

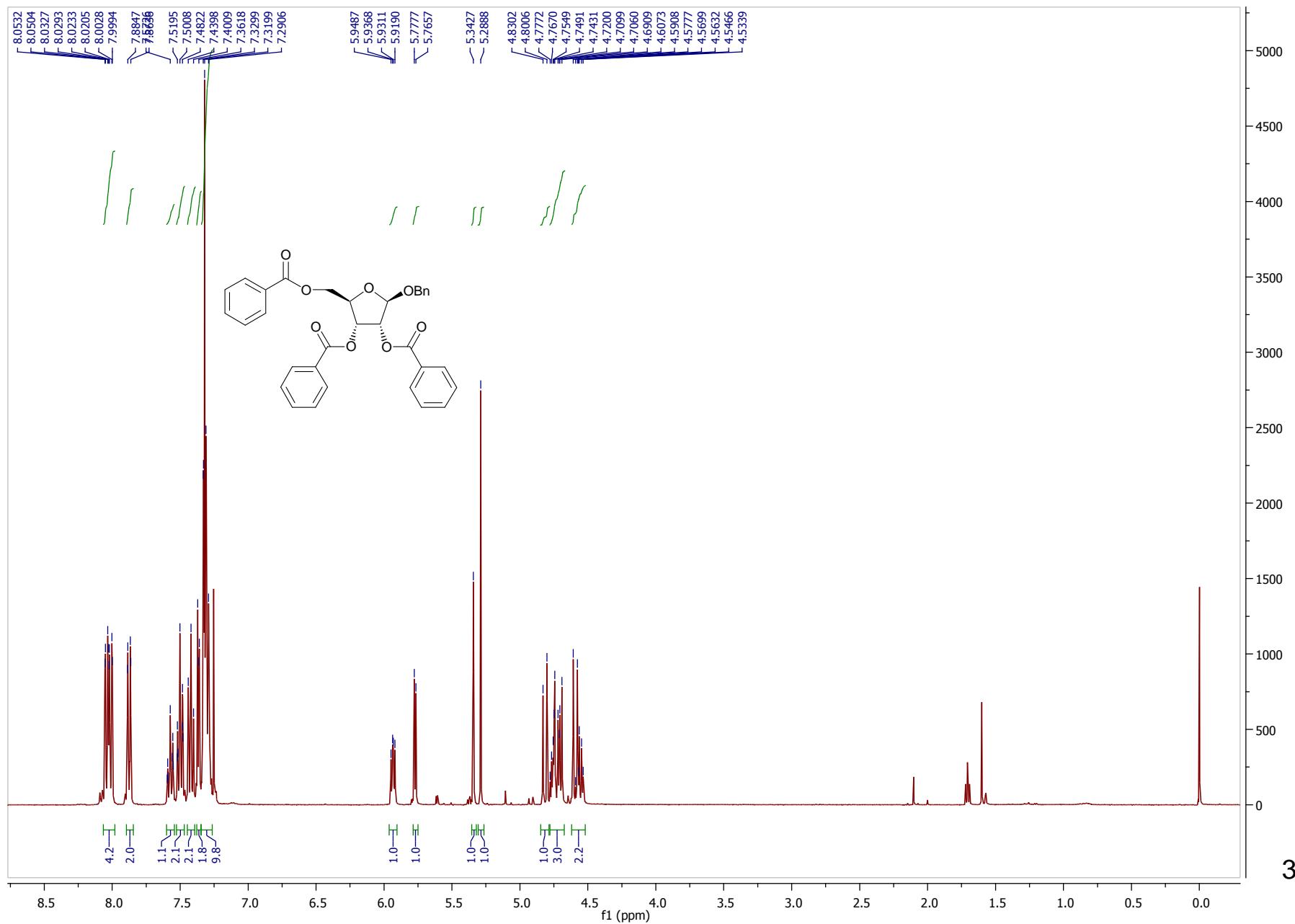
## Electronic Supplementary Information

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of all new compounds are provided below

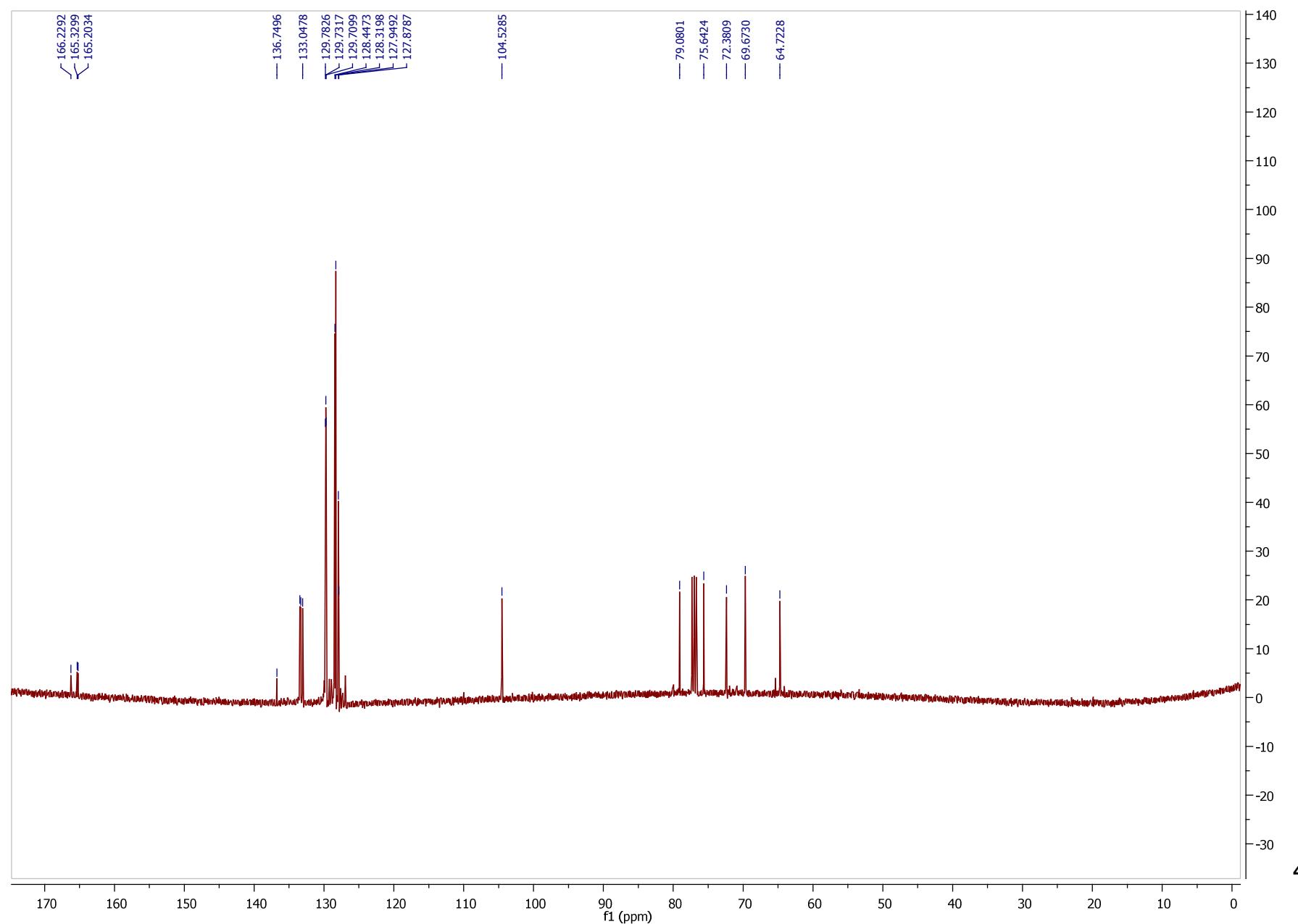
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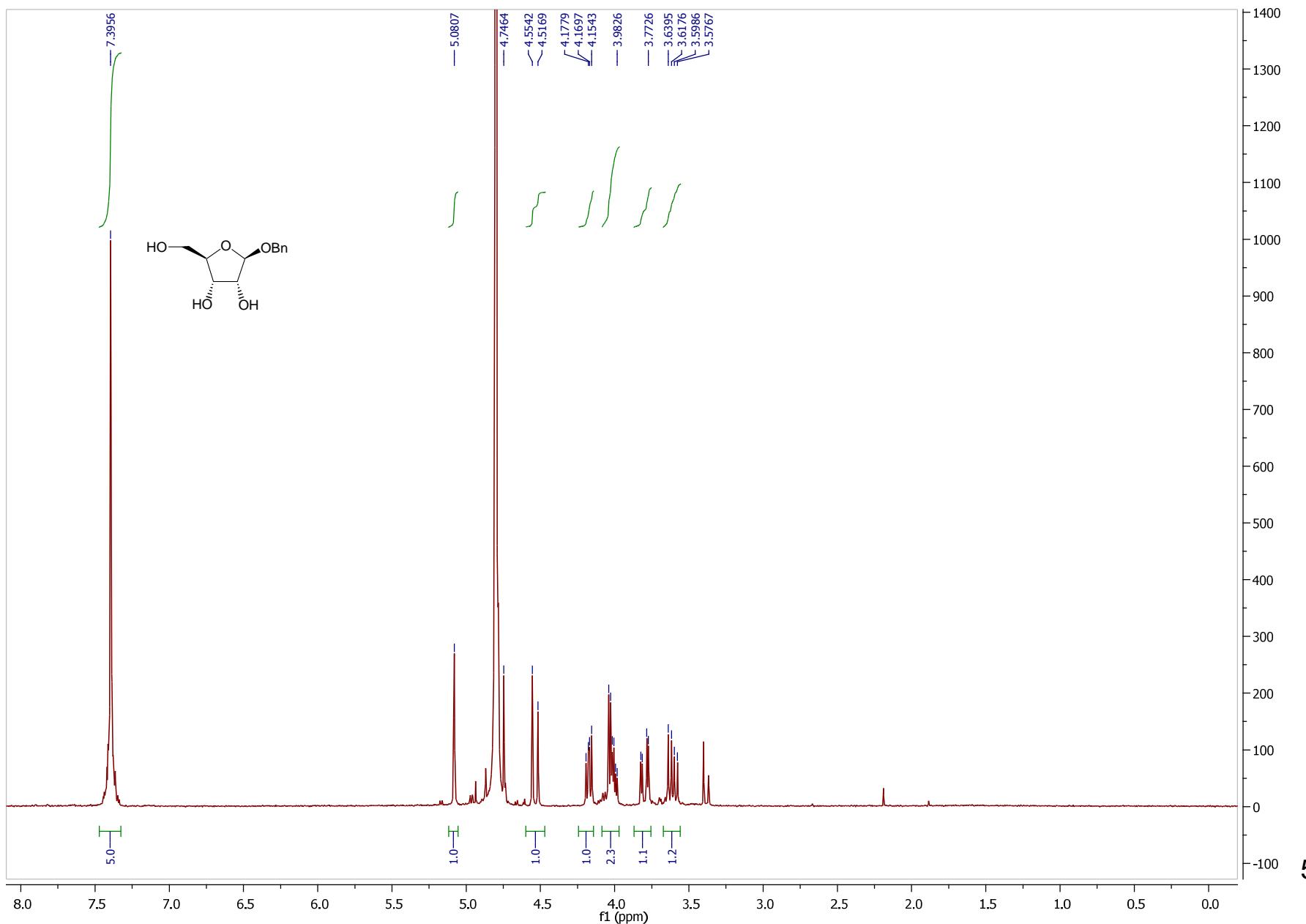
**2,3,5-tri-O-benzoyl-1-O-benzyl- $\beta$ -D-ribofuranoside 2:  $^1\text{H-NMR}$**



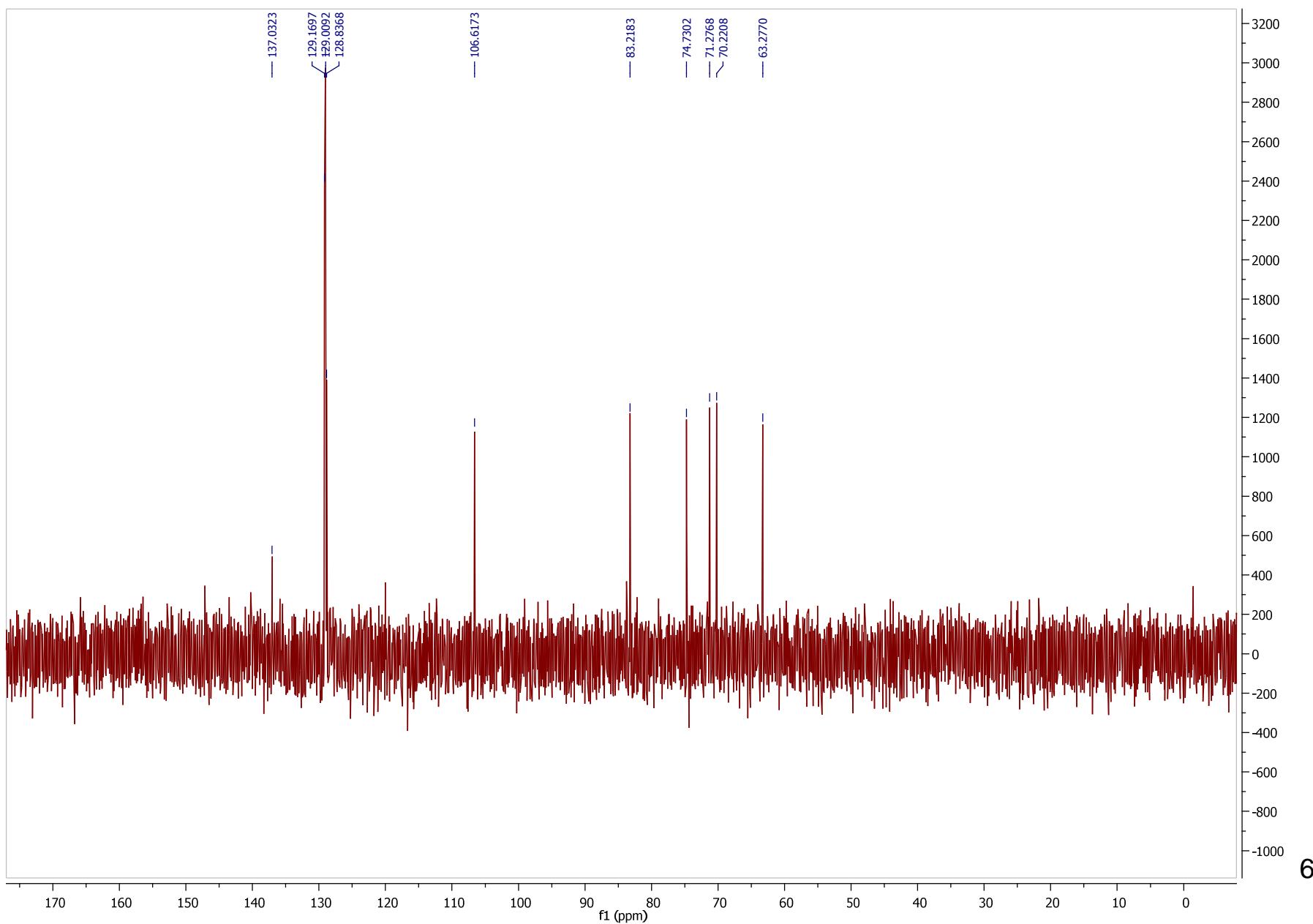
**2,3,5-tri-O-benzoyl-1-O-benzyl- $\beta$ -D-ribofuranoside 2:  $^{13}\text{C}$ -NMR**



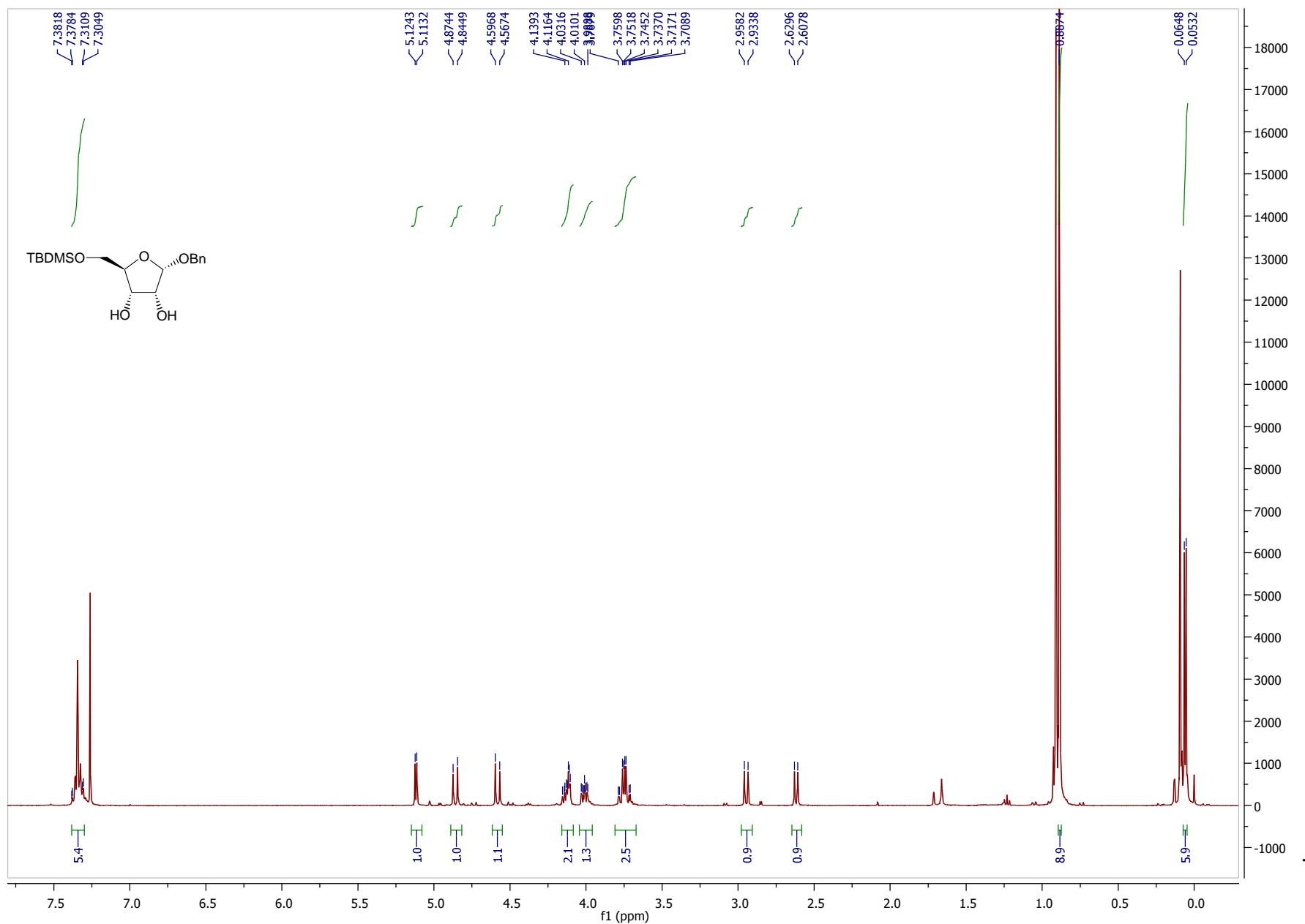
**1-O-benzyl- $\beta$ -D-ribofuranoside 3:  $^1\text{H}$ -NMR**



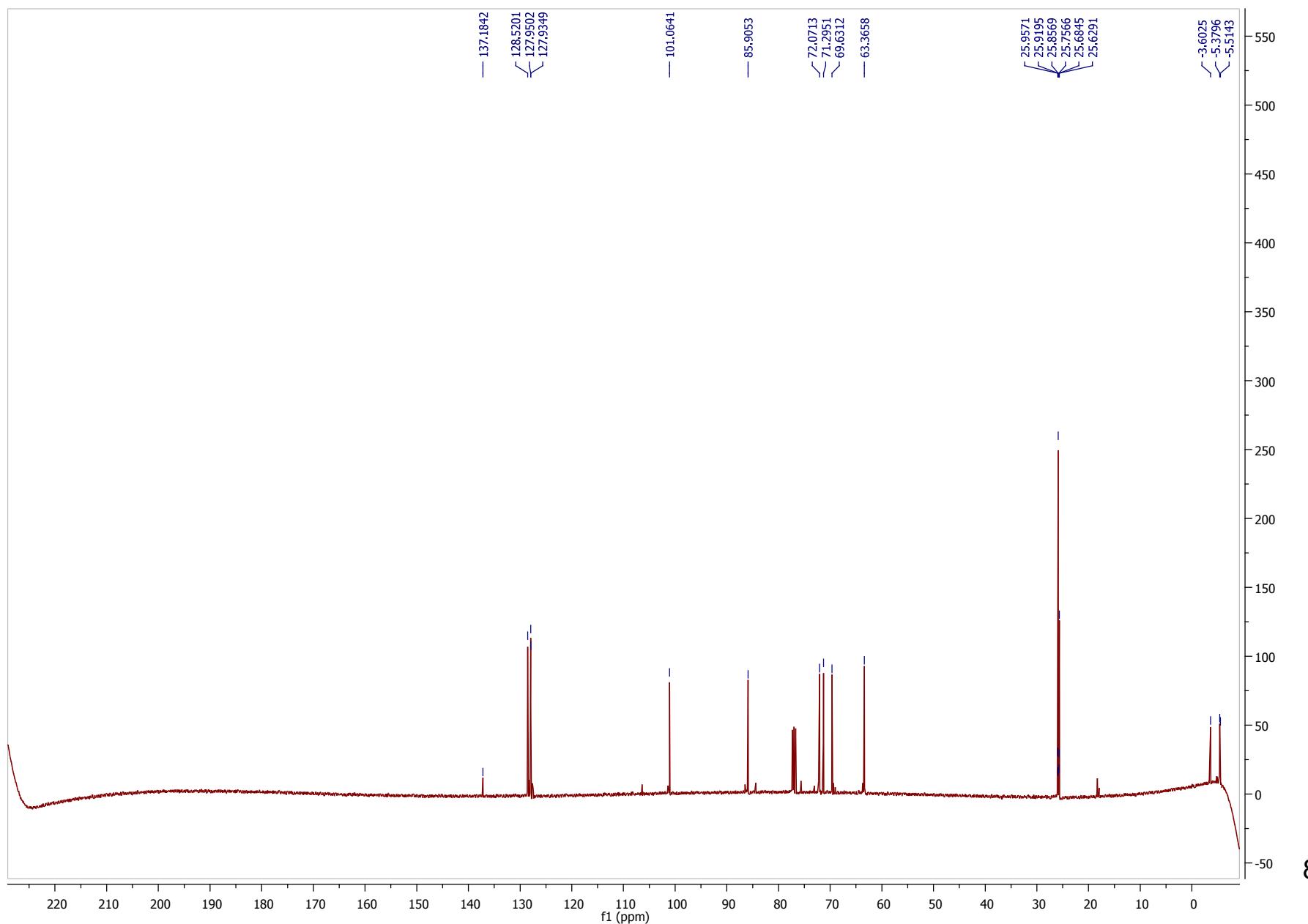
**1-O-benzyl- $\beta$ -D-ribofuranoside 3:  $^{13}\text{C}$ -NMR**



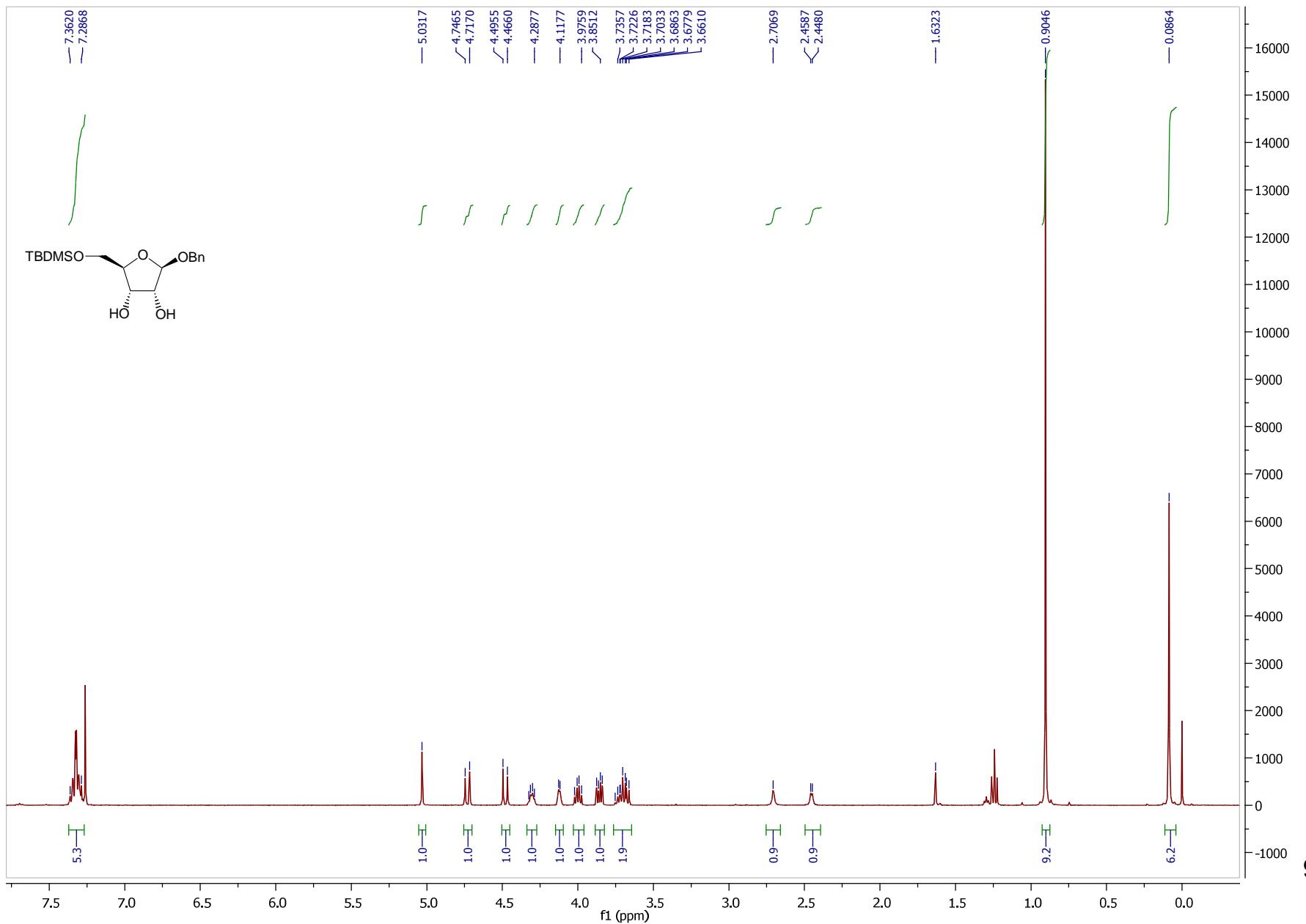
**1-O-benzyl-5-O-tert-butylidemethylsilyl- $\beta$ -D-ribofuranoside 4 $\alpha$ :**  $^1\text{H}$ -NMR



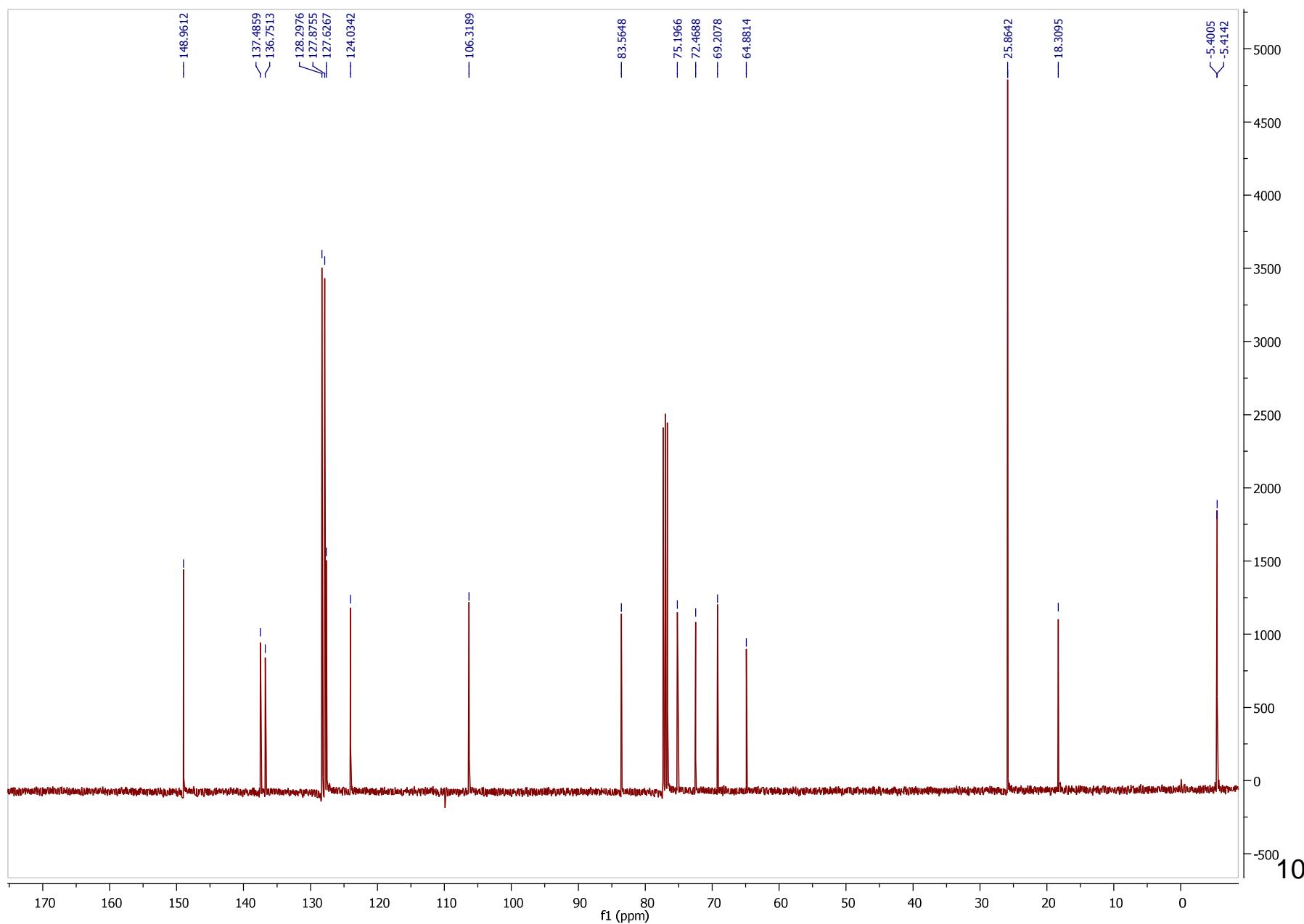
**1-O-benzyl-5-O-tert-butyldimethylsilyl- $\beta$ -D-ribofuranoside 4 $\alpha$ :**  $^{13}\text{C}$ -NMR



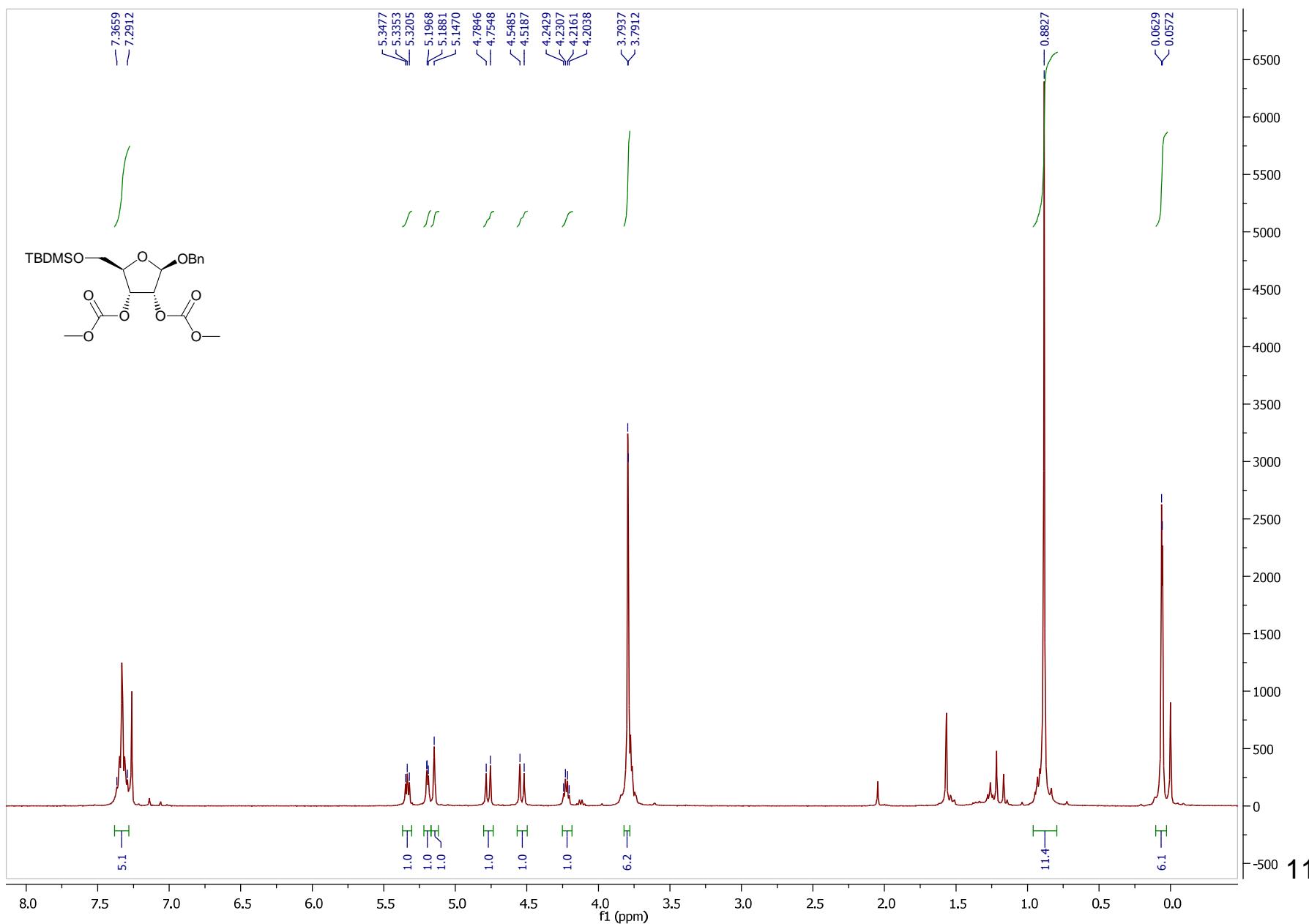
**1-O-benzyl-5-O-tert-butyldimethylsilyl- $\beta$ -D-ribofuranoside 4 $\beta$ :**  $^1\text{H-NMR}$



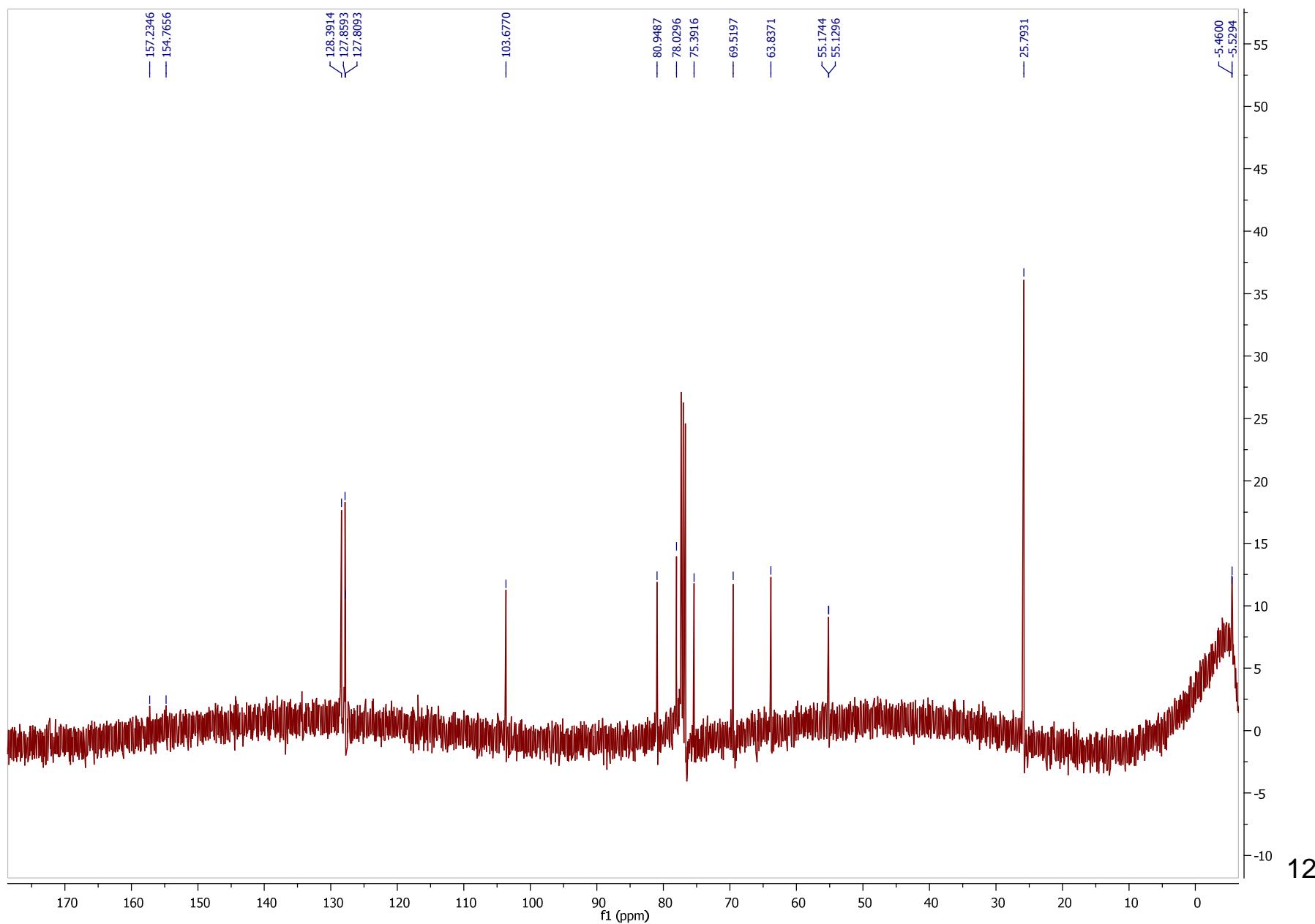
**1-O-benzyl-5-O-tert-butylidemethylsilyl- $\beta$ -D-ribofuranoside 4 $\beta$ :  $^{13}\text{C}$ -NMR**



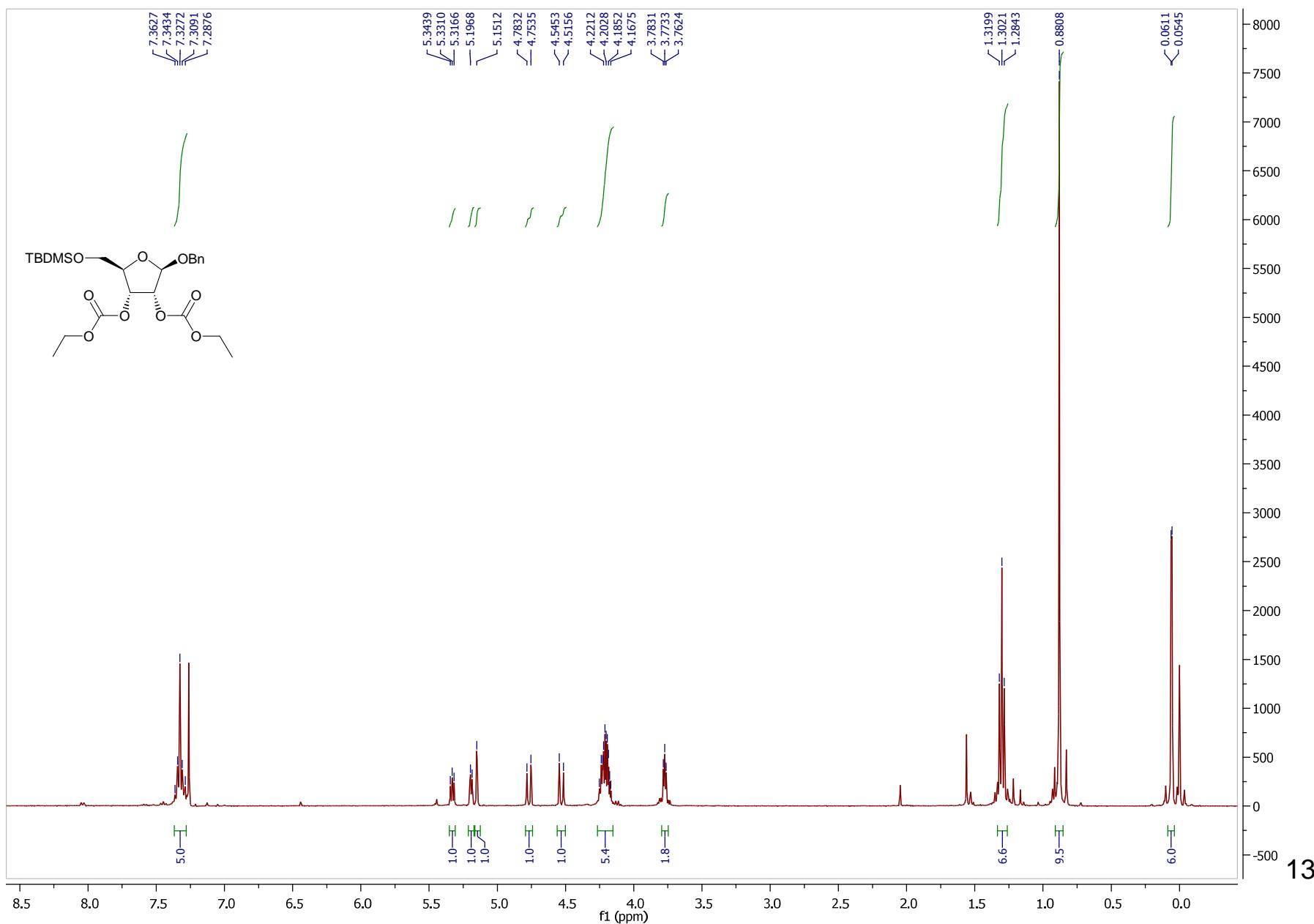
**1-O-benzyl-2,3-O-bis(methylcarbonate)-5-O-tert-butyldimethylsilyl- $\beta$ -D-ribofuranoside 5a:  $^1\text{H}$ -NMR**



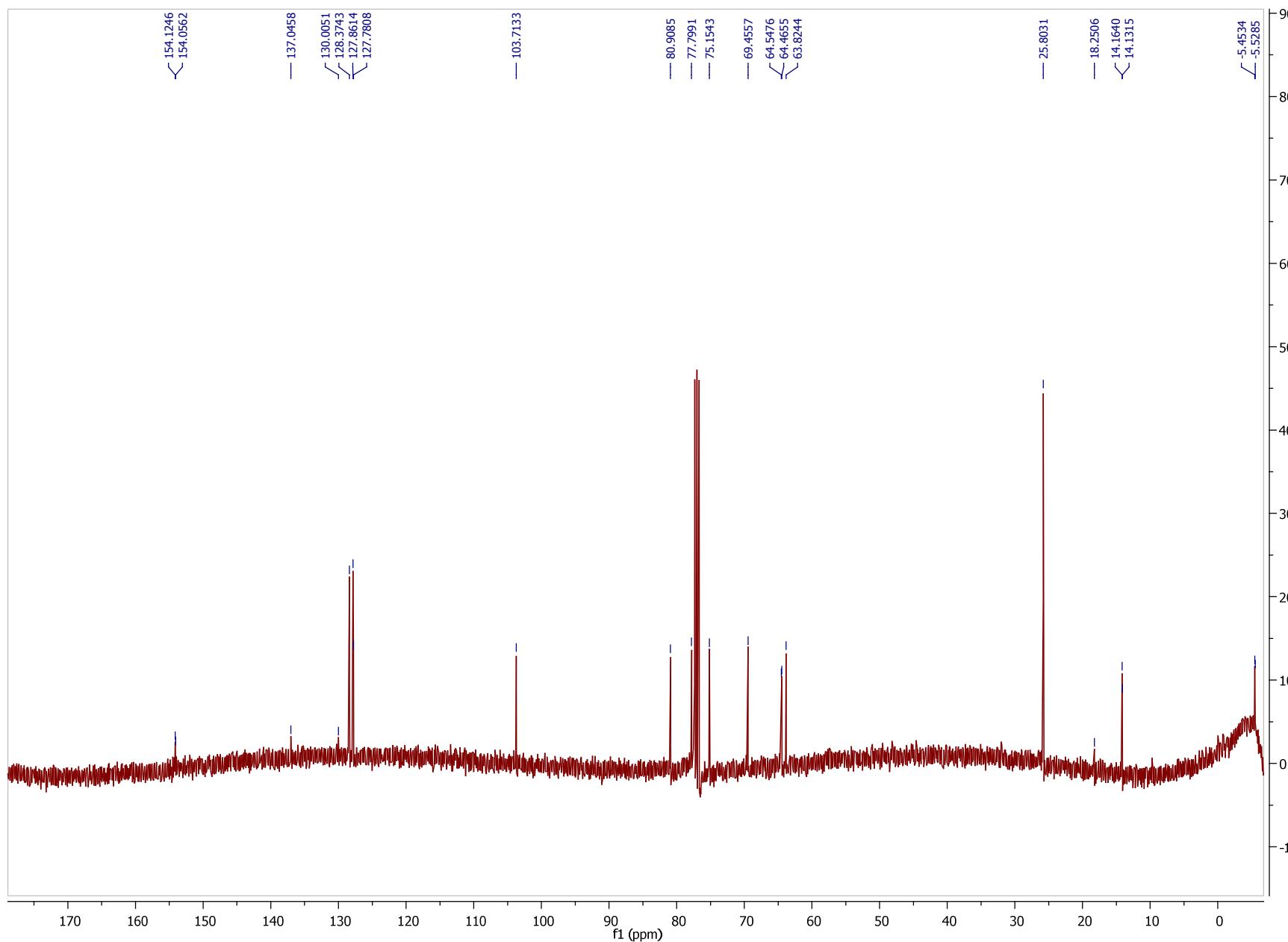
1-O-benzyl-2,3-O-bis(methylcarbonate)-5-O-tert-butyldimethylsilyl- $\beta$ -D-ribofuranoside **5a:**  $^{13}\text{C}$ -NMR



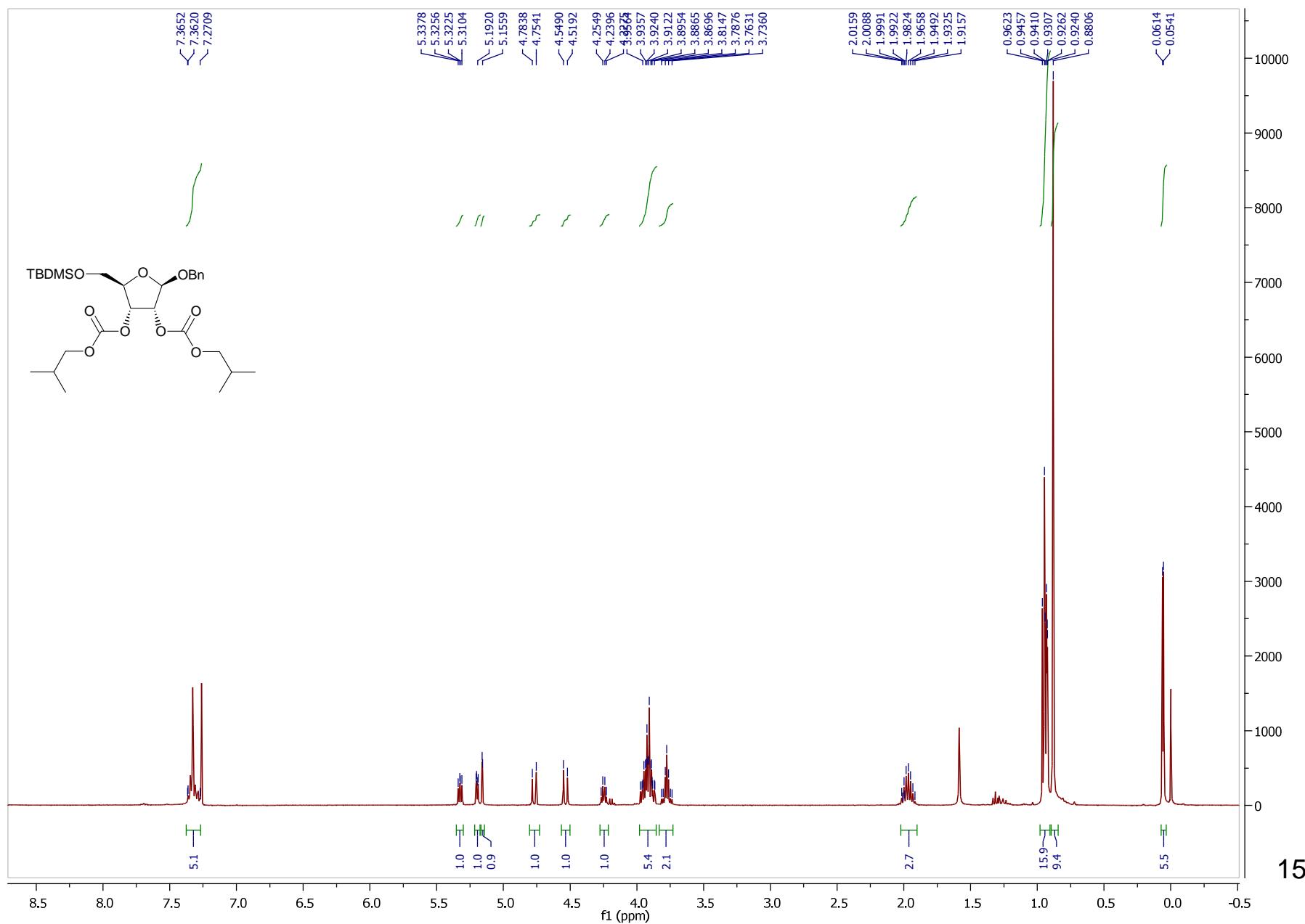
1-O-benzyl-2,3-O-bis(ethylcarbonate)-5-O-tert-butyldimethylsilyl- $\beta$ -D-ribofuranoside **5b**:  $^1\text{H}$ -NMR



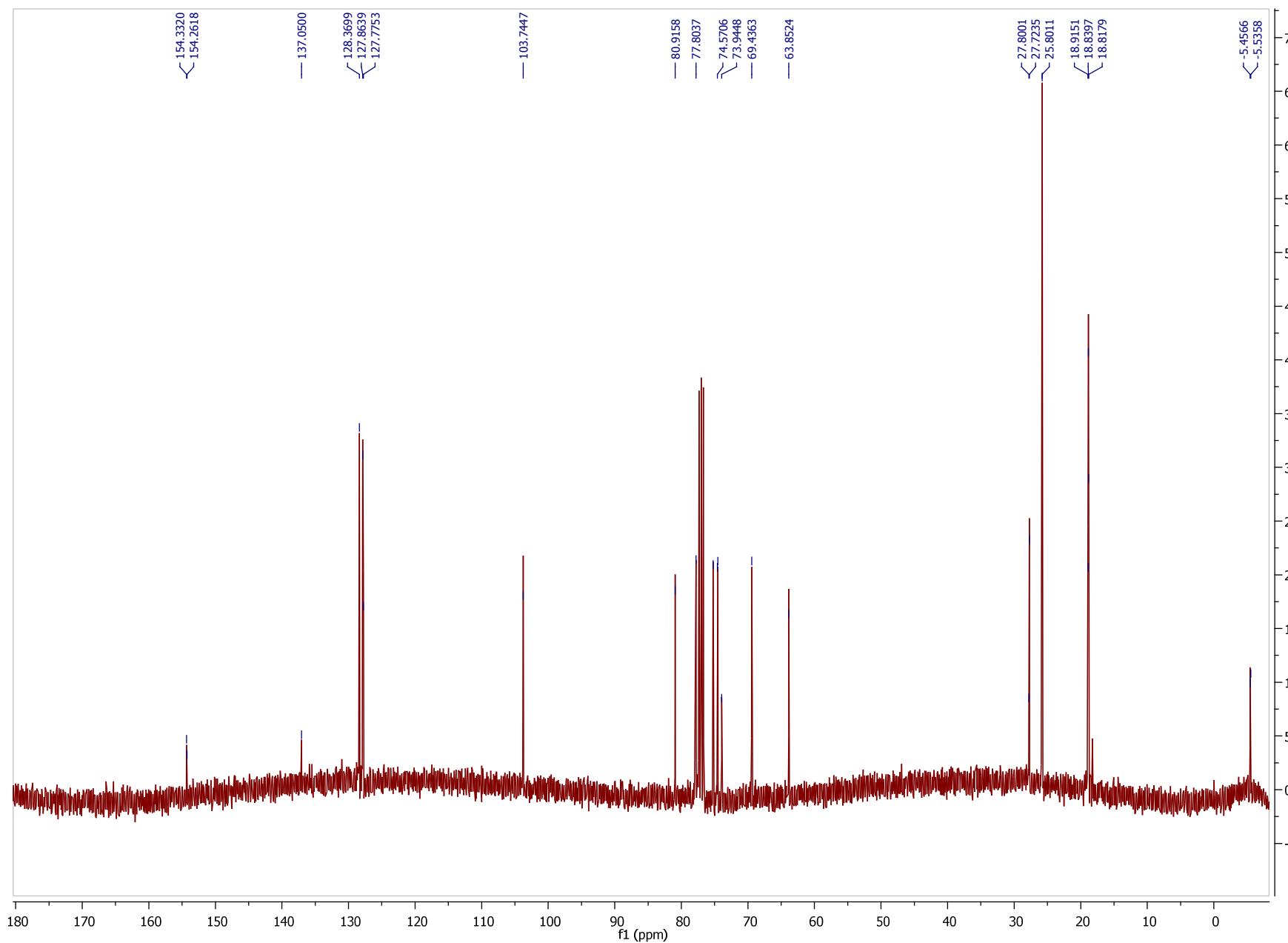
**1-O-benzyl-2,3-O-bis(ethylcarbonate)-5-O-tert-butyldimethylsilyl- $\beta$ -D-ribofuranoside 5b:  $^{13}\text{C}$ -NMR**



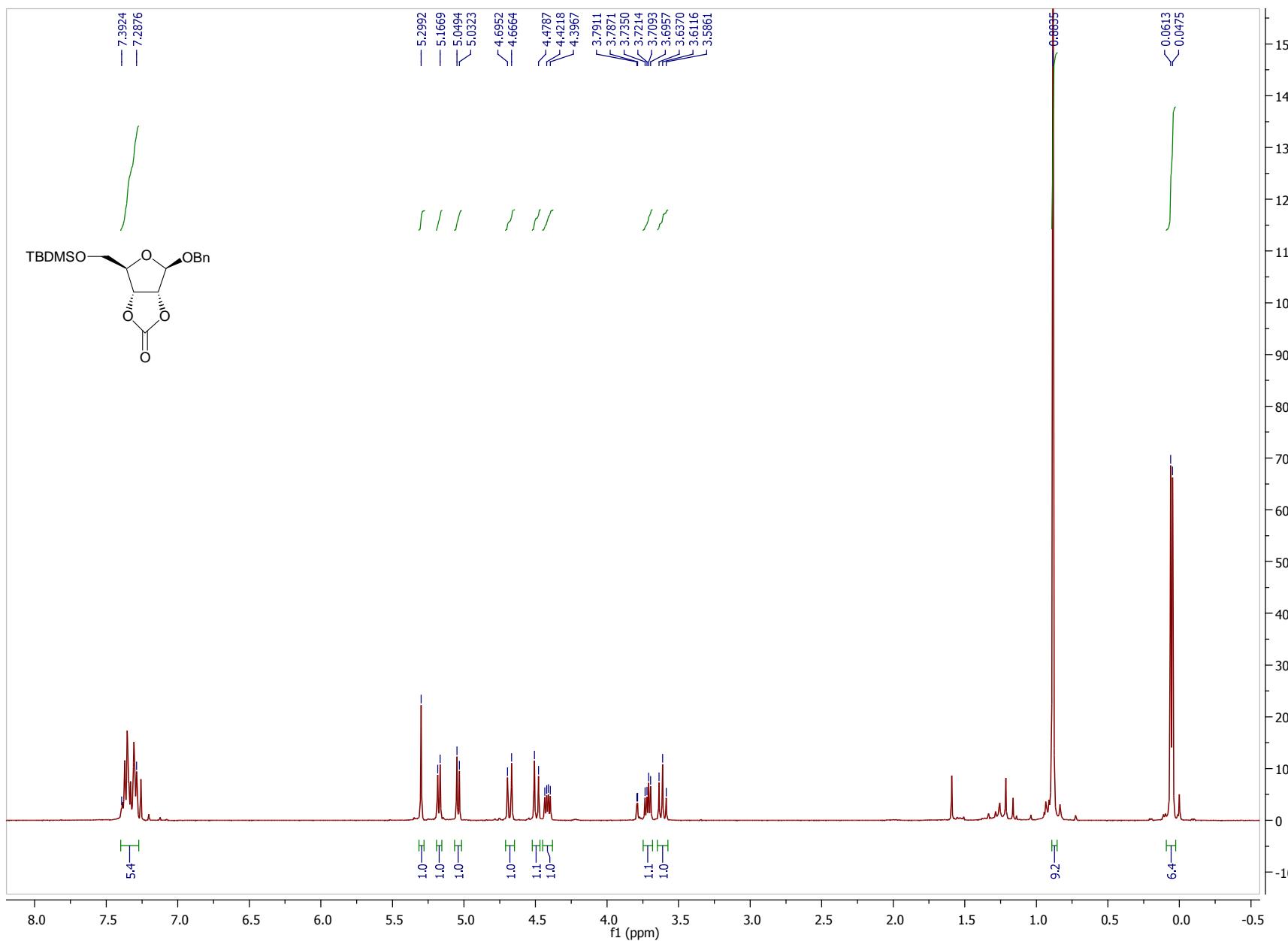
1-O-benzyl-2,3-O-bis(isobutylcarbonate)-5-O-tert-butyldimethylsilyl- $\beta$ -D-ribofuranoside **5c**:  $^1\text{H}$ -NMR



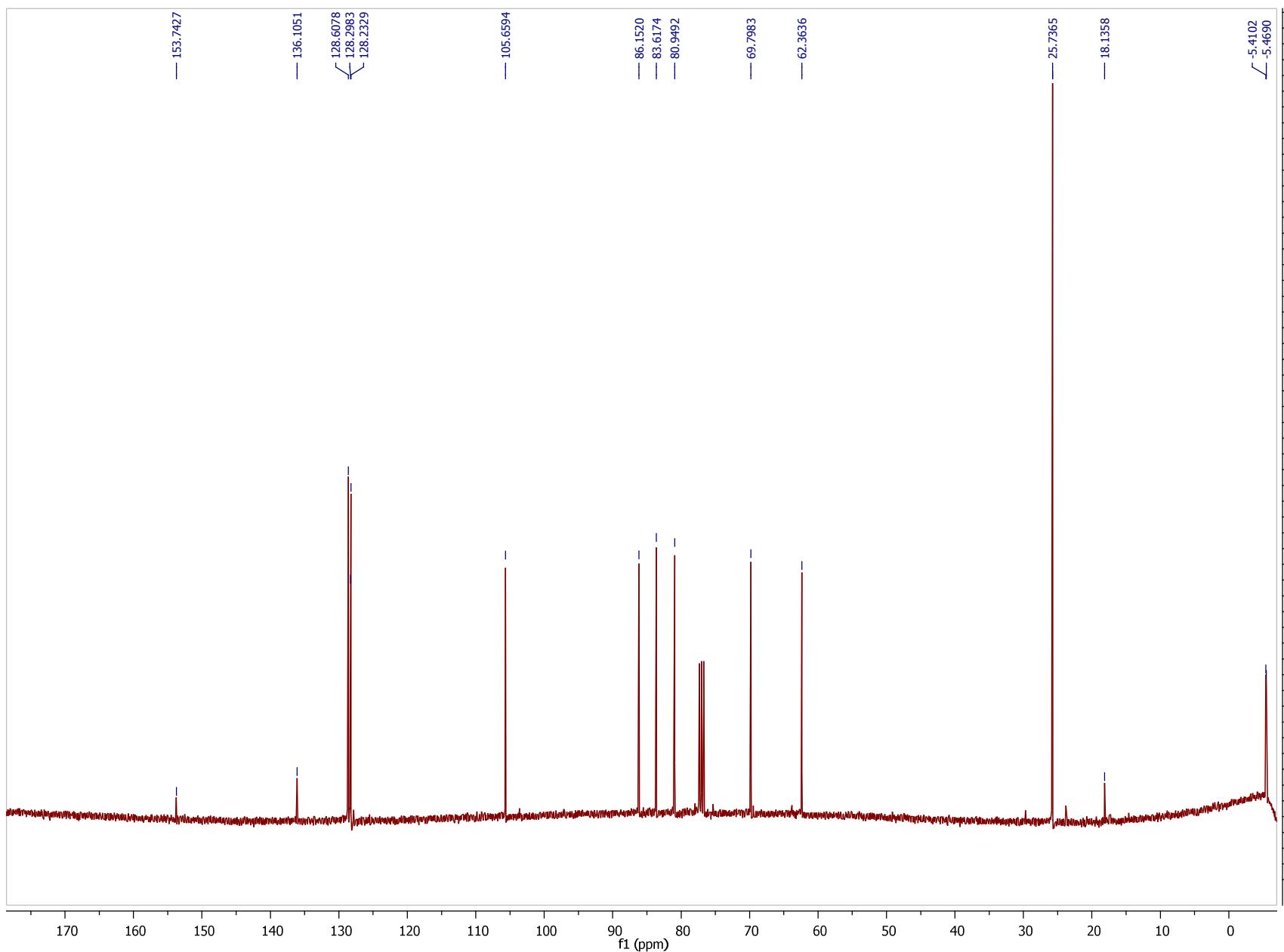
**1-O-benzyl-2,3-O-bis(isobutylcarbonate)-5-O-tert-butyldimethylsilyl- $\beta$ -D-ribofuranoside 5c:  $^{13}\text{C}$ -NMR**



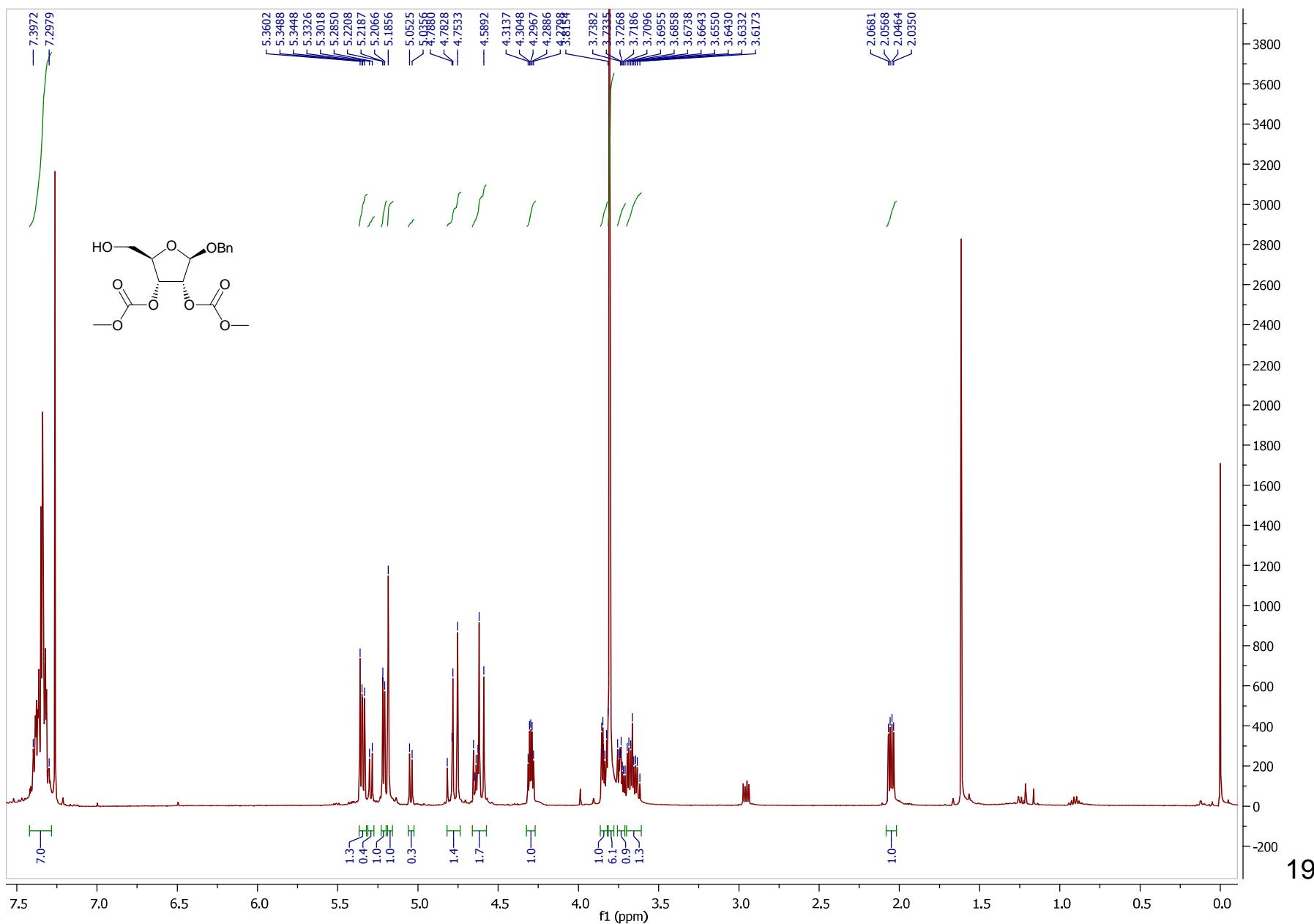
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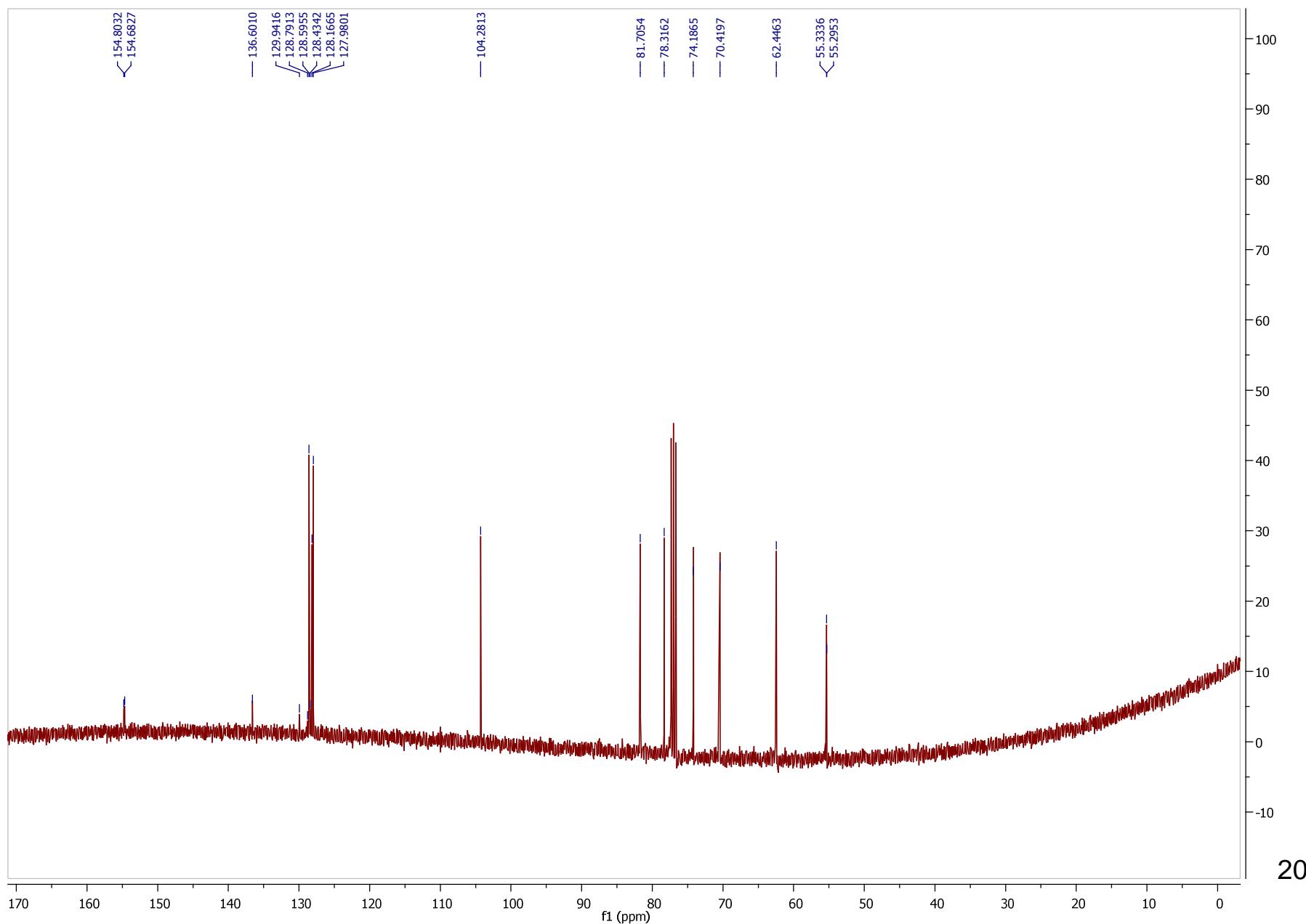
**1-O-benzyl-2,3-O-carbonate-5-O-tert-butyldimethylsilyl- $\beta$ -D-ribofuranoside 5d:  $^{13}\text{C}$ -NMR**



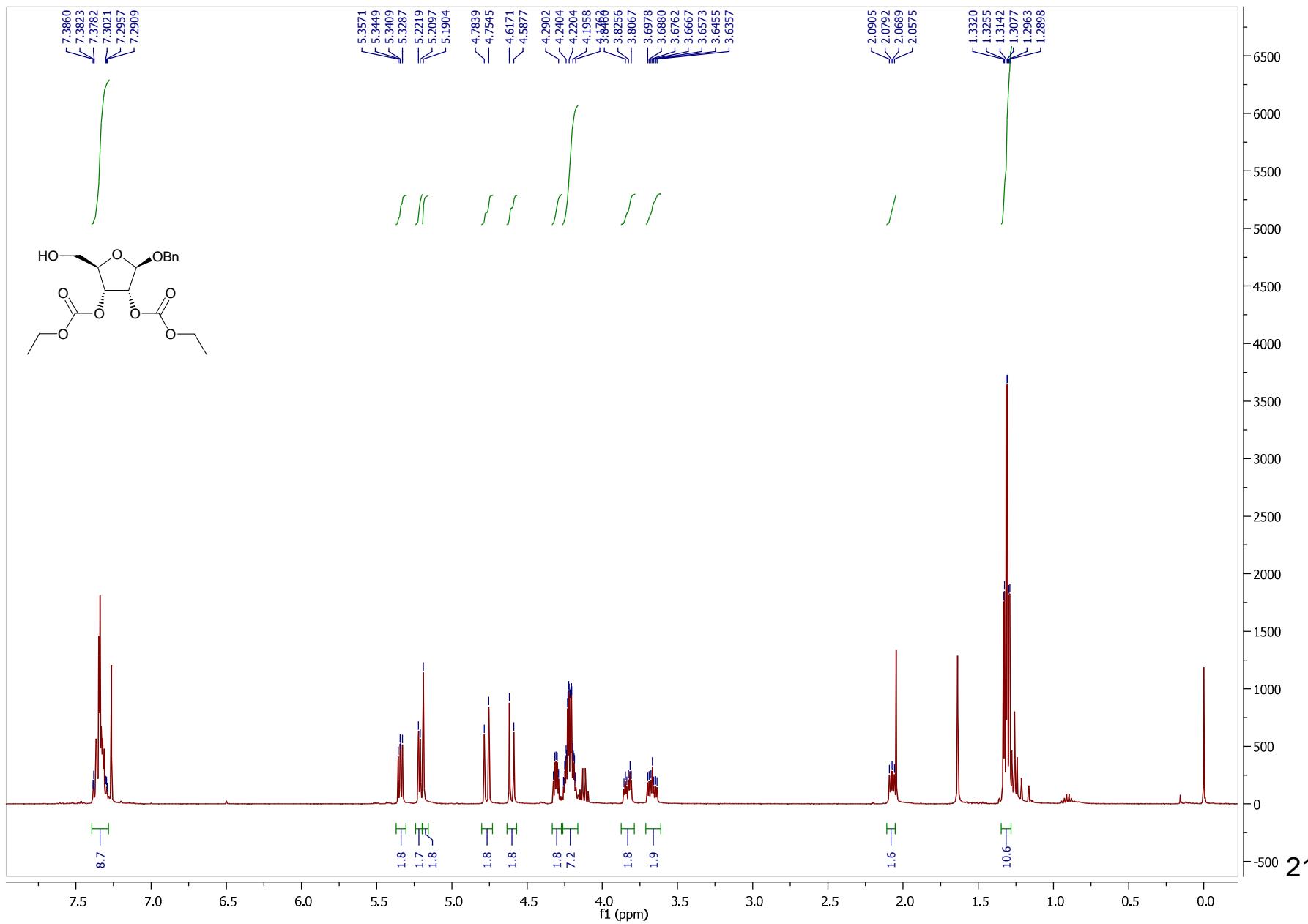
1-O-benzyl-2,3-O-bis(methylcarbonate)- $\beta$ -D-ribofuranoside 7a:  $^1\text{H}$ -NMR



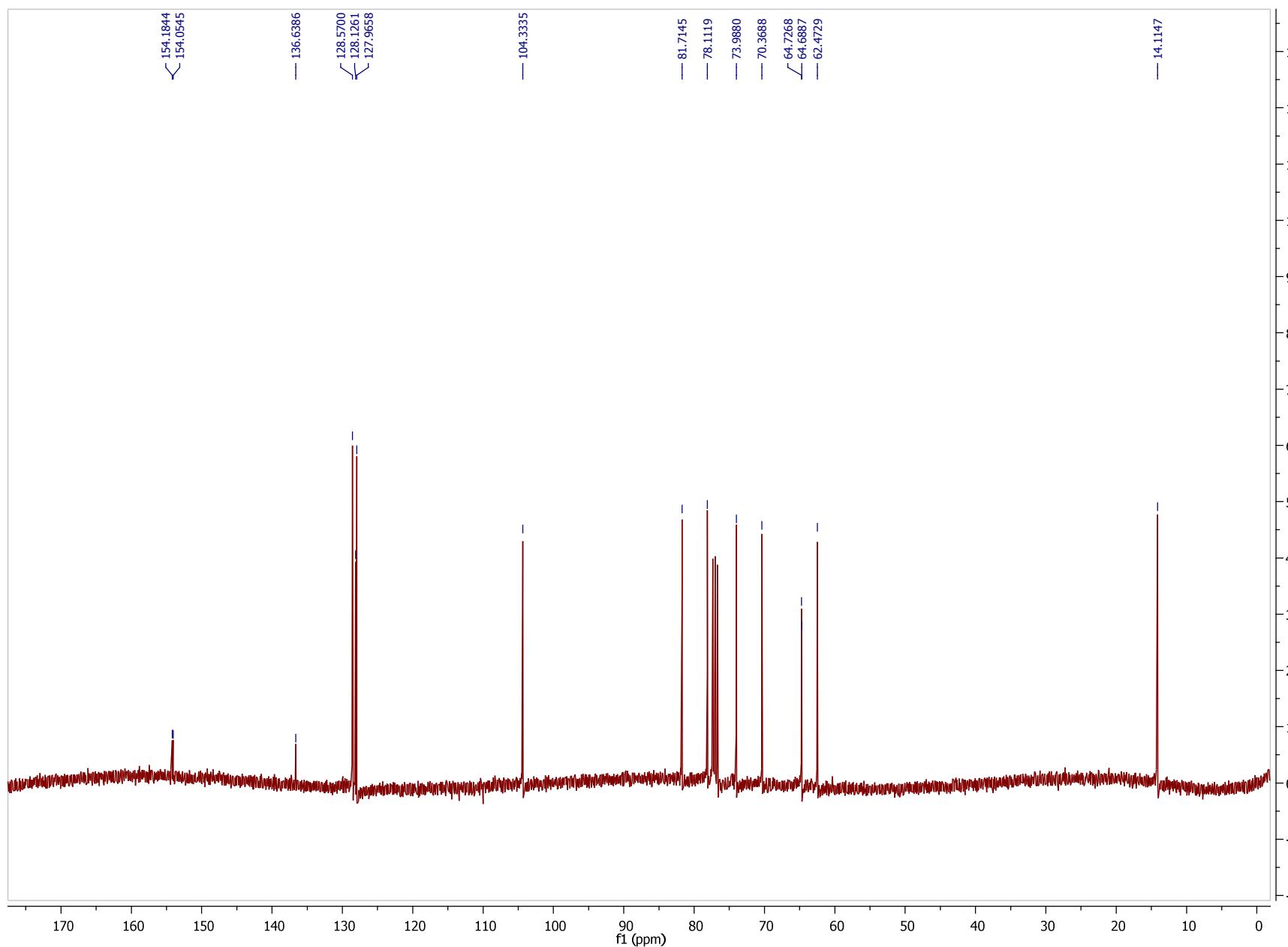
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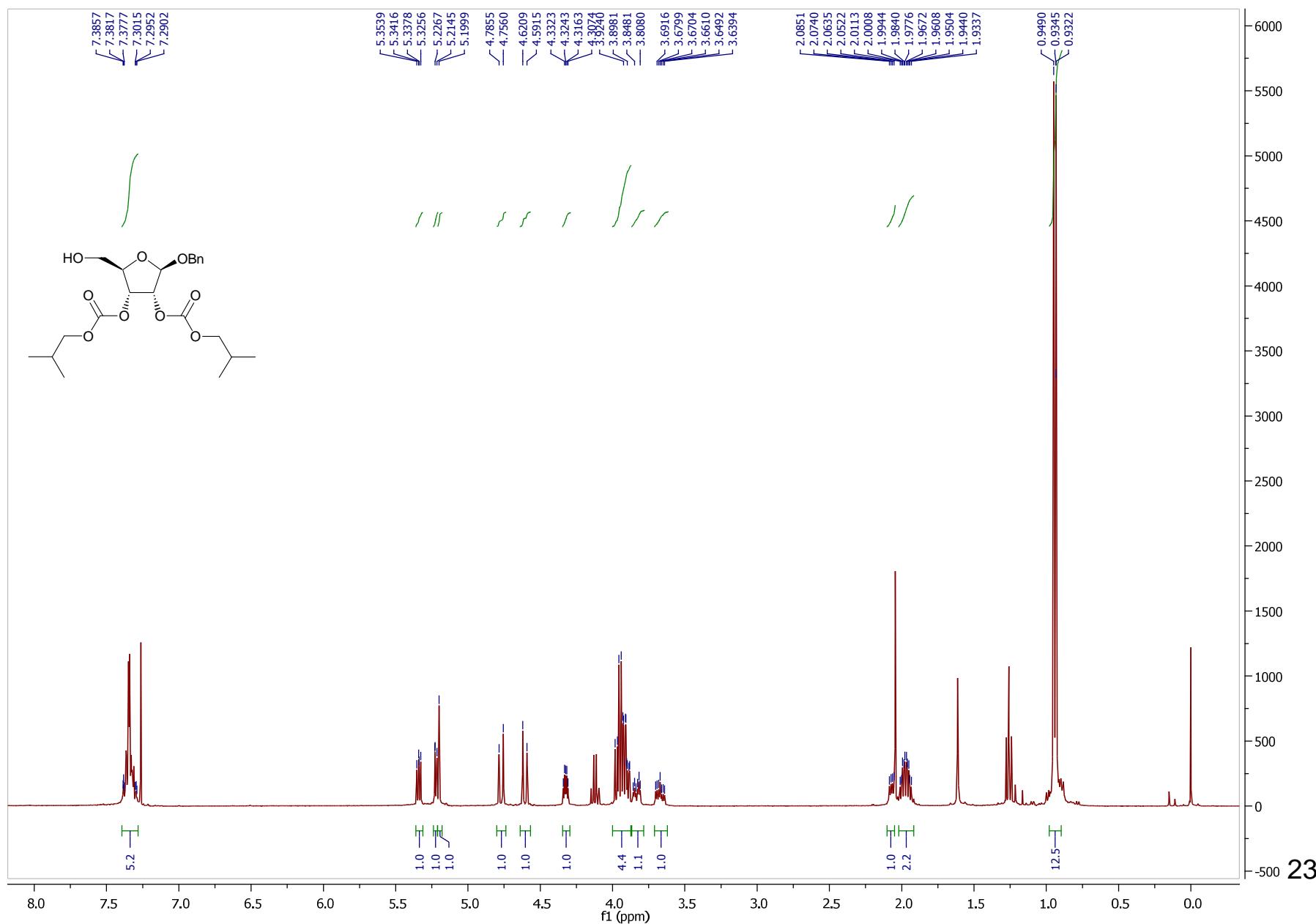
**1-O-benzyl-2,3-O-bis(ethylcarbonate)- $\beta$ -D-ribofuranoside 7b:**  $^1\text{H-NMR}$



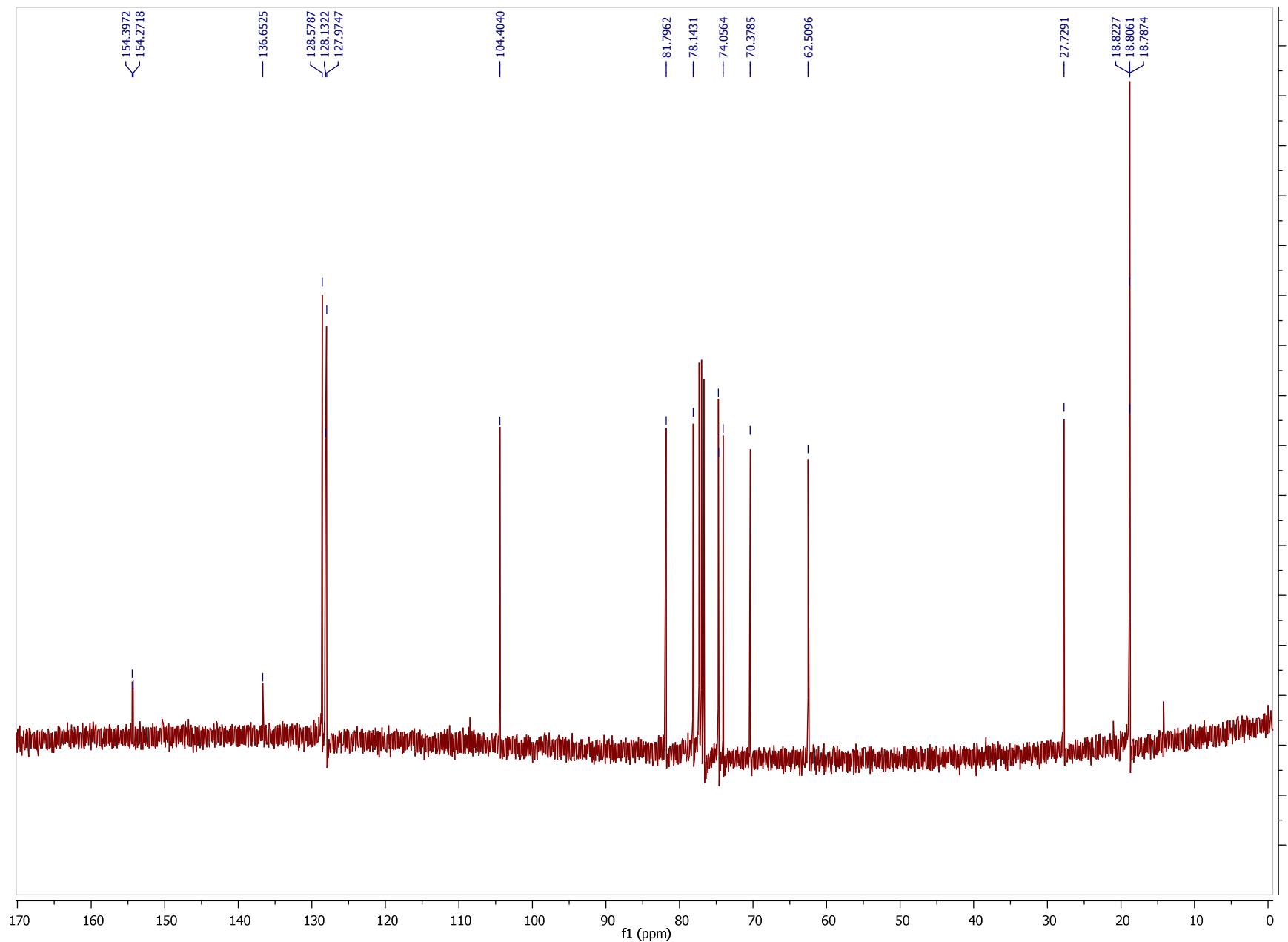
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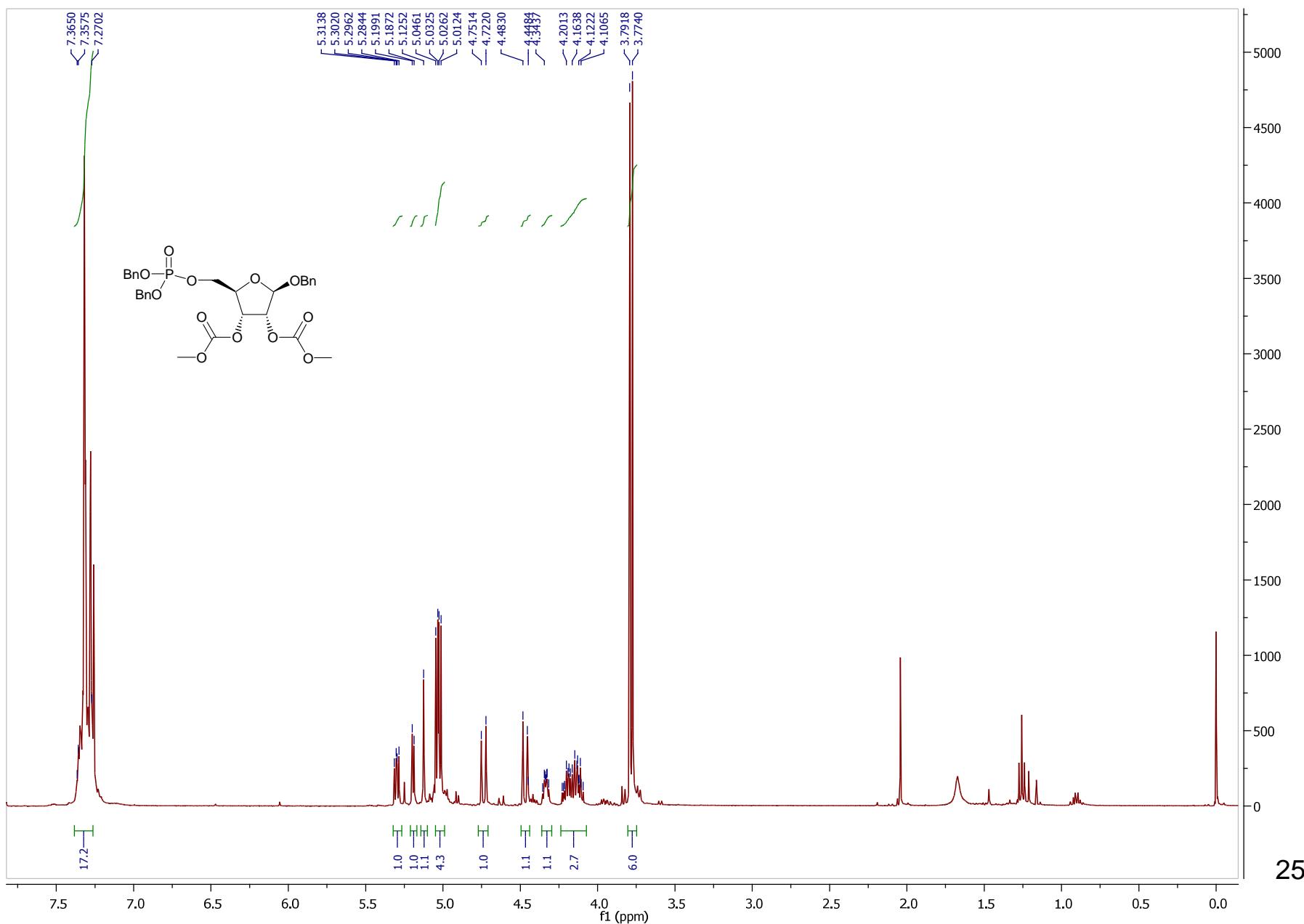
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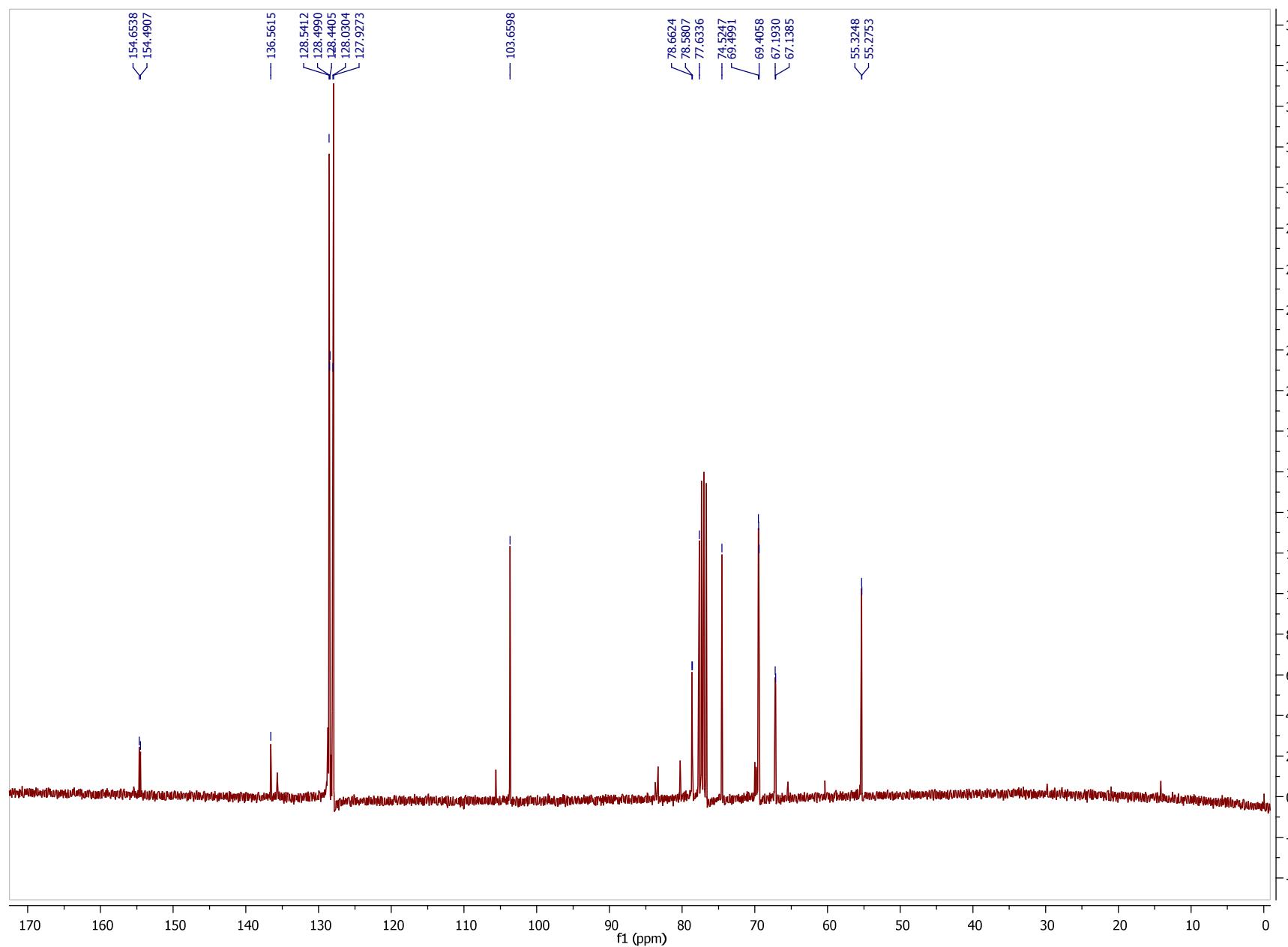
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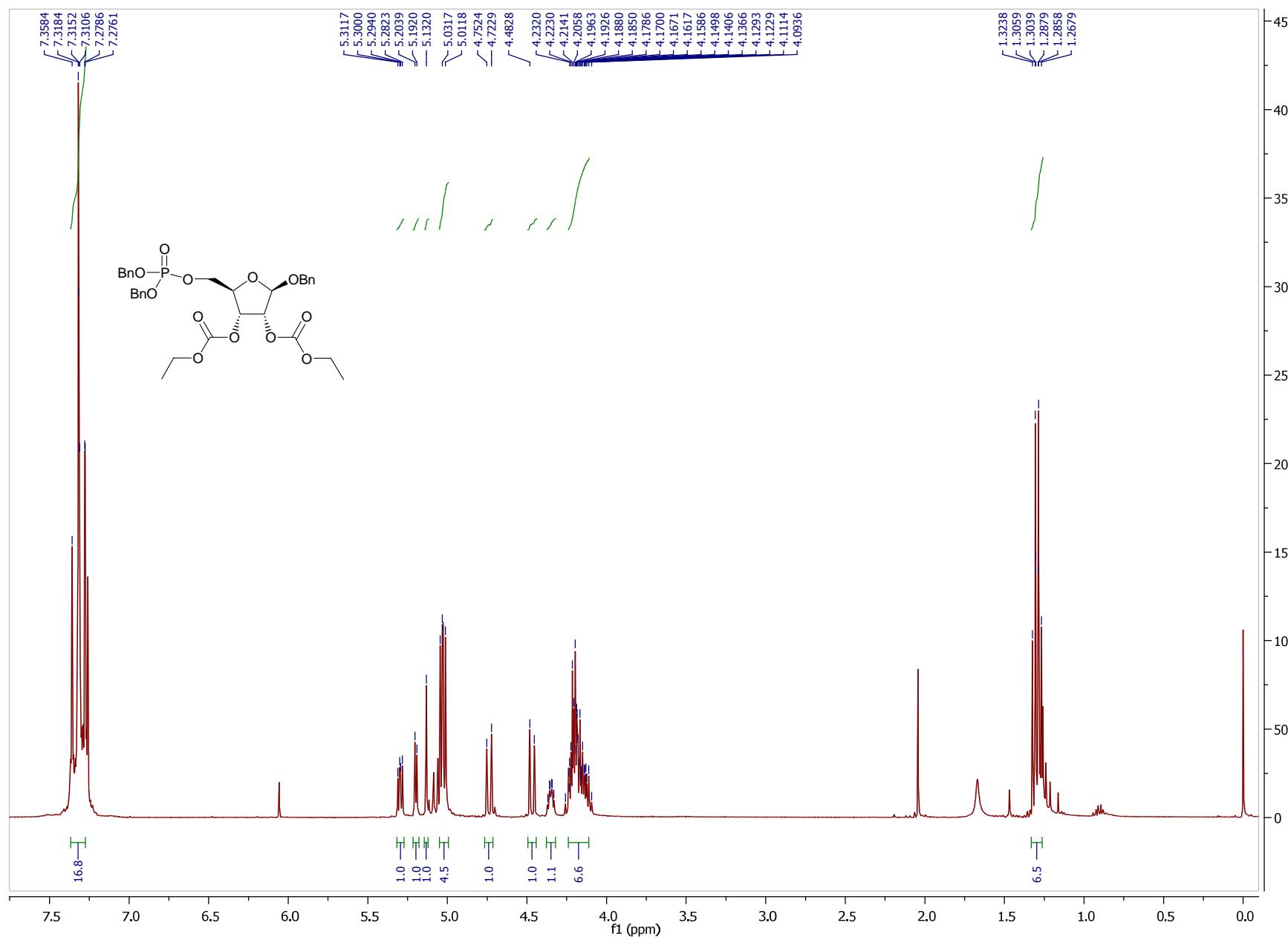
5-O-dibenzylphosphate-1-O-benzyl-2,3-O-bis(methylcarbonate)- $\beta$ -D-ribofuranoside **9a**:  $^1\text{H}$ -NMR



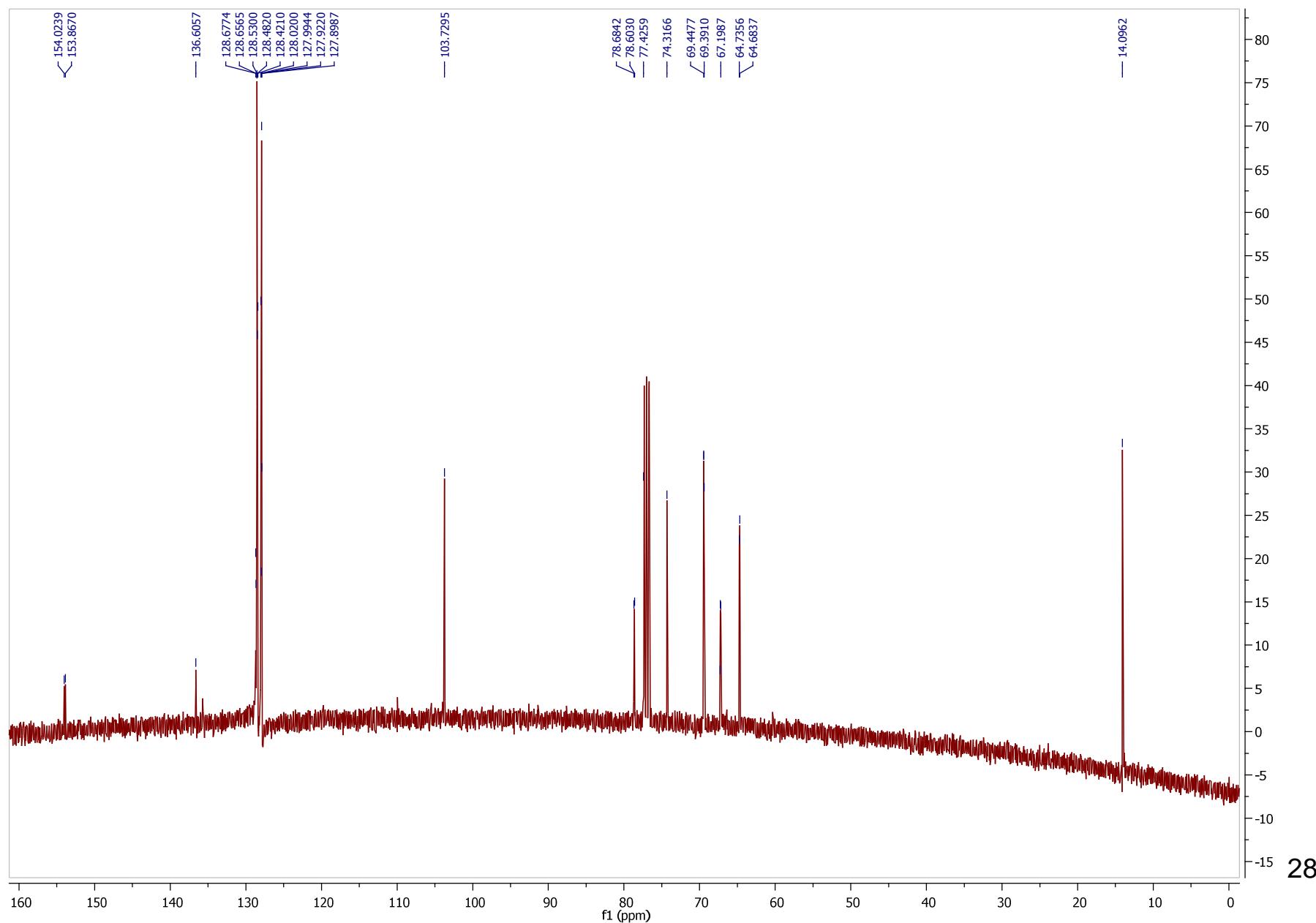
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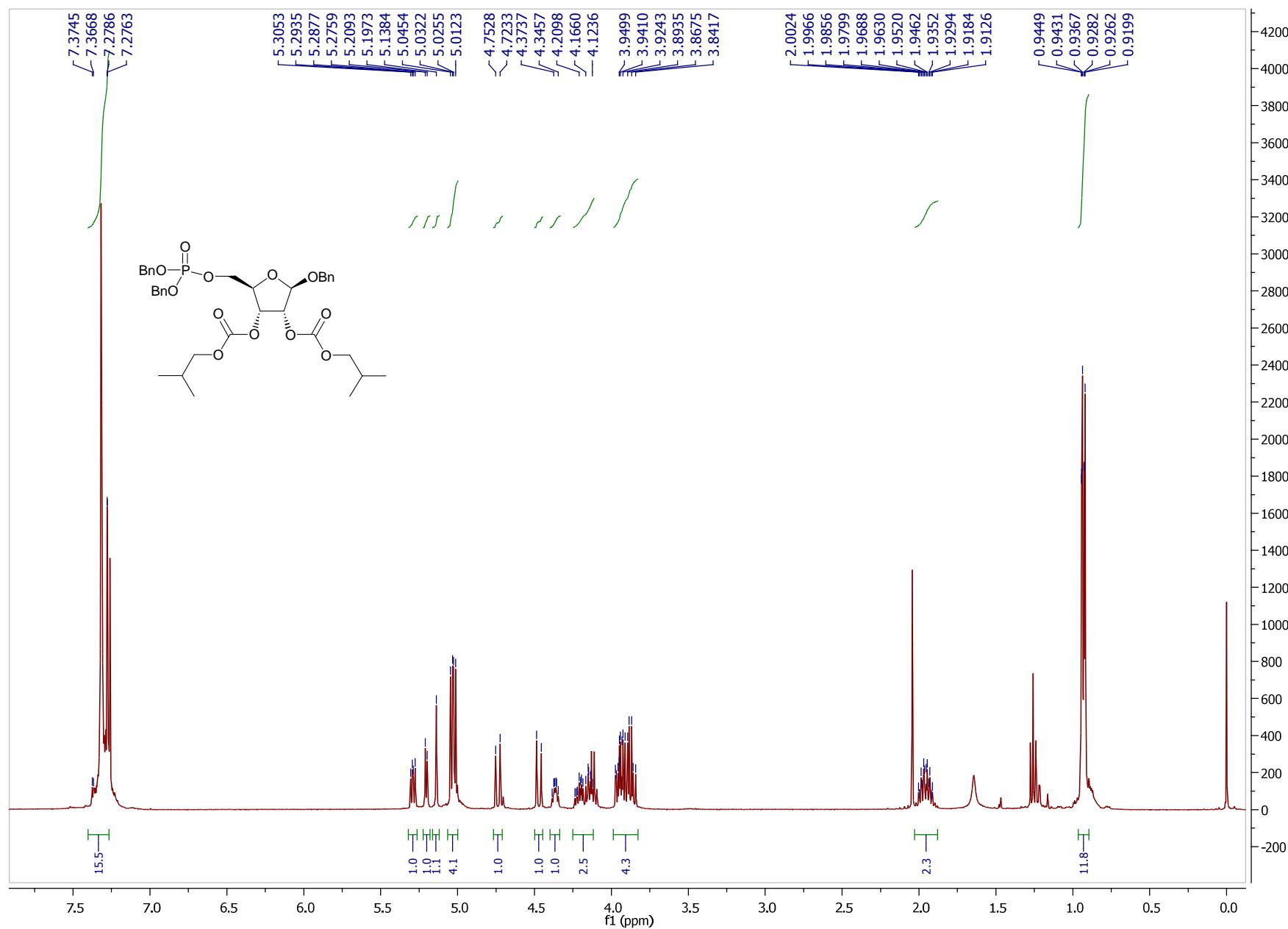
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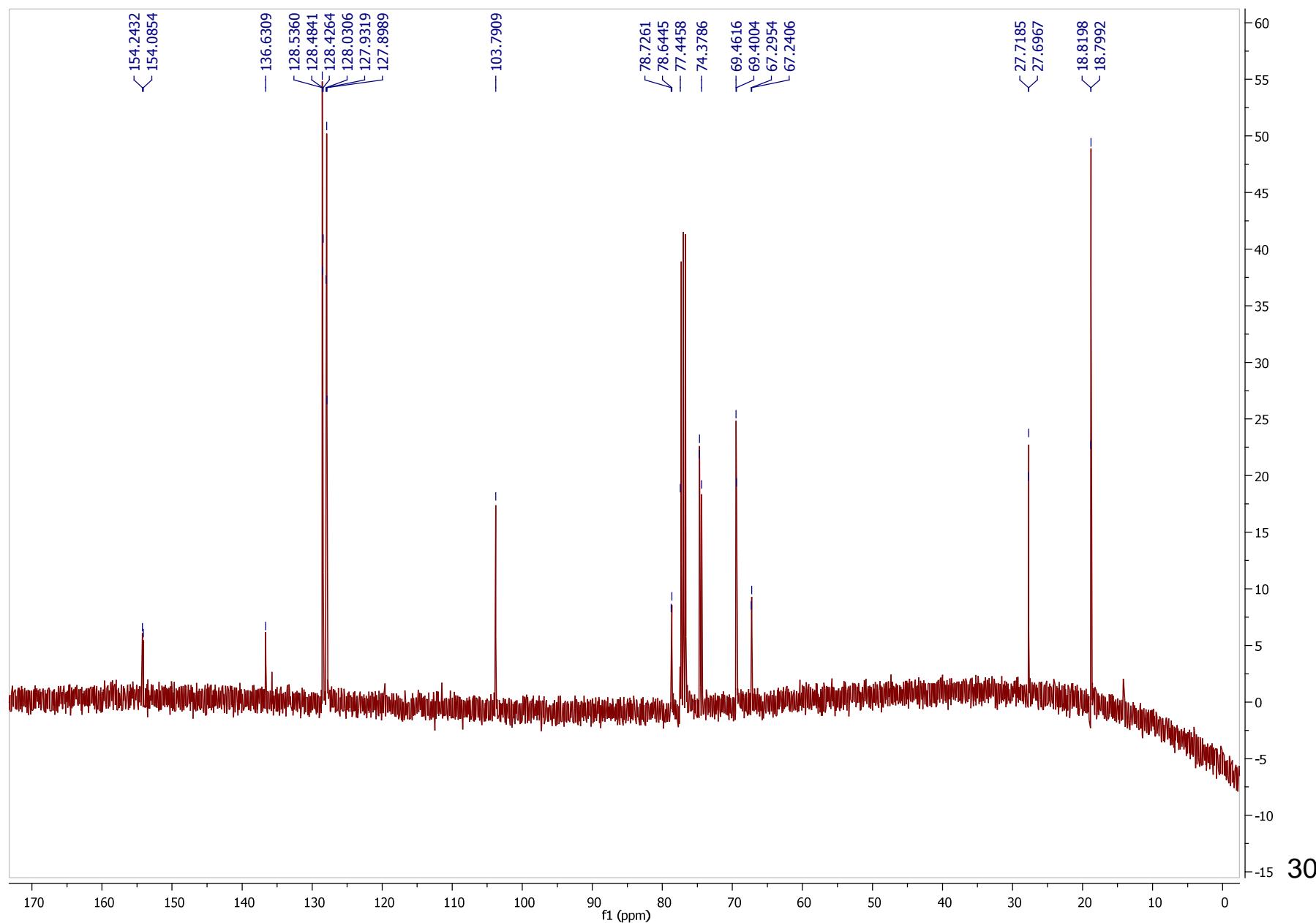
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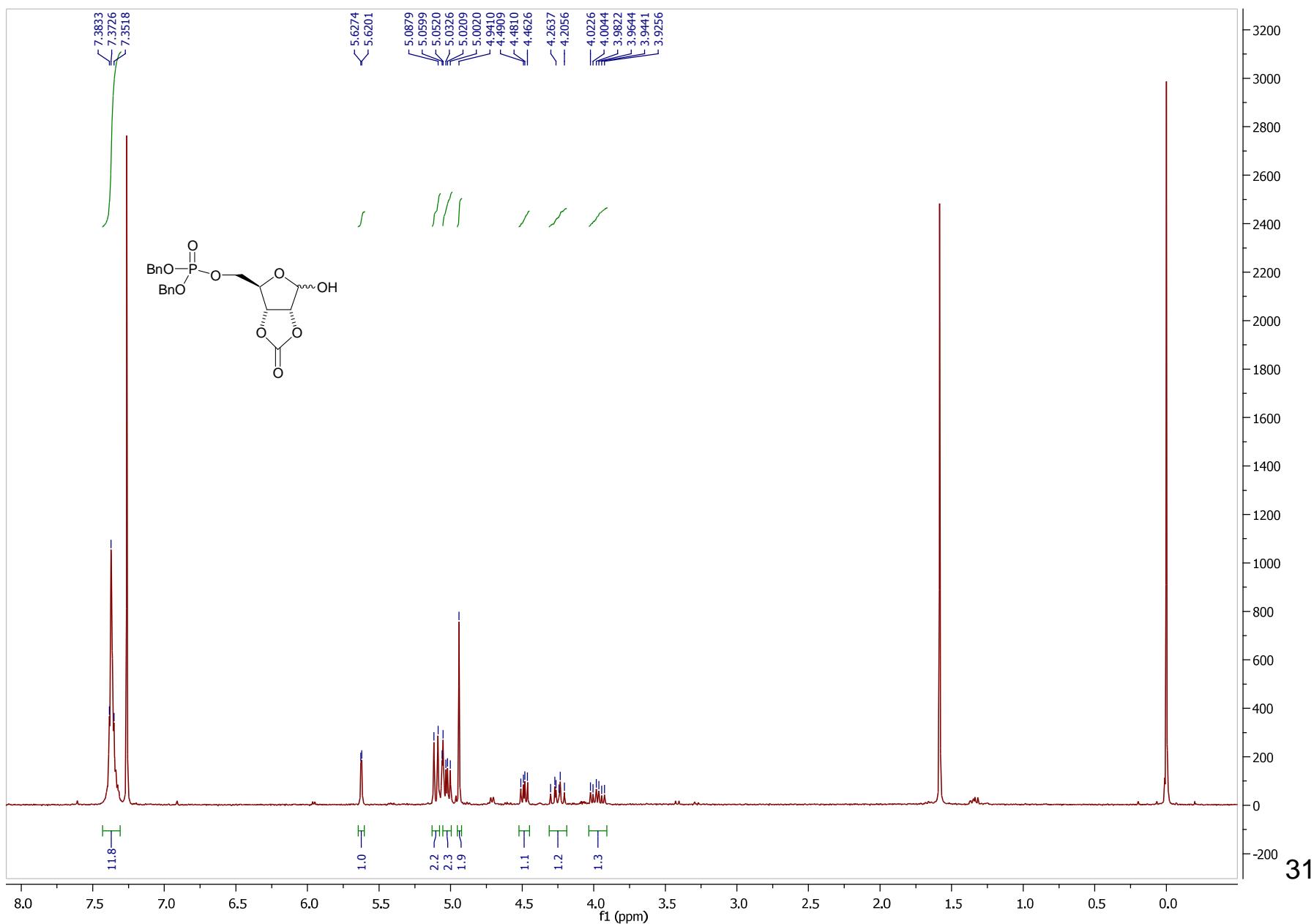
5-O-dibenzylphosphate-1-O-benzyl-2,3-O-bis(isobutylcarbonate)- $\beta$ -D-ribofuranoside **9c**:  $^1\text{H-NMR}$



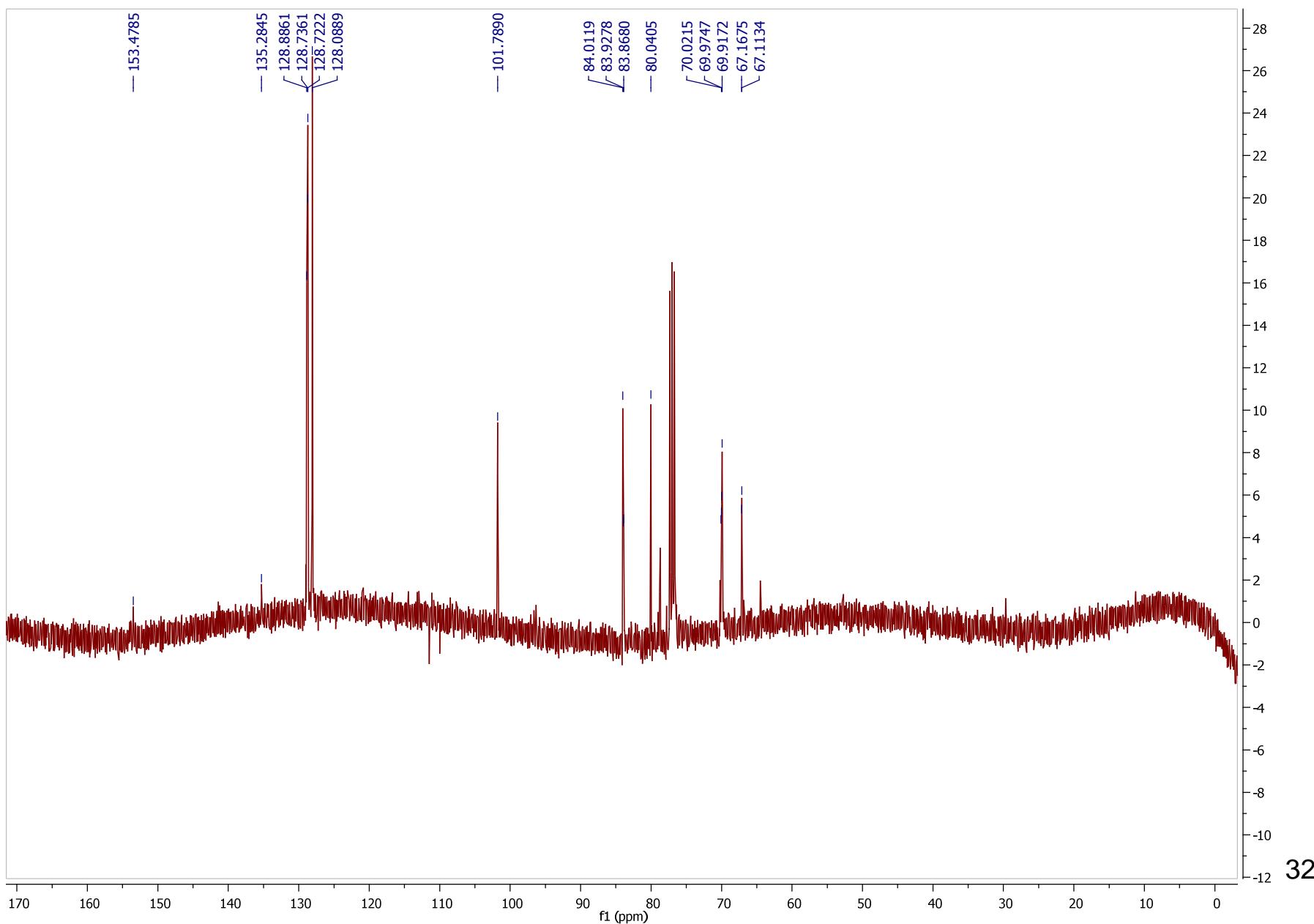
5-O-dibenzylphosphate-1-O-benzyl-2,3-O-bis(isobutylcarbonate)- $\beta$ -D-ribofuranoside **9c**:  $^1\text{H}$ -NMR



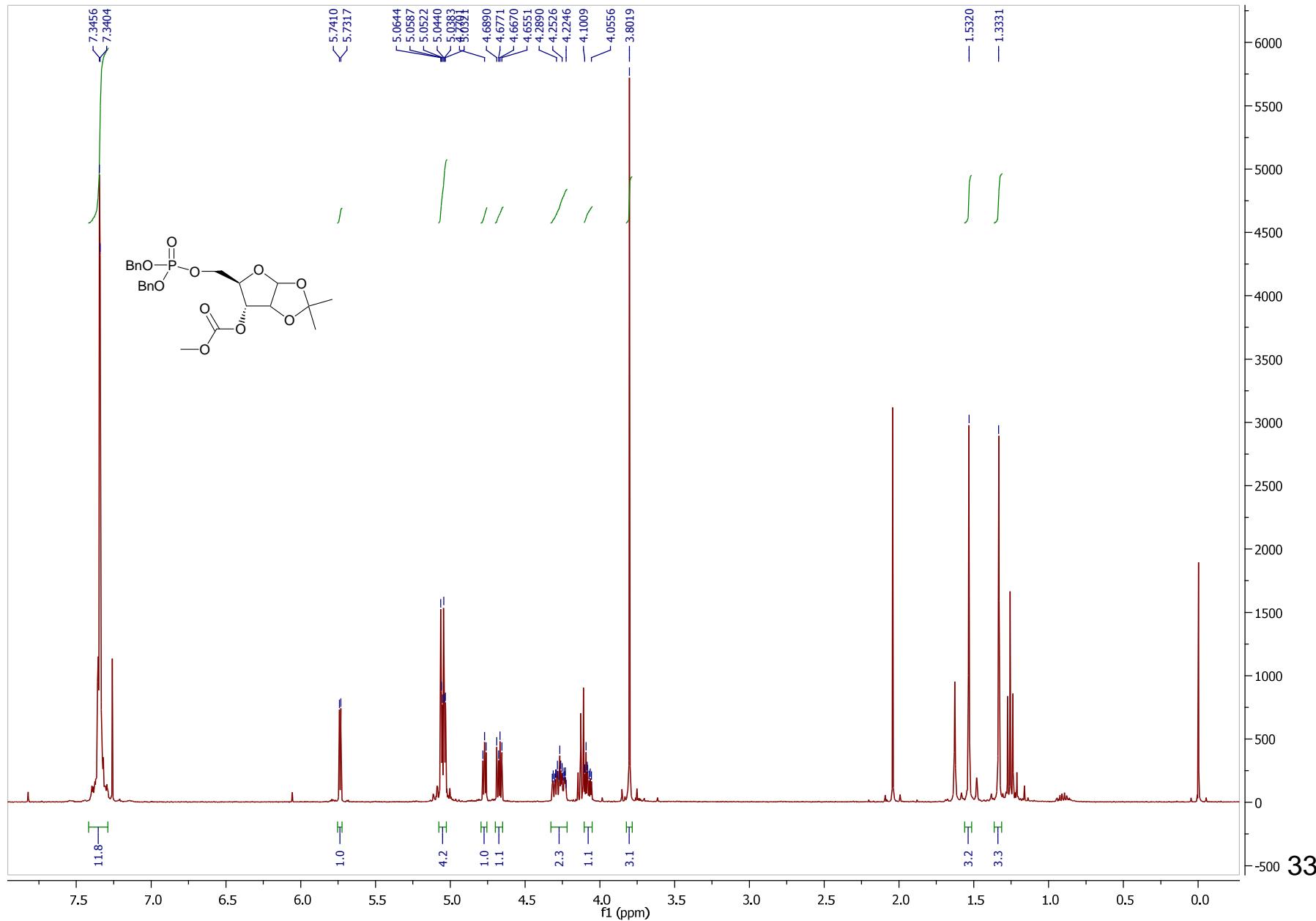
5-O-dibenzylphosphate-2,3-O-carbonate- $\beta$ -D-ribofuranose **9d**:  $^1\text{H}$ -NMR



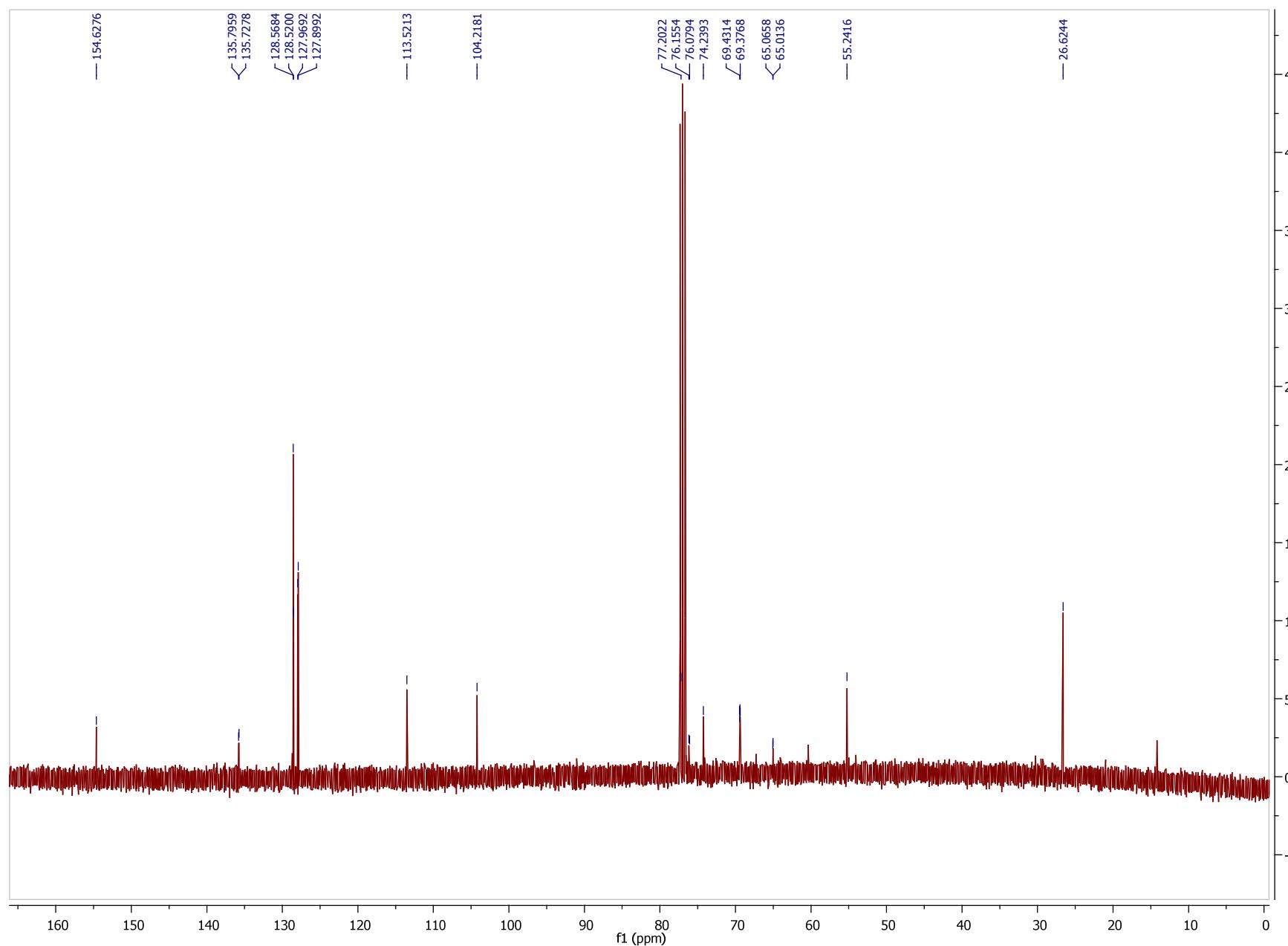
5-O-dibenzylphosphate-2,3-O-carbonate- $\beta$ -D-ribofuranose **9d**:  $^{13}\text{C}$ -NMR



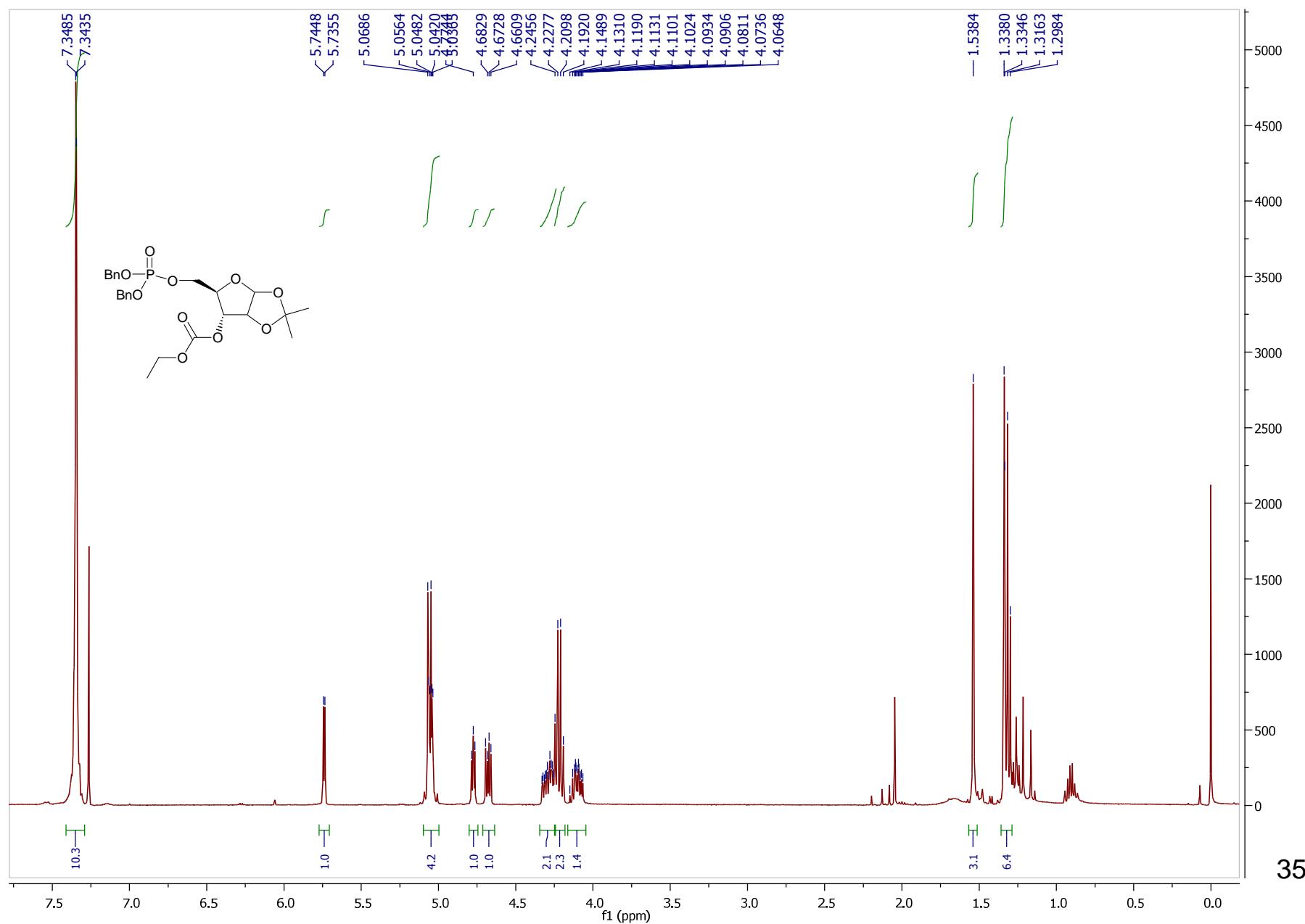
**5-O-dibenzylphosphate-1,2-O-isopropylidene-3-O-methylcarbonate- $\alpha$ -D-ribofuranoside 10a:**  $^1\text{H-NM}$



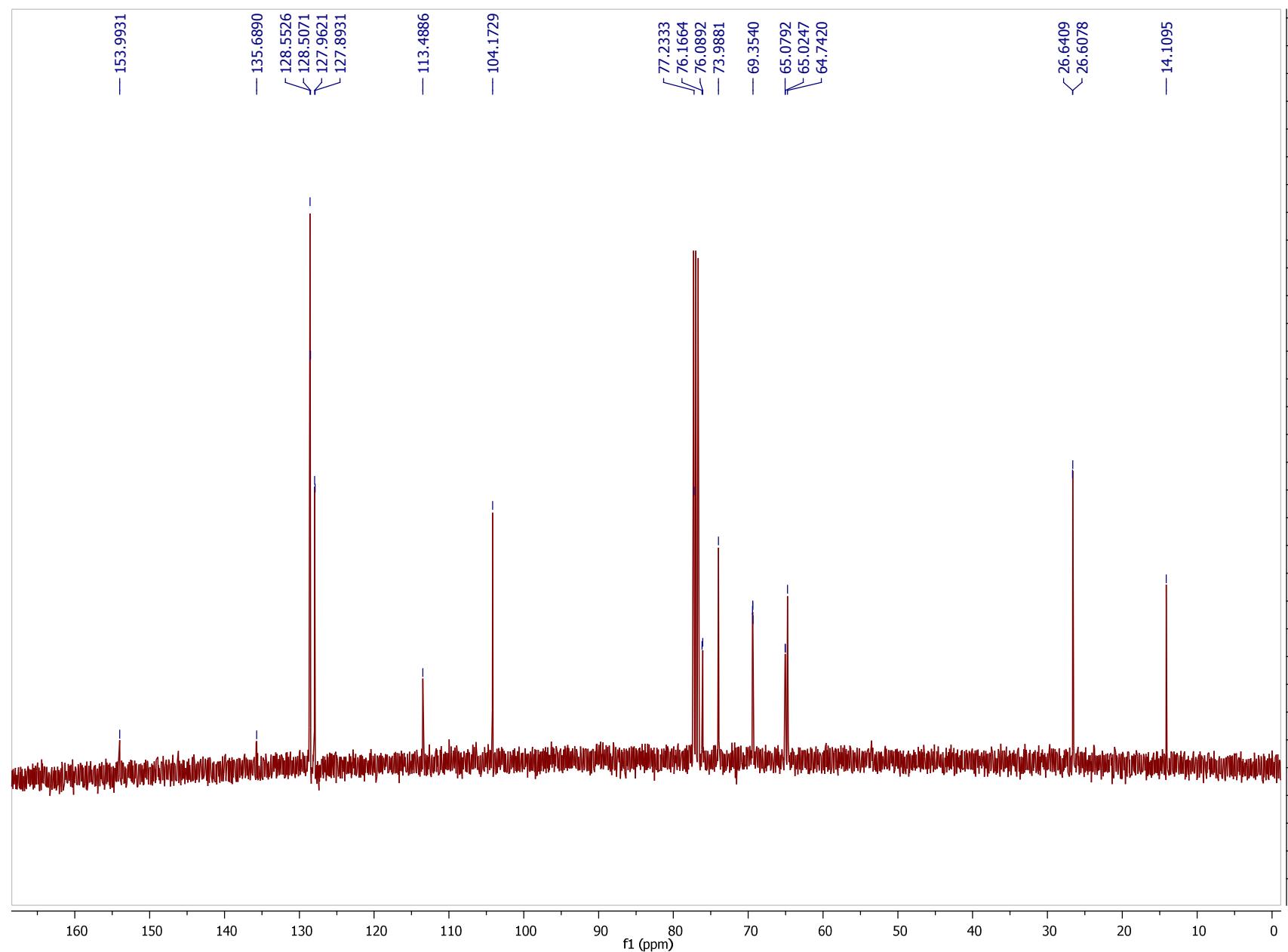
5-O-dibenzylphosphate-1,2-O-isopropylidene-3-O-methylcarbonate- $\alpha$ -D-ribofuranoside **10a**:  $^1\text{H}$ -NMR



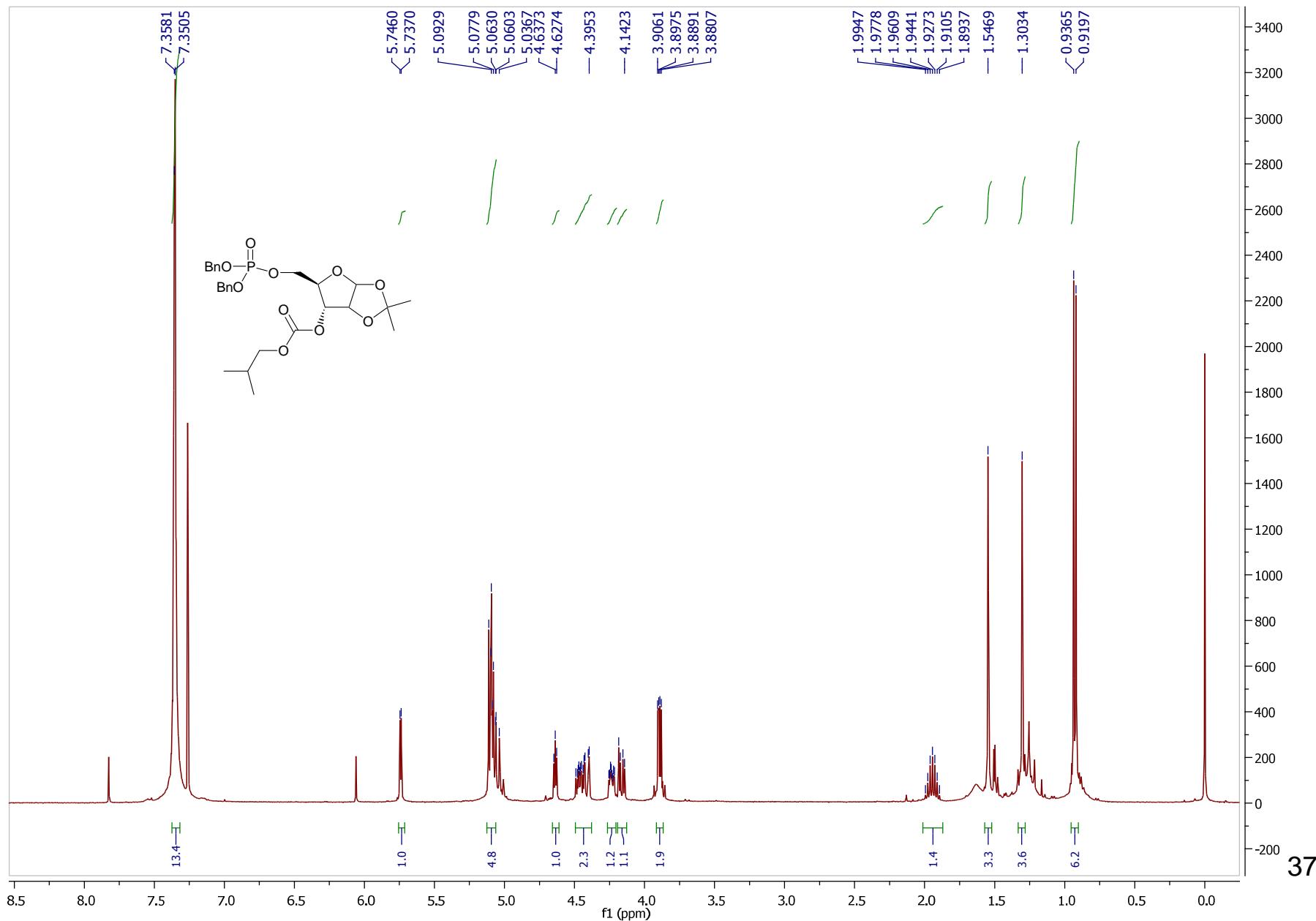
5-O-dibenzylphosphate-1,2-O-isopropylidene-3-O-ethylcarbonate- $\alpha$ -D-ribofuranoside **10b**:  $^1\text{H}$ -NMR



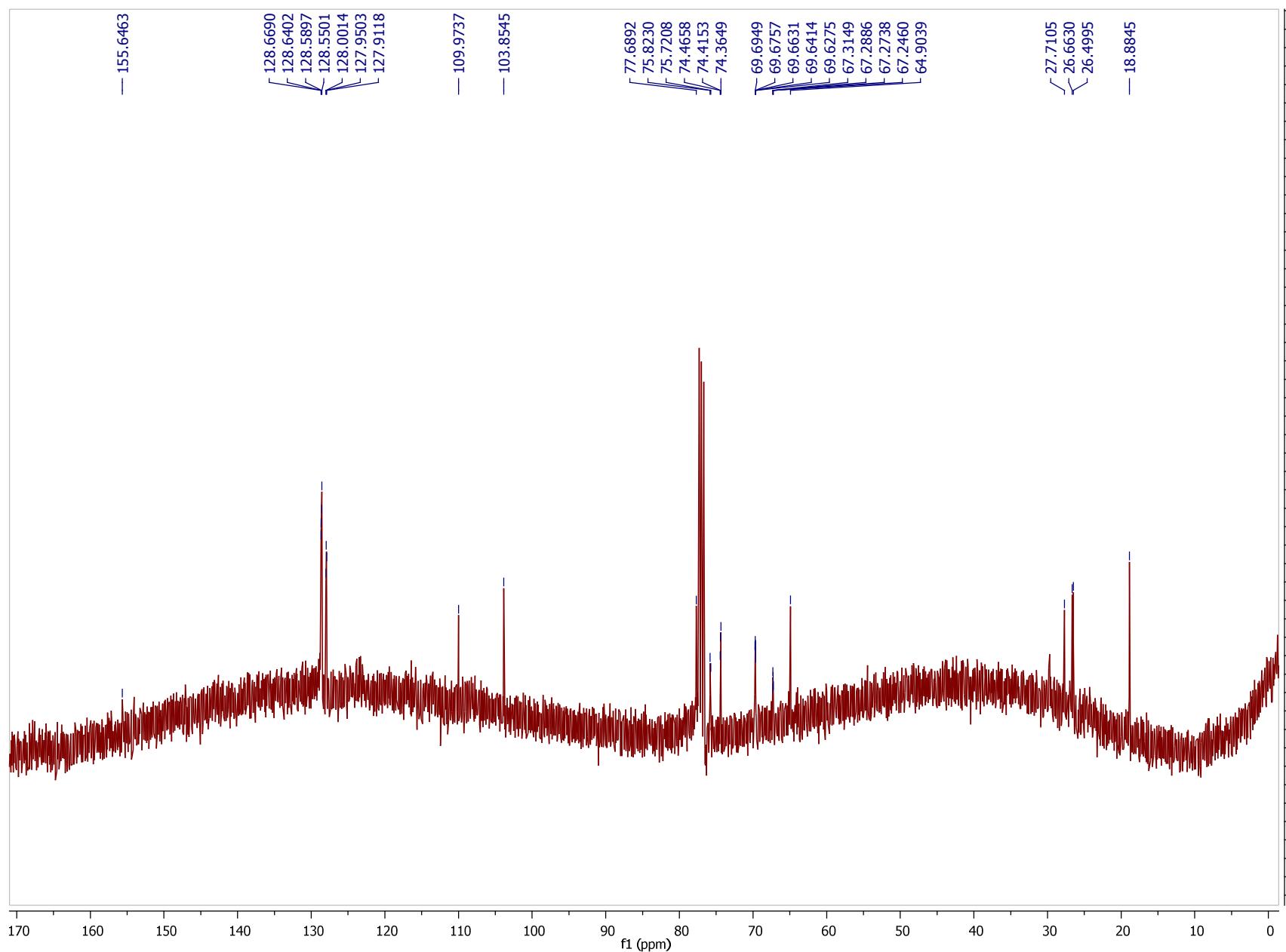
5-O-dibenzylphosphate-1,2-O-isopropylidene-3-O-ethylcarbonate- $\alpha$ -D-ribofuranoside **10b**:  $^{13}\text{C}$ -NMR



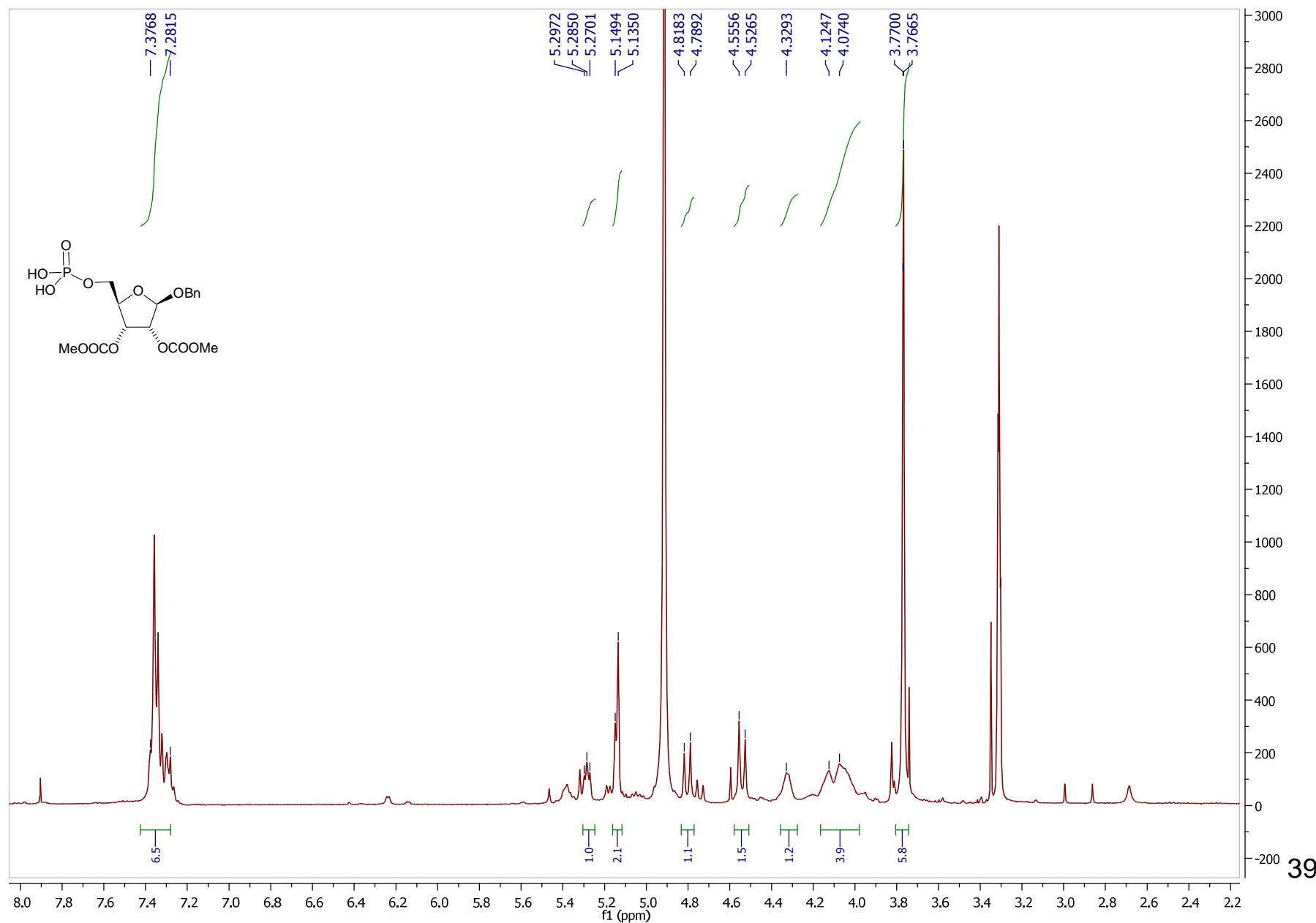
5-O-dibenzylphosphate-1,2-O-isopropylidene-3-O-isobutylcarbonate- $\alpha$ -D-ribofuranoside **10c**:  $^1\text{H}$ -NMR



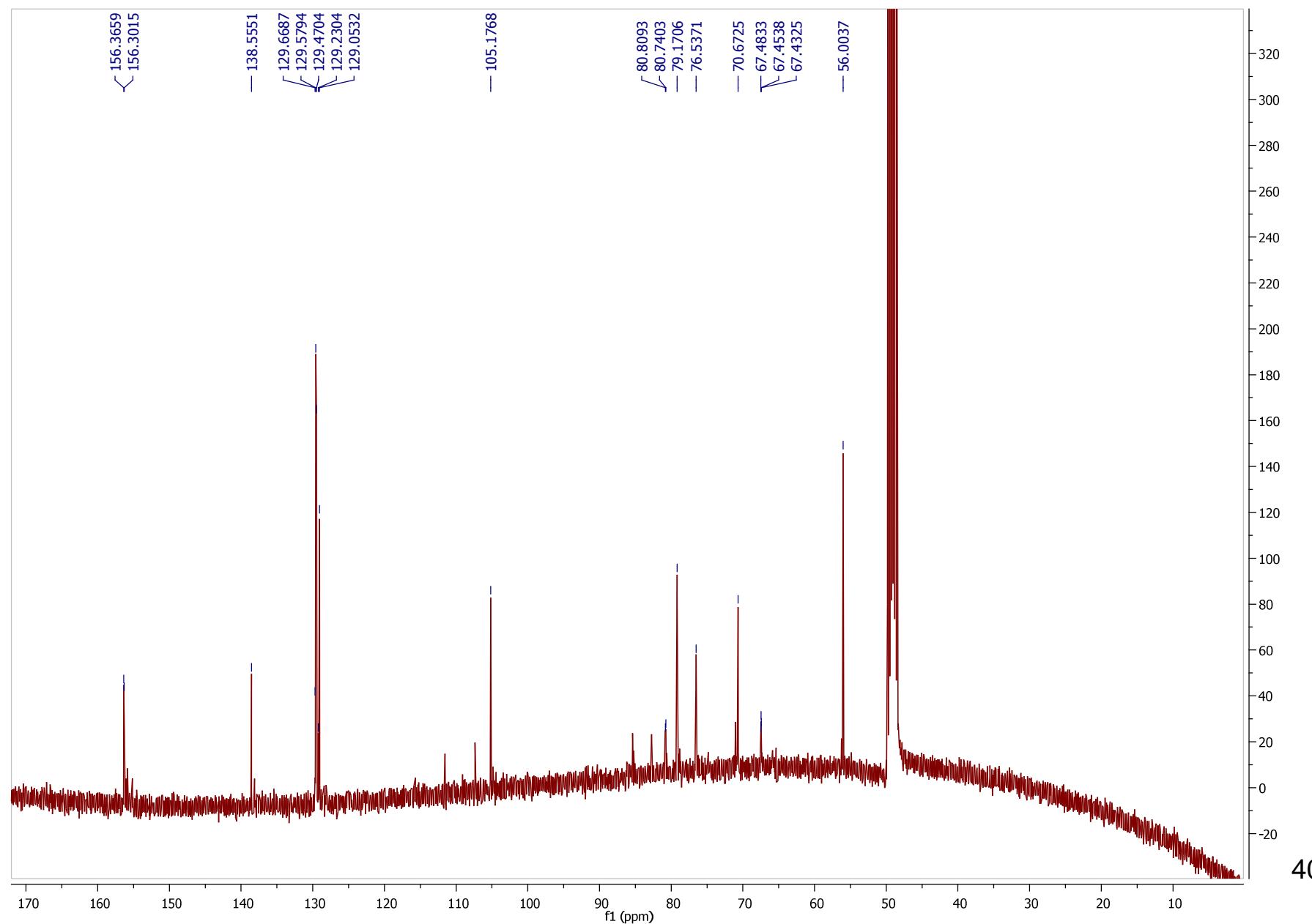
5-O-dibenzylphosphate-1,2-O-isopropylidene-3-O-isobutylcarbonate- $\alpha$ -D-ribofuranoside **10c**:  $^{13}\text{C}$ -NMR



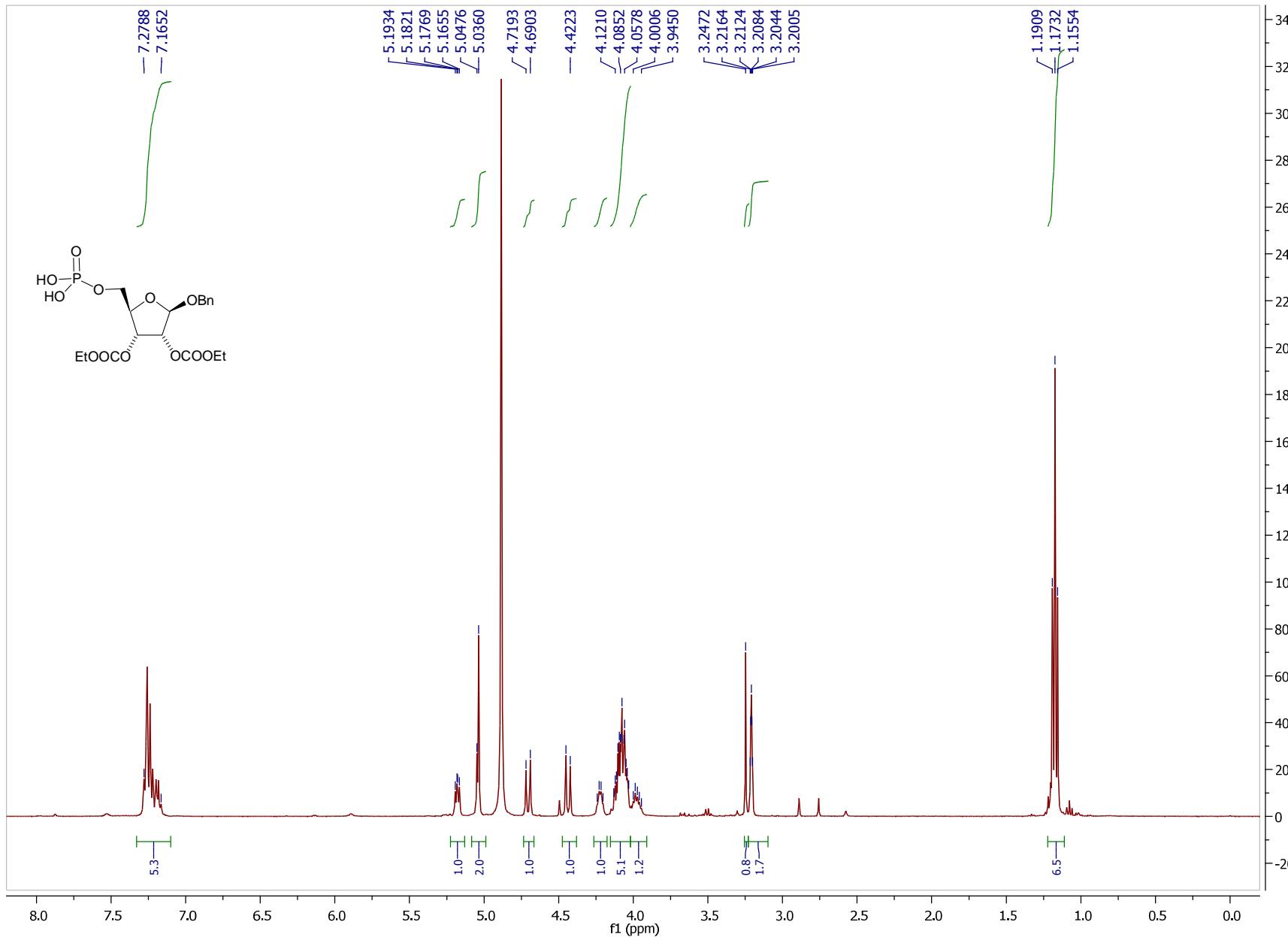
5-O-phosphate-1-O-benzyl-2,3-O-bis(methylcarbonate)- $\beta$ -D-ribofuranoside **12a**:  $^1\text{H}$ -NMR



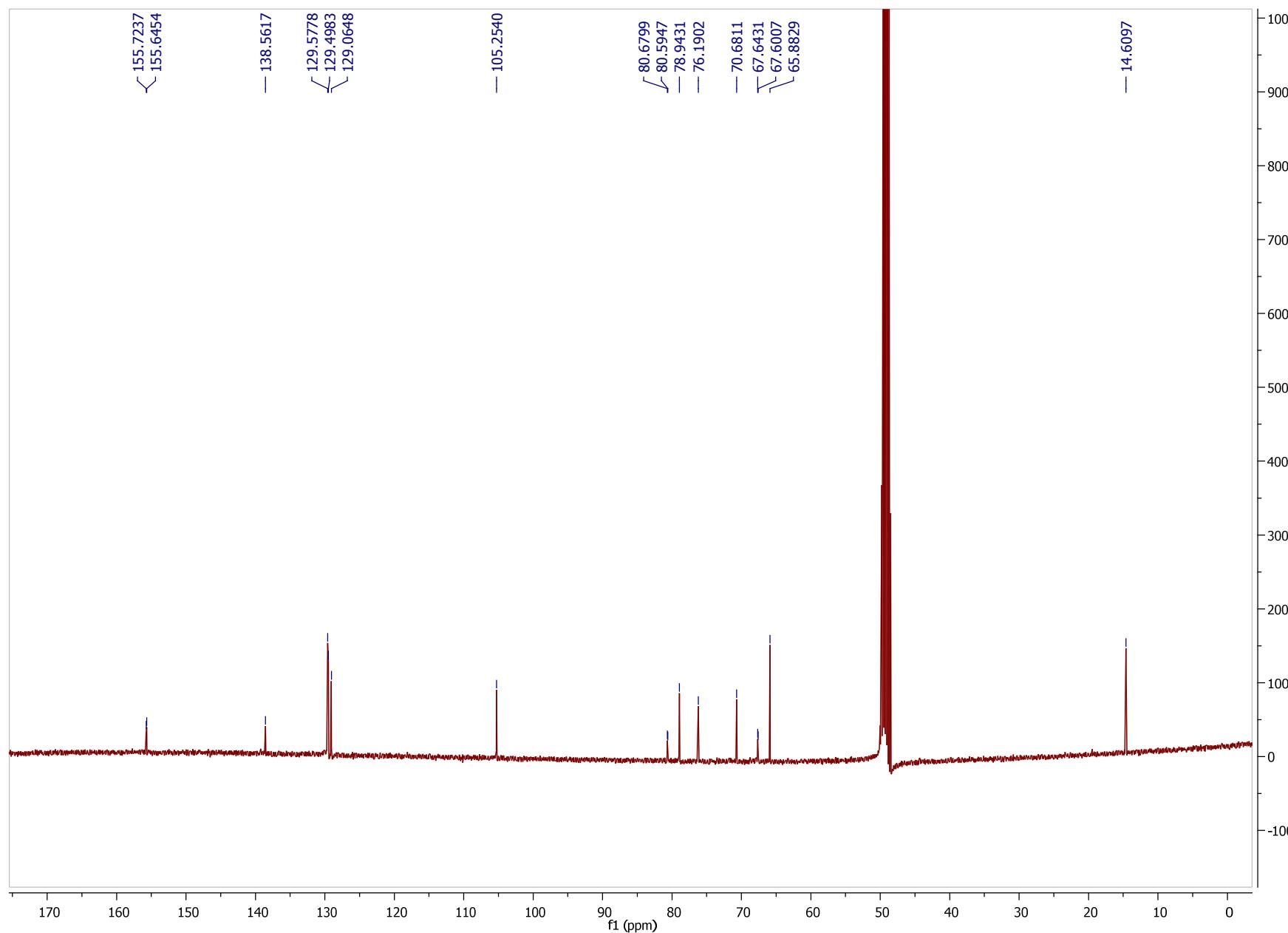
5-O-phosphate-1-O-benzyl-2,3-O-bis(methylcarbonate)- $\beta$ -D-ribofuranoside **12a**:  $^{13}\text{C}$ -NMR



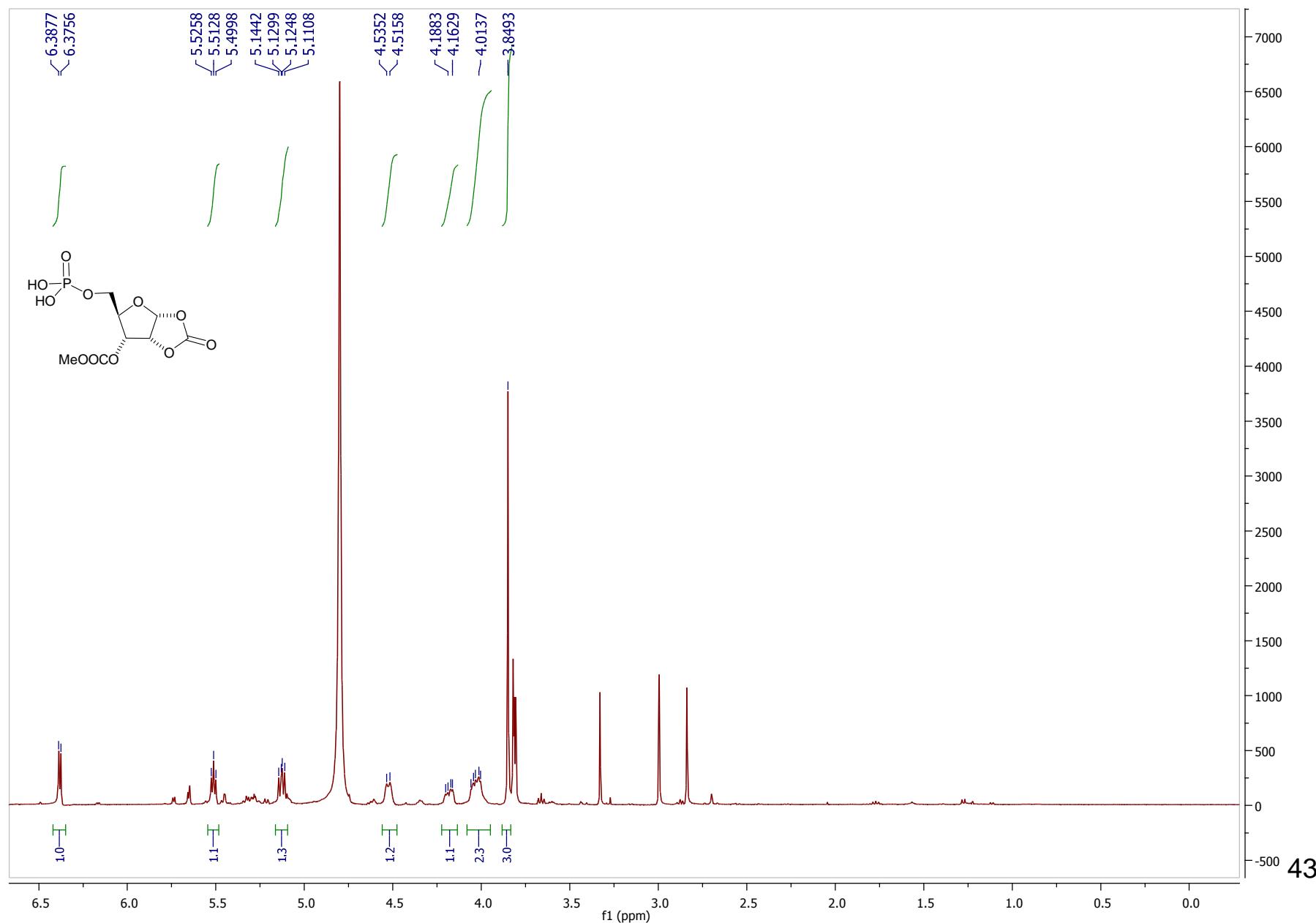
**5-O-phosphate-1-O-benzyl-2,3-O-bis(ethylcarbonate)- $\beta$ -D-ribofuranoside 12b:  $^1\text{H}$ -NMR**



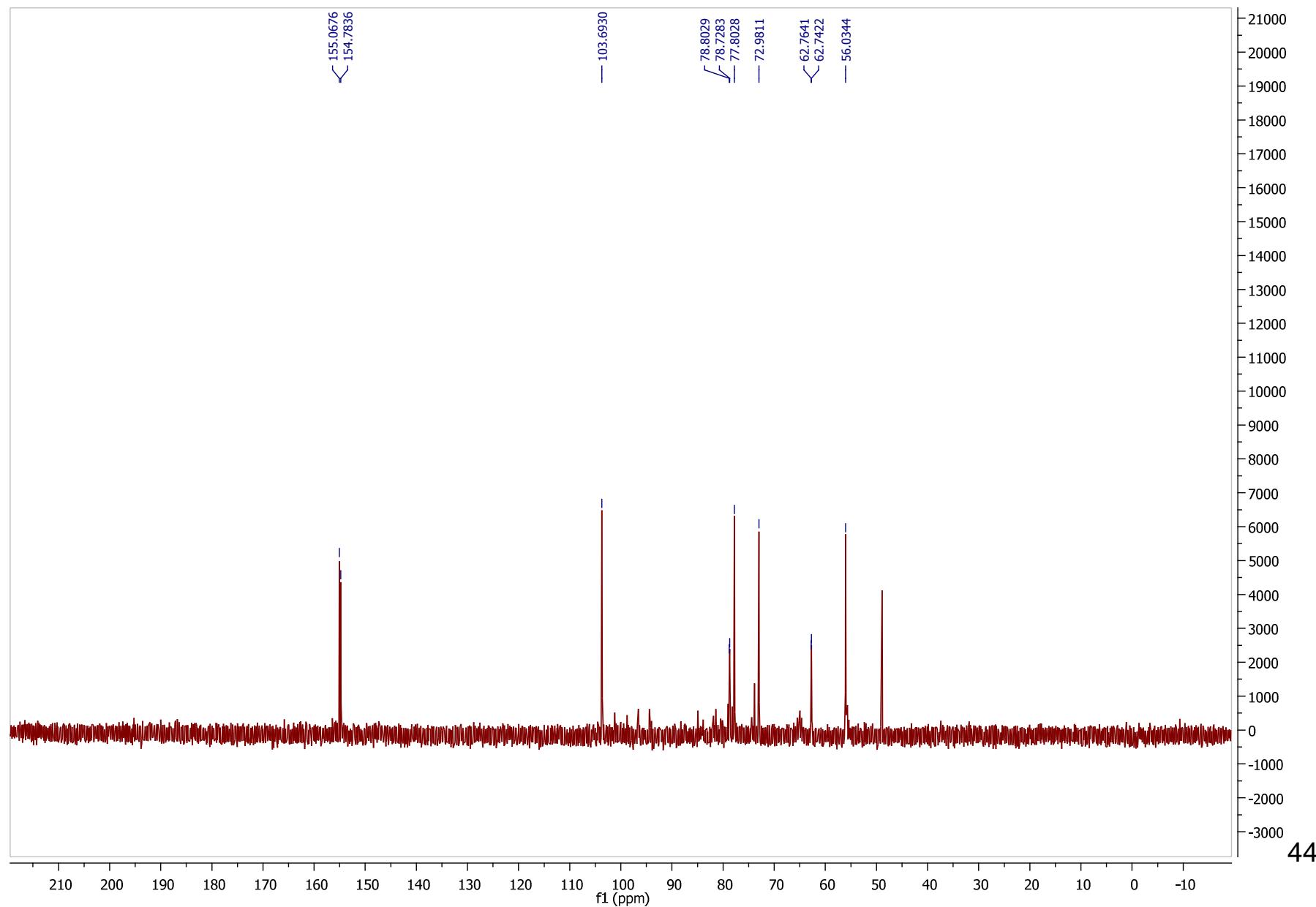
5-O-phosphate-1-O-benzyl-2,3-O-bis(ethylcarbonate)- $\beta$ -D-ribofuranoside **12b**:  $^{13}\text{C}$ -NMR



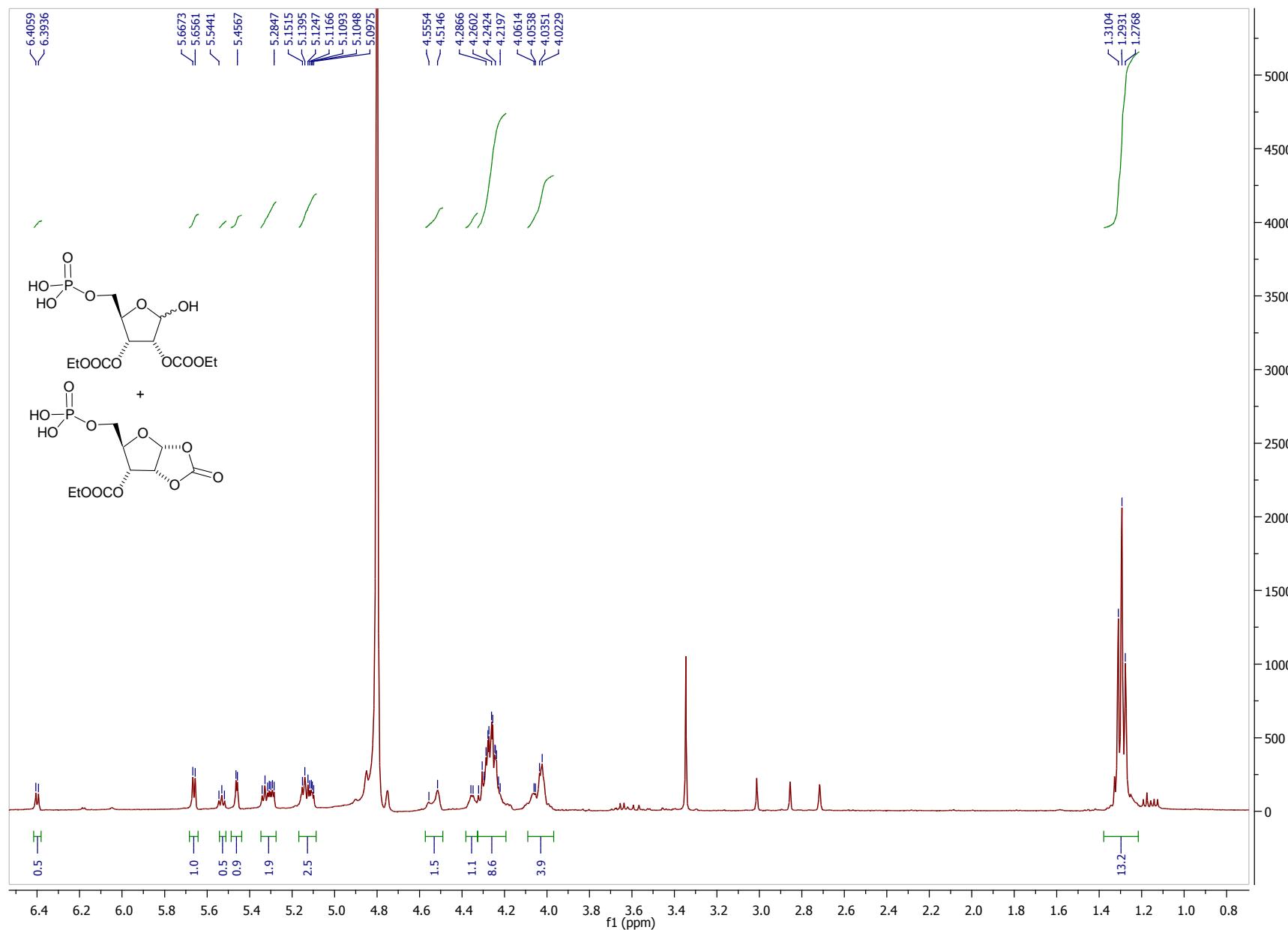
5-O-phosphate-1,2-O-carbonate-3-O-methylcarbonate- $\beta$ -D-ribofuranoside **15a**:  $^1\text{H}$ -NMR



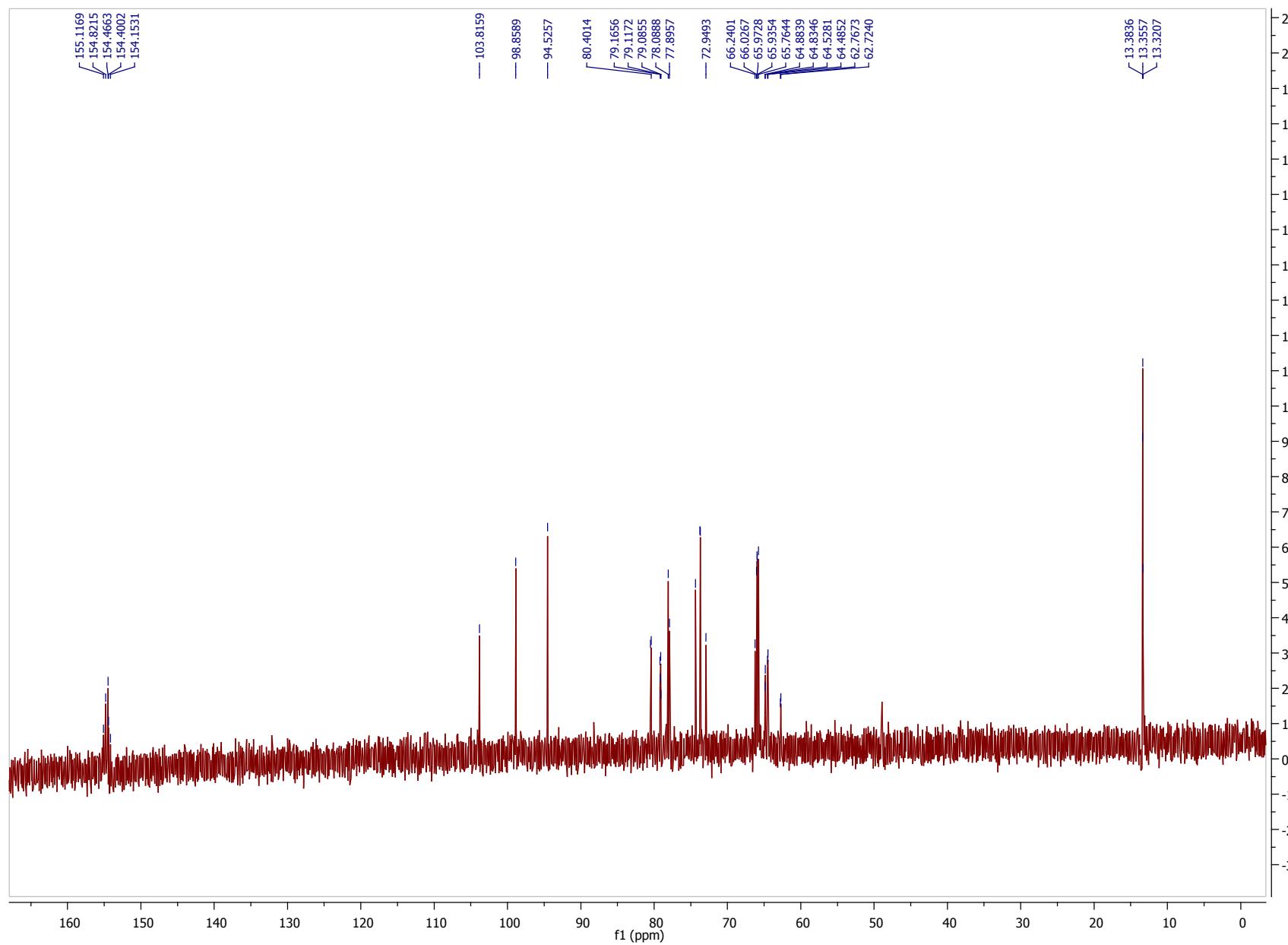
5-O-phosphate-1,2-O-carbonate-3-O-methylcarbonate- $\beta$ -D-ribofuranoside **15a**:  $^{13}\text{C}$ -NMR



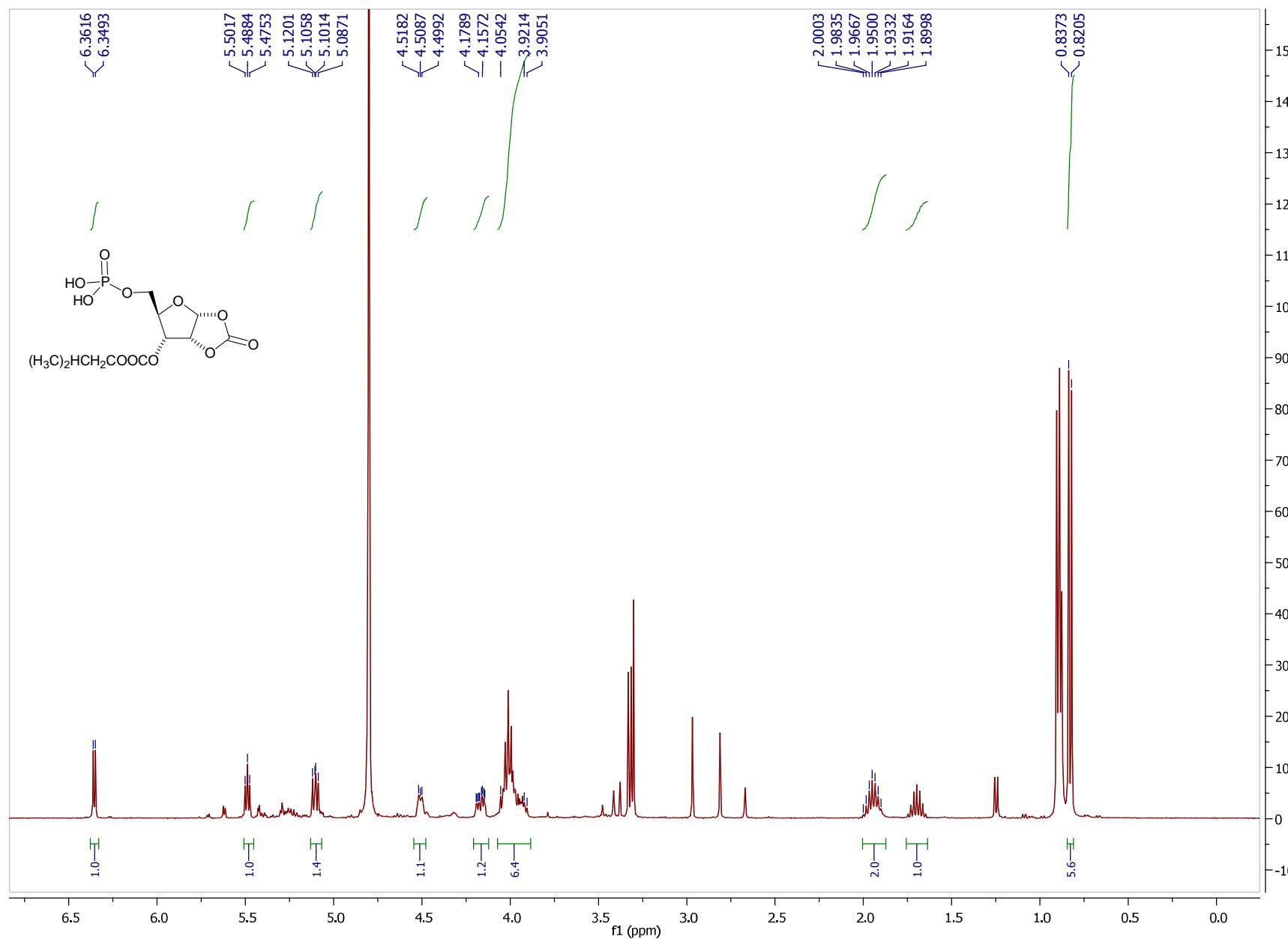
**5-O-phosphate-2,3-O-bis(ethylcarbonate)-D-ribofuranoside 13b** in  $\alpha$ - (A) and  $\beta$ - (B) form,  
**and 5-O-phosphate-1,2-O-carbonate-3-O-ethylcarbonate- $\beta$ -D-ribofuranoside 15b:**  $^1\text{H-NMR}$



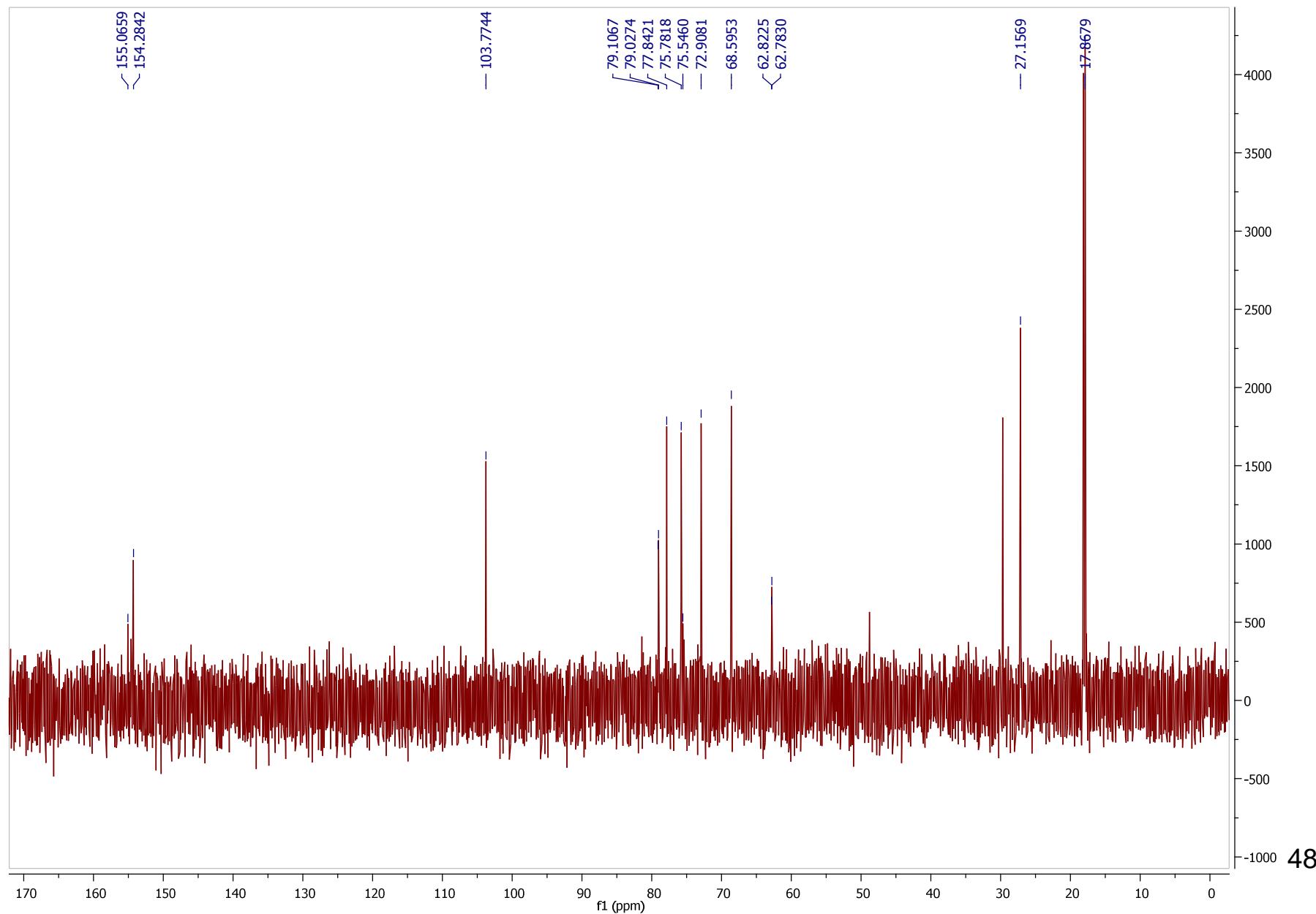
5-O-phosphate-2,3-O-bis(ethylcarbonate)-D-ribofuranoside **13b** in  $\alpha$ - (A) and  $\beta$ - (B) form,  
and 5-O-phosphate-1,2-O-carbonate-3-O-ethylcarbonate- $\beta$ -D-ribofuranoside **15b**:  $^{13}\text{C}$ -NMR



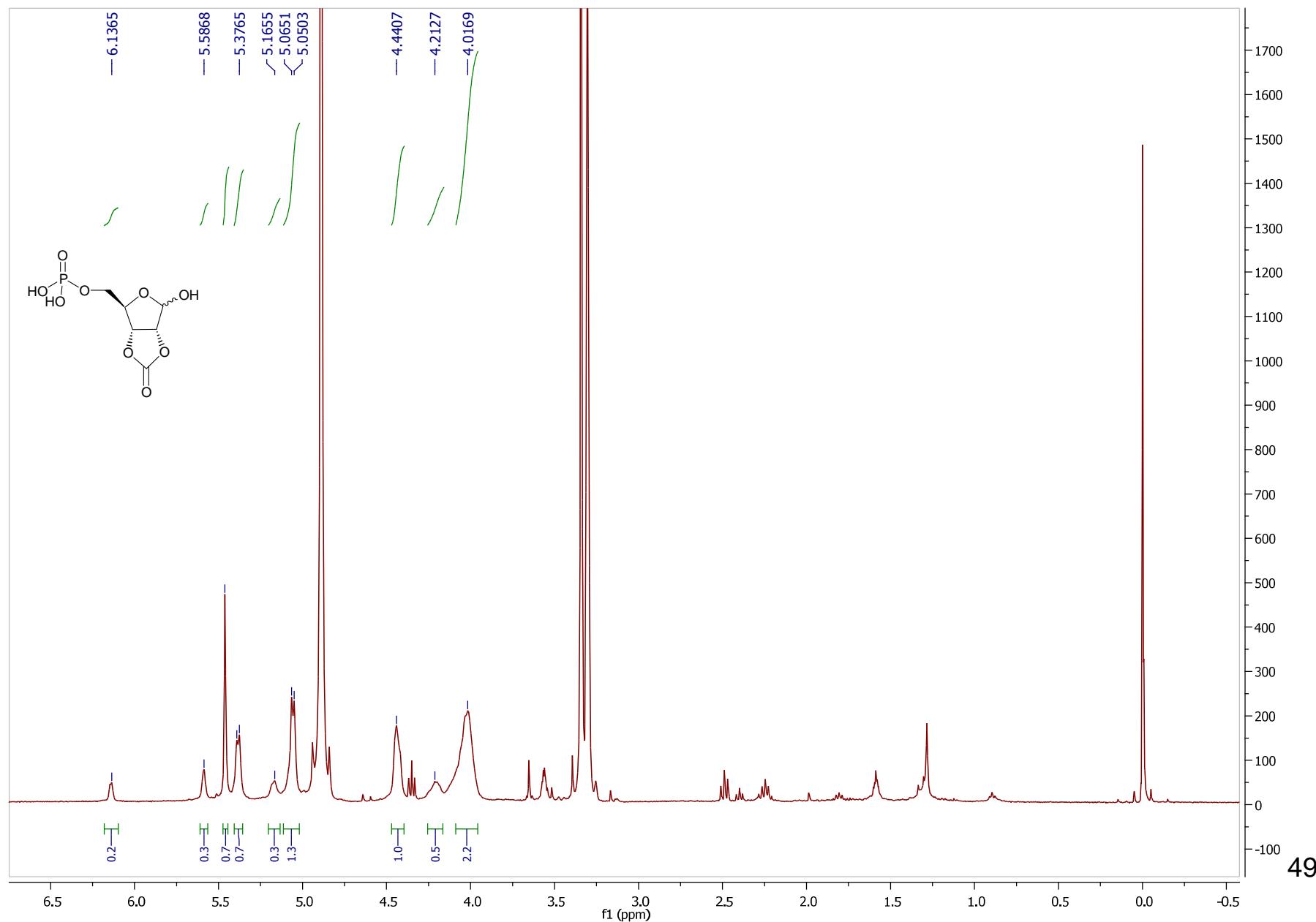
5-O-phosphate-1,2-O-carbonate-3-O-isobutylcarbonate- $\beta$ -D-ribofuranoside 15c:  $^1\text{H}$ -NMR



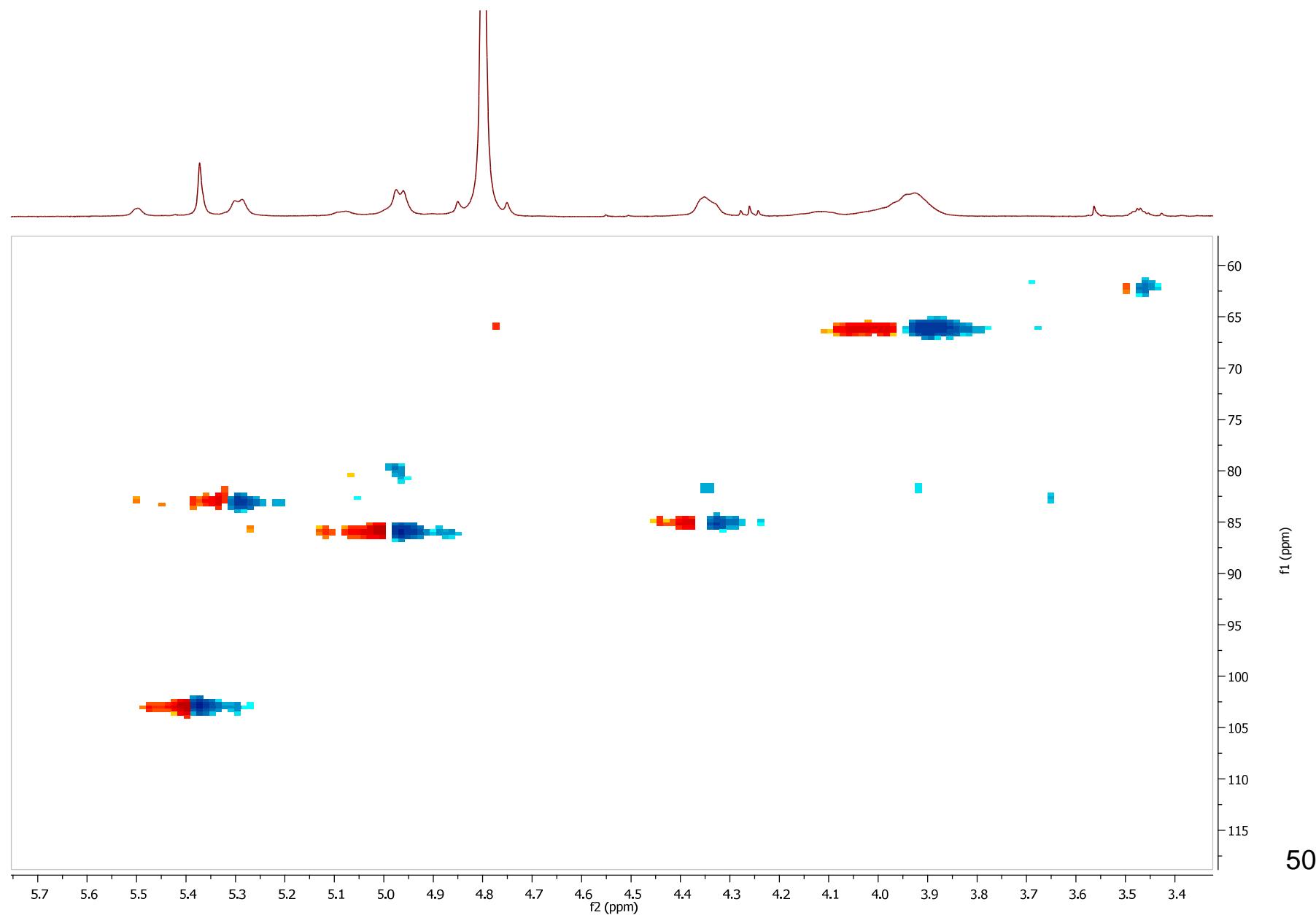
**5-O-phosphate-1,2-O-carbonate-3-O-isobutylcarbonate- $\beta$ -D-ribofuranoside 15c:  $^{13}\text{C}$ -NMR**



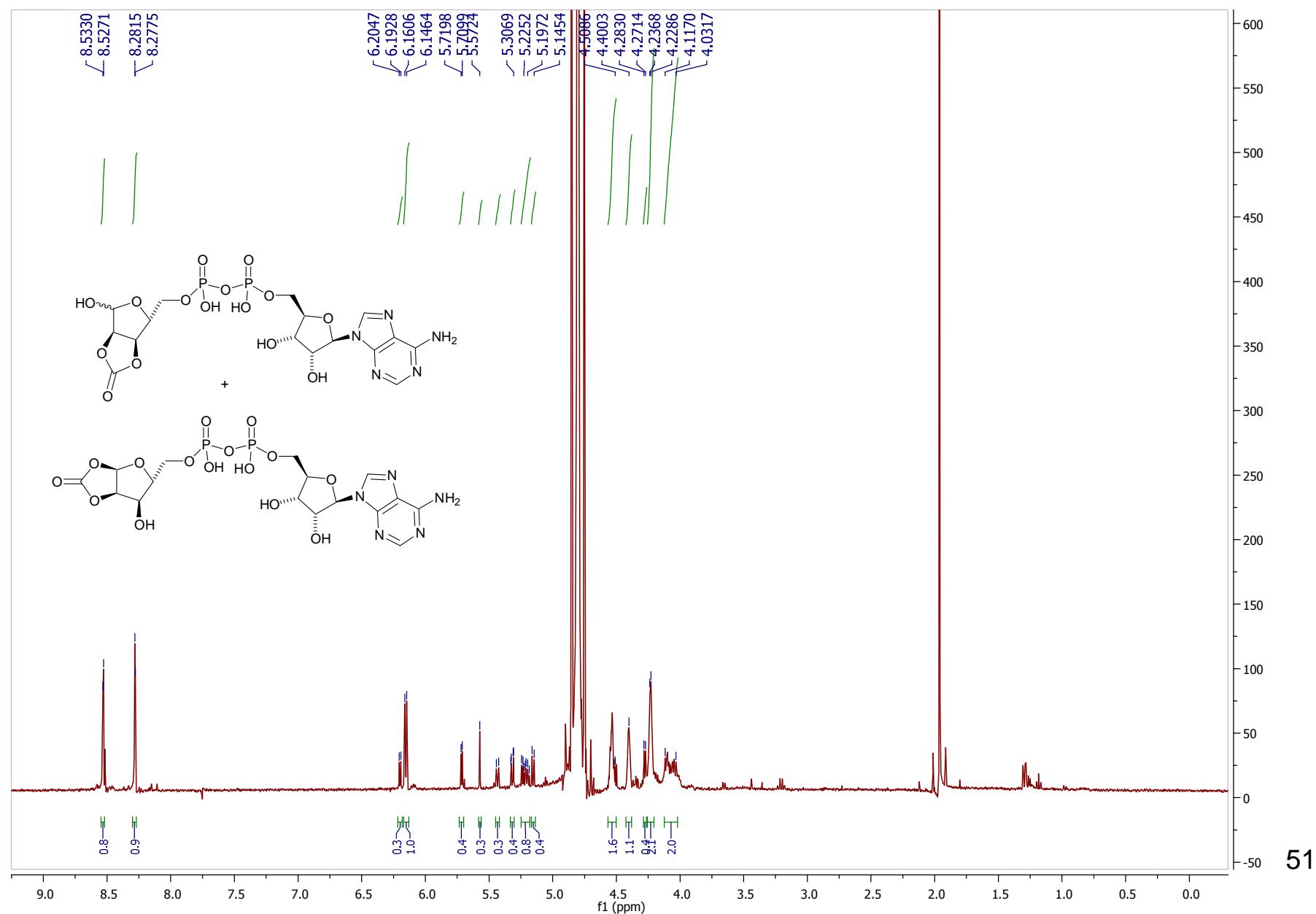
5-O-phosphate-2,3-O-carbonate- $\beta$ -D-ribofuranose 11d:  $^1\text{H}$ -NMR



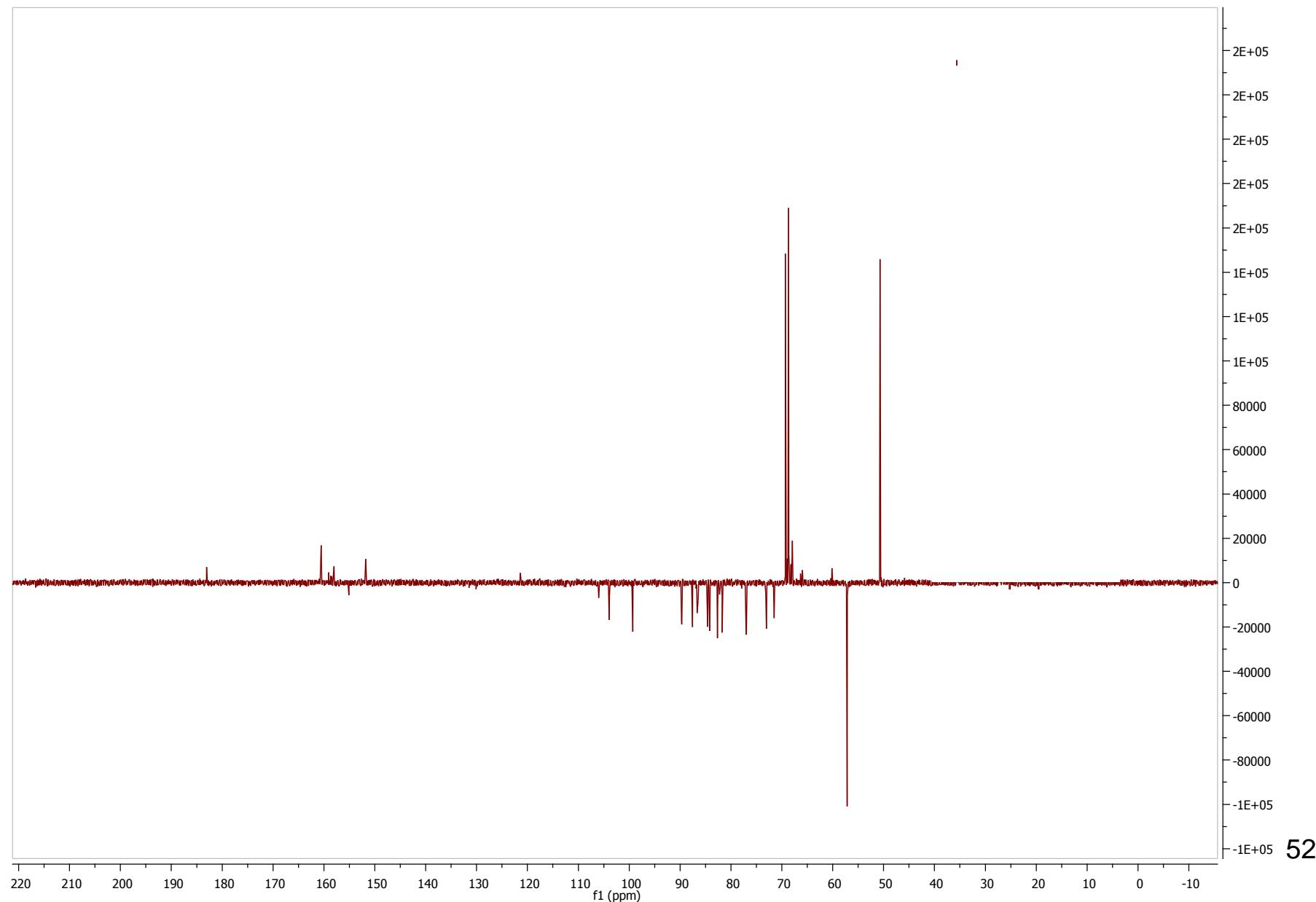
5-O-phosphate-2,3-O-carbonate- $\beta$ -D-ribofuranose 11d: HSQC



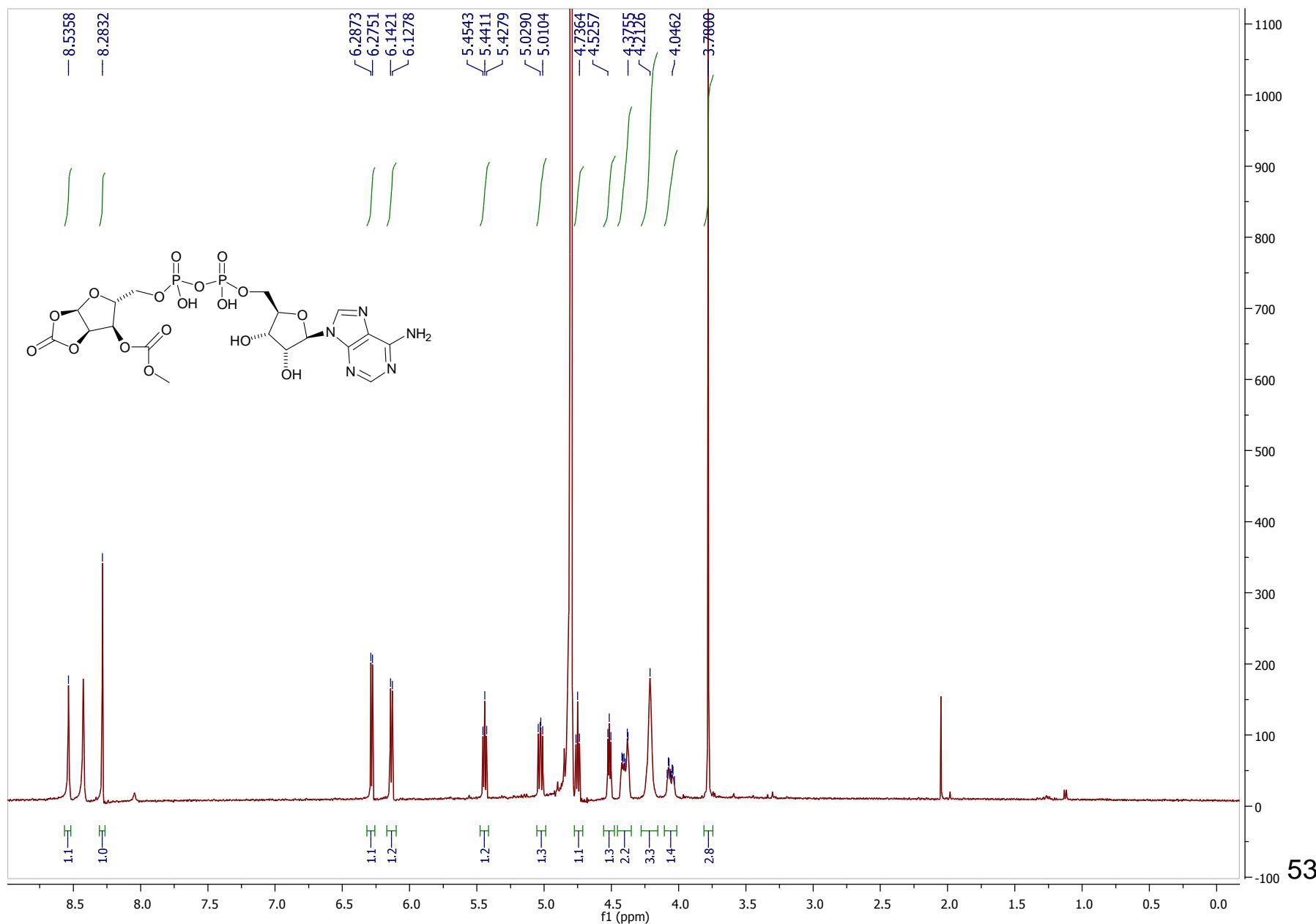
2',3'-O-carbonate-ADP-ribose **13d** ( $\alpha$ - and  $\beta$ -anomers) + 1',2'-O-carbonate-ADP-riboside **13e**:  $^1\text{H}$ -NMR



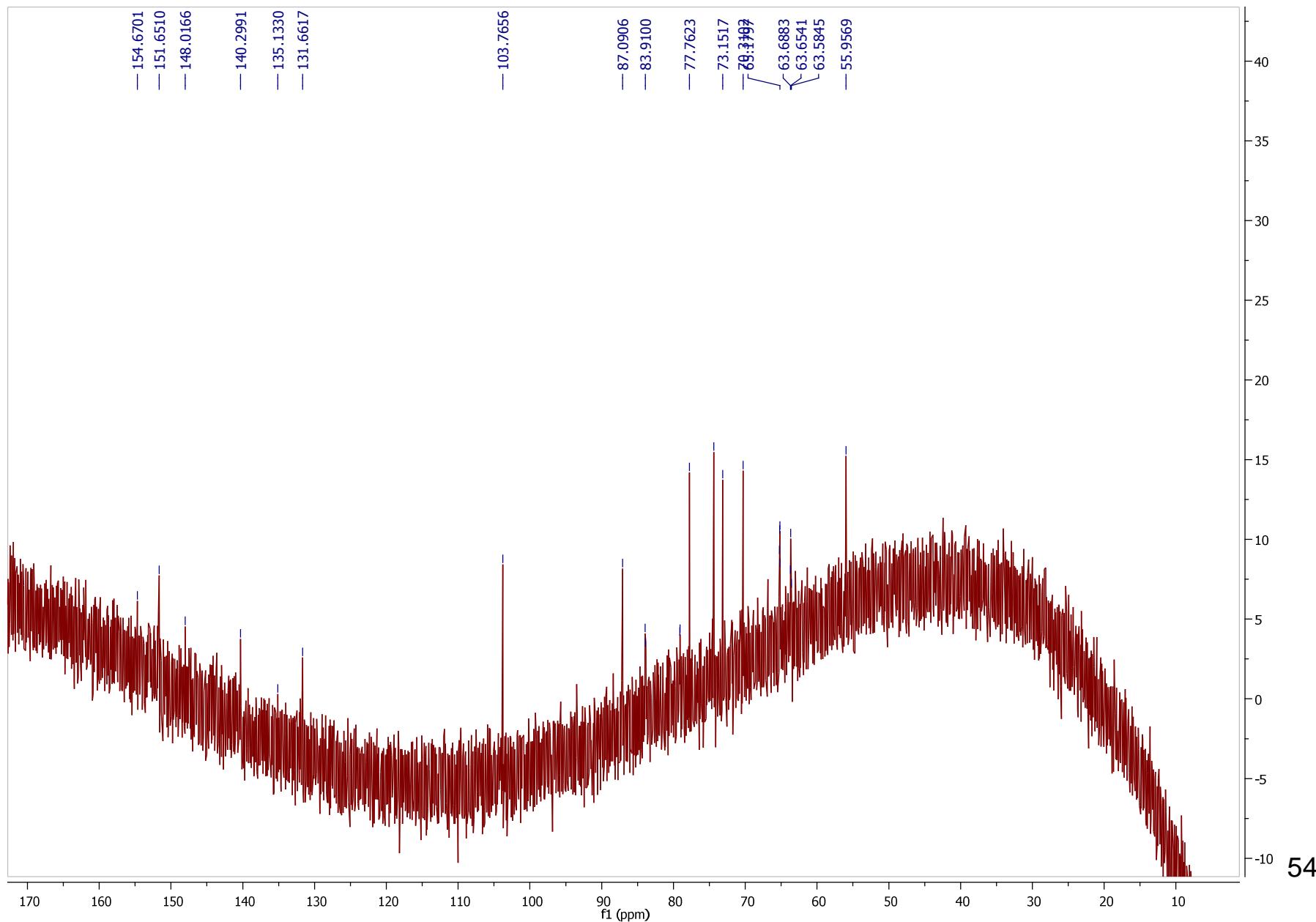
**2',3'-O-carbonate-ADP-ribose 13d ( $\alpha$ - and  $\beta$ -anomers) + 1',2'-O-carbonate-ADP-ribofuranose 13e:  $^{13}\text{C}$ -NMR**



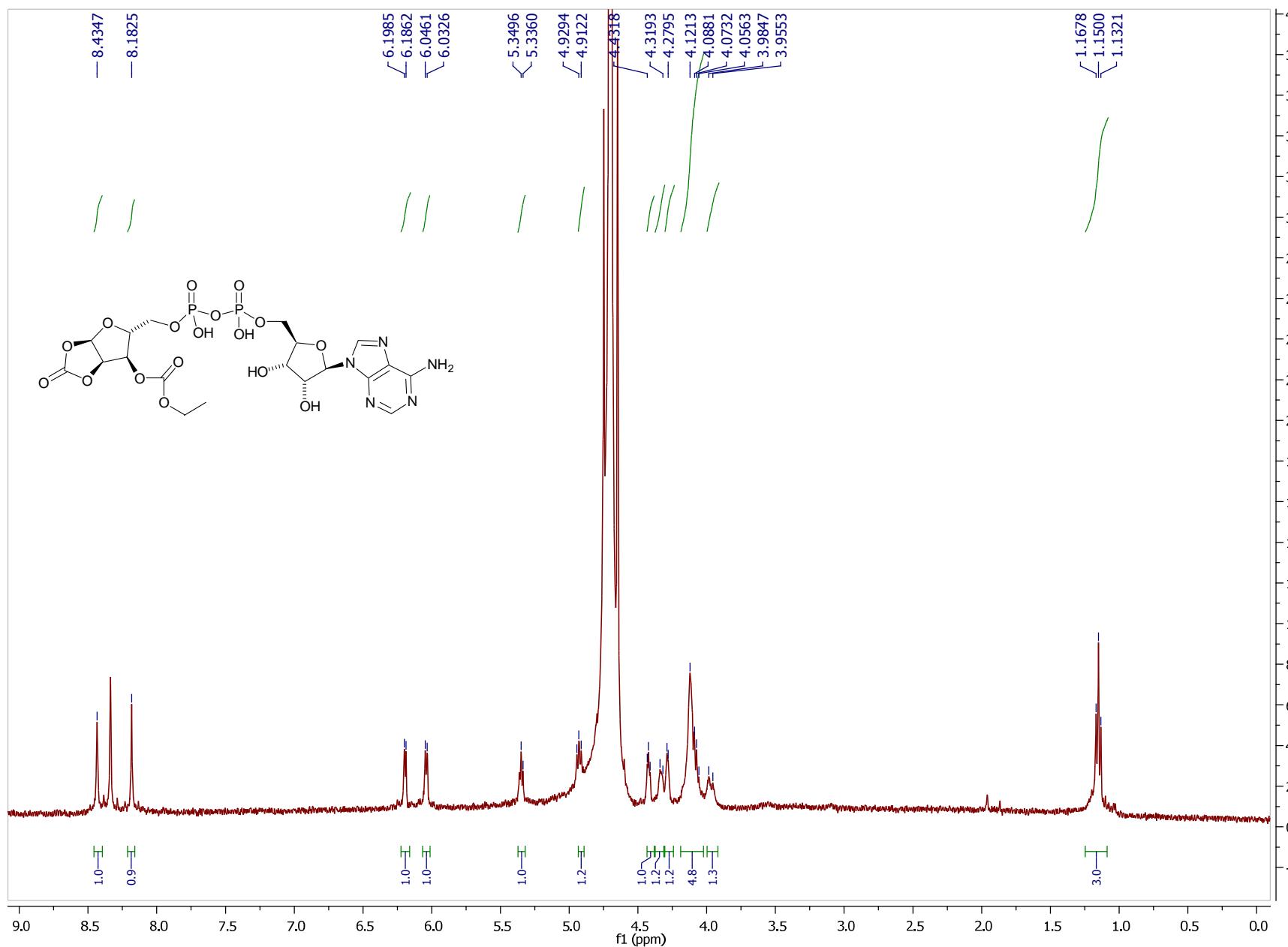
**1',2'-O-carbonate-3'-O-methylcarbonate-ADP-ribofuranoside 16a:  $^1\text{H}$ -NMR**



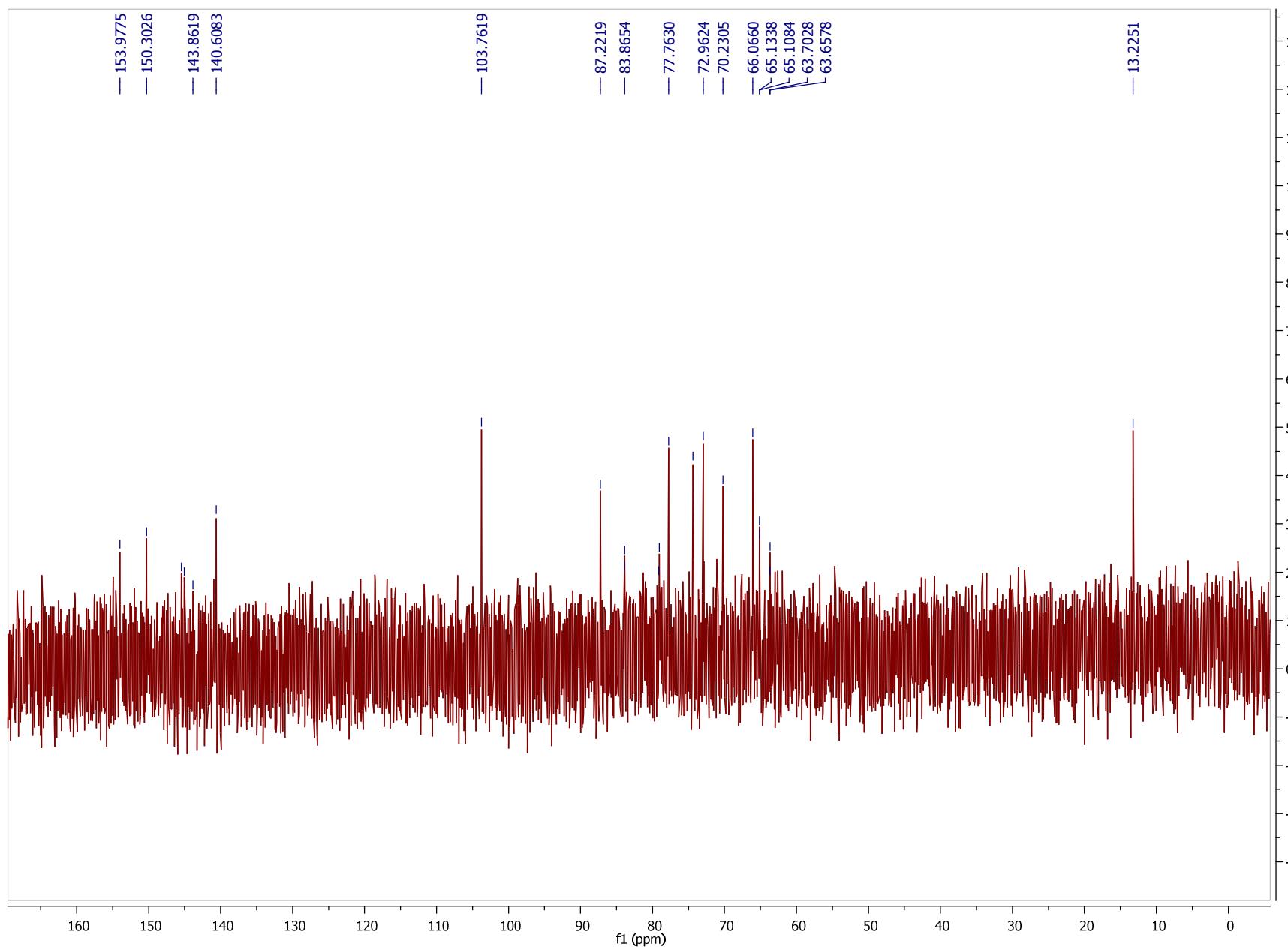
**1',2'-O-carbonate-3'-O-methylcarbonate-ADP-ribofuranoside 16a:  $^{13}\text{C}$ -NMR**



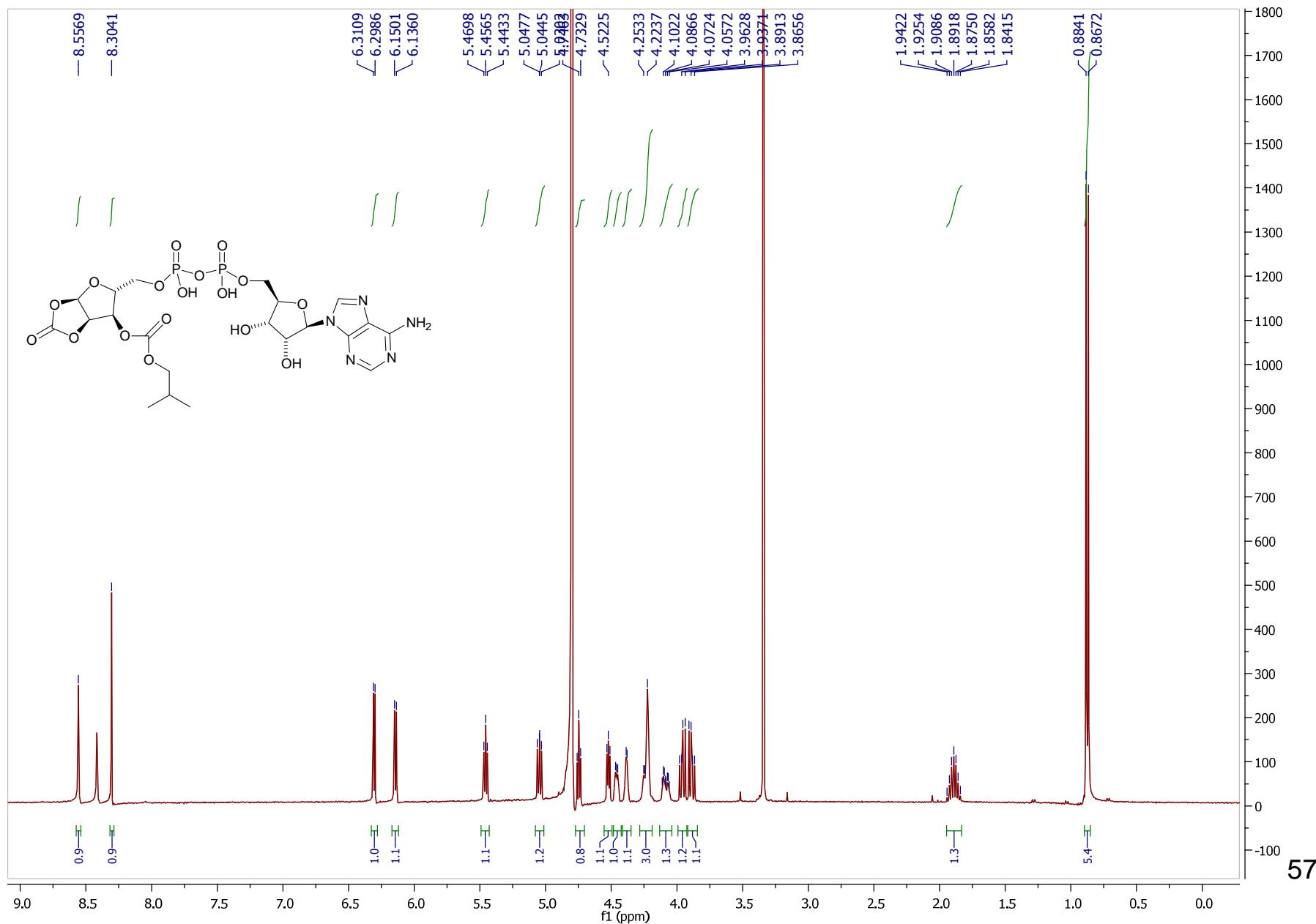
*1',2'-O-carbonate-3'-O-ethylcarbonate-ADP-ribofuranoside 16b: <sup>1</sup>H-NMR*



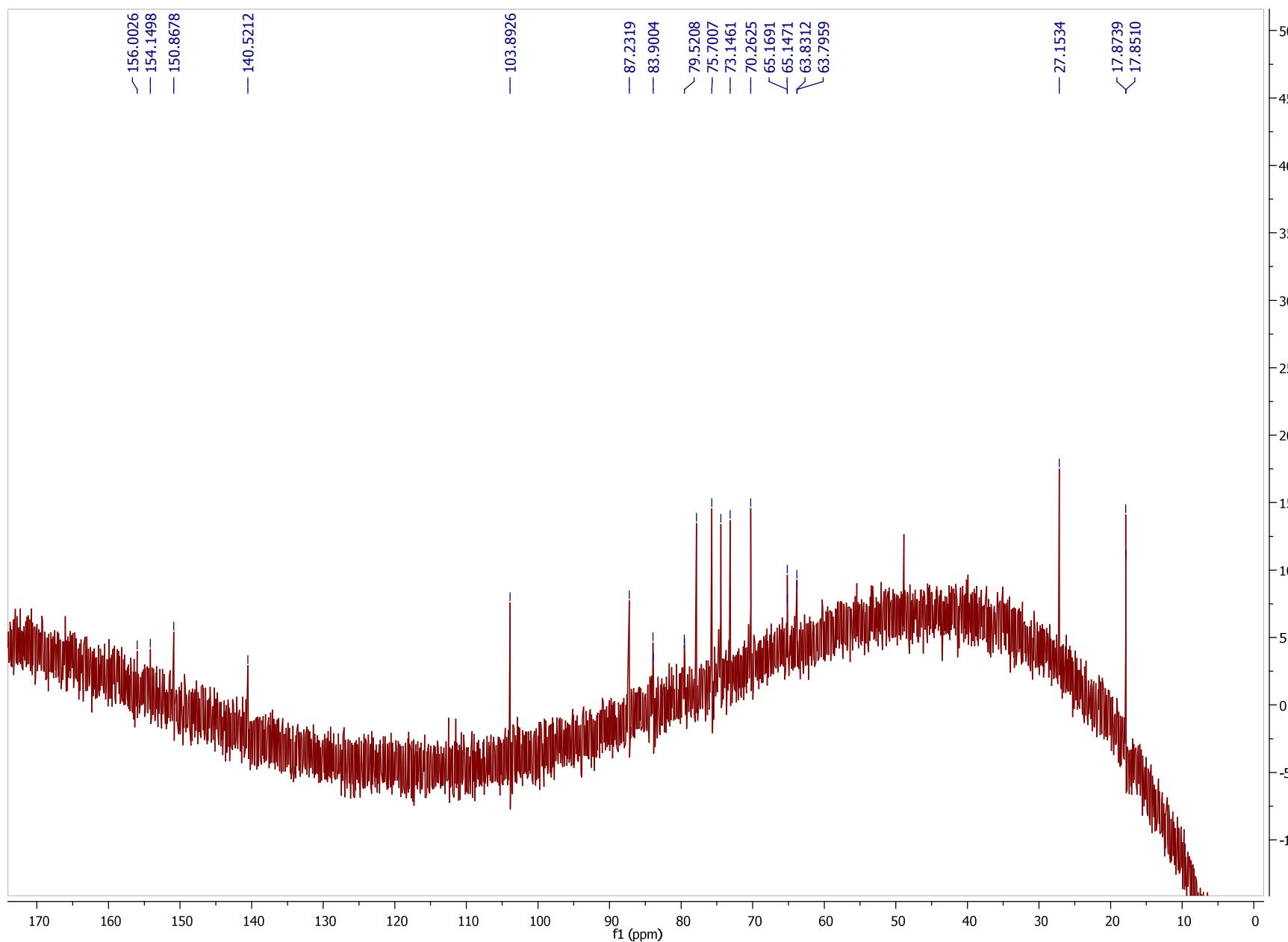
**1',2'-O-carbonate-3'-O-ethylcarbonate-ADP-ribofuranoside 16b:  $^{13}\text{C}$ -NMR**



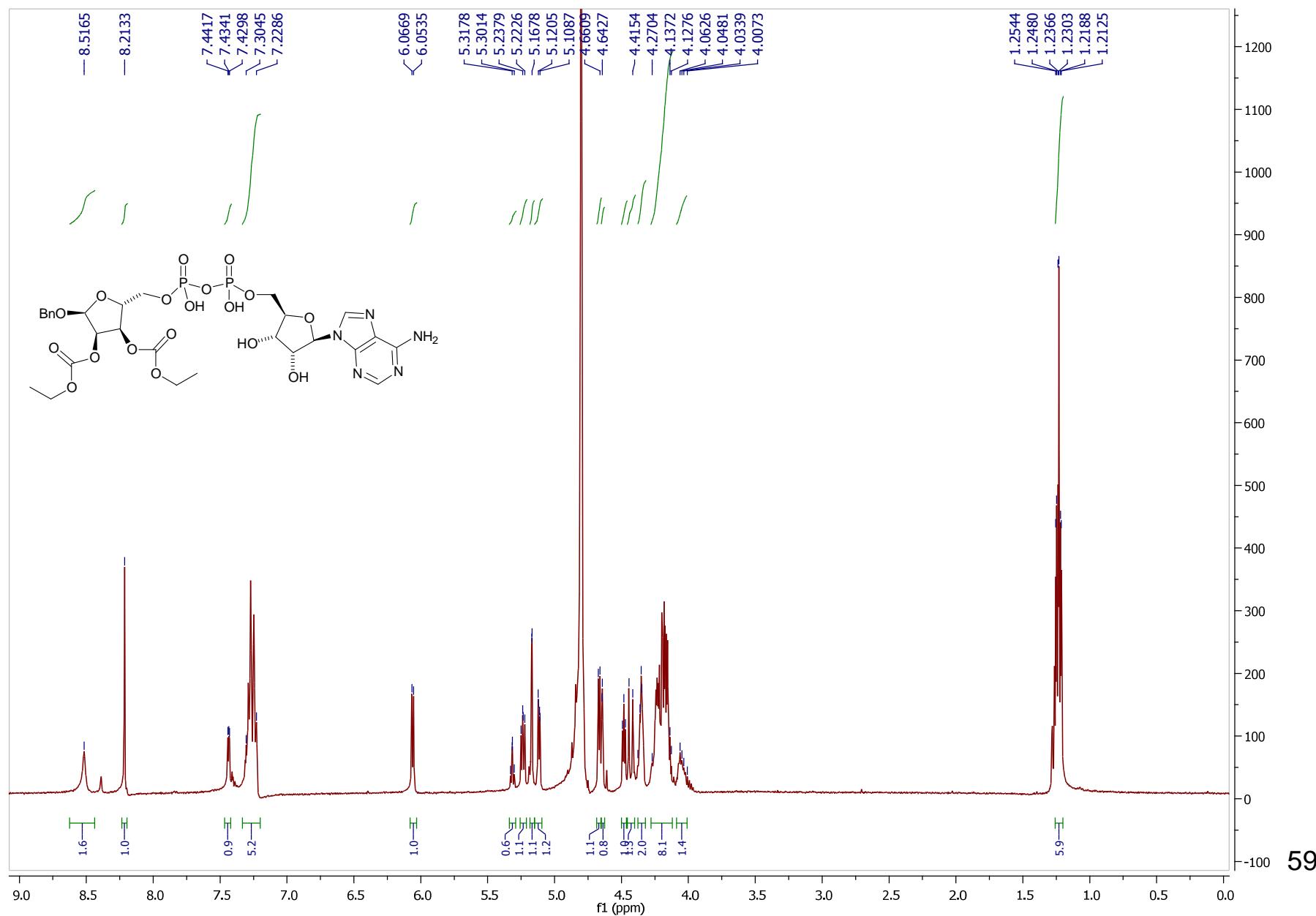
**1',2'-O-carbonate-3'-O-isobutylcarbonate-ADP-ribofuranoside 16c:  $^1\text{H}$ -NMR**



**1',2'-O-carbonate-3'-O-isobutylcarbonate-ADP-ribofuranoside 16c:  $^{13}\text{C}$ -NMR**



**1'-O-benzyl-2',3'-O-bis(ethylcarbonate)-ADP-ribofuranoside 17b:  $^1\text{H}$ -NMR**



**1'-O-benzyl-2',3'-O-bis(ethylcarbonate)-ADP-ribofuranoside 17b:  $^1\text{H}$ -NMR**

