

# Supporting Information

## Spectra

### **Protecting Group-Free Glycoligation by the Desulfurative Rearrangement of Allylic Disulfides as a Means of Assembly of Oligosaccharide Mimetics**

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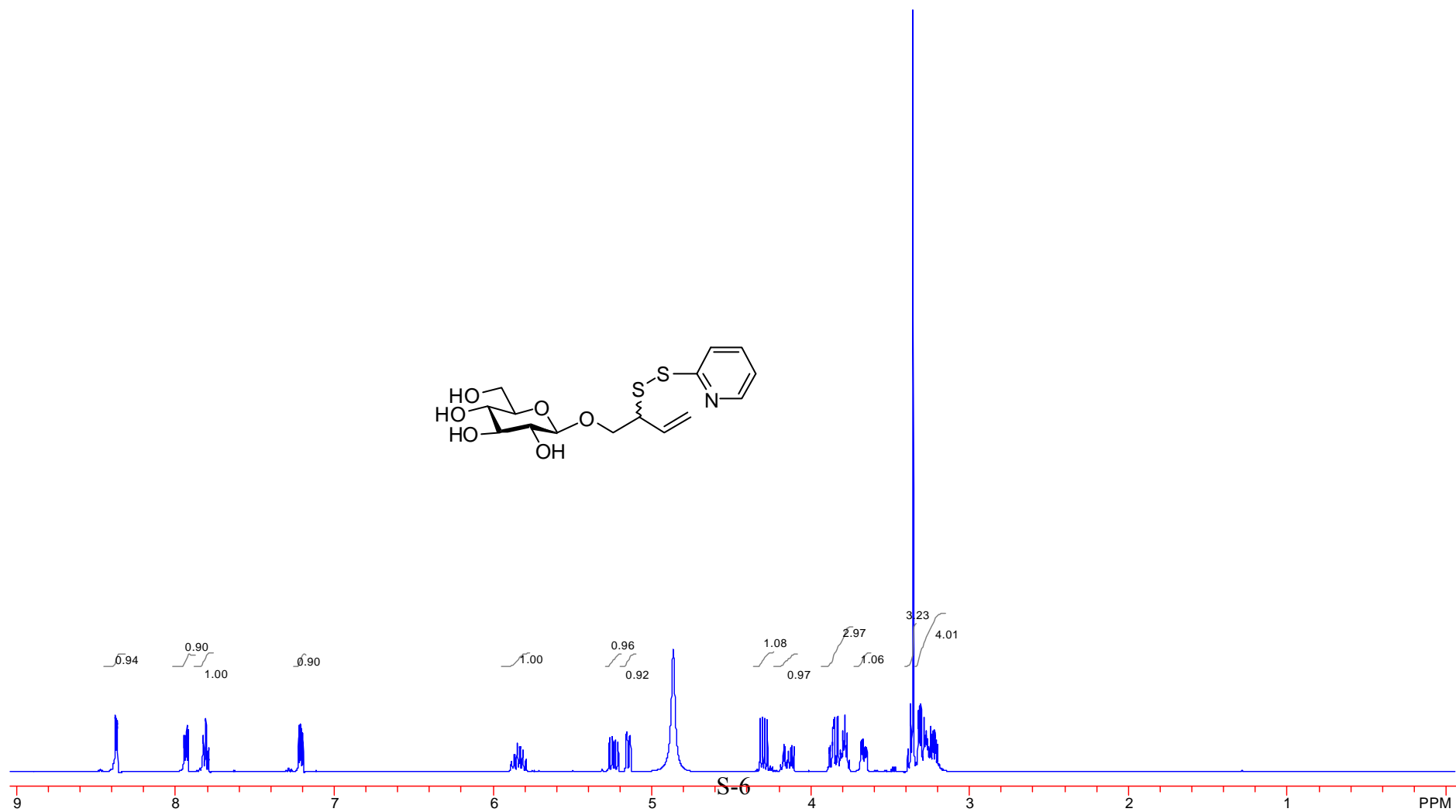
	<sup>1</sup> H	<sup>13</sup> C
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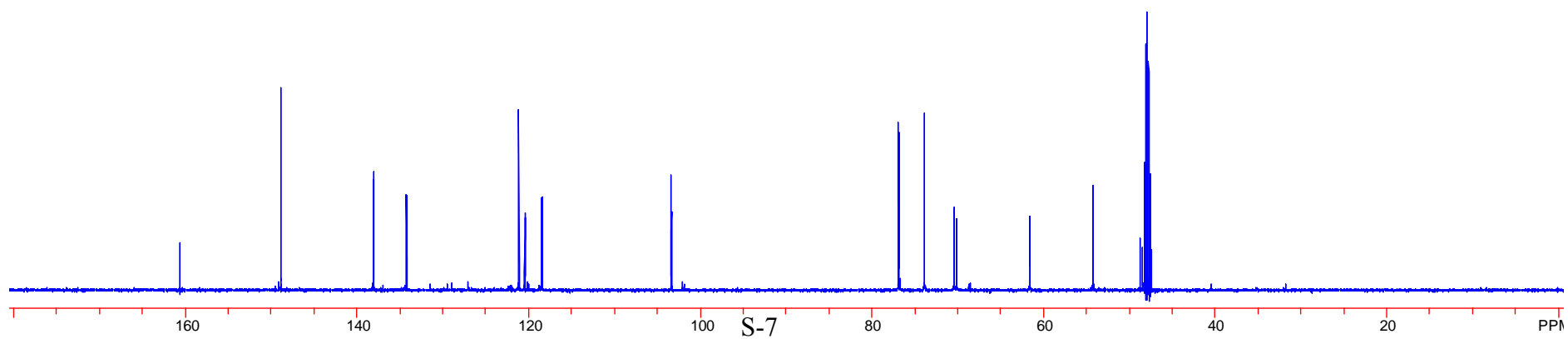
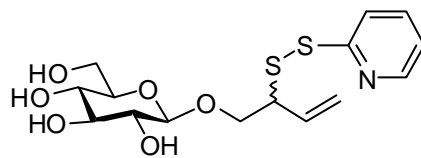
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Phenyl 2-azido-2-deoxy-3,4- <i>O</i> -(2,3-dimethoxybutane-2,3-diyl)-1-thio-[2'-azido-2'-deoxy-3',4',6'-tri- <i>O</i> -( <i>p</i> -methoxybenzyl)]- $\beta$ -D-gentiobioside <i>S</i> -Oxide ( <b>50</b> ).	S-98	S-99
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2-(Phenyloxycarbonylthioxy)but-3-enyl 3',4',6'-tri- <i>O</i> -acetyl-2,2'-dideoxy-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobioside ( <b>86</b> ).	S-112	S-113
2-(2-Pyridyldithio)but-3-enyl 2,2'-dideoxy-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobioside ( <b>62</b> ).	S-114	S-115
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2,2',4,4',6,6'-Hexa- <i>O</i> -acetyl-3'- <i>O</i> -[4-(2-naphthylmethyloxy)but-2- <i>Z</i> -enyl]- $\alpha$ -D-laminaribiosyl trichloroacetimidate ( <b>89</b> ).	S-124	S-125
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Methyl 2,2',4,4',6,6'-hexa- <i>O</i> -acetyl-3'- <i>O</i> -[4-hydroxybut-2- <i>Z</i> -enyl]- $\beta$ -D-laminaribioside ( <b>91</b> ).	S-128	S-129
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Methyl 6-[4- <i>O</i> -(2,2'-azido-2,2'-dideoxy- $\beta$ -D-gentiobiosyloxy)but-2- <i>E</i> -enyl]thio-2,2'-azido-2,2'-dideoxy- $\alpha$ -D-gentiobioside ( <b>66</b> ).	S-142	S-143
Methyl 6-[4- <i>O</i> -(2,2'-dideoxy-2,2'-(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobiosyloxy)but-2- <i>E</i> -enyl]thio-2,2'-dideoxy-(2,2,2-trichloroethoxycarbonylamino)- $\alpha$ -D-gentiobioside ( <b>67</b> ).	S-144	S-145
Benzyl 3-deoxy-3-[4-( $\beta$ -D-laminaribiosyloxy)but-2- <i>E</i> -enylthio]- $\beta$ -D-laminaribioside ( <b>68</b> ).	S-146	S-147
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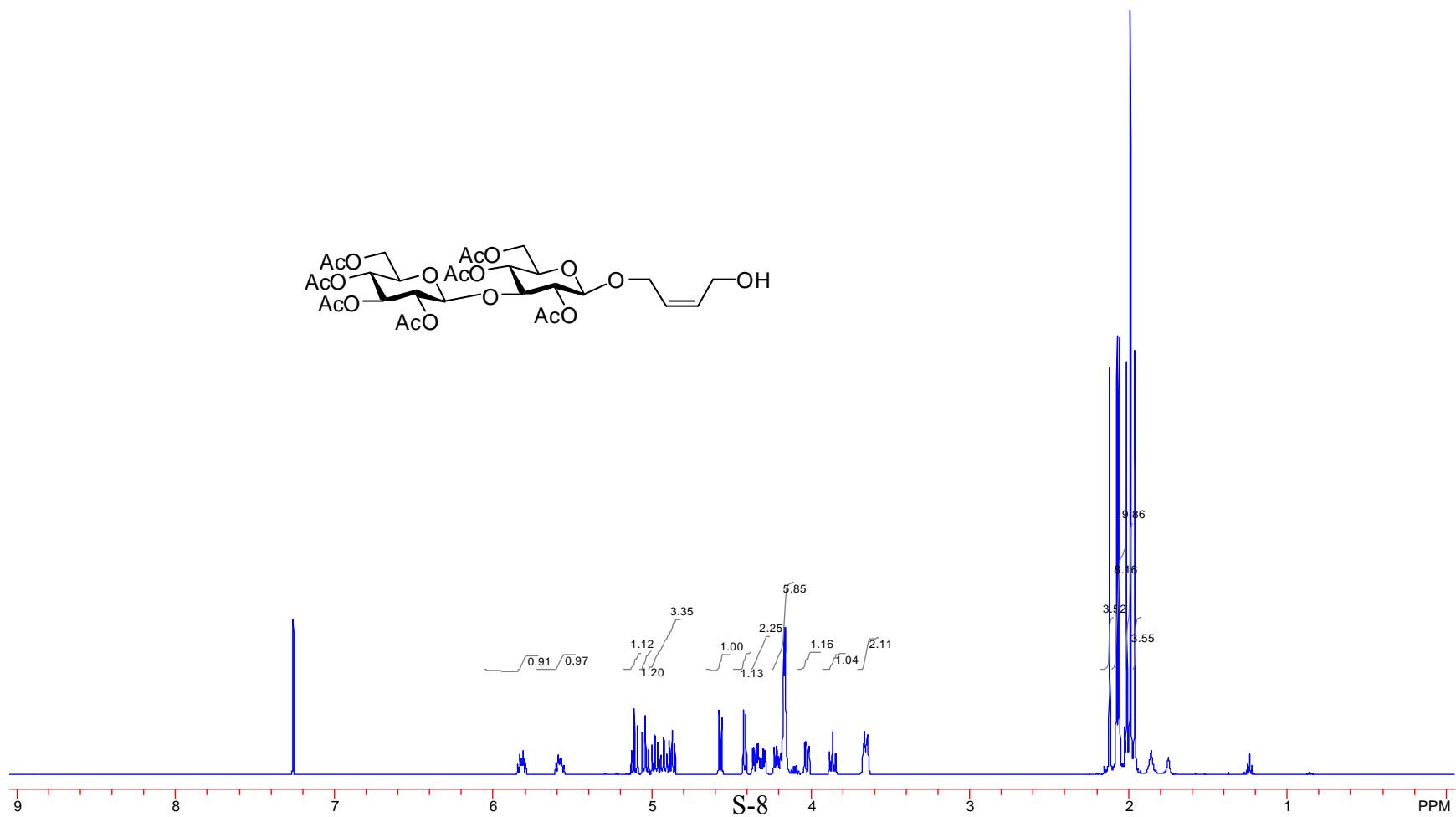
$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 500 MHz) of 2-(2-Pyridyldithio)-3-butenyl  $\beta$ -D-glucopyranoside (**13**)



$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) of 2-(2-Pyridyldithio)-3-butenyl  $\beta$ -D-glucopyranoside (**13**)

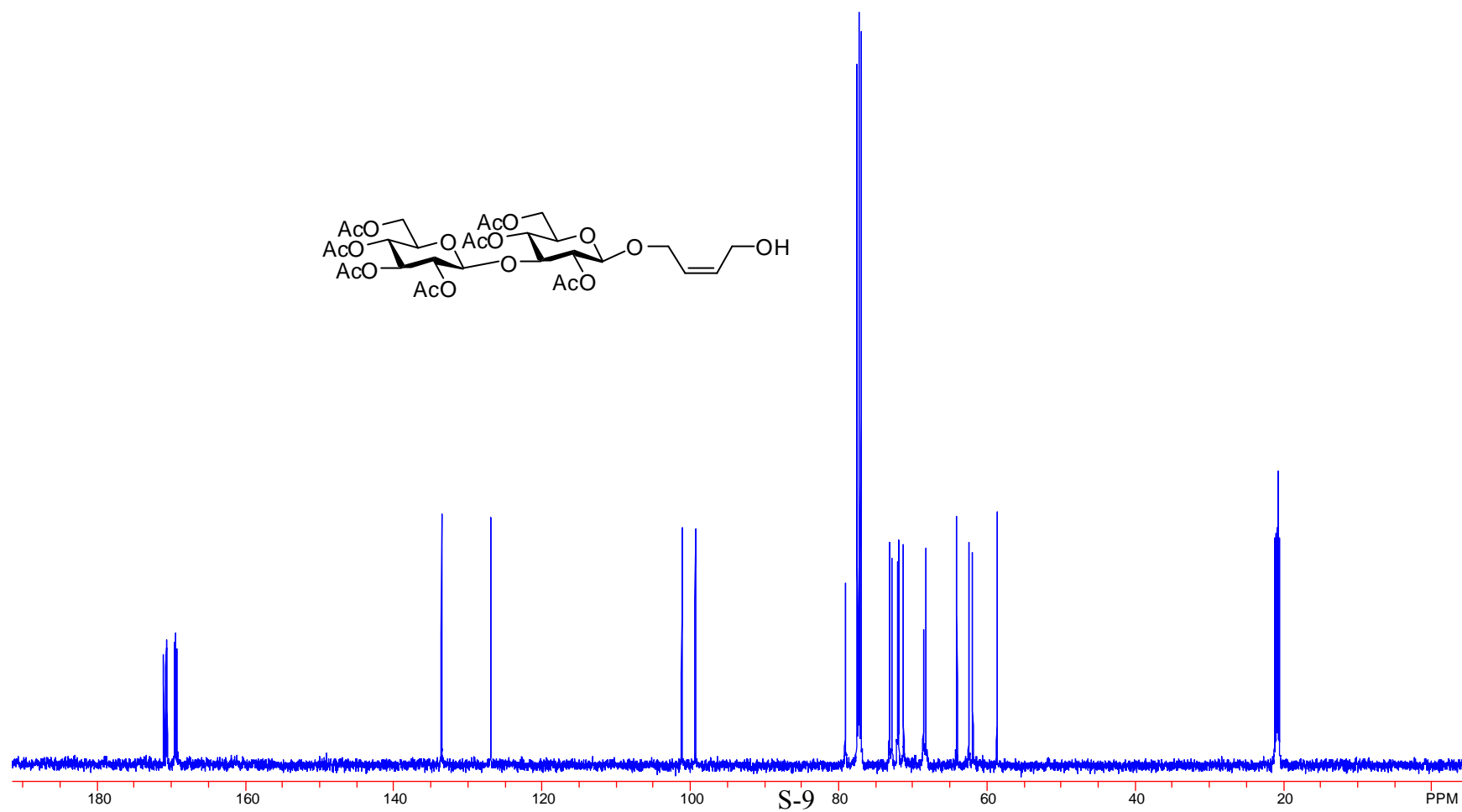


$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) of 4-Hydroxy-but-2Z-enyl hepta-*O*-acetyl- $\beta$ -D-laminaribioside (**8**).

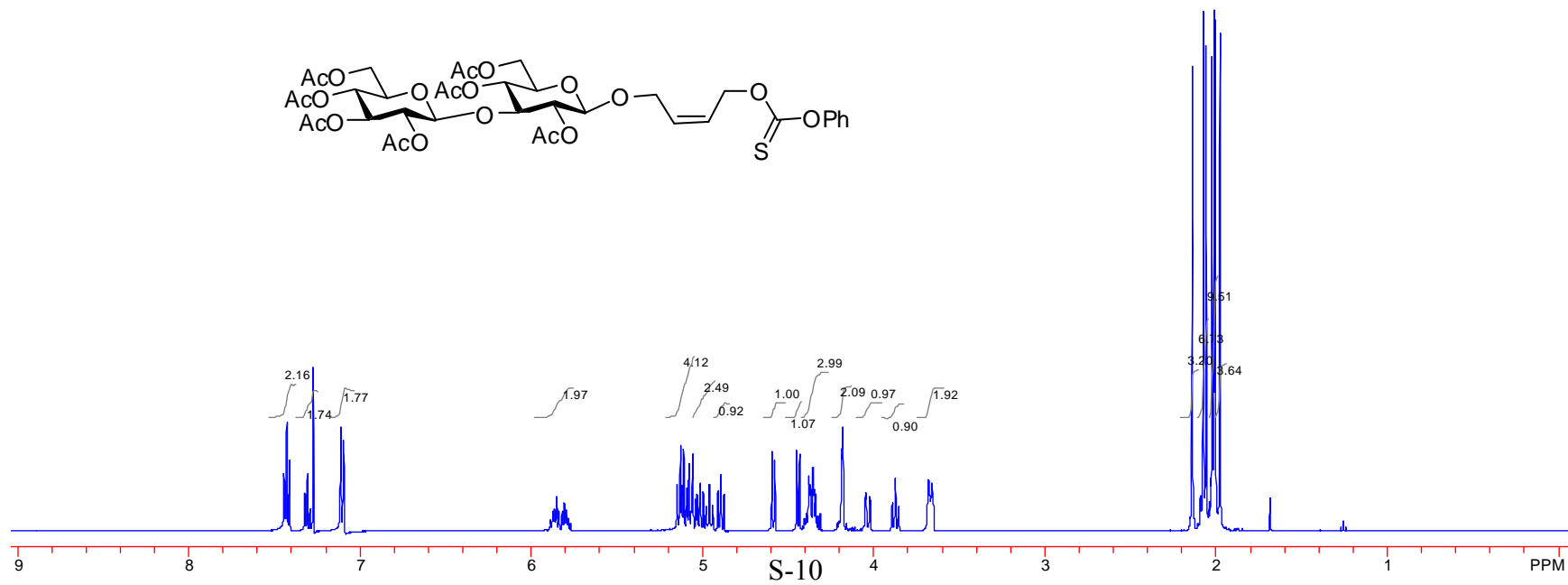




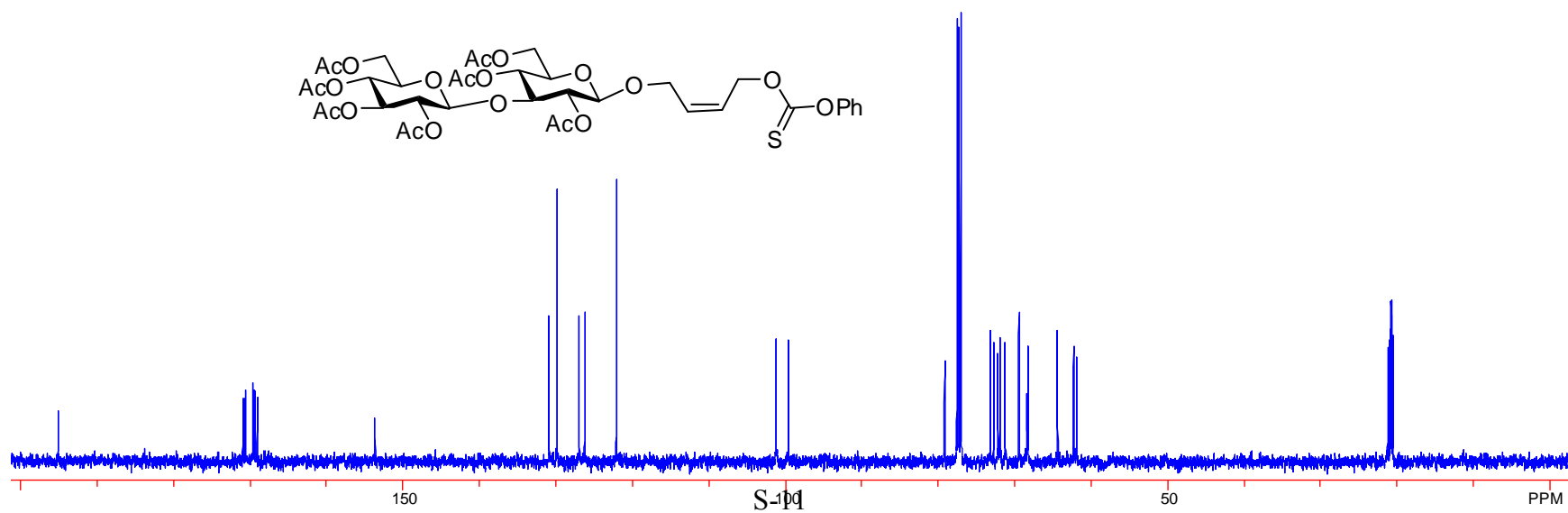
$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) of 4-Hydroxy-but-2Z-enyl hepta-*O*-acetyl- $\beta$ -D-laminaribioside (**8**).



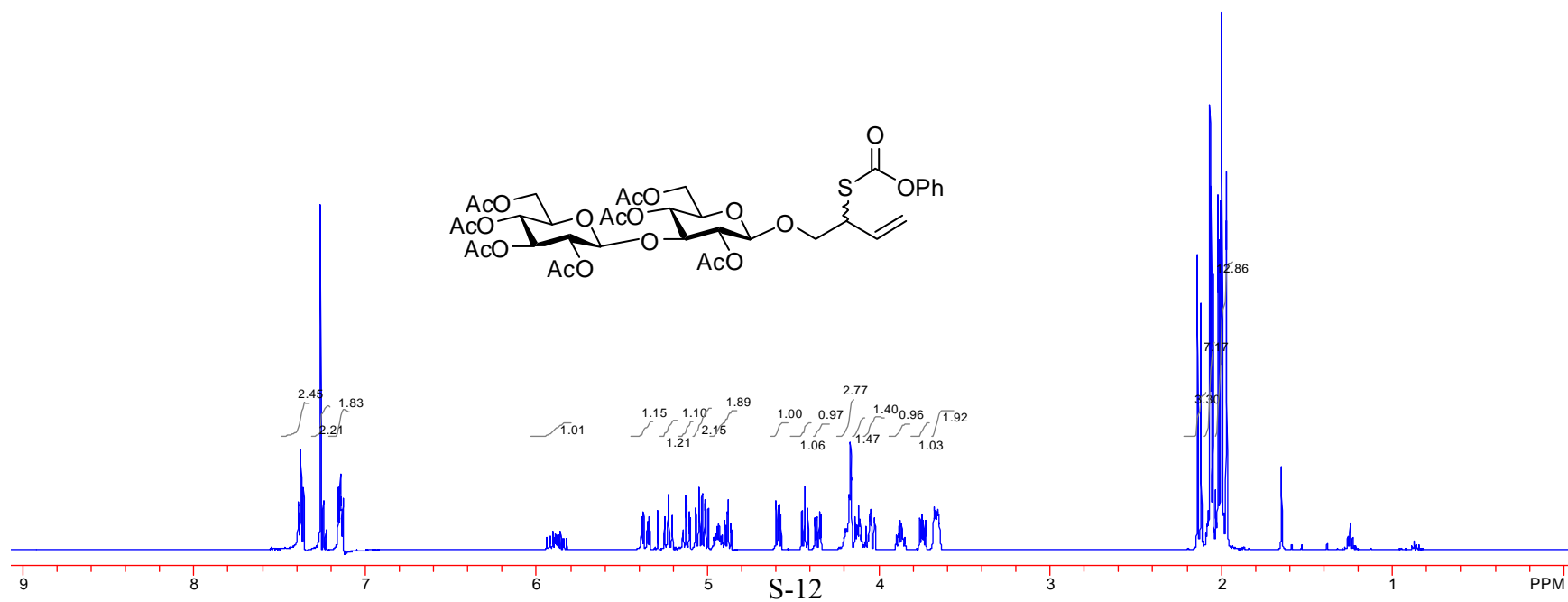
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) of 4-(Phenyloxythionocarbonyloxy)-2Z-butenyl hepta-*O*-acetyl- $\beta$ -D-laminaribioside (**10**).



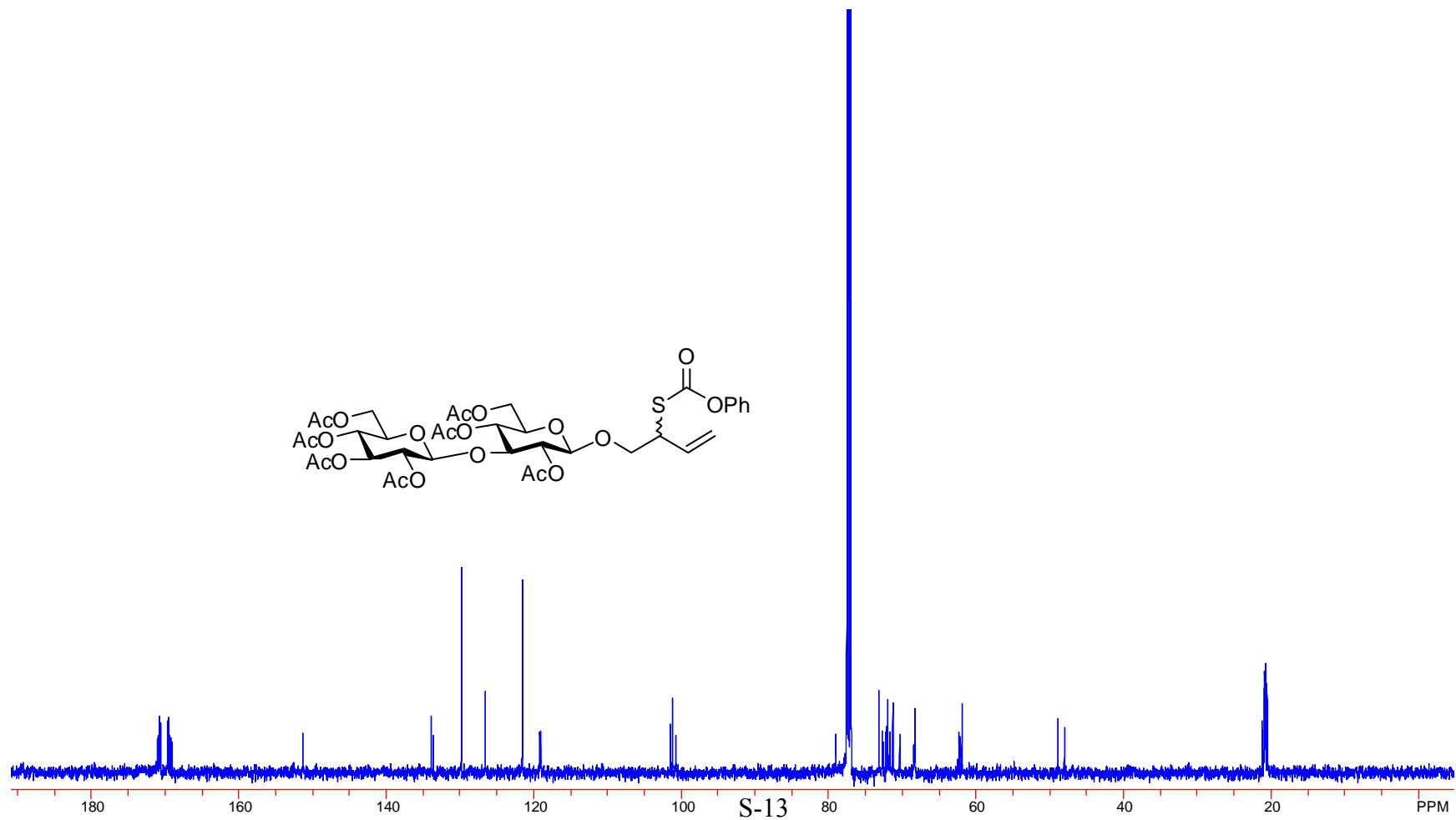
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of 4-(Phenyloxythionocarbonyloxy)-2Z-butenyl hepta-O-acetyl- $\beta$ -D-laminaribioside (**10**).



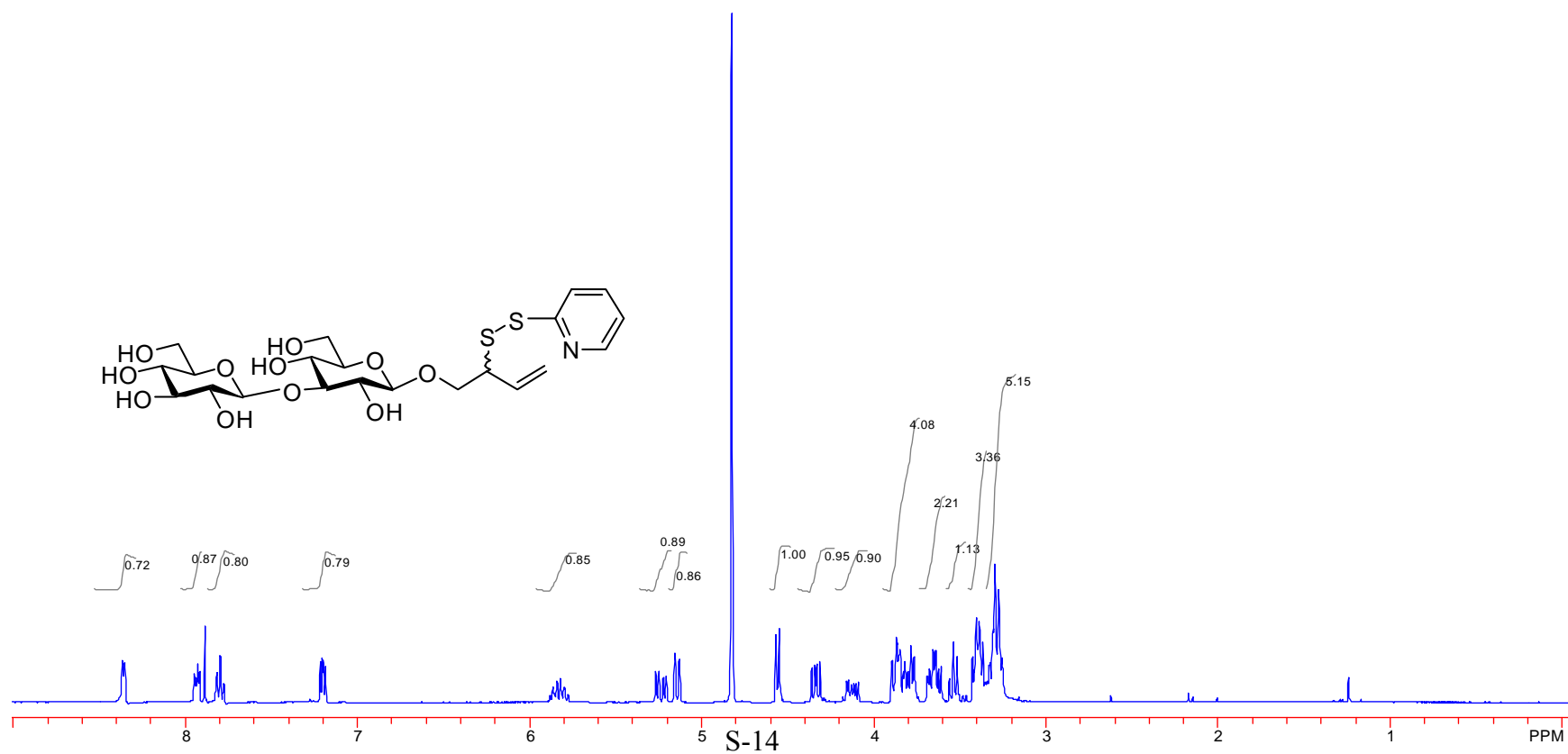
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) of 2-(Phenyloxycarbonylthioxy)-3-butenyl tetra-*O*-acetyl- $\beta$ -D-laminaribioside (**12**).



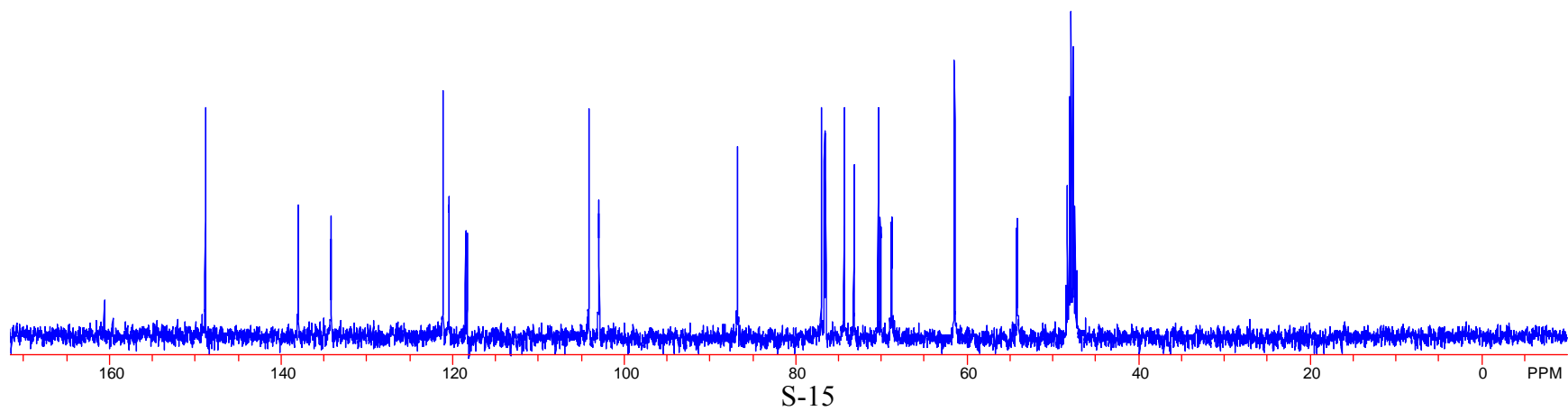
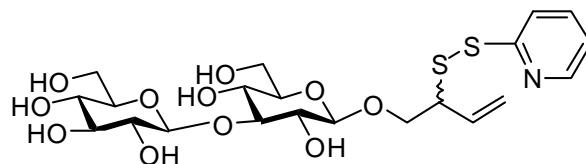
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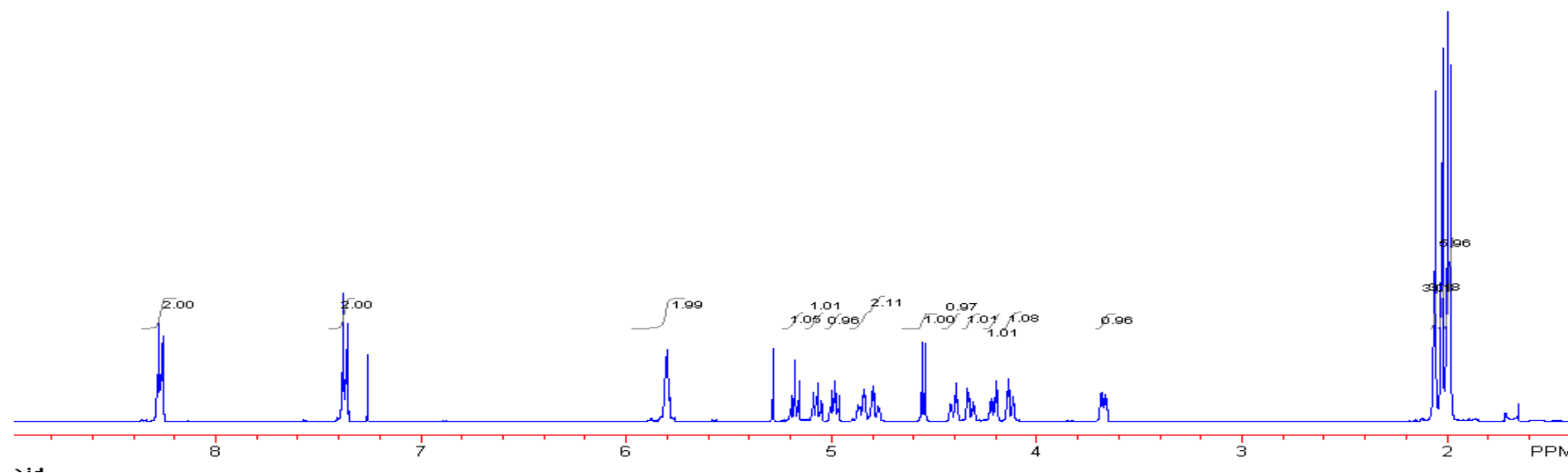
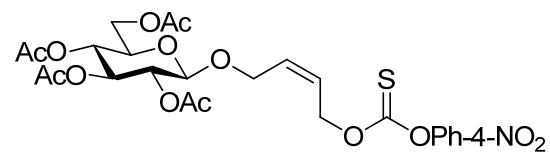
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$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) of 2-(2-Pyridyldithio)-3-butenyl  $\beta$ -D-laminaribioside (**14**).

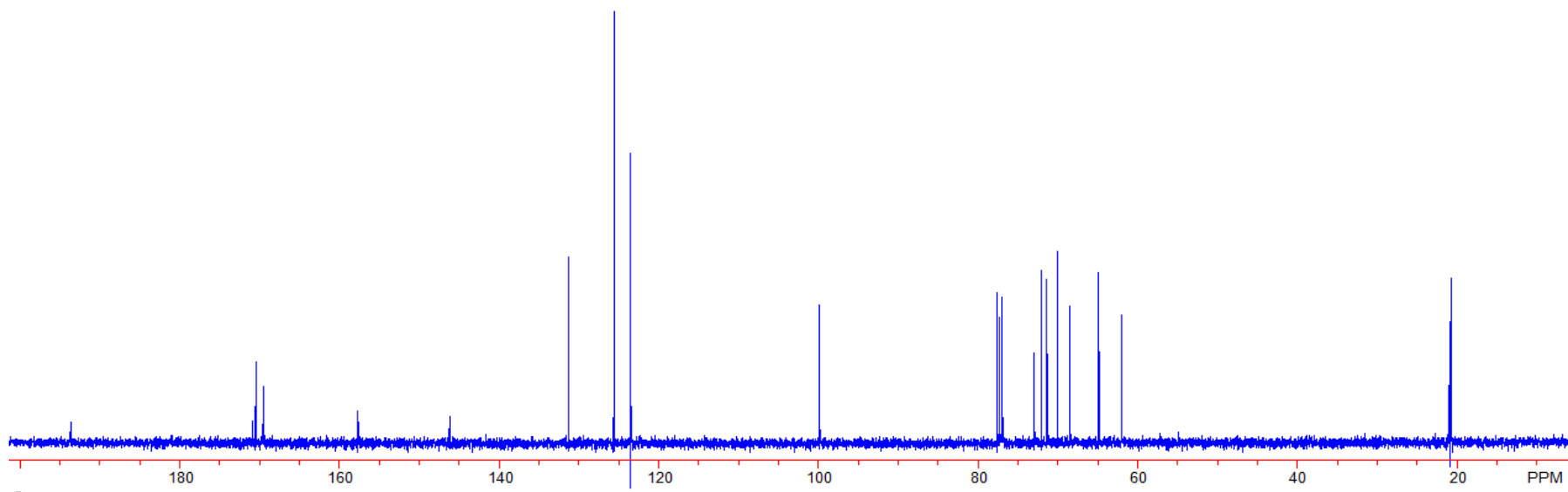
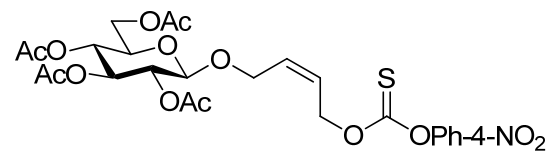


$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) of 4-(4-Nitrophenyloxythionocarbonyloxy)-2Z-butenyl tetra-O-acetyl- $\beta$ -D-glucopyranoside (**15**).



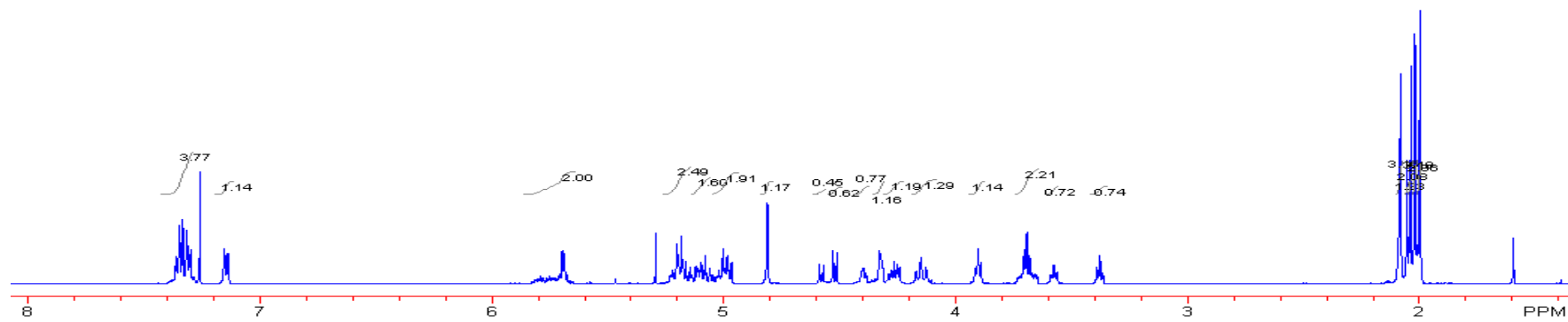
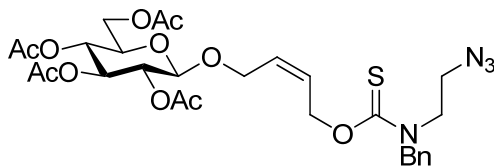


$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of 4-(4-Nitrophenoxythionocarbonyloxy)-2Z-butenyl tetra-O-acetyl- $\beta$ -D-glucopyranoside (**15**).



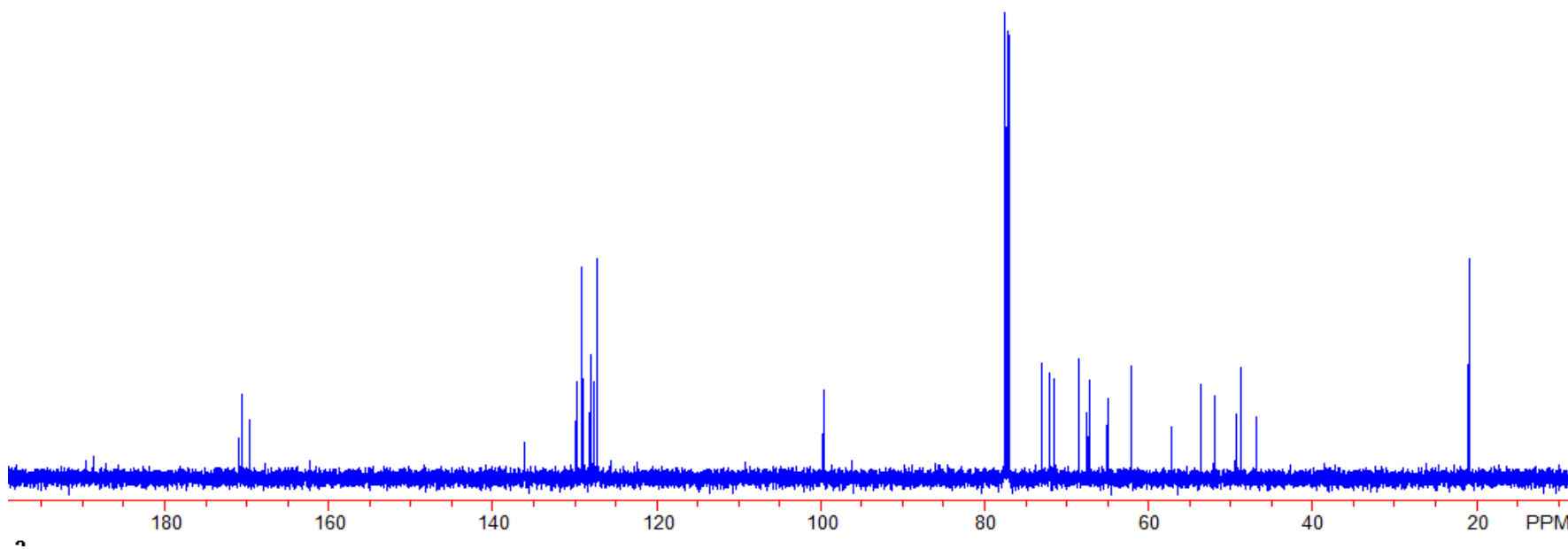
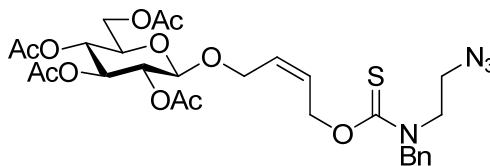
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<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 500 MHz) 4-[*N*-(2-Azidoethyl)-*N*-(benzyl)thionocarbamoyloxy]-2*Z*-butenyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside (**16**).

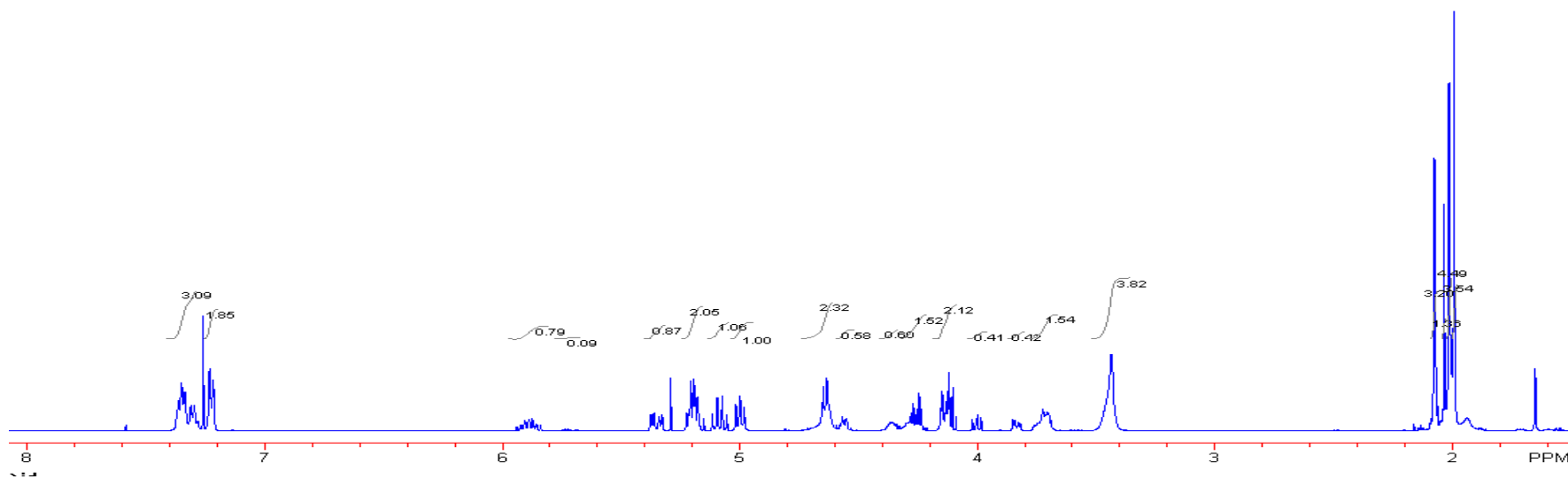
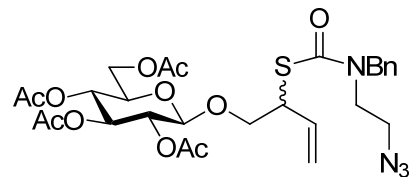


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$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 4-[*N*-(2-Azidoethyl)-*N*-(benzyl)thionocarbamoyloxy]-2*Z*-butenyl 2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranoside (**16**).

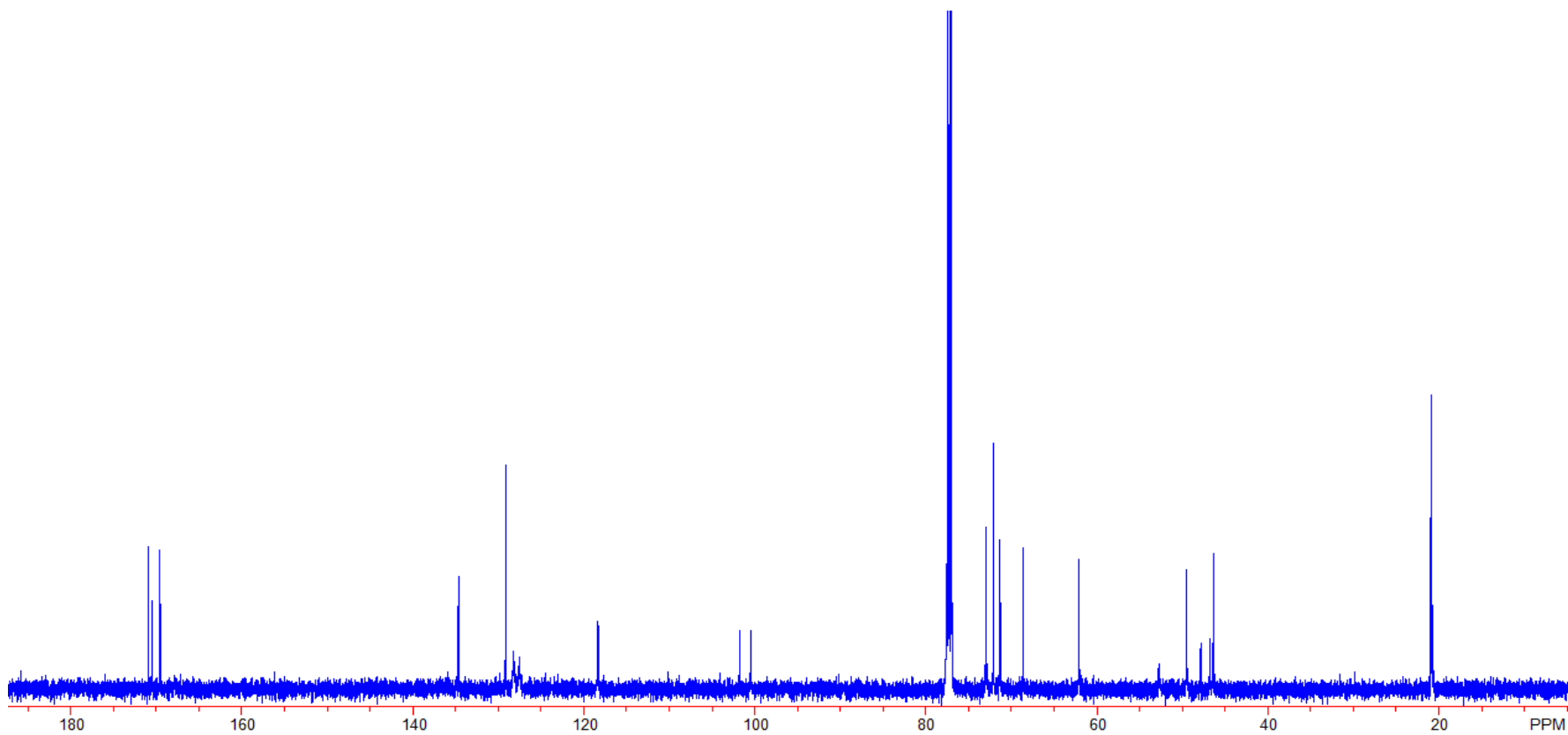
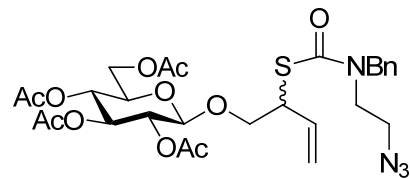


<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 500 MHz) 2-[*N*-(2-Azidoethyl)-*N*-(benzyl)carbamoylthioxy]-3-butenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (17).



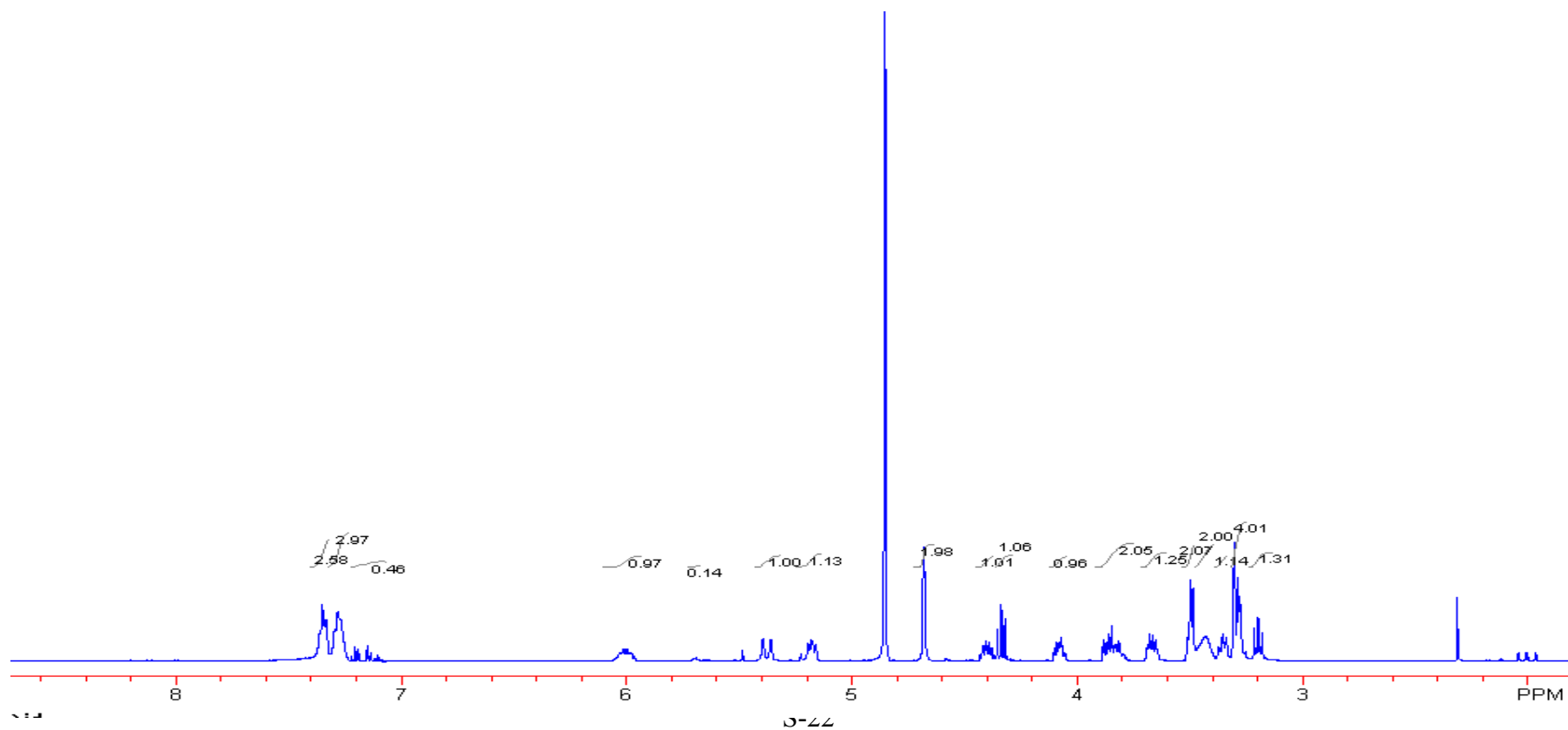
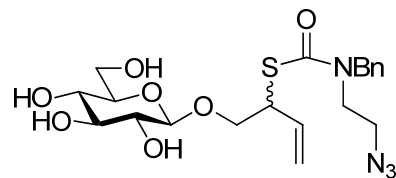
S-20

$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 2-[*N*-(2-Azidoethyl)-*N*-(benzyl)carbamoylthioxy]-3-butenyl 2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranoside (17).

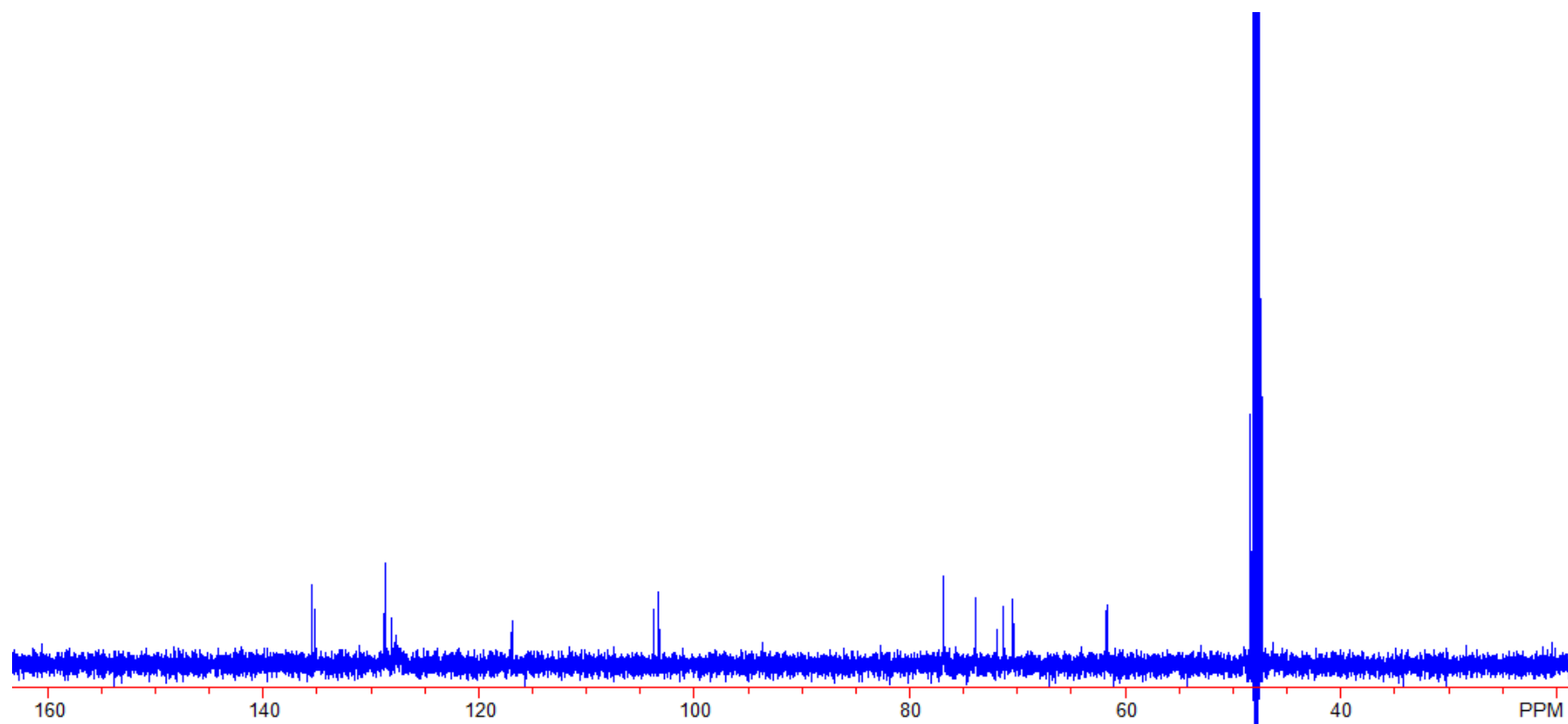
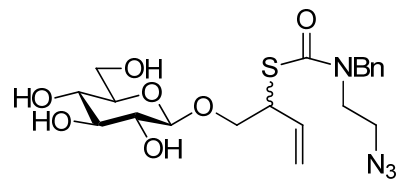


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$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 500 MHz) 2-[*N*-(2-Azidoethyl)-*N*-(benzyl)carbamoylthioxy]-3-butenyl  $\beta$ -D-glucopyranoside (**18**).

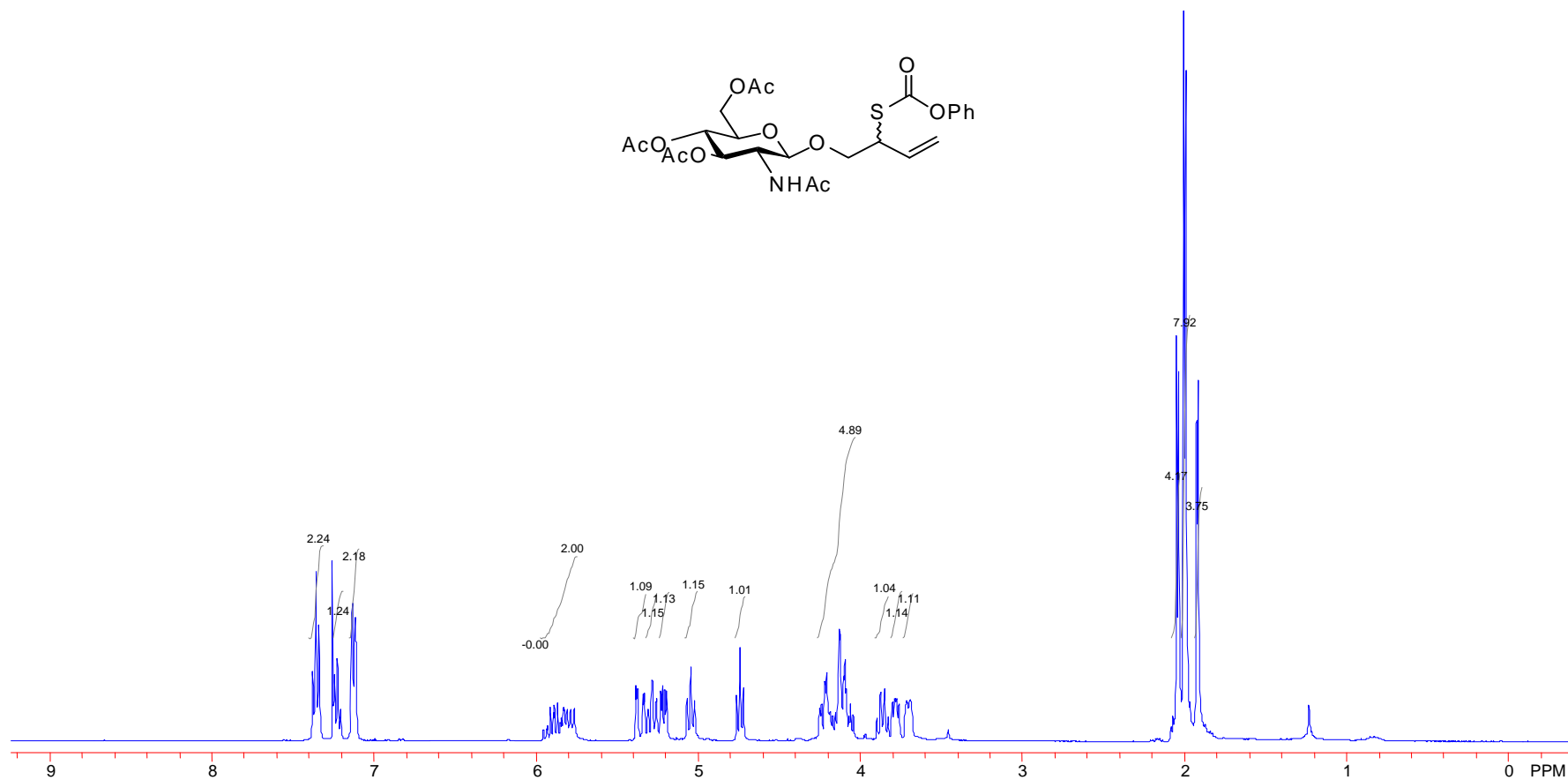
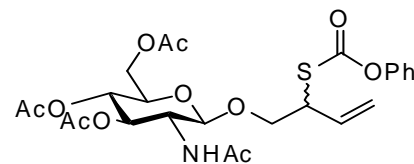


$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) 2-[*N*-(2-Azidoethyl)-*N*-(benzyl)carbamoylthioxy]-3-butenyl  $\beta$ -D-glucopyranoside (**18**).



<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) 2-(Phenyloxycarbonylthioxy)-3-butenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside

(21)

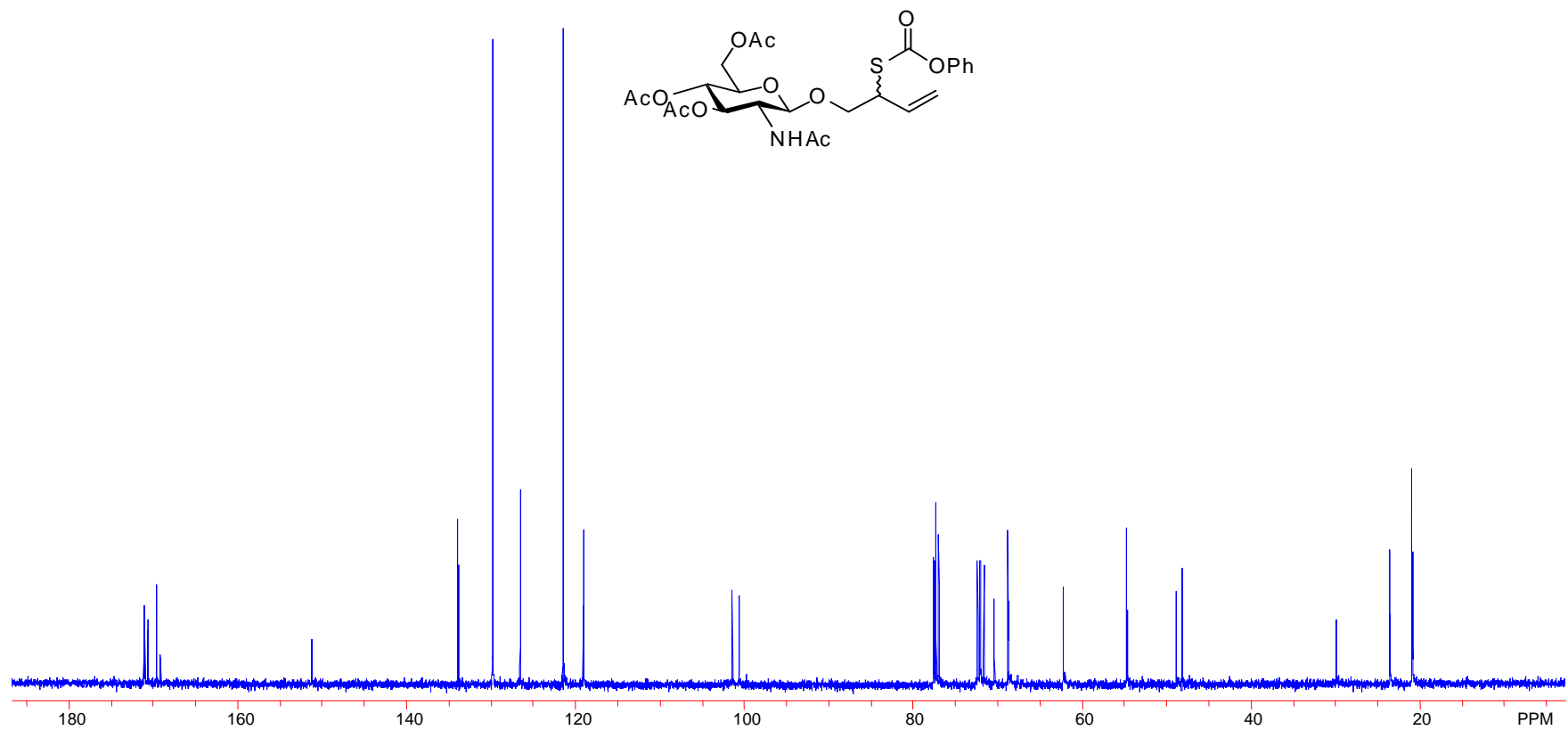
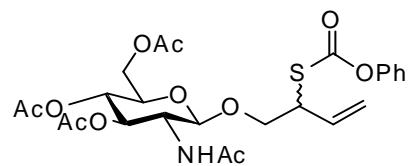


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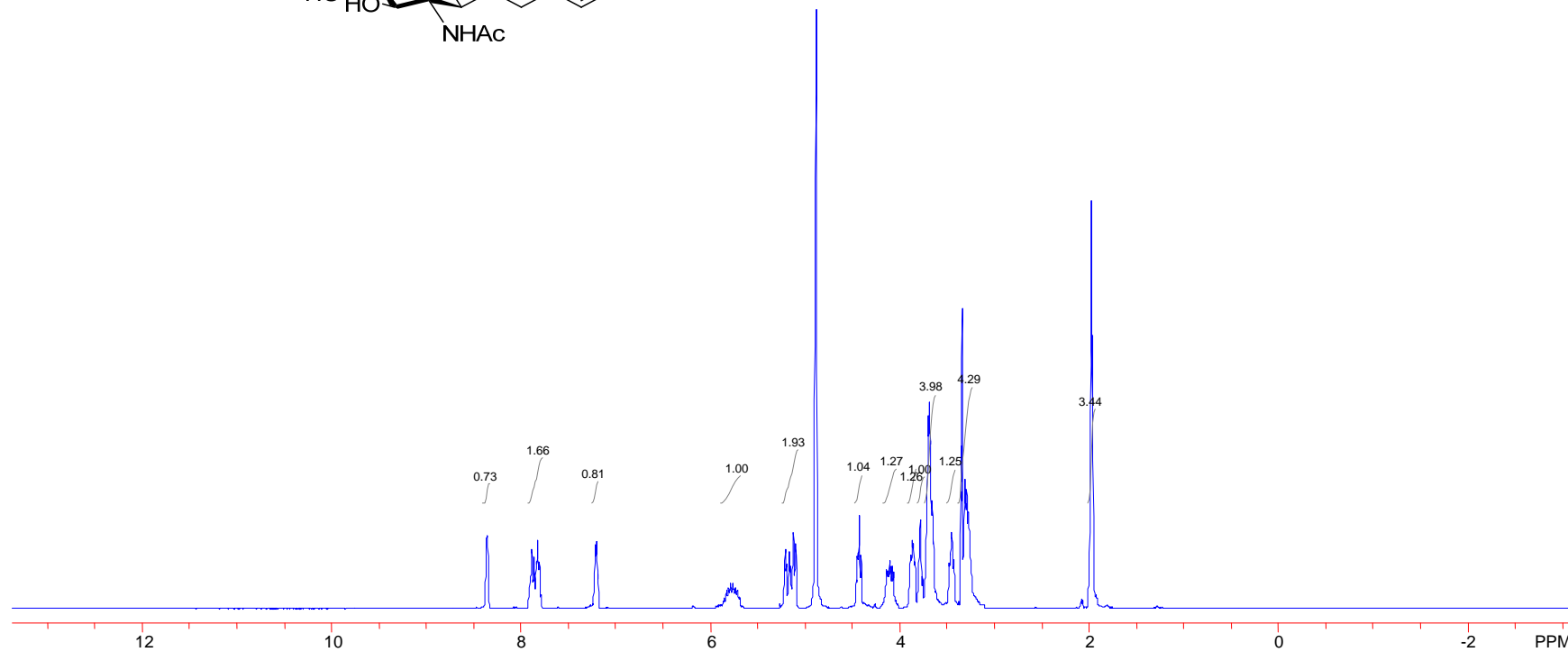
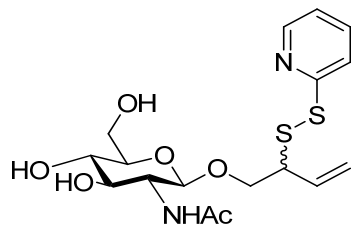
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) 2-(Phenyloxycarbonylthioxy)-3-butenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- $\beta$ -D-glucopyranoside

(21)

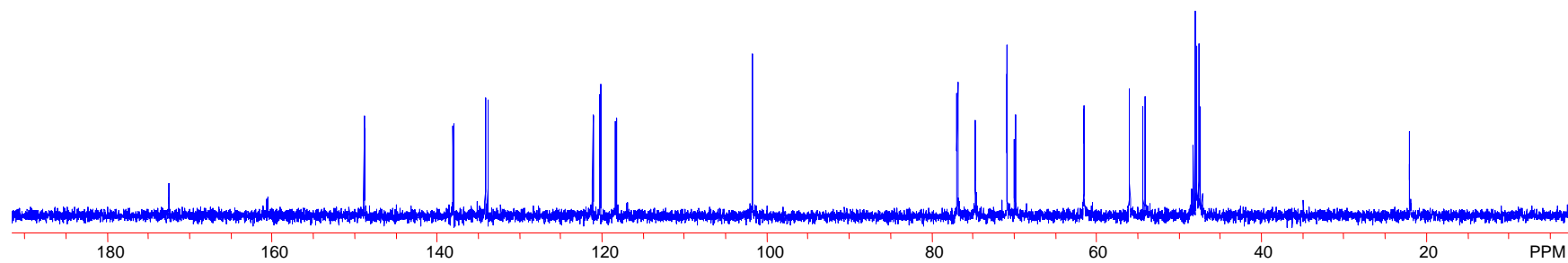
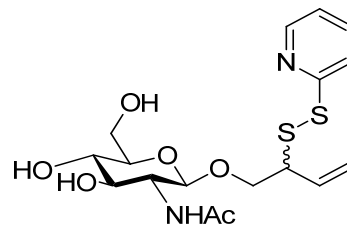


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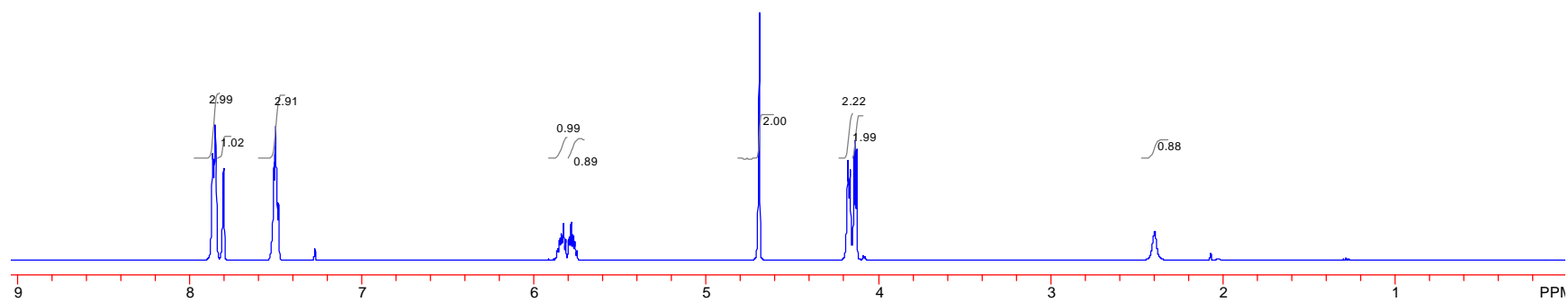
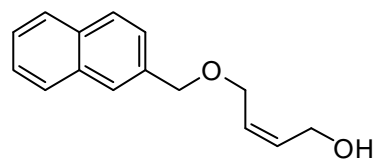
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) 2-(2-Pyridyldithio)-3-butenyl 2-acetamido-2-deoxy- $\beta$ -D-glucopyranoside (**22**).



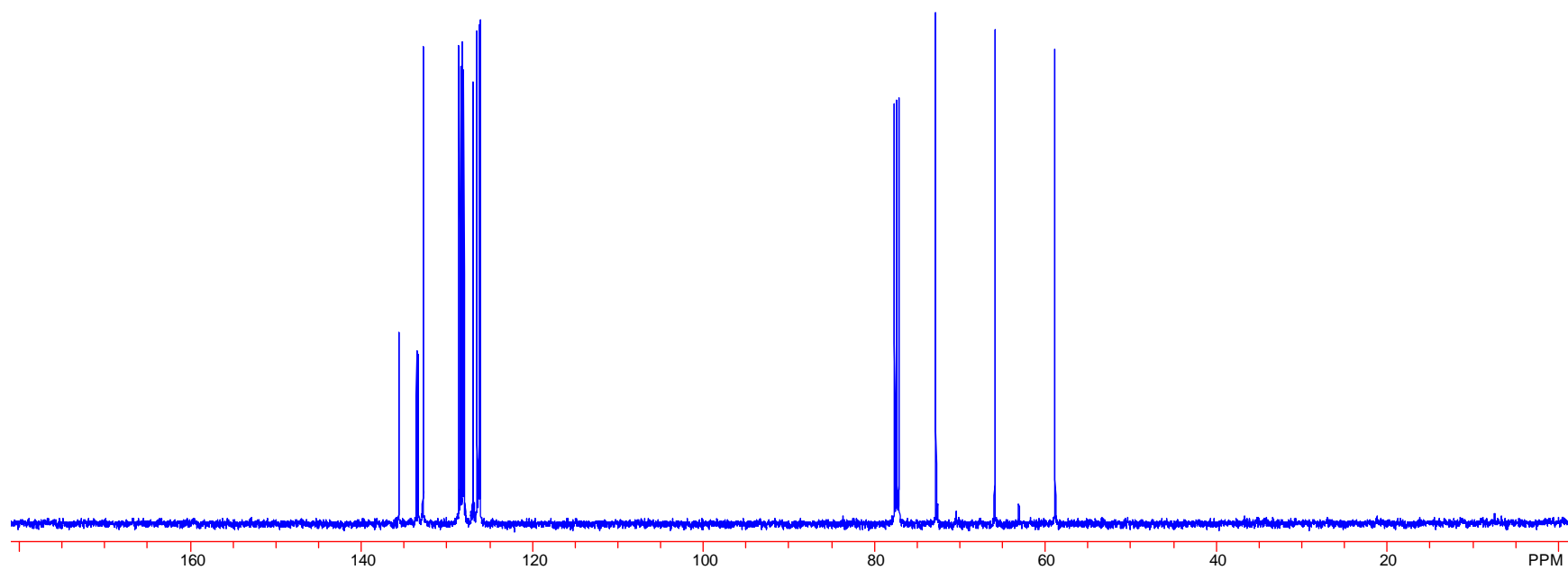
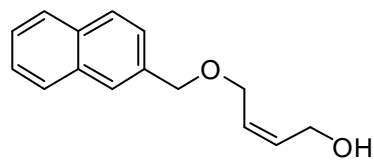
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) 2-(2-Pyridyldithio)-3-butenyl 2-acetamido-2-deoxy- $\beta$ -D-glucopyranoside (**22**).



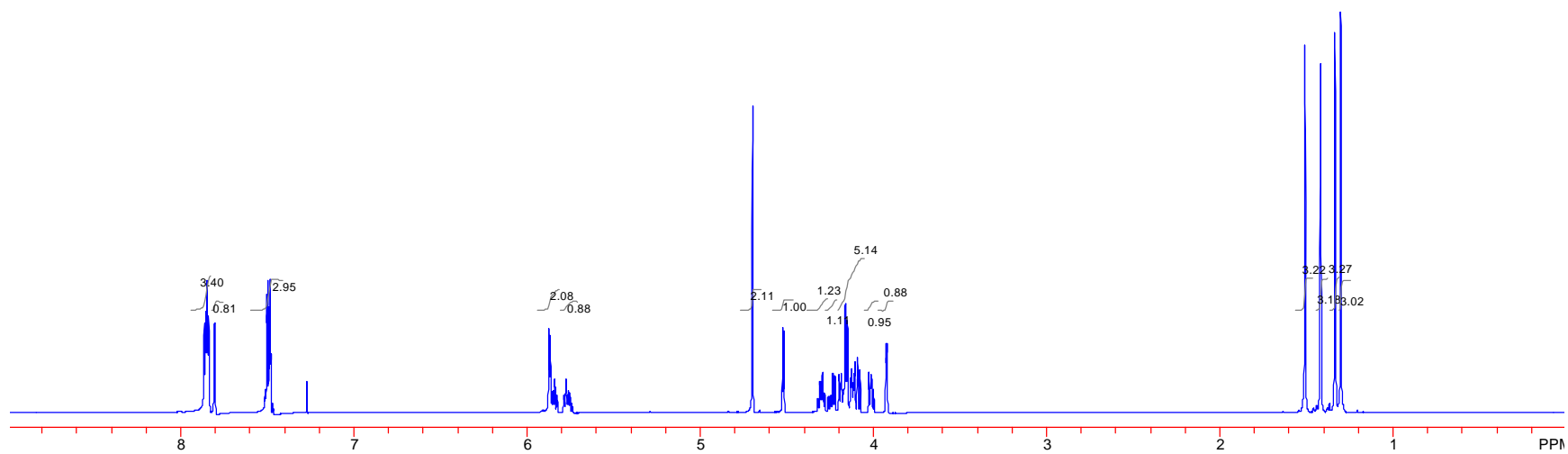
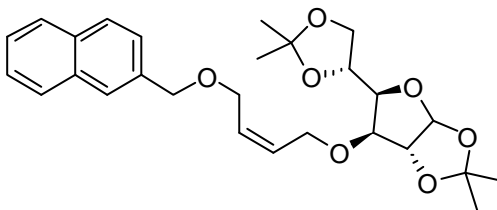
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 500 MHz) 4-(2-Naphthylmethoxy)-2-Z-butene-1-ol (**23**).



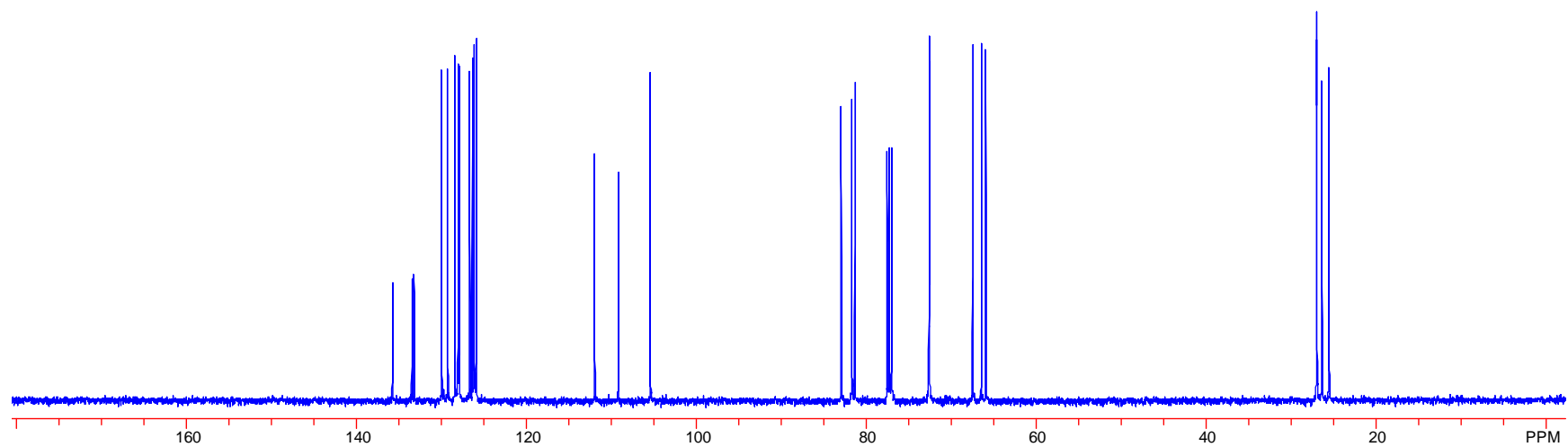
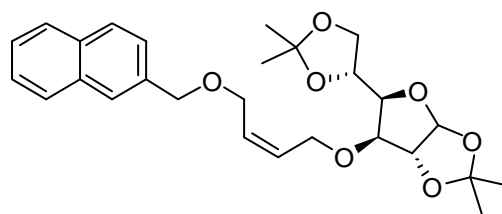
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 4-(2-Naphthylmethoxy)-2-Z-butene-1-ol (**23**).



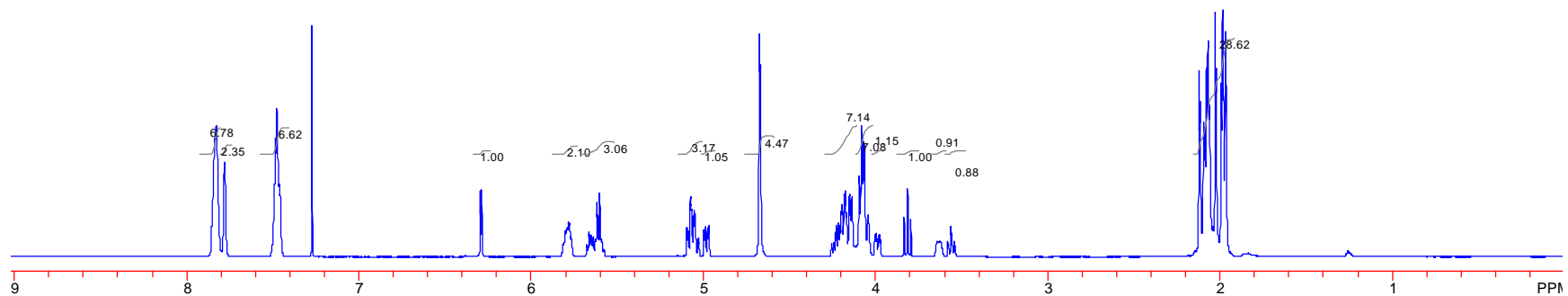
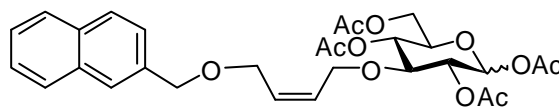
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 500 MHz) 1,2:5,6-Di-*O*-isopropylidene-3-*O*-4-(2-naphthylmethoxy)-2-*Z*-butenyl- $\alpha$ -D-glucofuranose (**24**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 1,2:5,6-Di-*O*-isopropylidene-3-*O*-4-(2-naphthylmethoxy)-2-*Z*-butenyl- $\alpha$ -D-glucofuranose (**24**).

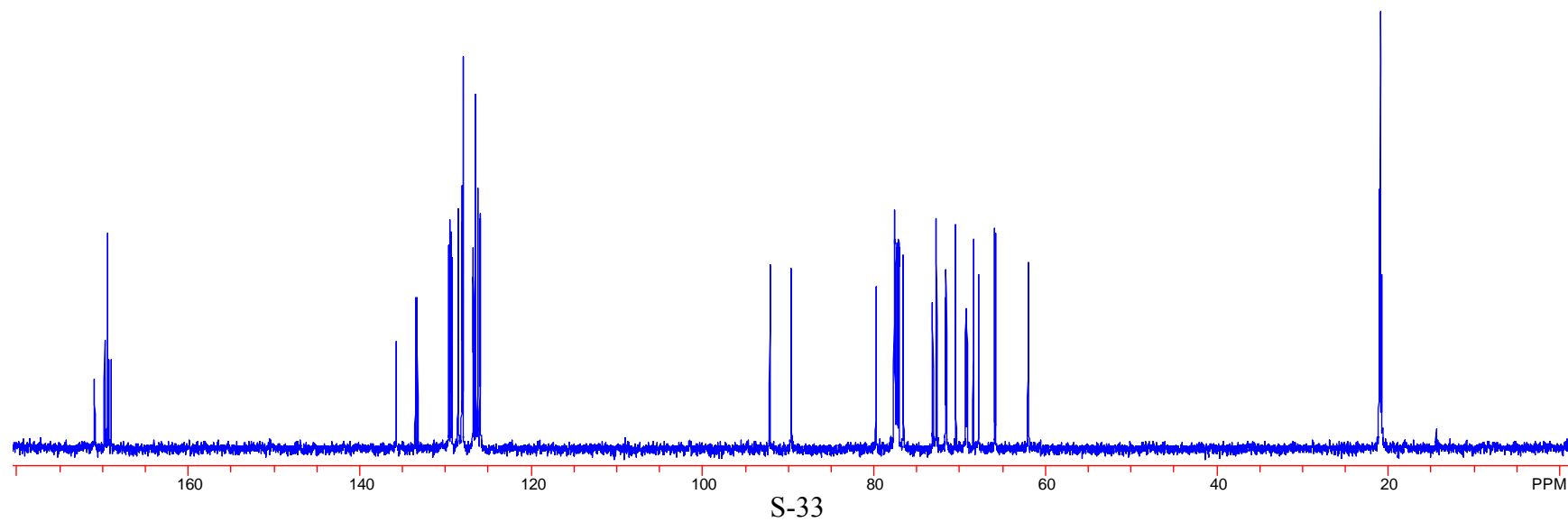
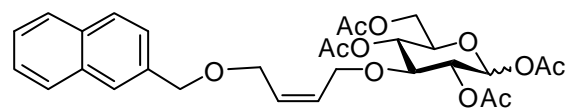


$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) 1,2,4,6-Tetra-*O*-acetyl-3-*O*-[4-(2-naphthylmethoxy)-2-*Z*-butenyl]-*D*- $\alpha,\beta$ -glucopyranose (**25**).

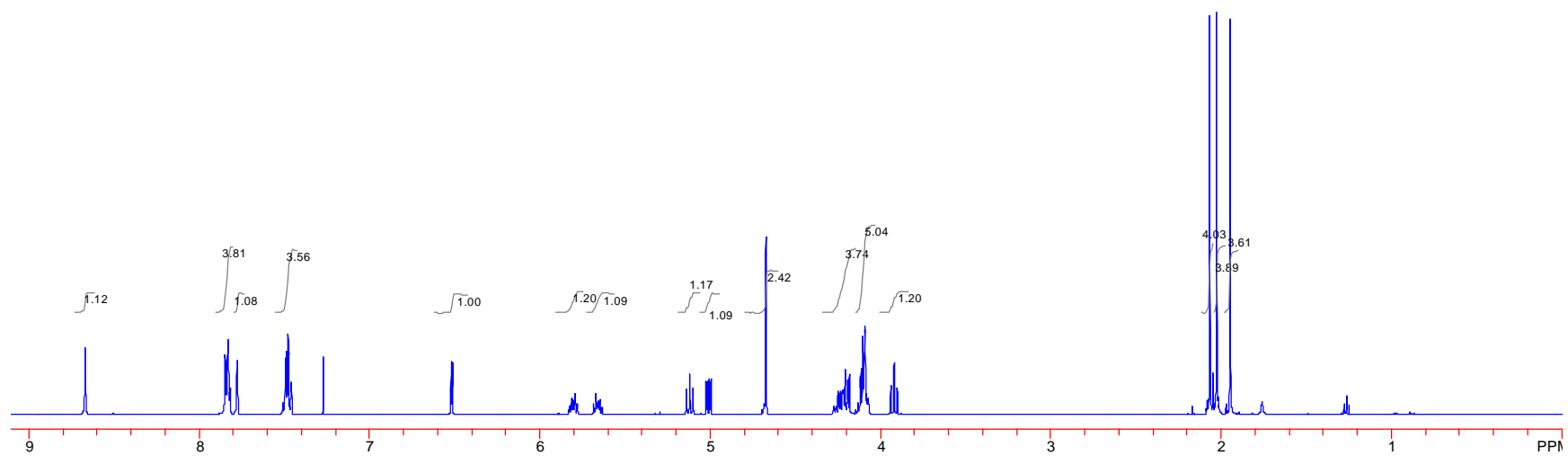
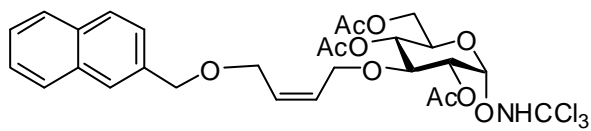




$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 1,2,4,6-Tetra-*O*-acetyl-3-*O*-[4-(2-naphthylmethoxy)-2-*Z*-butenyl]-*D*- $\alpha,\beta$ -glucopyranose (**25**).

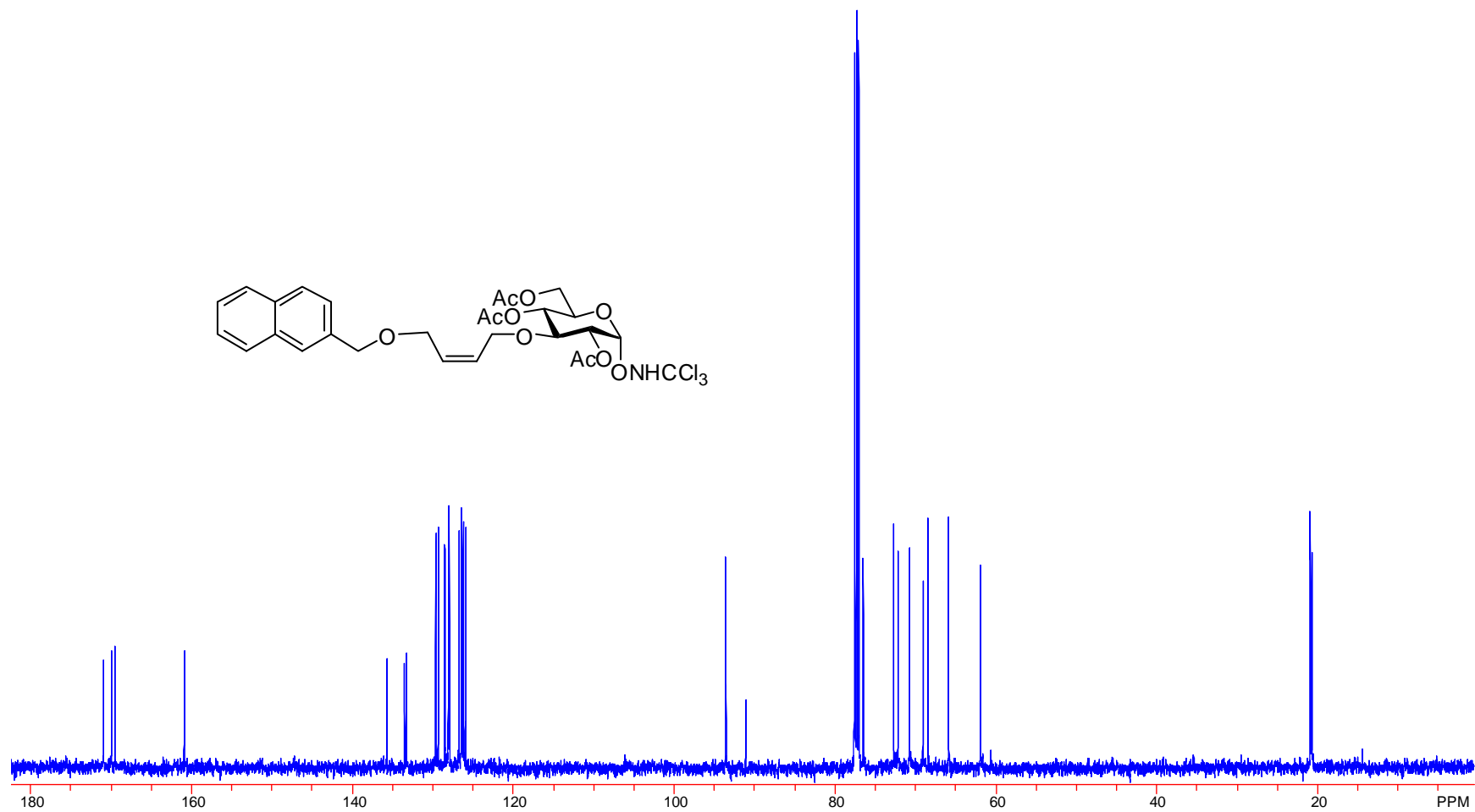


<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 500 MHz) 2,4,6-Tri-*O*-acetyl-3-*O*-[4-(2-naphthylmethoxy)-2-*Z*-butenyl]- $\alpha$ -D-glucopyranosyl trichloroacetimidate (26).

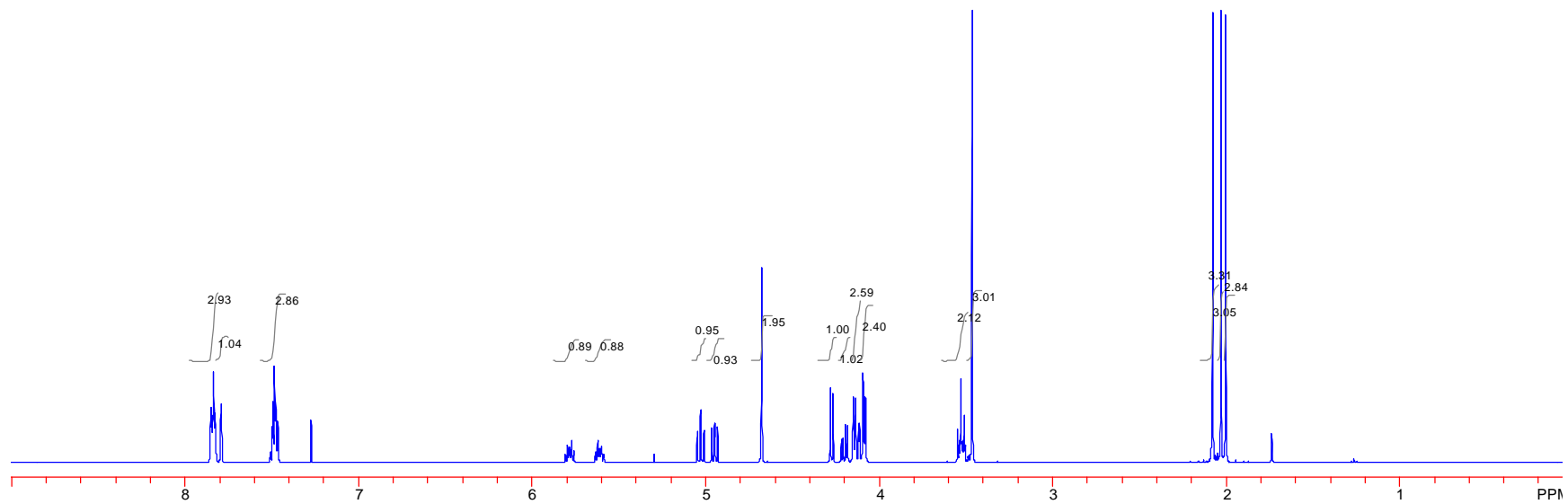
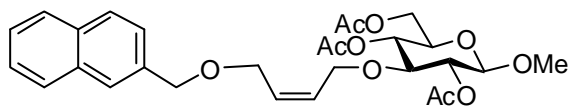


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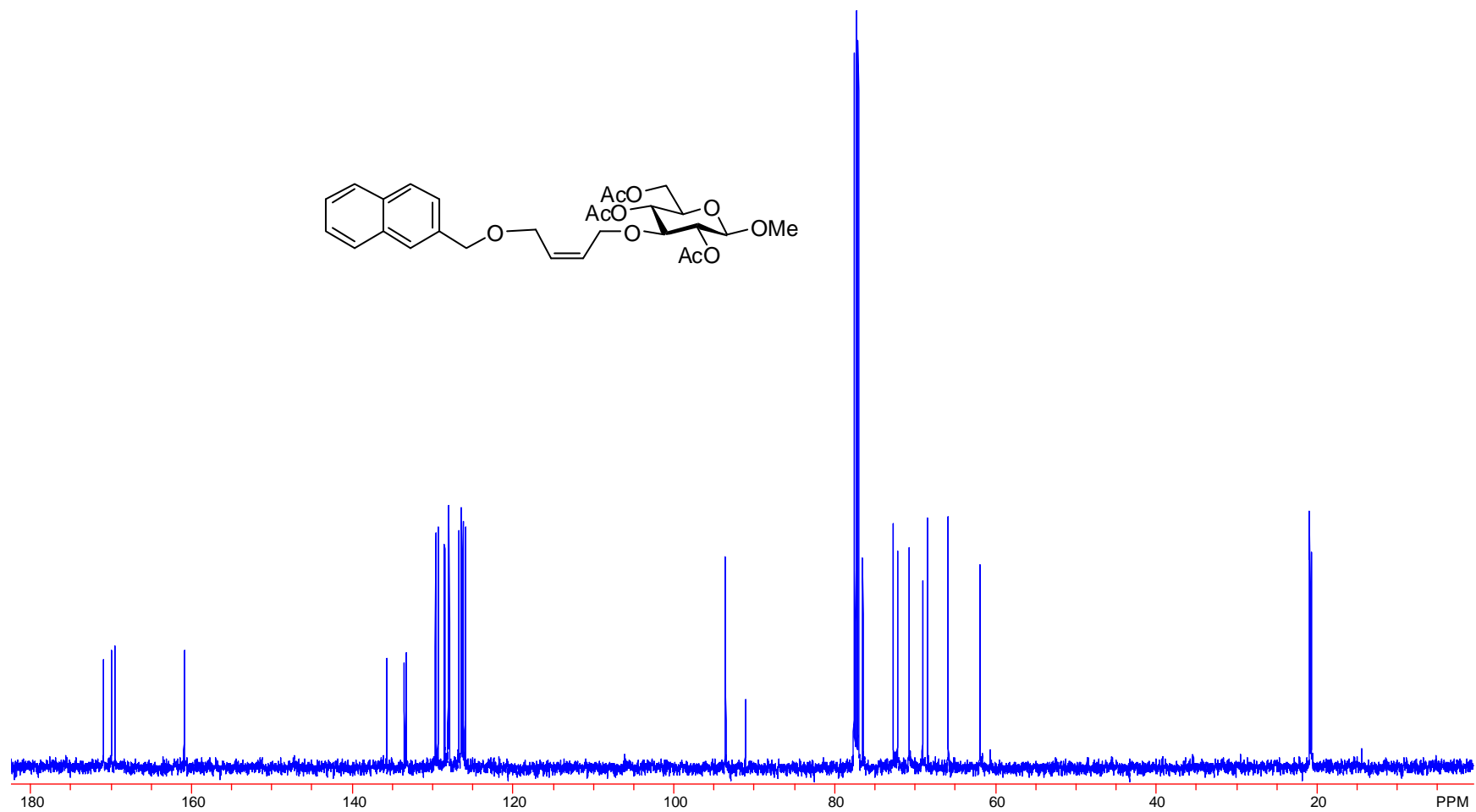
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 2,4,6-Tri-*O*-acetyl-3-*O*-[4-(2-naphthylmethoxy)-2-*Z*-butenyl]- $\alpha$ -D-glucopyranosyl trichloroacetimidate (26).



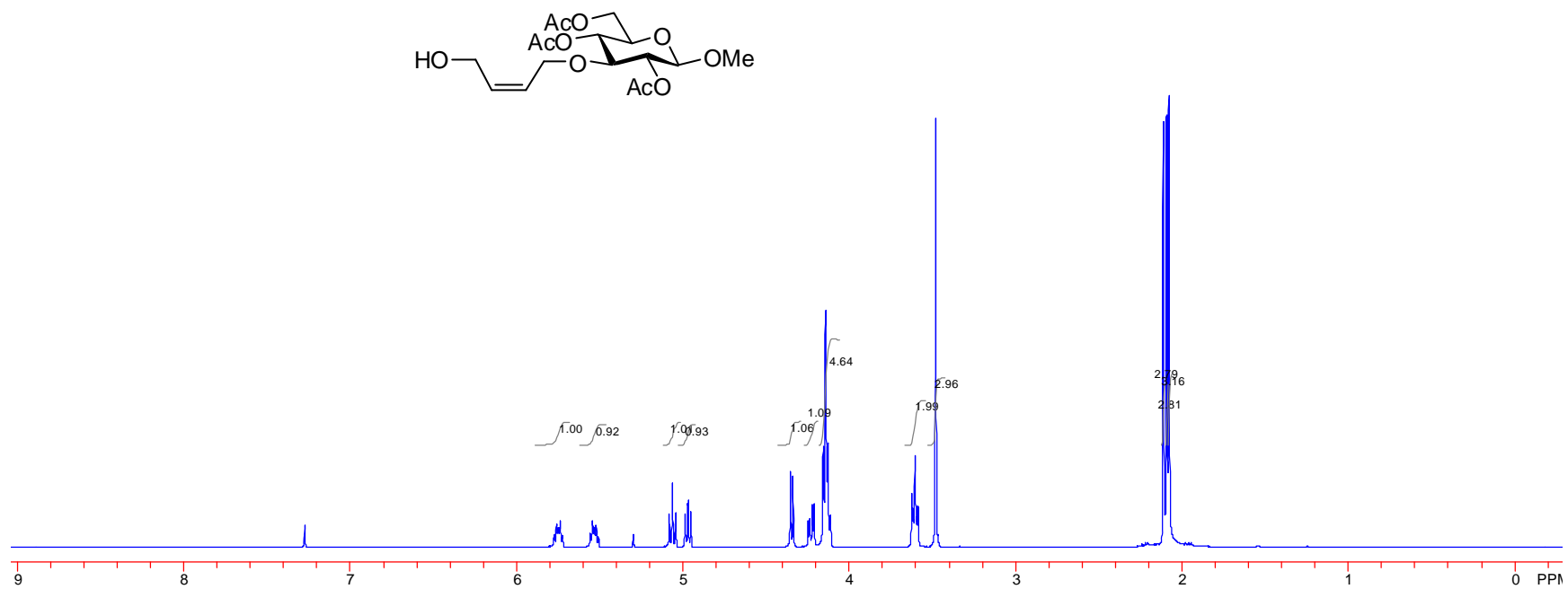
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 500 MHz) Methyl 2,4,6-tri-*O*-acetyl-3-*O*-[4-(2-naphthylmethoxy)-2-*Z*-butenyl]-β-D-glucopyranoside (**27**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) Methyl 2,4,6-tri-*O*-acetyl-3-*O*-[4-(2-naphthylmethoxy)-2-*Z*-butenyl]- $\beta$ -D-glucopyranoside (**27**).

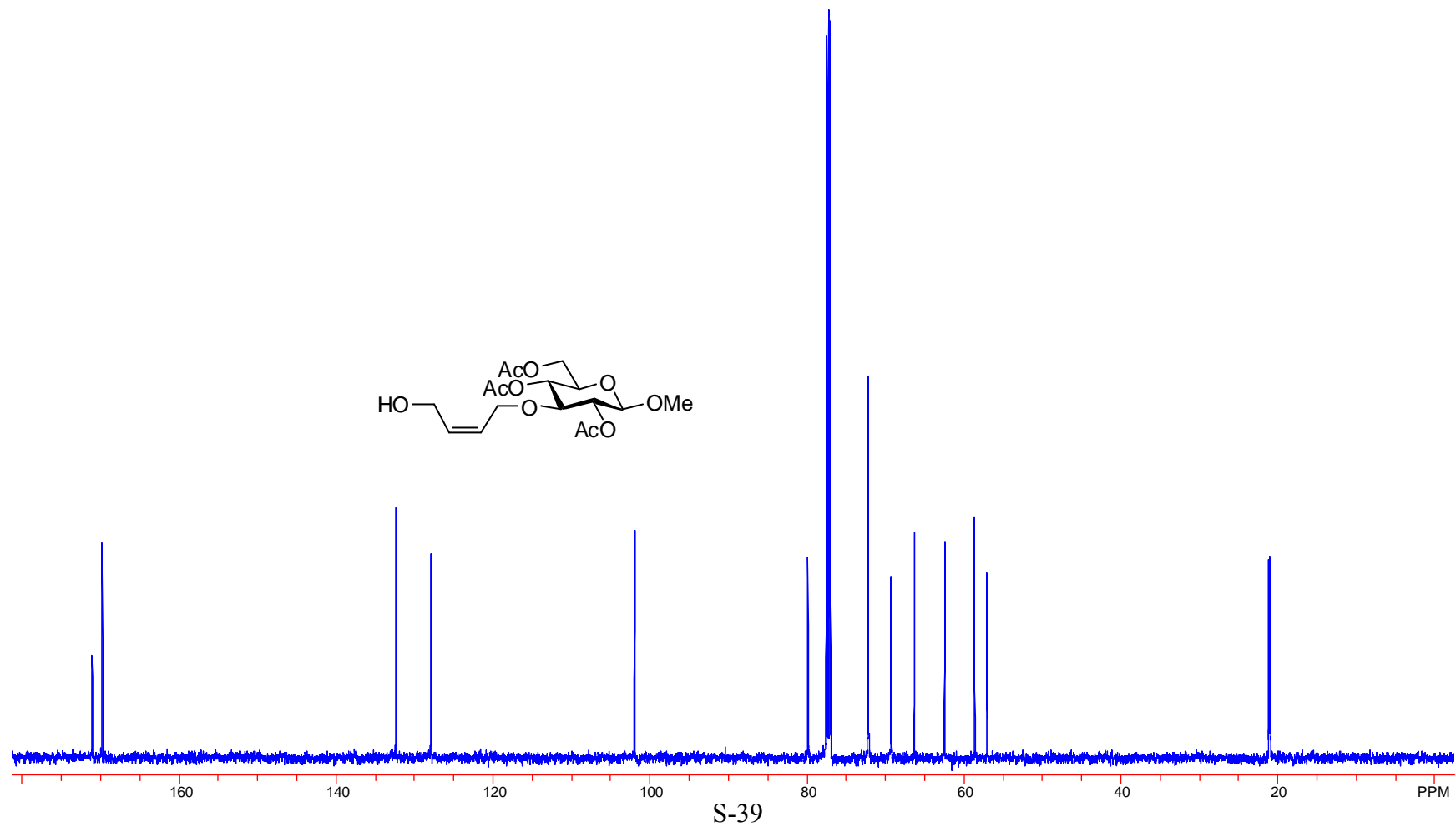


$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) Methyl 2,4,6-tri-*O*-acetyl-3-*O*-[4-hydroxy-2-*Z*-butenyl]- $\beta$ -D-glucopyranoside (**28**).

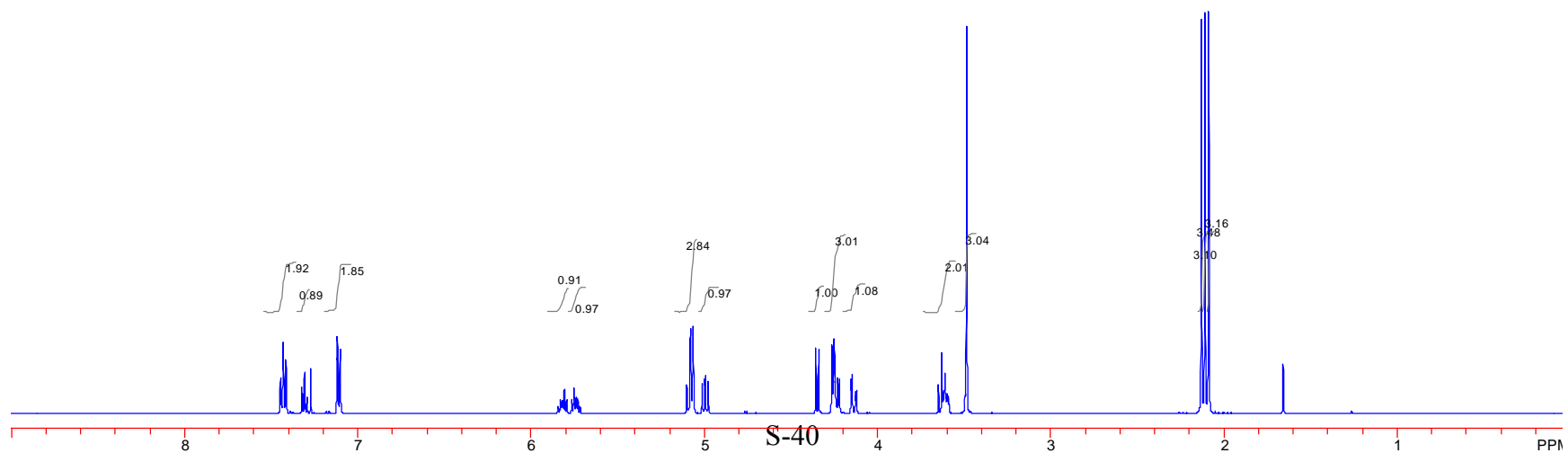
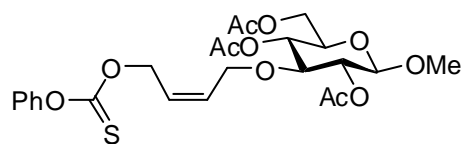


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$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) Methyl 2,4,6-tri-*O*-acetyl-3-*O*-[4-hydroxy-2-*Z*-butenyl]- $\beta$ -D-glucopyranoside (**28**).

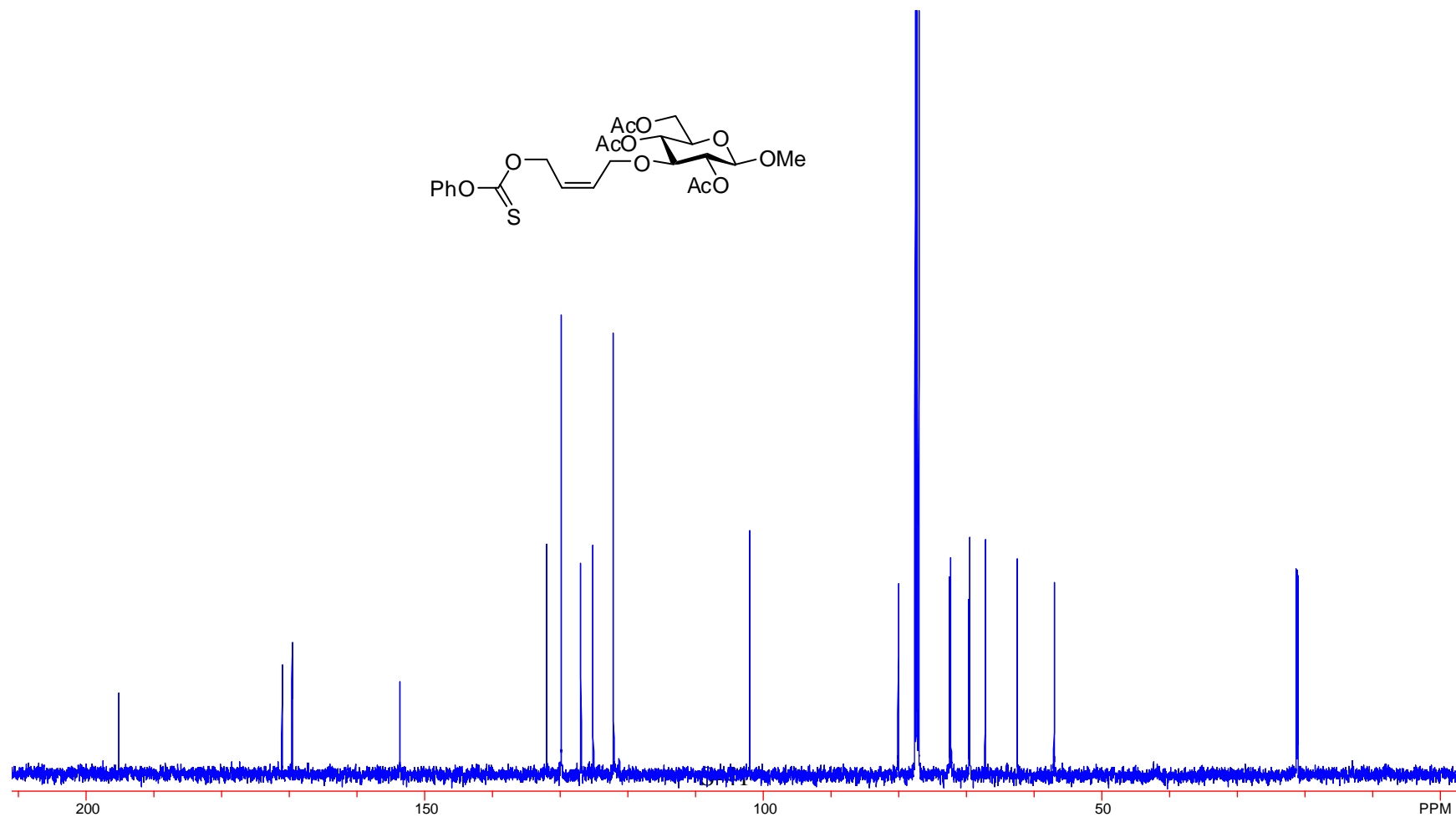
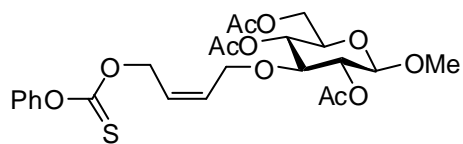


<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 500 MHz) Methyl 2,4,6-tri-*O*-acetyl-3-*O*-[4-(phenyloxythionocarbonyloxy)-2-*Z*-butenyl]-β-D-glucopyranoside (**29**).

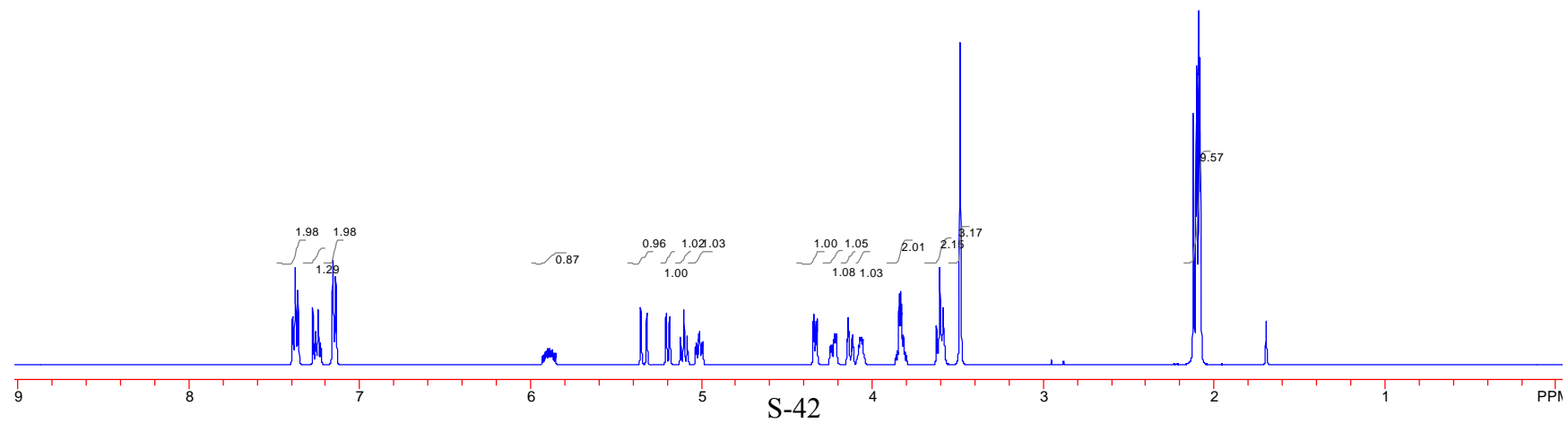
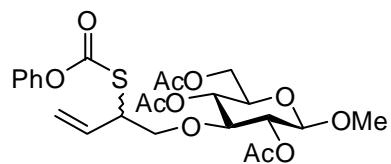




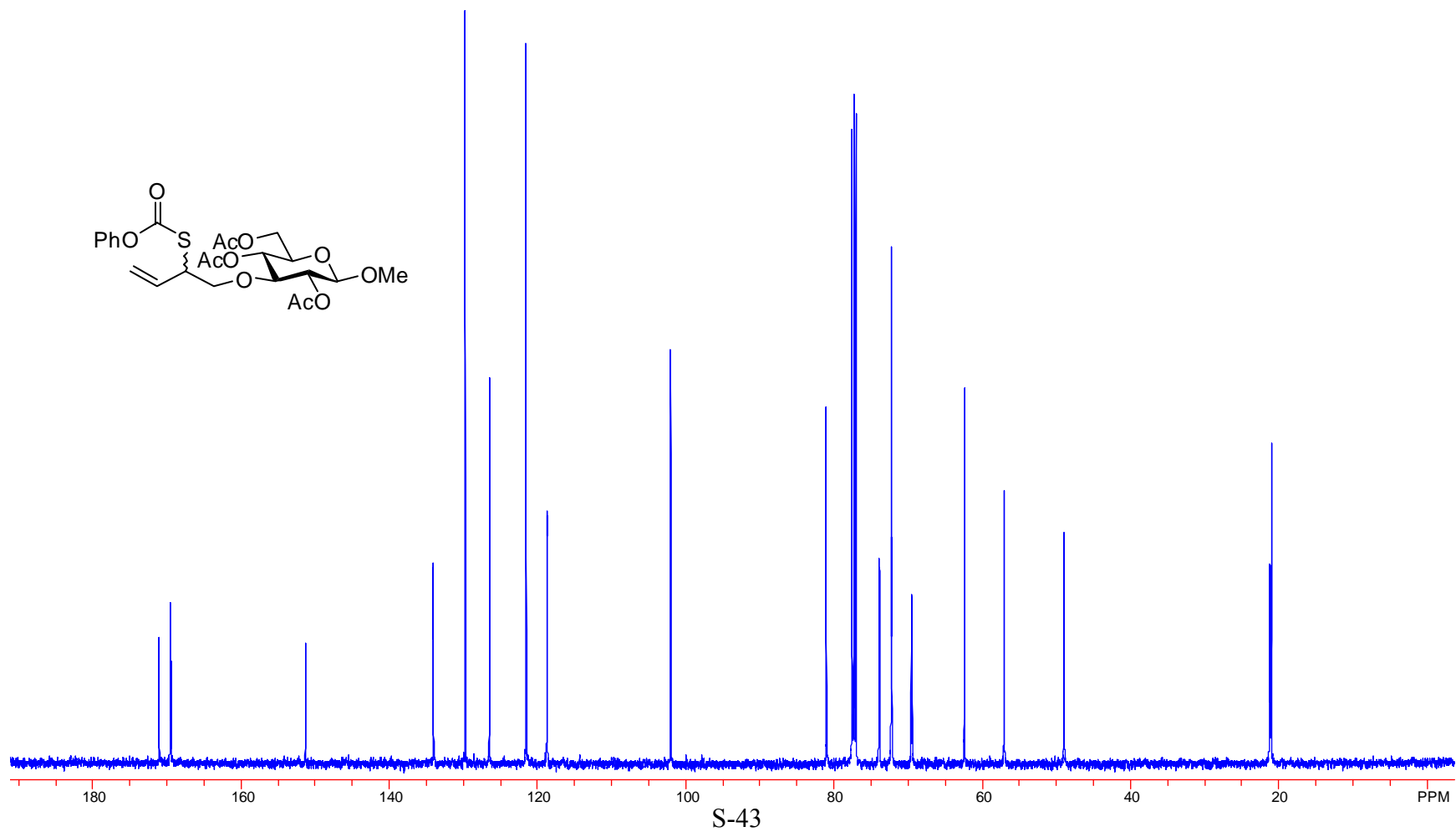
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) Methyl 2,4,6-tri-*O*-acetyl-3-*O*-[4-(phenyloxythionocarbonyloxy)-2-*Z*-butenyl]- $\beta$ -D-glucopyranoside (**29**).



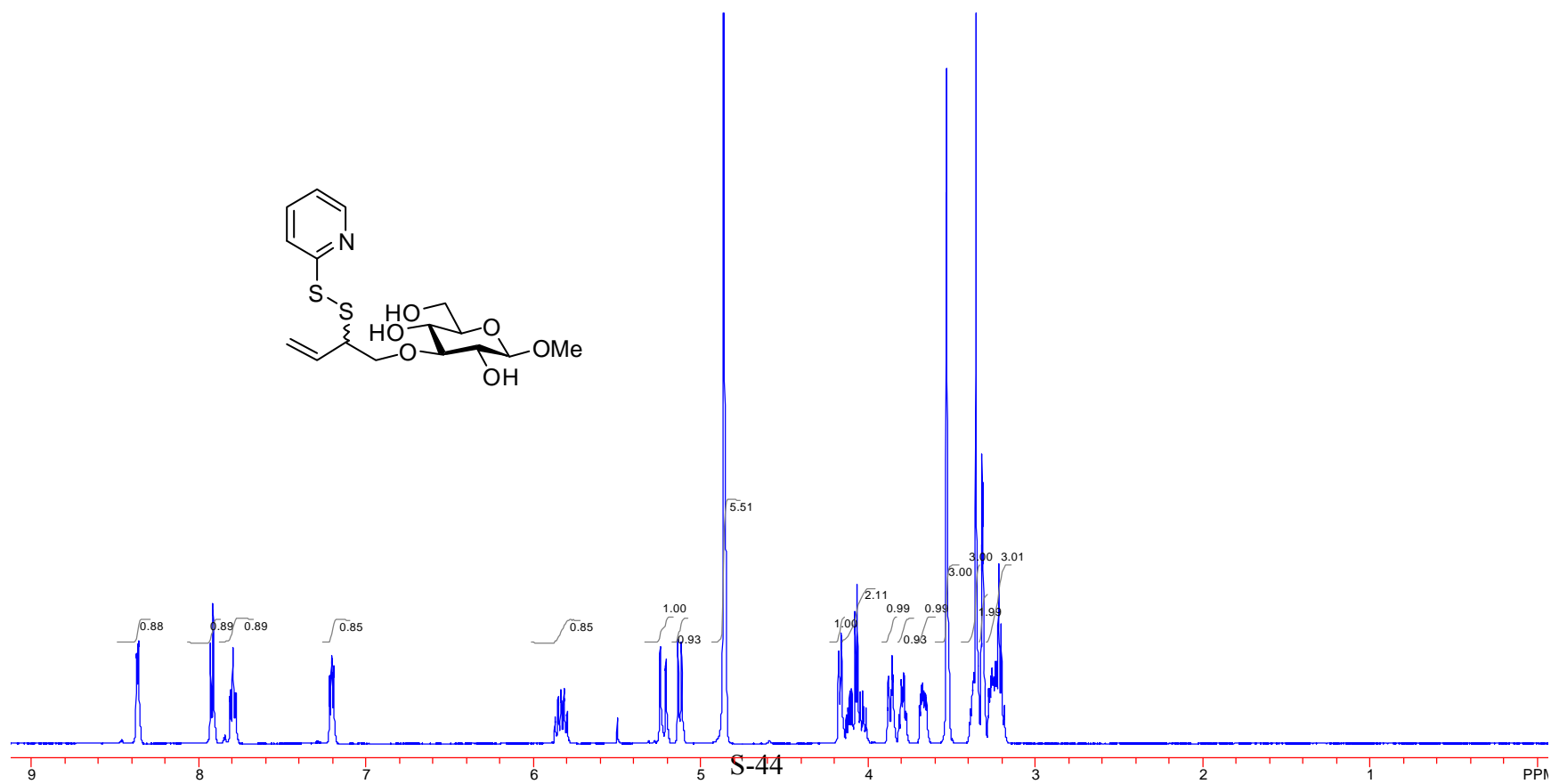
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) Methyl 2,4,6-tri-*O*-acetyl-3-*O*-[(2-phenyloxycarbonylthioxy)-3-butenyl]- $\beta$ -D-glucopyranoside (**30**).



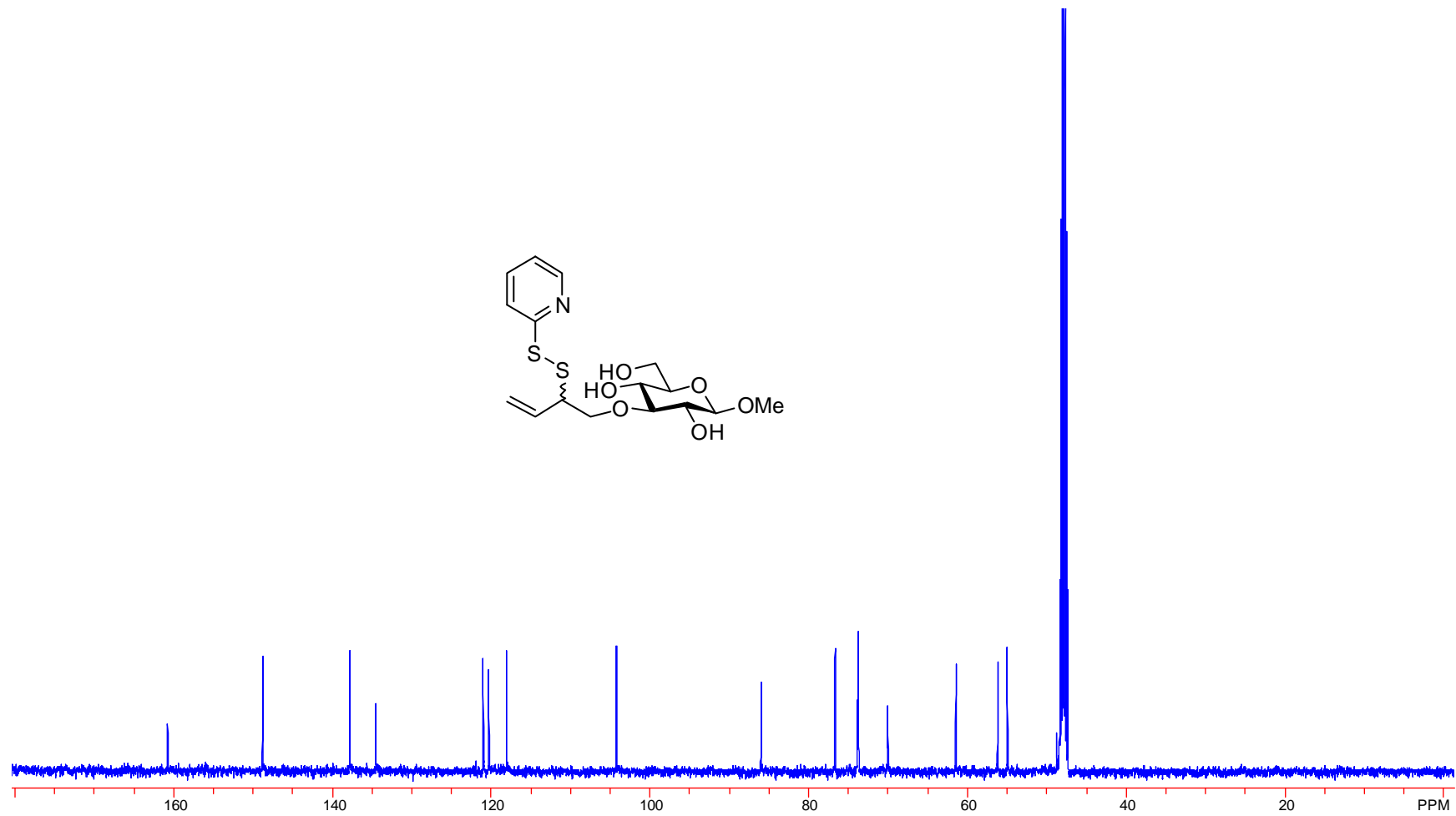
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) Methyl 2,4,6-tri-*O*-acetyl-3-*O*-[(2-phenyloxycarbonylthioxy)-3-butenyl]- $\beta$ -D-glucopyranoside (**30**).



$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 500 MHz) Methyl 3-*O*-[(2-pyridyldithio)-3-butenyl]- $\beta$ -D-glucopyranoside (**31**).

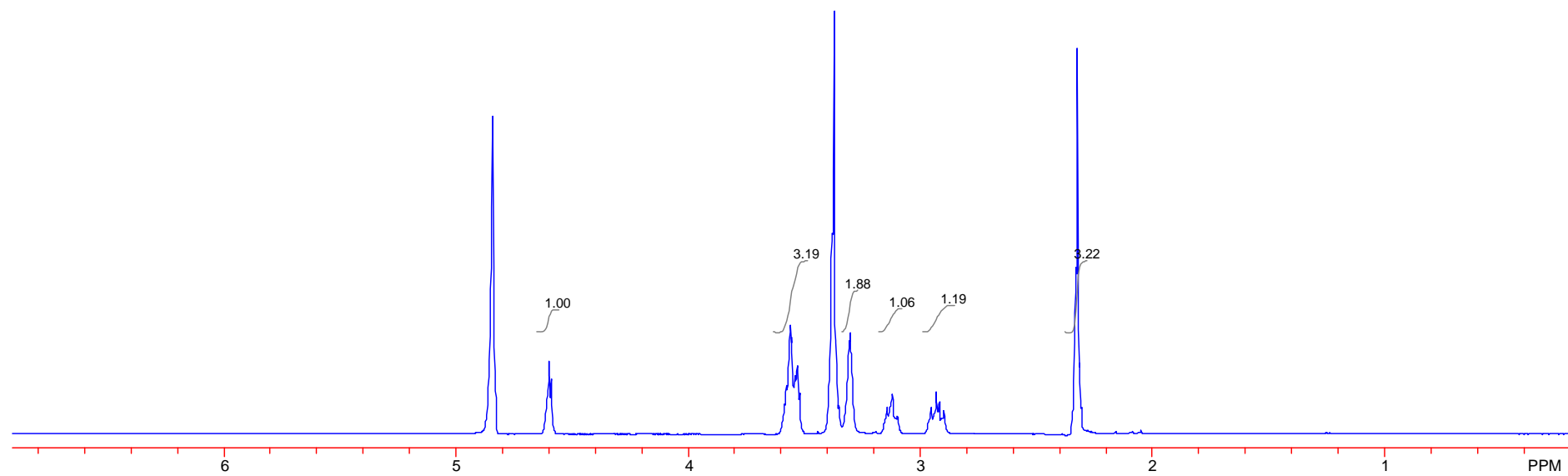
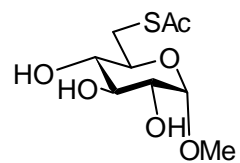


$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) Methyl 3-*O*-[(2-pyridyldithio)-3-butenyl]- $\beta$ -D-glucopyranoside (**31**).

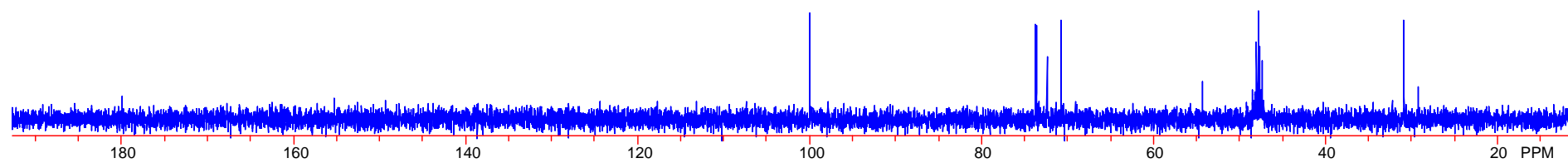
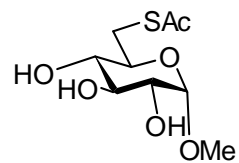


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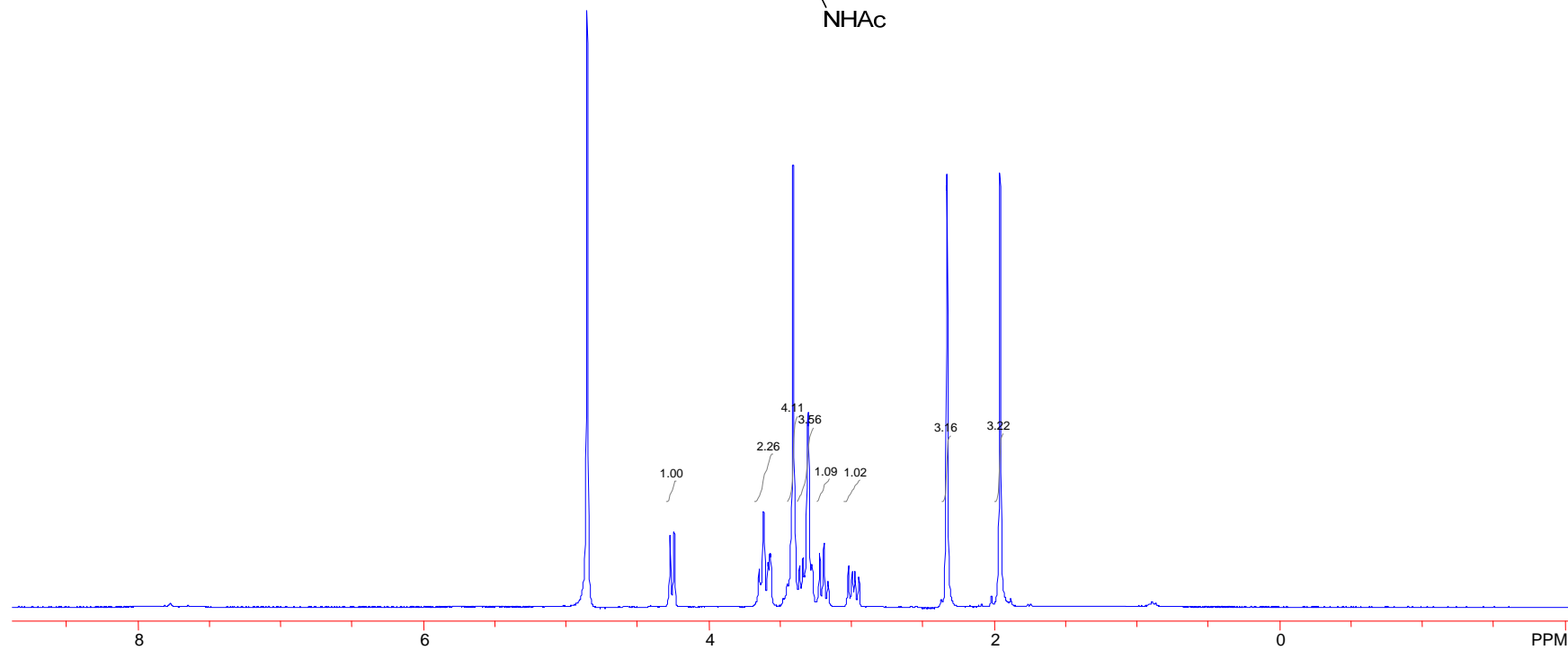
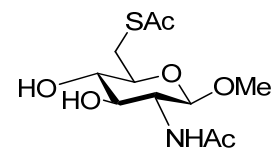
$^1\text{H}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 400 MHz) Methyl 6-acetylthio- $\alpha$ -D-glucopyranoside (**32**)



$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 100 MHz) Methyl 6-acetylthio- $\alpha$ -D-glucopyranoside (**32**)

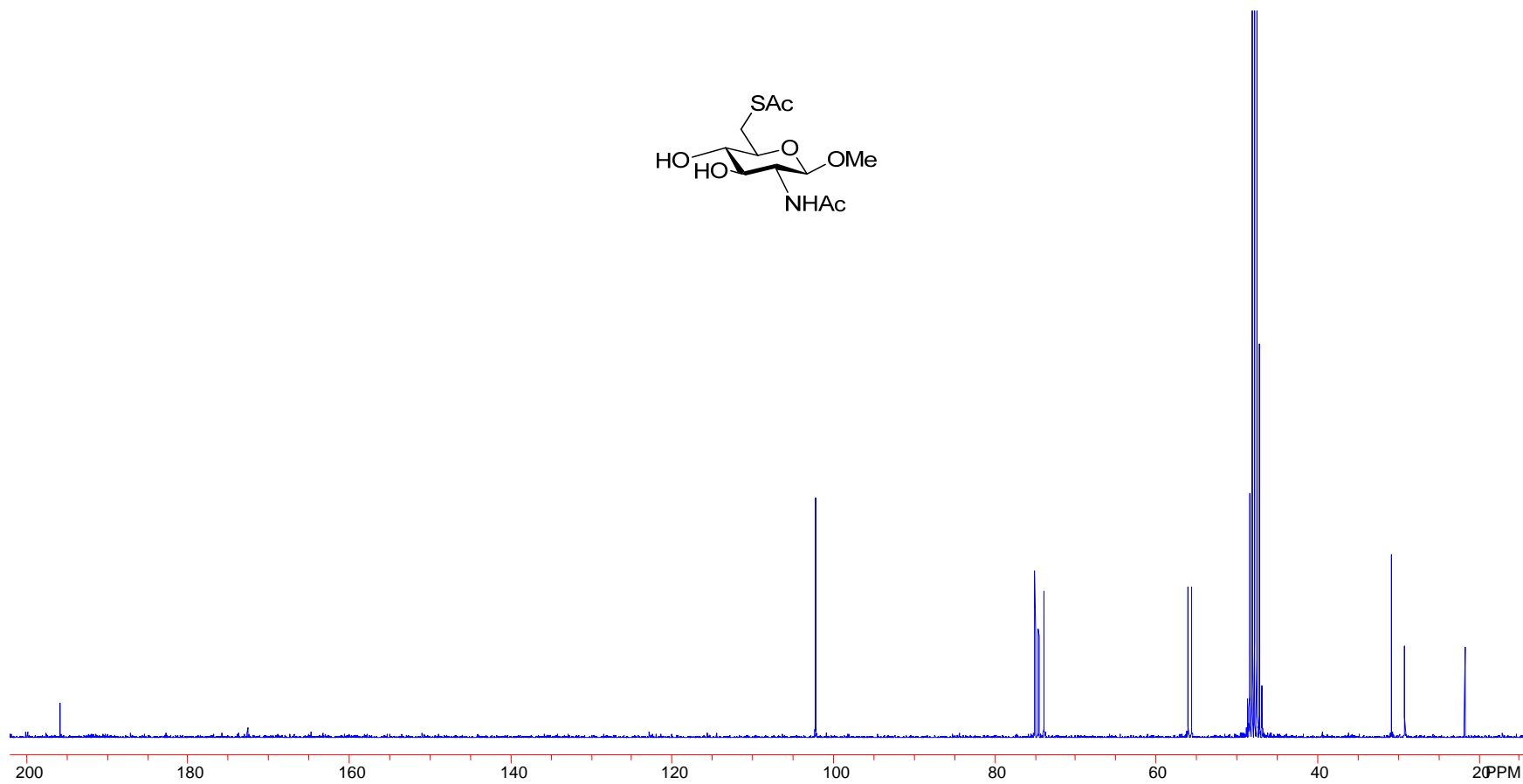
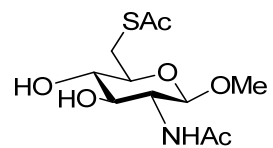


$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 400 MHz) Methyl 2-acetamido-6-acetylthio-2-deoxy- $\beta$ -D-glucopyranoside (**33**).

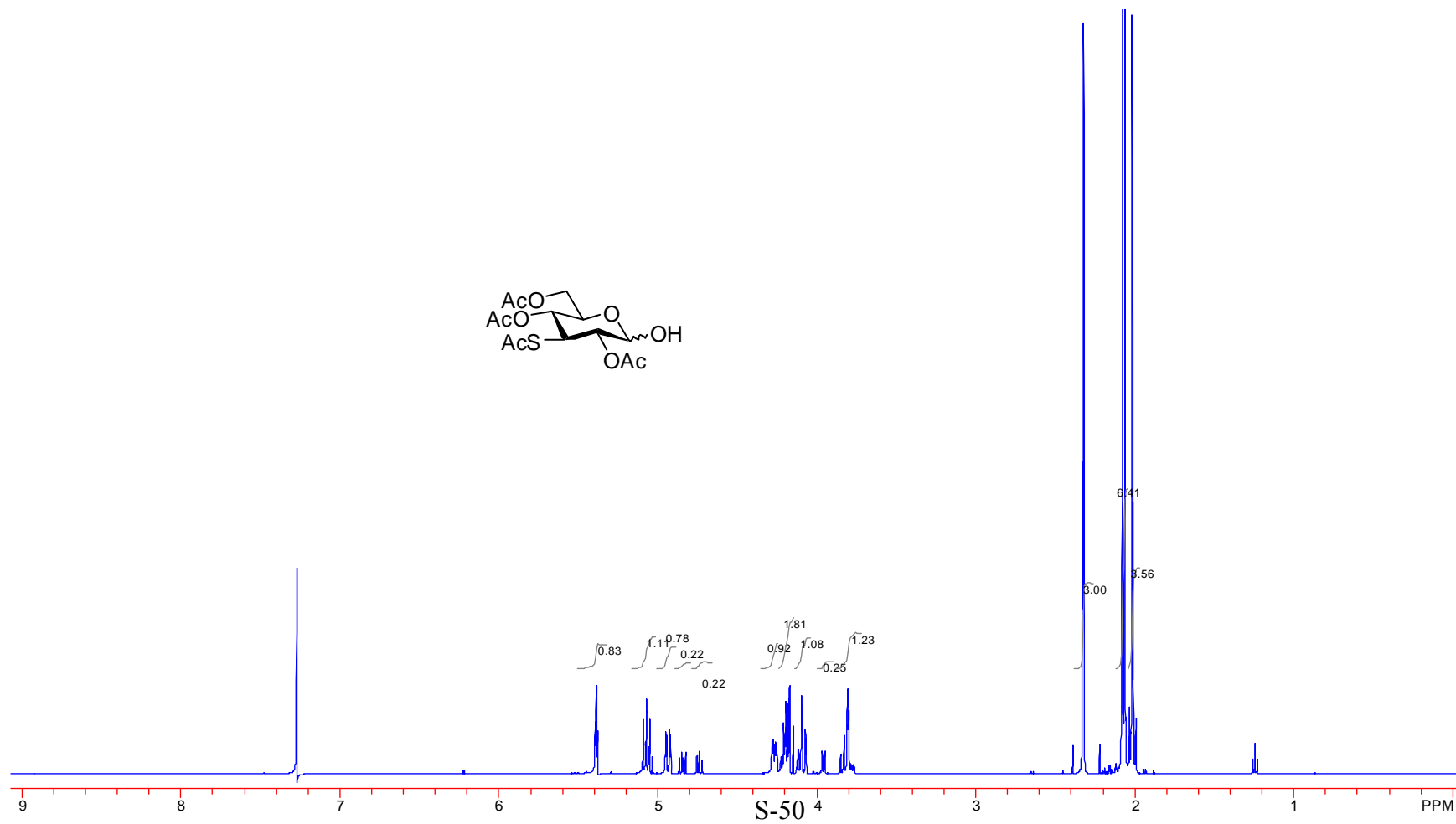




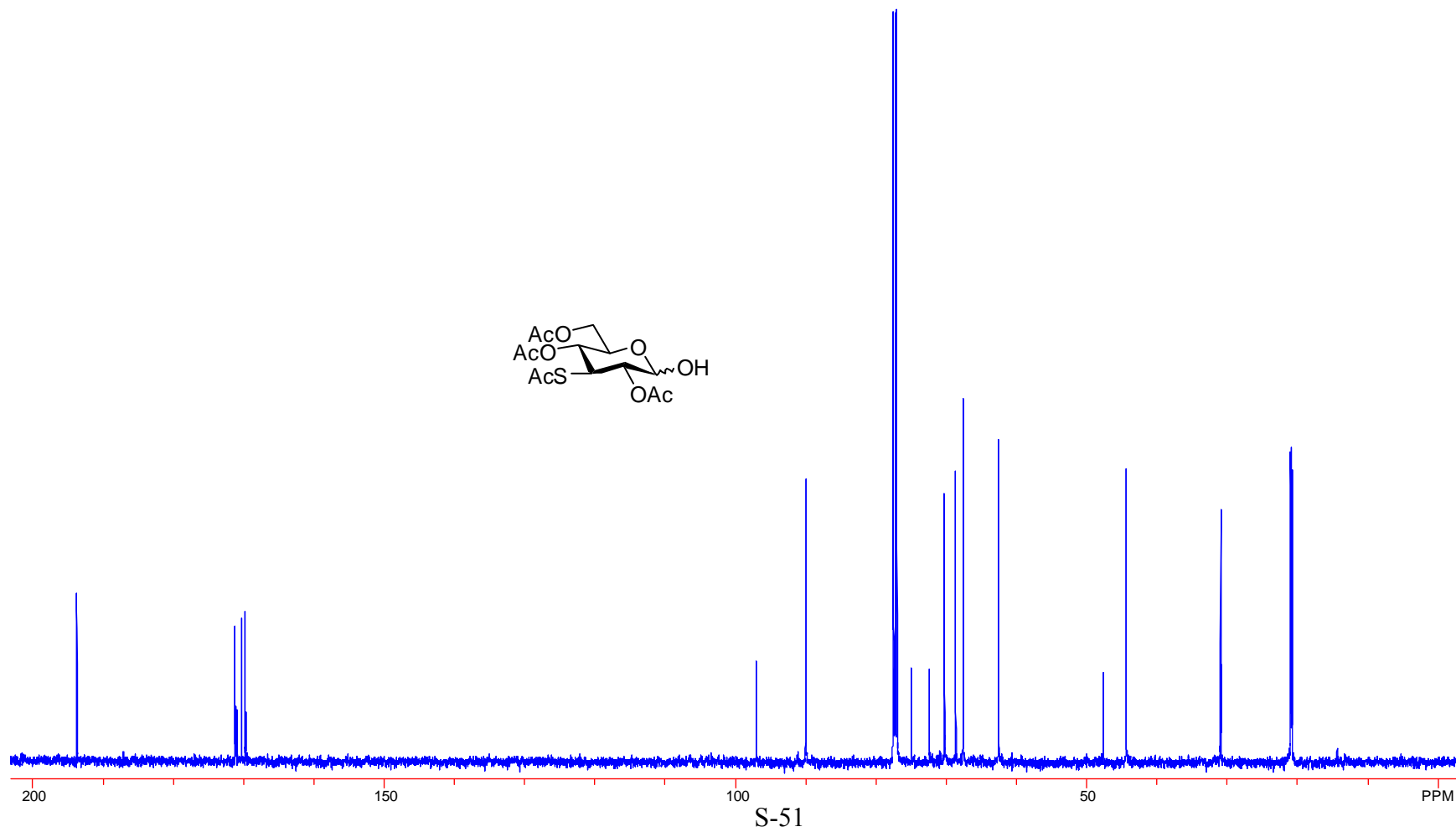
$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 100 MHz) Methyl 2-acetamido-6-acetylthio-2-deoxy- $\beta$ -D-glucopyranoside (**33**).



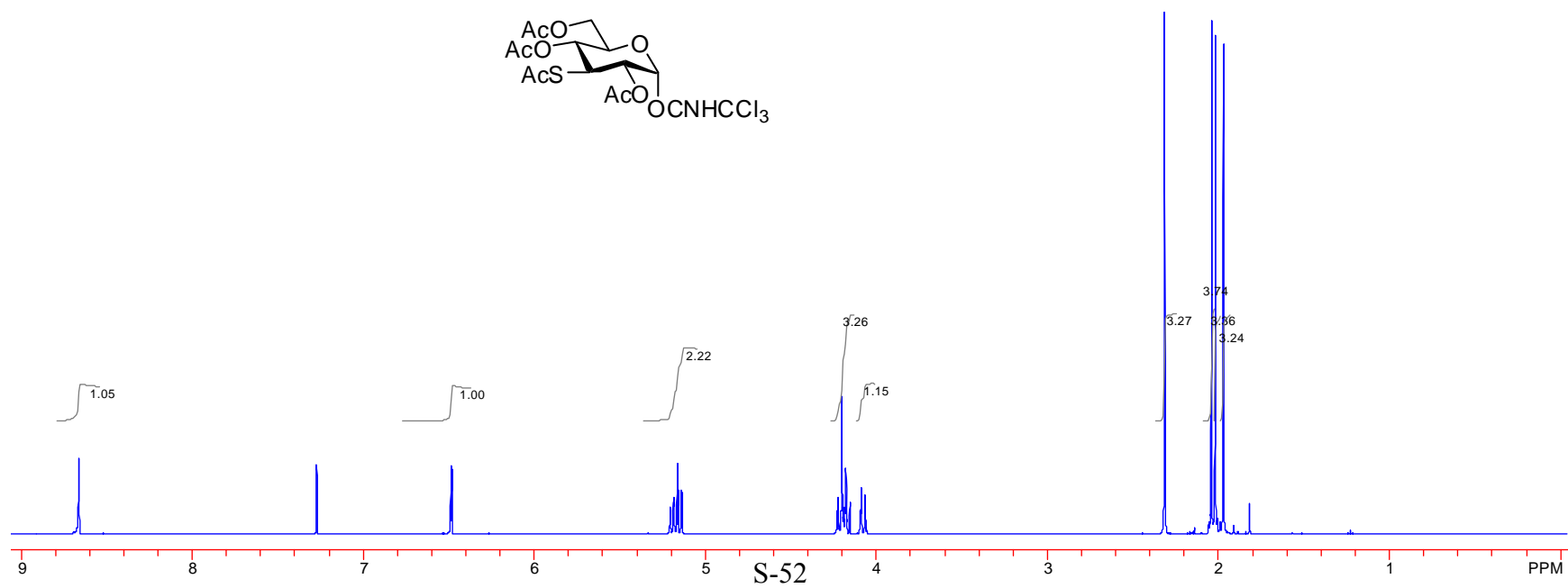
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) 2,4,6-Tri-*O*-acetyl-3-acetylthio- $\alpha,\beta$ -D-glucopyranose (**35**).



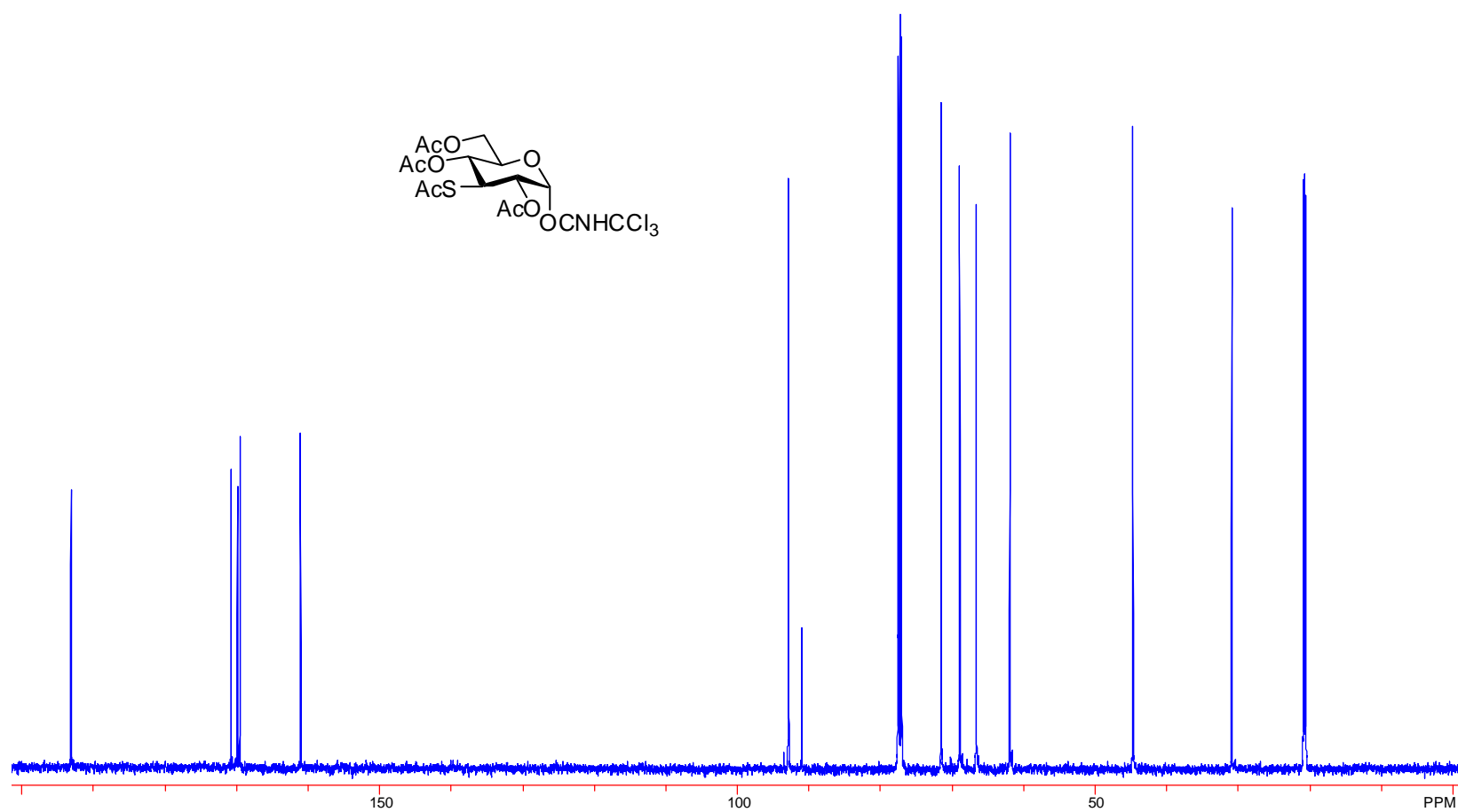
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 2,4,6-Tri-*O*-acetyl-3-acetylthio- $\alpha,\beta$ -D-glucopyranose (**35**).



$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) 2,4,6-Tri-*O*-acetyl-3-acetylthio- $\alpha$ -D-glucopyranosyl trichloroacetimidate (**36**).

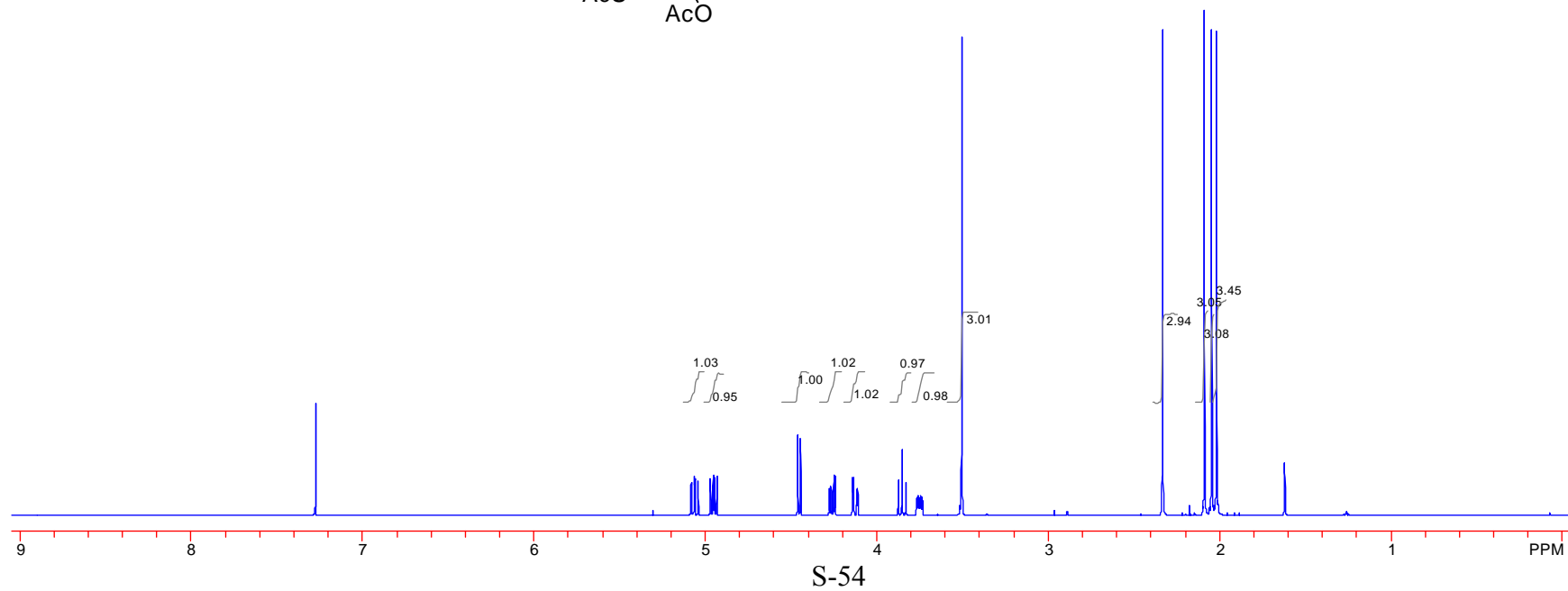
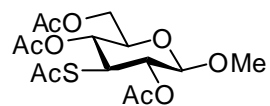


$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 2,4,6-Tri-*O*-acetyl-3-acetylthio- $\alpha$ -D-glucopyranosyl trichloroacetimidate (**36**).

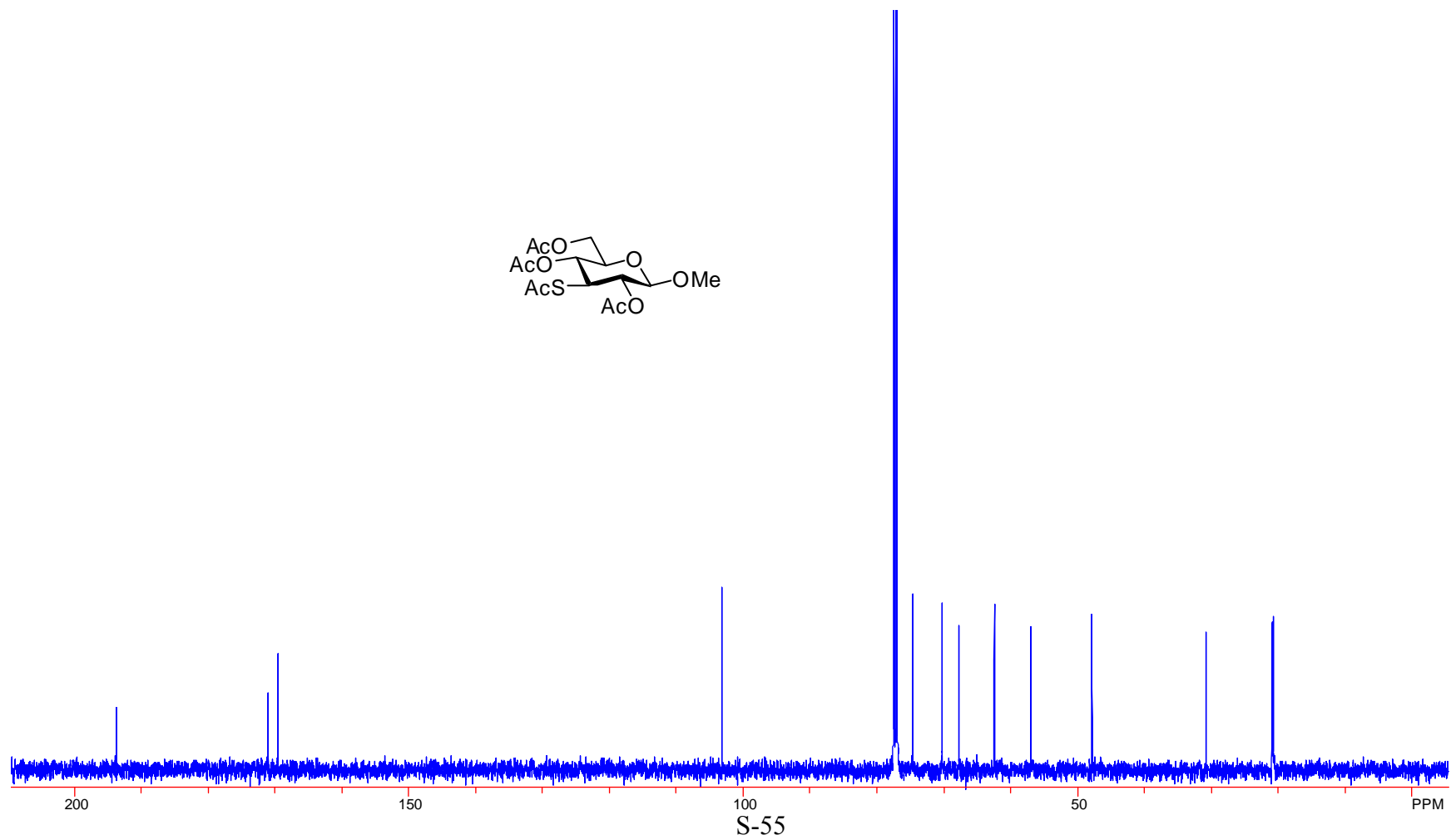
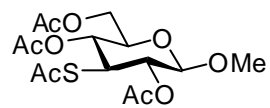


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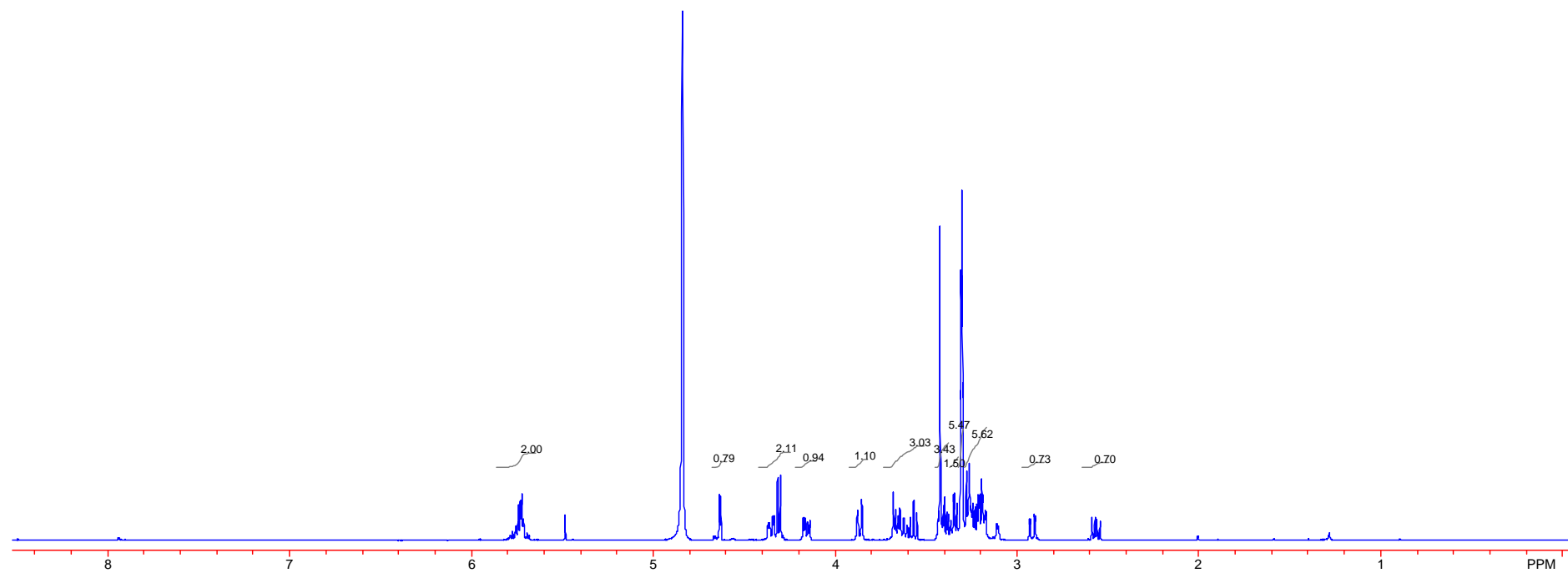
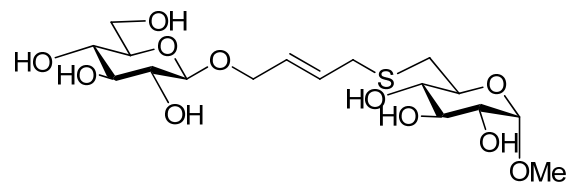
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) Methyl 2,4,6-tri-*O*-acetyl-3-acetylthio- $\beta$ -D-glucopyranoside (**37**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) Methyl 2,4,6-tri-*O*-acetyl-3-acetylthio- $\beta$ -D-glucopyranoside (**37**).



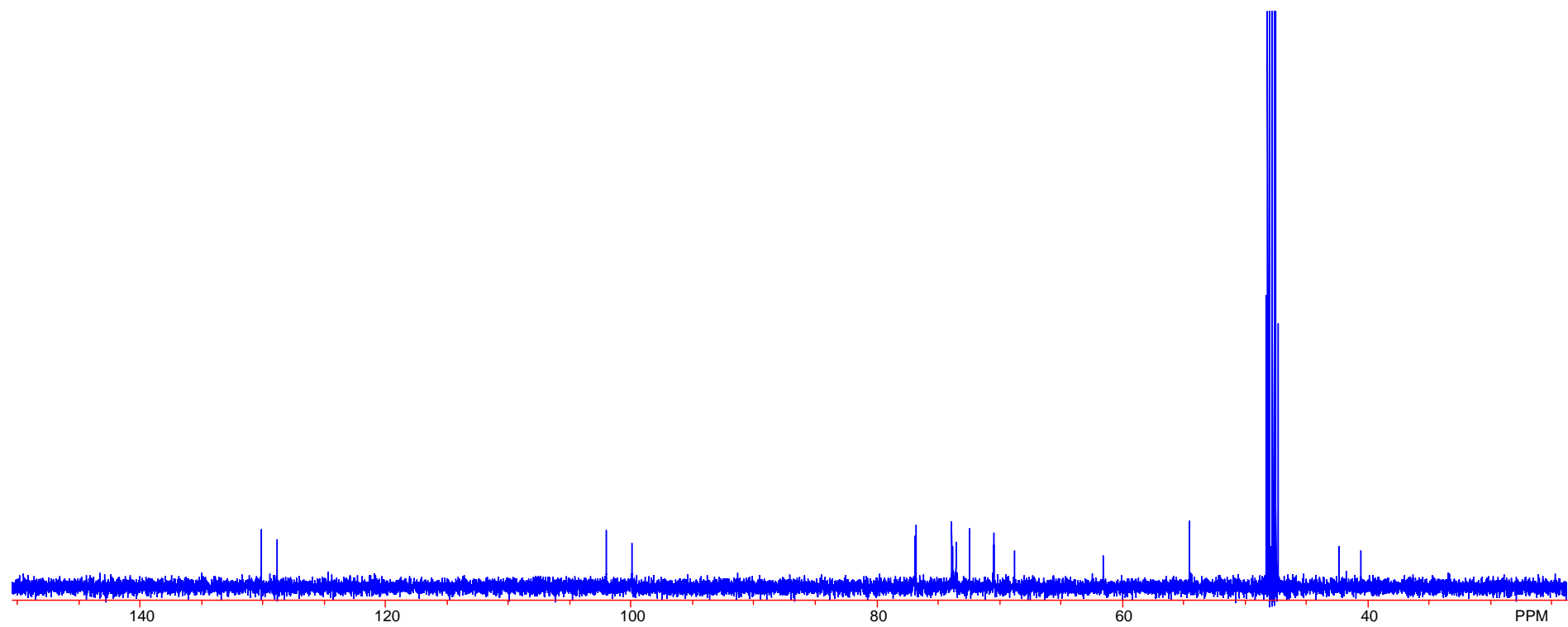
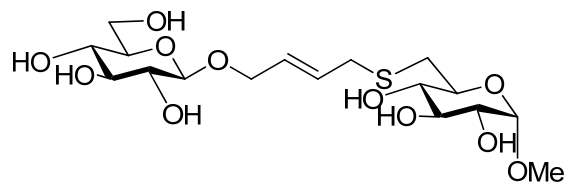
$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 500 MHz) Methyl 6-[4-( $\beta$ -D-glucopyranosyloxy)-2*E*-butenyl]-thio- $\alpha$ -D-glucopyranoside (**40**)



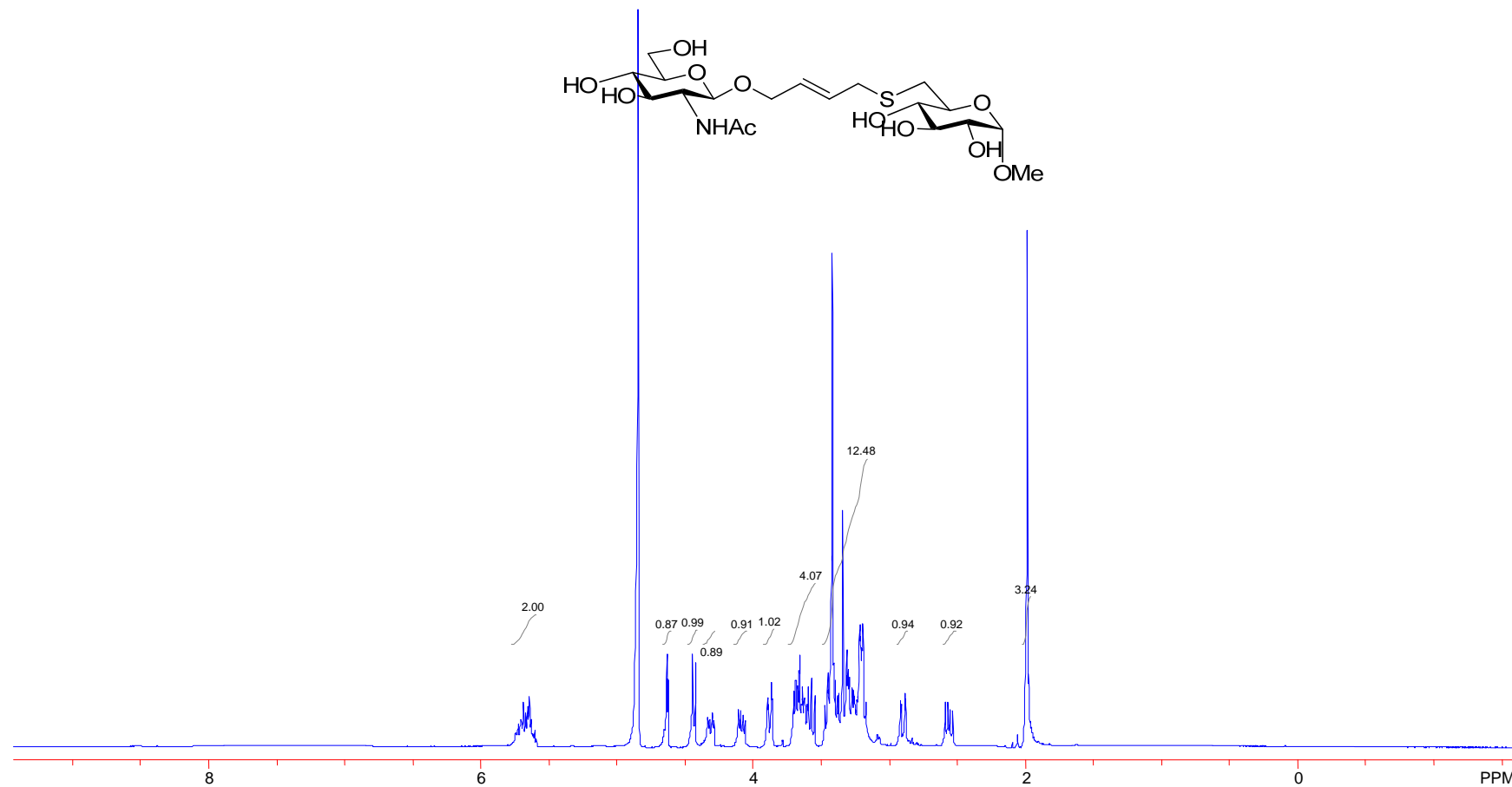
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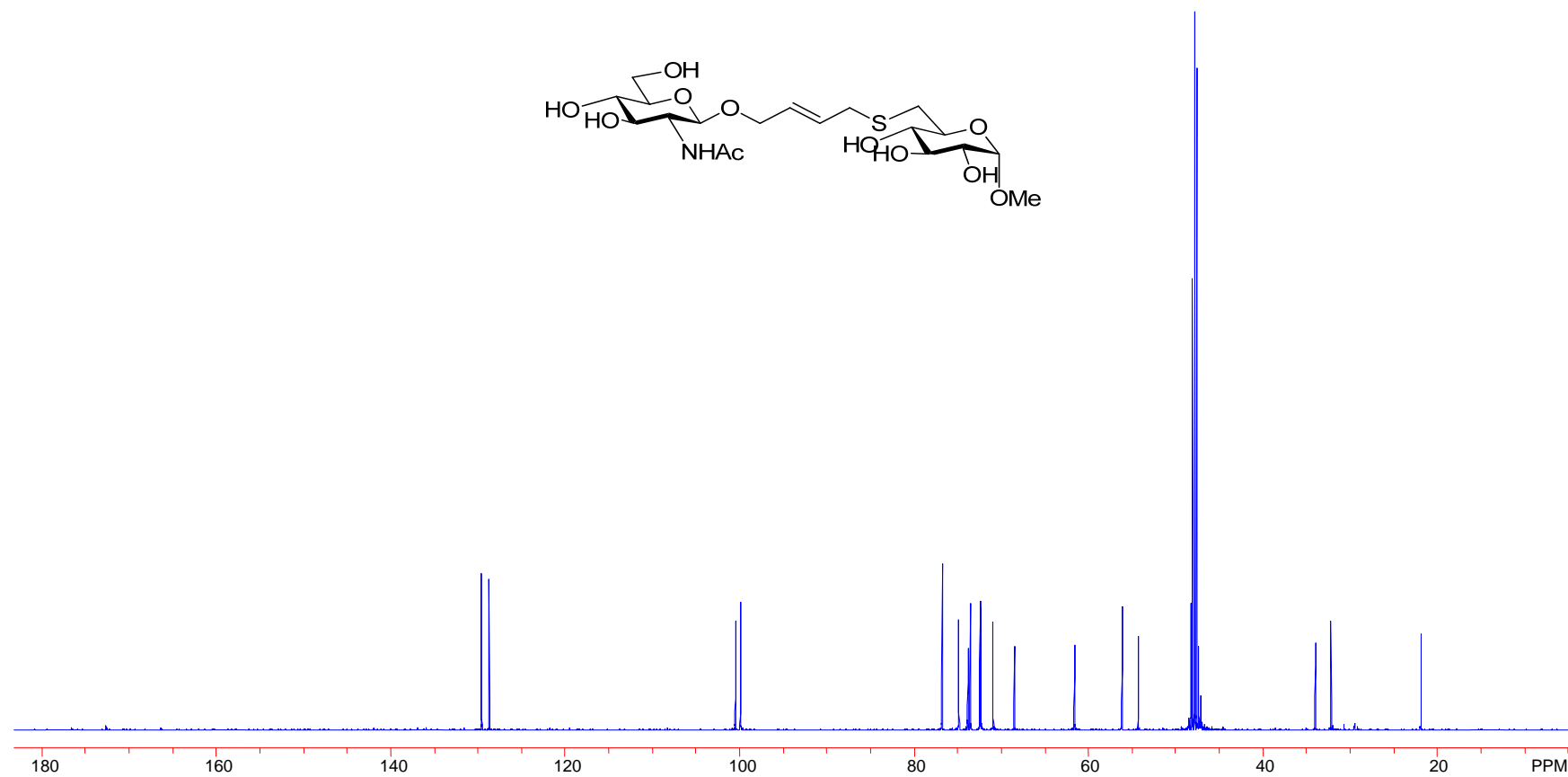
$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) Methyl 6-[4-( $\beta$ -D-glucopyranosyloxy)-2*E*-butenyl]-thio- $\alpha$ -D-glucopyranoside (**40**)



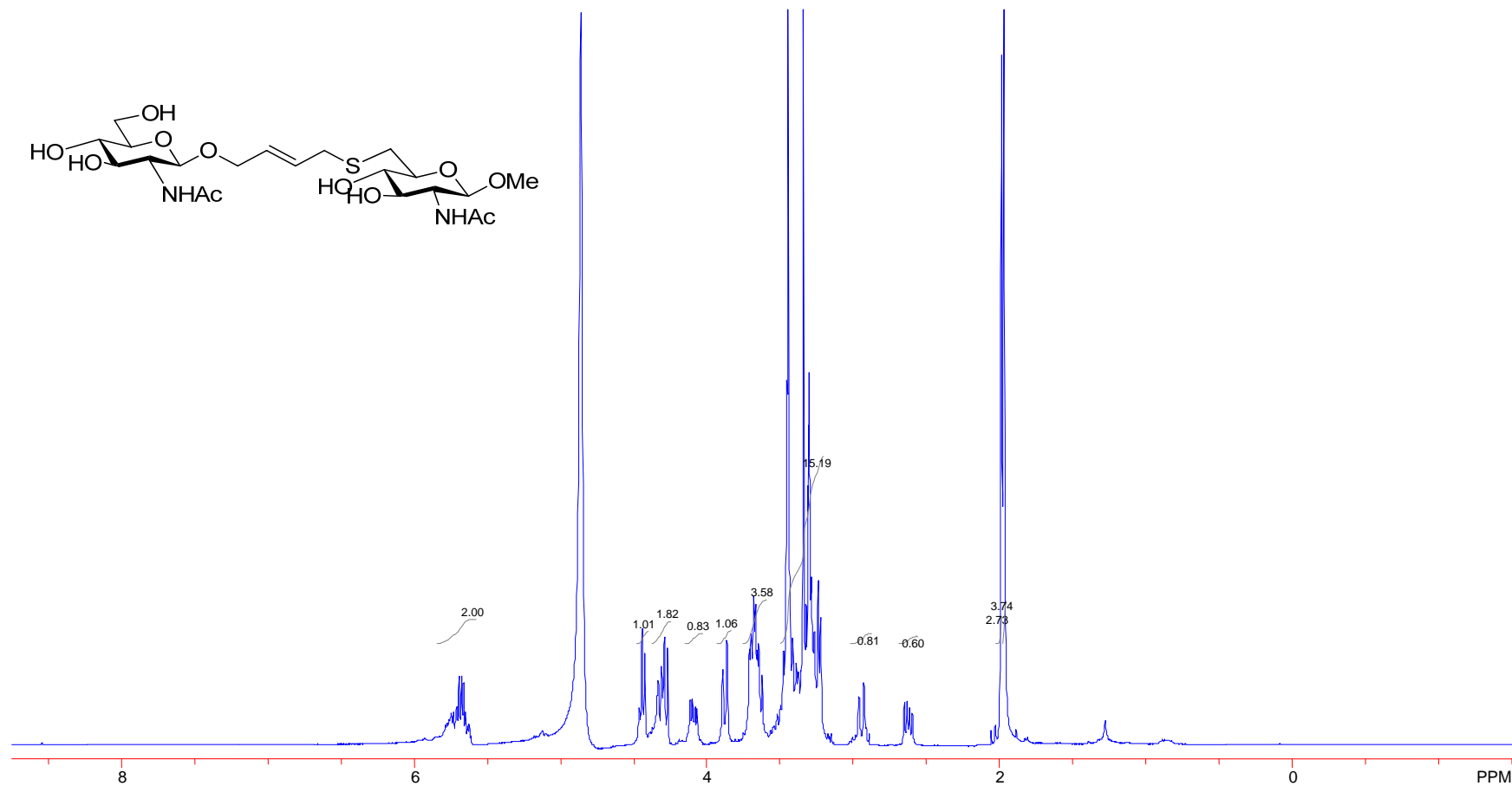
$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 400 MHz) Methyl 6-[4-(2-acetamido-2-deoxy- $\beta$ -D-glucopyranosyloxy)-2*E*-buteny]-thio-2-deoxy- $\beta$ -D-glucopyranoside (**41**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 100 MHz) Methyl 6-[4-(2-acetamido-2-deoxy- $\beta$ -D-glucopyranosyloxy)-2*E*-butenyl]-thio-2-deoxy- $\beta$ -D-glucopyranoside (**41**).

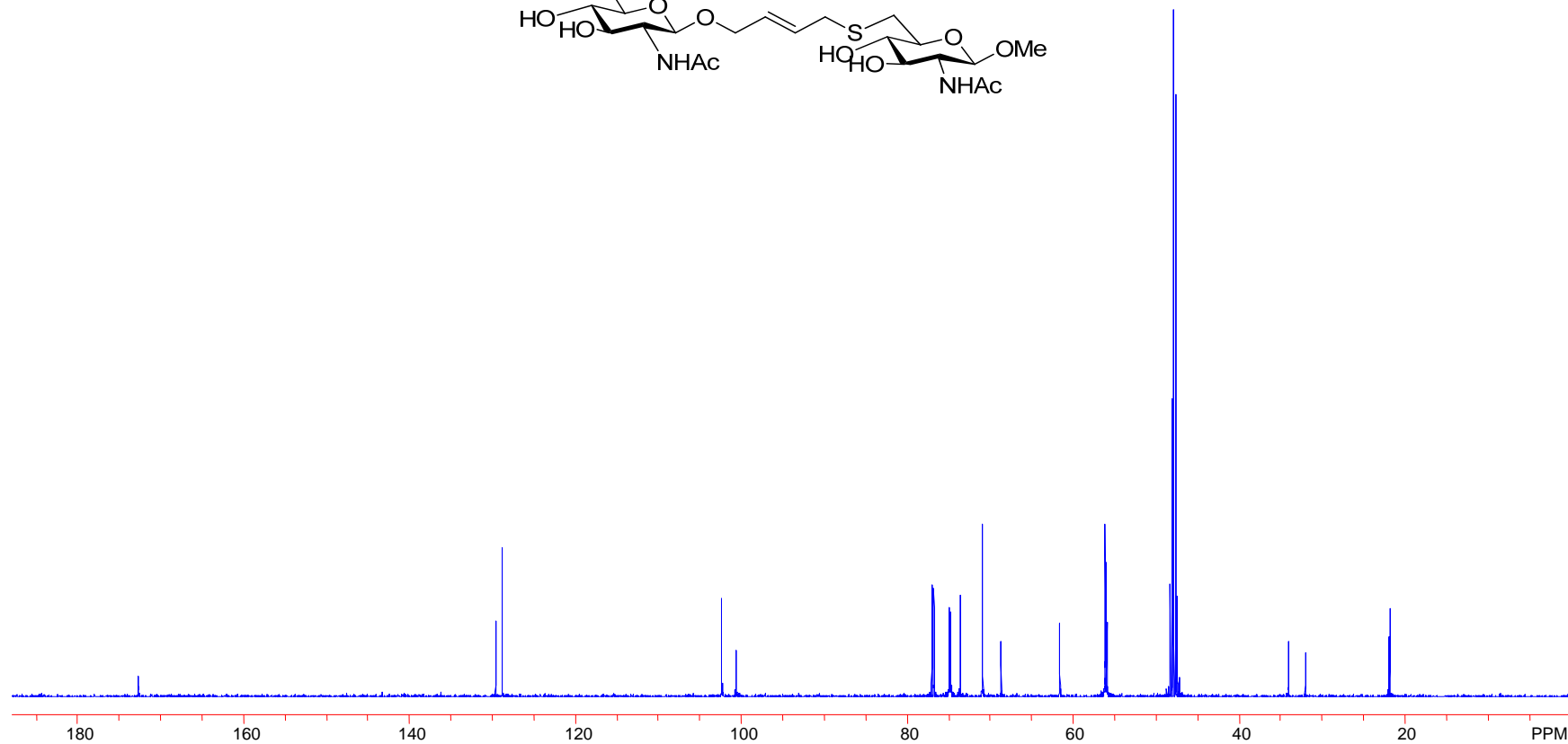
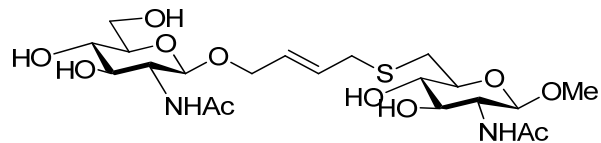


<sup>1</sup>H-NMR spectrum (CD<sub>3</sub>OD, 400 MHz) Methyl 6-[4-(2-acetamido-2-deoxy-β-D-glucopyranosyloxy)-2*E*-butenyl]-thio-2-acetamido-2-deoxy-β-D-glucopyranoside (**42**).

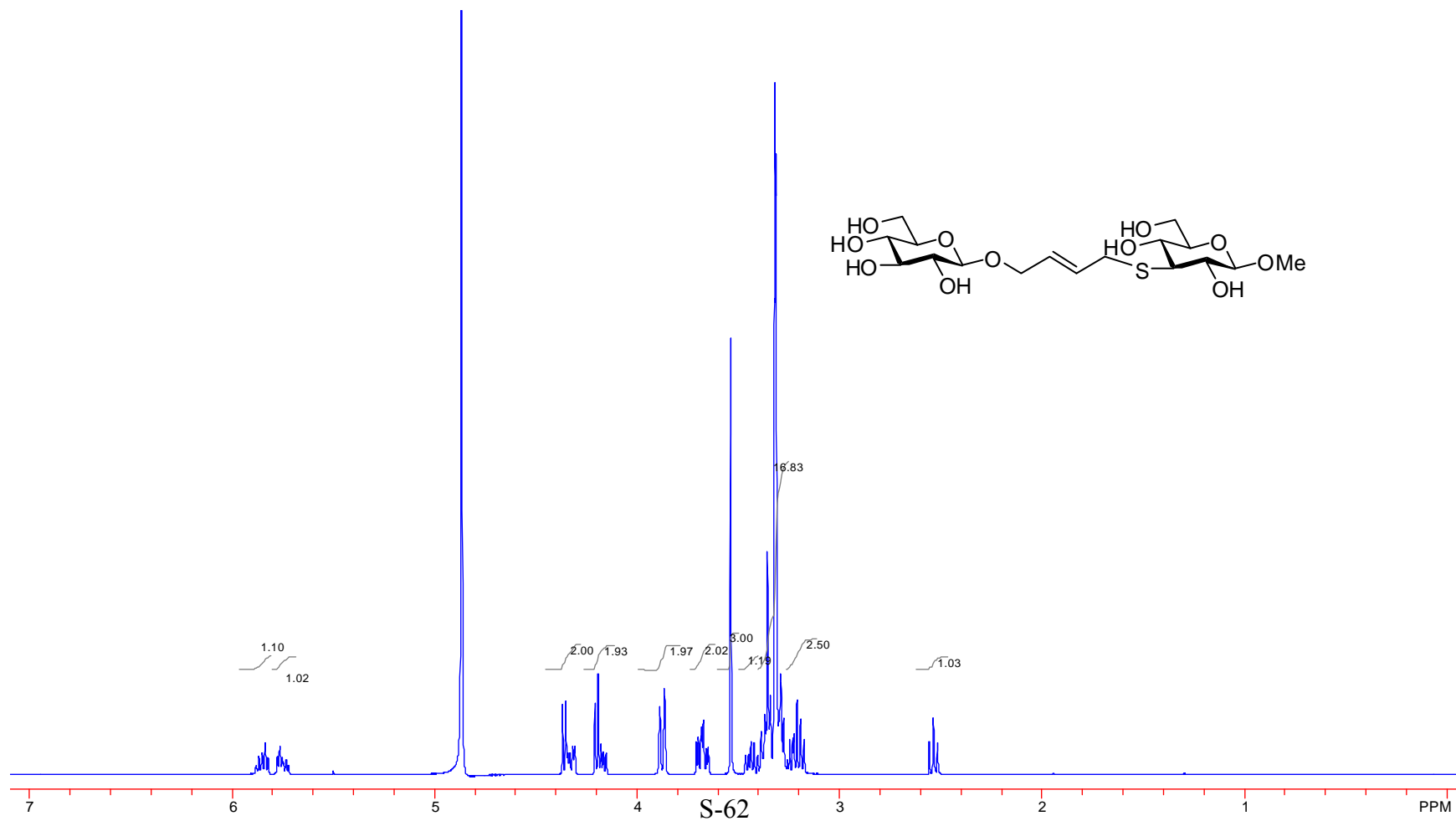


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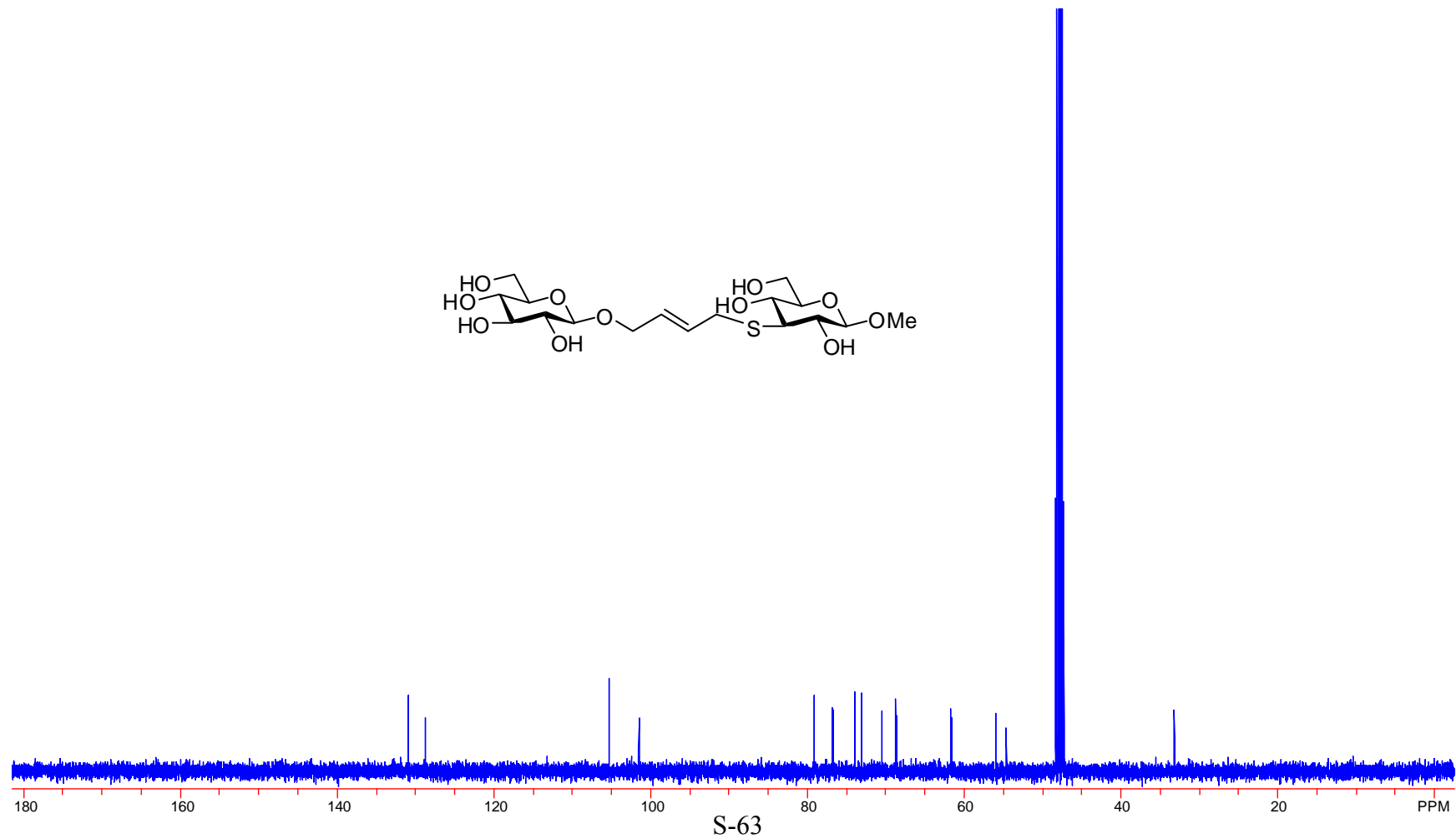
$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 100 MHz) Methyl 6-[4-(2-acetamido-2-deoxy- $\beta$ -D-glucopyranosyloxy)-2*E*-butenyl]-thio-2-acetamido-2-deoxy- $\beta$ -D-glucopyranoside (**42**).



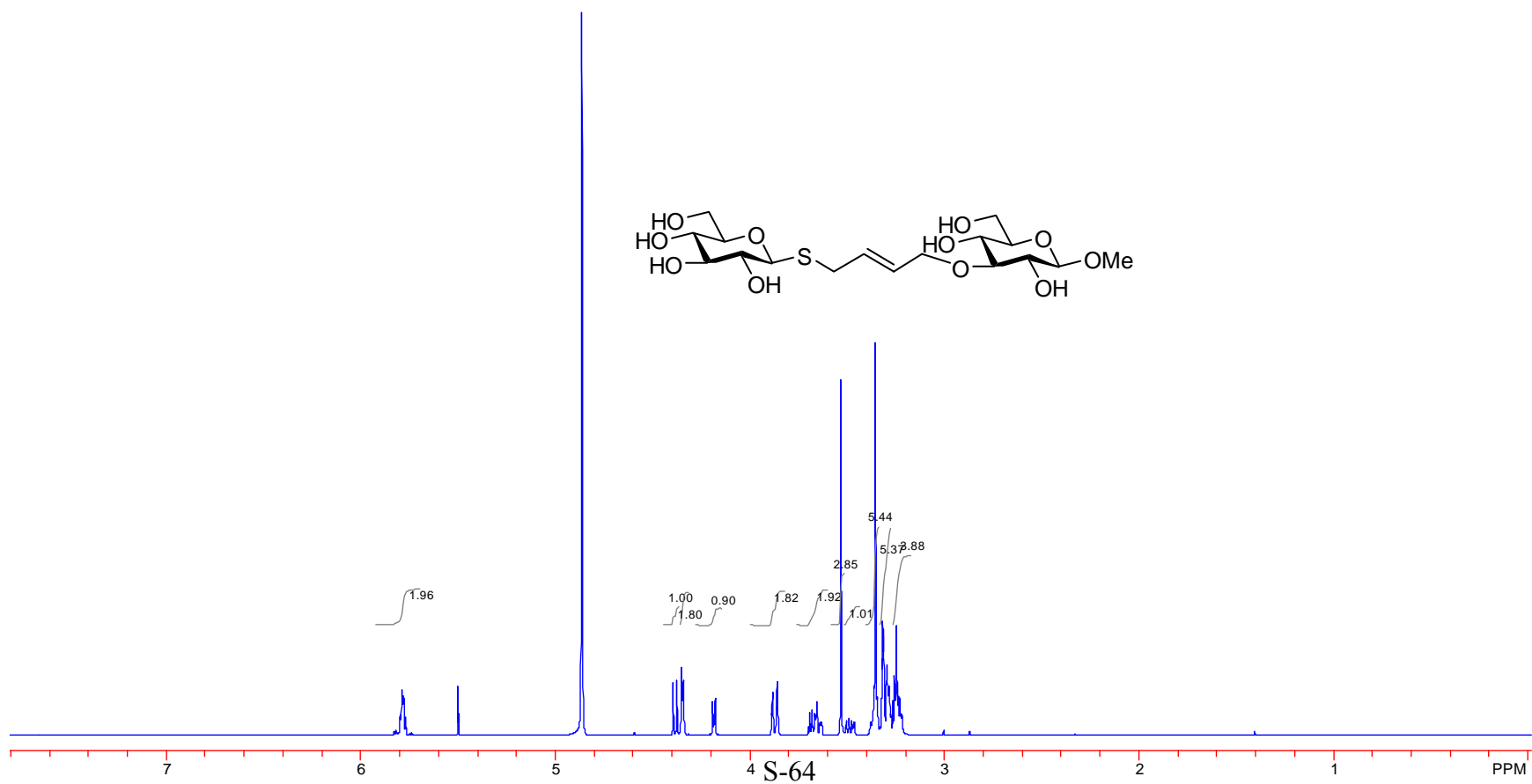
<sup>1</sup>H-NMR spectrum (CD<sub>3</sub>OD, 500 MHz) Methyl 3-deoxy-3-[4-(β-D-glucopyranosyloxy)but-2*E*-enylthio]-β-D-glucopyranoside (**43**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) Methyl 3-deoxy-3-[4-( $\beta$ -D-glucopyranosyloxy)but-2*E*-enylthio]- $\beta$ -D-glucopyranoside (**43**).

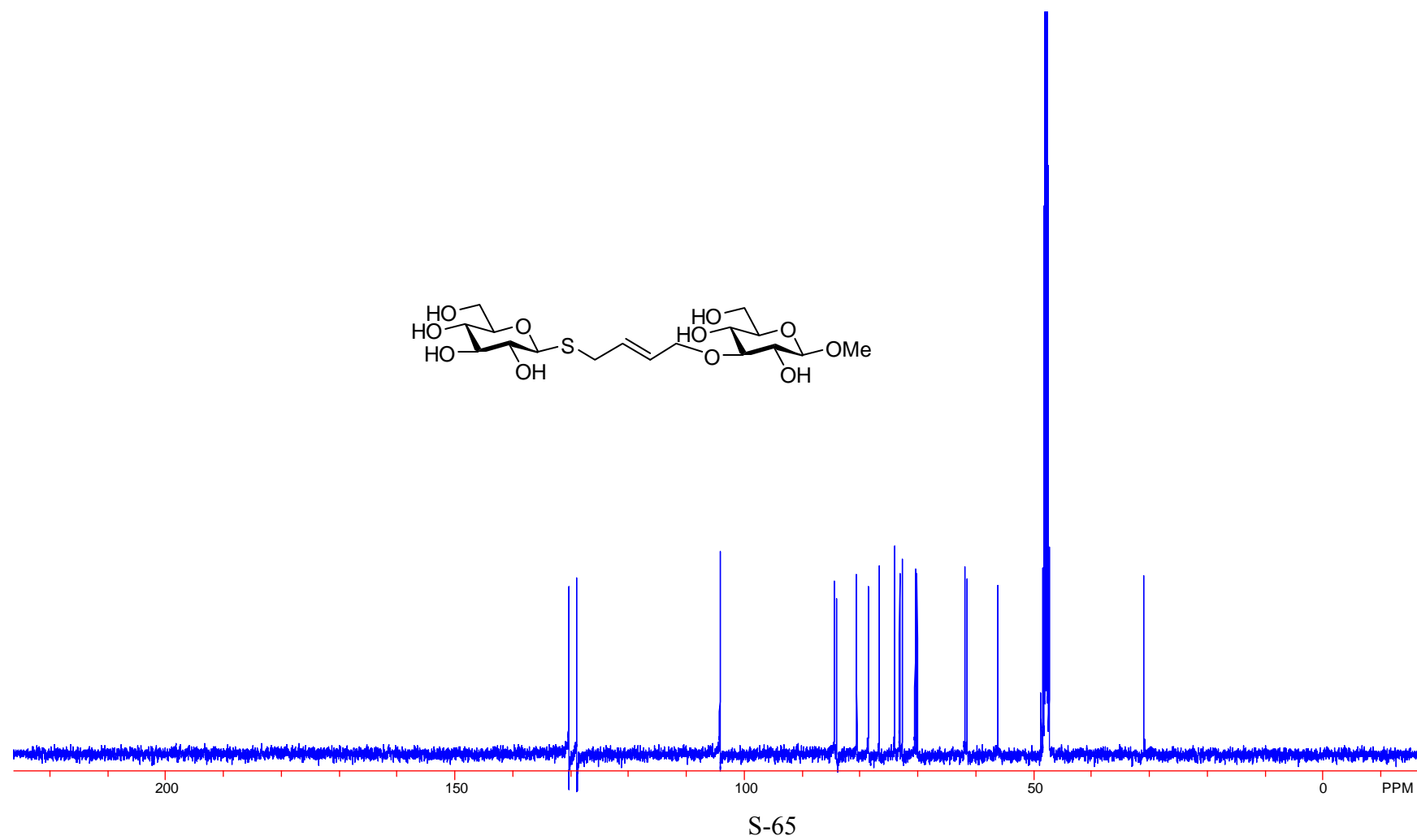


$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 500 MHz) Methyl 3-*O*-[4-(1-thio- $\beta$ -D-glucopyranosyl)-2*E*-butenyl]- $\beta$ -D-glucopyranoside (**44**).

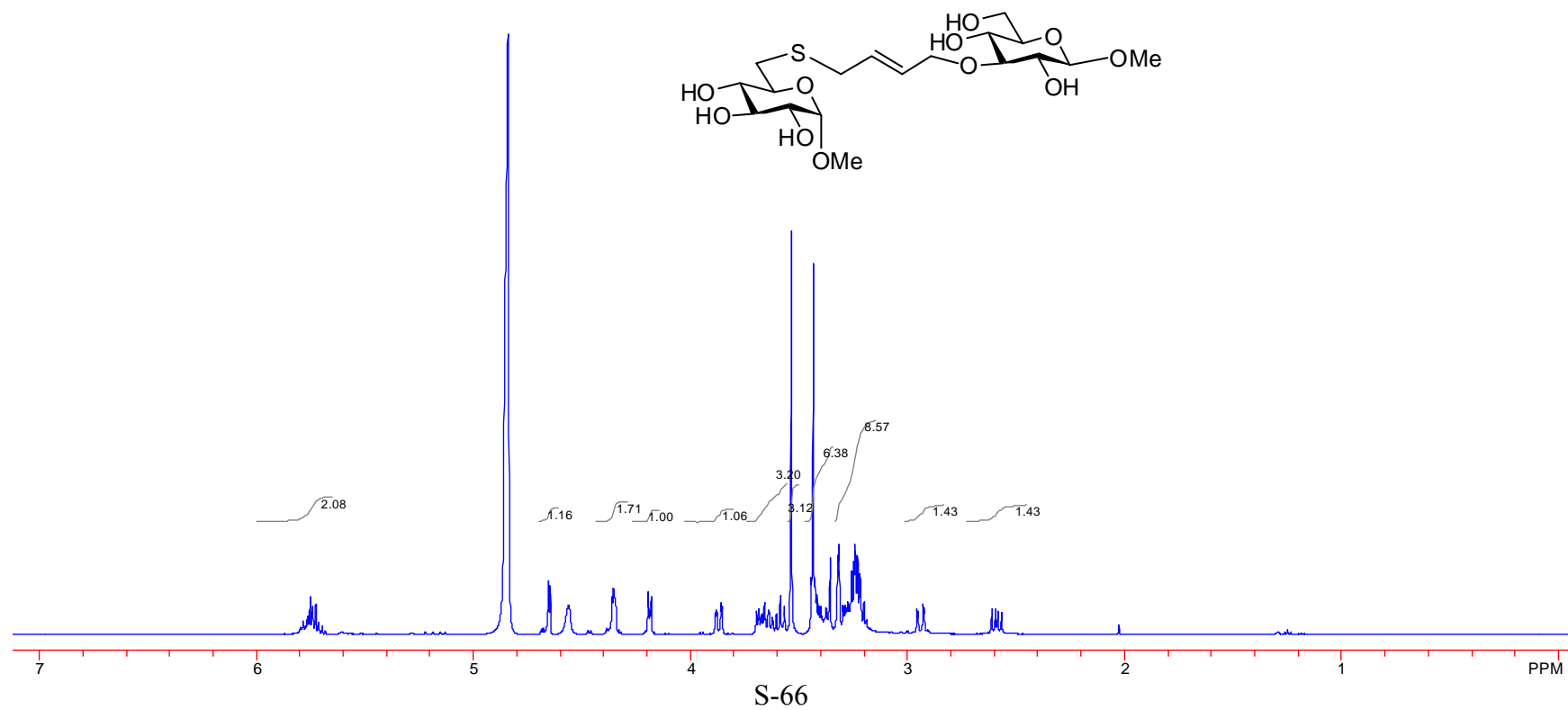




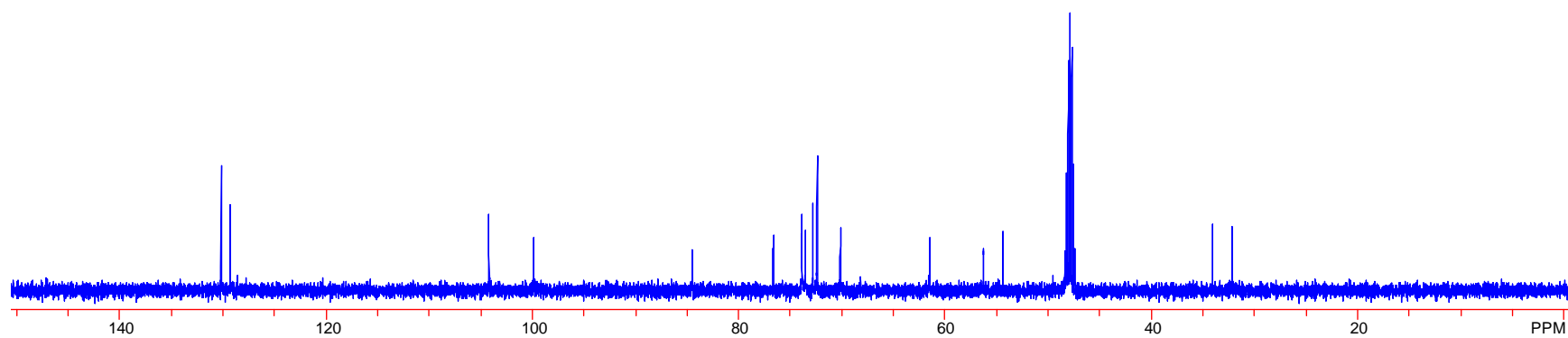
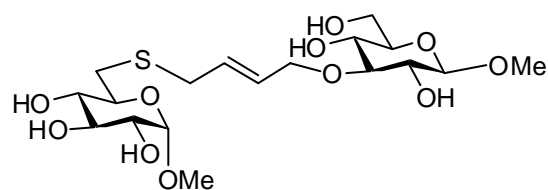
$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) Methyl 3-*O*-[4-(1-thio- $\beta$ -D-glucopyranosyl)-2*E*-butenyl]- $\beta$ -D-glucopyranoside (**44**).



$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 500 MHz) Methyl 3-*O*-[4-(methyl  $\alpha$ -D-glucopyranosid-6-thio)but-2*E*-enyl]- $\beta$ -D-glucopyranoside (**45**).

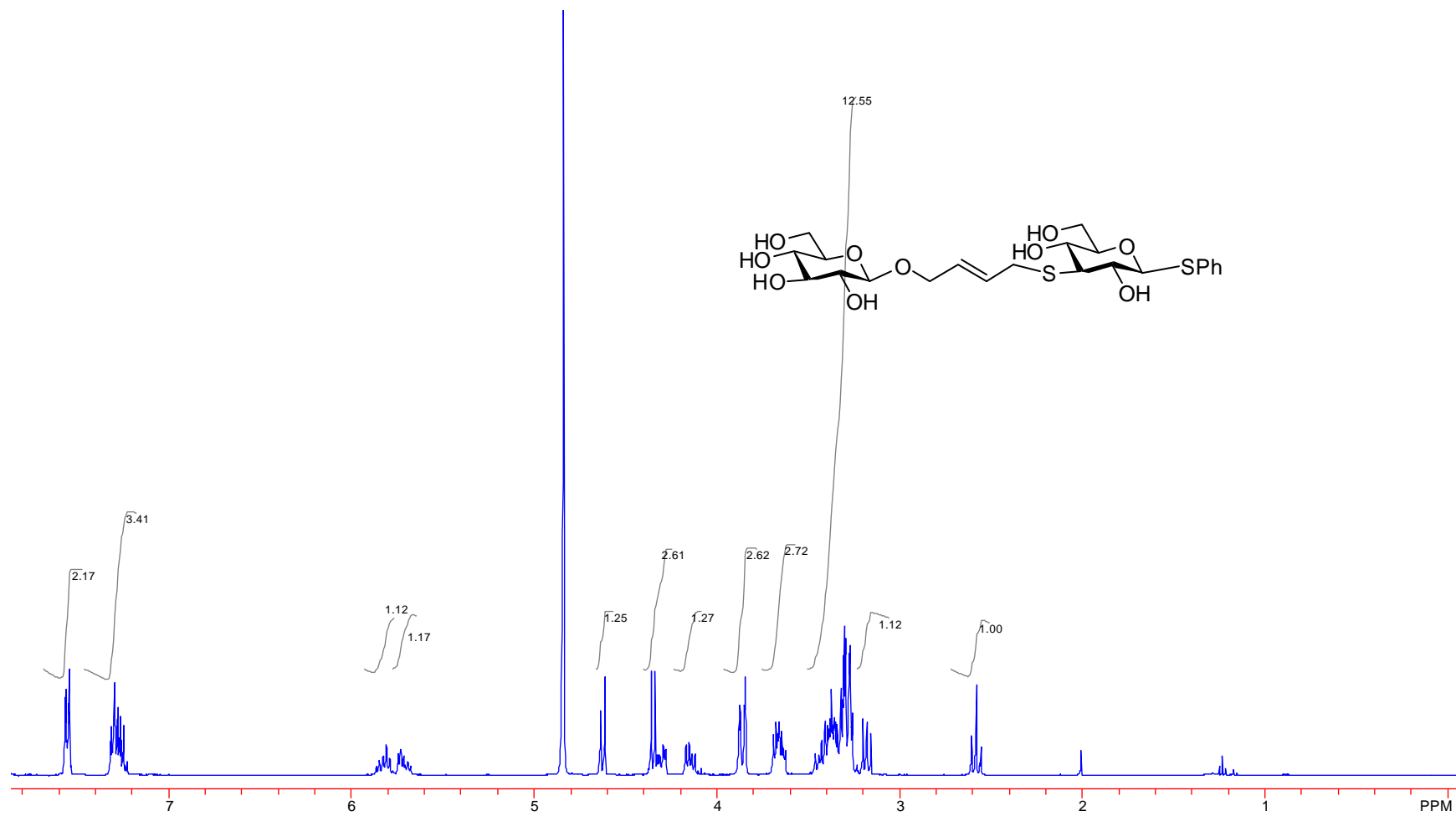


$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) Methyl 3-*O*-[4-(methyl  $\alpha$ -D-glucopyranosid-6-thio)but-2*E*-enyl]- $\beta$ -D-glucopyranoside (**45**).



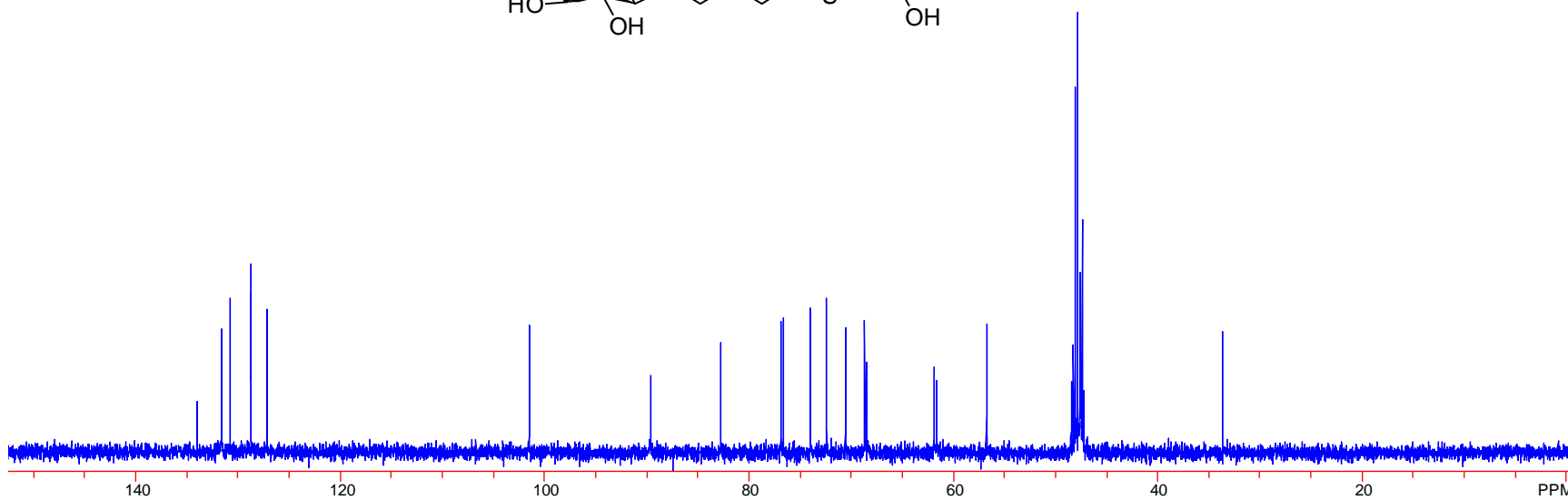
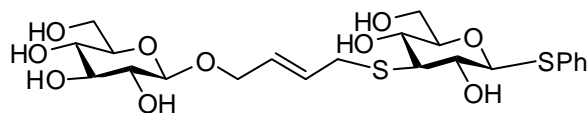
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$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 500 MHz) Phenyl 3-deoxy-3-[4-( $\beta$ -D-glucopyranosyloxy)but-2*E*-enylthio]-1-thio- $\beta$ -D-glucopyranoside (**46**).



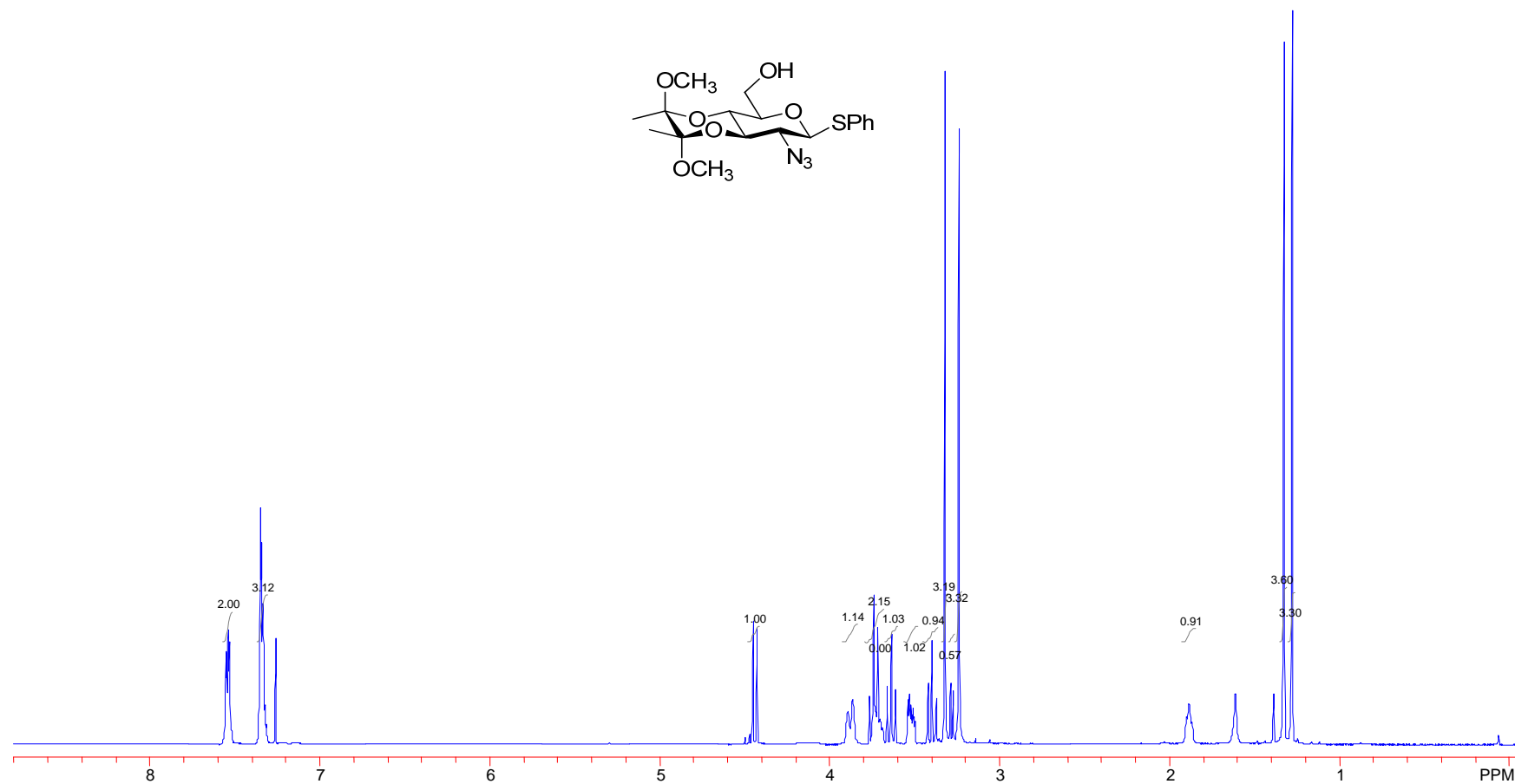
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$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) Phenyl 3-deoxy-3-[4-( $\beta$ -D-glucopyranosyloxy)but-2*E*-enylthio]-1-thio- $\beta$ -D-glucopyranoside (**46**).

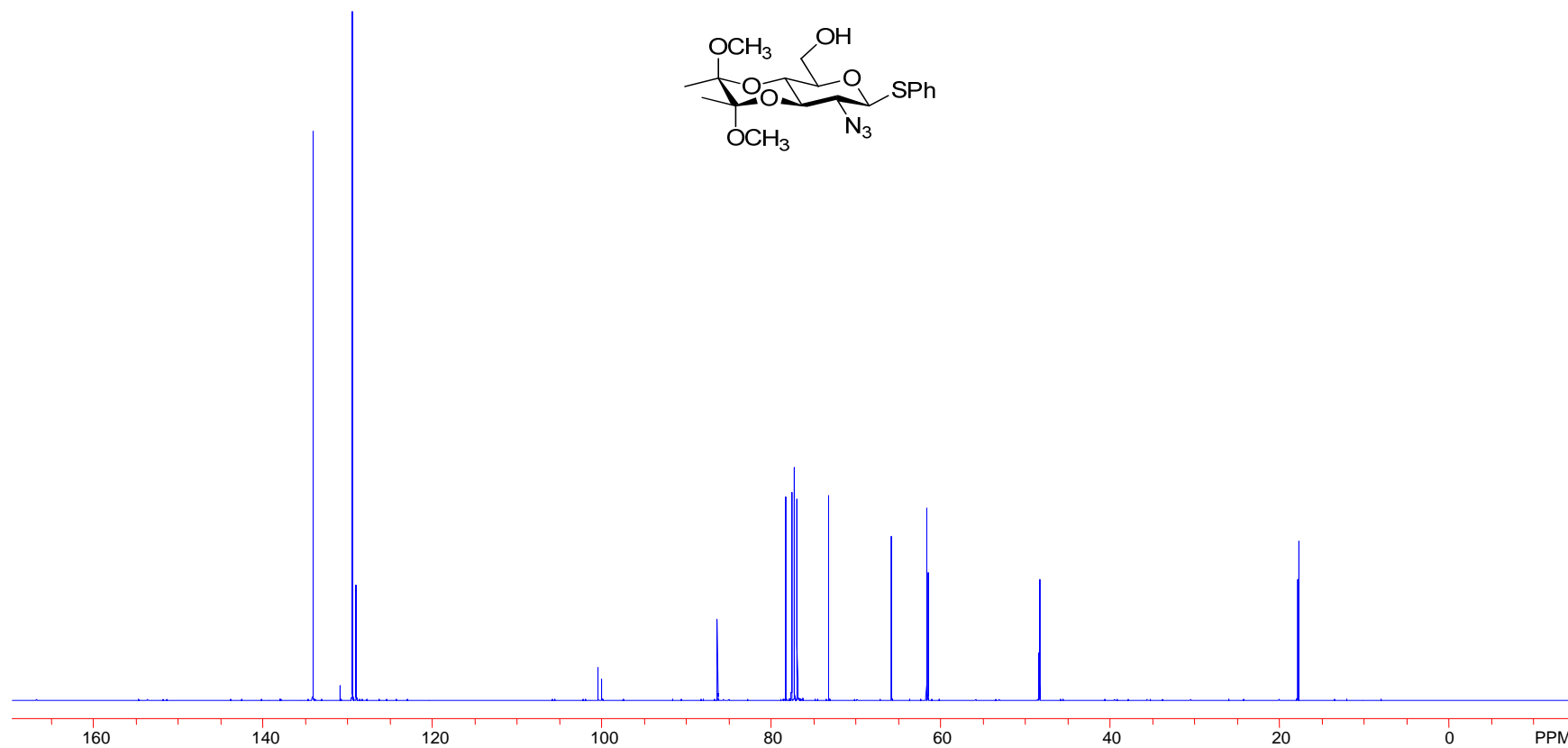


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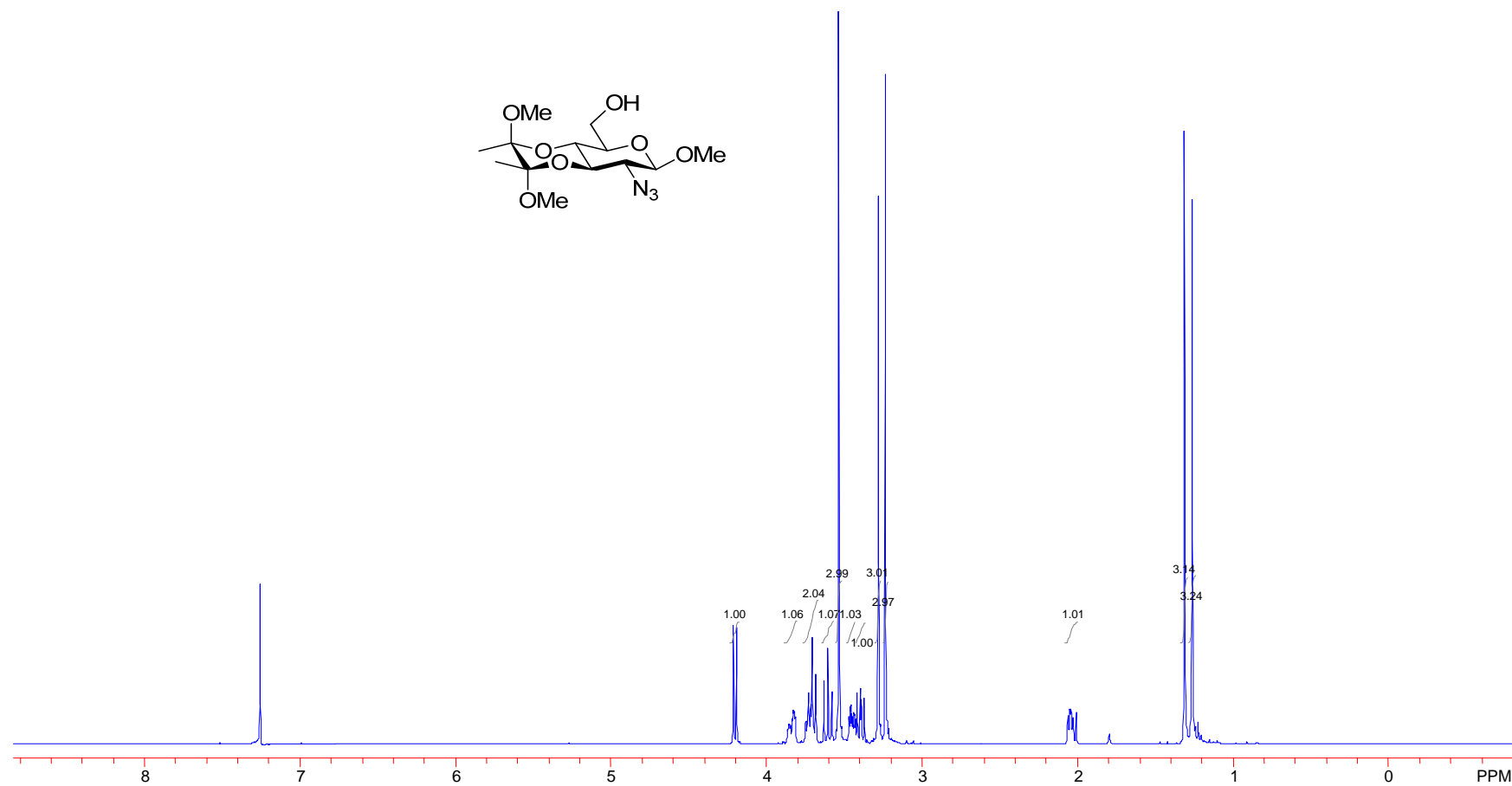
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Phenyl 2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-β-D-glucopyranoside (**48**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio- $\beta$ -D-glucopyranoside (**48**).

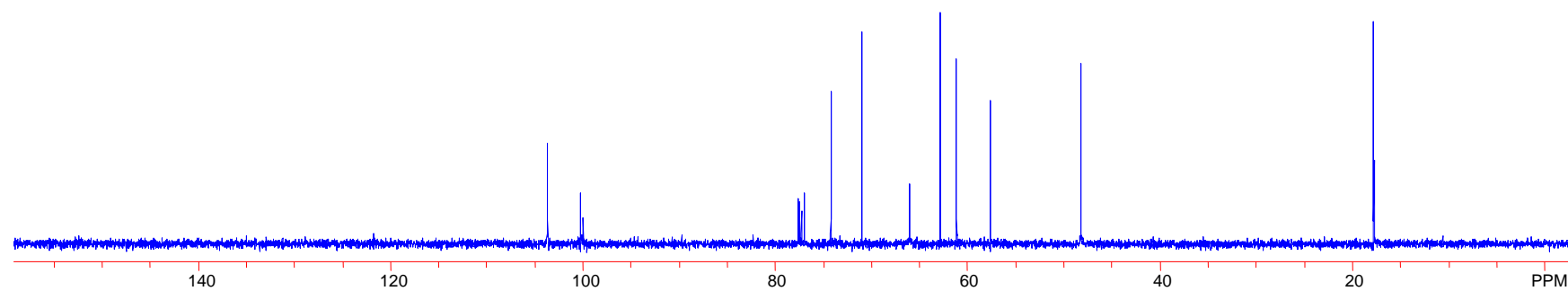
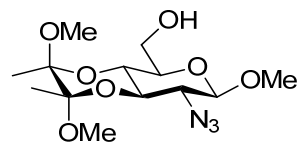


<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Methyl 2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-β-D-glucopyranoside (**55**).

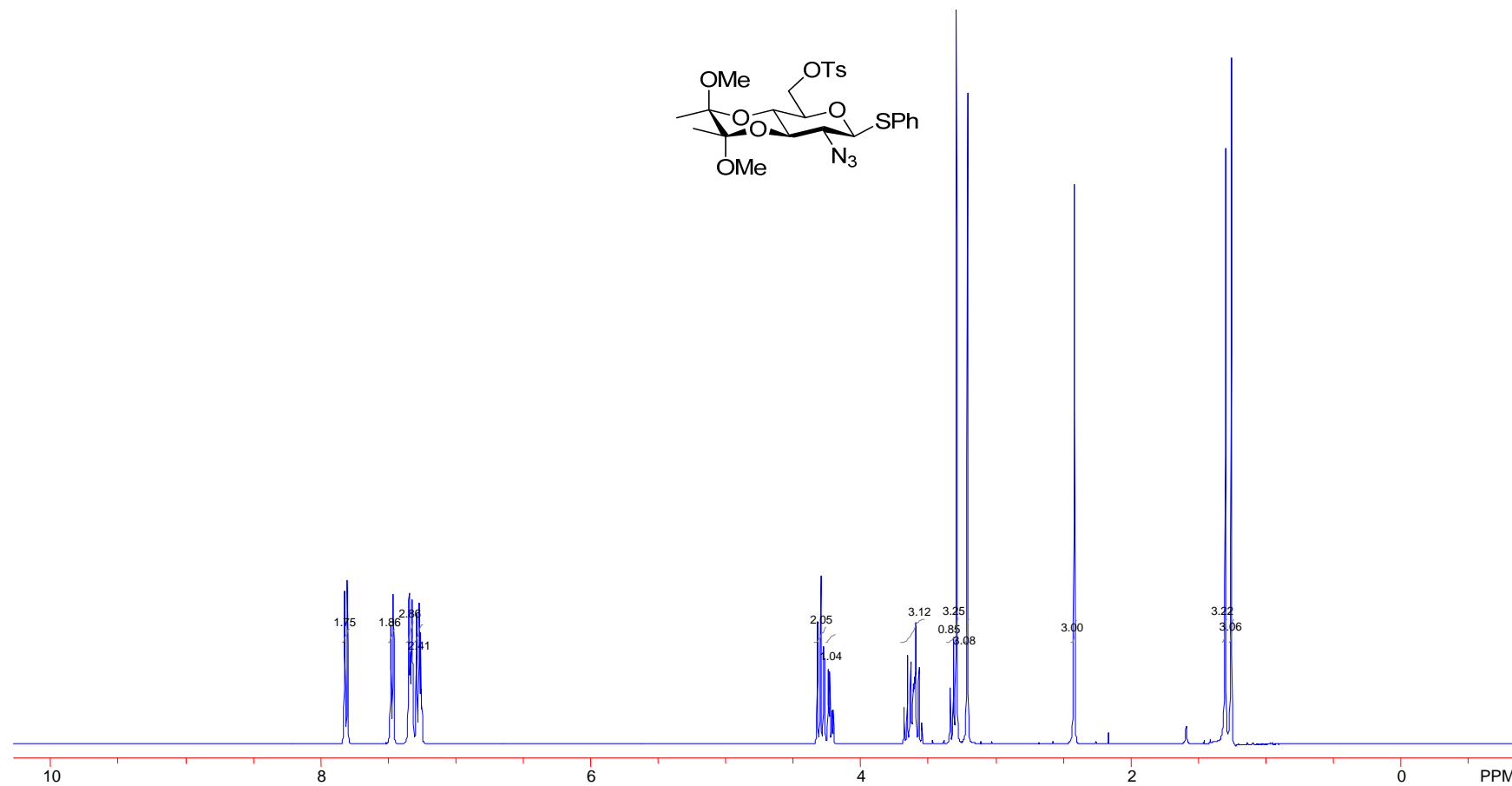




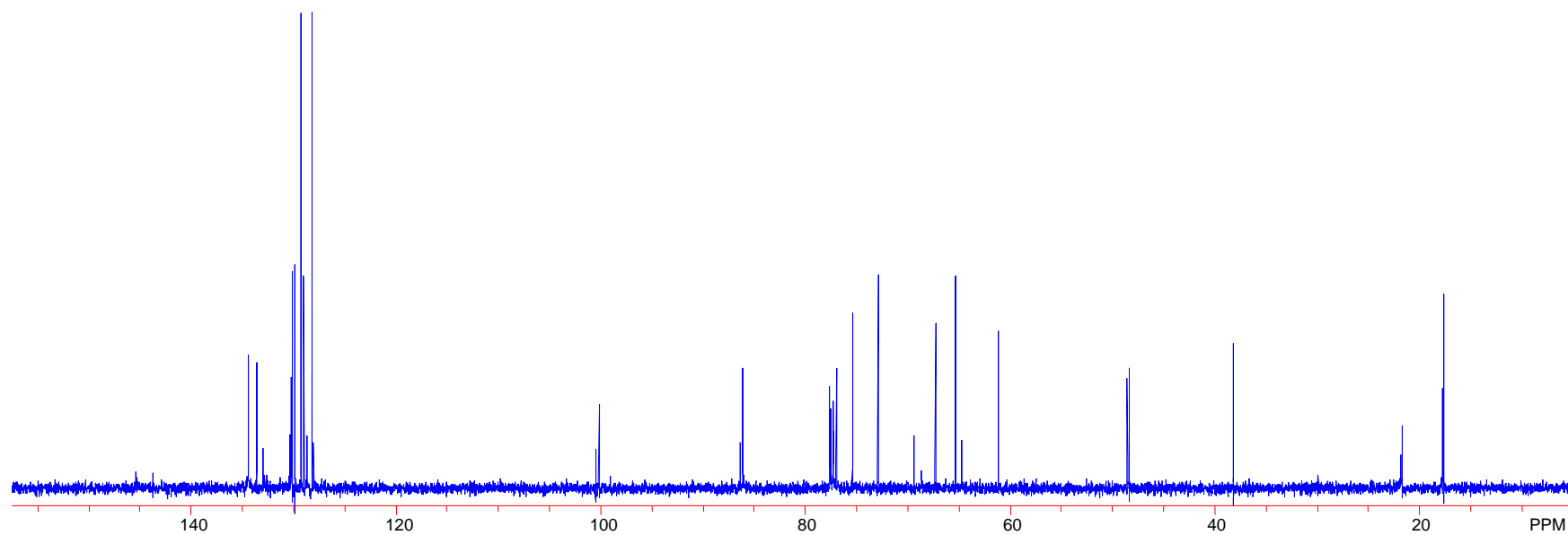
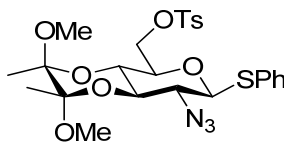
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Methyl 2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)- $\beta$ -D-glucopyranoside (**55**).



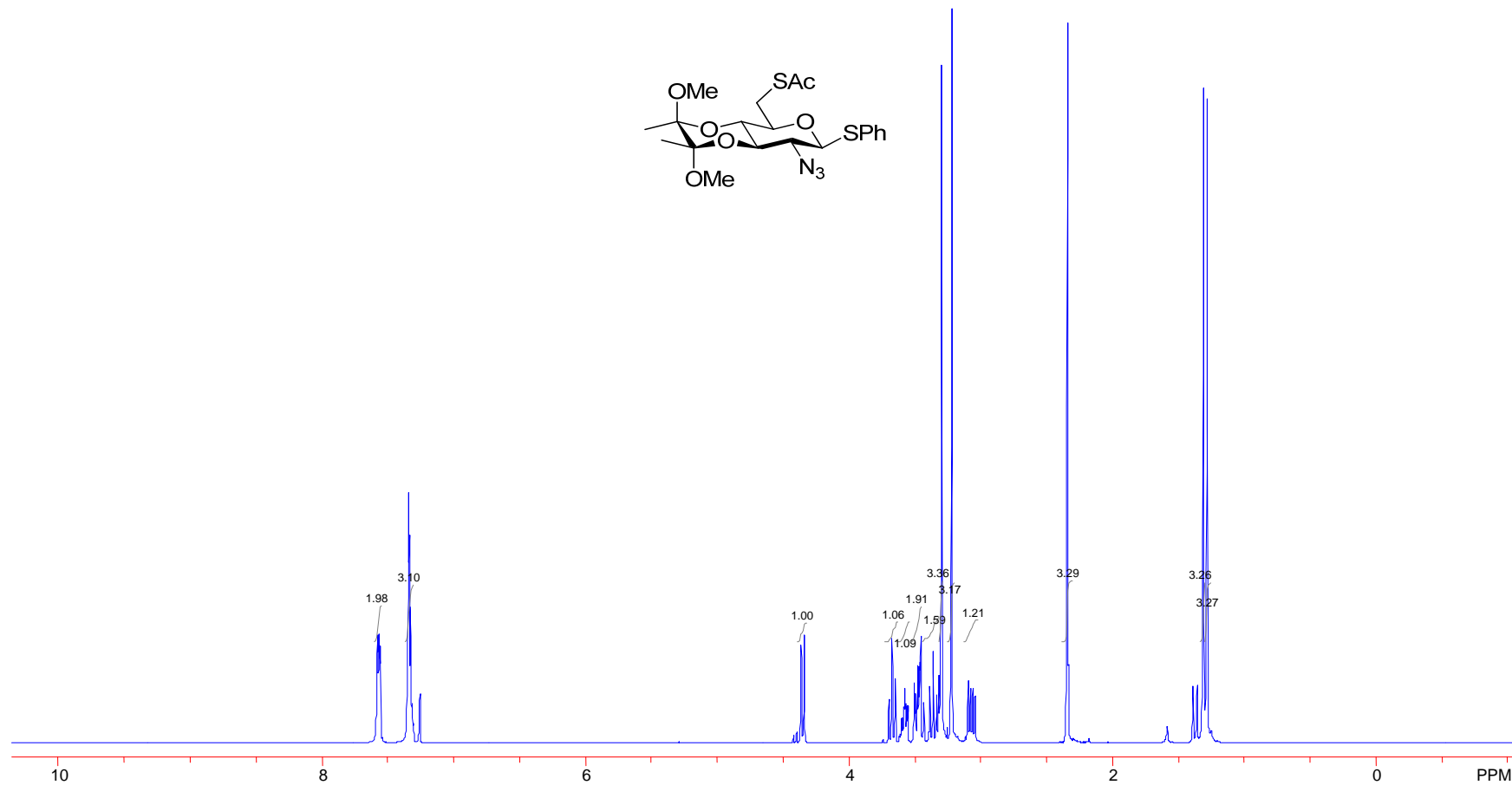
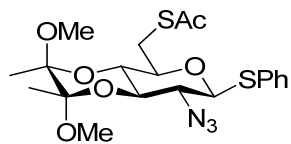
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Phenyl 2-azido-2-deoxy-3,4-O-(2,3-dimethoxybutane-2,3-diyl)-1-thio-6-O-p-toluenesulfonyl-β-D-glucopyranoside (**73**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 2-azido-2-deoxy-3,4-O-(2,3-dimethoxybutane-2,3-diyl)-1-thio-6-O-p-toluenesulfonyl- $\beta$ -D-glucopyranoside (**73**).

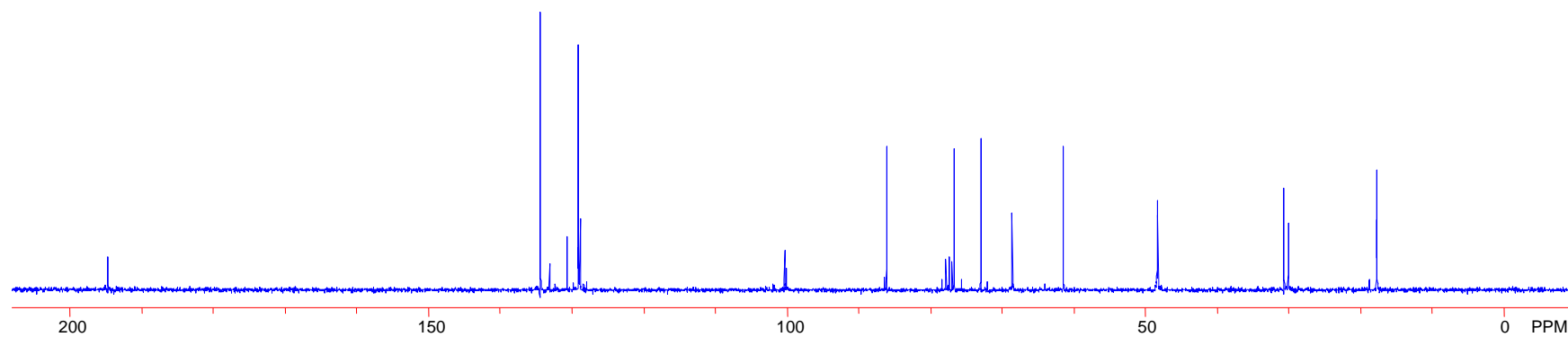
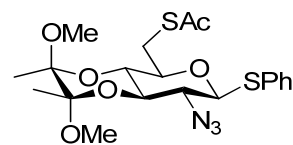


<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Phenyl 2-azido-2-deoxy-6-acetylthio-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-β-D-glucopyranoside (74).

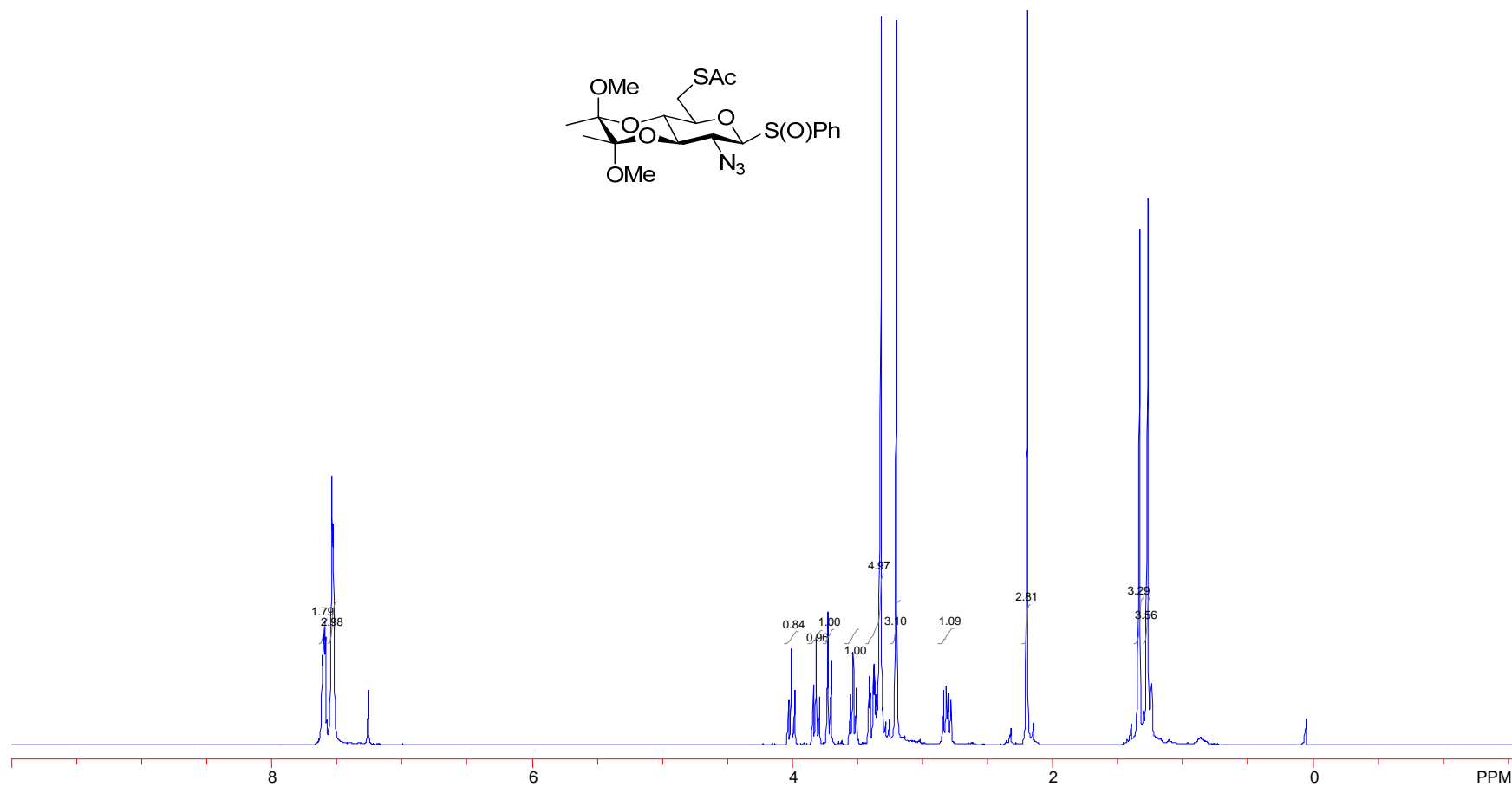


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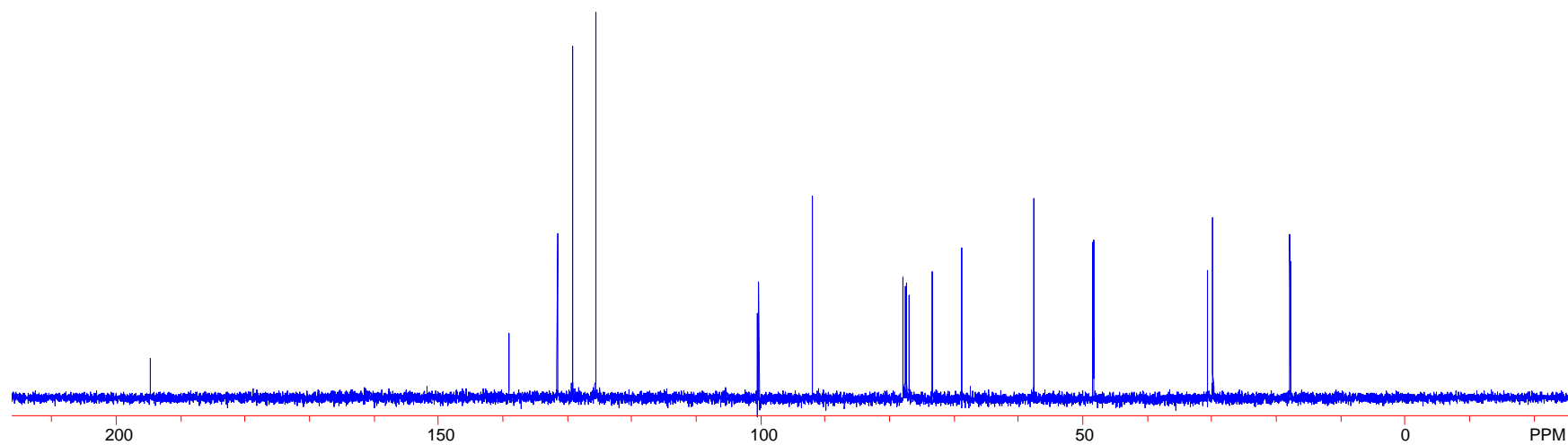
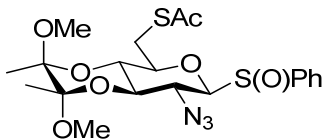
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 2-azido-2-deoxy-6-acetylthio-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio- $\beta$ -D-glucopyranoside (74).



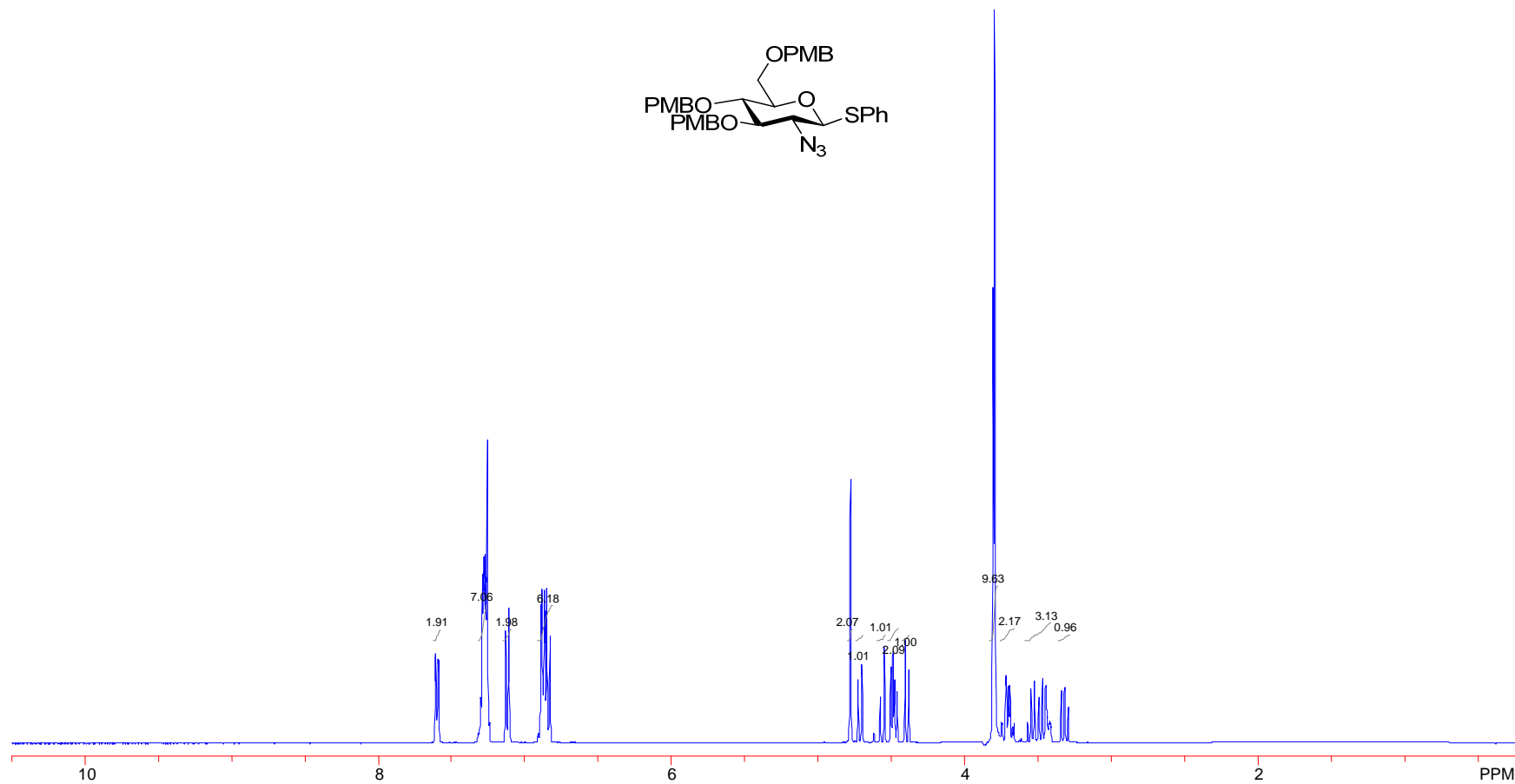
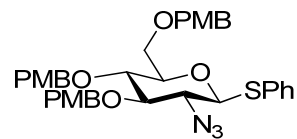
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Phenyl 6-acetylthio-2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-β-D-glucopyranoside *S*-Oxide (**54**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 6-acetylthio-2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio- $\beta$ -D-glucopyranoside *S*-Oxide (**54**).

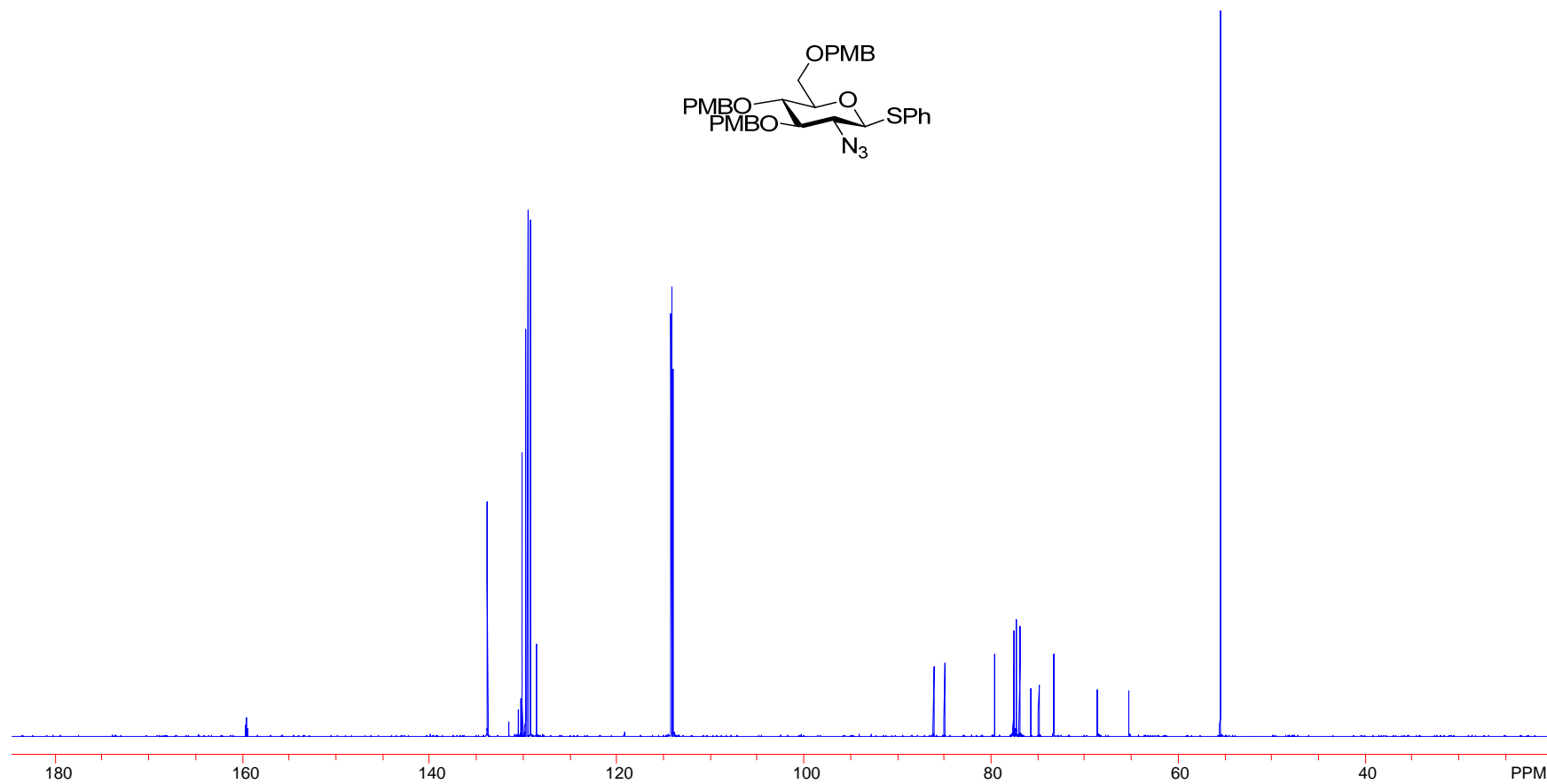


$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) Phenyl 2-azido-2-deoxy-3,4,6-tri-*O*-(*p*-methoxybenzyl)-1-thio- $\beta$ -D-glucopyranoside (**75**).

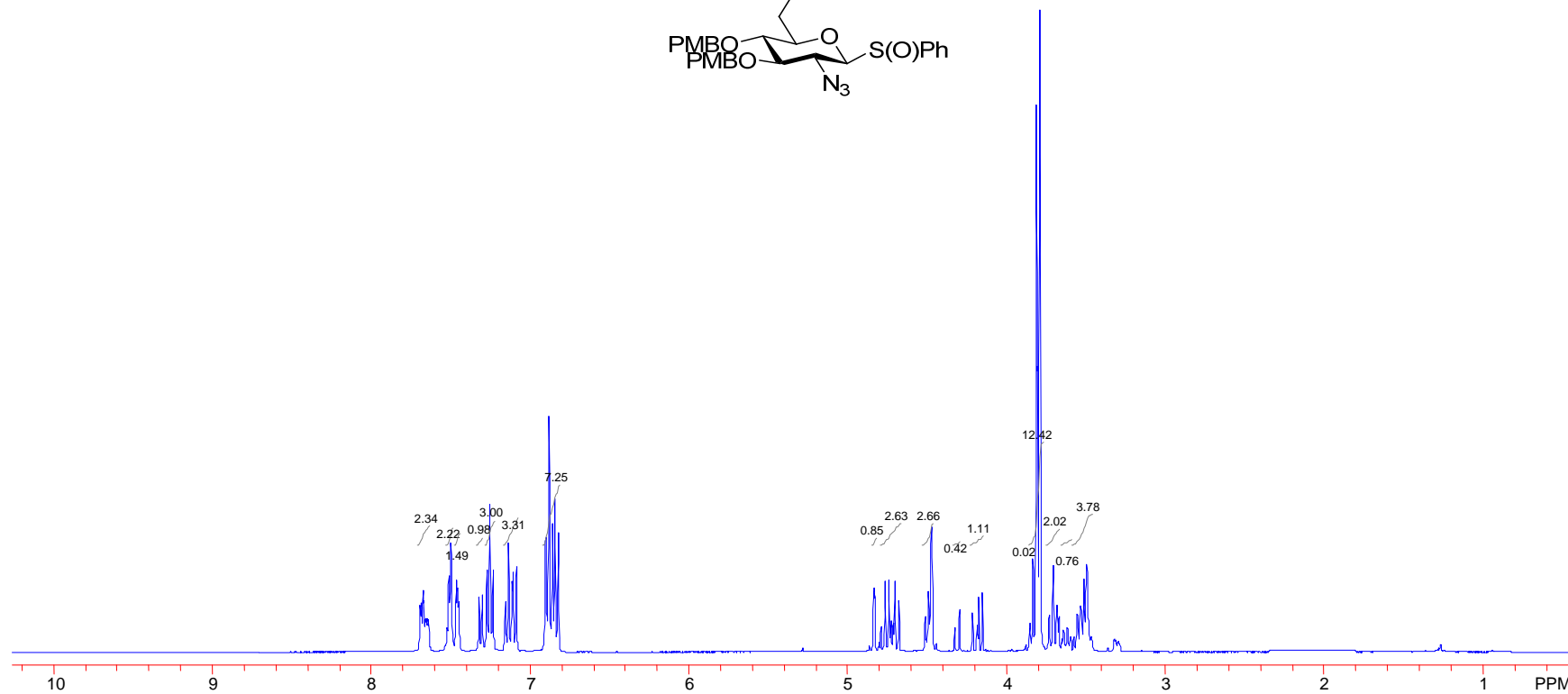
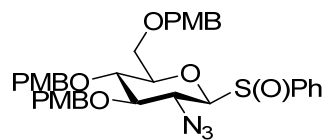




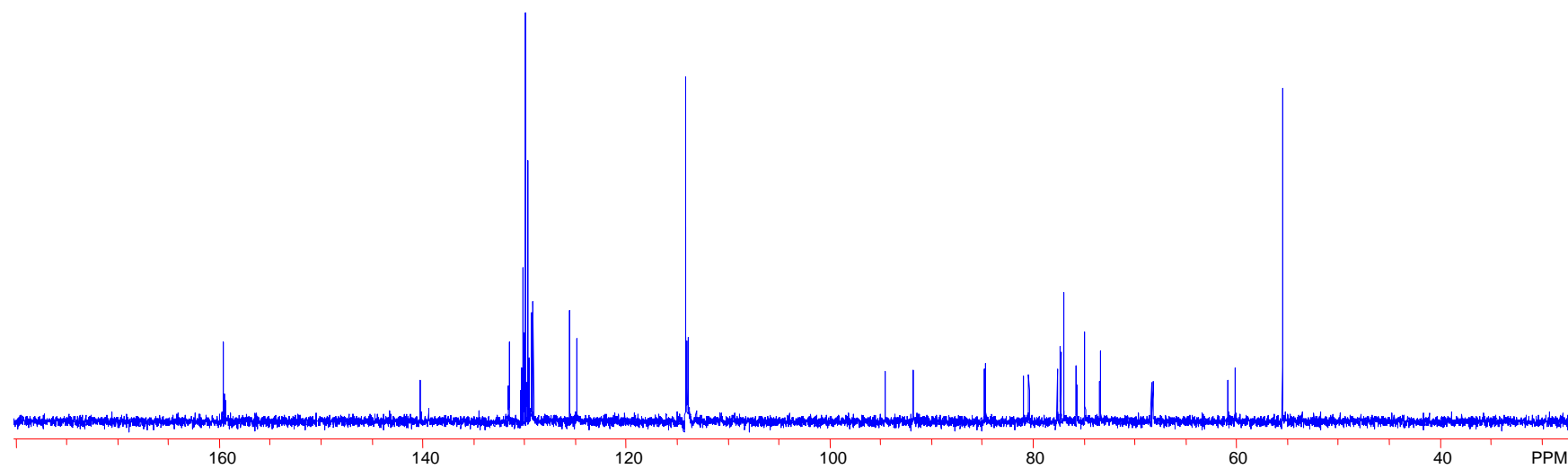
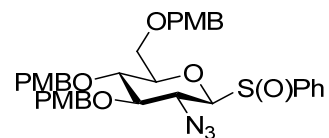
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 2-azido-2-deoxy-3,4,6-tri-*O*-(*p*-methoxybenzyl)-1-thio- $\beta$ -D-glucopyranoside (**75**).



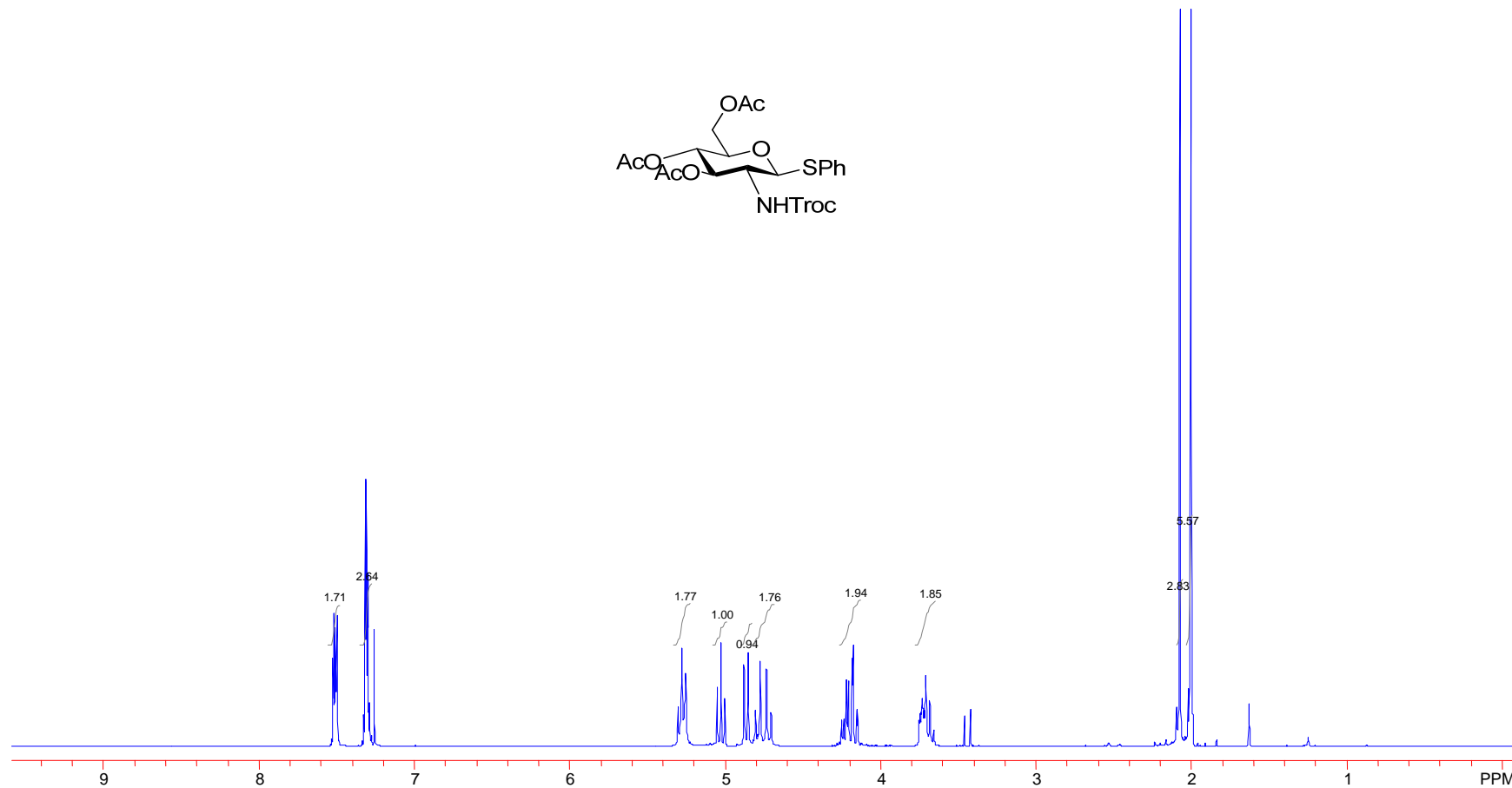
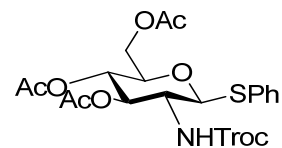
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Phenyl 2-azido-2-deoxy-3,4,6-tri-*O*-(*p*-methoxybenzyl)-1-thio-β-D-glucopyranoside *S*-Oxide (**47**).



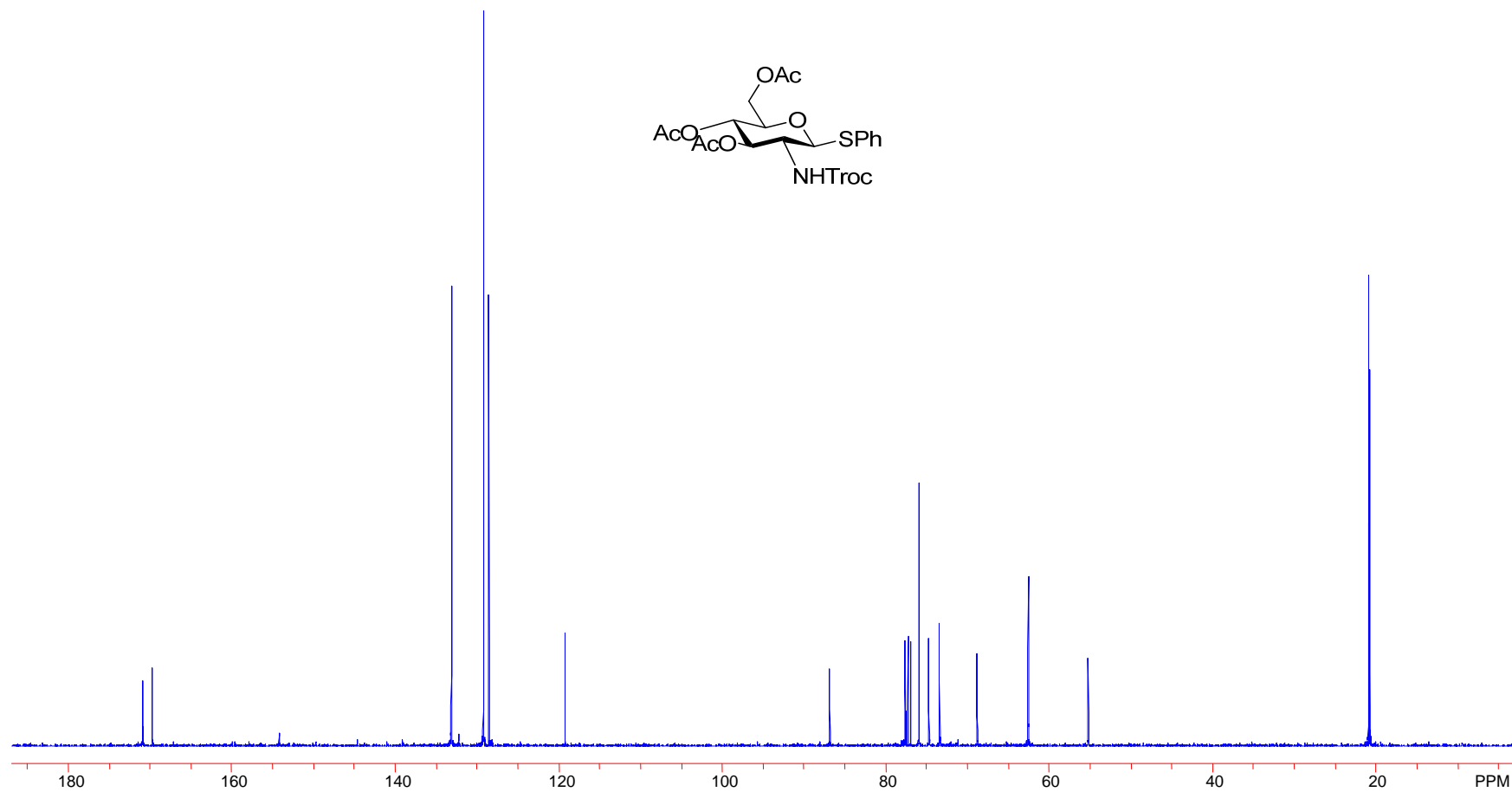
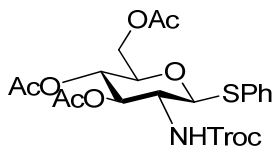
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 2-azido-2-deoxy-3,4,6-tri-*O*-(*p*-methoxybenzyl)-1-thio- $\beta$ -D-glucopyranoside *S*-Oxide (**47**).



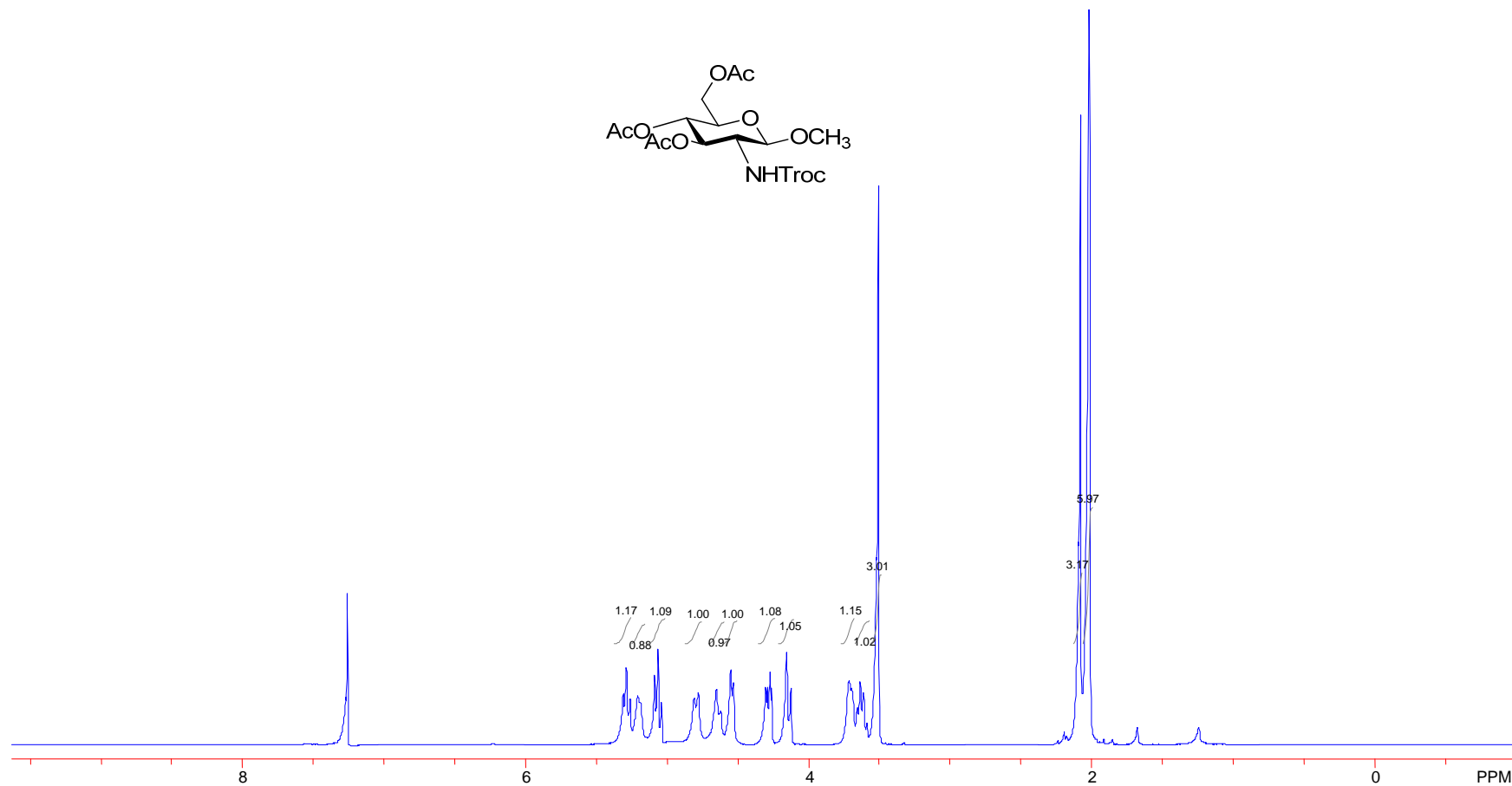
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (77).



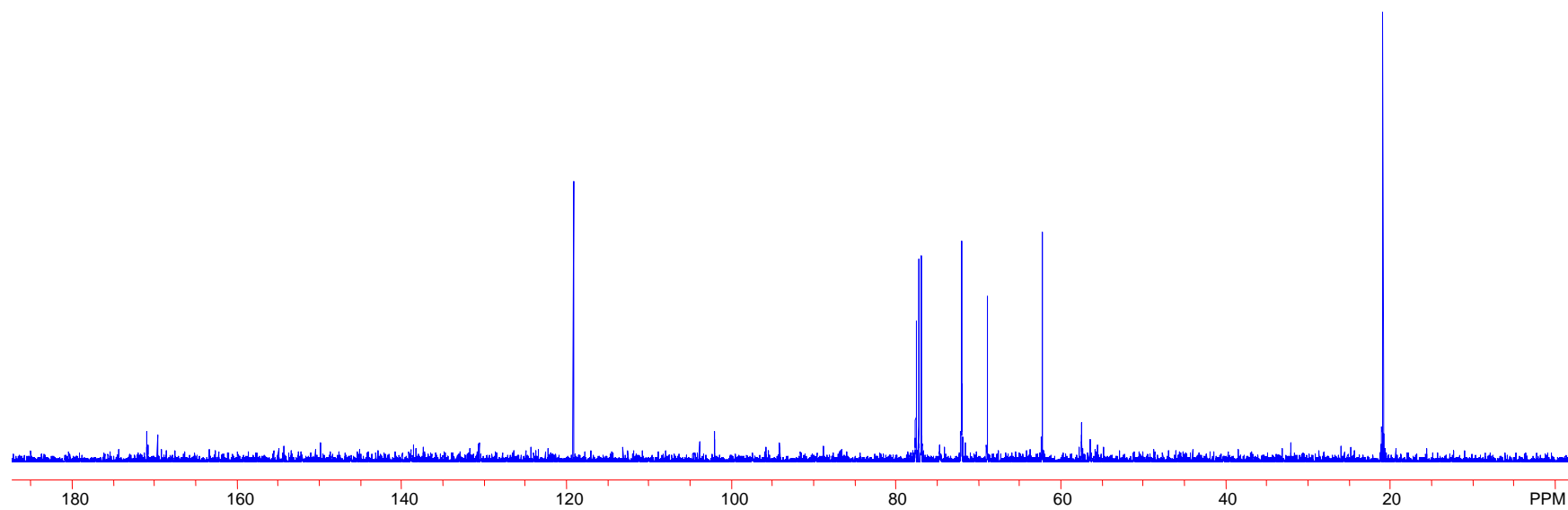
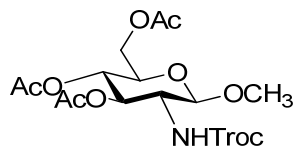
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-2-(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-glucopyranoside (77).



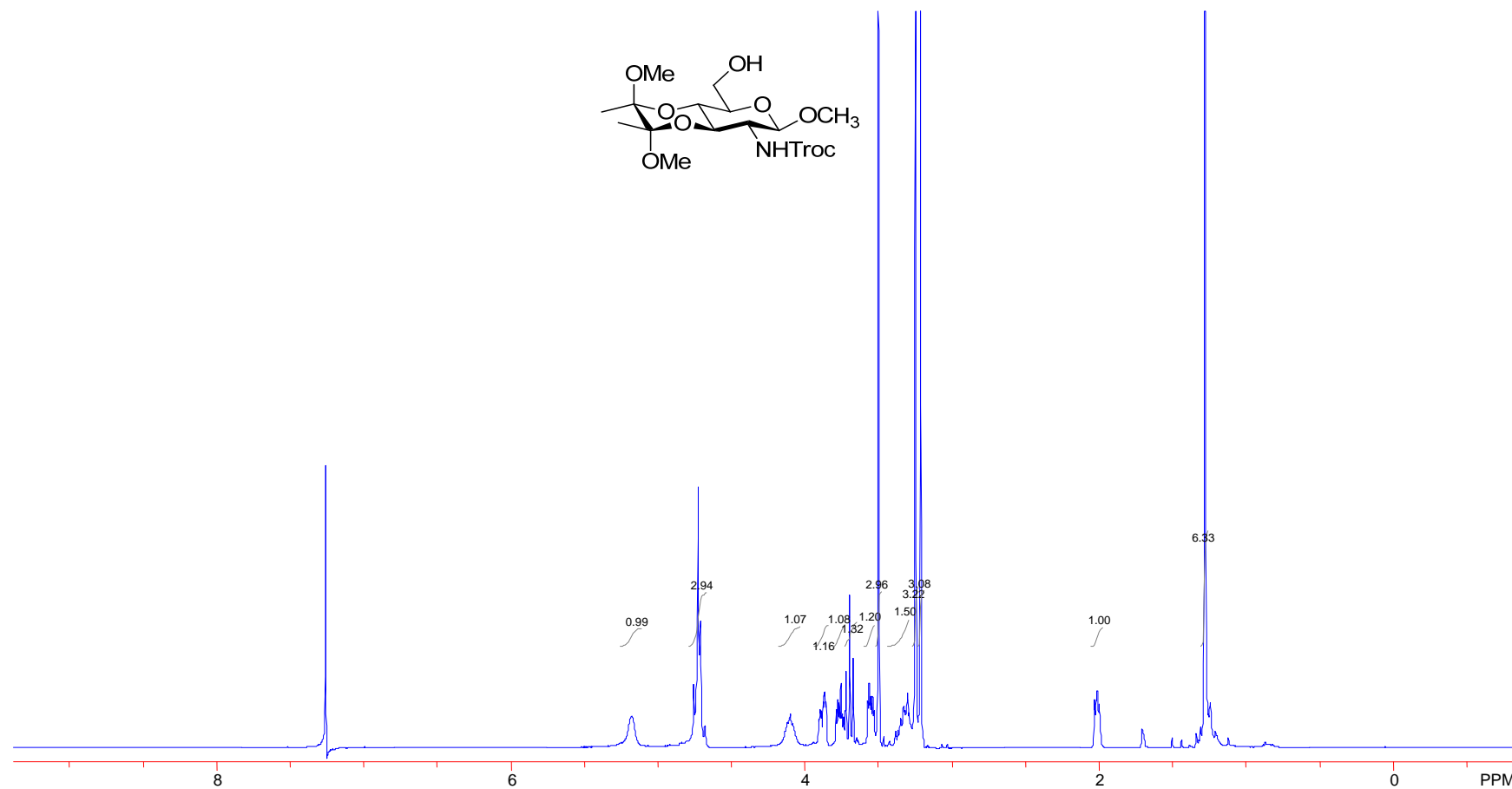
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Methyl 3,4,6-tri-*O*-acetyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-β-D-glucopyranoside (**79**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Methyl 3,4,6-tri-*O*-acetyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy- $\beta$ -D-glucopyranoside (**79**).



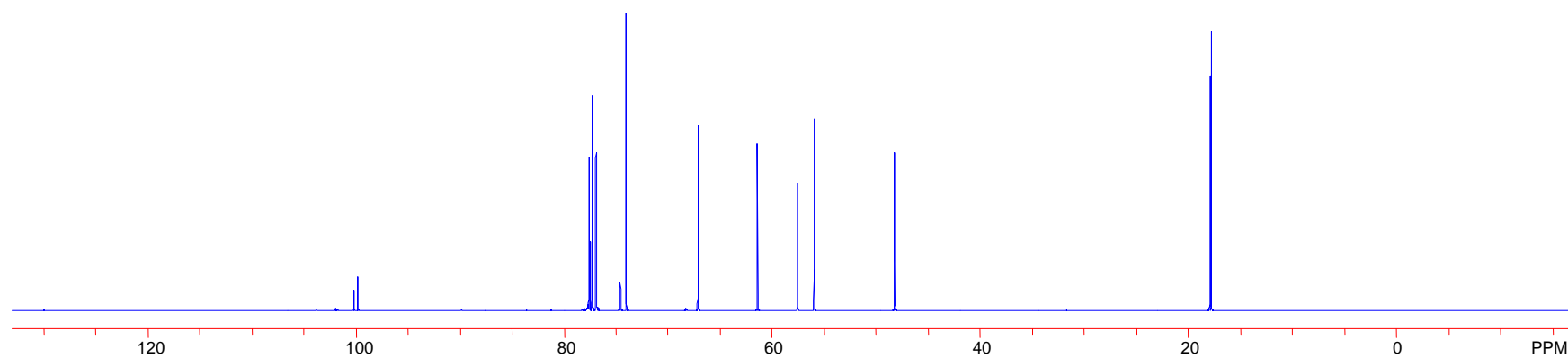
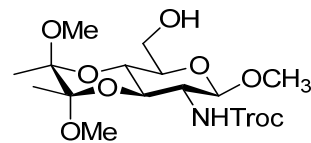
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) Methyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy- $\beta$ -D-glucopyranoside (**81**).



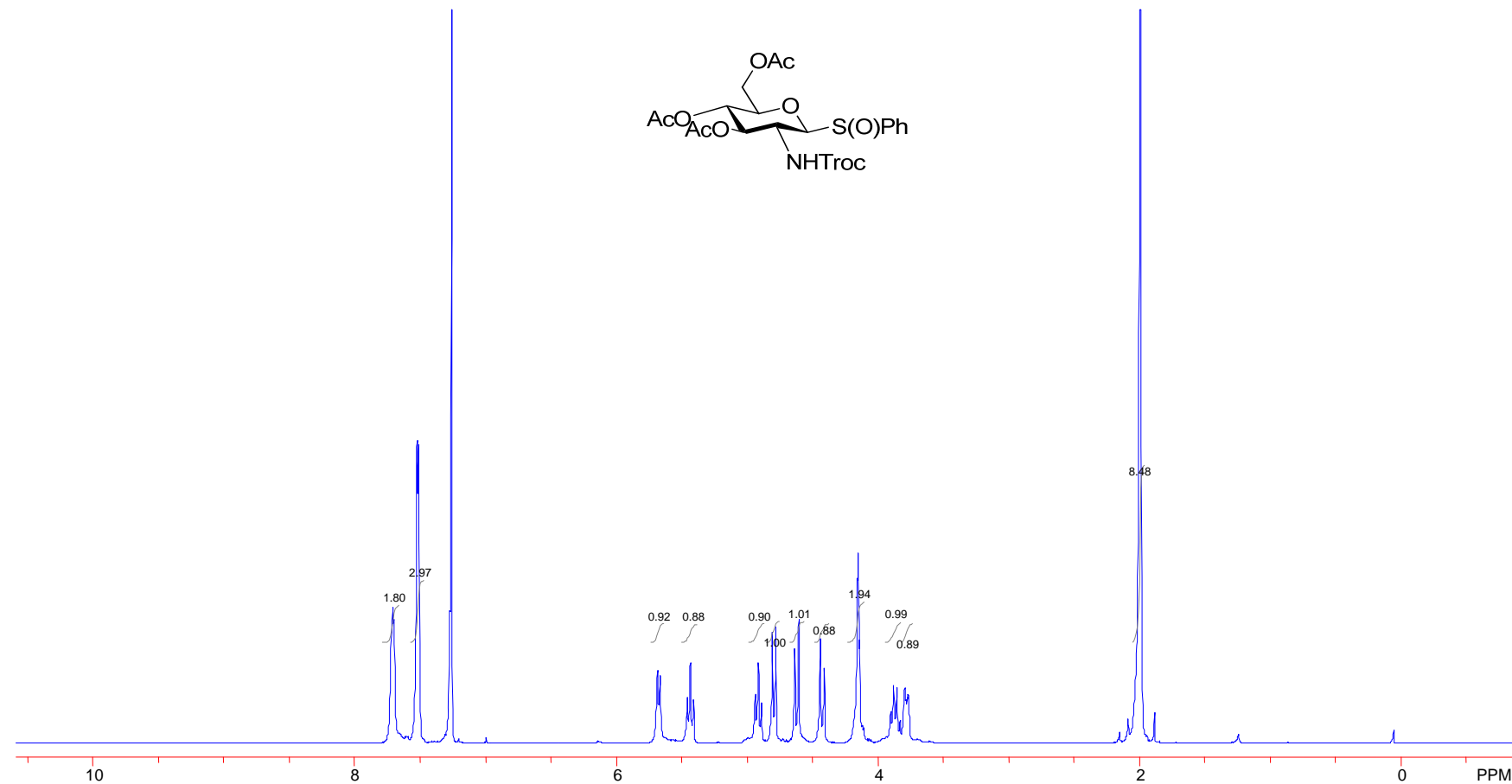
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$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Methyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy- $\beta$ -D-glucopyranoside (**81**).

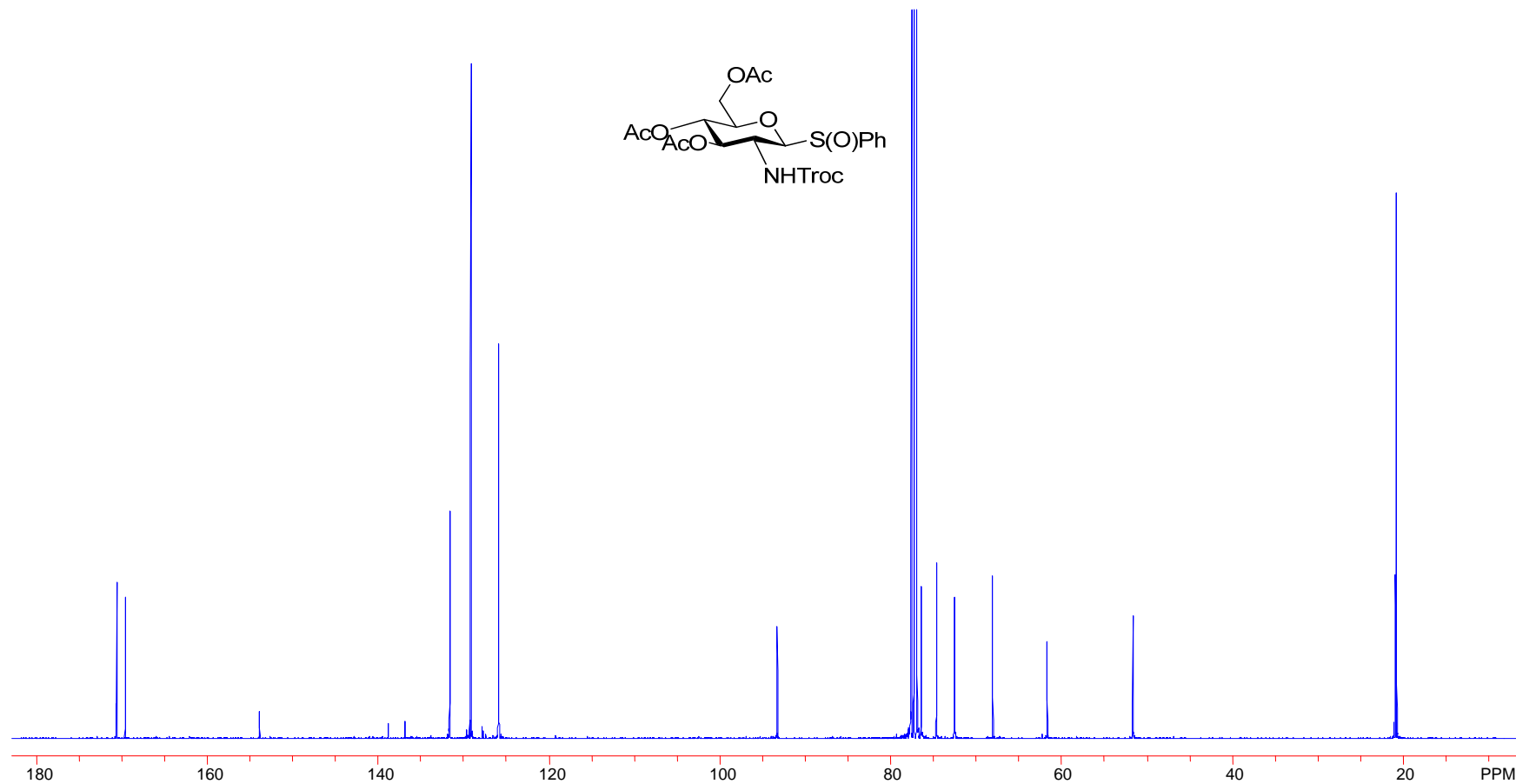


<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Phenyl 3,4,6-*O*-acetyl-2-deoxy-1-thio-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside *S*-Oxide (**78**).

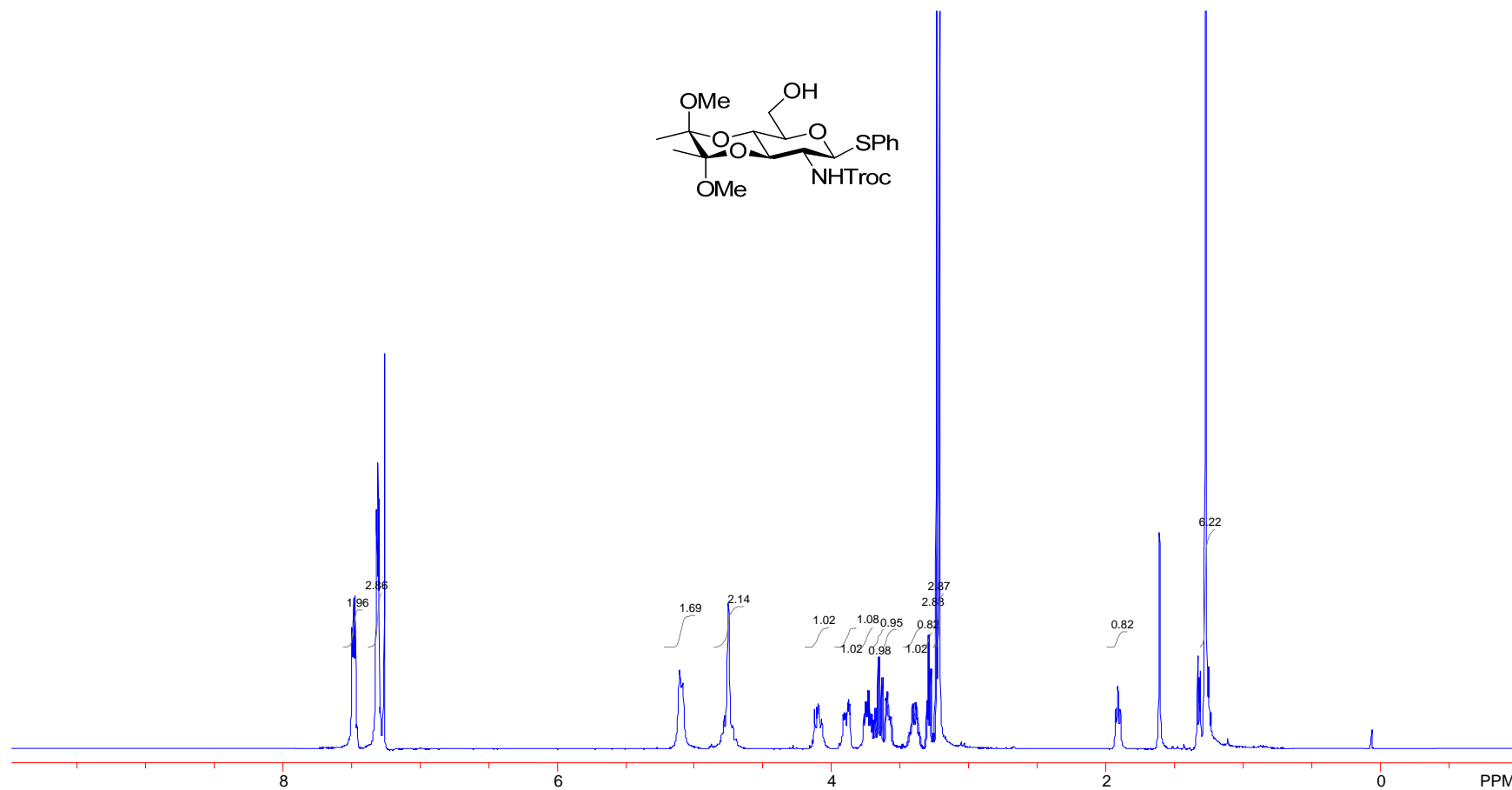


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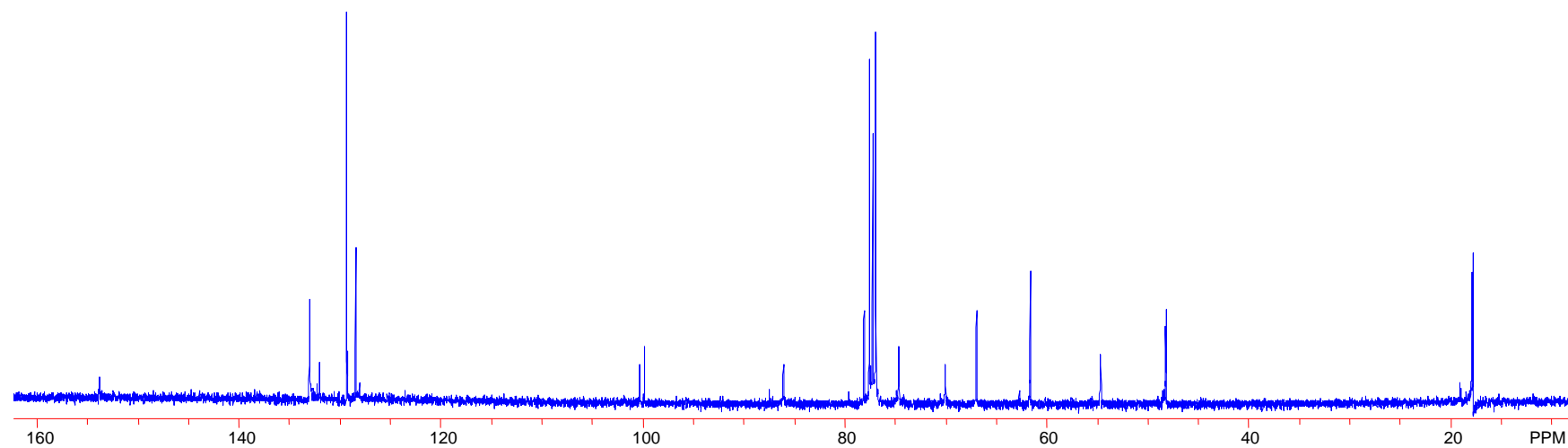
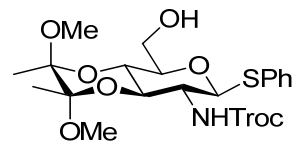
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 3,4,6-*O*-acetyl-2-deoxy-1-thio-2-(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-glucopyranoside *S*-Oxide (**78**).



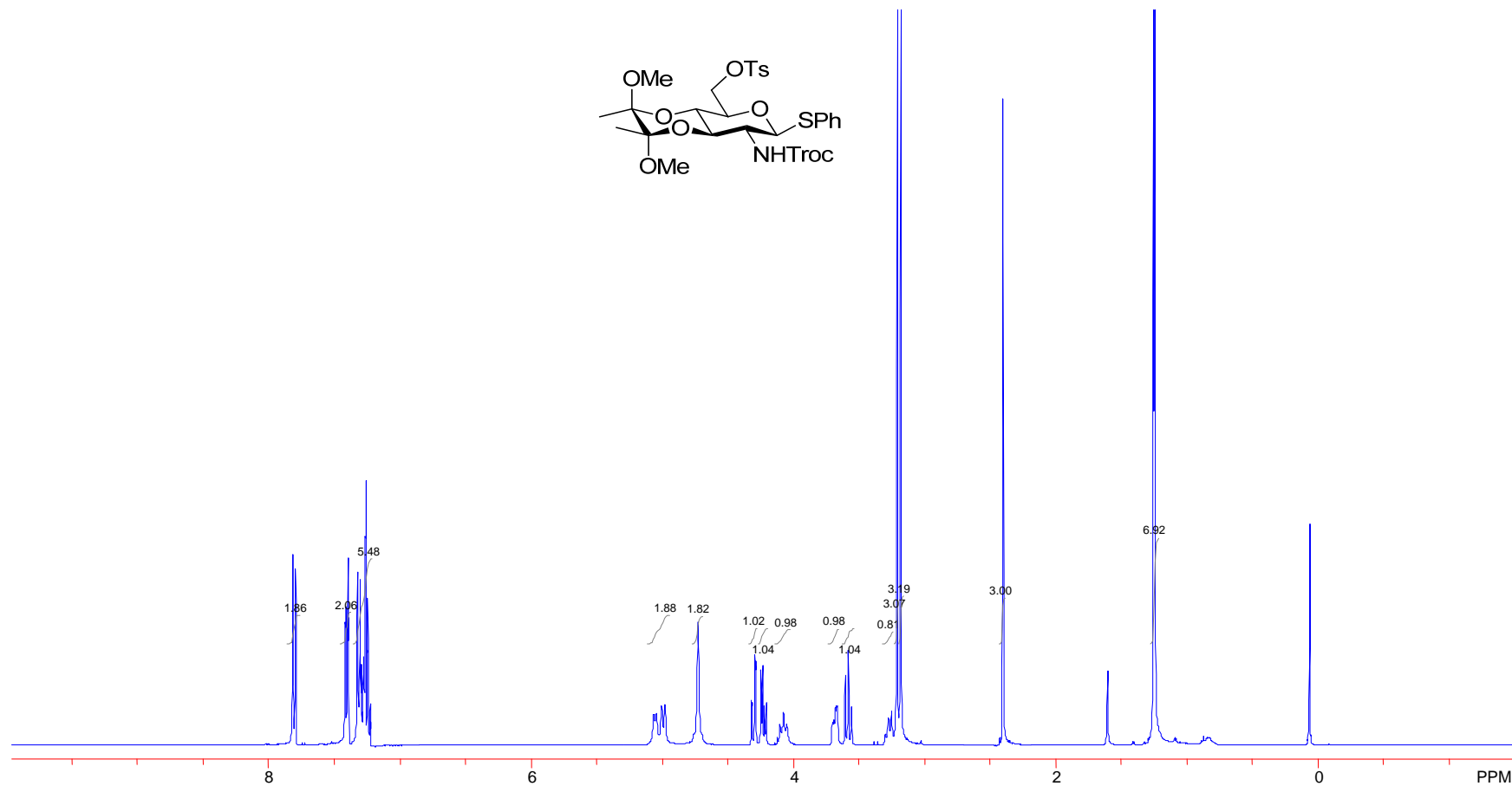
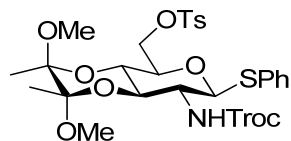
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Phenyl 2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (**83**).



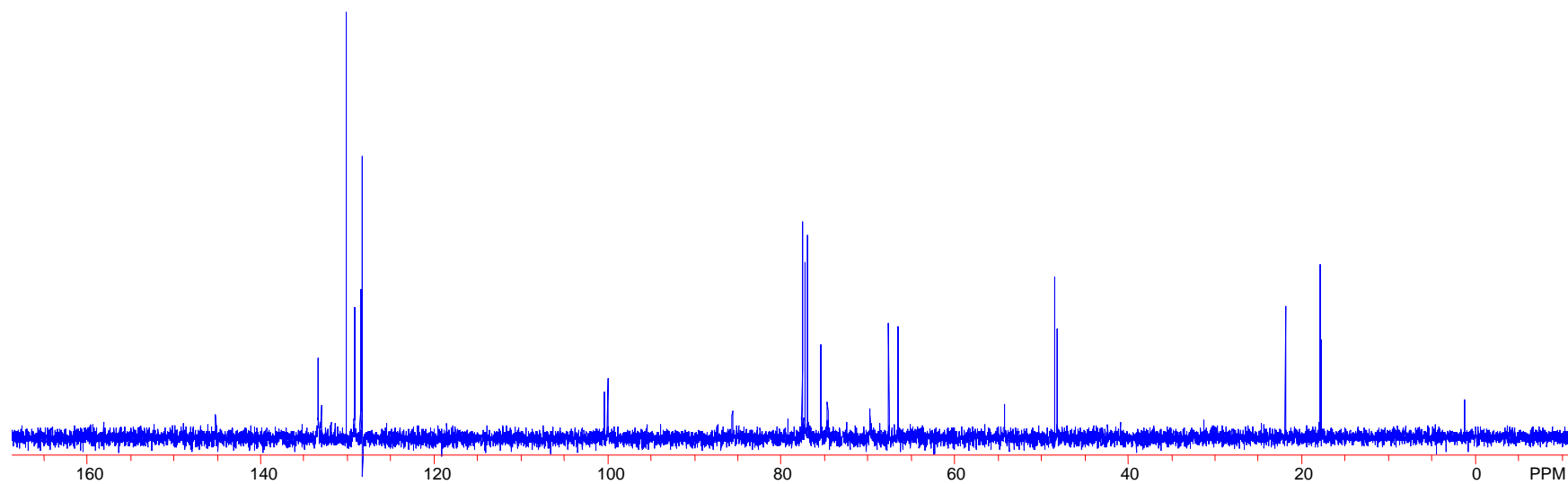
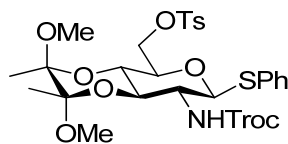
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-2-(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-glucopyranoside (**83**).



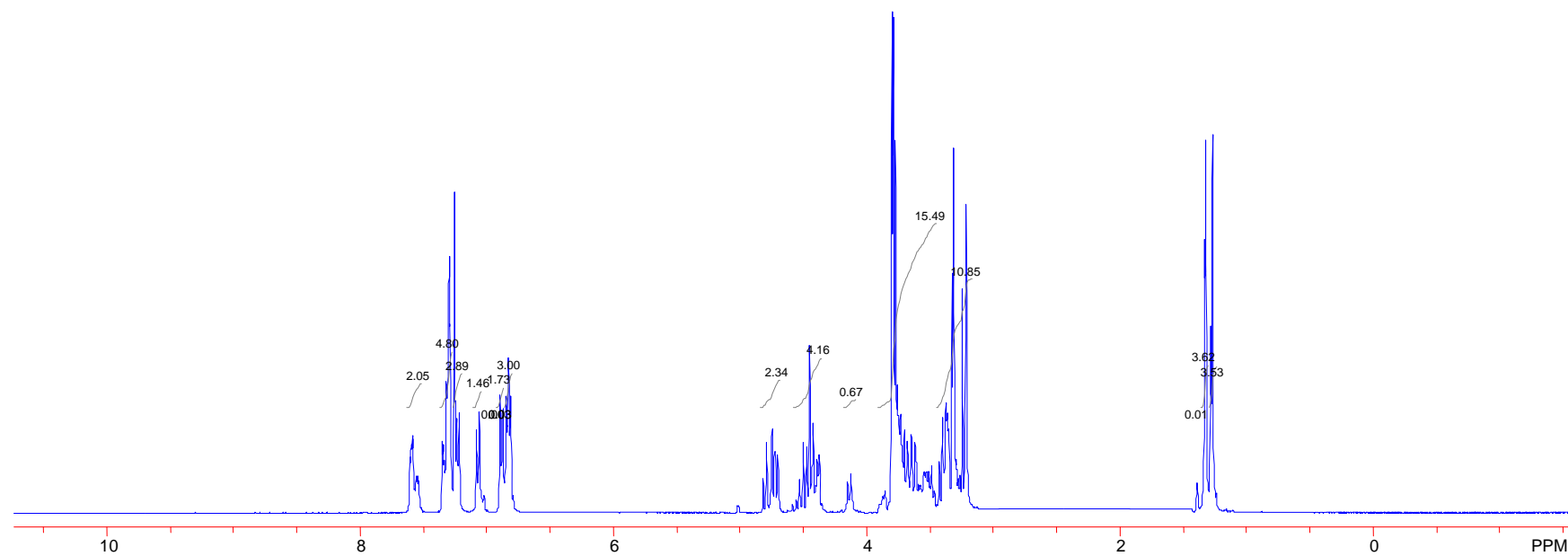
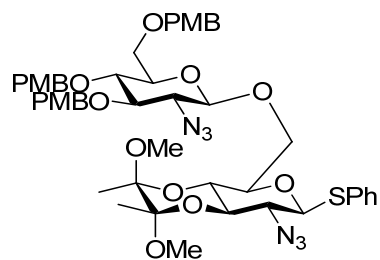
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Phenyl 2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-6-*O*-*p*-toluenesulfonyl-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (**57**).



$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) Phenyl 2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-6-*O*-*p*-toluenesulfonyl-2-(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-glucopyranoside (**57**).

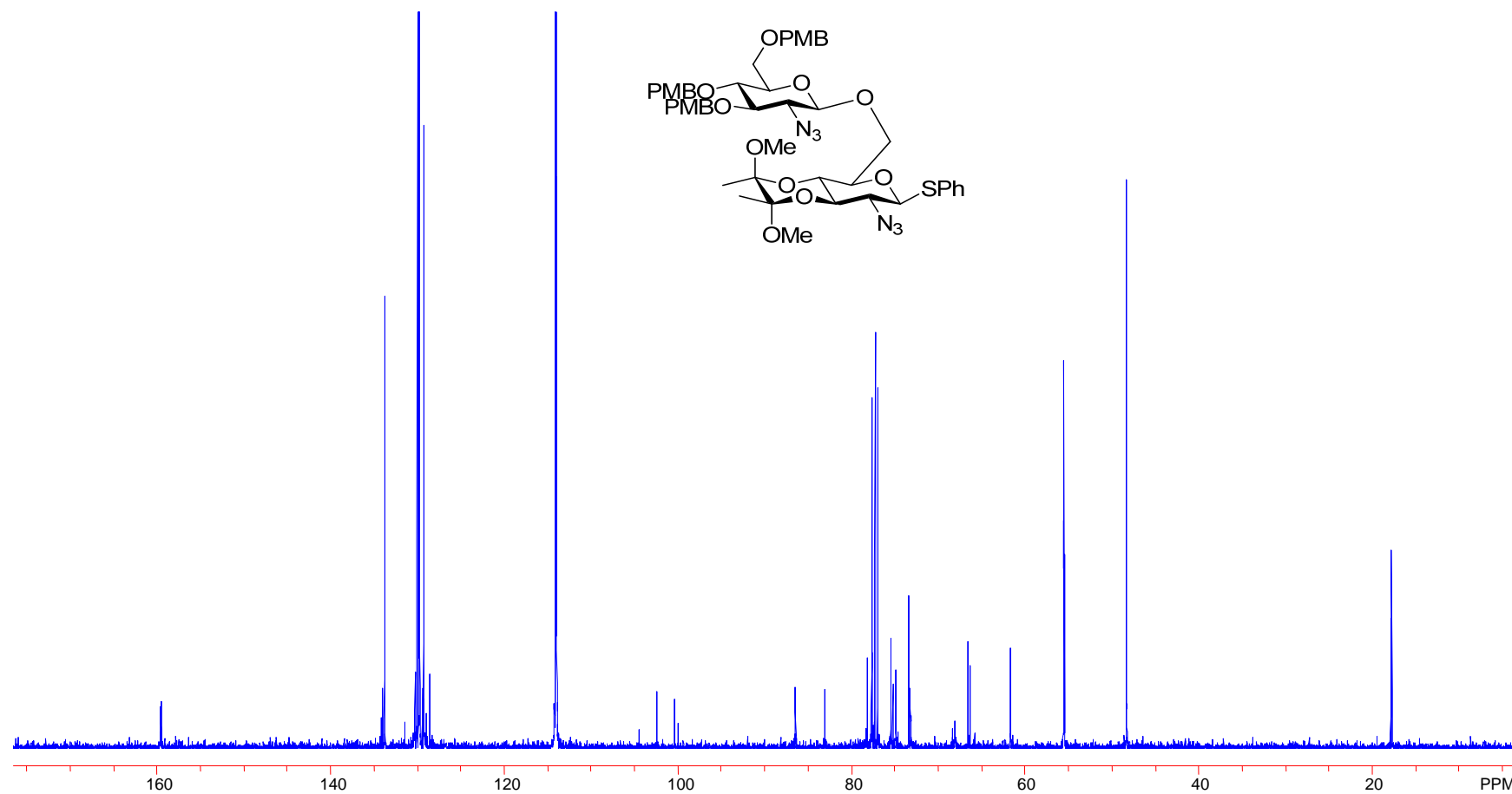


$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) Phenyl 2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-2'-azido-2'-deoxy-3',4',6'-tri-*O*-(*p*-methoxybenzyl)]- $\beta$ -D-gentiobioside (**49**).

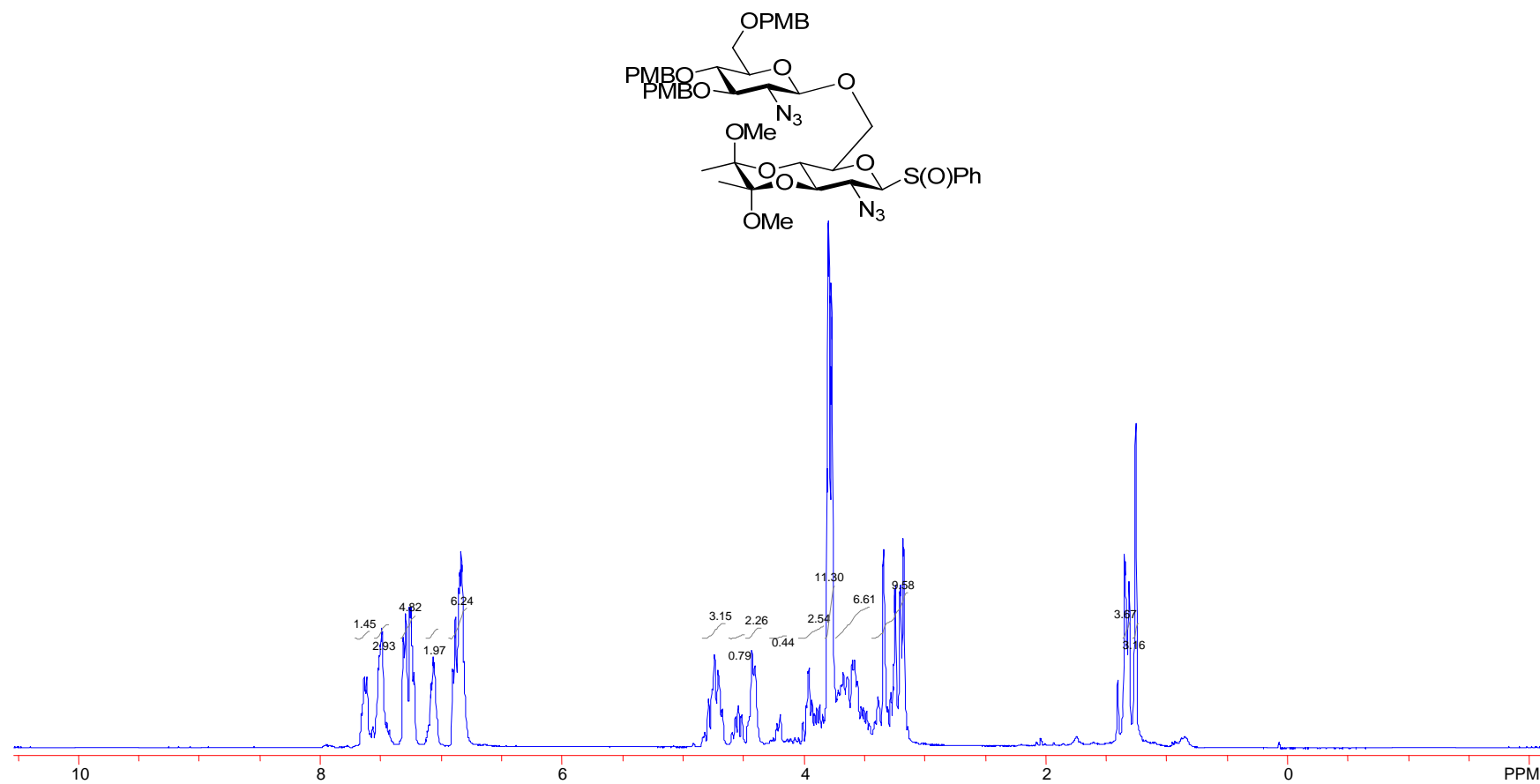




$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-2'-azido-2'-deoxy-3',4',6'-tri-*O*-(*p*-methoxybenzyl)]- $\beta$ -D-gentiobioside (**49**).

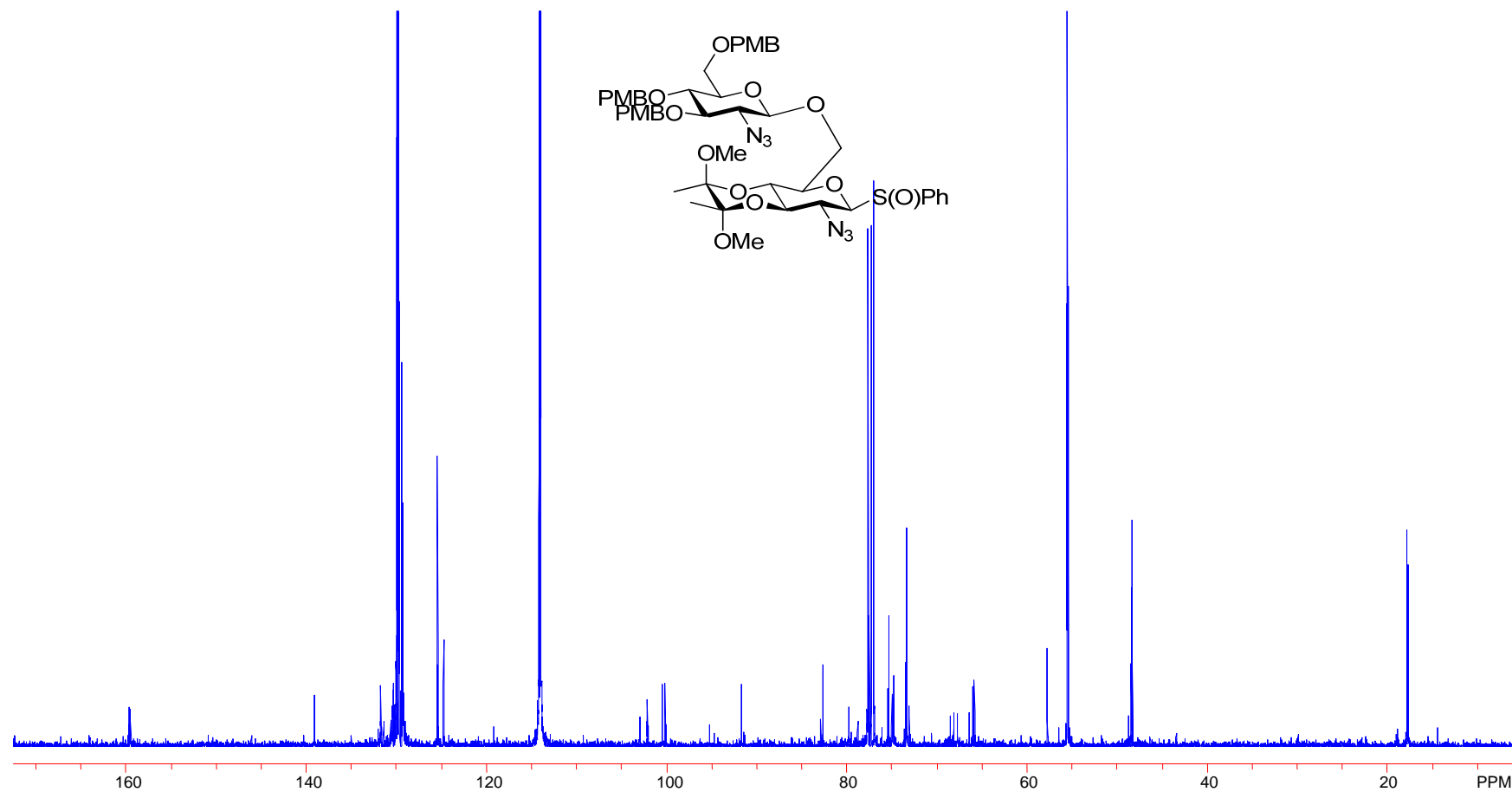


<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Phenyl 2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-[2'-azido-2'-deoxy-3',4',6'-tri-*O*-(*p*-methoxybenzyl)]-β-D-gentiobioside *S*-Oxide (**50**).

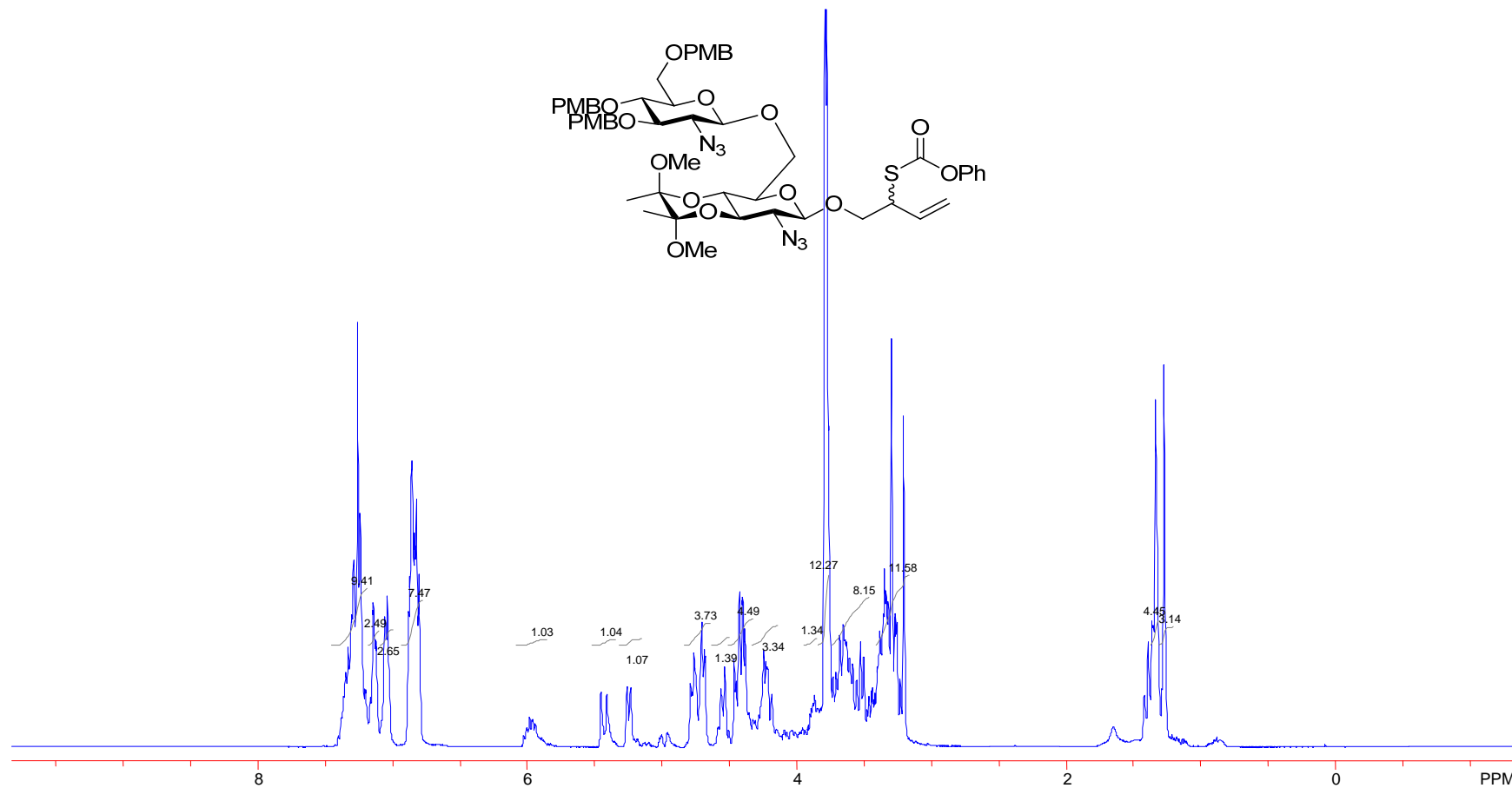


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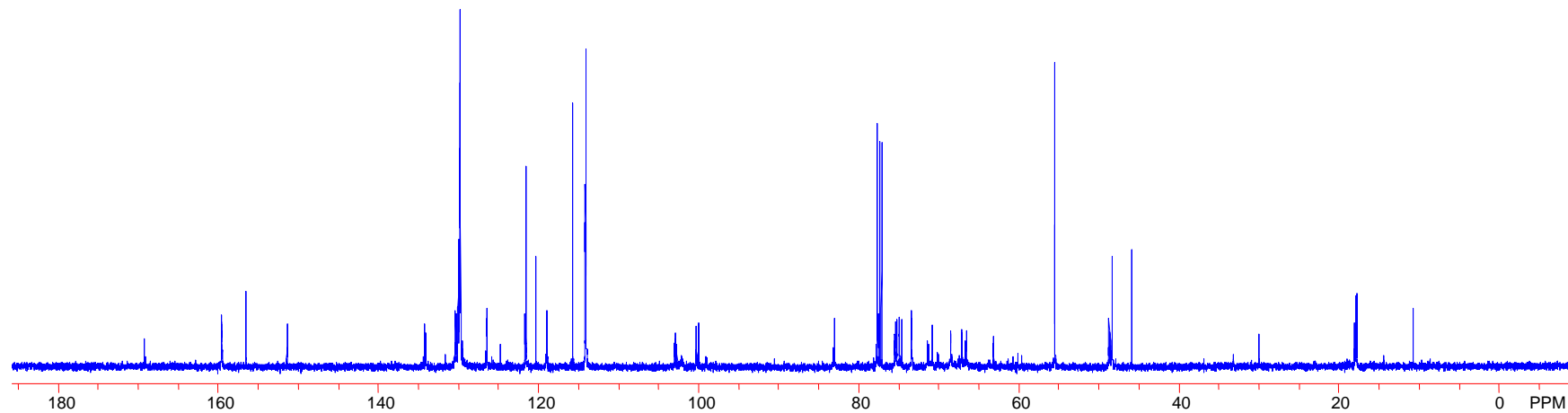
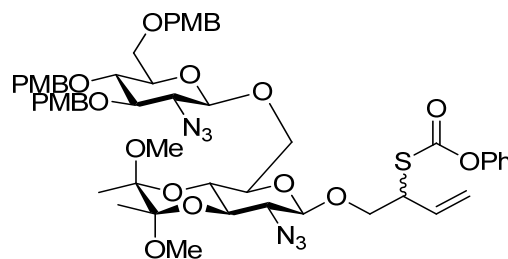
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-[2'-azido-2'-deoxy-3',4',6'-tri-*O*-(*p*-methoxybenzyl)]- $\beta$ -D-gentiobioside *S*-Oxide (**50**).



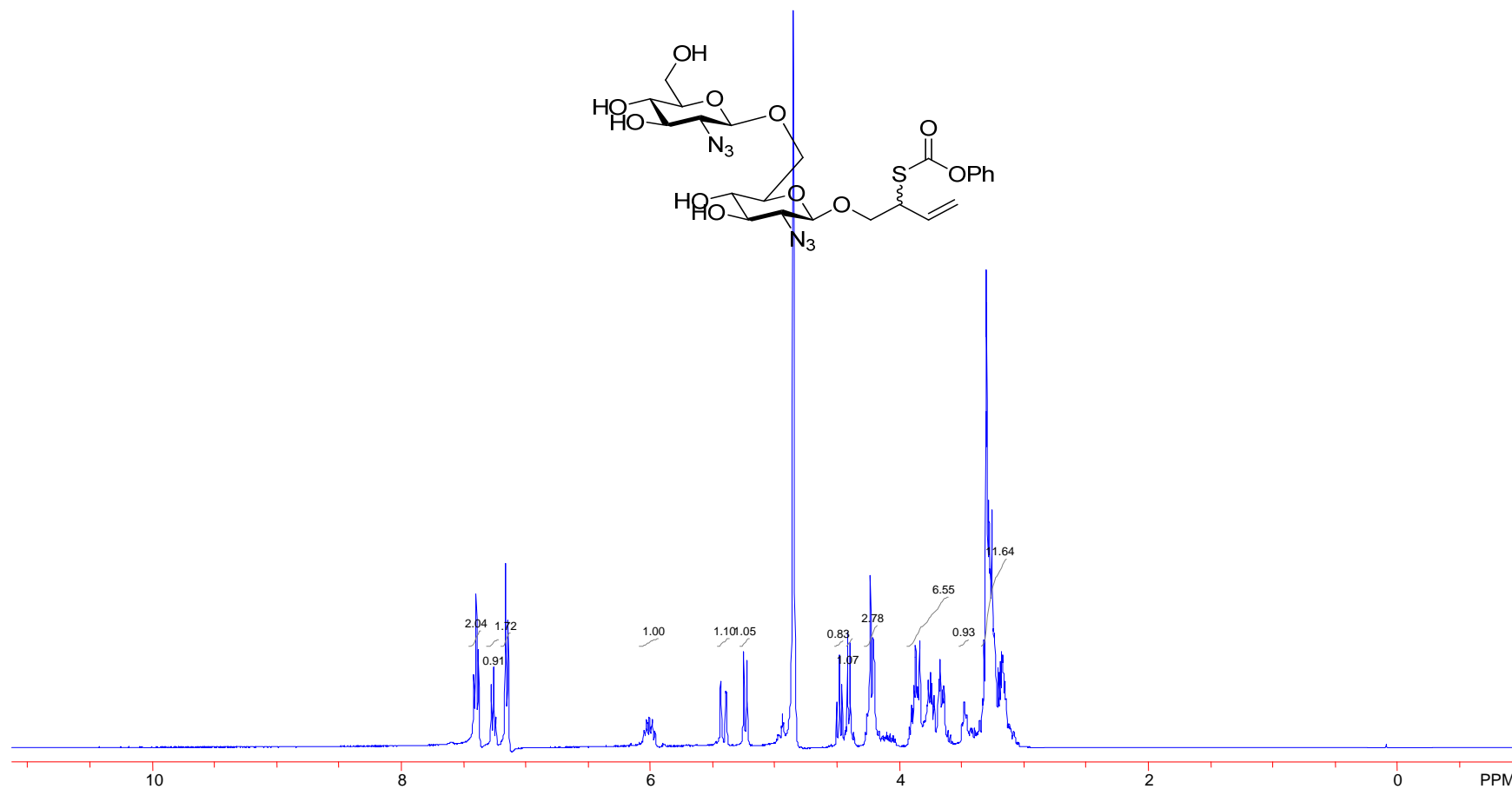
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) 2-(Phenyloxycarbonylthioxy-but-3-enyl 2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-[2'-azido-2'-deoxy-3',4',6'-tri-*O*-(*p*-methoxybenzyl)]- $\beta$ -D-gentiobioside (**51**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 2-(Phenyloxycarbonylthioxy-but-3-enyl 2-azido-2-deoxy-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-[2'-azido-2'-deoxy-3',4',6'-tri-*O*-(*p*-methoxybenzyl)]- $\beta$ -D-gentiobioside (**51**).

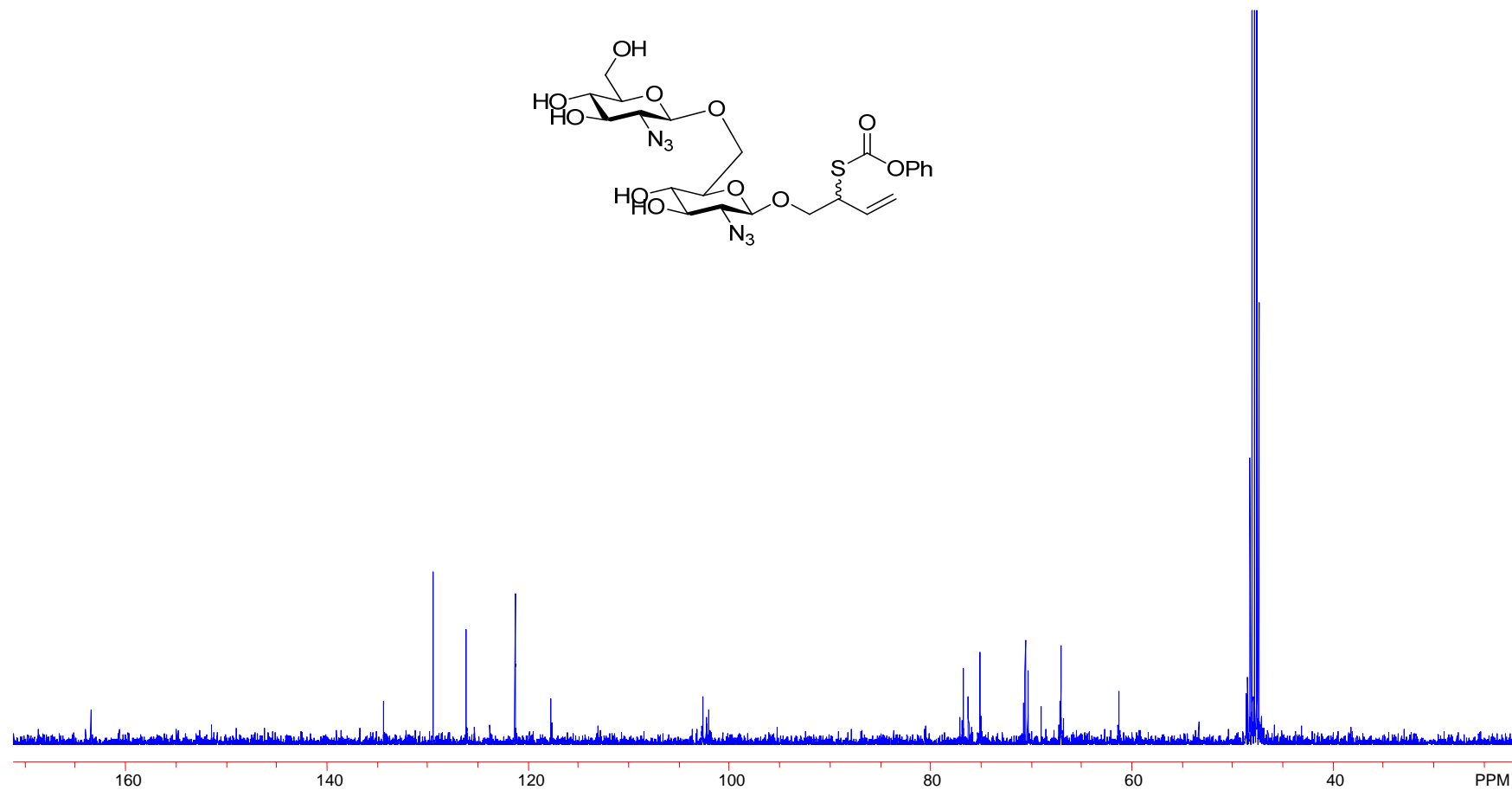
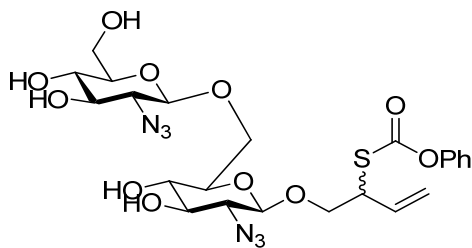


$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 400 MHz) 2-(Phenyloxycarbonylthioxy)but-3-enyl 2,2'-diazido-2,2'-dideoxy- $\beta$ -D-gentiobioside (**52**).

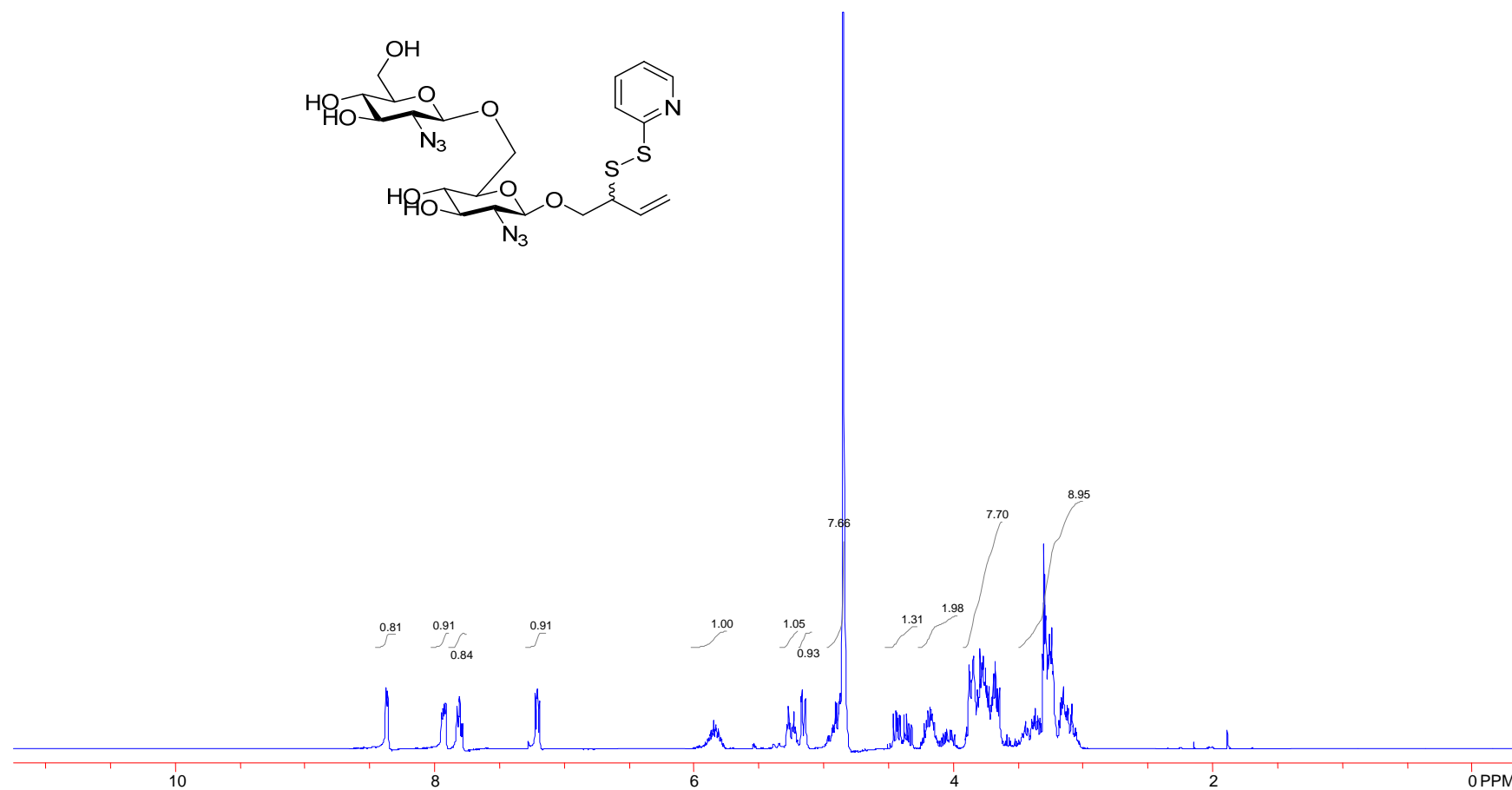


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$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 100 MHz) 2-(Phenyloxycarbonylthioxy)but-3-enyl 2,2'-diazido-2,2'-dideoxy- $\beta$ -D-gentiobioside (**52**).

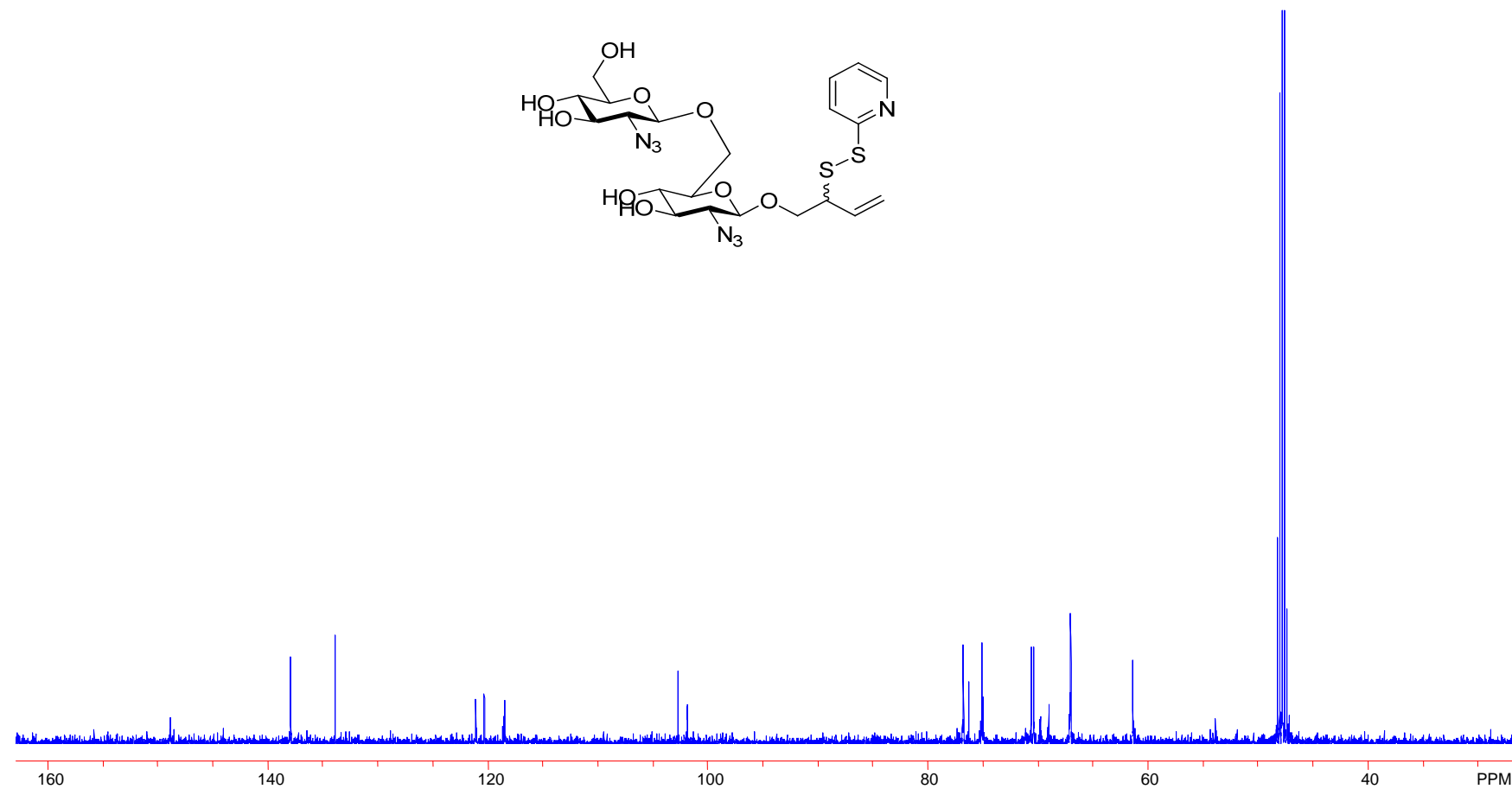


<sup>1</sup>H-NMR spectrum (CD<sub>3</sub>OD, 400 MHz) 2-(Pyridyldithio)but-3-enyl 2,2'-diazido-2,2'-dideoxy-β-D-gentiobioside (**53**).

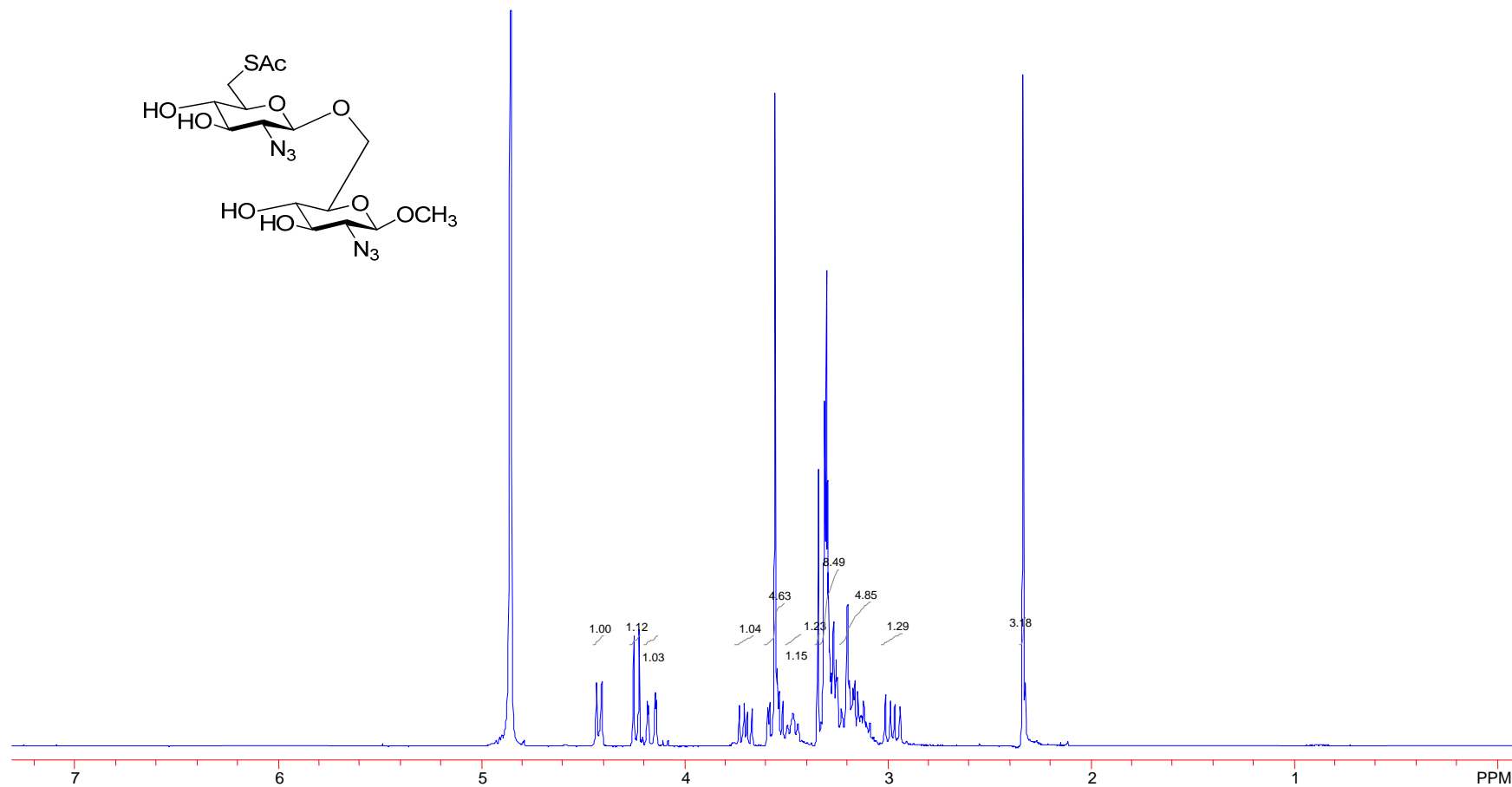




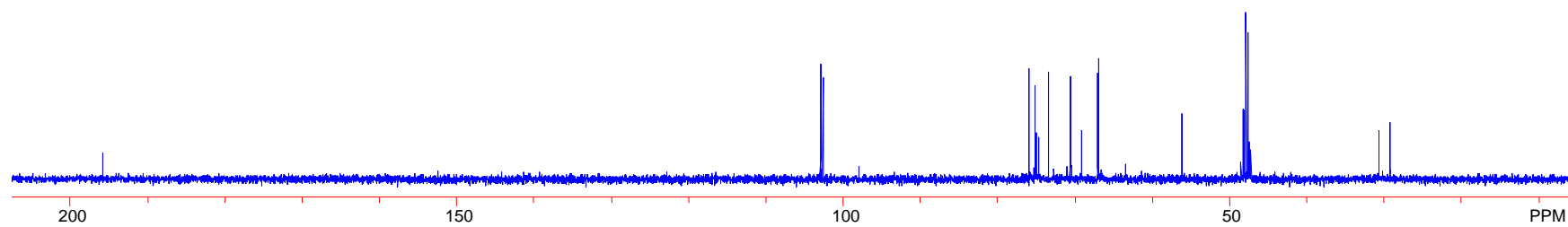
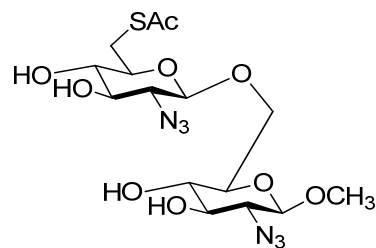
$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 100 MHz) 2-(Pyridyldithio)but-3-enyl 2,2'-diazido-2,2'-dideoxy- $\beta$ -D-gentiobioside (**53**).



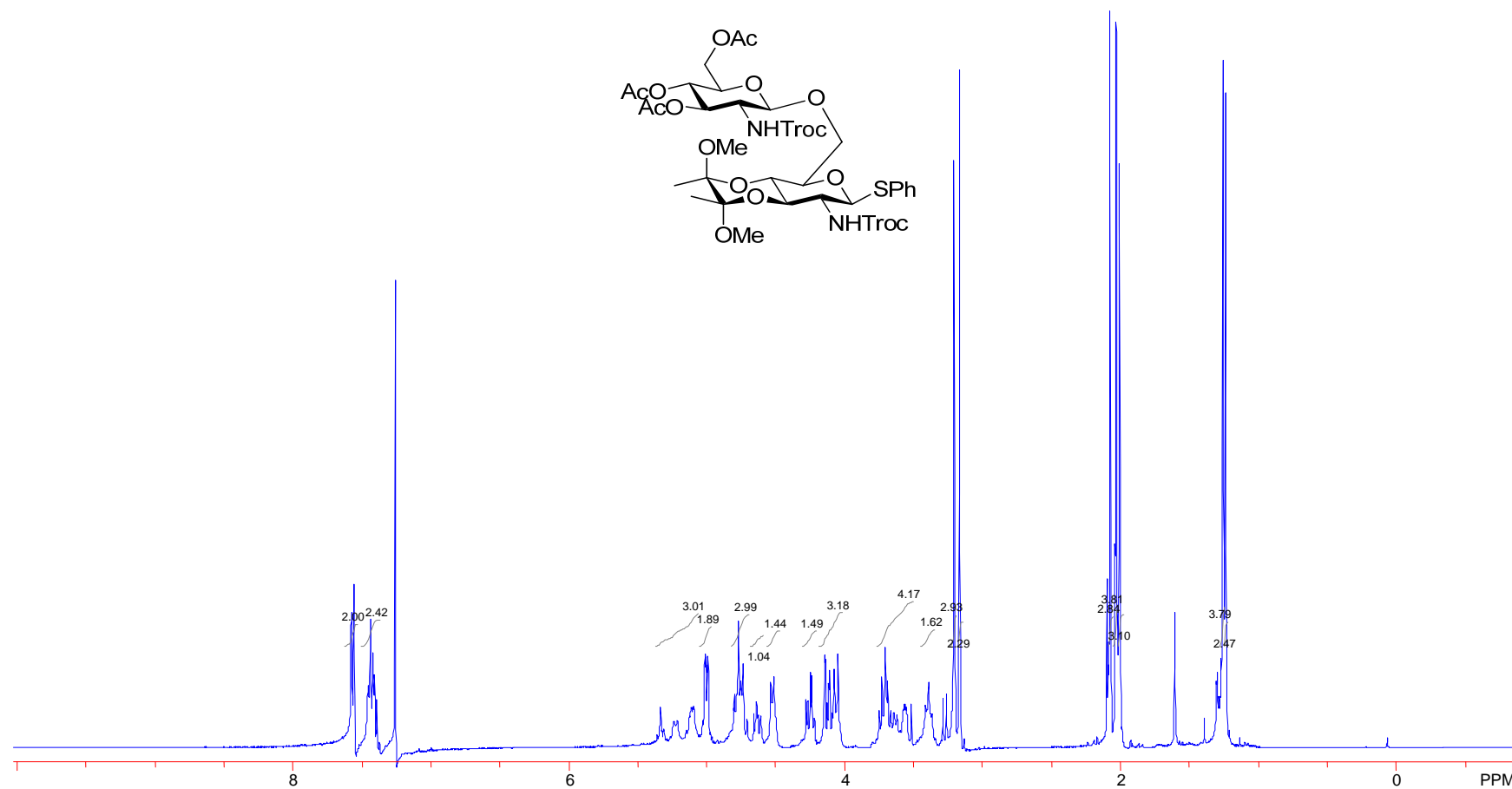
$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 400 MHz) Methyl 2,2'-diazido-2,2'-dideoxy-6'-acetylthio- $\beta$ -D-gentiobioside (**56**).



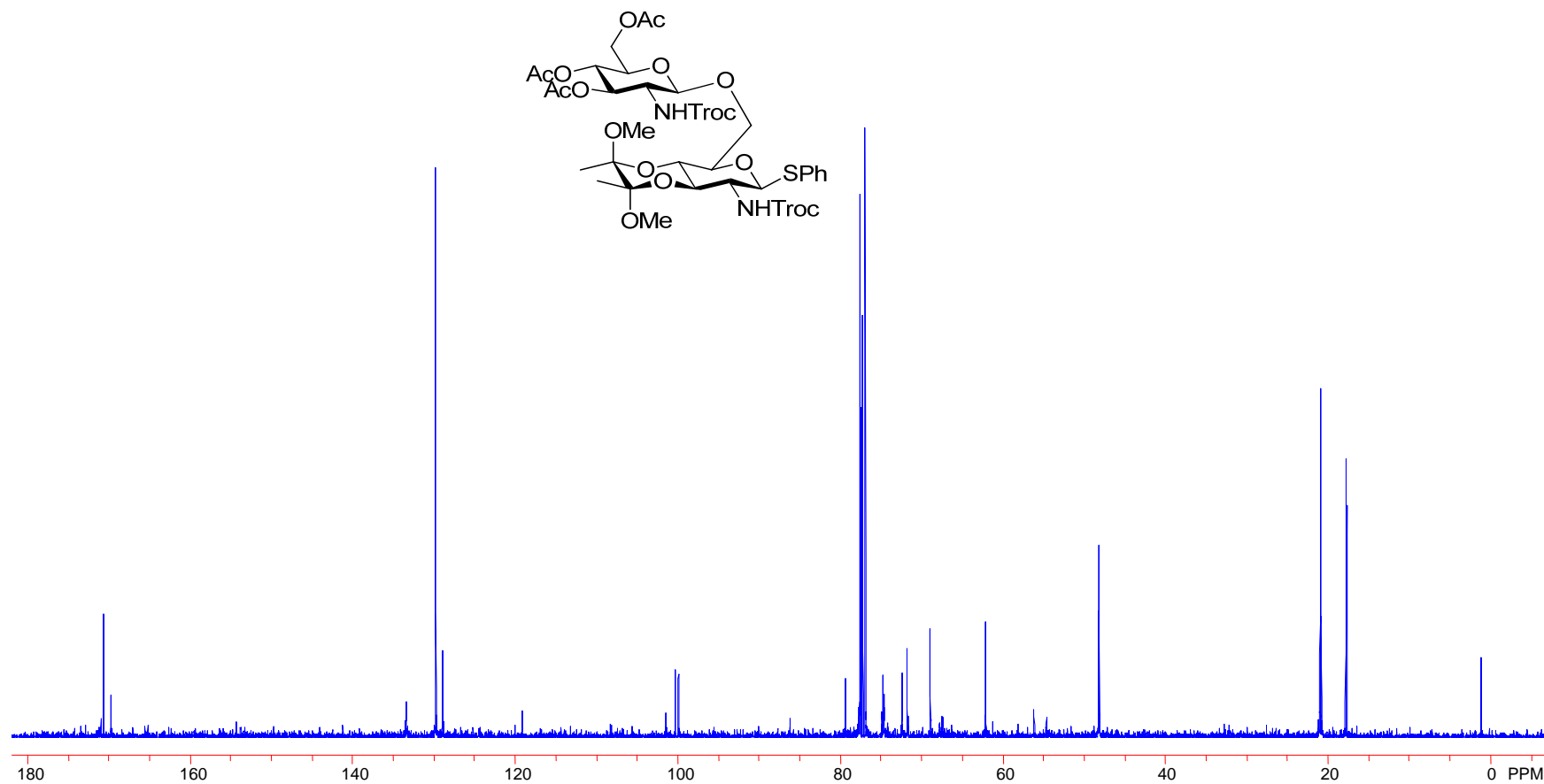
$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 100 MHz) Methyl 2,2'-diazido-2,2'-dideoxy-6'-acetylthio- $\beta$ -D-gentiobioside (**56**).



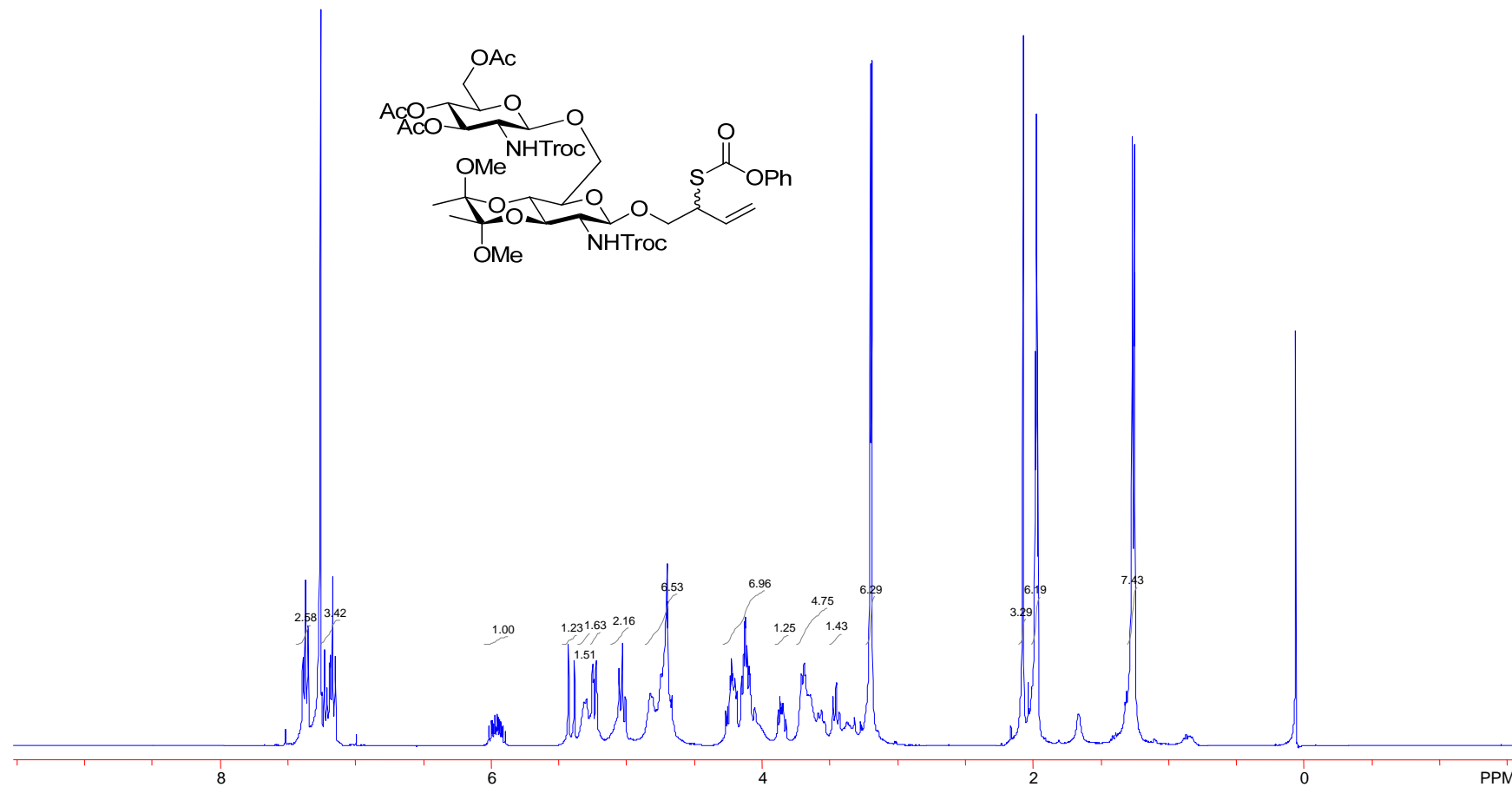
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) Phenyl 3',4',6'-tri-*O*-acetyl-2,2'-dideoxy-3,4-*O*-(2,3-dimethoxybutan-2,3-diyl)-1-thio-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobioside (**84**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Phenyl 3',4',6'-tri-*O*-acetyl-2,2'-dideoxy-3,4-*O*-(2,3-dimethoxybutan-2,3-diyl)-1-thio-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobioside (**84**).

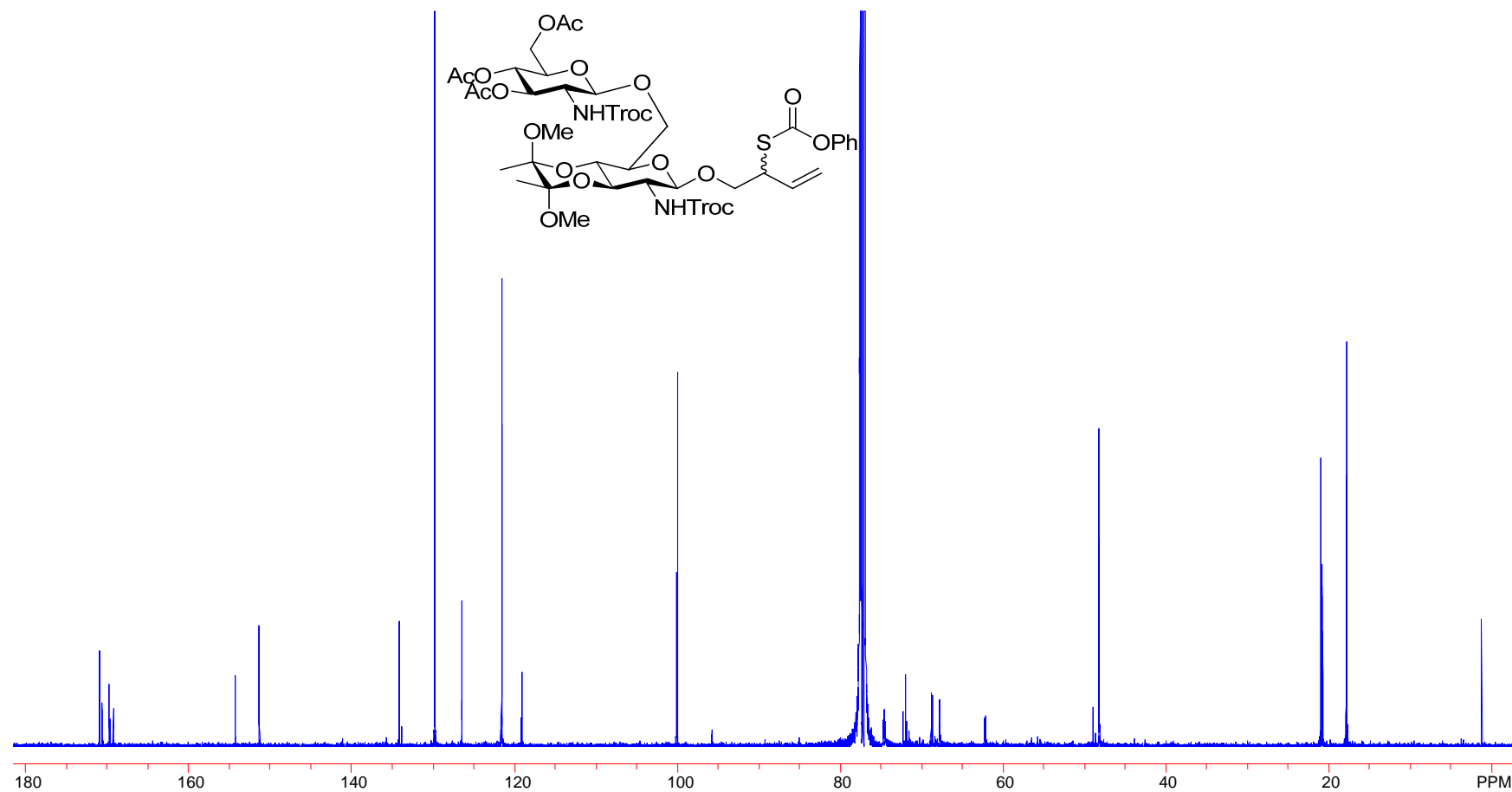


<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) 2-(Phenyloxycarbonylthioxy)but-3-enyl 3',4',6'-tri-*O*-acetyl-2,2'-dideoxy-3,4-*O*-(2,3-dimethoxybutan-2,3-diyl)-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)-β-D-gentiobioside (**85**)

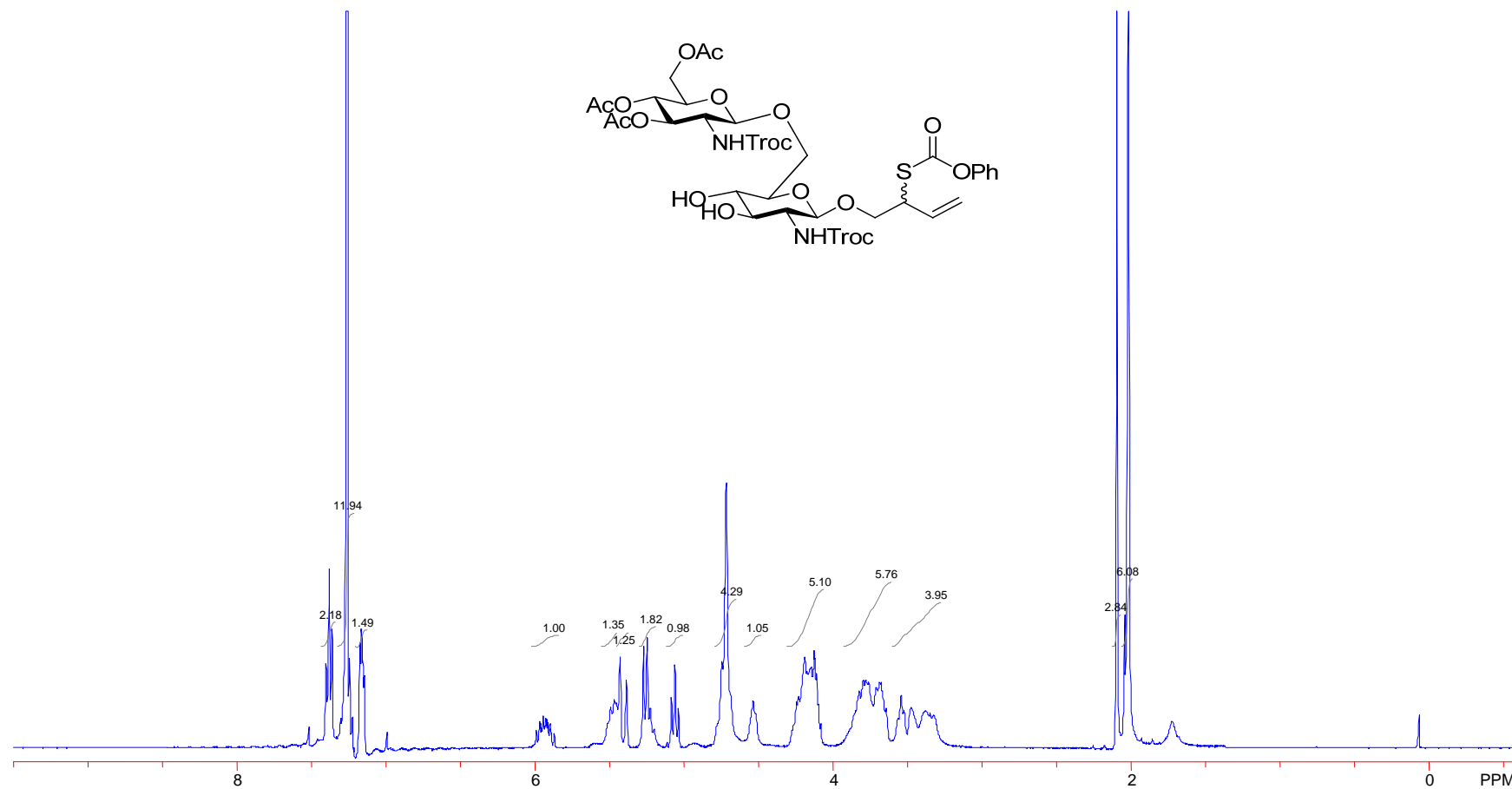


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$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) 2-(Phenyloxycarbonylthioxy)but-3-enyl 3',4',6'-tri-*O*-acetyl-2,2'-dideoxy-3,4-*O*-(2,3-dimethoxybutan-2,3-diyl)-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobioside (**85**)



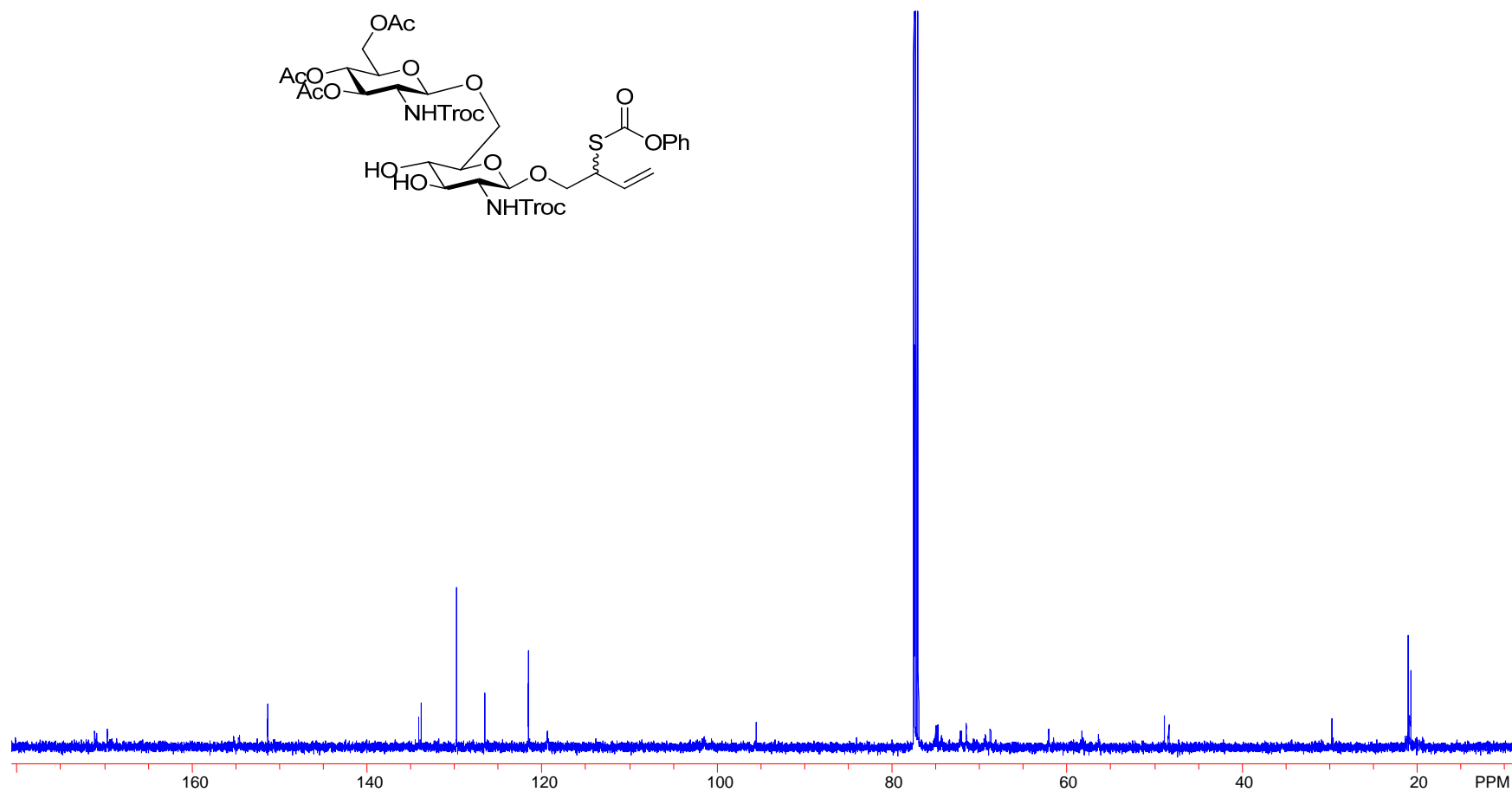
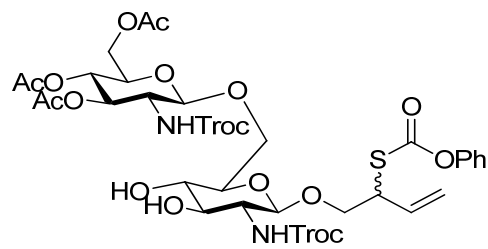
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 400 MHz) 2-(Phenyloxycarbonylthioxy)but-3-enyl 3',4',6'-tri-*O*-acetyl-2,2'-dideoxy-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobioside (**86**)



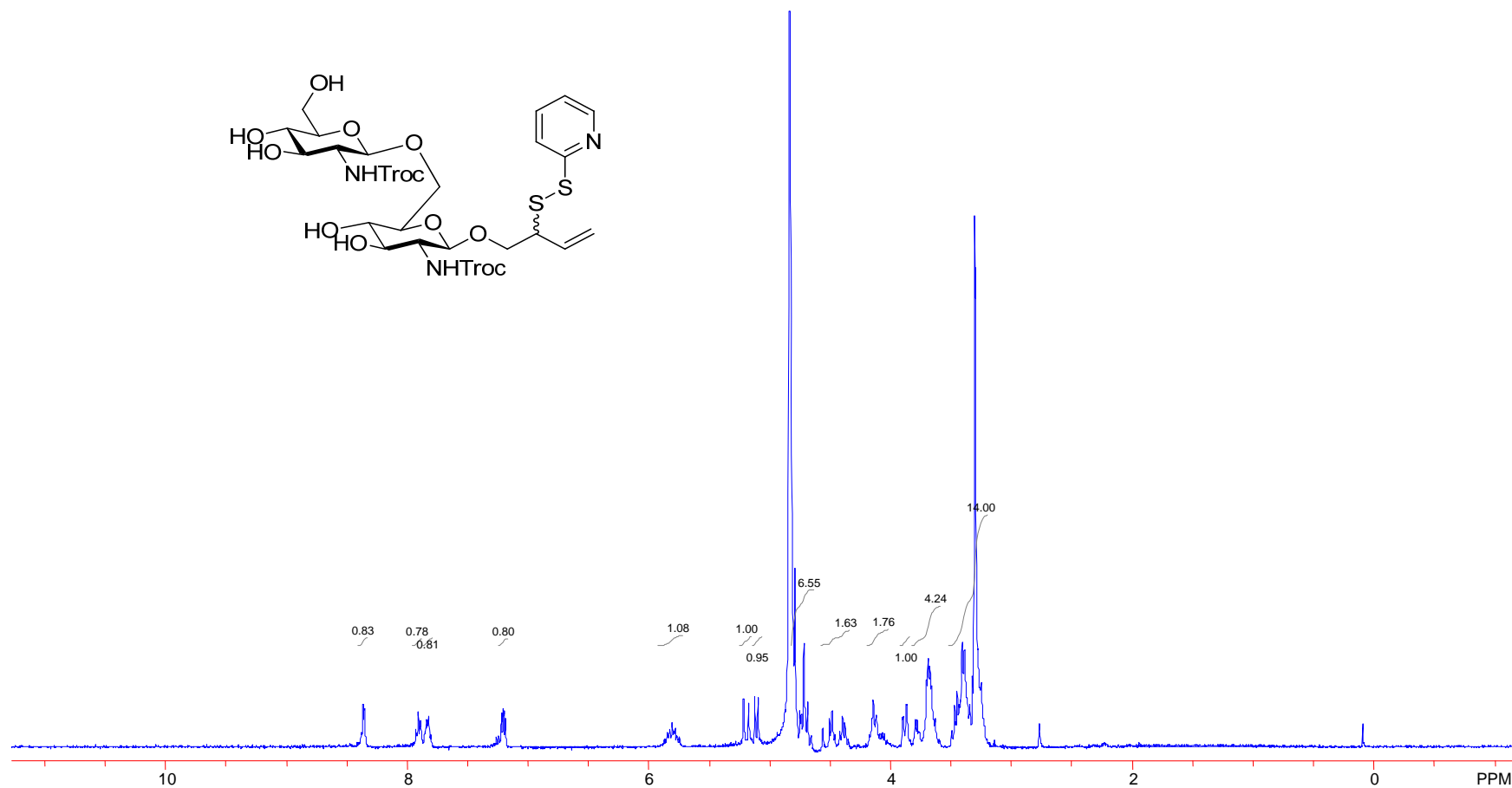
S-112



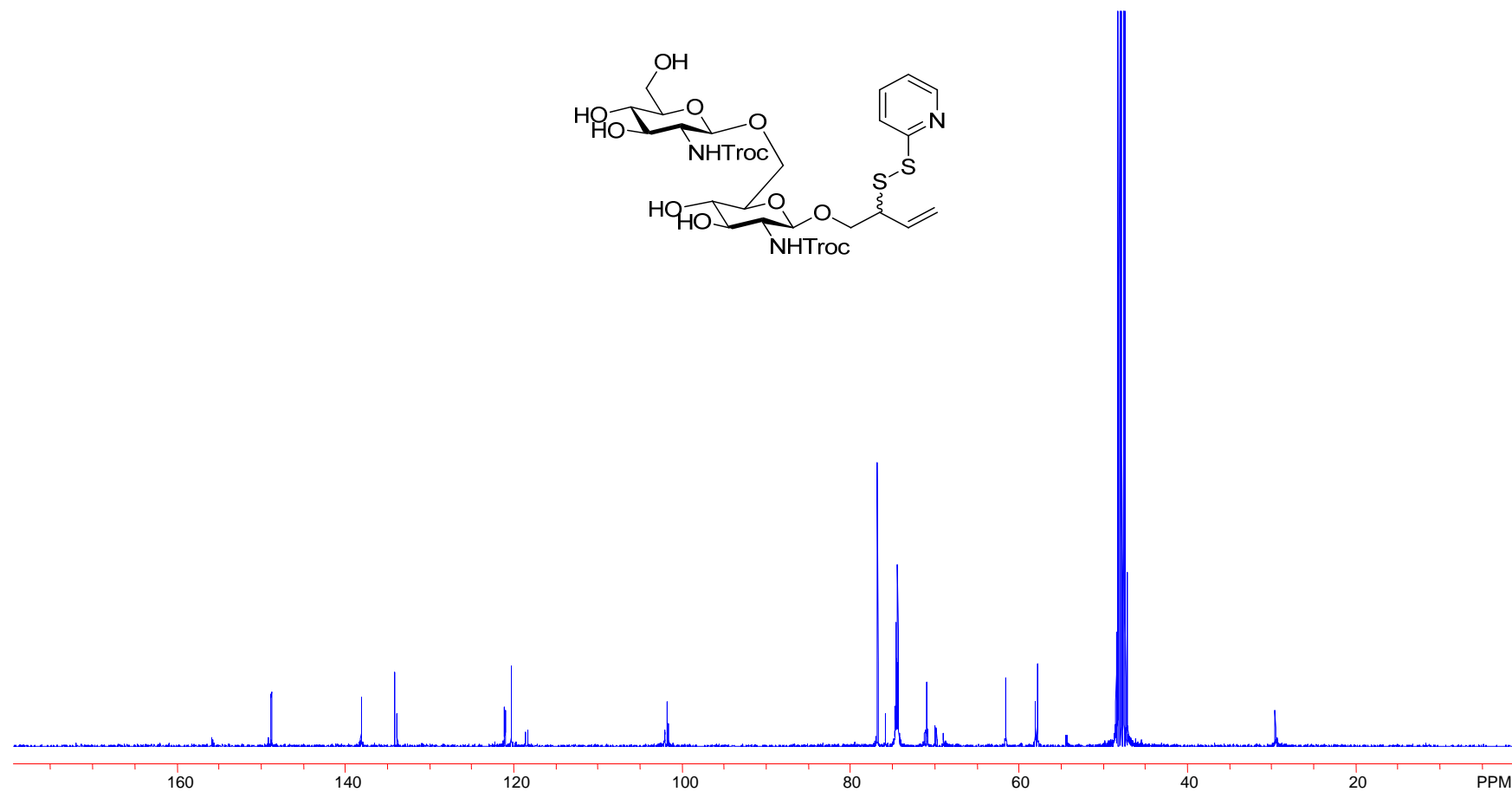
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 2-(Phenyloxycarbonylthioxy)but-3-enyl 3',4',6'-tri-*O*-acetyl-2,2'-dideoxy-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobioside (**86**)



$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 400 MHz) 2-(2-Pyridyldithio)but-3-enyl 2,2'-dideoxy-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobioside (**62**).

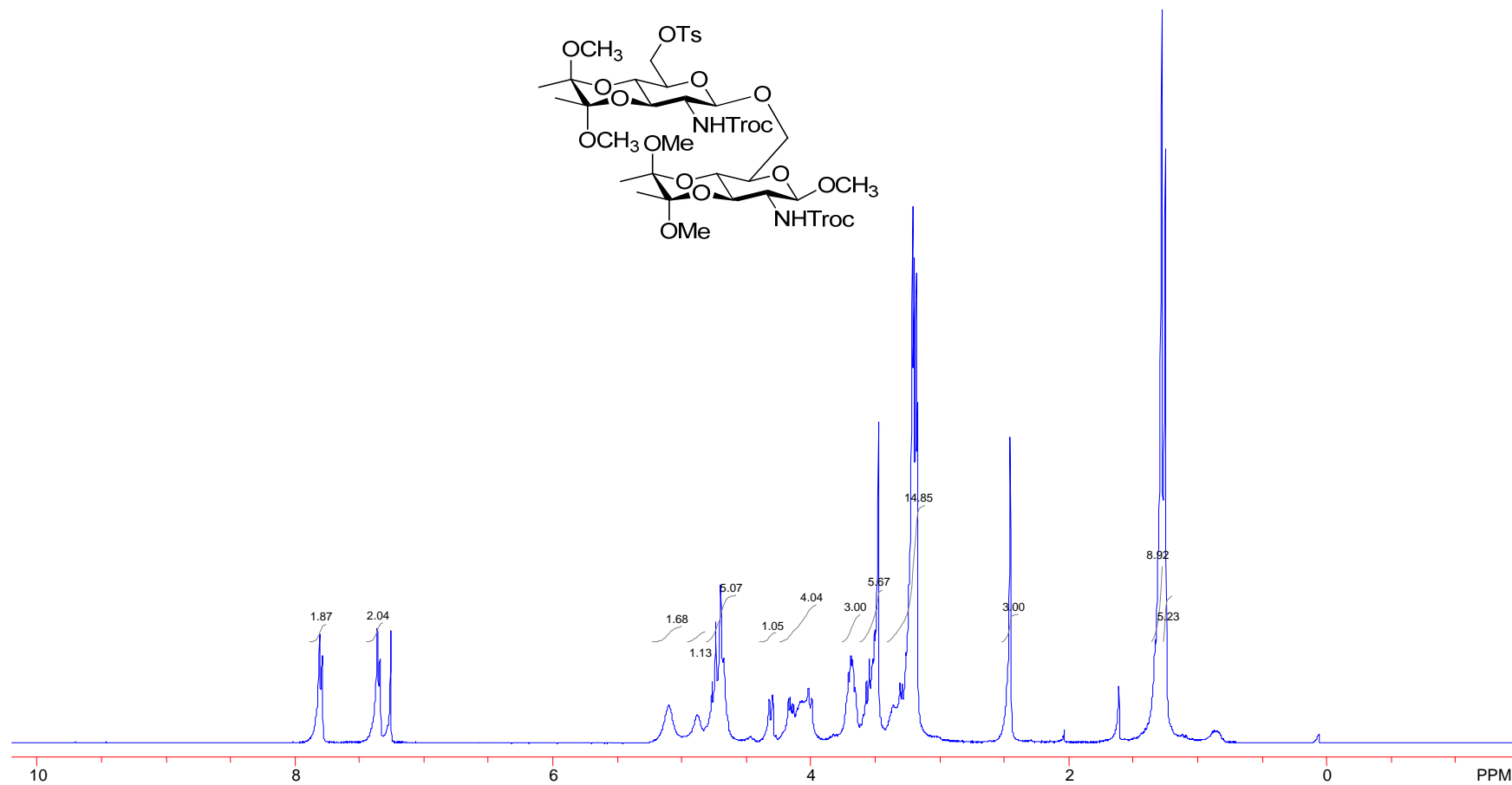


$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 100 MHz) 2-(2-Pyridyldithio)but-3-enyl 2,2'-dideoxy-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobioside (**62**).



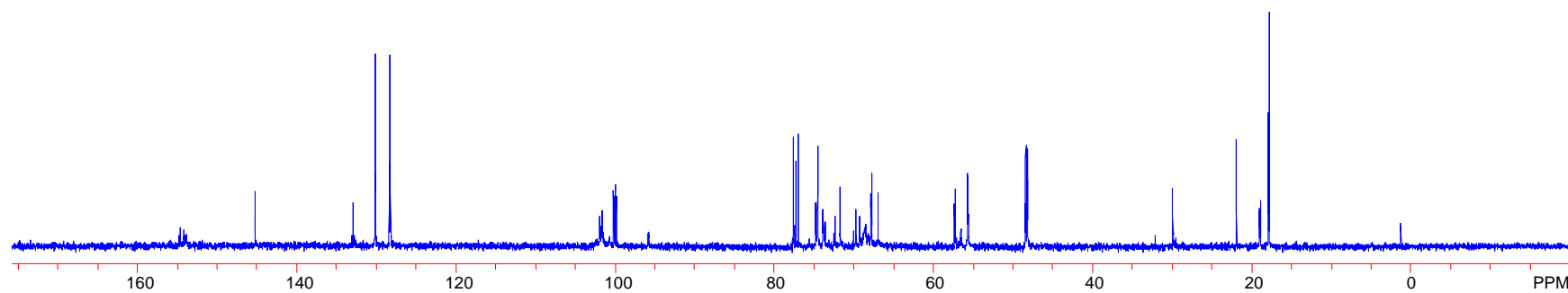
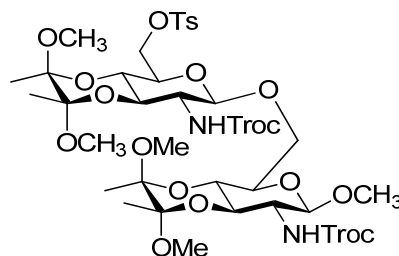
S-115

<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Methyl 2,2'-dideoxy-3,4;3',4'-di-*O*-(2,3-dimethoxybutan-2,3-diyl)-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)-6'-*O*-*p*-toluenesulfonyl-β-D-gentiobioside (**59**)



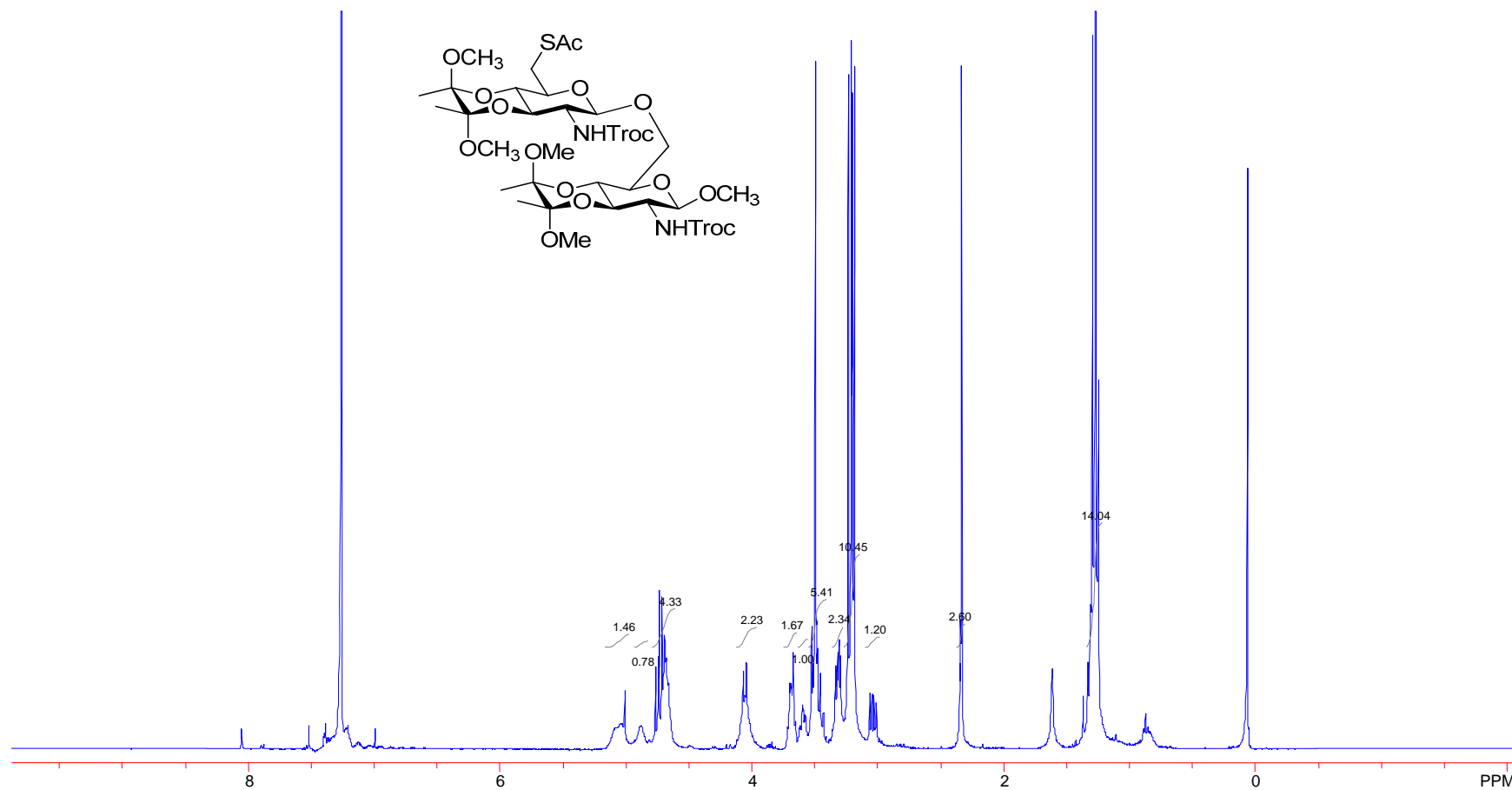
S-116

$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Methyl 2,2'-dideoxy-3,4;3',4'-di-*O*-(2,3-dimethoxybutan-2,3-diyl)-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)-6'-*O*-*p*-toluenesulfonyl- $\beta$ -D-gentiobioside (**59**)

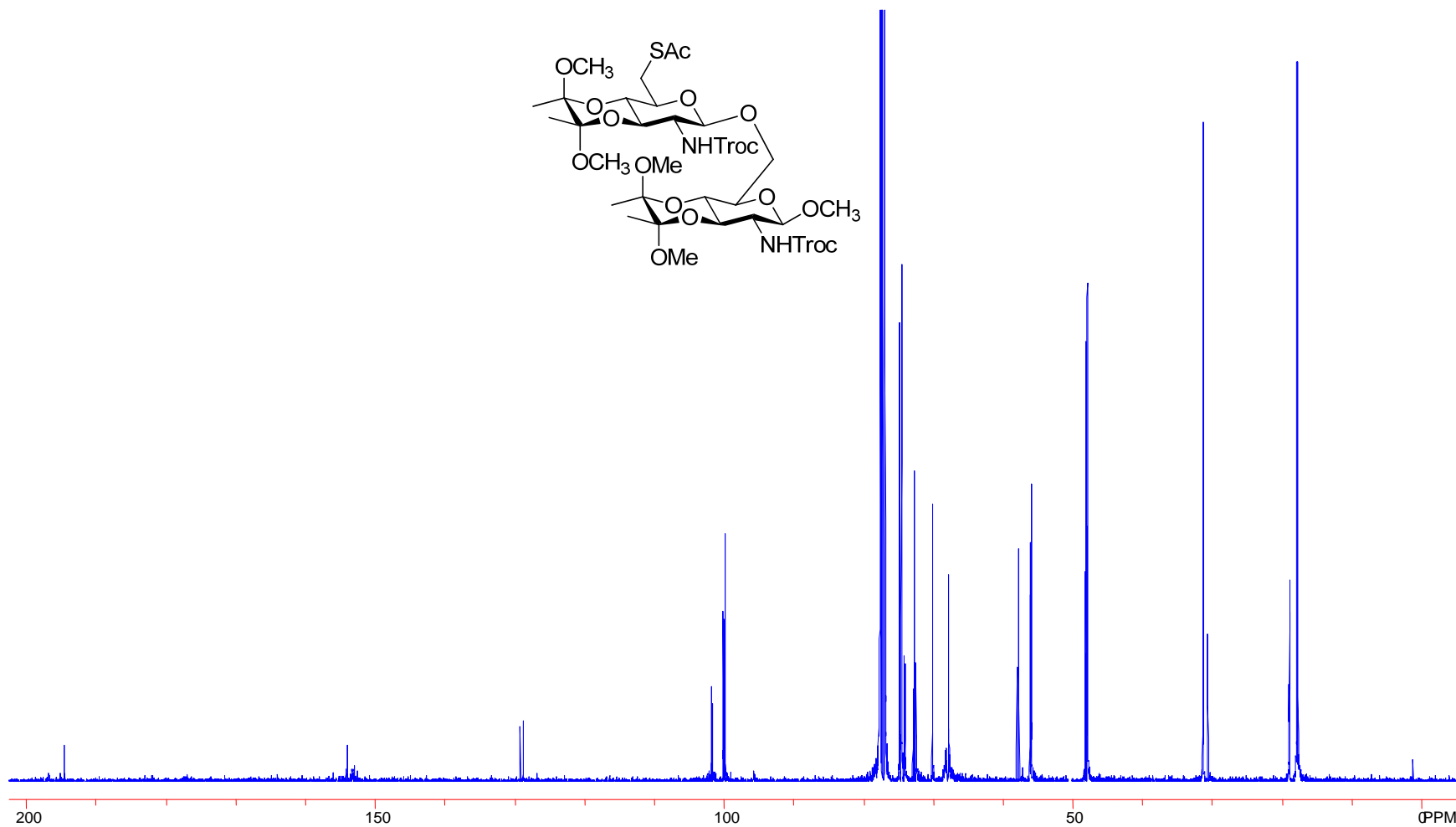


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<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Methyl 6'-acetylthio-2,2'-dideoxy-3,4;3',4'-di-O-(2,3-dimethoxybutan-2,3-diyl)-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)-β-D-gentiobioside (**60**).

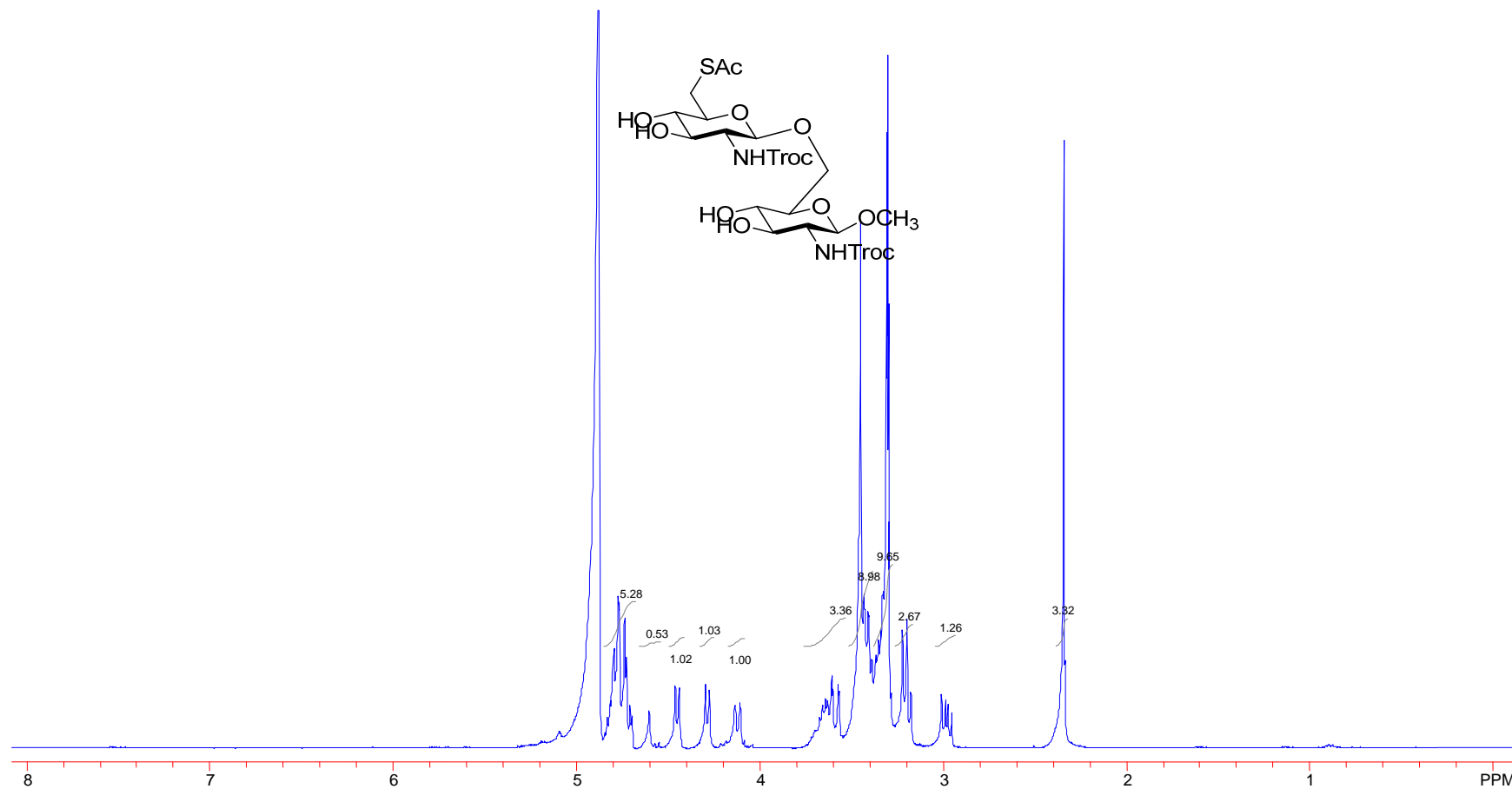


$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Methyl 6'-acetylthio-2,2'-dideoxy-3,4;3',4'-di-*O*-(2,3-dimethoxybutan-2,3-diyl)-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobioside (**60**).



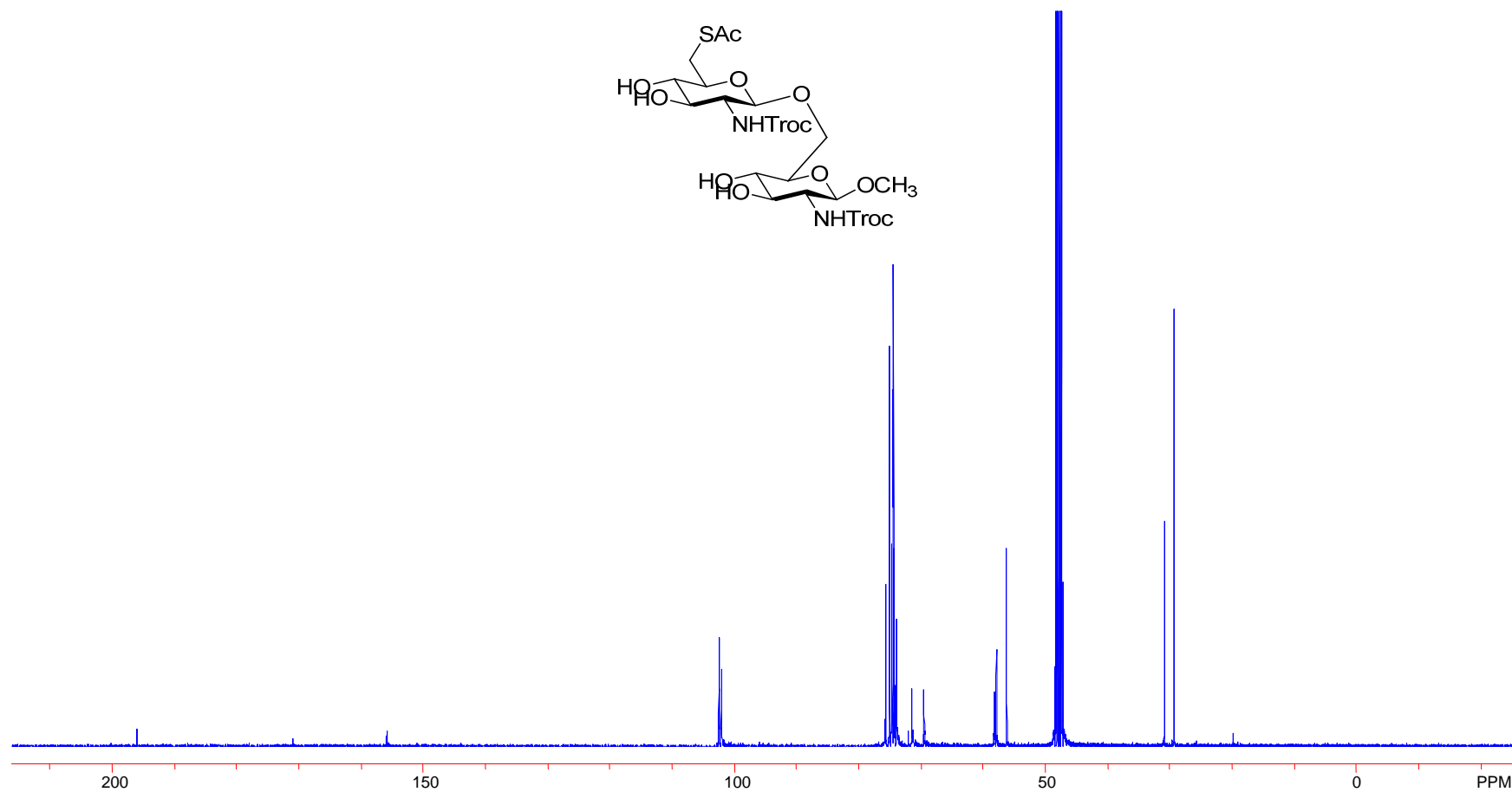
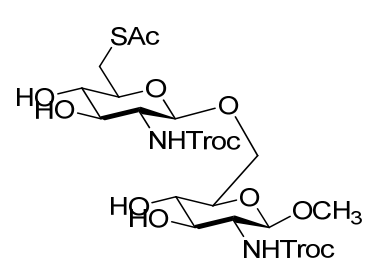
S-119

$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 400 MHz) Methyl 2,2'-dideoxy-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)-6'-acetylthio- $\beta$ -D-gentiobioside (**61**).

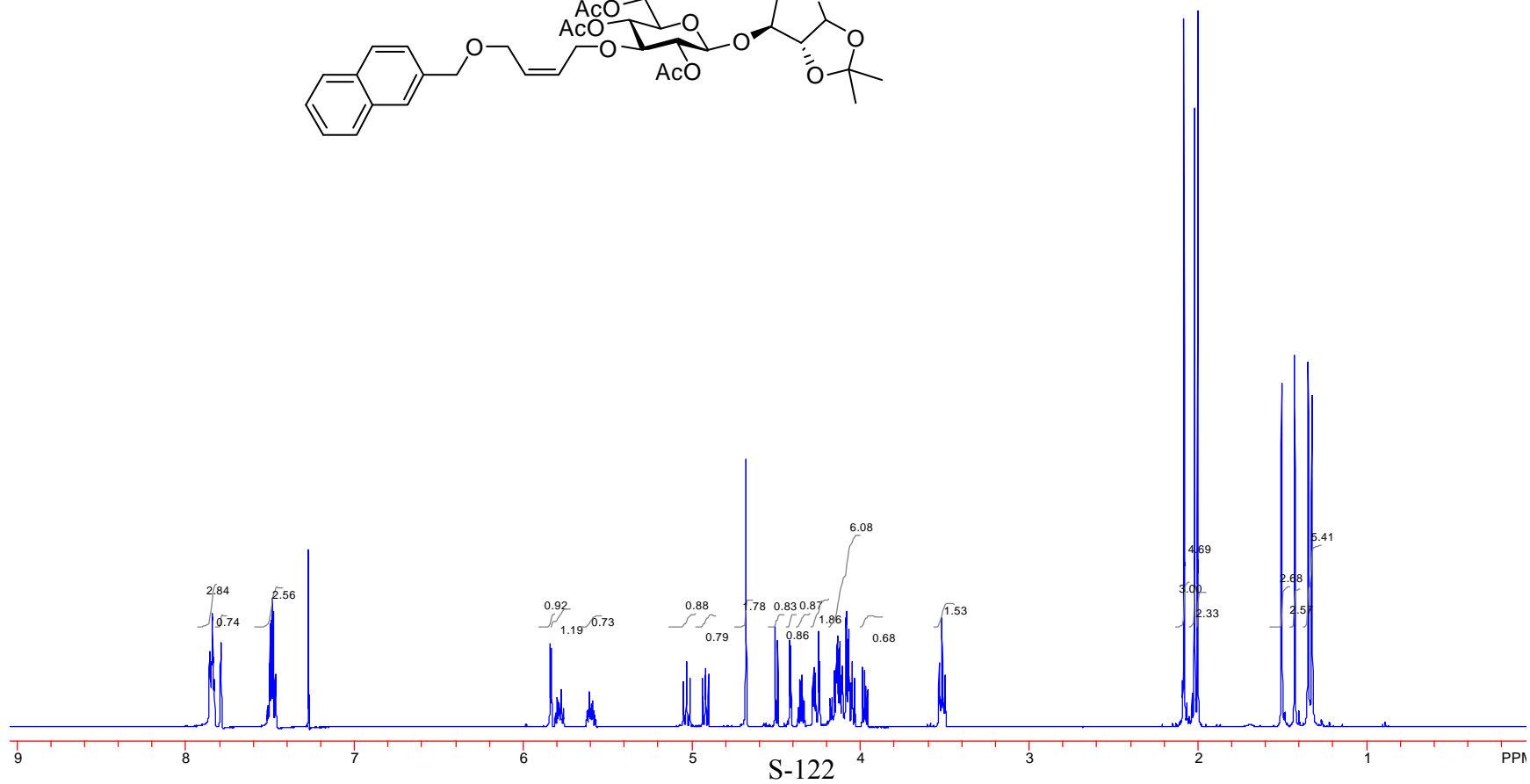
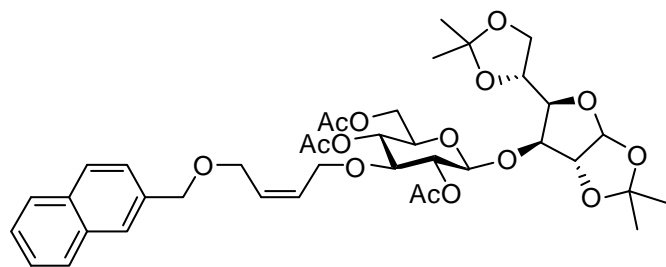




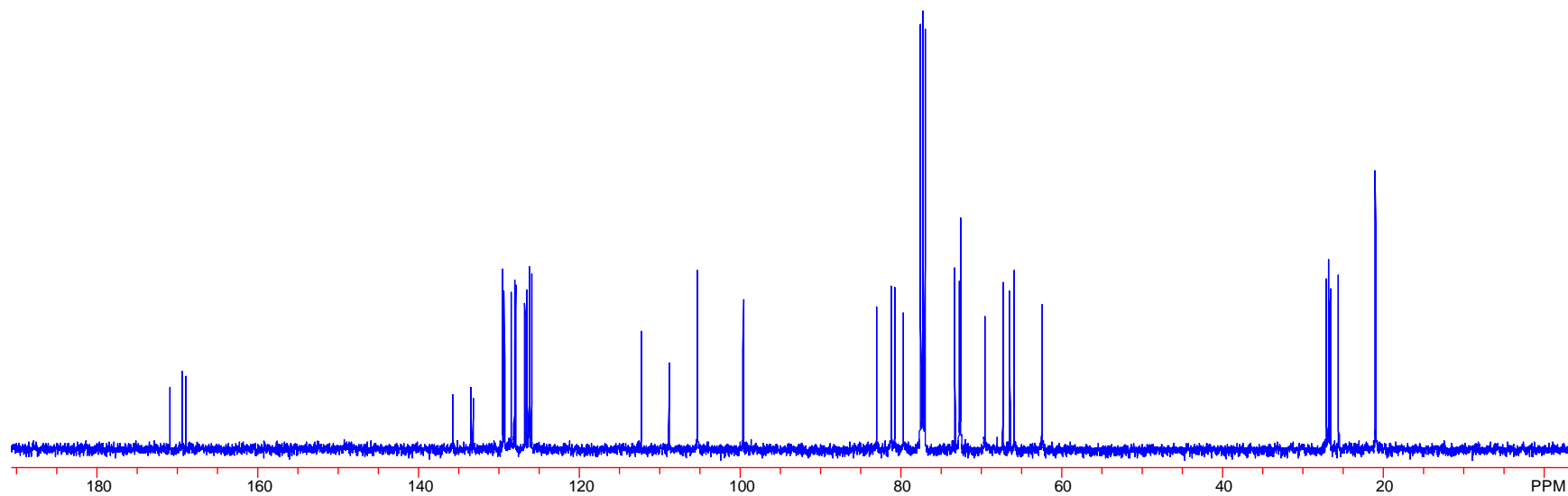
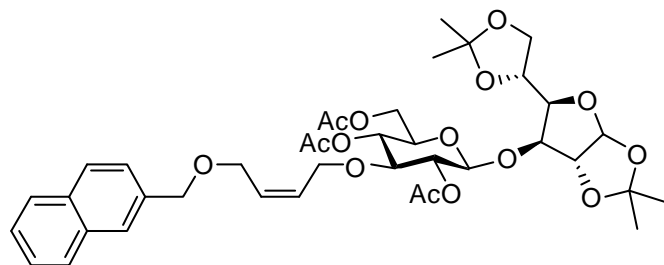
$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 100 MHz) Methyl 2,2'-dideoxy-2,2'-bis(2,2,2-trichloroethoxycarbonylamino)-6'-acetylthio- $\beta$ -D-gentiobioside (61).



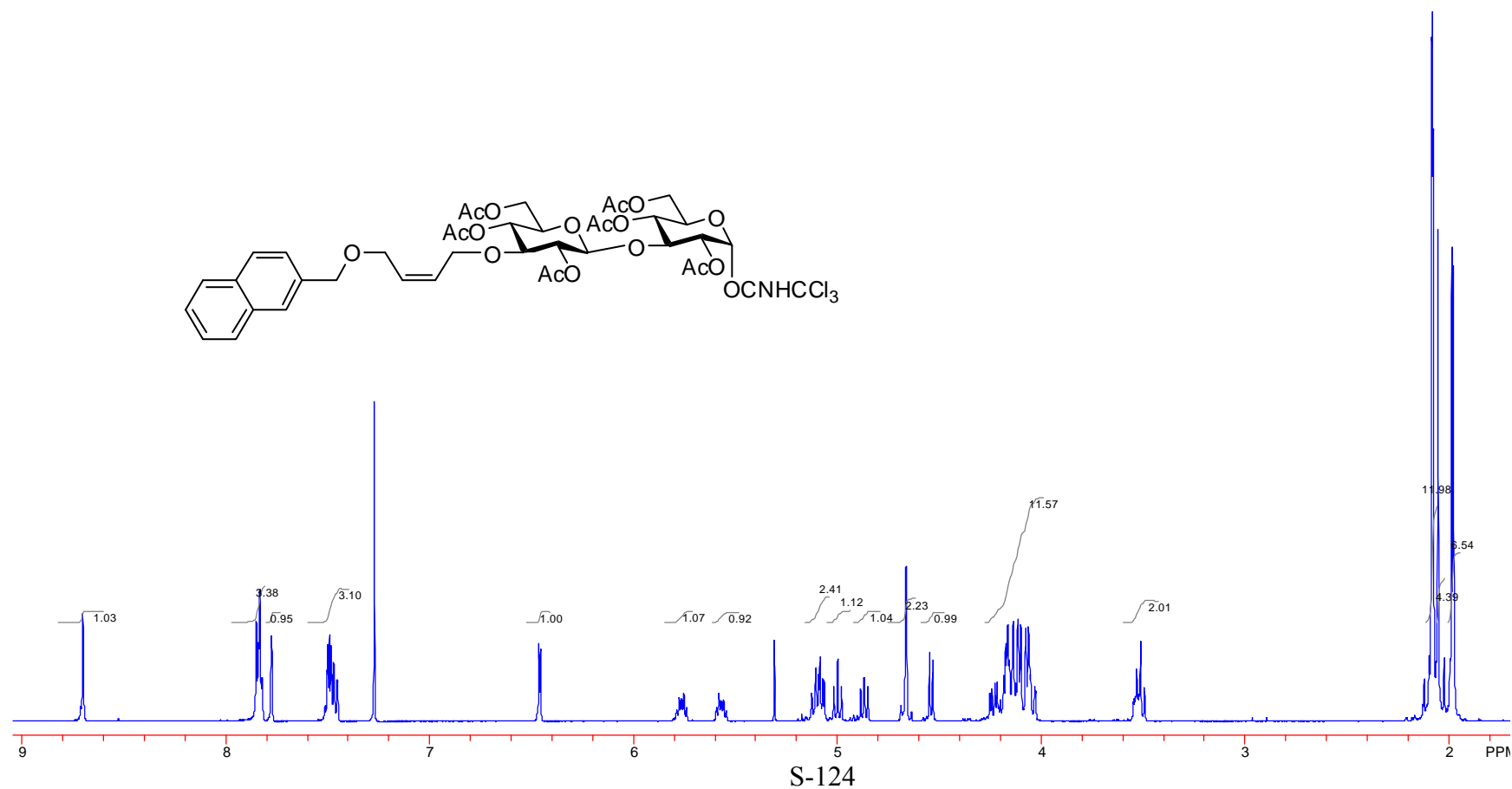
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) 3-*O*-{2,4,6-Tri-*O*-acetyl-3-*O*-[4-(2-naphthylmethoxy)but-2-*Z*-enyl]- $\beta$ -D-glycopyranosyl}-1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-glucofuranose (**87**).



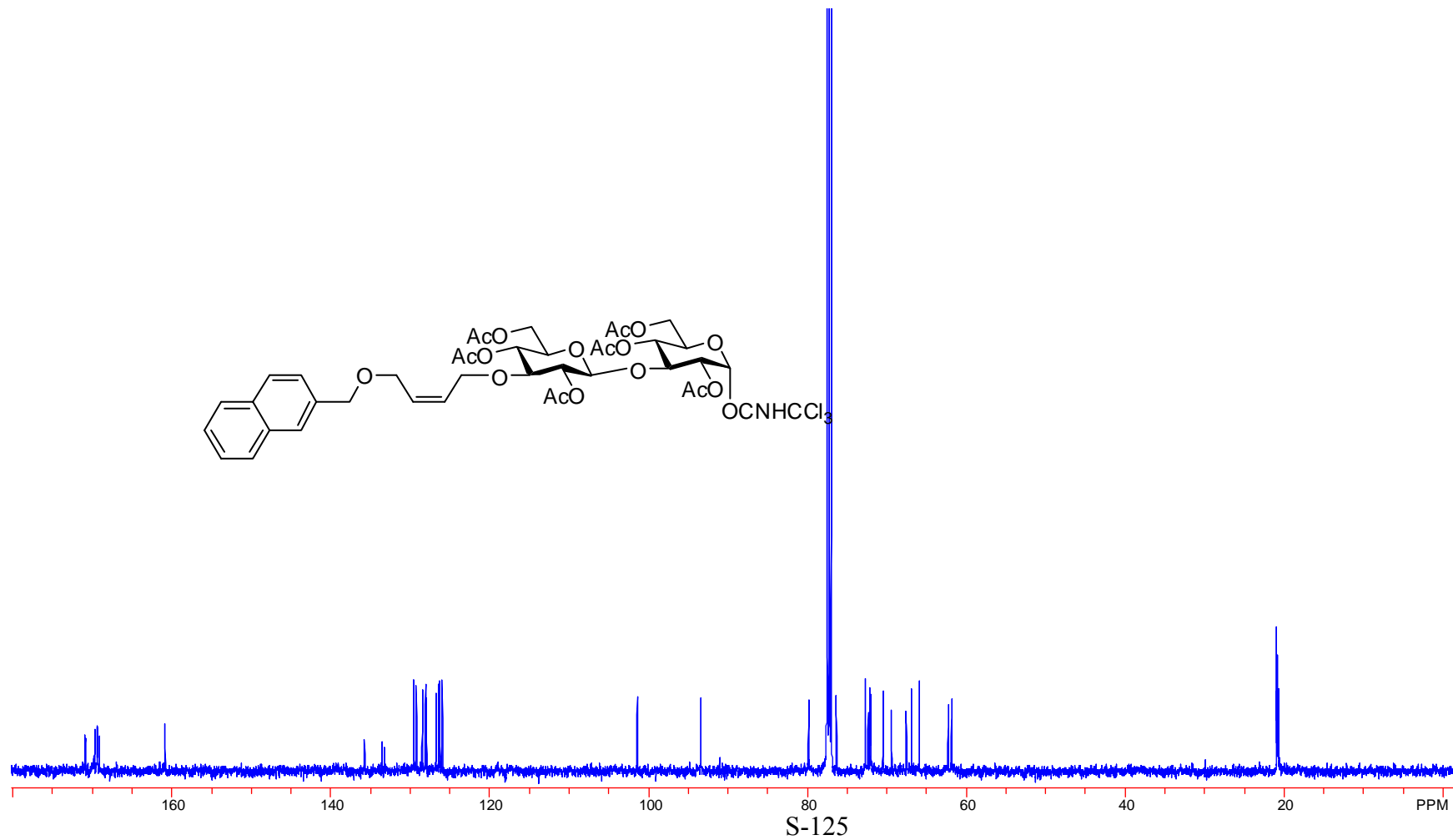
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 3-*O*-{2,4,6-Tri-*O*-acetyl-3-*O*-[4-(2-naphthylmethoxy)but-2-*Z*-enyl]- $\beta$ -D-glycopyranosyl}-1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-glucofuranose (**87**).



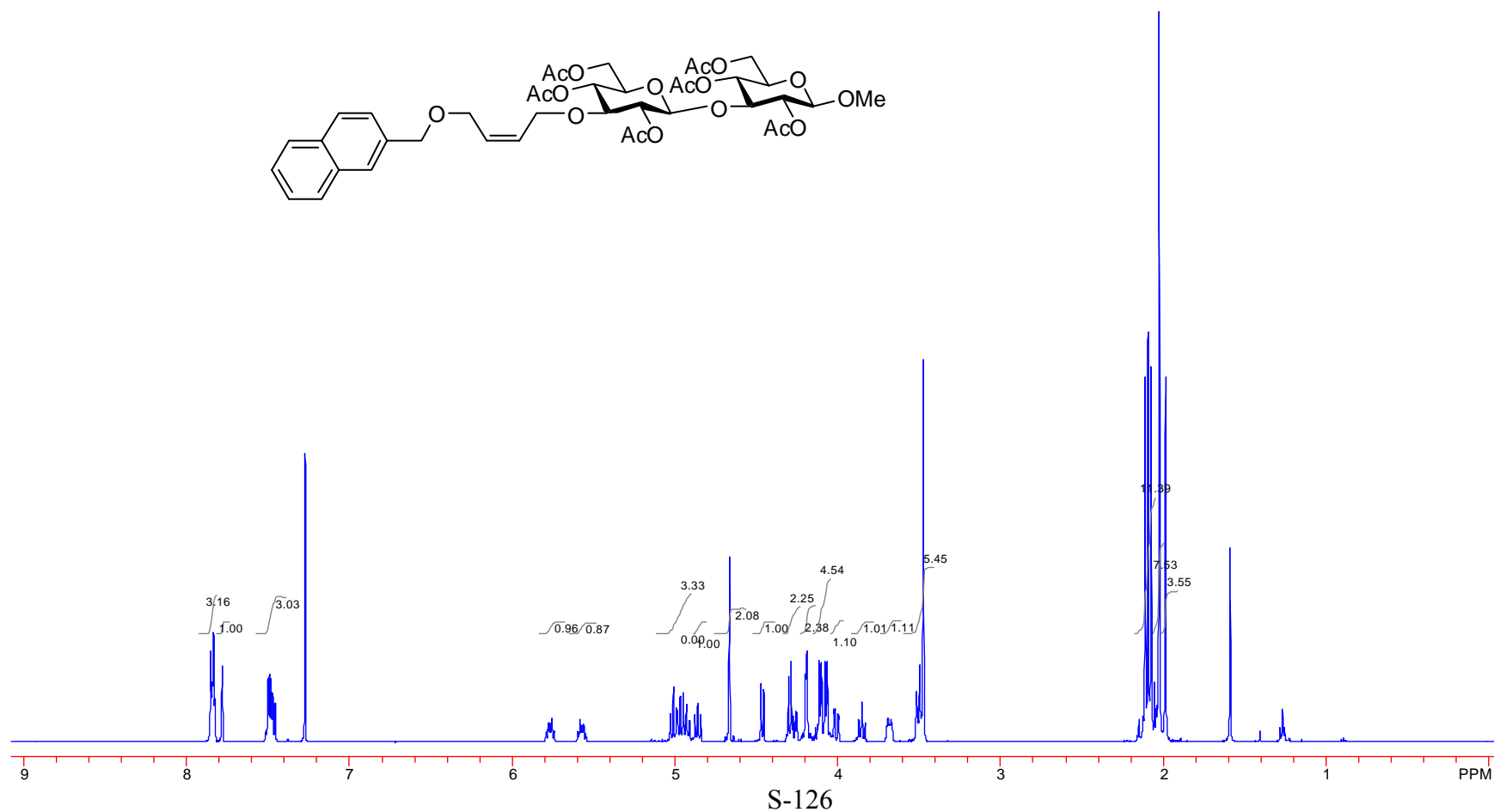
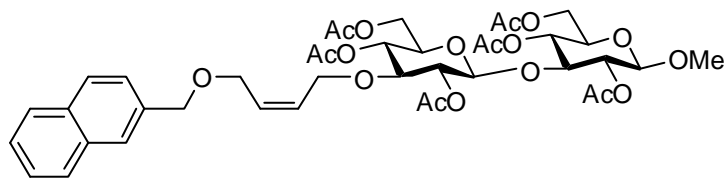
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) 2,2',4,4',6,6'-Hexa-*O*-acetyl-3'-*O*-[4-(2-naphthylmethoxy)but-2-*Z*-enyl]- $\alpha$ -D-lamaribiosyl trichloroacetimidate (**89**).



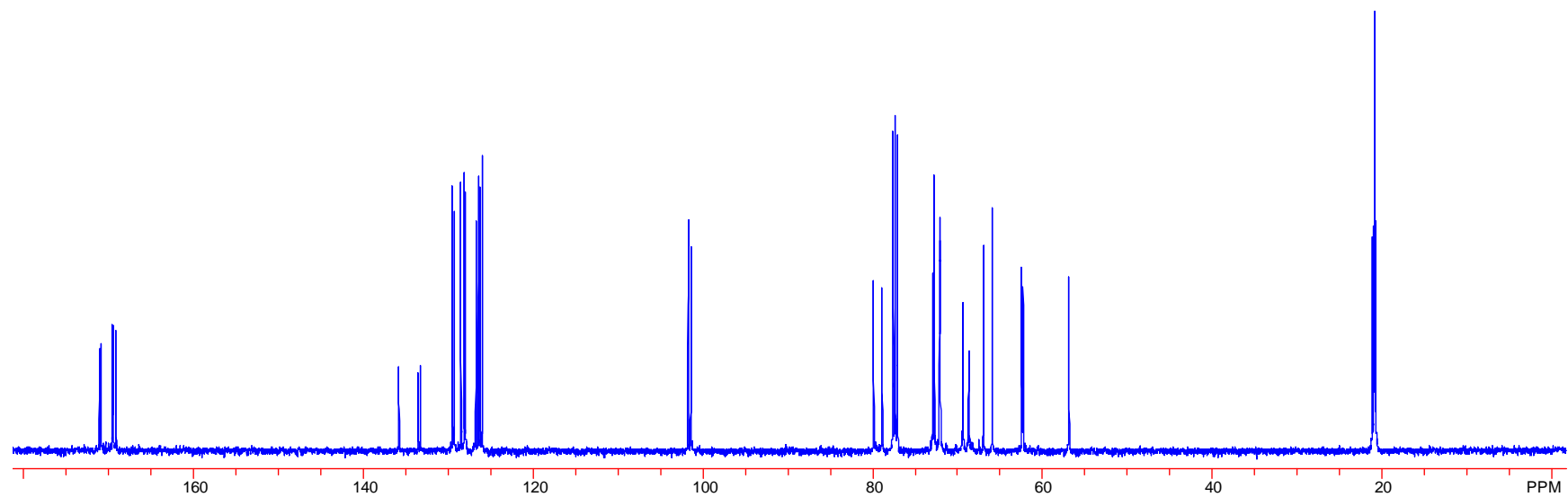
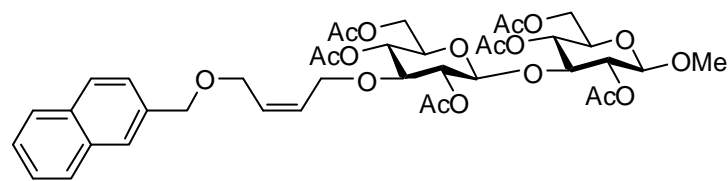
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 2,2',4,4',6,6'-Hexa-*O*-acetyl-3'-*O*-[4-(2-naphthylmethoxy)but-2-*Z*-enyl]- $\alpha$ -D-laminaribiosyl trichloroacetimidate (**89**).



<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 500 MHz) Methyl 2,2',4,4',6,6'-hexa-*O*-acetyl-3'-*O*-[4-(2-naphthylmethoxy)but-2*Z*-enyl]-β-D-laminaribioside (90).

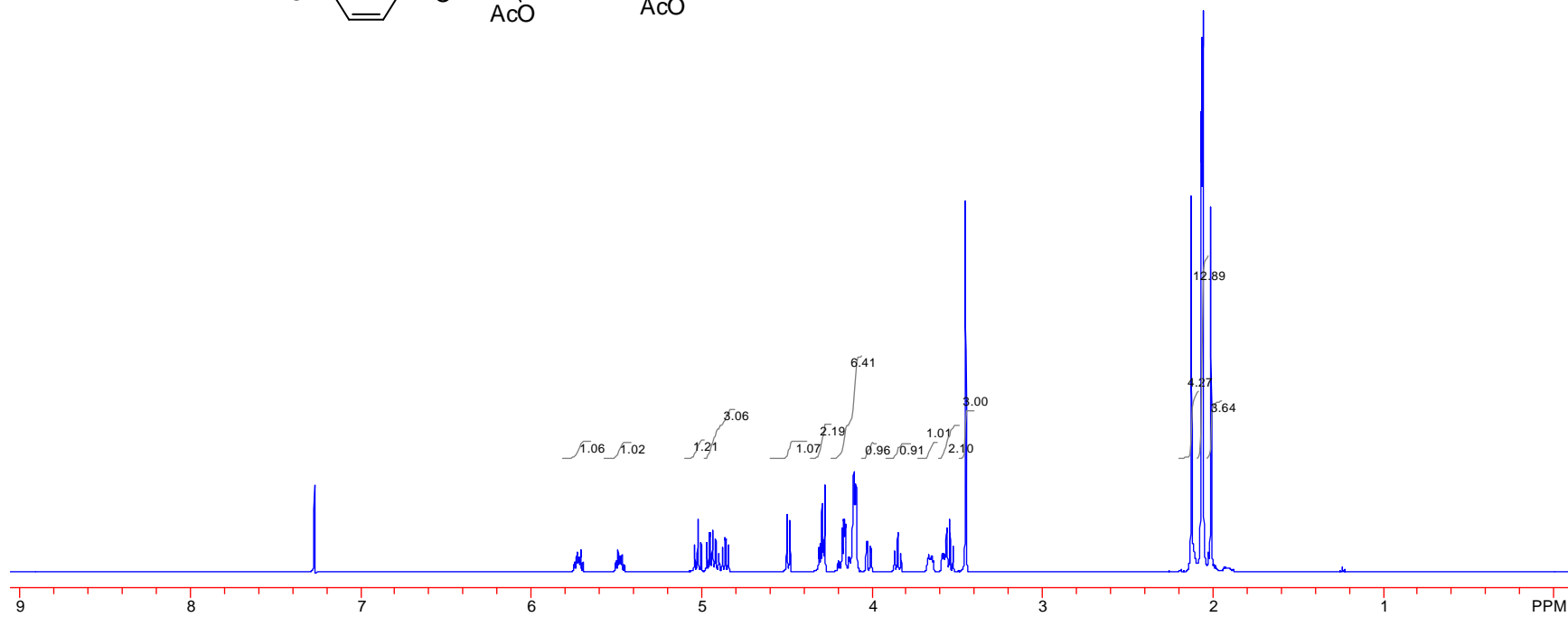
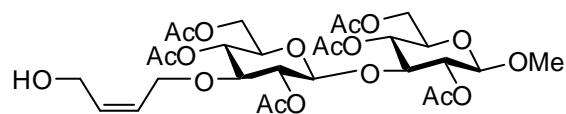


$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) Methyl 2,2',4,4',6,6'-hexa-*O*-acetyl-3'-*O*-[4-(2-naphthylmethoxy)but-2*Z*-enyl]- $\beta$ -D-laminaribioside (90).



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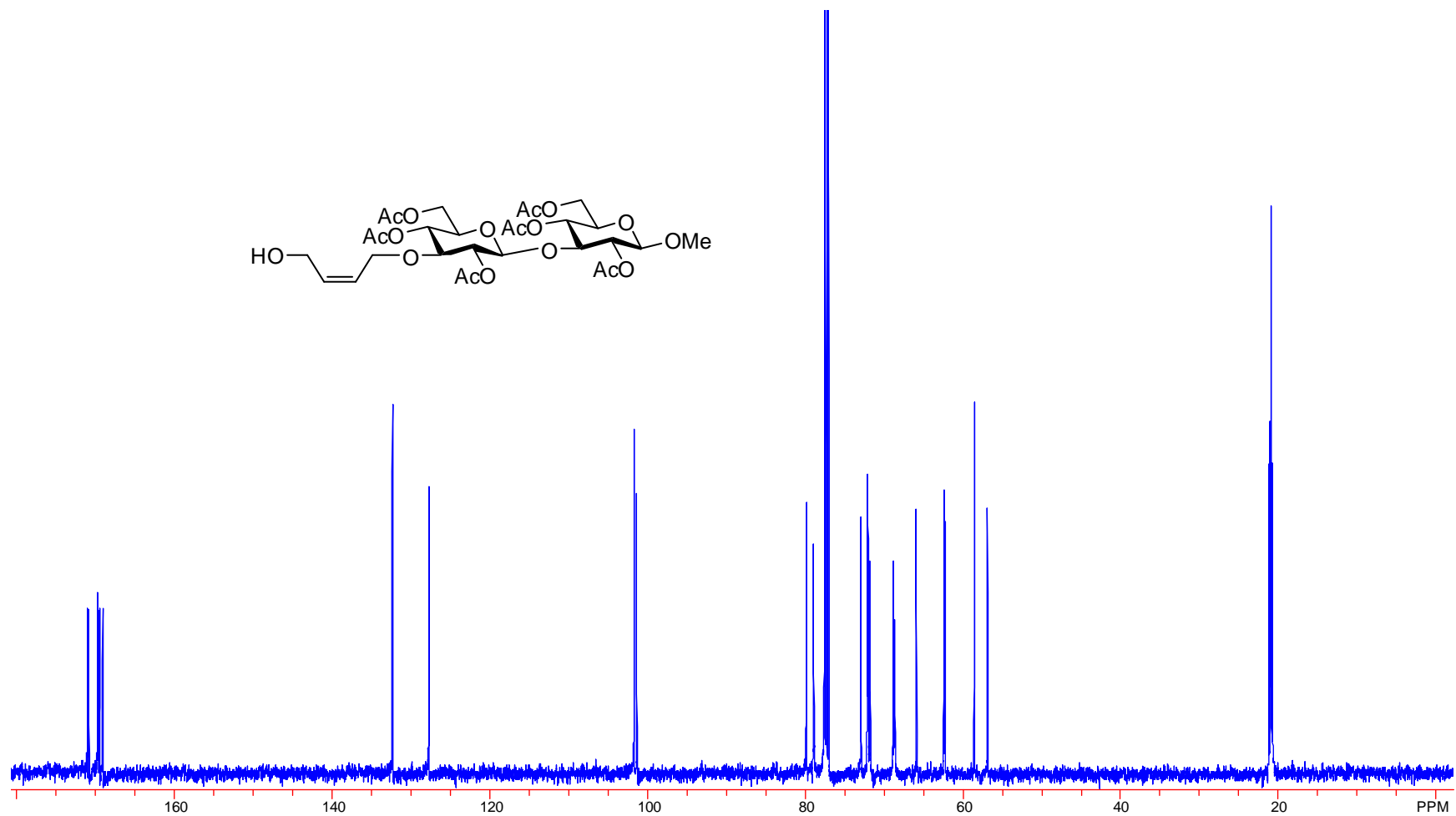
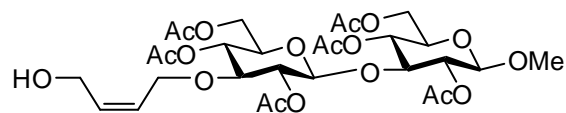
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 500 MHz) Methyl 2,2',4,4',6,6'-hexa-*O*-acetyl-3'-*O*-[4-hydroxybut-2*Z*-enyl]-β-D-laminaribioside (**91**).



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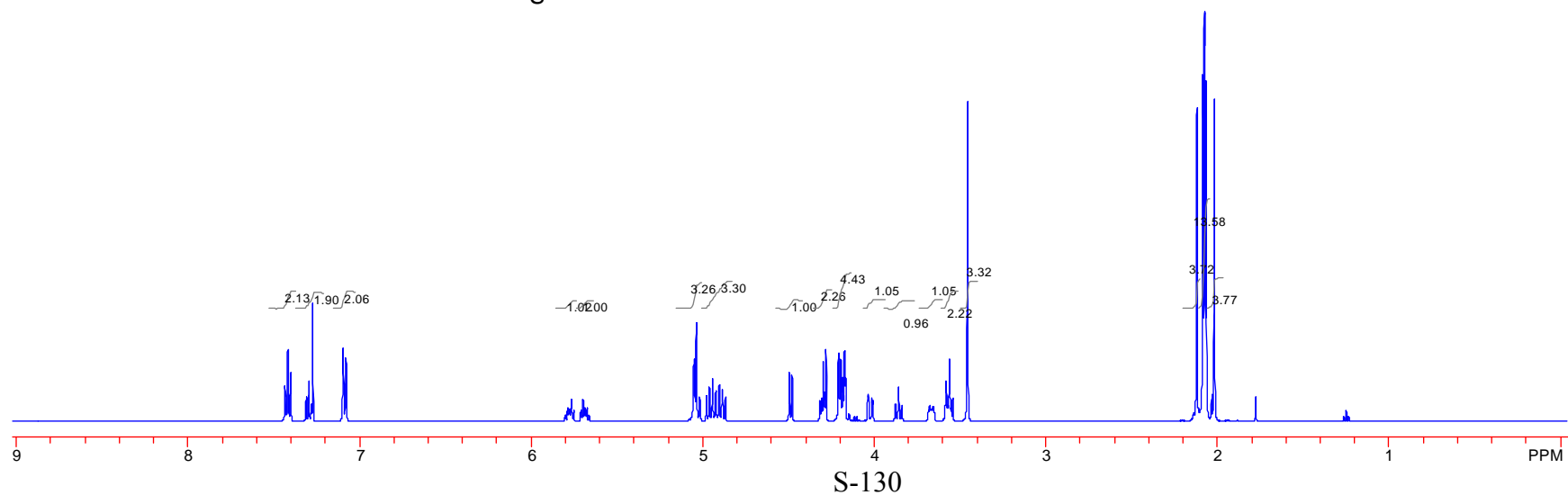
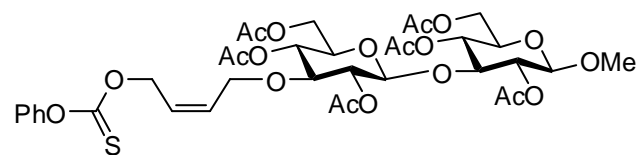


$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) Methyl 2,2',4,4',6,6'-hexa-*O*-acetyl-3'-*O*-[4-hydroxybut-2*Z*-enyl]- $\beta$ -D-laminaribioside (**91**).

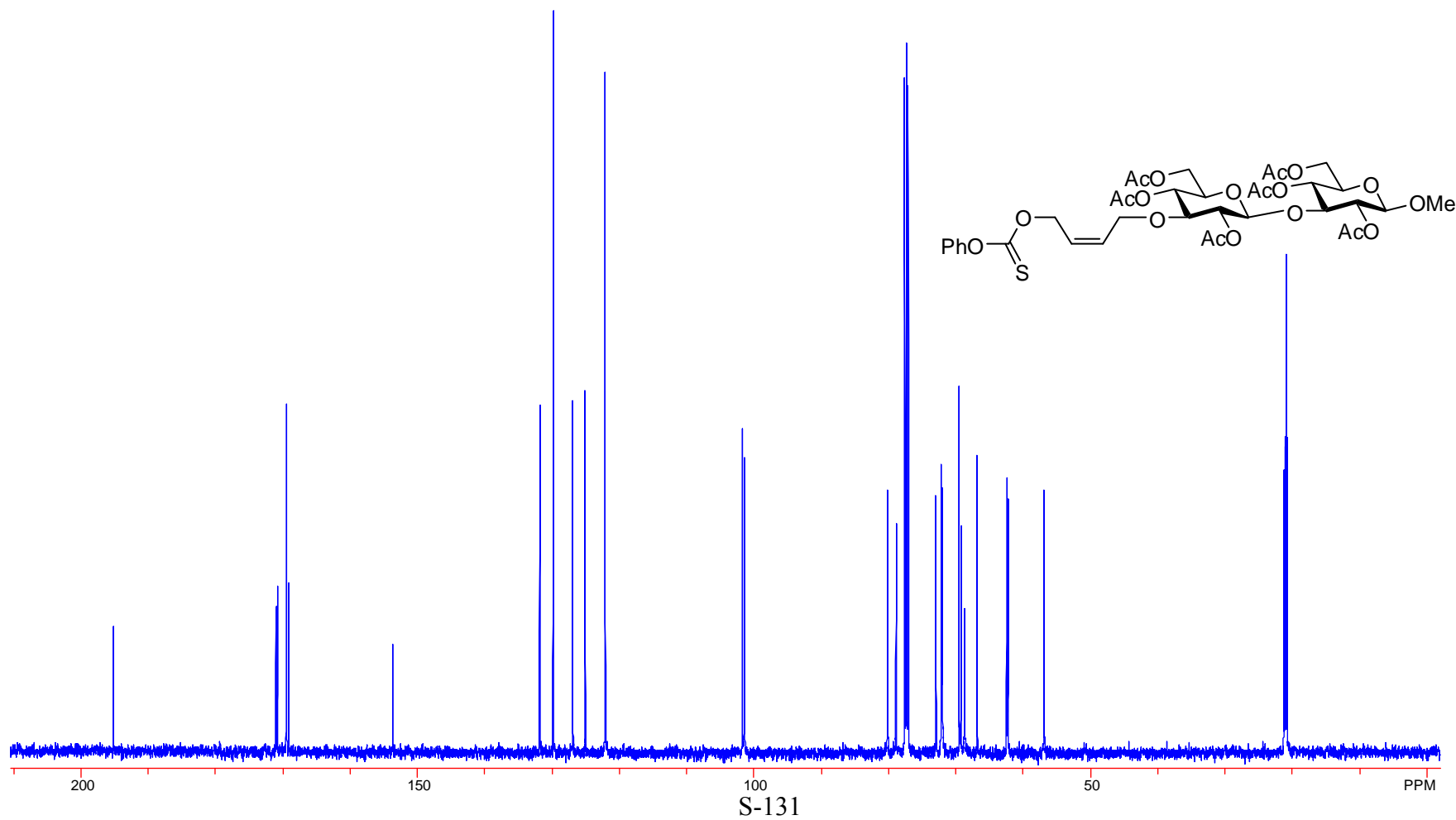


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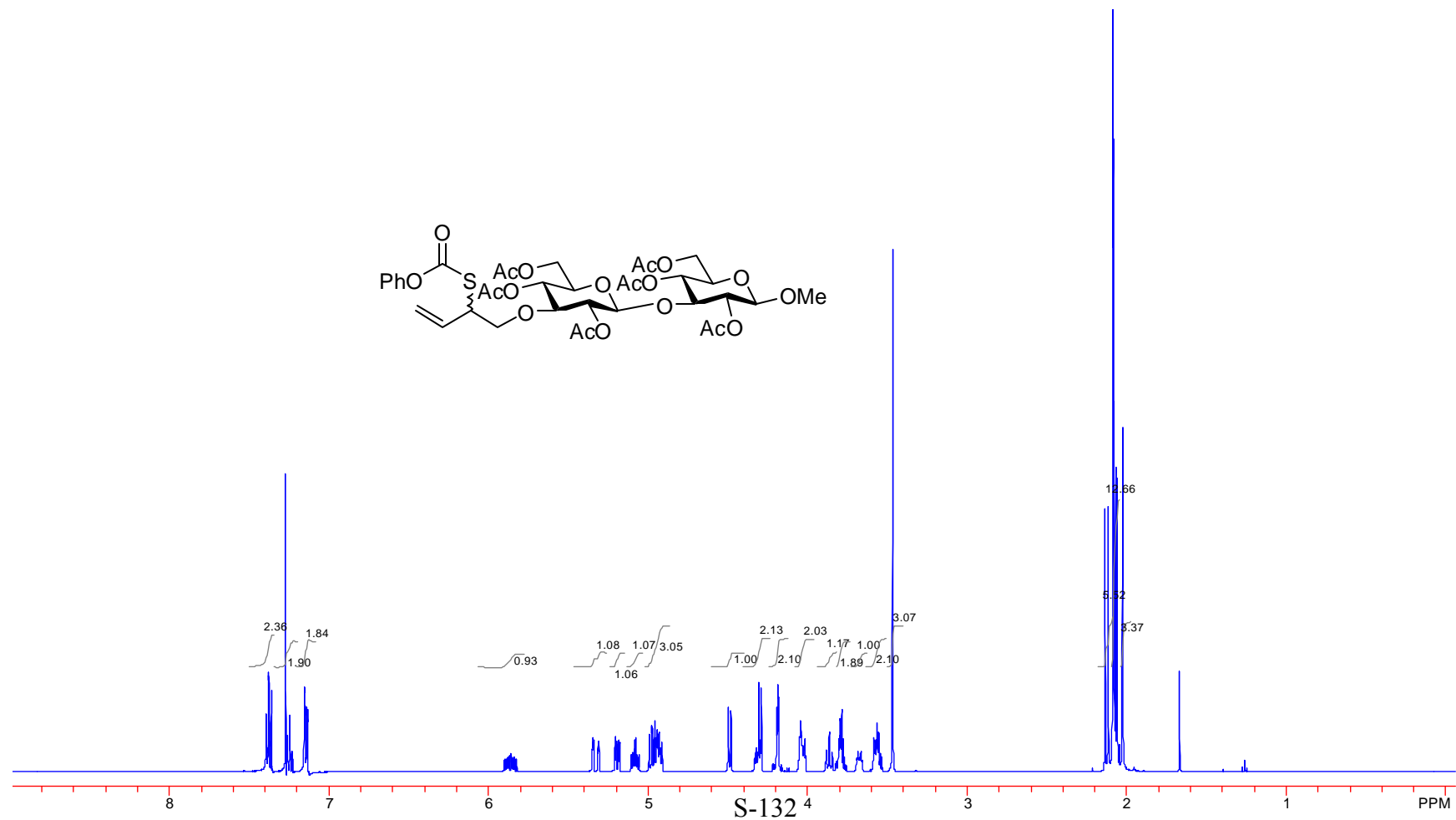
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) Methyl 2,2',4,4',6,6'-hexa-*O*-acetyl-3'-*O*-[4-(phenylthionocarbonyloxy)but-2*Z*-enyl]- $\beta$ -D-laminaribioside (**92**).



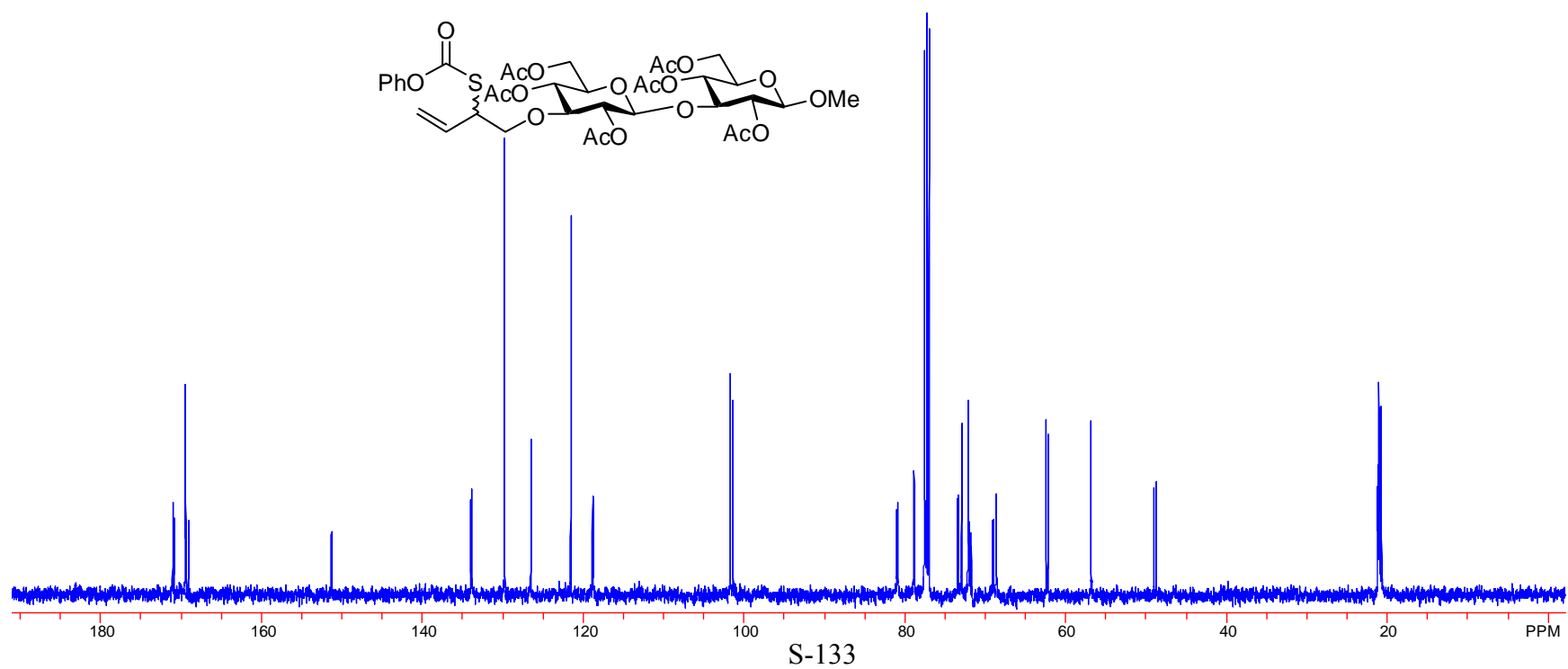
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) Methyl 2,2',4,4',6,6'-hexa-*O*-acetyl-3'-*O*-[4-(phenylthionocarbonyloxy)but-2*Z*-enyl]- $\beta$ -D-laminaribioside (**92**).



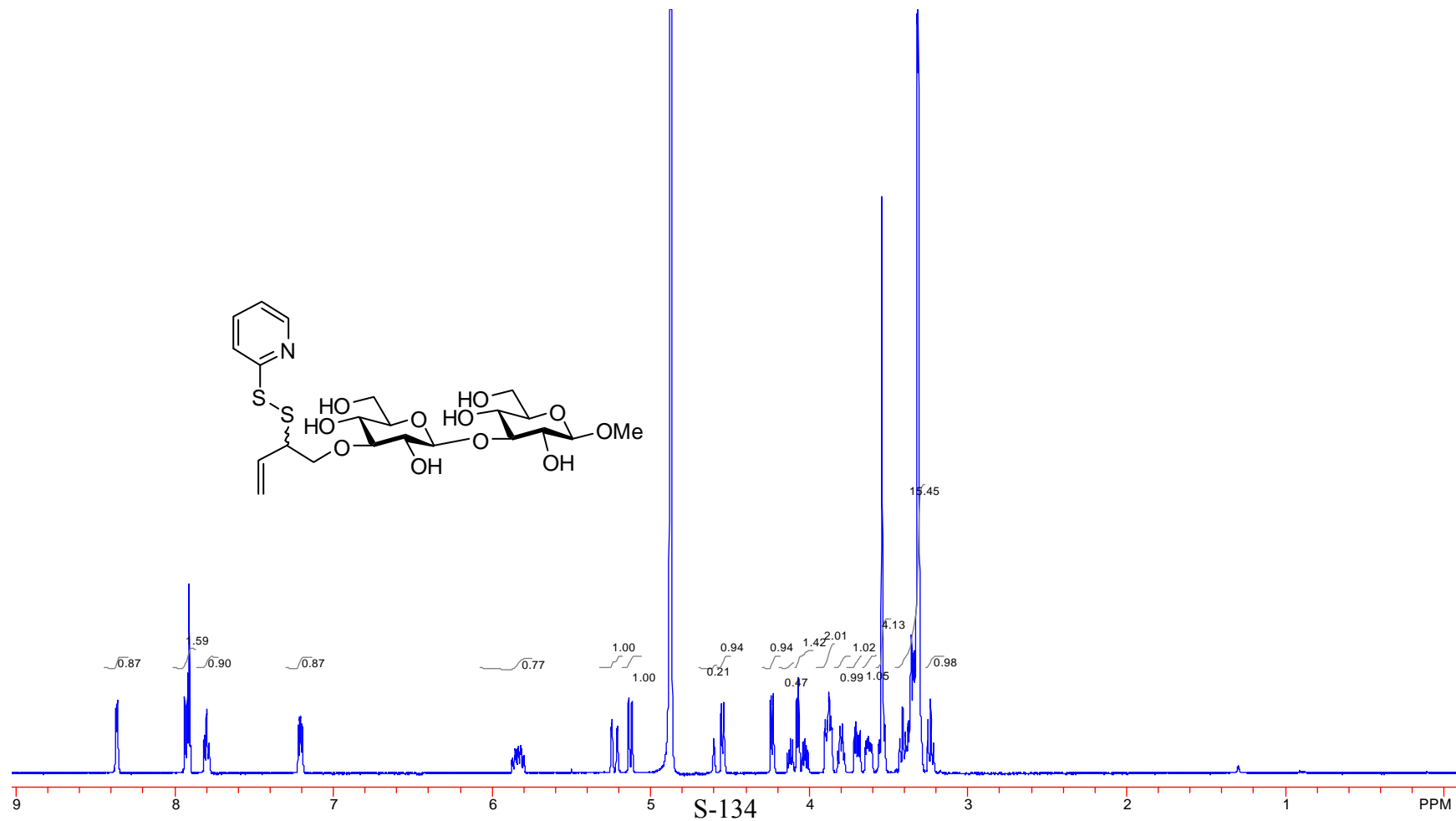
<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 500 MHz) Methyl 2,2',4,4',6,6'-hexa-*O*-acetyl-3'-*O*-[2-phenyloxycarbonylthioxy]but-3-enyl]-β-D-laminaribioside (93).



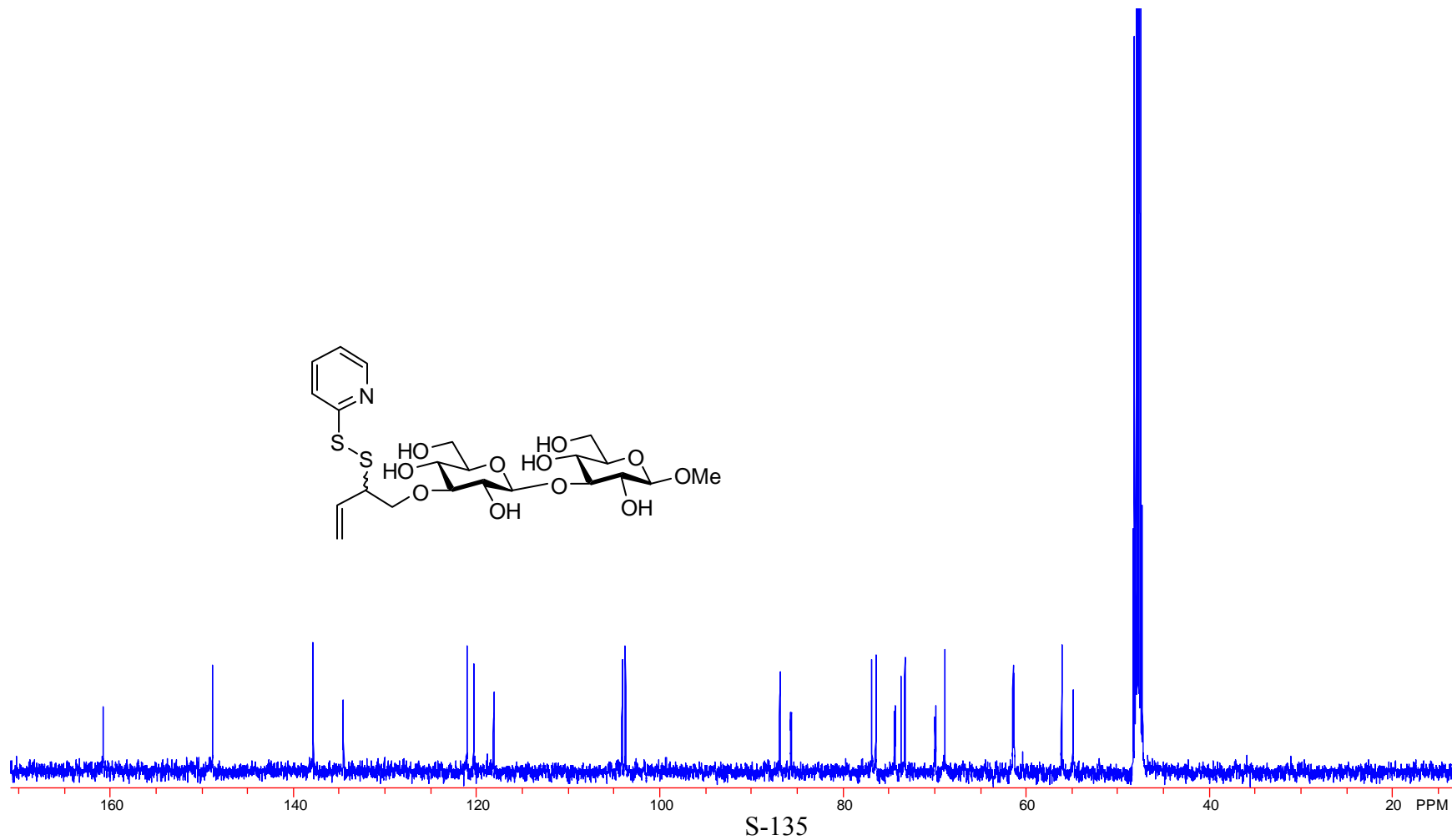
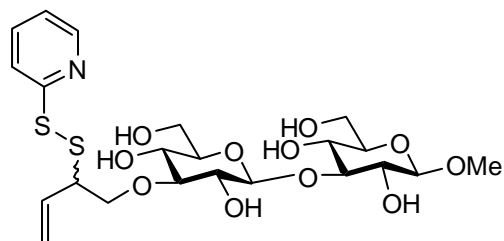
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) Methyl 2,2',4,4',6,6'-hexa-*O*-acetyl-3'-*O*-[2-phenyloxycarbonylthioxy]but-3-enyl]- $\beta$ -D-laminaribioside (93).



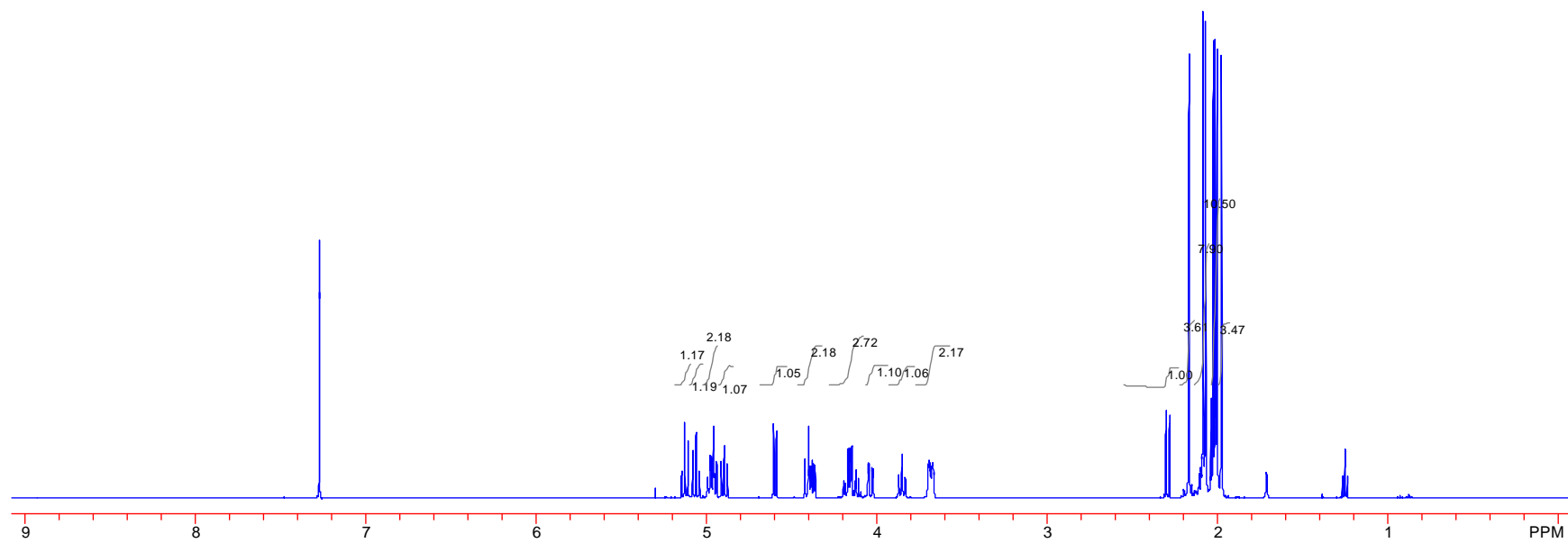
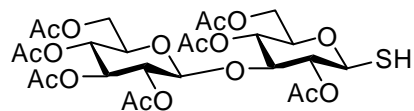
$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 500 MHz) Methyl 3'-*O*-(2-pyridin-2-ylthio)-but-3-enyl- $\beta$ -D-laminaribioside (**63**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) Methyl 3'-*O*-(2-pyridin-2-ylthio)-but-3-enyl- $\beta$ -D-laminaribioside (**63**).



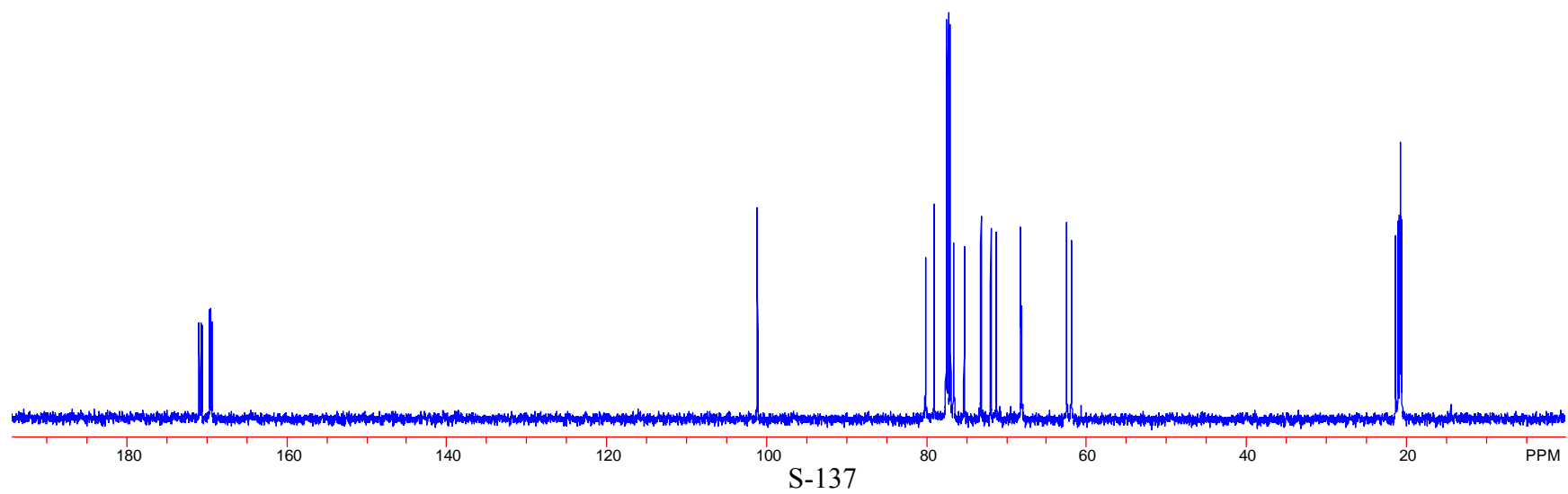
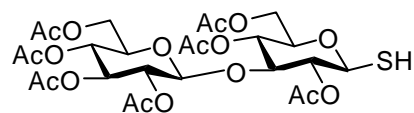
$^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , 500 MHz) 1-Thio-hepta-*O*-acetyl- $\beta$ -D-lamaribiose (**65**).



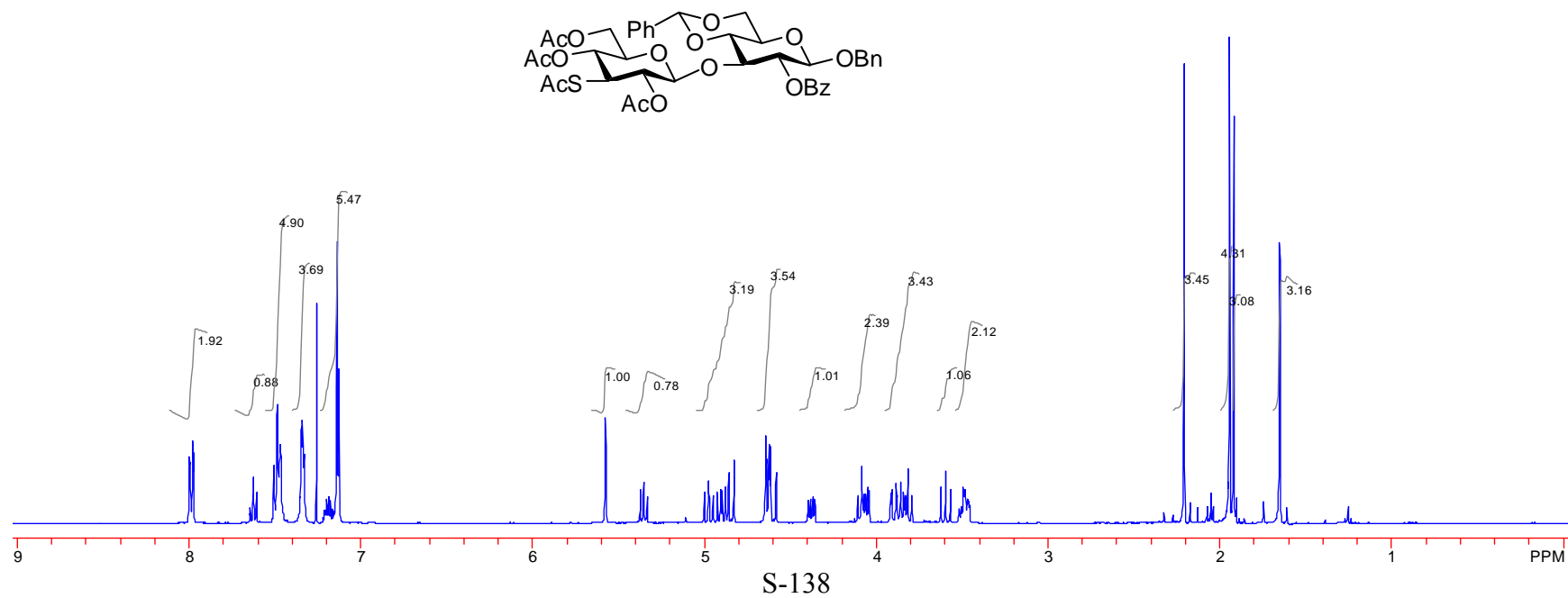
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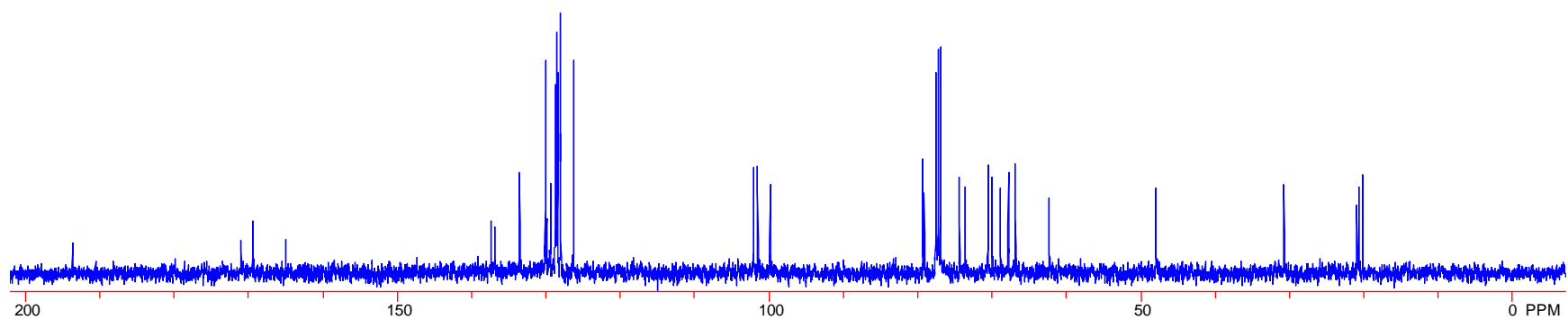
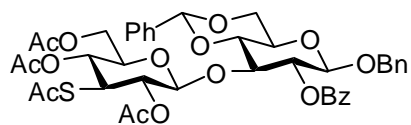
$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) 1-Thio-hepta-*O*-acetyl- $\beta$ -D-laminaribiose (**65**).



<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-2',4',6'-tri-*O*-acetyl-3'-acetylthio-β-D-laminaribioside (**95**).

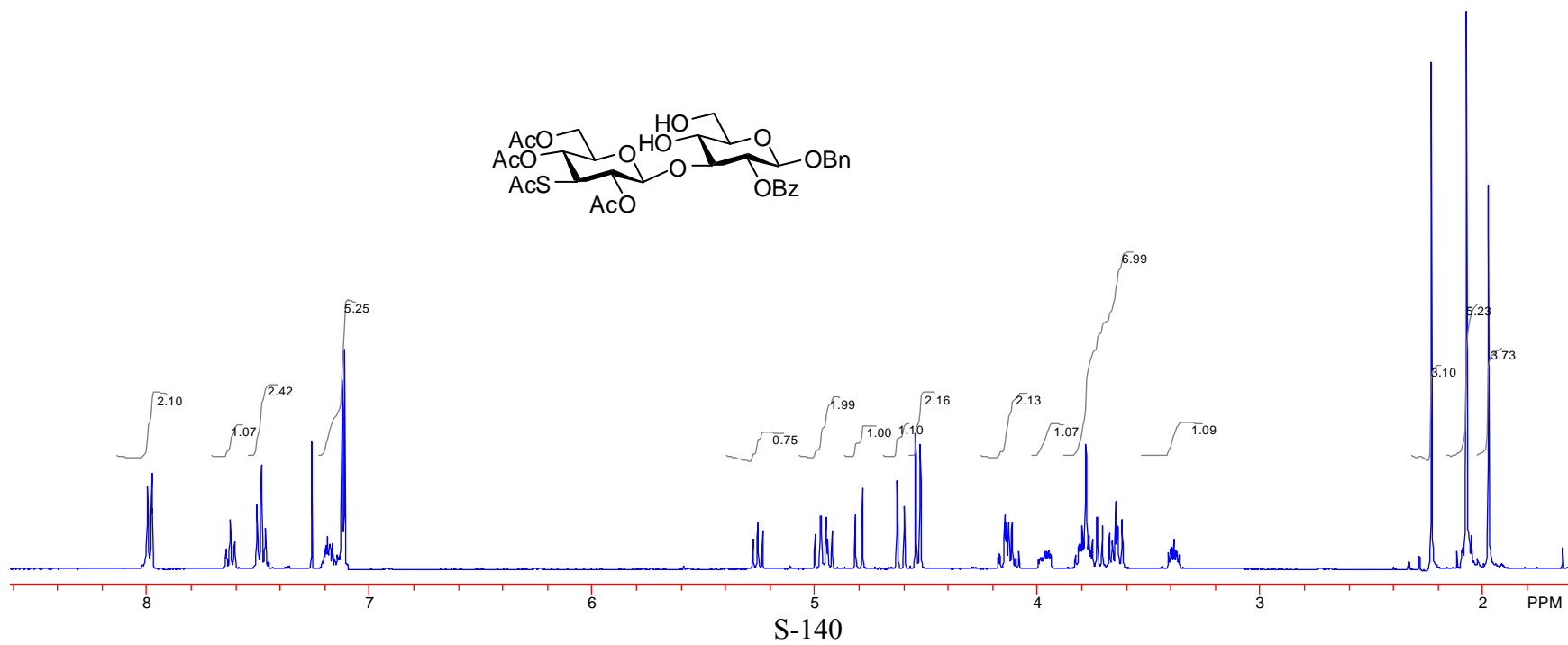


$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-2',4',6'-tri-*O*-acetyl-3'-acetylthio- $\beta$ -D-laminaribioside (**95**).

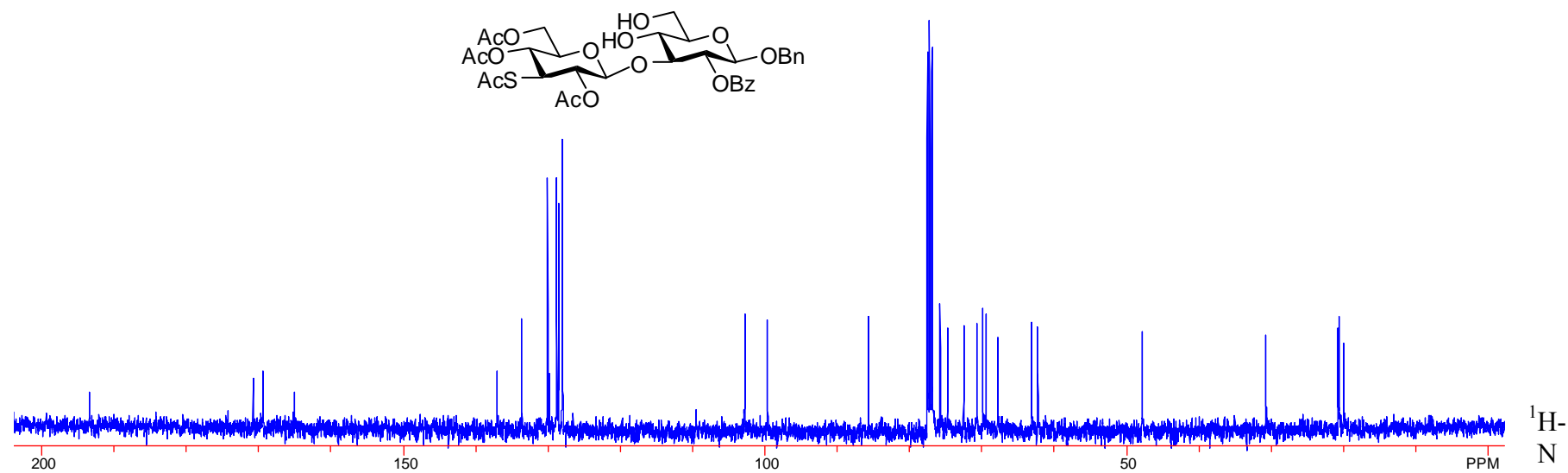


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<sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz) Benzyl 2-*O*-benzoyl-2',4',6'-tri-*O*-acetyl-3'-acetylthio-β-D-laminaribioside (**64**).

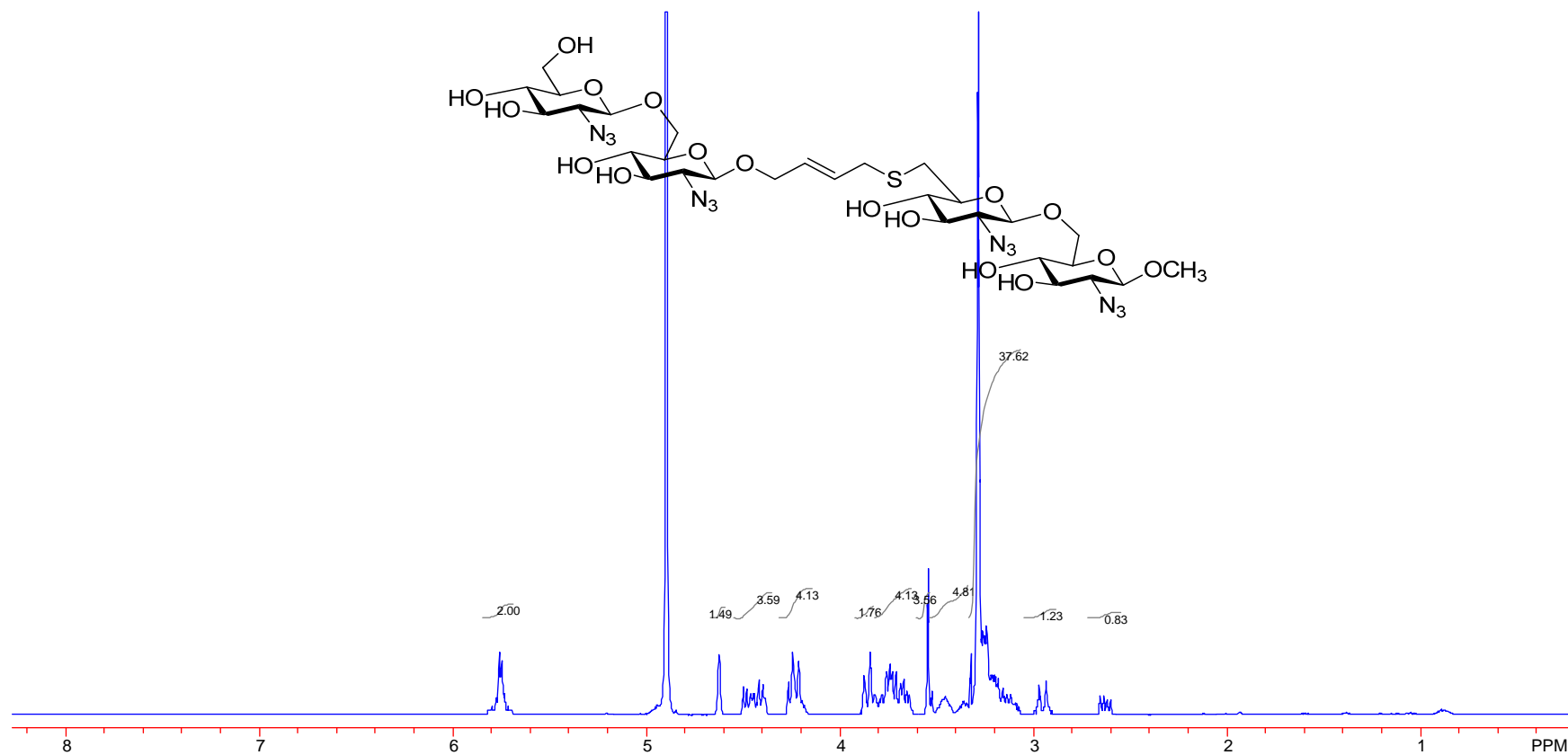


$^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) Benzyl 2-*O*-benzoyl-2',4',6'-tri-*O*-acetyl-3'-acetylthio- $\beta$ -D-laminaribioside (**64**).

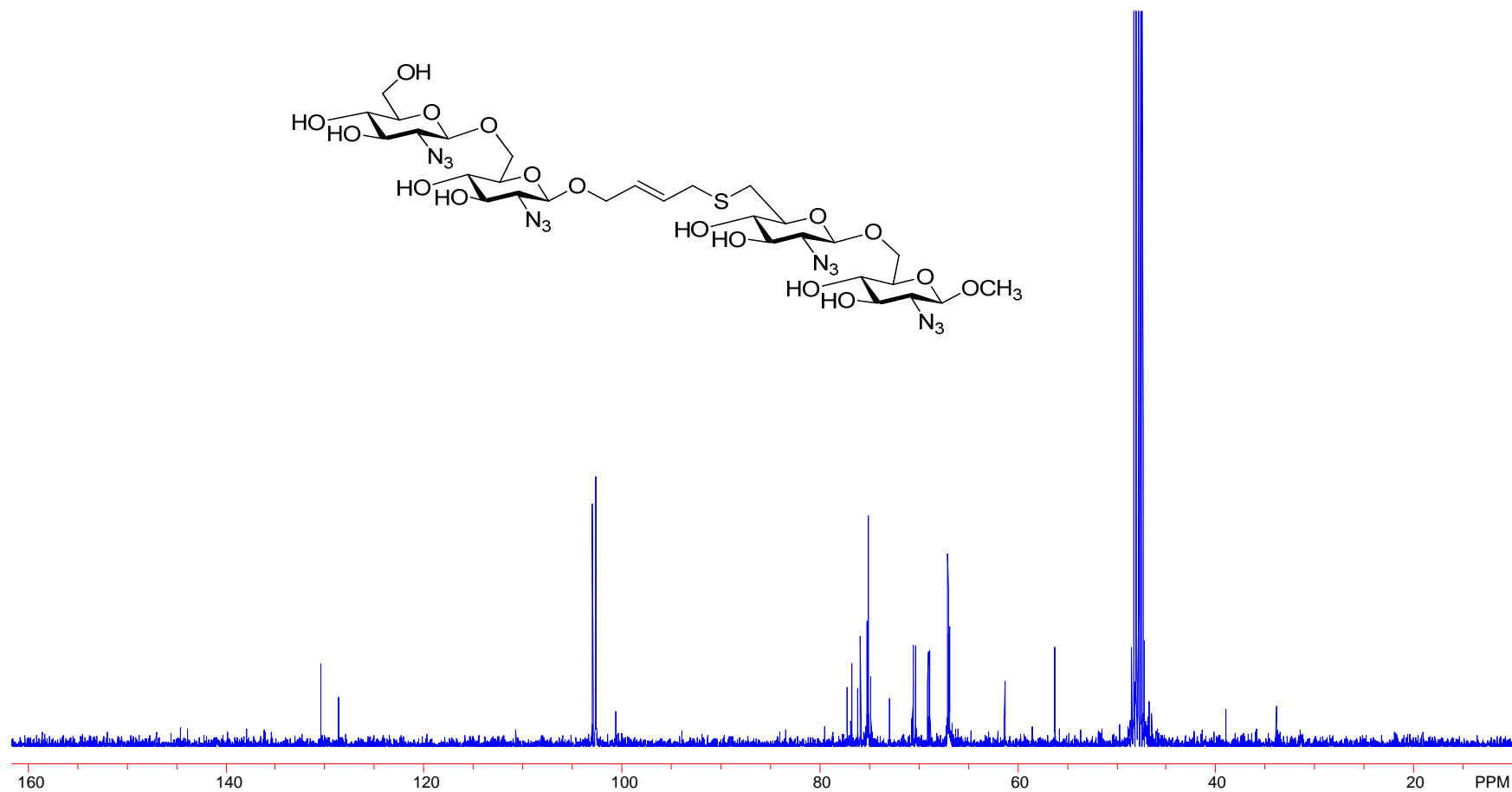


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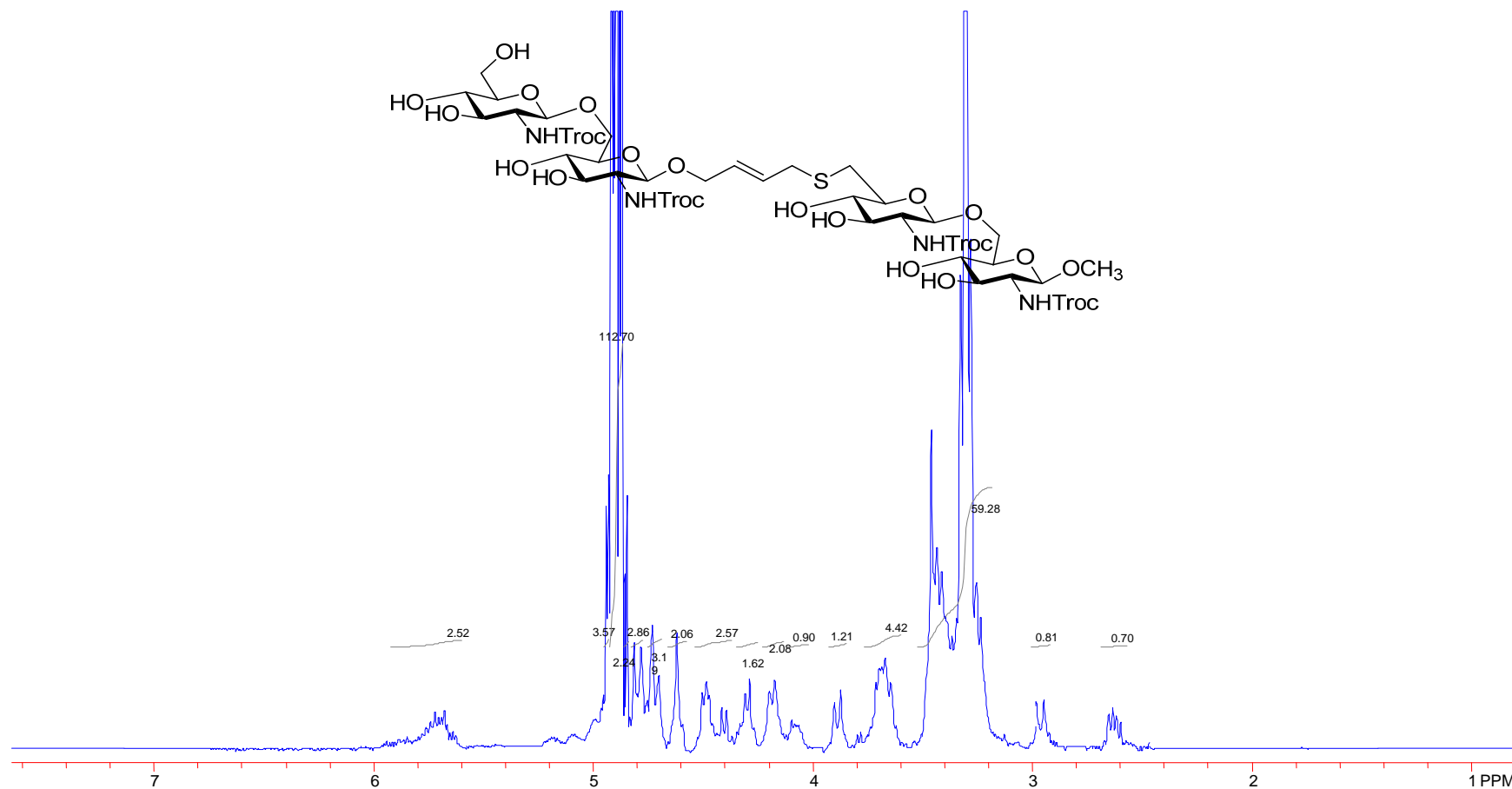
MR spectrum (CD<sub>3</sub>OD, 400 MHz) Methyl 6-[4-*O*-(2,2'-azido-2,2'-dideoxy- $\beta$ -D-gentiobiosyloxy)but-2-*E*-enyl]thio-2,2'-azido-2,2'-dideoxy- $\alpha$ -D-gentiobioside (**66**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 100 MHz) Methyl 6-[4-*O*-(2,2'-azido-2,2'-dideoxy- $\beta$ -D-gentiobiosyloxy)but-2*E*-enyl]thio-2,2'-azido-2,2'-dideoxy- $\alpha$ -D-gentiobioside (**66**).

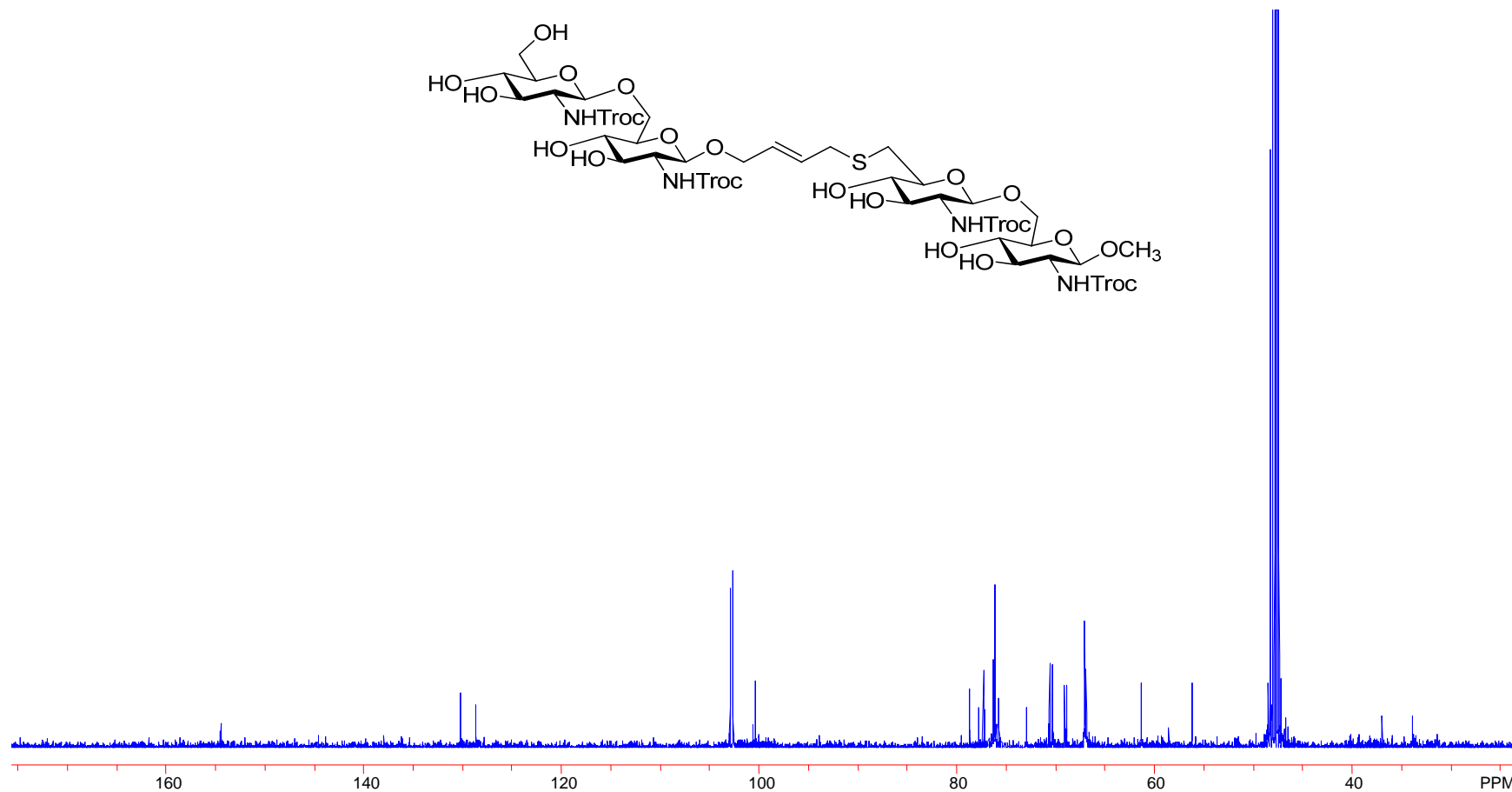


$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 400 MHz) Methyl 6-[4-*O*-(2,2'-dideoxy-2,2'-(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobiosyloxy)but-2*E*-enyl]thio-2,2'-dideoxy-(2,2,2-trichloroethoxycarbonylamino- $\alpha$ -D-gentiobioside (**67**).

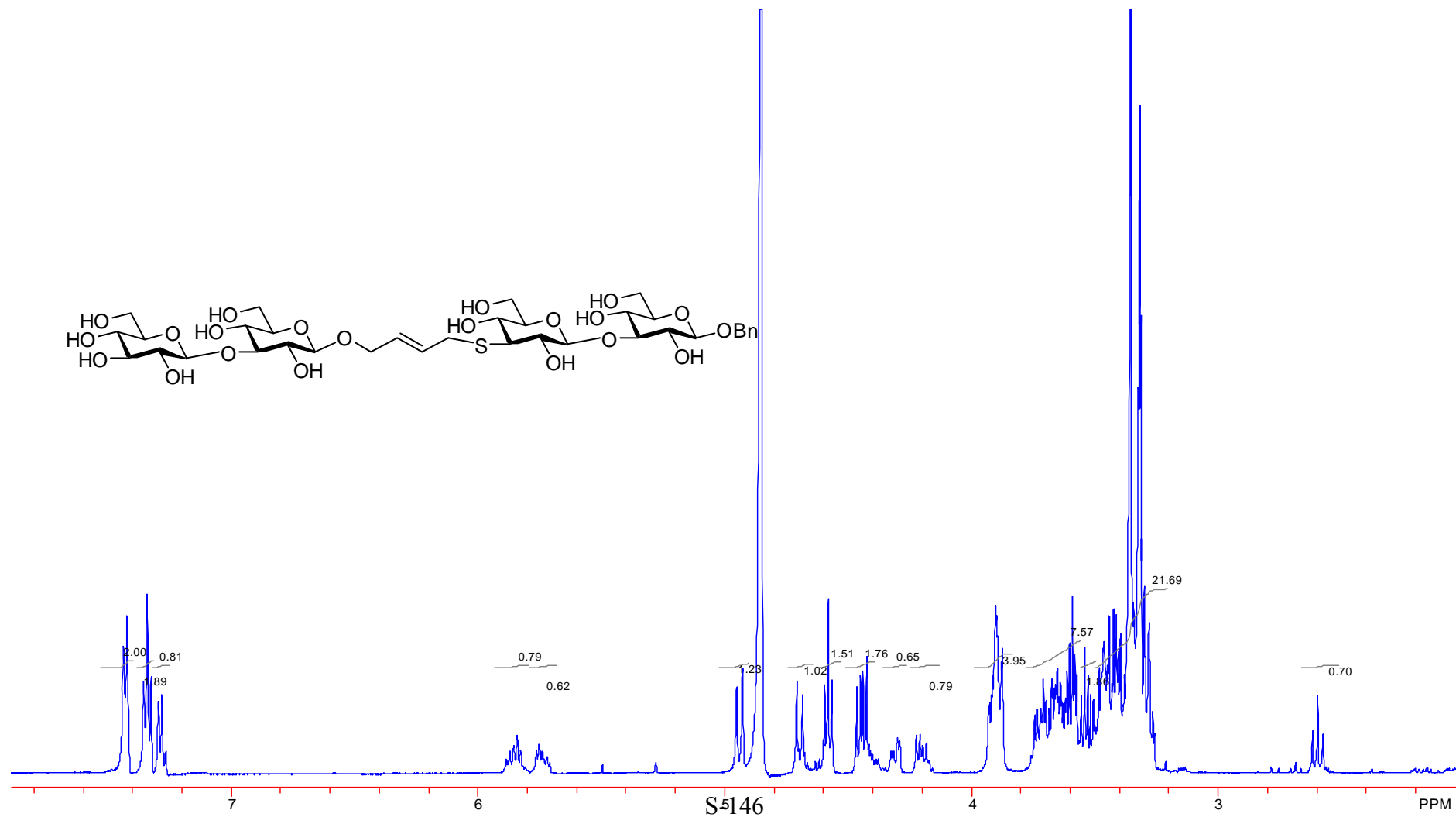




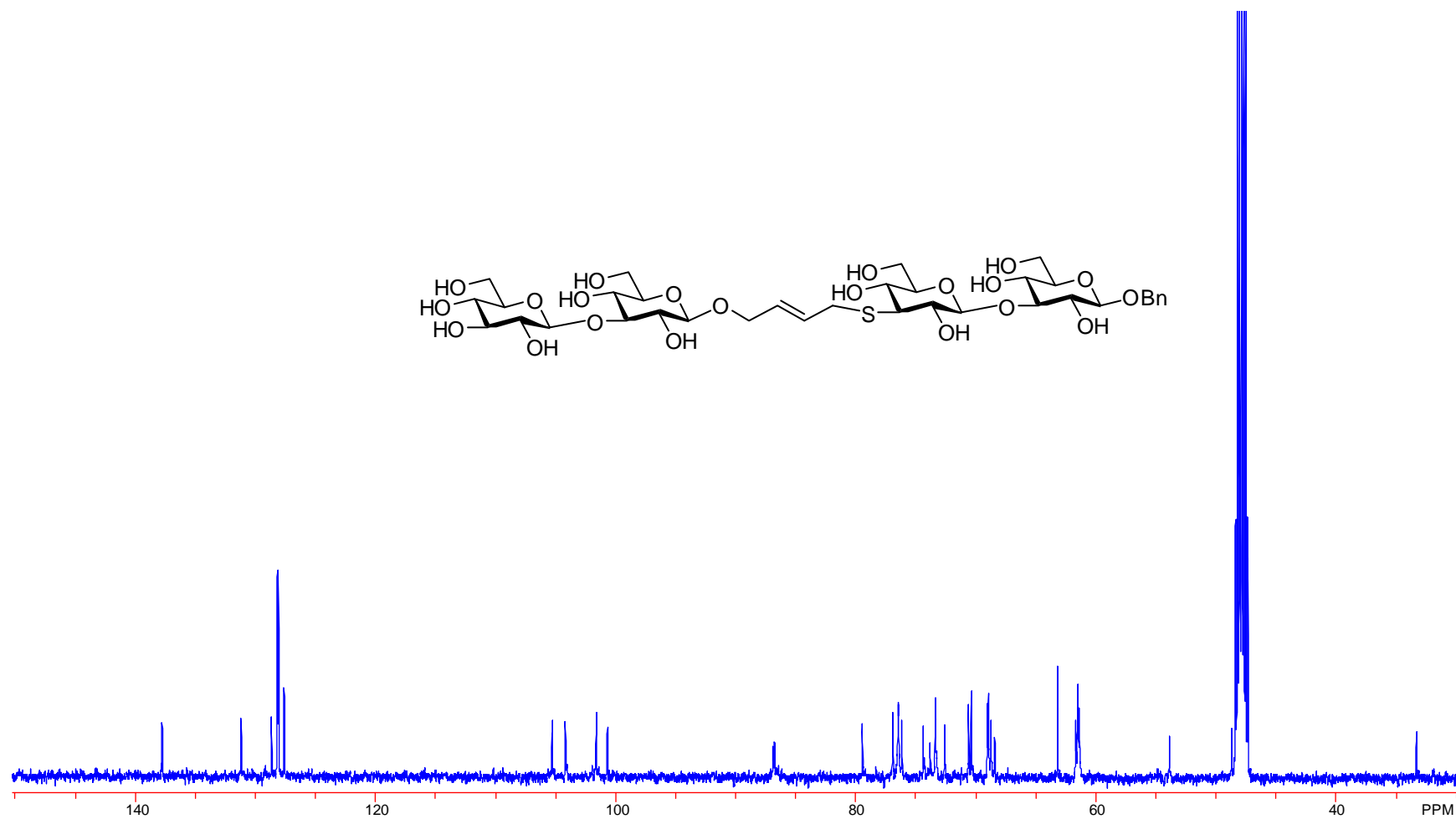
$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 100 MHz) Methyl 6-[4-*O*-(2,2'-dideoxy-2,2'-(2,2,2-trichloroethoxycarbonylamino)- $\beta$ -D-gentiobiosyloxy)but-2*E*-enyl]thio-2,2'-dideoxy-(2,2,2-trichloroethoxycarbonylamino- $\alpha$ -D-gentiobioside (**67**).



$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 500 MHz) Benzyl 3-deoxy-3-[4-( $\beta$ -D-laminaribiosyloxy)but-2-*E*-enylthio]- $\beta$ -D-laminaribioside (**68**).

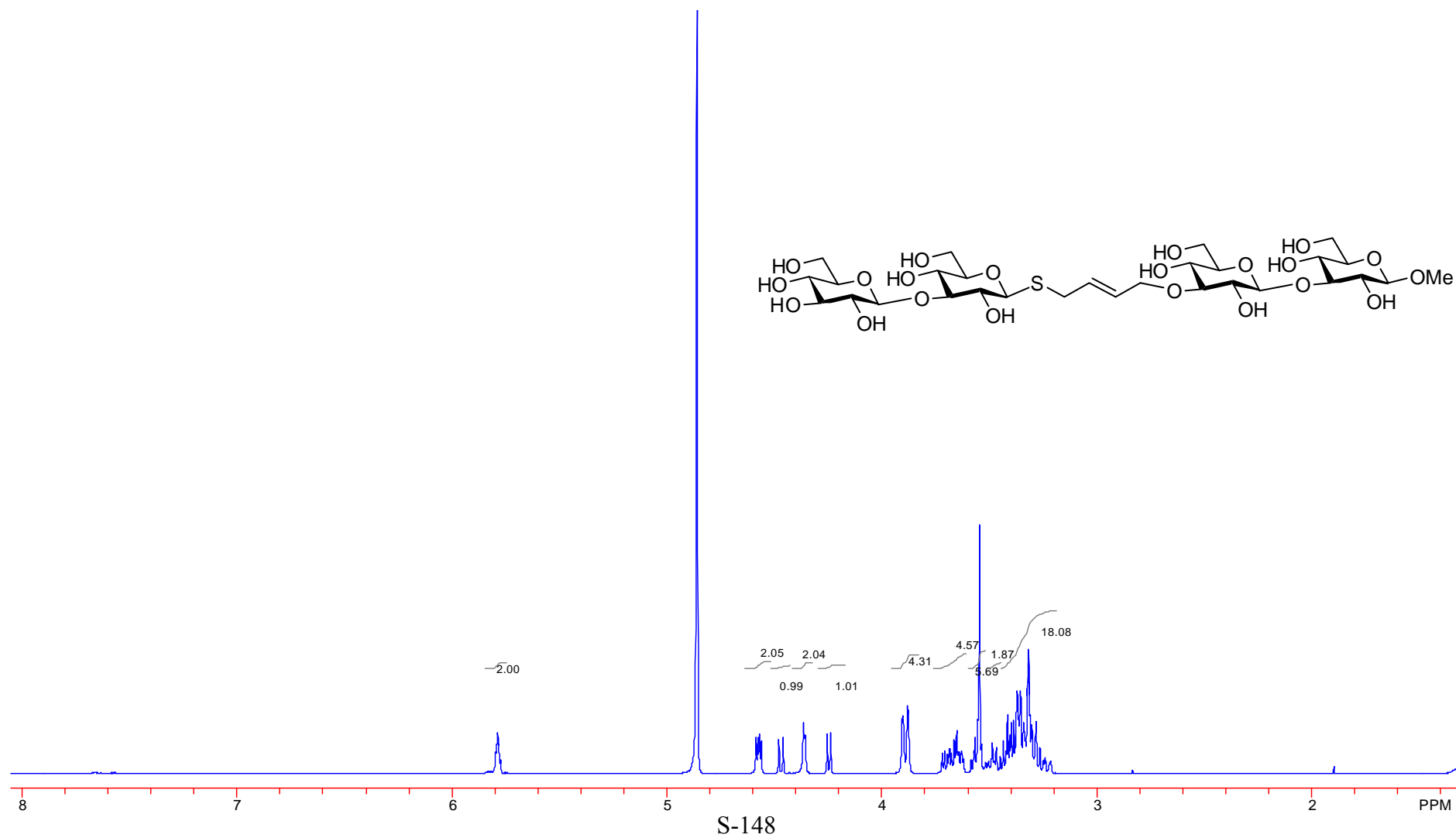


$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) Benzyl 3-deoxy-3-[4-( $\beta$ -D-laminaribiosyloxy)but-2-*E*-enylthio]- $\beta$ -D-laminaribioside (**68**).

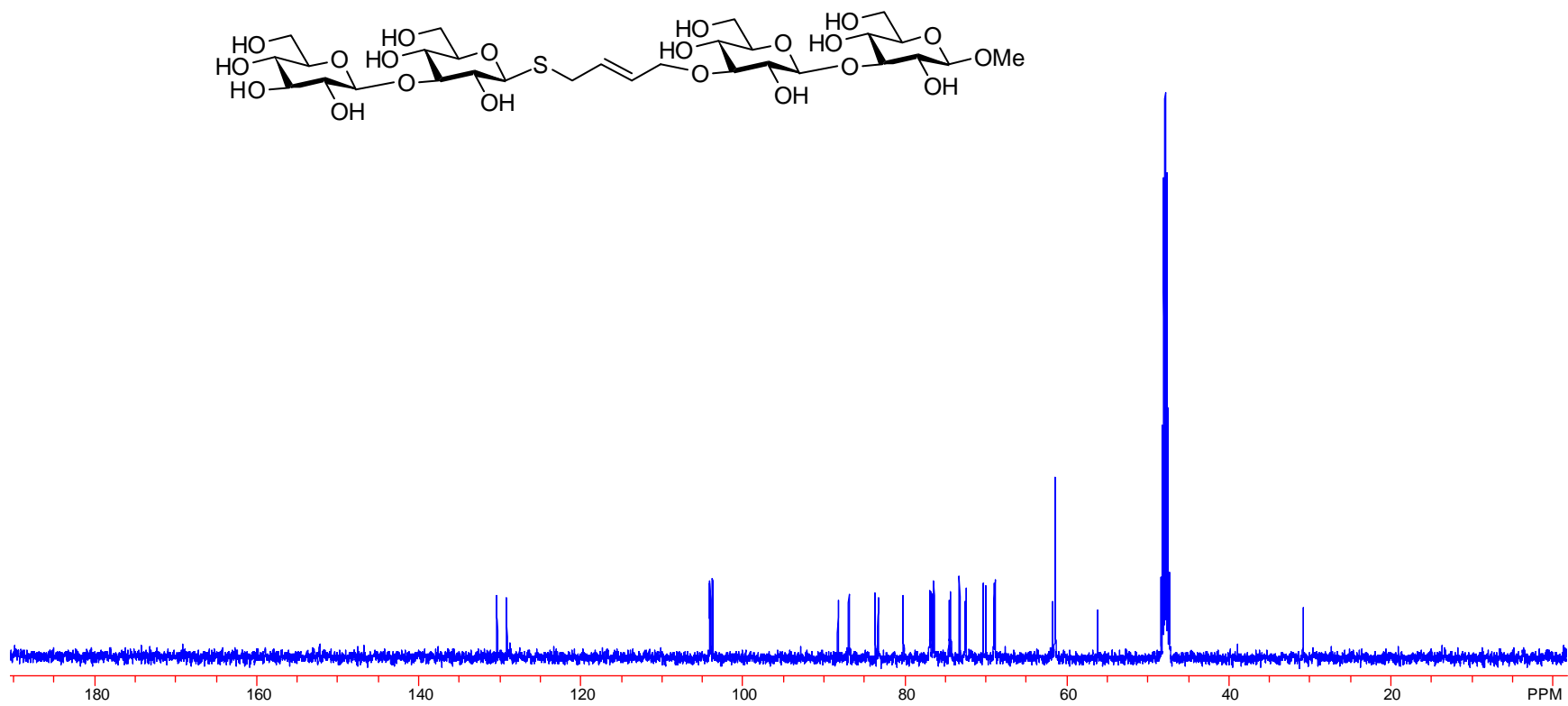


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<sup>1</sup>H-NMR spectrum (CD<sub>3</sub>OD, 500 MHz) Methyl 3-*O*-[4-(1-thio-β-D-laminaribiosyl)but-2-*E*-enyl]-β-D-laminariboside (**69**).

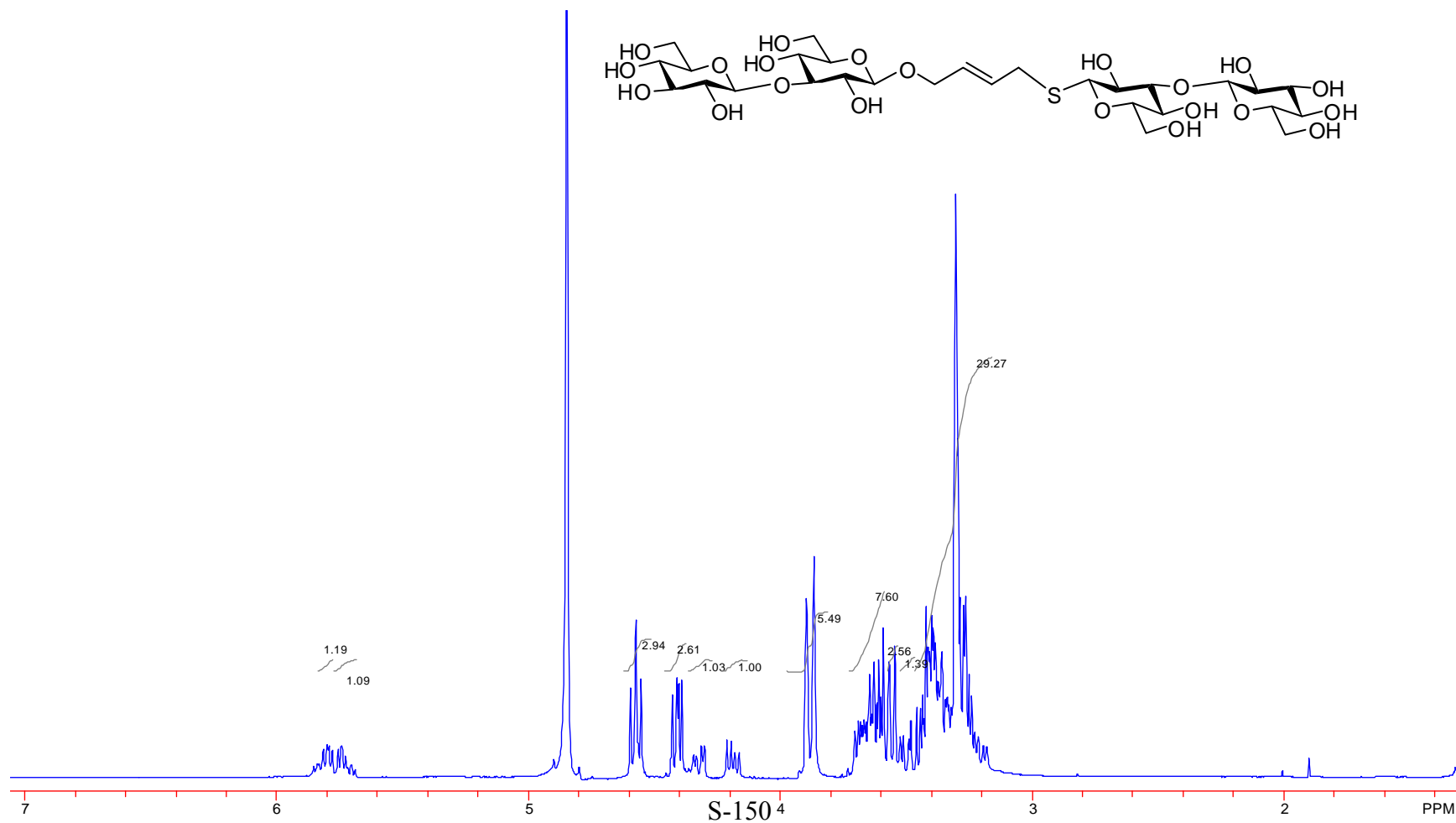


$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) Methyl 3-*O*-[4-(1-thio- $\beta$ -D-laminaribiosyl)but-2-*E*-enyl]- $\beta$ -D-laminaribioside (**69**).

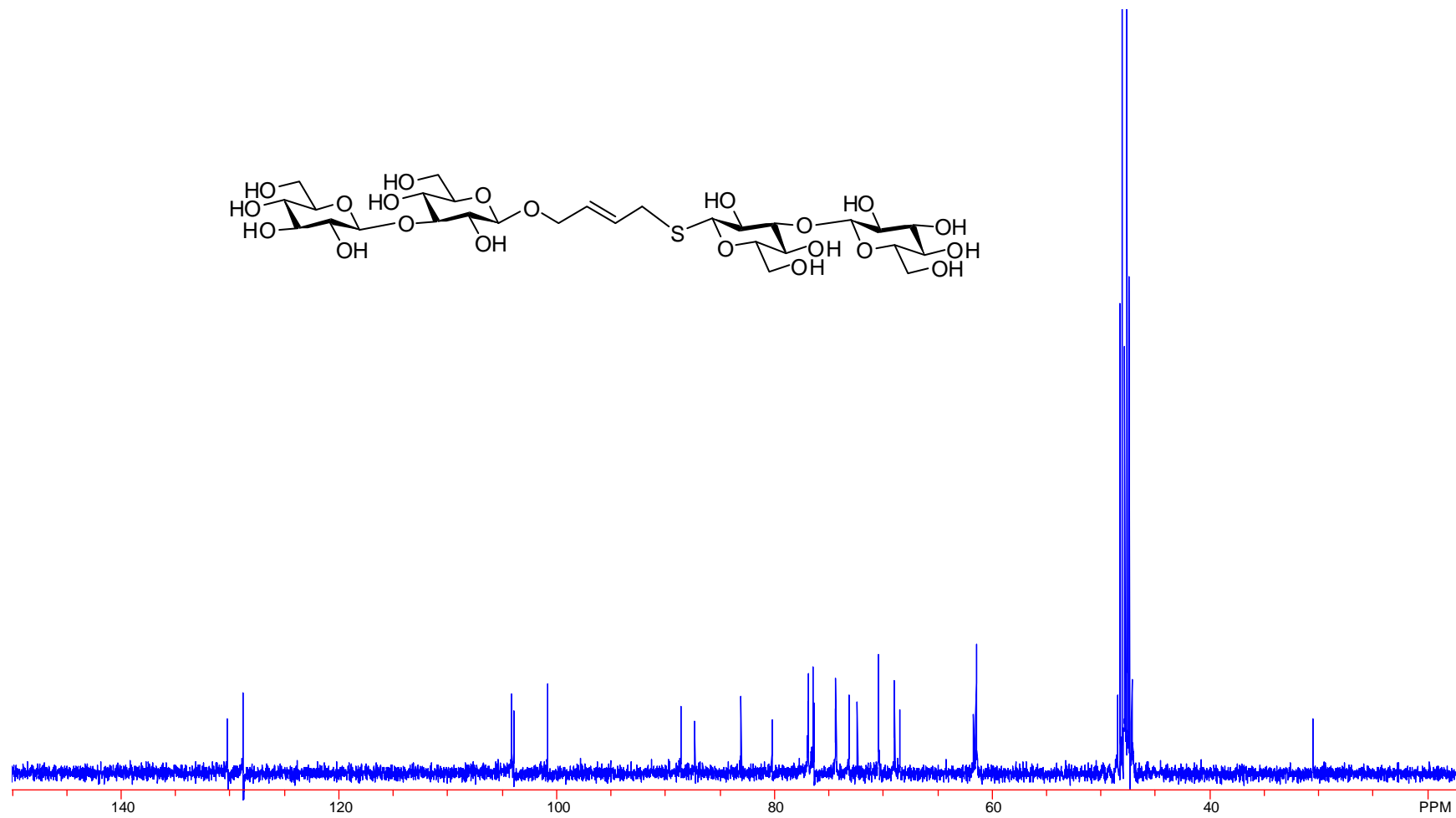


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$^1\text{H-NMR}$  spectrum ( $\text{CD}_3\text{OD}$ , 500 MHz) 4-(1-Thio- $\beta$ -D-laminaribiosyl)but-2-*E*-enyl  $\beta$ -D-laminaribioside (**70**).



$^{13}\text{C}$ -NMR spectrum ( $\text{CD}_3\text{OD}$ , 125 MHz) 4-(1-Thio- $\beta$ -D-laminaribosyl)but-2-*E*-enyl  $\beta$ -D-laminaribioside (**70**).



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