

## Electronic Supplementary Information (ESI)

Synthesis of methylphosphorylated oligomannosides structurally related to lipopolisaccharide O-antigens of *Klebsiella pneumoniae* serotype O3 and their application for detection of specific antibodies in rabbit and human sera

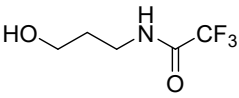
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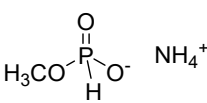
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## Synthetic procedures

### 3-N-trifluoroacetamido-1-propanol


 Ethyl trifluoroacetate (26.5 g, 185 mmol) was added dropwise to 3-amino-1-propanol (11.0 g, 151 mmol) cooled to 0°C. The reaction mixture was stirred for 1 h at 0°C, after that volatiles were removed by rotary evaporation at 7 mbar and 45°C over 30 minutes. The residue was purified by vacuum distillation at 124°C (4 mmHg) to give 3-N-trifluoroacetamido-1-propanol (22.8 g, 90%).  $n_D$  (20°C) = 1.405; lit.<sup>1</sup>  $n_D$  (20°C) = 1.4052.

### Ammonium methyl H-phosphonate


 A mixture of dry methanol (2.9 mL) with dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added dropwise to a mixture of PCl<sub>3</sub> (2.5 mL) and dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL) in a two-necked flask covered with drying tube. The reaction mixture was concentrated *in vacuo* and volatiles were condensed in a cold trap cooled with liquid nitrogen. Then concentrated ammonia (25%, 7.5 mL) was added dropwise to the residue. The reaction mixture was concentrated *in vacuo* and volatiles were condensed in a cold trap cooled with liquid nitrogen. The residue was co-evaporated 3 times with toluene and dried *in vacuo* at 50°C.

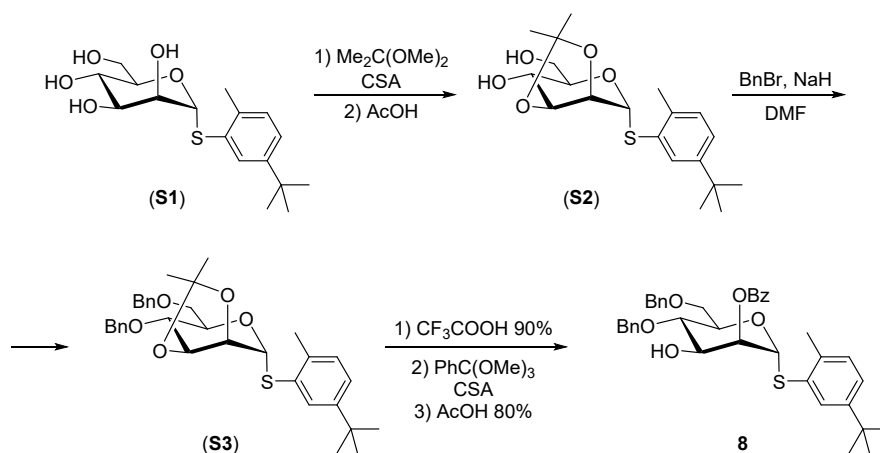
<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): 4.70 (3H, s, CH<sub>3</sub>), 3.47 (1H, d, J = 12 Hz, PH).

<sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O): 50.5 (J=4.2 Hz).

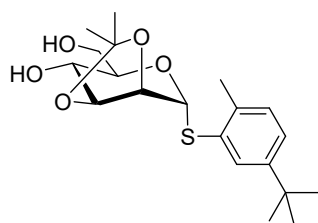
<sup>31</sup>P NMR (162 MHz, D<sub>2</sub>O): 8.46.

### (2-methyl-5-tert-butylthiophenyl) 4,6-di-O-benzyl-2-O-benzoyl-1-thia- $\alpha$ -D-mannopyranoside (8)

Thioglycoside **8** was synthesized according to a scheme described for similar compounds<sup>2,3</sup>.



### (2-methyl-5-tert-butylthiophenyl) 2,3-O-isopropylidene-1-thia- $\alpha$ -D-mannopyranoside (S2)

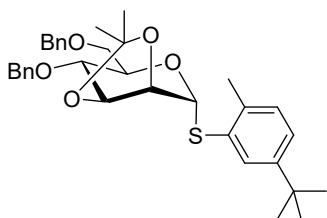


To a solution of monosaccharide **S1**<sup>4</sup> (9.9 g, 27.6 mmol) in acetone (10 mL), 2,2-dimethoxypropane (10 mL, 41 mmol) and camphorsulfonic acid (510 mg, 2.2 mmol) were added, and the reaction mixture was stirred at room temperature for 1 hour. The reaction was stopped with triethylamine (0.9 mL, 6.5 mmol) and the solution was concentrated *in vacuo*. The residue was dissolved in acetic acid (100 mL, 80% v/v with water) and the reaction mixture was stirred for 2 hours at 45°C. After that the solution was concentrated *in vacuo*. The residue was co-evaporated with toluene (50 mL twice) and purified via flash chromatography (40 g Silica Gel 60, toluene : EtOAc, 33% EtOAc over 8 CV) to give monosaccharide **S2** (4.95 g, 48%) as colorless oil.  $R_f = 0.45$  (toluene : EtOAc = 1:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 (d,  $J = 1.5$  Hz, 1H, Ar), 7.30-7.06 (m, 2H, Ar), 5.80 (s, 1H, H-1), 4.39 (d,  $J_{2,3} = 5.7$  Hz, 1H, H-2), 4.23 (dd,  $J_{3,4} = 7.2$  Hz, 1H, H-3), 4.05 (dt,  $J = 3.9, 9.9$  Hz, 1H, H-5), 3.85-3.70 (m, 3H, H-4, H-6a, H-6b), 2.41 (s, 3H, ArCH<sub>3</sub>), 1.55 (s, 3H, CH<sub>3</sub>), 1.39 (s, 3H, CH<sub>3</sub>), 1.30 (s, 9H, CH<sub>3</sub> tert-butyl).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.9, 137.0, 131.3, 130.4, 130.0, 125.4 (Ar), 110.0, 83.0 (C-1), 78.6 (C-3), 76.6 (C-2), 70.7 (C-5), 70.3 (C-4), 62.2 (C-6), 31.4 (CH<sub>3</sub> tert-butyl), 28.3 (CH<sub>3</sub>), 26.5 (CH<sub>3</sub>), 20.3 (ArCH<sub>3</sub>).

### (2-methyl-5-tert-butylthiophenyl) 4,6-di-O-benzyl-2,3-O-isopropylidene-1-thia- $\alpha$ -D-mannopyranoside (S3)

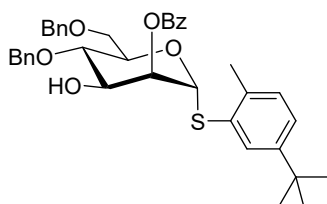


To a stirred solution of monosaccharide **S2** (5.13 g, 13.4 mmol) in DMF (20 mL) 60% suspension of NaH in mineral oil (2.15 g, 53.6

mmol) was added. After 10 minutes benzyl bromide (6.4 mL, 53.6 mmol) was added dropwise and the reaction mixture was stirred for 1.5 hours at room temperature. The reaction mixture was carefully poured into water (50 mL) and the crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL three times). The organic layer was filtered through a layer of anhydrous CaCl<sub>2</sub> and concentrated *in vacuo*. The residue was purified via flash chromatography (40 g Silica Gel 60, toluene : EtOAc, 5% EtOAc over 3 CV) to give monosaccharide **S3** (8.5 g) as colorless viscous liquid. R<sub>f</sub> = 0.58 (toluene : EtOAc = 10:1). The product contained some amount of mineral oil and benzyl bromide which were separated on the next step.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60-7.09 (m, Ar), 5.84 (s, 1H, H-1), 4.88 (d, *J* = 11.3 Hz, 1H, PhCH<sub>2</sub>), 4.59-4.37 (m, 5H, H-2, H-3, PhCH<sub>2</sub>), 4.23-4.18 (m, 1H, H-5), 3.79-3.72 (m, 2H, H-4, H-6a), 3.57 (d, *J* = 10.9 Hz, 1H, H-6b), 2.38 (s, 1H), 1.53 (s, 1H), 1.40 (s, 1H), 1.27 (s, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 130.1, 129.5, 128.6, 128.4, 128.4, 128.1, 127.9, 127.8, 127.6, 124.8 (Ar), 83.7 (C-1), 78.8 (C-3), 77.0 (C-2), 76.1 (C-4), 73.6 (PhCH<sub>2</sub>), 73.3 (PhCH<sub>2</sub>), 70.3 (C-5), 68.9 (C-6), 31.5 (CH<sub>3</sub> tert-butyl), 28.2 (CH<sub>3</sub>), 26.7 (CH<sub>3</sub>), 20.3 (ArCH<sub>3</sub>).



To a solution of monosaccharide **S3** (8.5 g, 15.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL), trifluoroacetic acid (3 mL, 90% v/v with water) was added and the reaction mixture was stirred for 1 hour at room temperature. After that the reaction mixture was diluted with toluene (50 mL), concentrated *in vacuo* and co-evaporated with toluene again (30 mL). The residue was purified via flash chromatography (40 g Silica Gel 60, toluene : EtOAc, 15% EtOAc over 2 CV, then 15% to 25% EtOAc over 6 CV) to give intermediate product. R<sub>f</sub> = 0.2 (toluene : EtOAc = 4:1). It was dissolved in acetonitrile (20 mL), and trimethylorthobenzoate (3.27 mL, 19 mmol) and camphorsulfonic acid (150 mg, 0.65 mmol) were added. The reaction mixture was stirred for 1.5 hours. After that acetic acid (27 mL) and water (6 mL) were added and the reaction mixture was stirred for 1.5 hours. The reaction mixture was poured into water (100 mL) at 0°C and then NaHCO<sub>3</sub> (40 g, 0.5 mol) was added in portions. The crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL three times), the solution was filtered through a layer of anhydrous CaCl<sub>2</sub> and the filtrate was concentrated *in vacuo*. The residue was purified via flash chromatography (40 g Silica Gel 60, petroleum ether : EtOAc, 10% EtOAc over 5 CV) to give monosaccharide **8** (4.55 g, 54% from **S2**) as colorless oil. R<sub>f</sub> = 0.25 (petroleum ether : EtOAc = 5:1).

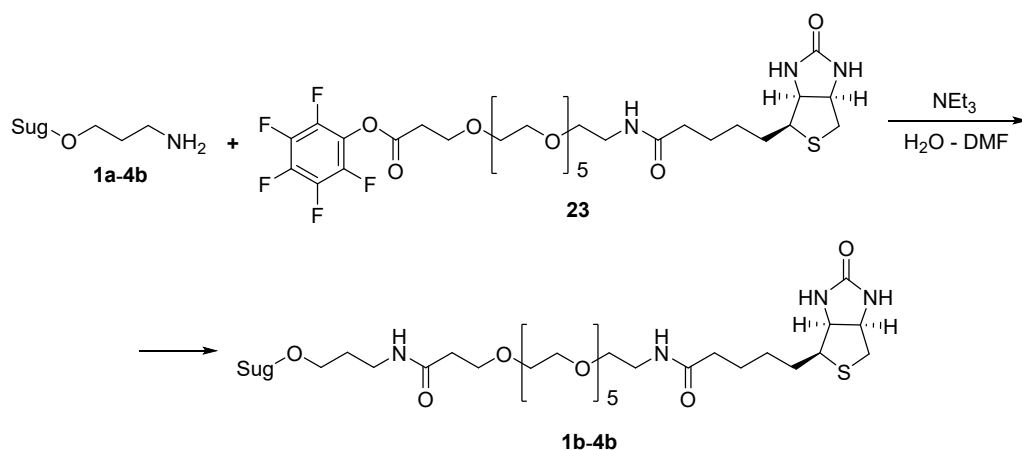
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 7.9 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.43-7.15 (m, 14H, Ar), 5.67 (s, 1H, H-2), 5.58 (s, 1H, H-1), 4.85 (d, *J* = 11.1 Hz, 1H, PhCH<sub>2</sub>), 4.75 (m, 2H, PhCH<sub>2</sub>), 4.55 (d, *J* = 11.9 Hz, 1H, PhCH<sub>2</sub>), 4.40 (br. d, *J*<sub>4,5</sub> = 9.4 Hz, 1H, H-5), 4.31 (m, 1H, H-3), 4.16 (t, *J*<sub>3,4</sub> = 9.5 Hz, 1H, H-4), 4.03 (dd, *J*<sub>5,6a</sub> = 3.4 Hz, *J*<sub>6a,6b</sub> = 11.1 Hz, 1H, H-6a), 3.77 (d,

$J = 11.1$  Hz, 1H, H-6b), 2.45 (s, 3H, ArCH<sub>3</sub>), 2.22 (d,  $J_{(O)H,2} = 5.0$  Hz, 1H, OH), 1.31 (s, 9H, CH<sub>3</sub>, tert-butyl).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  166.2 (CO), 149.9, 138.4, 138.3, 137.2, 133.4, 132.5, 130.6, 130.2, 130.0, 129.8, 128.7, 128.6, 128.5, 128.3, 128.1, 127.8, 127.7, 125.4 (Ar), 86.3 (C-1), 76.0 (C-4), 75.1 (PhCH<sub>2</sub>), 74.9 (C-2), 73.7 (PhCH<sub>2</sub>), 72.9 (C-5), 71.4 (C-3), 69.1 (C-6), 31.5 (CH<sub>3</sub> tert-butyl), 20.5 (ArCH<sub>3</sub>).

ESI HRMS: calculated  $m/z$  for [C<sub>38</sub>H<sub>42</sub>O<sub>6</sub>S+NH<sub>4</sub>]<sup>+</sup> 644.3040, found 644.3031; calculated  $m/z$  for [C<sub>38</sub>H<sub>42</sub>O<sub>6</sub>S+Na]<sup>+</sup> 649.2594, found 649.2589; calculated  $m/z$  for [C<sub>38</sub>H<sub>42</sub>O<sub>6</sub>S+K]<sup>+</sup> 665.2334, found 665.2328.

### Synthesis of biotinylated conjugates 1b-4b



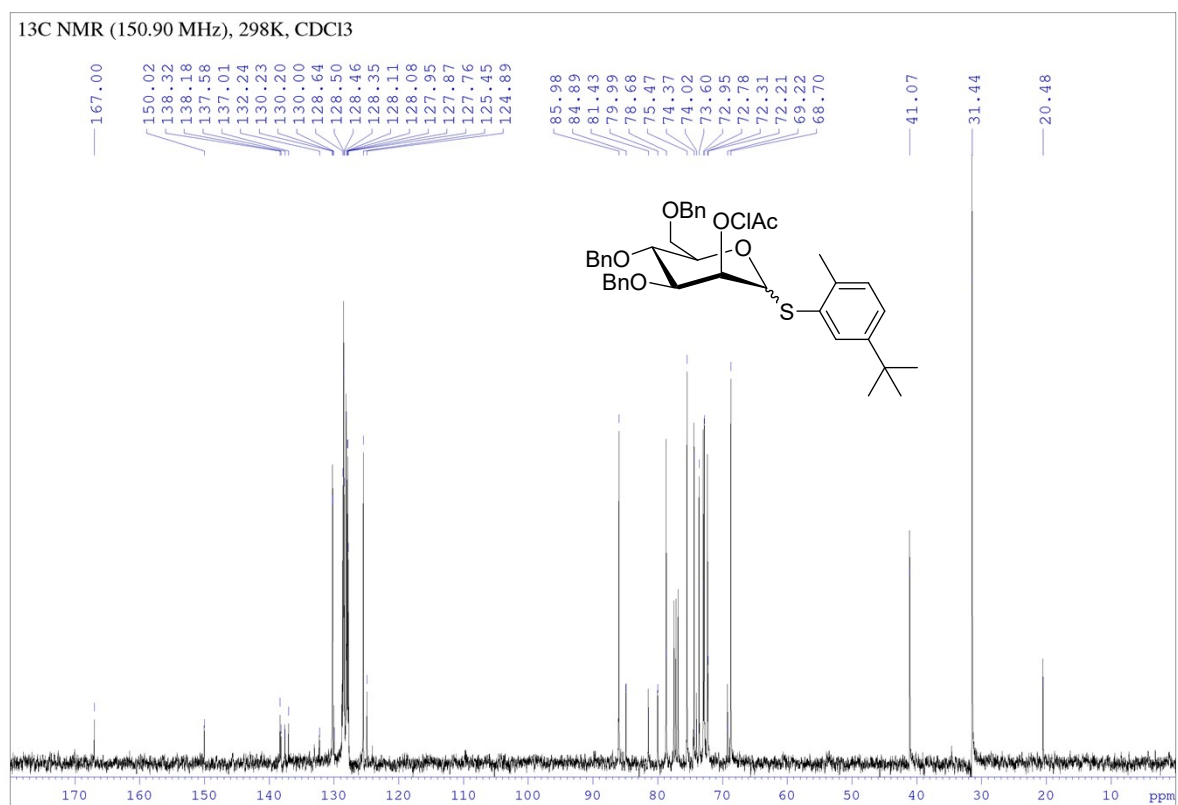
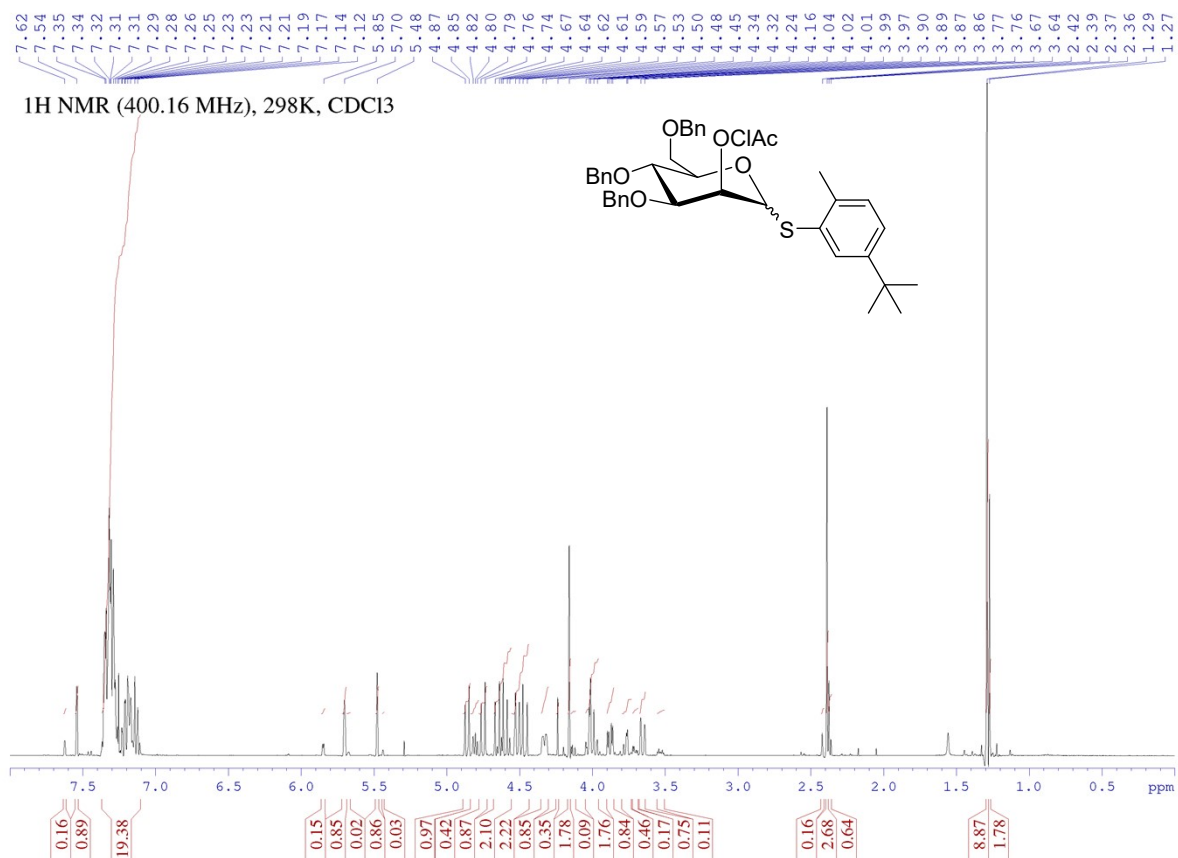
To a solution of starting compound (1-4, 1 eq.) in water (50  $\mu$ L) Et<sub>3</sub>N (10 eq.) and solution of active ester of biotin **23** in DMF (1.1 eq.,  $c = 62$   $\mu$ mol/ $\mu$ L) were added, the mixture was thoroughly shaken and then left for 1 hour. Then solvents were concentrated in vacuo and size-exclusion chromatography afforded desired biotin conjugates. Characteristic signals of biotin moiety:

<sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O)  $\delta$  4.62 (dd,  $J_{6a,3a} = 8.0$  Hz,  $J_{6a,6} = 4.9$  Hz, 1H, H6a), 4.42 (dd,  $J_{6a,3a} = 8.0$  Hz,  $J_{3a,4} = 4.5$  Hz, 1H, H3a), 3.02 (dd,  $J_{6,6'} = 13.1$  Hz,  $J_{6,6a} = 5.0$  Hz, 1H, H6), 2.81 (d,  $J_{6,6'} = 13.0$  Hz, 1H, H6'); 2.27 (t,  $J = 7.3$  Hz, 2H, NHCOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). Yields and HRMS data are in table below.

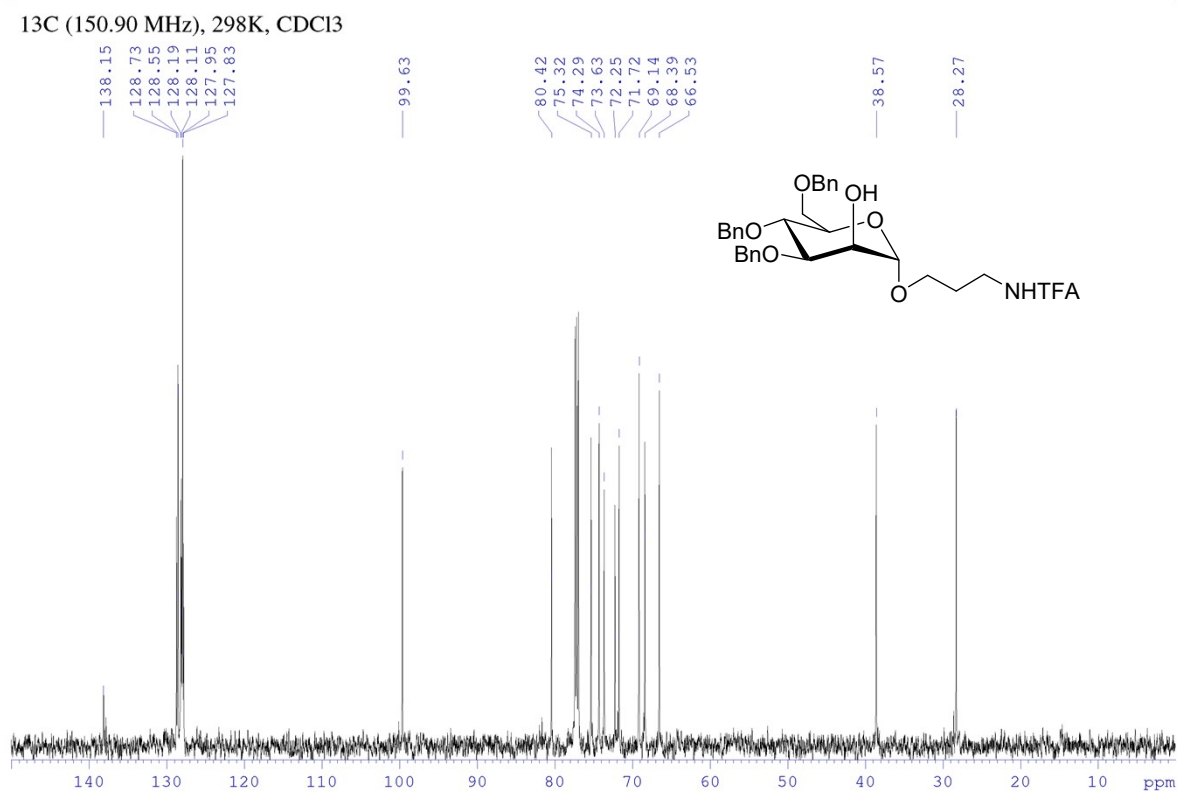
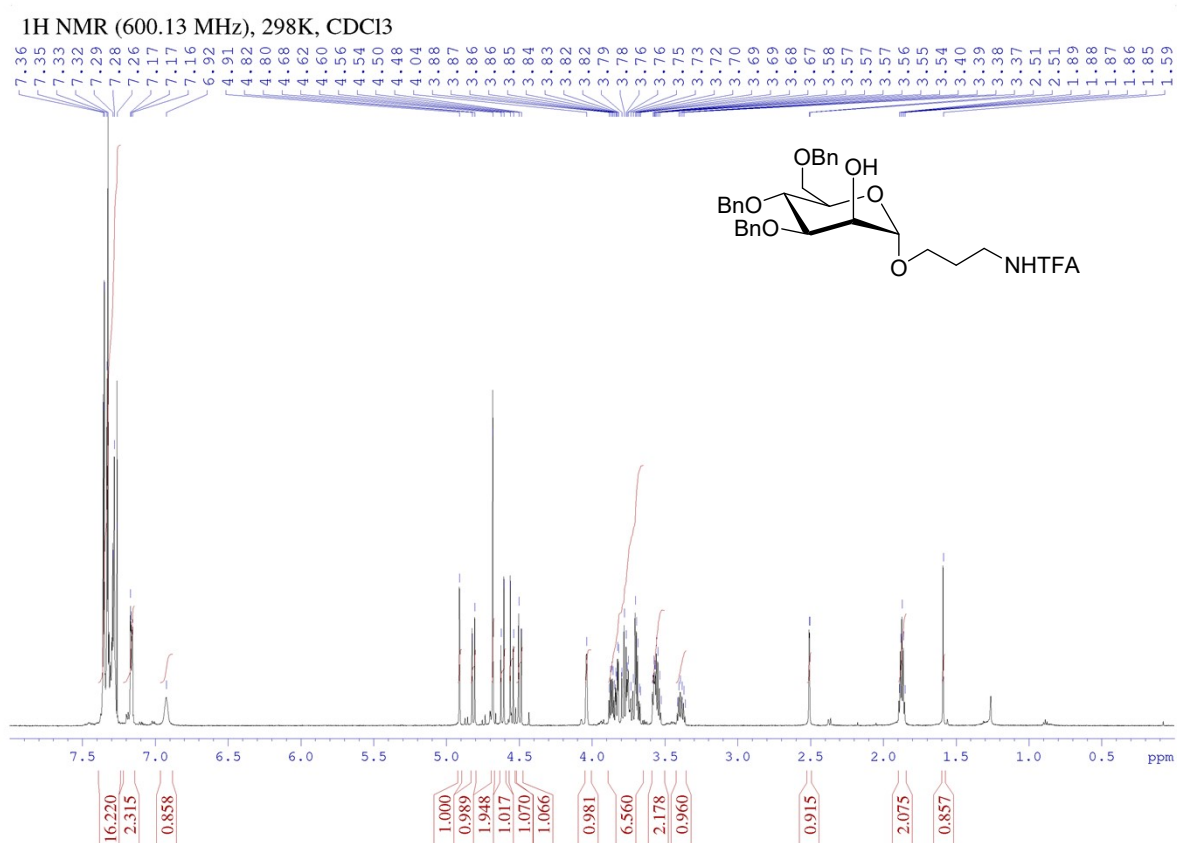
Entry	Starting compound			Product			HRMS $m([M + nH^+])/n$	
	N	mg	$\mu$ mol	N	mg	yield (%)	calculated	found
1	<b>1a</b>	1.2	3.7	<b>1b</b>	1.6	50	893.3825	893.3822
2	<b>2a</b>	0.7	1.3	<b>2b</b>	0.6	40	1055.4353	1055.4347
3	<b>3a</b>	0.9	1.4	<b>3b</b>	0.9	55	609.2477	609.2484
4	<b>4a</b>	1.1	1.7	<b>4b</b>	1.0	55	1217.4881	1217.4870

# NMR spectra copies

## (2-methyl-5-tert-butylthiophenyl) 2-O-chloroacetyl-3,4,6-tri-O-benzyl-1-thio-D-mannopyranoside (6)

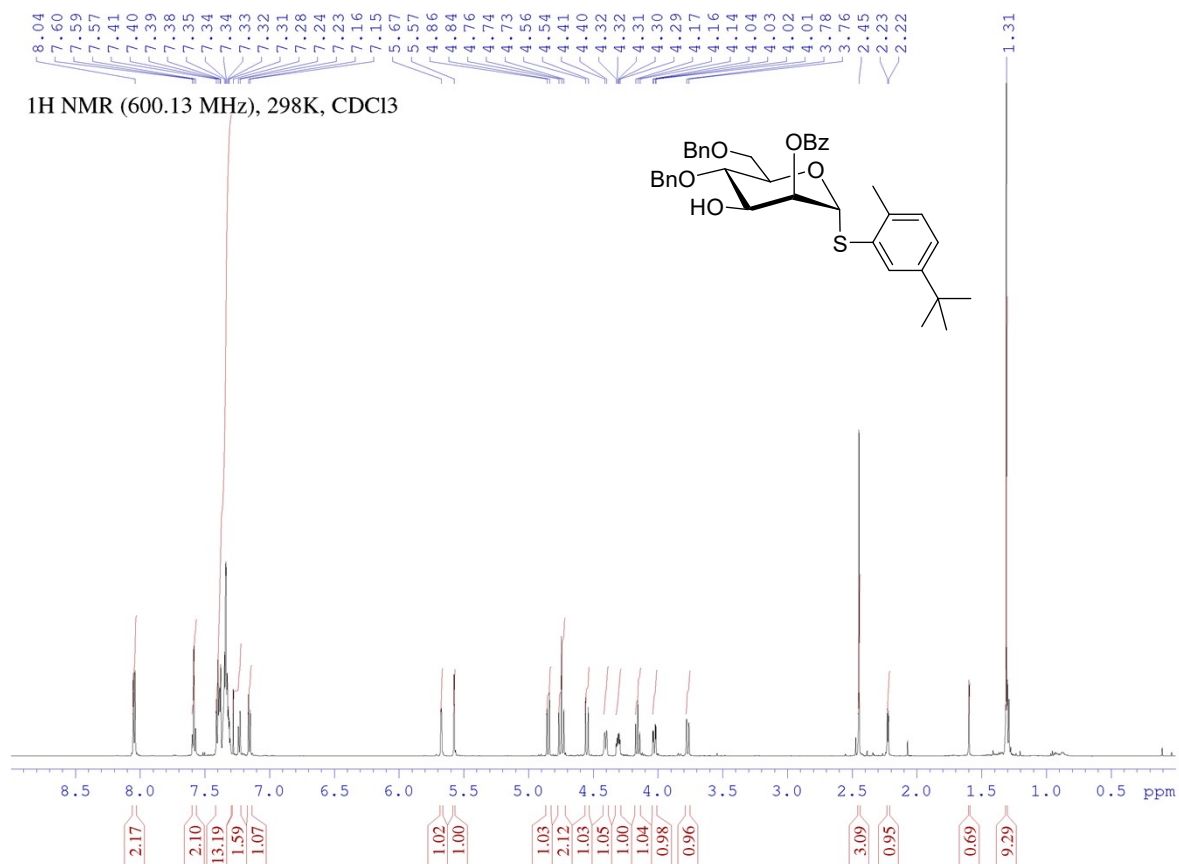


### 3-N-trifluoroacetylaminopropyl 3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranoside (7)

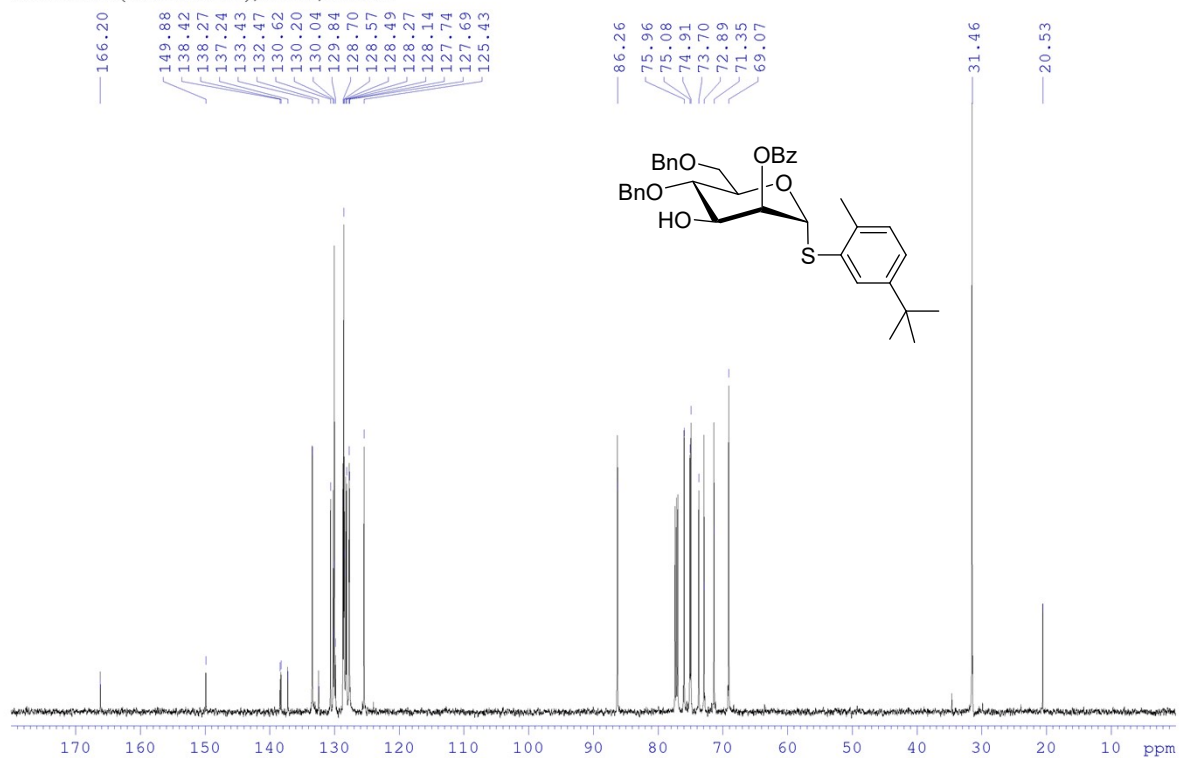




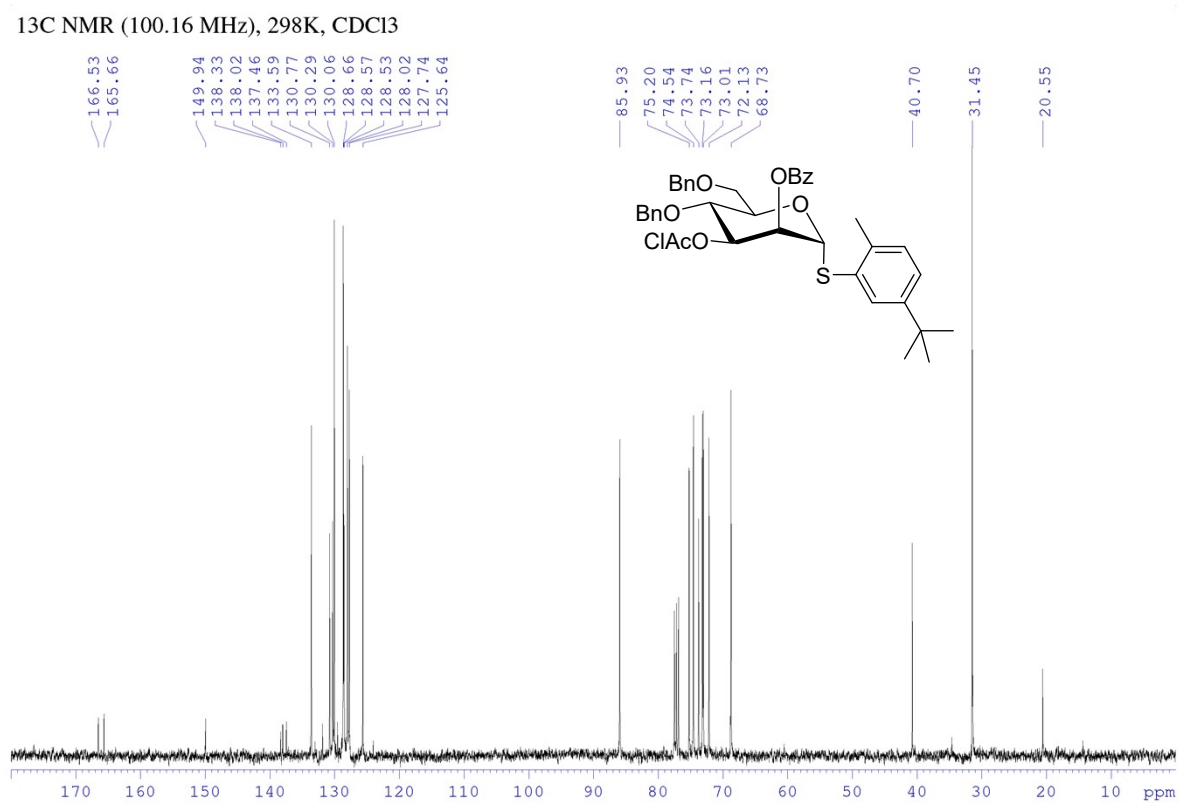
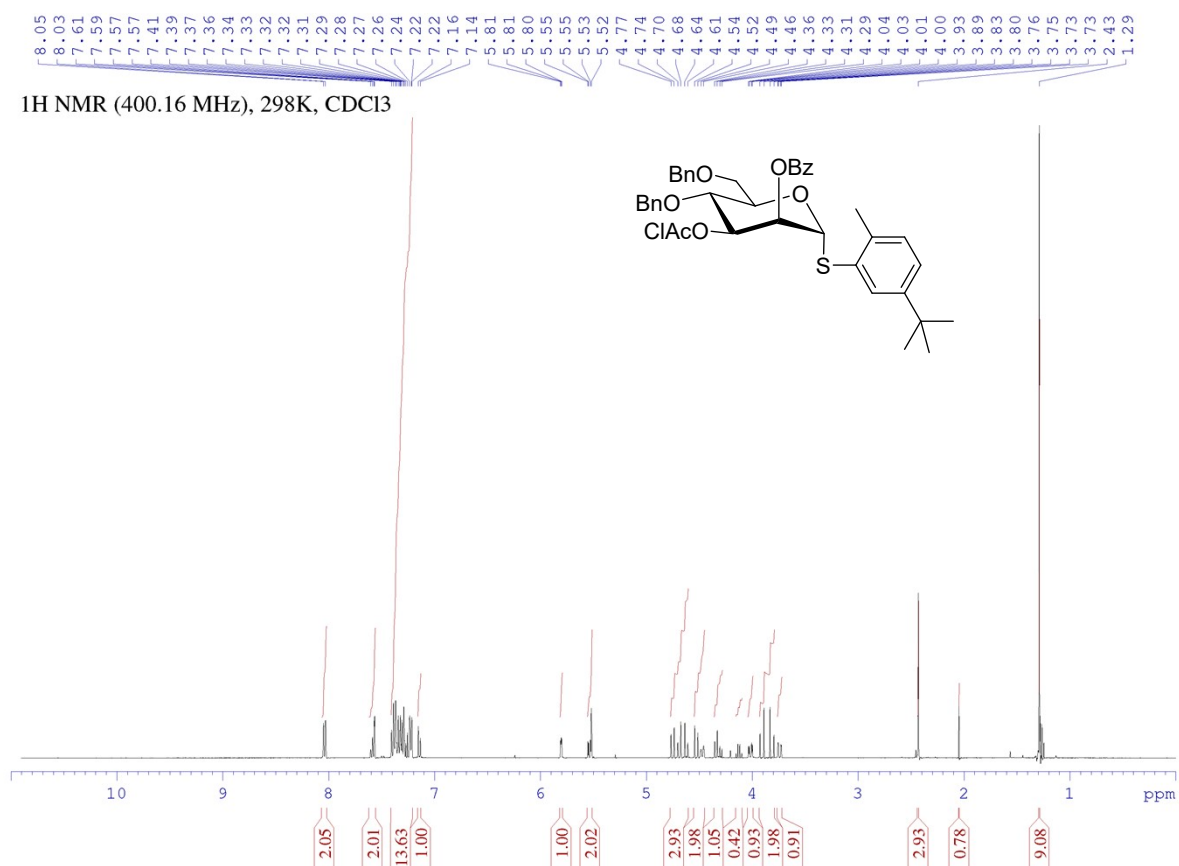
**(2-methyl-5-tert-butylthiophenyl) 4,6-di-O-benzyl-2-O-benzoyl-1-thia- $\alpha$ -D-mannopyranoside (8)**



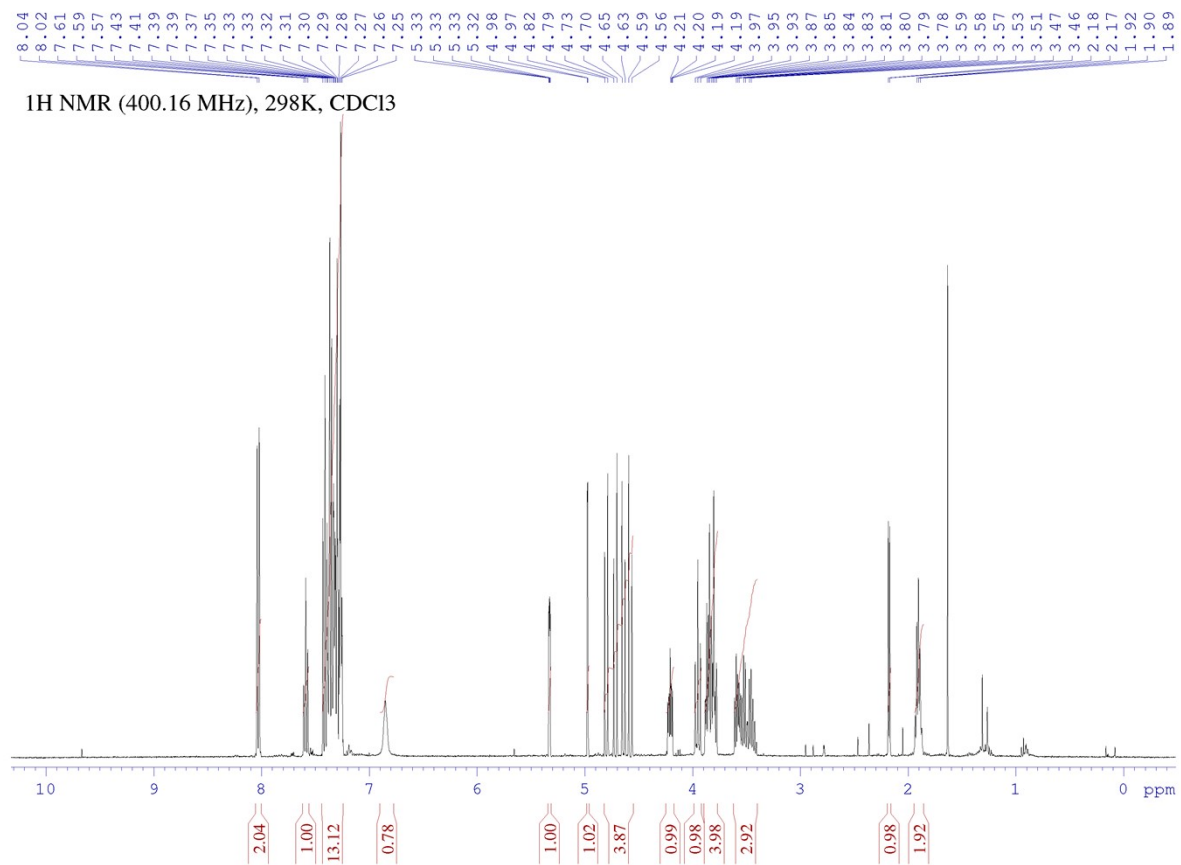
<sup>13</sup>C NMR (150.90 MHz), 298K, CDCl<sub>3</sub>



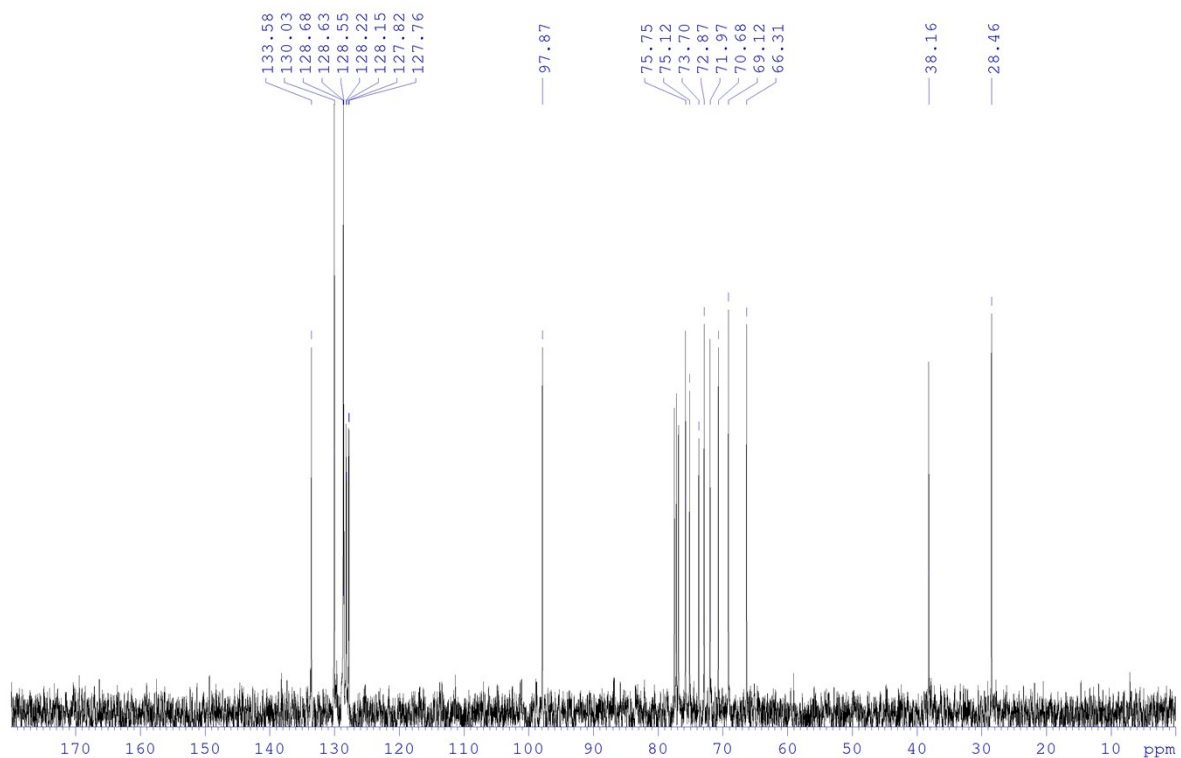
**(2-methyl-5-tert-butylthiophenyl) 4,6-di-O-benzyl-2-O-benzoyl-3-O-chloroacetyl-1-thia- $\alpha$ -D-mannopyranoside (9)**



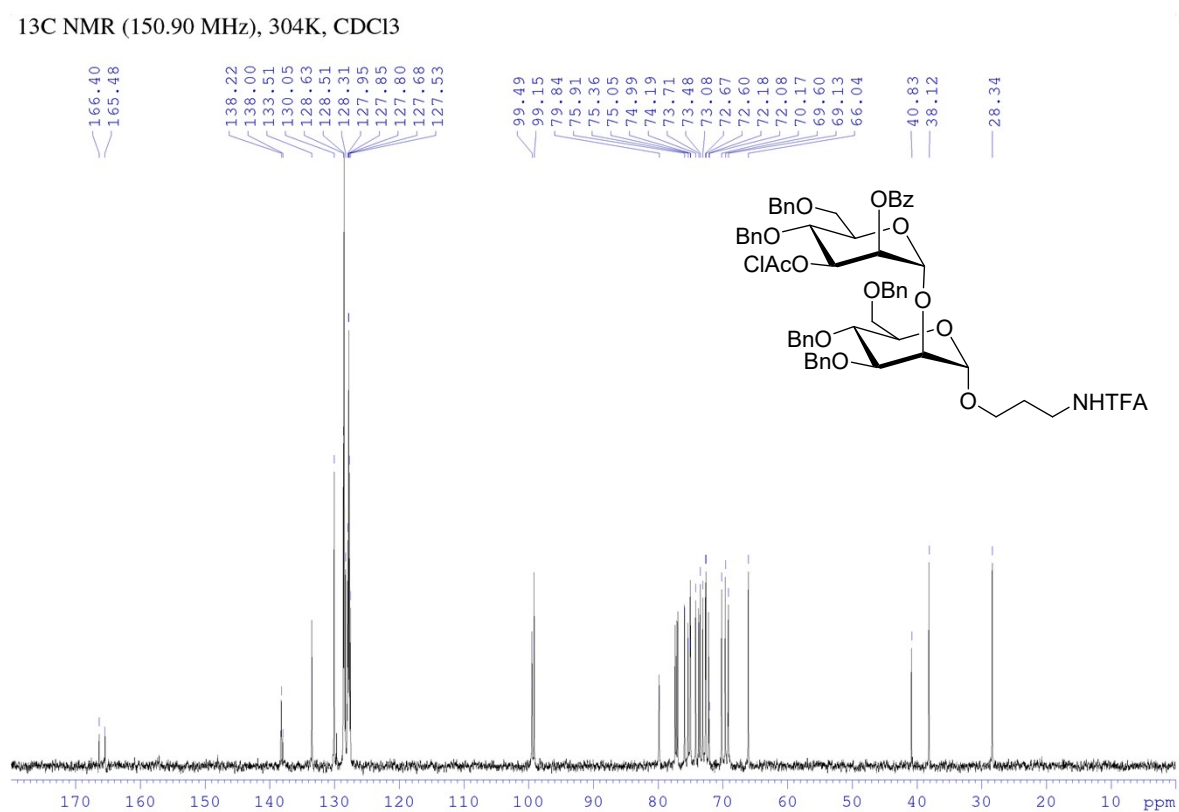
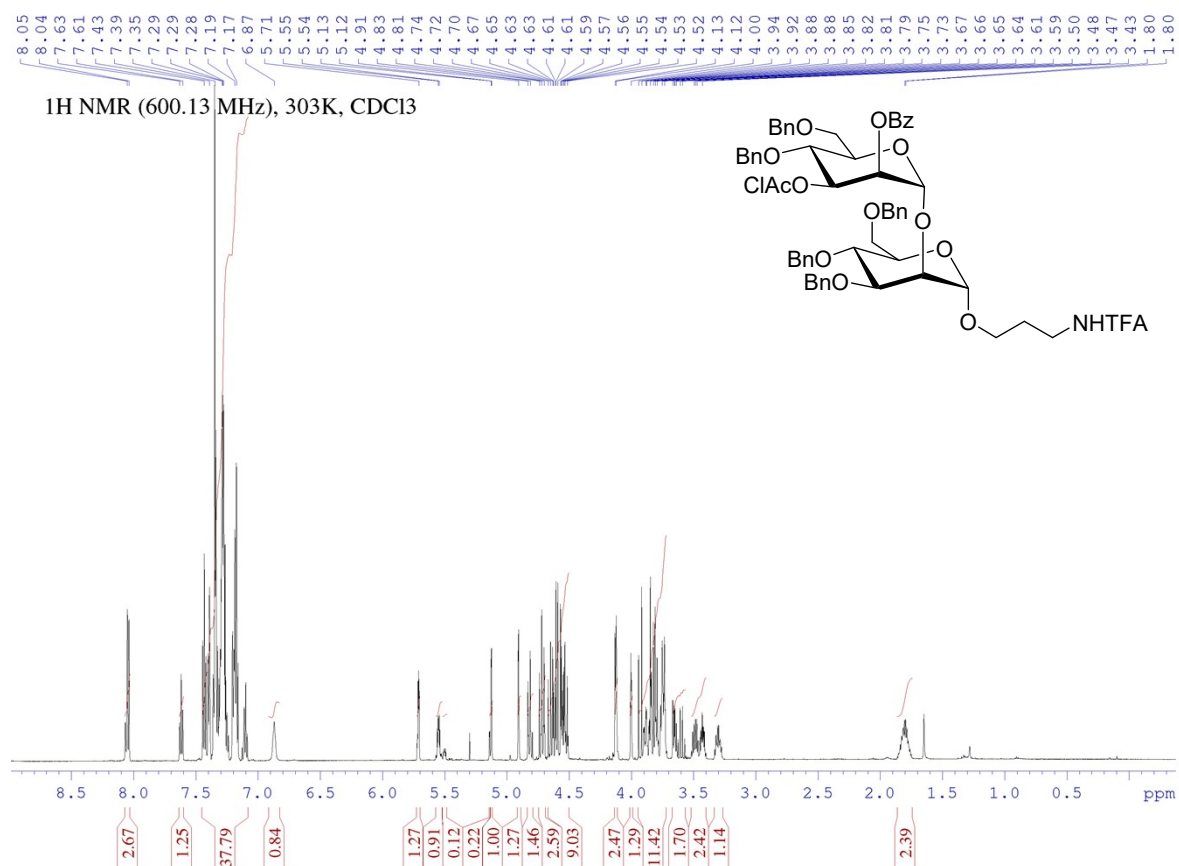
### 3-N-trifluoroacetylaminopropyl 4,6-di-O-benzyl-2-O-benzoyl- $\alpha$ -D-mannopyranoside (10)



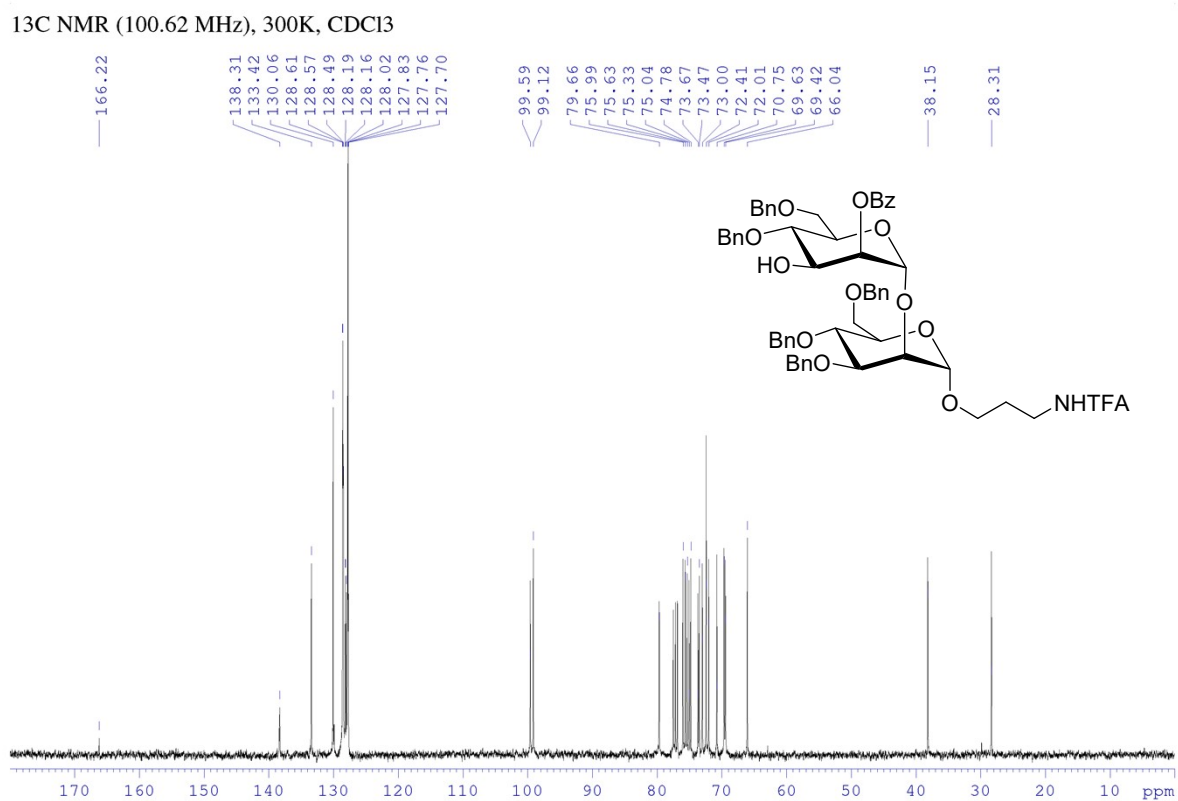
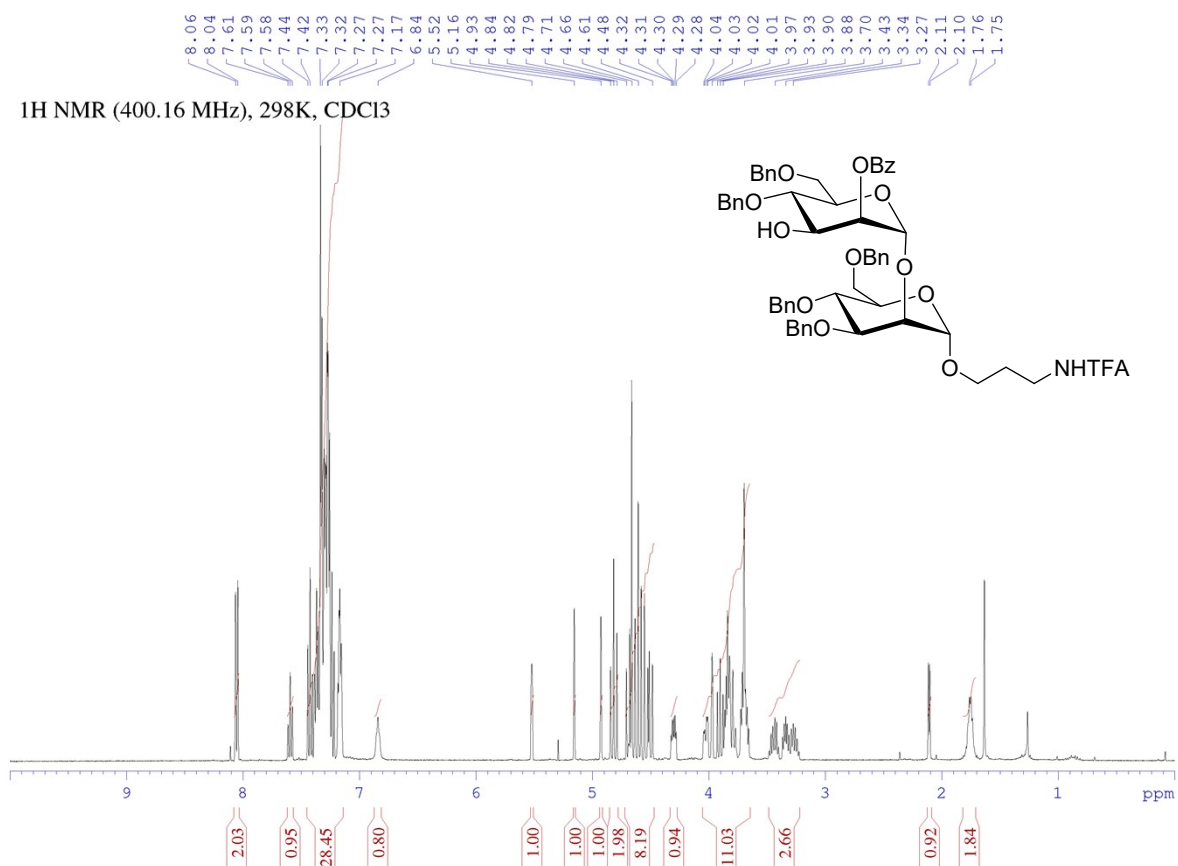
<sup>13</sup>C NMR (100.62 MHz), 298K, CDCl<sub>3</sub>



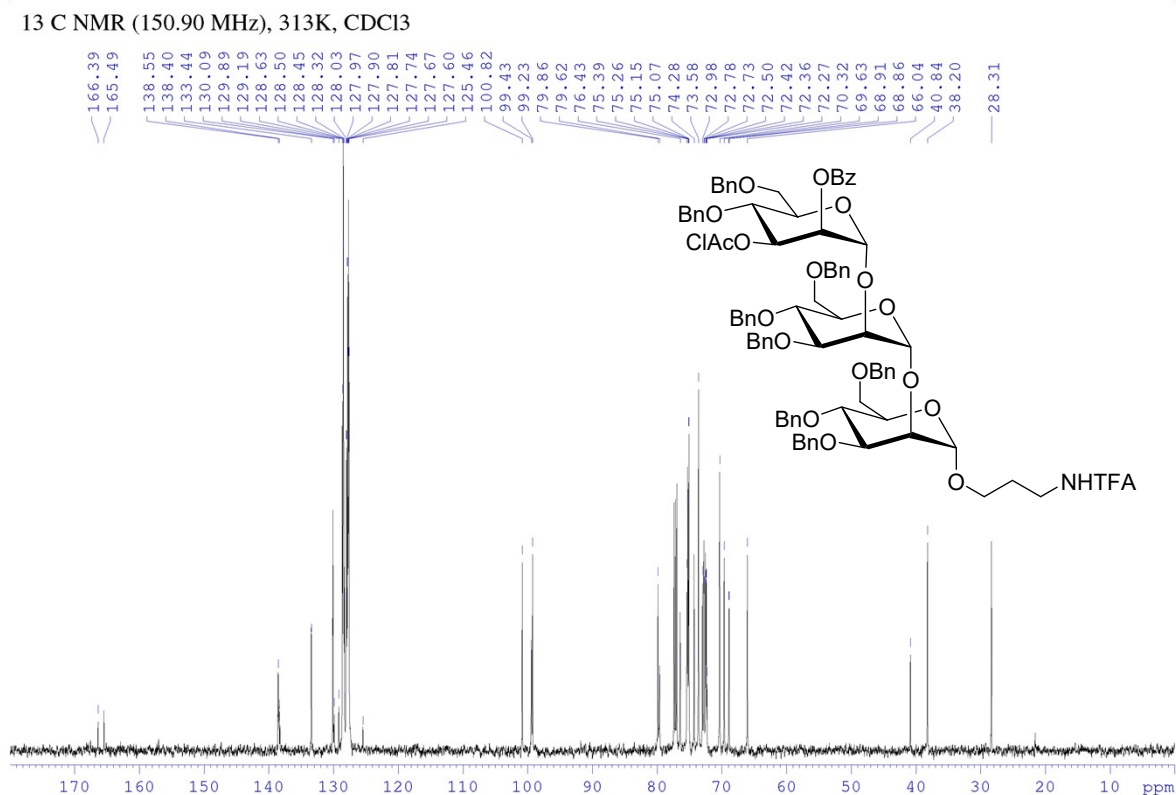
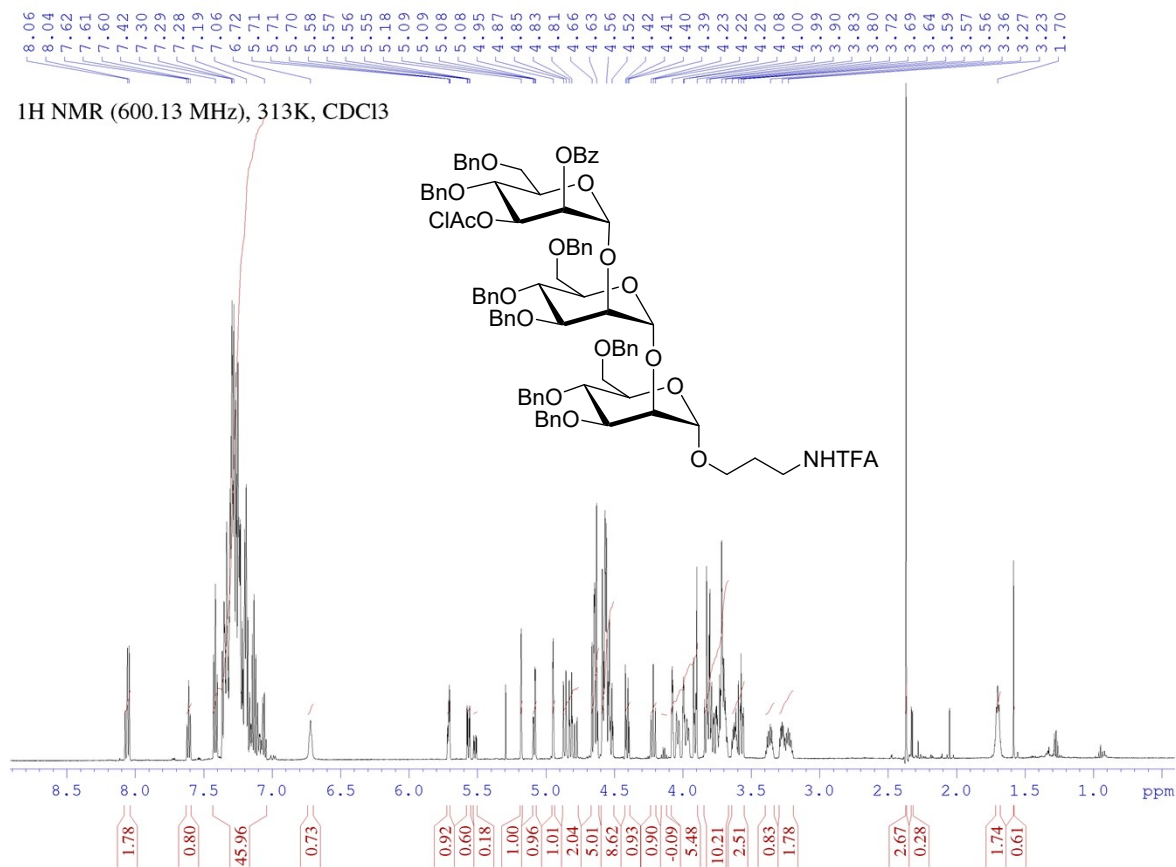
**3-N-trifluoroaminopropyl 4,6-di-O-benzyl-2-O-benzoyl-3-O-chloroacetyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranoside (11)**



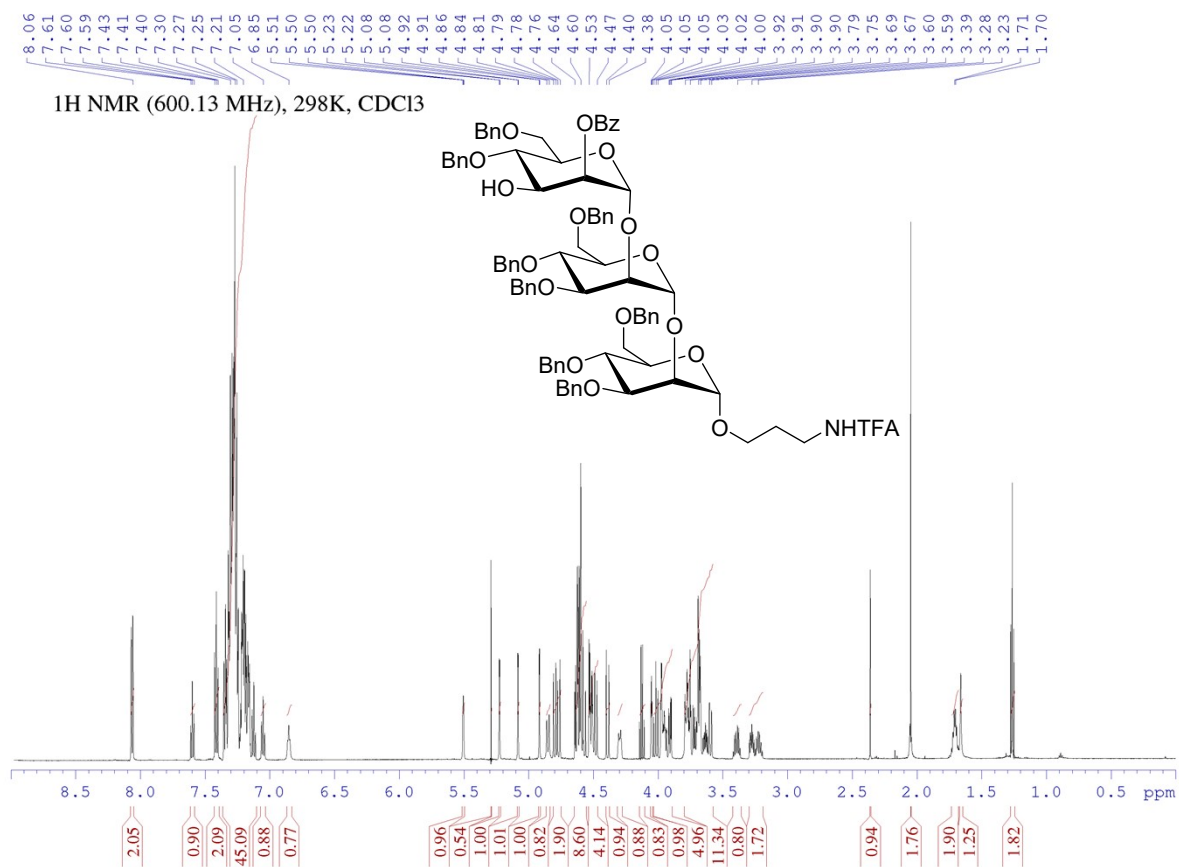
**3-N-trifluoroacetylaminopropyl 4,6-di-O-benzyl-2-O-benzoyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranoside (12)**



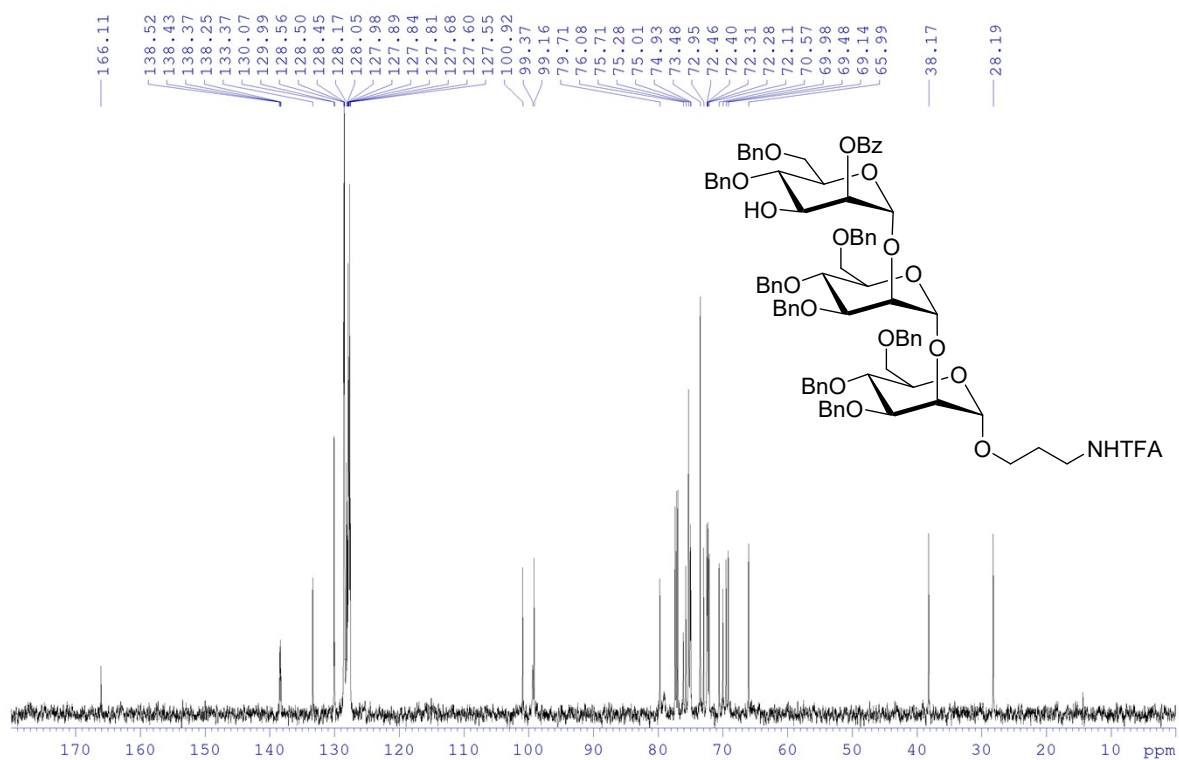
**3-N-trifluoroacetylaminopropyl 4,6-di-O-benzyl-2-O-benzoyl-3-O-chloroacetyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranoside (14)**



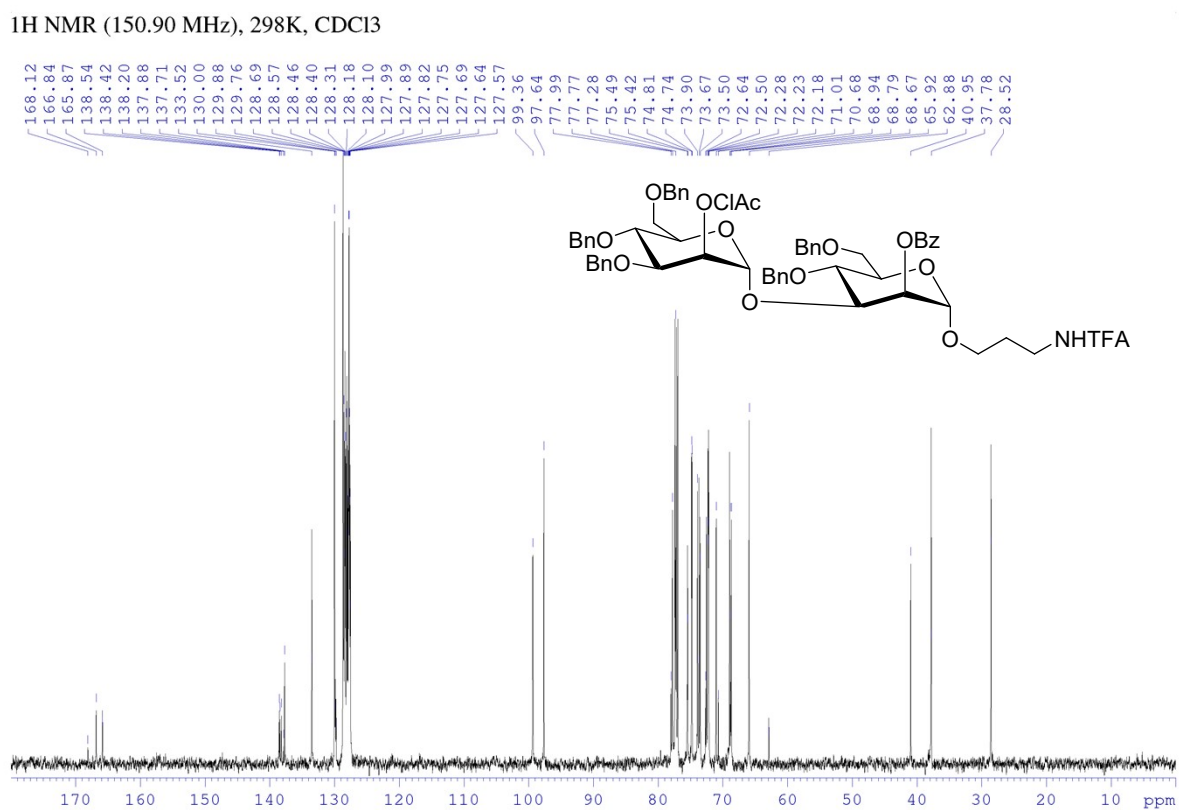
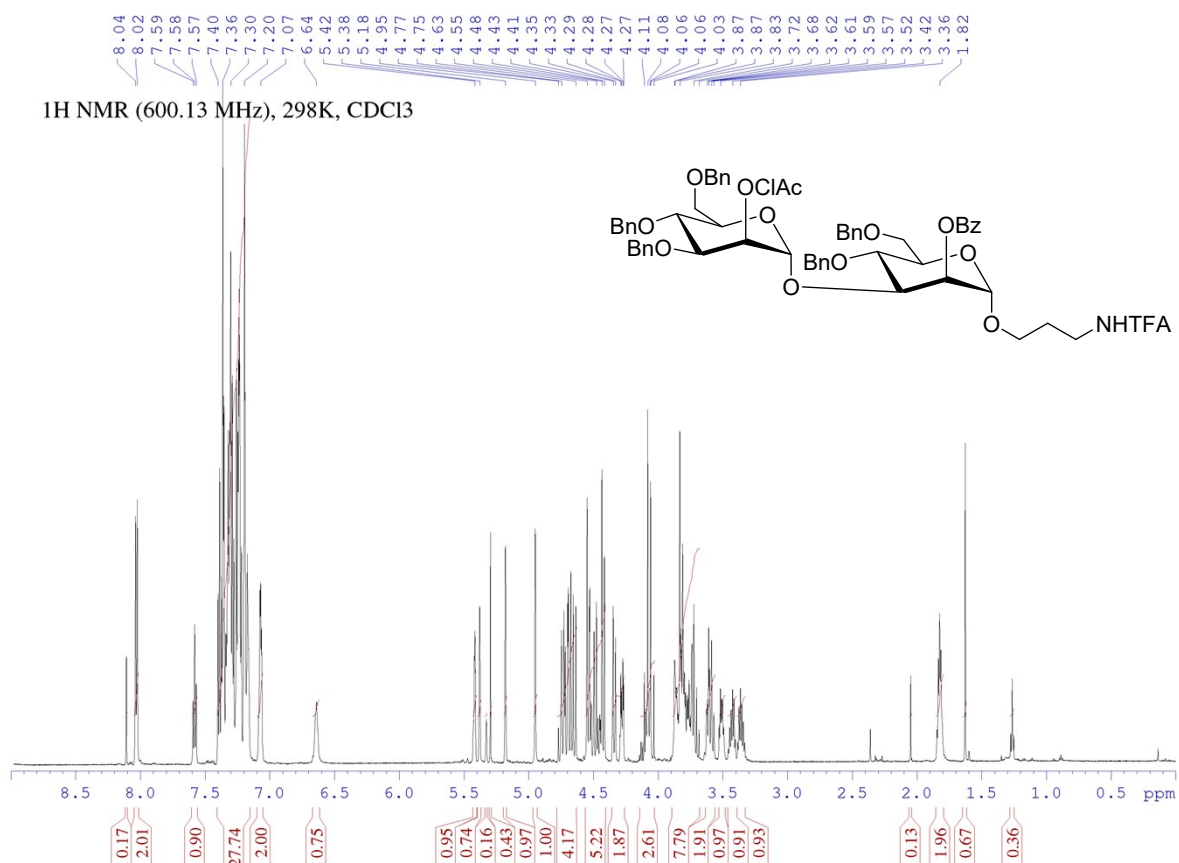
**3-N-trifluoroaminopropyl 4,6-di-O-benzyl-2-O-benzoyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranoside (15)**



<sup>13</sup>C NMR (150.90 MHz), 298K, CDCl<sub>3</sub>

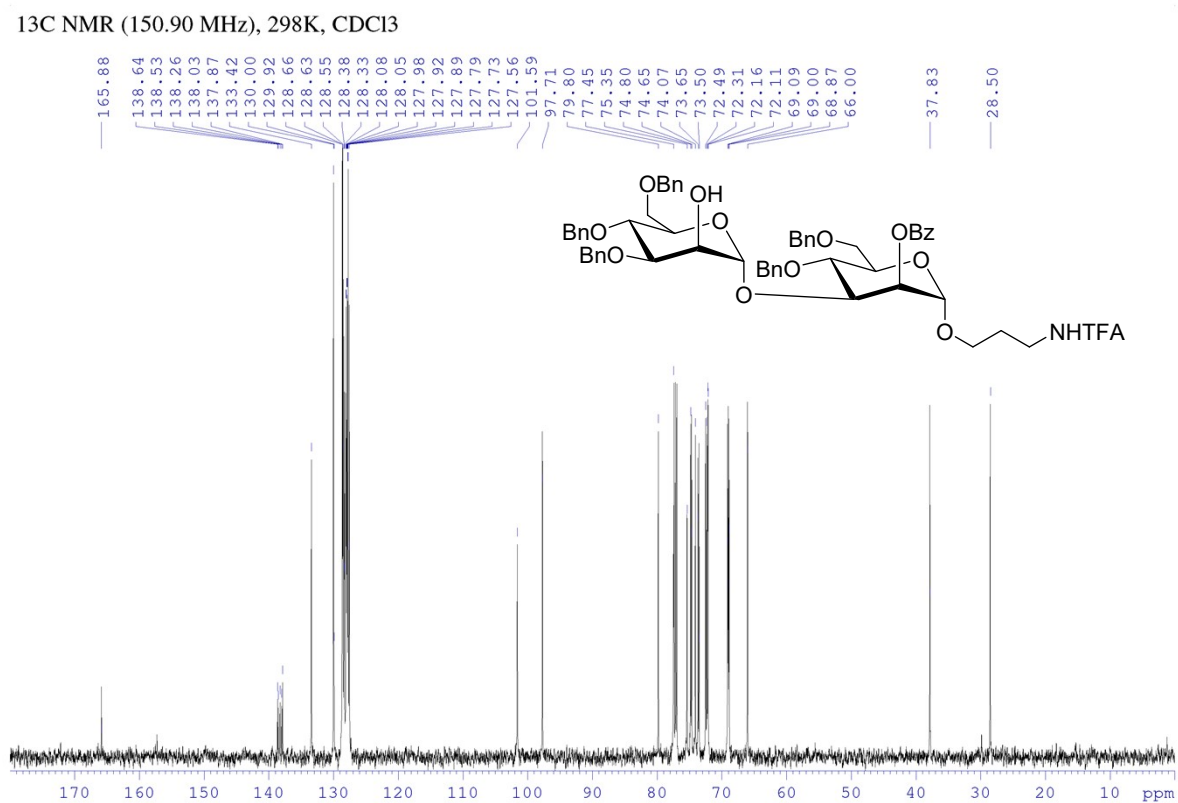
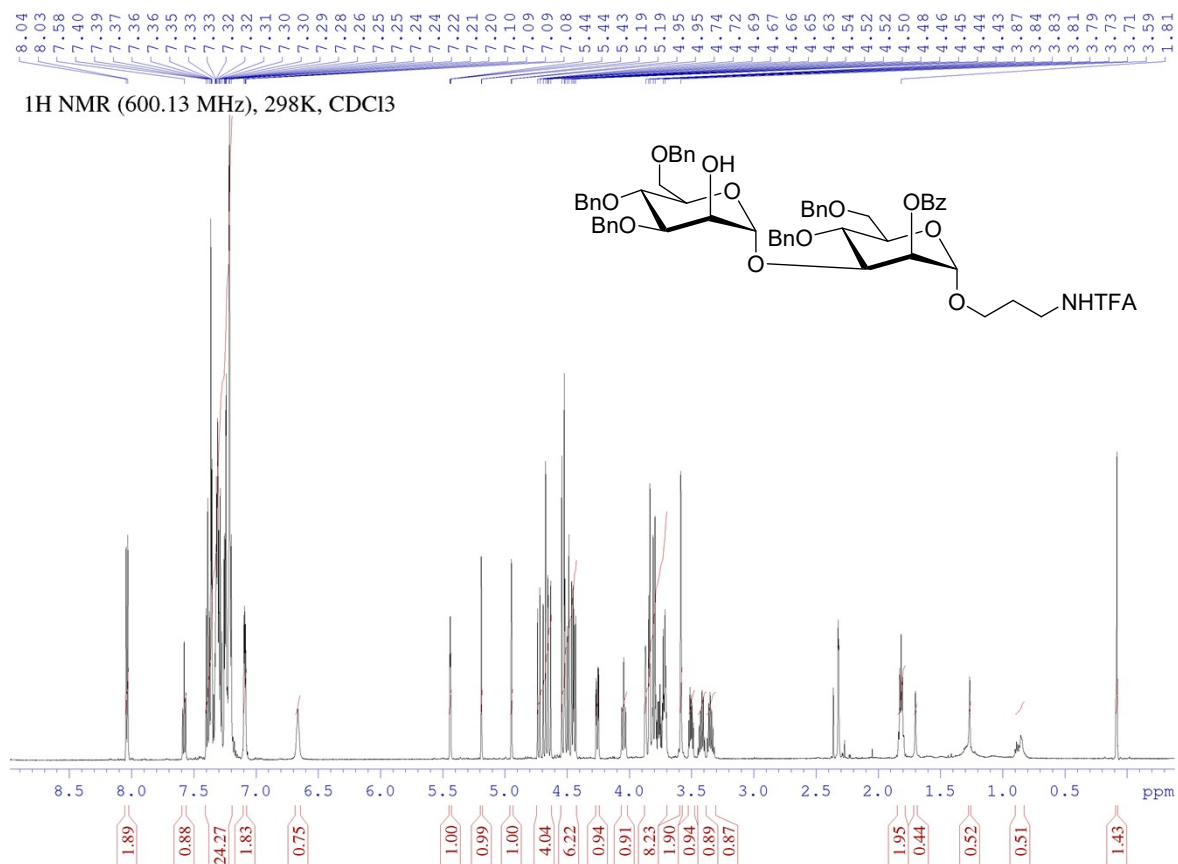


**3-N-trifluoroaminopropyl 3,4,6-tri-O-benzyl-2-O-chloroacetyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-di-O-benzyl-2-O-benzoyl- $\alpha$ -D-mannopyranoside (16)**

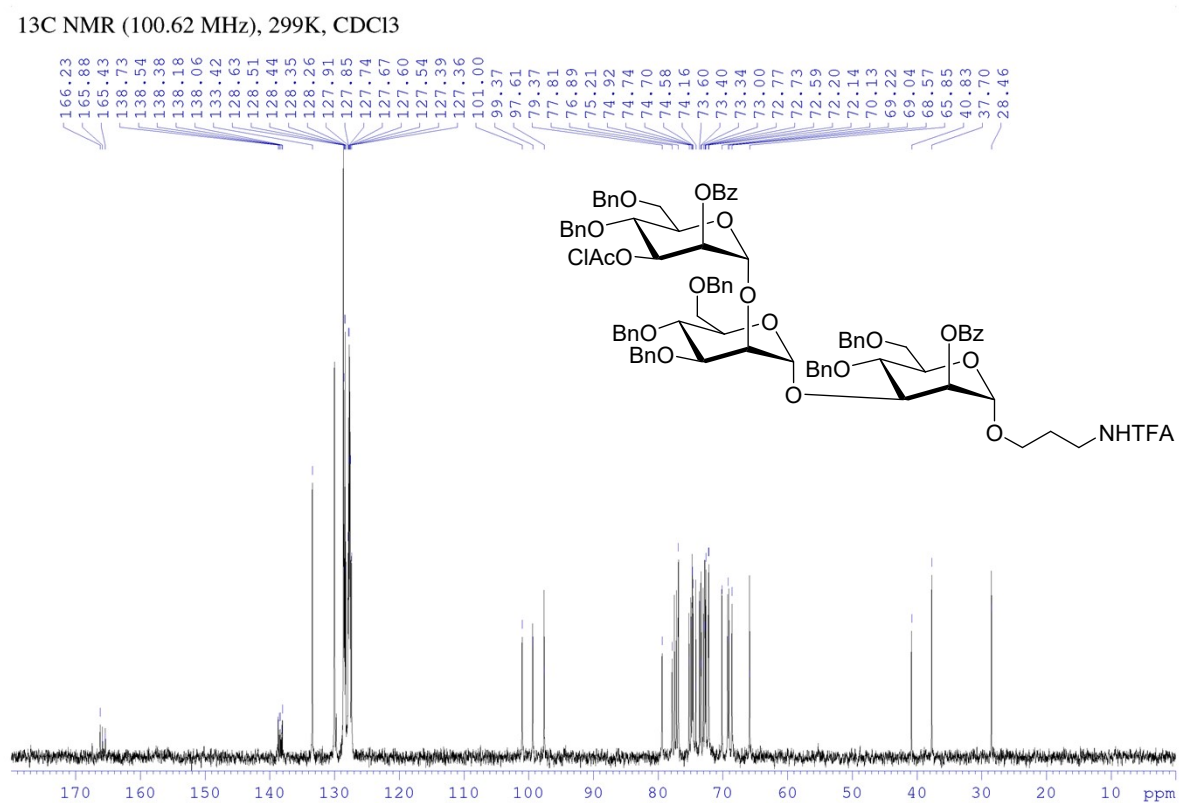
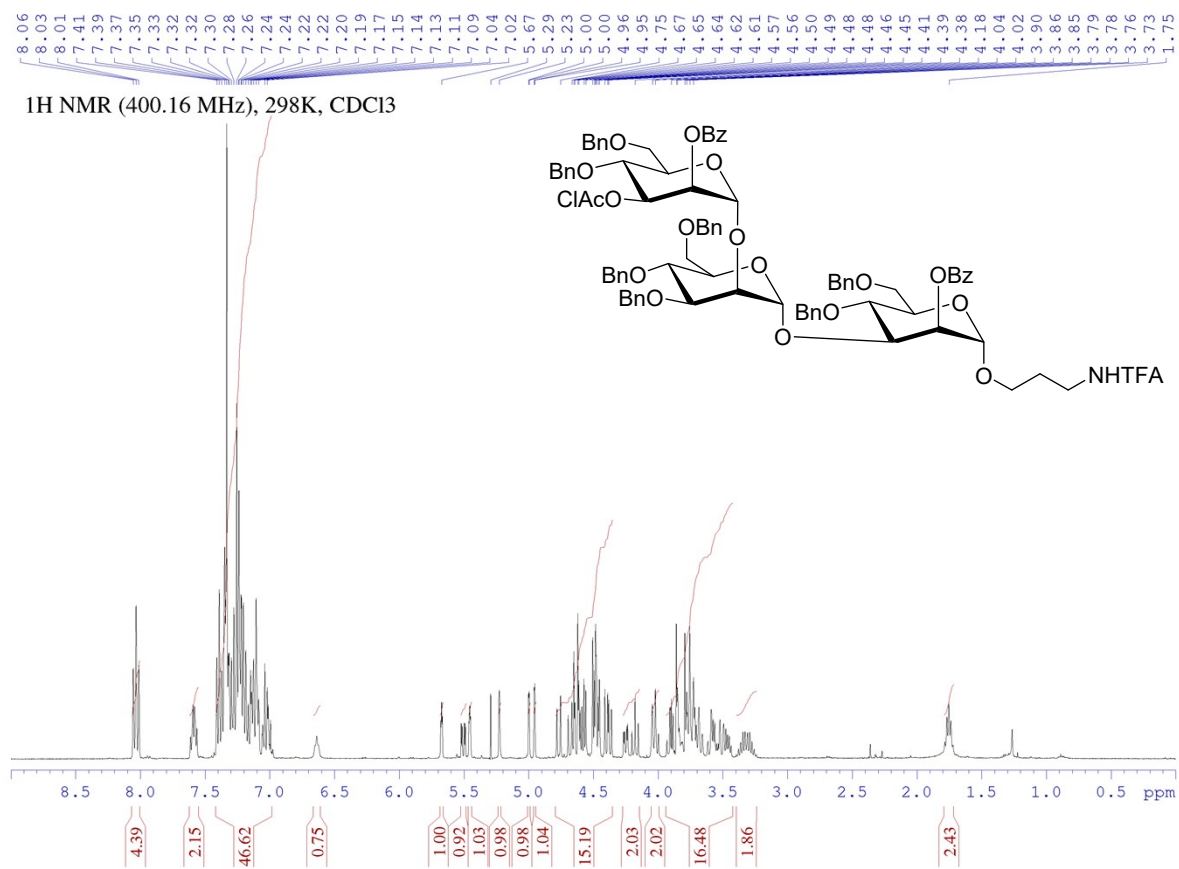




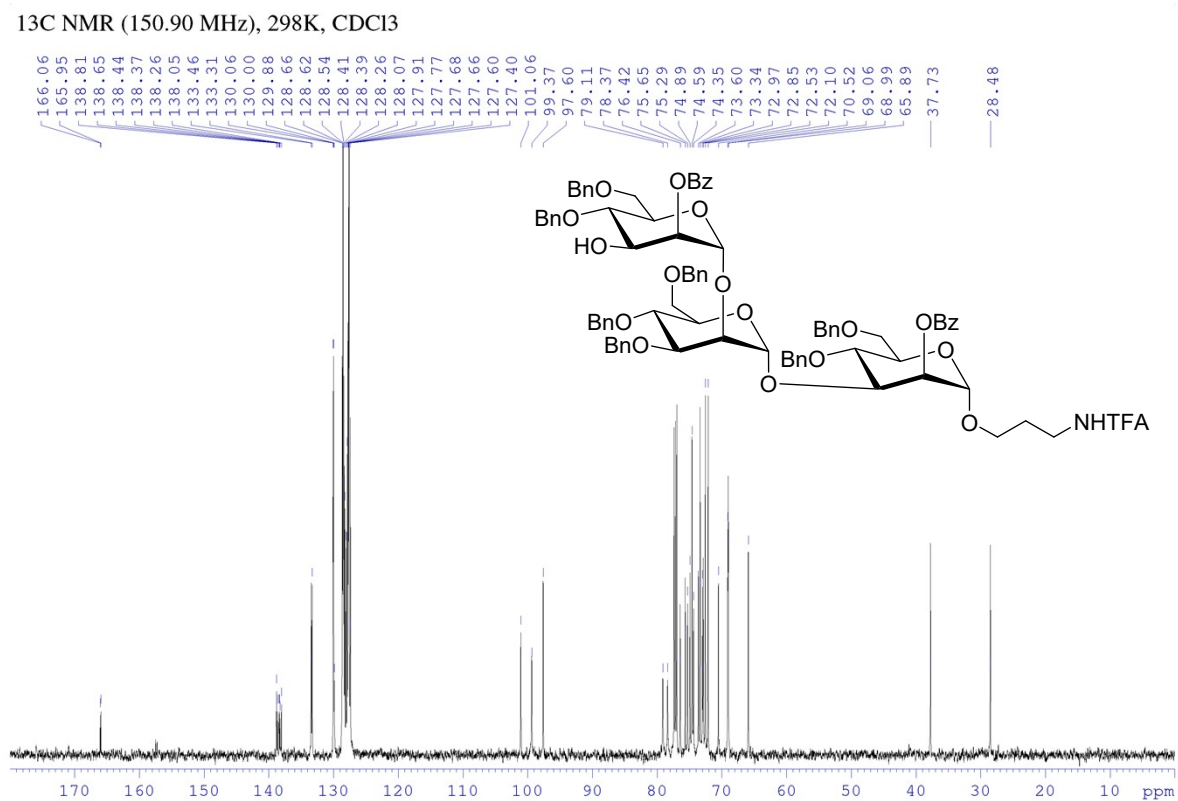
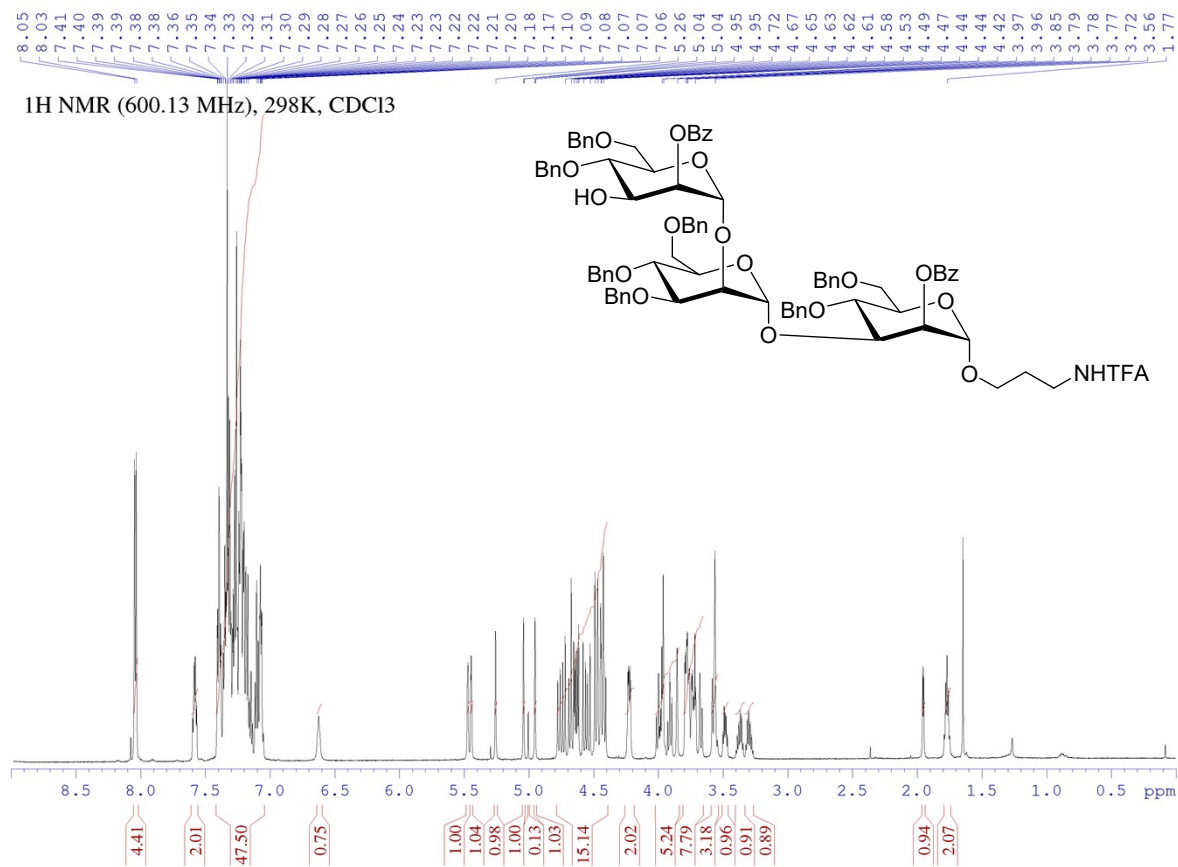
### 3-N-trifluoroacetylaminopropyl 3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-di-O-benzyl-2-O-benzoyl- $\alpha$ -D-mannopyranoside (17)



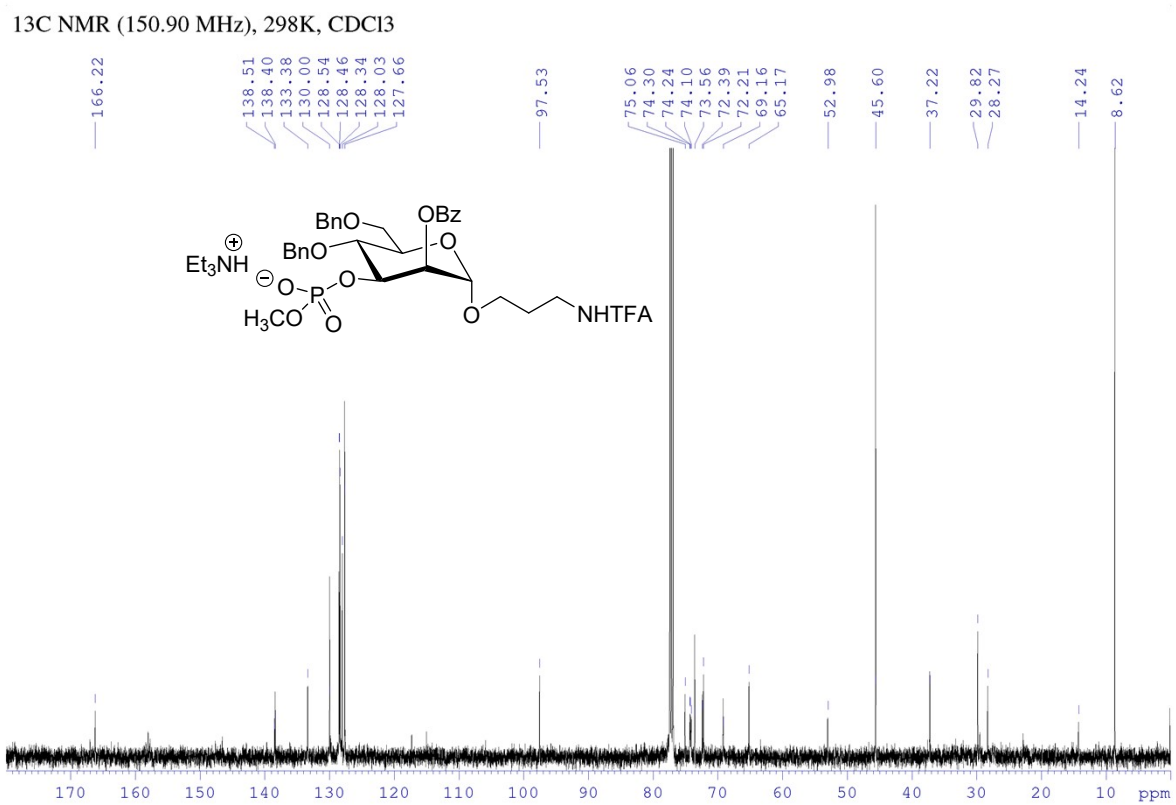
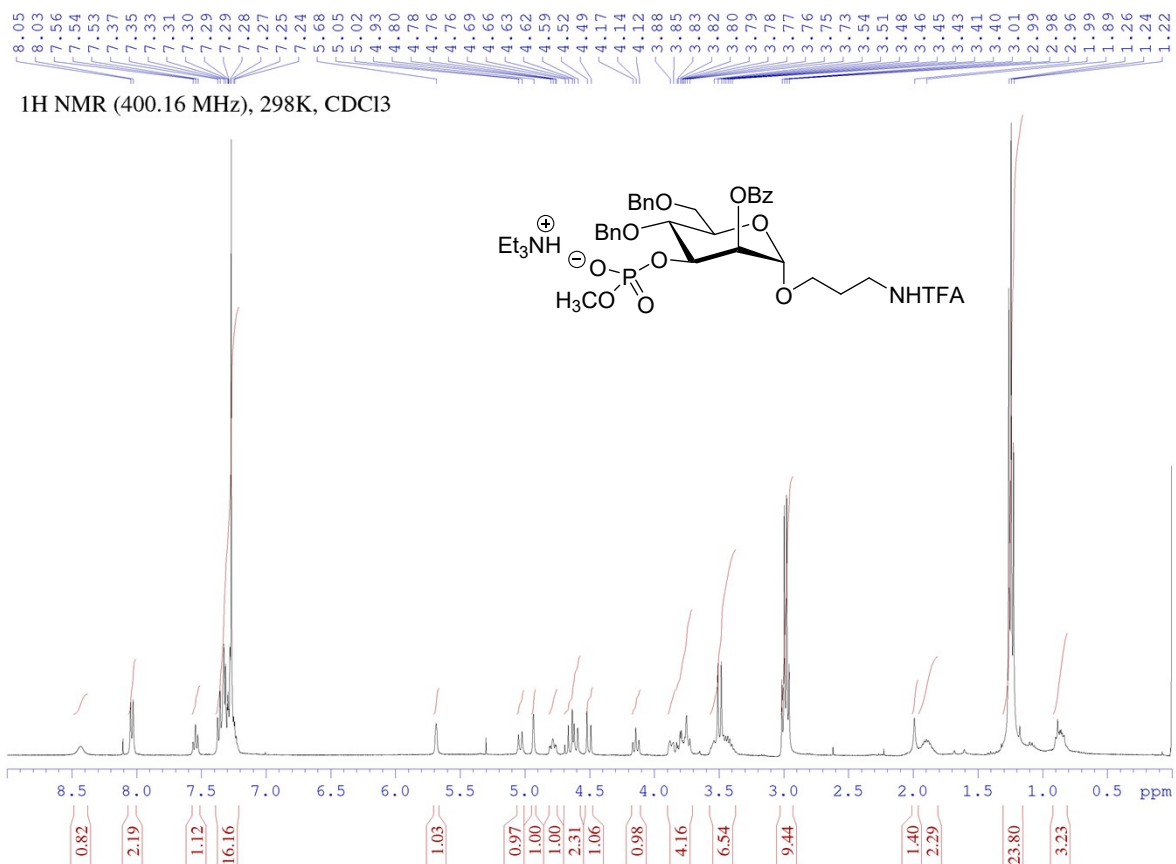
**3-N-trifluoroaminopropyl 4,6-di-O-benzyl-2-O-benzoyl-3-O-chloroacetyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-di-O-benzyl-2-O-benzoyl- $\alpha$ -D-mannopyranoside (18)**



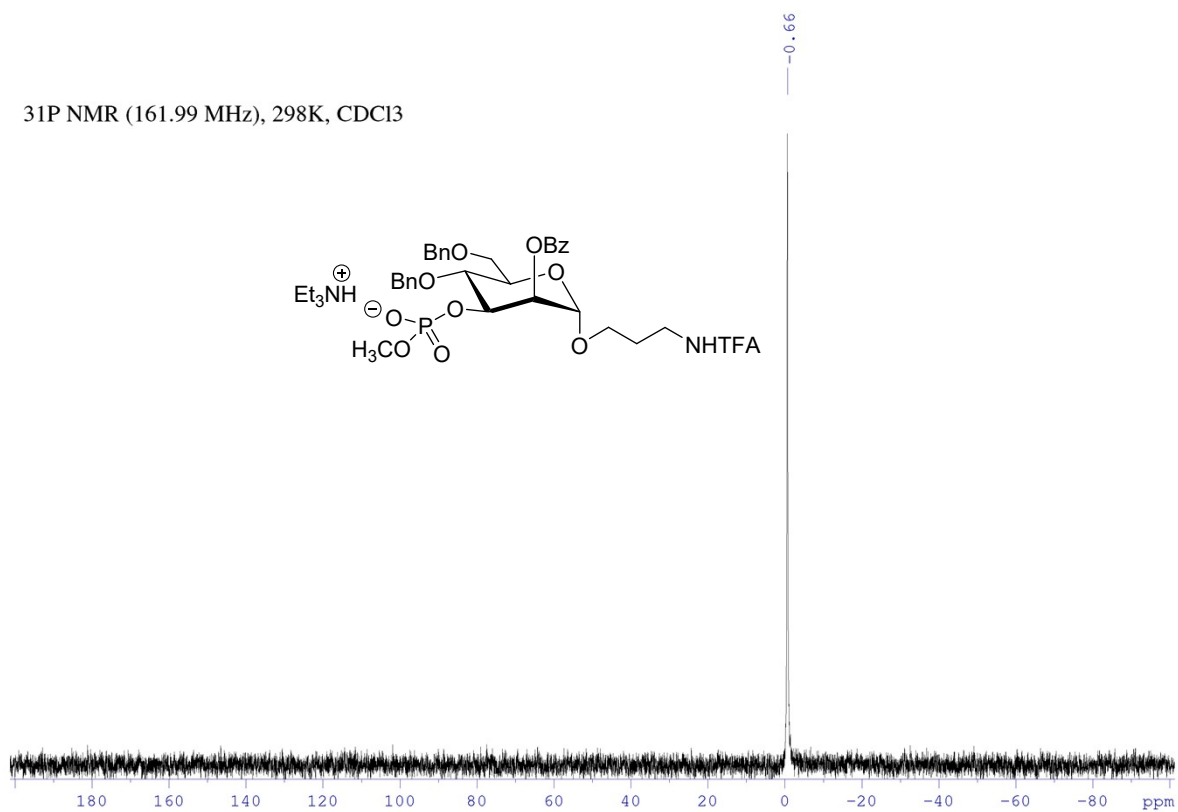
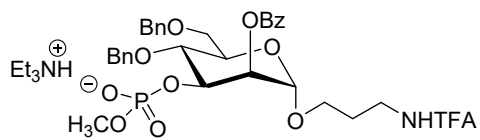
**3-N-trifluoroaminopropyl 4,6-di-O-benzyl-2-O-benzoyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-di-O-benzyl-2-O-benzoyl- $\alpha$ -D-mannopyranoside (19)**



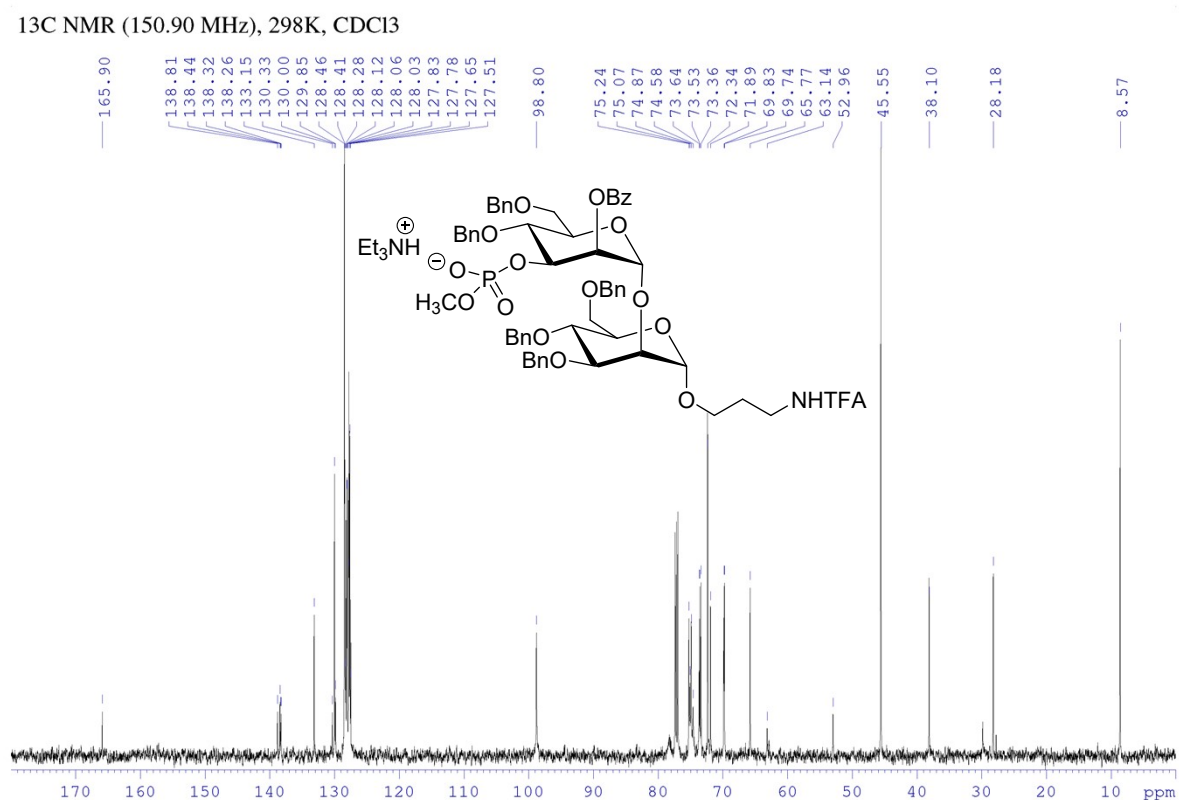
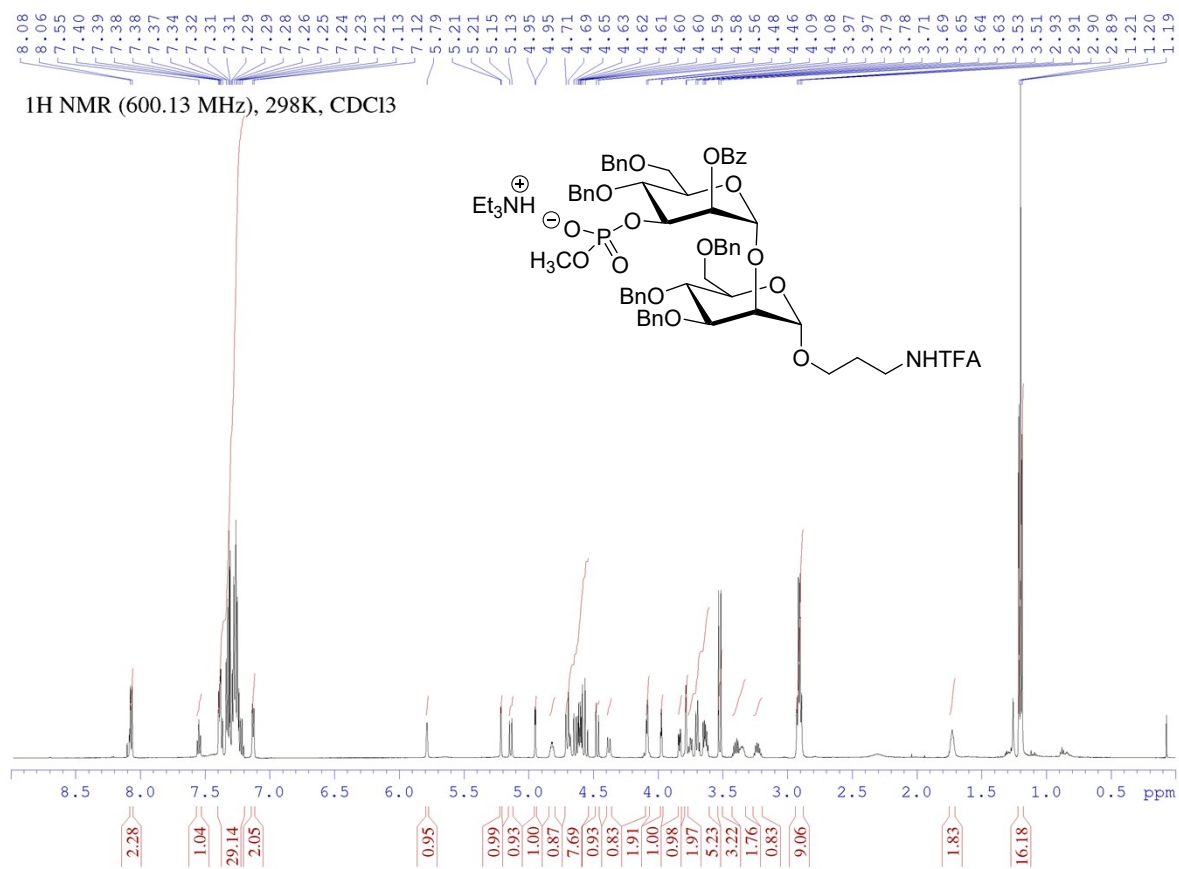
**Triethylammonium 3-N-trifluoroacetylaminopropyl 4,6-di-O-benzyl-2-O-benzoyl-3-O-(methylphosphonato)- $\alpha$ -D-mannopyranoside (20)**



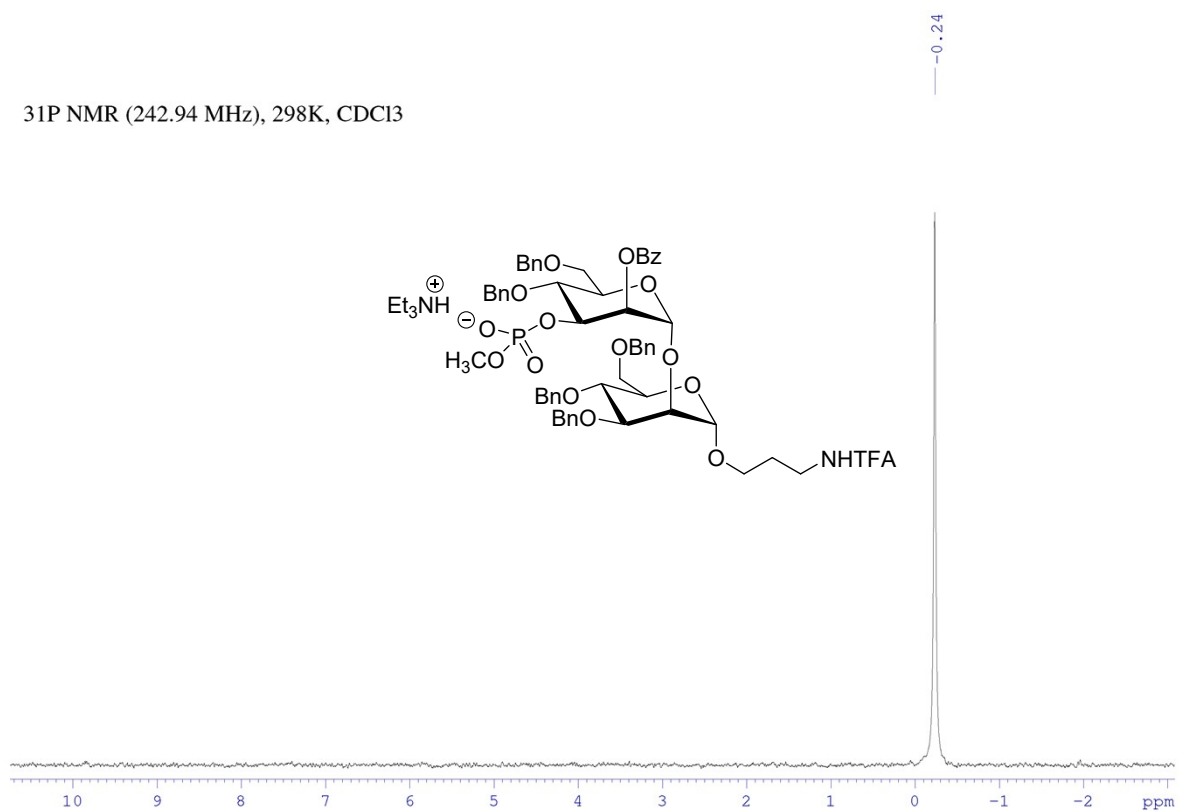
31P NMR (161.99 MHz), 298K, CDCl3



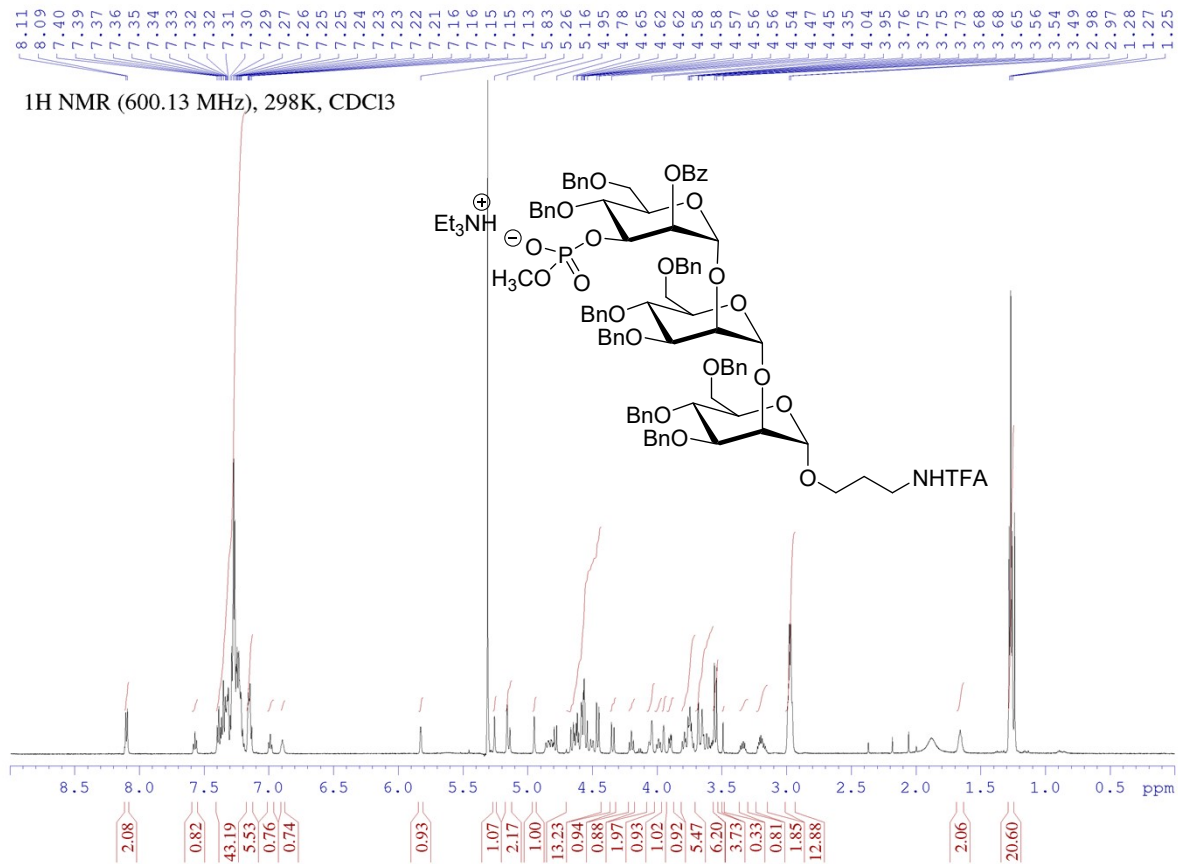
**Triethylammonium 3-N-trifluoroacetylaminopropyl 4,6-di-O-benzyl-2-O-benzoyl-3-O-(methylphosphonato)- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranoside (21)**



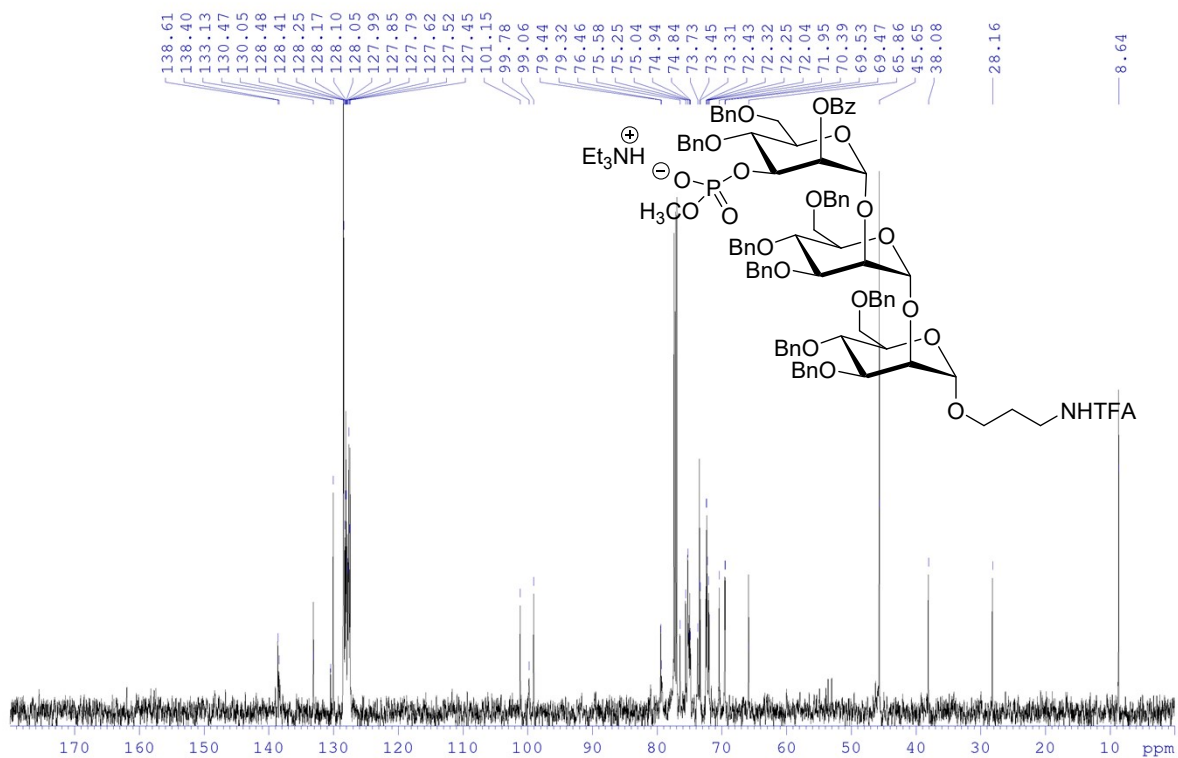
31P NMR (242.94 MHz), 298K, CDCl3



**Triethylammonium 3-N-trifluoroaminopropyl 4,6-di-O-benzyl-2-O-benzoyl-3-O-(methylphosphonato)- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranoside (22)**

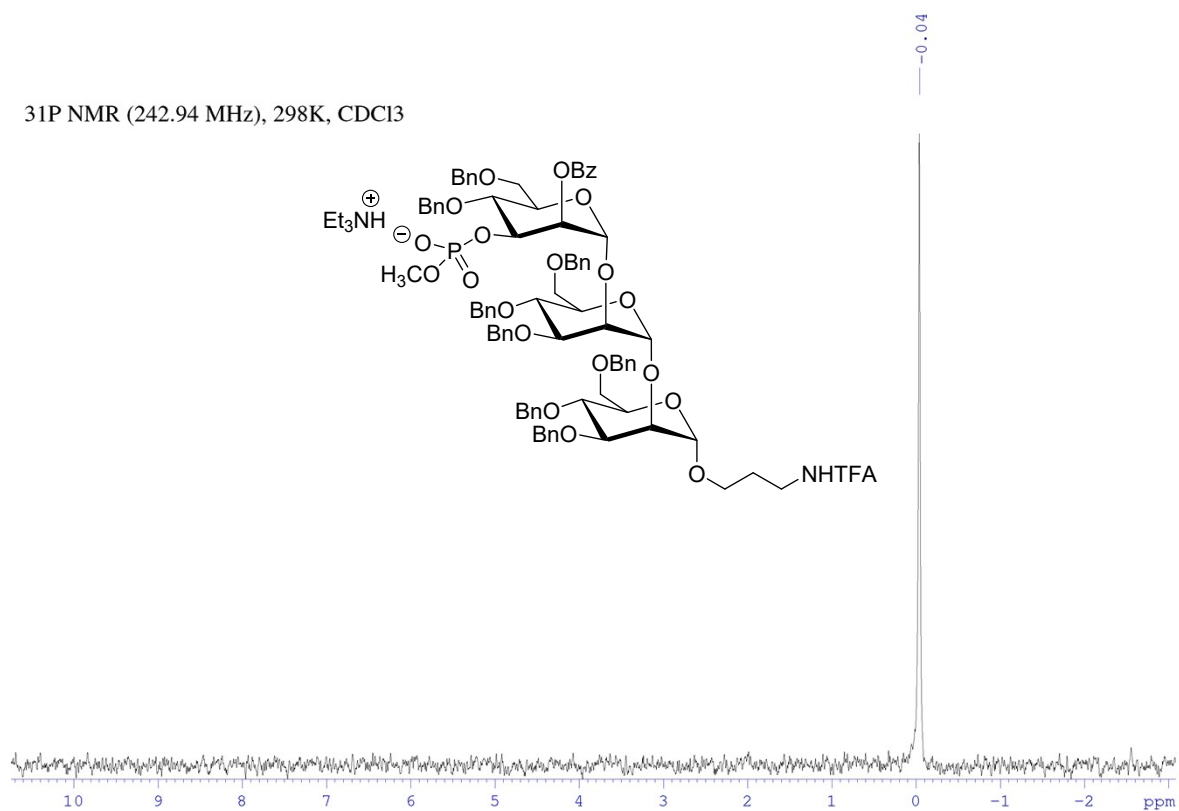


13C NMR (150.90 MHz), 298K, CDCl<sub>3</sub>

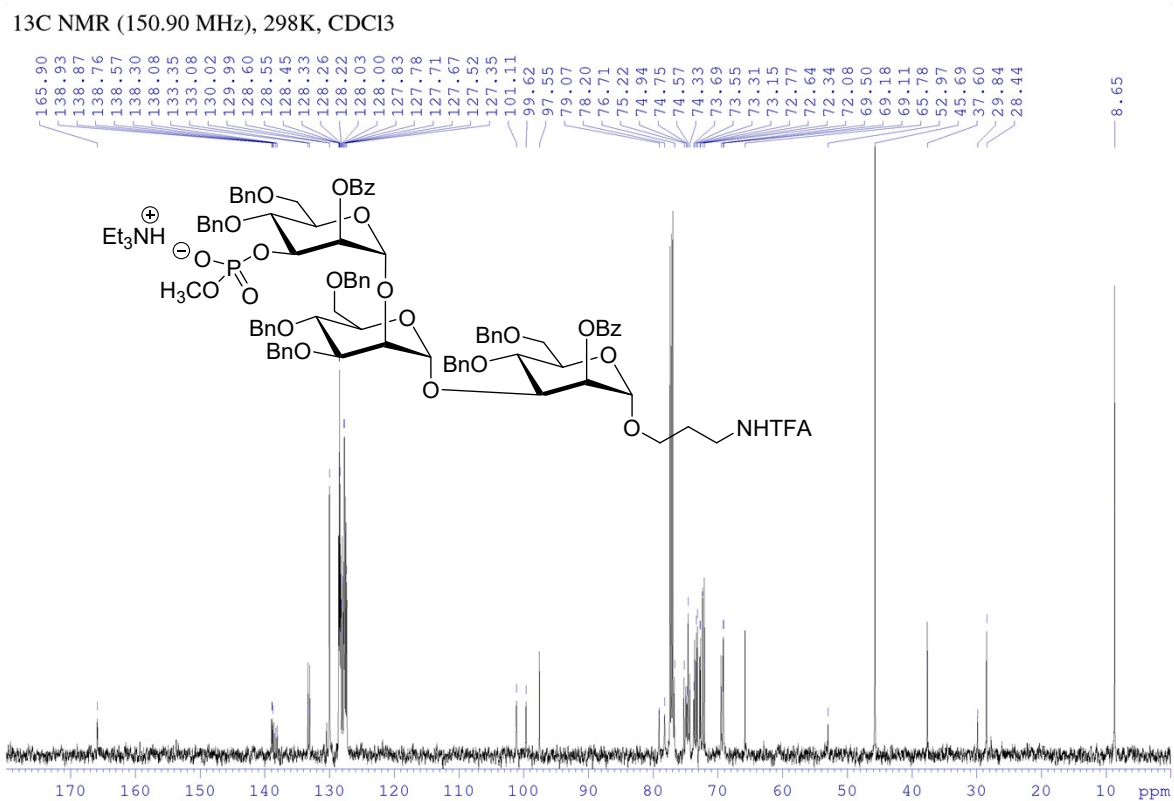
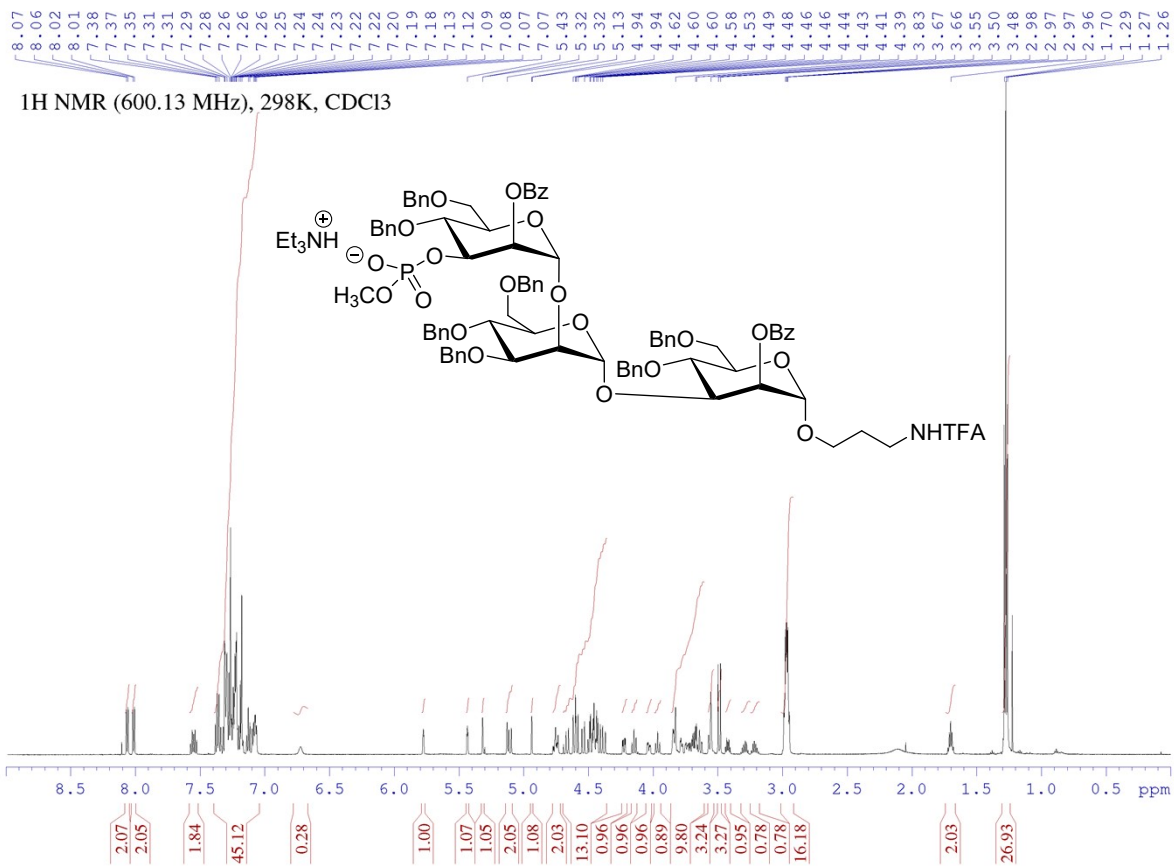




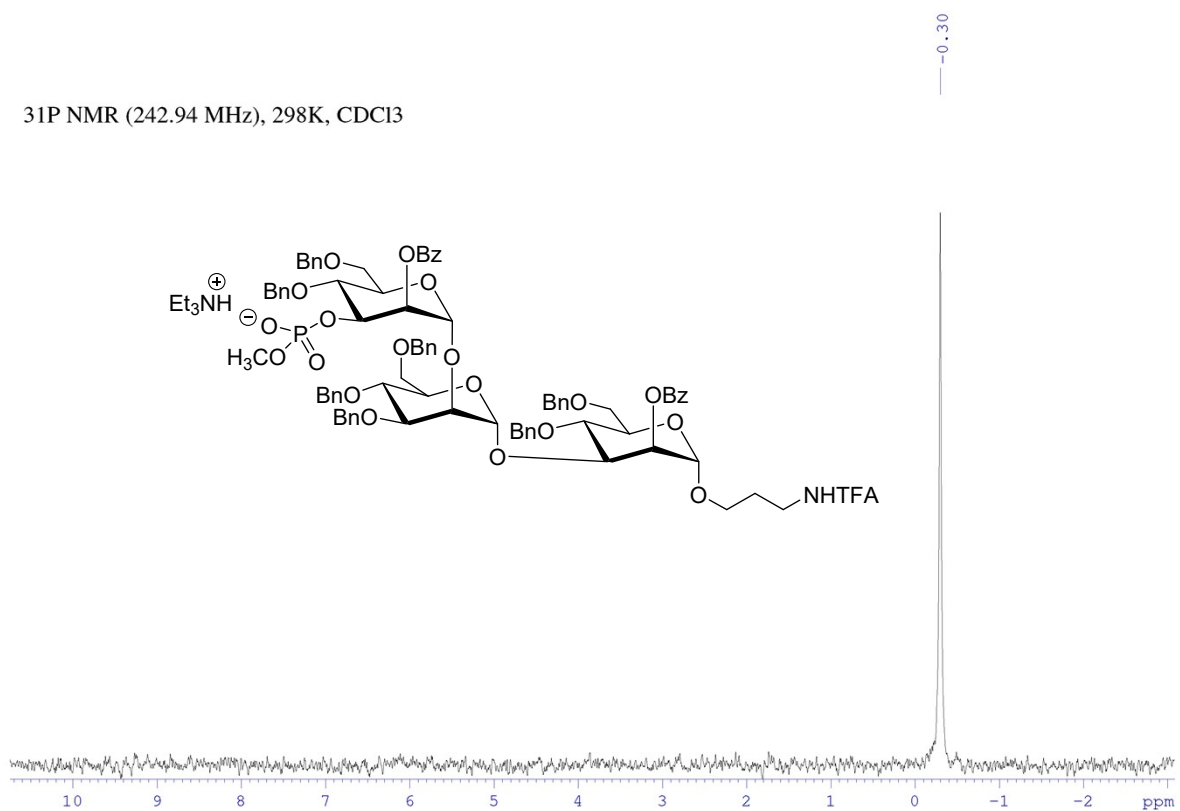
31P NMR (242.94 MHz), 298K, CDCl3



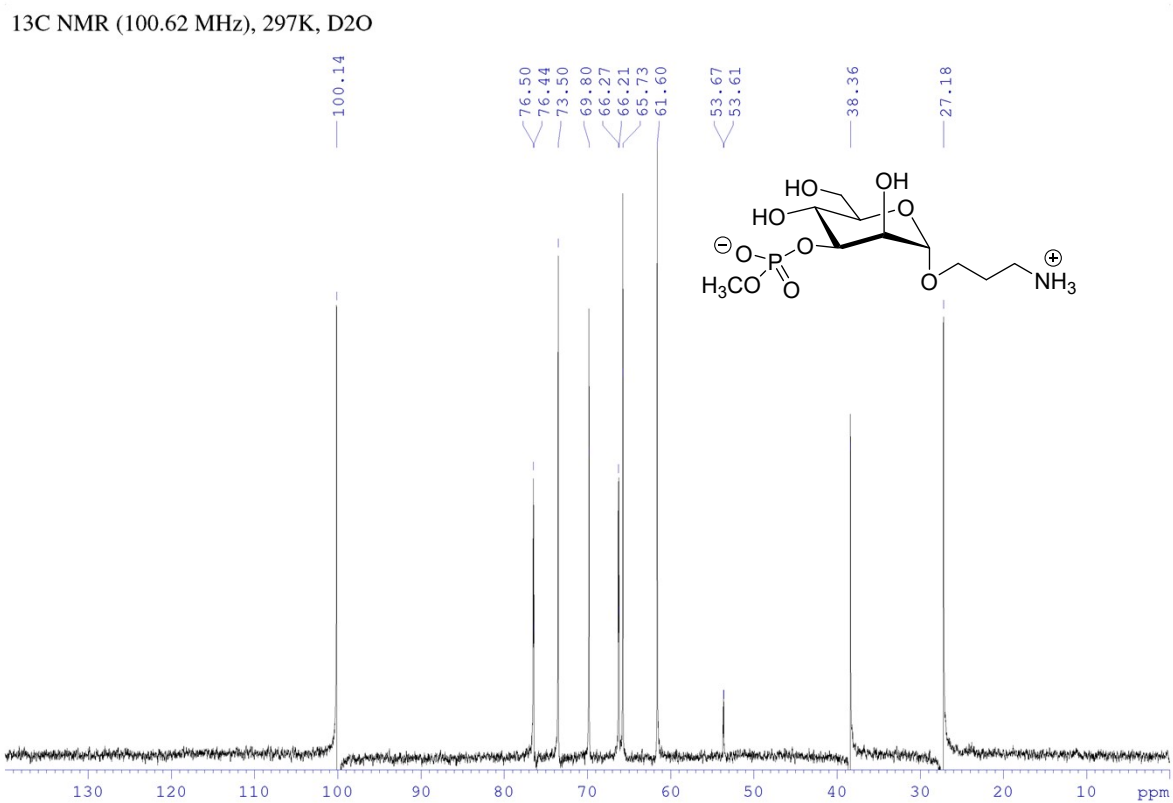
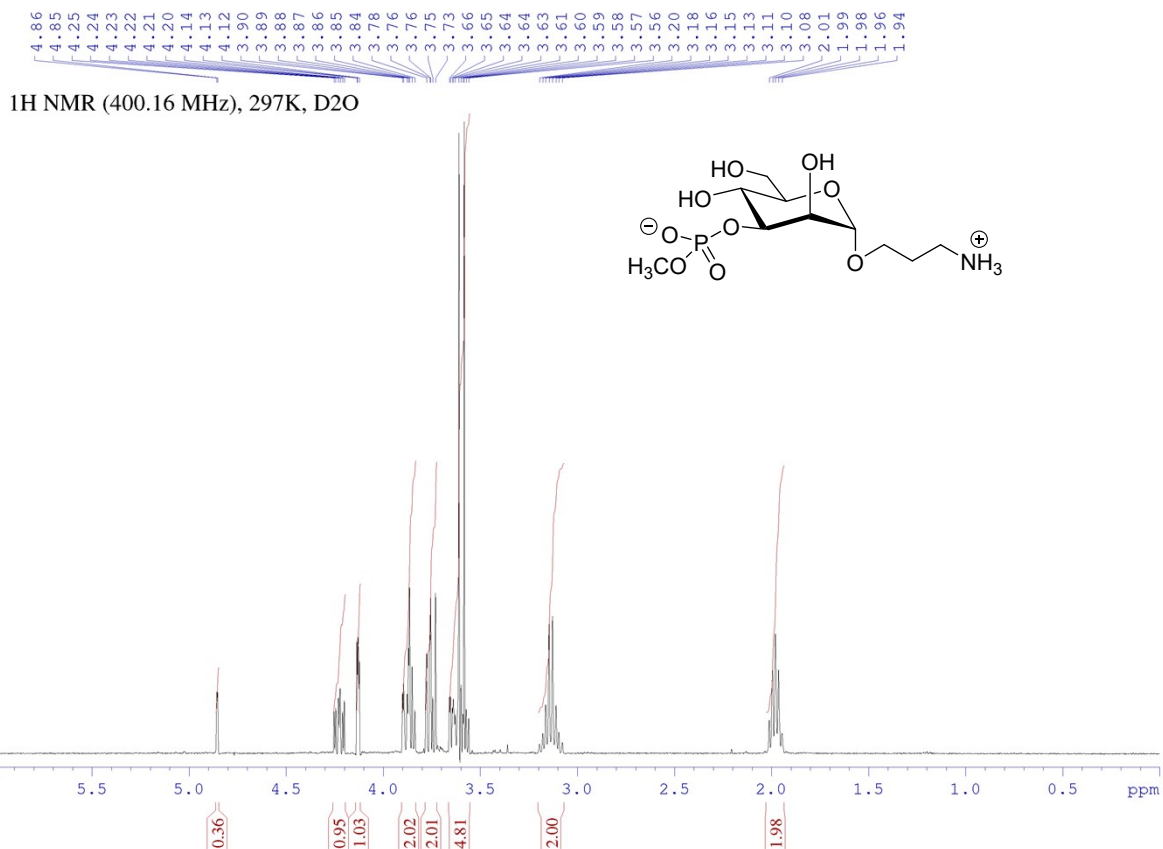
**Triethylammonium 3-N-trifluoroacetylaminopropyl 4,6-di-O-benzyl-2-O-benzoyl-3-O-(methylphosphonato)- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-O-benzyl- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 3)-4,6-di-O-benzyl-2-O-benzoyl- $\alpha$ -D-mannopyranoside (23)**



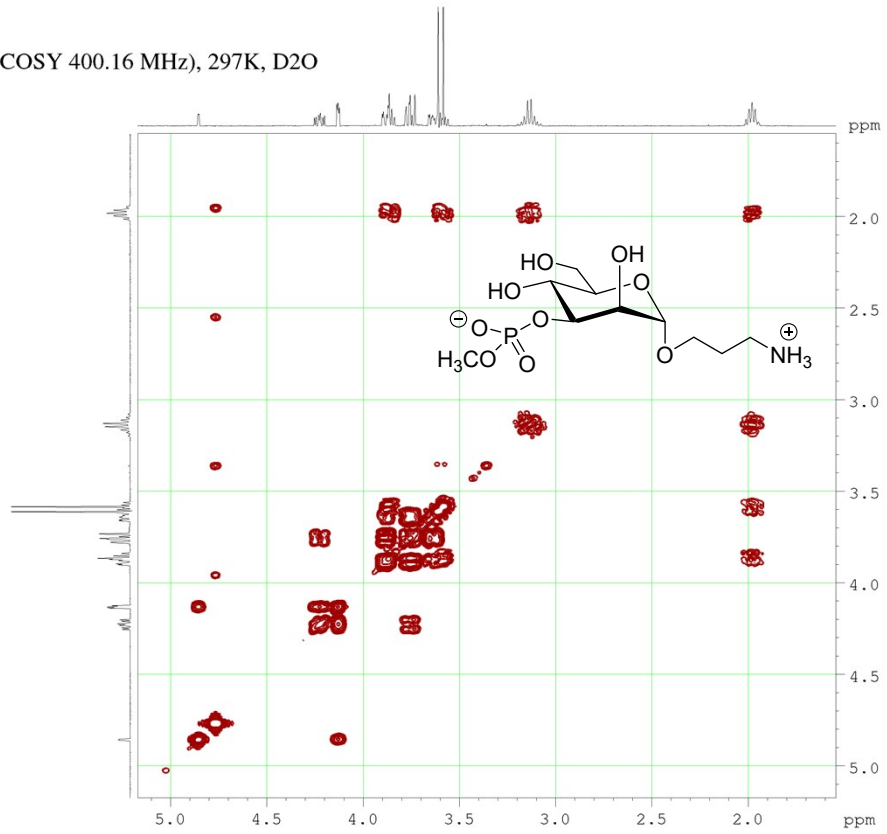
31P NMR (242.94 MHz), 298K, CDCl3



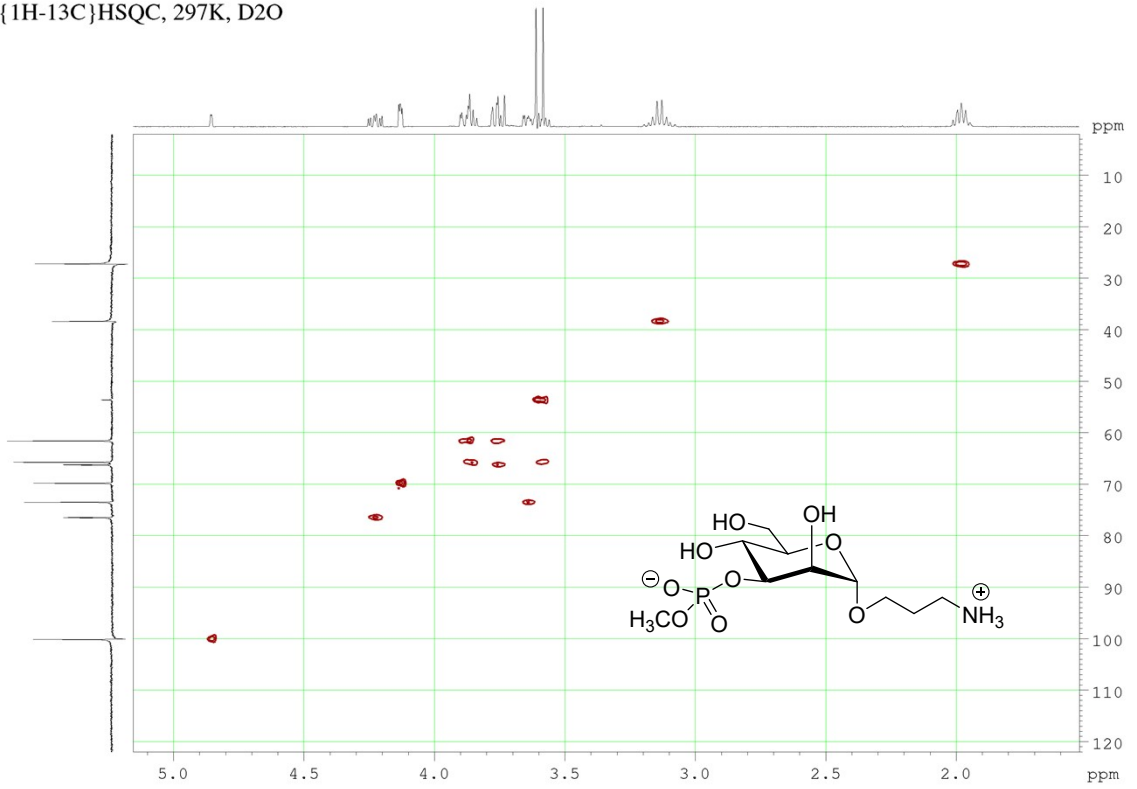
### 3-aminopropyl 3-O-(methylphosphonato)- $\alpha$ -D-mannopyranoside (1a)



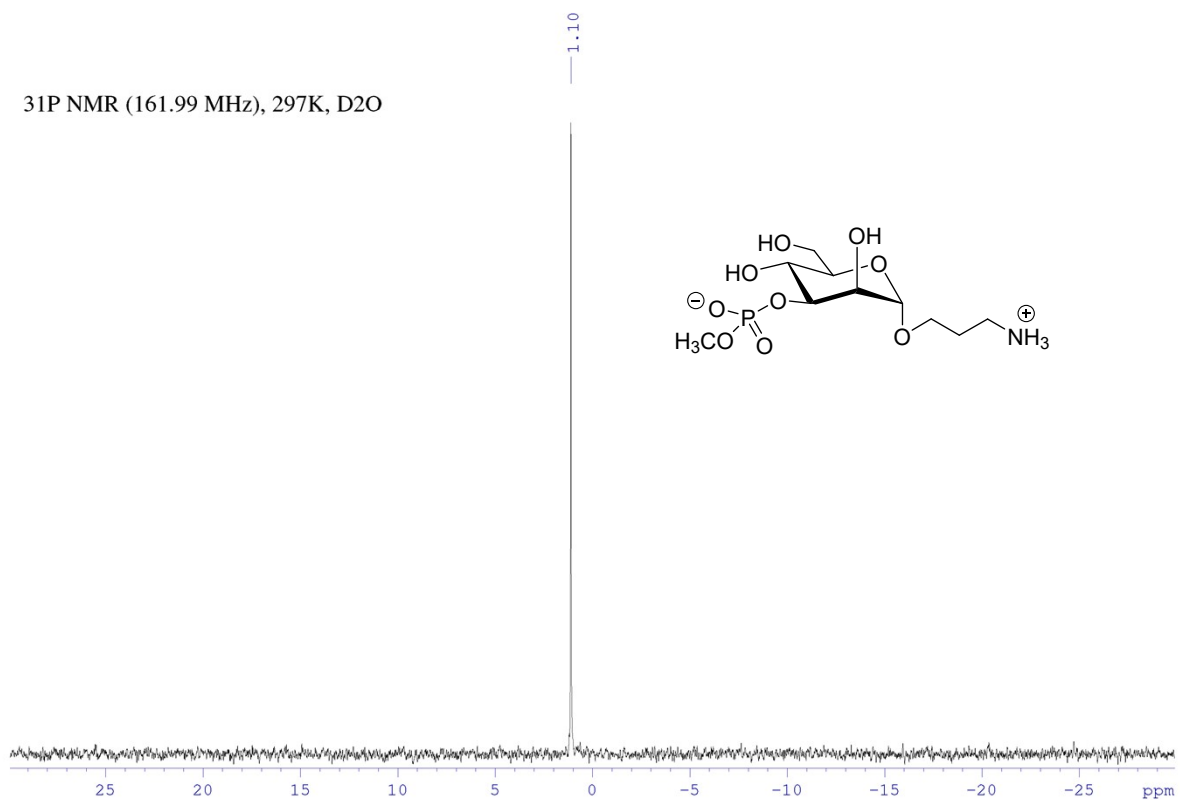
{1H-1H}COSY 400.16 MHz, 297K, D2O



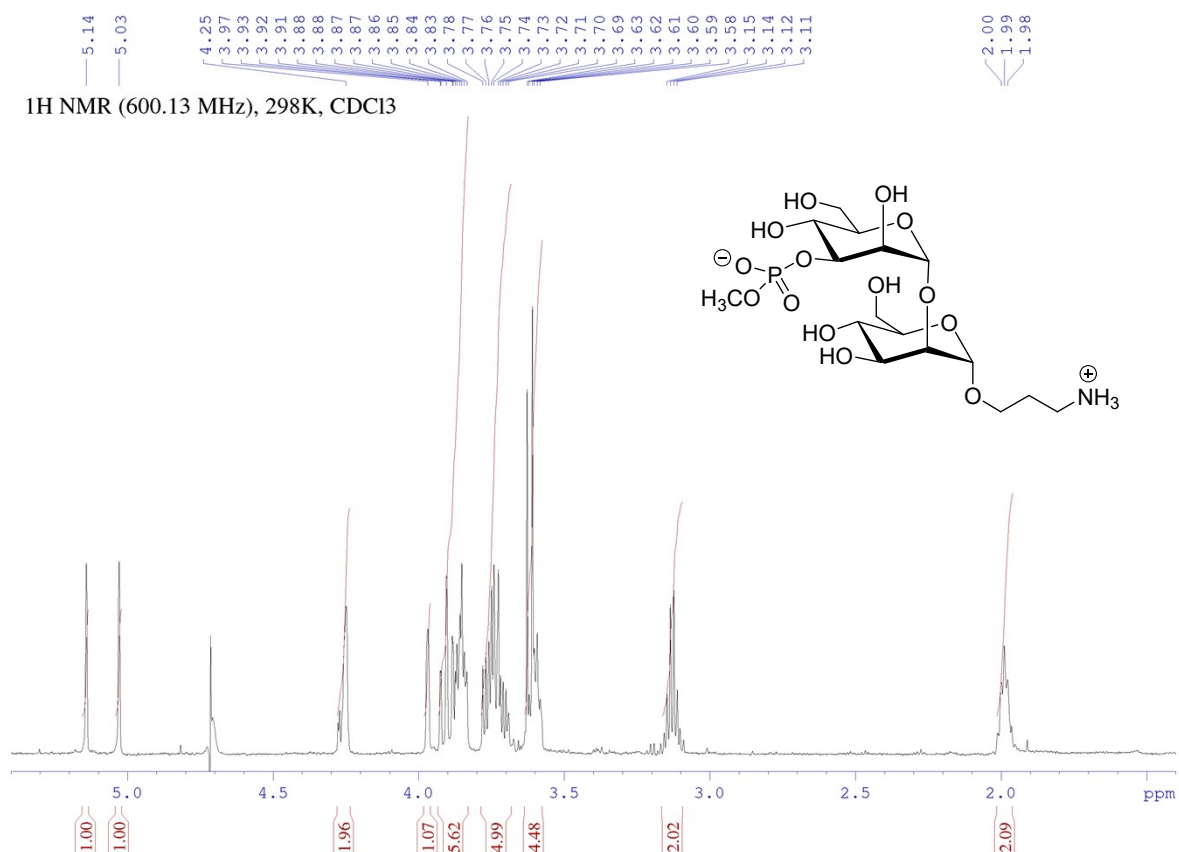
{1H-13C}HSQC, 297K, D2O



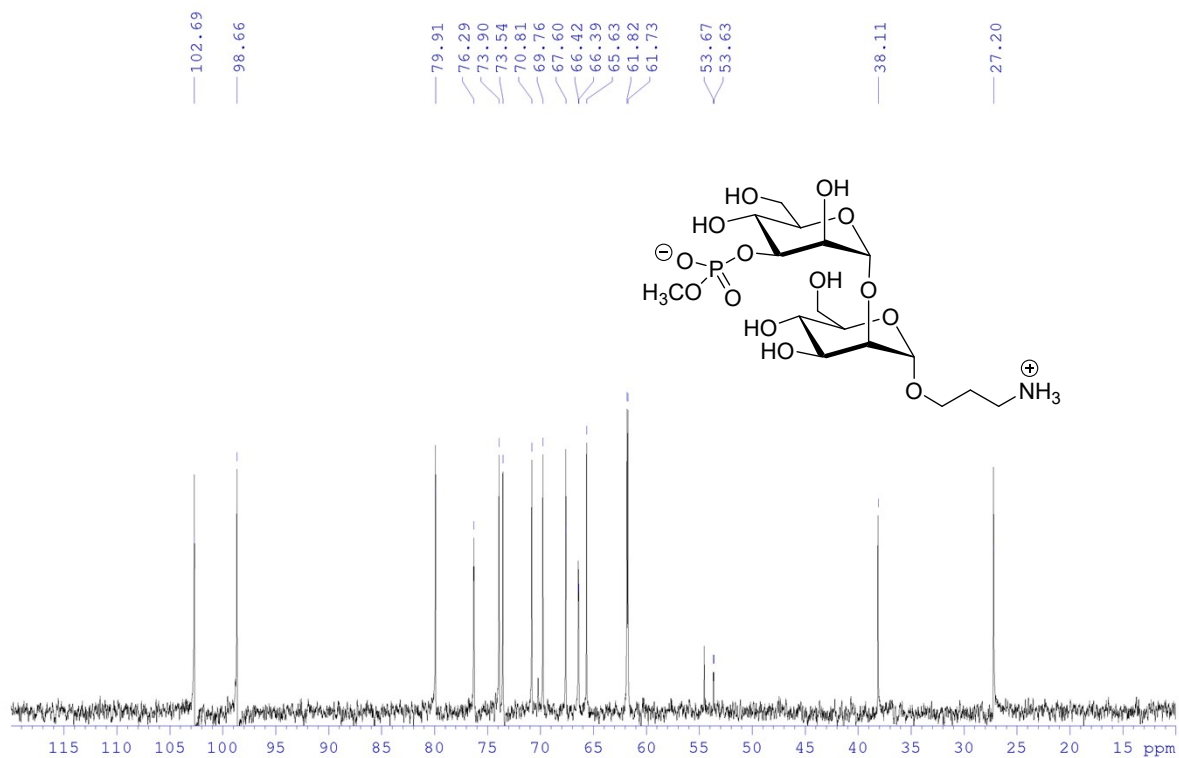
31P NMR (161.99 MHz, 297K, D2O)



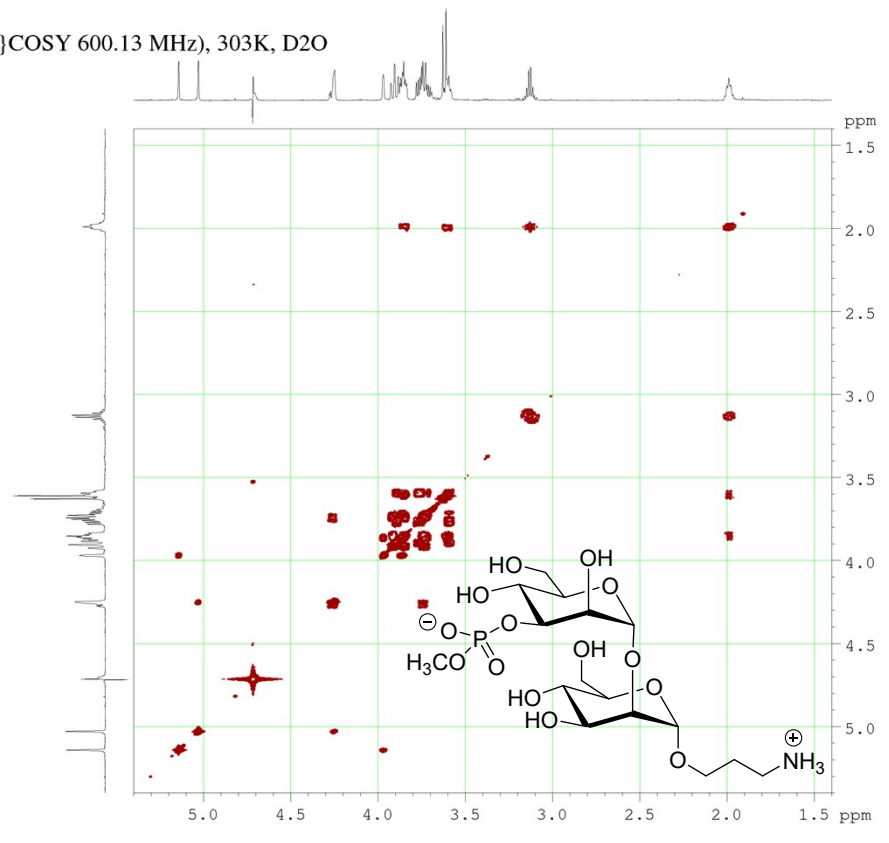
### 3-aminopropyl 3-O-(methylphosphonato)- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -D-mannopyranoside (2a)



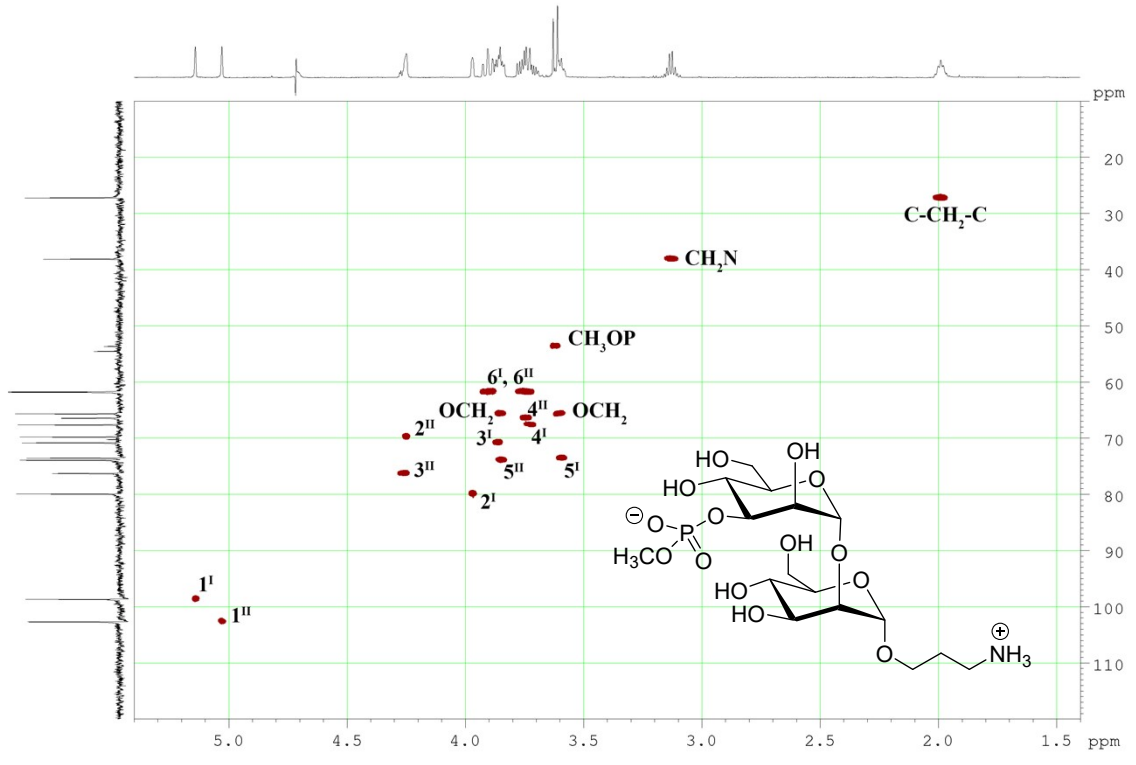
<sup>13</sup>C NMR (150.90 MHz), 303K, D<sub>2</sub>O



{1H-1H}COSY 600.13 MHz, 303K, D2O

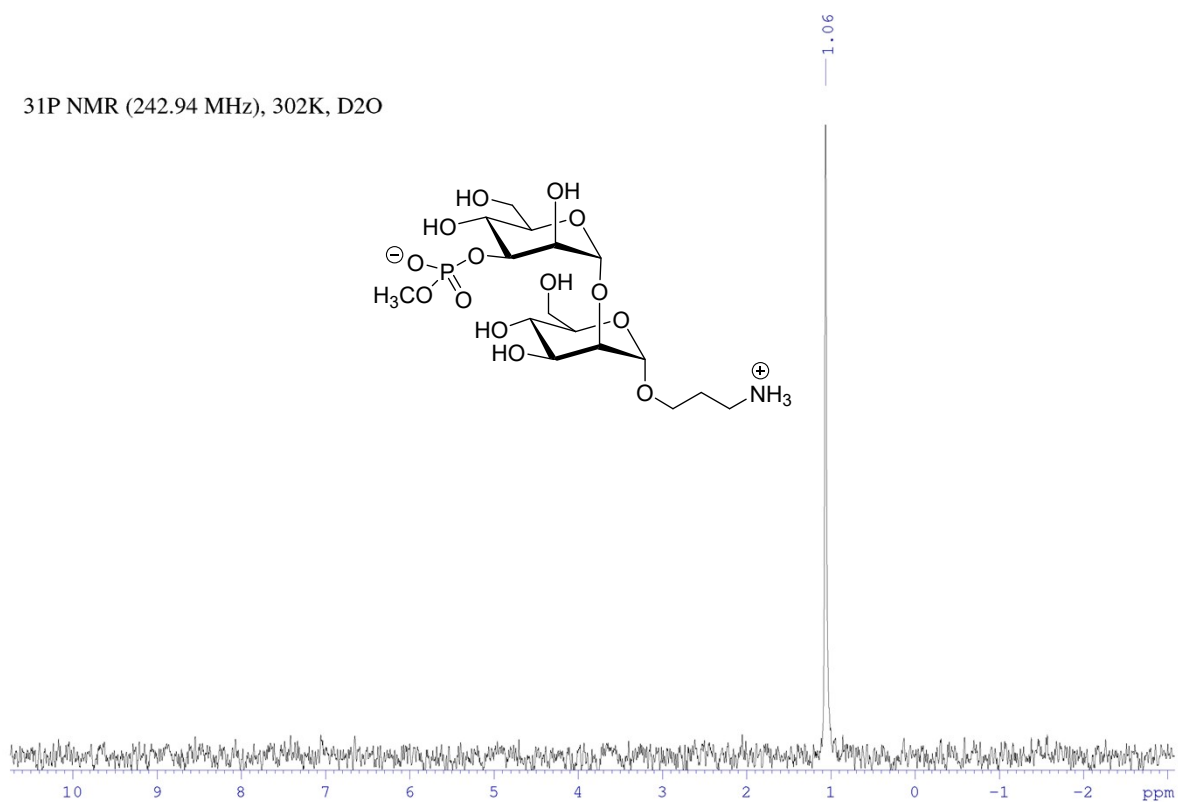


{1H-13C}HSQC, 303K, D2O

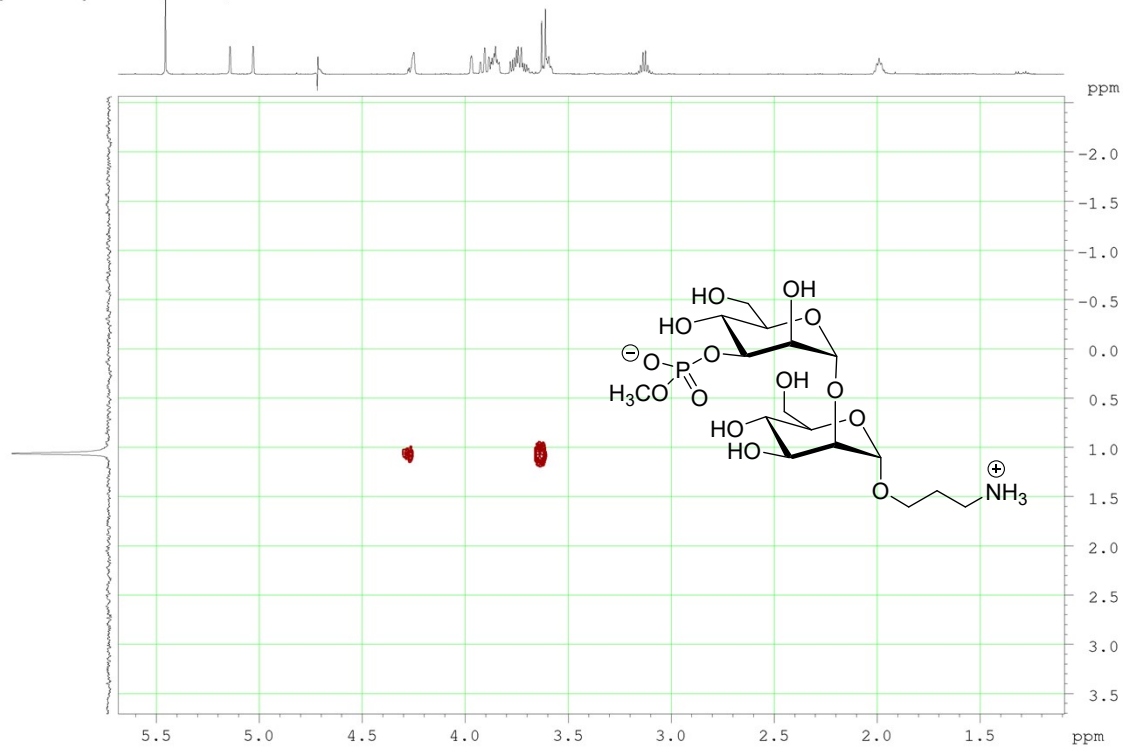




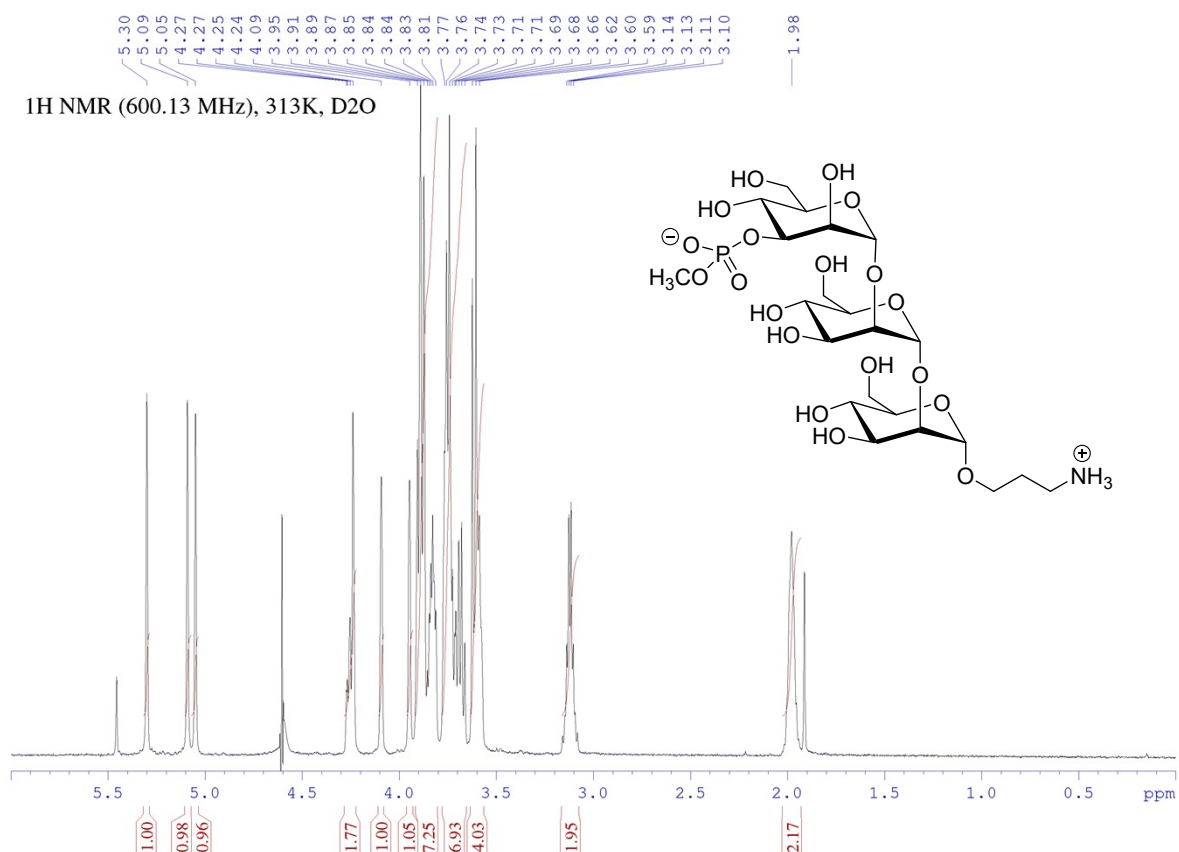
$^{31}\text{P}$  NMR (242.94 MHz, 302K, D<sub>2</sub>O)



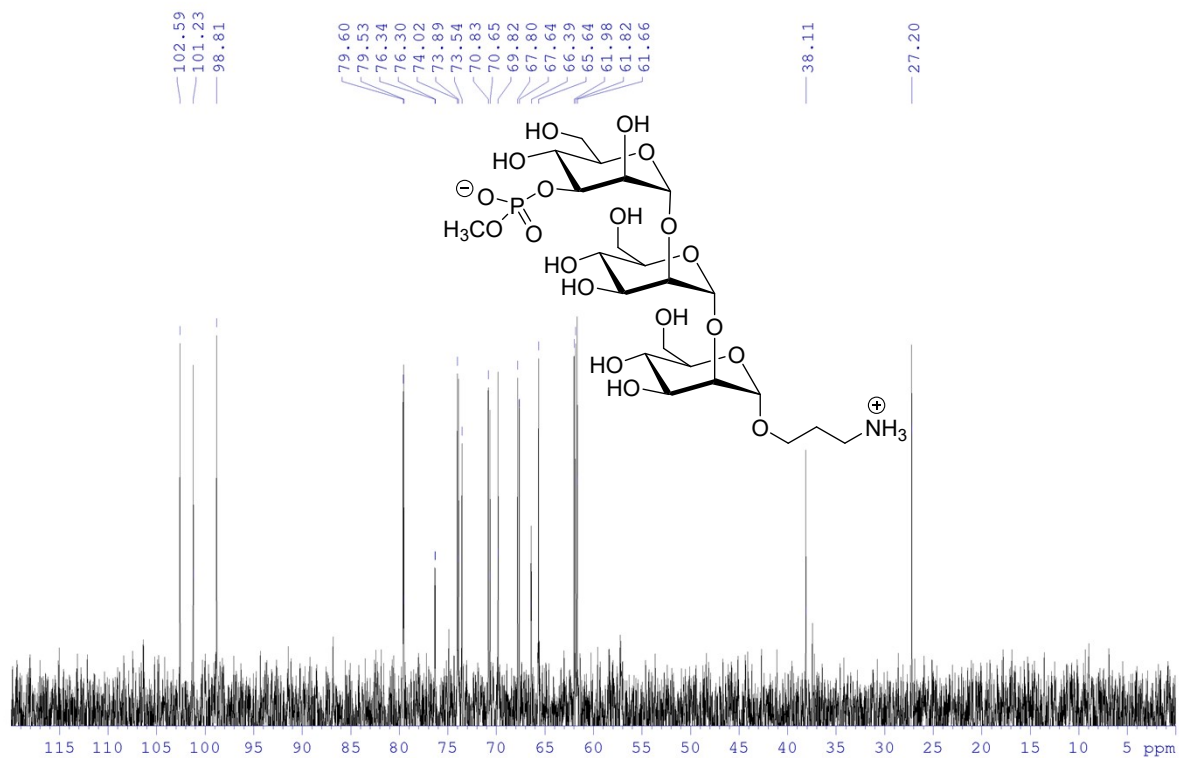
{ $^1\text{H}$ - $^{31}\text{P}$ }HMBC, 302K, D<sub>2</sub>O

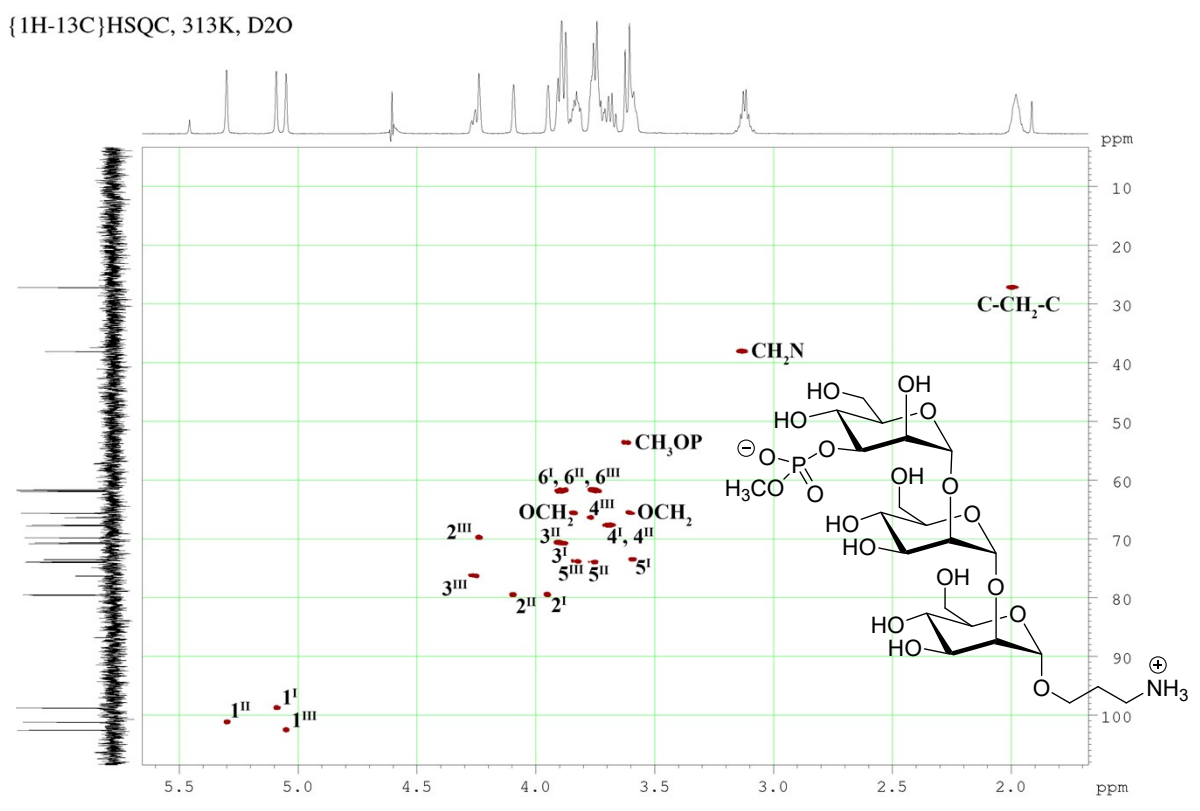
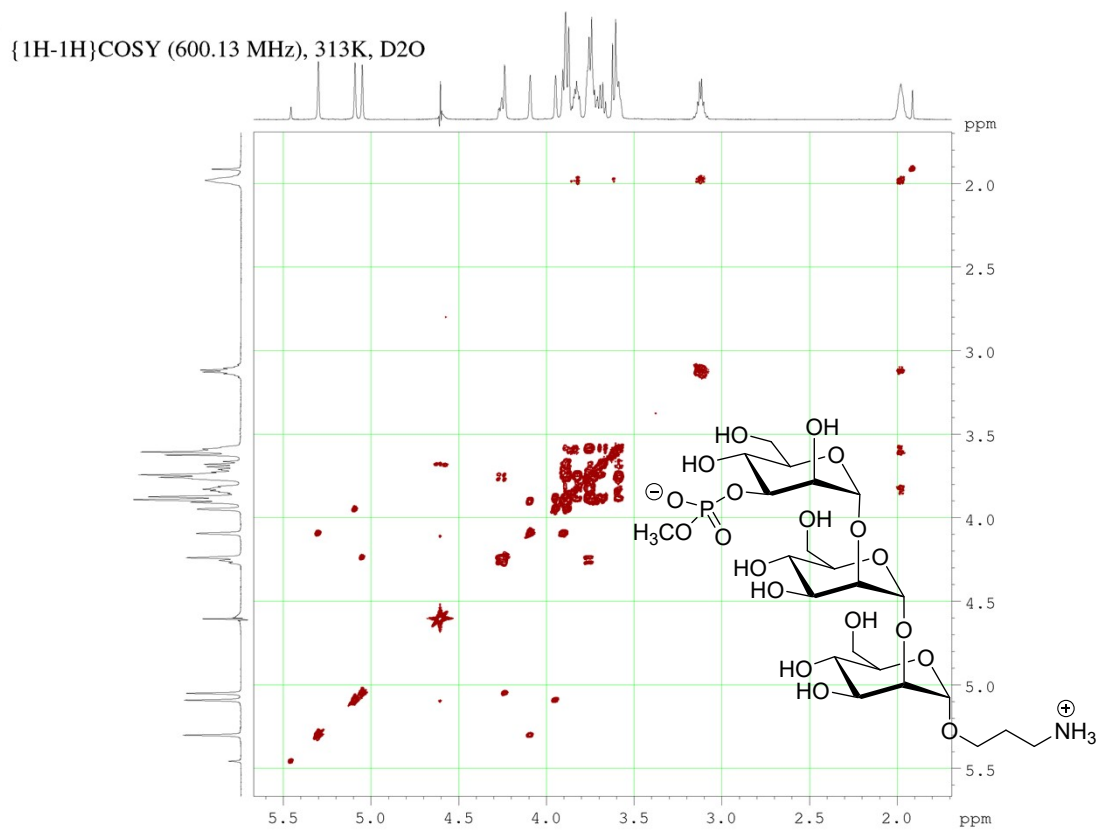


### 3-aminopropyl 3-O-(methylphosphonato)- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -D-mannopyranoside (3a)

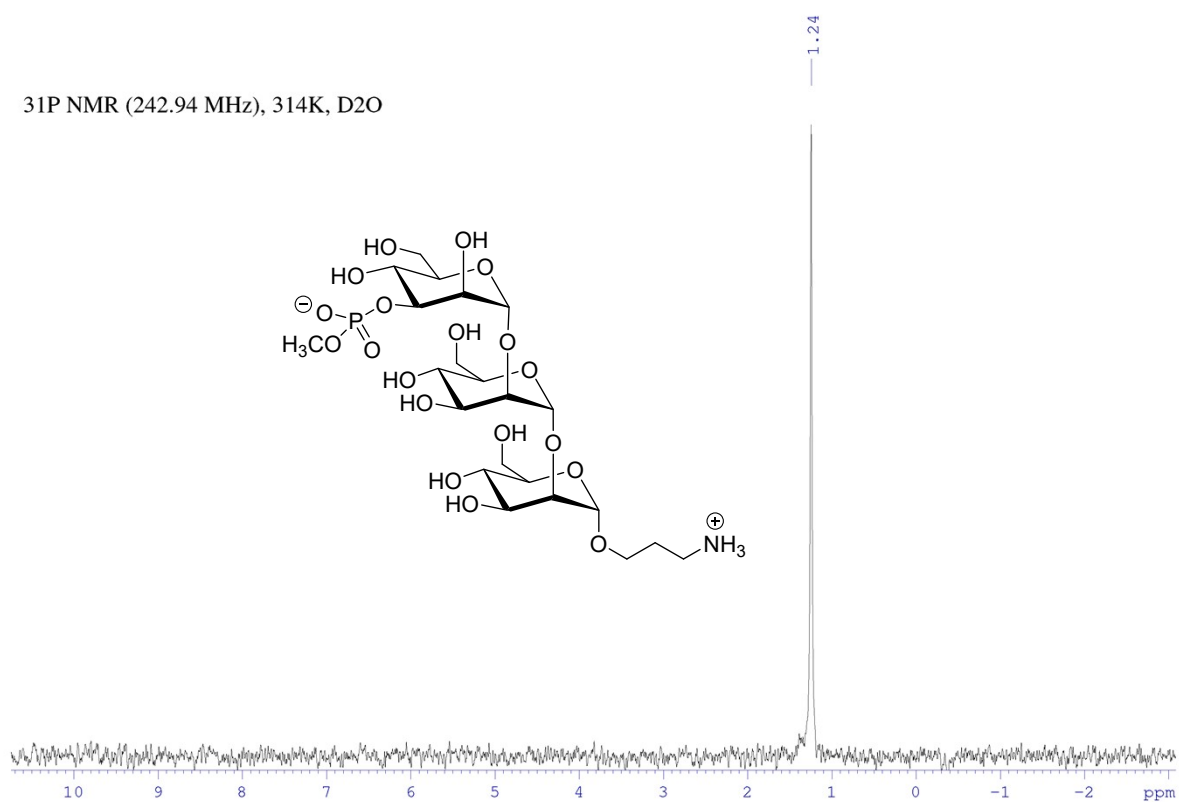


<sup>13</sup>C NMR (150.90 MHz), 313K, D<sub>2</sub>O

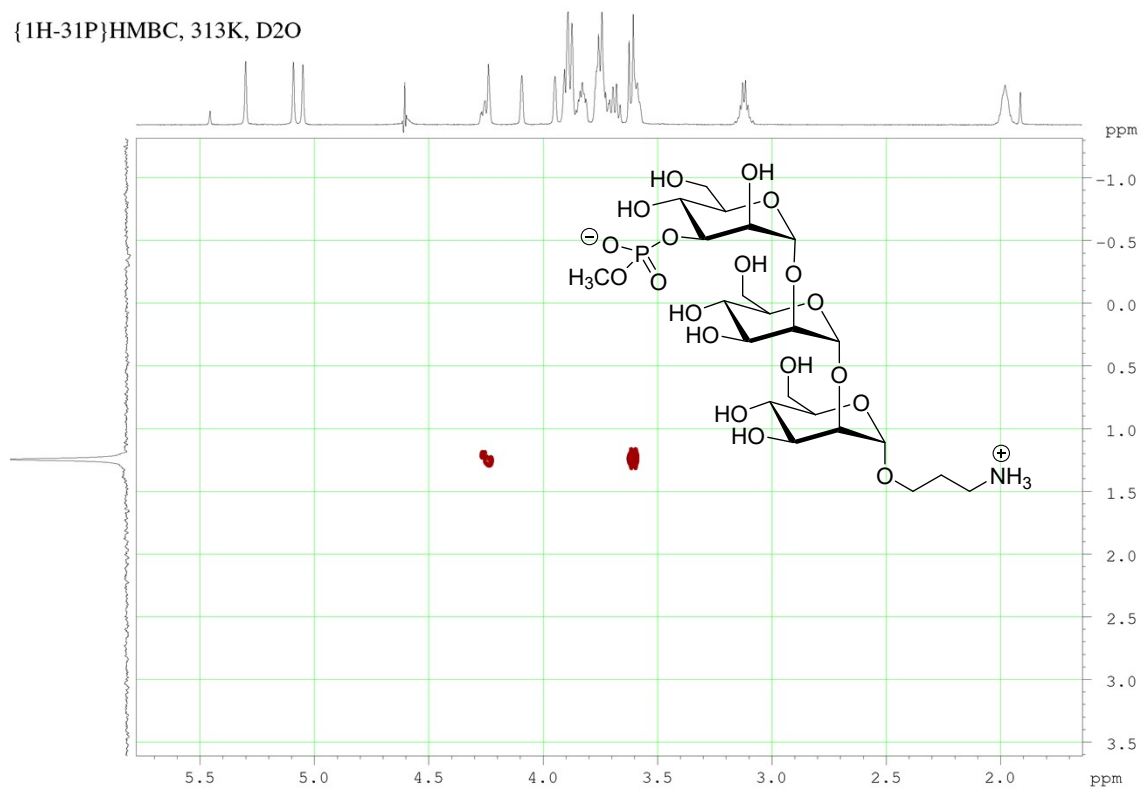




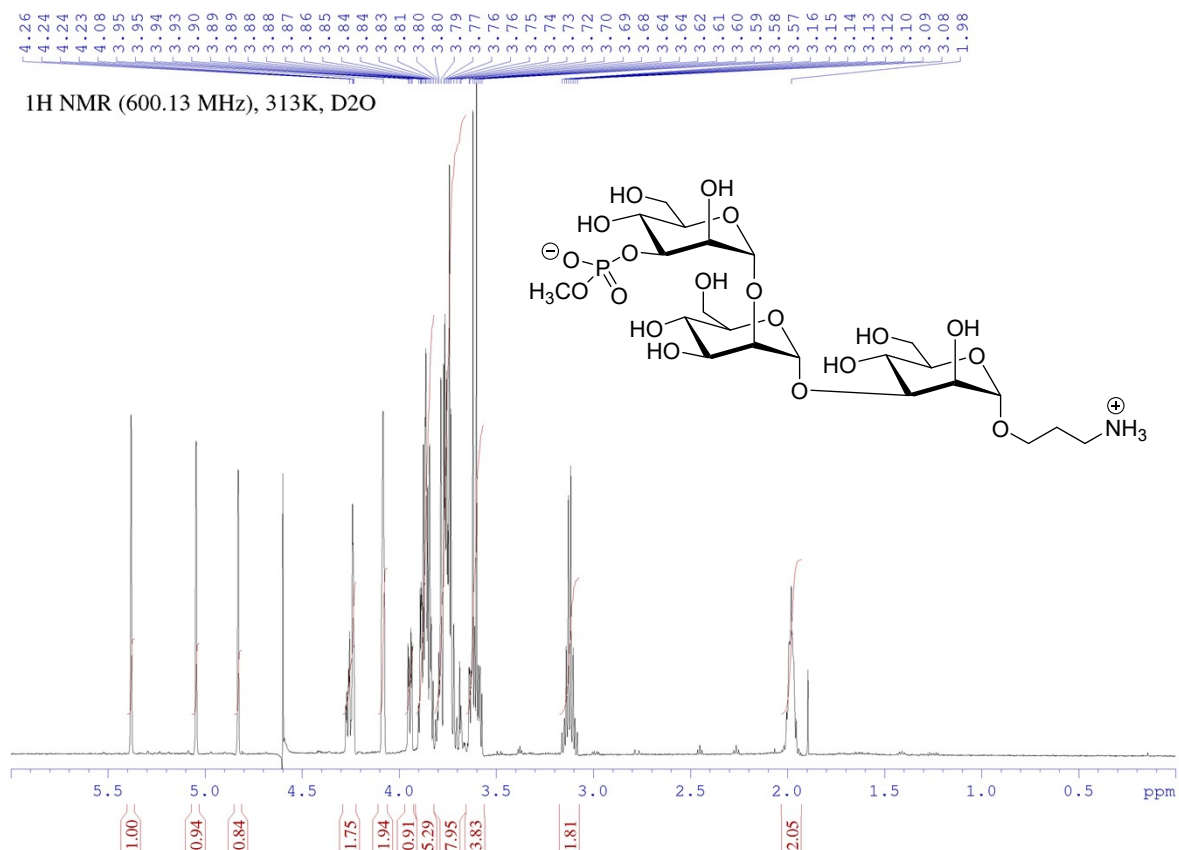
31P NMR (242.94 MHz), 314K, D2O



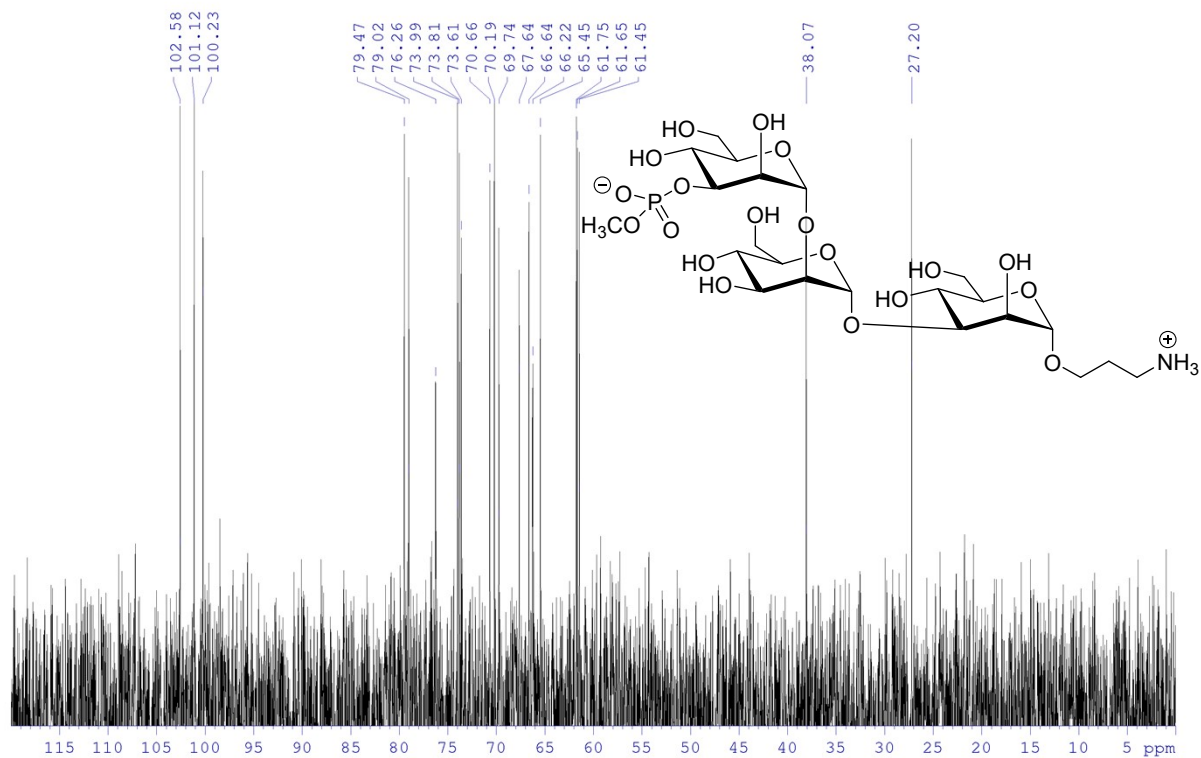
{1H-31P}HMBC, 313K, D2O



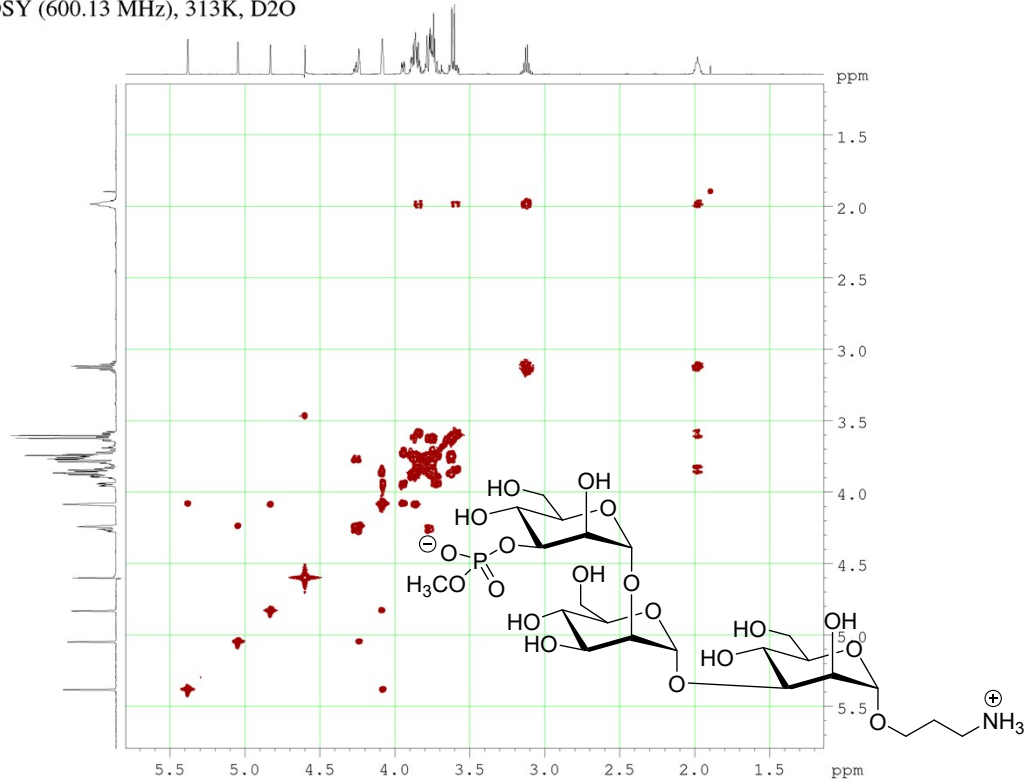
### 3-aminopropyl 3-O-(methylphosphonato)- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 3)- $\alpha$ -D-mannopyranoside (4a)



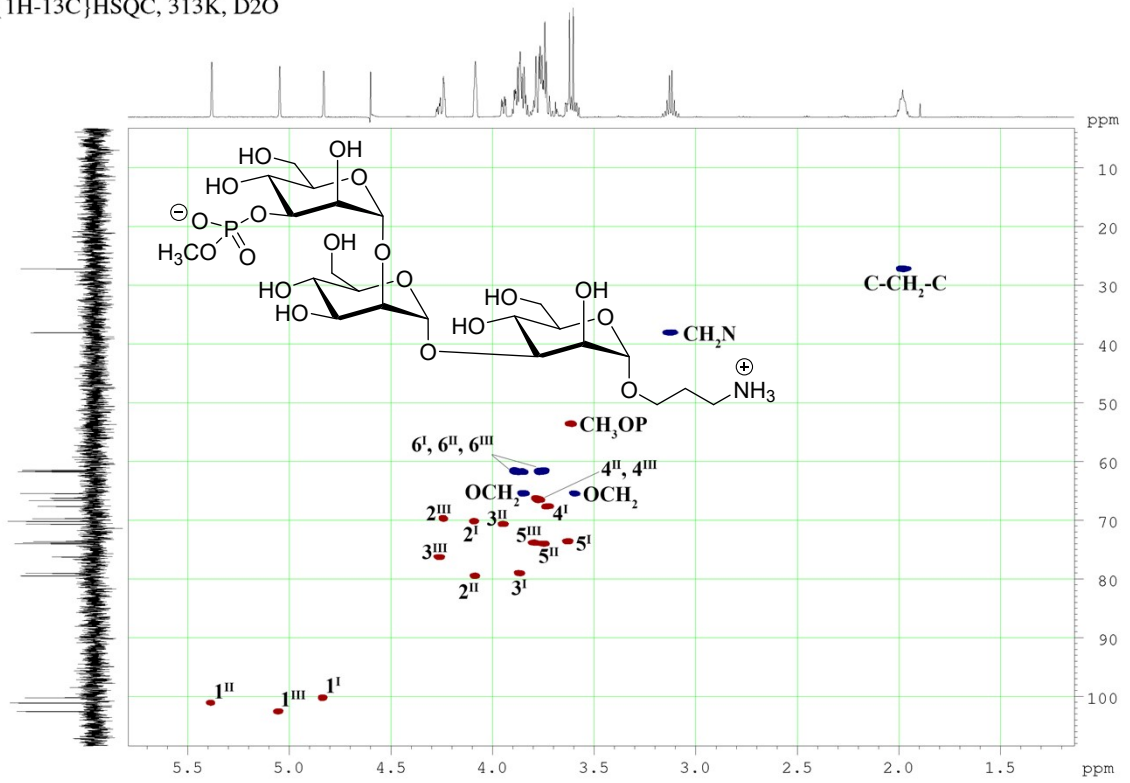
13C NMR (150.90 MHz), 313K, D2O



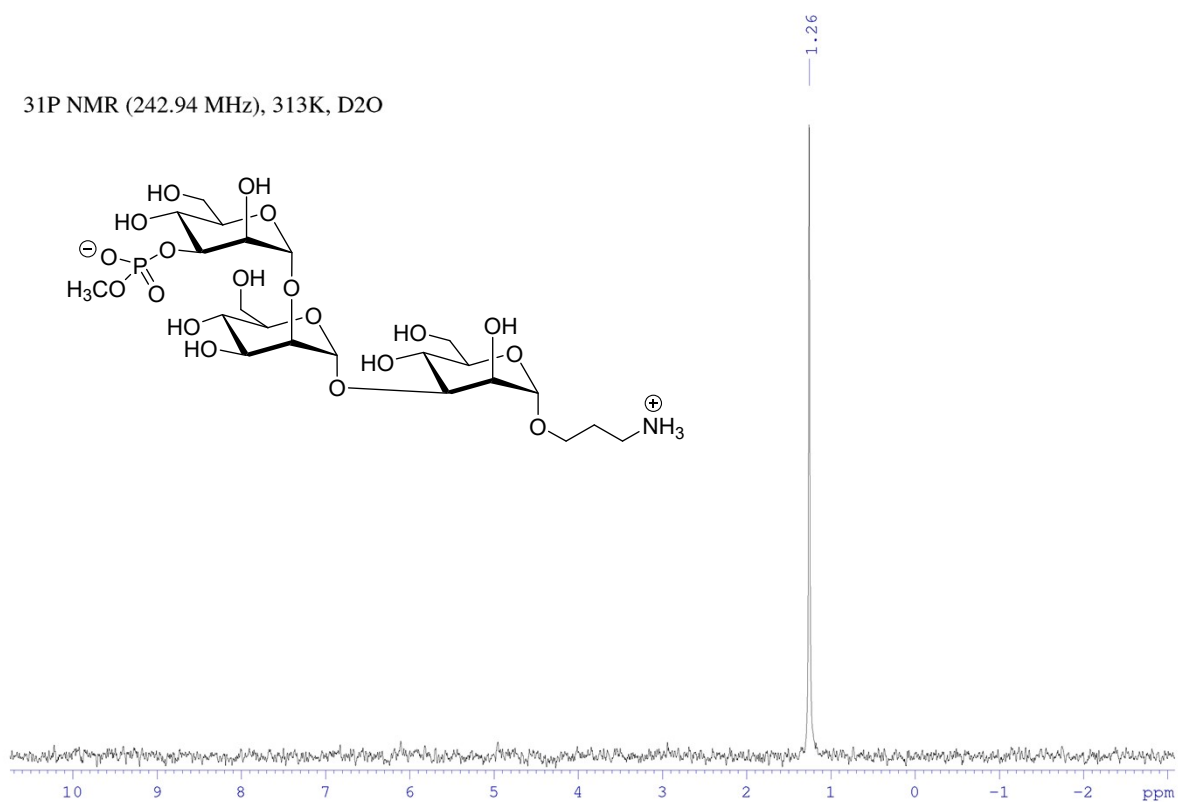
{1H-1H}COSY (600.13 MHz), 313K, D2O



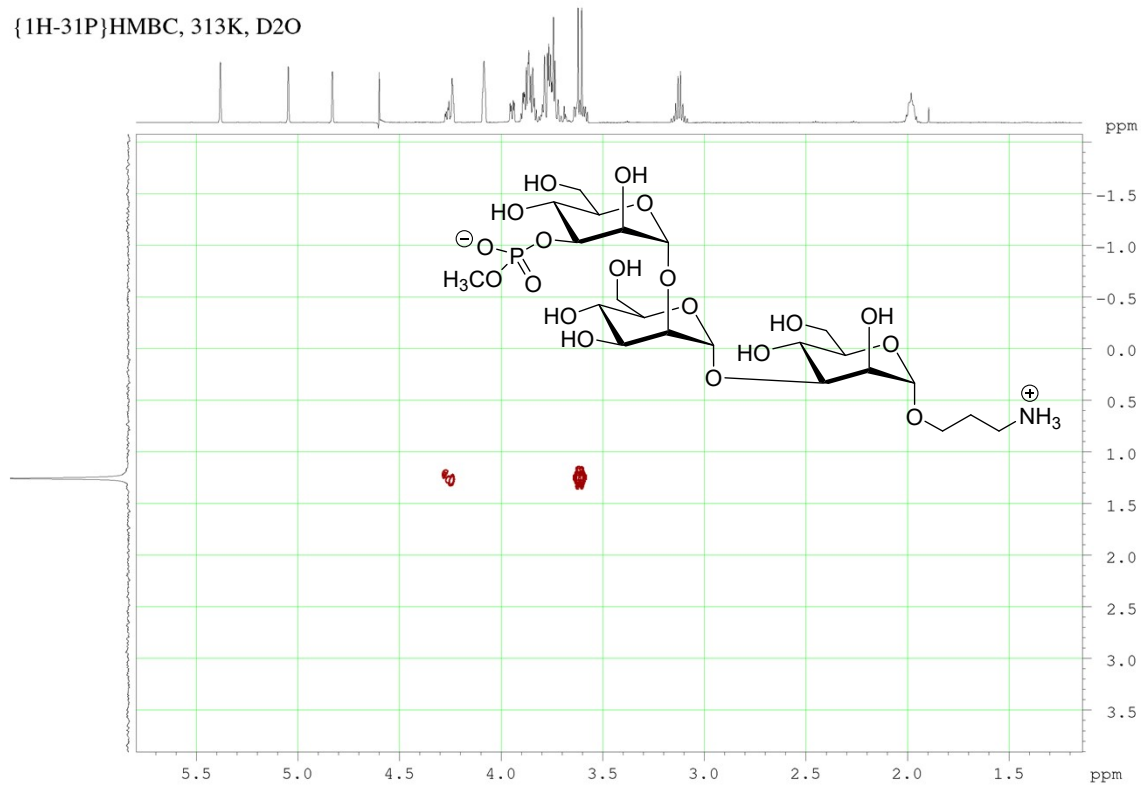
{1H-13C}HSQC, 313K, D2O



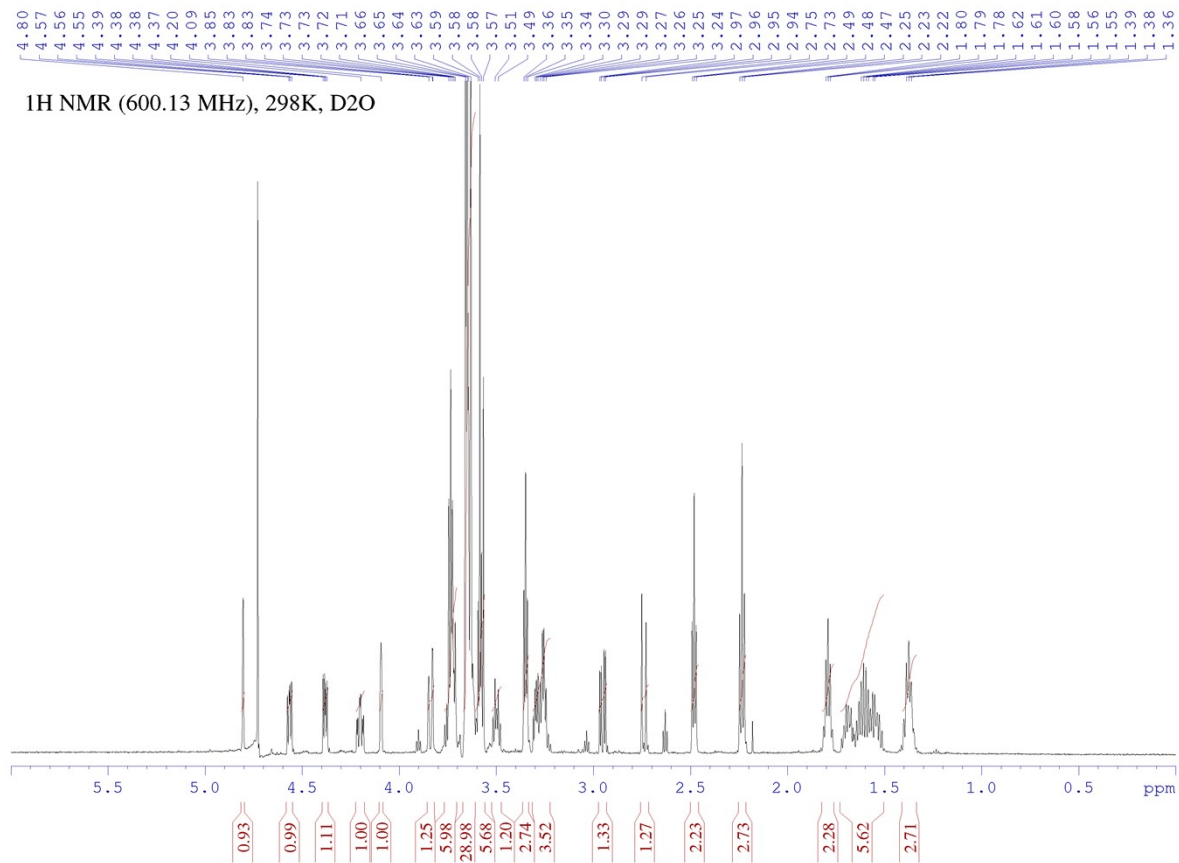
31P NMR (242.94 MHz), 313K, D2O



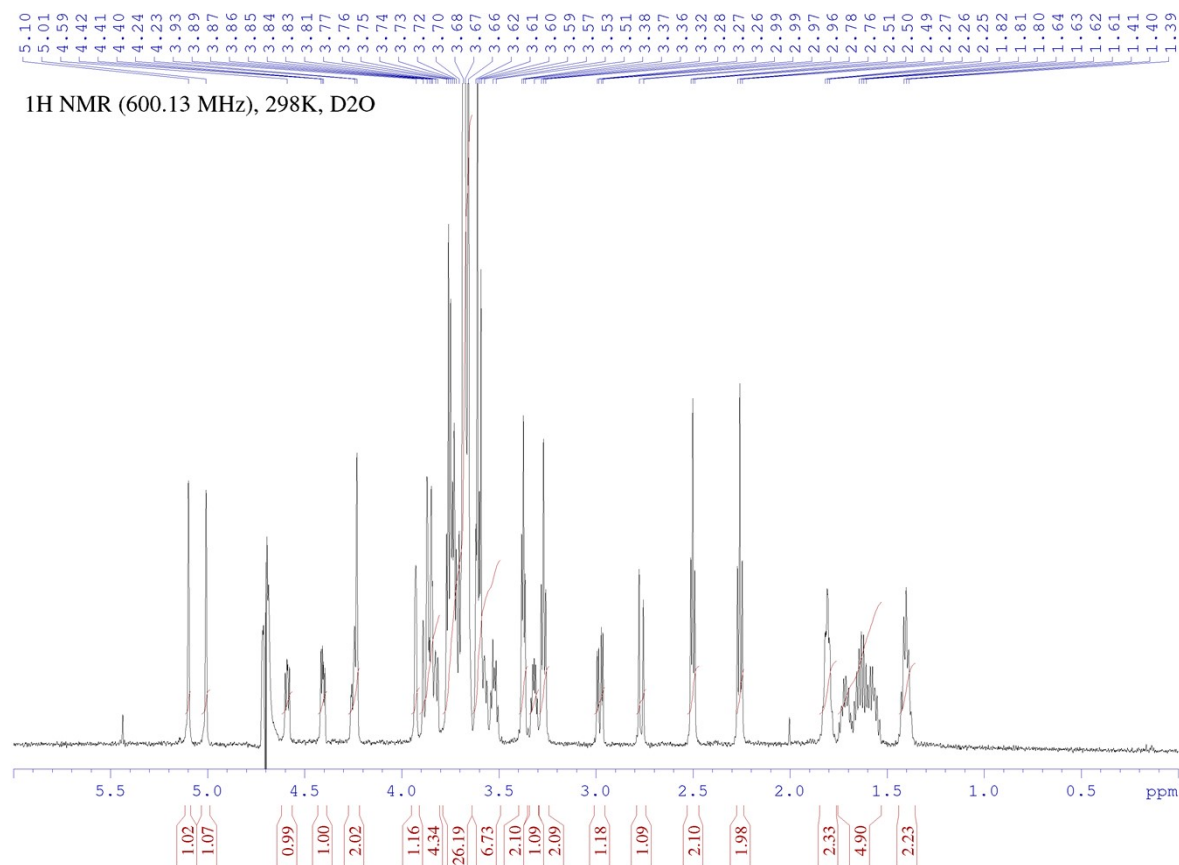
{1H-31P}HMBC, 313K, D2O



### Biotinylated monosaccharide 1b

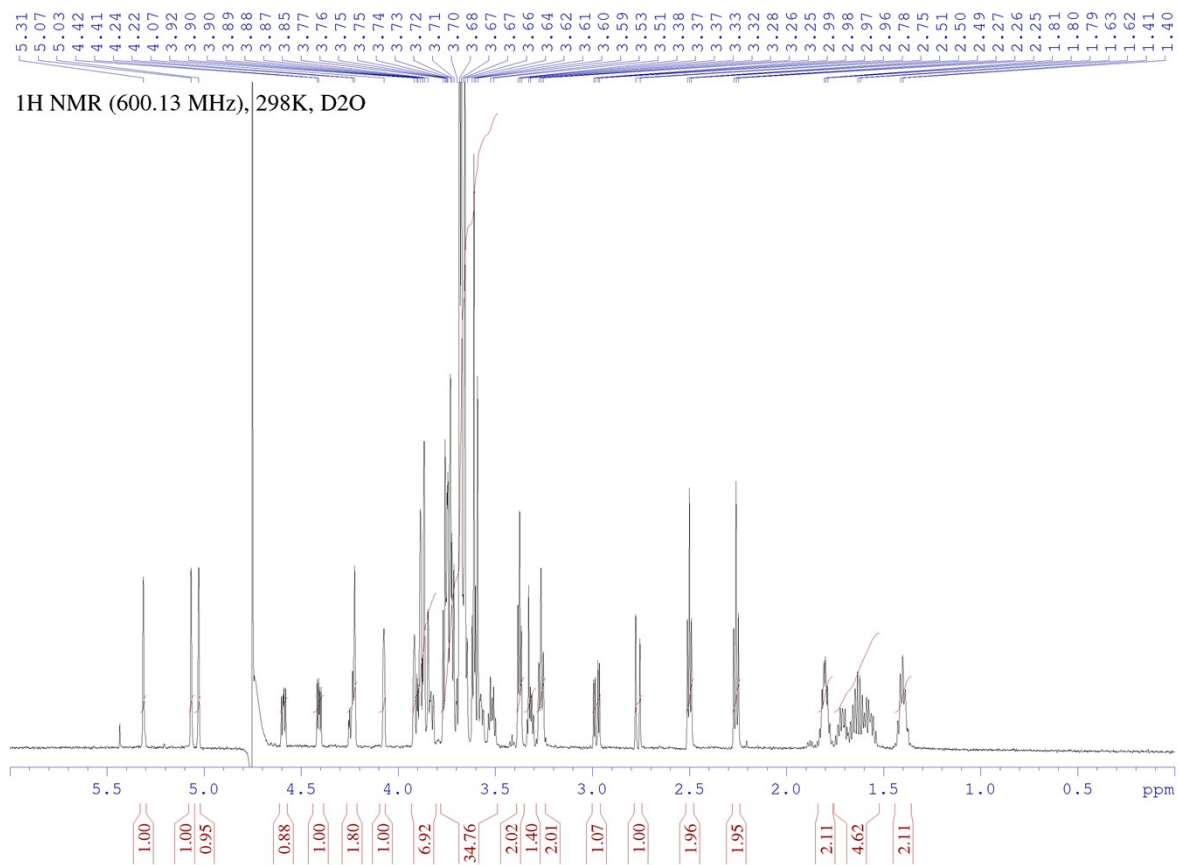


### Biotinylated disaccharide 2b

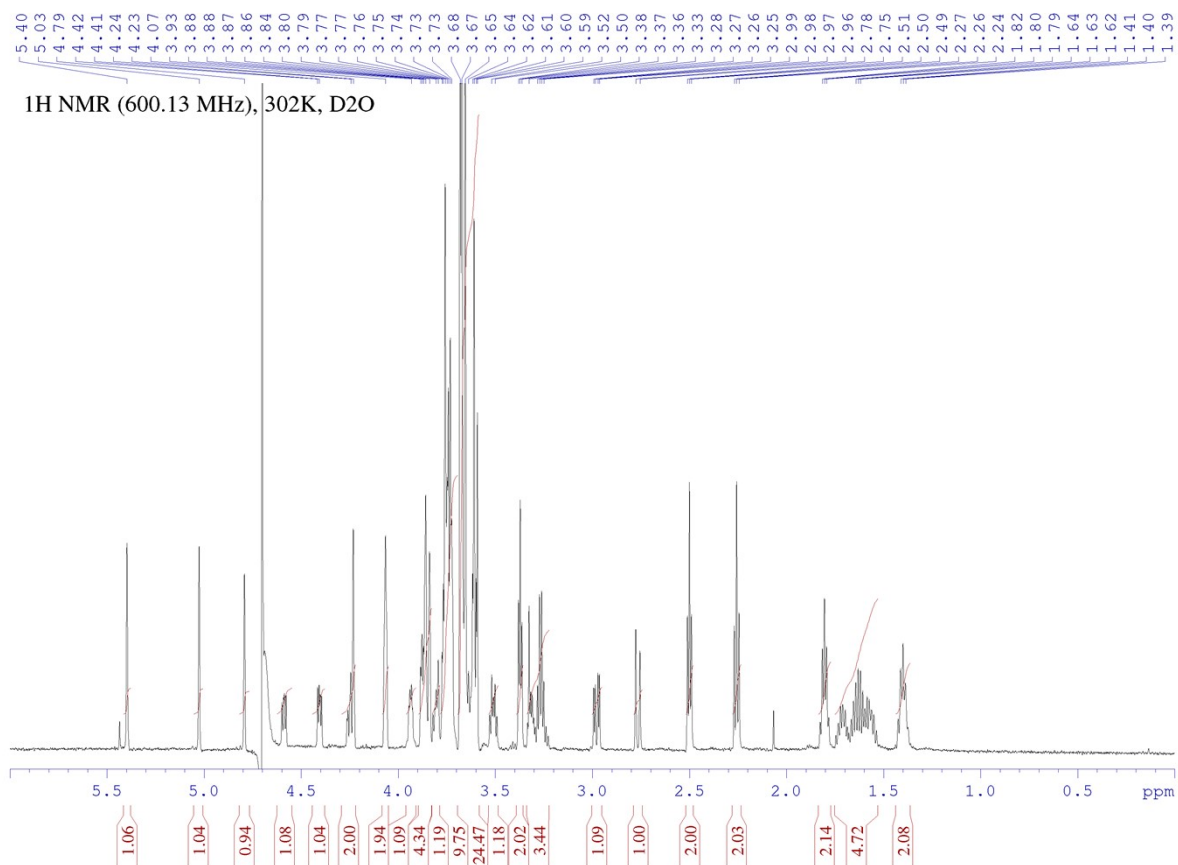




### Biotinylated trisaccharide 3b



### Biotinylated trisaccharide 4b



**Table S1.** ELISA screening of specific IgG level in human sera from patients with confirmed *K. pneumoniae* infection (mean OD(450 nm) raw data).

	Oligosaccharide ligand										Control
	1	2	3	4	5	6	7	8	9	10	
Case 1	0,1683	0,5913	1,0692	0,4338	0,0851	0,0869	0,1050	0,1084	0,1174	0,2263	0,0953
Case 2	0,1049	0,1111	0,1157	0,1138	0,1131	0,1197	0,1207	0,1172	0,3379	1,0676	0,1185
Case 3	0,1424	0,1404	0,1672	0,1429	0,1213	0,1091	0,2142	0,1092	0,1267	0,1589	0,1002
Case 4	0,0929	0,1504	0,1125	0,1033	0,1075	0,0994	0,1230	0,1134	0,1638	0,6808	0,0946
Case 5	0,1221	0,1434	0,1430	0,1381	0,1434	0,1424	0,1393	0,1481	0,1443	0,1432	0,1157
Case 6	0,0933	0,1126	0,1107	0,1005	0,1139	0,1233	0,1106	0,1151	0,1098	0,1455	0,1003
Case 7	0,0677	0,0820	0,0761	0,0888	0,0785	0,0820	0,1016	0,0886	0,3934	0,7701	0,0802
Case 8	0,0749	0,0761	0,0721	0,0722	0,0785	0,0775	0,0829	0,0873	0,0861	0,1739	0,0799
Case 9	0,1120	0,1249	0,1184	0,1061	0,0980	0,1410	0,1261	0,1160	0,1147	0,1590	0,1310
Case 10	0,0818	0,0996	0,1381	0,0931	0,0750	0,0688	0,1042	0,0821	0,0879	0,0874	0,0752
Case 11	0,0853	0,1330	0,1435	0,1120	0,0879	0,0945	0,1124	0,0910	0,1991	0,3668	0,0924
Case 12	0,0833	0,0905	0,1336	0,0948	0,1050	0,0897	0,1136	0,1013	0,1198	0,2431	0,0959
Case 13	0,1148	0,1239	0,1257	0,1170	0,1109	0,1329	0,1250	0,1218	0,1247	0,1412	0,1117
Case 14	0,0867	0,0884	0,1148	0,0892	0,0910	0,0992	0,1003	0,0984	0,1130	0,9039	0,1128
Case 15	0,0924	0,0947	0,0975	0,0966	0,0885	0,0968	0,0976	0,1058	0,1015	0,1288	0,0948

## References

- (1) Lobanova, N. A.; Stankevich, V. K.; Kukharev, B. F. Synthesis of Acetals Containing a Primary Amino Group. *Russ. J. Org. Chem.* **2012**, *48* (10), 1289–1296. <https://doi.org/10.1134/S1070428012100053>.
- (2) Karelin, A. A.; Tsvetkov, Y. E.; Kogan, G.; Bystricky, S.; Nifantiev, N. E. Synthesis of Oligosaccharide Fragments of Mannan from *Candida Albicans* Cell Wall and Their BSA Conjugates. *Russ. J. Bioorganic Chem.* **2007**, *33* (1), 110–121. <https://doi.org/10.1134/S106816200701013X>.
- (3) Lemanski, G.; Ziegler, T. Prearranged Glycosides. Part 12. Intramolecular Mannosylations of Glucose Derivatives via Prearranged Glycosides. *Helv. Chim. Acta* **2000**, *83* (10), 2655–2675. [https://doi.org/10.1002/1522-2675\(20001004\)83:10<2655::AID-HLCA2655>3.0.CO;2-U](https://doi.org/10.1002/1522-2675(20001004)83:10<2655::AID-HLCA2655>3.0.CO;2-U).
- (4) Picard, S.; Crich, D. Improved Methods for the Stereoselective Synthesis of Mannoheptosyl Donors and Their Glycosides: Toward the Synthesis of the Trisaccharide Repeating Unit of the *Campylobacter* Jejuni RM1221 Capsular Polysaccharide. *Tetrahedron* **2013**, *69* (26), 5501–5510. <https://doi.org/10.1016/j.tet.2013.04.094>.