

Supporting Information

Bismuth(III) triflate as a novel and efficient activator for glycosyl halides

Hayley B. Steber, Yashapal Singh,* and Alexei V. Demchenko*

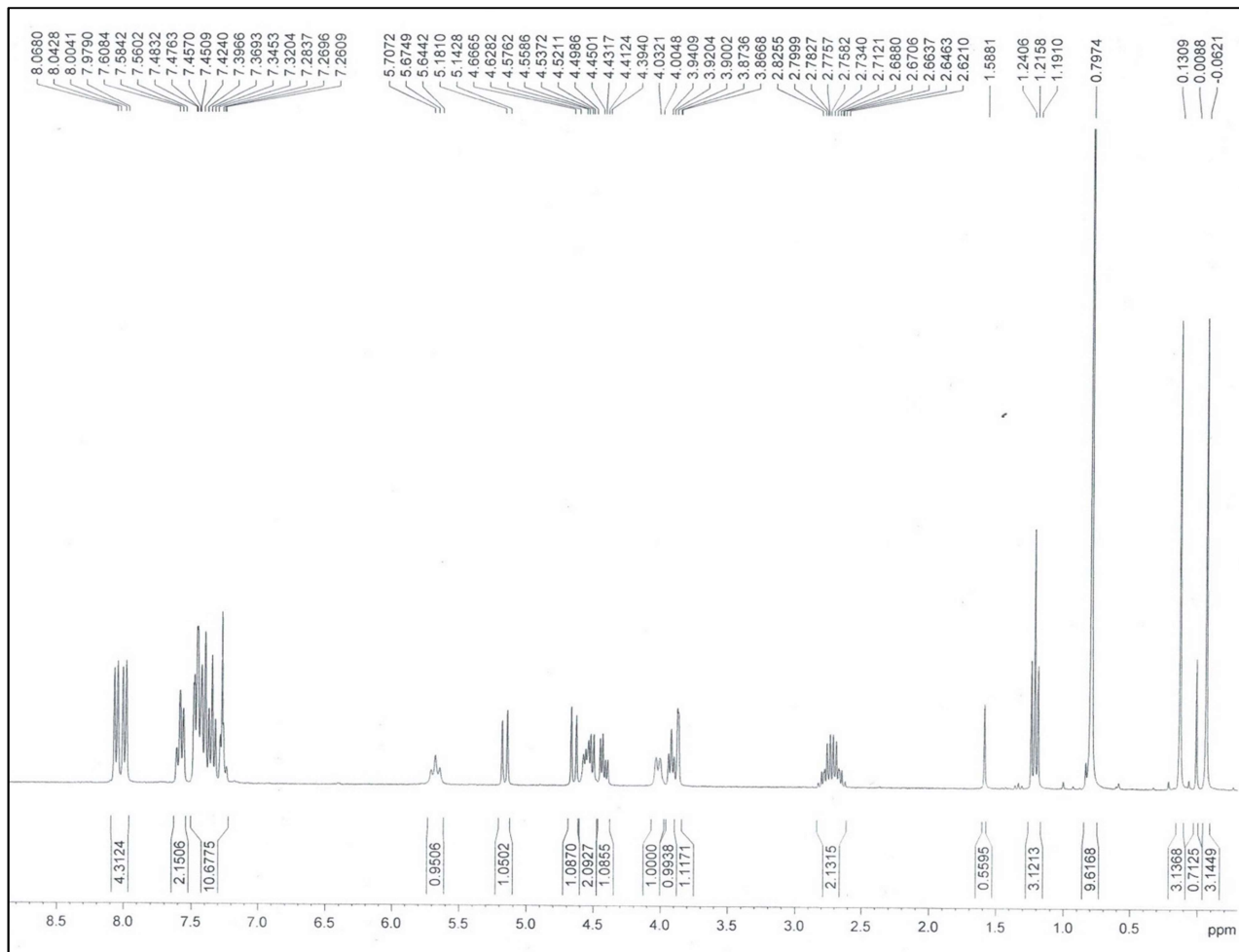
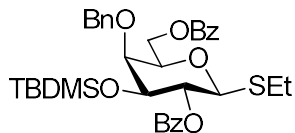
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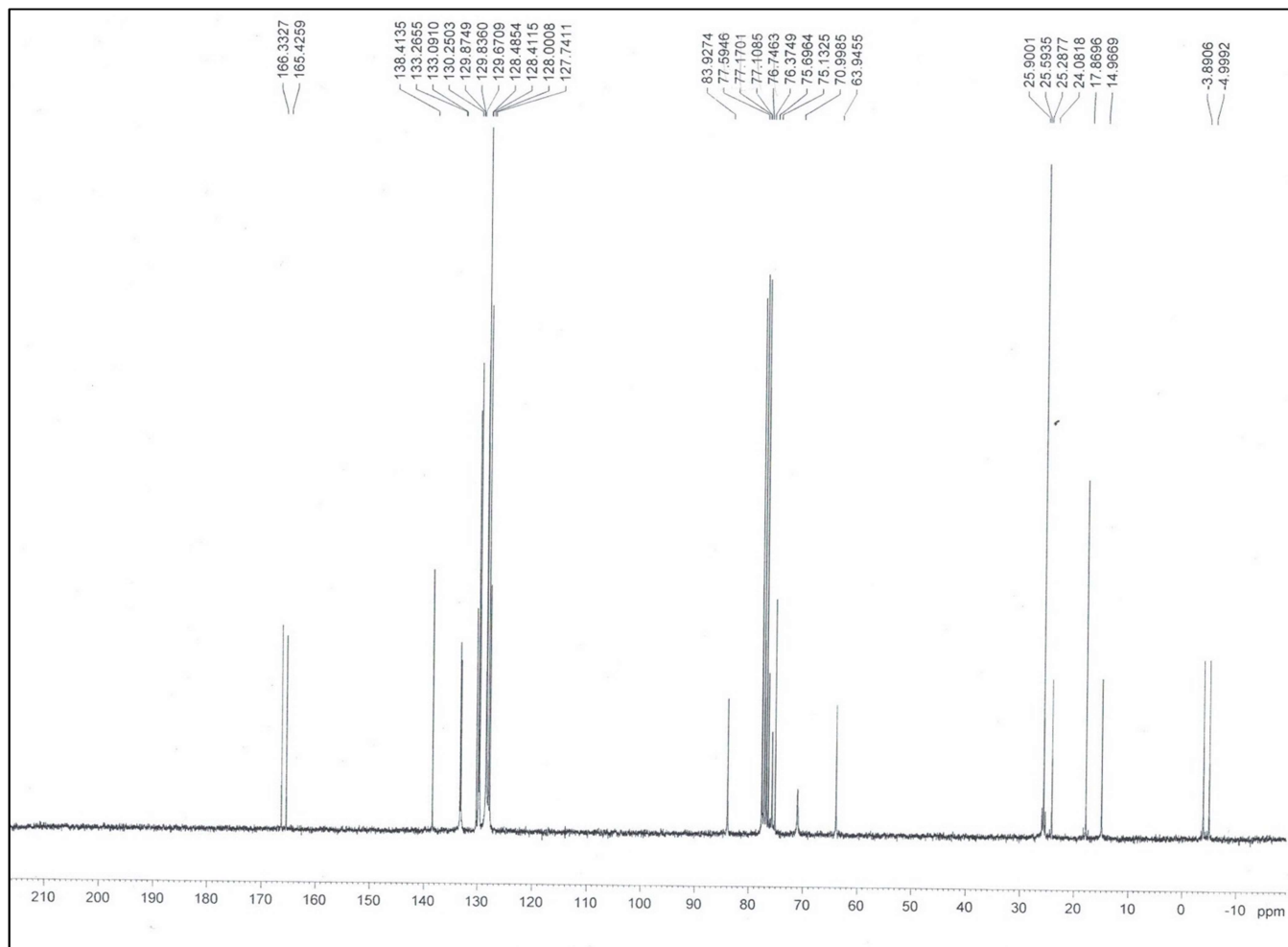
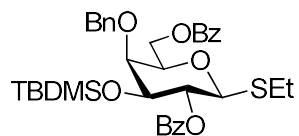
NMR Spectra for New Compounds

Ethyl 2,6-di-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-1-thio- β -D-galactopyranoside (33)



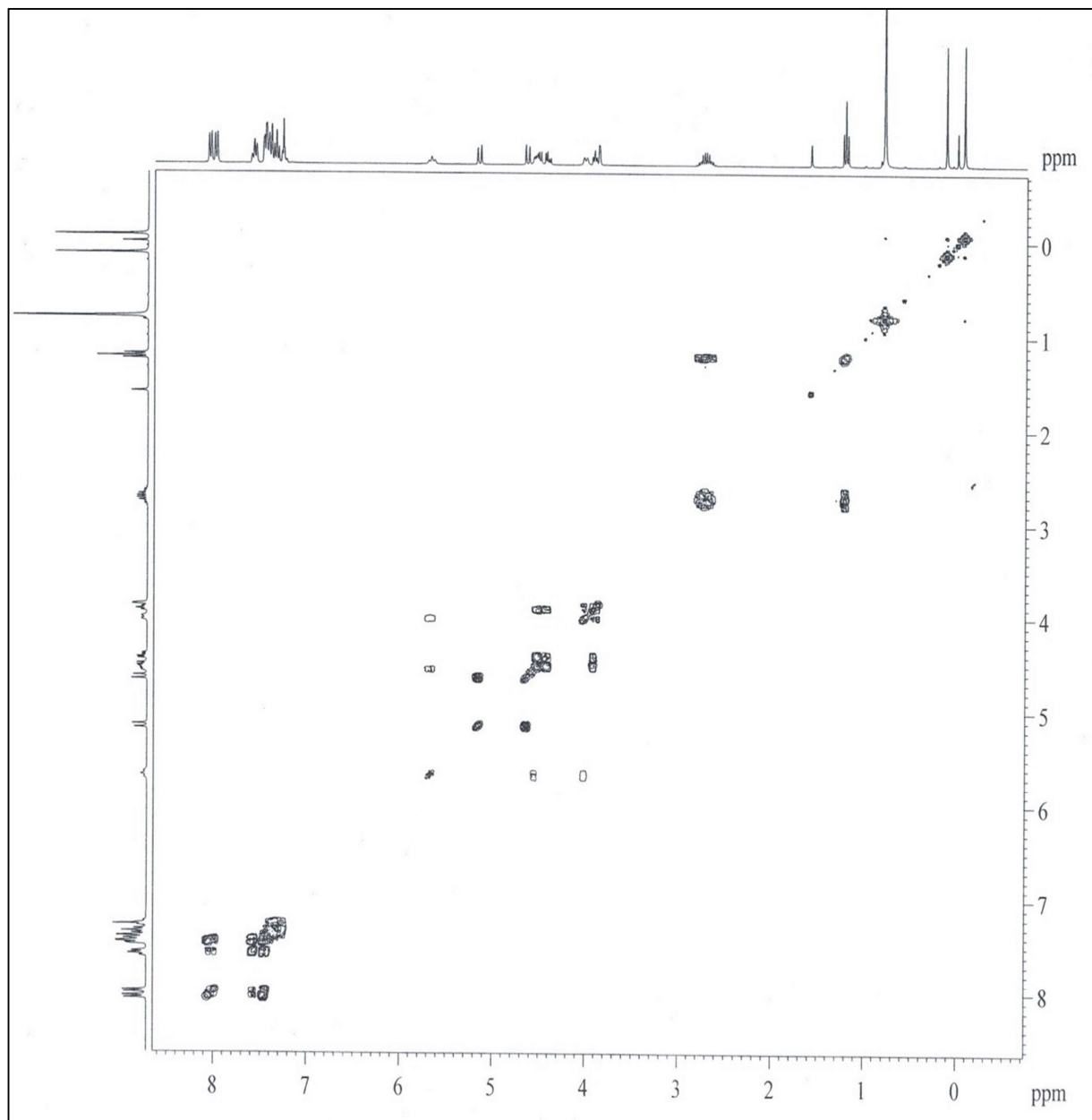
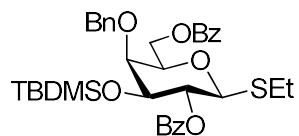
¹H NMR spectrum (CDCl₃, 300 MHz)

Ethyl 2,6-di-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-1-thio- β -D-galactopyranoside (33)



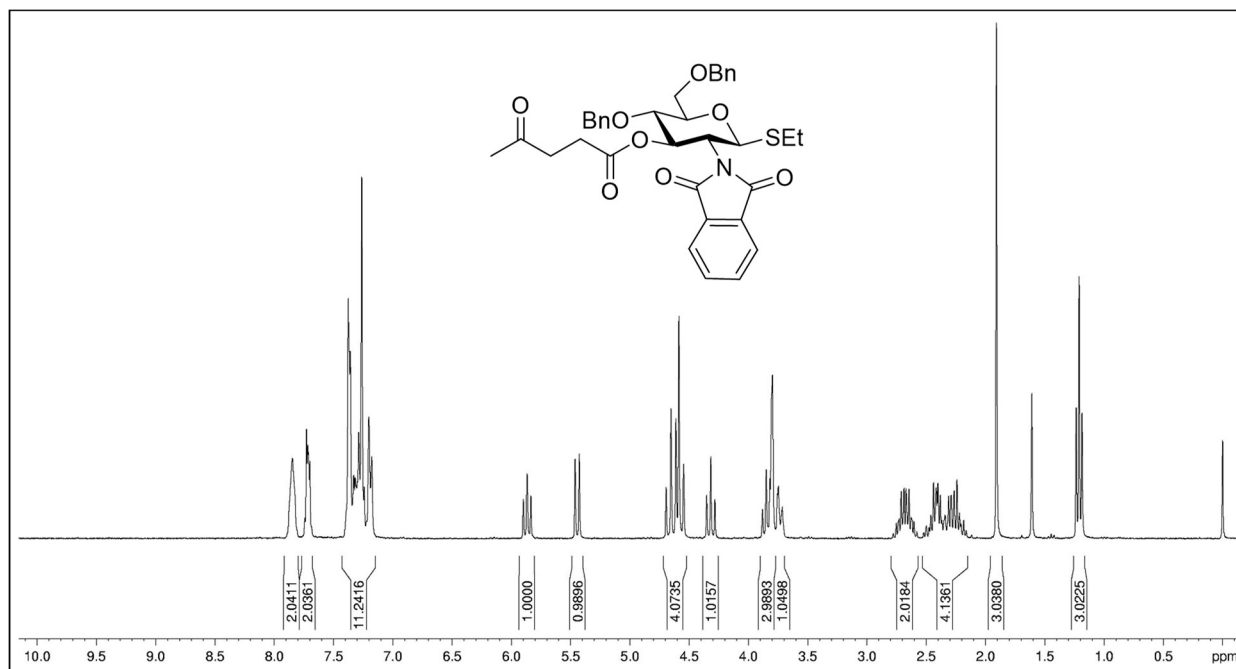
^{13}C NMR spectrum (75 MHz, CDCl_3)

Ethyl 2,6-di-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-1-thio- β -D-galactopyranoside (33)

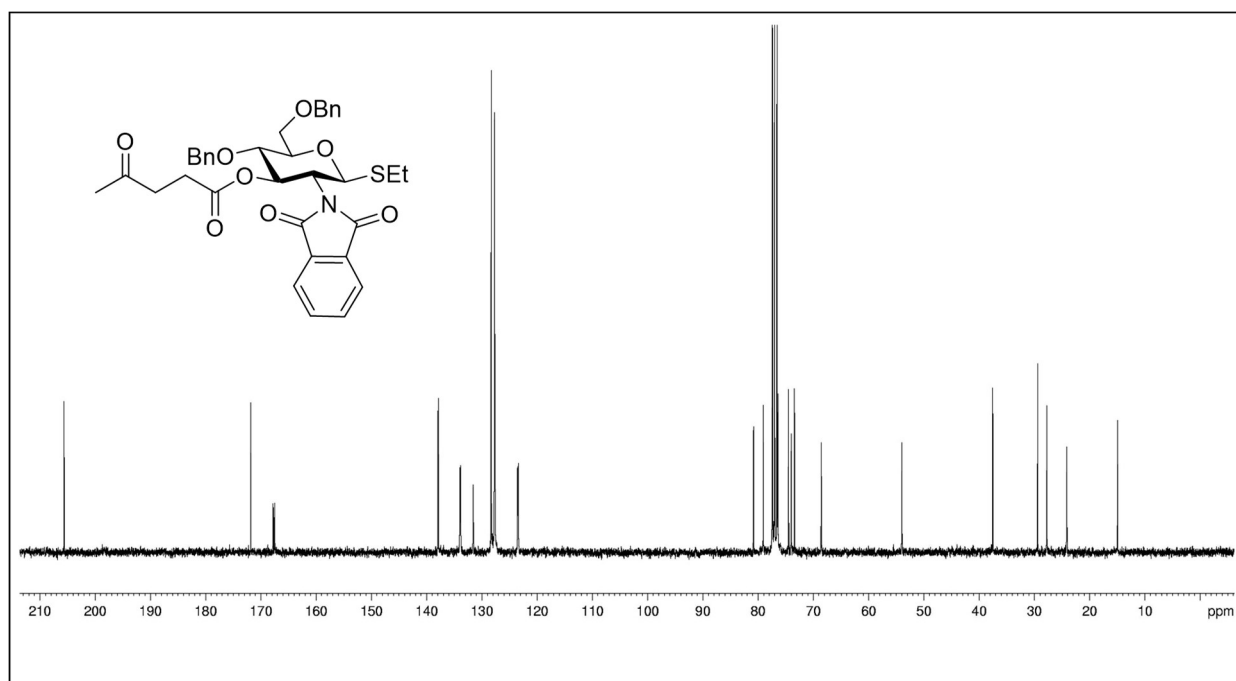


2D NMR (300 MHz, CDCl_3)

Ethyl 4, 6-di-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-phthalimido-1-thio- β -D-glucopyranoside (34)

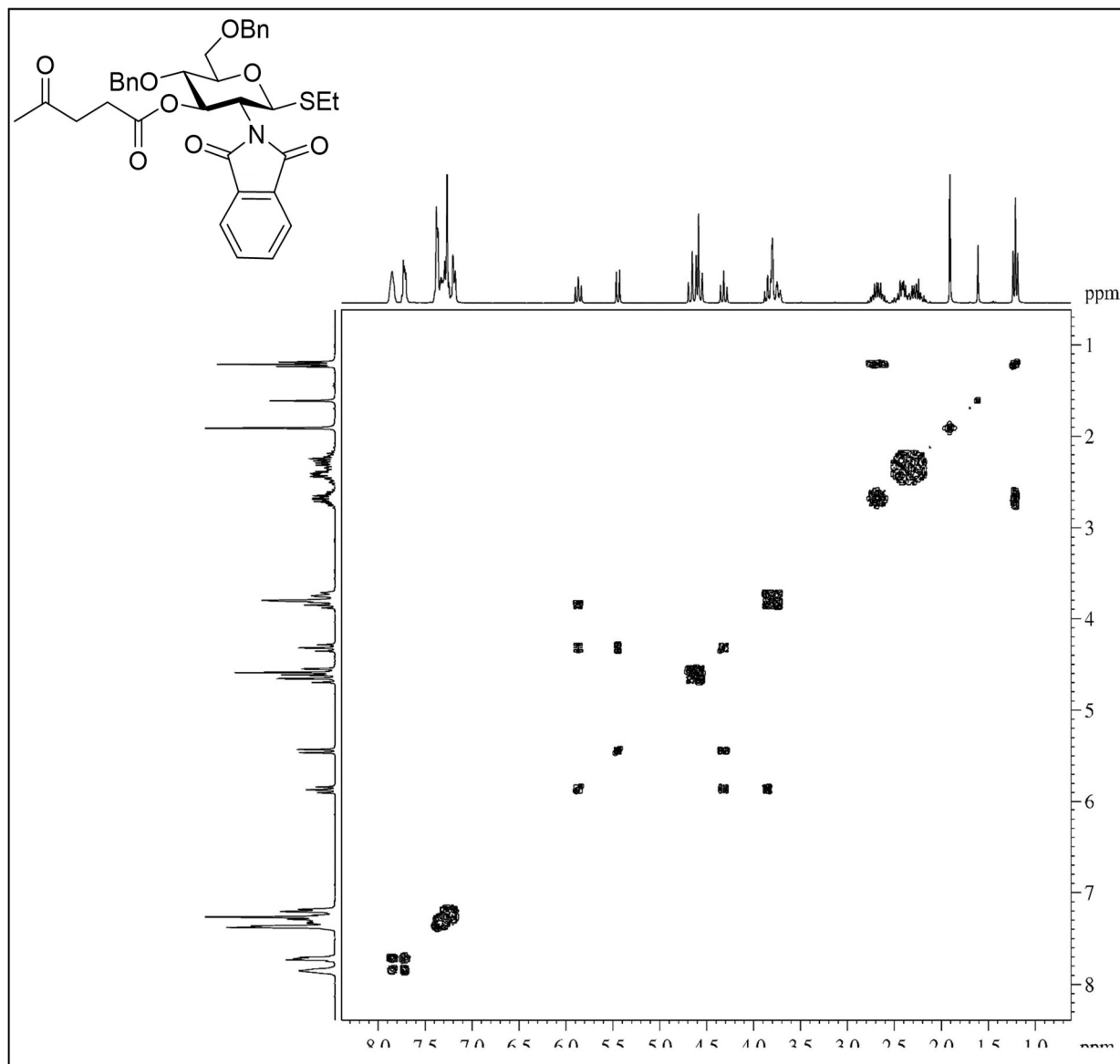


¹H NMR spectrum (CDCl₃, 300 MHz)



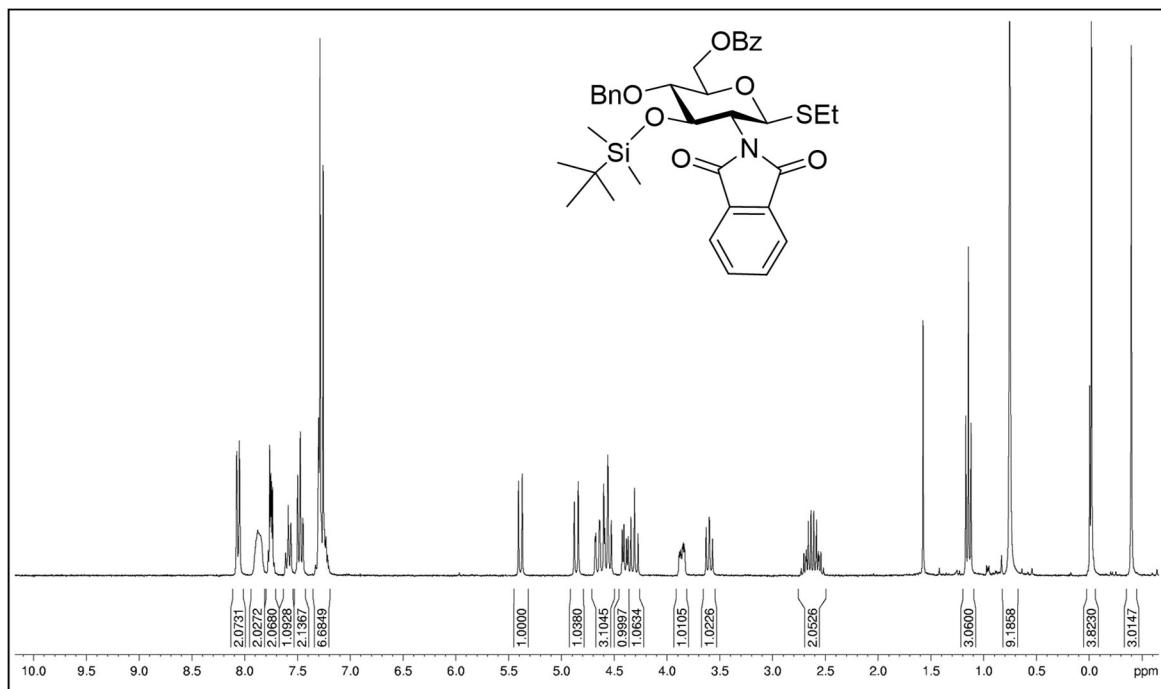
¹³C NMR spectrum (75 MHz, CDCl₃)

Ethyl 4, 6-di-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-phthalimido-1-thio- β -D-glucopyranoside (34)

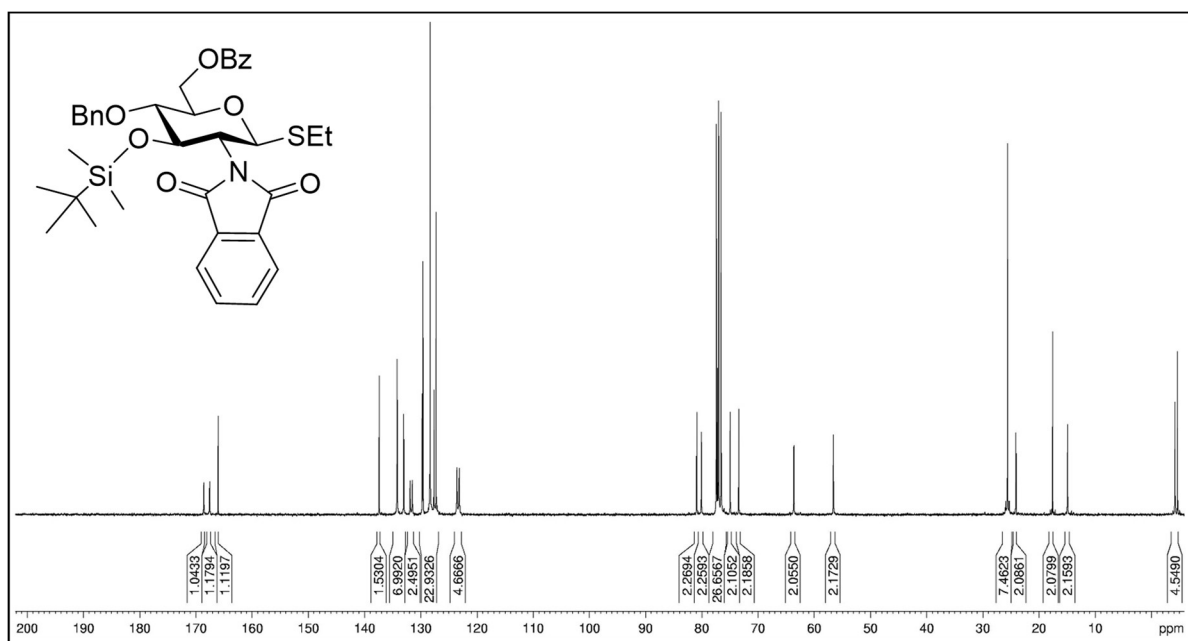


2D NMR (300 MHz, CDCl₃)

Ethyl 6-O-benzoyl-4-O-benzyl-2-deoxy-2-phthalimido-3-O-tert-butyldimethylsilyl-1-thio-β-D-glucopyranoside (49)

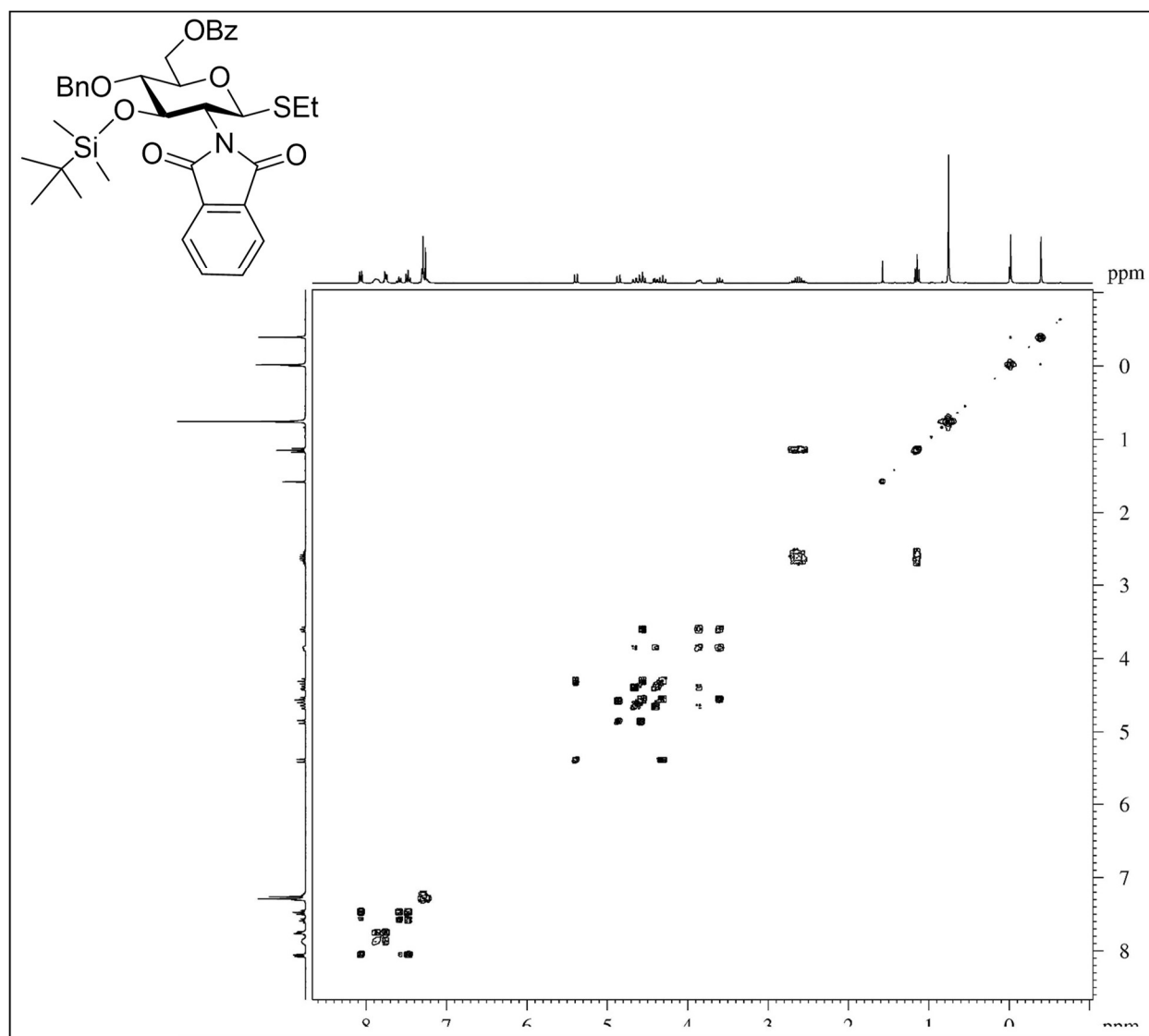


¹H NMR spectrum (CDCl₃, 300 MHz)



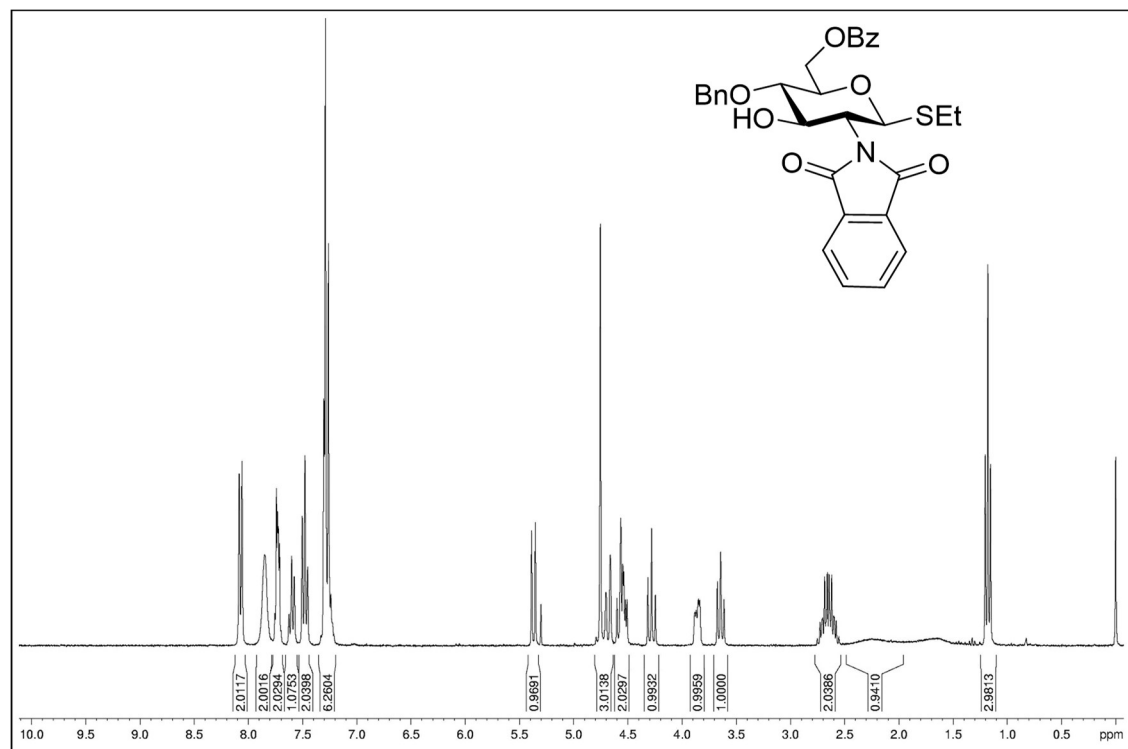
¹³C NMR spectrum (75 MHz, CDCl₃).

Ethyl 6-O-benzoyl-4-O-benzyl-2-deoxy-2-phthalimido-3-O-tert-butyldimethylsilyl-1-thio-β-D-glucopyranoside (49)

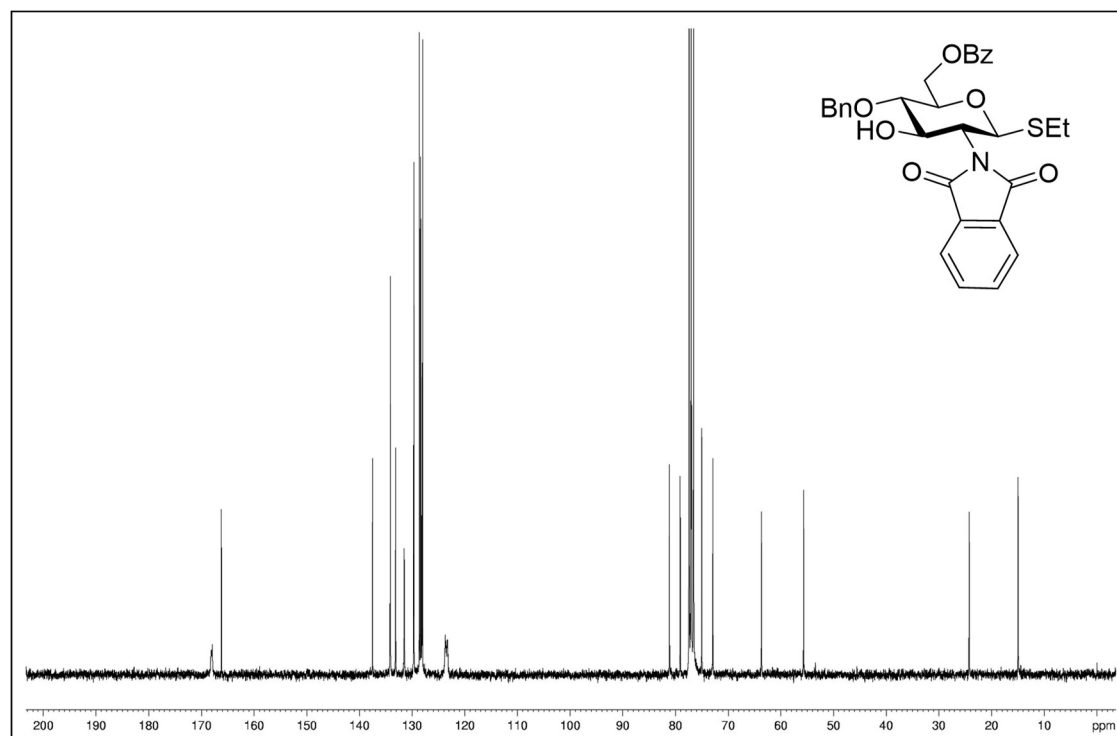


2D NMR (300 MHz, CDCl₃)

Ethyl 6-*O*-benzoyl-4-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (50)

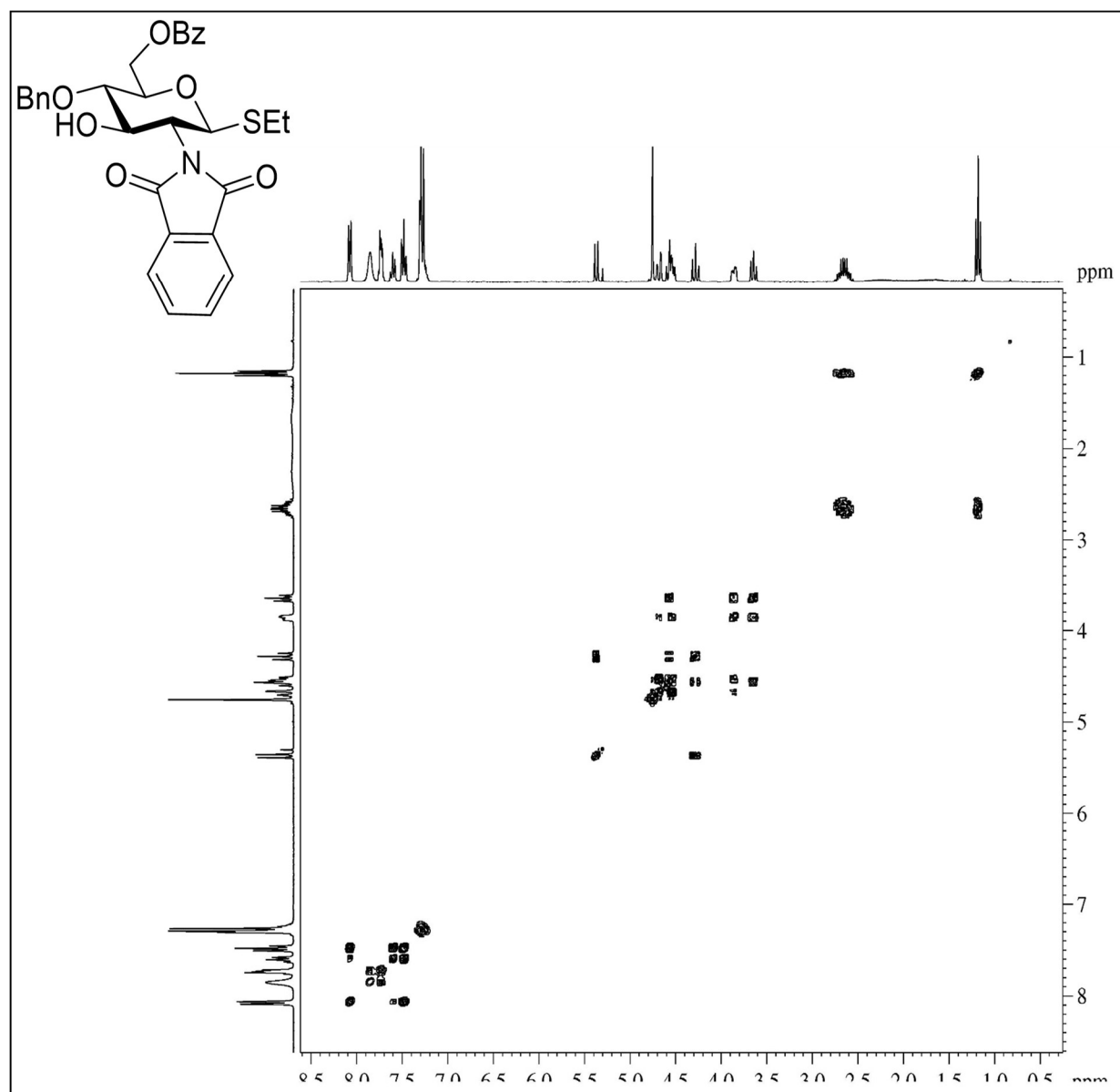


¹H NMR spectrum (CDCl₃, 300 MHz)



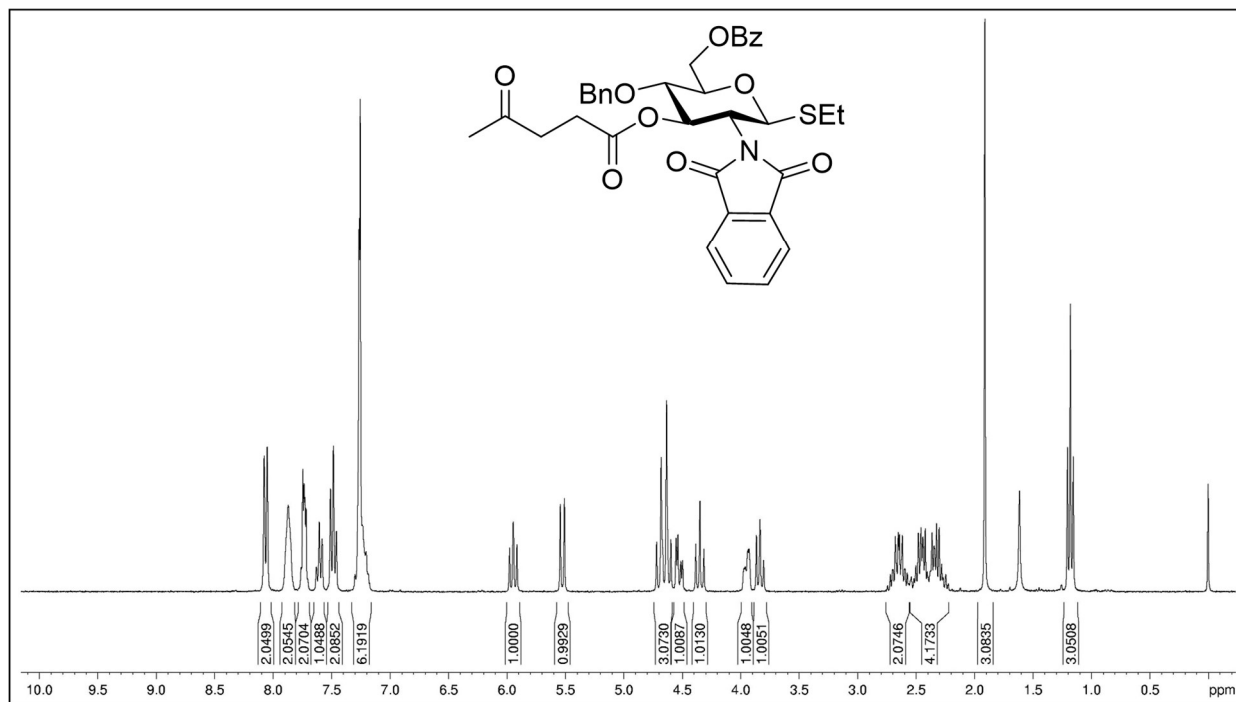
¹³C NMR spectrum (75 MHz, CDCl₃)

Ethyl 6-*O*-benzoyl-4-*O*-benzyl-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (**50**)

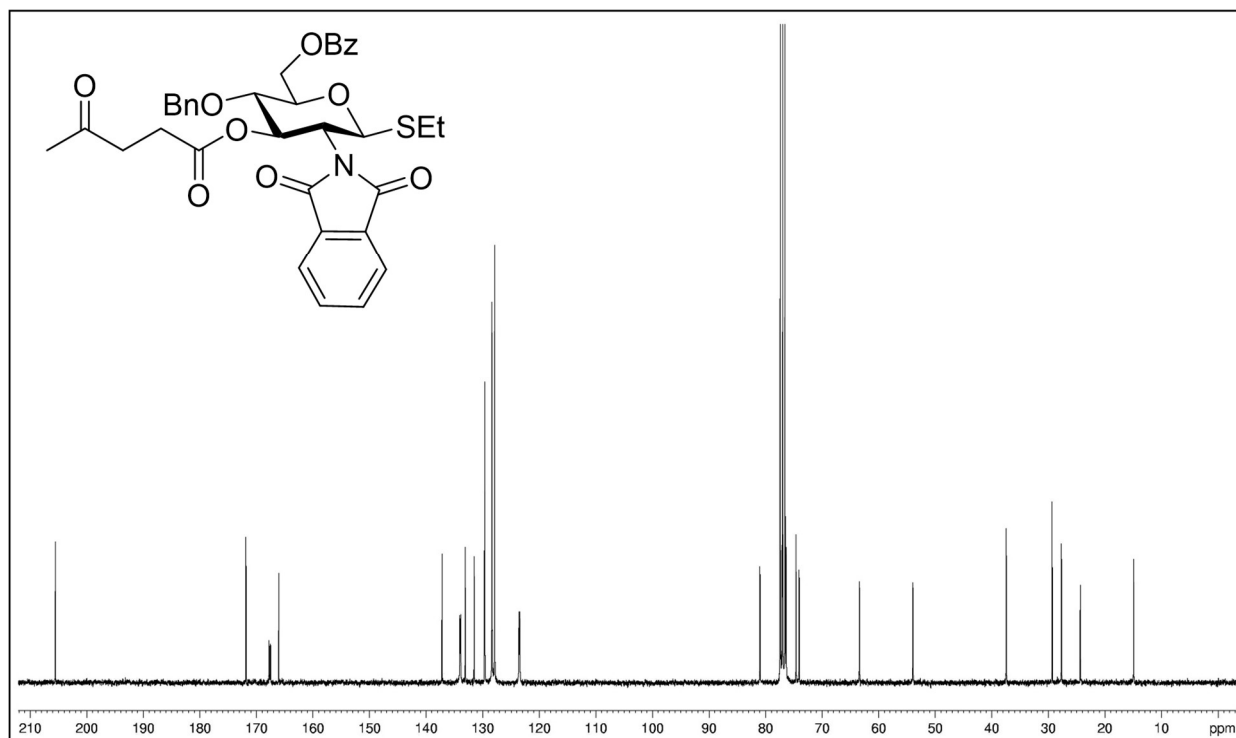


2D NMR (300 MHz, CDCl_3)

Ethyl 6-O-benzoyl-4-O-benzyl-2-deoxy-3-O-levulinoyl-2-phthalimido-1-thio-β-D-glucopyranoside (35)

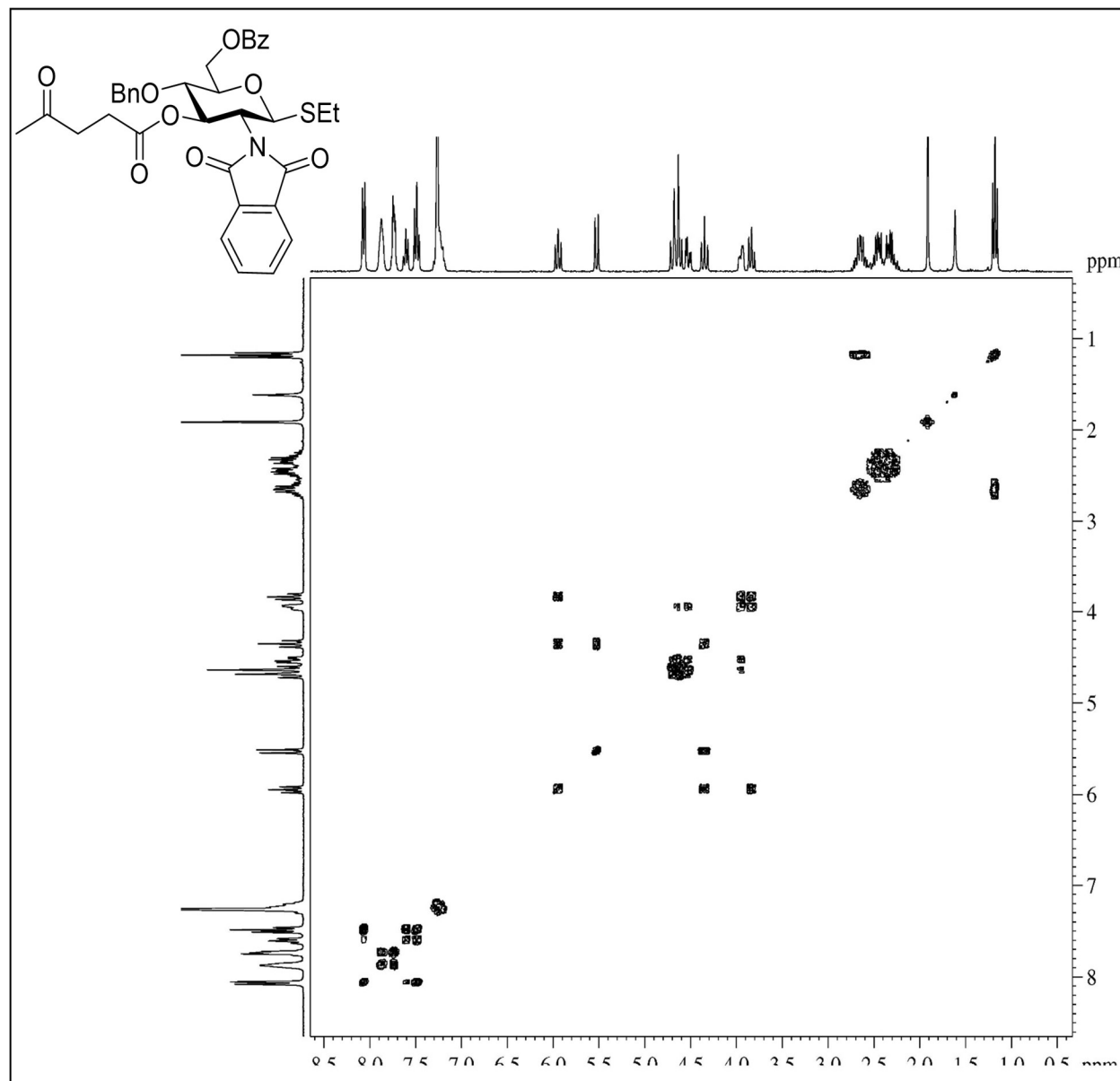


¹H NMR spectrum (CDCl₃, 300 MHz)



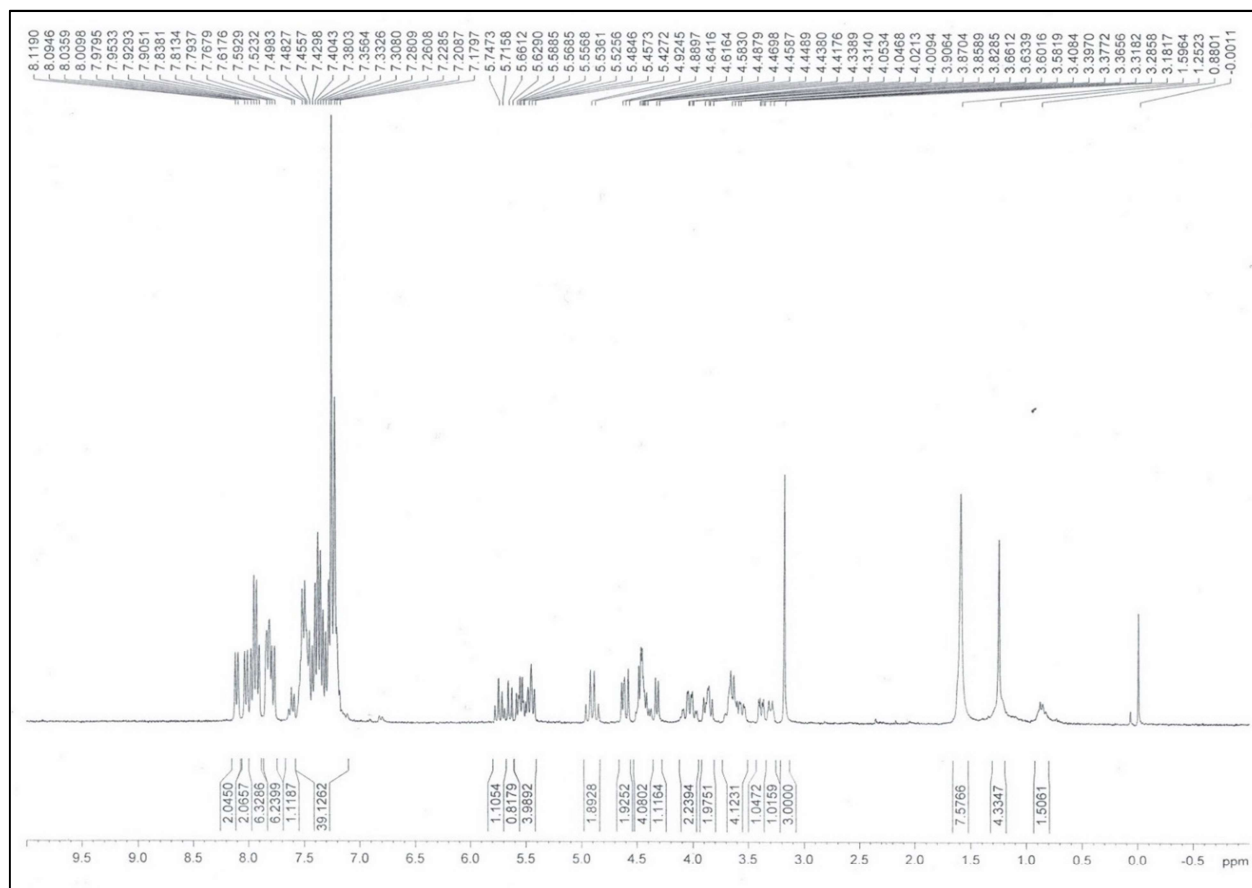
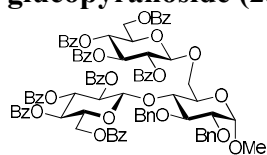
¹³C NMR spectrum (75 MHz, CDCl₃)

Ethyl 6-*O*-benzoyl-4-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-phthalimido-1-thio- β -D-glucopyranoside (35)

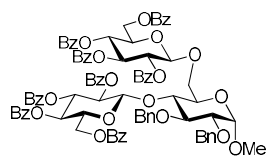


2D NMR (300 MHz, CDCl_3)

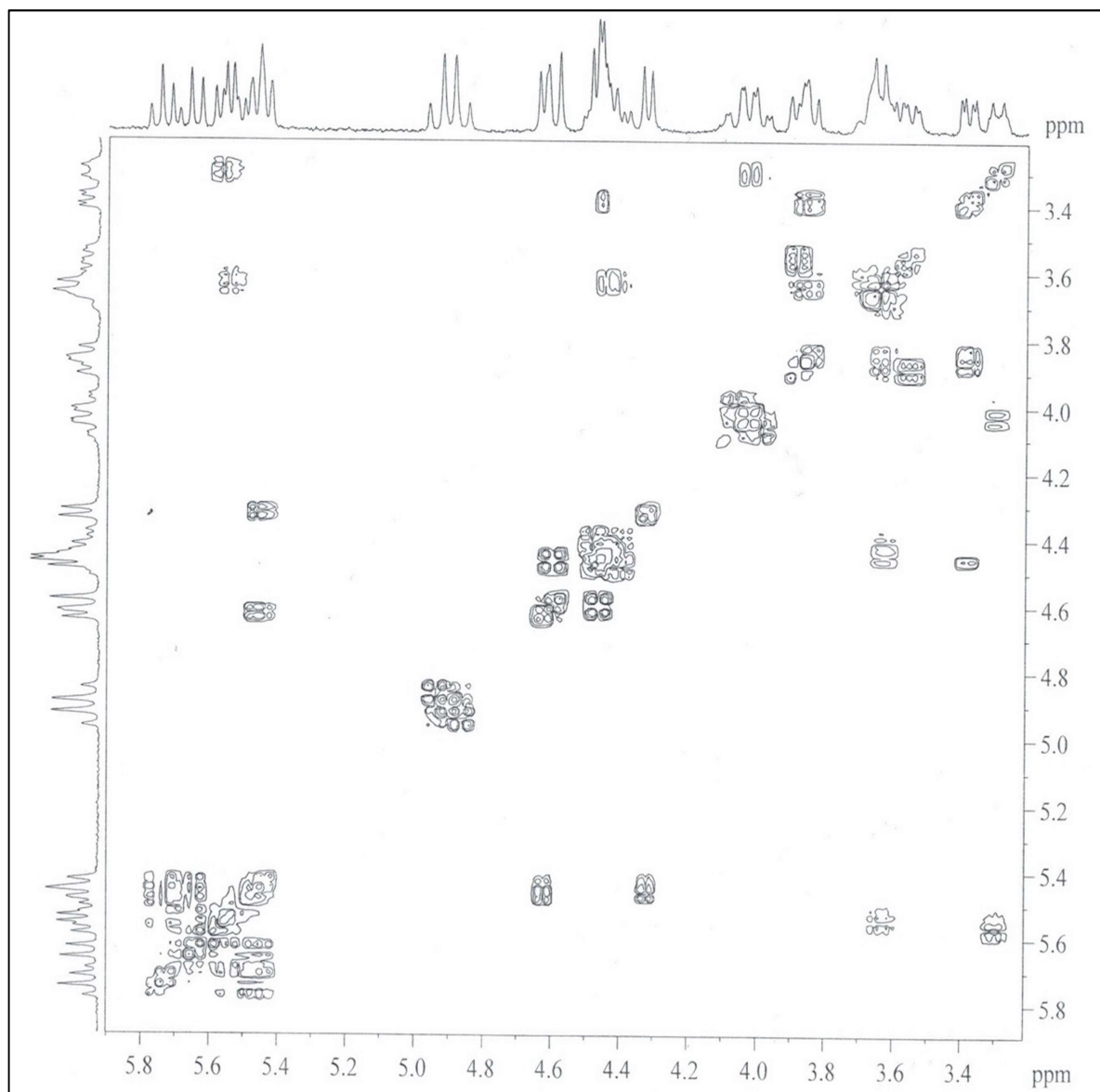
Methyl 4,6-di-*O*-(2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranosyl)-2,3-di-*O*-benzyl- α -D-glucopyranoside (25)



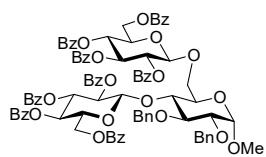
¹H NMR (300 MHz, CDCl₃)



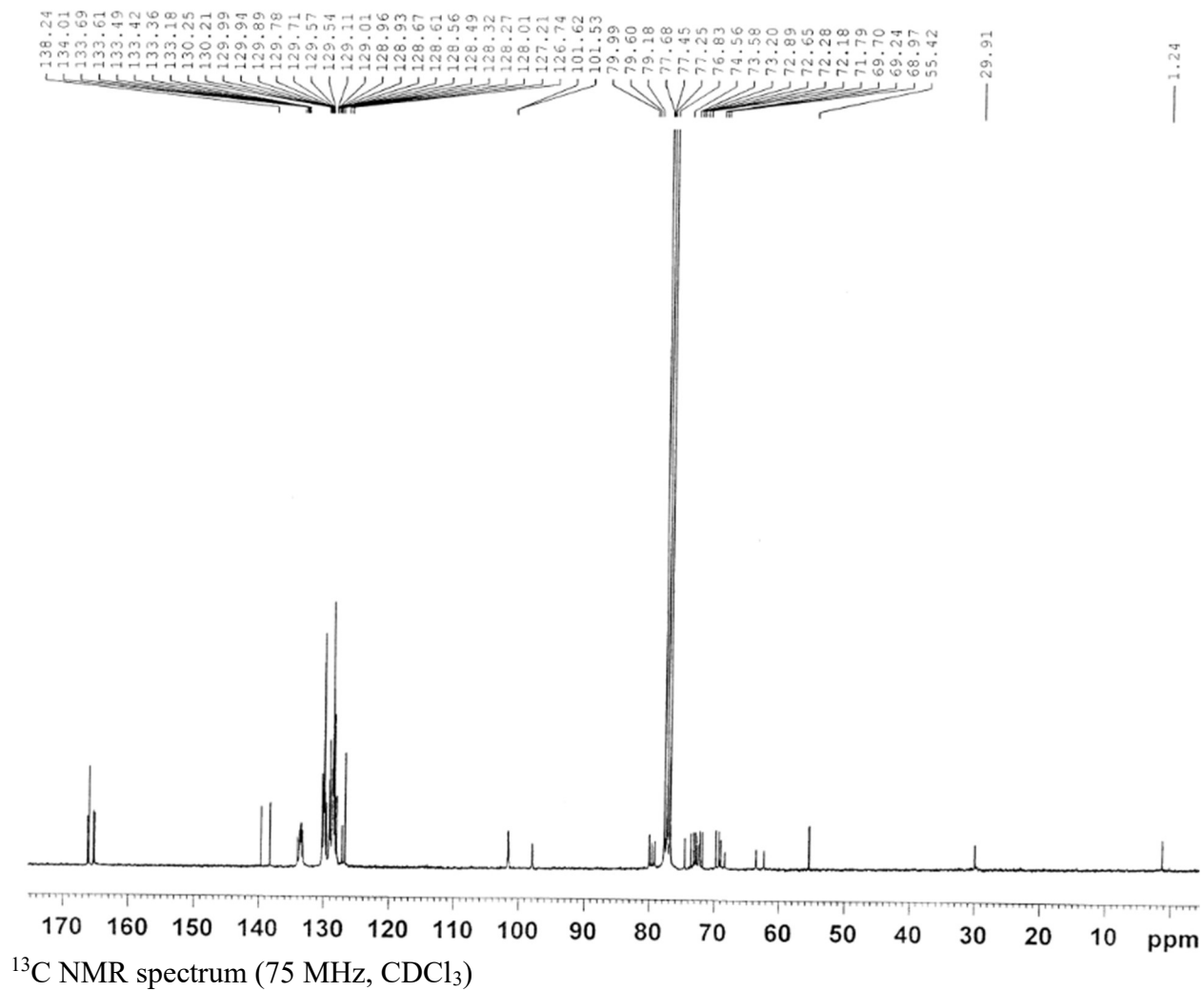
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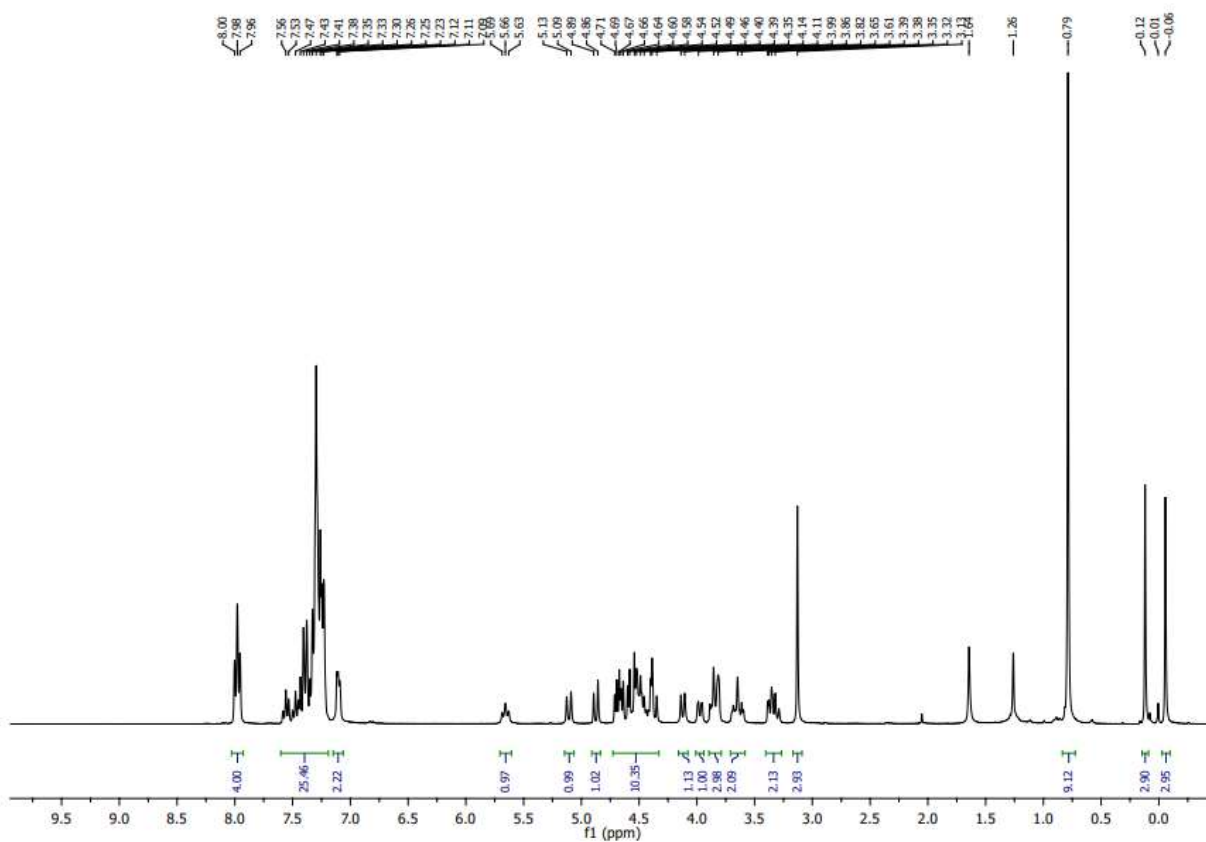
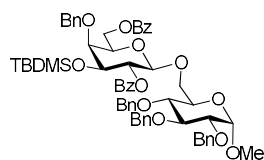
2D NMR (300 MHz, CDCl₃)



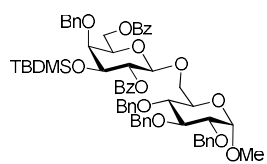
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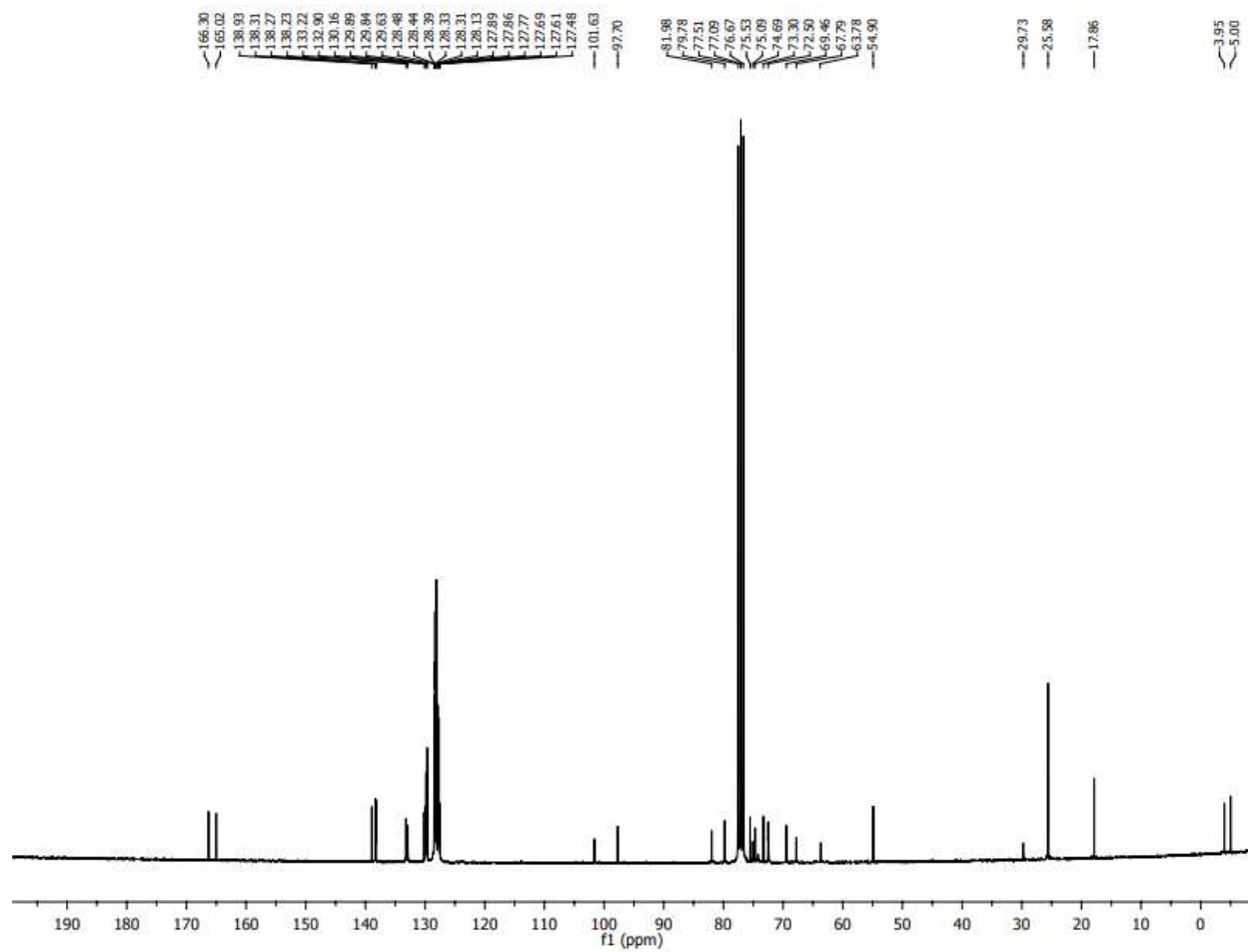
Methyl 6-O-(2,6-di-O-benzoyl-4-O-benzyl-3-O-tert-butyl dimethylsilyl)- β -D-galactopyranosyl)-2,3,4-tri-O-benzyl- α -D-glucopyranoside (42)



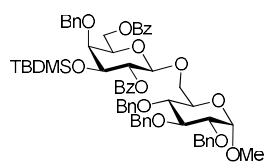
^1H NMR (300 MHz, CDCl_3)



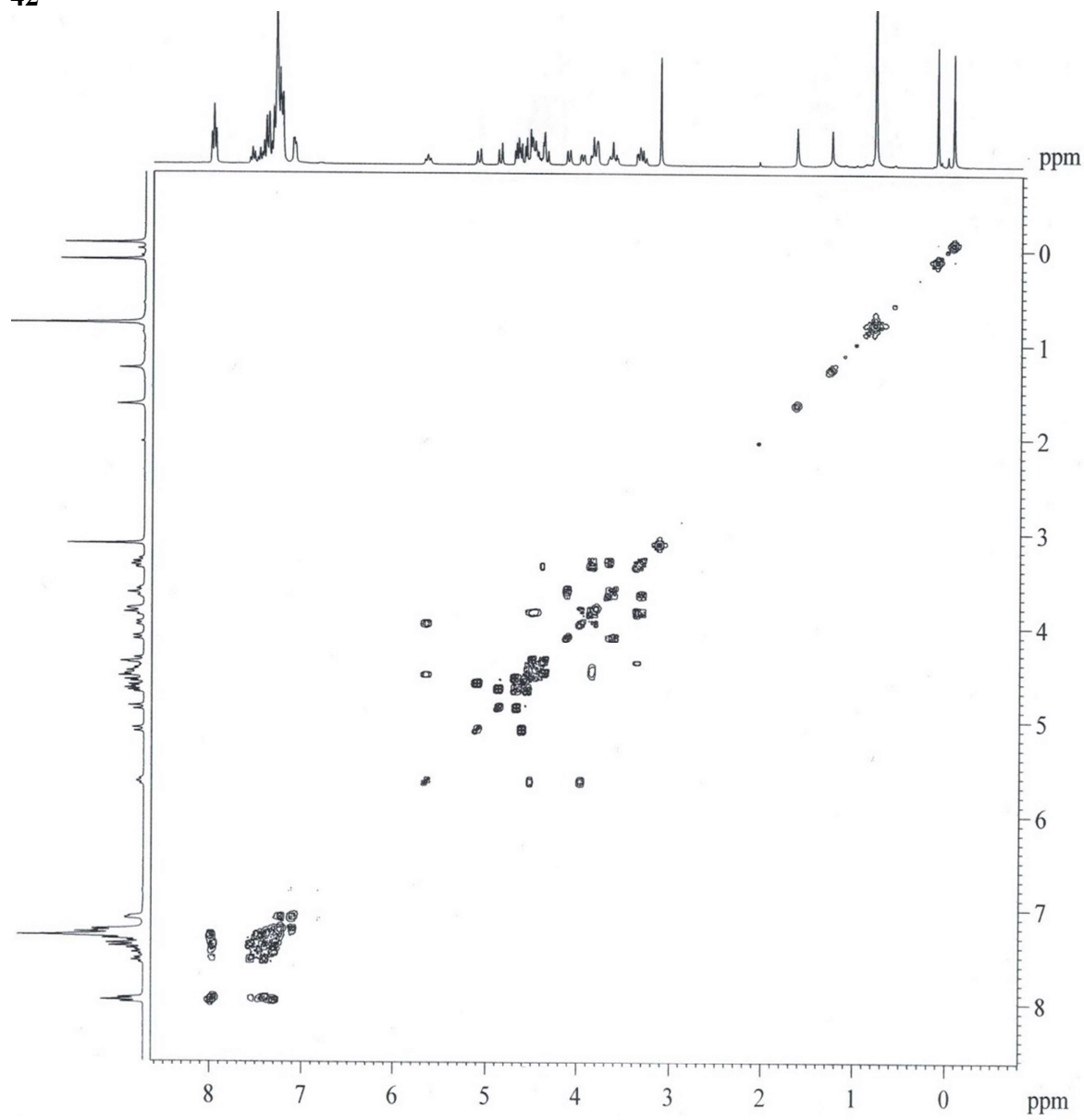
42



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

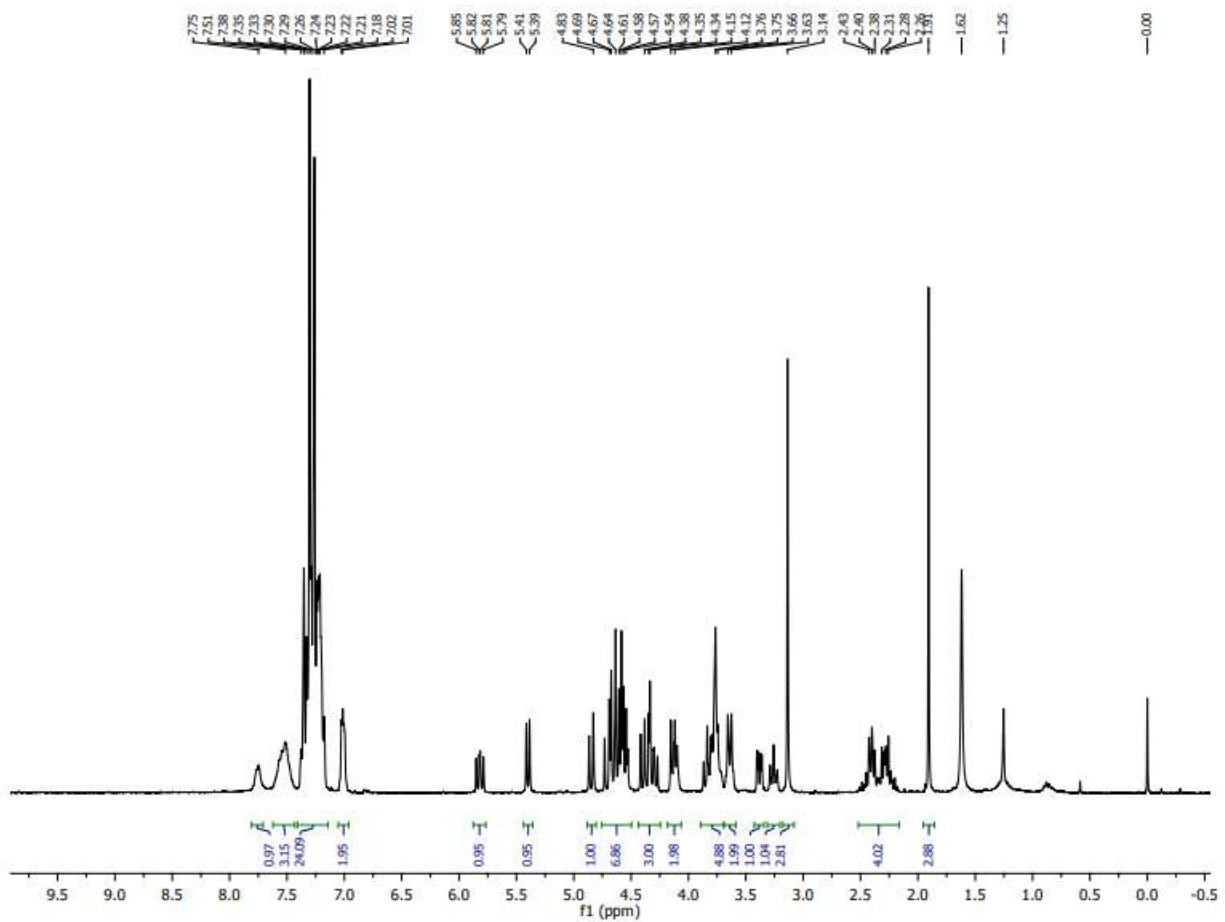
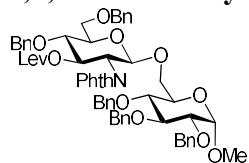


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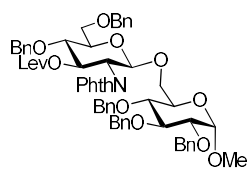


2D NMR (300 MHz, CDCl₃)

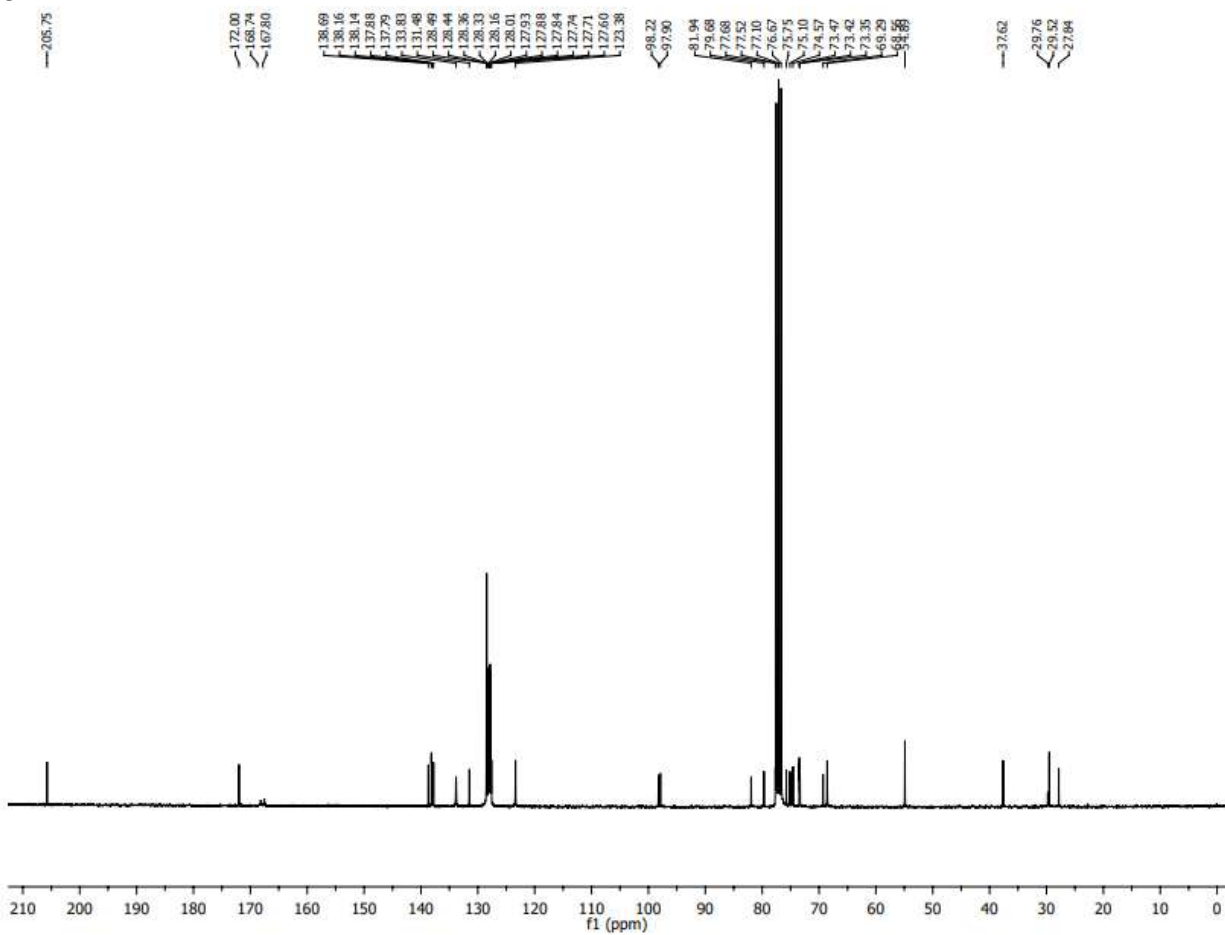
Methyl 6-O-(4,6-di-O-benzyl-2-deoxy-3-O-levulinoyl-2-phthalimido-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (43)



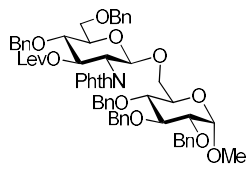
¹H NMR (300 MHz, CDCl₃)



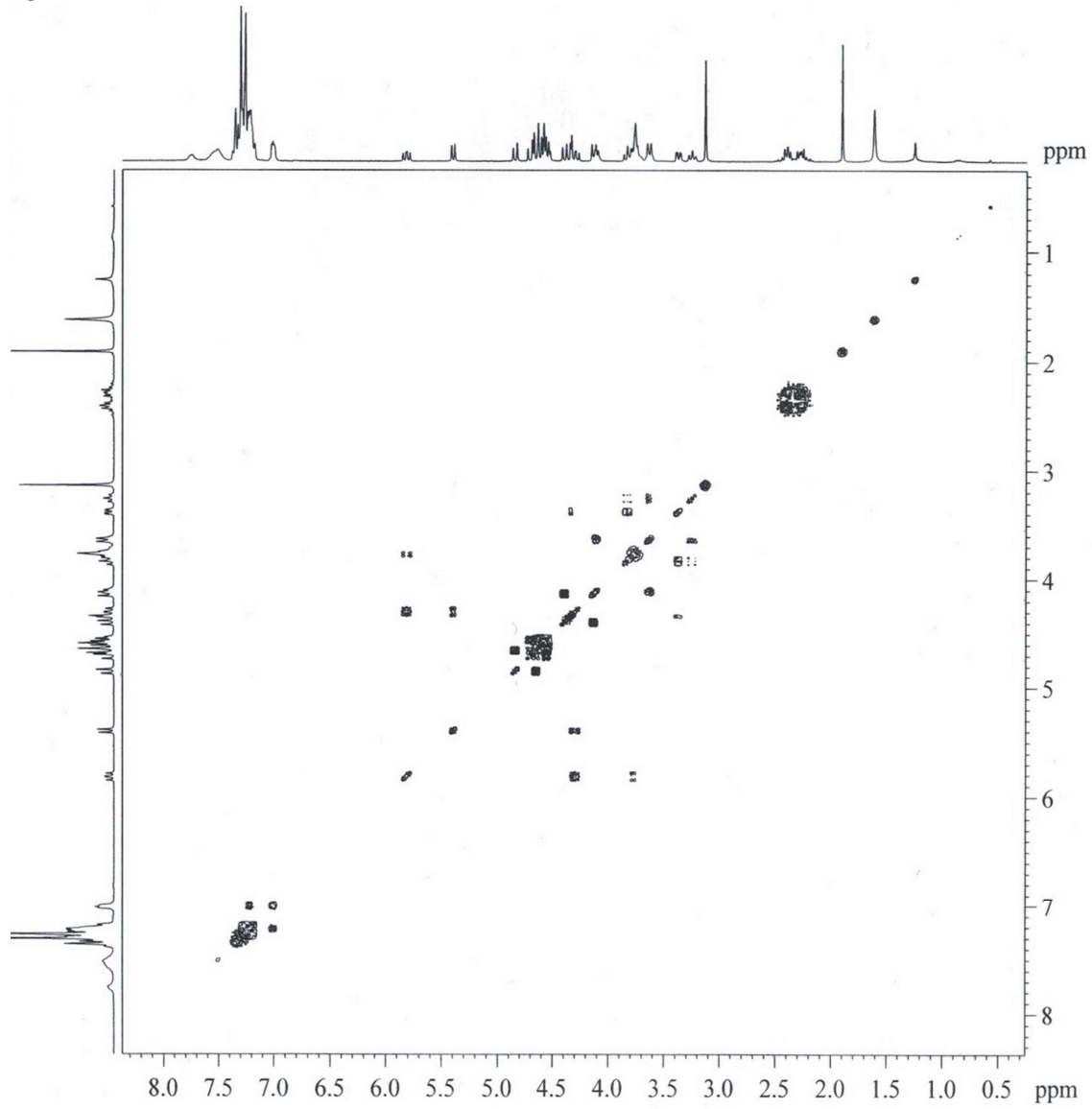
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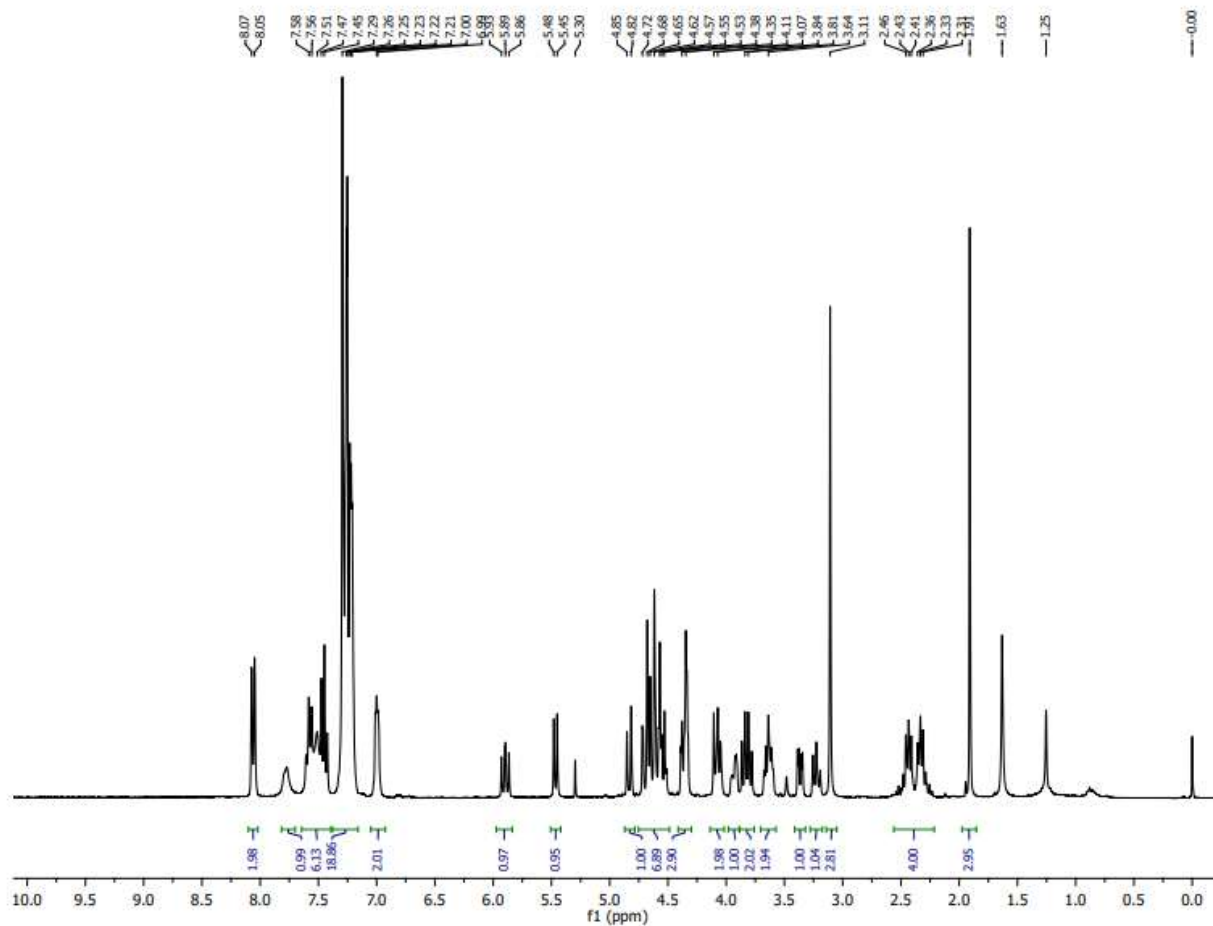
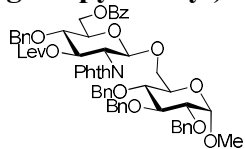
^{13}C NMR (75 MHz, CDCl_3)



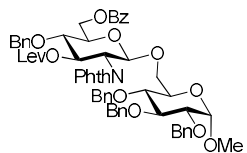
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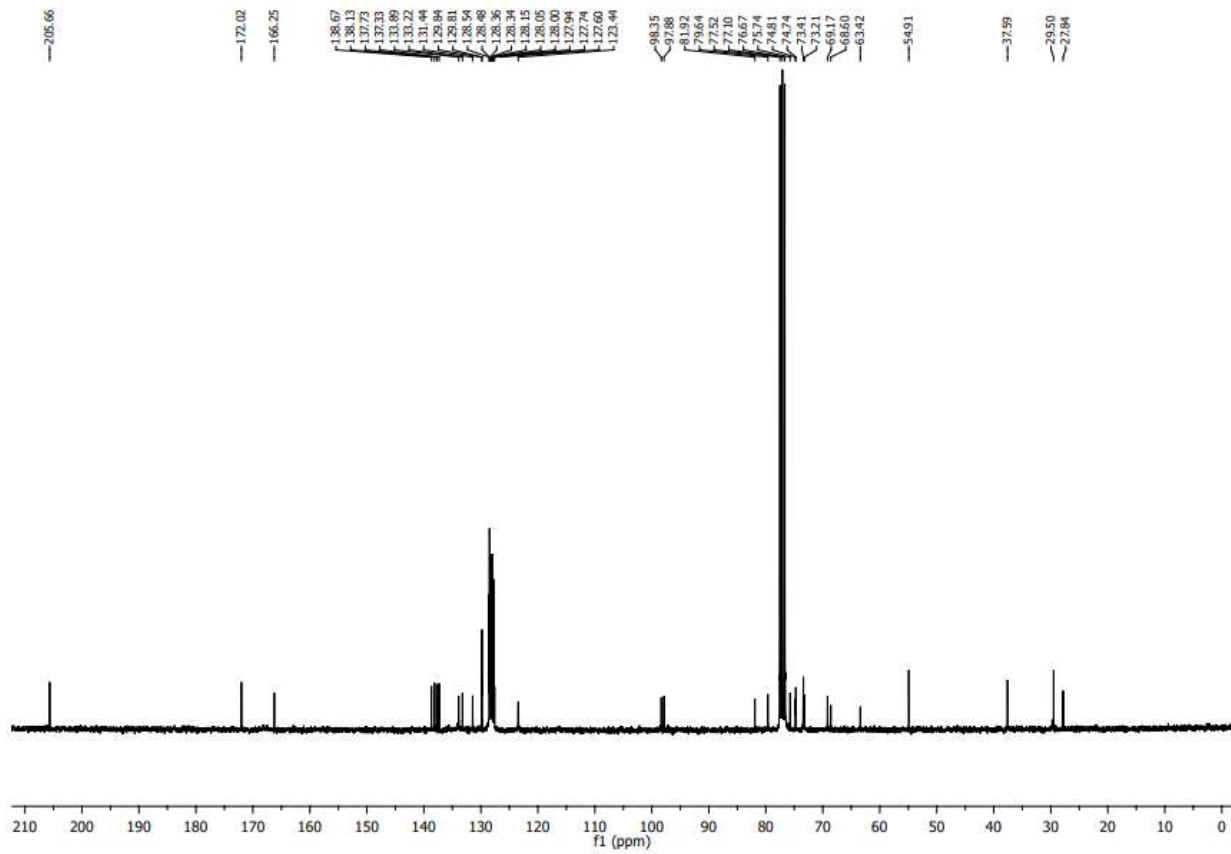
Methyl 6-O-(6-O-benzoyl-4-O-benzyl-2-deoxy-3-O-levulinoyl-2-phthalimido-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (44)



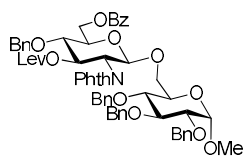
$^1\text{H NMR}$ (300 MHz, CDCl_3)



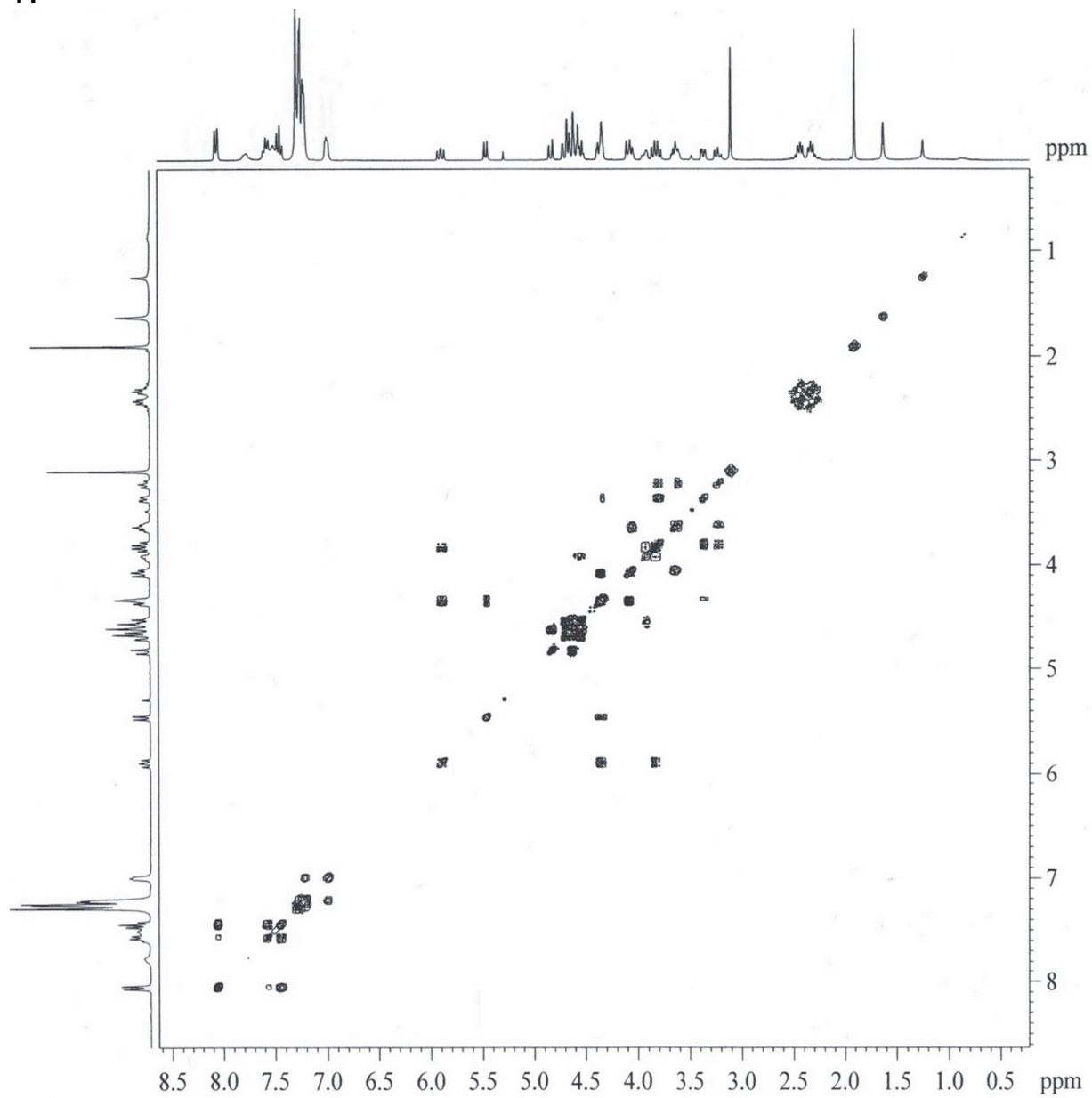
44



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



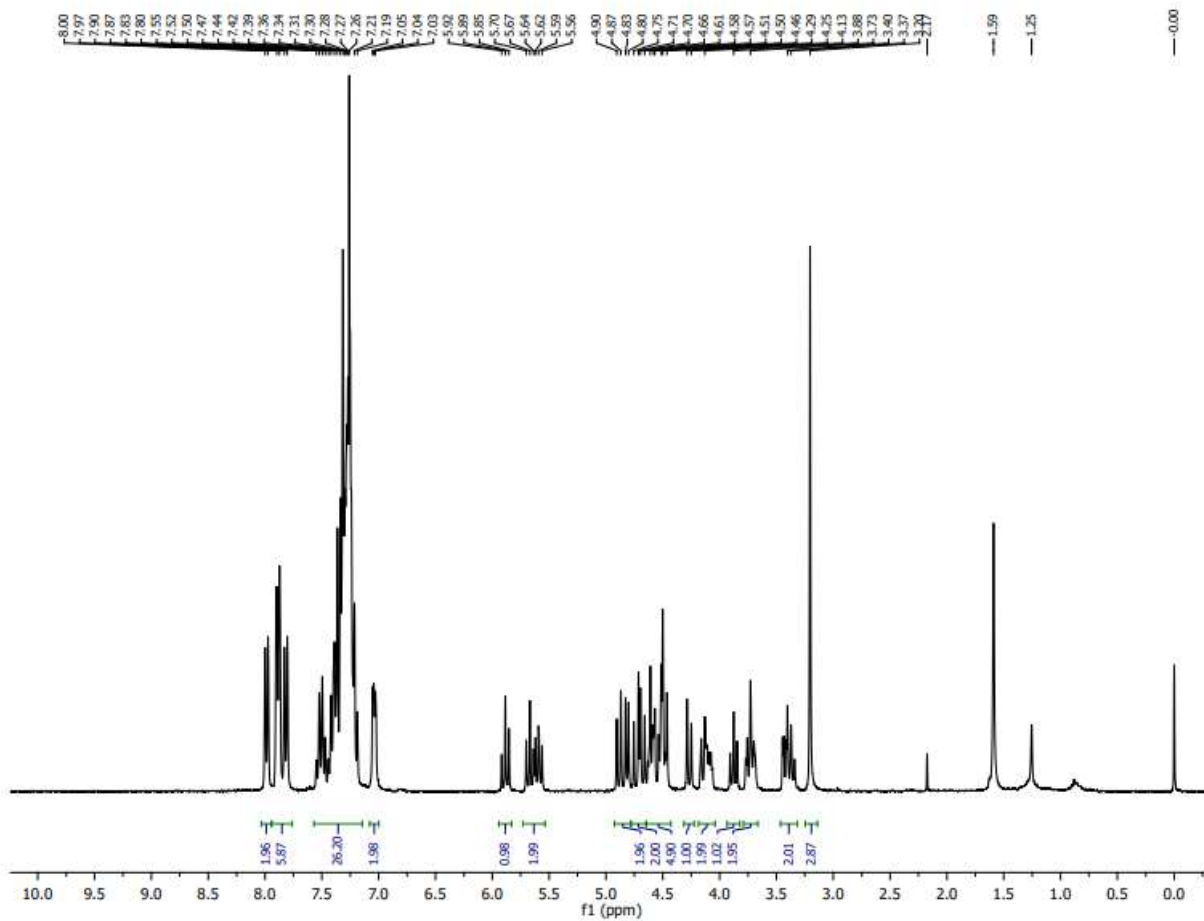
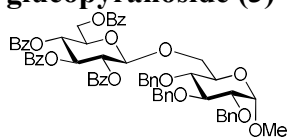
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2D NMR (300 MHz, CDCl₃)

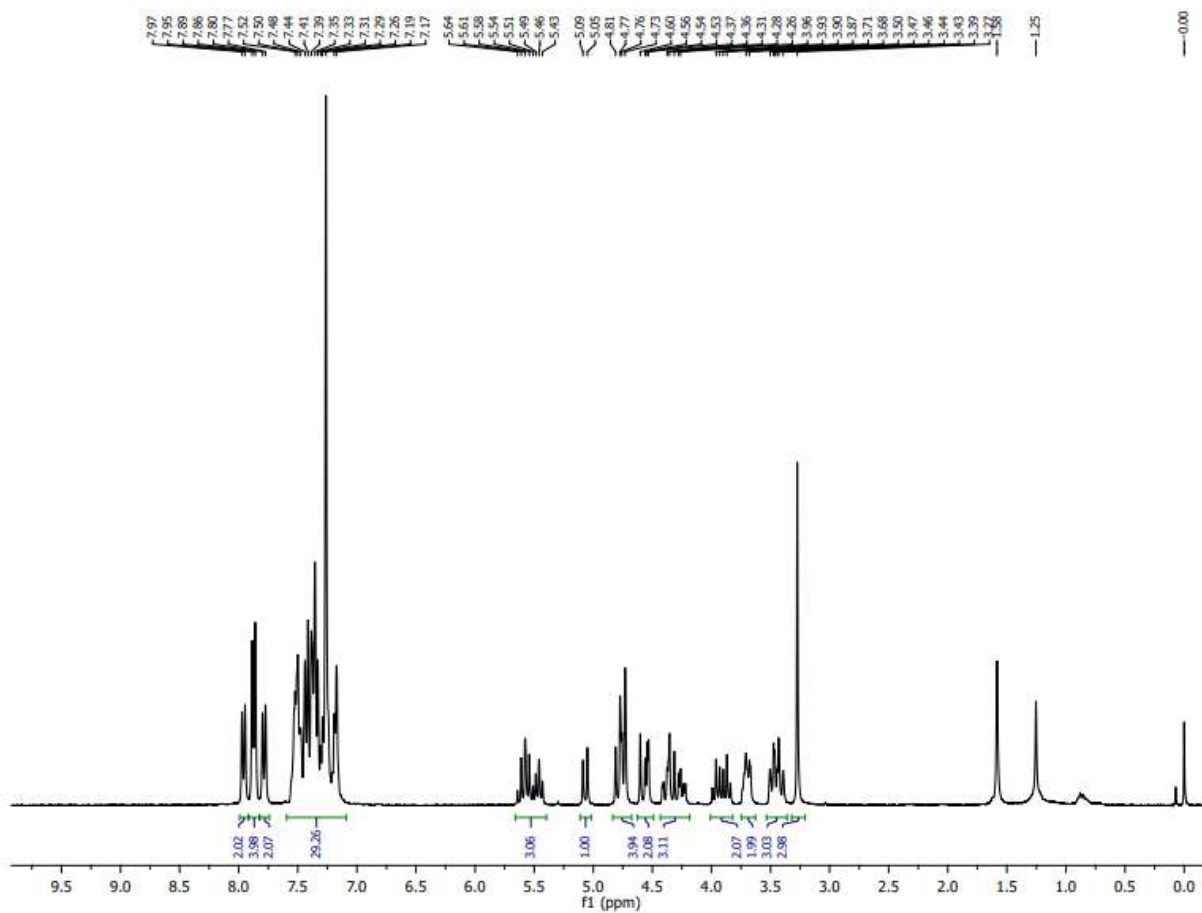
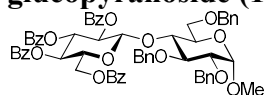
¹H NMR Spectra of Known Oligosaccharides

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



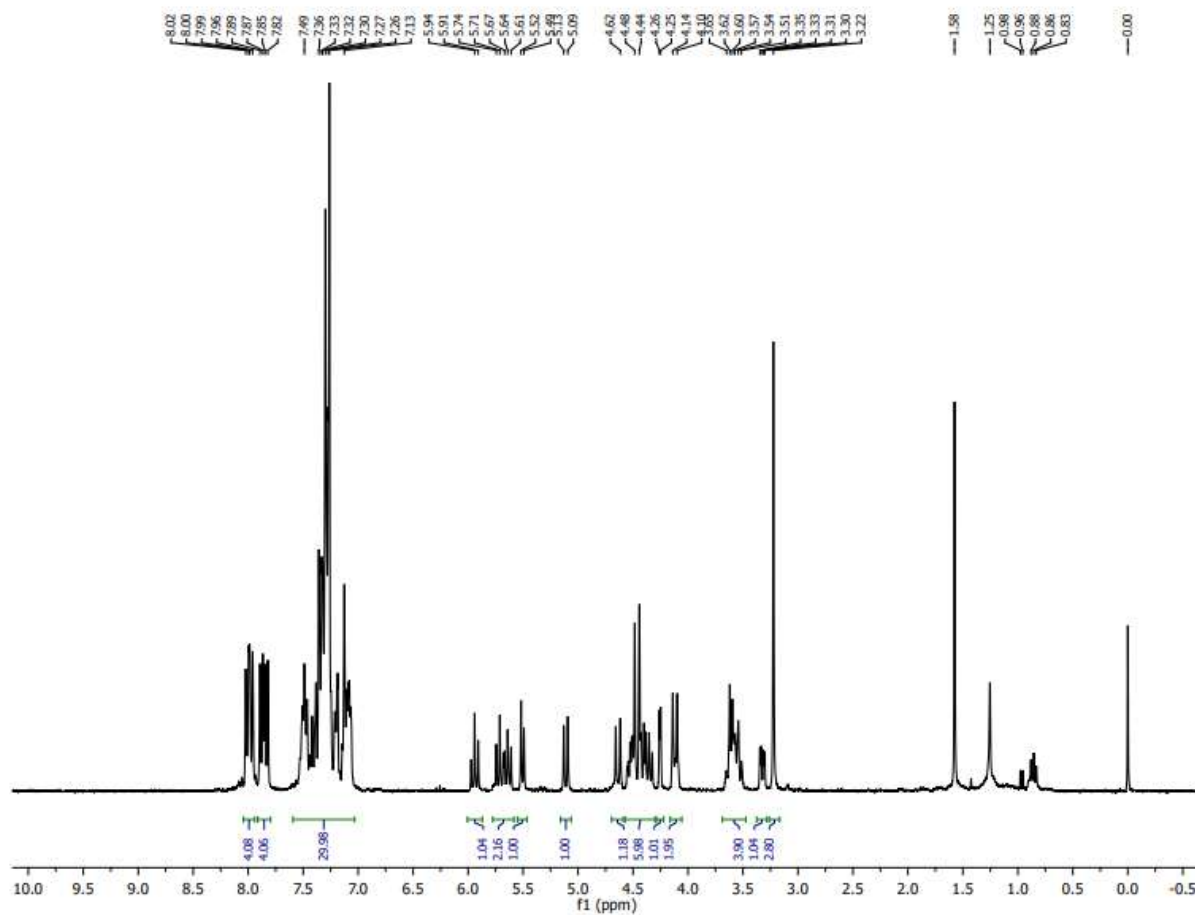
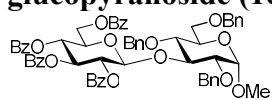
¹H NMR (300 MHz, CDCl₃)

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

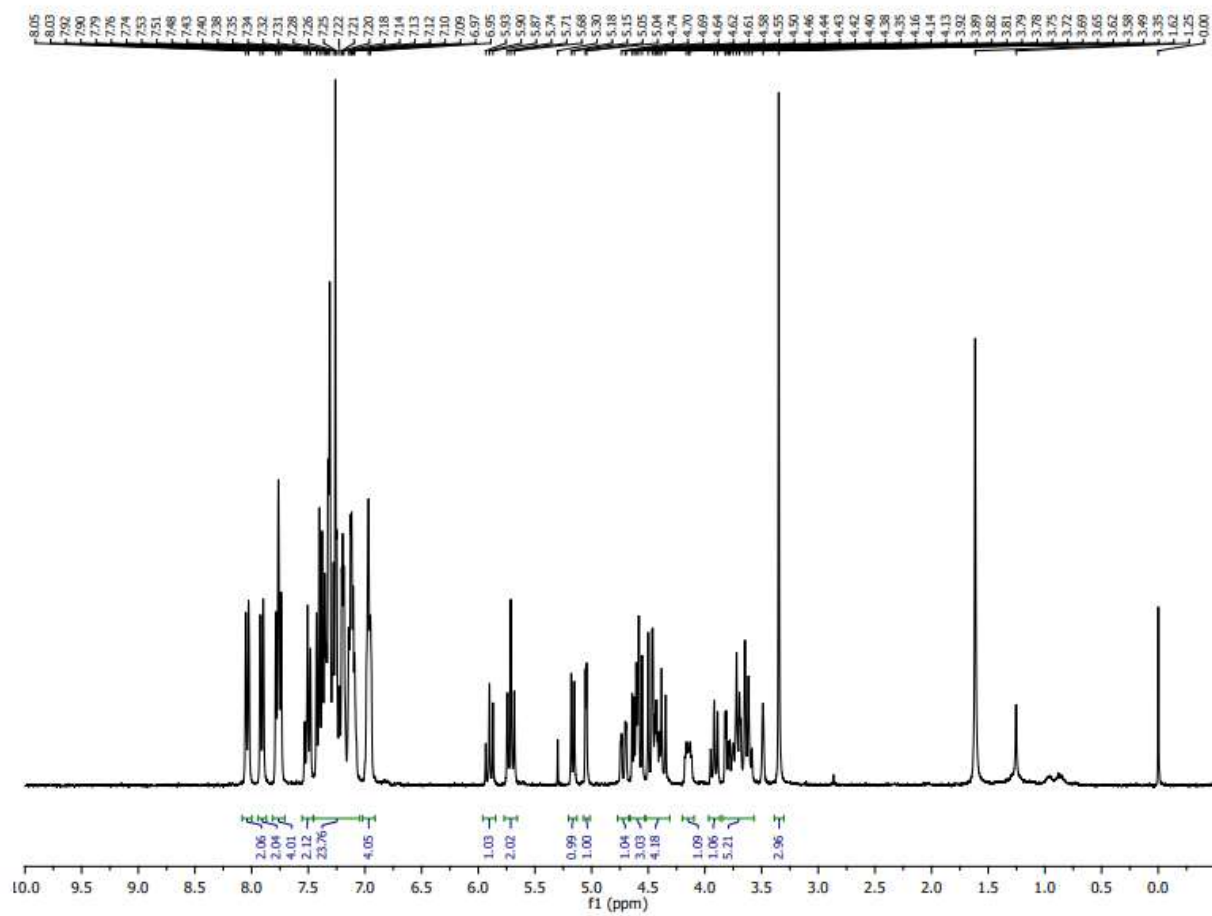
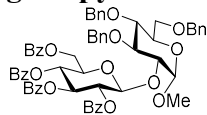


$^1\text{H NMR}$ (300 MHz, CDCl_3)

Methyl 3-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-2,4,6-tri-O-benzyl-α-D-glucopyranoside (16)

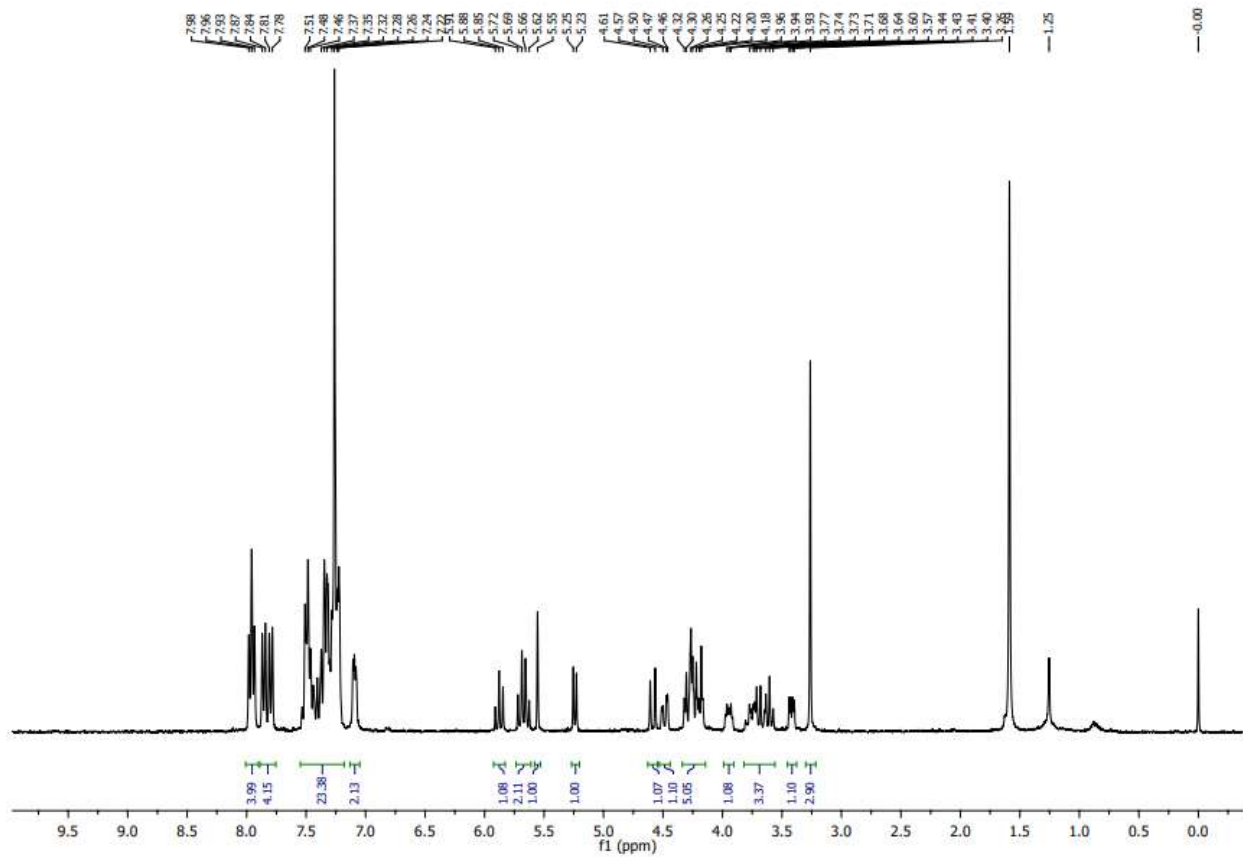
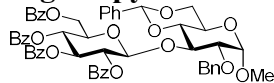


Methyl 2-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-3,4,6-tri-O-benzyl-α-D-glucopyranoside (17)



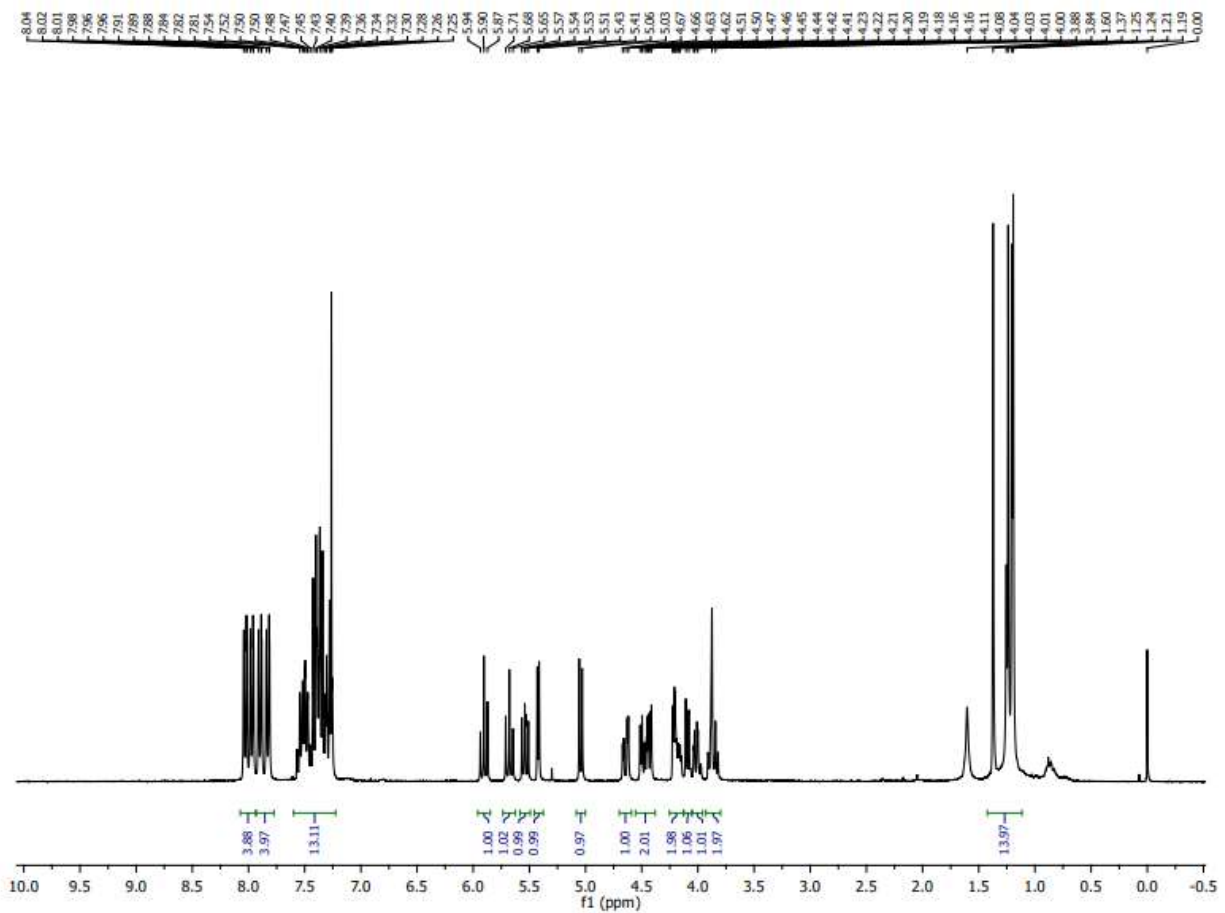
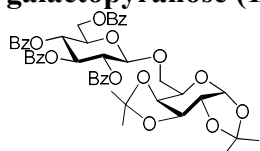
^1H NMR (300 MHz, CDCl_3)

Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside (18)



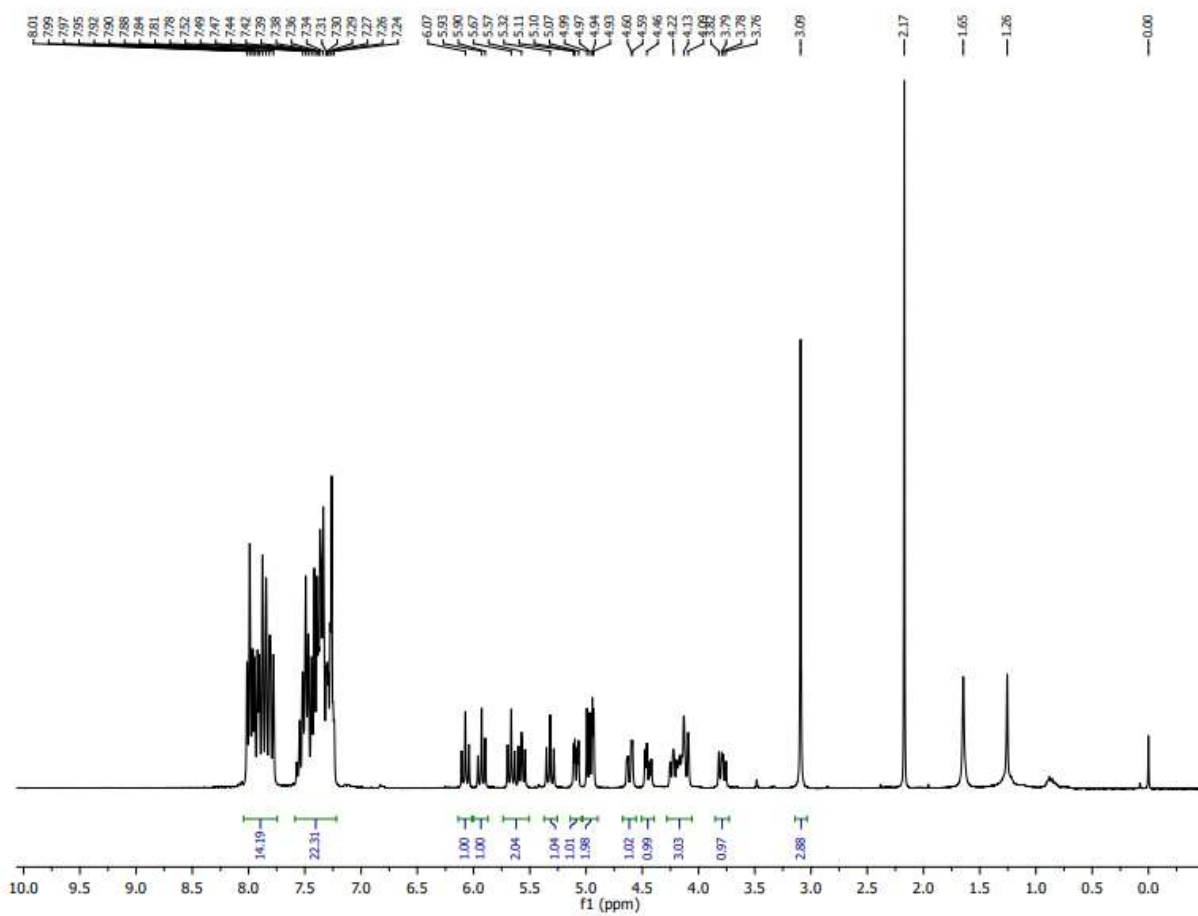
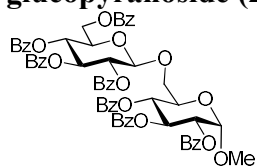
^1H NMR (300 MHz, CDCl_3)

6-*O*-(2,3,4,6-Tetra-*O*-benzoyl- β -D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (19)



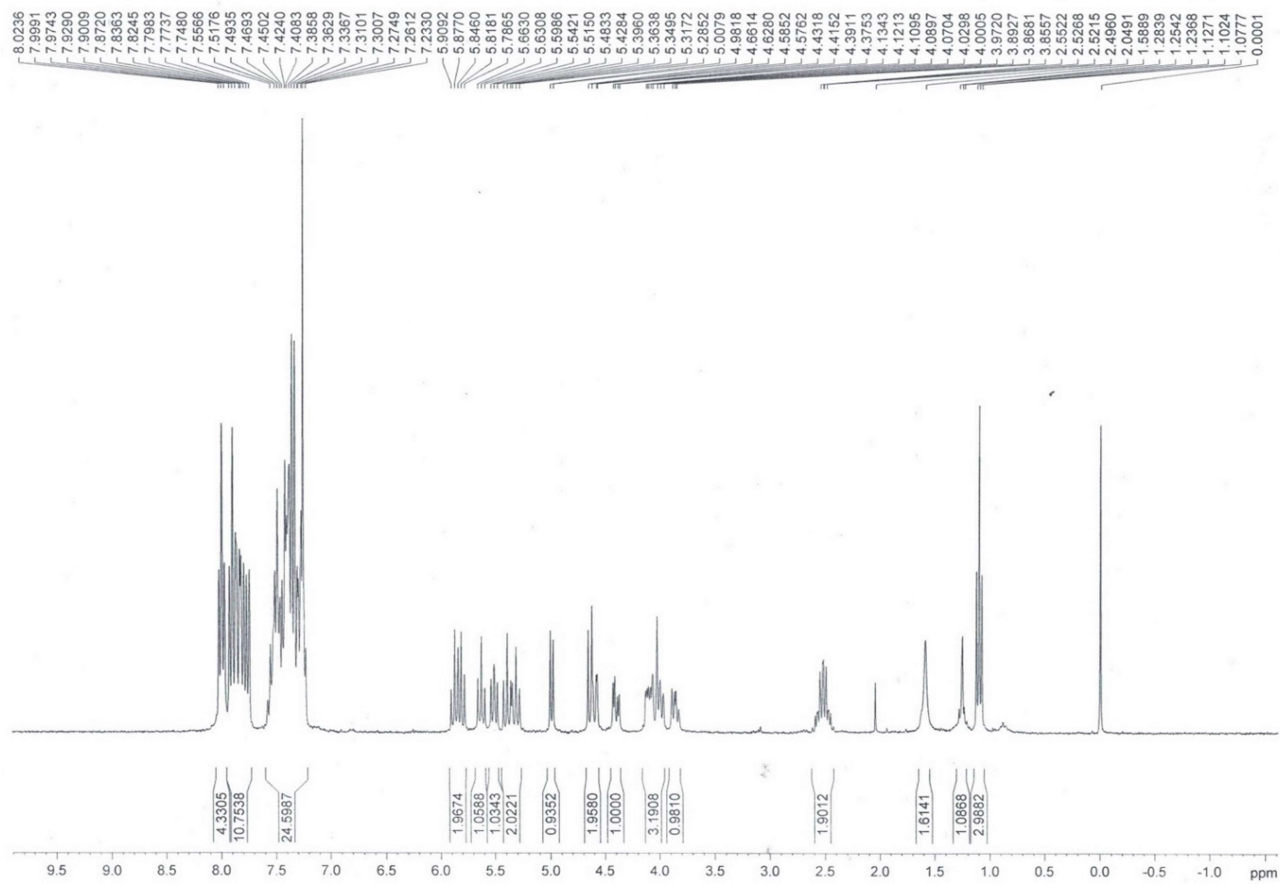
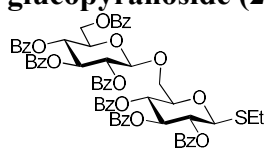
^1H NMR (300 MHz, CDCl_3)

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranosyl)- α -D-glucopyranoside (20)



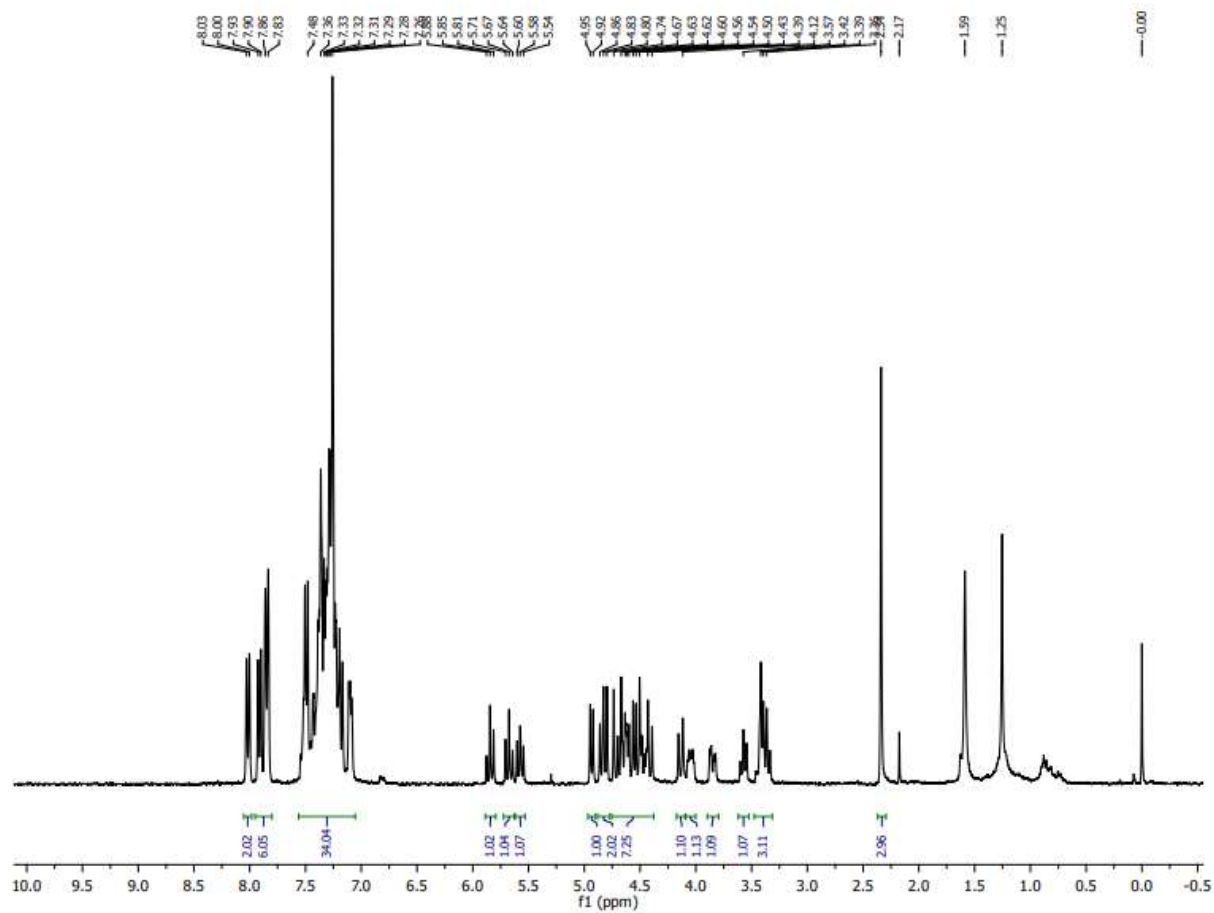
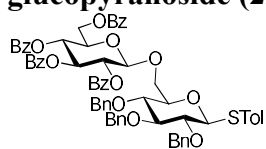
^1H NMR (300 MHz, CDCl_3)

Ethyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (21)



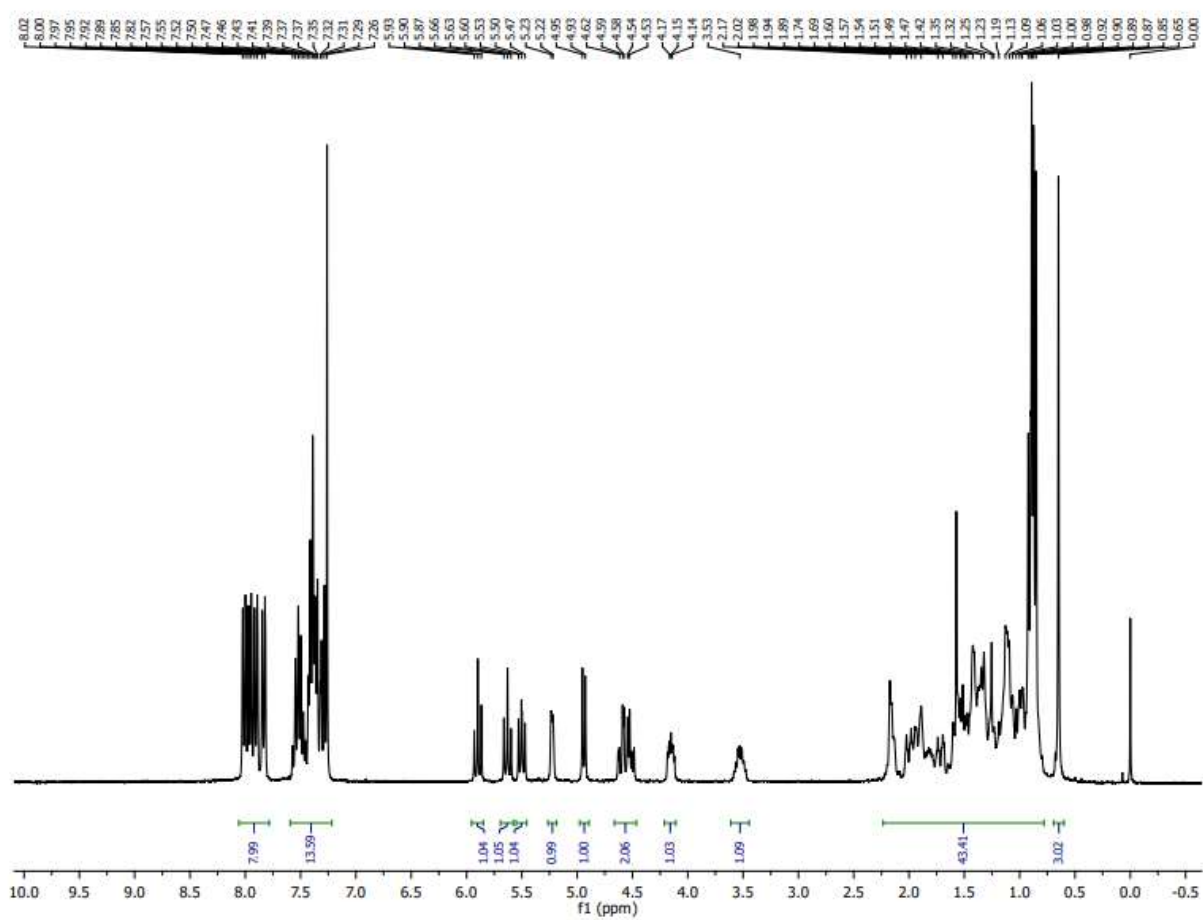
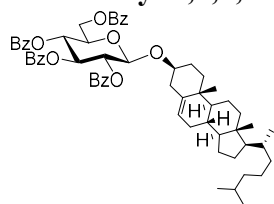
¹H NMR (300 MHz, CDCl₃)

p-Tolyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranosyl)-1-thio- β -D-glucopyranoside (22)



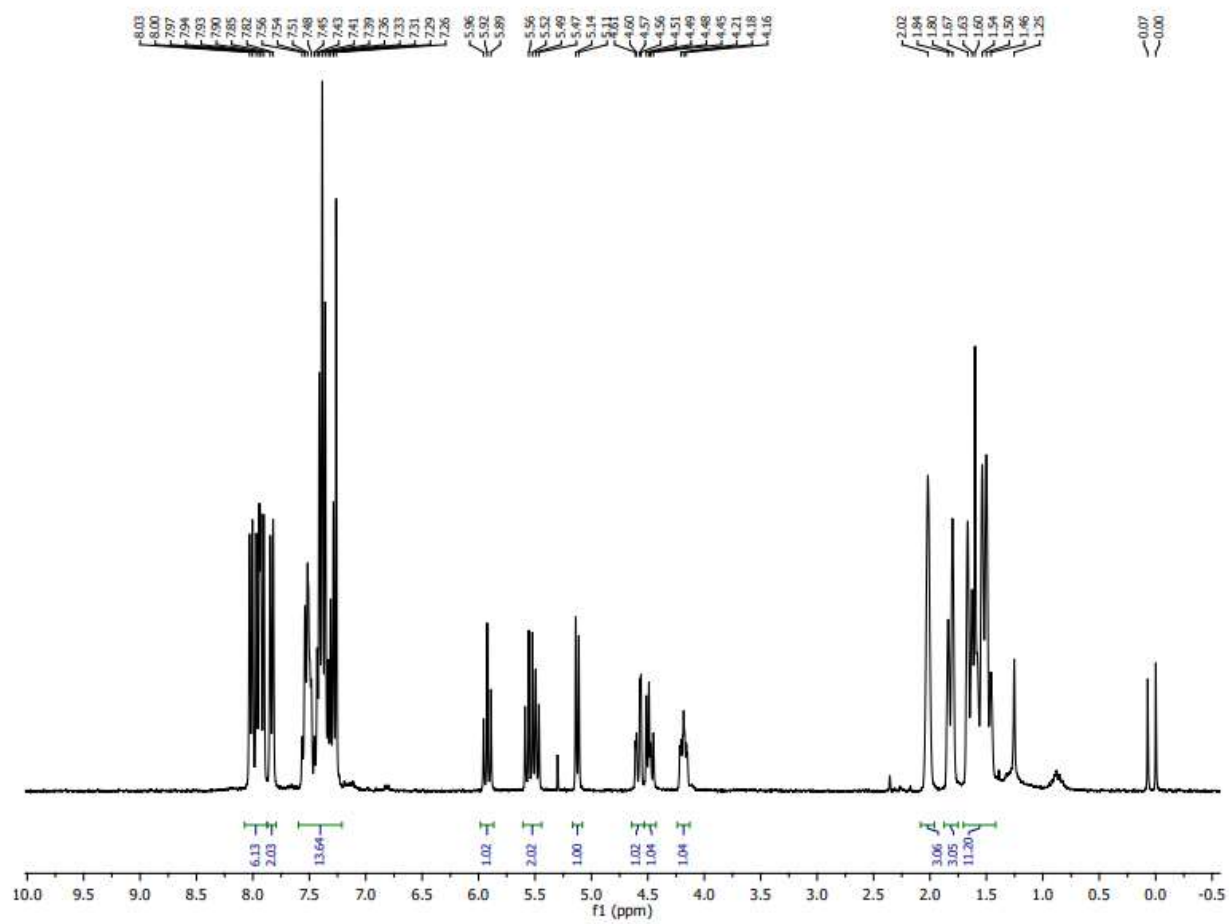
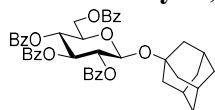
$^1\text{H NMR}$ (300 MHz, CDCl_3)

Cholesteryl 2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranoside (23)



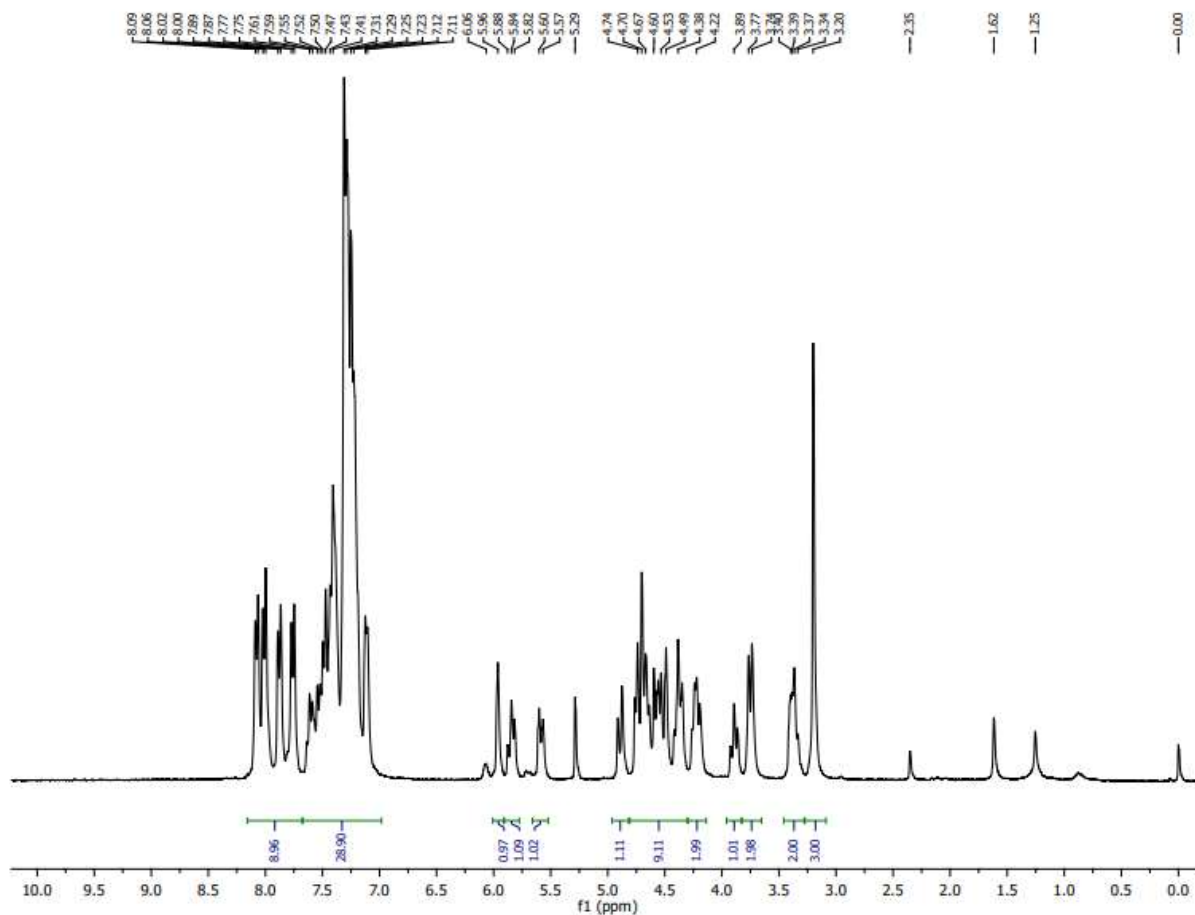
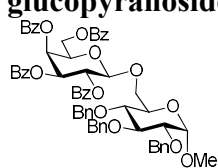
^1H NMR (300 MHz, CDCl_3)

1-Adamantyl 2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranoside (24)



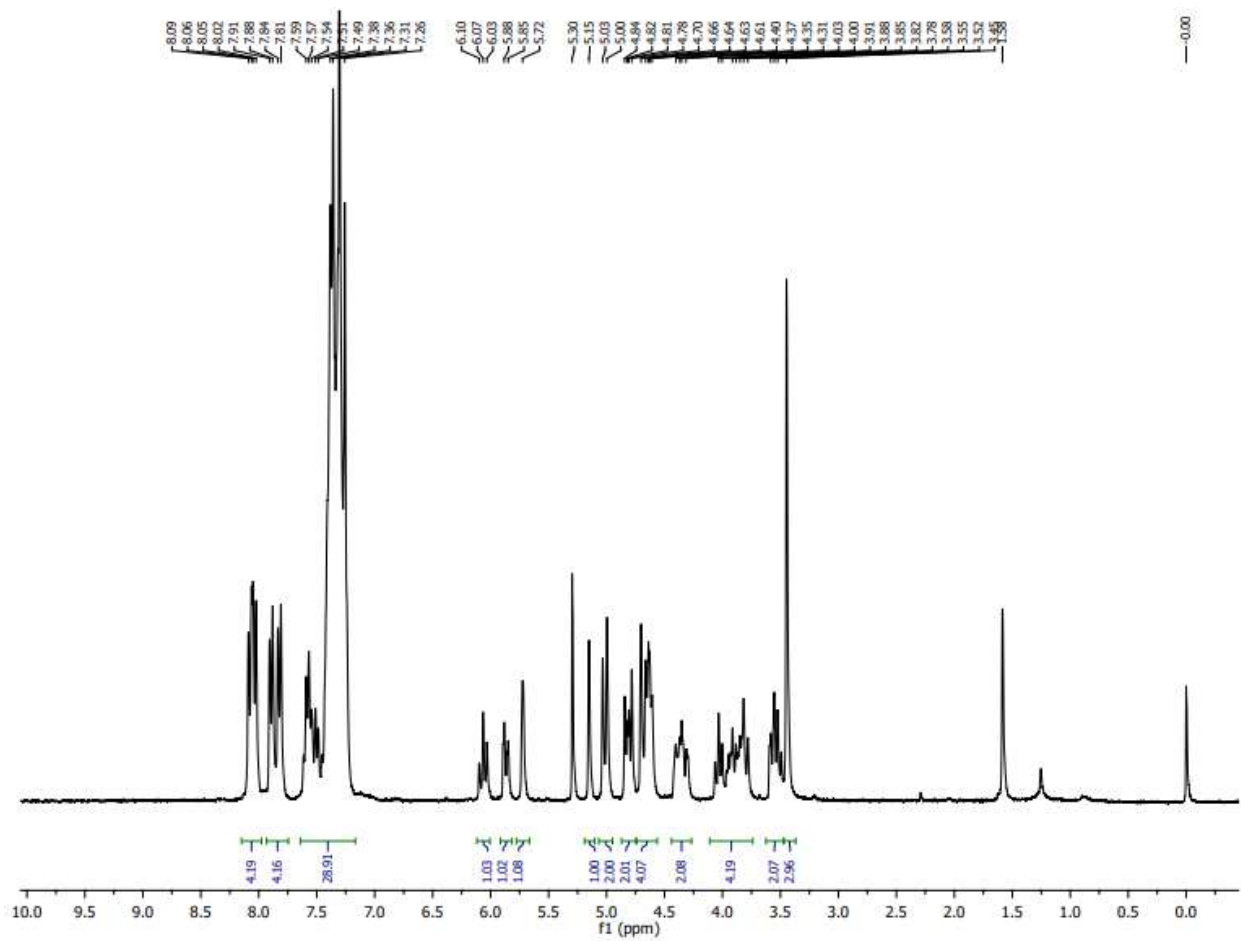
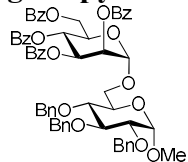
^1H NMR (300 MHz, CDCl_3)

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl- β -D-galactopyranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (37)



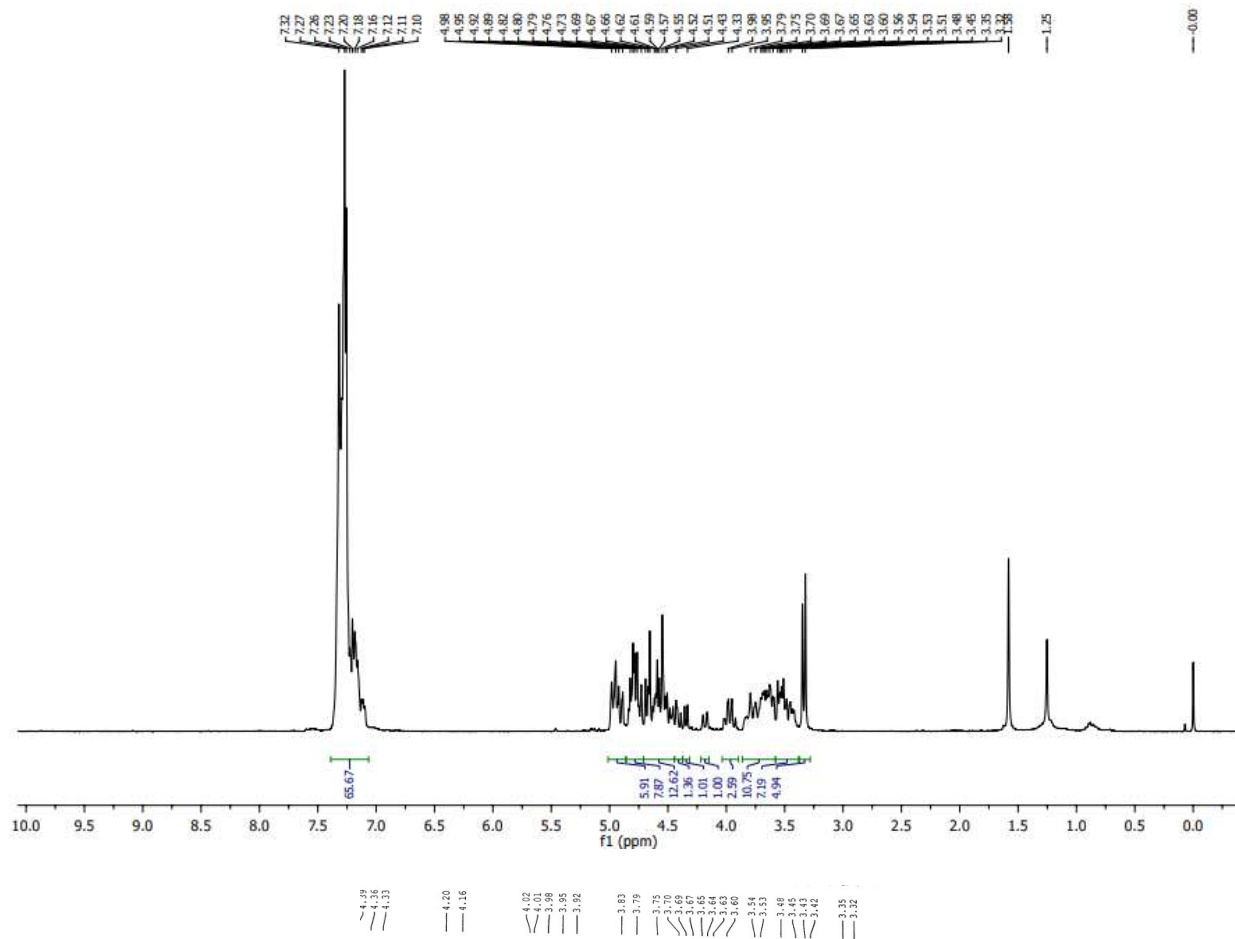
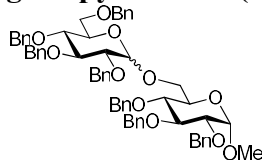
$^1\text{H NMR}$ (300 MHz, CDCl_3)

Methyl 6-O-(2,3,4,6-tetra-O-benzoyl- α -D-mannopyranosyl)-2,3,4-tri-O-benzyl- α -D-glucopyranoside (38)

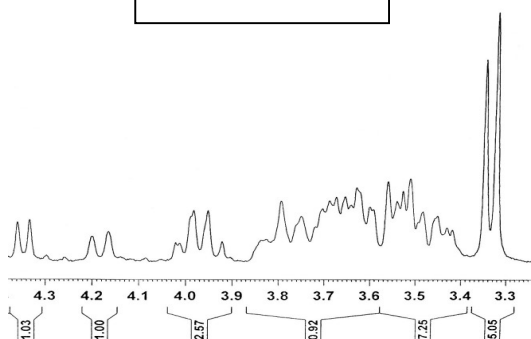


^1H NMR (300 MHz, CDCl_3)

Methyl 6-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranosyl)-2,3,4-tri-O-benzyl- α -D-glucopyranoside (39) ($\alpha/\beta = 1/1.5$)

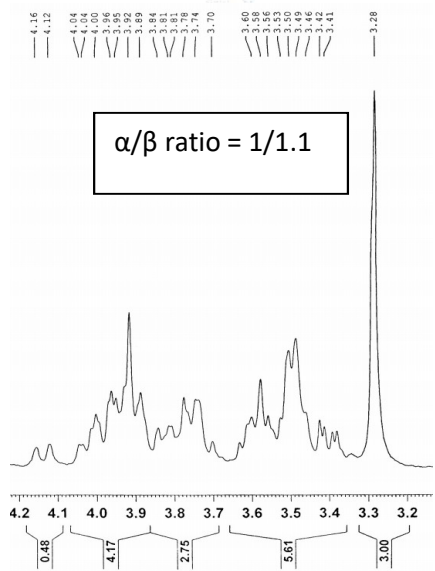
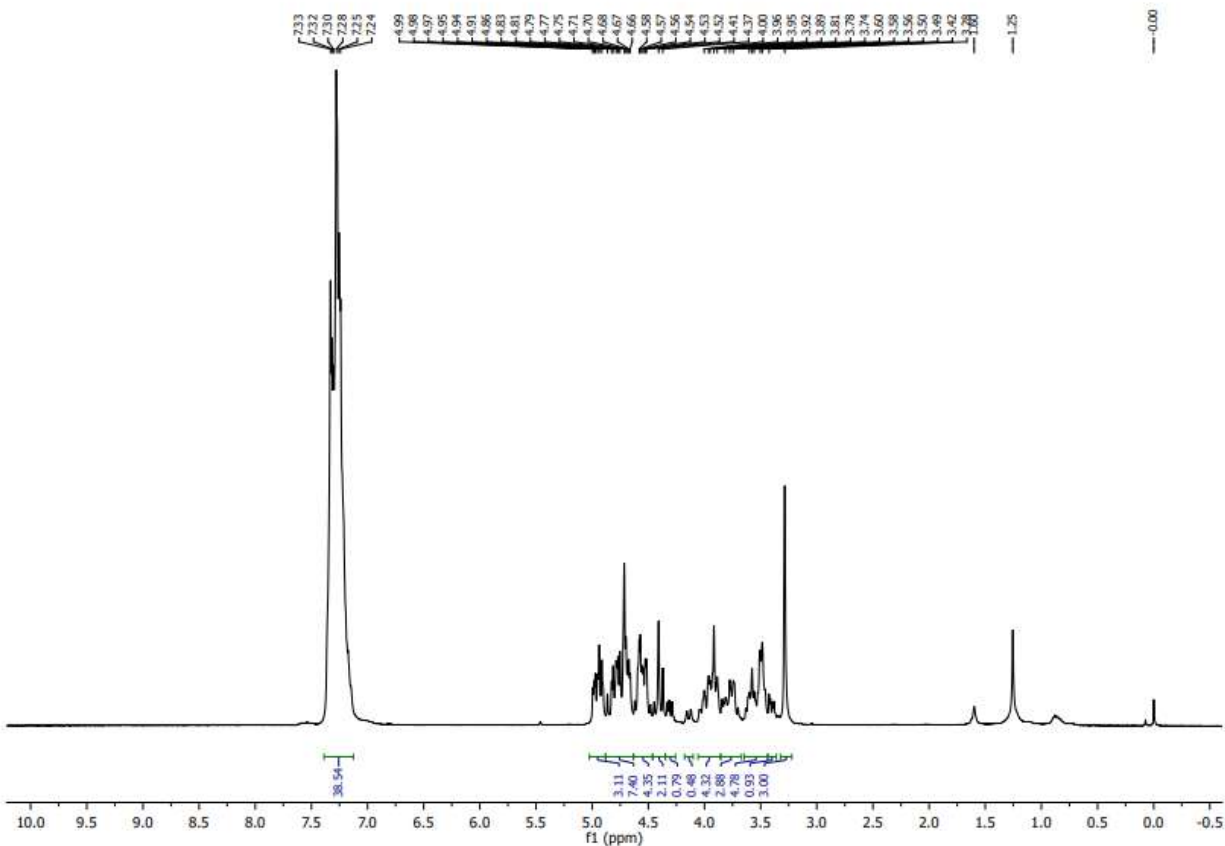
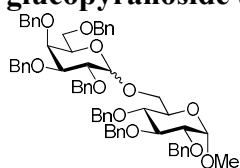


α/β ratio = 1/1.5



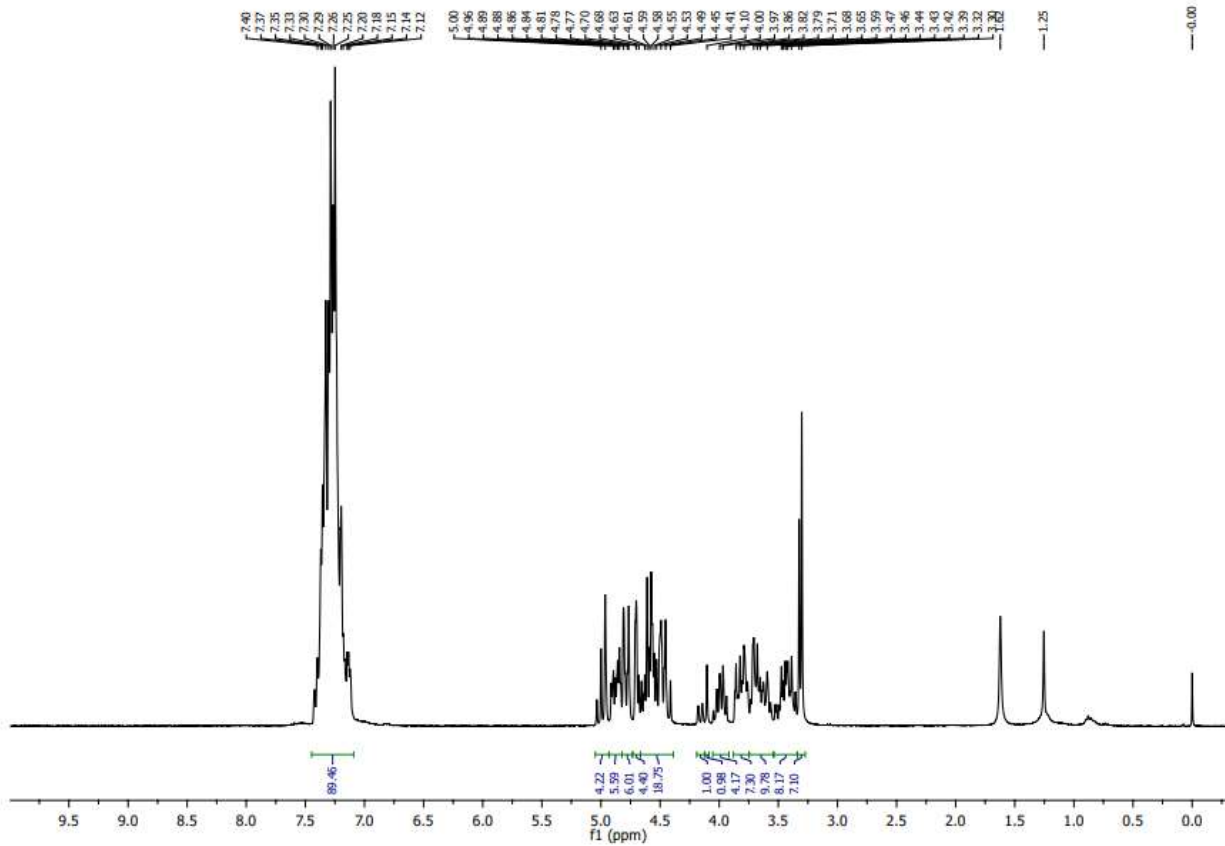
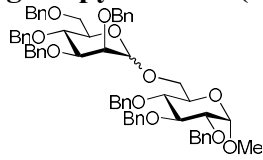
$^1\text{H NMR}$ (300 MHz, CDCl_3)

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (40) ($\alpha/\beta = 1/1.1$)



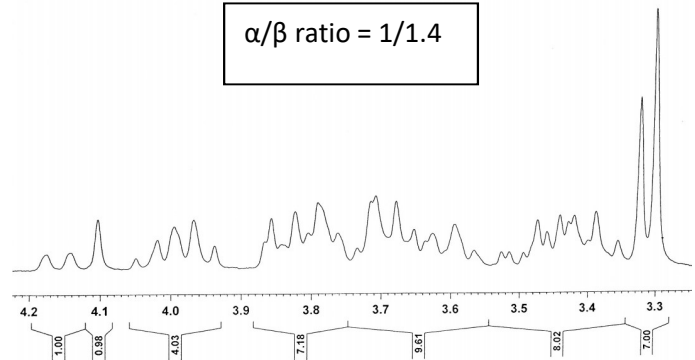
$^1\text{H NMR}$ (300 MHz, CDCl_3)

Methyl 6-O-(2,3,4,6-tetra-O-benzyl-D-mannopyranosyl)-2,3,4-tri-O-benzyl- α -D-glucopyranoside (41) ($\alpha/\beta = 1/1.4$)



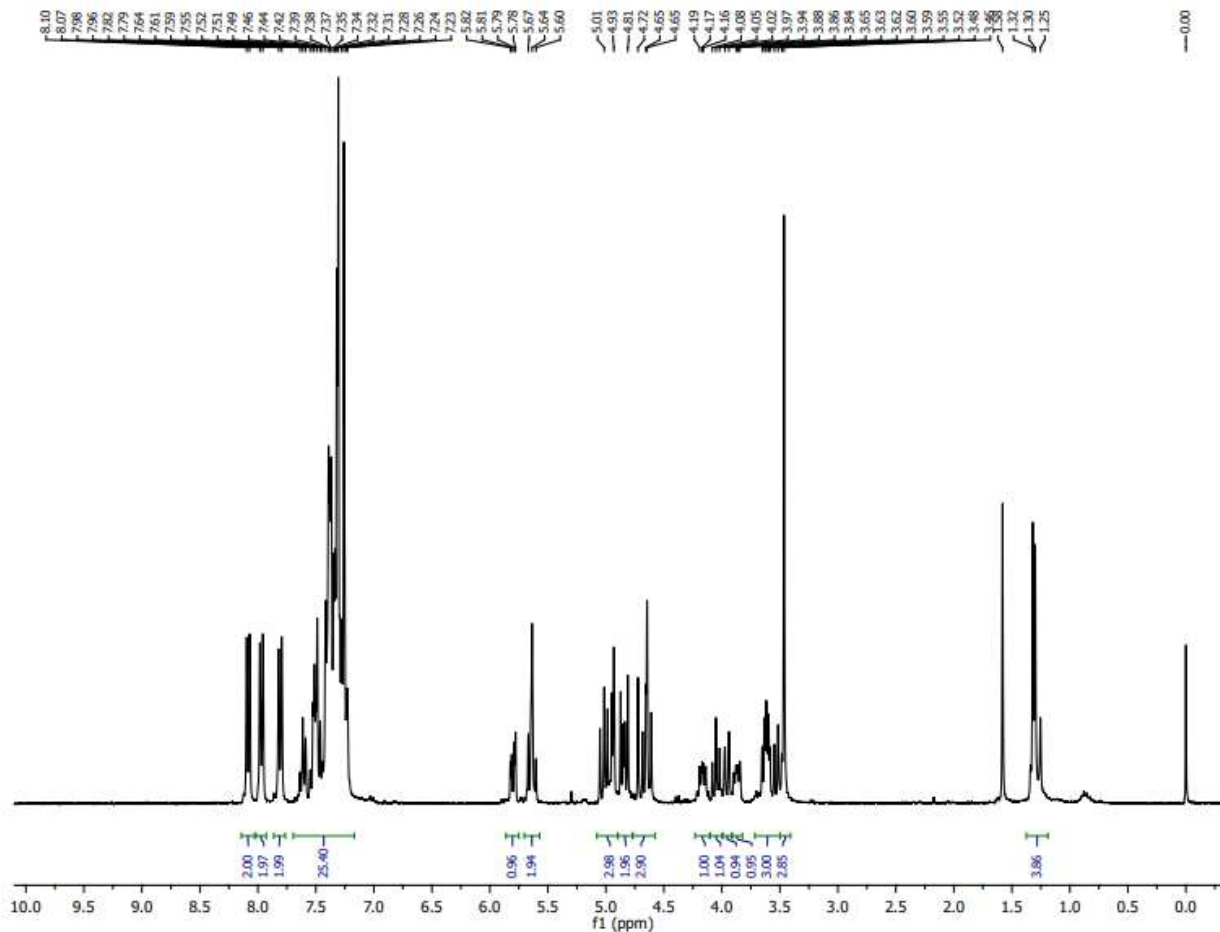
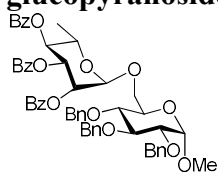
6.18
6.14
6.10
6.05
6.02
6.00
5.97
5.94
3.86
3.84
3.82
3.80
3.79
3.76
3.73
3.71
3.71
3.68
3.65
3.63
3.59
3.57
3.53
3.51
3.49
3.47
3.46
3.43
3.42
3.39
3.36
3.32
3.30

α/β ratio = 1/1.4



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

Methyl 6-*O*-(2,3,4-tri-*O*-benzoyl- α -L-rhamnopyranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (45)



^1H NMR (300 MHz, CDCl_3)