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Supporting Information

Evaluating Dihydroazulene/Vinylheptafulvene Photoswitches for Solar Energy Storage Applications

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Supplementary Information

Table of contents:

I. Determination of the solubility of DHA in PhMe, MeCN, and EtOH

General:

A modified version of a literature procedure was adopted.[1] For internal standard, 1,4-dinitrobenzene (>99% purity) was chosen.[2] The employed **DHA1** (2-phenylazulene-1,1(8a*H*)-dicarbonitrile) was recrystallized from boiling *n*-heptane (HPLC grade) to >99% purity by ^{1}H NMR. All weighings were performed on a Sartorius Extend ED2245 d=0.1 mg analytical balance. All quantitative ^{1}H NMR (qHNMR) experiments were performed at 298 K on a Varian 400/54 spectrometer operating at 399.94 MHz for ^{1}H. The total time occupied on the NMR instrument (including overhead for sample changes, locking, shimming, etc.) for the entire range of measurements in this investigation was ca. 9 h. Chemical shifts are referenced to residual $CHCl_3$ (δ 7.26 ppm).[3]

Preparation of internal standard solution:

Into a 10-mL volumetric flask was weighed 1,4-dinitrobenzene (168.11 gmol^{-1}, 18.8 mg, 11.2 mmol, >99% purity), after which ca. 5 mL $CDCl_3$ was added. The flask was thoroughly swirled, and upon complete dissolution of all solids additional $CDCl_3$ was added to reach a total of 10.00 mL. Finally, the flask was stoppered and inverted several times to ensure full mixing. Resulting concentration of internal standard, $c_{standard}$ = 11.2 mM in $CDCl_3$.

*Preparation of saturated **DHA1** solutions:*

An array of 2 × 3 ordinary 2-mL screw cap vials was set up and charged each with ca. 50 mg **DHA1** and ca. 0.5 mL solvent to provide two duplicates of saturated solutions of DHA in each tested solvent.

PhMe I *ca*. 50 mg DHA *ca*. 0.5 mL PhMe	**MeCN I** *ca*. 50 mg DHA *ca*. 0.5 mL MeCN	**EtOH I** *ca*. 50 mg DHA *ca*. 0.5 mL EtOH
PhMe II *ca*. 50 mg DHA *ca*. 0.5 mL PhMe	**MeCN II** *ca*. 50 mg DHA *ca*. 0.5 mL MeCN	**EtOH II** *ca*. 50 mg DHA *ca*. 0.5 mL EtOH

The six vials were capped and stirred gently (150 rpm) in the dark at room temperature for 24 h. Next, they were centrifuged (5000 rpm, 5 min) in order to settle undissolved DHA residues at the bottom and leave above a saturated DHA solution.

Preparation of qNMR samples:

Each individual NMR sample was prepared as quickly as possible to minimize evaporative losses and kept in the dark. Each of the six saturated DHA solutions was sampled twice in order to have a comparable estimate of sampling precision for each vial, giving a total of 12 NMR samples. An aliquot of saturated DHA solution (100 μL) was withdrawn from the vial without disturbing the solid layer in the bottom and weighed precisely into a standard 5-mm NMR tube. Into the same NMR tube was furthermore weighed a precise amount of the standard solution (600 μL).

qHNMR studies:

The above 12 prepared NMR samples of saturated DHA solutions were each investigated by two different qNMR experiments for reasons of securing satisfactory data:

Experiment series labelled "PROTON_01"
Acquisition parameters: *ns* = 128, *d1* = 9.0 s, *at* = 2.6 s, *pw* =3.17 μs (θ = 33°), *sw* = 6410.3 Hz, t_2 = 16K datapoints.
Processing parameters: Zero-filling to 64K datapoints, *lb* = 0.4 Hz.

Experiment series labelled "PROTON_02"
Acquisition parameters: *ns* = 8, *d1* = 27.0 s, *at* = 3.0 s, *pw* =4.75 μs (θ = 45°), *sw* = 6410.3 Hz, t_2 = 19231 datapoints.
Processing parameters: Zero-filling to 64K datapoints, *lb* = 0.3 Hz.

The experimental series labelled *PROTON_01* was pre-programmed on the spectrometer as standard walk-up qHNMR experiment.
The experimental series labelled *PROTON_02* was programmed by the author in order to secure acceptable qHNMR data (full spin relaxation and sufficient digital resolution), should the standard experiment prove inadequate.

No significant deviations were found, however, between the two experimental series, and therefore, both were used in the subsequent analysis. Indeed, it has been shown that running qHNMR experiments with AT + DE < $5T_1$ can provide acceptable integration values with only a minor increase of error.[4]

qHNMR analysis
A total of 24 ^{1}H NMR spectra were obtained (12 samples × 2 exp/sample), each providing "*DHA/solvent/standard*" molar ratios.

Selected signals were carefully integrated to give molar ratios of the sample constituents, i.e. standard, DHA, and solvent. The molar ratios were then converted to solubility figures. This was done in two ways: 1) using 1.4-DNB peak as internal standard; 2) using solvent peak(s) as internal standard. Finally, the obtained figures were averaged to give the results listed in Table X.

Calculations:
To calculate the solubility of DHA in a given solvent, we must determine the *amount of DHA* and the *amount of solvent* in each saturated aliquot.

$$S = \frac{m_{\mathrm{DHA}}}{V_{\mathrm{aliquot}}} \qquad \left[\frac{\mathrm{mg}}{\mathrm{mL}}\right]$$

When an aliquot of a saturated DHA solution is added to the NMR tube, the ratio DHA-to-solvent is fixed.

Thus, the *amount of DHA* (m_{DHA}) is found by comparing the NMR integrals of DHA to either *internal standard* (method 1) or to *solvent* (method 2; solvent considered as another internal standard. (In fact, it is not necessary to add an internal standard *per se*, but it is proper to do so as it provides a double-check measure.)

The *amount of solvent* (V_{solvent}) is found either from the *mass* (via density) or the *volume* of the *"sat DHA soln aliquot"* used for the NMR sample preparation. In practice, this is done by pipetting a fixed volume of

solution directly into the NMR tube while this in on the balance. Both the pipetted volume and the NMR tube mass increase is then noted.

$$V_{\text{solvent}} = \frac{m_{\text{sat DHA soln aliquot}}}{\rho_{\text{solvent}}} \qquad \text{(assuming that } \rho_{\text{solvent}} = \rho_{\text{sat DHA sol}}\text{)}$$

or

$$V_{\text{solvent}} = V_{\text{sat DHA soln aliquot}} \qquad \text{(assuming that } V_{\text{sat DHA soln aliquot}} \text{ is accurate)}$$

Method 1) assumes the density of solvent to be the same for the pure solvent as for the saturated solution of DHA-in-solvent. Method 2) assumes the pipetting of organic solvents/solutions to be performed reliably. Obviously, the two methods should give the same number; however, it is wise to do both series of calculations, since the assumption in 1) might be invalid or the pipetting in 2) might be imprecise (pipette tips do not always handle organic solvents well, and pipetting is notoriously less precise than weighing). It is observed for this experiment that the calculations with 1) and 2) show agreement.

Method 1: From DHA-to-standard ratios

$$m_{\text{DHA}} = n_{\text{DHA}} \cdot M_{\text{DHA}}$$

where

$$\begin{aligned} n_{\text{DHA}} &= \frac{A_{\text{DHA}}}{A_{\text{standard}}} \cdot n_{\text{standard}} \\ &= \frac{A_{\text{DHA}}}{A_{\text{standard}}} \cdot c_{\text{standard}} \cdot V_{\text{standard soln}} \\ &= \frac{A_{\text{DHA}}}{A_{\text{standard}}} \cdot c_{\text{standard}} \cdot \frac{m_{\text{standard soln}}}{\rho_{\text{CDCl}_3}} \end{aligned} \qquad \text{(assuming that } \rho_{\text{CDCl}_3} = \rho_{\text{standard solution}}\text{)}$$

Method 2: from DHA-to-solvent ratios

$$m_{\text{DHA}} = w\%_{\text{DHA}} \cdot m_{\text{sat DHA soln aliquot}}$$

where

$$w\%_{\text{DHA}} = \frac{x_{\text{DHA}} \cdot M_{\text{DHA}}}{x_{\text{DHA}} \cdot M_{\text{DHA}} + x_{\text{solvent}} \cdot M_{\text{solvent}}} \qquad \left(x_{\text{DHA}} = \frac{A_{\text{DHA}}}{A_{\text{DHA}} + A_{\text{solvent}}}\,;\; x_{\text{solvent}} = \frac{A_{\text{solvent}}}{A_{\text{DHA}} + A_{\text{solvent}}}\right)$$

Measured quantities:

Control no.	**Solution**	$m_{\text{sat DHA soln aliquot}}$		$m_{\text{standard solution}}$	
A	PhMe Ia	86,8	mg	768,9	mg
D	PhMe Ib	88,5	mg	764,6	mg
G	PhMe IIa	84,0	mg	770,6	mg
J	PhMe IIb	86,4	mg	777,2	mg
B	MeCN Ia	77,9	mg	777,5	mg
E	MeCN Ib	77,6	mg	786,4	mg
H	MeCN IIa	77,3	mg	759,2	mg
K	MeCN IIb	77,2	mg	785,2	mg
C	EtOH 99.5% Ia	73,0	mg	715,5	mg
F	EtOH 99.5% Ib	75,0	mg	786,4	mg
I	EtOH 99.5% IIa	80,4	mg	773,6	mg

L	EtOH 99.5% Iib	67,8	mg	789,7	mg

(For ^{1}H NMR integrals, see spectra enclosed.)

^{1}H NMR resonances:

	δ($CDCl_3$) observed*	**mult**	**#H**
1,4-Dinitrobenzene	8.4	s	4H
DHA	7.8 – 7.7	m	2H
	7.5 – 7.4	m	3H
	6.9	s	1H
	6.6	ddd	1H
	6.5	dd	1H
	6.4 – 6.3	m	2H
	5.8	dd	1H
	3.8	dt	1H
PhMe	7.4	m	2H
	7.3	m	3H
	2.5	s	3H
MeCN	1.9	s	3H
EtOH	3.6	q	2H
	3.4	s	1H
	1.1	q	3H

* Chemical shifts are quite dependent on co-solutes. In the solubility experiments, there are always several species present simultaneously and in varying concentrations; namely, standard, analyte, analyte solvent, and NMR solvent. The values given here may deviate from the chemical shifts observed in a sample of pure compound and are therefore given with one decimal only as a means for proper peak identification.

Results

Solvent	**Solubility of DHA**	
PhMe	54.8 ± 1.0 mg/mL	54.8 mg/mL ± 2%
MeCN	36.2 ± 0.7 mg/mL	36.2 mg/mL ± 2%
EtOH 99.5%	4.9 ± 0.2 mg/mL	4.9 mg/mL ± 4%

II. NMR spectra

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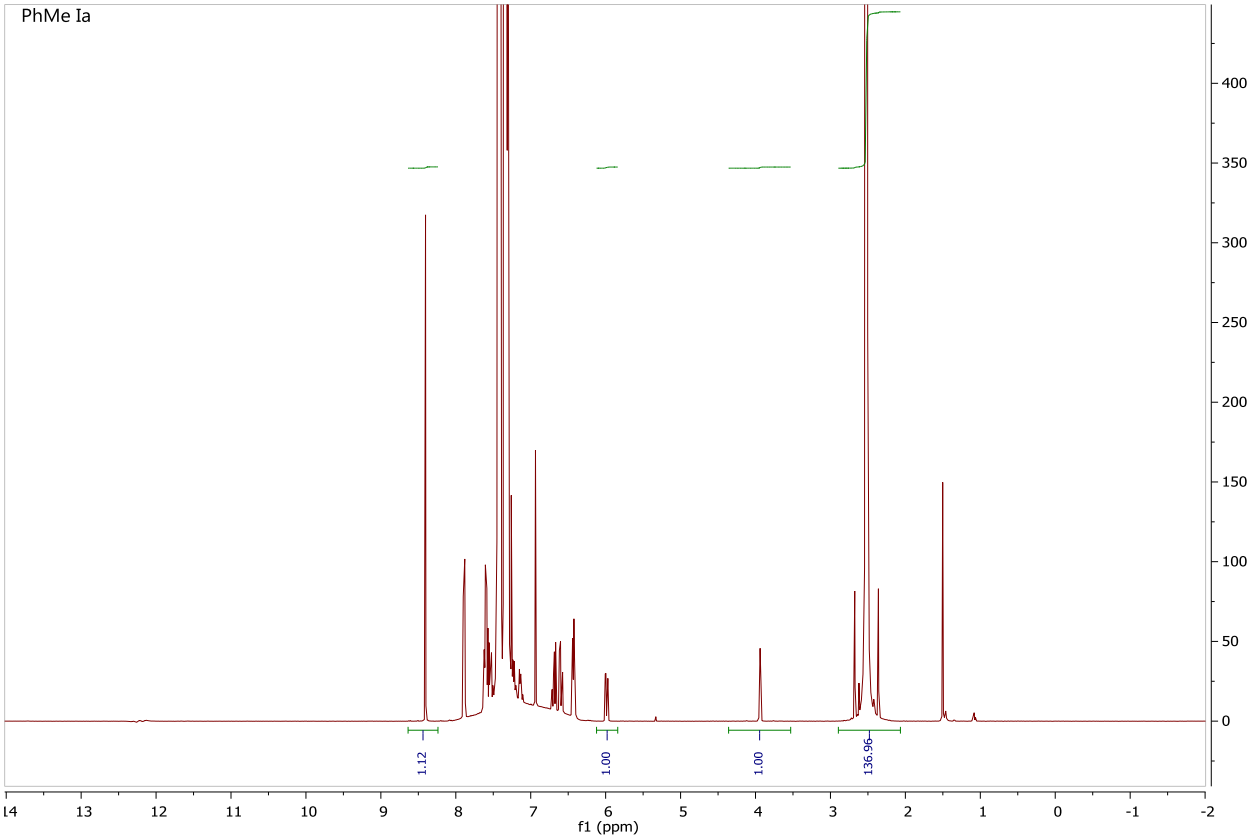

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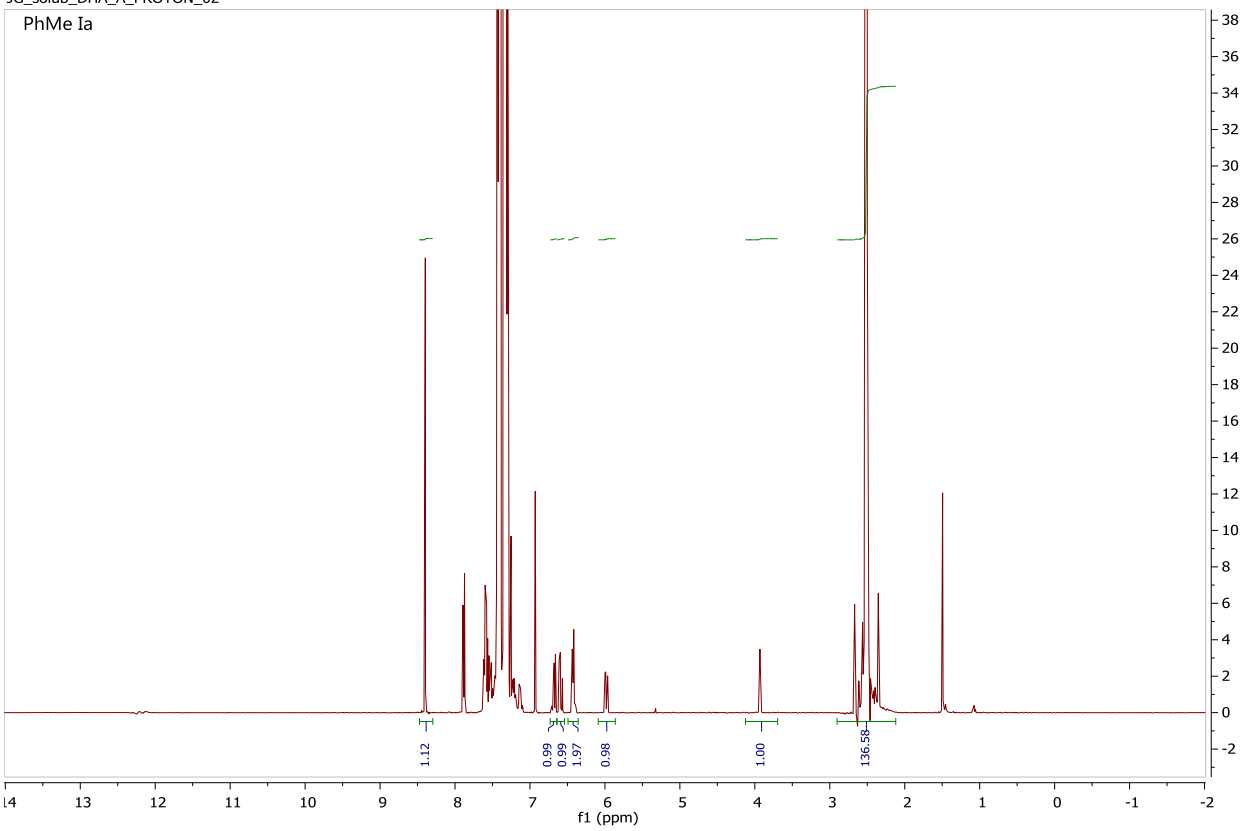

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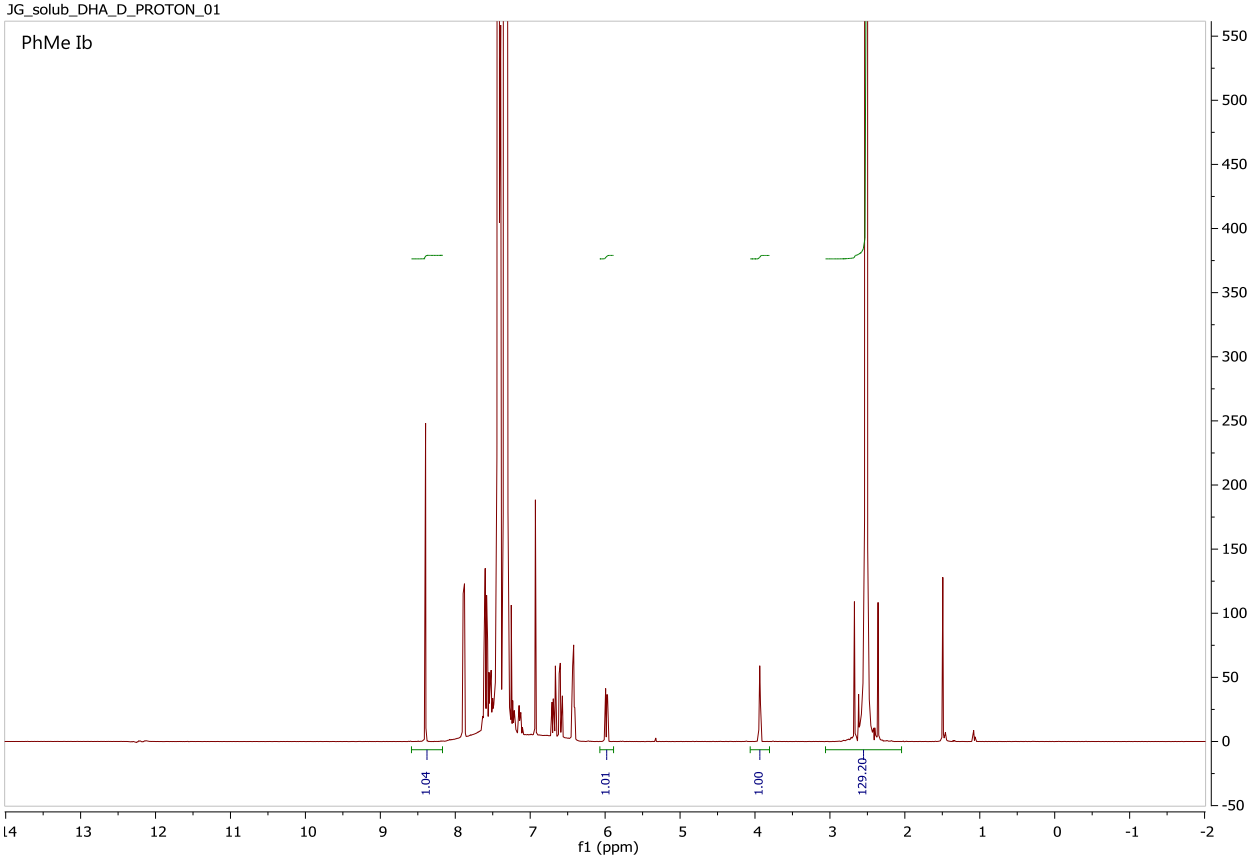

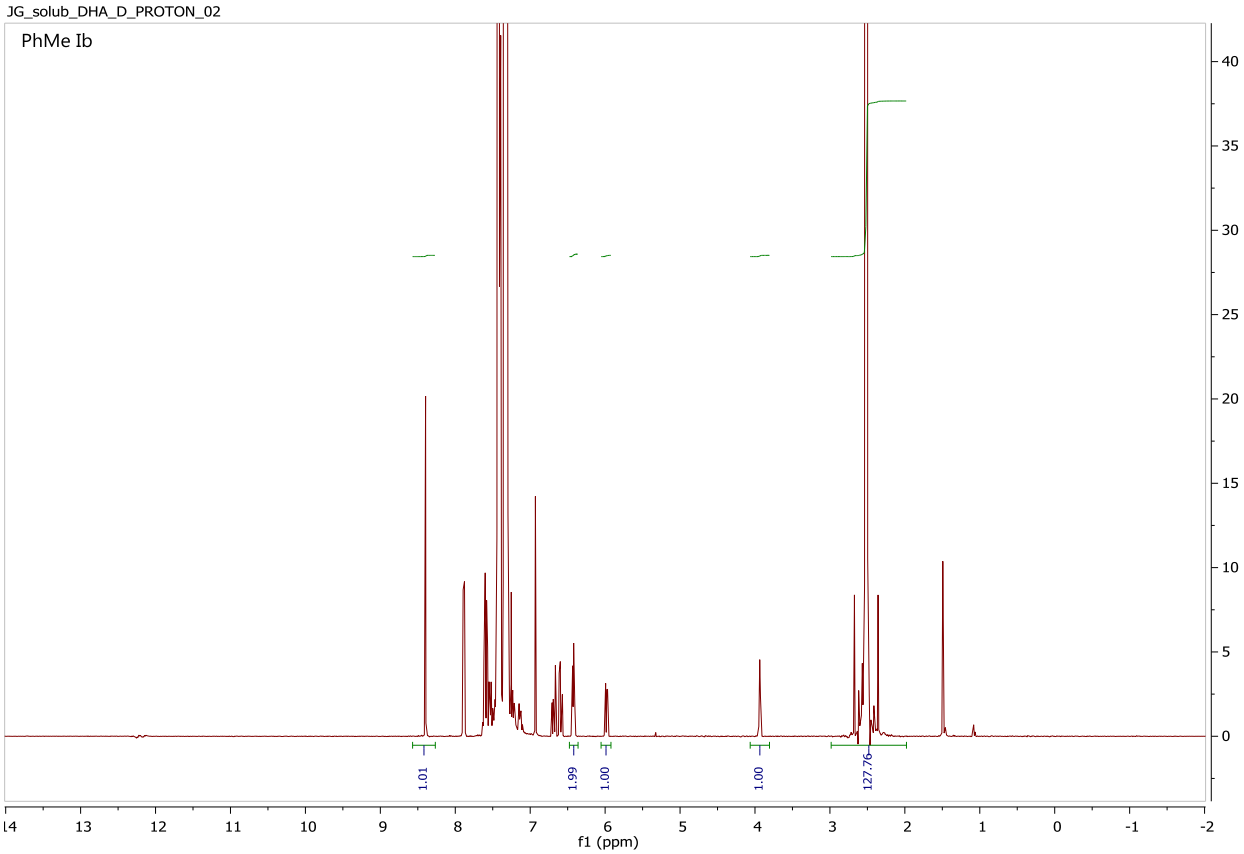
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PhMe Ib
1.01
1.99
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127.76
f1 (ppm)

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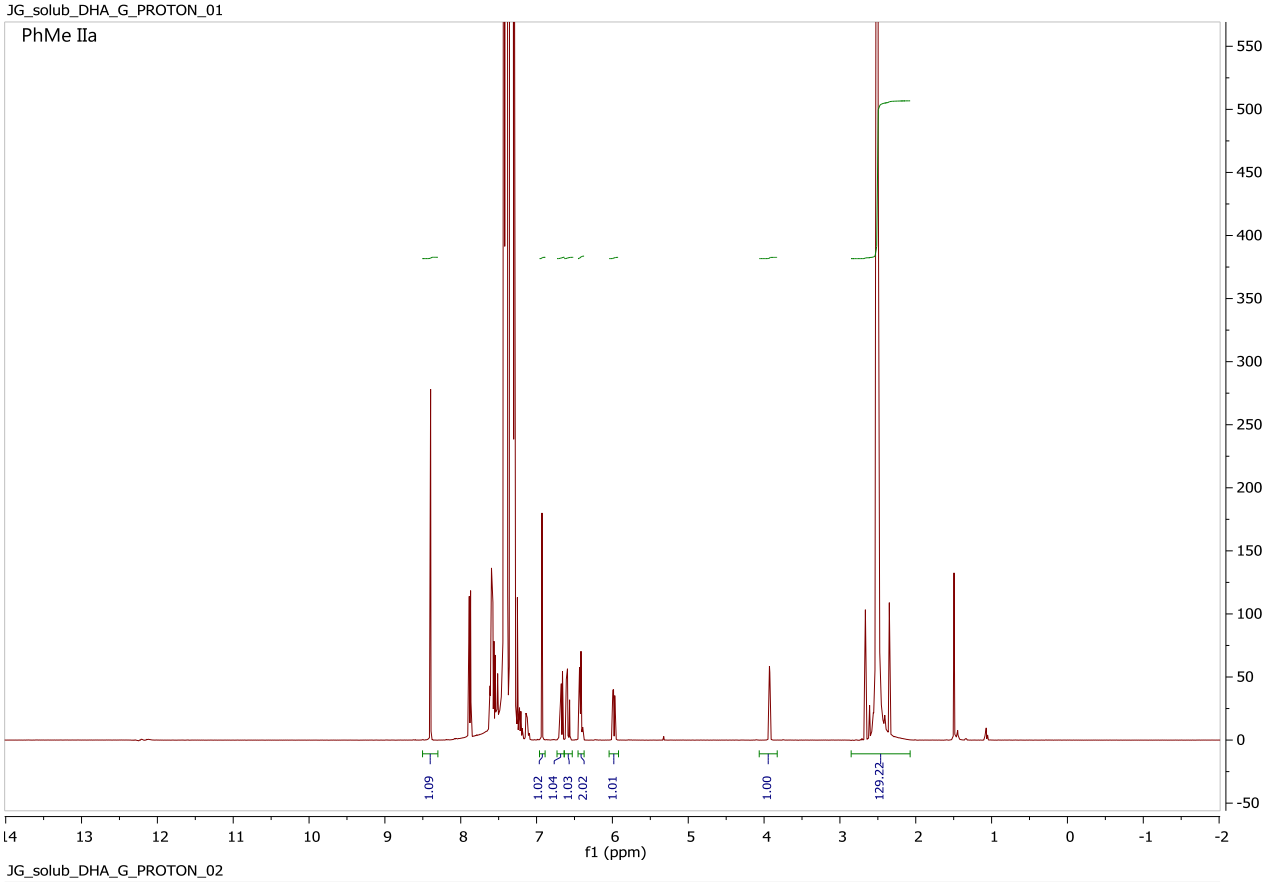

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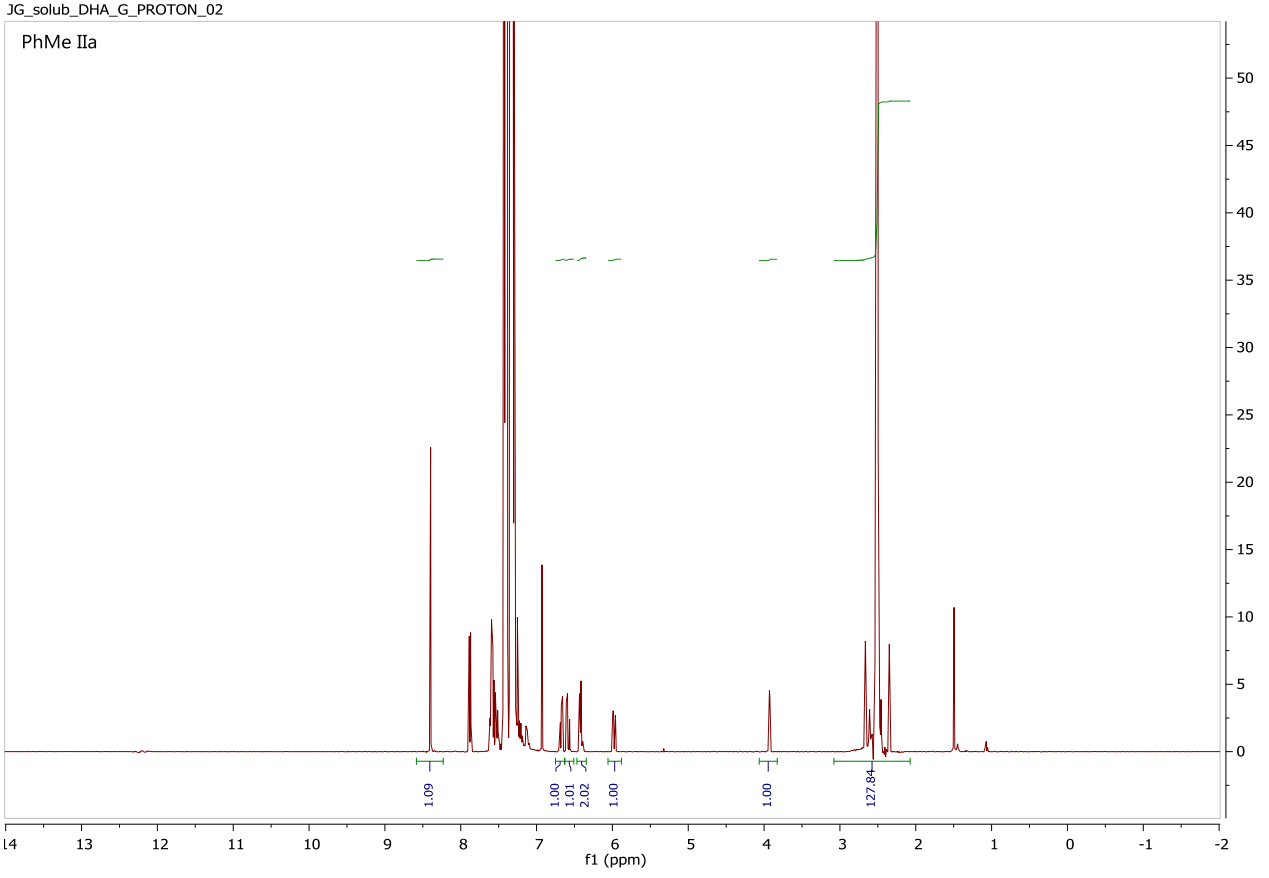

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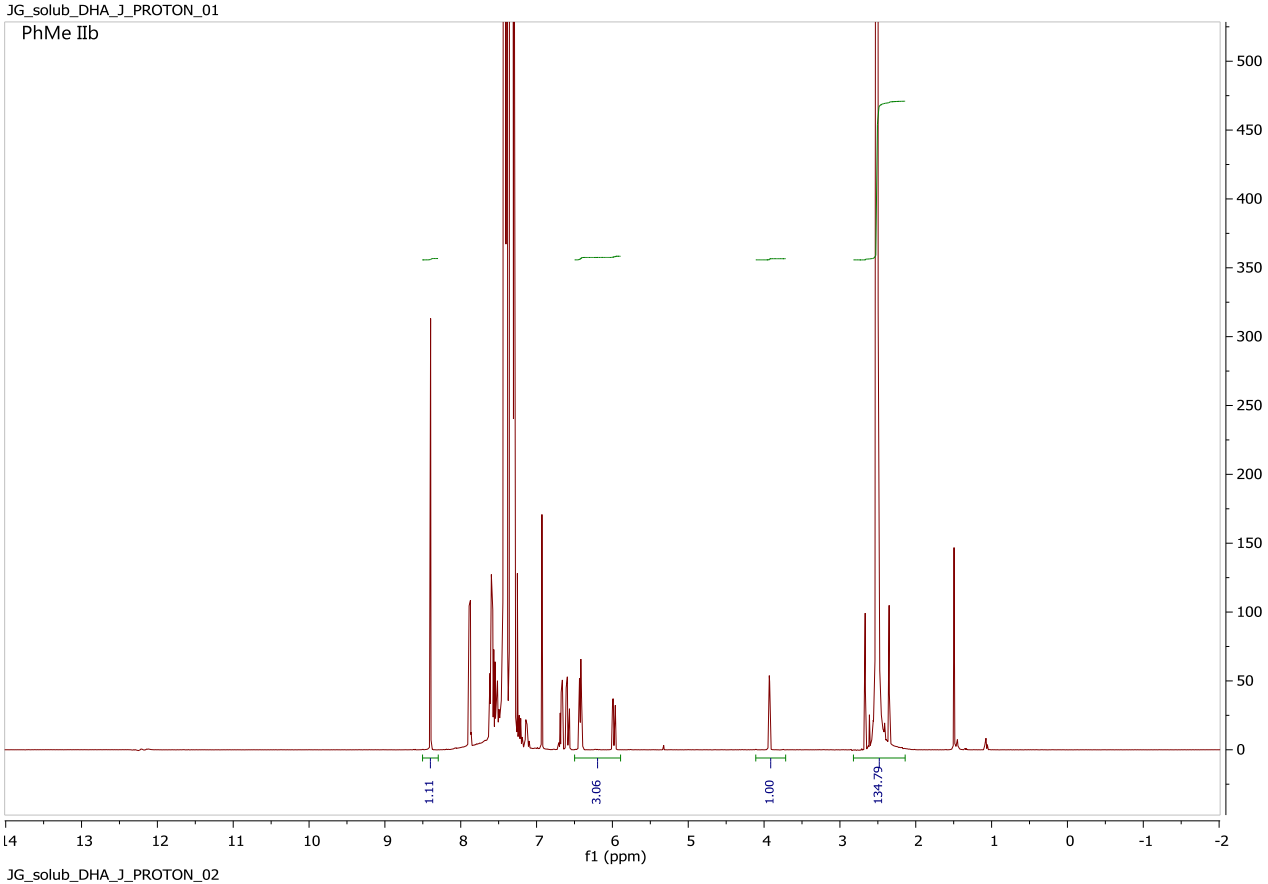

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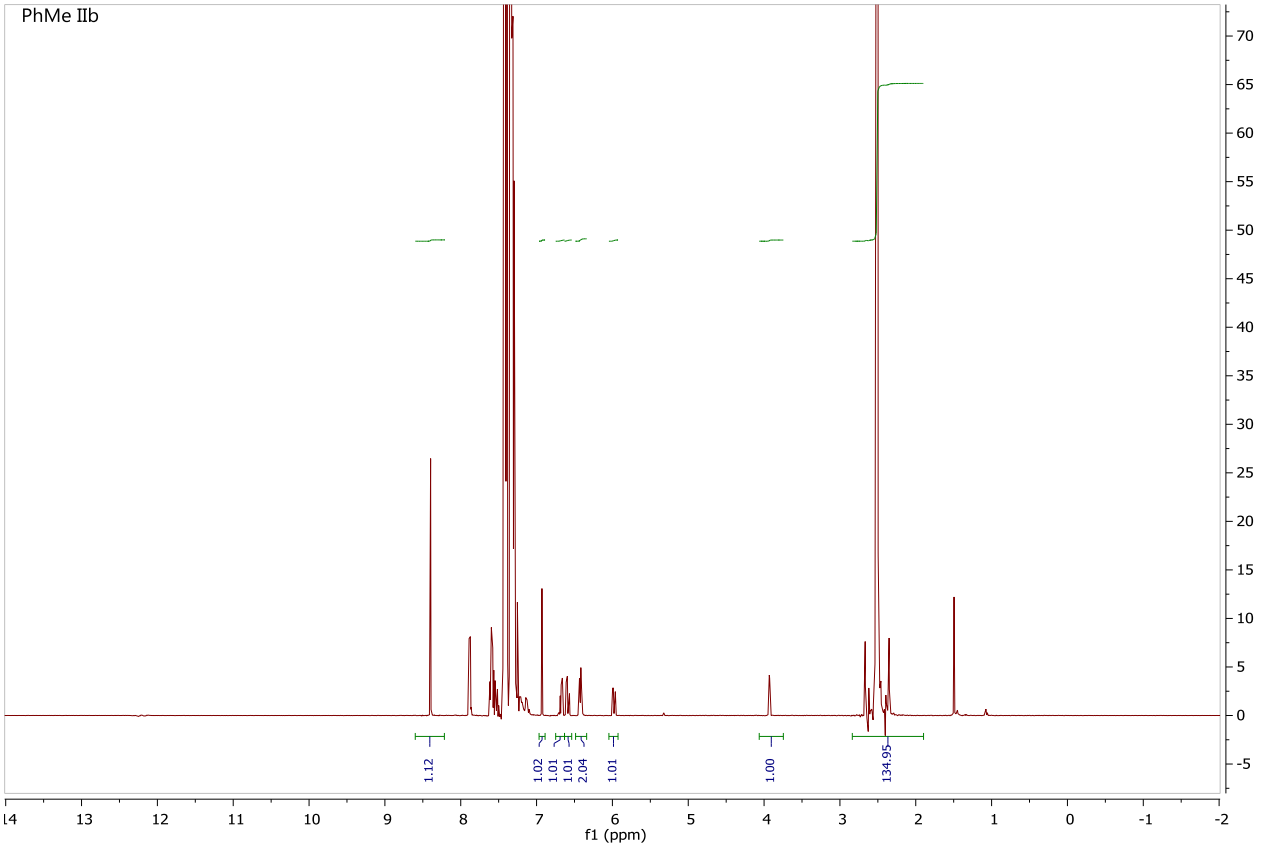

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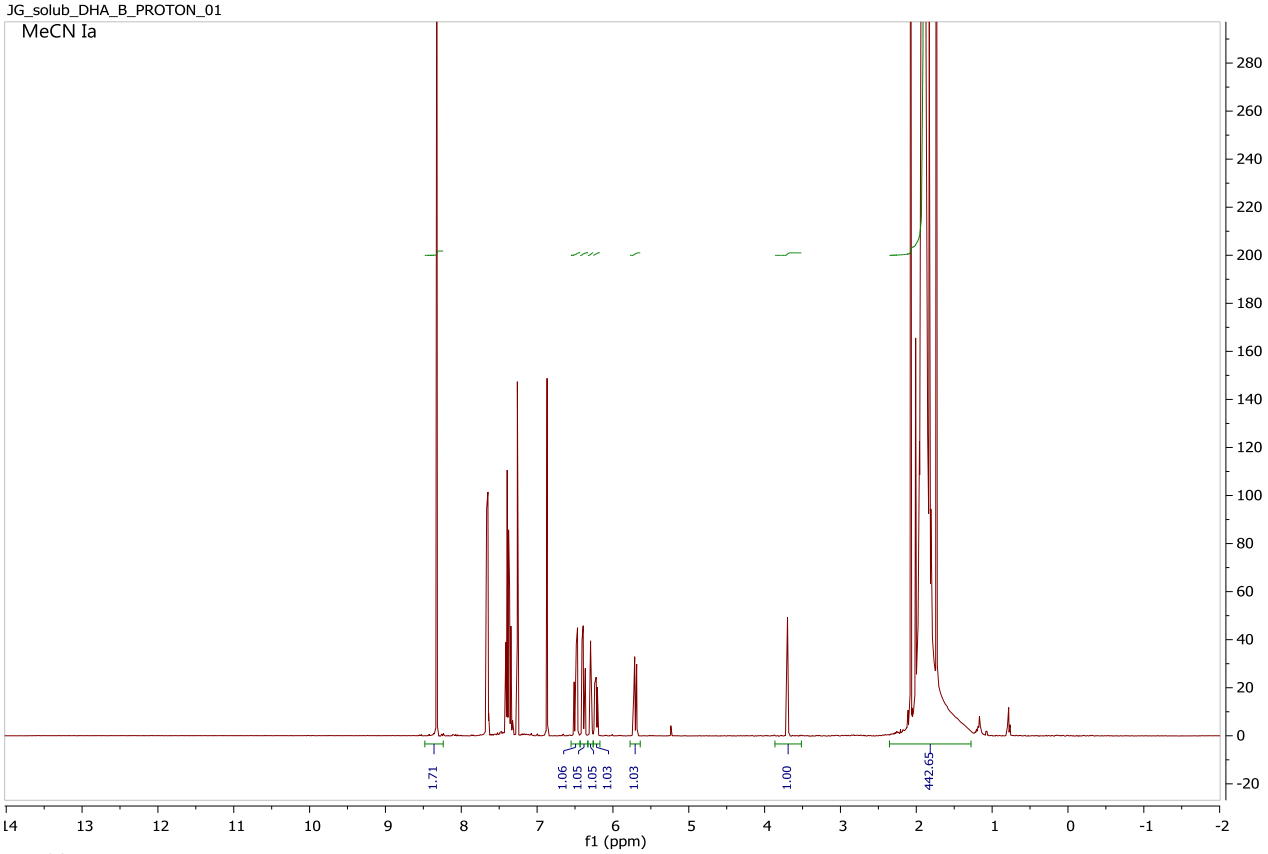

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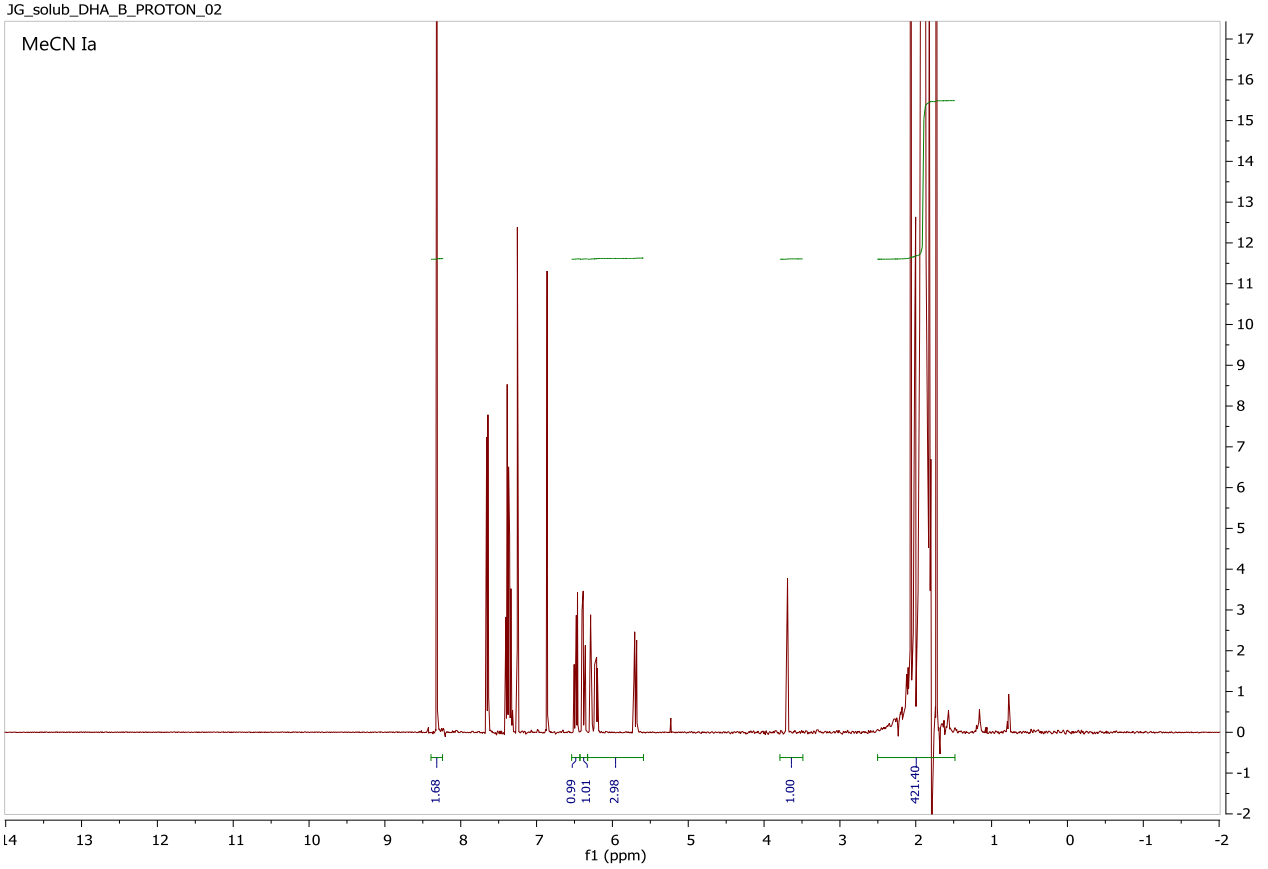

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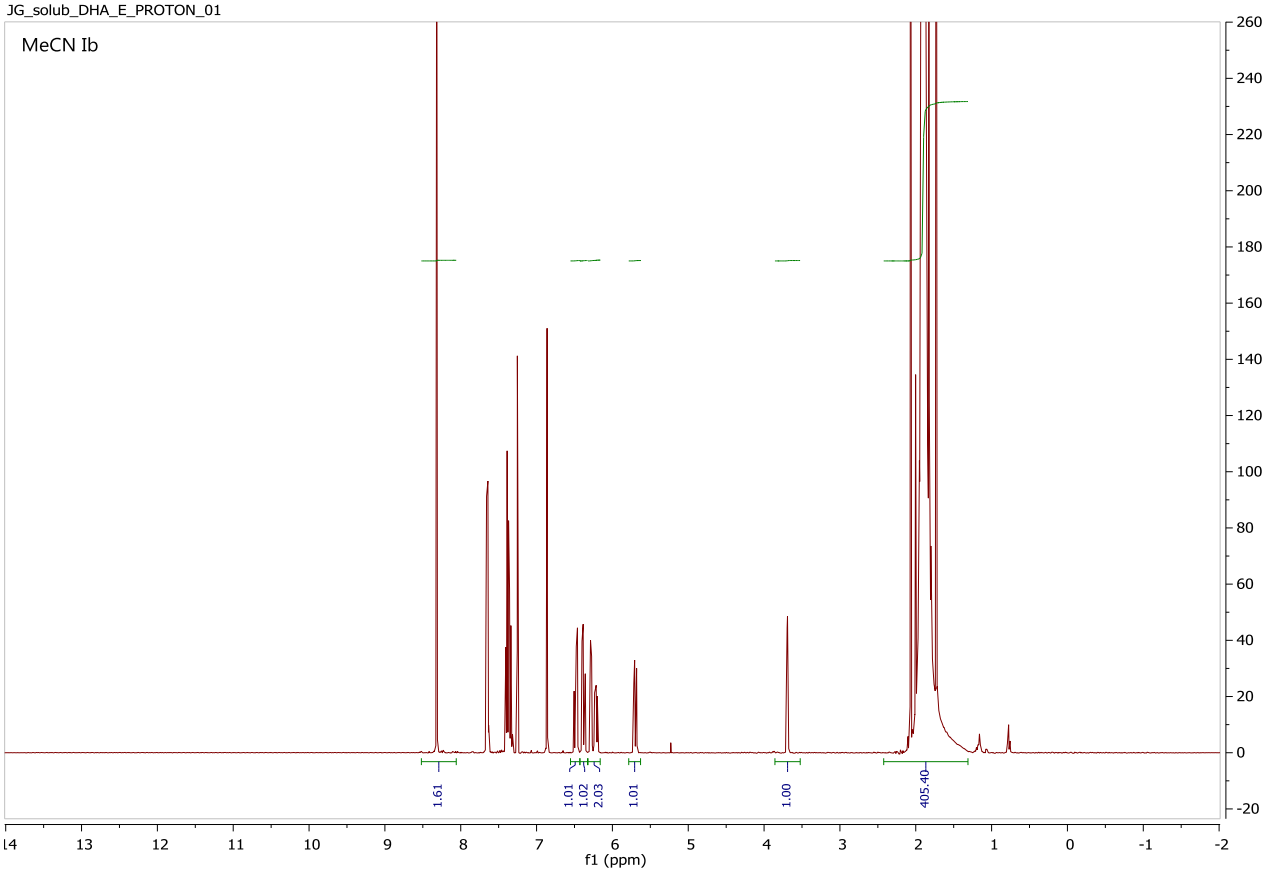

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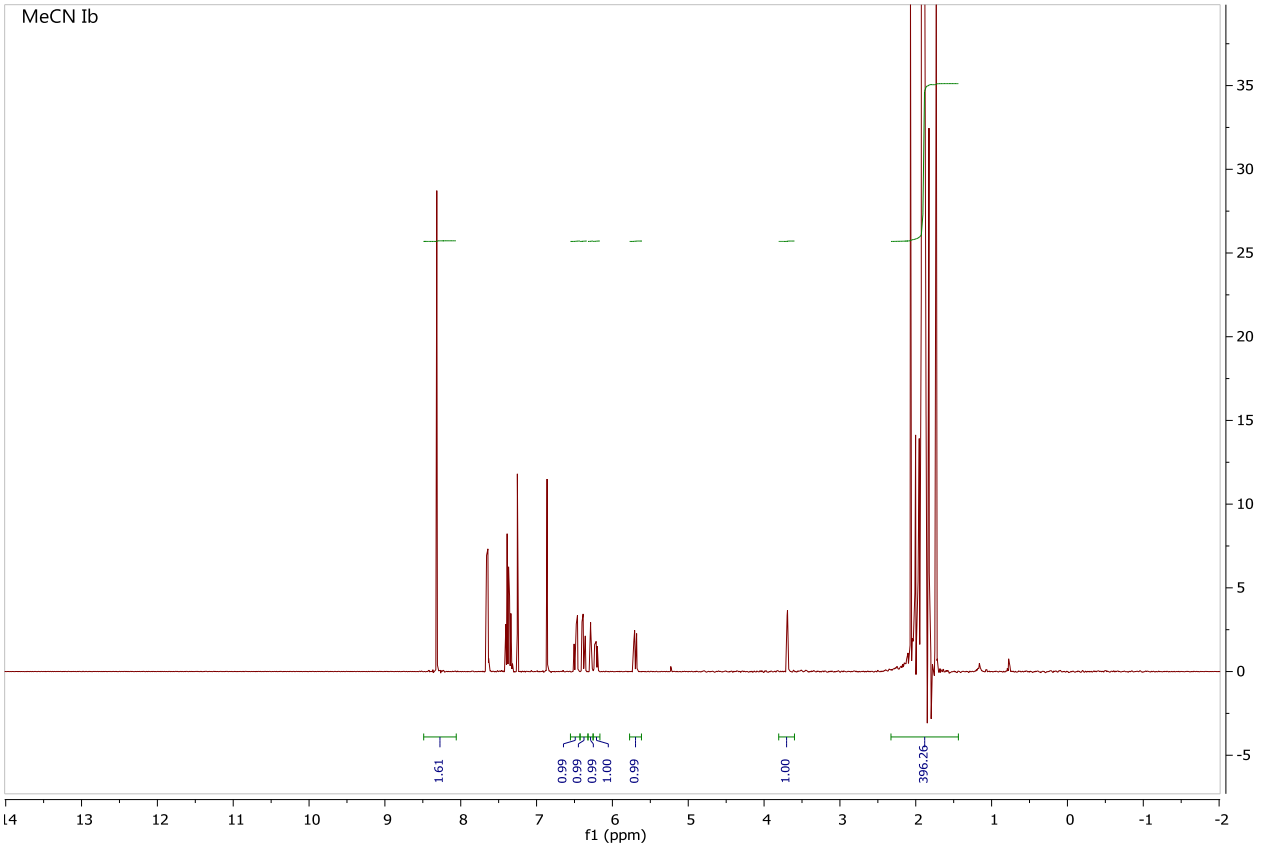

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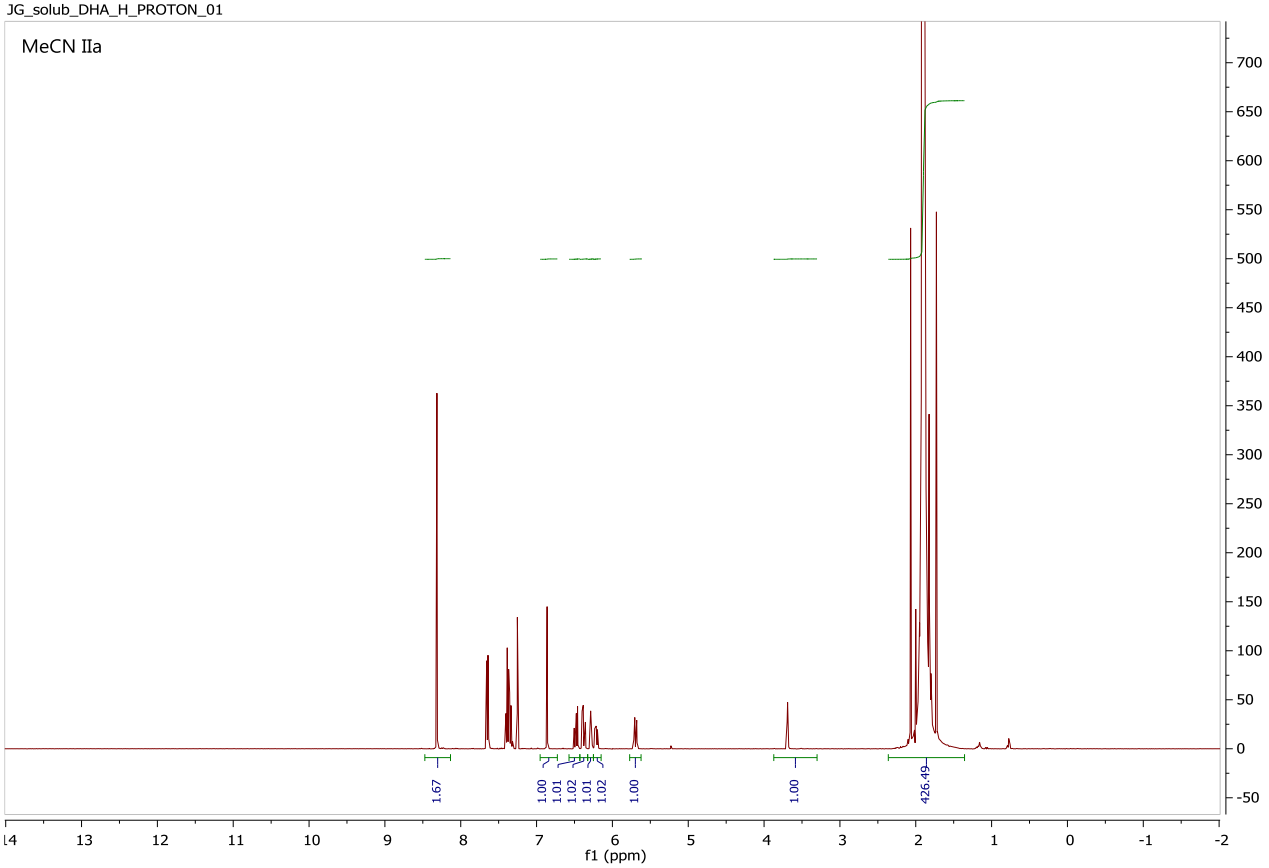

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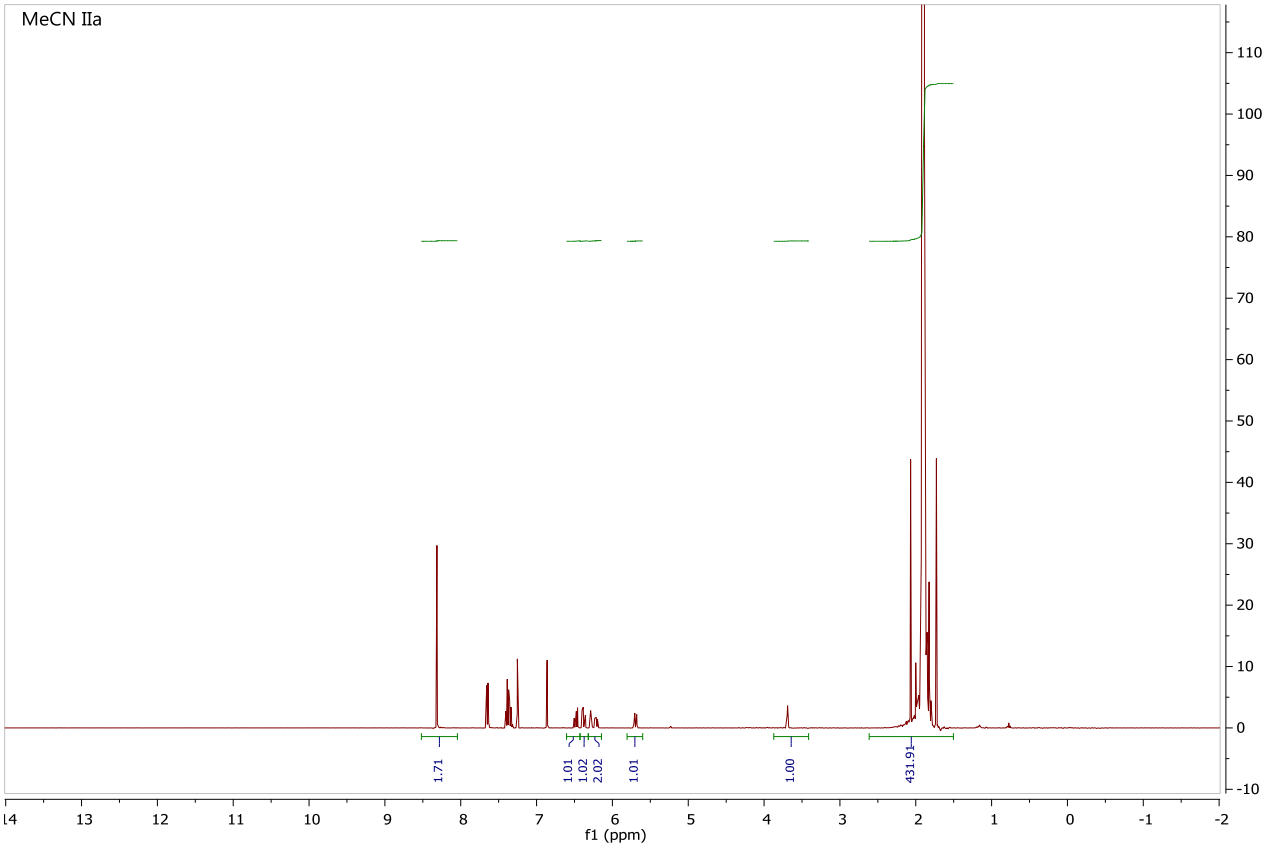

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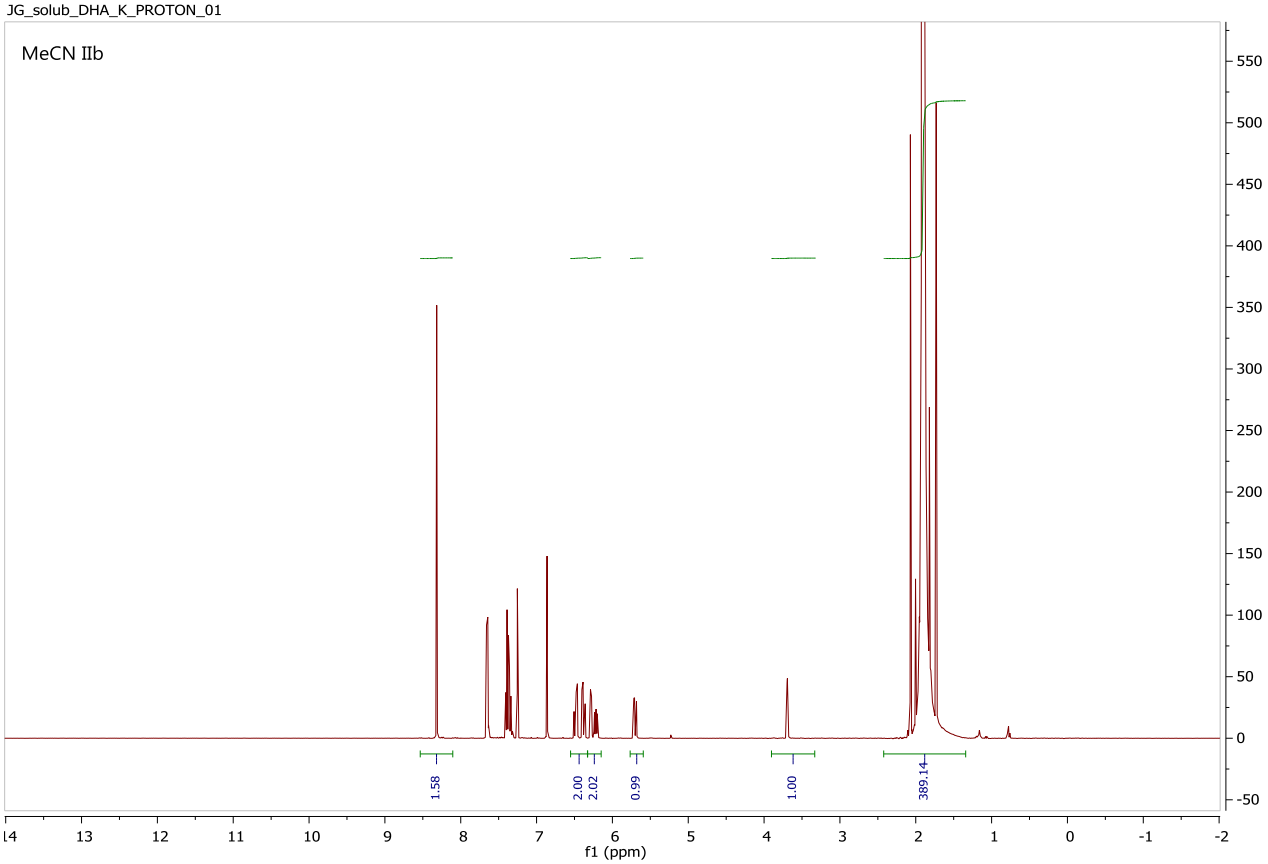

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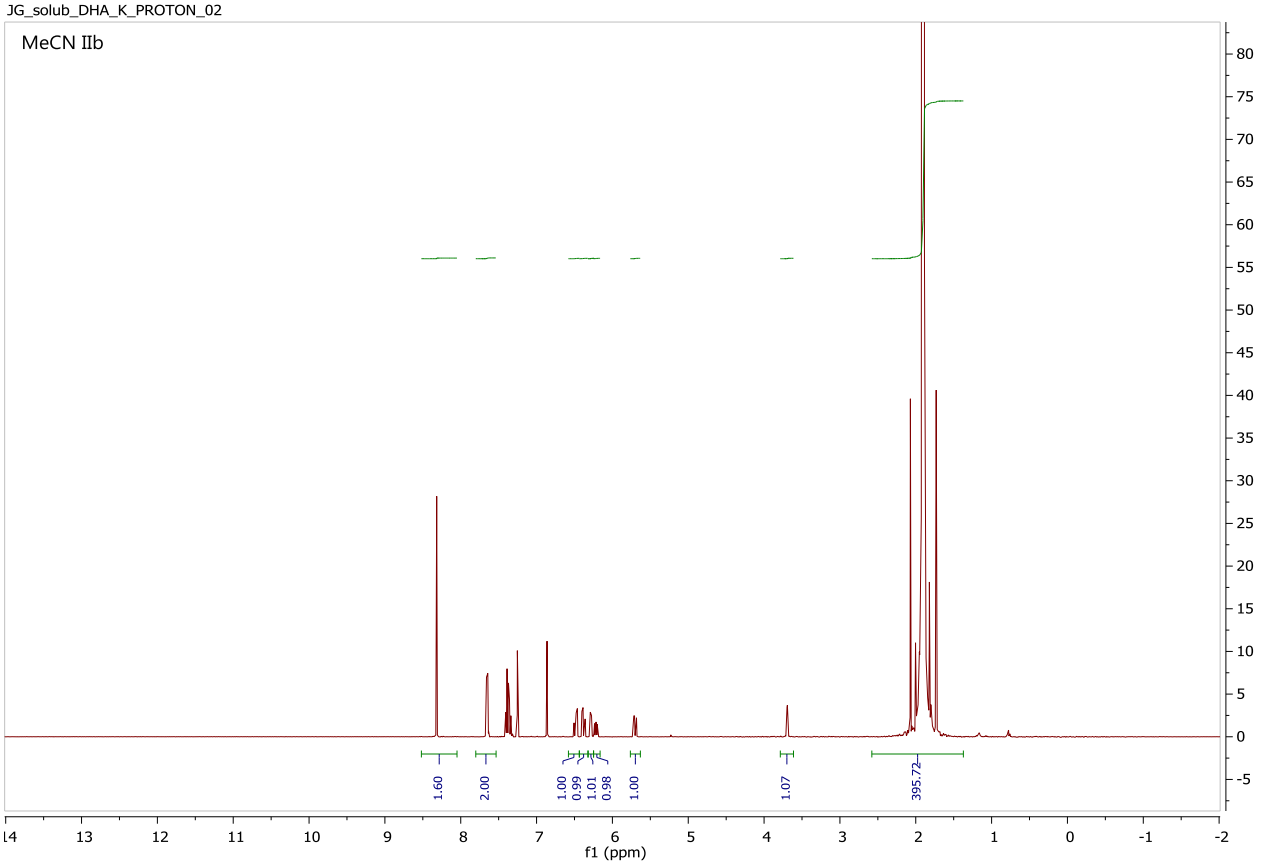

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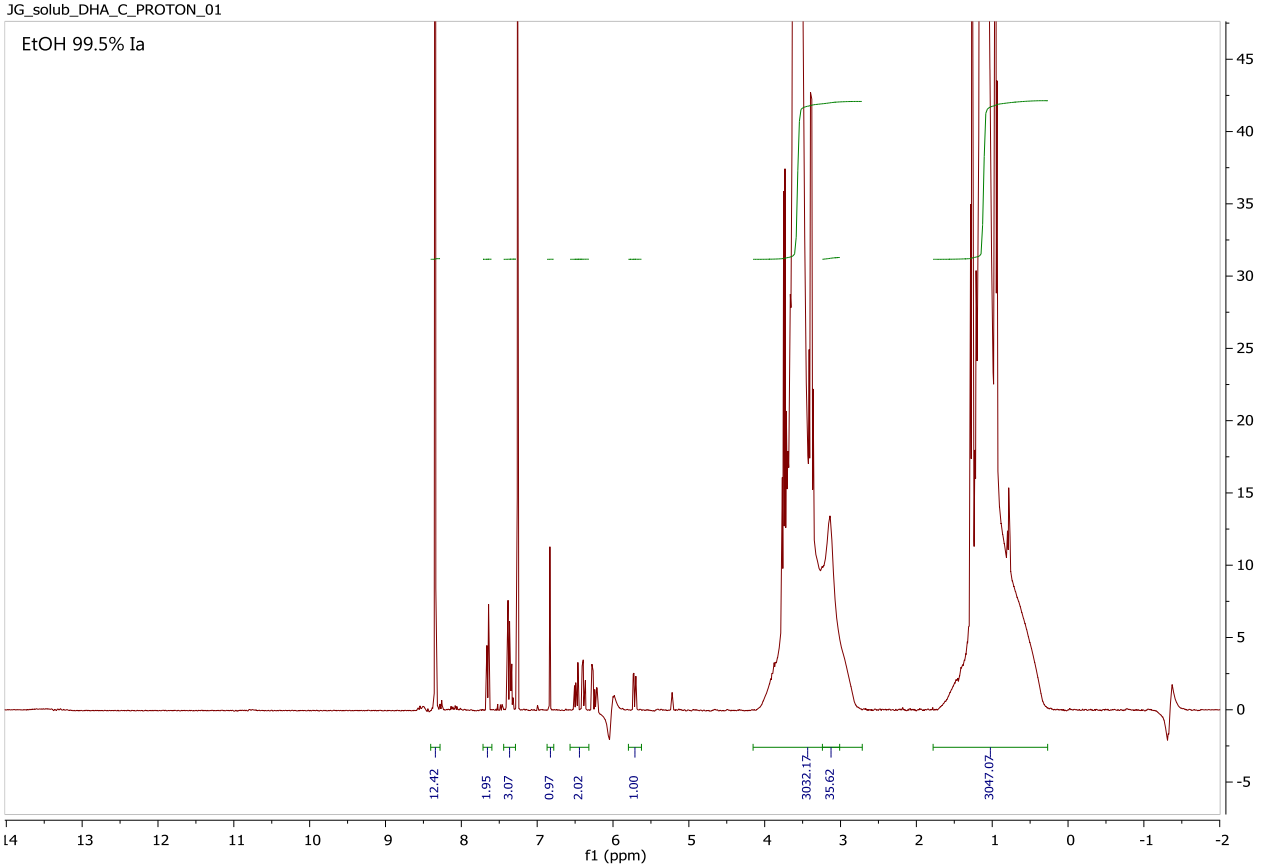

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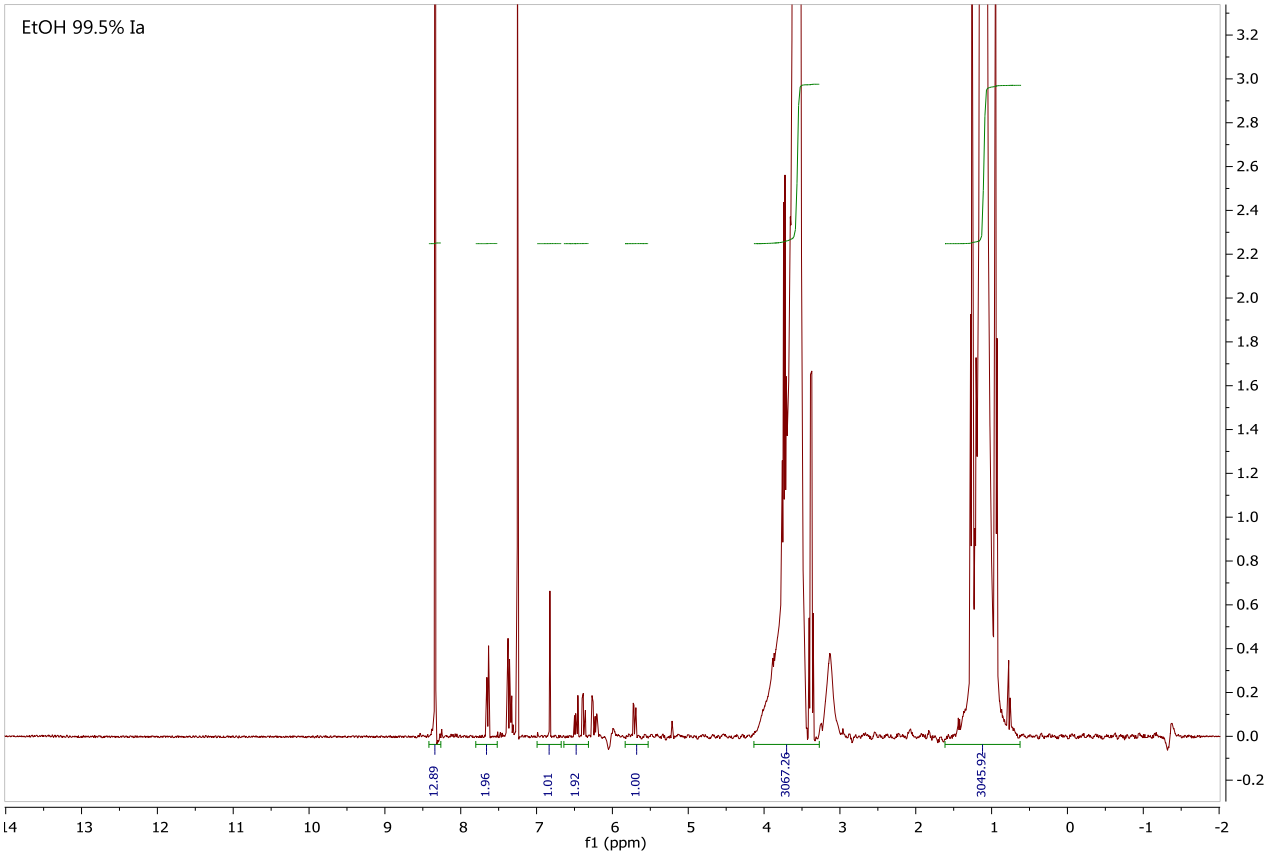

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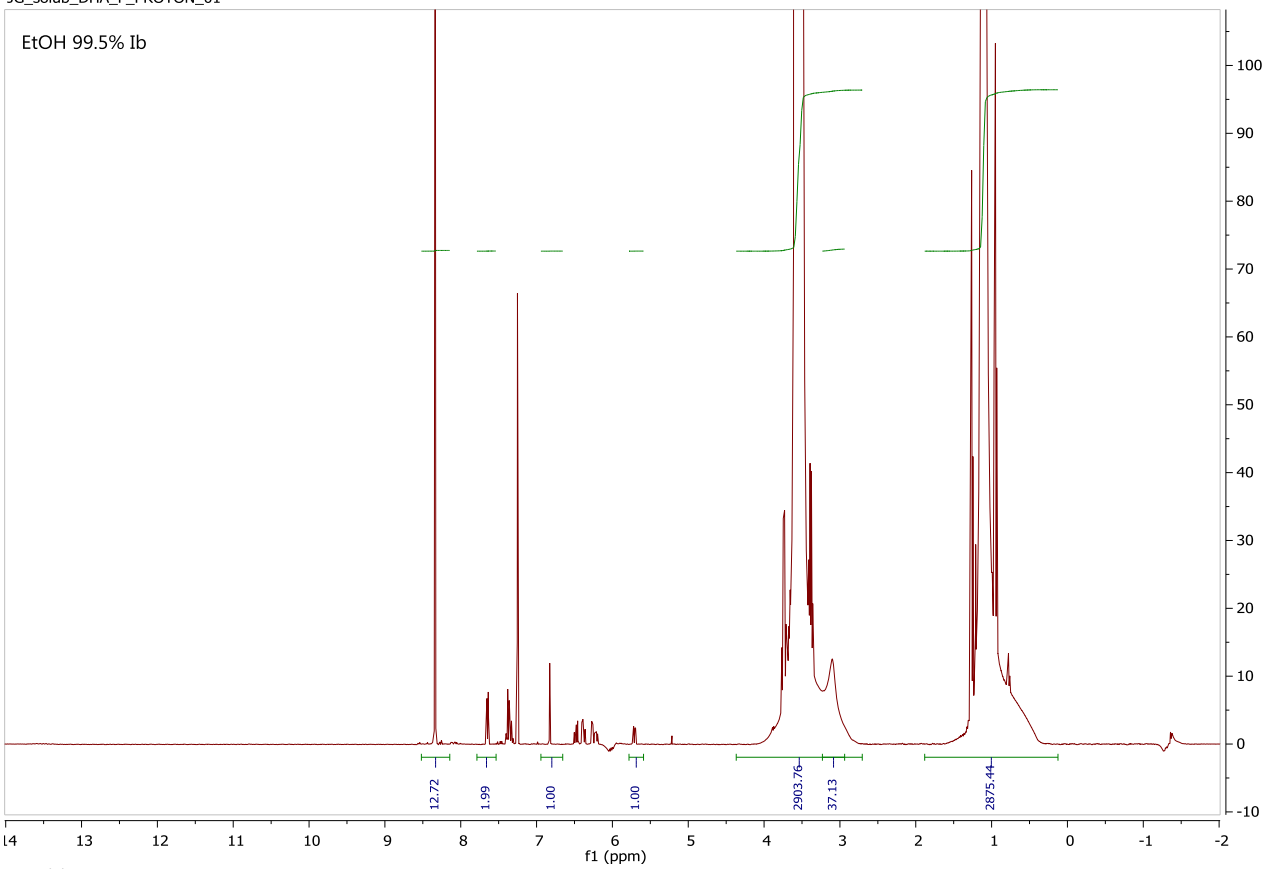

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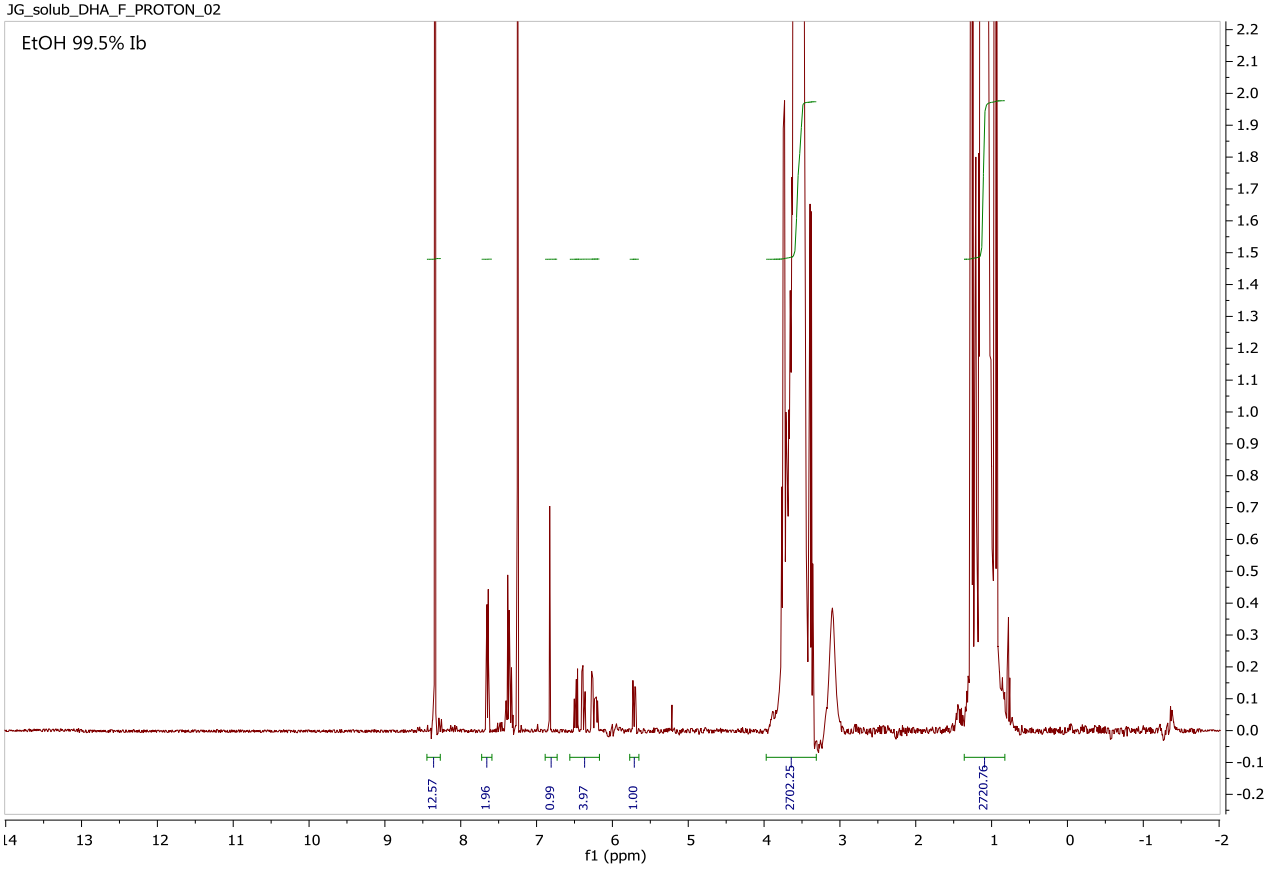

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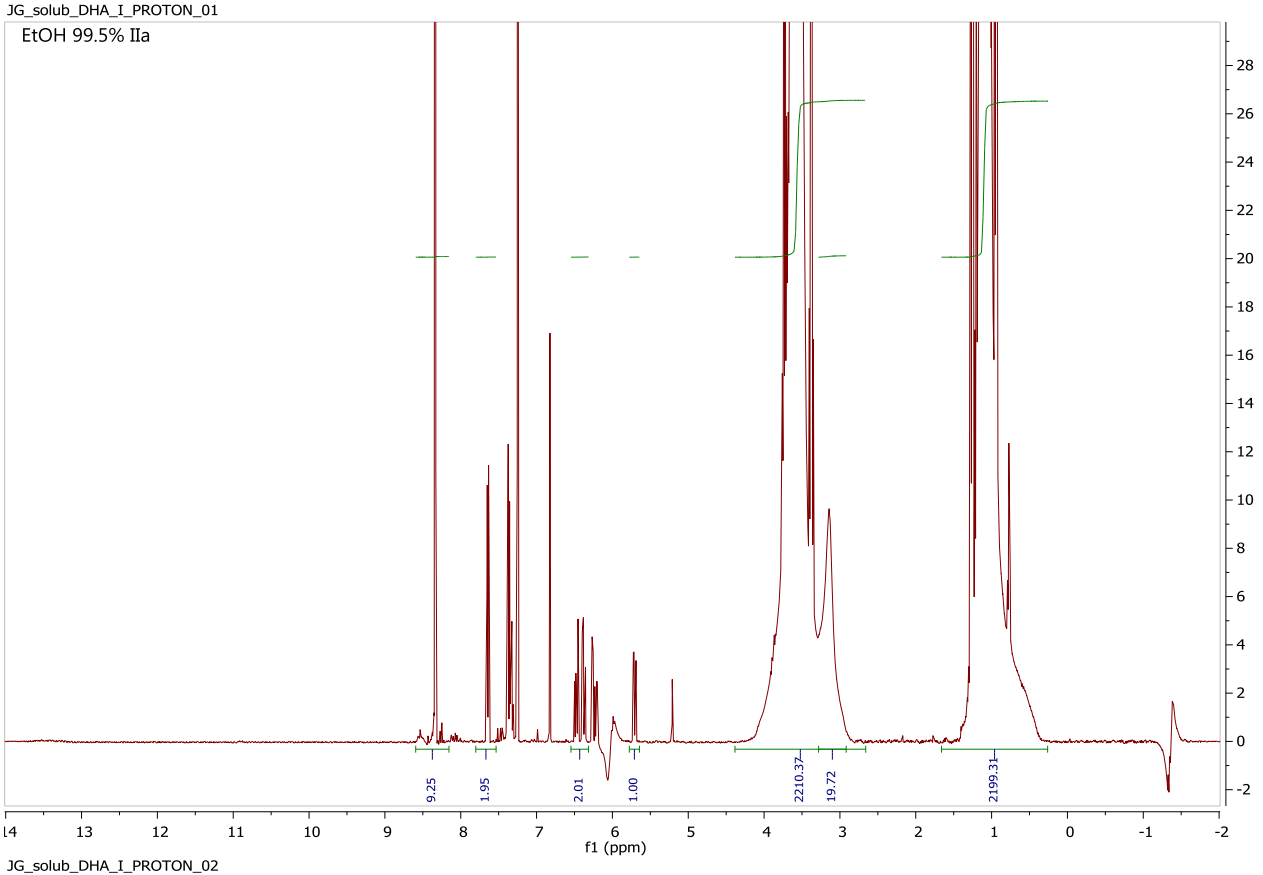

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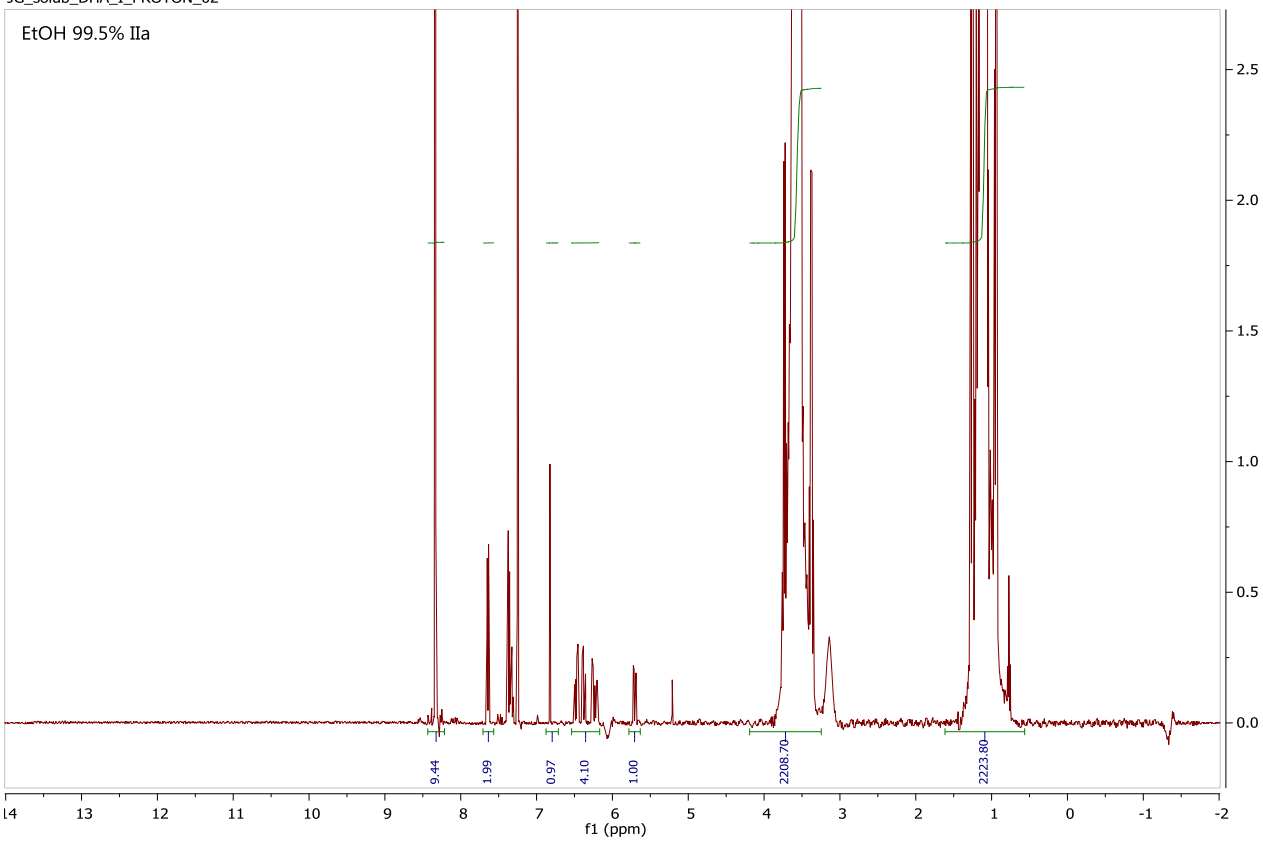

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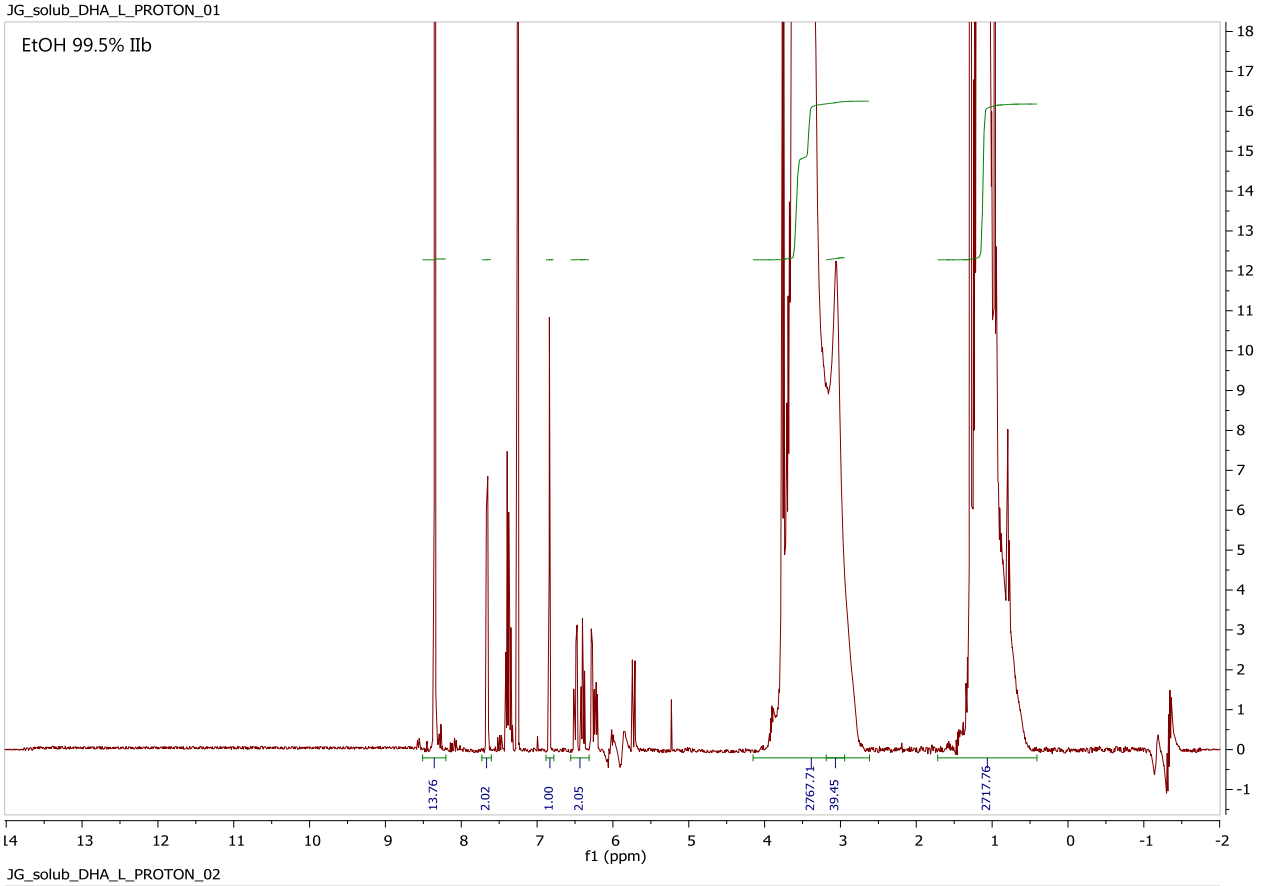

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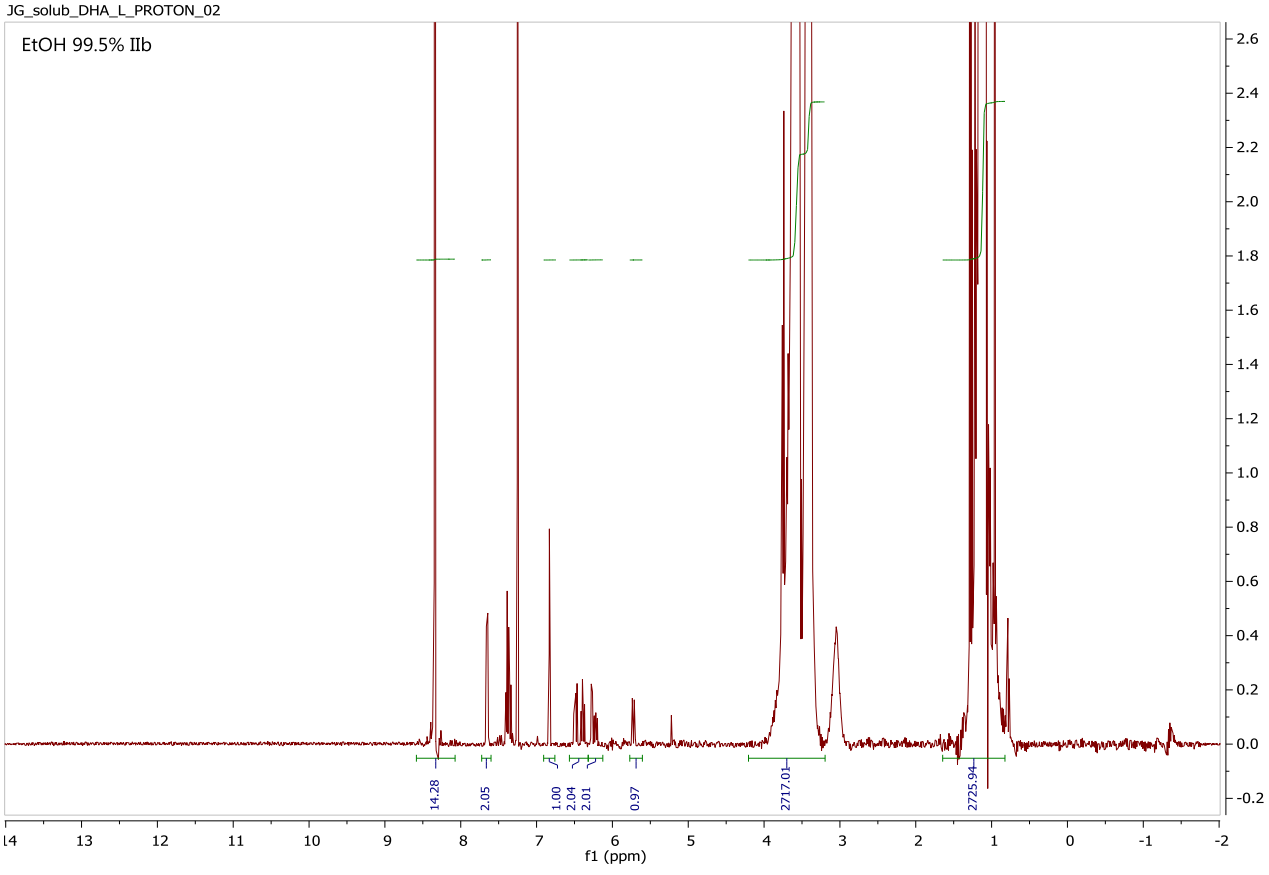

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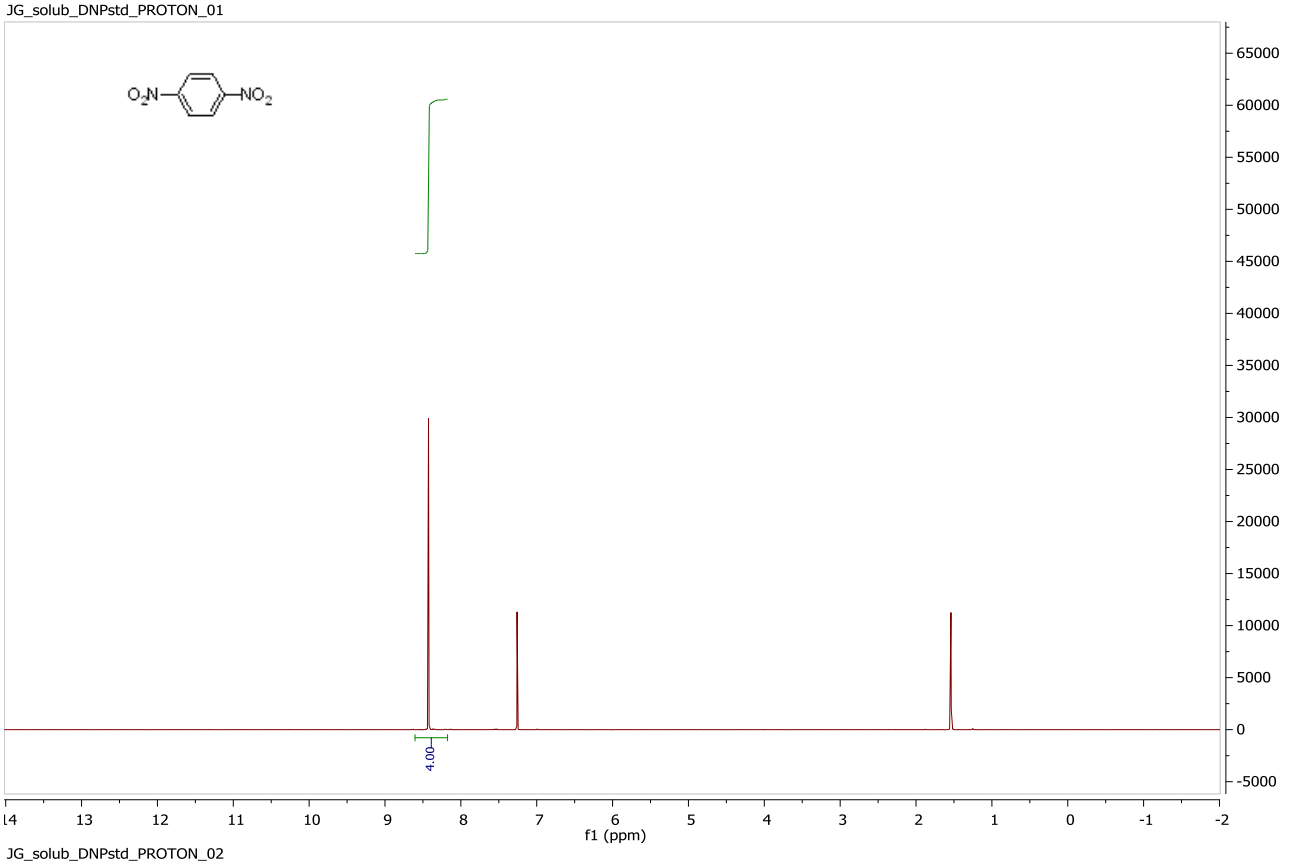

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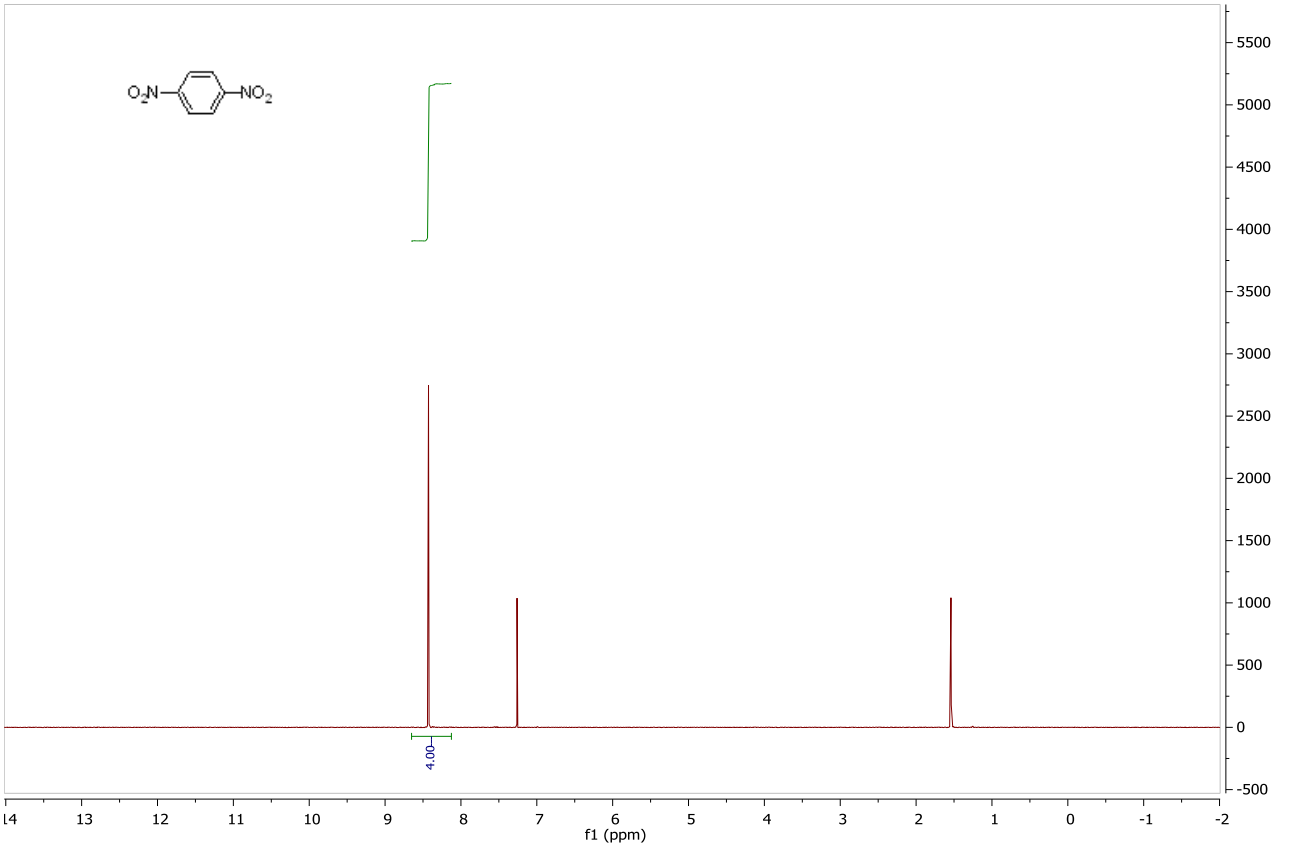

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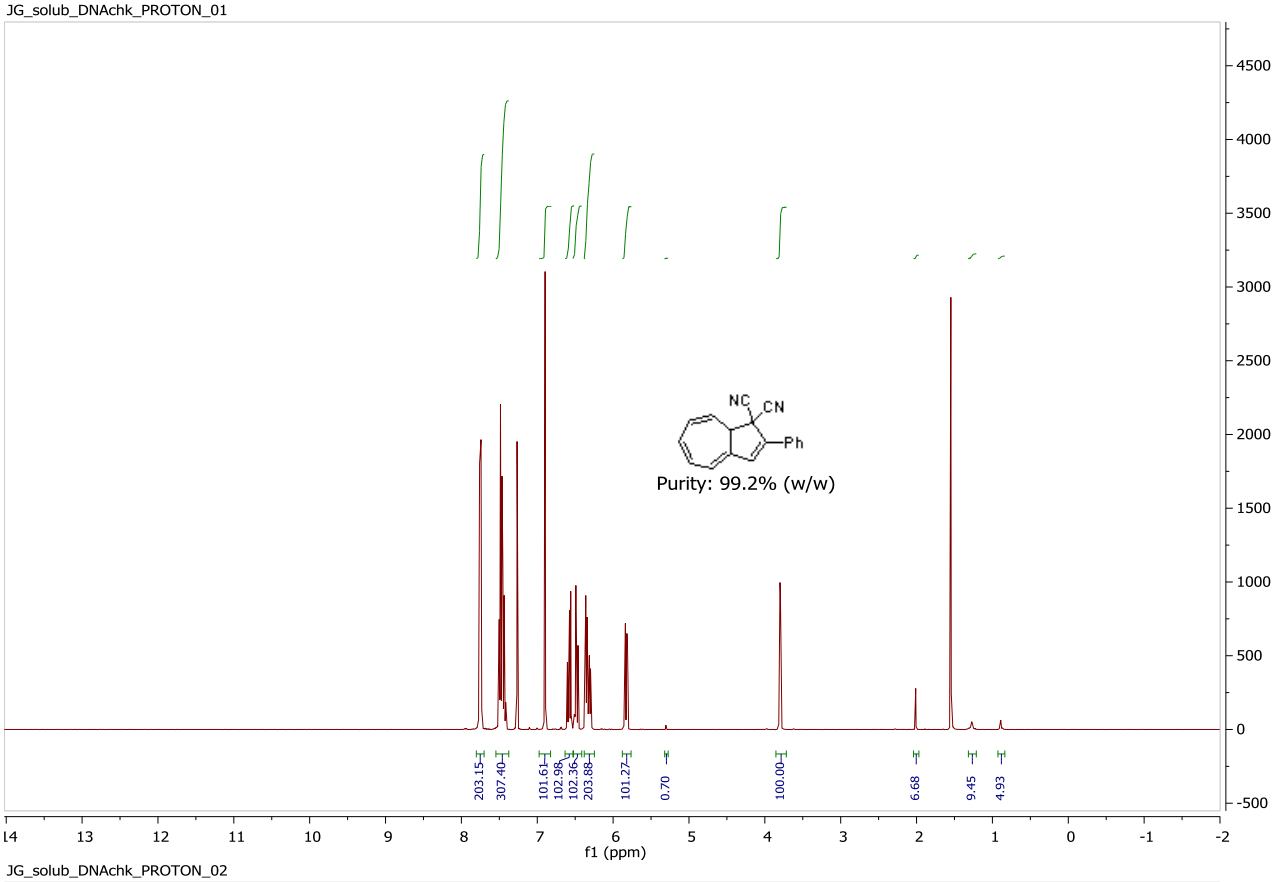

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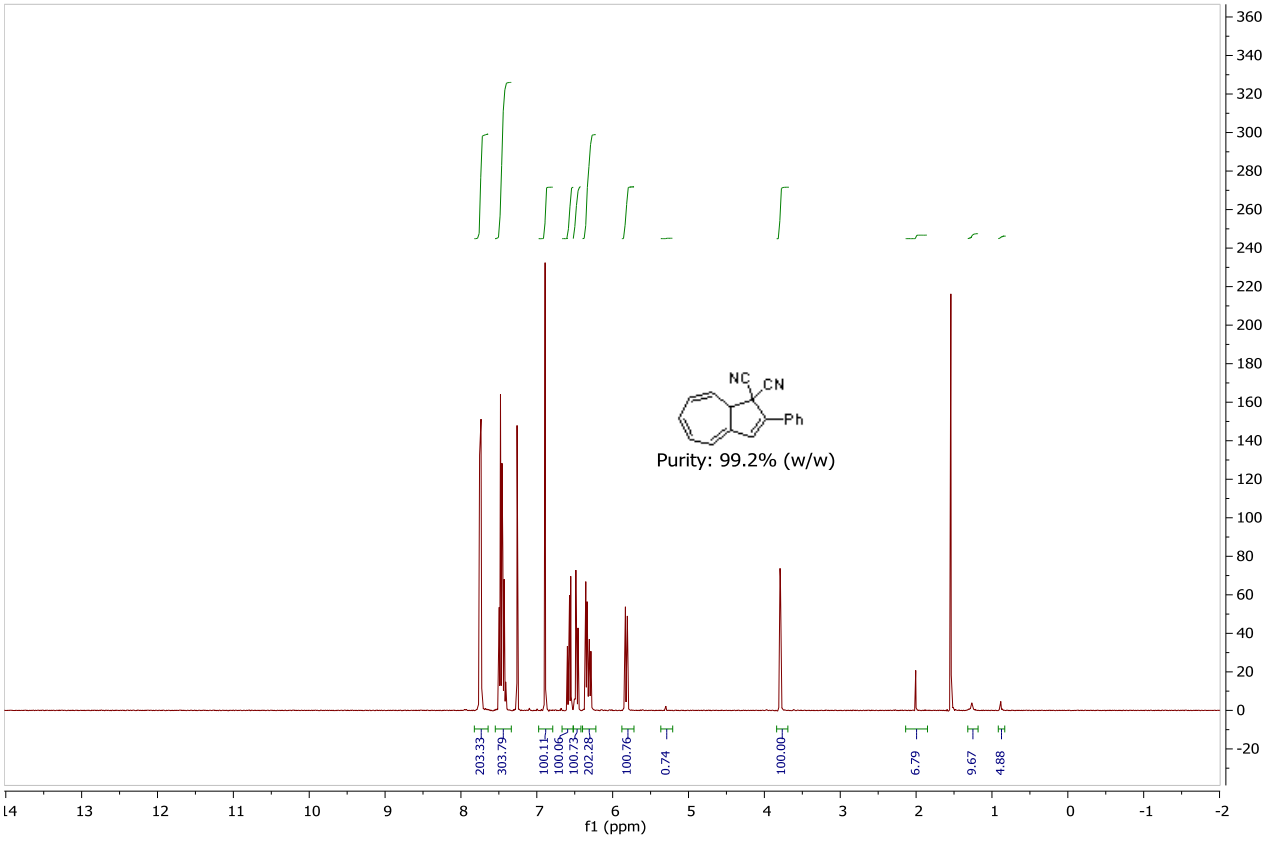

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[1] M. Lin, M. Tesconi, M. Tischler, *Int. J. Pharm.* **2009**, *369*, 47-52.

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[3] a) G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179; b) H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512-7515.

[4] C. Szantay, *Trends Anal. Chem.* **1992**, *11*, 332-344.