Supporting information

Palladium(II)-Assisted Activation of Thioglycosides

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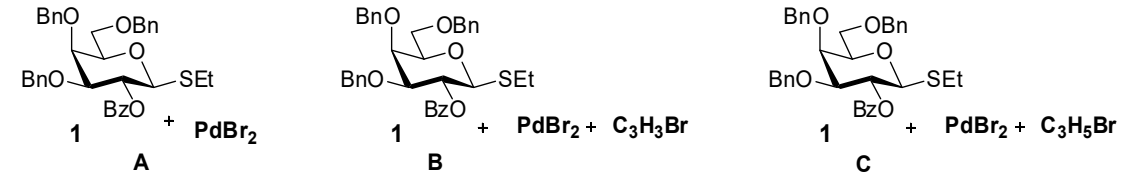
[1]H NMR Experiments



1 (1.0 equiv)
$PdBr_2$ (1.0 equiv)
C_3H_3Br (1.0 equiv) or **C_3H_5Br**

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[1]H-NMR study of $PdBr_2$ complexation with thioglycoside 1 in $CDCl_3$ (A). To a solution of **1** (10 mg, 0.01 mmol) in 0.5 mL $CDCl_3$, **$PdBr_2$** (4.4 mg, 0.01 mmol) was added and the mixture stirred at rt for 12 h, then the sample was immediately taken for NMR analysis.

[1]H-NMR study of $PdBr_2$ with thioglycoside 1 in presence of C_3H_3Br in $CDCl_3$ (B). To a solution of **1** (10 mg, 0.01 mmol) in 0.5 mL $CDCl_3$, **C_3H_3Br** (1.5µL, 0.01 mmol) and **$PdBr_2$** (4.4 mg, 0.01 mmol) were added and the mixture stirred at rt for 12 h, then the sample was immediately taken for NMR analysis (Fig 1).

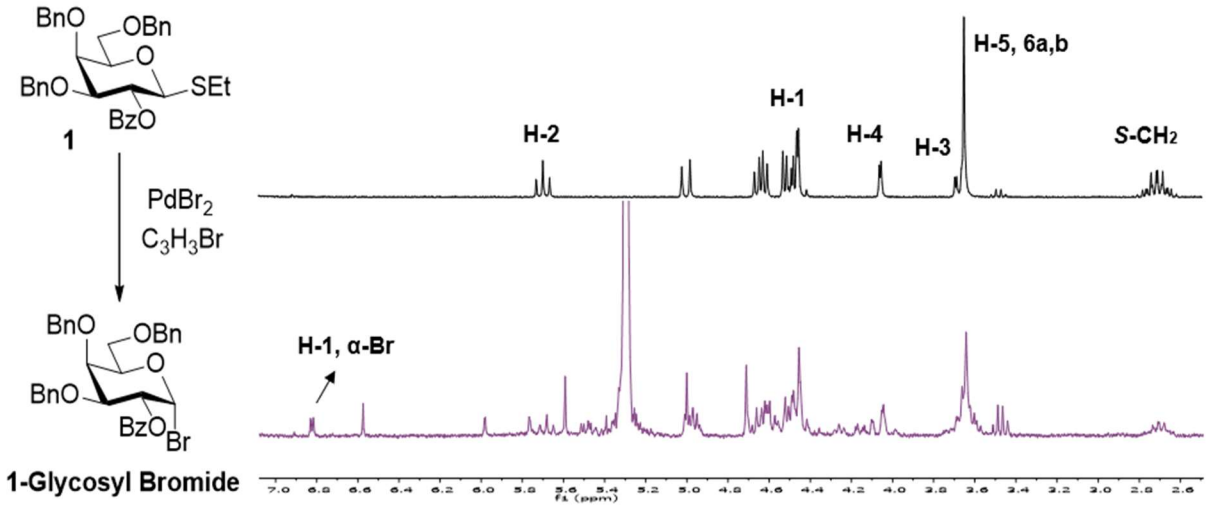


Figure 1. [1]H NMR studies of $PdBr_2$ in the presence of C_3H_3Br with donor **1** in $CDCl_3$ at rt.

The [1]H NMR experiment was conducted in the presence of propargyl bromide (Fig 1) show an entirely new set of proton signals were appeared along with signals of donor **1**. The above observation revealed that thiogalactoside **1** partially converted to corresponding *α*-galactosyl bromide (H-1 at 6.81 ppm) in the presence of propargyl bromide and absence of glycosyl acceptor.

^{1}H-NMR study of $PdBr_2$ with thioglycoside 1 in presence of C_3H_5Br (allyl bromide) in $CDCl_3$ (C) To a solution of **1**(10 mg, 0.01 mmol) in 0.5 mL $CDCl_3$, **C_3H_5Br** (1.4µL, 0.01 mmol) and **$PdBr_2$** (4.4 mg, 0.01 mmol) were added and the mixture stirred at rt for 12 h, then the sample was immediately taken for NMR analysis (Fig 2).

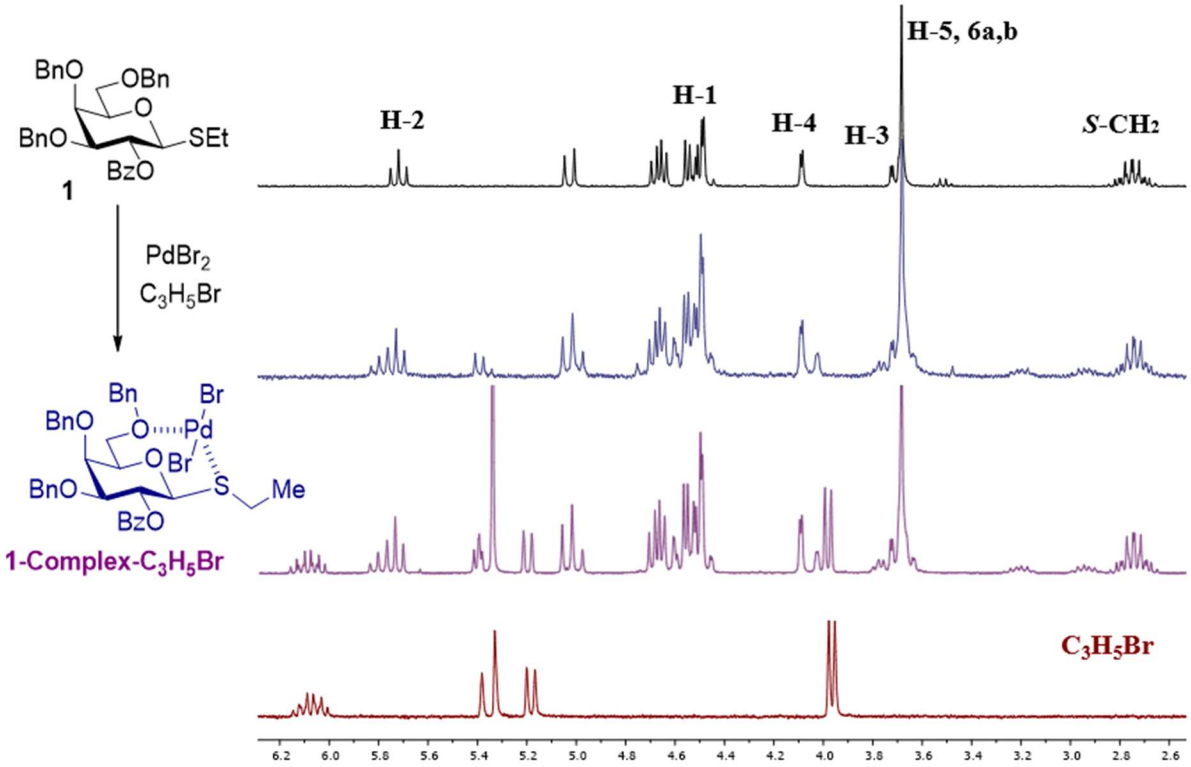
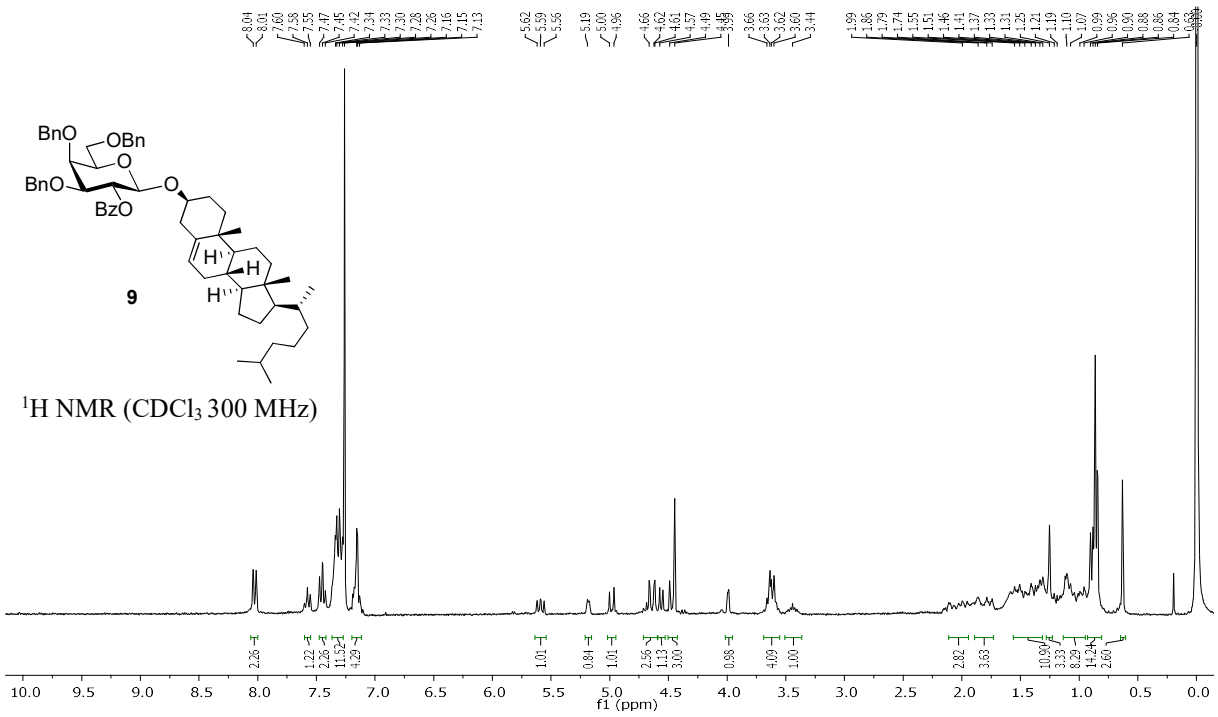


Figure 2. ^{1}H NMR studies of $PdBr_2$ in the presence of C_3H_5Br with donor **1** in $CDCl_3$ at rt.

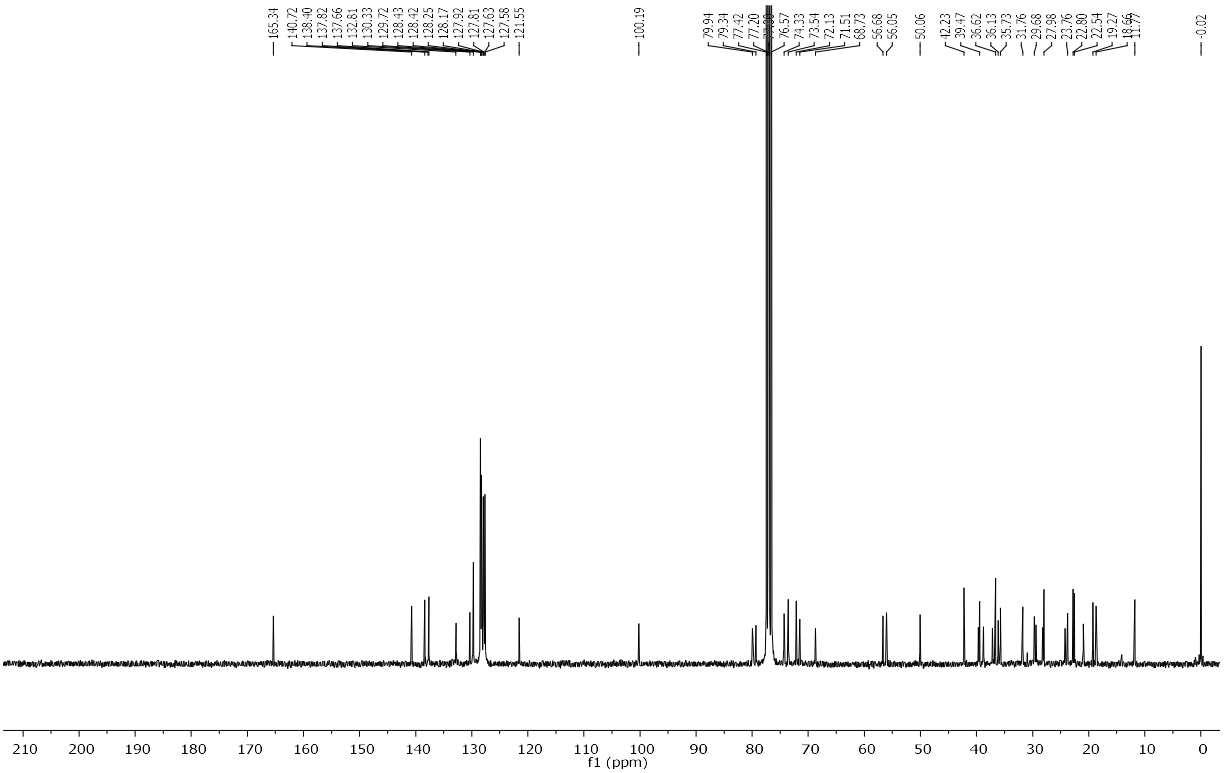
The ^{1}H NMR experiment conducted in the presence of allyl bromide (Fig 2, 3rd spectrum) show the complexation of $PdBr_2$ with thiogalactoside **1** without an interaction between the additive and $PdBr_2$; thus, the formation of corresponding *α*-galactosyl bromide was not observed in absence of glycosyl acceptor.

NMR Spectra for New Compounds

Cholesteryl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranoside (9).

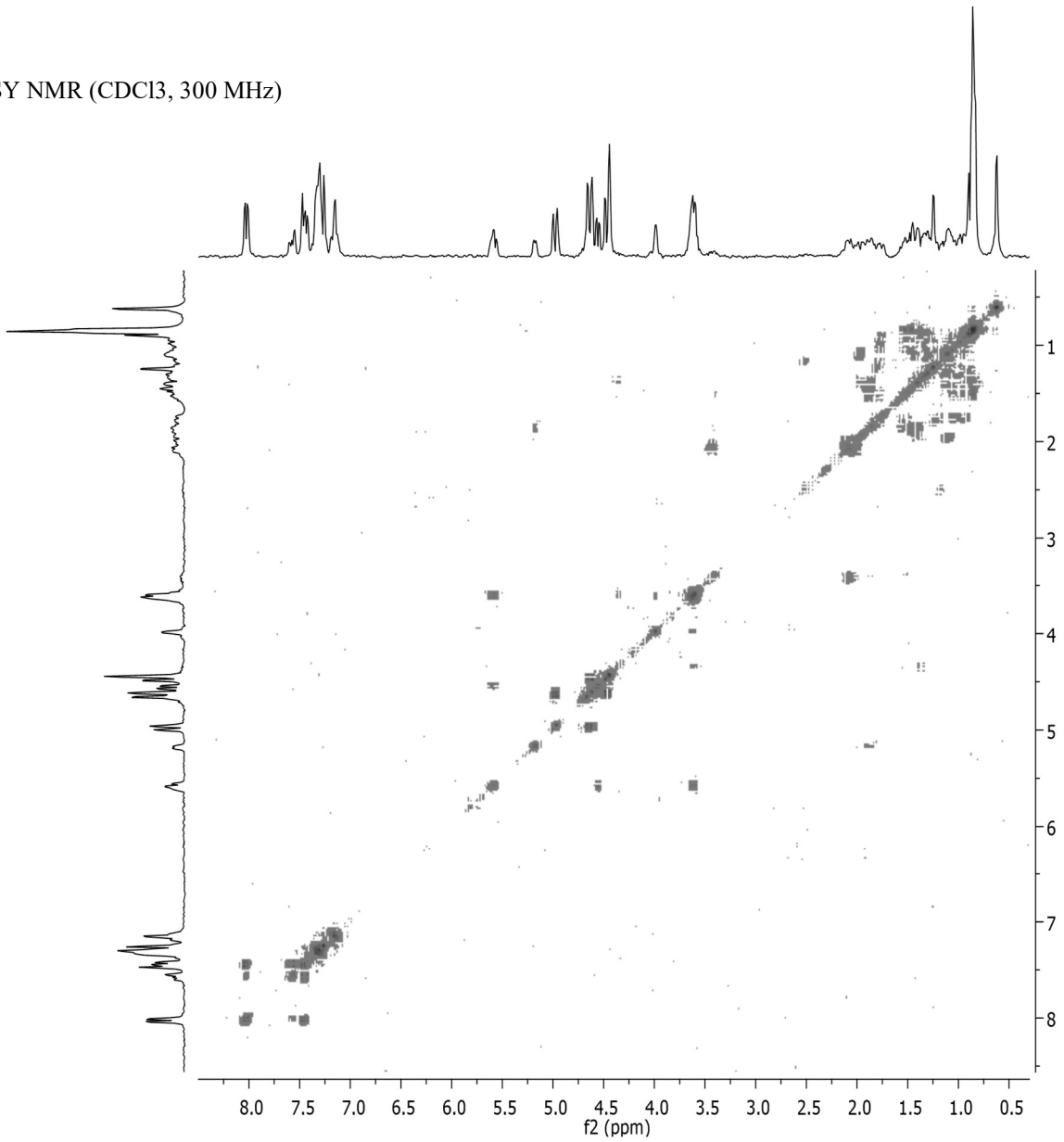


^{1}H NMR ($CDCl_3$ 300 MHz)

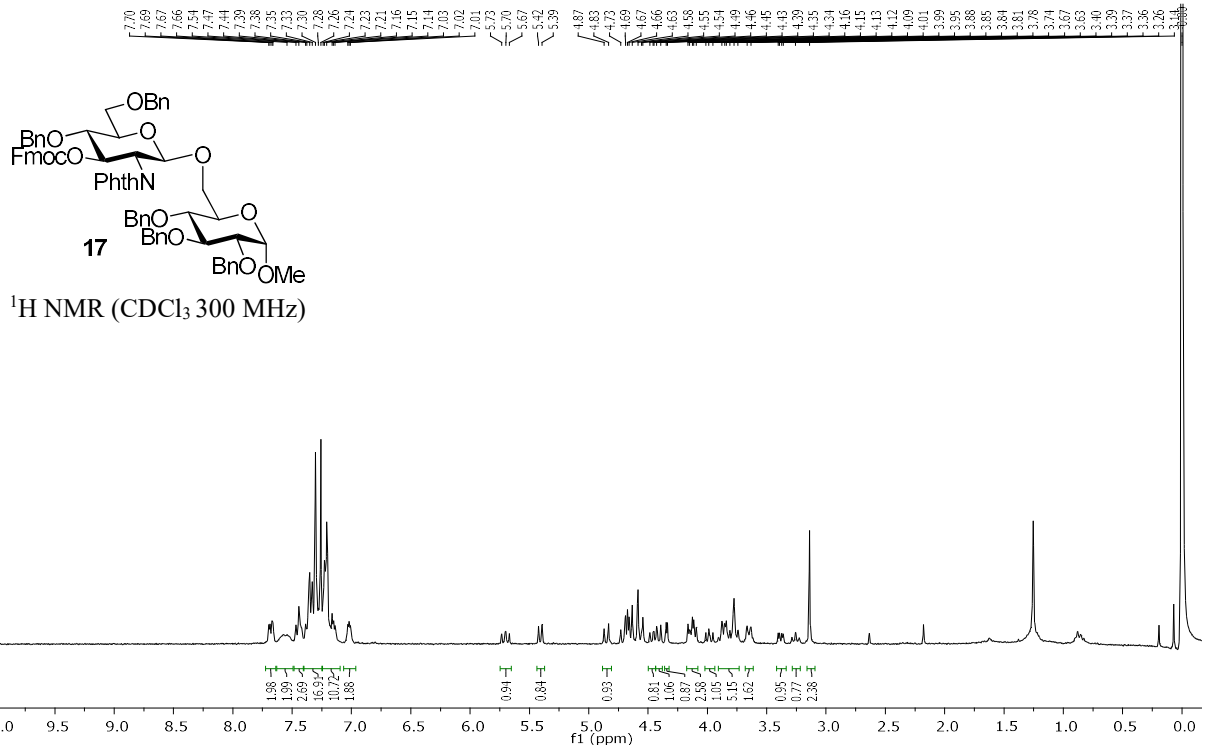


^{13}C NMR ($CDCl_3$ 75 MHz)

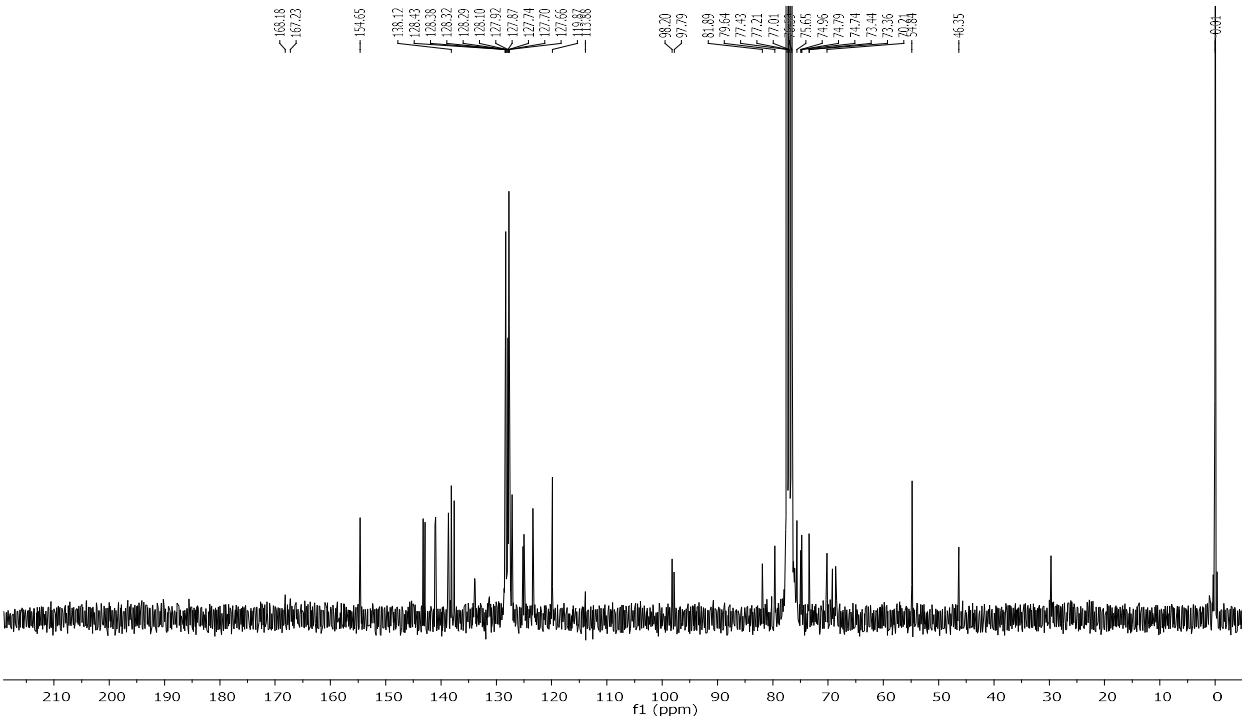
COSY NMR (CDCl3, 300 MHz)



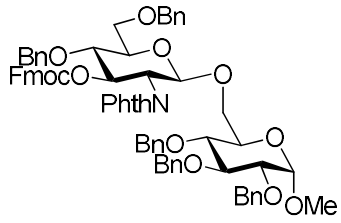
Methyl 6-*O*-(4,6-di-*O*-benzyl-2-deoxy-3-*O*-fluorenylmethoxycarbonyl-2-phthalimido-*β*-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (17).



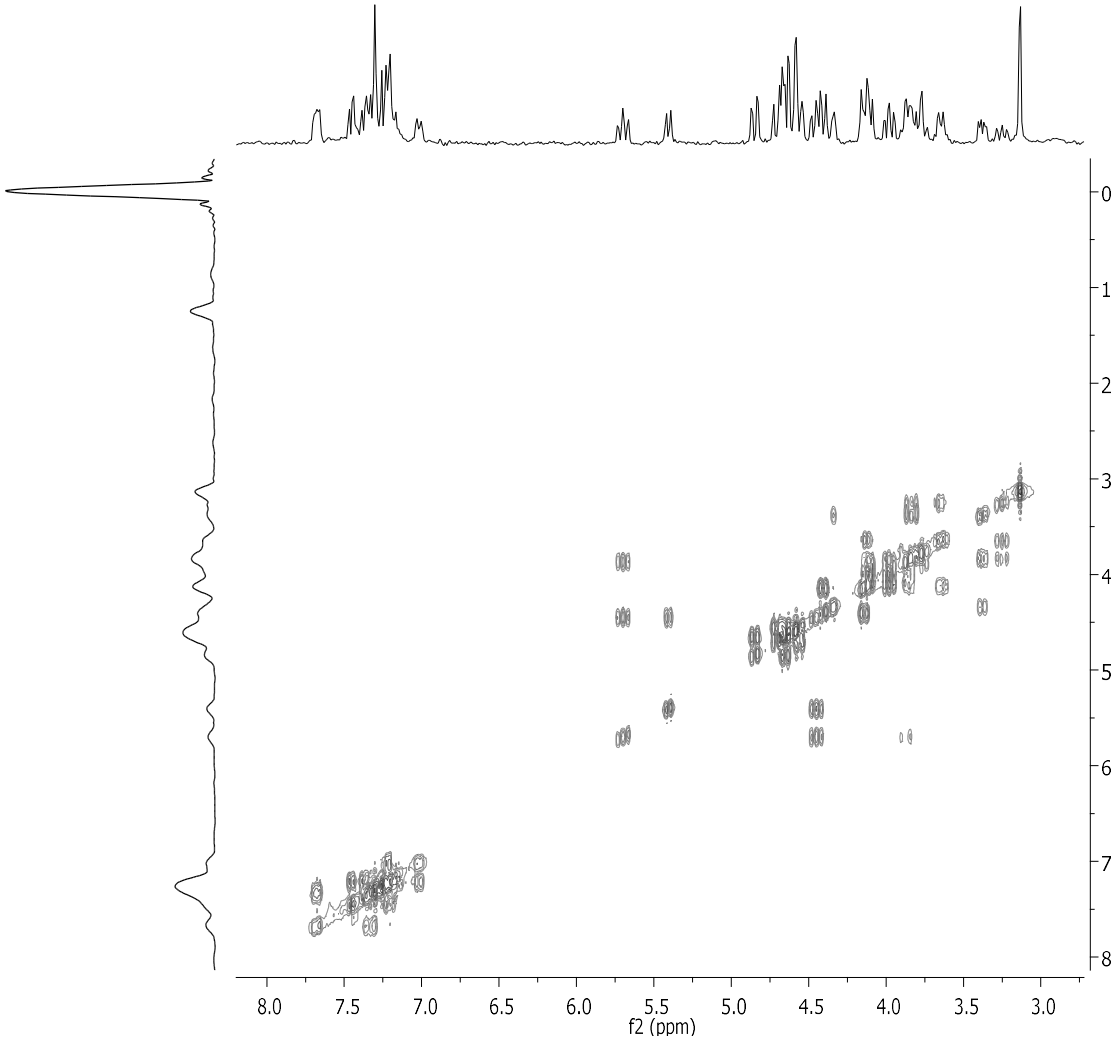
^{1}H NMR ($CDCl_3$ 300 MHz)



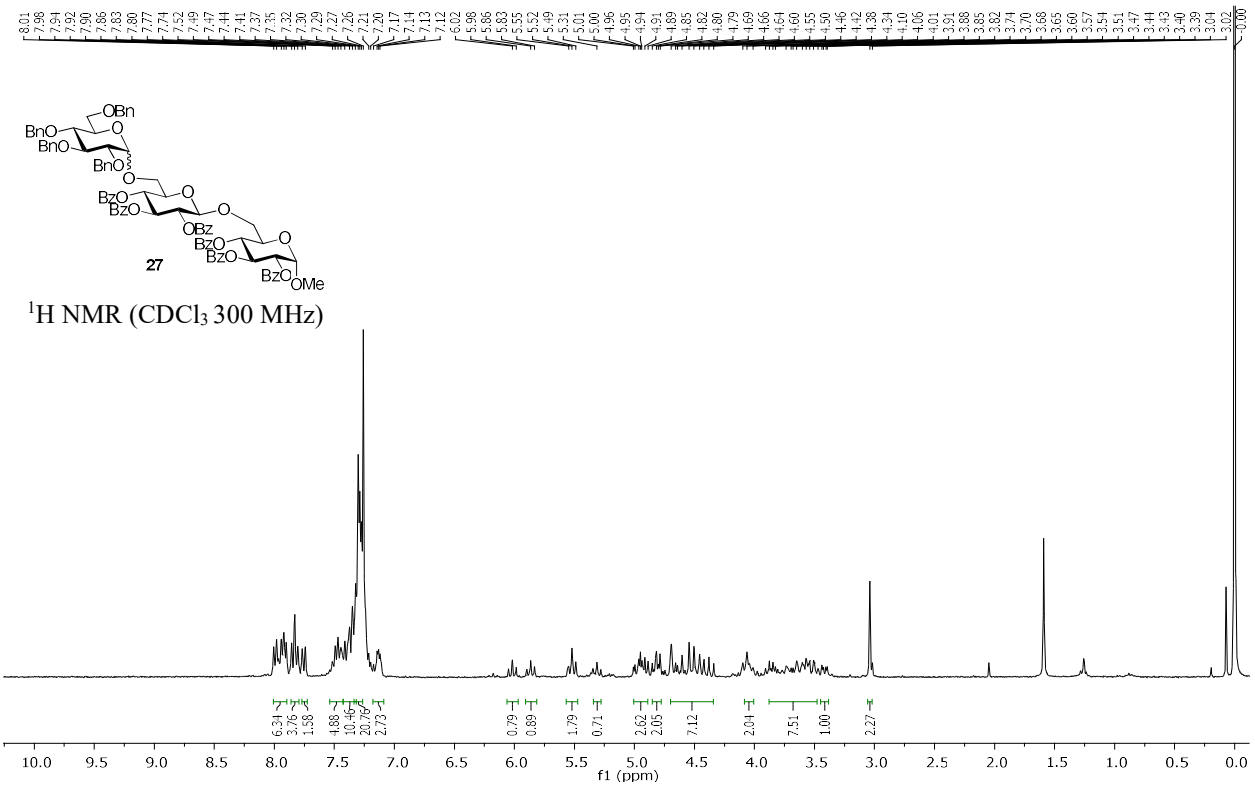
^{13}C NMR ($CDCl_3$ 75 MHz)



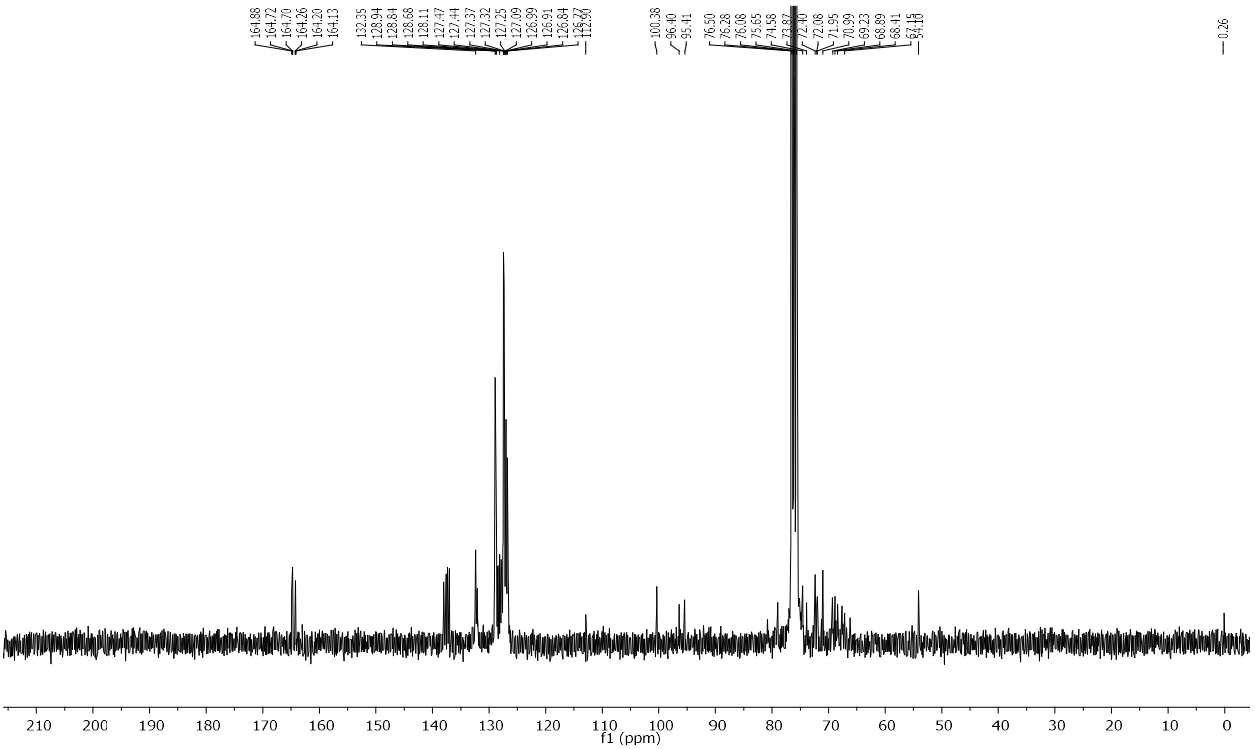
COSY NMR (CDCl3, 300 MHz)



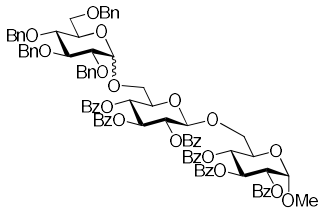
Methyl 2,3,4,6-tetra-*O*-benzyl-*α/β*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-*β*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside (27).



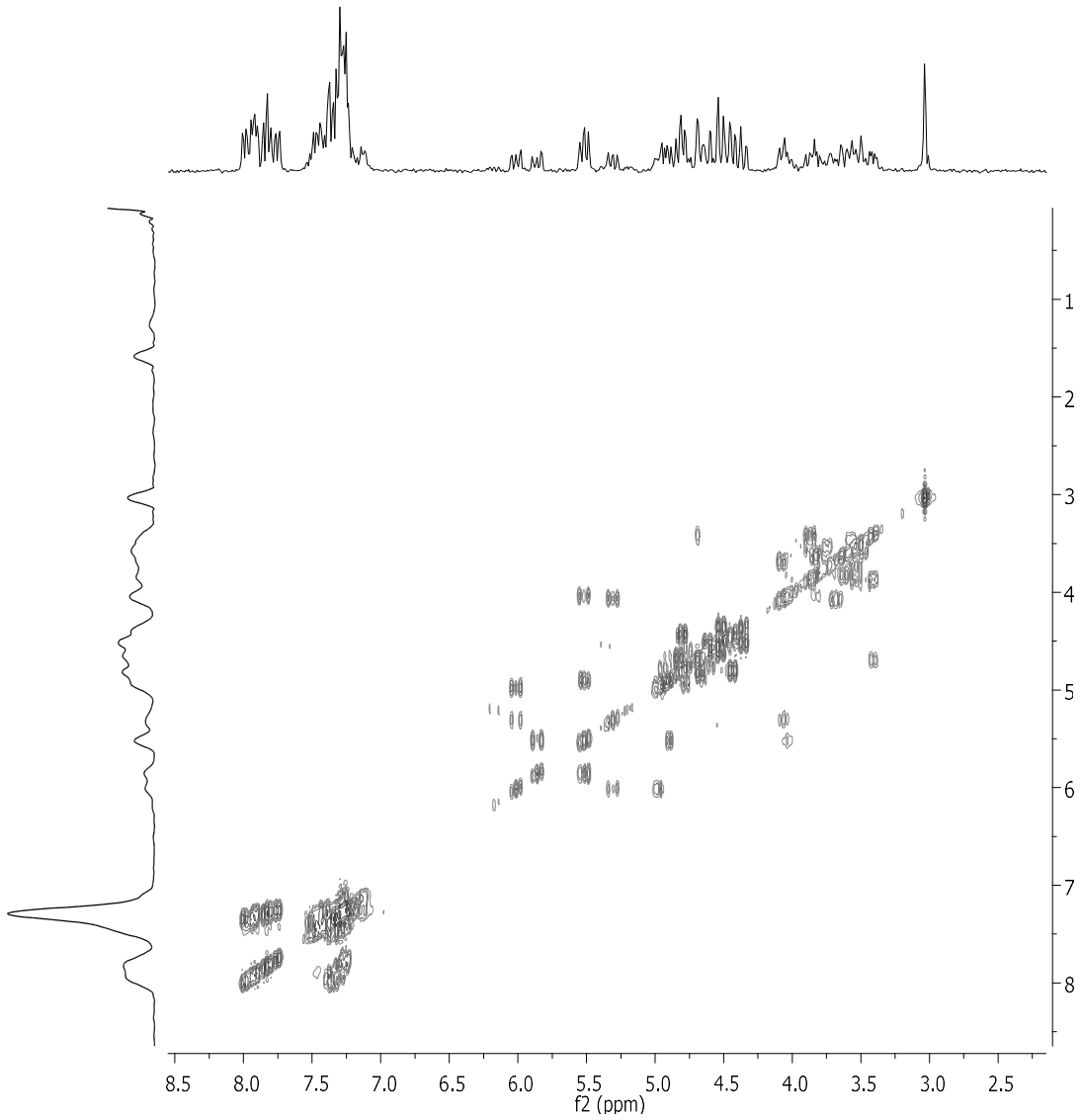
^{1}H NMR ($CDCl_3$ 300 MHz)



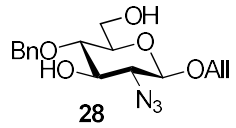
^{13}C NMR ($CDCl_3$ 75 MHz)



COSY NMR (CDCl3, 300 MHz)

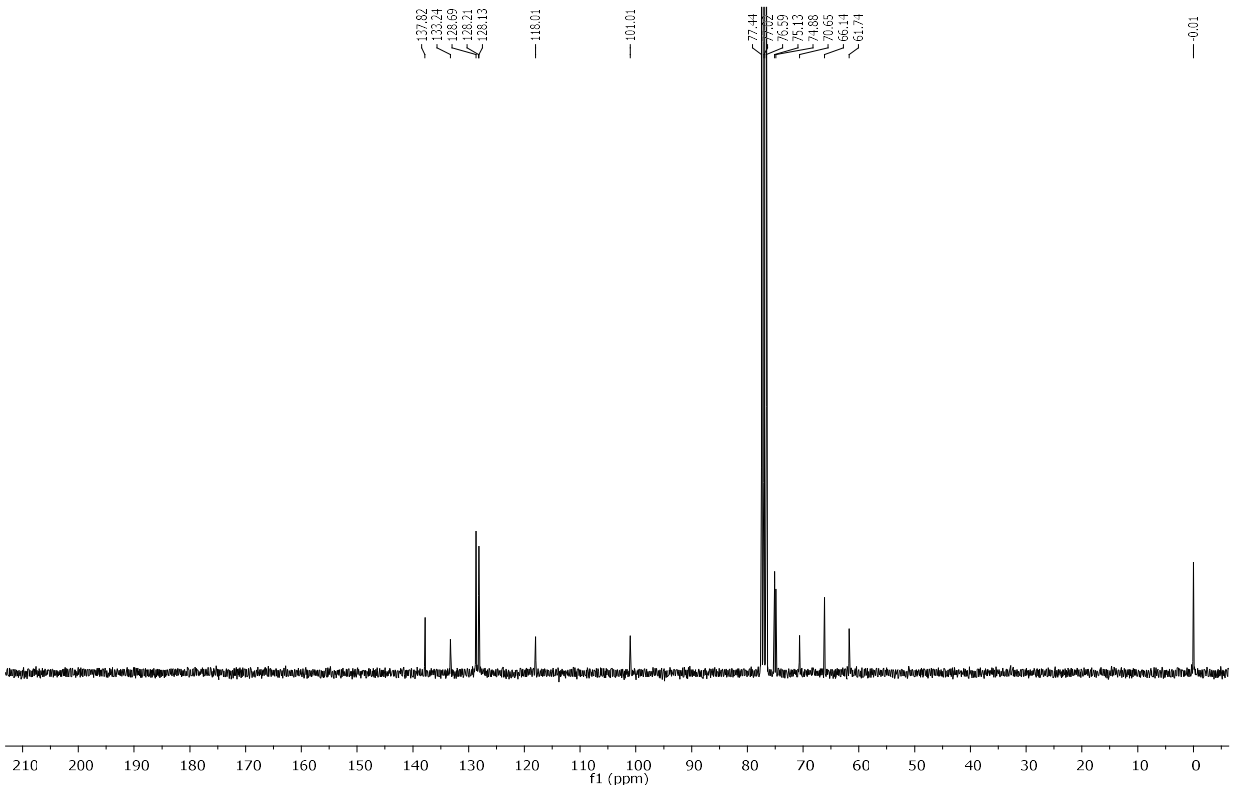


Allyl 2-azido-4-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (28).

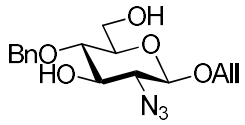


28

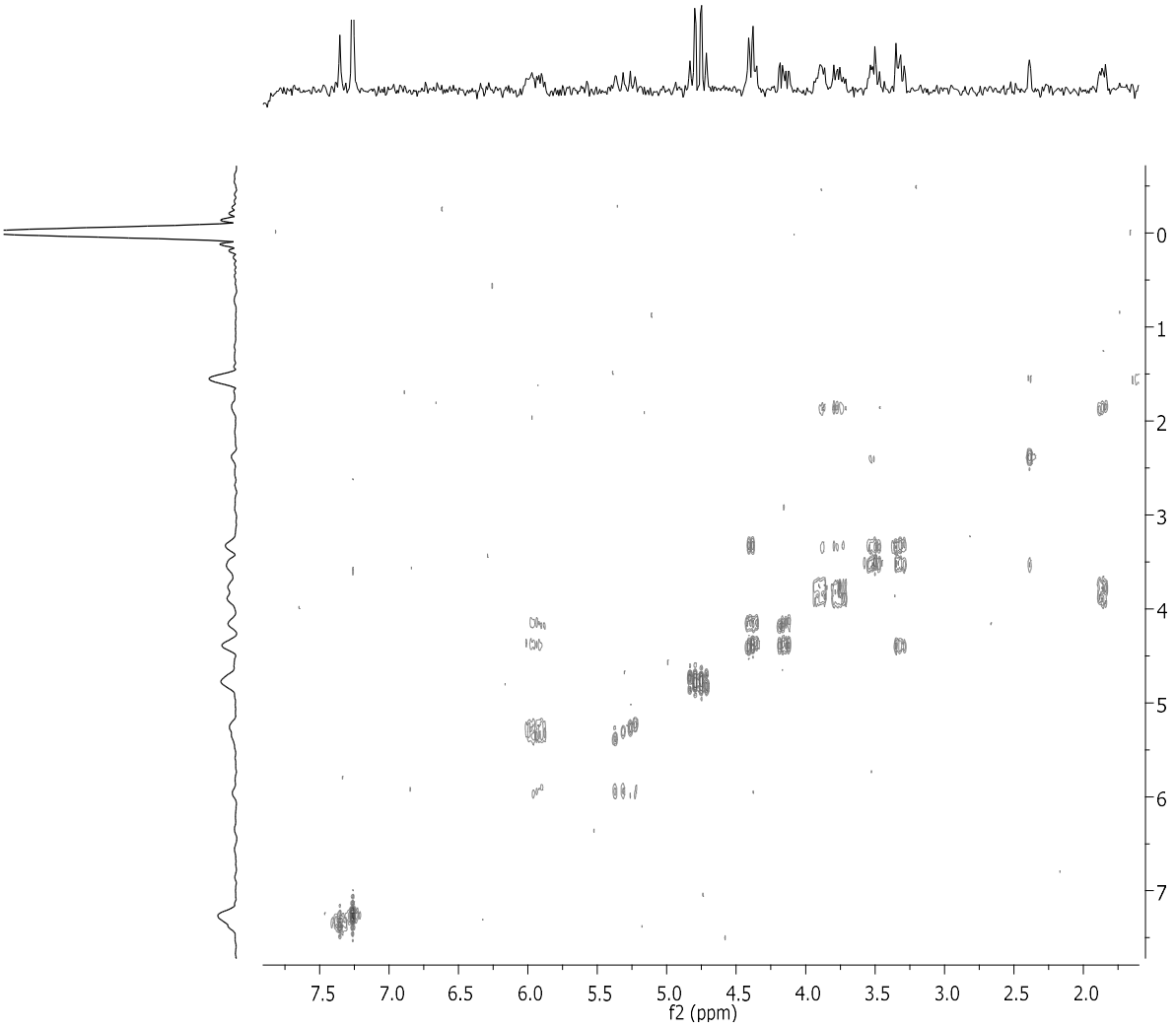
^{1}HNMR ($CDCl_3$ 300 MHz)



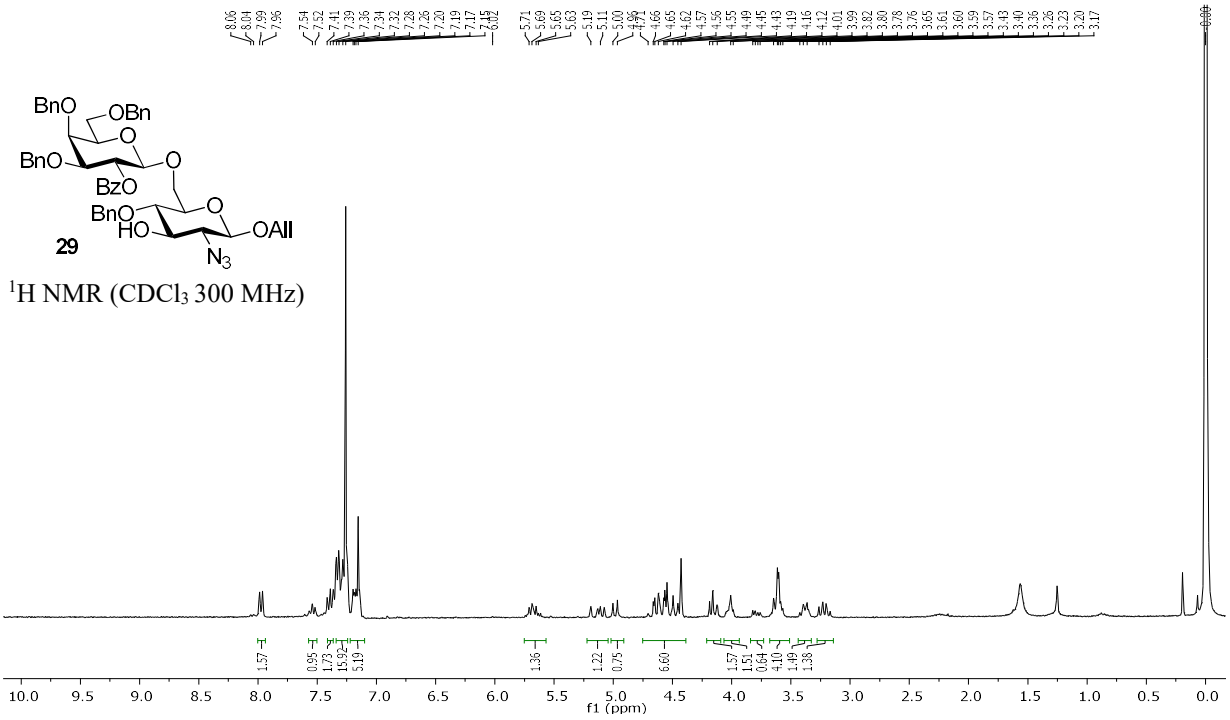
^{13}C NMR ($CDCl_3$ 75 MHz)



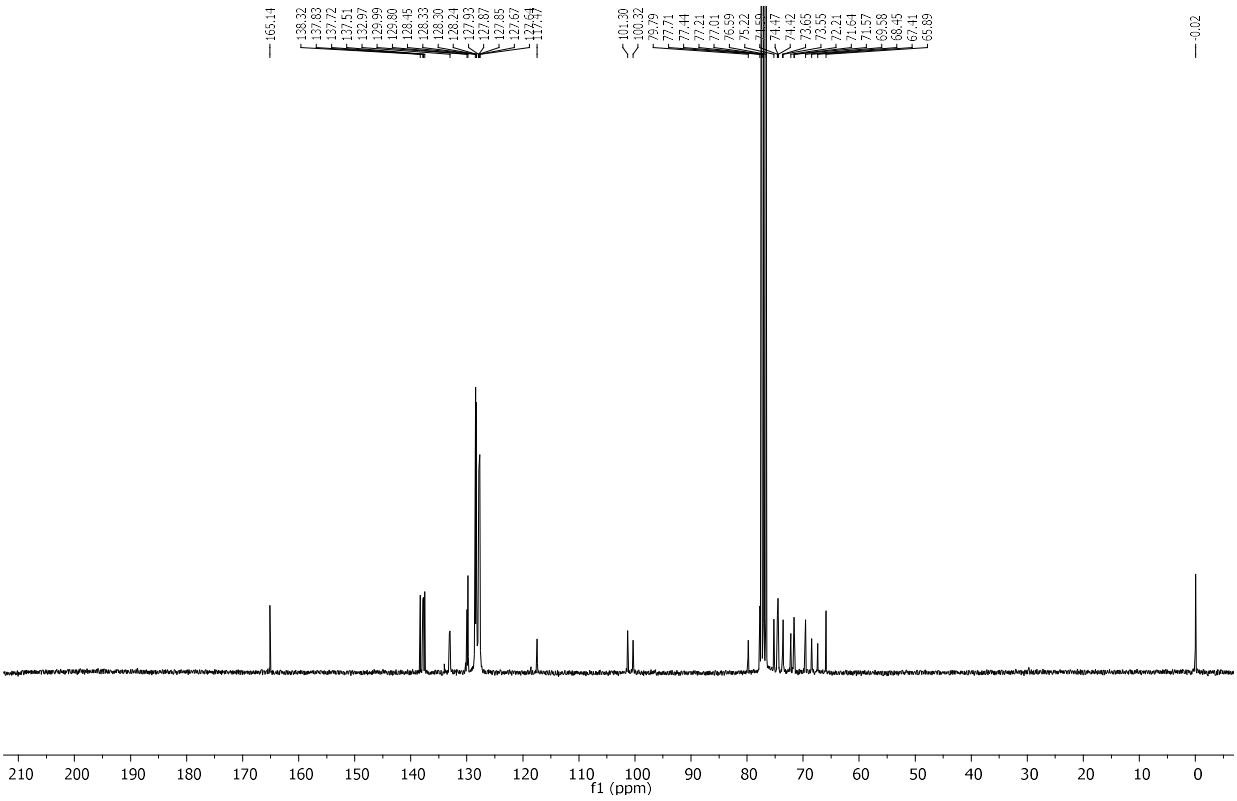
COSY NMR ($CDCl_3$, 300 MHz)



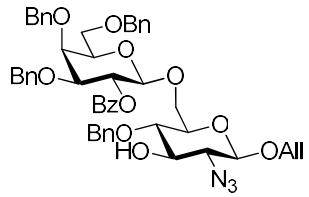
Allyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-2-azido-4-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (29).



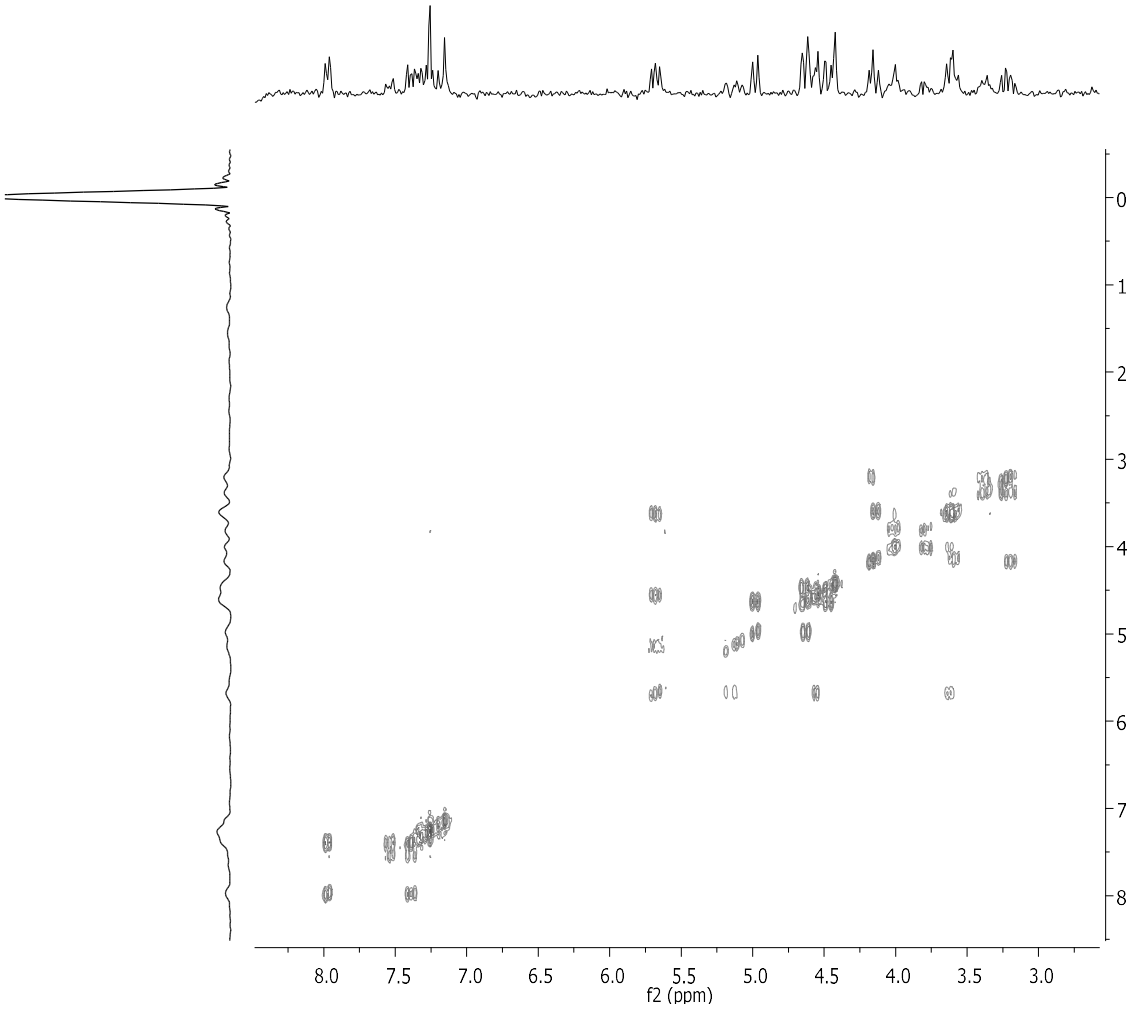
^{1}H NMR ($CDCl_3$ 300 MHz)



^{13}C NMR ($CDCl_3$ 75 MHz)

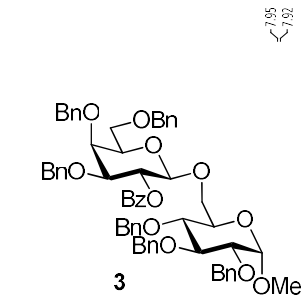


COSY NMR (CDCl3, 300 MHz)



NMR Proton Spectra for Known Compounds

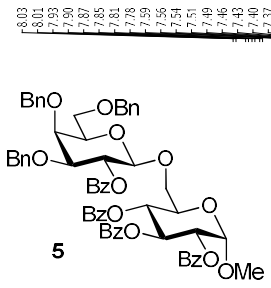
Methyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (3).



3

^{1}H NMR ($CDCl_3$ 300 MHz)

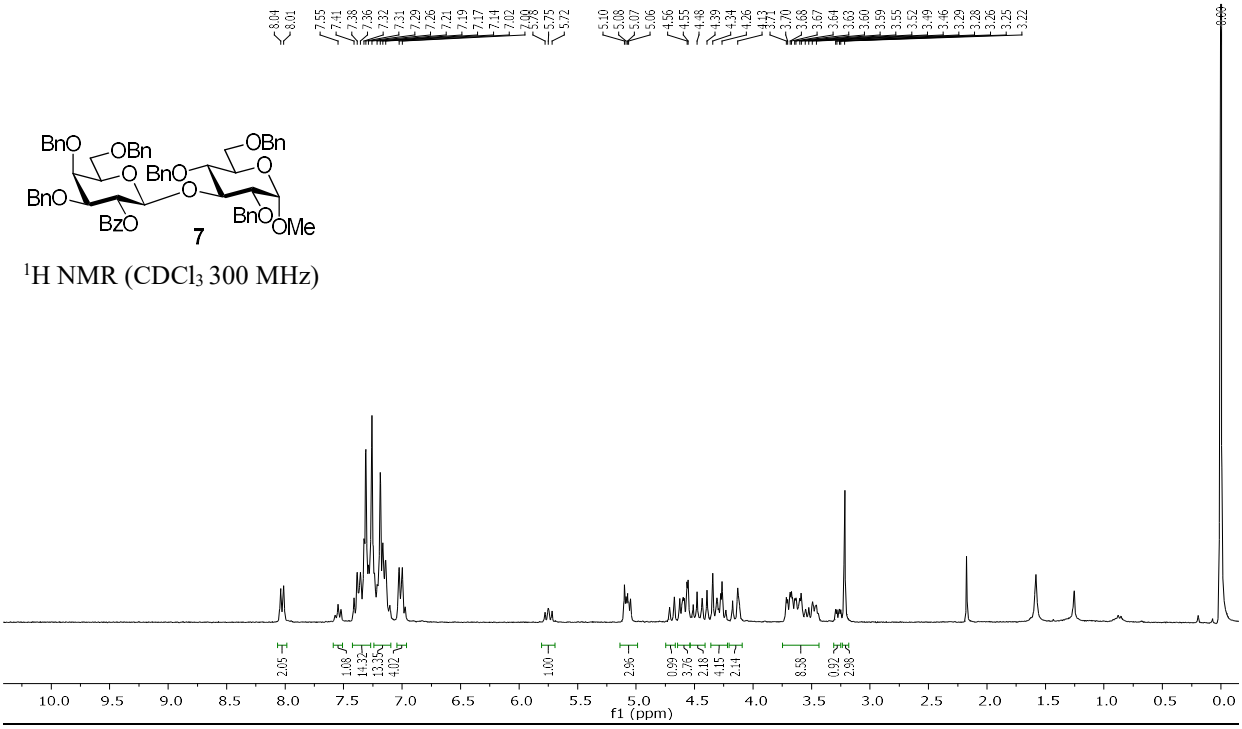
Methyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside (5).



5

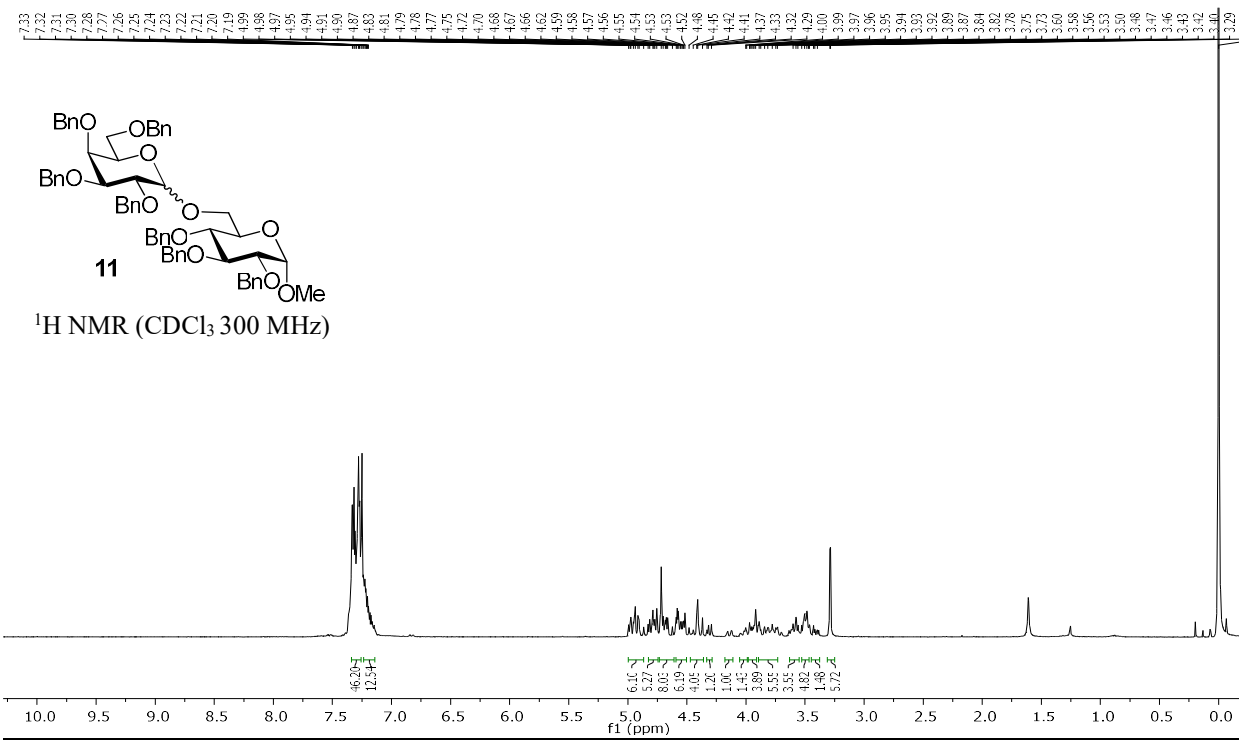
^{1}H NMR ($CDCl_3$ 300 MHz)

Methyl 3-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-2,4,6-tri-*O*-benzyl-*α*-D-glucopyranoside (7).



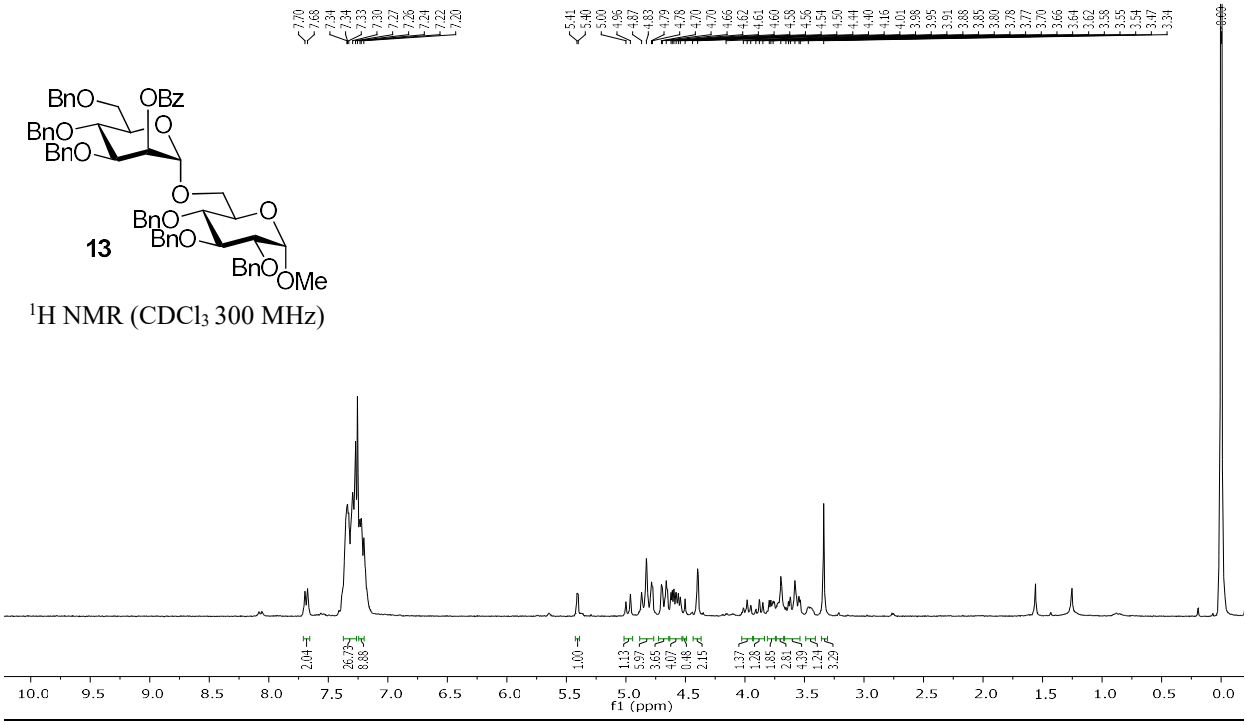
^{1}H NMR ($CDCl_3$ 300 MHz)

Methyl 6-*O*-(2,3,4,6-tetra-*O*-Benzyl-*α/β*-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (11).



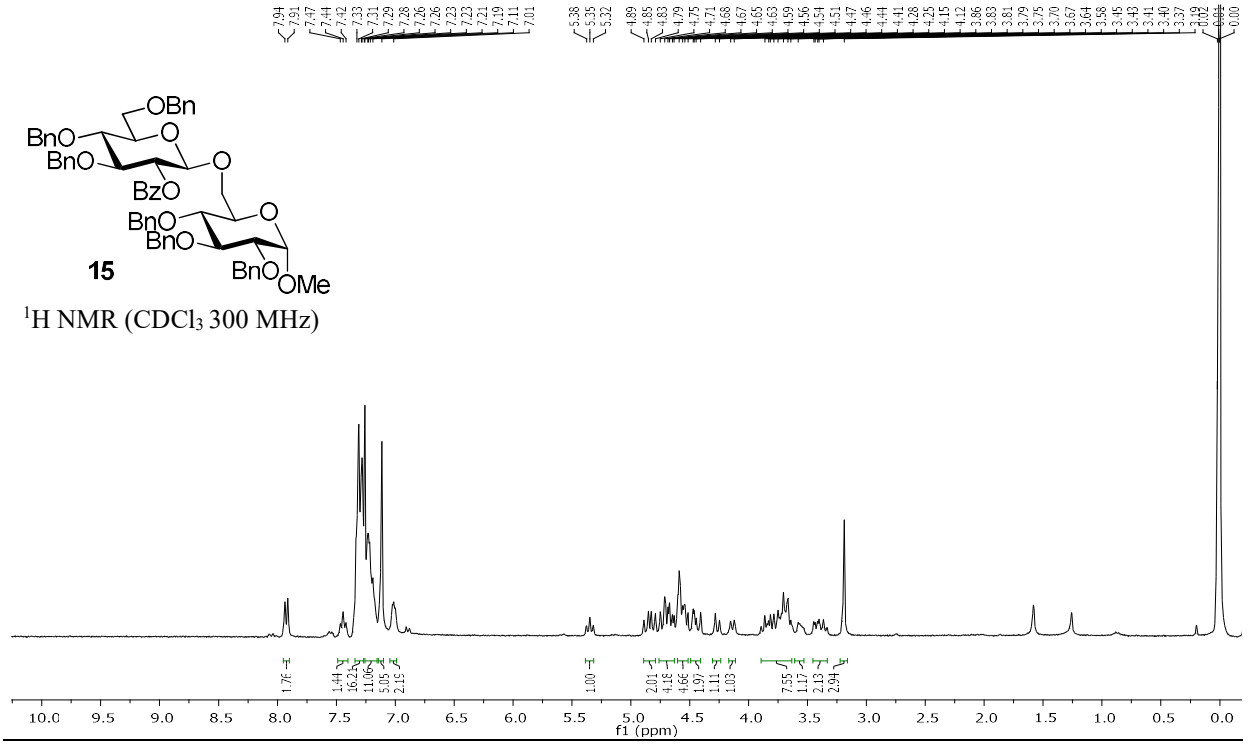
^{1}H NMR ($CDCl_3$ 300 MHz)

Methyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (13).



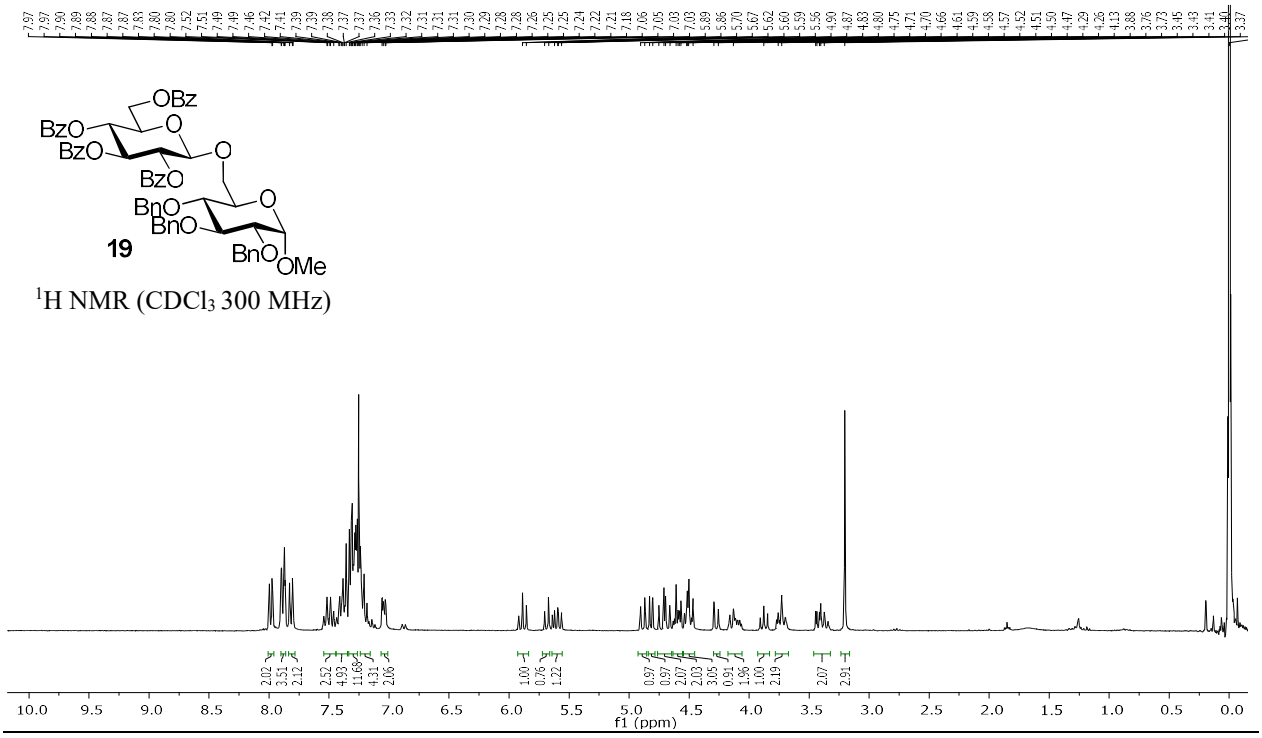
^{1}H NMR ($CDCl_3$ 300 MHz)

Methyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (15).



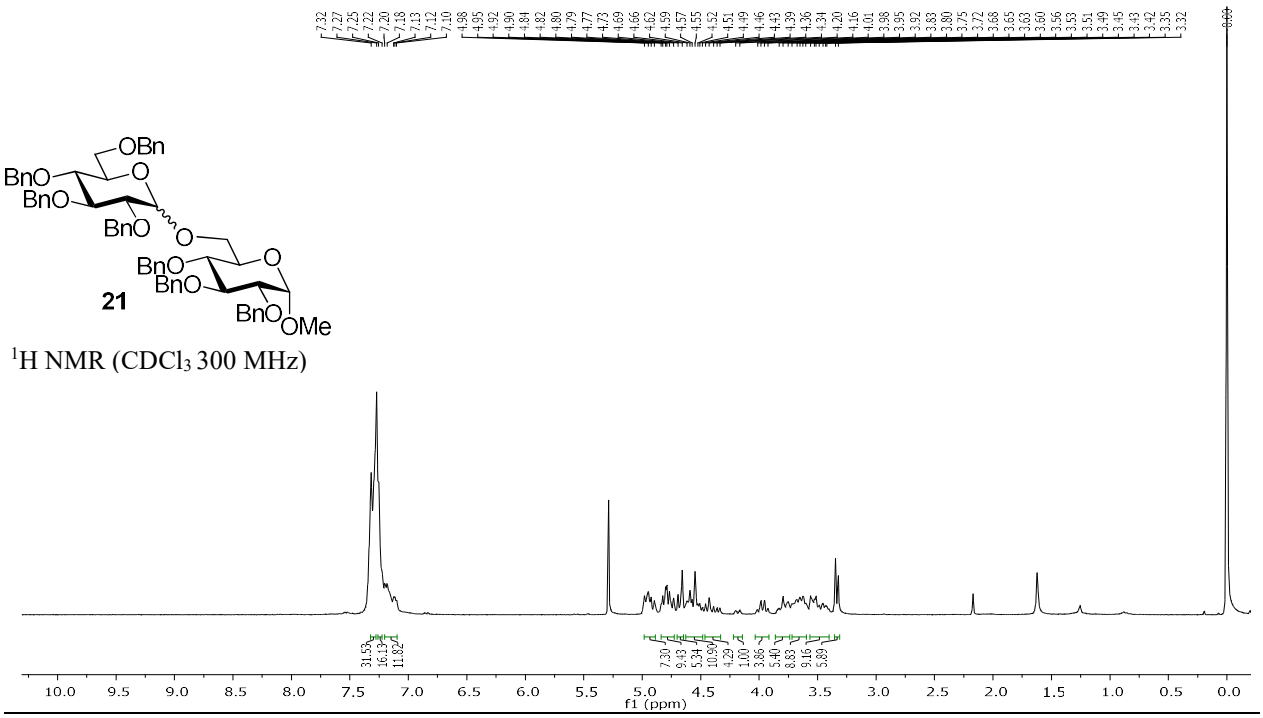
^{1}H NMR ($CDCl_3$ 300 MHz)

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-*β*-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (19).



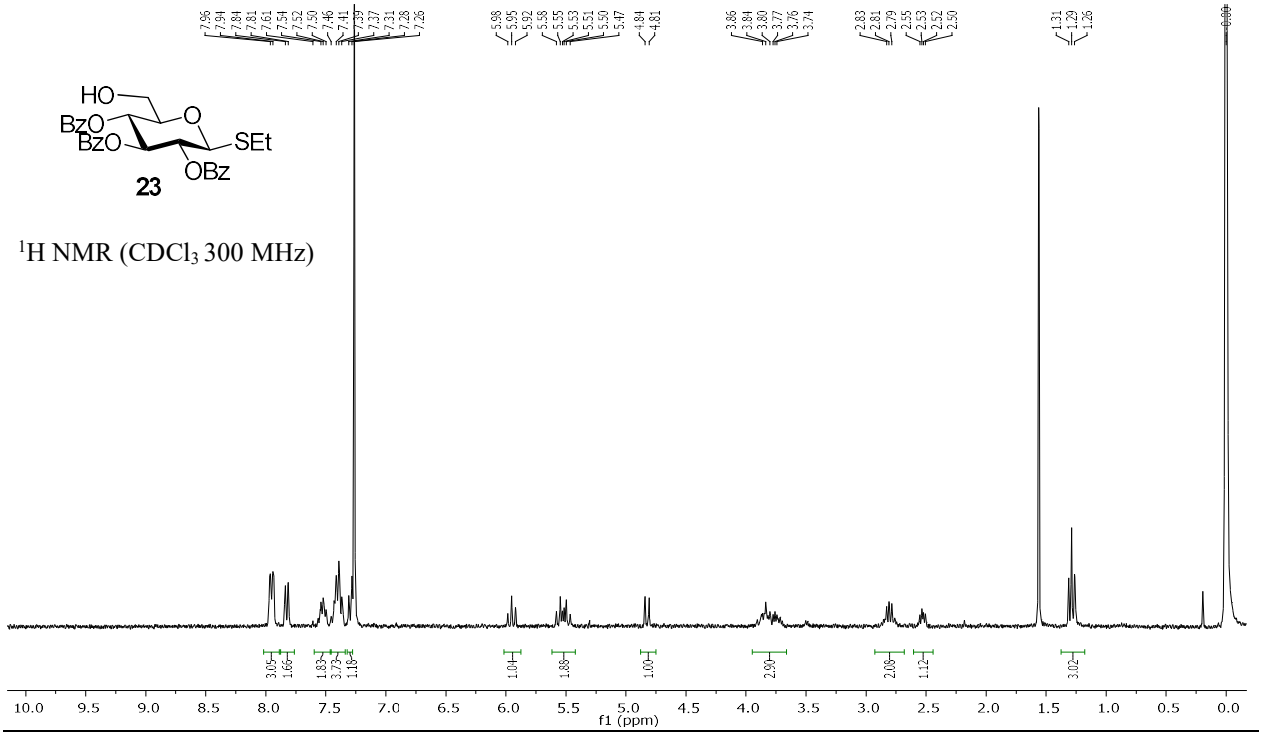
^{1}H NMR ($CDCl_3$ 300 MHz)

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-*α/β*-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (21).



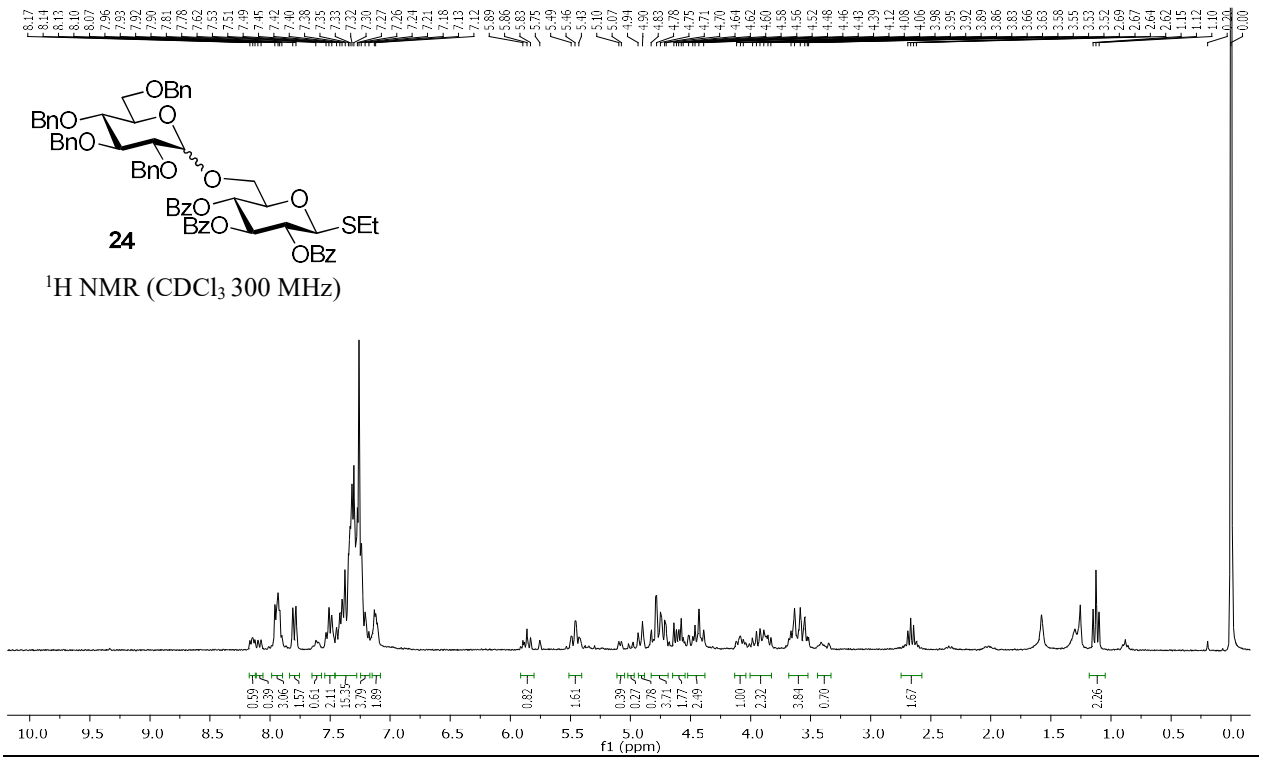
^{1}H NMR ($CDCl_3$ 300 MHz)

Ethyl 2,3,4-tri-*O*-benzoyl-*β*-D-glucopyranoside (23).



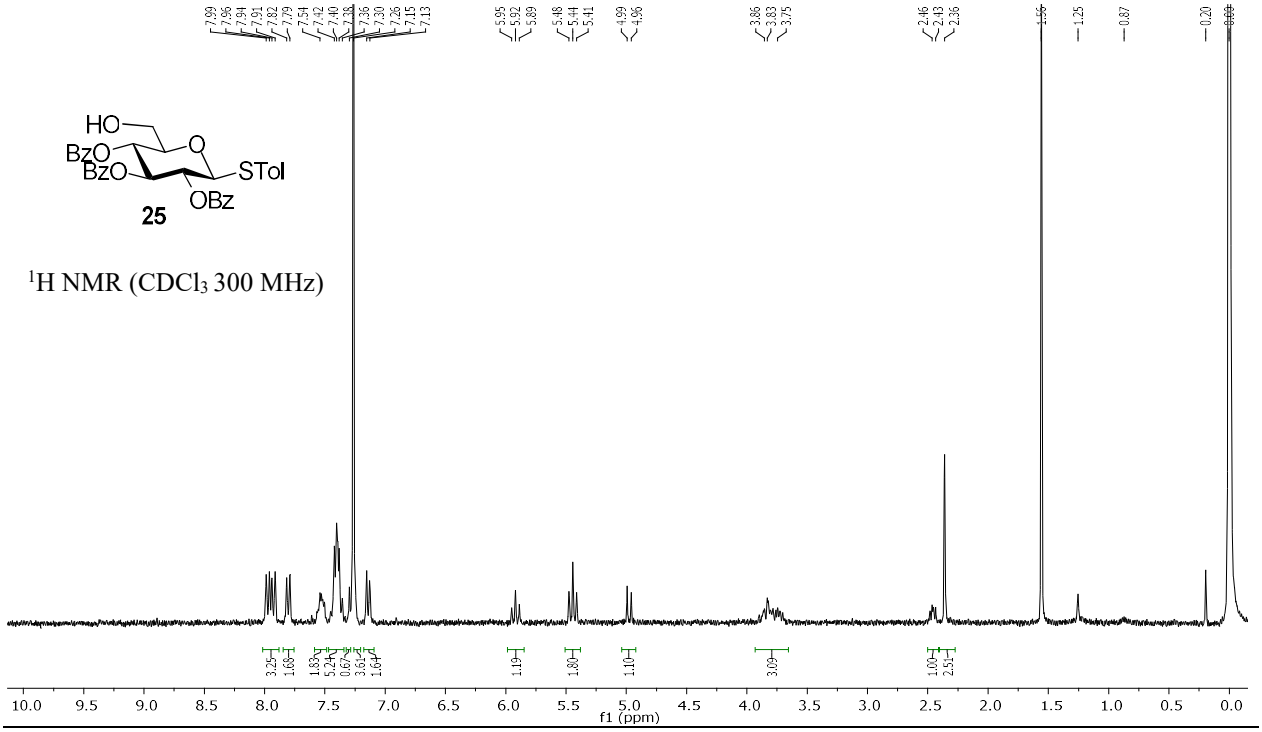
^{1}H NMR ($CDCl_3$ 300 MHz)

Ethyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-*α/β*-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-*β*-D-glucopyranoside (24).



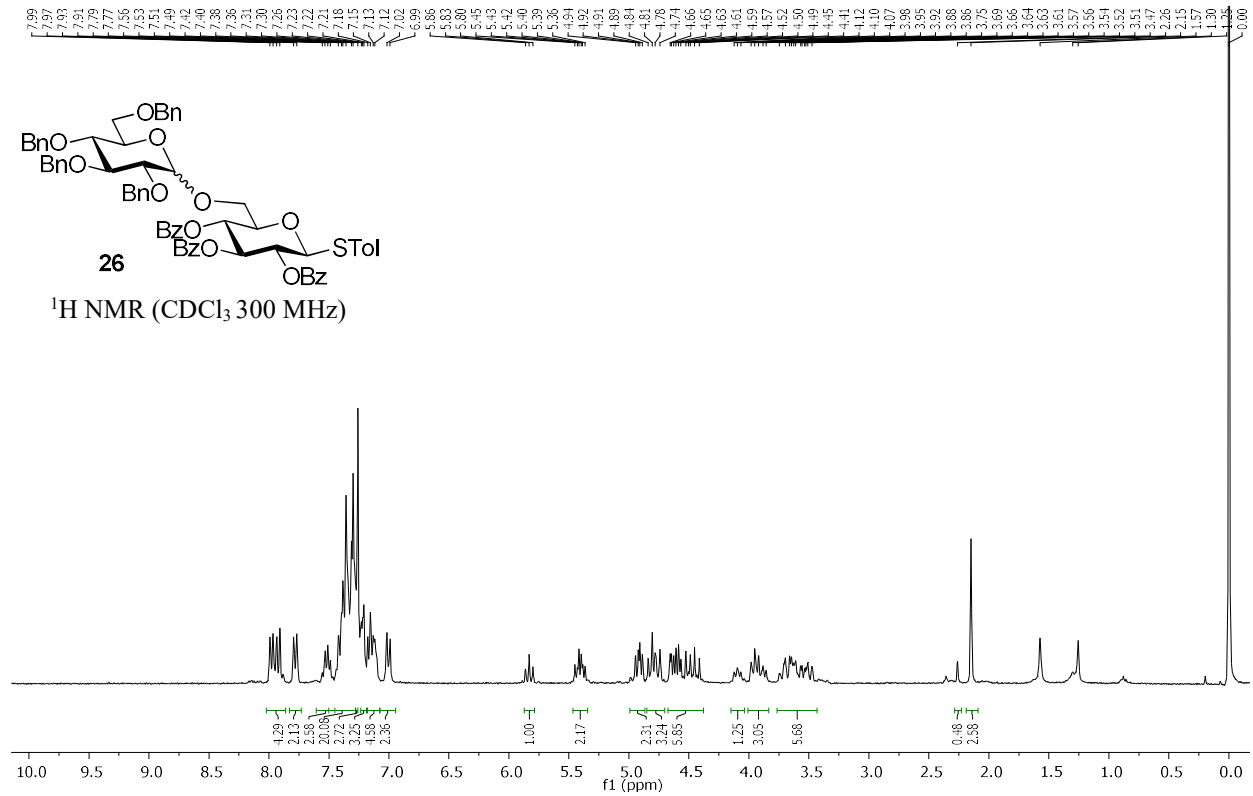
^{1}H NMR ($CDCl_3$ 300 MHz)

Tolyl 2,3,4-tri-*O*-benzoyl-*β*-D-glucopyranoside (25).



^{1}H NMR ($CDCl_3$ 300 MHz)

Tolyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-*α/β*-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-*β*-D-glucopyranoside (26).



^{1}H NMR ($CDCl_3$ 300 MHz)