

## Supporting Information

### **Regenerative Glycosylation**

Yashapal Singh, Tinghua Wang, Scott A. Geringer, Keith J. Stine, and Alexei V. Demchenko\*

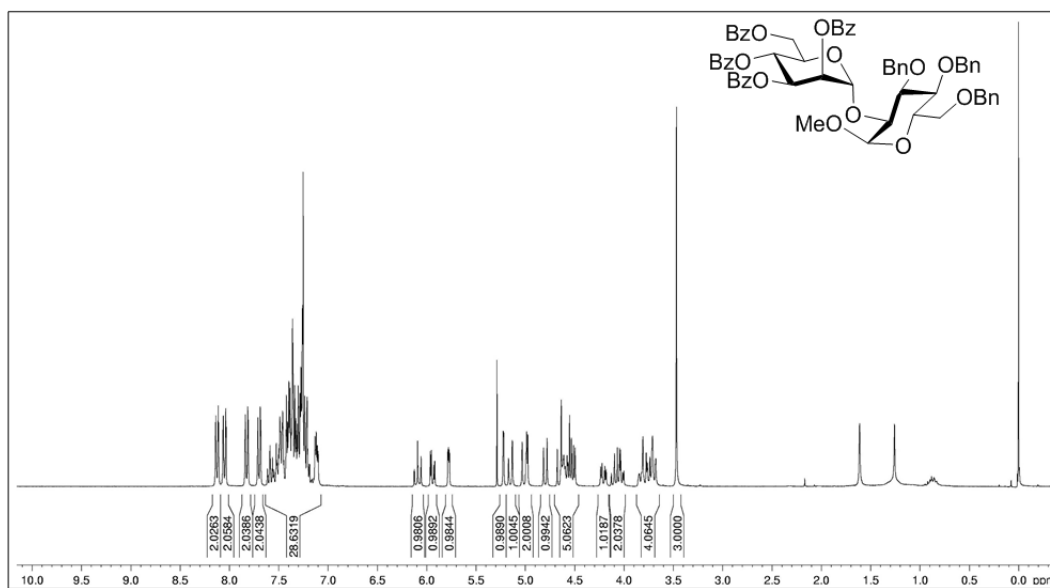
*Department of Chemistry and Biochemistry, University of Missouri - St. Louis  
One University Boulevard, St. Louis, Missouri 63121, USA  
Fax: (+) 1-314-516-5342; E-mail: [demchenkoa@umsl.edu](mailto:demchenkoa@umsl.edu)*

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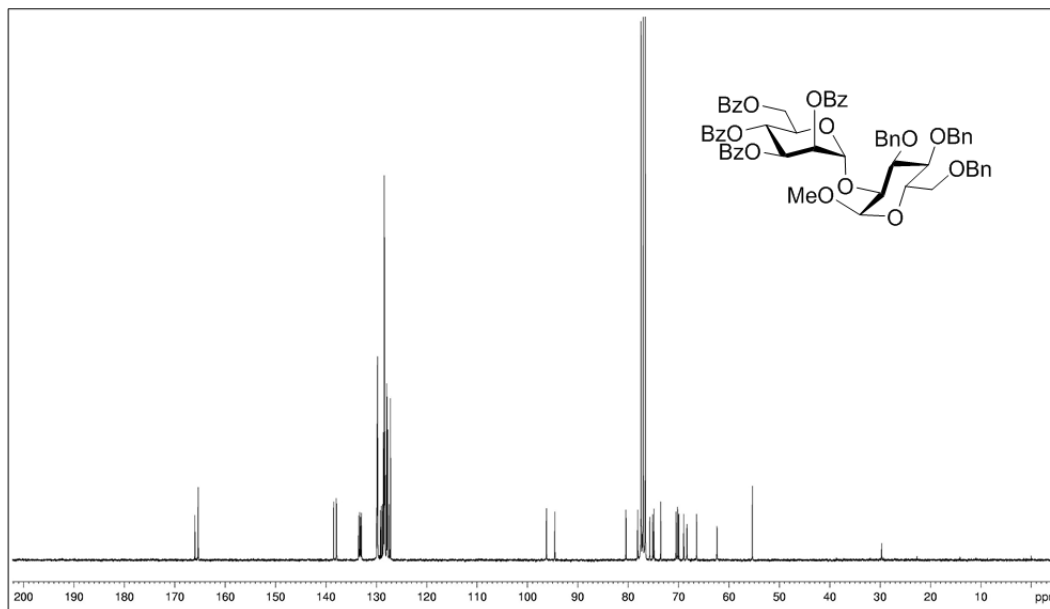
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## NMR Spectra for new compounds

### Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)-3,4,6-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (21)

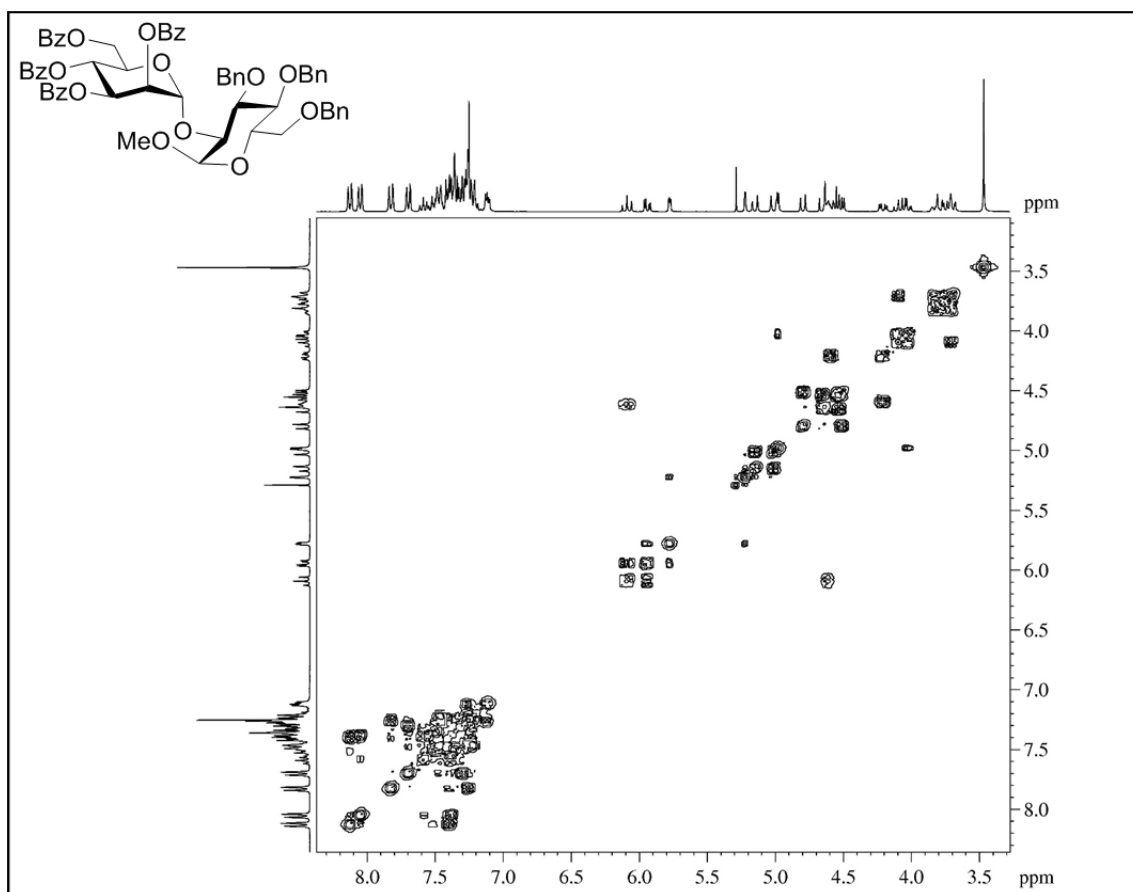


<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 300 MHz)



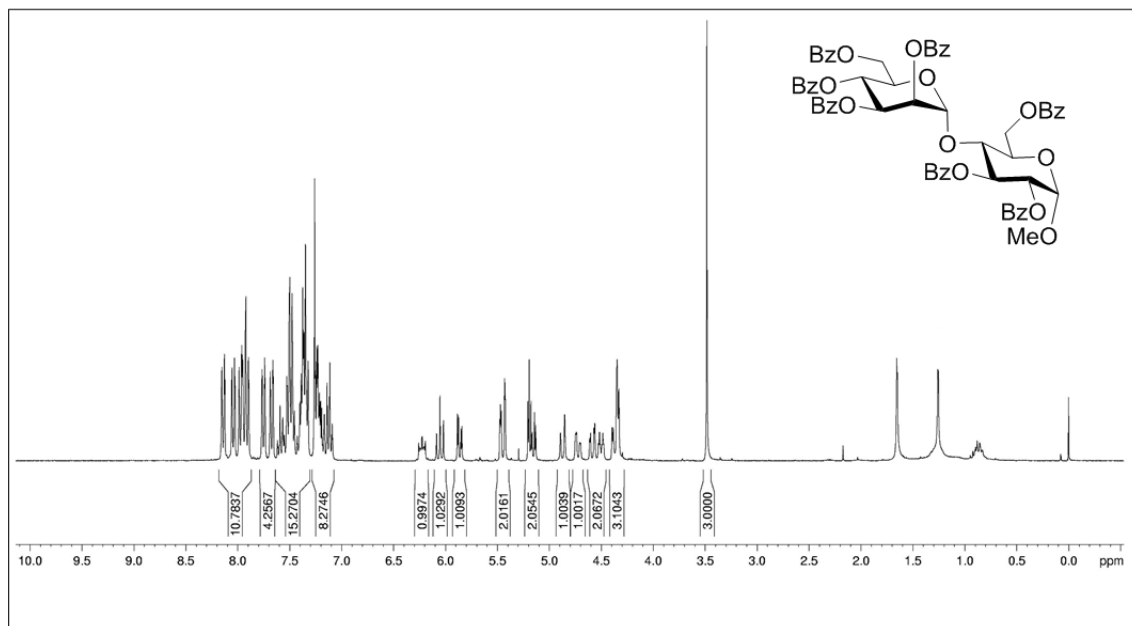
<sup>13</sup>C NMR spectrum (75 MHz, CDCl<sub>3</sub>)

**Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)-3,4,6-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (21)**

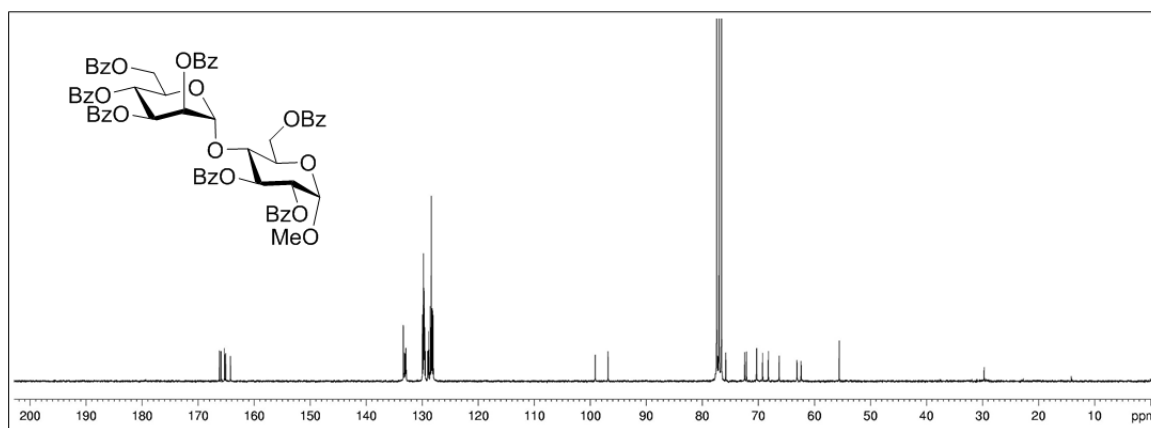


2D NMR (300 MHz, CDCl<sub>3</sub>)

**Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)-2,4,6-tri-*O*-benzoyl- $\alpha$ -D-glucopyranoside (29)**

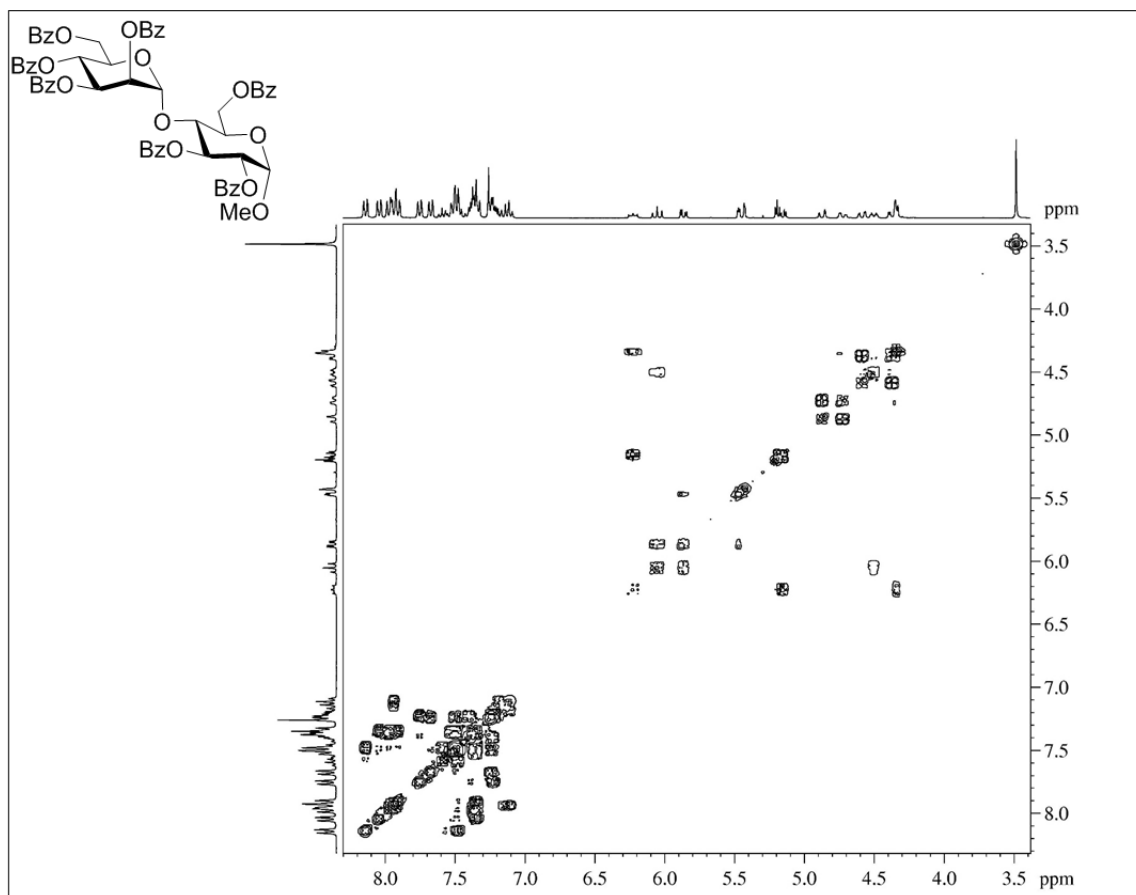


<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)



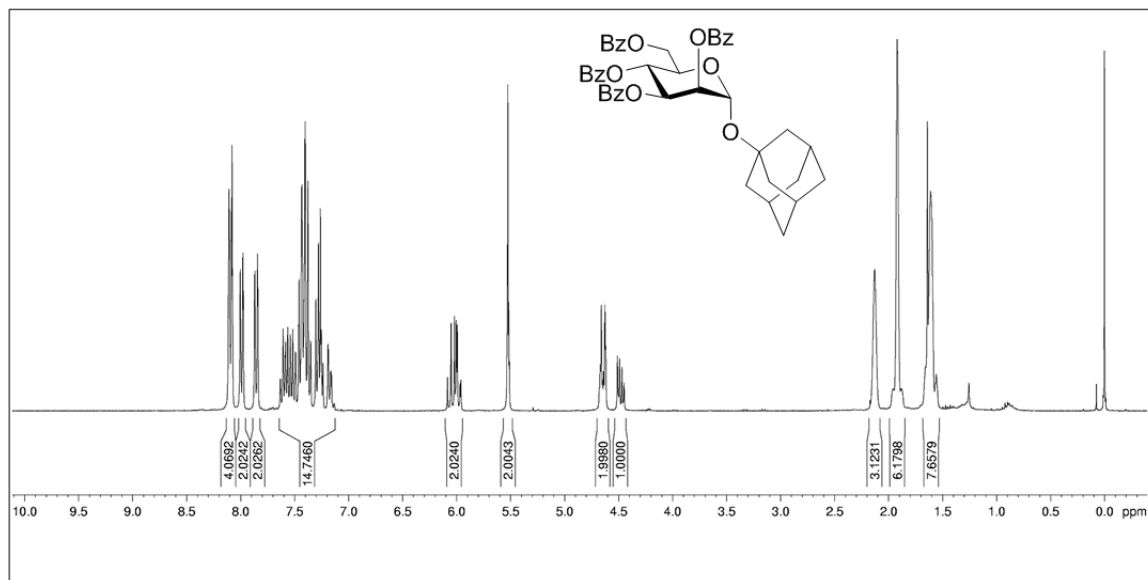
<sup>13</sup>C NMR spectrum (75 MHz, CDCl<sub>3</sub>)

**Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)-2,4,6-tri-*O*-benzoyl- $\alpha$ -D-glucopyranoside (29)**

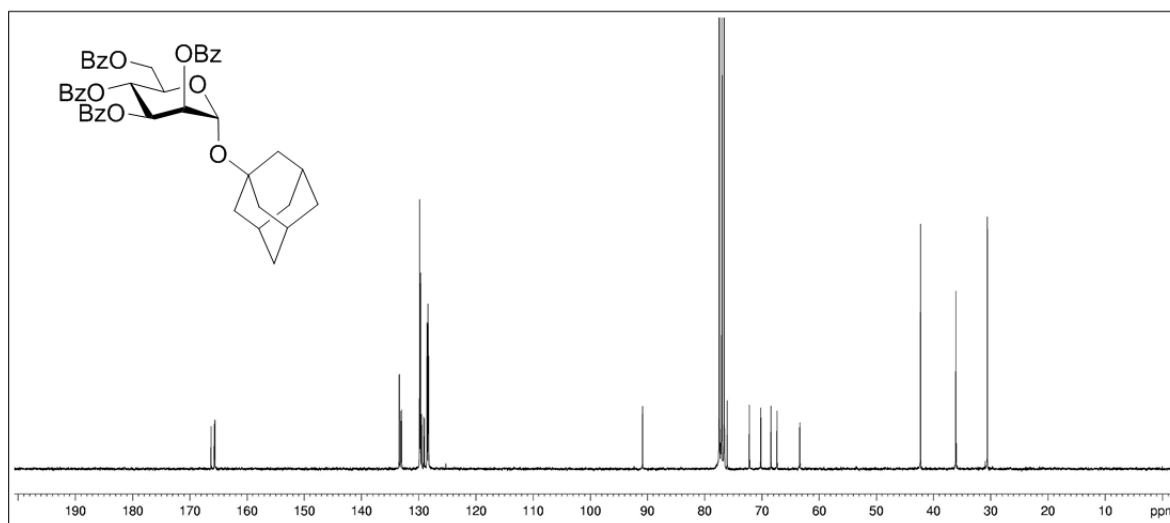


2D NMR (300 MHz, CDCl<sub>3</sub>)

### 1-Adamantyl 2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranoside (19)

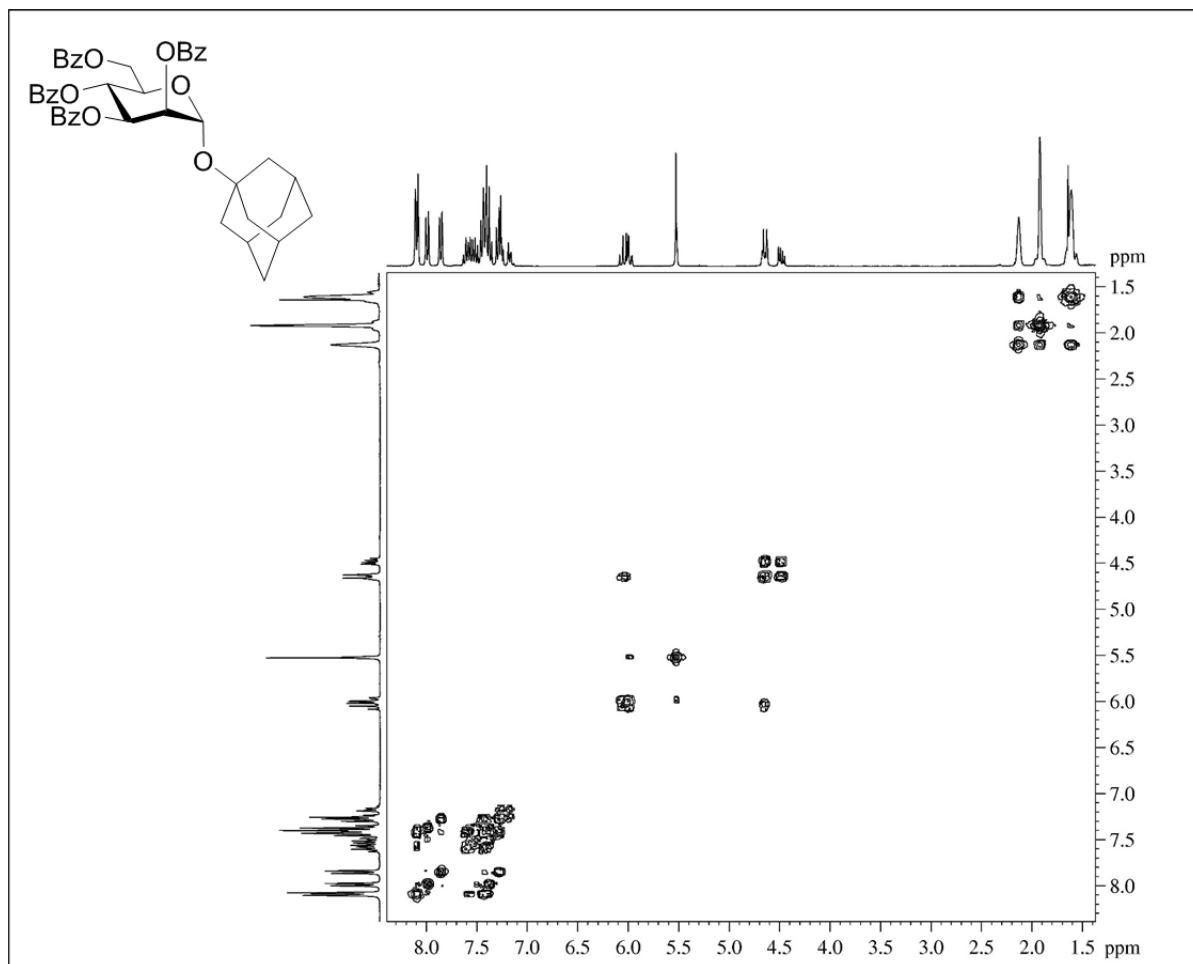


<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)



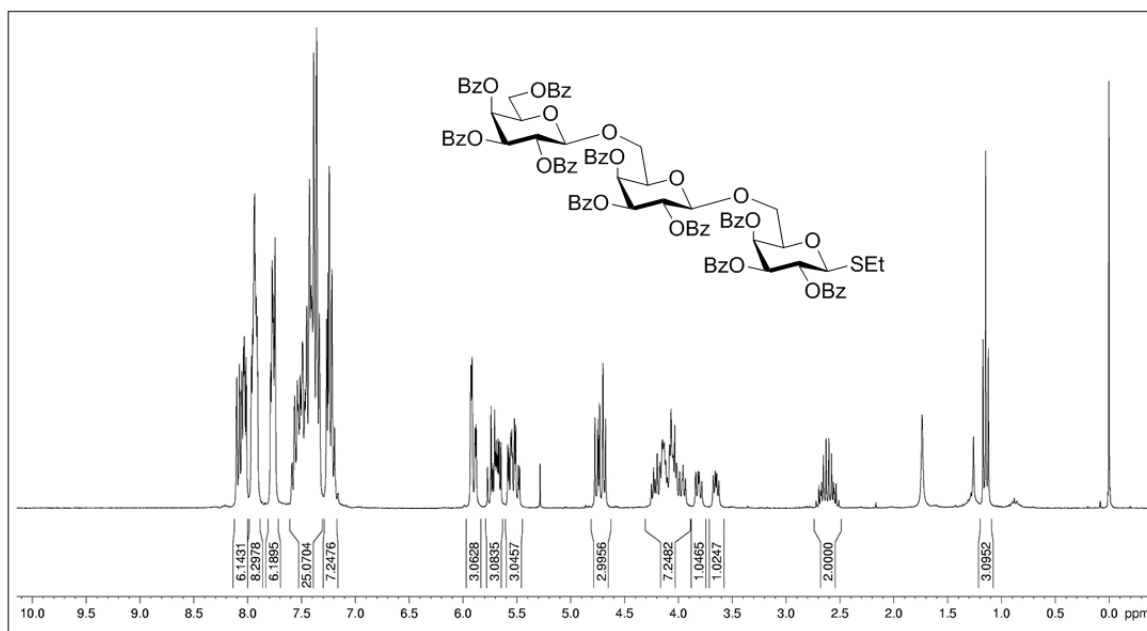
<sup>13</sup>C NMR spectrum (75 MHz, CDCl<sub>3</sub>).

**1-Adamantyl 2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranoside (19)**

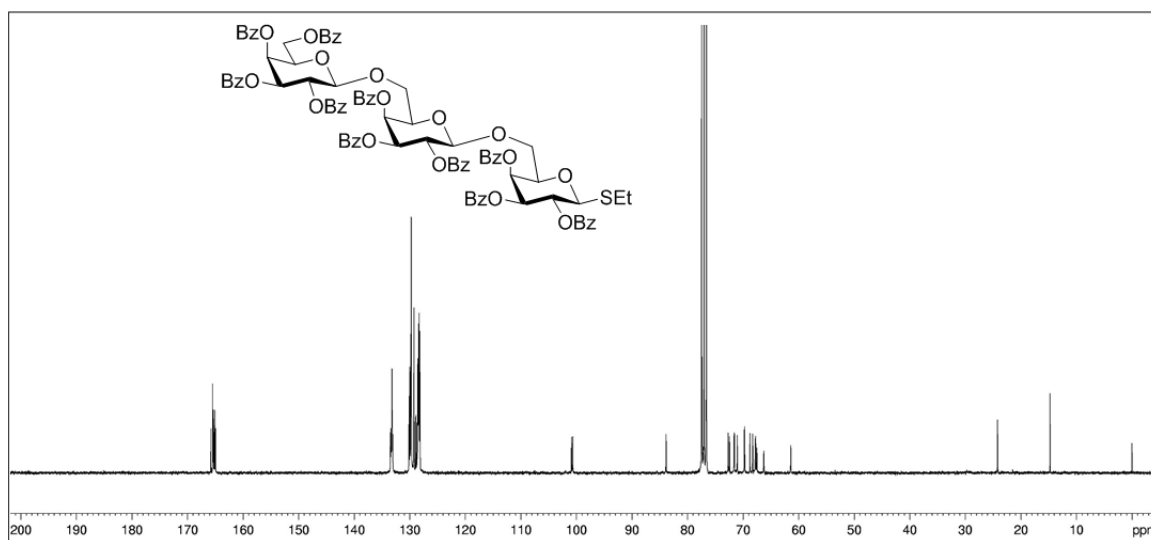


2D NMR (300 MHz, CDCl<sub>3</sub>)

**Ethyl *O*-(2,3,4-Tri-*O*-benzoyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzoyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl-1-thio- $\beta$ -D-galactopyranoside (37)**



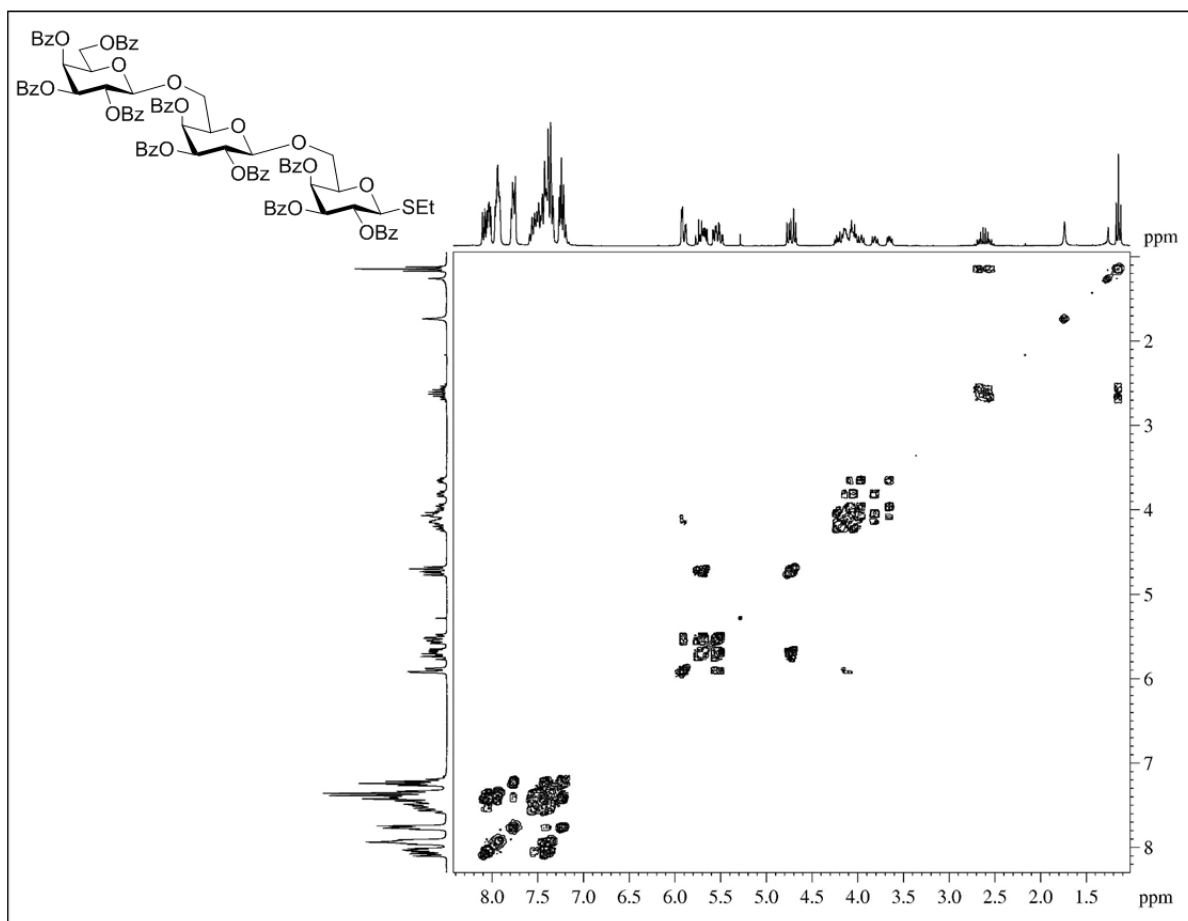
<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR spectrum (75 MHz, CDCl<sub>3</sub>)

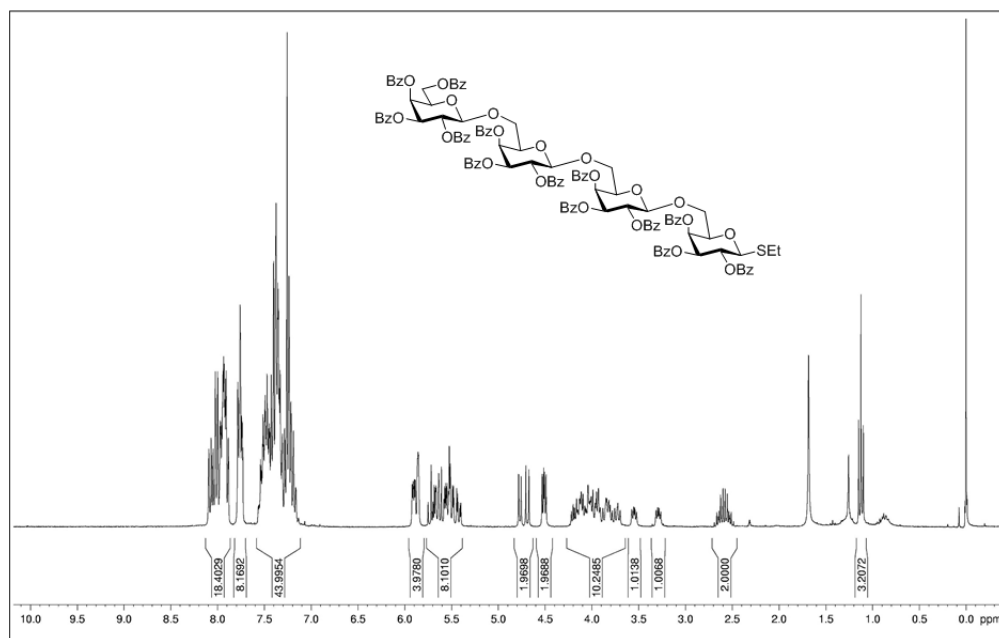


**Ethyl *O*-(2,3,4-Tri-*O*-benzoyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzoyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl-1-thio- $\beta$ -D-galactopyranoside (37)**

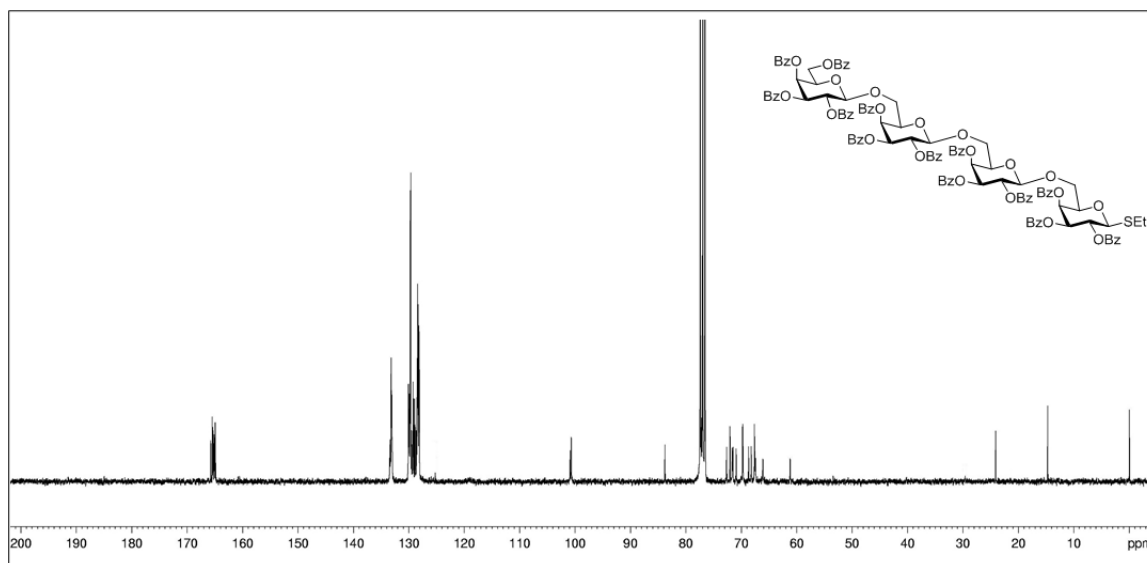


2D NMR (300 MHz, CDCl<sub>3</sub>)

**Ethyl *O*-(2,3,4-Tri-*O*-benzoyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzoyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl-1-thio- $\beta$ -D-galactopyranoside (38)**

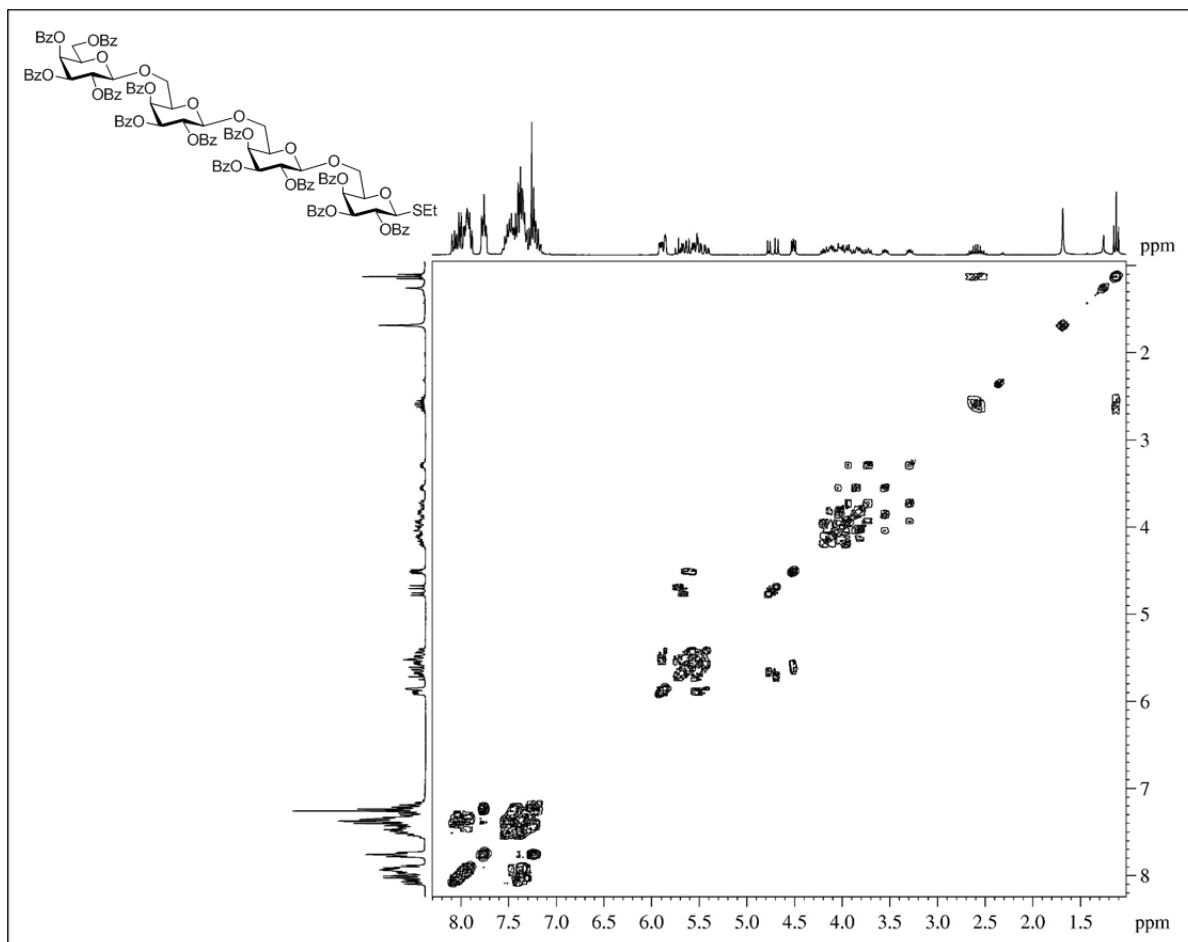


$^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR spectrum (75 MHz,  $\text{CDCl}_3$ )

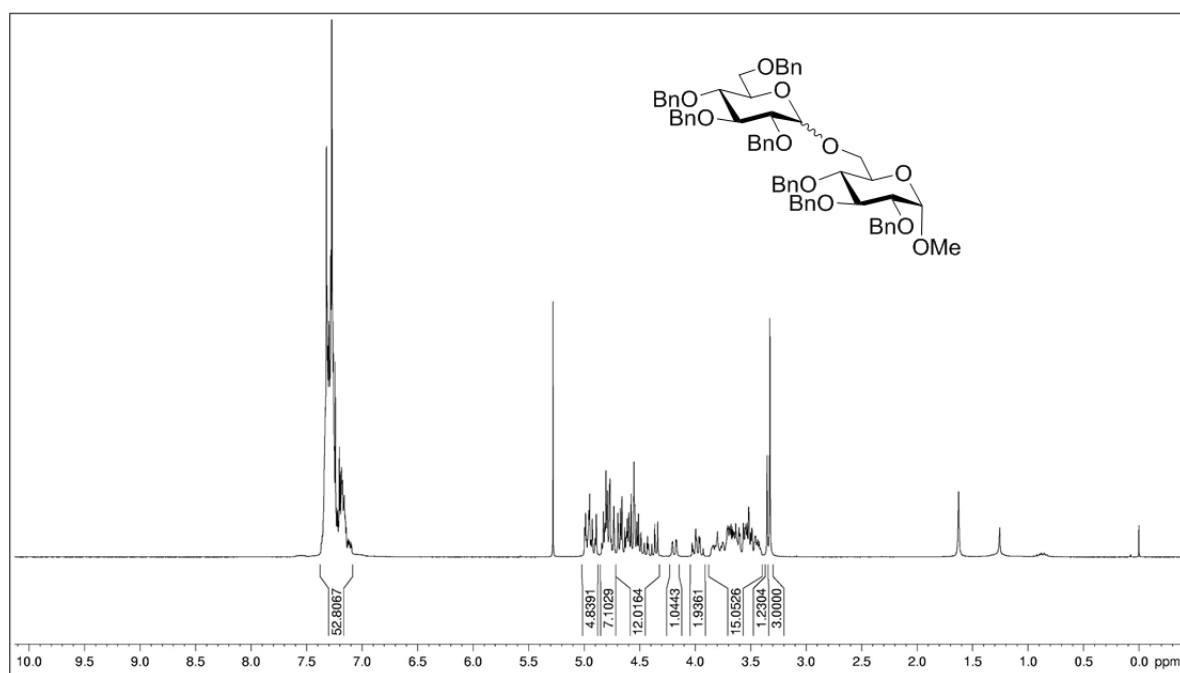
**Ethyl *O*-(2,3,4-Tri-*O*-benzoyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzoyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl-1-thio- $\beta$ -D-galactopyranoside (38)**



2D NMR (300 MHz, CDCl<sub>3</sub>)

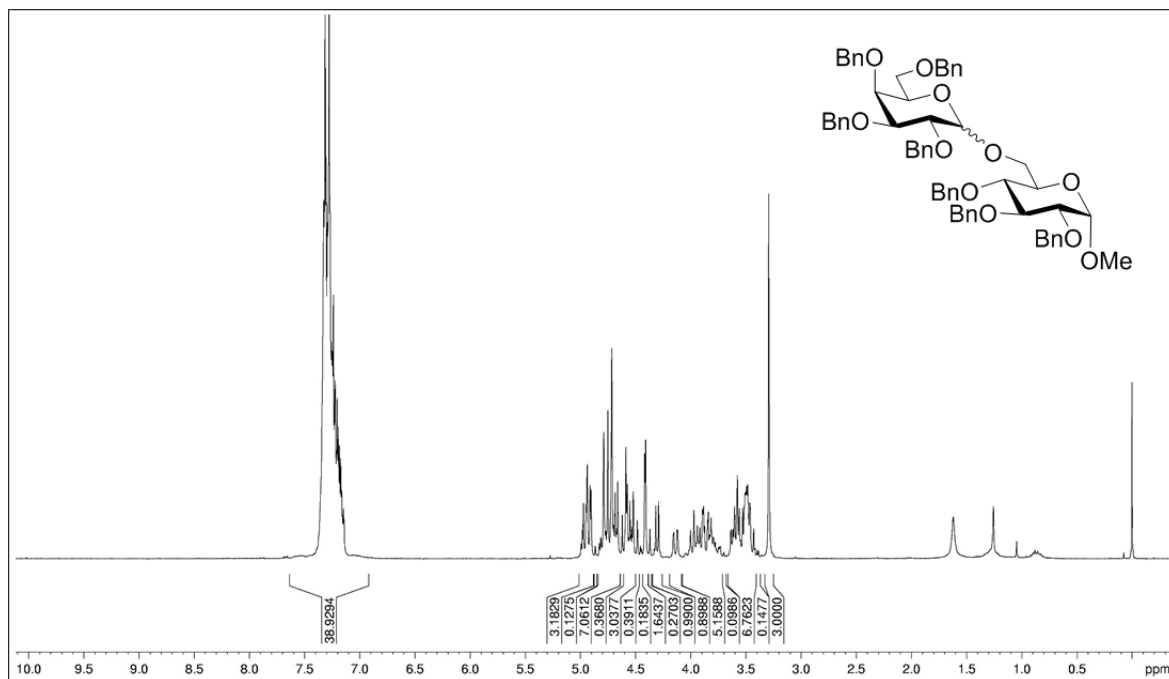
## Proton NMR Spectra for known compounds

### Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl- $\beta$ -D-glucopyranosyl)-2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (5)



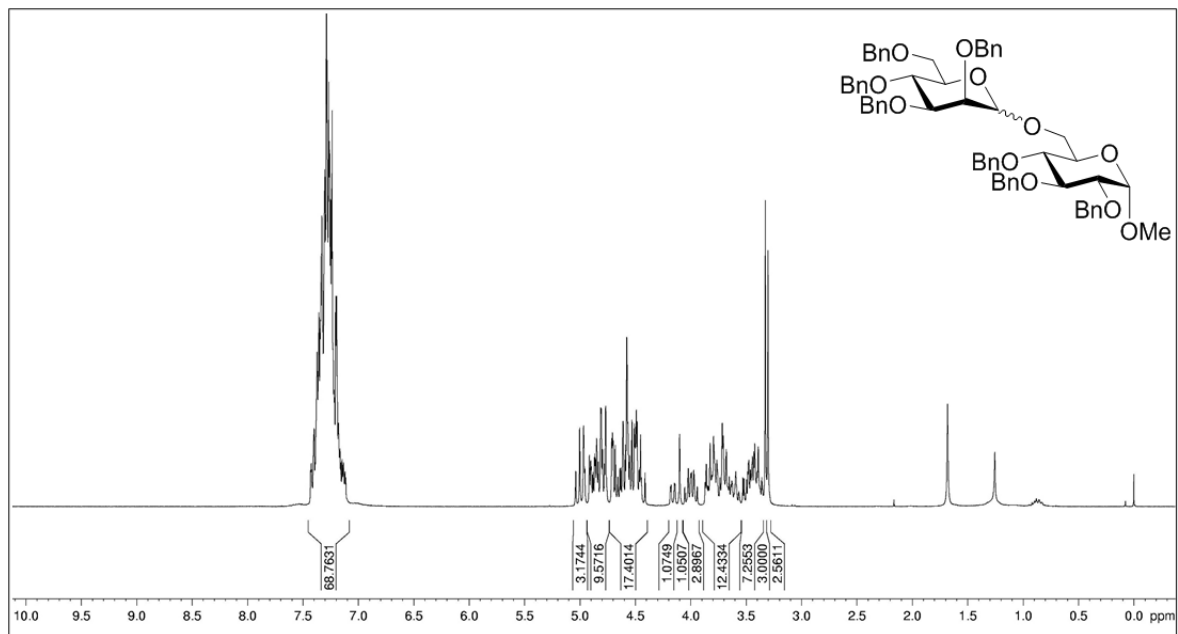
<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)

**Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl- $\beta$ -D-galacopyranosyl)-2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (7)**



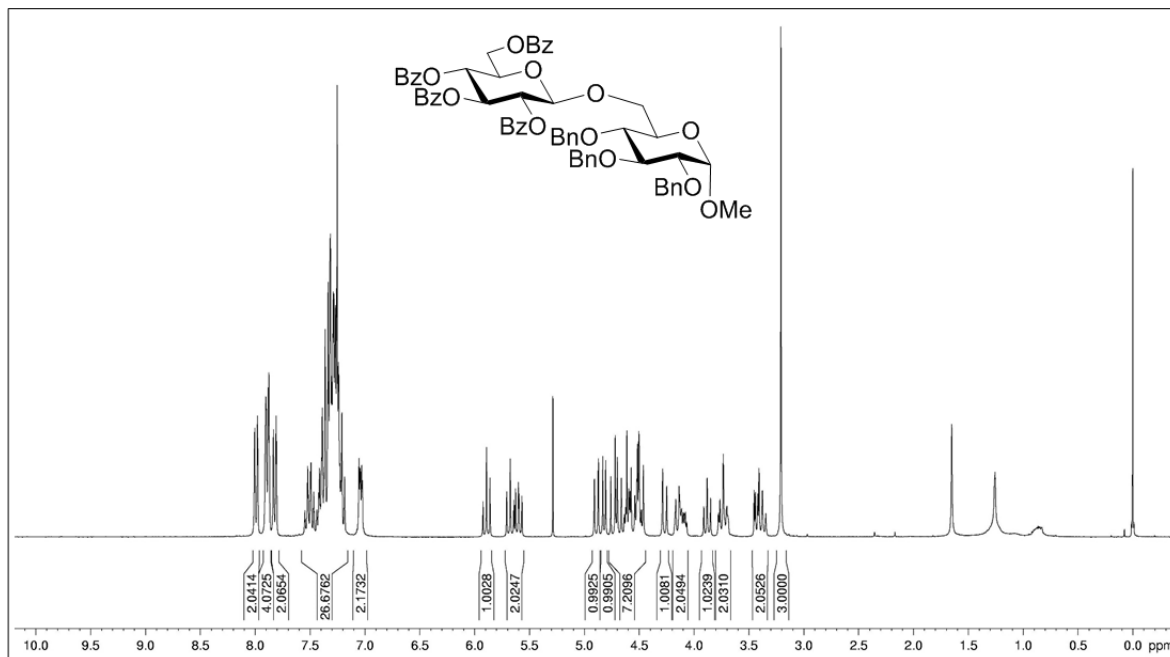
<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)

**Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl- $\alpha$ -D-mannopyranosyl)- $\alpha$ -D-glucopyranoside (9)**



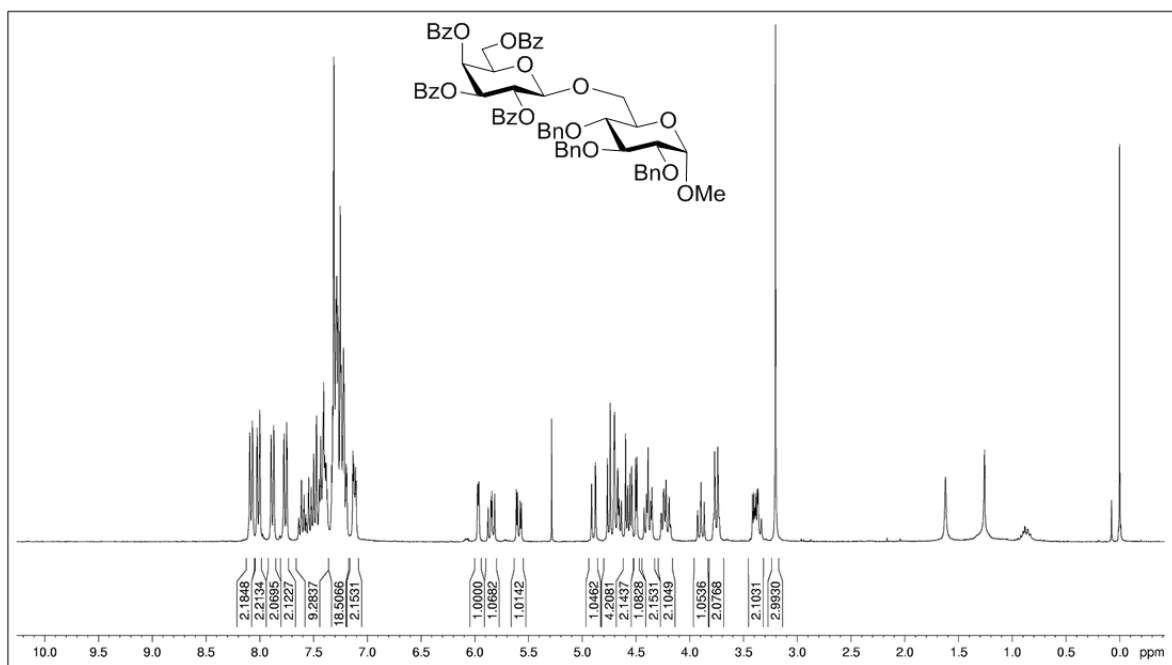
$^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ )

**Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\beta$ -D-glucopyranosyl)-2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (11)**



<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)

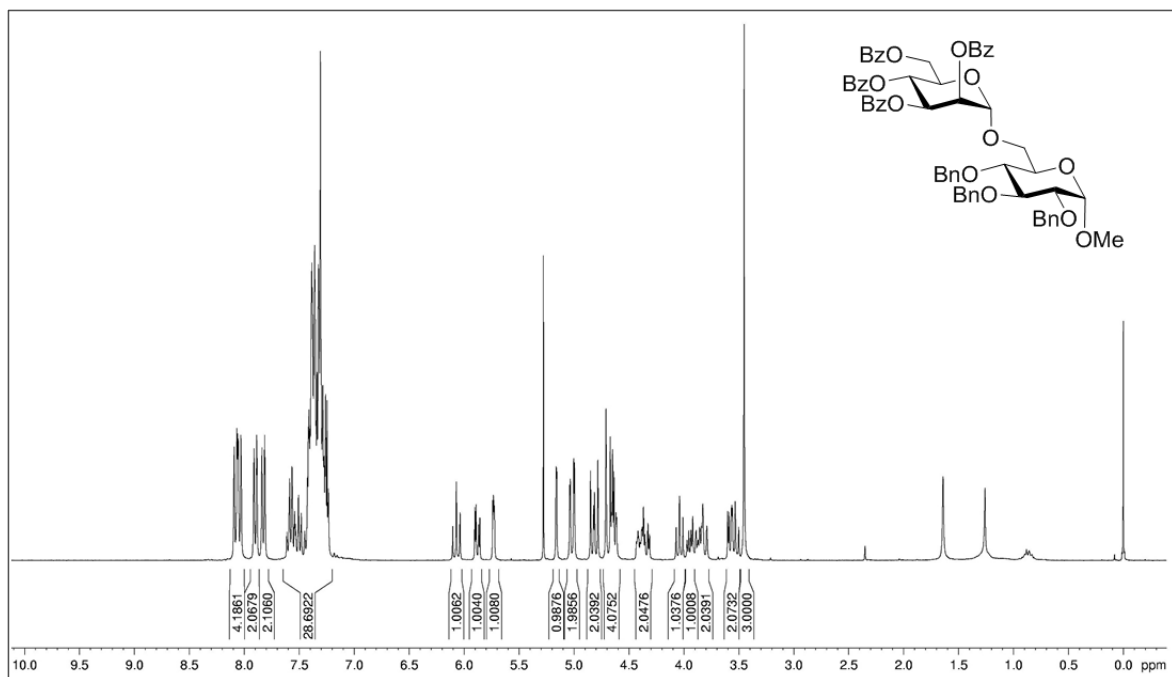
**Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\beta$ -D-galactopyranosyl)-2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (13)**



<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)

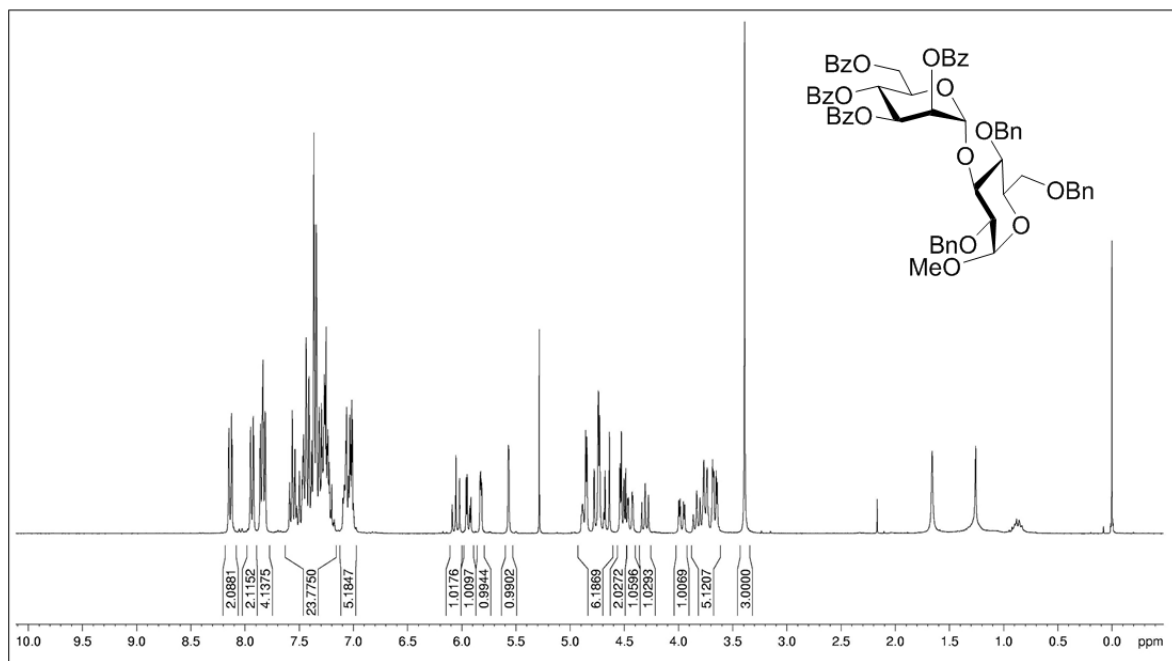


**Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)- $\alpha$ -D-glucopyranoside (15)**



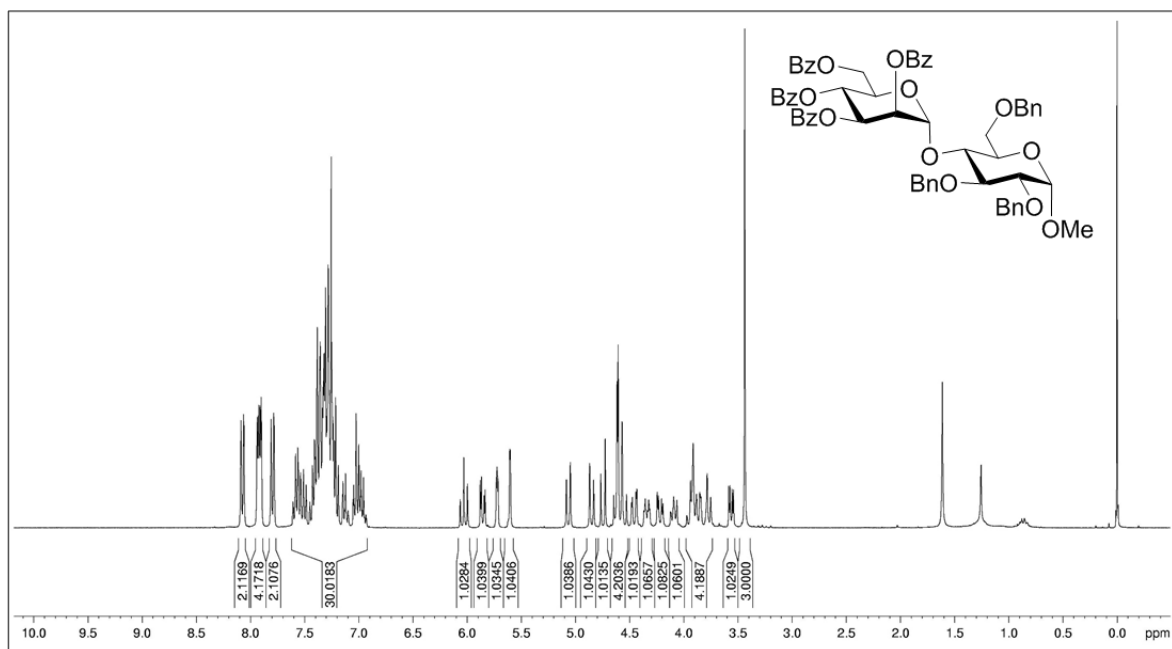
<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)

**Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)- $\alpha$ -D-glucopyranoside (23)**



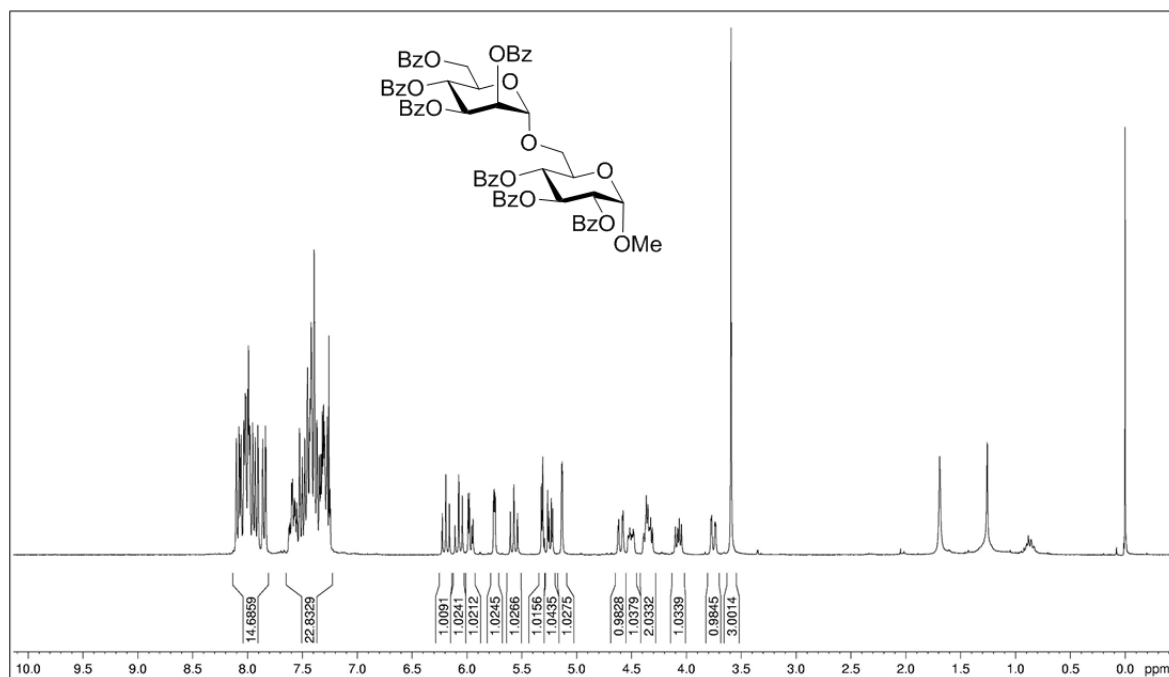
$^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ )

**Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)- $\alpha$ -D-glucopyranoside (25)**



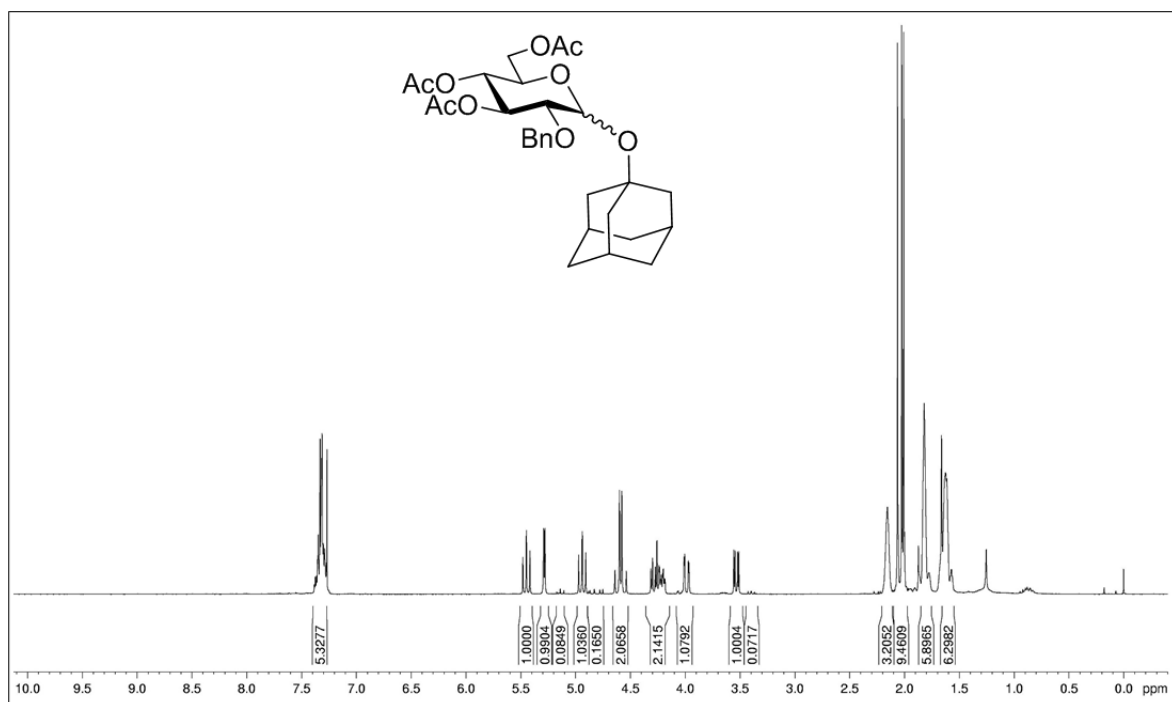
$^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ )

**Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)- $\alpha$ -D-glucopyranoside (27)**



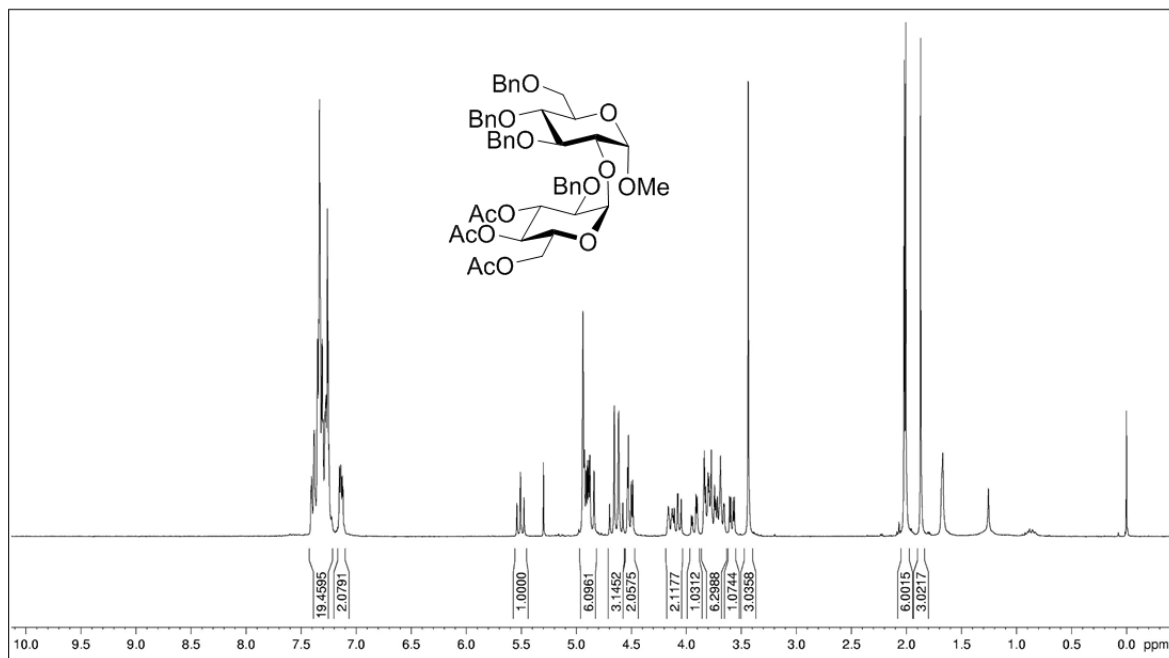
<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)

**1-Adamantyl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl- $\alpha$ -D-glucopyranoside (30)**



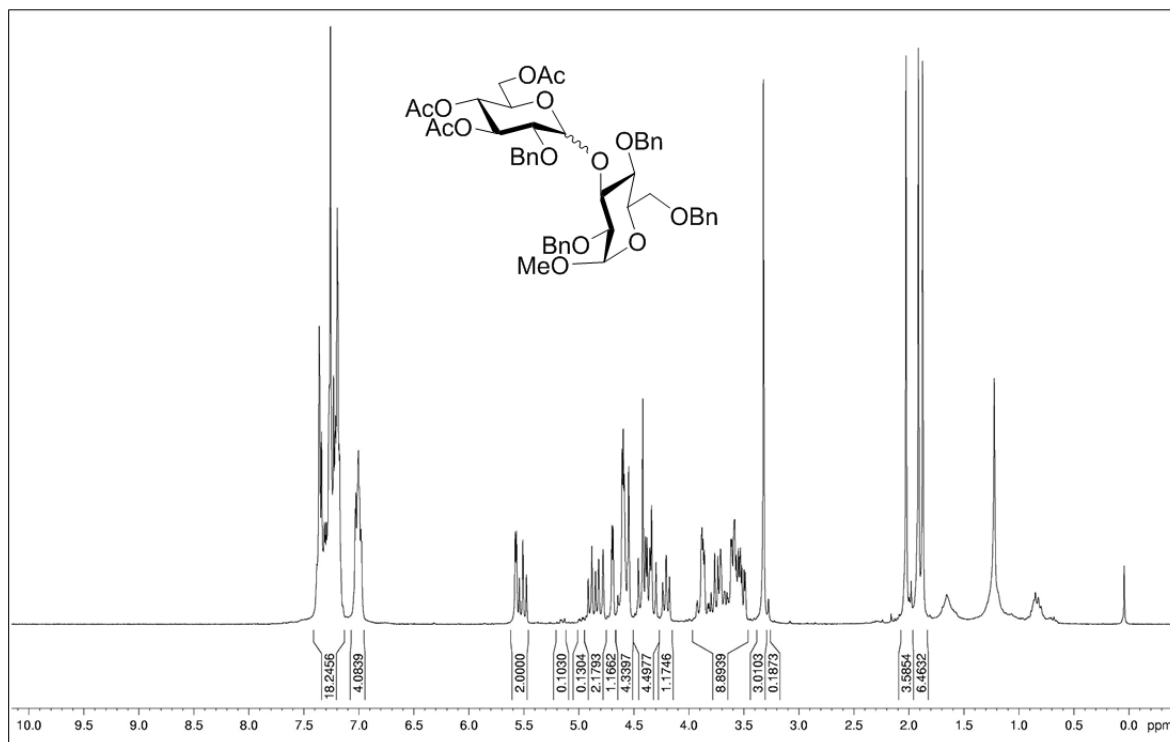
$^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ )

**Methyl 2-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl- $\alpha$ -D-glucopyranosyl)-3,4,6-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (31)**



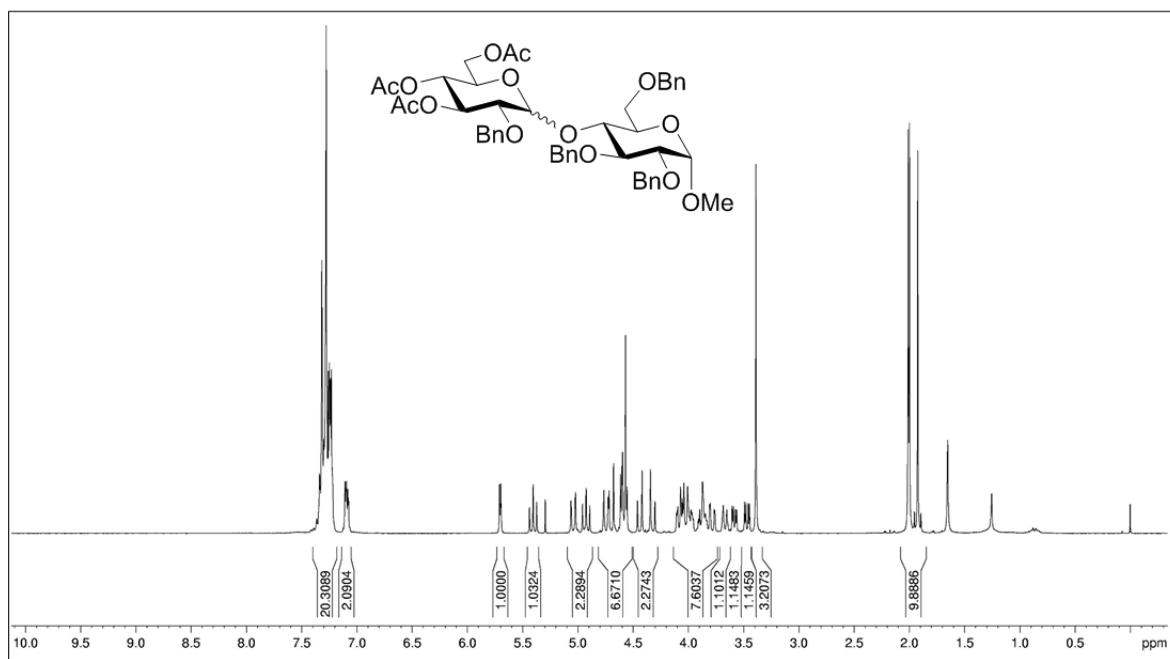
<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)

**Methyl 3-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl- $\alpha$ -D-glucopyranosyl)-2,4,6-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (32)**



<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)

**Methyl 4-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl- $\alpha$ -D-glucopyranosyl)-2,3,6-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (33)**



<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>)