

Supporting Information

Reusable, Homogeneous Water Soluble Photoredox Catalyzed Oxidative Dehydrogenation of N-heterocycles in Biphasic System: Applications to Synthesis of Biologically Active Natural Products

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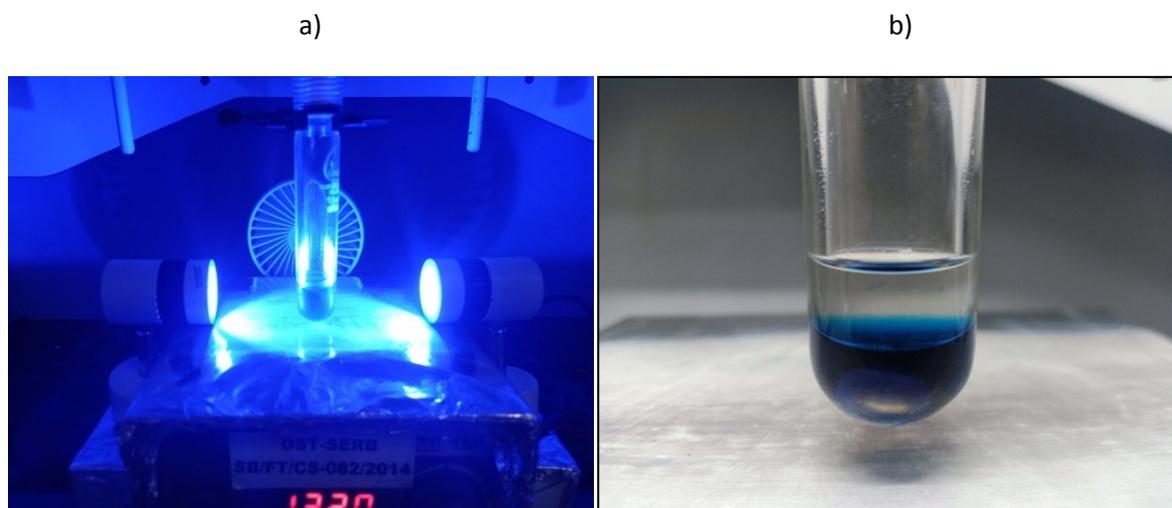


Figure 1. a) Photochemical reaction set up b) Biphasic layer of the reaction mixture

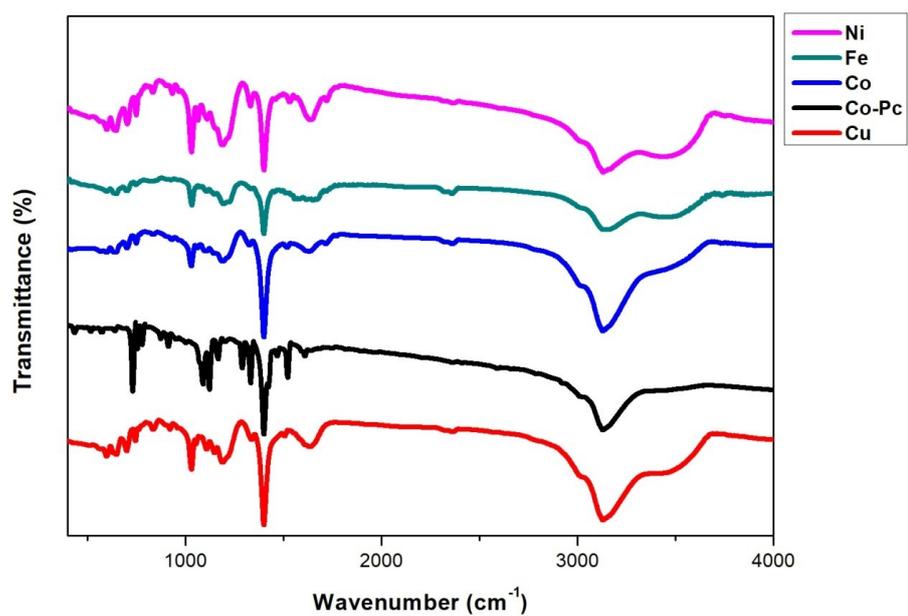


Figure 2 IR spectra of CoPc (**3a**) and different water soluble MPc(SO₃Na)₄ [M = Co (**3b**), Fe (**3c**), Ni (**3d**) and Cu (**3e**)] photoredox catalysts measured using KBr pellet.

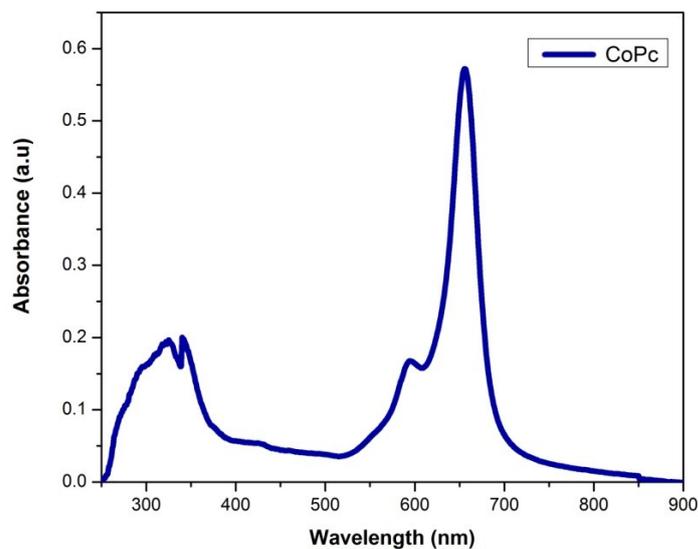


Figure 3 UV-Visible spectral absorbance of CoPc (**3a**) photoredox catalyst measured in DMSO.

Cyclic Voltammetric Experiment:

The Voltammetric experiments are analyzed in Biologic SP-300 electrochemical workstation using Glassy carbon as working electrode, Standard calomel electrode as reference electrode, Pt wire as counter electrode and 0.1 M TBAPF₆ as supporting electrolyte in DMF with 2.0 mM solution of the sample. Ferrocene was used as an internal standard (Fig. 4). All the experiments are performed using argon purged solutions at room temperature. High purity dimethylformamide (DMF) was purchased from SRL. The supporting electrolyte, tetrabutylammoniumhexafluoro phosphate (TBAPF₆), was purchased from Sigma Aldrich.

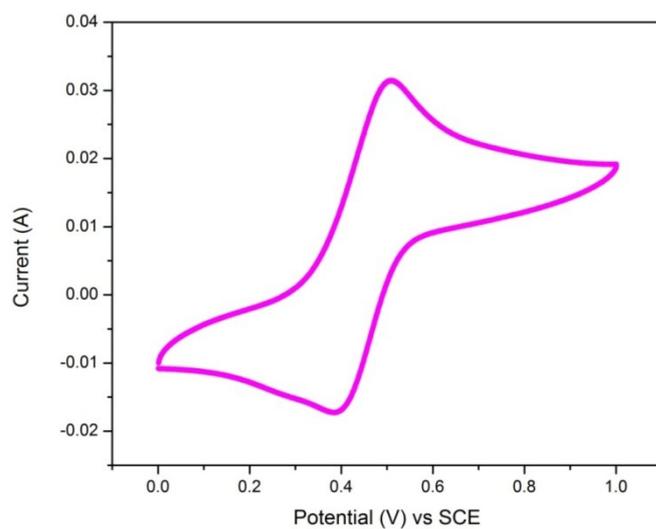


Figure 4. Cyclic Voltammogram of Ferrocene

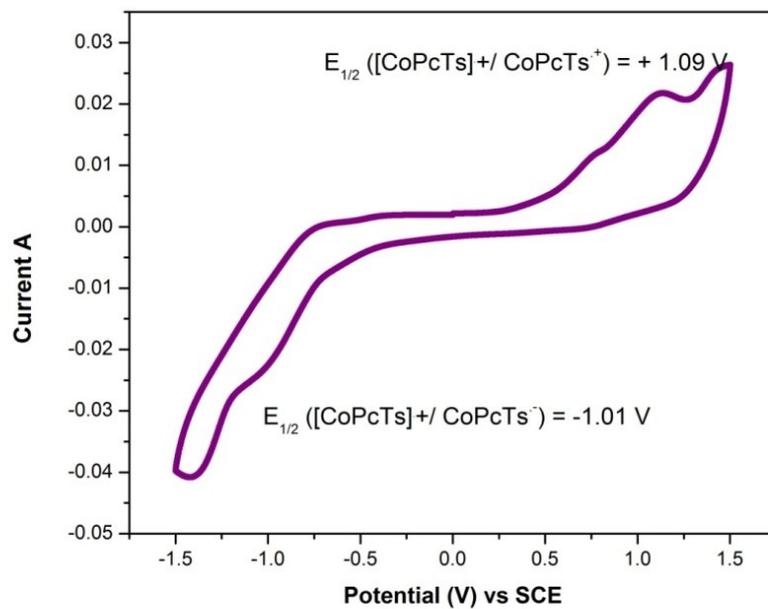


Figure 5. Cyclic Voltammogram of CoPc(SO₃Na)₄ [CoPcTs]

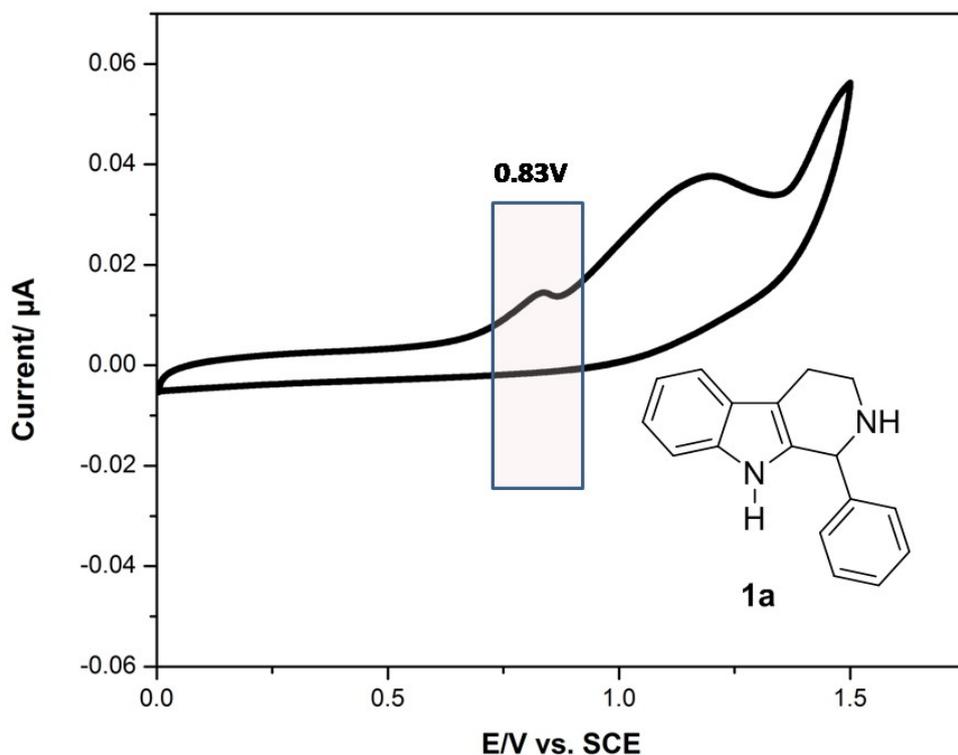


Figure 6. Cyclic voltammogram of substrate **1a** measured in DMF

Calculation of the Excited State Potential of the Catalyst:

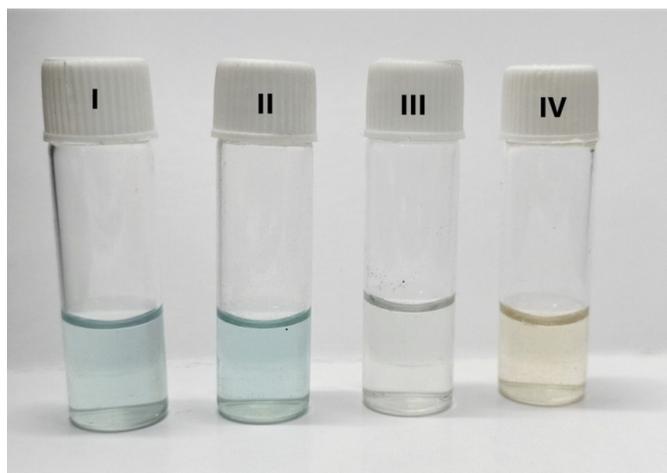
The excited state potential of the catalyst can be calculated using the Rehm–Weller formalism by employing the following equation.

$$(E(I^*/I^-) = E(I/I^-) + E_{0,0}(I^*/I))$$

$E(I/I^-)$ is the ground state reduction potential of the catalyst. $E_{0,0}(I^*/I)$ is the excited state energy of catalyst which was estimated spectroscopically. $E_{0,0}(I^*/I)$ was calculated to be **2.74 eV**.

Thereby,

$$E(I^*/I^-) = -1.01 + 2.74 = +1.73V \text{ (vs SCE)}$$



I- (Without Irradiation)
Photocatalyst + Substrate + KI

II-(Without Irradiation)
Photocatalyst + Substrate

III-(Irradiation) Photocatalyst +
Substrate

IV-(Irradiation) Photocatalyst +
Substrate + KI

Figure 7 Detection of superoxide anion radical through KI experiment

The produced H_2O_2 can be detected in the photocatalyzed dehydrogenation of tetrahydro- β -carboline using the procedure reported in the literature¹. The color of the dehydrogenation reaction after using KI solution denotes the presence of H_2O_2 which can be compared to non-illuminated reactions.

The experimental steps are:

1) Four of ethanol:water (2:1) solutions (3 mL) each containing tetrahydro- β -carboline (10 mM) and Co catalyst (500 μ M, catalyst) were prepared. Then two of them were illuminated under standard conditions in white LED. The remaining samples are placed as such without illumination.

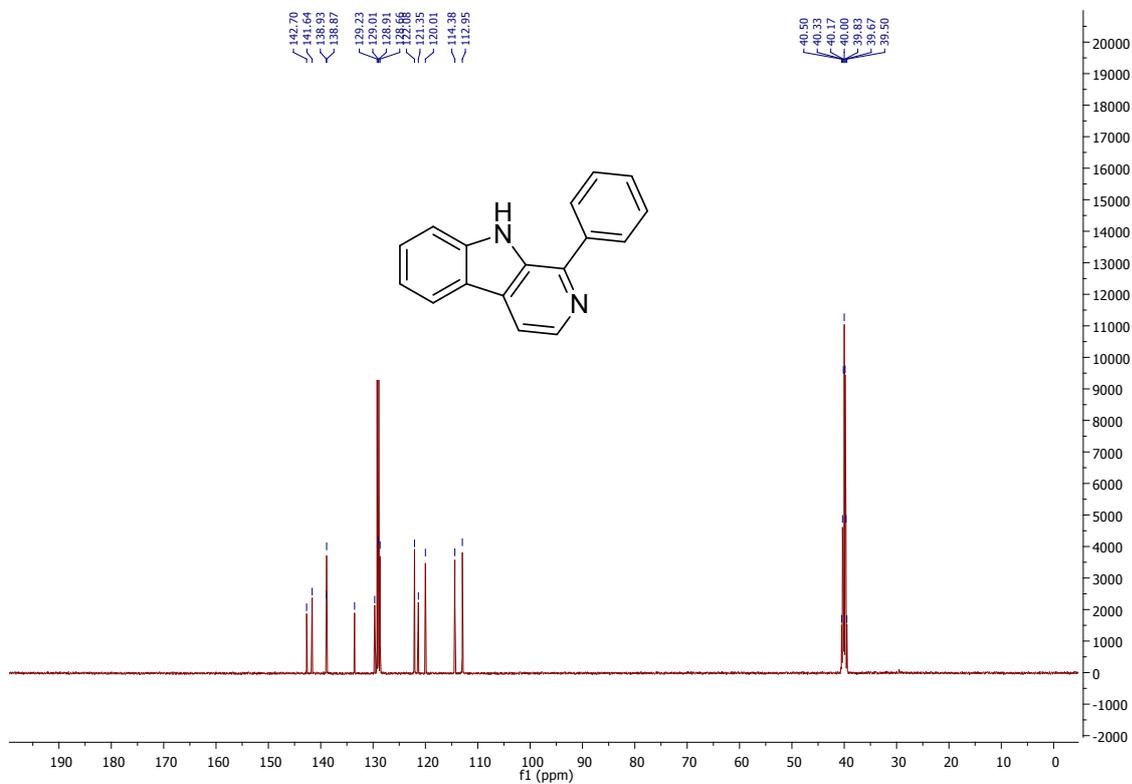
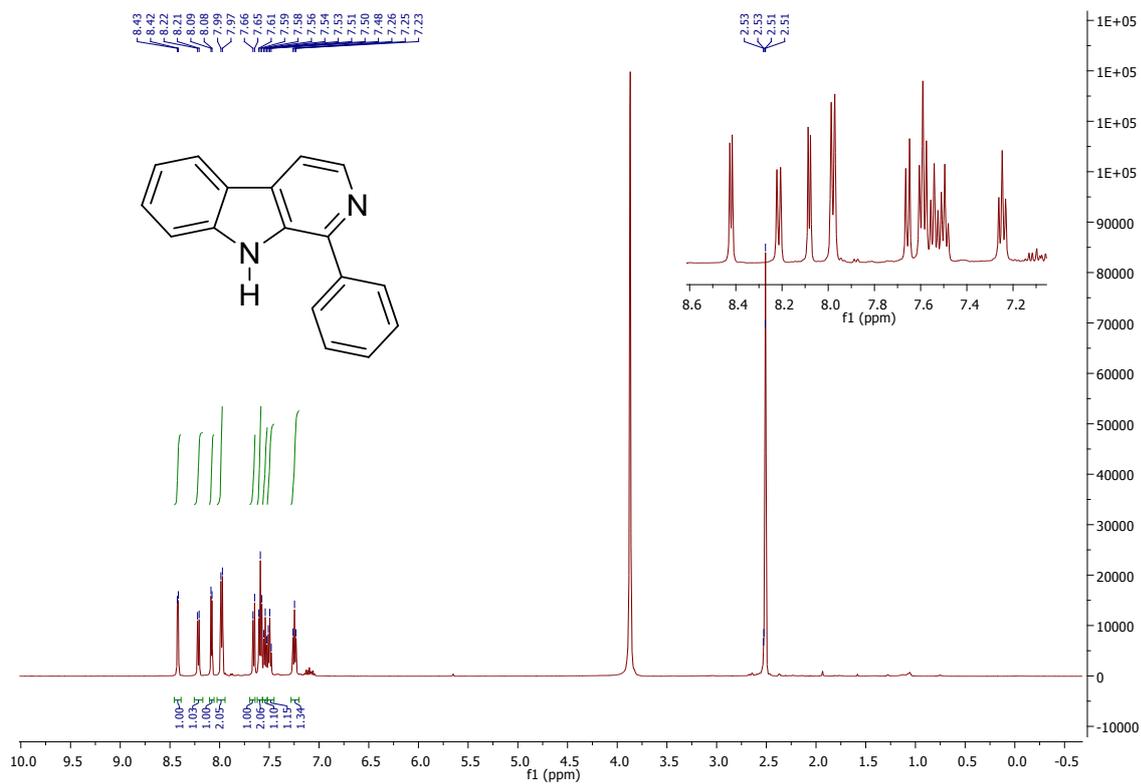
2) Each of the four solutions (0.04 ml) above was diluted with water (0.9 ml).

3) 0.06 ml of KI aqueous solution (0.6M) was added into one of the diluted irradiated (IV) and non-irradiated (I) samples respectively. The other two samples are diluted with 0.06 ml water (II and III). It can be clearly observed that the solution in sample IV gets deeper yellow colour than the other samples which is due to the presence of H_2O_2 produced in the reaction. The sample irradiated under light without KI doesn't produce any colour change due to the absence of the reaction between KI and H_2O_2 .

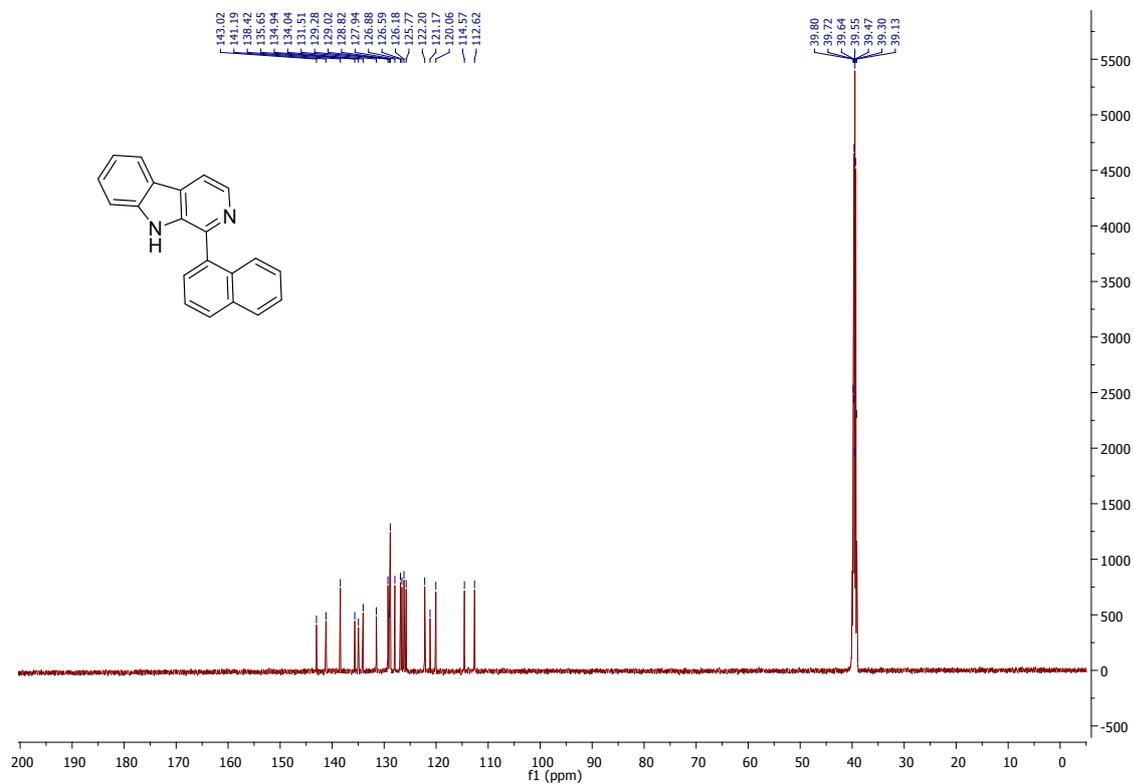
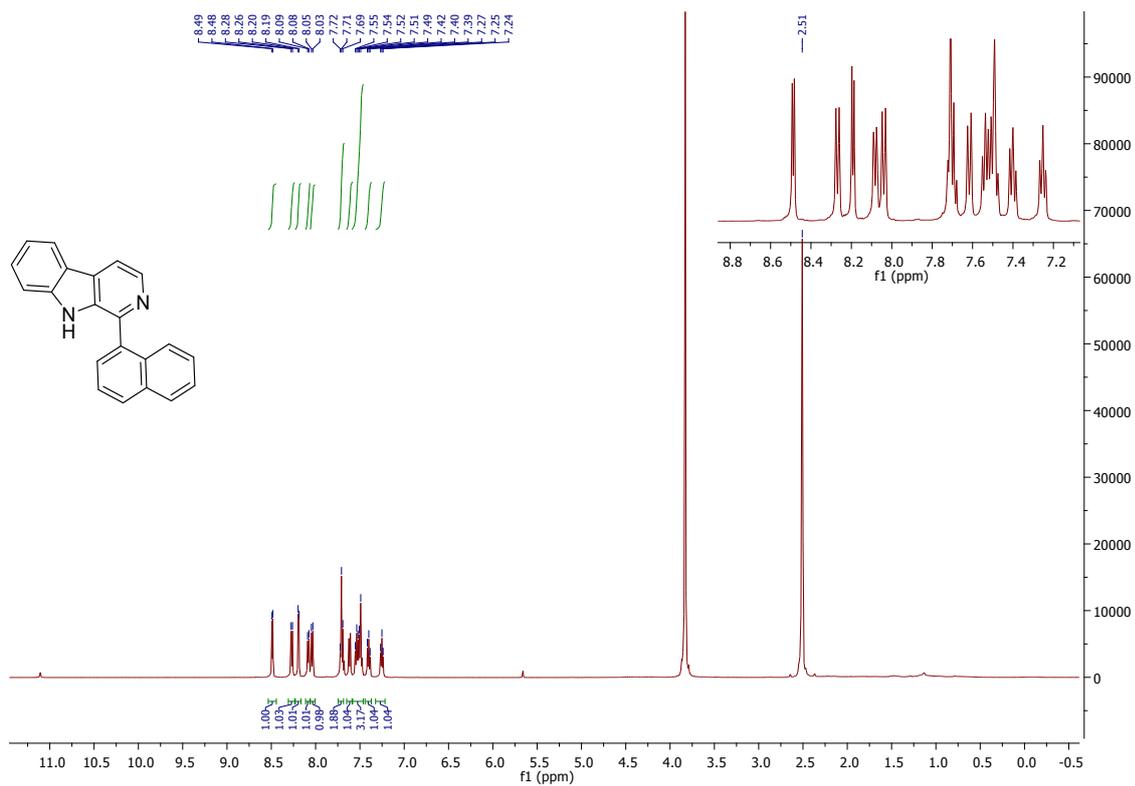
References:

1. S. Chen, Q. Wan, A. K. Badu-Tawiah, *Angew. Chem. Int. Ed.*, 2016, **55**, 9345-9349.

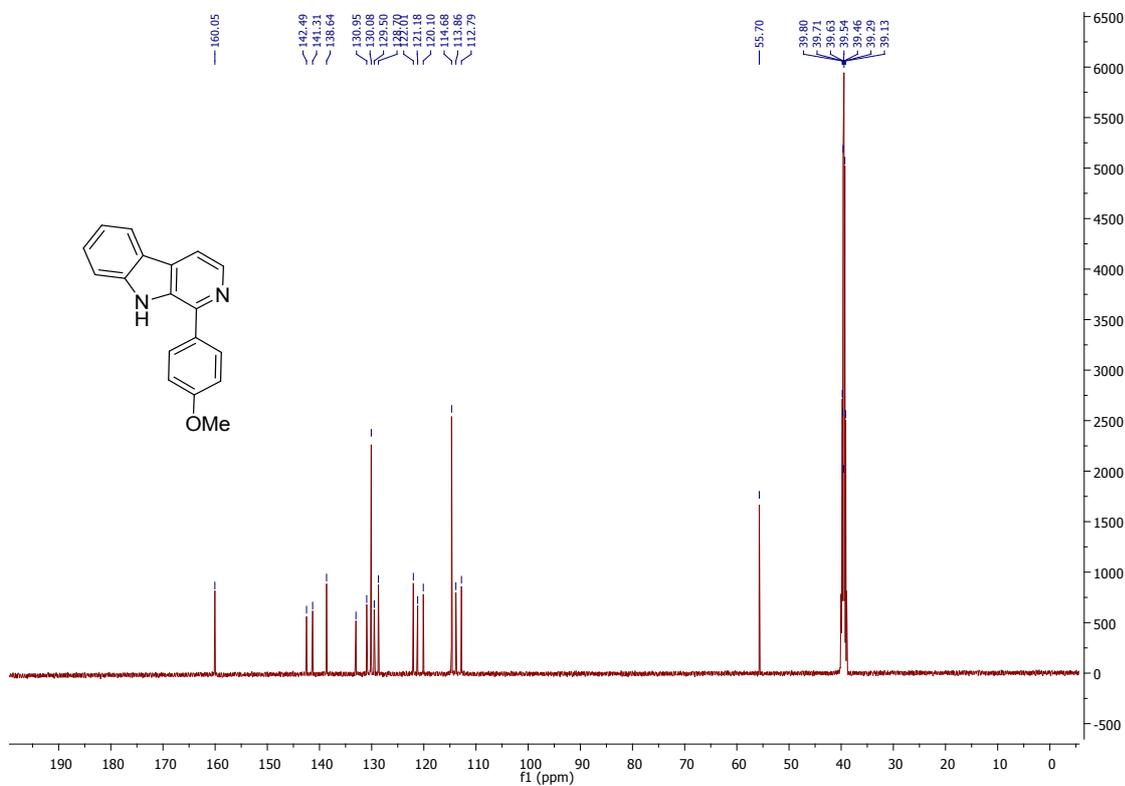
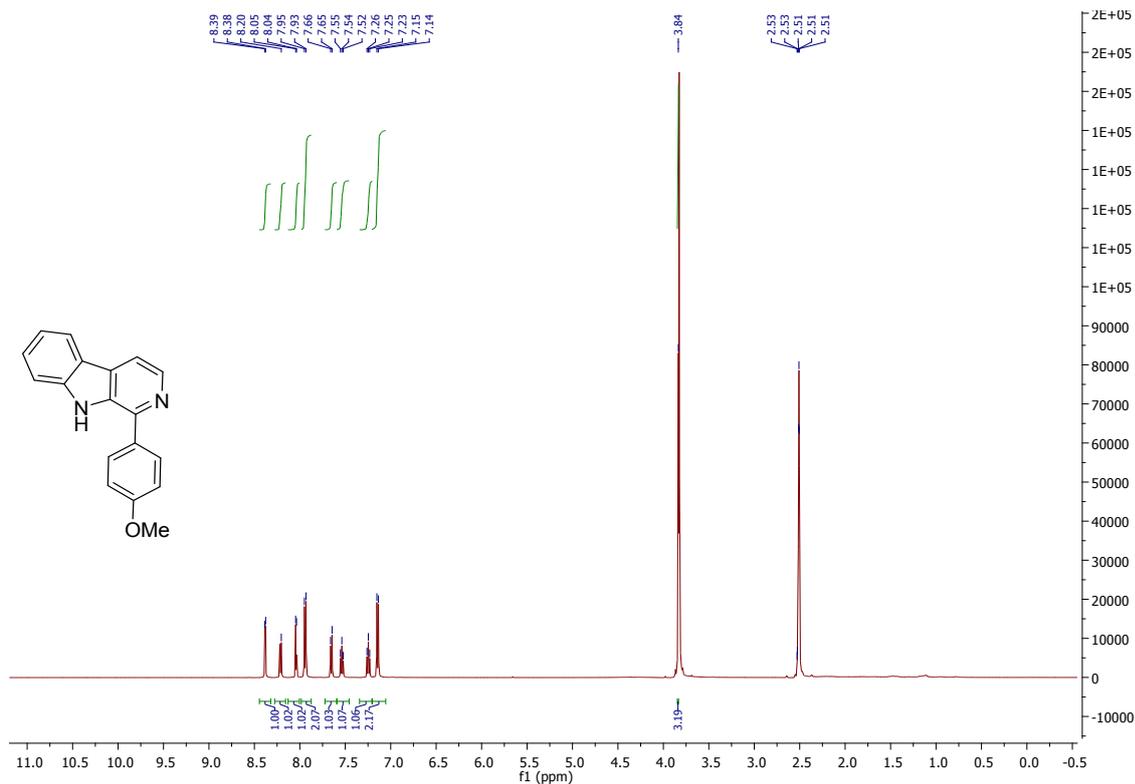
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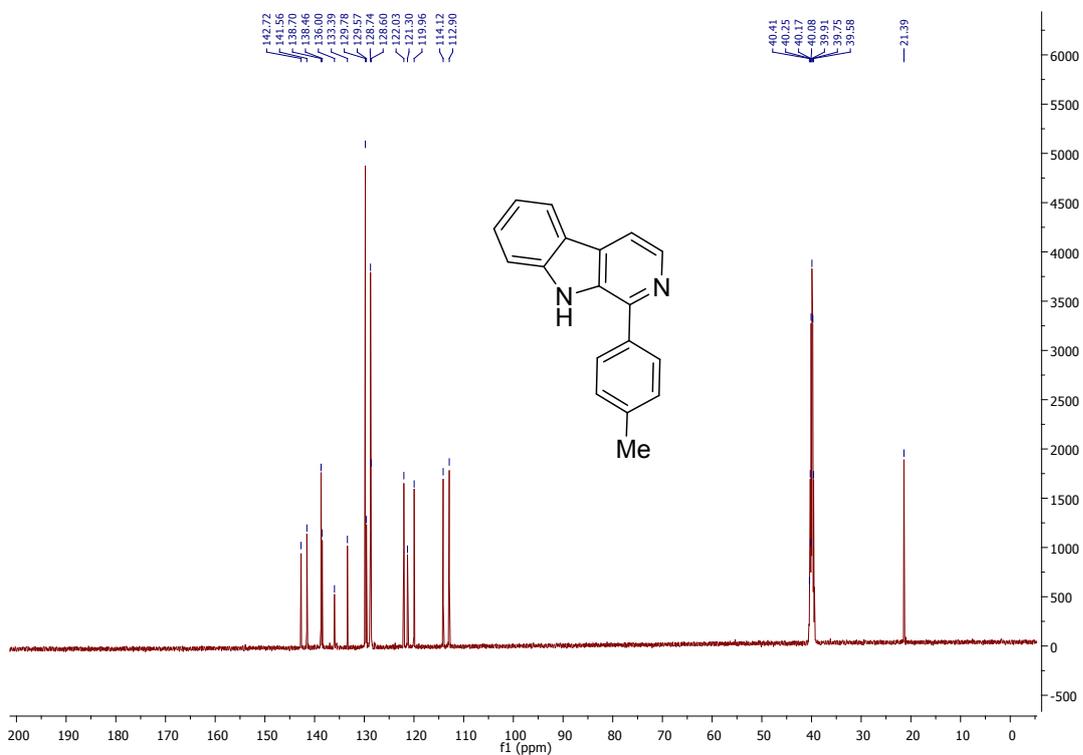
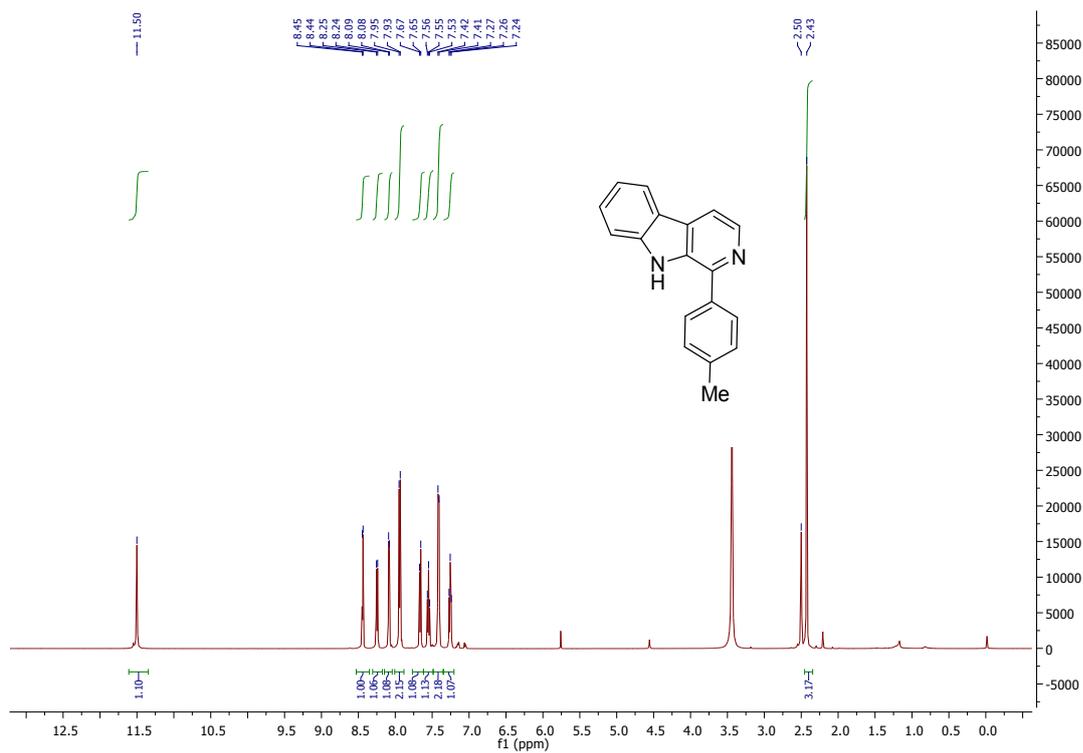
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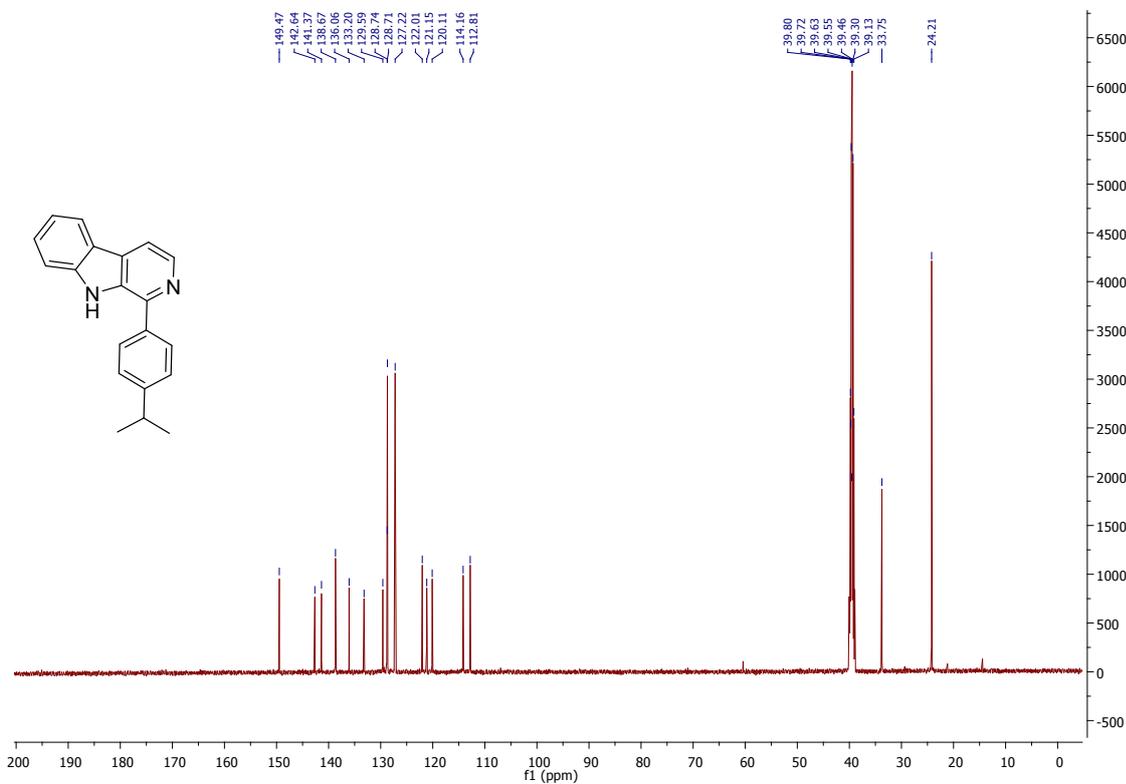
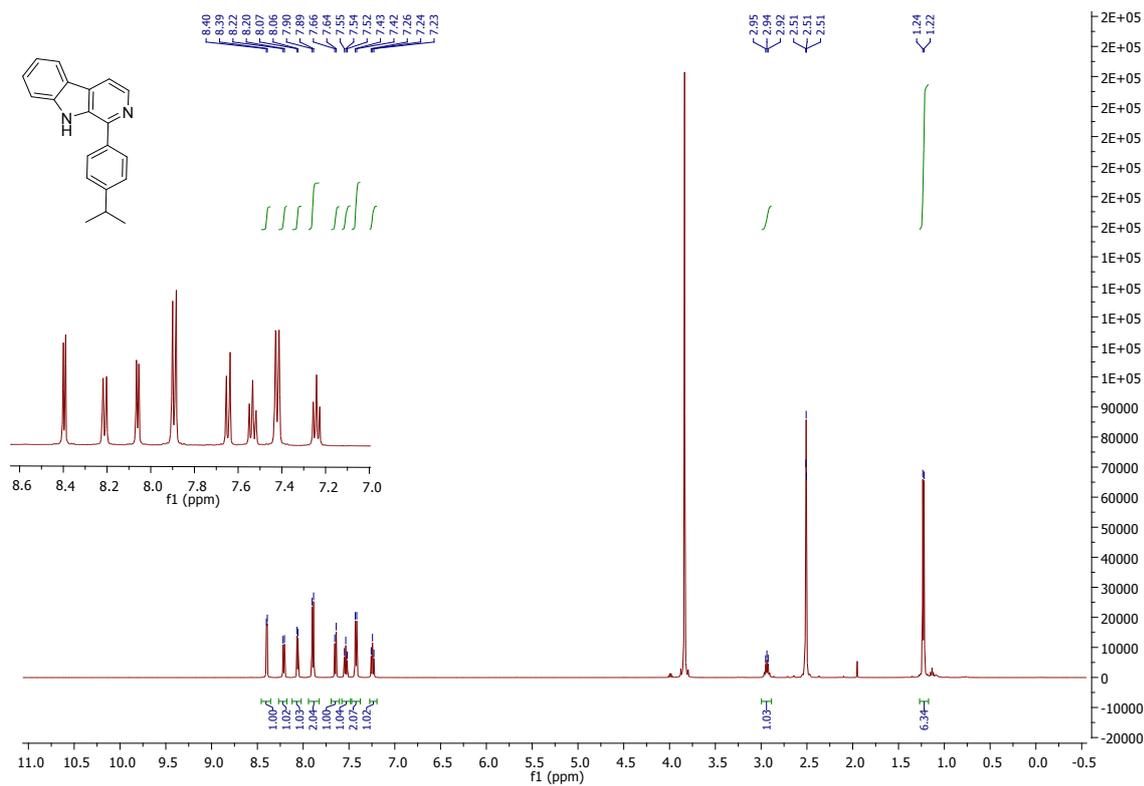
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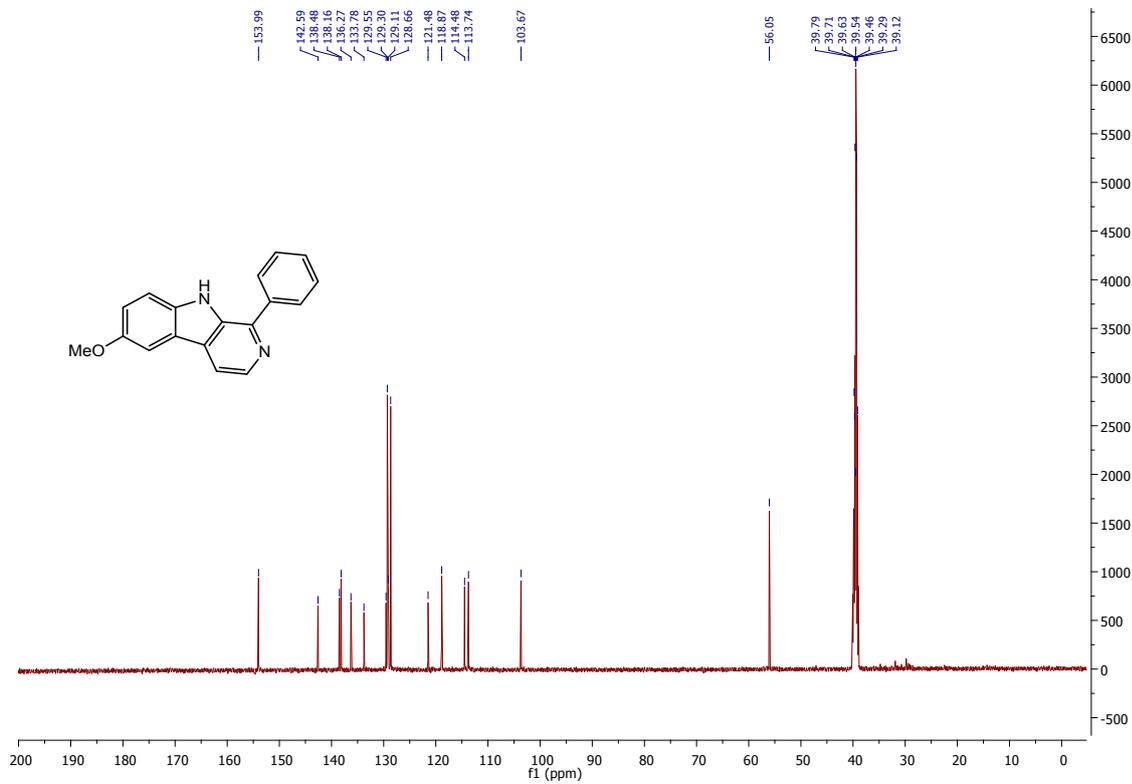
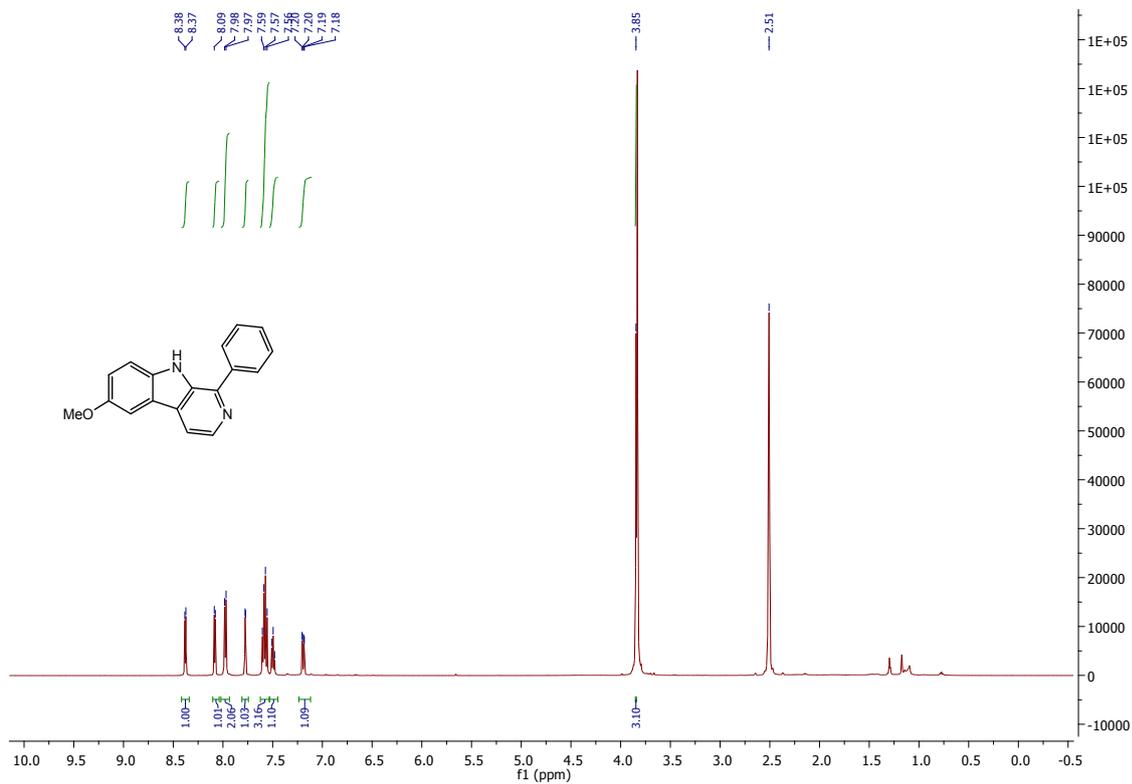
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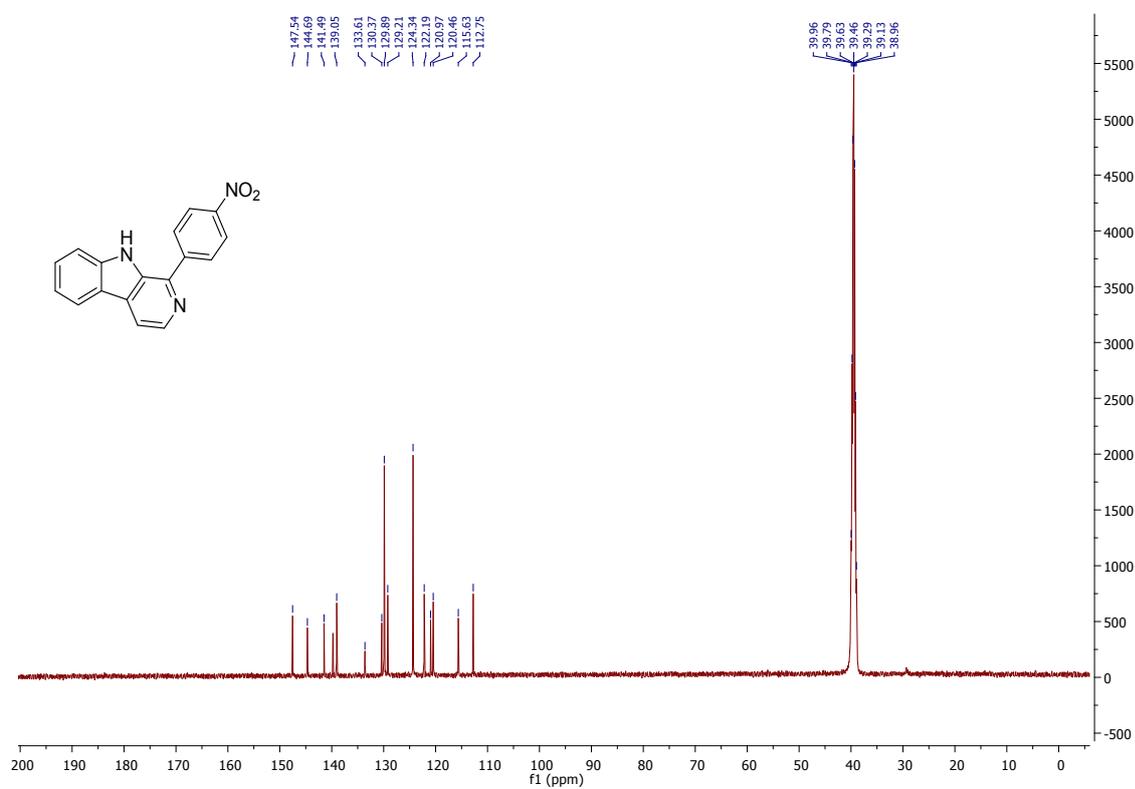
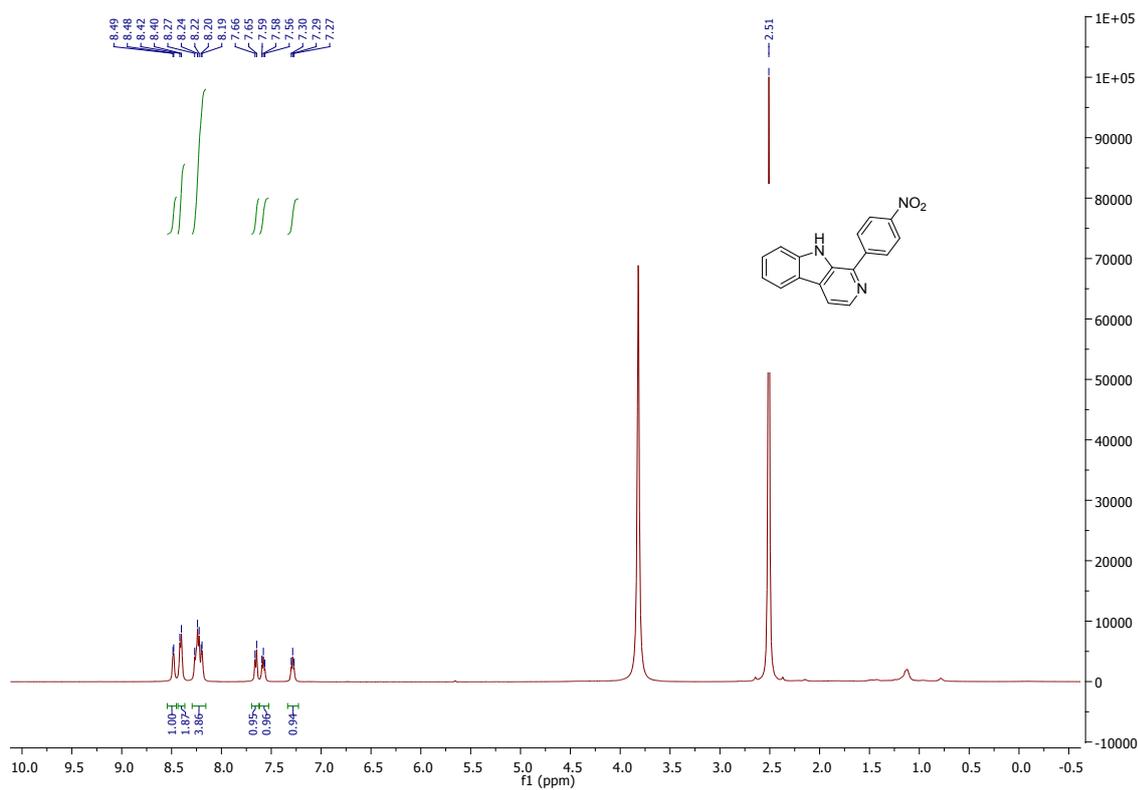
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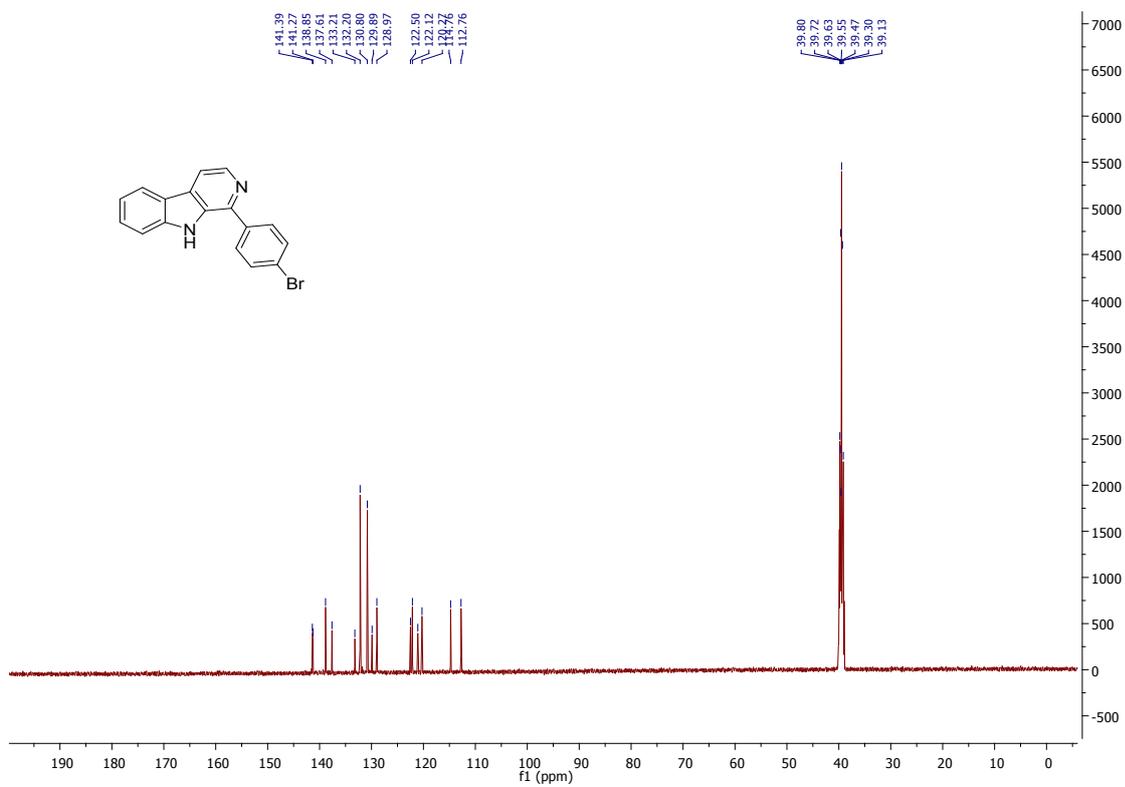
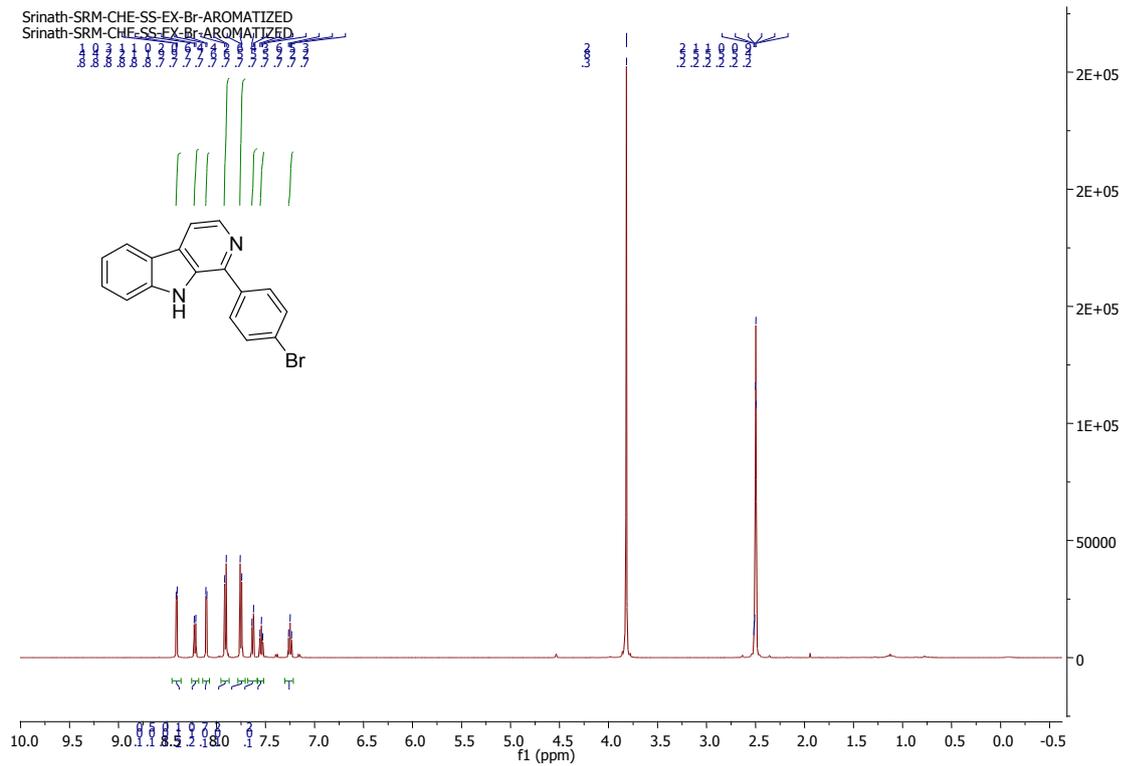
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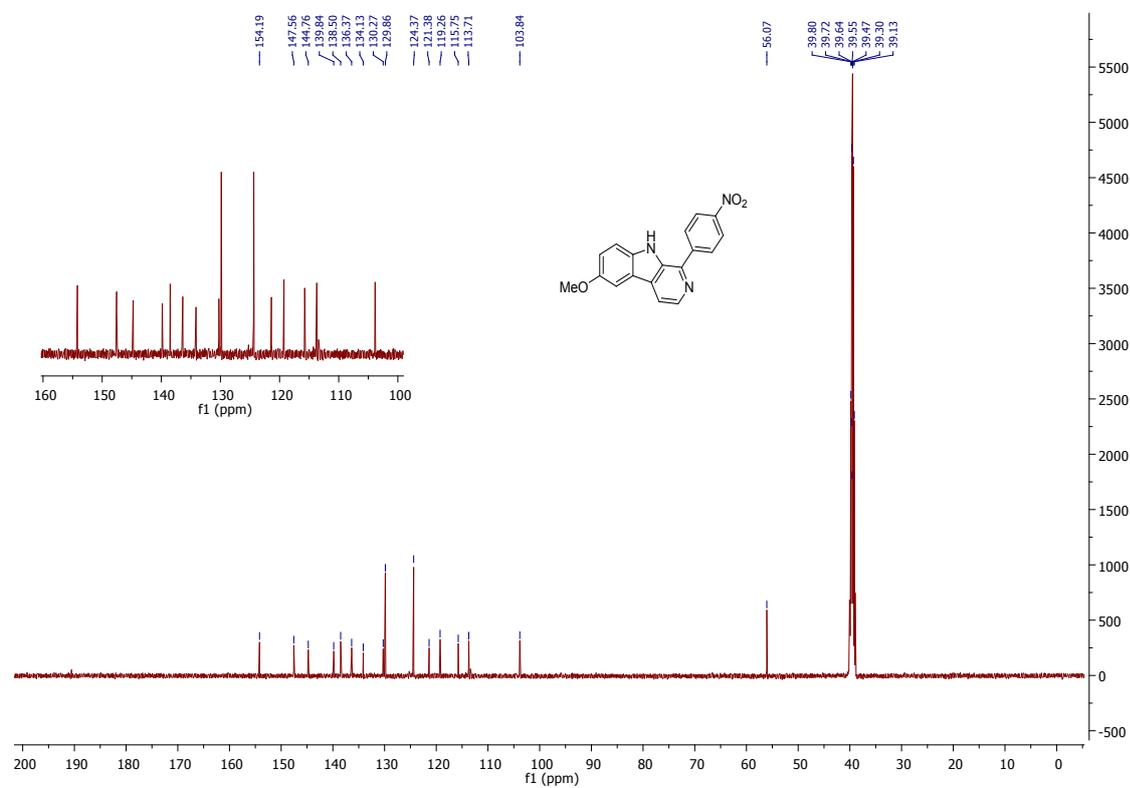
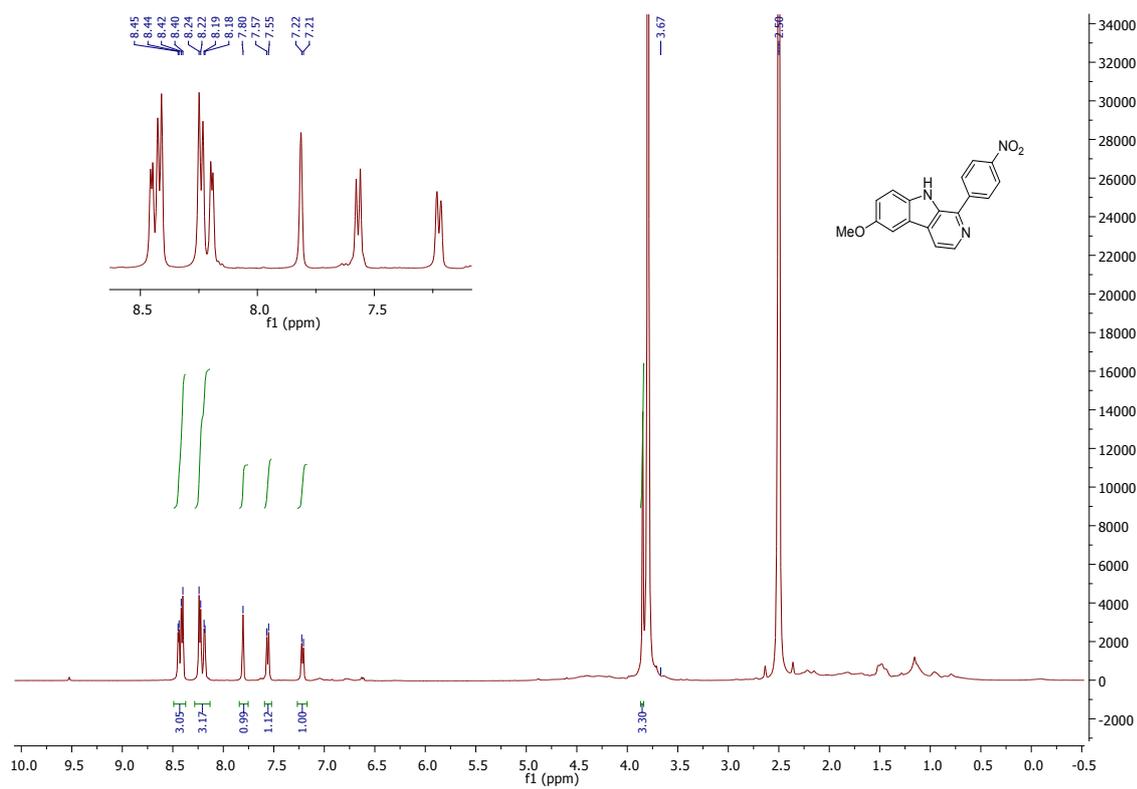
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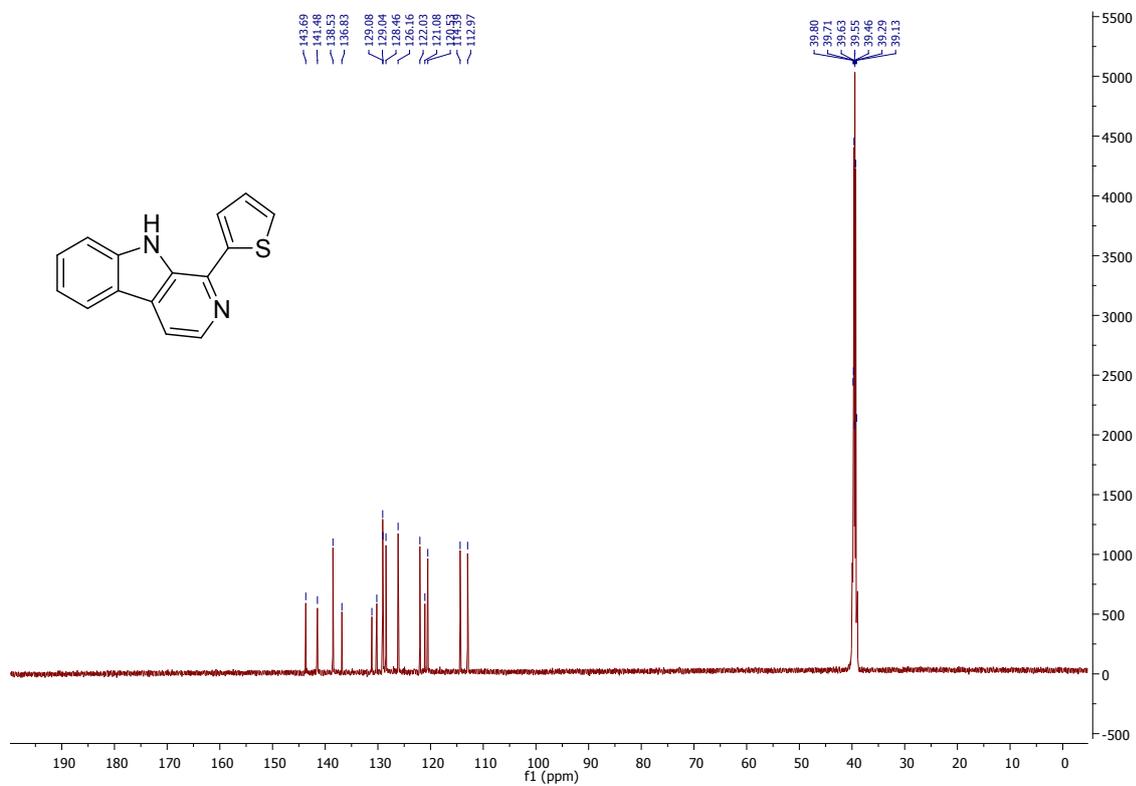
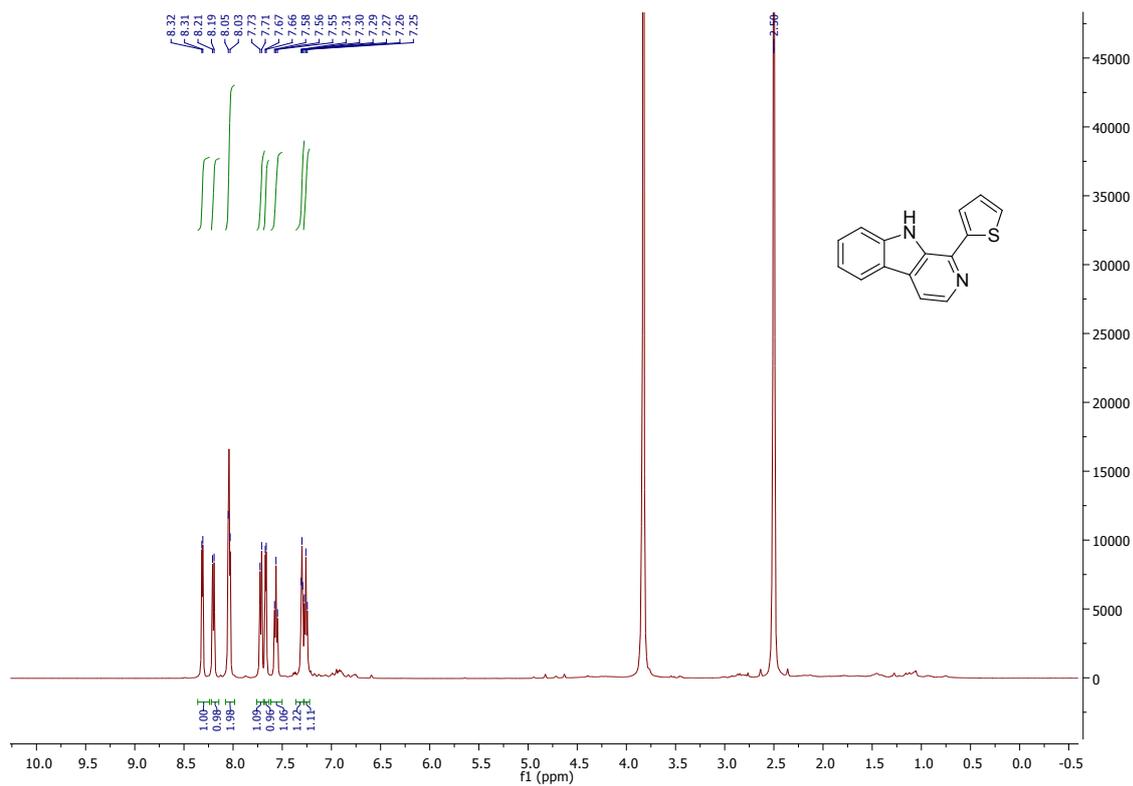
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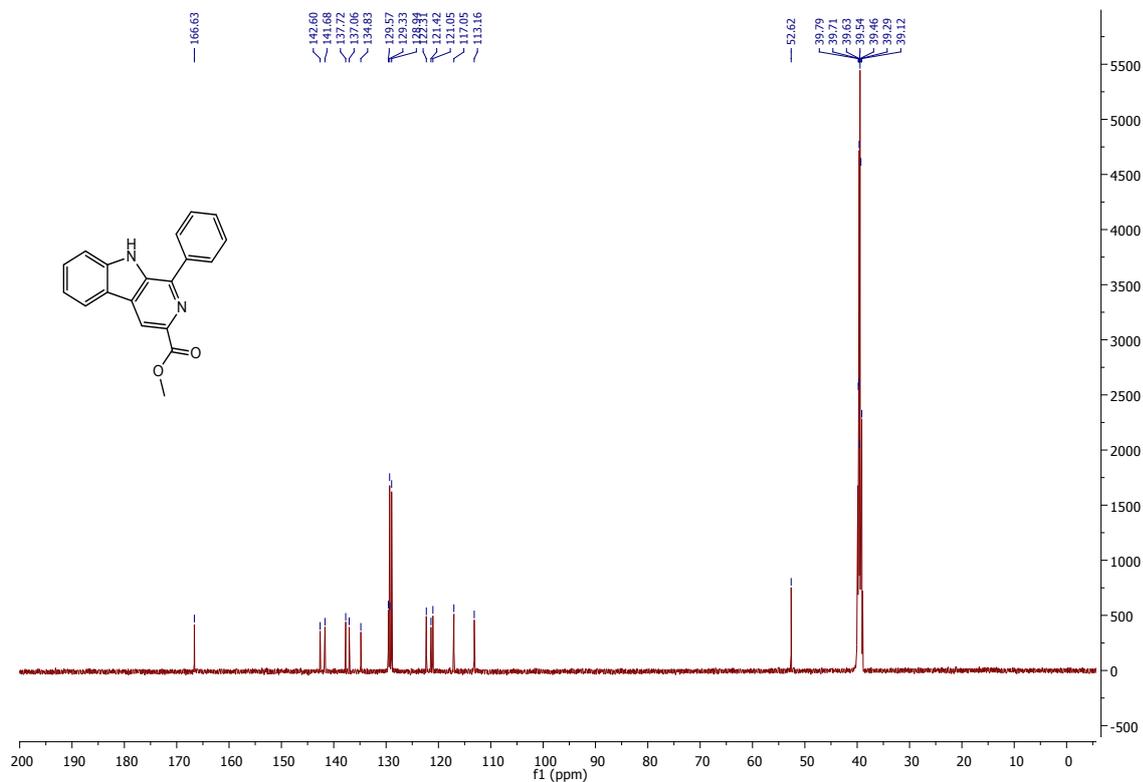
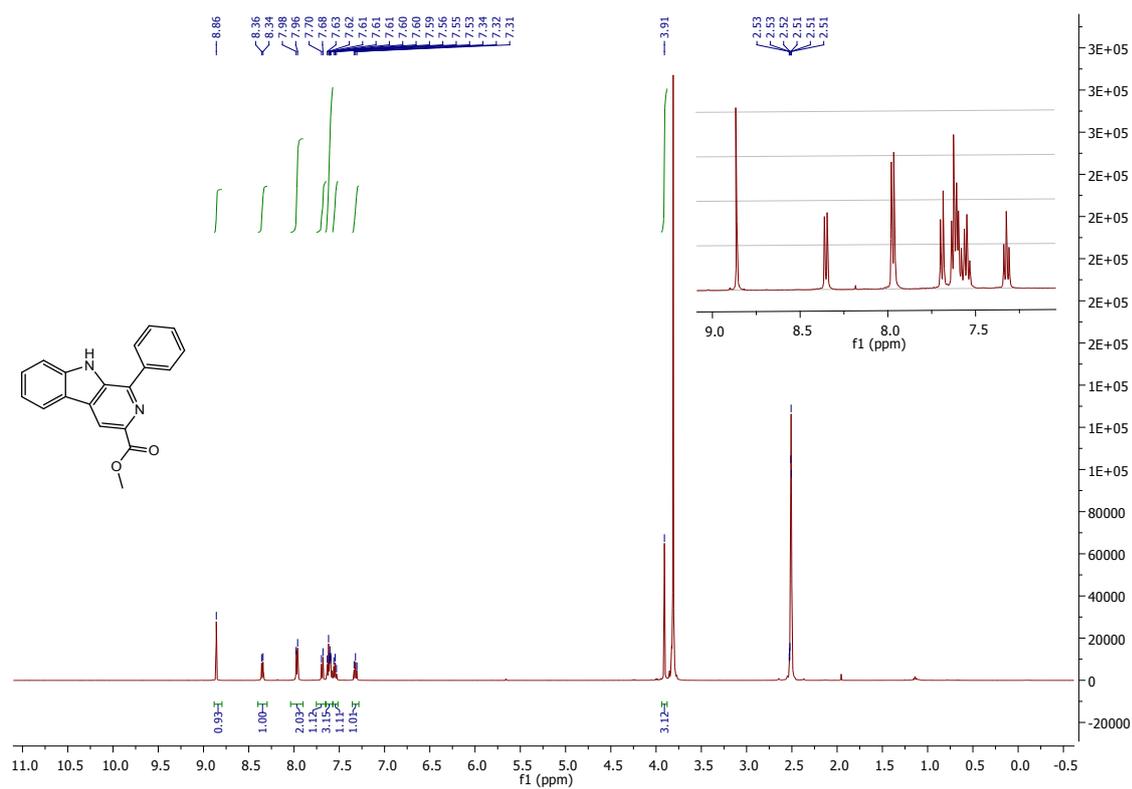
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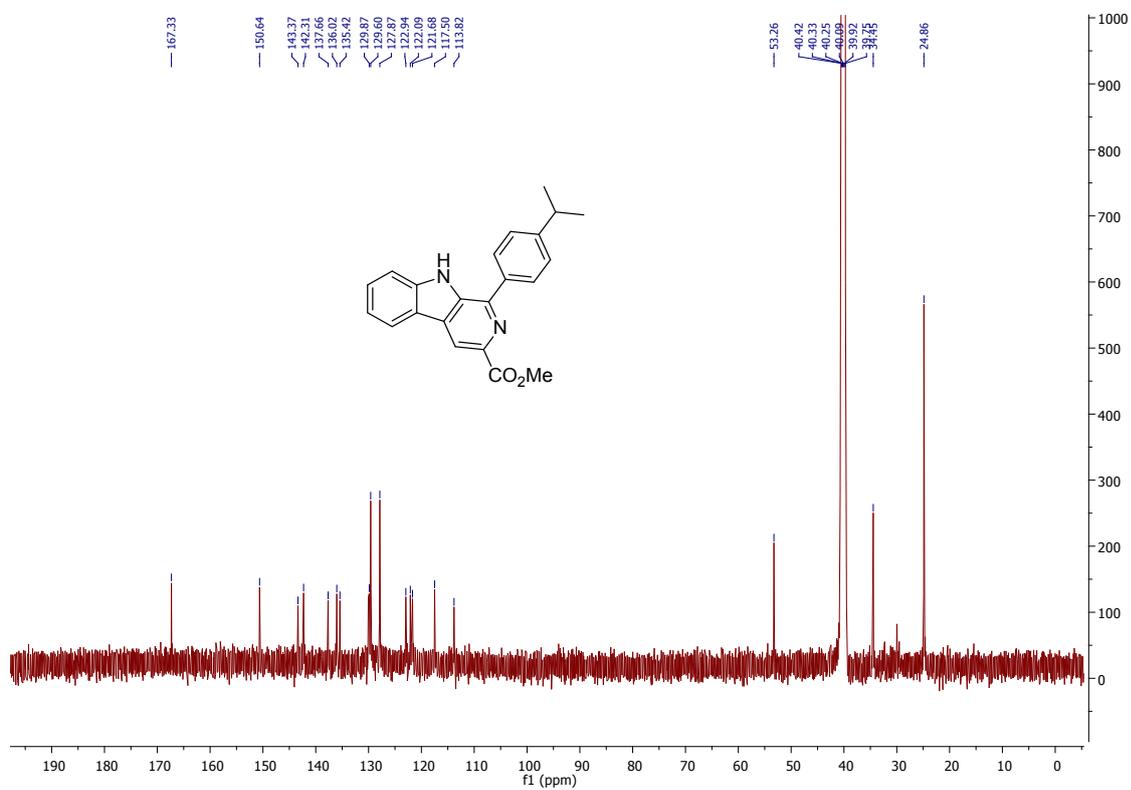
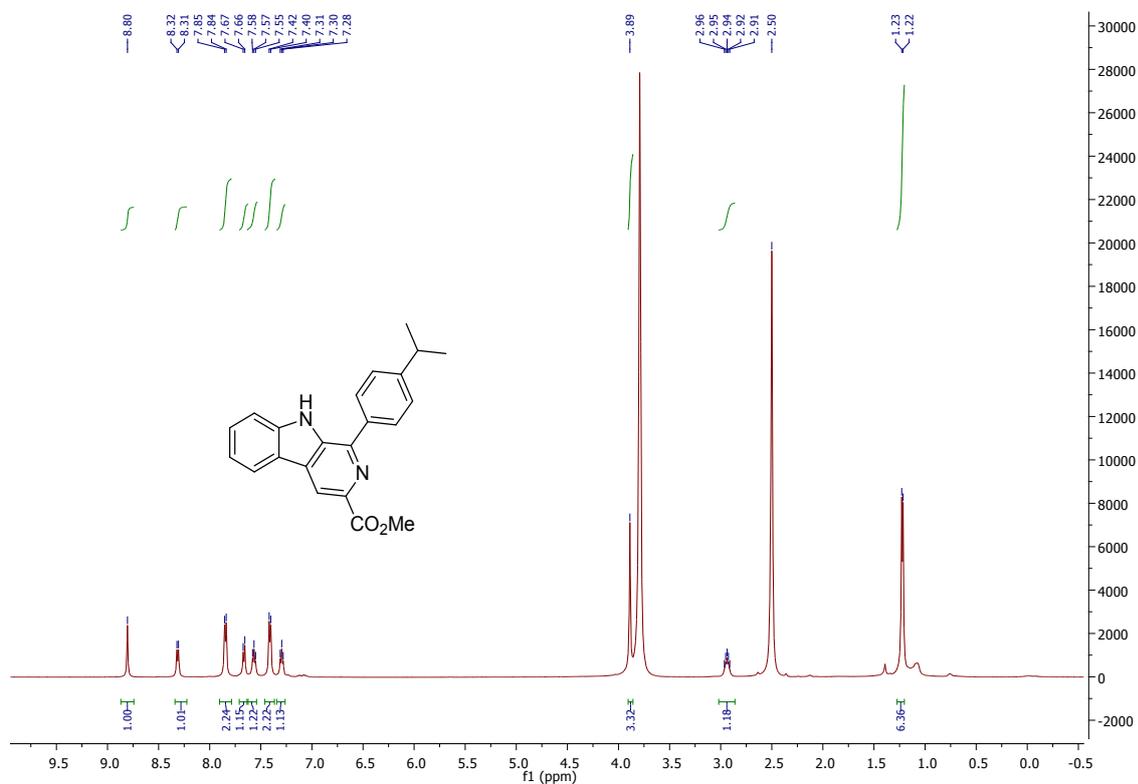
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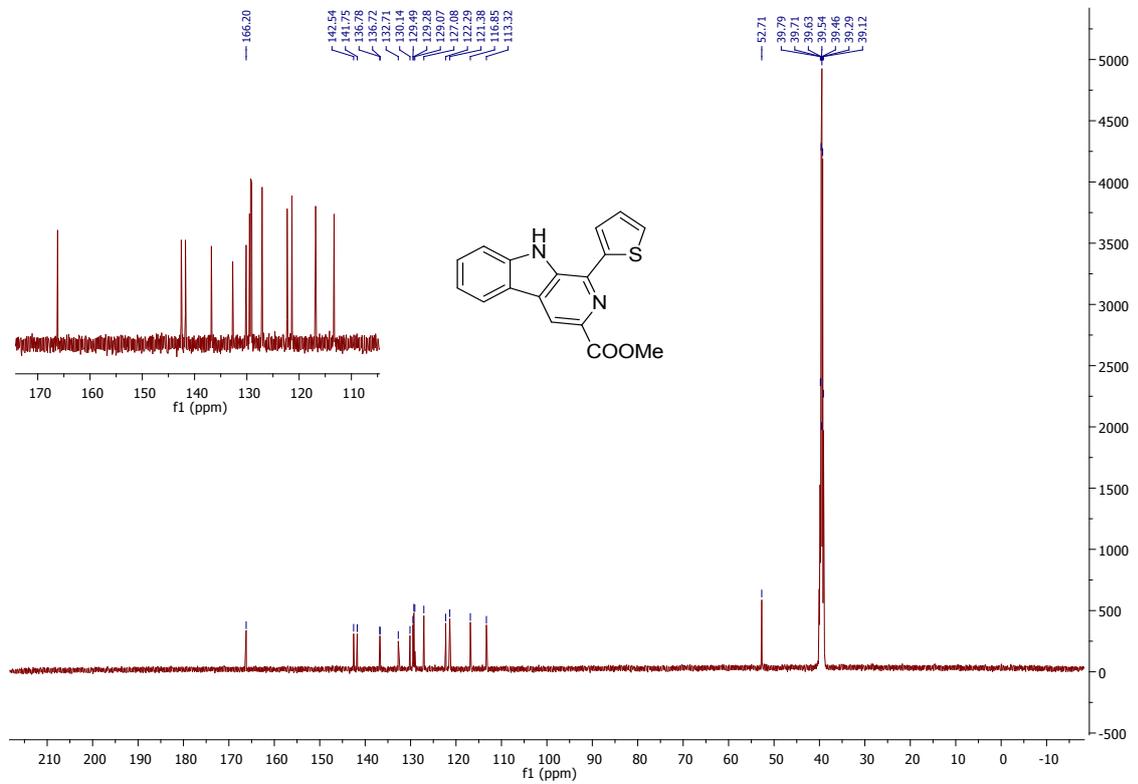
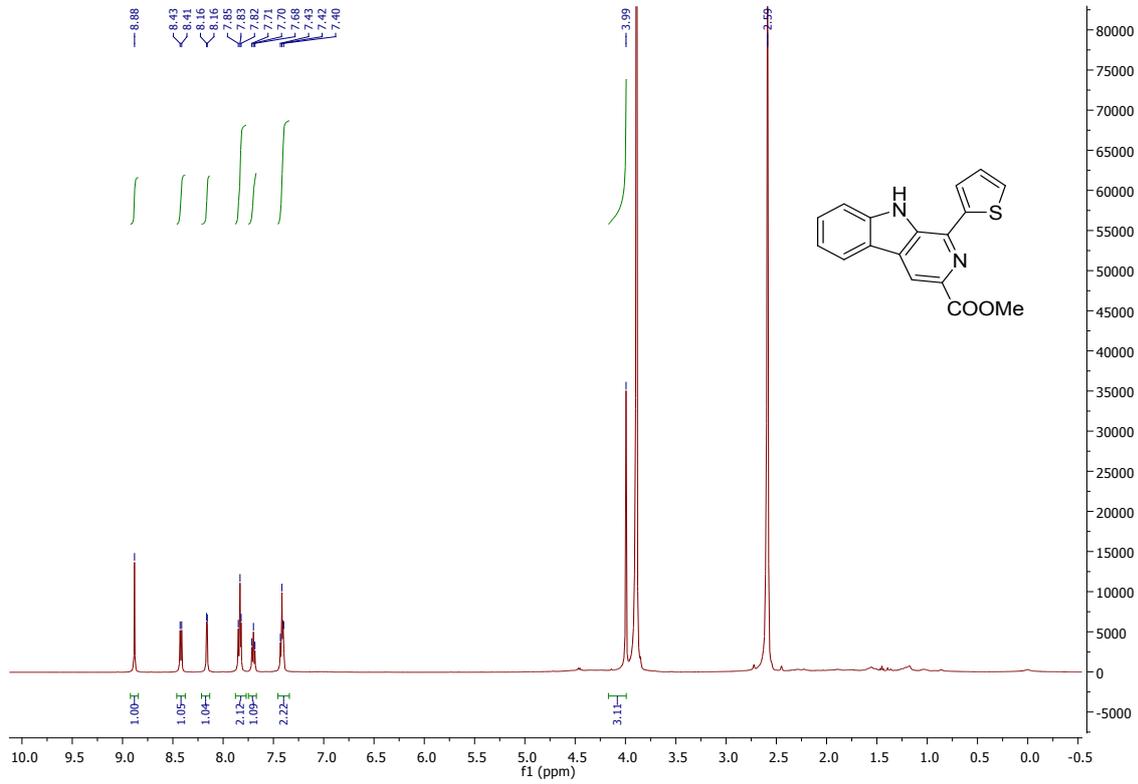
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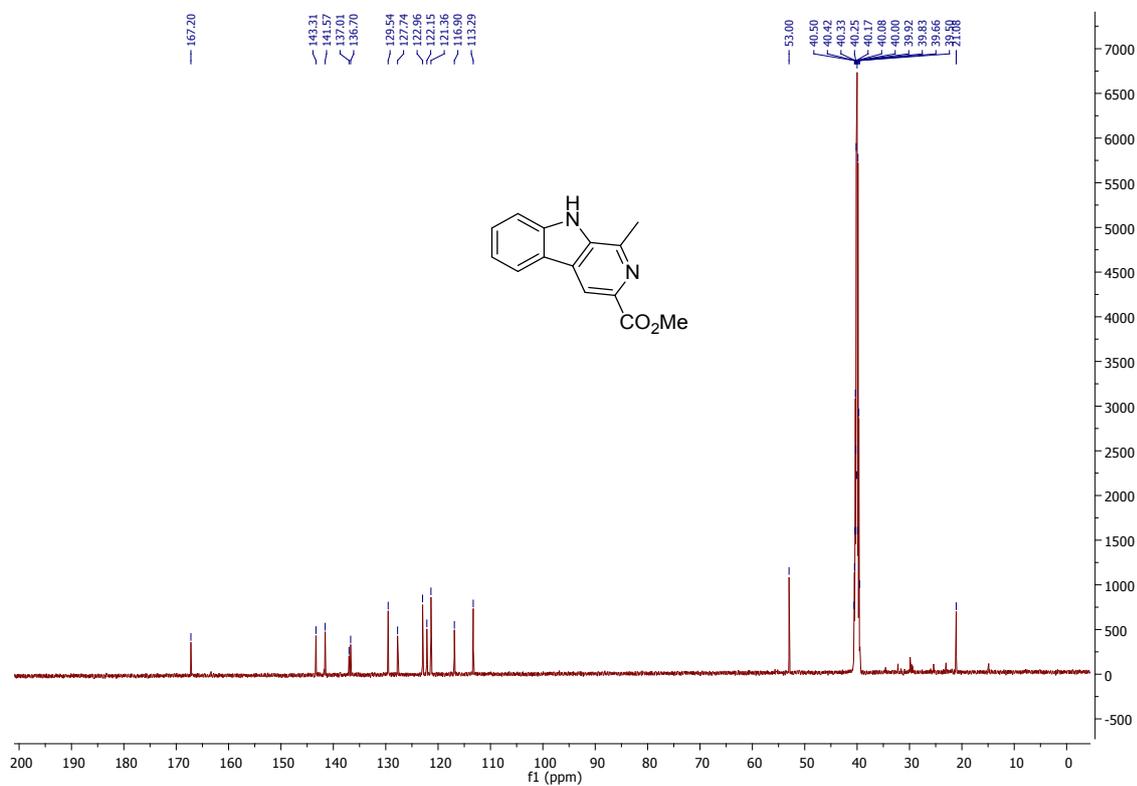
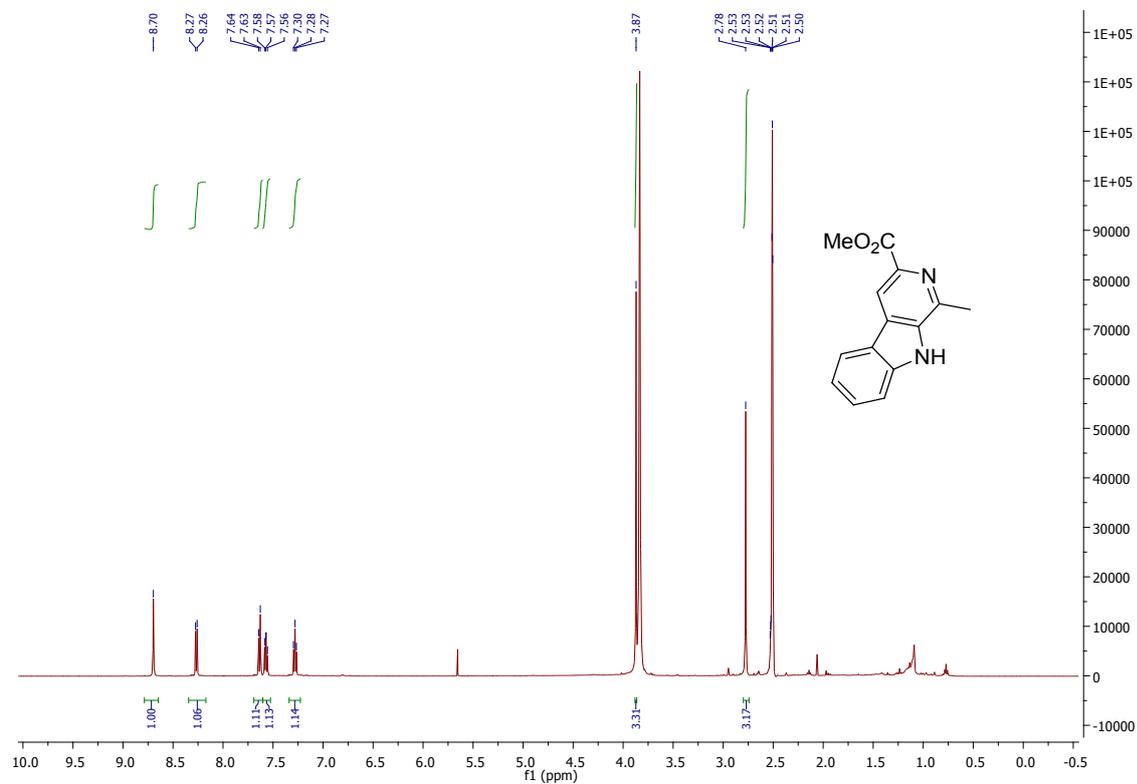
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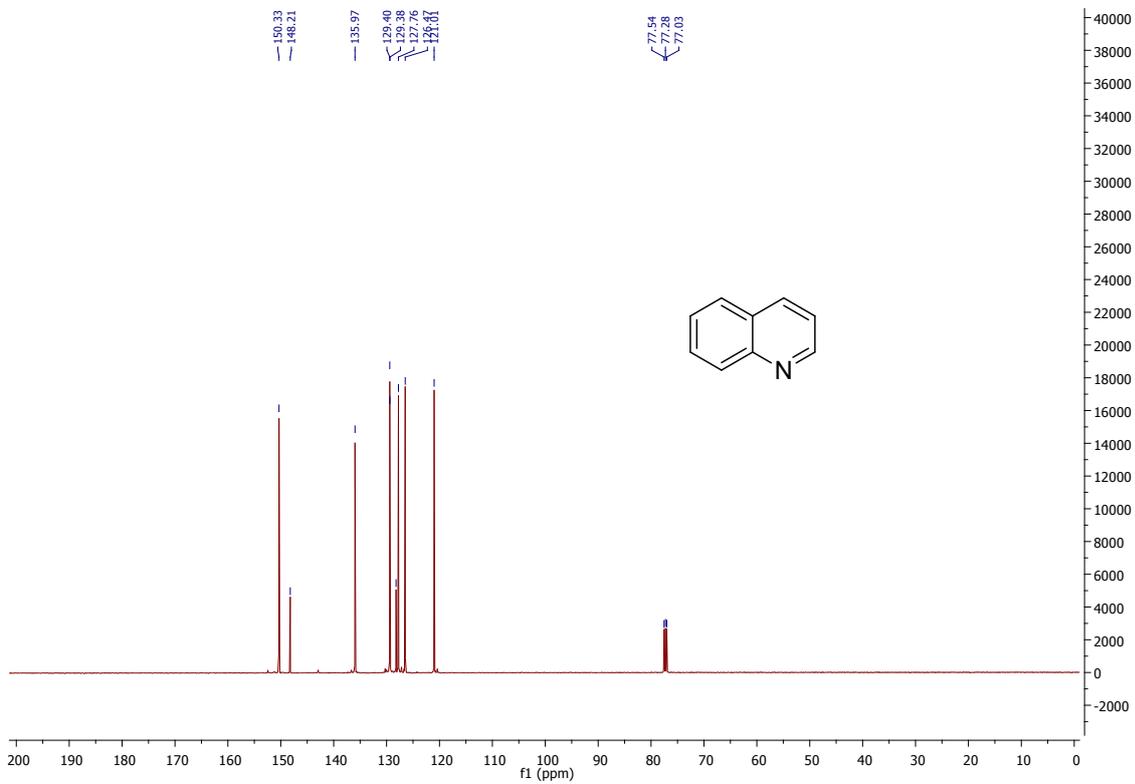
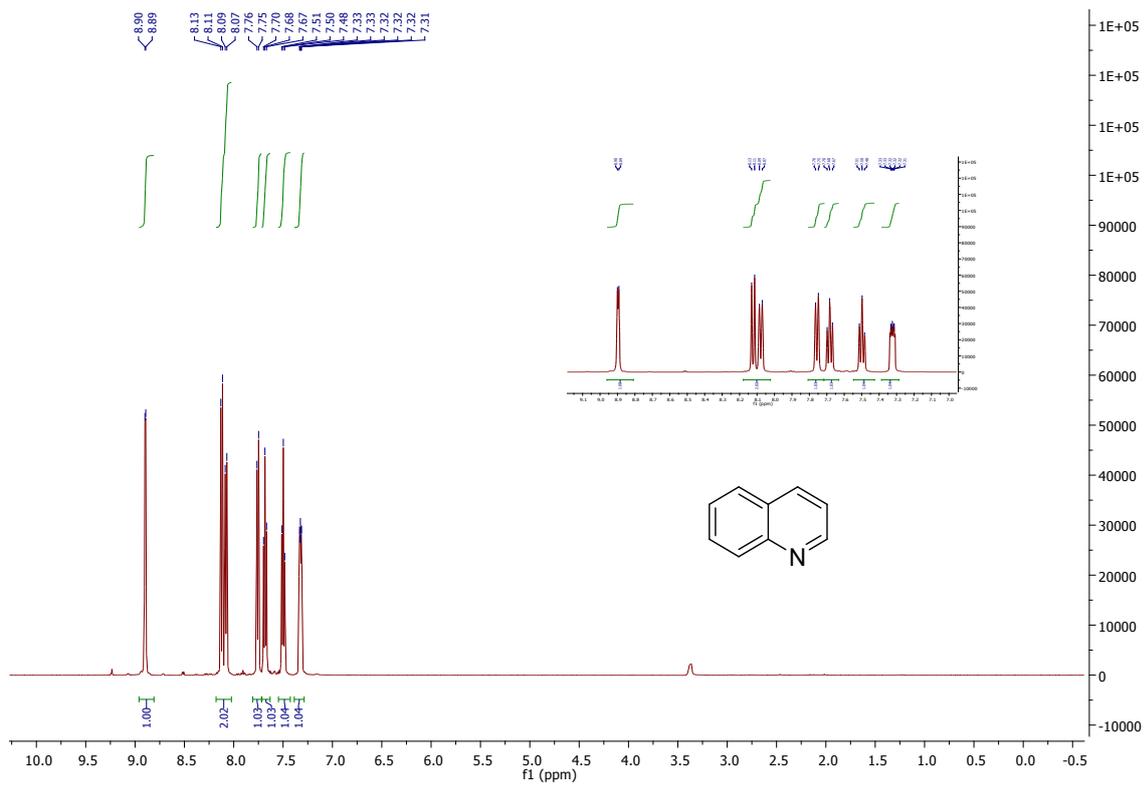
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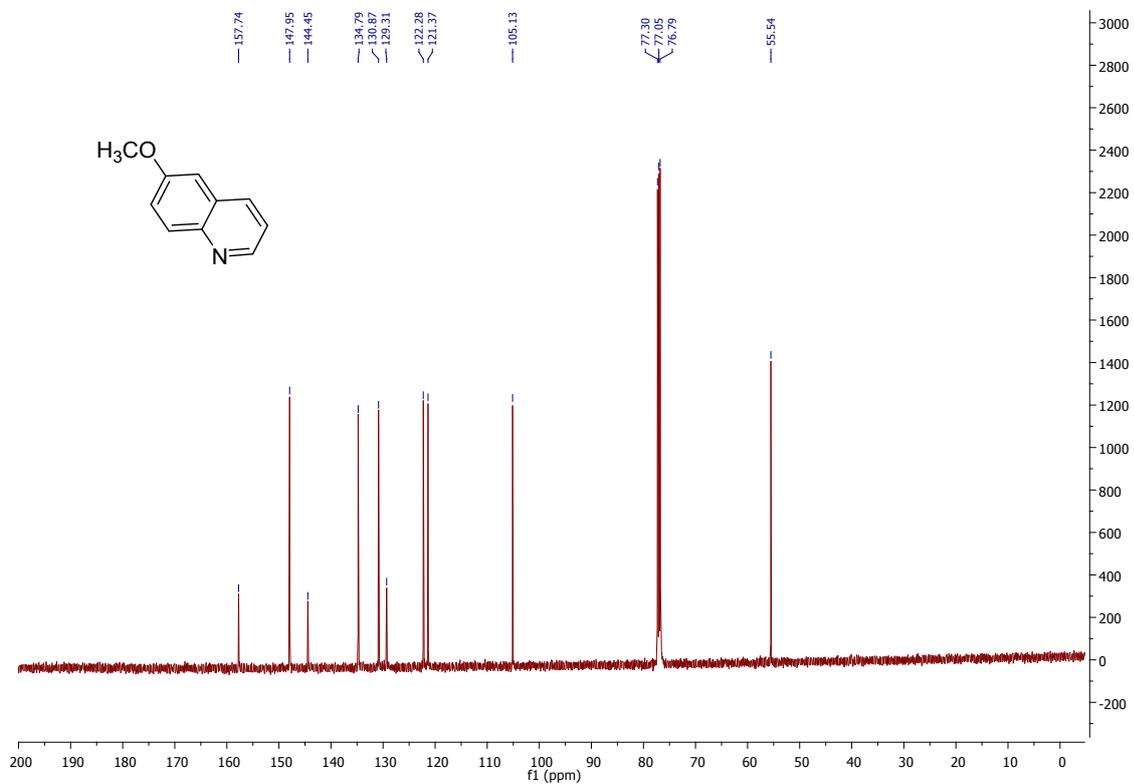
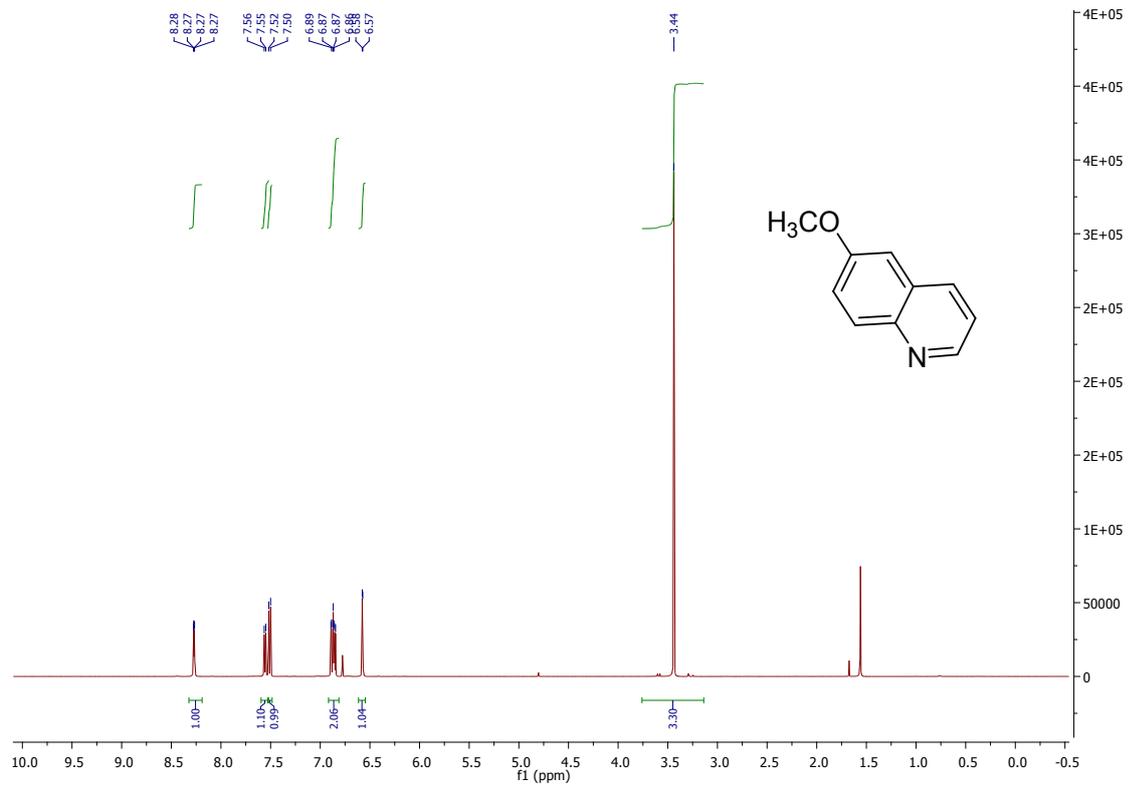
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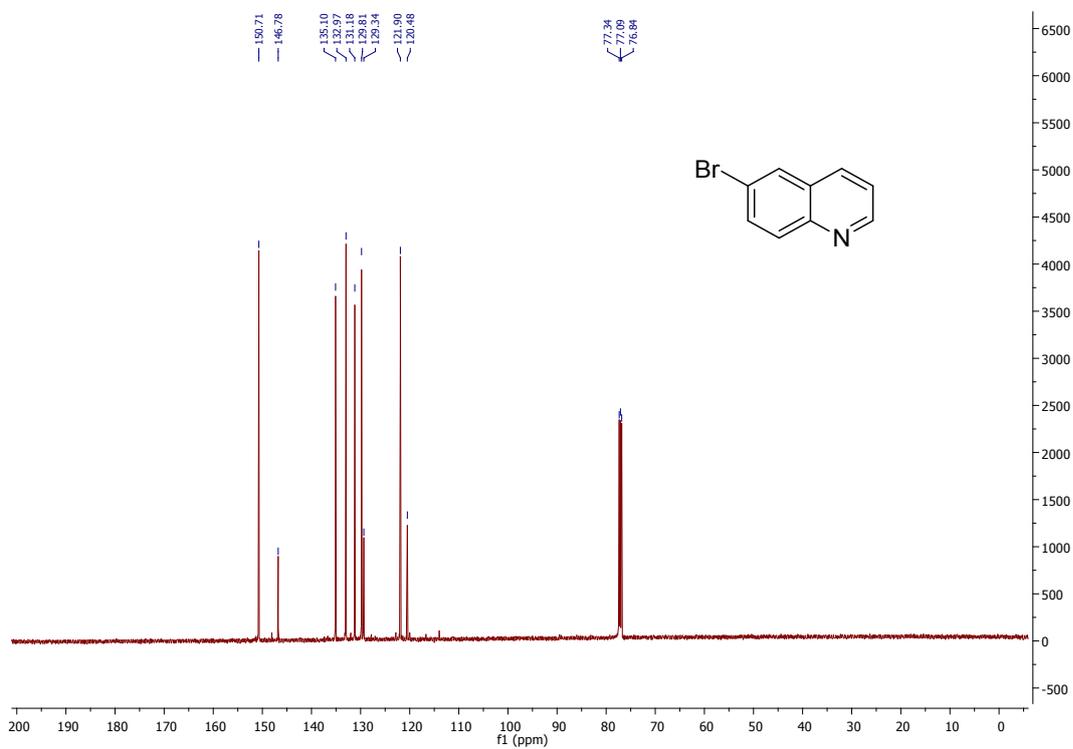
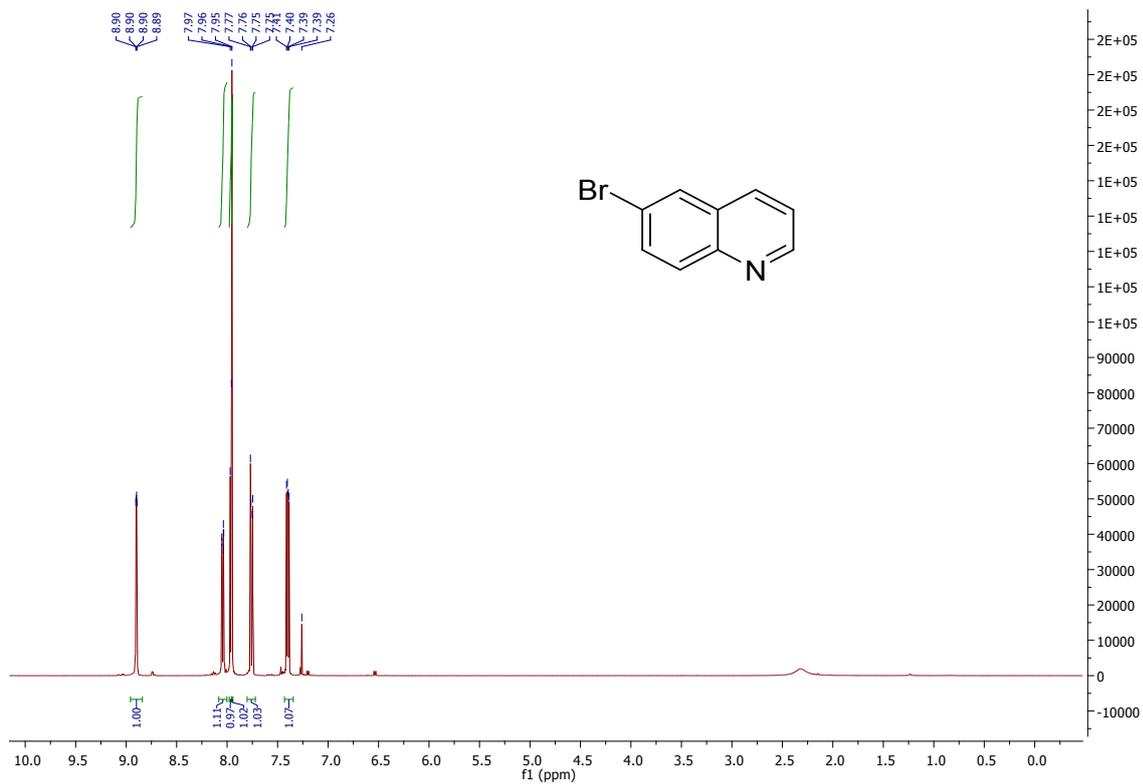
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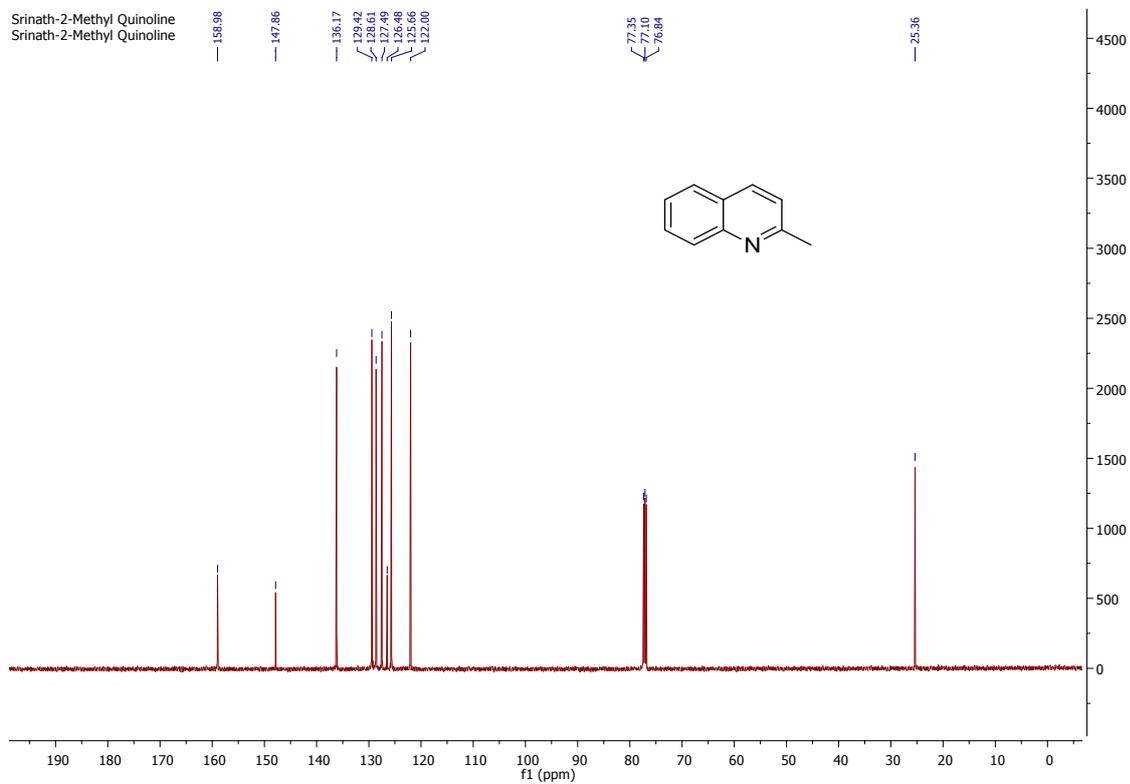
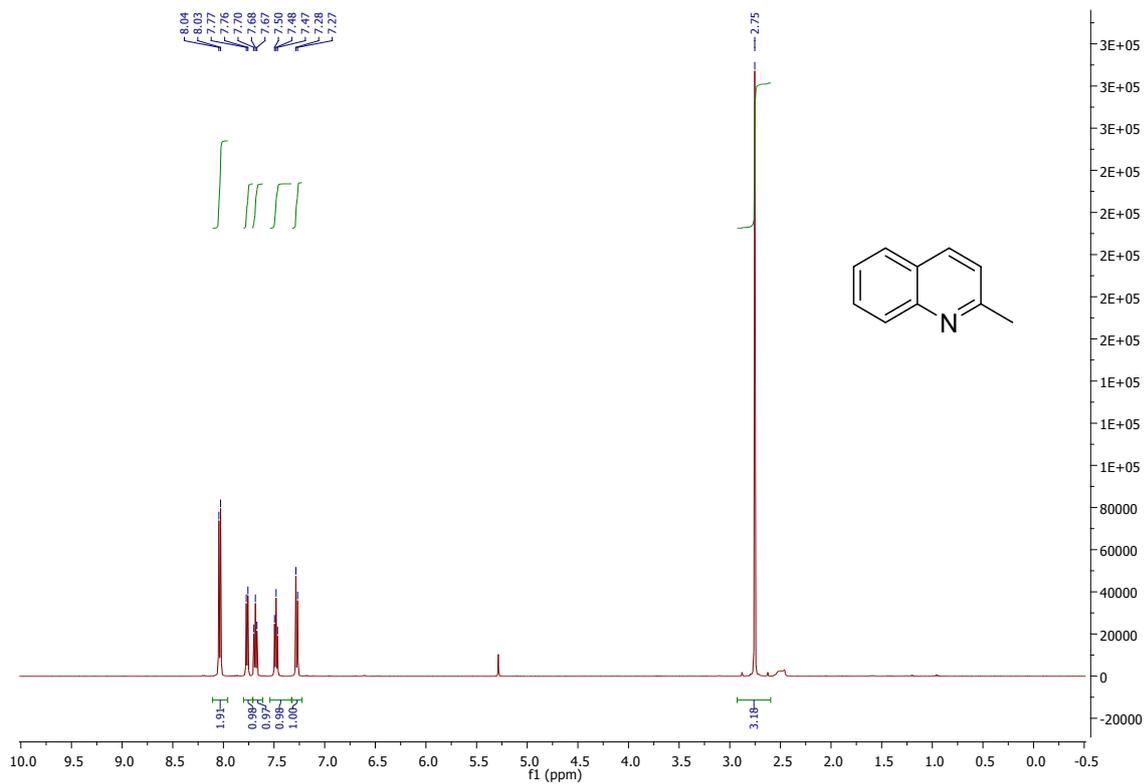
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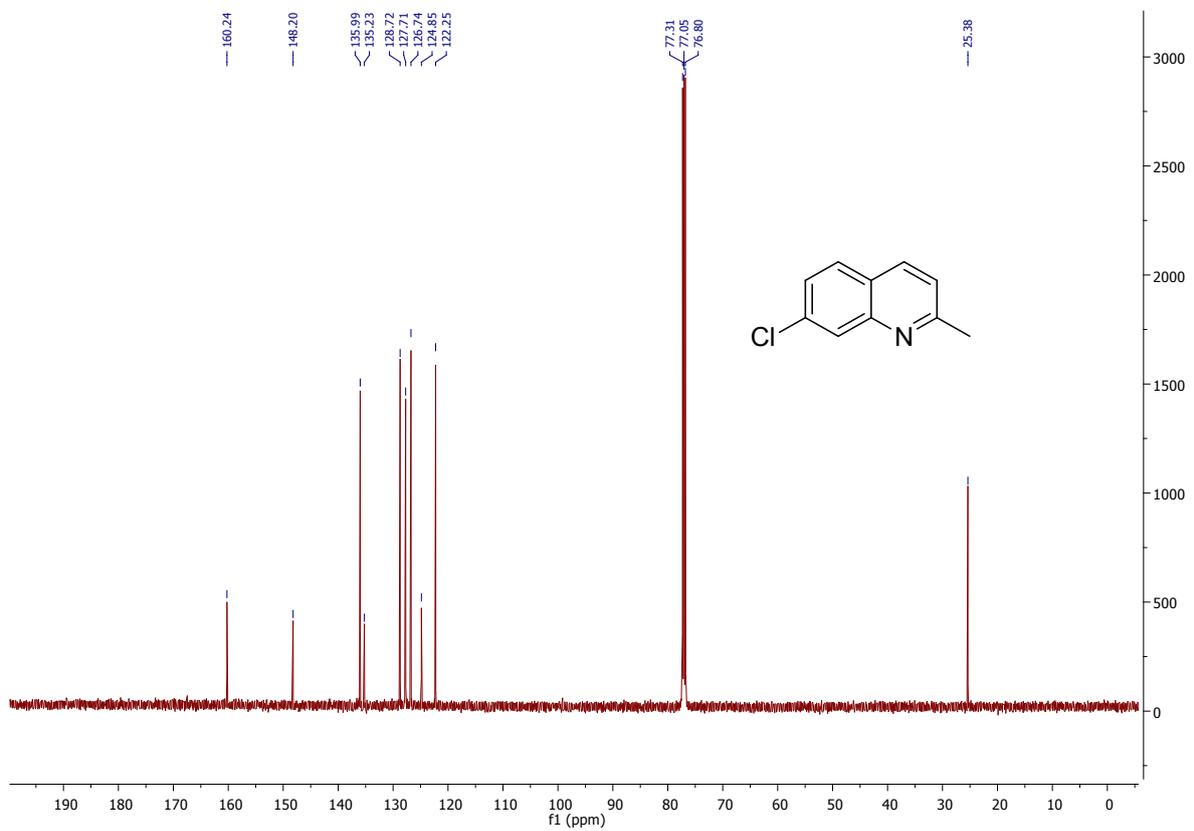
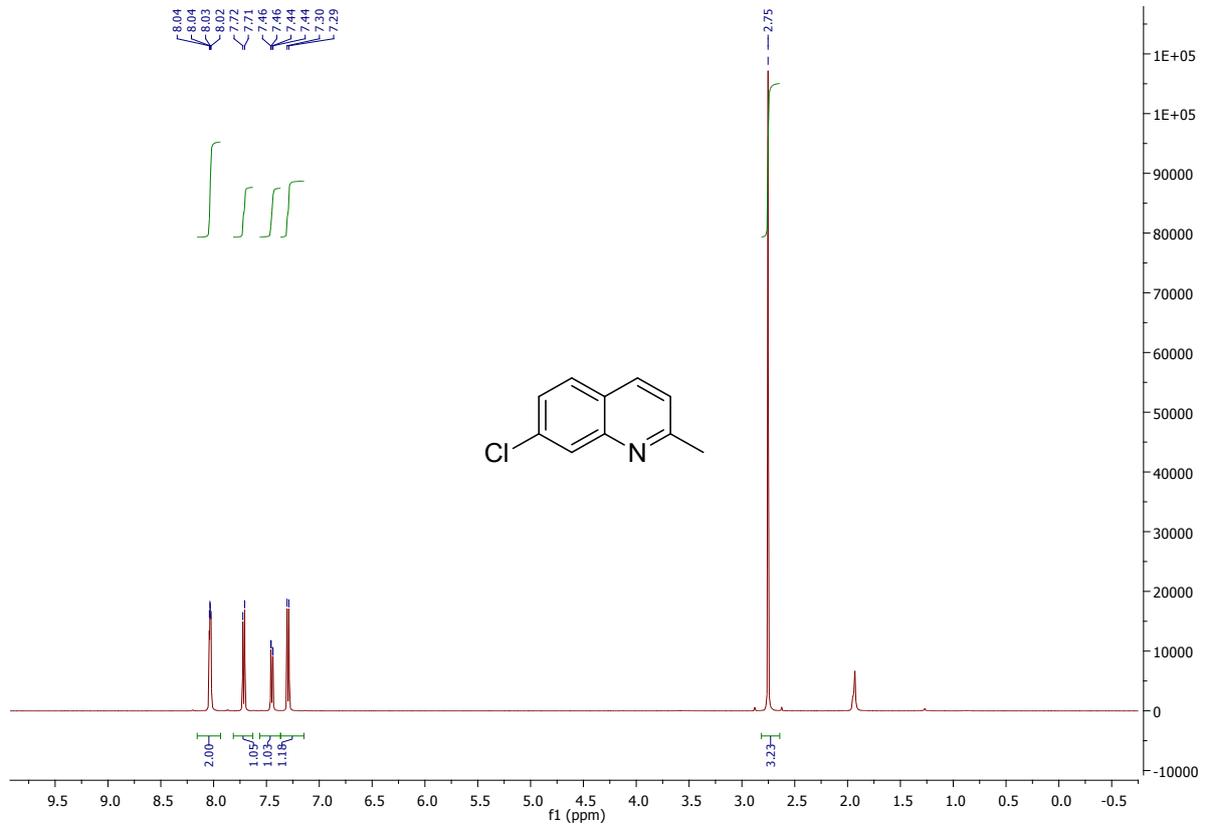
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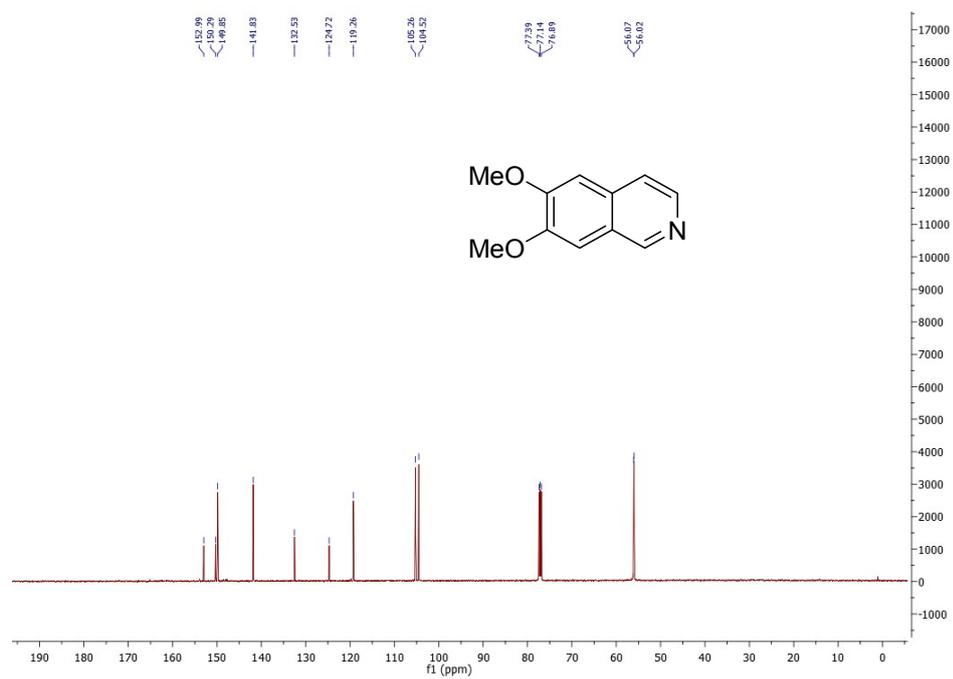
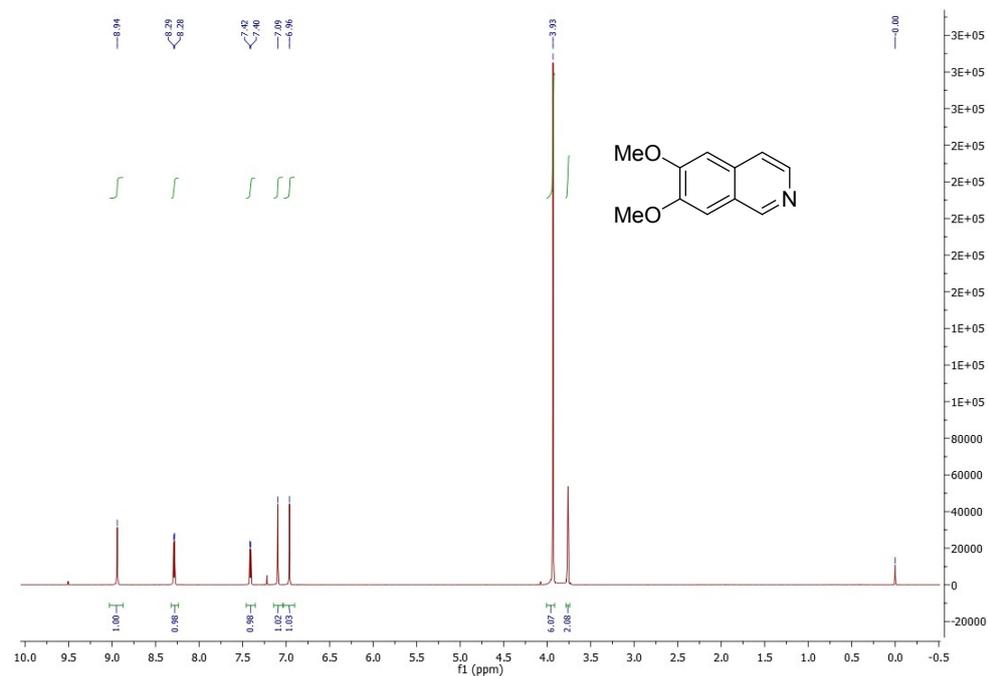
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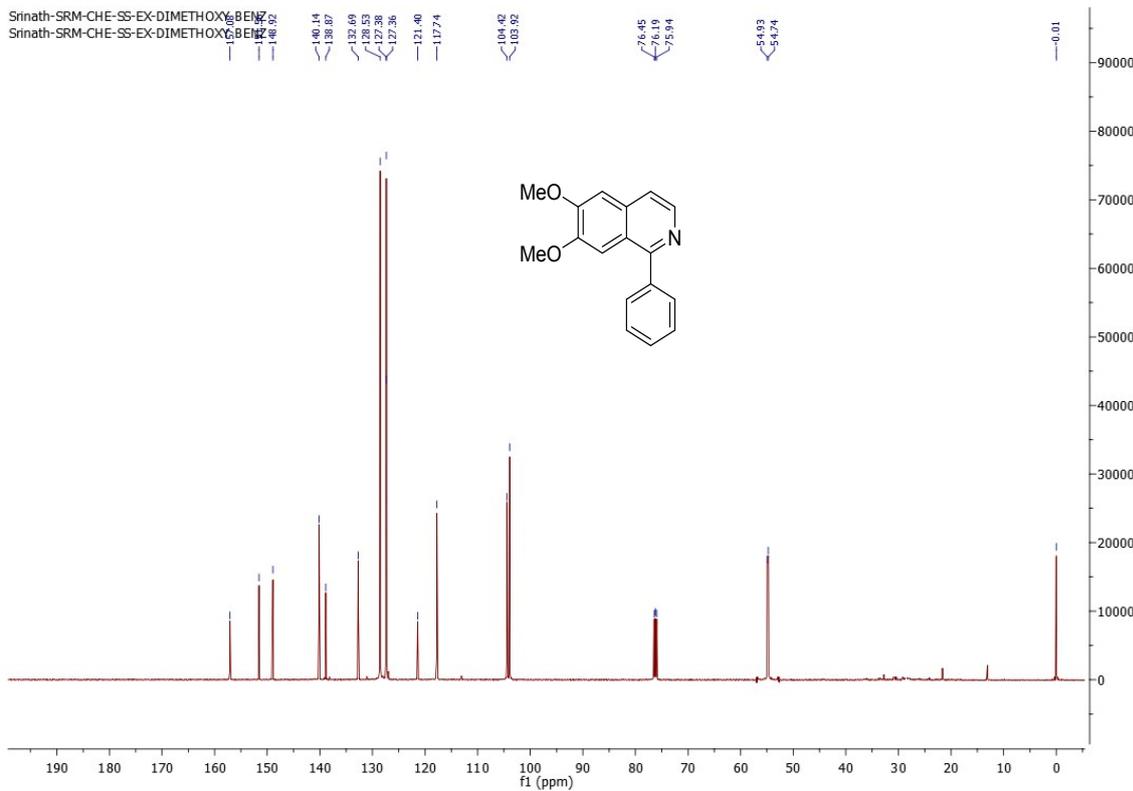
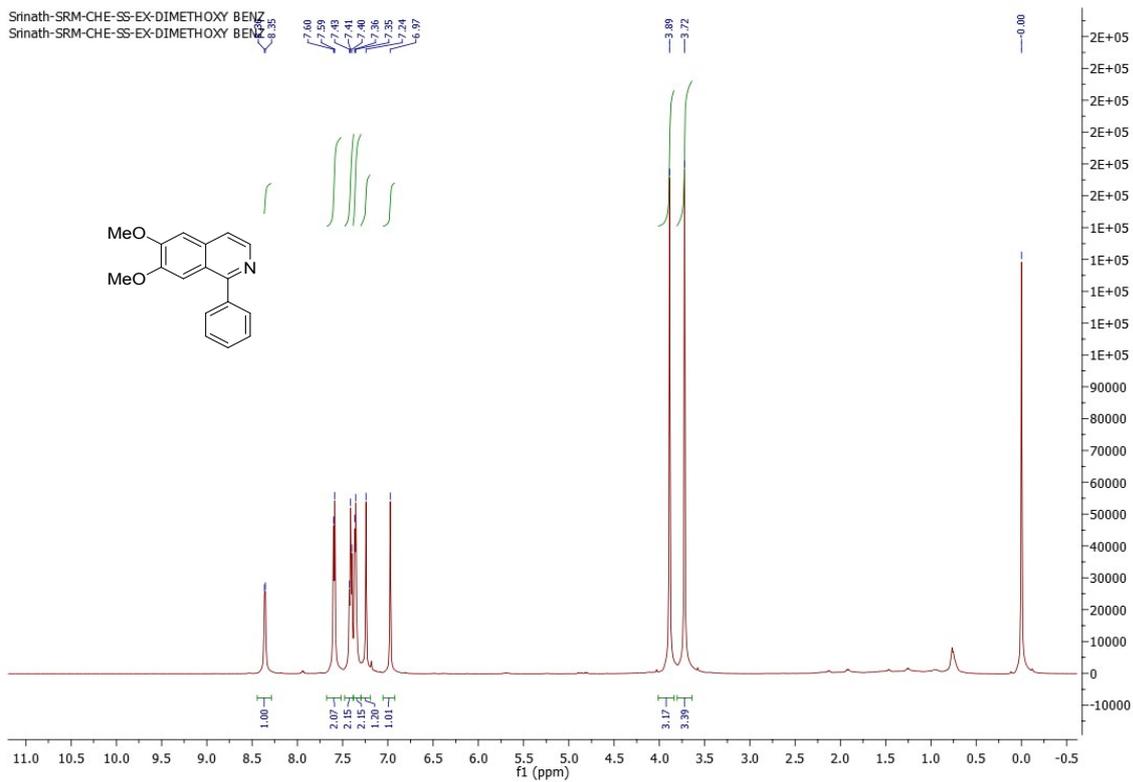
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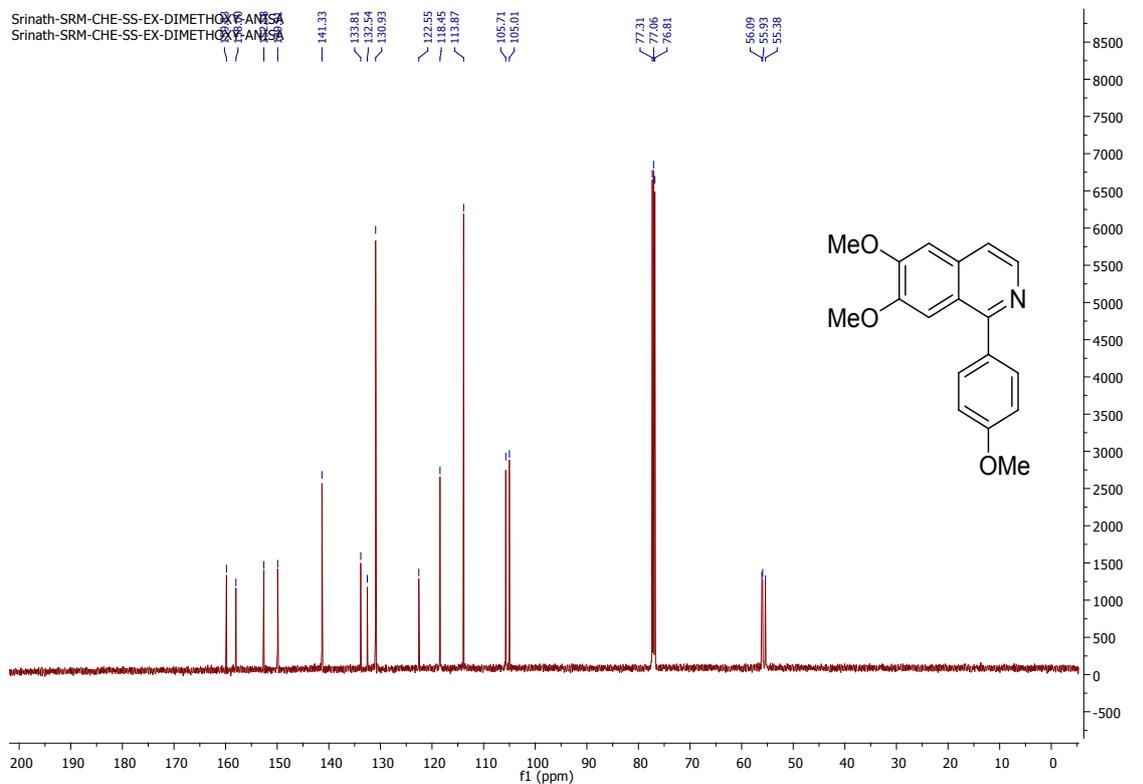
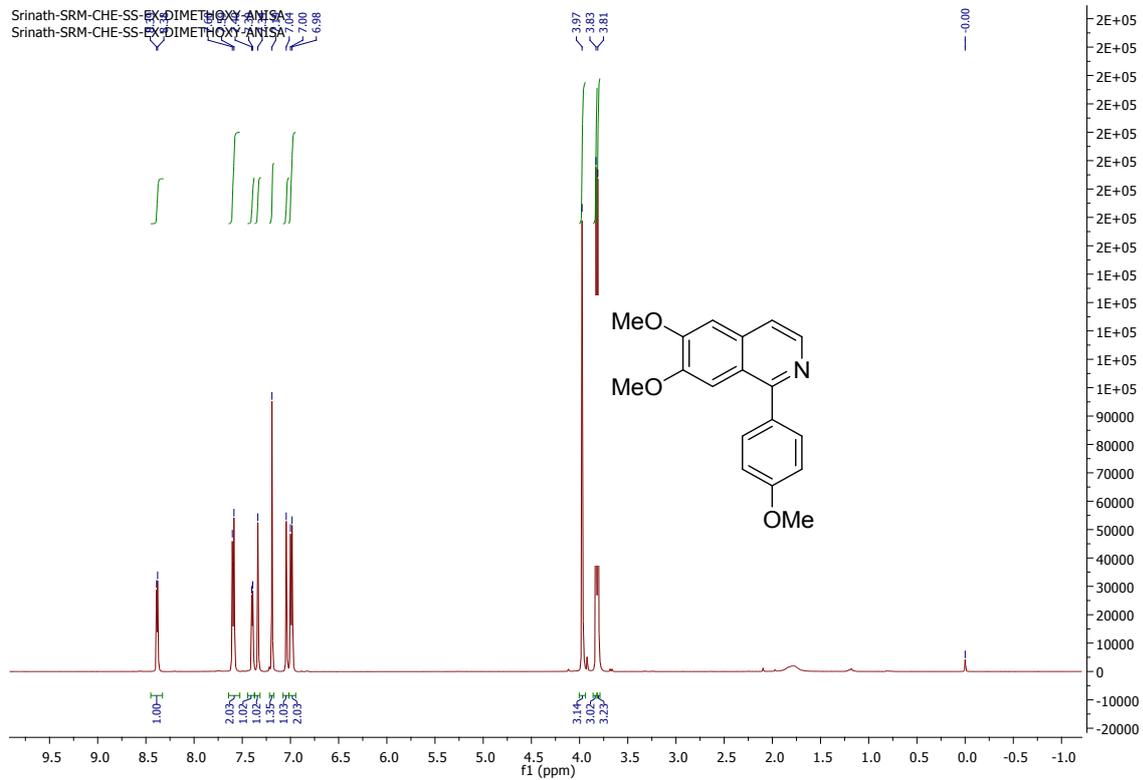
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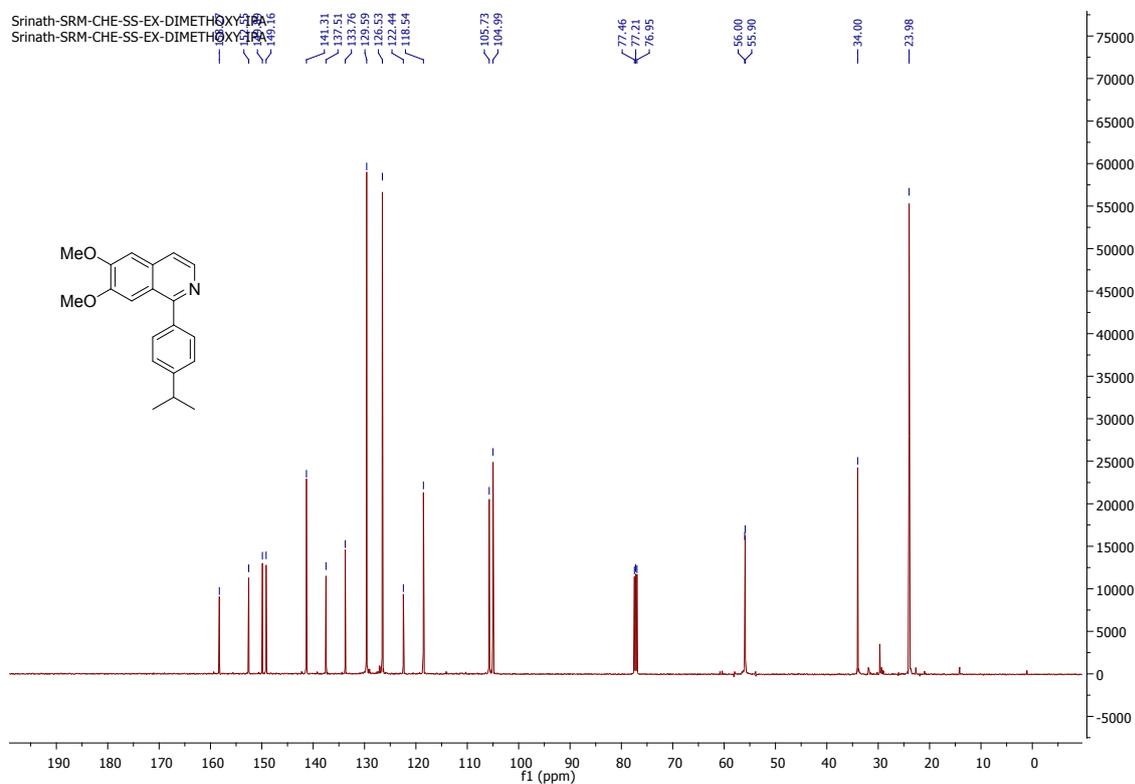
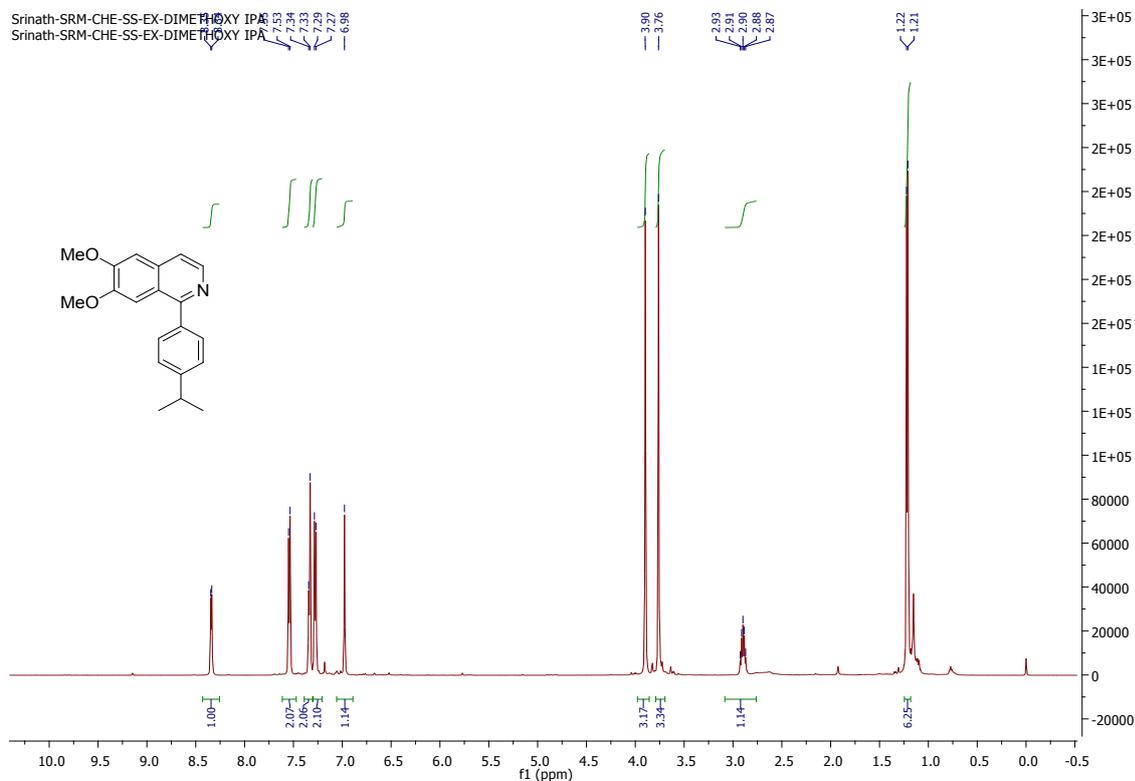
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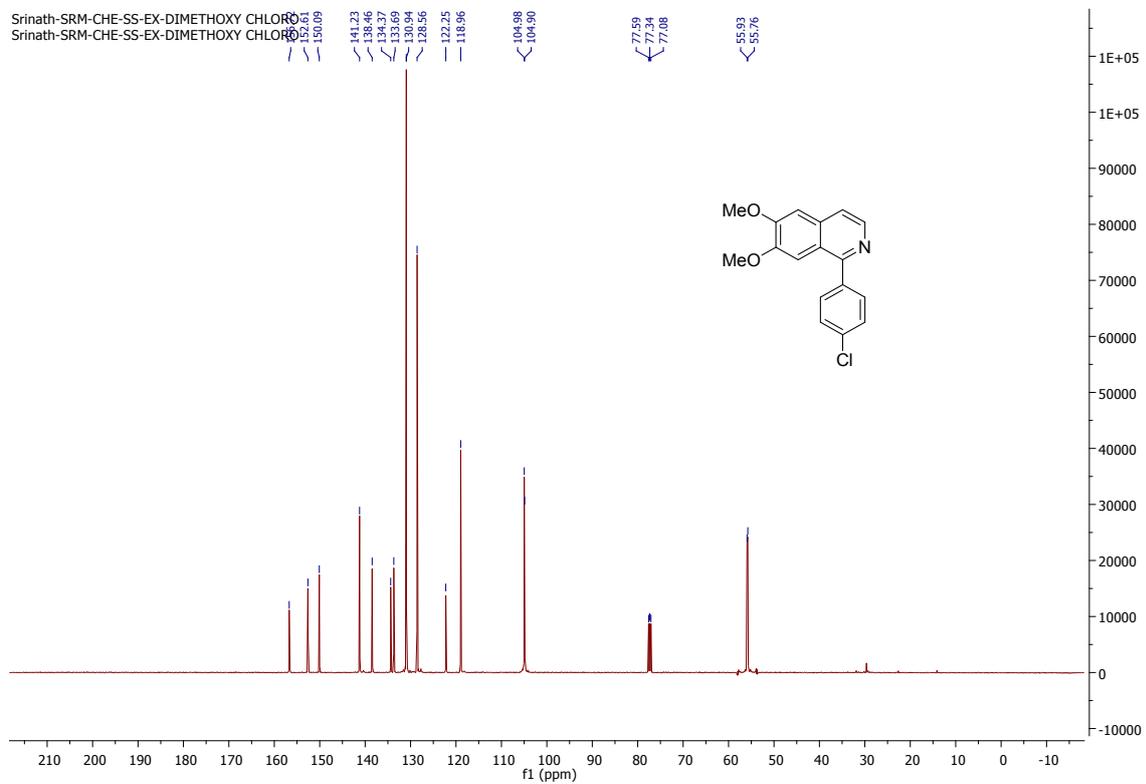
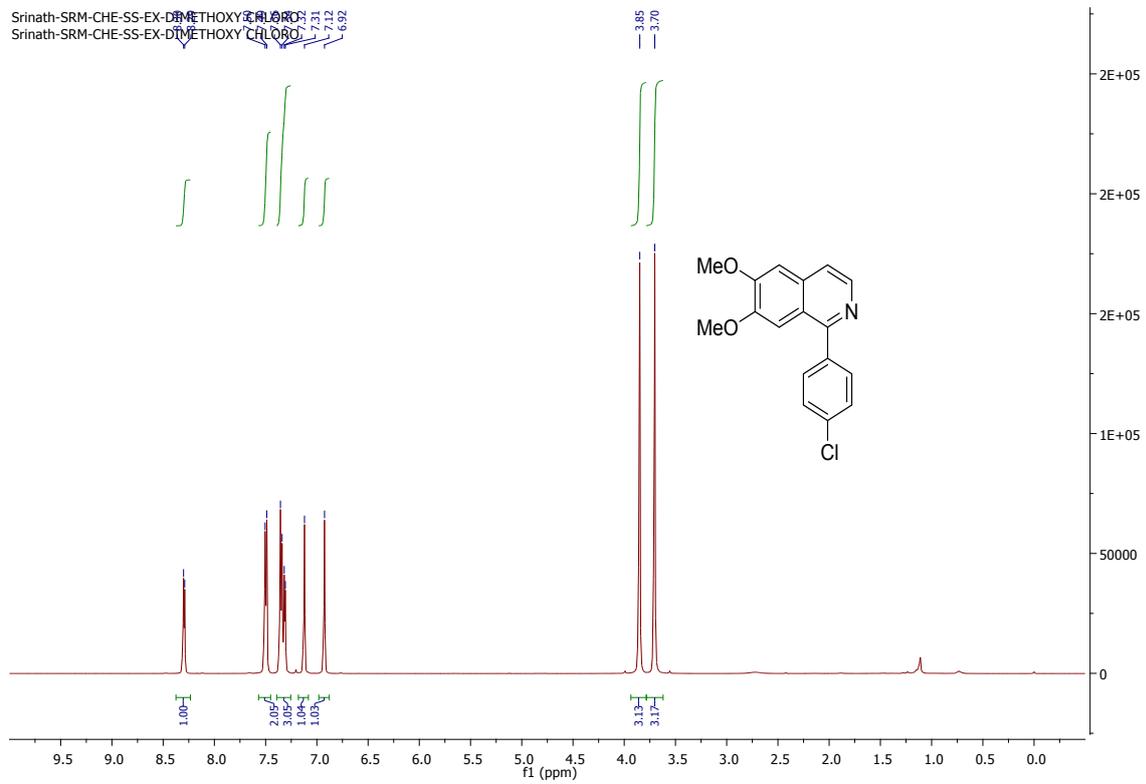
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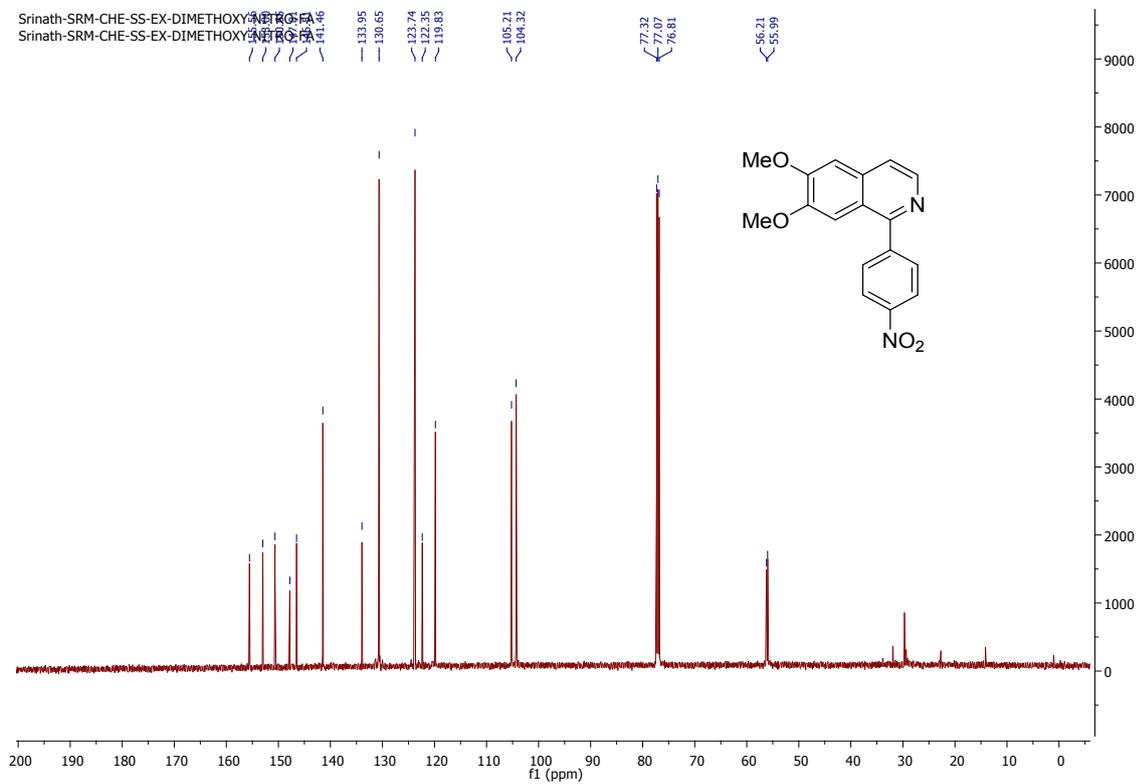
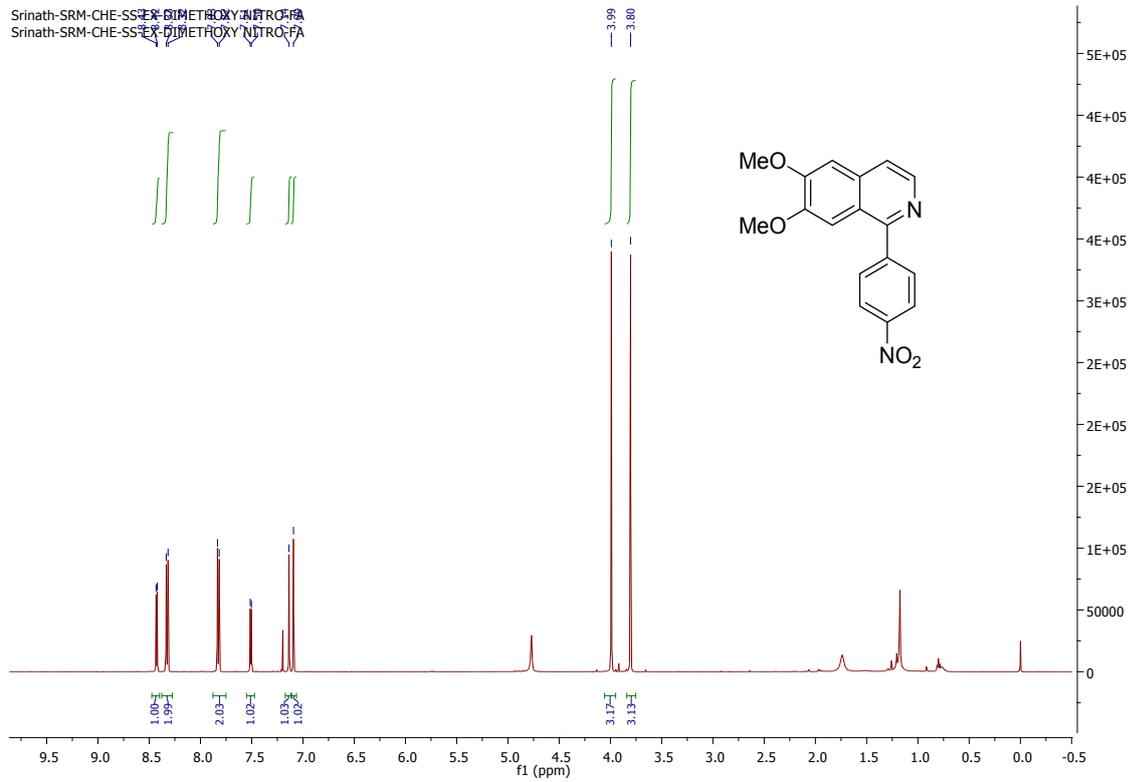
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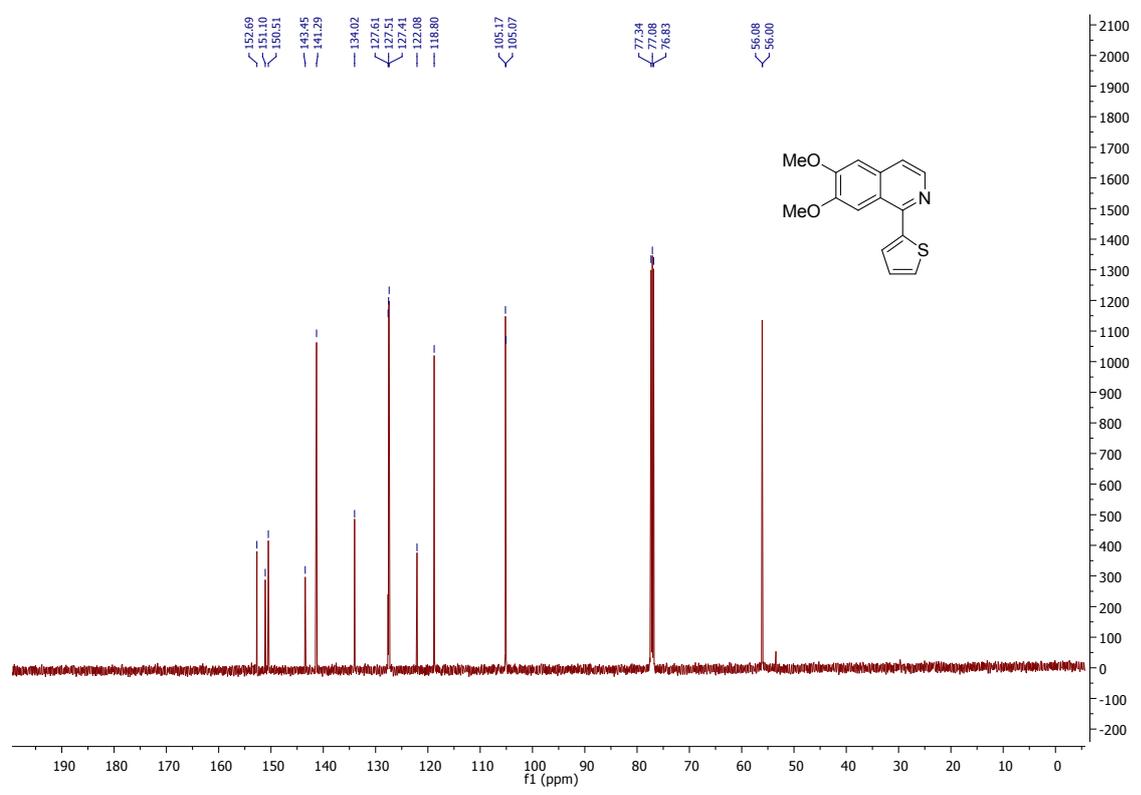
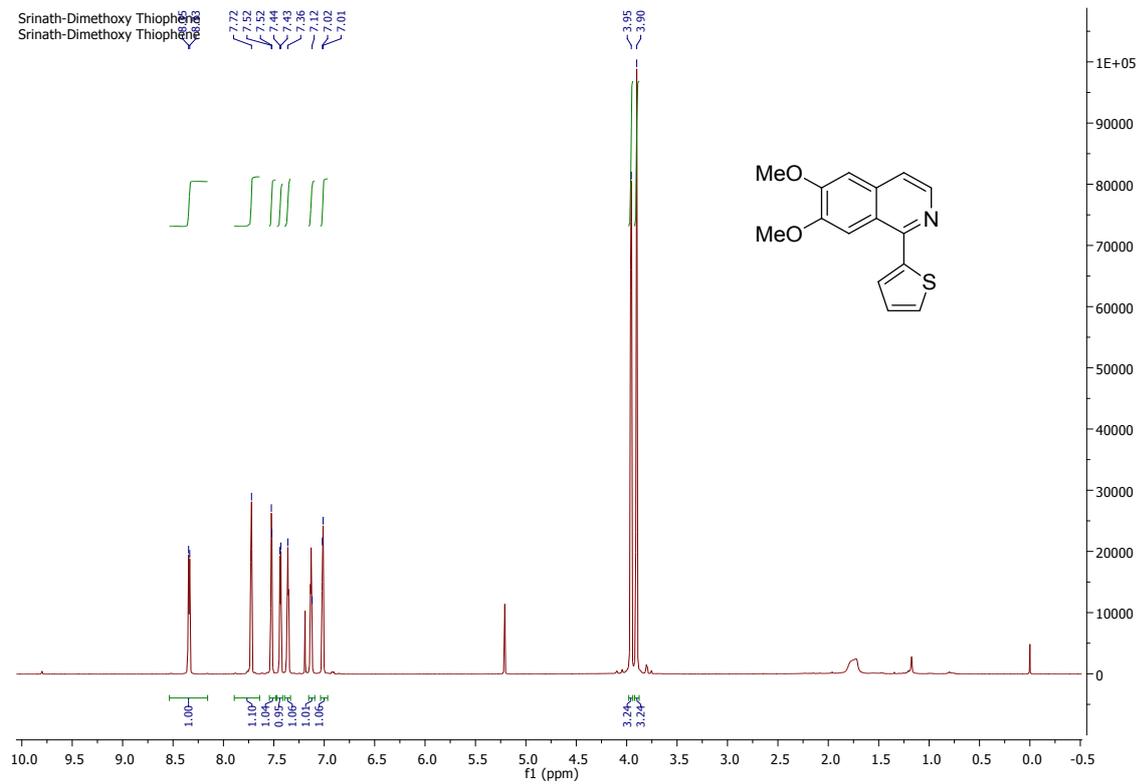
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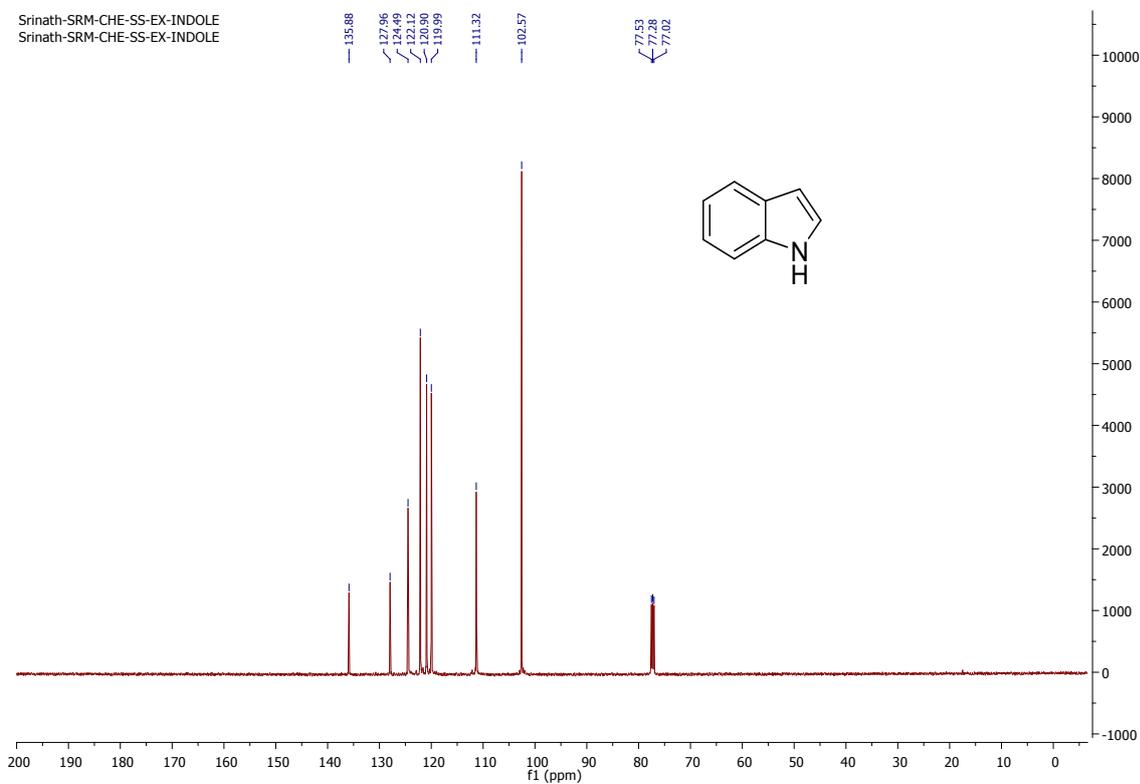
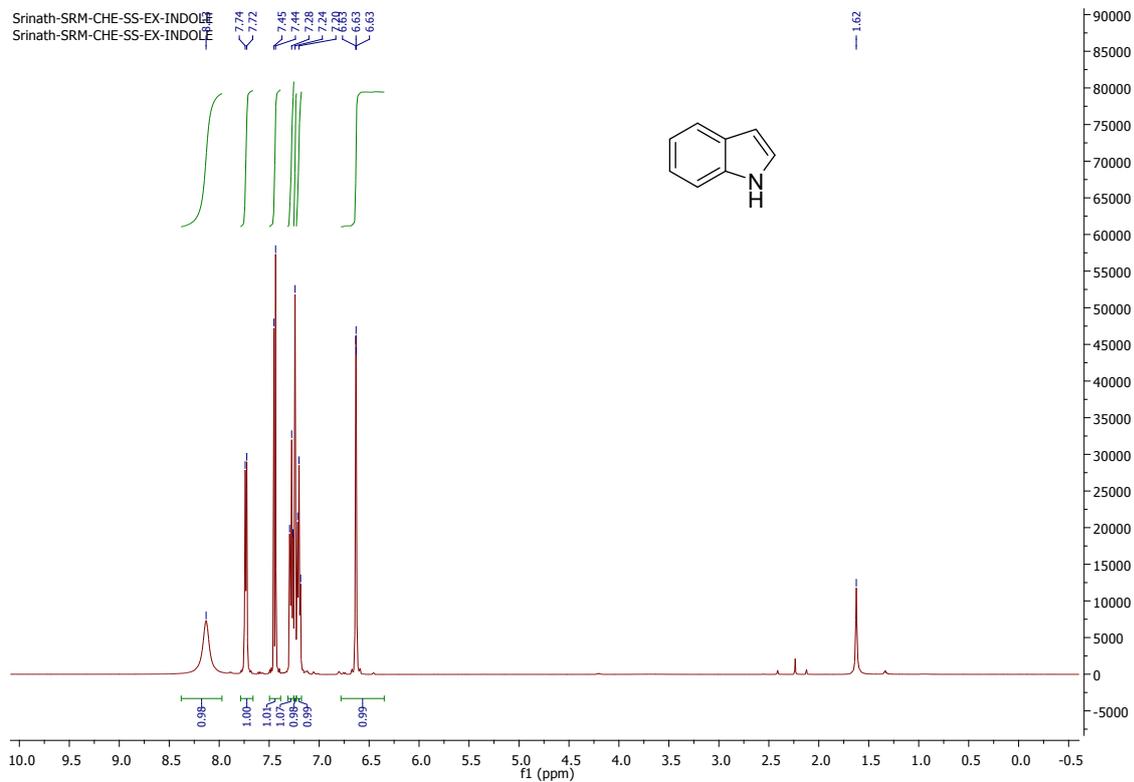
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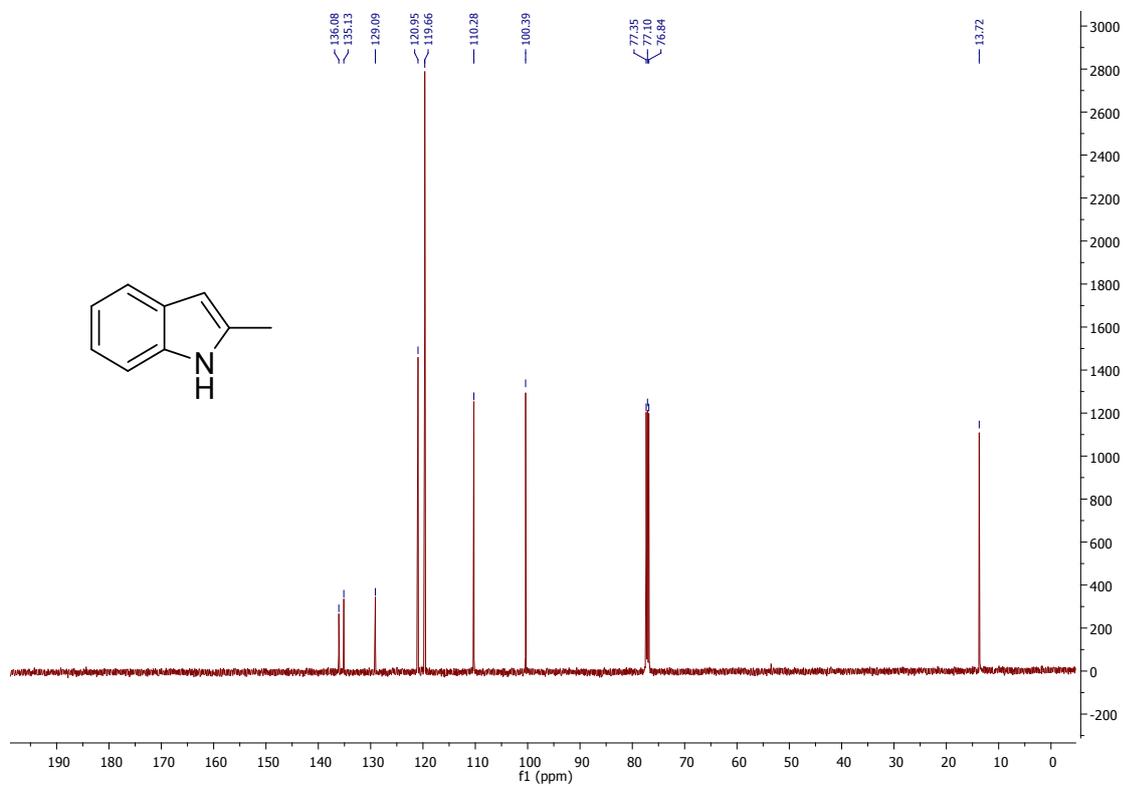
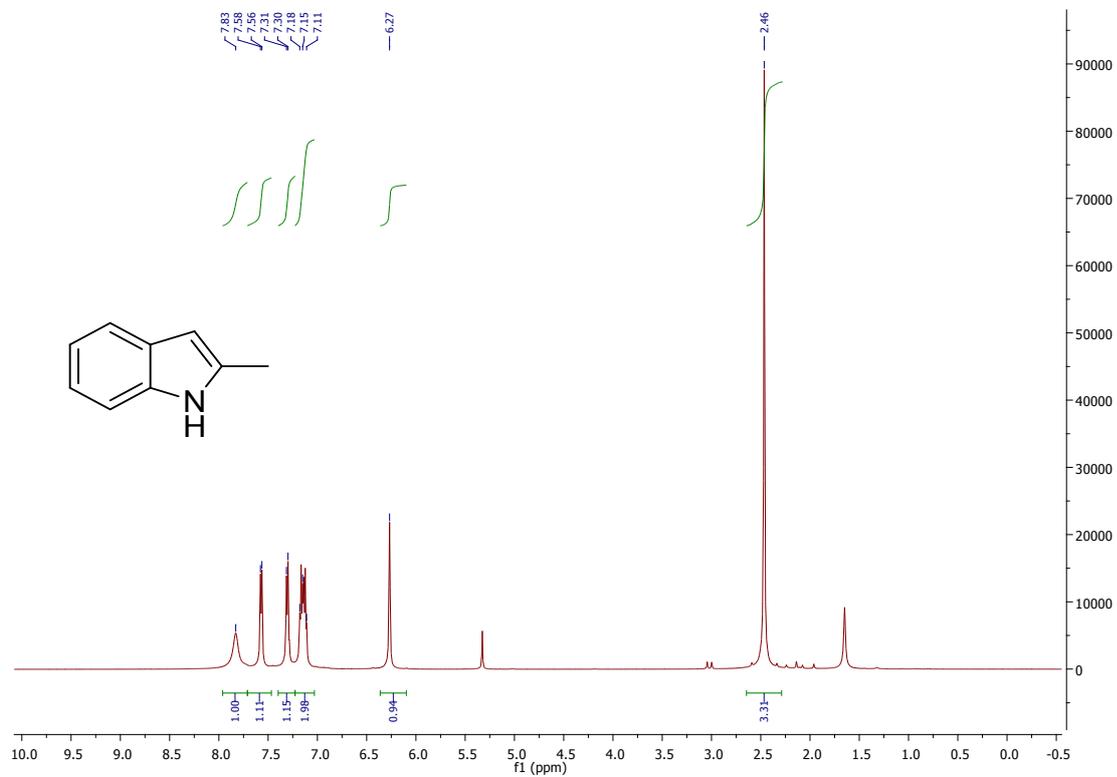
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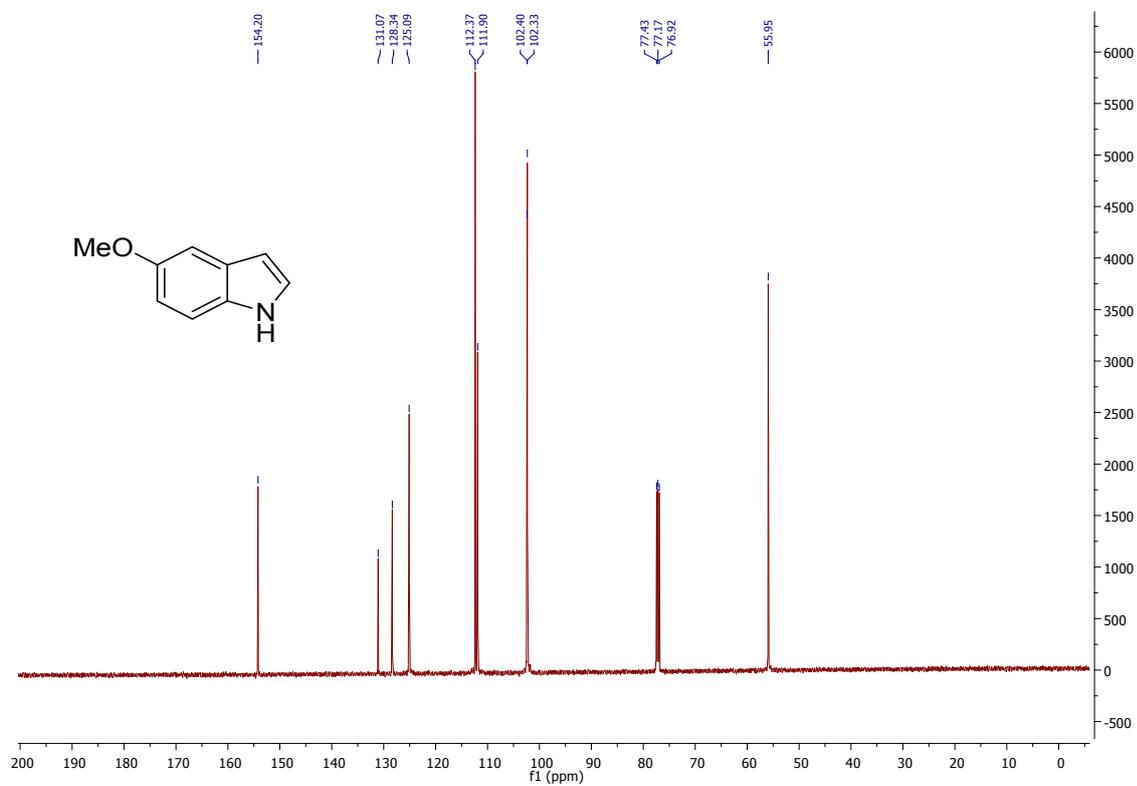
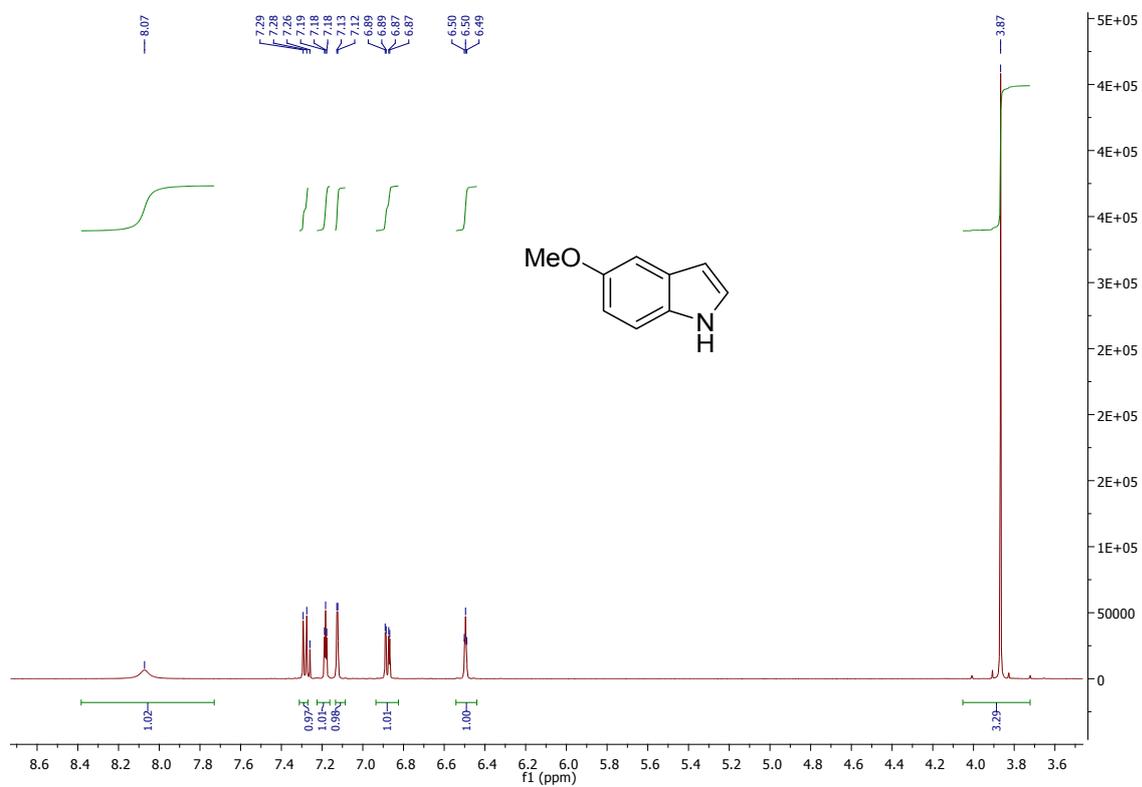
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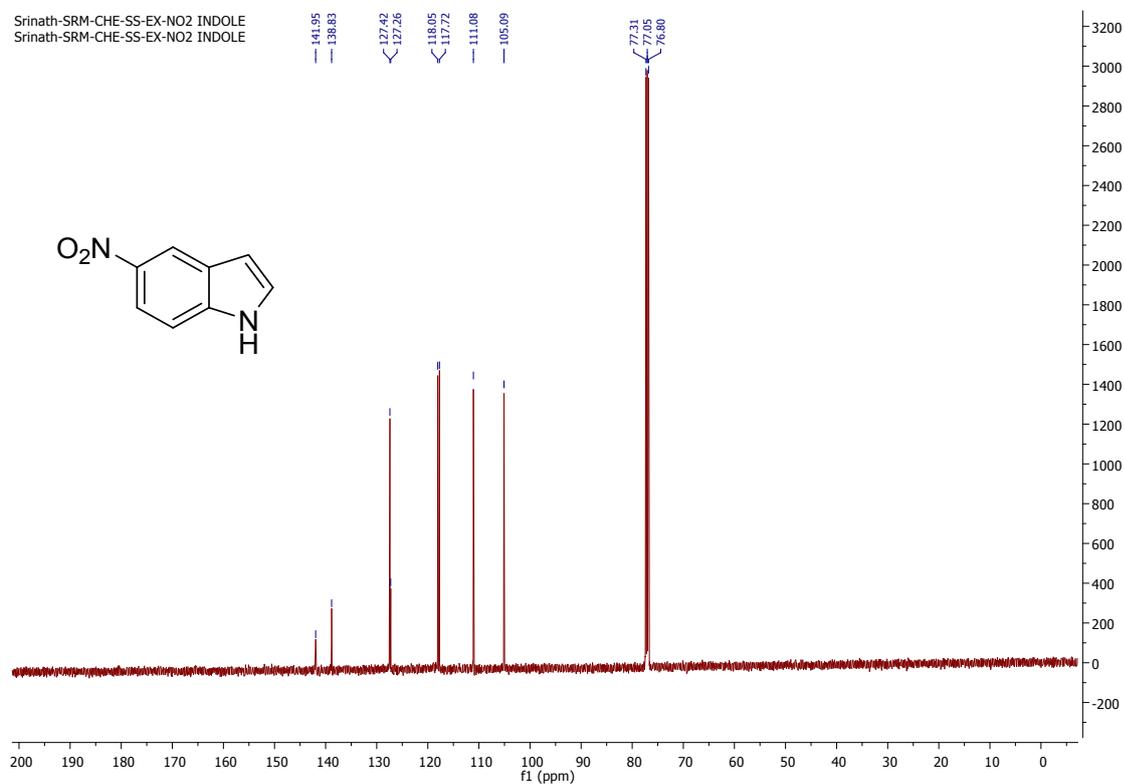
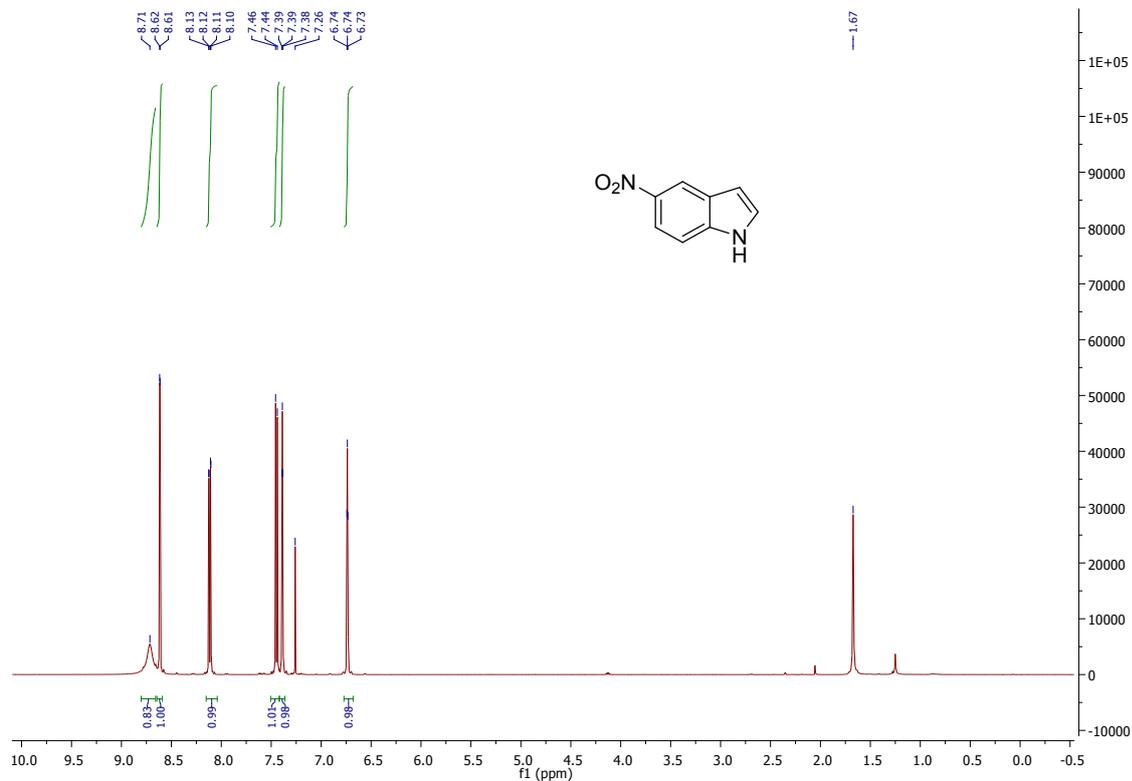
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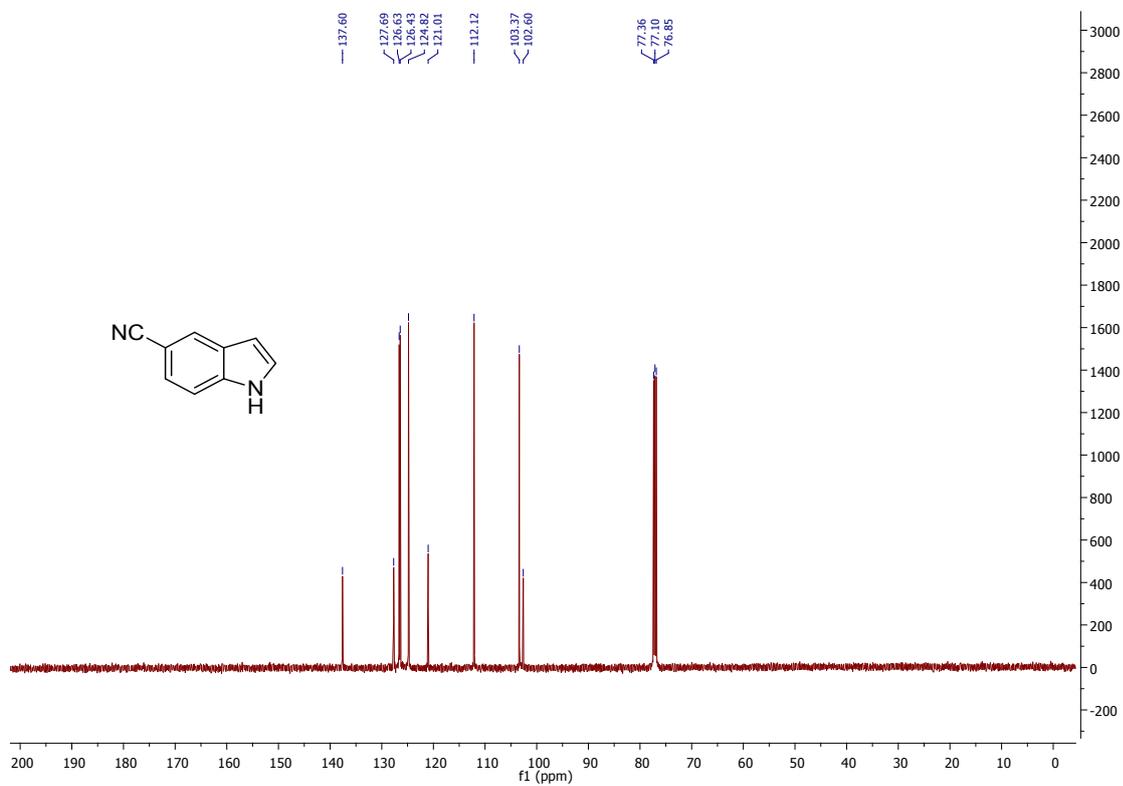
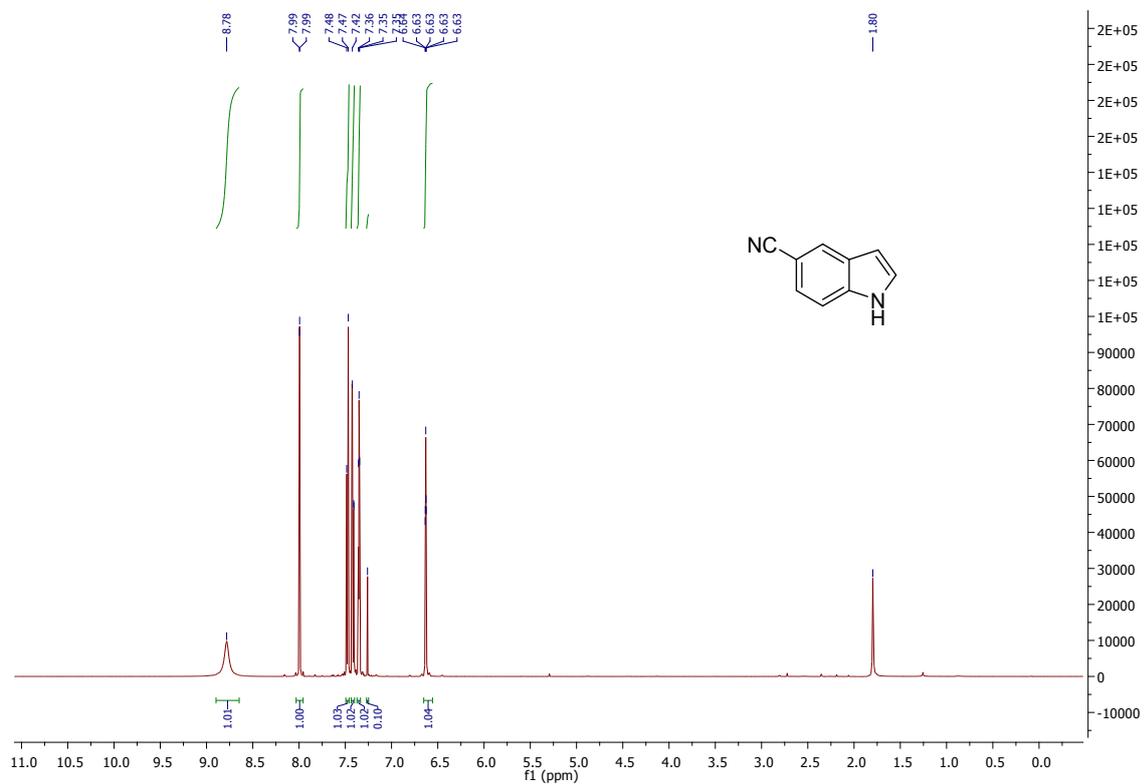
5-Methoxyindole (7c):



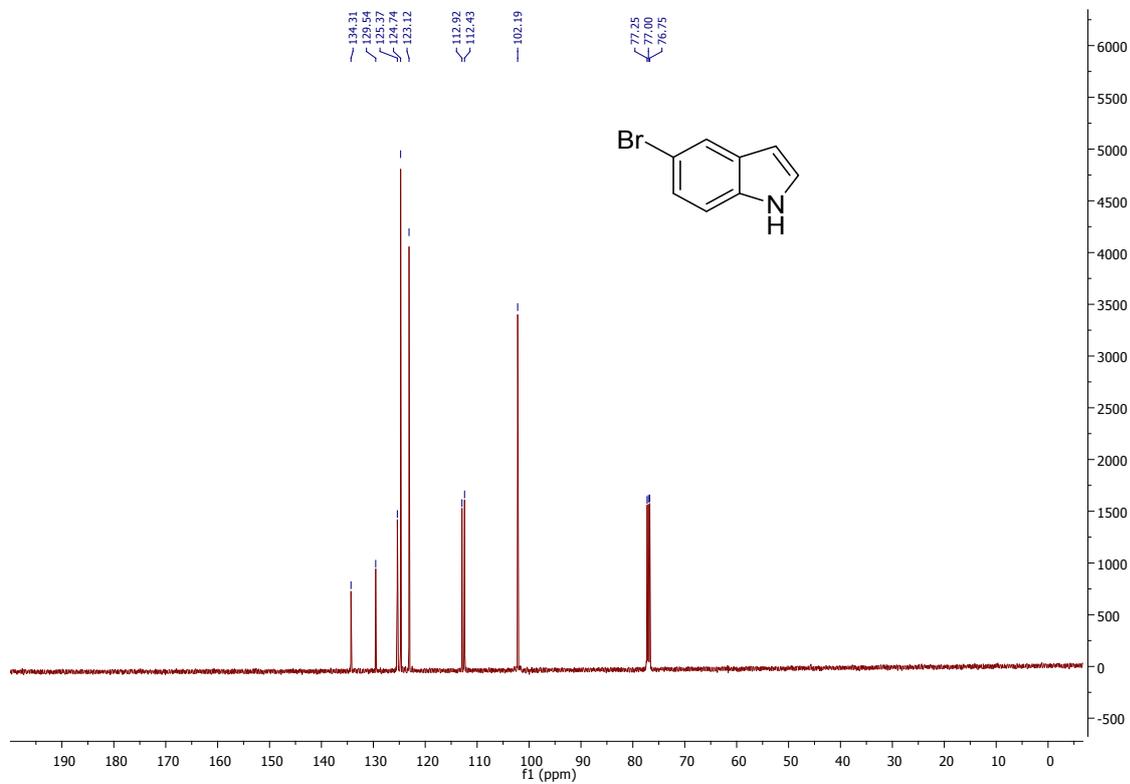
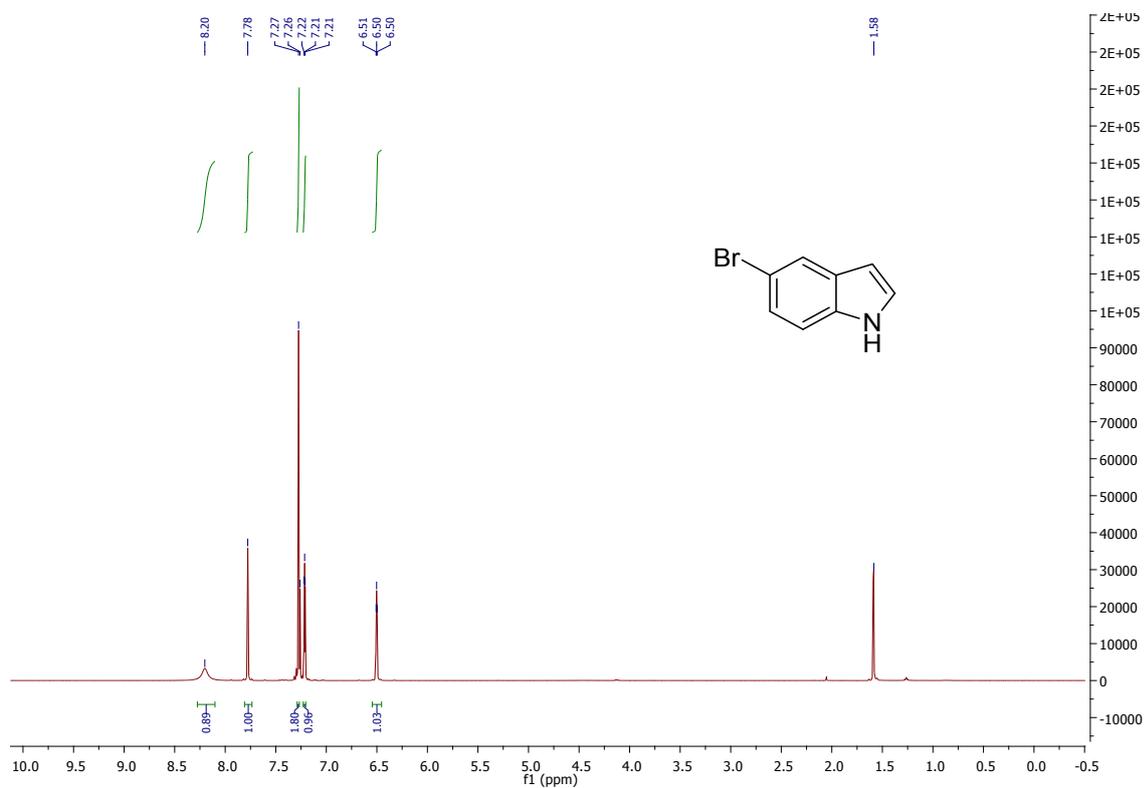
5-Nitroindole (7d):



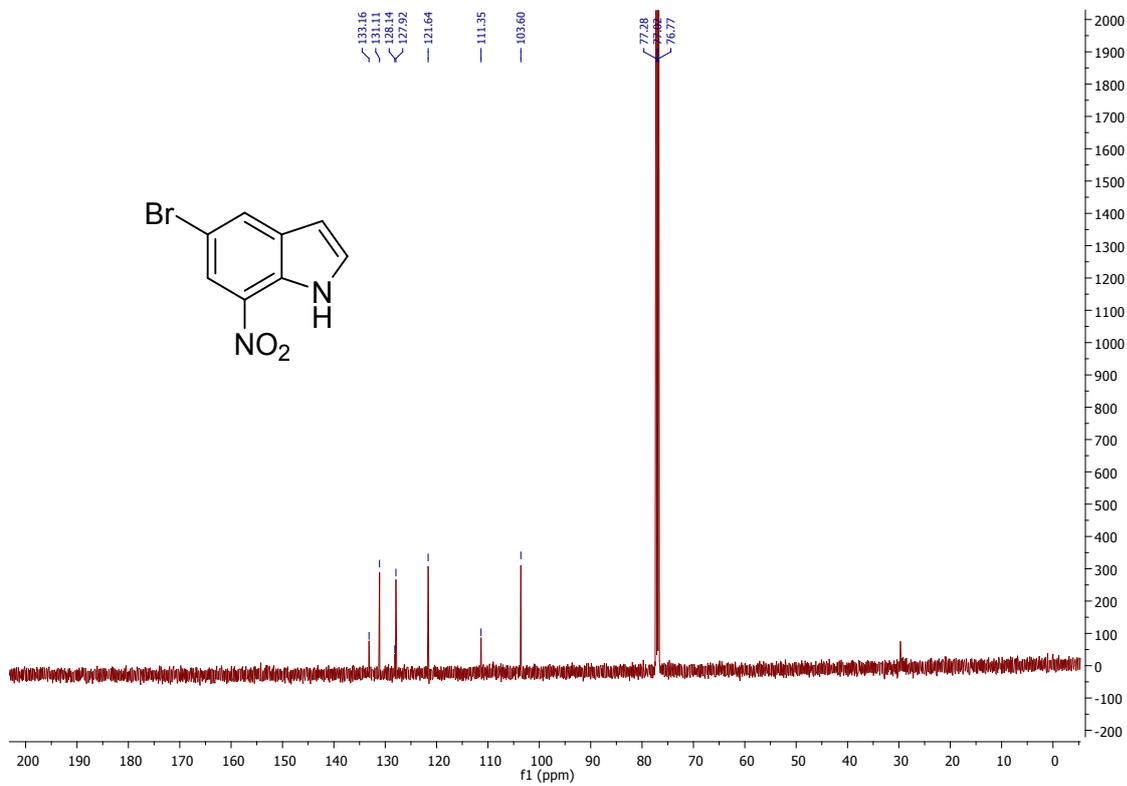
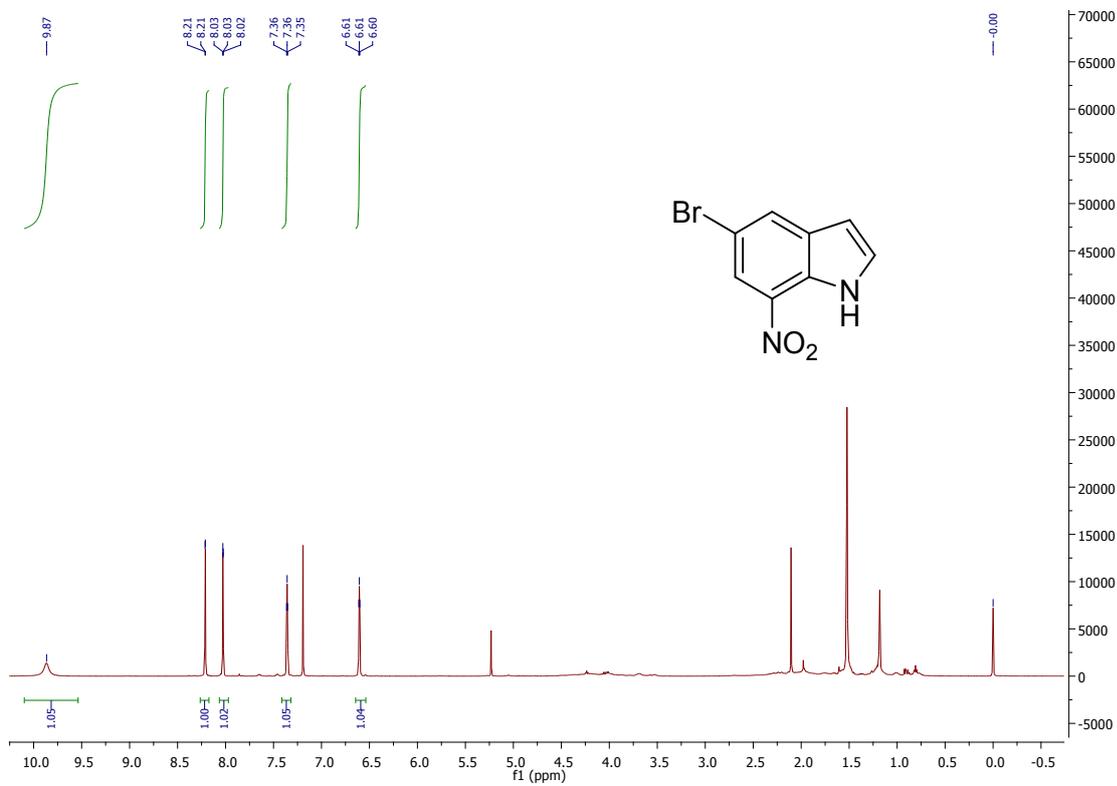
5-Cyanoindole (7e):



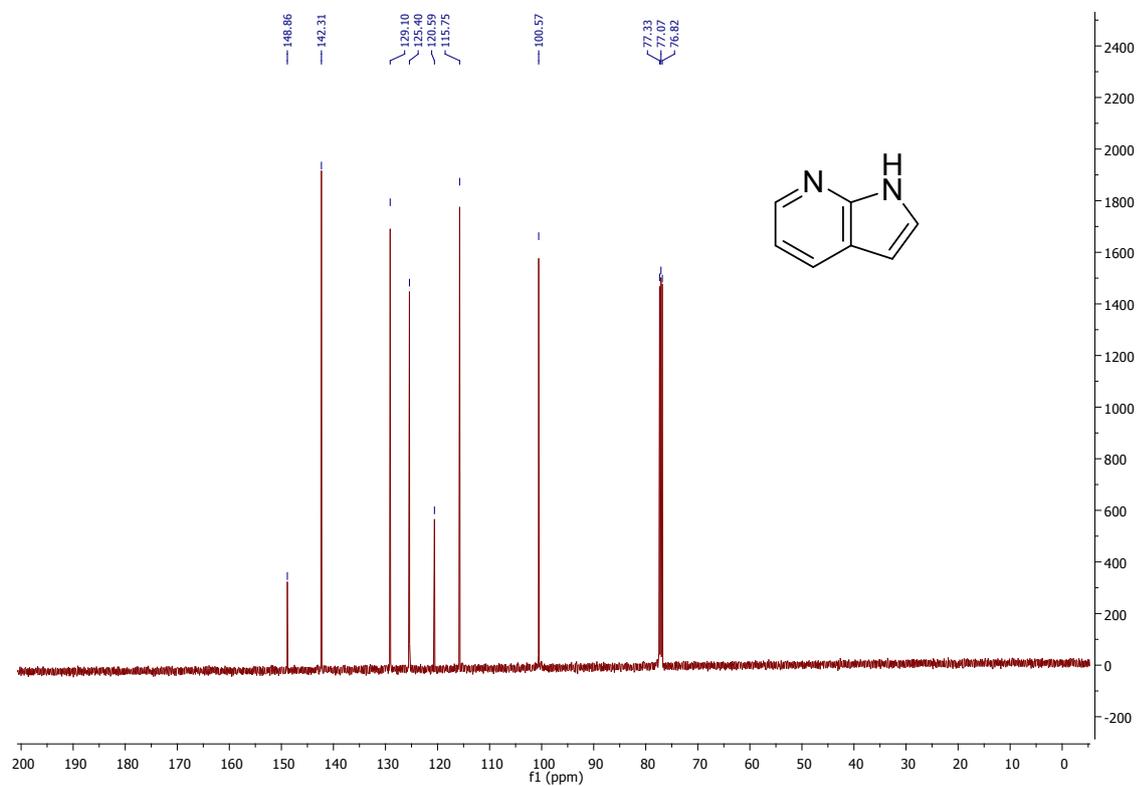
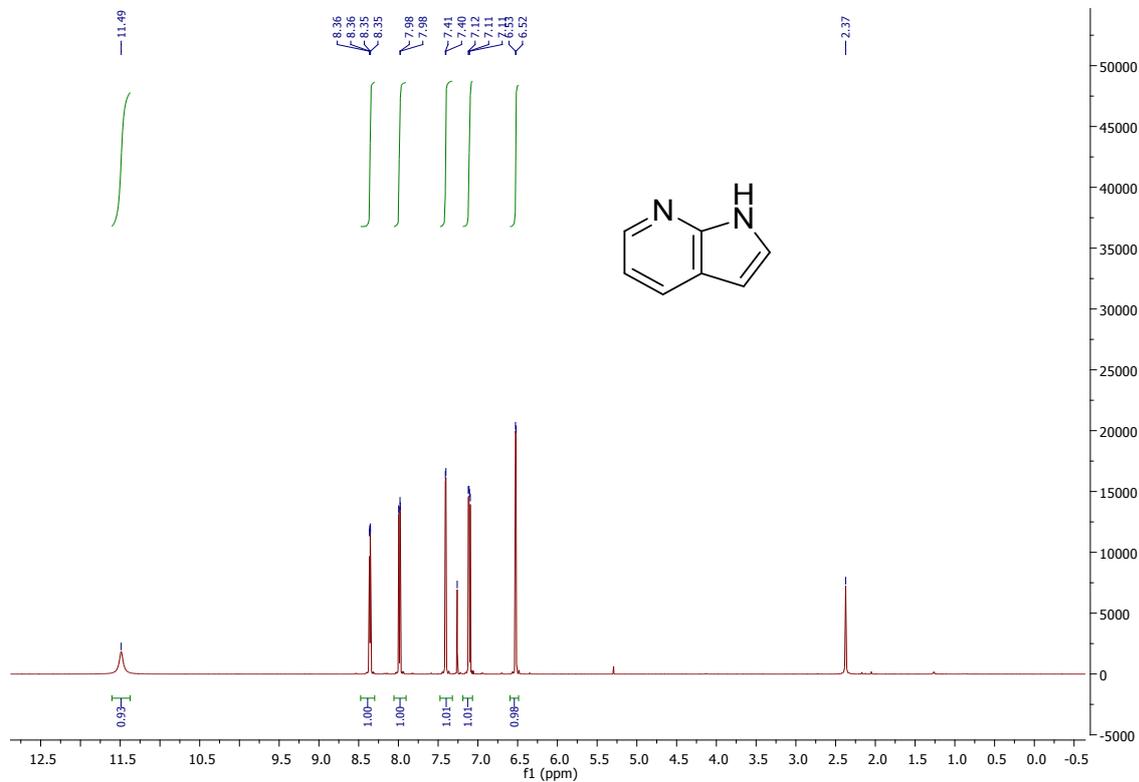
5- Bromoindole (7f):



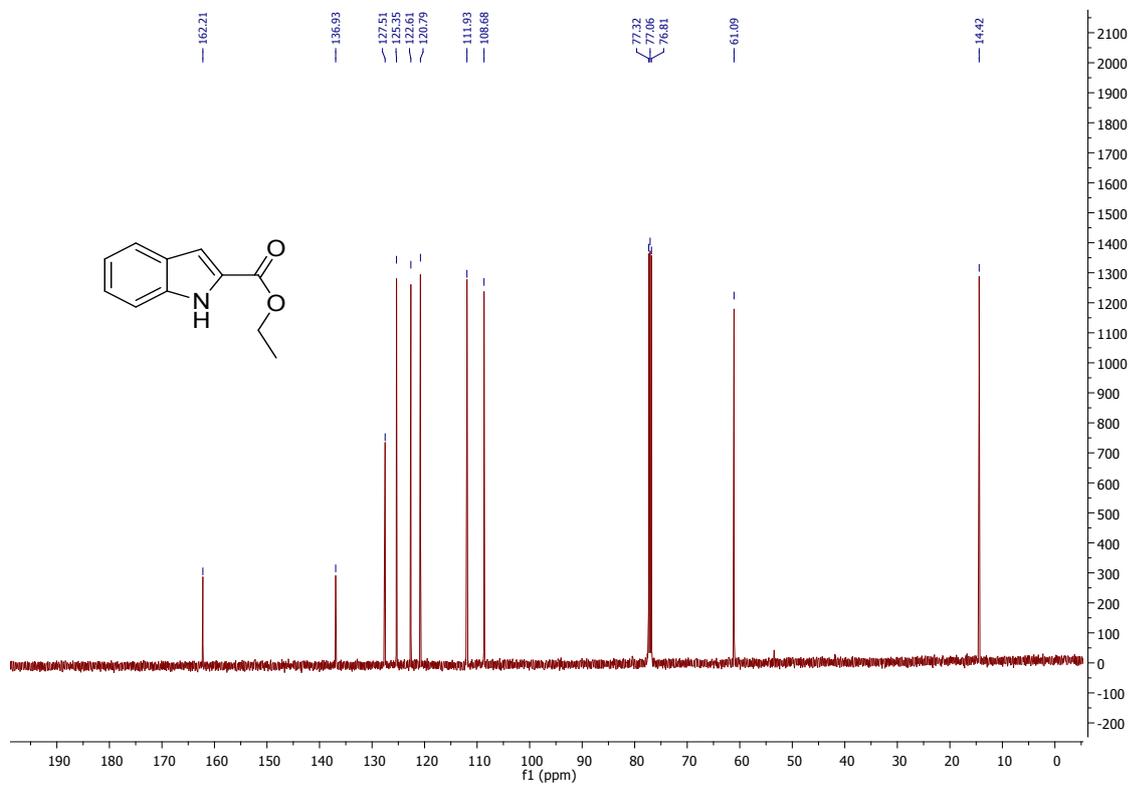
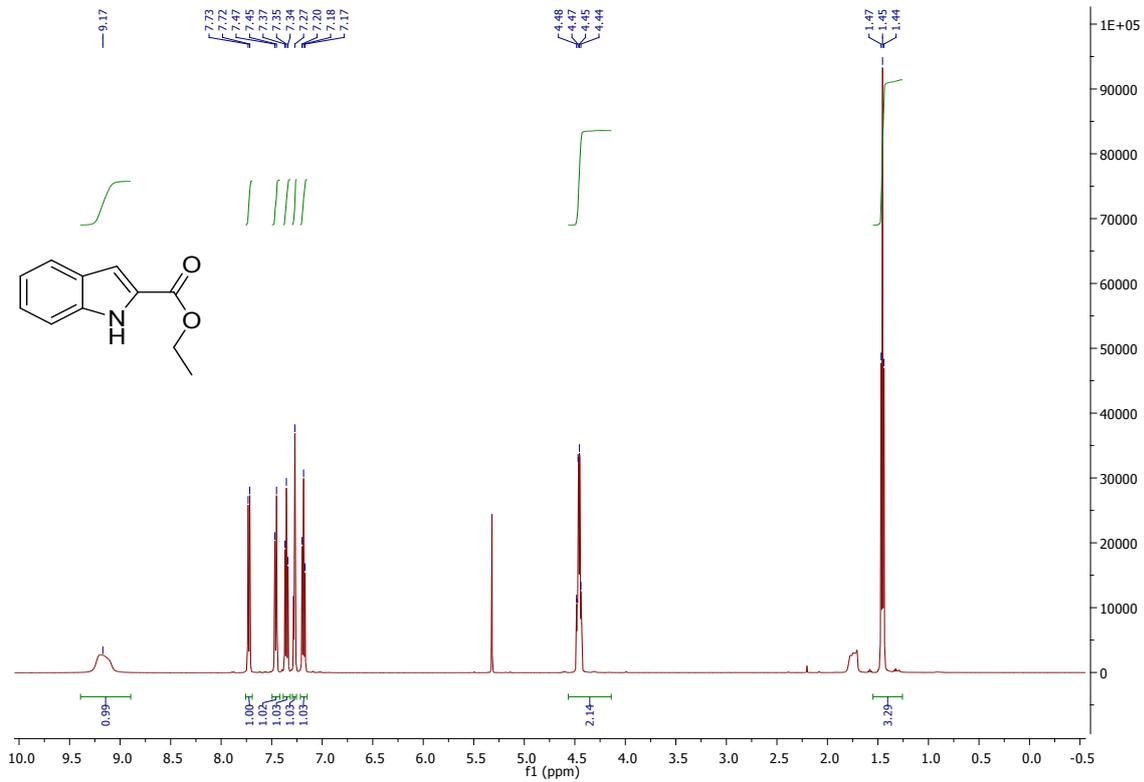
5-Bromo-7-nitro indole (7g):



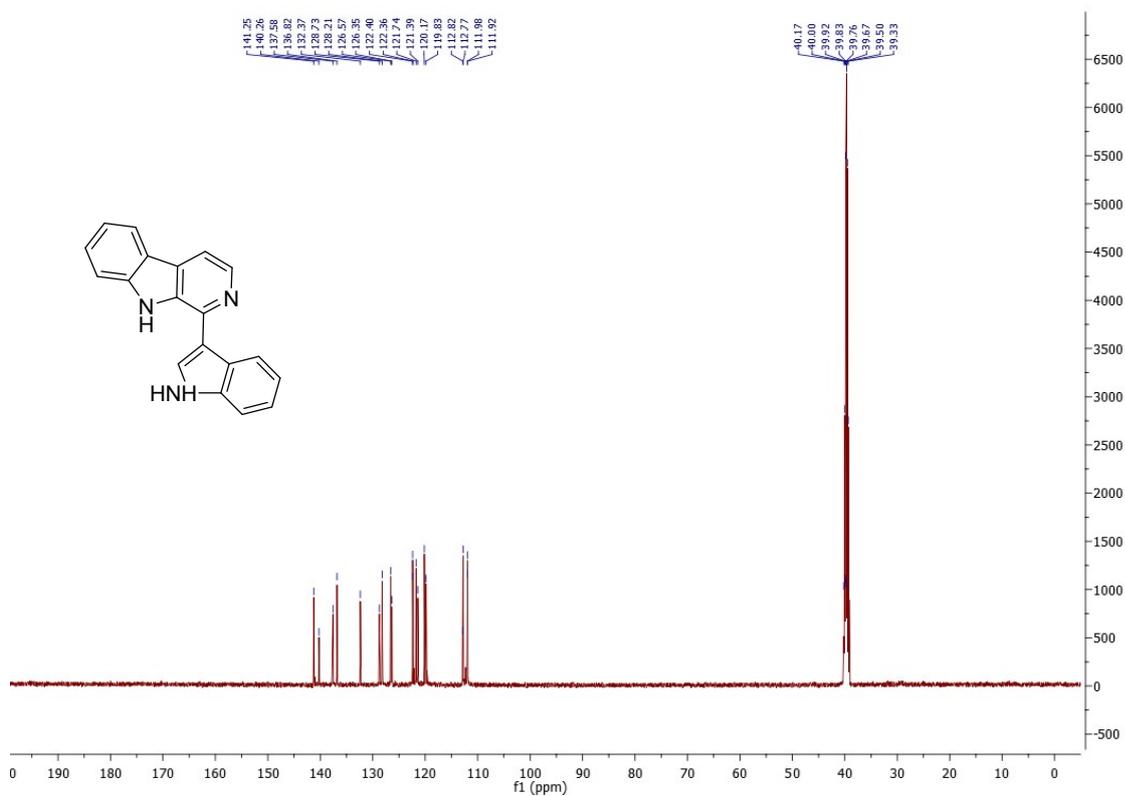
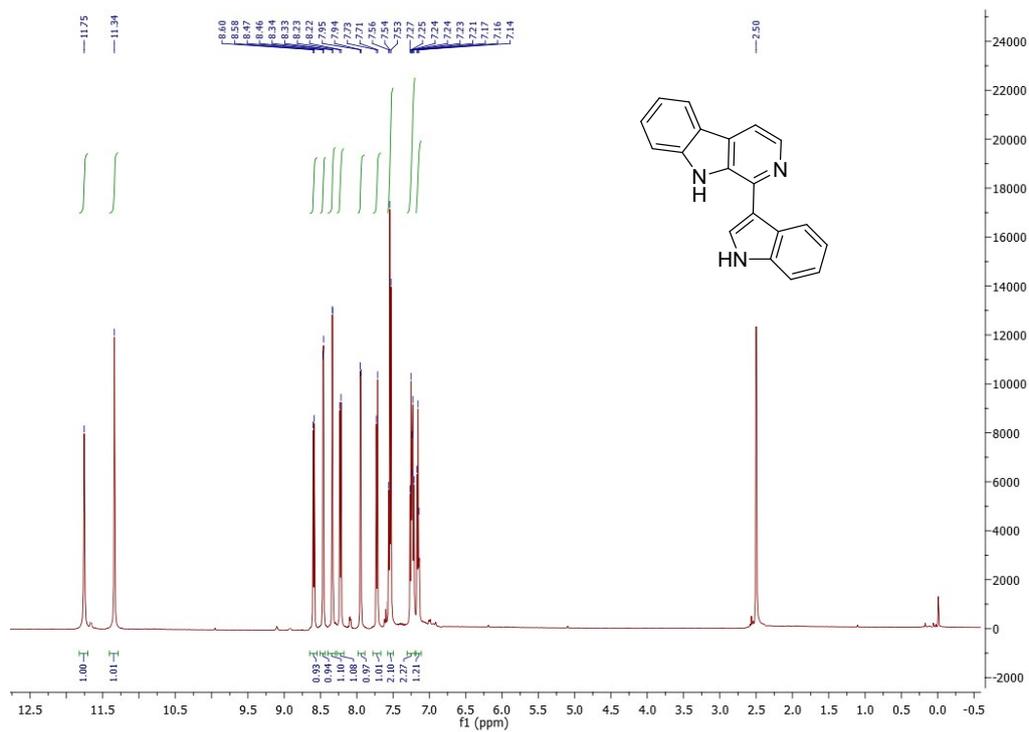
7-Azaindole (7h):



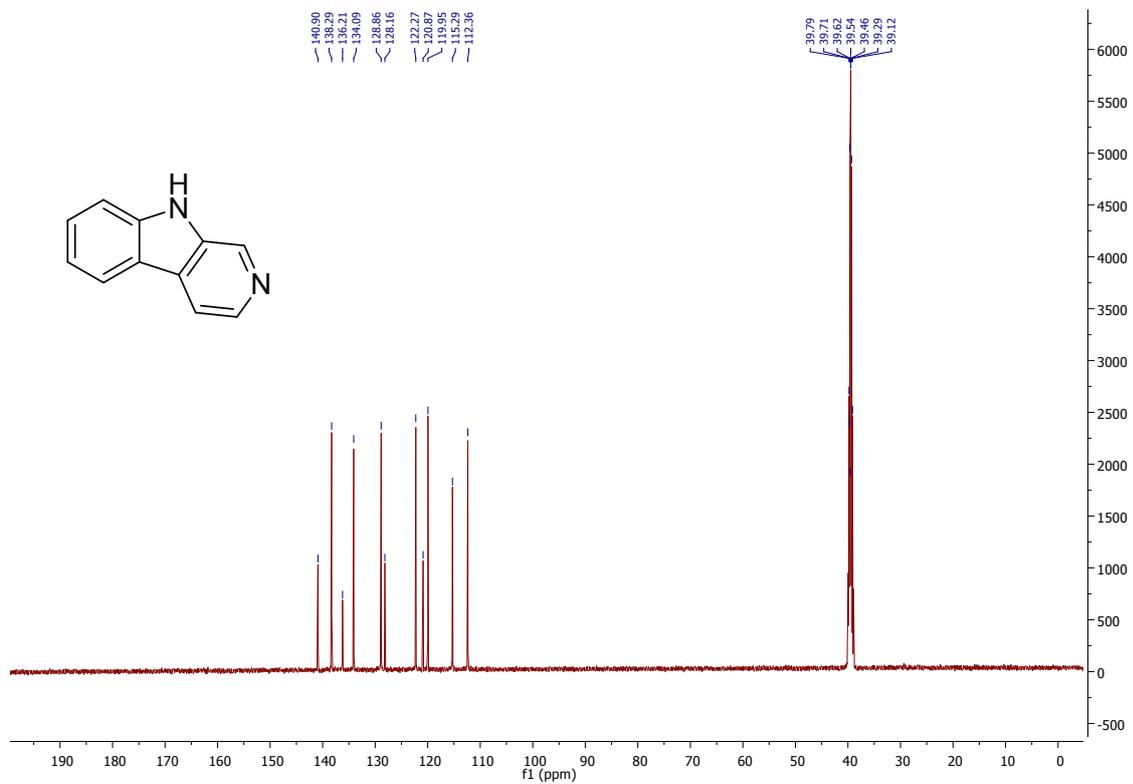
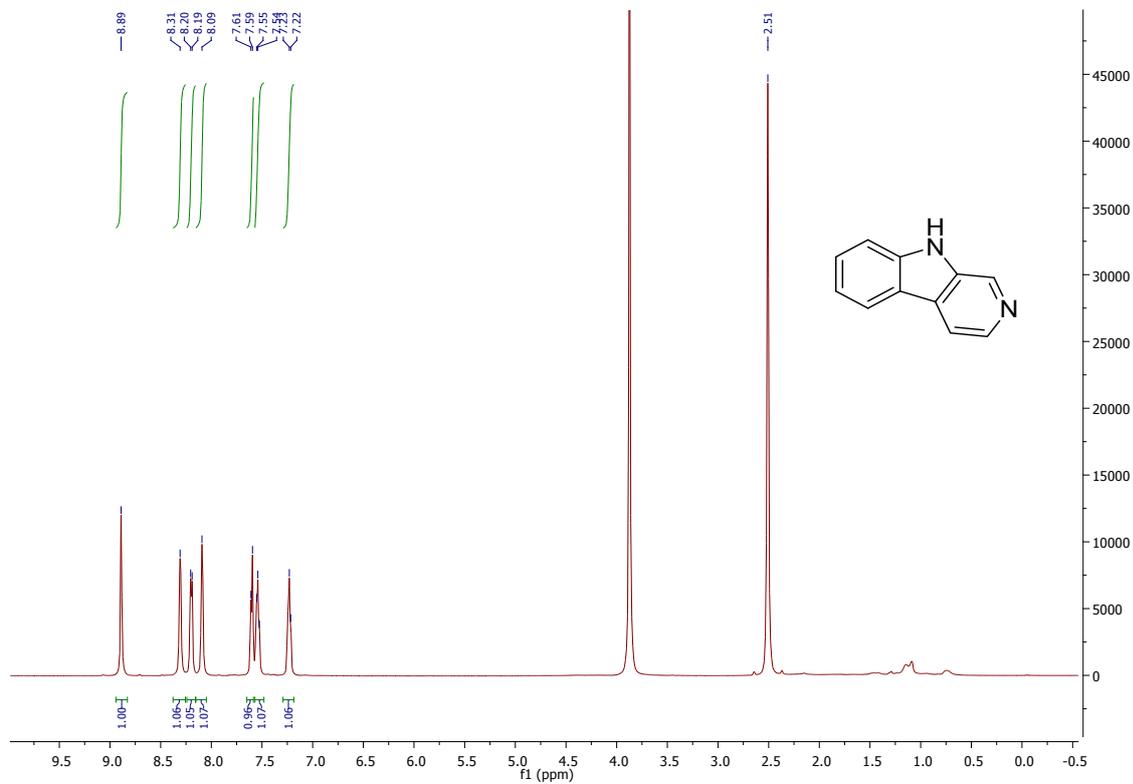
Ethyl indole-2-carboxylate (7i):



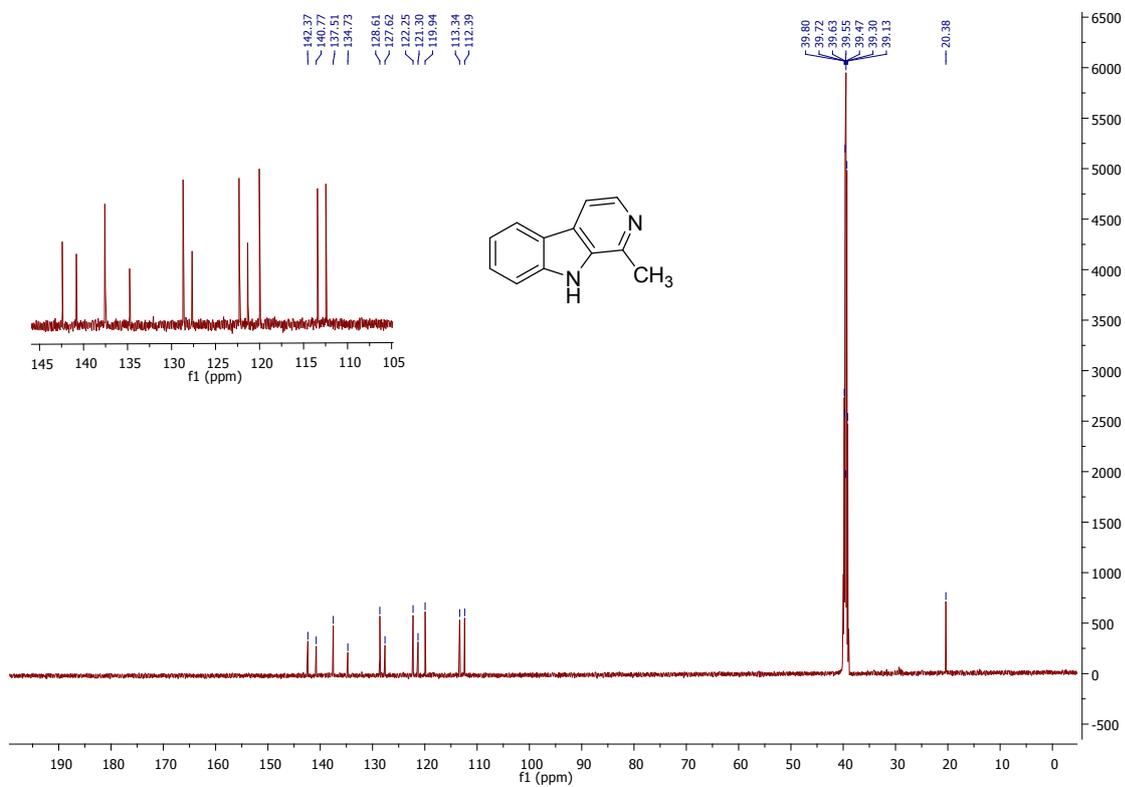
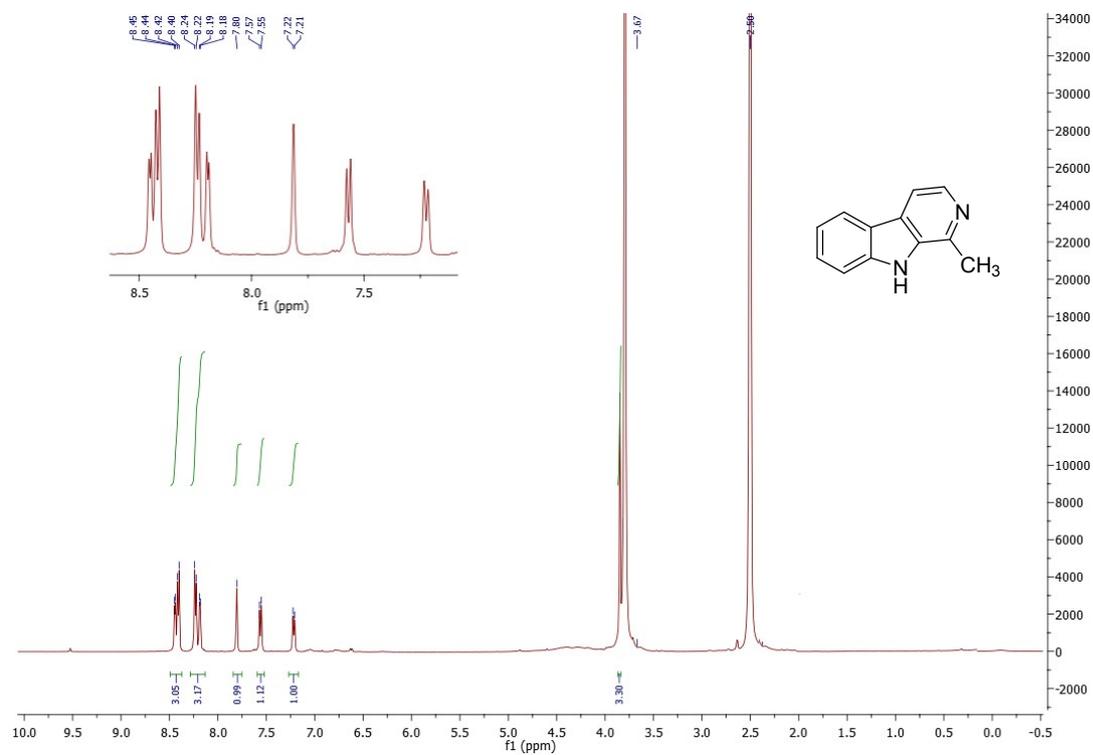
Eudistomin U (9a)



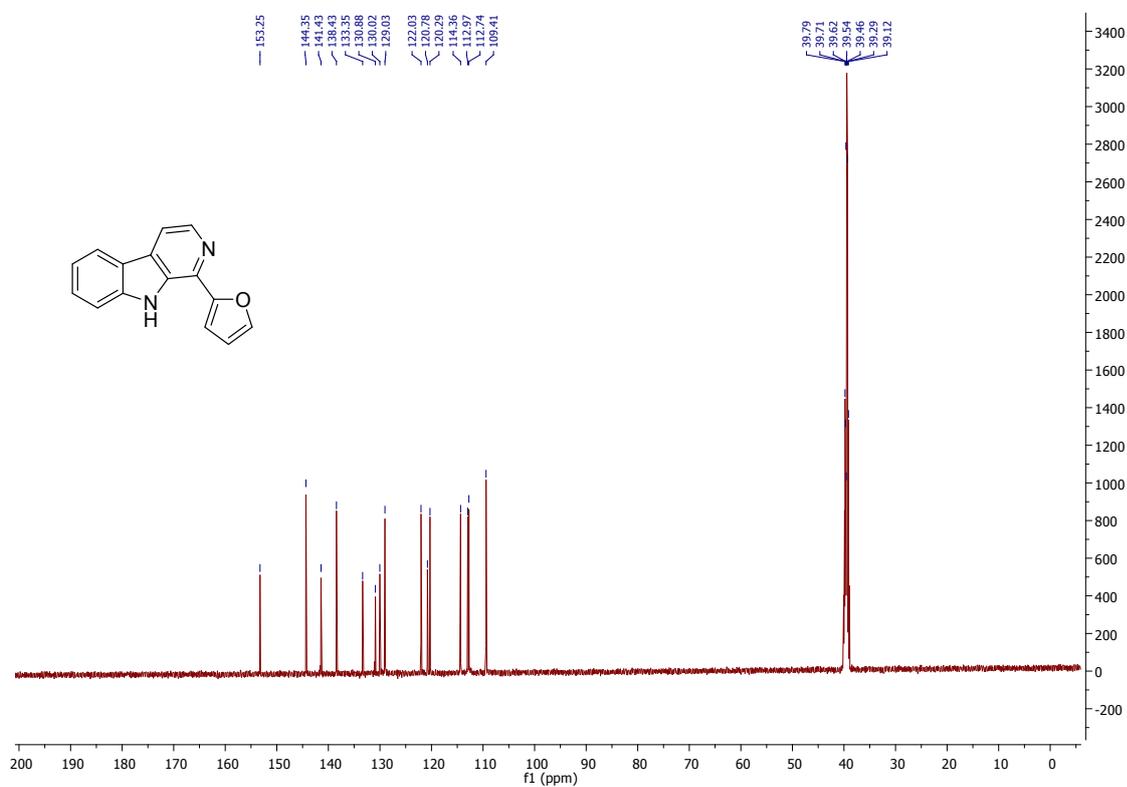
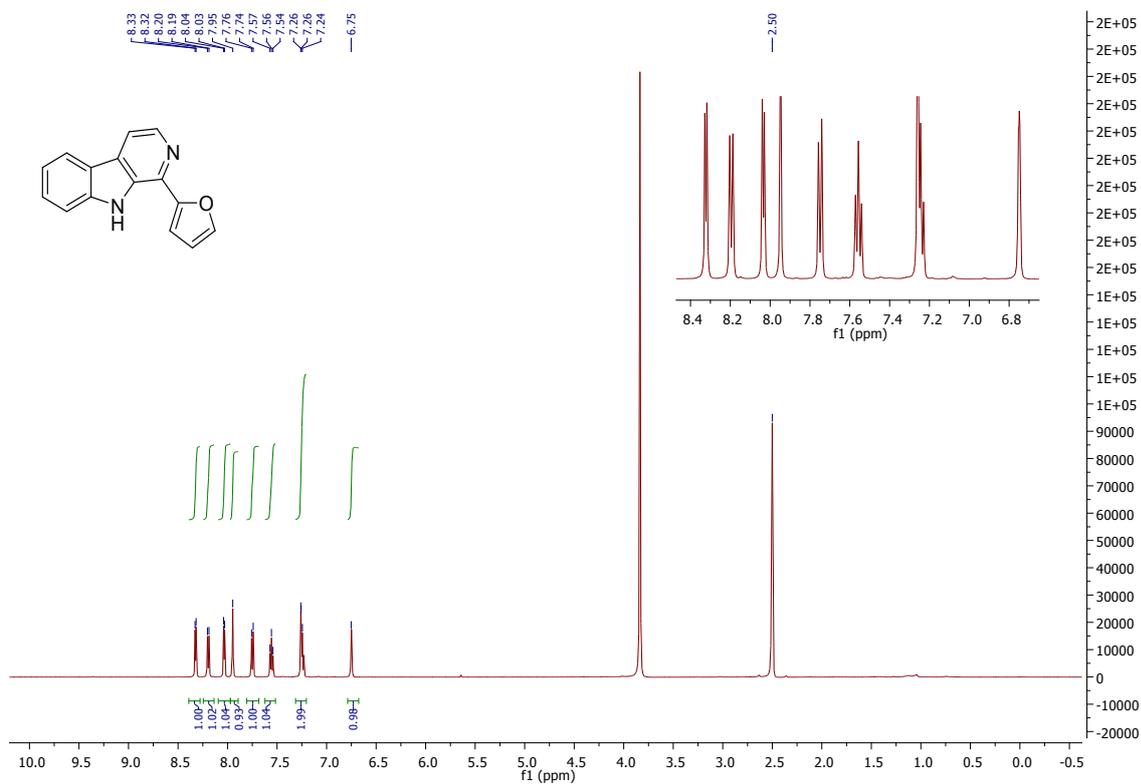
9H-pyrido[3,4-b]indole (11a):



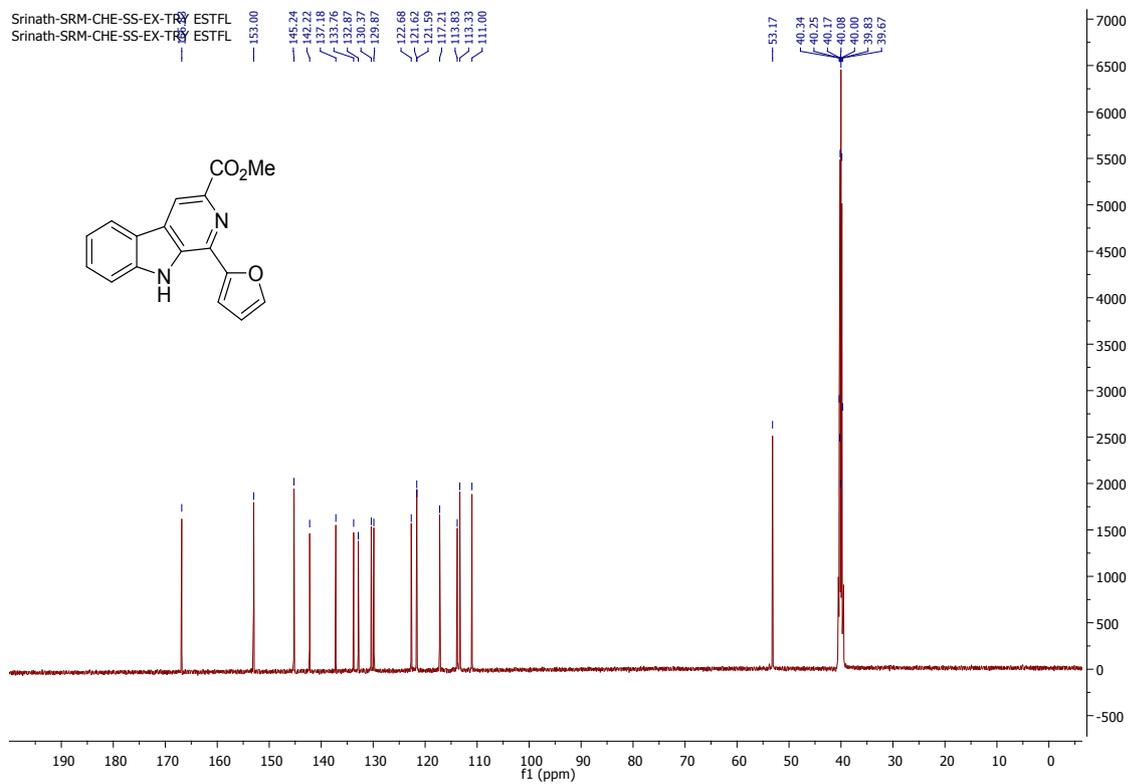
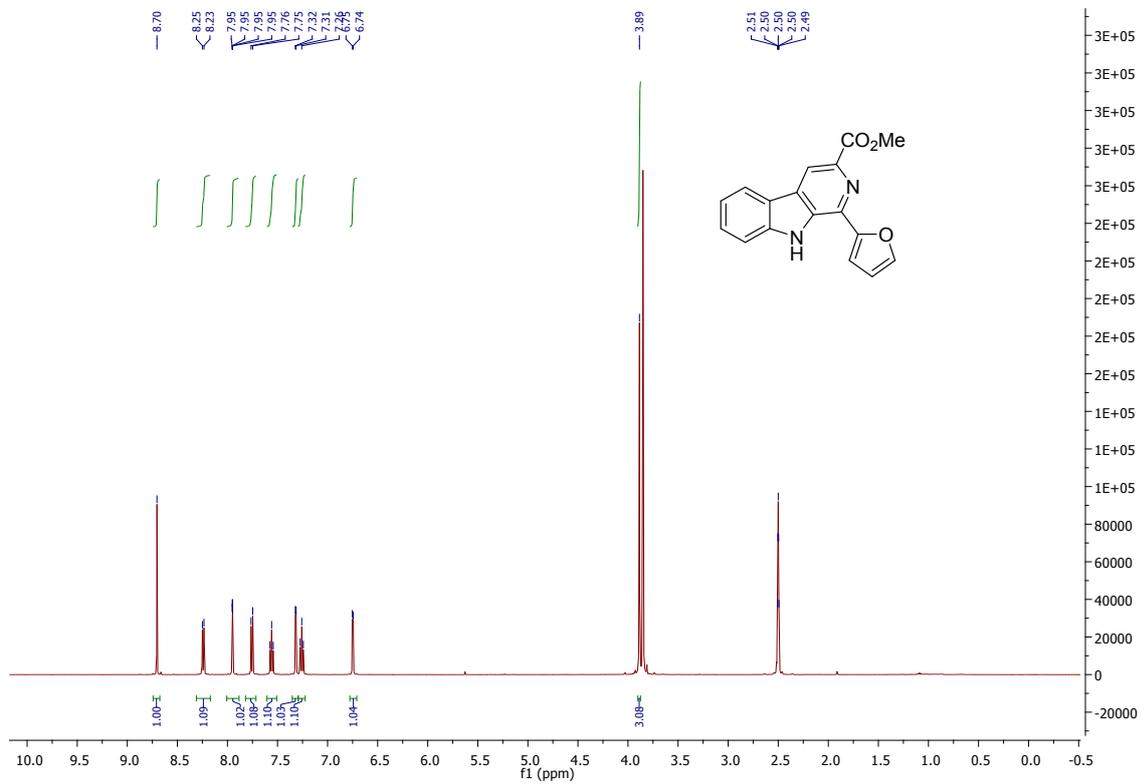
1-Methyl-9H-pyrido[3,4-b]indole (13a):



1-(Furan-2-yl)-9H-pyrido[3,4-b]indole (15a):



Methyl 1-(furan-2-yl)-9H-pyrido[3,4-b]indole-3-carboxylate (18a):



1-(3,4-Dihydroquinolin-1(2H)-yl)ethanone (20)

Srinath-1-Acetyl quinoline
Srinath-1-Acetyl quinoline

