**Supporting Information**

# Ruthenium-Catalyzed (Spiro)Annulation of *N*-Aryl-2,3-dihydrophthalazine-1,4-diones with Quinones to Access Pentacyclic Spiro-Indazolones and Fused-Cinnolines

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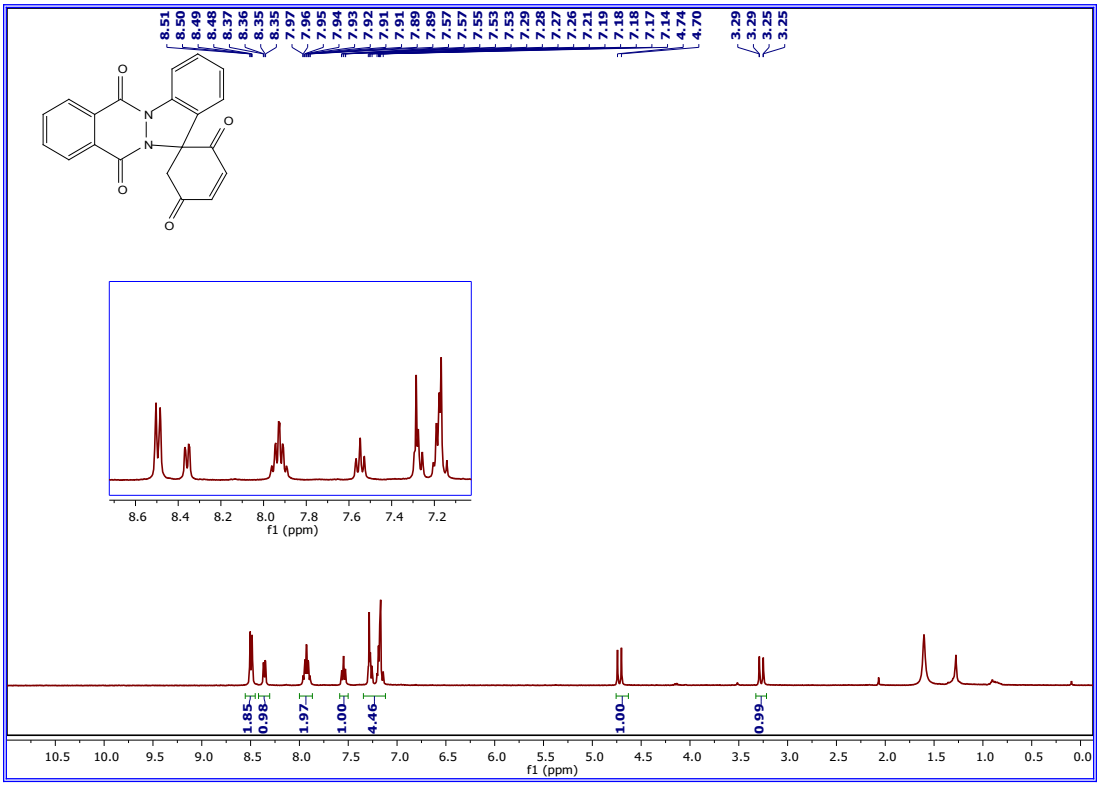
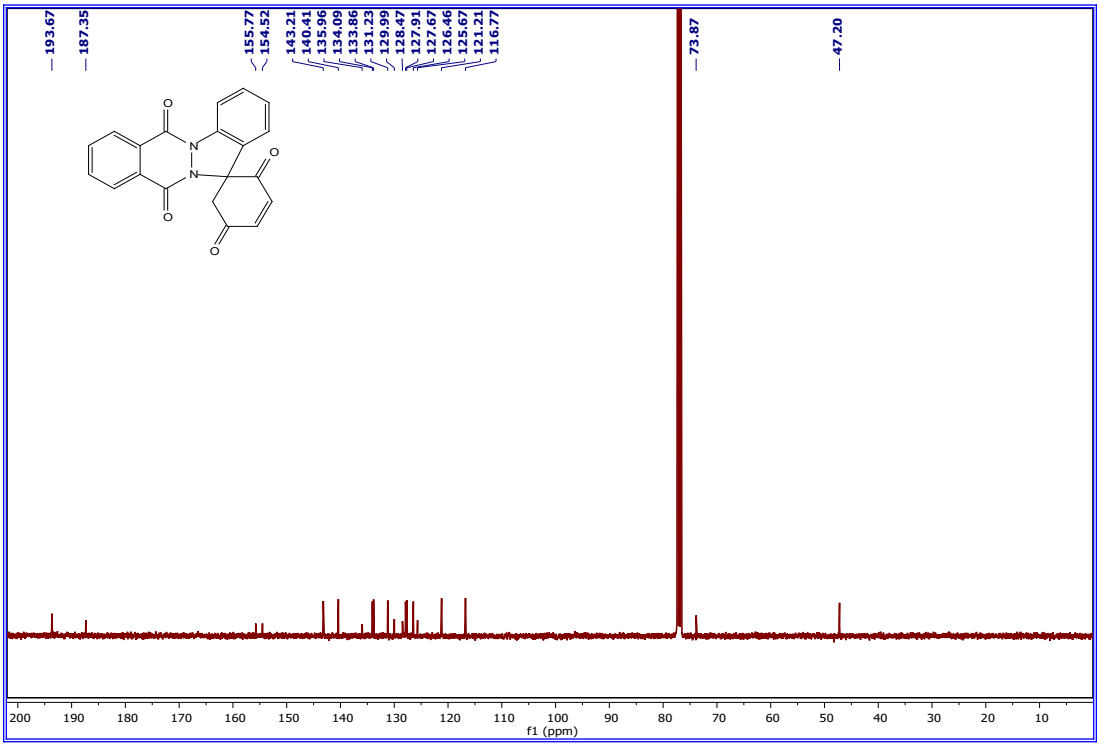
## 1. $^{1}H$ and $^{13}C$ Spectra of 3 & 4

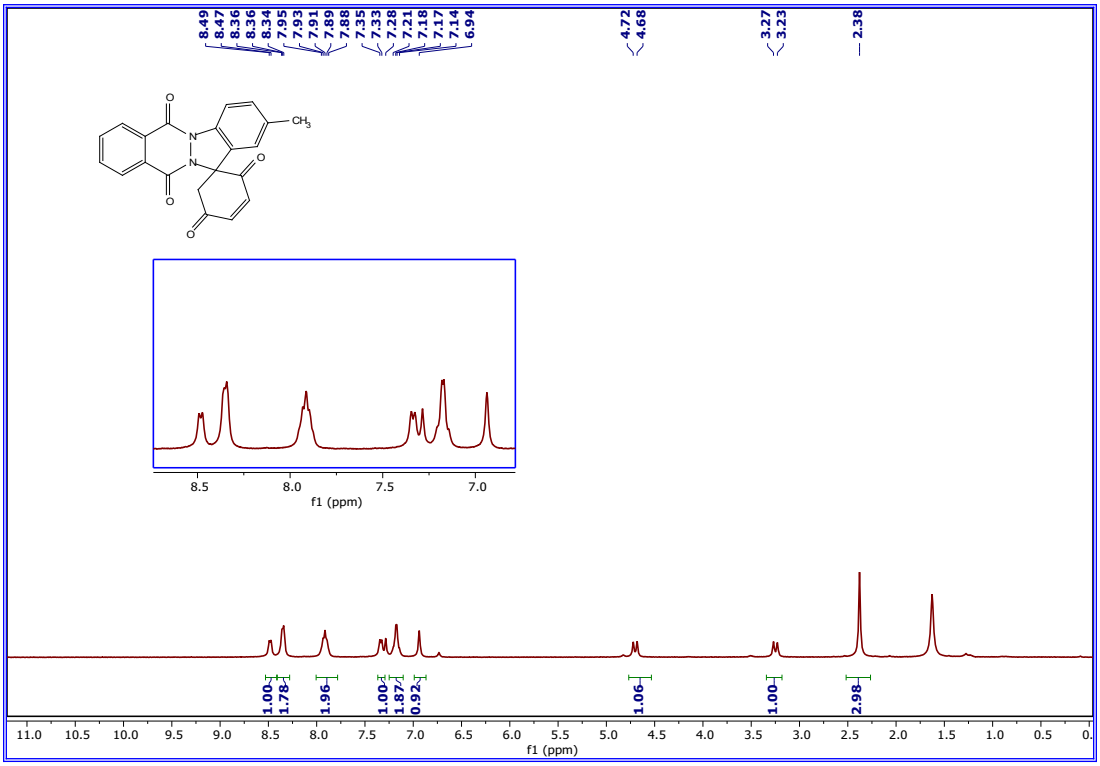
### $^{1}H$ NMR of 3aa



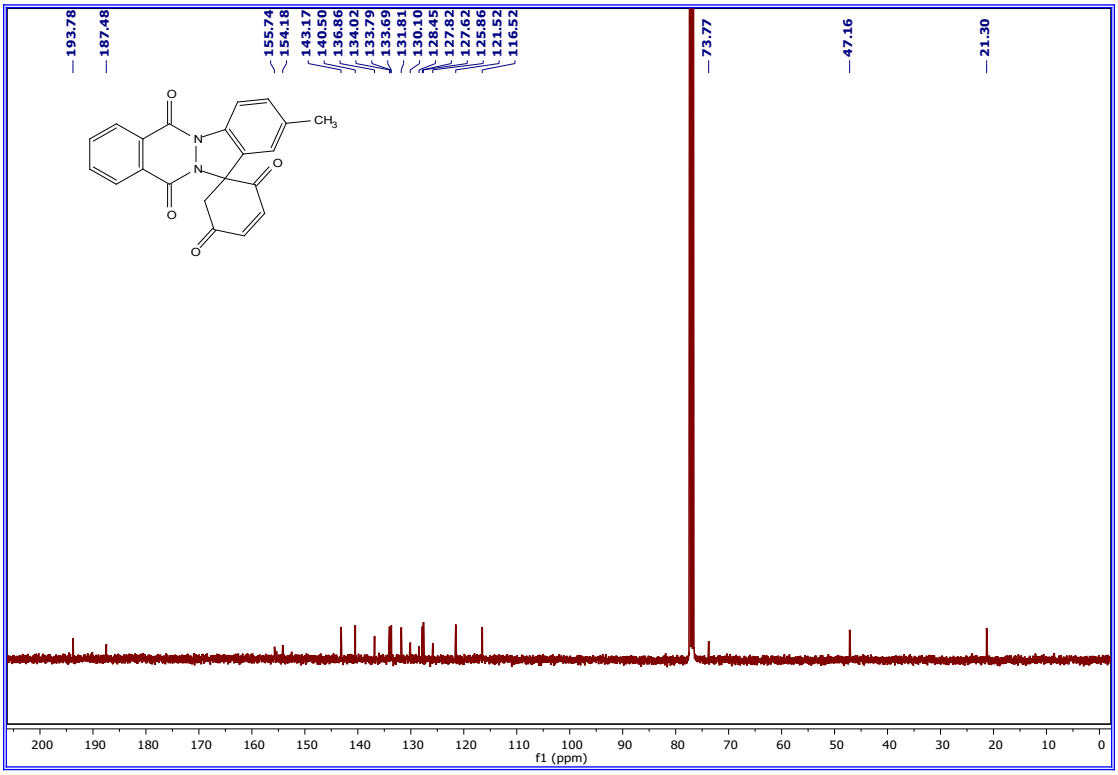

### $^{13}C$ NMR of 3aa



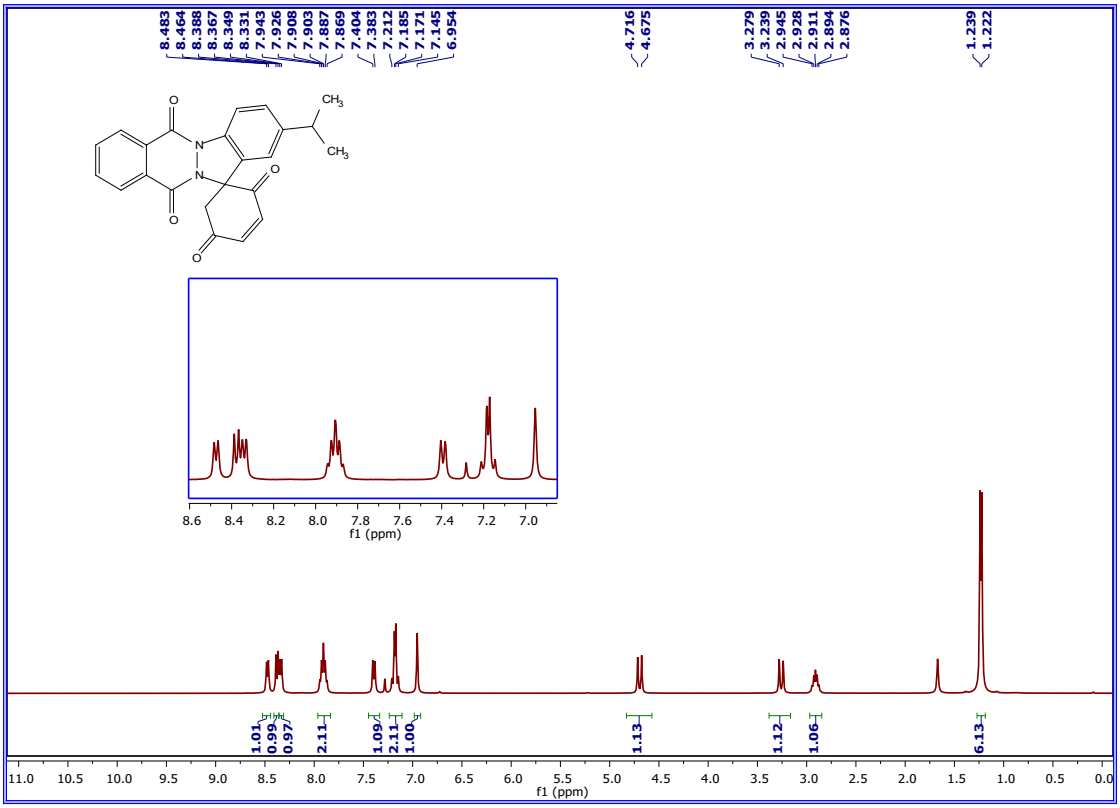
## $^{1}$H NMR of 3ba




## $^{13}$C NMR of 3ba



## $^{1}$H NMR of 3ca

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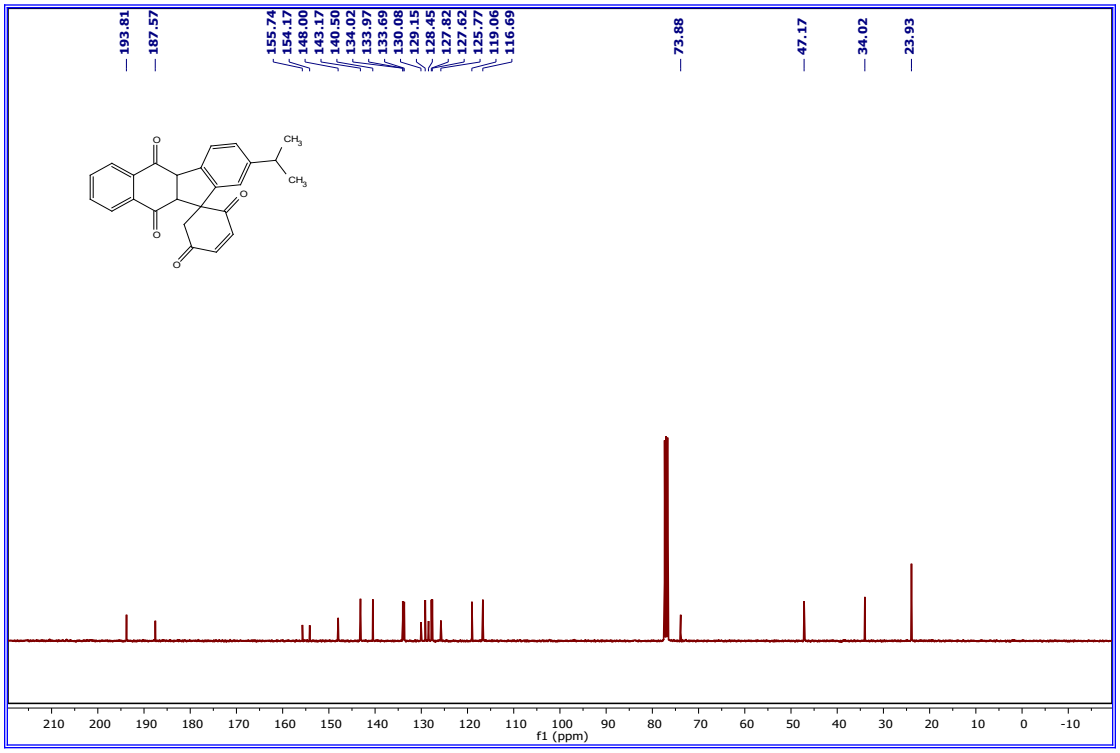
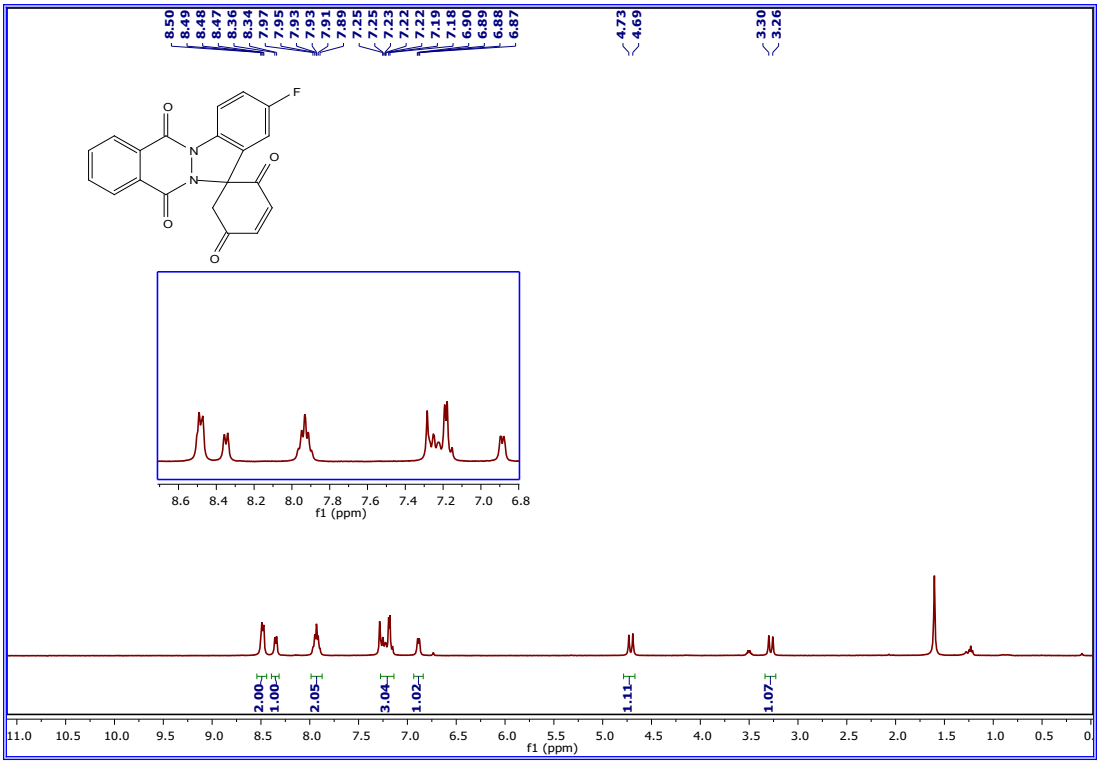


## $^{1}$H NMR of 3da

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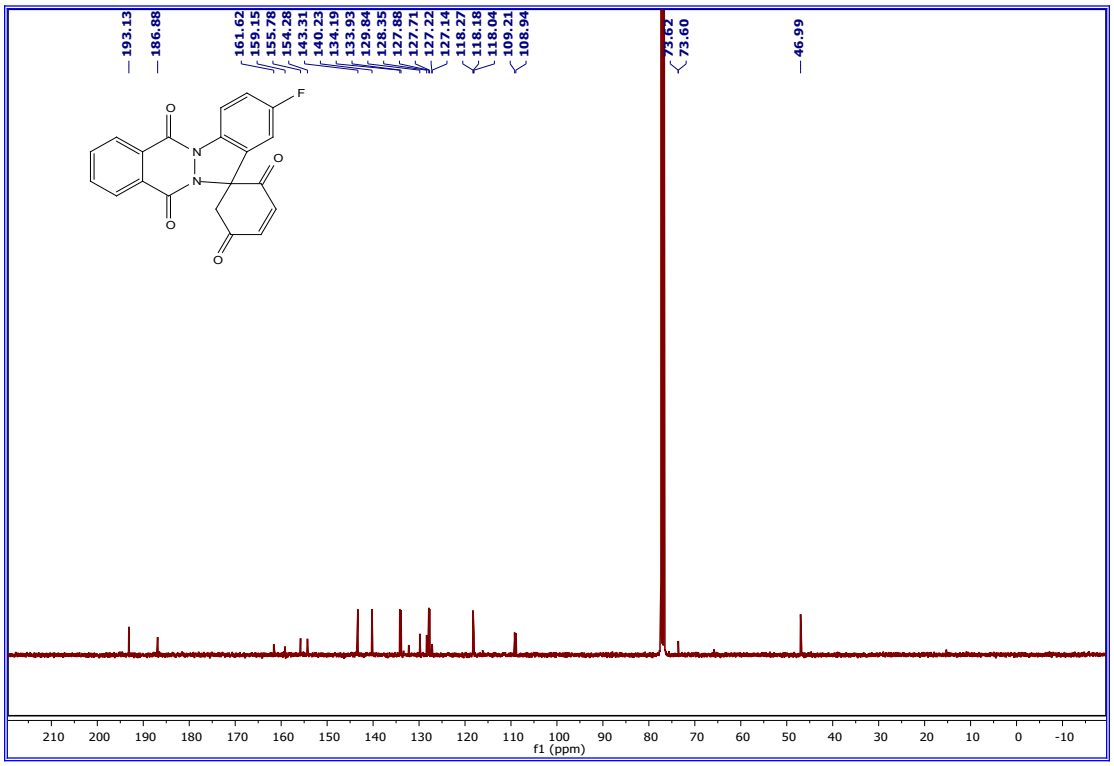

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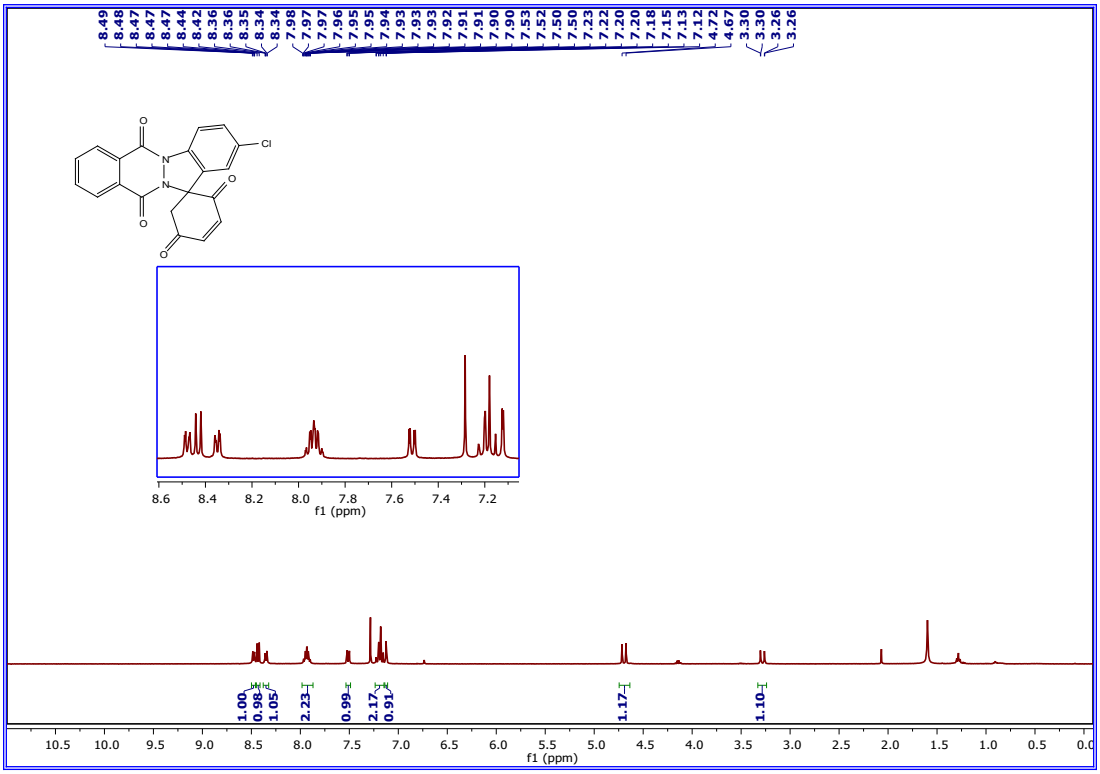


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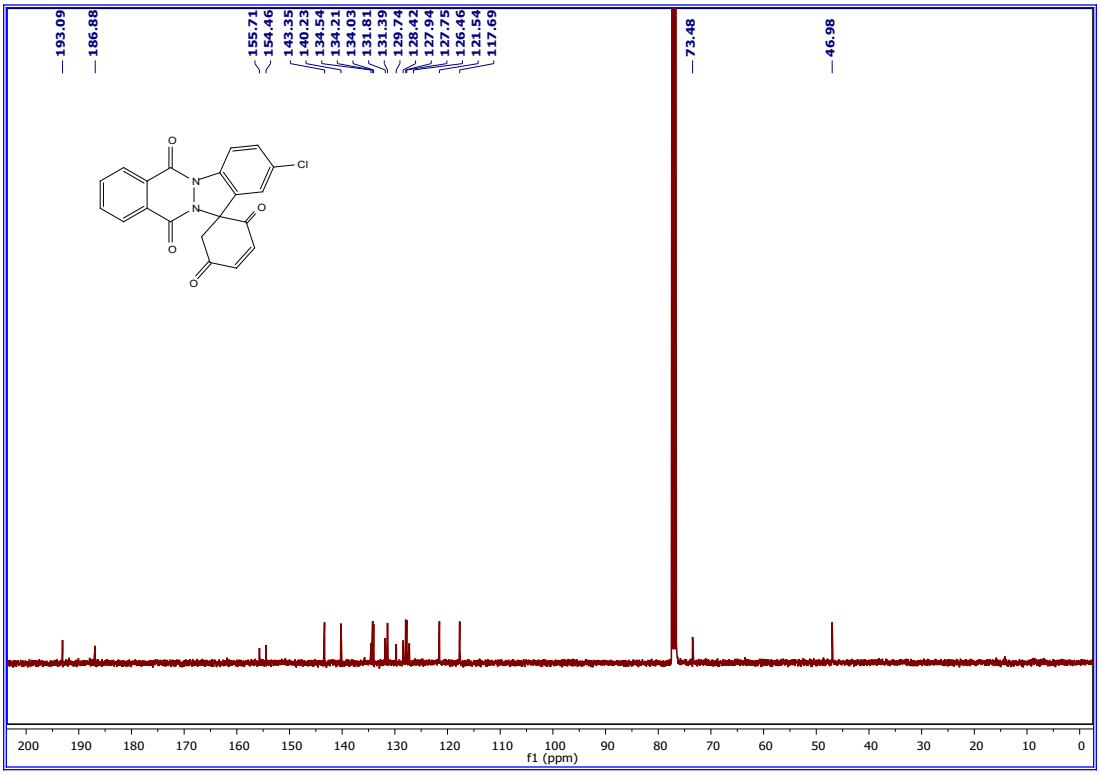

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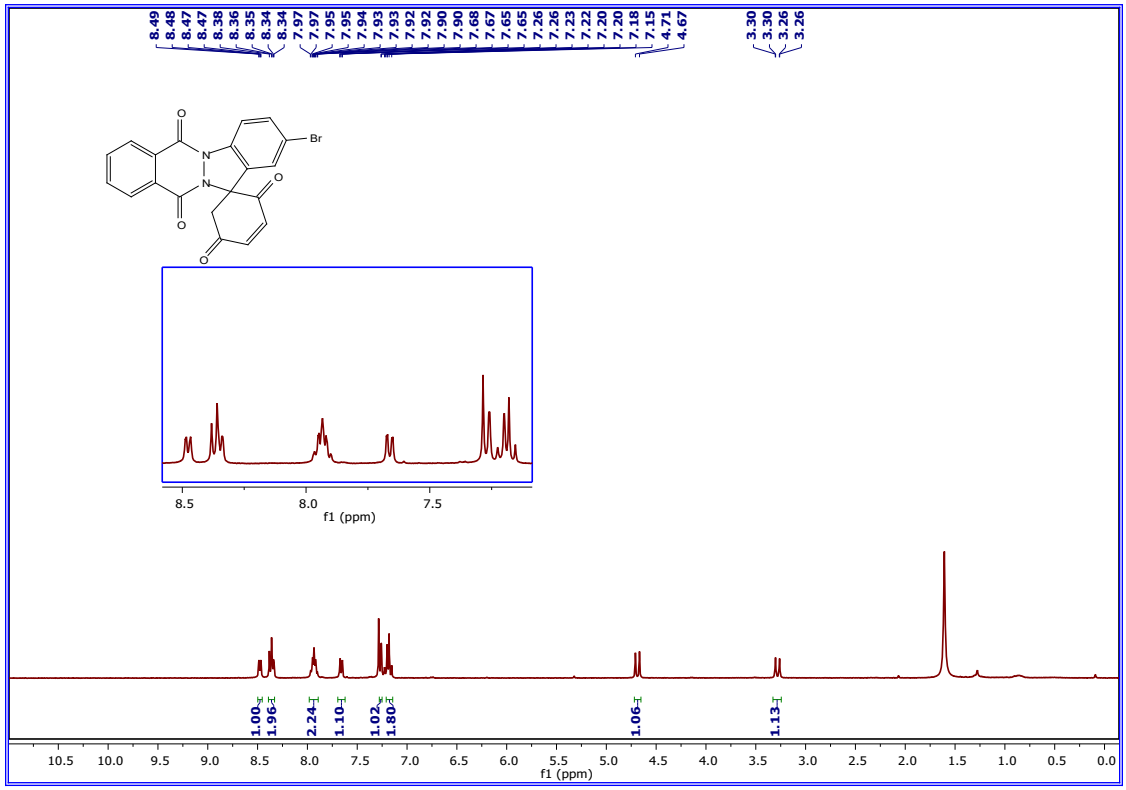
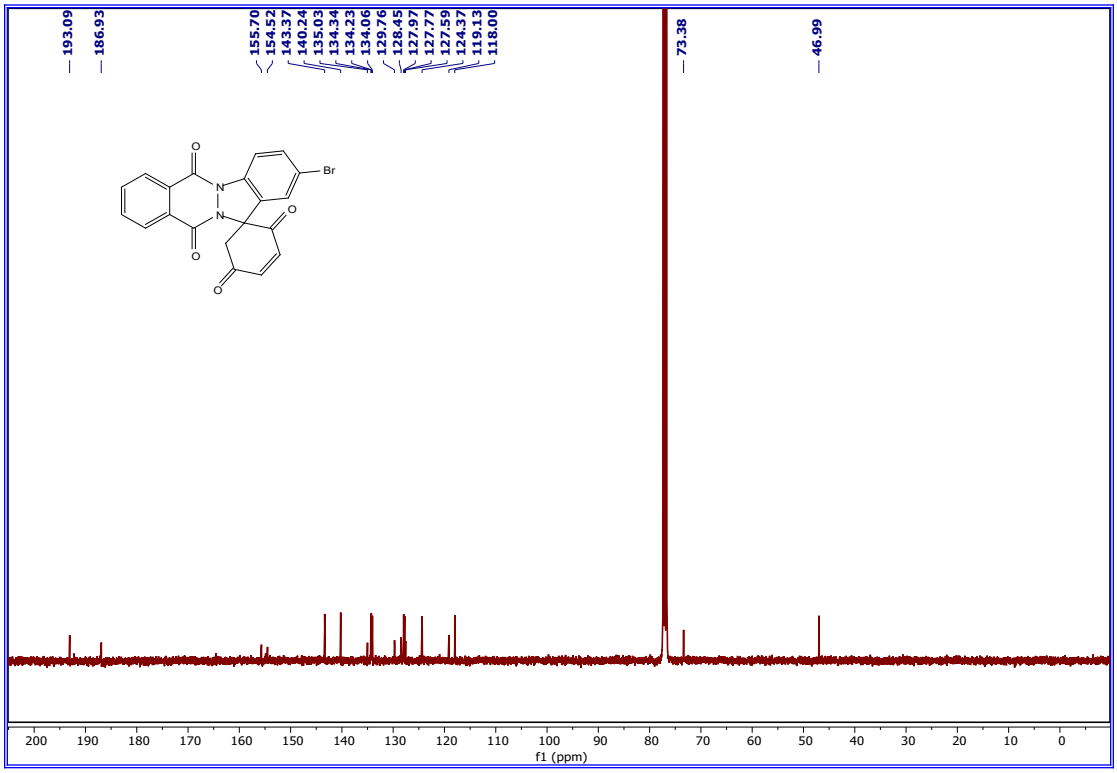



## $^{13}$C NMR of 3fa



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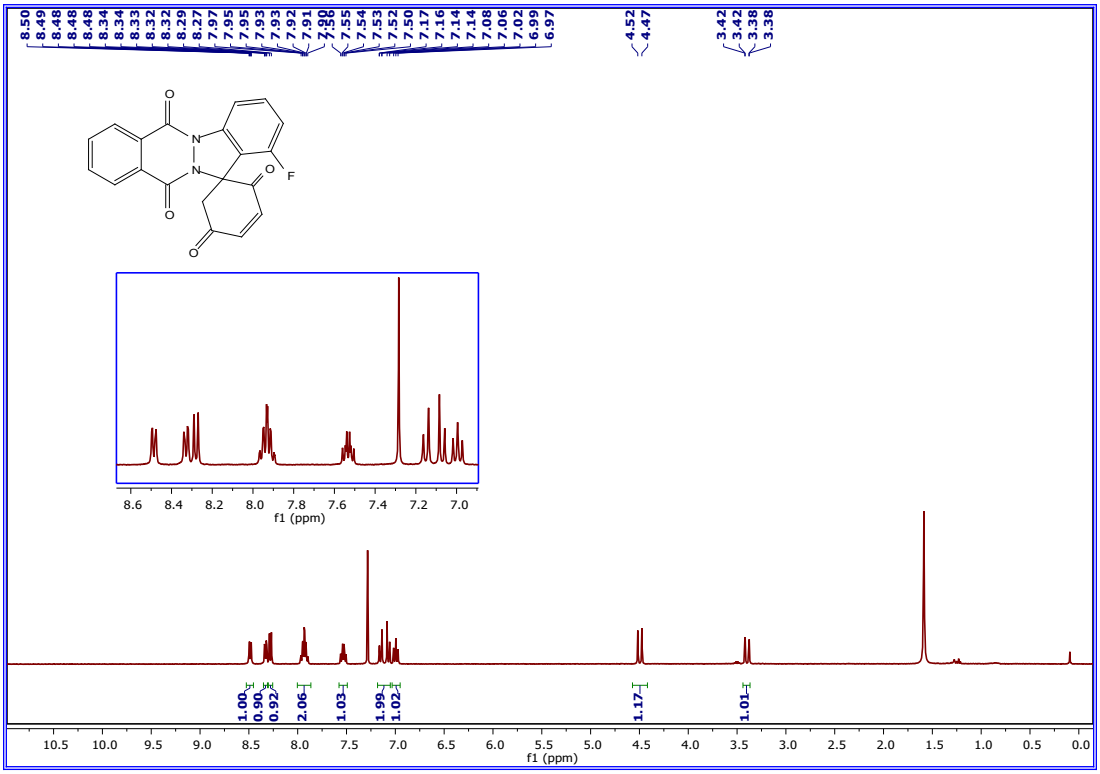
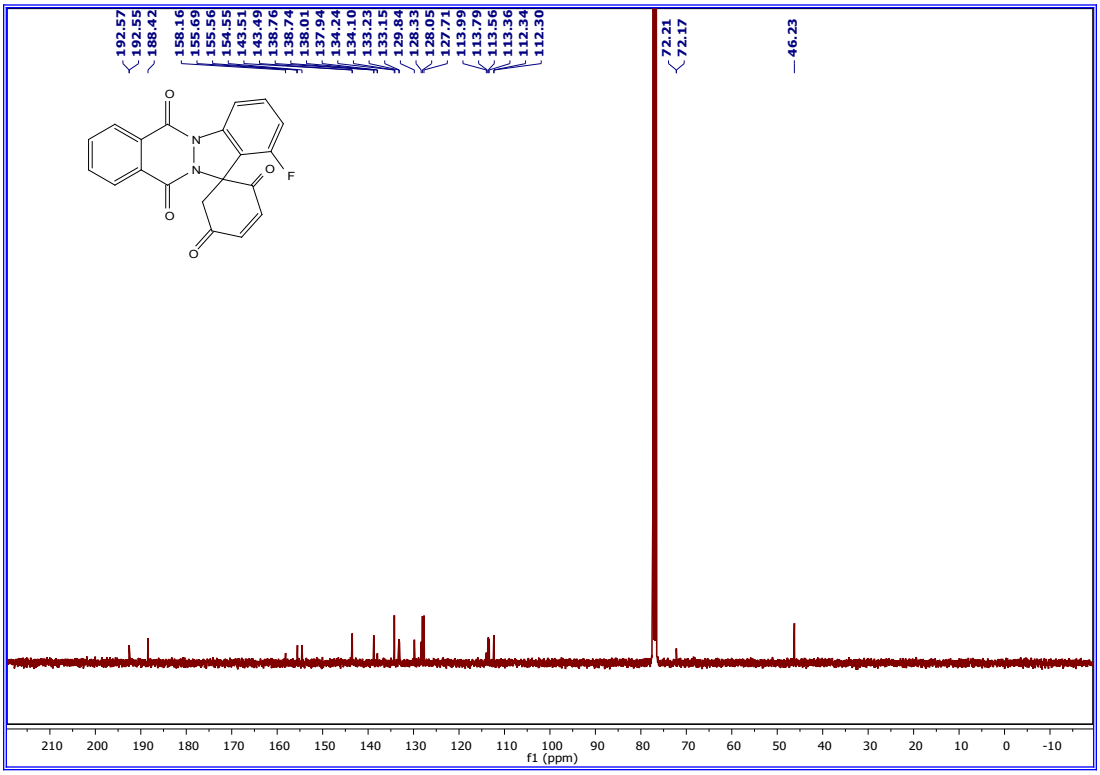
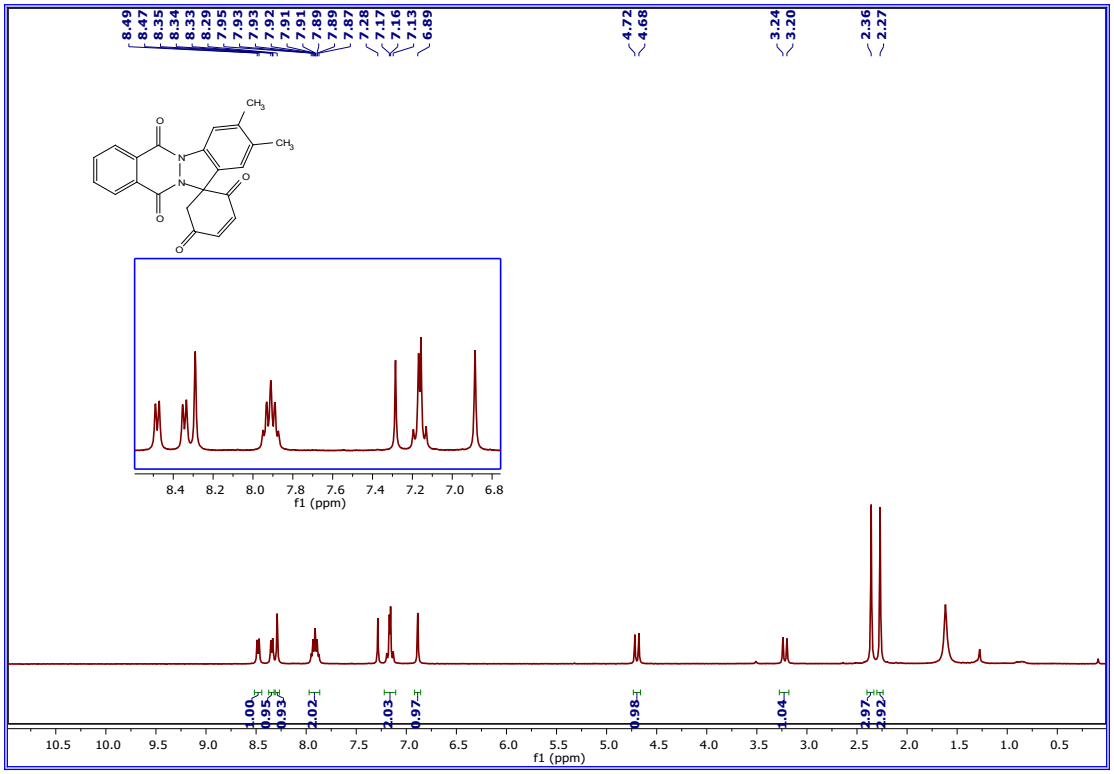


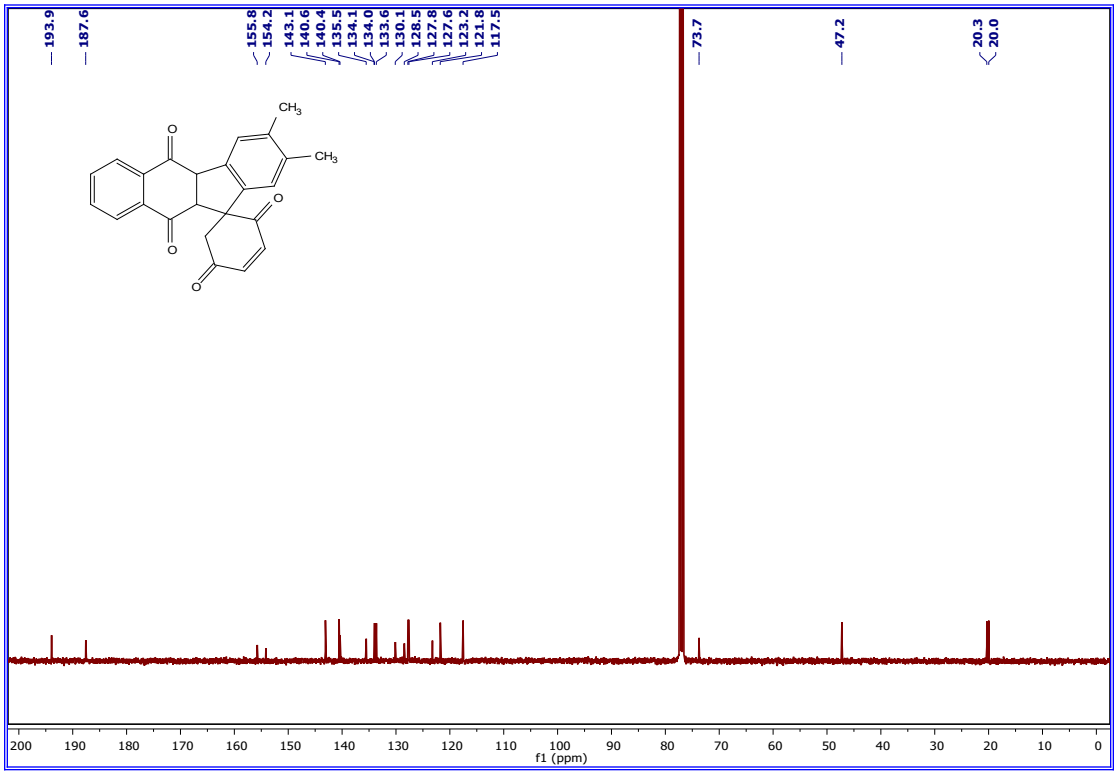

## $^{13}$C NMR of 3ga



## $^{1}$H NMR of 3ha




## $^{13}$C NMR of 3ha



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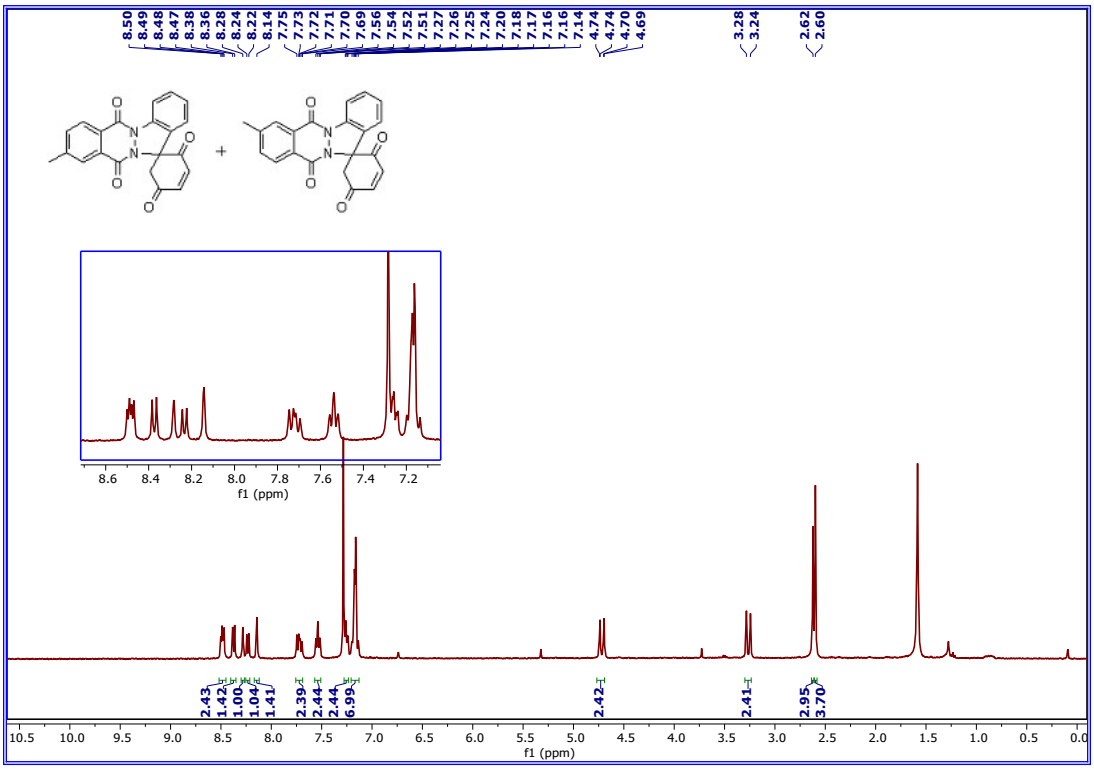


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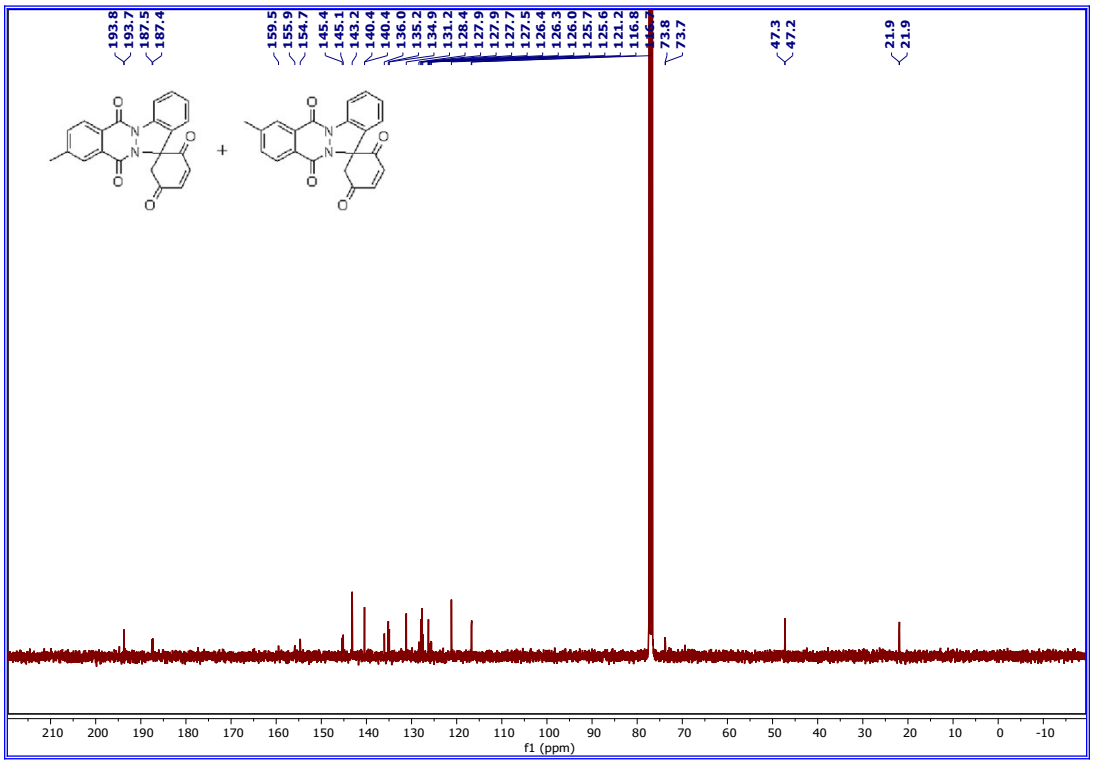
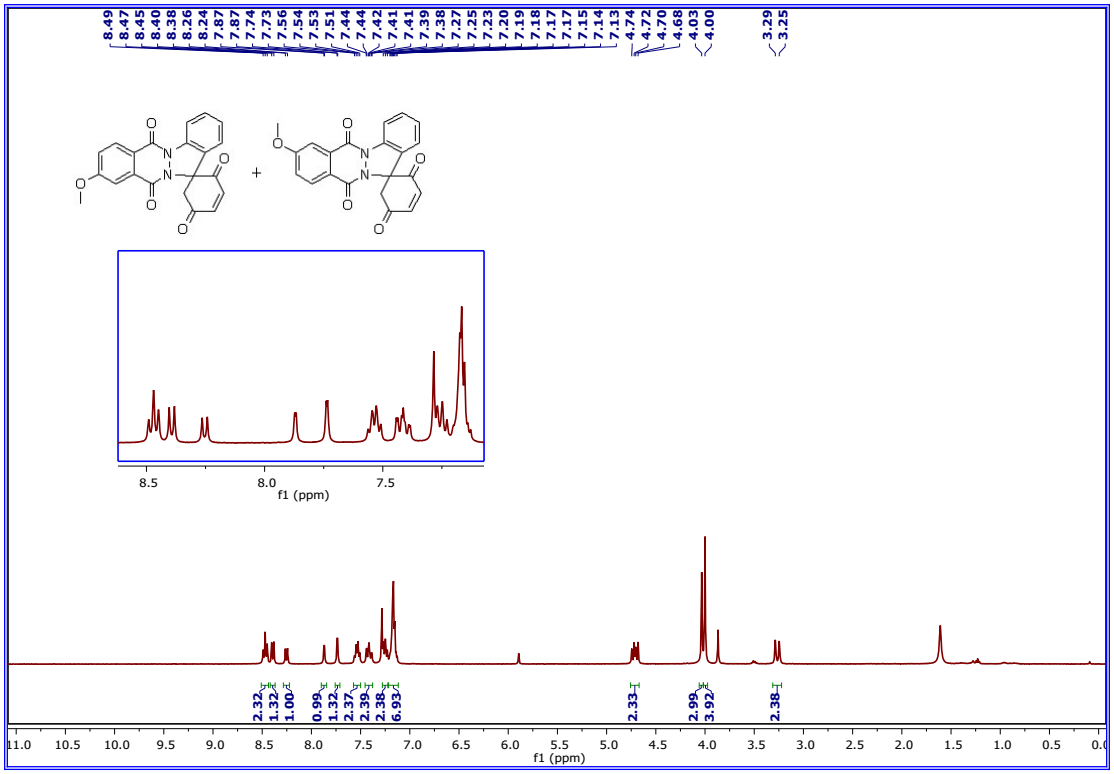


## $^{1}$H NMR of 3ja

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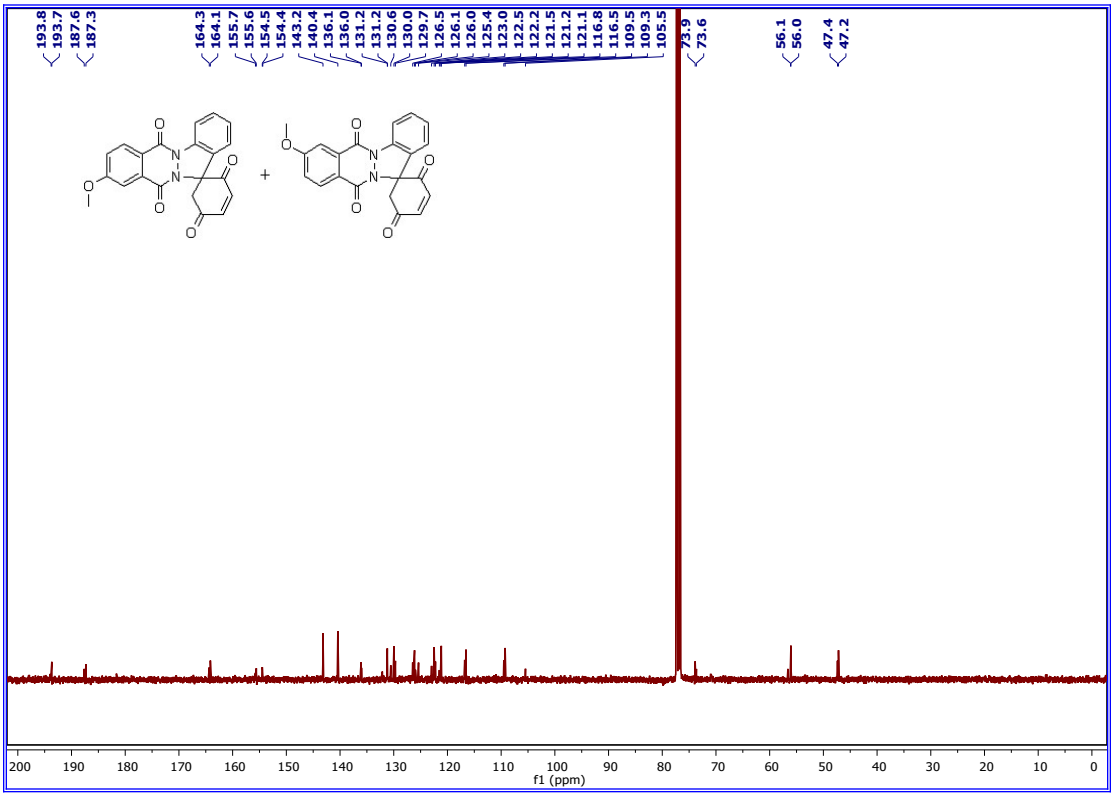

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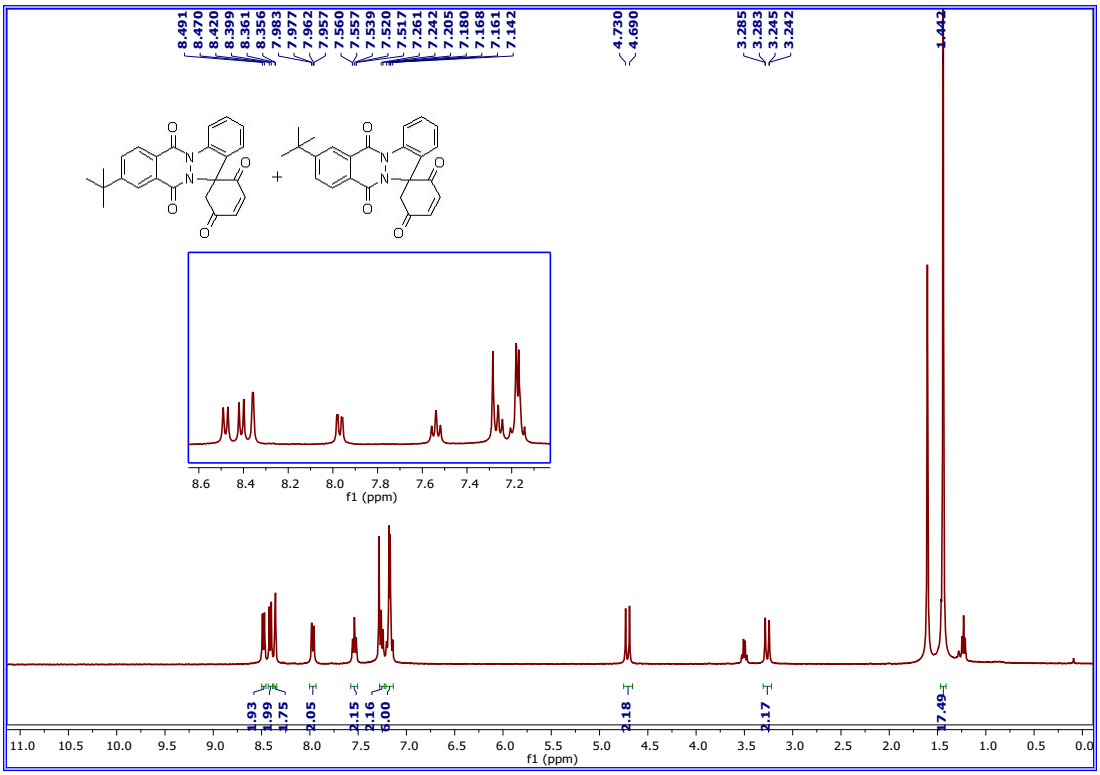


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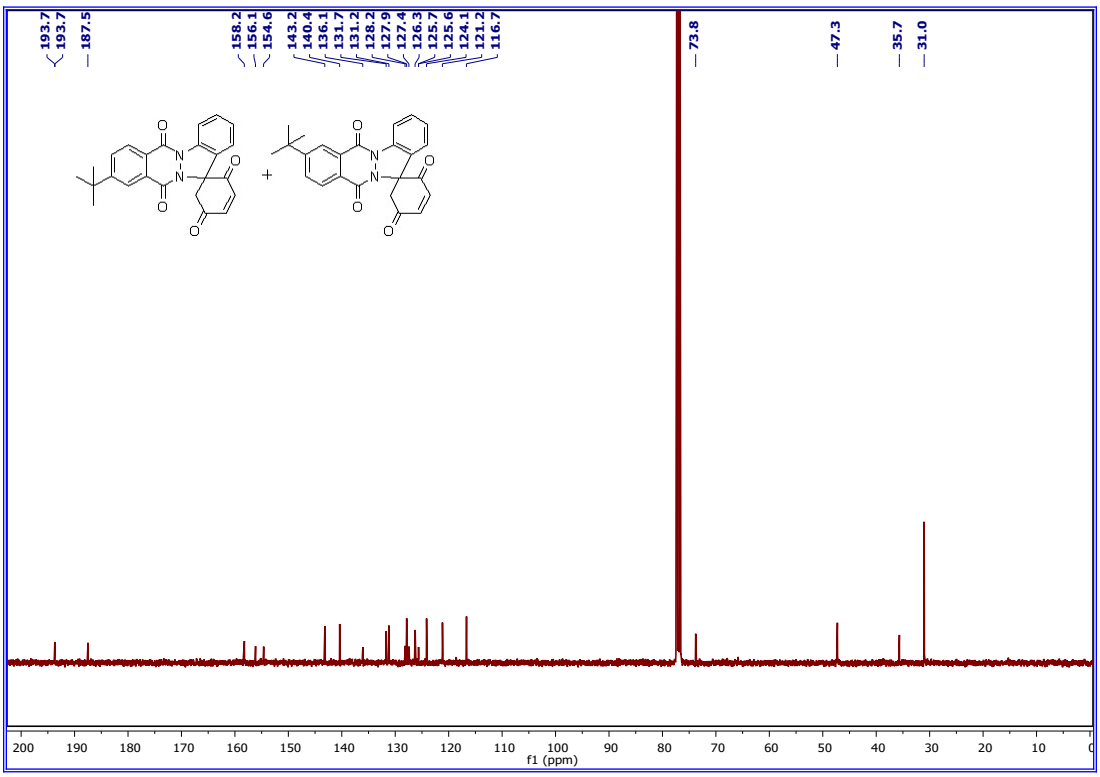

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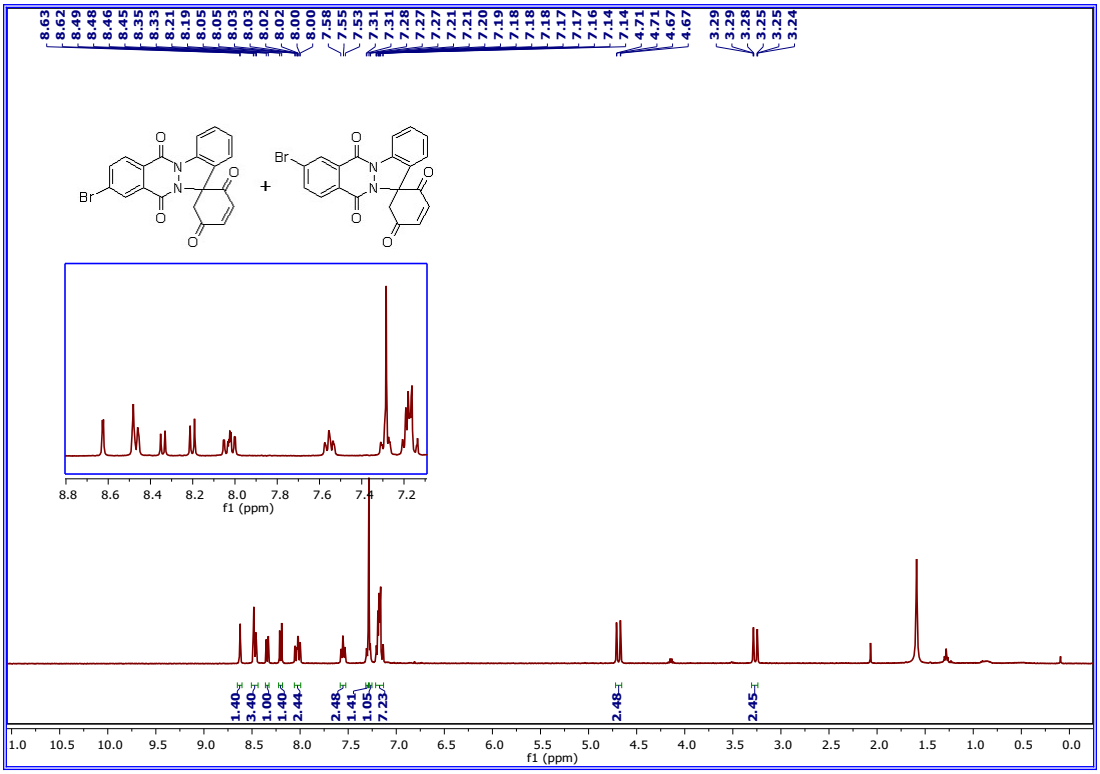

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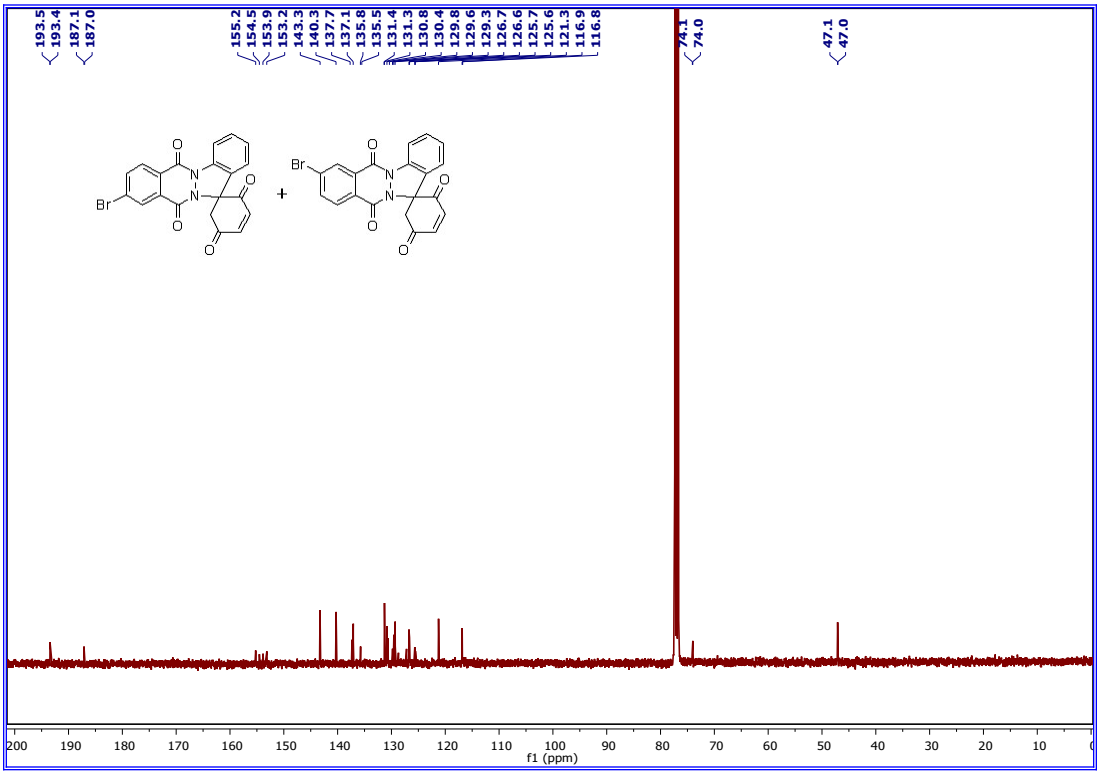

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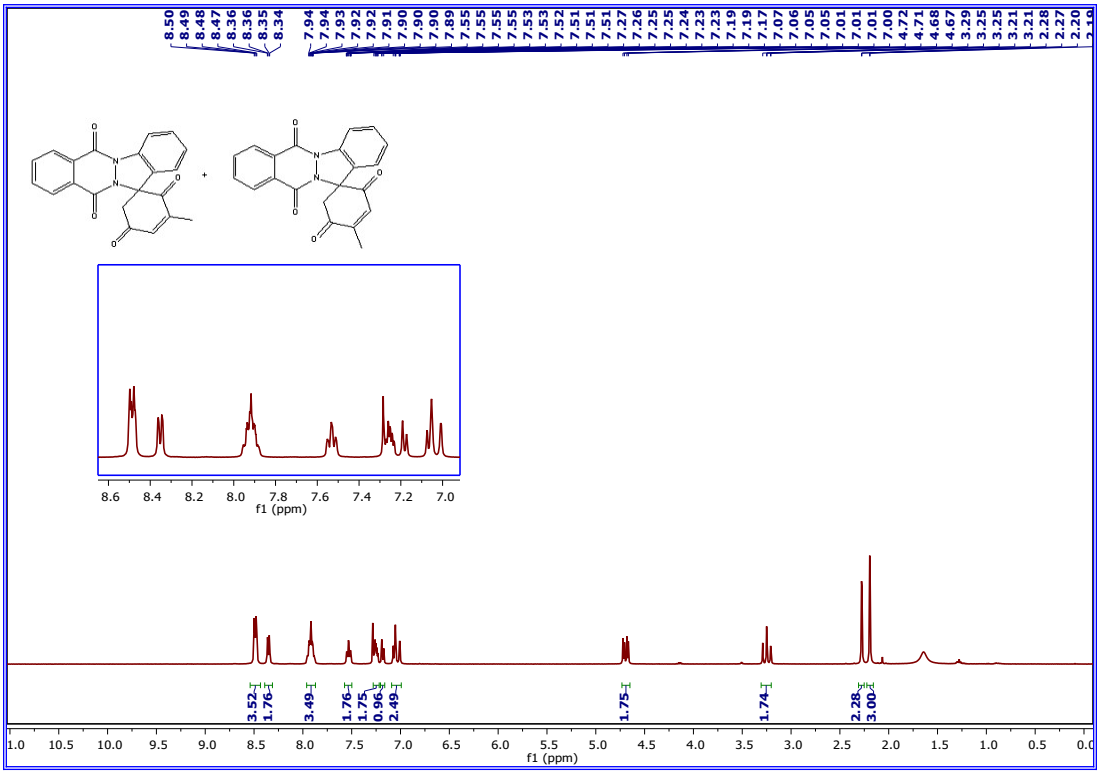


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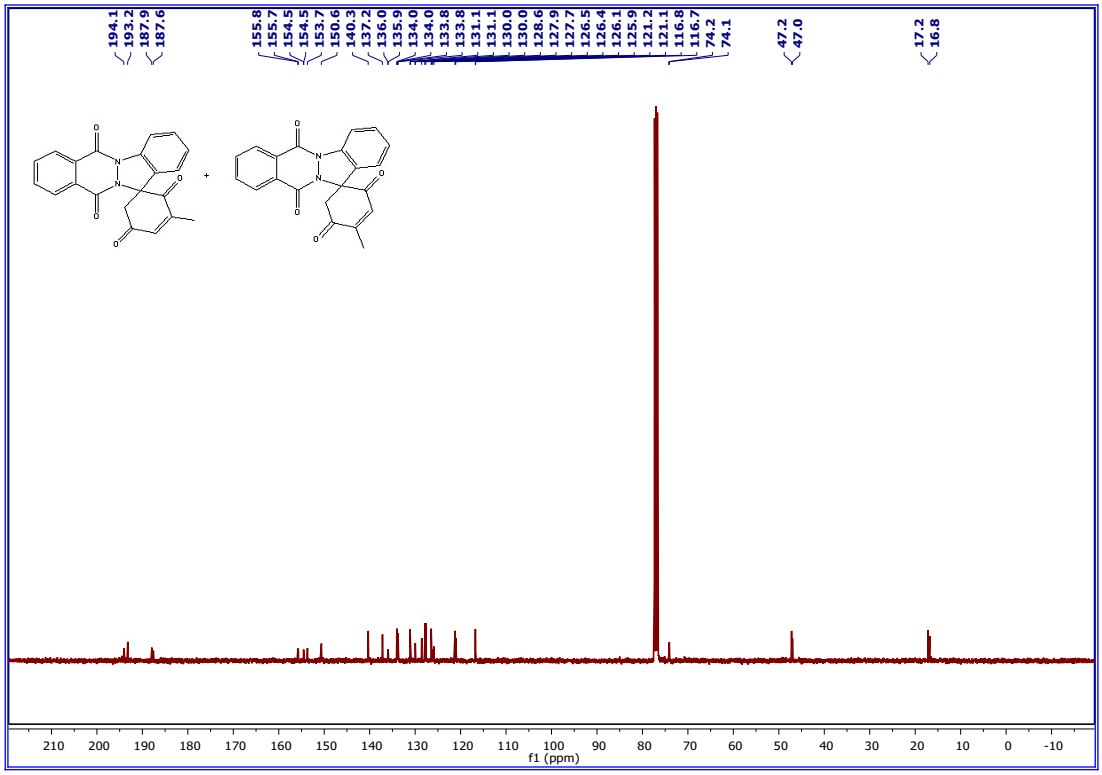

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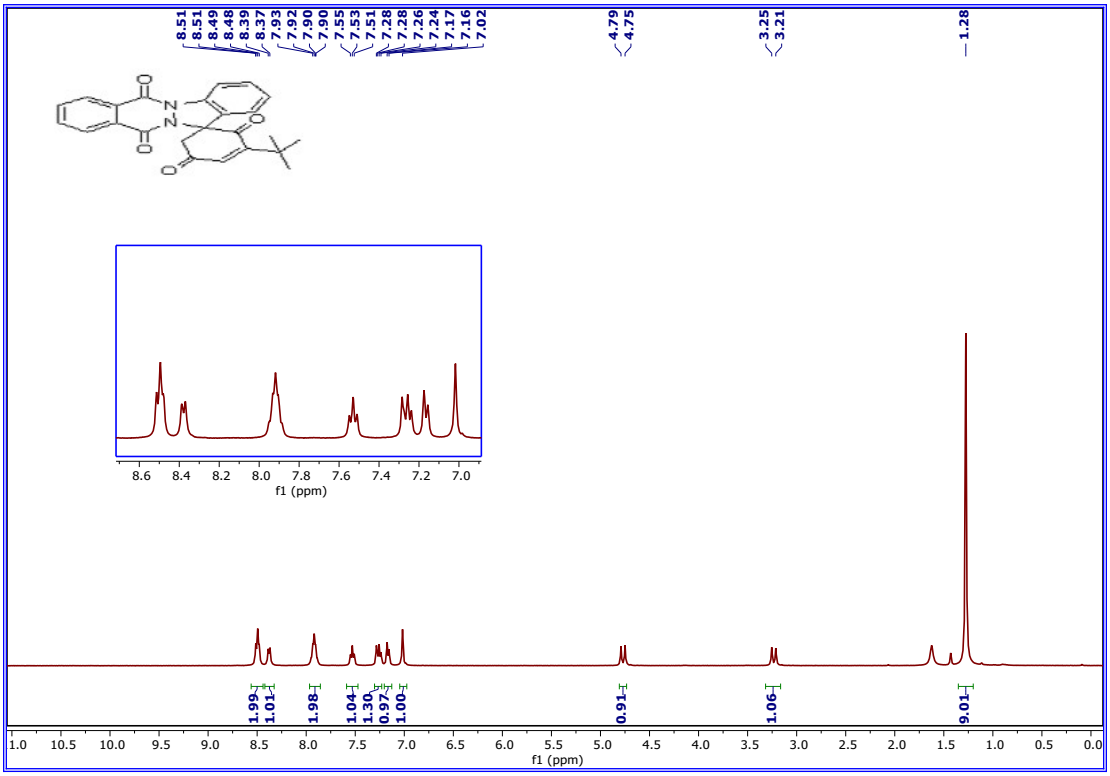
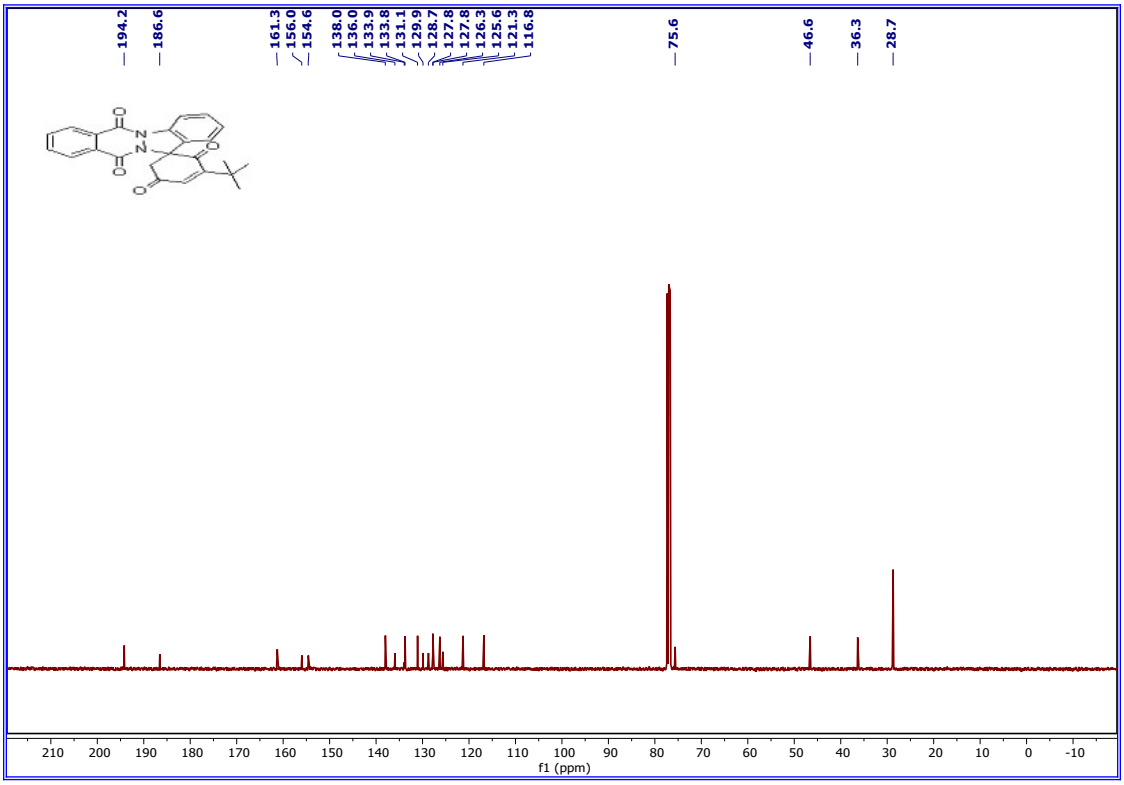



## $^{13}$C NMR of 3ac



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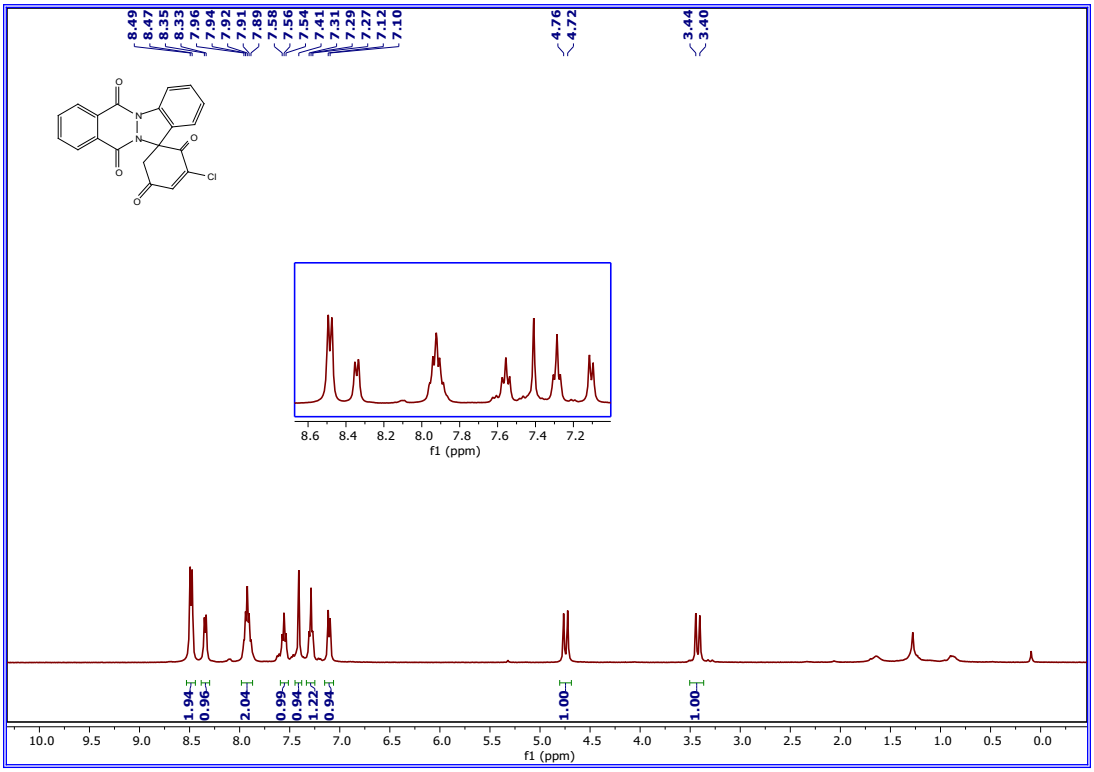


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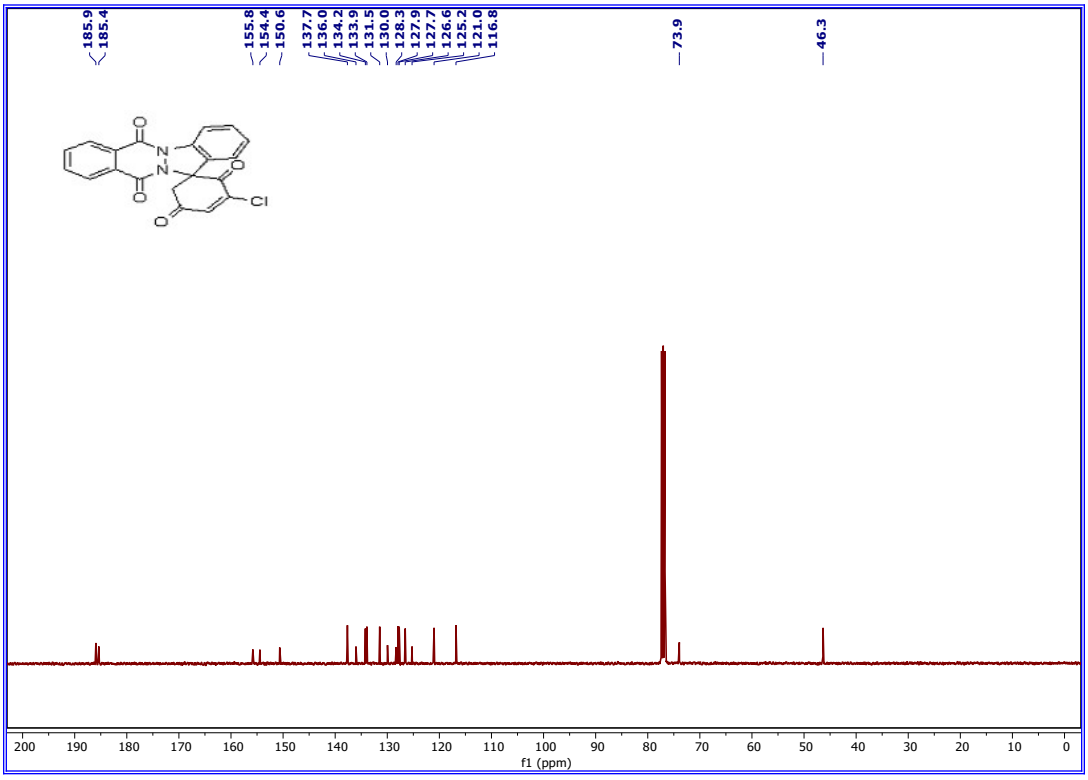
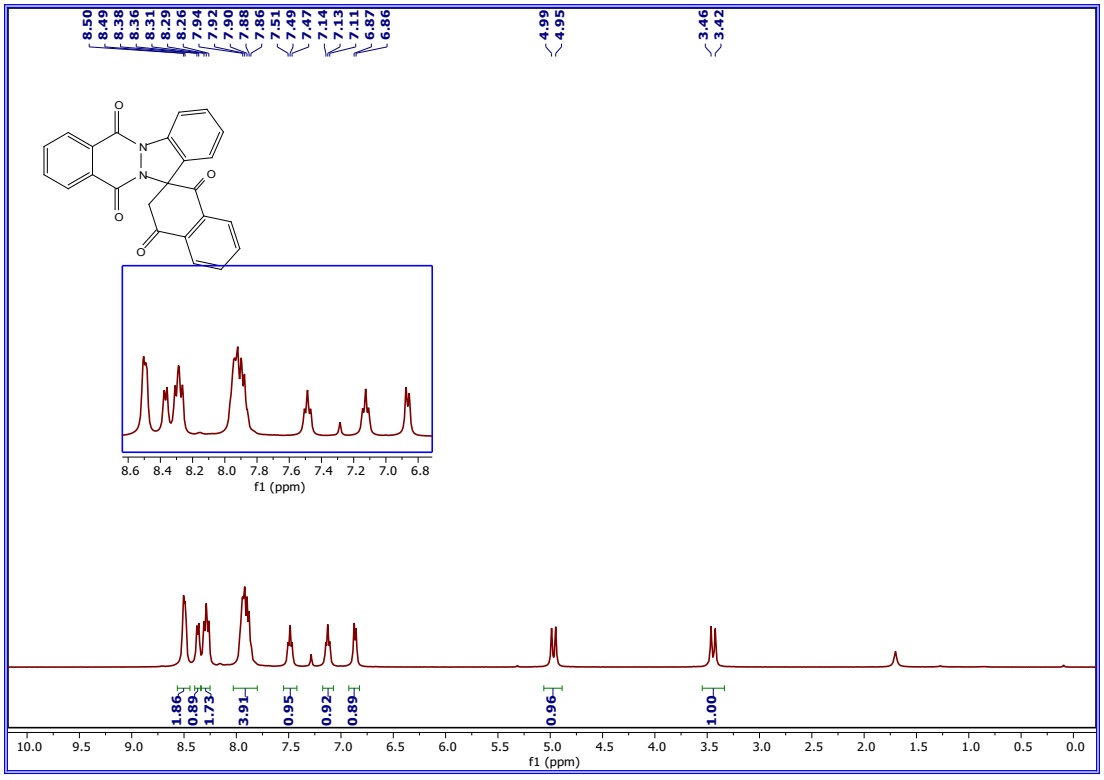


## $^{1}$H NMR of 3ae

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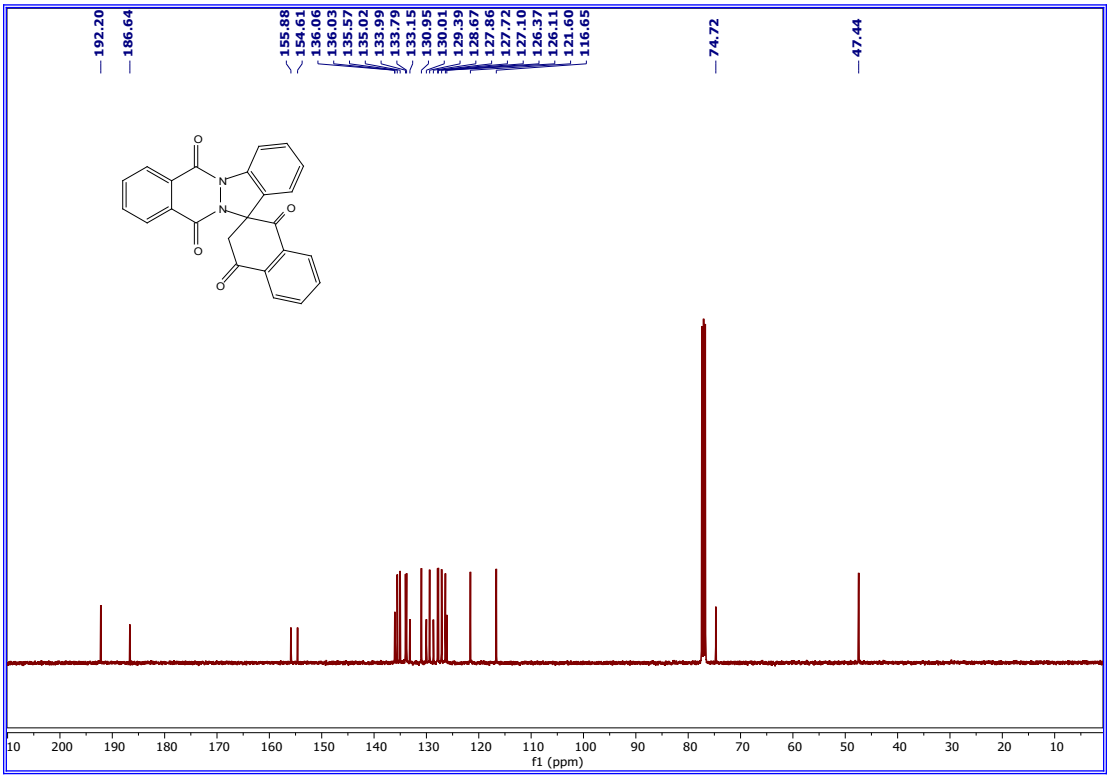
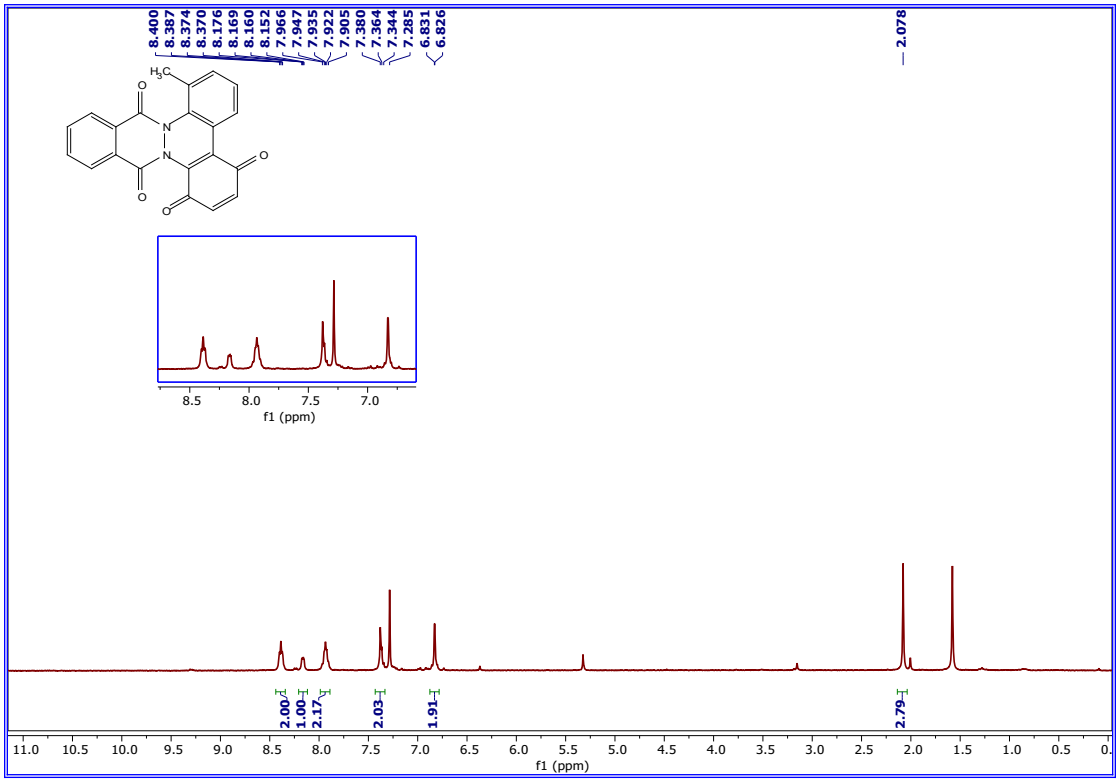
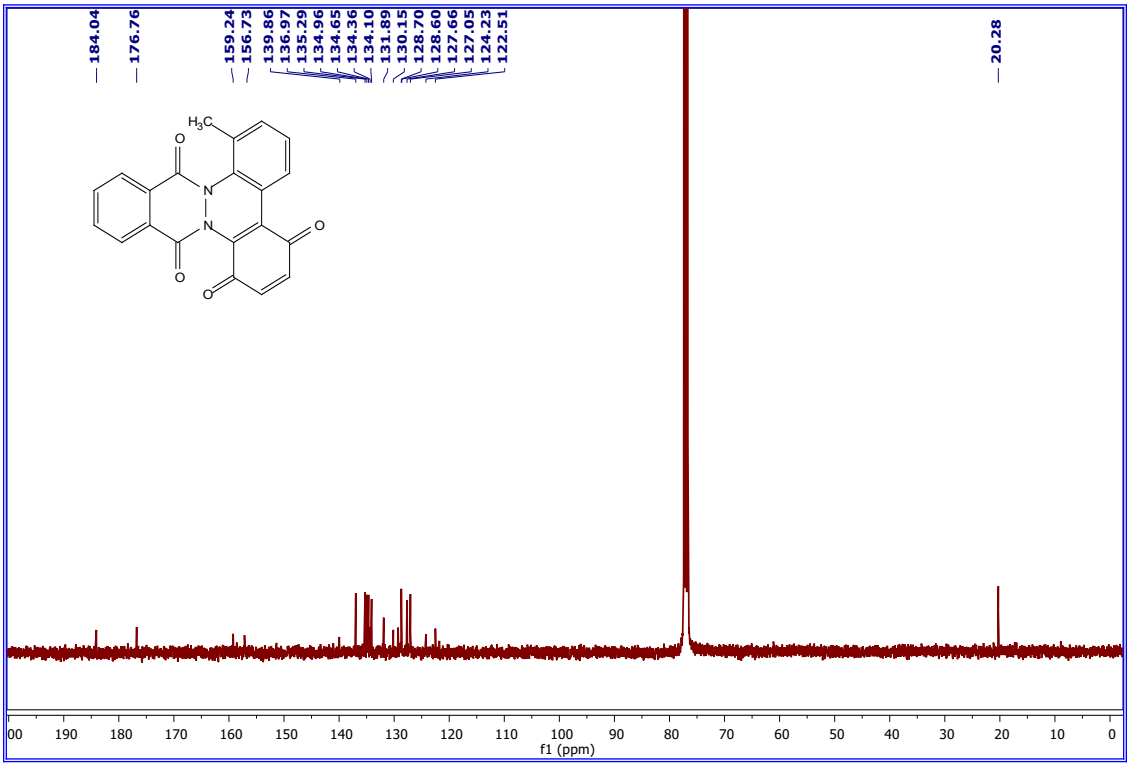


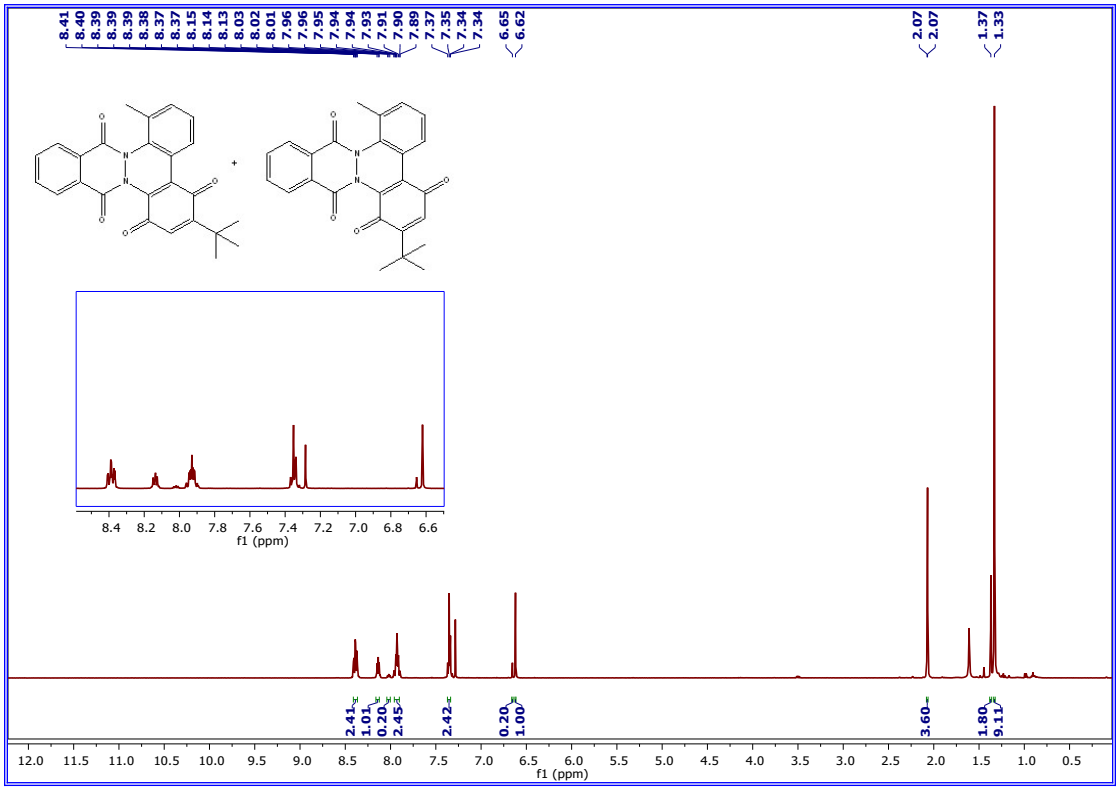
## $^{1}$H NMR of 4ma




## $^{13}$C NMR of 4ma



## $^{1}$H NMR of 4mc

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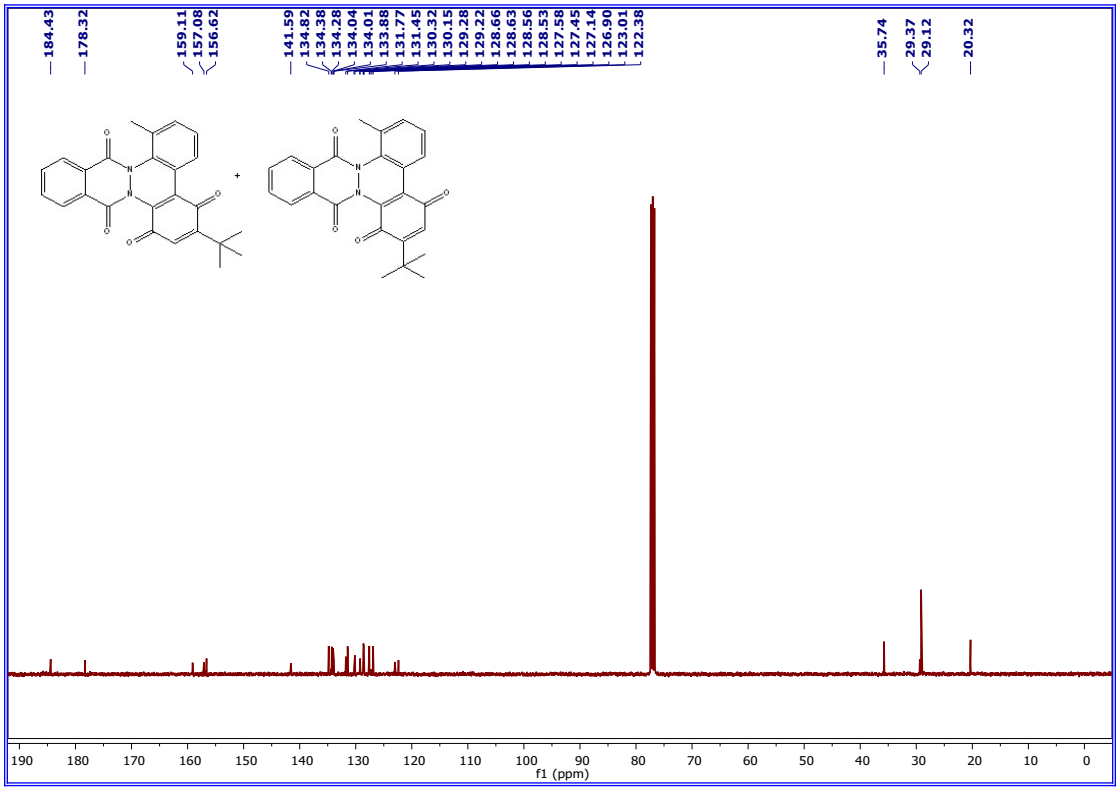

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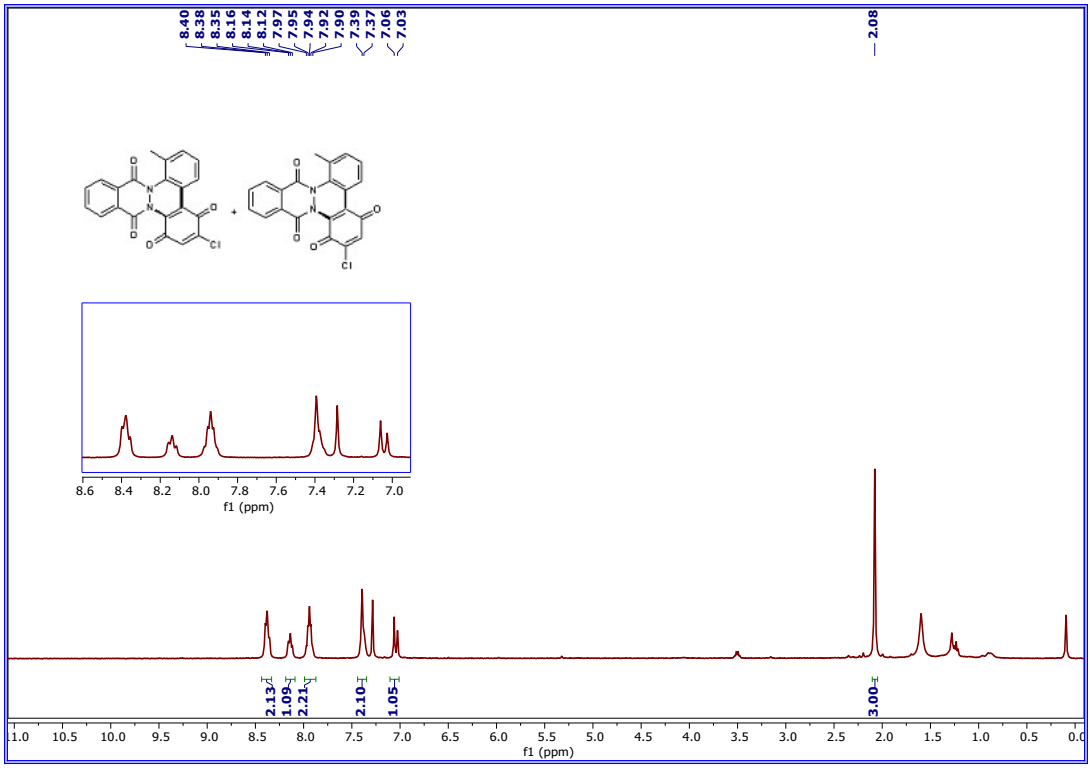


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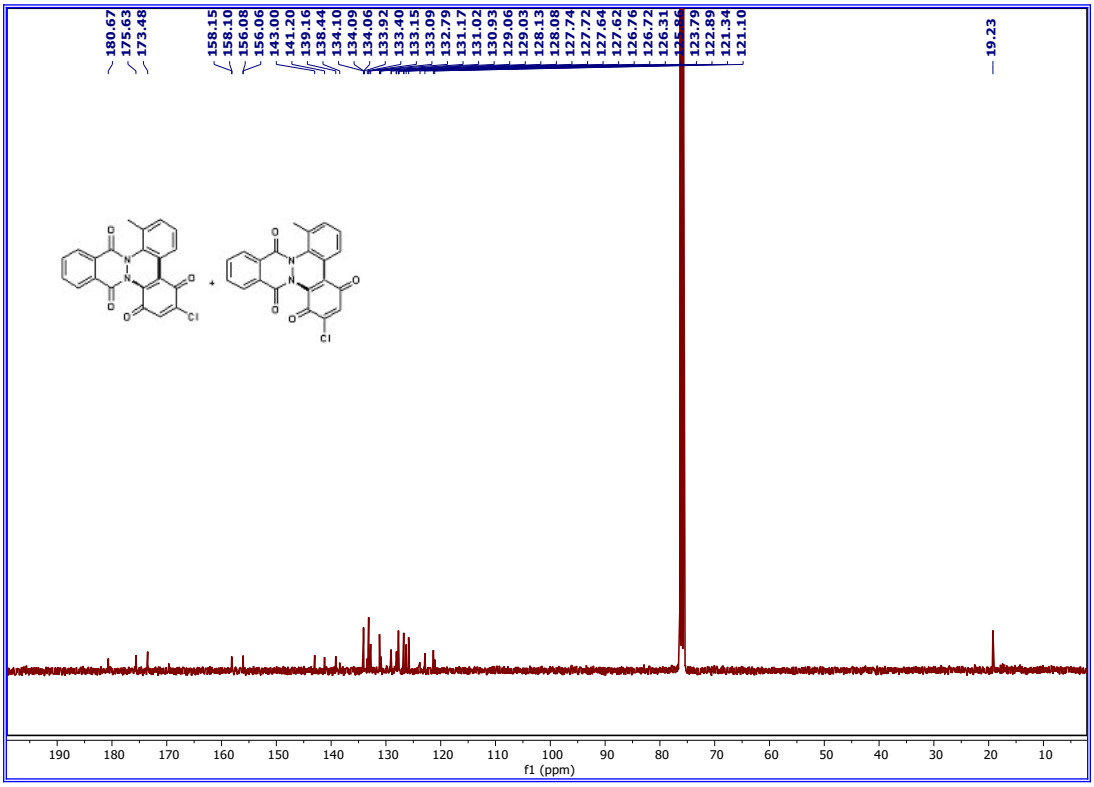

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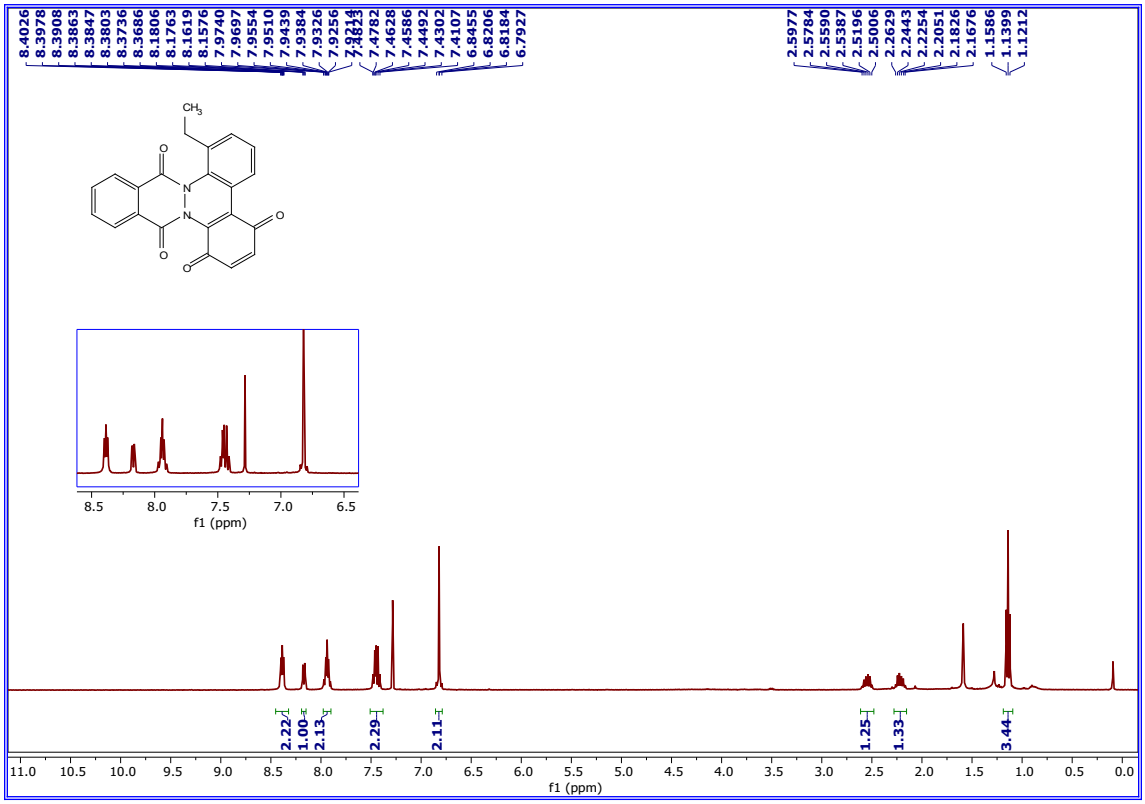
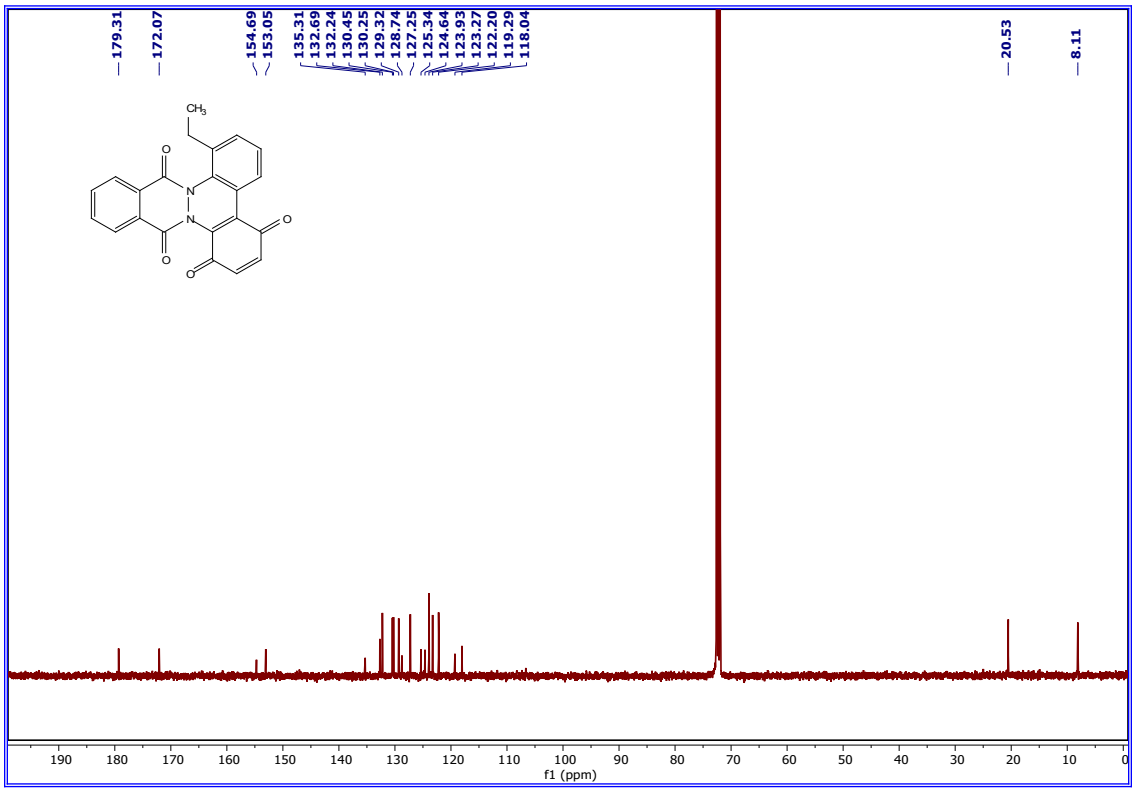



## $^{13}$C NMR of 4na



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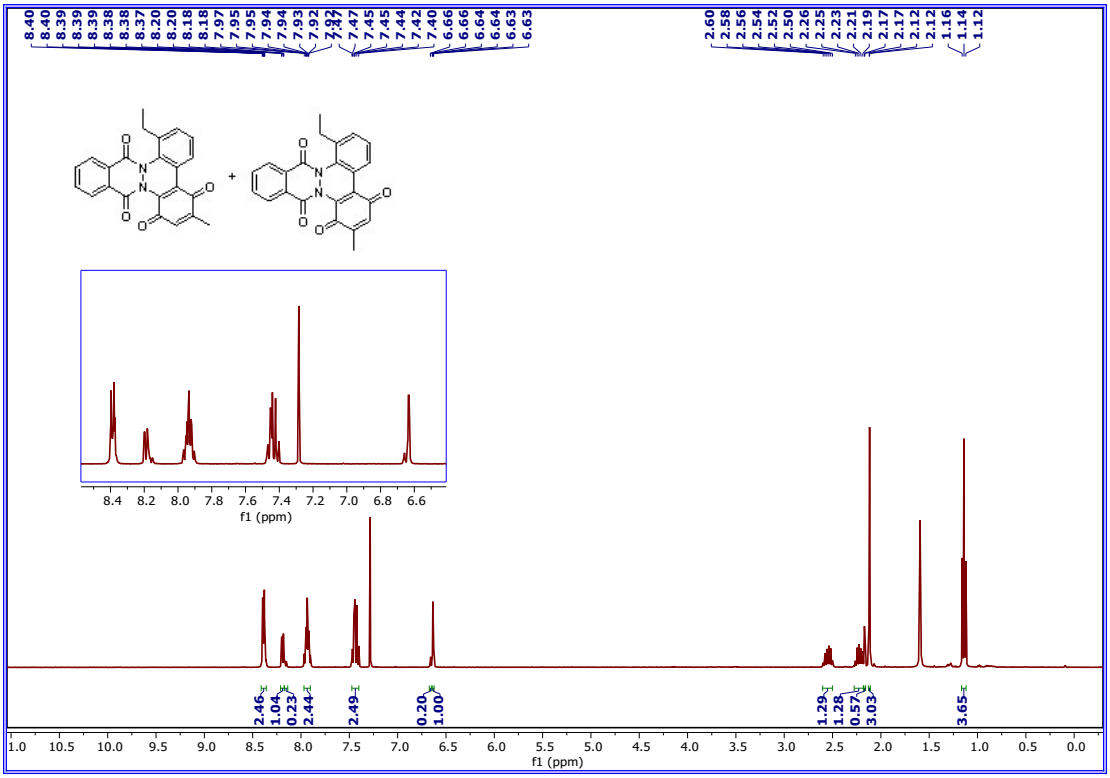

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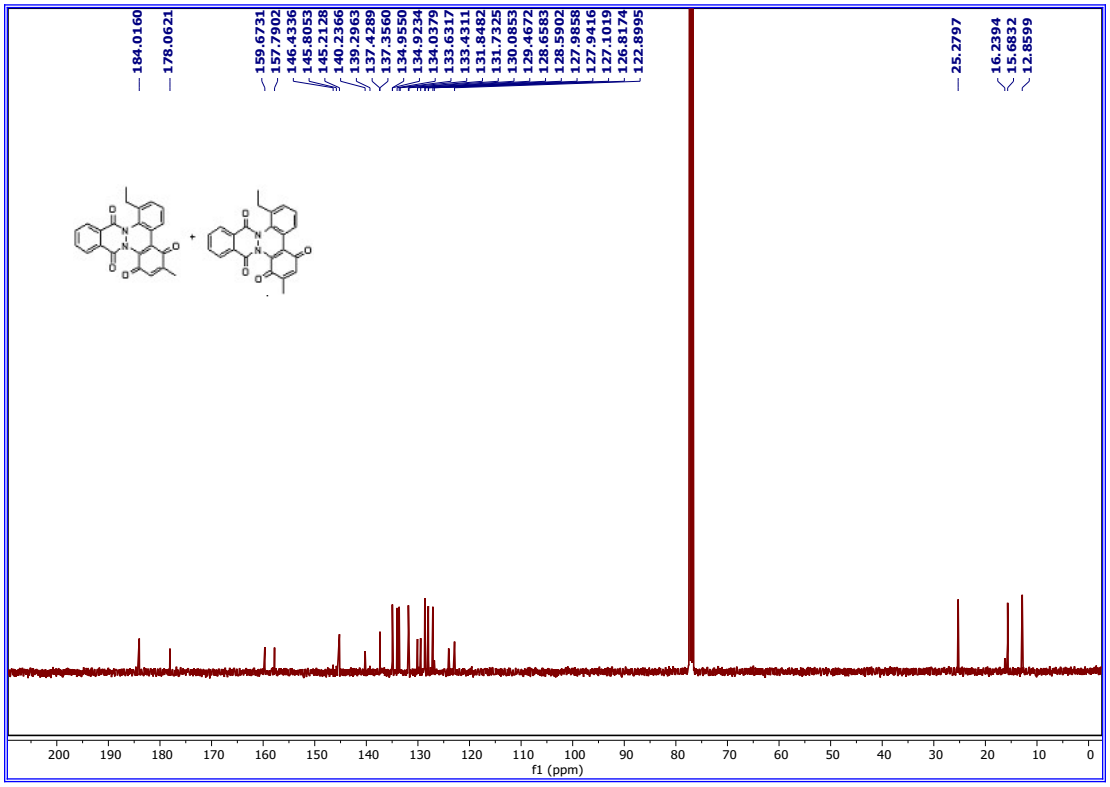

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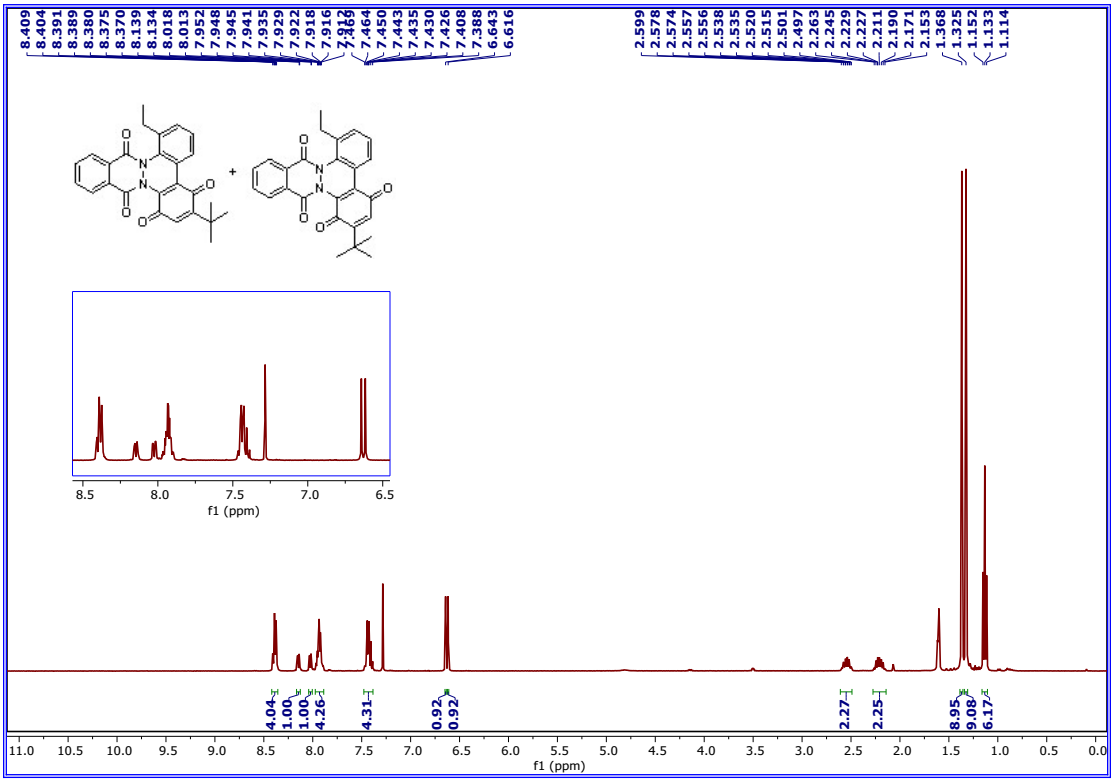
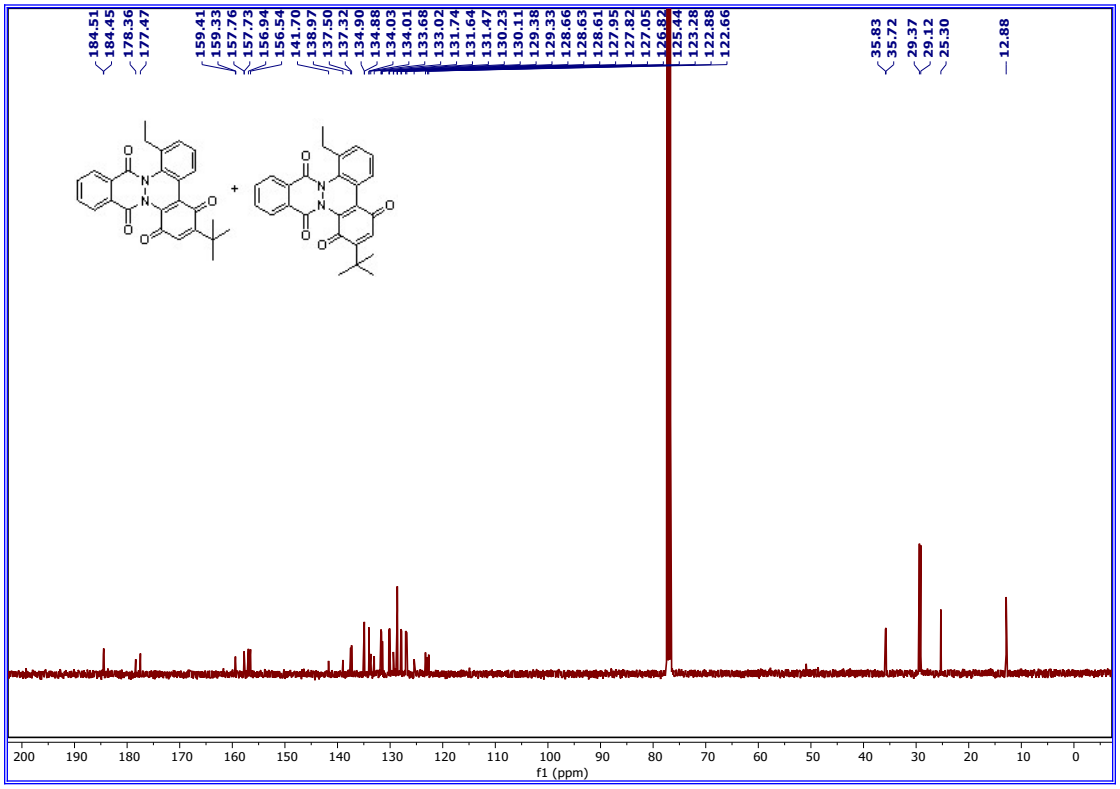



## $^{13}$C NMR of 4nc



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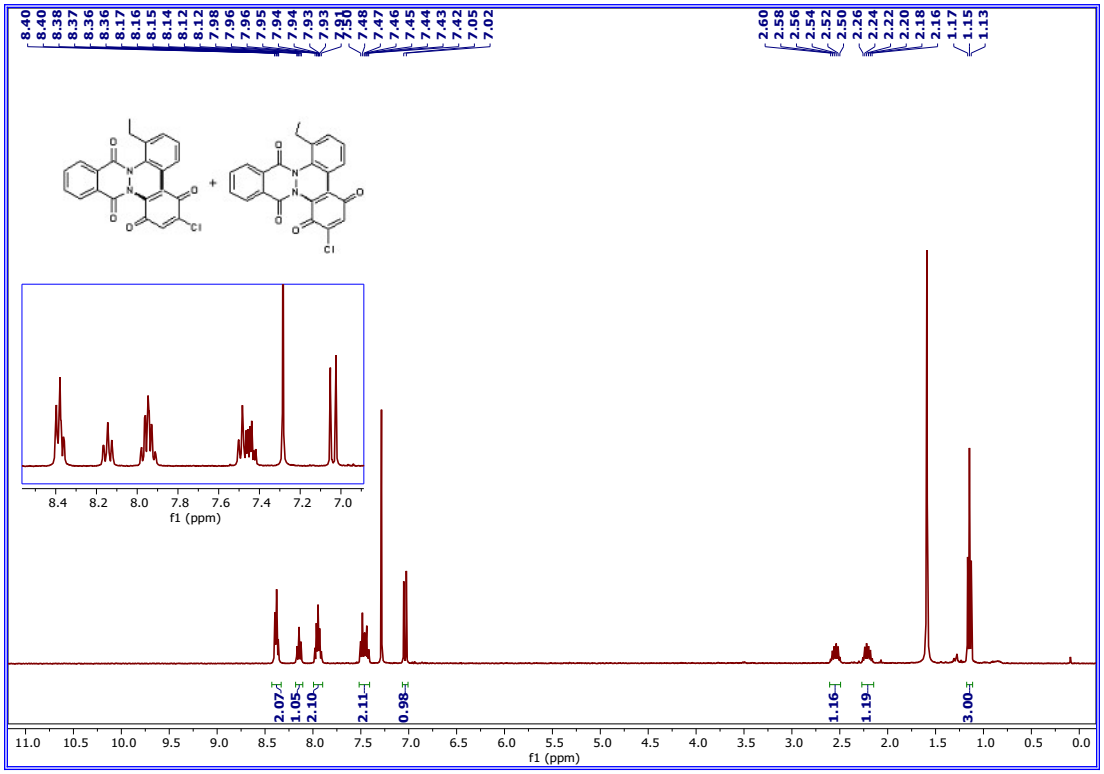


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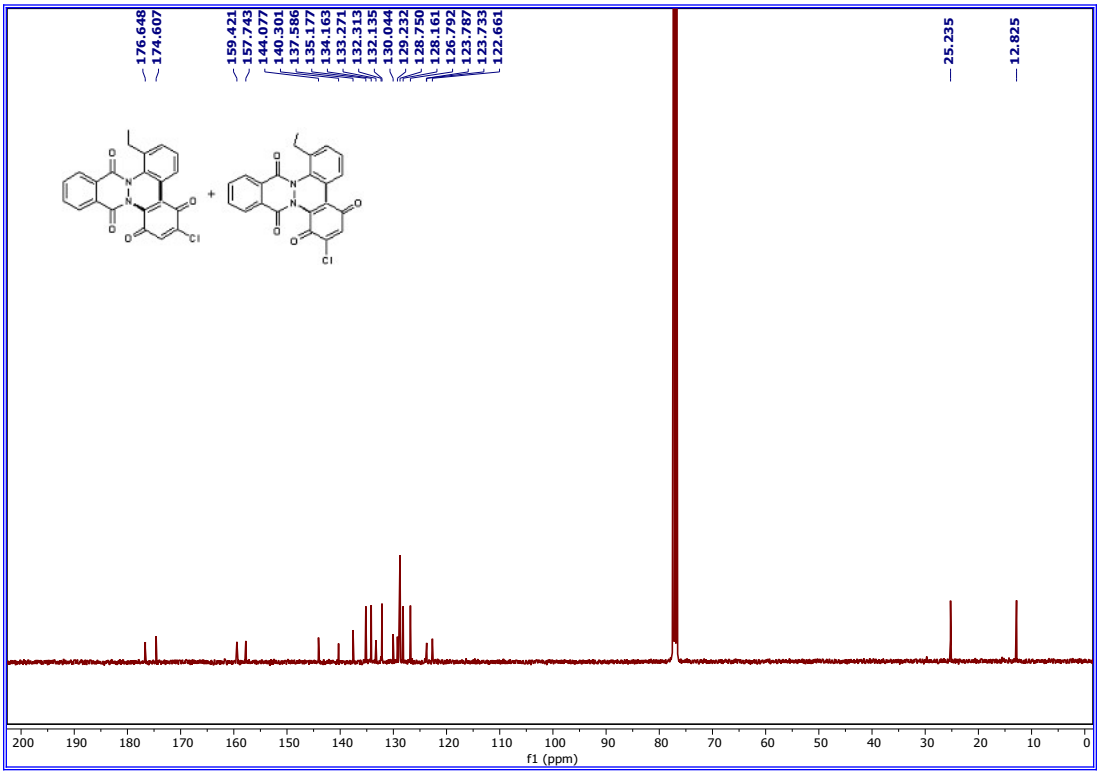

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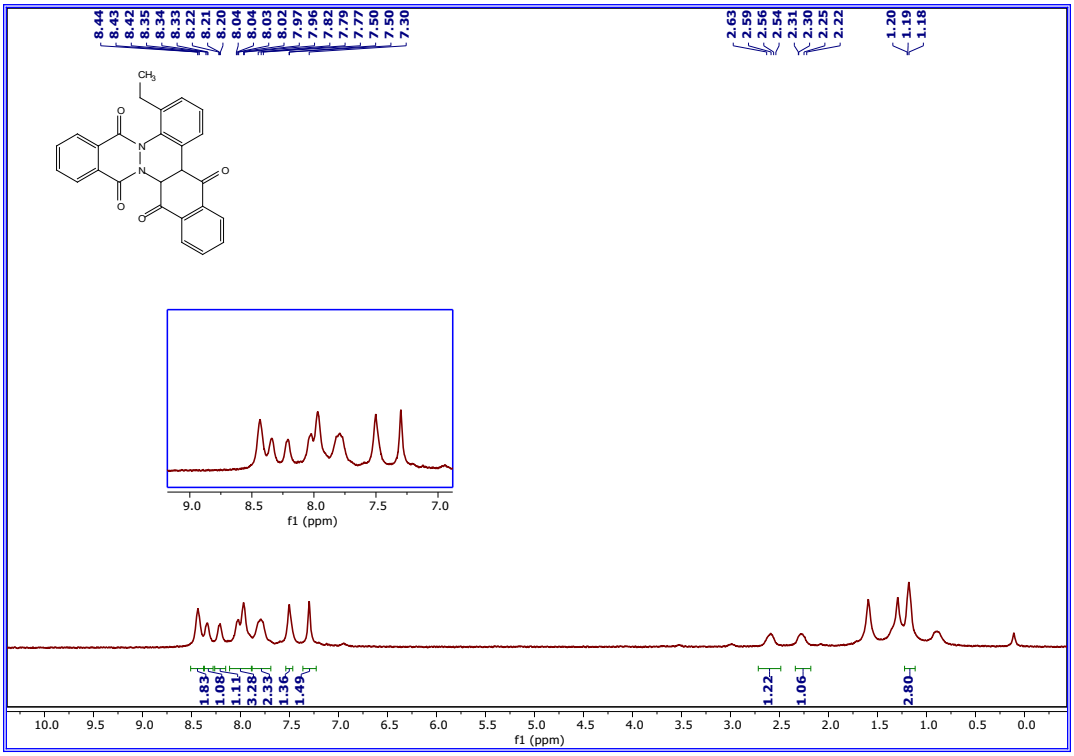
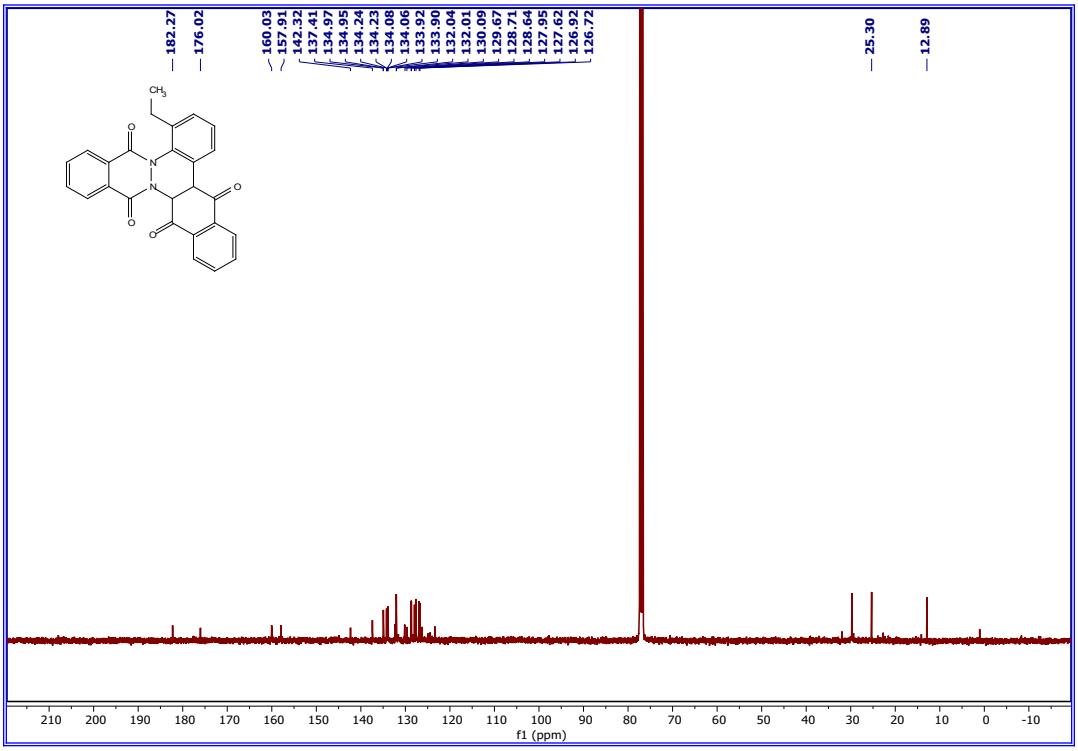



## $^{13}$C NMR of 4ne



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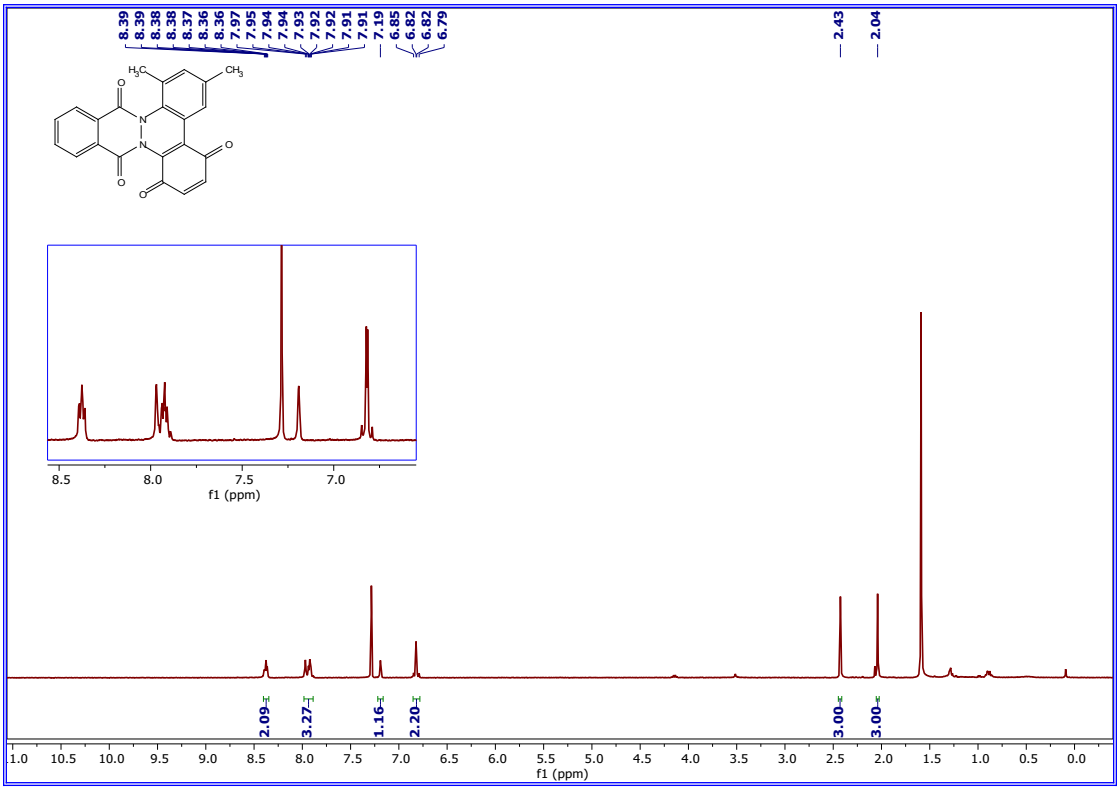


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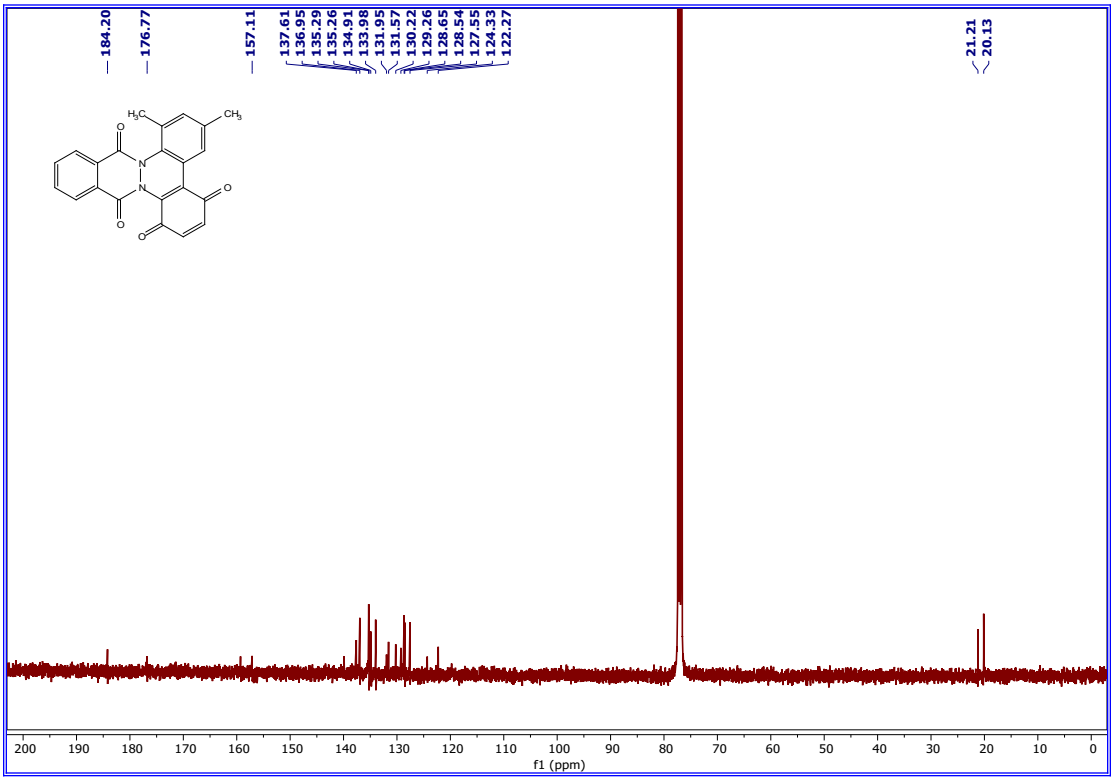

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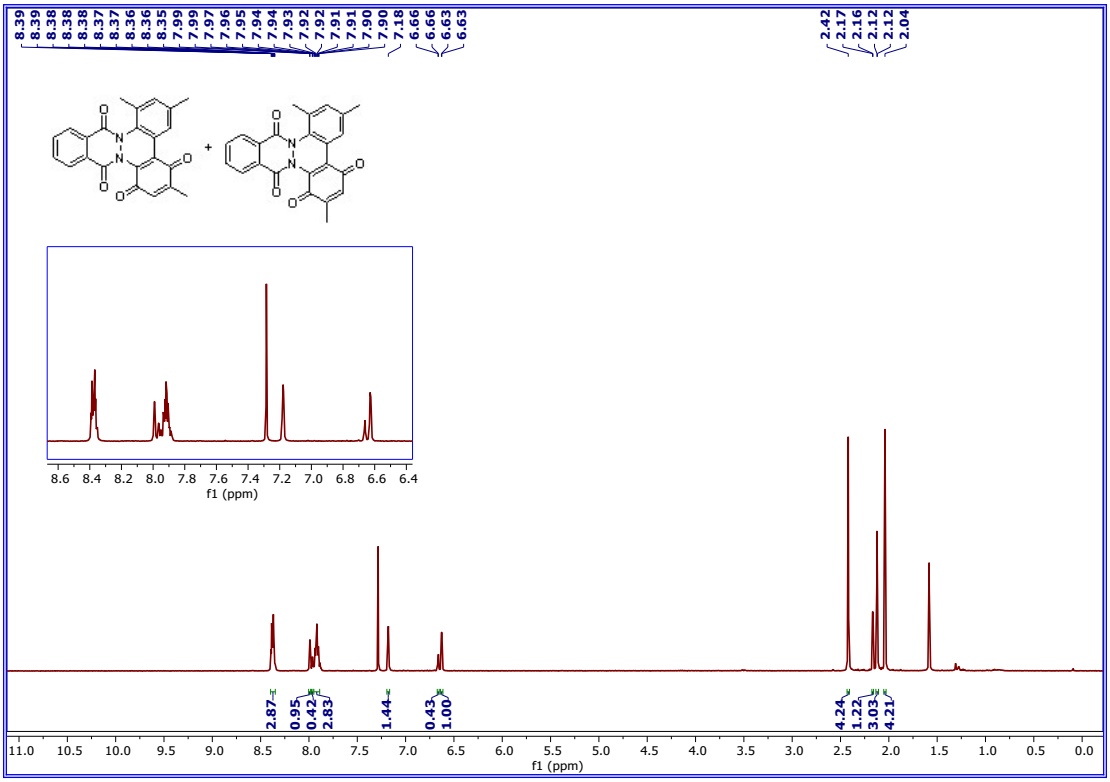
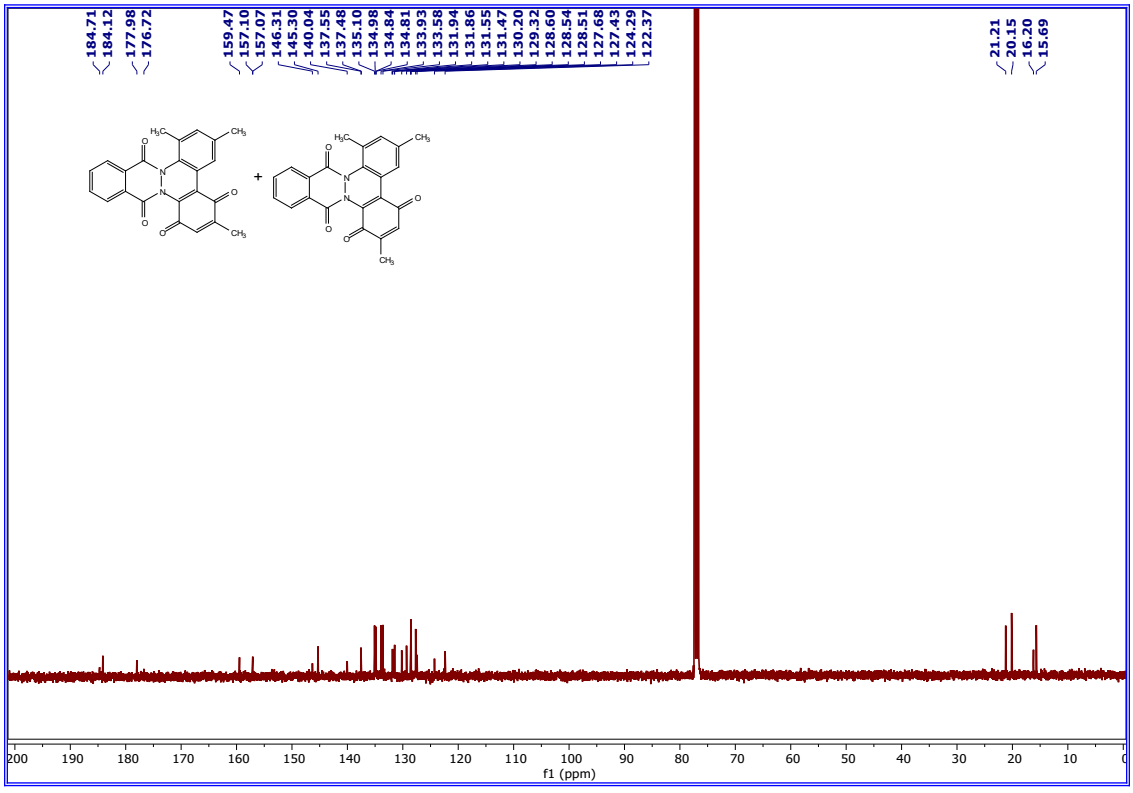
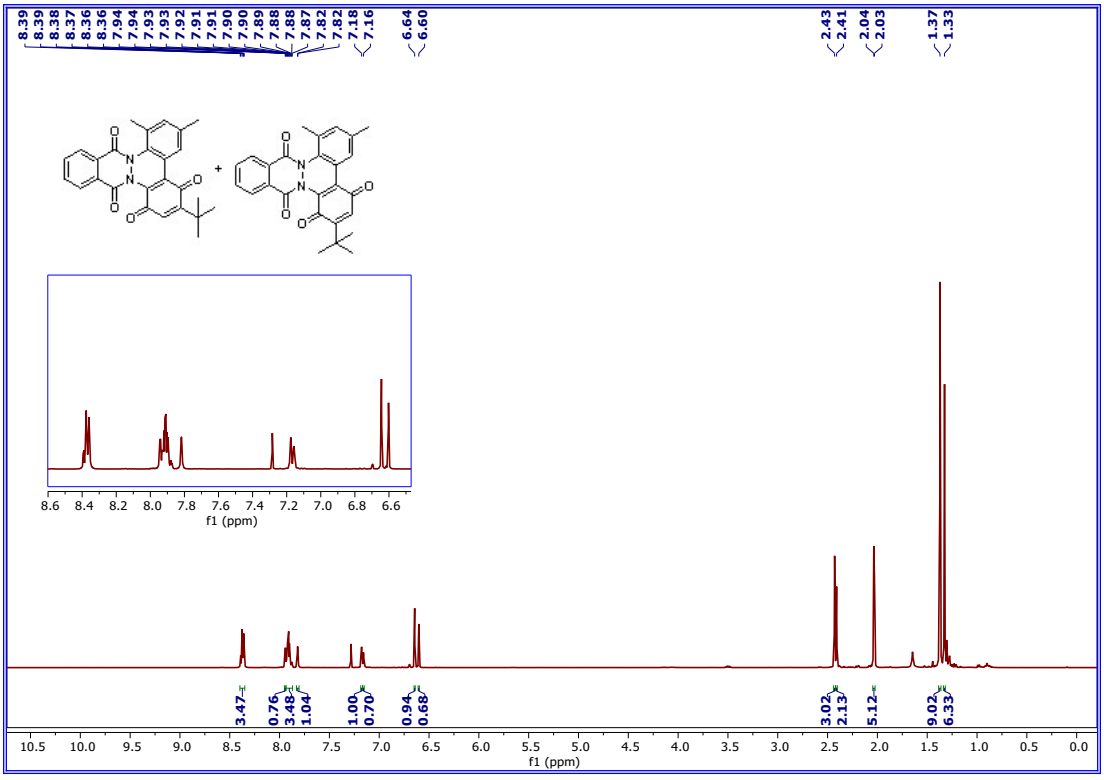


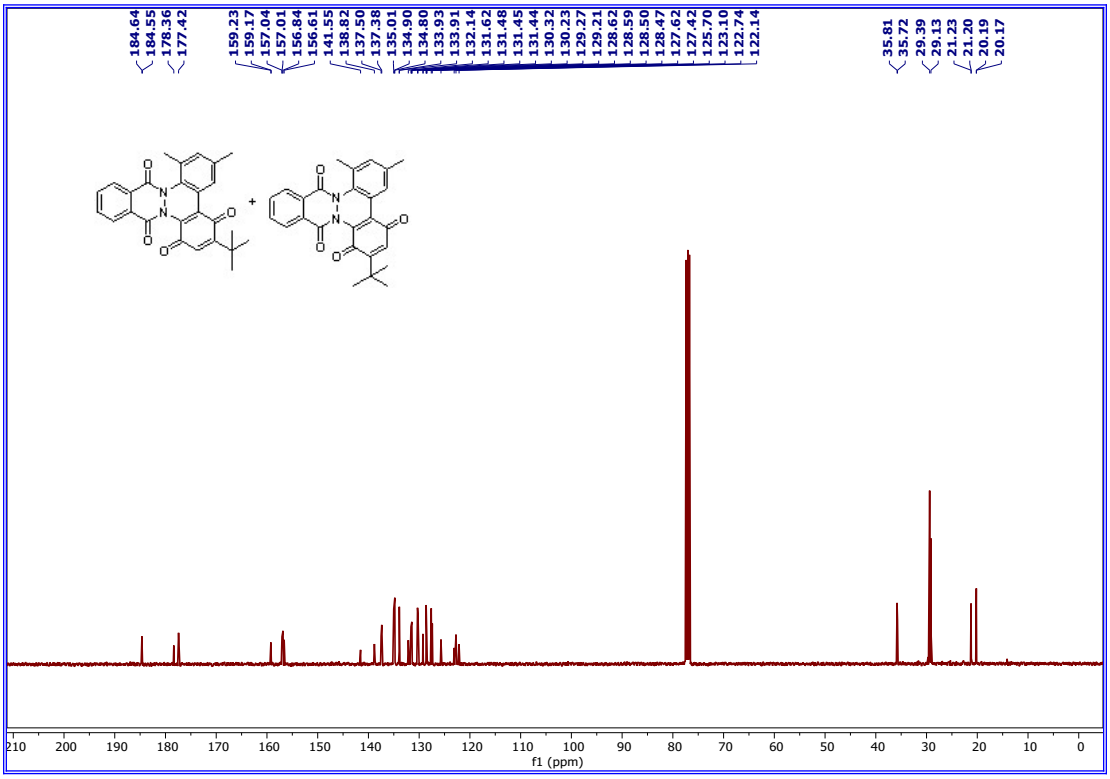

## $^{13}$C NMR of 4ob



## $^{1}$H NMR of 4oc




## $^{13}$C NMR of 4oc



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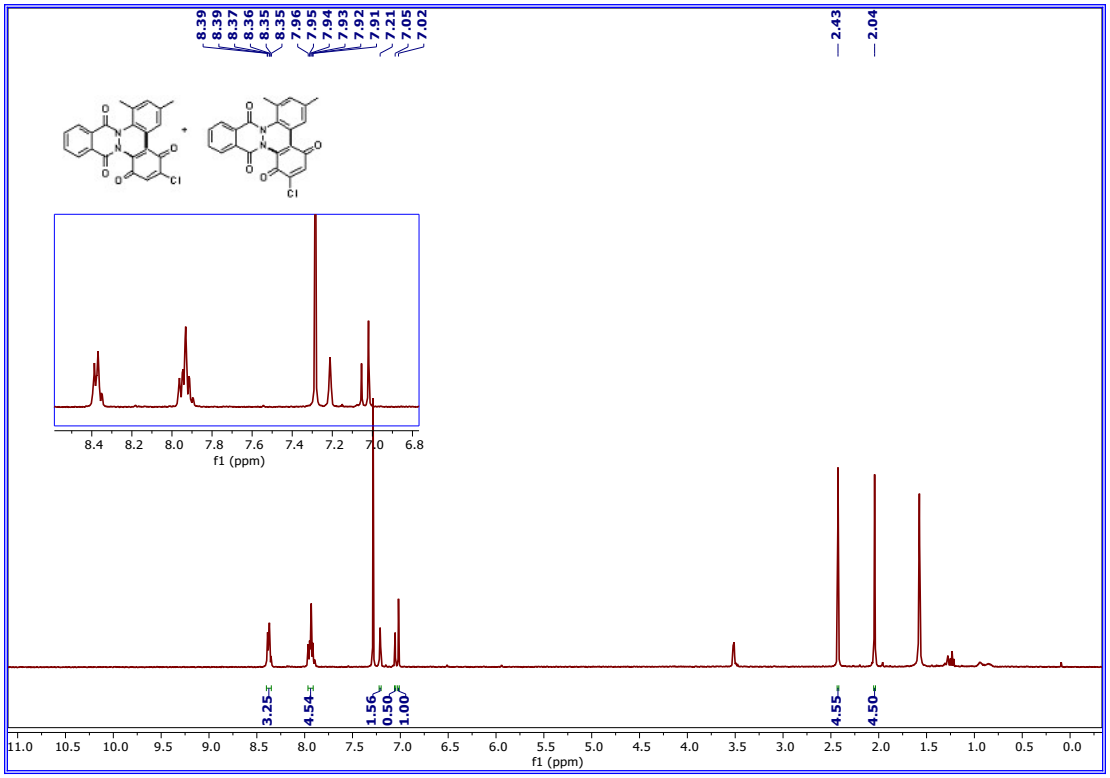
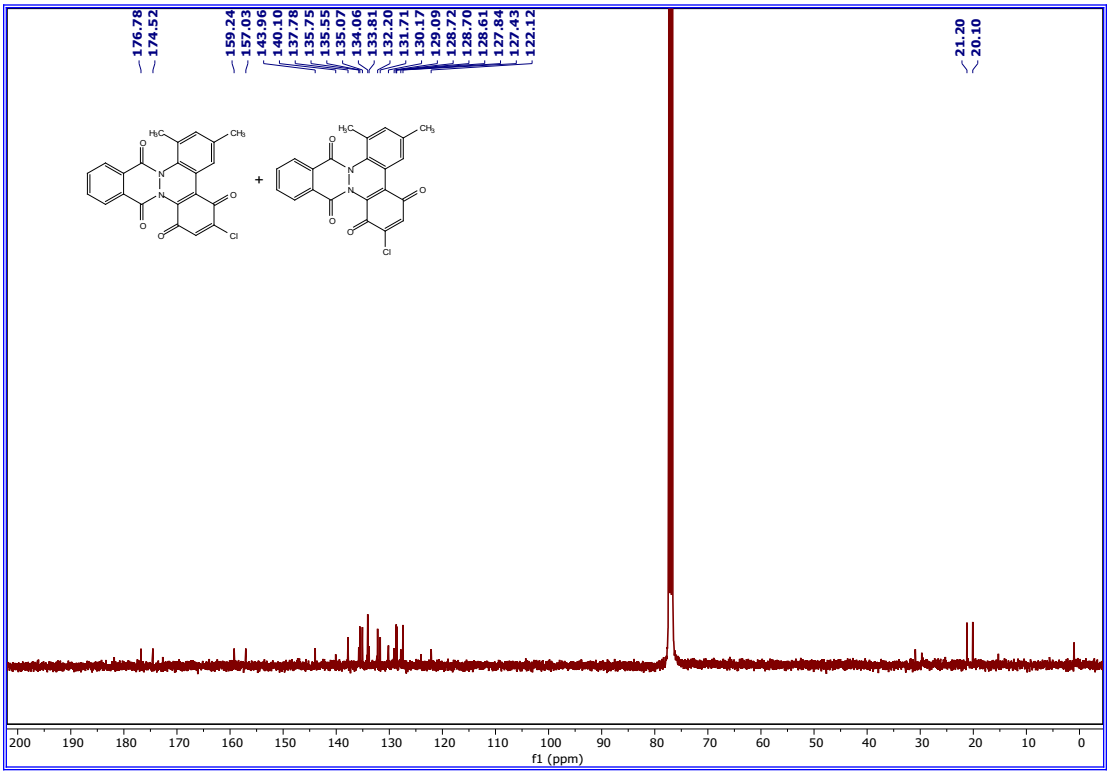
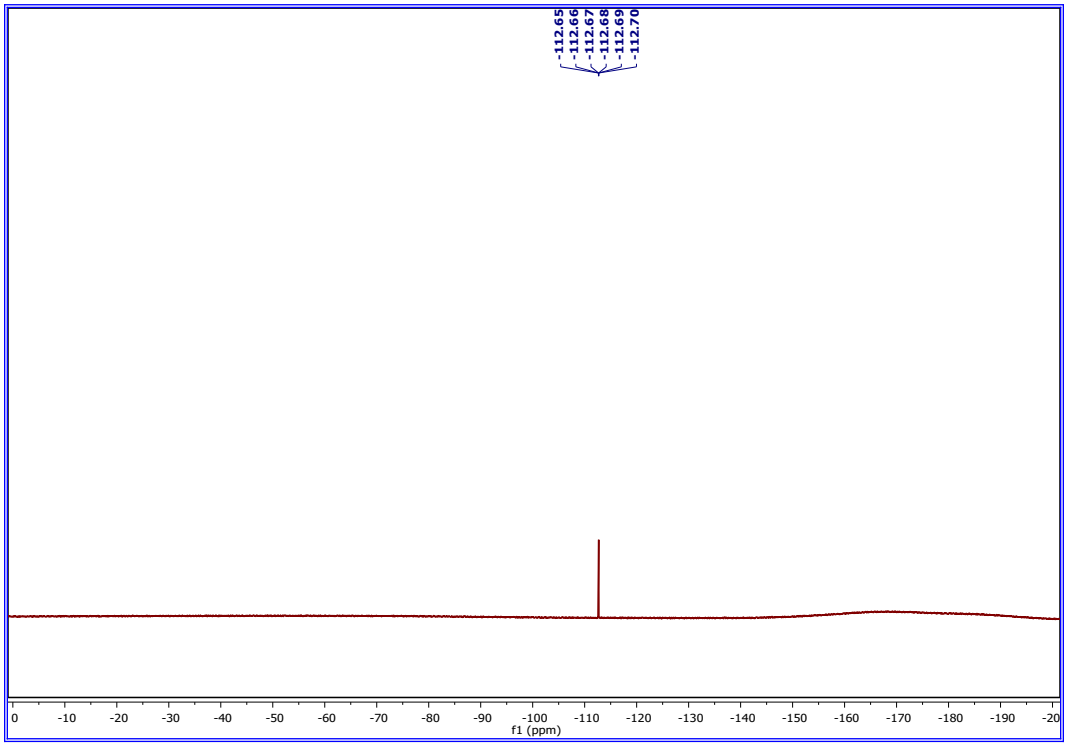



## $^{13}$C NMR of 4od

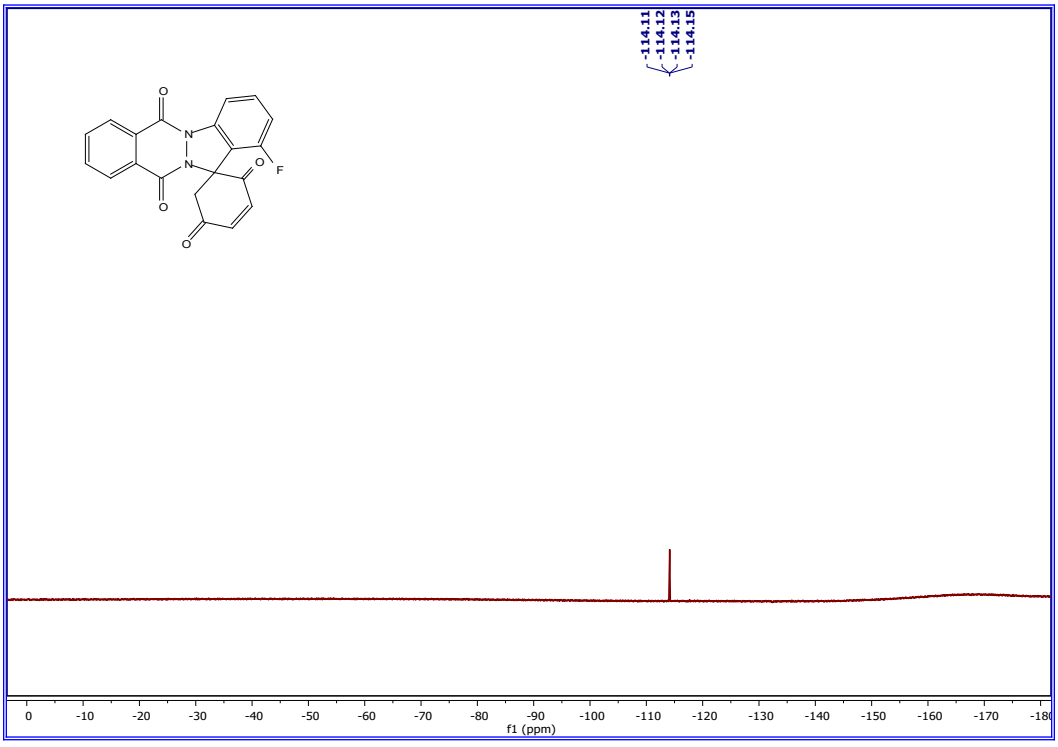


## 2. $^{19}F$ NMR of 3da and 3ga

**$^{19}F$ NMR of 3da (376 MHz, $CDCl_3$)**

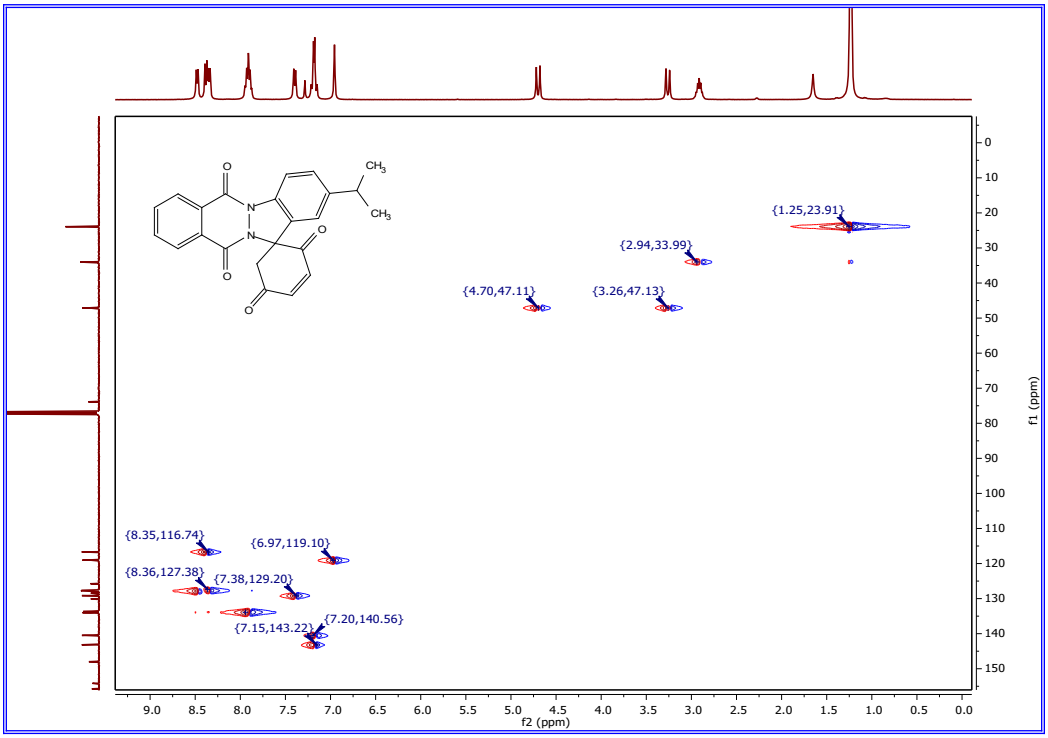



**$^{19}F$ NMR of 3ga (376 MHz, $CDCl_3$)**

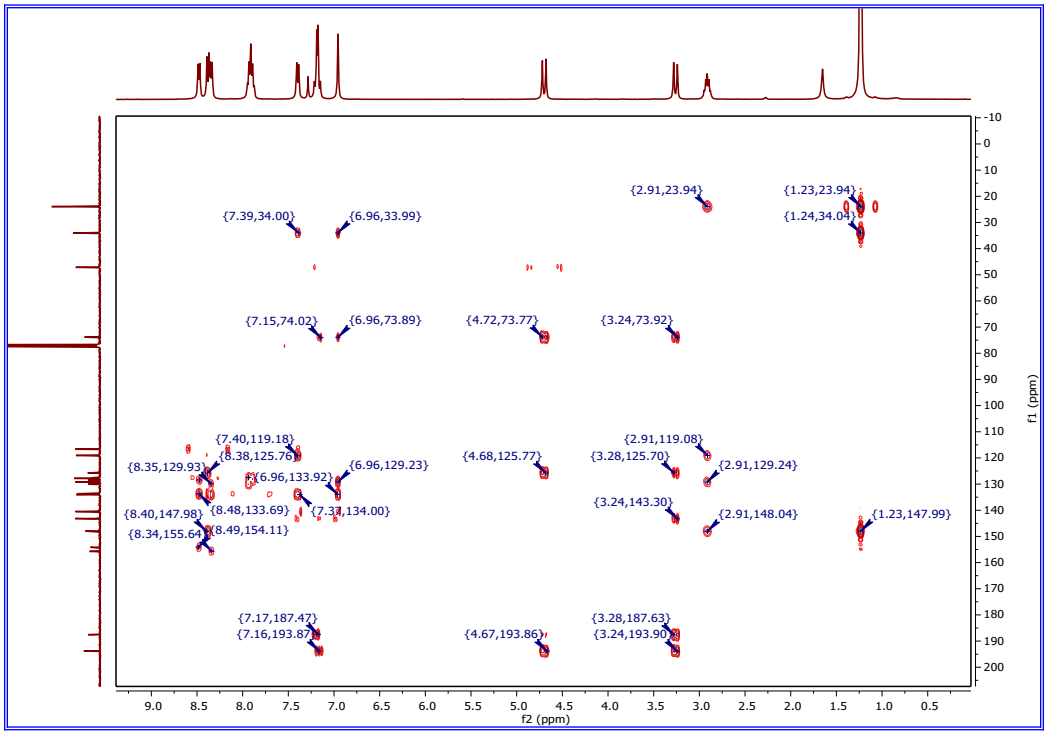


## 3. COSY and HSQC of 3ca

### HSQC of 3ca

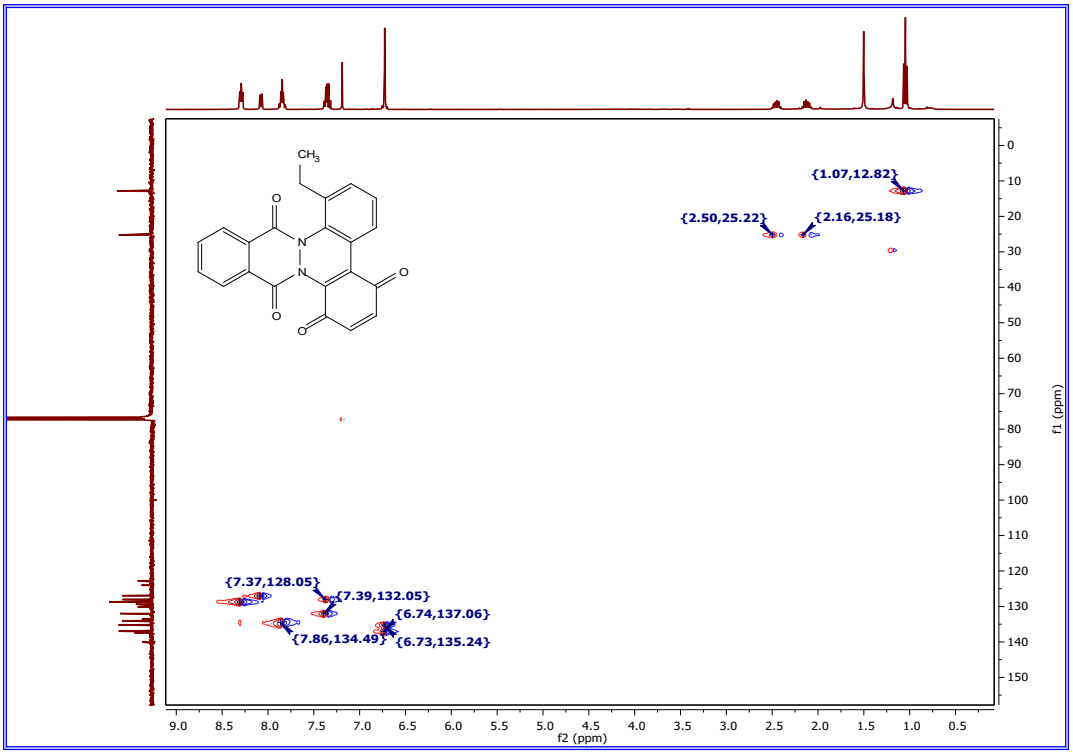



### HMBC of 3ca

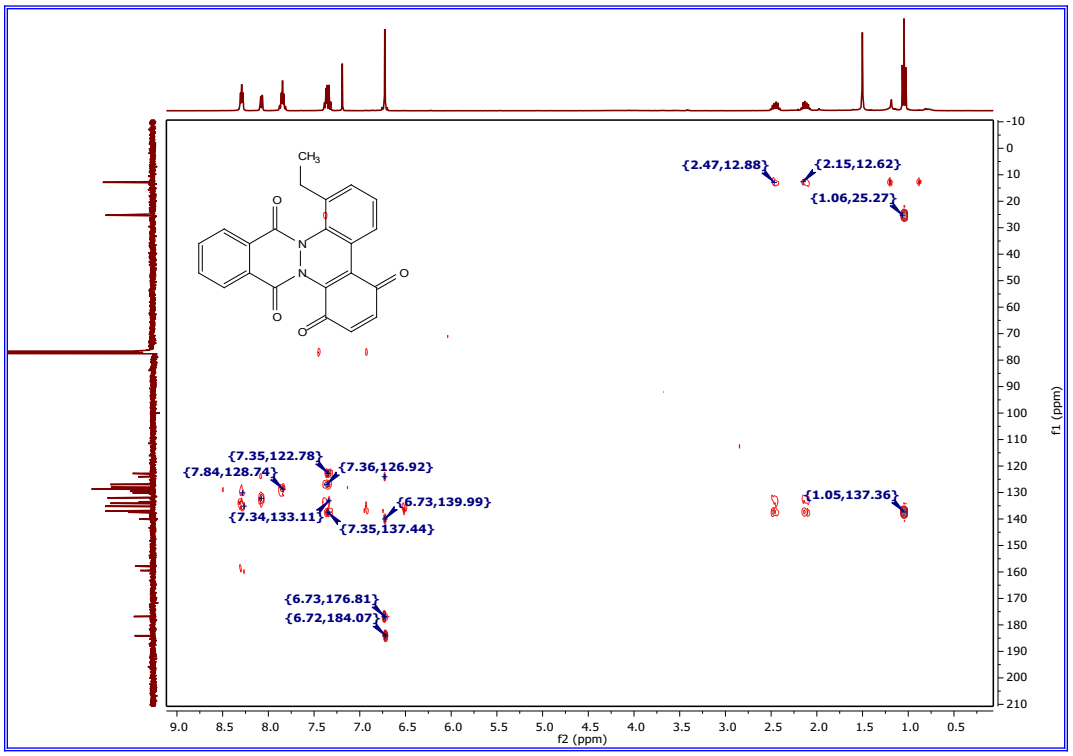


## 4. COSY and HSQC of 4na

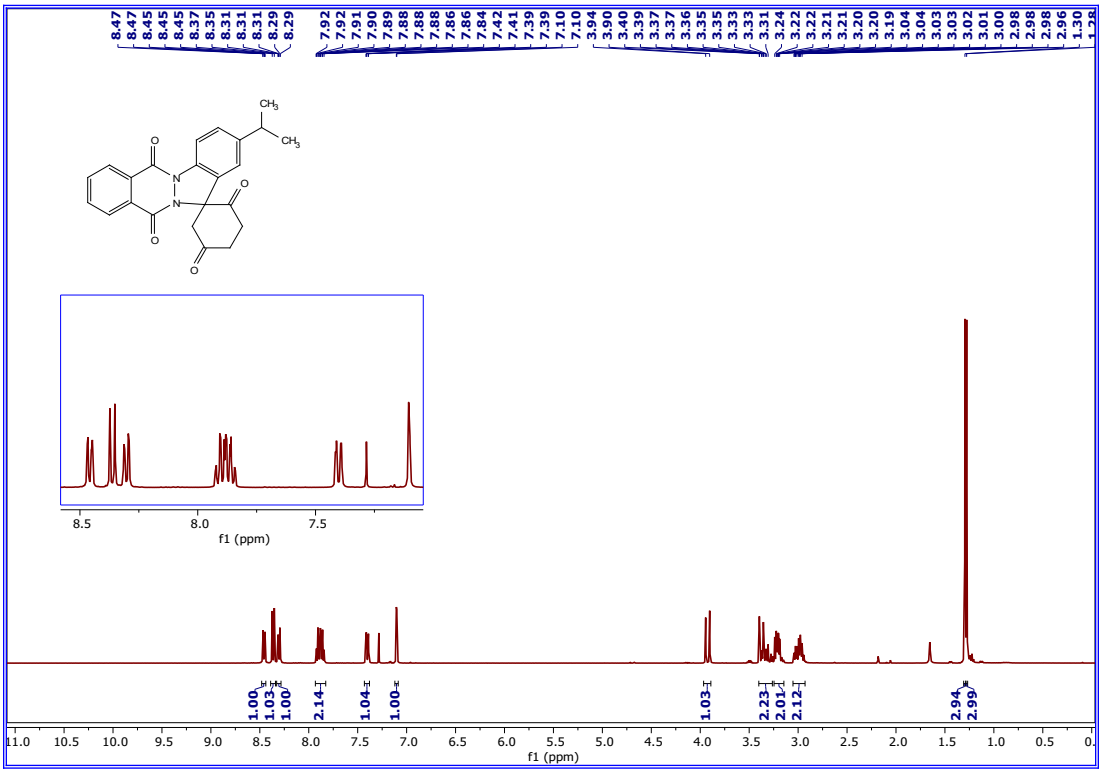
### HSQC of 4na

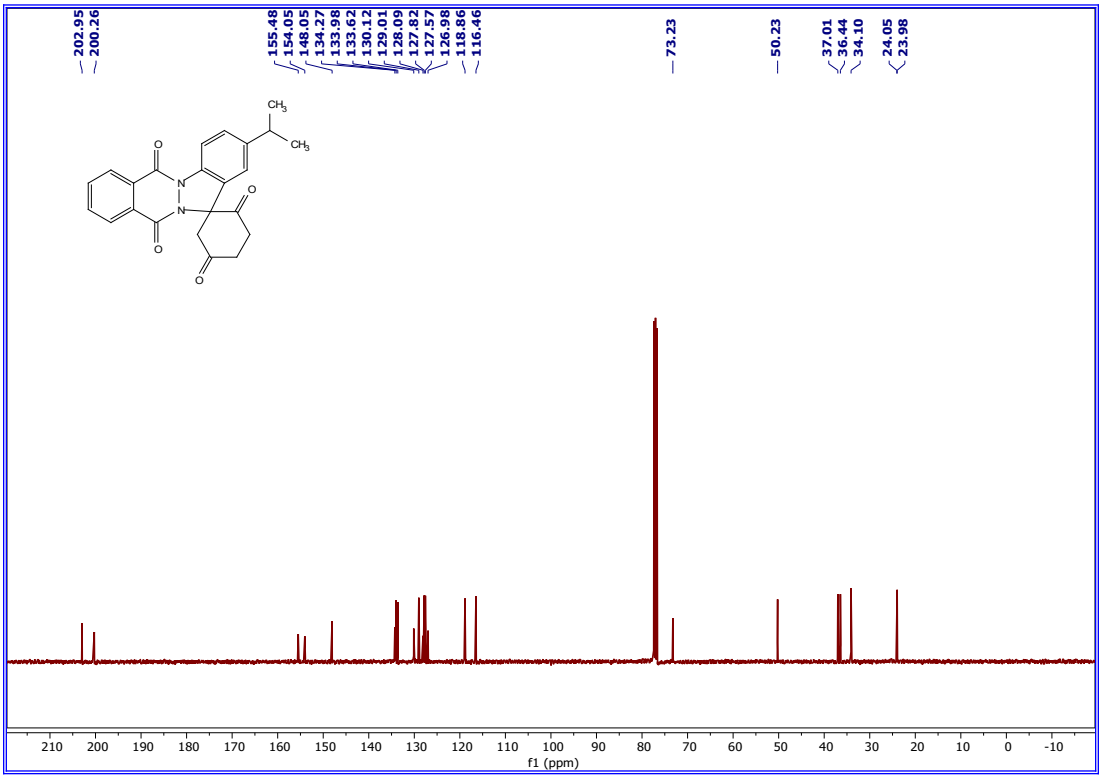



### HMBC of 4na

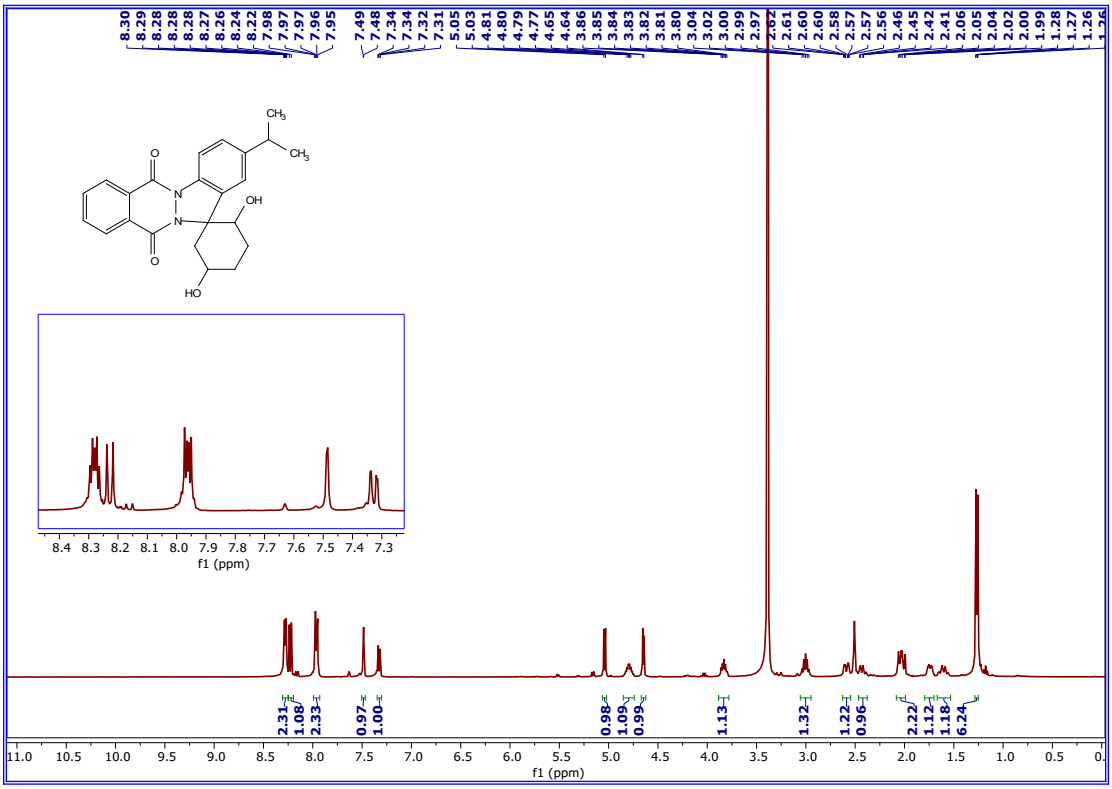


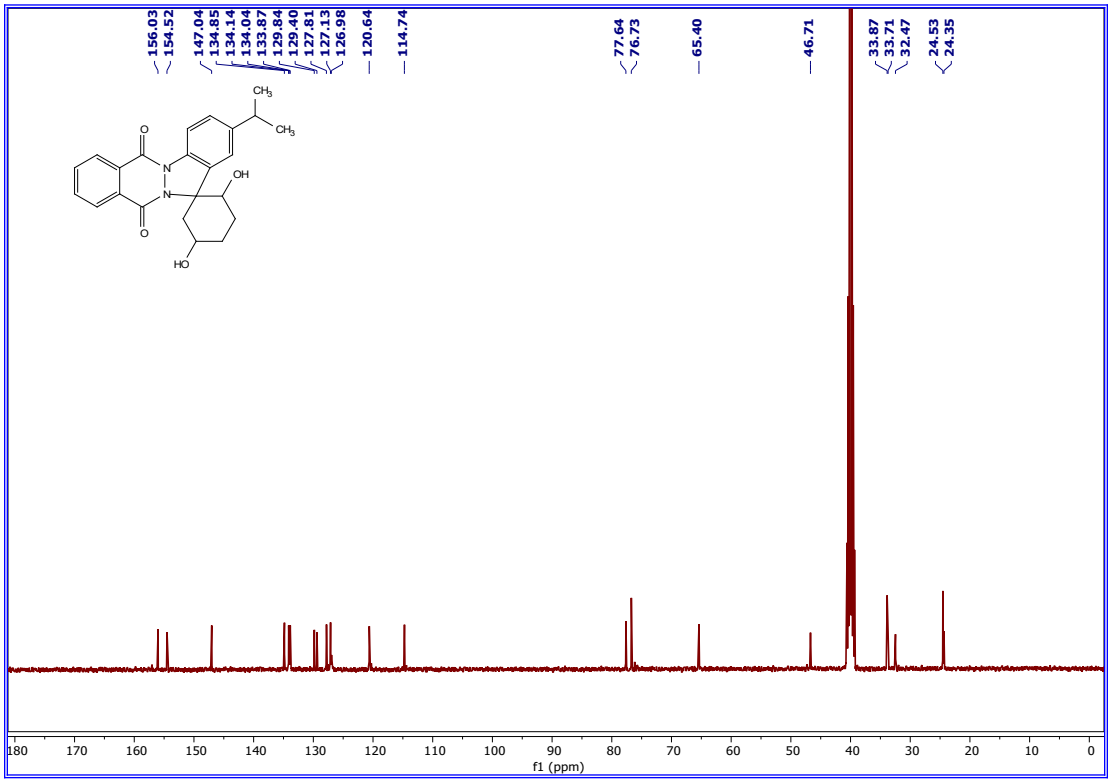
## 5, $^{1}$H NMR and $^{13}$C NMR spectra of 3'ca



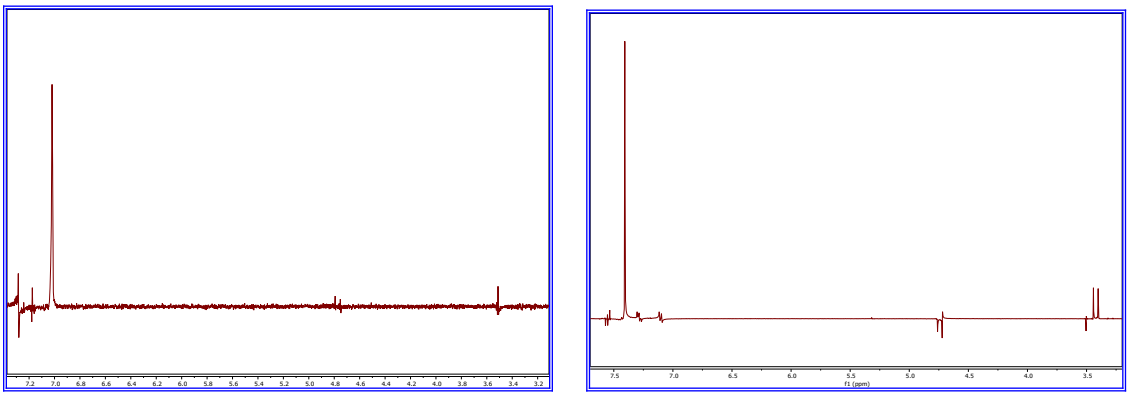
## 6. $^{1}$H NMR and $^{13}$C NMR spectra of 3''ca



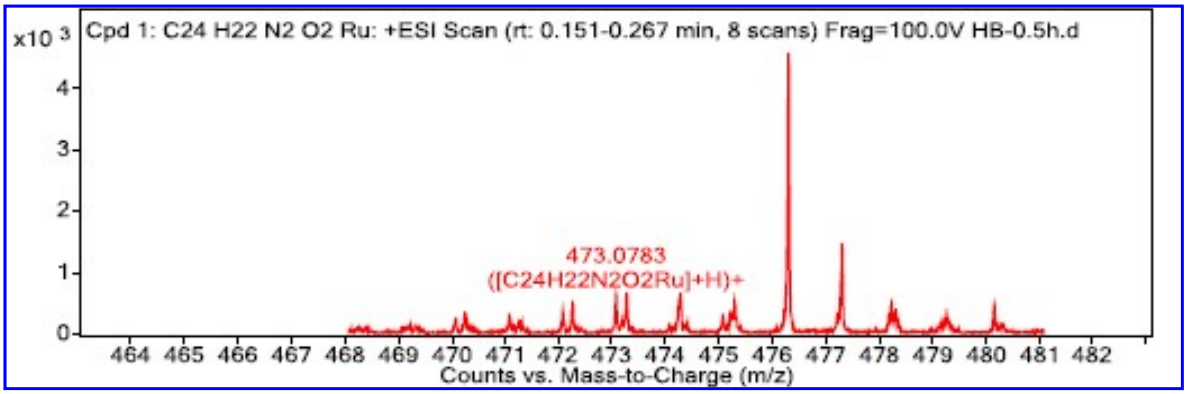
## 7. NOE spectra of 3ac and 3ad

1D gradient NOE spectrum of **3ac** *(left)* with an initial selective pulse at $\delta$ 4.77 ppm creates a significant intensified peak at 7.02 ppm. 1D gradient NOE spectrum of **3ad** *(right)* with an initial selective pulse at $\delta$ 4.74 ppm creates a significant intensified peak at 7.41 ppm.

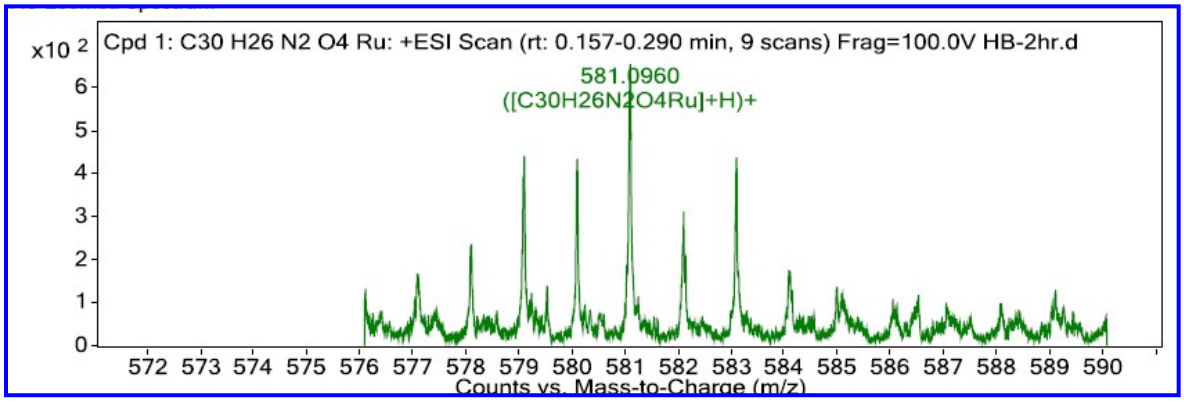


## 8. HRMS Analysis of Crude Reaction Mixture

**HRMS data of intermediate 3A**

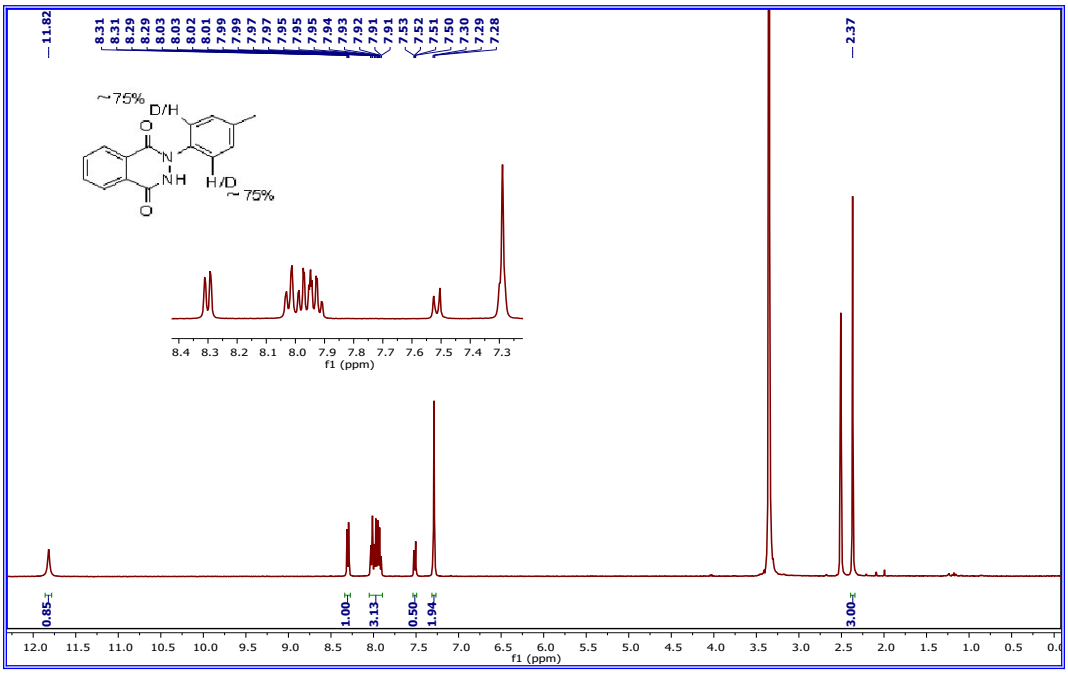



**HRMS data of intermediate 3B**



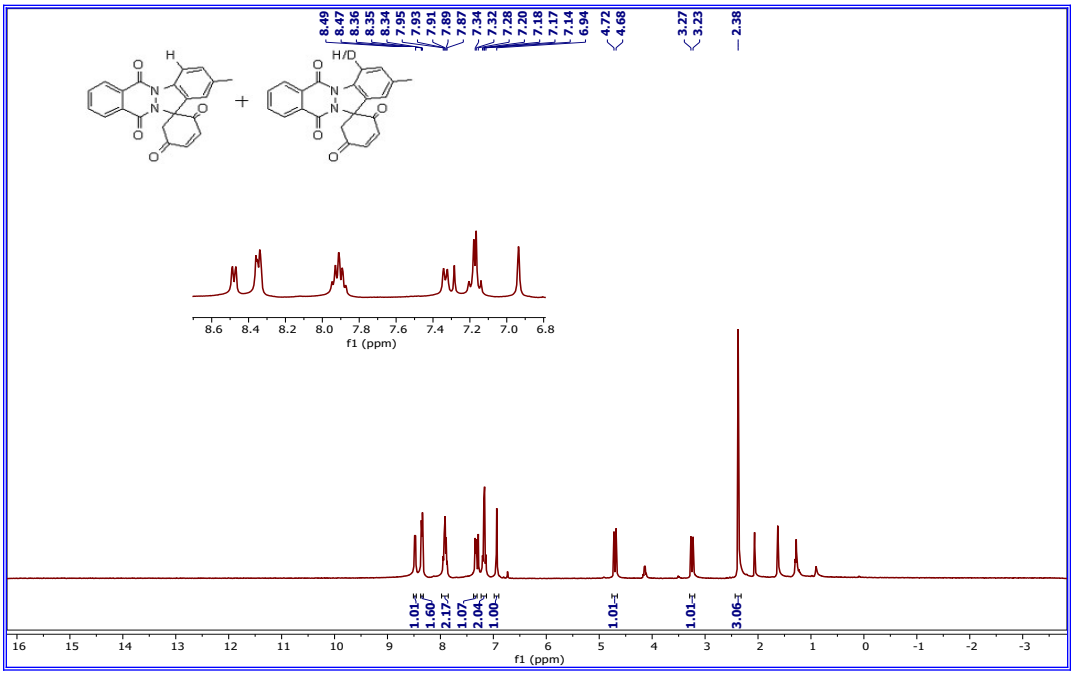
## 9. Deuterium Labelling & Kinetic Isotope Studies

### $^1$H NMR of 1b/1b-$d_2$




### Intermolecular Competitive Experiment

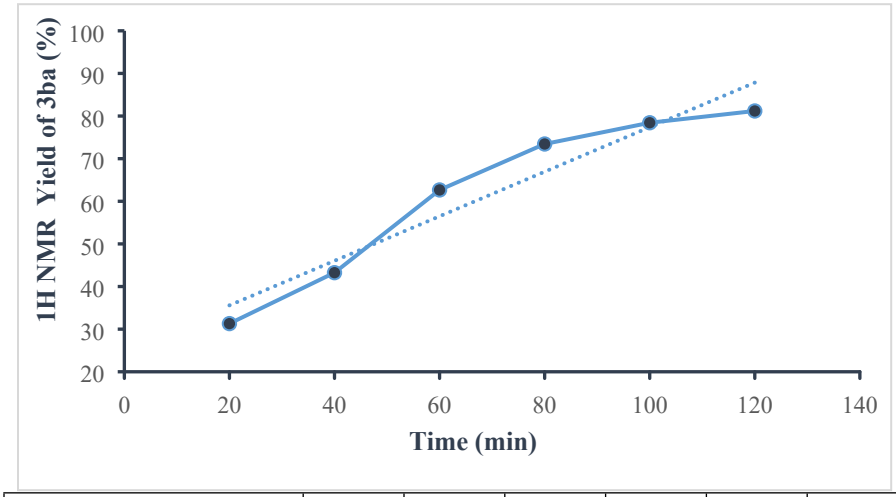
### $^1$H NMR of 3ba + 3ba-$d_1$




$P_H/P_D$ = 0.60/0.40 = 1.5

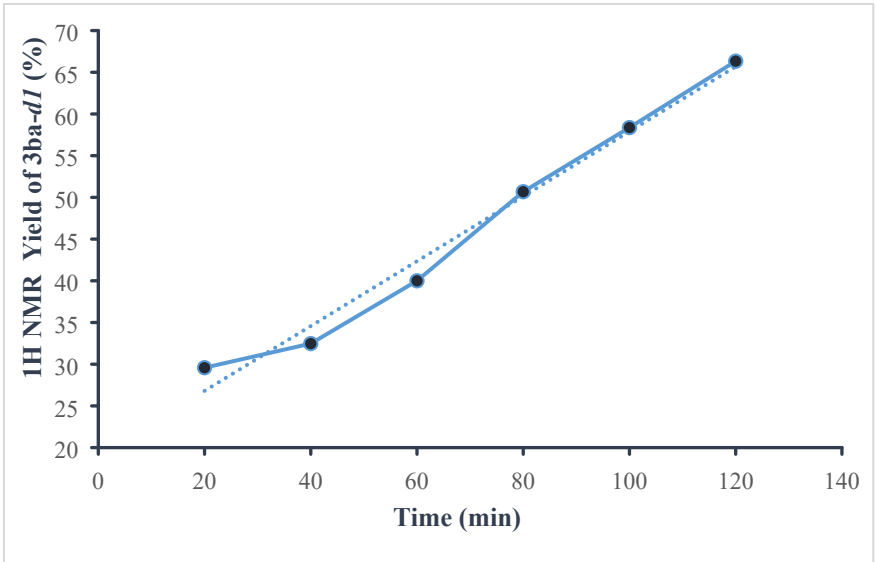
## Parallel Experiments

### Protonated Kinetics




| Time (Min) | 20 | 40 | 60 | 80 | 100 | 120 |
|---|---|---|---|---|---|---|
| $^1$H NMR Yield of 3ba (%) | 31.30 | 43.25 | 62.66 | 73.44 | 78.43 | 81.19 |

### Deuterated Kinetics

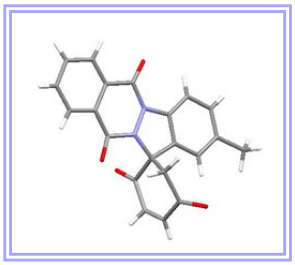



| Time (Min) | 20 | 40 | 60 | 80 | 100 | 120 |
|---|---|---|---|---|---|---|
| $^1$H NMR Yield of 3ba-$d_1$ (%) | 29.58 | 32.47 | 40.00 | 50.68 | 58.37 | 66.33 |

**KIE = $k_H/k_D$ = 0.5225/0.3888= 1.34**

## 10. Single Crystal X-ray Diffraction Studies

A suitable crystal was chosen with the help of a light microscope for mounting in a nylon loop to attach to a goniometer head. A Kappa APEX II diffractometer equipped with a CCD detector (with the crystal-to-detector distance fixed at 60 mm) and sealed-tube monochromated MoKα radiation was used for centering, initial crystal evaluation and data collection by the program APEX2.[1] All data were integrated, and reflections were fitted and values of $F^2$ and $\sigma(F^2)$ for each reflection were obtained by using the program SAINT.[1] Finally, data were also corrected for the Lorentz and polarization effects. Using the subroutine XPREP[1] the space group was determined, and an absorption correction (SADABS)[1] and merging of data were performed to generate the necessary files for solution and refinement. A structure solution was obtained by direct methods using the SHELXS program of the SHELXTL package and was refined using SHELXL[2,3] within the OLEX2 crystallographic software suite.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. All figures were drawn using MERCURY V 3.0[5]



Crystal data for **3ba**. $C_{21}H_{14}N_2O_4$, Mr = 358.34 g/mol, monoclinic, space group $P2_1$, a = 10.8392(10) Å, b = 6.9084(6) Å, c = 13.2121(11) Å, α = 90°, β = 108.035(3)°, γ = 90°, V = 940.73(14) $Å^3$, Z = 2, T = 298(2) K, $D_{calcd}$ = 1.265 $g/cm^3$; Full matrix least-square on $F^2$; $R_1$ = 0.1450, $wR_2$ = 0.3879 for 2762 observed reflections [$I > 2\sigma(I)$] and $R_1$ = 0.1600, $wR_2$ = 0.4121 for all 3301 reflections; number of parameters = 240; GOF = 1.715. CCDC No. 2169711.

### References


1. *APEX2*, *SADABS and SAINT*; Bruker AXS inc: Madison, WI, USA, **2008**.
2. G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Adv., 2015, **71**, 3-8.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. C: Found. Adv.*, 2015, **71**, 3-8.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* 2009, **42**, 339−341
5. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edginton, P. McCabe, E. Pidocck, L. Rodriguez-Monge, T. Taylor, J. Van de Streek, P. A. Wood, *J. Appl. Cryst.,* 2008, **41**, 466.