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

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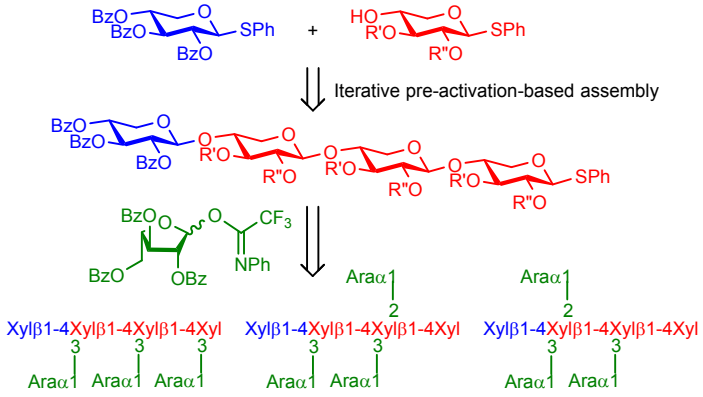


Abstract

A concise synthetic strategy has been developed for assembling densely substituted arabinoxylan oligosaccharides, which are valuable substrates for characterizing hemicellulose-degrading enzymes. The xylan backbone has been prepared by an iterative pre-activation-based glycosylation approach with phenyl thioglycosides. The pre-activation has been performed with in situ generated *p*-nitrobenzenesulfenyl triflate prior to addition of the acceptor. The glycosylation temperature was shown to have an important impact on the yield of the coupling. The arabinose substituents have been introduced in one high-yielding glycosylation with a *N*-phenyl trifluoroacetimidate donor. The strategy has been successfully employed for the

synthesis of three heptasaccharides in seven steps and overall yields of 24 – 36% from the corresponding monosaccharide building blocks.

INTRODUCTION

The hemicellulose polysaccharides comprise 15 – 35% by weight of the plant cell wall which is the main source of lignocellulosic biomass.[1] The largest group of polysaccharides in hemicellulose are the xylans which are characterized by a common backbone of β(1→4)-linked xylopyranosides.[1] The xylan structures are highly complex and heterogeneous due to the differences in the substitution patterns. One of the most abundant xylan subclasses are the arabinoxylans where some of the xylose units are substituted with L-arabinofuranosyl residues through either single substitution by α(1→2) or α(1→3) linkages or double substitution by both linkages.[1,2]

The arabinoxylans are dietary fibers that are not hydrolyzed by the digestive enzymes.[3] Instead they are fermented by microbes in the gut and in this way influences the composition and abundance of the colonic microbiota.[3] The result is a prebiotic effect where the health of the host is benefitted. Arabinoxylans have been shown to

strengthen the immune system and to lower the risk for obesity, type 2 diabetes, colon cancer and cardiovascular diseases.[3] The physiological functions, however, are strongly connected to the structure of the arabinoxylans, i.e. the length of the xylan backbone and the distribution of the arabinose units.[3] Besides food applications arabinoxylans are also used as a renewable source to prepare biodegradable materials such as films and hydrogels.[1,4]

Arabinoxylans are cleaved by glycosyl hydrolases (GH) to form smaller saccharides. The hydrolysis of the xylose linkages can be achieved with GH10 and GH11 xylanases, which prefer several unsubstituted xylose units, and with GH5 xylanases where an arabinose substituent is allowed close to the cleavage site.[5] Hydrolysis of the arabinose residues can be performed with GH43, GH51 and GH62 arabinofuranosidases where some of the enzymes exclusively cleave arabinoses linked to the 2 or the 3 position of single substituted xylose residues, whereas others are able to remove the pentose from disubstituted xylose moieties.[5,6] All the enzyme classes, however, suffer from poor access in the densely substituted regions of arabinoxylans and the difficulties are

further complicated by the lack of well-defined substrates with multiple arabinose substituents.

Arabinoxylan-degrading enzymes are usually investigated with rather heterogeneous polysaccharides isolated from natural sources by suitable pretreatment procedures. A few saccharides containing 2 – 4 xylose units and 1 – 2 arabinose residues can be isolated from enzymatic degradation of arabinoxylans,[7] but these simple substrates do not resemble the more densely substituted regions. Thus, well-defined xylans with several arabinose substituents would be valuable tools for mapping the active site of enzymes implicated in arabinoxylan degradation and to understand the interplay between different enzymes in order to achieve the most efficient deconstruction.

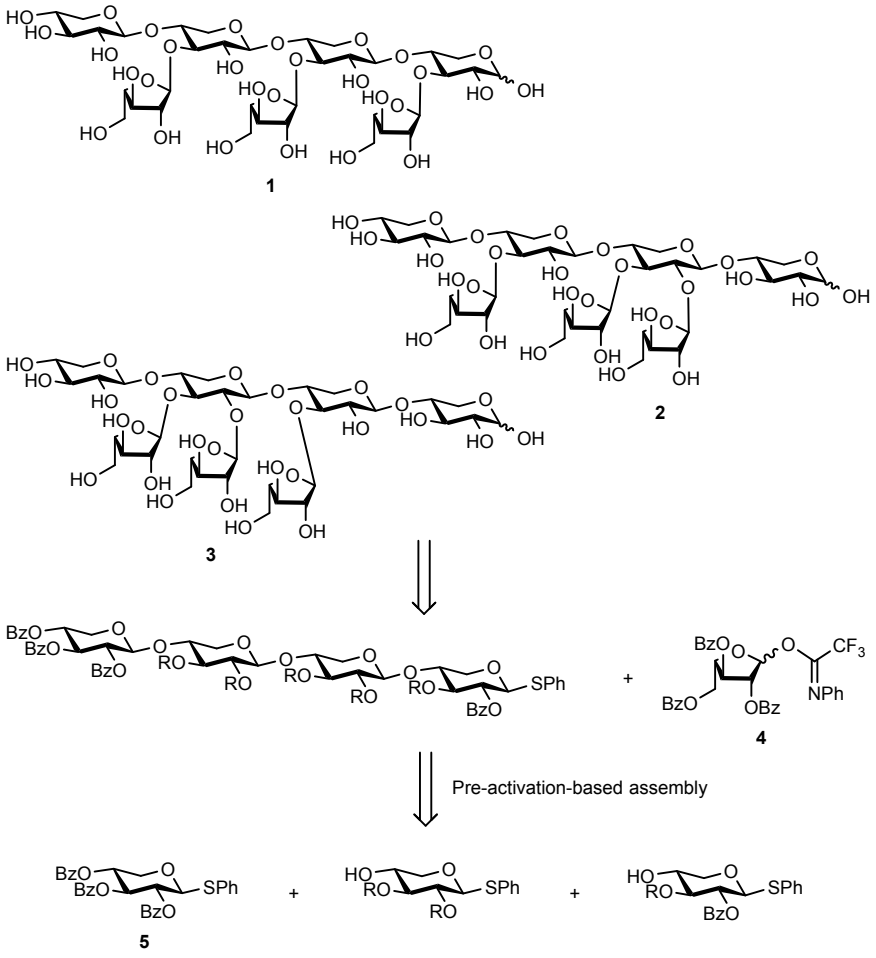
Chemical synthesis offers the possibility to prepare pure and well-defined oligosaccharides, but the arabinoxylans have so far received relatively little attention. Xylobiose has been glycosylated with one or two equiv. of an arabinofuranosyl donor to afford tri- and tetrasaccharides.[8] Recently, arabinoxylans with up to 6 xylose residues and 1 – 2 arabinose units were prepared by solid-phase synthesis and used for

determining the epitopes for monoclonal antibodies and the substrate specificity for xylanases and arabinofuranosidases.[9] In one case, two arabinoses were glycosylated onto the 2 and the 3 position of the same xylose residue although a very low yield was obtained illustrating the challenge of producing more densely substituted arabinoxylans. Linear xylans, on the other hand, where no additional substituents are present, are more readily assembled by either stepwise or blockwise approaches[10] and so far linear xylans up to decaxylans have been prepared,[11] which includes an approach by cleaving the hydroxymethyl group of glucans[12] and the assembly of *S*-linked oligoxylans.[13]

Herein, we report a novel pre-activation-based synthetic strategy for assembling arabinoxylans, which has led to the preparation of heptasaccharides **1** – **3** with three arabinose substituents (Scheme 1). A tetraxylan is chosen as the backbone since this constitutes a sufficient length to give the necessary enzyme activities.[5,9a] The three arabinose substituents are connected to either a xylotriose unit (as in **1**) or a xylobiose moiety (as in **2** and **3**) in order to resemble the densely substituted region. The

preparation of **1** – **3** extends our work on the synthesis of plant cell wall components where we have previously assembled oligomers of rhamnogalacturonan I and homogalacturonan by using *n*-pentenyl glycosides as glycosyl donors.[14]

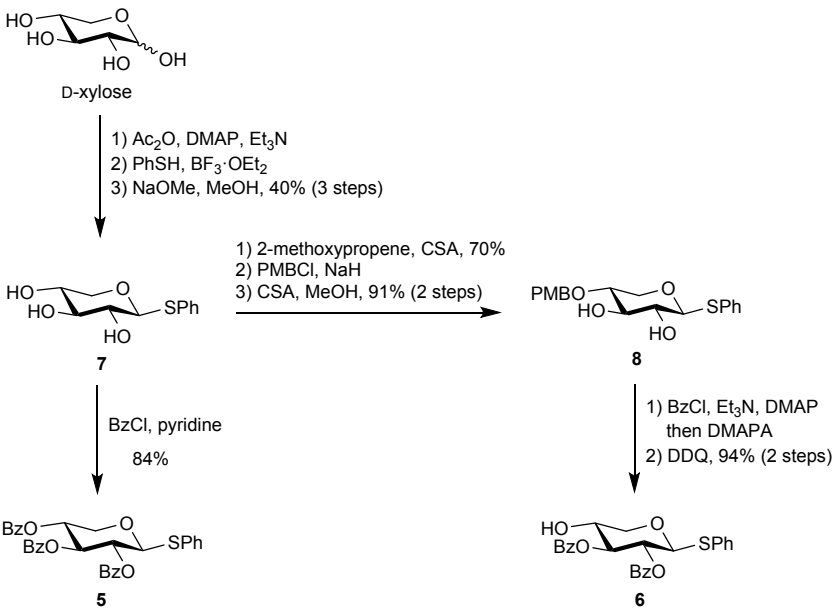
Scheme 1. Structures of Arabinoxylans 1 – 3 and Retrosynthetic Strategy



RESULTS AND DISCUSSION

The recent solid-phase synthesis of arabinoxylans was achieved by a stepwise approach where one xylose or arabinose unit was glycosylated at a time onto the growing oligosaccharide chain followed by cleavage from the resin and global deprotection.[9] Up to ten equiv. of a xylopyranosyl phosphate (prepared from the corresponding tolyl thioglycoside) or an ethyl 1-thioarabinofuranoside was used as the donor for each glycosylation reaction. We opted for a solution-phase strategy involving fewer steps where all the arabinose units are introduced in one coupling reaction (Scheme 1). The linear xylan backbone will be prepared by a pre-activation-based synthesis[15] from the appropriate phenyl 1-thioxylopyranosides where deprotection steps will not be necessary after each glycosylation reaction.[16] The pre-activation-based thioglycoside protocol has previously been used for coupling of a variety of monosaccharides[15,17] including arabinofuranosides,[18] but it has so far not been applied to the coupling of xylose units. The benzoyl group will serve as a permanent protecting group for the xylose residues since it allows for neighboring group participation from the 2 position to afford the β-linkage in the glycosylations. The arabinose units will also be protected with benzoyl groups and the corresponding *N*-phenyl trifluoroacetimidate **4** will serve as the donor since it has previously given high yields in the coupling with different secondary alcohols.[19]

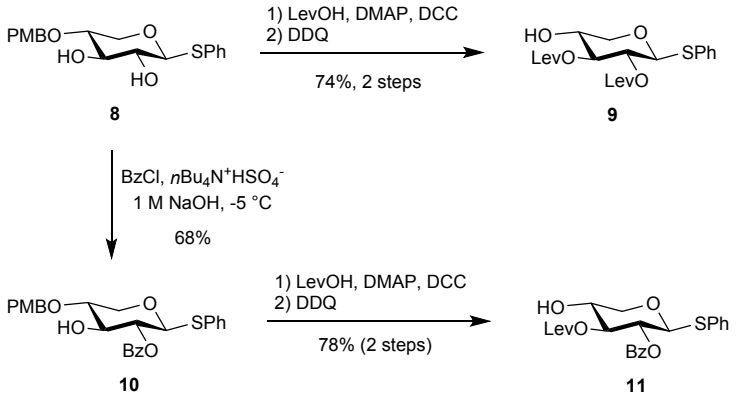
Scheme 2. Synthesis of Building Blocks 5 and 6



Several phenyl 1-thioxylopyranoside building blocks were required for the xylan assembly by the pre-activation-based approach. This involves fully benzoylated glycoside **5**, 2,3-di-*O*-benzoylated glycoside **6** and two glycosides with different protecting groups at position 2 and 3. The building blocks were all prepared from phenyl 1-thio-β-D-xylopyranoside (**7**), which is available from xylose in three simple steps involving peracetylation in the presence of 4-(*N*,*N*-dimethylamino)pyridine (DMAP), thiolation and deacetylation[20] with no purification of the intermediates (Scheme 2). Perbenzoylation of **7** then afforded tribenzoate **5** while the preparation of dibenzoate **6** required selective transformations of the hydroxy groups. In xylopyranosides the three hydroxy groups are all equatorial and similar in reactivity making regioselective reactions a particular challenge.[21] One of the most effective procedures is to block the 2 and the 3 position with an isopropylidene group, which affords only minor amounts of the corresponding 3,4-acetal.[22] Thus, treatment of triol **7** with 2-methoxyprop-1-ene and camphorsulfonic acid (CSA) led to the acetonide at position 2 and 3 as the major product.

Subsequently, a *para*-methoxybenzyl group (PMB) was installed at position 4 and the acetonide was removed under acidic conditions to provide diol **8**.[23] The hydroxy groups were benzoylated and excess benzoyl chloride removed with 3-(dimethylamino)-1-propylamine (DMAPA).[24] Without further purification the crude product was subjected to PMB deprotection with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to afford dibenzoate **6**.

Scheme 3. Synthesis of Building Blocks 8 and 10



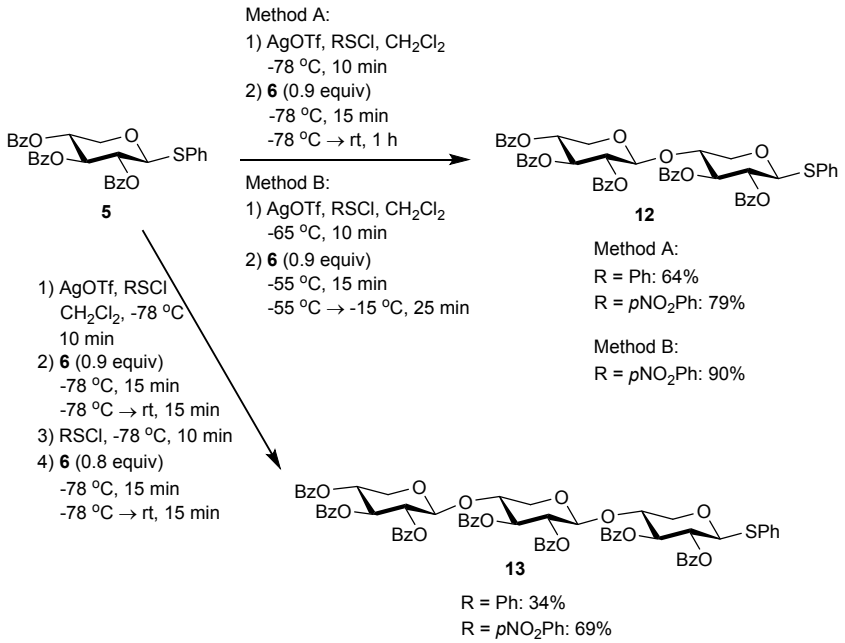
The two remaining building blocks required a different protecting group to be installed at position 3 as well as at position 2 and 3 since these sites will be linked to the arabinose units. The temporary protecting group should be an ester to ensure neighboring group participation in the glycosylation, but should at the same time be removable in the presence of the benzoates. A chloroacetate was first considered and installed selectively at position 3, but the following glycosylation with **5** under the pre-activation protocol only furnished a moderate yield of the disaccharide. This was attributed to the use of a silver salt in the glycosylation and a levulinyl (Lev) group was therefore chosen instead. *N,N'*-Dicyclohexylcarbodiimide (DCC) coupling of diol **8** with levulinic acid followed by direct treatment with DDQ furnished dilevulinate **9**

(Scheme 3). For the selective introduction of the temporary protecting group, diol **8** was first subjected to regioselective benzoylation at position 2. With benzoyl chloride in pyridine the esterification was slow and actually produced the dibenzoate as the main product. However, when diol **8** was submitted to 1.3 equiv. of benzoyl chloride in a mixture of CH_2Cl_2 and 1 M NaOH under phase transfer catalysis,[25] 2-benzoate **10** was obtained in 68% yield with only minor amounts of the corresponding 3-benzoate as a byproduct. Subsequent esterification with levulinic acid and deprotection of the PMB group gave the desired 3-levulinate **11**.

The stage was now set for assembling the xylan backbone by the pre-activation-based protocol. The original procedure with tolylthio glycosides called for activation of the donor with *p*-toluenesulfenyl chloride and silver triflate at a temperature of –60 °C to generate the reactive electrophile.[16] The acceptor was then added followed by stirring for 15 min and warming to rt. The procedure was later on modified with the formation of the reactive electrophile at –78 °C followed by adding the acceptor and raising the temperature to rt.[17] Using this latest protocol, donor **5** was coupled to acceptor **6** with phenylsulfenyl chloride and silver triflate[26] to give disaccharide **12** in 64% yield (Scheme 4, Method A). The coupling could also be carried out in a one-pot iterative manner[16] by adding more promoter and acceptor to furnish trisaccharide **13** although the yield in this case was only 34% since disaccharide **12** was also formed in 59% yield. Attempts to improve the glycosylations by using Me_2S_2/Tf_2O[27] or 1-benzenesulfinyl piperidine/Tf_2O[28] as the promoter were unsuccessful and only led to a mixture of products. However, when *p*-nitrobenzenesulfenyl chloride and silver triflate[29] was employed as the promoter, the yield of **12** and **13** in the two reactions increased to 79 and 69%, respectively. *p*-Nitrobenzenesulfenyl chloride is commercially available as opposed to phenylsulfenyl chloride and *p*-toluenesulfenyl chloride which are prepared from the corresponding thiols with sulfuryl

chloride. In addition, *p*-nitrobenzenesulfenyl chloride is a solid making this reagent procedurally more convenient to deliver while the other two sulfenyl chlorides are liquids. The quality of commercial *p*-nitrobenzenesulfenyl chloride, however, varied and we obtained lower glycosylation yields when using light brown samples with a mp of ~43 °C. Attempts to recrystallize the compound failed, but sublimation yielded material with a light yellow color and a mp of 47 – 51 °C which could be stored at 5 °C for months. When *p*-nitrobenzenesulfenyl chloride purified by sublimation was used, the yields in the glycosylations were consistent. During the couplings, the disulfide byproduct from the activation (i.e. *p*NO_2PhSSPh) precipitated and did therefore not take part in any additional reactions.

Scheme 4. Synthesis of Saccharides 12 and 13



To further improve the glycosylation outcome the influence of the temperature was also investigated. These experiments were performed in a two-neck Schlenk flask that allowed for

measuring the internal temperature in the reaction mixture at any time during the glycosylation. The activation of donor **5** was observed to be quick and goes to completion in less than 10 min at –78 °C according to TLC analysis. This is in accordance with investigations on the activation of similar thioglycosides under these conditions.[30] However, in the ensuing glycosylation reaction after adding acceptor **6** the reaction temperature becomes important. If the temperature is kept at –78 °C the glycosylation is sluggish and an intermolecular aglycon transfer[31] becomes a competing reaction leading to the regeneration of donor **5**.[32] Under these conditions disaccharide **12** was only obtained in 54% yield together with 10% of donor **5** although full activation of the donor had been achieved. Thus, at very low temperature the hydroxy group and the sulfur in acceptor **6** are both able to serve as a nucleophile in the reaction with the donor. Further experiments revealed that the aglycon transfer was mainly observed when the temperature was kept below –60 °C. Therefore, three separate experiments were set up where acceptor **6** was added at –55 °C (Figure 1). In the first experiment, the temperature was immediately raised to rt over 1 h while in the two other experiments the temperature was first maintained at –55 °C for 10 – 15 min before being raised. The first reaction gave 73% yield of disaccharide **12** whereas 85 and 90% yield were obtained in the two other experiments (Figure 1 and Scheme 4, Method B). This is a notable difference and illustrates the significance of the temperature in securing an optimal coupling reaction. If the temperature is too low the aglycon transfer becomes a side reaction while if the temperature is too high the activated intermediate of donor **5** (which is mostly the corresponding 1,2-benzoxonium ion)[33] presumably decomposes. Thus, a coupling temperature of –55 °C was included in the protocol in the following experiments. The reactions were moinitored by TLC at –55 °C and the temperature was only raised when the coupling had gone to completion.

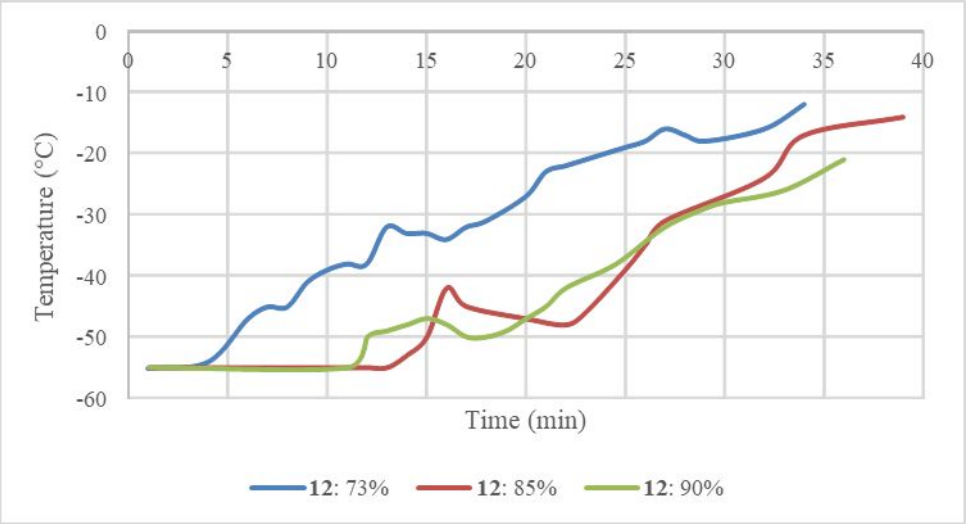
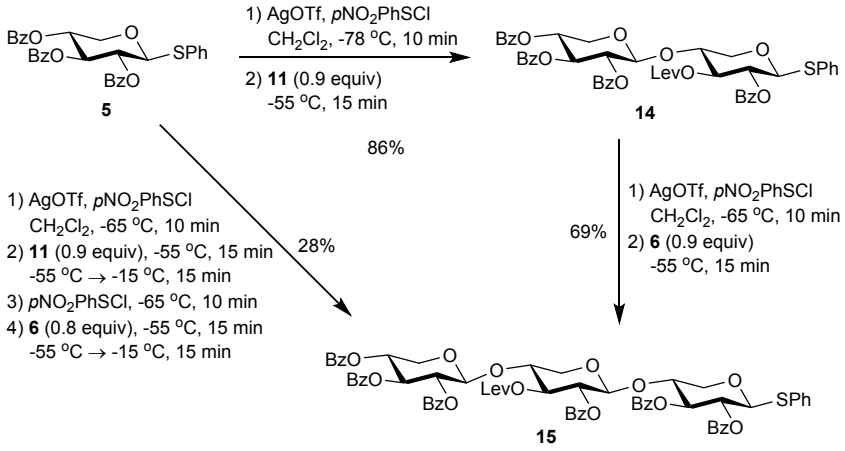


Figure 1. Reaction Temperatures and Yields for Coupling of 5 and 6 to afford 12

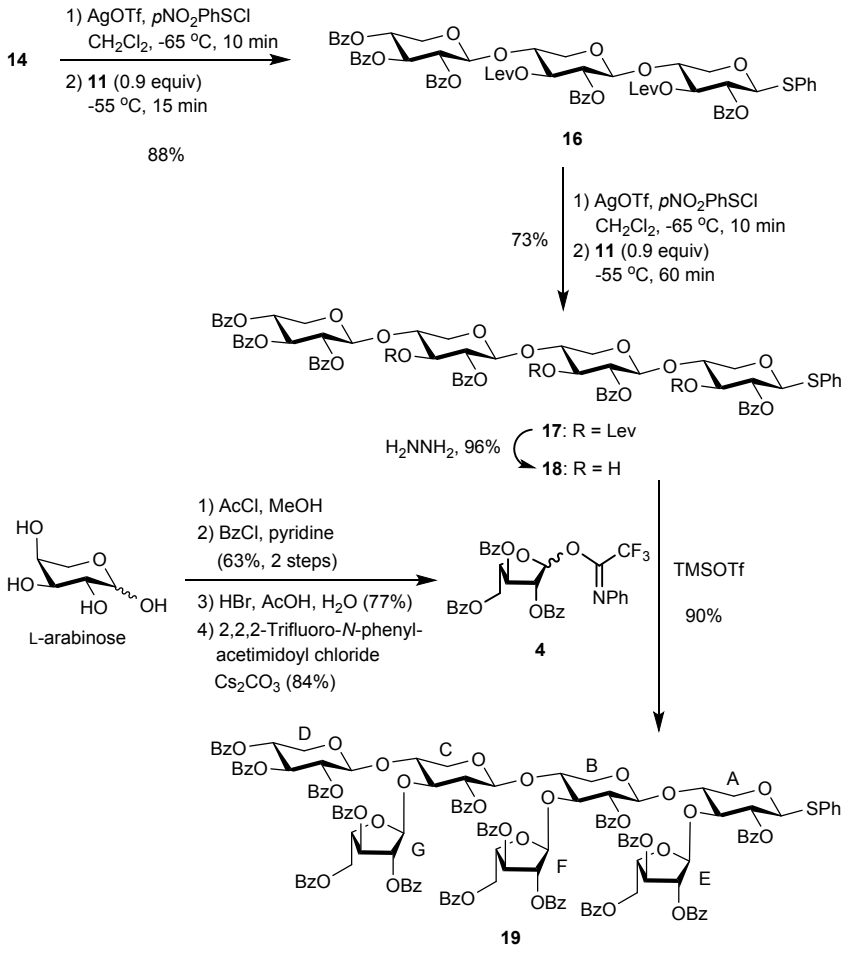
Using this optimized procedure donor **5** was then coupled to Lev-protected acceptor **11** to afford disaccharide **14** in 86% yield (Scheme 5). Unfortunately, when the same coupling was performed in a one-pot fashion with the further addition of acceptor **6**, trisaccharide **15** was only obtained in 28% yield. The addition of 2,4,6-tri-*tert*-butylpyrimidine[15,34] to mitigate the possible influence of the increasing amount of acid lowered the yield even further to 17%. Instead, large amounts of unreacted acceptor **6** were recovered in both cases. The low yield was not caused by the inability of Lev-protected thioglycosides to serve as donors since the coupling between disaccharide donor **14** and acceptor **6** gave rise to trisaccharide **15** in 69% yield. Possibly, the mediocre result is caused by the Lev group undergoing further transformations due to the longer reaction time in the one-pot protocol. Therefore, the xylan backbones in targets **1** – **3** will be assembled by an iterative glycosylation approach with pre-activation where the glycosylation products once isolated will be immediately used as donors for the next glycosylation step without any further modifications.

Scheme 5. Synthesis of Saccharides 14 and 15



Accordingly, to prepare arabinoxylan **1** disaccharide **14** was then coupled twice with Lev-protected acceptor **11** to afford trisaccharide **16** and tetrasaccharide **17** in 88 and 73% yields, respectively (Scheme 6). The three Lev groups in the 3 positions were removed with hydrazine to give triol **18** in 96% yield. Subsequent glycosylation with four equiv. of imidate donor **4** afforded protected arabinoxylan **19** in 90% yield. The arabinofuranose donor **4** was prepared in four straightforward steps from the parent pentose.[35,19b] Thus, heptasaccharide **19** has been assembled from monosaccharides **4**, **5** and **11** in a total of five steps and 48% overall yield, which illustrates the advantage of the iterative pre-activation-based strategy.

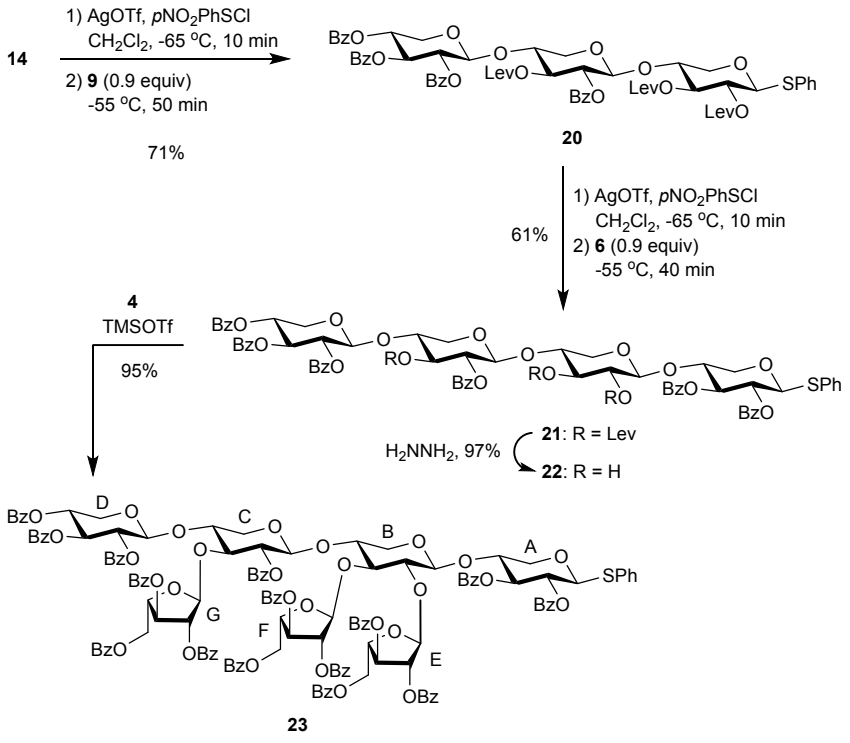
Scheme 6. Synthesis of Heptasaccharide 19



The same sequence of reactions were then employed to prepare the protected forms of arabinoxylans **2** and **3**. To assemble the former, disaccharide **14** was used again and now coupled with 2,3-Lev-protected acceptor **9** to give trisaccharide **20** in 71% yield (Scheme 7). Further glycosylation with acceptor **6** produced 61% yield of tetrasaccharide **21**, which was subjected to Lev deprotection to afford triol **22**. The arabinoses were then installed with donor **4** to afford heptasaccharide **23** in 95% yield. Likewise, the route to arabinoxylan **3** began with the coupling between donor **5** and 2,3-Lev-protected acceptor **9** to furnish disaccharide **24** in 95% yield (Scheme 8). The following glycosylation with acceptor **11** produced trisaccharide **25** in 52% yield. The moderate yield in this coupling as well as between **20** and **6** in Scheme 7 may

indicate a lower stability of the activated species with a Lev group at the 2 position. Next, trisaccharide **25** was reacted with acceptor **6** to give tetrasaccharide **26** in 75% yield, which was followed by Lev deprotection to provide triol **27**. The final triple glycosylation with arabinose donor **4** gave heptasaccharide **28** in 91% yield. Thus, protected heptasaccharides **23** and **28** have each been prepared in five steps from monosaccharides **4**, **5**, **9** and **11** and with overall yields of 34 and 33%, respectively. In all cases, the three arabinoses were installed in very high yields with imidate donor **4** proving the strength of this method even for forming densely substituted substrates.

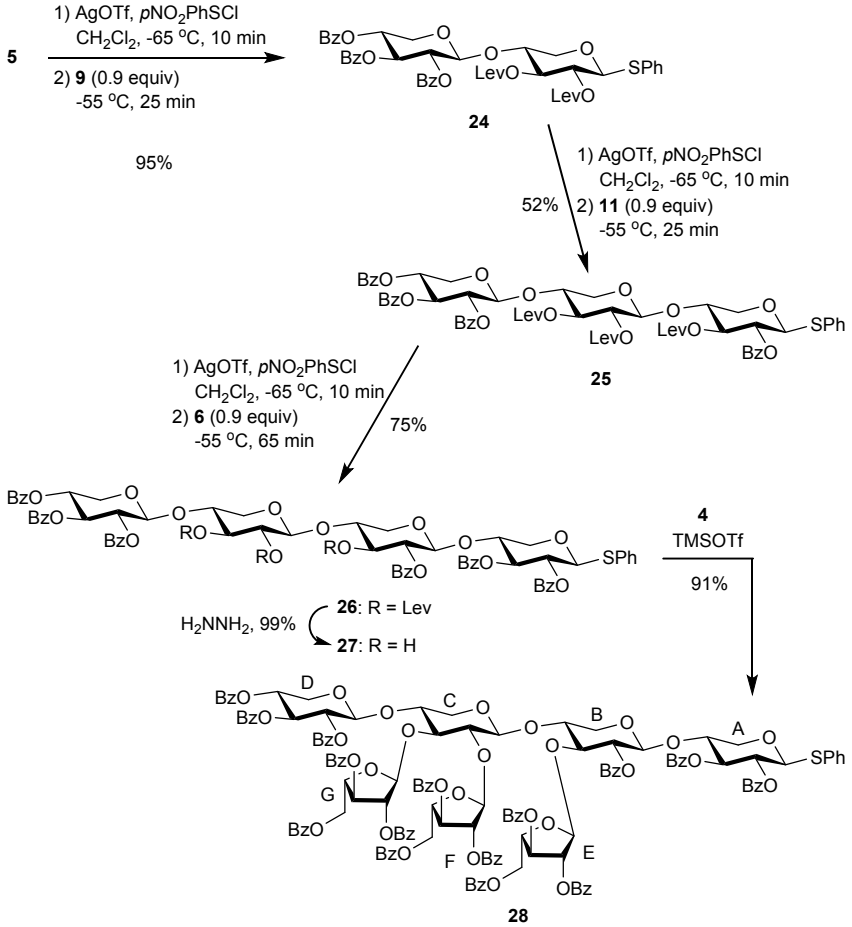
Scheme 7. Synthesis of Heptasaccharide 23



The β-linkages of the xylose backbones were confirmed by measuring the J_{CH} coupling constants for the anomeric carbon atoms, which were found to be between 155 and 165 Hz

where a coupling around 160 Hz is characteristic of a β-glycosidic bond.[36] The anomeric carbon atoms for the β-glycosidic linkages were located in the δ = 99.0 – 102.5 ppm range, which is in accordance with earlier observations.[11] Xylopyranosides are more conformationally flexible than e.g. glucopyranosides[21] and the $J_{H\text{-}1,H\text{-}2}$ coupling constants can therefore not always be used to determine their anomeric configuration. On the contrary, for the arabinofuranose substituents the $J_{H\text{-}1,H\text{-}2}$ coupling constants could be used to verify the α-linkages since small values of 0 – 2 Hz are characteristic for the α anomers.[37]

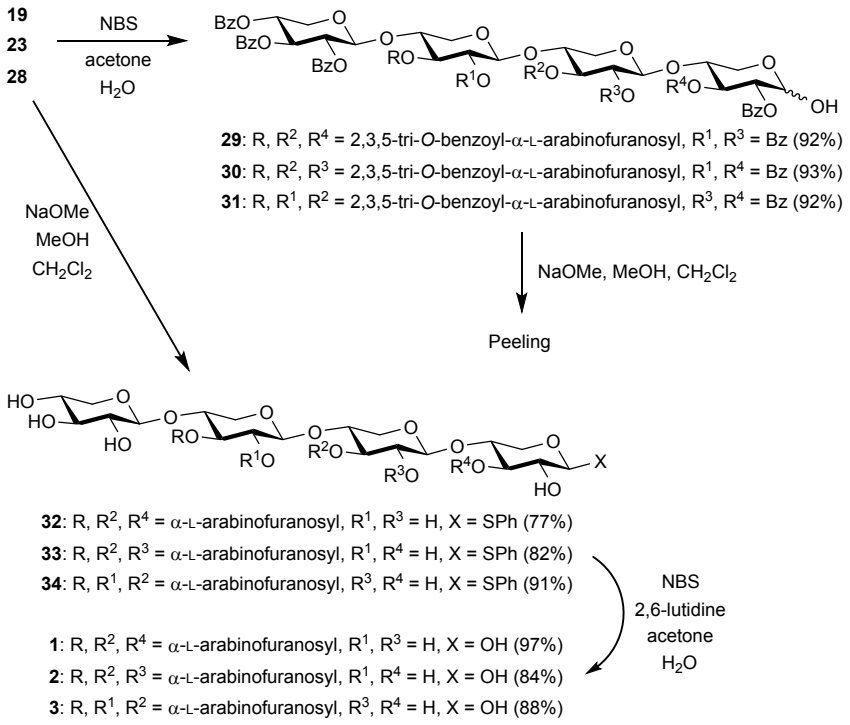
Scheme 8. Synthesis of Heptasaccharide 28



Deprotection of the three heptasaccharides is a two-step process since the thiophenyl moiety and the benzoates are removed under different conditions. In the first approach, the thiophenyl group was cleaved in the first step with NBS in a mixture of acetone and water.[38] This transformation proceeded uneventfully for all three heptasaccharides and gave rise to reducing sugars **29** – **31** in 92 – 93% yield (Scheme 9). The products were isolated as α/β mixtures with the α anomers as the major components according to NMR. The following Zemplén reaction to remove the benzoates[39] was carried out with approx. 20 equiv. of NaOMe in a 1:1 methanol – dichloromethane solution for up to 7 days to achieve complete deprotection of all benzoyl groups. Unfortunately, a mixture of saccharides of different length were obtained and it became apparent that the alkaline deprotection procedure had been accompanied by a so-called peeling reaction (endwise degradation).[40] In this process reducing saccharides are degraded with one monosaccharide at the time from the reducing end through aldose – ketose isomerizations and β-alkoxy eliminations.[40] To circumvent this side reaction, the order of the deprotections were reversed. First, the protected heptasaccharides were subjected to cleavage of the benzoyl groups, which proceeded cleanly to give compounds **32** – **34** in 77 – 91% yield. Then, attempts were made to remove the thiophenyl moiety under the same conditions as applied to the perbenzoylated substrates. However, these conditions now resulted in partial hydrolysis of the arabinofuranose residues, which is presumably due to the higher acid lability of these substituents in the absence of the benzoyl groups. Hence, 2,6-lutidine was added during the deprotections[41] to ensure a pH of the reaction media around 6, which led to clean removal of the thiophenyl groups to afford the completely deprotected target structures **1** – **3** in 84 – 97% yield. Heptasaccharides **1** – **3** were fully characterized by 800 MHz NMR spectroscopy and although they were obtained as α/β mixtures, the differences in the ^{1}H and the ^{13}C chemical shifs between

the α and the β anomers were only observed for the reducing end xylose unit and when an arabinose residue was attached to this moiety (as in **1**).

Scheme 9. Deprotection of Heptasaccharides 19, 23 and 28



In conclusion, three arabinoxylan heptasaccharides have been assembled in seven steps from monosaccharide building blocks in overall yields of 36 (**1**), 24 (**2**) and 27% (**3**). The key transformations are the pre-activation-based thioglycoside glycosylation to prepare the tetraxylan backbones and the triple glycosylation with imidate donor **4** to install the arabinose substituents. *p*-Nitrobenzenesulfenyl chloride was employed as a potent and convenient source of the sulfenium electrophile for the pre-activation of the phenyl thioglycoside donors. In the ensuing glycosylation reaction, temperature monitoring revealed an optimum temperature for the coupling where side reactions are diminished. The strategy allows for the expeditious

preparation of a diverse set of densely substituted arabinoxylans in good overall yields as valuable substrates for characterization of hemicellulose-degrading enzymes.

EXPERIMENTAL SECTION

General Information. Starting materials, reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. All solvents were of analytical HPLC grade. Anhyd solvents were obtained from an Innovative Technology PS-MD-7 PureSolv solvent purification system except for CH_2Cl_2 and toluene for glycosylations, which were dried over 3Å mol sieves prior to use. All reactions were performed under inert atm (N_2) in oven-dried glassware. TLC was carried out using Merck aluminium sheets pre-coated with 0.25 mm silica gel, C-60 F_{254} plates. TLC plates were inspected under UV light or visualized by charring after dipping in a cerium ammonium sulfate solution (1% cerium(IV)sulfate and 2.5% ammonium heptamolybdate in a 10% sulfuric acid solution). Flash column chromatography was performed using Merck Geduran silica gel 60 Å (40–63 μm) while dry column chromatography[42] was accomplished using Merck silica gel 60 Å (15–40 μm). NMR spectra were recorded with a Bruker Ascend™ 400 or a Bruker Ascend™ 800 spectrometer. The chemical shift are reported in ppm relative to the residual solvent peak from $CDCl_3$ (δ_H = 7.26 ppm, δ_C = 77.16 ppm), CD_3OD (δ_H = 4.87 ppm, δ_C = 49.00 ppm) or D_2O (δ_H = 4.79 ppm). Assignment of ^1H and ^{13}C resonances were based on APT, DQF-COSY, HSQC, H2BC, HMBC, TOCSY and HSQC-TOSCY experiments. Xylose residues are numbered A – D from the reducing end while arabinose substituents are labelled E – G as shown in Scheme 6 – 8. Optical rotation was measured on a Perkin Elmer Model 341 polarimeter. HRMS analysis

was performed on either a UHPLC-QTOF system (Dionex UltiMate 3000 and Bruker MaXis) with an electrospray ionization (ESI) source or a MALDI-TOF system (Bruker Solarix XR 7T).

Phenyl 1-thio-β-D-xylopyranoside (7). D-Xylose (29.9 g, 199 mmol), Et_3N (223 mL, 160 mmol) and DMAP (4.90 g, 40.1 mmol) were suspended in CH_2Cl_2 (300 mL) at 0 °C. Upon dropwise addition of Ac_2O (94.0 mL, 996 mmol) the solution turned yellow. After stirring for 2 h at rt TLC analysis (hexane/EtOAc 1:1) showed the consumption of the starting material and formation of the product. The mixture was washed with 1 M HCl and brine followed by concentration in vacuo. The crude xylose tetraacetate was dissolved in dry CH_2Cl_2 (160 mL) followed by addition of PhSH (25.0 mL, 243 mmol) and $BF_3{\cdot}OEt_2$ (76.0 mL, 600 mmol) at 0 °C under N_2 atm. The reaction was stirred overnight at rt where it turned purple. TLC analysis (hexane/EtOAc 2:1) showed full consumption of the starting material and formation of the product. The solution was diluted with CH_2Cl_2 and washed with saturated aq $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concd in vacuo. The residue was dissolved in methanol (160 mL) and solid sodium was added until a basic medium was obtained. After 1 h TLC analysis (hexane/EtOAc 2:1) showed the consumption of the starting material and formation of the product. The solution was neutralized with Amberlite IR-120 (H^+), filtered and concd in vacuo. The residue was purified by dry column chromatography (10% acetone in toluene, 5% gradient) followed by crystallization from hexane and acetone to afford a white crystalline product (19.2 g, 40%). R_f 0.27 (toluene/acetone 1:1). Mp 142.3–143.8 °C (lit.[20] 143–145 °C). ^{1}H NMR (400 MHz, CD_3OD) δ 7.54–7.51 (m, 2H), 7.34–7.26 (m, 3H), 4.56 (d, $J_{1,2}$ = 9.3 Hz, 1H, H1), 3.95 (dd, $J_{5,5'}$ = 11.3 Hz, $J_{4,5}$ = 5.2 Hz, 1H, H5), 3.51–3.45 (m, 1H, H4), 3.38–3.31 (m, 3H, H3, OH), 3.26–3.19 (m, 2H, H2, H5'). ^{13}C{^{1}H} NMR (101 MHz, CD_3OD) δ 134.9, 133.1 (×2),

129.9 (×2), 128.5, 90.1 (C1), 79.2 (C3), 73.7 (C2), 70.9 (C4), 70.4 (C5). NMR data are in accordance with literature values.[43]

*Phenyl 2,3,4-tri-O-benzoyl-1-thio-β-D-xylopyranoside (**5**).* Triol **7** (5.12 g, 21.1 mmol) was dissolved in pyridine (45 mL) and BzCl (7.4 mL, 63.4 mmol) was added. The reaction was stirred at rt for 1 h and excess of BzCl was quenched by the addition of methanol (10 mL) followed by stirring for an additional 10 min. The mixture was diluted with CH_2Cl_2 and washed with 1 M HCl and water, dried over Na_2SO_4, filtered, and concd in vacuo. The residue was purified by flash column chromatography to afford **5** as write crystals (5.1 g, 84%). R_f 0.28 (heptane/EtOAc 7:3). Mp 102.9–104.3 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.2, 1.1 Hz, 2H), 8.01–7.98 (m, 4H), 7.56–7.51 (m, 5H), 7.42–7.32 (m, 9H), 5.78 (t, J = 6.6 Hz, 1H, H3), 5.46 (t, J = 6.3 Hz, 1H, H2), 5.33–5.26 (m, 2H, H1, H4), 4.71 (dd, $J_{5eq,5ax}$ = 12.3 Hz, $J_{5eq,4}$ = 4.0 Hz, 1H, $H5_{eq}$), 3.83 (dd, $J_{5ax,5eq}$ = 12.3 Hz, $J_{5ax,4}$ = 6.5 Hz, 1H, $H5_{ax}$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6, 165.3, 165.3, 133.6, 133.5, 133.5, 133.2, 132.8 (×2), 130.2 (×2), 130.1 (×2), 130.1 (×2), 129.3 (×2), 129.2 (×2), 129.1, 128.6 (×2), 128.6 (×2), 128.5 (×2), 128.3, 86.5 (C1), 70.6 (C3), 70.1 (C2), 68.8 (C4), 63.7 (C5). Anal. calcd for $C_{32}H_{26}O_7S$: C, 69.30; H, 4.73; S, 5.78. Found: C, 69.26; H, 4.70; S, 5.66. NMR data are in accordance with literature values.[44]

*Phenyl 4-O-(p-methoxy)benzyl-1-thio-β-D-xylopyranoside (**8**).* To a solution of triol **7** (29.5 g, 122 mmol) in dry DMF (200 mL) was added CSA (2.83 g, 12.0 mmol) and the mixture was heated to 60 °C. 2-Methoxy prop-1-ene (37.5 mL, 366 mmol) was added slowly to the solution. The reaction was stirred for 1 h and then cooled to rt and quenched with Et_3N (30 mL).

Concentration in vacuo followed by purification of the residue by flash column chromatography (heptane/EtOAc/CH_2Cl_2 4:1:1) afforded phenyl 2,3-*O*-isopropylidene-1-thio-β-D-xylopyranoside as a colorless oil (24.1 g, 70%). R_f 0.62 (toluene/acetone 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.55 (m, 2H), 7.34–7.30 (m, 3H), 4.80 (d, $J_{1,2}$ = 9.6 Hz, 1H, H1), 4.13 (dd, $J_{5,5'}$ = 11.6 Hz, $J_{4,5}$ = 5.3 Hz, 1H, $H5_{eq}$), 4.03–3.96 (m, 1H, H4), 3.54 (t, J = 9.1 Hz, 1H, H3), 3.27–3.22 (m, 2H, H2, $H5_{ax}$), 2.17 (d, $J_{OH,4}$ = 4.0 Hz, 1H, OH), 1.49 (s, 3H), 1.45 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 133.0 (×2), 132.0, 129.0 (×2), 128.3, 111.5, 85.6 (C1), 83.0 (C3), 75.3 (C2), 70.0 (C5), 69.2 (C4), 26.8, 26.7. NMR data are in accordance with literature values.[45] The intermediate (17.5 g, 62.0 mmol) was dissolved in dry DMF (120 mL) and NaH (3.0 g, 74.4 mmol, 60% in mineral oil) was added at 0 °C. After 10 min PMBCl (10.9 mL, 80.6 mmol, 1.3 equiv.) was added. The mixture was stirred at rt for 16 h and then quenched with 10% HCl (28 mL) and diluted with CH_2Cl_2. The solution was washed with saturated aq $NaHCO_3$, dried over Na_2SO_4, filtered, and concd in vacuo. The crude residue was dissolved in CH_2Cl_2/MeOH 1:1 (200 mL), CSA (14.4 g, 62.0 mmol) was added and the mixture was allowed to stir at rt overnight. The reaction was quenched by addition of Et_3N and concd in vacuo. The residue was purified by flash column chromatography (heptane/EtOAc 3:2) to furnish compound **8** as a white crystalline solid (20.5 g, 91% over 2 steps). R_f 0.47 (hexane/EtOAc 1:1). Mp 72.7–75.6 °C (EtOH). $[\alpha]^{25}_D$ –55.9 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.33–7.29 (m, 3H), 7.27–7.23 (m, 2H), 6.90–6.86 (m, 2H), 4.61 (d, J_{gem} = 11.4 Hz, 1H, PMB), 4.58–4.54 (m, 2H, H1 ($J_{1,2}$ = 8.9 Hz) PMB), 4.07 (dd, $J_{5eq,5ax}$ = 11.5 Hz, $J_{5eq,4}$ = 4.8 Hz, 1H, $H5_{eq}$), 3.80 (s, 3H, OMe), 3.66 (t, J = 8.4 Hz, 1H, H3), 3.49–3.43 (m, 1H, H4), 3.40 (t, J = 8.6 Hz, 1H, H2), 3.27 (dd, $J_{5ax,5eq}$ = 11.5 Hz, $J_{5ax,4}$ = 9.7 Hz, 1H, $H5_{ax}$), 2.52 (bs, 2H, OH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.7, 132.8 (×2), 132.3, 130.1, 129.7 (×2), 129.2 (×2),

128.3, 114.2 (×2), 88.8 (C1), 76.6 (C4), 76.5 (C3), 72.8 (PMB), 72.1 (C2), 67.1 (C5), 55.4 (OMe). HRMS: *m*/*z* calcd for $C_{19}H_{22}O_5SNa$ $[M + Na]^+$ 385.1080, found 385.1090.

*Phenyl 2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**6**).* Compound **8** (1.97 g, 5.43 mmol) was dissolved in CH_2Cl_2 (32 mL) and Et_3N (2.4 mL, 17.2 mmol), DMAP (0.069 g, 0.56 mmol) and BzCl (1.9 mL, 16.4 mmol) were added at 0°C. After 5 min the reaction was left to stir at rt overnight. 3-(Dimethylamino)-1-propylamine (2.2 mL, 17.5 mmol) was added and the mixture was stirred for 1.5 h followed by washing with 1 M HCl and brine, drying over $MgSO_4$, filtration, and concentration in vacuo. The product phenyl 2,3-di-*O*-benzoyl-4-*O*-(*p*-methoxy)benzyl-1-thio-β-D-xylopyranoside (3.12 g, 100%) was obtained as a light yellow syrup and used without further purification. R_f 0.28 (hexane/EtOAc 4:1). $[\alpha]^{25}_D$ +62.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) β 7.99–7.95 (m, 3H), 7.56–7.27 (m, 12H), 7.15–7.12 (m, 2H), 6.74–6.71 (m, 2H), 5.60 (t, J = 8.0 Hz, 1H, H3), 5.34 (t, J = 8.0 Hz, 1H, H2), 5.04 (d, $J_{1,2}$ = 8.1 Hz, 1H, H1), 4.56 (d, J_{gem} = 11.9 Hz, 1H, PMB), 4.52 (d, J_{gem} = 11.8 Hz, 1H, PMB), 4.28 (dd, $J_{5eq,5ax}$ = 11.9 Hz, $J_{5eq,4}$ = 4.6 Hz, 1H, $H5_{eq}$), 3.80–3.76 (m, 1H, H4), 3.75 (s, 3H, OMe), 3.57 (dd, $J_{5ax,5eq}$ = 11.9 Hz, $J_{5ax,4}$ = 8.5 Hz, 1H, $H5_{ax}$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.7, 165.4, 159.5, 133.4 (×2), 133.2, 132.5 (×2), 130.1 (×2), 130.0 (×2), 129.7, 129.7 (×2), 129.5, 129.4, 129.1 (×2), 128.5 (×2), 128.5 (×2), 128.1, 113.9 (×2), 87.0 (C1), 73.9 (C4), 73.6 (C3), 72.5 (PMB), 70.6 (C2), 66.4 (C5), 55.4 (OMe). HRMS: *m*/*z* calcd for $C_{33}H_{30}O_7SNa$ $[M + Na]^+$ 593.1604, found 593.1617. NMR data are in accordance with literature values.[13] To a well stirred emulsion of the above PMB ether (0.696 g, 1.22 mmol) in CH_2Cl_2 (10 mL) and H_2O (1.0 mL), DDQ (0.415 g, 1.83 mmol) was added. The reaction was stirred in the dark for 7 h and then filtered through a large pad of Celite. The filtrate was washed with saturated aq $NaHCO_3$

and brine, filtered and concd in vacuo. Purification by flash column chromatography (pentane/EtOAc 4:1) yielded **6** as a white crystalline compound (0.514 g, 94%). R_f 0.53 (hexane/EtOAc 2:1). Mp 133.1–134.0 °C (EtOH). $[\alpha]^{25}_D$ +66.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.99 (m, 4H), 7.57–7.49 (m, 4H), 7.43–7.39 (m, 4H), 7.35–7.29 (m, 3H), 5.43 (t, J = 7.4 Hz, 1H, H2), 5.33 (t, J = 7.4 Hz, 1H, H3), 5.09 (d, $J_{1,2}$ = 7.3 Hz, 1H, H1), 4.45 (dd, $J_{5eq,5ax}$ = 12.0 Hz, $J_{5eq,4}$ = 4.4 Hz, 1H, $H5_{eq}$), 4.00 (q, J = 6.9 Hz, 1H, H4), 3.61 (dd, $J_{5ax,5eq}$ = 12.0 Hz, $J_{5ax,4}$ = 7.9 Hz, 1H, $H5_{ax}$), 3.03 (s, 1H, OH). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.1, 165.2, 133.8, 133.6, 133.0, 132.8 (×2), 130.2 (×2), 130.0 (×2), 129.3, 129.2 (×2), 128.9, 128.7 (×2), 128.7 (×2), 128.3, 86.8 (C1), 76.0 (C3), 70.2 (C2), 68.4 (C4), 67.6 (C5). HRMS: *m*/*z* calcd for $C_{25}H_{22}O_6SNa$ $[M + Na]^+$ 473.1029, found 473.1048.

*Phenyl 2,3-di-O-levulinoyl-1-thio-β-D-xylopyranoside (**9**).* A solution of diol **8** (1.98 g, 5.47 mmol) and 4-oxopentanoic acid (1.61 g, 13.8 mmol) in CH_2Cl_2 (8.5 mL) was cooled to 0 °C. Then a solution of DMAP (0.070 g, 0.58 mmol) and DDC (3.42 g, 16.8 mmol) in CH_2Cl_2 (1.0 mL) was added. The reaction stirred at rt overnight and then filtered and concd. The residue was dissolved in CH_2Cl_2 (20 mL) and H_2O (2.0 mL) and stirred vigorously. DDQ (1.86 g, 8.21 mmol) was added and the mixture was stirred at rt for 4.5 h. Then the solution was filtered through a large pad of Celite and washed with saturated aq $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concd in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc 1:1) to provide **9** as a light yellow wax (1.78 g, 74% over 2 steps). R_f 0.58 (EtOAc). $[\alpha]^{25}_D$ –23.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.33–7.29 (m, 3H), 5.02 (t, J = 8.4 Hz, 1H, H3), 4.94 (t, J = 8.7 Hz, 1H, H2), 4.73 (d, $J_{1,2}$ = 8.8 Hz, 1H, H1), 4.19 (dd, $J_{5eq,5ax}$ = 11.7 Hz, $J_{5eq,4}$ = 5.1 Hz, 1H, $H5_{eq}$), 3.84–3.79 (m, 1H, H4), 3.39

(dd, $J_{5ax,5eq}$ = 11.7 Hz, $J_{5ax,4}$ = 9.5 Hz, 1H, $H5_{ax}$), 3.16 (bs, 1H, OH), 2.89–2.51 (m, 8H), 2.17 (2 × s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 208.0, 206.4, 173.0, 171.4, 132.7, 132.6 (×2), 129.1 (×2), 128.2, 86.8 (C1), 76.5 (C3), 69.7 (C2), 68.6 (C5), 68.5 (C4), 38.4, 37.9, 29.9, 29.9, 28.3, 28.1. HRMS: *m*/*z* calcd for $C_{21}H_{26}O_8SNa$ $[M + Na]^+$ 461.1241, found 461.1242.

*Phenyl 2-O-benzoyl-4-O-(p-methoxy)benzyl-1-thio-β-D-xylopyranoside (**10**).* To a vigorously stirred solution of diol **8** (1.0 g, 2.76 mmol), tetrabutylammonium hydrogen sulfate (0.187 g, 0.55 mmol) and BzCl (0.43 mL, 3.72 mmol) in CH_2Cl_2 (50 mL) at –5 °C was added a 1 M aq NaOH solution (7.0 mL, 7.0 mmol). The mixture was stirred for 30 min (TLC indicated traces of **8** and the dibenzoylated product). The organic layer was separated, washed with H_2O, dried over Na_2SO_4, filtered, and concd in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc 8.5:1.5) affording compound **10** as white crystals (0.877 g, 68%). R_f 0.35 (hexane/EtOAc 3:1). Mp 101.7–102.4 °C (EtOH). $[\alpha]^{25}_D$ –13.2 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.09–8.07 (m, 2H), 7.61–7.57 (m, 1H), 7.48–7.41 (m, 4H), 7.29–7.24 (m, 5H), 6.89–6.86 (m, 2H), 5.04 (dd, $J_{1,2}$ = 9.5 Hz, $J_{2,3}$ = 9.0 Hz, 1H, H2), 4.78 (d, $J_{1,2}$ = 9.6 Hz, 1H, H1), 4.65 (d, J_{gem} = 11.5 Hz, 1H, PMB), 4.60 (d, J_{gem} = 11.5 Hz, 1H, PMB), 4.10 (dd, $J_{5eq,5ax}$ = 11.5 Hz, $J_{5eq,4}$ = 5.1 Hz, 1H, $H5_{eq}$), 3.85 (t, J = 8.8 Hz, 1H, H3), 3.81 (s, 3H, OMe), 3.61–3.55 (m, 1H, H4), 3.30 (dd, $J_{5ax,5eq}$ = 11.5 Hz, $J_{5ax,4}$ = 10.1 Hz, 1H, $H5_{ax}$), 2.62 (bs, 1H, OH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.1, 159.7, 133.5, 132.8 (×2), 132.7, 130.1 (×2), 130.1, 129.8, 129.7 (×2), 129.1 (×2), 128.6 (×2), 128.2, 114.2 (×2), 86.8 (C1), 77.4 (C4), 76.1 (C3), 73.1 (PMB), 73.0 (C2), 67.6 (C5), 55.4 (OMe). HRMS: *m*/*z* calcd for $C_{26}H_{26}O_6SNa$ $[M + Na]^+$ 489.1342, found 489.1343.

*Phenyl 2-O-benzoyl-3-O-levulinoyl-1-thio-β-D-xylopyranoside (**11**).* To a solution of **10** (3.94 g, 8.45 mmol) and 4-oxopentanoic acid (1.22 g, 10.5 mmol) in CH_2Cl_2 (14 mL) cooled to 0 °C was added DMAP (0.104 g, 0.85 mmol) and DCC (2.61 g, 12.6 mmol). The solution was left to stir at rt for 3.5 h, then filtered and concd in vacuo. The residue was dissolved in CH_2Cl_2 (60 mL) and H_2O (6.0 mL) and stirred vigorously. DDQ (2.88 g, 12.7 mmol) was added and the mixture was left to stir at rt overnight in the dark. Then the solution was filtered through a large pad of Celite and washed with saturated aq $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concd in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc 2:1) affording **11** as a white crystalline solid (2.935 g, 78% over 2 steps). R_f 0.28 (hexane/EtOAc 1:1). Mp 88.7–90.3 °C (EtOH). $[\alpha]^{25}_D$ –1.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.01 (m, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47–7.44 (m, 4H), 7.29–7.28 (m, 3H), 5.23–5.16 (m, 2H, H2, H3), 4.94–4.91 (m, 1H, H1), 4.29 (dd, $J_{5eq,5ax}$ = 11.8 Hz, $J_{5eq,4}$ = 4.9 Hz, 1H, $H5_{eq}$), 3.94–3.89 (m, 1H, H4), 3.49 (dd, $J_{5ax,5eq}$ = 11.7 Hz, $J_{5ax,4}$ = 9.1 Hz, 1H, $H5_{ax}$), 3.14 (bs, 1H, OH), 2.81–2.65 (m, 2H), 2.58–2.51 (m, 1H), 2.44–2.37 (m, 1H), 2.11 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 207.7, 172.8, 165.3, 133.6, 132.9, 132.7 (×2), 130.0 (×2), 129.4, 129.1 (×2), 128.7 (×2), 128.2, 87.0 (C1), 76.4 (C3), 70.3 (C2), 68.5 (C4), 68.3 (C5), 38.5, 29.8, 28.3. HRMS: m/z calcd for $C_{23}H_{24}O_7SNa$ $[M + Na]^+$ 467.1135, found 467.1136.

Temperature Screening (General Procedure A). Crushed mol sieves (3Å, 1.0 g) were added a 2-neck Schlenk flask, where the middle neck was fitted with a glass stopper and the other with a septum. The flask was placed under vacuum, heated with a heatgun and then subjected to an atm of N_2 and cooled to rt. Donor **5** (0.200 g, 0.36 mmol) dissolved in dry CH_2Cl_2 (3.0 mL) was added to the flask together with AgOTf (0.185 g, 0.72 mmol) dissolved in dry toluene (2.0 mL).

Stirring of the reaction was initiated and the glass stopper was exchanged for a thermometer, and the solution was cooled to –65 °C. *p*NO_2PhSCl (0.068 g, 0.36 mmol) was dissolved in dry CH_2Cl_2 (0.5 mL) and slowly added followed by stirring for an additional 10 min. Acceptor **6** (0.146 g, 0.33 mmol) was dissolved in dry CH_2Cl_2 (0.5 mL) and added quickly. The temperature was raised as indicated in Figure 1, where the reaction was allowed to warm to –15 °C at which point Et_3N (0.15 mL, 1.08 mmol) was added. The solution was filtered through a pad of Celite and concd in vacuo. The residue was purified by flash column chromatography to afford the product **12**.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**12**).* To a Schlenk flask containing 3Å mol sieves (1.20 g) was added donor **5** (0.200 g, 0.36 mmol) dissolved in dry CH_2Cl_2 (6.0 mL) and AgOTf (0.185 g, 0.72 mmol) dissolved in dry Et_2O (5.0 mL). The mixture was stirred for 1 h at rt and then cooled to –78 °C at which point PhSCl (0.062 g, 0.43 mmol) or *p*NO_2PhSCl (0.082 g, 0.43 mmol) dissolved in dry CH_2Cl_2 (1.0 mL) was added dropwise followed by stirring for 10 min. Acceptor **6** (0.146 g, 0.33 mmol) dissolved in dry CH_2Cl_2 (0.5 mL) was then added slowly. The reaction was stirred at –78 °C for 15 min, then for 15 min at rt after which Et_3N (0.21 mL, 2.88 mmol) was added. The mixture was filtered through a pad of Celite, concd in vacuo, and purified by flash column chromatography (pentane/EtOAc 3:2) to give **12** as a white amorphous solid (0.186 g, 64% with PhSCl and 0.229 g, 79% with *p*NO_2PhSCl). Alternatively, general procedure A was employed to afford 0.260 g (90%) of **12**. R_f 0.18 (heptane/EtOAc 7:3). $[\alpha]^{25}_D$ –22 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.92 (m, 10H), 7.56–7.50 (m, 5H), 7.45–7.27 (m, 15H), 5.69–5.62 (m, 2H, $H3^A$, $H3^B$), 5.34 (t, J = 8.0 Hz, 1H, $H2^A$), 5.24 (dd, $J_{2B,3B}$ = 6.5 Hz, $J_{1B,2B}$ = 5.0 Hz, 1H,

H2^{B}), 5.06–5.01 (m, 2H, H1^{A}, H4^{B}), 4.95 (d, $J_{1B,2B}$ = 4.8 Hz, 1H, H1^{B}), 4.27 (dd, $J_{5Aeq,5Aax}$ = 12.2 Hz, $J_{5Aeq,4A}$ = 4.7 Hz, 1H, H5$^{A}_{eq}$), 4.09 (td, J = 8.3 Hz, $J_{5Aeq,4A}$ = 4.9 Hz, 2H, H4^{A}), 4.03 (dd, $J_{5Beq,5Bax}$ = 12.4 Hz, $J_{5Beq,4B}$ = 3.9 Hz, 1H, H5$^{B}_{eq}$), 3.55 (dd, $J_{5Aax,5Aeq}$ = 12.1 Hz, $J_{5Aax,4A}$ = 8.6 Hz, 1H, H5$^{A}_{ax}$), 3.43 (dd, $J_{5Bax,5Beq}$ = 12.4 Hz, $J_{5Bax,4B}$ = 6.3 Hz, 1H, H5$^{B}_{ax}$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6, 165.5, 165.4, 165.4, 165.2, 133.5 (×2), 133.5, 133.4 (×2), 132.8, 132.7 (×2), 130.1 (×2), 130.0 (×2), 130.0 (×2), 129.9 (×2), 129.9 (×2), 129.5, 129.4, 129.3, 129.2, 129.1 (×2), 129.0, 128.6 (×6), 128.5 (×4), 128.2, 99.8 (C1^{B}), 86.8 (C1^{A}), 75.2 (C4^{A}), 73.1 (C3^{A}), 70.6 (C2^{A}), 70.2 (C2^{B}), 69.7 (C3^{B}), 68.6 (C4^{B}), 65.6 (C5^{A}), 60.9 (C5^{B}). HRMS: *m*/*z* calcd for $C_{51}H_{42}O_{13}SNa$ $[M + Na]^+$ 917.2238, found 917.2258.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**13**).* To a Schlenk flask containing 3Å mol sieves (1.20 g) was added donor **5** (0.200 g, 0.36 mmol) dissolved in dry CH_2Cl_2 (6.0 mL) and AgOTf (0.185 g, 0.72 mmol) dissolved in dry Et_2O (5.0 mL). The mixture was stirred for 1 h at rt and then cooled to –78 °C at which point PhSCl (0.062 g, 0.43 mmol) or *p*NO_2PhSCl (0.082 g, 0.43 mmol) dissolved in dry CH_2Cl_2 (1.0 mL) was added dropwise followed by stirring for 10 min. Acceptor **6** (0.146 g, 0.33 mmol) dissolved in dry CH_2Cl_2 (0.5 mL) was then added slowly. The reaction was stirred at –78 °C for 15 min and then for 15 min at rt. AgOTf (0.093 g, 0.36 mmol) dissolved in dry Et_2O (2.0 mL) was added and the mixture was cooled to –78 °C over 20 min. PhSCl (0.058 g, 0.40 mmol) or *p*NO_2PhSCl (0.075 g, 0.40 mmol) dissolved in dry CH_2Cl_2 (1.0 mL) was added dropwise followed by stirring for 10 min. Acceptor **6** (0.132 g, 0.29 mmol) dissolved in dry CH_2Cl_2 (0.4 mL) was added slowly. The reaction was stirred at –78 °C for 15 min, then for 15 min at rt after which Et_3N (0.4 mL, 5.44 mmol) was added. The mixture was

filtered through a pad of Celite, concd in vacuo, and purified by flash column chromatography (pentane/acetone 7.5:2.5) to give a mixture of **12** (0.169 g, 59%) and **13** (0.134 g, 34%) (with PhSCl) or only **13** as a white amorphous solid (0.249 g, 69%, with *p*NO_2PhSCl). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.89 (m, 14H), 7.57–7.47 (m, 7H), 7.42–7.25 (m, 19H), 5.62–5.57 (m, 2H, $H3^A$, $H3^C$), 5.52 (t, J = 8.1 Hz, 1H, $H3^B$), 5.31–5.27 (m, 1H, $H2^A$), 5.19–5.14 (m, 2H, $H2^B$, $H2^C$), 5.01 (td, J = 6.4 Hz, J = 4.1 Hz, 1H, $H4^C$), 4.97 (d, J = 8.1 Hz, 1H, $H1^A$), 4.74–4.71 (m, 2H, $H1^B$, $H1^C$), 4.14 (dd, $J_{5Aeq,5Aax}$ = 12.0 Hz, $J_{5Aeq,4A}$ = 4.7 Hz, 1H, $H5^A{}_{eq}$), 4.00–3.94 (m, 2H, $H4^A$, $H5^C{}_{eq}$), 3.82 (td, J = 8.4, 5.0 Hz, 1H, $H4^B$), 3.55 (dd, $J_{5Beq,5Bax}$ = 12.3 Hz, $J_{5Beq,4B}$ = 4.8 Hz, 1H, $H5^B{}_{eq}$), 3.46 (dd, $J_{5Aax,5Aeq}$ = 12.1 Hz, $J_{5Aax,4A}$ = 8.7 Hz, 1H, $H5^A{}_{ax}$), 3.35 (dd, $J_{5Cax,5Ceq}$ = 12.3 Hz, $J_{5Cax,4C}$ = 6.3 Hz, 1H, $H5^C{}_{ax}$), 3.16 (dd, $J_{5Bax,5Beq}$ = 12.3 Hz, $J_{5Bax,4B}$ = 8.6 Hz, 1H, $H5^B{}_{ax}$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.5, 165.5, 165.5, 165.4, 165.3, 165.2, 165.0, 133.5 (×2), 133.5, 133.5, 133.4 (×2), 133.3, 132.8, 132.6 (×2), 130.1 (×2), 130.0 (×2), 130.0 (×2), 129.9 (×2), 129.9 (×2), 129.8 (×2), 129.8 (×2), 129.6, 129.5, 129.5, 129.3 (×2), 129.2, 129.1 (×2), 129.0, 128.6 (×2), 128.6 (×2), 128.6 (×4), 128.5 (×2), 128.5 (×2), 128.4 (×2), 128.2, 101.1 ($C1^B$), 99.6 ($C1^C$), 86.8 ($C1^A$), 75.8 ($C4^A$), 74.9 ($C4^B$), 73.1 ($C3^A$), 72.1 ($C3^B$), 71.6 ($C2^B$), 70.5 ($C2^A$), 70.2 ($C2^C$), 69.7 ($C3^C$), 68.6 ($C4^C$), 65.9 ($C5^A$), 62.3 ($C5^B$), 60.9 ($C5^C$). HRMS: *m*/*z* calcd for $C_{70}H_{58}O_{19}SNa$ $[M + Na]^+$ 1257.3185, found 1257.3192.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-3-O-levulinoyl-1-thio-β-D-xylopyranoside (**14**).* Disaccharide **14** was obtained in 86% yield as a light yellow amorphous solid following general procedure A. R_f 0.42 (hexane/EtOAc 1:1). $[\alpha]^{25}_D$ –60.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–8.00 (m, 4H), 7.97–7.92 (m, 4H), 7.62–7.45 (m, 4H), 7.42–7.32 (m, 10H), 7.28–7.25 (m, 3H), 5.70 (t, J = 6.5 Hz, 1H, $H3^B$), 5.40 (t, J = 8.3 Hz, 1H,

H3^{A}), 5.28–5.23 (m, 2H, H2^{B}, H4^{B}), 5.16 (t, J = 8.4 Hz, 1H, H2^{A}), 4.94 (d, $J_{1B,2B}$ = 4.7 Hz, 1H, H1^{B}), 4.89 (d, $J_{1A,2A}$ = 8.6 Hz, 1H, H1^{A}), 4.48 (dd, $J_{5Beq,5Bax}$ = 12.4, Hz, $J_{5Beq,4B}$ = 3.8 Hz, 1H, H5$^{B}_{eq}$), 4.19 (dd, $J_{5Aeq,5Aax}$ = 12.0 Hz, $J_{5Aeq,4A}$ = 4.9 Hz, 1H, H5$^{A}_{eq}$), 3.99 (td, J = 8.7, Hz, $J_{5Aeq,4A}$ = 5.0 Hz, 1H, H4^{A}), 3.75 (dd, $J_{5Bax,5Beq}$ = 12.4 Hz, $J_{5Bax,4B}$ = 6.1 Hz, 1H, H5$^{B}_{ax}$), 3.44 (dd, $J_{5Aax,5Aeq}$ = 12.0 Hz, $J_{5Aax,4A}$ = 9.1 Hz, 1H, H5$^{A}_{ax}$), 2.65–2.41 (m, 4H), 1.97 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.9, 171.8, 165.6, 165.4, 165.4, 165.2, 133.6, 133.5 (×2), 133.5, 132.8 (×2), 132.5, 130.1 (×2), 130.1 (×2), 130.1 (×2), 130.0 (×2), 129.5, 129.4, 129.2, 129.1, 129.1 (×2), 128.6 (×2), 128.6 (×2), 128.6 (×3), 128.2, 99.4 (C1^{B}), 86.7 (C1^{A}), 74.6 (C4^{A}), 73.2 (C3^{A}), 70.7 (C2^{A}), 70.3 (C2^{B}), 69.6 (C3^{B}), 68.7 (C4^{B}), 66.1 (C5^{A}), 61.1 (C5^{B}), 37.9, 29.6, 28.1. HRMS: m/z calcd for $C_{49}H_{44}O_{14}SNa$ $[M + Na]^+$ 911.2344, found 911.2340.

Glycosylation with a Thiophenyl Donor (General Procedure B). Crushed mol sieves (3Å) were added to a 2-neck Schlenk flask, where the middle neck was fitted with a glass stopper and the other with a septum. The flask was placed under vacuum, heated with a heatgun and then subjected to an atm of N_2 and cooled to rt. The donor (1.0 equiv) dissolved in dry CH_2Cl_2 (c = 0.12 M) was added to the flask together with AgOTf (2.0 equiv.) dissolved in dry toluene (c = 0.36 M). Stirring of the reaction was initiated and the glass stopper was exchanged for a thermometer, and the solution was cooled to –65 °C. $p$$NO_2$PhSCl (1.0 equiv) was dissolved in dry CH_2Cl_2 (c = 0.72 M) and slowly added to avoid raising the temperature above –60 °C. The mixture was left to stir for approximately 10 min or until complete activation. The acceptor (0.9 equiv.) was dissolved in dry CH_2Cl_2 (c = 0.65 M) and added quickly. The temperature was kept between –55 °C and –50 °C until TLC analysis showed completion of the reaction. Afterwards the mixture was allowed to warm to –15 °C over 10 min at which point Et_3N (3.0 equiv) was

added. The solution was filtered through a pad of Celite and concd in vacuo. The residue was then purified by flash column chromatography to afford the product.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-3-O-levulinoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**15**).* Crushed mol sieves (3Å, 1.0 g) were added a 2-neck Schlenk flask, where the middle neck was fitted with a glass stopper and the other with a septum. The flask was placed under vacuum, heated with a heatgun and then subjected to an atm of N_2 and cooled to rt. Donor **5** (0.200 g, 0.36 mmol) dissolved in dry CH_2Cl_2 (3.0 mL) and AgOTf (0.185 g, 0.72 mmol) dissolved in dry toluene (2.0 mL) were added. Stirring of the reaction was initiated and the glass stopper was exchanged for a thermometer, and the solution was cooled to –65 °C. *p*NO_2PhSCl (0.068 g, 0.36 mmol) dissolved in dry CH_2Cl_2 (0.5 mL) was added dropwise followed by stirring for an additional 10 min. Acceptor **11** (0.144 g, 0.33 mmol) dissolved in dry CH_2Cl_2 (0.5 mL) was quickly added. The reaction was stirred at a temperature between –55 °C and –50 °C for 15 min and then for 15 min at rt. The mixture was cooled to –65 °C. AgOTf (0.093 g, 0.36 mmol) dissolved in dry toluene (1.0 mL) was added followed by stirring for an additional 20 min. *p*NO_2PhSCl (0.062 g, 0.33 mmol) dissolved in dry CH_2Cl_2 (0.4 mL) was added dropwise followed by stirring for 10 min. Acceptor **6** (0.132 g, 0.29 mmol) dissolved in dry CH_2Cl_2 (0.4 mL) was added quickly. The reaction was stirred at a temperature between –55 °C and –50 °C for 15 min and then allowed to warm to –15 °C over 15 min, at which point Et_3N (0.8 mL, 0.54 mmol) was added. The mixture was filtered through a pad of Celite, concd in vacuo, and purified by flash column chromatography (heptane/acetone 3:2). The product **15** was obtained as a white amorphous solid (0.124 g, 28%). Alternatively, general procedure B was employed with crushed mol sieves (1.0

g), donor **14** (0.490 g, 0.551 mmol), AgOTf (0.283 g, 1.10 mmol), *p*NO_2PhSCl (0.105 g, 0.551 mmol) and acceptor **6** (0.223 g, 0.496 mmol). Reaction time 15 min then Et_3N (0.232 mL, 1.65 mmol). Purification by flash column chromatography gave product **15** (0.420 g, 69%). R_f 0.22 (heptane/acetone 3:2). $[\alpha]^{25}_D$ –24.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.90 (m, 12H), 7.60–7.25 (m, 23H), 5.65 (t, J = 6.6 Hz, 1H, H3^C), 5.58 (t, J = 7.9 Hz, 1H, H3^A), 5.31–5.20 (m, 3H, H2^A, H3^B, H4^C), 5.16 (dd, $J_{2C,3C}$ = 6.4 Hz, $J_{1C,2C}$ = 4.9 Hz, 1H, H2^C), 5.02 (dd, $J_{2B,3B}$ = 8.2 Hz, $J_{1B,2B}$ = 6.6 Hz, 1H, H2^B), 4.96 (d, $J_{1A,2A}$ = 8.1 Hz, 1H, H1^A), 4.71 (d, $J_{1C,2C}$ = 4.7 Hz, 1H, H1^C), 4.66 (d, $J_{1B,2B}$ = 6.4 Hz, 1H, H1^B), 4.40 (dd, $J_{5Ceq,5Cax}$ = 12.4 Hz, $J_{5Ceq,4C}$ = 3.8 Hz, 1H, H5$^C_{eq}$), 4.13 (dd, $J_{5Aeq,5Aax}$ = 12.0 Hz, $J_{5Aeq,4A}$ = 4.7 Hz, 1H, H5$^A_{eq}$), 3.95 (td, J = 8.2 Hz, $J_{5Aeq,4A}$ = 4.9 Hz, 1H, H4^A), 3.74–3.65 (m, 2H, H4^B, H5$^C_{ax}$), 3.51 (dd, $J_{5Beq,5Bax}$ = 12.2 Hz, $J_{5Beq,4B}$ = 4.8 Hz, 1H, H5$^B_{eq}$), 3.45 (dd, $J_{5Aax,5Aeq}$ = 12.0 Hz, $J_{5Aax,4A}$ = 8.6 Hz, 1H, H5$^A_{ax}$), 3.09 (dd, $J_{5Bax,5Beq}$ = 12.2 Hz, $J_{5Bax,4B}$ = 8.7 Hz, 1H, H5$^B_{ax}$), 2.64–2.37 (m, 4H, 1.97 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.9, 171.8, 165.6, 165.4, 165.3, 165.3, 165.2, 165.0, 133.6, 133.5 (×2), 133.5, 133.4, 133.3, 132.8, 132.6 (×2), 130.1 (×3), 130.0 (×2), 129.9 (×2), 129.8 (×2), 129.6, 129.4, 129.4, 129.4, 129.3, 129.2, 129.1 (×2), 128.6 (×2), 128.6 (×3), 128.5 (×3), 128.5 (×2), 128.4 (×2), 128.2, 101.0 (C1^B), 99.1 (C1^C), 86.7 (C1^A), 75.6 (C4^A), 74.2 (C4^B), 73.1 (C3^A), 71.9 (C3^B), 71.6 (C2^B), 70.4 (C2^A), 70.1 (C2^C), 69.6 (C3^C), 68.7 (C4^C), 65.9 (C5^A), 62.2 (C5^B), 61.0 (C5^C), 37.8, 29.6, 28.0. HRMS: *m*/*z* calcd. for $C_{68}H_{60}O_{20}SNa$ $[M + Na]^+$ 1251.3291, found 1251.3308.

*2,3,5-Tri-O-benzoyl-L-arabinofuranosyl N-phenyl-2,2,2-trifluoroacetimidate (**4**).* AcCl (5.0 mL, 70.3 mmol) was slowly added to methanol (60.0 mL) cooled to 0 °C. The methanolic HCl solution was then added to a vigorously stirred suspension of L-arabinose (10.0 g, 66.8 mmol) in

methanol (200 mL). The reaction was left to stir at rt for 4.5 h, then the mixture was concd under co-evaporation with CH_2Cl_2. The resulting residue was cooled to 0 °C and dissolved in pyridine (60.0 mL). BzCl (62.0 mL, 534 mmol) was slowly added over 25 min and the reaction was left to stir at rt overnight. H_2O (5.0 mL) was added to quench the reaction which was stirred for an additional 5 min. The mixture was then diluted with CH_2Cl_2 (500 mL) and washed with H_2O, 1 M HCl, and $NaHCO_3$, dried over $MgSO_4$, filtered, and concd in vacuo under co-evaporation with toluene. The residue was crystallized from absolute EtOH with the addition of pentane to promote the crystallization. The intermediate methyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranoside was obtained as white crystals (14.13 g, 44% over 2 steps). R_f 0.44 (hexane/EtOAc 2:1). Mp 95.3–97.7 °C (EtOH) (lit.[35] 106 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.00 (m, 6H), 7.62–7.56 (m, 2H), 7.53–7.49 (m, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 5.59 (d, J = 5.2 Hz, 1H, H3), 5.52 (d, J = 1.3 Hz, 1H, H2), 5.18 (s, 1H, H1), 4.85 (dd, $J_{5,5'}$ = 11.9 Hz, $J_{4,5}$ = 3.4 Hz, 1H, H5), 4.70 (dd, $J_{5',5}$ = 11.9 Hz, $J_{4,5'}$ = 4.8 Hz, 1H, H5'), 4.59–4.56 (m, 1H, H4), 3.50 (s, 3H, OMe). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.4, 166.0, 165.6, 133.7, 133.6, 133.2, 130.1 (×2), 130.0 (×2), 129.9 (×2), 129.2, 129.2, 128.7 (×2), 128.6 (×2), 128.5 (×2), 107.0 (C1), 82.4 (C2), 81.0 (C4), 78.1 (C3), 63.9 (C5), 55.2 (OMe). NMR data are in accordance with literature values.[35] The above glycoside (1.92 g, 4.03 mmol) was dissolved in 80% AcOH (13.0 mL) and 33% HBr·AcOH (11.0 mL, 60.7 mmol) was added under an atm of N_2. The solution was let stir at rt for 3.5 h. EtOAc was added and the mixture washed with brine and H_2O, dried over $MgSO_4$, filtered, and concd in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc 7:1) to afford 2,3,5-tri-*O*-benzoyl-L-arabinofuranose (α:β ratio 1:0.35) as a white foam (1.445 g, 77%). R_f 0.41 (hexane/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–8.03 (m, 8H), 7.66–7.32 (m, 12H),

5.91 (t, J = 5.4 Hz, 0.35H, H3$_\beta$), 5.86 (d, J = 4.4 Hz, 0.34H, H1$_\beta$), 5.71 (s, 1H, H1$_\alpha$), 5.61–5.57 (m, 2.35H, H2$_\alpha$, H3$_\alpha$, H2$_\beta$), 4.89–4.75 (m, 2.70H, H4$_\alpha$, H5$_\alpha$, H5$_\beta$, H5'$_\beta$), 4.69 (dd, J = 11.5, 5.2 Hz, 1H, H5'$_\alpha$), 4.51–4.47 (m, 0.34H, H4$_\beta$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.6, 166.4, 166.1, 166.0, 165.9, 165.7, 134.0, 133.8, 133.7, 133.7, 133.3, 133.3, 132.2, 130.3, 130.1, 130.1, 130.0, 129.9, 129.9 129.8, 129.1, 129.1, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 101.2 (C1$_\alpha$), 95.7 (C1$_\beta$), 82.6 (C2$_\alpha$), 81.6 (C4$_\alpha$), 79.3 (C4$_\beta$), 78.1 (C3$_\alpha$), 77.8 (C2$_\beta$), 76.7 (C3$_\beta$), 65.9 (C5$_\beta$), 64.1 (C5$_\alpha$). NMR data are in accordance with literature values.[19a] The above hemiacetal (0.500 g, 1.08 mmol) was dissolved in acetone (4.0 mL) followed by addition of Cs_2CO_3 (0.704 g, 2.16 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (0.35 mL, 2.21 mmol). The mixture was left to stir at rt for 2 h and then filtered through a pad of Celite, concd in vacuo, and purified by flash column chromatography (hexane/EtOAc 10:1). The product **4** was obtained a yellow foam. It was possible to separate some of the α isomer (0.281 g, 41%) from the mixture (α/β ratio 1:2) (0.292 g, 43%) (overall α/β ratio 2:1). R_f(α) 0.57 and R_f(β) 0.52 (hexane/EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–8.08 (m, 5H), 8.06–8.04 (m, 3H), 8.01 (d, J = 7.5 Hz, 1H), 7.66–7.38 (m, 11.5H), 7.32–7.26 (m, 3H), 7.17 (t, J = 7.8 Hz, 2H), 7.09 (t, J = 7.5 Hz, 0.5H), 7.03 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.83 (bs, 1H, H1$_\beta$), 6.58 (d, J = 7.7 Hz, 2H), 6.02–5.99 (m, 1H, H3$_\beta$), 5.93–5.91 (m, 1H, H2$_\beta$), 5.80 (s, 0.5H, H2$_\alpha$), 5.67–5.66 (m, 0.5H, H3$_\alpha$), 4.84–4.80 (m, 2H, H4$_\alpha$, H5$_\alpha$, H5$_\beta$), 4.76–4.71 (m, 1.5H, H5'$_\alpha$, H5'$_\beta$), 4.67–4.63 (m, 1H, H4$_\beta$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.3, 166.2, 165.9, 165.7, 165.6, 165.2, 143.5, 143.4, 134.0, 134.0 (×2), 133.9 (×2), 133.3 (×2), 130.1 (×4), 130.1 (×4), 130.0 (×4), 129.9 (×4), 129.7, 129.7, 129.0, 128.9 (×2), 128.8 (×4), 128.7, 128.5 (×4), 124.6, 124.3, 119.7, 119.3, 102.4 (C1$_\alpha$), 97.0 (C1$_\beta$), 84.4 (C4$_\alpha$), 80.9 (C2$_\alpha$), 80.7 (C4$_\beta$), 77.4 (C3$_\alpha$), 76.3 (C2$_\beta$), 75.7 (C3$_\beta$), 65.0

($C5_\beta$), 63.7 ($C5_\alpha$). HRMS: *m*/*z* calcd for $C_{34}H_{26}F_3NO_8Na$ $[M + Na]^+$ 656.1503, found 656.1499. NMR data are in accordance with literature values.[19]

Deprotection of Levulinoyl Groups (General Procedure C). The linear xylan saccharide (1.0 equiv) was dissolved in AcOH (*c* = 0.40 M) and pyridine (*c* = 0.20 M). A mixture of a 50% solution of hydrazine hydrate (10.0 equiv) in AcOH (*c* = 20 M) and pyridine (*c* = 10 M) was added. The reaction was left to stir at rt until TLC showed consumption of the starting material and formation of the product. The reaction was stopped by the addition of acetone (300 equiv) and left to stir at rt for 30 min. EtOAc was added and the mixture was washed with 1 M HCl, $NaHCO_3$, and H_2O, dried over Na_2SO_4, filtered, and concd in vacuo. The product was obtained in sufficient purity and did not need further purification.

Glycosylation with *N*-Phenyl-2,2,2-trifluoroacetimidate 4 (General Procedure D). The partially deprotected xylan (1.0 equiv) and donor **4** (4.0 equiv) were co-evaporated twice with toluene and left under high vacuum overnight. The mixture was dissolved in dry CH_2Cl_2 (20 mL/0.1 g deprotected xylan) and cooled to –40 °C. TMSOTf (0.1 equiv) was added from a freshly made stock solution of TMSOTf in dry CH_2Cl_2. The reaction was kept at –40 °C for the time indicated after which Et_3N (0.7 equiv) was added, and the mixture was concd in vacuo. The residue was purified by flash column chromatography to afford the desired product.

Deprotection of Anomeric Thiophenyl Group to Prepare 29 – 31 (General Procedure E). The arabinoxylan saccharide (1.0 equiv) was dissolved in acetone/H_2O 9:1 (15 mL/mmol) and NBS (4.0 equiv) was added. The mixture was left to stir at rt until TLC analysis showed

completion of the reaction. EtOAc was added to the mixture, which was then washed with $NaHCO_3$ and H_2O, dried over Na_2SO_4, filtered, and concd in vacuo. The residue was purified by flash column chromatography.

Deprotection of Benzoyl Groups (General Procedure F). The arabinoxylan saccharide (1.0 equiv) was dissolved in CH_2Cl_2/MeOH 1:1 (c = 0.01 M). A 1 M NaOMe solution was added until the solution had obtained a pH of 11. The reaction was stirred at rt until TLC analysis (EtOAc/MeOH/H_2O/AcOH 6:3:0.8:0.2) showed completion of the reaction (about 1 – 3 h). The mixture was diluted with water and washed with Et_2O and EtOAc and concd followed by purification with Sep-Pak C18 Plus Short Cartridge (Waters) with a gradient of H_2O to H_2O/MeOH 1:1.

Deprotection of Anomeric Thiophenyl Group to Prepare 1 – 3 (General Procedure G). The partially deprotected arabinoxylan saccharide (1.0 equiv) was dissolved in MeCN/H_2O 5:1 (c = 0.02 M) followed by addition of 2,6-lutidine (1.5 equiv) and NBS (3.0 equiv). The mixture was stirred at rt until TLC analysis (EtOAc/MeOH/H_2O/AcOH 6:3:0.8:0.2) showed completion of the reaction. The mixture was concd in vacuo. The crude residue was dissolved in MeOH (0.5 mL) followed by addition of ice-cold Et_2O, and precipitation for 30 min in the freezer. The mixture was then centrifuged and the supernatant removed. The precipitation process was repeated three times in total. The resulting residue was purified by gel filtration (PD miniTrap G-10 column).

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-3-O-levulinoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-3-O-levulinoyl-1-thio-β-D-xylopyranoside (**16**)*. General procedure B with crushed mol sieves (1.0 g), donor **14** (0.250 g, 0.28 mmol), AgOTf (0.145 g, 0.56 mmol), *p*NO_2PhSCl (0.053 g, 0.28 mmol) and acceptor **11** (0.113 g, 0.25 mmol). Reaction time 15 min then Et_3N (0.12 mL, 0.84 mmol). Purification by flash column chromatography (heptane/EtOAc 4:3) gave **16** as a white amorphous solid (0.274 g, 88%). R_f 0.37 (heptane/EtOAc 1:1). $[\alpha]^{25}_D$ –57.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.95 (m, 10H), 7.63–7.46 (m, 9H), 7.43–7.35 (m, 8H), 7.29–7.25 (m, 3H), 5.73 (t, J = 6.6 Hz, 1H, H3^C), 5.37–5.26 (m, 4H, H3^A, H3^B, H2^C, H4^C), 5.13 (t, $J_{1A,2A}$ = 8.3 Hz, 1H, H2^A), 5.05 (dd, $J_{2B,3B}$ = 8.3 Hz, $J_{1B,2B}$ = 6.5 Hz, 1H, H2^B), 4.96 (d, $J_{1C,2C}$ = 4.7 Hz, 1H, H1^C), 4.86 (d, $J_{1A,2A}$ = 8.4 Hz, 1H, H1^A), 4.67 (d, $J_{1B,2B}$ = 6.4 Hz, 1H, H1^B), 4.48 (dd, $J_{5Ceq,5Cax}$ = 12.4 Hz, $J_{5Ceq,4C}$ = 3.9 Hz, 1H, H5$^C{}_{eq}$), 4.11–4.04 (m, 2H, H5$^A{}_{eq}$, H5$^B{}_{eq}$), 3.98–3.97 (m, 1H, H4^B), 3.88–3.82 (m, 1H, H4^A), 3.77 (dd, $J_{5Cax,5Ceq}$= 12.4 Hz, $J_{5Cax,4C}$ = 6.2 Hz, 1H, H5$^C{}_{ax}$), 3.42 (dd, $J_{5Bax,5Beq}$ = 12.1 Hz, $J_{5Bax,4B}$ = 8.4 Hz, 1H, H5$^B{}_{ax}$), 3.36 (dd, $J_{5Aax,5Aeq}$ = 11.9 Hz, $J_{5Aax,4A}$ = 9.0 Hz, 1H, H5$^A{}_{ax}$), 2.66–2.39 (m, 8H), 2.06 (s, 3H), 2.01 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.0, 205.9, 171.8, 171.6, 165.6, 165.3, 165.3, 165.1 (×2), 133.5, 133.5, 133.4, 133.4, 132.6 (×2), 132.6, 130.1 (×2), 130.0 (×2), 130.0 (×2), 129.9 (×2), 129.9 (×2), 129.5, 129.4, 129.4, 129.2, 129.1, 129.0 (×2), 128.6 (×2), 128.5 (×4), 128.5 (×4), 128.1, 100.5 (C1^B), 99.2 (C1^C), 86.5 (C1^A), 74.9 (C4^A), 74.3 (C4^B), 73.0 (C3^A), 71.9 (C3^B), 71.4 (C2^B), 70.4, 70.2 (C2^A, C2^C), 69.7 (C3^C), 68.7 (C4^C), 66.1 (C5^A), 62.4 (C5^B), 61.1 (C5^C), 37.8, 37.8, 29.8, 29.6, 28.0, 28.0. HRMS: *m*/*z* calcd for $C_{66}H_{62}O_{21}SNa$ $[M + Na]^+$ 1245.3396, found 1245.3379.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-3-O-levulinoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-3-O-levulinoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-3-O-levulinoyl-1-thio-β-D-xylopyranoside (**17**).* General procedure B with crushed mol sieves (1.5 g), donor **16** (0.794 g, 0.65 mmol), AgOTf (0.332 g, 1.29 mmol), *p*NO_2PhSCl (0.123 g, 0.65 mmol) and acceptor **11** (0.262 g, 0.59 mmol). Reaction time 60 min then Et_3N (0.27 mL, 1.95 mmol). Purification by flash column chromatography (heptane/acetone 2:1) gave **17** as a white amorphous solid (0.670 g, 73%). R_f 0.34 (hexane/acetone 1:1). $[\alpha]^{25}_D$ –46.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.92 (m, 12H), 7.60–7.31 (m, 20H), 7.25–7.21 (m, 3H), 5.70 (t, J = 6.5 Hz, 1H, H3^D), 5.32 (t, $J_{2B,3B}$ = 8.2 Hz, 1H, H3$_B$), 5.28–5.24 (m, 3H, H3^A, H2^D, H4^D), 5.20 (t, $J_{2C,3C}$ = 8.0 Hz, 1H, H3^C), 5.08 (t, $J_{1A,2A}$ = 8.3 Hz, 1H, H2^A), 5.04 (dd, $J_{2B,3B}$ = 8.4 Hz, $J_{1B,2B}$ = 6.5 Hz, 1H, H2^B), 4.97 (dd, $J_{2C,3C}$ = 8.3 Hz, $J_{1C,2C}$ = 6.4 Hz, 1H, H2^C), 4.93 (d, $J_{1D,2D}$ = 4.7 Hz, 1H, H1^D), 4.81 (d, $J_{1A,2A}$ = 8.4 Hz, 1H, H1^A), 4.64 (d, $J_{1B,2B}$ = 6.5 Hz, 1H, H1^B), 4.57 (d, $J_{1C,2C}$ = 6.3 Hz, 1H, H1^C), 4.46 (dd, $J_{5Deq,5Dax}$ = 12.4 Hz, $J_{5Deq,4D}$ = 3.9 Hz, 1H, H5$^D{}_{eq}$), 4.05–4.00 (m, 2H, H5^A, H5$^B{}_{eq}$), 3.95–3.89 (m, 2H, H4^B, H5^C), 3.80–3.72 (m, 3H, H4^A, H4^C, H5$^D{}_{ax}$), 3.38 (dd, $J_{5Bax,5Beq}$ = 12.1 Hz, $J_{5Bax,4B}$ = 8.5 Hz, 1H, H5$^B{}_{ax}$), 3.33–3.25 (m, 2H, H5'^{A}, H5'^{C}), 2.66–2.32 (m, 12H), 2.03 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.1, 206.0, 205.9, 171.8, 171.7, 171.5, 165.6, 165.3, 165.2, 165.2, 165.1, 165.1, 133.5, 133.5 (×2), 133.4 (×2), 132.6 (×2), 132.5, 130.1 (×2), 130.0 (×2), 130.0 (×2), 129.9 (×3), 129.9 (×3), 129.5, 129.4 (×2), 129.4, 129.2, 129.1, 129.0 (×2), 128.6 (×3), 128.5 (×4), 128.5 (×4), 128.1, 100.4 (×2, C1^B, C1^C), 99.2 (C1^D), 86.5 (C1^A), 74.7 (C4^A), 74.5, 74.3 (C4^B, C4^C), 72.9 (C3^A), 71.9 (C3^B), 71.6 (C3^C), 71.4 (C2^B), 71.1 (C2^C), 70.4 (C2^A), 70.2 (C2^D), 69.6 (C3^D), 68.7 (C4^D), 66.0 (C5^A), 62.4 (2C, C5^B, C5^C), 61.0 (C5^D), 37.8, 37.8, 37.8, 29.8, 29.8, 29.6, 28.0, 28.0, 27.9. HRMS: *m*/*z* calcd for $C_{83}H_{80}O_{28}SNa$ $[M + Na]^+$ 1579.4449, found 1579.4427.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-1-thio-β-D-xylopyranoside (**18**).* General procedure C with tetrasaccharide **17** (0.146 g, 0.094 mmol) and 50% solution of hydrazine hydrate (59 μL, 0.94 mmol). Reaction time 3 h. Eluent for TLC (heptane/EtOAc 1:1). The product obtained was a white powder (0.113 g, 96%). R_f 0.37 (heptane/acetone 1:1). $[\alpha]^{25}_D$ –36.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.00 (m, 6H), 7.96–7.90 (m, 6H), 7.62–7.32 (m, 22H), 7.24–7.20 (m, 1H), 5.82 (t, J = 8.9 Hz, 1H, H3^D), 5.42 (dd, $J_{2D,3D}$ = 9.0 Hz, $J_{1D,2D}$ = 7.0 Hz, 1H, H1^D), 5.37 (td, $J_{3D,4D}$ = 8.9 Hz, J = 4.5 Hz, 1H, H4^D), 5.11–5.07 (m, 1H, H2^C), 5.05–5.00 (m, 2H, H2^A, H2^B), 4.83 (d, $J_{1D,2D}$ = 7.0 Hz, 1H, H1^D), 4.64 (d, $J_{1A,2A}$ = 9.9 Hz, 1H, H1^A), 4.50 (d, $J_{1C,2C}$ = 7.9 Hz, 1H, H1^C), 4.47–4.43 (m, 2H, H1^B, H5^D), 3.87–3.77 (m, 4H, H3^A, H3^C, H4^C, H5^C), 3.75–3.55 (m, 7H, H3^A, H4^A, H3^B, H4^B, H5^B, H5'^{D}), 3.31–3.15 (m, 3H, H5'^{A}, H5'^{B}, H5'^{C}). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6 (×2), 165.5, 165.5, 165.4, 165.2, 133.8, 133.7, 133.6, 133.5, 133.5, 133.3, 132.8 (×3), 132.3, 130.0 (×2), 129.9 (×2), 129.9 (×2), 129.9 (×2), 129.8 (×2), 129.7 (×4), 129.5, 129.4, 129.1, 129.0, 129.0 (×3), 128.9, 128.9, 128.9, 128.8 (×2), 128.7 (×2), 128.6 (×2), 128.6 (×2), 128.5 (×2), 128.5 (×2), 128.3, 128.1, 102.2, 102.1 (C1^B, C1^C, J_{C-H} = 157 Hz, J_{C-H} = 163 Hz), 101.8 (C1^D, J_{C-H} = 162 Hz), 86.6 (C1^A, J_{C-H} = 155 Hz), 80.6 (C4^A), 80.3 (C4^B), 80.1 (C4^C), 74.8 (C3^A), 73.2, 73.1, 73.0, 73.0 (C2^B, C3^B, C2^C, C3^C), 72.0 (C2^A), 71.3 (C3^D), 71.1 (C2^D), 69.3 (C4^D), 67.1 (C5^A), 63.5 (2C, C5^B, C5^C), 62.8 (C5^D). HRMS: *m*/*z* calcd for $C_{68}H_{62}O_{22}SNa$ $[M + Na]^+$ 1285.3346, found 1285.3346.

Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-

*arabinofuranosyl-(1→3)]-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-2-O-benzoyl-1-thio-β-D-xylopyranoside (**19**).* General procedure D with acceptor **18** (0.054 g, 0.043 mmol), donor **4** (0.109 g, 0.17 mmol) and TMSOTf in dry CH_2Cl_2 (0.11 mL, c = 0.04 mmol/mL). Reaction time 75 min then Et_3N (0.02 mL, 0.11 mmol). Eluent TLC (heptane/acetone 1:1) and flash column chromatography (heptane/acetone 2:1). The product **19** was isolated as a white amorphous solid (0.100 g, 90%). R_f 0.41 (heptane/acetone 1:1). $[\alpha]^{25}_D$ –46.9 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18–8.16 (m, 2H), 8.09–7.87 (m, 28H), 7.83 (t, J = 7.4 Hz, 1H), 7.64–7.16 (m, 49H), 5.71 (t, $J_{3D,4D}$ = 9.3 Hz, 1H, H3^D), 5.52 (d, J = 5.5 Hz, 1H), 5.49 (d, J = 5.3 Hz, 1H), 5.45 (d, J = 4.6 Hz, 1H), 5.43 (s, 1H), 5.37 (d, J = 1.0 Hz, 1H), 5.35–5.34 (m, 2H), 5.30–5.28 (m, 2H, H2^D), 5.26–5.24 (m, 2H, H2^A), 5.15 (td, $J_{3D,4D}$ = 9.3 Hz, $J_{4D,5D}$ = 4.7 Hz, 1H, H4^D), 5.07–4.83 (m, 2H, H2^B, H2^C), 4.68 (d, J = 8.8 Hz, 1H, H1^A), 4.23 (d, J = 8.0 Hz, 1H, H1^B), 4.10 (d, J = 7.4 Hz, 1H, H1^D), 4.08–3.99 (m, 2H, H3^A, H5^A), 3.88–3.82 (m, 3H, H3^B, H3^C, H5^D), 3.76 (td, J = 8.8, 4.8 Hz, 1H, H4^A), 3.59–3.53 (m, 2H, H1^C, H4^C), 3.33 (dd, J = 11.8, 5.1 Hz, 1H, H5^C), 3.29–3.19 (m, 2H, H4^B, H5'^{D}), 3.10–3.02 (m, 2H, H5'^{A}, H5^B), 2.67–2.56 (m, 2H, H5'^{B}, H5'^{C}). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.4, 166.4, 166.4, 166.1, 165.9, 165.8, 165.7, 165.1, 165.1 (×3), 165.0, 164.7, 164.4, 164.2, 133.9, 133.7, 133.5, 133.4, 133.3, 133.2, 133.2, 133.1, 133.0, 132.9, 132.5, 130.4, 130.2, 130.2, 130.1, 130.1, 130.0, 129.9, 129.9, 129.9, 129.9, 129.8, 129.8, 129.7, 129.7, 129.7, 129.6, 129.5, 129.3, 129.2, 129.1, 129.1, 129.0, 129.0, 129.0, 129.0, 128.9, 128.9, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 127.9, 106.1, 105.7, 105.6 (C1^E, C1^F, C1^G), 100.3 (C1^B), 100.1 (C1^C), 99.9 (C1^B), 86.7 (C1^A), 82.8, 82.7, 82.5, 82.1, 81.5, 80.8, 78.3, 78.2 (×2), 76.0 (C3^A), 75.3 (C3^B/C3^C), 75.2 (C3^B/C3^C), 74.5 (C4^C), 74.2 (C4^B), 73.7(C4^A), 73.3 (C2^B), 73.0 (C2^C), 72.2 (C2^A/C3^D), 72.0 (C2^A/C3^D), 71.2 (C2^D), 69.8 (C4^D), 66.1 (C5^A), 64.0, 63.9, 63.8 (C5^E, C5^F,

C5^{G}), 63.1, 63.1, 63.0 (C5^{B}, C5^{C}, C5^{D}). HRMS: *m*/*z* calcd for $C_{146}H_{122}O_{43}SNa$ $[M + Na]^+$ 2617.6973, found 2617.6976.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-3-O-levulinoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-levulinoyl-1-thio-β-D-xylopyranoside (**20**).* General procedure B with crushed mol sieves (2.6 g), donor **14** (1.00 g, 1.12 mmol), AgOTf (0.579 g, 2.25 mmol) and *p*NO_2PhSCl (0.214 g, 1.12 mmol). Activation time 40 min then acceptor **9** (0.447 g, 1.02 mmol). Reaction time 50 min then Et_3N (0.47 mL, 3.37 mmol). Purification by flash column chromatography (hexane/toluene/EtOAc 3:1:4) gave **20** as a white amorphous solid (0.883 g, 71%). In addition, donor **14** was reisolated (0.119 g, 12%). R_f 0.48 (hexane/acetone 3:2). $[\alpha]^{25}_D$ –60.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.92 (m, 8H), 7.61–7.43 (m, 6H), 7.41–7.32 (m, 8H), 7.28–7.26 (m, 3H), 5.70 (t, J = 6.5 Hz, 1H, H3^{C}), 5.31 (t, J = 8.1 Hz, 1H, H3^{B}), 5.28–5.24 (m, 2H, H2^{C}, H4^{C}), 5.11 (t, $J_{2A,3A}$ = 8.7 Hz, 1H, H3^{A}), 5.00 (dd, $J_{2B,3B}$ = 8.3 Hz, $J_{1B,2B}$ = 6.4 Hz, 1H, H2^{B}), 4.97 (d, $J_{1C,2C}$ = 4.7 Hz, 1H, H1^{C}), 4.84 (t, $J_{2A,3A}$ = 9.0 Hz, 1H, H2^{A}), 4.61–4.58 (m, 2H, H1^{A}, H1^{B}), 4.46 (dd, $J_{5Ceq,5Cax}$ = 12.4 Hz, $J_{5Ceq,4C}$ = 3.8 Hz, 1H, H5$^{C}_{eq}$), 4.06 (dd, $J_{5Beq,5Bax}$ = 11.9 Hz, $J_{5Beq,4B}$ = 4.8 Hz, 1H, H5$^{B}_{eq}$), 4.02–3.98 (m, 1H, H4^{B}), 3.94 (dd, $J_{5Aeq,5Aax}$ = 11.9 Hz, $J_{5Aeq,4A}$ = 5.2 Hz, 1H, H5$^{A}_{eq}$), 3.77–3.71 (m, 2H, H4^{A}, H5$^{c}_{ax}$), 3.38 (dd, $J_{5Bax,5Beq}$ = 11.9 Hz, $J_{5Bax,4B}$ = 8.1 Hz, 1H, H5$^{B}_{ax}$), 3.21 (dd, $J_{5Aax,5Aeq}$ = 11.8 Hz, $J_{5Aax,4A}$ = 9.8 Hz, 1H, H5$^{A}_{ax}$), 2.85–2.39 (m, 12H), 2.17 (s, 3H), 2.16 (s, 3H), 1.98 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.5, 206.4, 206.0, 171.9, 171.7, 171.5, 165.6, 165.4, 165.2, 165.1, 133.5, 133.5, 133.5, 133.5, 132.8 (×2), 132.3, 130.1 (×2), 130.0 (×2), 130.0 (×2), 129.9 (×2), 129.4, 129.4, 129.3, 129.2, 129.1 (×2), 128.7 (×2), 128.5 (×4), 128.2, 100.6 (C1^{B}), 99.3 (C1^{C}), 86.5 (C1^{A}), 75.2 (C4^{A}), 74.3 (C4^{B}), 73.4 (C3^{A}), 71.9 (C3^{B}), 71.4 (C2^{B}), 70.2, 70.0 (C2^{A}, C2^{C}), 69.7

(C3^{C}), 68.8 (C4^{C}), 66.6 (C5^{A}), 62.5 (C5^{B}), 61.1 (C5^{C}), 37.9, 37.9, 37.8, 30.0, 29.9, 29.7, 28.1, 28.0, 28.0. HRMS: *m*/*z* calcd for $C_{64}H_{64}O_{22}SNa$ $[M + Na]^+$ 1239.3502, found 1239.3489.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-3-O-levulinoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-levulinoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**21**).* General procedure B with crushed mol sieves (2.1 g), donor **20** (1.21 g, 0.99 mmol), AgOTf (0.510 g, 1.98 mmol), *p*NO_2PhSCl (0.187 g, 0.99 mmol) and acceptor **6** (0.402 g, 0.89 mmol). Reaction time 40 min then Et_3N (0.40 mL, 2.97 mmol). Purification by flash column chromatography (heptane/toluene/acetone 3:2:2) gave **21** as a white amorphous solid (0.851 g, 61%). R_f 0.40 (hexane/acetone 3:2). $[\alpha]^{25}_D$ –38.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.91 (m, 12H), 7.61 (t, J = 7.4 Hz, 1H), 7.56–7.45 (m, 9H), 7.41–7.32 (m, 10H), 7.29–7.24 (m, 2H), 7.18–7.16 (m, 1H), 5.70 (t, J = 6.5 Hz, 1H, H3^{D}), 5.53 (t, J = 7.6 Hz, 1H, H3^{A}), 5.30–5.24 (m, 4H, H2^{A}, H3^{C}, H2^{D}, H4^{D}), 5.03 (d, $J_{1A,2A}$ = 7.7 Hz, 1H, H1^{A}), 4.99–4.91 (m, 3H, H3^{B}, H2^{C}, H1^{D}), 4.70 (dd, $J_{2B,3B}$ = 8.9 Hz, $J_{1B,2B}$ = 7.0 Hz, 1H, H2^{B}), 4.45 (dd, $J_{5Deq,5Dax}$ = 12.4 Hz, $J_{5Deq,4D}$ = 3.8 Hz, 1H, H5$^{D}_{eq}$), 4.41 (d, $J_{1B,2B}$ = 6.9 Hz, 1H, H1^{B}), 4.36 (d, $J_{1C,2C}$ = 6.5 Hz, 1H, H1^{C}), 4.30 (dd, $J_{5Aeq,5Aax}$ = 12.1 Hz, $J_{5Aeq,4A}$ = 4.6 Hz, 1H, H5$^{A}_{eq}$), 4.01–3.86 (m, 3H, H4^{A}, H4^{C}, H5^{C}), 3.74 (dd, $J_{5Dax,5Deq}$ = 12.4 Hz, $J_{5Dax,4D}$ = 6.1 Hz, 1H, H5$^{D}_{ax}$), 3.58 (dd, $J_{5Aax,5Aeq}$ = 12.1 Hz, $J_{5Aax,4A}$ = 8.2 Hz, 1H, H5$^{A}_{ax}$), 3.49–3.44 (m, 1H, H4^{B}), 3.34–3.28 (m, 2H, H5$^{B}_{eq}$, H5^{C}), 2.89 (dd, $J_{5Bax,5Beq}$ = 12.0 Hz, $J_{5Bax,4B}$ = 9.4 Hz, 1H, H5$^{B}_{ax}$), 2.71–2.35 (m, 12H), 2.14 (bs, 6H), 1.97 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.4, 206.4, 205.9, 171.8, 171.7, 171.3, 165.6, 165.4, 165.3 (×2), 165.2, 165.0, 133.5, 133.5, 133.5, 133.5, 133.3, 133.2, 133.0, 132.6 (×2), 130.1 (×3), 130.0 (×2), 130.0 (×2), 129.9 (×2), 129.8 (×2), 129.6, 129.5, 129.4, 129.4, 129.2, 129.2, 129.1, 129.1 (×2), 128.6 (×2), 128.6 (×3), 128.5 (×4), 128.5

(×2), 128.4 (×2), 128.3, 128.1, 100.9 ($C1^B$), 100.3 ($C1^C$), 99.2 ($C1^D$), 86.6 ($C1^A$), 75.4 ($C4^A$), 74.8 ($C4^B$), 74.4 ($C4^C$), 72.7 ($C3^A$), 72.1, 71.9 ($C3^B$, $C2^A$/$C3^C$/$C2^D$), 71.3, 71.2 ($C2^B$, $C2^C$), 70.4, 70.2 ($C2^A$/$C3^C$/$C2^D$), 69.6 ($C3^D$), 68.7 ($C4^D$), 65.5 ($C5^A$), 62.6, 62.5 ($C5^B$, $C5^C$), 61.1 ($C5^D$), 37.8, 37.8, 37.7, 30.0, 29.9, 29.6, 28.0, 27.9, 27.9. HRMS: *m*/*z* calcd for $C_{83}H_{80}O_{28}SNa$ $[M + Na]^+$ 1579.4449, found 1579.4430.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**22**).* General procedure C with tetrasaccharide **21** (0.507 g, 0.33 mmol) and 50% solution of hydrazine hydrate (0.20 mL, 3.21 mmol). Reaction time 20 min. Eluent for TLC (hexane/toluene/acetone 2:1:2). The product was a white powder (0.400 g, 97%). R_f 0.24 (hexane/acetone 3:2). $[\alpha]^{25}_D$ –15.4 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.04–7.92 (m, 12H), 7.63 (t, J = 7.4 Hz, 1H), 7.57–7.26 (m, 22H), 5.84 (t, $J_{2D,3D}$ = 8.8 Hz, 1H, $H3^D$), 5.57 (t, $J_{2A,3A}$ = 7.5 Hz, 1H, $H3^A$), 5.43 (dd, $J_{2D,3D}$ = 8.7 Hz, $J_{1D,2D}$ = 7.1 Hz, 1H, $H2^D$), 5.38–5.30 (m, 2H, $H2^A$, $H4^D$), 5.10 (d, $J_{1A,2A}$ = 7.4 Hz, 1H, $H1^A$), 5.05 (t, J = 8.2 Hz, 1H, $H2^C$), 4.88 (d, $J_{1D,2D}$ = 6.9 Hz, 1H, $H1^D$), 4.42–4.36 (m, 2H, $H5^A$, $H5^D$), 4.33 (d, J = 7.6 Hz, 1H, $H1^C$), 4.27 (d, J = 6.7 Hz, 1H, $H1^B$), 3.97–3.92 (m, 1H, $H4^A$), 3.89–3.81 (m, 3H, $H3^C$, $H4^C$, $H5^C$), 3.73–3.62 (m, 4H, $H5'^A$, $H5'^D$, OH), 3.45 (t, J = 8.1 Hz, 1H, $H3^B$), 3.33–3.19 (m, 4H, $H2^B$, $H4^B$, $H5^B{}_{eq}$, $H5'^C$), 3.05 (bs, 1H, OH) 2.89 (dd, $J_{5Bax,5Beq}$ = 11.5 Hz, $J_{5bax,4B}$ = 9.2 Hz, 1H, $H5^B{}_{ax}$). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.6, 165.6, 165.6, 165.6, 165.3, 165.2, 133.8, 133.7, 133.5 (×2), 133.4, 133.3, 133.0, 132.6 (×3), 130.0 (×4), 129.9 (×4), 129.9 (×2), 129.8 (×2), 129.6, 129.5, 129.5, 129.1 (×2), 129.0, 129.0, 128.9, 128.7 (×2), 128.7 (×2), 128.6 (×2), 128.5 (×2), 128.5 (×2), 128.4 (×2), 128.2, 102.1 ($C1^B$, J_{C-H} = 160 Hz), 101.8 ($C1^D$, J_{C-H} = 163 Hz), 101.4 ($C1^C$, J_{C-H} = 163 Hz), 86.6 ($C1^A$, J_{C-H} = 159 Hz), 80.2 ($C4^C$), 79.0

(C4^{B}), 74.1 (C4^{A}), 73.3, 73.1, 73.0 (C3^{B}, C2^{C}, C3^{C}), 72.5, 72.3 (C3^{A}, C2^{B}), 71.4, 71.2 (C2^{D}, C3^{D}), 70.2 (C2^{A}), 69.4 (C4^{D}), 65.1 (C5^{a}), 63.4 (C5^{C}), 62.8 (C5^{D}), 62.0 (C5^{B}). HRMS: *m*/*z* calcd for $C_{68}H_{62}O_{22}SNa$ $[M + Na]^+$ 1285.3345, found 1285.3334.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-[(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→2)]-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**23**).* General procedure D with acceptor **22** (0.201 g, 0.16 mmol), donor **4** (0.401 g, 0.63 mmol) and TMSOTf in dry CH_2Cl_2 (0.16 mL, *c* = 0.10 mmol/mL). Reaction time 1 h then Et_3N (0.02 mL, 0.11 mmol). Eluent TLC analysis (hexane/toluene/acetone 2:1:1) and eluent flash column chromatography (hexane/toluene/acetone 3:2:1→2:1:1). The product was a white amorphous solid (0.393 g, 95%). R_f 0.42 (hexane/toluene/acetone 2:1:1). $[\alpha]^{25}_{D}$ –52.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.3 Hz, 2H), 8.09–7.73 (m, 28H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.58–7.05 (m, 48H), 5.76 (s, 1H, H1^{F}), 5.69 (t, *J* = 9.1 Hz, 1H, H3^{D}), 5.65 (s, 1H, H1^{E}), 5.54–5.47 (m, 6H, H3^{A}), 5.34–5.34 (m, 1H, H2^{E}), 5.25 (s, 1H, H1^{G}), 5.25–5.20 (m, 2H, H2^{A}, H2^{D}), 5.19–5.13 (m, 1H, H4^{D}), 5.10–5.06 (m, 2H), 5.04–4.96 (m, 3H, H2^{C}), 4.94–4.85 (m, 3H, H1^{A}), 4.79 (dd, *J* = 11.4, 3.0 Hz, 1H), 4.71–4.62 (m, 2H), 4.31 (d, $J_{1B,2B}$ = 6.9 Hz, 1H, H1^{B}), 4.17–4.13 (m, 2H, H5^{A}, H1^{D}), 3.88–3.81 (m, 4H, H3^{B}, H1^{C}, H3^{C}, H5^{D}), 3.79–3.74 (m, 1H, H4^{A}), 3.65 (dd, $J_{2B,3B}$ = 9.5 Hz, $J_{1B,2B}$ = 7.0 Hz, 1H, H2^{B}), 3.53–3.47 (m, 2H, H5'^{A}, H4^{C}), 3.32–3.26 (m, 3H, H4^{B}, H5^{B}, H5'^{D}), 3.03 (dd, $J_{5C,5C'}$ = 11.8 Hz, $J_{5C,4C}$ = 5.1 Hz, 1H, H5^{C}), 2.73–2.67 (m, 1H, H5'^{B}), 2.53 (t, *J* = 11.1 Hz, 1H, H5'^{C}). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.5, 166.3, 166.3, 166.0, 165.8, 165.8, 165.7, 165.6, 165.3, 165.2 (×2), 165.0, 165.0, 164.5, 164.2, 133.6, 133.6, 133.6, 133.5,

133.4, 133.4, 133.3, 133.2, 133.1, 133.0, 132.9, 132.8, 132.2, 130.3, 130.1, 130.1, 130.0, 129.9, 129.9, 129.8, 129.8, 129.7, 129.7, 129.5, 129.2, 129.1, 129.1, 129.0, 129.0, 129.0, 128.9, 128.9, 128.6, 128.6, 128.4, 128.4, 128.3, 128.3, 128.2, 127.9, 106.9 ($C1^{E}$), 106.2 ($C1^{G}$), 105.4 ($C1^{F}$), 101.7 ($C1^{B}$), 99.8 ($C1^{D}$), 99.5 ($C1^{C}$), 86.2 ($C1^{A}$), 82.6 ($C2^{F}$), 82.3, 82.2, 81.8, 81.8, 80.7, 79.7 ($C2^{B}$), 78.6, 78.1, 77.8, 76.0 ($C3^{B}$/$C3^{C}$), 75.8 ($C3^{B}$/$C3^{C}$), 74.6 ($C4^{C}$), 73.8 ($C4^{B}$), 73.6 ($C4^{A}$), 73.1 ($C2^{C}$), 71.9 ($C3^{D}$), 71.8 ($C3^{A}$), 71.1 ($C2^{D}$), 70.2 ($C2^{A}$), 69.7 ($C4^{D}$), 64.6 ($C5^{A}$), 64.2, 64.0, 63.9 ($C5^{E}$, $C5^{F}$, $C5^{G}$), 63.0 ($C5^{C}$/$C5^{D}$), 62.8 ($C5^{C}$/$C5^{D}$), 62.3 ($C5^{B}$). HRMS: *m*/*z* calcd for $C_{146}H_{122}O_{43}S(Na^{+})_2$ $[M + 2Na]^{2+}$ 1320.3432; found *m/z* 1320.3463.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-levulinoyl-1-thio-β-D-xylopyranoside (**24**).* General procedure B with crushed mol sieves (2.0 g), donor **5** (0.402 g, 0.72 mmol), AgOTf (0.378 g, 1.47 mmol), *p*NO_2PhSCl (0.141 g, 0.74 mmol) and acceptor **9** (0.286 g, 0.65 mmol). Reaction time 25 min then Et_3N (0.30 mL, 2.15 mmol). Purification by flash column chromatography (pentane/EtOAc 3:2) gave **24** as a white amorphous solid (0.547 g, 95%). R_f 0.42 (hexane/EtOAc 1:1). $[\alpha]^{25}_{D}$ –28.1 (*c* 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.2 Hz, 2H), 7.94 (d, J = 7.4 Hz, 4H), 7.59–7.49 (m, 3H), 7.45–7.28 (m, 11H), 5.69 (t, J = 6.4 Hz, 1H, $H3^{B}$), 5.30 (td, J = 6.1 Hz, $J_{5Beq,4B}$ = 4.0 Hz, 1H, $H4^{B}$), 5.25 (d, J = 8.8 Hz, 1H, $H3^{A}$), 5.22–5.19 (m, 1H, $H2^{B}$), 4.92–4.87 (m, 2H, $H2^{A}$, $H1^{B}$), 4.66 (d, $J_{A1,A2}$ = 9.3 Hz, 1H, $H1^{A}$), 4.49 (dd, $J_{5Beq,5Bax}$ = 12.4 Hz, $J_{5Beq,4B}$ = 3.8 Hz, 1H, $H5^{B}_{eq}$), 4.09 (dd, $J_{5Aeq,5Aax}$ = 11.9 Hz, $J_{5Aeq,4A}$ = 5.2 Hz, 1H, $H5^{A}_{eq}$), 3.90 (td, J = 9.4 Hz, $J_{5Aeq,4A}$ = 5.2 Hz, 1H, $H4^{A}$), 3.75 (dd, $J_{5Bax,5Beq}$ =12.4 Hz, $J_{5Bax,4B}$ = 6.0 Hz, 1H, $H5^{B}_{ax}$), 3.32 (dd, $J_{5Aax,5Aeq}$ = 11.7 Hz, $J_{5Aeq,4A}$ = 9.9 Hz, 1H, $H5^{A}_{ax}$), 2.88–2.53 (m, 8H), 2.19 (s, 3H), 2.08 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 206.5, 206.4, 171.9, 171.5, 165.7, 165.4, 165.2, 133.6, 133.5, 133.5, 132.9 (×2), 132.2, 130.1

(×2), 130.1 (×2), 129.9 (×2), 129.4, 129.2, 129.1, 129.1 (×2), 128.6 (×4), 128.3, 99.4 ($C1^B$), 86.6 ($C1^A$), 74.9 ($C4^A$), 73.5 ($C3^A$), 70.3 ($C2^A$), 70.2 ($C2^B$), 69.6 ($C3^B$), 68.7 ($C4^B$), 66.7 ($C5^A$), 61.1 ($C5^B$), 37.9, 37.8, 30.0, 29.8, 28.1, 28.0. HRMS: *m*/*z* calcd for $C_{47}H_{46}O_{15}SNa$ $[M + Na]^+$ 905.2449, found 905.2444.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-levulinoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-3-O-levulinoyl-1-thio-β-D-xylopyranoside (**25**).* General procedure B with crushed mol sieves (1.2 g), donor **24** (0.252 g, 0.29 mmol), AgOTf (0.148 g, 0.58 mmol), *p*NO_2PhSCl (0.054 g, 0.28 mmol) and acceptor **11** (0.114 g, 0.26 mmol). Reaction time 25 min then Et_3N (0.12 mL, 0.86 mmol). Purification by flash column chromatography (heptane/toluene/EtOAc 2:1:1) gave **25** as a light yellow amorphous solid (0.162 g, 52%). R_f 0.35 (hexane/EtOAc 1:1). $[\alpha]^{25}_D$ –53.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.99 (m, 6H), 7.96–7.93 (m, 4H), 7.60–7.50 (m, 5H), 7.47–7.32 (m, 12H), 7.28–7.26 (m, 3H), 5.69 (t, J = 6.6 Hz, 1H, $H3^C$) 5.30–5.25 (m, 2H, $H3^A$, $H4^C$), 5.22 (dd, $J_{2C,3C}$ = 6.5 Hz, $J_{1C,2C}$ = 4.8 Hz, 1H, $H2^C$), 5.17–5.10 (m, 2H, $H2^A$, $H3^B$), 4.93 (d, $J_{1A,2A}$ = 8.1 Hz, 1H, $H1^A$), 4.87 (d, $J_{1C,2C}$ = 4.7 Hz, 1H, $H1^C$), 4.77 (dd, J = 8.9, 7.0 Hz, 1H, $H2^B$), 4.48–4.44 (m, 2H, $H1^B$, $H5^C$), 4.22 (dd, $J_{5Aeq,5Aax}$ = 12.0 Hz, $J_{5Aeq,4A}$ = 4.7 Hz, 1H, $H5^A{}_{eq}$), 3.95 (dd, $J_{5Beq,5Bax}$ = 12.0 Hz, $J_{5Beq,4B}$ = 5.0 Hz, 1H, $H5^B{}_{eq}$), 3.86–3.76 (m, 2H, $H4^A$, $H4^B$), 3.73 (dd, $J_{5C',5C}$ = 12.4 Hz, $J_{5C',4C}$ = 6.2 Hz, 1H, $H5'^C$), 3.50 (dd, $J_{5Aax,5Aeq}$ = 12.0 Hz, $J_{5ax,4A}$ = 8.6 Hz, 1H, $H5^A{}_{ax}$), 3.27 (dd, $J_{5Bax,5Beq}$ = 12.0 Hz, $J_{5Bax,4B}$ = 9.1 Hz, 1H, $H5^B{}_{ax}$), 2.75–2.69 (m, 4H), 2.62–2.36 (m, 8H), 2.17 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 206.5, 206.4, 206.1, 172.0, 171.5, 171.3, 165.7, 165.4, 165.3, 165.2, 133.5, 133.5, 133.5, 133.4, 132.8, 132.7 (×2), 130.1 (×2), 130.1 (×2), 130.0 (×2), 129.9 (×2), 129.5, 129.4, 129.2, 129.1, 129.1 (×2), 128.6 (×4), 128.1, 100.8 ($C1^B$),

99.3 ($C1^C$), 86.5 ($C1^A$), 75.0 ($C4^A$), 74.7 ($C4^B$), 72.7 ($C3^A$), 72.2 ($C3^B$), 71.4 ($C2^B$), 70.4 ($C2^A$), 70.2 ($C2^C$), 69.7 ($C3^C$), 68.8 ($C4^C$), 65.8 ($C5^A$), 62.9 ($C5^B$), 61.1 ($C5^C$), 37.9, 37.8, 37.8, 29.9, 29.8, 29.8, 28.1, 28.0, 27.9. HRMS: *m*/*z* calcd for $C_{64}H_{64}O_{22}SNa$ $[M + Na]^+$ 1239.3502, found 1239.3483.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-levulinoyl-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-3-O-levulinoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**26**).* General procedure B with crushed mol sieves (1.2 g), donor **25** (0.414 g, 0.34 mmol), AgOTf (0.175 g, 0.68 mmol), *p*NO_2PhSCl (0.064 g, 0.34 mmol) and acceptor **6** (0.139 g, 0.31 mmol). Reaction time 65 min then Et_3N (0.14 mL, 1.02 mmol). Purification by flash column chromatography (hexane/toluene/acetone 3:2:1) gave **26** as a white amorphous solid (0.358 g, 75%). In addition, donor **25** was reisolated (0.064 g, 15%). R_f 0.32 (hexane/EtOAc 1:1). $[\alpha]^{25}_D$ –35.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.92 (m, 12H), 7.58–7.50 (m, 6H), 7.45–7.31 (m, 14H), 7.28–7.24 (m, 3H), 5.69 (t, J = 6.6 Hz, 1H, $H3^D$), 5.60 (t, J = 8.0 Hz, 1H, $H3^A$), 5.32–5.26 (m, 2H, $H2^A$, $H4^D$), 5.21 (dd, $J_{2D,3D}$ = 6.5 Hz, $J_{1D,2D}$ = 4.8 Hz, 1H, $H2^D$), 5.13–5.07 (m, 2H, $H3^B$, $H3^C$), 4.98–4.95 (m, 2H, $H1^A$, $H2^B$), 4.84 (d, $J_{1D,2D}$ = 4.7 Hz, 1H, $H1^D$), 4.73–4.68 (m, 2H, $H1^B$, $H2^C$), 4.46 (dd, $J_{5Deq,5Dax}$ = 12.4 Hz, $J_{5Deq,4D}$ = 3.9 Hz, 1H, $H5^D{}_{eq}$), 4.21–4.15 (m, 2H, $H5^A$, $H1^C$), 4.02–3.96 (m, 1H, $H4^A$), 3.88 (dd, $J_{5C,5'C}$ = 11.9 Hz, $J_{5C,4C}$ = 5.1 Hz, 1H, $H5^C$), 3.83–3.77 (m, 1H, $H4^C$), 3.72 (dd, $J_{5Dax,5Dax}$ = 12.4 Hz, $J_{5Dax,4D}$ = 6.2 Hz, 1H, $H5^D{}_{ax}$), 3.56 (dd, $J_{5Beq,5Bax}$ = 11.9 Hz, $J_{5Beq,4B}$ = 4.6 Hz, 1H, $H5^B{}_{eq}$), 3.52–3.44 (m, 2H, $H5'^A$, $H4^B$), 3.20–3.14 (m, 2H, $H5'^C$, $H5^B{}_{ax}$), 2.73–2.69 (m, 4H), 2.60–2.31 (m, 8H), 2.17 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.4, 206.3, 206.1, 172.0, 171.6, 171.3, 165.6, 165.4, 165.4, 165.3, 165.1, 165.1, 133.6, 133.5, 133.5, 133.4, 133.4, 133.3,

132.8, 132.6 (×2), 130.1 (×2), 130.0 (×2), 130.0 (×2), 129.9 (×2), 129.9 (×2), 129.9 (×2), 129.6, 129.5, 129.4, 129.4, 129.2, 129.1, 129.1 (×2), 128.6 (×2), 128.6 (×4), 128.5 (×2), 128.1, 100.5 ($C1^C$, J_{C-H} = 161 Hz), 100.3 ($C1^B$, J_{C-H} = 164 Hz), 99.3 ($C1^D$, J_{C-H} = 165 Hz), 86.7 ($C1^A$, J_{C-H} = 159 Hz), 75.0 ($C4^A$), 74.7 ($C4^C$), 74.5 ($C4^B$), 73.0 ($C3^A$), 72.2 ($C3^C$), 71.4 ($C3^B$), 71.2 ($C2^C$), 71.0 ($C2^B$), 70.4, 70.2 ($C2^D$, $C4^D$), 69.7 ($C3^D$), 68.8 ($C2^A$), 65.8 ($C5^A$), 62.9 ($C5^C$), 62.0 ($C5^B$), 61.1 ($C5^D$), 37.8, 37.8 (×2), 29.9, 29.8, 29.8, 28.0, 27.9, 27.8. HRMS: *m*/*z* calcd for $C_{83}H_{80}O_{28}SNa$ $[M + Na]^+$ 1579.4449, found 1579.4425.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**27**).* General procedure C with tetrasaccharide **26** (0.252 g, 0.16 mmol) and 50% solution of hydrazine hydrate (0.10 mL, 1.59 mmol). Reaction time 10 min. Eluent for TLC (hexane/toluene/acetone 2:1:1). The product was a white powder (0.202 g, 99%). R_f 0.64 (hexane/acetone 1:1). $[\alpha]^{25}_D$ –9.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.91 (m, 12H), 7.59–7.33 (m, 20H), 7.28–7.25 (m, 3H), 5.80 (t, *J* = 8.5 Hz, 1H, $H3^D$), 5.58 (t, $J_{2A,3A}$ = 7.7 Hz, 1H, $H3^A$), 5.40–5.34 (m, 2H, $H2^D$, $H4^D$), 5.31 (t, *J* = 7.8 Hz, 1H, $H2^A$), 4.99 (d, $J_{1A,2A}$ = 7.8 Hz, 1H, $H1^A$), 4.92 (dd, $J_{2B,3B}$ = 8.6 Hz, $J_{1B,2B}$ = 7.0 Hz, 1H, $H2^B$), 4.79 (d, $J_{1D,2D}$ = 6.6 Hz, 1H, $H1^D$), 4.63 (d, $J_{1B,2B}$ = 6.9 Hz, 1H, $H1^B$), 4.50 (dd, $J_{5Deq,5Dax}$ = 11.9 Hz, $J_{5Deq,4D}$ = 4.9 Hz, 1H, $H5^D{}_{eq}$), 4.18 (dd, $J_{5Aeq,5Aax}$ = 12.1 Hz, $J_{5Aeq,4A}$ = 4.6 Hz, 1H, $H5^A{}_{eq}$), 4.14 (d, $J_{1C,2C}$ = 7.4 Hz, 1H, $H1^C$), 4.01–3.95 (m, 1H, $H4^A$), 3.75–3.42 (m, 9H, $H5^A{}_{ax}$, $H3^B$, $H4^B$, $H5^B$, $H3^C$, $H4^C$, $H5^C$, $H5^D{}_{ax}$), 3.37–3.33 (m, 1H, $H2^C$), 3.15–3.09 (m, 2H, $H5'^B$, $H5'^C$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.7, 165.6, 165.6, 165.5, 165.3, 165.2, 133.7, 133.6, 133.5, 133.4, 133.3, 133.3, 132.9, 132.5 (×2), 130.0 (×2), 130.0 (×2), 129.9 (×2), 129.9 (×3), 129.8 (×2), 129.6, 129.6, 129.4, 129.1 (×2), 129.0, 129.0, 128.9, 128.7 (×2), 128.6

(×3), 128.5 (×2), 128.5 (×3), 128.1, 102.5 ($C1^C$), 101.4 ($C1^B$), 101.0 ($C1^D$), 86.6 ($C1^A$), 78.8 ($C4^C$), 77.4 ($C4^B$), 75.7 ($C4^A$), 74.0 ($C3^C$), 73.7 ($C2^B$), 72.8 , 72.7 ($C3^A$, $C3^B$), 72.1 ($C2^C$), 71.1, 70.9 ($C2^D$, $C3^D$), 70.3 ($C2^A$), 69.3 ($C4^D$), 65.7 ($C5^A$), 63.1 ($C5^B$/$C5^C$), 63.0 ($C5^B$/$C5^C$), 62.5 ($C5^D$). HRMS: *m*/*z* calcd for $C_{68}H_{62}O_{22}SNa$ $[M + Na]^+$ 1285.3345, found 1285.3335.

*Phenyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→2)]-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-1-thio-β-D-xylopyranoside (**28**).* General procedure D with acceptor **27** (0.088 g, 0.069 mmol), donor **4** (0.175 g, 0.28 mmol) and TMSOTf in dry CH_2Cl_2 (0.17 mL, *c* = 0.04 mmol/mL). Reaction time 105 min then Et_3N (0.02 mL, 0.14 mmol). Purification by flash column chromatography (hexane/toluene/acetone 3:3:1) gave **28** as a white amorphous solid (0.168 g, 91%). R_f 0.26 (hexane/toluene/acetone 3:3:1). $[\alpha]^{25}_D$ –58.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 2H), 8.12–8.07 (m, 6H), 8.03–7.93 (m, 14H), 7.86–7.79 (m, 8H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.62–7.10 (m, 46H), 7.03 (t, *J* = 7.8 Hz, 1H), 5.69 (s, 1H, $H1^F$), 5.63 (t, *J* = 9.6 Hz, 1H, $H4^D$), 5.58 (s, 1H, $H1^G$), 5.53 (s, 1H), 5.51 (d, *J* = 4.4 Hz, 1H), 5.40–5.39 (m, 3H, $H3^A$), 5.37–5.34 (m, 2H), 5.21–5.16 (m, 4H, $H2^A$, $H2^D$, $H1^E$), 5.13–5.03 (m, 3H, $H2^B$, $H4^D$), 5.00–4.93 (m, 2H), 4.86–4.74 (m, 7H, $H1^A$), 4.31 (d, $J_{B1,B2}$ = 6.6 Hz, 1H, $H1^B$), 4.02–3.96 (m, 2H, $H5^A$, $H1^D$), 3.90 (t, *J* = 8.7 Hz, 1H, $H3^B$), 3.83–3.78 (m, 2H, $H1^C$, $H3^C$), 3.58–3.52 (m, 2H, $H4^B$, $H2^C$), 3.45 (td, *J* = 9.5, 5.0 Hz, 1H, $H4^C$), 3.41–3.35 (m, 2H, $H4^A$, $H5^D$), 3.32–3.24 (m, 2H, $H5'^A$, $H5^B_{eq}$), 3.09–3.00 (m, 2H, $H5^C$, $H5'^D$), 2.92 (dd, $J_{5Bax,5Beq}$ = 12.2 Hz, $J_{5Bax,4B}$ = 7.5 Hz, 1H, $H5^B_{ax}$), 2.45 (t, *J* = 10.8 Hz, 1H, $H5'^C$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.6 (×2), 166.4, 166.3, 165.9, 165.8, 165.8,

165.6, 165.5, 165.3, 165.2, 164.9, 164.9, 164.9, 164.4, 134.1, 134.0, 133.5, 133.4, 133.4, 133.3, 133.3, 133.1, 133.0, 132.9, 132.8, 132.1, 130.3, 130.2, 130.1, 130.1, 130.0, 130.0, 130.0, 129.9, 129.9, 129.9, 129.8, 129.8, 129.7, 129.7, 129.6, 129.5, 129.3, 129.3, 129.2, 129.1, 129.0, 129.0, 129.0, 128.9, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.2, 106.1 ($C1^{G}$), 105.7 ($C1^{F}$), 105.4 ($C1^{E}$), 100.1 ($C1^{B}$), 99.8 ($C1^{D}$), 99.6 ($C1^{C}$), 86.2 ($C1^{A}$), 82.0, 81.9, 81.9 (×2), 81.7, 81.6, 78.9, 78.7, 78.4, 77.4 ($C2^{C}$), 76 ($C3^{C}$), 75.5 ($C3^{B}$), 74.7 ($C4^{C}$), 73.6, 73.3, 73.1 (×2), ($C3^{A}$, $C4^{A}$, $C2^{B}$, $C4^{B}$), 72.4 ($C3^{D}$), 71.1, 70.3 ($C2^{A}$, $C2^{D}$), 69.8 ($C4^{D}$), 66.1 ($C5^{A}$), 64.4, 64.1, 64.1 ($C5^{E}$, $C5^{F}$, $C5^{G}$), 63.1, 62.8 ($C5^{C}$, $C5^{D}$), 62.0 ($C5^{B}$). HRMS: *m*/*z* calcd for $C_{146}H_{122}O_{43}SNa$ $[M + Na]^+$ 2617.6973, found 2617.6916.

*2,3,4-Tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-2-O-benzoyl-D-xylopyranose (**29**).* General procedure E with thioglycoside **19** (0.081 g, 0.031 mmol), NBS (0.030 g, 0.17 mmol), additional NBS added after 2 h and 15 min (0.026 g, 0.15 mmol). Reaction time 3 h. Purification by flash column chromatography (heptane/acetone 3:2) gave **29** as a white amorphous solid (0.072 g, α/β ratio ~1:0.3, 92%). R_f 0.42 (heptane/EtOAc 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18–7.80 (m, 39H), 7.64–7.19 (m, 58.5H), 5.78 (t, J = 8.9 Hz, 0.2H) 5.71 (t, J = 9.3 Hz, 1H, $H3^{D}$), 5.53–5.49 (m, 4H, $H1^{E}$/$H1^{F}$), 5.46–5.42 (m, 2H), 5.39–5.35 (m, 4H, $H1^{A}$), 5.30–5.28 (m, 2H, $H2^{D}$, $H1^{G}$), 5.26 (s, 1H, $H1^{E}$/$H1^{F}$), 5.16 (td, J = 9.3, 5.5 Hz, 1H, $H4^{D}$), 5.09–4.84 (m, 15H, $H2^{A}$, $H2^{B}$, $H2^{C}$), 4.48 (d, J = 7.8 Hz, 0.3H, $H1^{A}{}_{\beta}$), 4.36 (t, J = 9.3 Hz, 1H, $H3^{A}$), 4.25 (dd, J = 8.0, 3.7 Hz, 1H, $H1^{B}$), 4.11–4.05 (m, 2H, $H1^{D}$), 3.91–3.81 (m, 4H, $H3^{B}$, $H3^{C}$, $H5^{D}$), 3.76 (td, J = 9.5, 5.0 Hz, 1H, $H4^{A}$), 3.58–3.46 (m, 4H,

H5^{A}, H5'^{A}, H1^{C}, H4^{C}), 3.37–3.29 (m, 2H, H4^{B}, H5^{C}), 3.24–3.19 (m, 1H, H5'^{D}), 3.12 (dd, J = 11.9, 5.6 Hz, 1H, H5^{B}), 2.99–2.94 (m, 0.3H), 2.66–2.59 (m, 2H, H5'^{B}, H5'^{C}). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.0, 166.4, 166.4, 166.4, 166.1, 165.9, 165.8, 165.8, 165.8, 165.6, 165.2, 165.1, 165.1, 165.0, 164.8, 164.5, 164.4, 164.2, 133.9, 133.9, 133.7, 133.7, 133.5, 133.4, 133.4, 133.3, 133.2, 133.2, 133.2, 133.0, 133.0, 132.9, 130.4, 130.4, 130.2, 130.2, 130.1, 130.1, 130.0, 129.9, 129.9, 129.8, 129.8, 129.8, 129.7, 129.6, 129.5, 129.5, 129.5, 129.3, 129.2, 129.2, 129.1, 129.1, 129.0, 129.0, 129.0, 128.9, 128.9, 128.9, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 106.1 (C1^{G}), 105.7, 105.6 (C1^{E}, C1^{F}), 100.4 (C_β), 100.3 (C1^{B}), 100.0 (C1^{C}), 100.0 (C_β), 99.9 (C1^{D}), 96.4 (C_β), 90.5 (C1^{A}), 82.8, 82.7, 82.7, 81.8 (C_β), 81.7, 81.5, 80.8, 78.3, 78.3, 78.2, 78.1 (C_β), 76.3 (C_β), 75.4 (C_β), 75.3, 73.3 (C3^{B}, C3^{C}), 74.7 (C_β), 74.5, 74.3, 74.3 (C4^{A}, C4^{B}, C4^{C}), 74.2 (C_β), 74.2 (C_β), 74.1 (C_β), 73.4 (C2^{B}), 73.0 (C2^{C}), 72.1, 72.0 (C2^{A}, C3^{D}), 71.2 (C2^{D}), 69.8 (C4^{D}), 64.0, 63.9, 63.9, 63.8 (C5^{E}, C5^{F}, C5^{G}), 63.3 (C_β), 63.1, 63.0, 63.0 (C5^{B}, C5^{C}, C5^{D}), 59.3 (C5^{A}). HRMS: *m*/*z* calcd for $C_{140}H_{118}O_{44}SNa$ $[M + Na]^+$ 2525.6888, found 2525.6876.

*2,3,4-Tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→2)]-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-α-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-D-xylopyranose (**30**).* General procedure E with thioglycoside **23** (0.200 g, 0.077 mmol), acetone/H_2O 9:1 (1.23 mL), NBS (0.055 g, 0.31 mmol), additional NBS added after 30 min (0.030 g, 0.17 mmol). Reaction time 60 min. Eluent for TLC and flash column chromatography (heptane/acetone 3:2). Product was isolated as a white amorphous solid (0.181 g, α/β ratio ~1:0.35, 93%). R_f 0.45 (heptane/EtOAc 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.19–8.18 (m, 2H), 8.10–7.80 (m, 27H), 7.78–7.74 (m, 1H), 7.69–7.64 (m, 2H), 7.59–7.20 (m, 39H), 7.18–7.07 (m, 4H), 5.86–5.82 (m, 1H, $H3^{A}$), 5.79–5.78 (m, 1H, $H1^{F}$), 5.69 (t, J = 9.2 Hz, 1H, $H3^{D}$), 5.63–5.61 (m, 1H, $H1^{E}$), 5.55–5.50 (m, 6H), 5.36–5.35 (m, 2H, $H1^{A}$), 5.26 (s, 1H, $H1^{G}$), 5.23 (dd, $J_{2D,3D}$ = 9.3 Hz, $J_{1D,2D}$ = 7.4 Hz, 1H, $H2^{D}$), 5.17 (td, $J_{3D,4D}$ = 9.2 Hz, $J_{4D,5D}$ = 5.5 Hz, 1H, $H4^{D}$), 5.12–5.07 (m, 2H), 5.05–4.81 (m, 7H, $H2^{A}$, $H2^{C}$), 4.76–4.64 (m, 2H), 4.57 (d, J = 7.3 Hz, 0.33H, $H1^{A}{}_{\beta}$), 4.31 (t, $J_{1B,2B}$ = 7.5 Hz, 1H, $H1^{B}$), 4.14 (d, $J_{1D,2D}$ = 7.3 Hz, 1H, $H1^{D}$), 4.00 (dd, J = 11.9, 5.3 Hz, 0.40H), 3.93–3.82 (m, 6H, $H4^{A}$, $H5^{A}$, $H3^{B}$, $H1^{C}$, $H3^{C}$, $H5^{D}$), 3.74–3.69 (m, 1H, $H5'^{A}$), 3.66 (dd, $J_{2B,3B}$ = 9.6 Hz, $J_{1B,2B}$ = 6.9 Hz, 1H, $H2^{B}$), 3.54–3.38 (m, 3H, $H4^{A}$, $H4^{C}$), 3.36–3.24 (m, 2H, $H5^{B}$, $H5'^{D}$), 3.07–3.00 (m, 1H, $H5^{C}$), 2.74–2.63 (m, 1H, $H5'^{B}$), 2.53 (t, J = 11.1 Hz, 1H, $H5'^{C}$). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 166.9, 166.7, 166.5, 166.4, 166.1, 165.9, 165.9, 165.8, 165.8, 165.7, 165.7, 165.6, 165.6, 165.4, 165.4, 165.4, 165.1, 165.0, 164.6, 164.2, 133.7, 133.6, 133.6, 133.5, 133.4, 133.4, 133.3, 133.2, 133.1, 133.0, 132.9, 132.8, 130.3, 130.2, 130.2, 130.1, 130.0, 130.0, 129.9, 129.9, 129.9, 129.8, 129.8, 129.8, 129.6, 129.6, 129.3, 129.2, 129.2, 129.2, 129.1, 129.1, 129.1, 129.0, 128.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 107.2 (C_{β}), 107.1 ($C1^{E}$), 106.2 ($C1^{G}$), 105.5 ($C1^{F}$), 101.3 (C_{β}), 100.9 ($C1^{B}$), 99.8 ($C1^{D}$), 99.6 ($C1^{C}$), 96.0 (C_{β}), 90.5 ($C1^{A}$), 82.7, 82.5 (C_{β}), 82.3 (C_{β}), 82.3, 82.0, 81.9, 81.8, 81.8 (C_{β}), 81.7 (C_{β}), 80.8, 80.3 (C_{β}) 80.0 ($C2^{B}$), 78.6, 78.2, 77.9, 77.8 (C_{β}), 76.0 ($C3^{B}$/$C3^{C}$), 75.9 (C_{β}), 75.7 ($C3^{B}$/$C3^{C}$), 74.6 ($C4^{C}$), 74.2, 74.0 ($C4^{A}$/$C4^{B}$), 74.0, 73.8 ($C4^{A}$/$C4^{B}$), 73.2 ($C2^{C}$), 72.4, 72.0 (2C, $C2^{A}$, $C3^{D}$), 71.2 ($C2^{D}$), 70.4 ($C3^{A}$), 69.7 ($C4^{D}$), 64.4 (C_{β}), 64.3, 64.1, 63.9 ($C5^{E}$, $C5^{F}$, $C5^{G}$), 63.1 (C_{β}), 63.0 ($C5^{C}$), 62.9 ($C5^{D}$), 62.4 ($C5^{B}$), 59.4 ($C5^{A}$). HRMS: *m*/*z* calcd for $C_{140}H_{118}O_{44}S(Na^{+})_2$ $[M + 2Na]^{2+}$ 1274.3390, found 1274.3381.

*2,3,4-Tri-O-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→2)]-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-[2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl-(1→3)]-2-O-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-O-benzoyl-D-xylopyranose (**31**).* General procedure E with thioglycoside **28** (0.190 g, 0.073 mmol), acetone/H_2O 9:1 (1.1 mL), NBS (0.057 g, 0.32 mmol), additional NBS added after 30 min (0.033 g, 0.19 mmol). Reaction time 60 min. Eluent for TLC and flash column chromatography (heptane/acetone 3:2). Product was isolated as a white amorphous solid (0.169 g, α/β ratio ~1:0.3, 92%). R_f 0.24 (heptane/EtOAc 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.1 Hz, 2H), 8.13–8.03 (m, 8H), 7.99–7.94 (m, 8H), 7.86–7.80 (m, 7H), 7.75–7.72 (m, 2H), 7.69 (d, J = 7.4 Hz, 2H), 7.65–7.59 (m, 5H), 7.56–7.25 (m, 31H), 7.20–7.11 (m, 8H), 7.08–7.03 (m, 2H), 5.79 (t, J = 9.5 Hz, 1H, H3^A), 5.71 (s, 1H, H1^G), 5.64 (t, J = 9.6 Hz, 1H, H3^D), 5.58 (d, J = 2.7 Hz, 1H, H1^F), 5.54 (s, 1H), 5.53–5.49 (m, 2H, H1^A), 5.45–5.41 (m, 2H), 5.37 (t, J = 4.8 Hz, 2H), 5.29 (s, 0.2H), 5.21–5.19 (m, 3H, H2^D, H1^E), 5.16–4.94 (m, 6H, H2^A, H2^B, H4^D), 4.87–4.83 (m, 3H), 4.81–4.75 (m, 2H), 4.71 (d, J = 7.7 Hz, 1H, H1$^A{}_\beta$), 4.38 (d, $J_{1B,2B}$ = 6.5 Hz, 1H, H1^B), 4.35 (d, J = 6.6 Hz, 0.3H), 3.98–3.92 (m, 2H, H3^B, H1^D), 3.84–3.79 (m, 2H, H1^C, H3^C), 3.76 (t, J = 11.0 Hz, 1H, H5^A), 3.62–3.30 (m, 7H, H4^A, H5'^{A}, H4^B, H5^B, H2^C, H4^C, H5^D), 3.23 (t, J = 11.2 Hz, 0.4H), 3.10–2.96 (m, 3H, H5'^{B}, H5^C, H5'^{D}), 2.49–2.44 (m, 1H, H5'^{C}). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.1, 166.6 (×2), 166.4, 166.3, 166.0, 165.9, 165.8, 165.8, 165.8, 165.8, 165.6, 165.5, 165.5, 165.4, 165.4, 165.0, 165.0, 164.9, 164.9, 164.9, 164.4, 164.4, 134.0, 133.5, 133.5, 133.5, 133.4, 133.4, 133.3, 133.3, 133.1, 133.0, 132.9, 132.9, 132.9, 130.3, 130.2, 130.1, 130.1, 130.0, 129.9, 129.9, 129.9, 129.8, 129.8, 129.7, 129.7, 129.6, 129.4, 129.3, 129.2, 129.1, 129.0, 129.0, 128.9, 128.9, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 106.1 (C1^F), 105.7 (C1^G), 105.4 (C1^E), 105.3 (C_β), 100.2 (C_β), 100.1 (C1^B), 99.8 (C1^D), 99.6 (C1^C), 96.3

(C_β), 90.5 ($C1^A$), 82.0, 82.0, 81.9, 81.8, 81.8 (C_β), 81.7, 81.5, 79.0, 78.6, 78.3, 77.4 ($C2^C$), 76.7 ($C3^C$), 75.4 ($C3^B$), 74.7, 74.5 ($C4^A$, $C4^C$), 74.3 (C_β), 74.2 (C_β), 73.1, 73.1 ($C2^B$, $C4^B$), 72.4, 72.3 ($C2^A$, $C3^D$), 71.1 ($C2^B$), 70.1 ($C3^C$), 69.7 ($C4^D$), 64.3, 64.1, 64.1 ($C5^E$, $C5^F$, $C5^G$), 63.5 (C_β), 63.0, 62.8 ($C5^C$, $C5^D$), 62.0 ($C5^B$), 59.3 ($C5^A$). HRMS: *m*/*z* calcd for $C_{140}H_{118}O_{44}S(Na^+)_2$ [M + 2Na]$^{2+}$ 1274.3390, found 1274.3378.

*Phenyl β-D-xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→3)]-1-thio-β-D-xylopyranoside (**32**).* General procedure F with heptasaccharide **19** (0.028 g, 0.011 mmol). The product was obtained as a white powder (0.009 g, 77%). R_f 0.63 (EtOAc/MeOH/H_2O/AcOH 6:3:0.8:0.2). $[\alpha]^{25}_D$ –30 (*c* 0.23, H_2O). ^{1}H NMR (800 MHz, D_2O) δ 7.60–7.57 (m, 2H), 7.47–7.43 (m, 3H), 5.43 (s, 1H, $H1^{arabinose}$), 5.41 (s, 1H, $H1^{arabinose}$), 5.40 (s, 1H, $H1^{arabinose}$), 4.82 (d, *J* = 9.6 Hz, 1H, $H1^A$), 4.49–4.48 (m, 2H, $H1^B$, $H1^C$), 4.45 (d, *J* = 7.8 Hz, 1H, $H1^D$), 4.30–4.27 (m, 3H, $H4^{arabinose}$), 4.19–4.17 (m, 4H, $H5^A$, $H2^{arabinose}$), 4.10–4.06 (m, 2H, $H5^B$, $H5^C$), 3.93–3.91 (m, 4H, $H5^D$, $H3^{arabinose}$), 3.82–3.79 (m, 7H, $H3^A$, $H4^A$, $H4^B$, $H4^C$, $H5^{arabinose}$), 3.76–3.72 (m, 5H, $H3^B$, $H3^C$, $H5'^{arabinose}$), 3.61 (td, *J* = 9.9, 5.5 Hz, 1H, $H4^D$), 3.53 (t, *J* = 8.8 Hz, 1H, $H2^A$), 3.46–3.41 (m, 4H, $H5'^A$, $H2^B$, $H2^C$, $H3^D$), 3.37 (t, *J* = 11.1 Hz, 2H, $H5'^B$, $H5'^C$), 3.28 (t, *J* = 11.1 Hz, 1H, $H5'^D$), 3.26–3.24 (m, 1H, $H2^D$). $^{13}C\{^1H\}$ NMR (201 MHz, D_2O) δ 132.4 (×2), 131.2, 129.4 (×2), 128.4, 107.7, 107.6, 107.6 ($C1^{arabinose}$), 101.4 ($C1^D$), 101.2, 101.2 ($C1^B$, $C1^C$), 87.8 ($C1^A$), 84.8, 84.7, 84.7 ($C4^{arabinose}$), 80.7, 80.7, 80.7 ($C2^{arabinose}$), 78.7 ($C3^A$), 77.3, 77.2, 77.2, 77.2 ($C3^B$, $C3^C$, $C3^{arabinose}$), 75.6 ($C3^D$), 73.6, 73.6, 73.5, 73.5, 73.5 ($C4^A$, $C2^B$, $C4^B$, $C2^C$, $C4^C$), 72.9 ($C2^D$), 71.9 ($C2^A$), 69.2 ($C4^D$), 66.3 ($C5^A$), 65.1 ($C5^D$), 62.7, 62.7

(C5^{B}, C5^{C}), 61.3 (C5^{arabinose}). HRMS: *m*/*z* calcd for $C_{41}H_{63}O_{28}S$ $[M + H]^+$ 1035.3221, found 1035.3214.

*Phenyl β-D-xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→2)]-[α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-1-thio-β-D-xylopyranoside (**33**).* General procedure F with heptasaccharide **23** (0.071 g, 0.027 mmol). The product was obtained as a white powder (0.023 g, 82%). R_f 0.53 (EtOAc/MeOH/H_2O/AcOH 6:3:0.8:0.2). $[\alpha]^{25}_D$ –36 (*c* 0.21, H_2O). ^{1}H NMR (800 MHz, D_2O) δ 7.59–7.58 (m, 2H), 7.46–7.42 (m, 3H), 5.42 (s, 1H, H1^{G}), 5.28 (s, 1H, H1^{F}), 5.23 (s, 1H, H1^{E}), 4.77 (d, *J* = 9.5 Hz, 1H, H1^{A}), 4.64 (d, *J* = 7.2 Hz, 1H, H1^{B}), 4.49 (d, *J* = 7.9 Hz, 1H, H1^{C}), 4.45 (d, *J* = 7.8 Hz, 1H, H1^{D}), 4.32 (q, *J* = 5.4 Hz, 1H, H4^{F}), 4.29 (q, *J* = 5.2 Hz, 1H, H4^{G}), 4.19–4.14 (m, 5H, H5^{A}, H5^{B}, H2^{E}, H2^{F}, H2^{G}), 4.12 (td, *J* = 5.8, 3.5 Hz, 1H, H4^{E}), 4.09 (dd, *J* = 11.8, 5.2 Hz, 1H, H5^{C}), 3.96–3.95 (m, 2H, H3^{E}, H3^{F}), 3.94–3.91 (m, 2H, H5^{D}, H3^{G}), 3.89 (td, *J* = 9.0, 5.1 Hz, 1H, H4^{B}), 3.84–3.77 (m, 6H, H4^{A}, H3^{B}, H4^{C}, H5^{E}, H5^{F}, H5^{G}), 3.77–3.70 (m, 4H, H3^{C}, H5'^{E}, H5'^{F}, H5'^{G}), 3.63–3.59 (m, 2H, H3^{A}, H4^{D}), 3.59–3.57 (m, 1H, H2^{B}), 3.47–3.36 (m, 6H, H2^{A}, H5'^{A}, H5'^{B}, H2^{C}, H5'^{C}, H3^{D}), 3.29 (t, *J* = 11.4 Hz, 1H, H5'^{D}), 3.26 (dd, *J* = 9.2, 8.0 Hz, 1H, H2^{D}). ^{13}C{^{1}H} NMR (201 MHz, D_2O) δ 132.1 (×2), 131.4, 129.4 (×2), 128.3, 108.7 (C1^{E}), 108.1 (C1^{F}), 107.6 (C1^{G}), 101.4 (C1^{D}), 101.2 (C1^{C}), 99.8 (C1^{B}), 88.0 (C1^{A}), 84.8 (C4^{G}), 84.4 (C4^{E}), 84.2 (C4^{F}), 81.2, 81.0, 80.7 (C2^{E}, C2^{F}, C2^{G}), 78.6 (C2^{B}), 77.6 (C3^{B}), 77.2, 77.2, 77.2 (C3^{C}, C3^{F}, C3^{G}), 76.6 (C3^{E}), 75.6 (C3^{D}), 75.4 (C4^{A}), 75.2 (C3^{A}), 73.8, 73.7, 73.6 (C4^{B}, C2^{C}, C4^{C}), 72.9 (C2^{D}), 71.6 (C2^{A}), 69.2 (C4^{D}), 66.5 (C5^{A}), 65.1 (C5^{D}), 62.7 (C5^{C}), 62.5 (C5^{B}), 61.3, 61.2, 61.1 (C5^{E}, C5^{F}, C5^{G}). HRMS: *m*/*z* calcd for $C_{41}H_{63}O_{28}S$ $[M + H]^+$ 1035.3221, found 1035.3216.

*Phenyl β-D-xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→2)]-[α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-1-thio-β-D-xylopyranoside (**34**).* General procedure F with heptasaccharide **28** (0.061 g, 0.024 mmol). Product was obtained as a white powder (0.022 g, 91%). R_f 0.53 (EtOAc/MeOH/H_2O/AcOH 6:3:0.8:0.2). $[\alpha]^{25}_D$ –22 (*c* 0.28, H_2O). ^{1}H NMR (800 MHz, D_2O) δ 7.59–7.58 (m, 2H), 7.46–7.43 (m, 3H), 5.43 (s, 1H, H1^E), 5.29 (s, 1H, H1^G), 5.25 (s, 1H, H1^F), 4.79 (d, *J* = 9.2 Hz, 1H, H1^A), 4.61 (d, *J* = 7.5 Hz, 1H, H1^C), 4.50 (d, *J* = 7.7 Hz, 1H, H1^B), 4.44 (d, *J* = 7.8 Hz, 1H, H1^D), 4.34–4.31 (m, 2H, H4^E, H4^G), 4.18–4.13 (m, 6H, H5^A, H5^B, H2^E, H2^F, H4^F, H2^G), 4.10 (dd, *J* = 11.9, 4.4 Hz, 1H, H5^C), 3.99 (dd, *J* = 5.8, 3.1 Hz, 1H, H3^F), 3.95–3.92 (m, 3H, H5^D, H3^E, H3^G), 3.86–3.73 (m, 11H, H4^A, H3^B, H4^B, H3^C, H4^C, H5^E, H5'^{E}, H5^F, H5'^{F}, H5^G, H5'^{G}), 3.63–3.60 (m, 2H, H3^A, H4^D), 3.57 (t, *J* = 7.8 Hz, 1H H2^C), 3.48–3.38 (m, 6H, H2^A, H5'^{A}, H2^B, H5'^{B}, H5'^{C}, H3^D), 3.30–3.25 (m, 2H, H2^D, H5'^{D}). ^{13}C{^{1}H} NMR (201 MHz, D_2O) δ 132.1 (×2), 131.4, 129.4 (×2), 128.4, 108.7 (C1^F), 108.0 (C1^G), 107.5 (C1^E), 101.6 (C1^B), 101.3 (C1^D), 99.8 (C1^C), 87.9 (C1^A), 85.0 (C4^E/C4^G), 84.3 (C4^F), 84.2 (C4^E/C4^G), 81.3 (C2^F), 80.9, 80.6 (C2^E, C2^G), 78.7 (C2^C), 77.7 (C3^C), 77.2, 77.2 (C3^E, C3^G), 77.0 (C3^B), 76.7 (C3^F), 76.1 (C4^A), 75.6 (C3^D), 75.2 (C3^A), 73.6, 73.3 (C4^B, C4^C), 73.3 (C2^B), 73.0 (C2^D), 71.6 (C2^A), 69.2 (C4^D), 66.5 (C5^A), 65.1 (C5^D), 62.8 (C5^B), 62.6 (C5^C), 61.3, 61.1, 61.1 (C5^E, C5^F, C5^G). HRMS: *m*/*z* calcd for $C_{41}H_{63}O_{28}S$ $[M + H]^+$ 1035.3221, found 1035.3218.

*β-D-Xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→3)]-D-xylopyranose (**1**).* General procedure G with partially deprotected heptasaccharide **32** (10.0 mg,

0.097 mmol), 2,6-lutidine (3 μL, 0.015 mmol) and NBS (5.3 mg, 0.030 mmol). Reaction time 1.5 h. The product was obtained as a white powder (8.8 mg, 97%). α/β ratio 0.7:1. R_f 0.45 (EtOAc/MeOH/H_2O/AcOH 6:3:0.8:0.2). ^{1}H NMR (800 MHz, D_2O) δ 5.41–5.41 (m, 4.01H, $H1^F$, $H1^G$), 5.36 (s, 0.73H, $H1^E{}_\alpha$), 5.19 (d, J = 3.5 Hz, 0.70H, $H1^A{}_\alpha$), 4.64 (d, J = 7.9 Hz, 1H, $H1^A{}_\beta$), 4.51–4.49 (m, 3.35H, $H1^B$, $H1^C$), 4.45–4.44 (m, 1.76H, $H1^D$), 4.31–4.28 (m, 4.90H, $H4^E$, $H4^F$, $H4^G$), 4.19–4.17 (m, 4.94H, $H2^E$, $H2^F$, $H2^G$), 4.10–4.07 (m, 4.29H, $H5^A{}_\beta$, $H5^B$, $H5^C$), 3.94–3.91 (m, 7.29H, $H3^A{}_\alpha$, $H5^D$, $H3^E$, $H3^F$, $H3^G$), 3.87–3.78 (m, 12.26H, $H4^A{}_\alpha$, $H4^A{}_\beta$, $H5^A{}_\alpha$, $H5'^A{}_\alpha$, $H4^B$, $H5^E$, $H5^F$, $H5^G$), 3.76–3.72 (m, 9.69H, $H3^A{}_\beta$, $H3^B$, $H3^C$, $H5'^E$, $H5'^F$, $H5'^G$), 3.70 (dd, J = 9.2, 3.6 Hz, 1.06H, $H2^A{}_\alpha$), 3.63–3.59 (m, 2H, $H4^D$), 3.47–3.36 (m, 10.88H, $H2^A{}_\beta$, $H5^A{}_\beta$, $H2^B$, $H5'^B$, $H2^C$, $H5'^C$, $H3^D$), 3.30–3.24 (m, 3.99H, $H2^D$, $H5'^D$). ^{13}C{^{1}H} NMR (201 MHz, D_2O) δ 107.8, 107.7, 107.7, 107.6 ($C1^E$, $C1^F$, $C1^G$), 101.4, 101.3, 101.3, 101.2 ($C1^B$, $C1^C$, $C1^D$), 96.4 ($C1^A{}_\beta$), 92.2 ($C1^A{}_\alpha$), 84.8, 84.7, 84.7, 84.6 ($C4^E$, $C4^F$, $C4^G$), 80.7, 80.7, 80.7 ($C2^E$, $C2^F$, $C2^G$), 77.7 ($C3^A{}_\beta$), 77.3, 77.3, 77.2, 77.2 ($C3^B$, $C3^C$, $C3^E$, $C3^F$, $C3^G$), 75.6 ($C3^D$), 75.2 ($C3^A{}_\alpha$), 74.5 ($C2^A{}_\beta$), 73.8, 73.7, 73.6, 73.6, 73.6, 73.5, 73.5 ($C4^A{}_\alpha$, $C4^A{}_\beta$, $C2^B$, $C4^B$, $C2^C$, $C4^C$), 72.9 ($C2^D$), 71.7 ($C2^A{}_\alpha$), 69.2 ($C4^D$), 65.1 ($C5^D$), 62.8, 62.7, 62.7, 62.7 ($C5^A{}_\beta$, $C5^B$, $C5^C$), 61.3 ($C5^E$, $C5^F$, $C5^G$), 59.1 ($C5^A{}_\alpha$). HRMS: *m*/*z* calcd for $C_{35}H_{58}O_{29}Na$ $[M + Na]^+$ 965.2956, found 965.2962.

*β-D-Xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→2)]-[α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-D-xylopyranose (**2**).* General procedure G with partially deprotected heptasaccharide **33** (13.4 mg, 0.013 mmol), 2,6-lutidine (4 μL, 0.019 mmol) and NBS (6.8 mg, 0.038 mmol). Reaction time 1.5 h. The product was obtained as a white powder (10.2 mg, 84%). α/β ratio 0.5:1. R_f 0.31

(EtOAc/MeOH/H_2O/AcOH 6:3:0.8:0.2). ^{1}H NMR (800 MHz, D_2O) δ 5.43 (s, 1.54H, H1^G), 5.29 (s, 1.40H, H1^F), 5.25 (s, 0.53H, H1 $^E{}_{\alpha/\beta}$), 5.25 (s, 0.86H, H1$^E{}_{\alpha/\beta}$), 5.21 (d, J = 3.6 Hz, 0.53H, H1$_\alpha$), 4.66 (d, J = 7.2 Hz, 1.37H, H1^B), 4.60 (d, J = 7.9 Hz, 1H, H1$^A{}_\beta$), 4.50 (d, J = 7.8 Hz, 1.43H, H1^C), 4.46 (d, J = 7.8 Hz, 1.49H, H1^D), 4.33 (td, J = 5.4, 3.8 Hz, 1.54H, H4^F), 4.30 (q, J = 5.3 Hz, 1.66H, H4^G), 4.19–4.09 (m, 11.09H, H5^A, H5^B, H5^C, H2^E, H4^E, H2^F, H2^G), 4.01–4.00 (m, 0.61H, H4$^A{}_\alpha$), 3.98 (dd, J = 5.8, 3.2 Hz, 1.14H, H3^E), 3.96 (dd, J = 5.5, 2.4 Hz, 1.62H, H3^F), 3.94–3.92 (m, 3.49H, H5^D, H3^G), 3.89 (dd, J = 9.1, 4.9 Hz, 1.58H, H4^B), 3.86–3.73 (m, 19.09H, H3$^A{}_\alpha$, H4$^A{}_\beta$, H5$^A{}_\alpha$, H5'$^A{}_\alpha$, H3^B, H3^C, H4^C, H5^E, H5'^{E}, H5^F*, H5'^{F}, H5^G, H5'^{G}), 3.63–3.57 (m, 4.95H, H2$^A{}_\alpha$, H3$^A{}_\beta$, H2^B, H4^D), 3.47–3.42 (m, 6.09H, H5'$^A{}_\beta$, H5^B, H2^C, H3^D), 3.40–3.37 (m, 1.75H, H5'^{C}), 3.31–3.25 (m, 4.64H, H2$^A{}_\beta$, H2^D, H5'^{D}). ^{13}C{^{1}H} NMR (201 MHz, D_2O) δ 108.7, 108.7 (C1^E), 108.1 (C1^F), 107.6 (C1^G), 101.4 (C1^D), 101.2 (C1^C), 99.9, 99.8 (C1^B), 96.5 (C1$^A{}_\beta$), 92.0 (C1$^A{}_\alpha$), 84.8 (C4^G), 84.4, 84.3 (C4^E), 84.3 (C4^F), 81.2, 81.2 (C2^E), 81.0 (C2^F), 80.7 (C2^G), 78.6, 78.6 (C2^B), 77.6, 77.5 (C3^B), 77.2, 77.2, 77.2 (C3^C, C3^F, C3^G), 76.6 (C3^E), 76.5 (C4$^A{}_\alpha$), 75.9 (C4$^A{}_\beta$), 75.8, 75.6 (C3^D), 74.0, 73.9, 73.8 (C2$^A{}_\beta$, C3$^A{}_\beta$, C4^B), 73.7, 73.6 (C2^C, C4^C), 72.9 (C2^D), 71.4 (C2$^A{}_\alpha$), 71.0 (C3$^A{}_\alpha$), 69.2 (C4^D), 65.1 (C5^D), 62.9, 62.7 (C5$^A{}_\beta$, C5^C), 62.5 (C5^B), 62.5, 61.3, 61.2, 61.1, 61.0 (C5^E, C5^F, C5^G), 58.7 (C5$^A{}_\alpha$). HRMS: *m*/*z* calcd for $C_{35}H_{58}O_{29}Na$ [M + Na]$^+$ 965.2956, found 965.2965.

*β-D-Xylopyranosyl-(1→4)-[α-L-arabinofuranosyl-(1→2)]-[α-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-[-L-arabinofuranosyl-(1→3)]-β-D-xylopyranosyl-(1→4)-D-xylopyranose (**3**).* General procedure G with partially deprotected heptasaccharide **34** (10.6 mg, 0.010 mmol), 2,6-lutidine (3 μL, 0.015 mmol) and NBS (5.5 mg, 0.031 mmol). Reaction time 1.5 h. The

product was obtained as a white powder (8.5 mg, 88%). α/β ratio 0.6:1. R_f 0.33 (EtOAc/MeOH/H_2O/AcOH 6:3:0.8:0.2). ^{1}H NMR (800 MHz, D_2O) δ 5.44–5.44 (m, 1.57H, $H1^E$), 5.30 (s, 1.56H, $H1^G$), 5.25 (s, 1.55H, $H1^F$), 5.21 (d, J = 3.6 Hz, 1H, $H1^A{}_\alpha$), 4.62–4.60 (m, 2.70H, $H1^A{}_\beta$, $H1^C$), 4.52–4.51 (m, 1.58H, $H1^B$), 4.45 (d, J = 7.8 Hz, 1.58H, $H1^D$), 4.34–4.31 (m, 3.29H, $H4^E$, $H4^G$), 4.19–4.18 (m, 3.20H, $H2^E$, $H2^F$), 4.17–4.15 (m, 5.36H, $H5^B$, $H2^F$, $H4^F$), 4.10 (dd, J = 11.9, 4.2 Hz, 1.60H, $H5^C$), 4.07 (dd, J = 11.8, 5.4 Hz, 1.09H, $H5^A{}_\beta$), 4.00 (dd, J = 5.9, 3.1 Hz, 1.57H, $H3^F$), 3.96–3.93 (m, 5.17H, $H5^D$, $H3^E$, $H3^G$), 3.87–3.73 (m, 22.09H, $H3^A{}_\alpha$, $H3^A{}_\beta$, $H4^A{}_\alpha$, $H5^A{}_\alpha$, $H5'^A{}_\alpha$, $H3^B$, $H4^B$, $H3^C$, $H4^C$), 3.63–3.55 (m, 5.31H, $H2^A{}_\alpha$, $H5^A{}_\beta$, $H2^C$, $H4^D$), 3.50–3.45 (m, 3.52H, $H2^B$, $H5'^B$), 3.43 (t, J = 9.3 Hz, 1.94H, $H3^D$), 3.41–3.38 (m, 2.99H, $H3^C$, $H5'^C$), 3.30–3.25 (m, 4.54H, $H2^A{}_\beta$, $H2^D$, $H5'^D$). ^{13}C{^{1}H} NMR (201 MHz, D_2O) δ 108.7 ($C1^F$), 108.0 ($C1^G$), 107.5 ($C1^E$), 101.6 ($C1^B$), 101.3 ($C1^D$), 99.8 ($C1^C$), 96.5 ($C1^A{}_\beta$), 92.0 ($C1^A{}_\alpha$), 85.0 ($C4^E$), 84.3, 84.2 ($C4^F$, $C4^G$), 81.3 ($C2^F$), 80.9 ($C2^G$), 80.5 ($C2^E$), 78.7 ($C2^C$), 77.7 ($C3^C$), 77.3, 77.2 ($C3^E$, $C3^G$), 77.0, 77.0 ($C3^B$), 76.7 ($C3^F$), 76.6 ($C4^A{}_\alpha$), 76.4 ($C4^A{}_\beta$), 75.6 ($C3^D$), 74.0, 73.9 ($C2^A{}_\beta$, $C3^A{}_\beta$), 73.6 ($C4^C$), 73.3 ($C2^B$, $C4^B$), 73.0 ($C2^D$), 71.3 ($C2^A{}_\alpha$), 70.9 ($C3^A{}_\alpha$), 69.2 ($C4^D$), 65.1 ($C5^D$), 62.9, 62.8, 62.8, 62.6 ($C3^C$) ($C5^A{}_\beta$, $C5^B$, $C5^C$), 61.4, 61.1, 61.1 ($C5^E$, $C5^F$, $C5^G$), 58.8 ($C5^A{}_\alpha$). HRMS: m/z calcd for $C_{35}H_{58}O_{29}Na$ $[M + Na]^+$ 965.2956, found 965.2966.

Supporting Information. Copies of ^{1}H and ^{13}C{^{1}H} NMR spectra for the prepared compounds as well as 2D NMR spectra for compounds **1** – **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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