

Supporting Information

For

**Sigmatropic Rearrangements as Tools for Amino Acid and Peptide Modification:
Application of the Allylic Sulfur Ylide Rearrangement to the Preparation of Neoglyco- and
Other Conjugates**

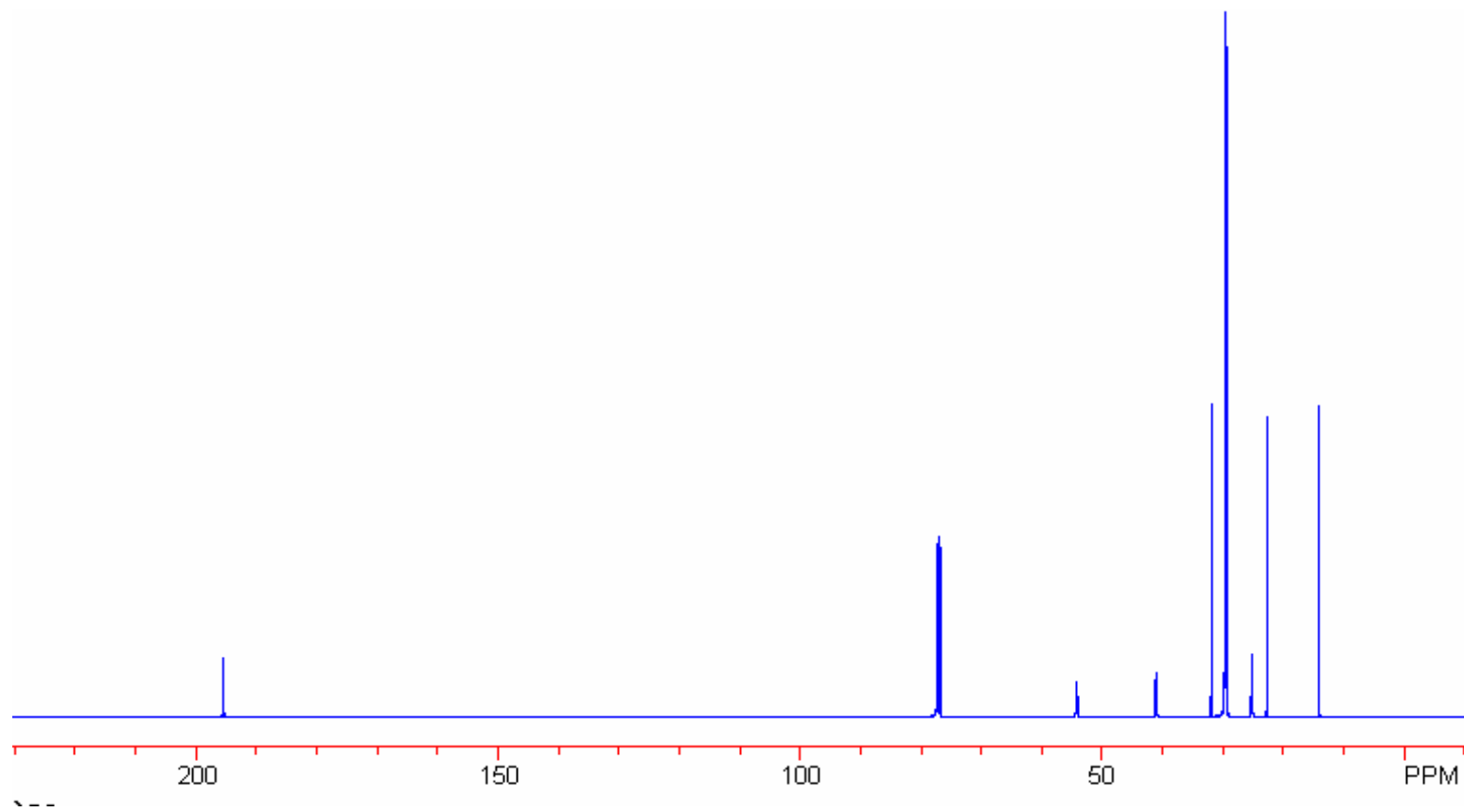
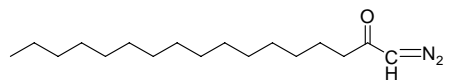
David Crich, Yekui Zou and Franck Brebion*

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Chicago Illinois 60607-7061

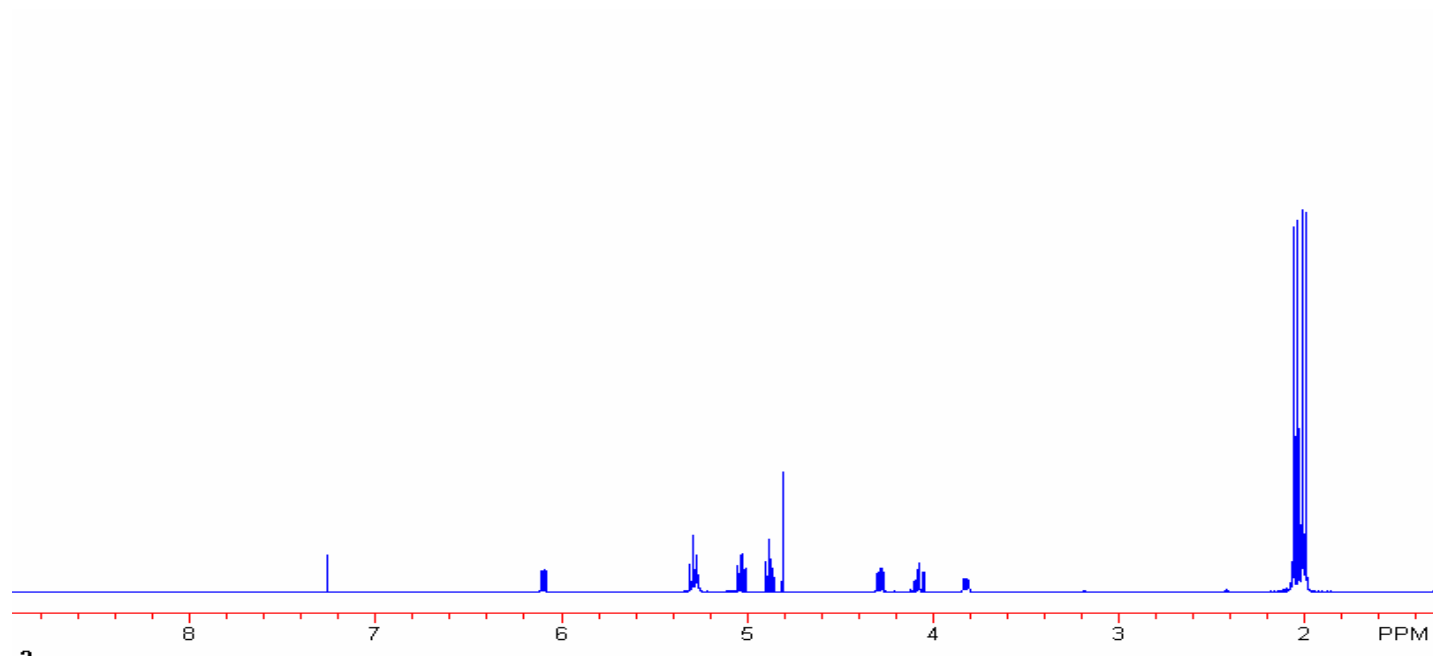
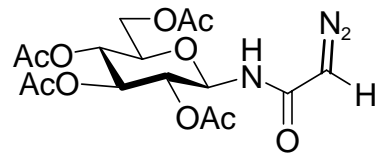
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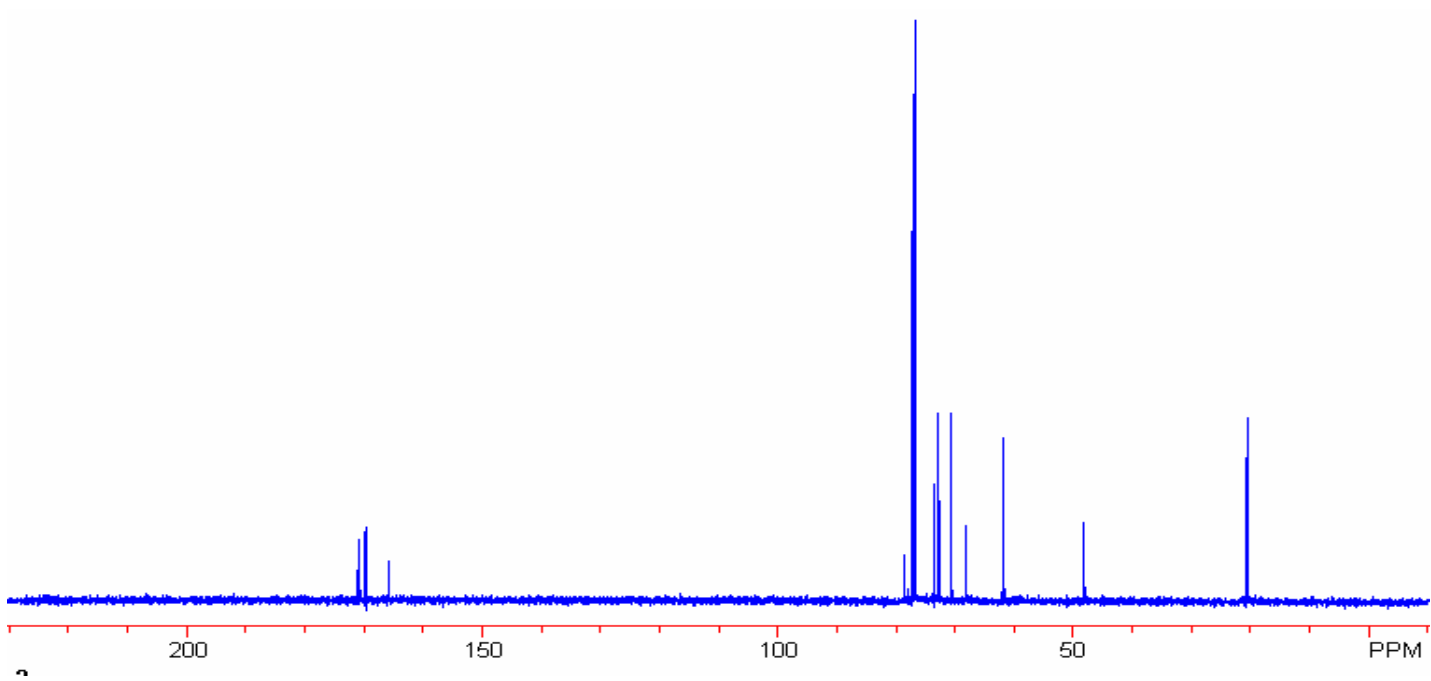
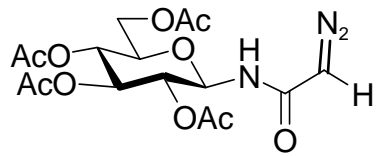
Compound	
General Experimental	S-3
1-Diazo-2-heptadecanone	S-4,5
<i>N</i> -(2,3,4,6-Tetra- <i>O</i> -acetyl- β -D-glucopyranosyl)-diazoacetamide	S-6,7
<i>N</i> -(2,3,6,2',3',4',6'-Hepta- <i>O</i> -acetyl- β -cellobiosyl)-diazoacetamide	S-8,9
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(4-ethoxycarbonyl-1-buten-4-yl)- <i>L</i> -cysteine ethyl ester (3)	S-10,11
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(4-ethoxycarbonyl-2-methyl-1-buten-4-yl)- <i>L</i> -cysteine ethyl ester (4)	S-12,13
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(4-trimethylsilanyl-1-buten-4-yl)- <i>L</i> -cysteine ethyl ester (5)	S-14,15
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(2-methyl-5-oxo-4-icosyl)- <i>L</i> -cysteine ethyl ester (6)	S-16,17
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(4-ethoxycarbonyl-1-buten-4-yl)-glutathione dimethyl ester (8)	S-18,19
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(4-phenyl-1-buten-4-yl)-glutathione dimethyl ester (9)	S-20,21
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(5-oxo-4-icosyl)-glutathione dimethyl ester (10)	S-22,23
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(1-tetradecen-4-yl)-glutathione dimethyl ester (11)	S-24,25
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(1-tridecafluorododecen-4-yl)-glutathione dimethyl ester (12)	S-26,27
<i>N</i> -(2,3,4,6-Tetra- <i>O</i> -acetyl- β -D-glucopyranosyl)-(2-Hexadecylsulfanyl)-4-pentenamide (16)	S-28,29
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(4- <i>N</i> -(2,3,4,6-Tetra- <i>O</i> -acetyl- β -D-glucopyranosyl)-aminocarbonyl-1-buten-4-yl)- <i>L</i> -cysteine ethyl ester (17)	S-30,31
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(4- <i>N</i> -(2,3,6,2',3',4',6'-hepta- <i>O</i> -acetyl- β -cellobiosyl)-aminocarbonyl-1-buten-4-yl)- <i>L</i> -cysteine ethyl ester (18)	S-32,33
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(4- <i>N</i> -(2,3,4,6-Tetra- <i>O</i> -acetyl- β -D-glucopyranosyl)-aminocarbonyl-1-buten-4-yl)-glutathione dimethyl ester (19)	S-34,35
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(4- <i>N</i> -(2,3,6,2',3',4',6'-hepta- <i>O</i> -acetyl- β -cellobiosyl)-aminocarbonyl-1-buten-4-yl)-glutathione dimethyl ester (20)	S-36,37
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(2-methyl-5-oxo-4-icosyl)- <i>L</i> -cysteinyl- <i>L</i> -alanyl- <i>L</i> -tryptophan methyl ester (21)	S-38,39
<i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>S</i> -(2-methylallyl)- <i>L</i> -cysteinyl- <i>L</i> -alanyl- <i>L</i> - N_{ω} -(2-oxo-heptadecyl)-tryptophan methyl ester (22)	S-40,41

General. Unless otherwise indicated, all reagents were obtained from commercial sources and used without further purification. All reactions were performed under a nitrogen atmosphere, unless otherwise indicated. All NMR spectra were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C with CDCl_3 as solvent, unless otherwise indicated.

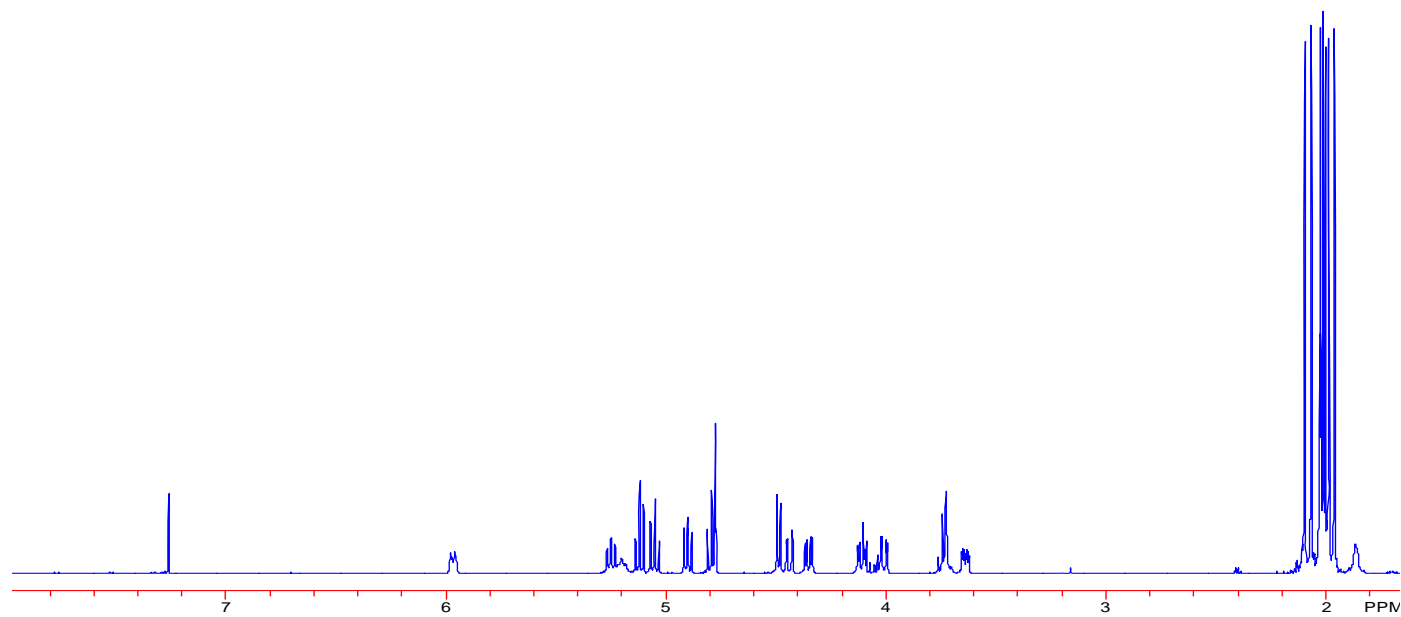
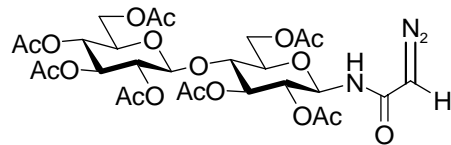


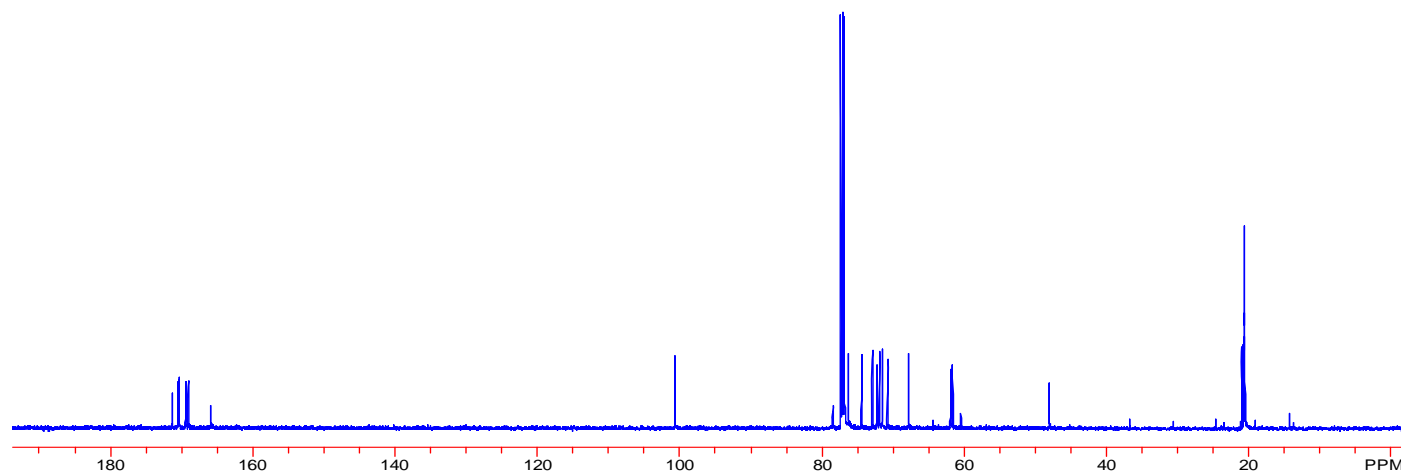
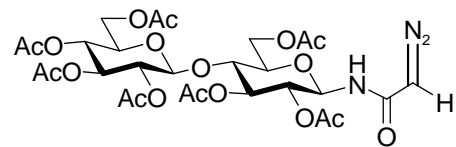
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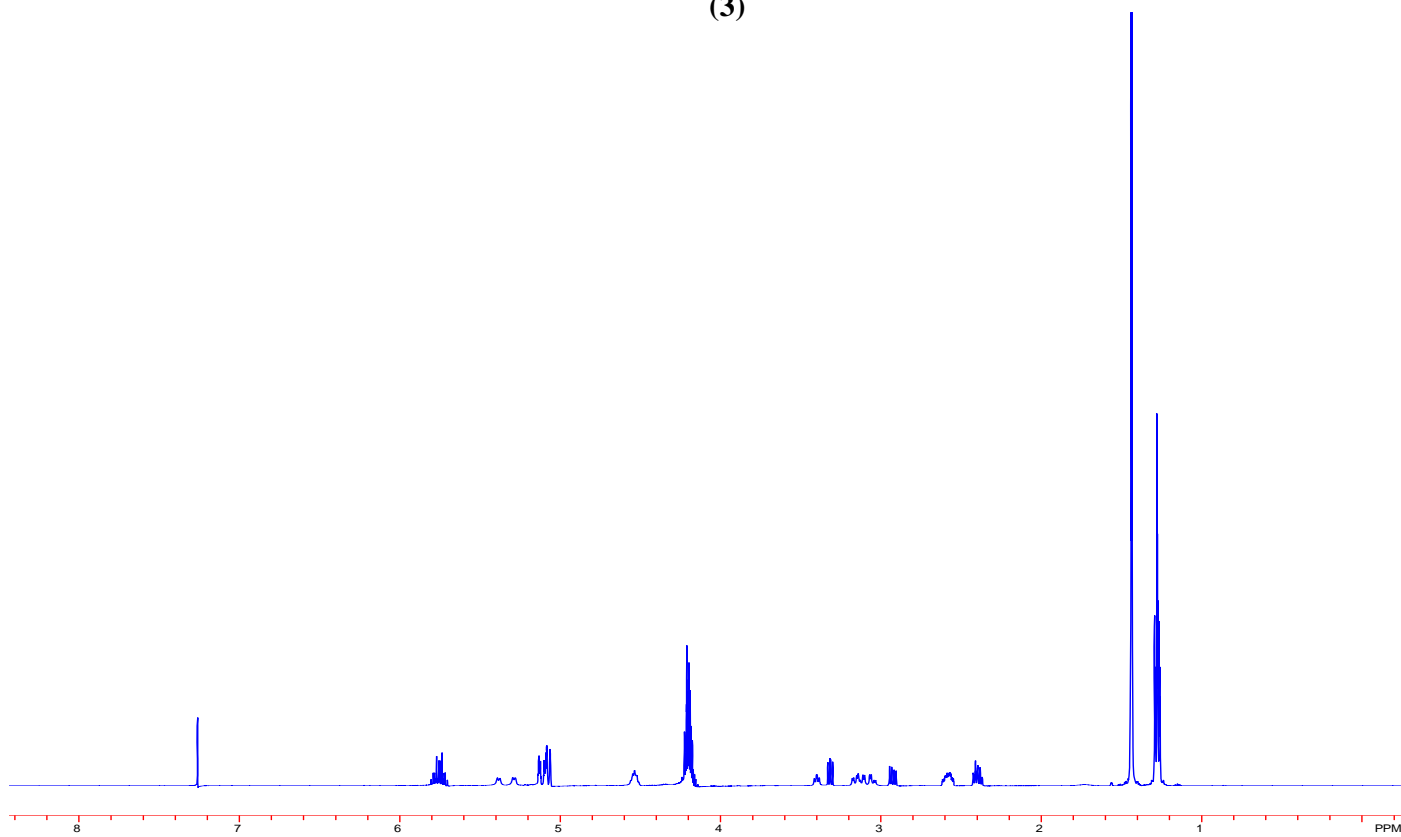
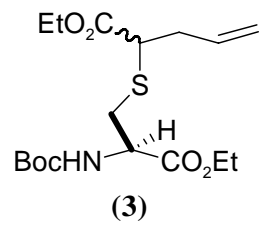


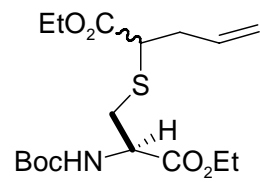


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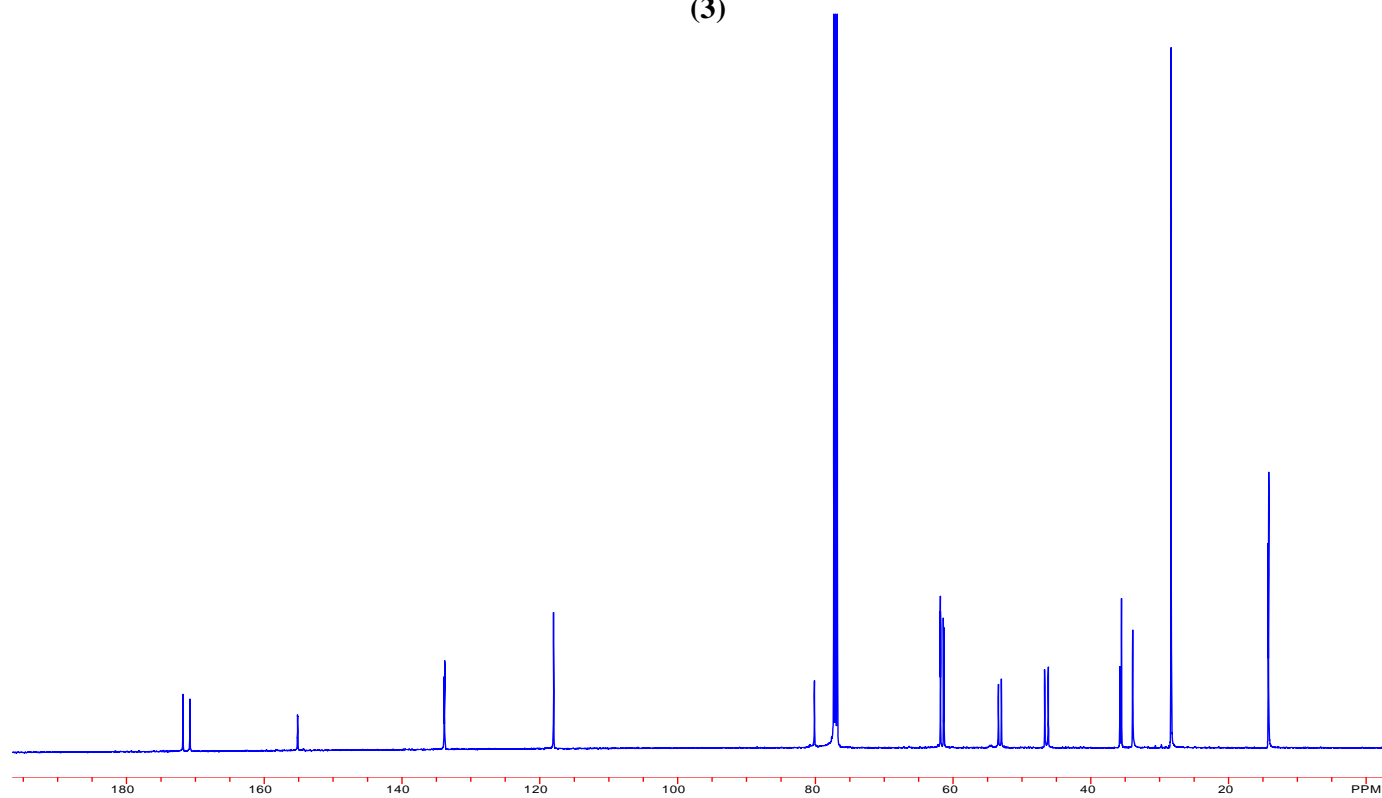


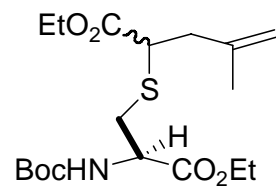




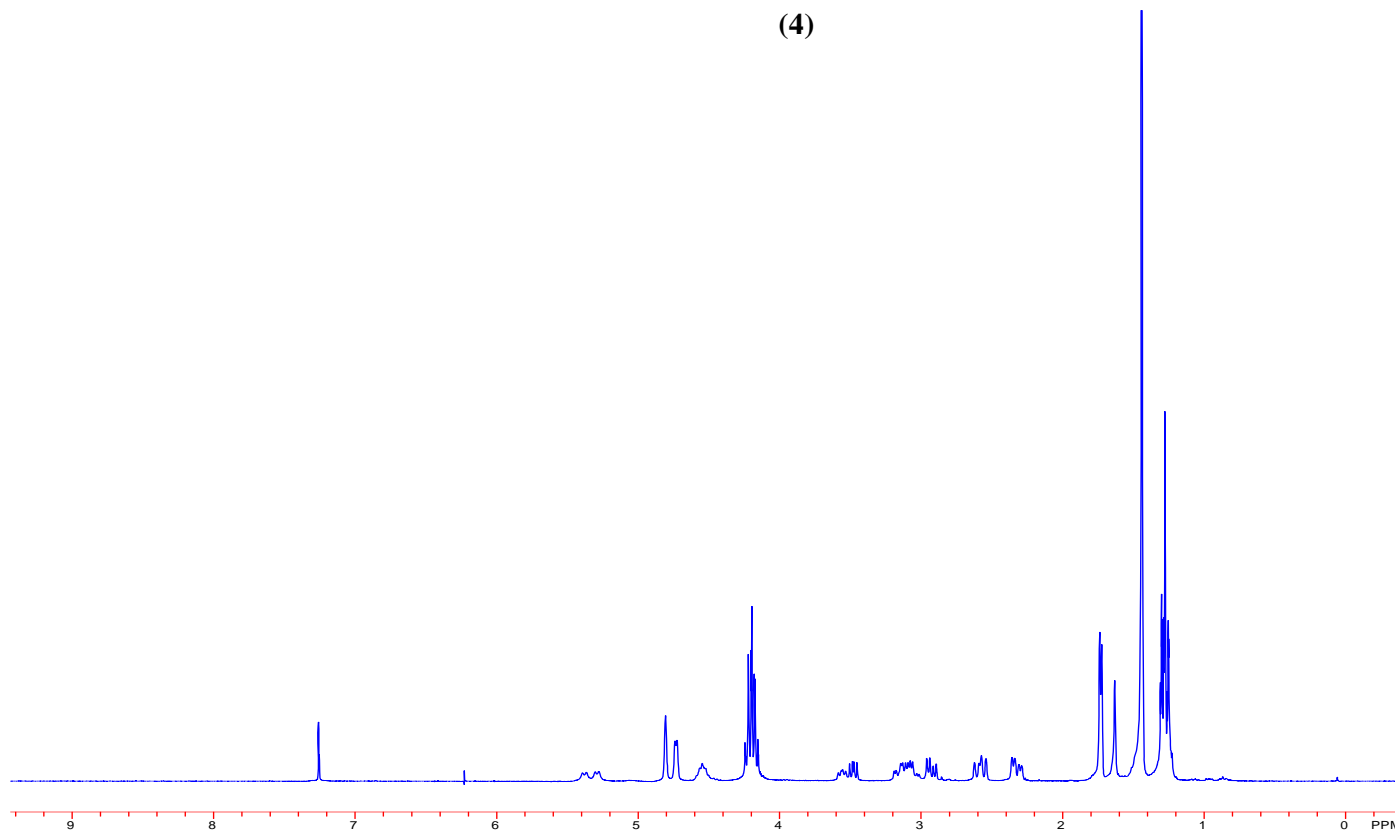


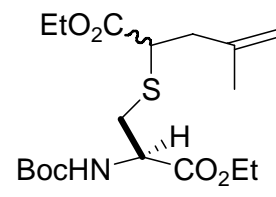
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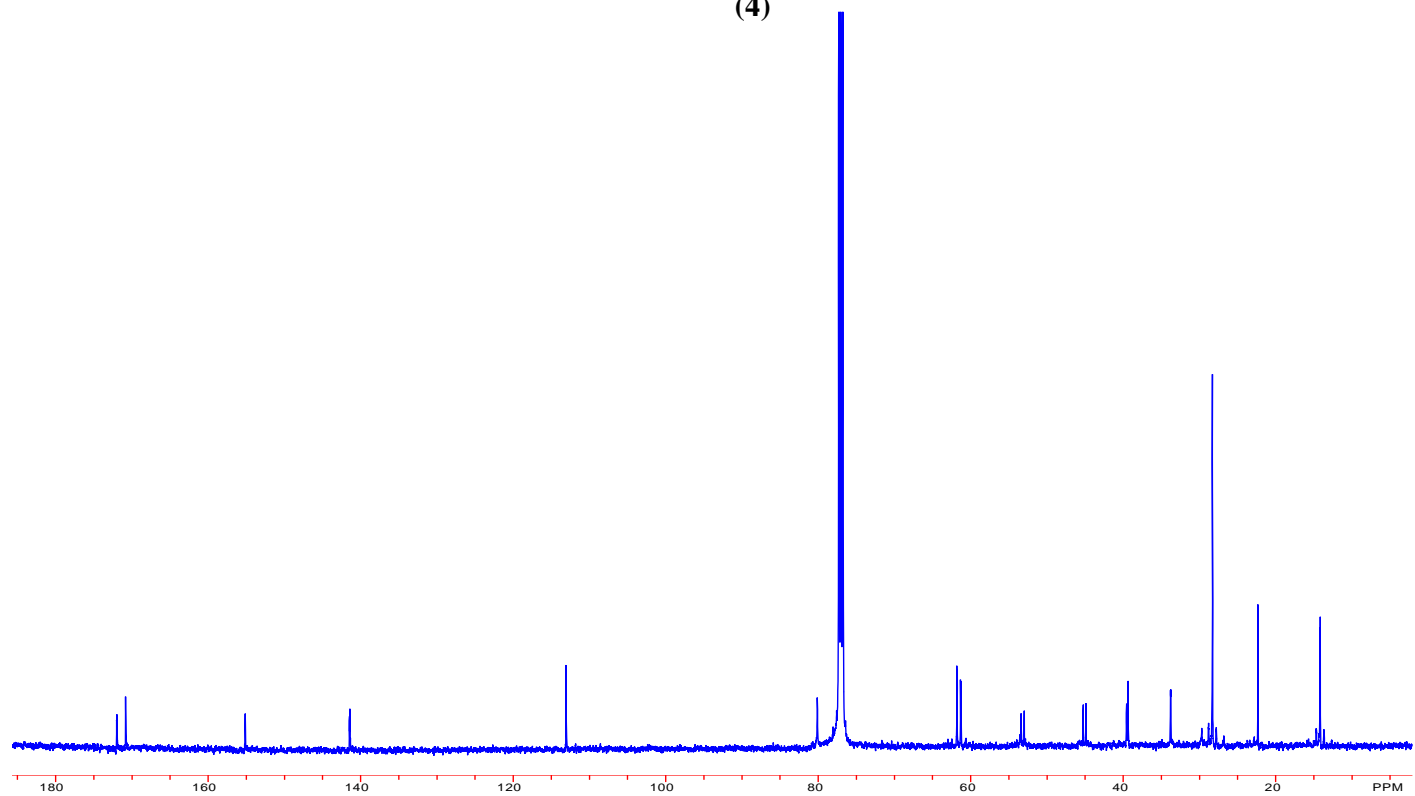


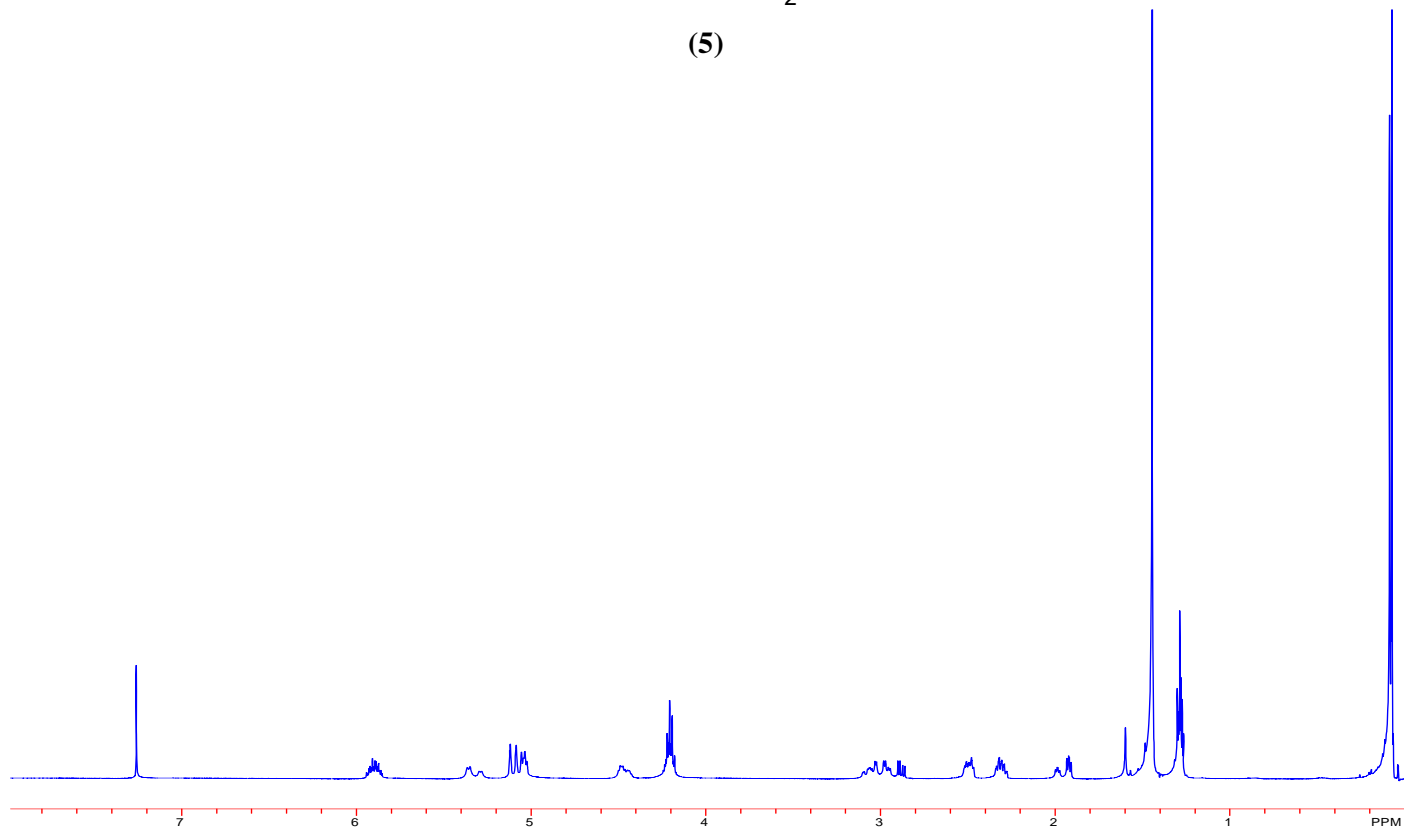
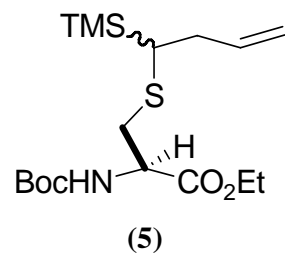
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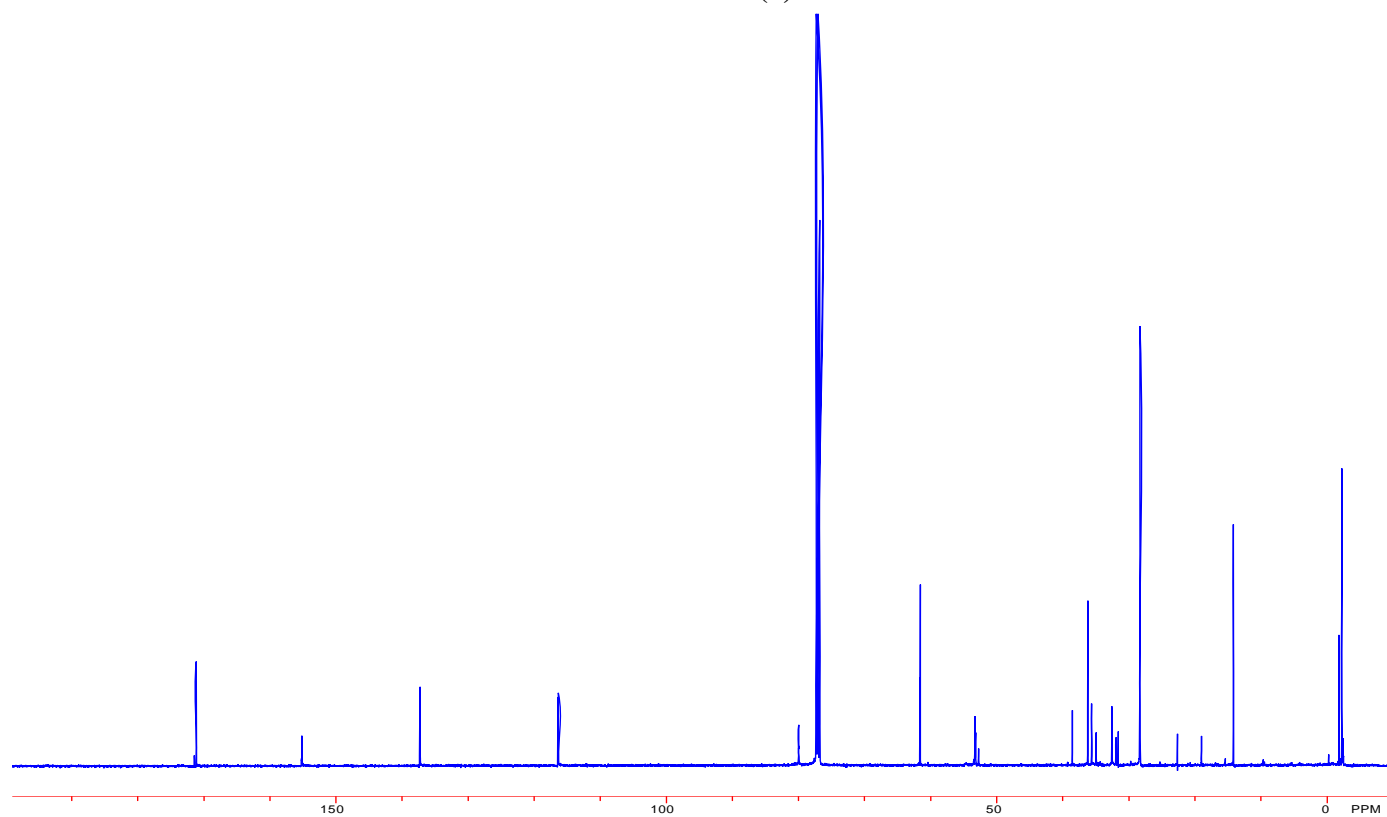
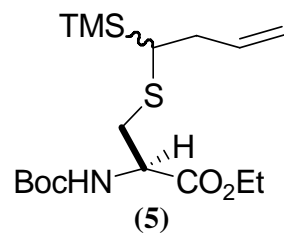


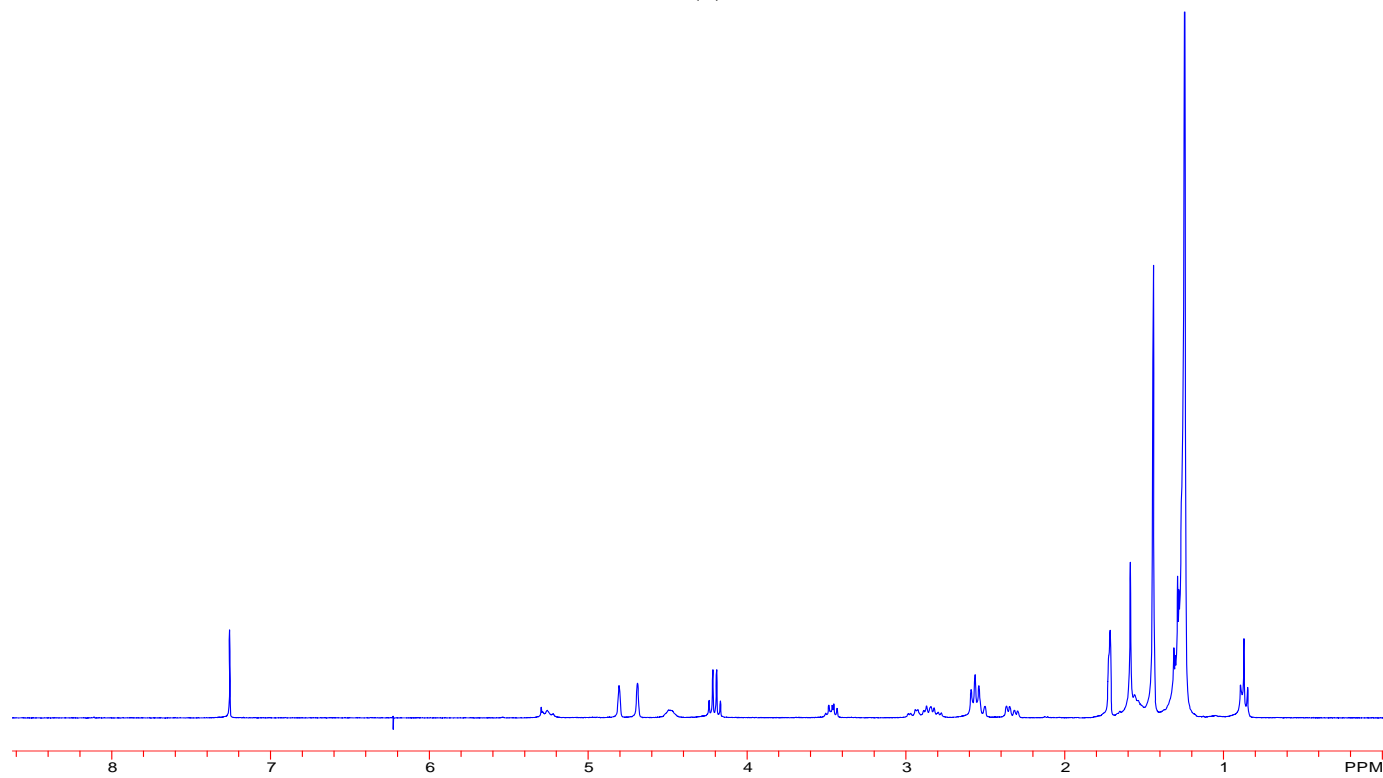
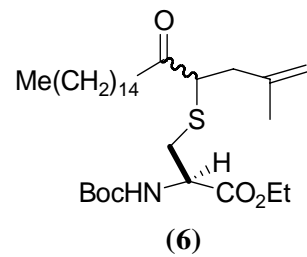


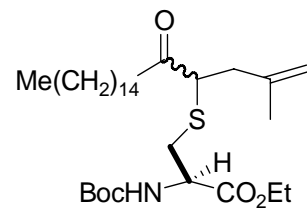
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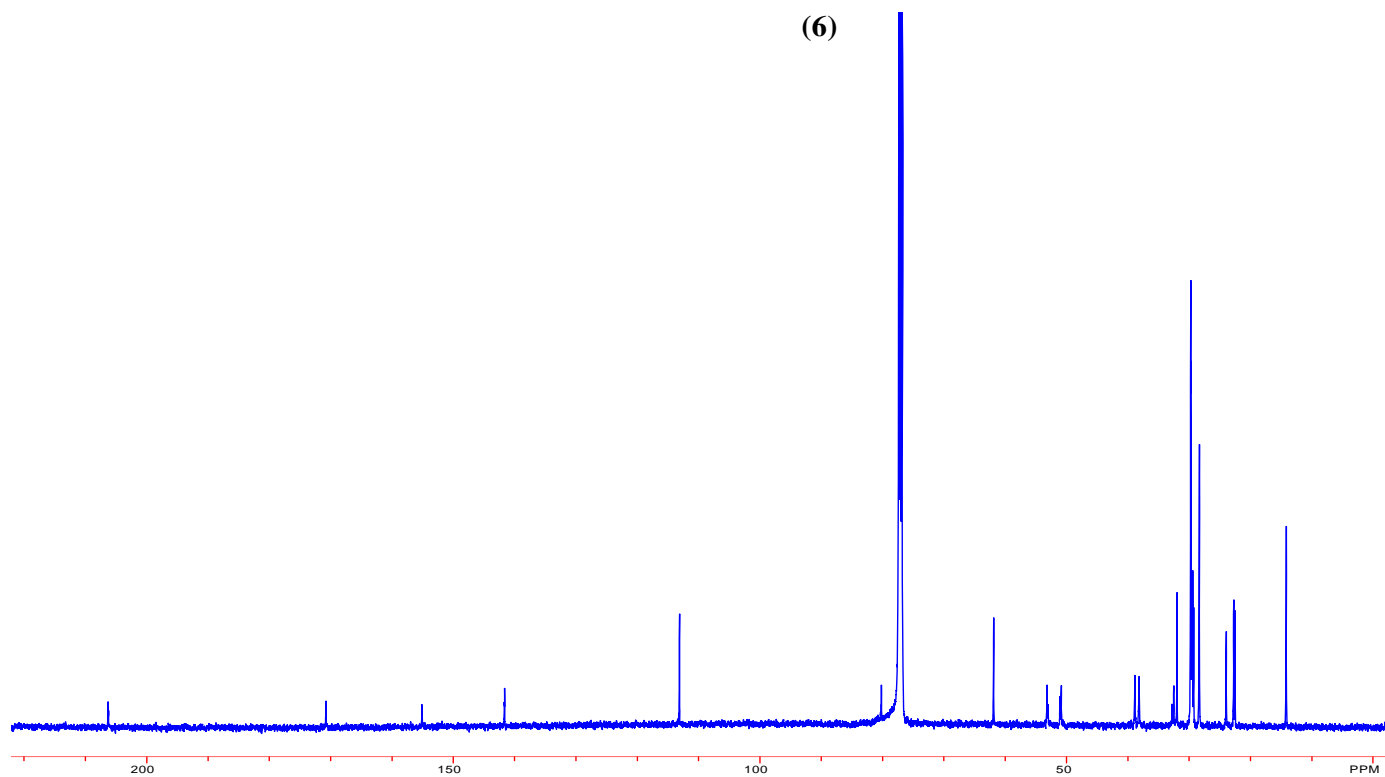


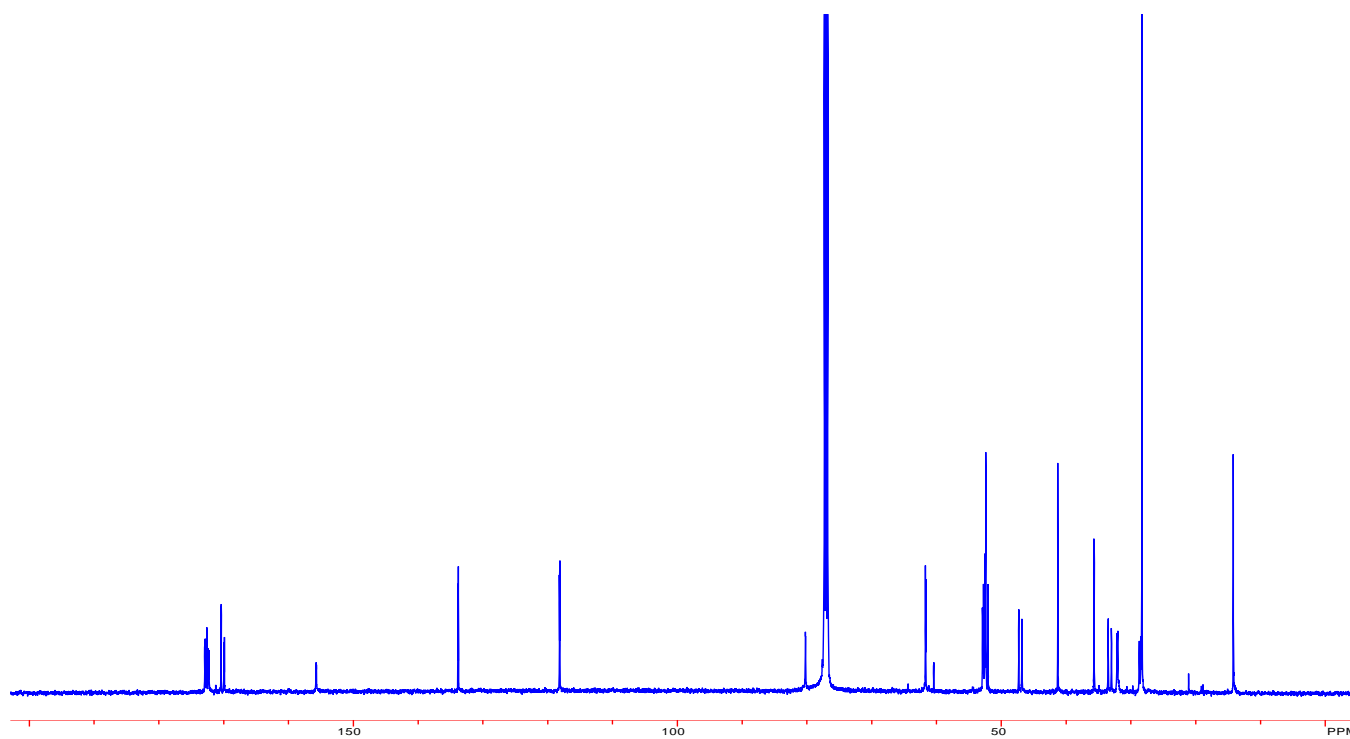
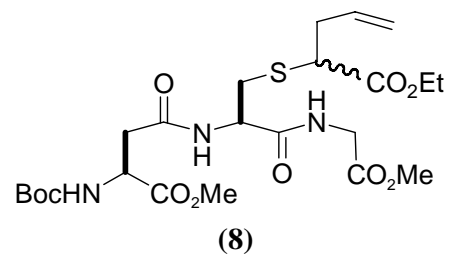


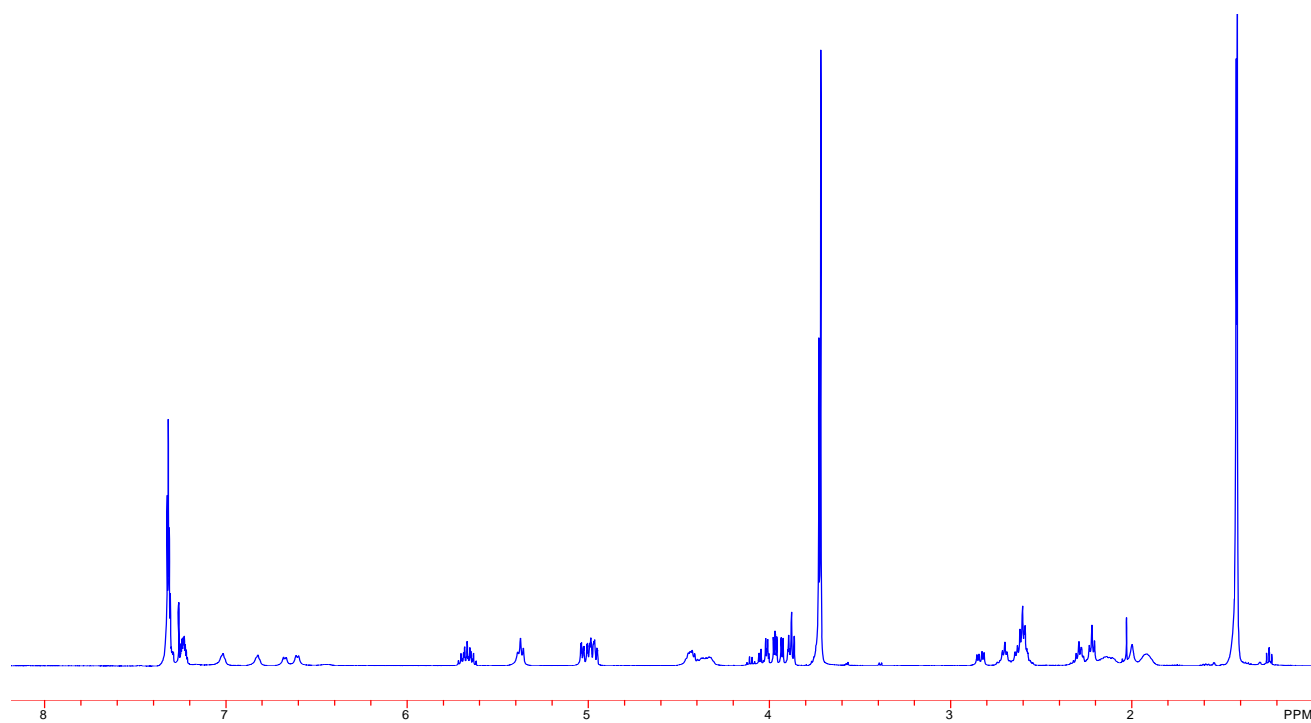
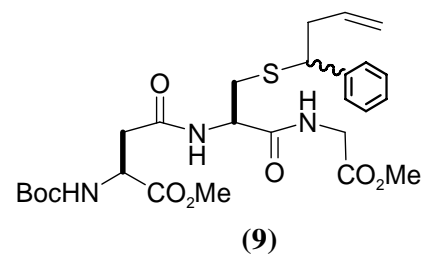


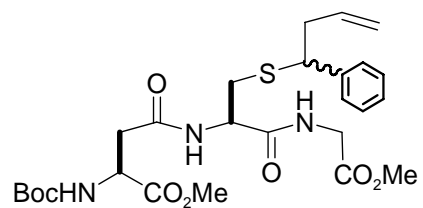


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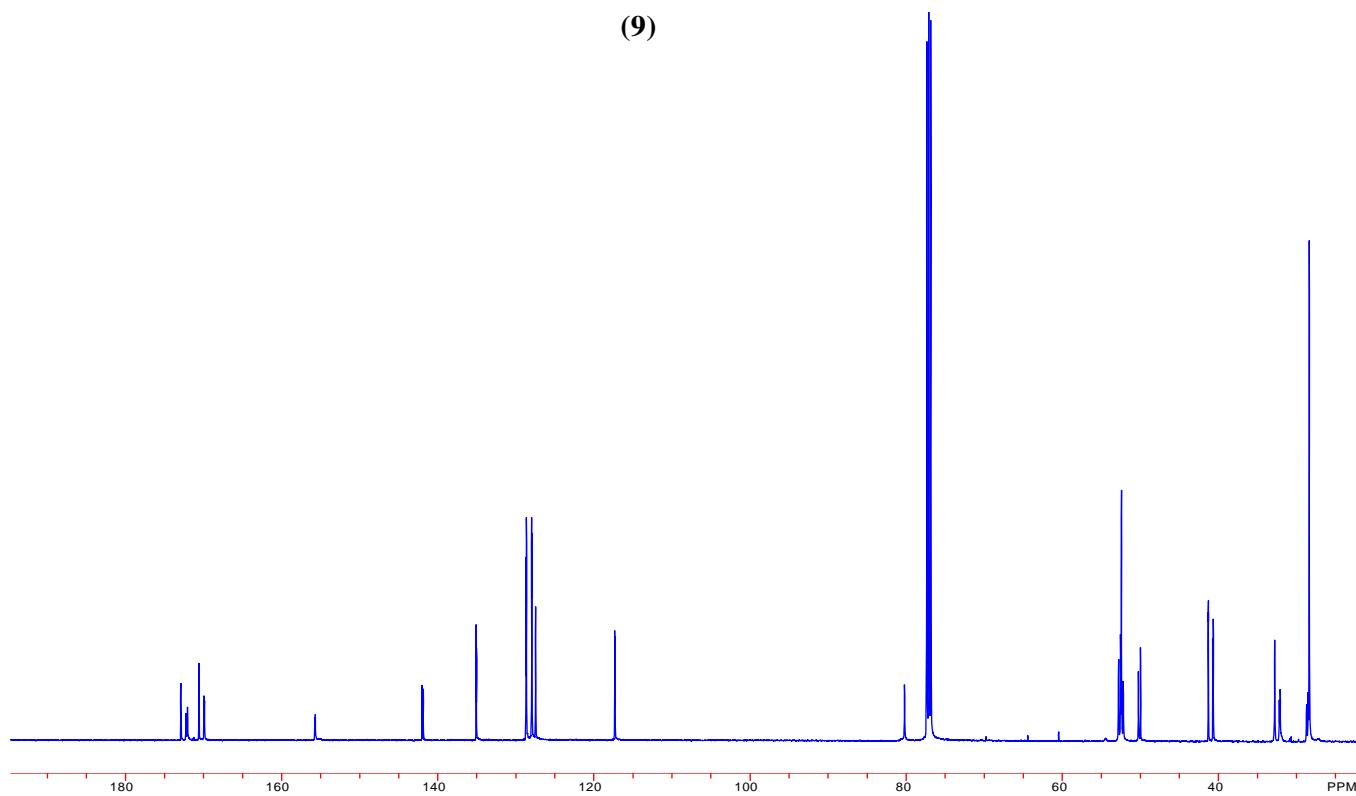


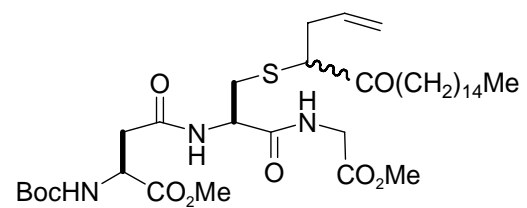




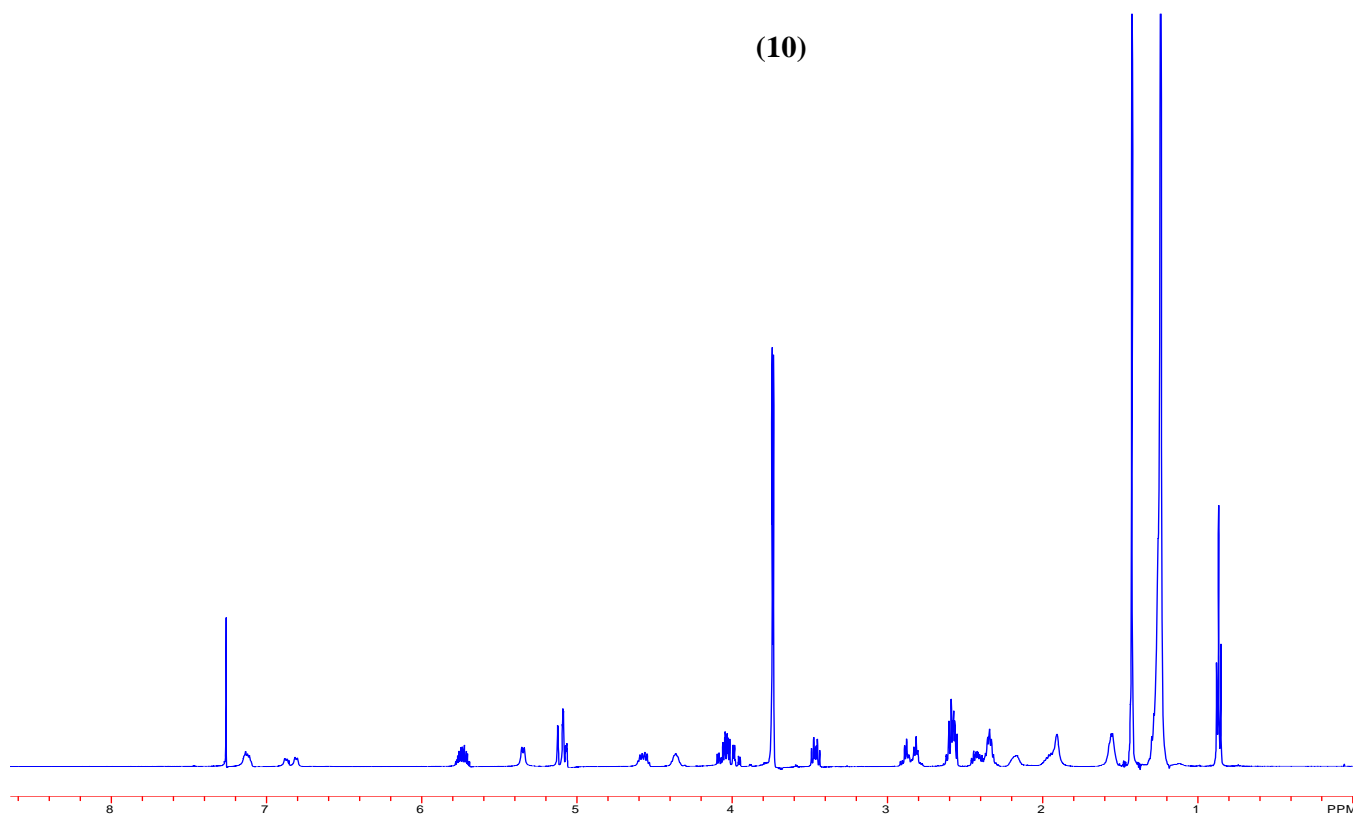


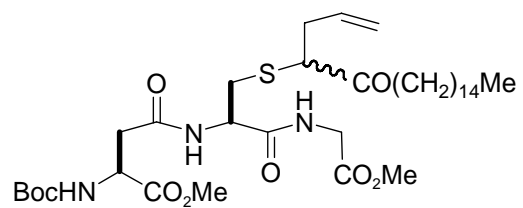
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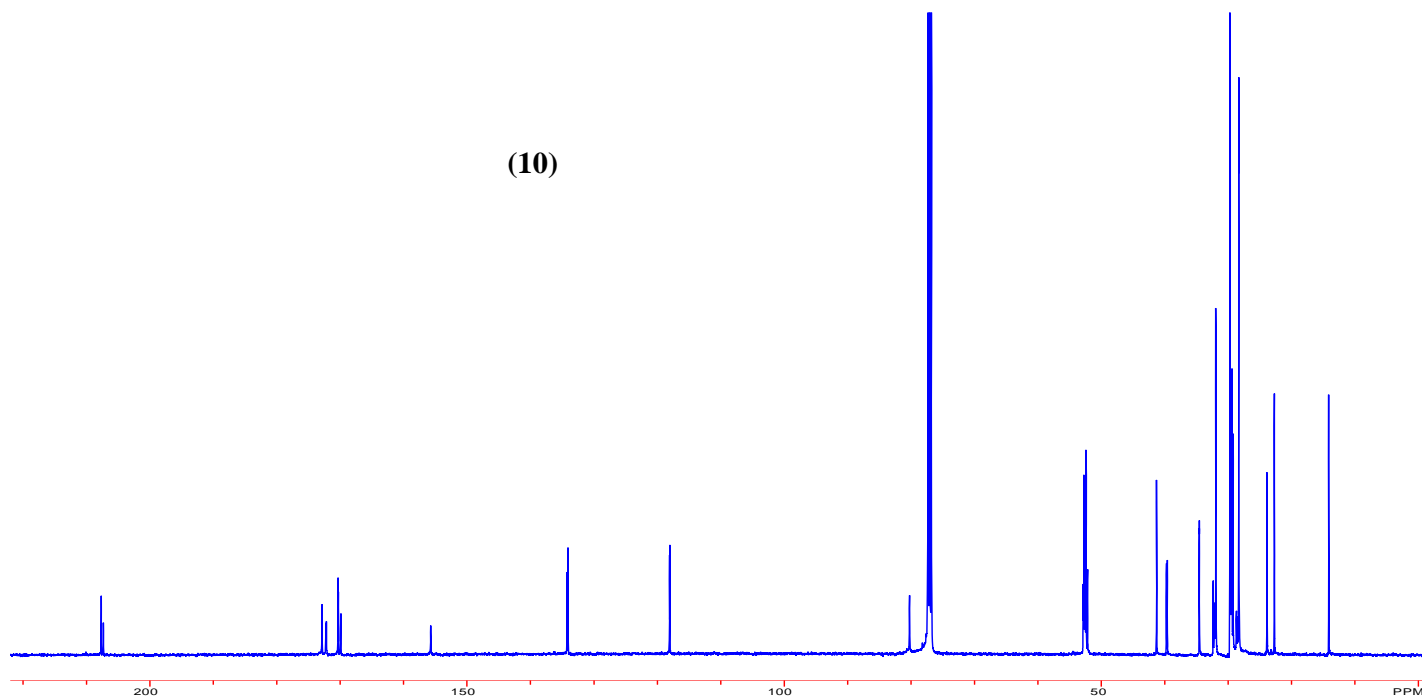


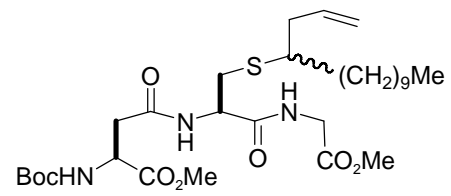
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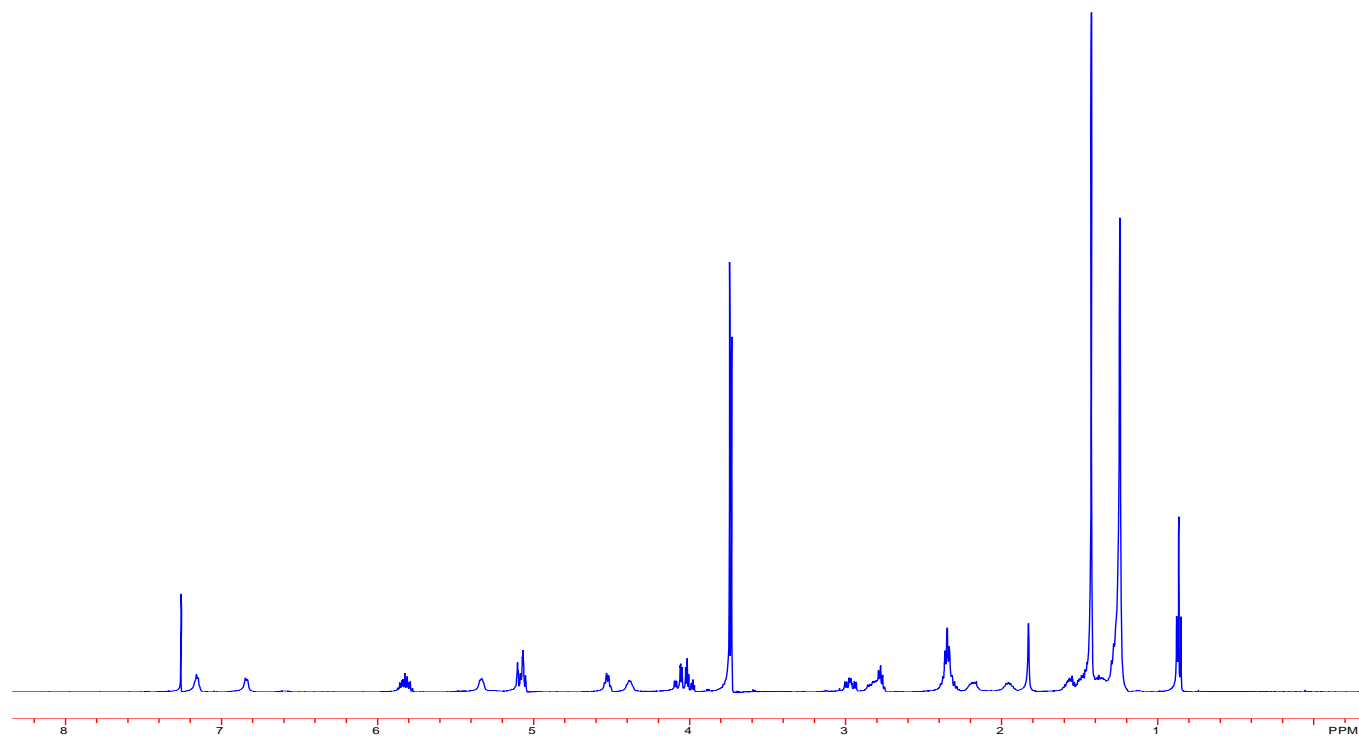


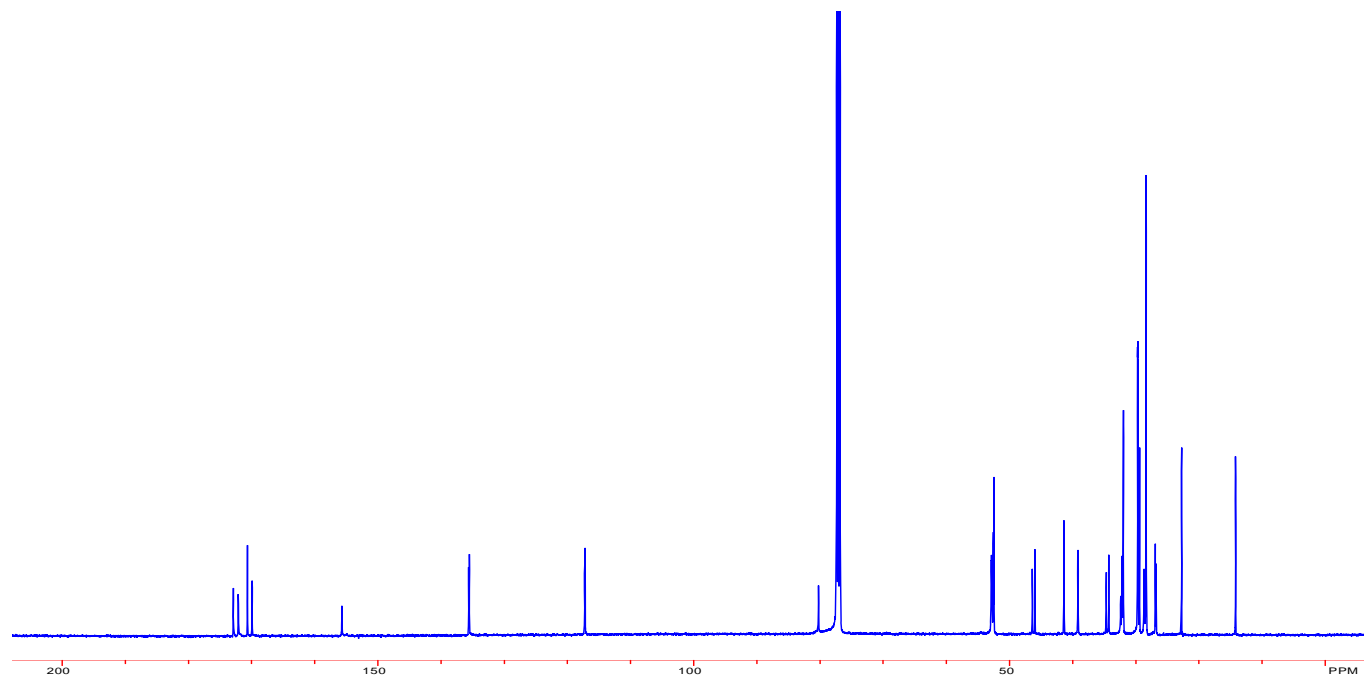
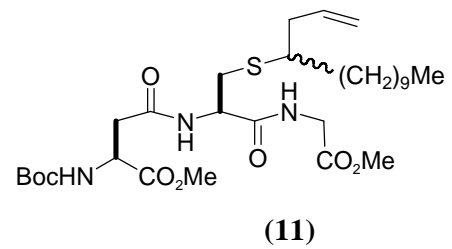
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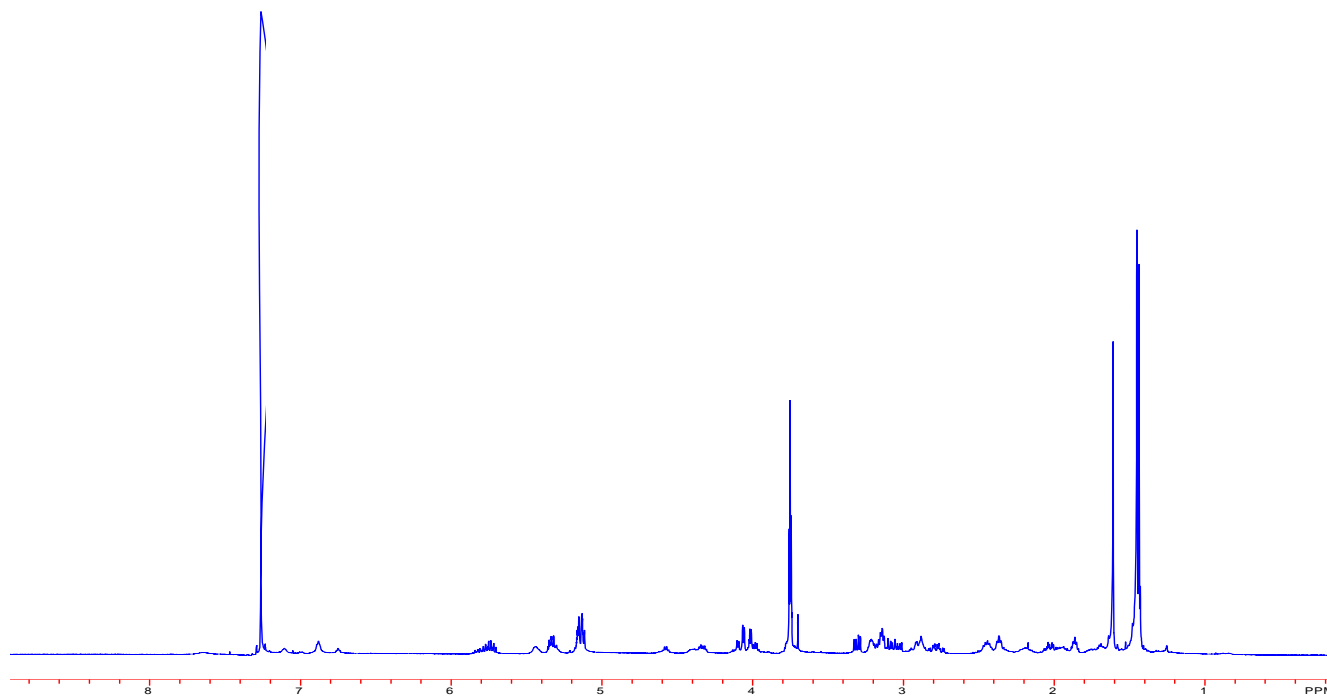
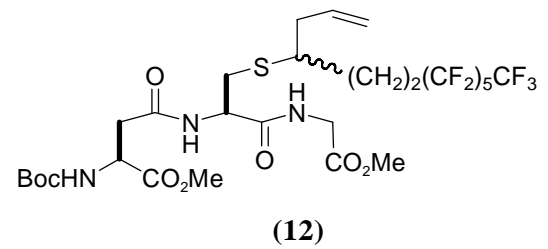


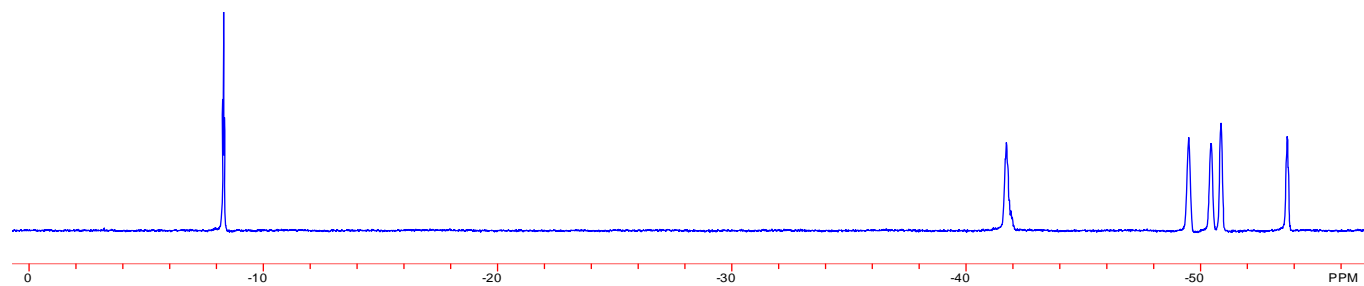
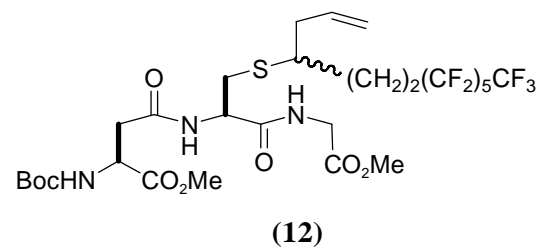


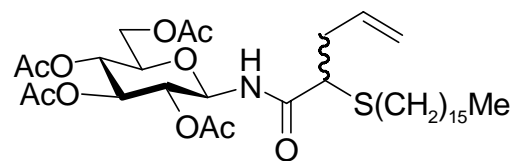
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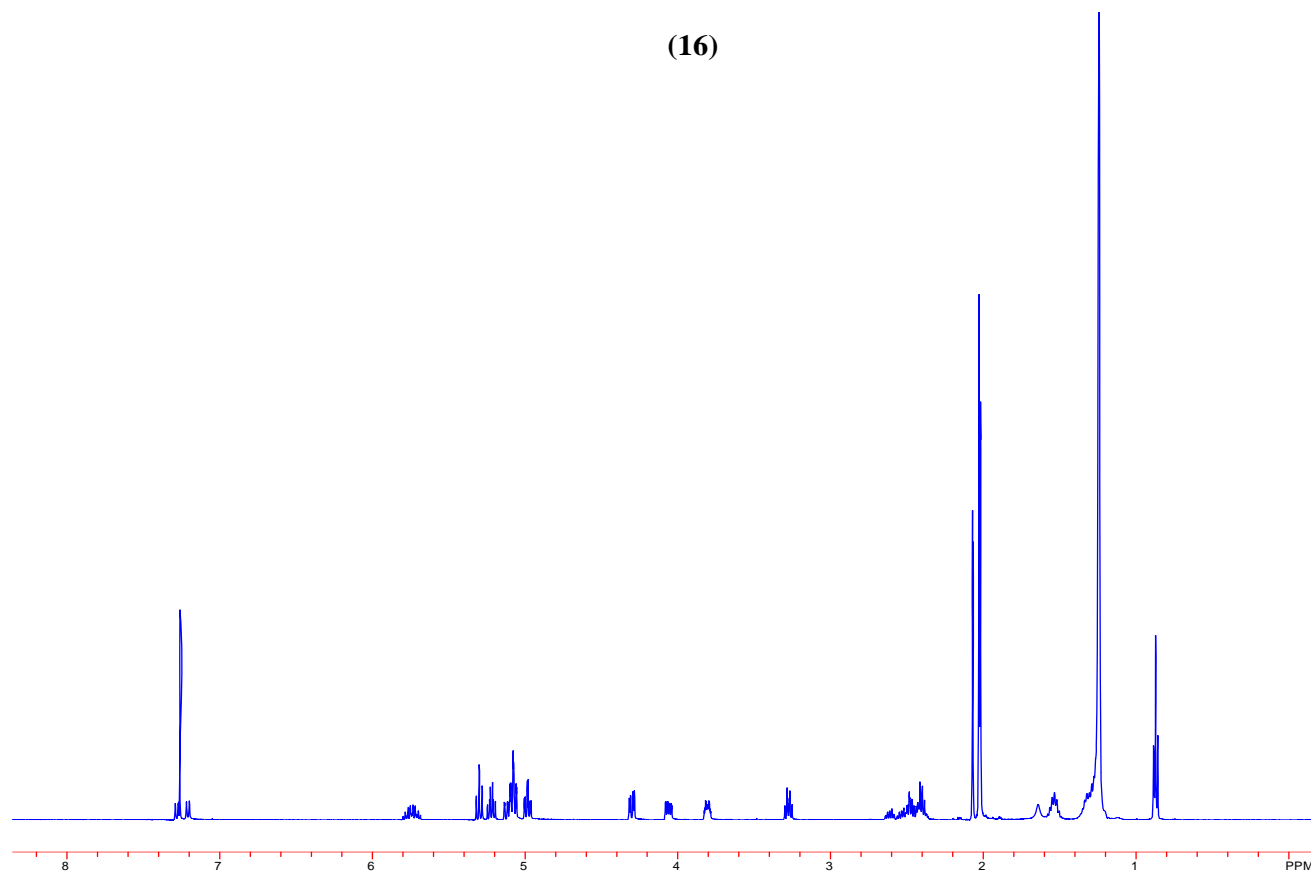


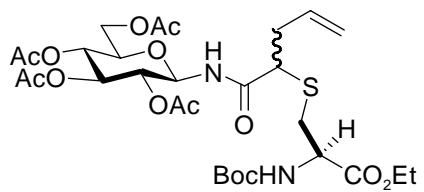




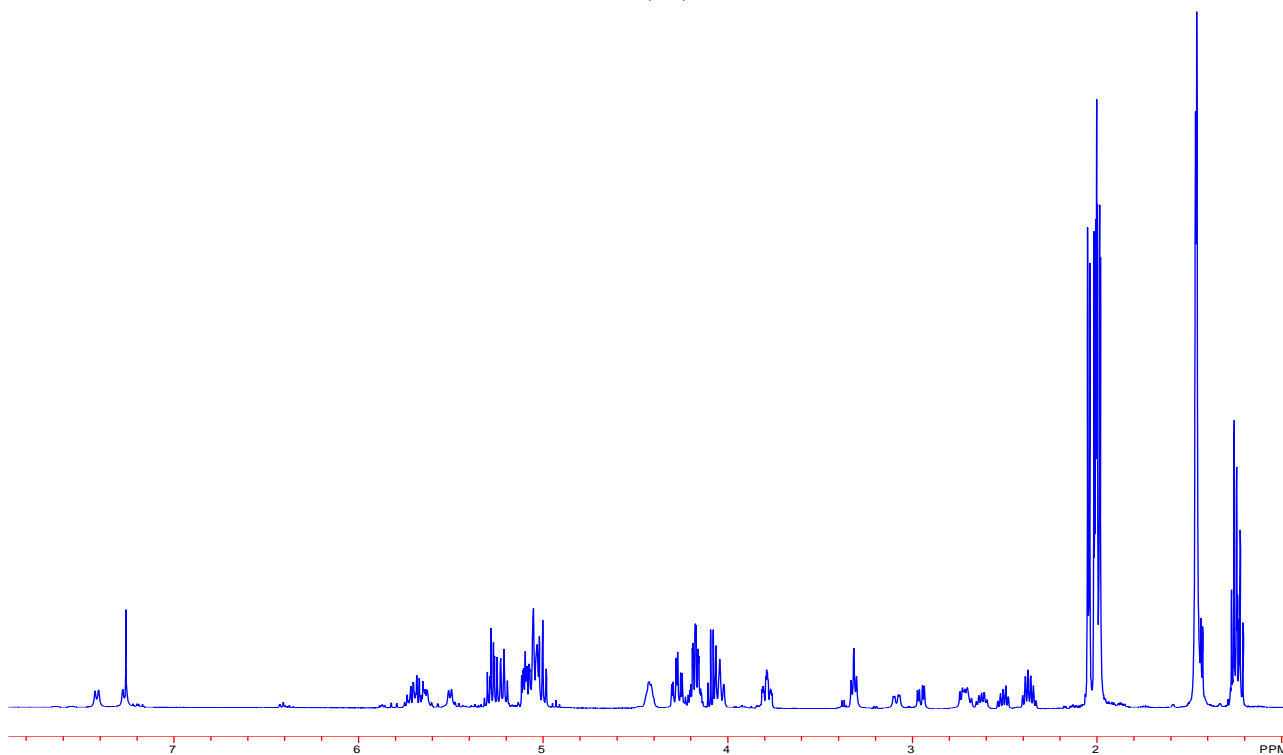


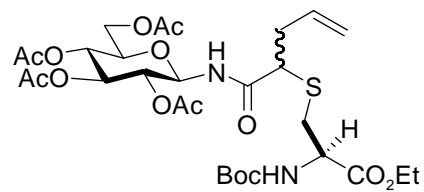
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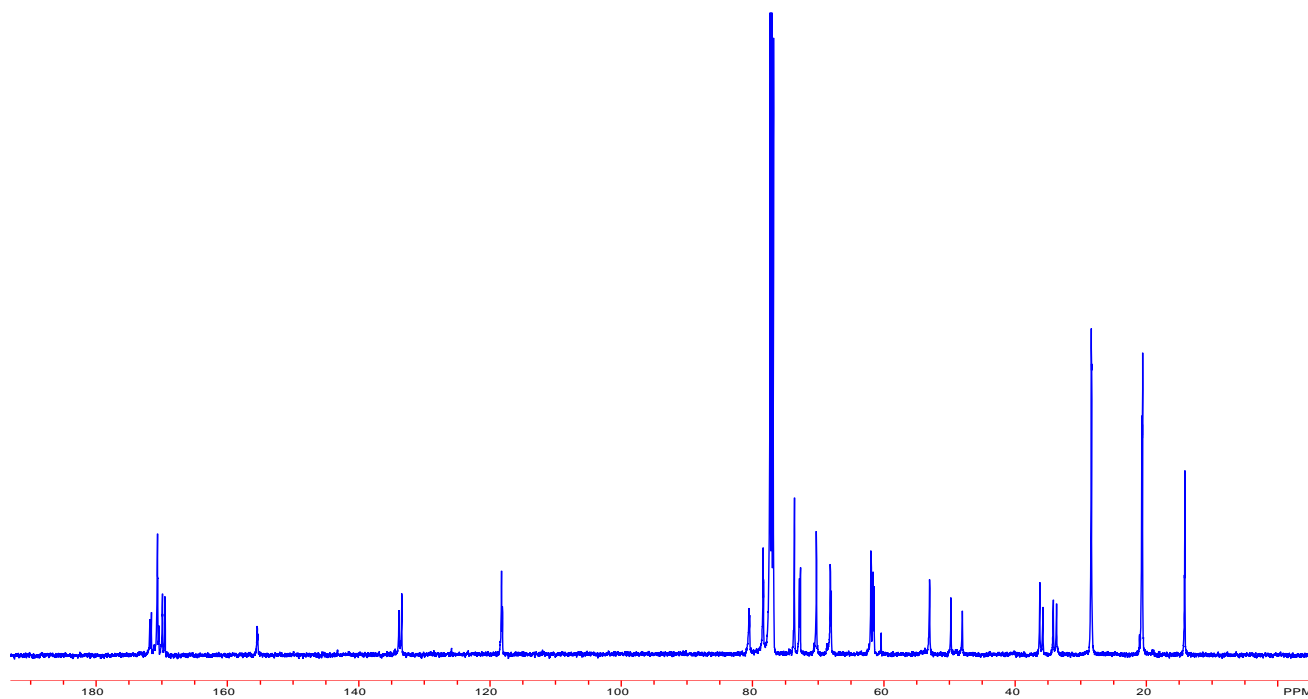


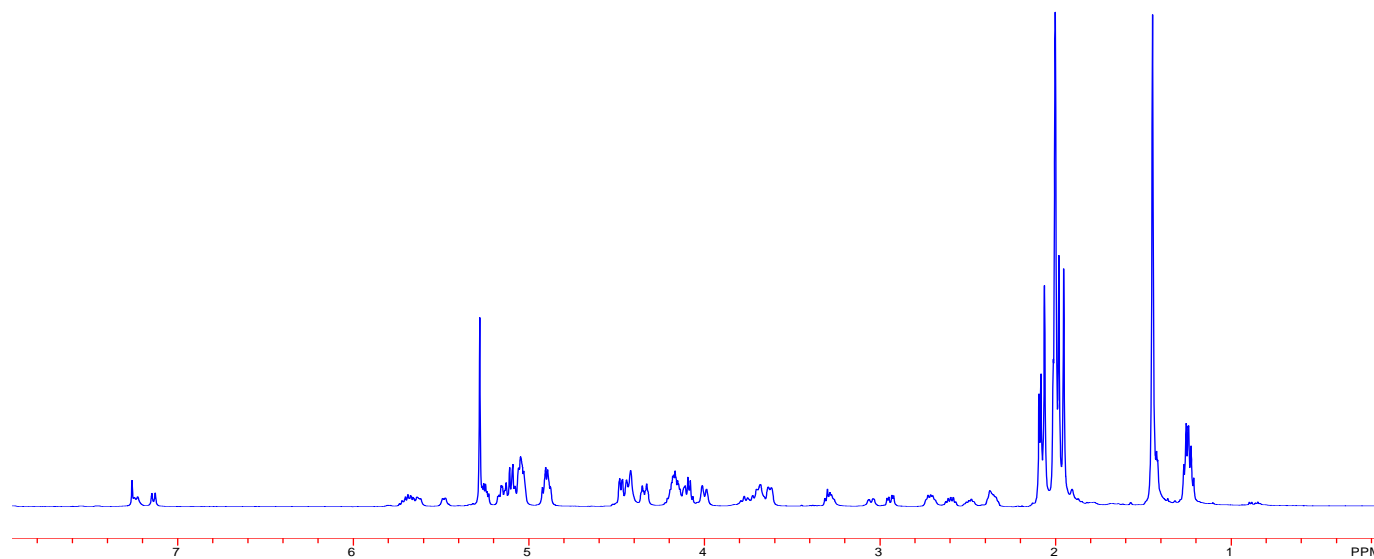
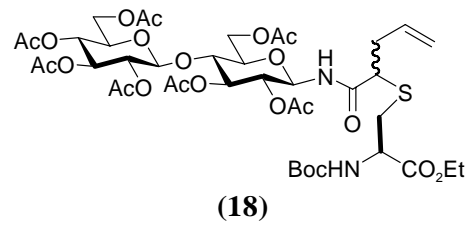
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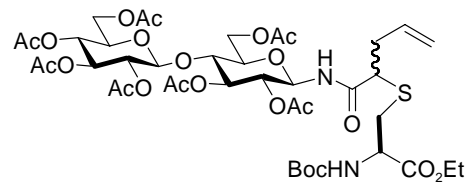




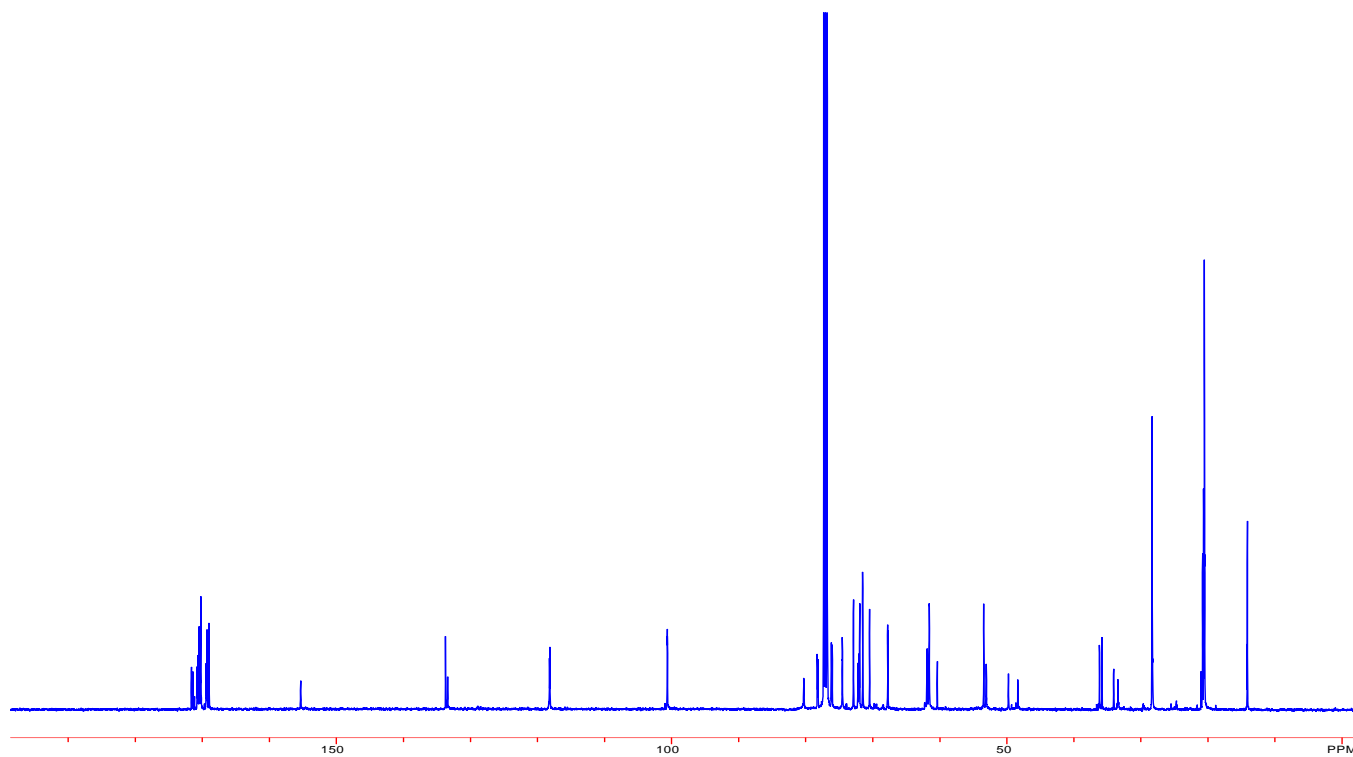
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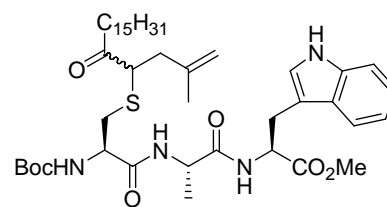




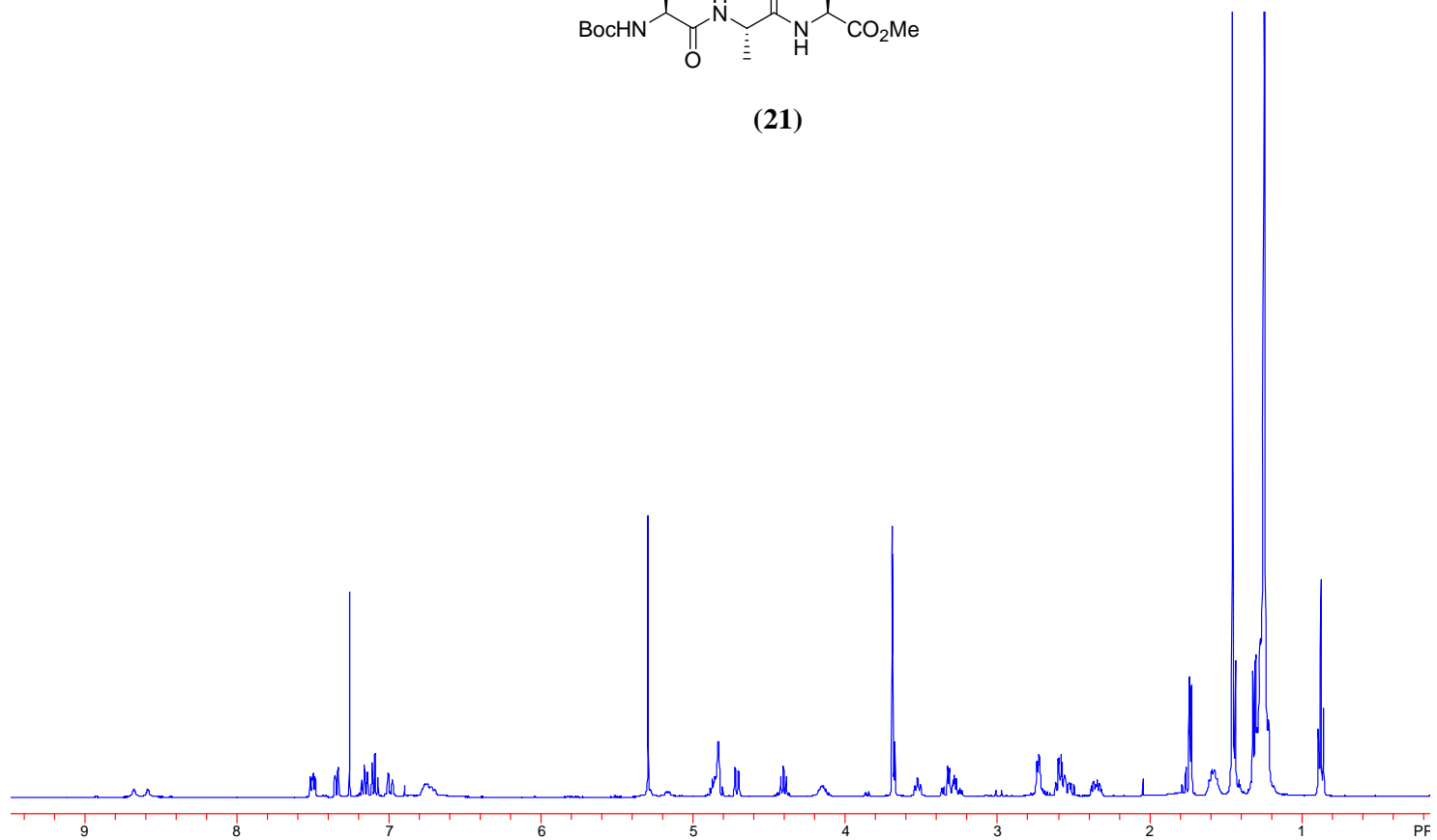


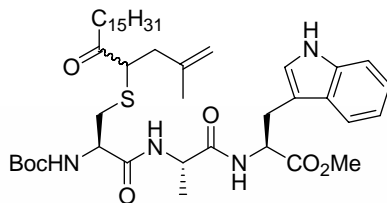
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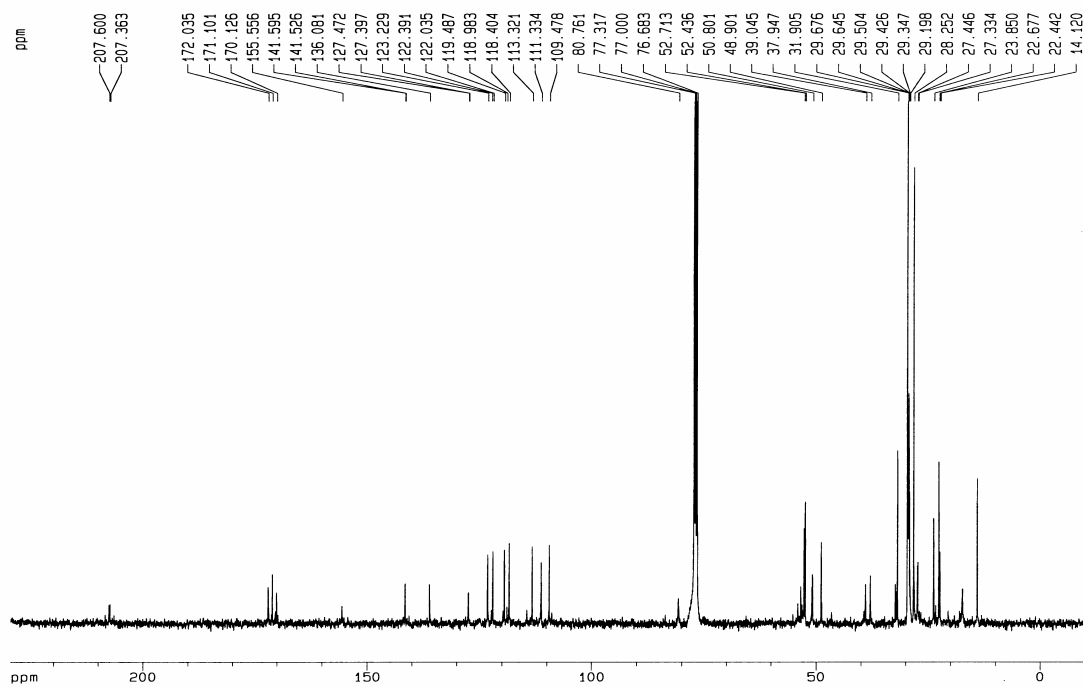


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Carbon-13 standard parameters, BBO probe
(21)

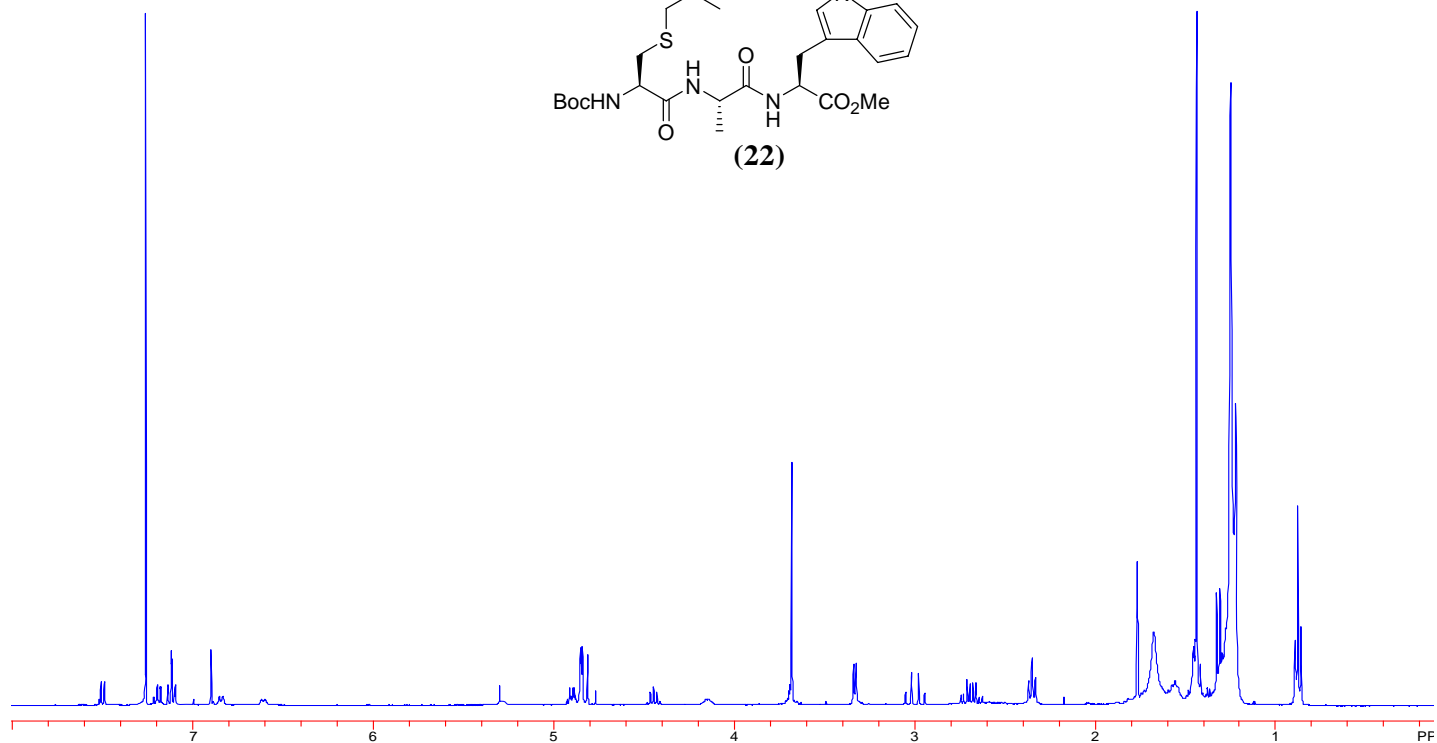
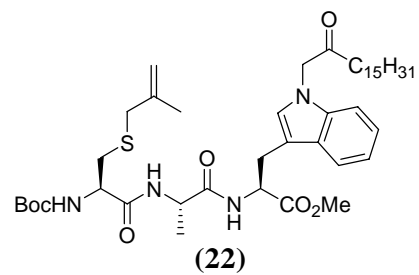


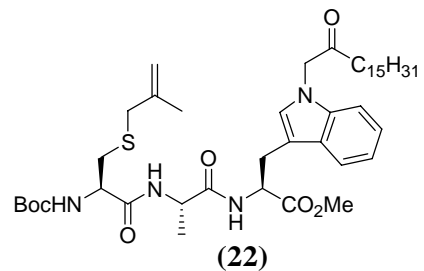
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PROCNO 1

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D1 2.0000000 sec
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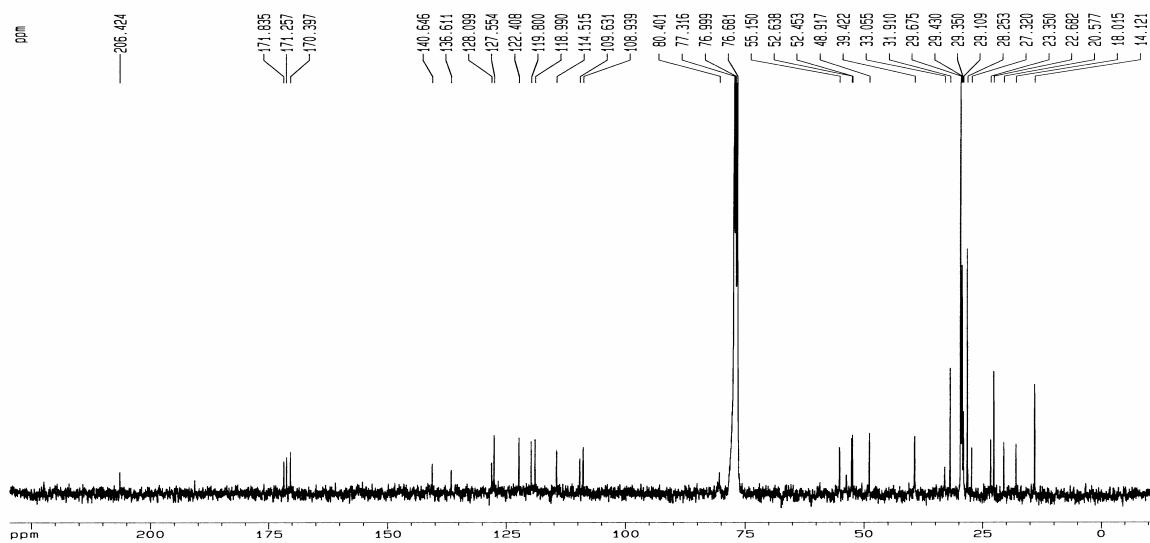
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Carbon-13 standard parameters, BBO probe



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PROCNO   1

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