

# SUPPORTING INFORMATION

## Synthesis of Arabinoxylan Oligosaccharides by Pre-Activation-Based Iterative Glycosylations

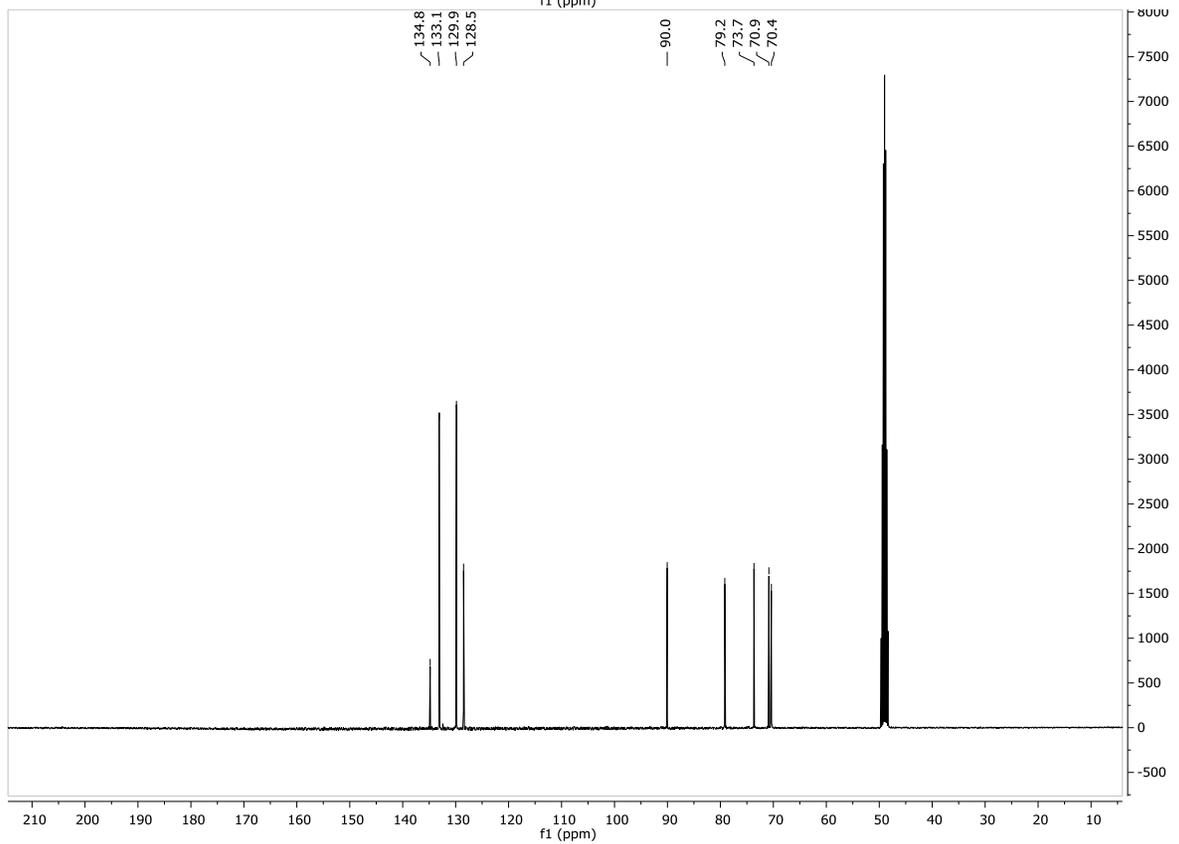
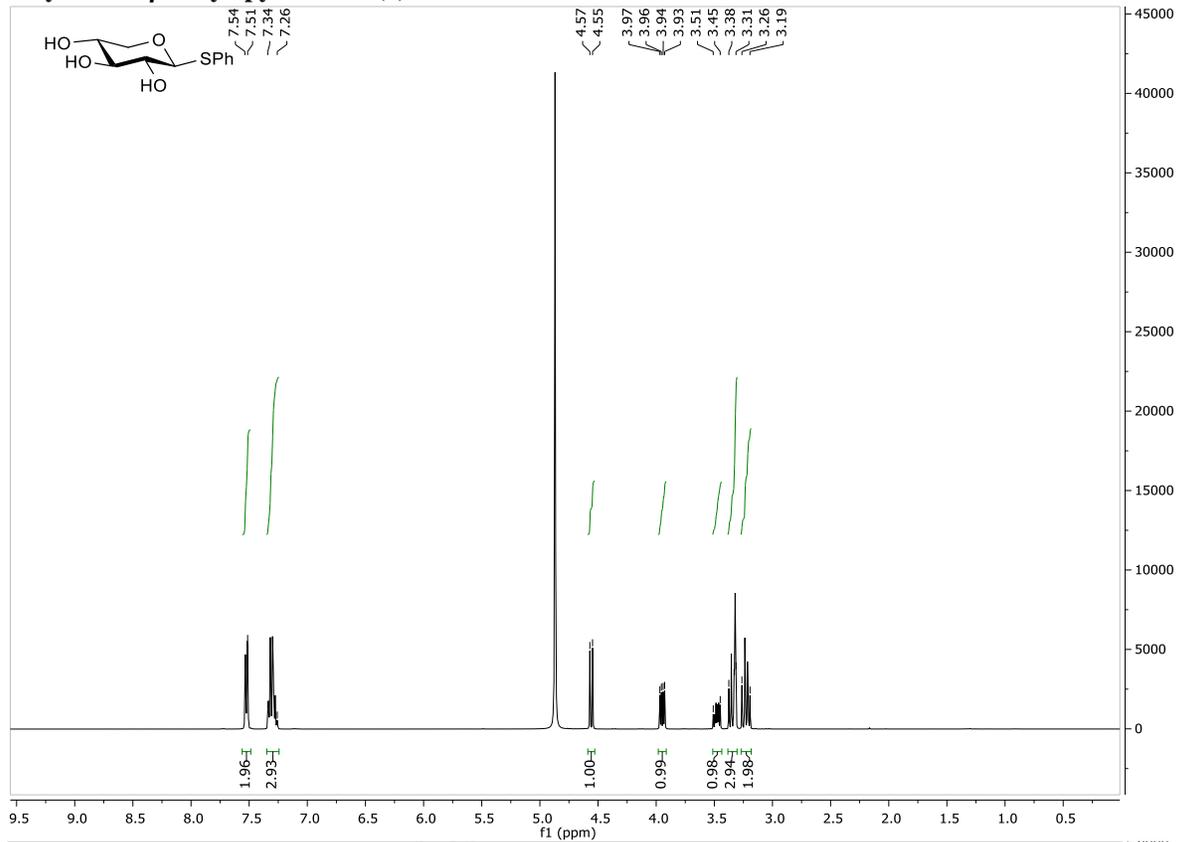
Emilie N. Underlin, Maximilian Böhm and Robert Madsen\*

*Department of Chemistry, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark*

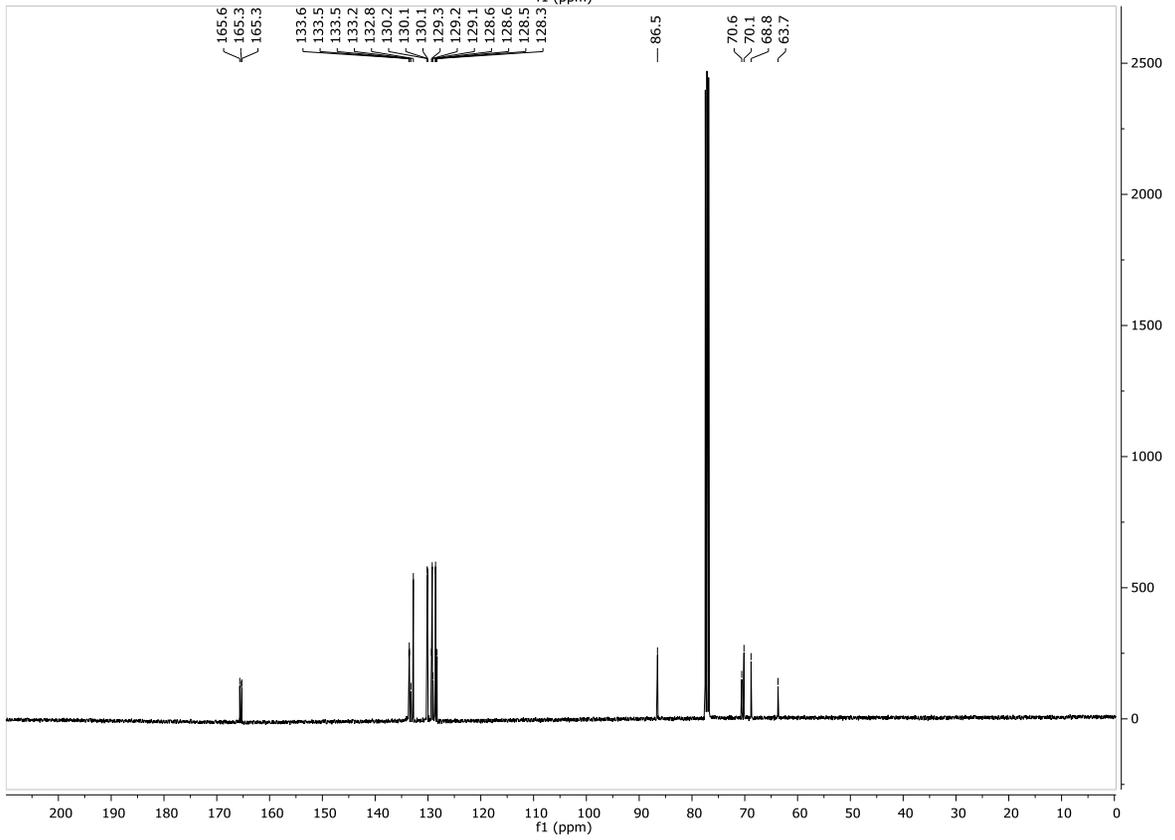
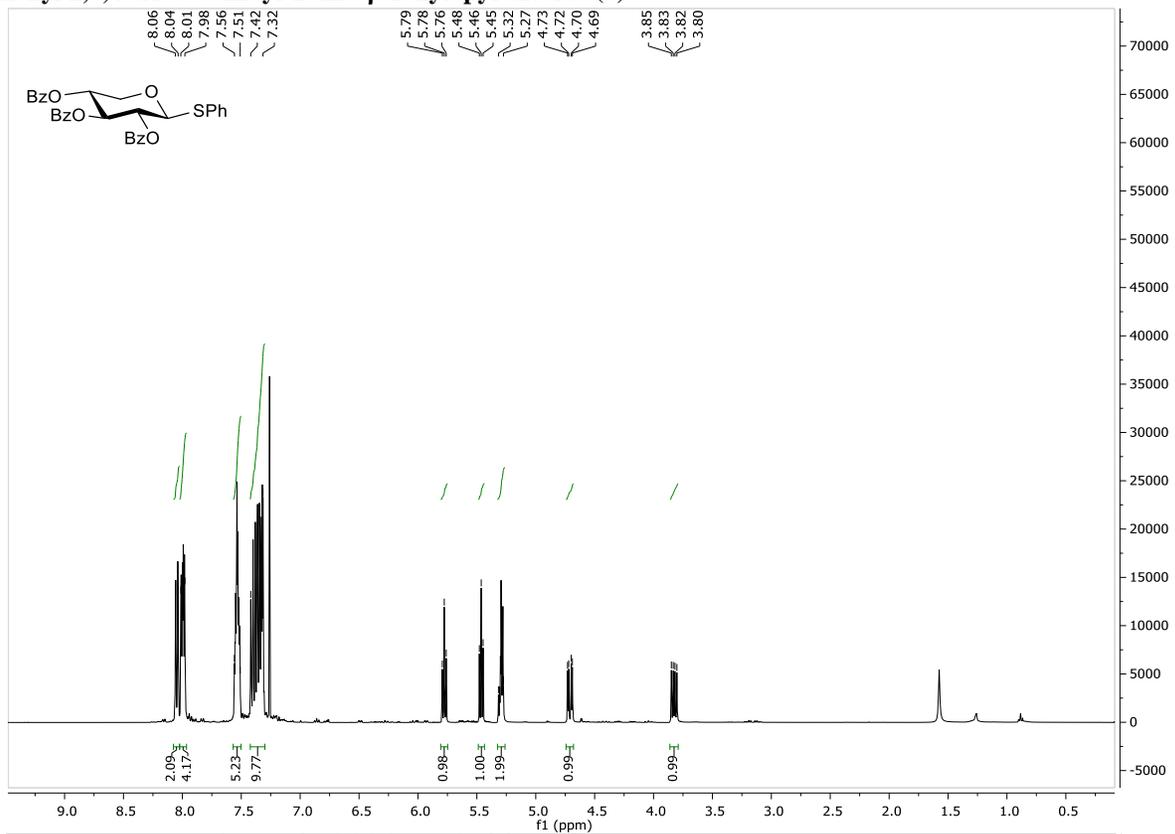
### Table of Contents

|  | Page     |
|--|----------|
| $^1\text{H}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for the prepared compounds<br>and 2D NMR spectra for compounds <b>1 – 3</b> | S2 – S48 |

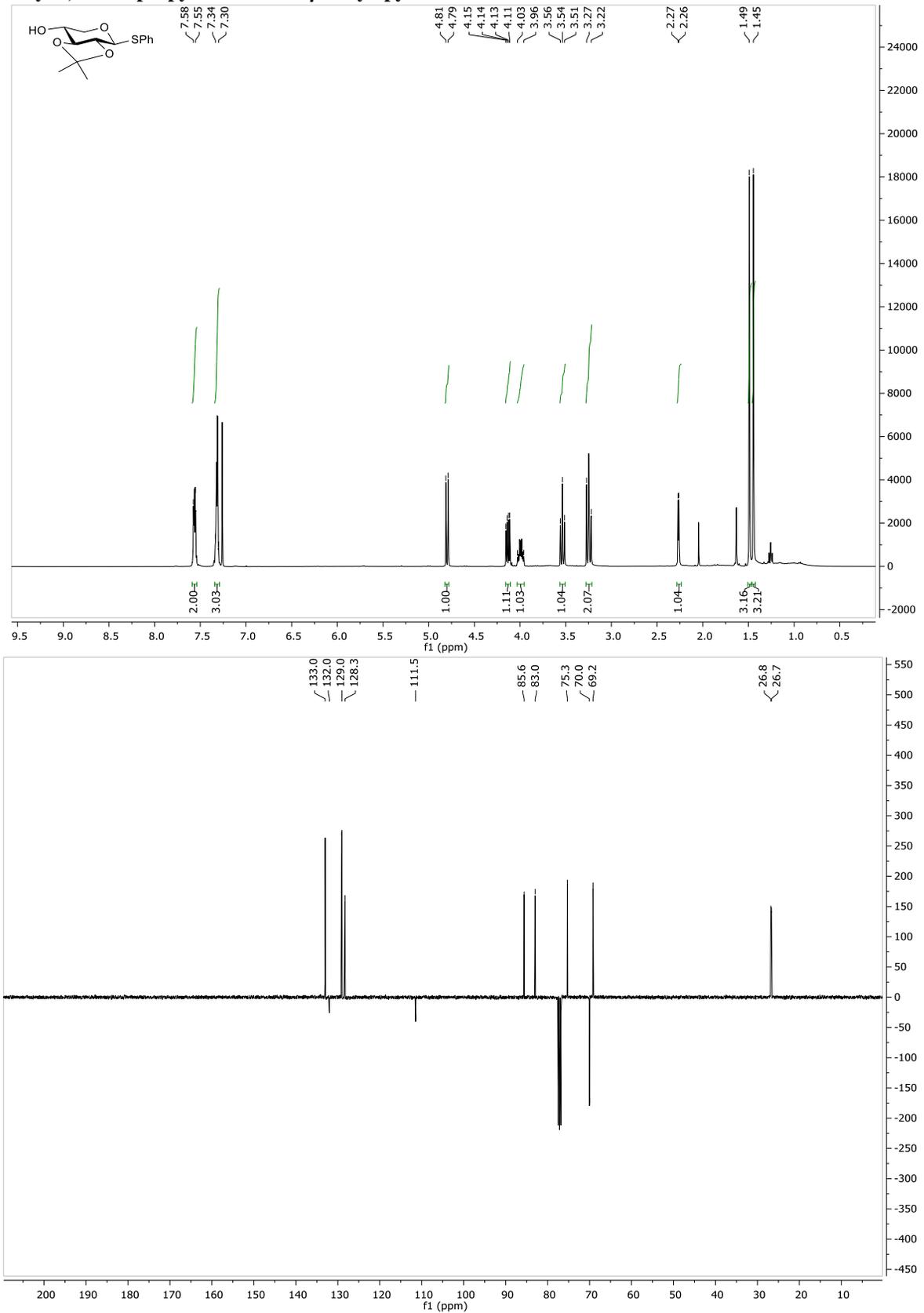
Phenyl 1-thio-β-D-xylopyranoside (7)



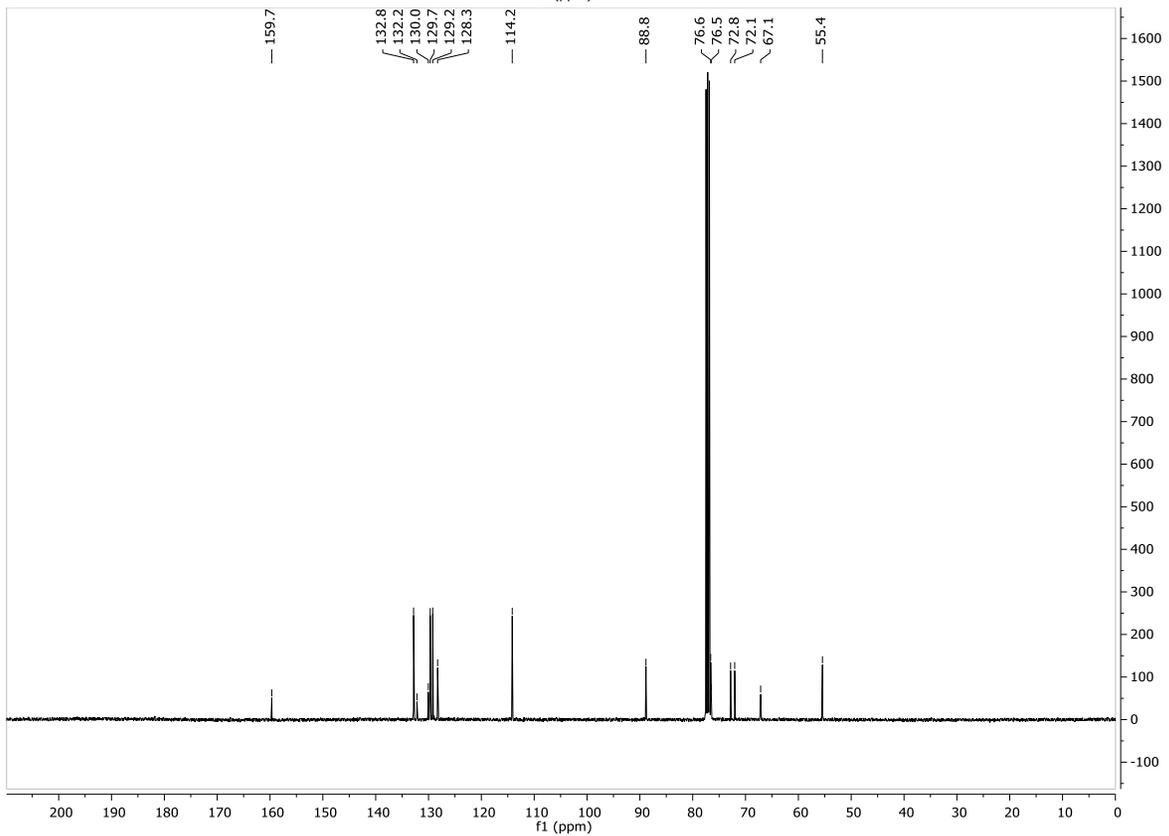
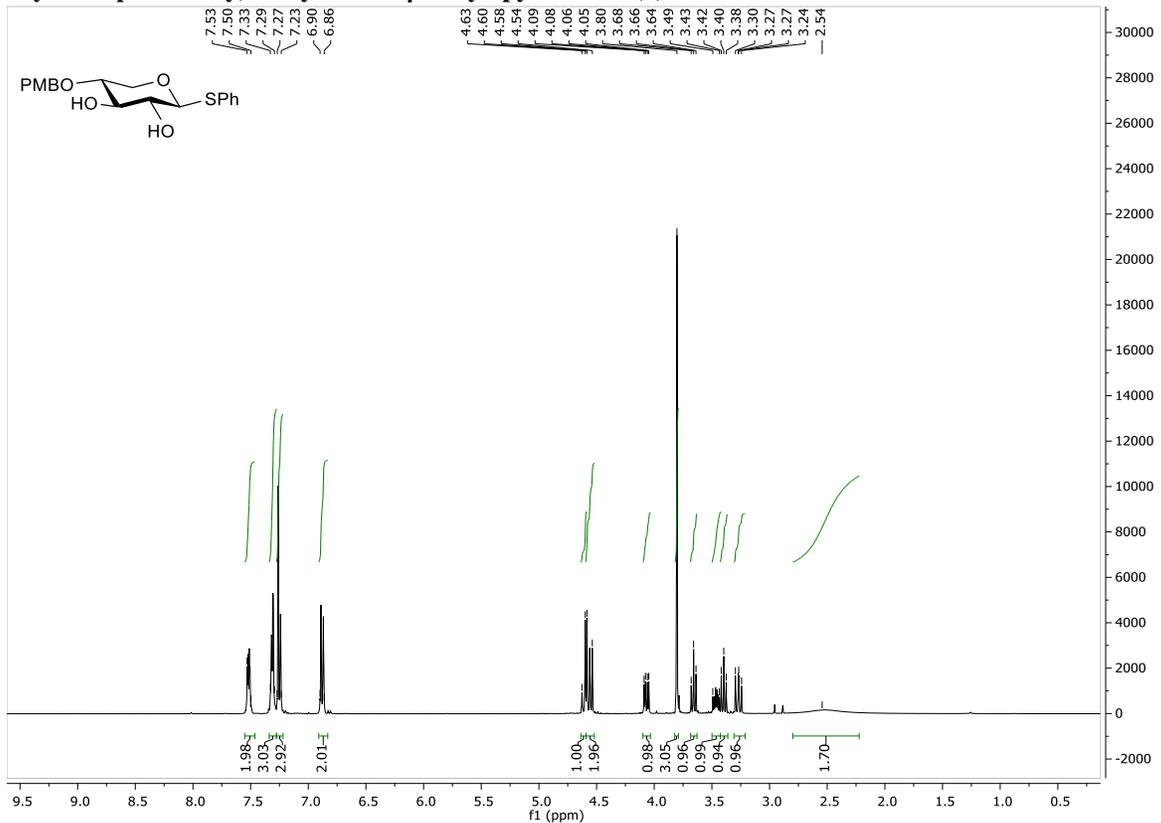
Phenyl 2,3,4-tri-*O*-benzoyl-1-thio- $\beta$ -D-xylopyranoside (5)



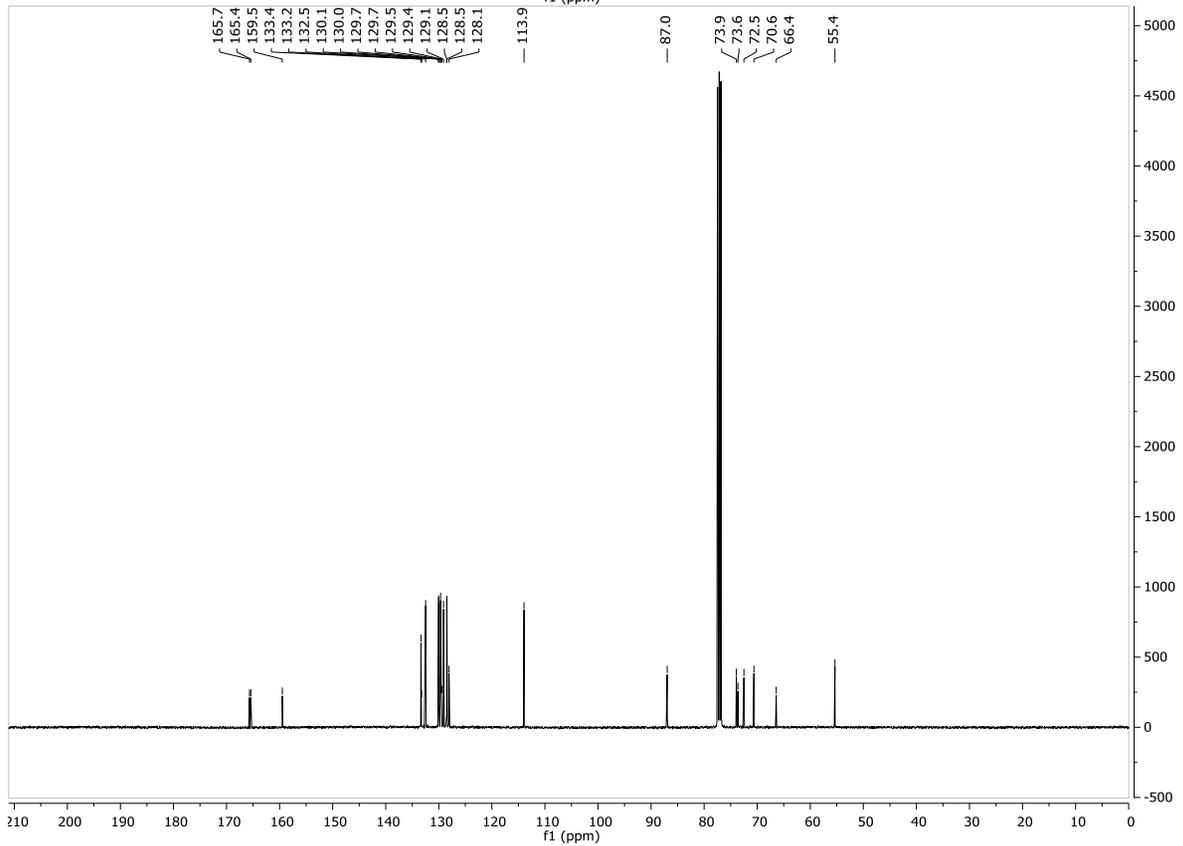
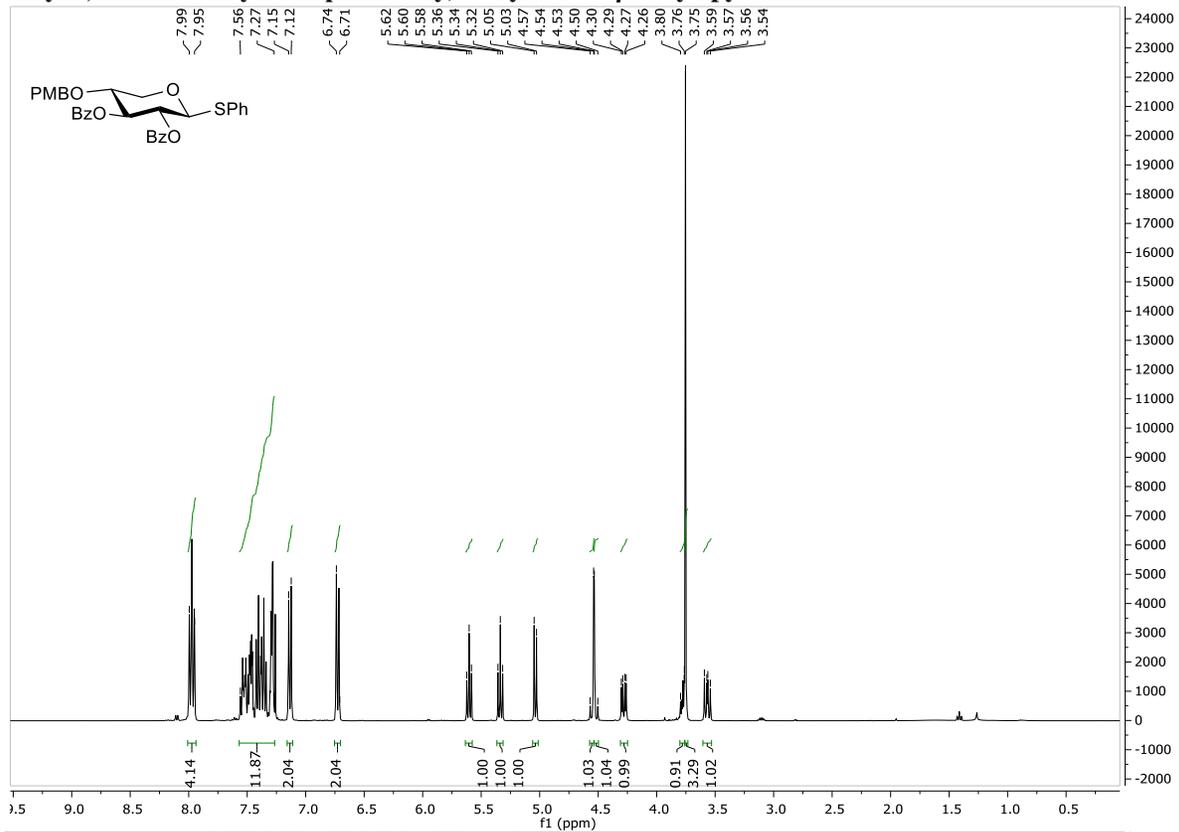
**Phenyl 2,3-*O*-isopropylidene-1-thio-β-D-xylopyranoside**



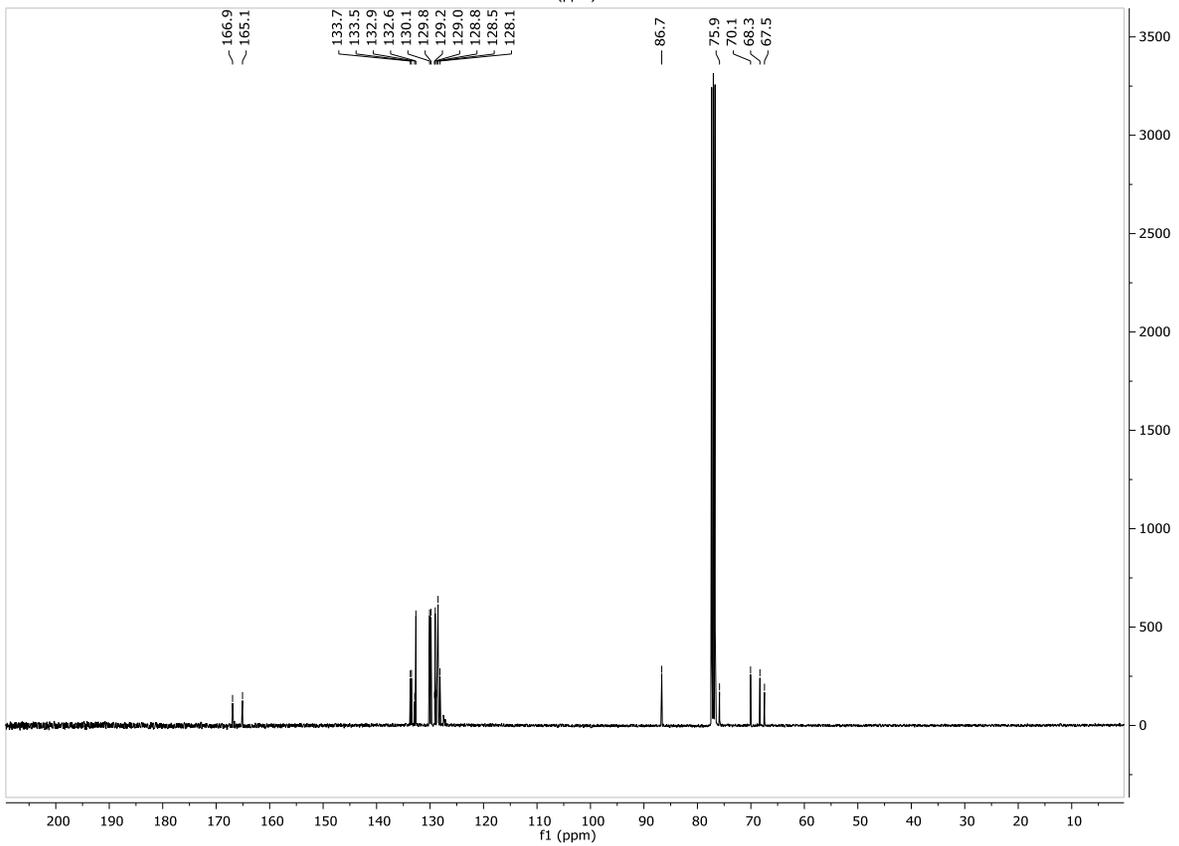
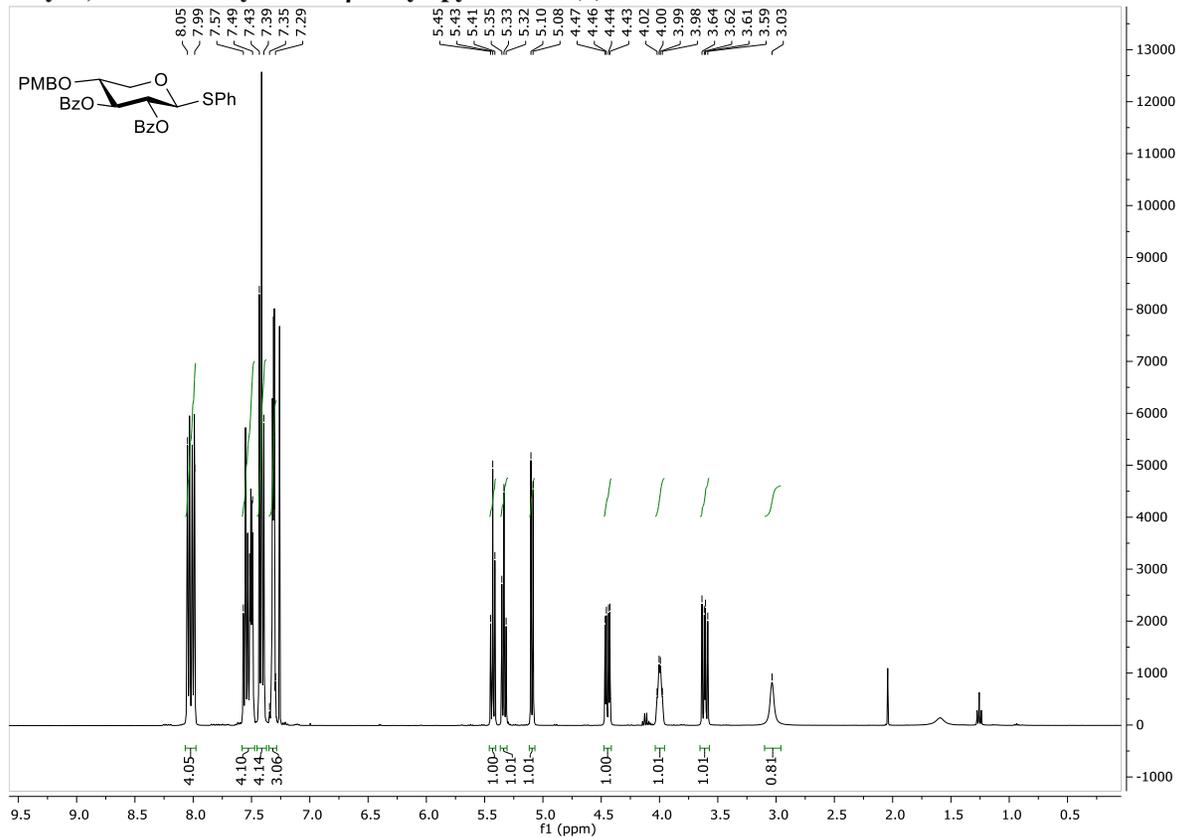
Phenyl 4-*O*-(*p*-methoxy)benzyl-1-thio- $\beta$ -D-xylopyranoside (8)



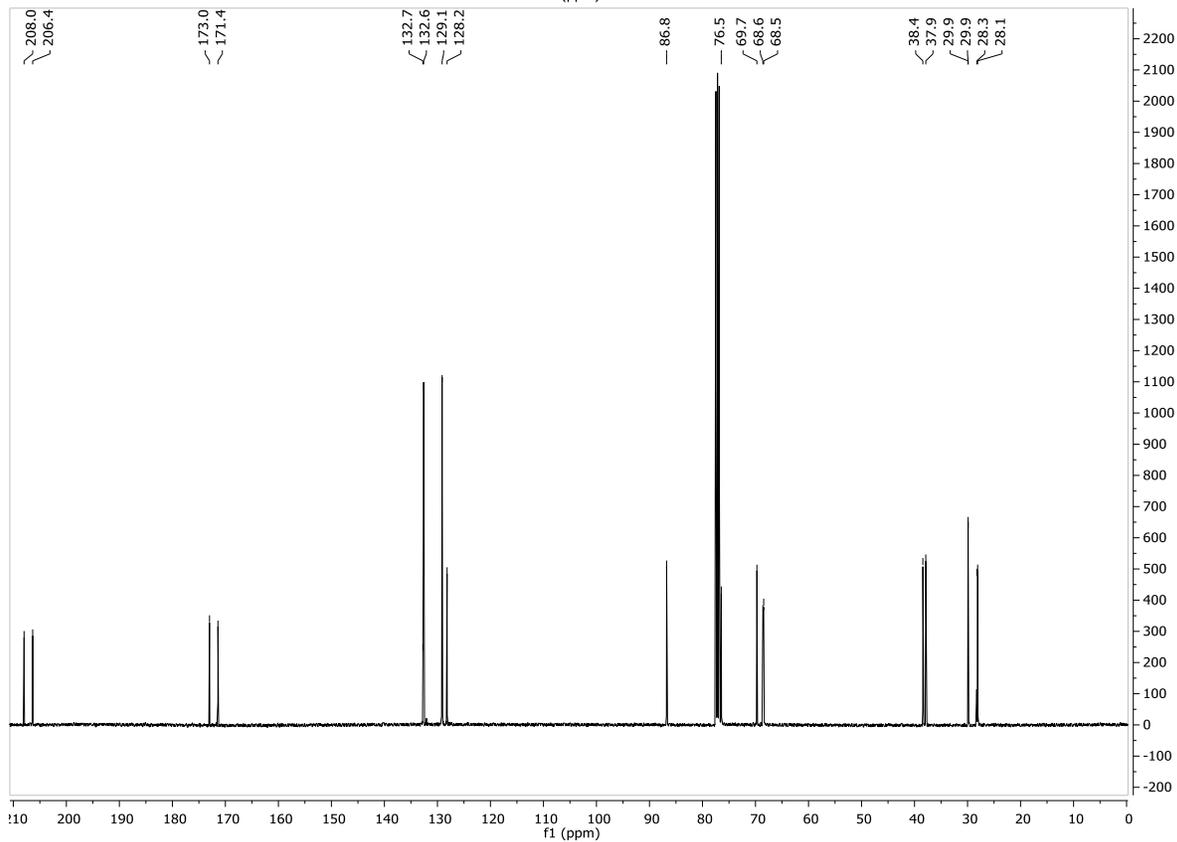
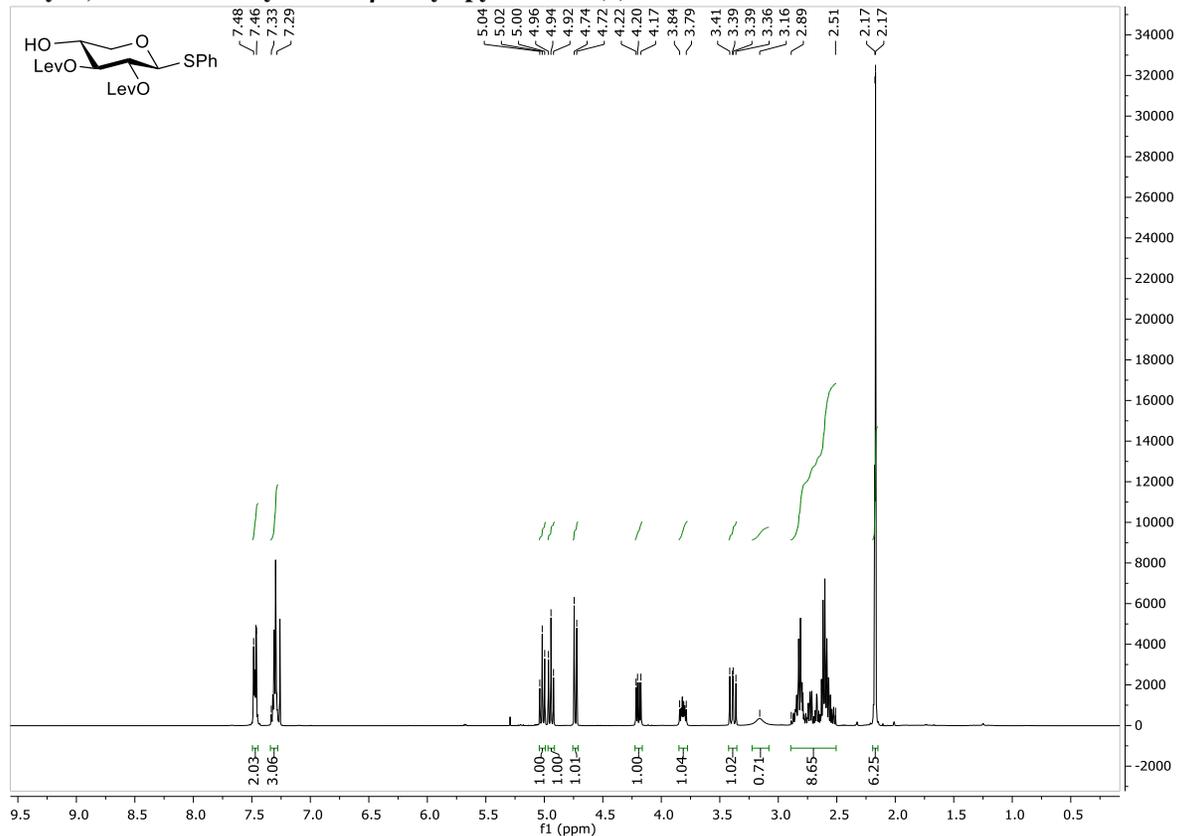
**Phenyl 2,3-di-O-benzoyl-4-O-(p-methoxy)benzyl-1-thio-β-D-xylopyranoside**



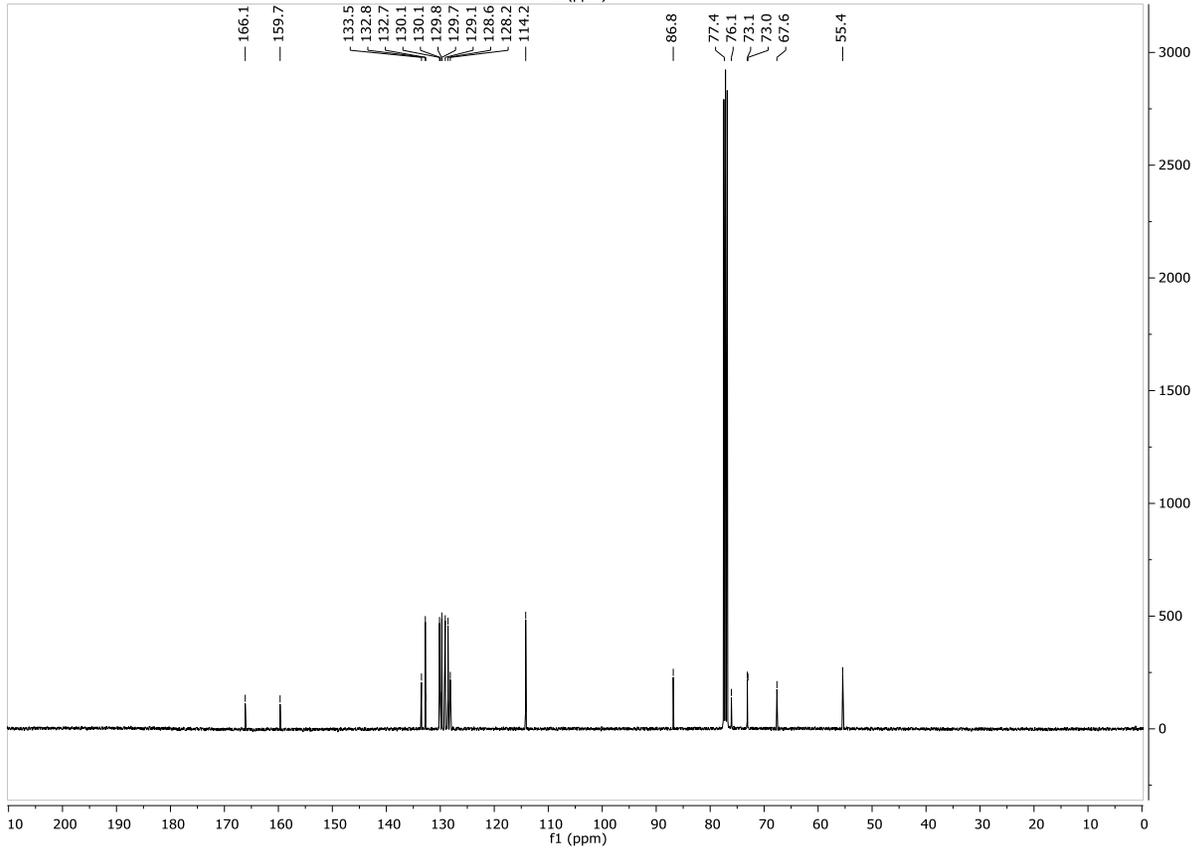
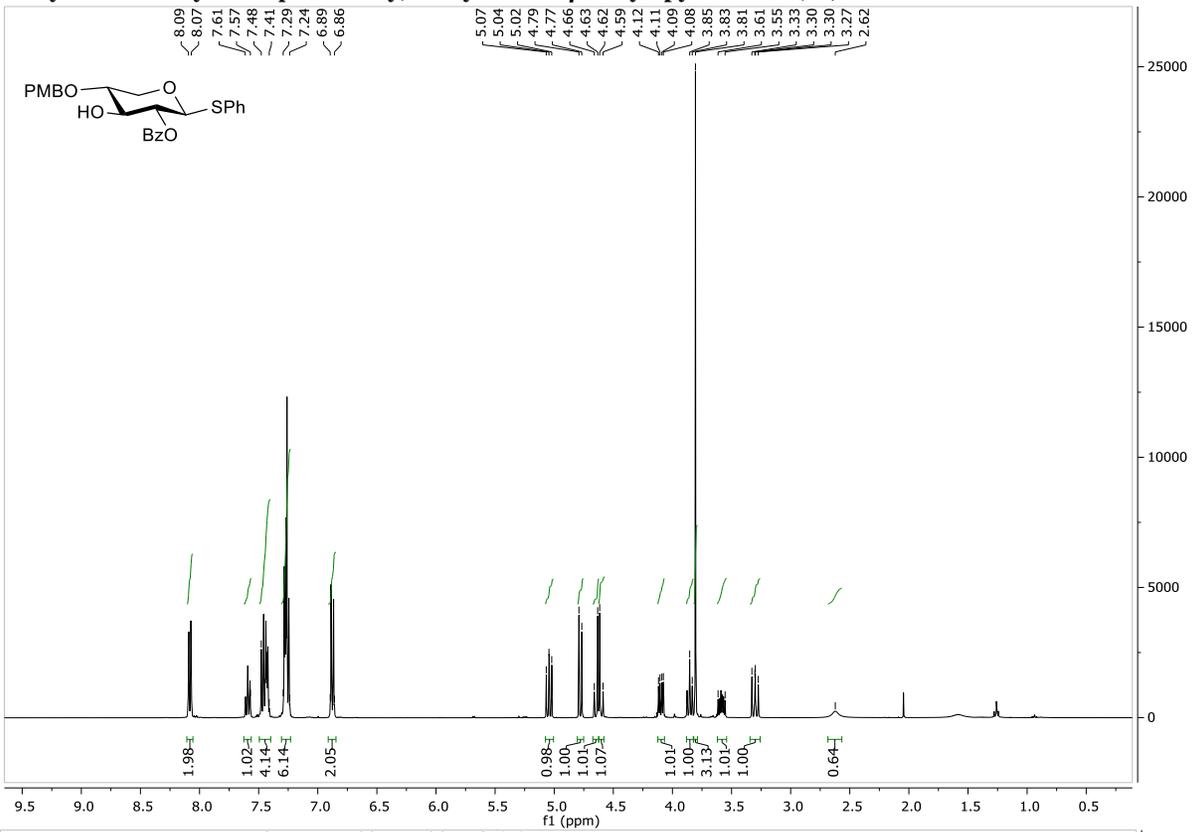
Phenyl 2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (6)



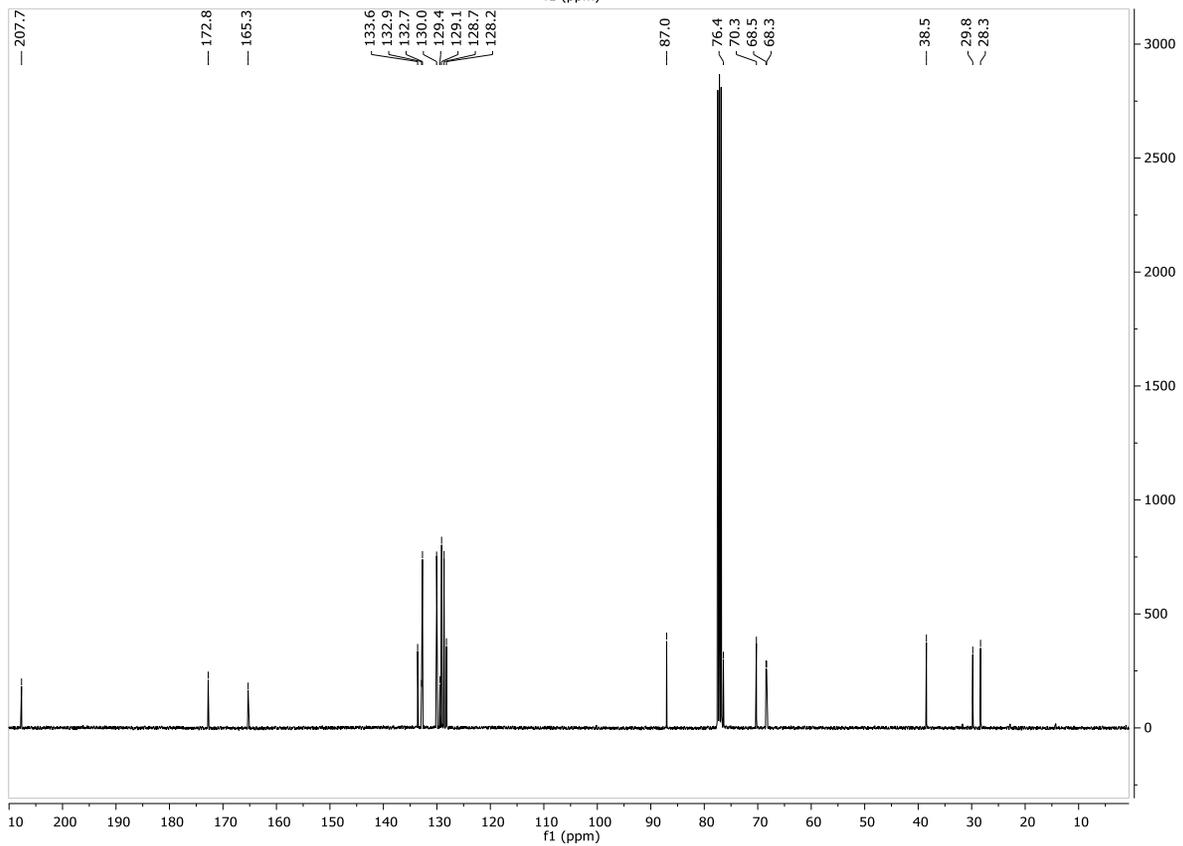
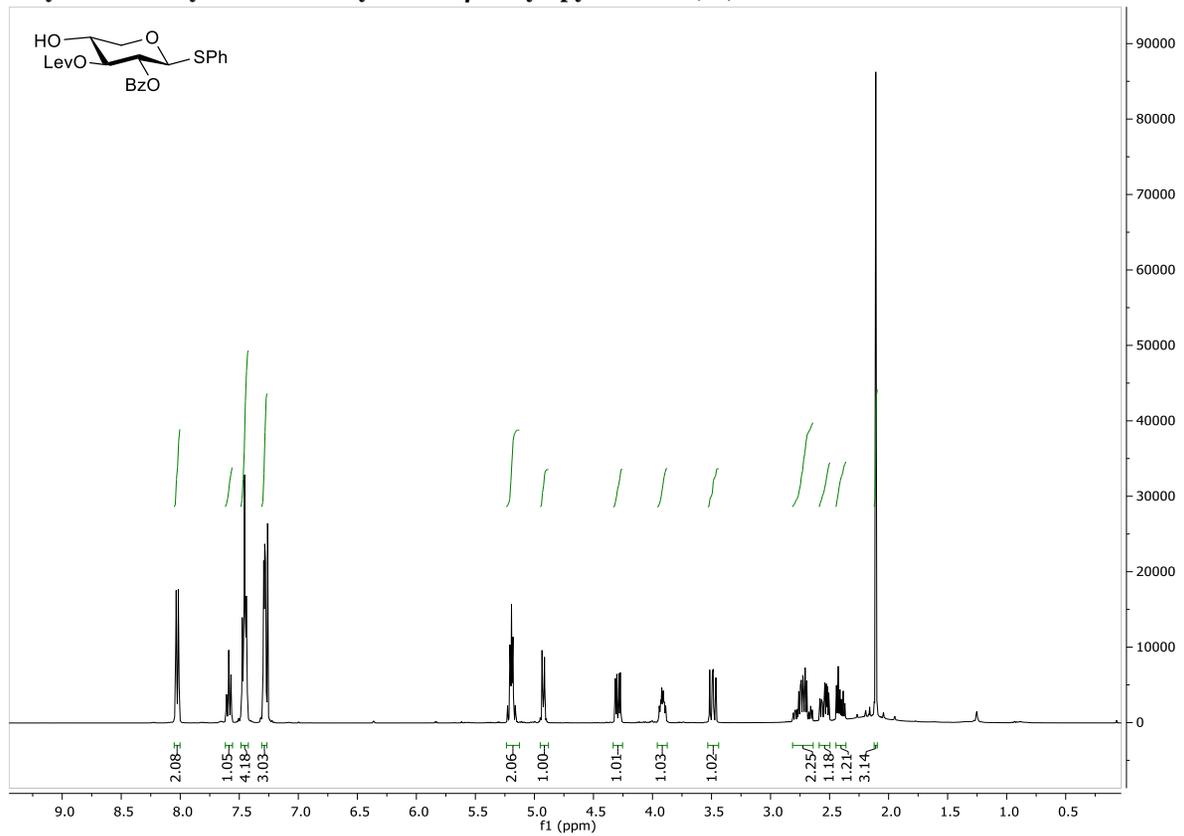
**Phenyl 2,3-di-*O*-levulinoyl-1-thio- $\beta$ -D-xylopyranoside (9)**



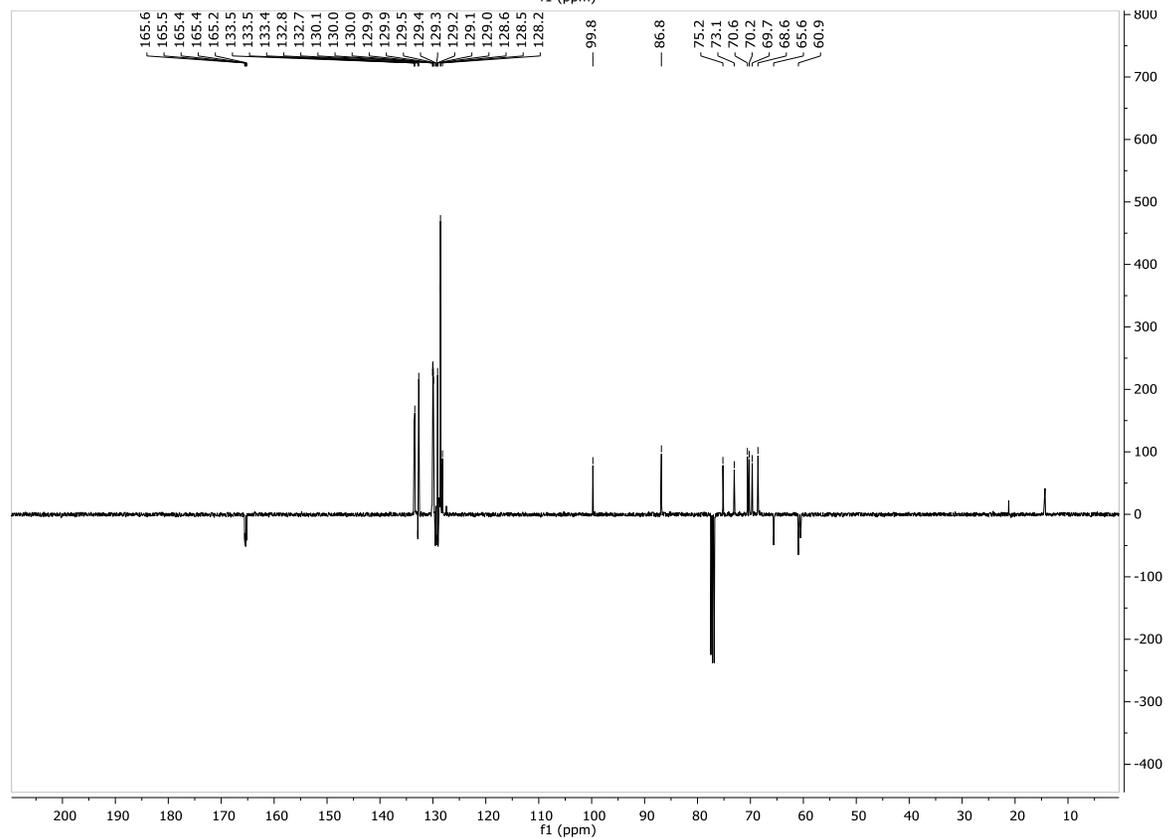
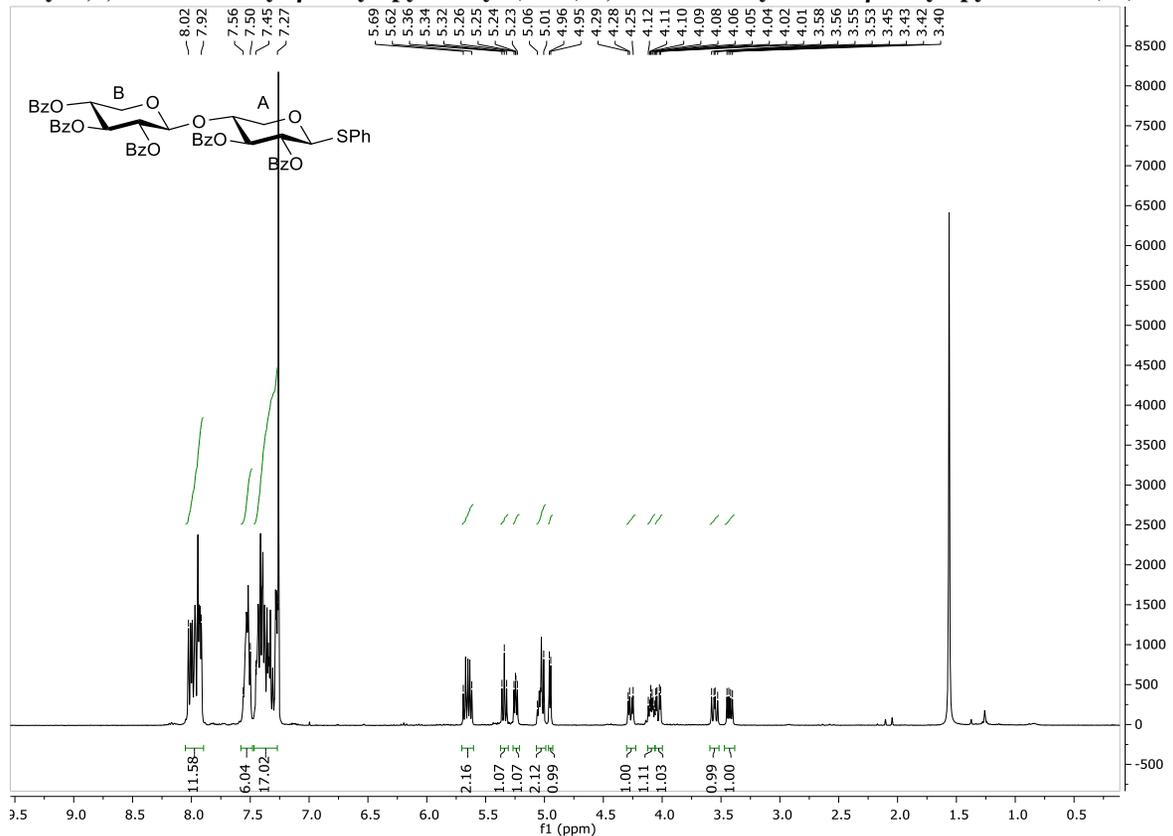
Phenyl 2-O-benzoyl-4-O-(*p*-methoxy)benzyl-1-thio- $\beta$ -D-xylopyranoside (10)



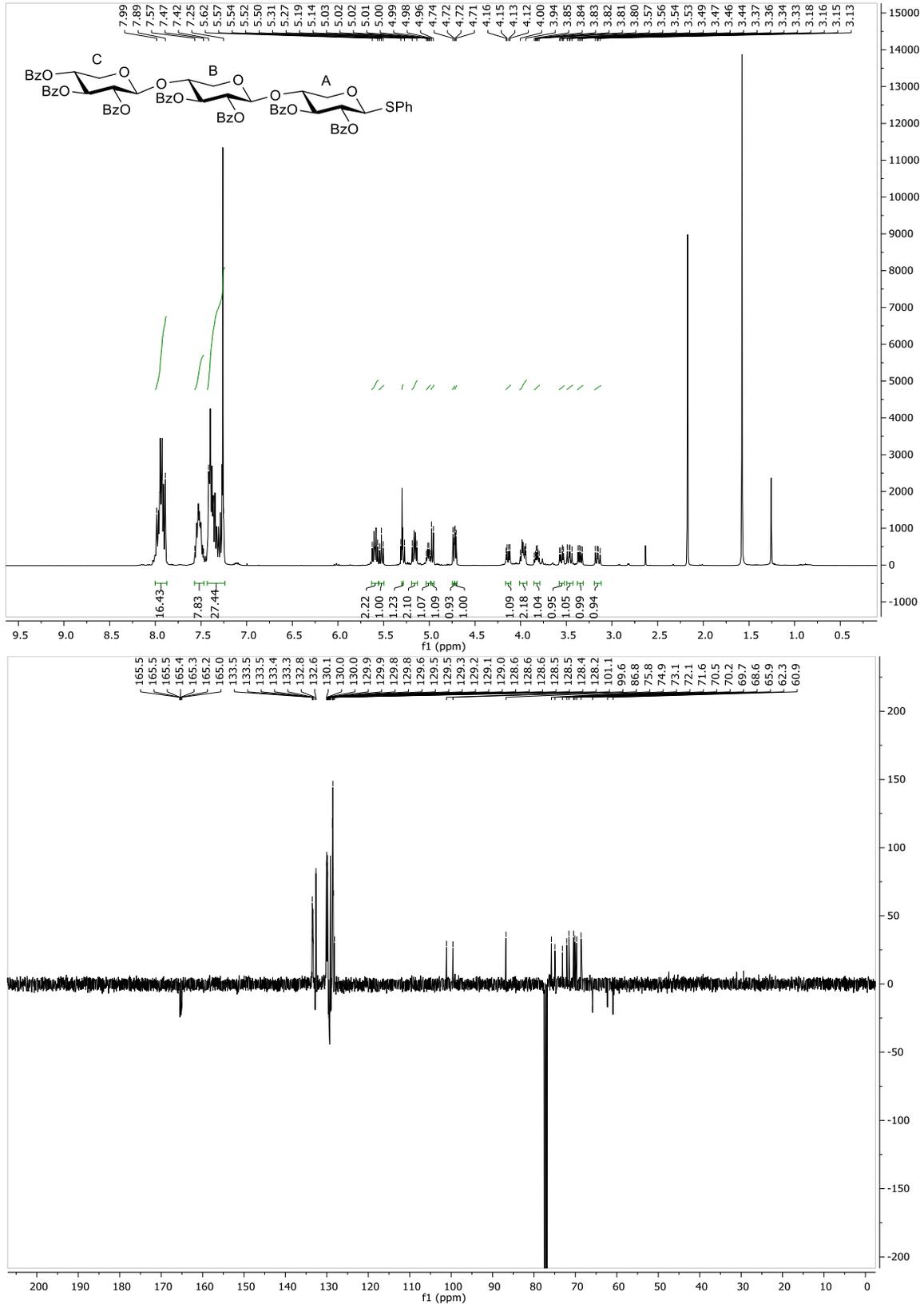
Phenyl 2-O-benzoyl-3-O-levulinoyl-1-thio-β-D-xylopyranoside (11)



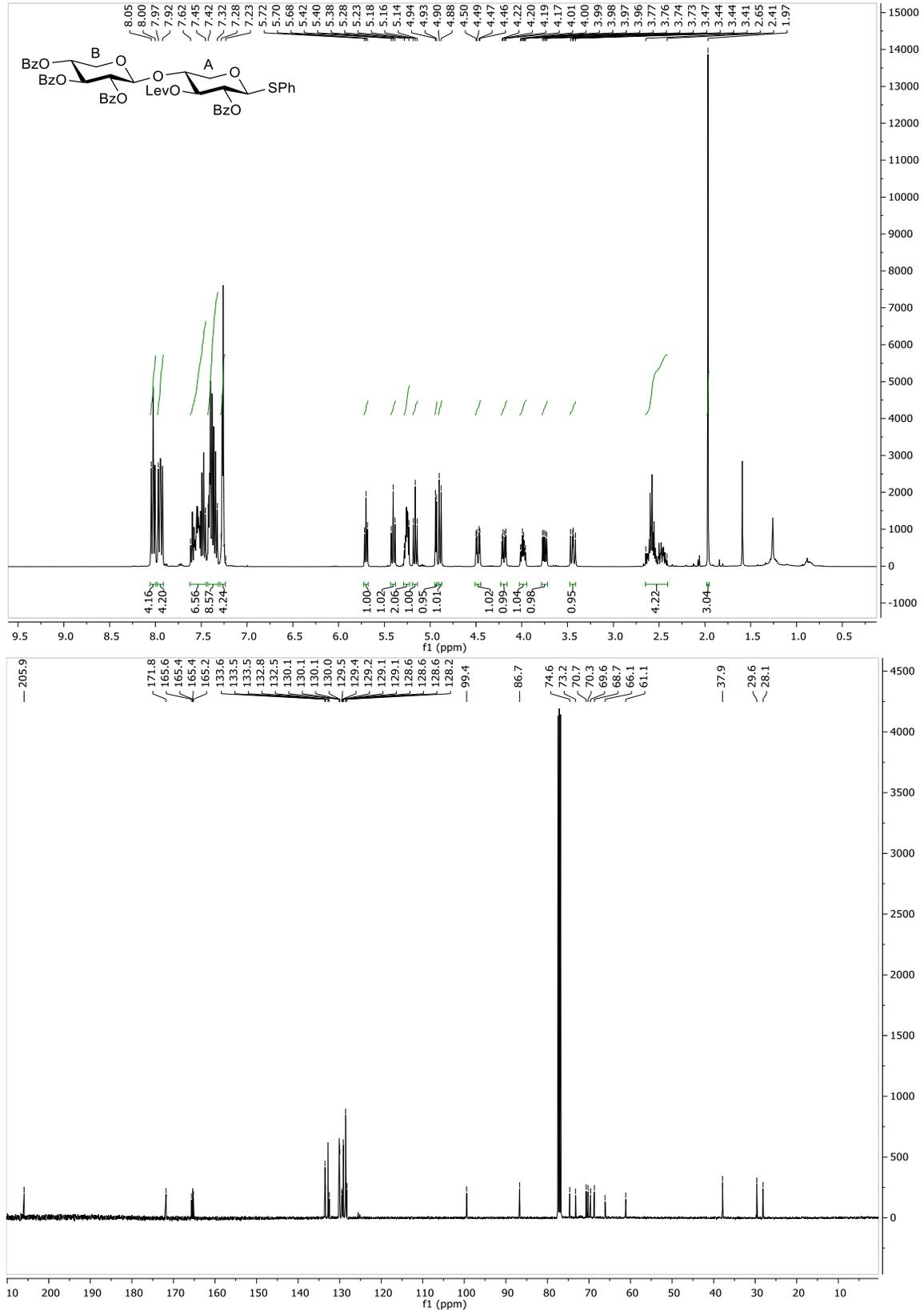
Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-1-thio- $\beta$ -D-xylopyranoside (12)



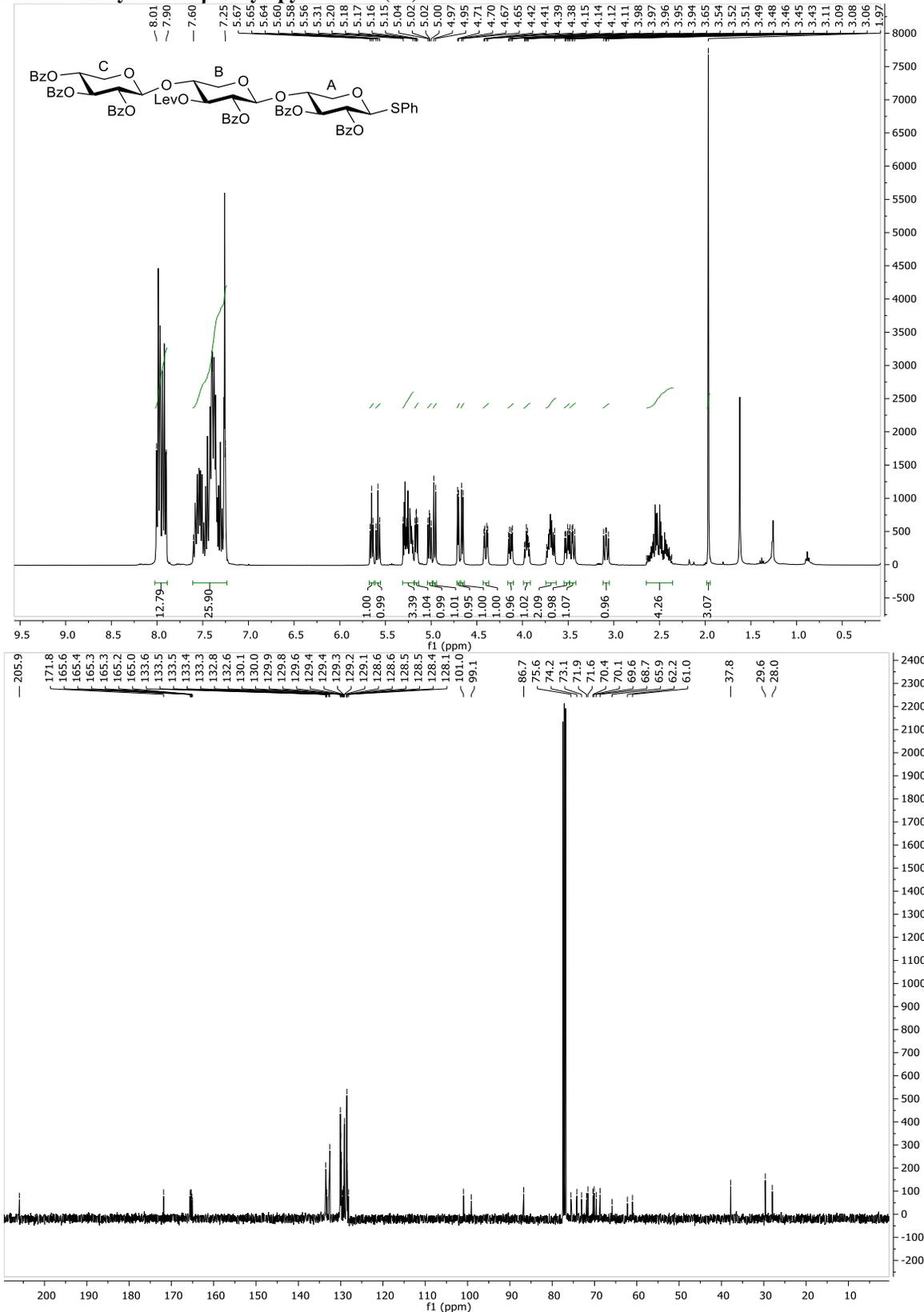
**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-1-thio- $\beta$ -D-xylopyranoside (13)**



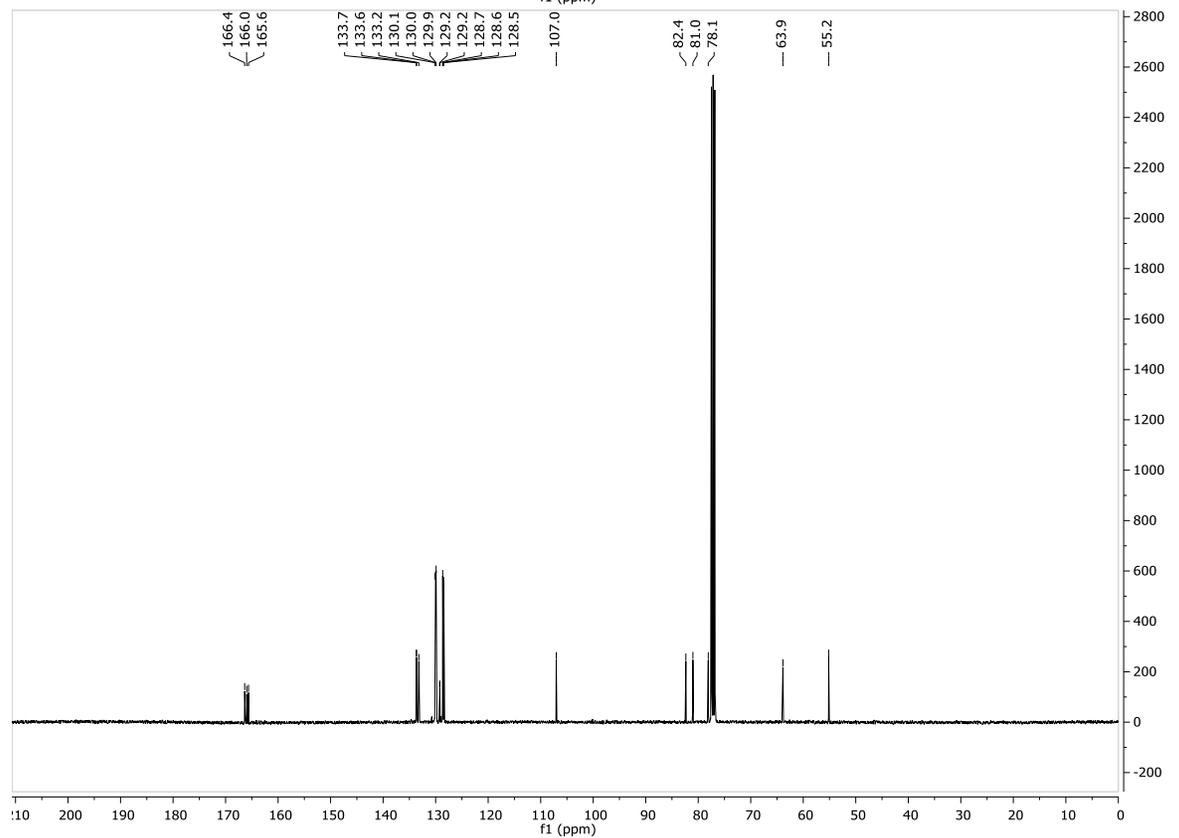
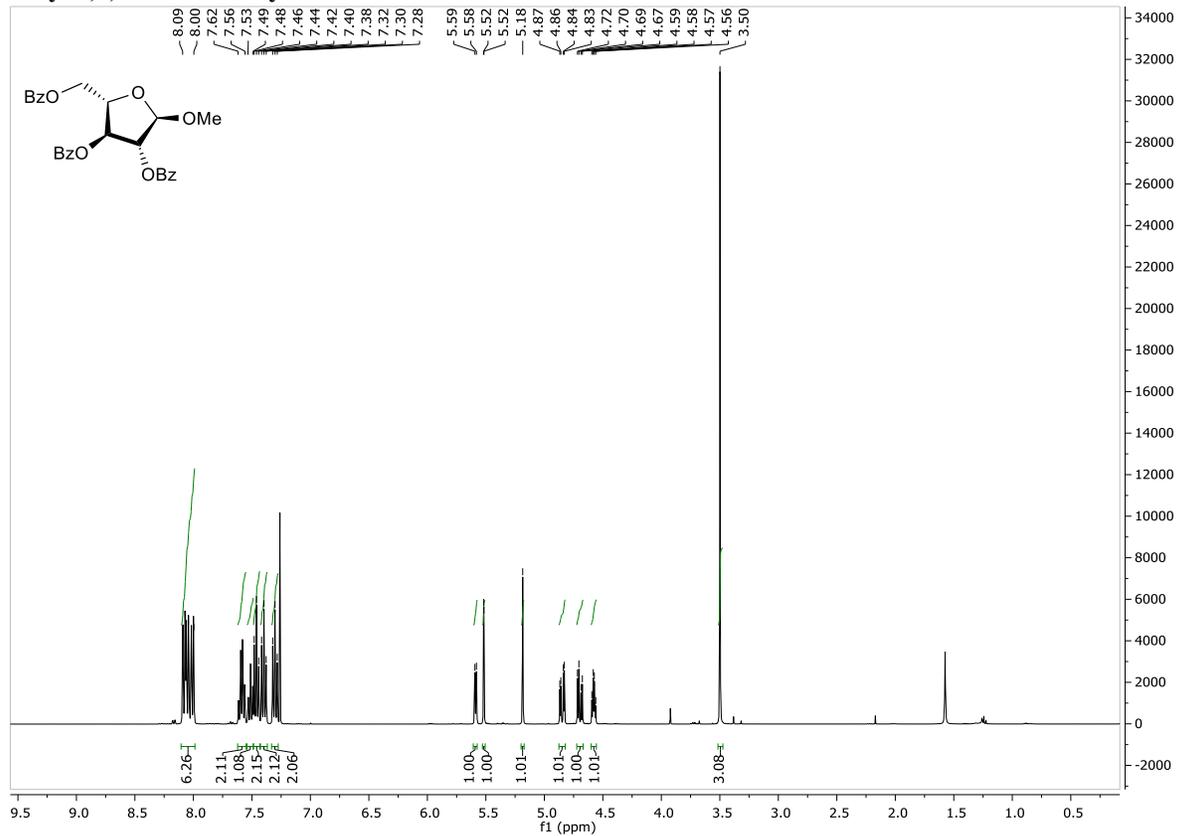
**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-3-*O*-levulinoyl-1-thio- $\beta$ -D-xylopyranoside (14)**



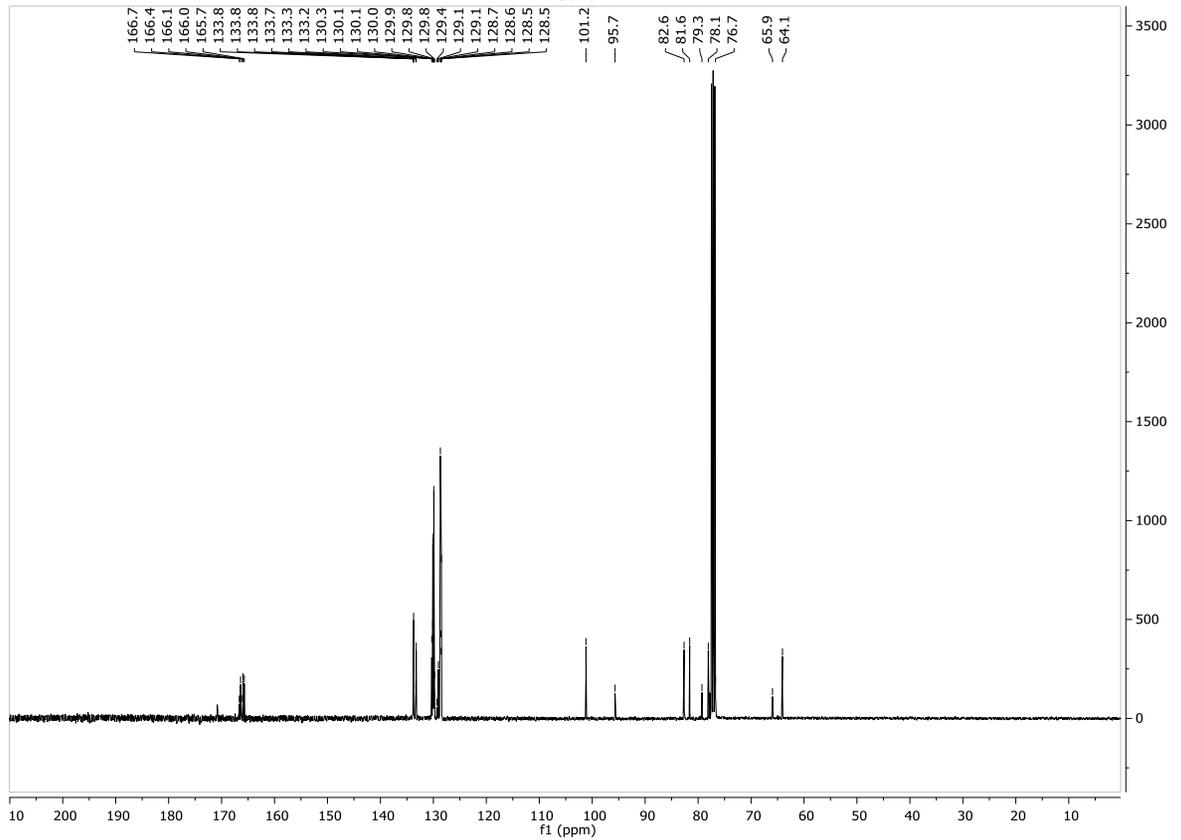
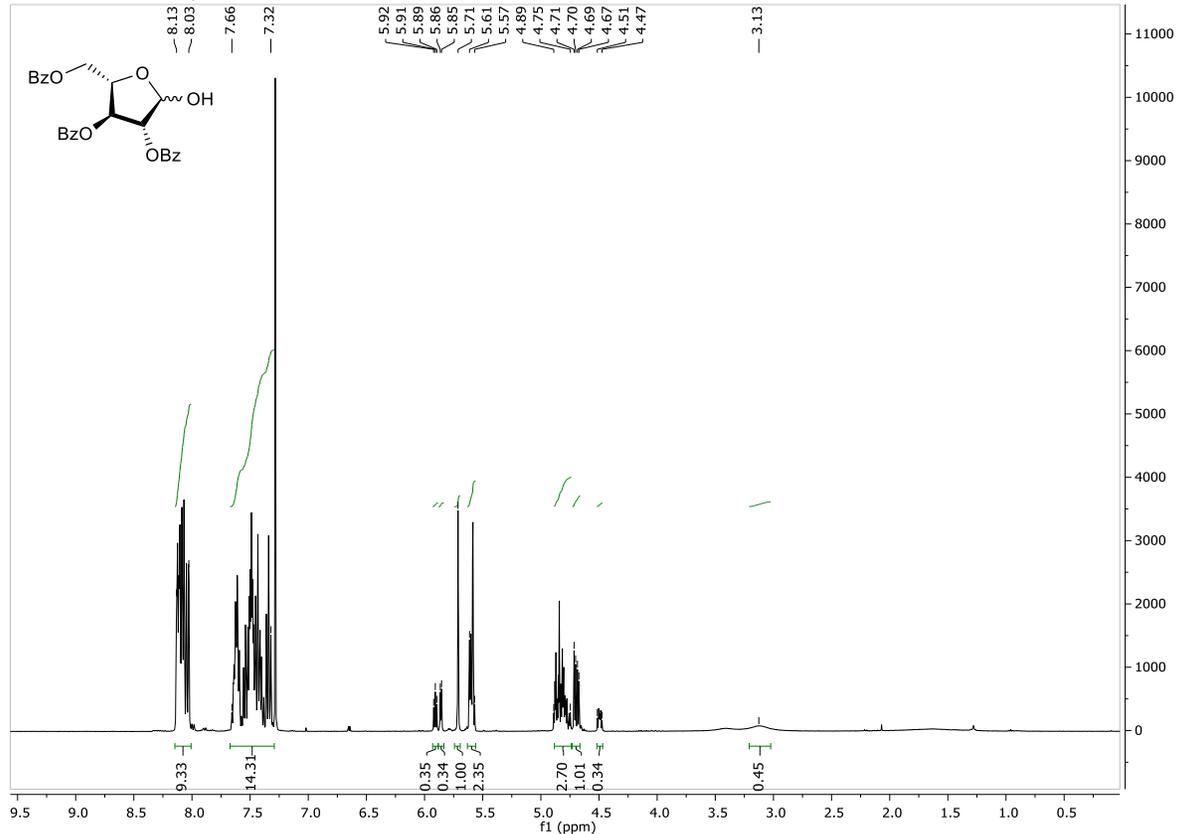
**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-3-*O*-levulinoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3 di-*O*-benzoyl-1-thio- $\beta$ -D-xylopyranoside (15)**



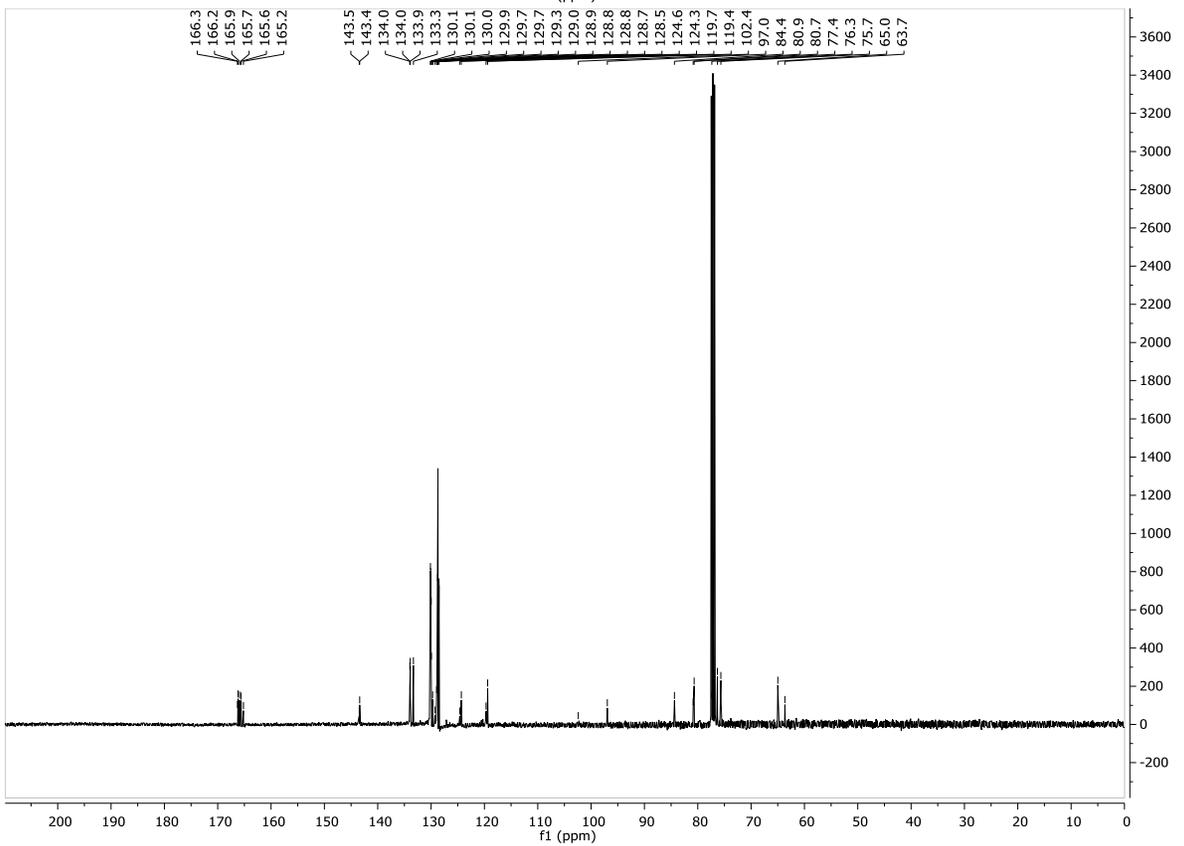
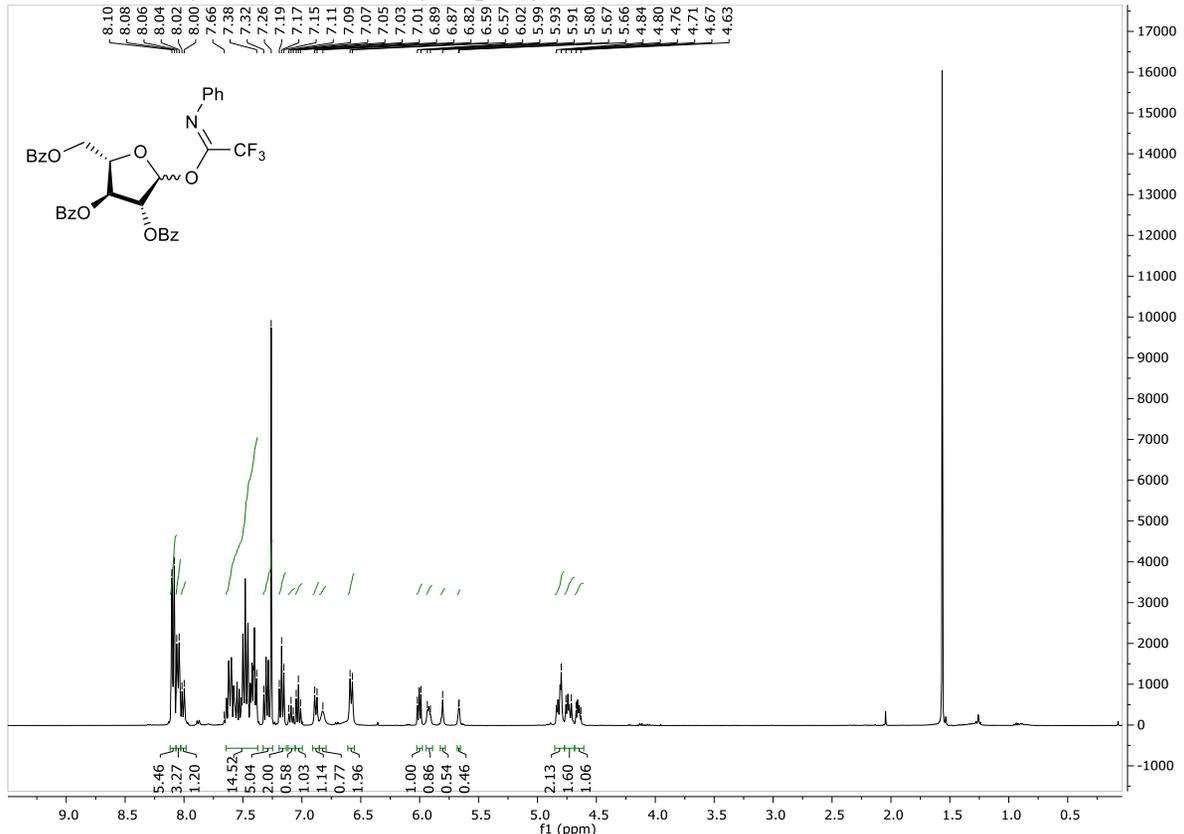
**Methyl 2,3,5-tri-O-benzoyl- $\alpha$ -L-arabinofuranoside**



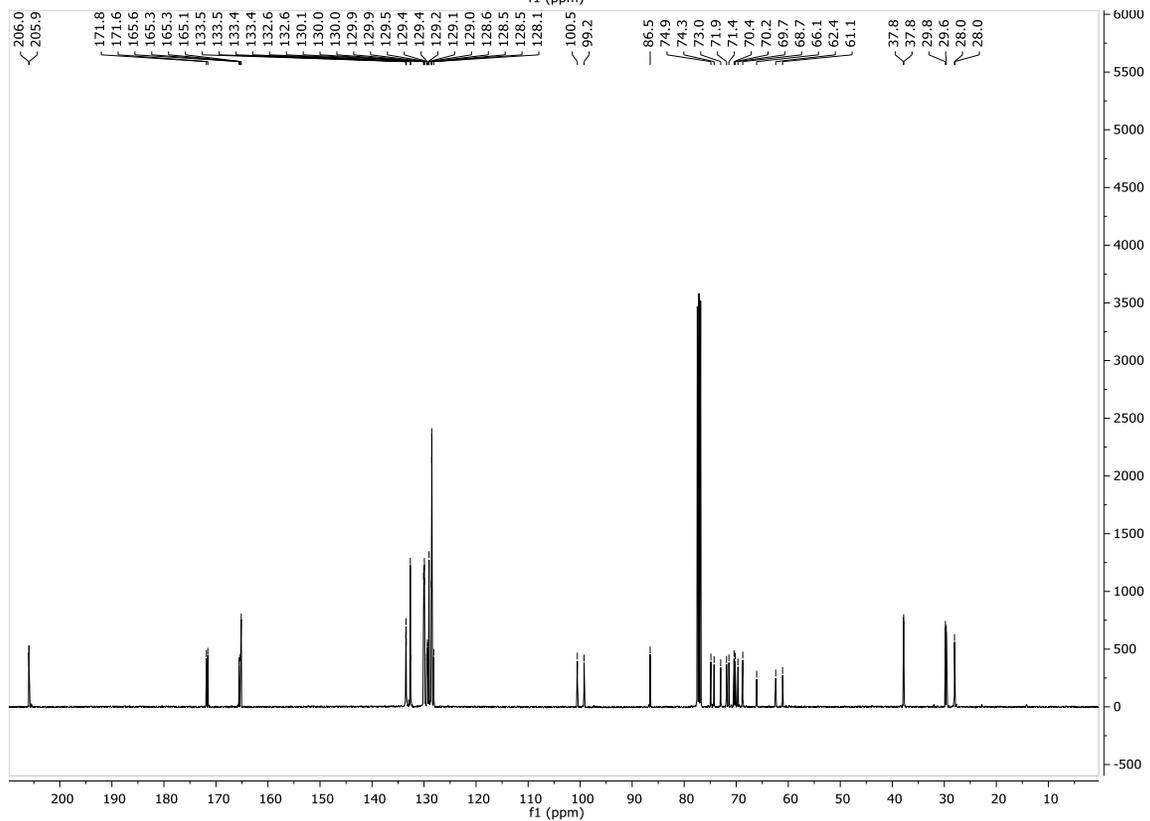
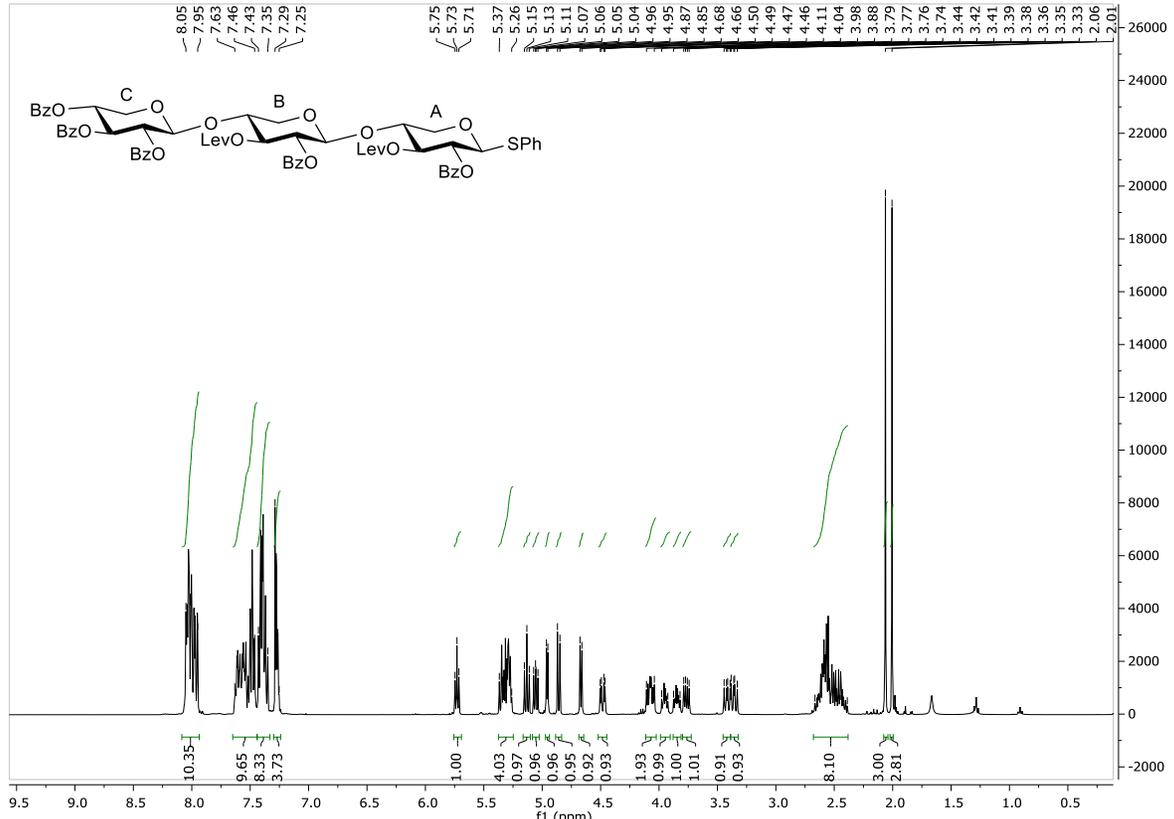
**2,3,5-Tri-*O*-benzoyl-L-arabinofuranose**



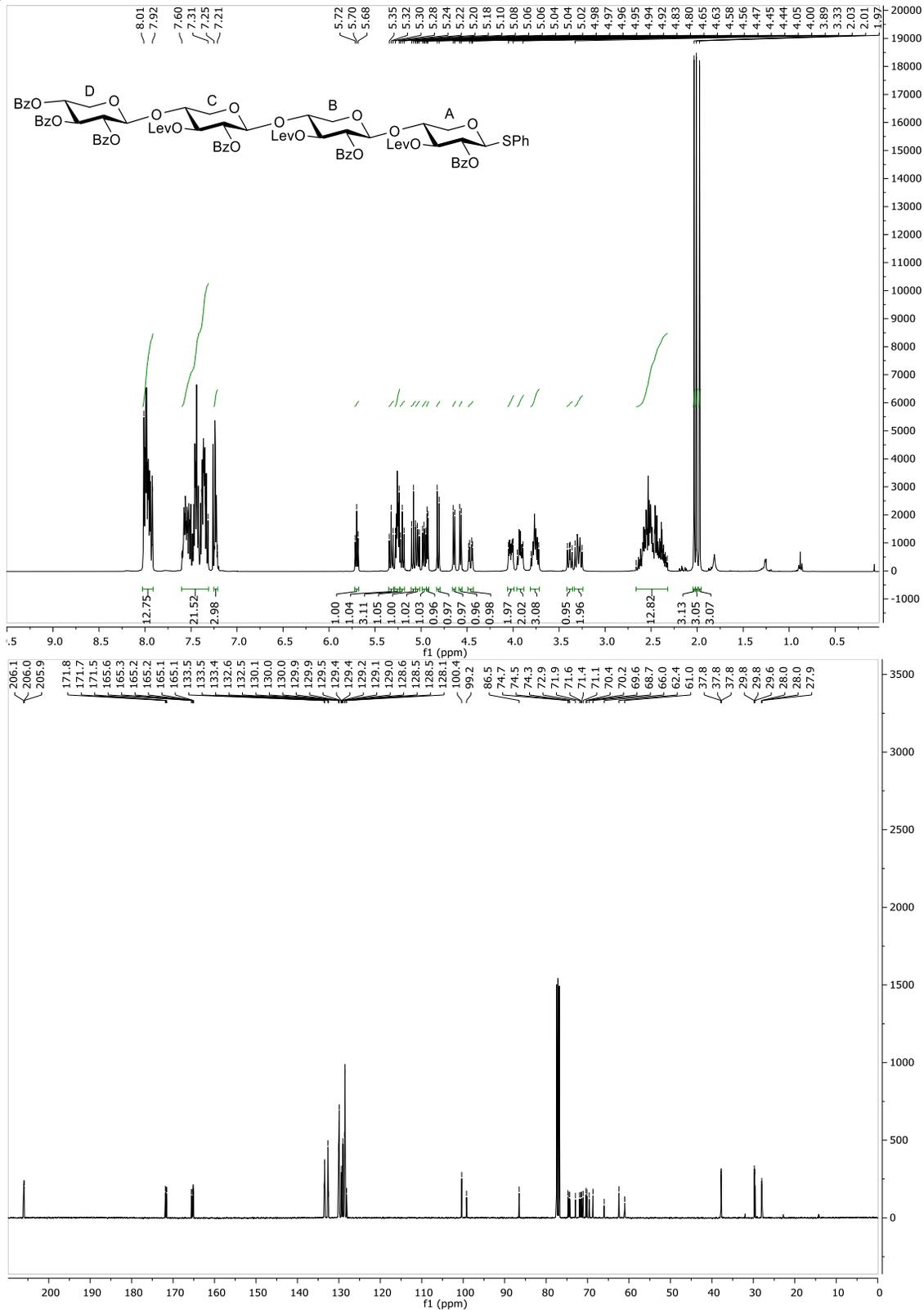
**2,3,5-Tri-*O*-benzoyl-L-arabinofuranosyl *N*-phenyl-2,2,2-trifluoroacetimidate (4)**



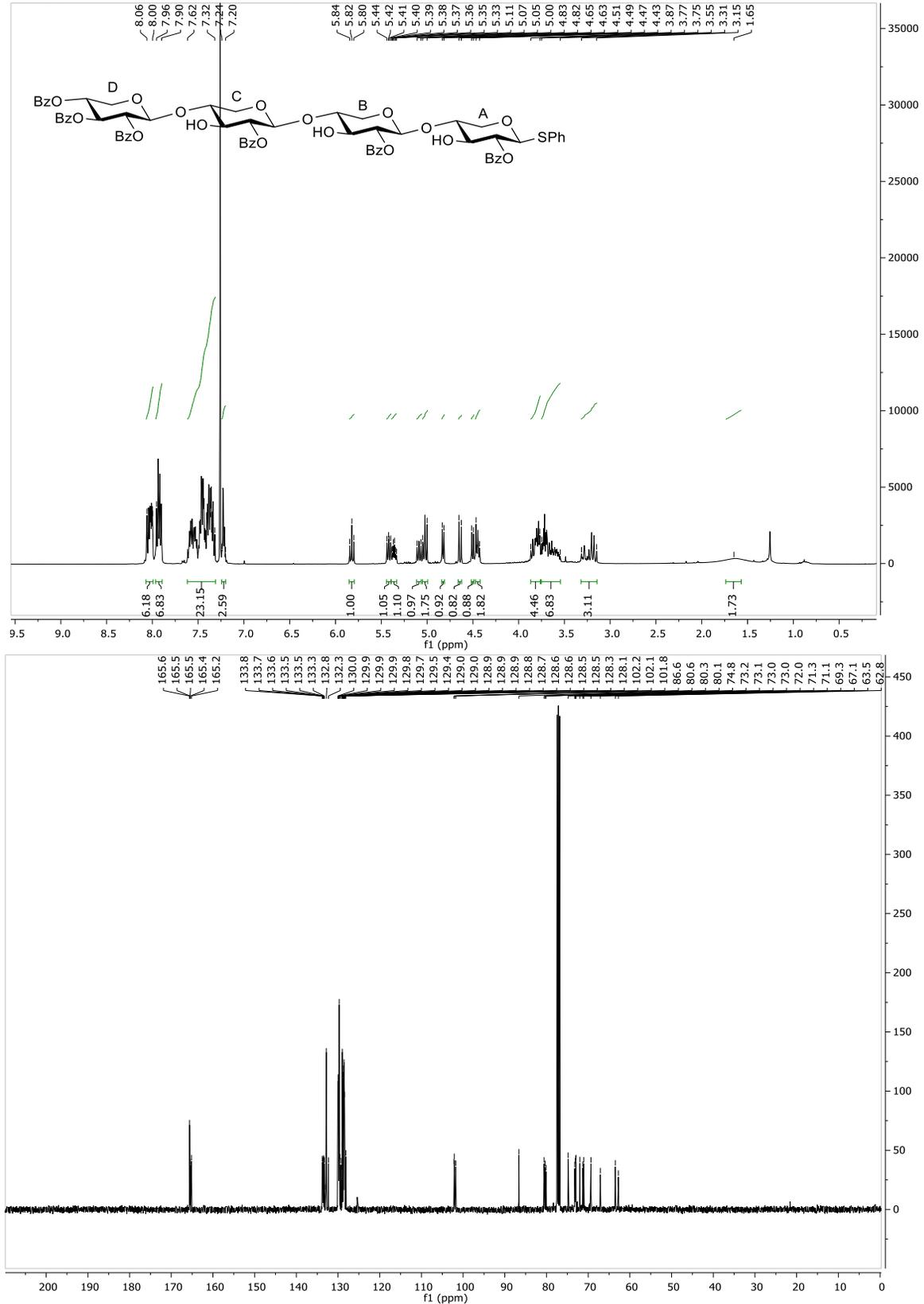
**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-3-*O*-levulinoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-3-*O*-levulinoyl-1-thio- $\beta$ -D-xylopyranoside (16)**



**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-3-*O*-levulinoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-3-*O*-levulinoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-3-*O*-levulinoyl-1-thio- $\beta$ -D-xylopyranoside (17)**

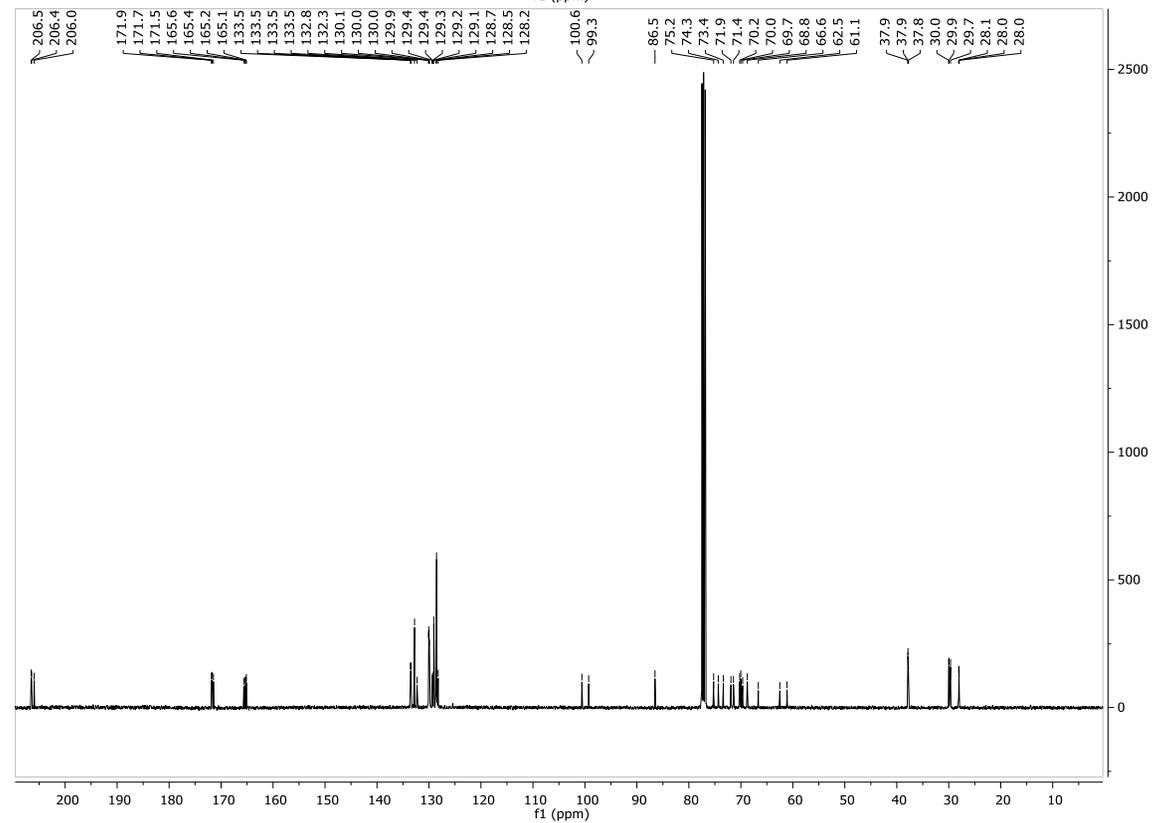
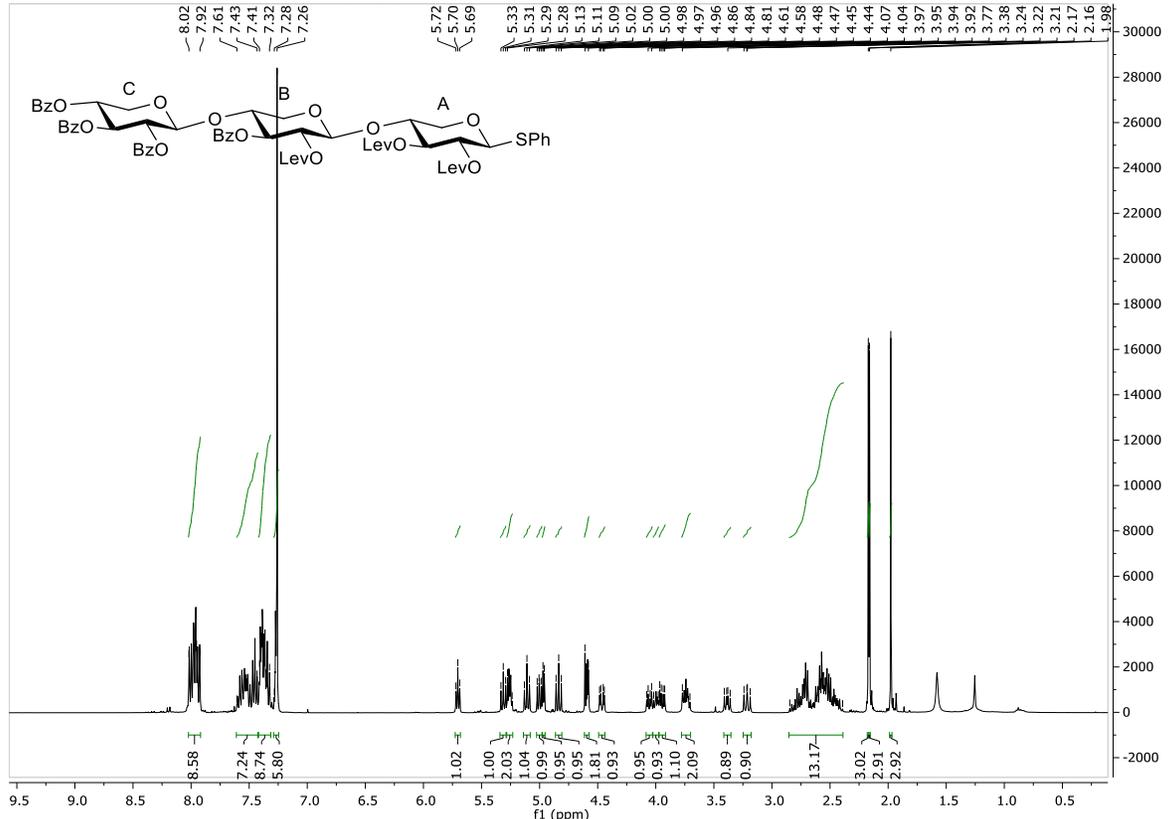


**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-1-thio- $\beta$ -D-xylopyranoside (18)**

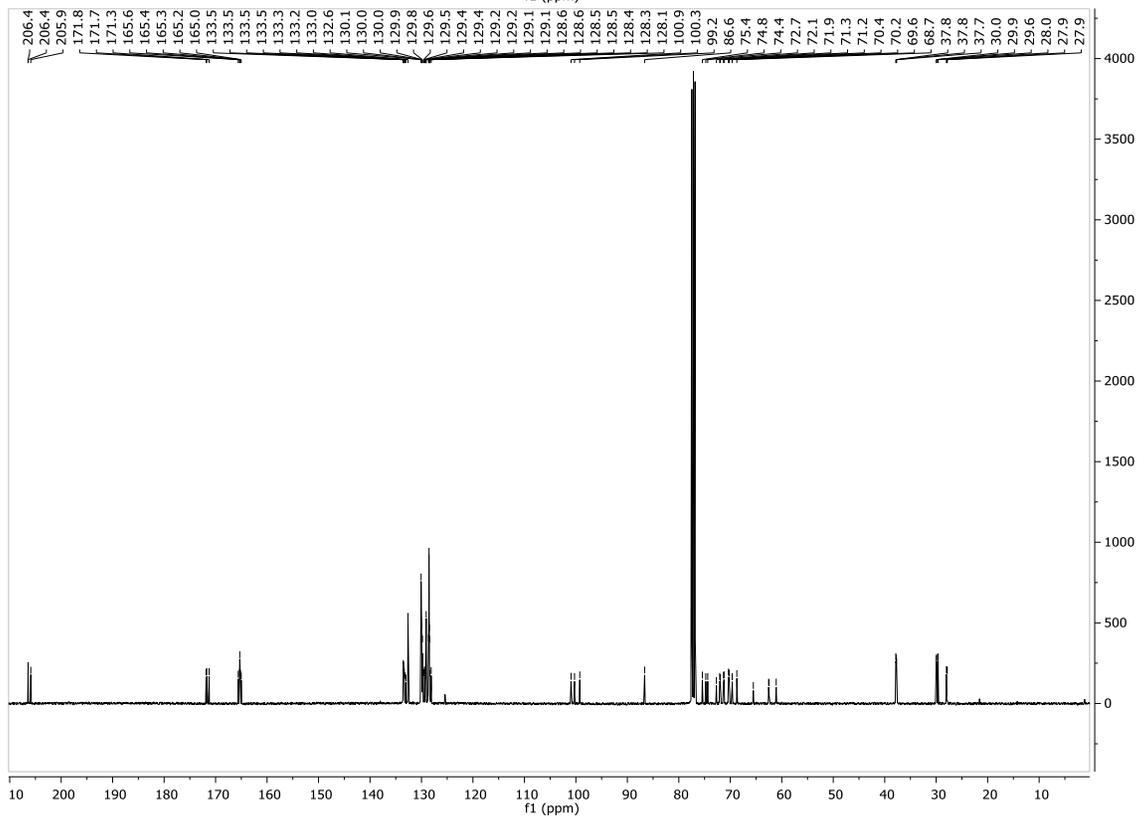
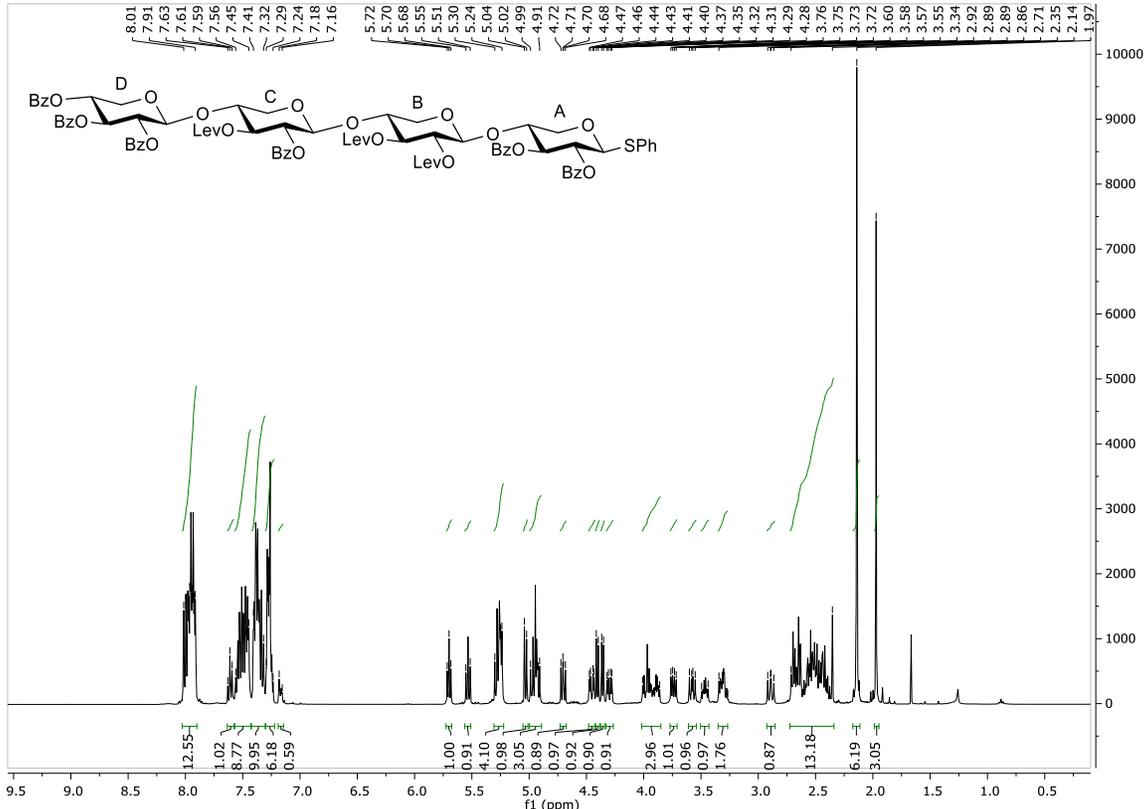




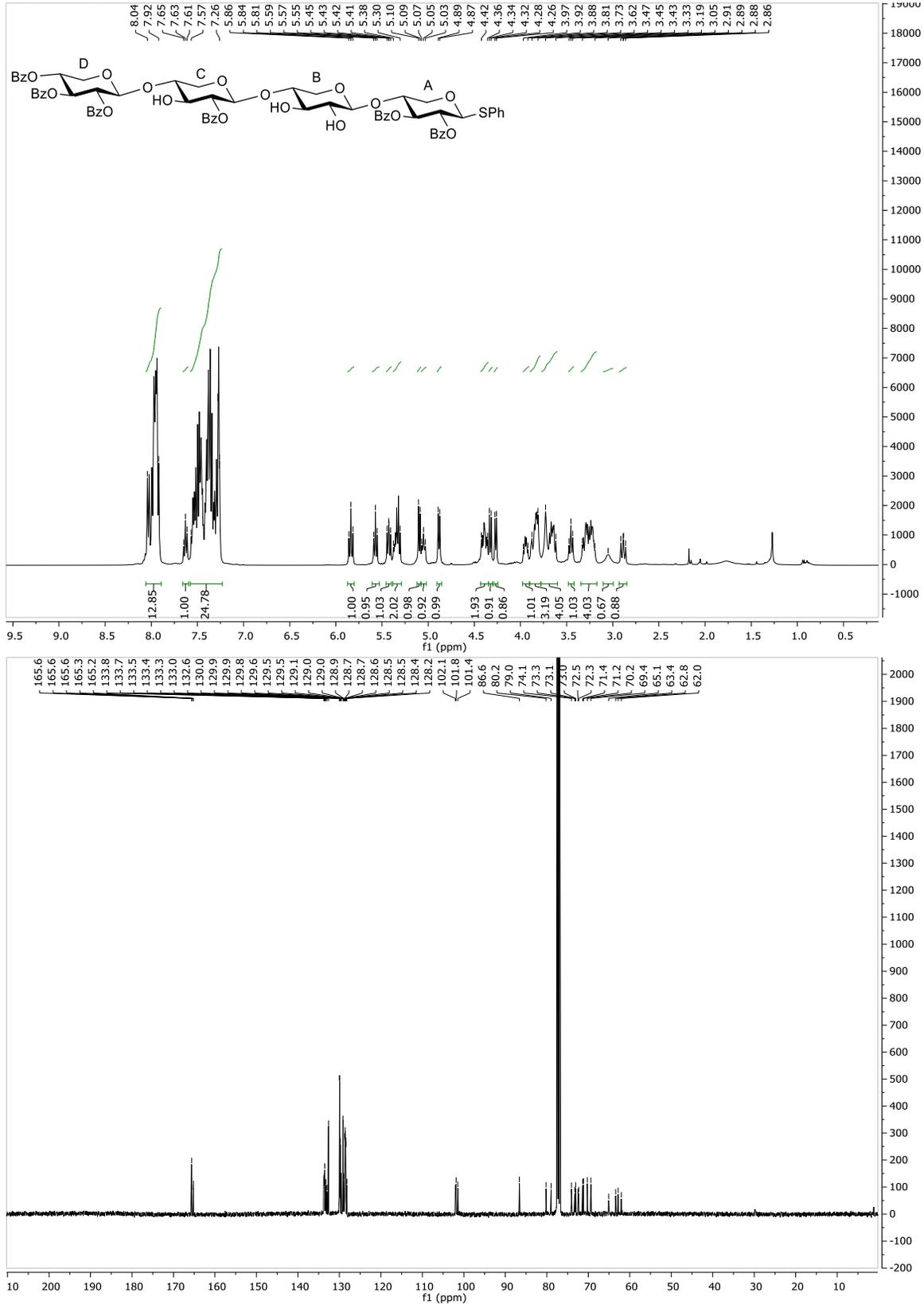
**Phenyl 2,3,4-tri-*O*-benzoyl-  $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-3-*O*-levulinoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-levulinoyl-1-thio- $\beta$ -D-xylopyranoside (20)**



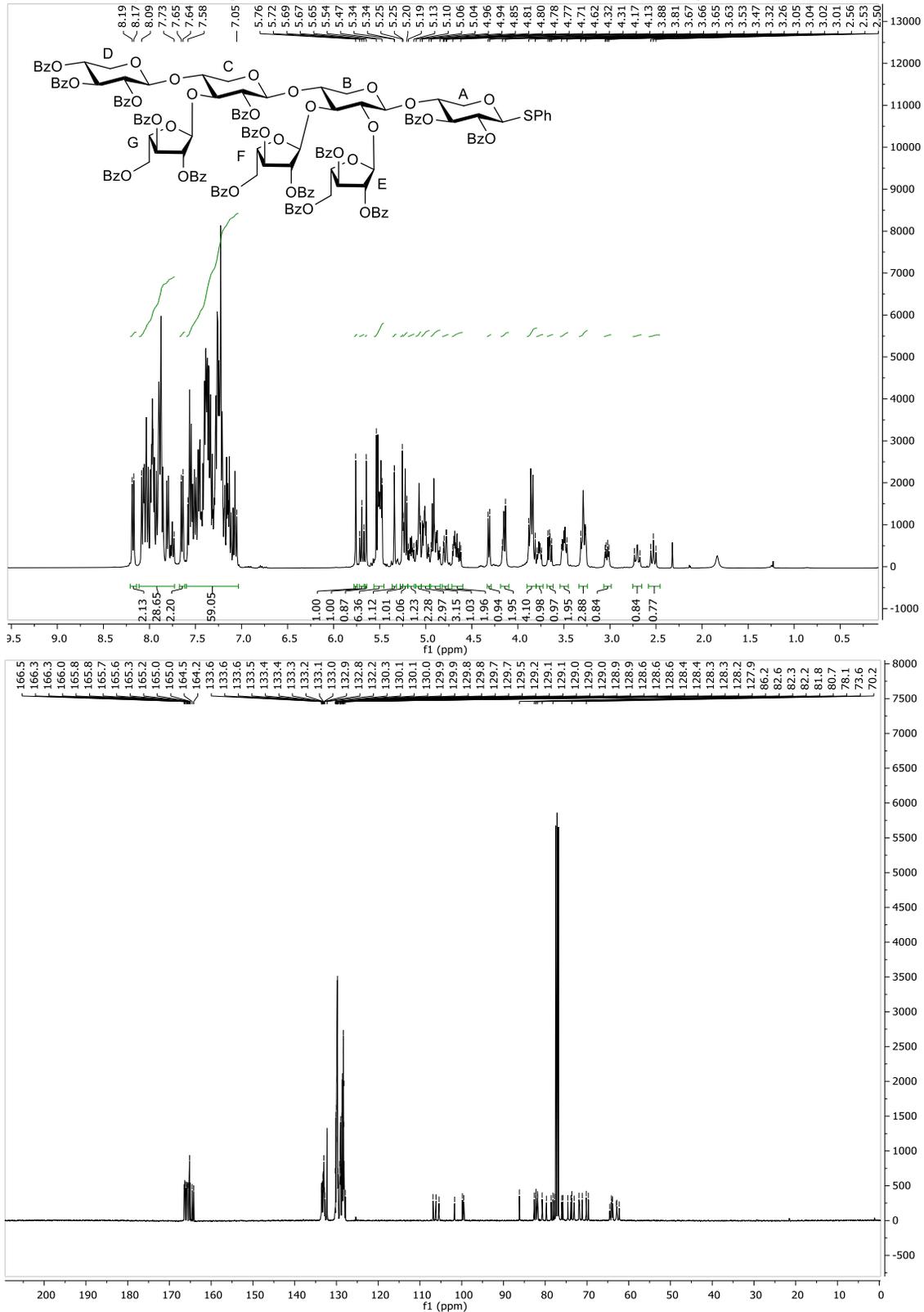
**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-3-*O*-levulinoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-levulinoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-1-thio- $\beta$ -D-xylopyranoside (21)**



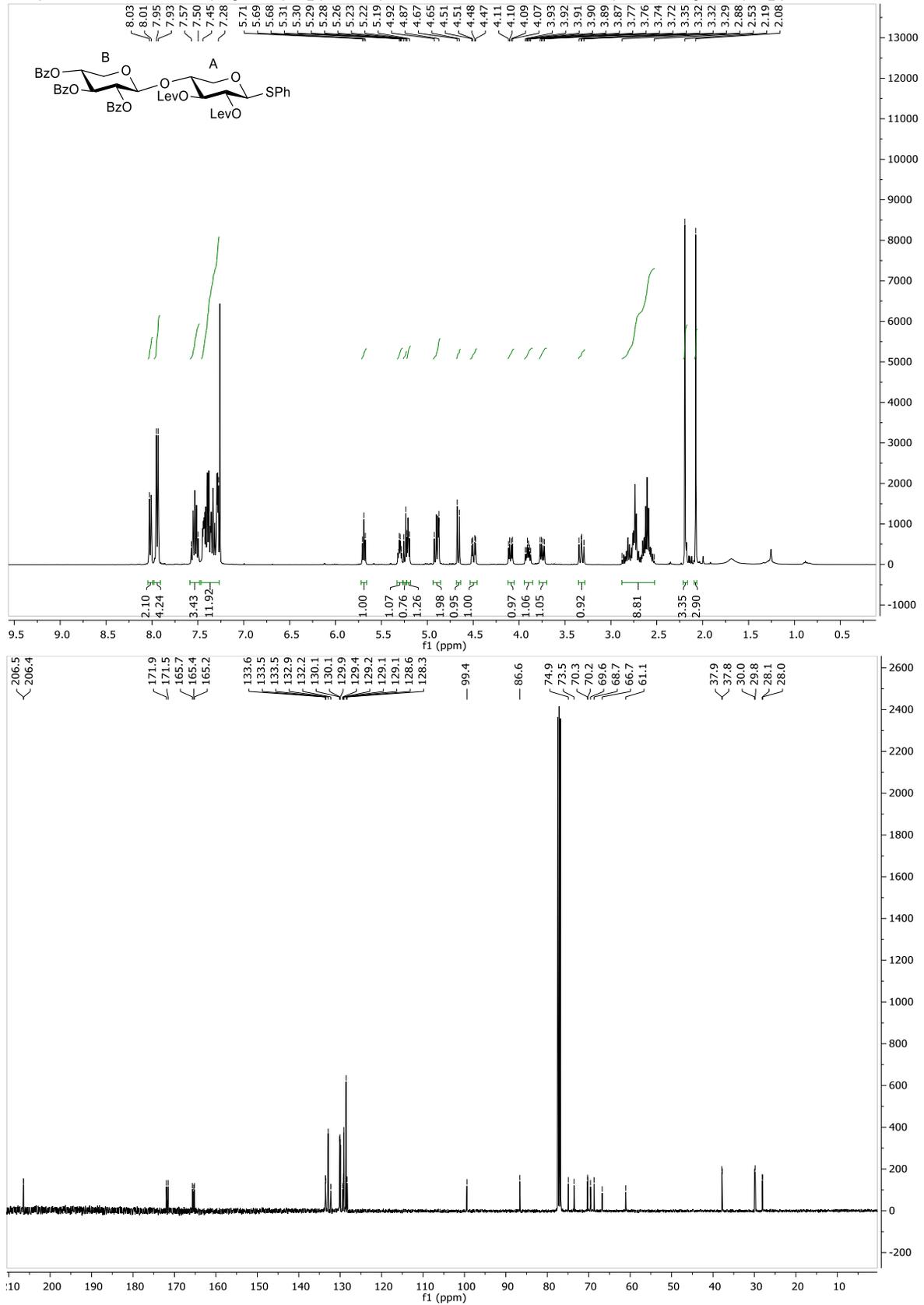
**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-1-thio- $\beta$ -D-xylopyranoside (22)**



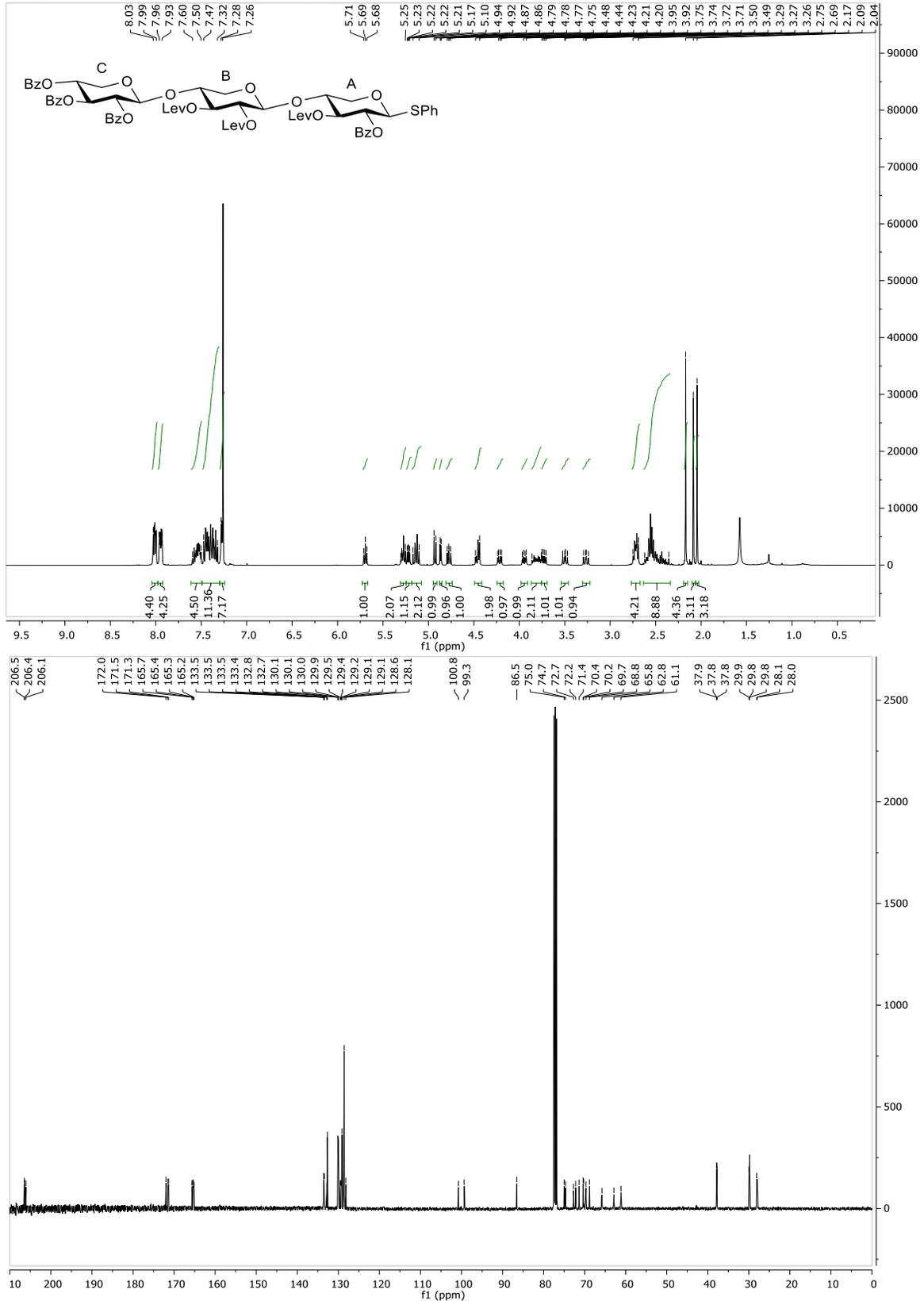
**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]-2-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 2)]-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-1-thio- $\beta$ -D-xylopyranoside (23)**



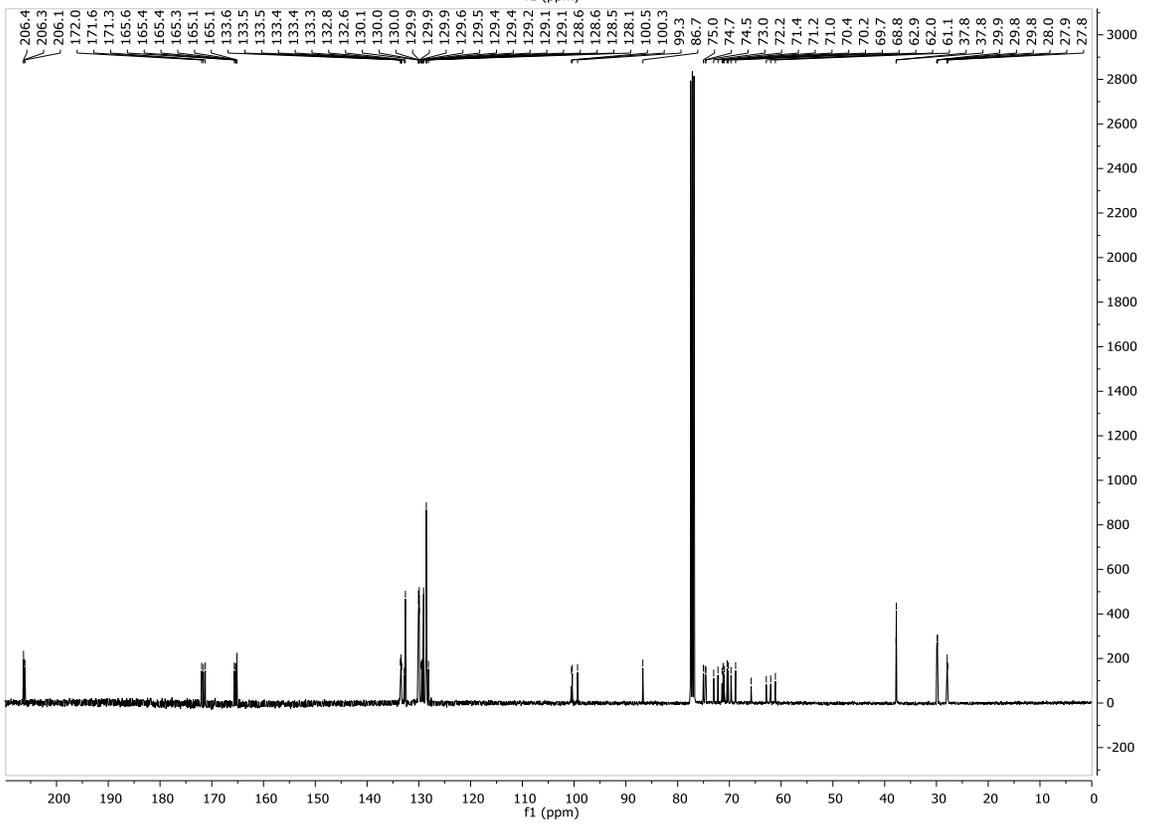
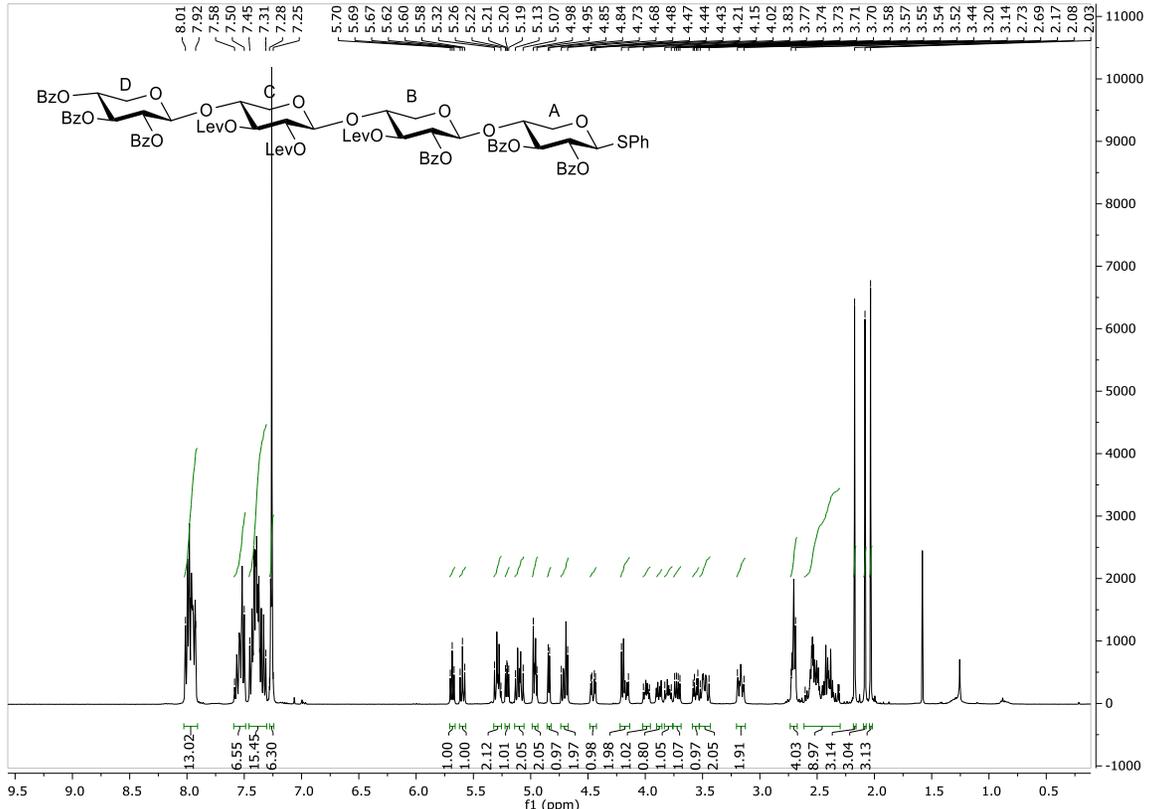
Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-levulinoyl-1-thio- $\beta$ -D-xylopyranoside (24)



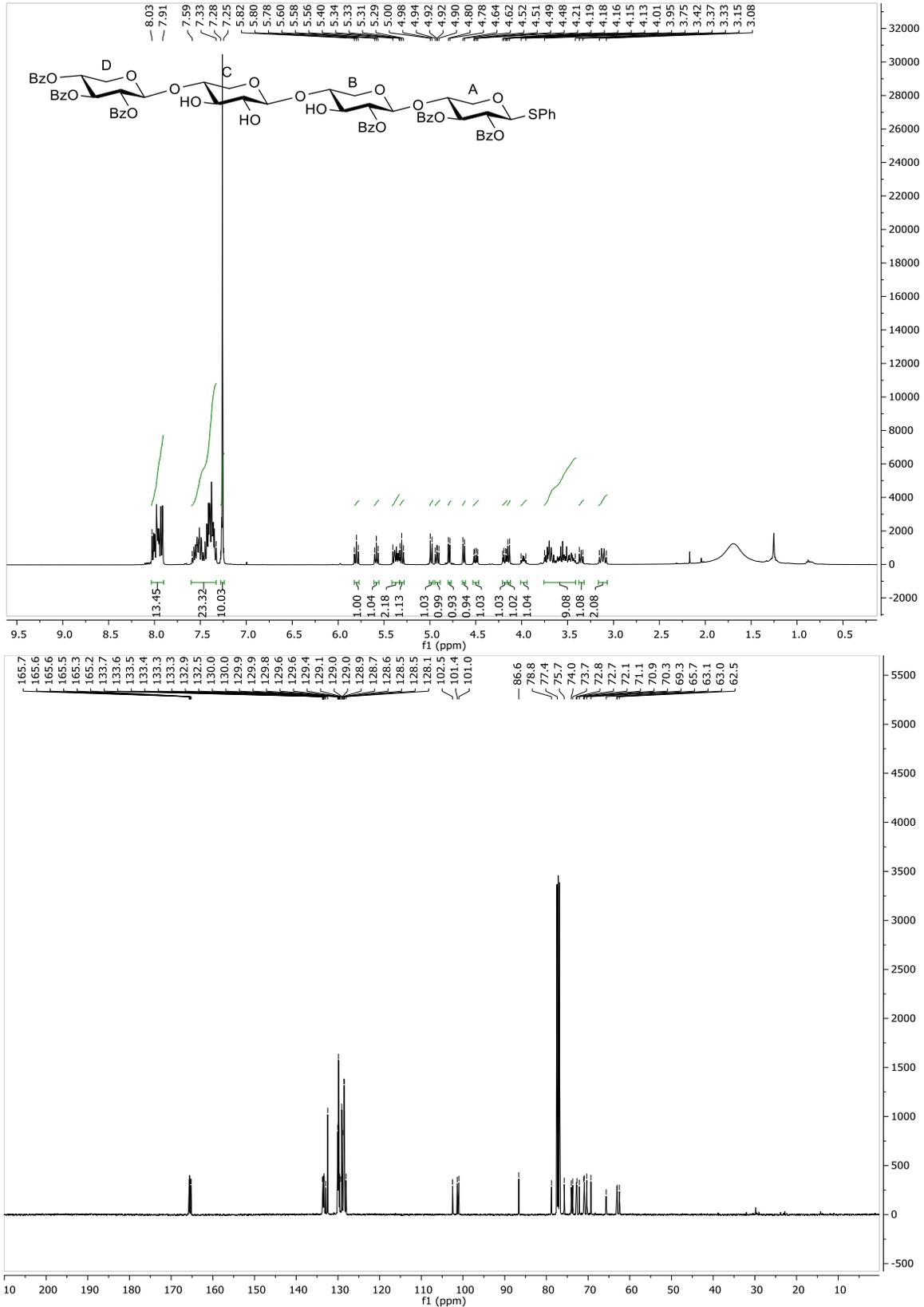
**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-levulinoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-3-*O*-levulinoyl-1-thio- $\beta$ -D-xylopyranoside (25)**



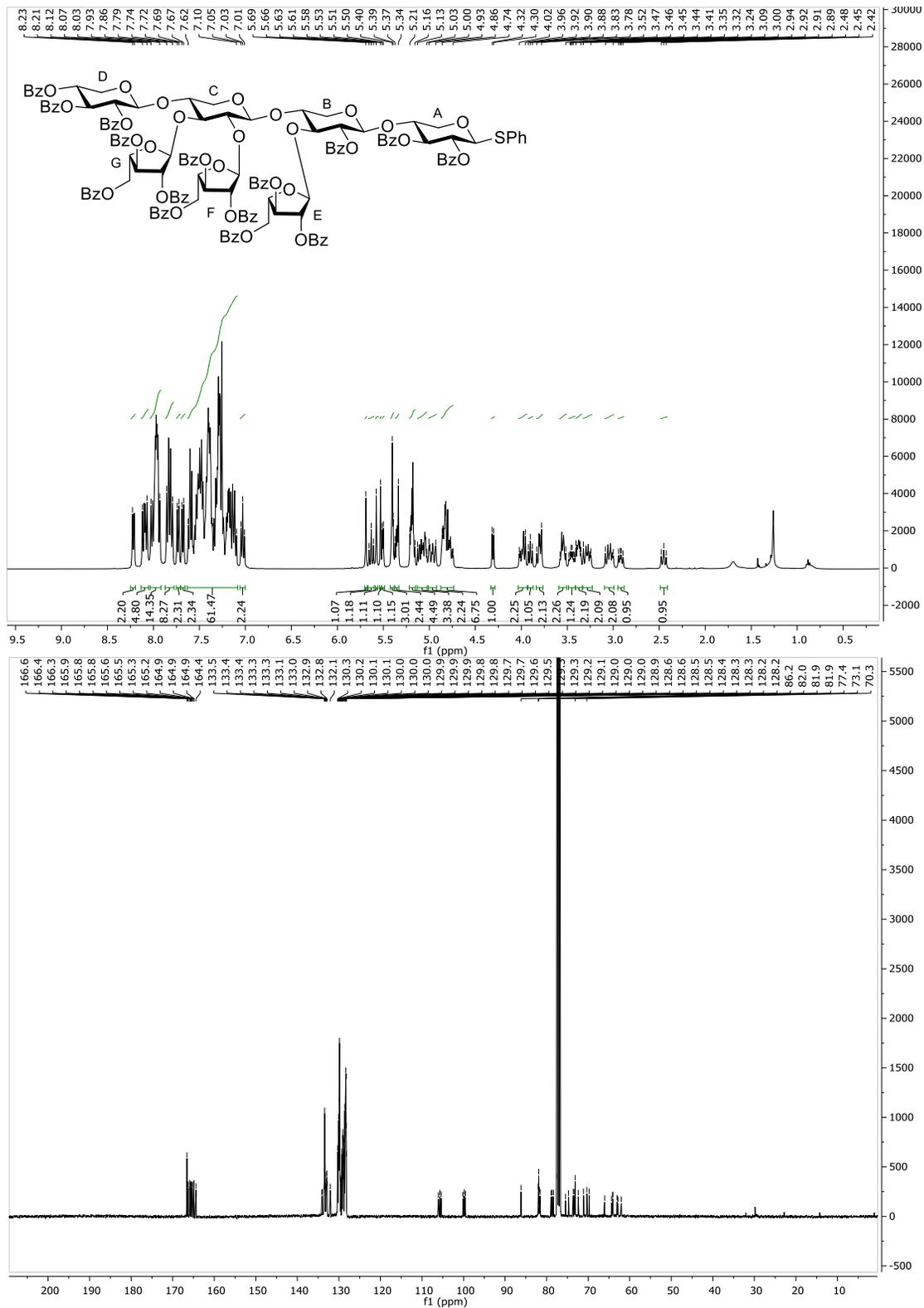
**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-levulinoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl-3-*O*-levulinoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-1-thio- $\beta$ -D-xylopyranoside (26)**



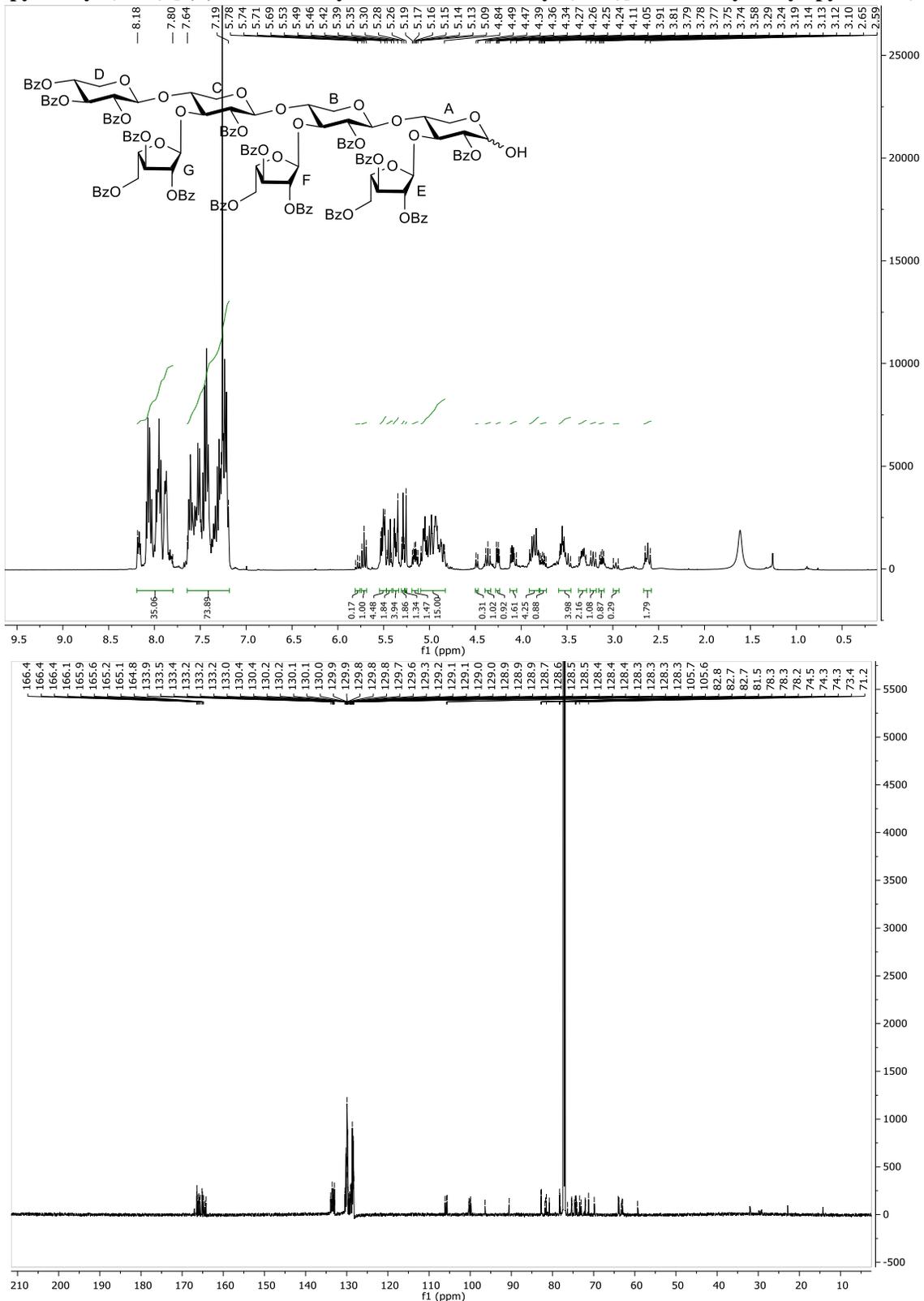
**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-1-thio- $\beta$ -D-xylopyranoside (27)**



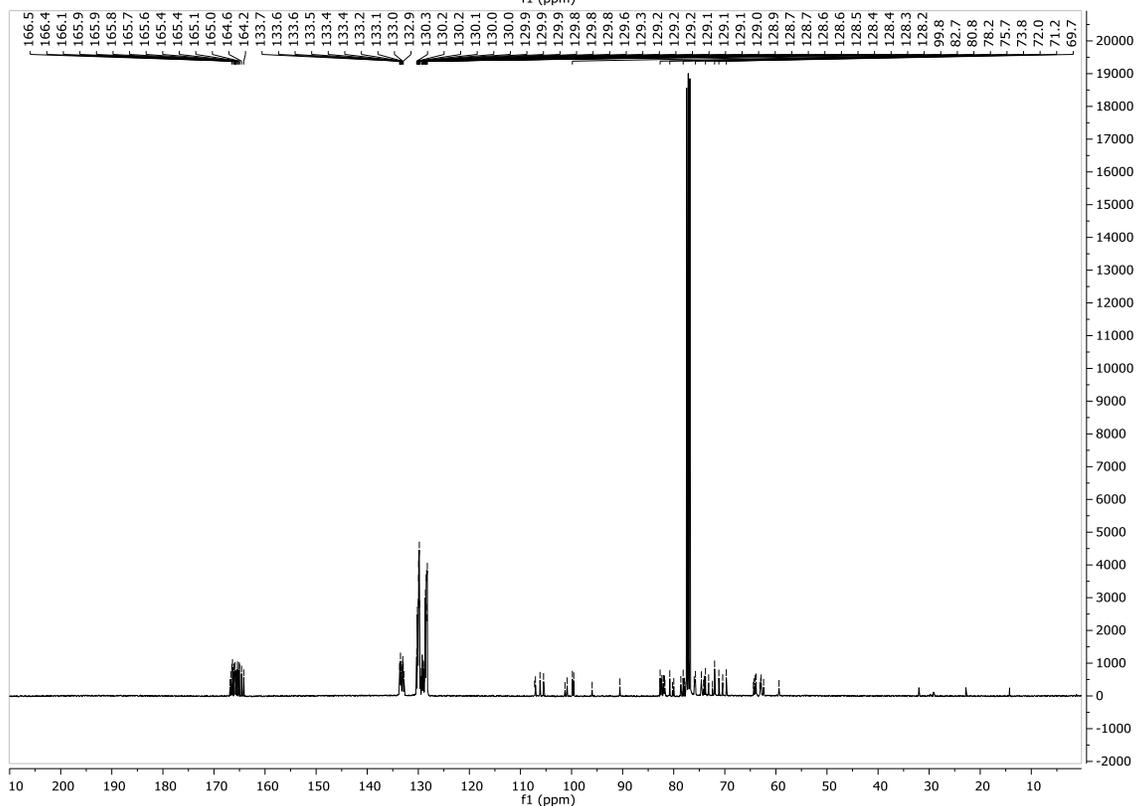
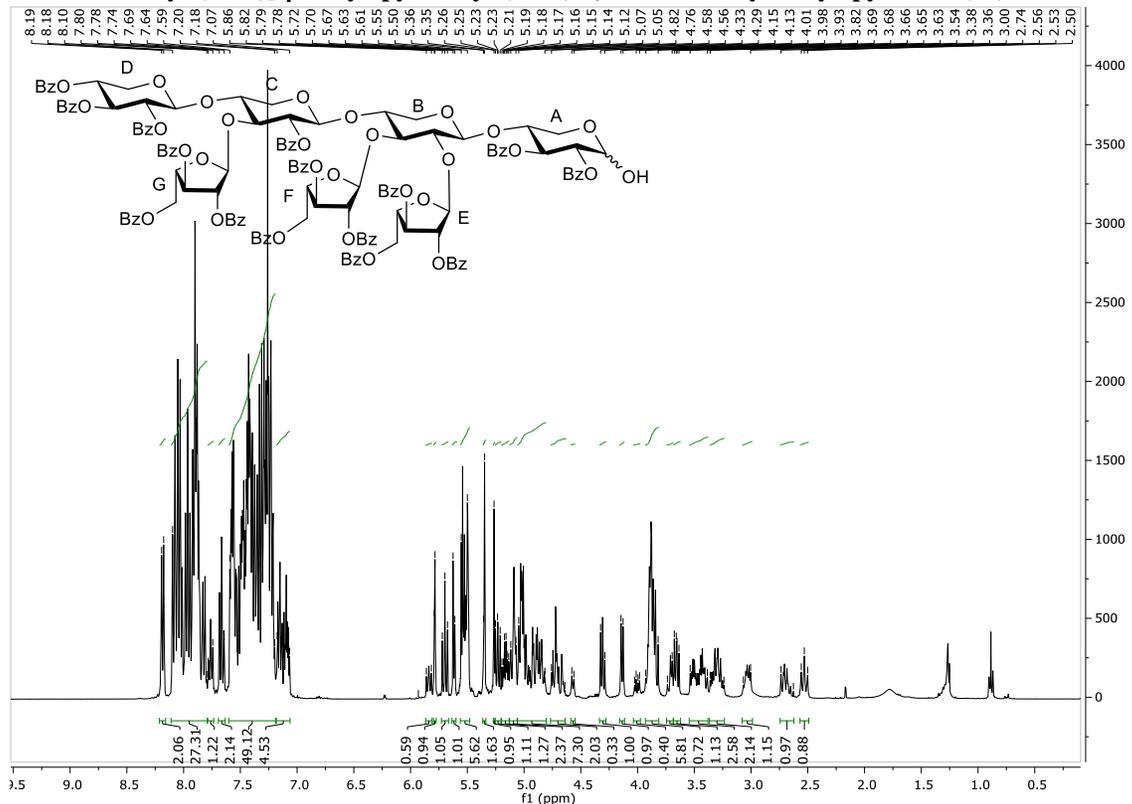
**Phenyl 2,3,4-tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 2)]-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]-2-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-1-thio- $\beta$ -D-xylopyranoside (28)**



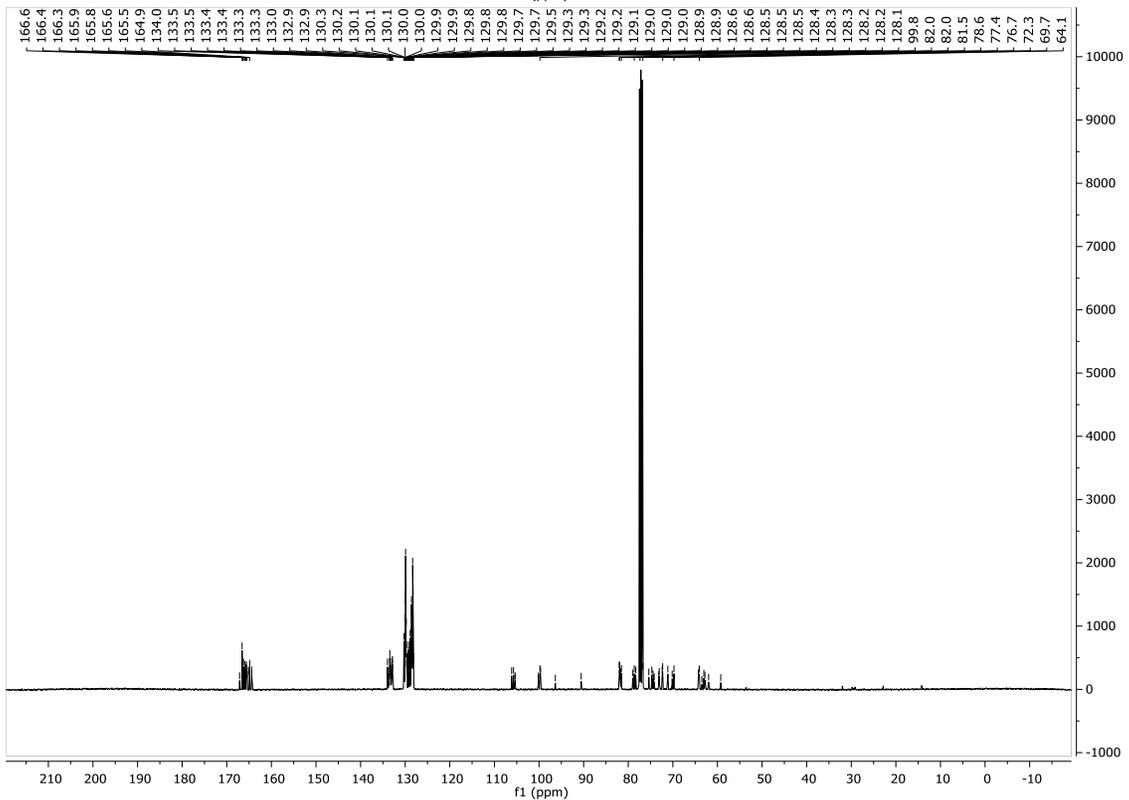
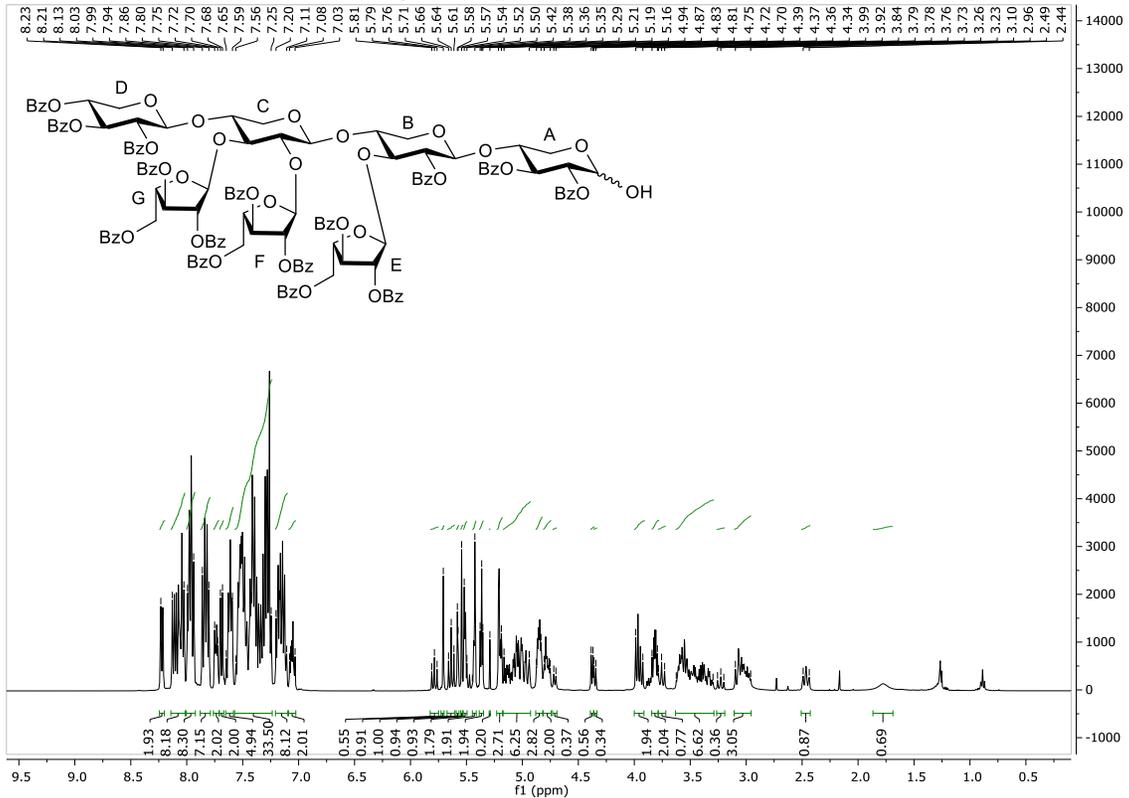
**2,3,4-Tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]-2-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]-2-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]-2-*O*-benzoyl- $\beta$ -D-xylopyranose (29)**



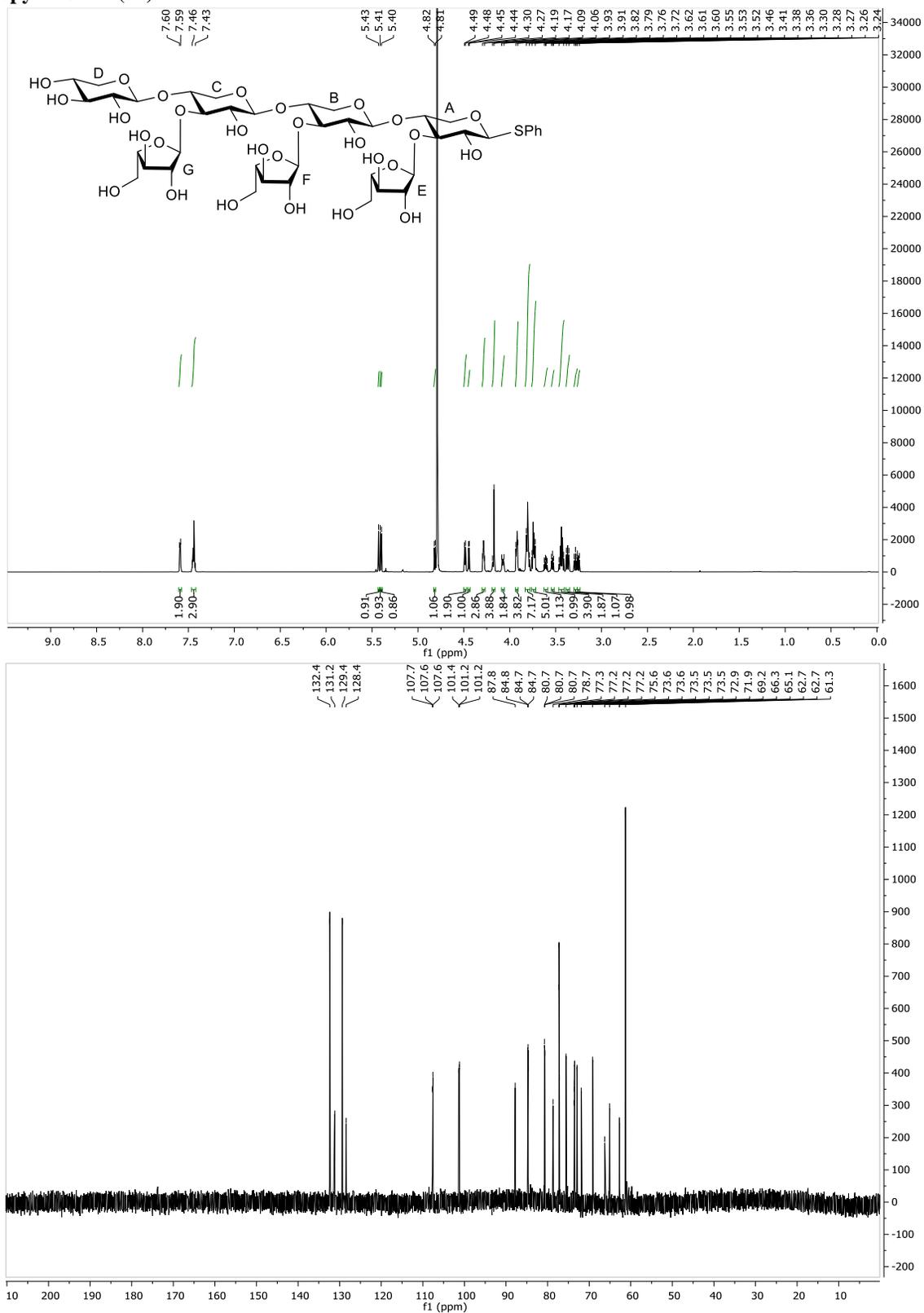
**2,3,4-Tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]-2-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 2)]-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-D-xylopyranose (30)**



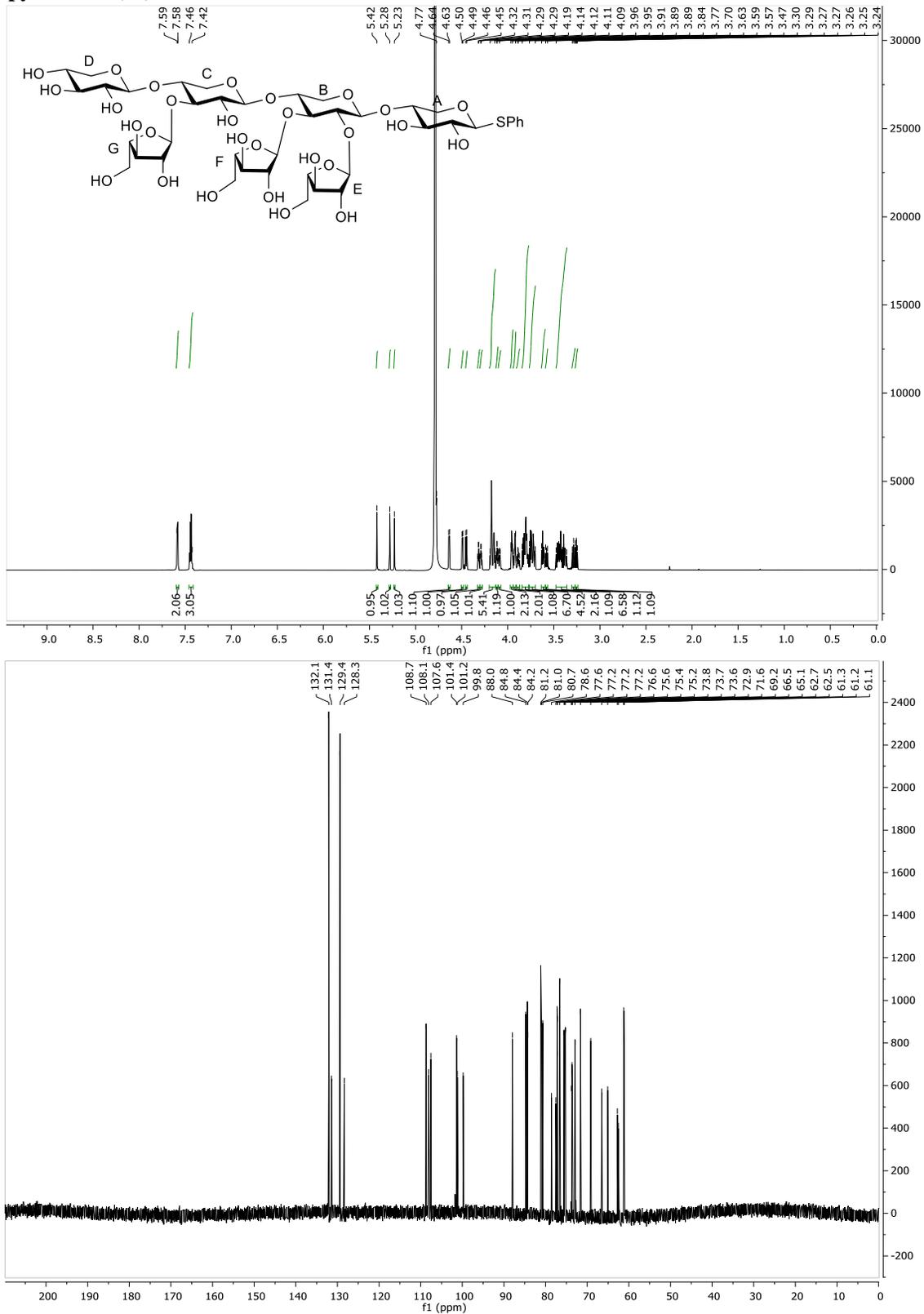
**2,3,4-Tri-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 2)]-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[2,3,5-tri-*O*-benzoyl- $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]-2-*O*-benzoyl- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-D-xylopyranose (31)**



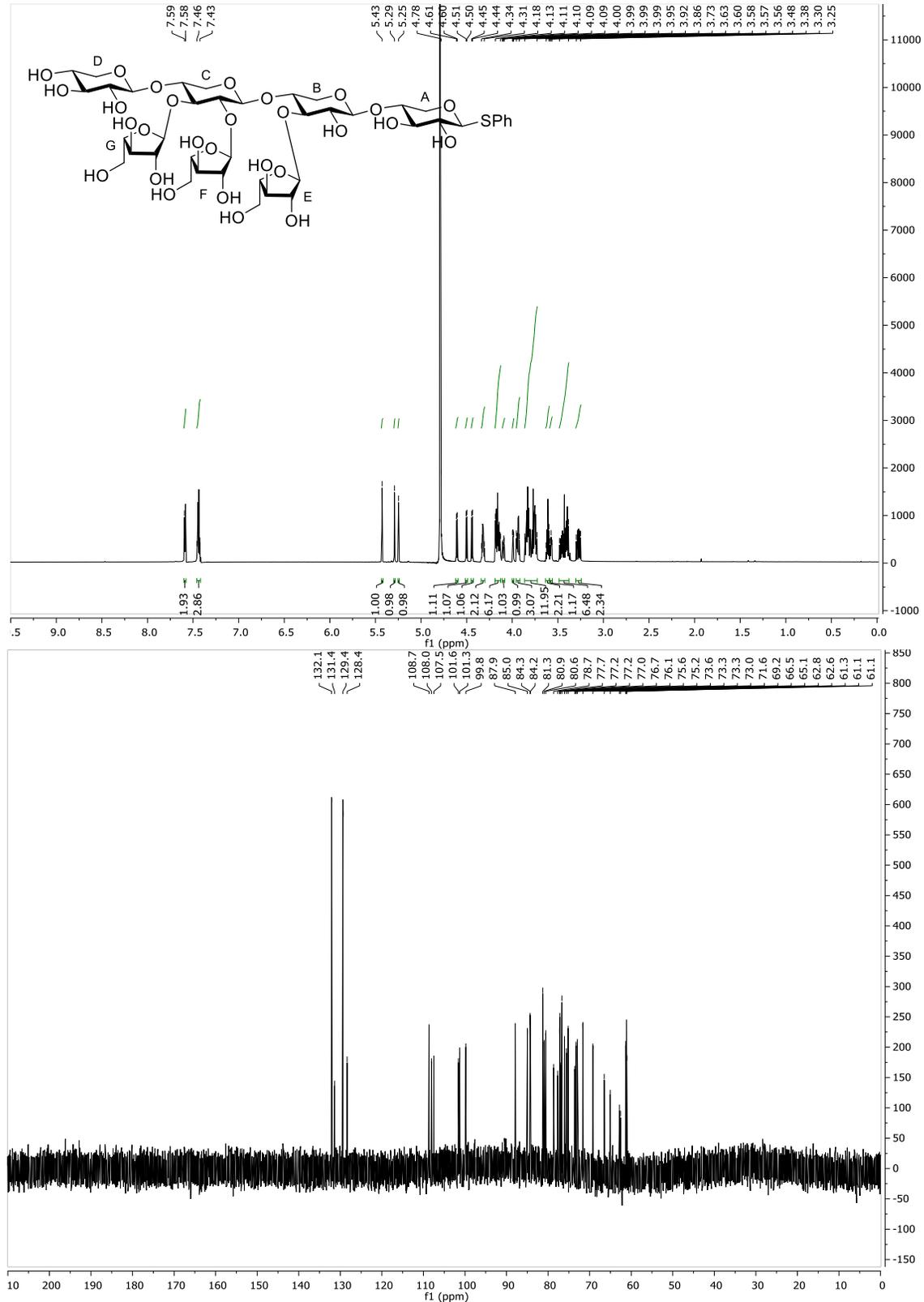
**Phenyl  $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]-1-thio- $\beta$ -D-xylopyranoside (32)**



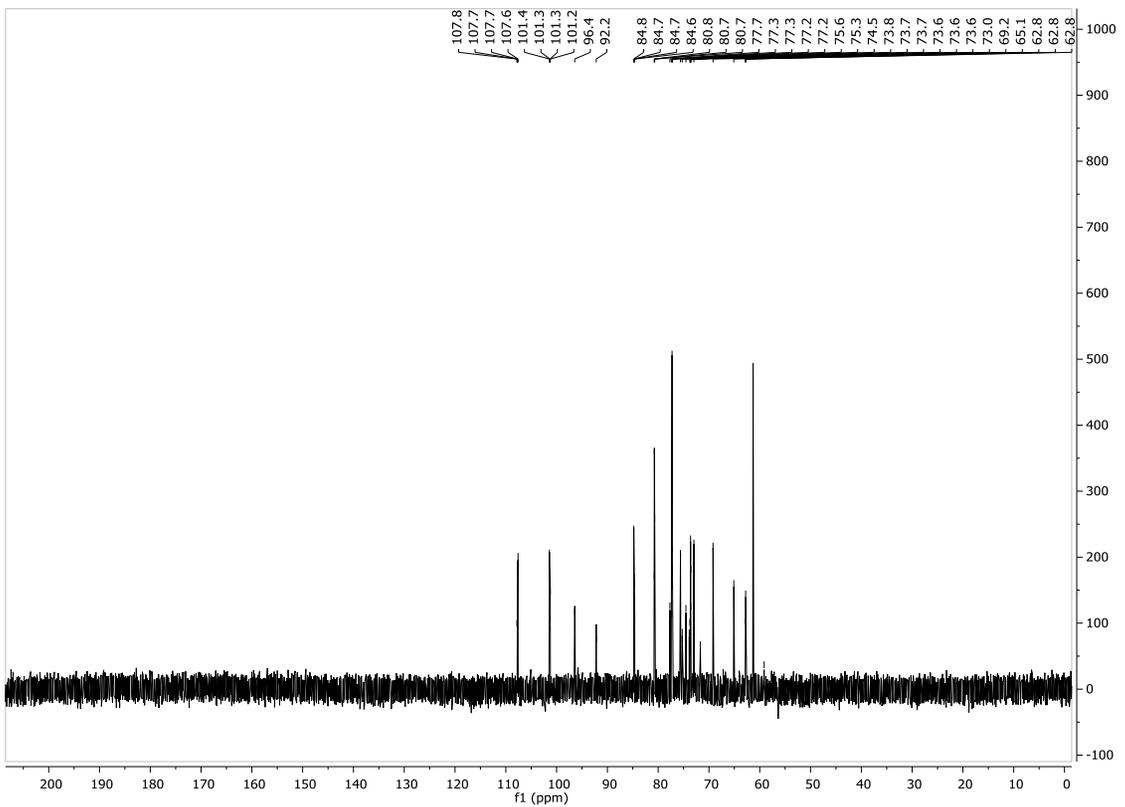
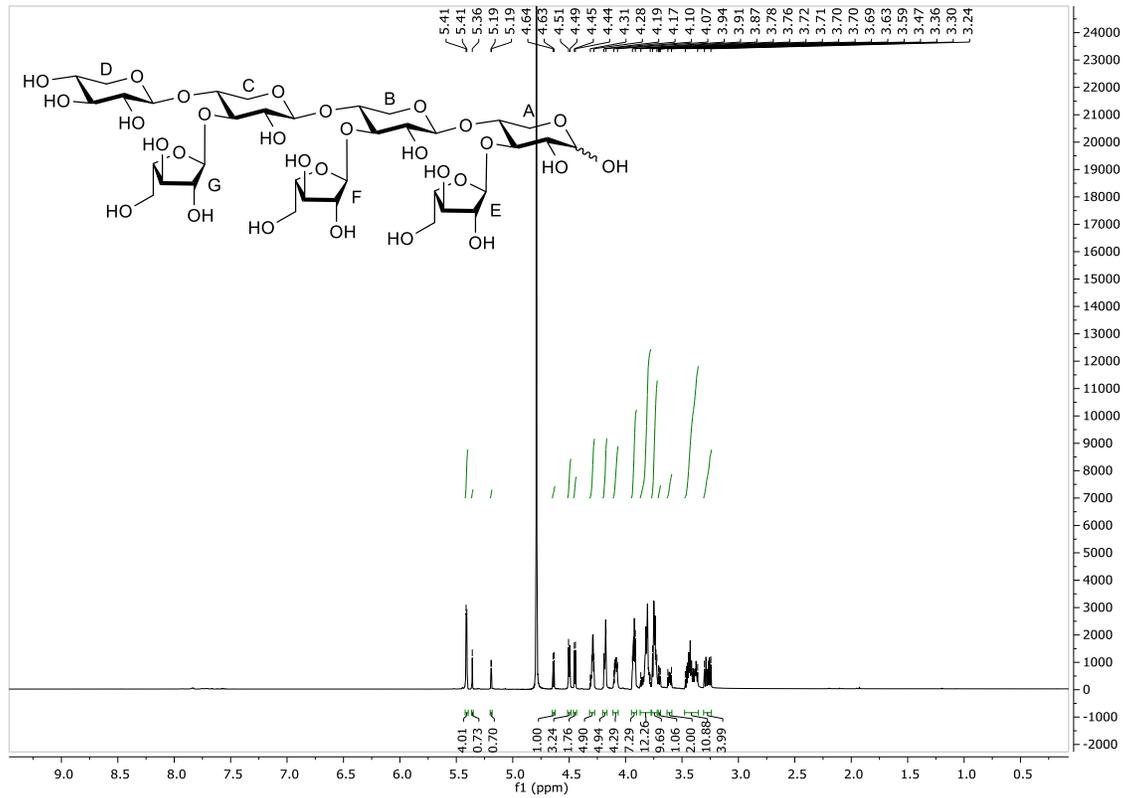
**Phenyl  $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 2)]-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-1-thio- $\beta$ -D-xylopyranoside (33)**



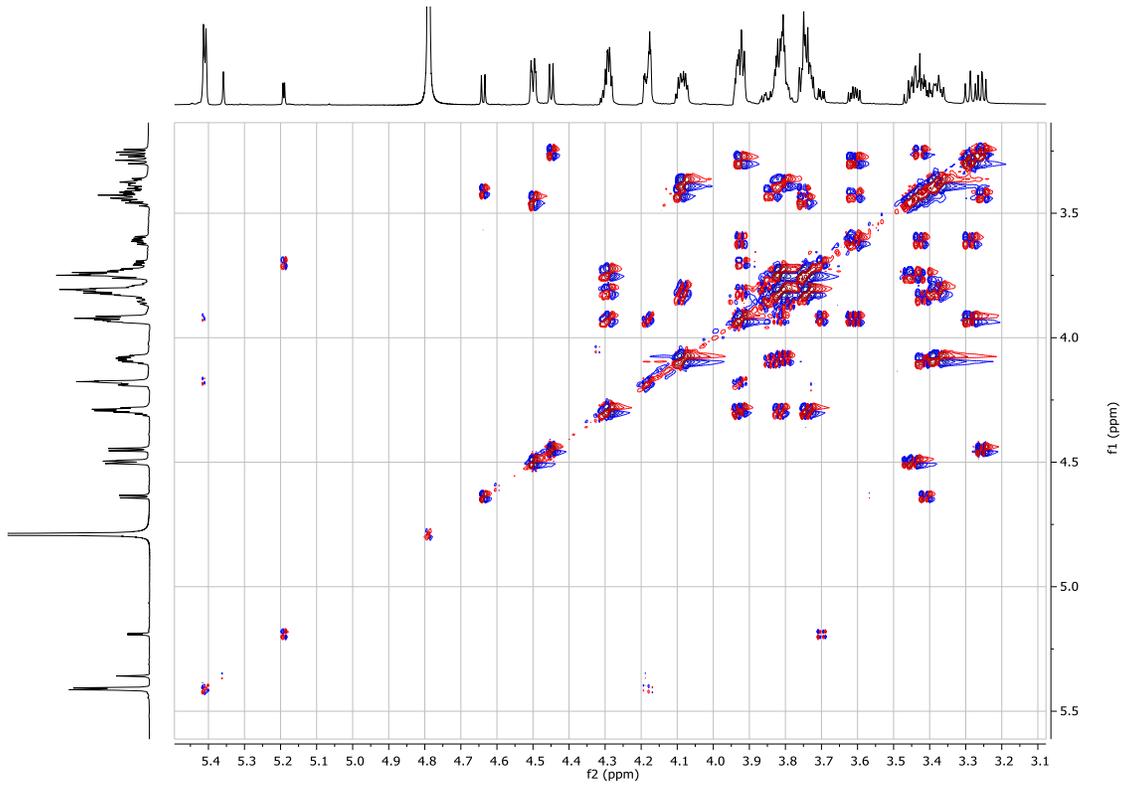
**Phenyl  $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 2)]-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-1-thio- $\beta$ -D-xylopyranoside (34)**



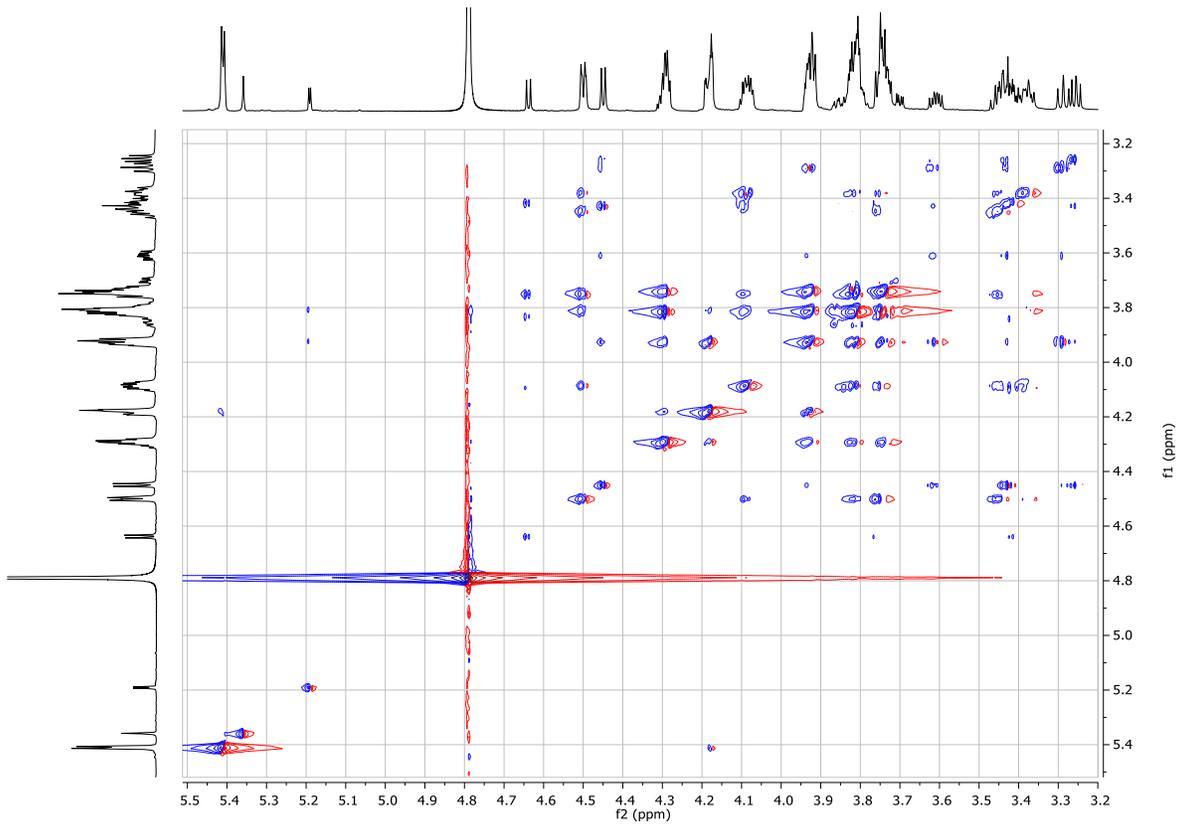
**$\beta$ -D-Xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]-D-xylopyranose (1)**



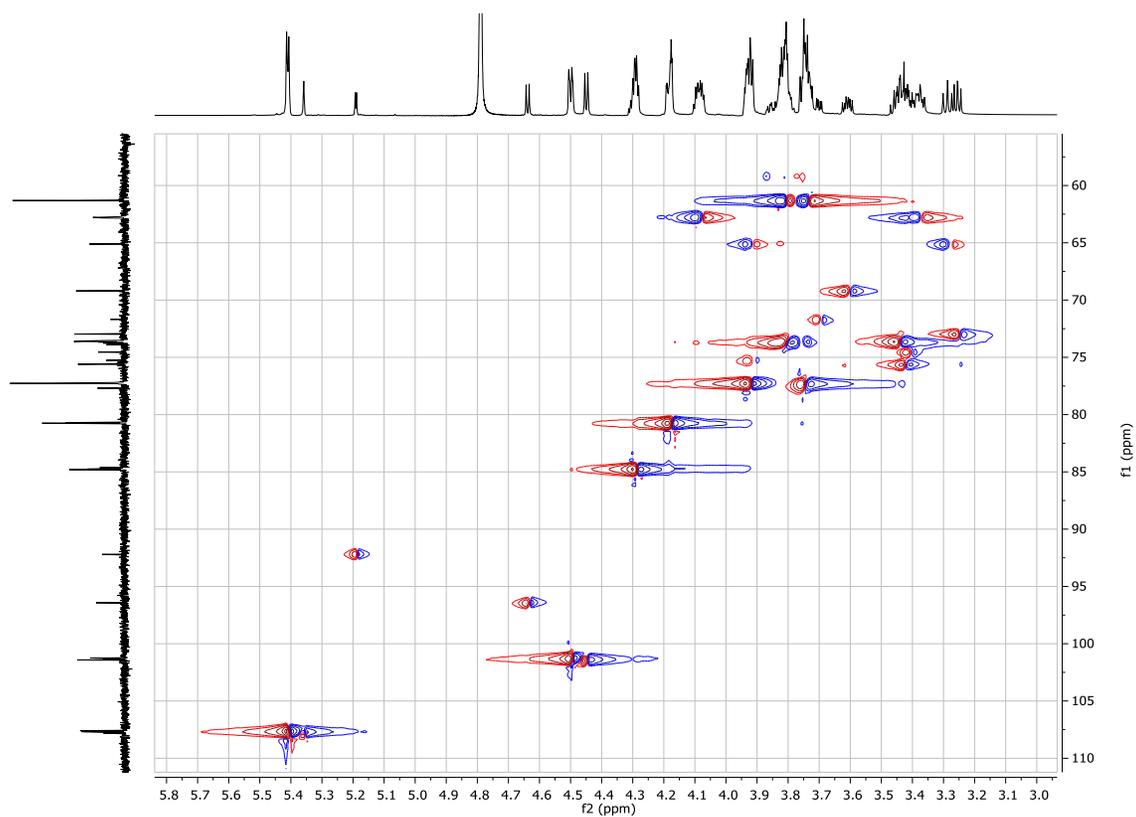
DQF-COSY



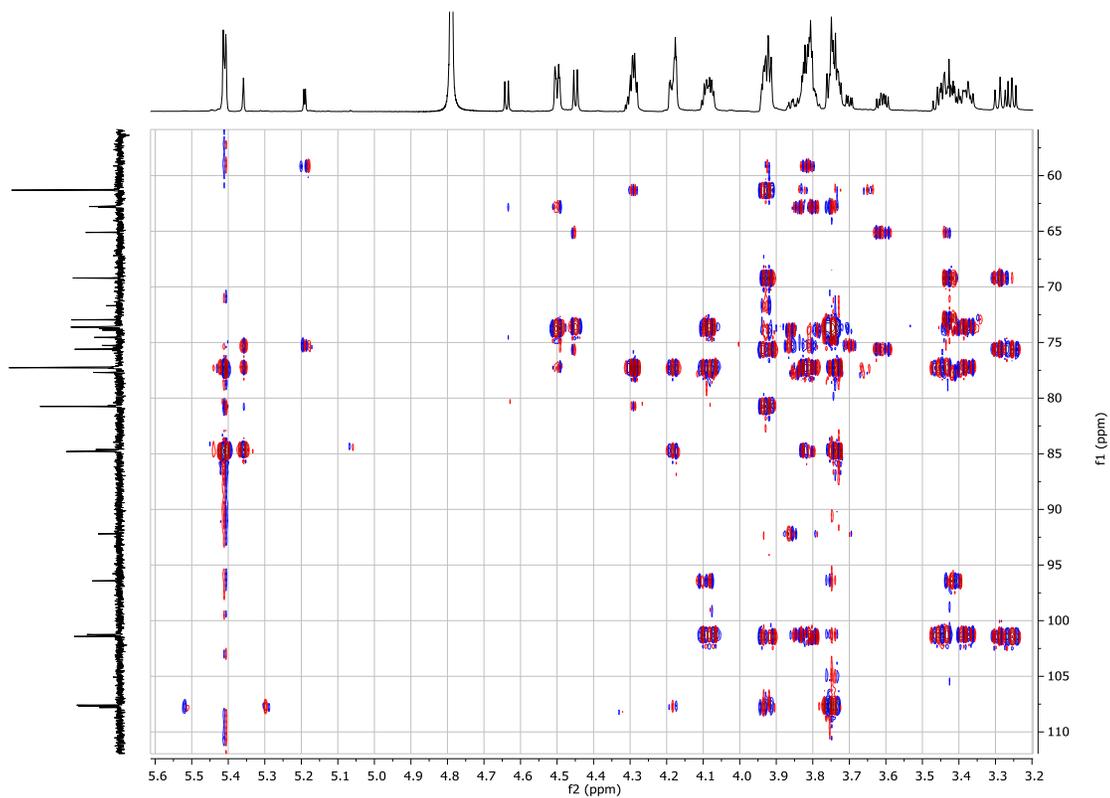
TOCSY



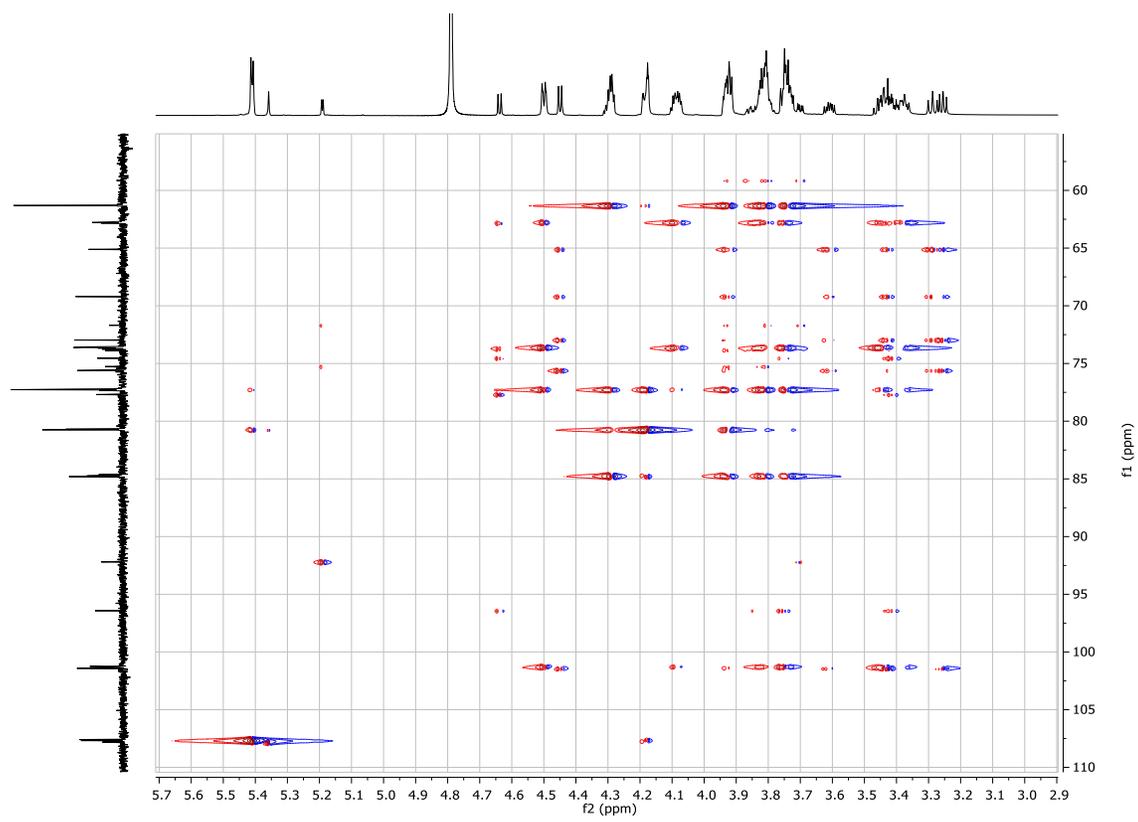
# HSQC



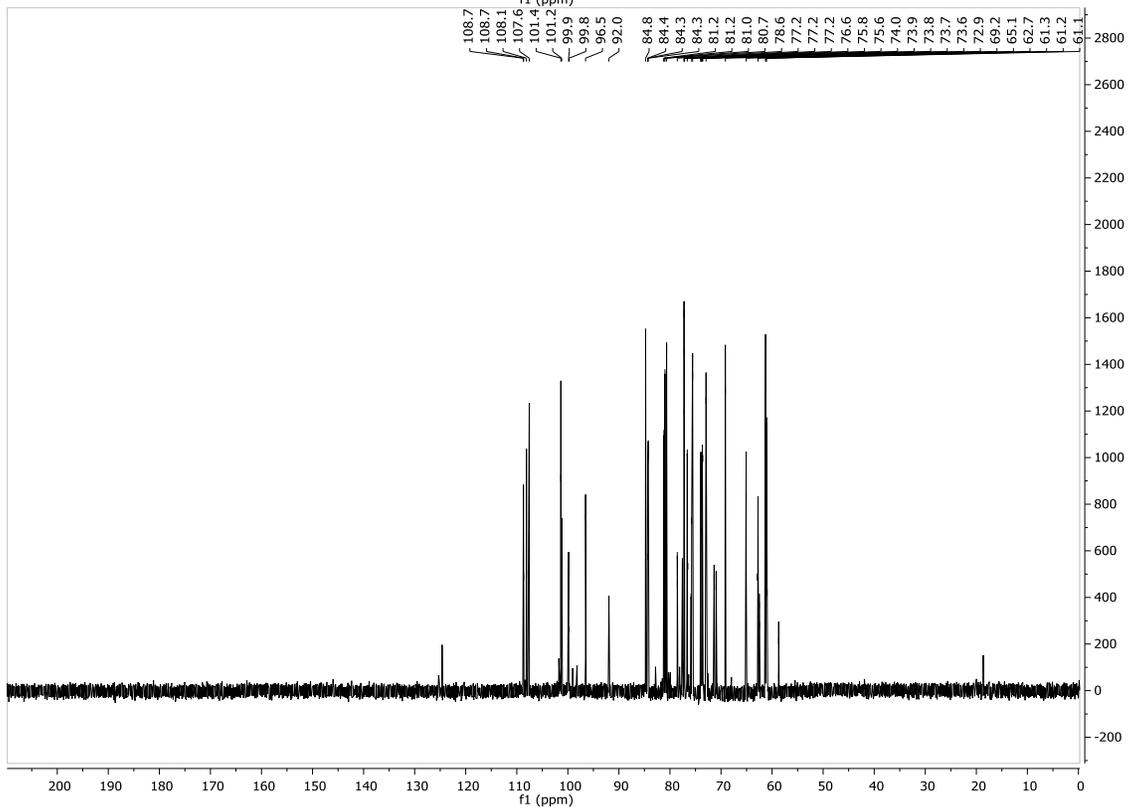
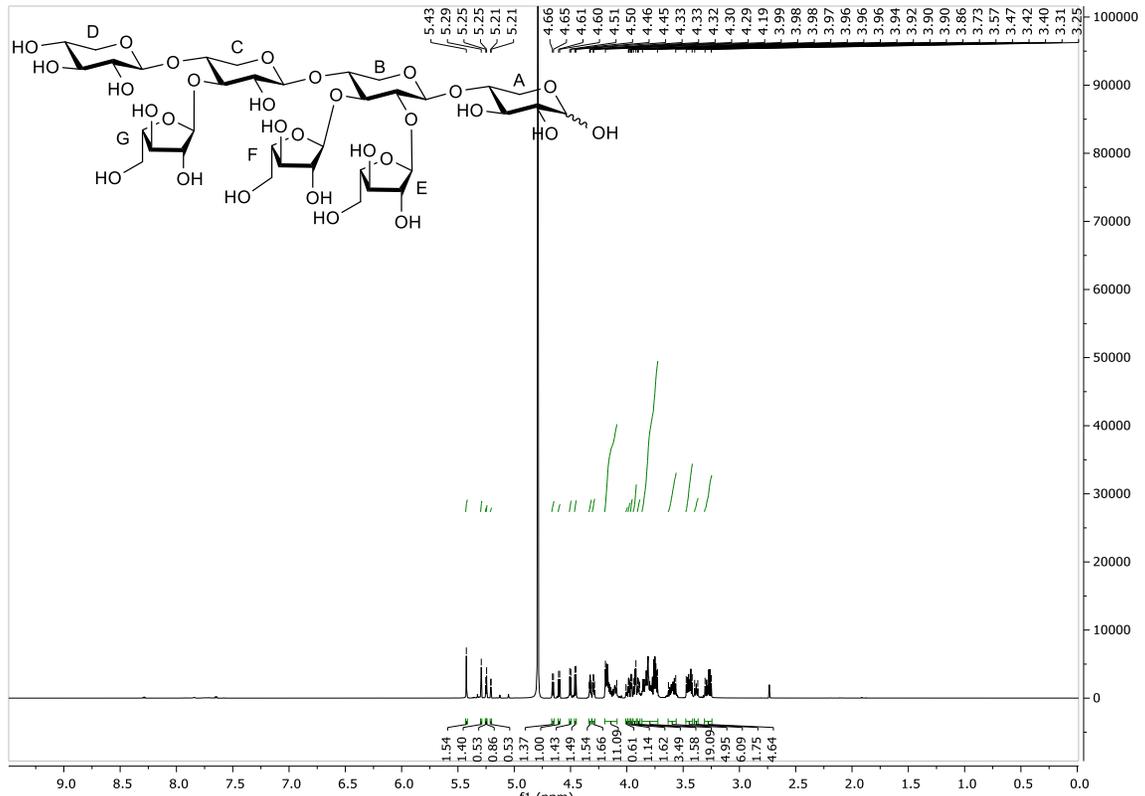
# HMBC



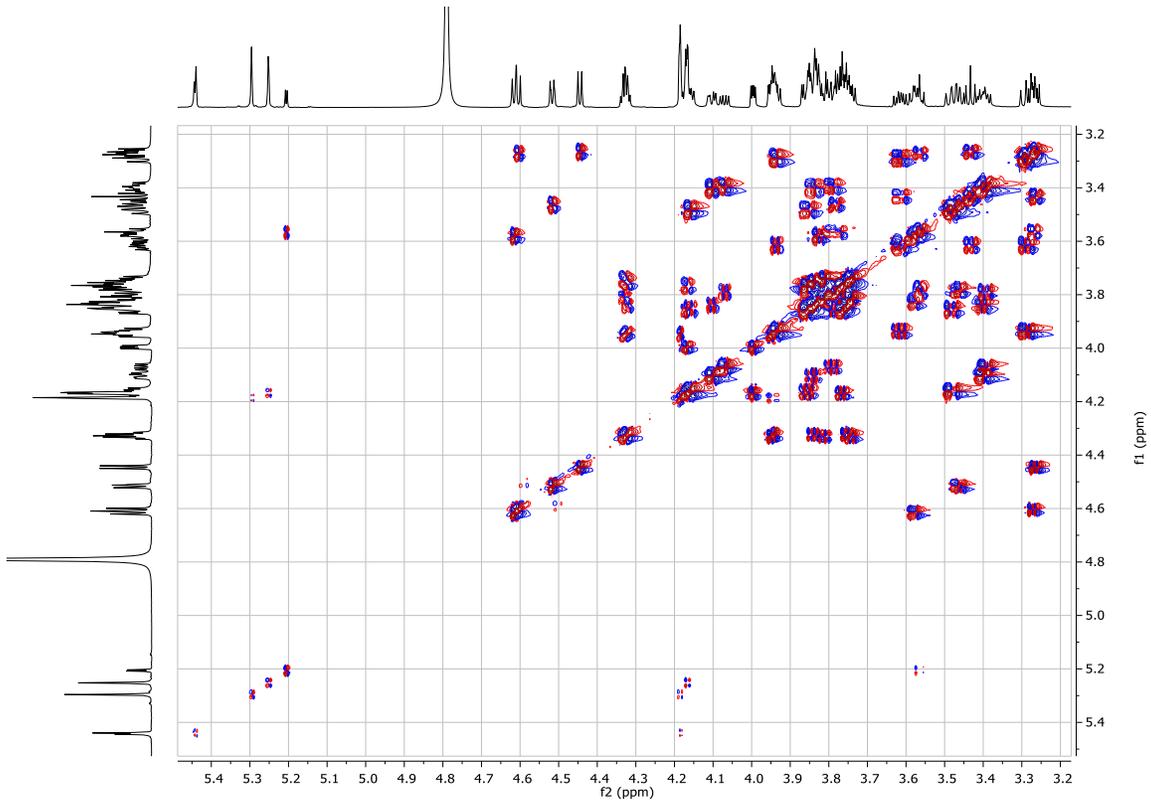
# HSQC-TOCSY



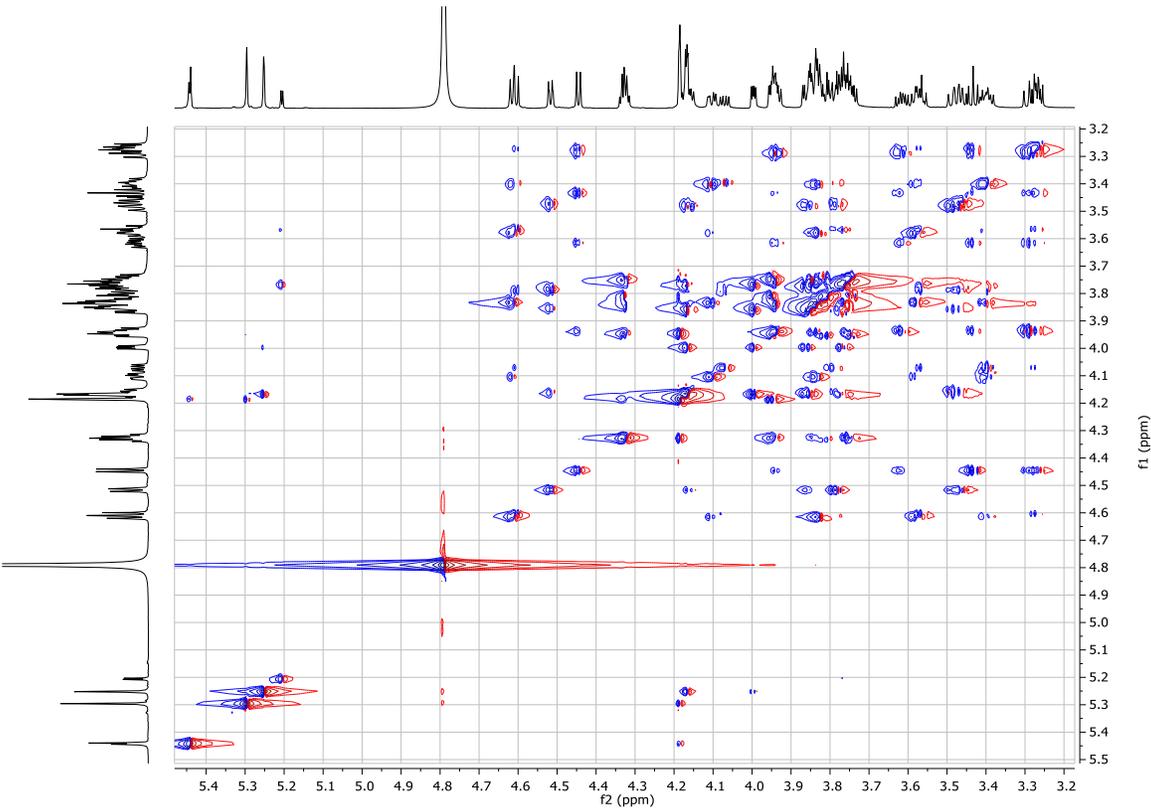
**$\beta$ -D-Xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 2)]-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-D-xylopyranose (2)**



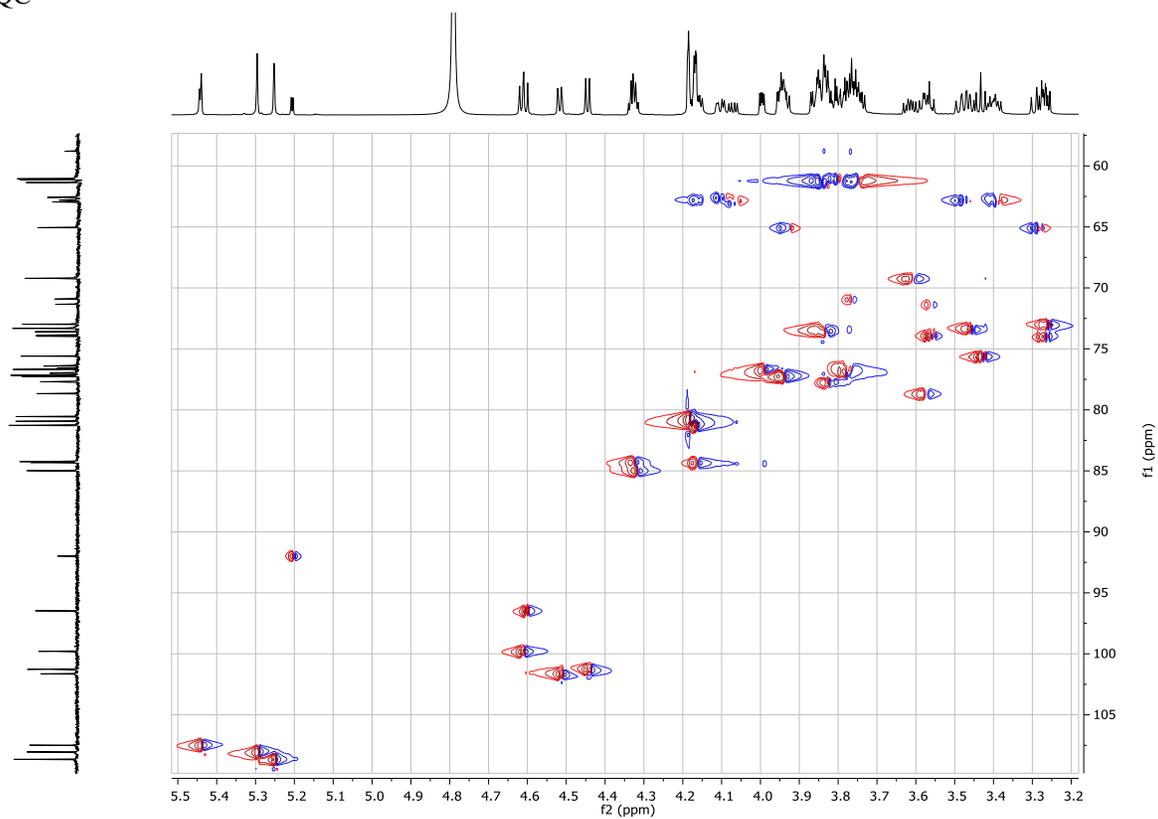
DQF-COSY



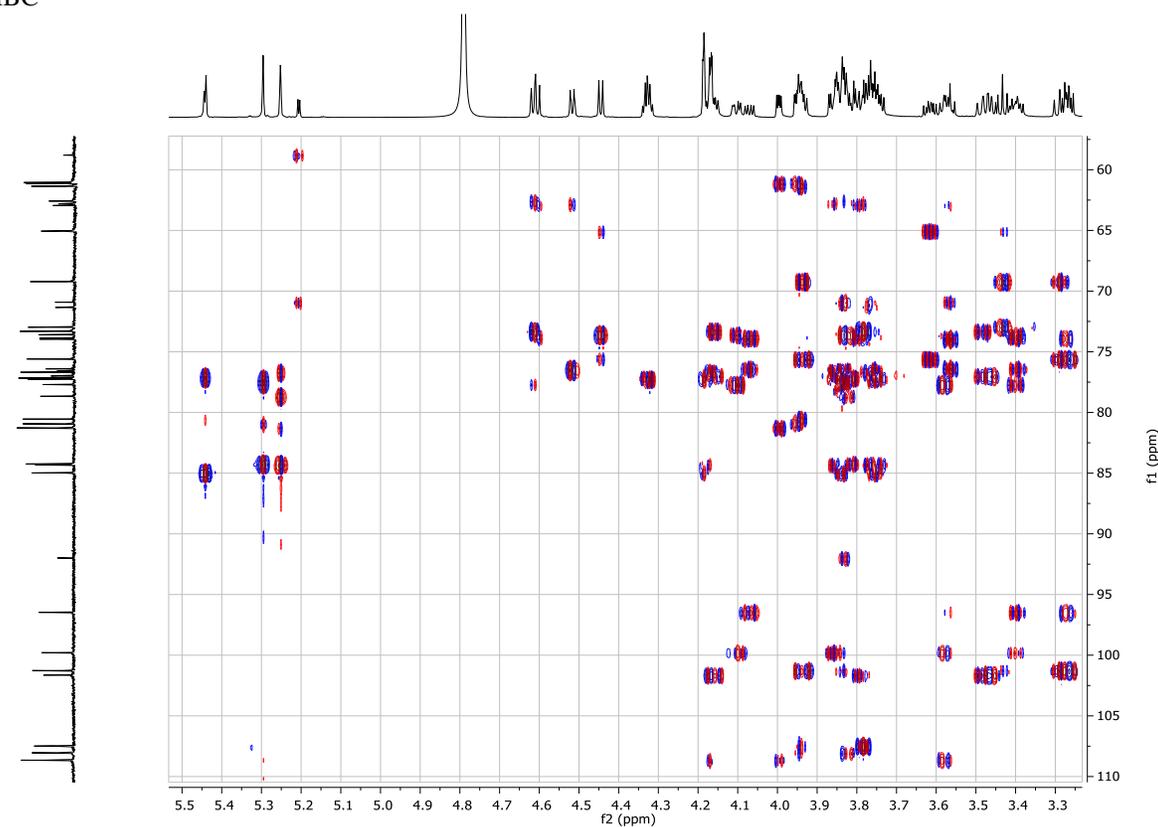
TOCSY



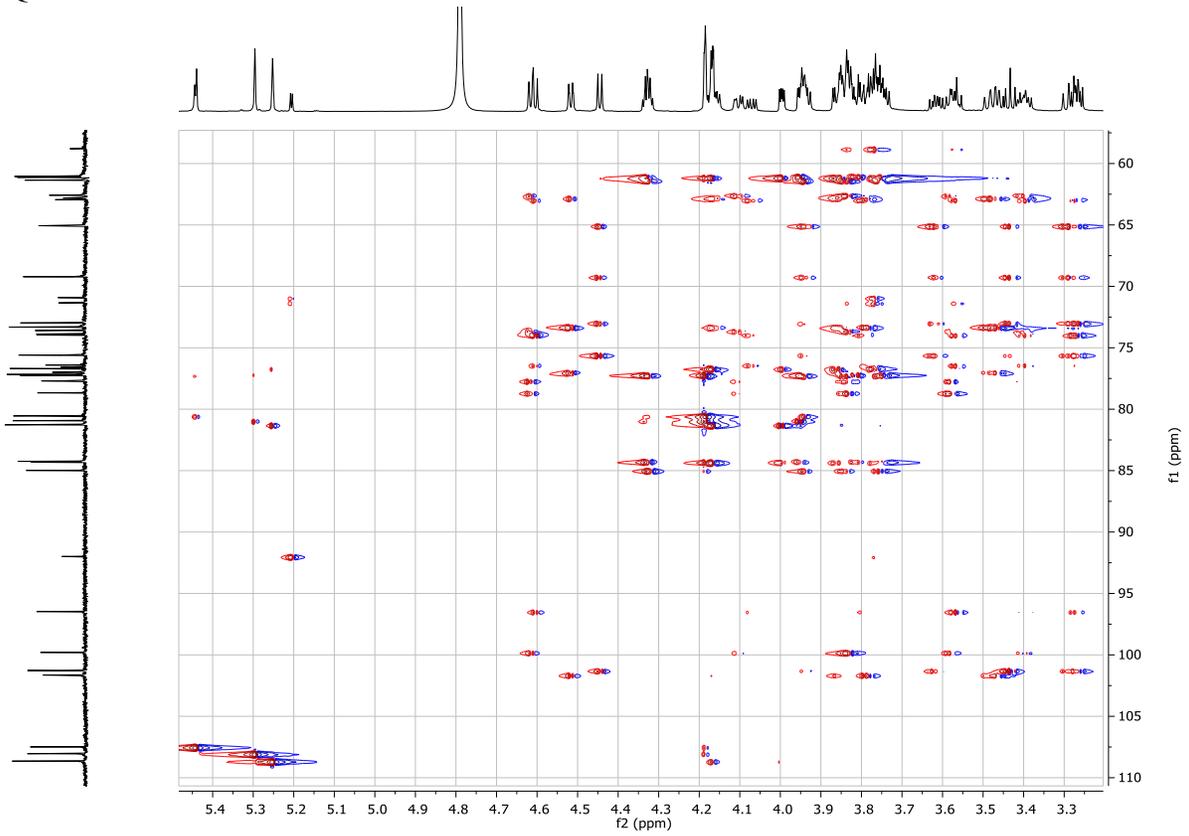
HSQC



HMBC



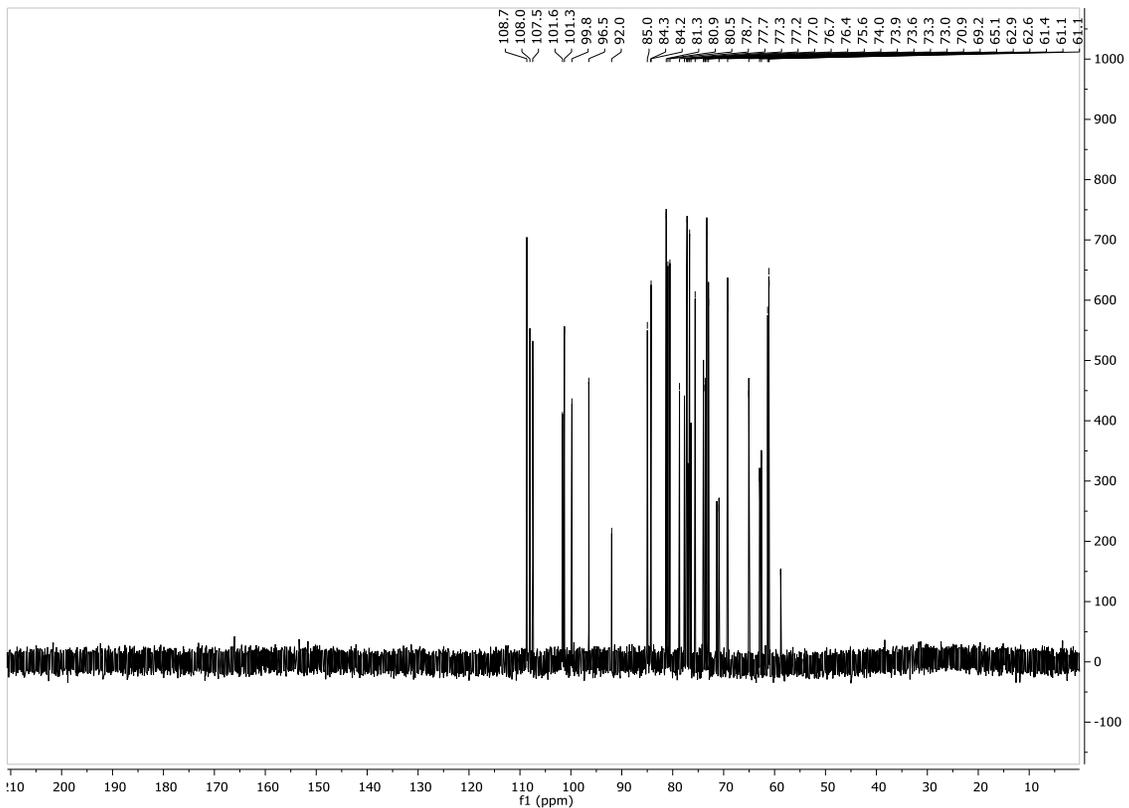
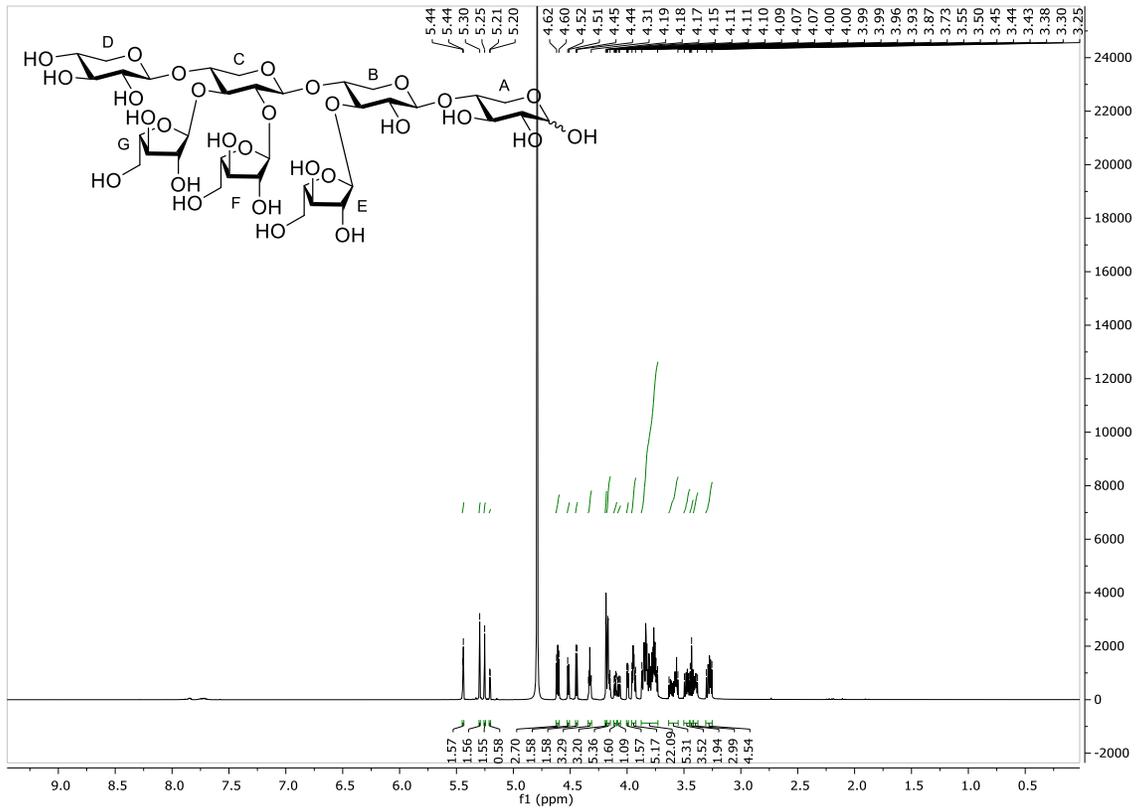
HSQC-TOCSY



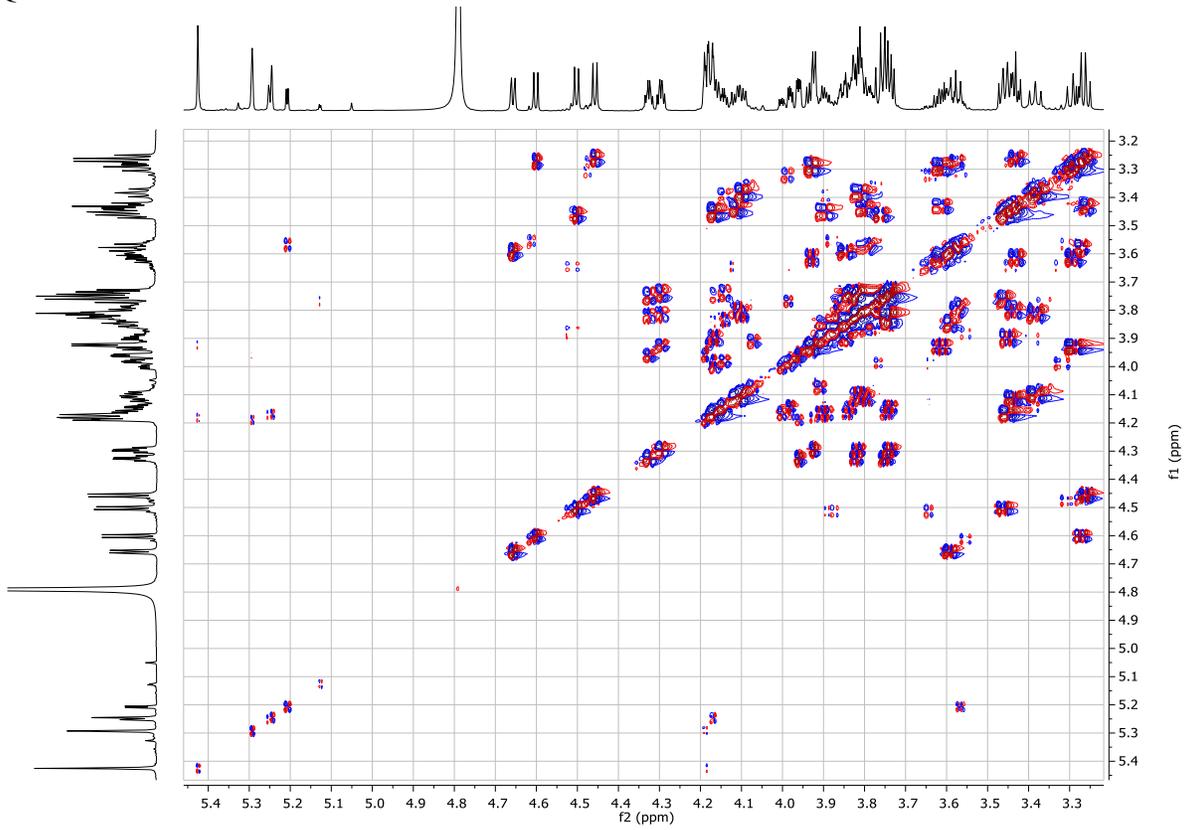
H2BC



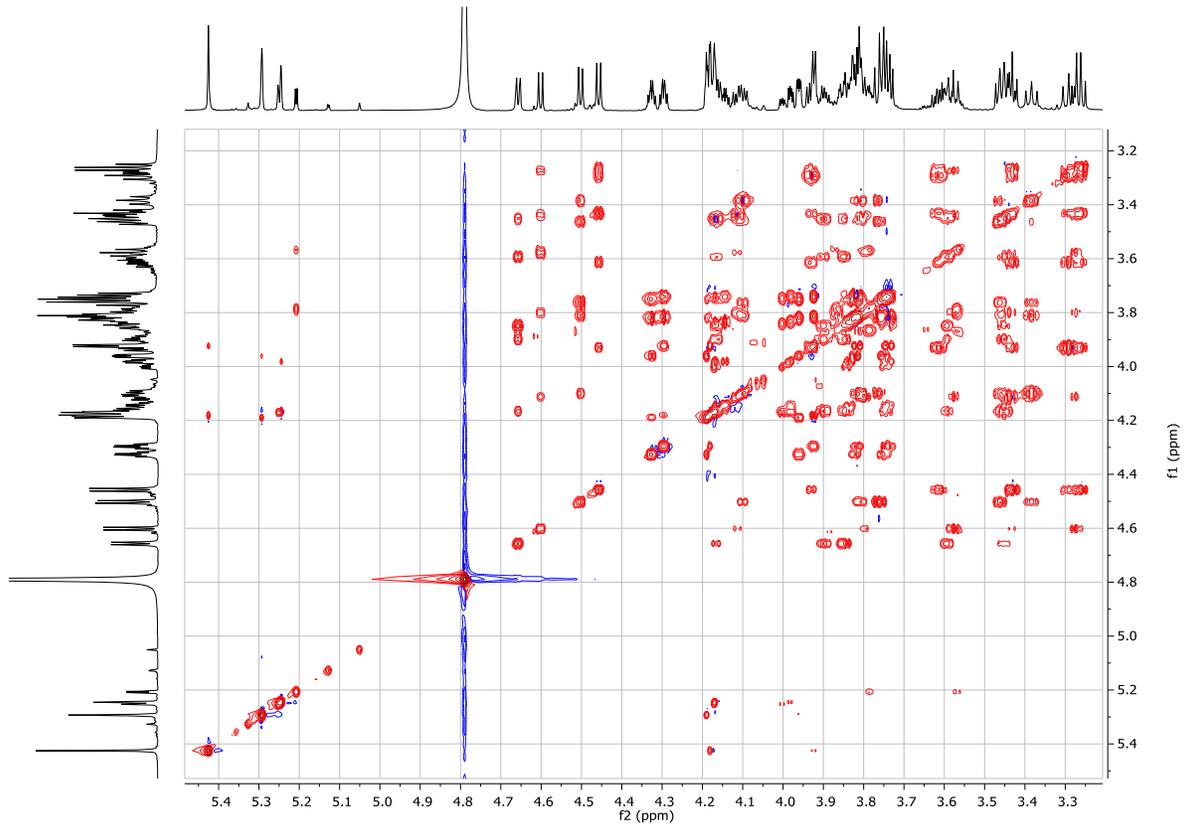
**$\beta$ -D-Xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 2)]-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-[ $\alpha$ -L-arabinofuranosyl-(1 $\rightarrow$ 3)]- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-D-xylopyranose (3)**



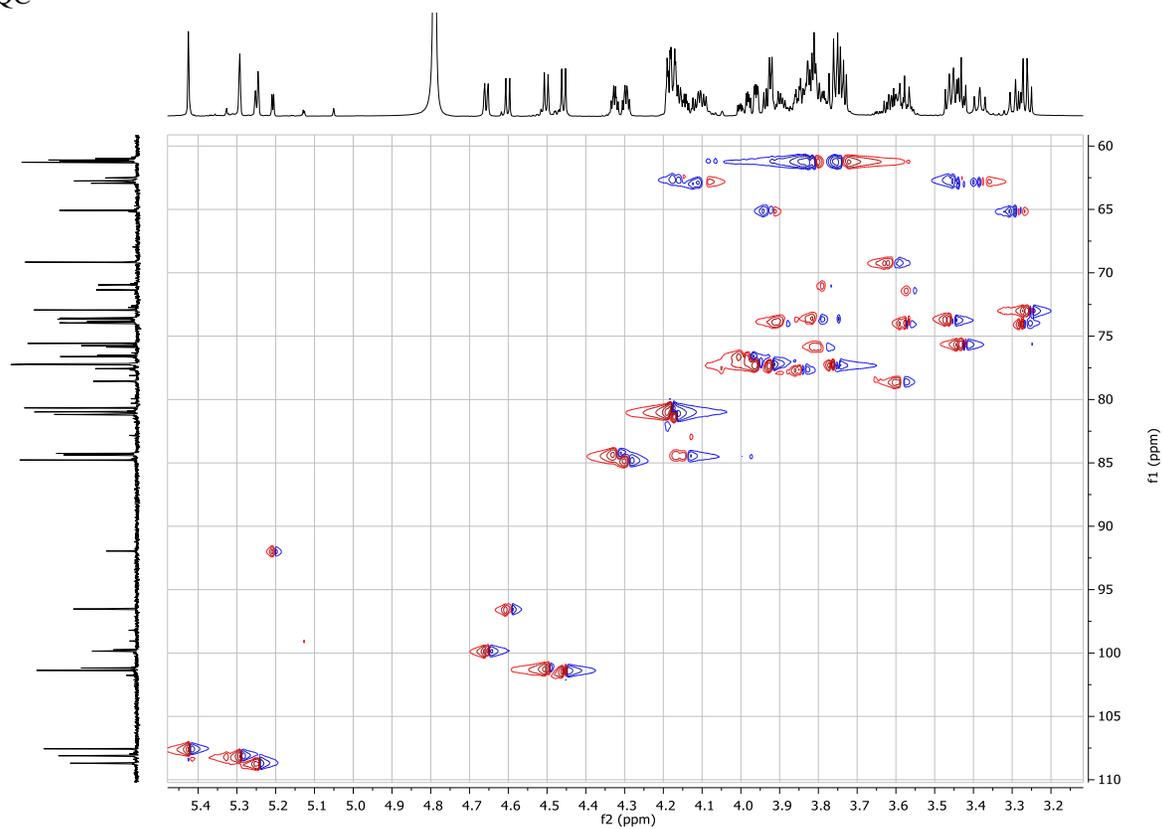
DQF-COSY



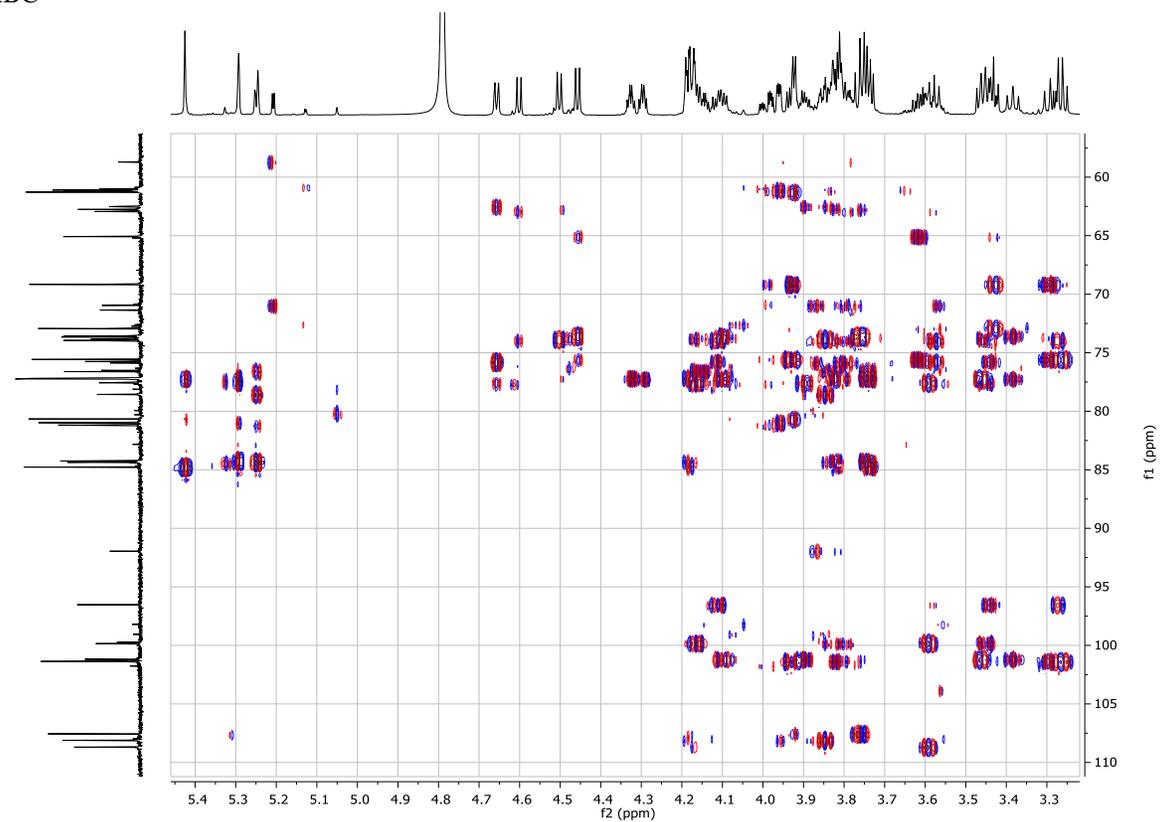
TOCSY



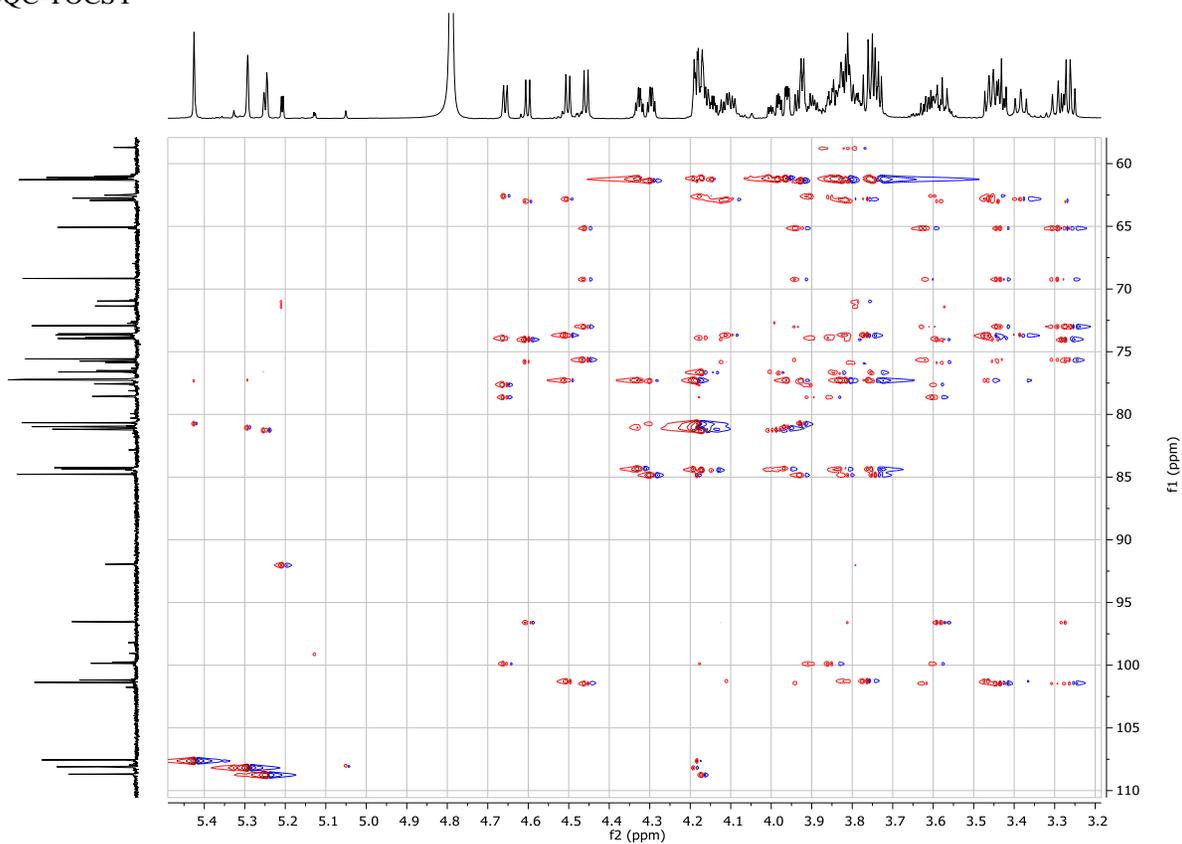
# HSQC



# HMBC



# HSQC-TOCSY



# H2BC

