Supporting Information

Direct Synthesis of *ortho*-Methylthio Allyl and Vinyl Ethers *via* Three Component Reaction of Aryne, Activated Alkene and DMSO

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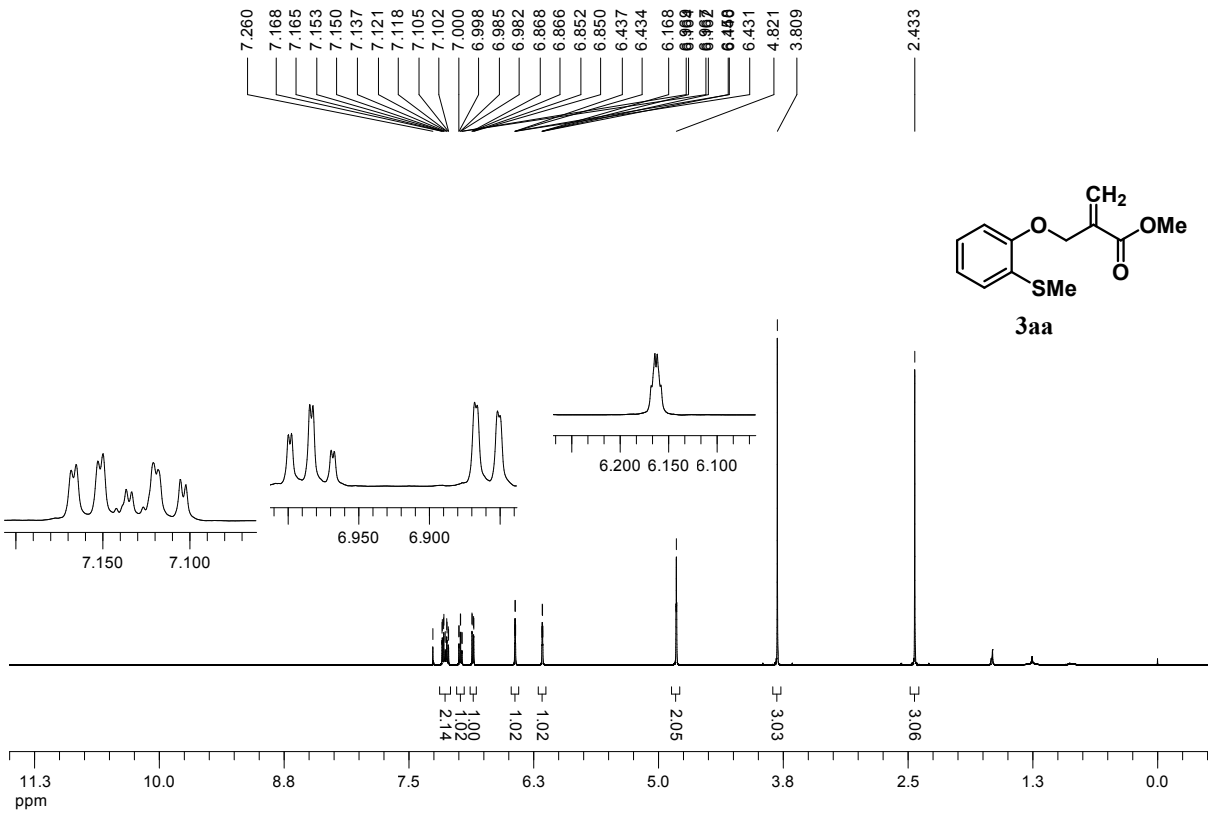
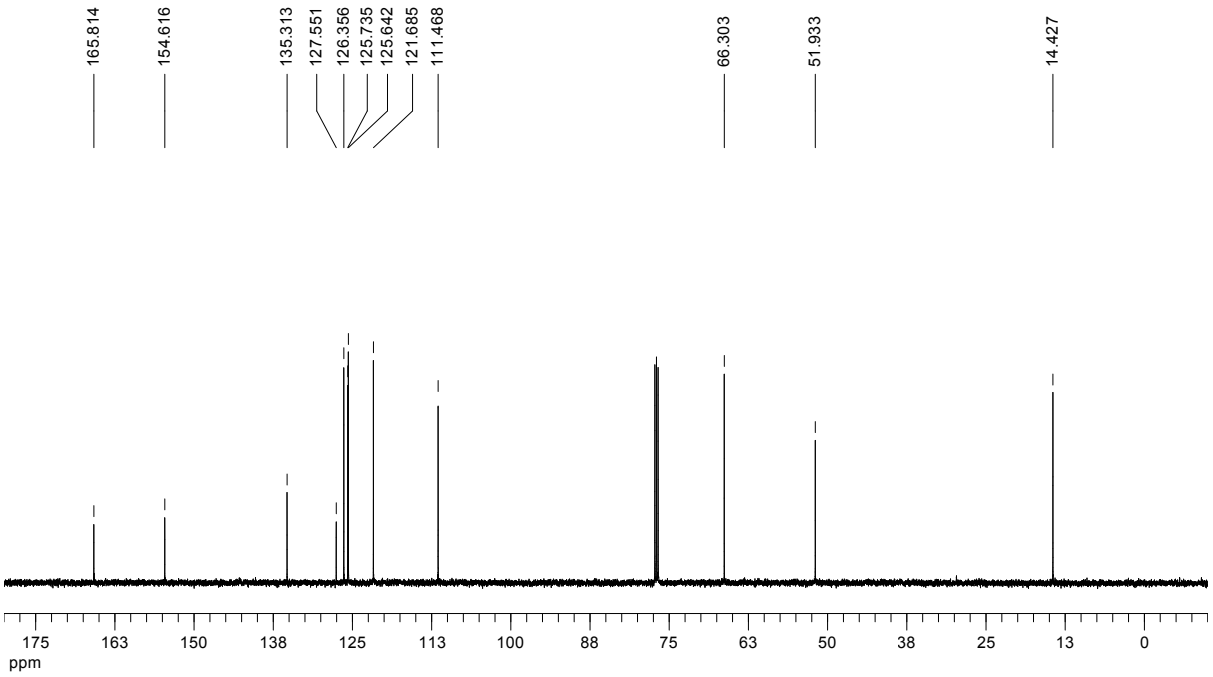
Copies of spectra (^{1}H, ^{13}C and HRMS) and Some independent experiments

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



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



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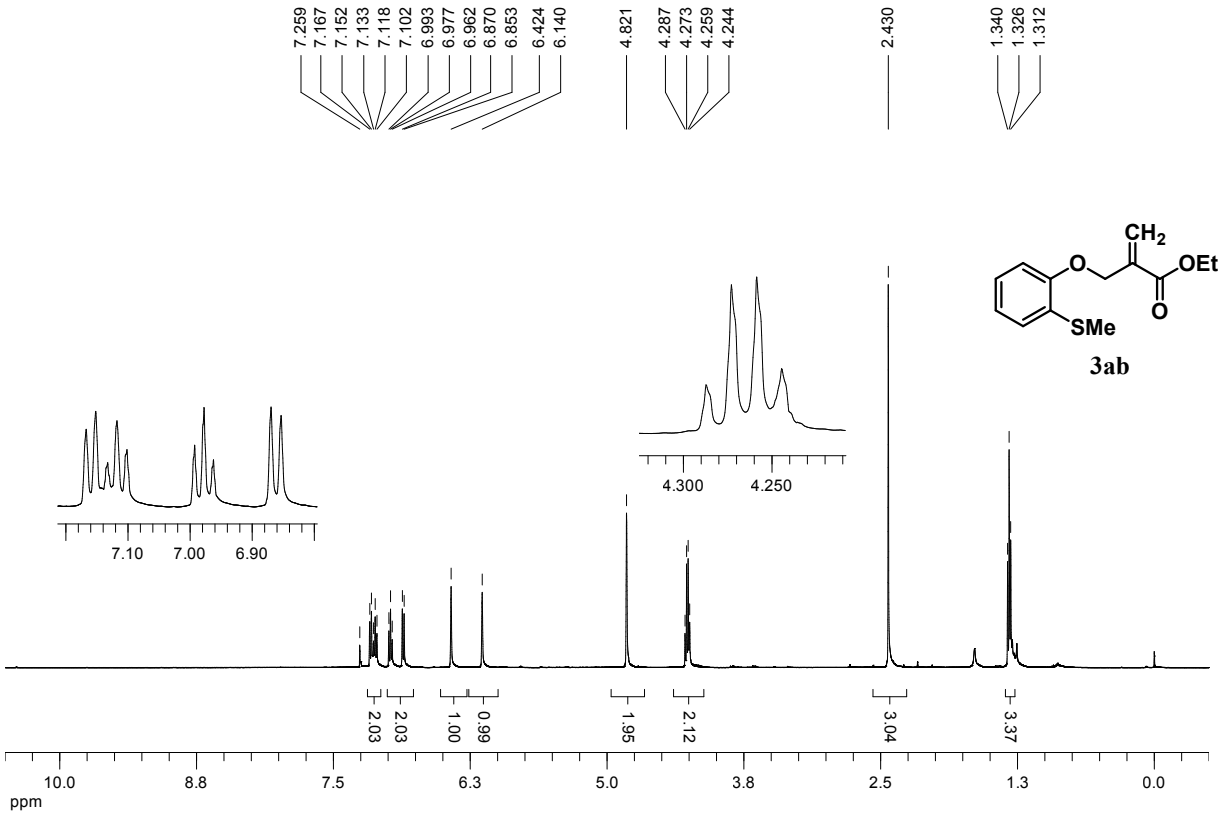

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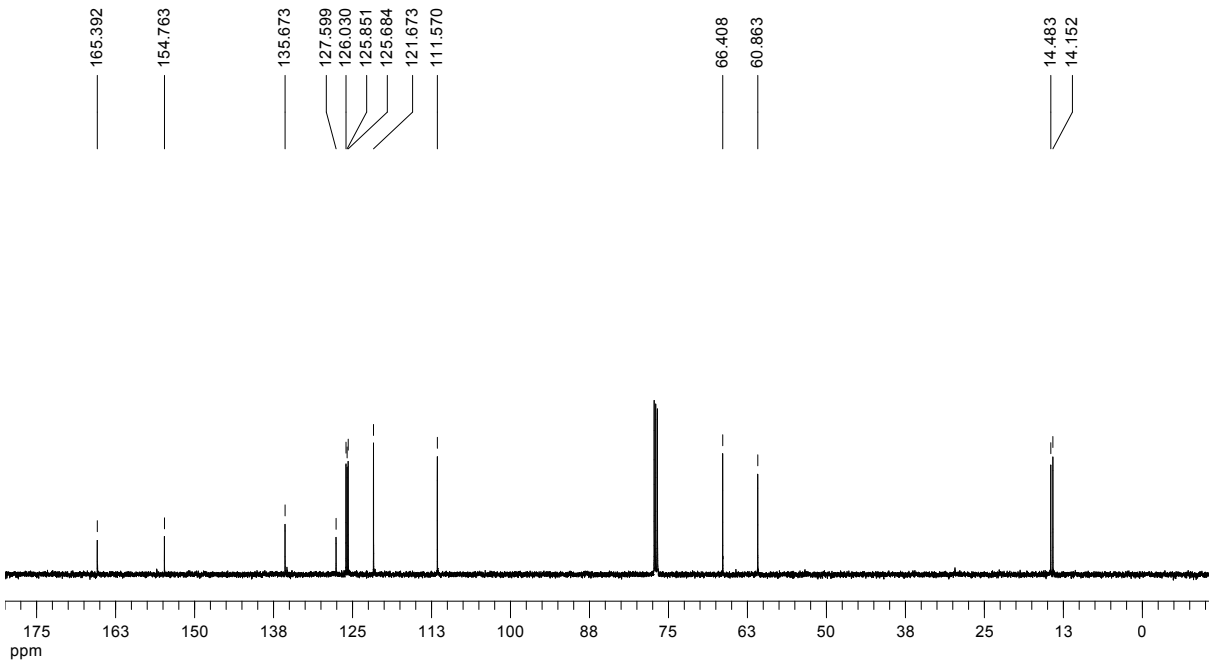

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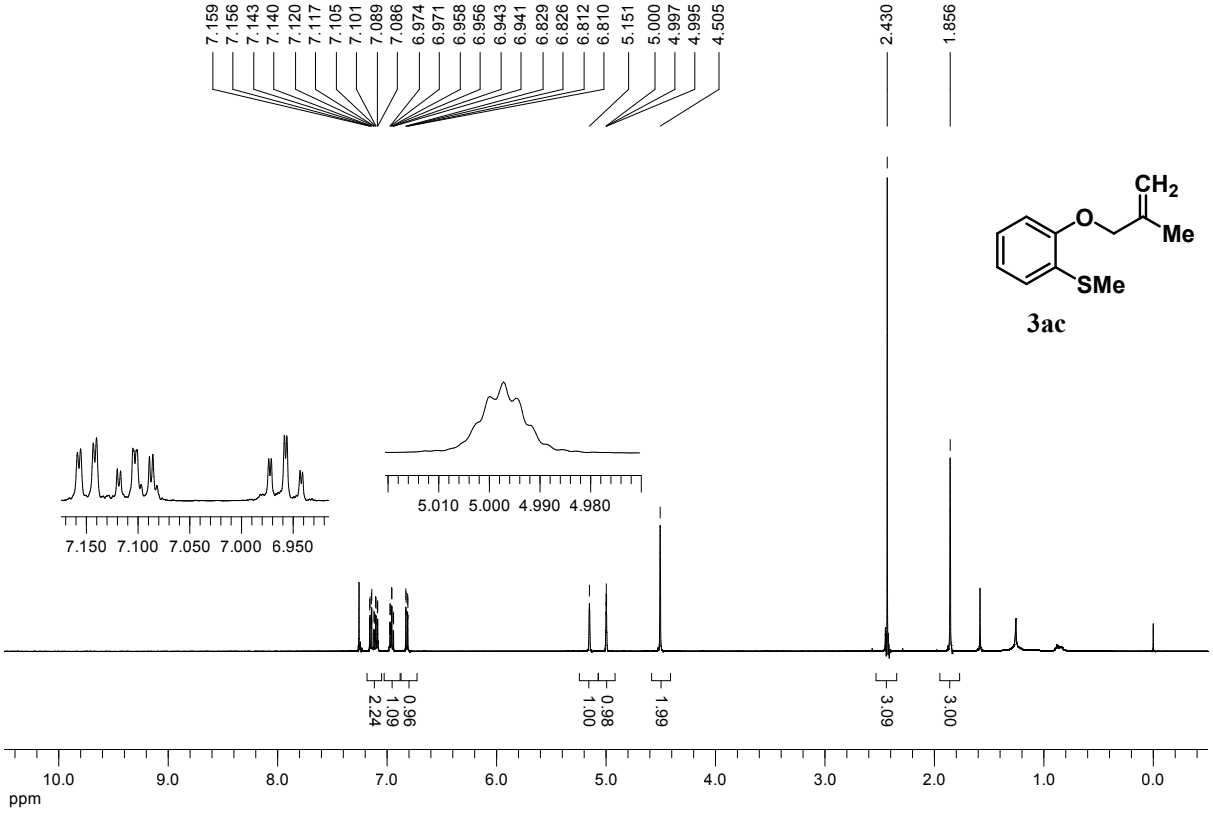

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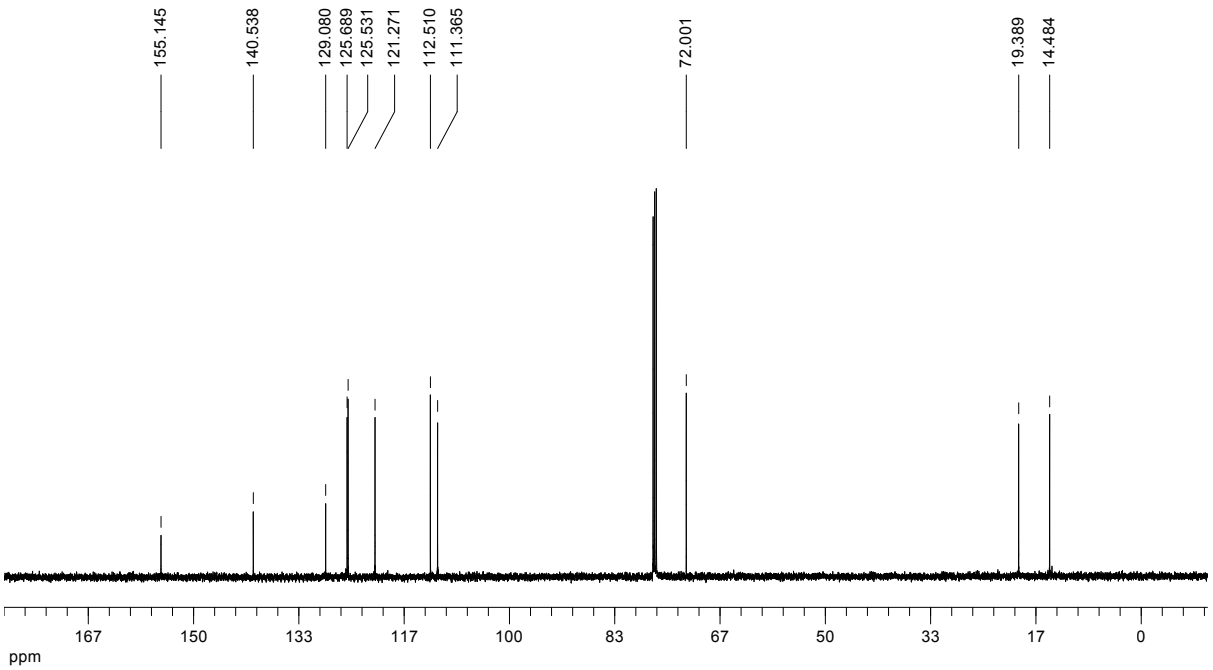

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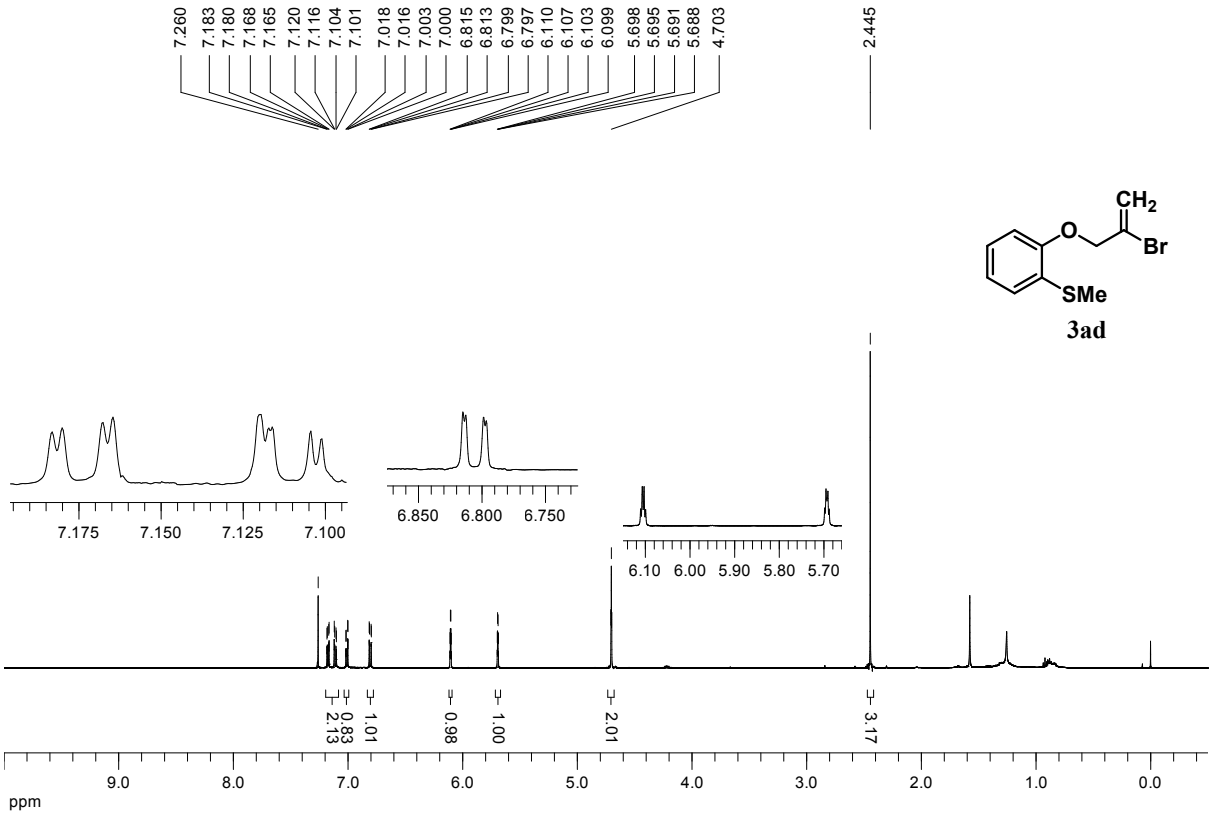

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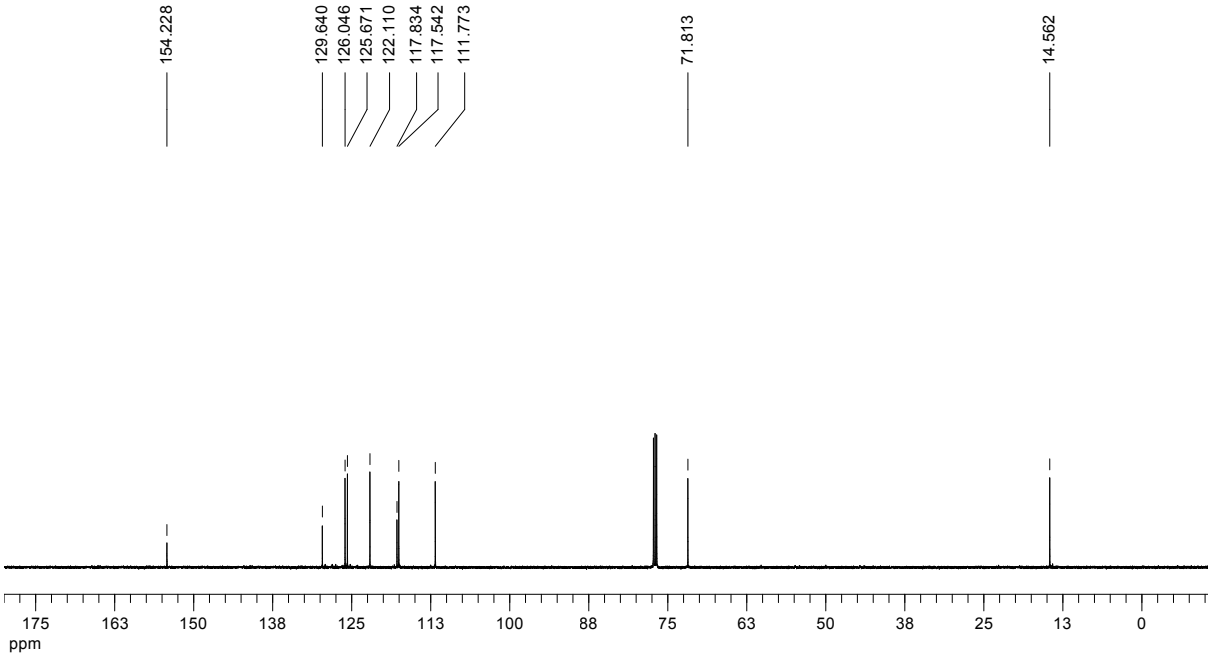

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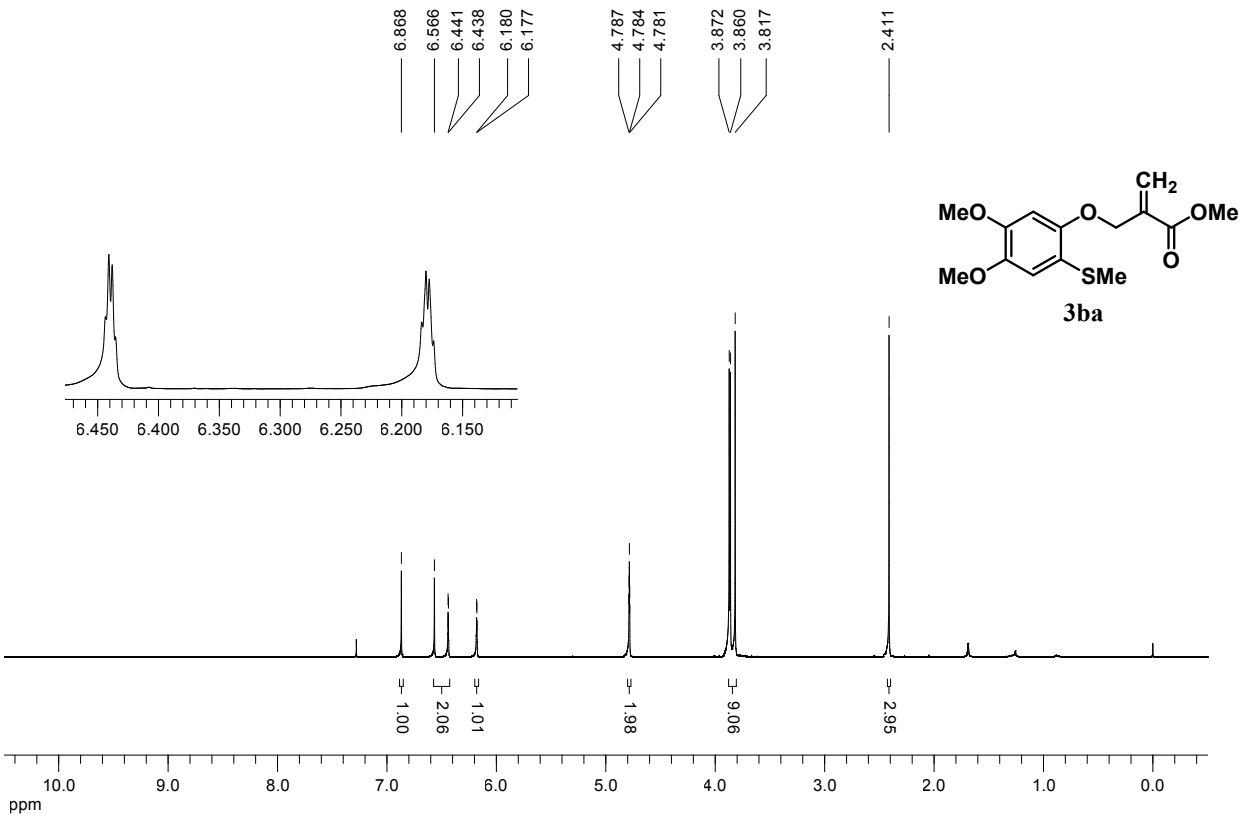

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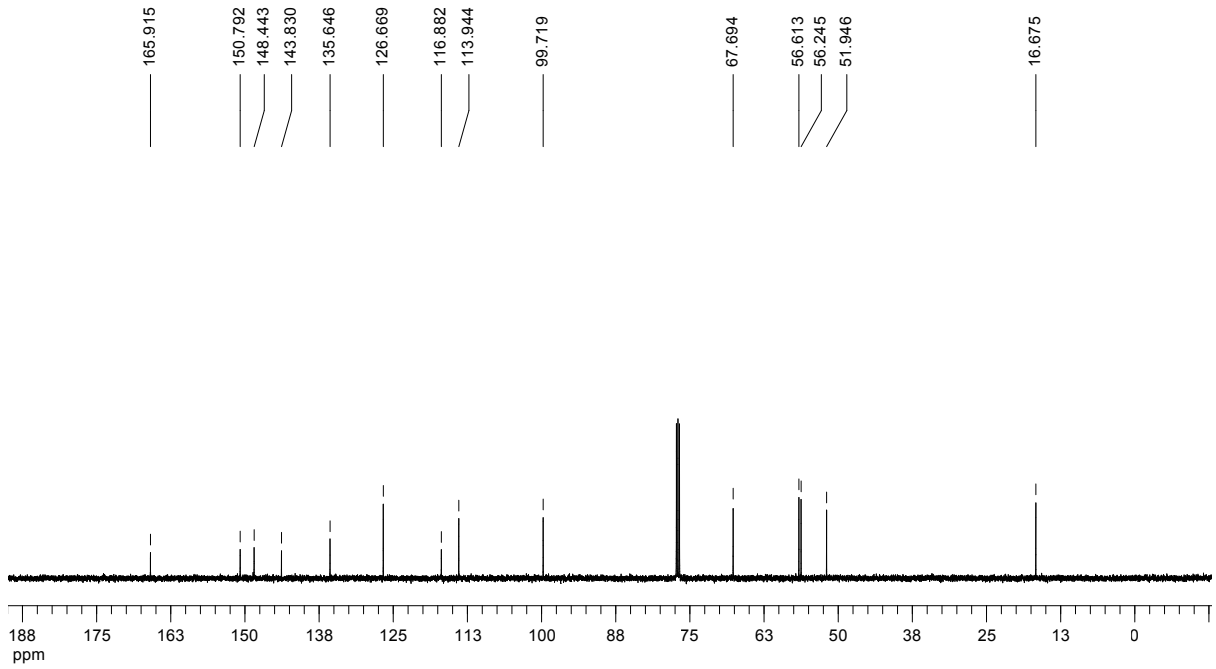

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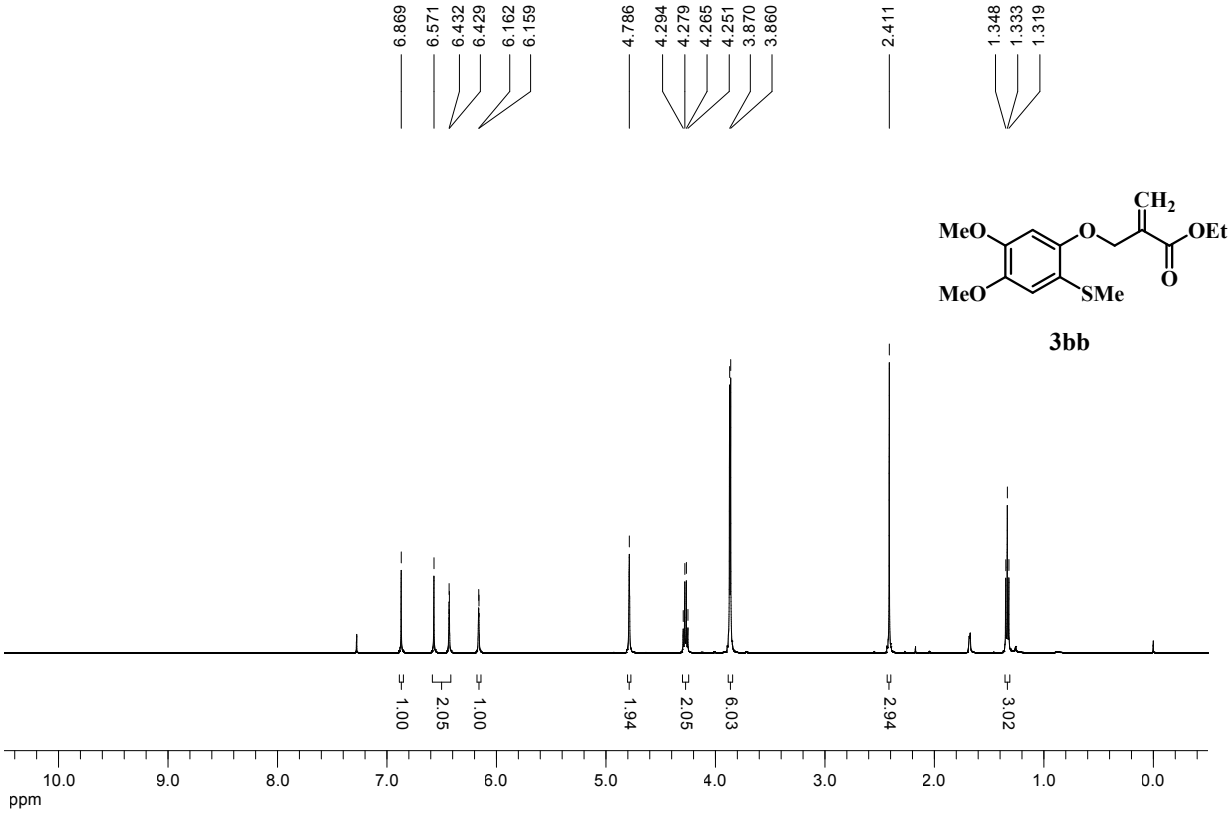

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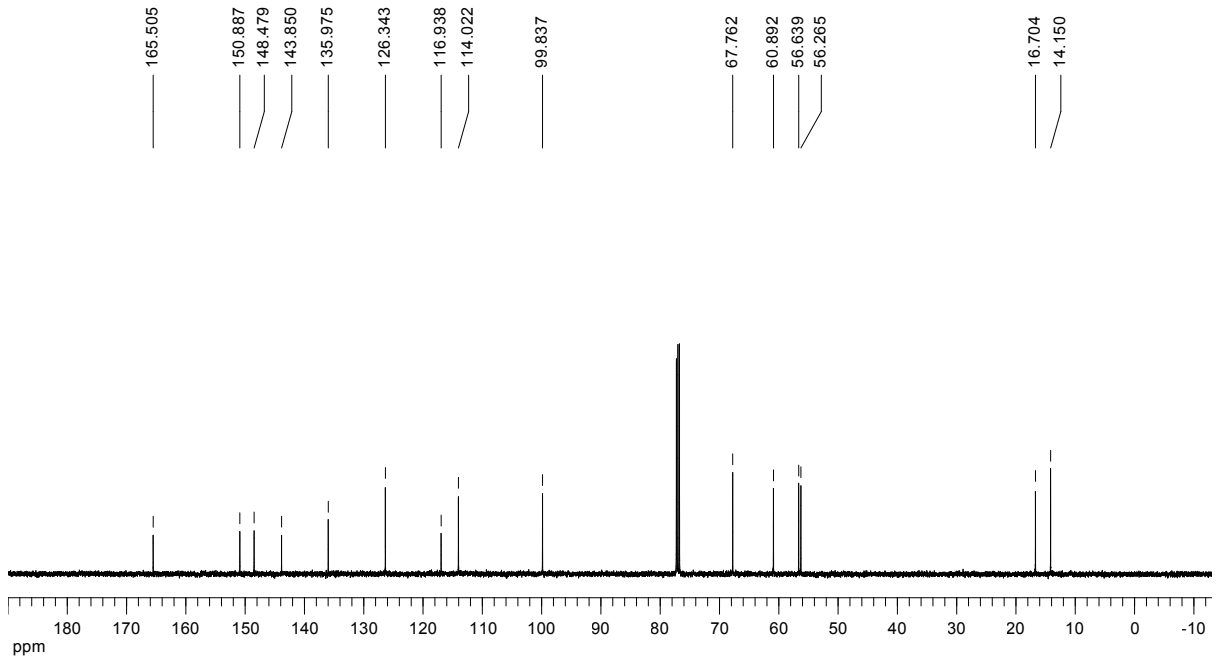

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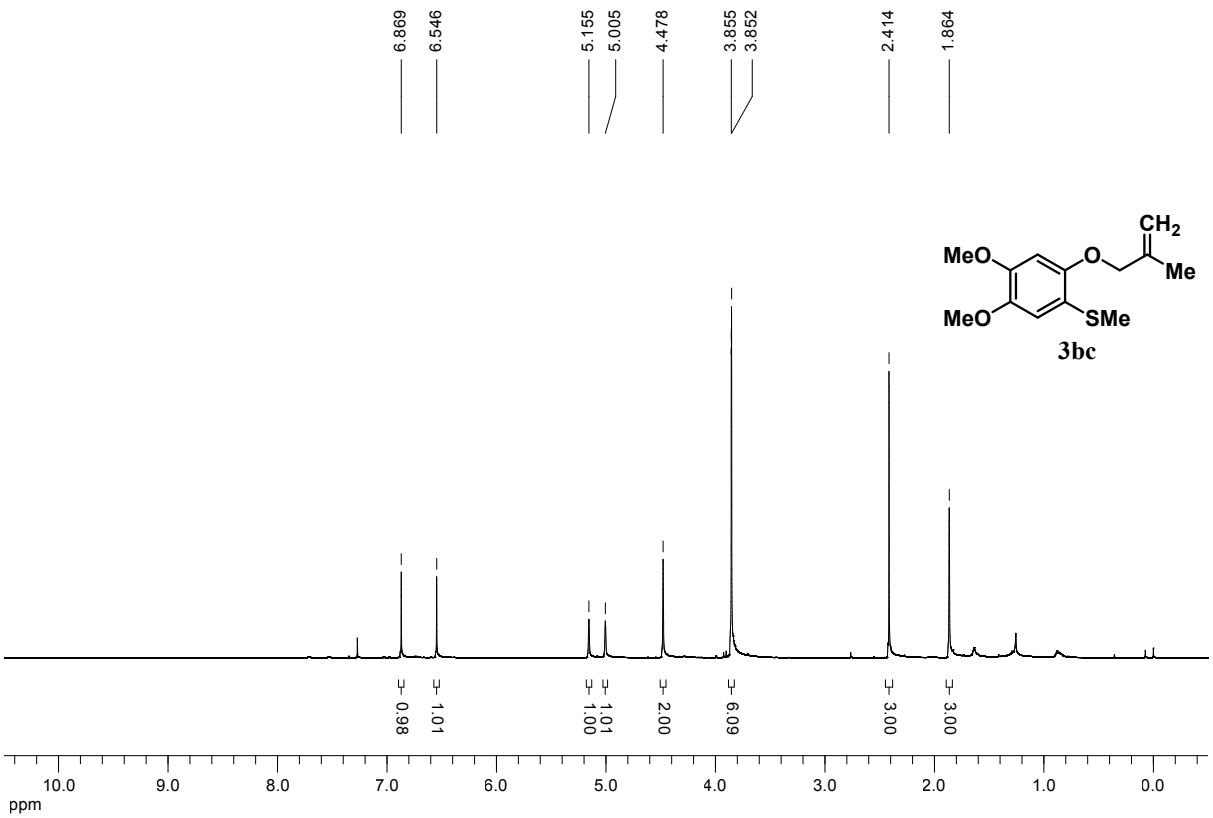

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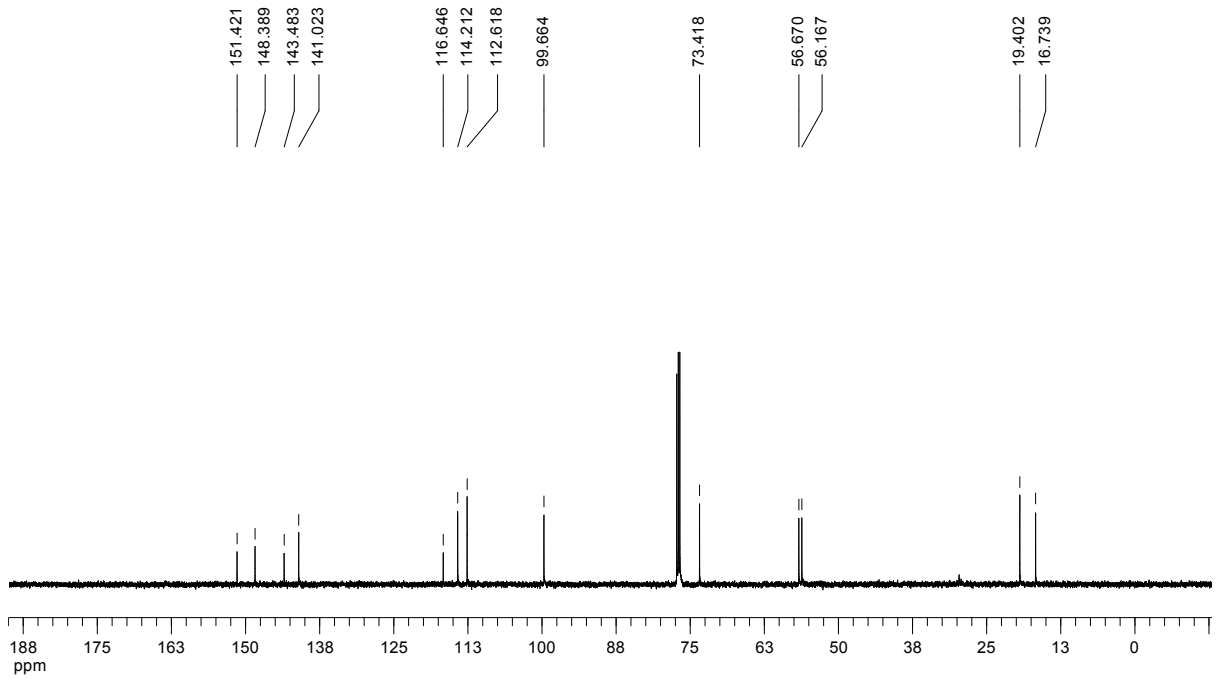

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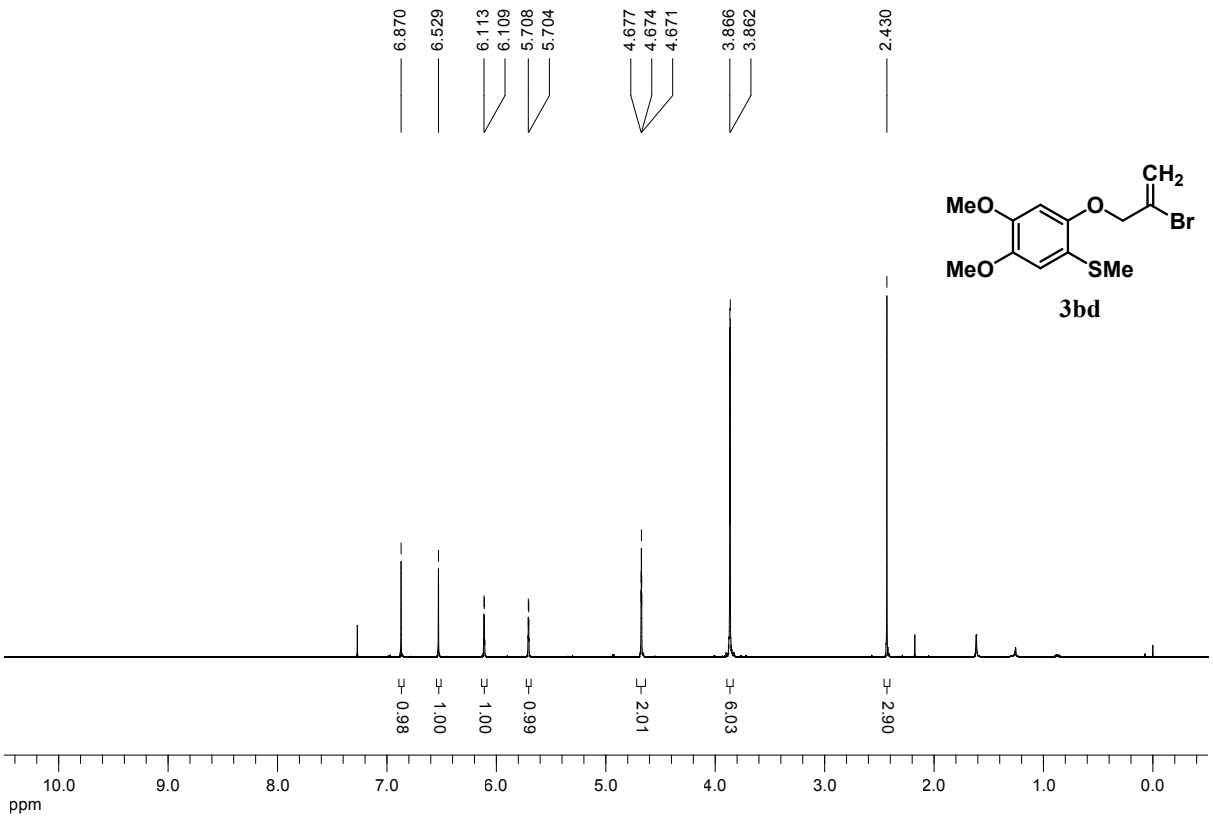

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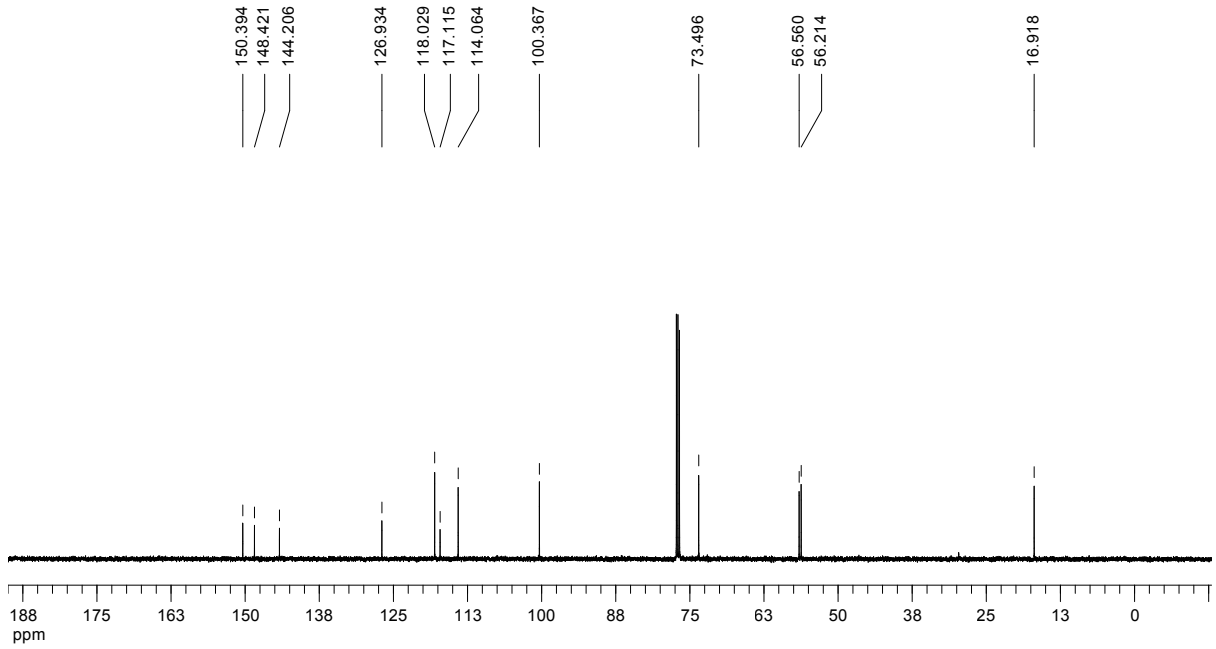

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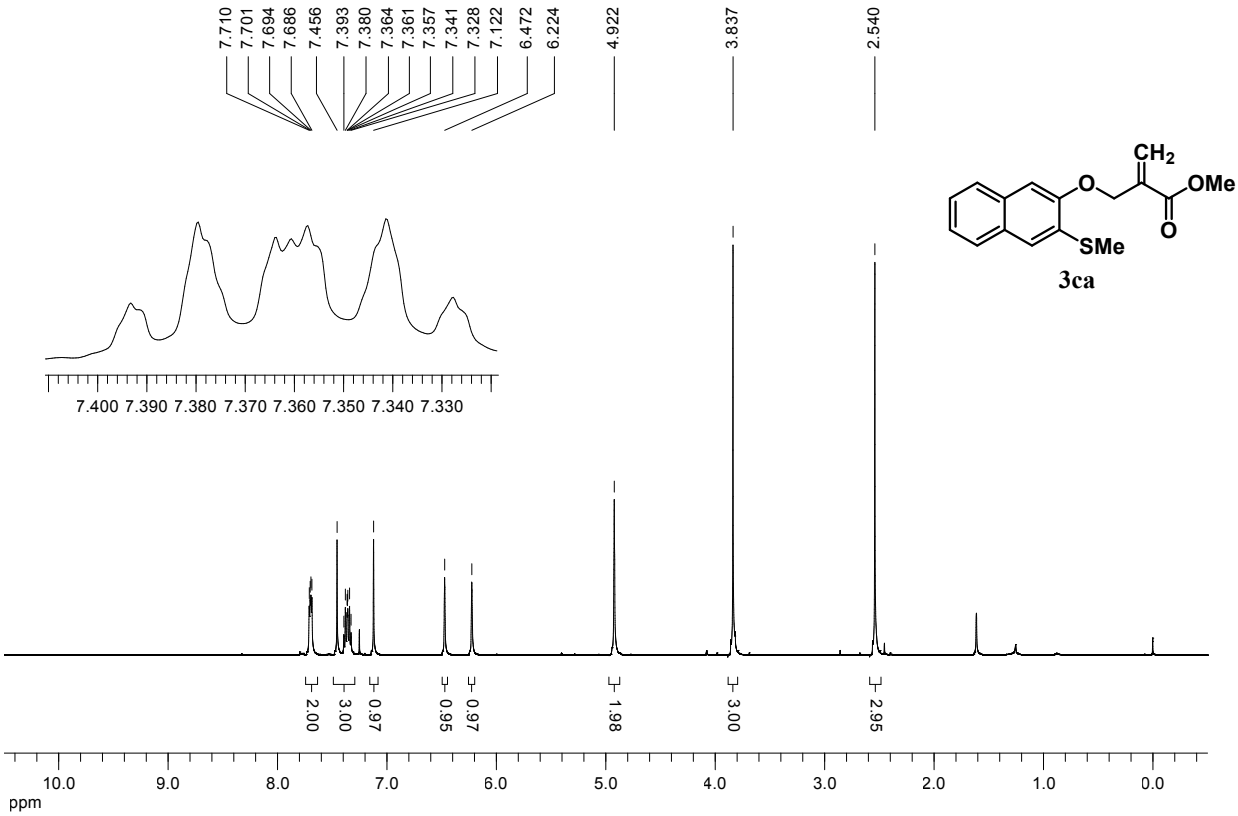

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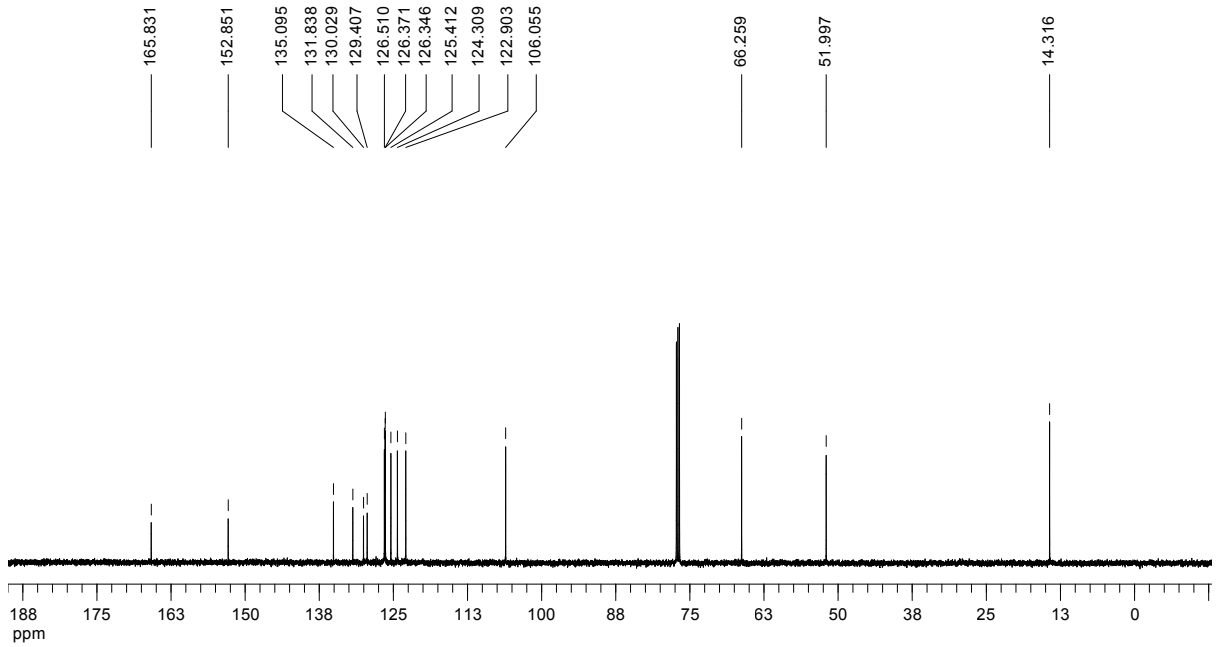

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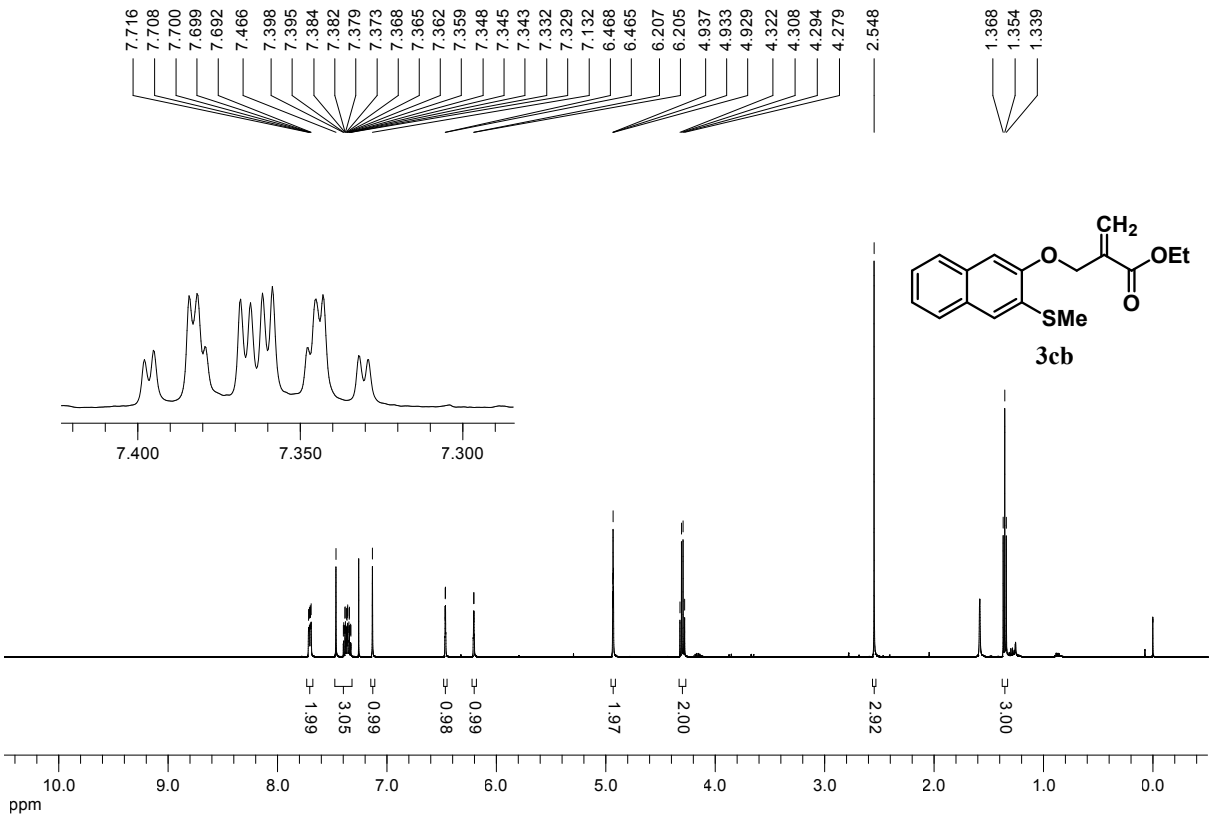

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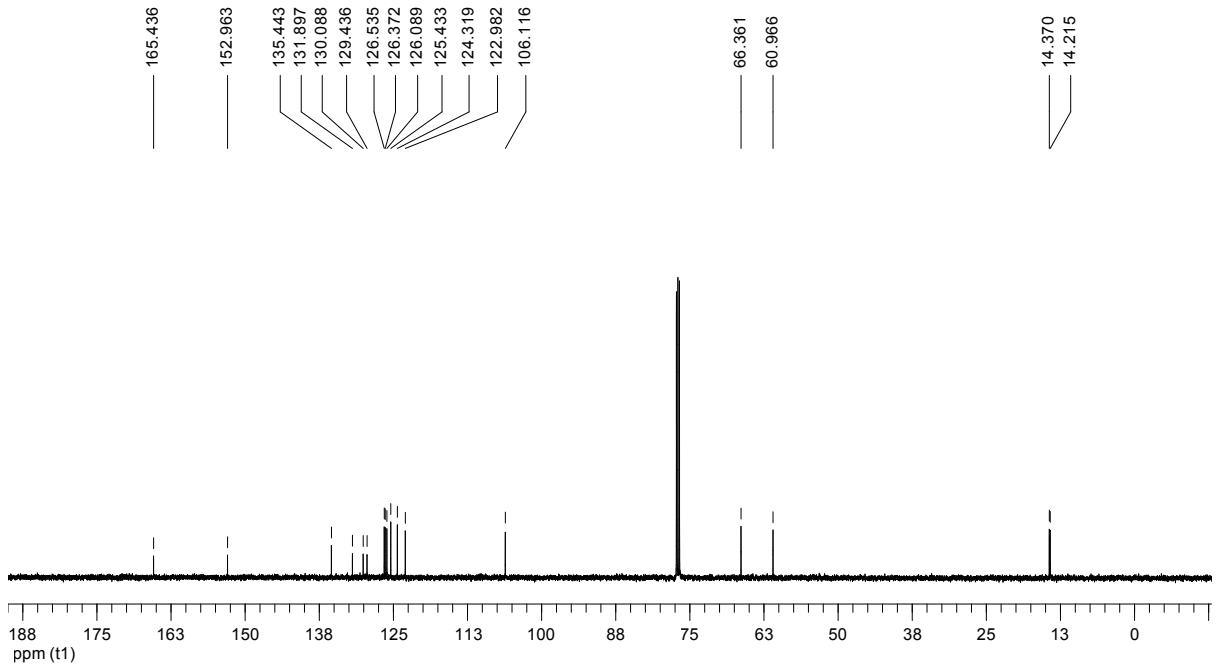

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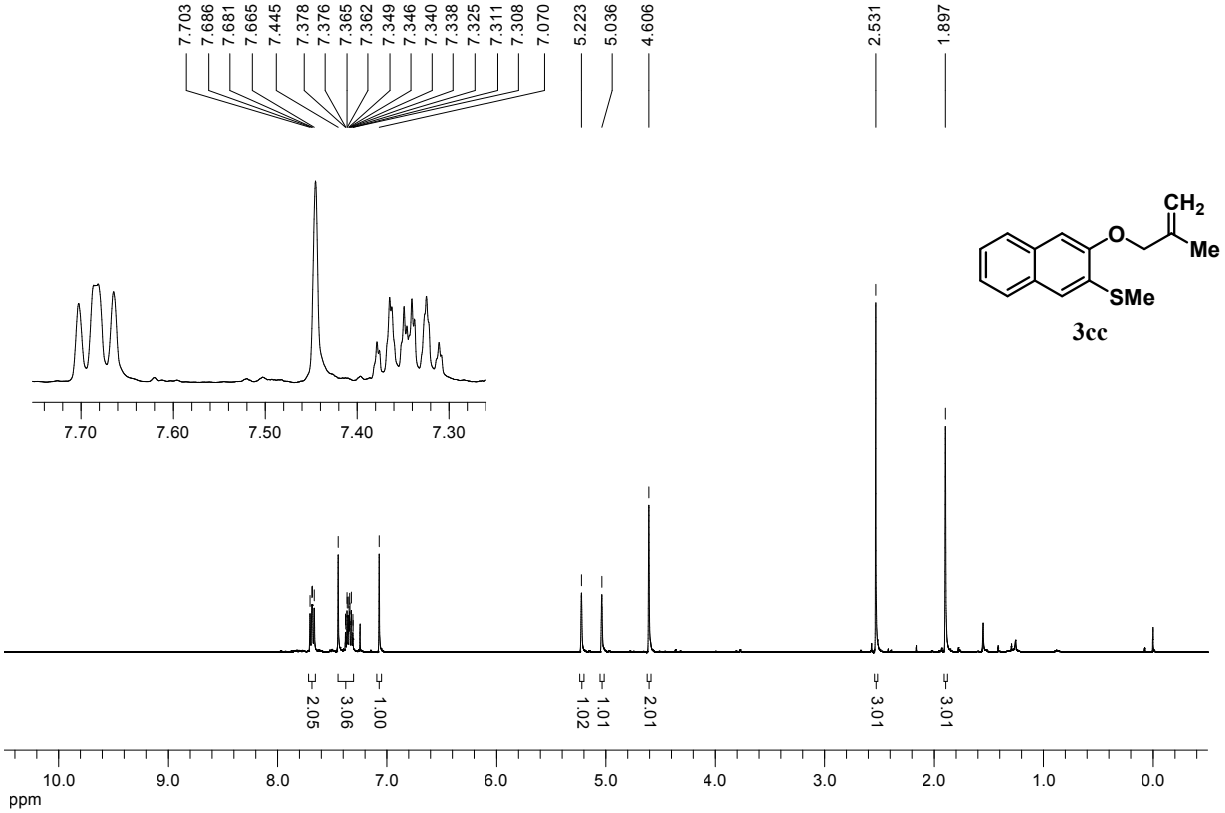

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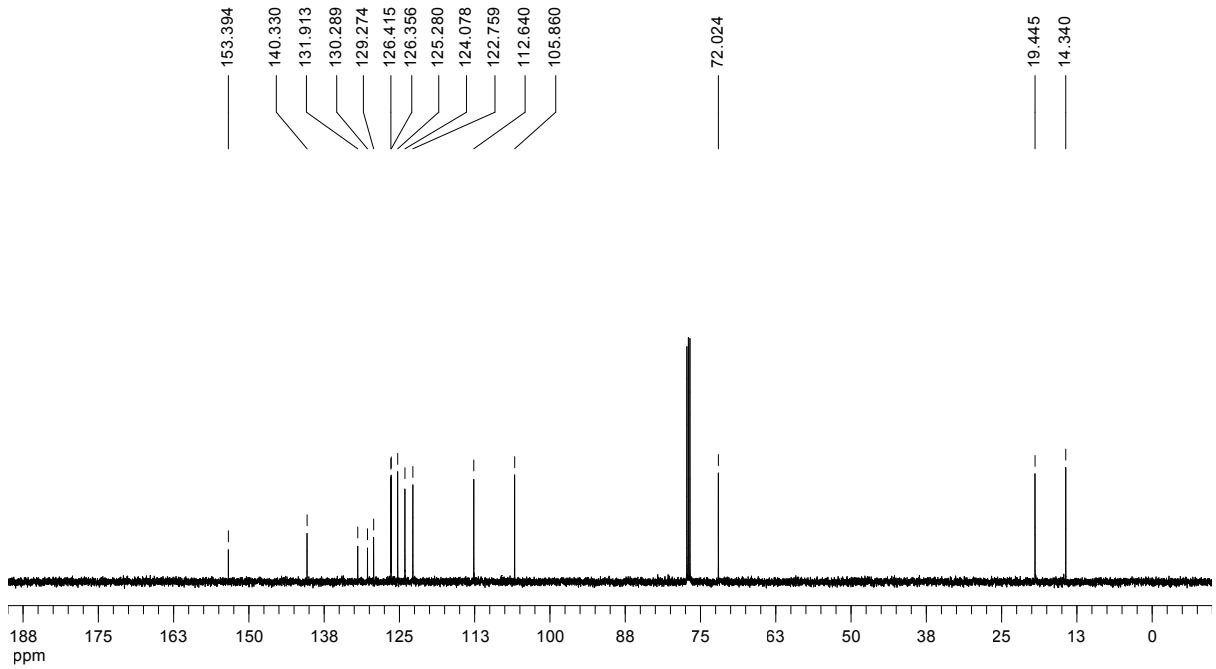

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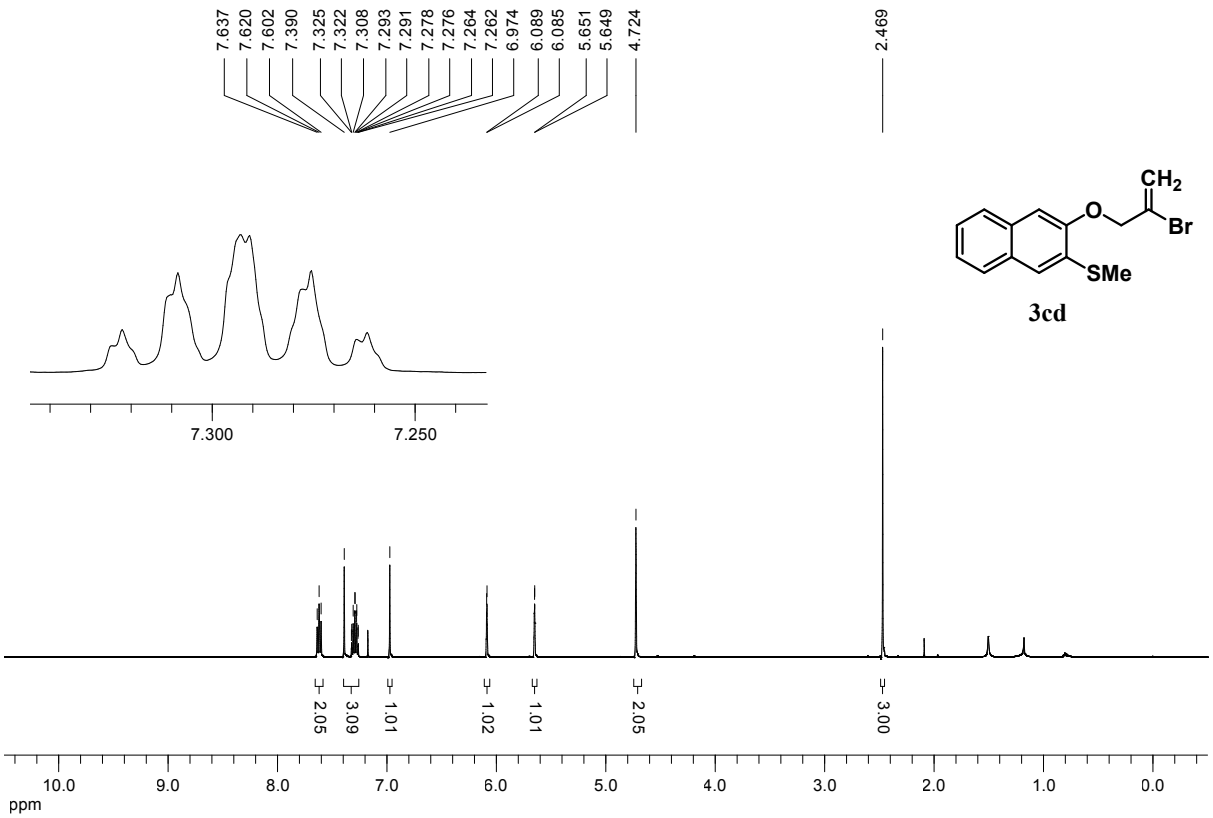

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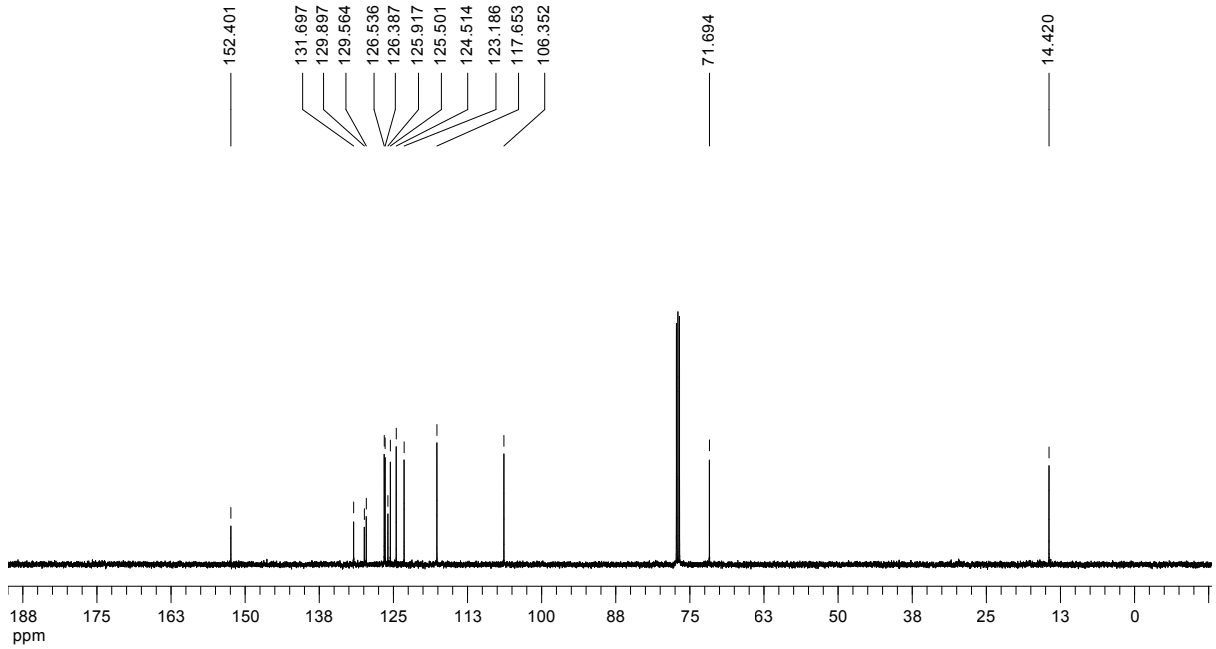

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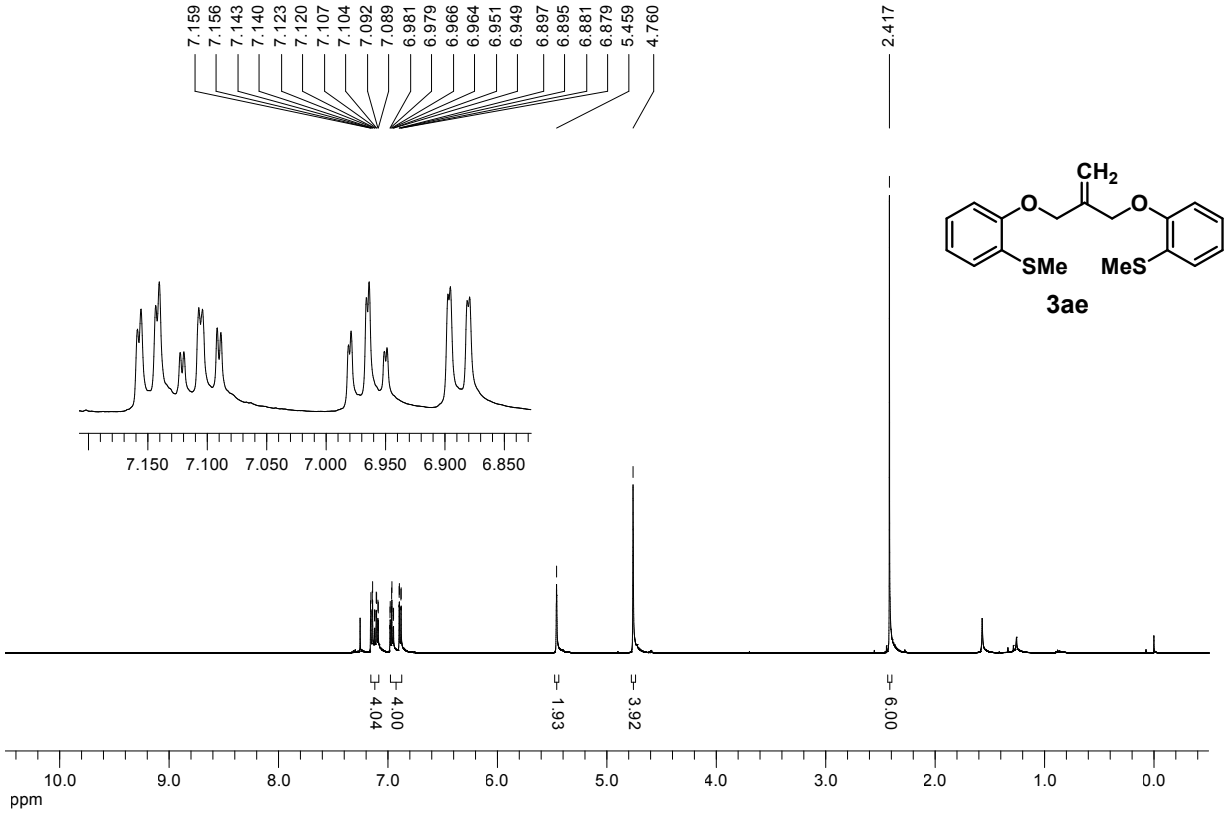

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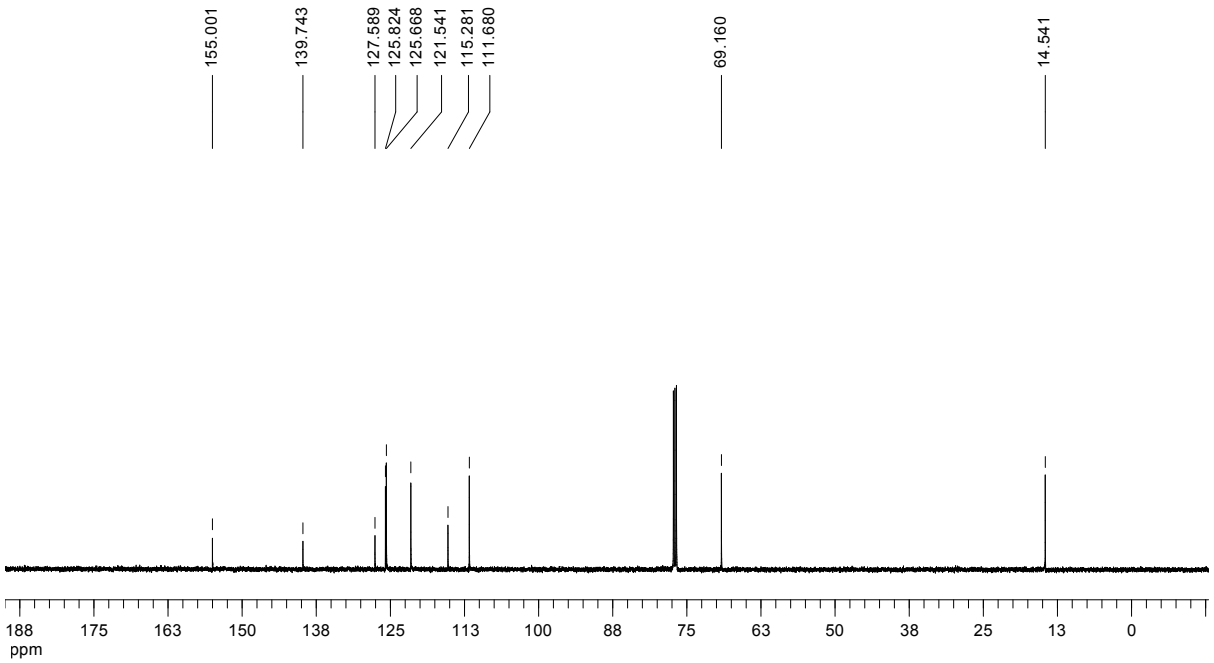

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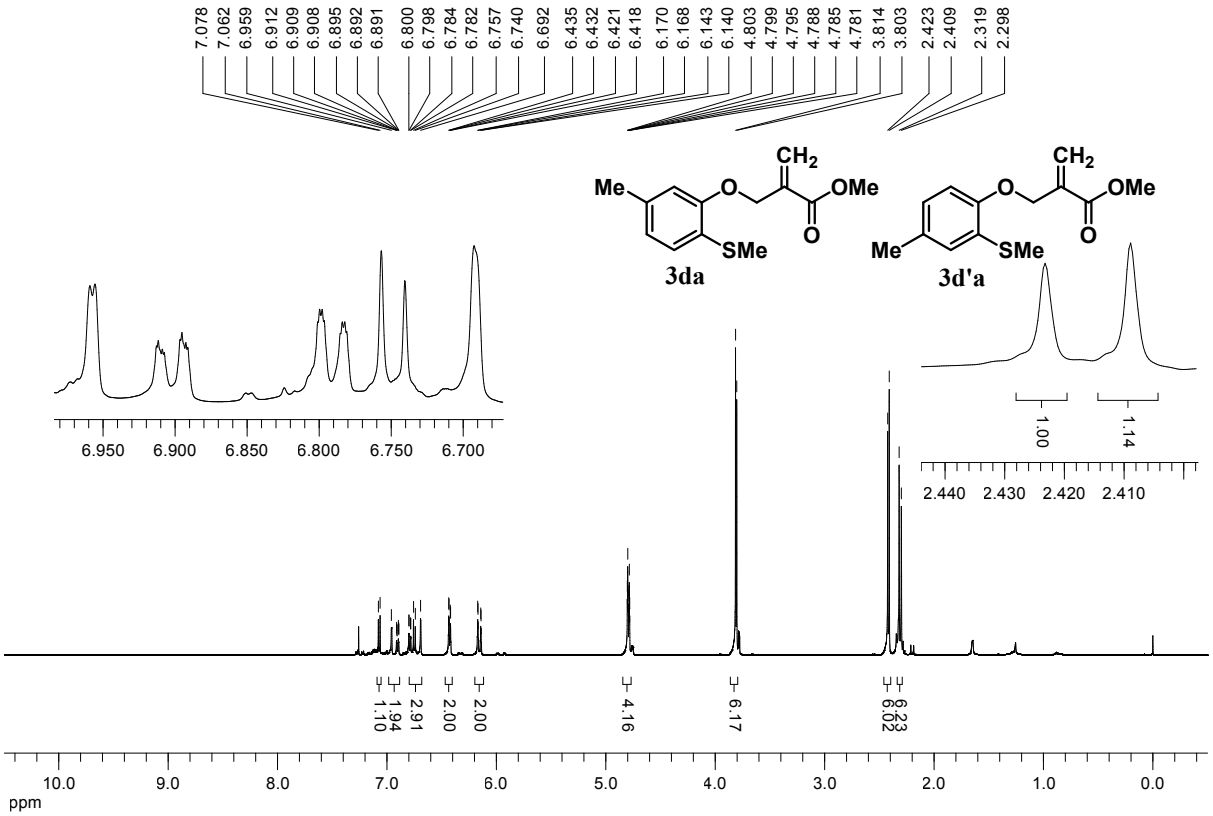

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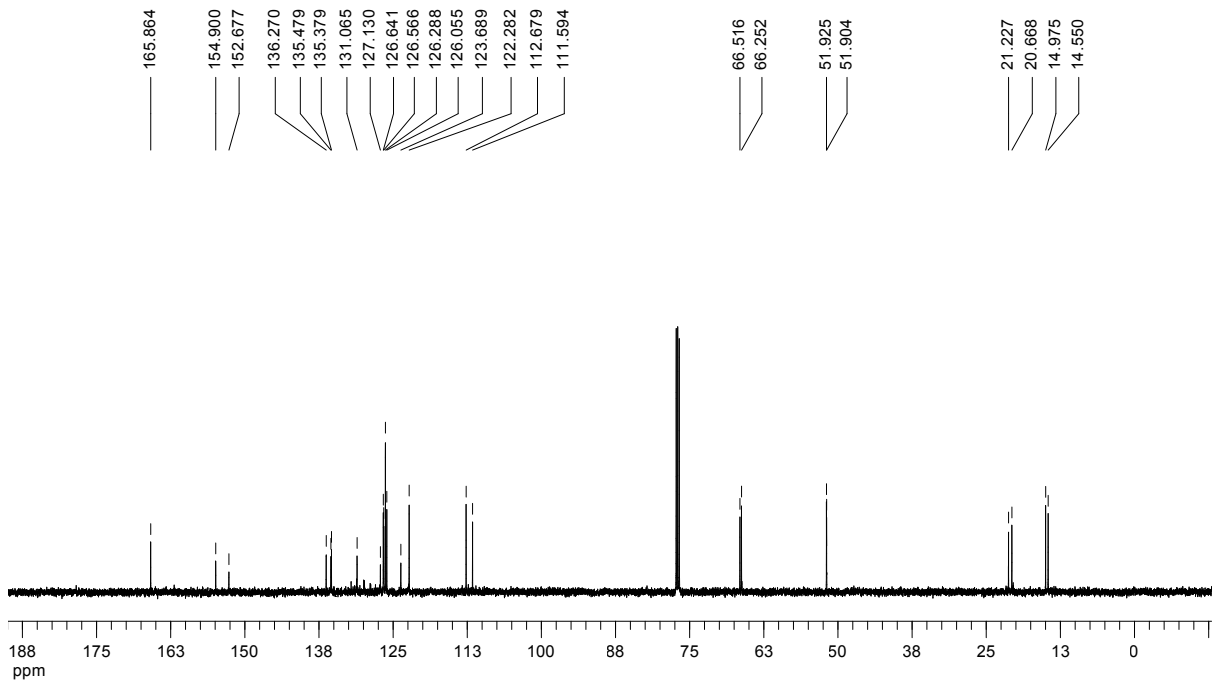

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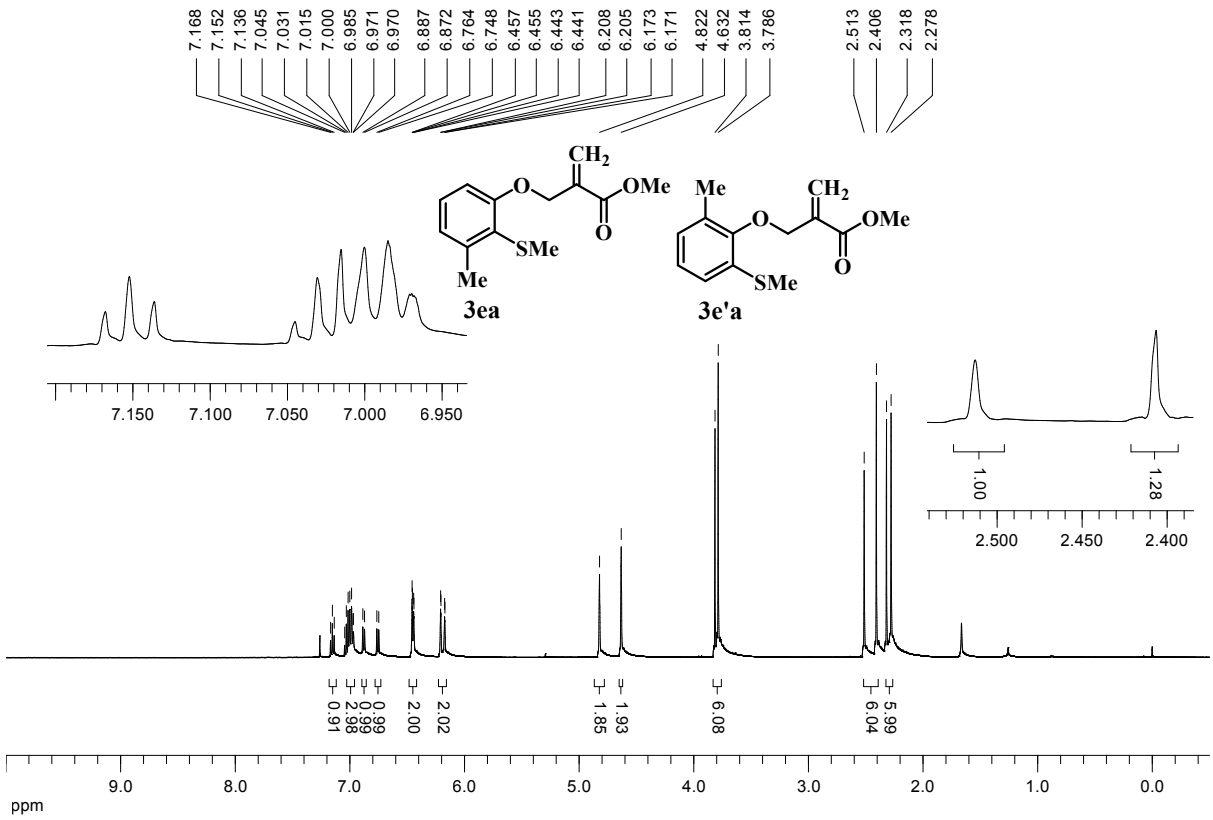

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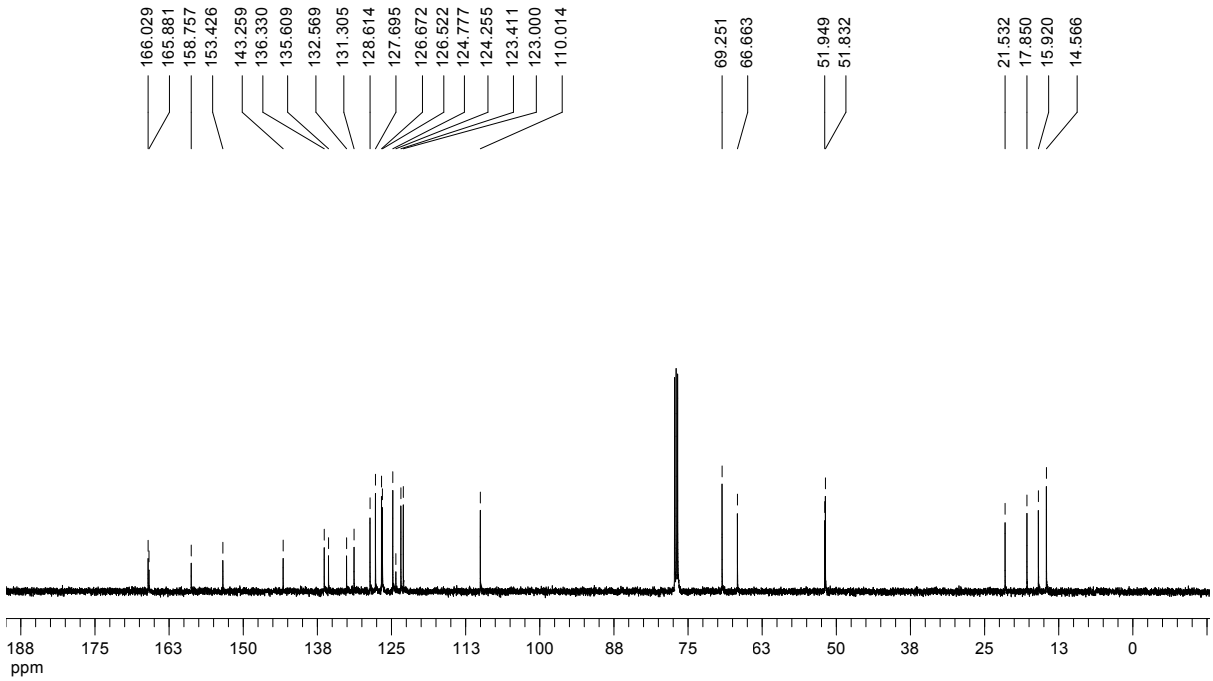

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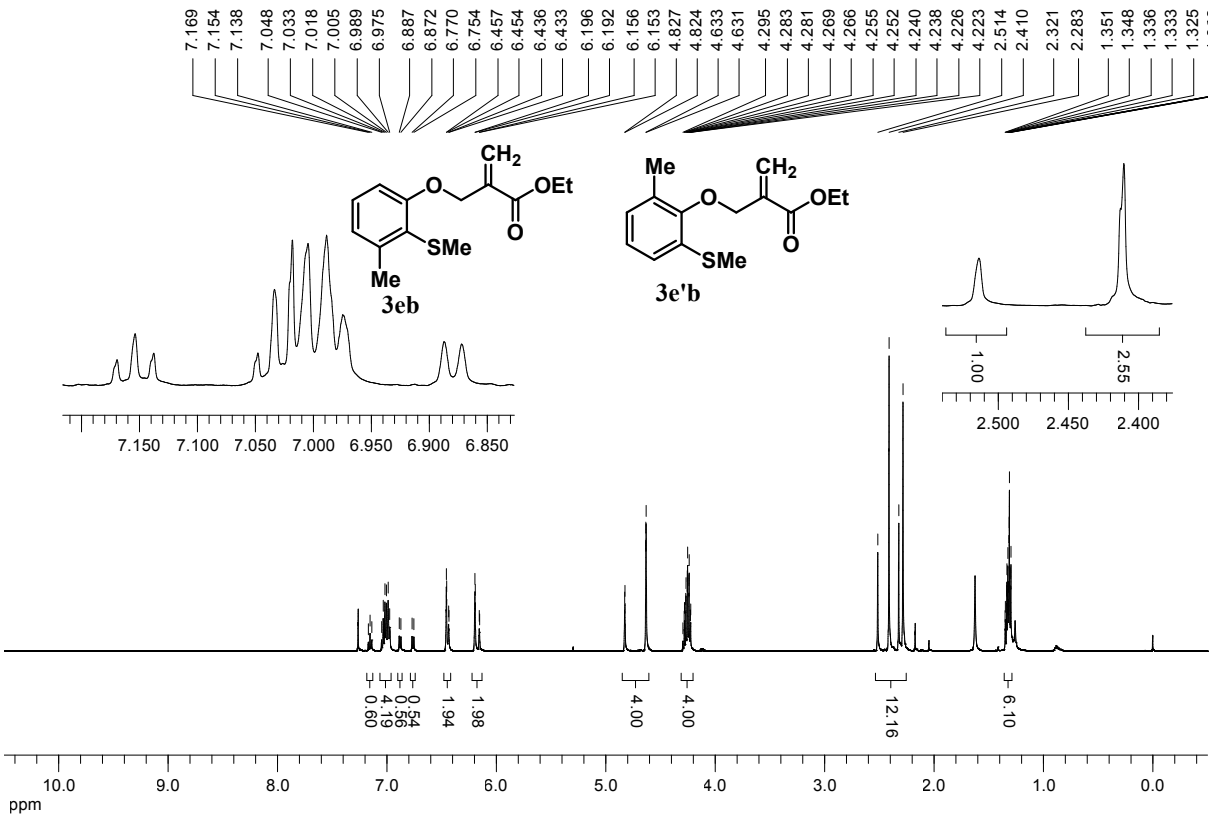

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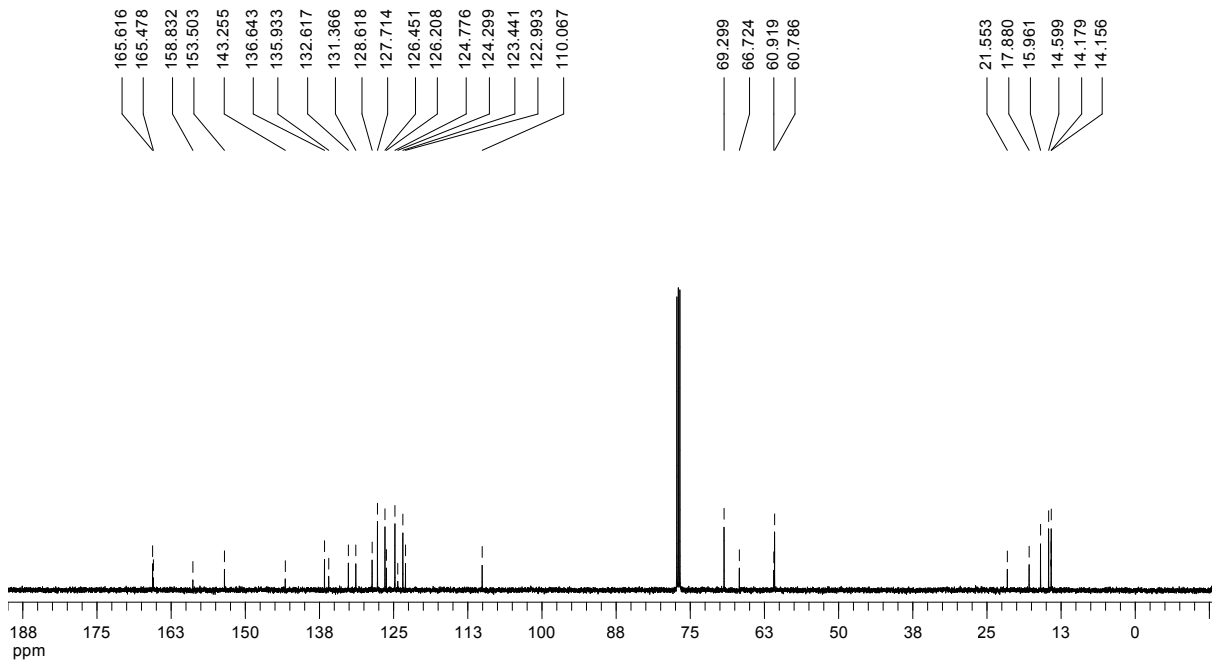

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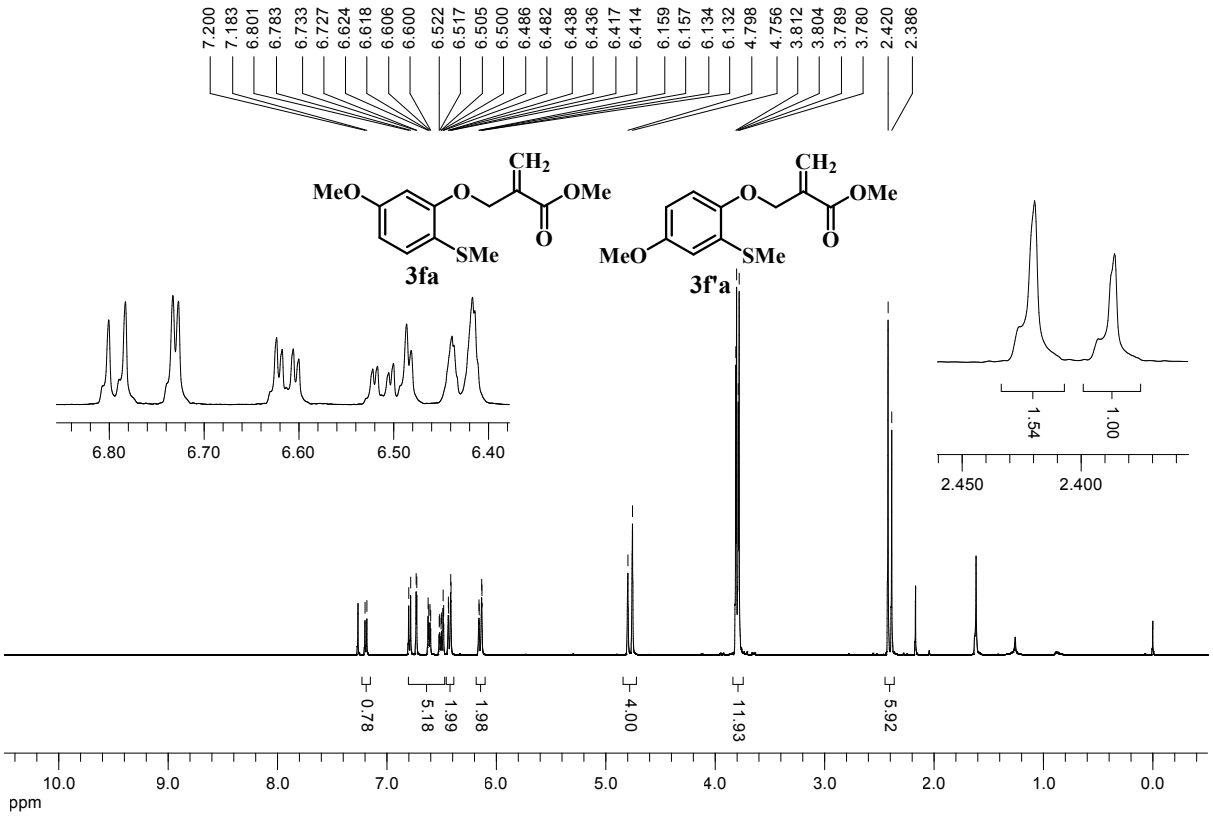

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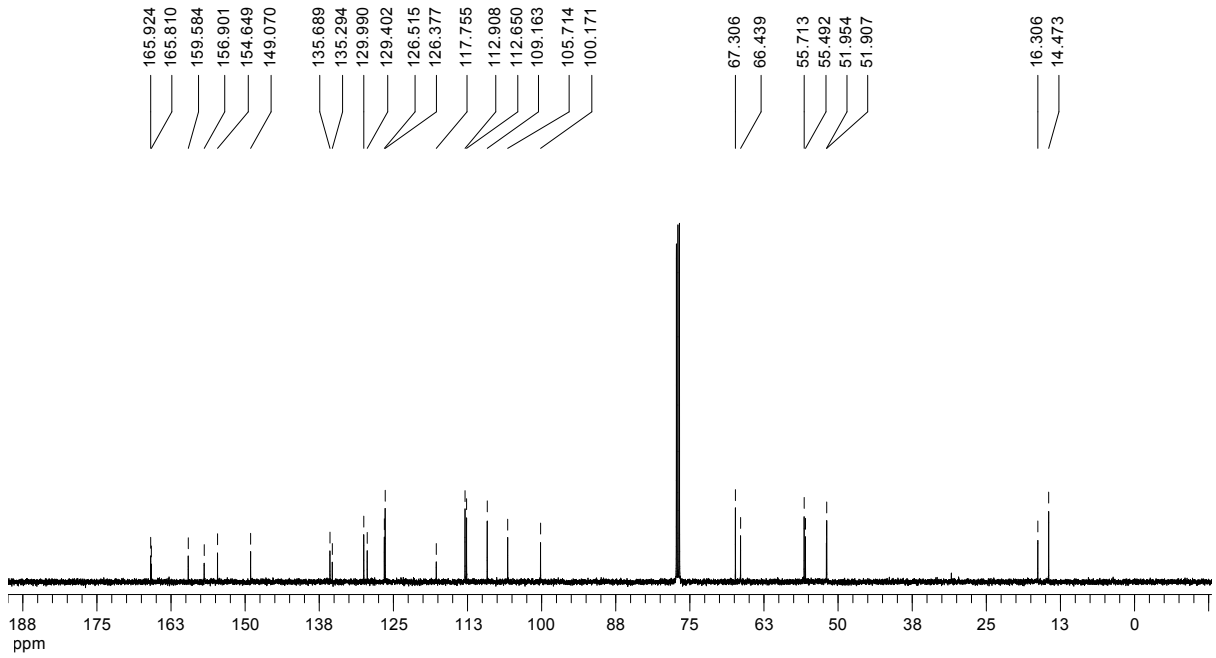

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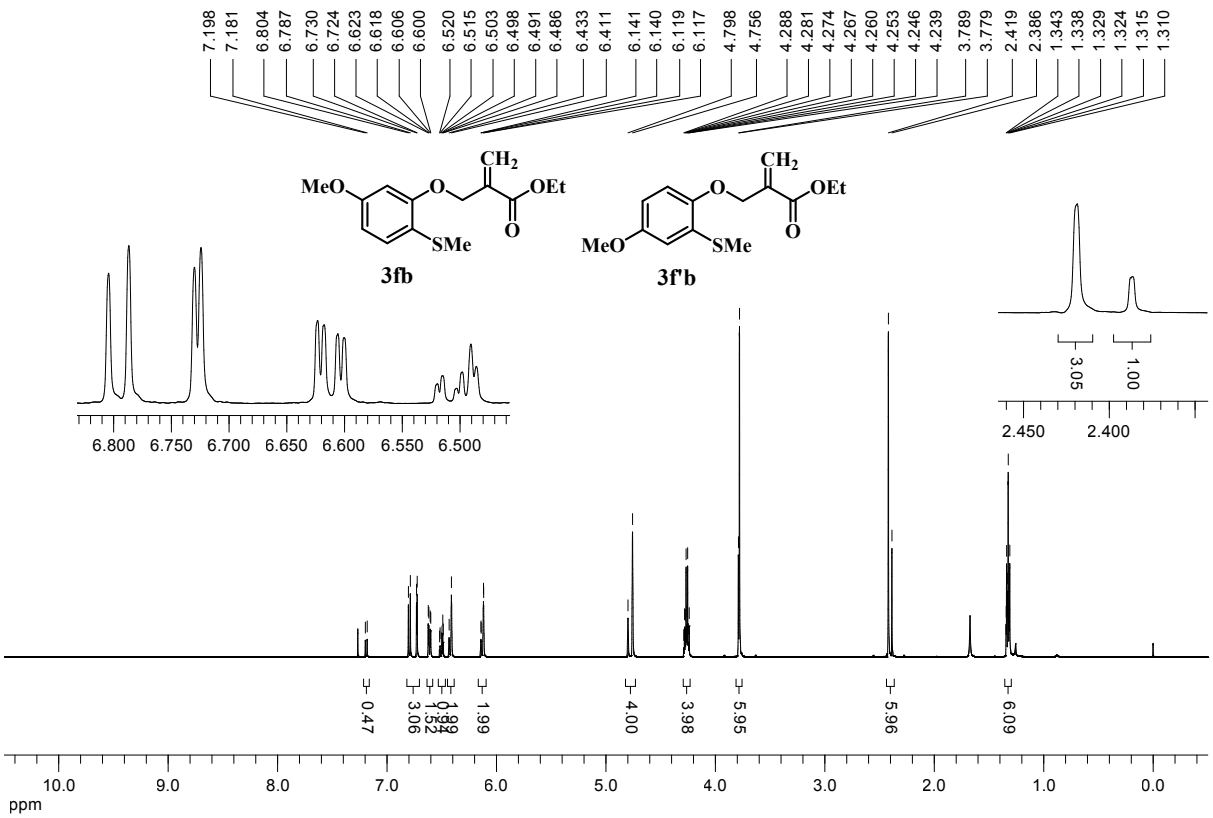

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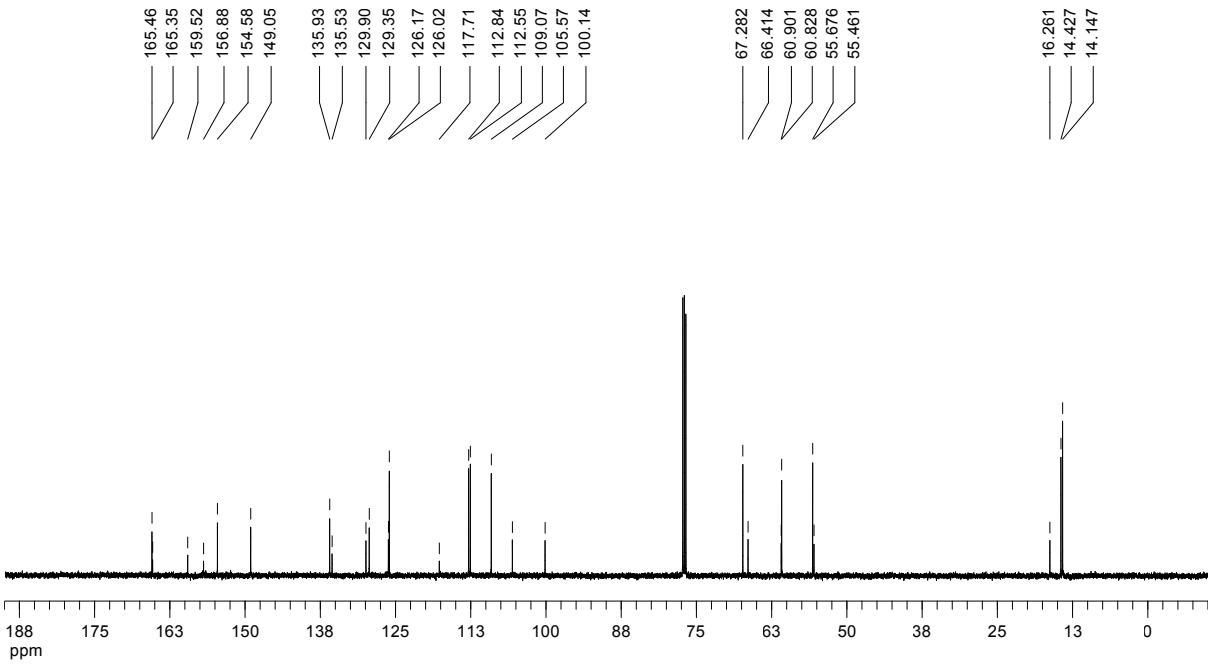

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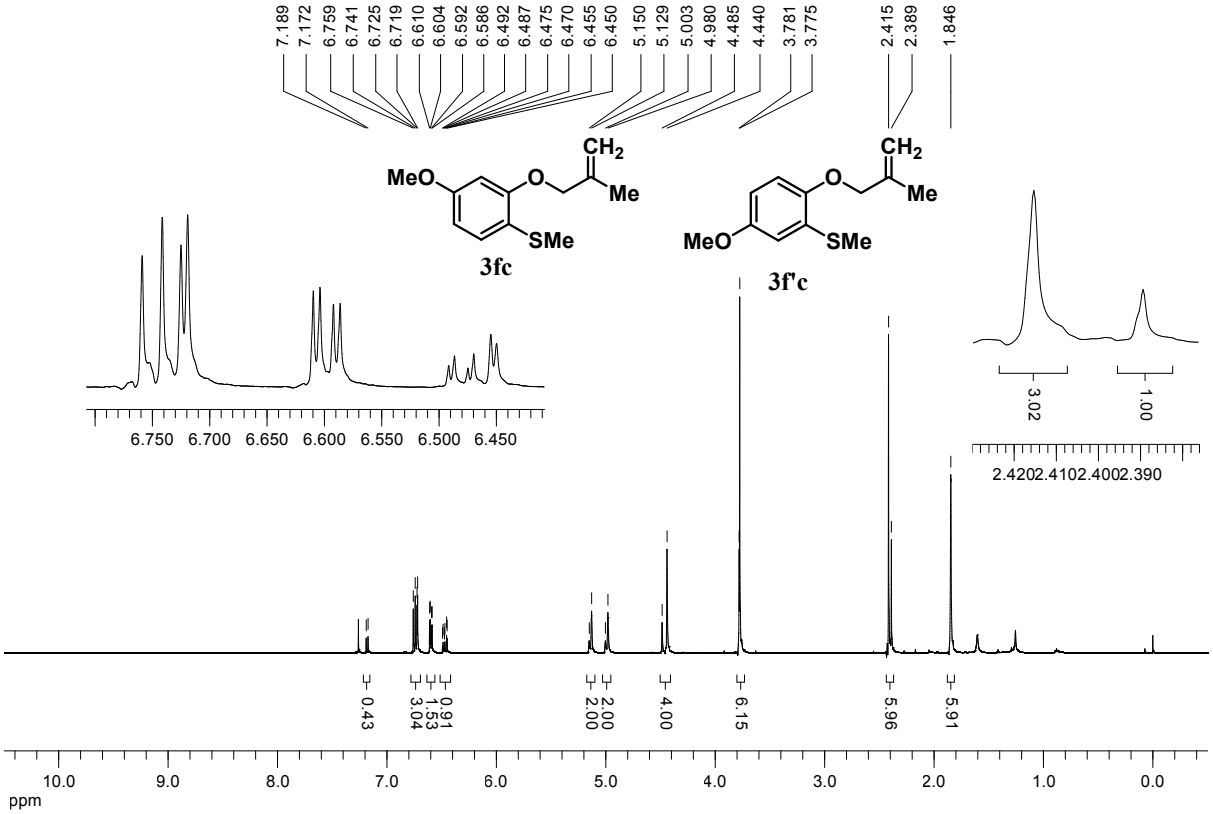

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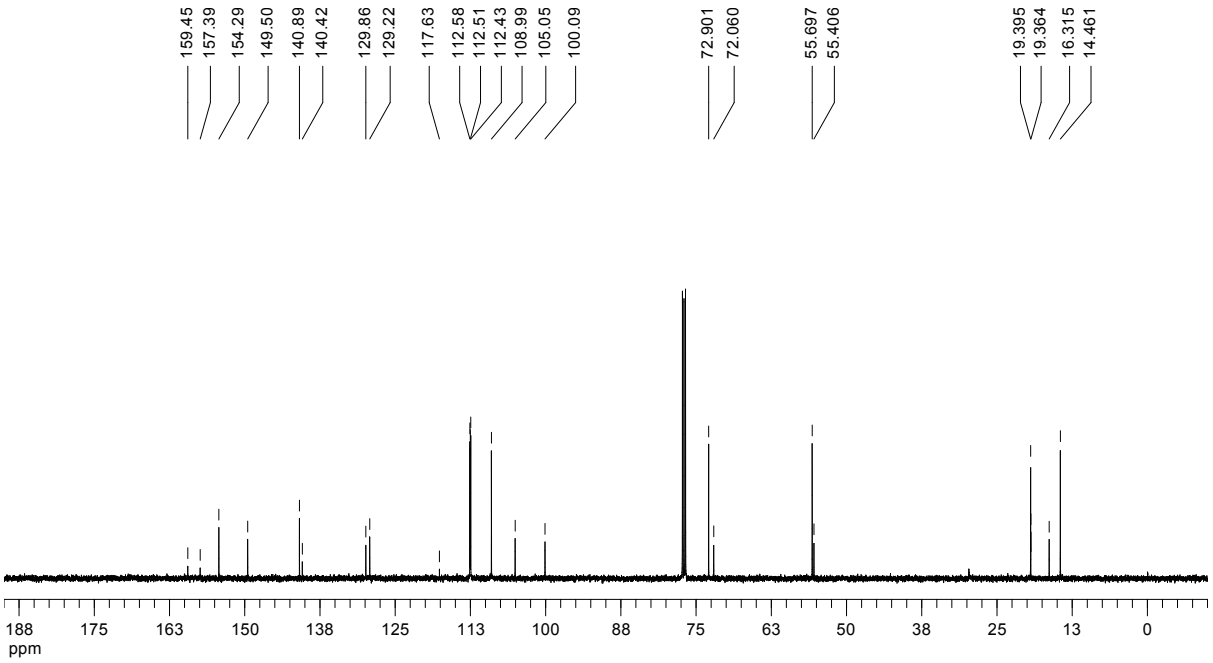

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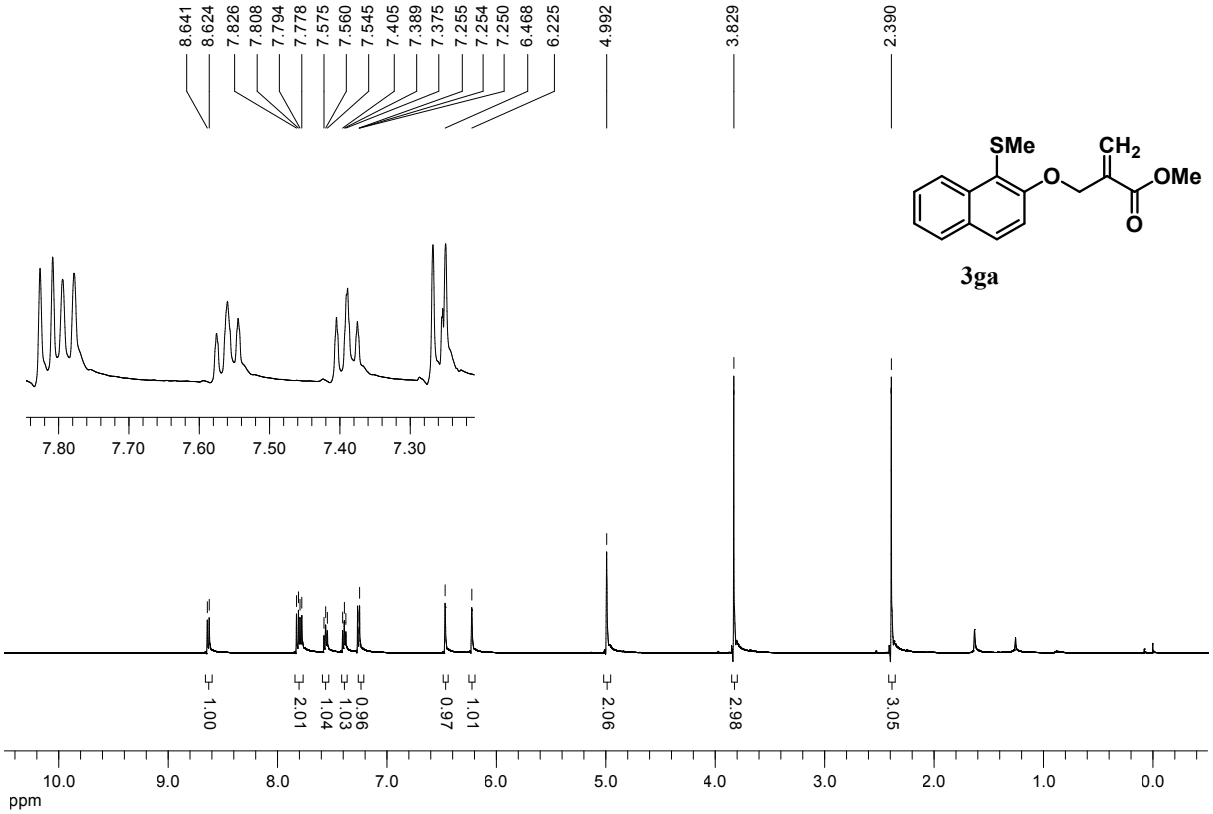

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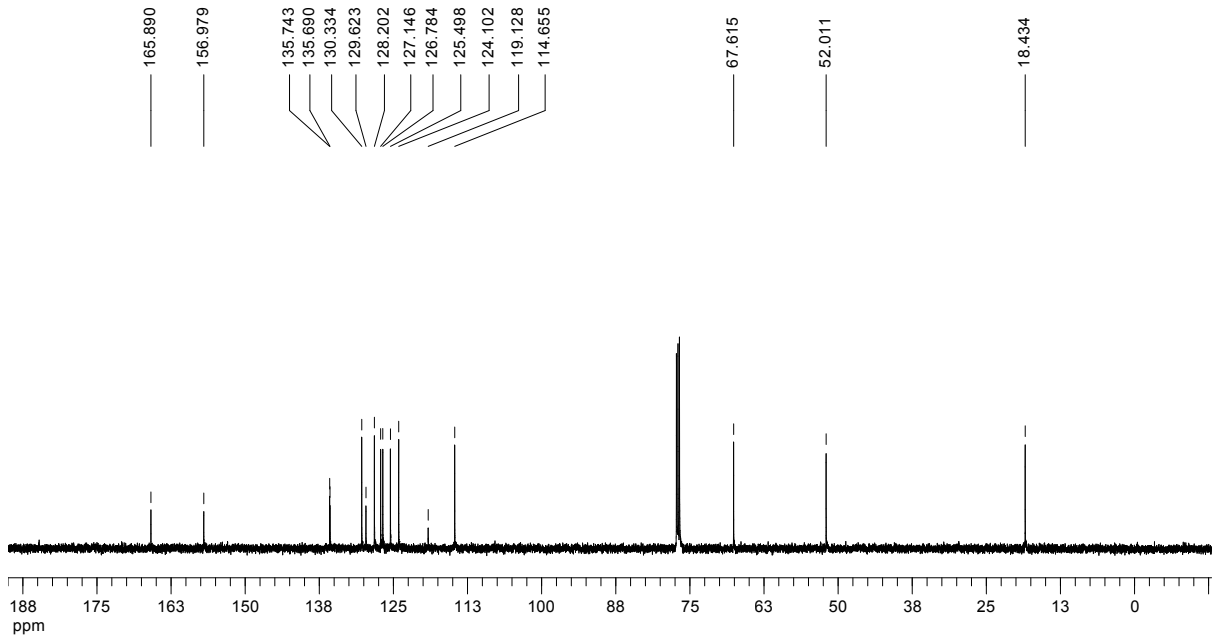

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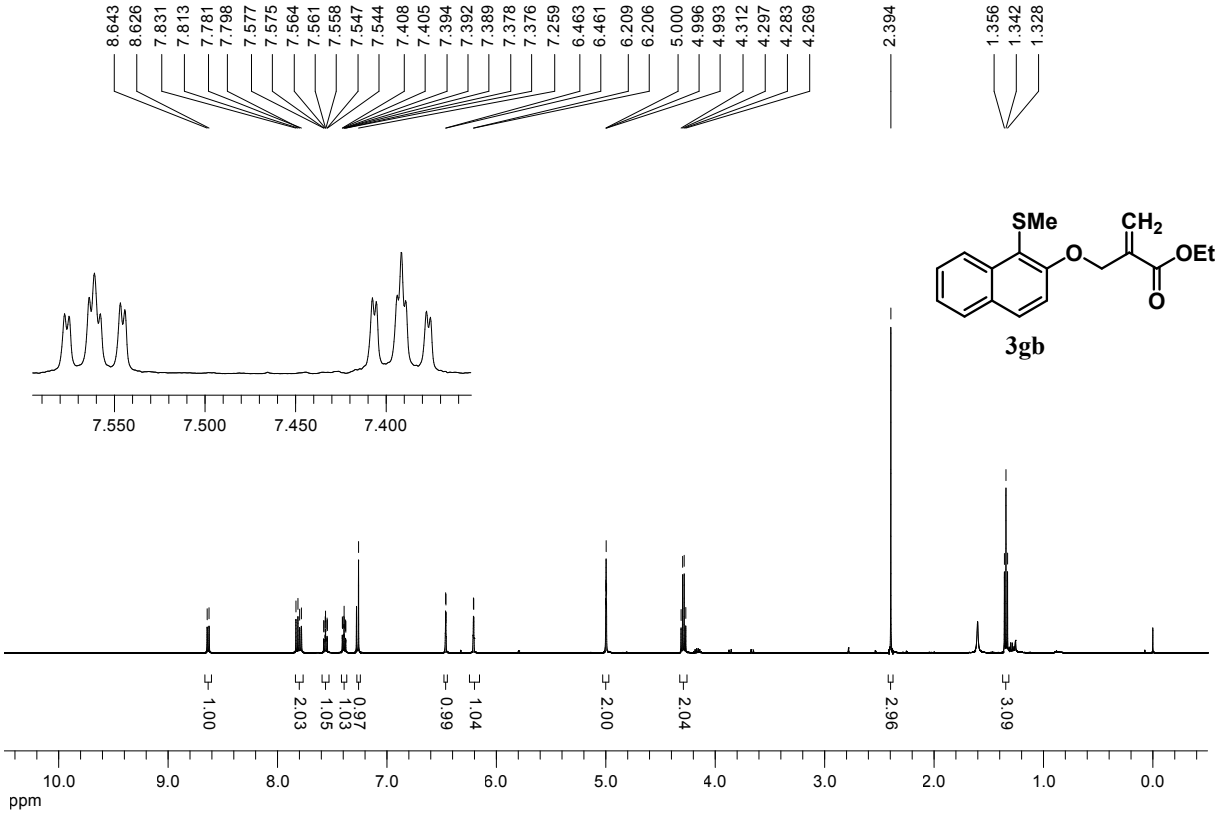

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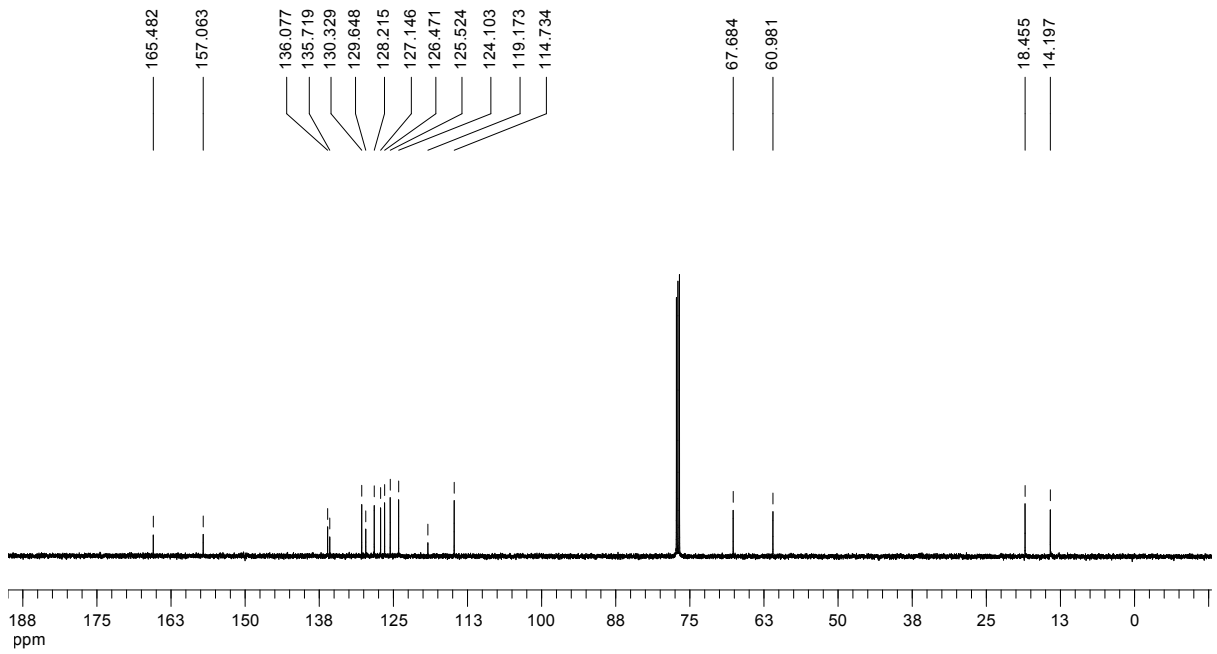

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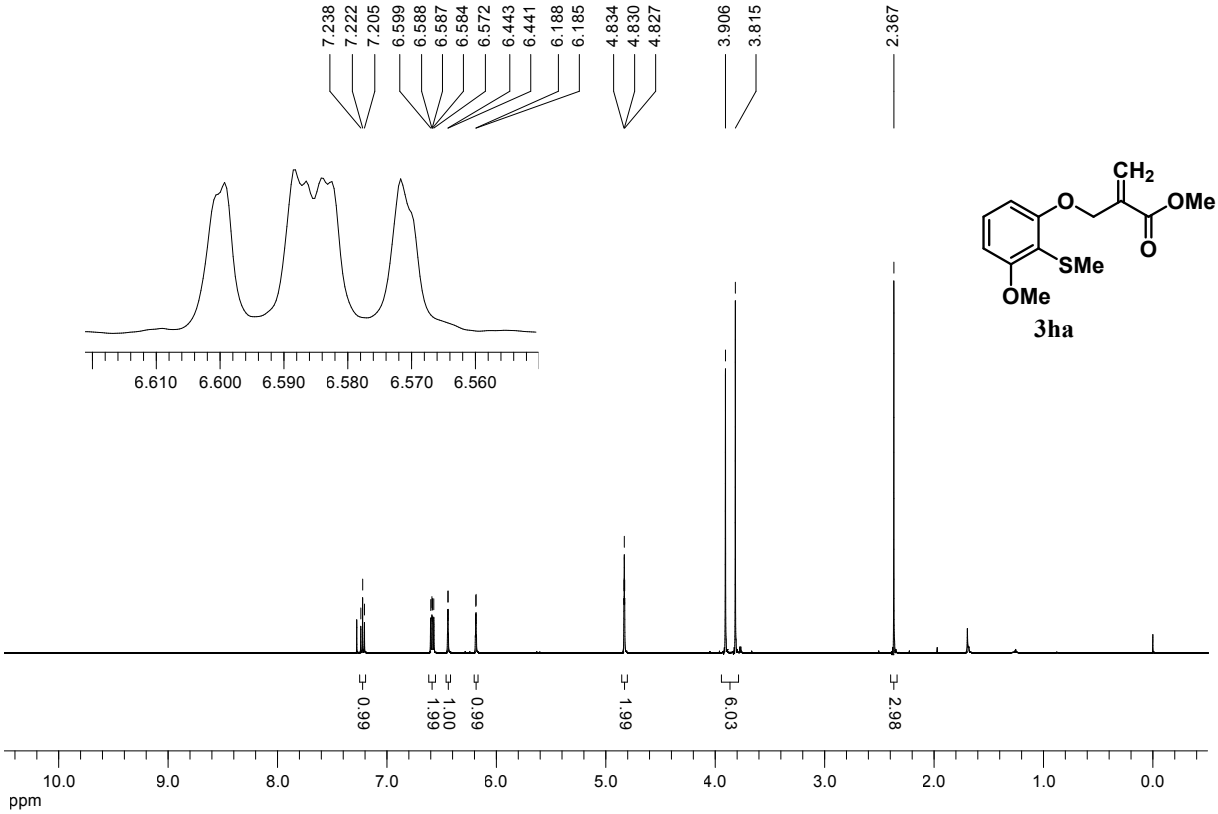

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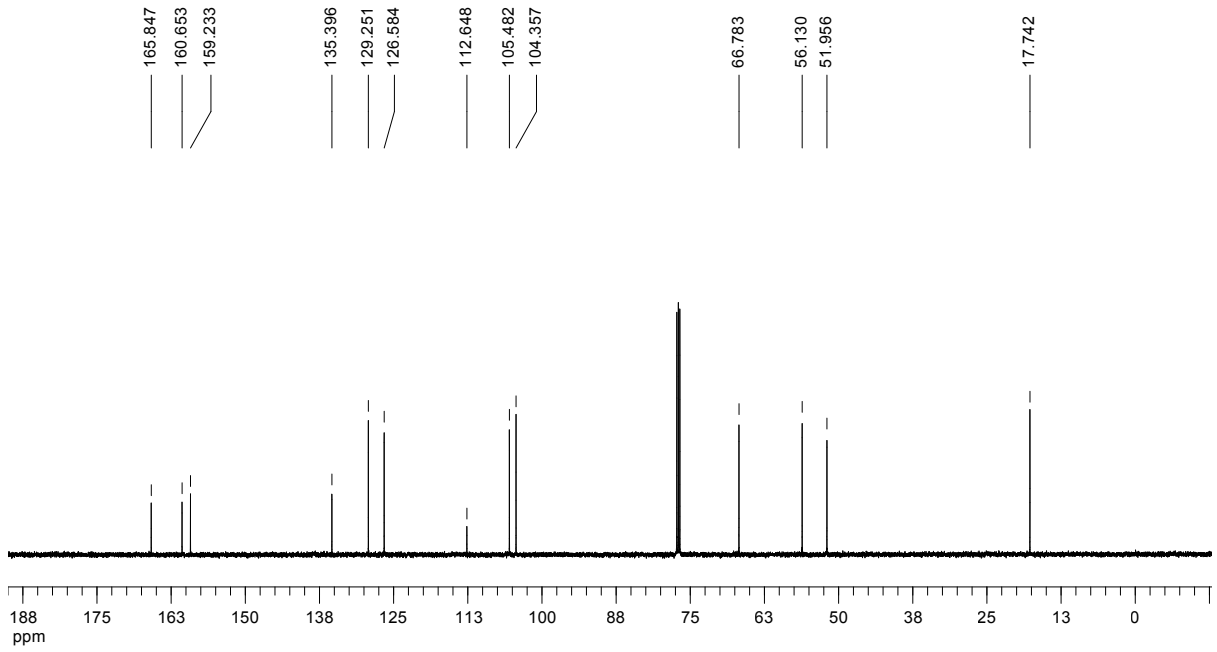

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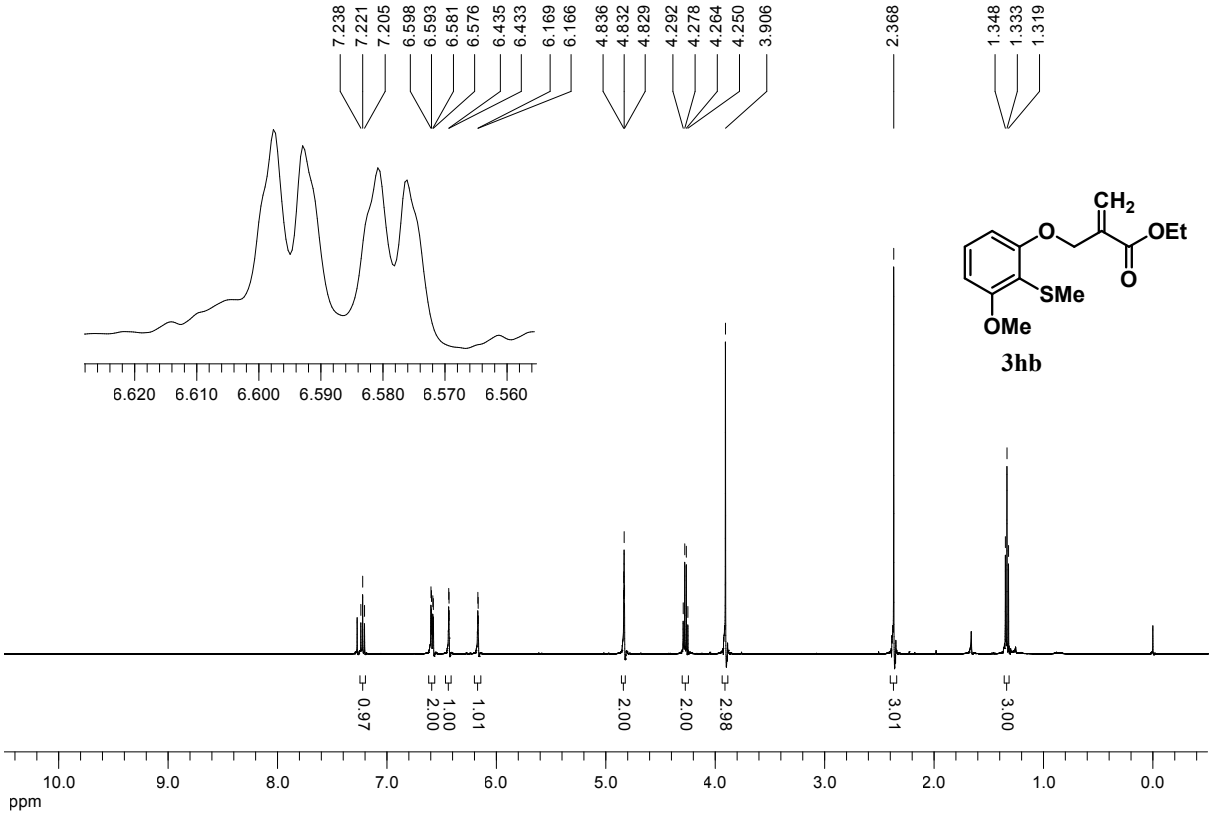

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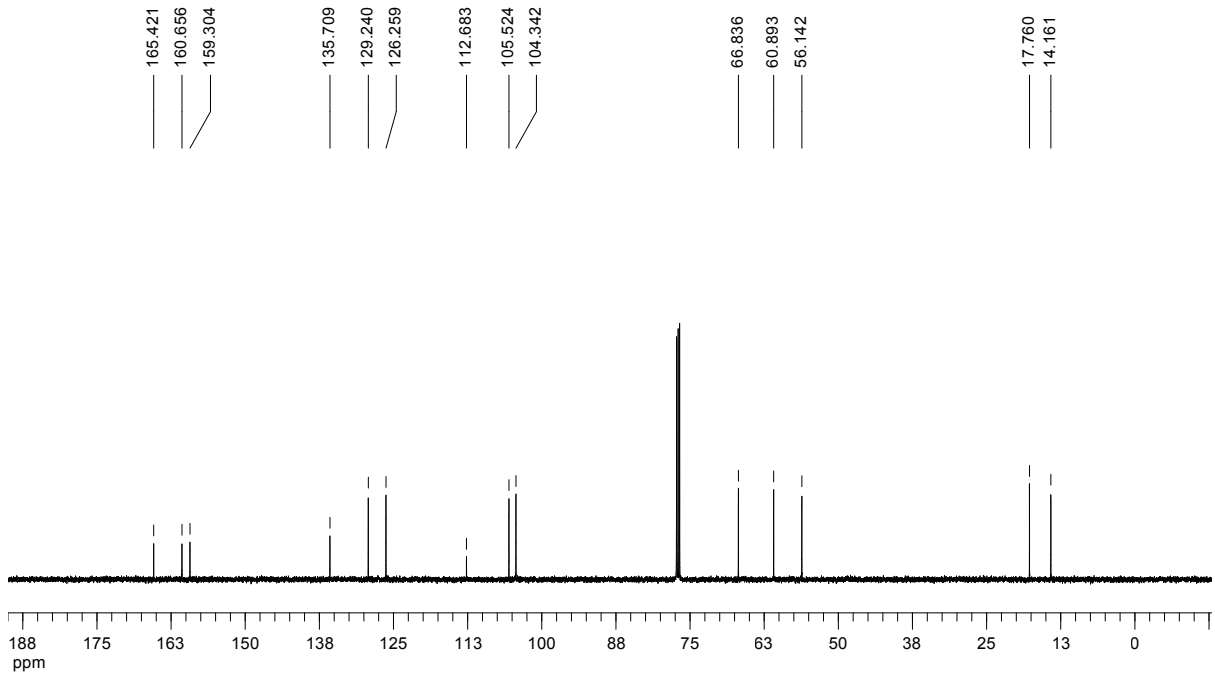

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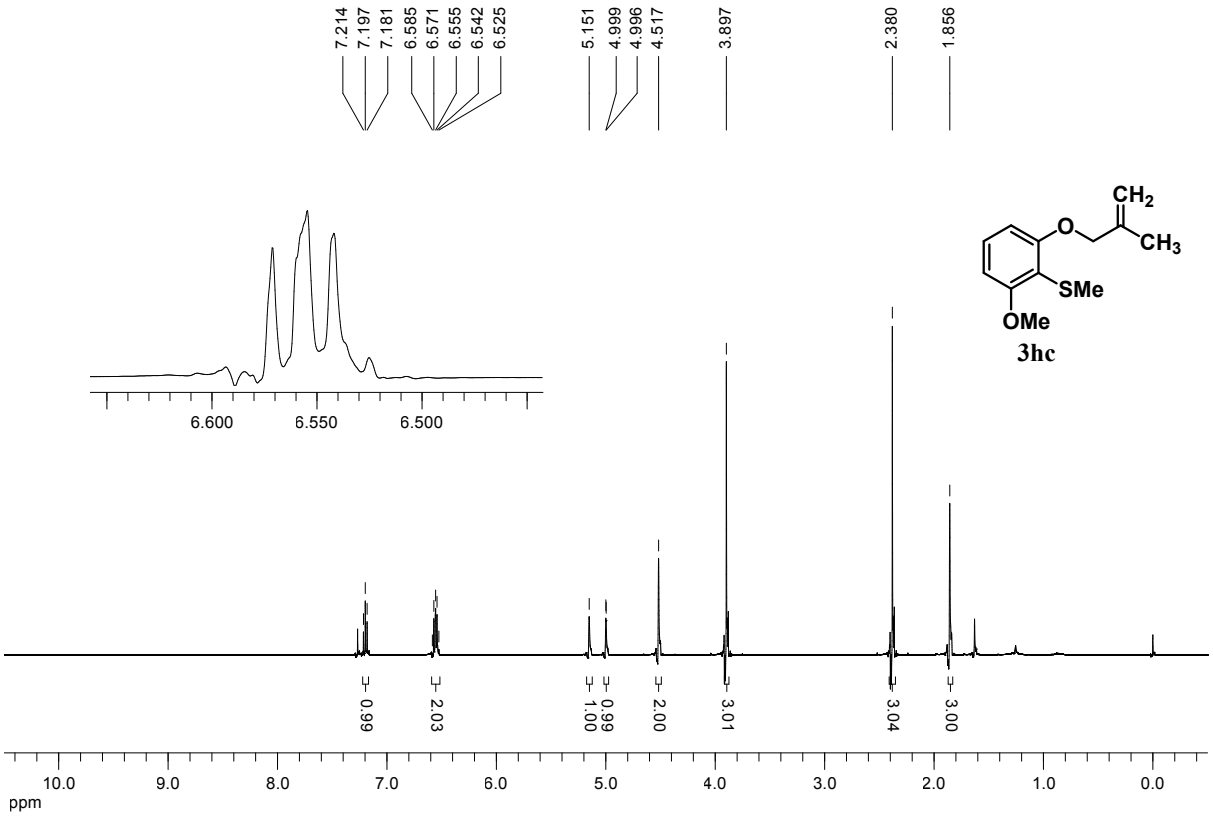

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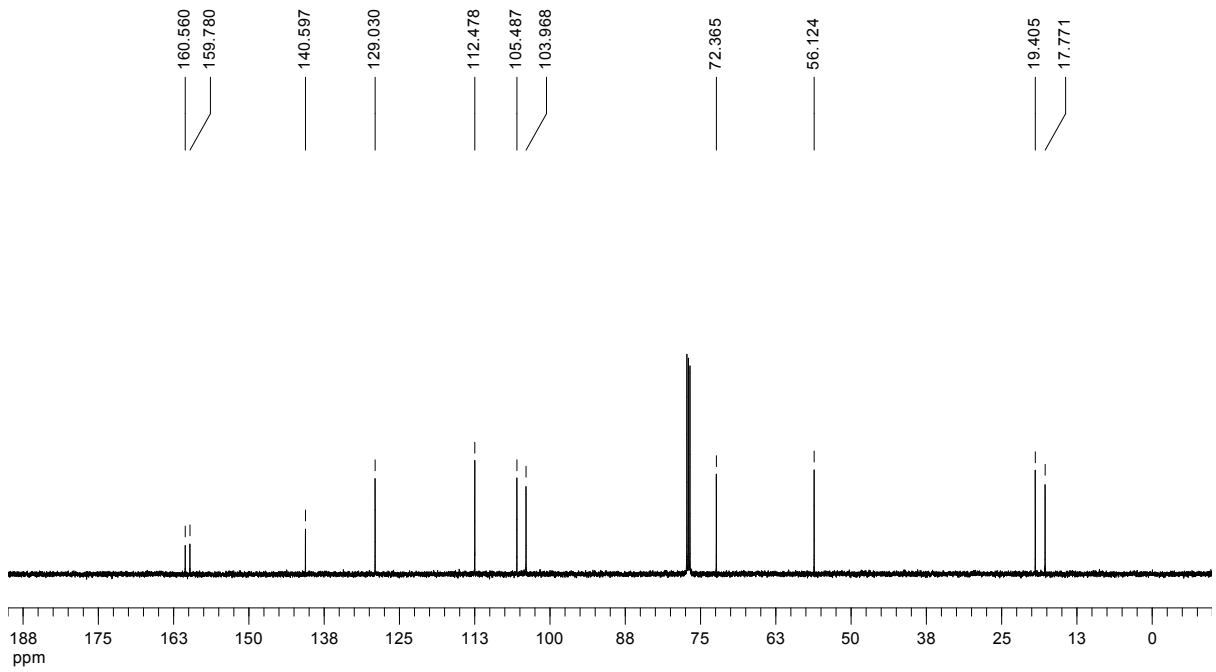

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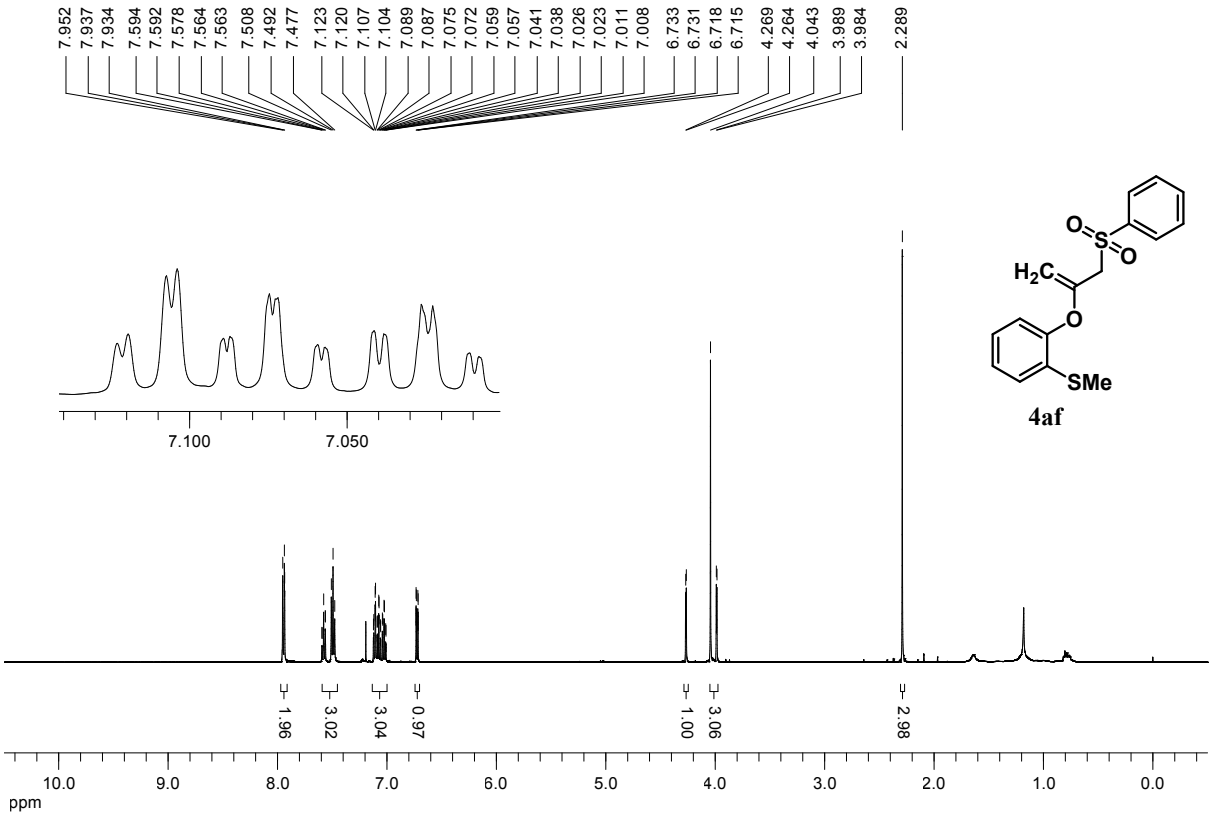

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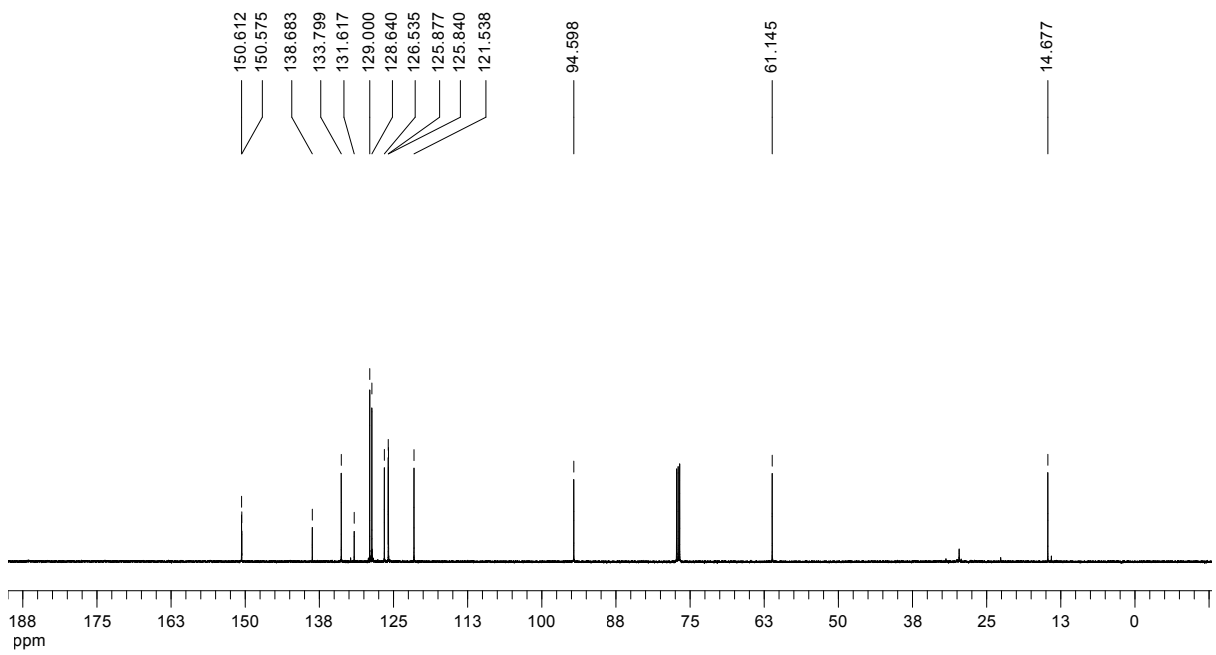

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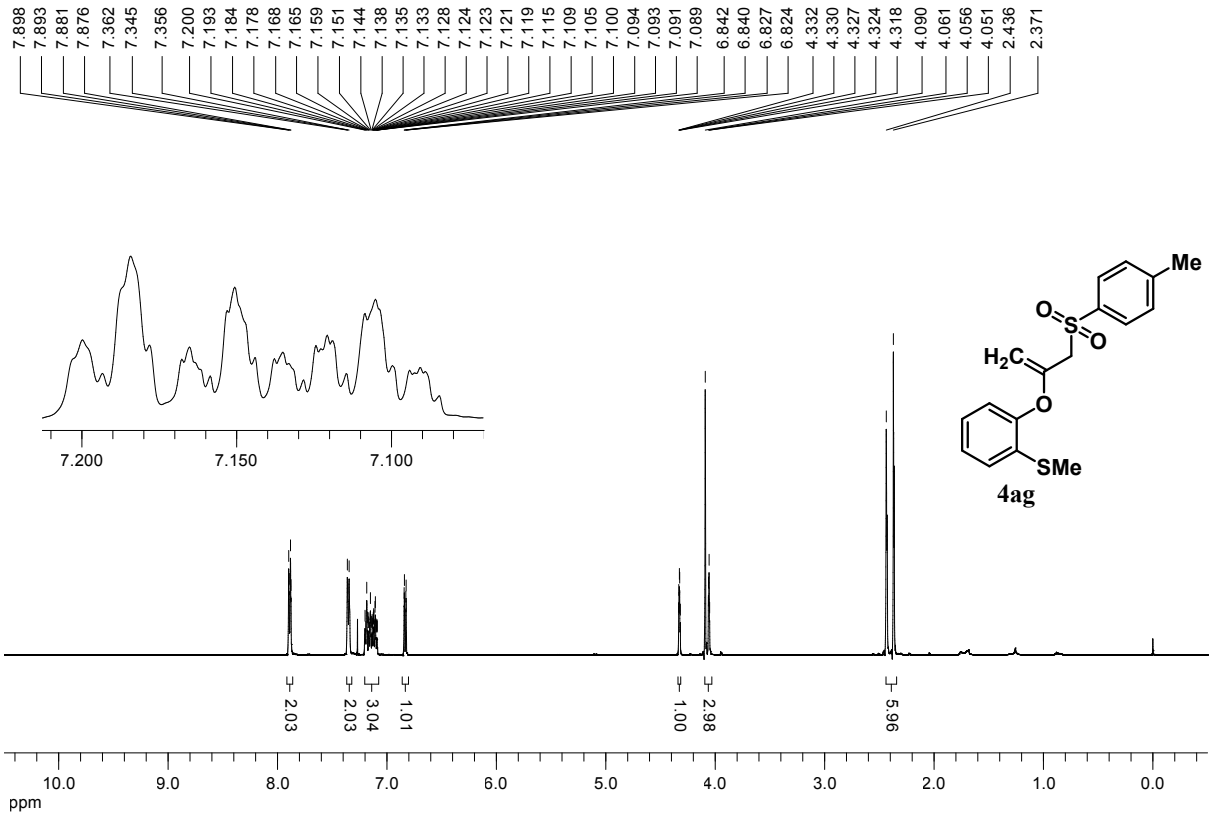

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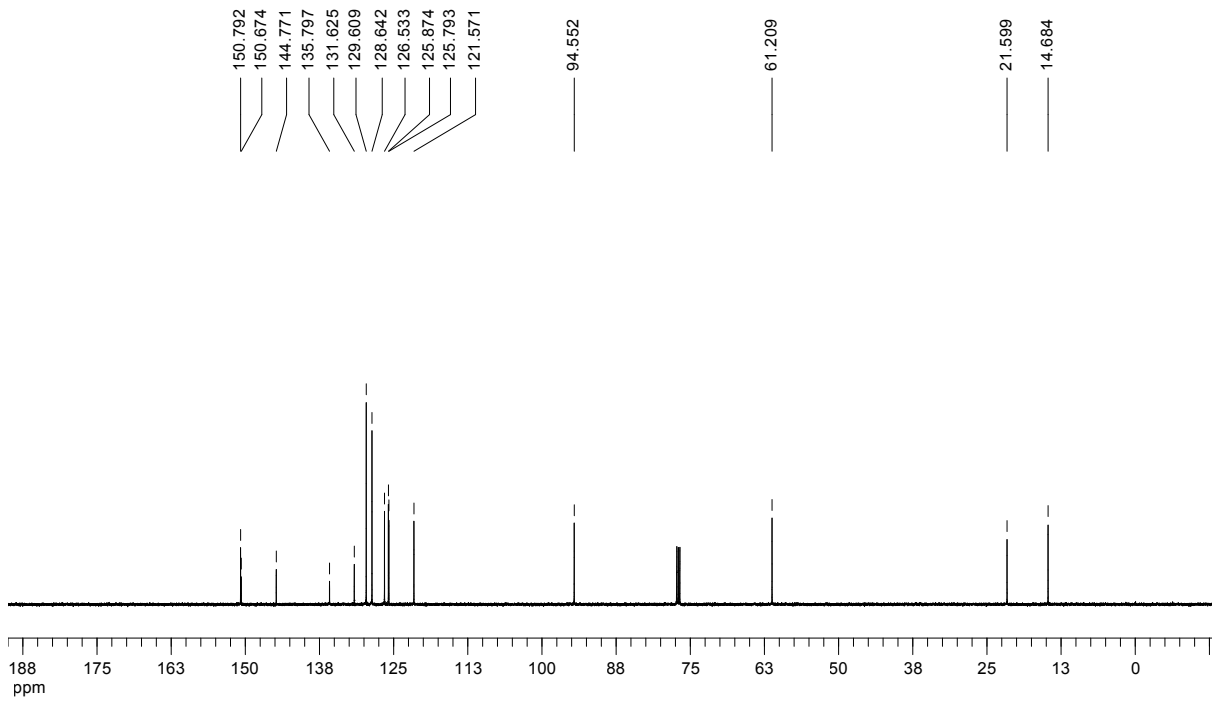

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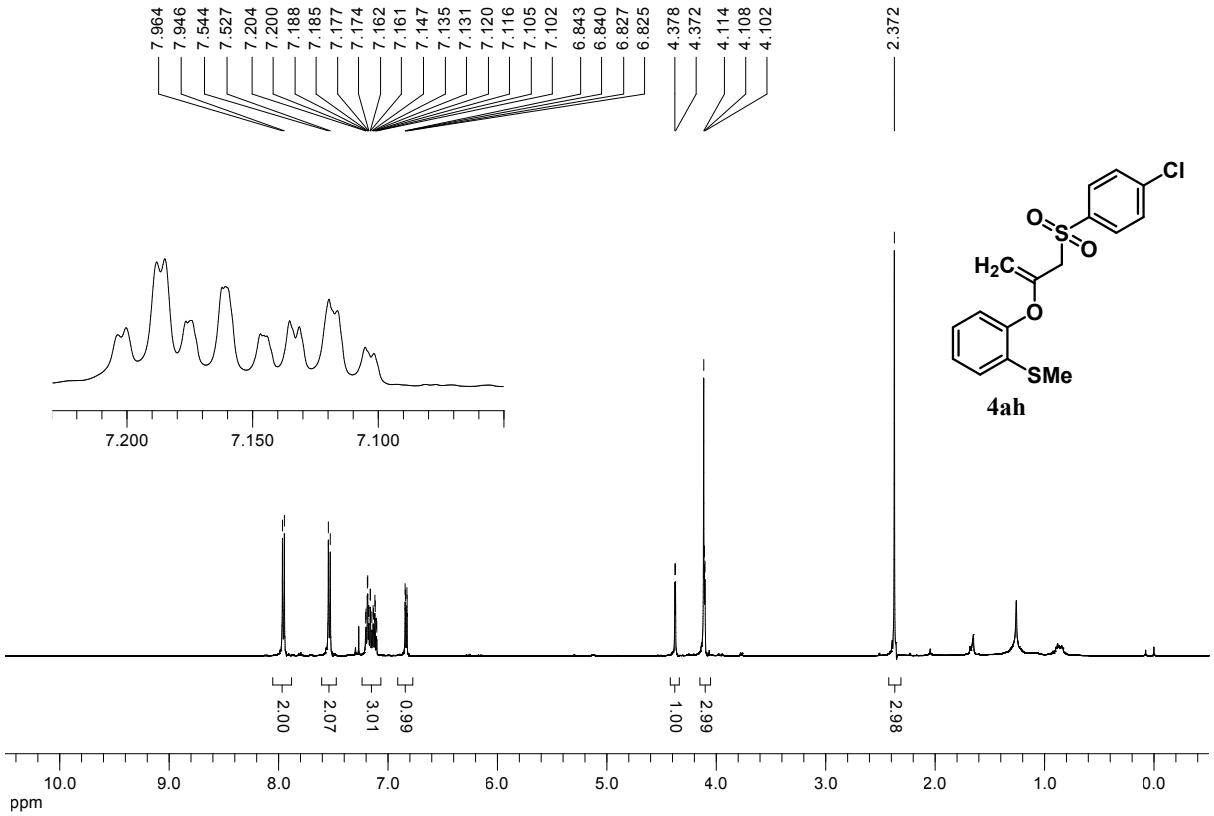
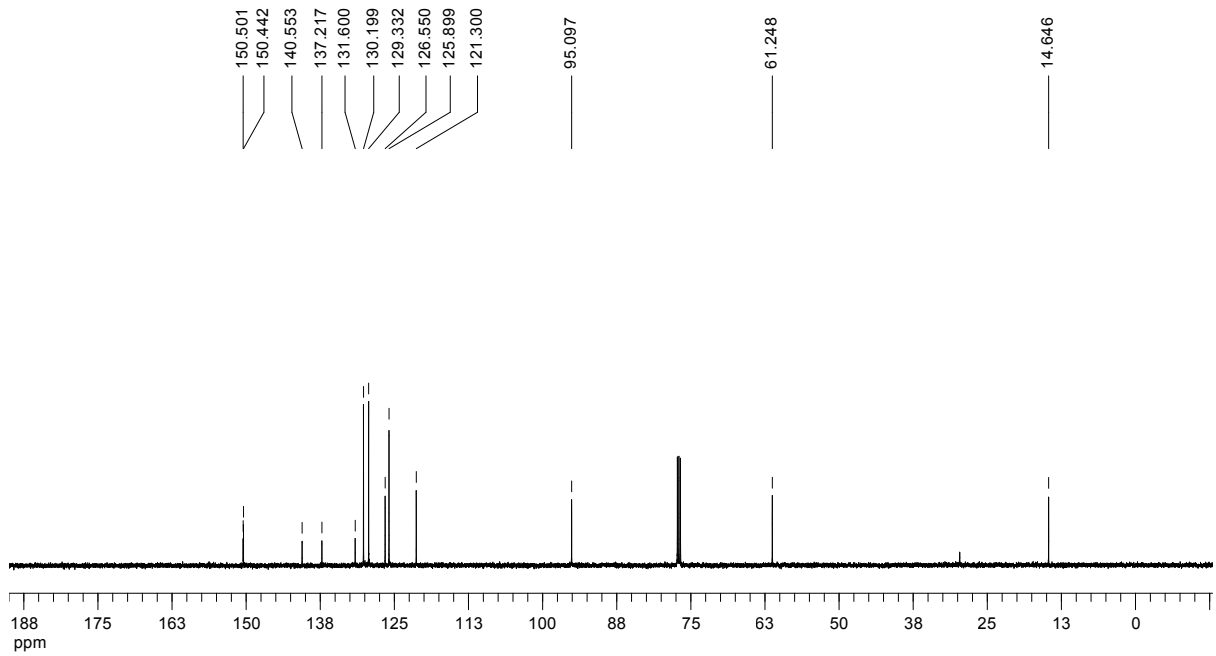
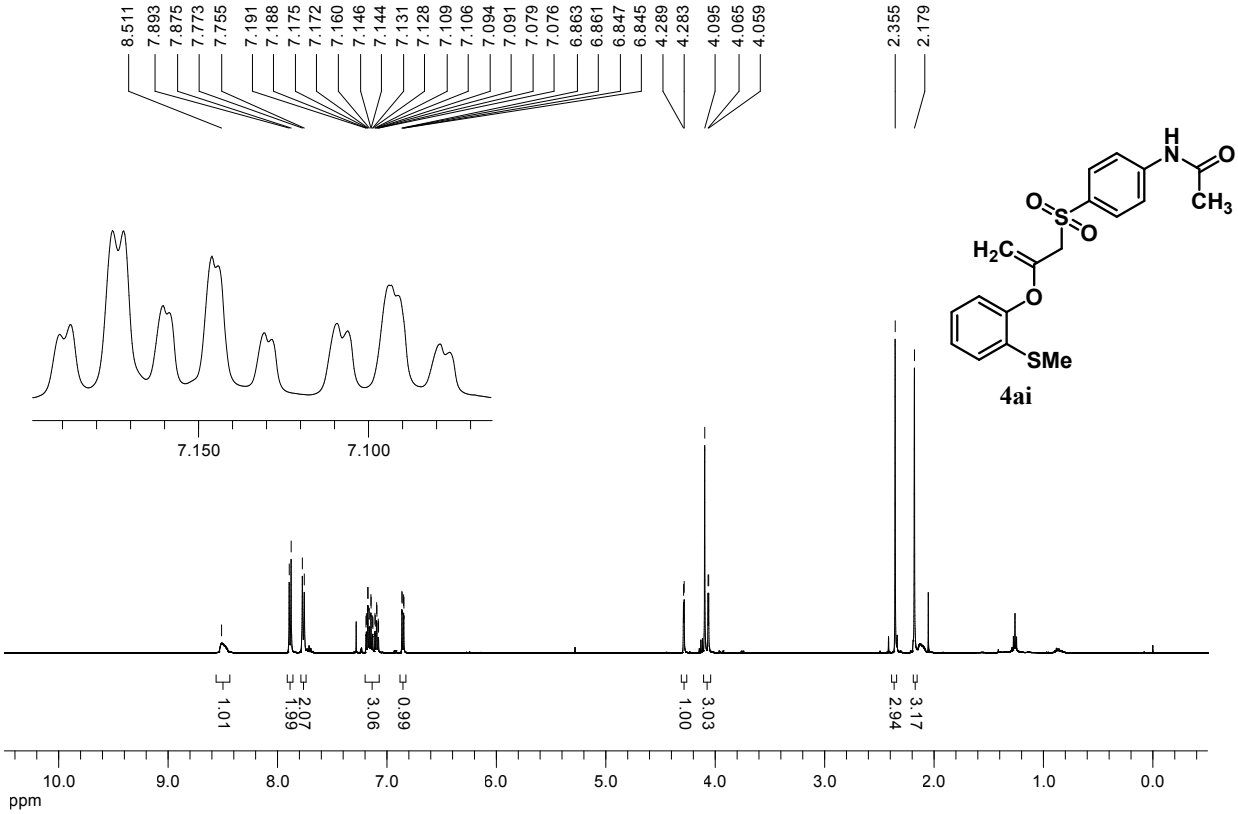


^{13}C NMR (126 MHz, $CDCl_3$)

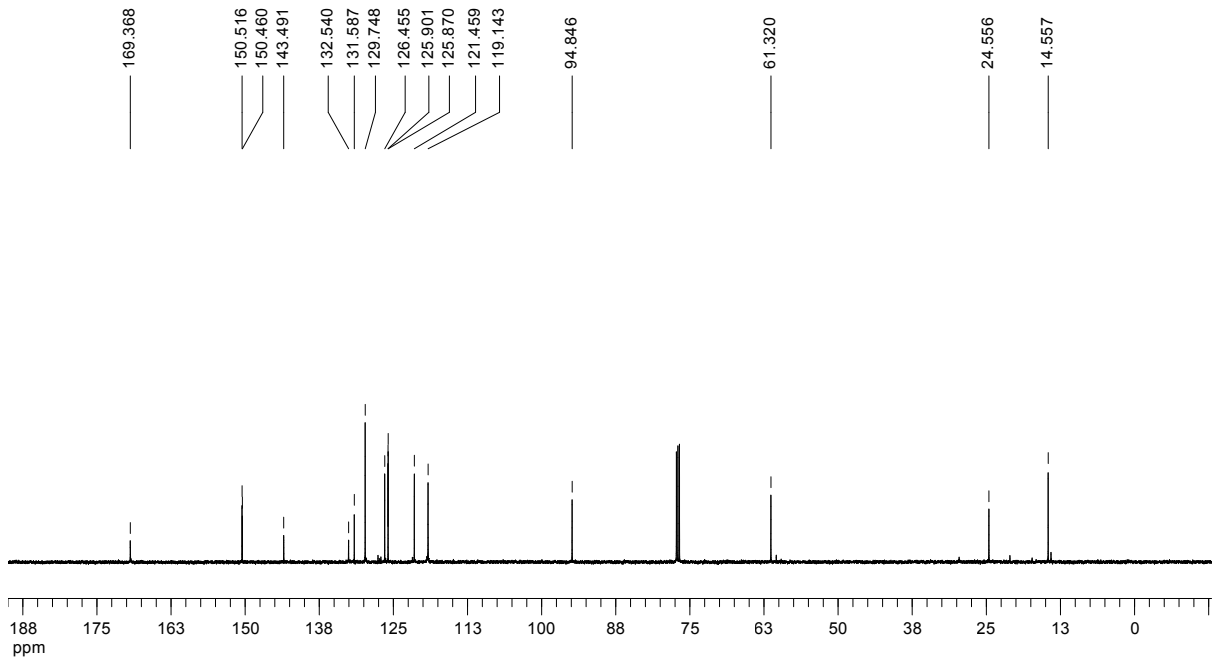


^{1}H NMR (500 MHz, $CDCl_3$)



4ai

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



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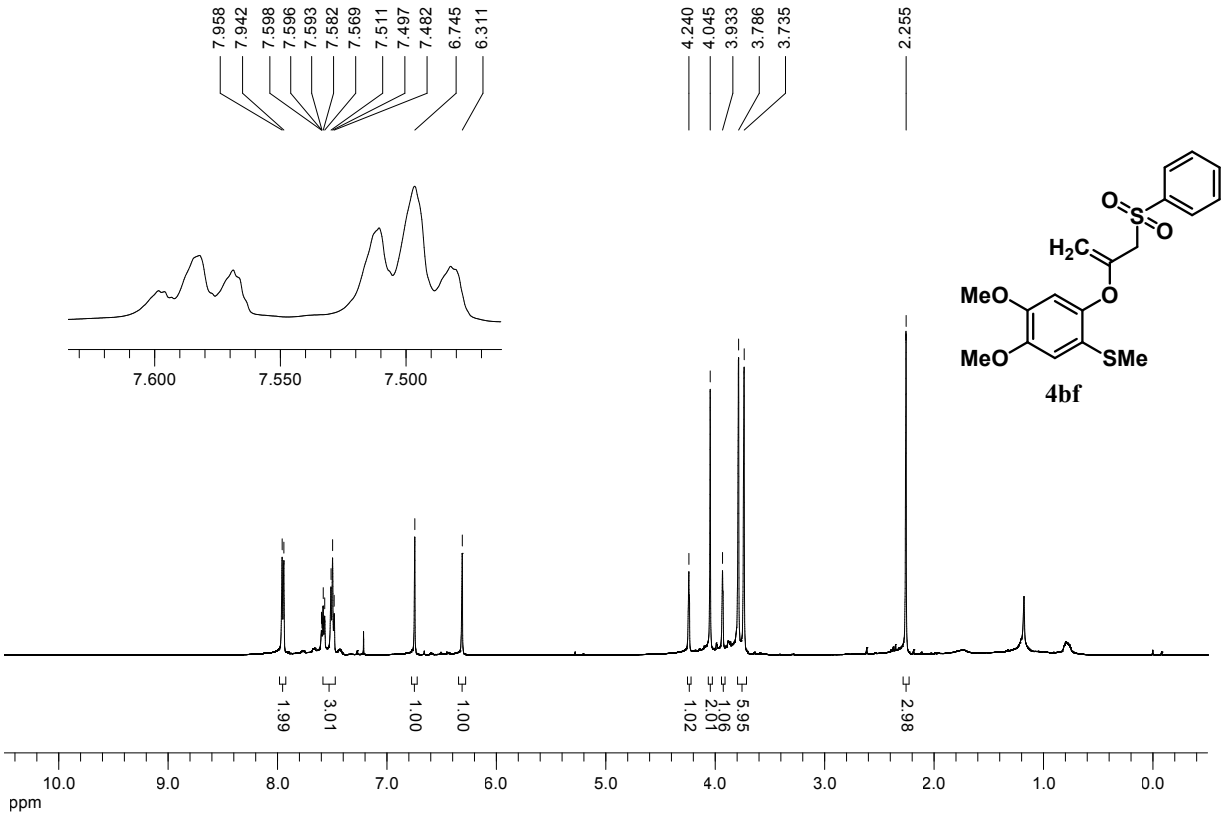
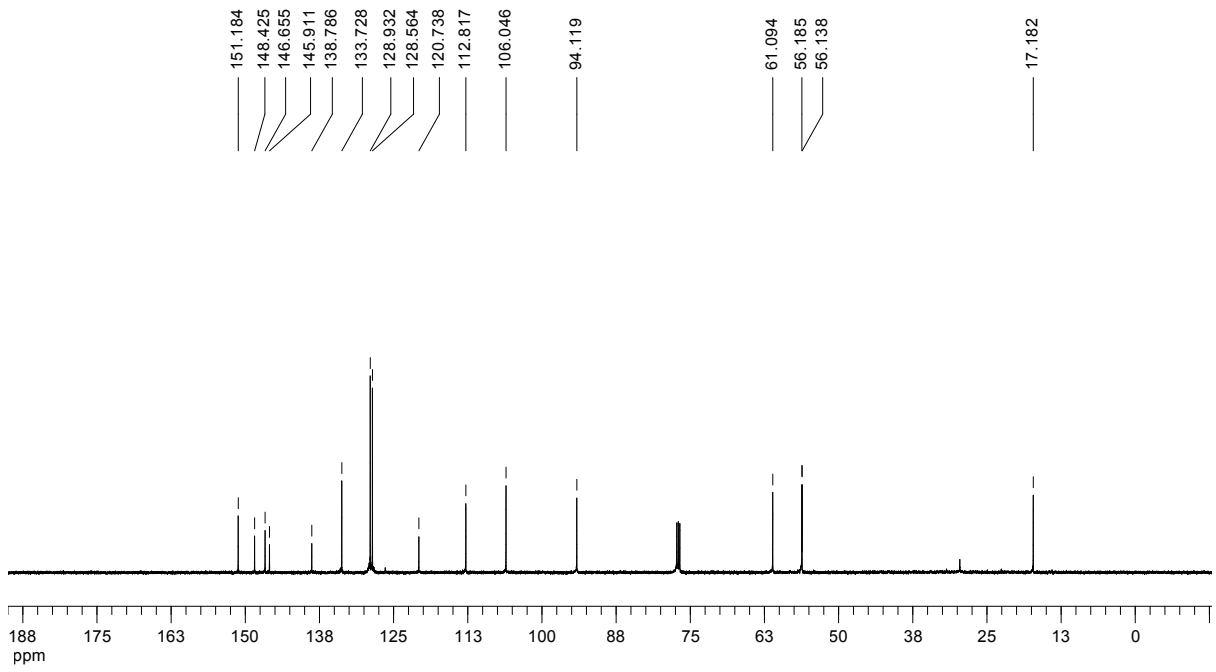
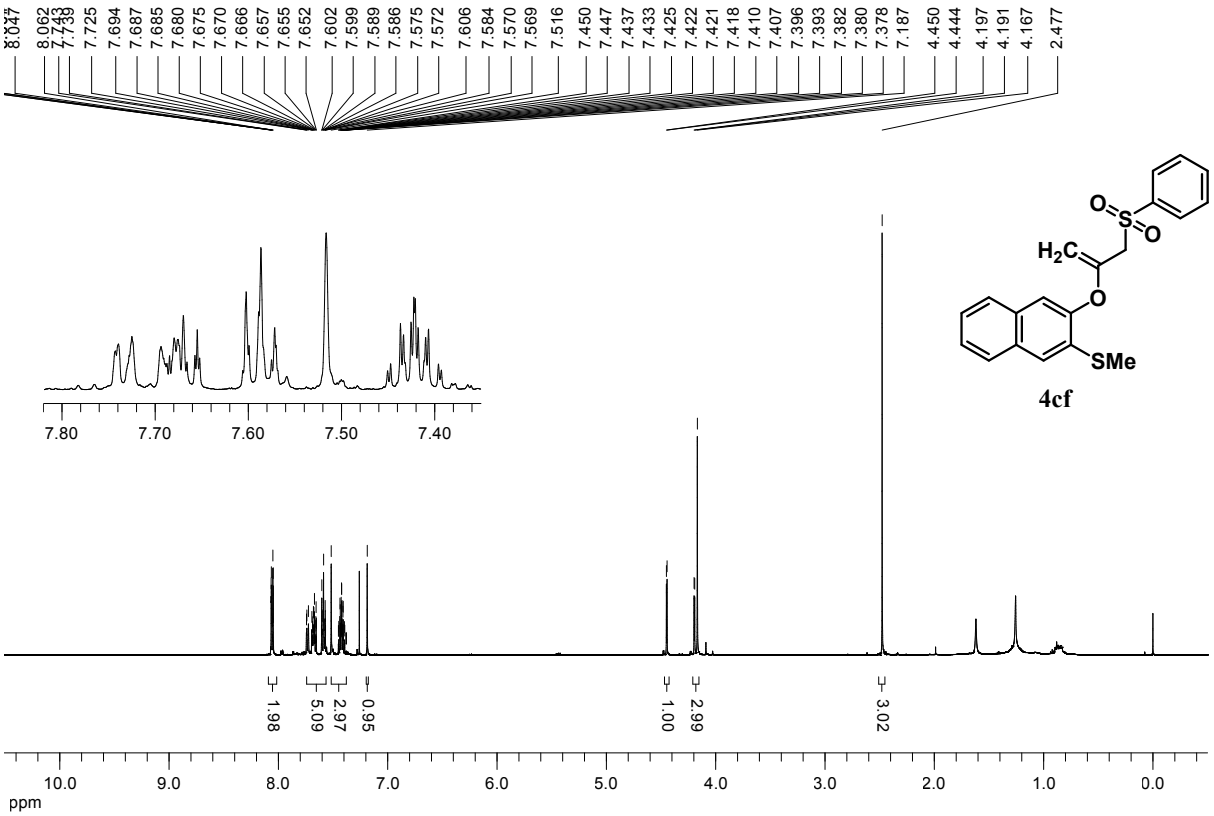


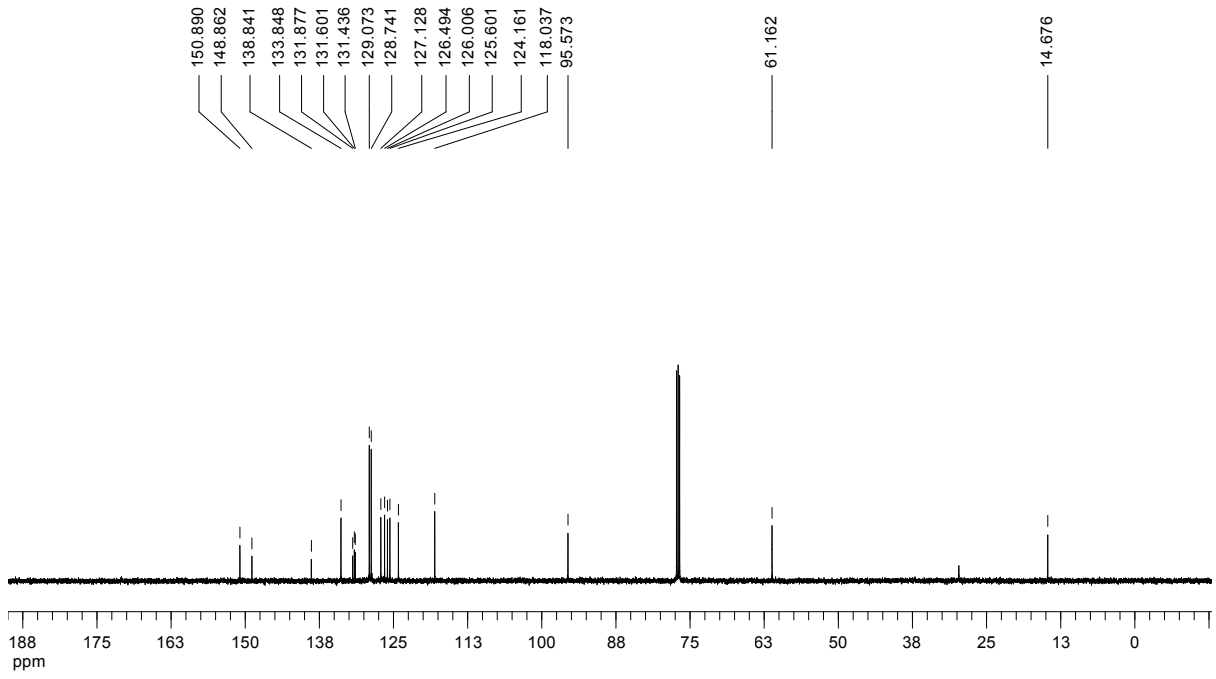
^{13}C NMR (126 MHz, $CDCl_3$)



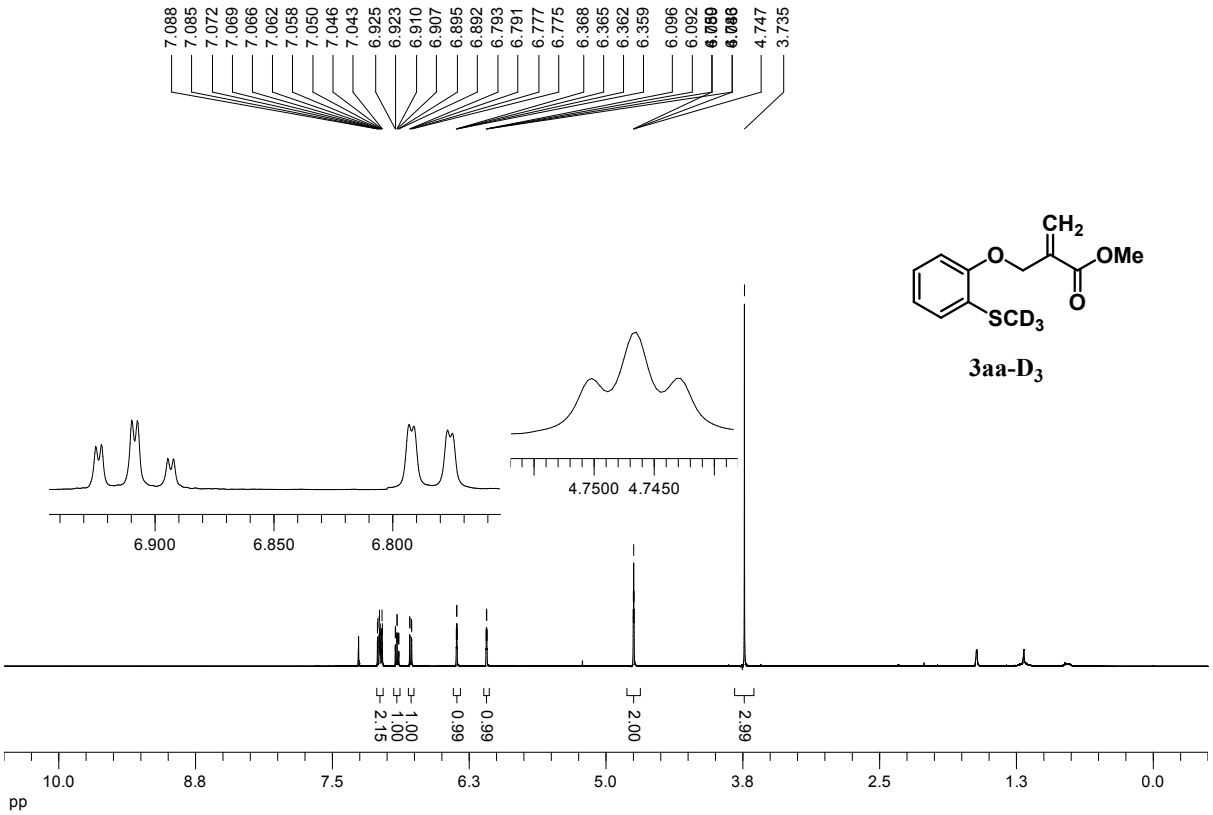
^{1}H NMR (500 MHz, $CDCl_3$)



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



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



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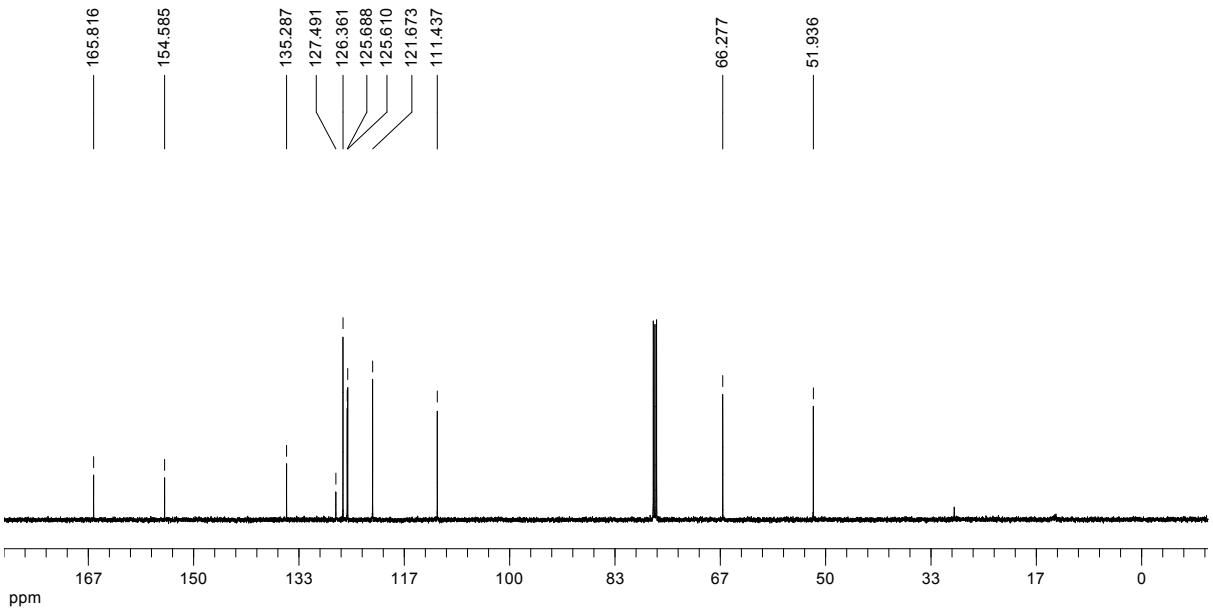

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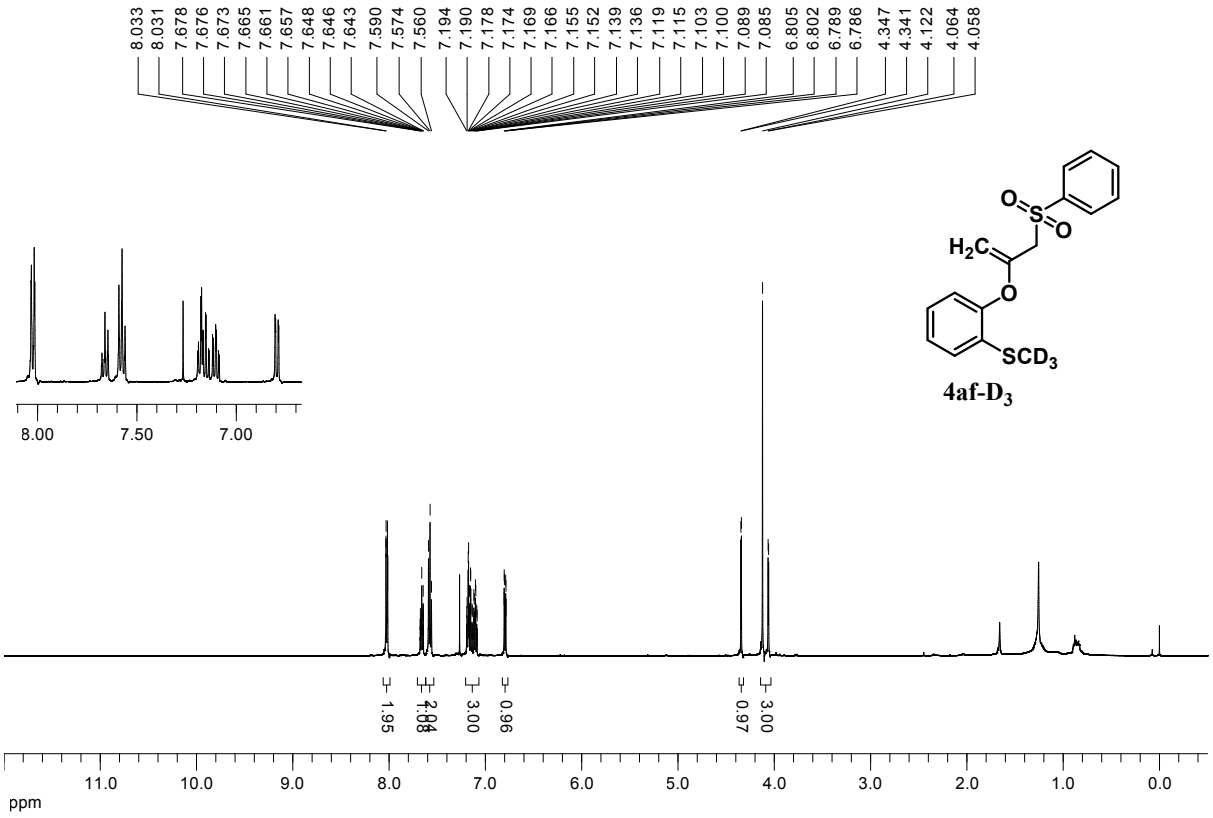

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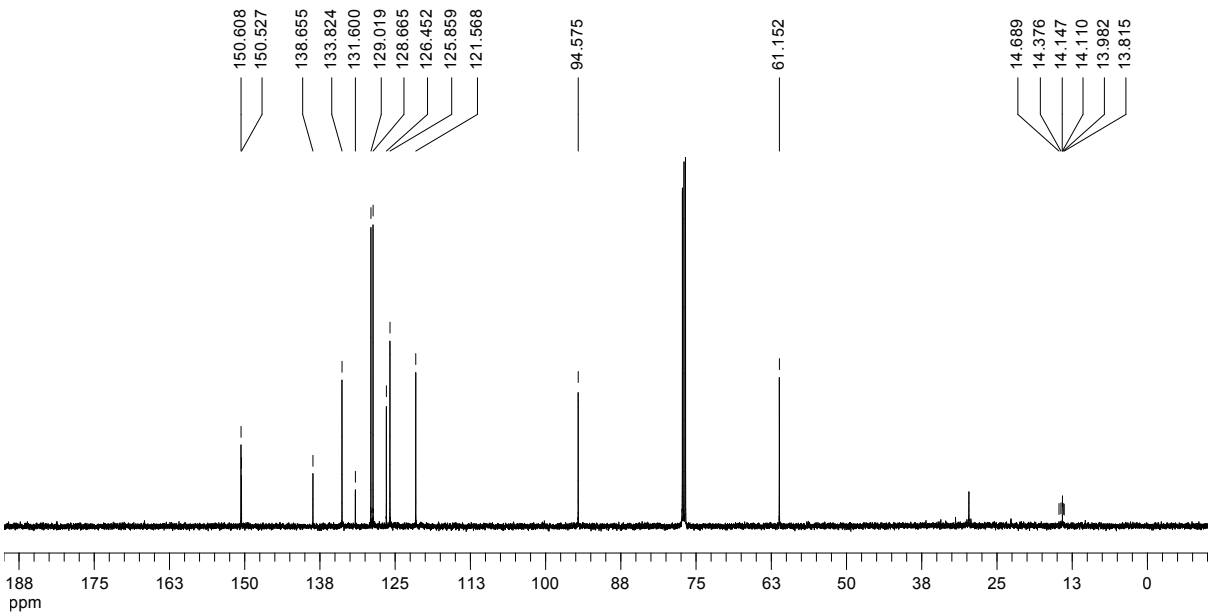
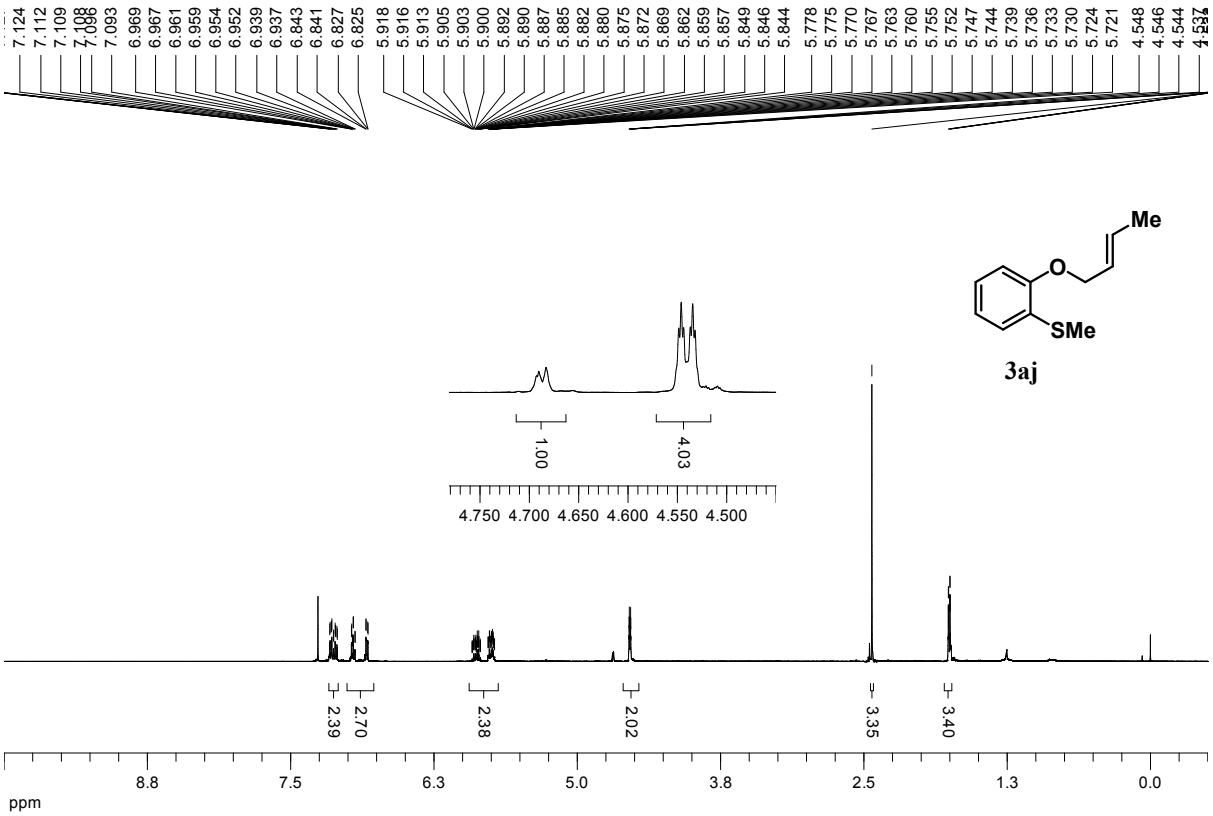
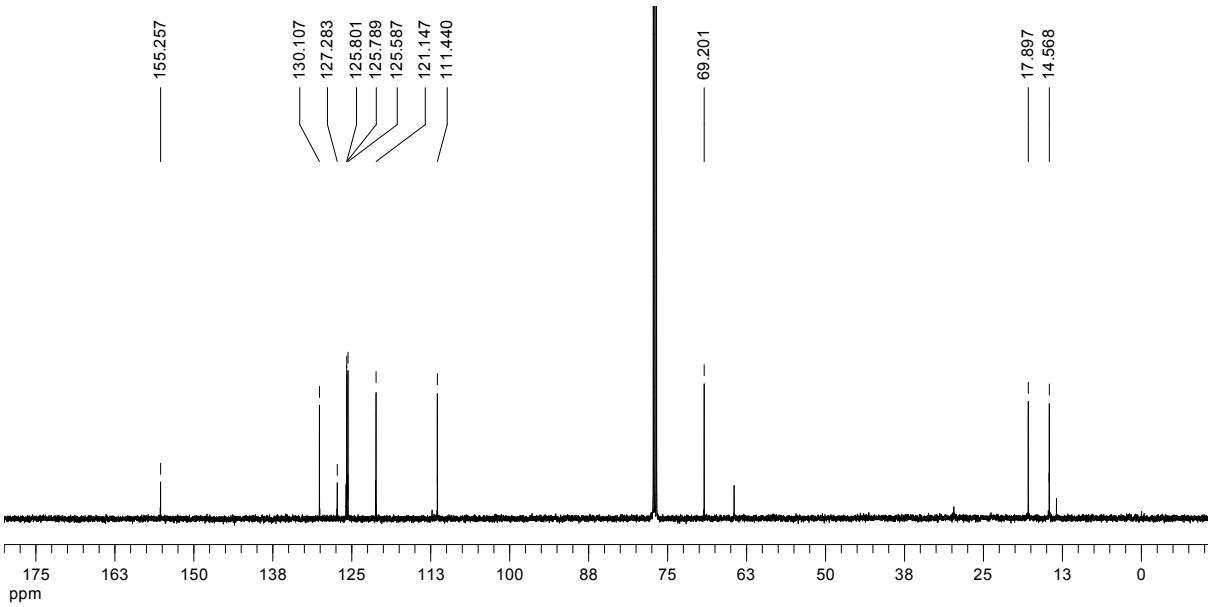


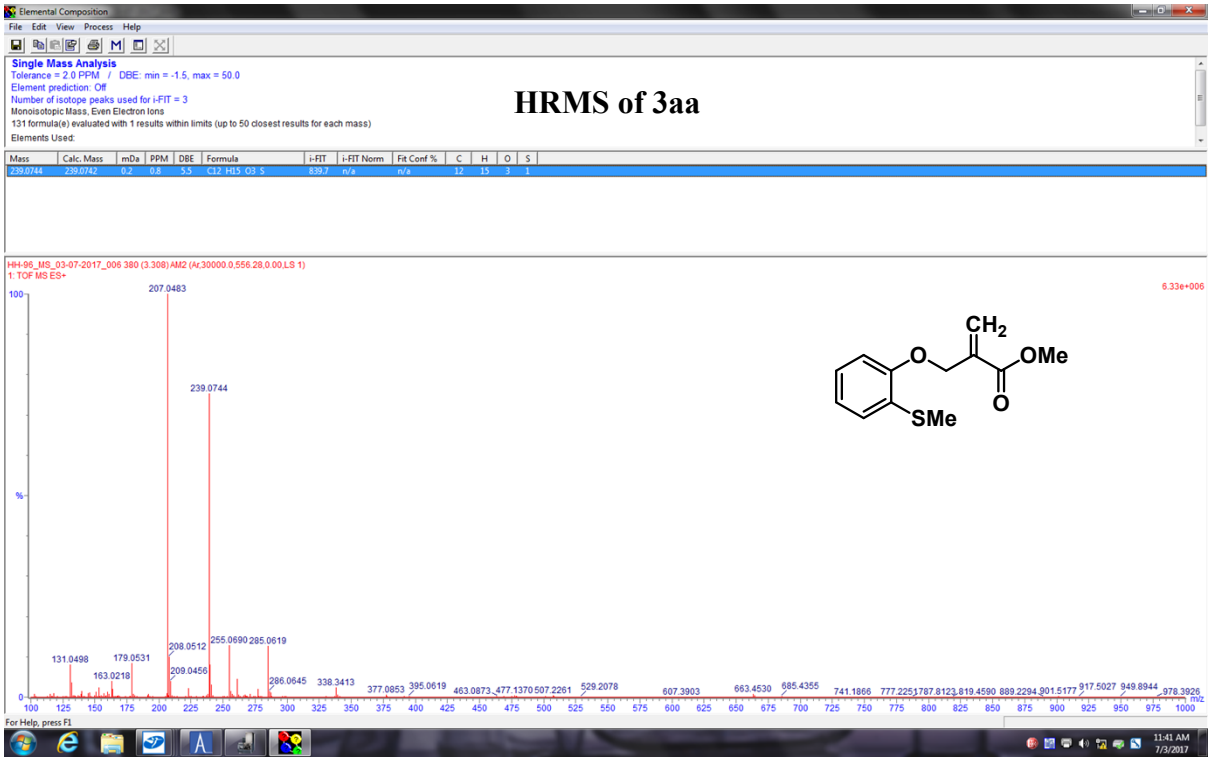
^{1}H NMR (500 MHz, $CDCl_3$)



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



HRMS of 3aa



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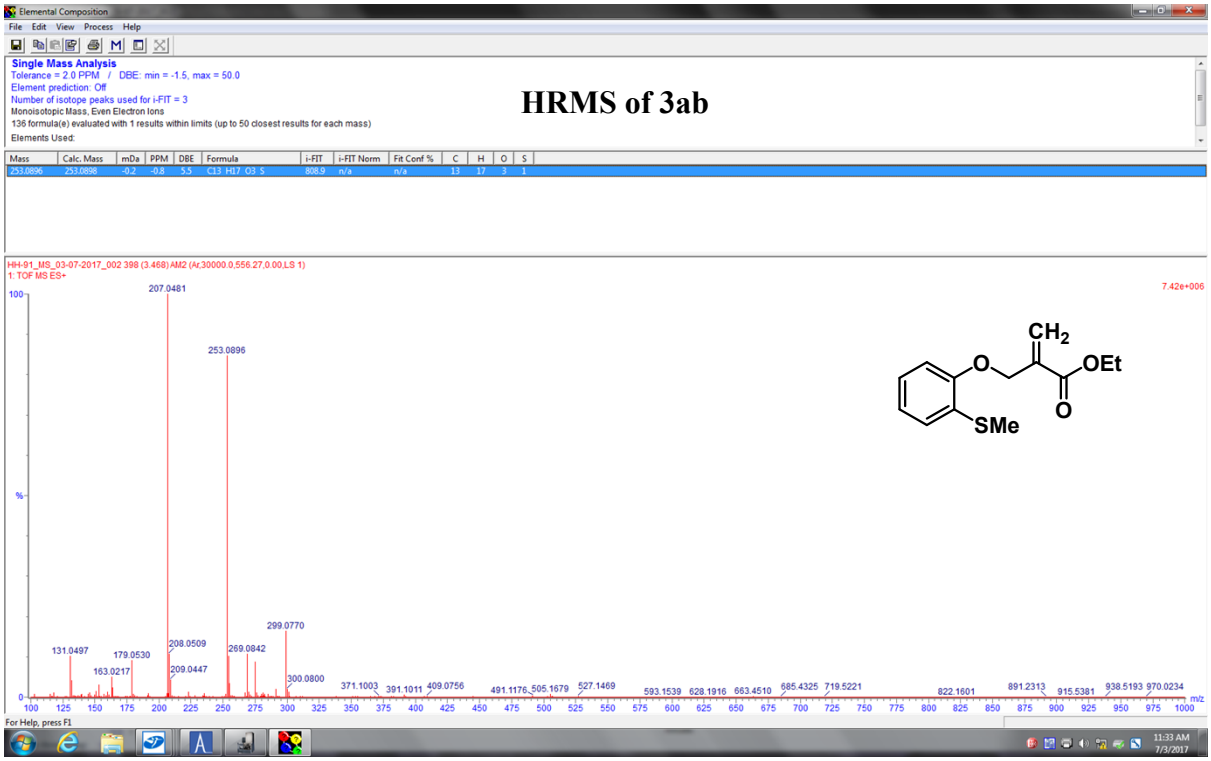
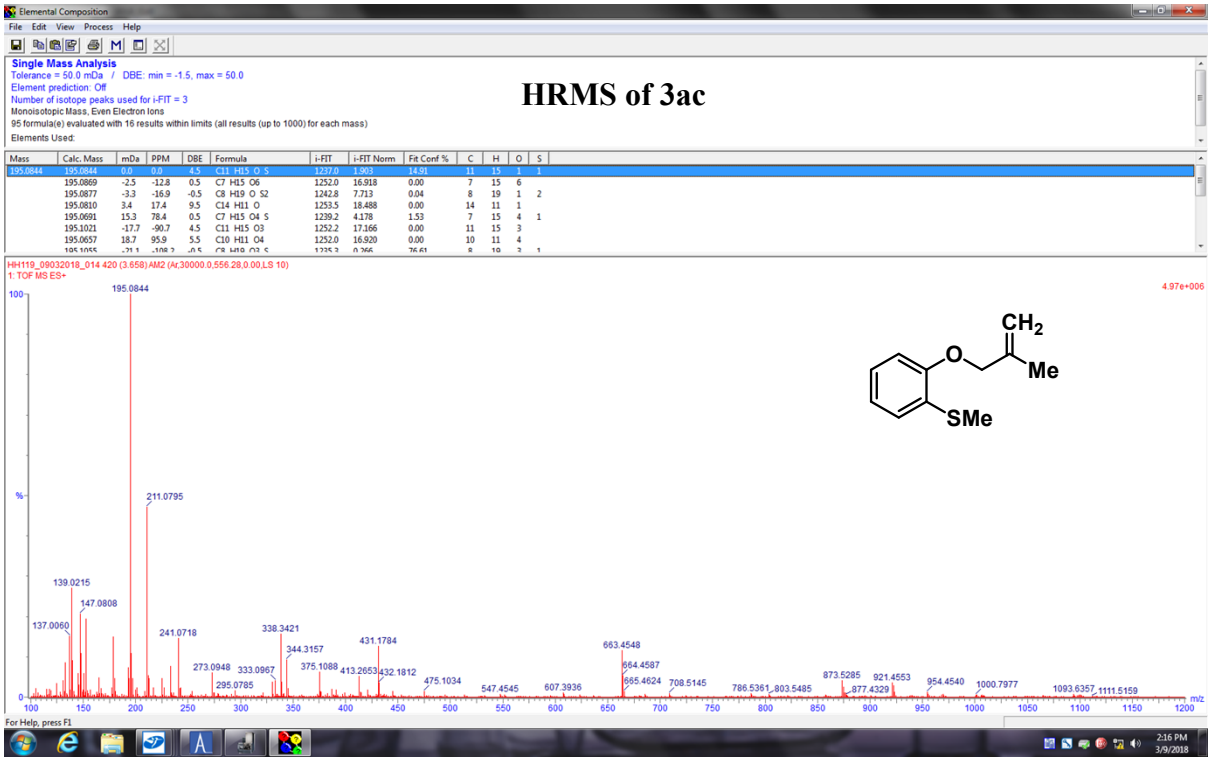
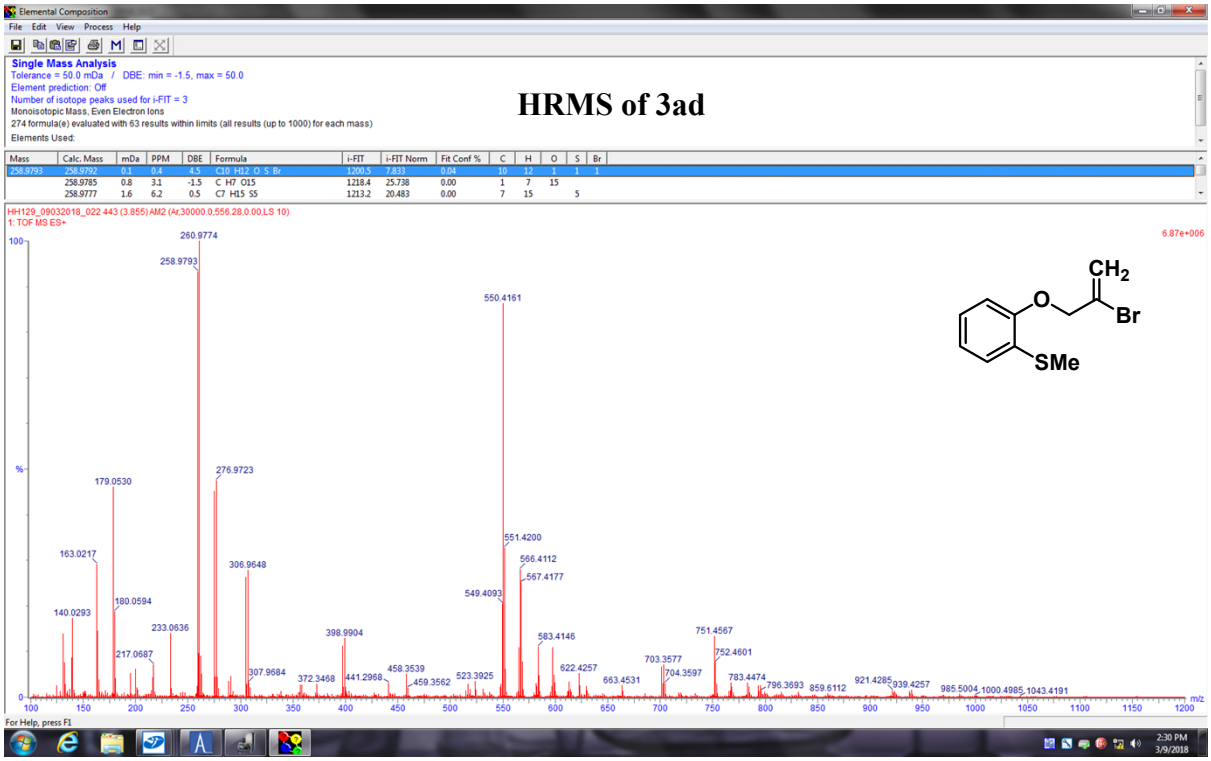


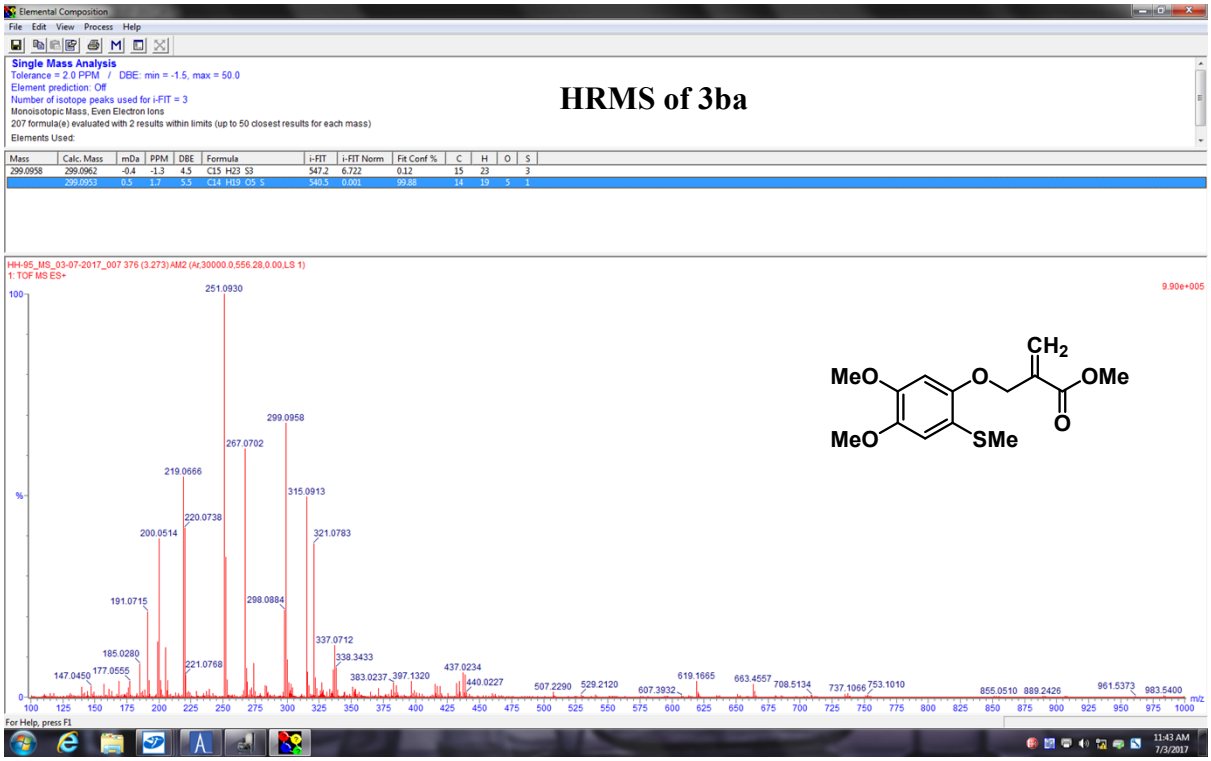
HRMS of 3ac



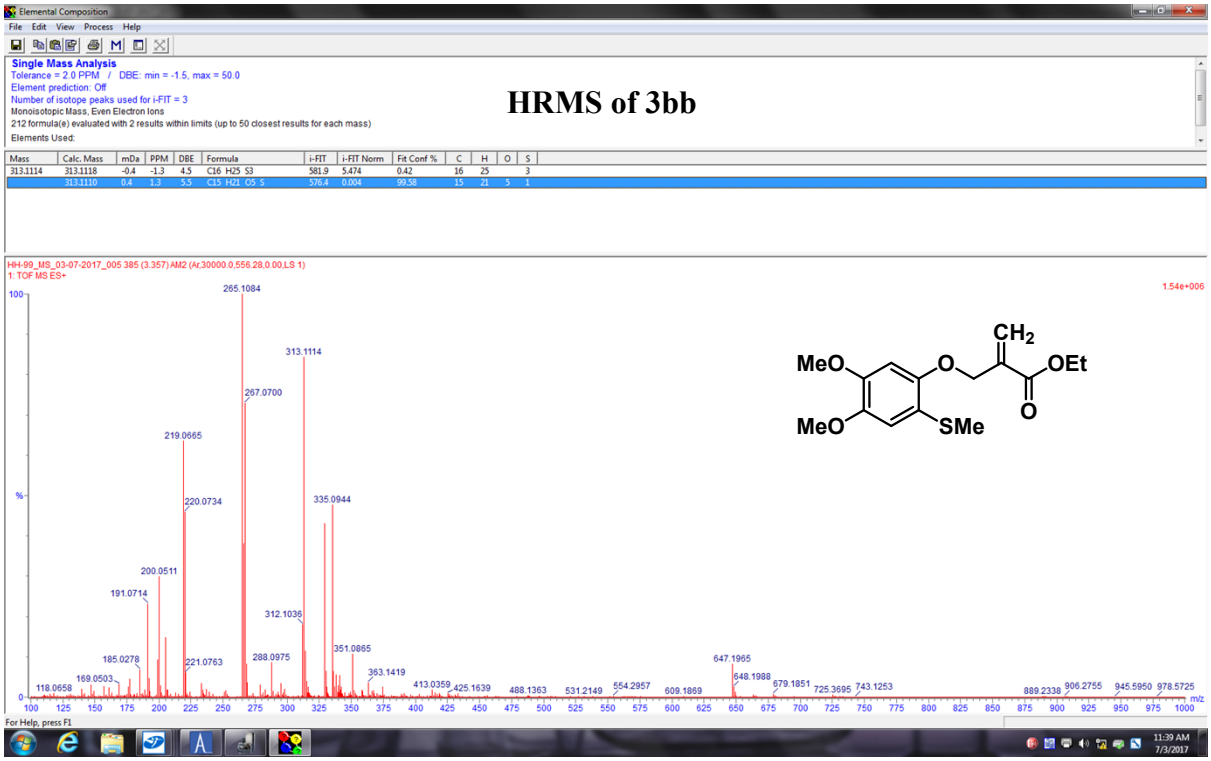
HRMS of 3ad



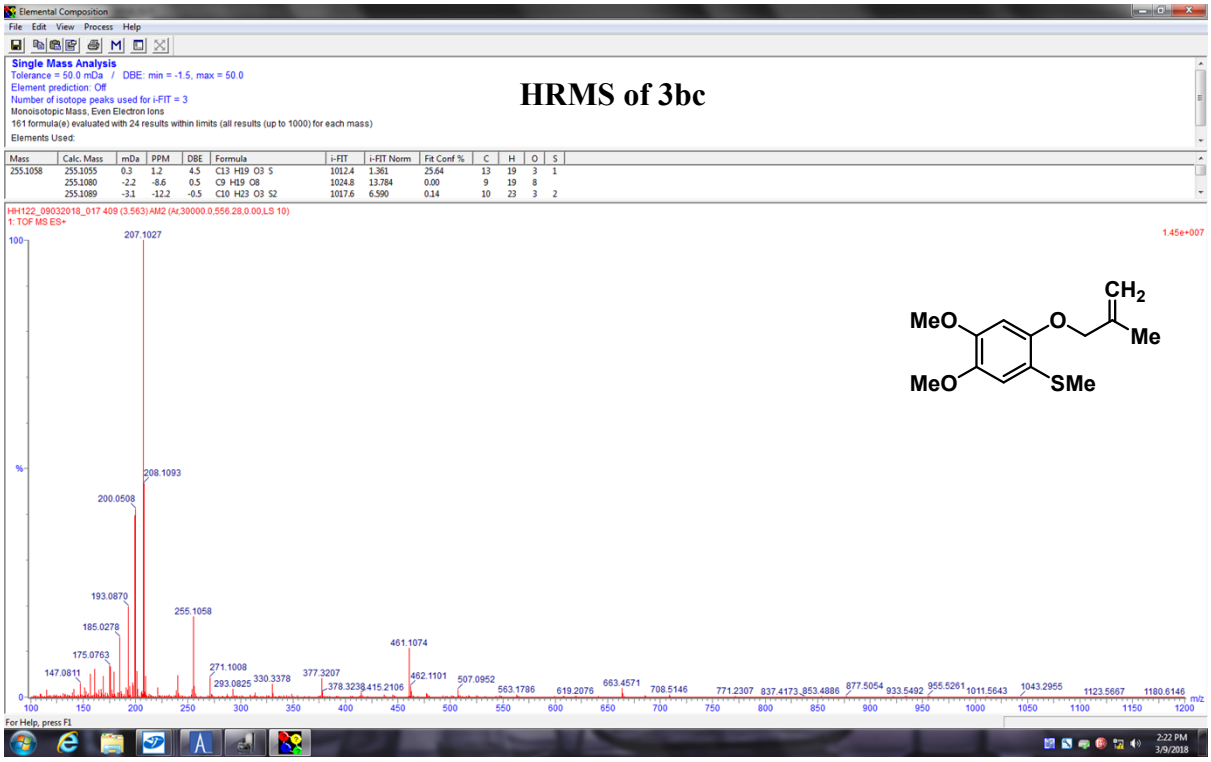
HRMS of 3ba



HRMS of 3bb



HRMS of 3bc



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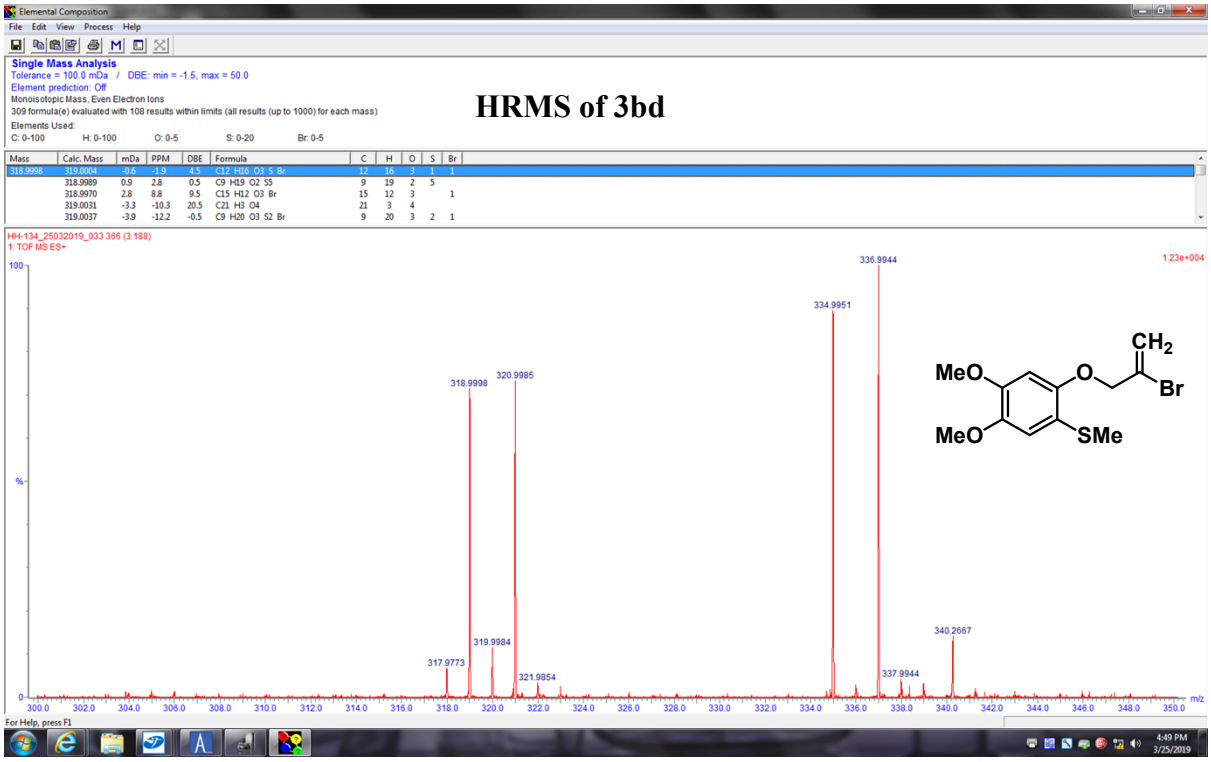
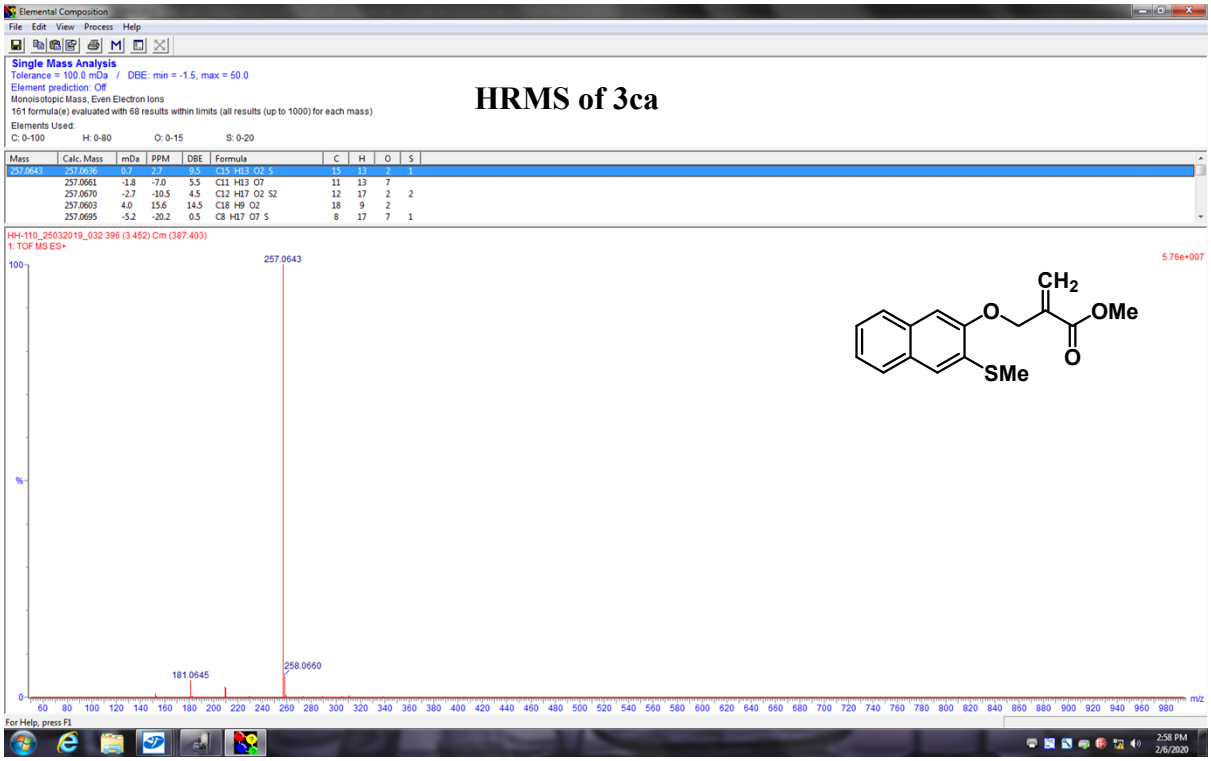
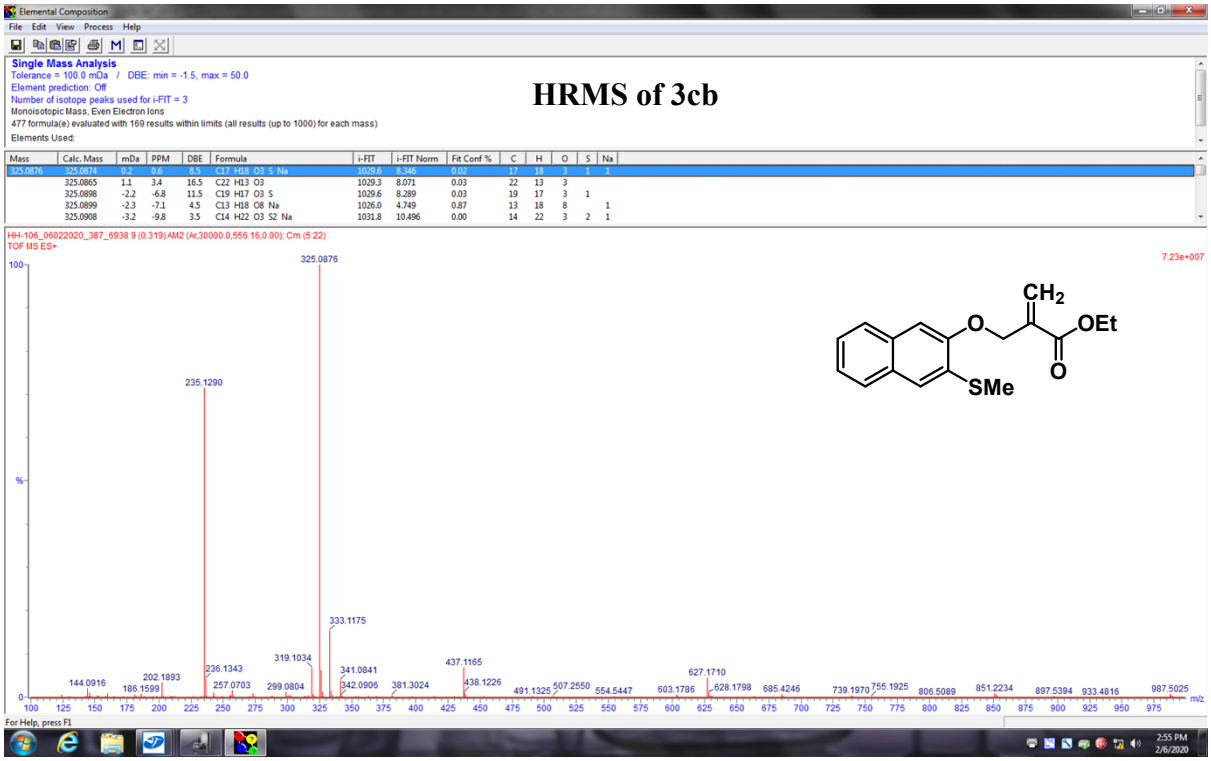


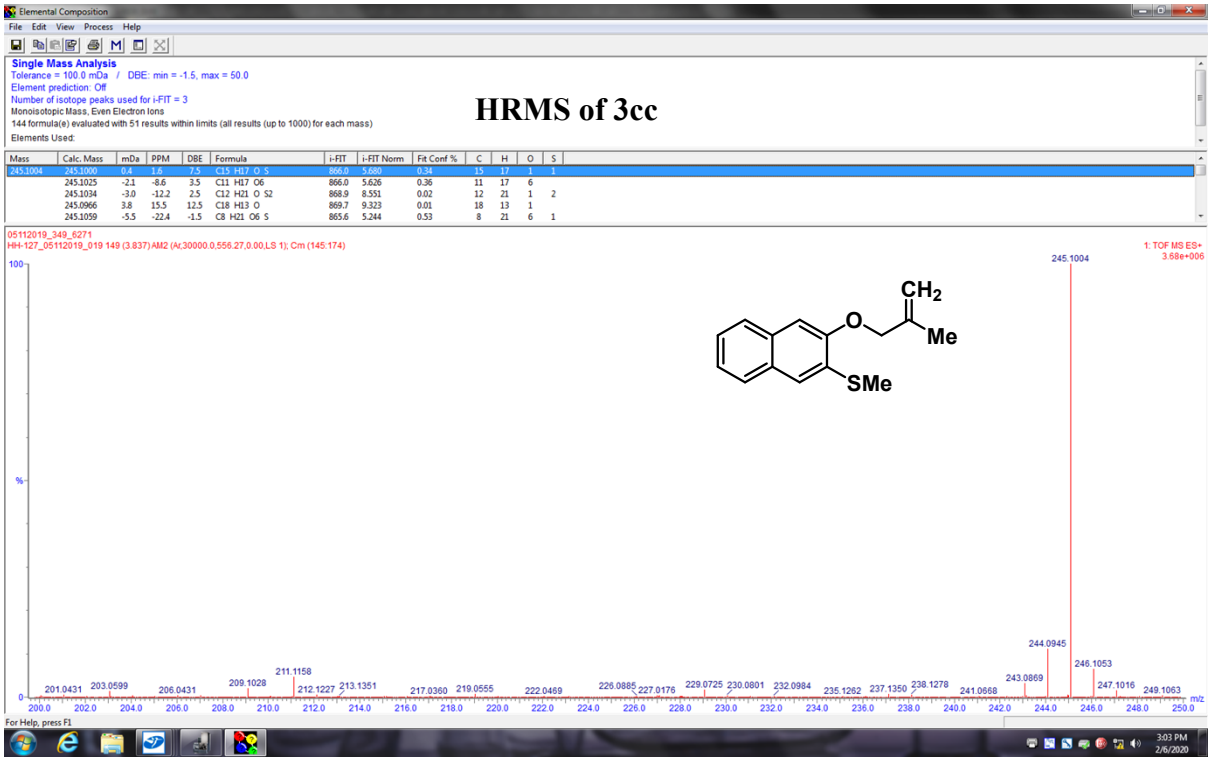
HRMS of 3ca



HRMS of 3cb



HRMS of 3cc



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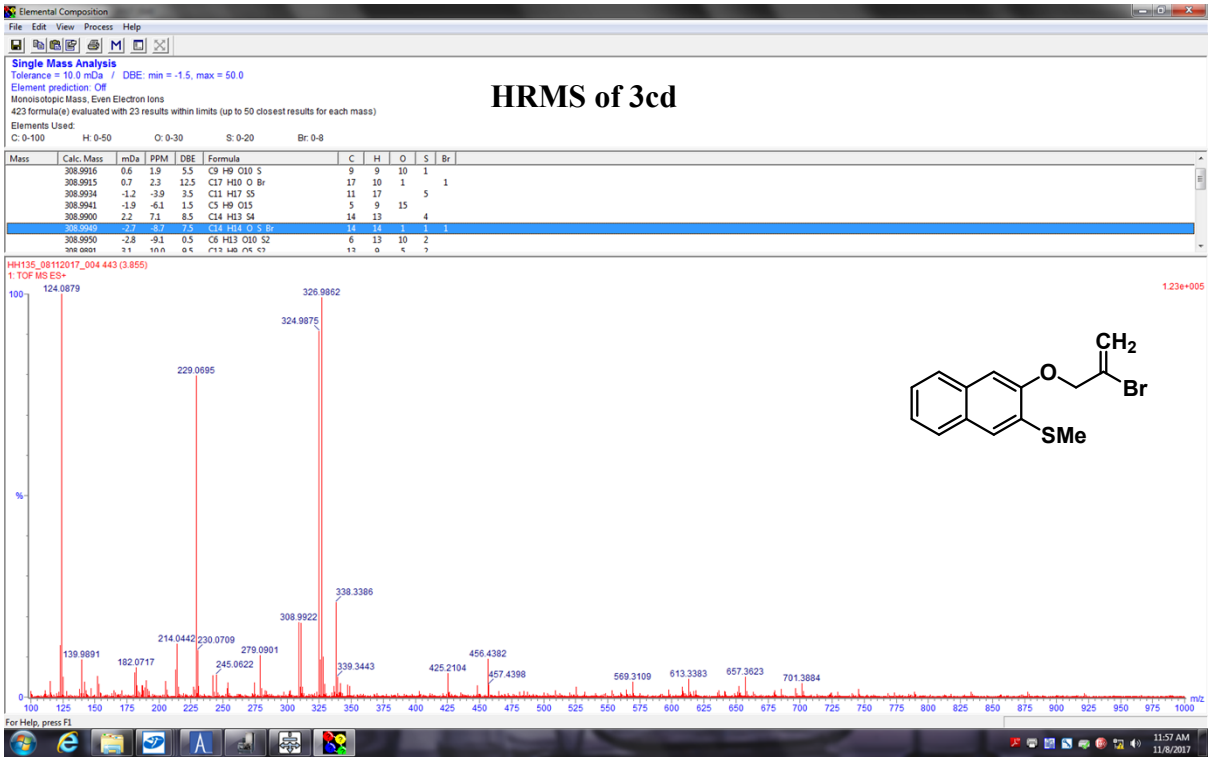

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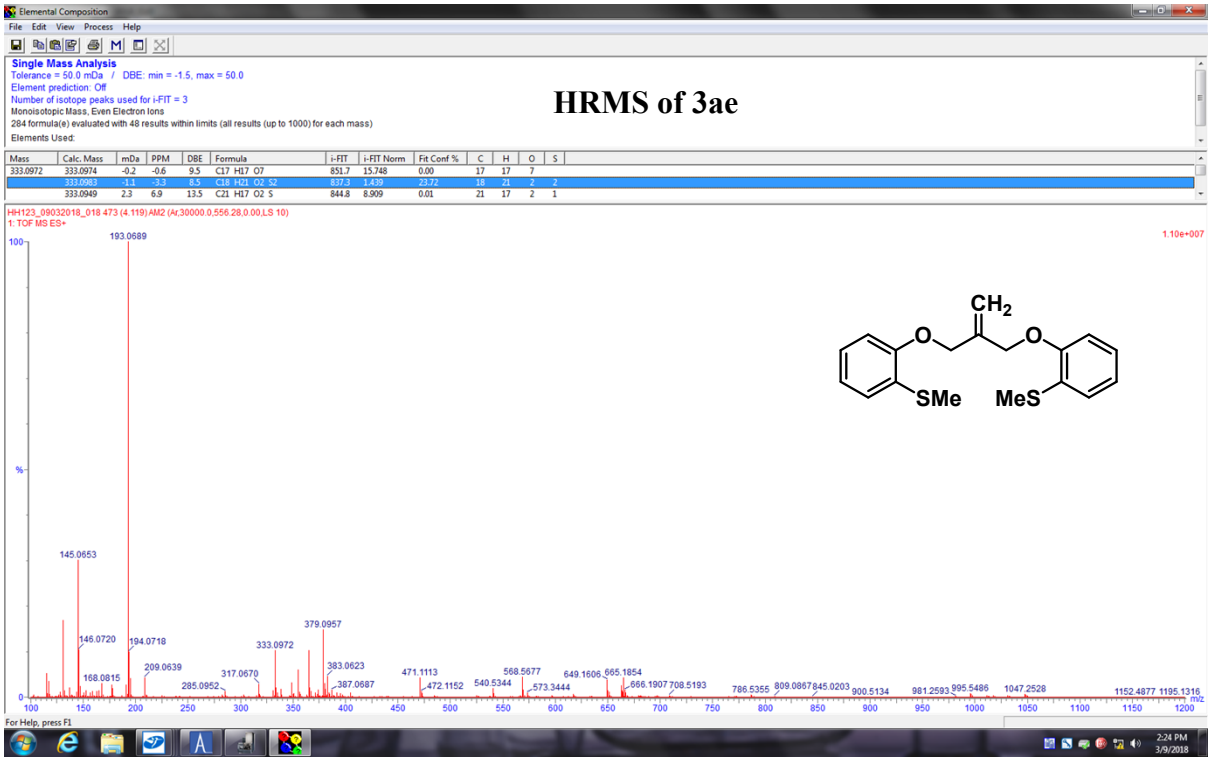
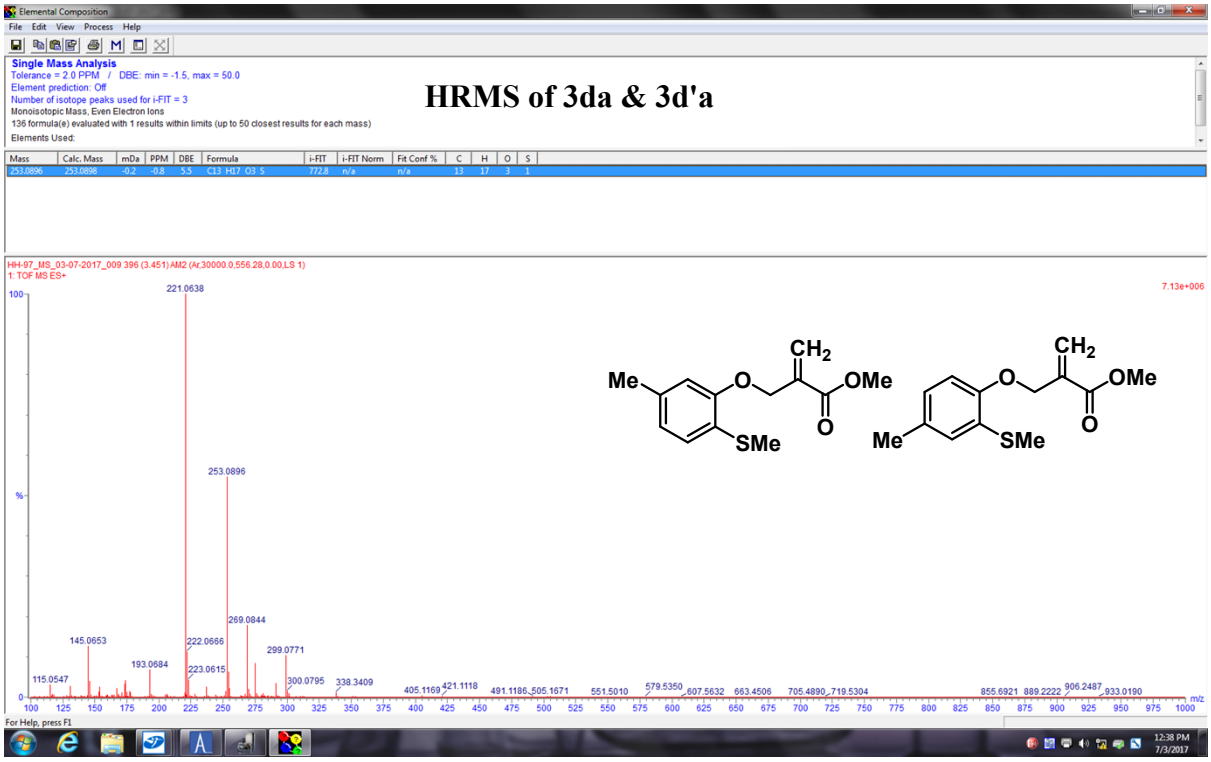


HRMS of 3da & 3d'a



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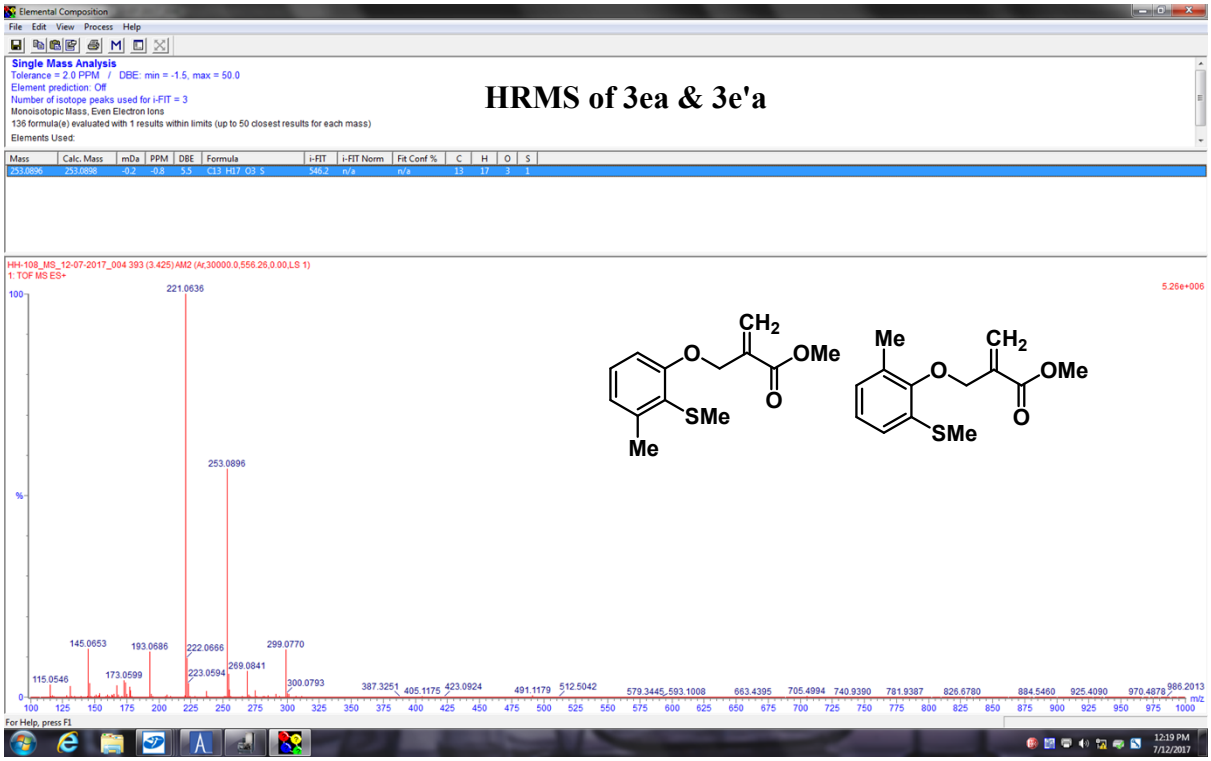

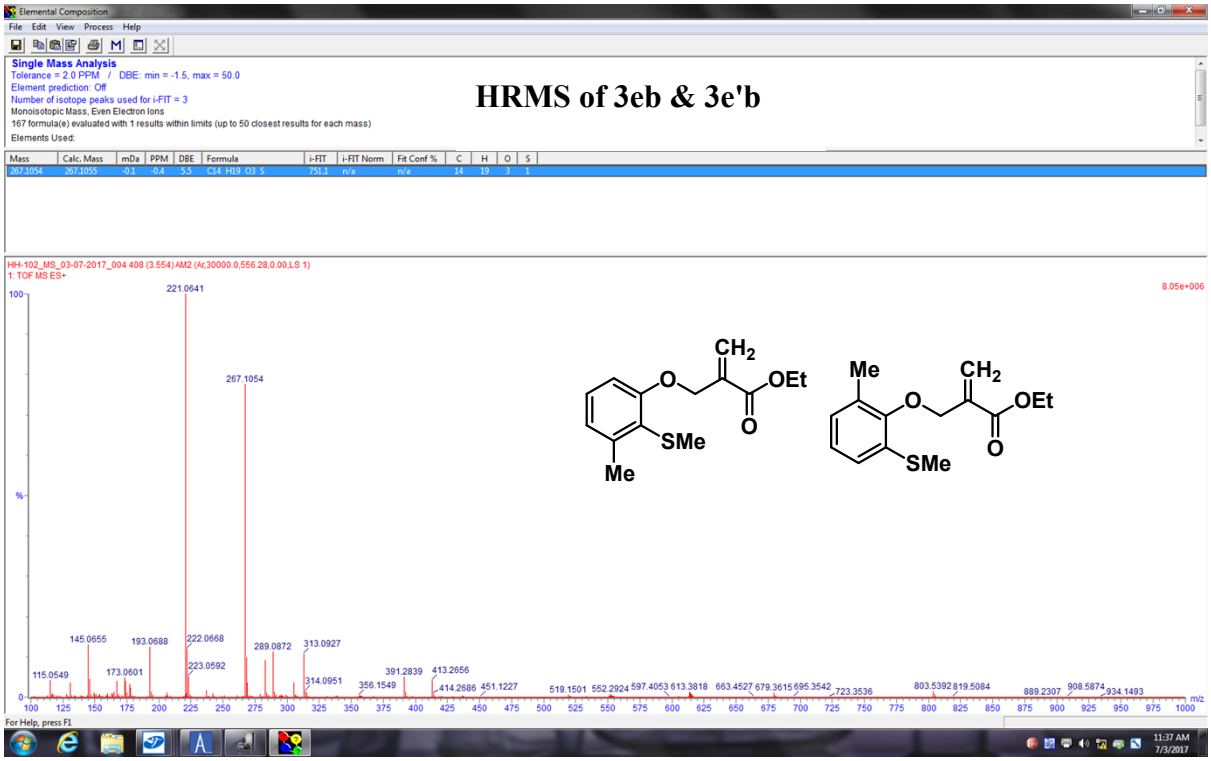

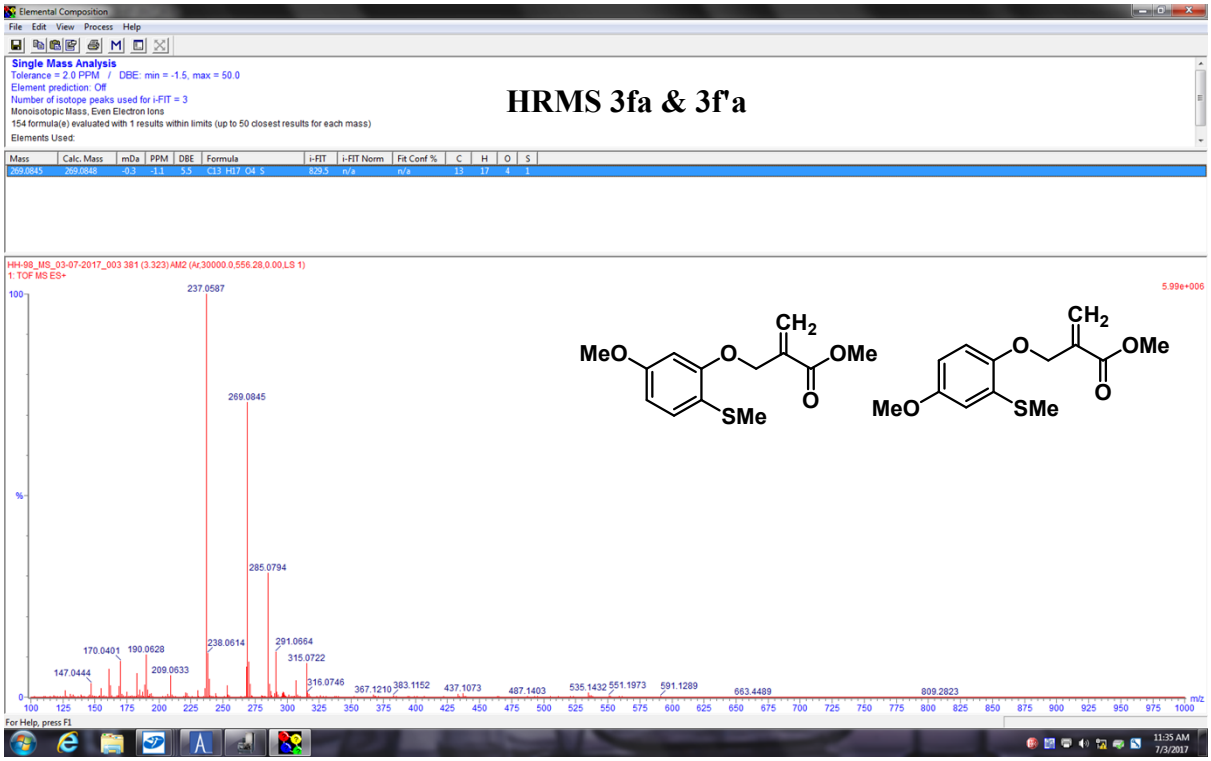

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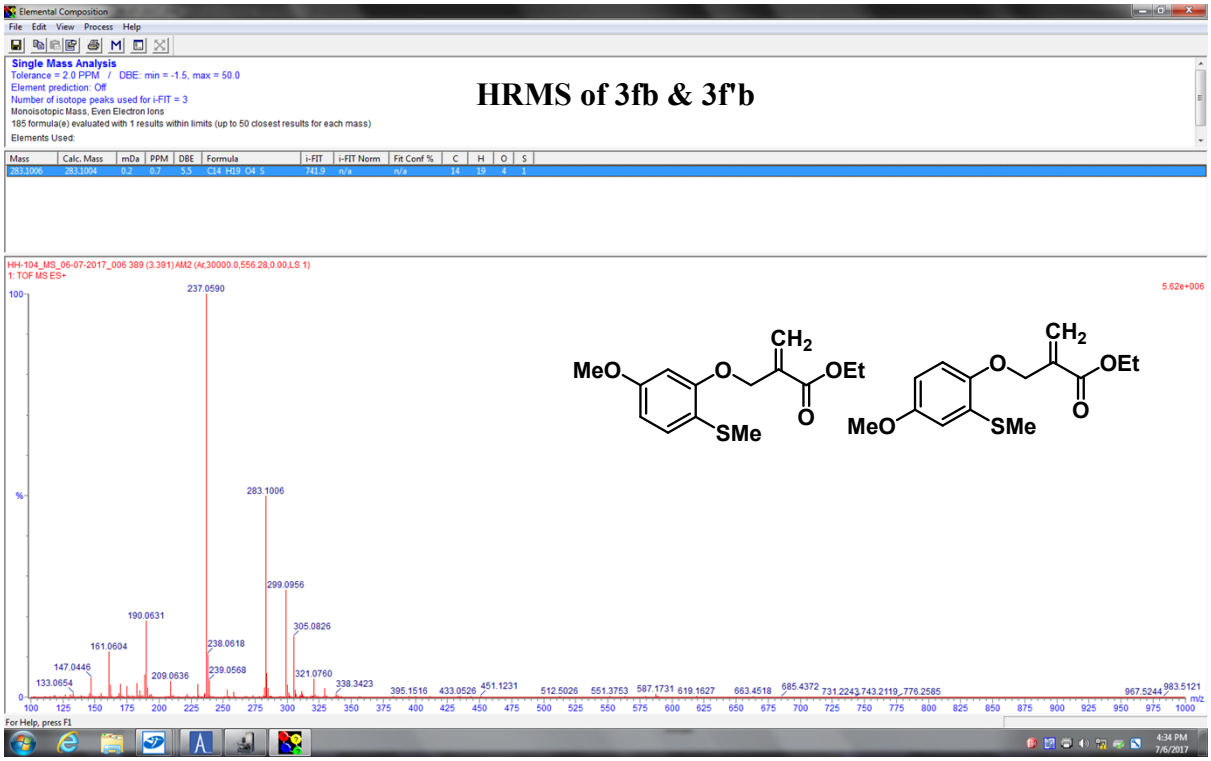

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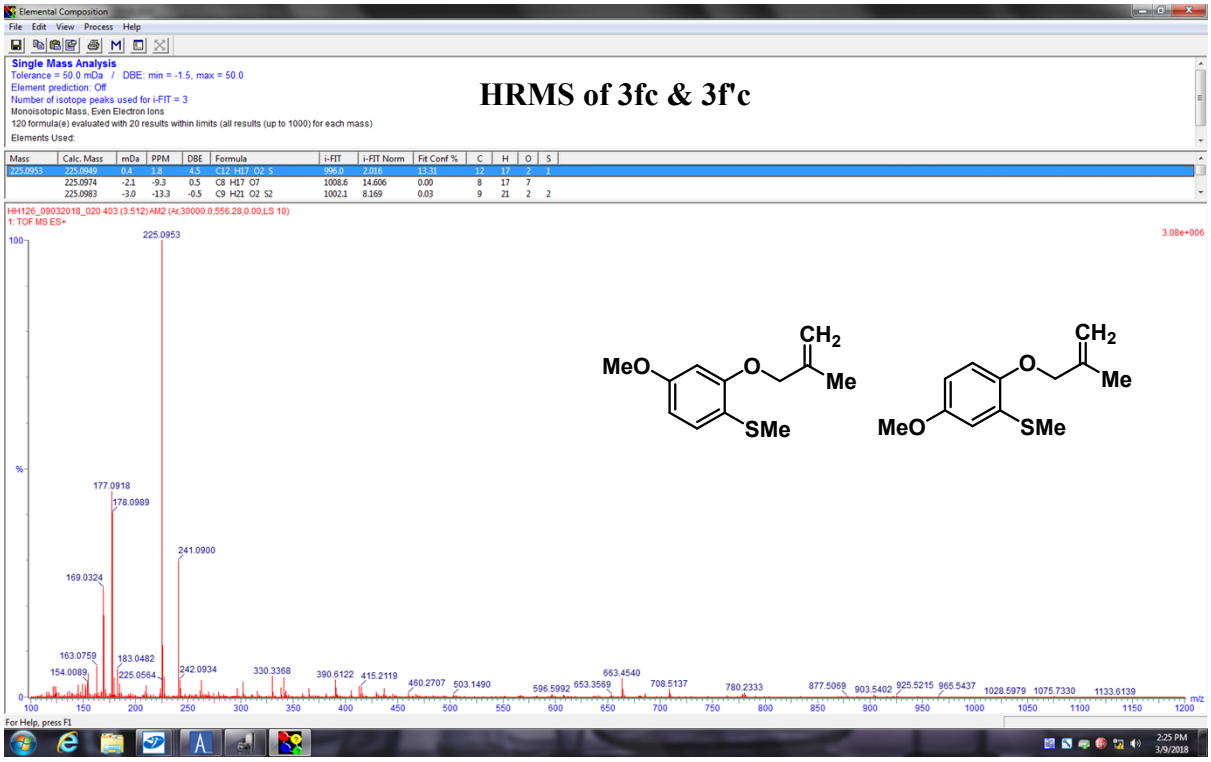
HRMS of 3fc & 3f'c



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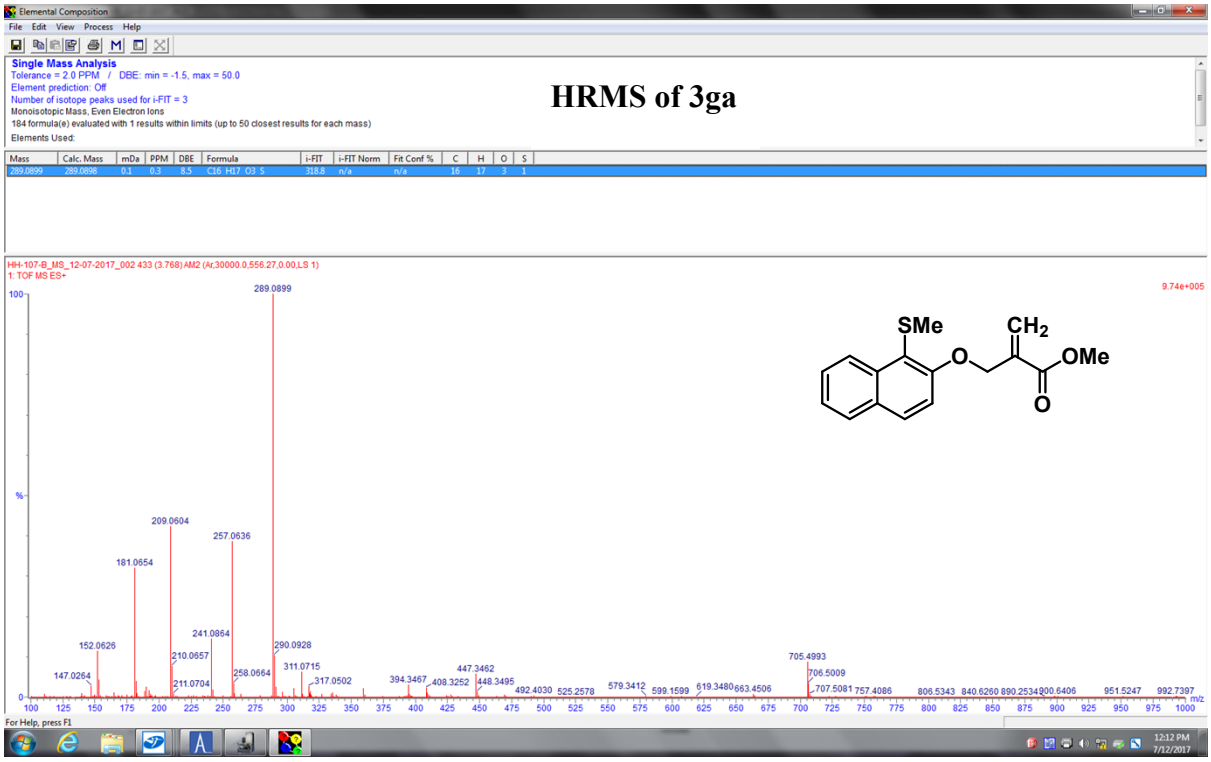

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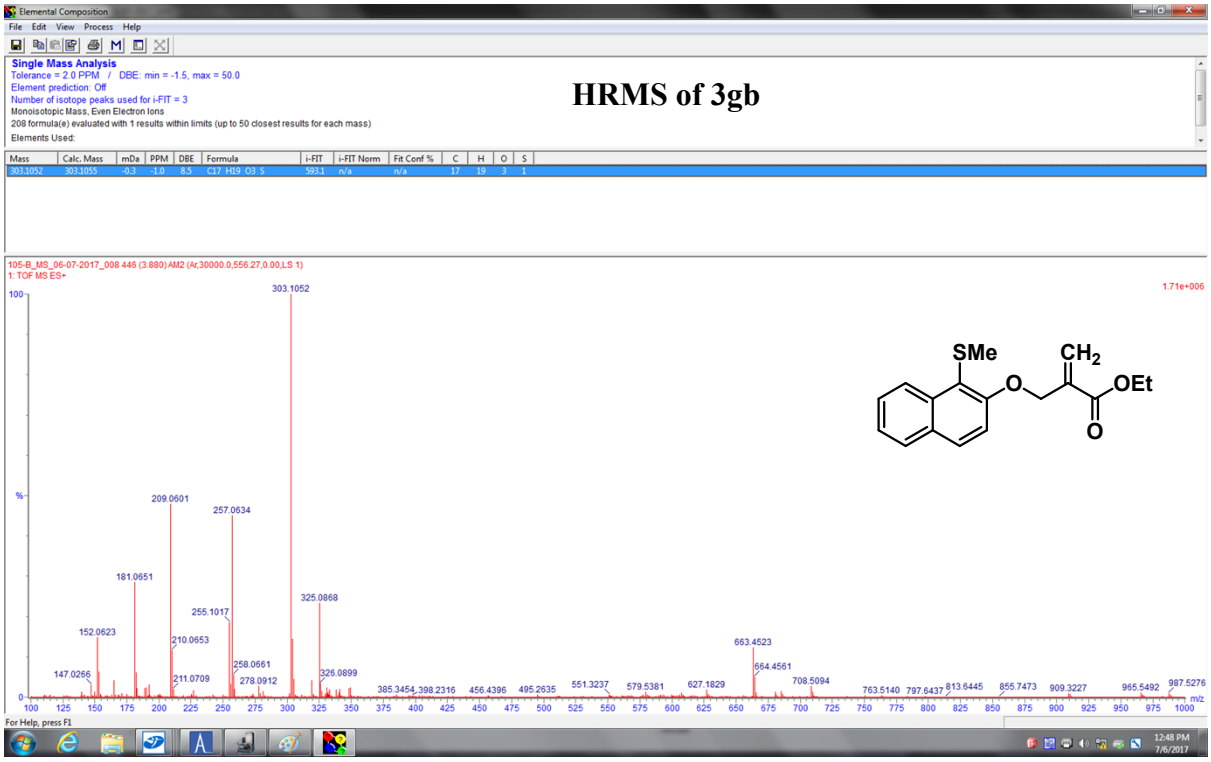

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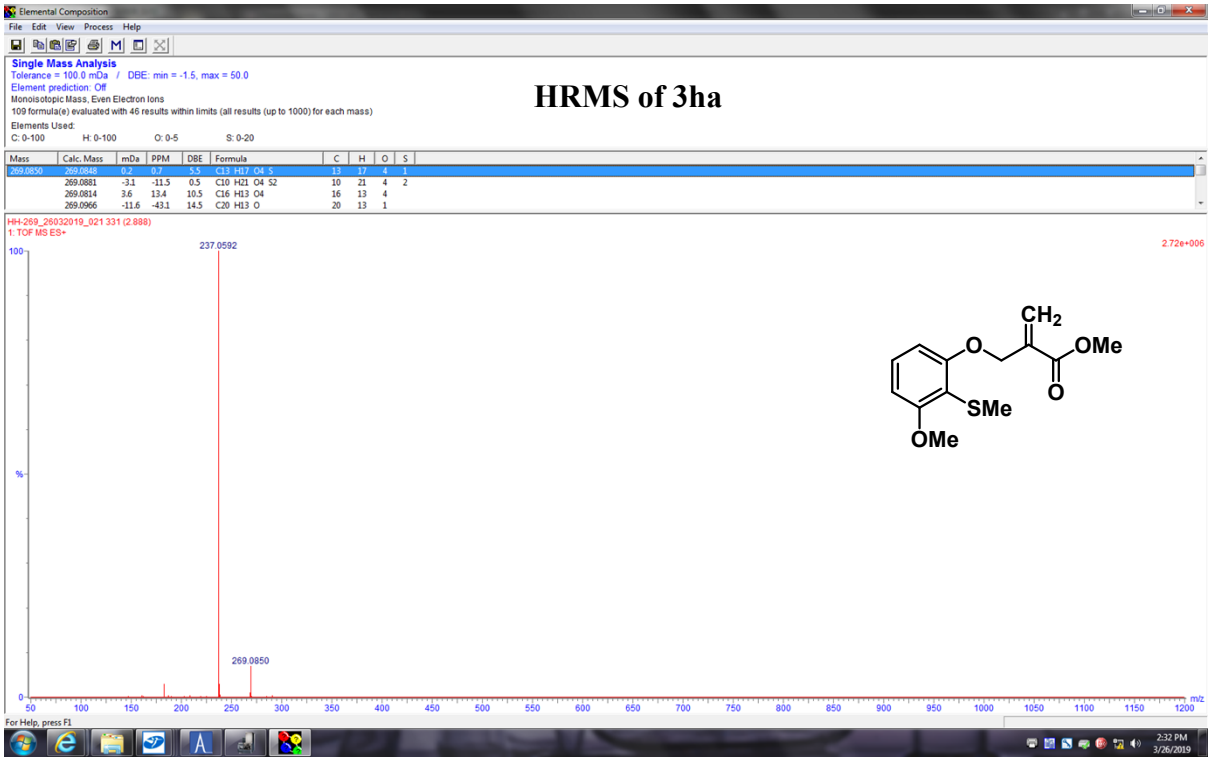

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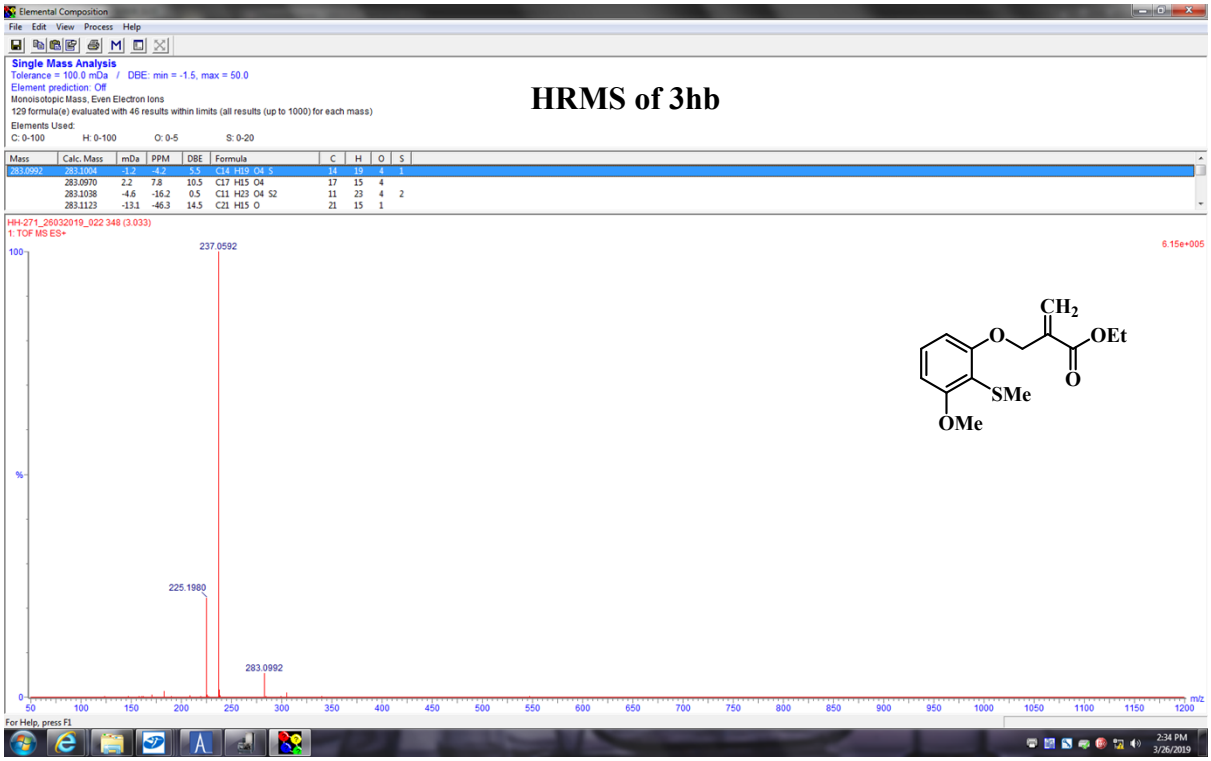
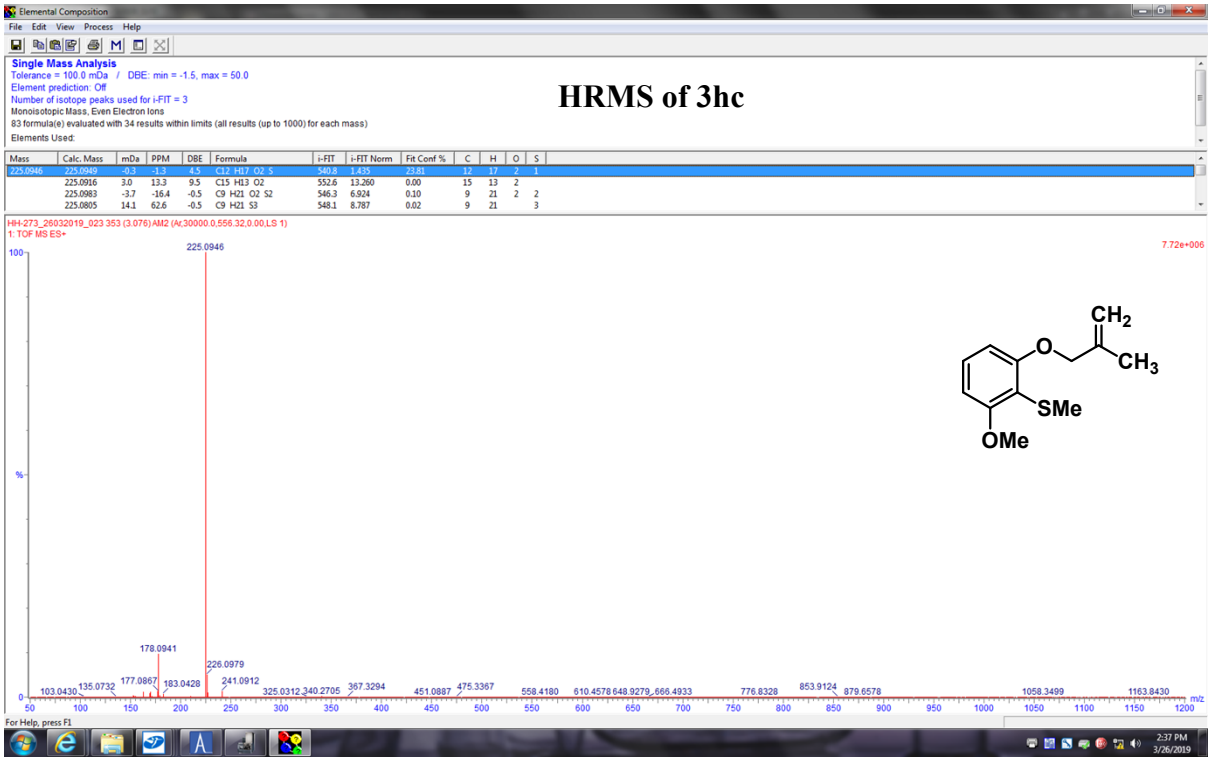
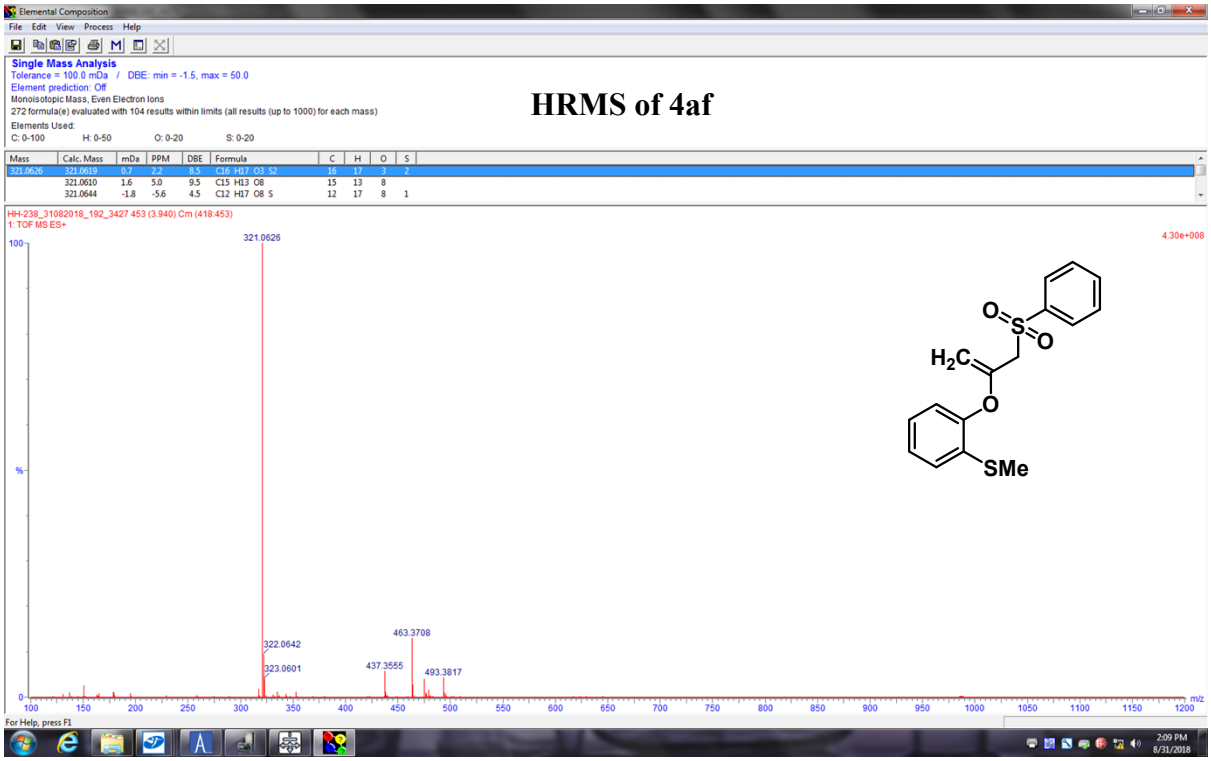


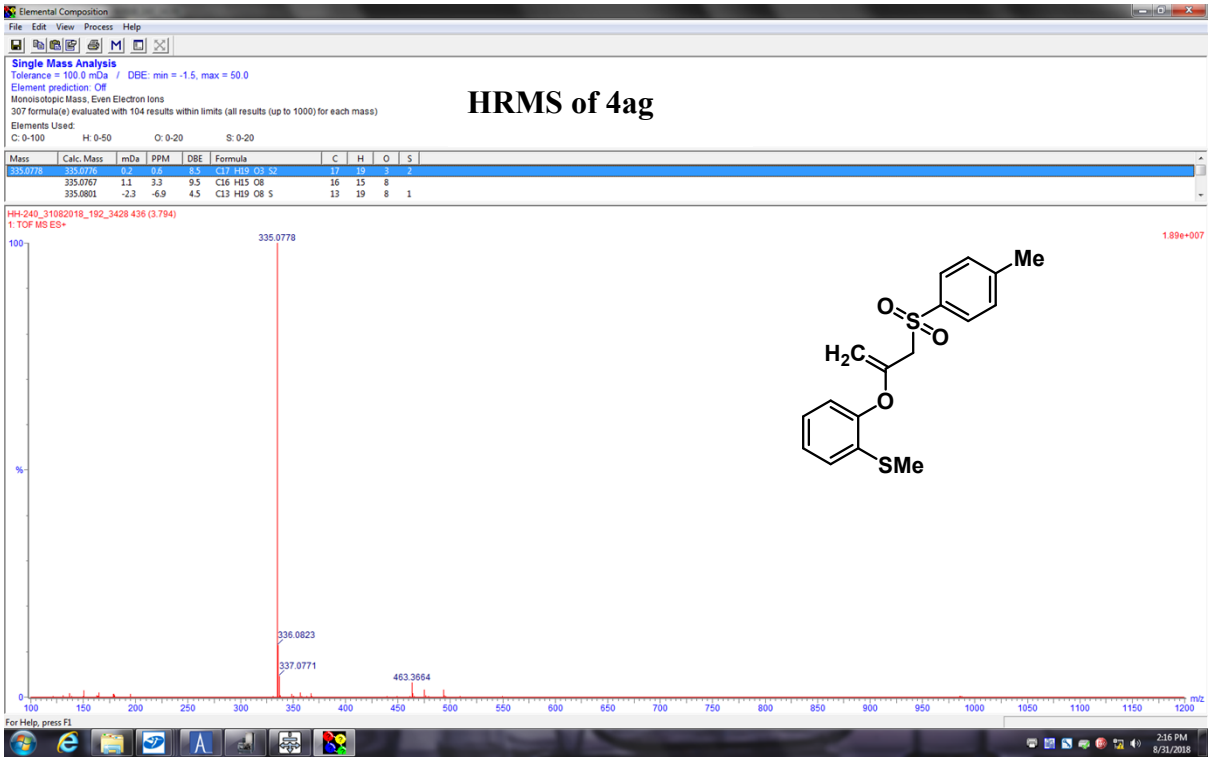
HRMS of 3hc



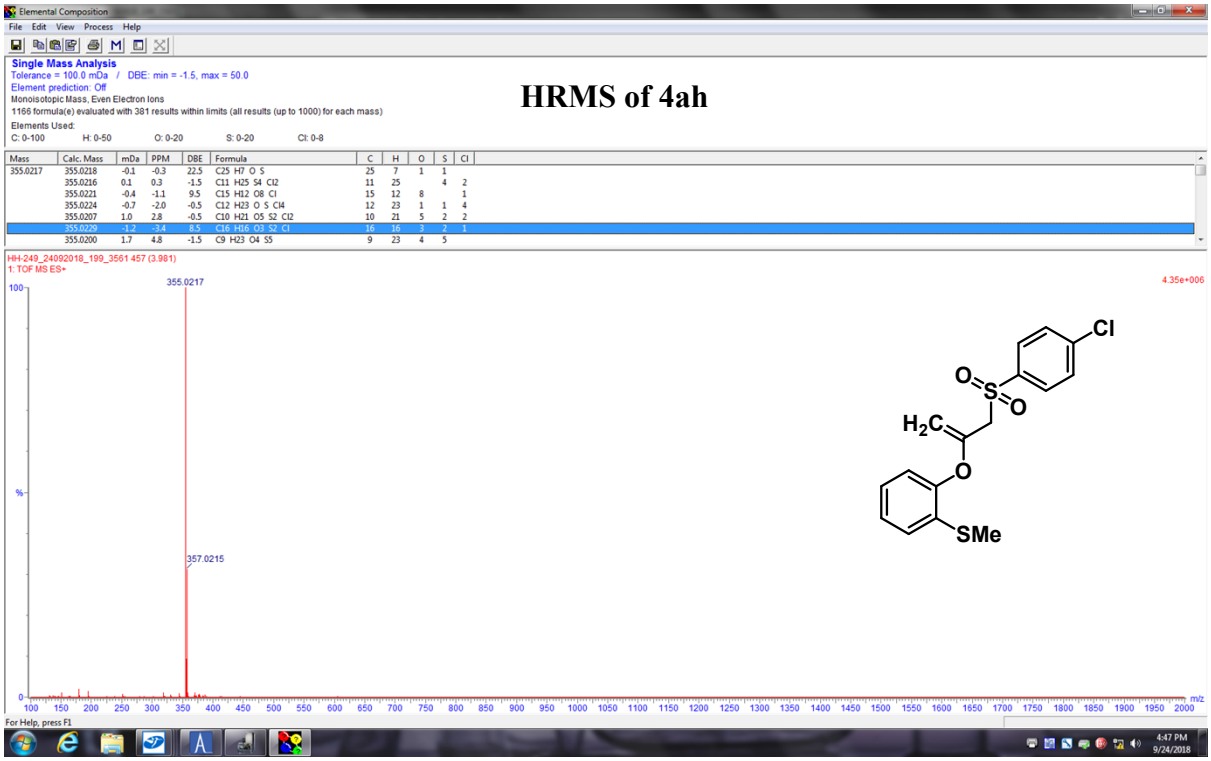
HRMS of 4af



HRMS of 4ag



HRMS of 4ah



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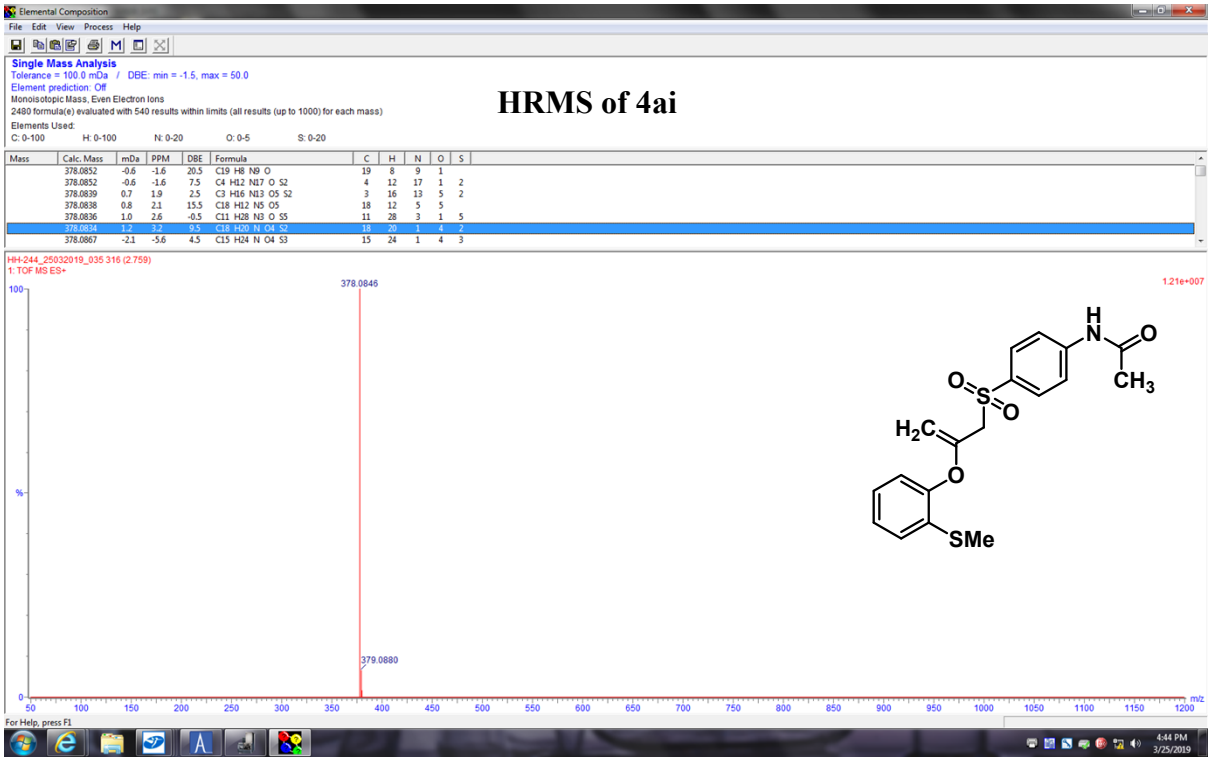

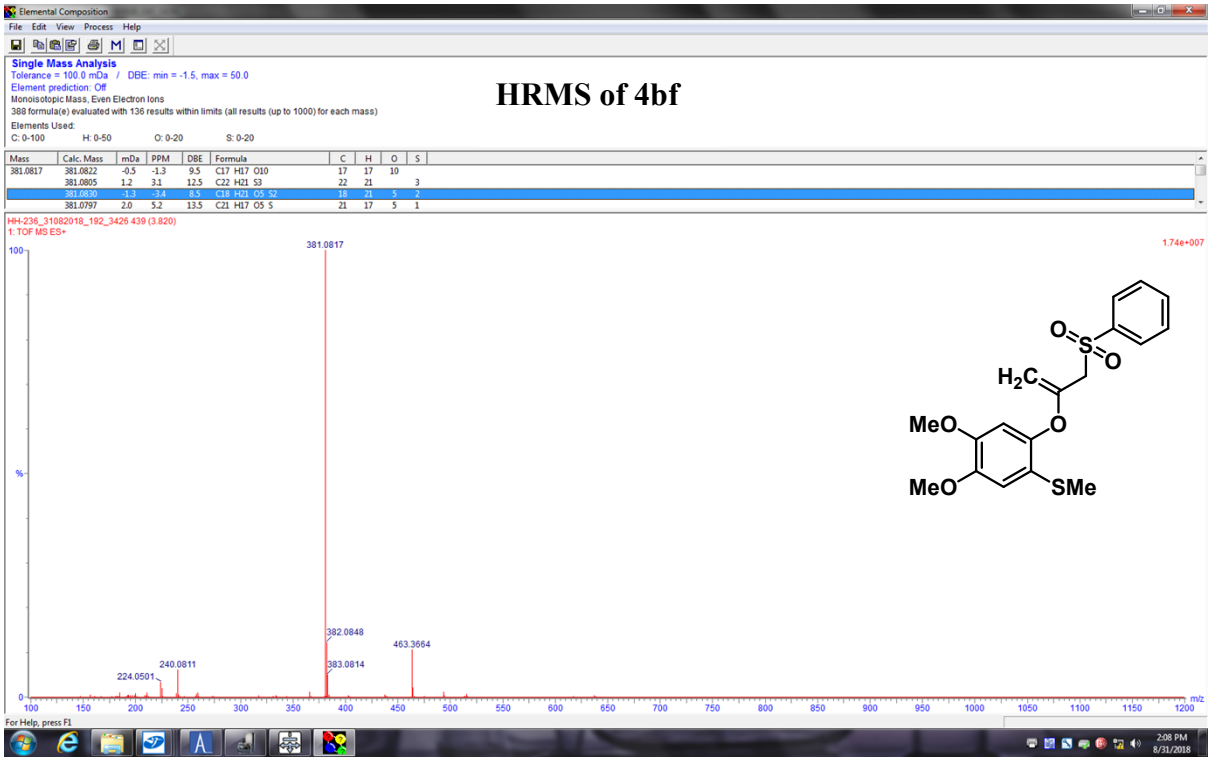

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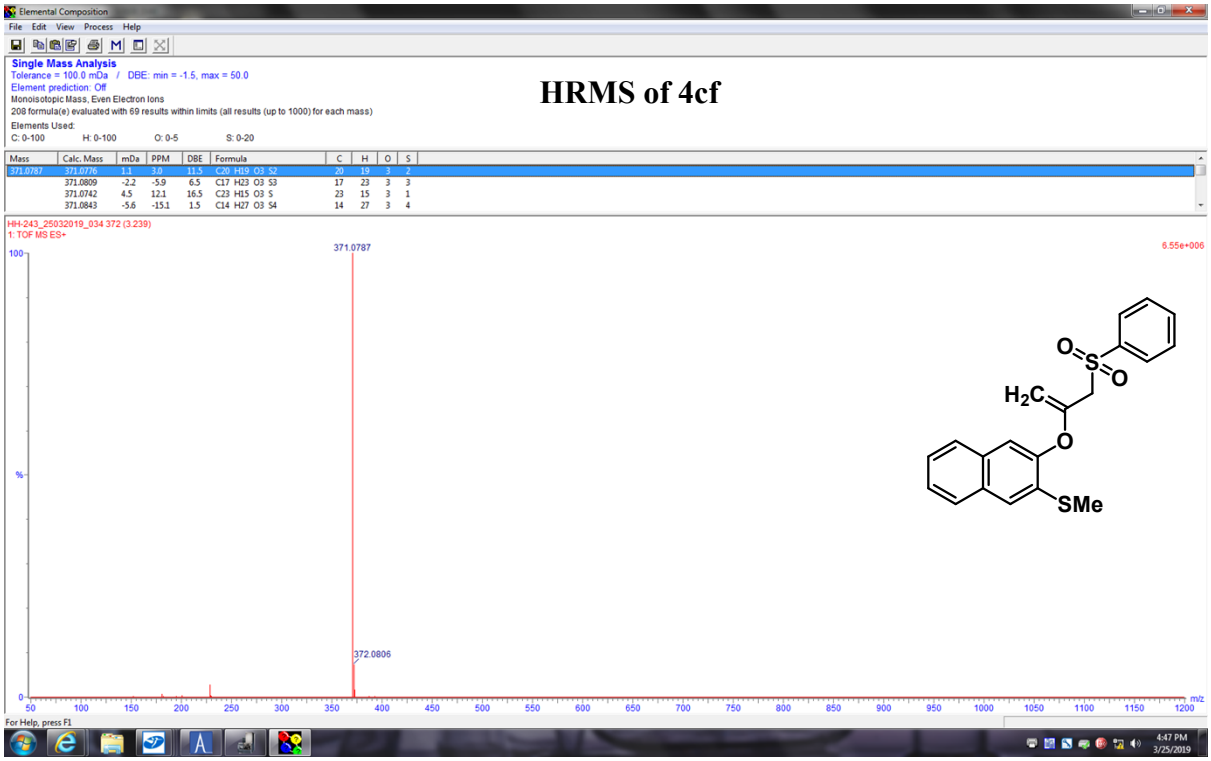
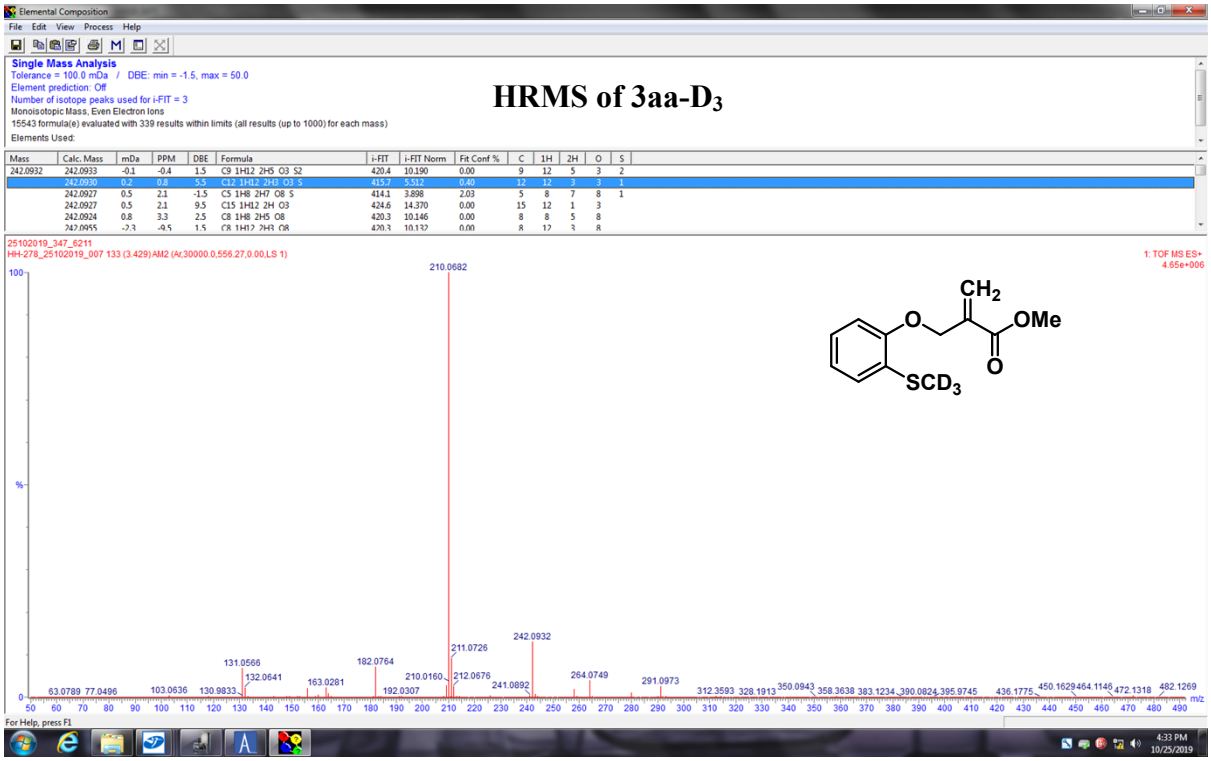
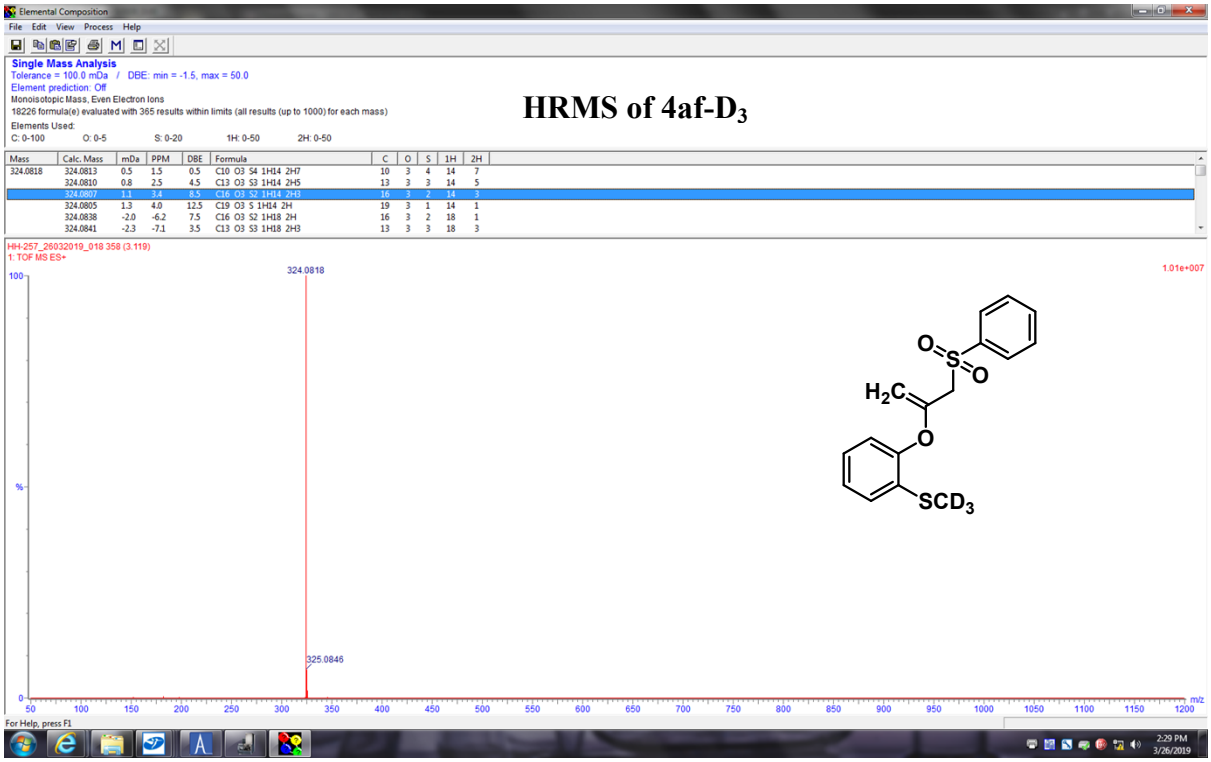


HRMS of 4cf

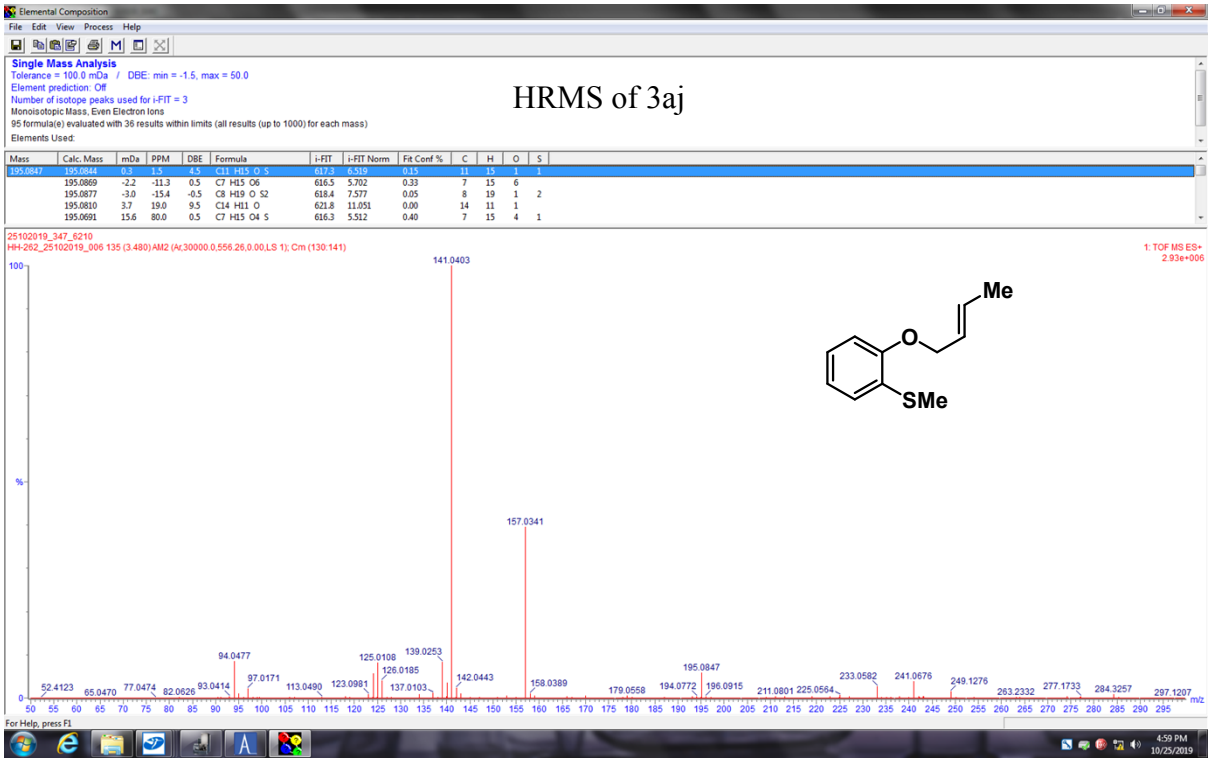
HRMS of 3aa-D_3



HRMS of 4af-D_3



HRMS of 3aj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Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
95 formula(e) evaluated with 36 results within limits (all results (up to 1000) for each mass)
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195.0869 -2.2 -11.3 0.5 C7 H15 O6 616.5 5.702 0.33 7 15 6
195.0877 -3.0 -15.4 -0.5 C8 H19 O S2 618.4 7.577 0.05 8 19 1 2
195.0810 3.7 19.0 9.5 C14 H11 O 621.8 11.051 0.00 14 11 1
195.0691 15.6 80.0 0.5 C7 H15 O4 S 616.3 5.512 0.40 7 15 4 1
25102019_347_6210
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1: TOF MS ES+
2.93e+006
141.0403
157.0341
Me
O
SMe
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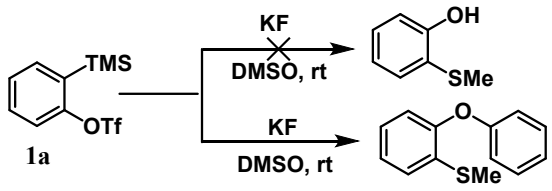
10/25/2019

Additional Experiments:

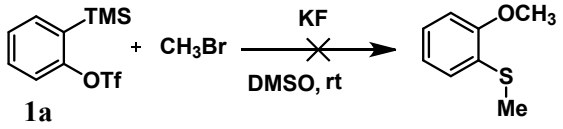
Few independent experiments were performed to know more about our synthetic protocol. The experiments are showing below.

Experiment 1:



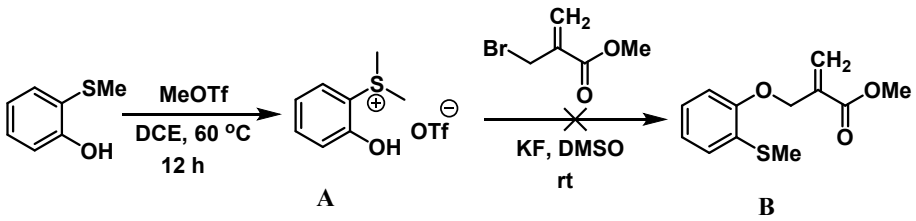
An independent experiment was performed by using aryne precursor **1a** (0.12 mL, 0.5 mmol), KF (0.116 g, 2 mmol) and DMSO (2 mL) under our optimized reaction conditions. Under these conditions, we did not get our expected 2-(methylthio)phenol. However, *o*-aryloxydiarylsulphide was isolated, which is already reported by Wang group.[1]

Experiment 2:



Another independent experiment was peformed by using methyl bromide as reactive partner instead of activated alkene. In a typical experimental procedure, aryne precursor **1a** (0.12 mL, 0.5 mmol), CH_3Br (0.04 mL, 0.75 mmol), KF (0.116 g, 2 mmol) and DMSO (2 mL) were treated under our optimized reaction conditions. Under these conditions, we did not get the desired product as shown in the above scheme.

Experiment 3:



In another experiment, sulfonium salt[2] **A** (0.15 g, 0.5 mmol, 1 equiv) was treated with methyl-2-(bromomethyl)acrylate (0.09 mL; 0.75 mmol, 1.5 equiv) and KF (0.116 g, 2 mmol) in DMSO (2 mL) under our optimized conditions. Under these conditions, the desired product **B** was not observed.

References:

1. H.-Y. Li, L.-J. Xing, M.-M. Lou, H. Wang, R.-H. Liu and B. Wang, *Org. Lett.*, 2015, **17**, 1098–1101.
2. C. Huang, J. Feng, R. Ma, S. Fang, T. Lu, W. Tang, D. Du and J. Gao, *Org. Lett.*, 2019, **21**, 9688-9692.