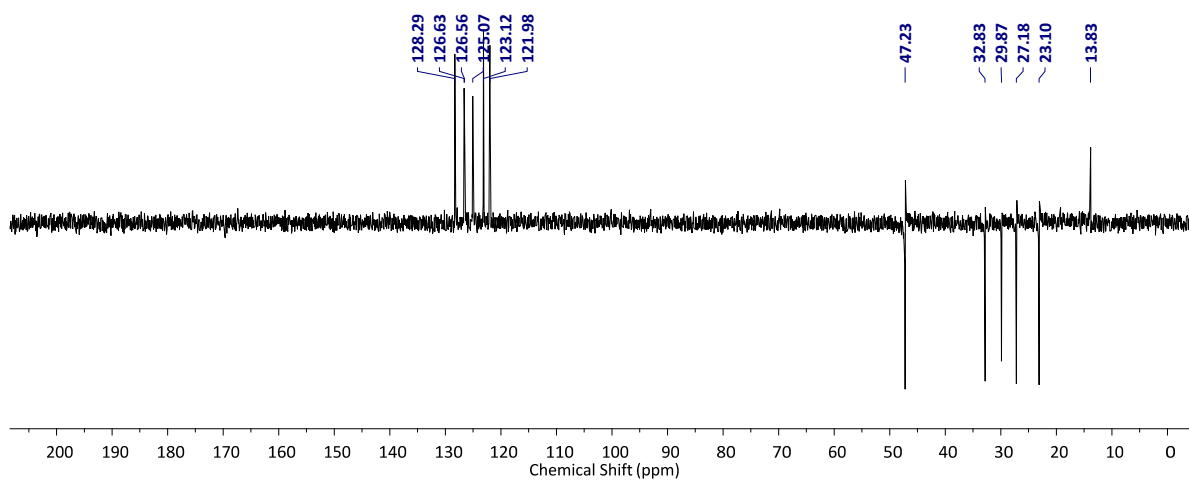
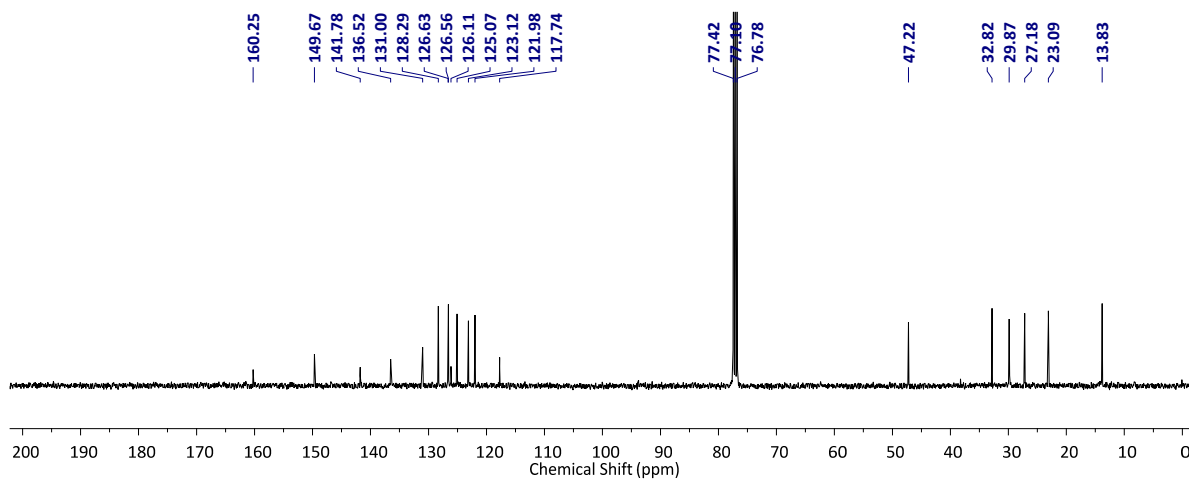
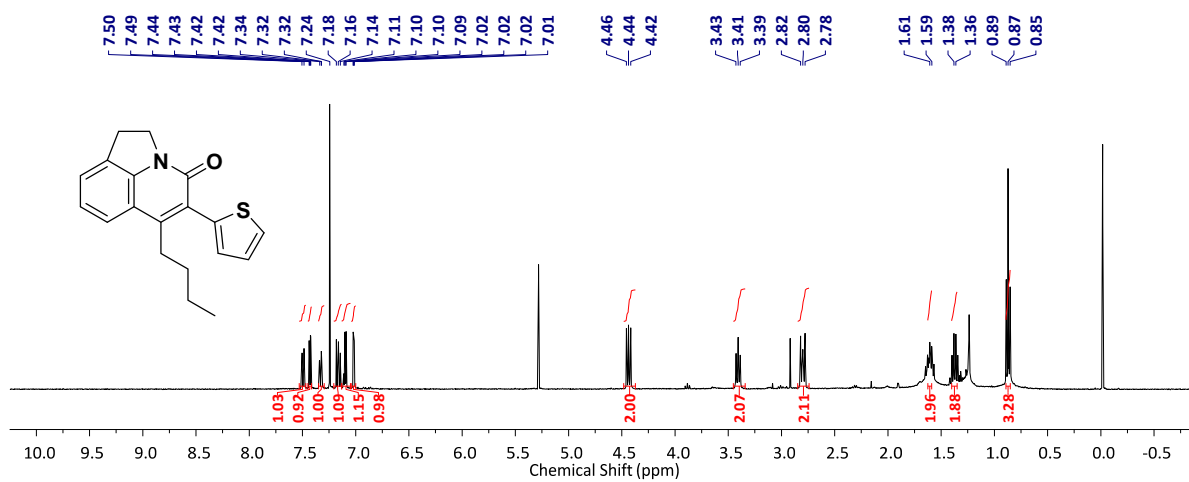
# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 3ab.



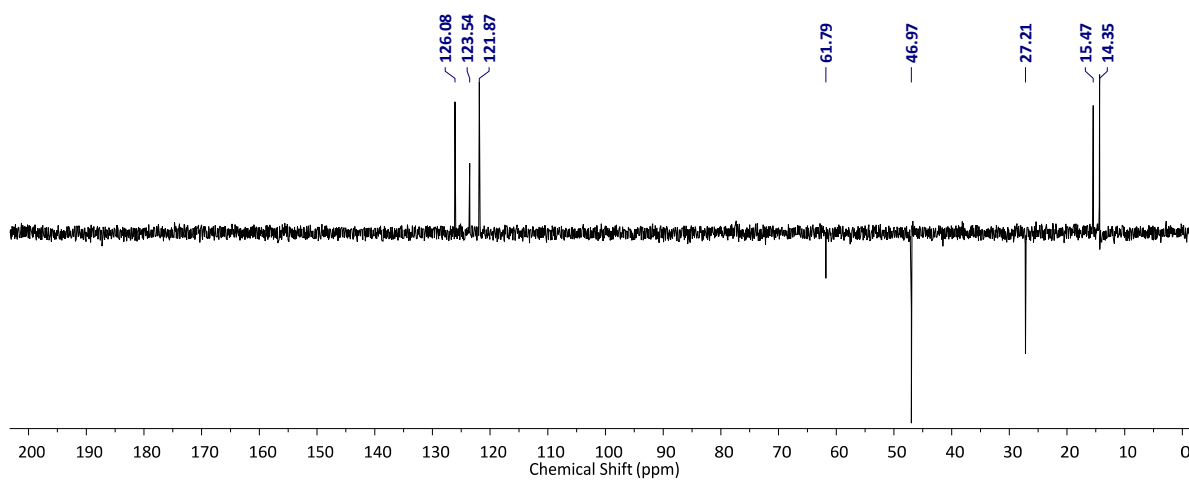
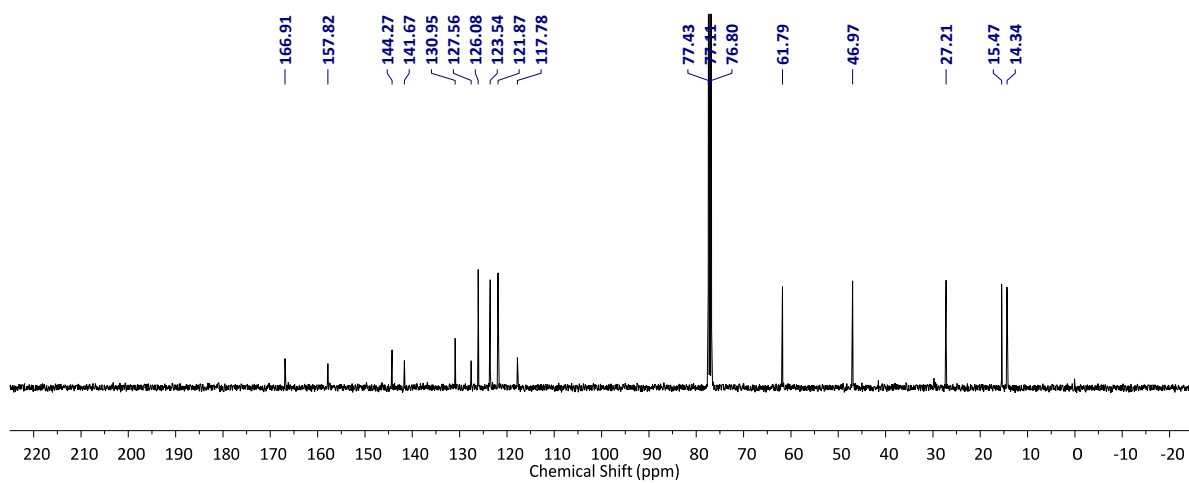
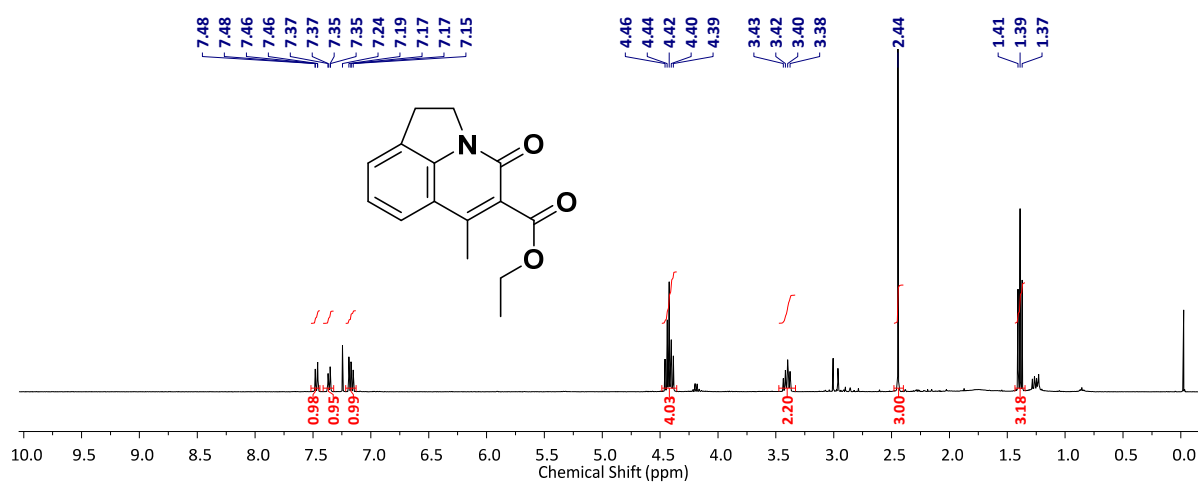
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ac.



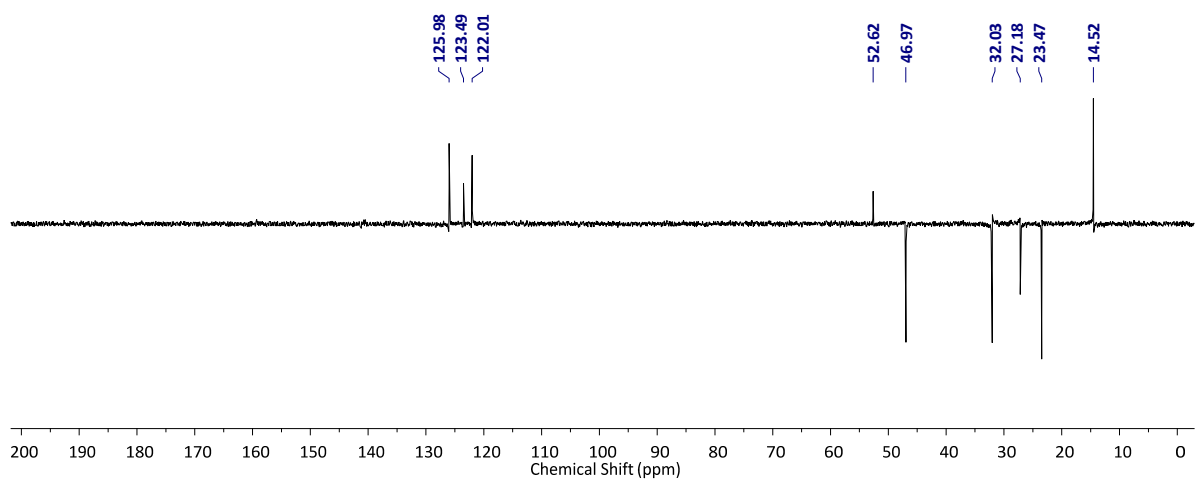
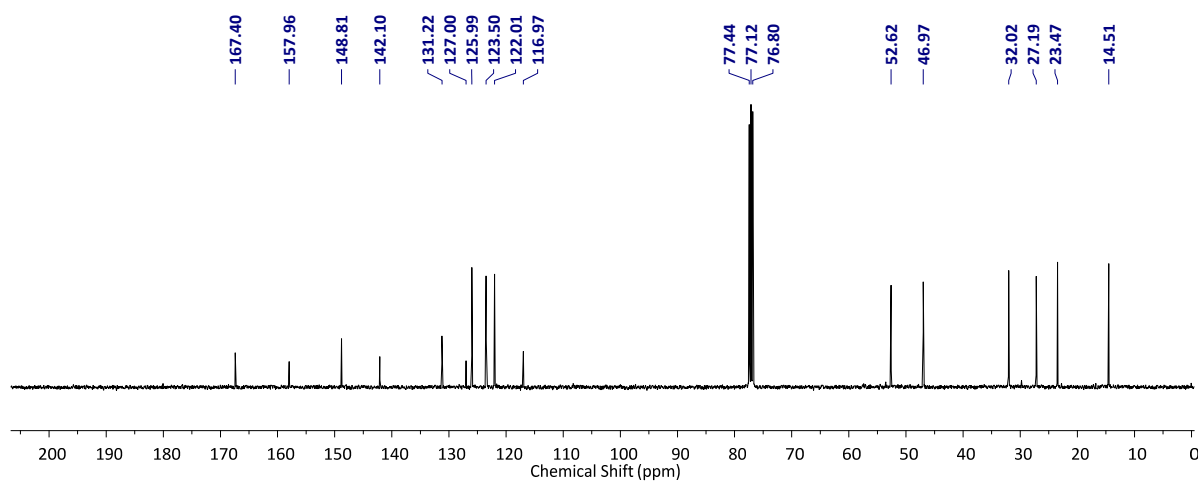
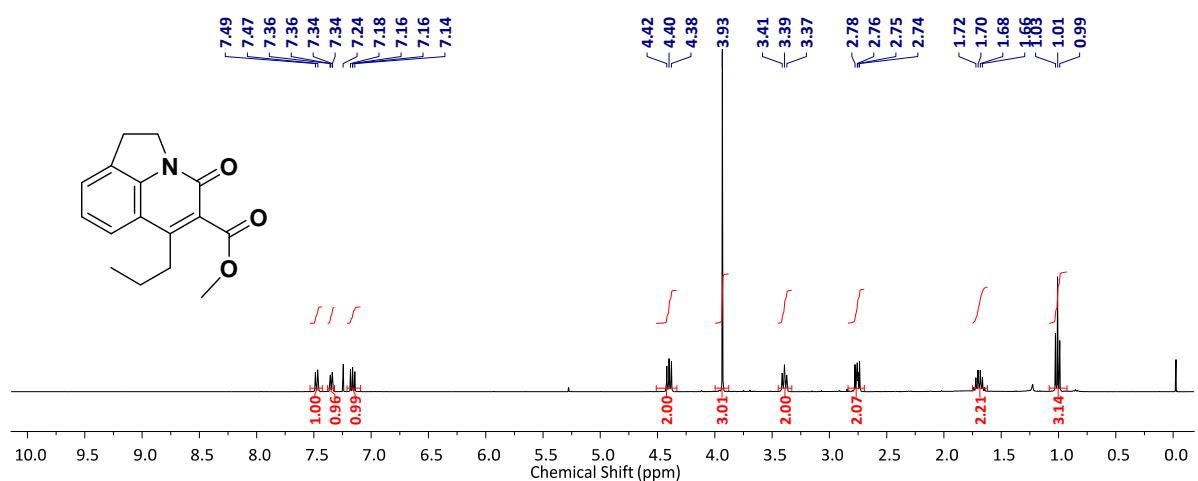
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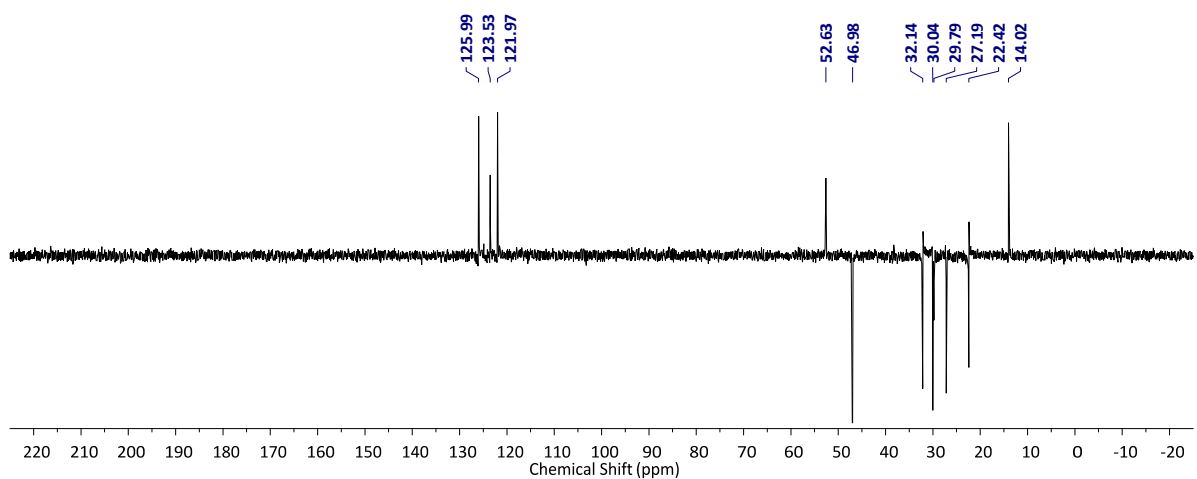
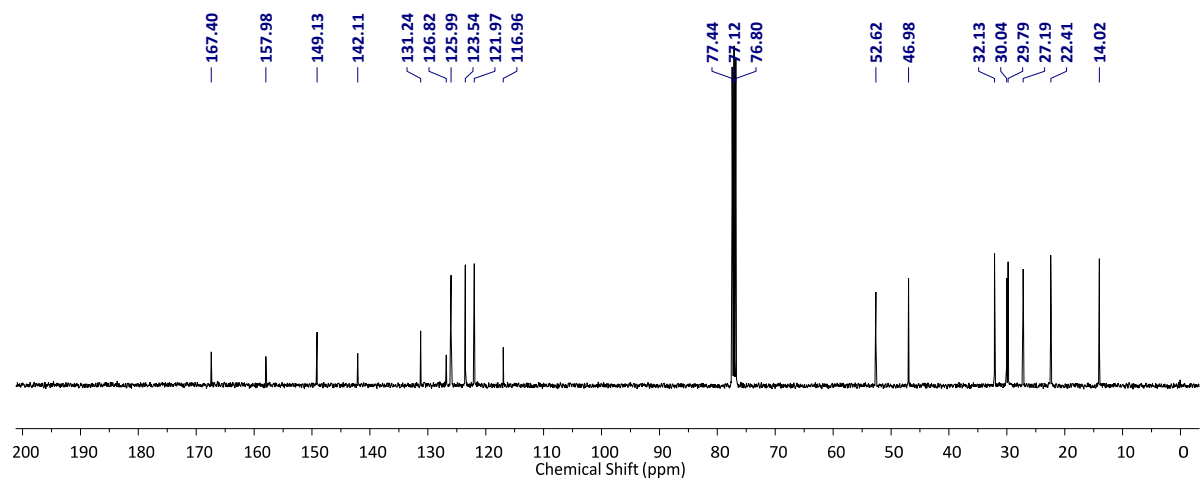
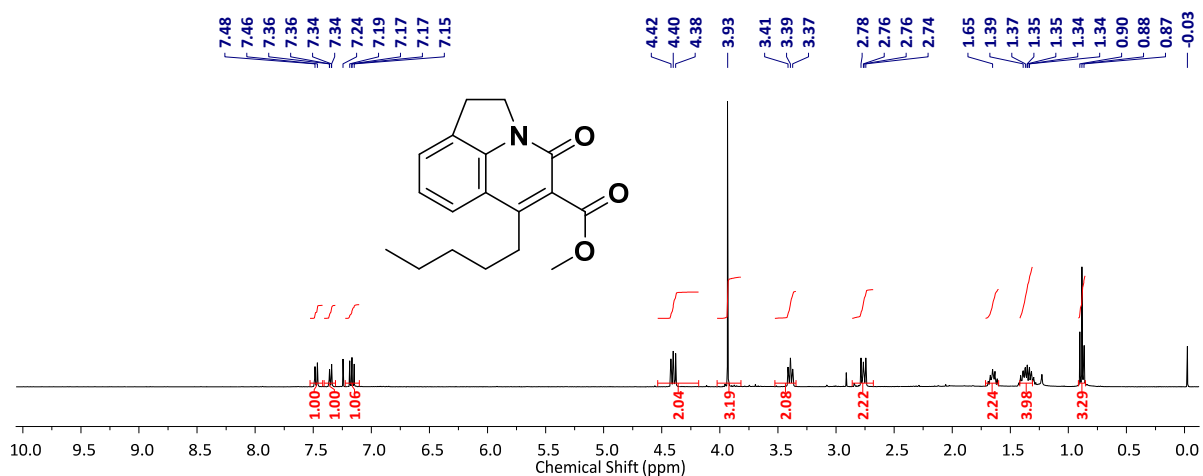
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ae.



# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 3af.

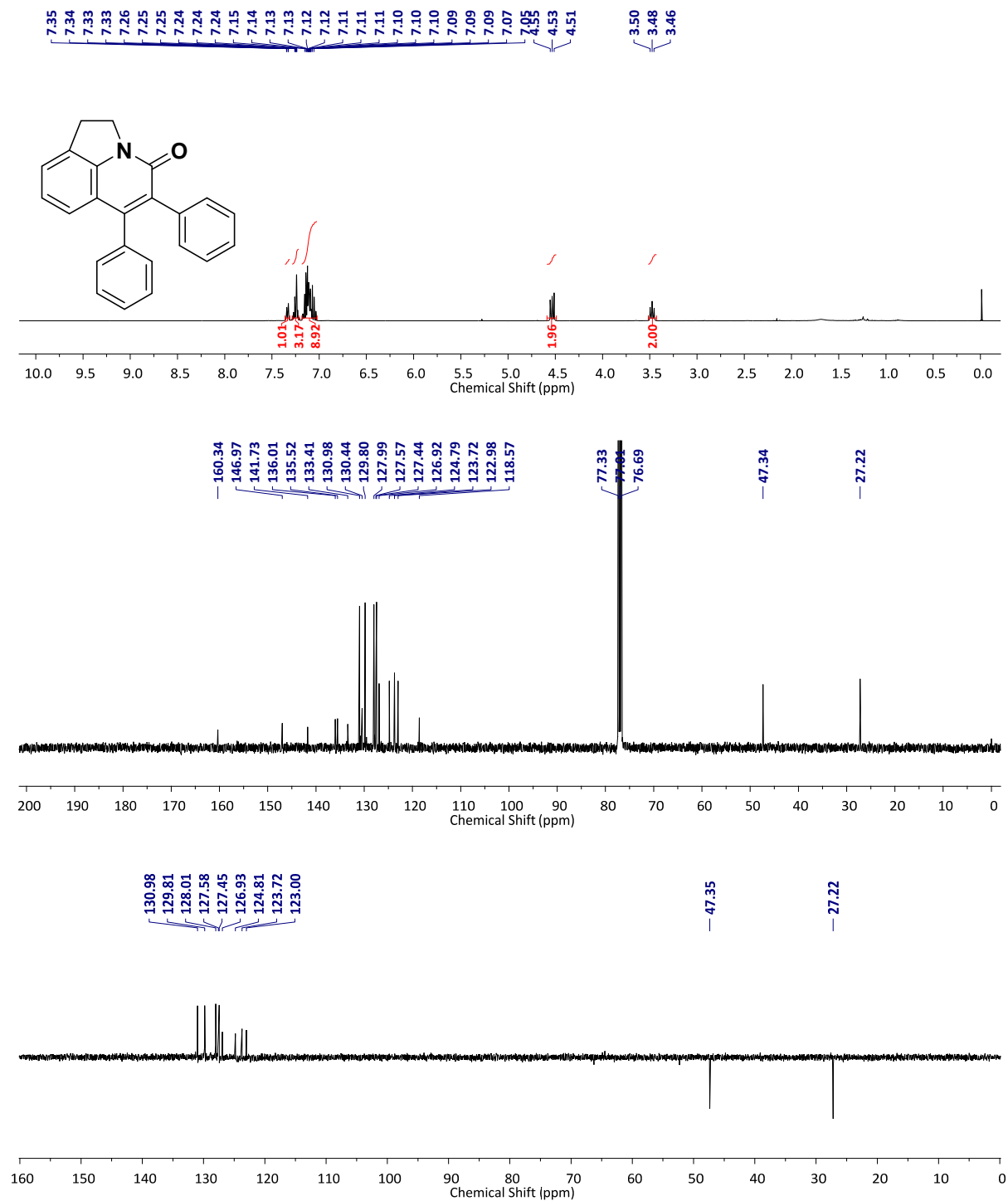


# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 3ag.

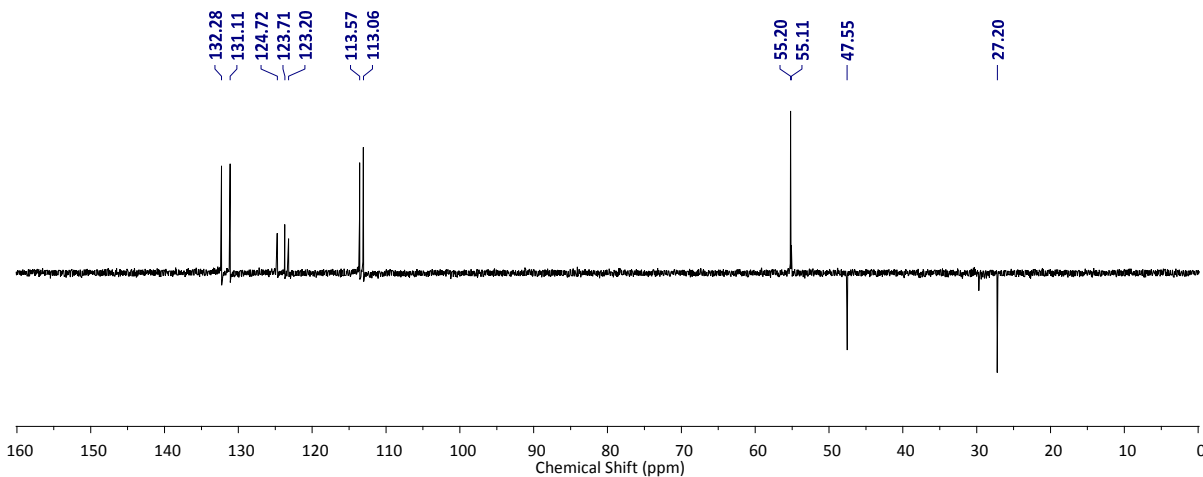
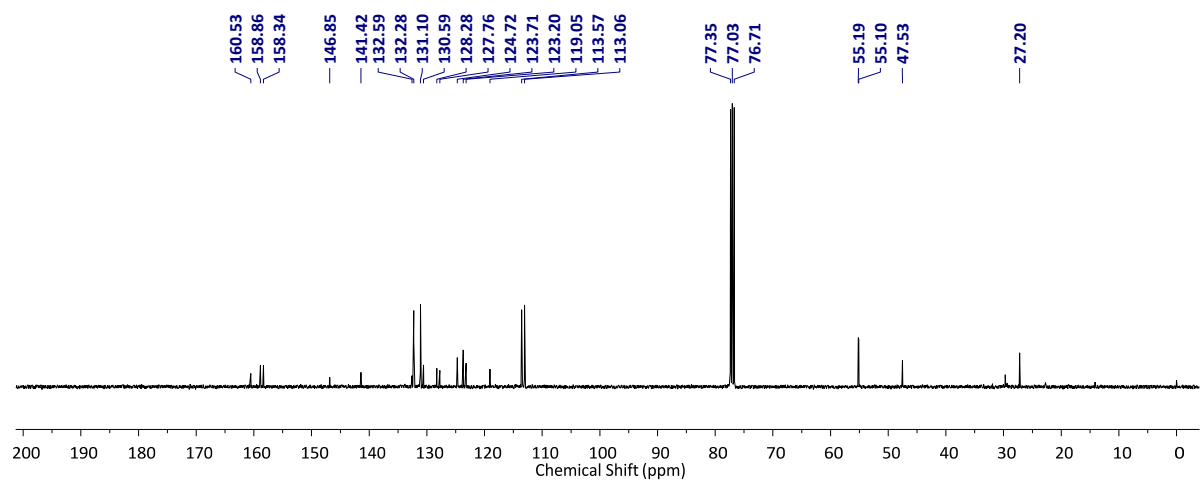
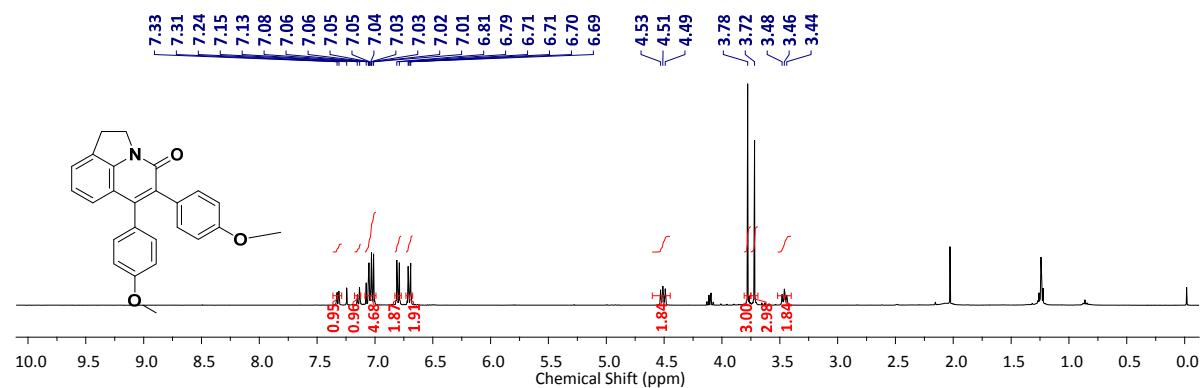




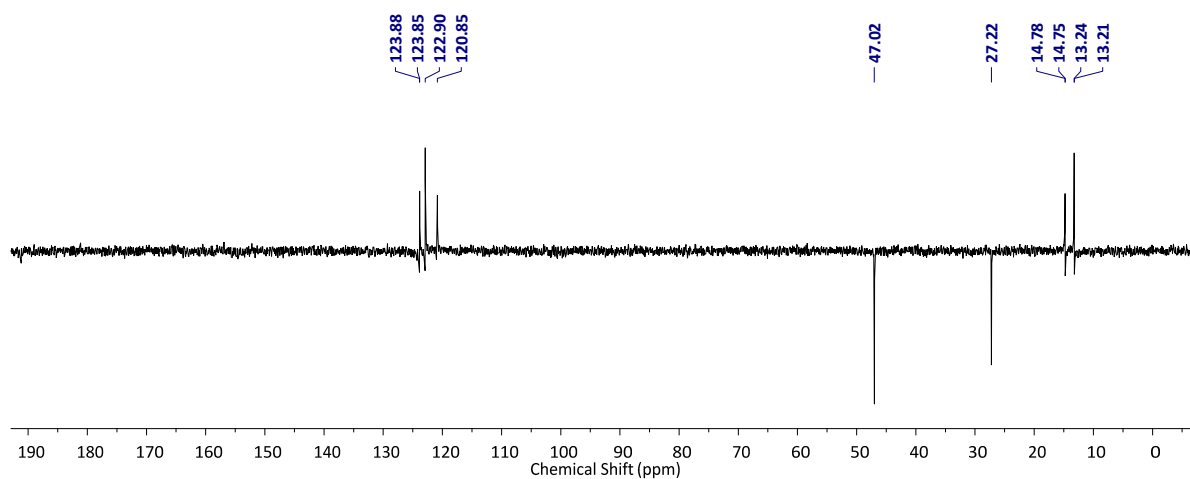
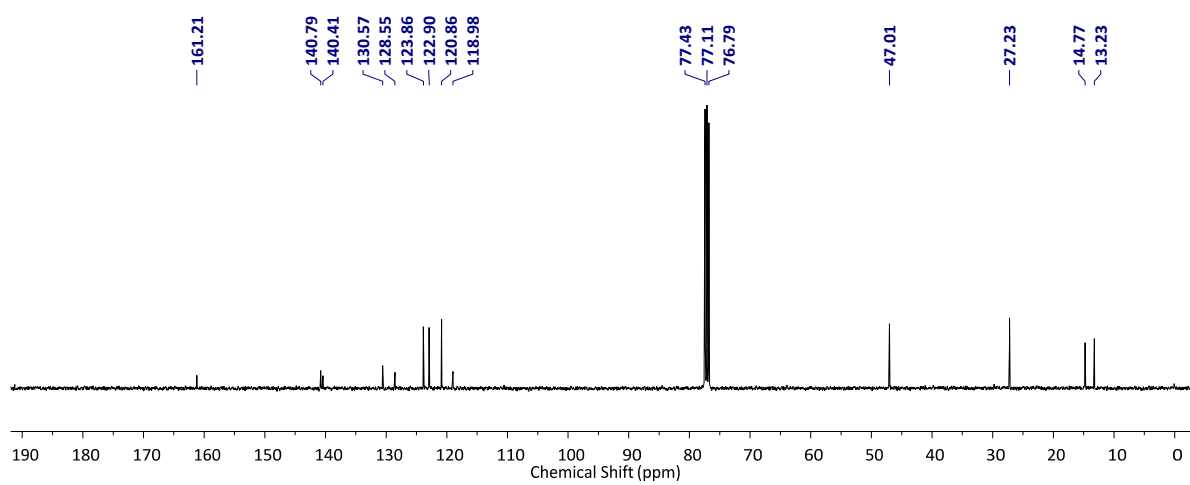
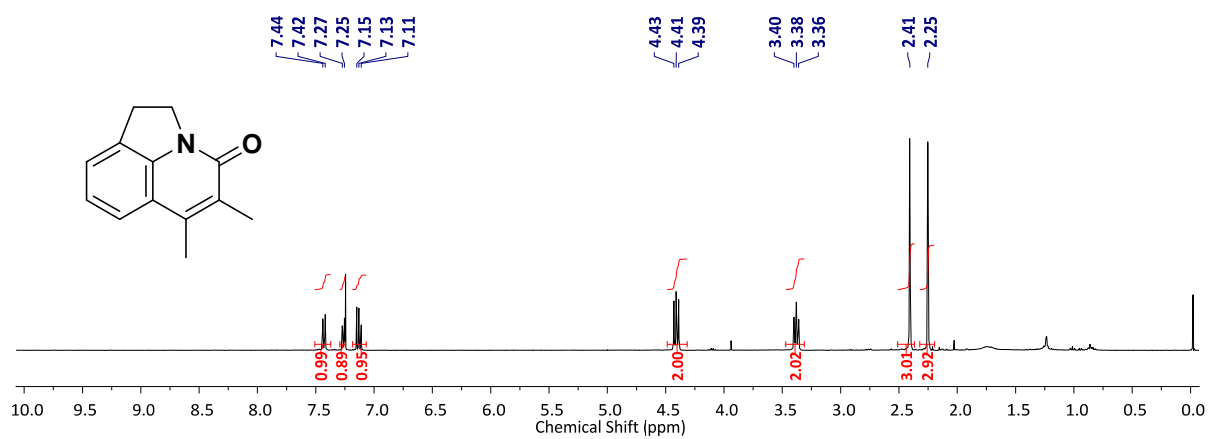
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ah.



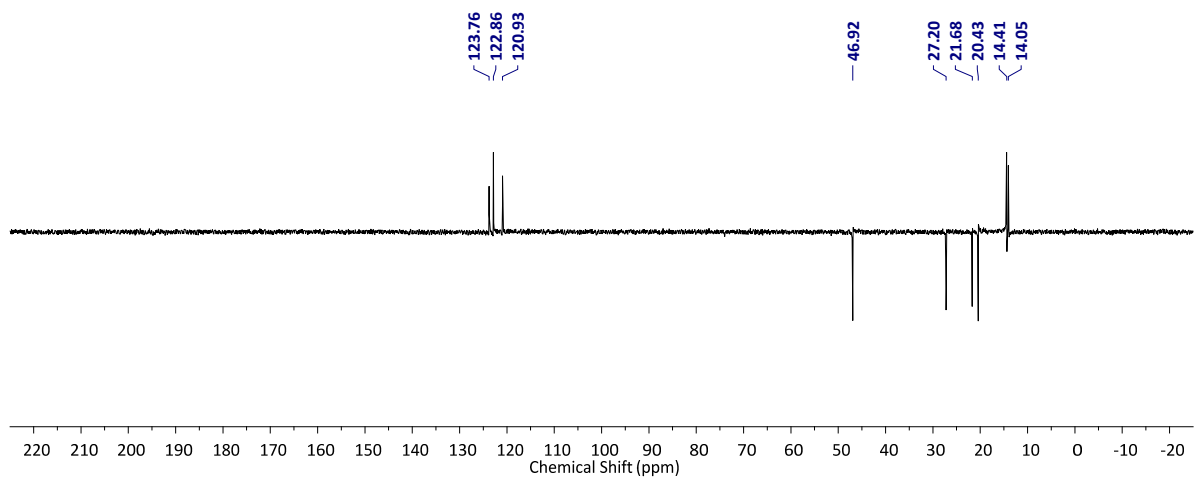
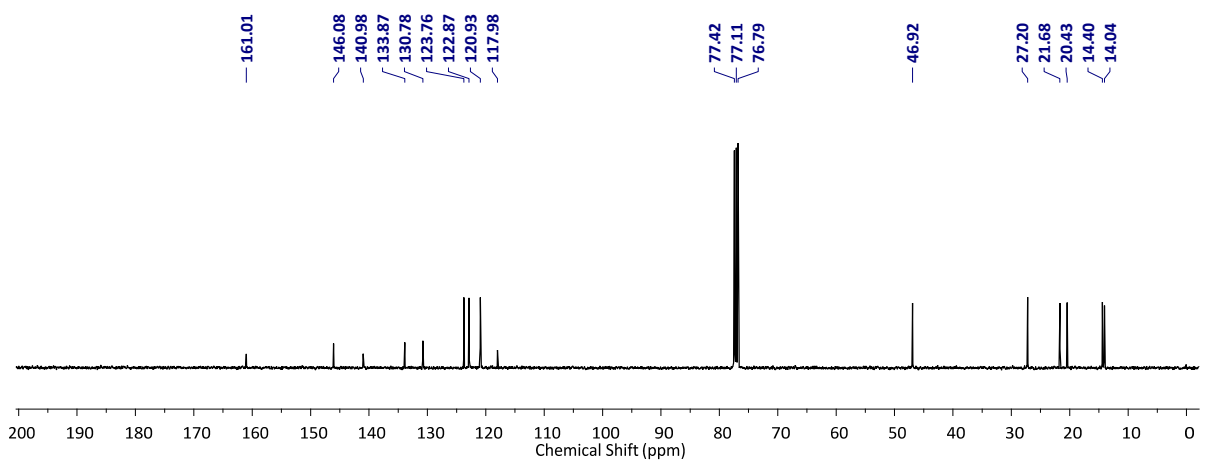
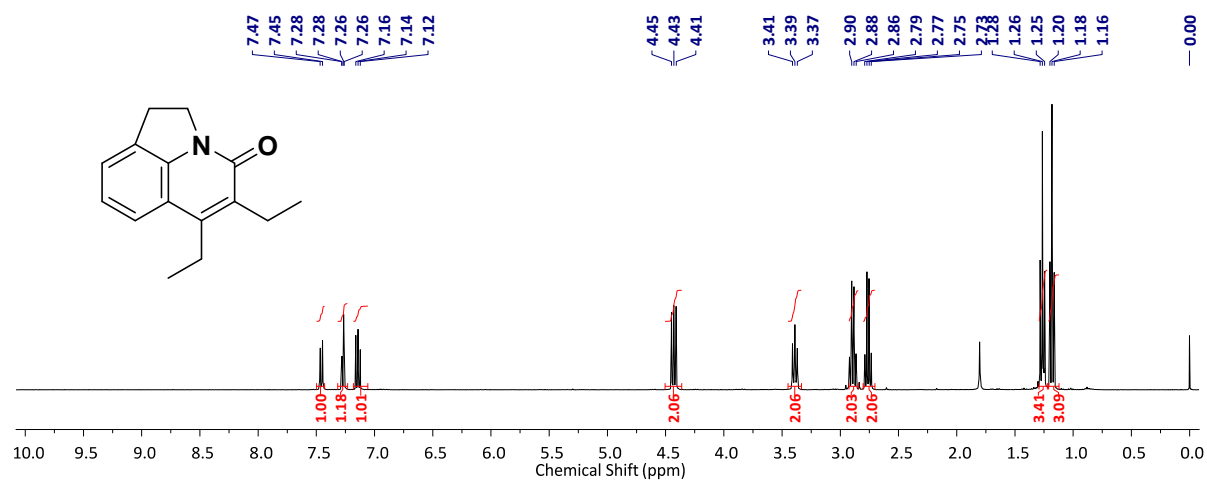
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ai.



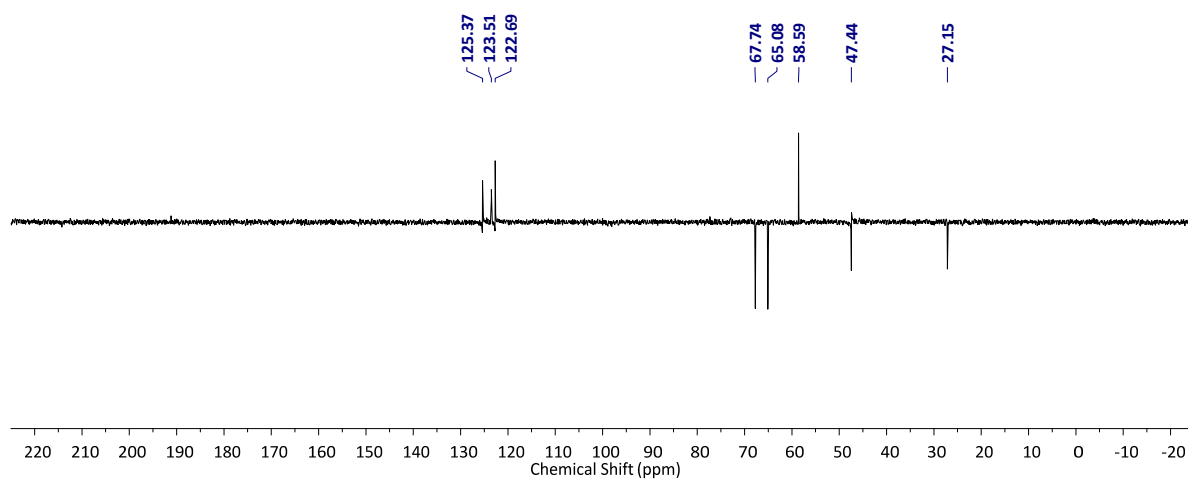
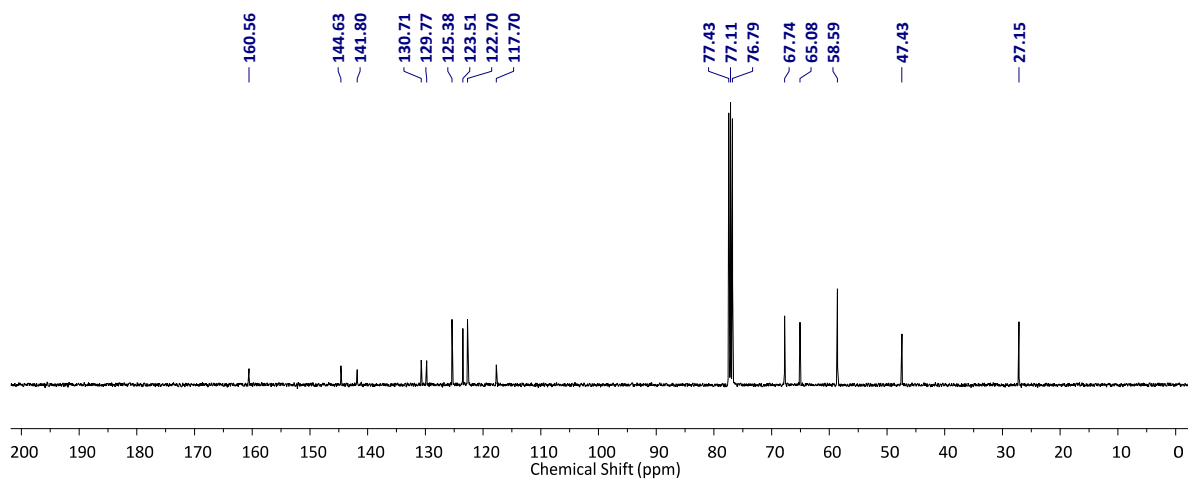
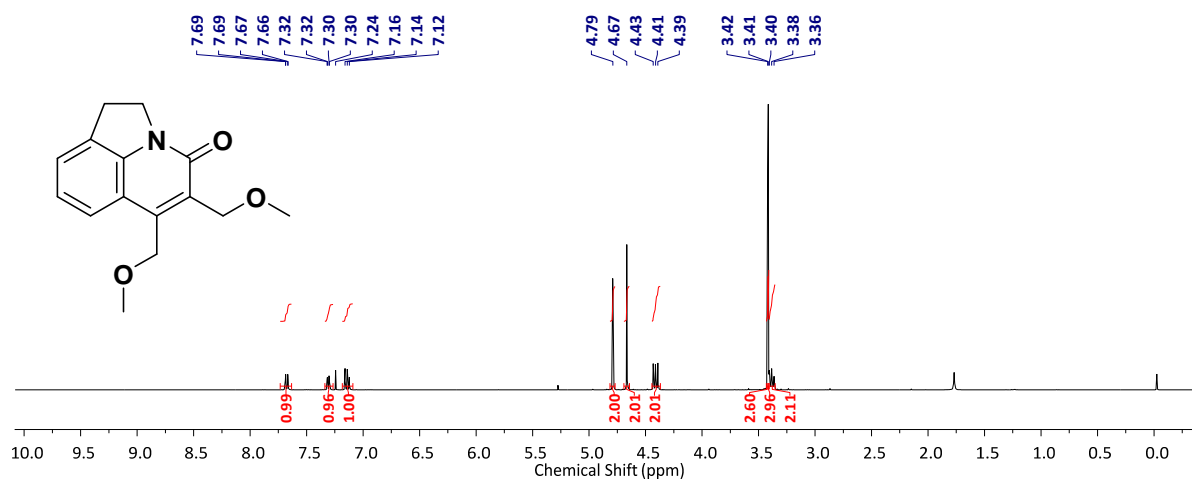
# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 3aj.



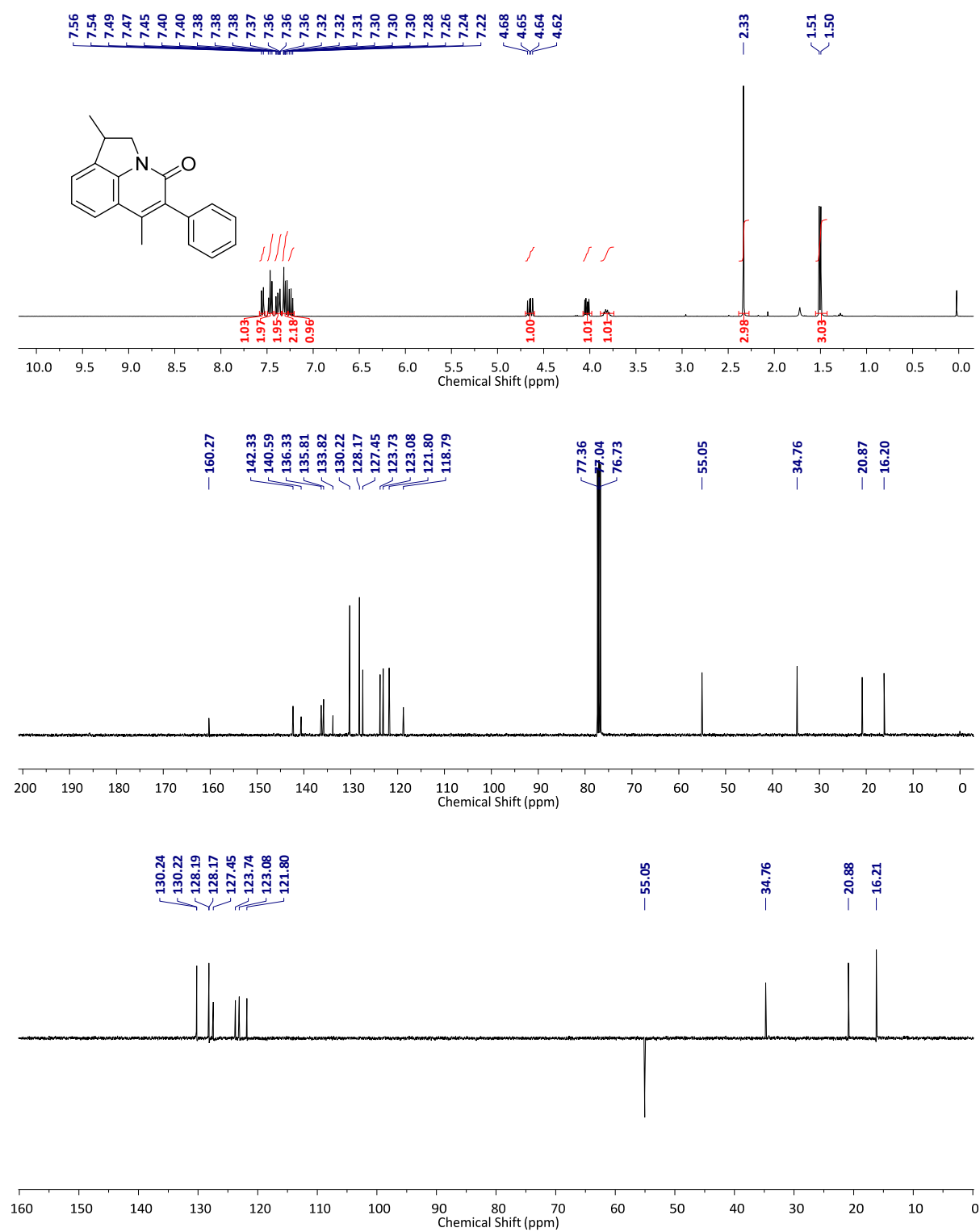
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ak.



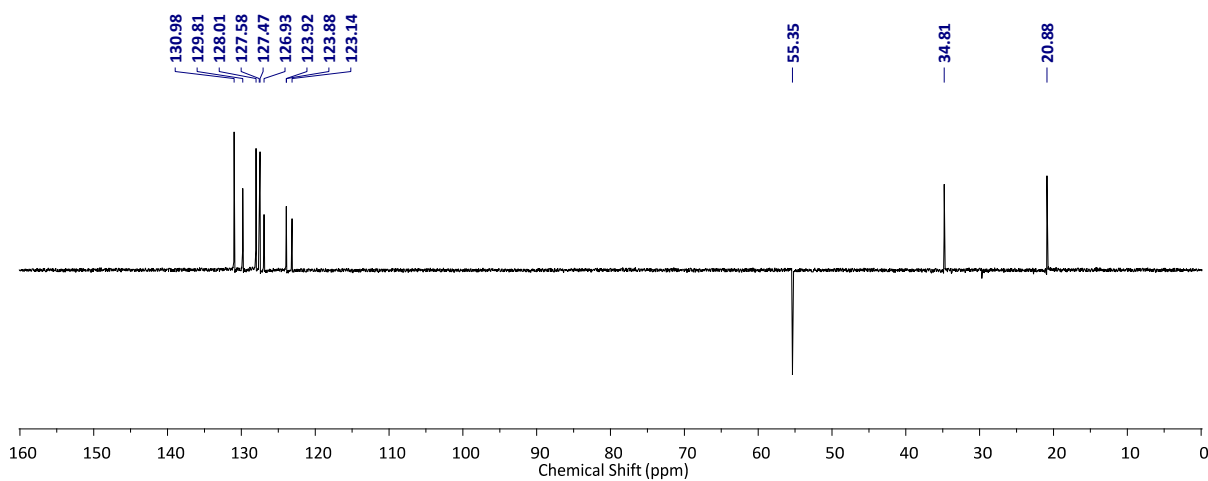
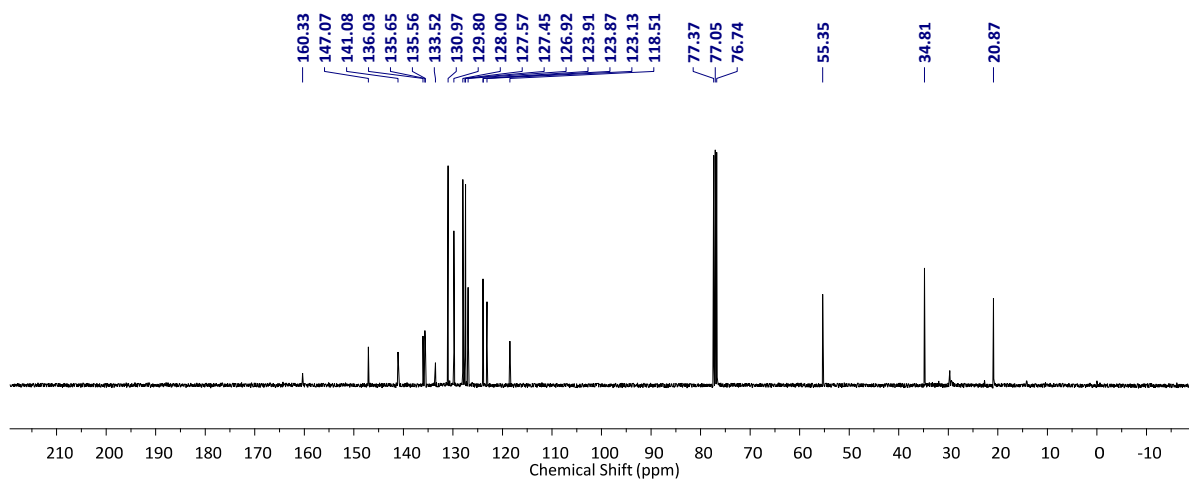
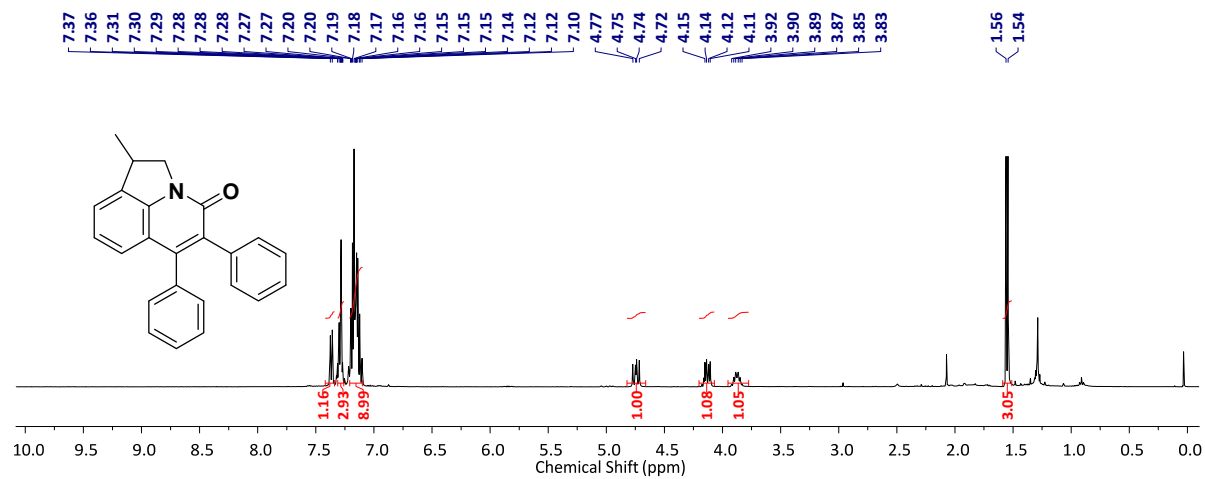
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3a.



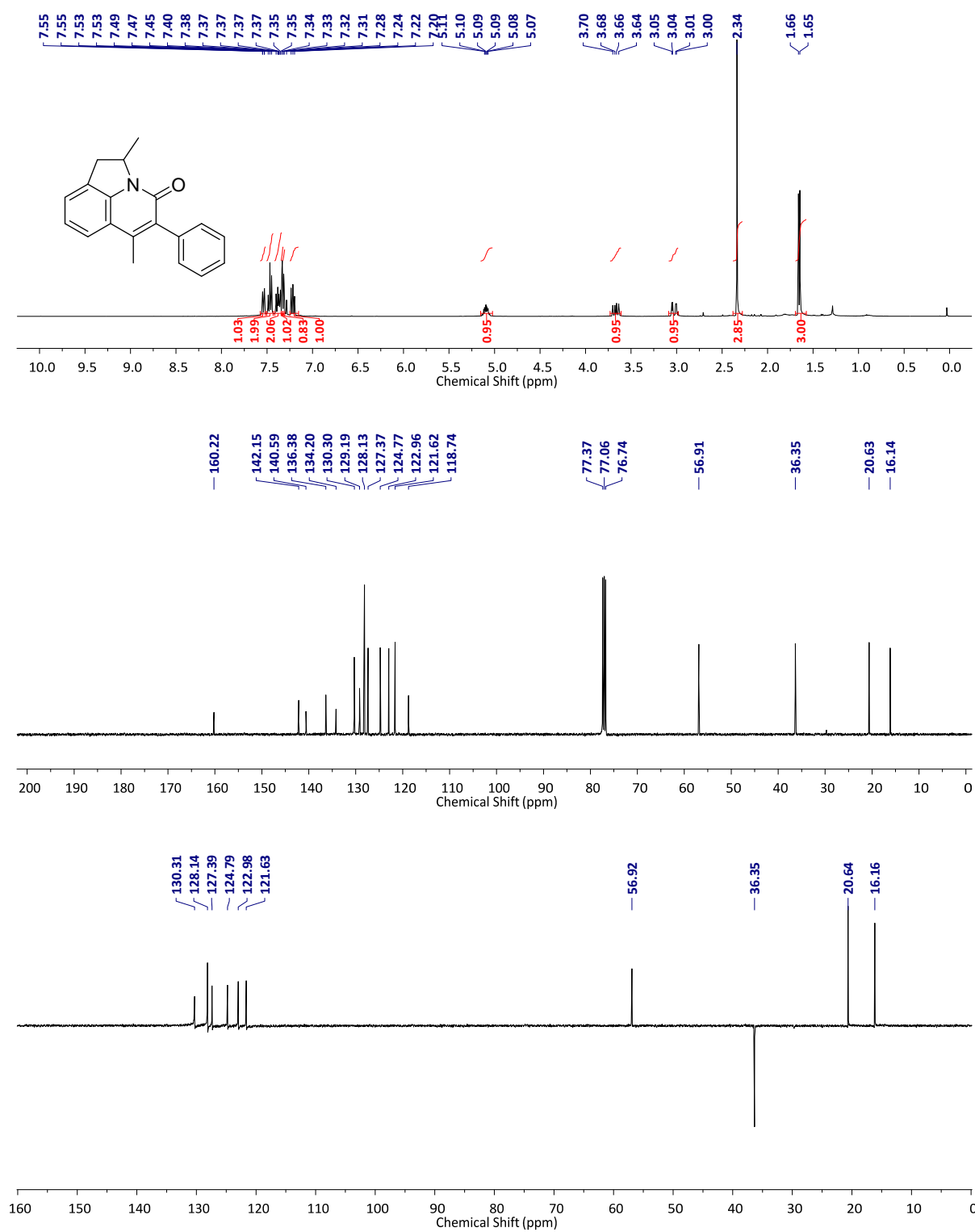
# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 3ba.



# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3bh.

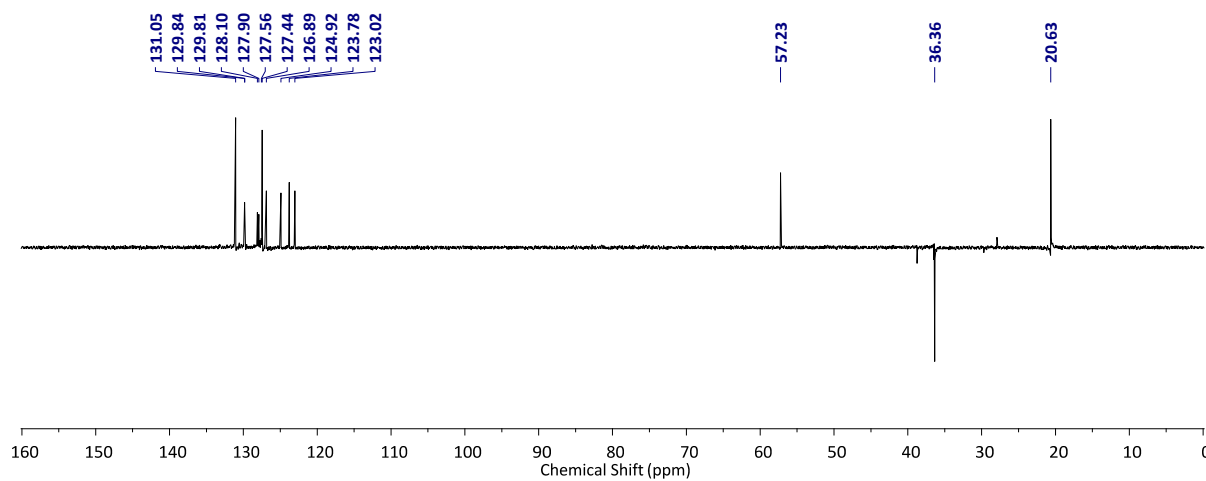
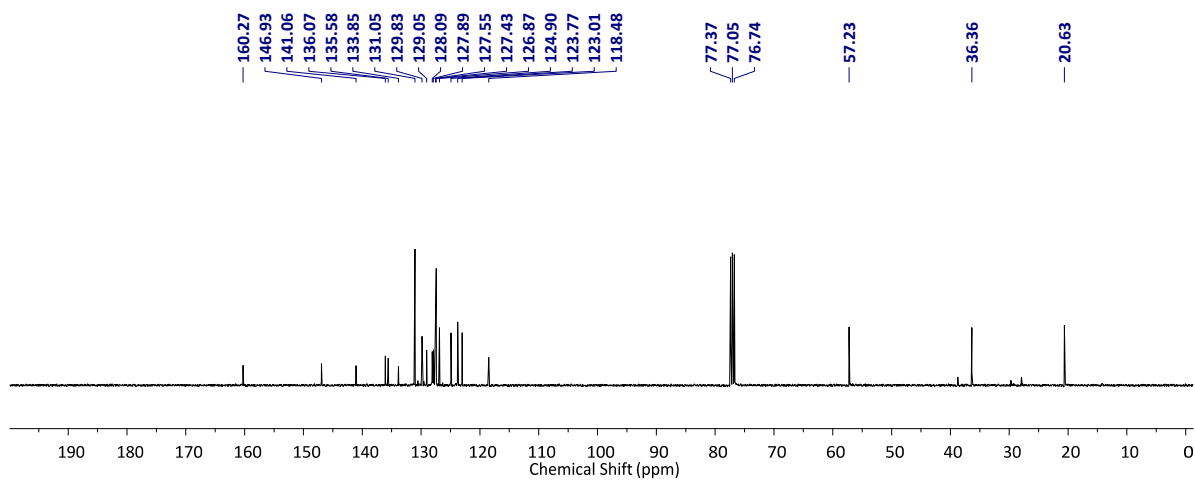
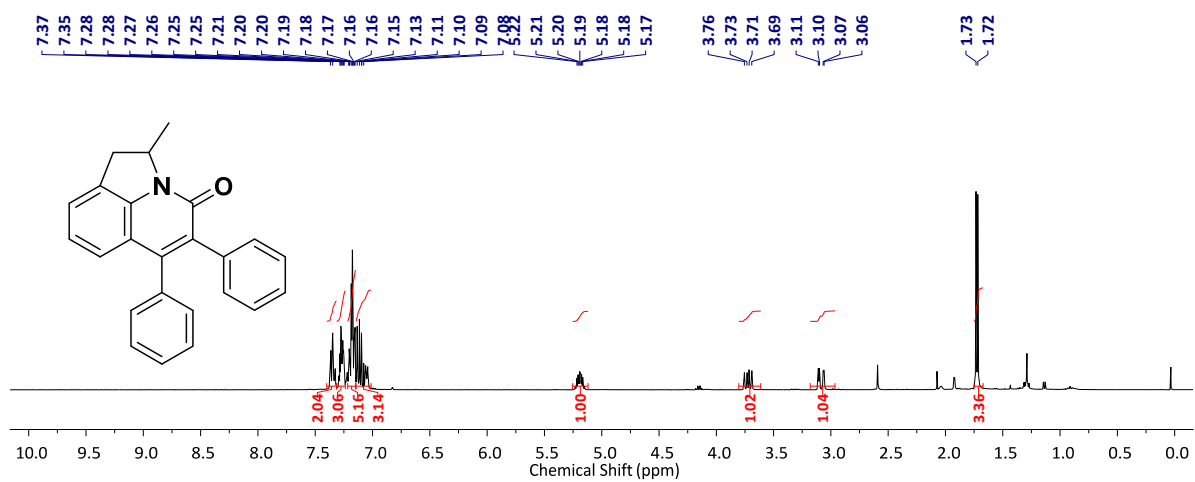


# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ca.

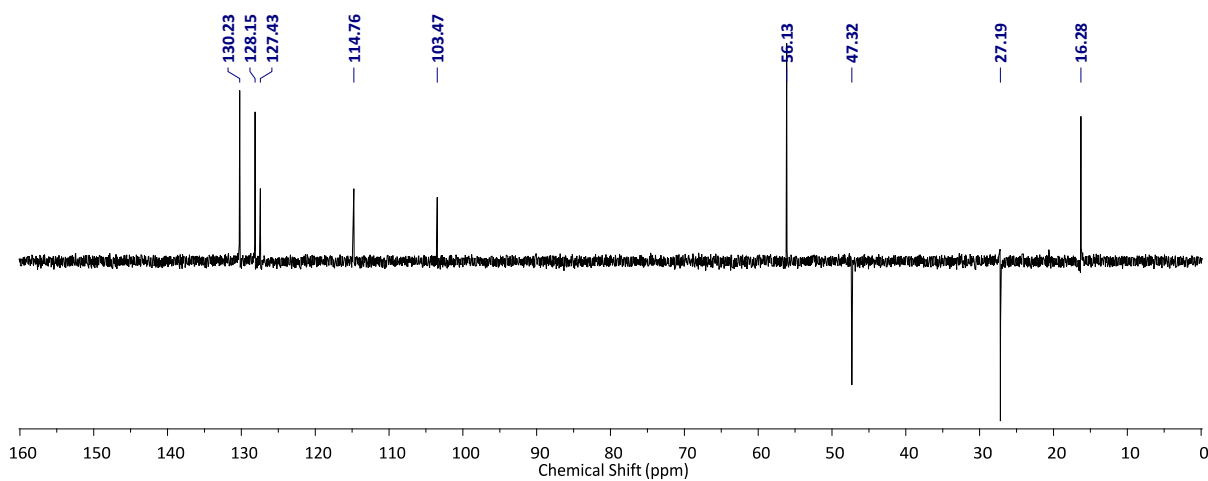
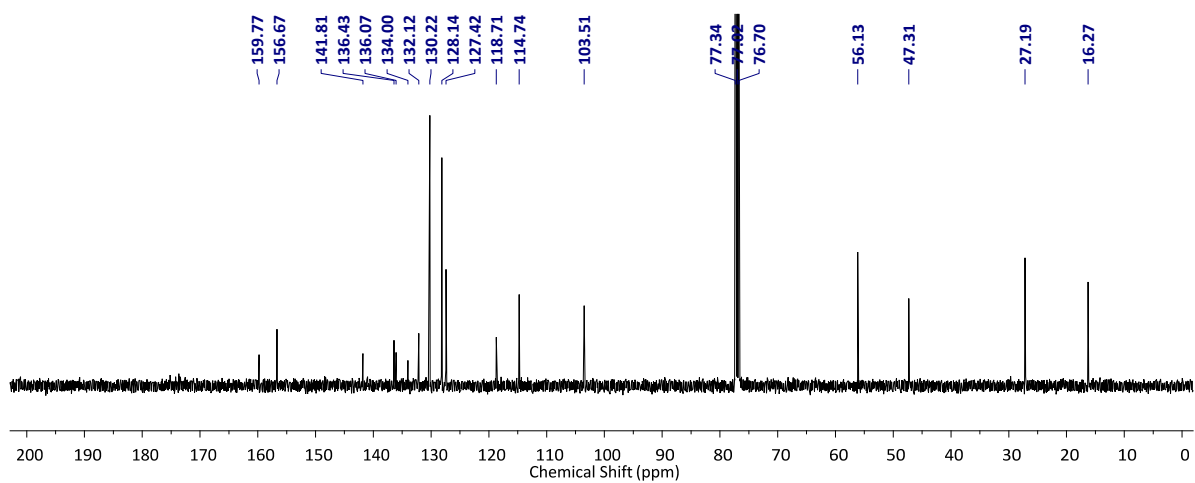
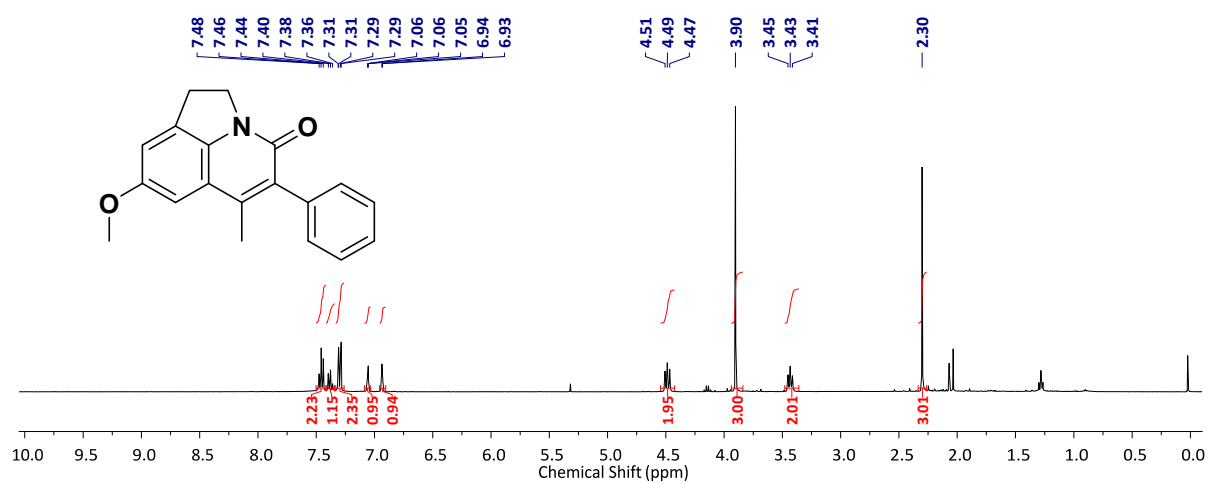




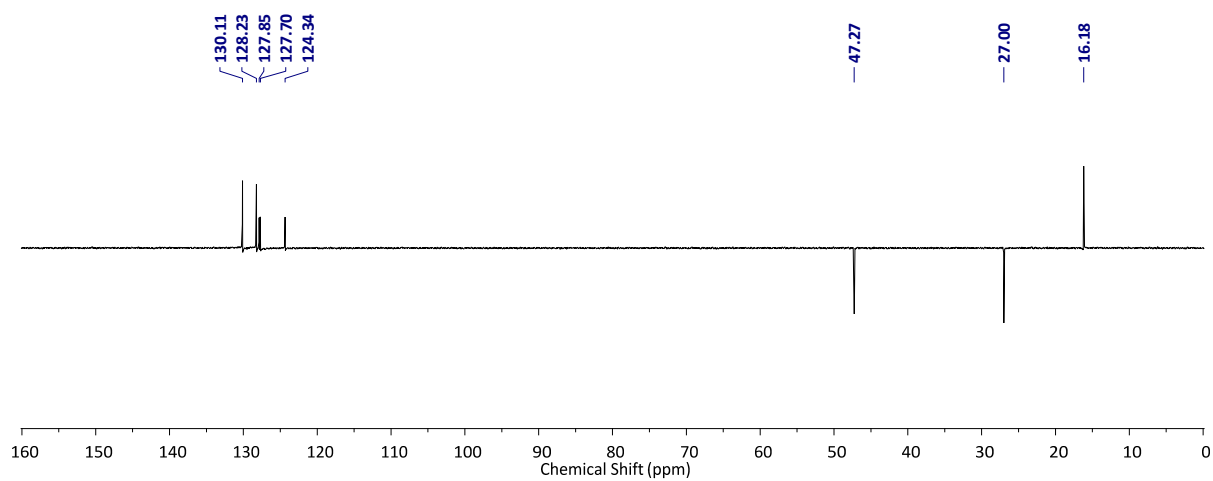
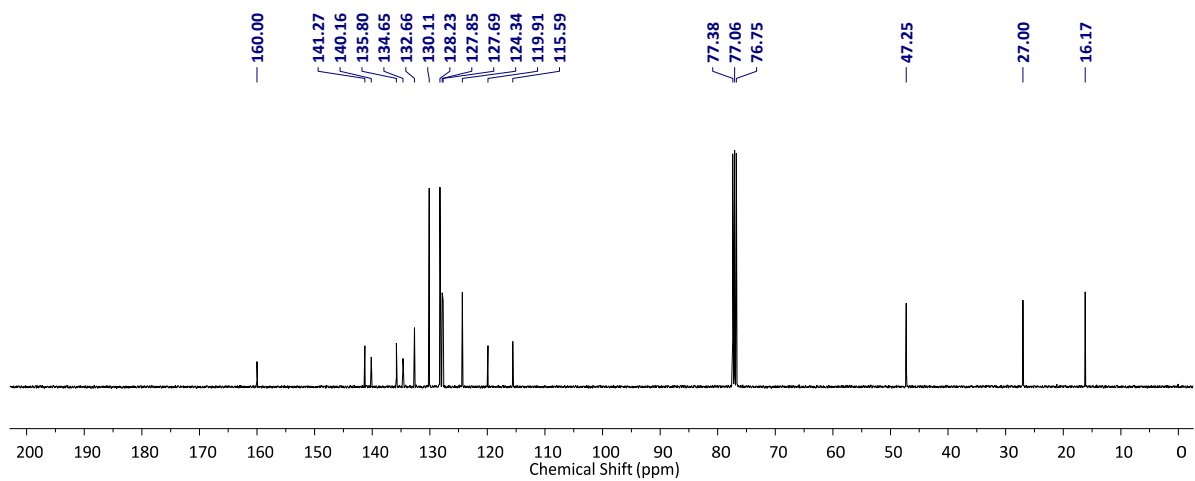
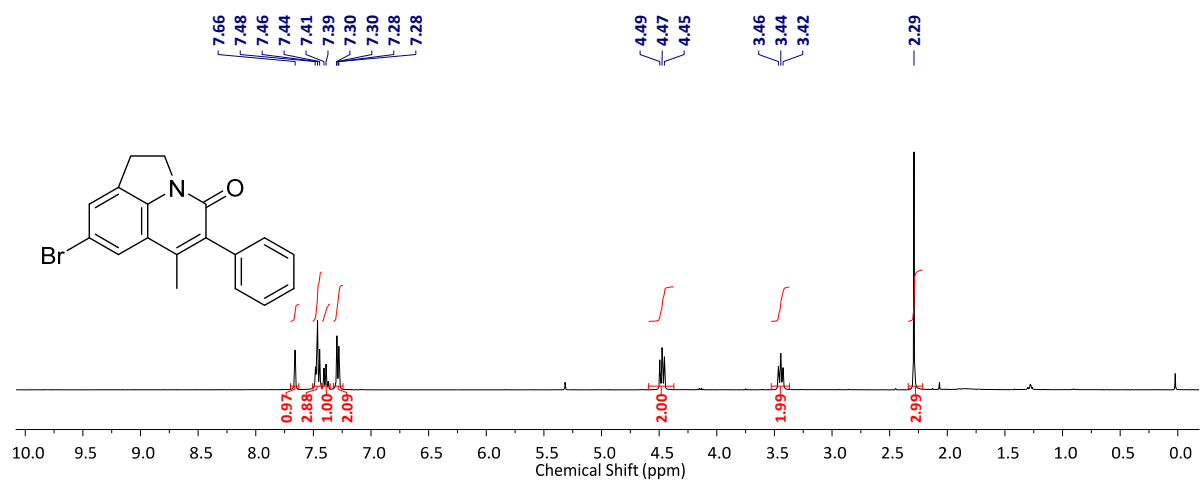
# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 3ch.



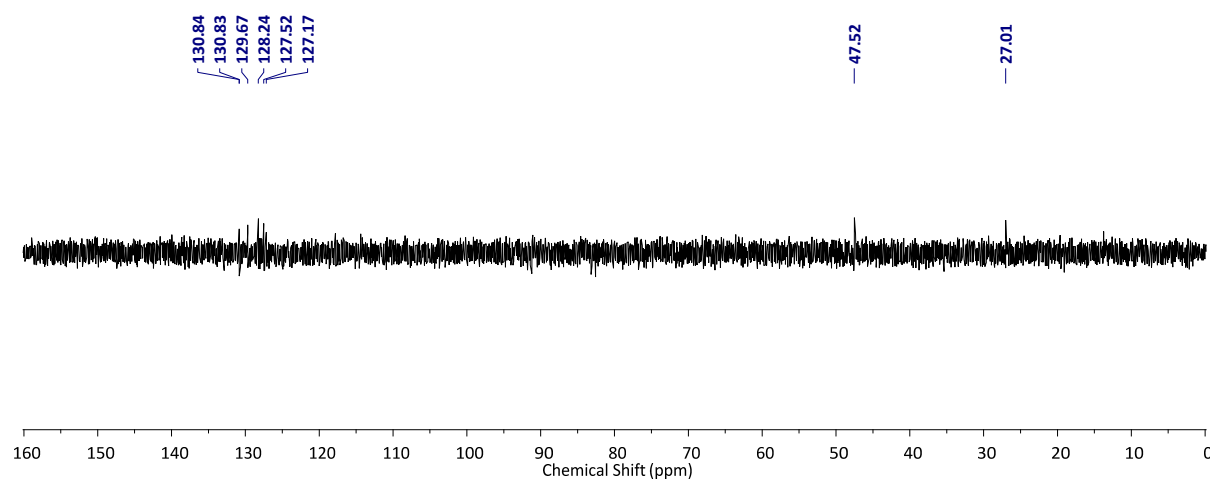
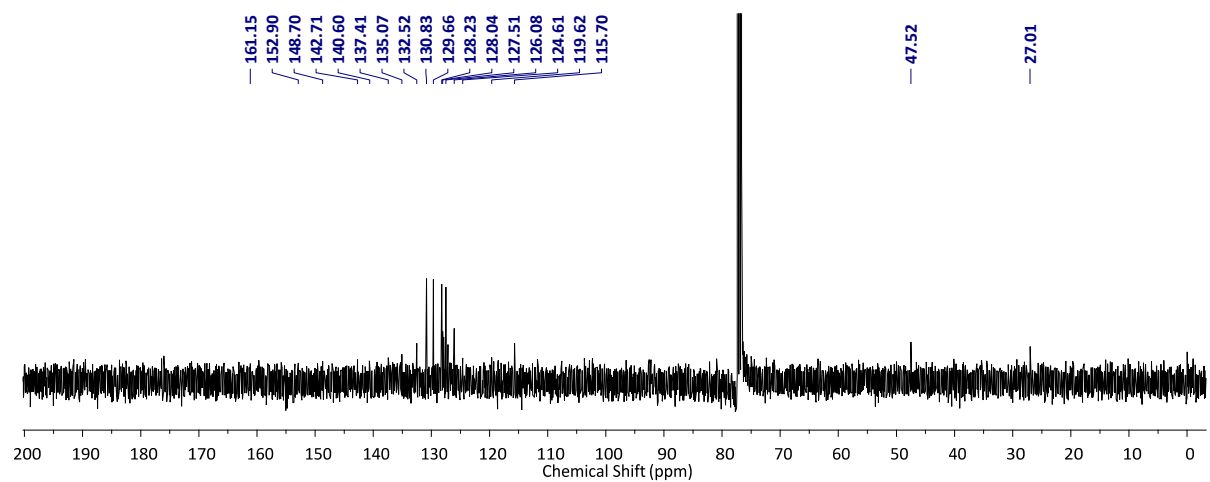
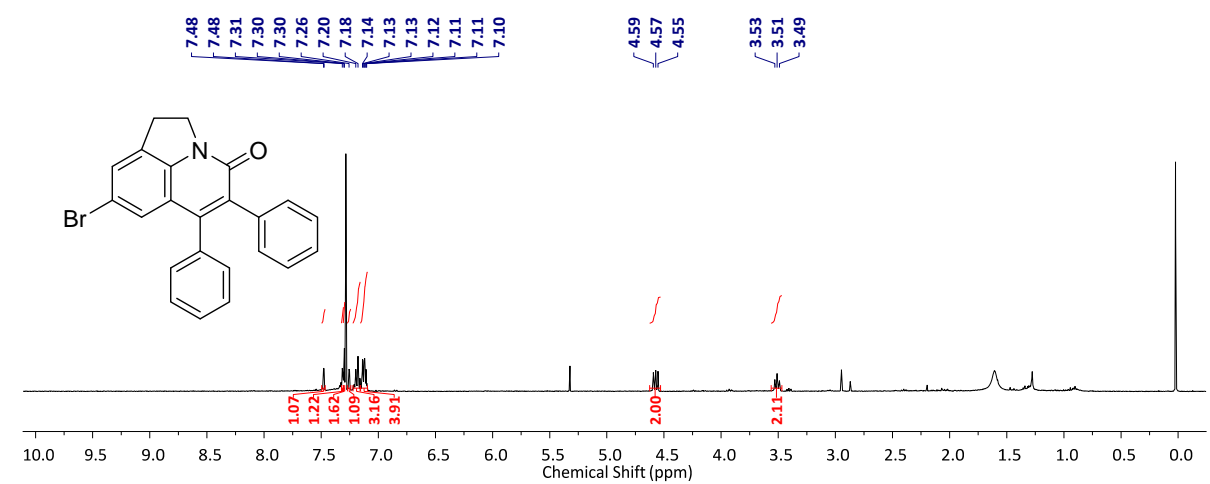
# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 3da.



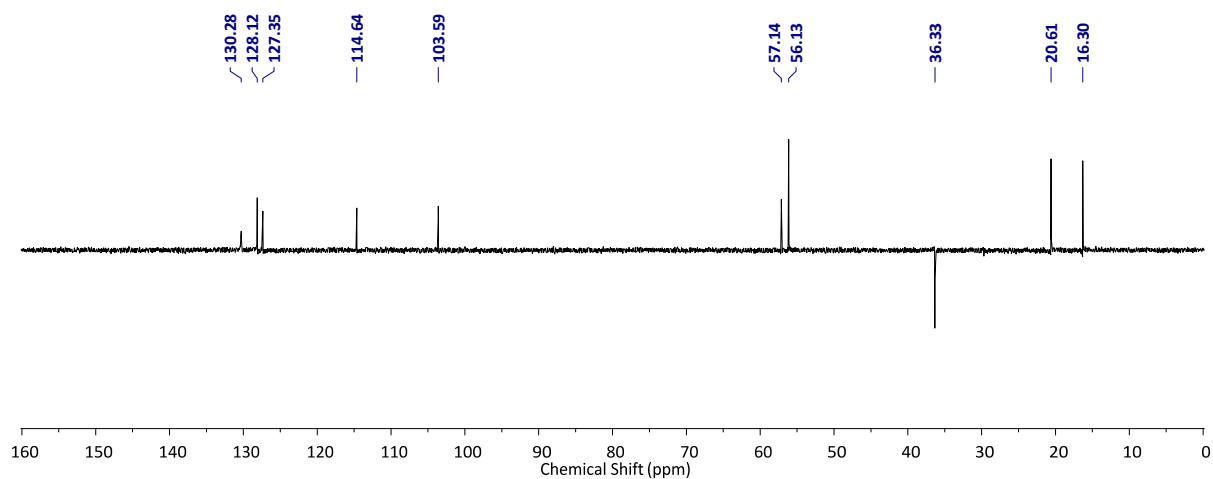
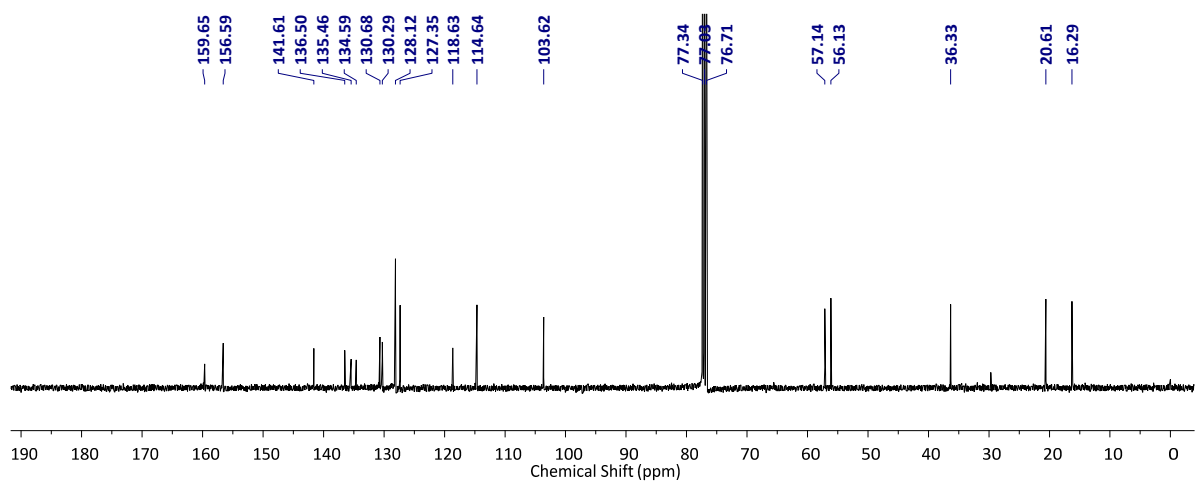
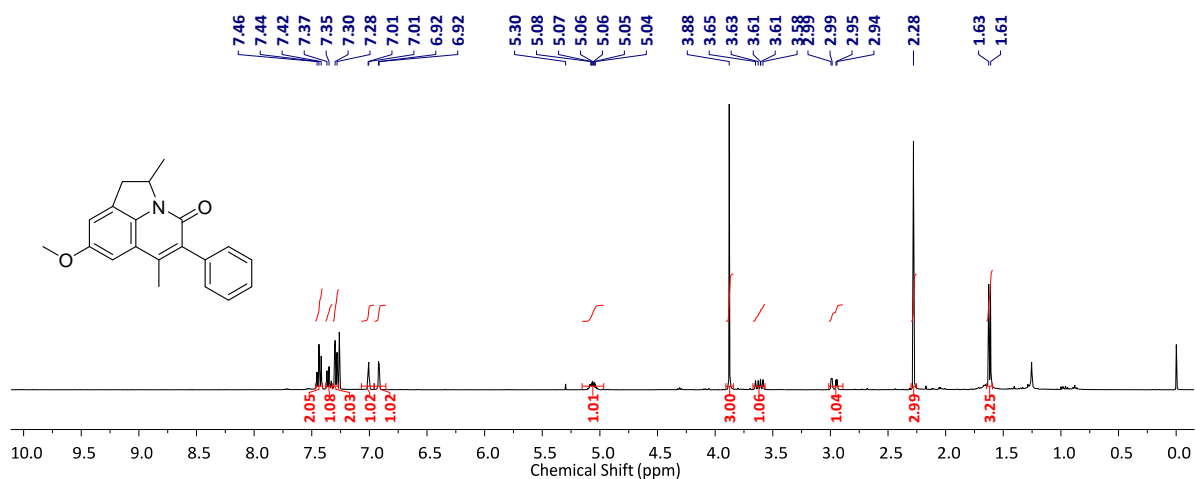
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ea.



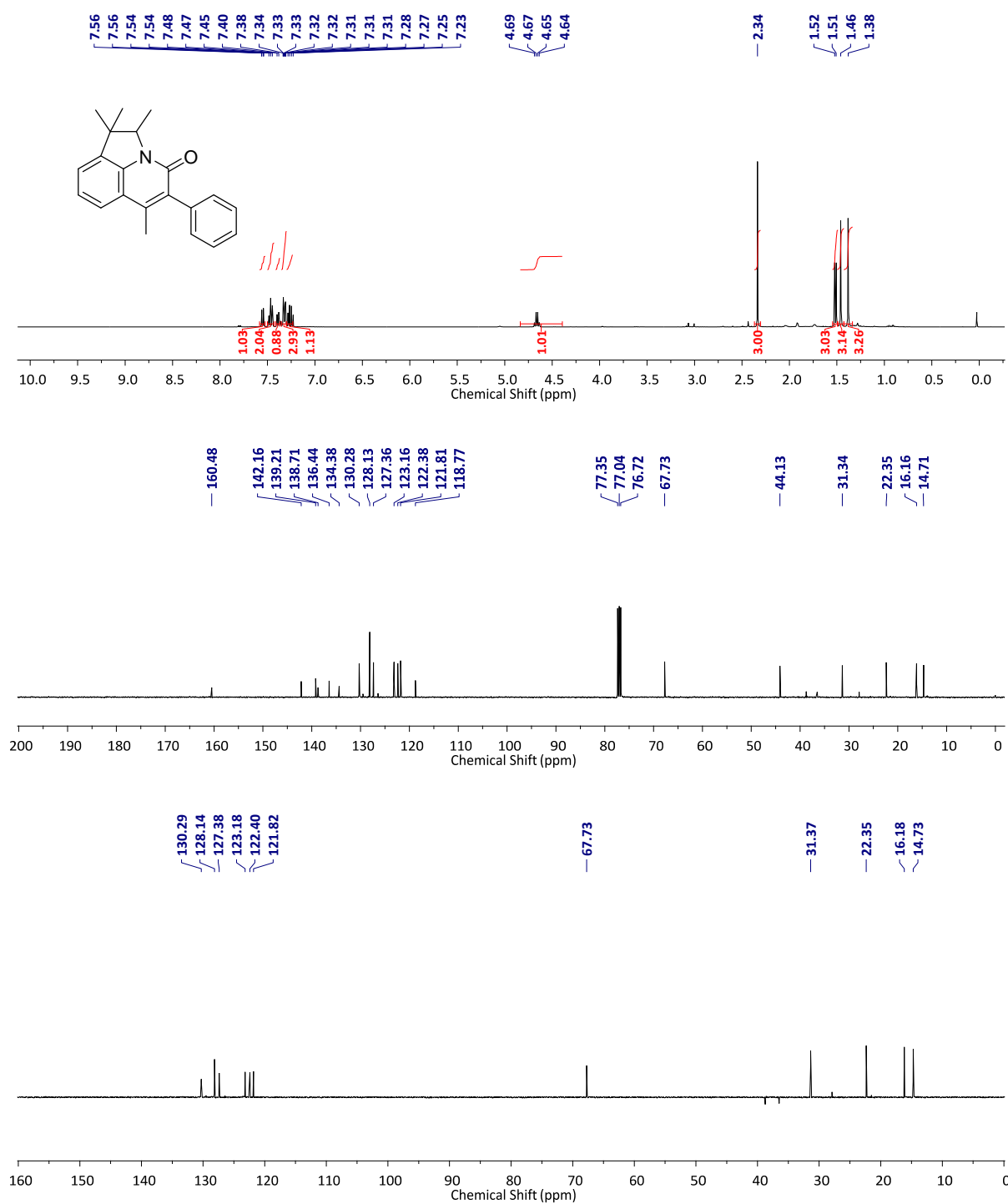
# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 3eh.



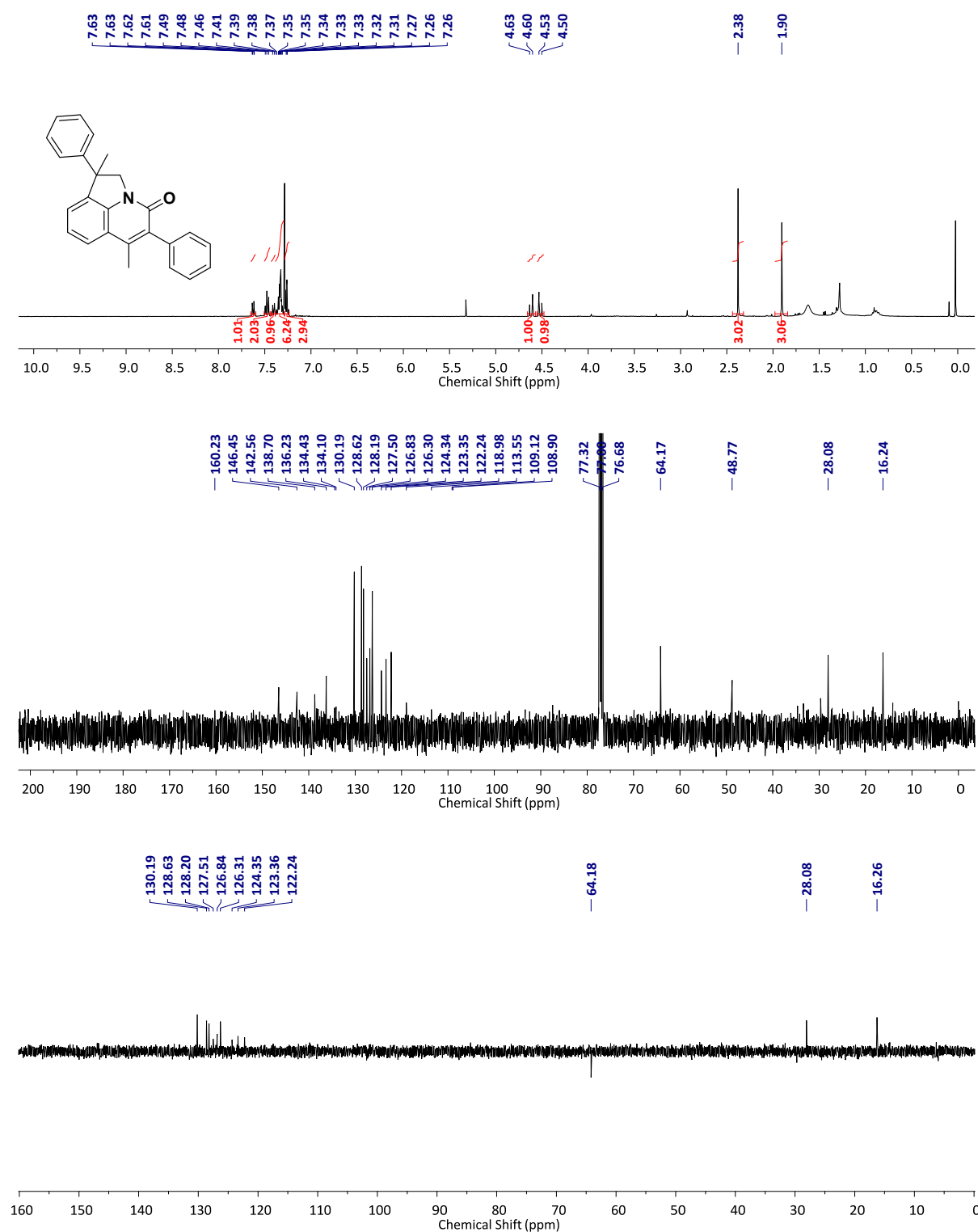
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3fa.



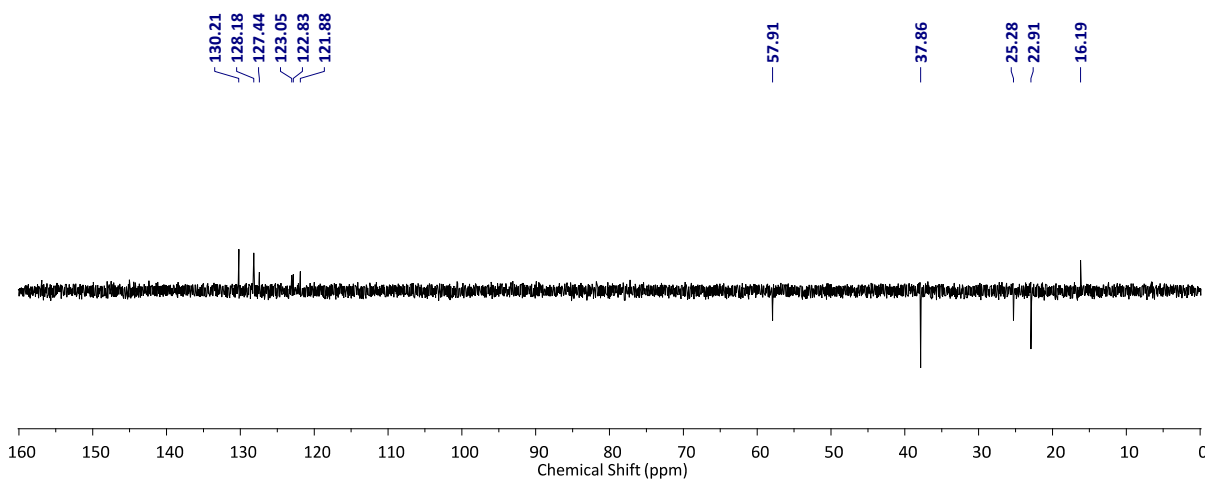
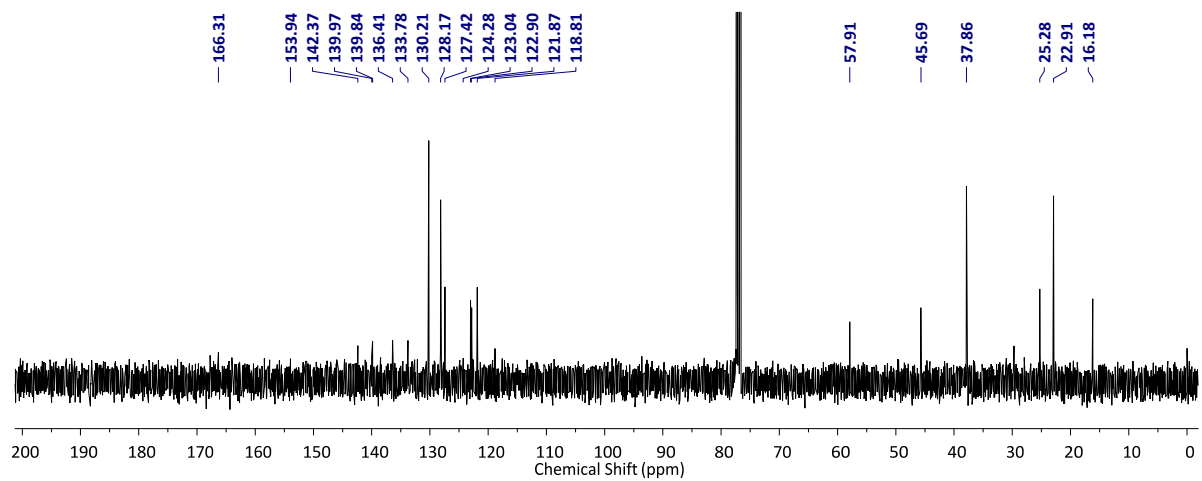
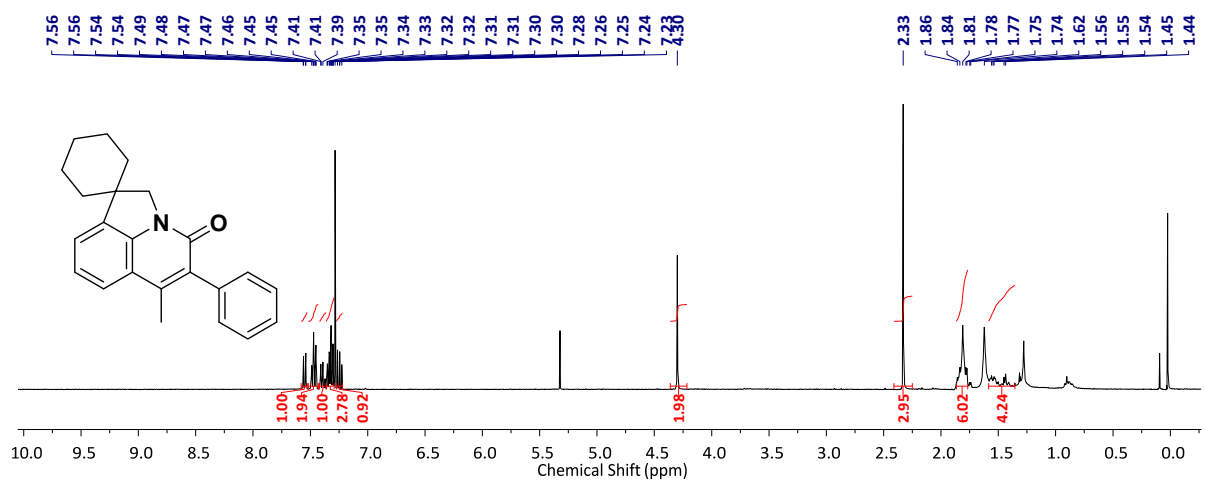
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ga.



# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 3ha.

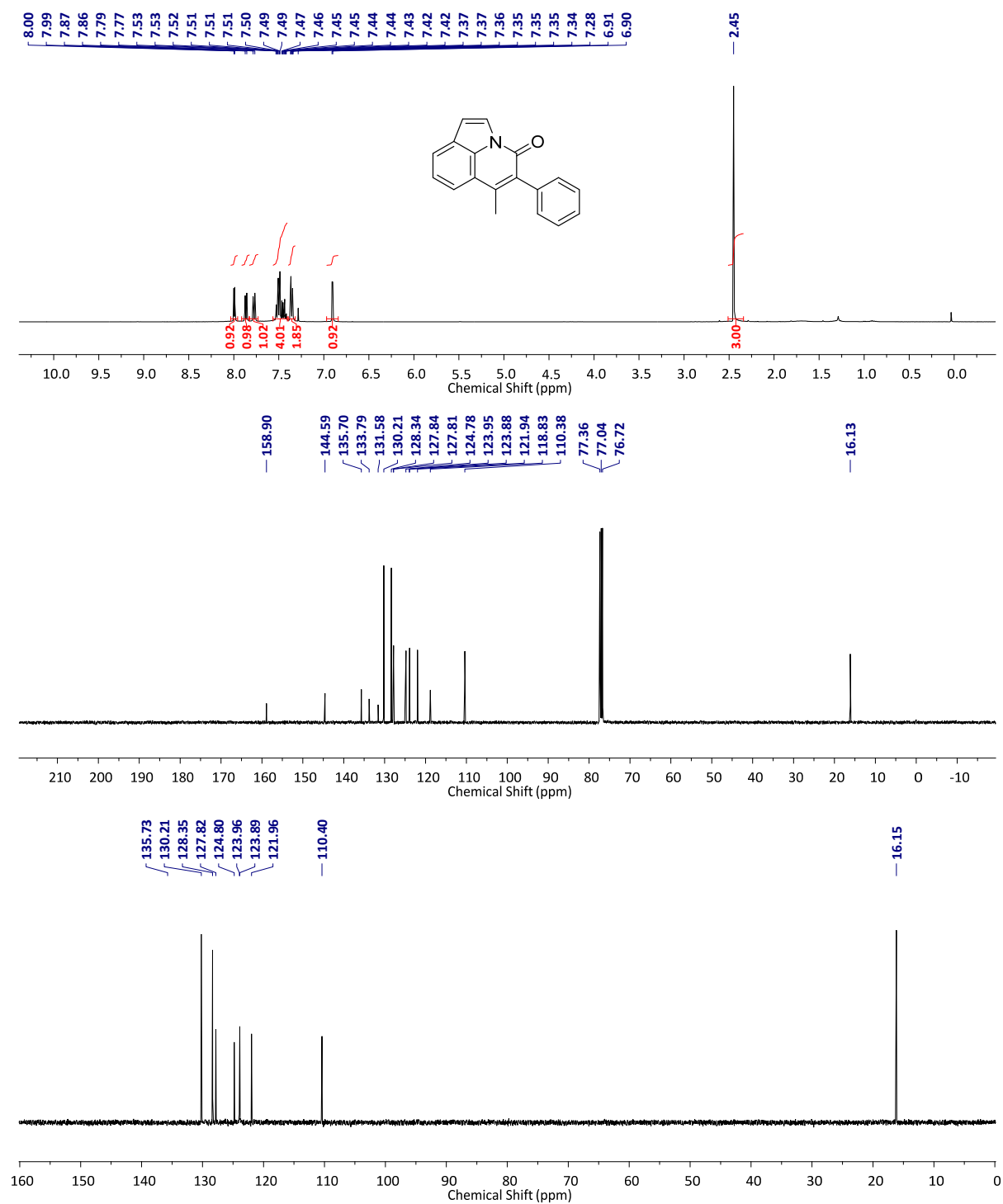


# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ia.





# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 4a.



# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 4b.

