

## Supporting Information

for

# The Amadori rearrangement as glycoconjugation method: Synthesis of non-natural C-glycosyl type glycoconjugates

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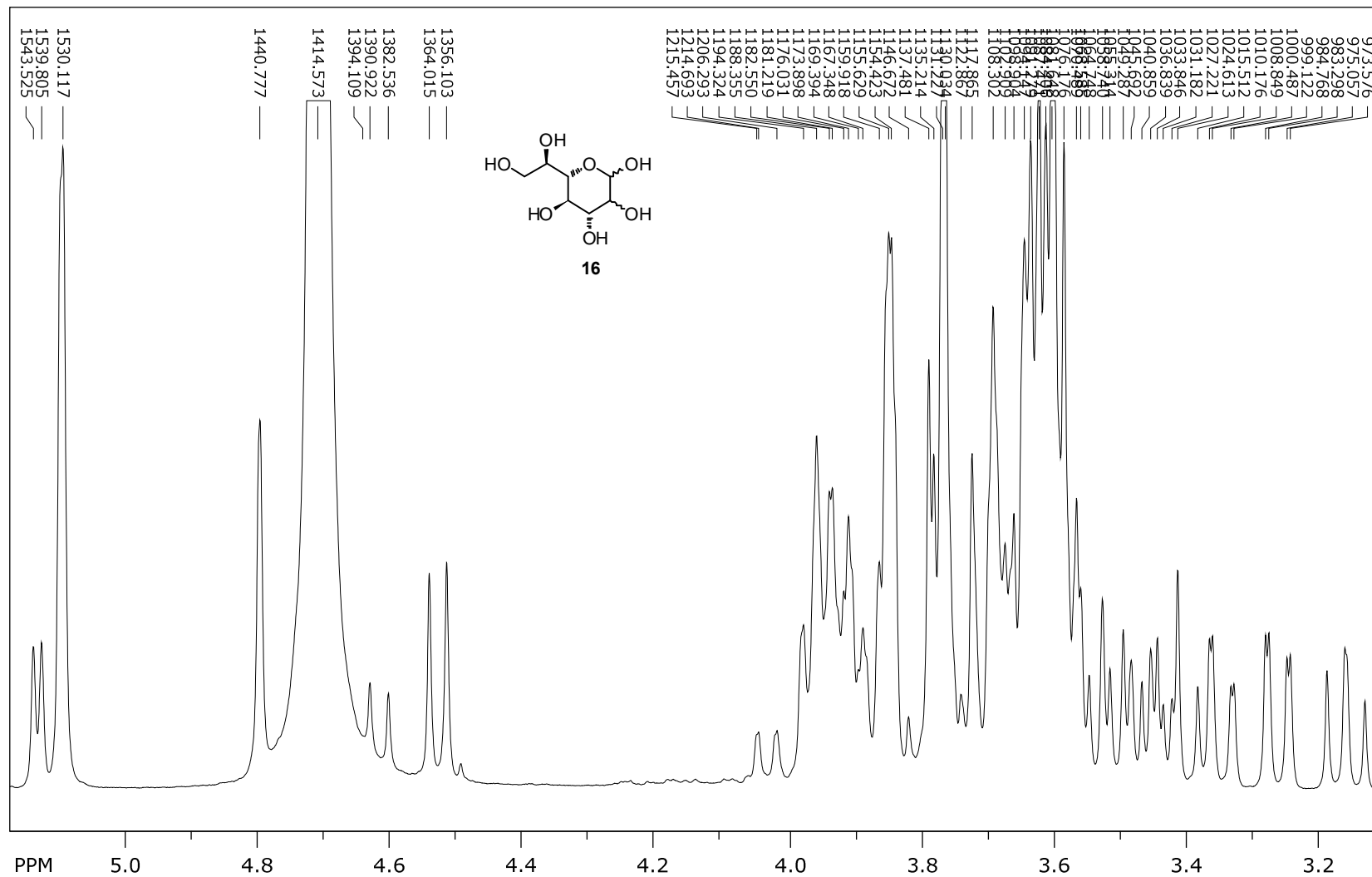
\* Corresponding author

## NMR data of compounds 16, 19, 23–36.

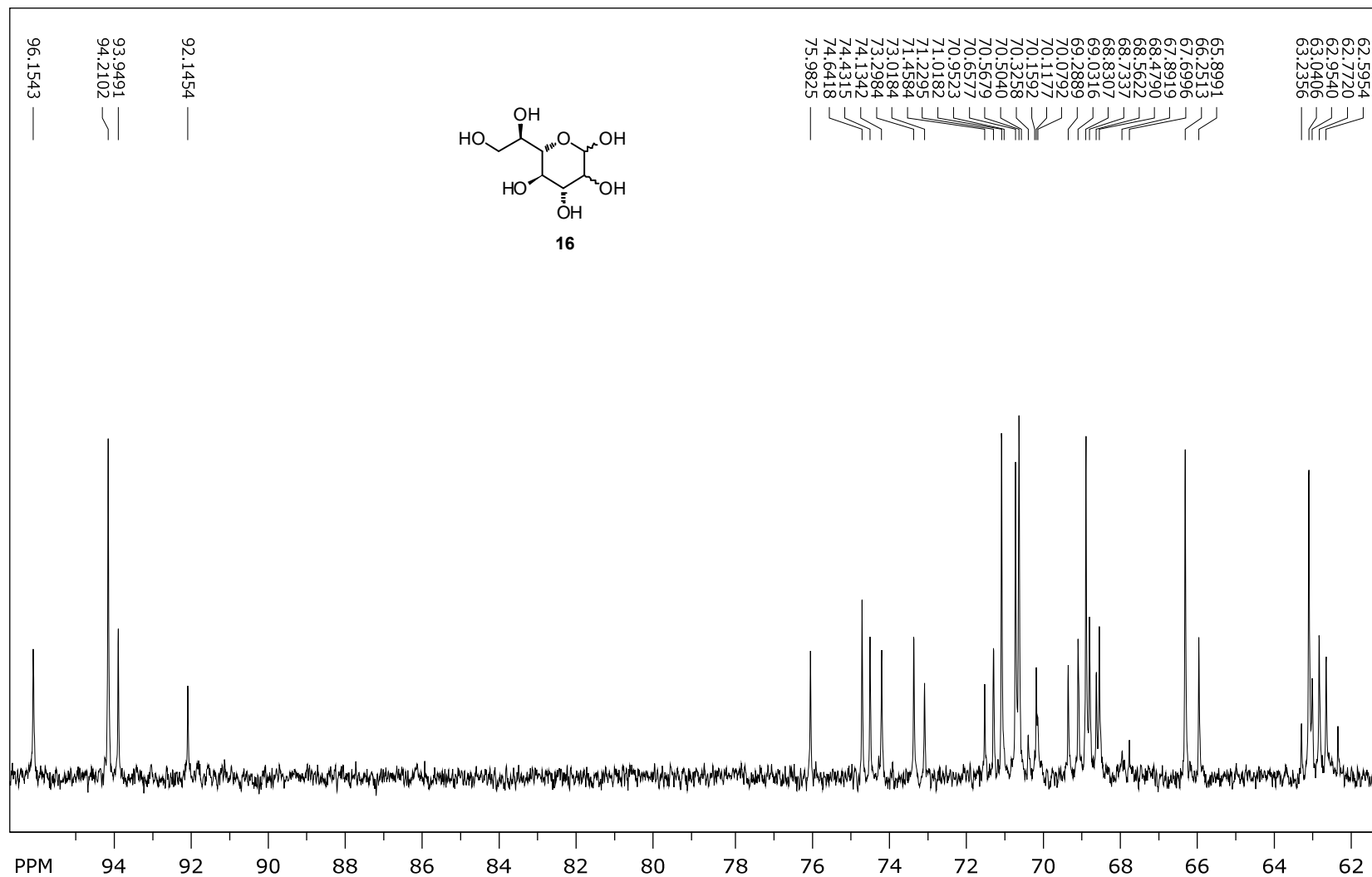
### General

NMR spectra were recorded on a Bruker Ultrashield spectrometer at 300.36 and 75.53 MHz, respectively in methanol-*d*<sub>4</sub> or D<sub>2</sub>O as indicated. Chemical shifts are listed in delta employing residual, non-deuterated solvent as the internal standard. Structures of crucial intermediates were unambiguously assigned by 1D-TOCSY and HSQC experiments.

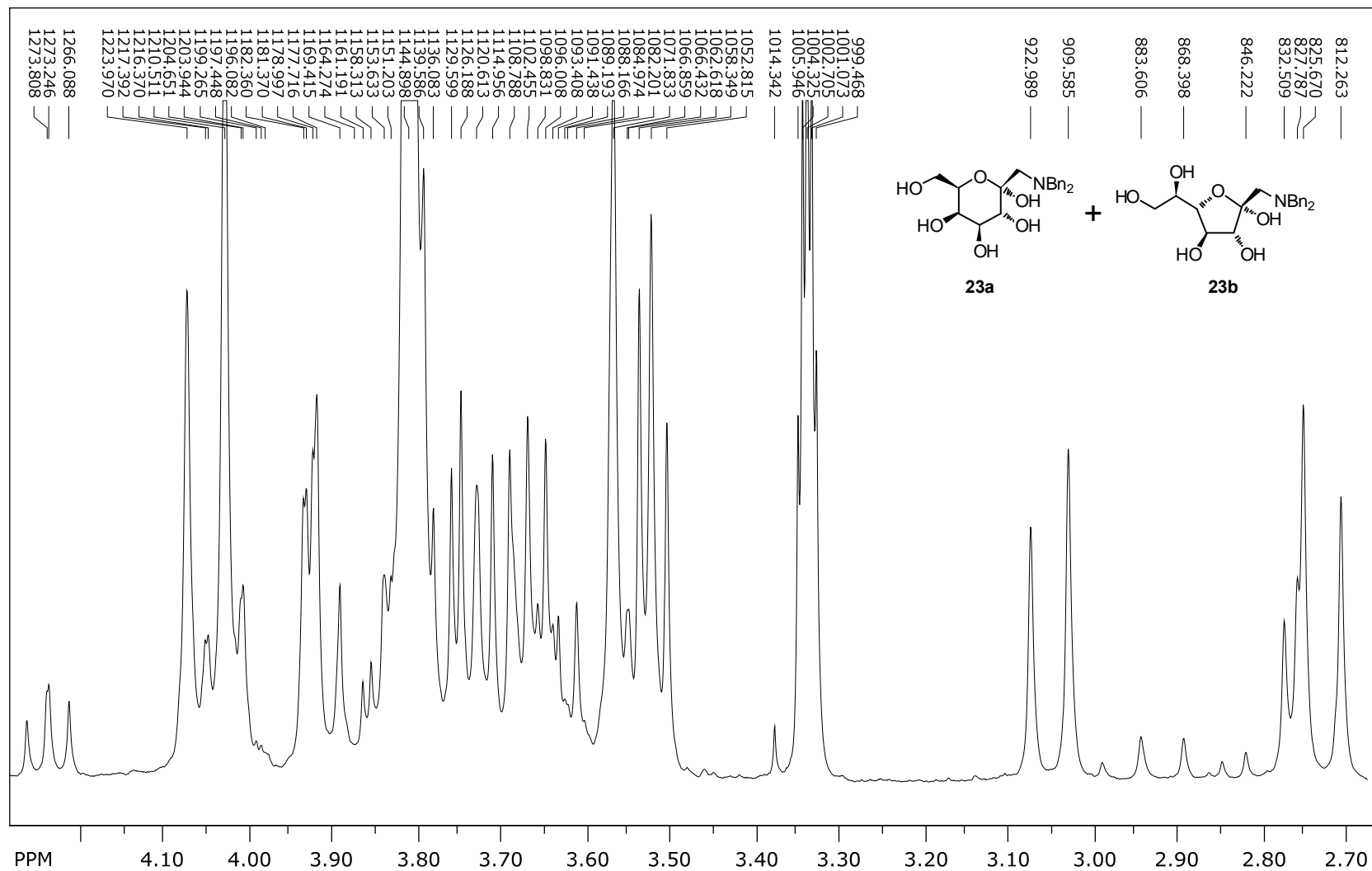
D-glycero-L-manno/L-gluco-heptopyranose 16a and 16b <sup>1</sup>H, 300 MHz, D<sub>2</sub>O



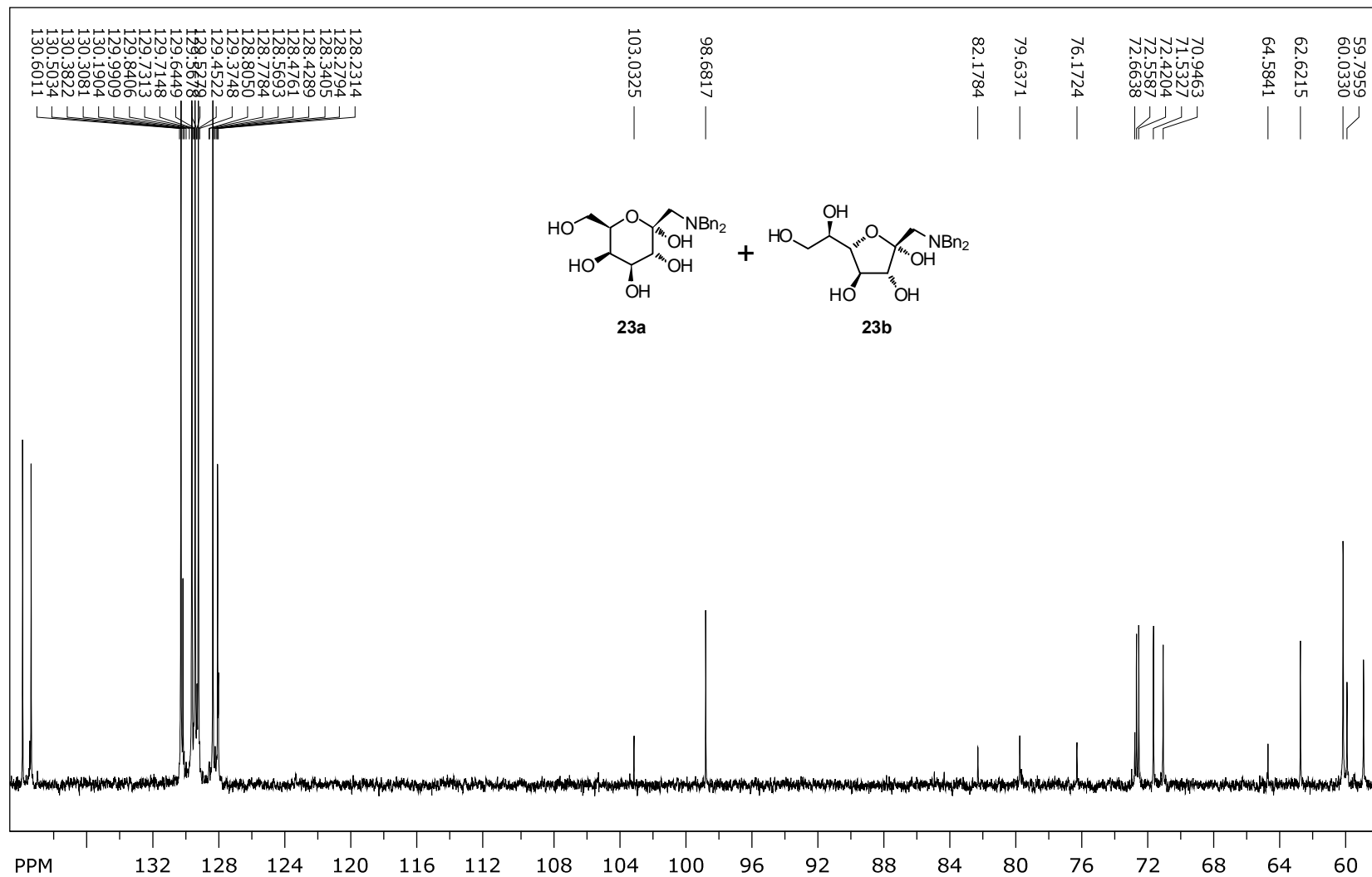
**D-glycero-L-manno/L-gluco-heptopyranose 16a and 16b <sup>13</sup>C, 75 MHz, D<sub>2</sub>O**



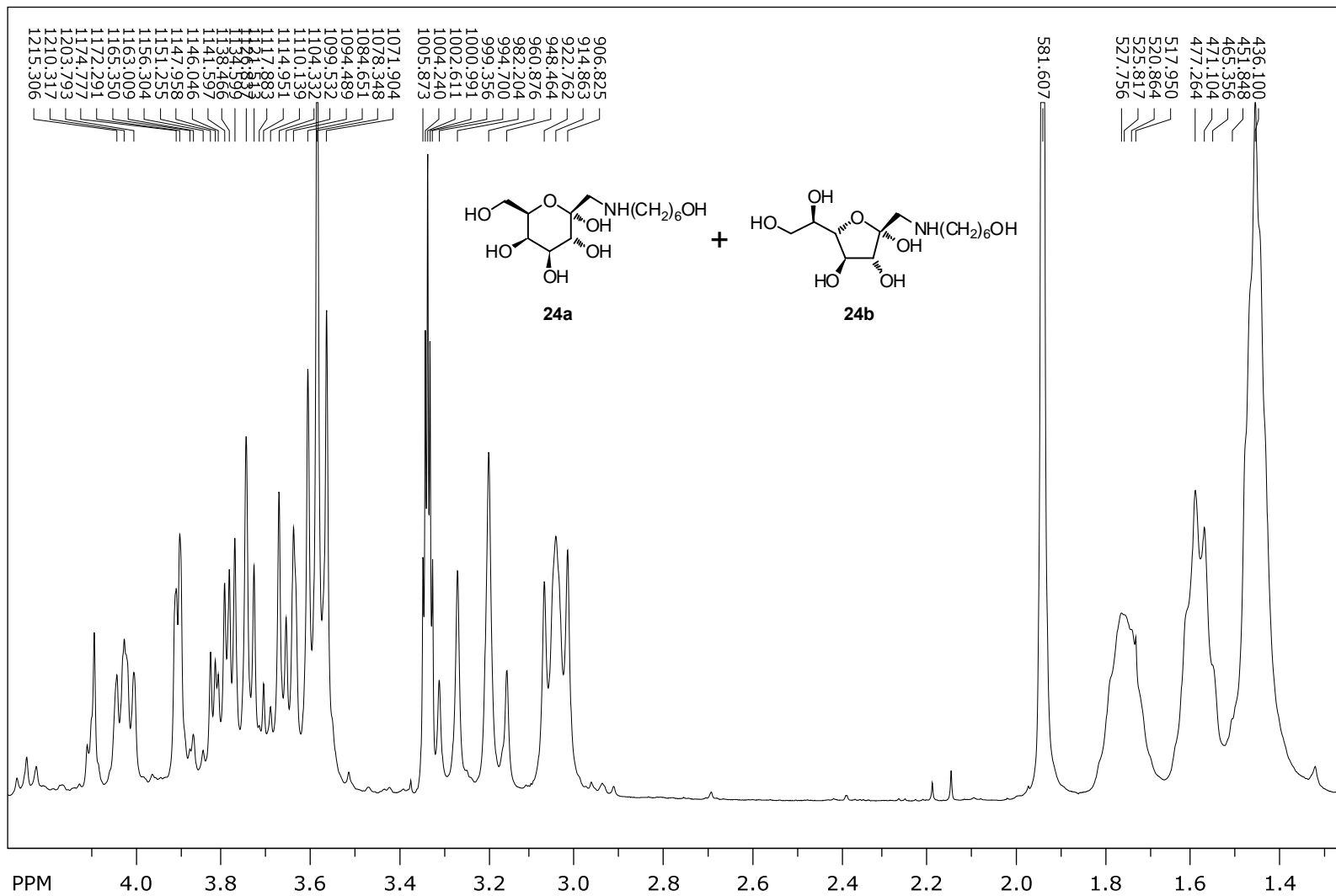
1-(*N,N*-Dibenzylamino)-1-deoxy- $\alpha$ -D-galacto-hept-2-ulopyranose (23a) and -furanose (23b),  $^1\text{H}$ , 300 MHz, MeOH- $d_4$



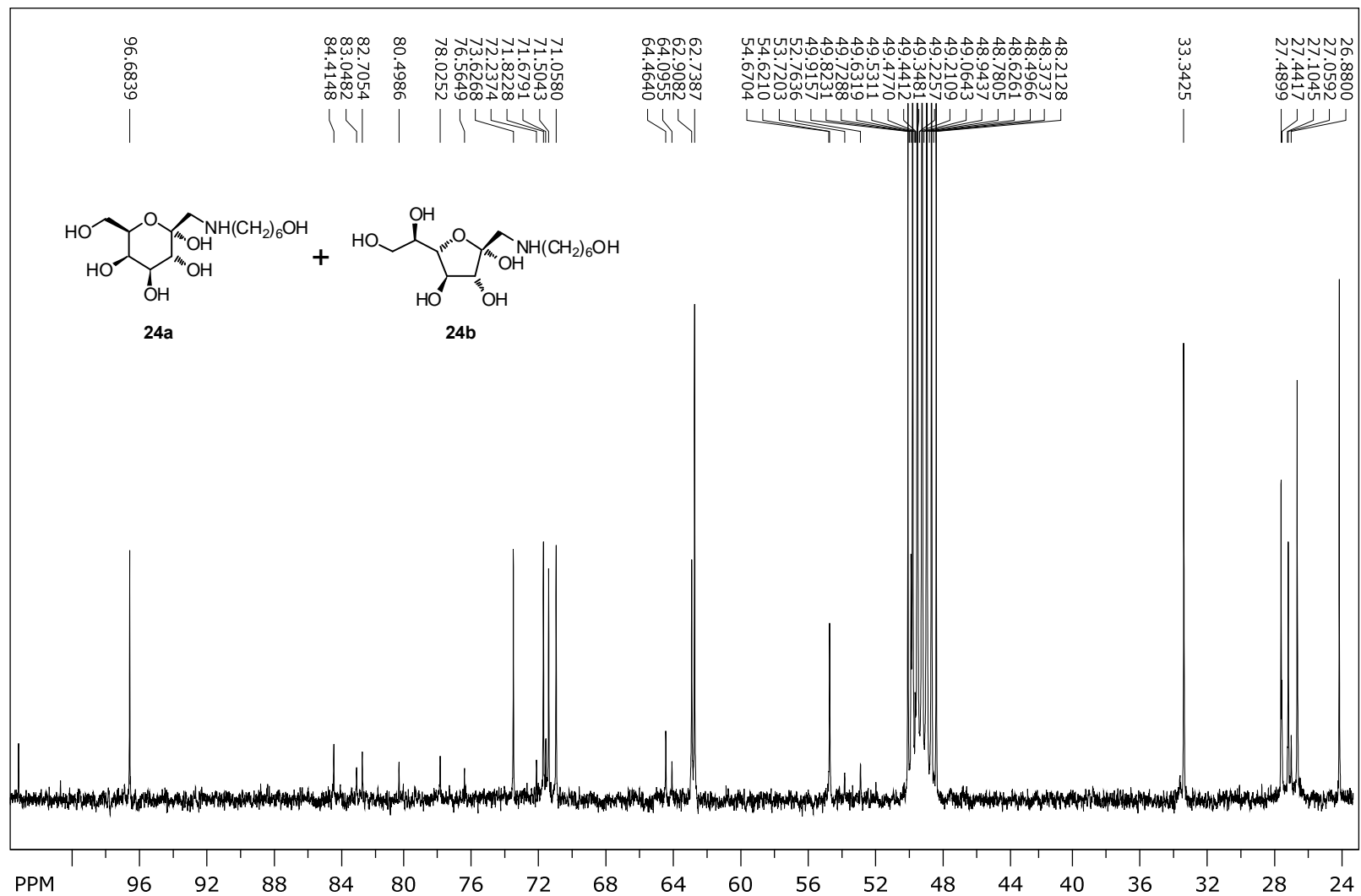
1-(*N,N*-Dibenzylamino)-1-deoxy- $\alpha$ -D-galacto-hept-2-ulopyranose (23a) and -furanose (23b),  $^{13}\text{C}$ , 75 MHz,  $\text{MeOH-}d_4$



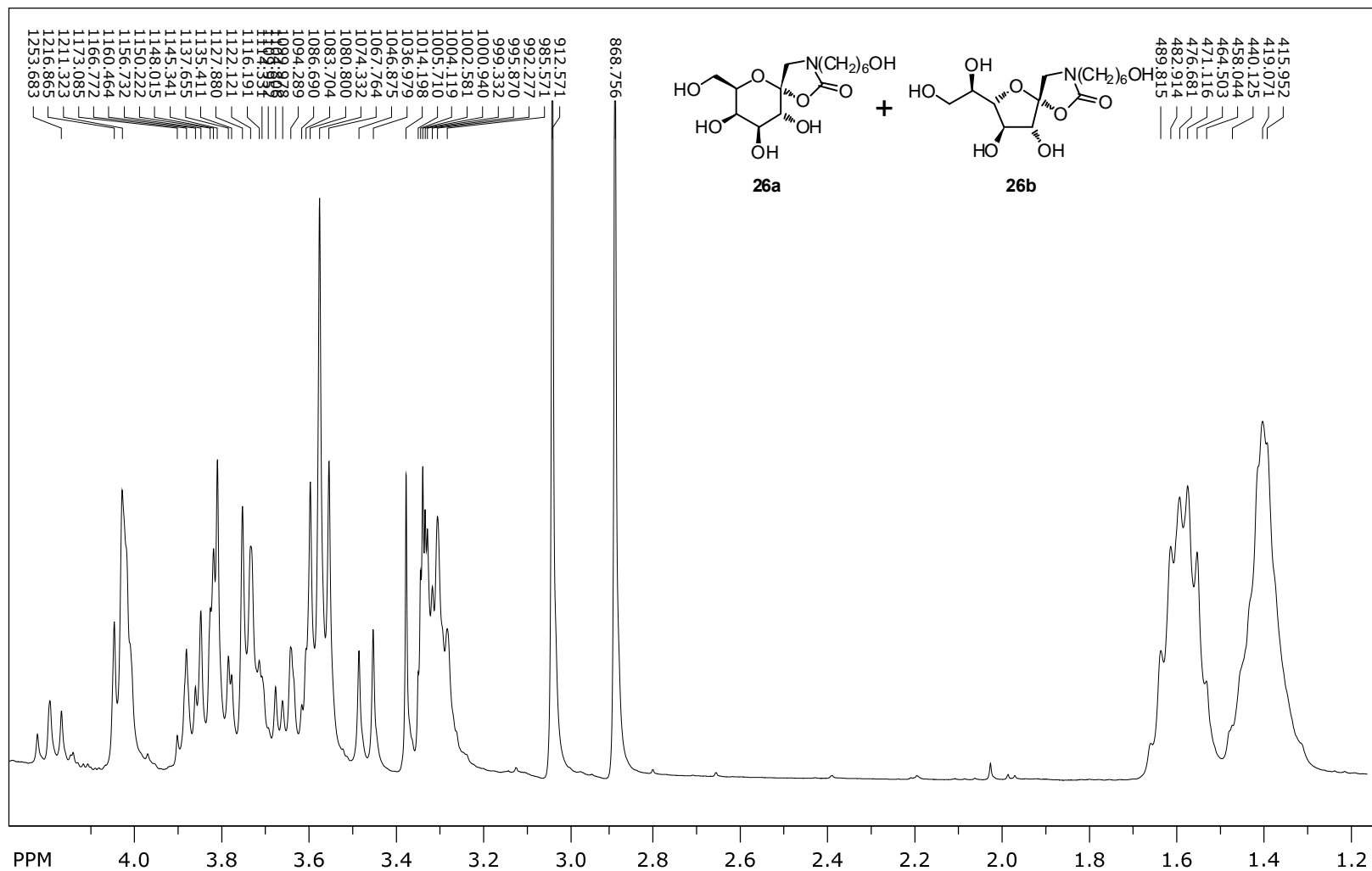
1-(*N*-(6-Hydroxyhexyl)amino)-1-deoxy- $\alpha$ -*D*-galacto-hept-2-ulopyranose (24a) and -furanose (24b)  $^1\text{H}$ , 300 MHz,  $\text{MeOH-}d_4$



1-(*N*-(6-Hydroxyhexyl)amino)-1-deoxy- $\alpha$ -*D*-galacto-hept-2-ulopyranose (24a) and -furanose (24b)  $^{13}\text{C}$ , 75 MHz, MeOH- $d_4$

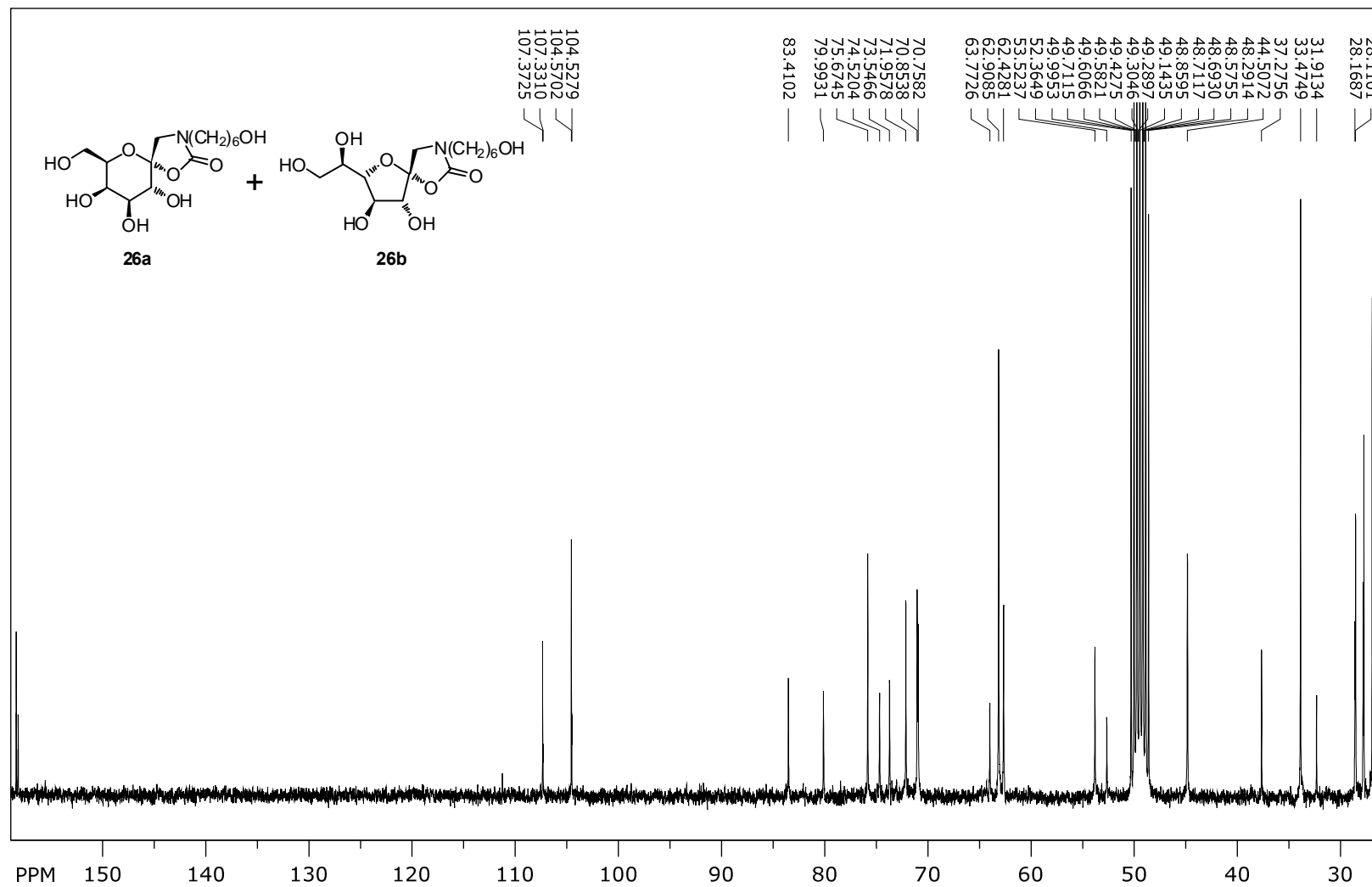


1-(N-(6-Hydroxyhexyl)amino)-1-N,2-O-carbonyl-1-deoxy- $\beta$ -D-galacto-hept-2-ulopyranose 26a and -furanose 26b  $^1\text{H}$ , 300 MHz,  $\text{MeOH-}d_4$

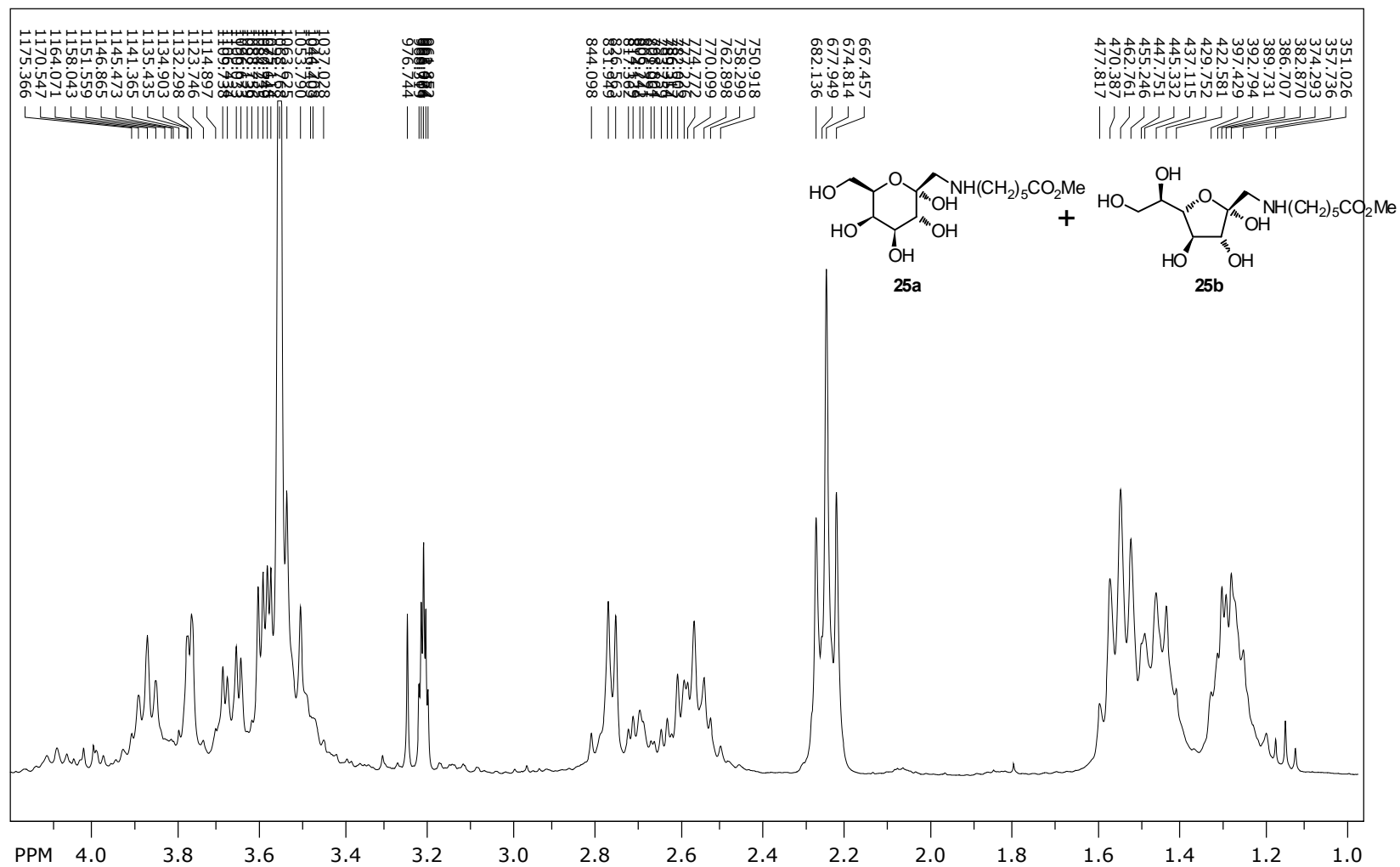




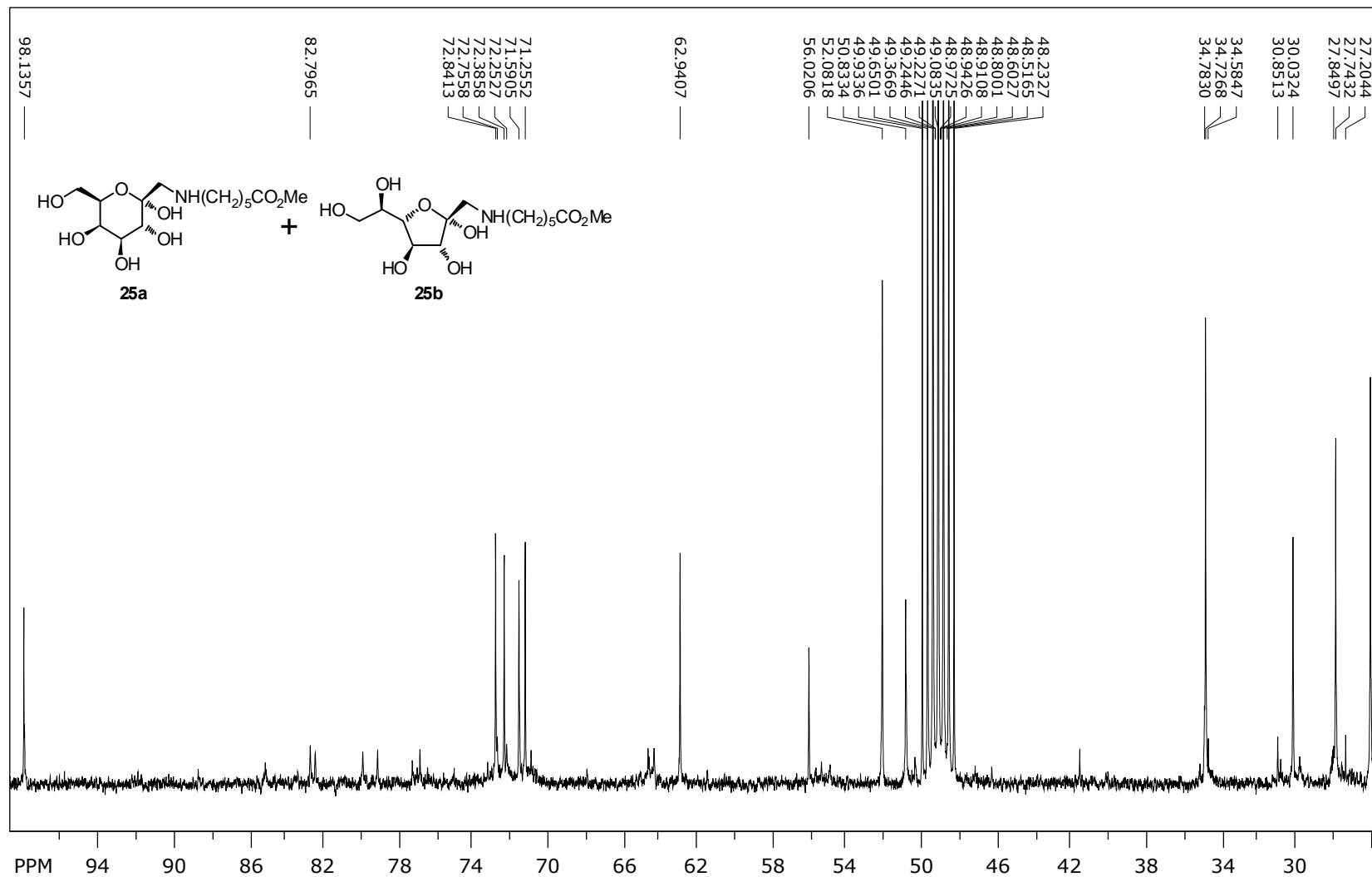
1-(*N*-(6-Hydroxyhexyl)amino)-1-*N*,2-*O*-carbonyl-1-deoxy- $\beta$ -D-galacto-hept-2-ulopyranose 26a and -furanose 26b  $^{13}\text{C}$ , 75 MHz, MeOH- $d_4$



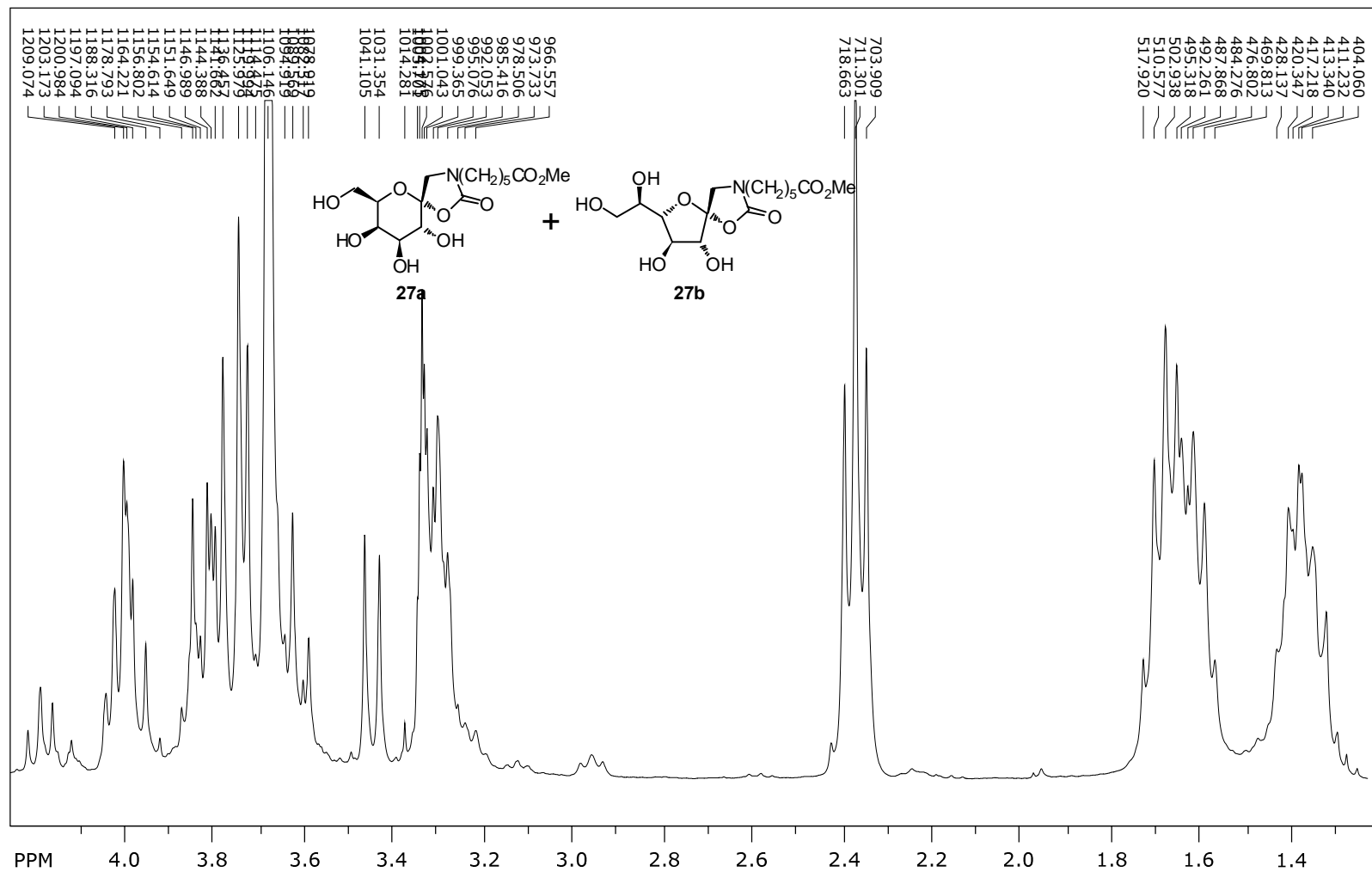
1-(N-(5-(Methoxycarbonyl)pentyl)amino)-1-deoxy- $\alpha$ -D-galacto-hept-2-ulopyranose (25a) and -furanose (25b)  $^1\text{H}$ , 300 MHz, MeOH- $d_4$



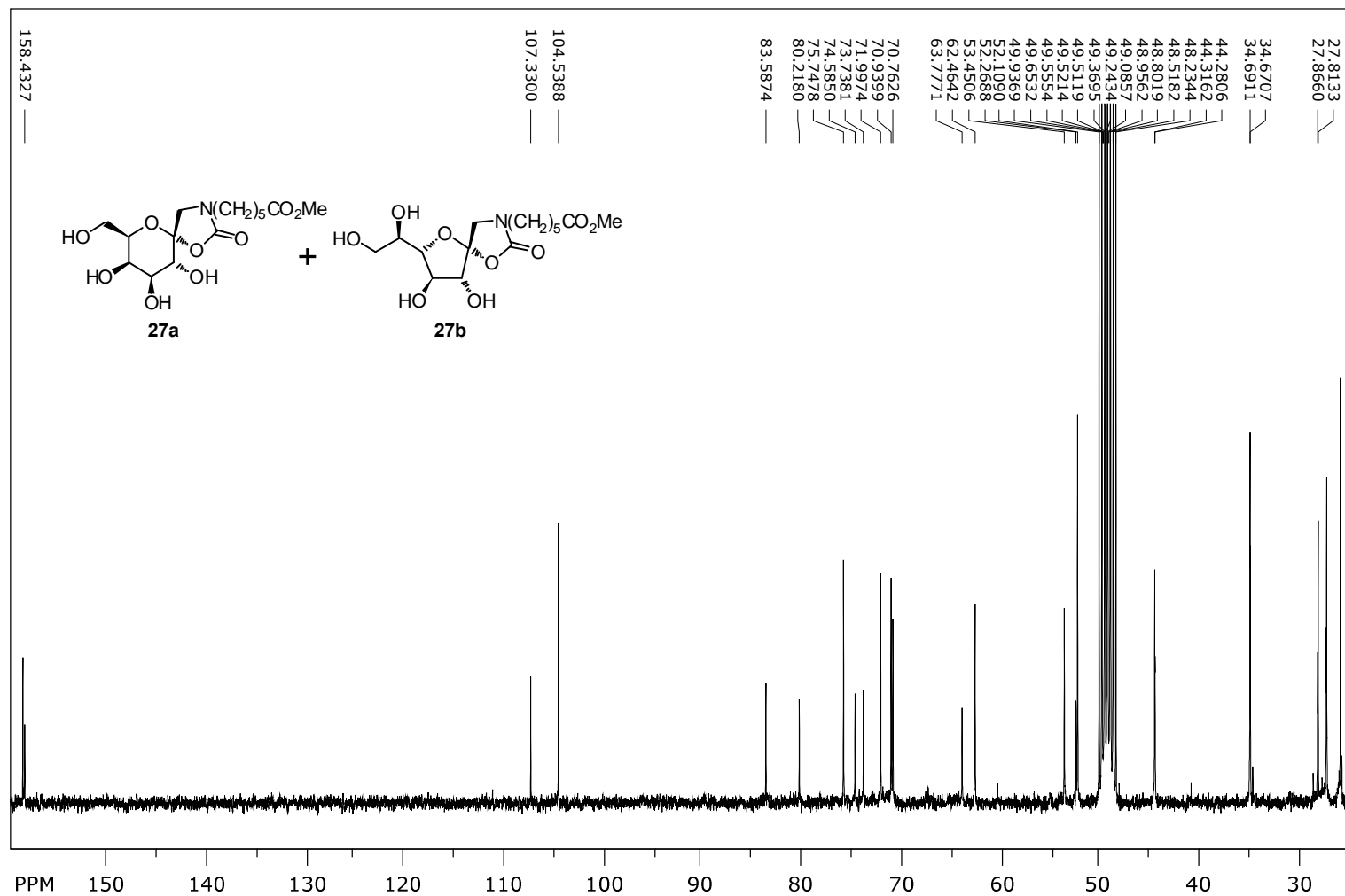
1-(*N*-(5-(Methoxycarbonyl)pentyl)amino)-1-deoxy- $\alpha$ -D-galacto-hept-2-ulopyranose (25a) and -furanose (25b)  $^{13}\text{C}$ , 75 MHz, MeOH- $d_4$



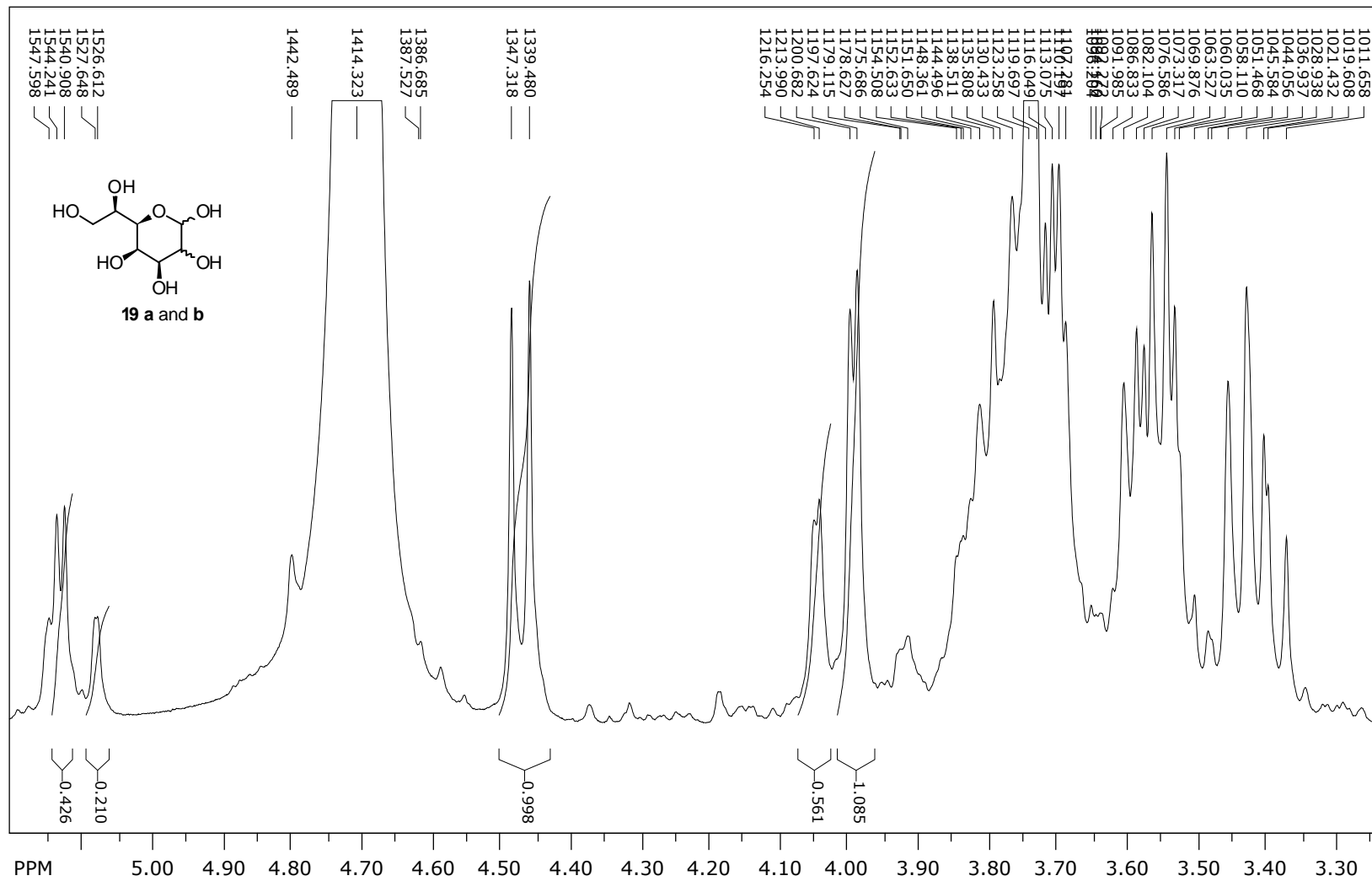
1-(*N*-(5-(Methoxycarbonyl)pentyl)amino)-1-*N*,2-*O*-carbonyl-1-deoxy- $\beta$ -D-galacto-hept-2-ulopyranose (27a) and -furanose (27b)  $^1\text{H}$ ,  
300 MHz, MeOH- $d_4$



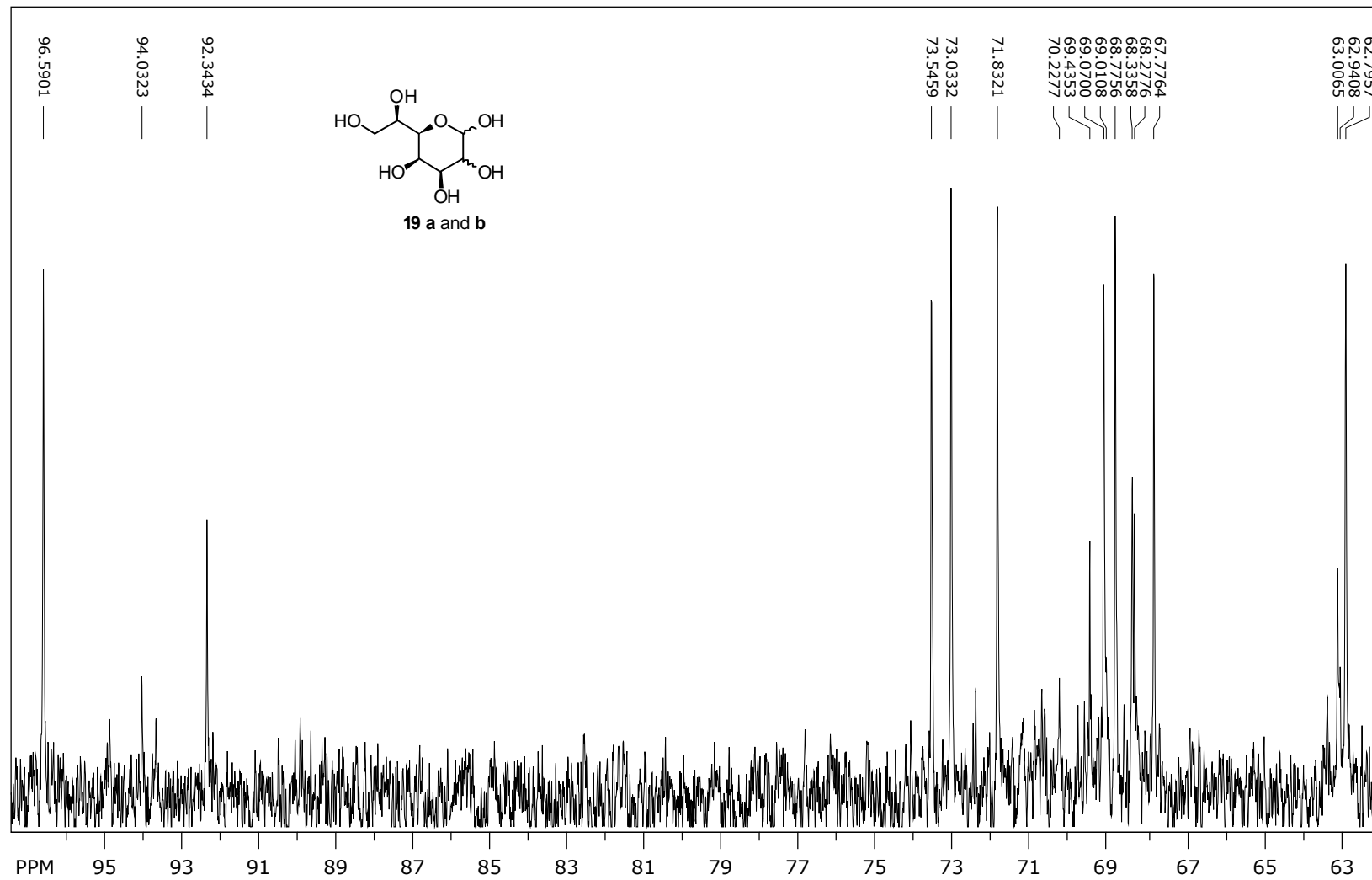
1-(*N*-(5-(Methoxycarbonyl)pentyl)amino)-1-*N*,2-*O*-carbonyl-1-deoxy- $\beta$ -D-galacto-hept-2-ulopyranose (27a) and -furanose (27b)  $^{13}\text{C}$ ,  
75 MHz, MeOH- $d_4$



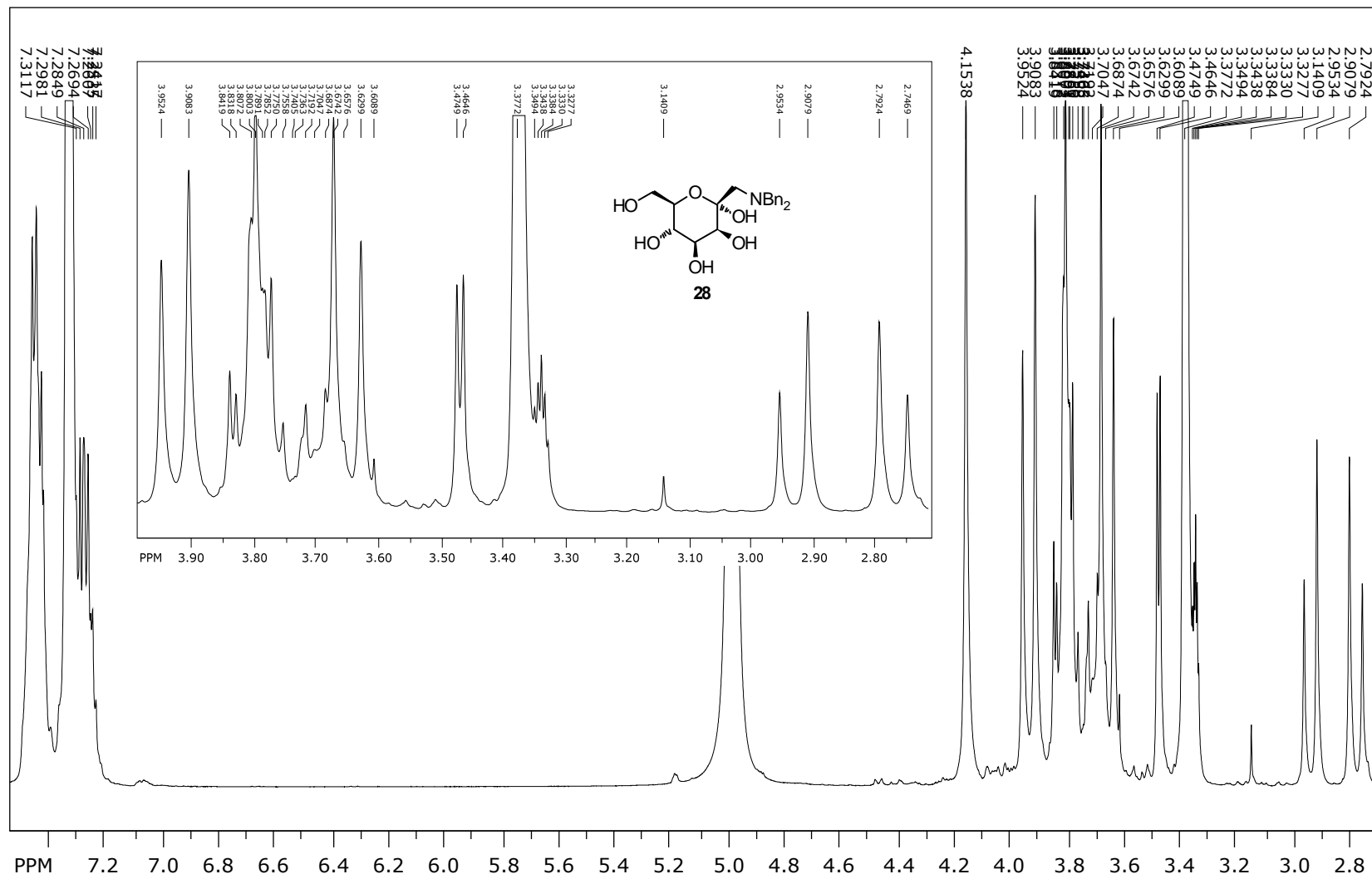
D-glycero-D-galacto/D-talo-heptopyranose 19a and 19b <sup>1</sup>H, 300 MHz, D<sub>2</sub>O



D-glycero-D-galacto/D-talo-heptopyranose 19a and 19b <sup>13</sup>C, 75 MHz, D<sub>2</sub>O

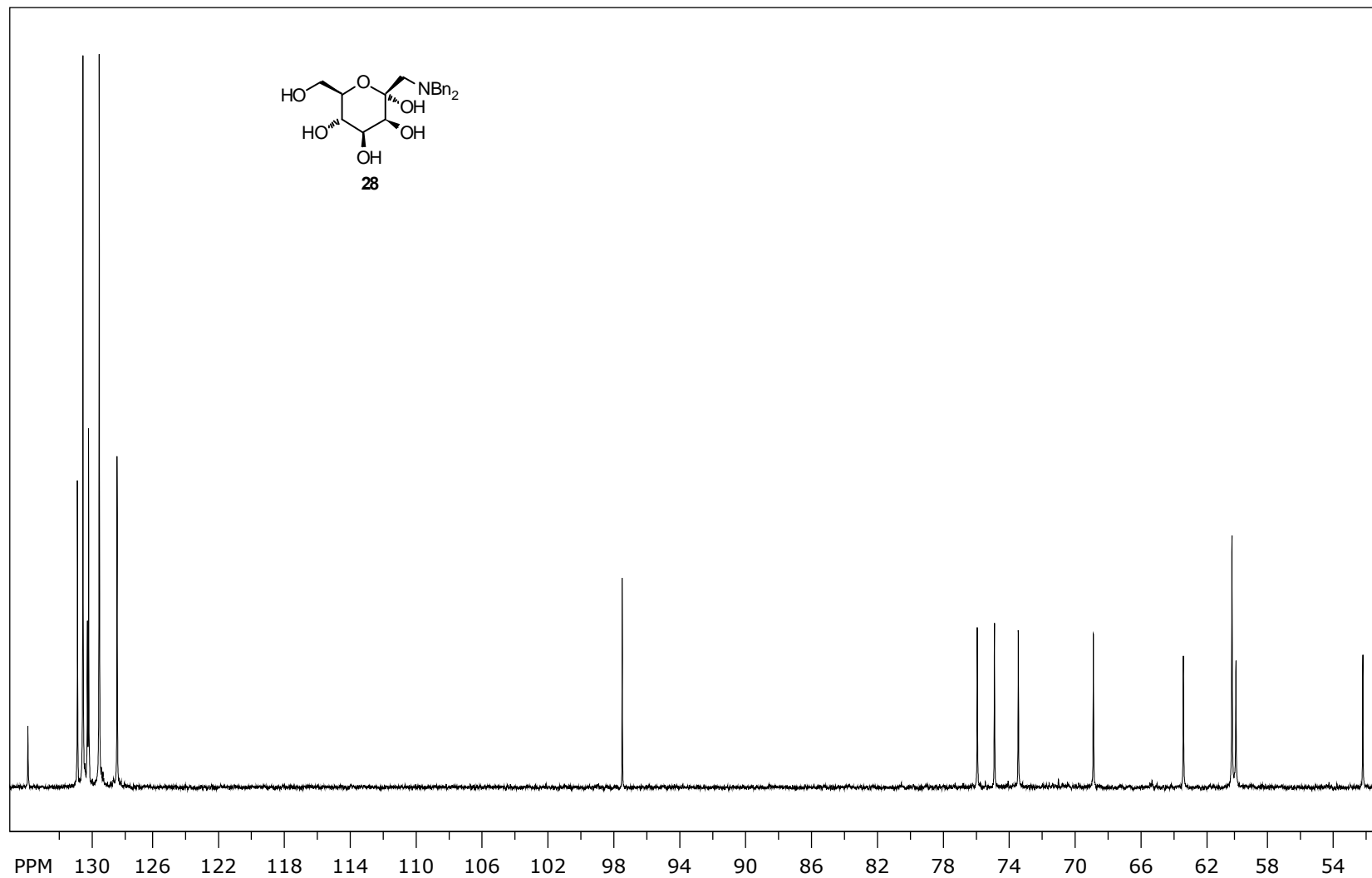


1-(*N,N*-Dibenzylamino)-1-deoxy- $\alpha$ -D-manno-hept-2-ulopyranose (**28**)  $^1\text{H}$ , 300 MHz,  $\text{MeOH-}d_4$

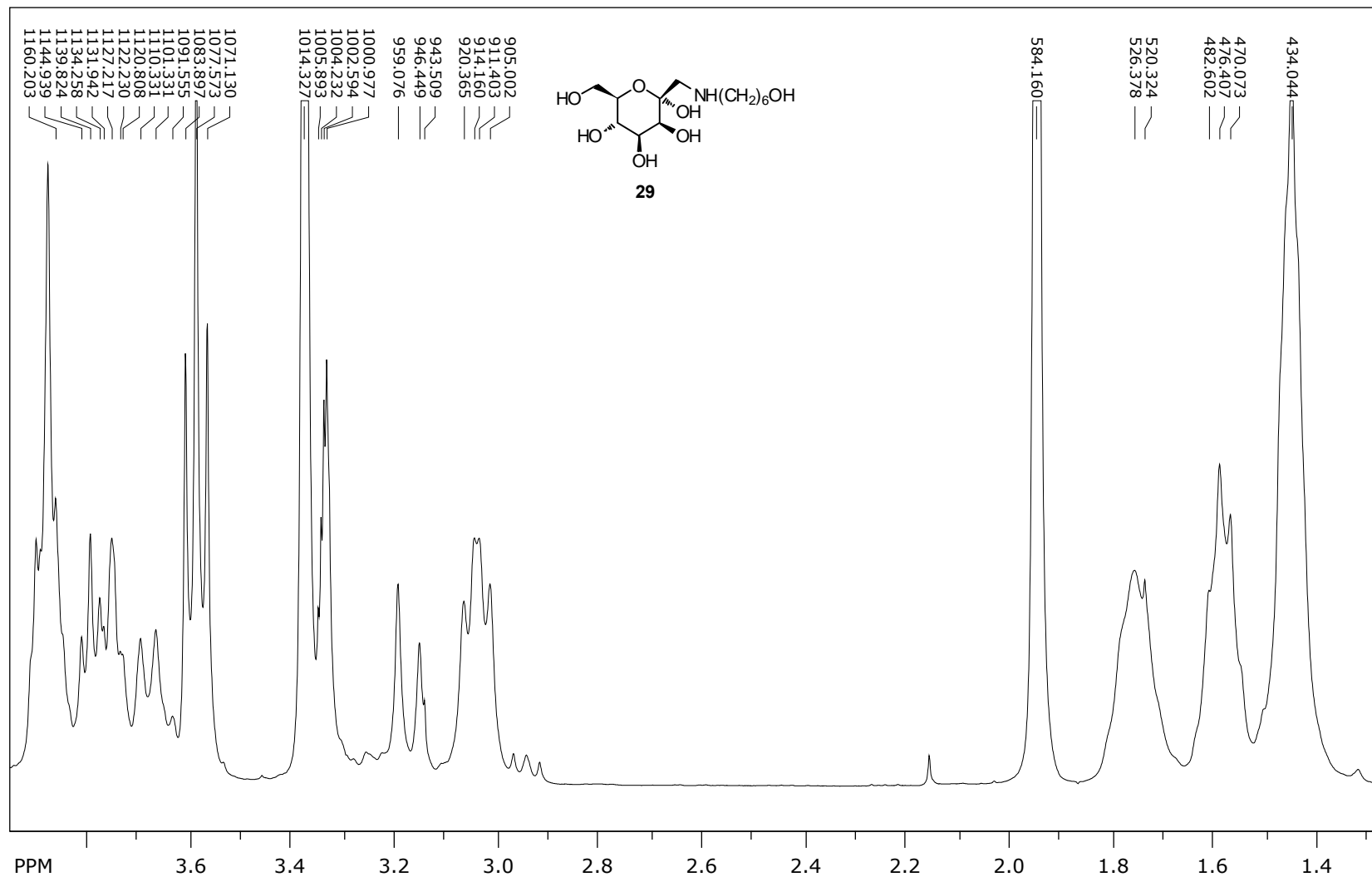




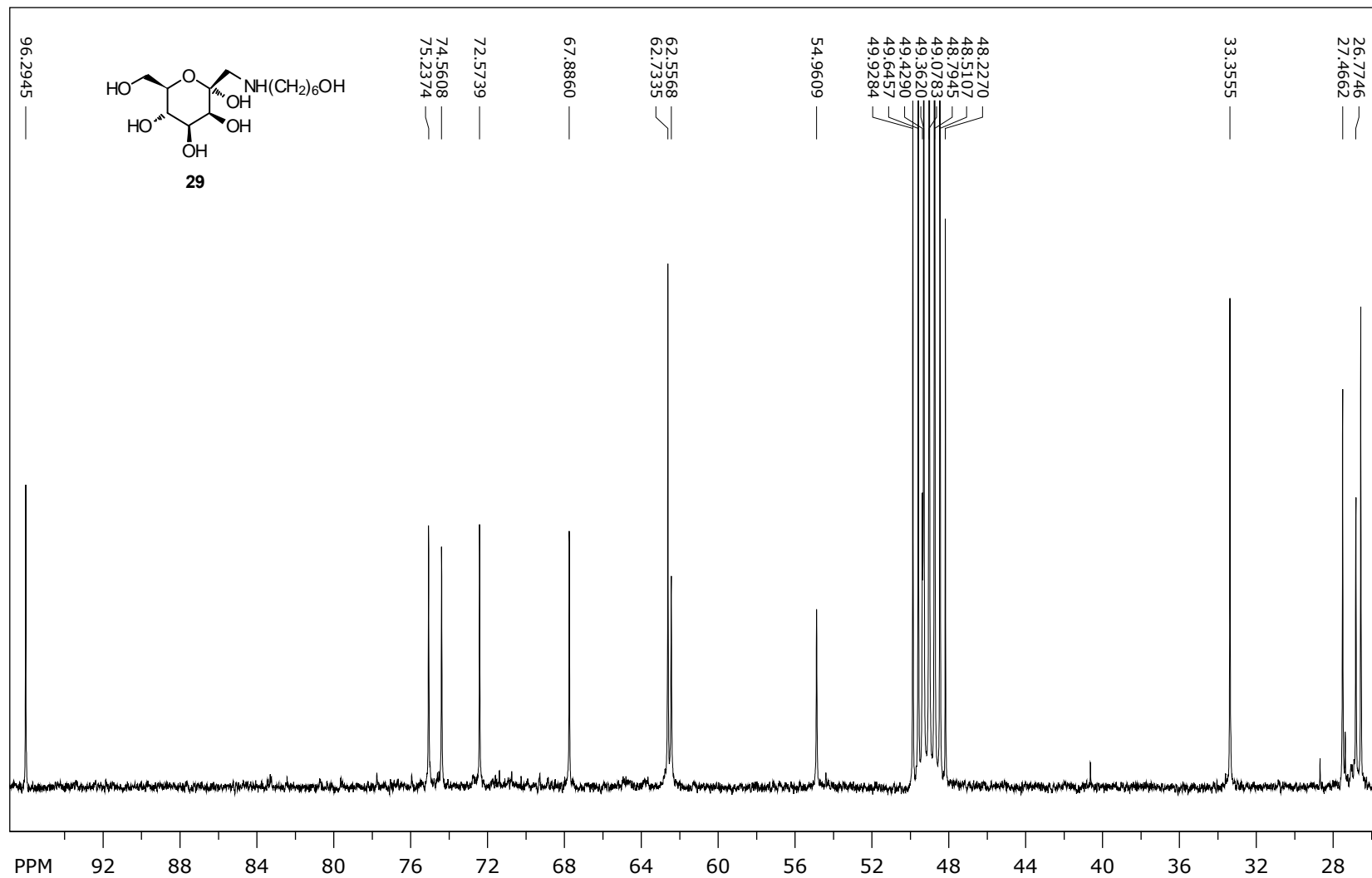
1-(*N,N*-Dibenzylamino)-1-deoxy- $\alpha$ -D-manno-hept-2-ulopyranose (**28**)  $^{13}\text{C}$ , 75 MHz, MeOH- $d_4$



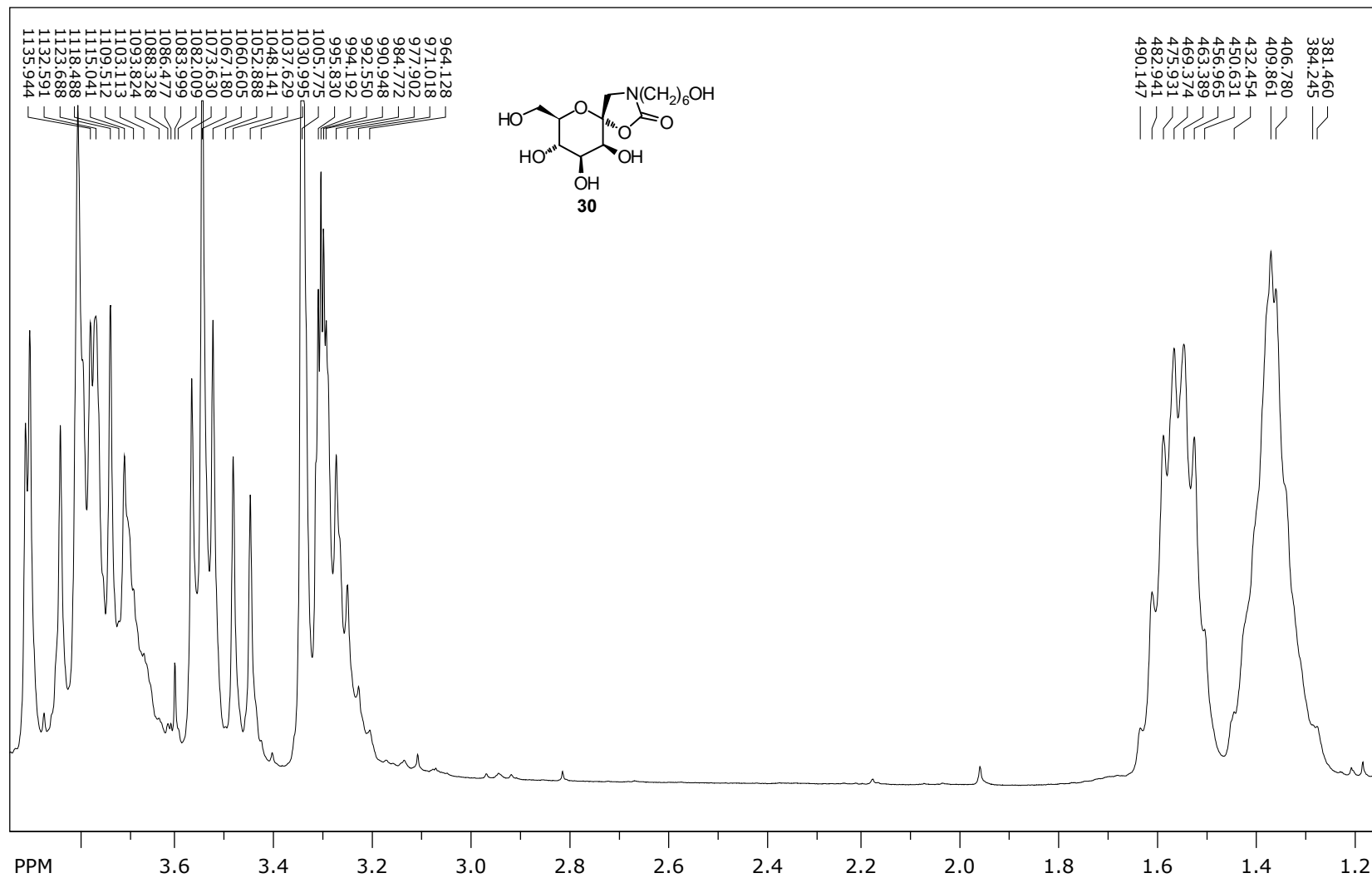
1-(N-(6-Hydroxyhexyl)amino)-1-deoxy- $\alpha$ -D-manno-hept-2-ulose (29)  $^1\text{H}$ , 300 MHz,  $\text{MeOH-}d_4$



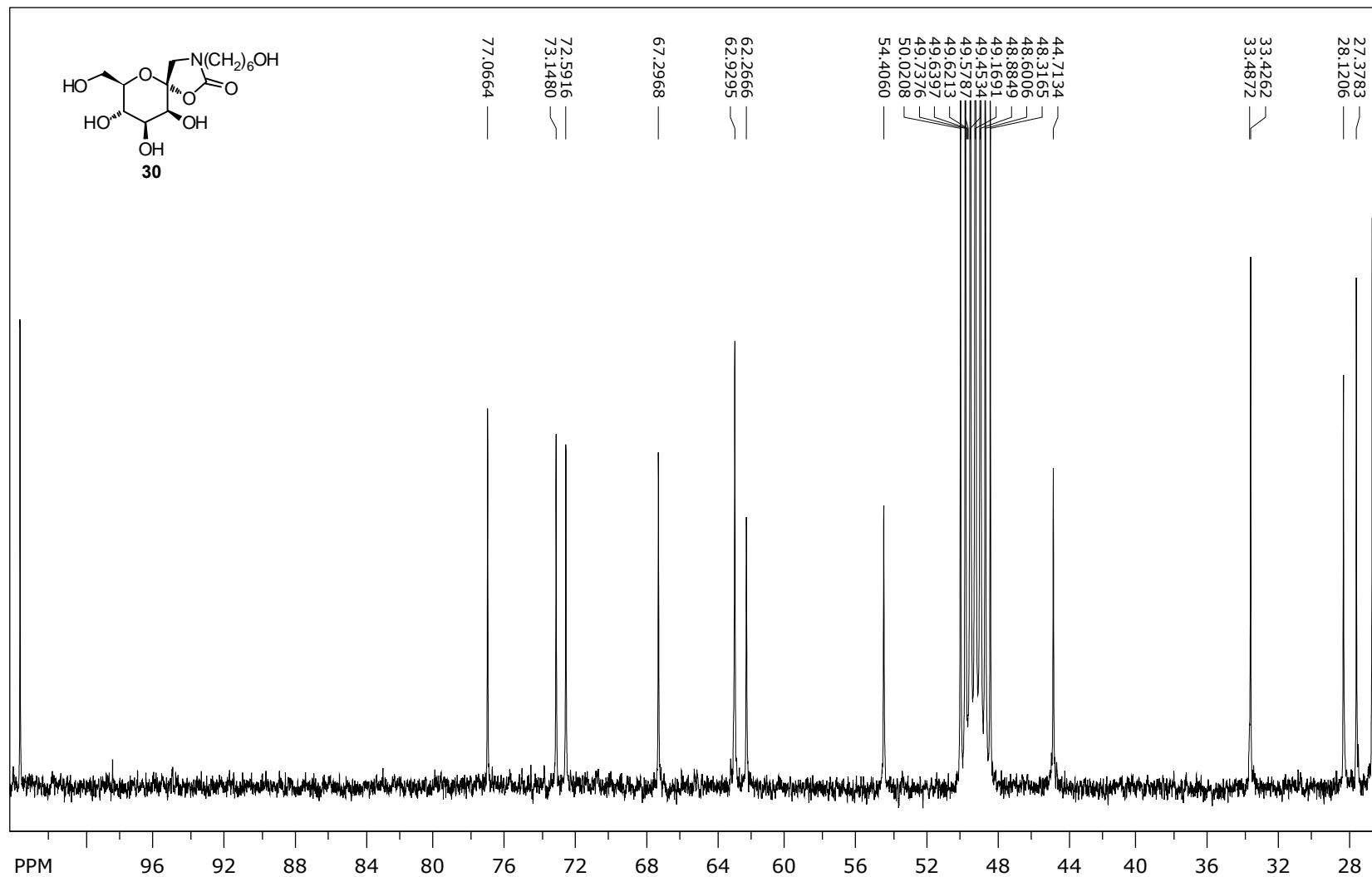
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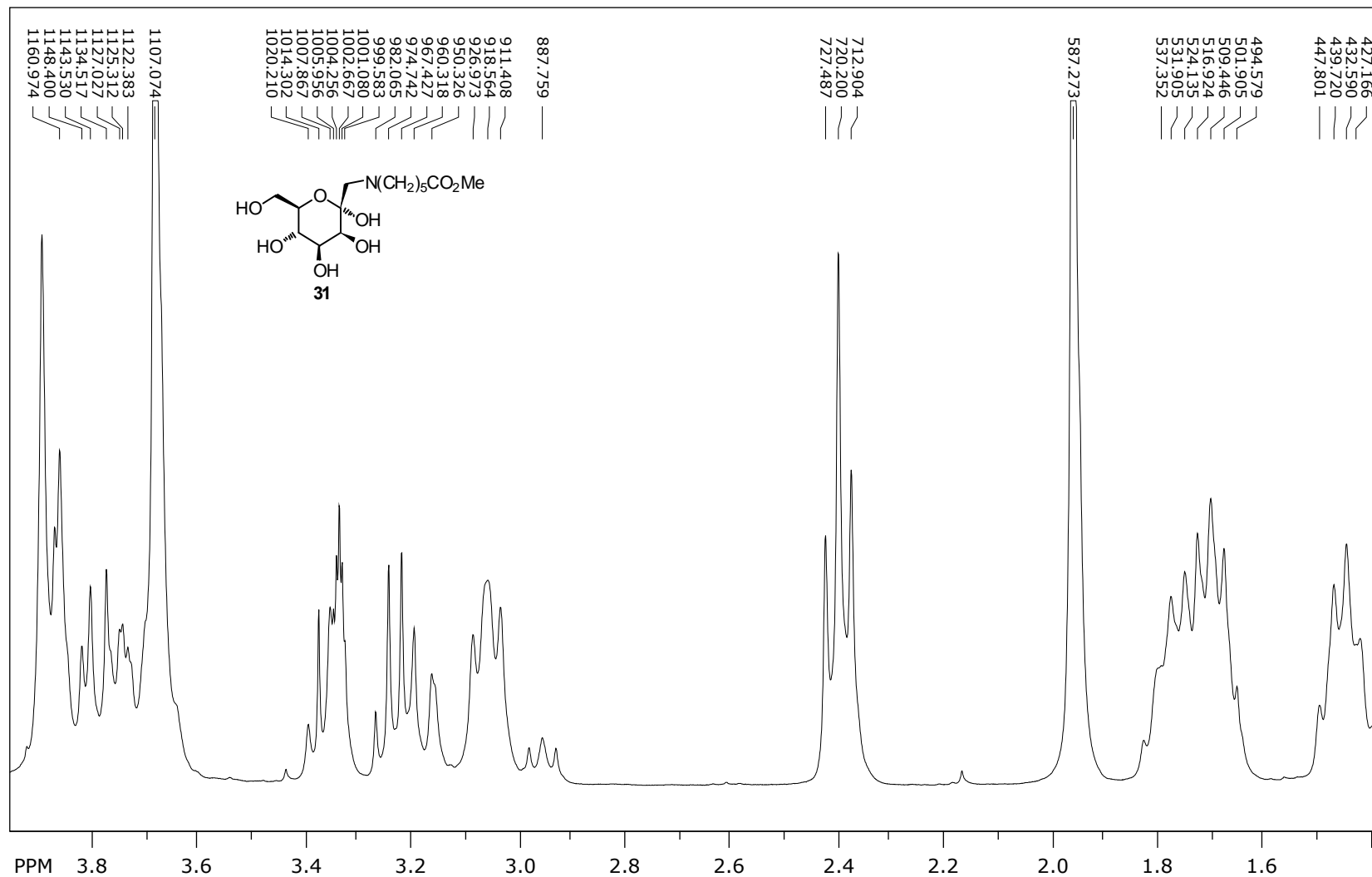
1-(*N*-(6-Hydroxyhexyl)amino)-1-*N*,2-*O*-carbonyl-1-deoxy- $\beta$ -D-manno-pyranose (**30**)  $^1\text{H}$ , 300 MHz,  $\text{MeOH-}d_4$



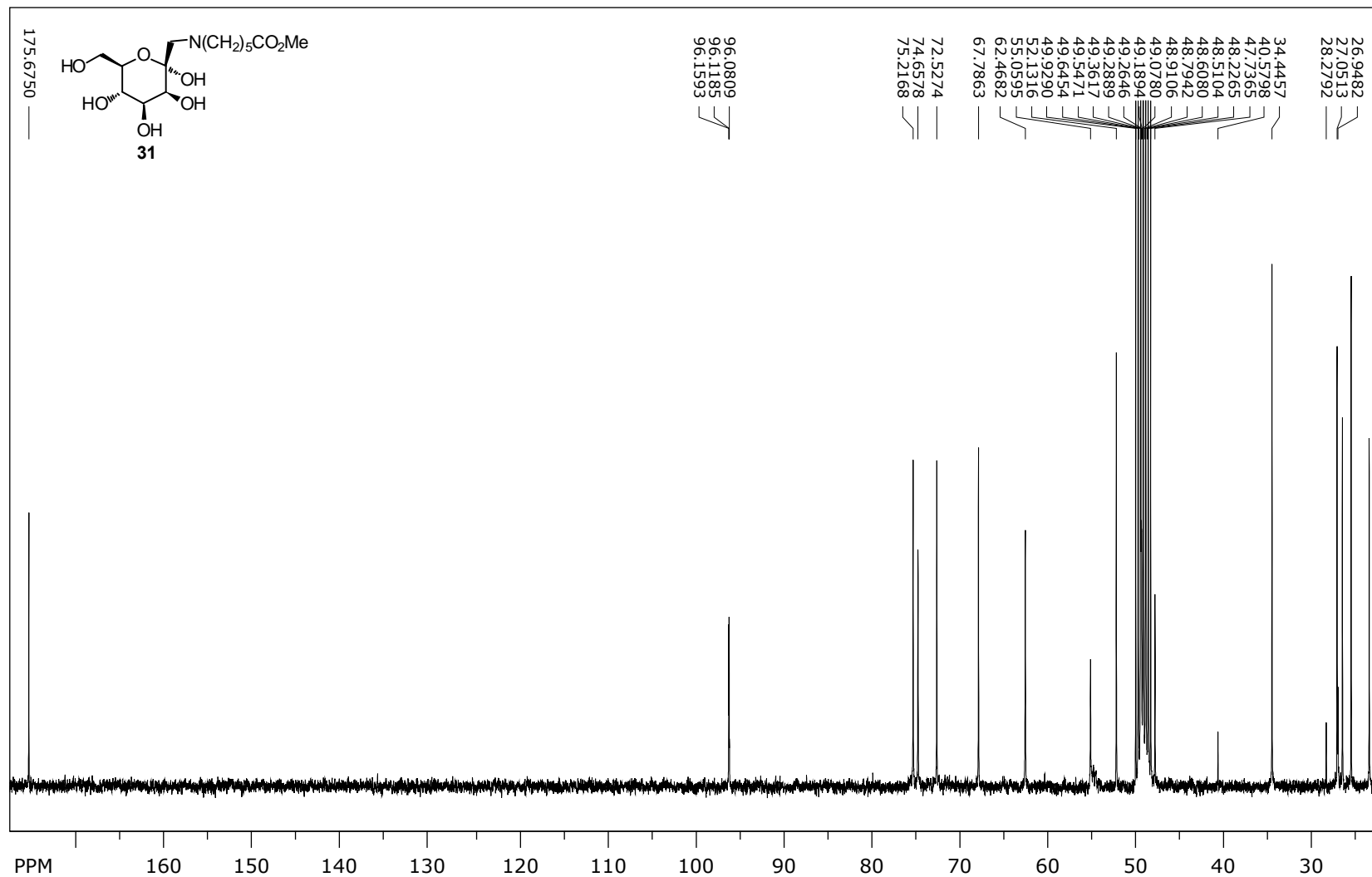
1-(*N*-(6-Hydroxyhexyl)amino)-1-*N*,2-*O*-carbonyl-1-deoxy- $\beta$ -D-*manno*-pyranose (30)  $^{13}\text{C}$ , 75 MHz, MeOH- $d_4$



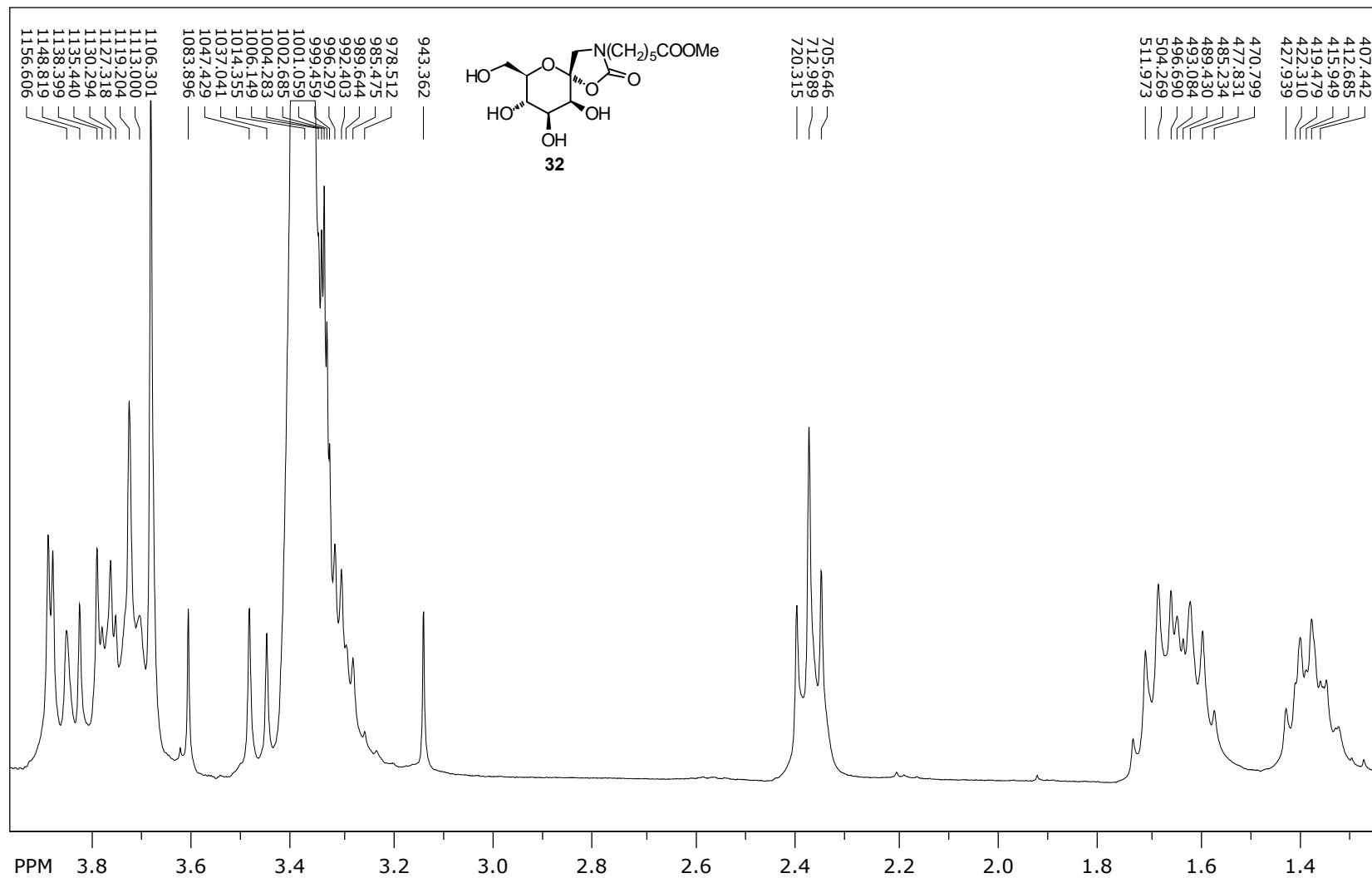
1-(*N*-(5-(Methoxycarbonyl)pentyl)amino)-1-deoxy- $\alpha$ -D-manno-hept-2-ulopyranose (31)  $^1\text{H}$ , 300 MHz,  $\text{MeOH-}d_4$



1-(N-(5-(Methoxycarbonyl)pentyl)amino)-1-deoxy- $\alpha$ -D-manno-hept-2-ulopyranose (31)  $^{13}\text{C}$ , 75 MHz, MeOH- $d_4$

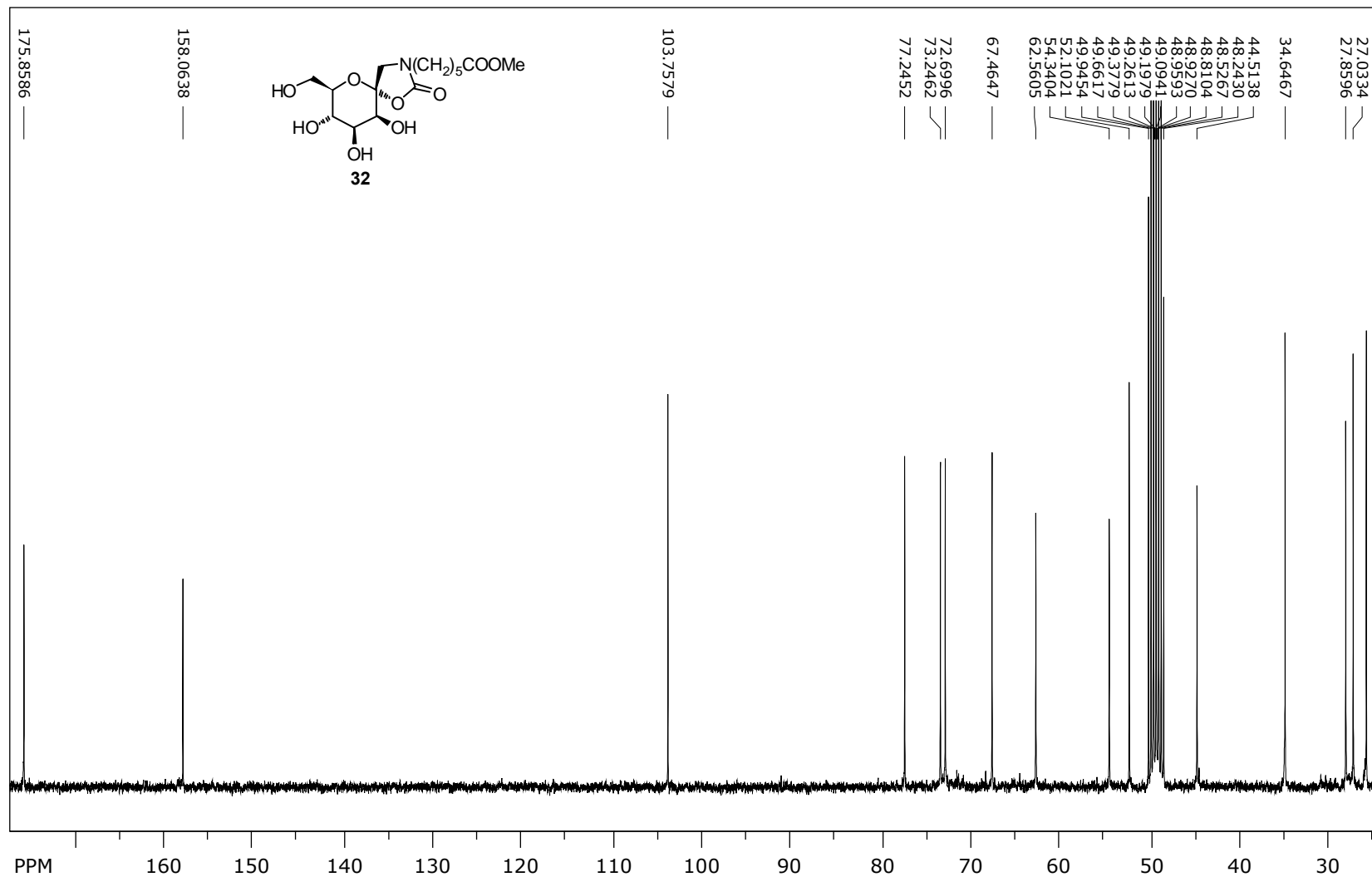


1-(*N*-(5-(Methoxycarbonyl)pentyl)amino)-1-*N*,2-*O*-carbonyl-1-deoxy- $\beta$ -D-manno-hept-2-ulopyranose (**32**)  $^1\text{H}$ , 300 MHz,  $\text{MeOH-}d_4$

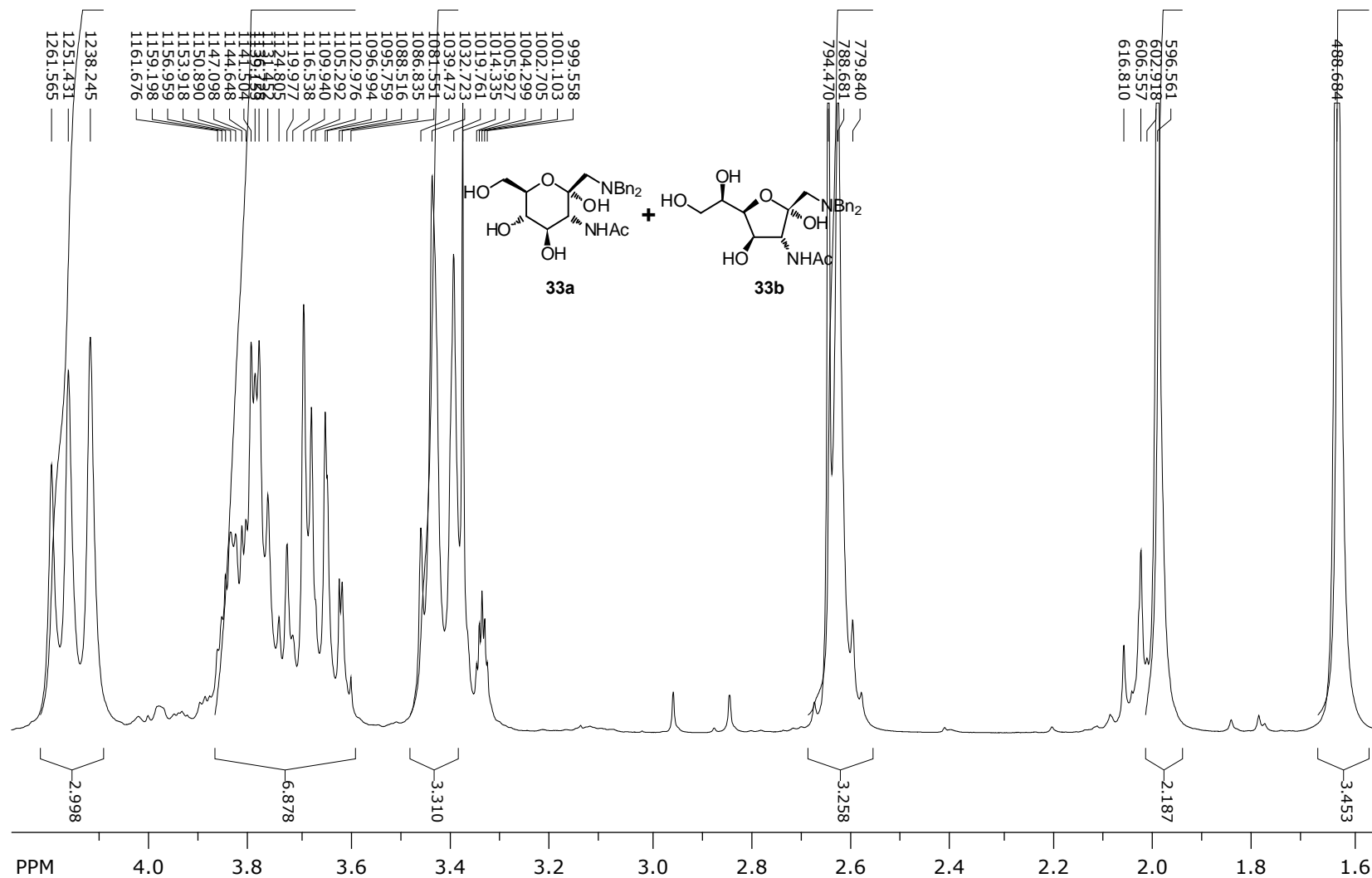




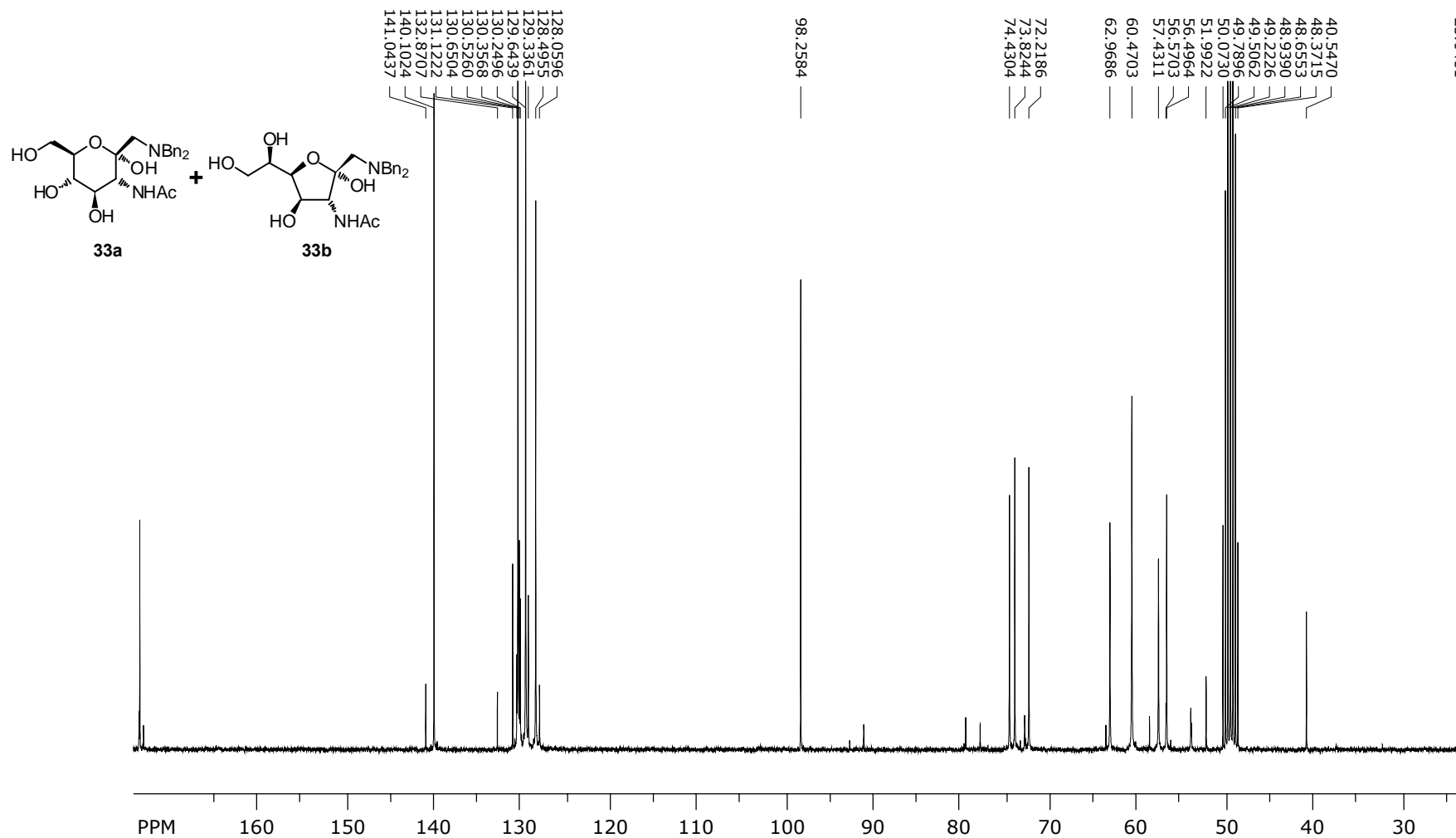
1-(*N*-(5-(Methoxycarbonyl)pentyl)amino)-1-*N*,2-*O*-carbonyl-1-deoxy- $\beta$ -D-manno-hept-2-ulopyranose (**32**)  $^{13}\text{C}$ , 75 MHz, MeOH- $d_4$



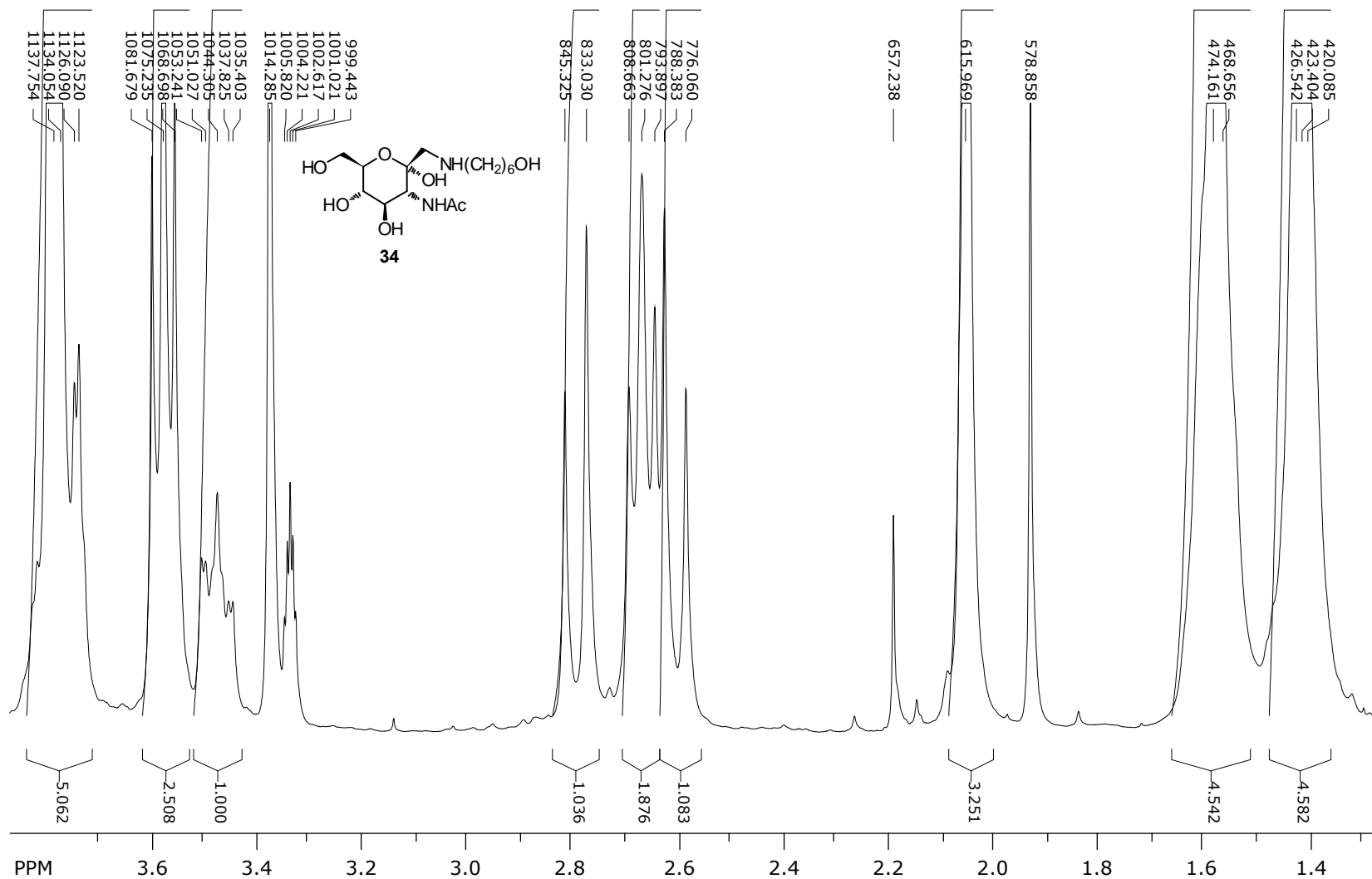
1-(*N,N*-Dibenzylamino)-3-acetamino-1,2-dideoxy- $\alpha$ ,*D*-gluco-hept-2-ulopyranose (33a) and -furanose (33b)  $^1\text{H}$ , 300 MHz,  $\text{MeOH-}d_4$



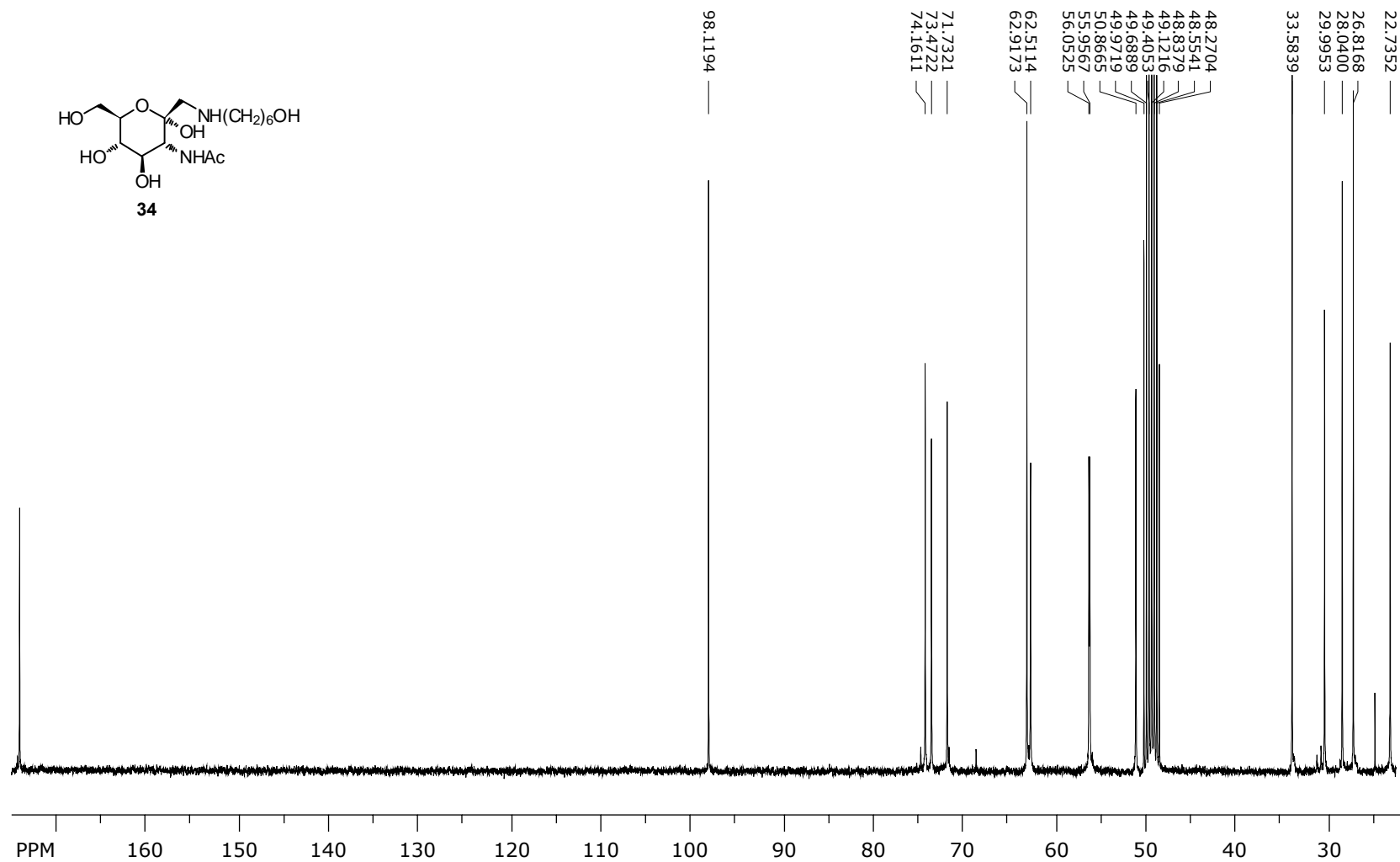
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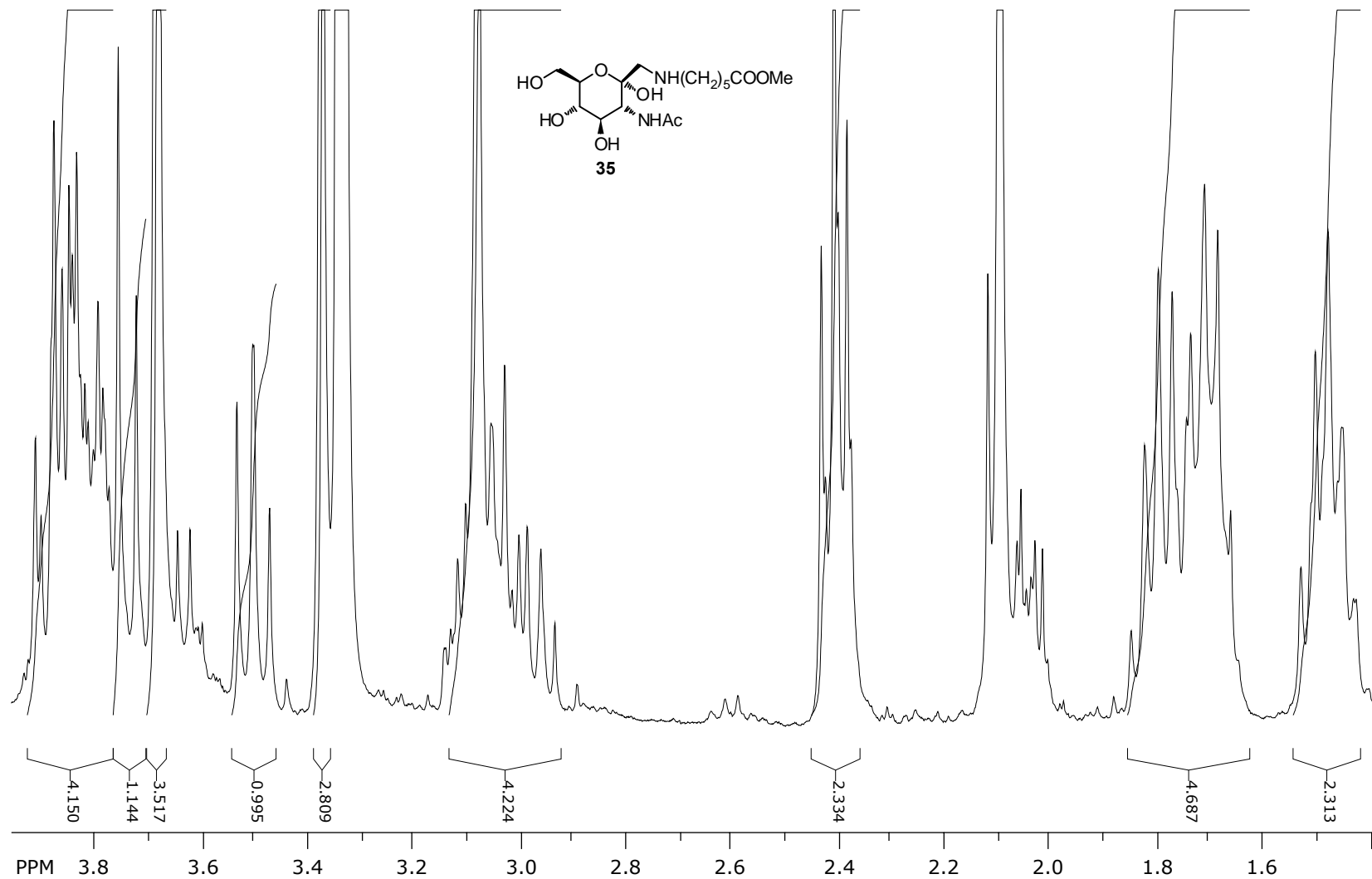
**1-(N-(6-Hydroxyhexyl)amino)-3-acetamido-1,2-dideoxy- $\alpha$ -D-gluco-hept-2-ulopyranose (34)  $^1\text{H}$ , 300 MHz,  $\text{MeOH-}d_4$**



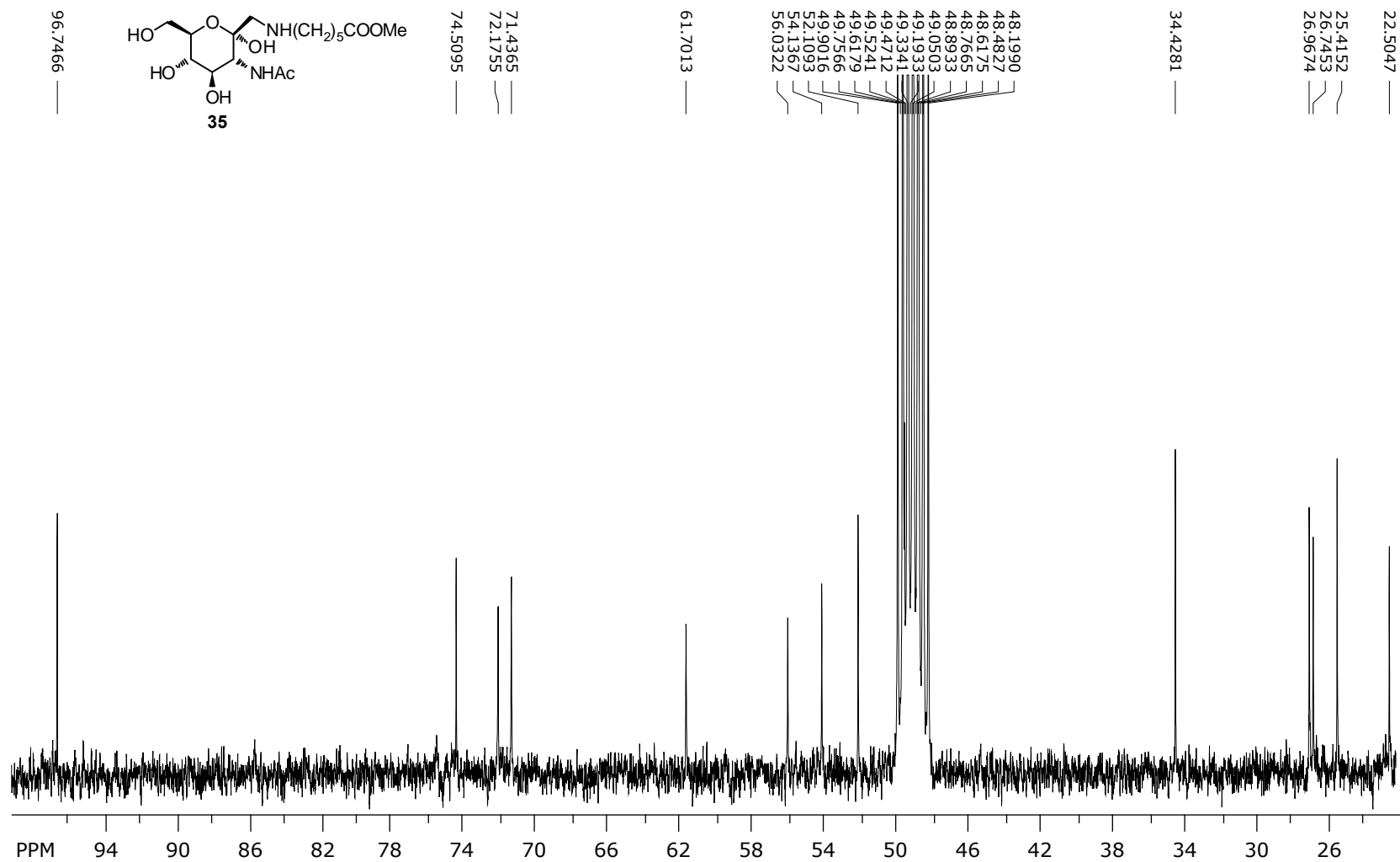
1-(N-(6-Hydroxyhexyl)amino)-3-acetamino-1,2-dideoxy- $\alpha$ -D-gluco-hept-2-ulopyranose (**34**)  $^{13}\text{C}$ , 75 MHz, MeOH- $d_4$



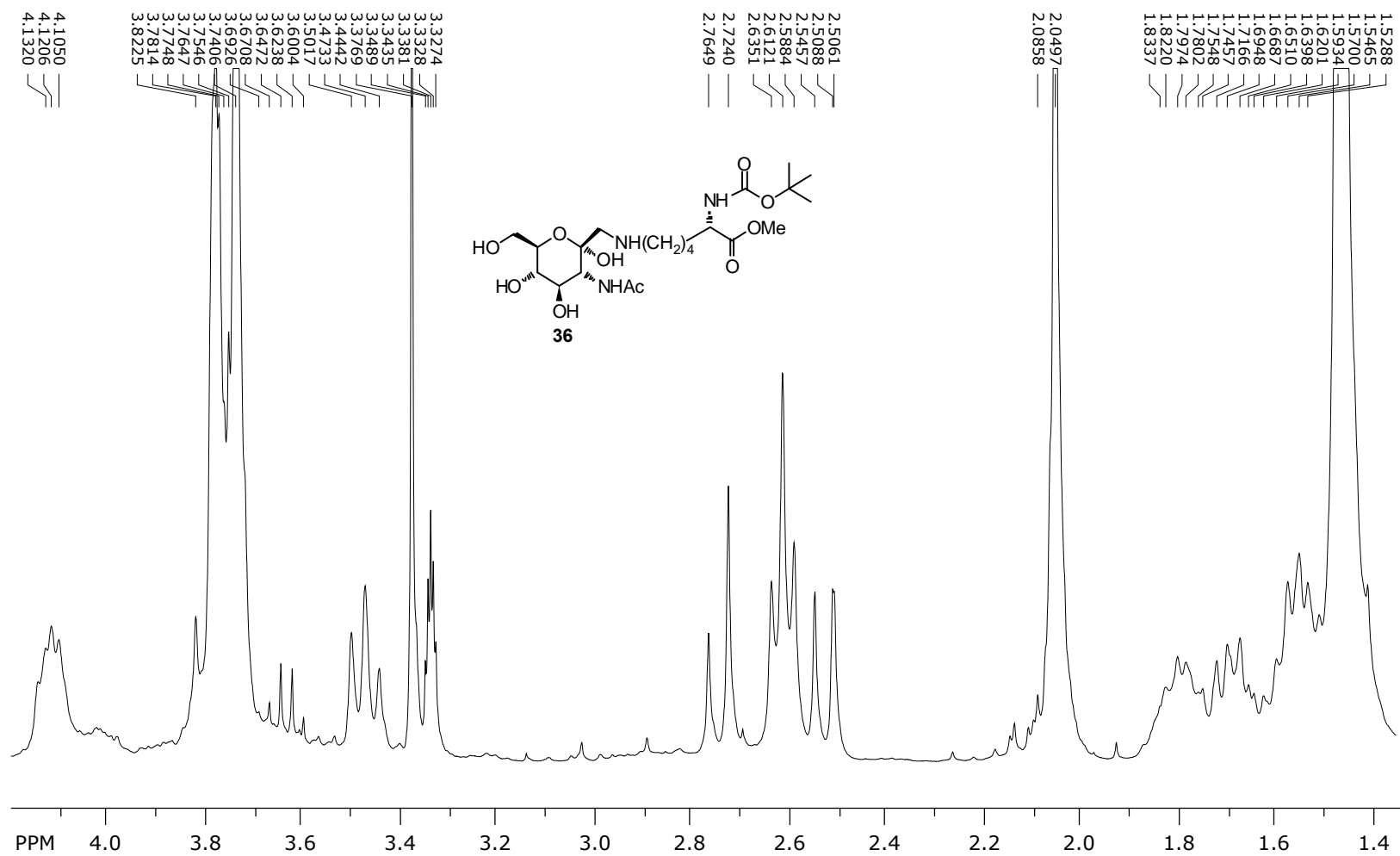
1-(*N*-(5-(Methoxycarbonyl)pentyl)amino)-2-acetamido-1,2-dideoxy- $\alpha$ -D-*gluco*-hept-2-ulopyranose (**35**)  $^1\text{H}$ , 300 MHz,  $\text{MeOH-}d_4$



1-(N-(5-(Methoxycarbonyl)pentyl)amino)-2-acetamino-1,2-dideoxy- $\alpha$ -D-gluco-hept-2-ulopyranose (35)  $^{13}\text{C}$ , 75 MHz, MeOH- $d_4$



**1-*N*-[(5*S*)-(tert-Butoxycarbonylamino)-5-(methoxycarbonyl)pentyl]amino-3-acetamino-1,2-dideoxy- $\alpha$ -D-gluco-hept-2-ulopyranose (36)**  
 **$^1\text{H}$ , 300 MHz, MeOH- $d_4$**





**1-N-[(5S)-(tert-Butoxycarbonylamino)-5-(methoxycarbonyl)pentyl]amino-3-acetamino-1,2-dideoxy- $\alpha$ -D-gluco-hept-2-ulopyranose (36)**  
 **$^{13}\text{C}$ , 75 MHz, MeOH- $d_4$**

