

## Supporting Information

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### From silylated trishomoallylic alcohols to dioxaspiroundecanes or oxocanes: catalyst and substitution influence

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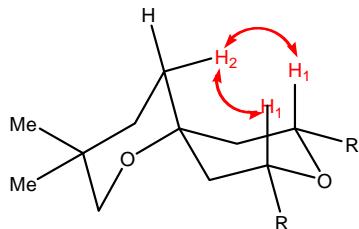
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#### *Table of Contents*

1. Relative stereochemistry of compounds.....	S-2
2. Copies of $^1\text{H}$ , $^{13}\text{C}$ and NOE spectra.....	S-4

## 1. Relative stereochemistry of compounds

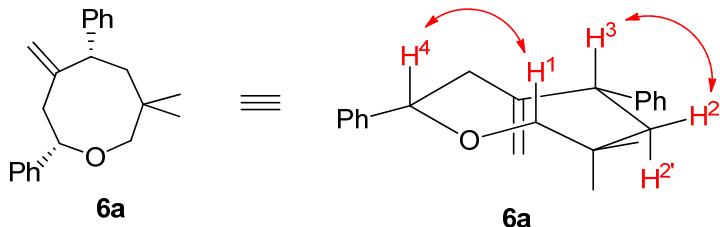
The relative stereochemistry of dioxaspiroundecanes was assigned based on the 1D-NOE experiments, considering the signals corresponding to the interactions highlighted in the figure:



The relative stereochemistry of oxocanes was assigned based on the 1D-NOE experiments, considering the signals corresponding to the interactions highlighted in the figure, and the coupling constants of the corresponding H:

### Oxocane 6a

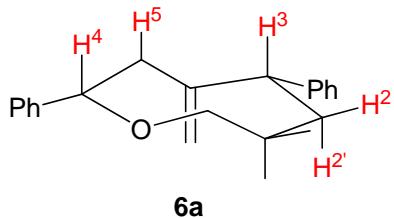
#### 1D-NOE crosspeaks



1D-crosspeak was found between H<sup>4</sup> and H<sup>1</sup>

1D-crosspeak was found between H<sup>2</sup> and H<sup>3</sup>

#### Relevant <sup>1</sup>H-NMR coupling constants

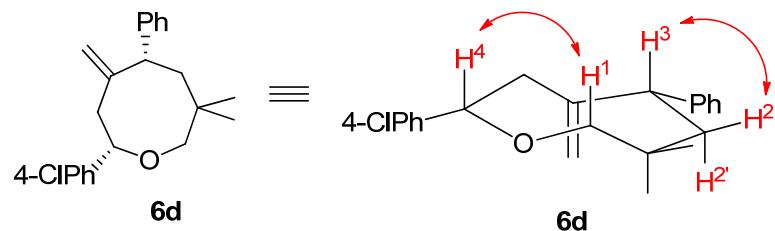
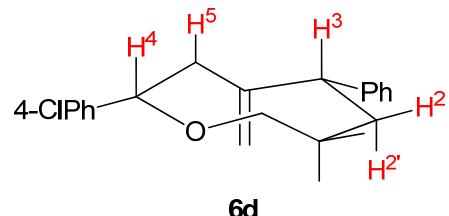
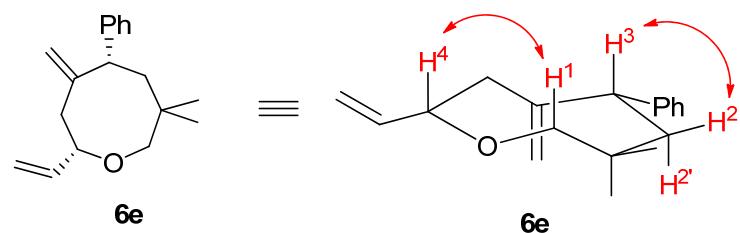


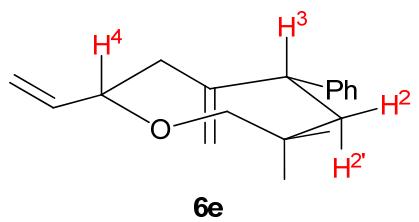
H<sup>2</sup>: 1.51 (dd,  $J = 14.2$  (gem) and 2.1 (ax<sup>3</sup>-eq<sup>2</sup>)

H<sup>2</sup>: 2.66 (dd,  $J = 14.2$  (gem) and 13.3 (ax<sup>3</sup>-ax<sup>2</sup>')

H<sup>3</sup>: 3.85 (dd,  $J = 13.3$  (ax<sup>3</sup>-ax<sup>2</sup>') and 2.7 (ax<sup>3</sup>-eq<sup>2</sup>)

H<sup>4</sup>: 4.62 (dd,  $J = 10.7$  (ax<sup>4</sup>-ax<sup>5</sup>) and 2.3 (ax<sup>4</sup>-eq)

**Oxocane 6d***1D-NOE crosspeaks*1D-crosspeak was found between H<sup>4</sup> and H<sup>1</sup>1D-crosspeak was found between H<sup>2</sup> and H<sup>3</sup>*Relevant <sup>1</sup>H-NMR coupling constants*H<sup>2</sup>: 1.47 (dd,  $J = 14.0$  (gem) and 1.9 (ax<sup>3</sup>-eq<sup>2</sup>)H<sup>2'</sup>: 2.57 (dd,  $J = 14.0$  (gem) and 13.3 (ax<sup>3</sup>-ax<sup>2</sup>))H<sup>4</sup>: 4.55 (dd,  $J = 10.6$  (ax<sup>4</sup>-ax<sup>5</sup>) and 2.4 (ax<sup>4</sup>-eq)**Oxocane 6e***1D-NOE crosspeaks*1D-crosspeak was found between H<sup>4</sup> and H<sup>1</sup>1D-crosspeak was found between H<sup>2</sup> and H<sup>3</sup>

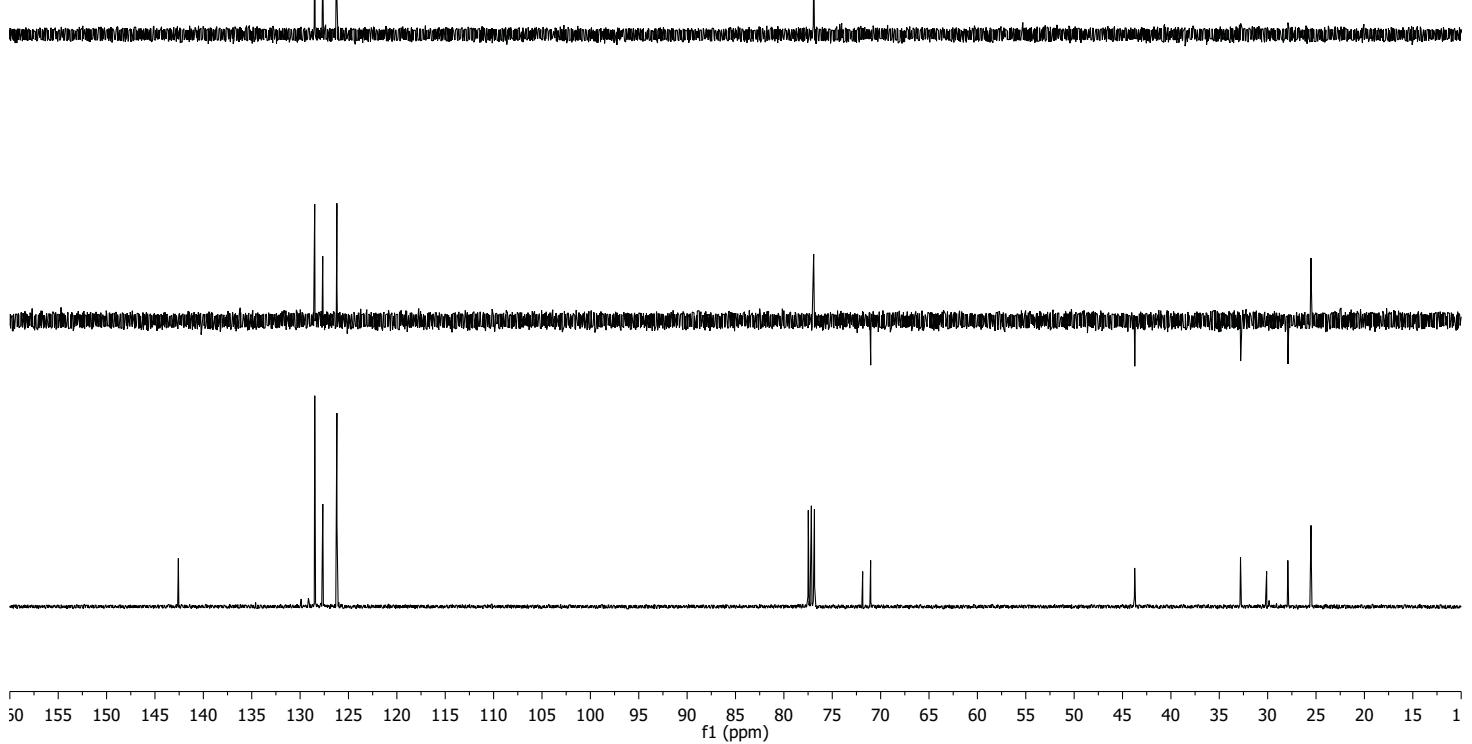
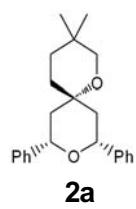
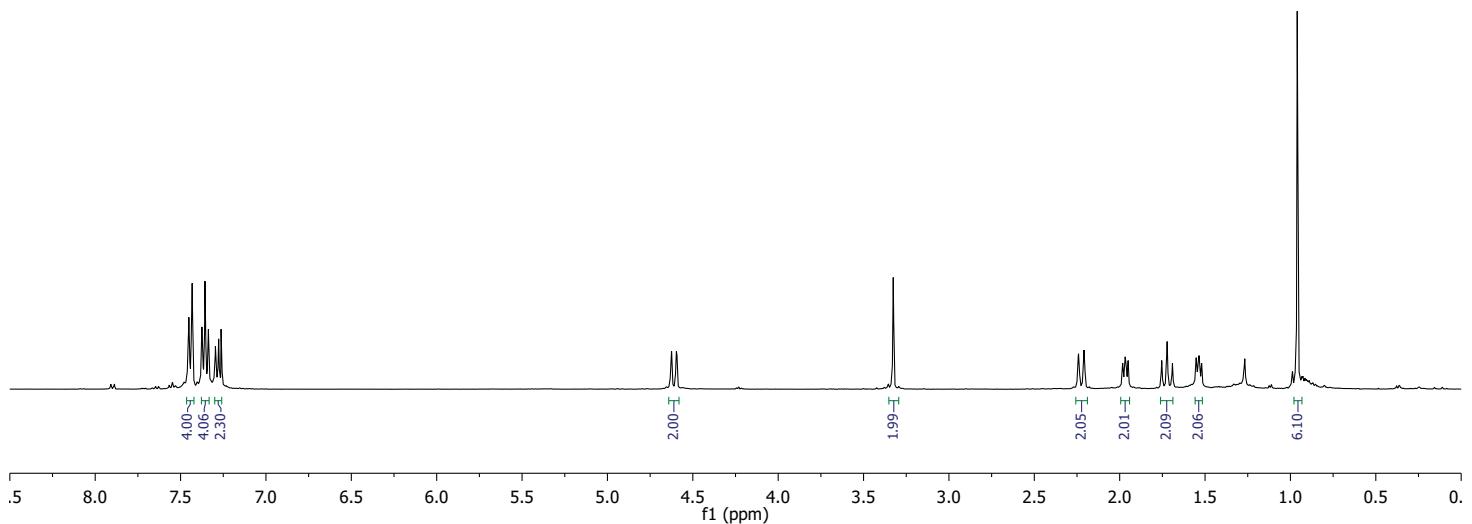
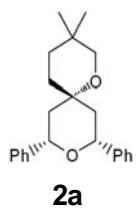
*Relevant <sup>1</sup>H-NMR coupling constants*

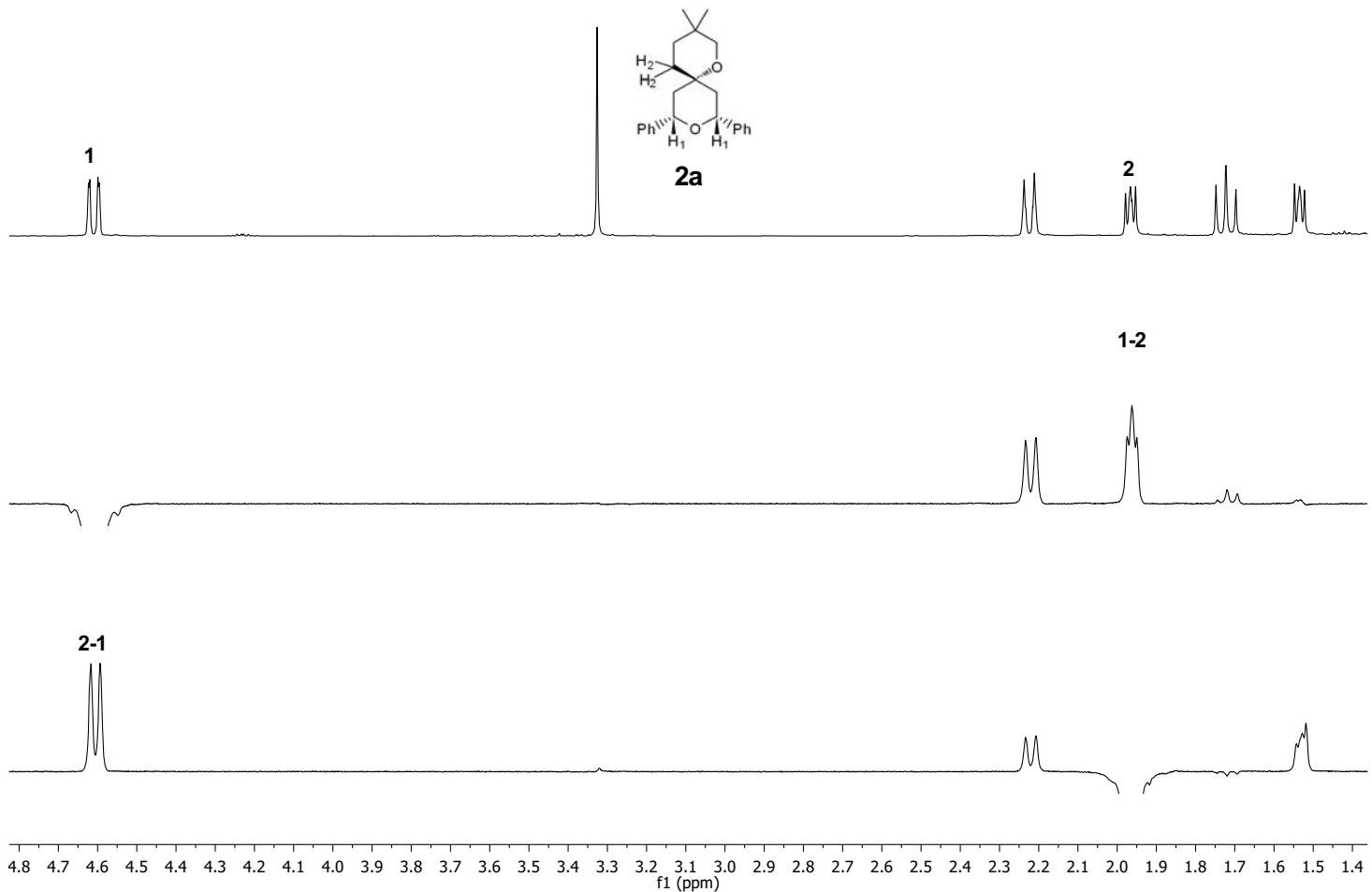
H<sup>2</sup>: 1.39 (dd,  $J = 13.9$  (gem) and 1.9 (ax<sup>3</sup>-eq<sup>2</sup>)

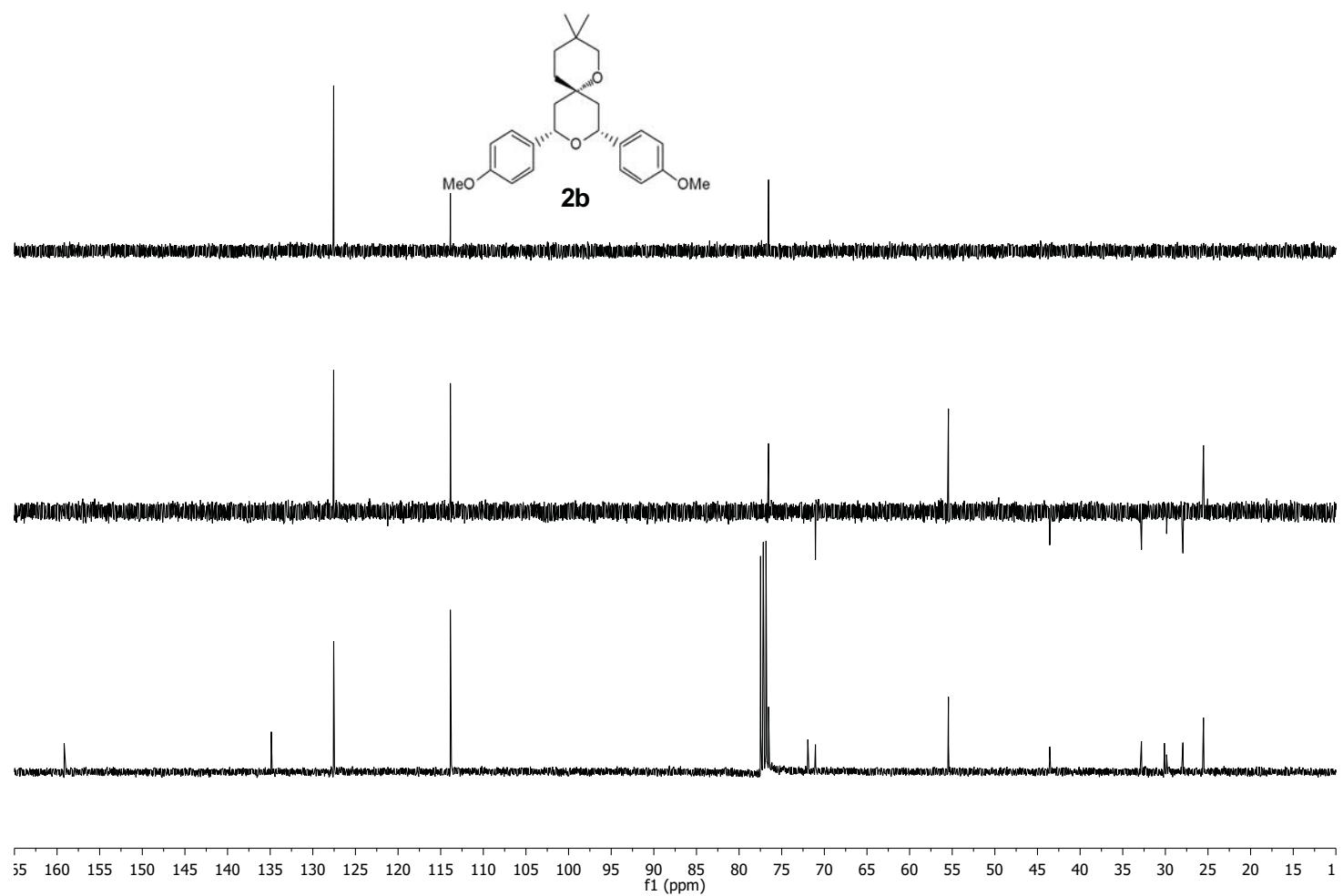
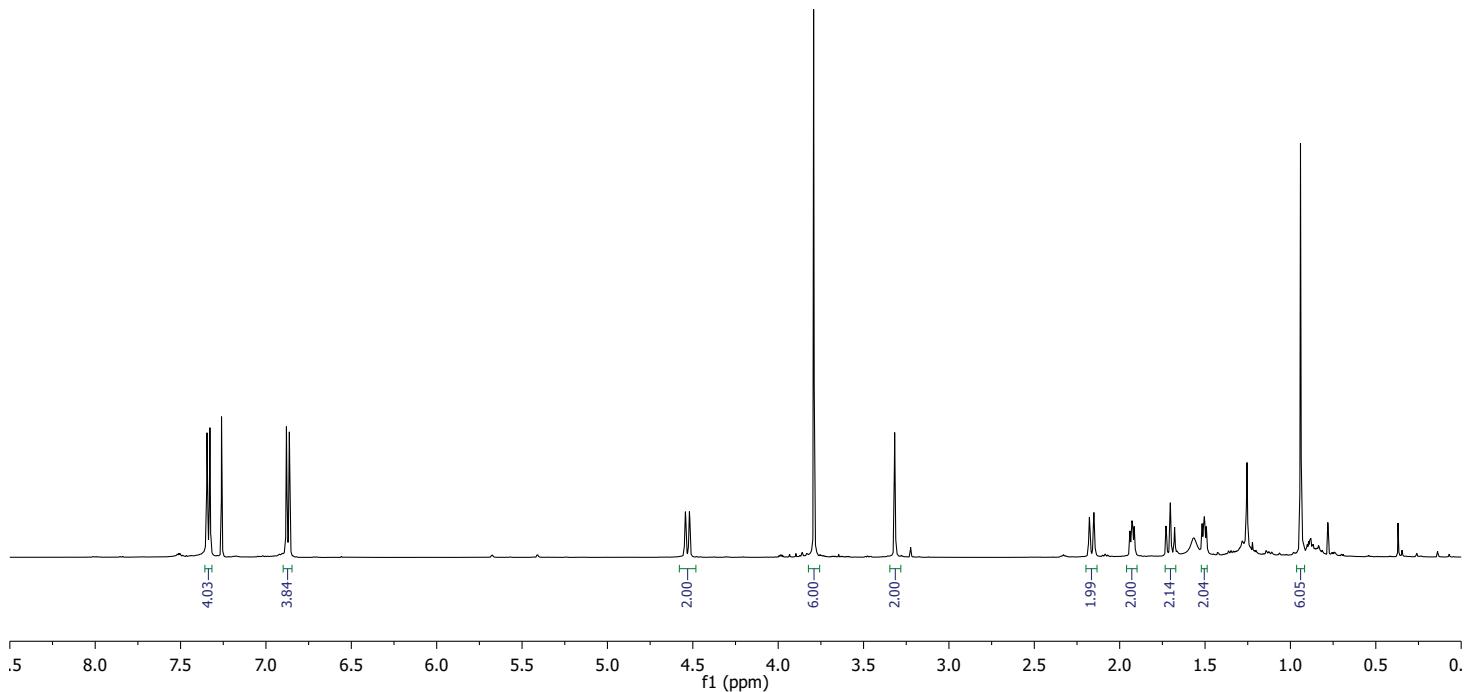
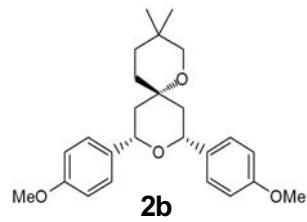
H<sup>2'</sup>: 2.48 (dd,  $J = 13.9$  (gem) and 13.3 (ax<sup>3</sup>-ax<sup>2</sup>))

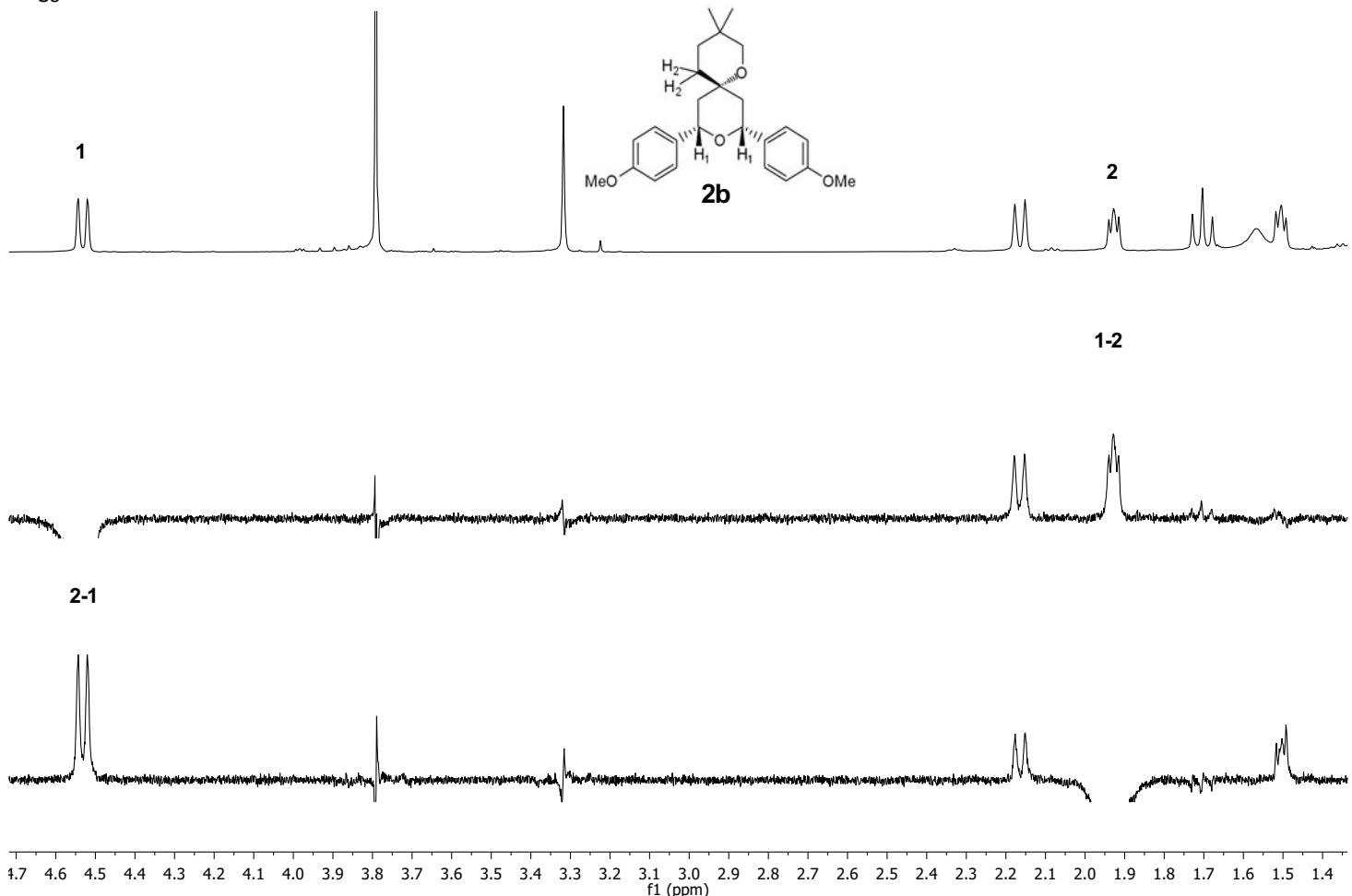
H<sup>3</sup>: 3.75 (dd,  $J = 13.3$  (ax<sup>3</sup>-ax<sup>2</sup>) and 2.7)

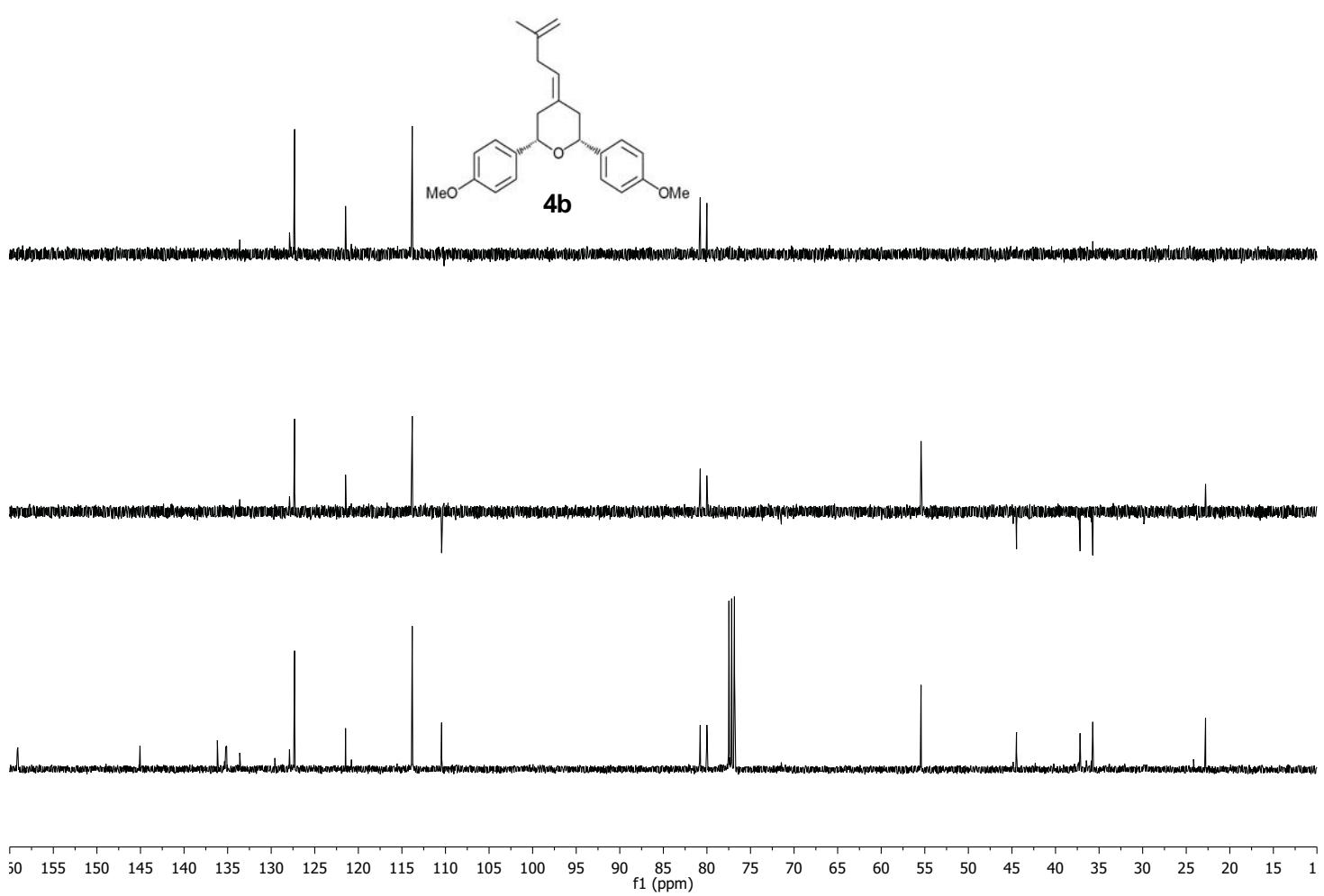
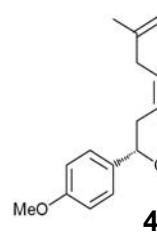
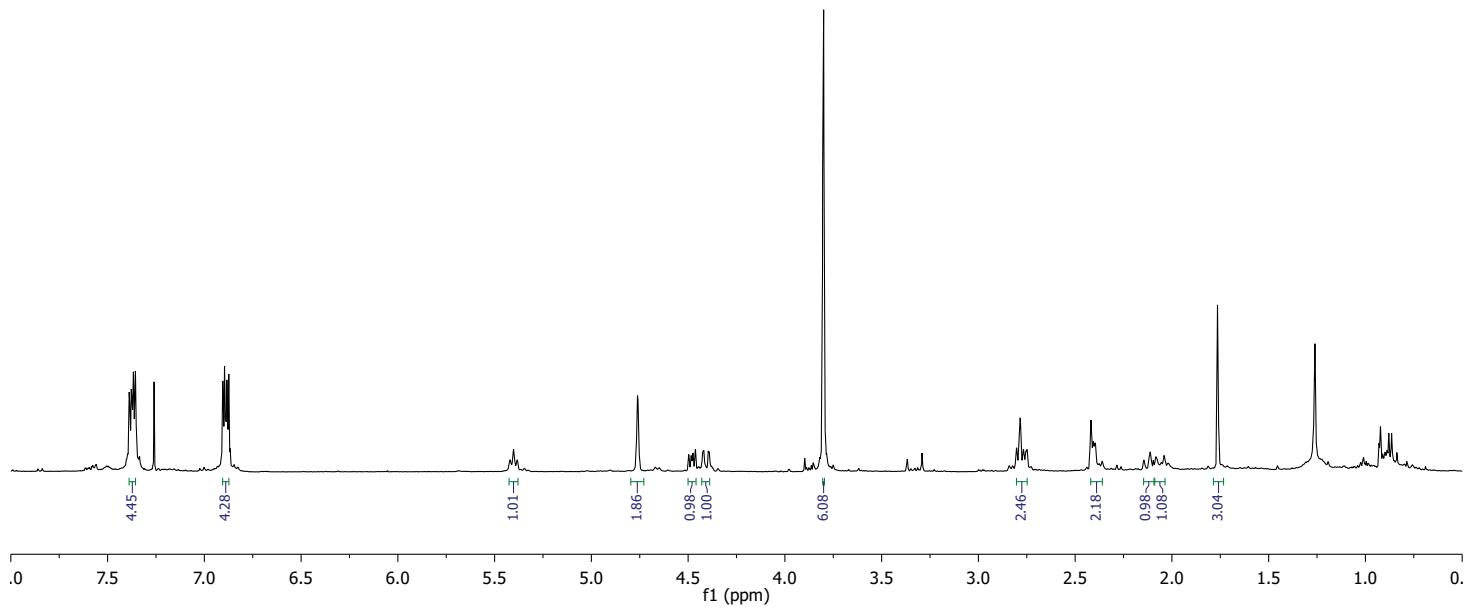
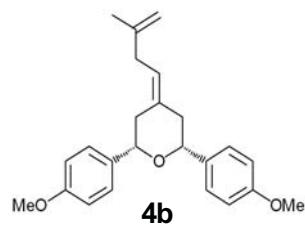
**2. Copies of <sup>1</sup>H, <sup>13</sup>C and NOE spectra**

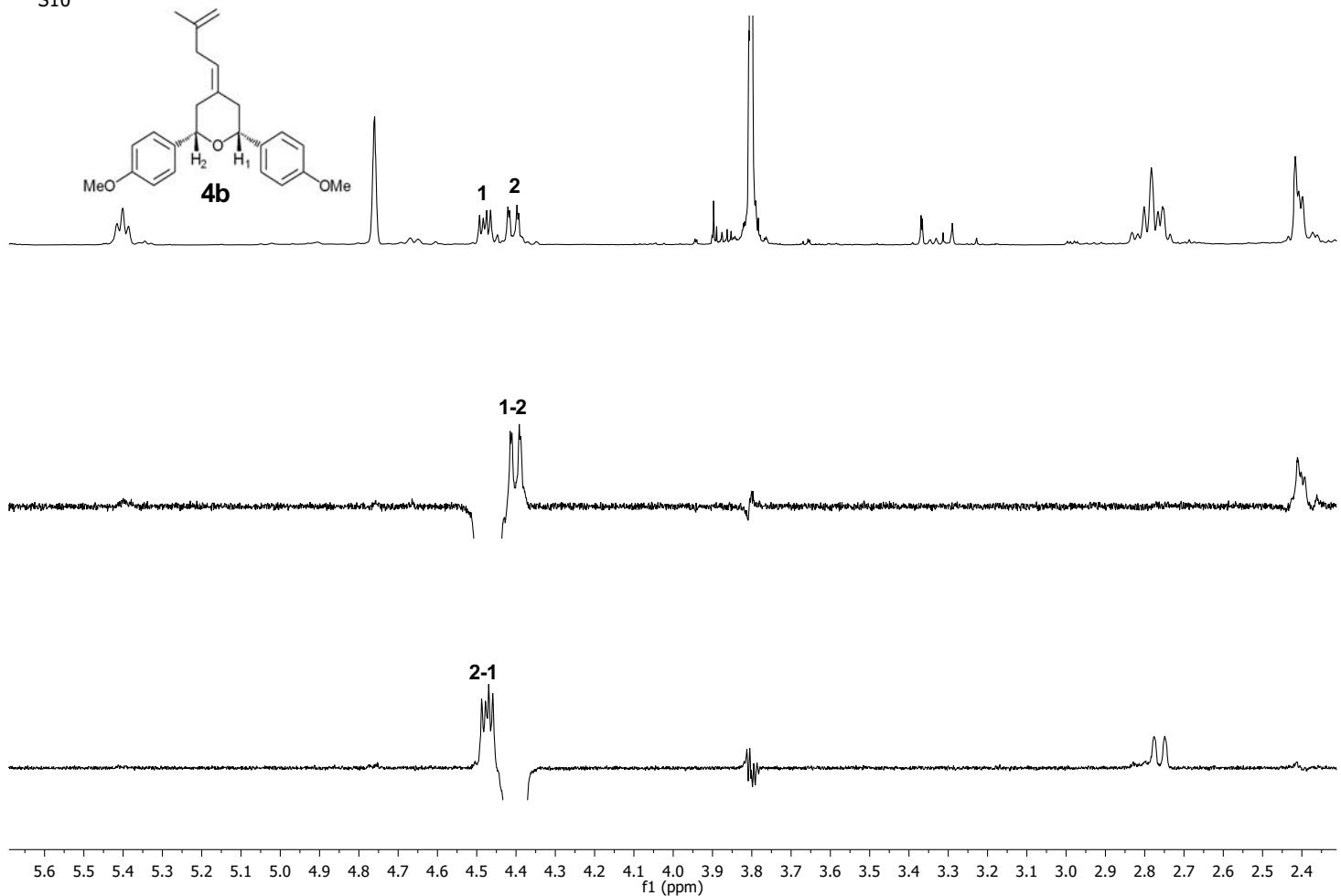


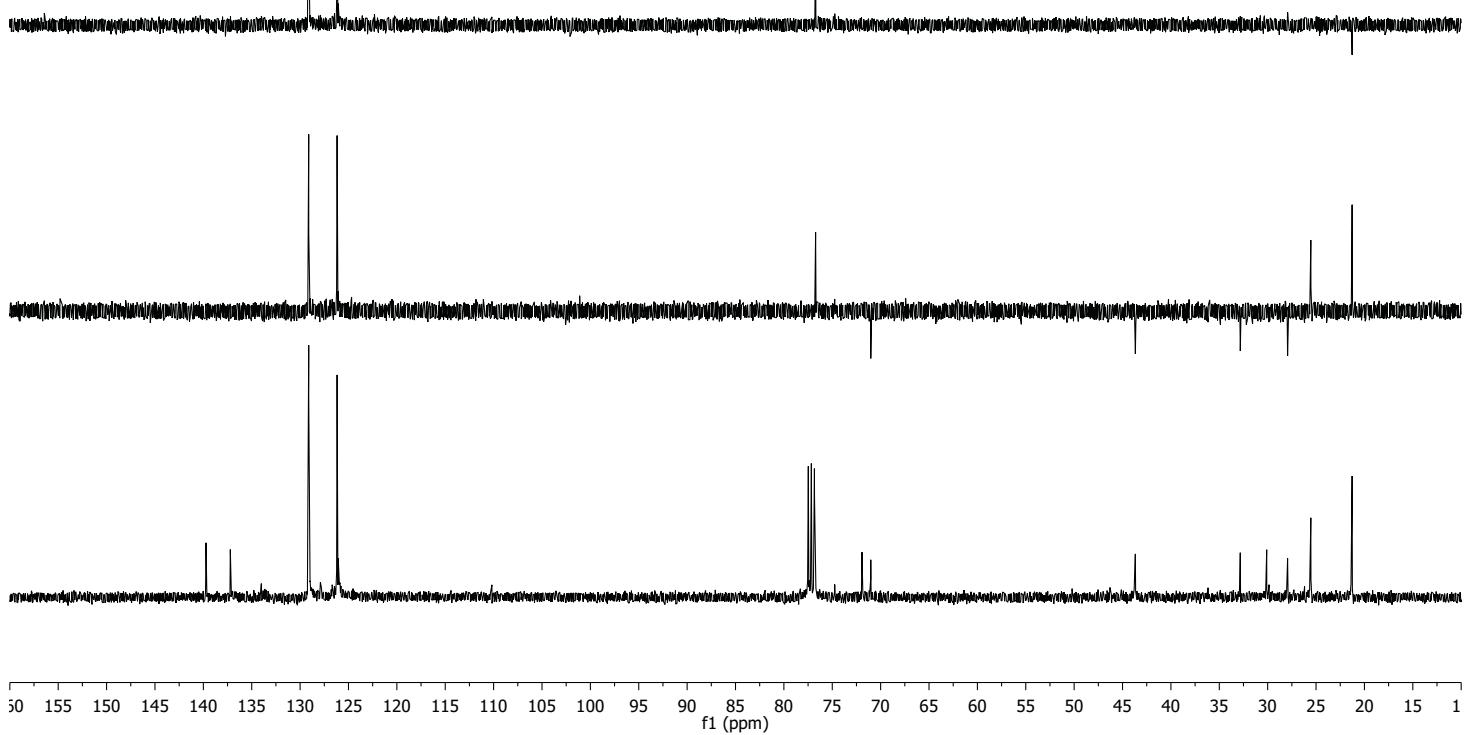
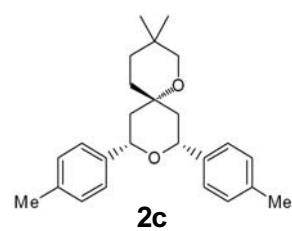
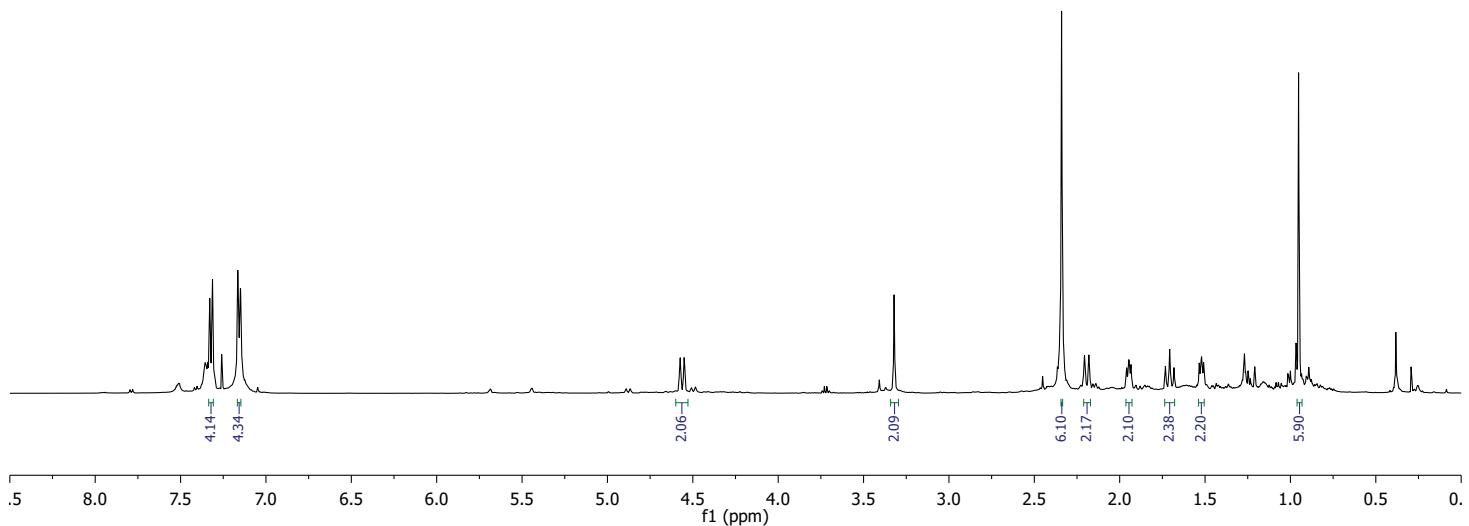
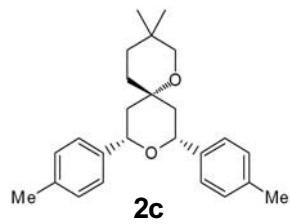


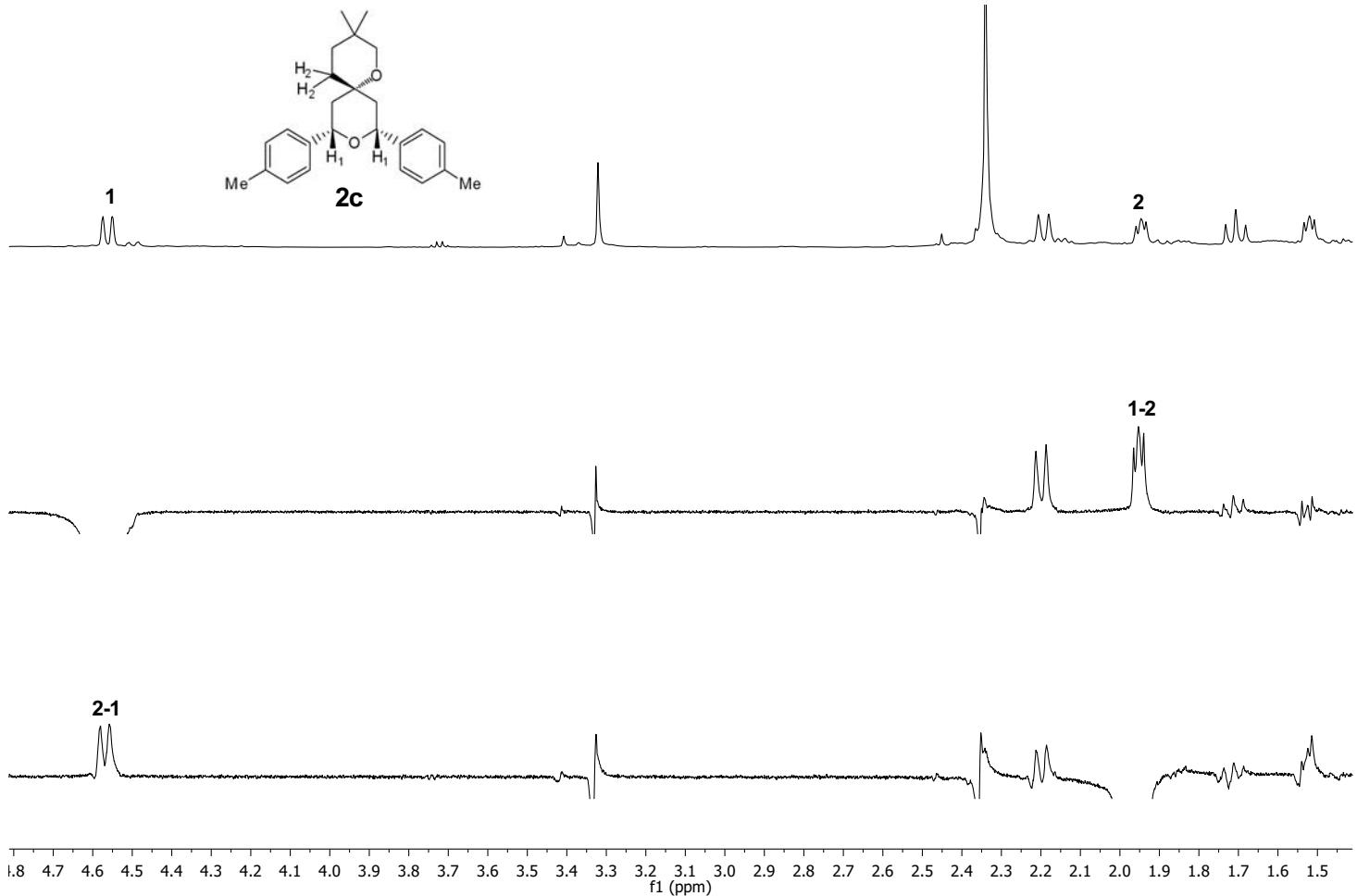


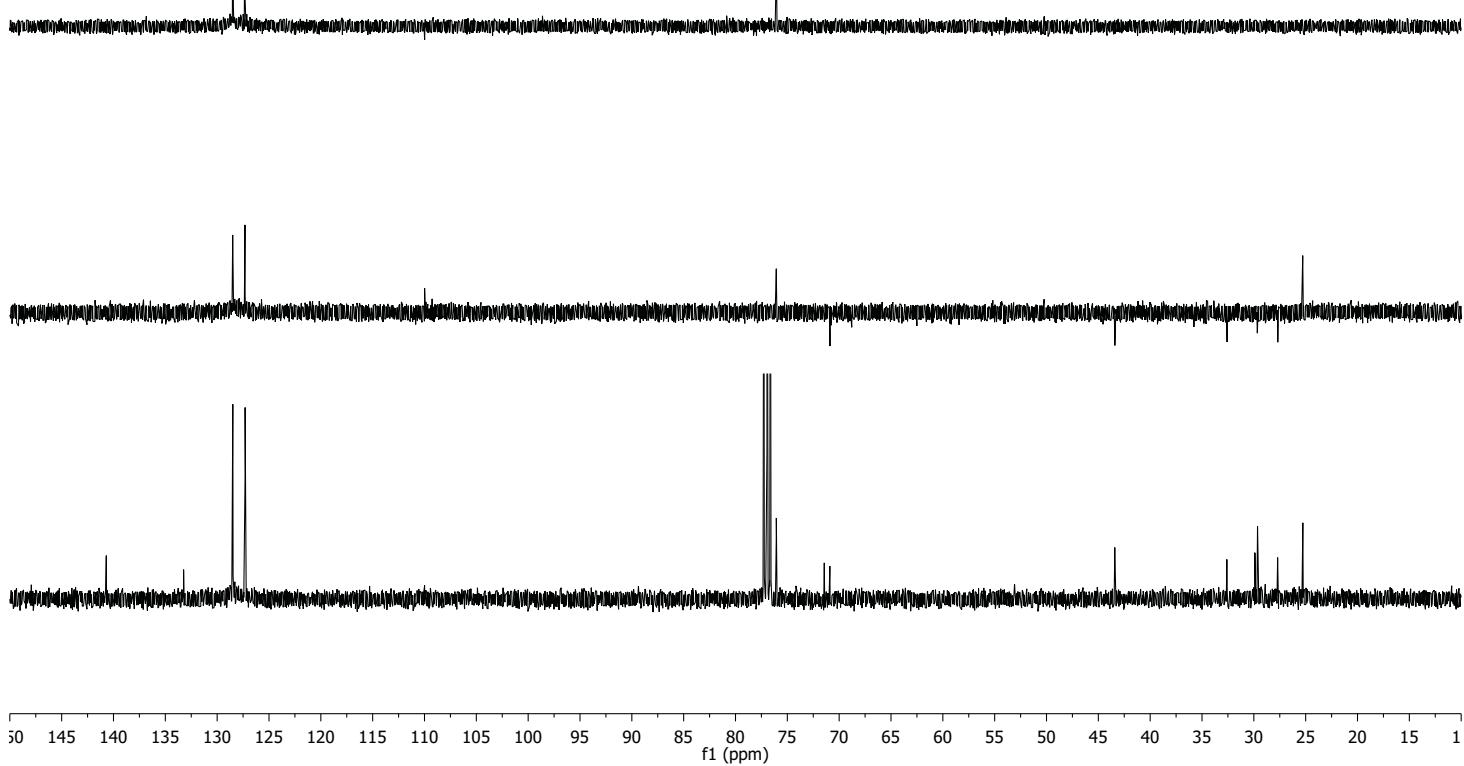
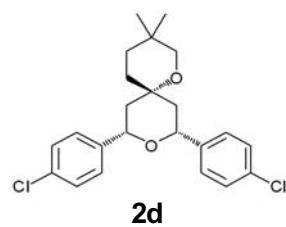
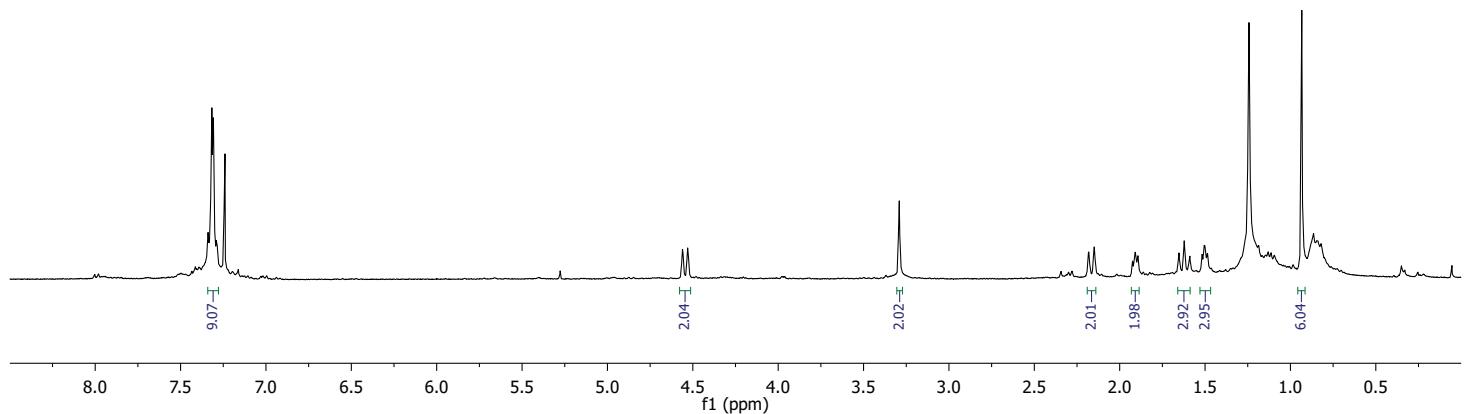
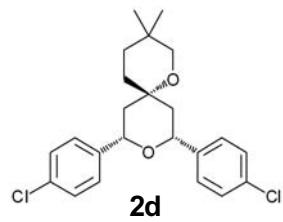


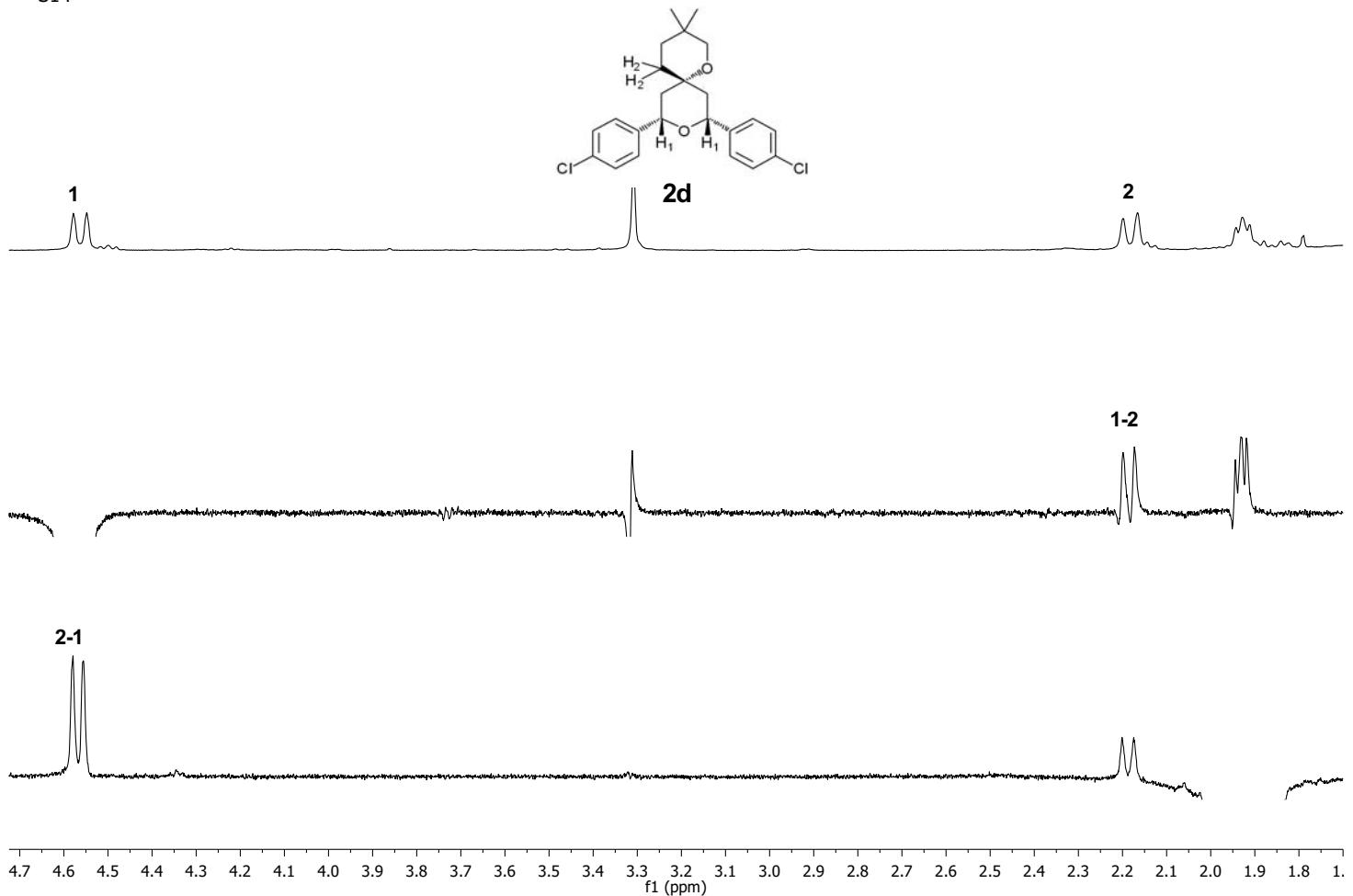


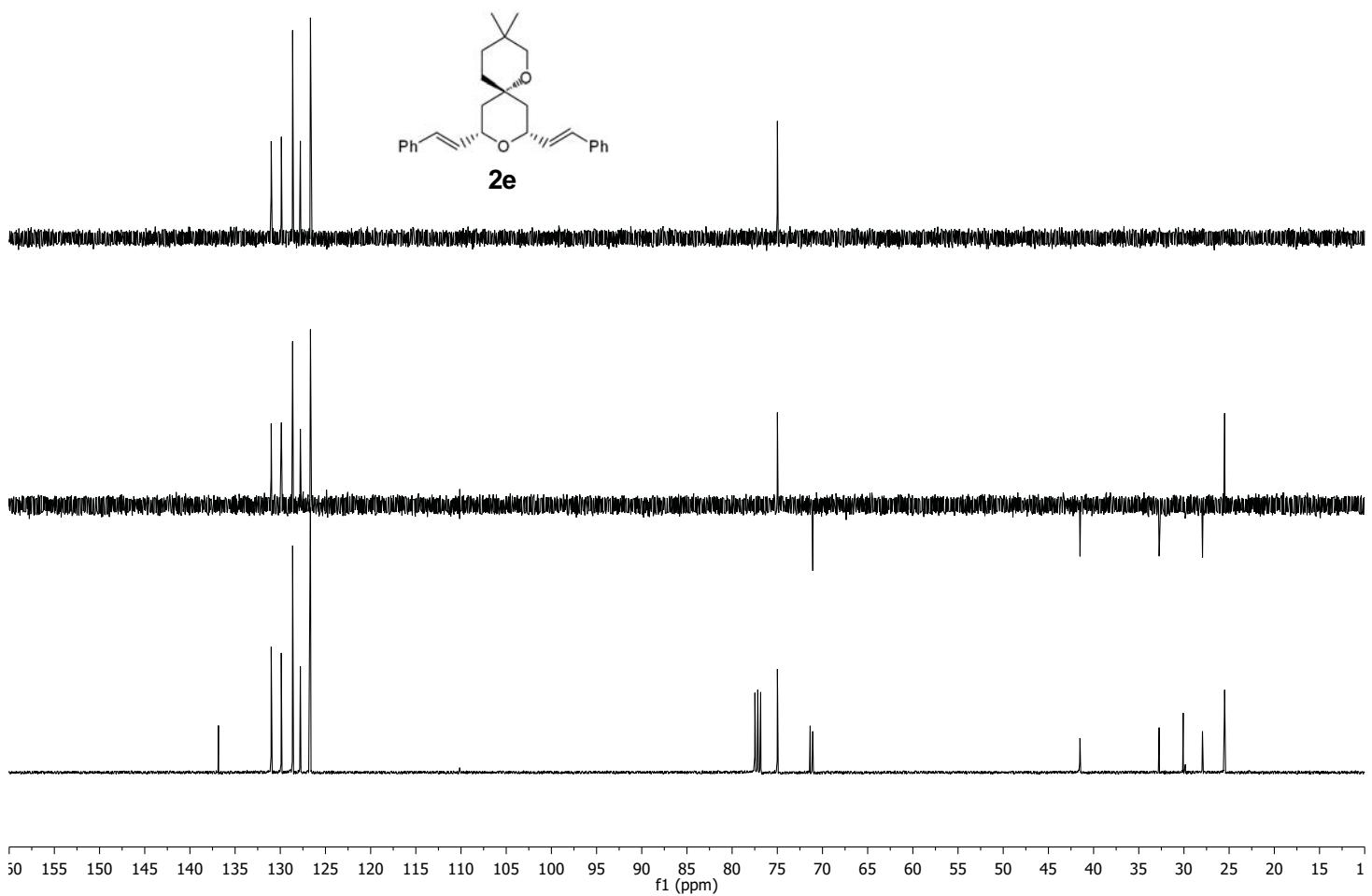
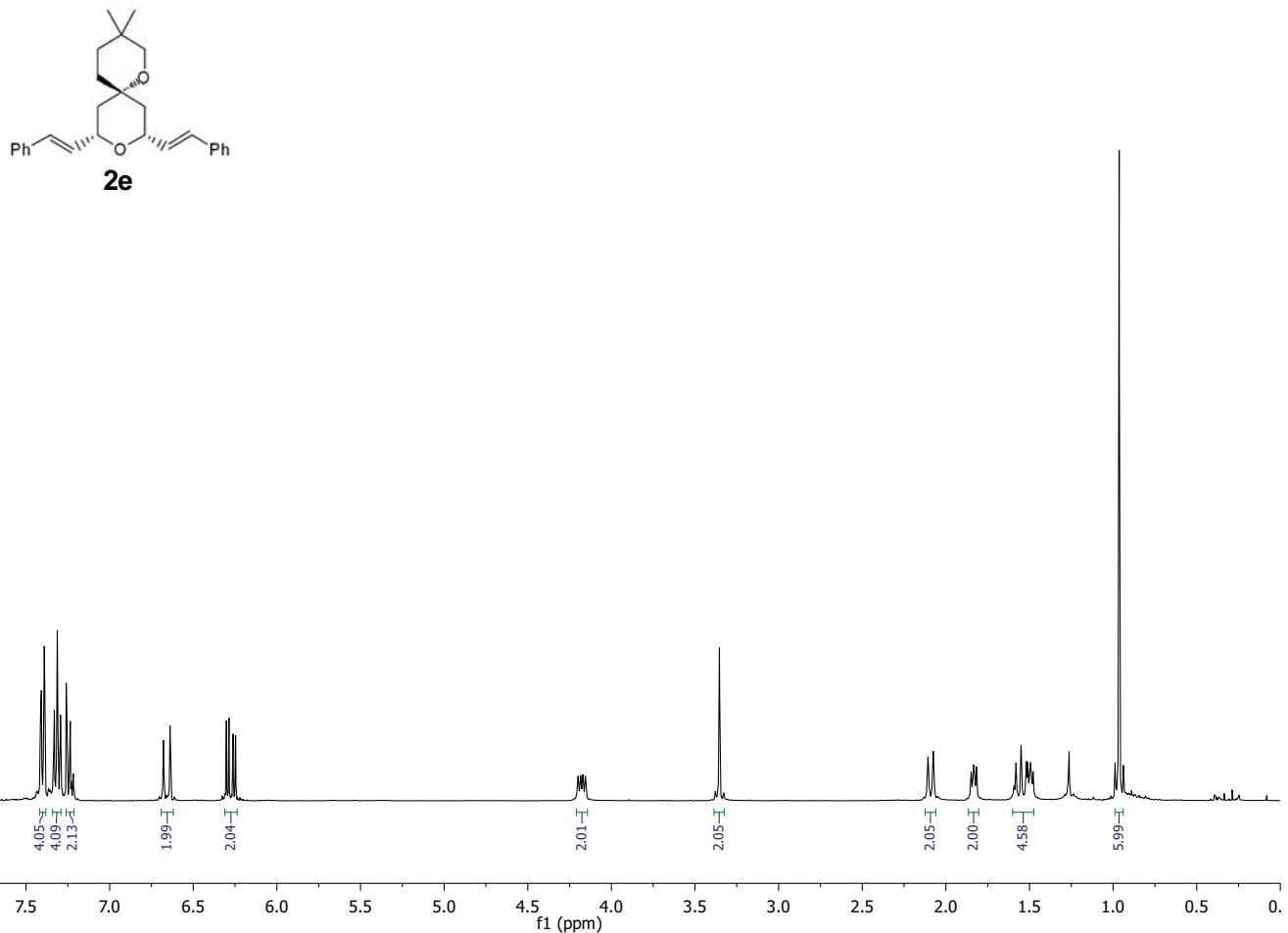


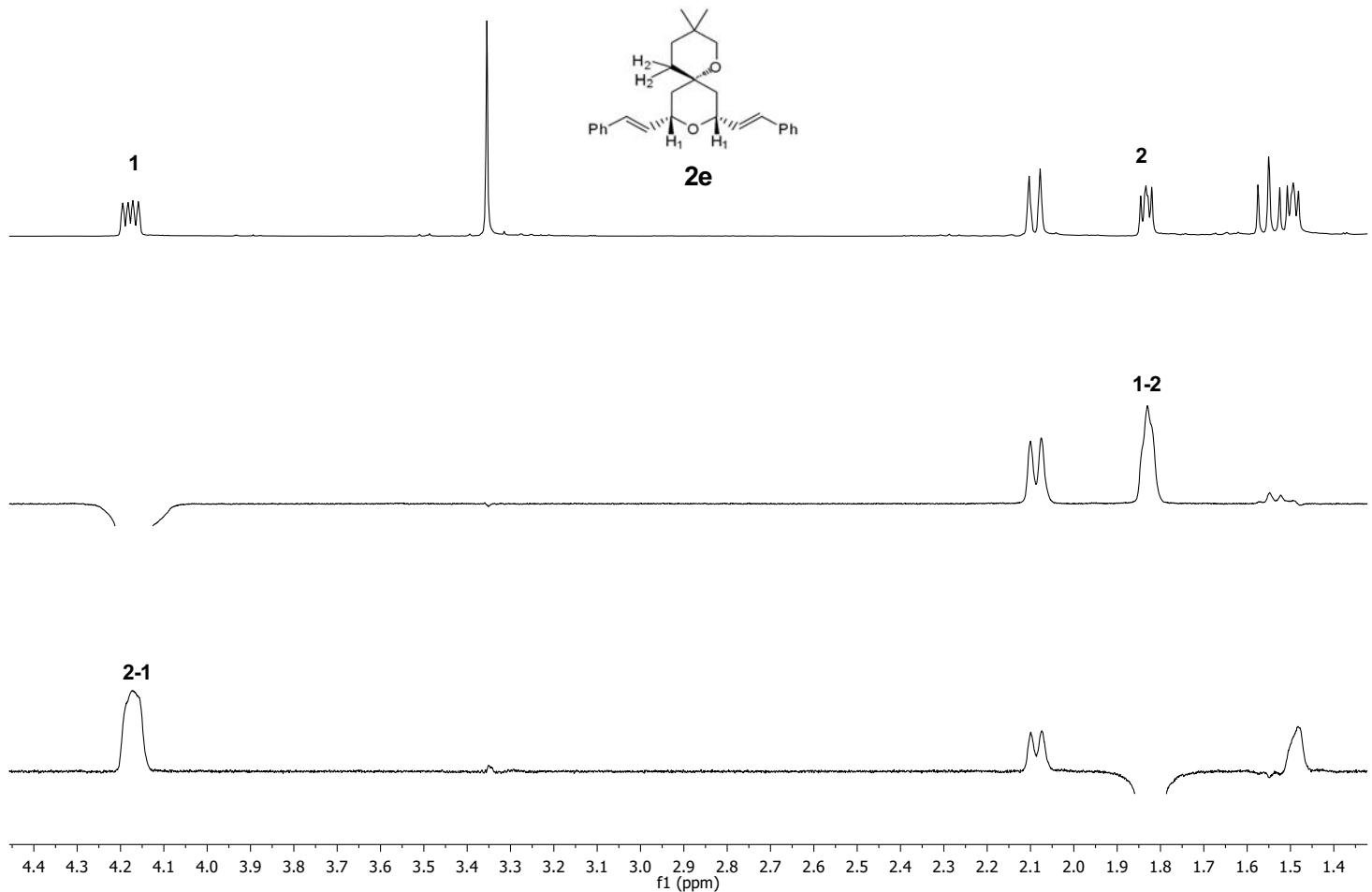


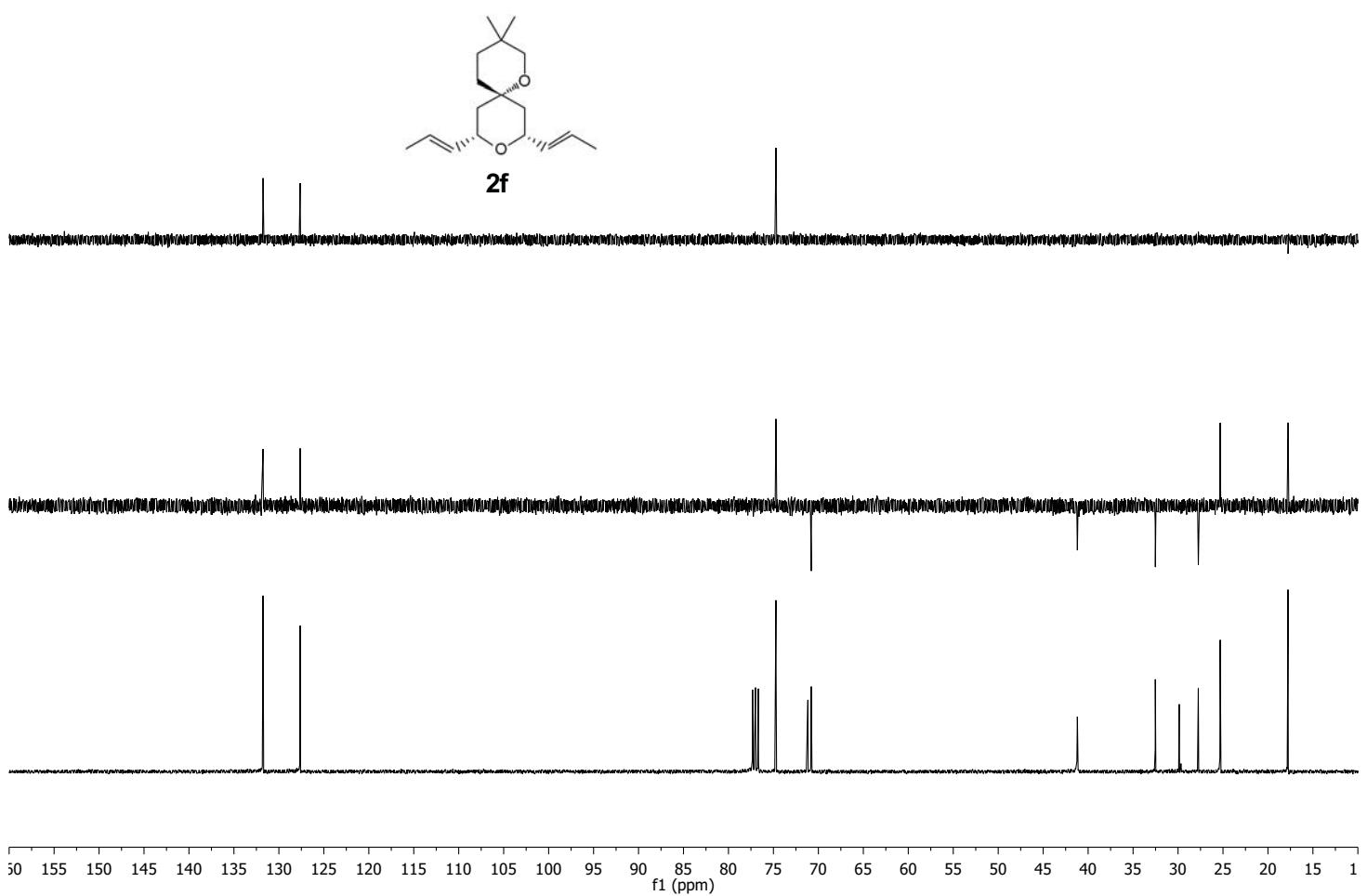
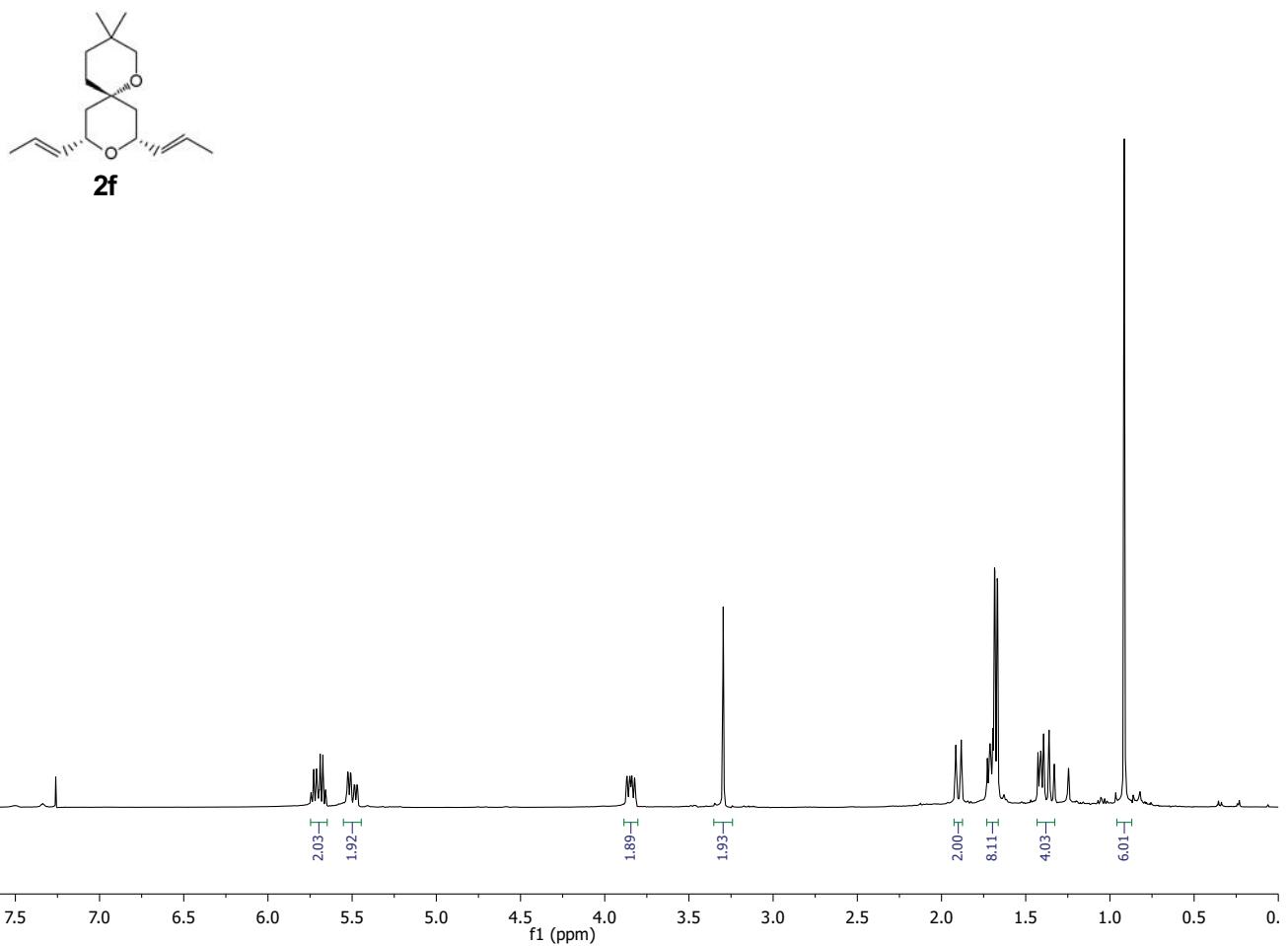


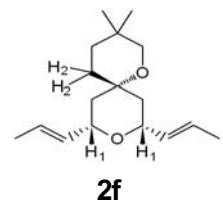
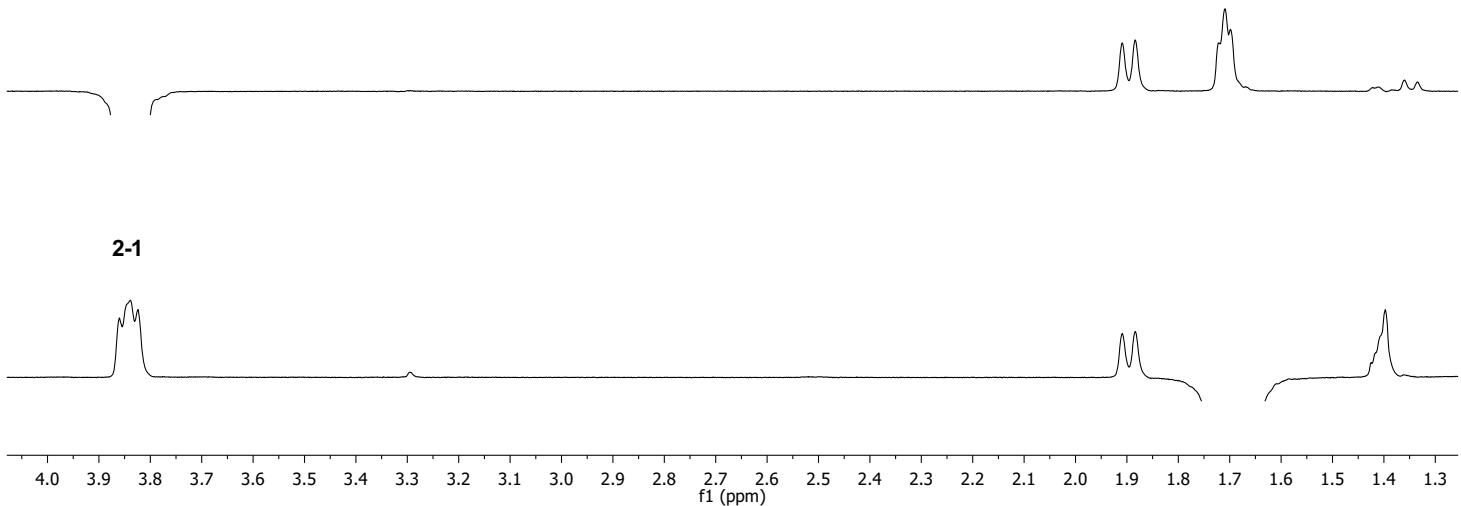


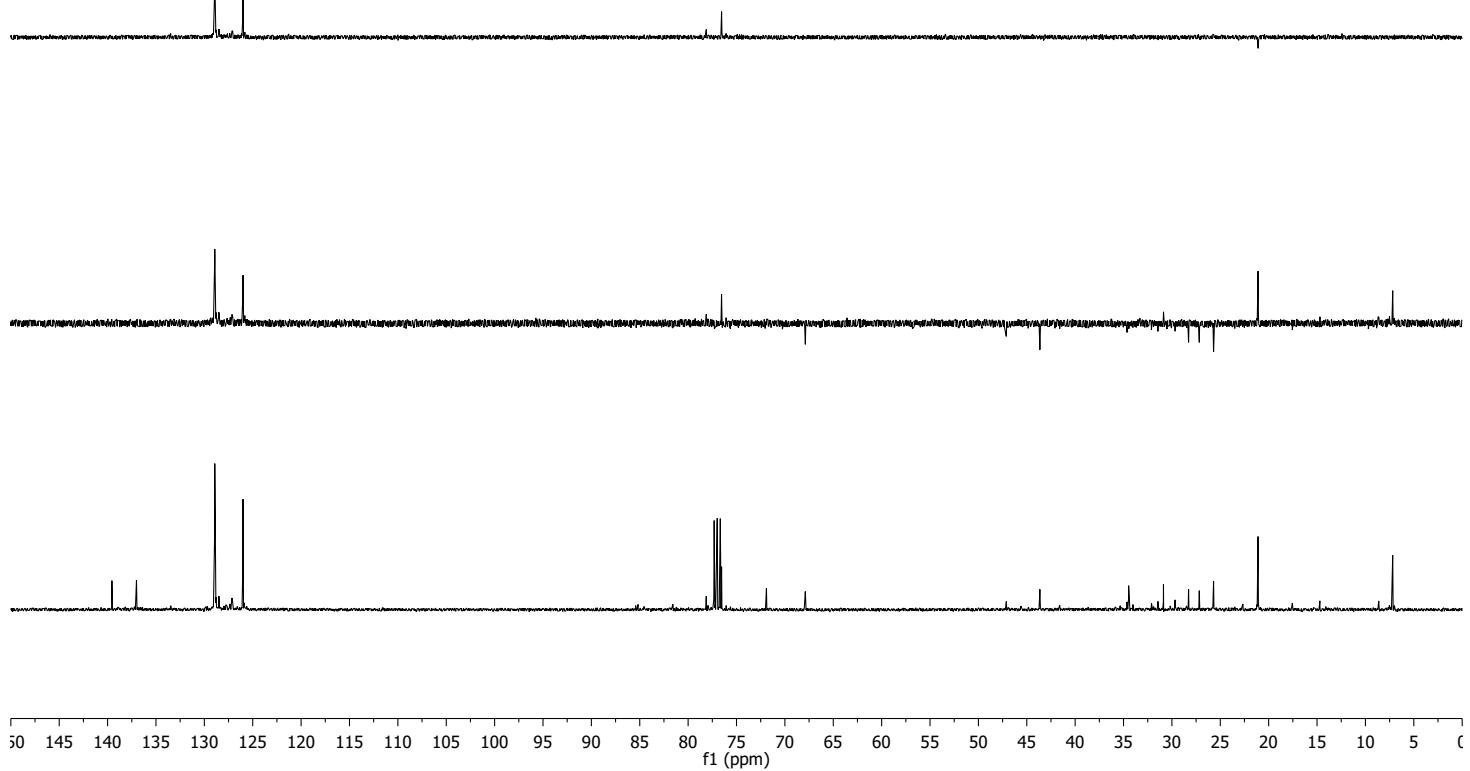
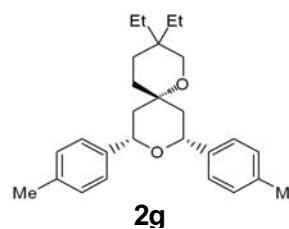
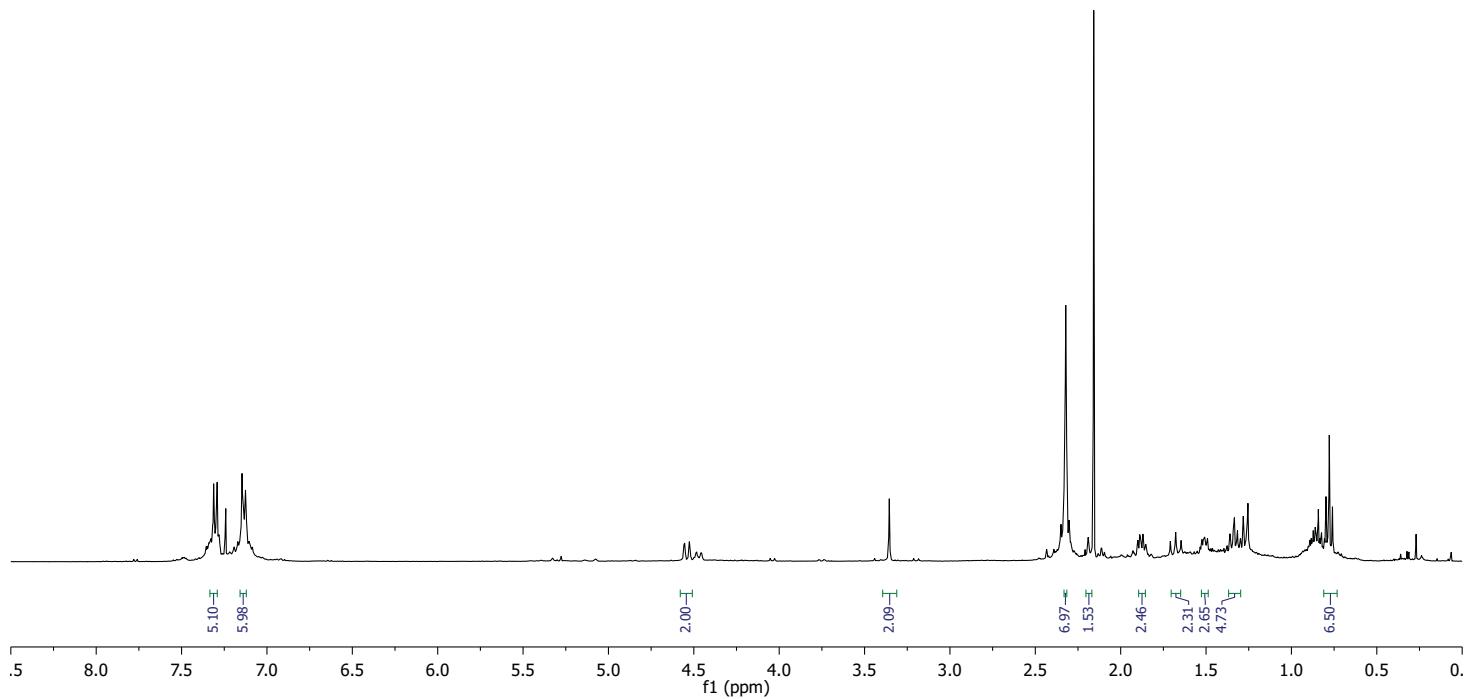
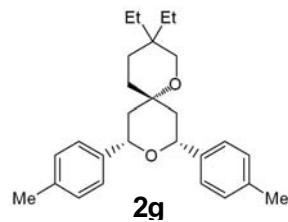


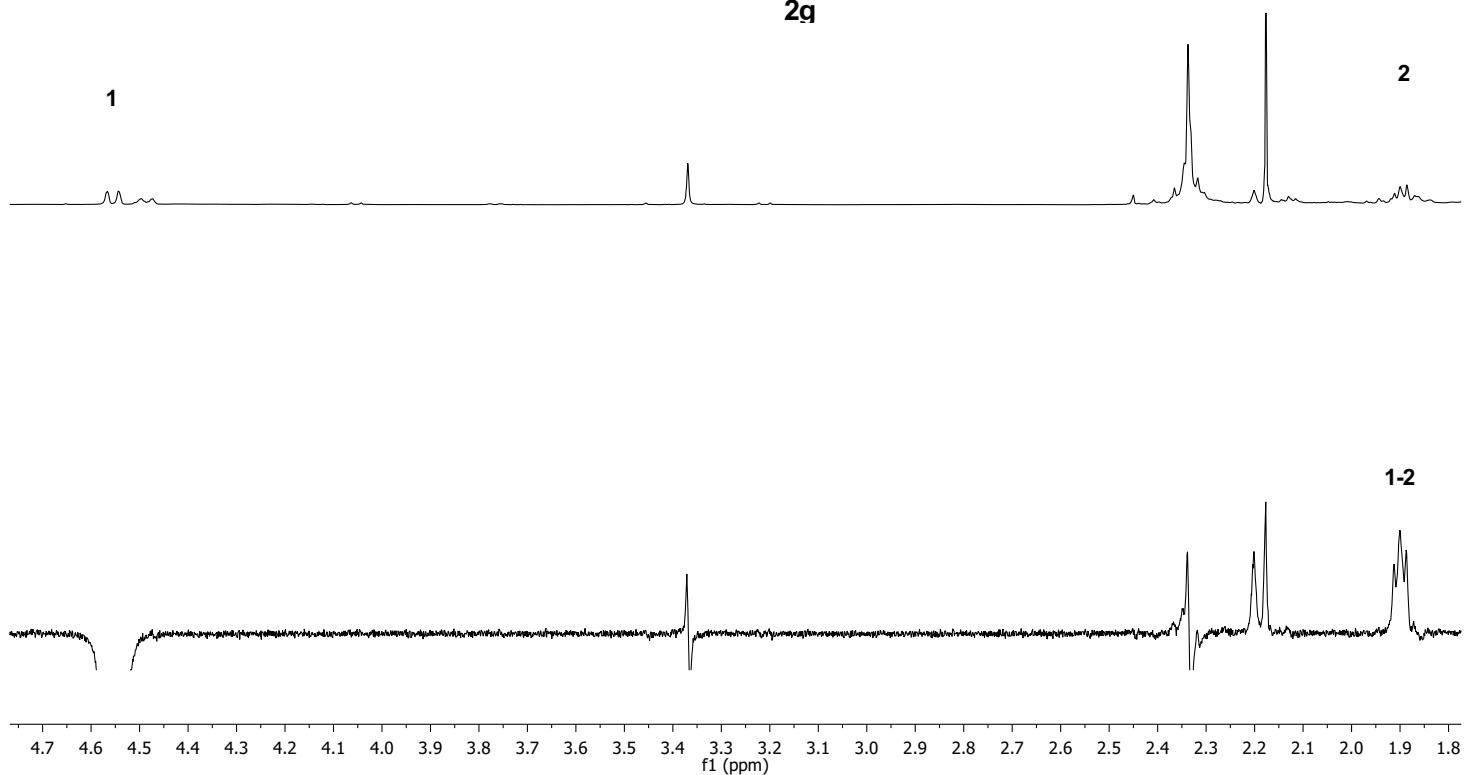
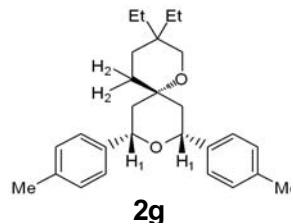


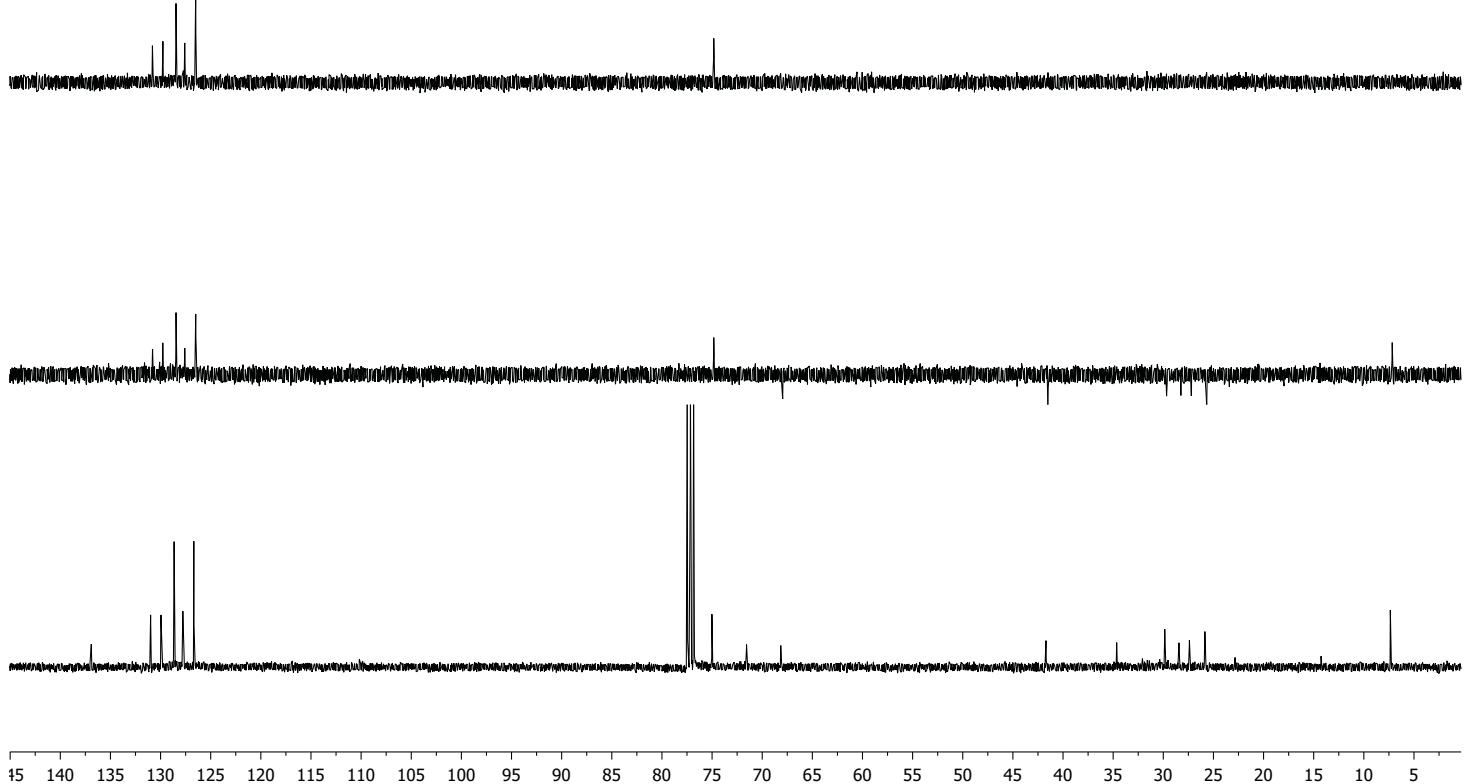
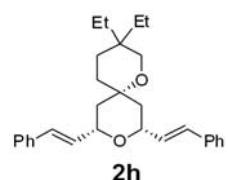
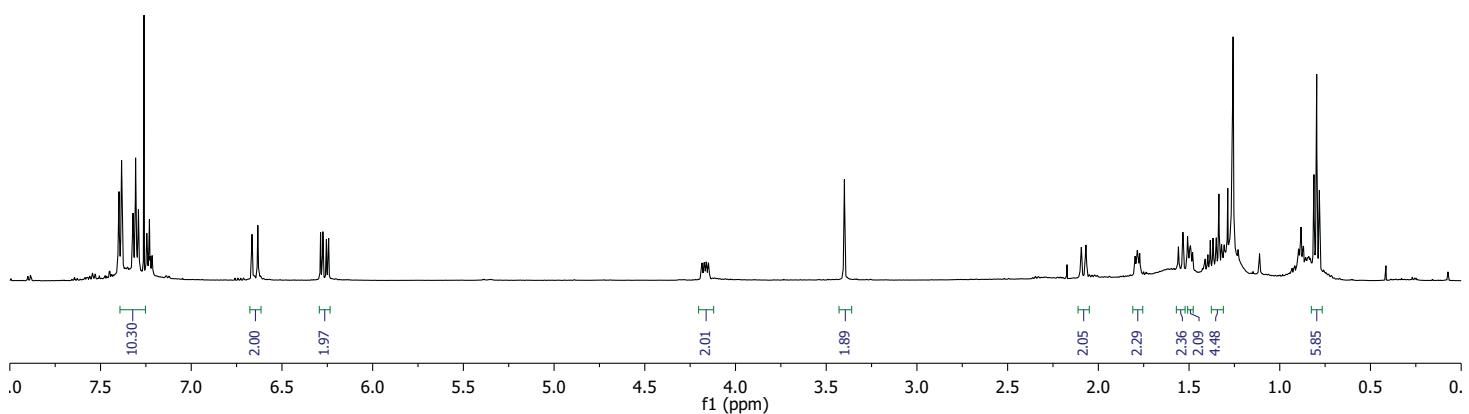
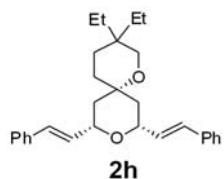


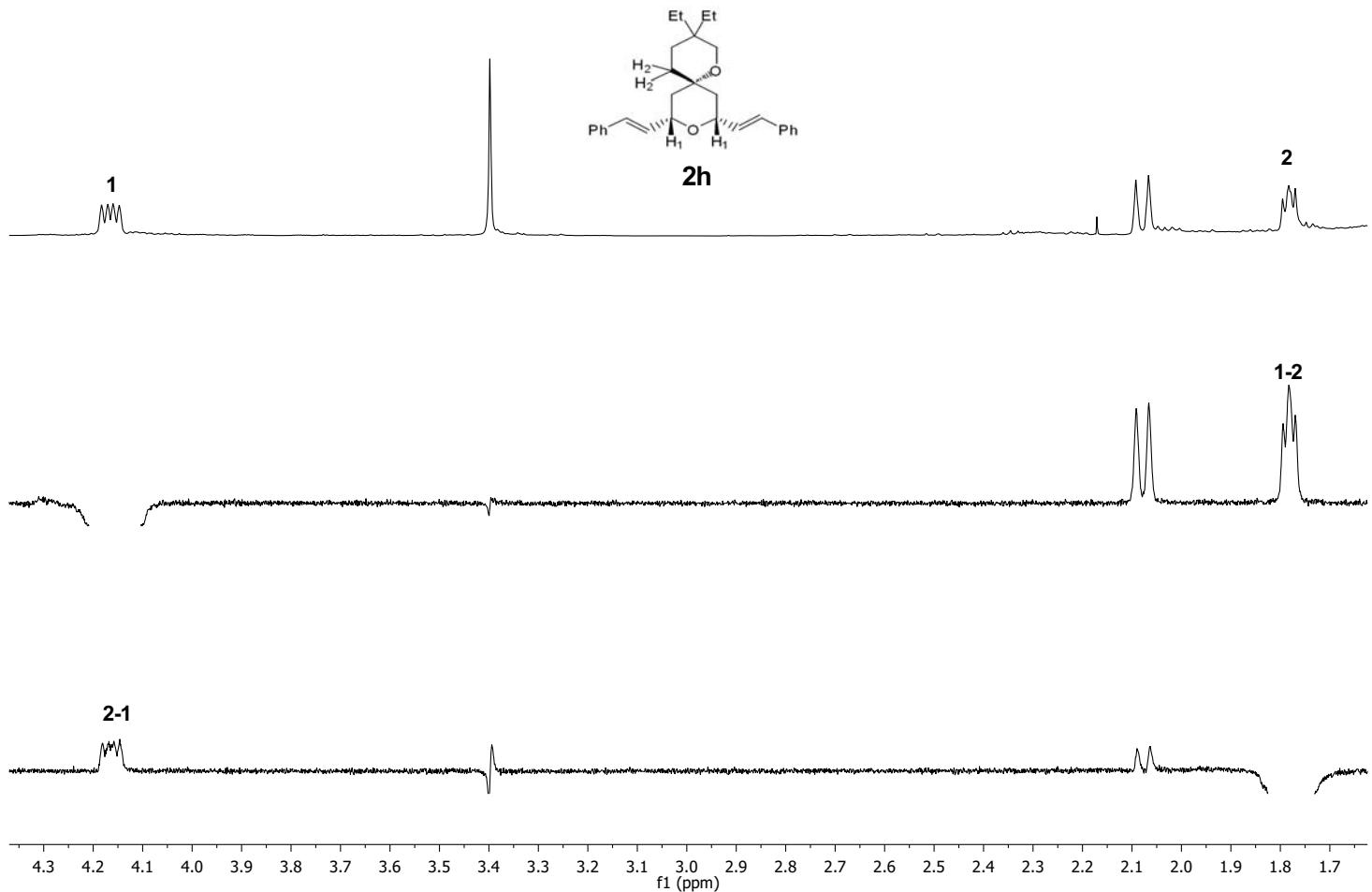


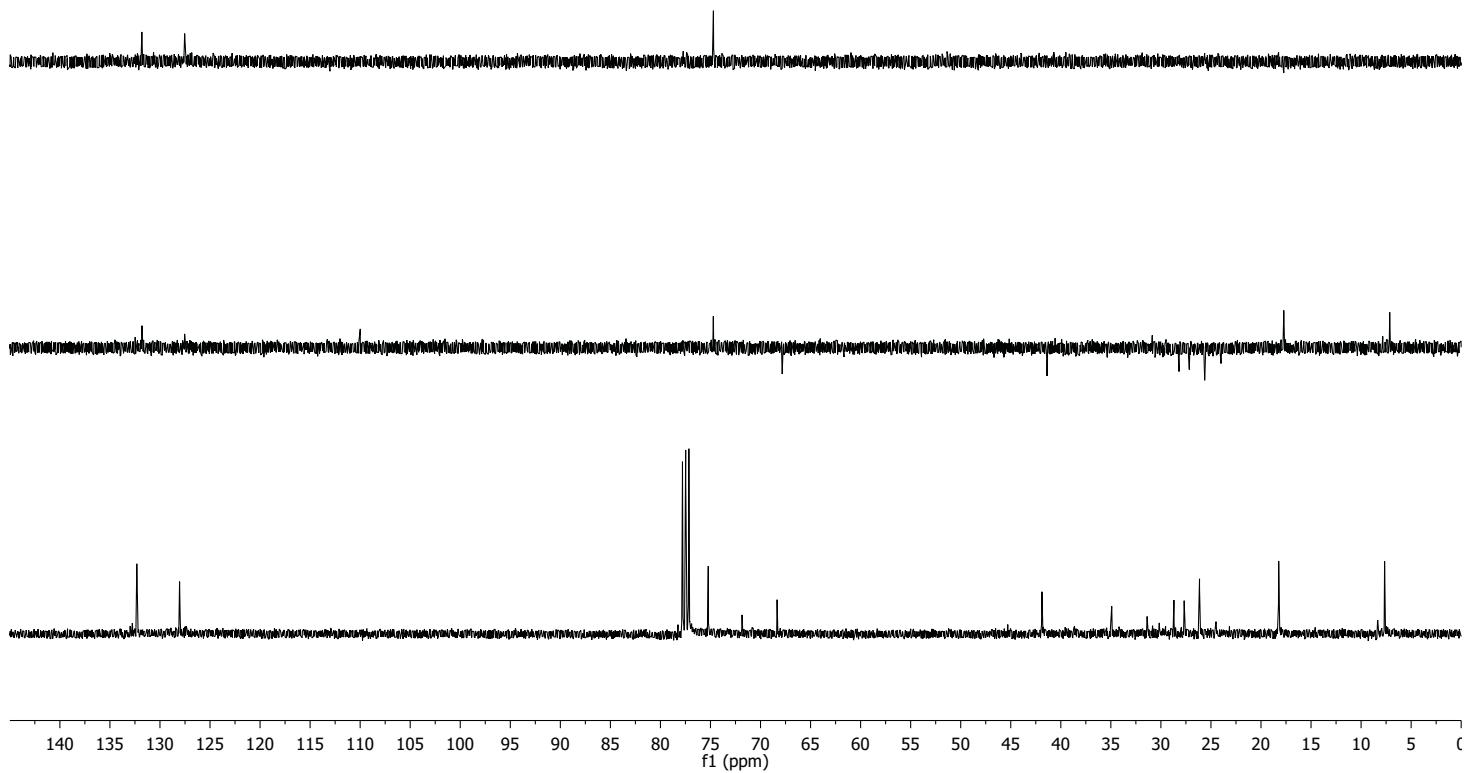
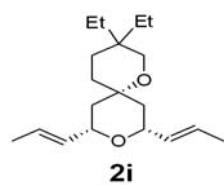
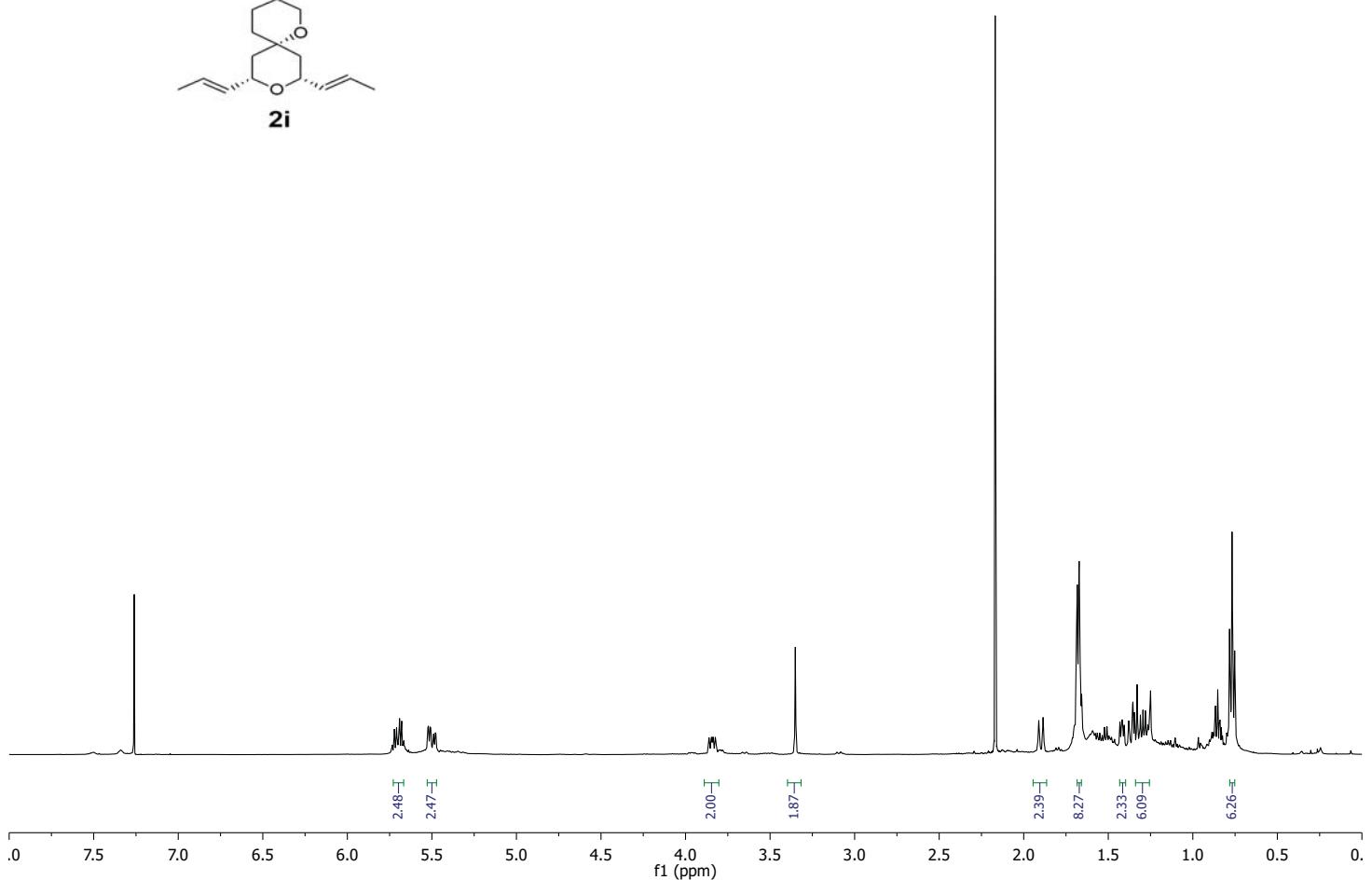
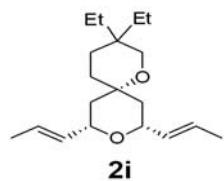
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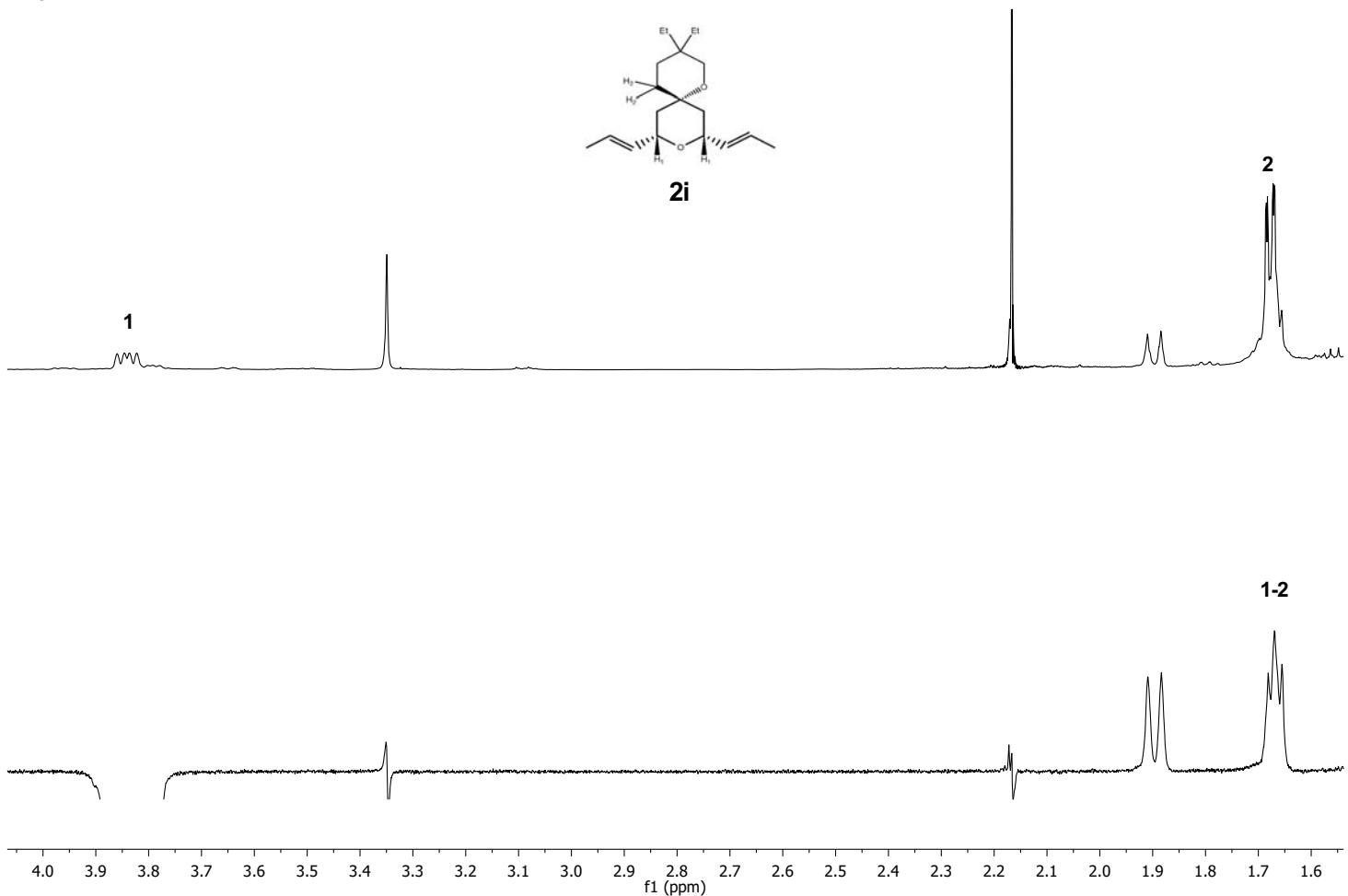
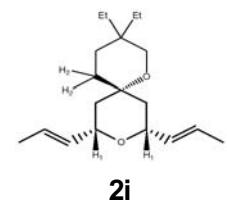


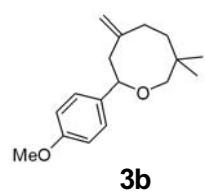
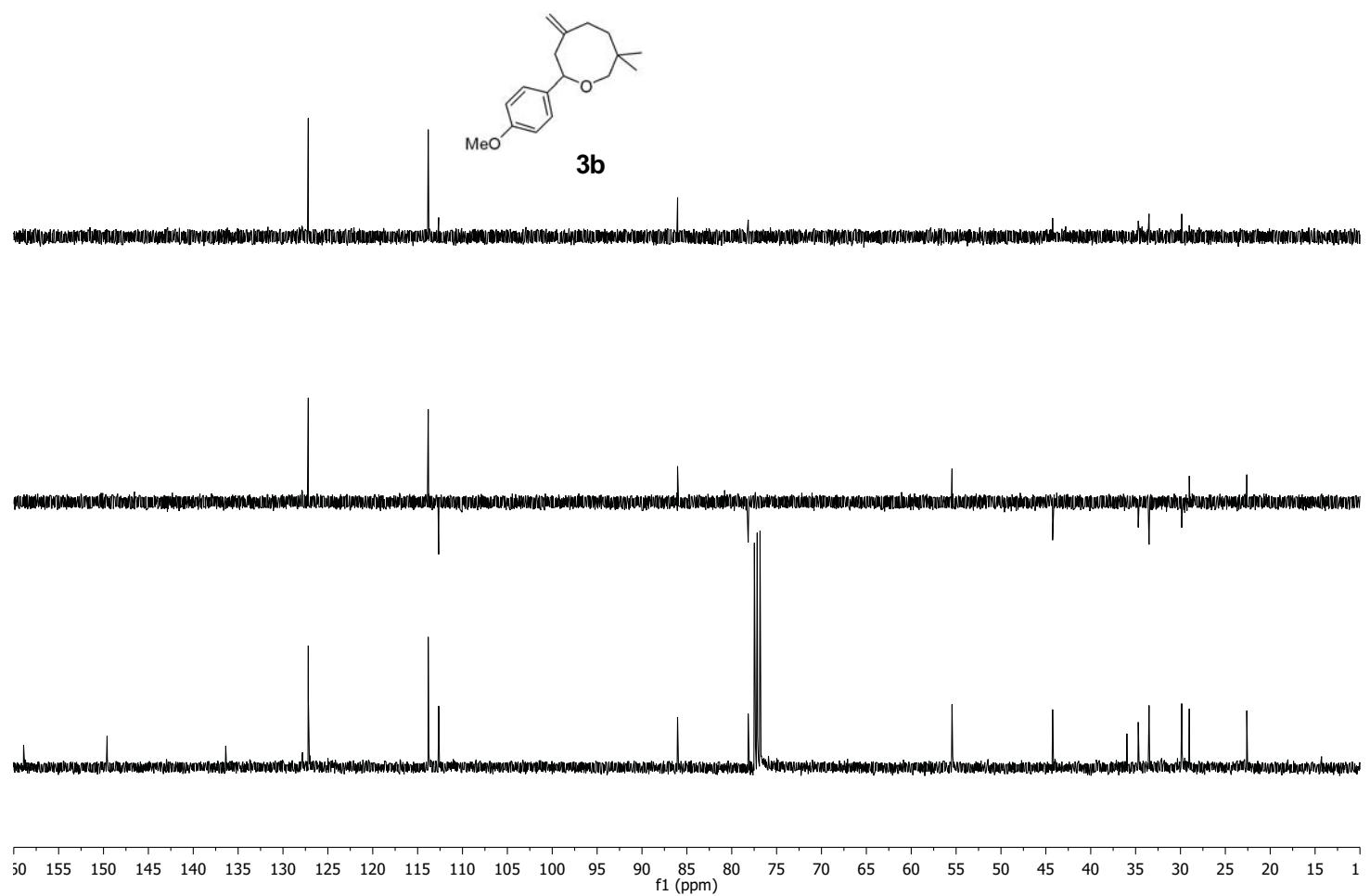
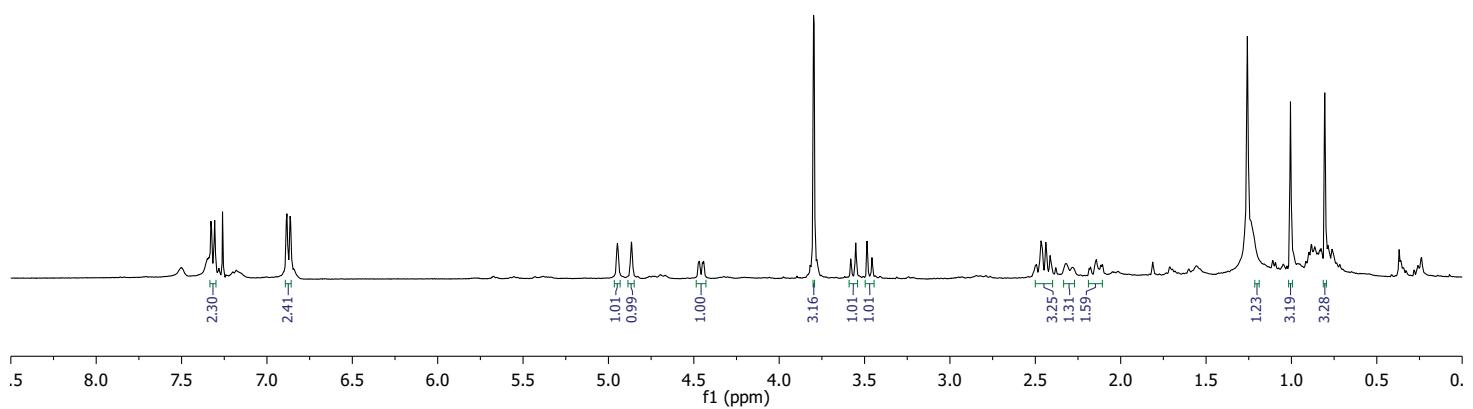


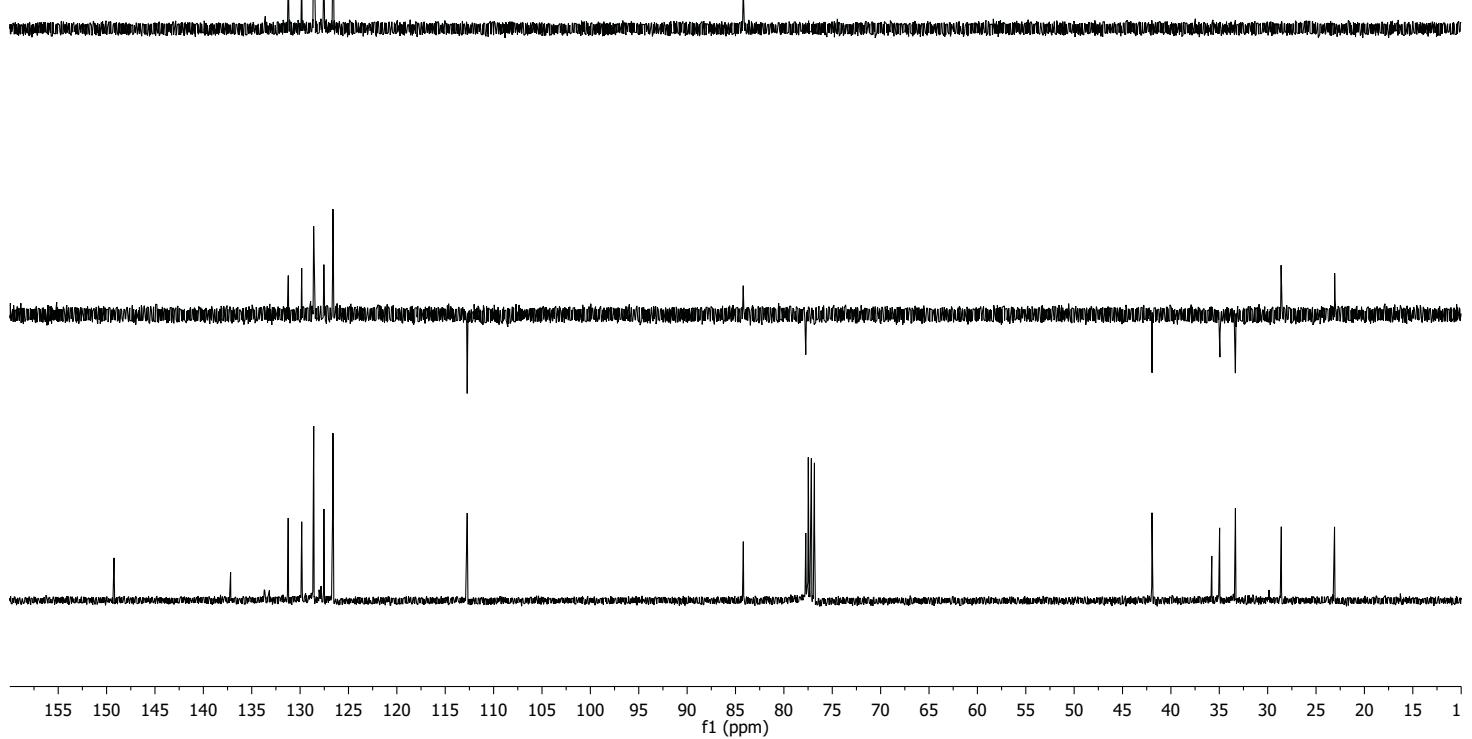
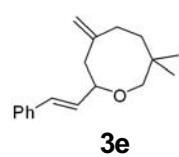
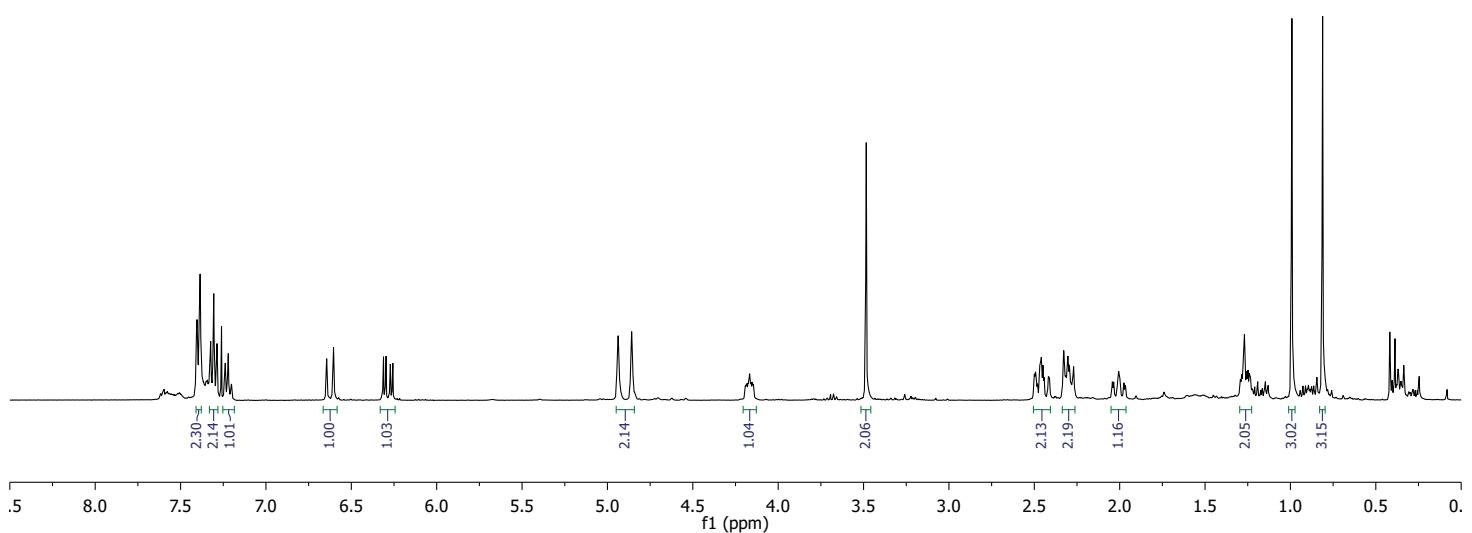
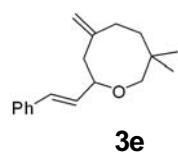


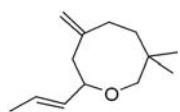
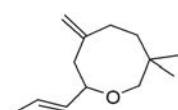
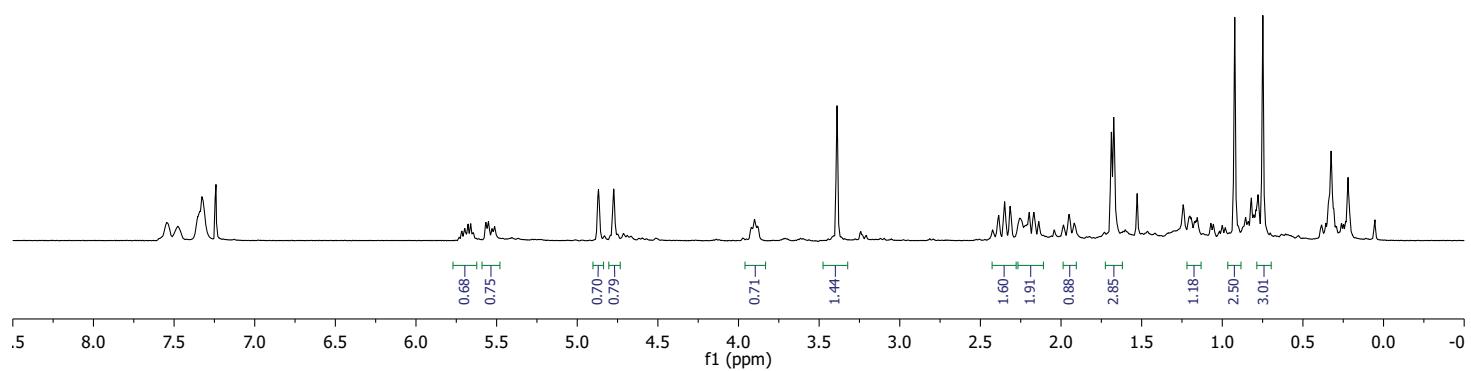
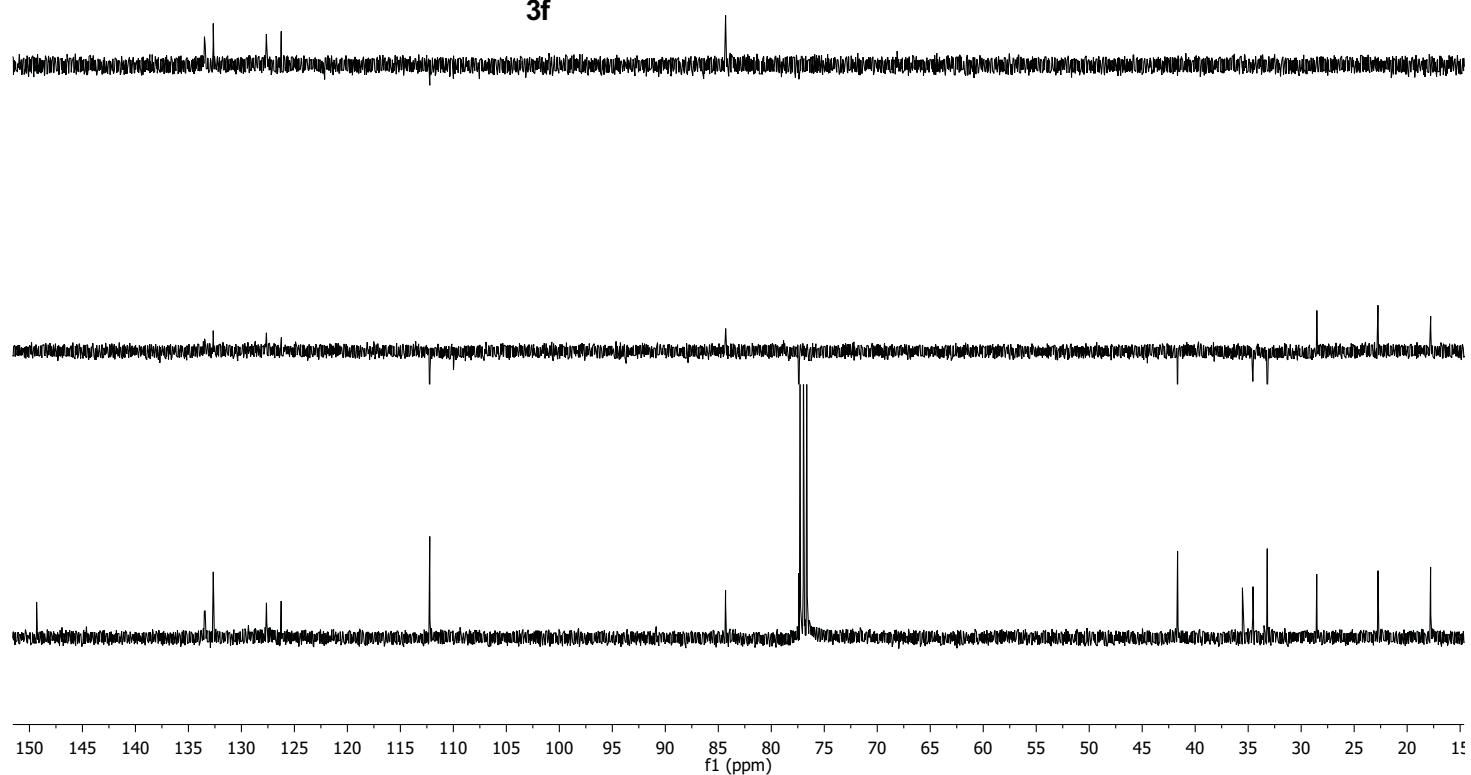


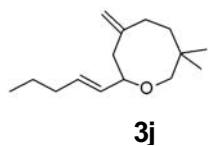
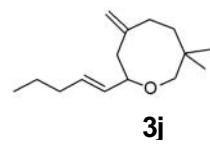
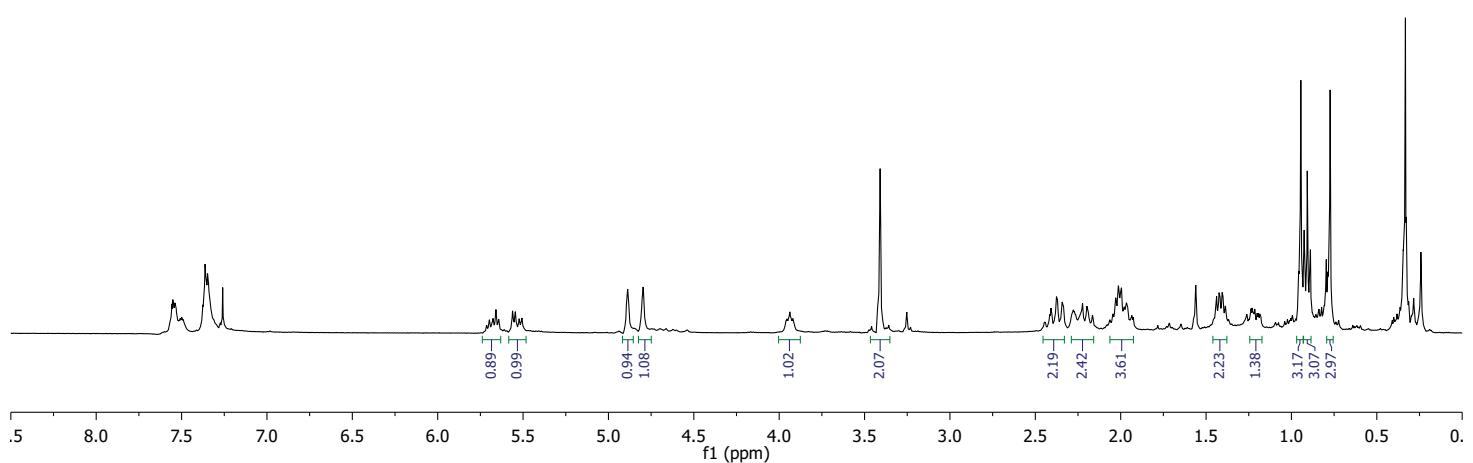
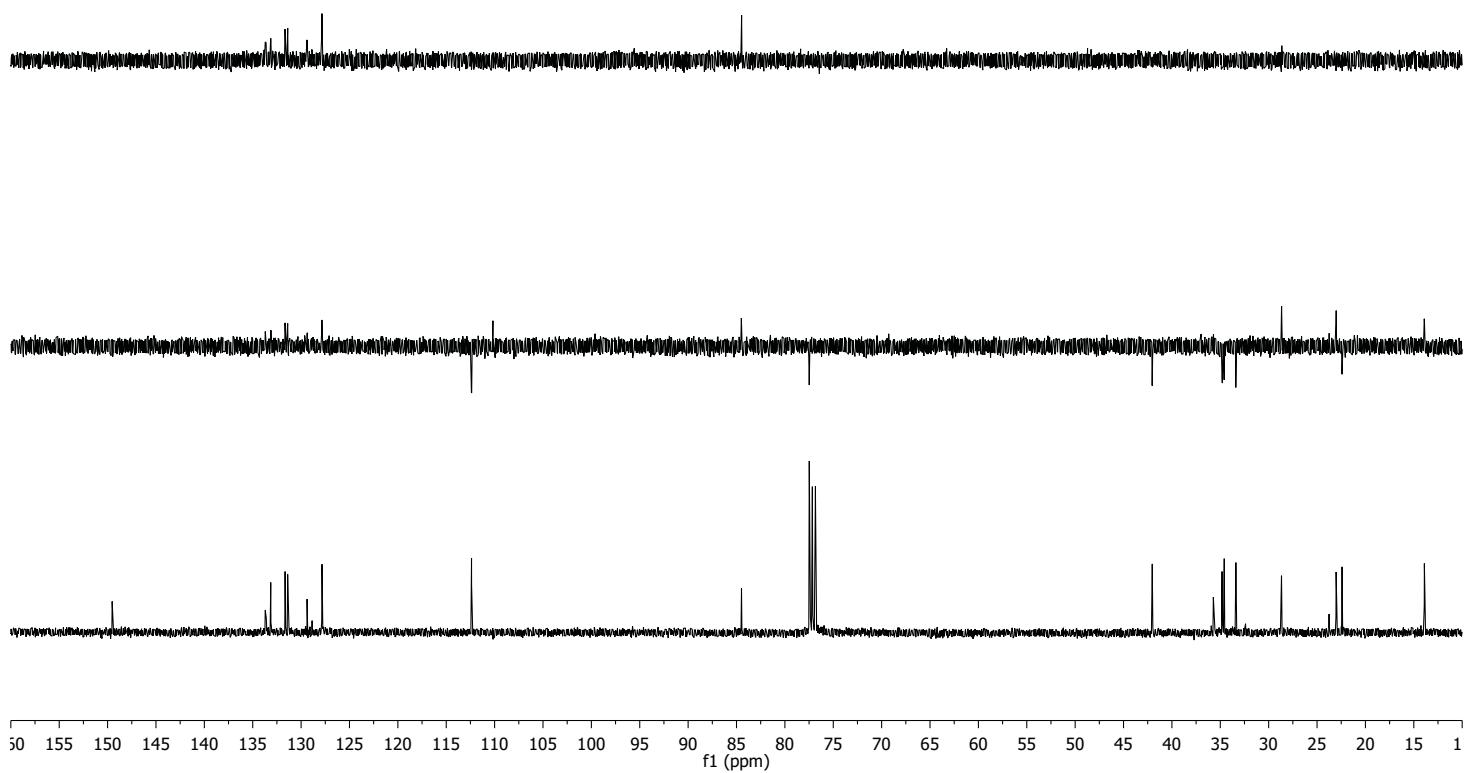


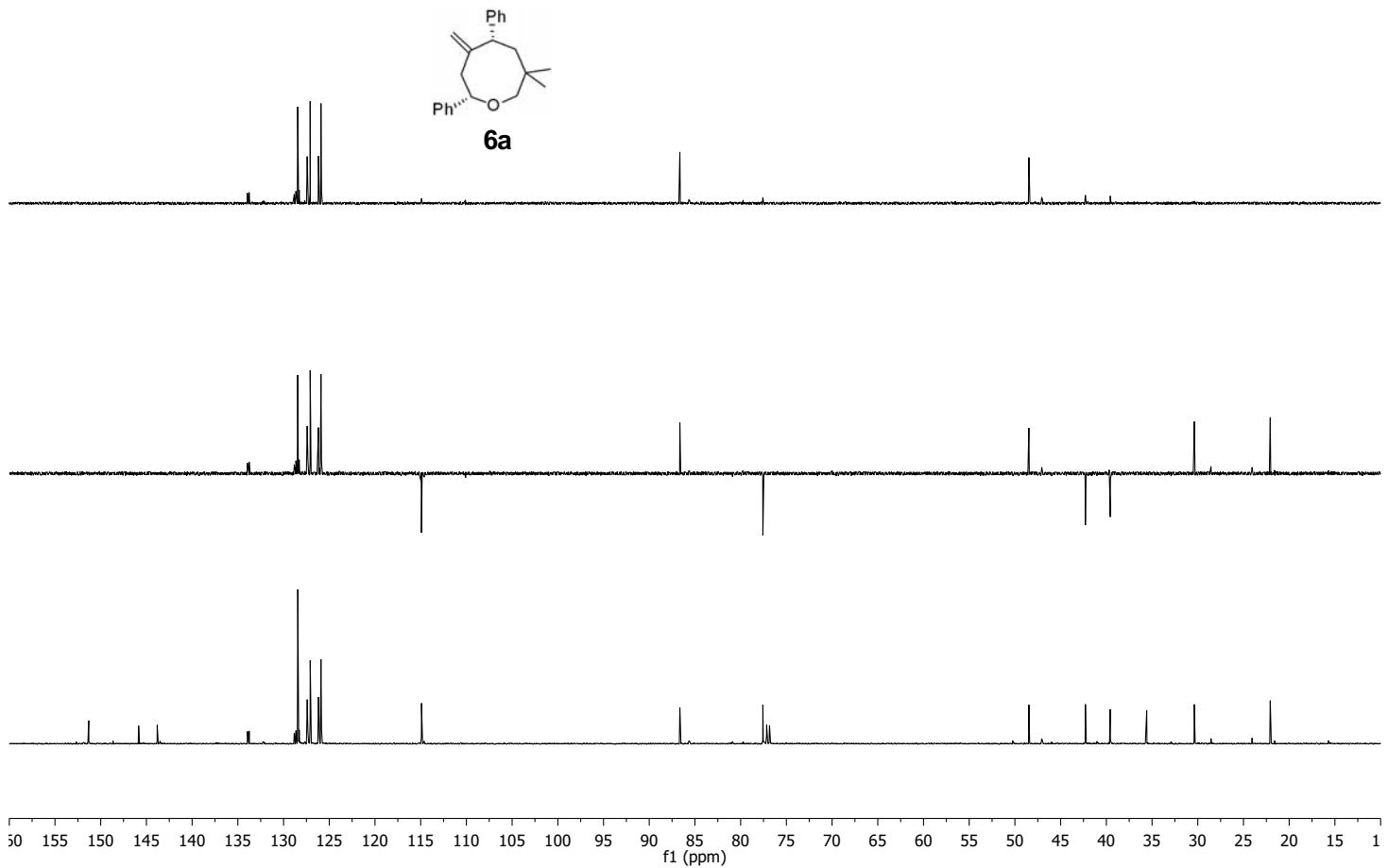
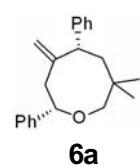
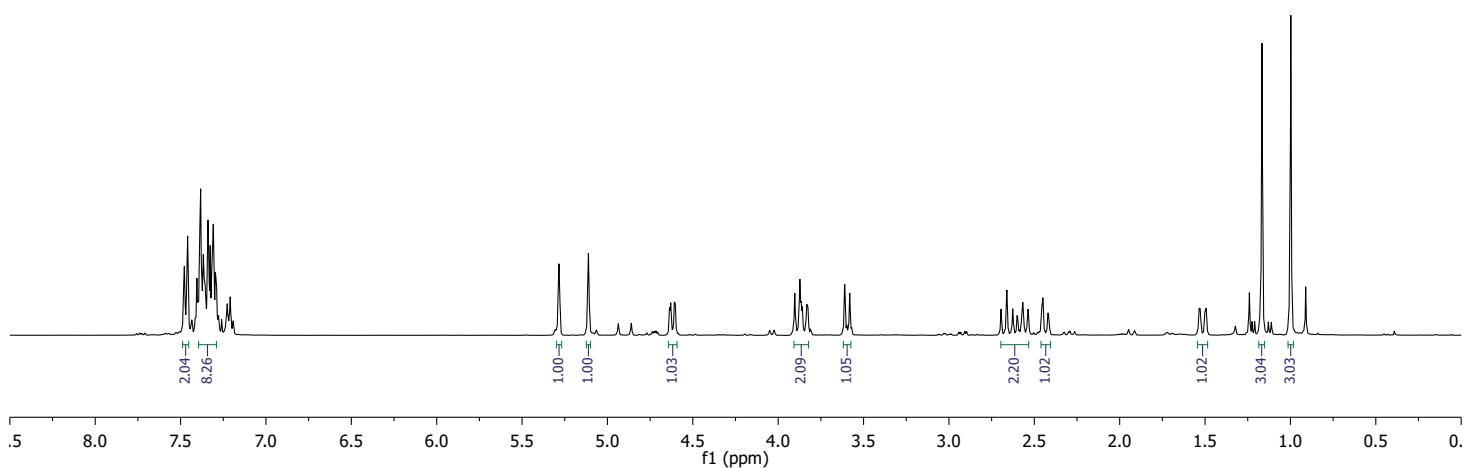
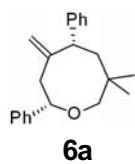


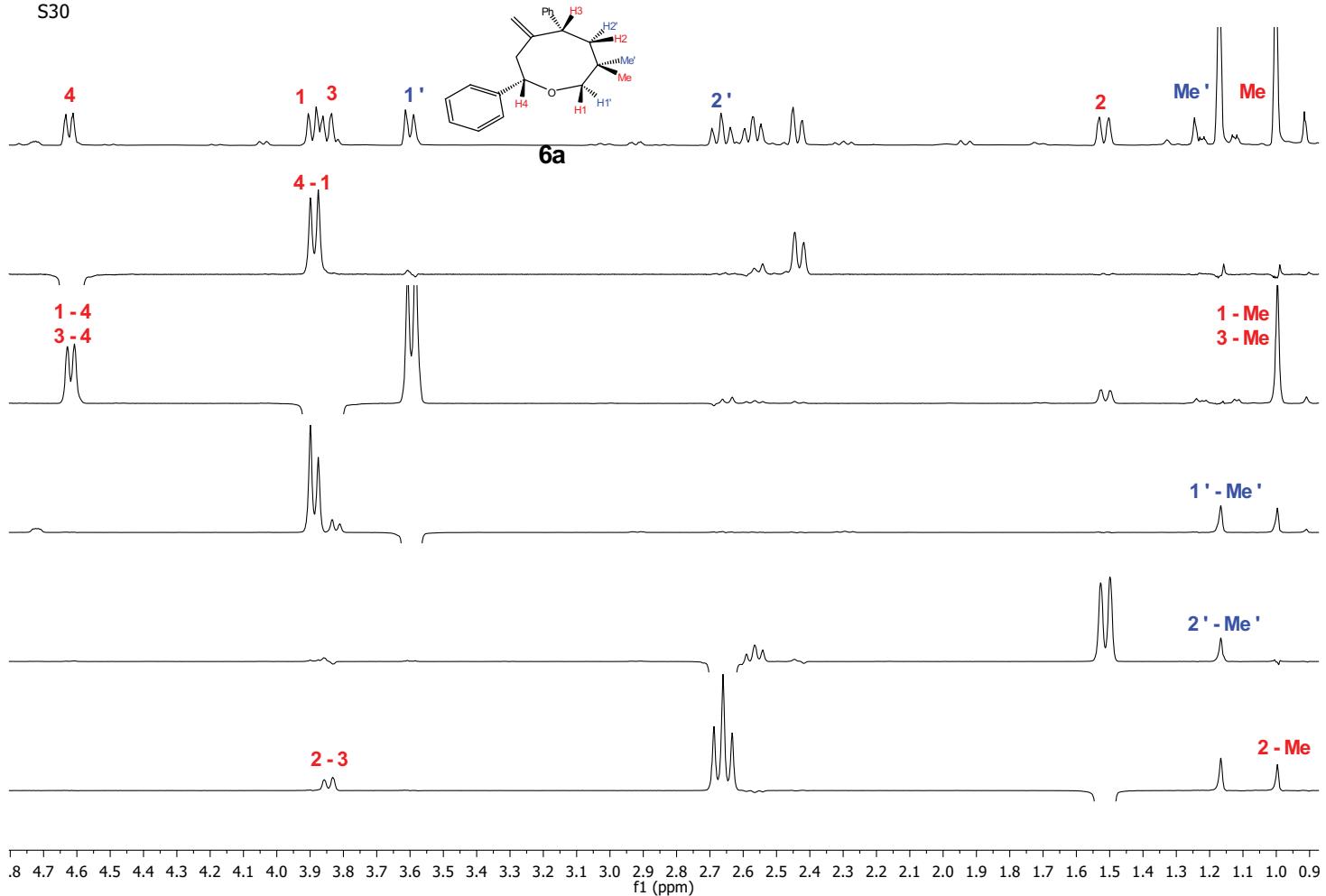
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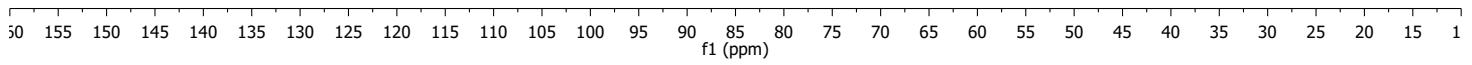
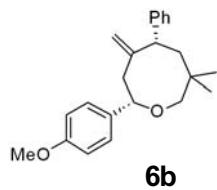
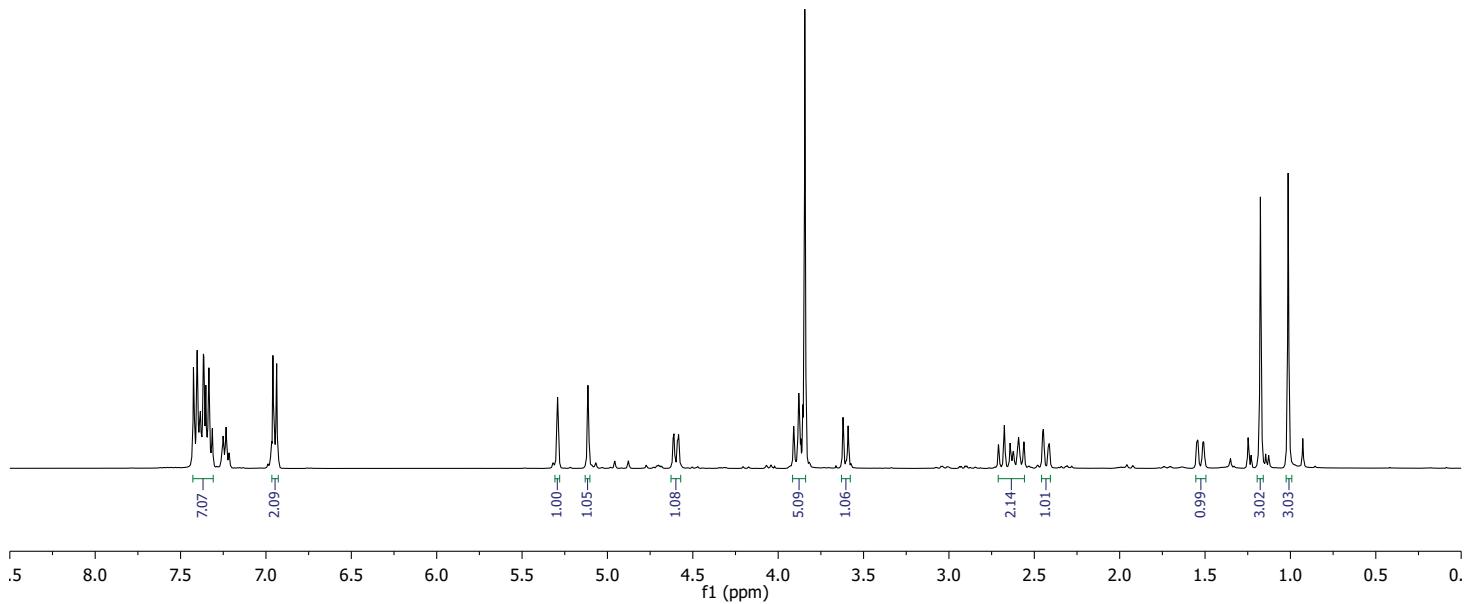
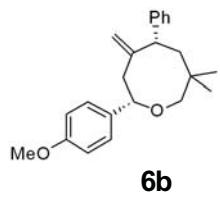


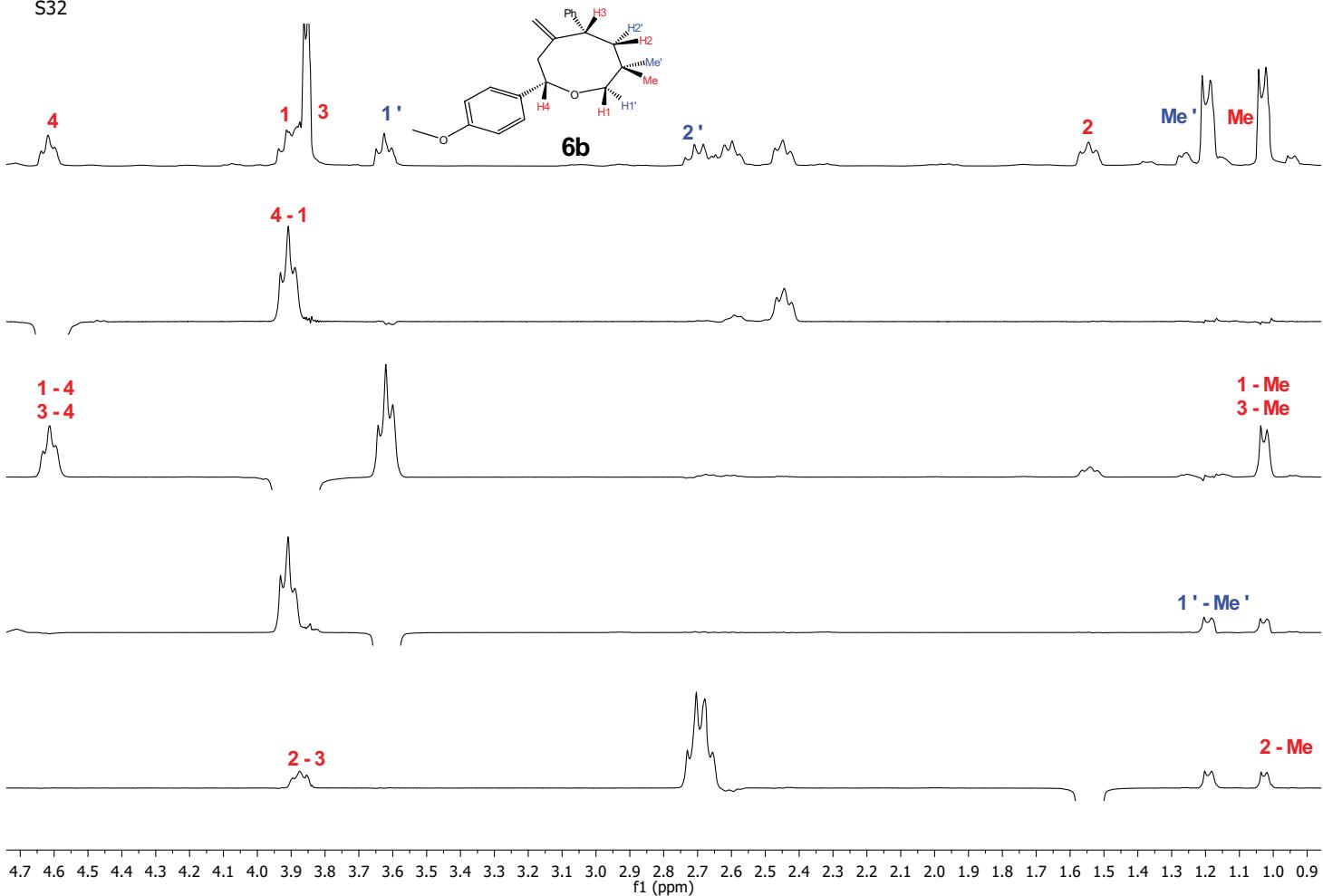
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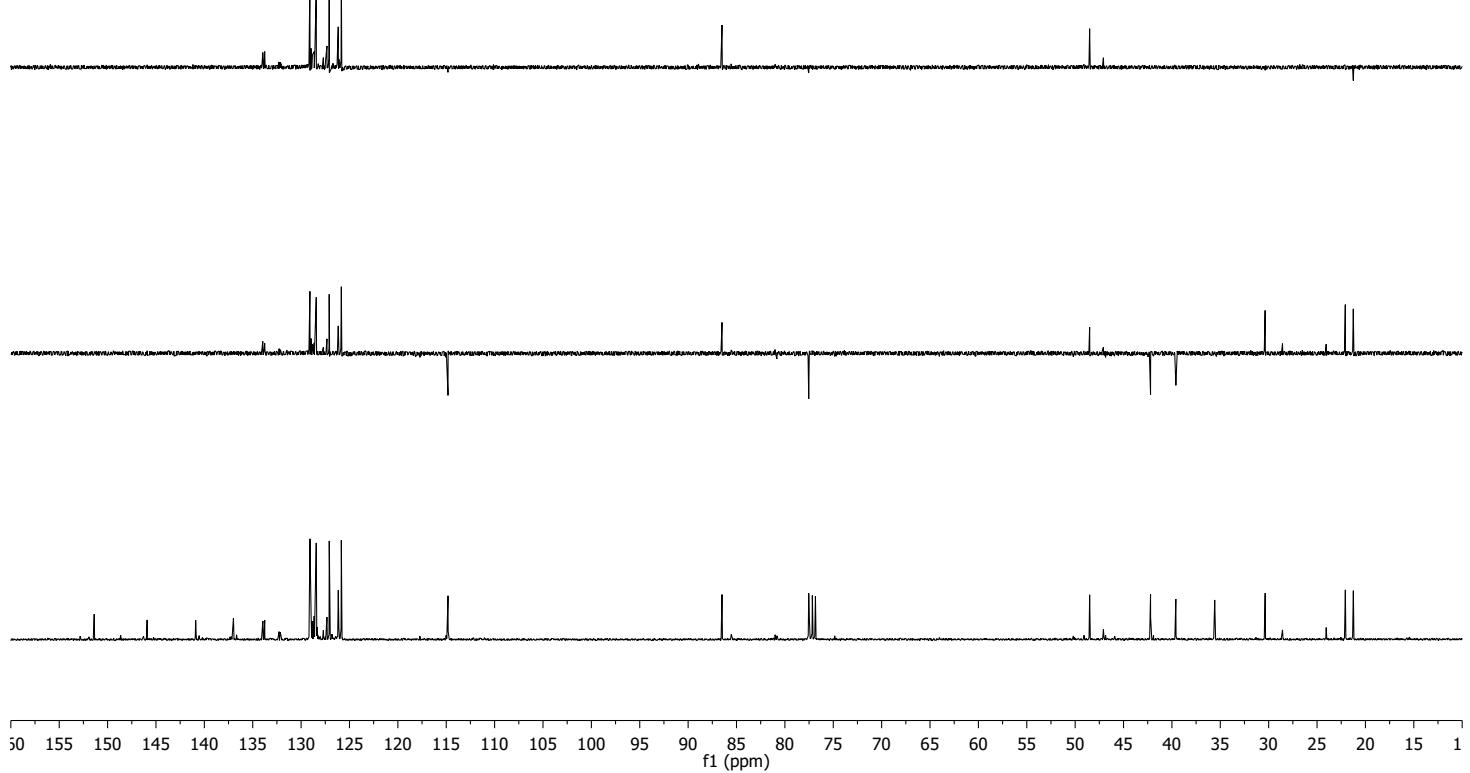
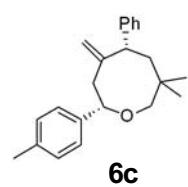
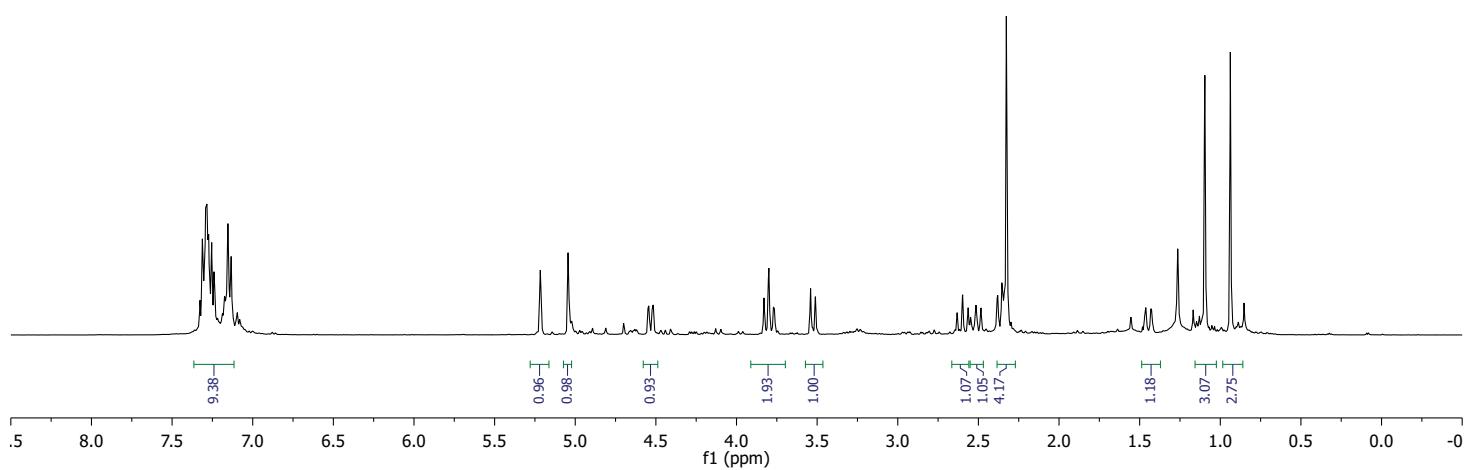
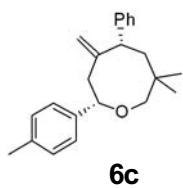
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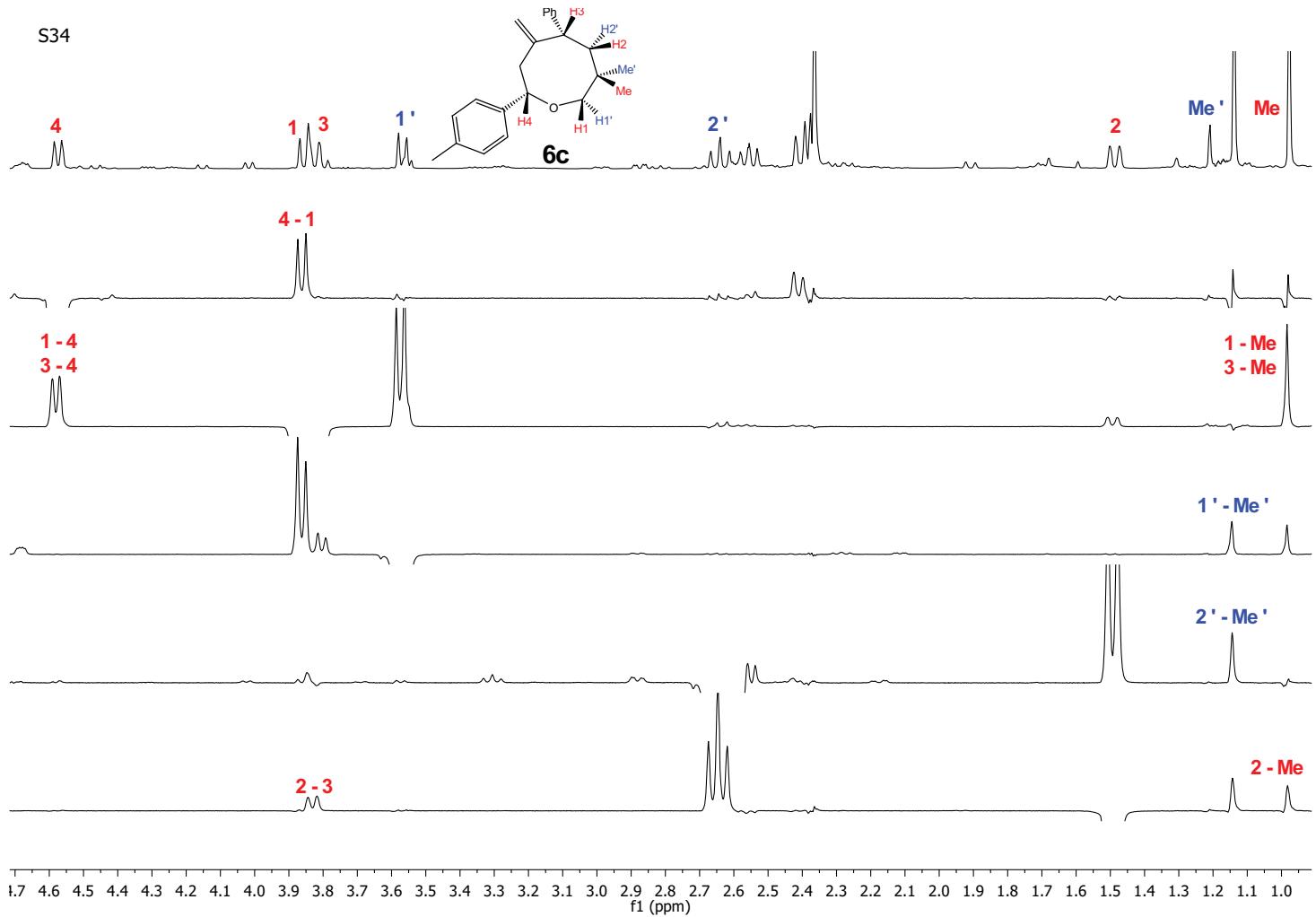


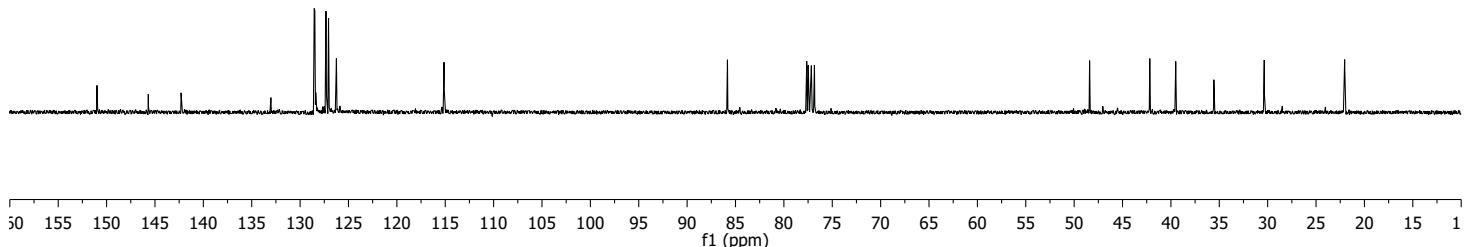
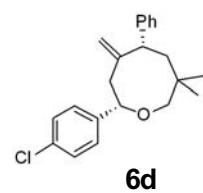
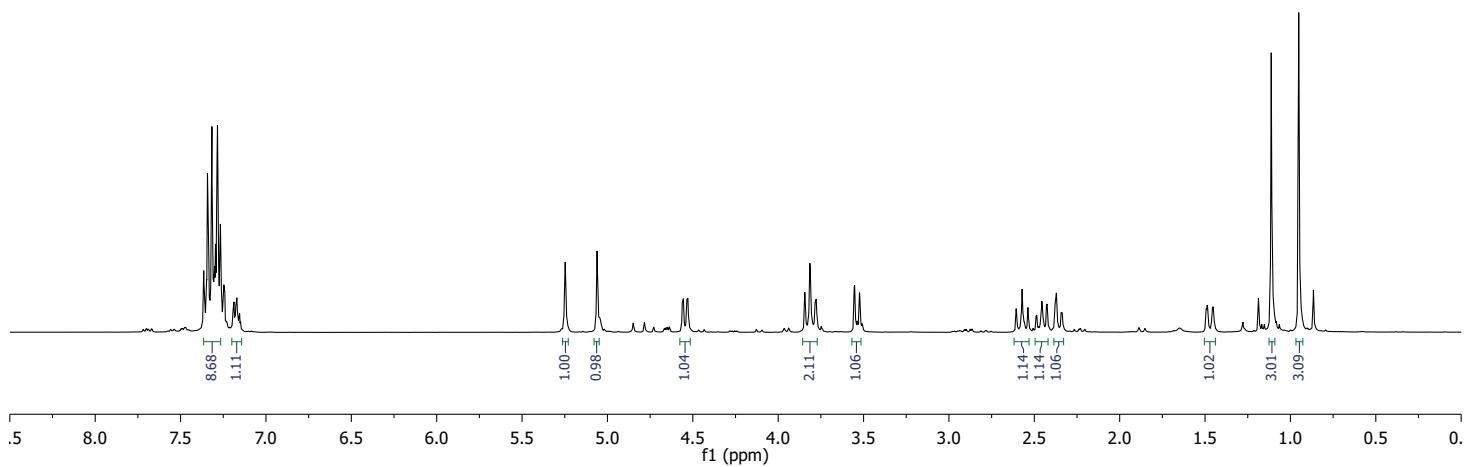
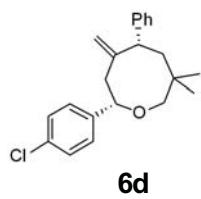




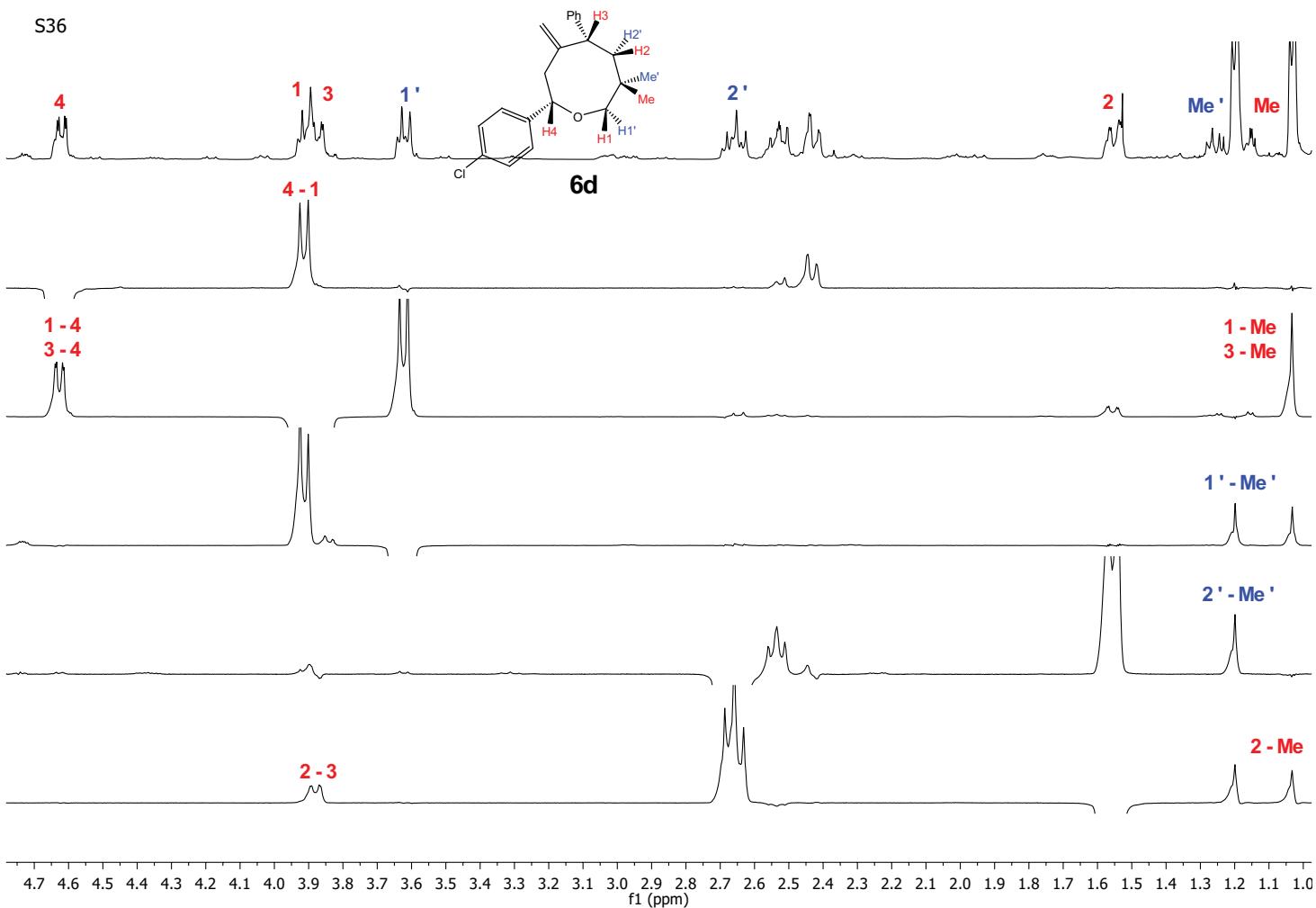


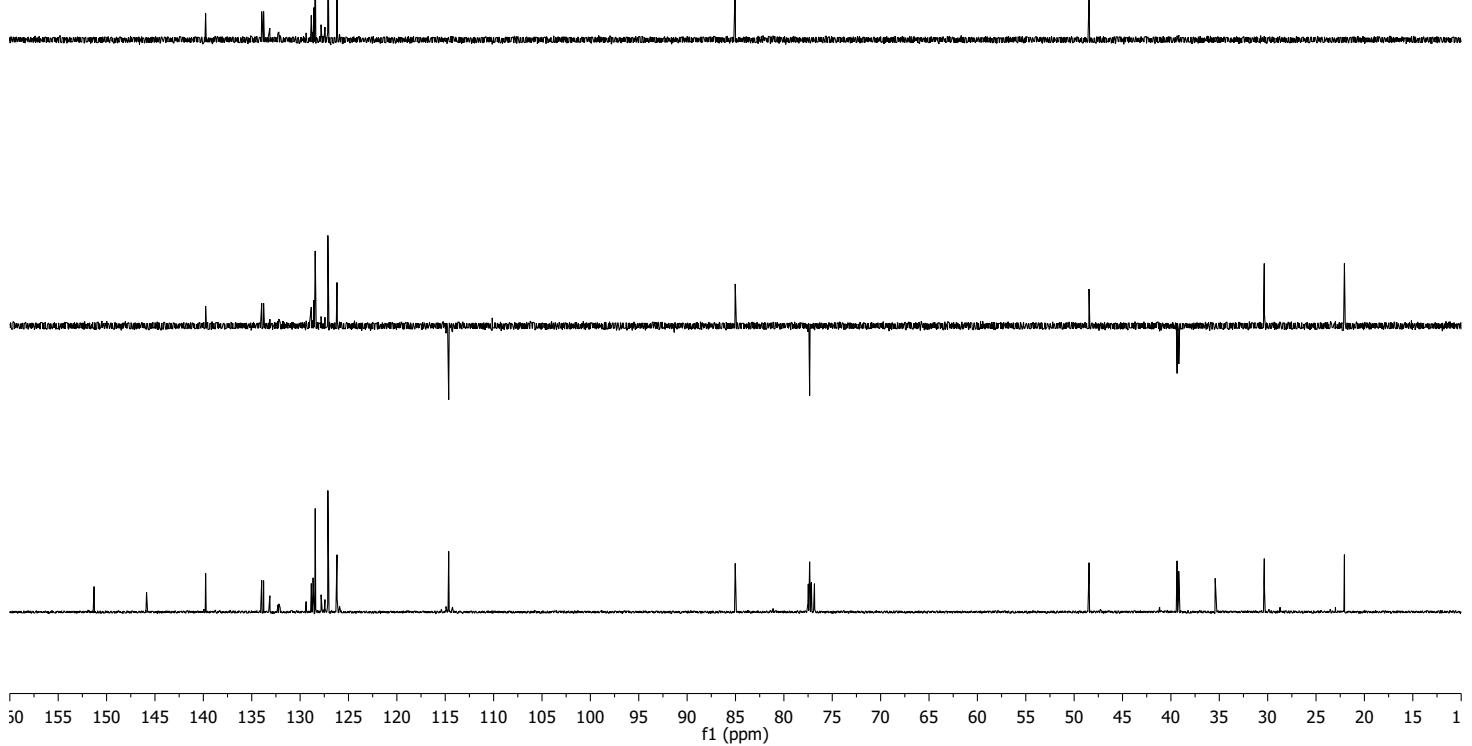
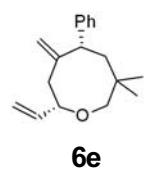
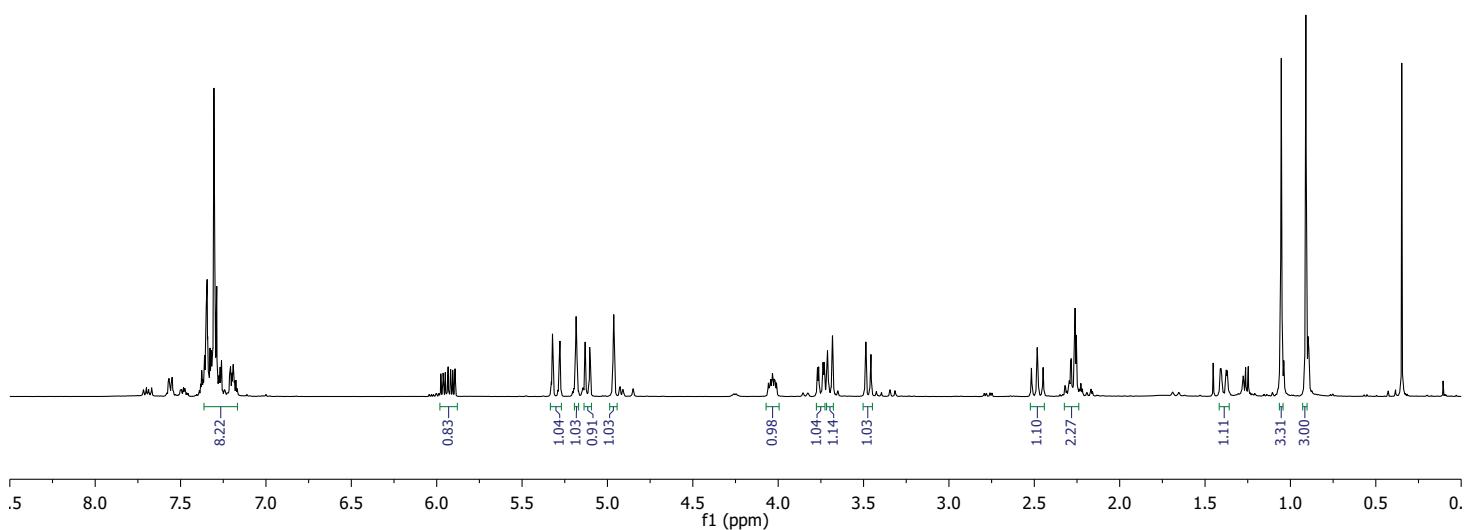
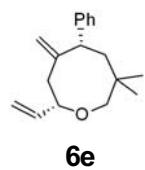


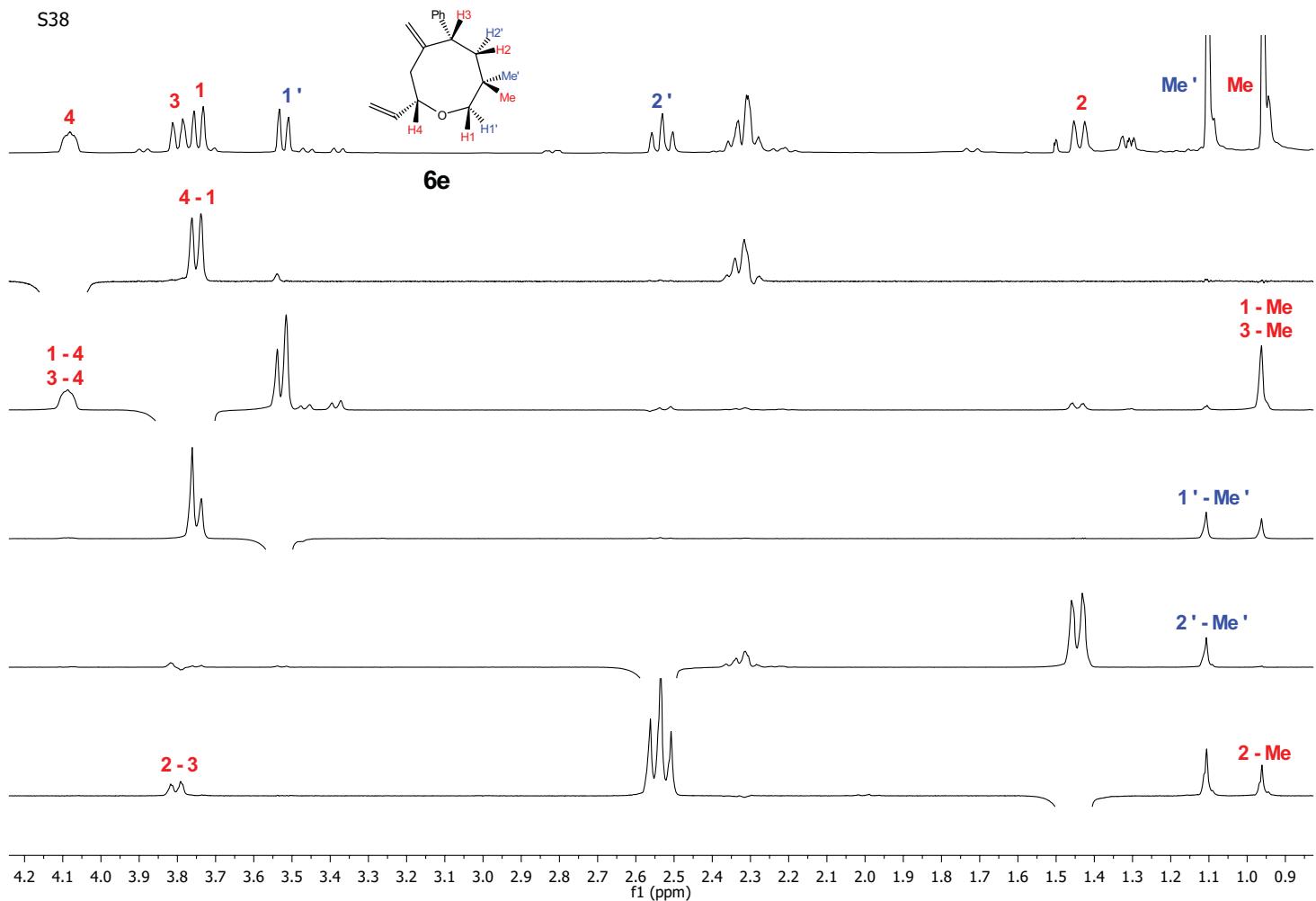


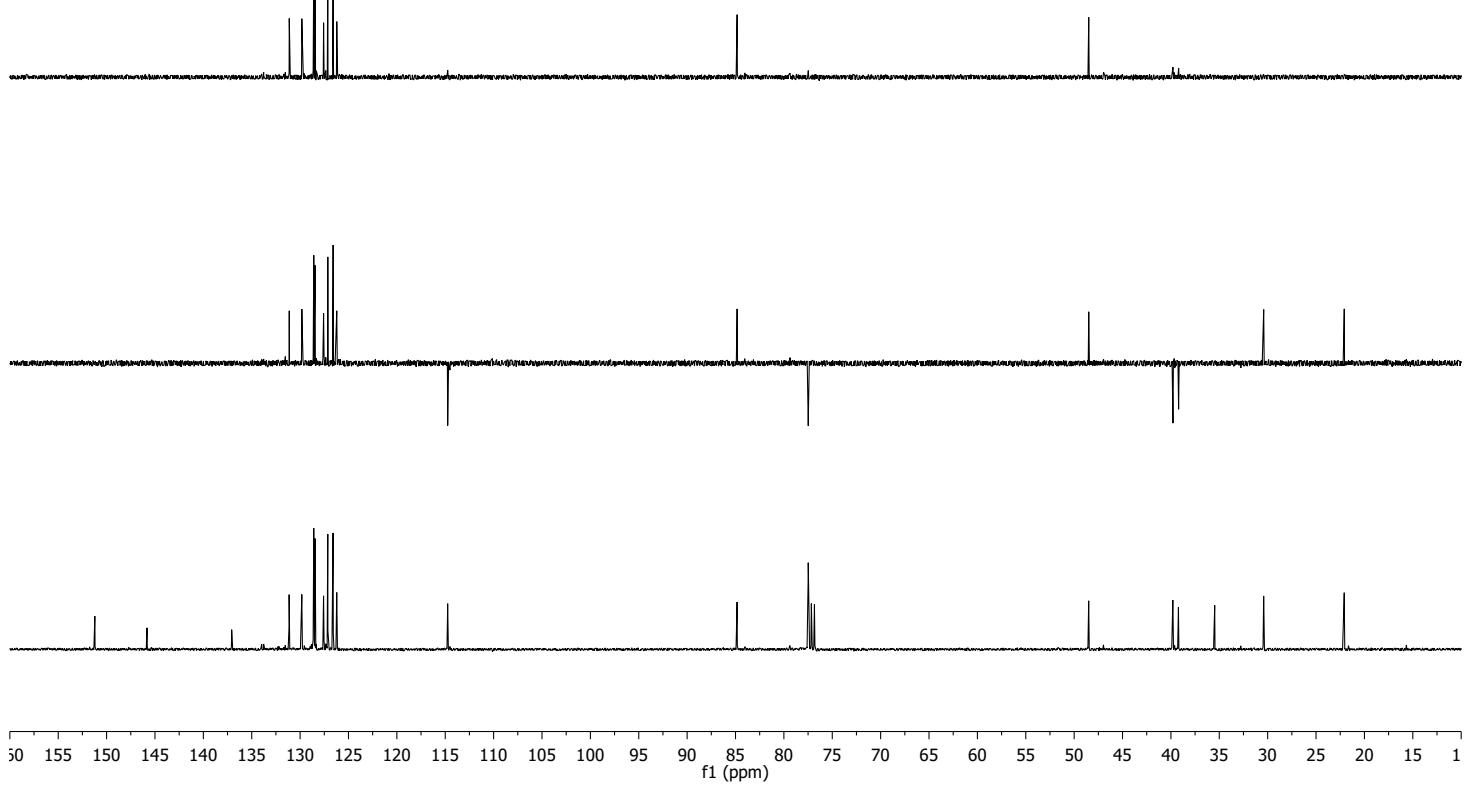
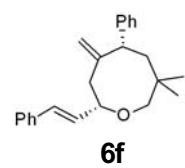
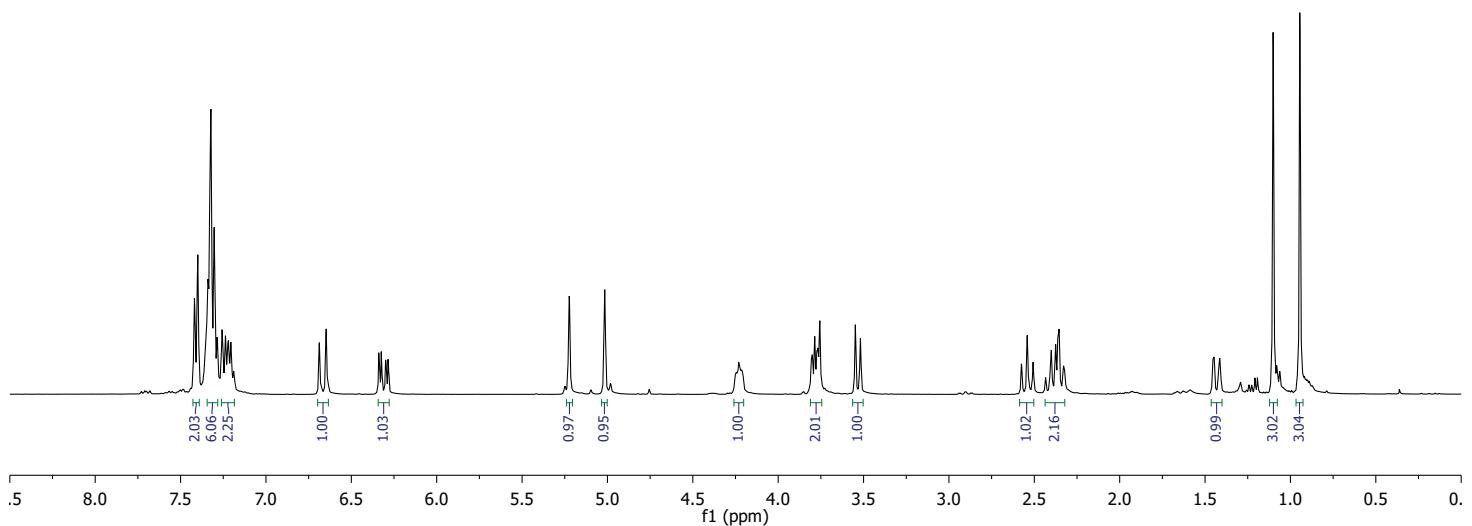
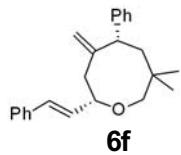


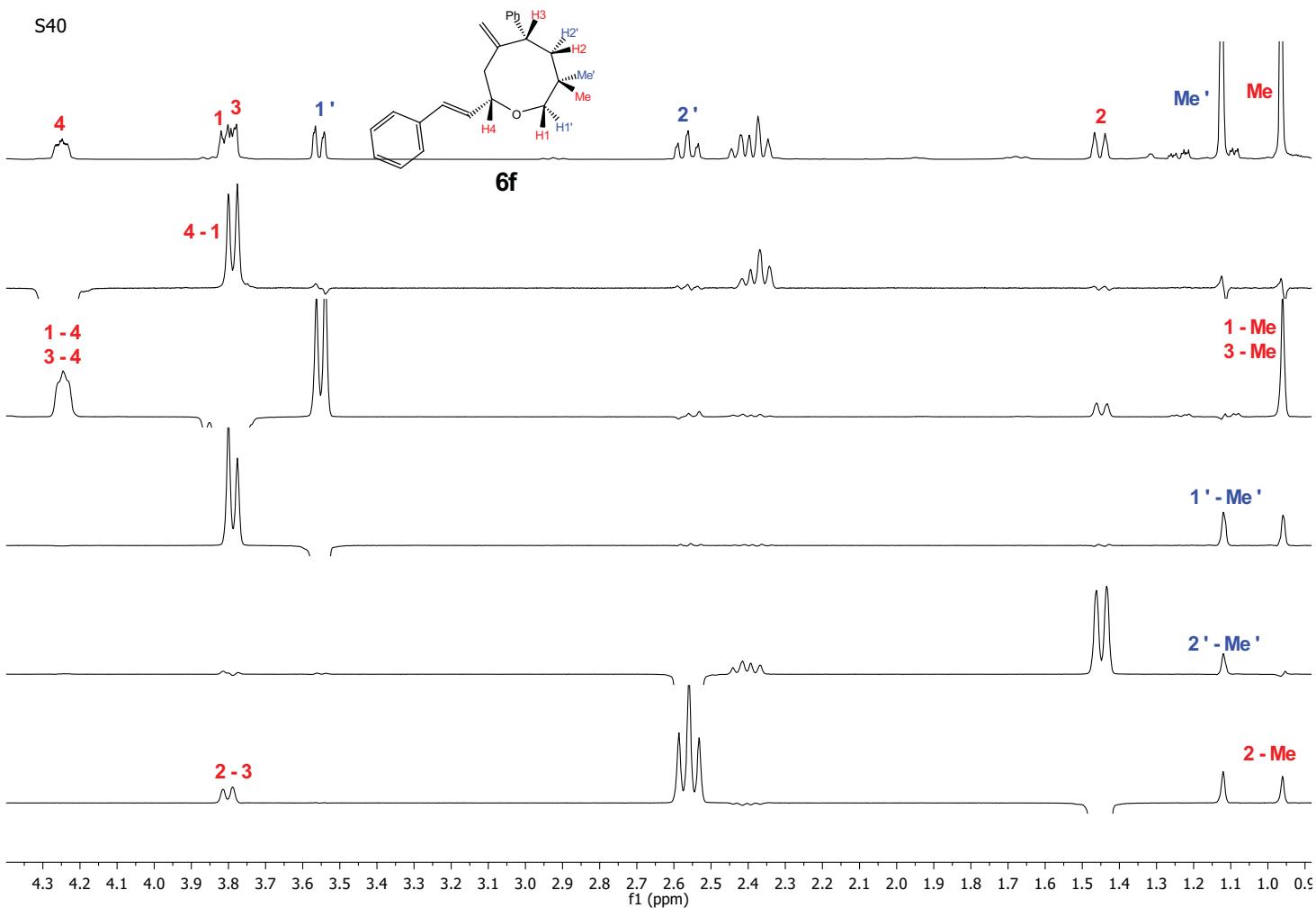
S36

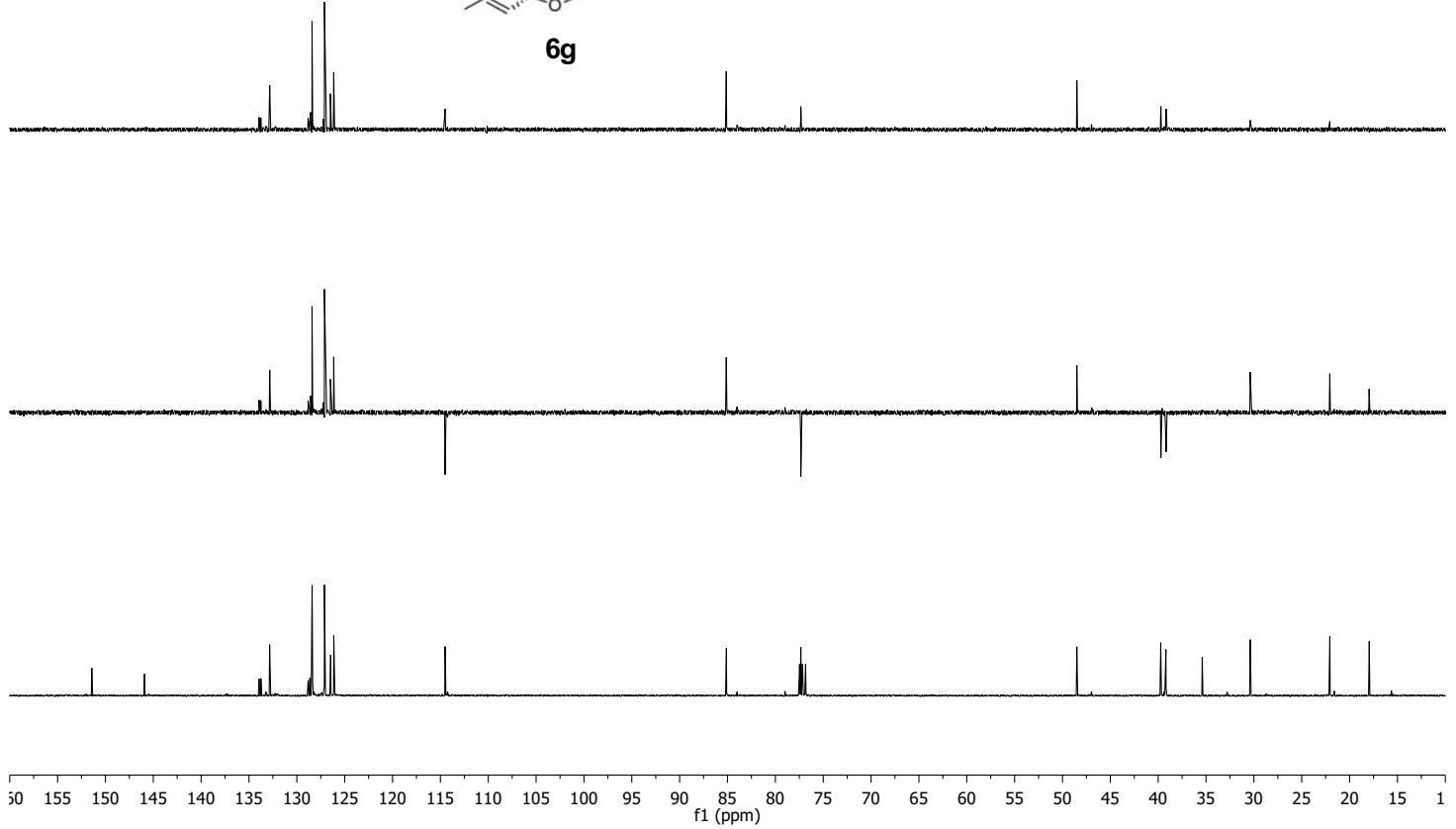
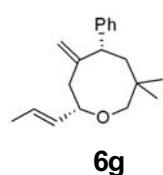
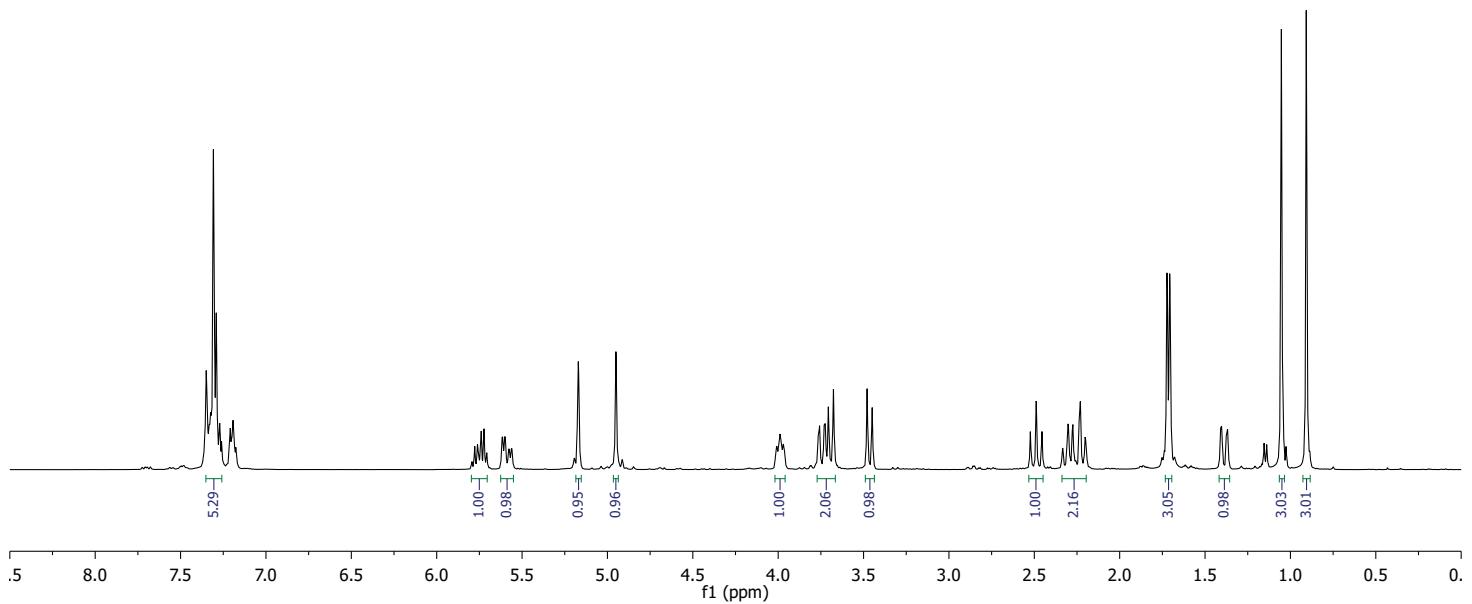
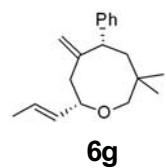


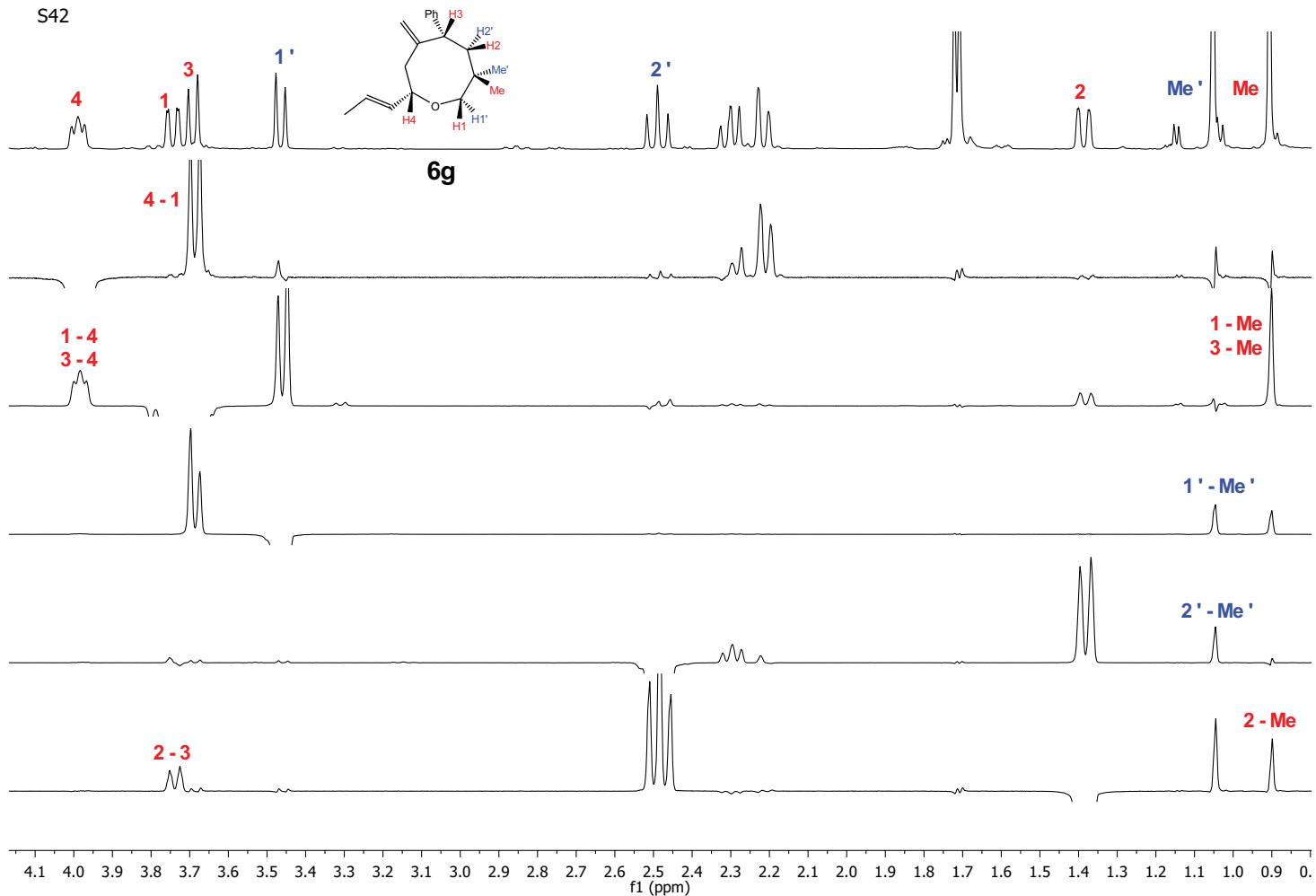


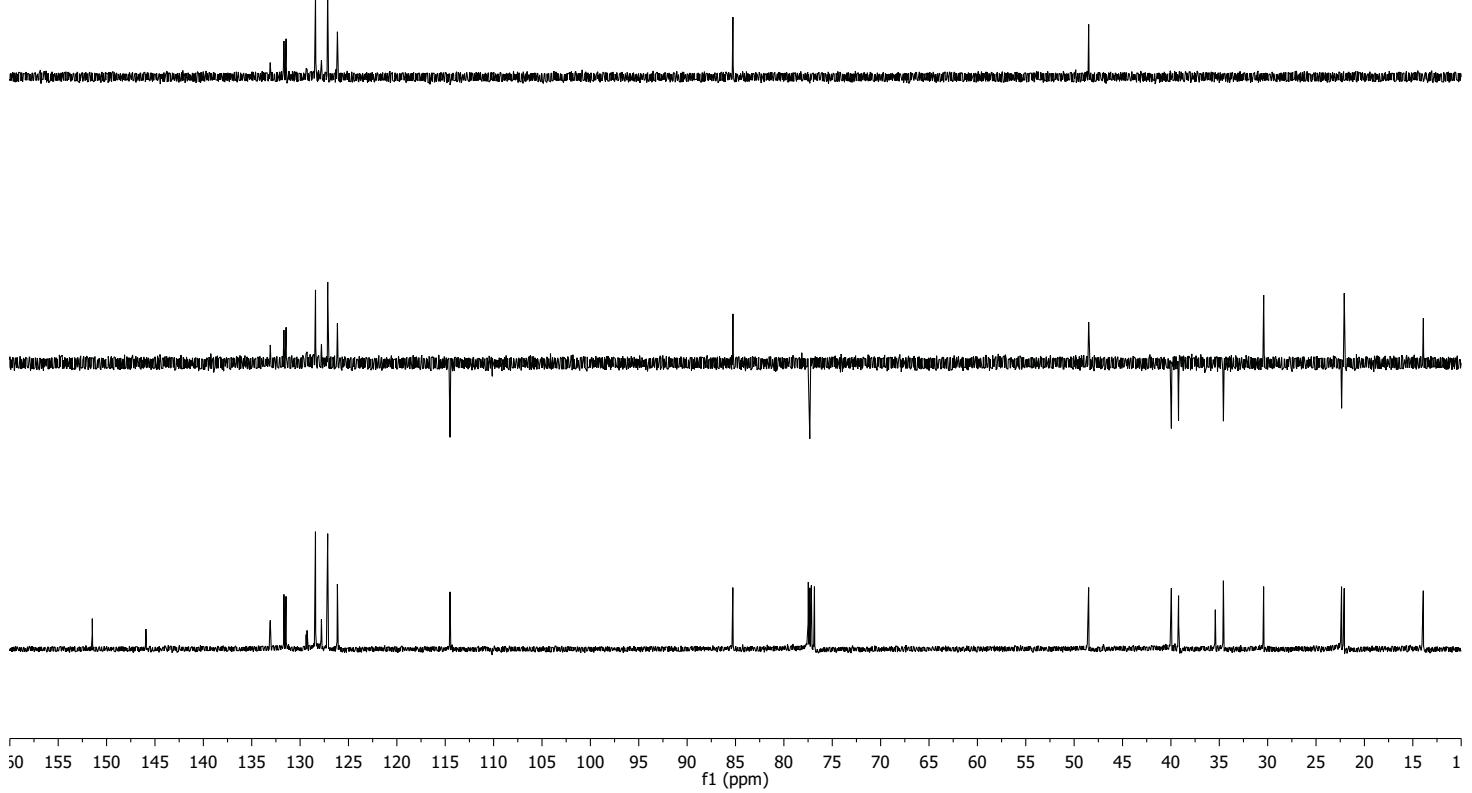
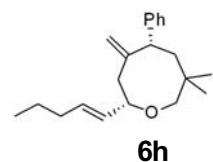
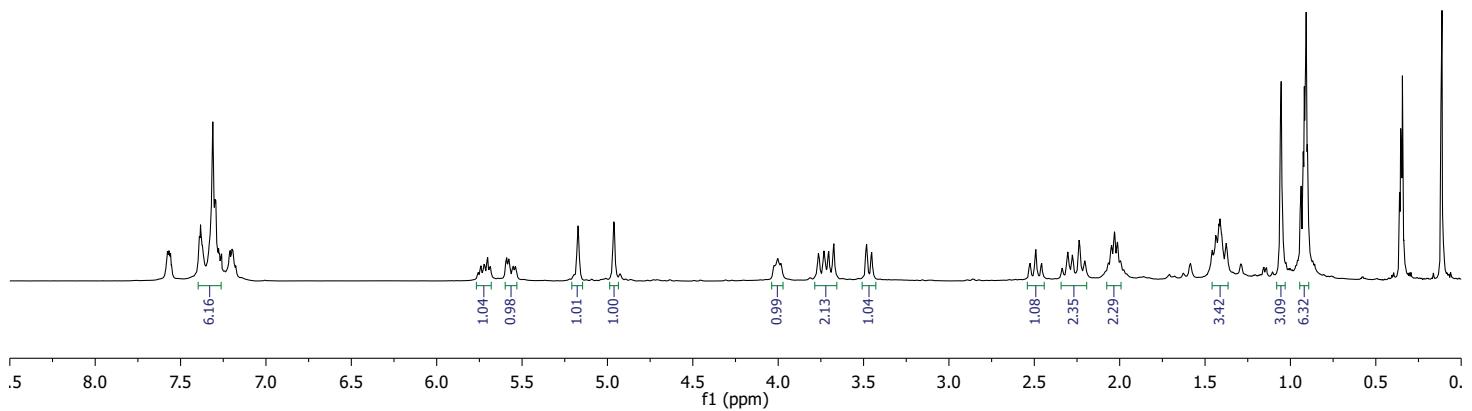
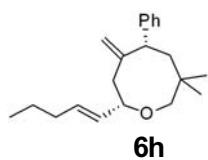


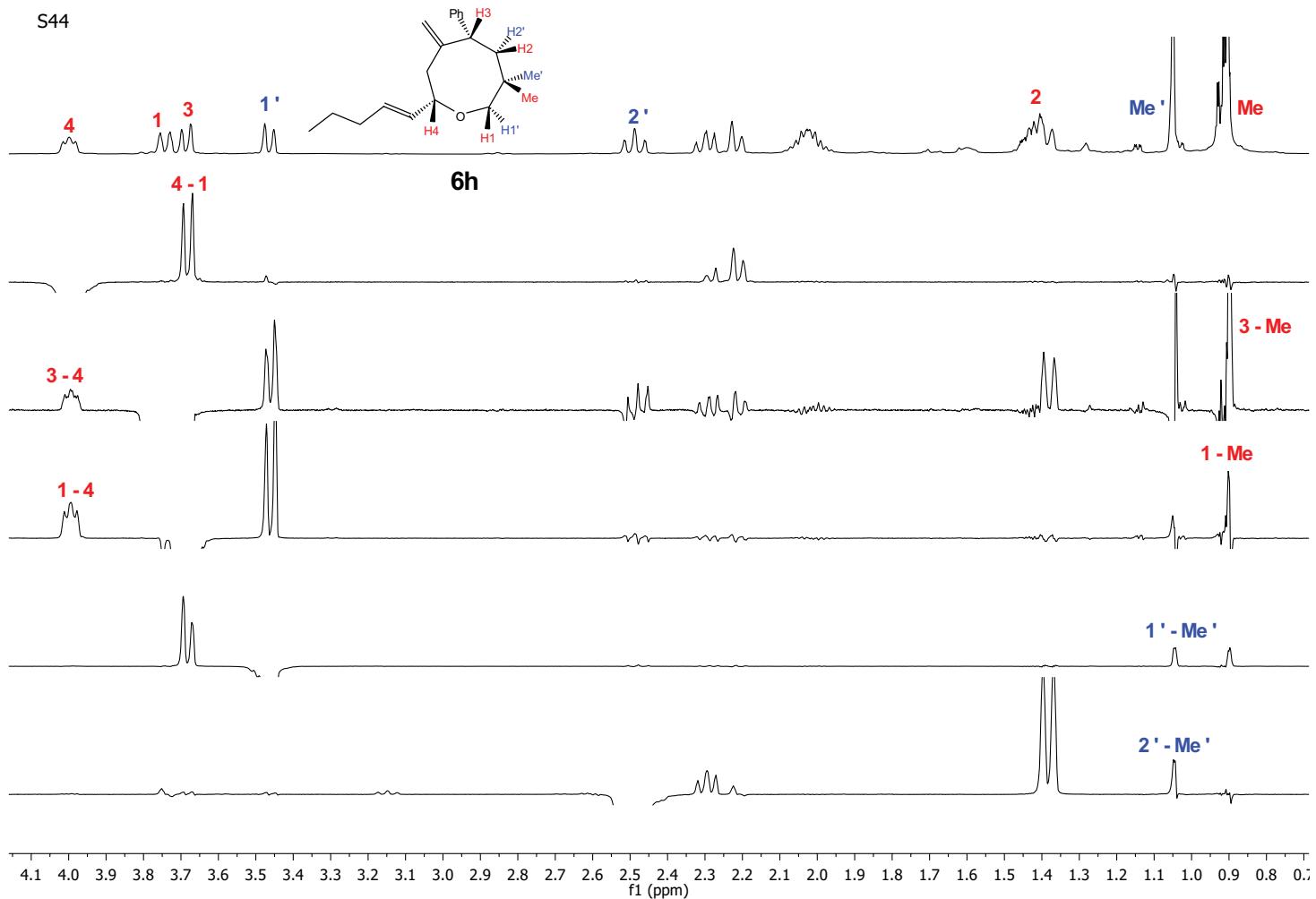


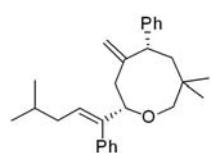
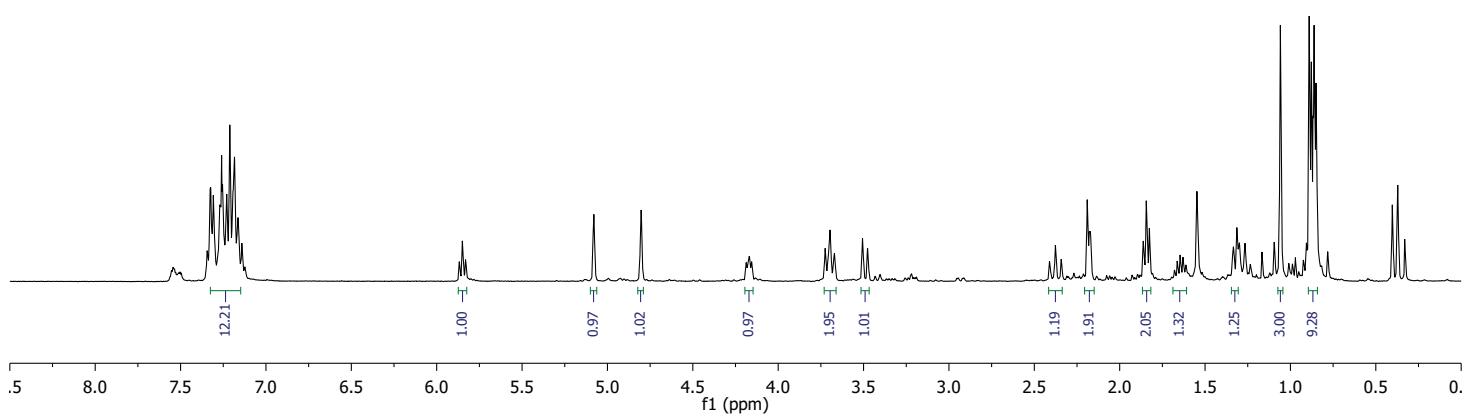
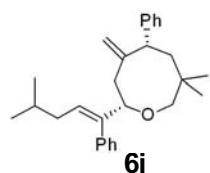
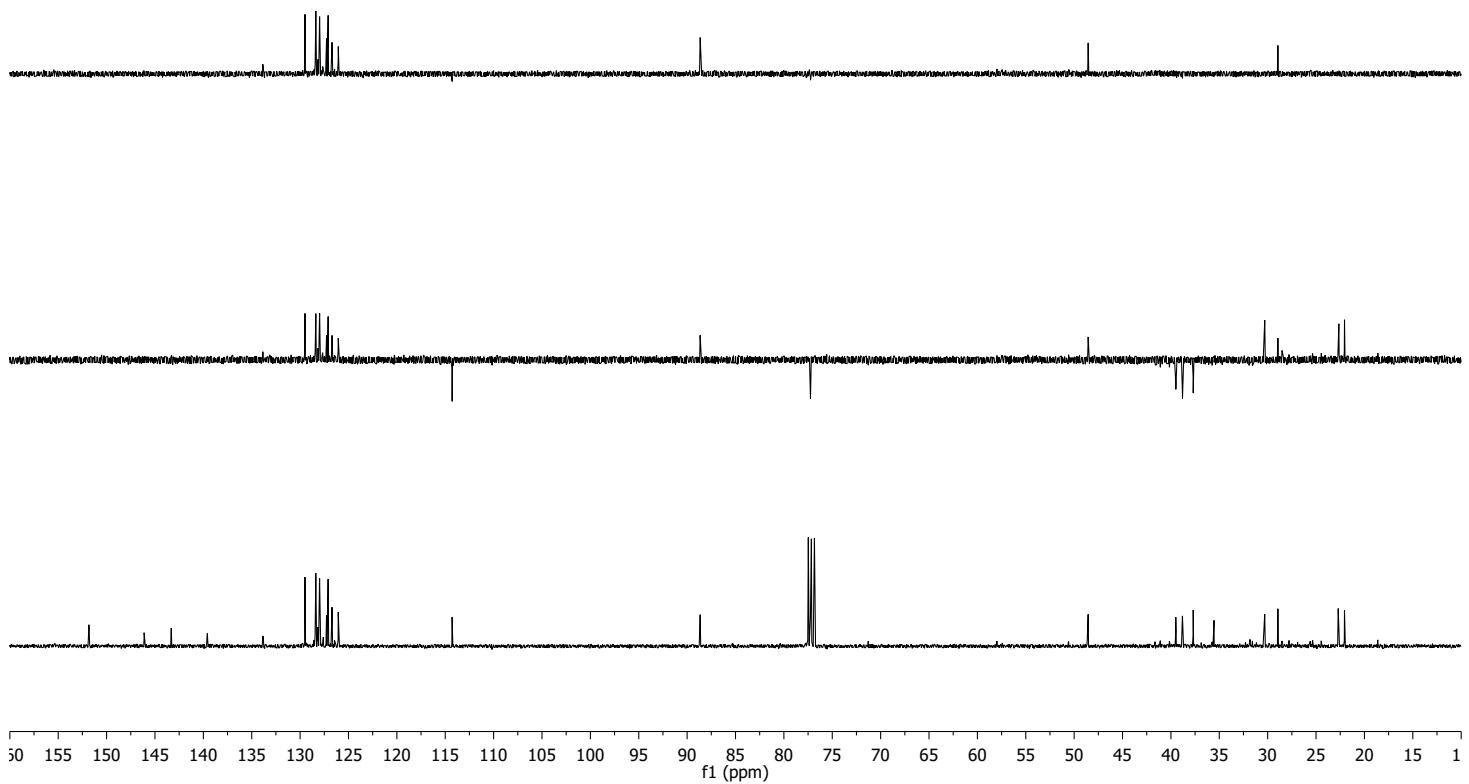


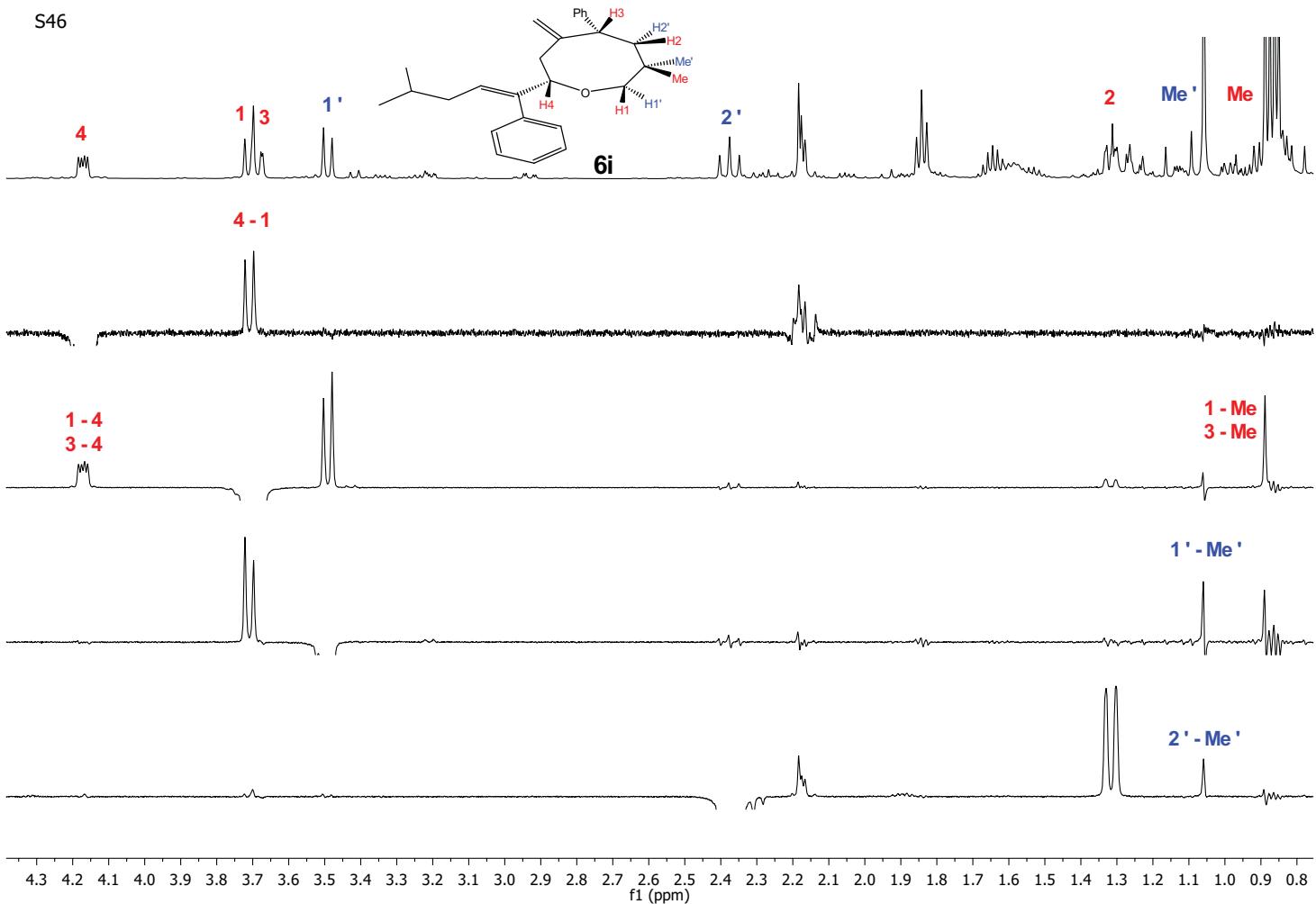


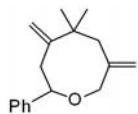
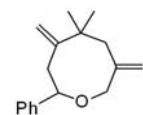
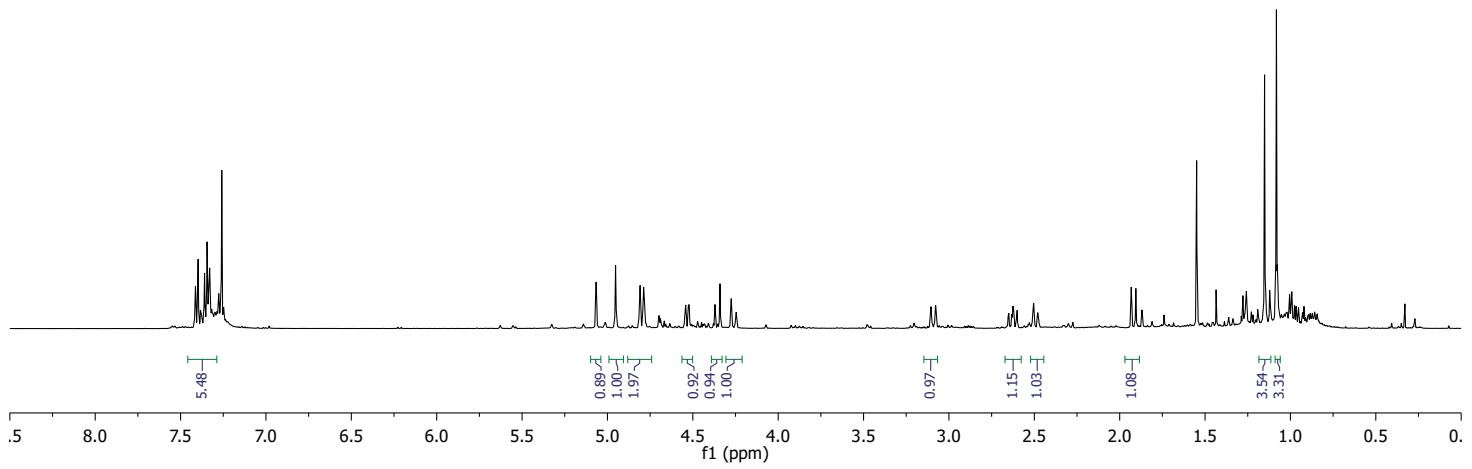
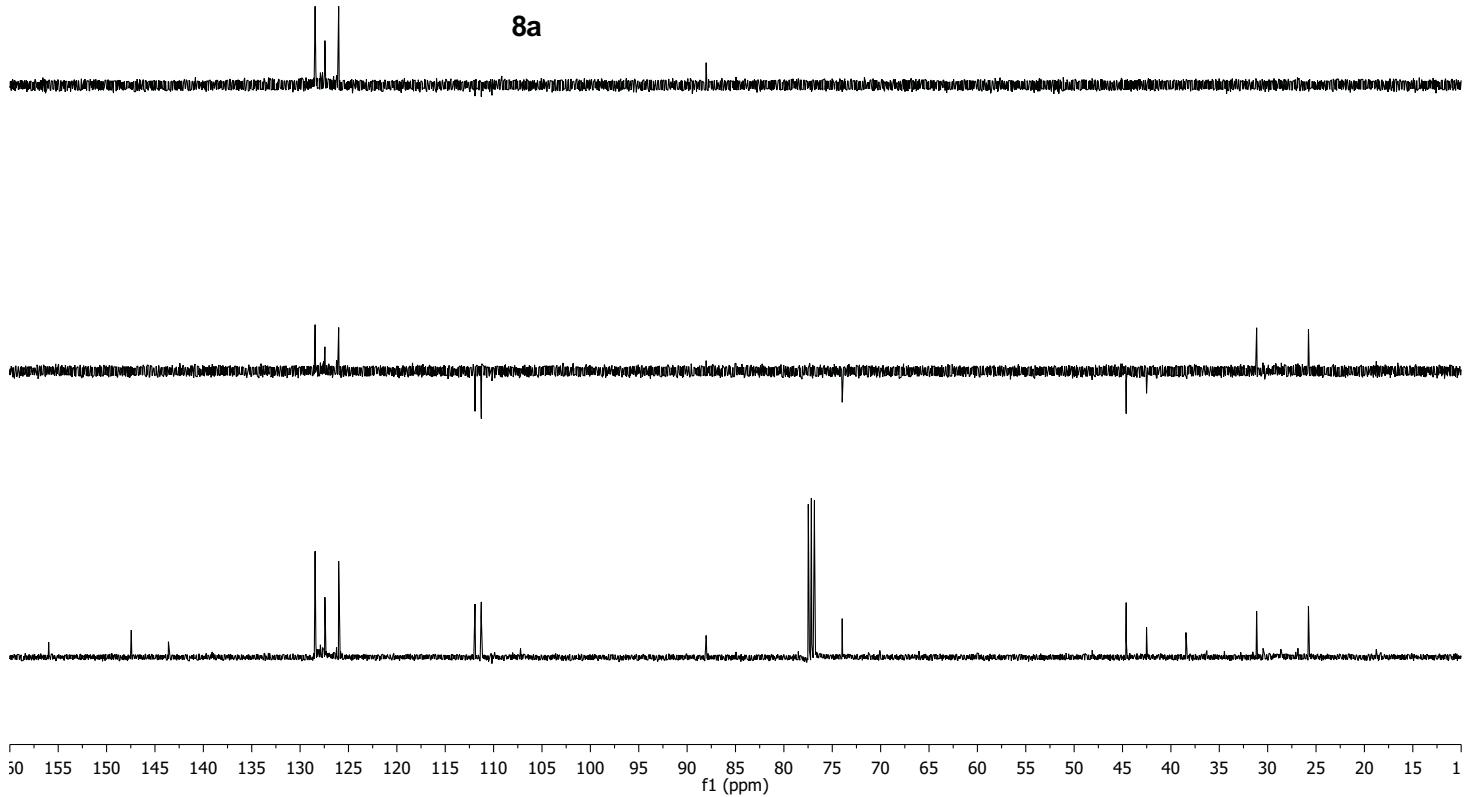


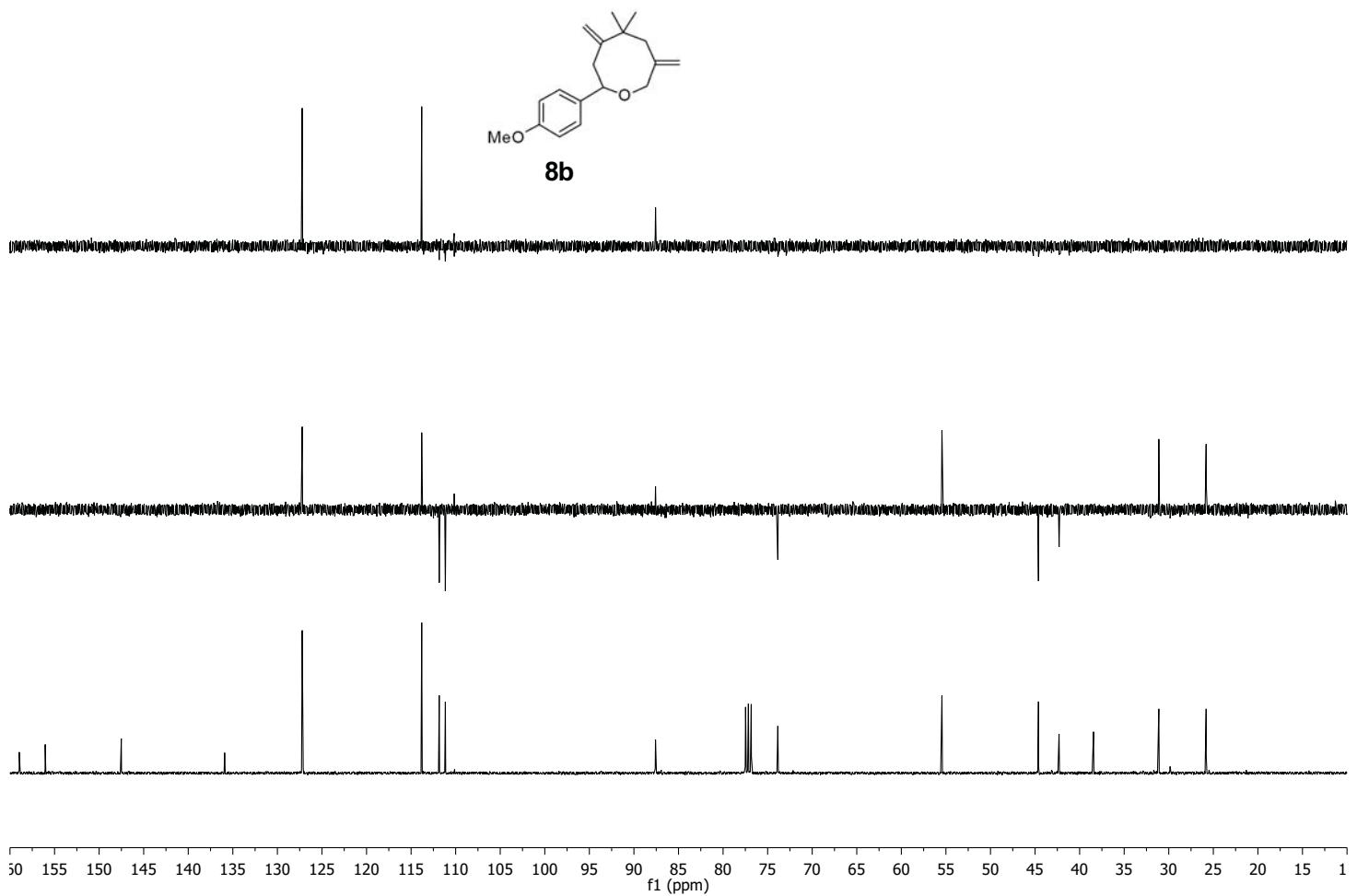
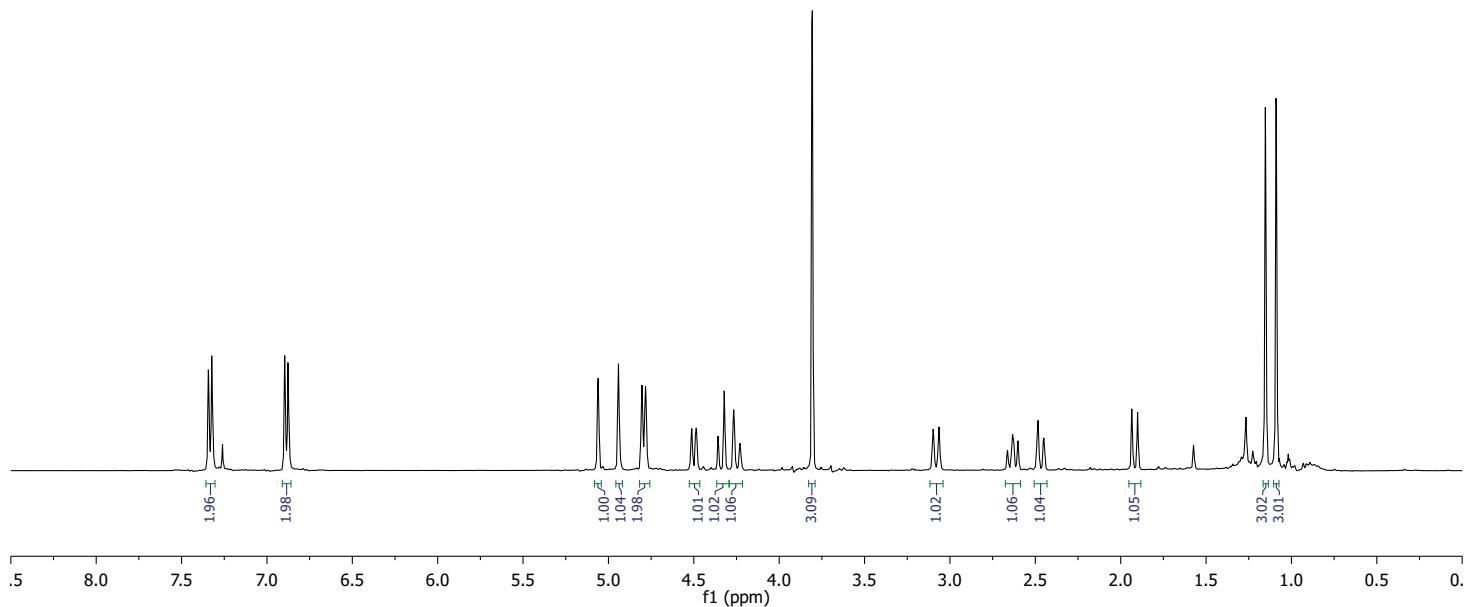
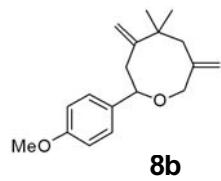


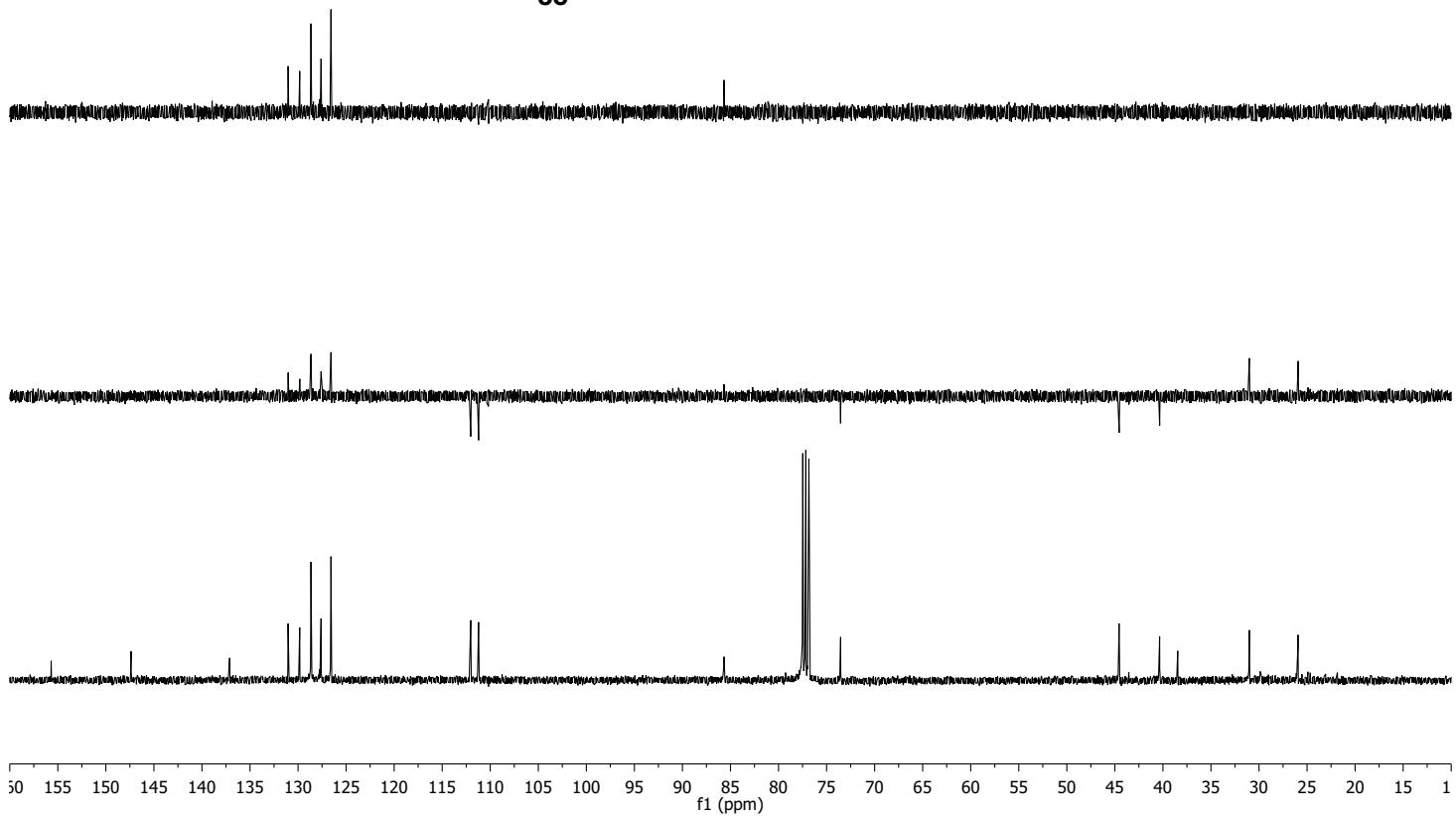
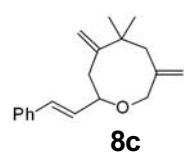
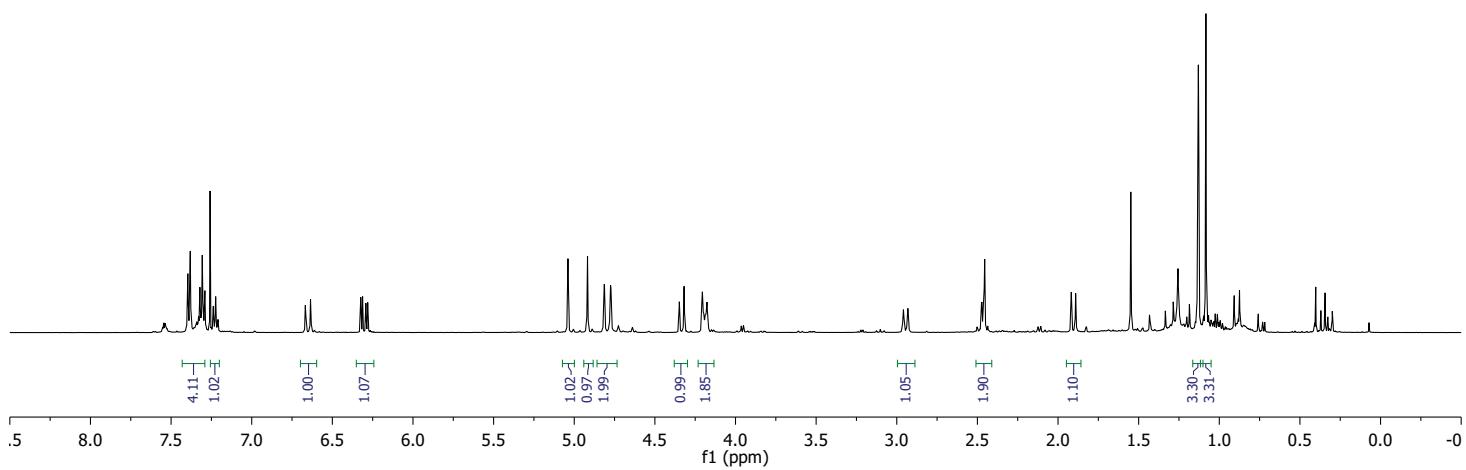
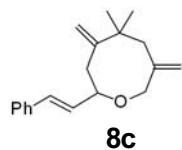


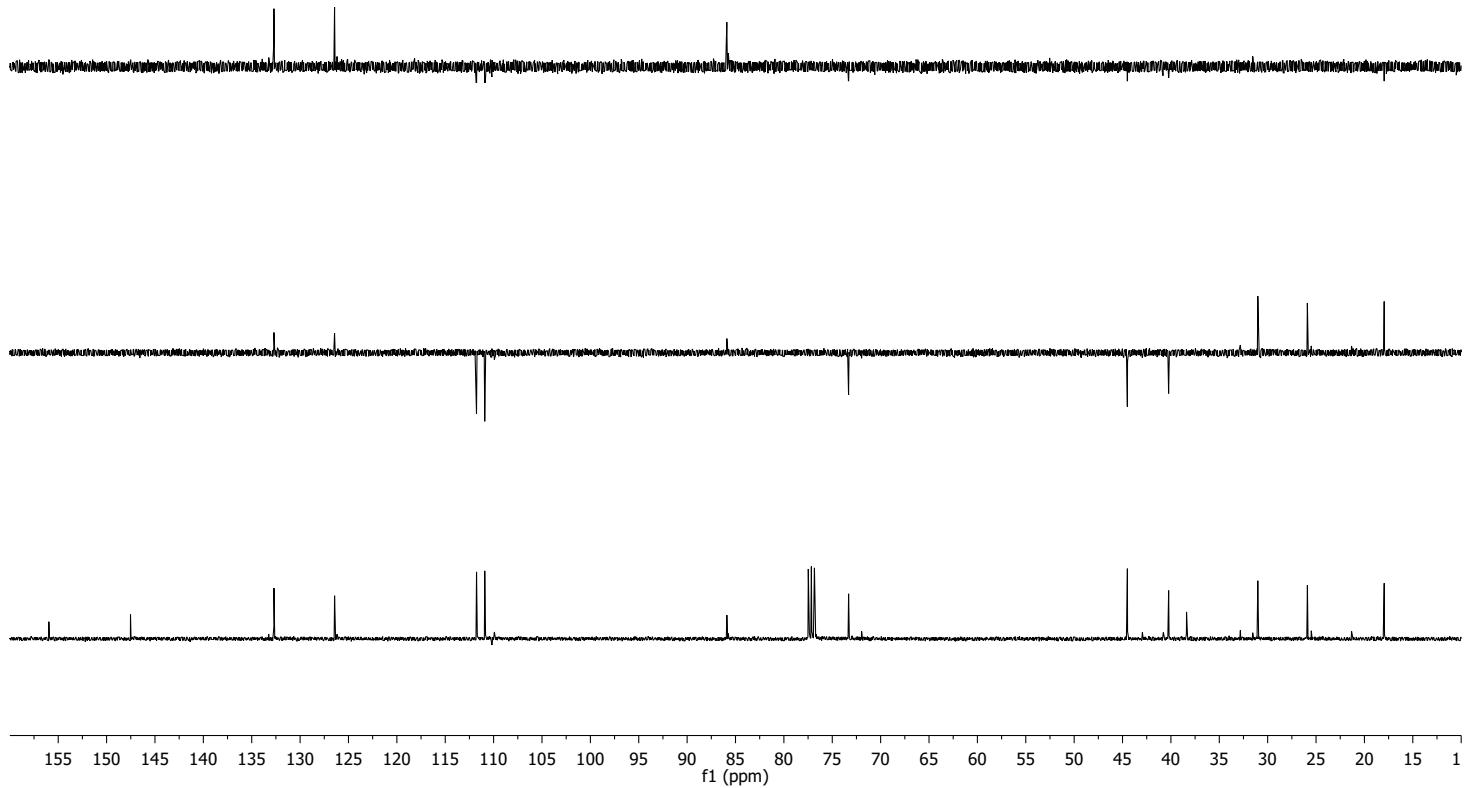
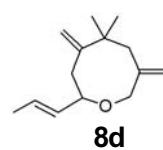
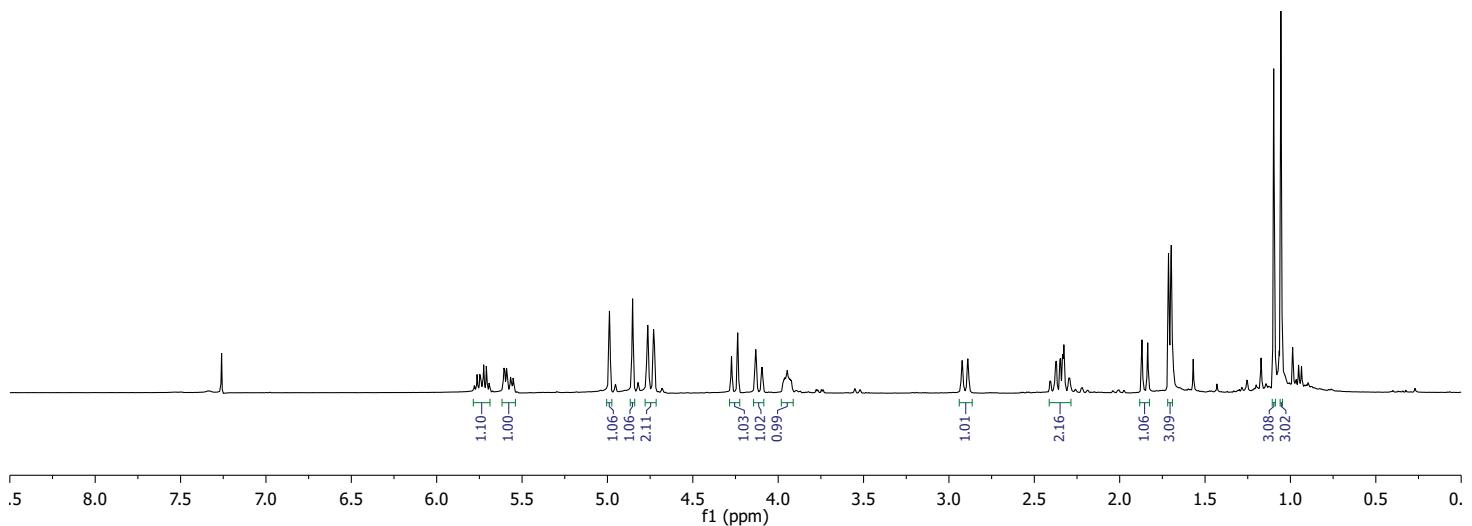
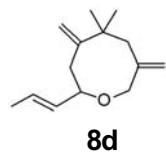
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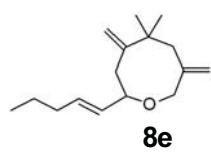


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**8e**

