

Supporting Information

A Cascade Process for the Synthesis of *ortho*-Formyl Allyl Aryl Ethers and 2*H*-Chromen-2-ol Derivatives from Arynes *via* Trapping of *o*-Quinone Methide with Activated Alkene

Abhilash Sharma^{a,b} and Pranjal Gogoi^{a,b*}

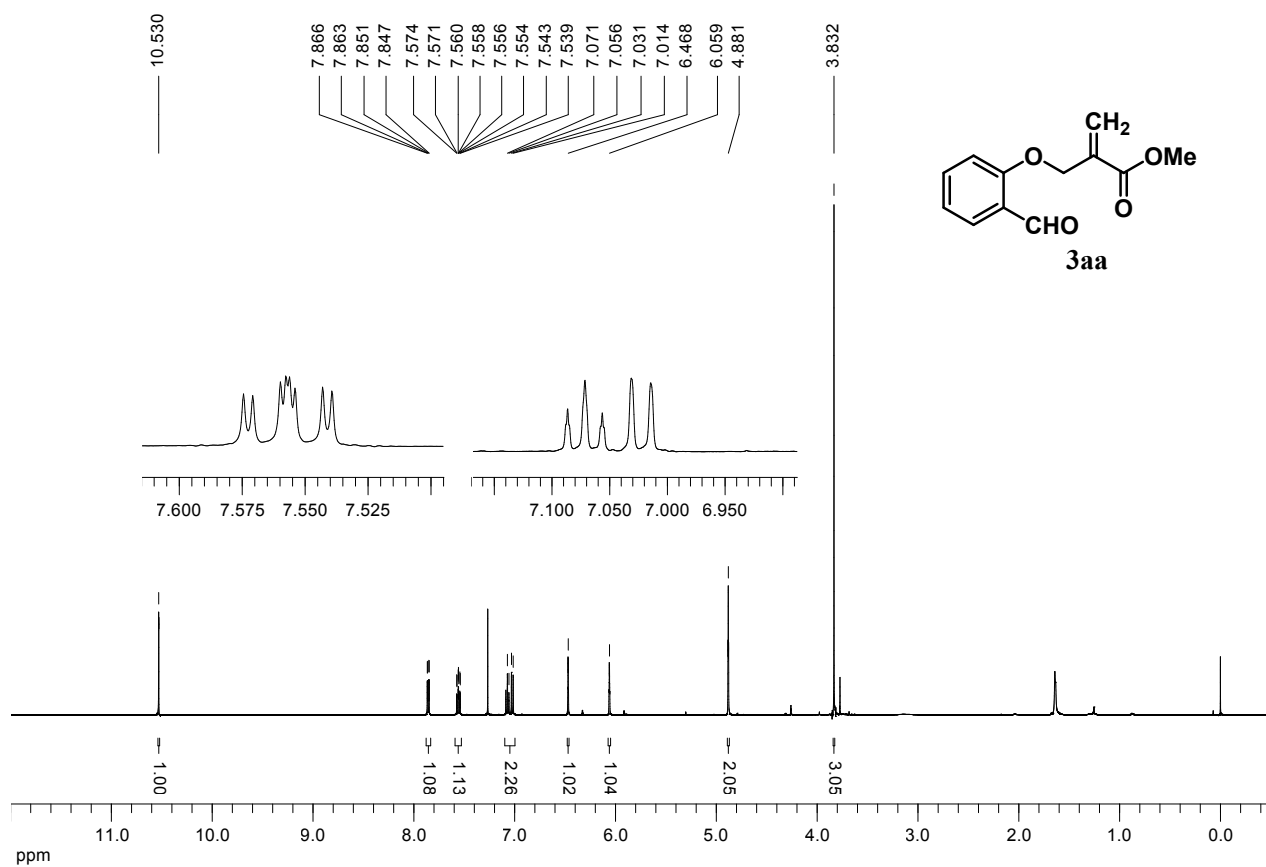
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^b*Academy of Scientific and Innovative Research (AcSIR), CSIR-NEIST Campus, India*

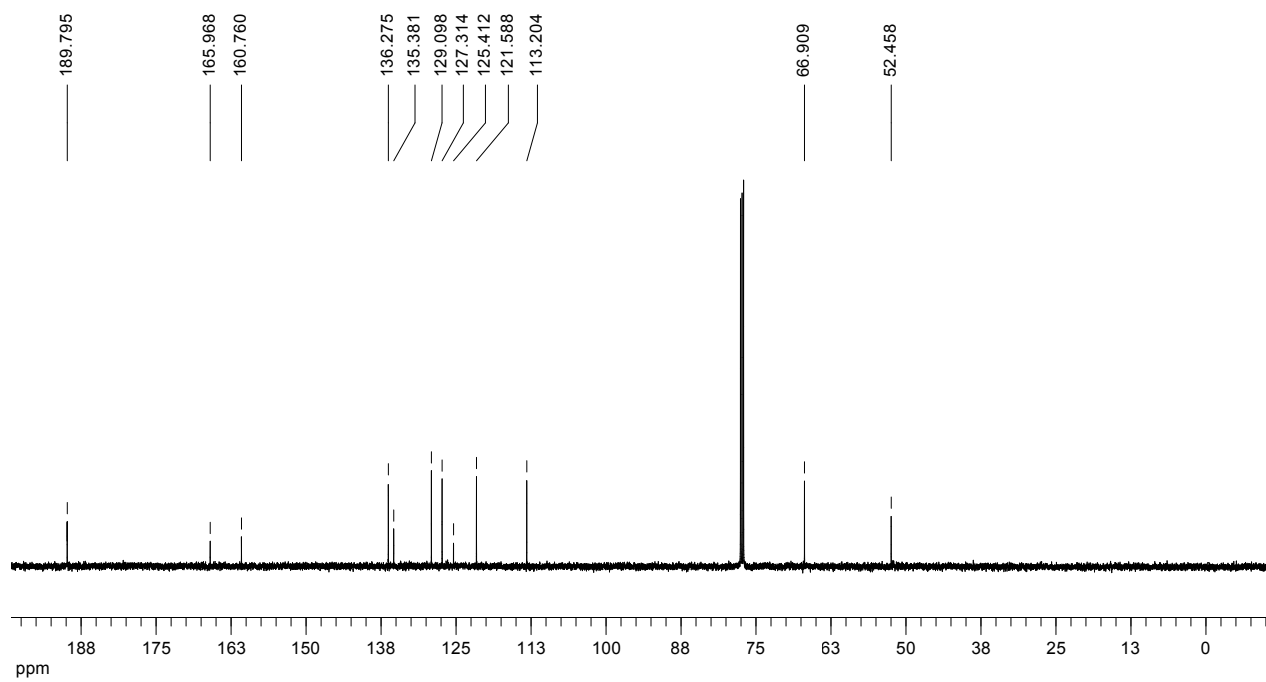
Email: gogoipranj@yahoo.co.uk; gogoipranj@gmail.com

Copies of ¹H, ¹³C NMR and HRMS spectra

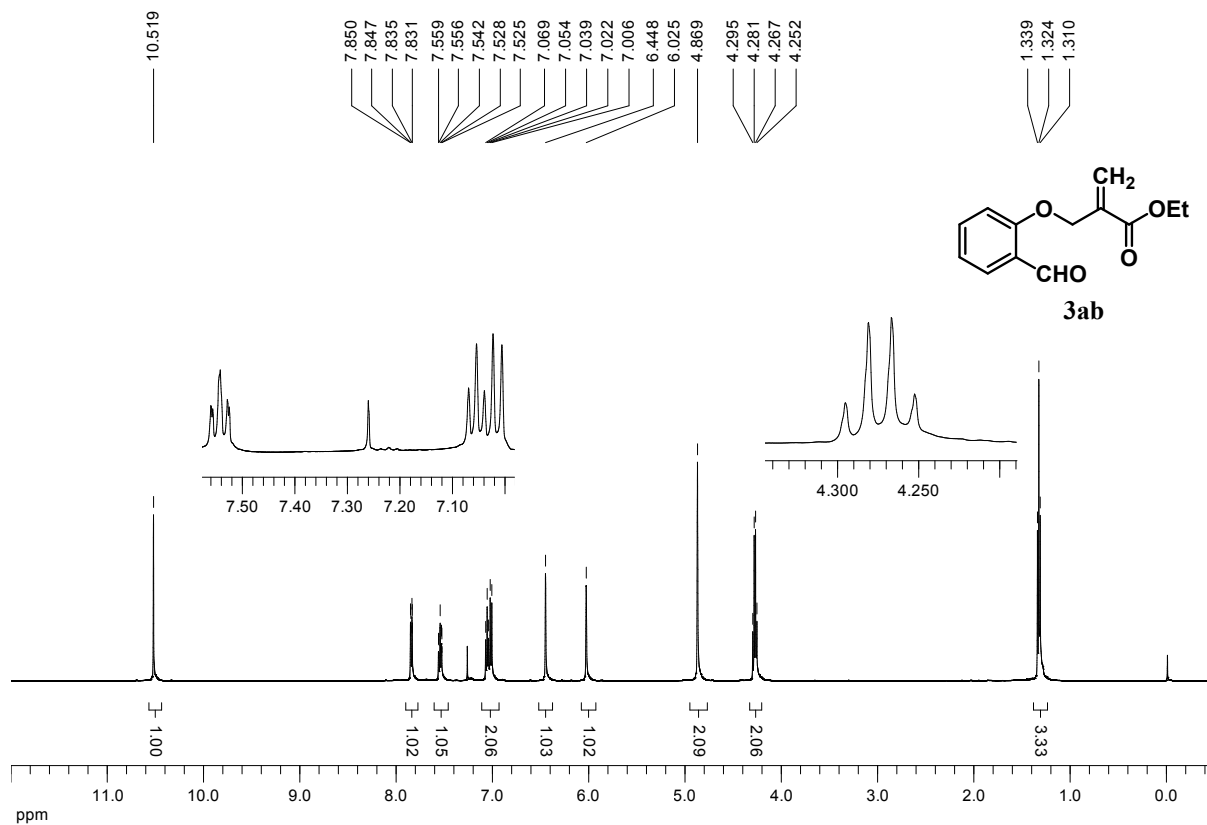
¹H-NMR (500 MHz, CDCl₃)



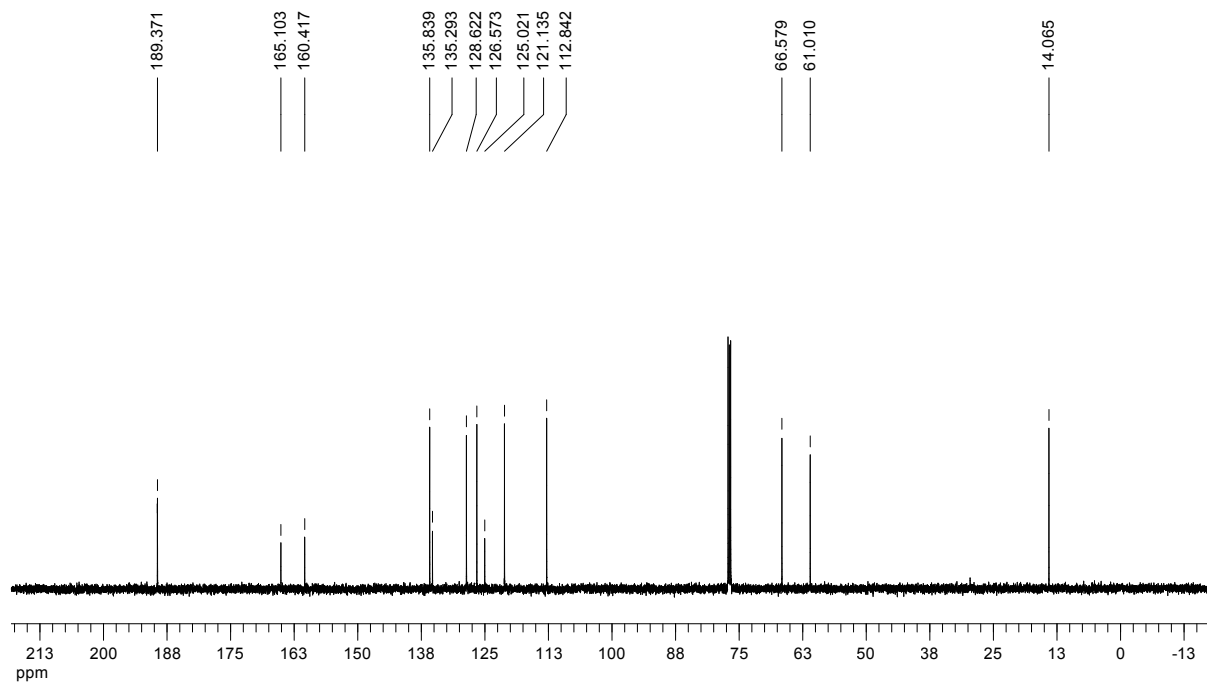
¹³C-NMR (126 MHz, CDCl₃)



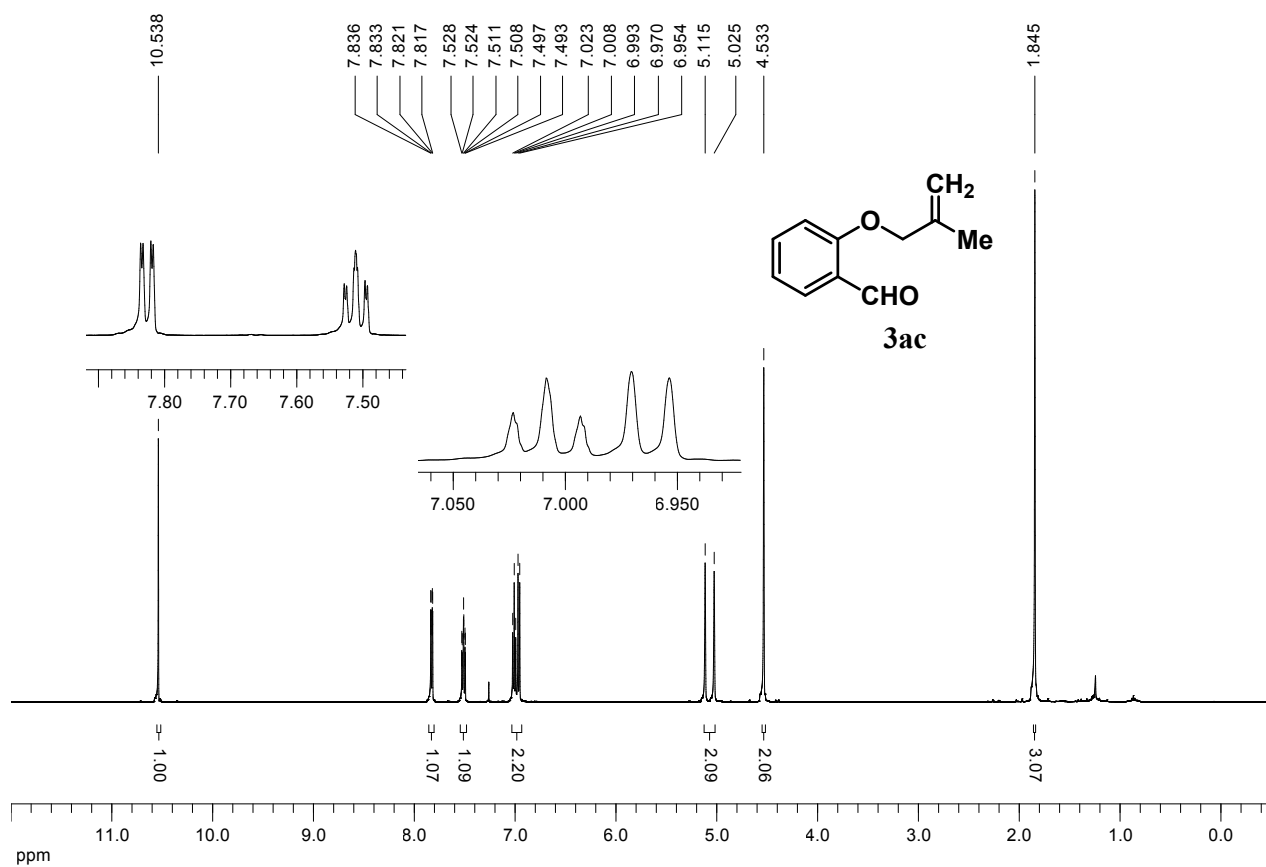
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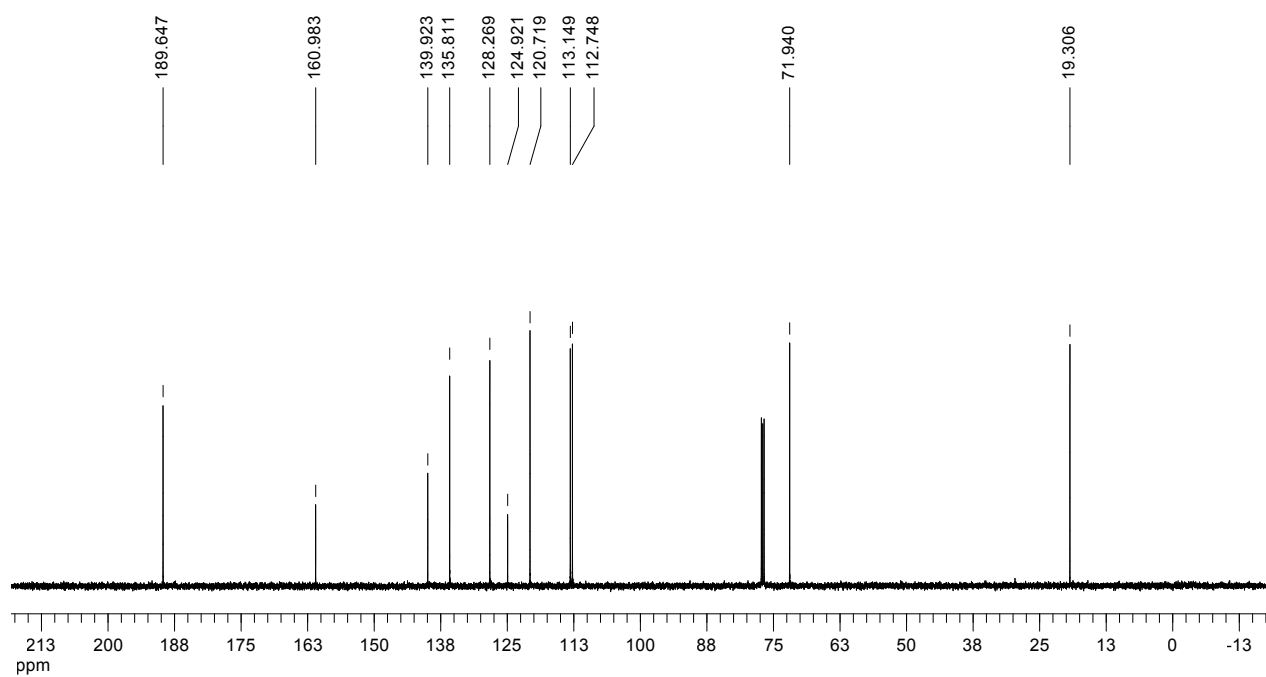
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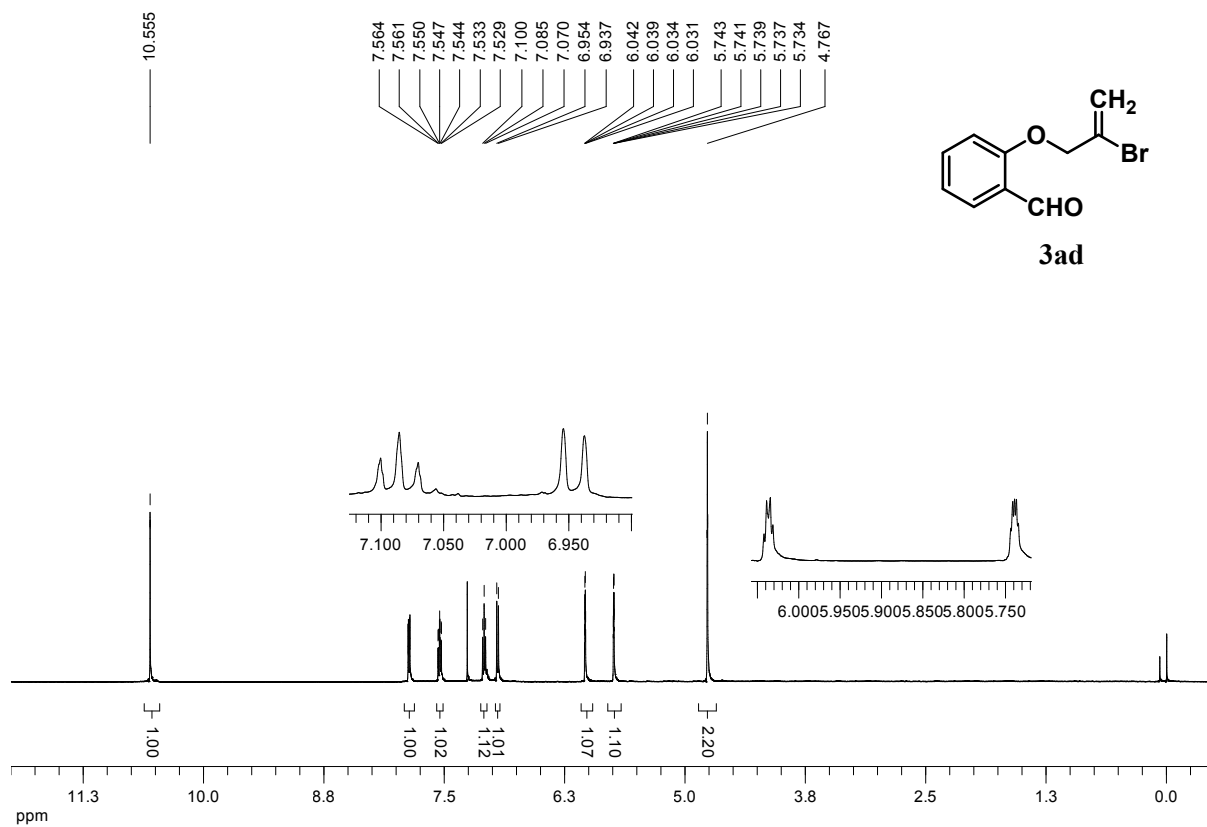
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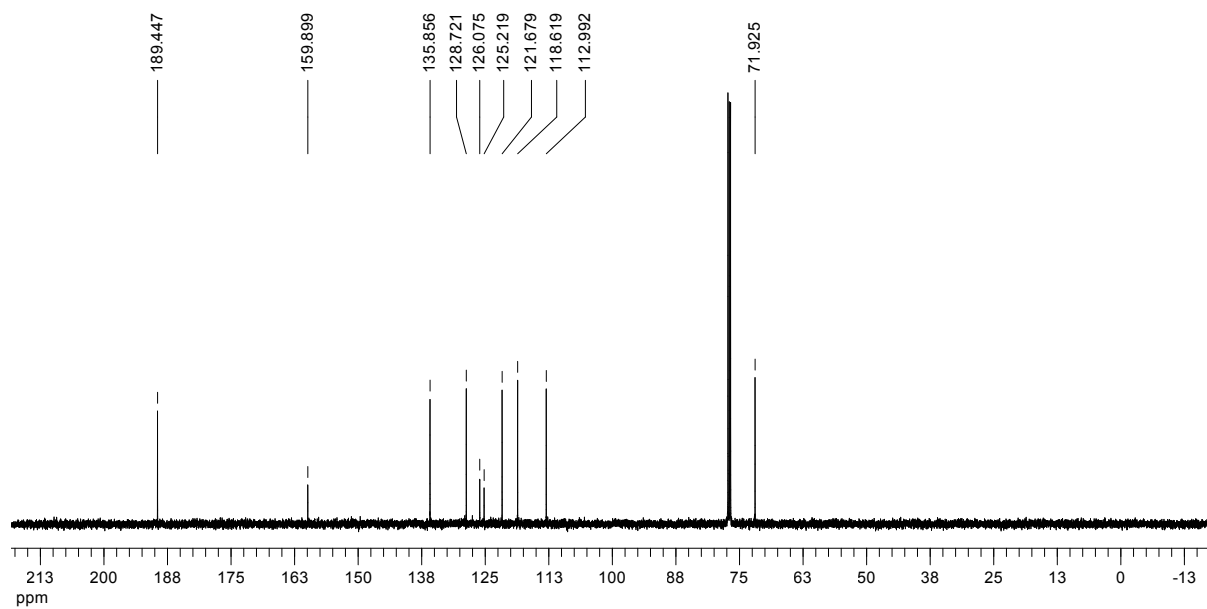
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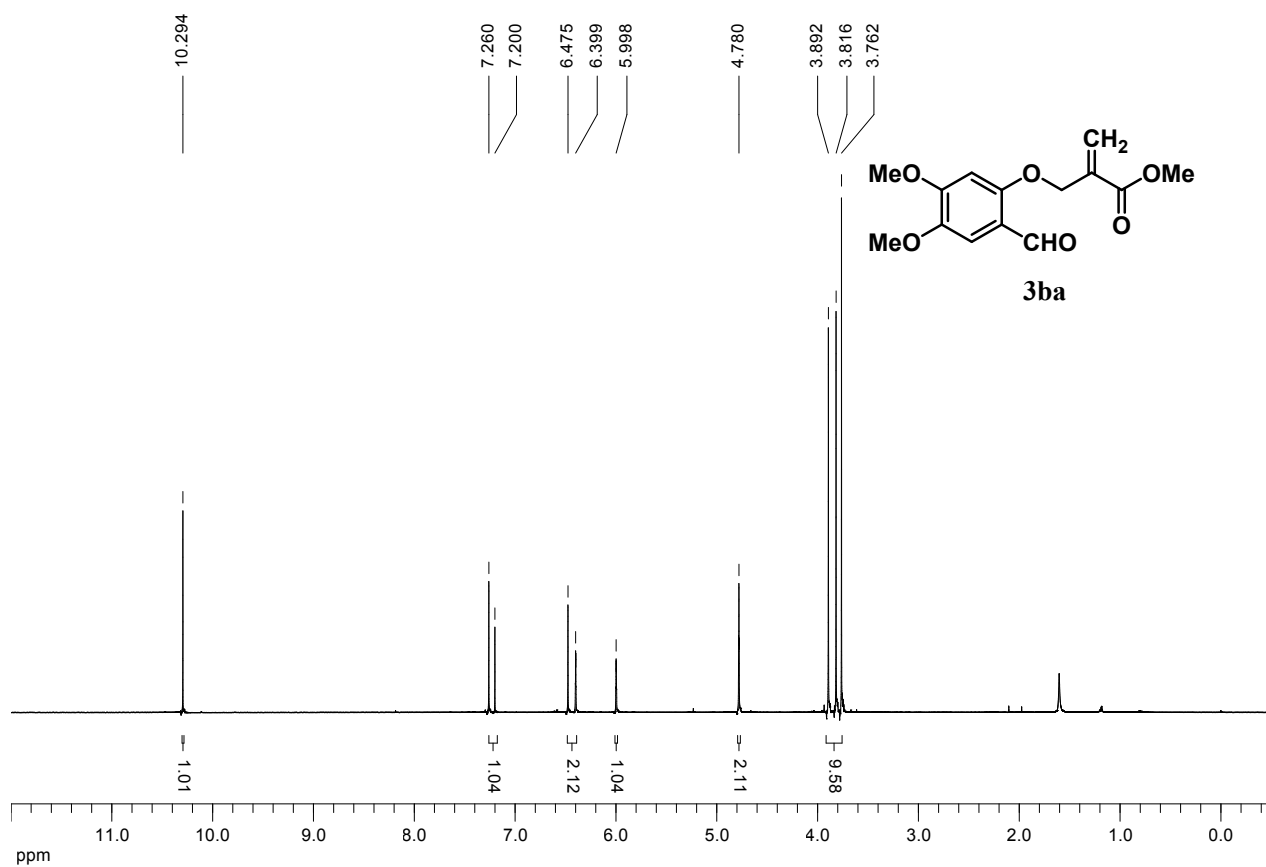
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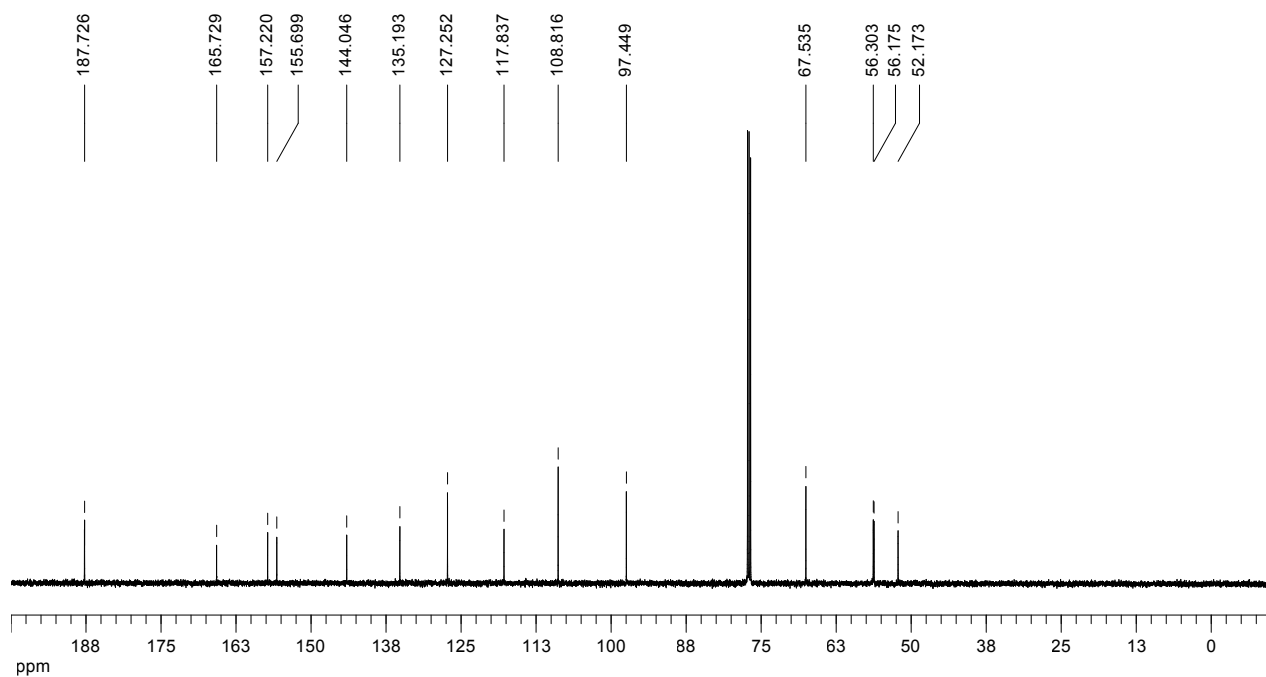
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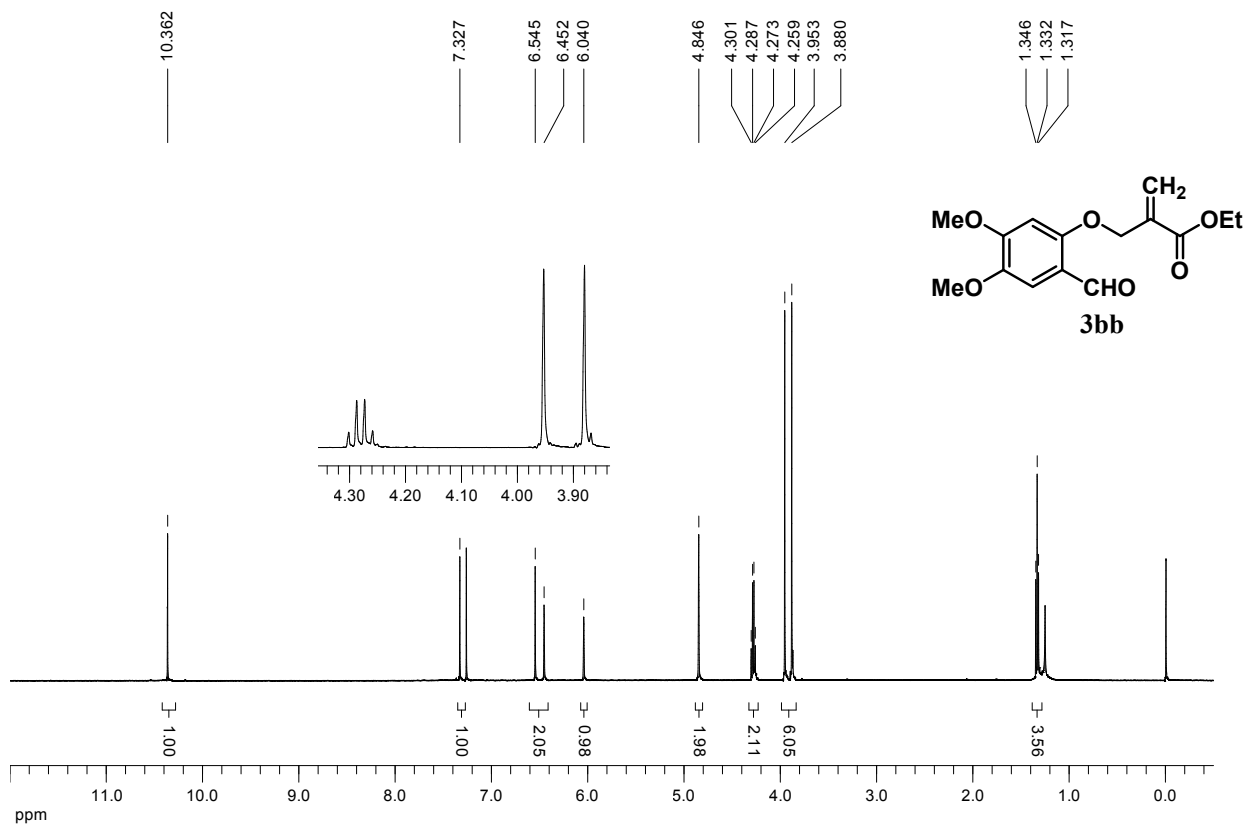
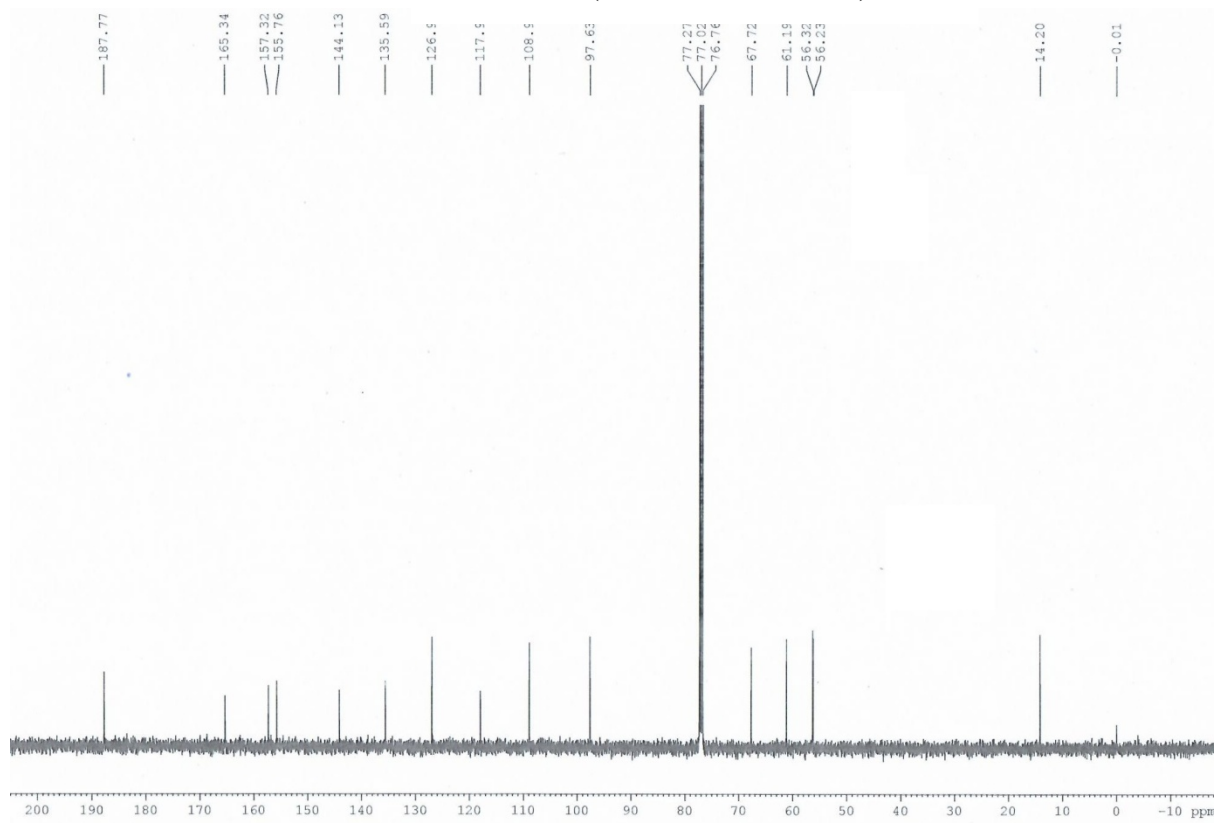


¹H-NMR (500 MHz, CDCl₃)

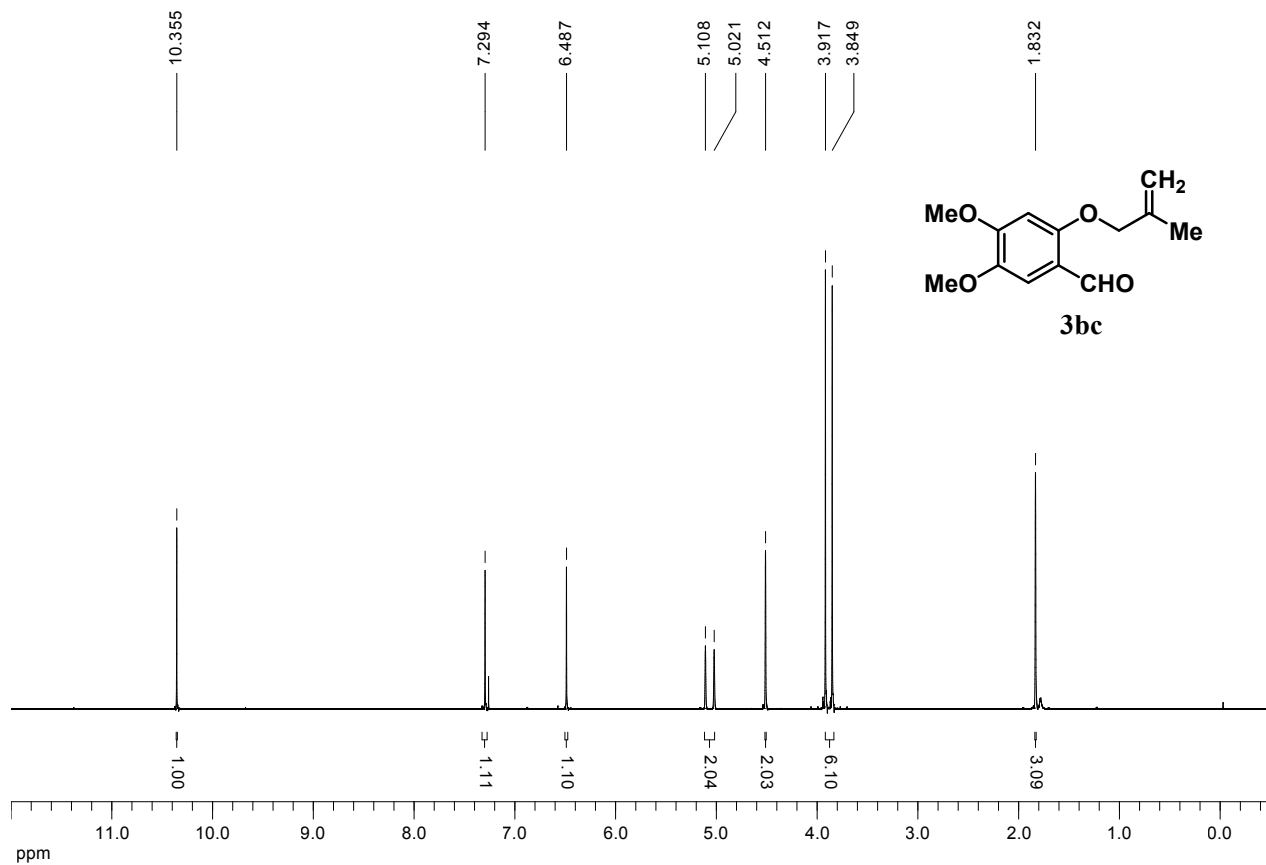


¹³C-NMR (126 MHz, CDCl₃)

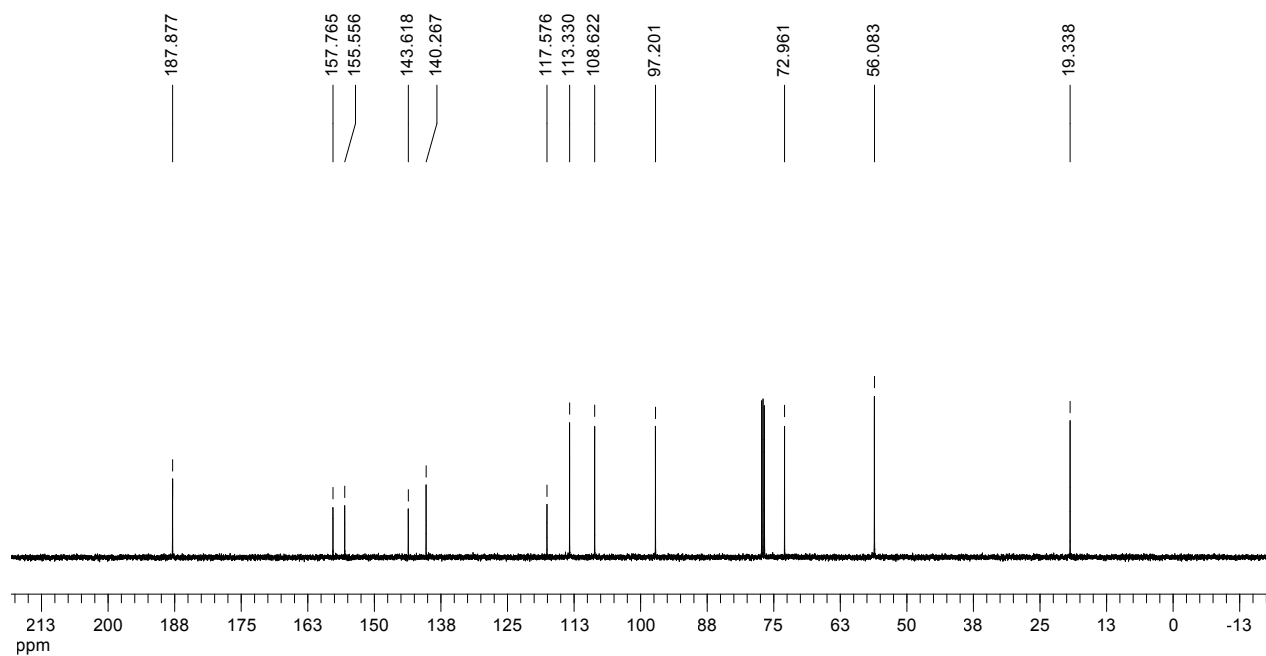


¹H-NMR (500 MHz, CDCl₃) ^{13}C -NMR (126 MHz, CDCl_3)

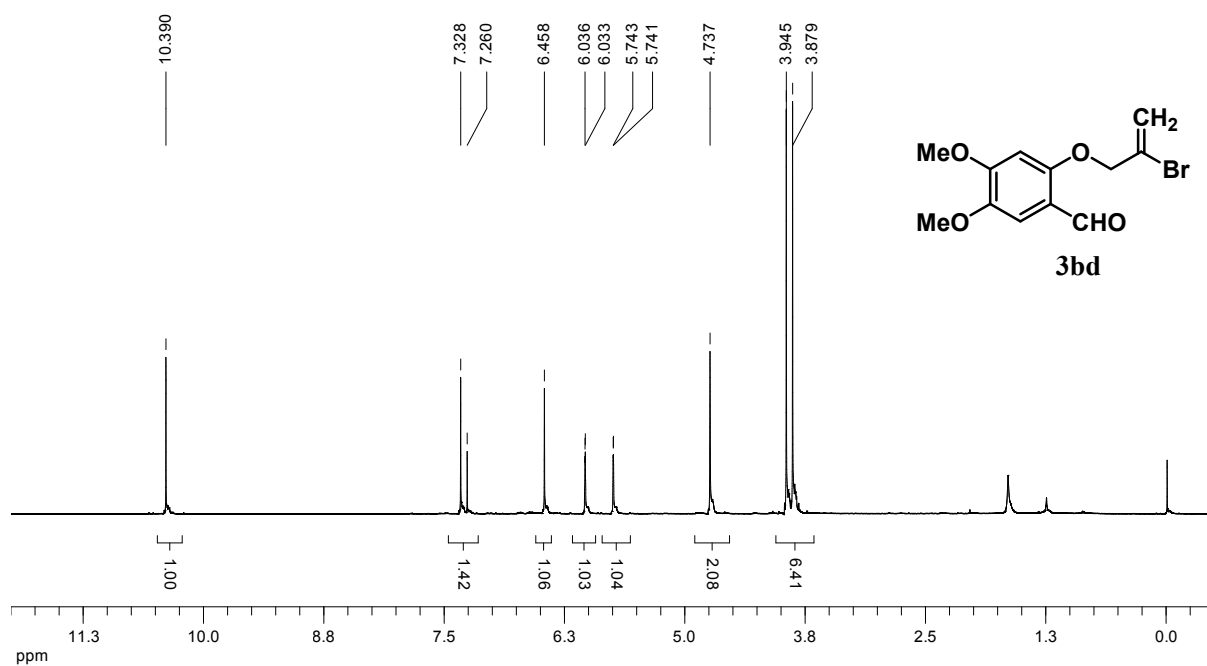
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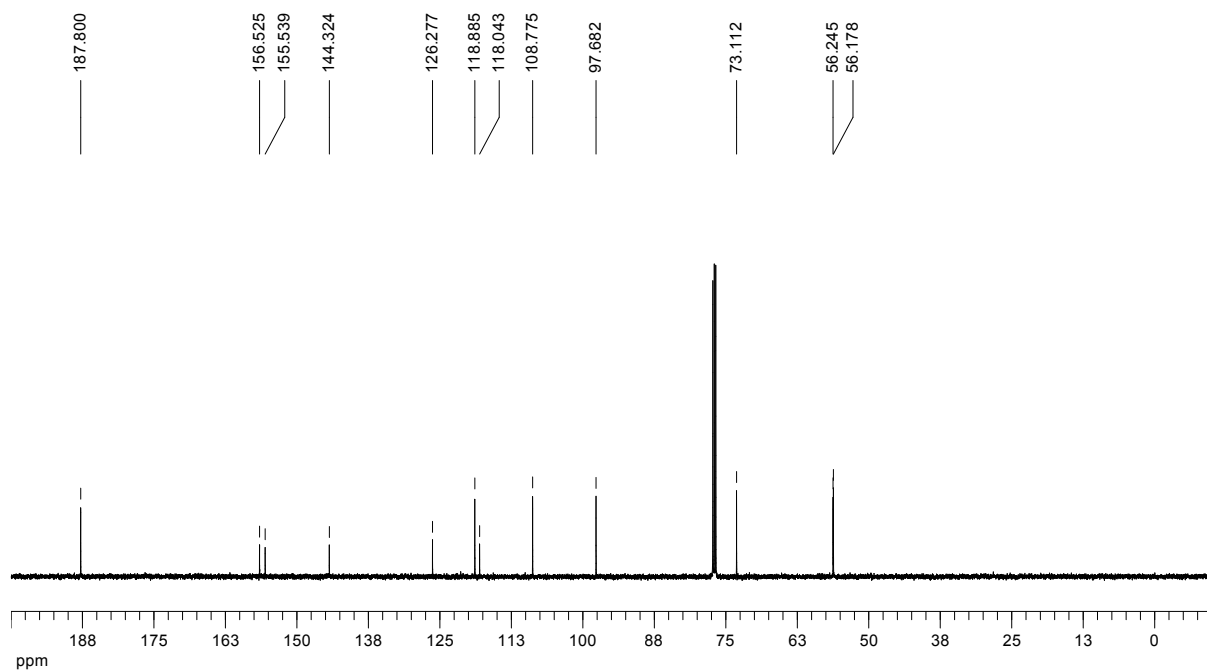
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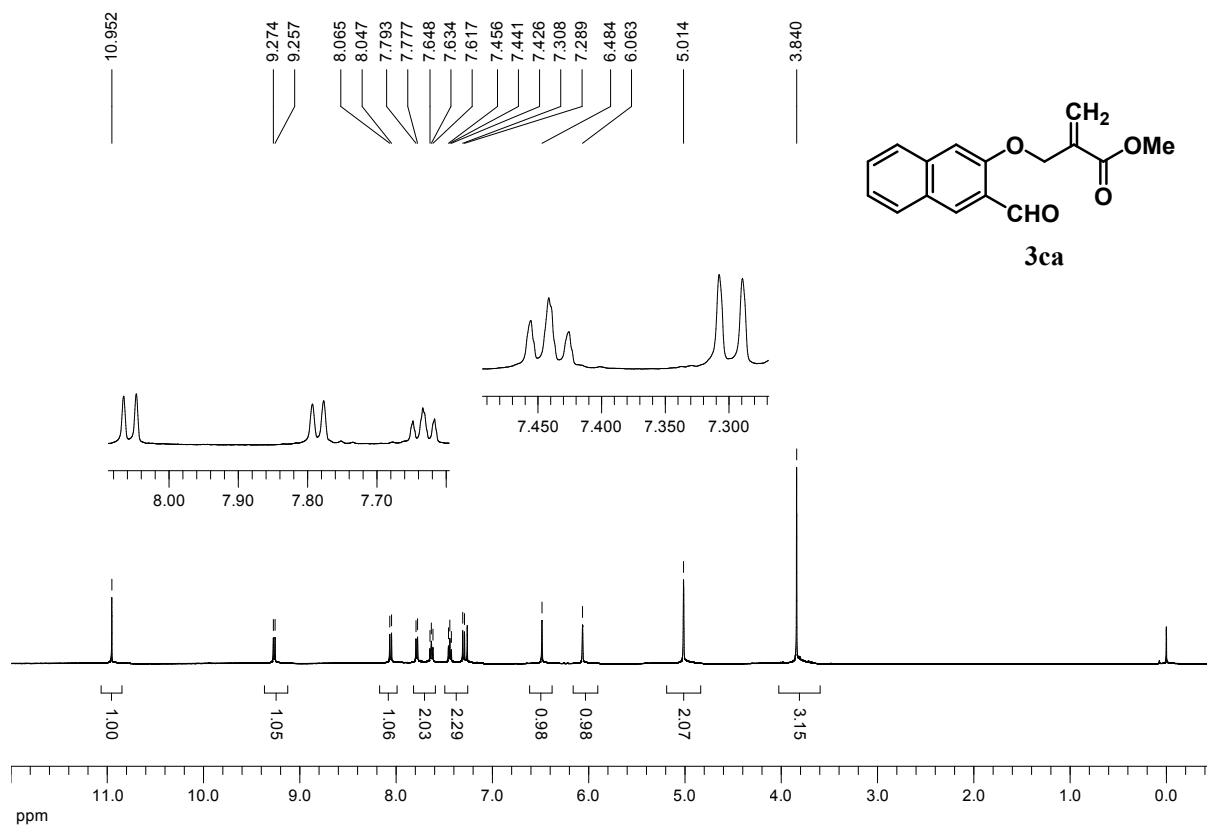
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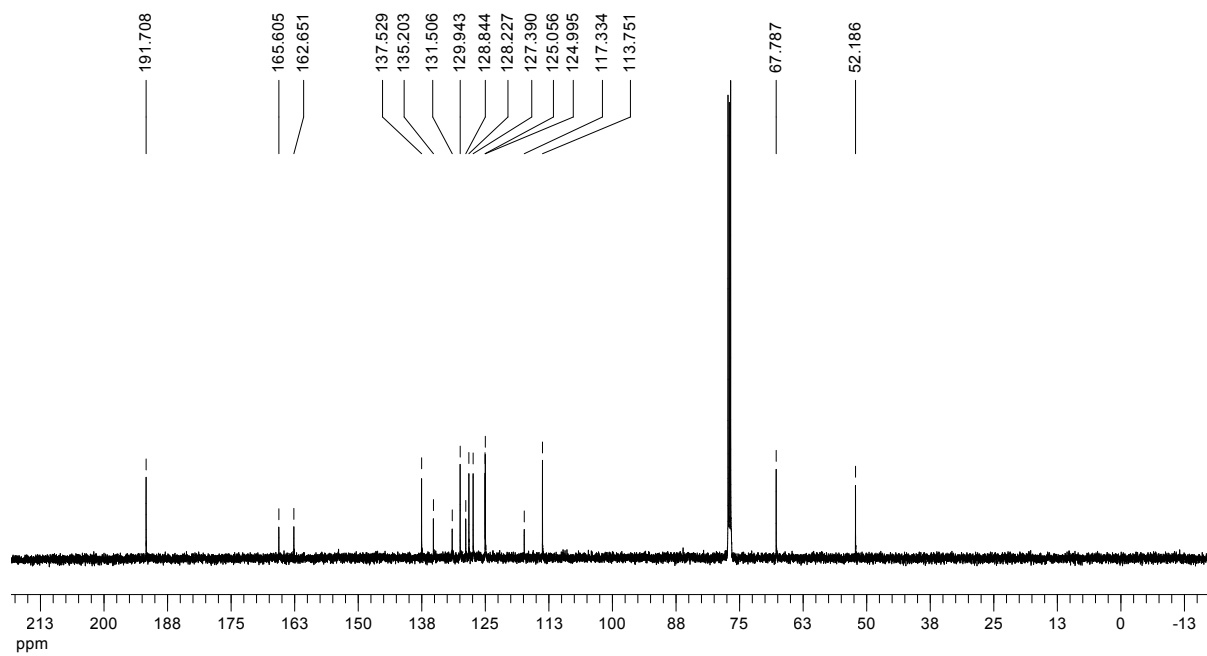
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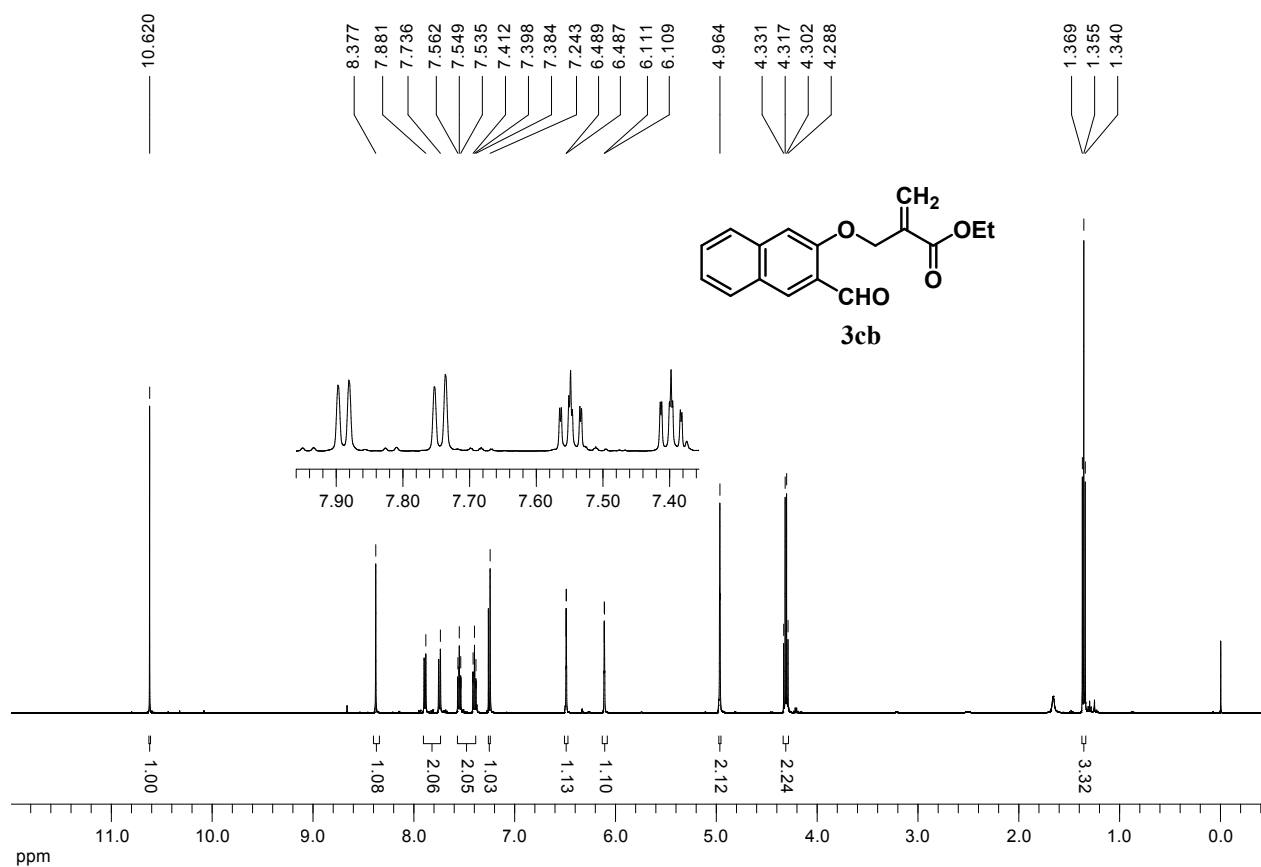
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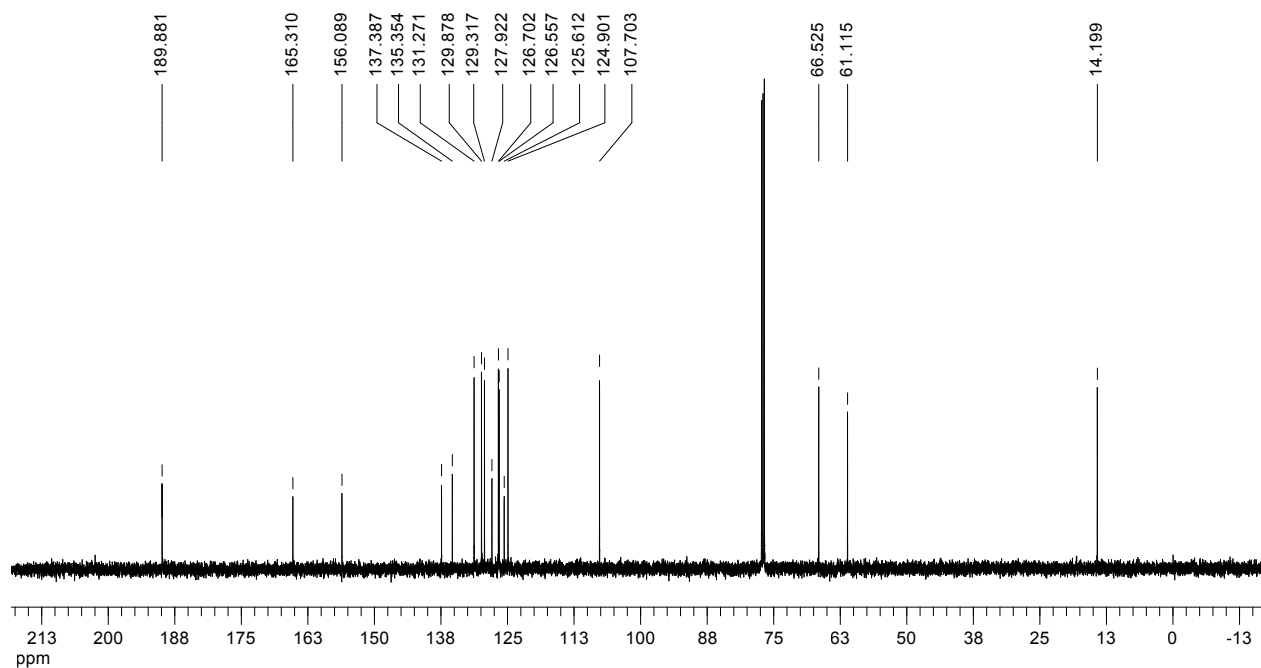
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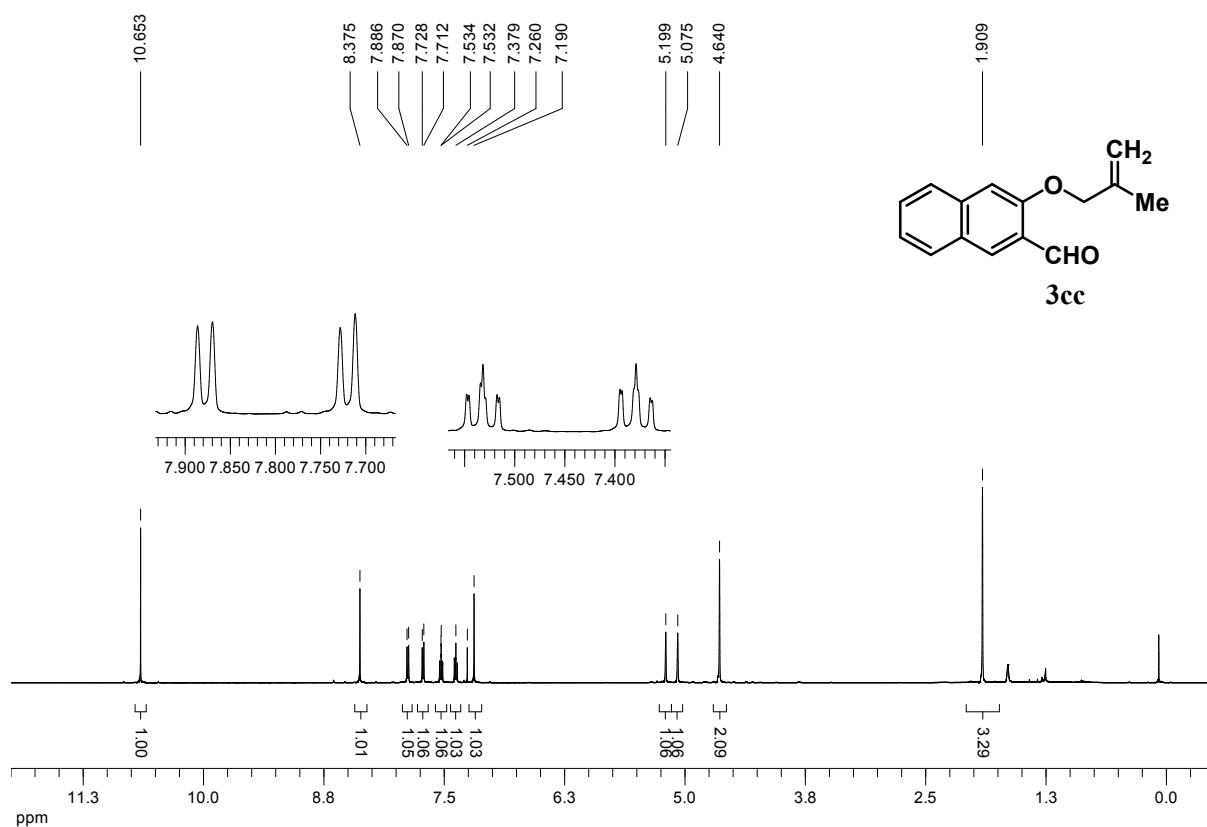
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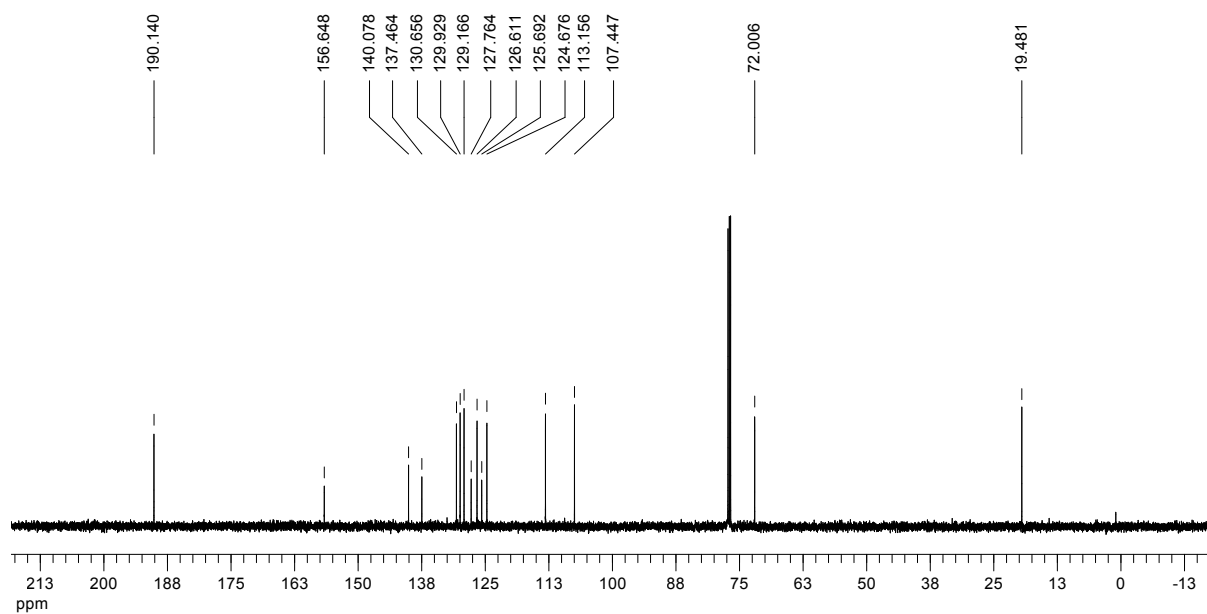
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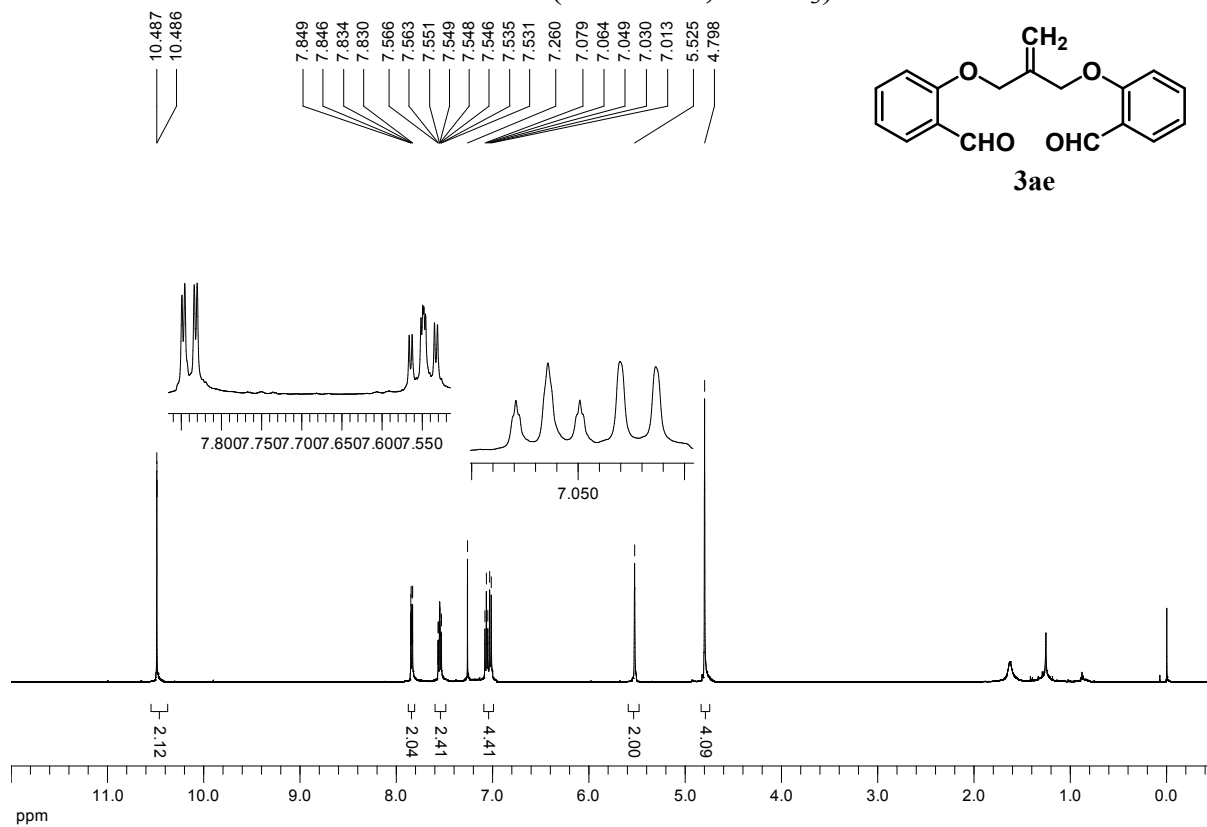
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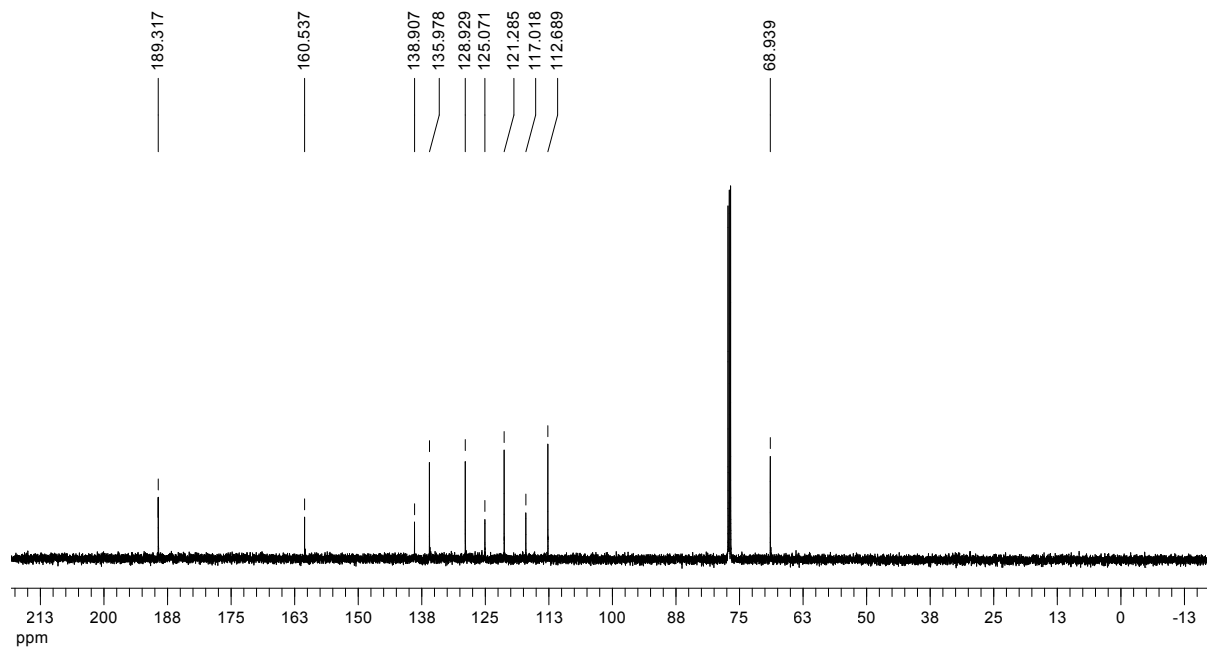
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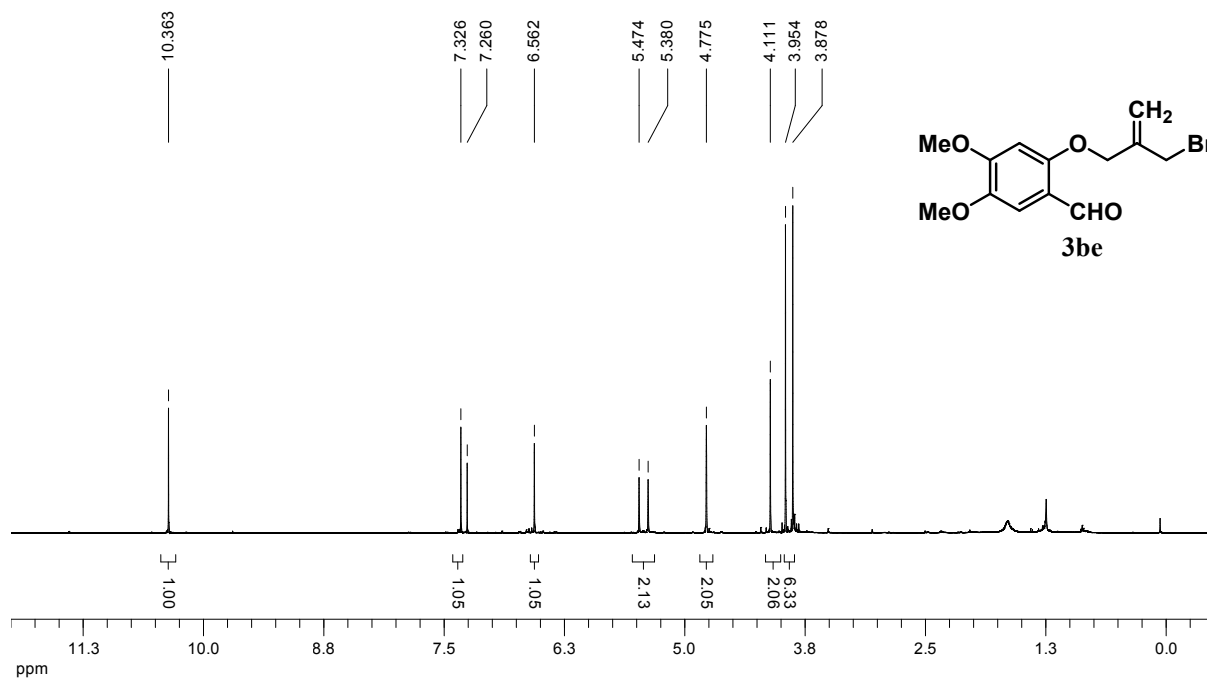
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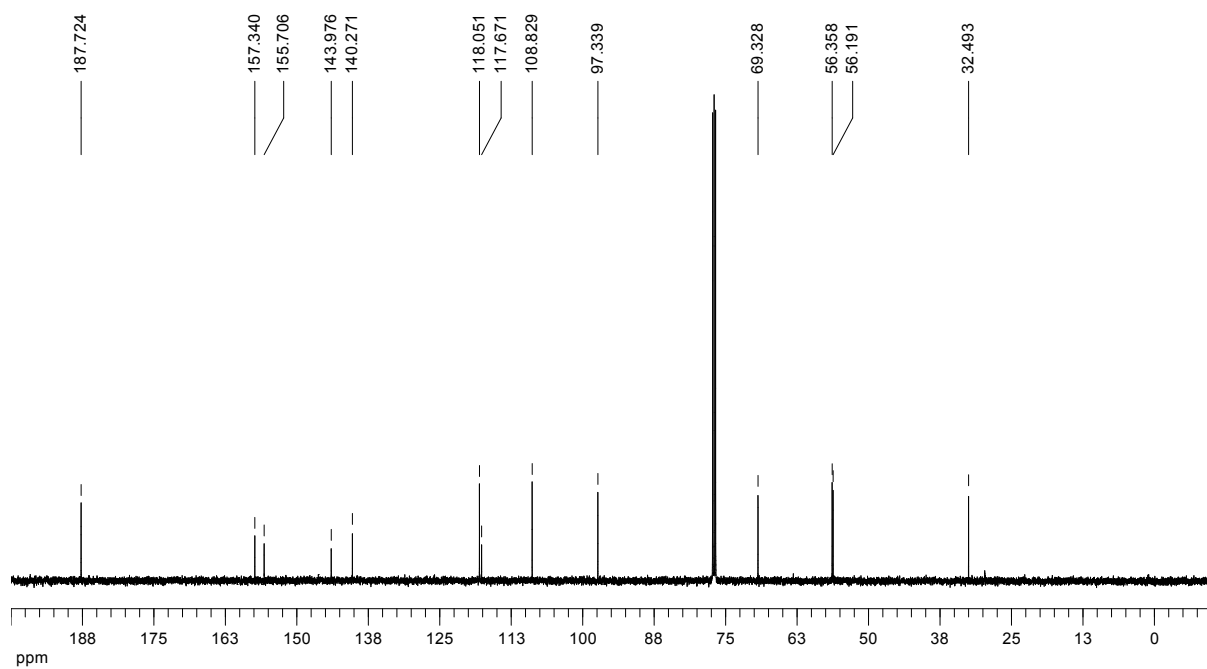
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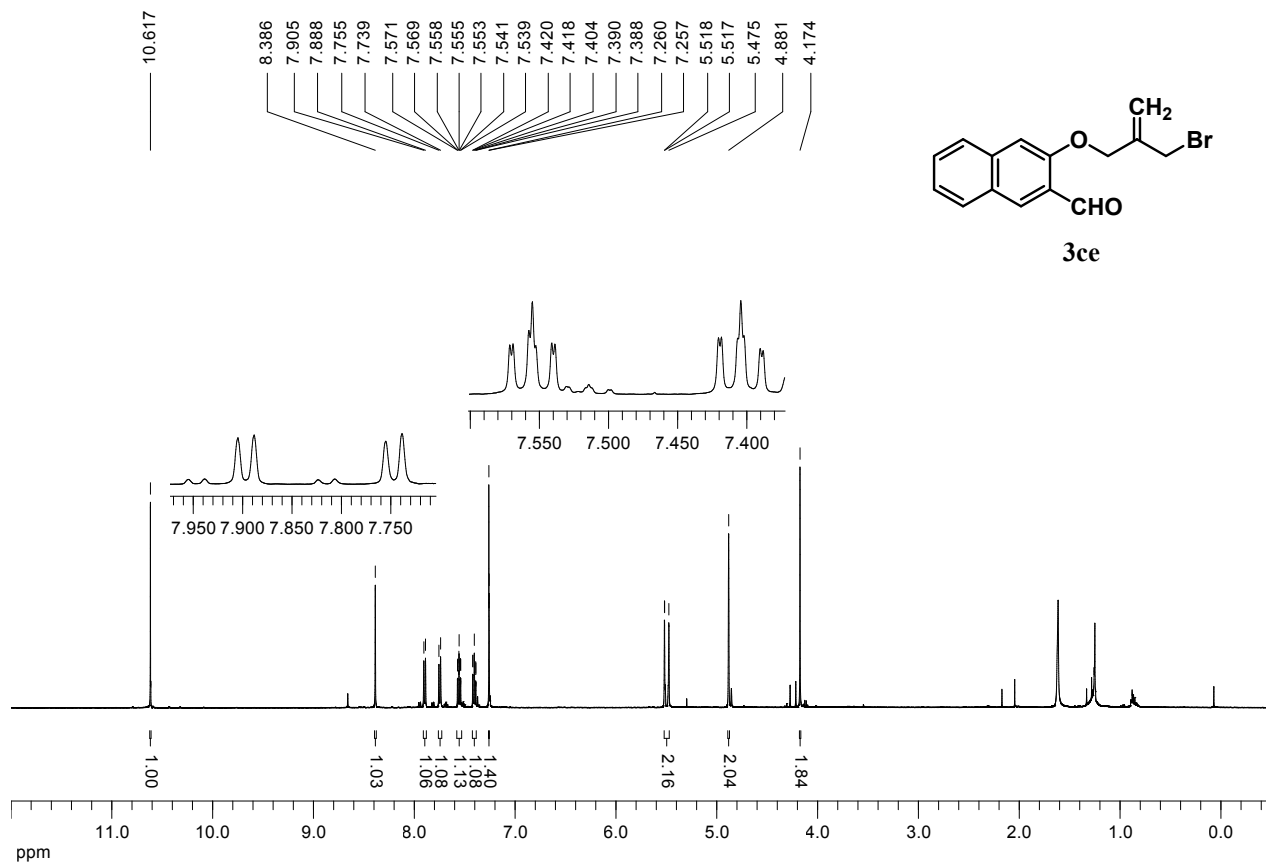
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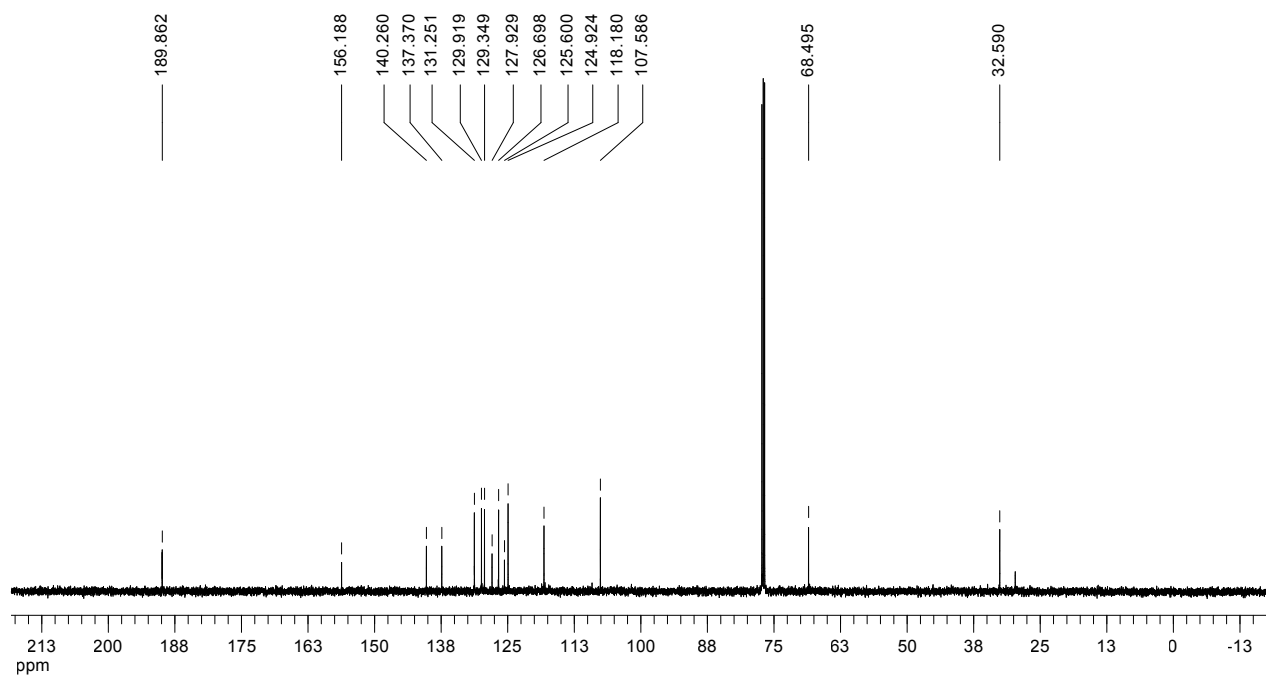
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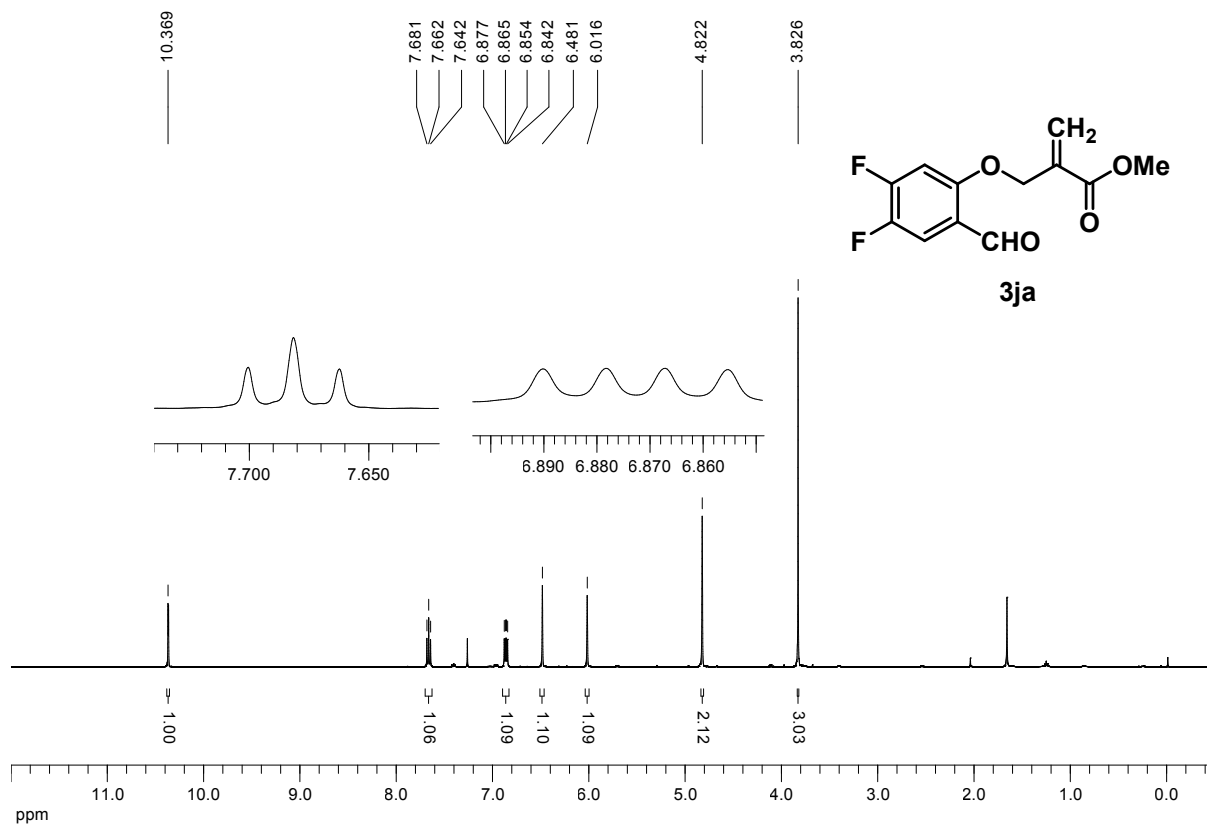
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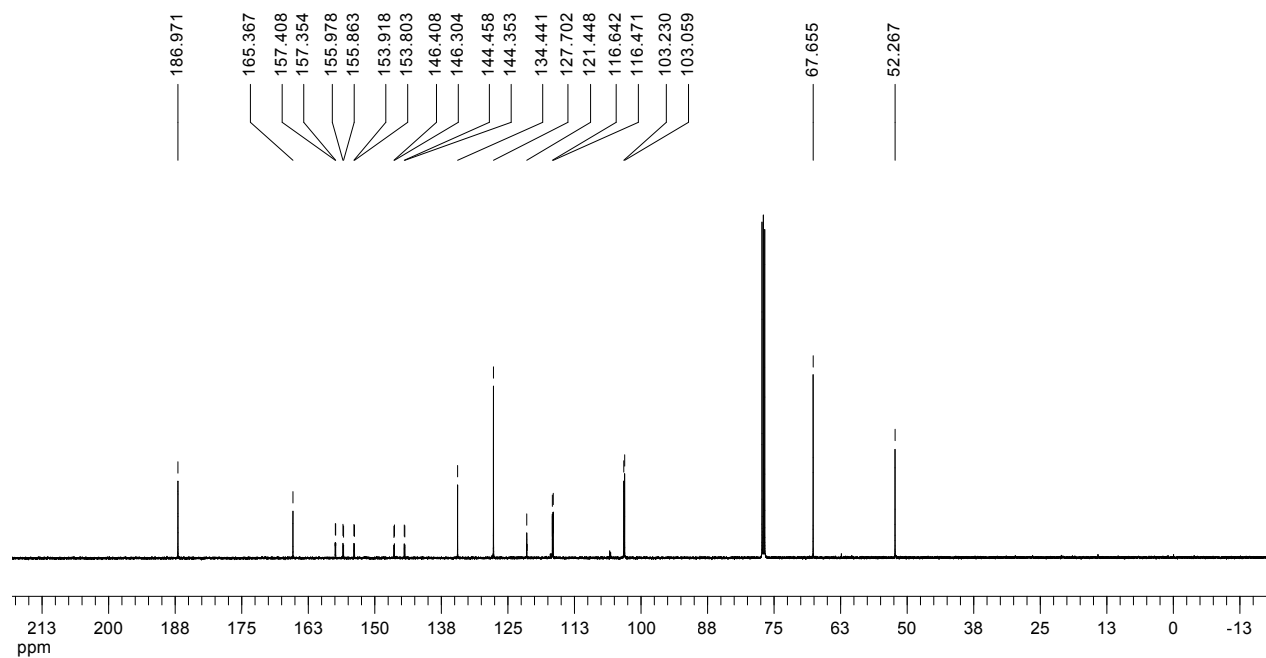
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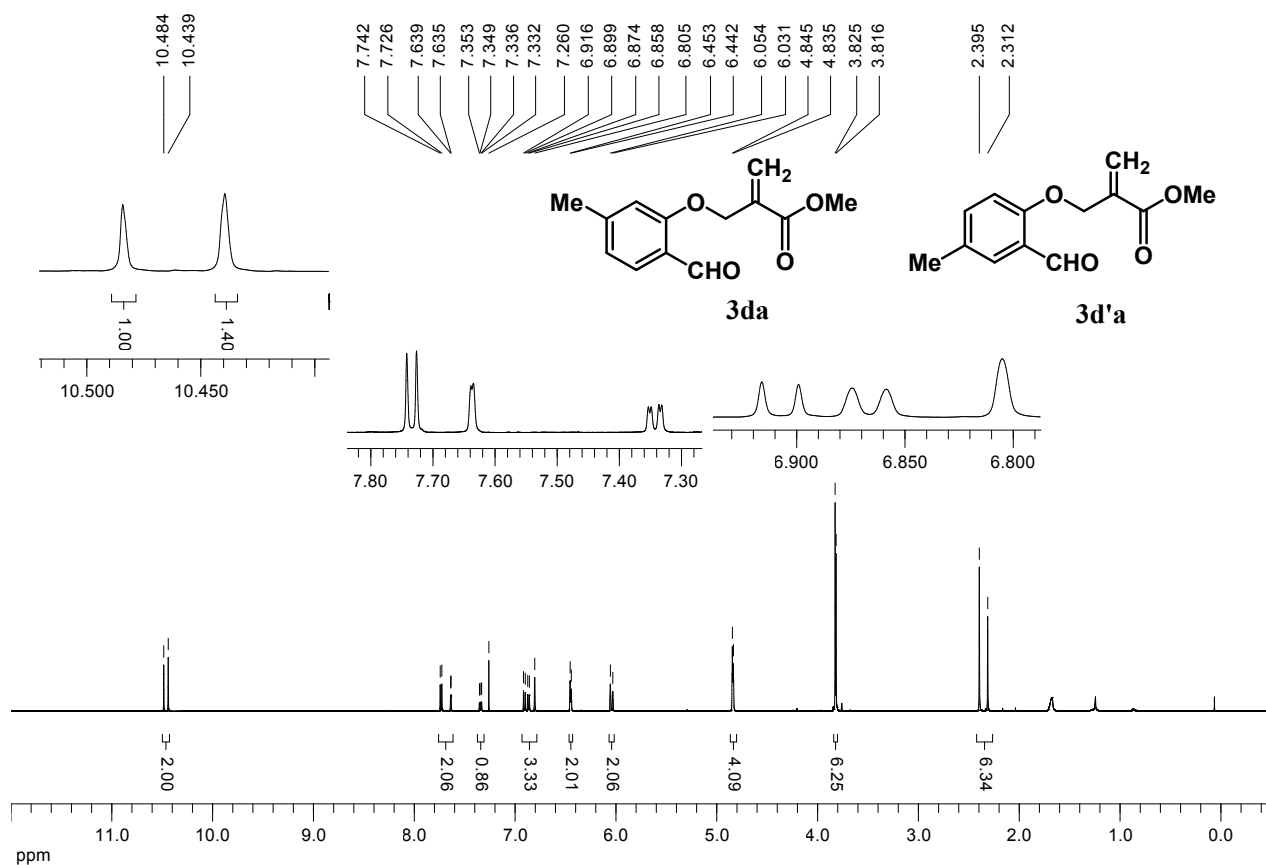
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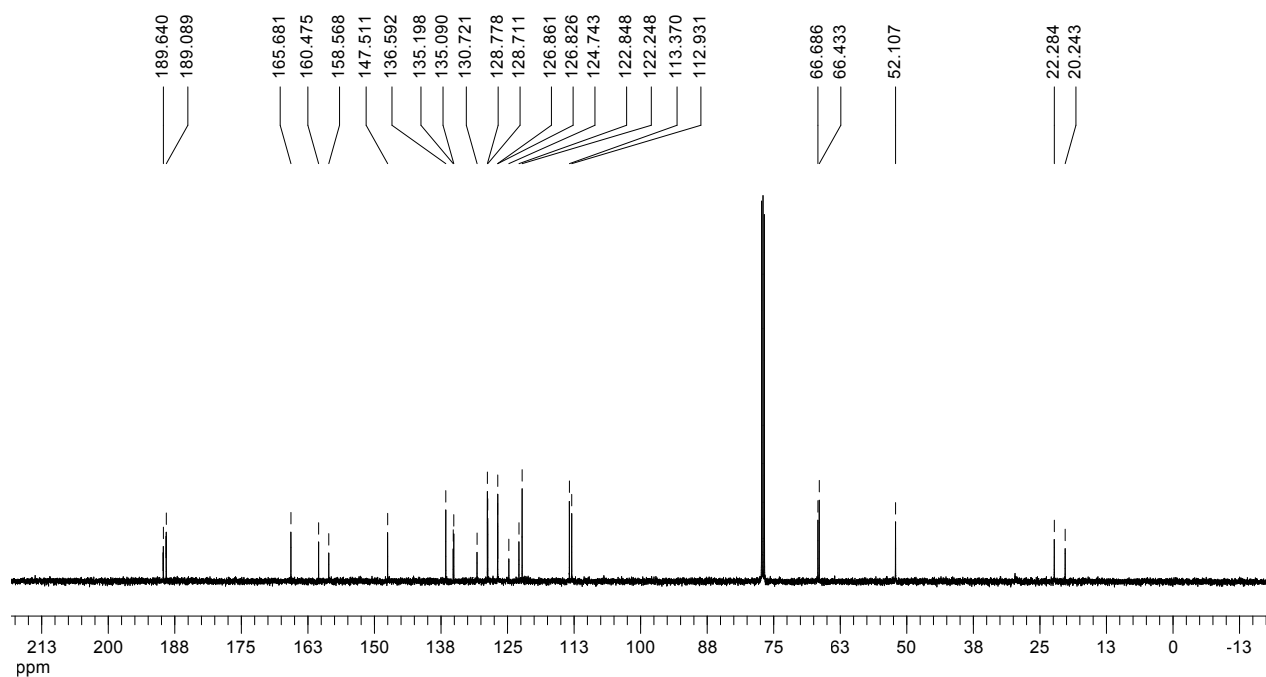
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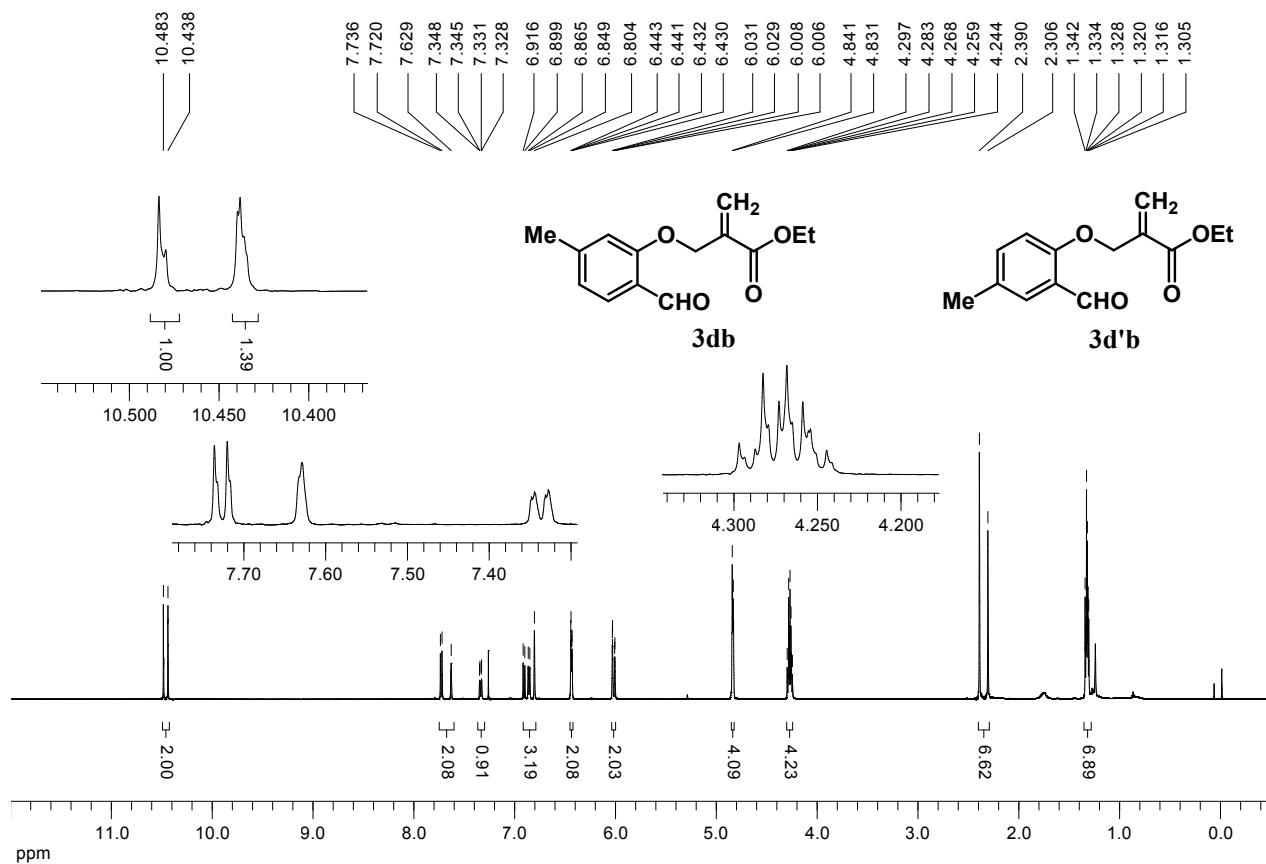
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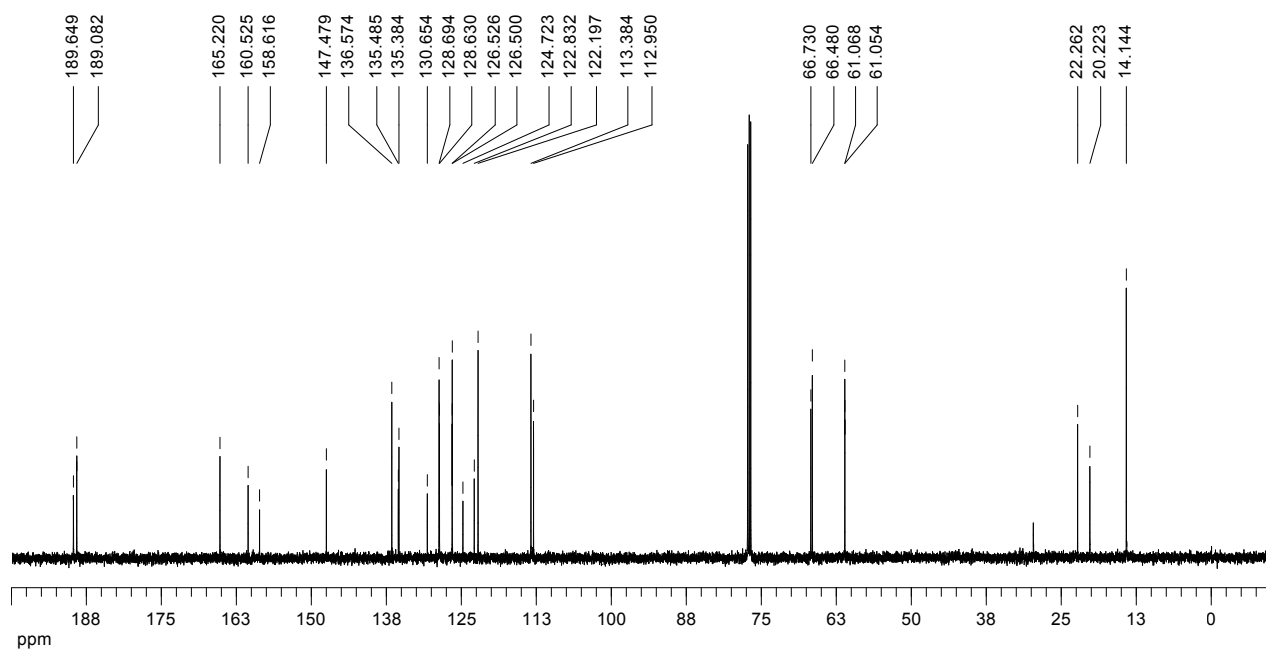
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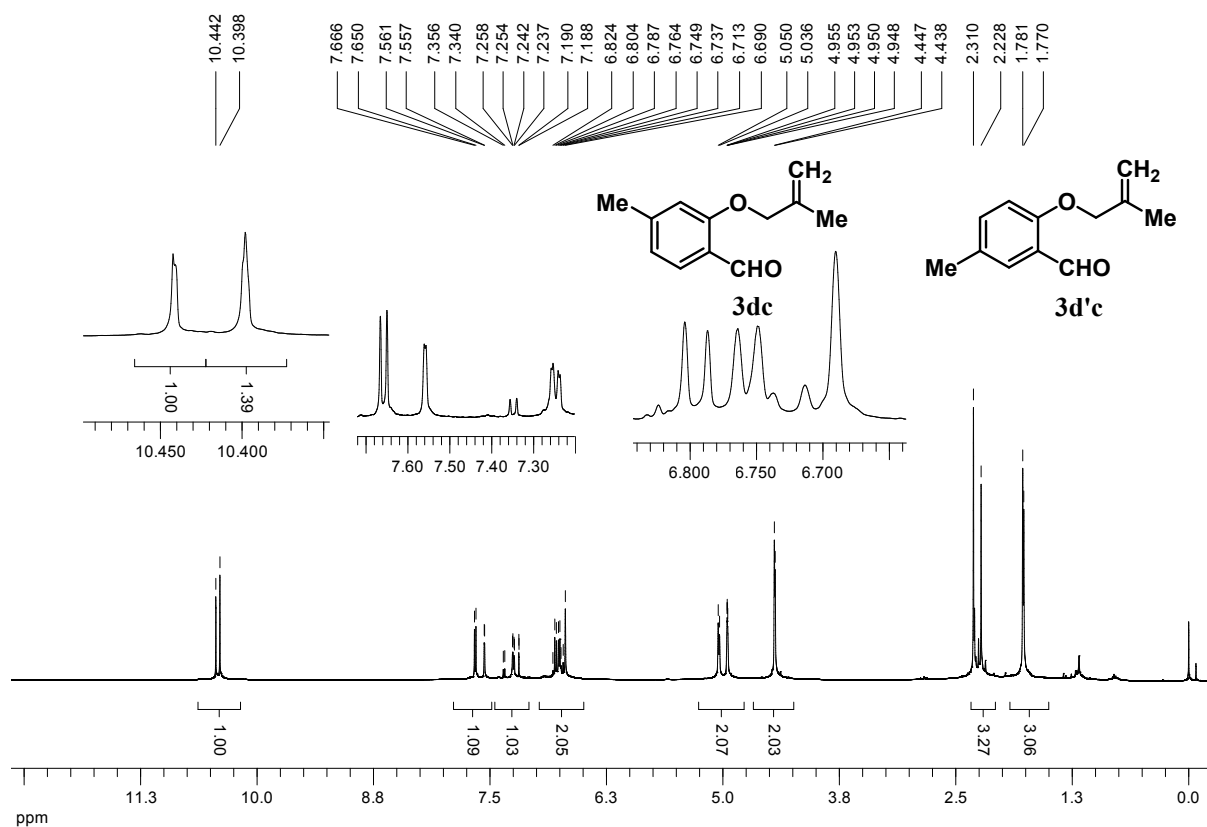
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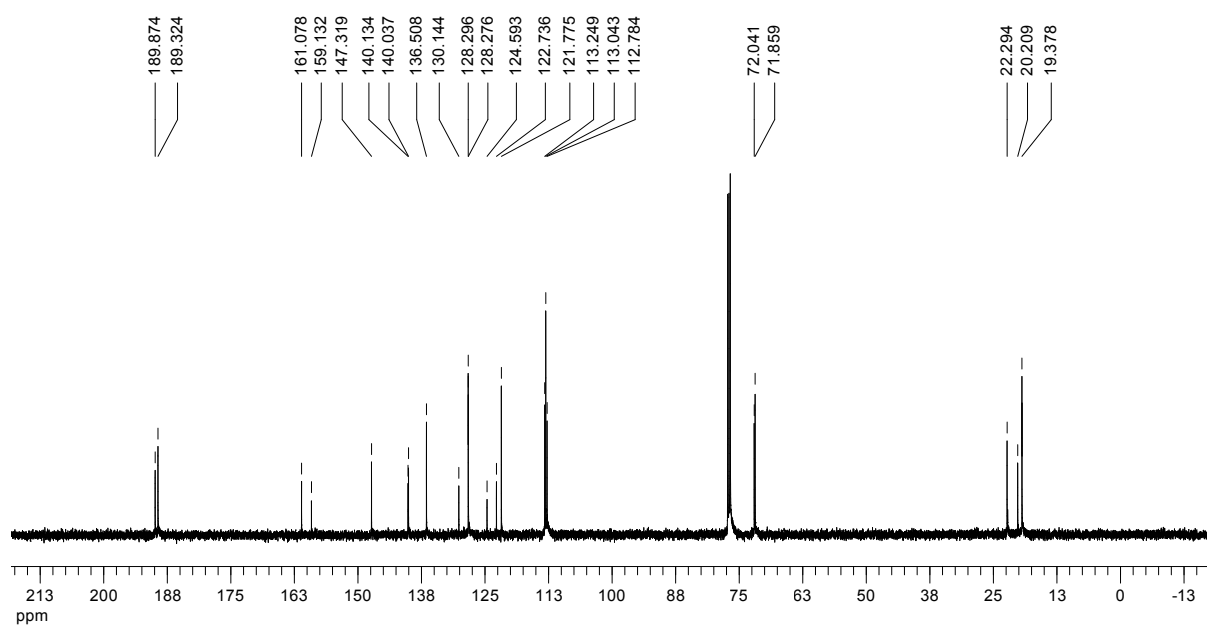
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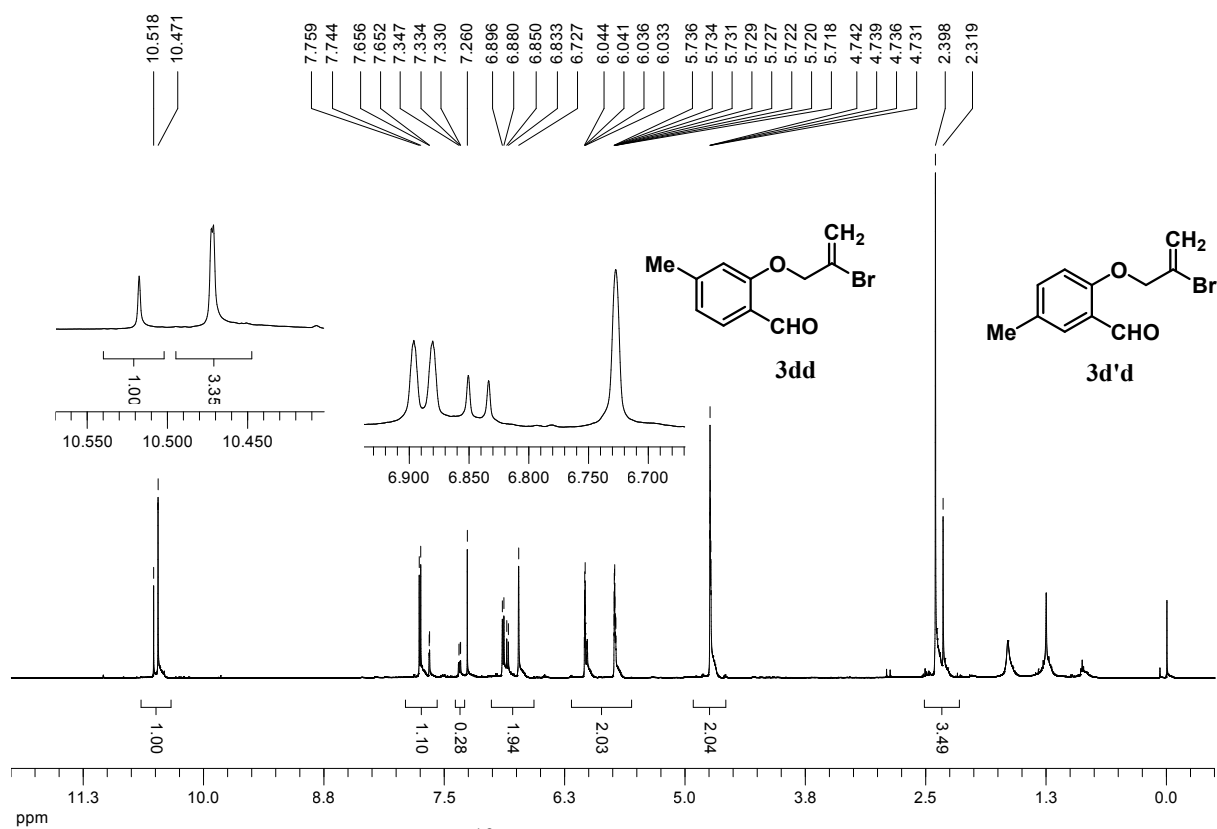
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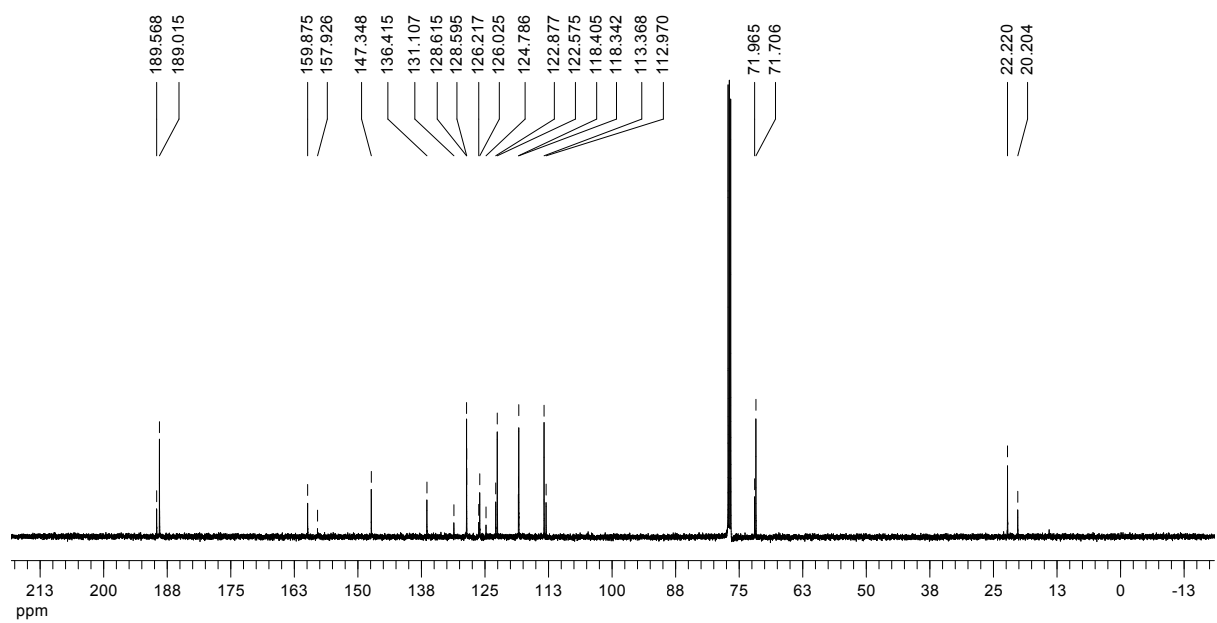
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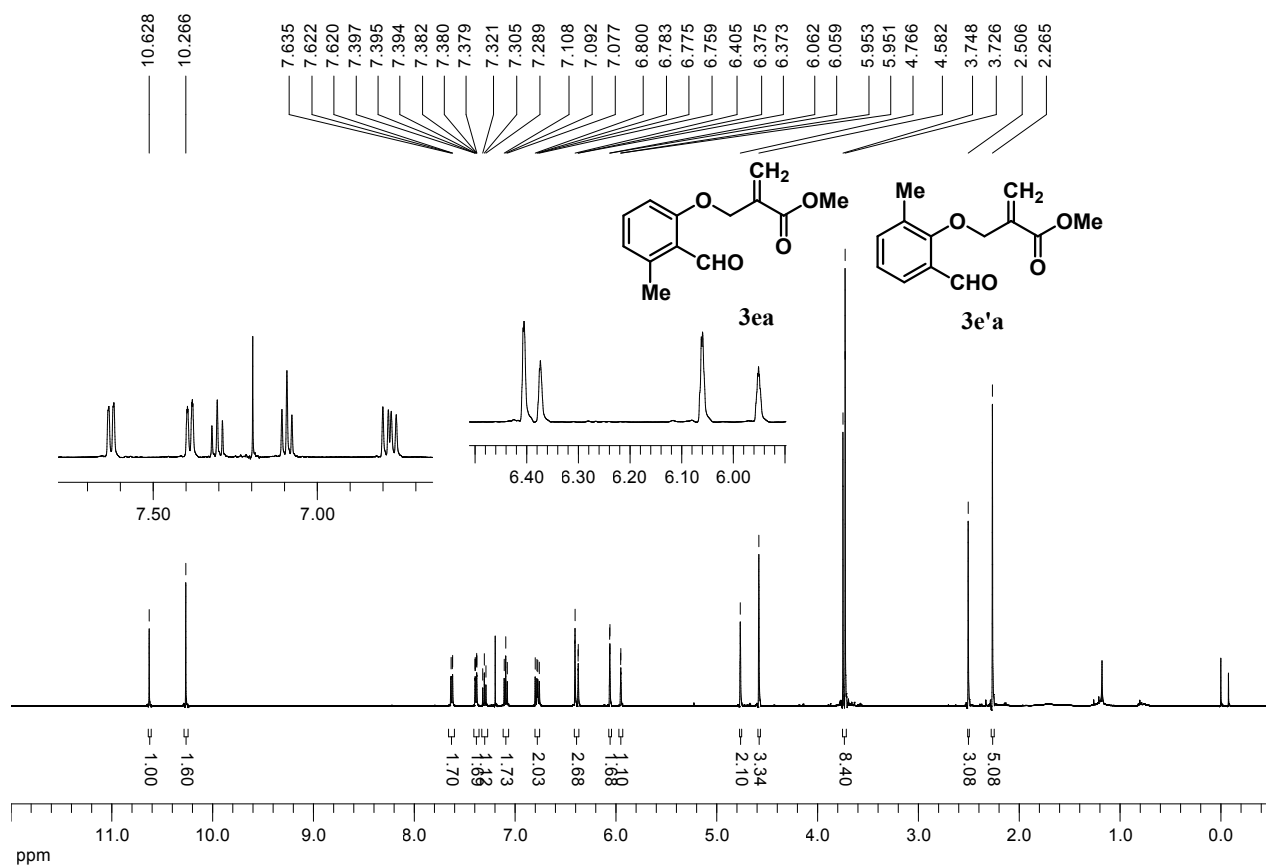
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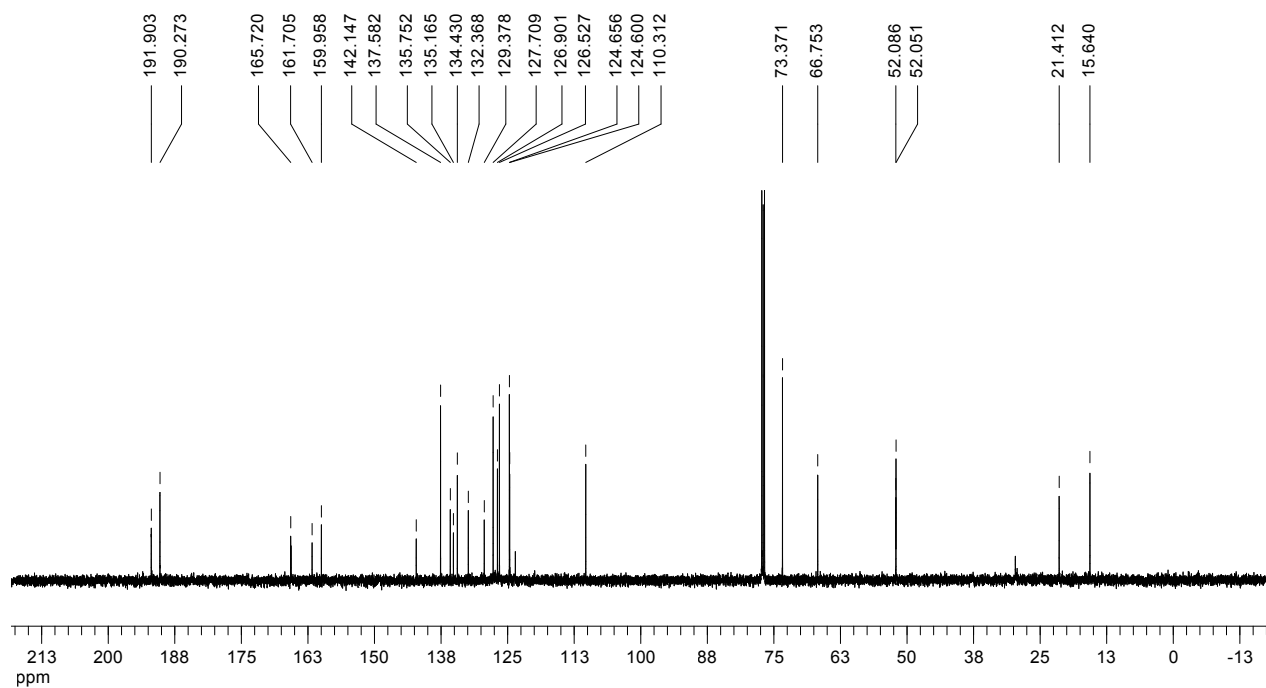
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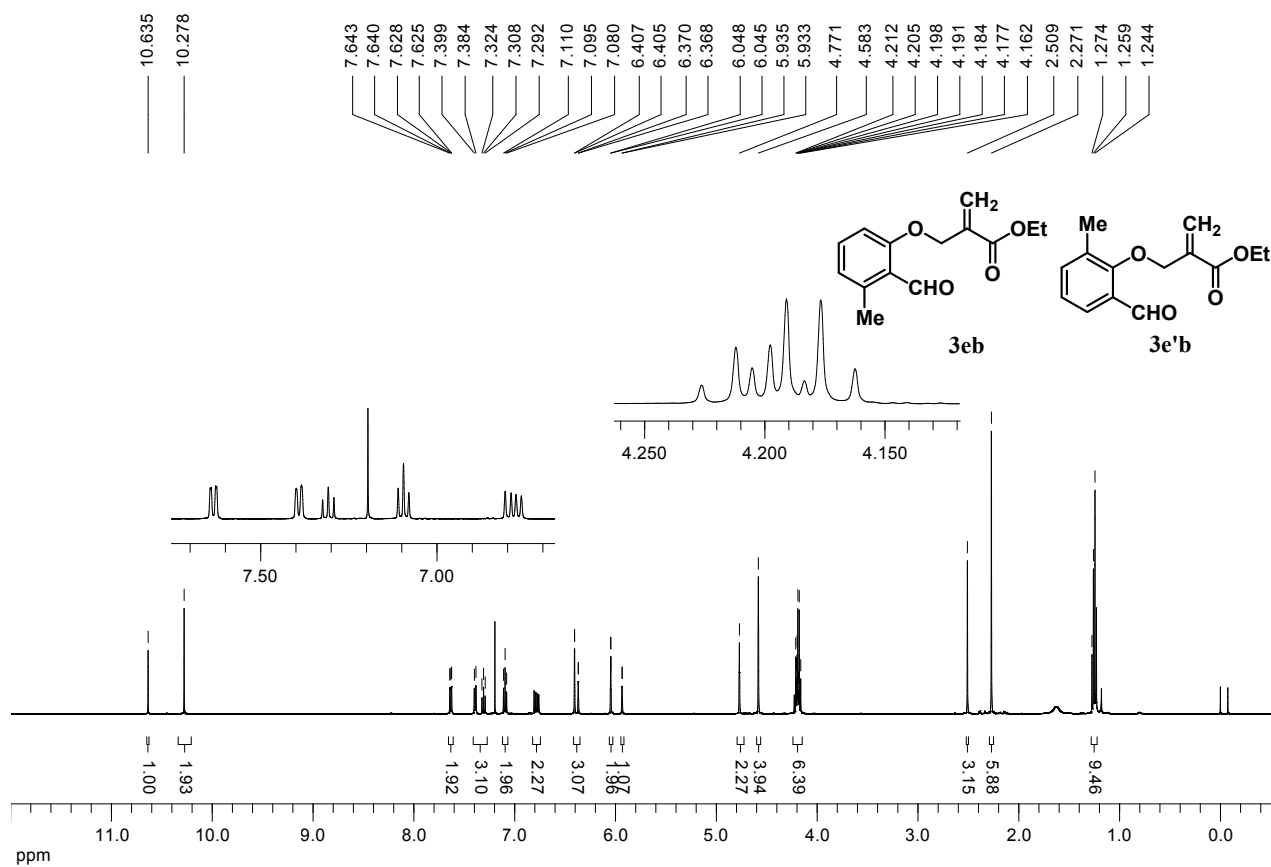
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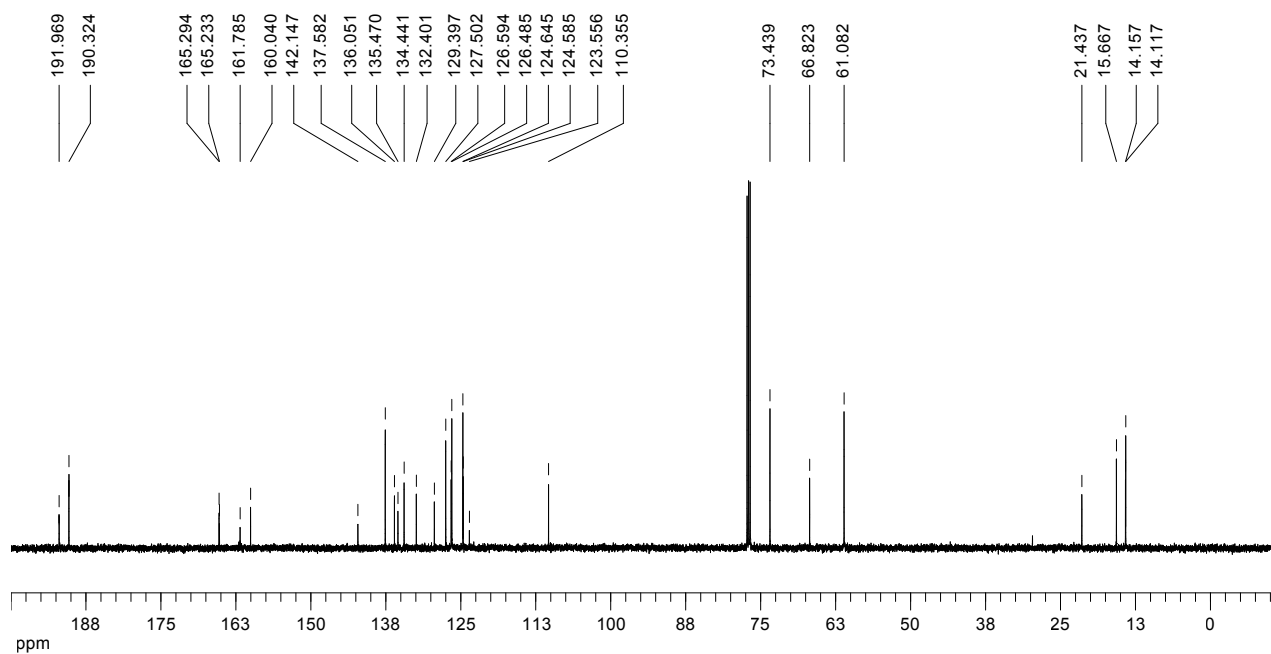
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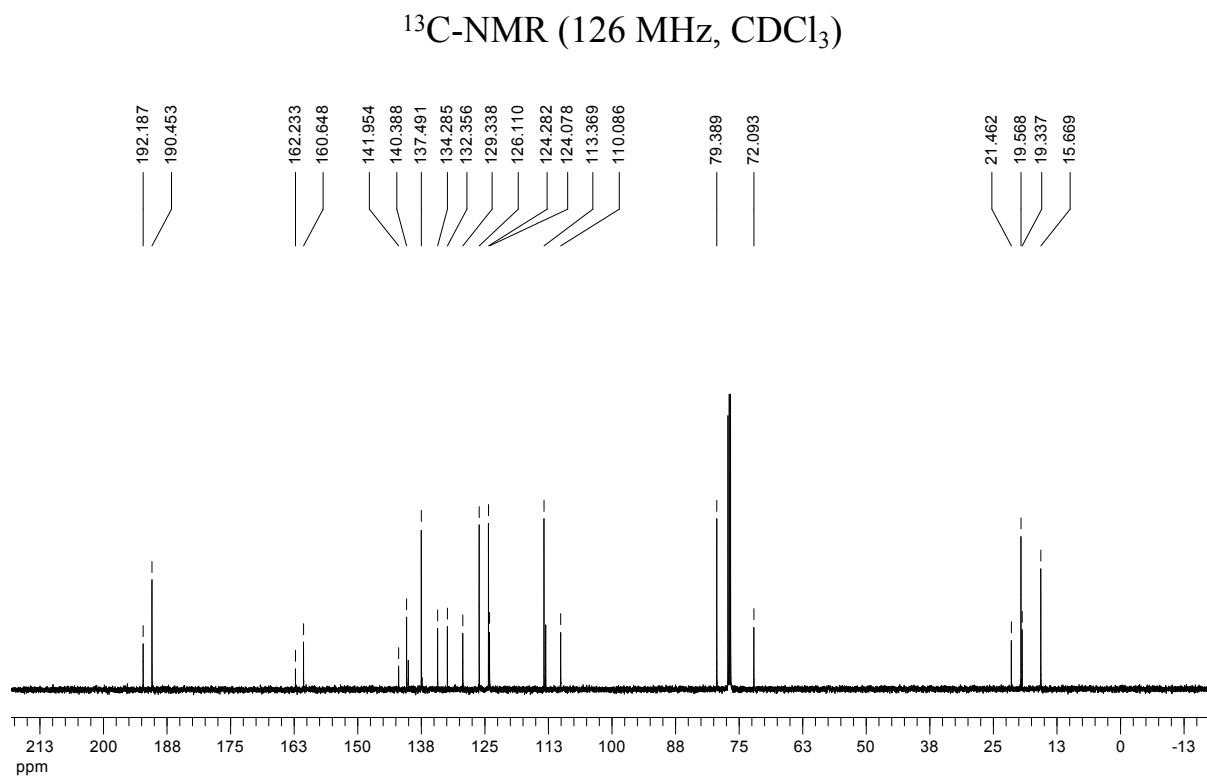
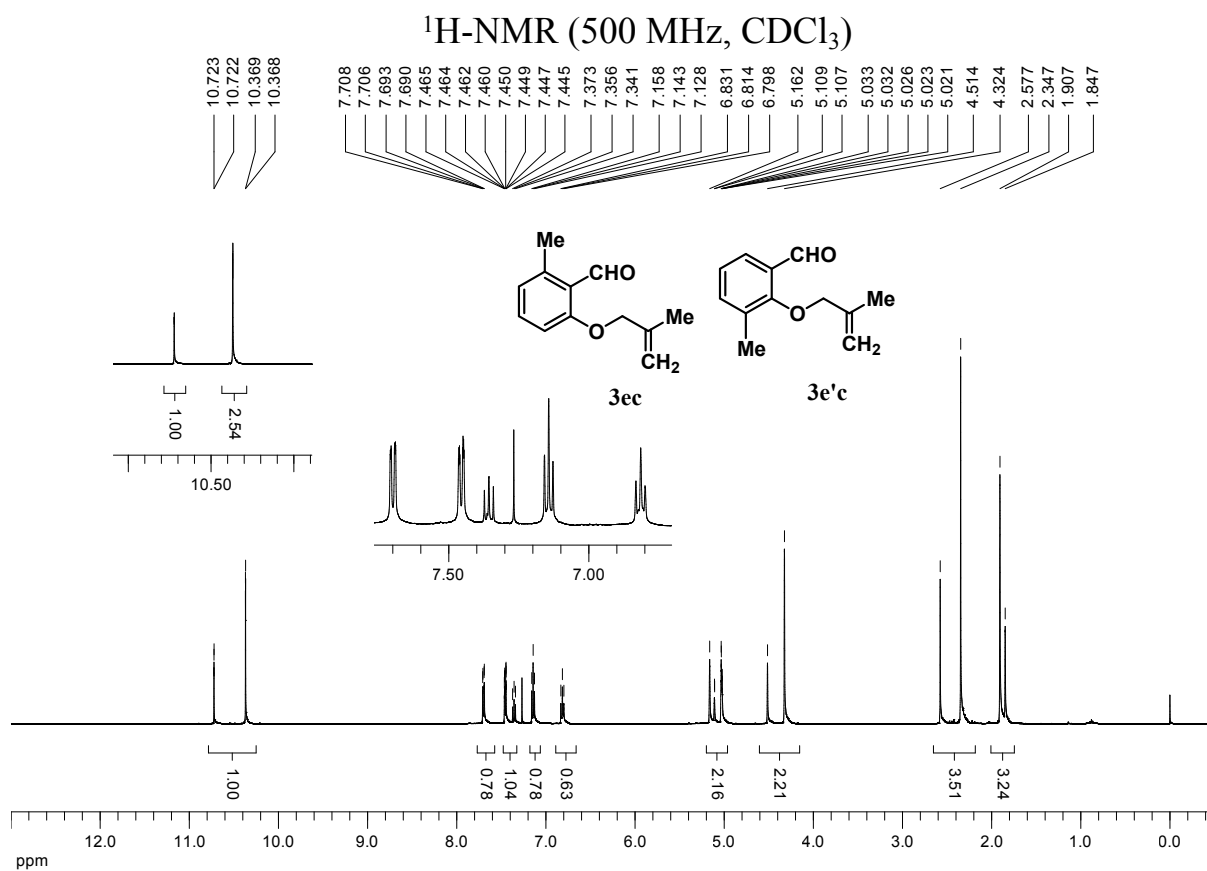


¹H-NMR (500 MHz, CDCl₃)



¹³C-NMR (126 MHz, CDCl₃)





Chemical structure of 3fa: COCC(=O)C=Cc1cc(=O)c2ccccc2c1

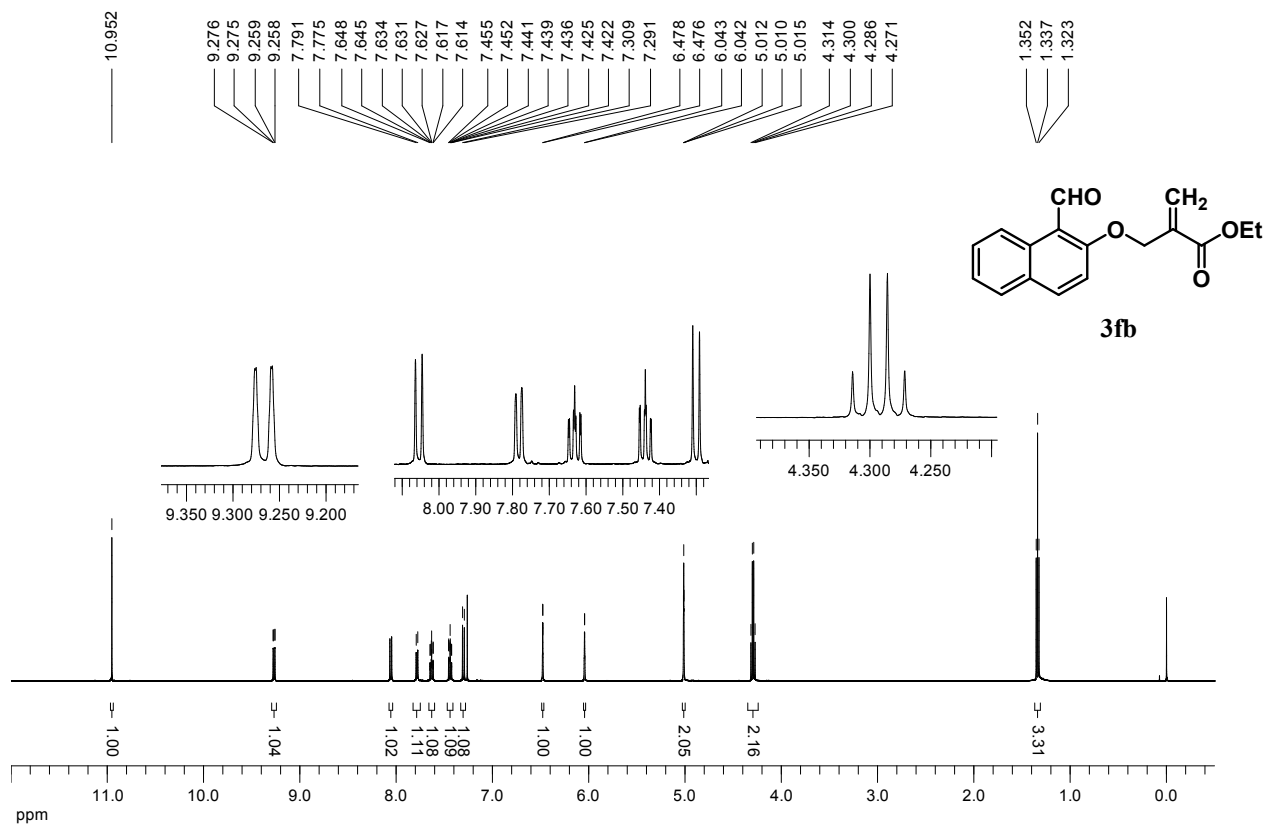
¹H NMR spectrum (CDCl₃):

- Chemical shift (ppm):** 10.943, 9.271, 9.253, 8.057, 8.039, 7.787, 7.771, 7.644, 7.629, 7.627, 7.613, 7.451, 7.435, 7.421, 7.296, 7.279, 6.481, 6.057, 5.003, 3.836.
- Integration values:** 1.00, 1.05, 1.07, 1.28, 1.11, 1.08, 1.08, 1.08, 2.05, 3.10.

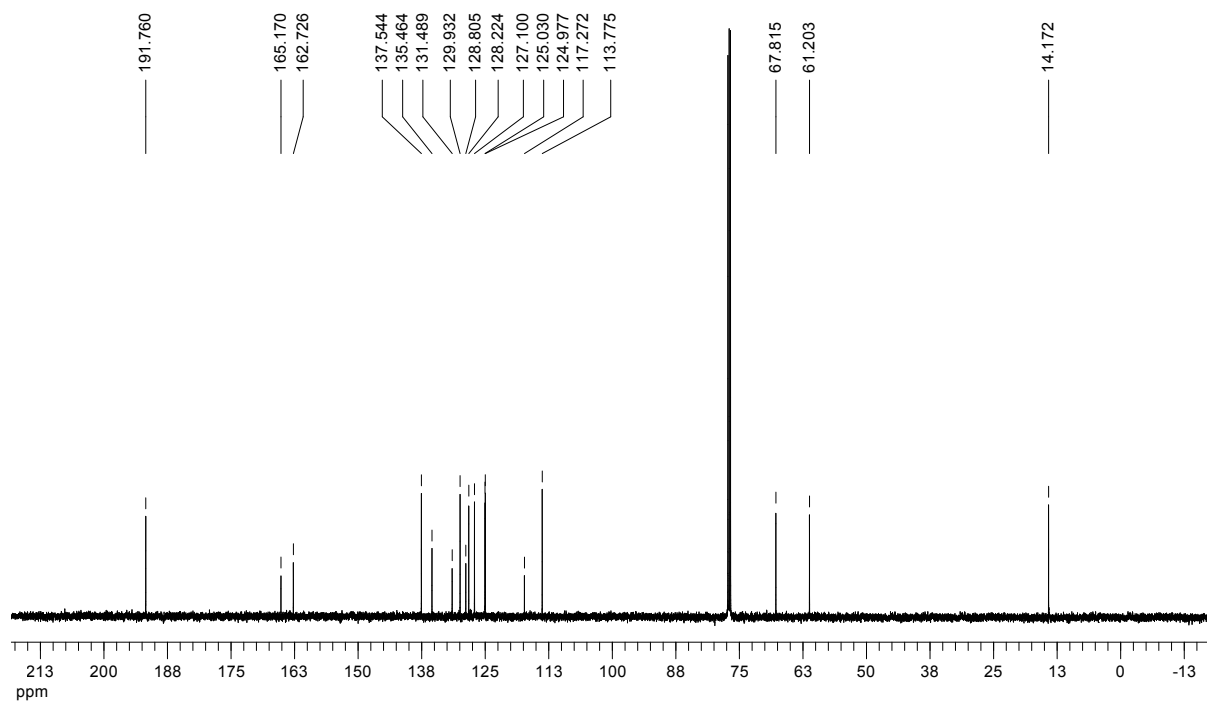
Mass spectrum of compound 10. The x-axis represents the mass-to-charge ratio (m/z) from 0 to 200, and the y-axis represents relative intensity from 0 to 100. The base peak is at m/z 77. Other significant peaks are labeled with their m/z values.

m/z	Relative Intensity (%)
191.707	~10
165.583	~10
162.627	~10
137.545	~10
135.129	~10
131.458	~10
129.928	~10
128.780	~10
128.217	~10
127.373	~10
125.023	~10
124.946	~10
117.216	~10
113.684	~10
77	100
67.701	~10
52.185	~10

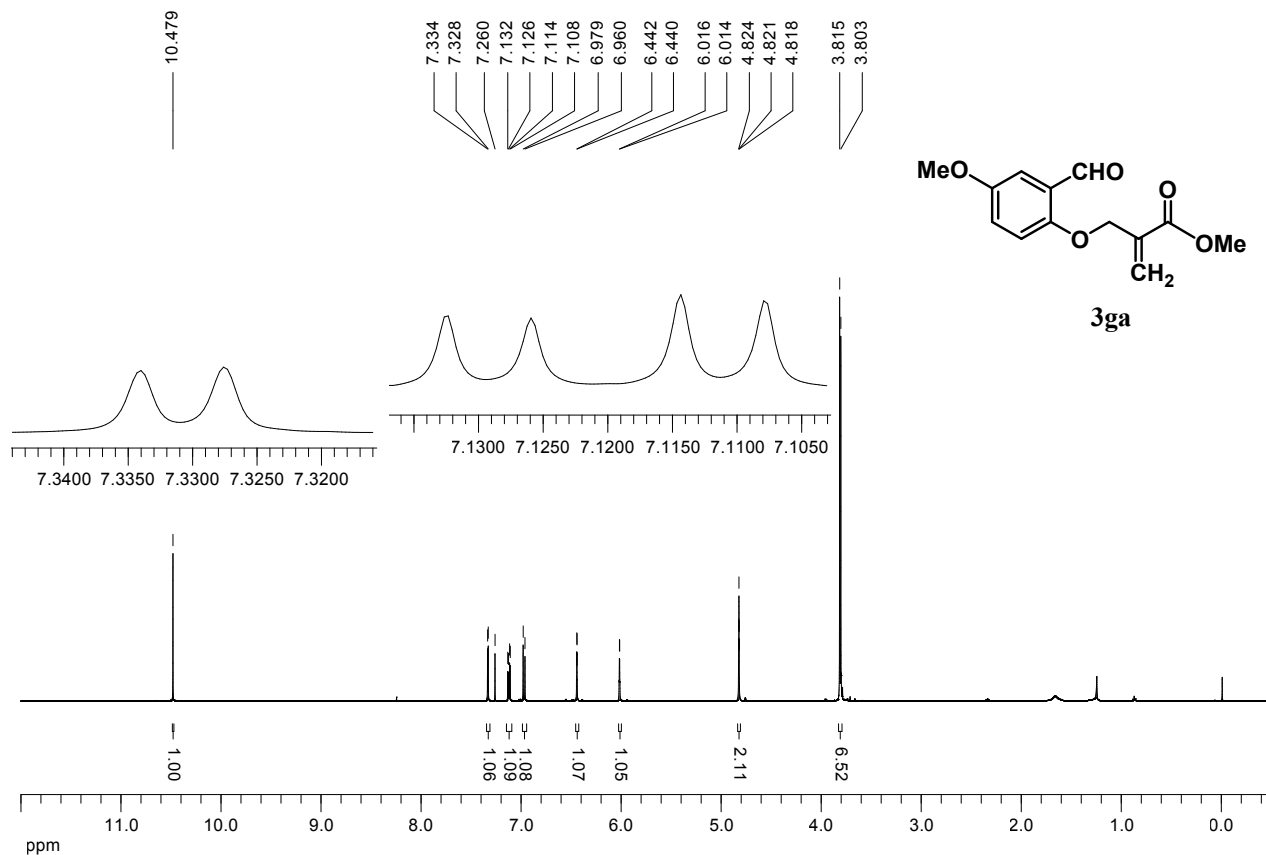
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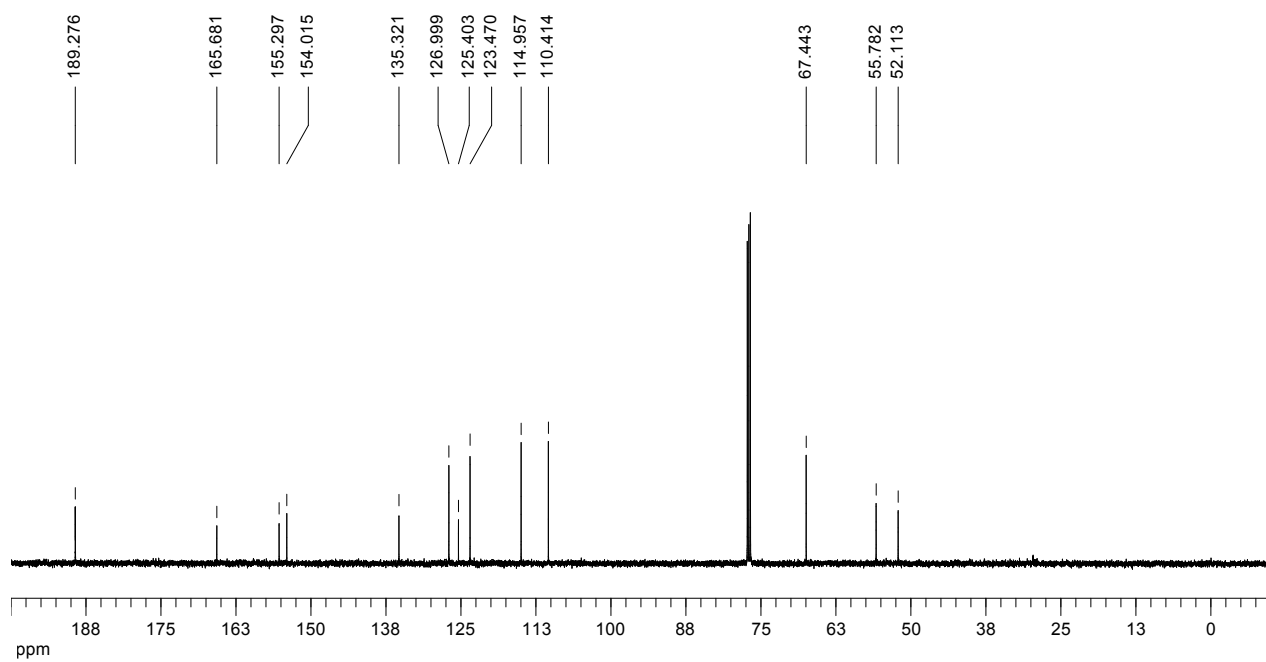
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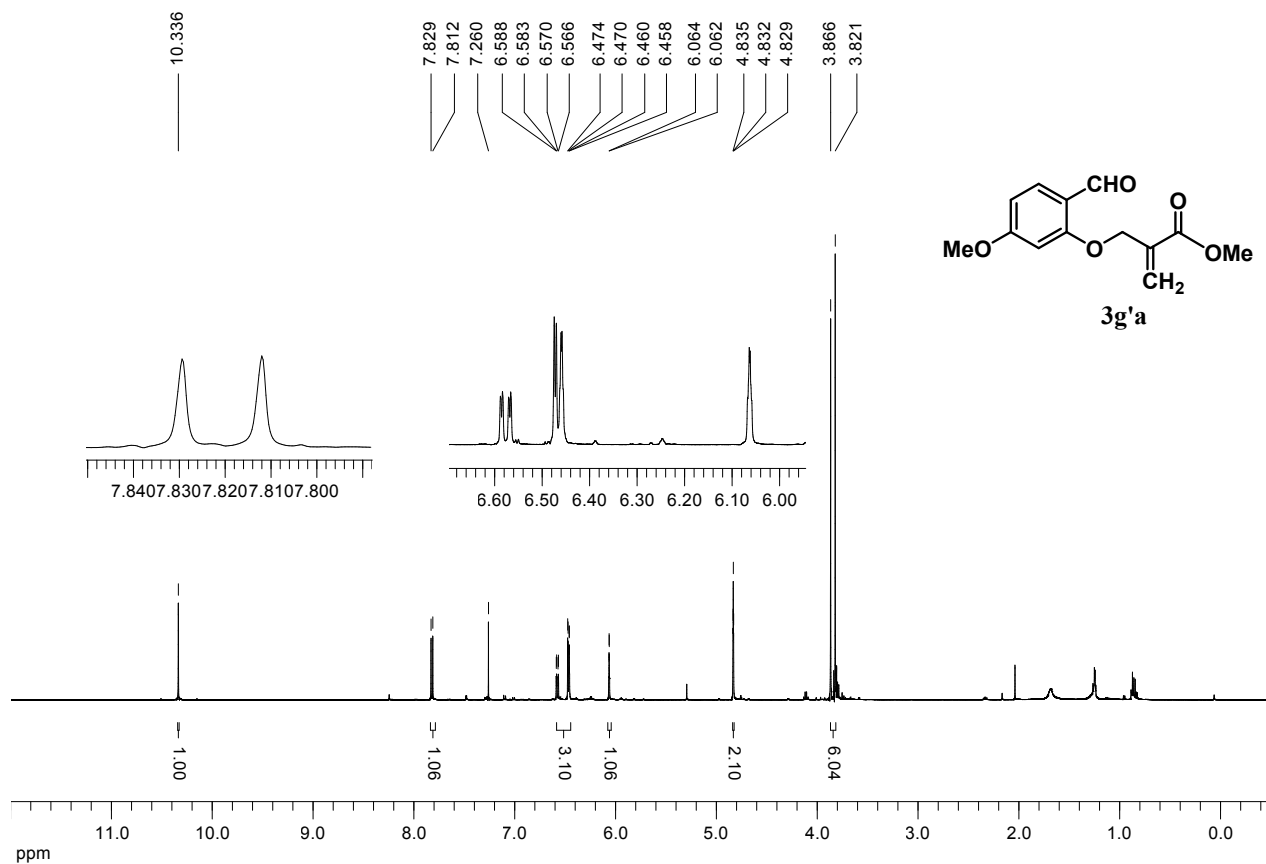
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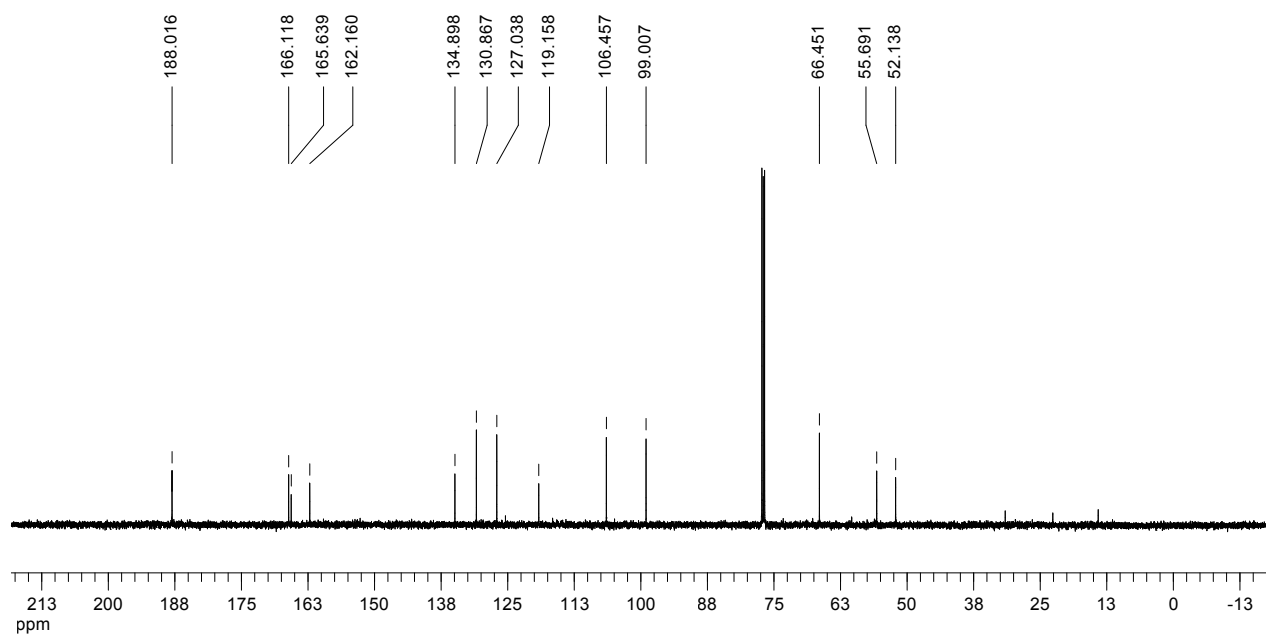
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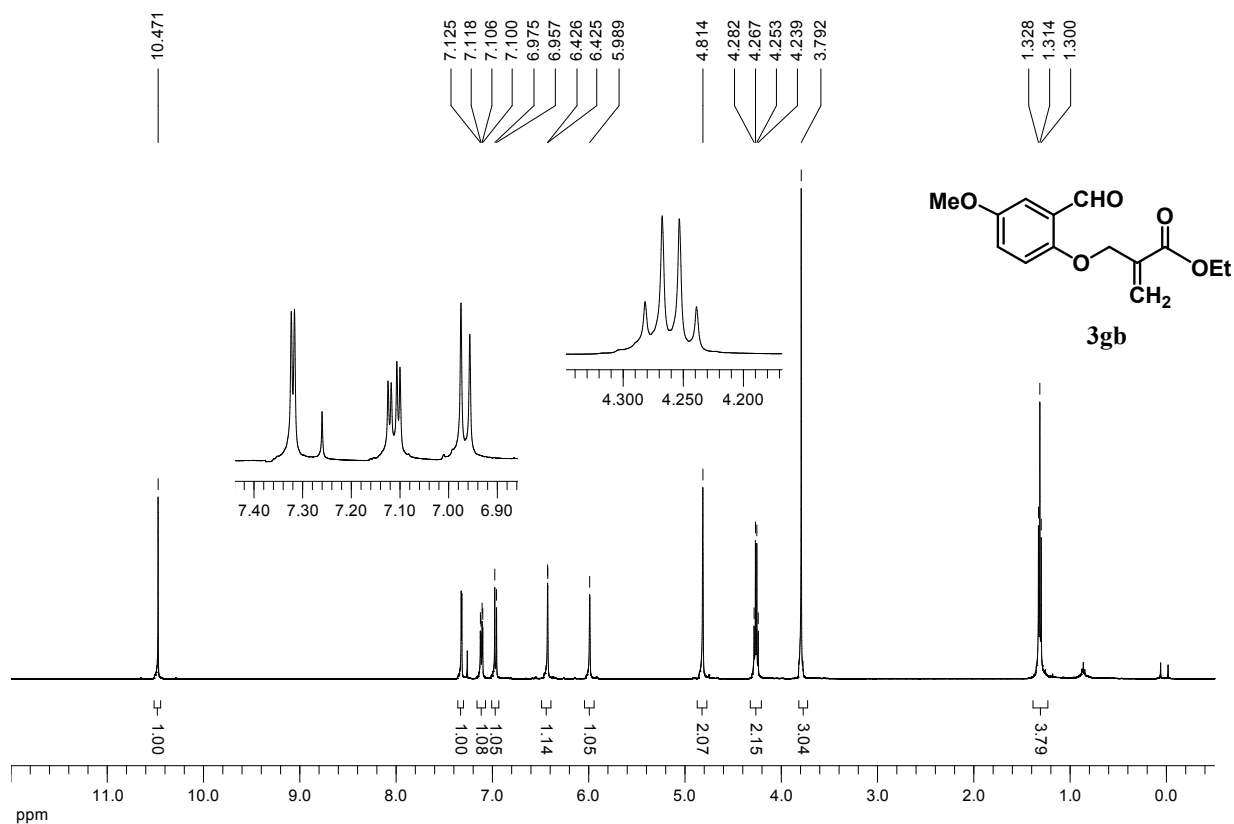
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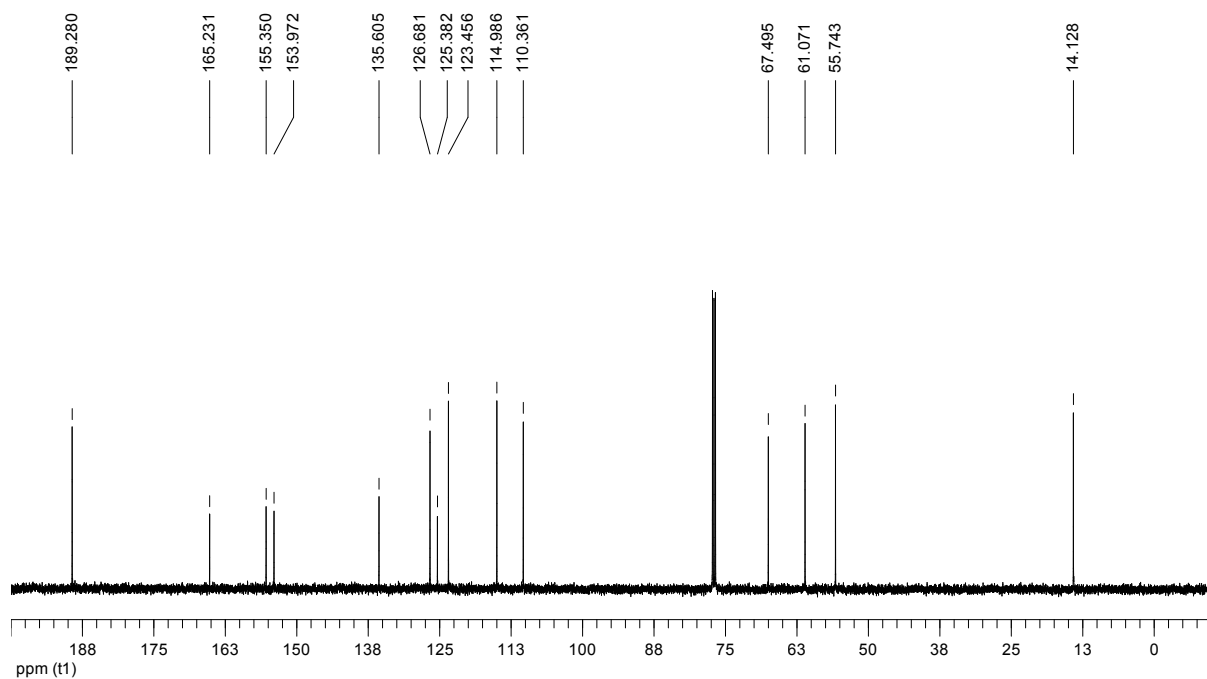
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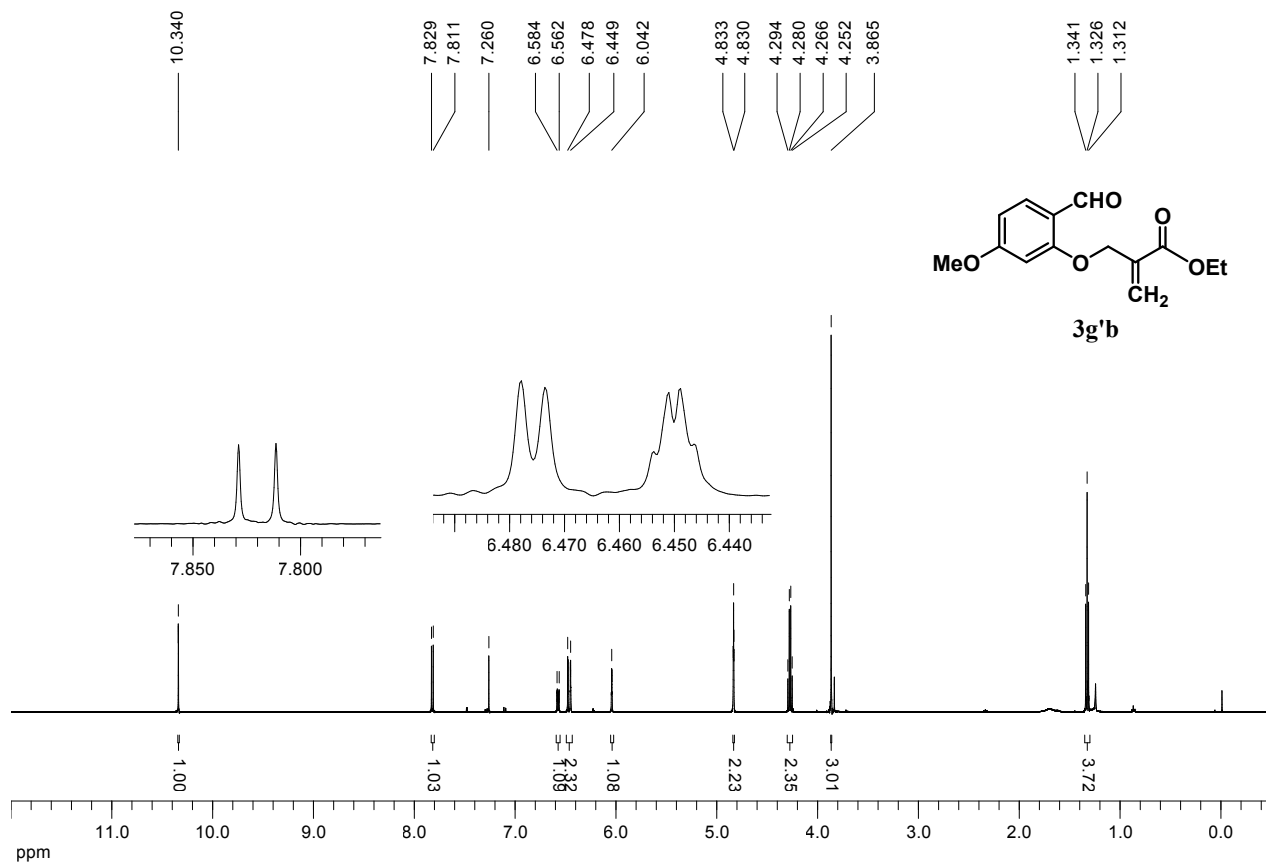
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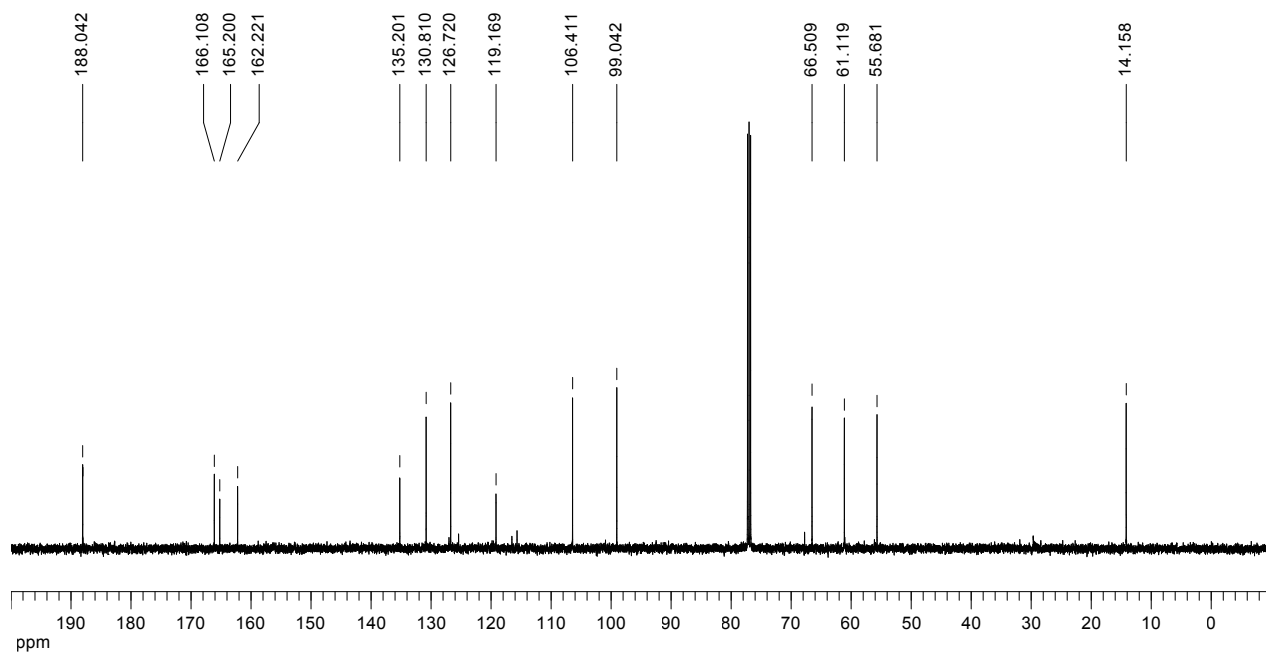
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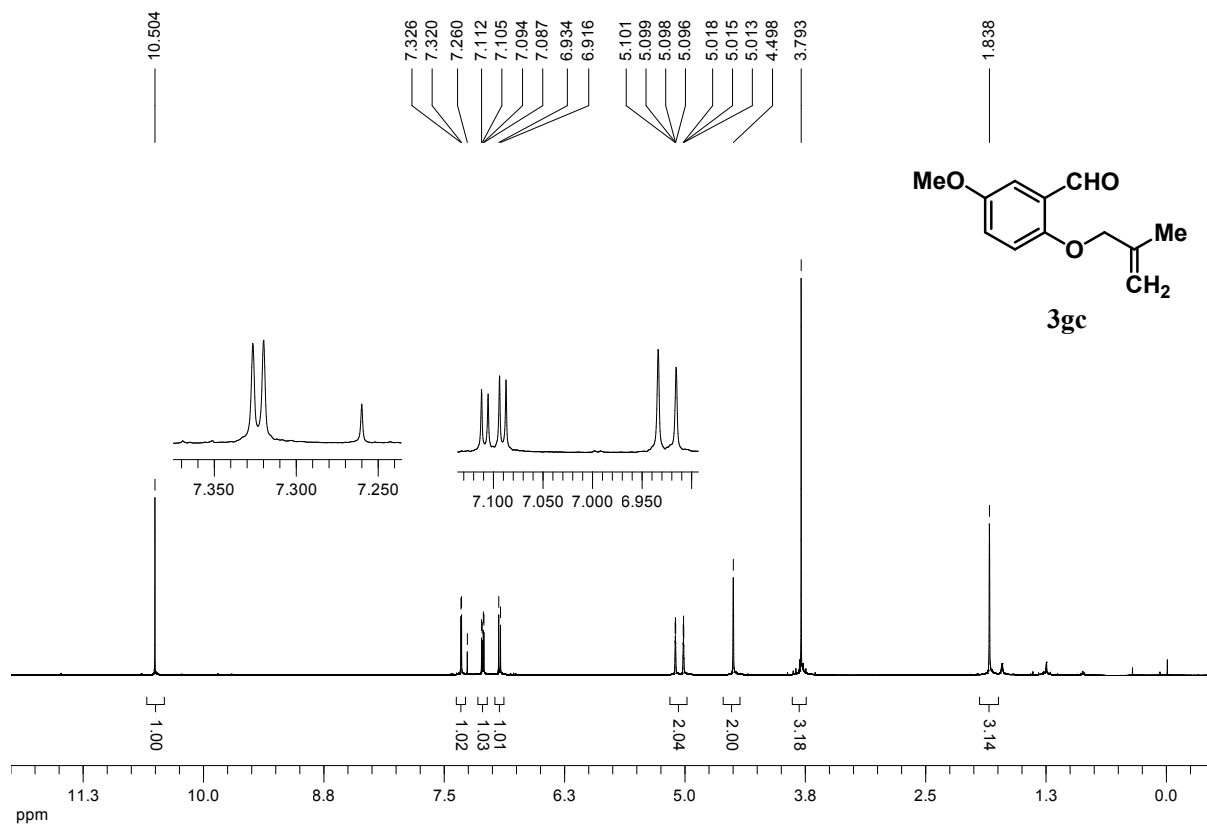
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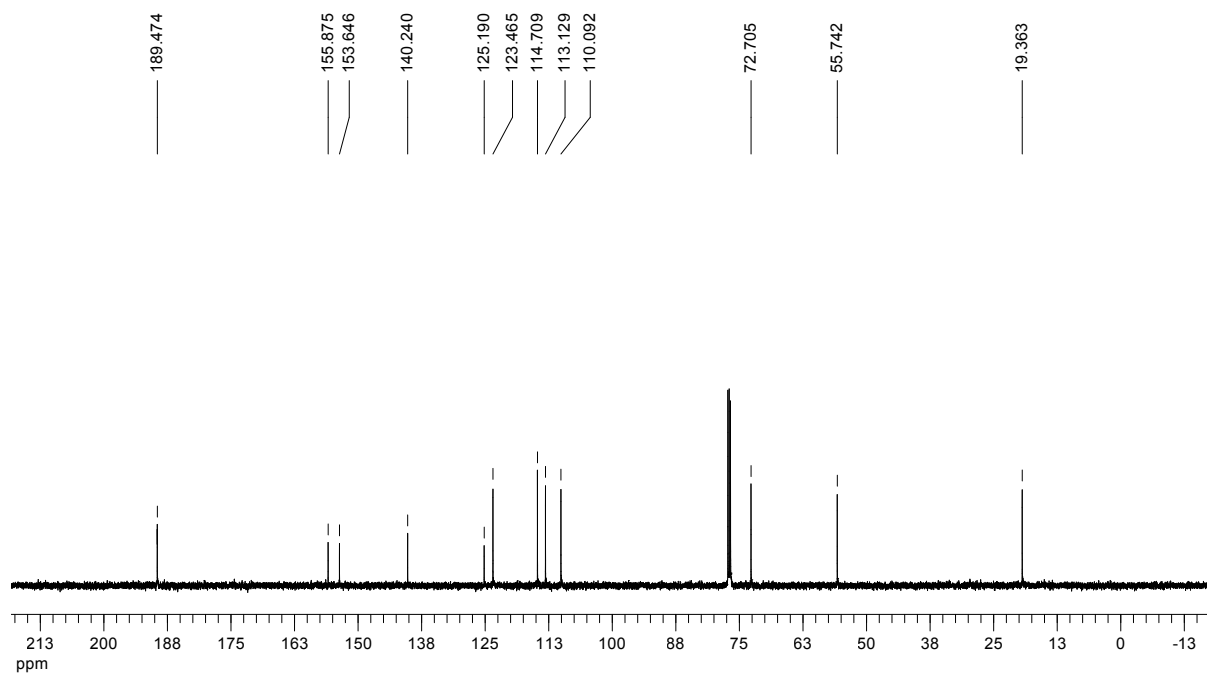
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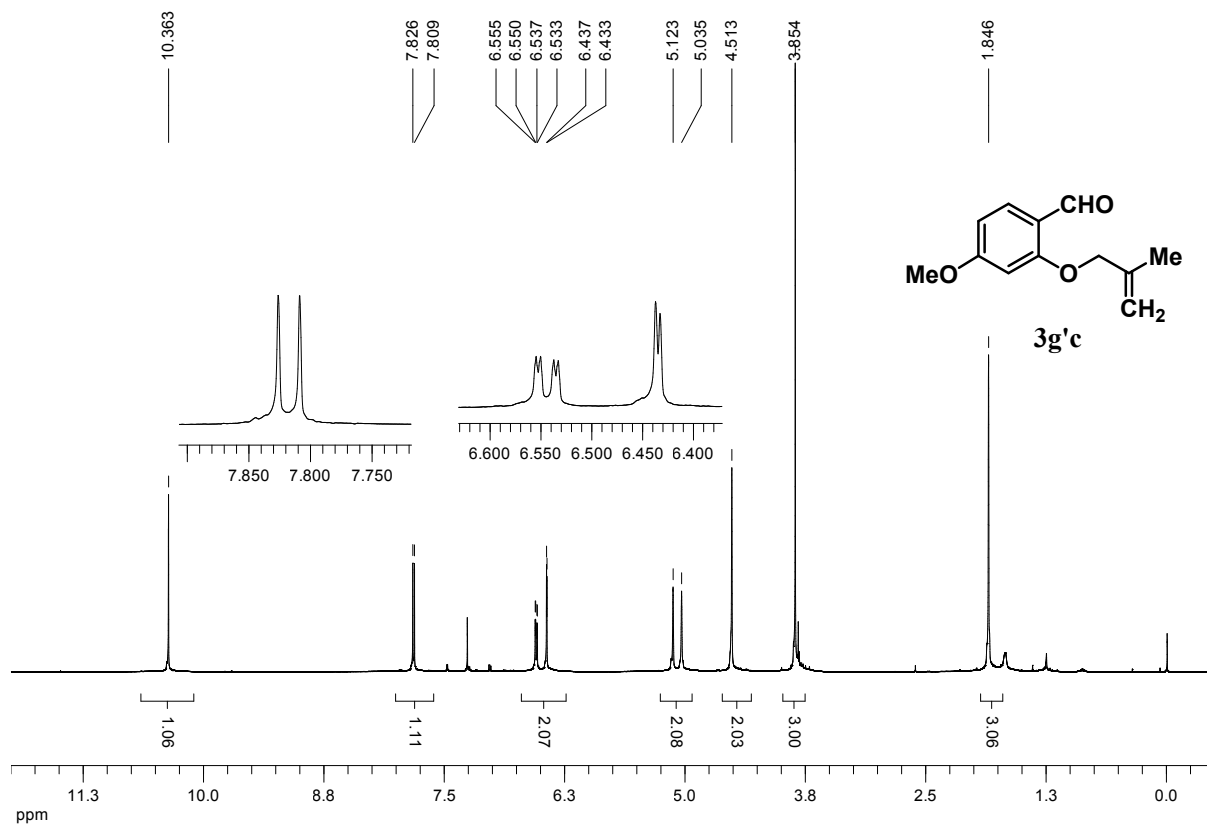
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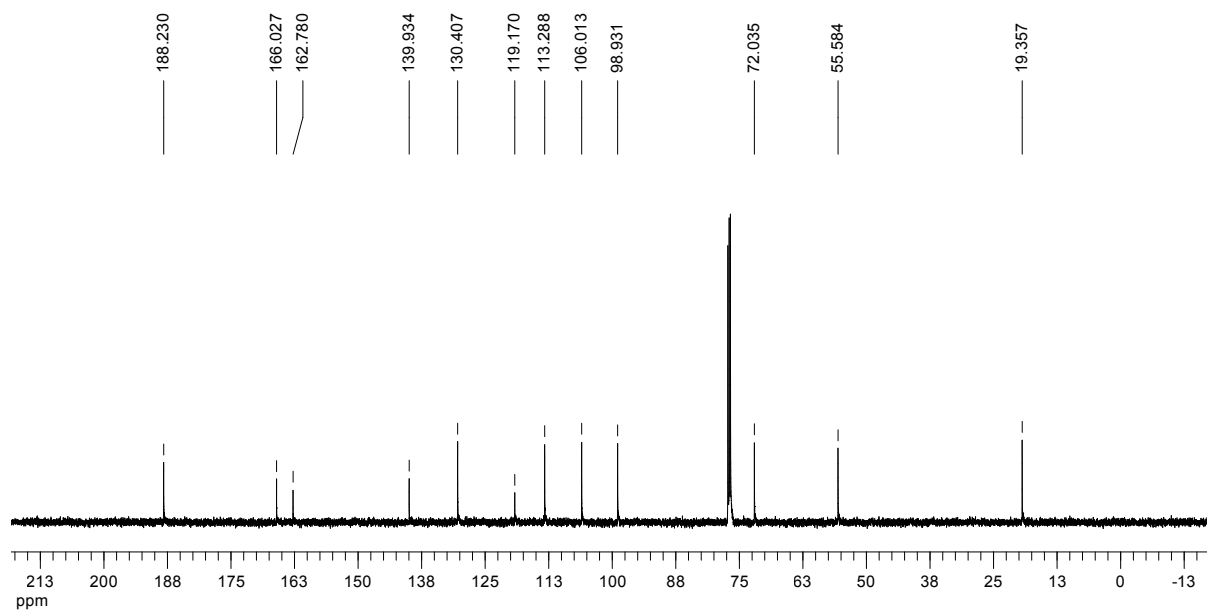
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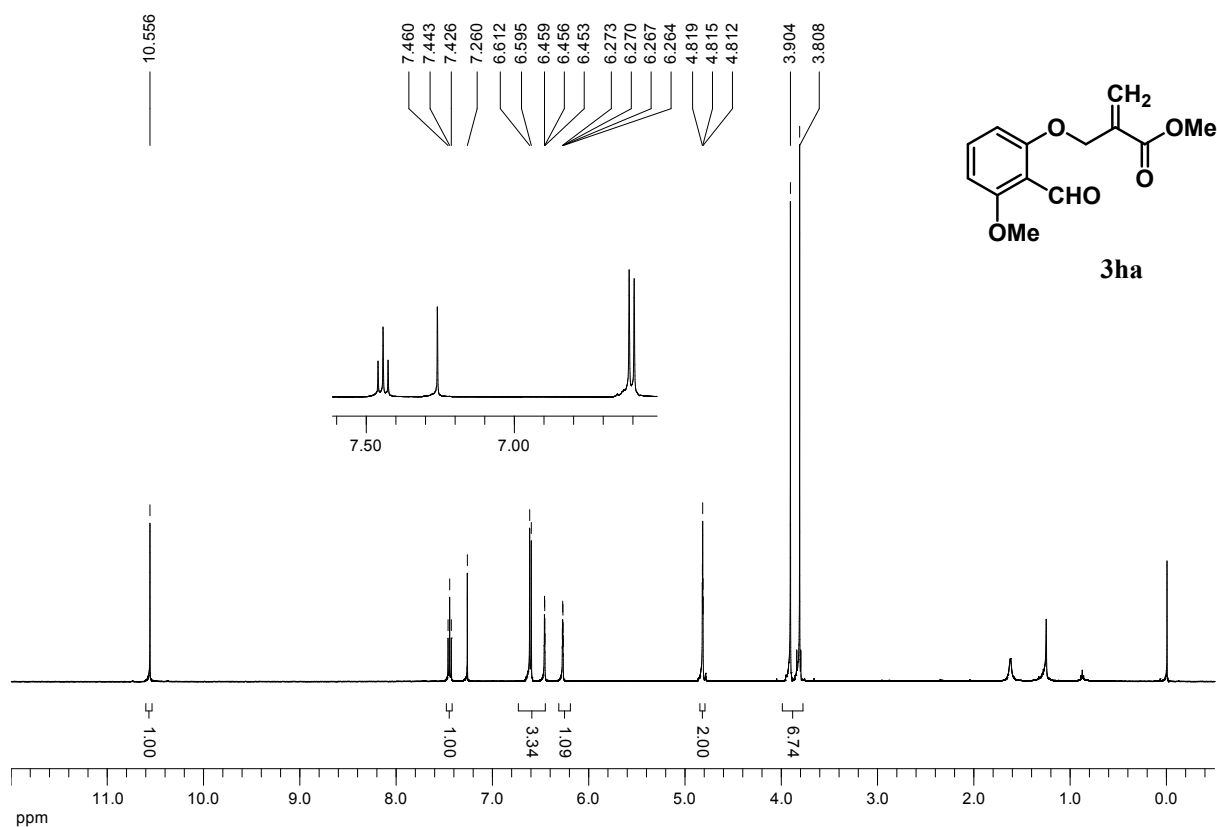
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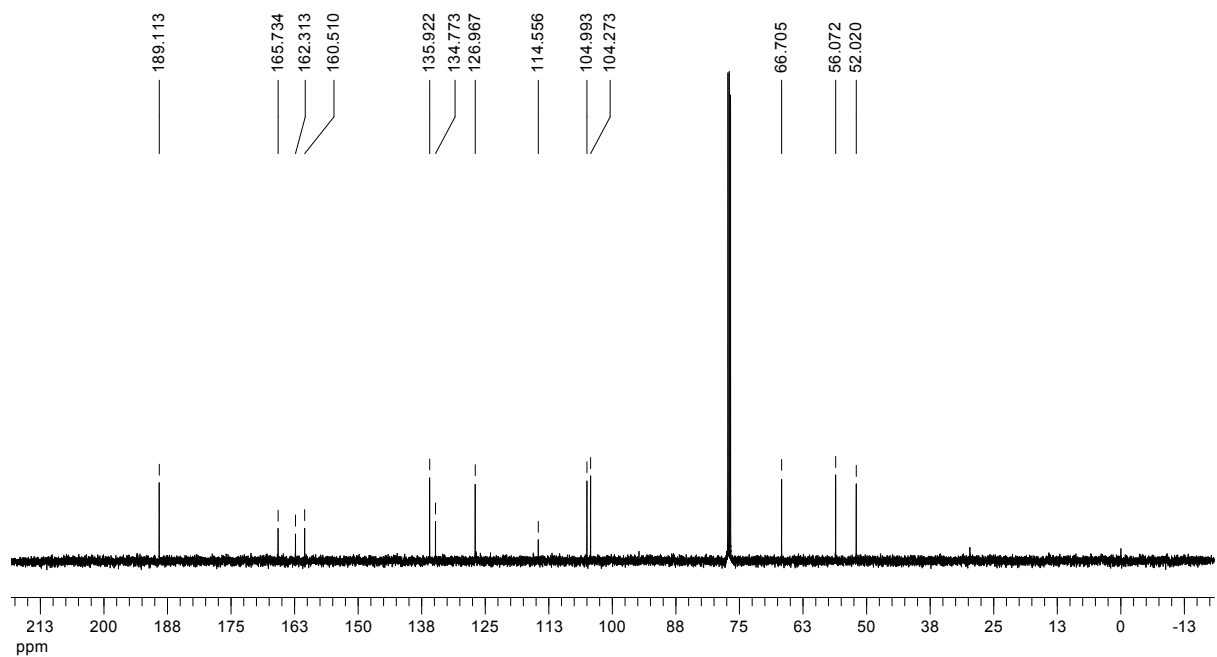
^{13}C -NMR (126 MHz, CDCl_3)



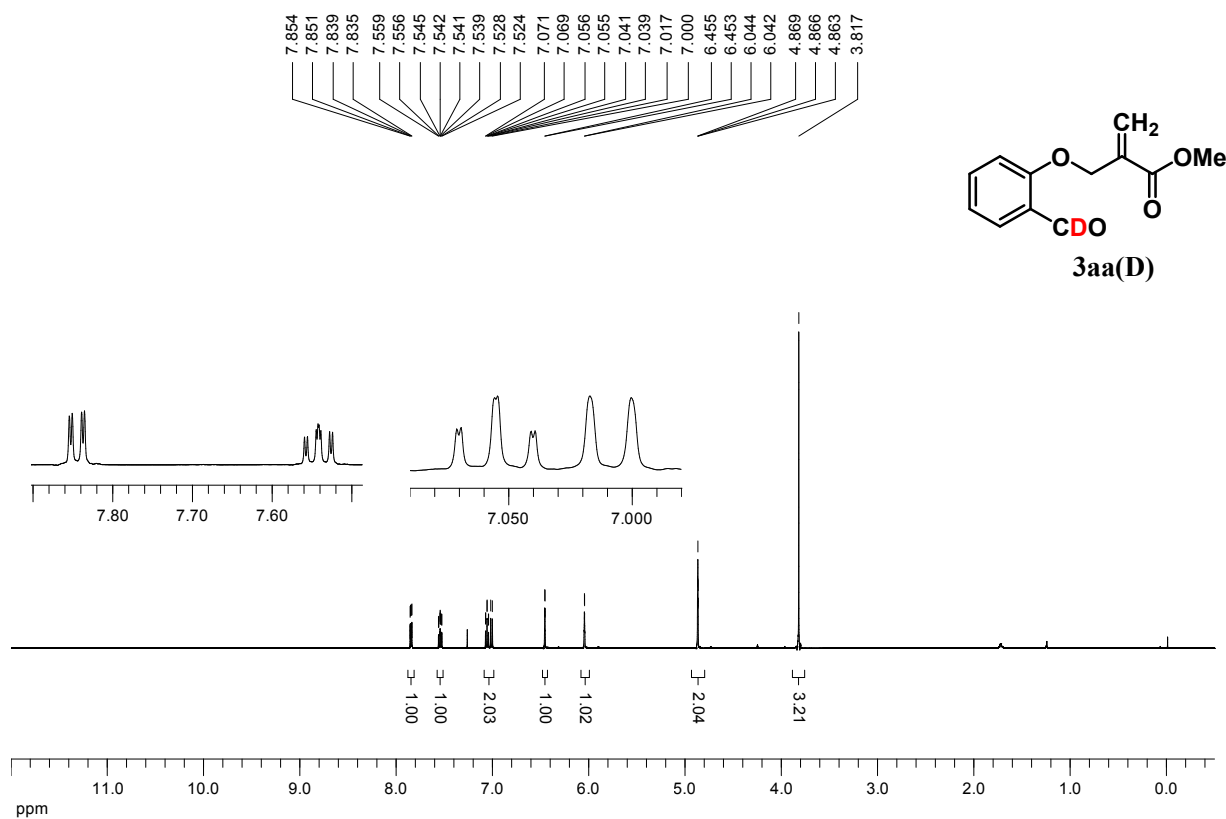
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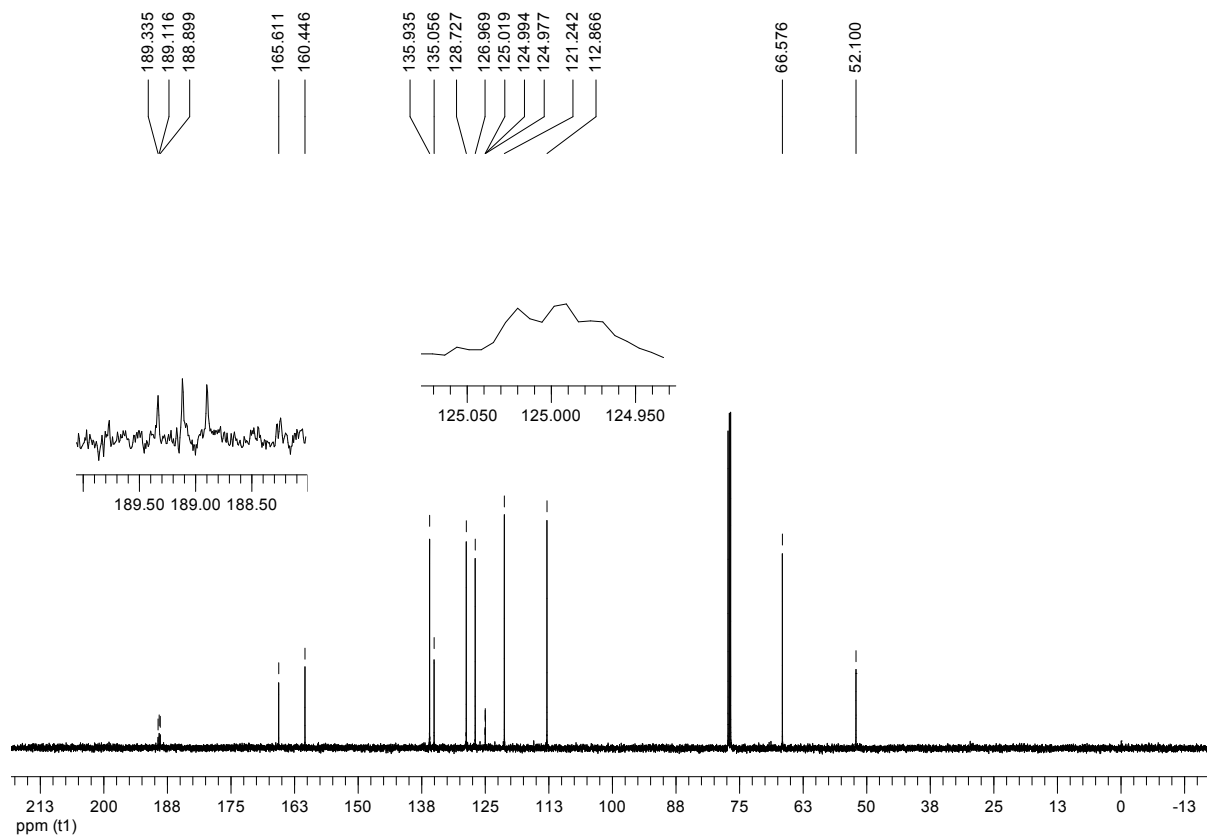
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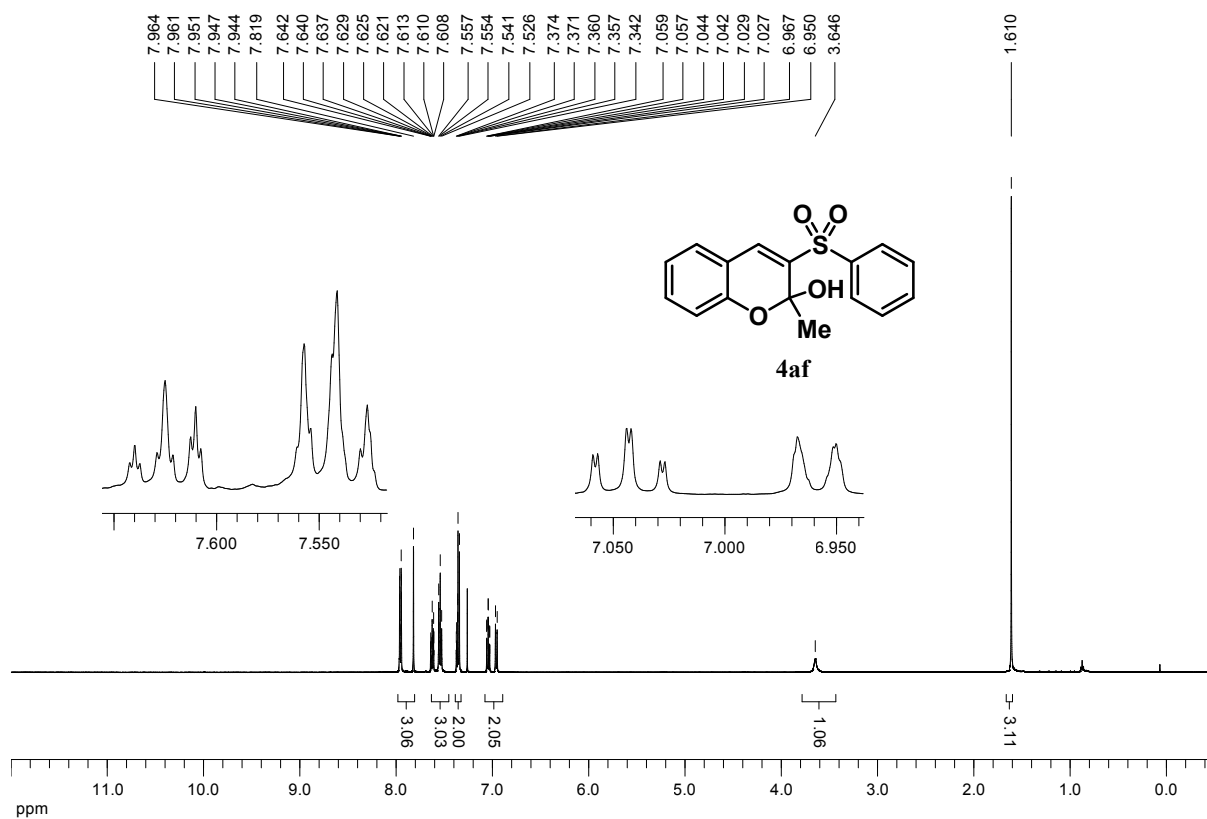
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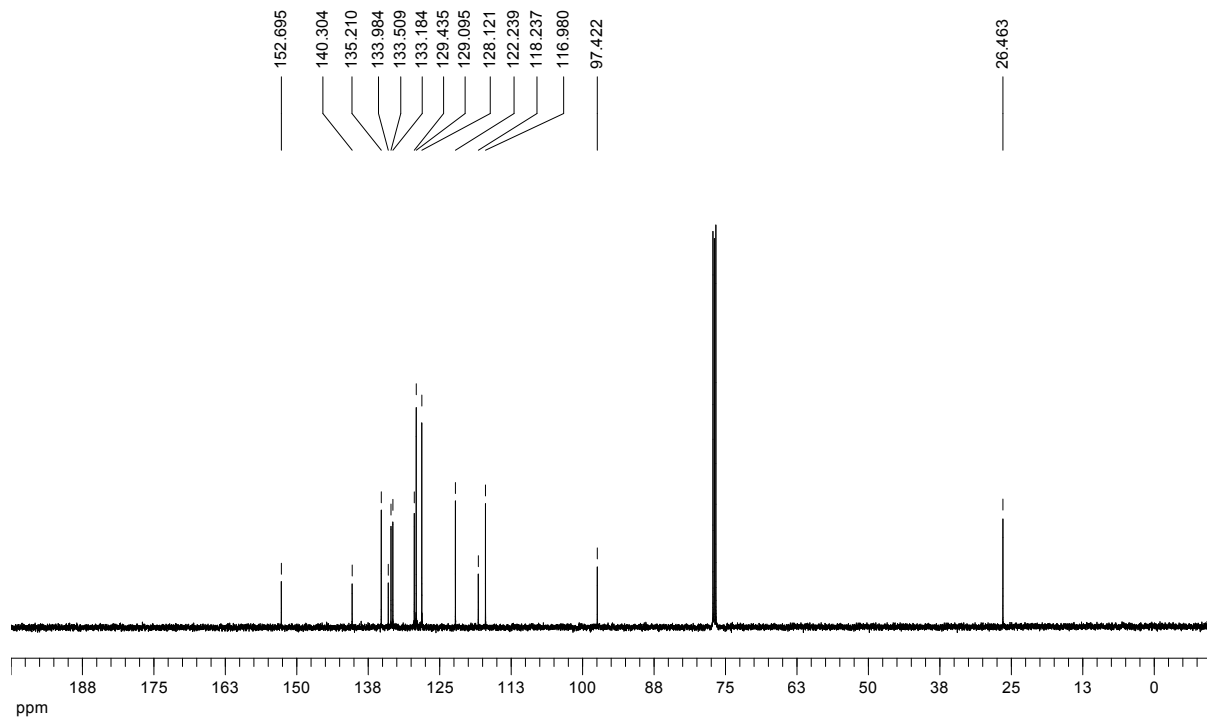
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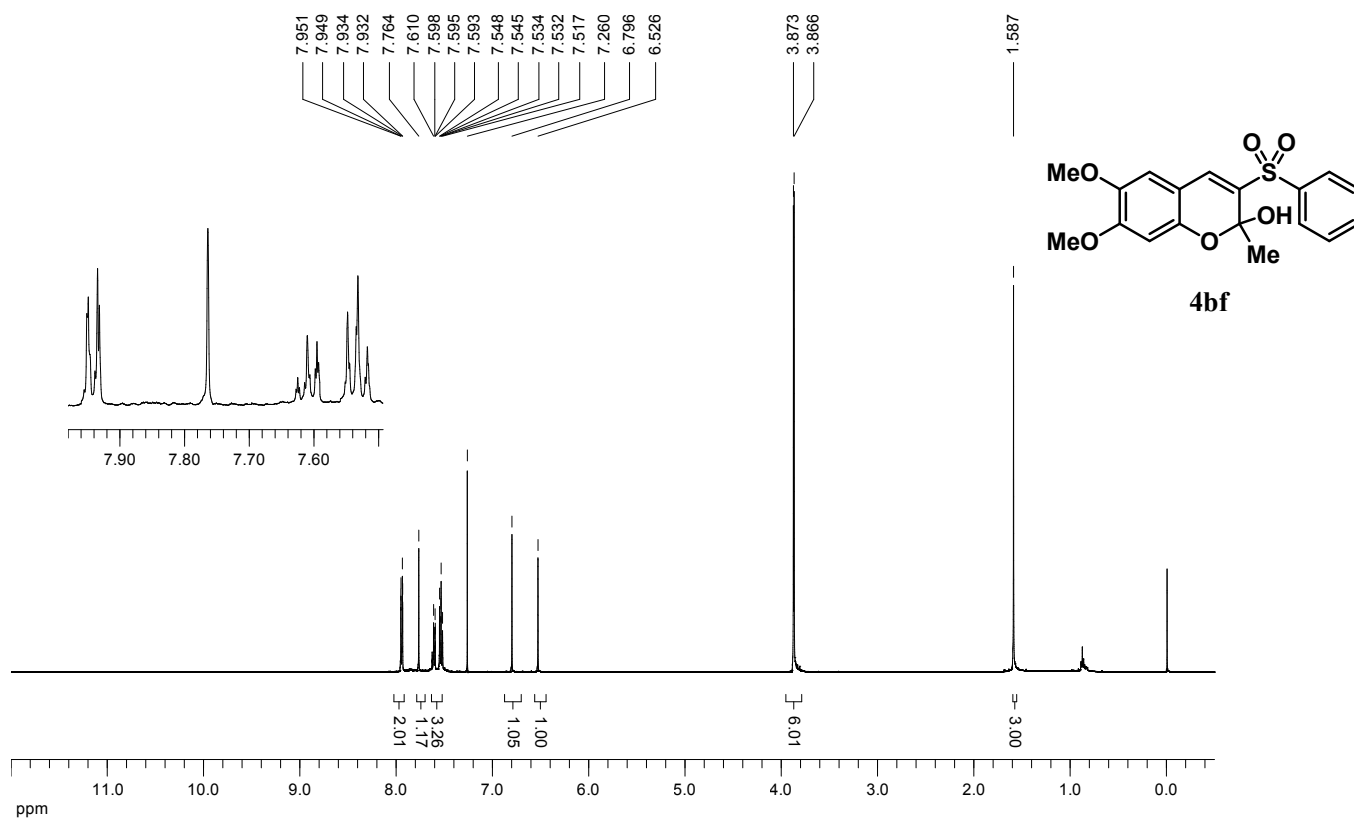
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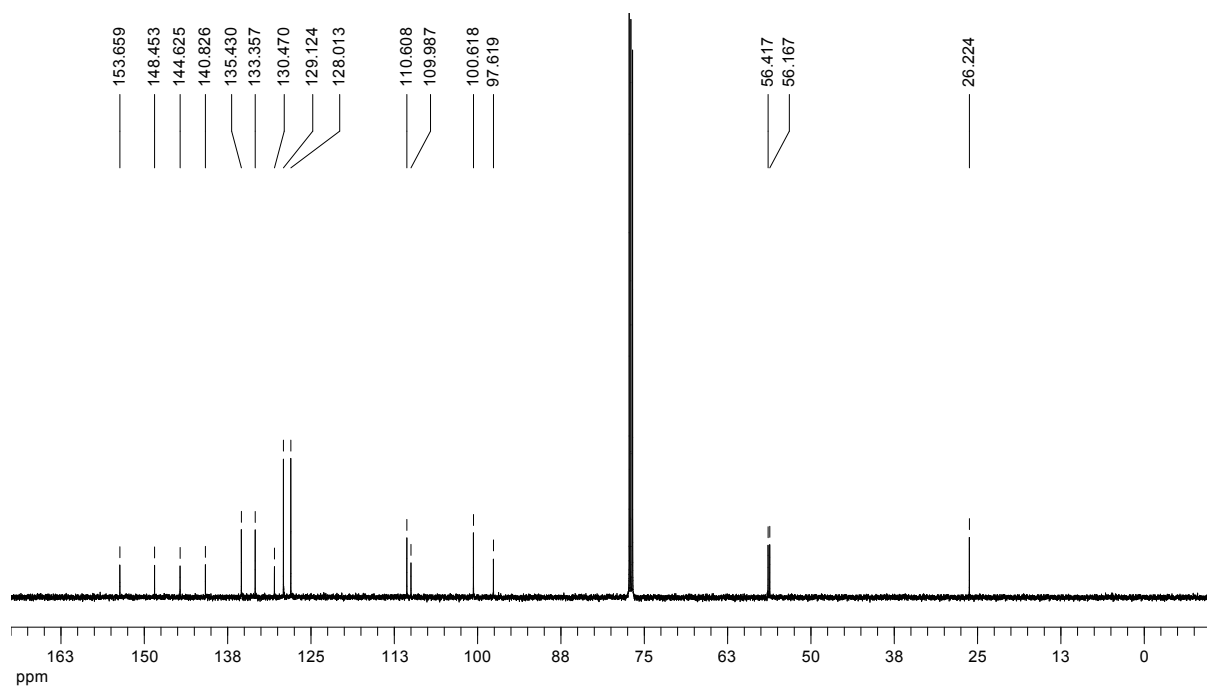
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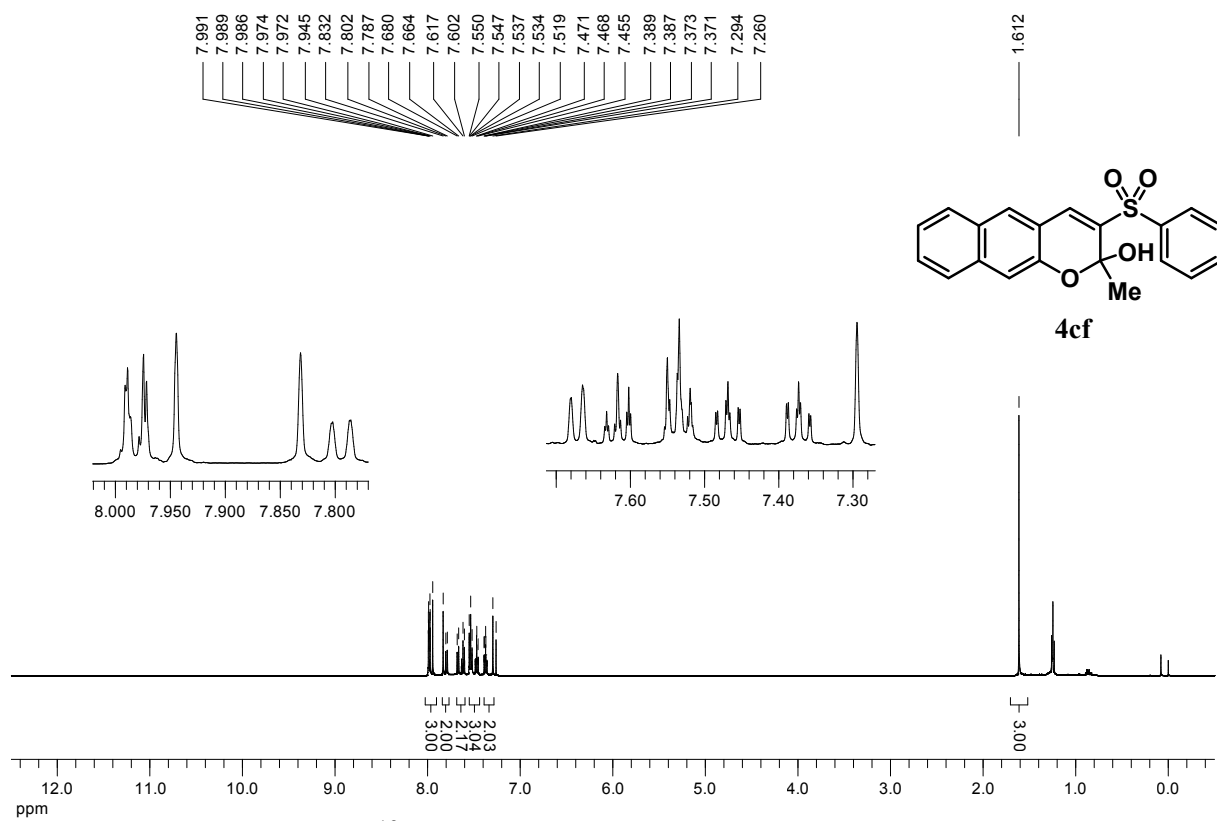
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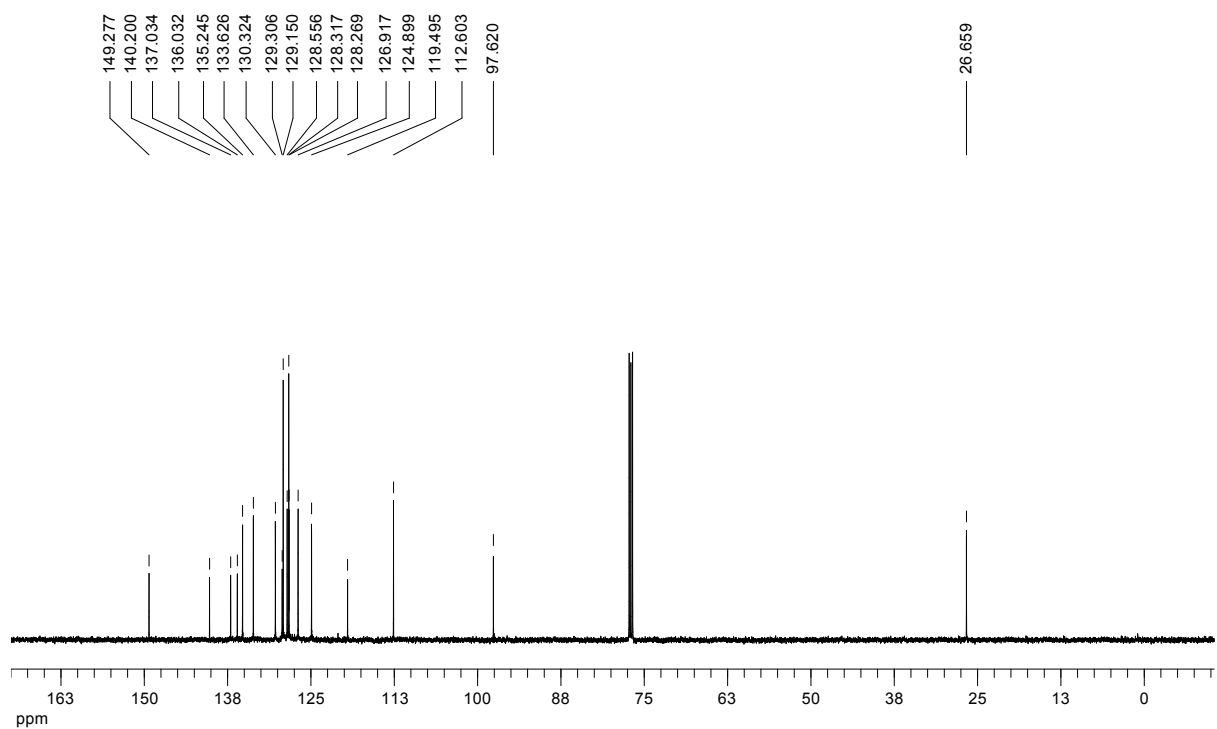
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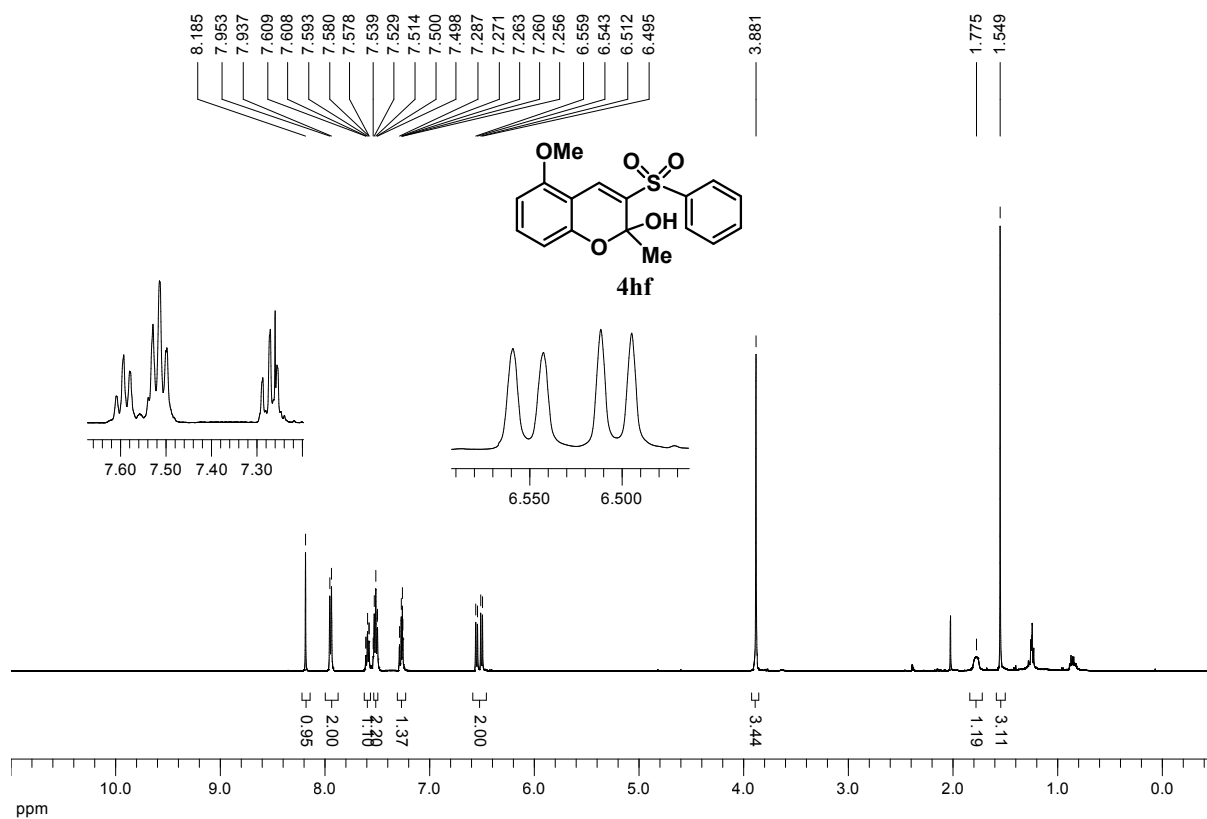
$^1\text{H-NMR}$ (500 MHz, CDCl_3)



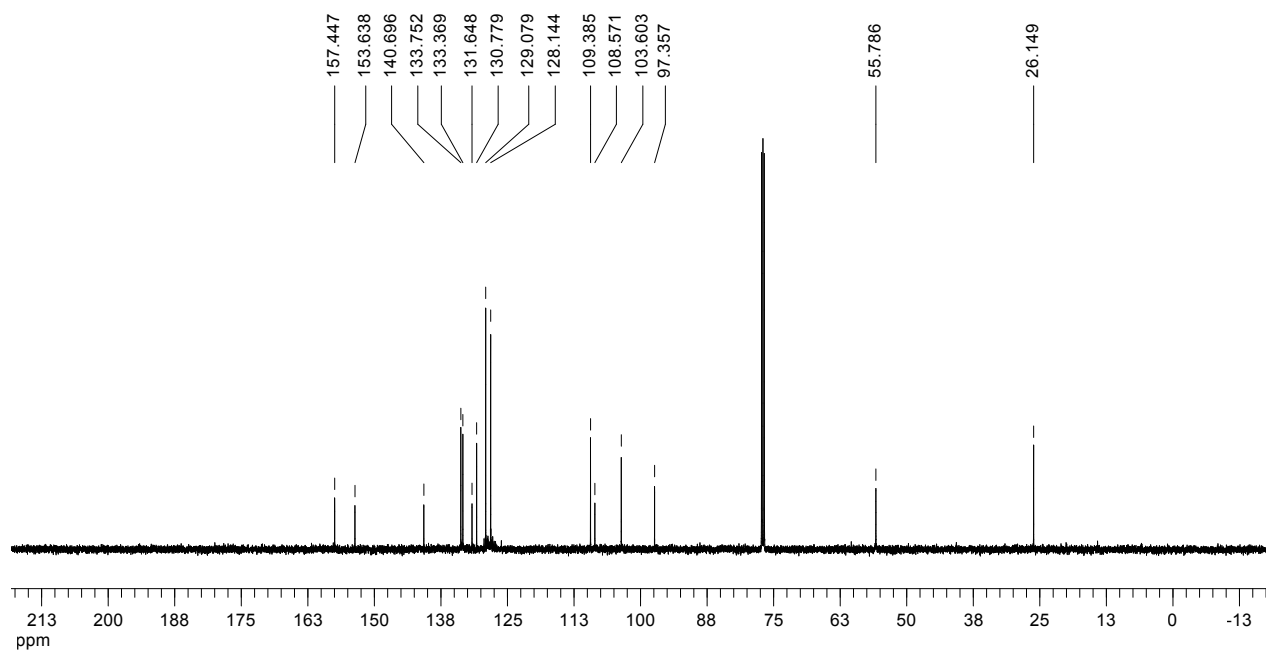
$^{13}\text{C-NMR}$ (126 MHz, CDCl_3)



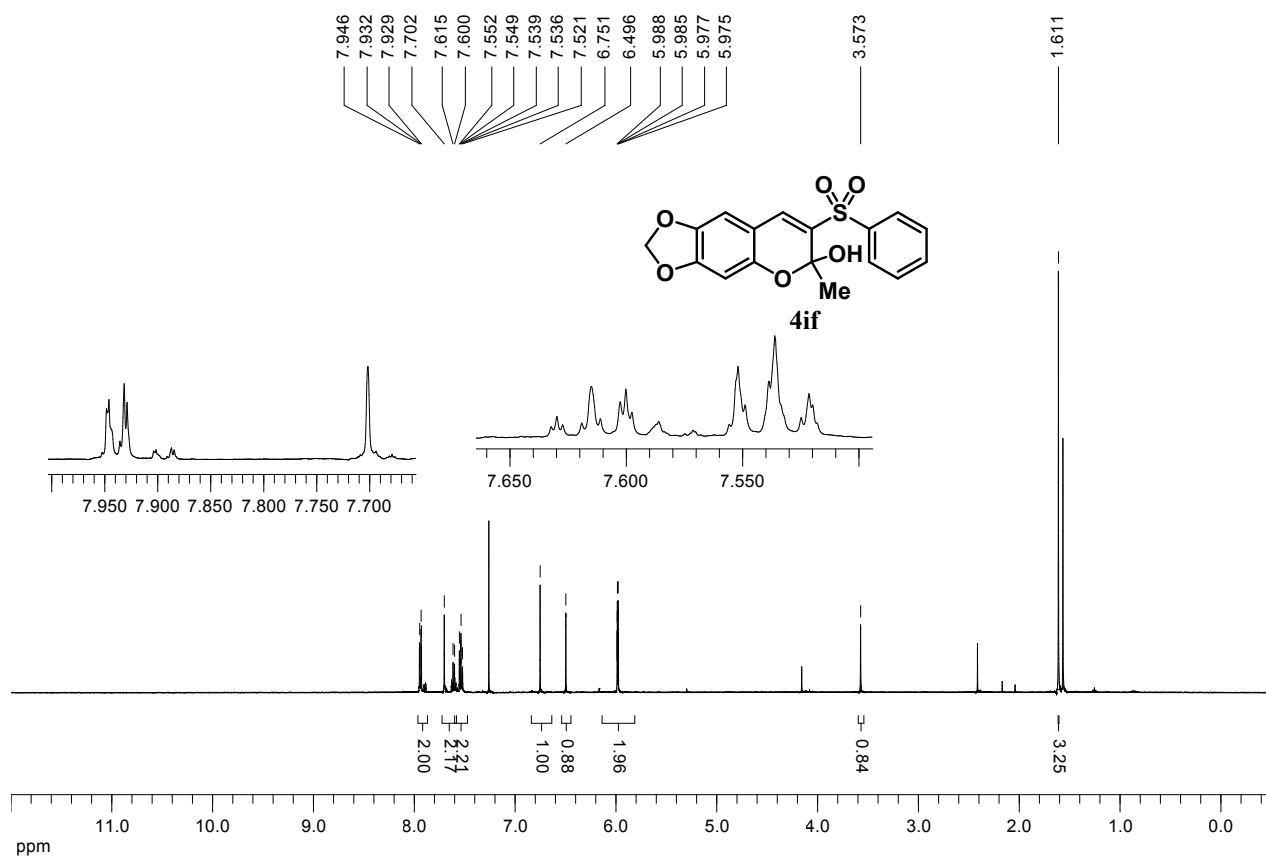
¹H-NMR (500 MHz, CDCl₃)



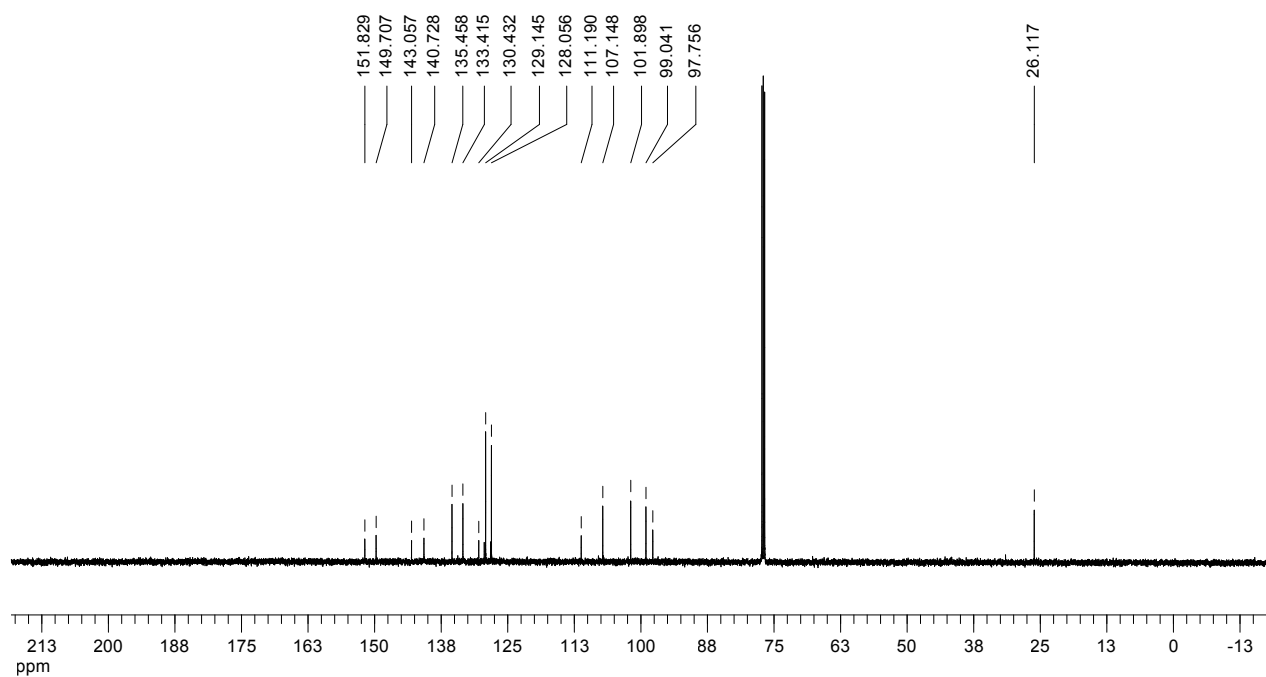
¹³C-NMR (126 MHz, CDCl₃)



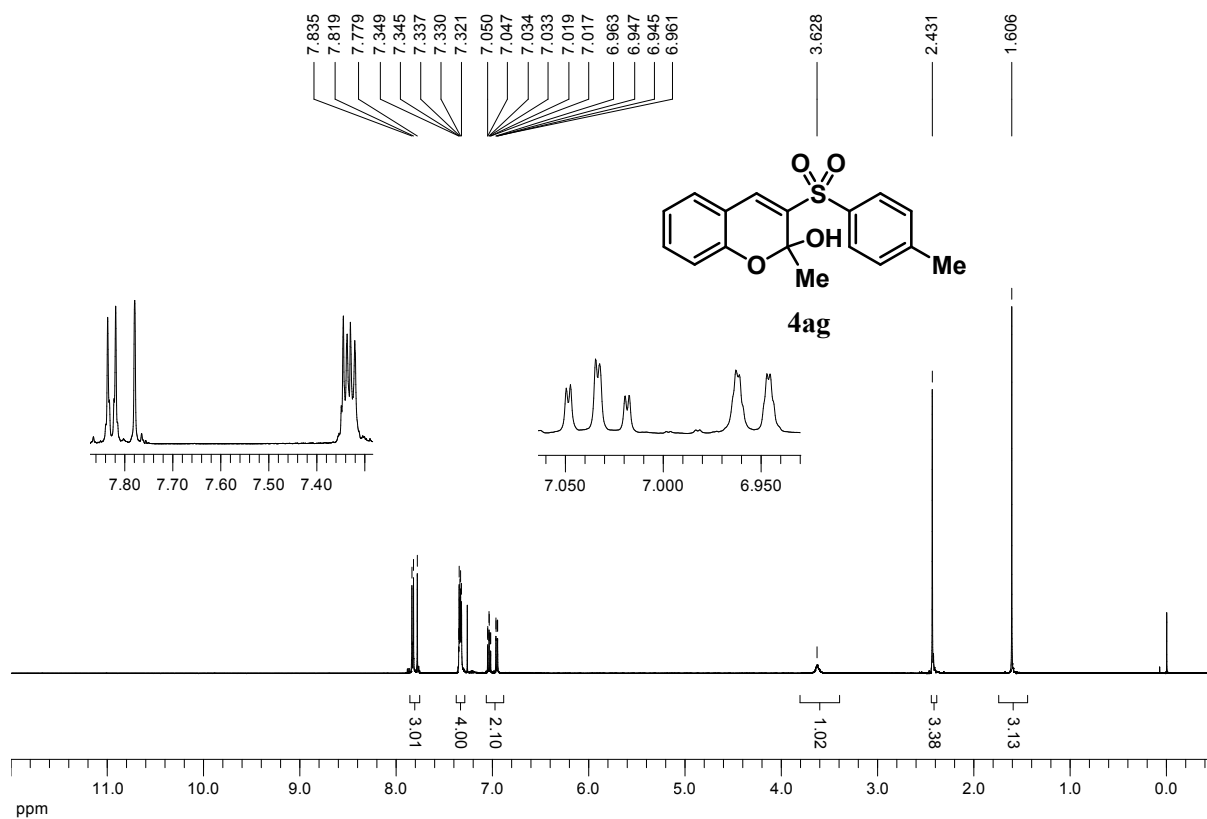
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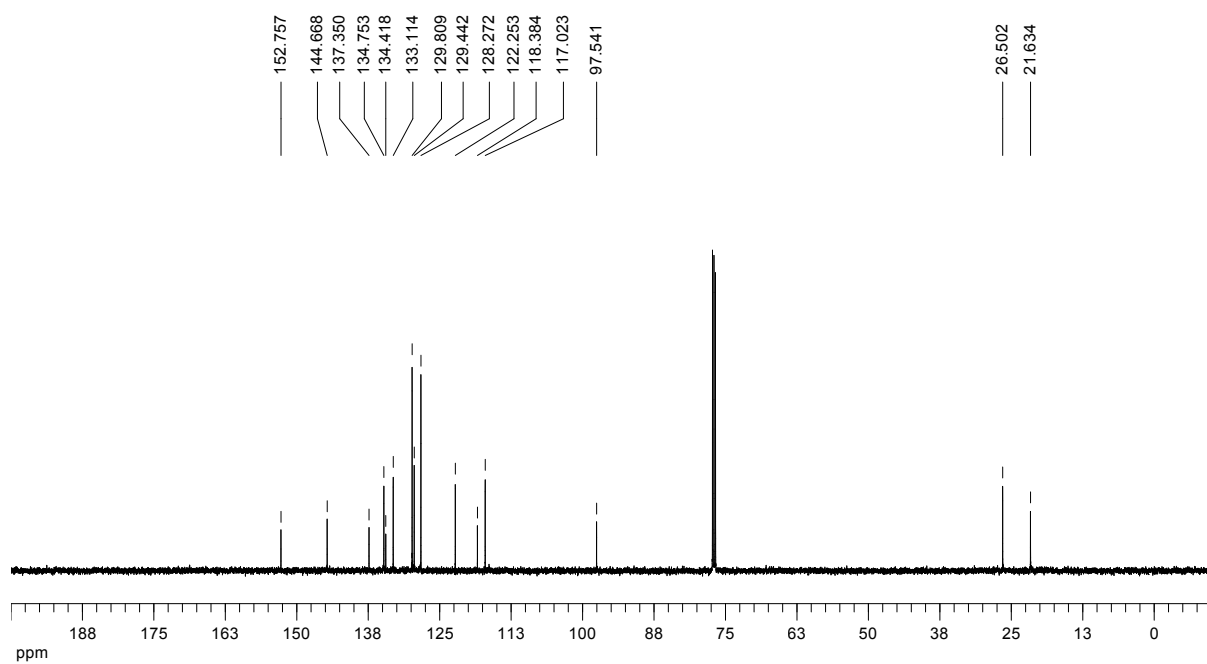
¹³C-NMR (126 MHz, CDCl₃)



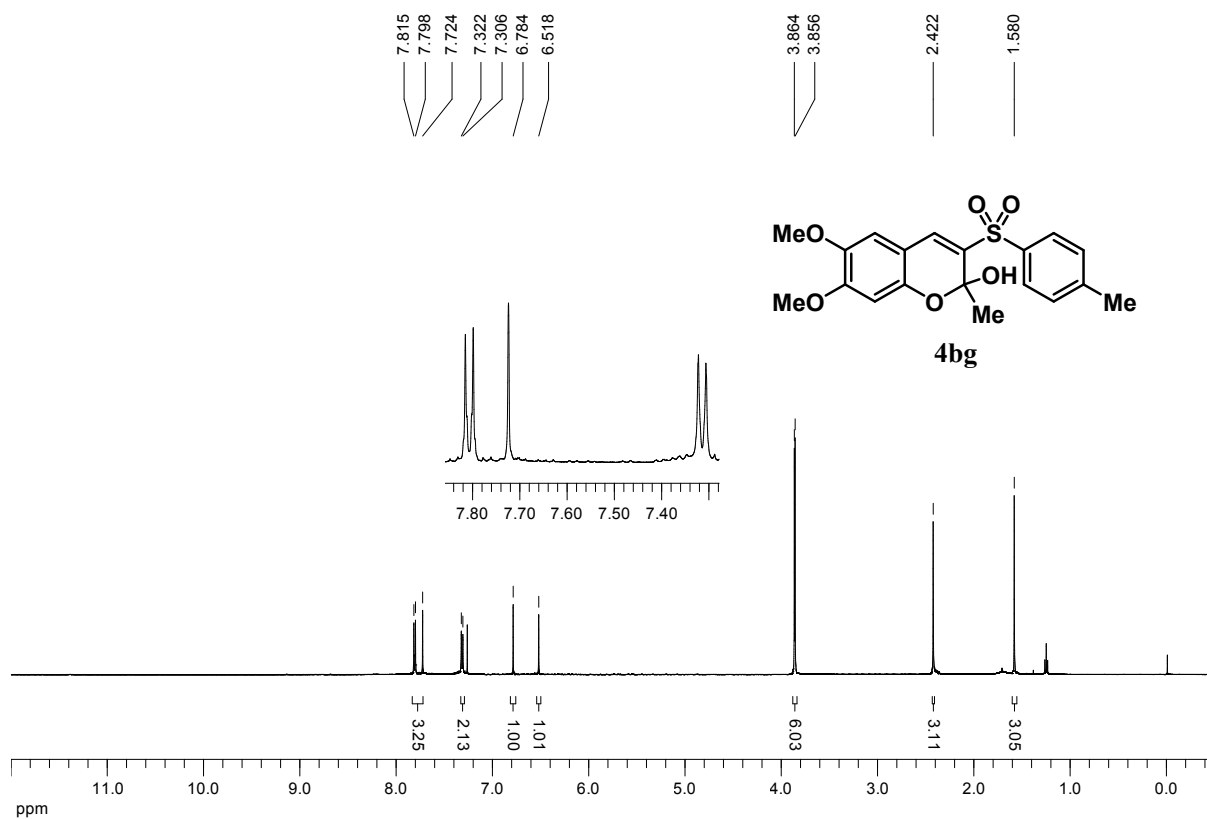
¹H-NMR (500 MHz, CDCl₃)



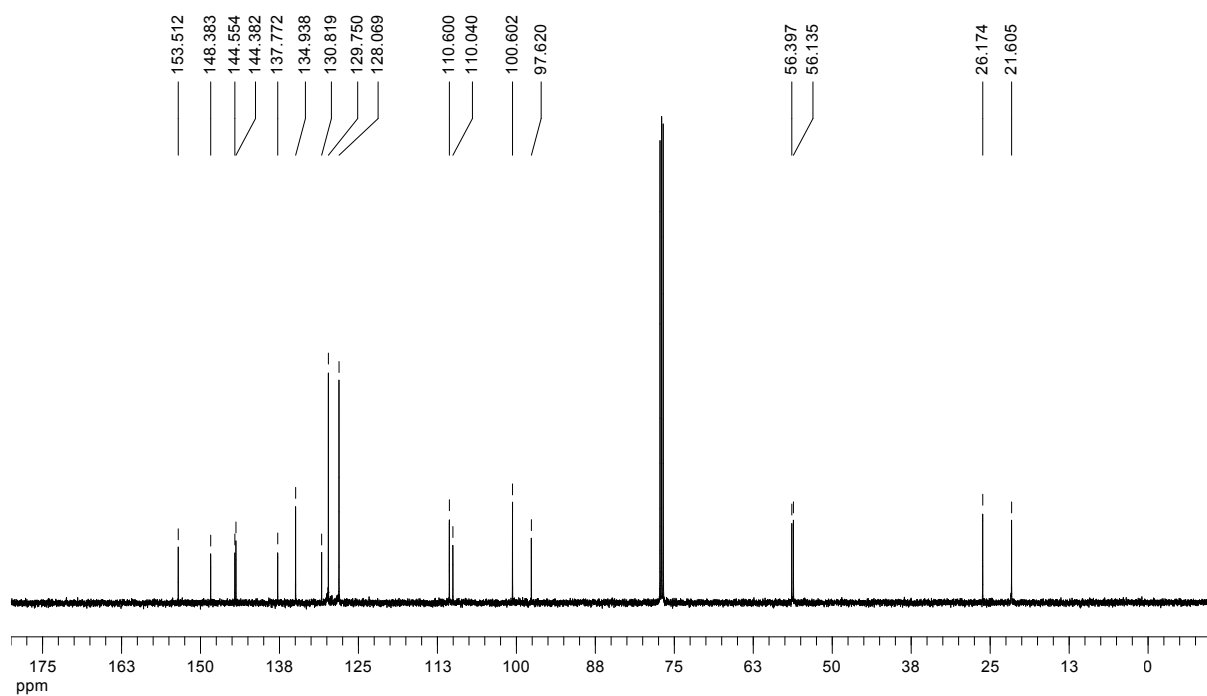
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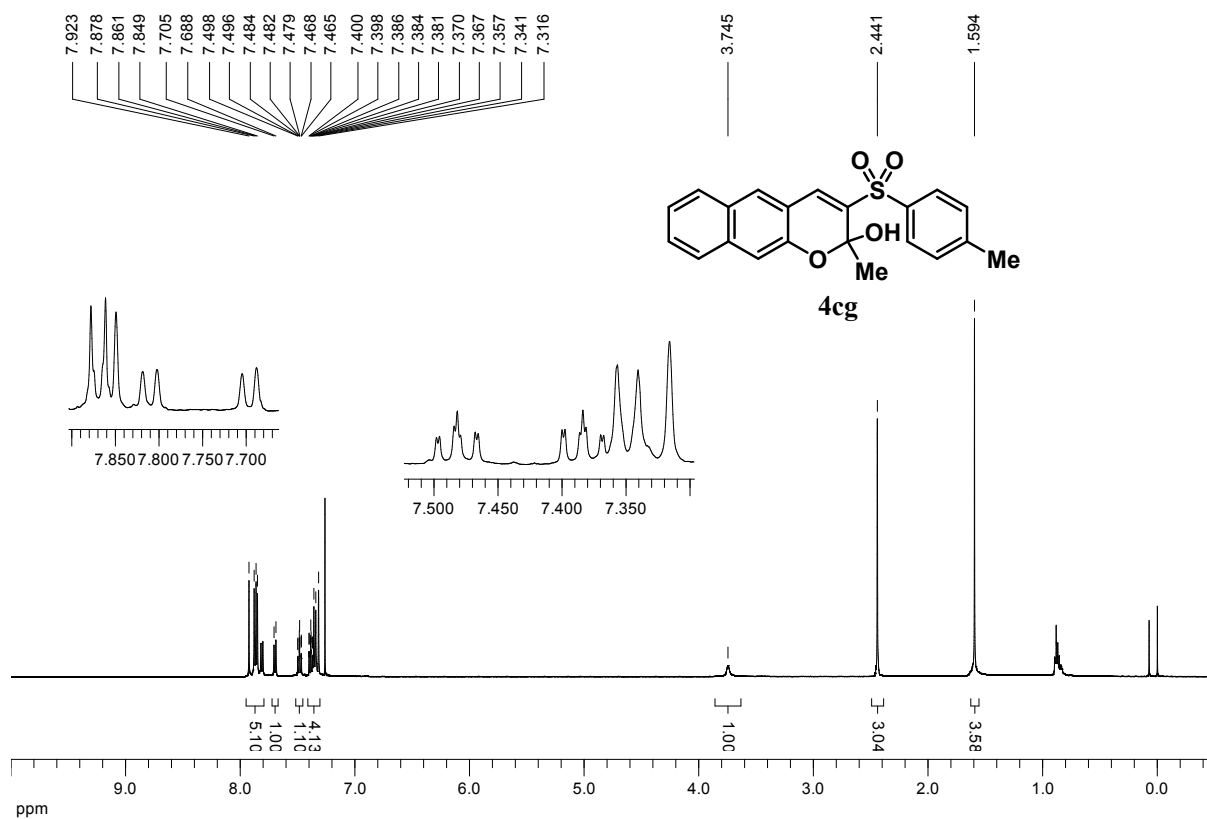
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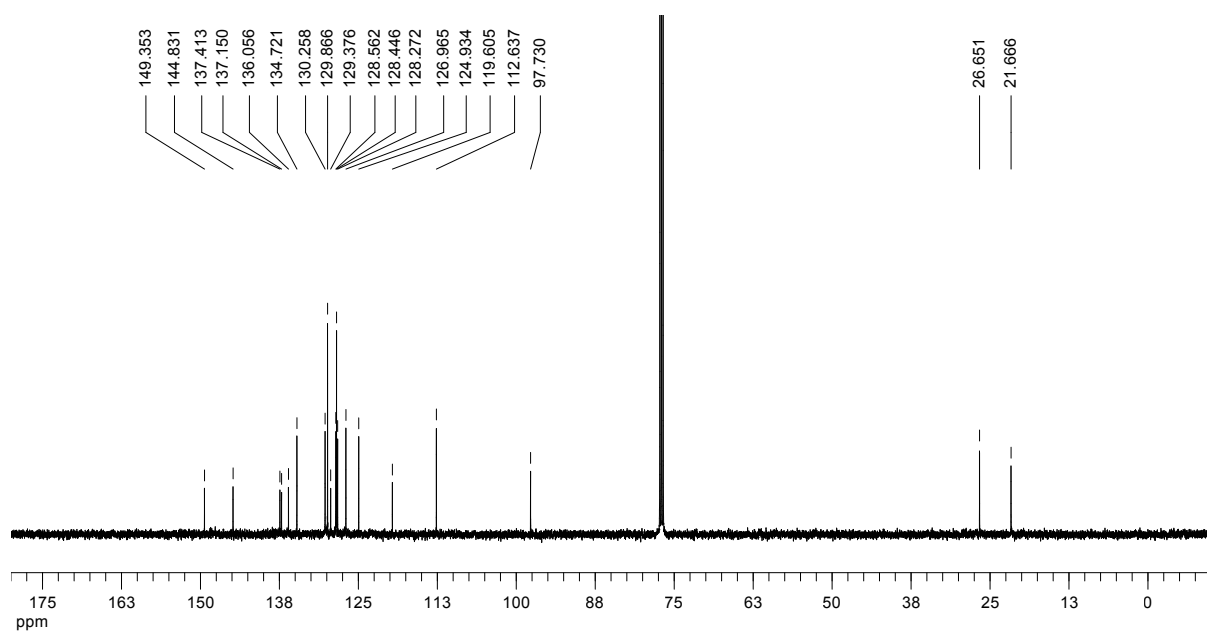
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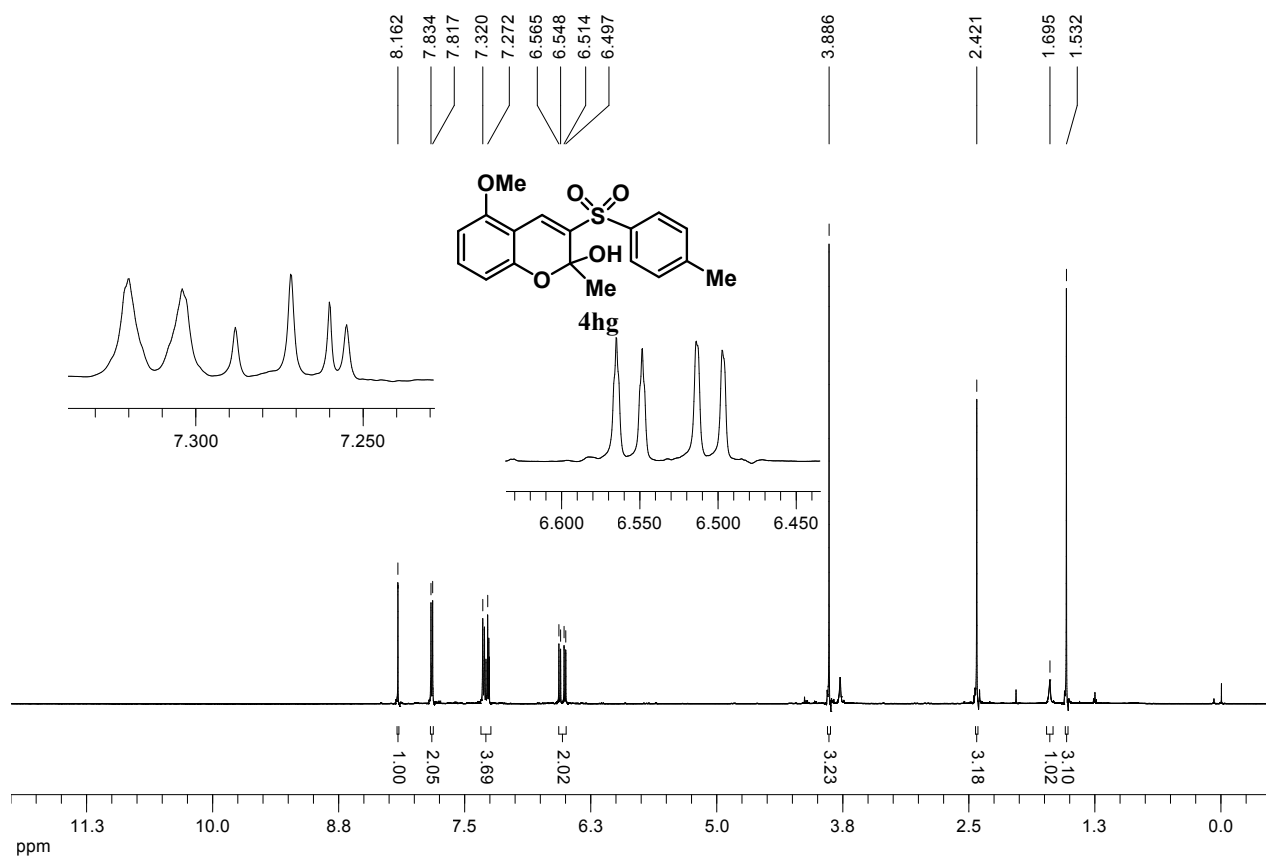
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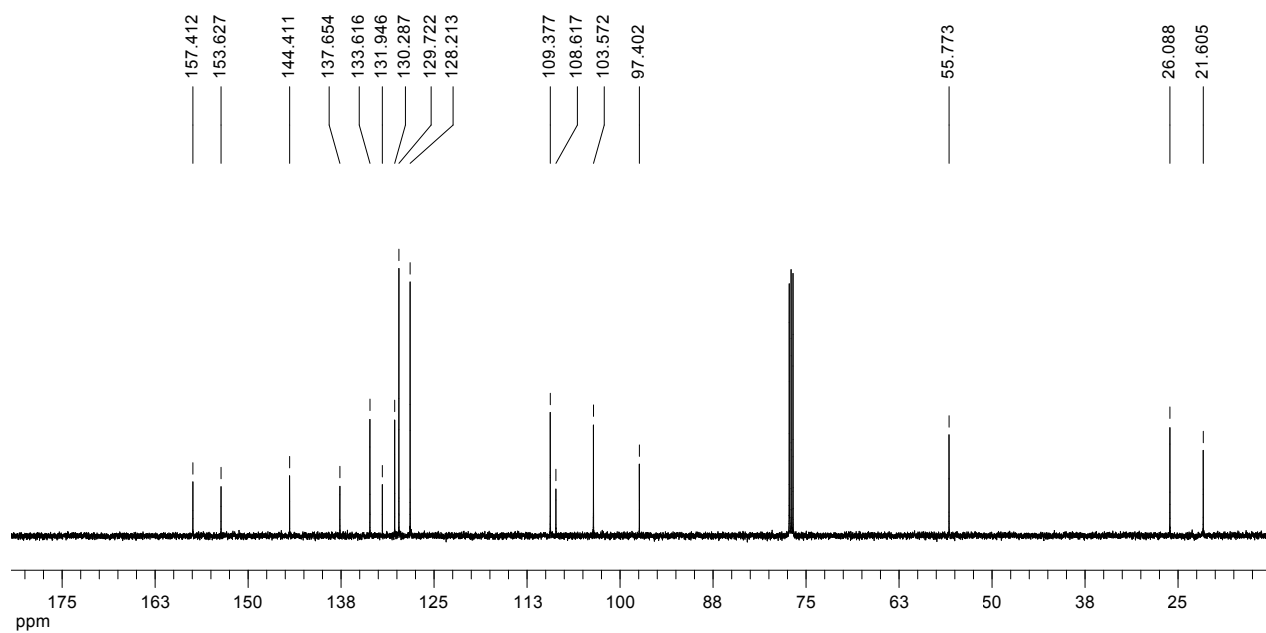
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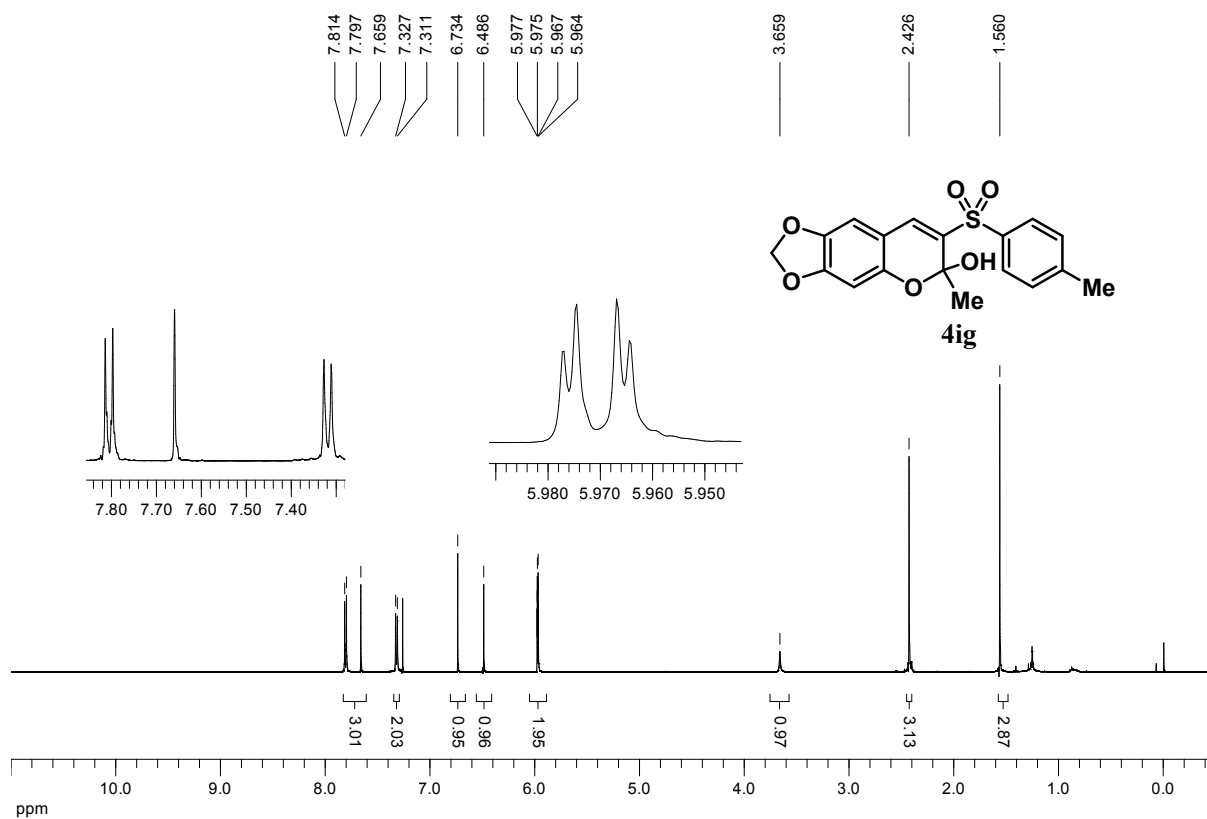
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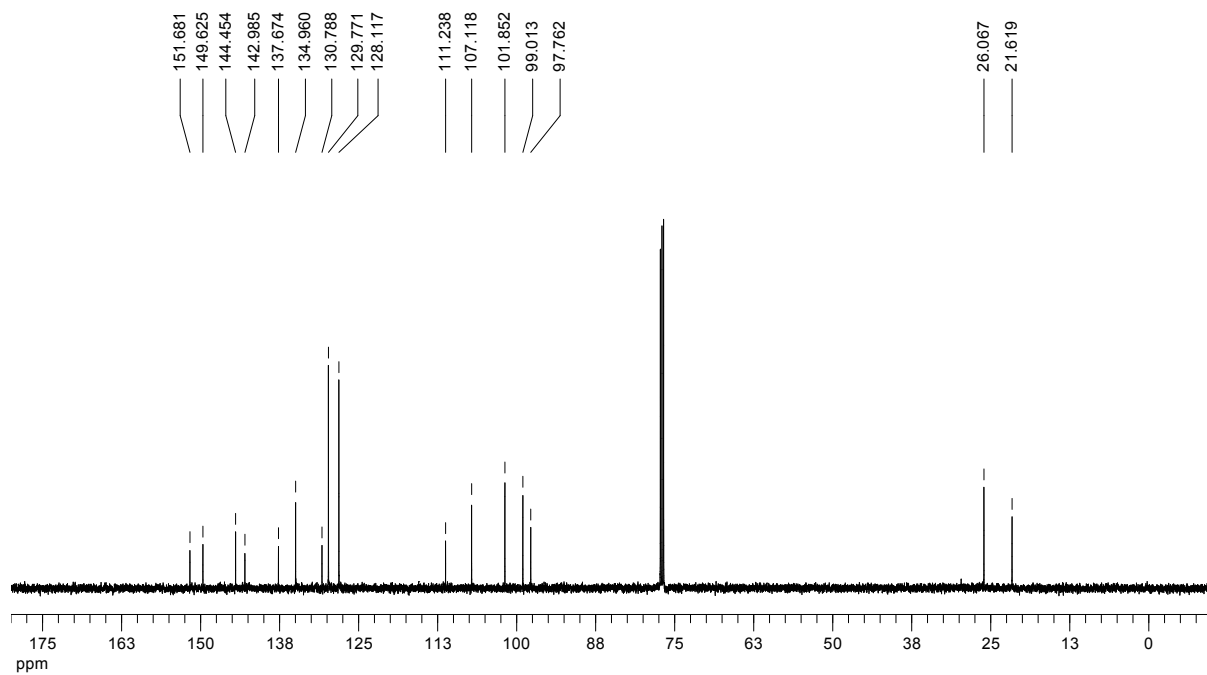
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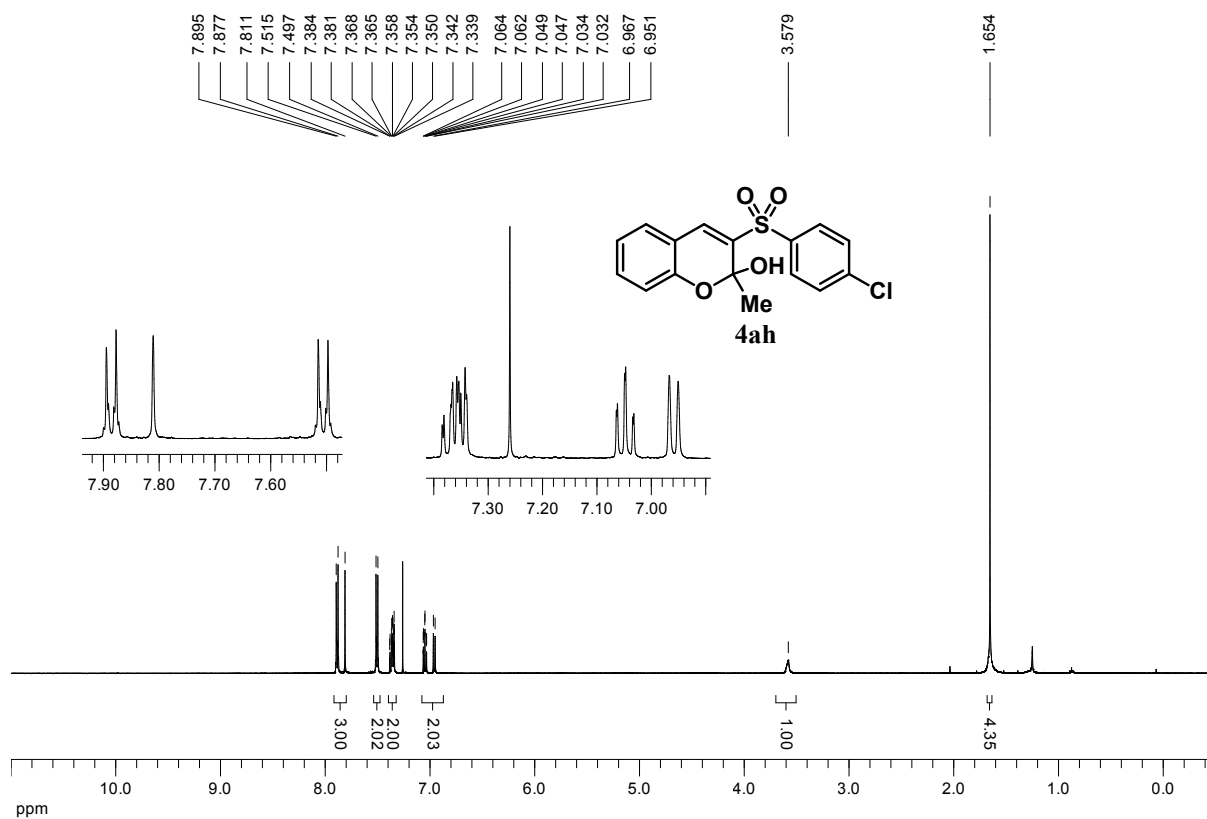
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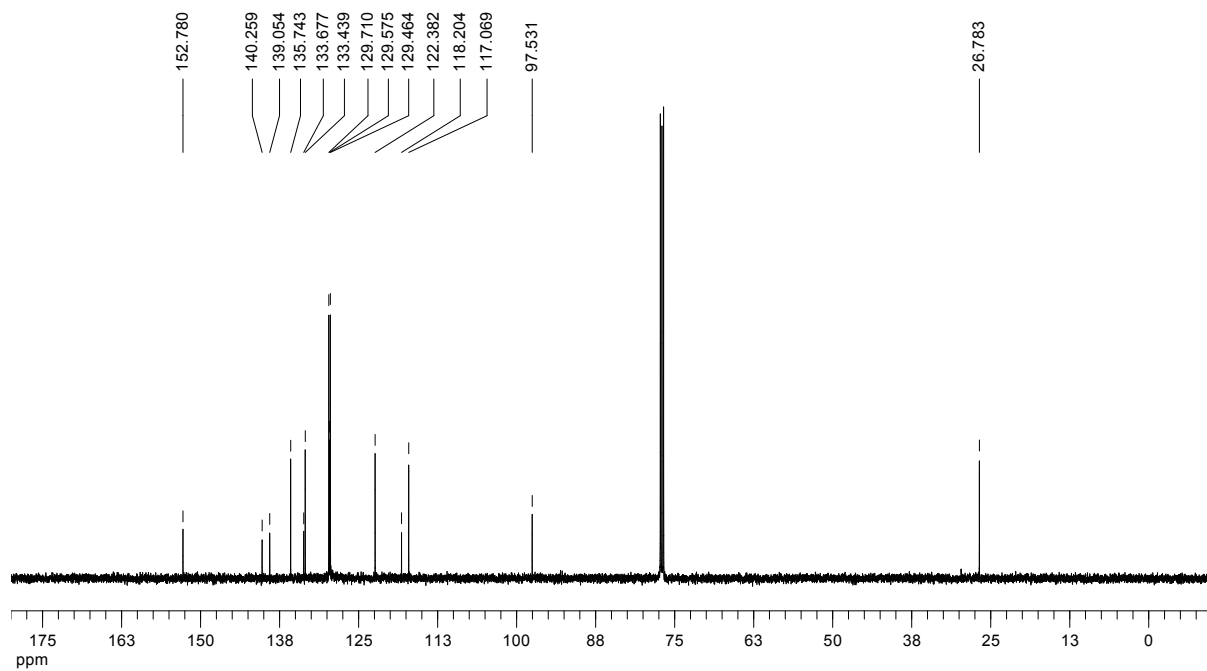
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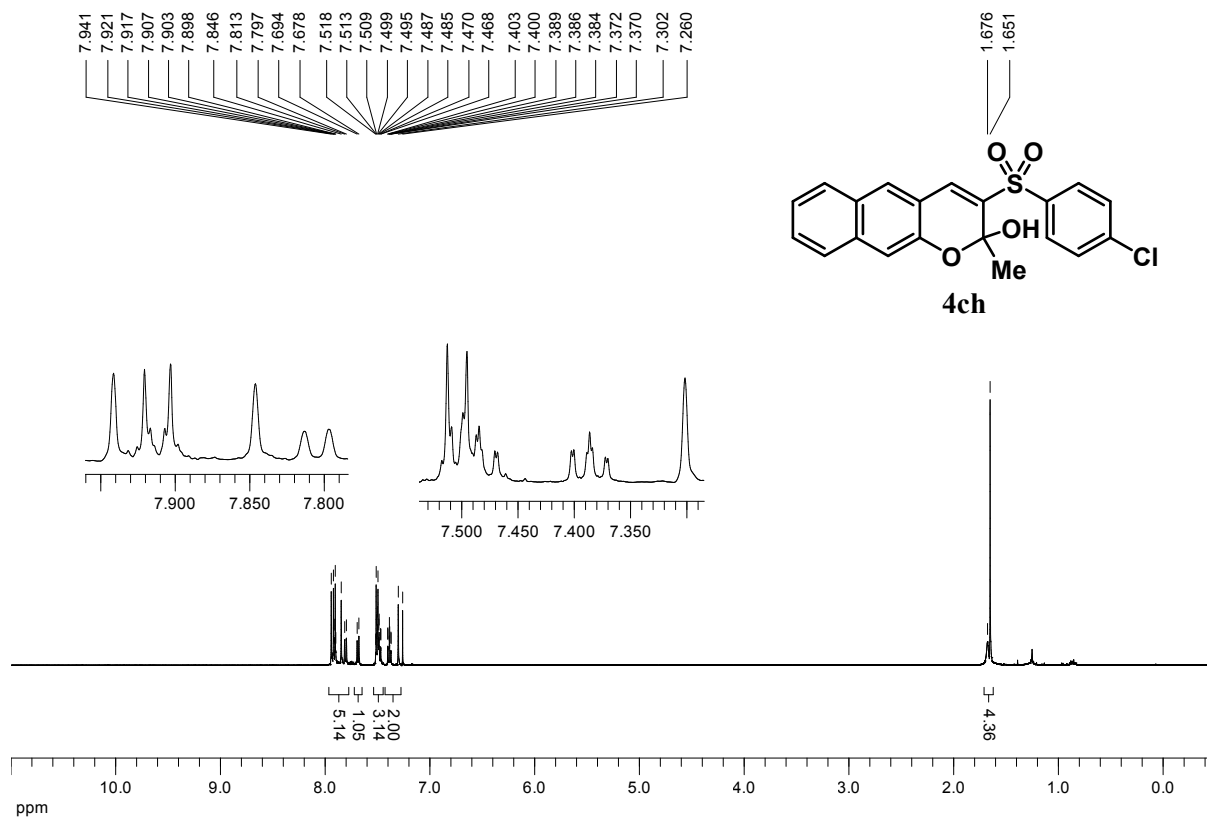
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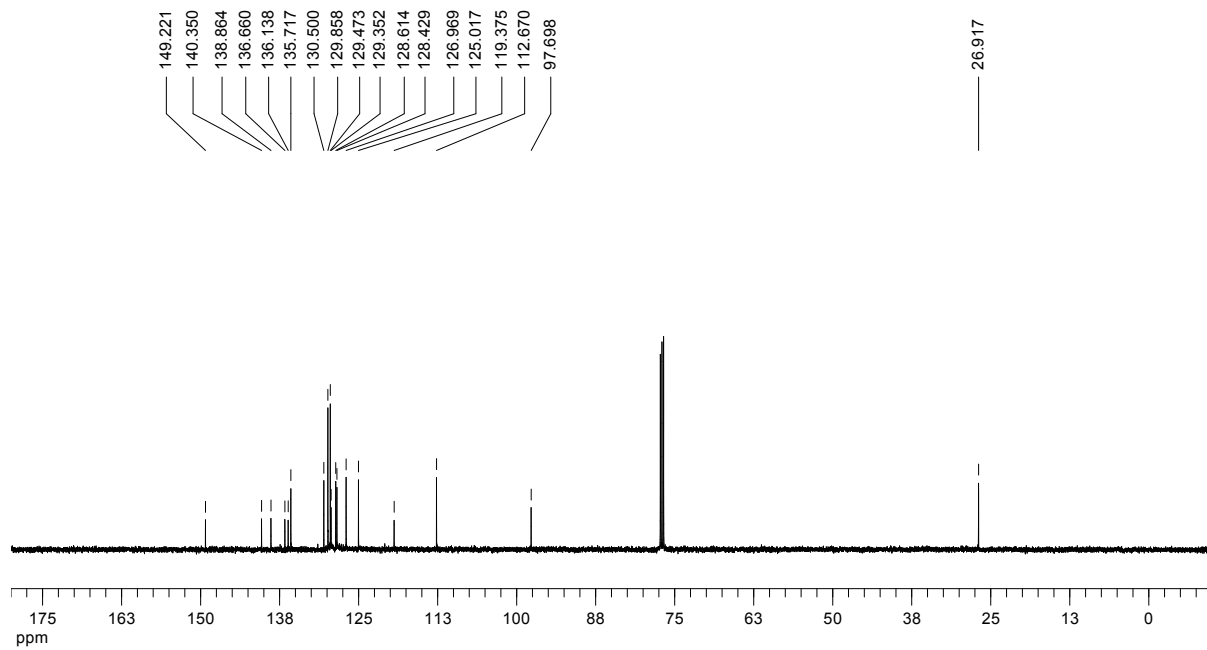
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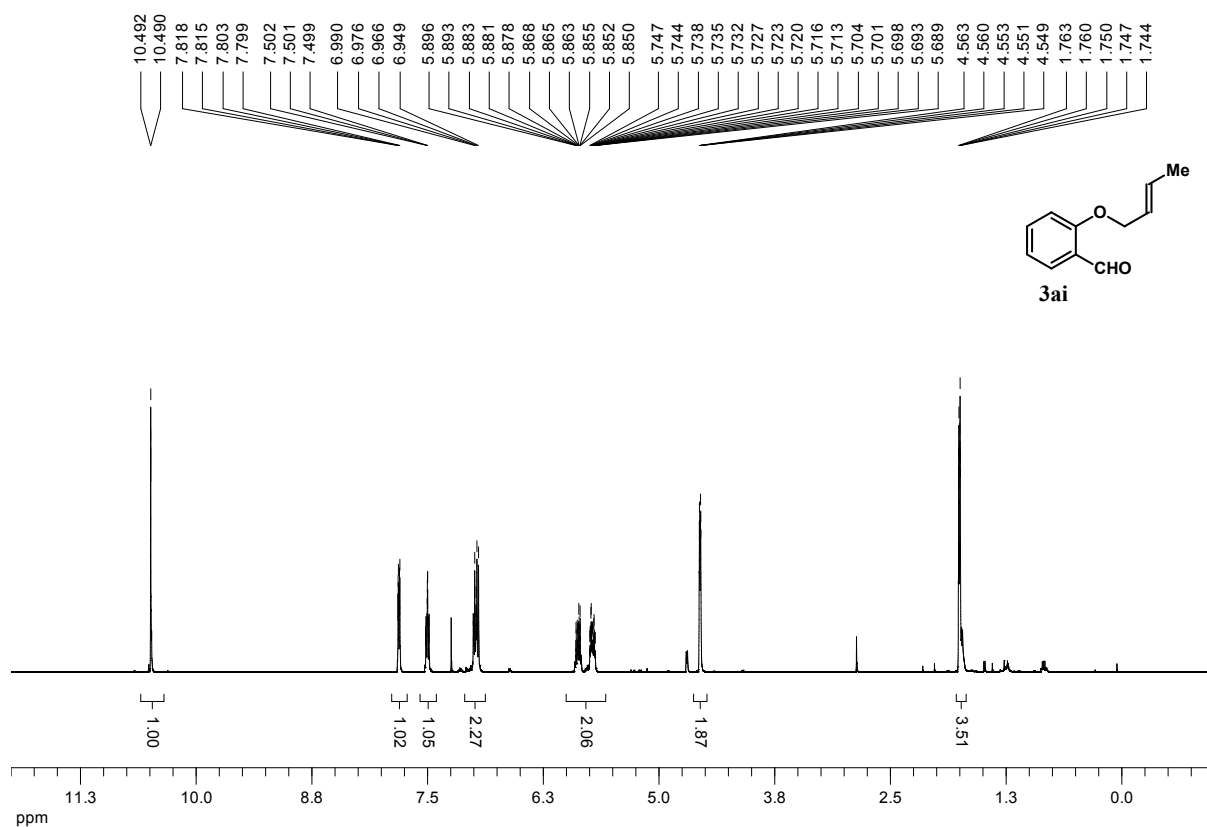
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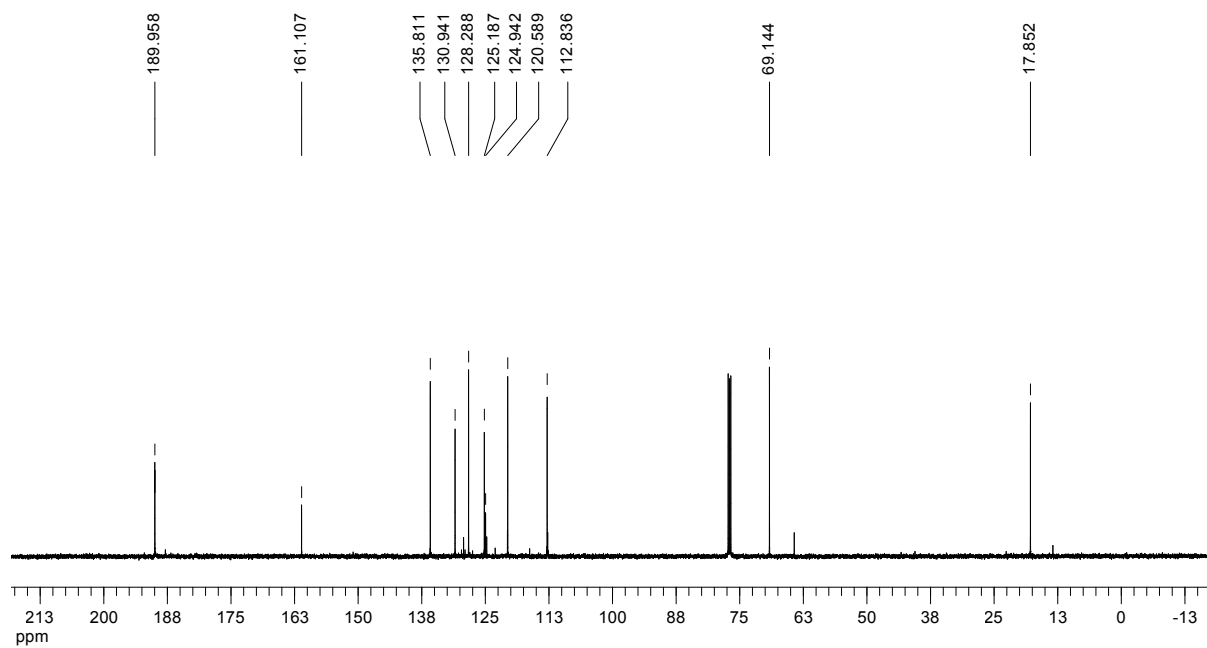
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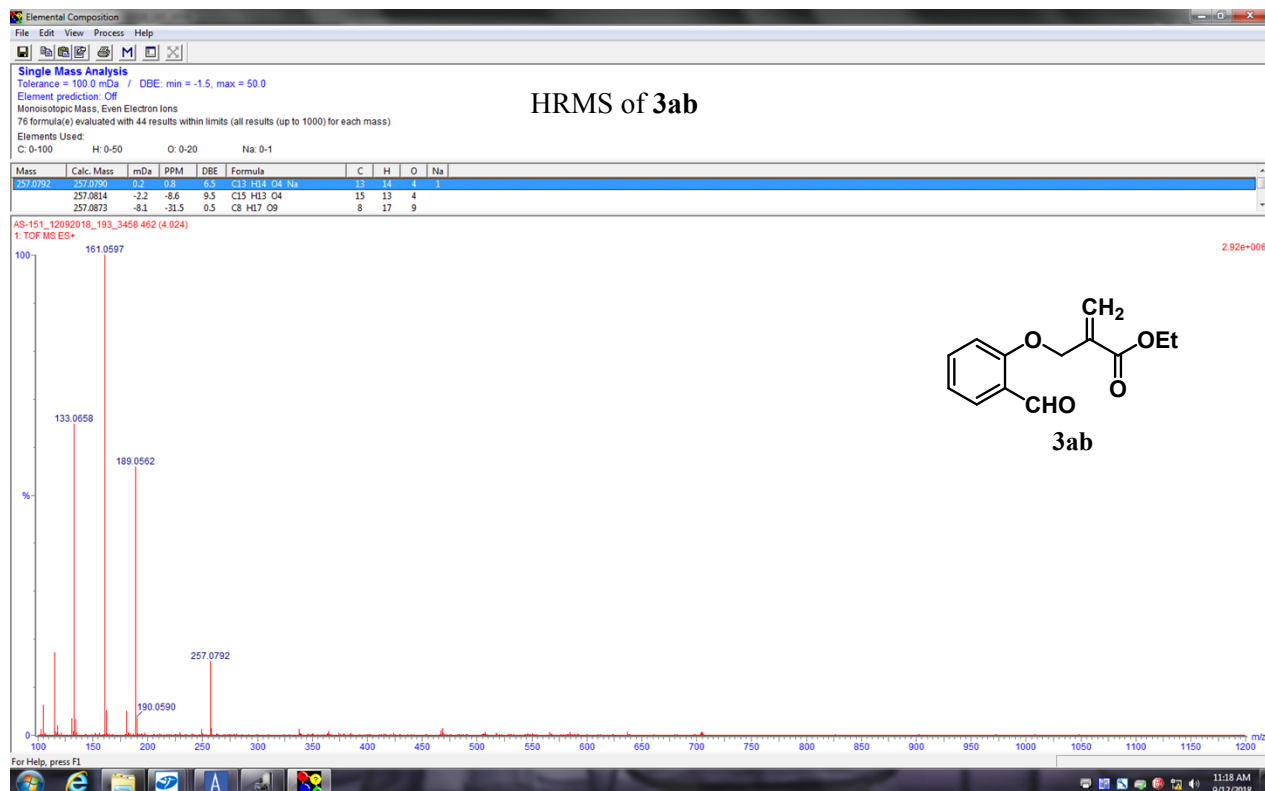
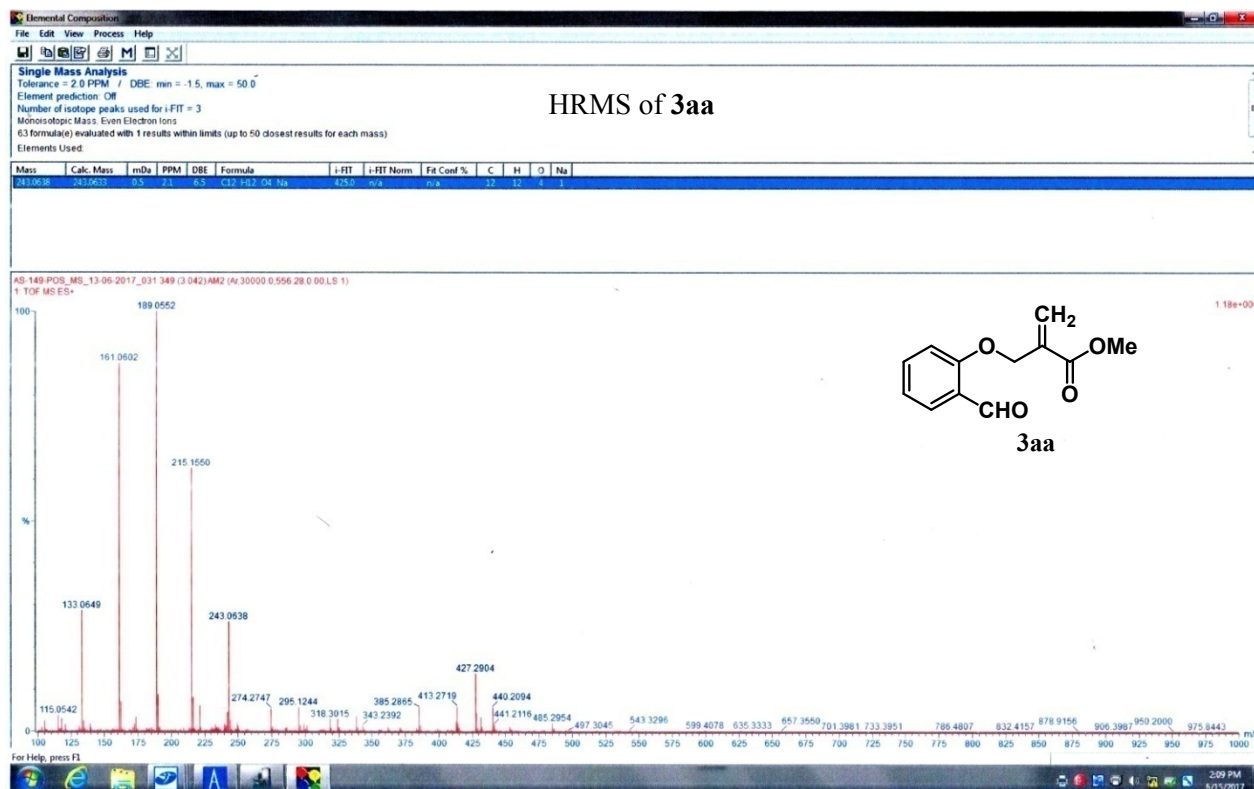


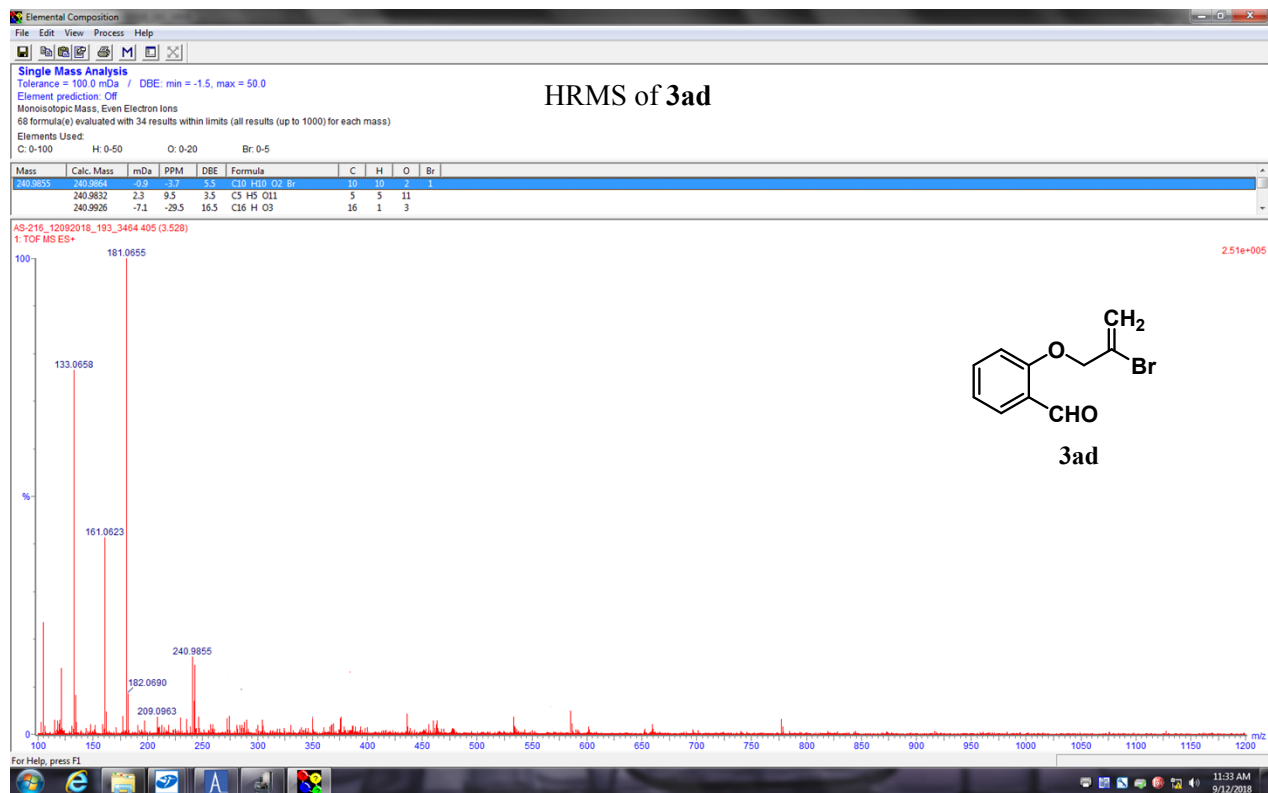
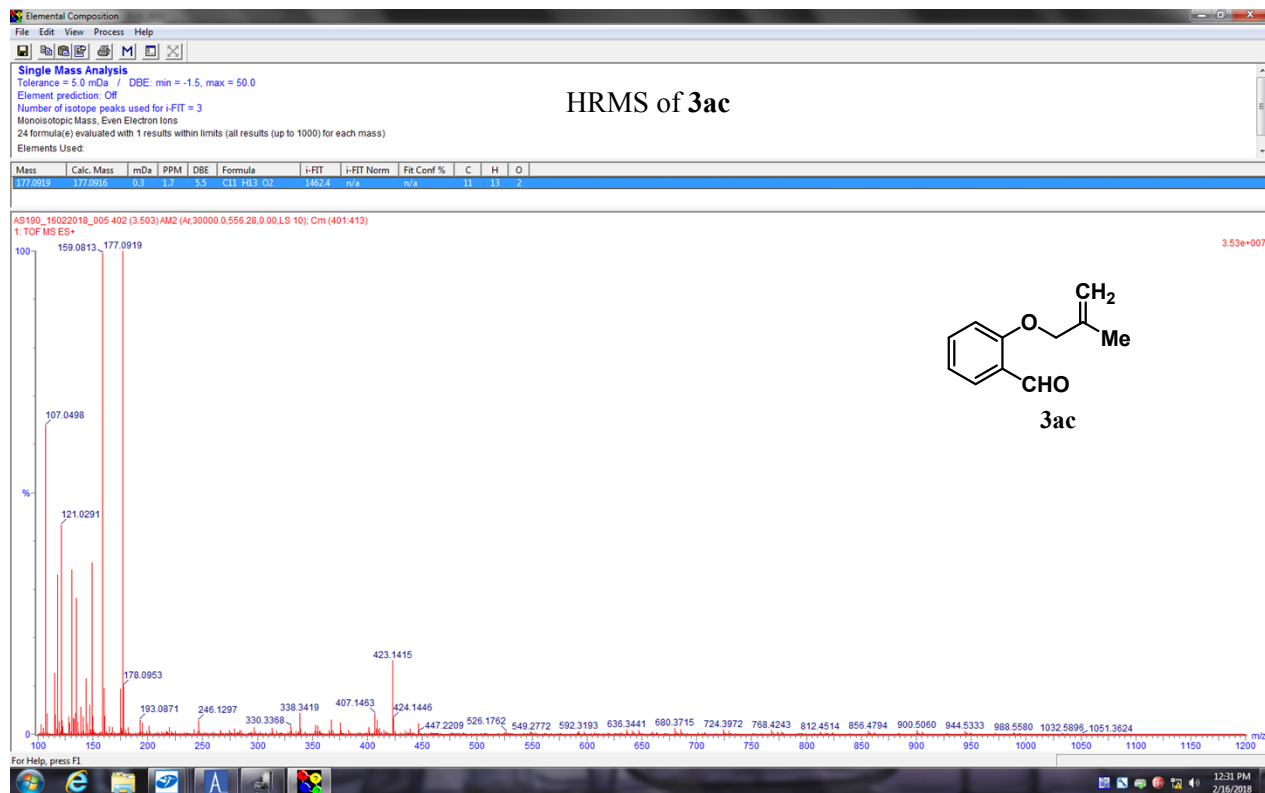
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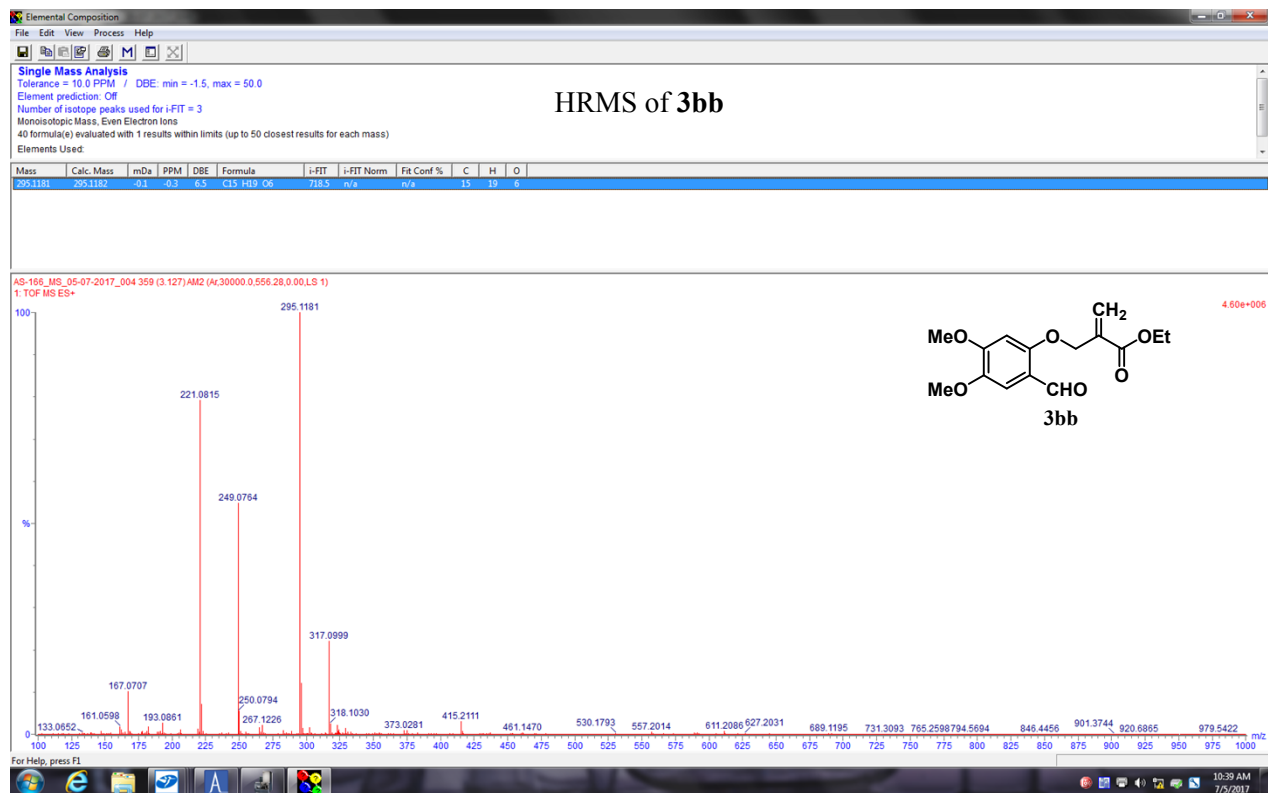
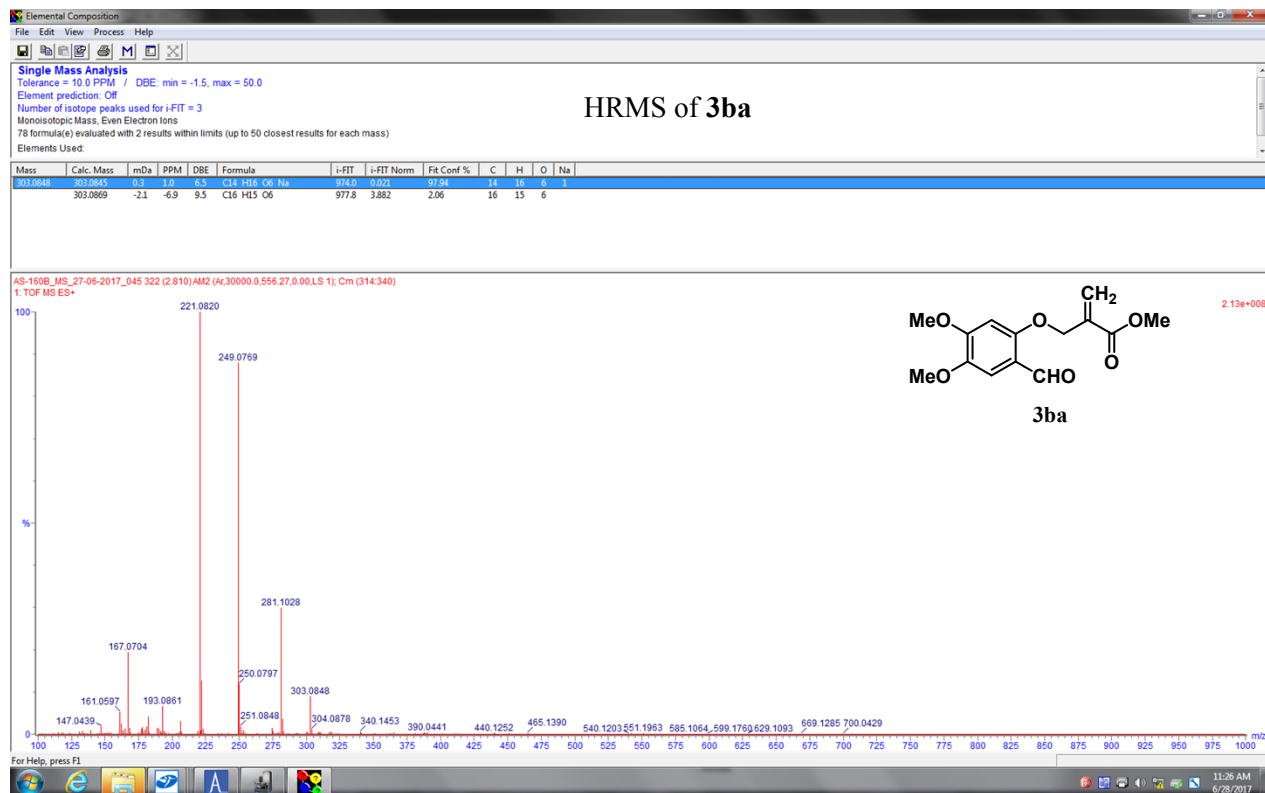


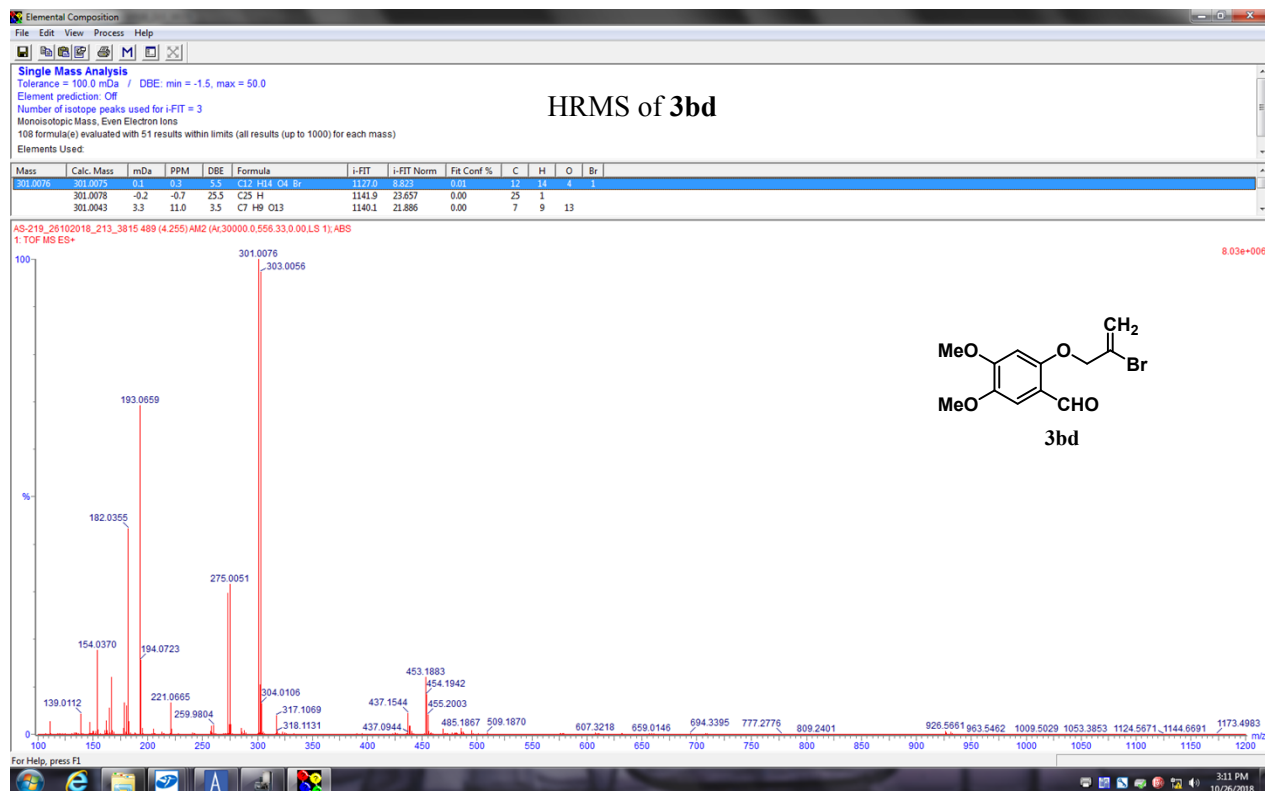
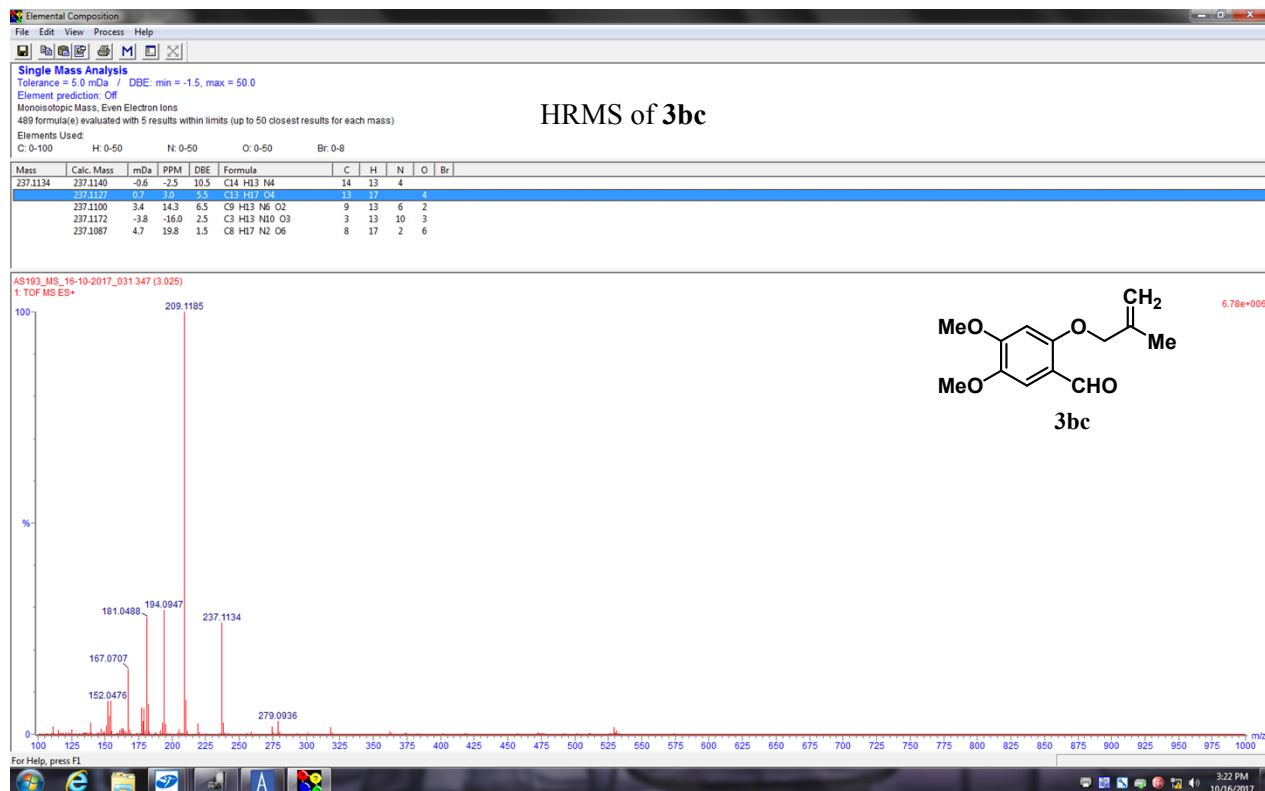
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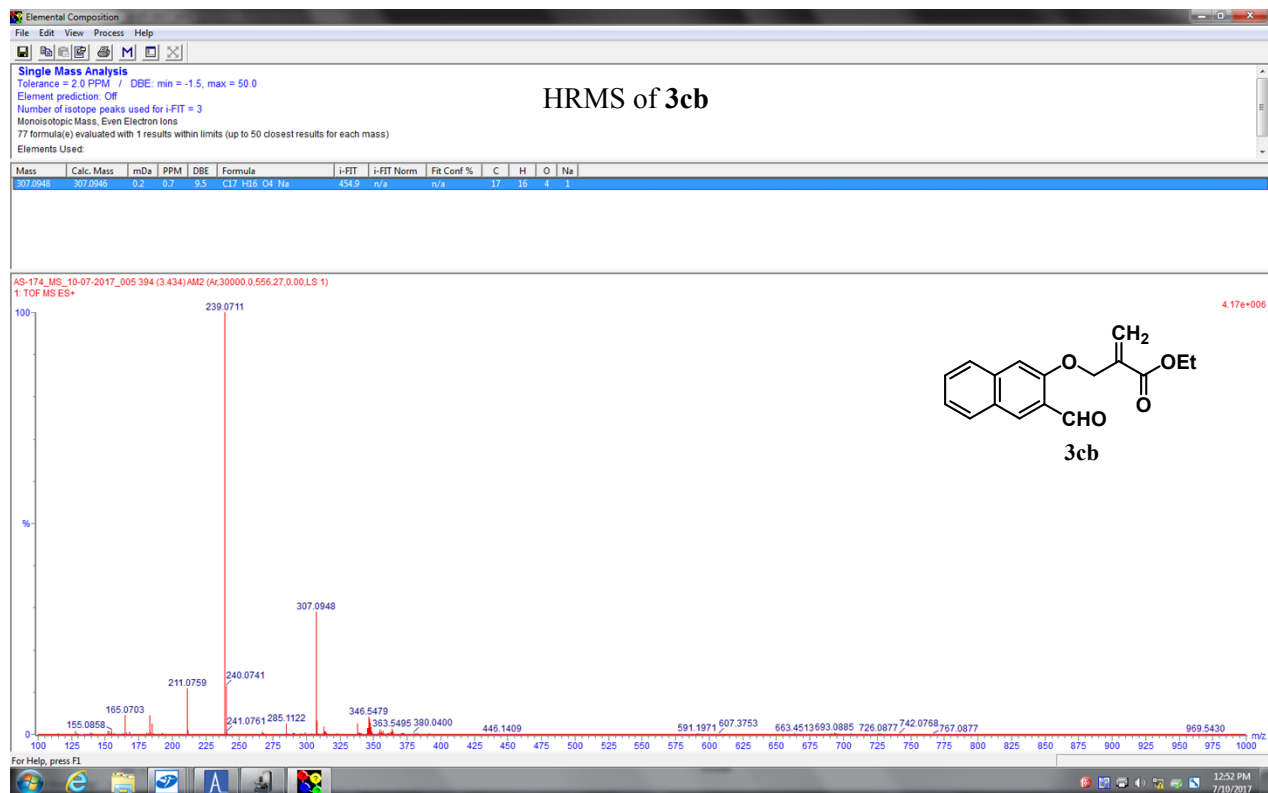
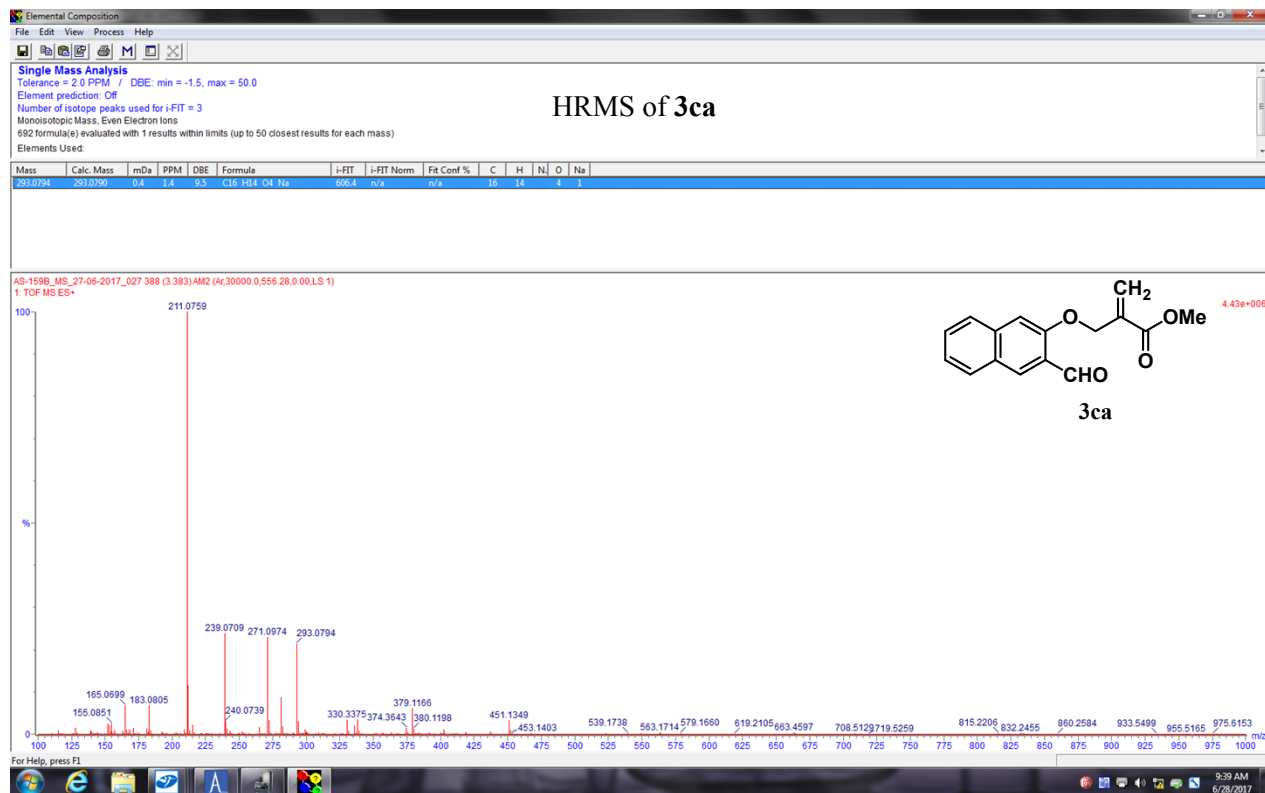


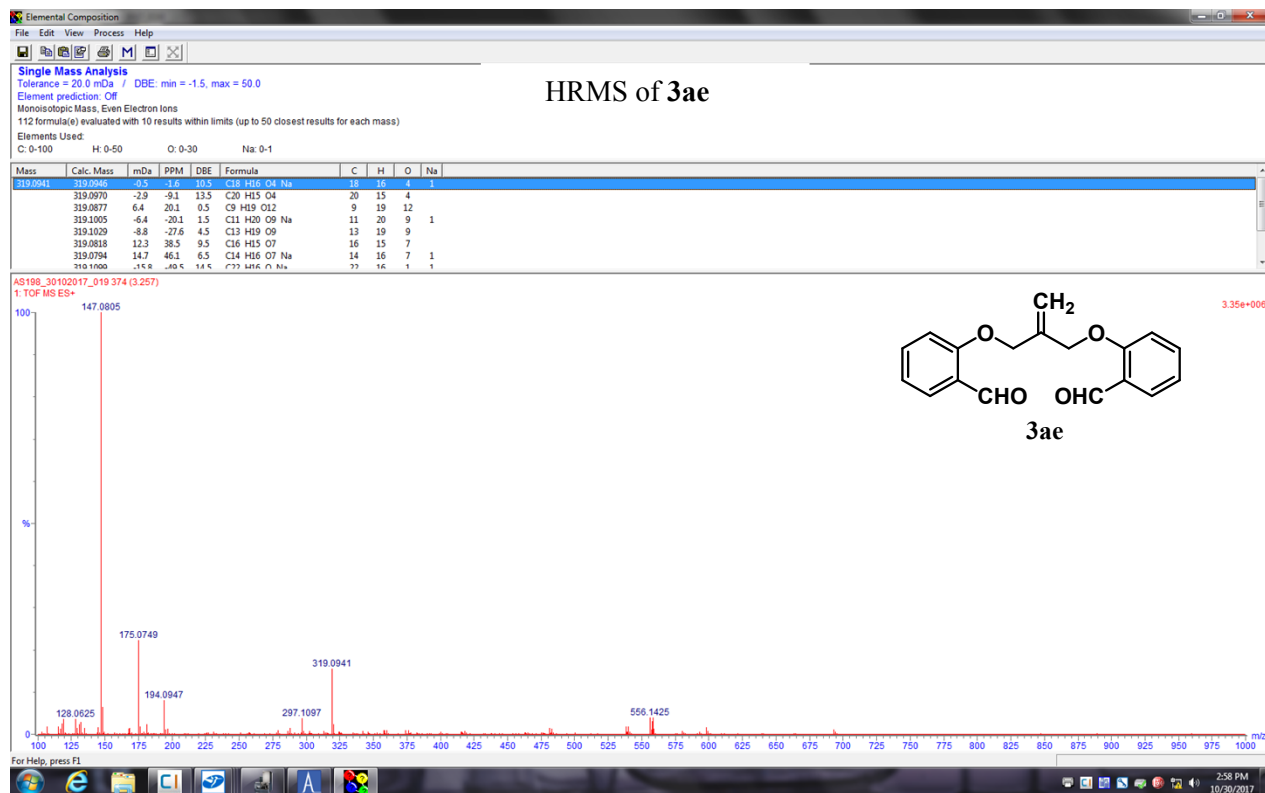
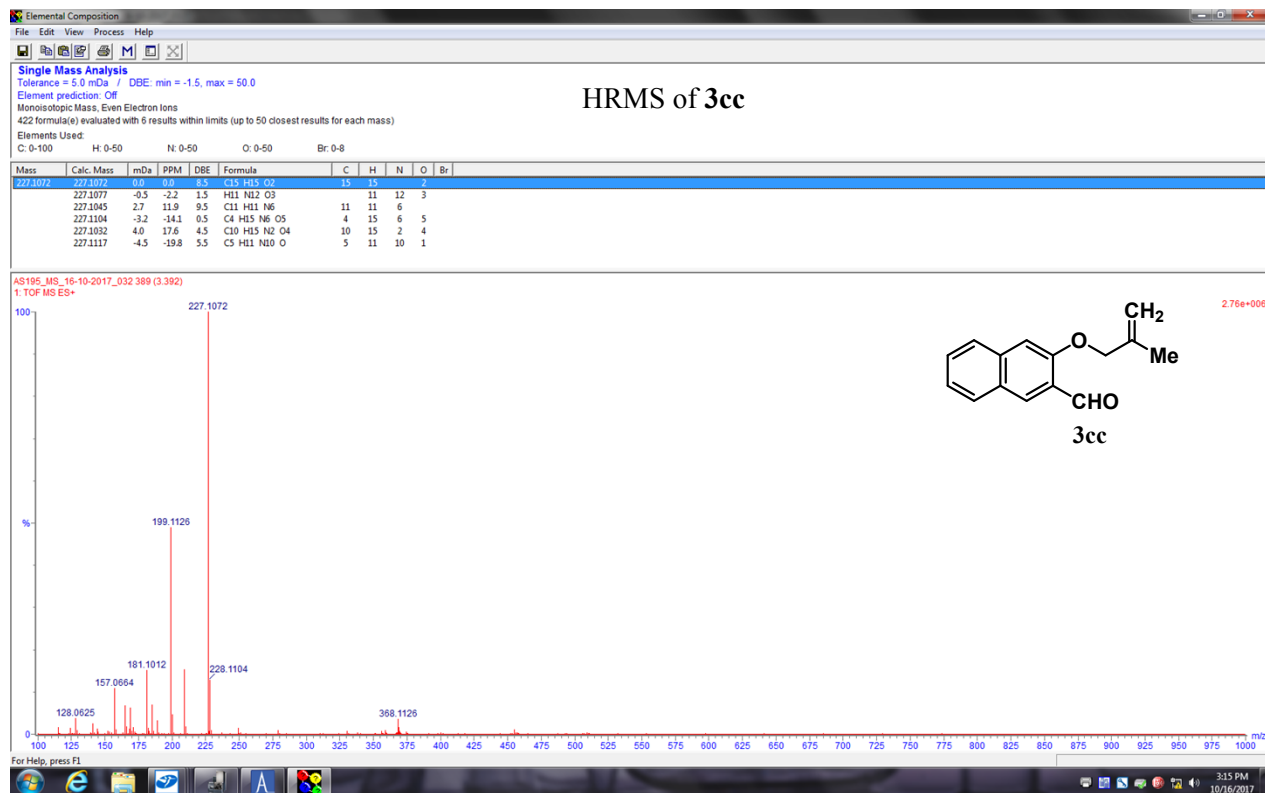


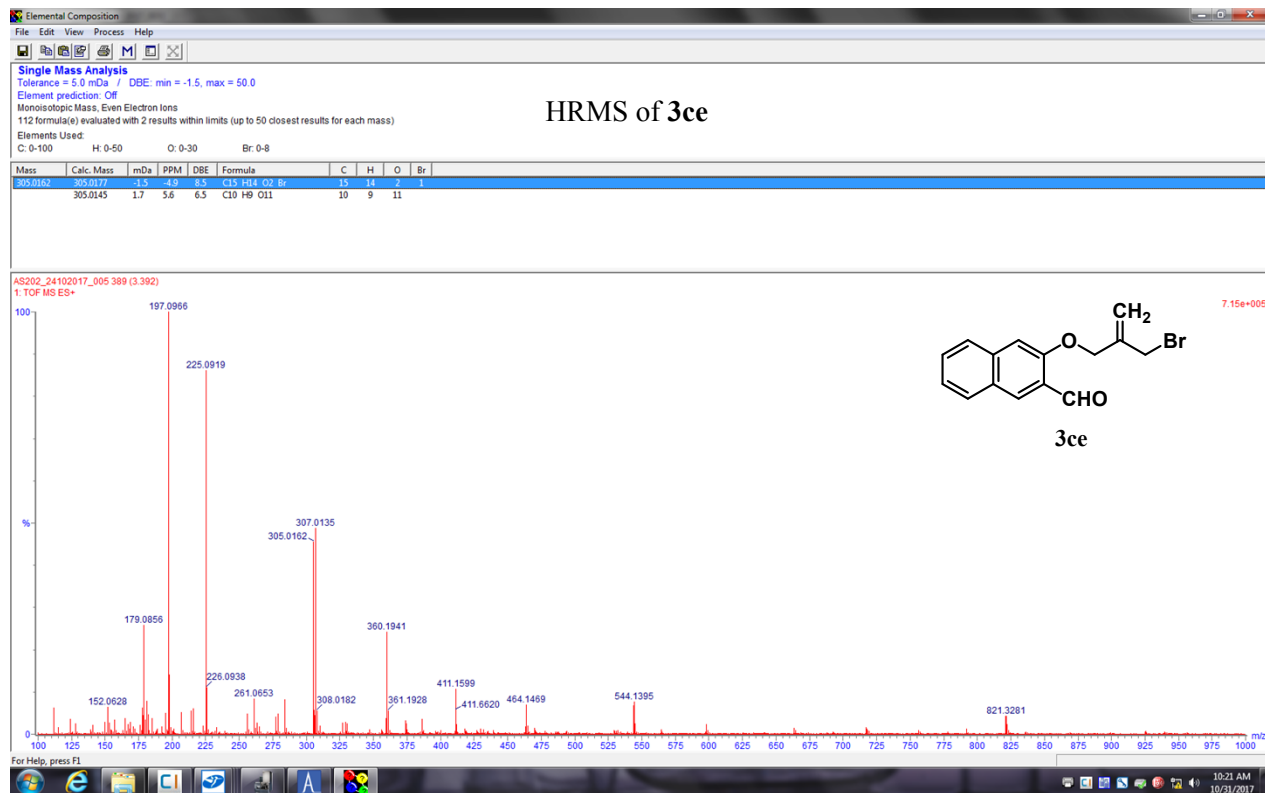
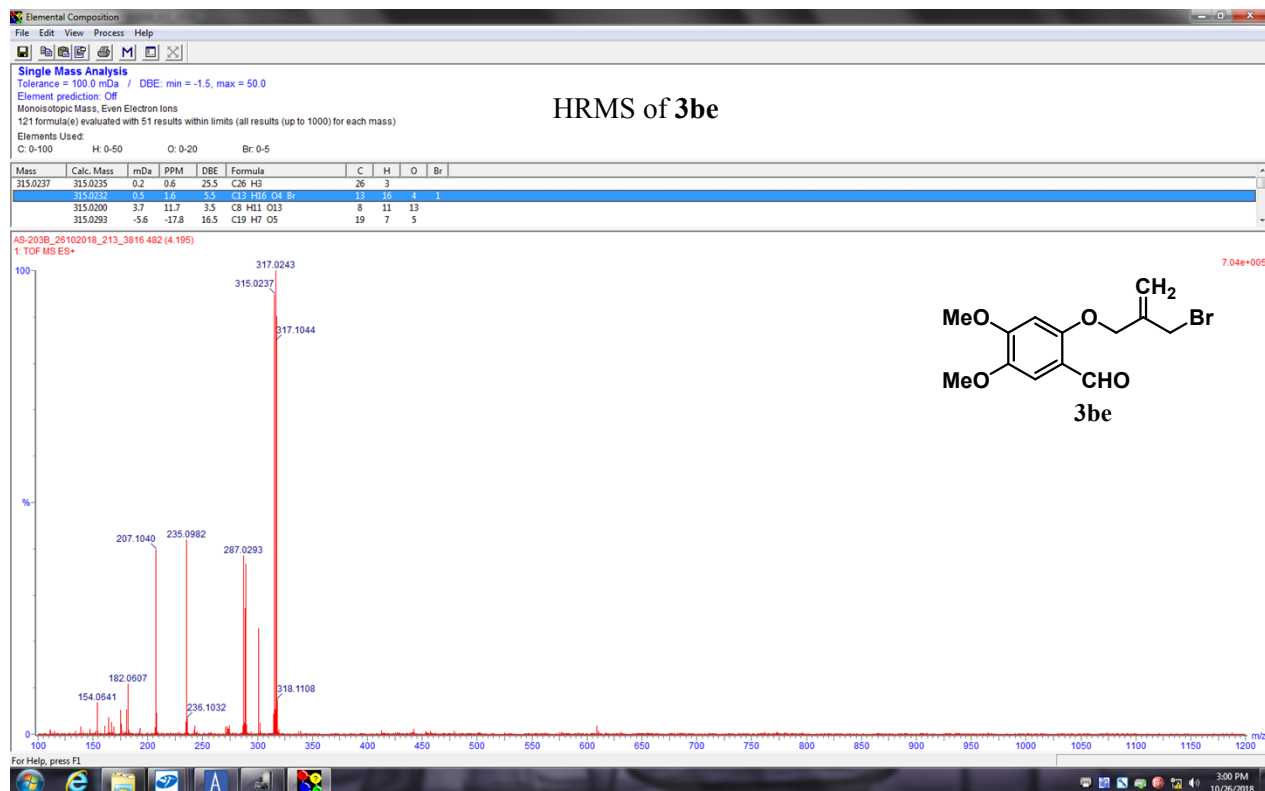


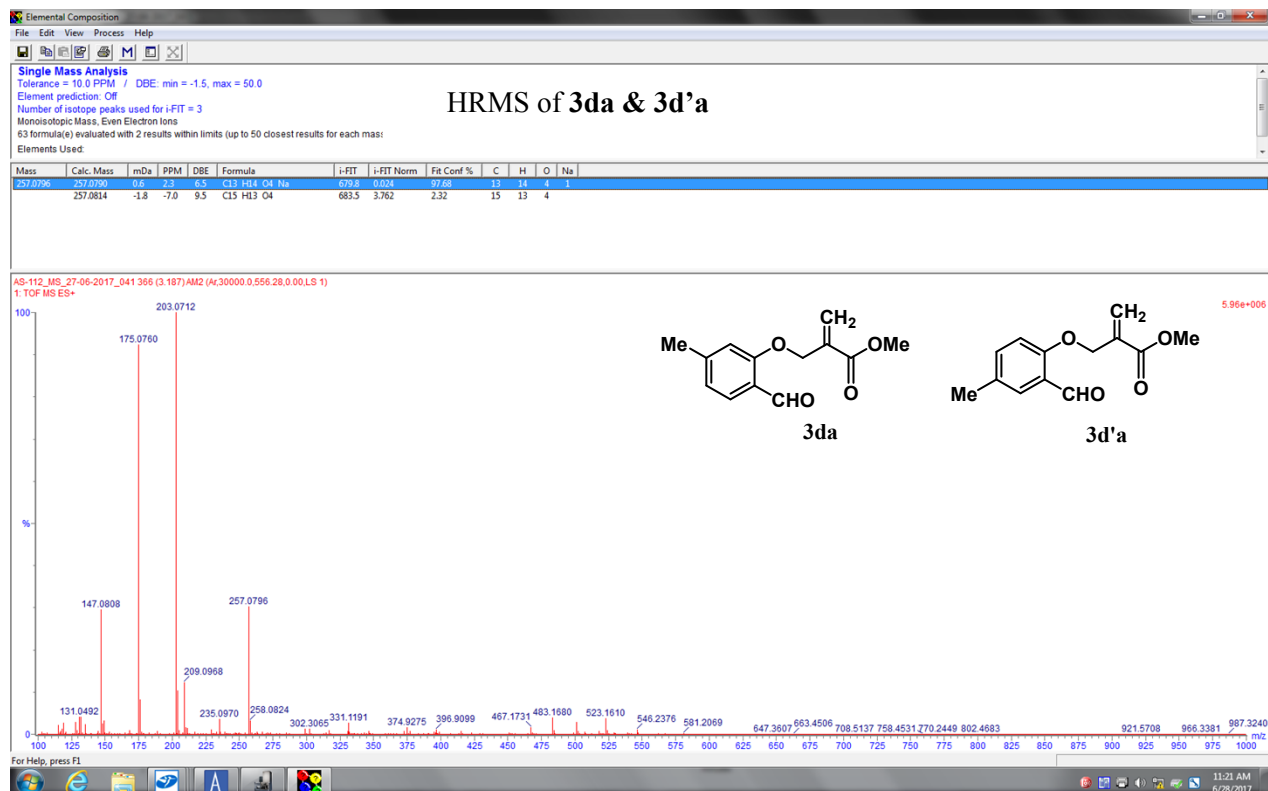
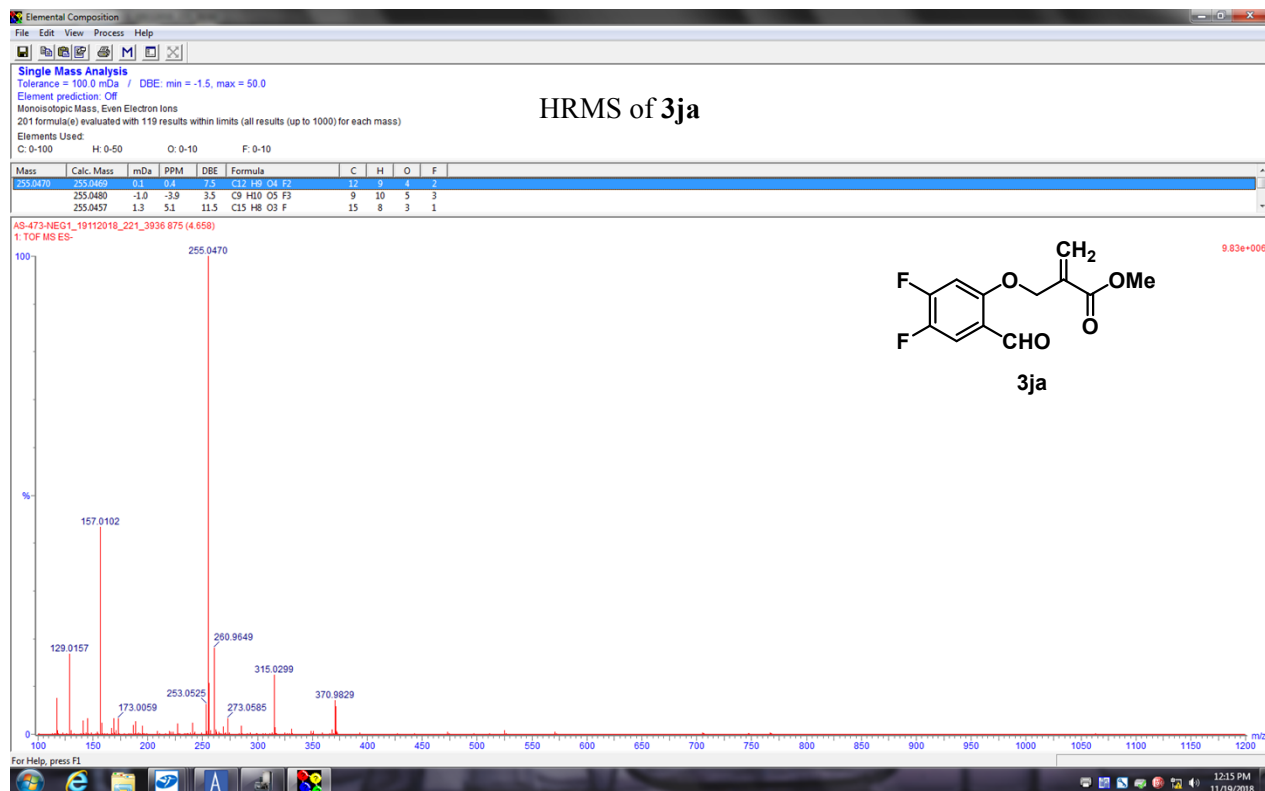


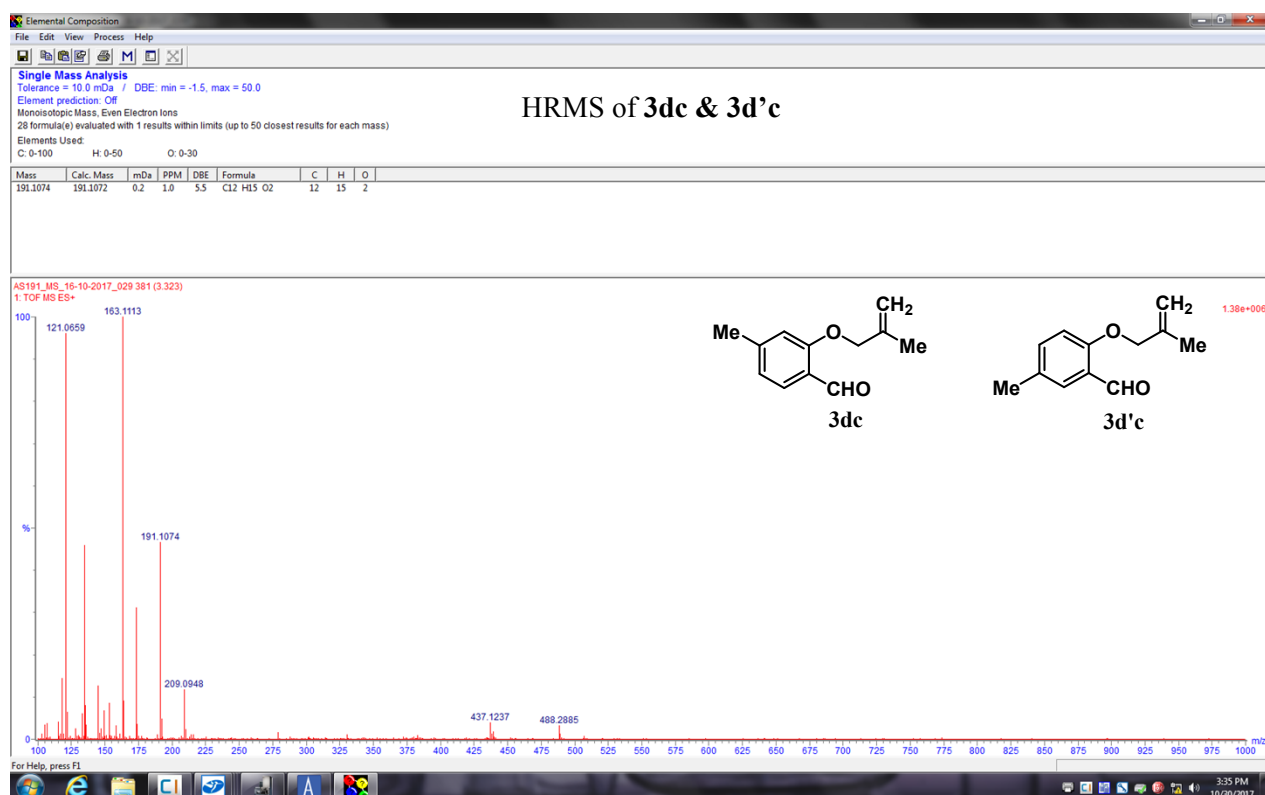
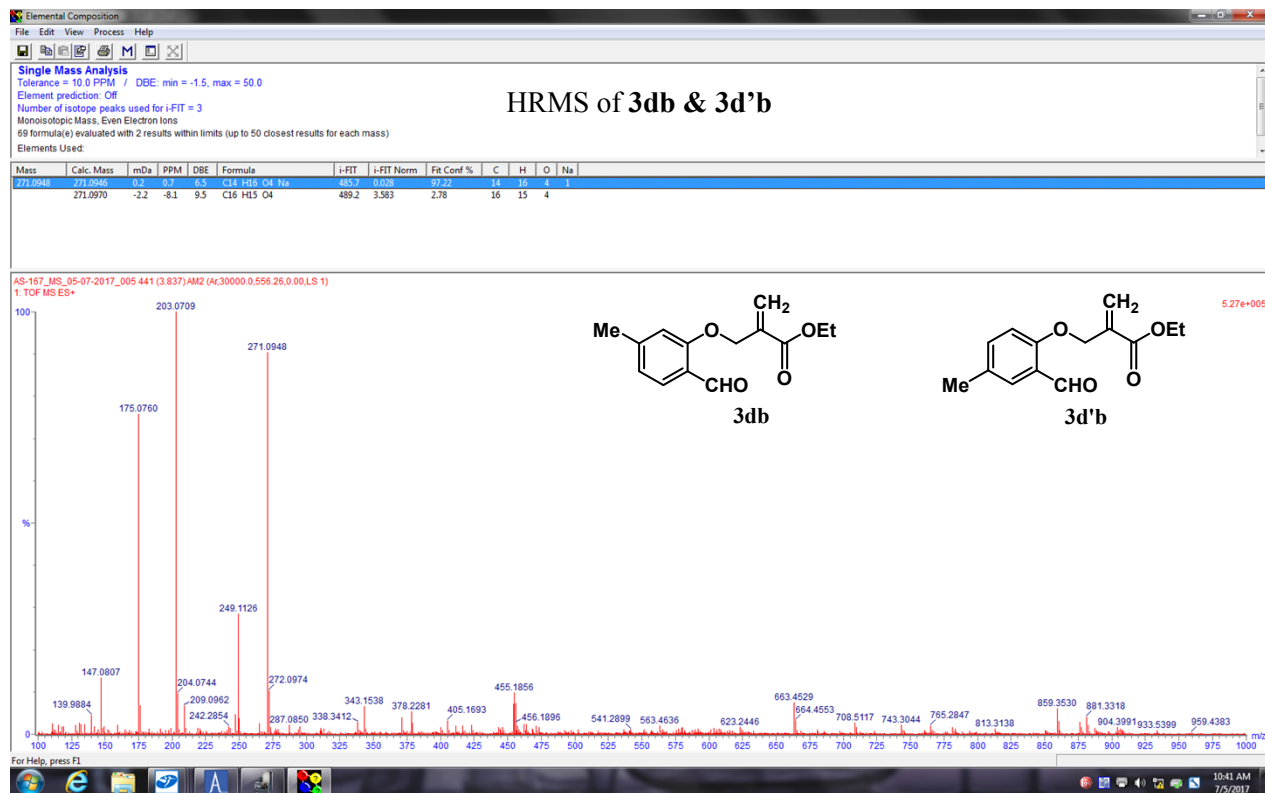


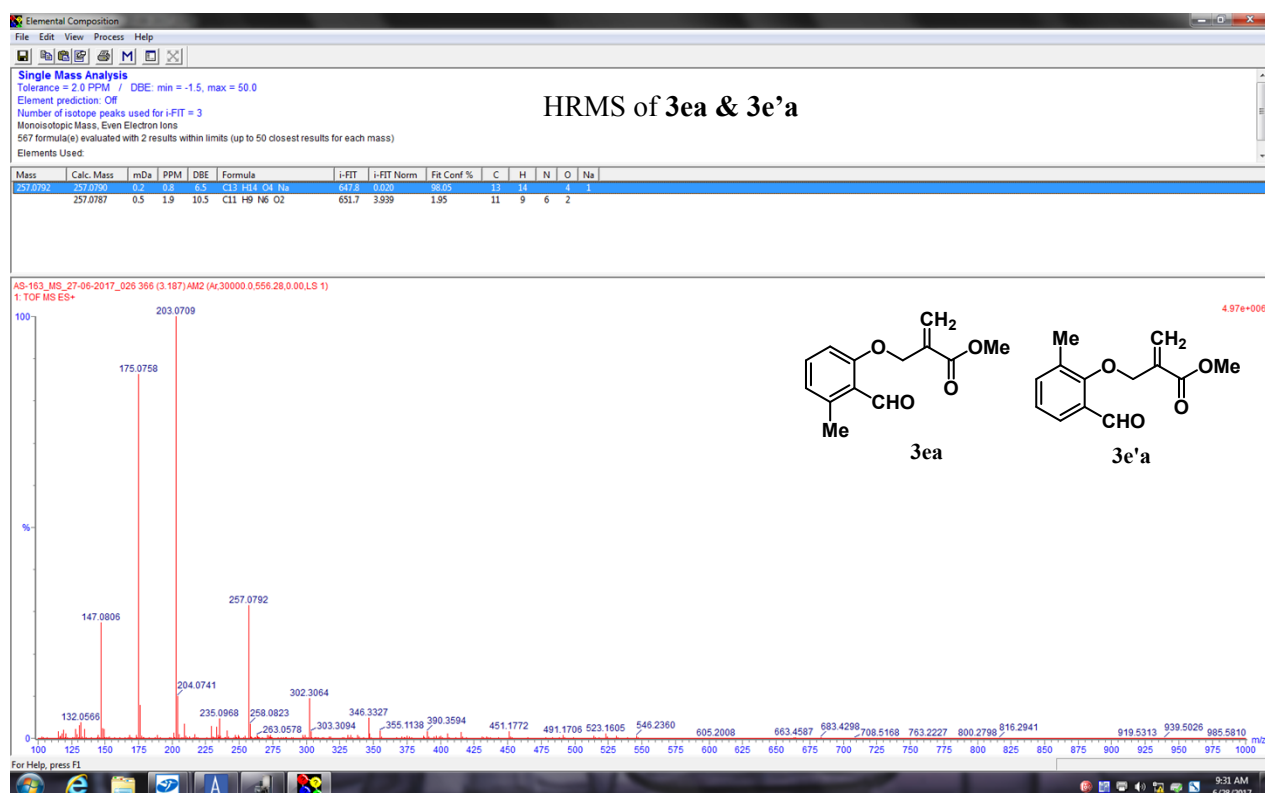
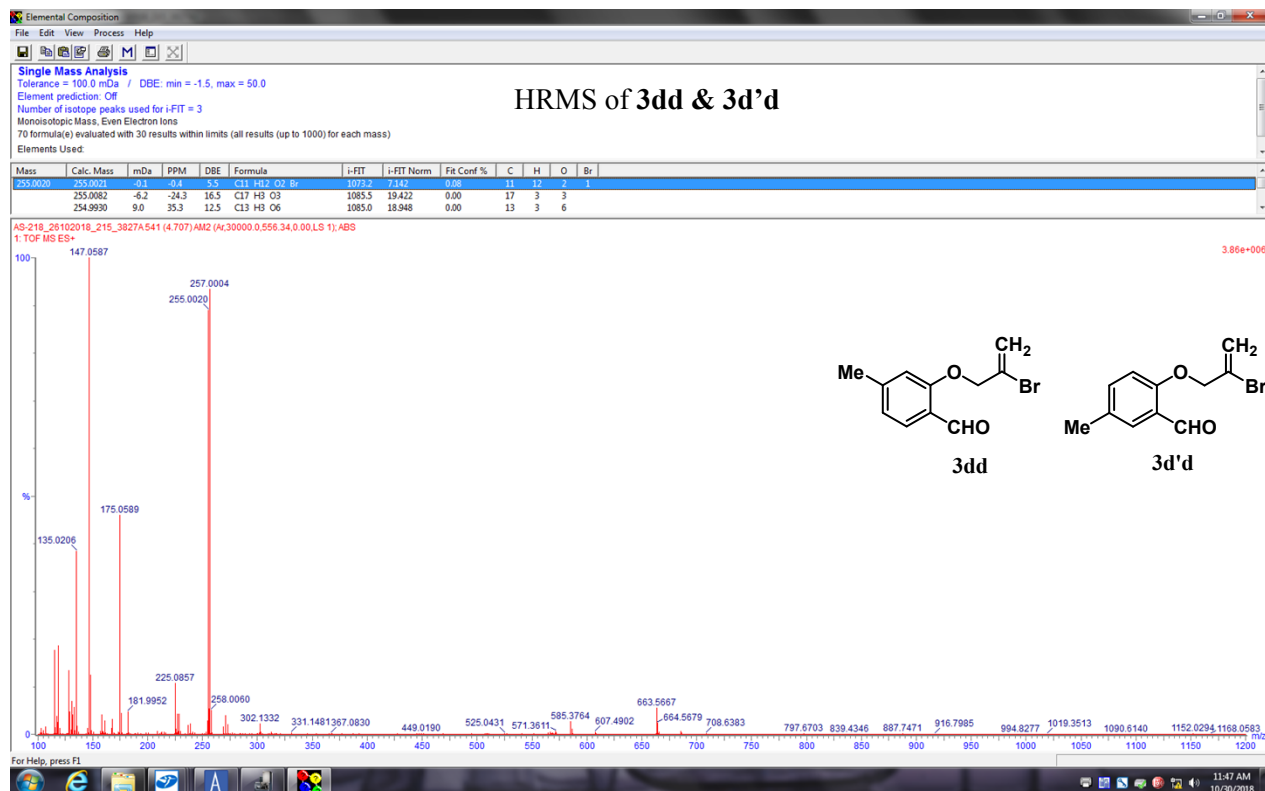


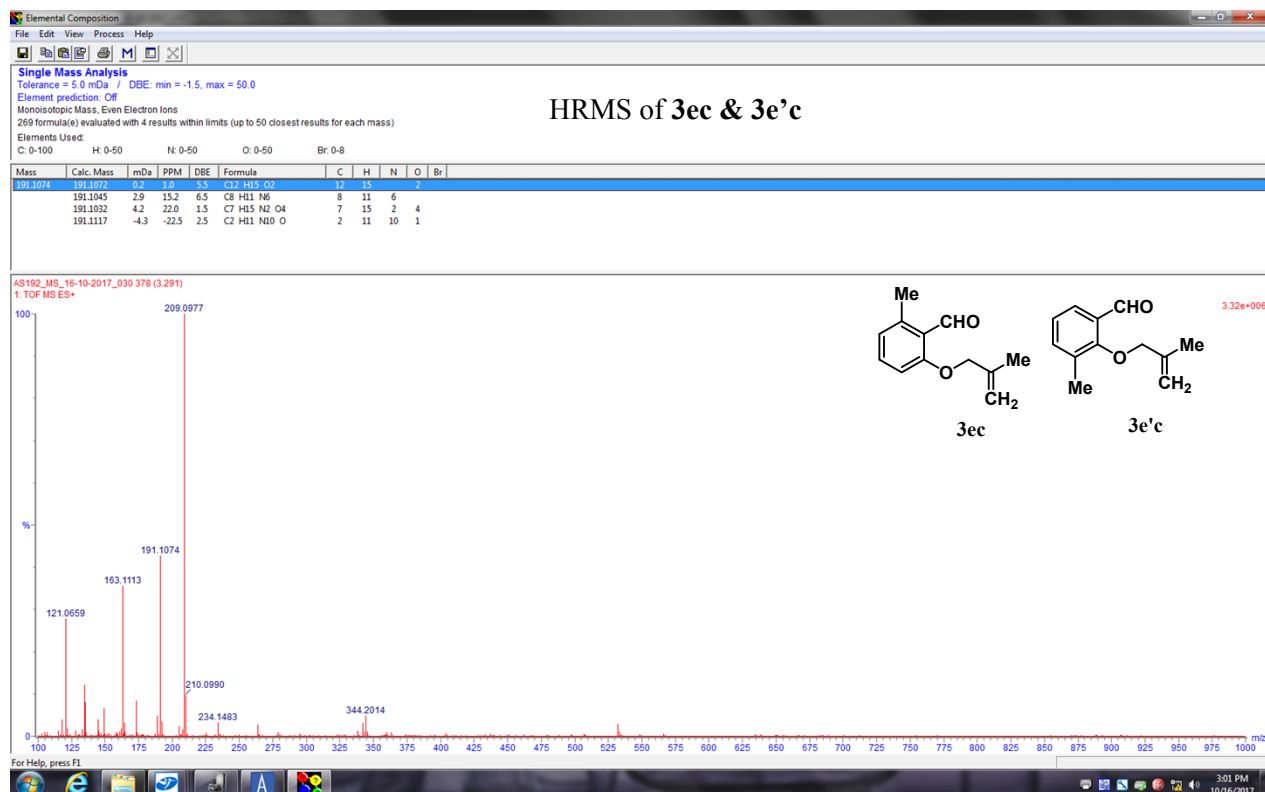
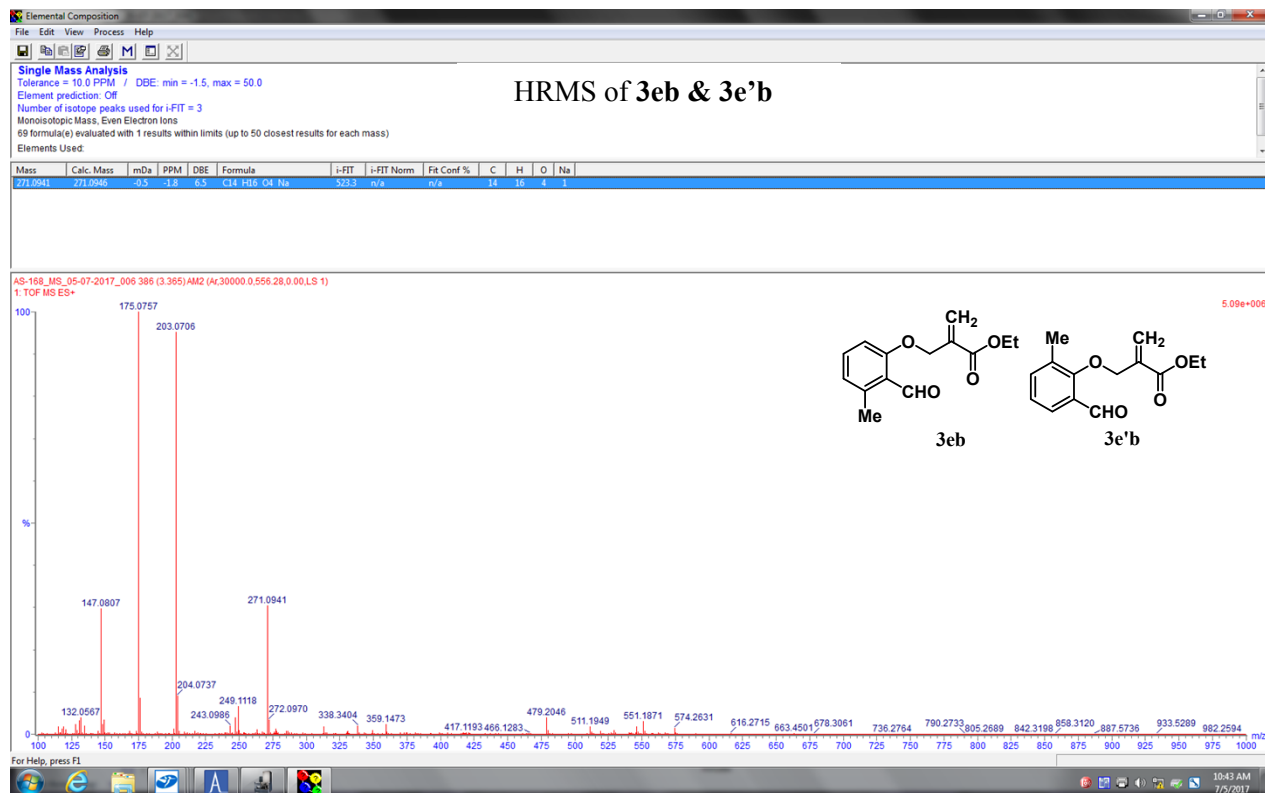


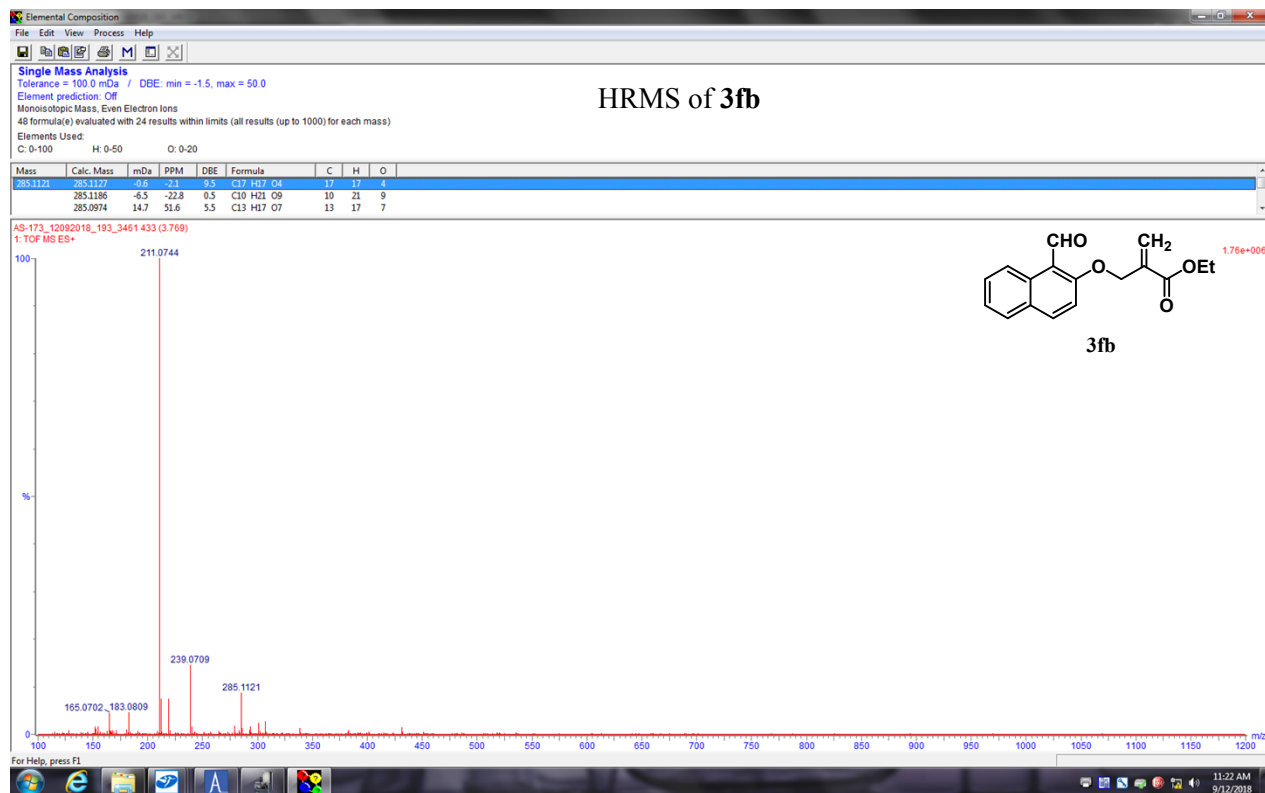
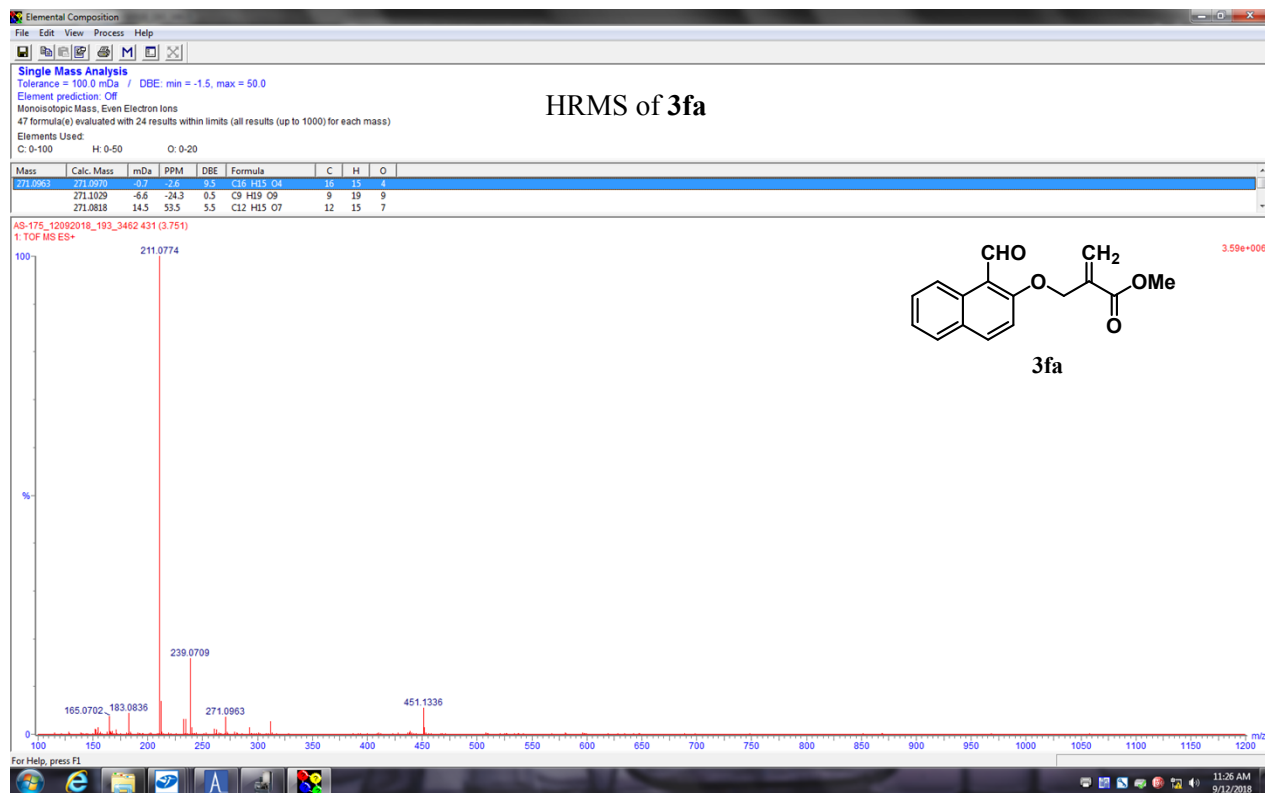


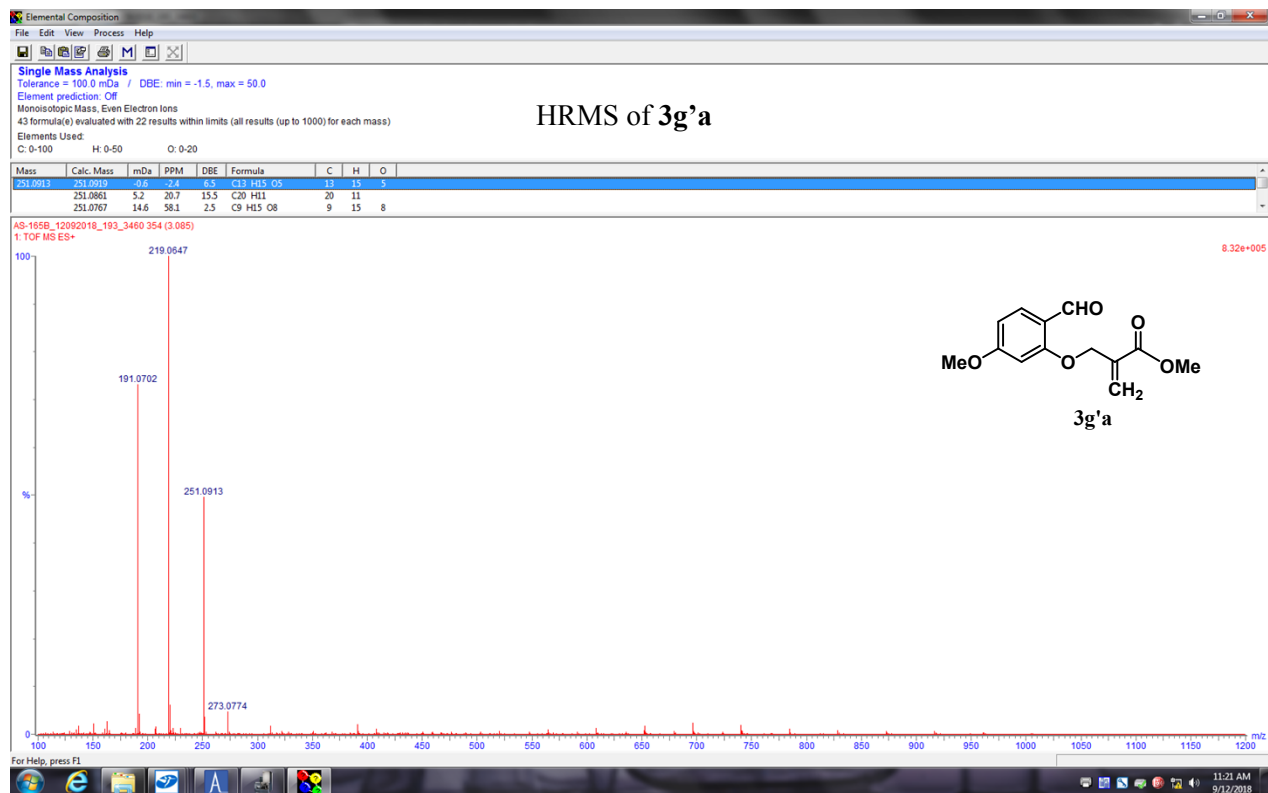
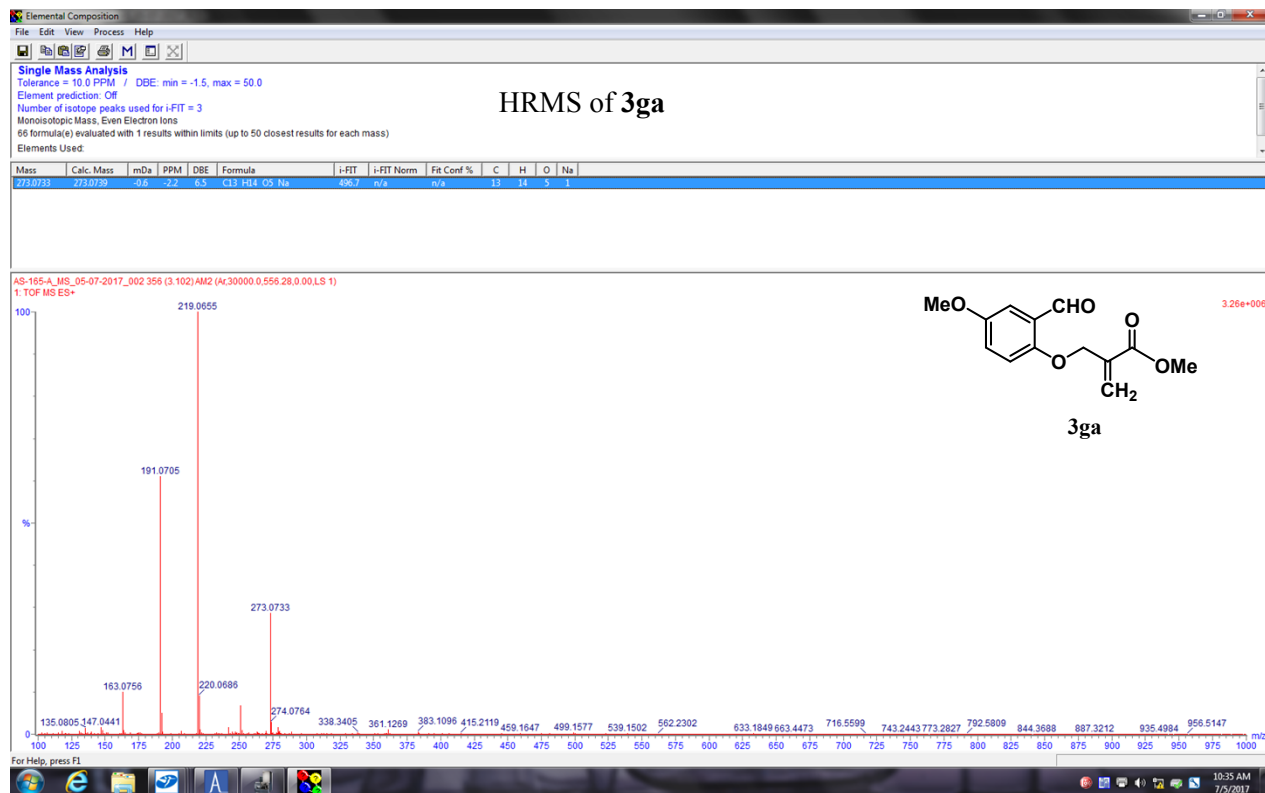


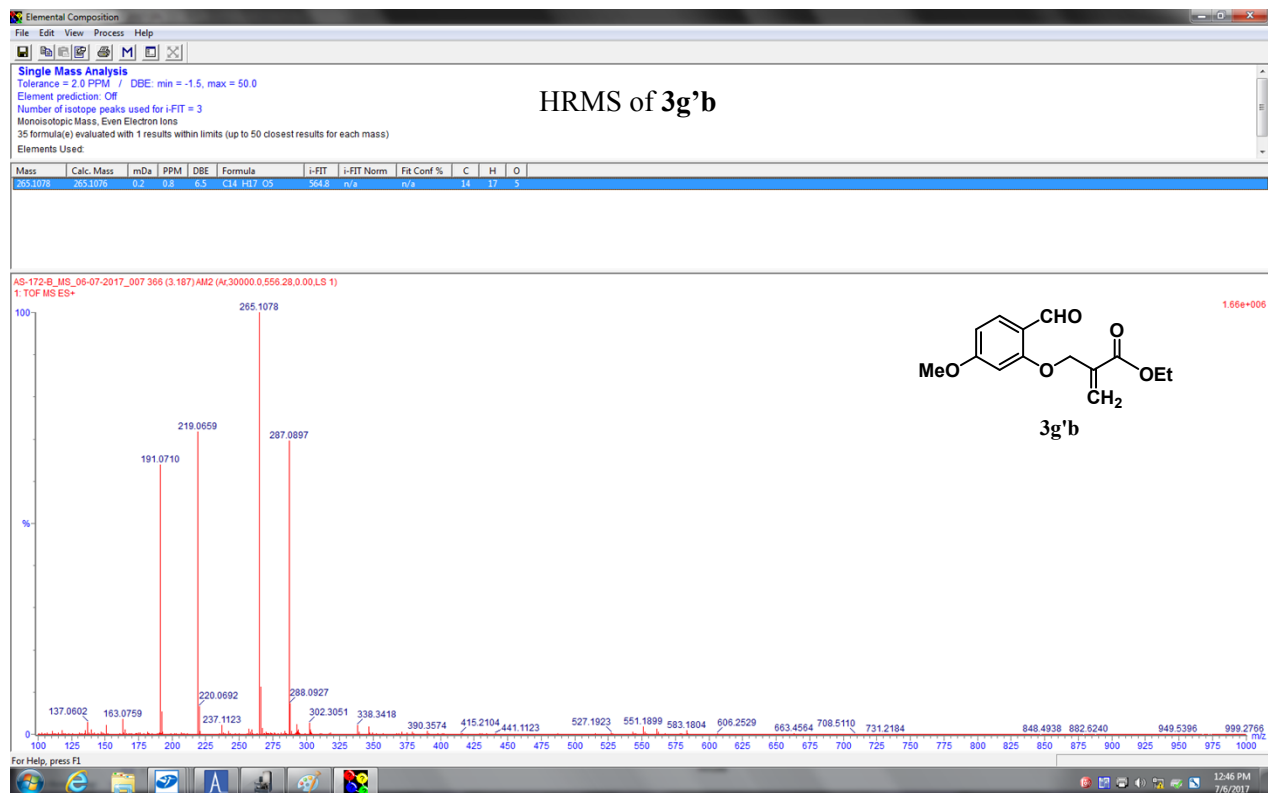
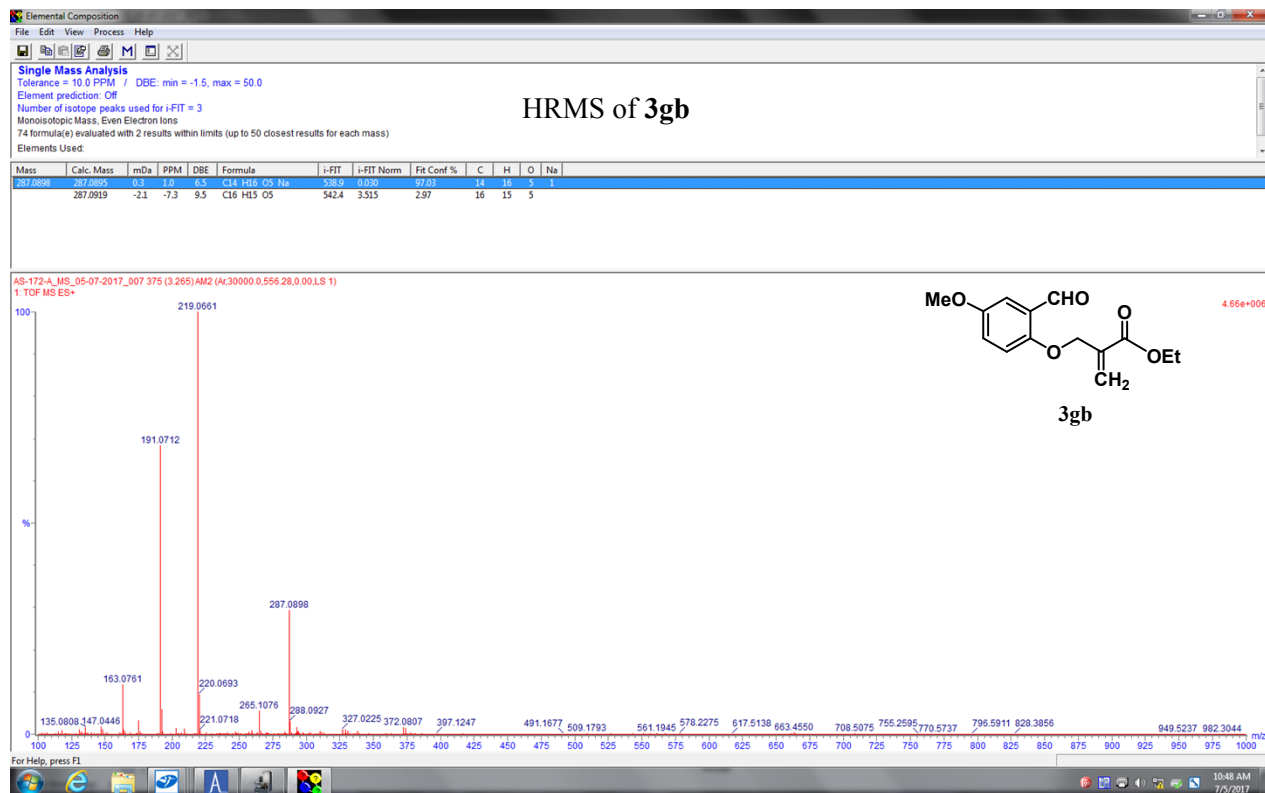


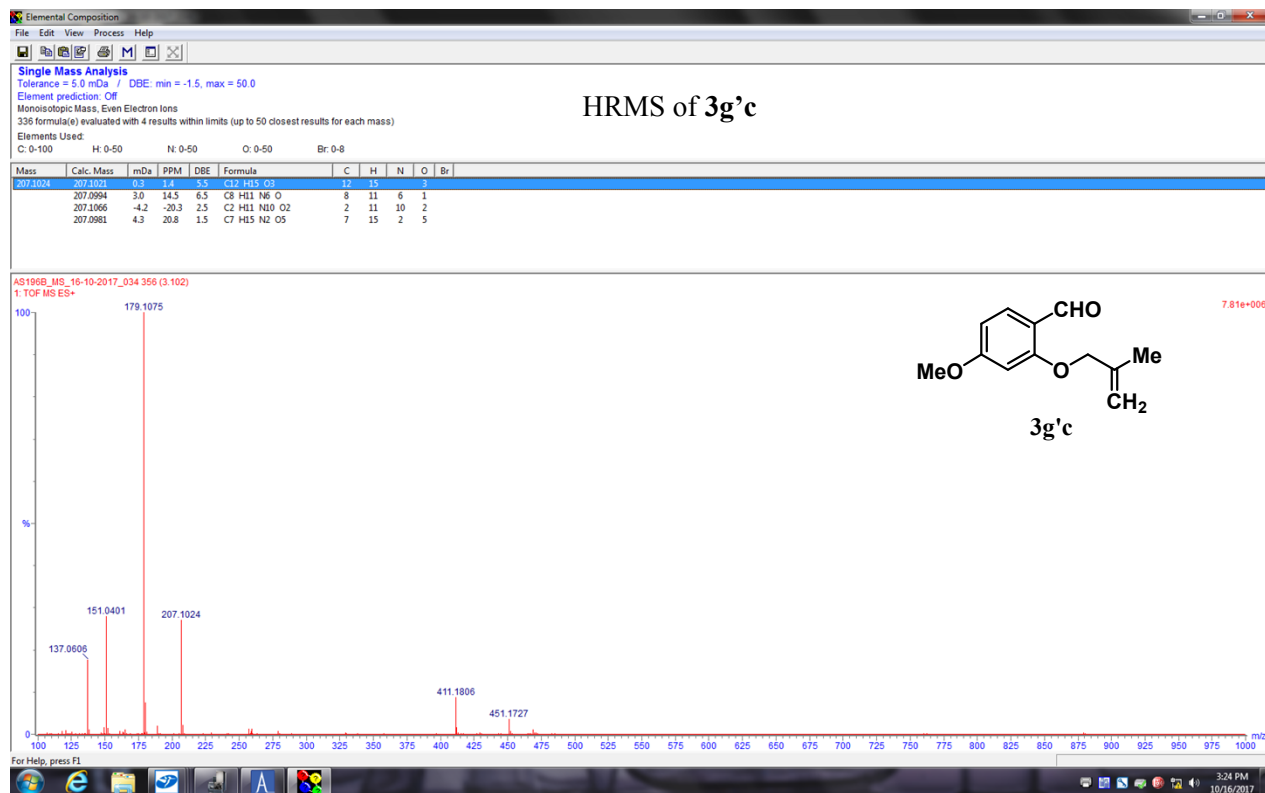
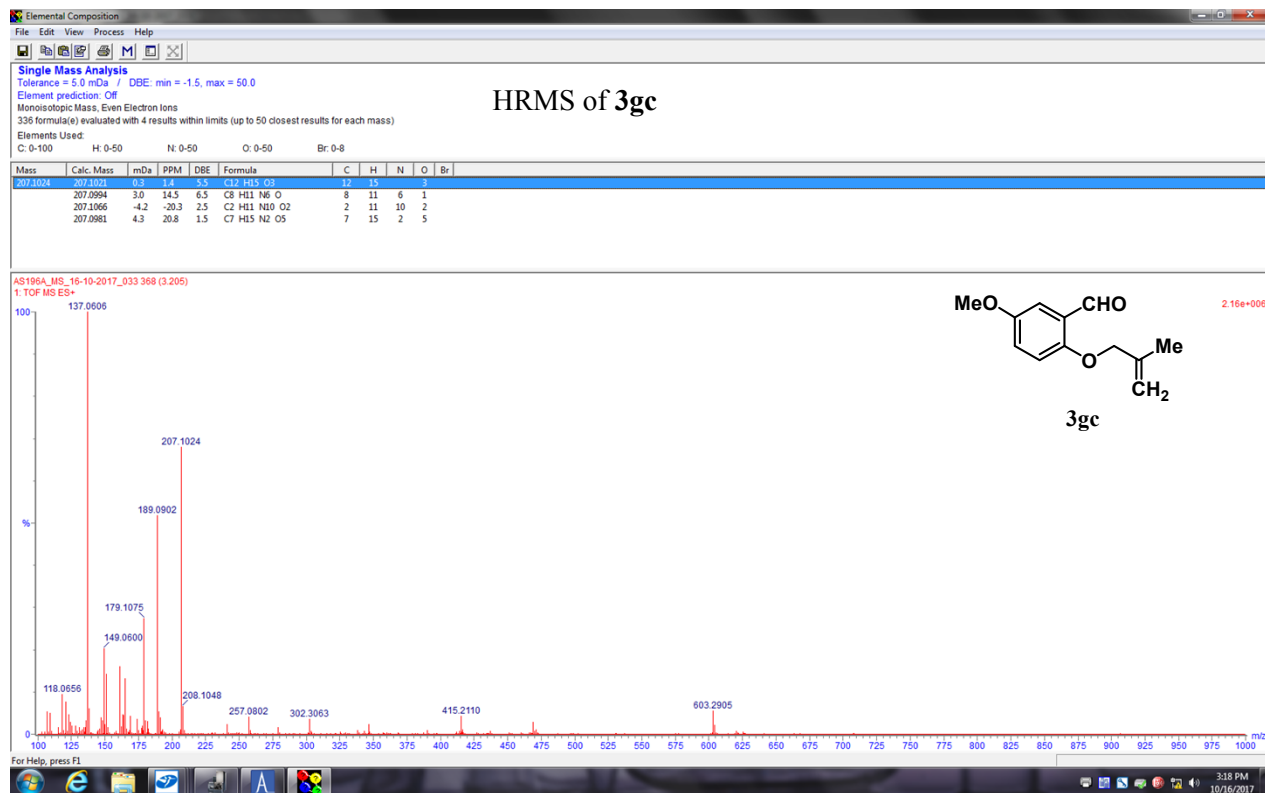


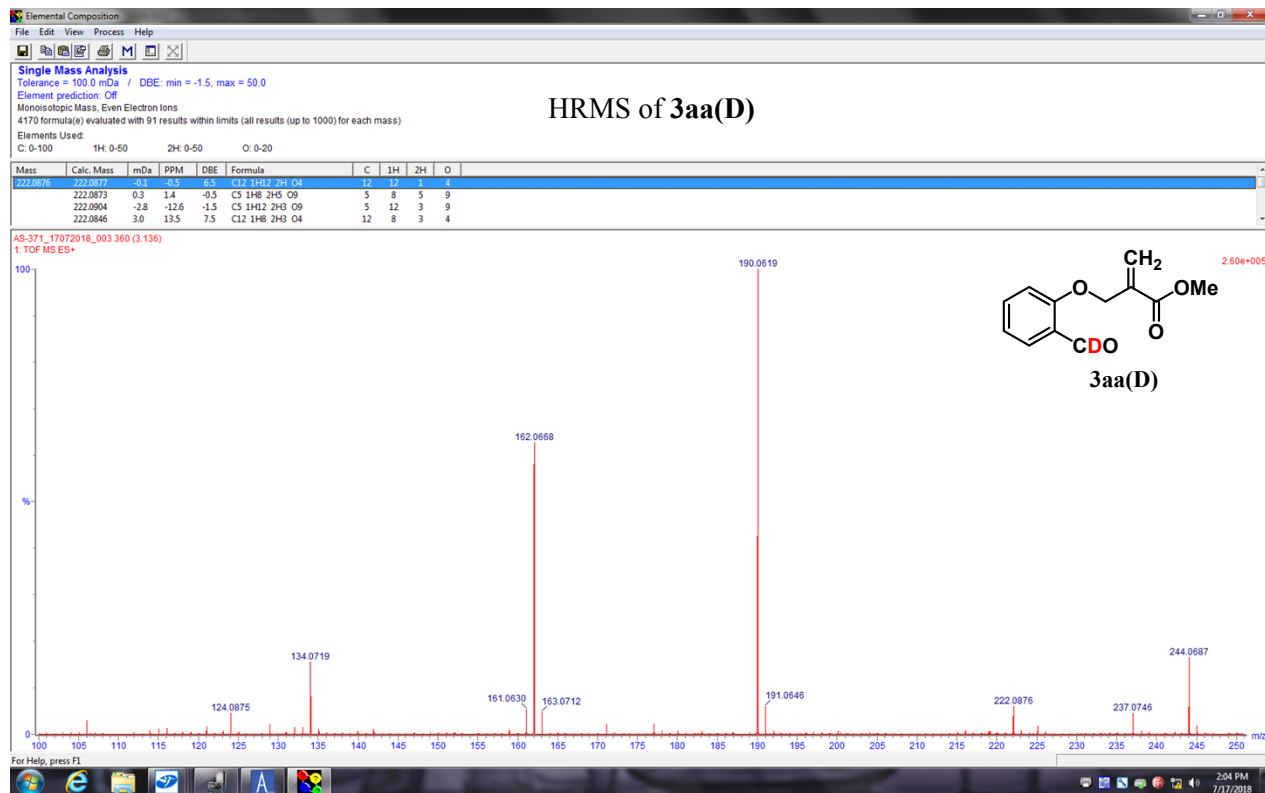
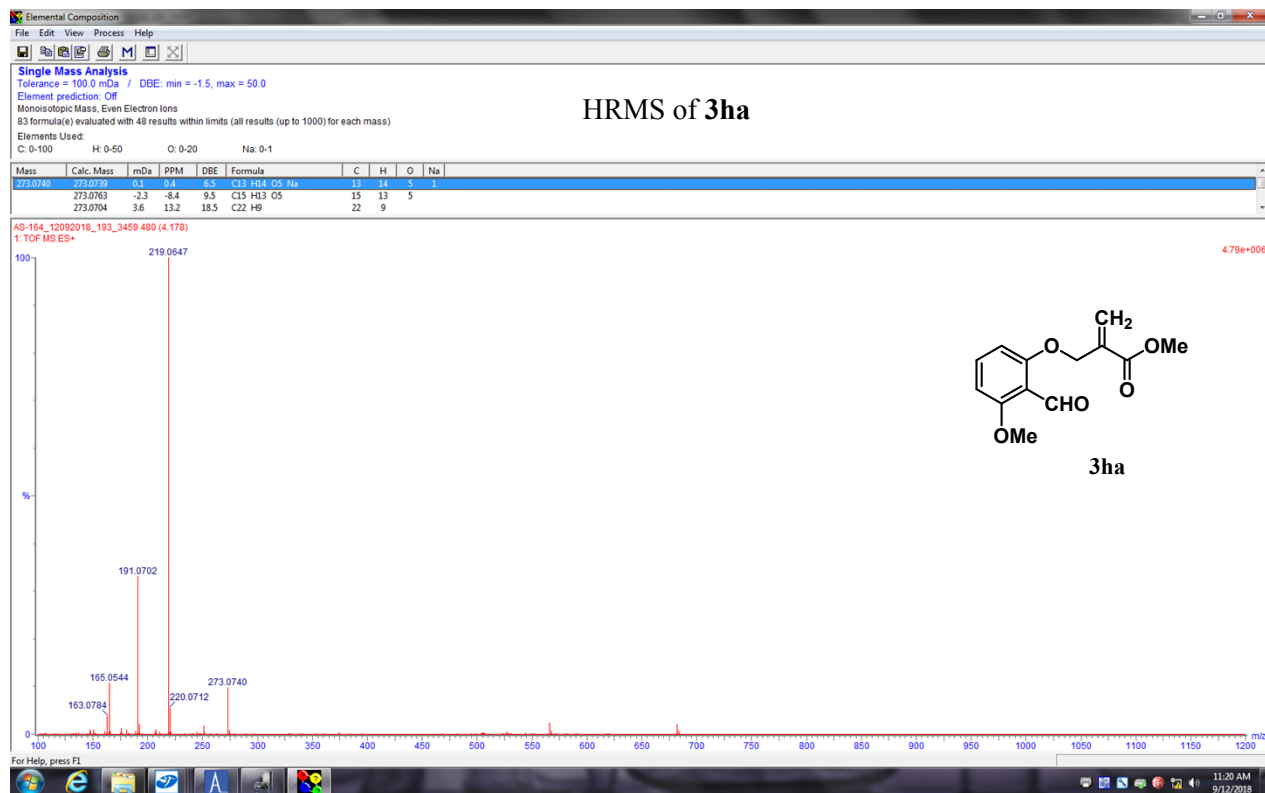


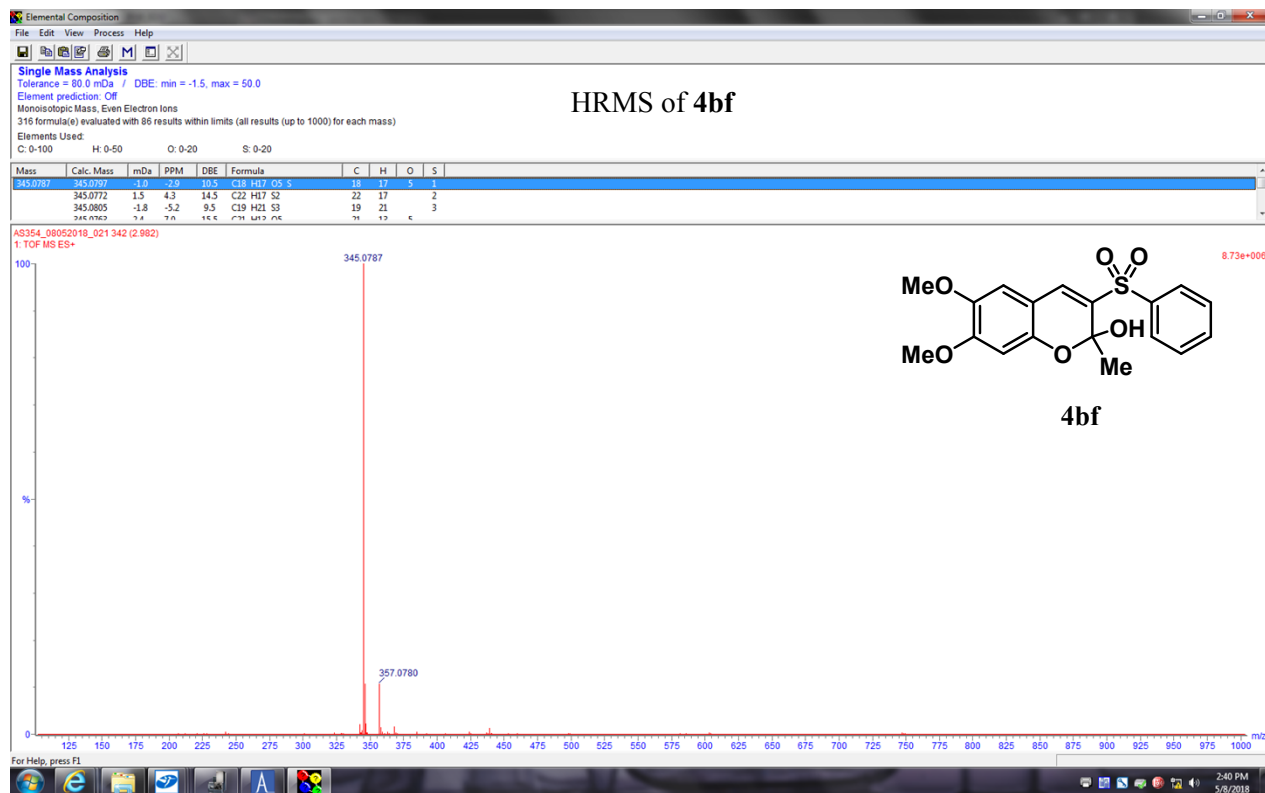
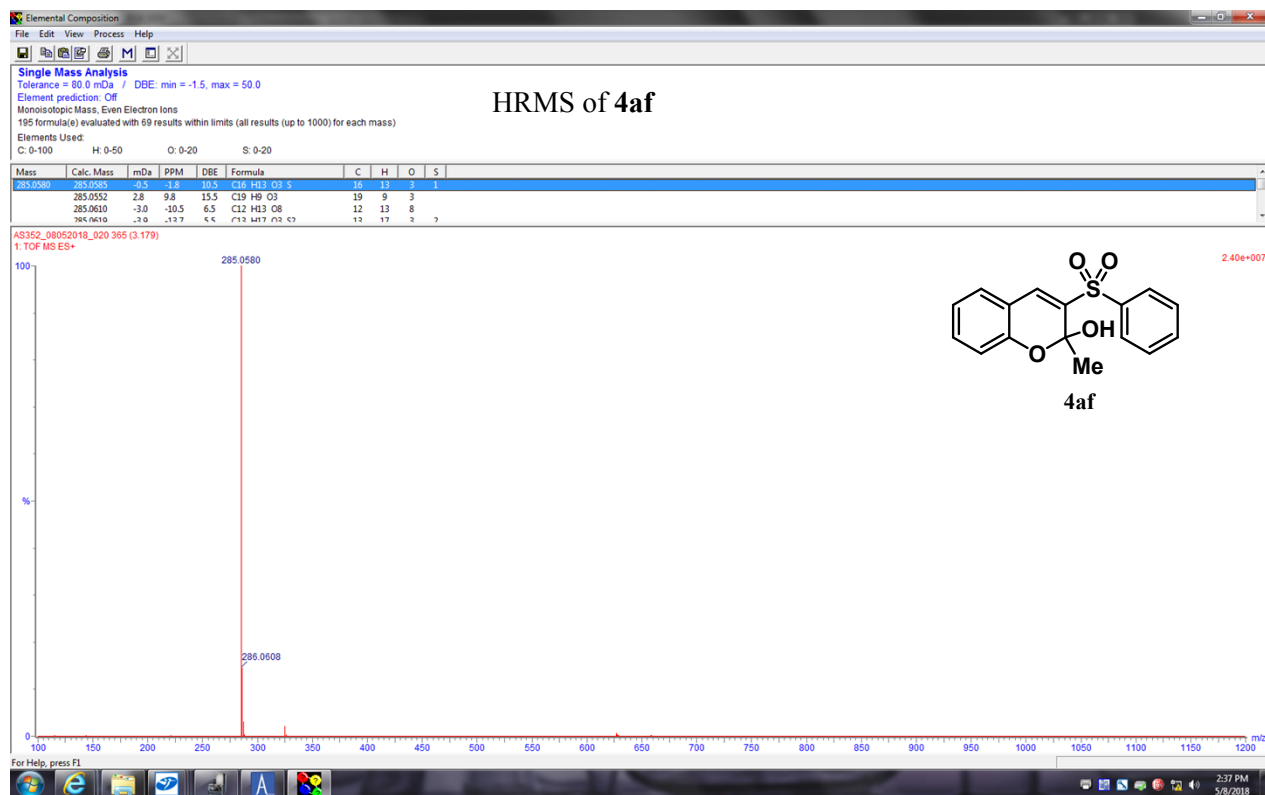


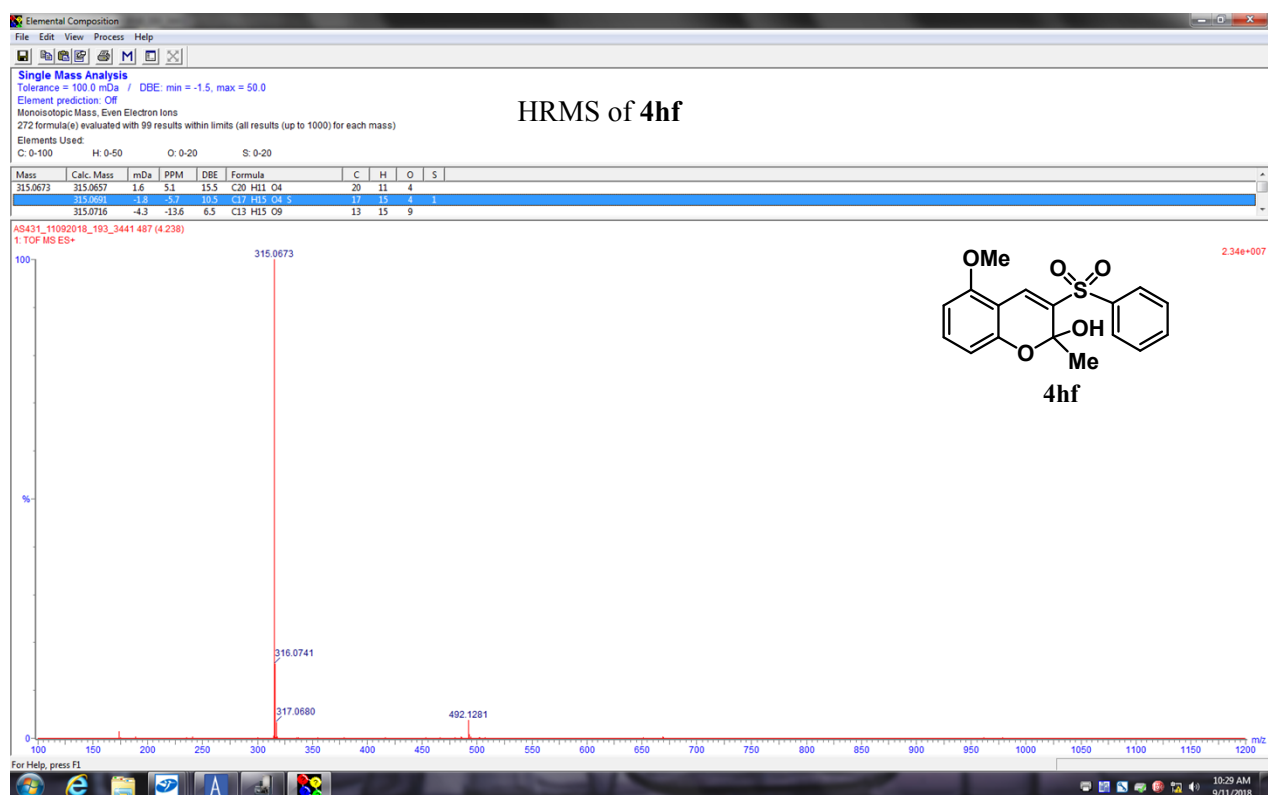
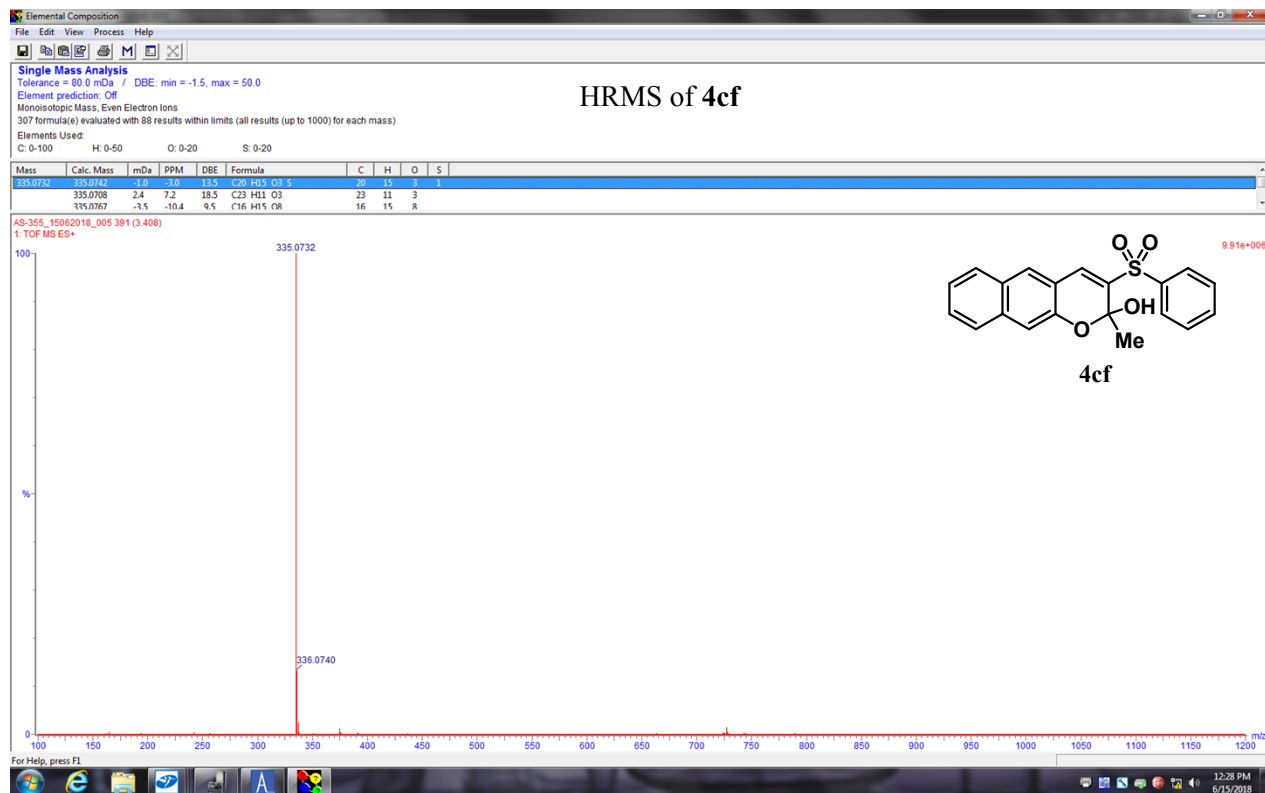


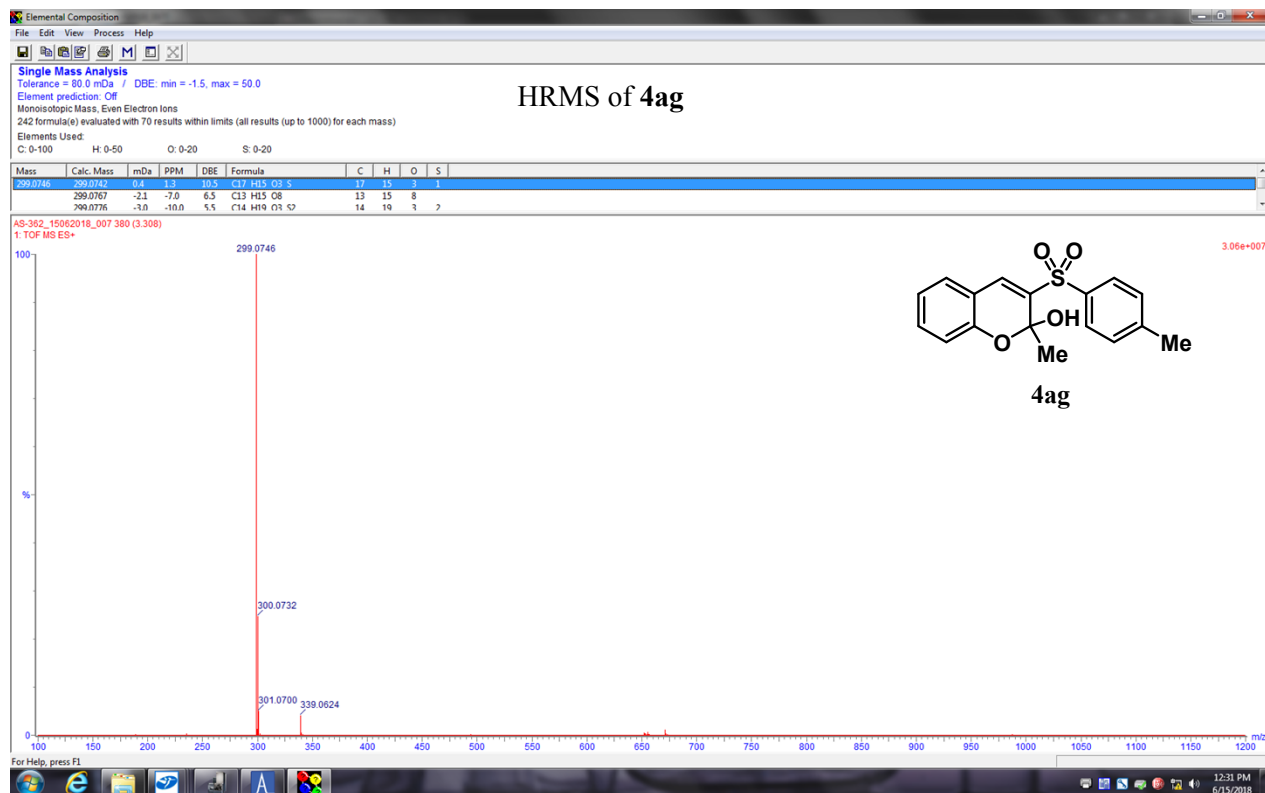
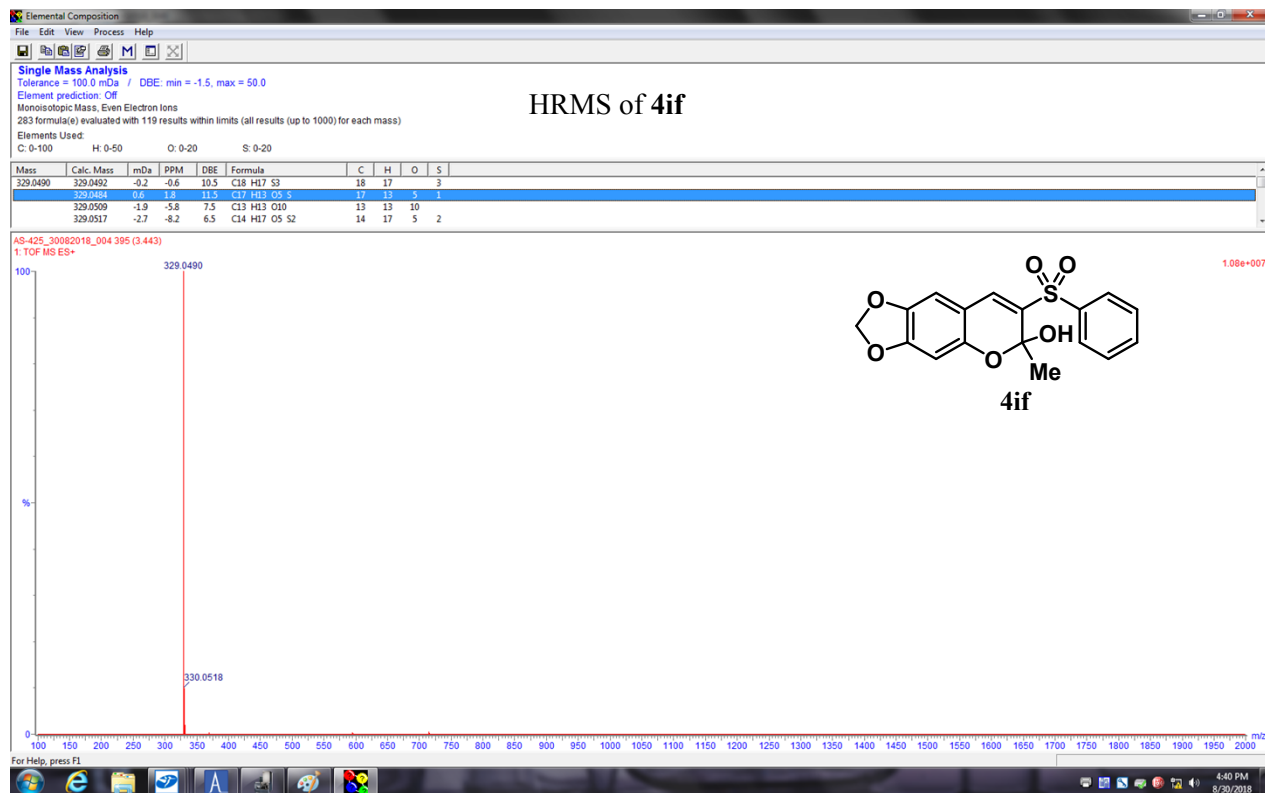


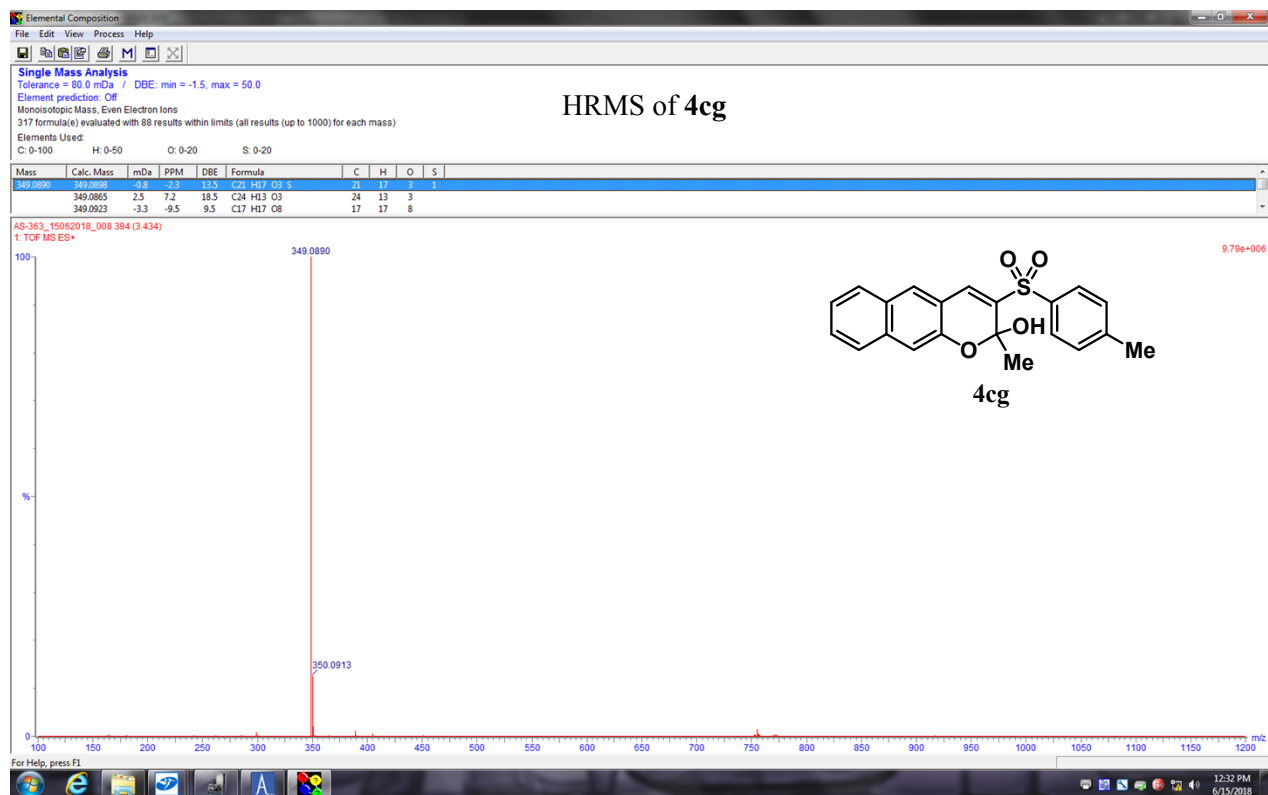
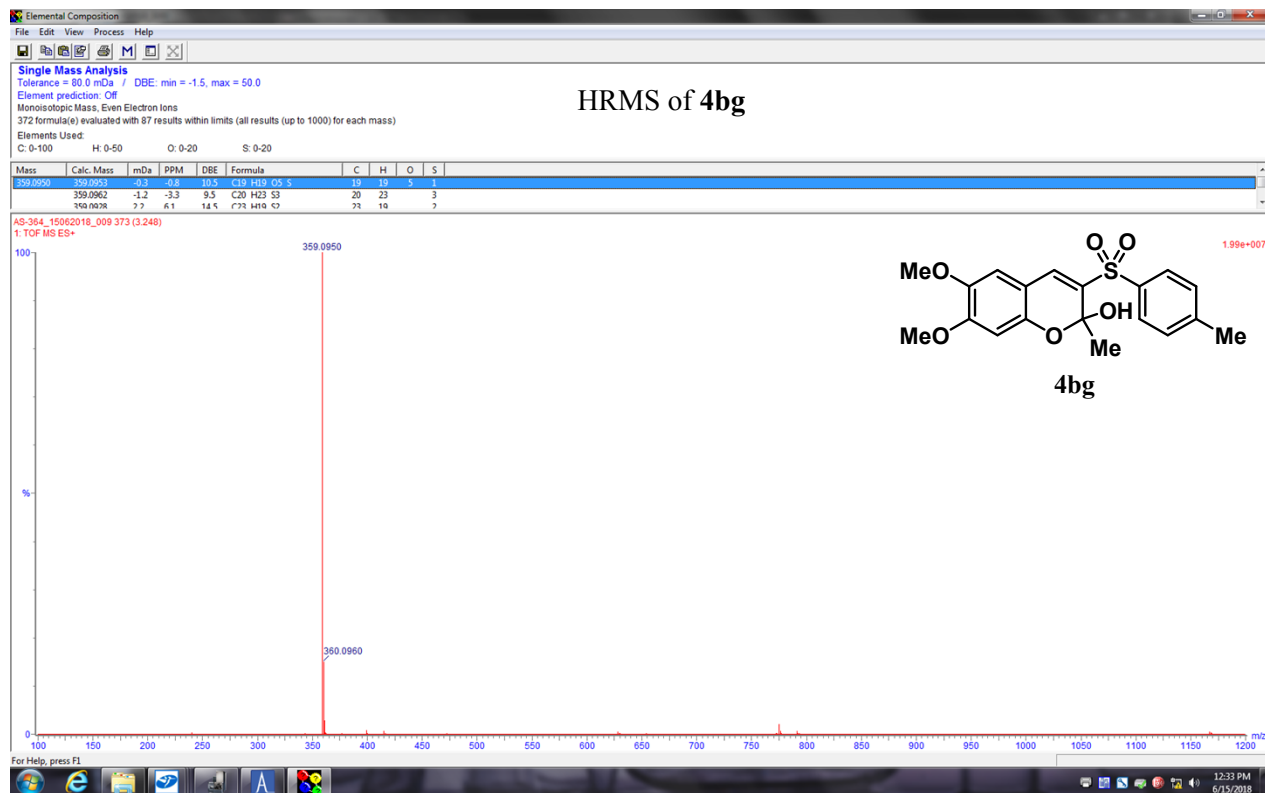


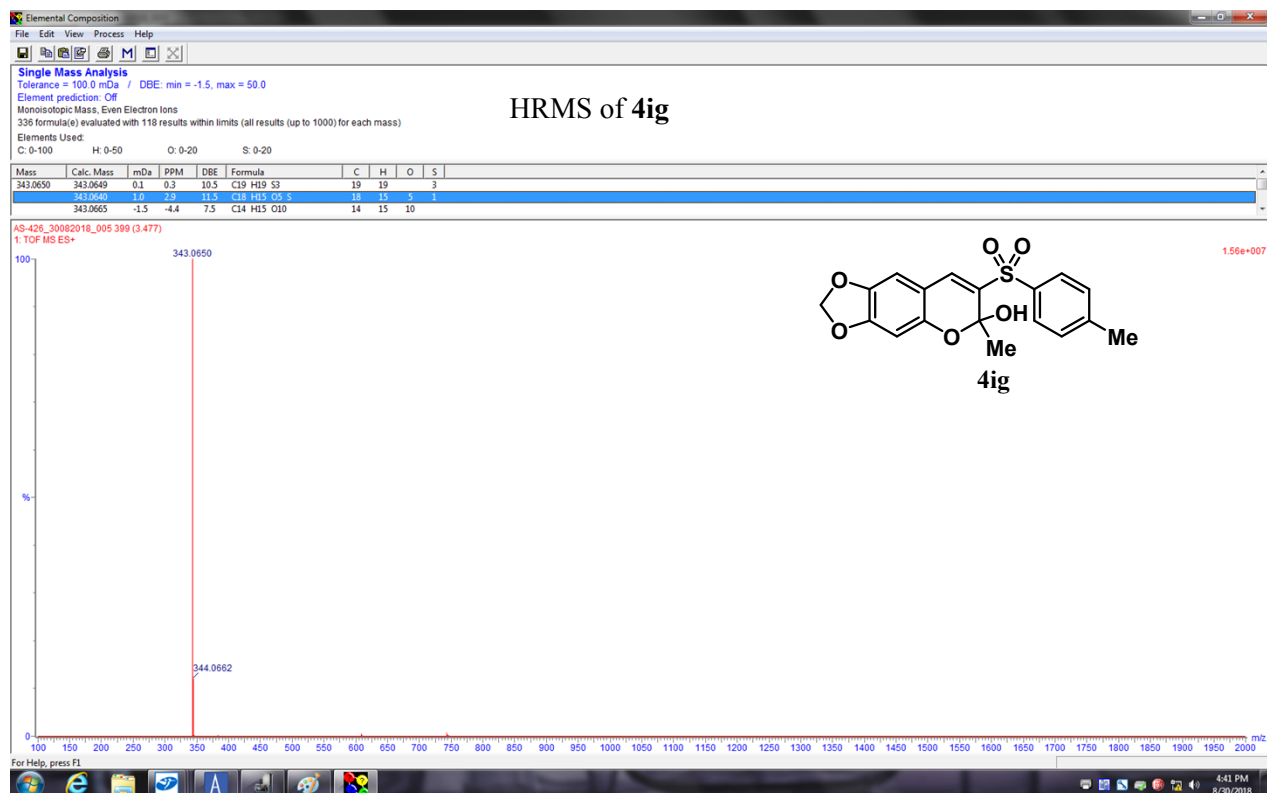
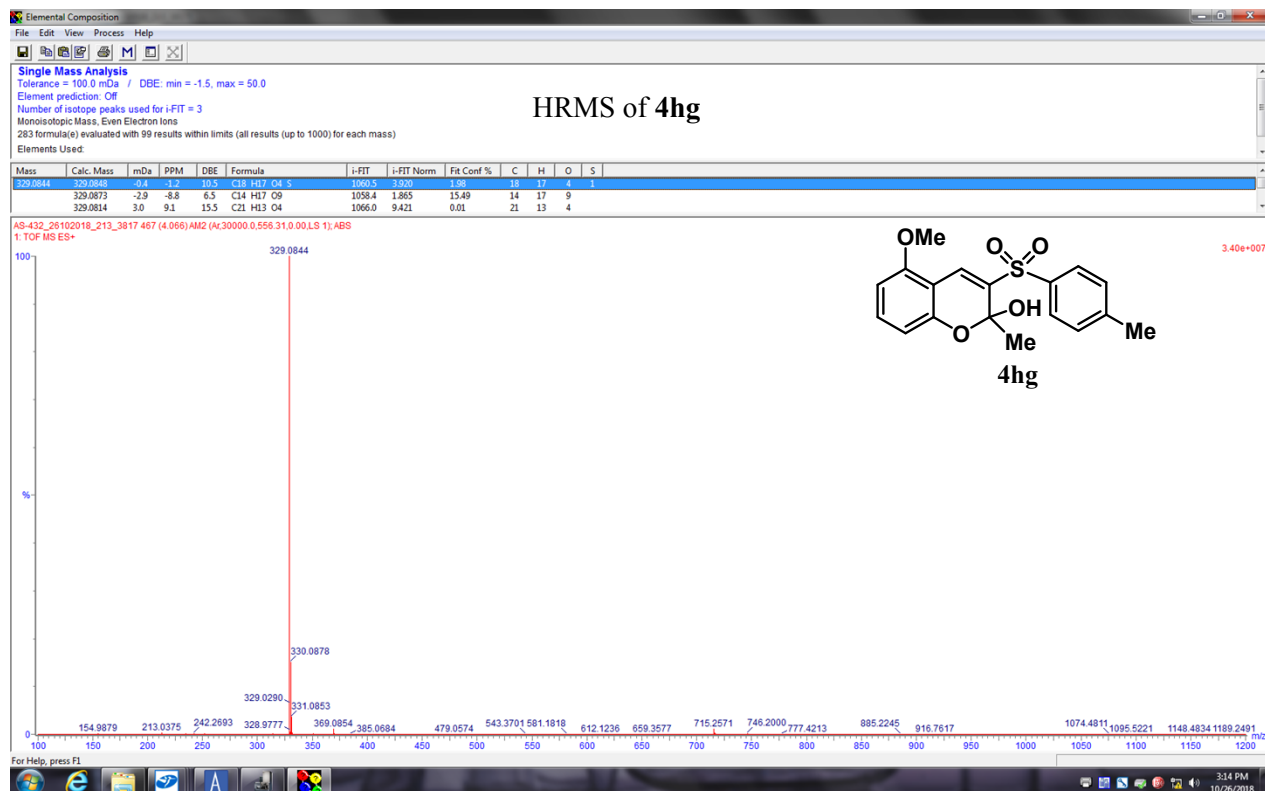


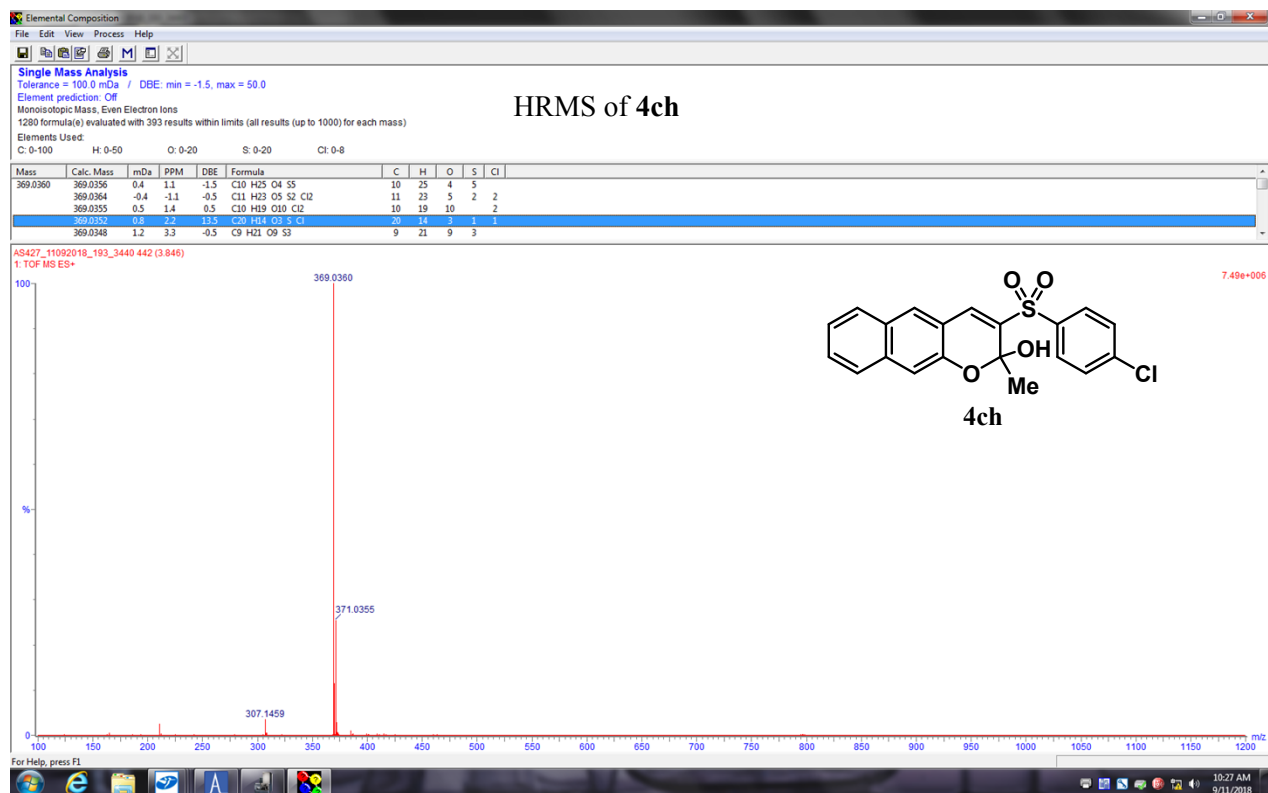
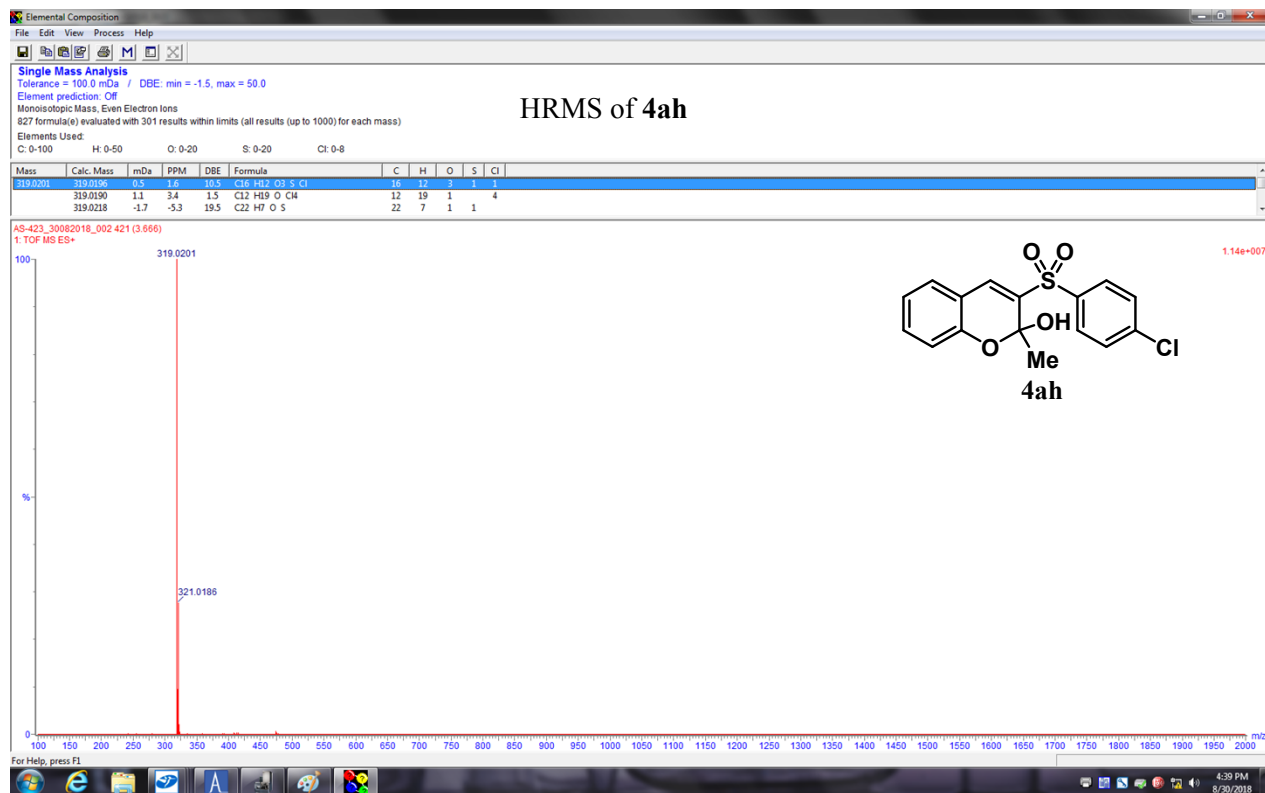


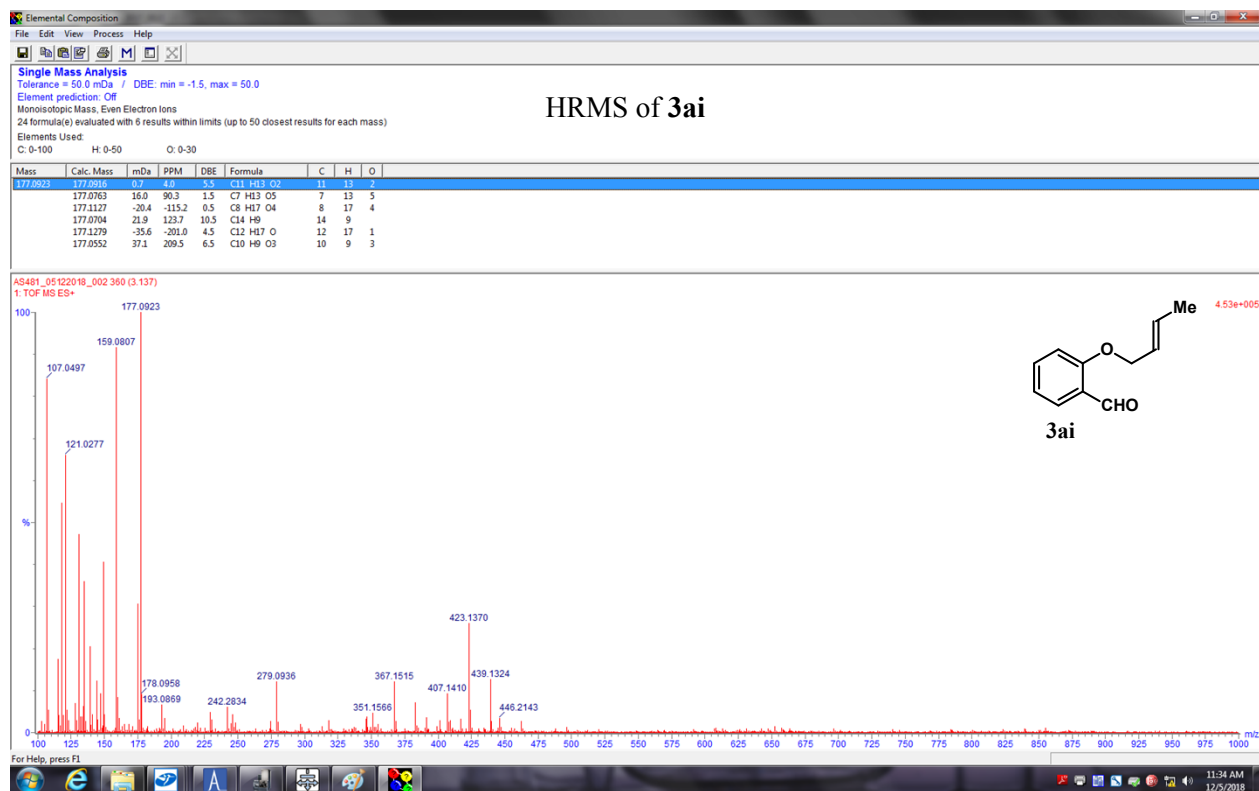










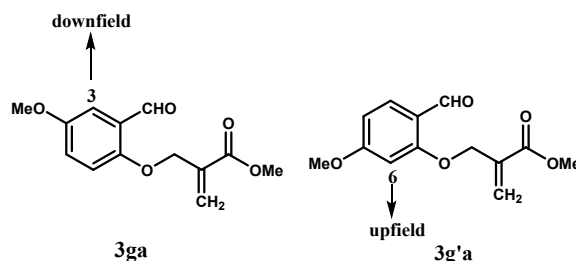


Assignment of product obtained from unsymmetrical arynes.

The products **3da/3d'a** - **3ec/3e'c** obtained from unsymmetrical aryne **1d** and **1e** are isolated as inseparable mixtures of two regioisomers. The regioisomers are not separated into individual isomers and their ratio was determined by ^1H NMR data.

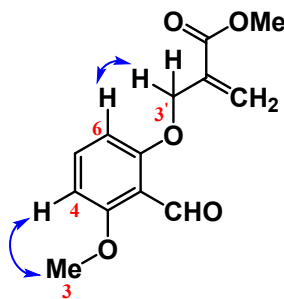
In order to confirm the product **3fa** obtained from unsymmetrical aryne **1f**, we have carried out an independent experiment to synthesize the same compound **3fa** alternatively using 2-hydroxy-1-naphthaldehyde and activated alkene methyl-2-(bromomethyl)acrylate. The product obtained from this independent experiment was characterized by ^1H and ^{13}C NMR data. This spectroscopic data resemble with our synthesized compound **3fa**, which confirmed our proposed structure. This suggests that the product obtained from **1f** results in single regioisomer **3fa** which is attributed to preferential attack of carbonyl oxygen atom of DMF at the less sterically hindered carbon atom of naphthalene.

The assignment of products **3ga** and **3g'a** obtained from unsymmetrical aryne precursor **1g** when treated with methyl-2-(bromomethyl)acrylate could be explained from ^1H NMR data. In case of compound **3ga**, the proton (3) resonates at 7.33 ppm whereas in case of compound **3g'a**, the proton (6) resonates at 6.47 ppm which appears to be more upfield due to the presence of ether groups on the adjacent position of the proton. This information from ^1H NMR data helps us to confirm our proposed structure.



The structure of the compound **3ha** was characterized by using 1D (^1H and ^{13}C) and 2D (^1H - ^1H NOESY experiment) NMR analysis.

The NOESY correlation between H-4/OMe-3 (Aromatic-ortho) protons and H-6/H-3' protons suggests that they are in spatial proximity which confirmed our proposed structure.



NOESY of 3ha

28980
AS-164

