Lewis acid promoted anomerisation of alkyl O- and S-xylo-, arabino- and fucopyranosides

Lewis Acid Promoted Anomerisation of Alkyl *O*- and *S*-Xylo-, Arabino- and Fucopyranosides

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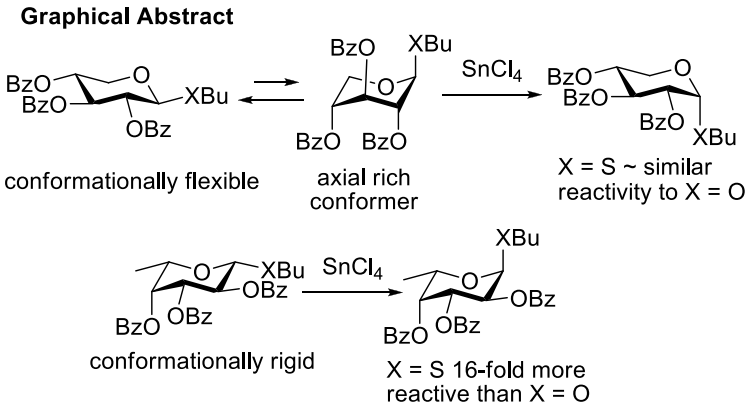
Abstract: Pentopyranoside and 6-deoxyhexopyranosides, such as those from D-xylose, L-arabinose and L-fucose are components of natural products, oligosaccharides or polysaccharides. Lewis acid promoted anomerisation of some of their alkyl *O*- and *S*-glycopyranosides is reported here. $SnCl_4$ was more successful than $TiCl_4$, with the latter giving glycosyl chloride in some cases, and both were reactive than BF_3OEt_2. Kinetic study using ^{1}H-NMR spectroscopy showed an order of reactivity: *O*-xylopyranoside > O-arabinopyranoside > O-fucopyranoside. Benzoylated glycosides were more reactive than acetylated glycosides. The reactivity of *S*-glycosides was greater than that of *O*-glycosides for both arabinose and fucose derivatives; reactivity of *O*- and *S*-xylopyranosides was similar. The highest stereoselectivities were observed for fucopyranosides. The β-D-xylopyranoside and α-L-arabinopyranoside reactants are conformationally more flexible than β-L-fucopyranosides.

Graphical Abstract



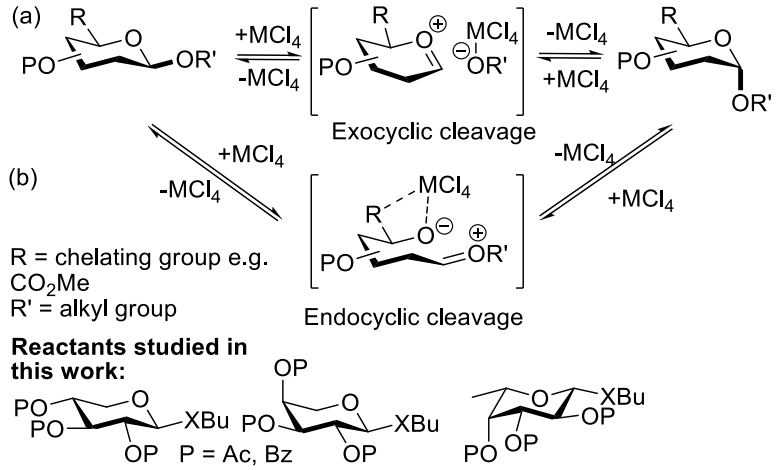
1. Introduction

The chemical reactivity of saccharides is influenced by their substituents.[1] For instance, whether a substituent is axial or equatorial on a pyranoside influences the rate of hydrolysis of the glycosidic linkage, with reactivity increasing if there are more axial OH groups present.[1a] The degree to which substituents are electron withdrawing influences glycosyl donor reactivity. Accordingly, it was established that presence of *O*-acyl substituents reduce reactivity of donors compared to *O*-benzyl substituents.[2] Substituents also influence the kinetics of anomerisation of *O*- and *S*-glycosides promoted by Lewis acids[3] and also influence anomeric preference in these reactions, which are presumed to be at equilibrium.[4]

Lewis acid promoted anomerisation[5] has been used for the stereoselective synthesis of glycosides,[6] but specific strategies are required to achieve success. For instance, the use of both 2,3-trans-carbamate and carbonate based protecting groups on pyranosides,[7] gives rise to a slight distortion in their $^4C_1$ conformations, which leads to an enhancement of the rate of anomerisation via endocyclic cleavage.[8] Alternatively, a CO_2R substituent at C-5, as found in glucuronic and galacturonic acid derivatives, coupled with the use of benzoyl protecting groups at other positions[9] enabled $TiCl_4$ induced anomerisation of the interglycosidic linkage in disaccharides and other linkages.[10,11] It was proposed in the latter case that the C-5 carbonyl group facilitates chelation by Lewis acids such as $TiCl_4$ or $SnCl_4$ and subsequent endocyclic cleavage (Scheme 1).[12] This chelation renders anomerisation of the uronic acids more efficient than for benzoylated gluco- and galactopyranosides.[12] Chelation, however, is not ruled out for (acylated) gluco- and galactopyranosides given they contain oxygen atoms at C-6 that can potentially chelate. Anomerisation can also proceed through an exocyclic cleavage pathway (Scheme 1).

The main aim of this study was to investigate the potential usefulness of anomerisation in generating α-xylopyranosides, β-arabinopyranosides and α-fucopyranosides. These

saccharides lack any C-5 chelating substituent, and was also considered of interest to compare their reactivity to that of other saccharides studied to date.[3] Aside from our recent study on glycosyl thiols,[13] there has not been a systematic study of Lewis acid anomerisation of these saccharides, that we are aware of. Mammalian glycans that contain α-L-fucopyranosides are involved in interactions between host cells and microorganisms, blood transfusion reactions, leukocyte adhesion and numerous ontogenic events.[14] The 1,2-*cis* linked fucopyranoside[15] is present in glycans such as blood group antigens A, B and H, Lewis^b, Lewis^y, sialyl Lewis^x and globo-H and α-L-fucosidases are of interest in biomedice.[16] β-L-Arabinopyranose is a component of arabinogalactan-proteins and a β-L-arabinopyranosidase has been identified.[17] The chemistry of xylopyranosides has been reviewed[18,19] and α-D-xylopyranoside has been found on the non-reducing terminal of the backbone of oligoxyloglucans, such as in the disaccharide isoprimeverose. α-Xylosidases and functions associated with them have been identified.[20]

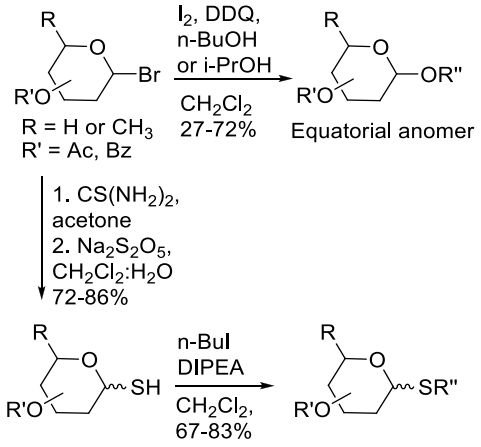


Scheme 1: Possible pathways for Lewis acid promoted O-glycoside anomerisation through (a) exocyclic or (b) endocyclic cleavage. Endocyclic cleavage may be promoted by chelation. The reactants investigated herein (X = O, S) lack chelating substituents at C-5.

Results and Discussion

2.1 Synthesis of O- *and* S-*glycosides for anomerisation study*

Butyl *O*- and *S*-glycosides, which are acetylated or benzoylated (Chart 1), were first synthesised (Scheme 2) so that reactivity and stereoselectivity comparisons could be compared with glycosides studied previously.[4,21] Acetyl and benzoyl groups were chosen as protecting groups as they are stable to $SnCl_4$ and $TiCl_4$ and they influence reactivity and stereoselectivity. Briefly, *O*-glycosides (**1-2β, 3-4α, 5-6β** and **12β-13β**) were prepared from the corresponding glycosyl bromide precursor according to the glycosylation method involving I_2 and DDQ as reported by Lehmler and co-workers.[22] The 1,2-*trans* anomer was generally obtained and the yields varied from 27-76%. The *S*-glycosides **7β-10β** were prepared via the appropriate glycosyl thiol, which was reacted with DIPEA and iodobutane to give the *S*-butyl glycosides (67-83%). Glycoside **11β** was prepared as described previously.[13]



Scheme 2 Summary of the synthesis of *O*-glycosides and *S*-glycosides

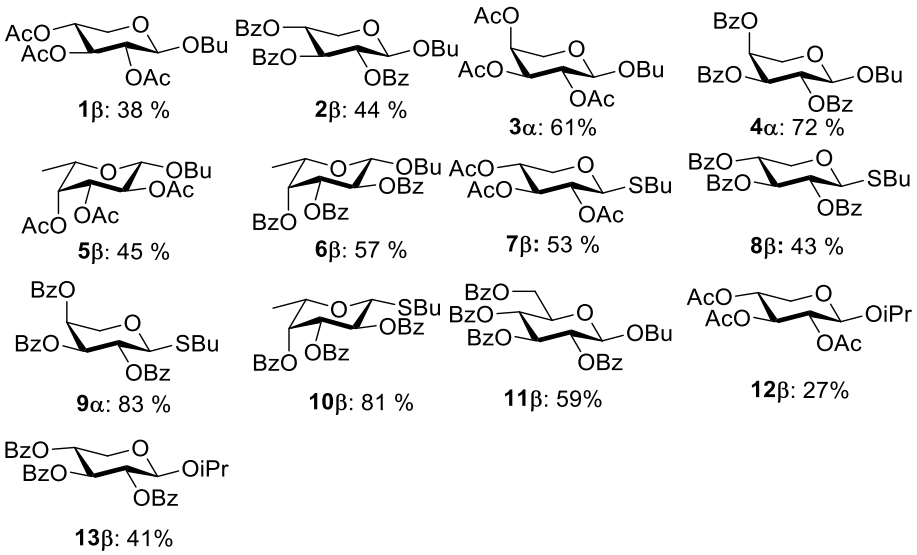


Chart 1 Structures of *O*- and *S*-glycosides. The yields from the glycosyl bromide are given in the case of the O-glycosides and from the thiol for the S-glycosides.

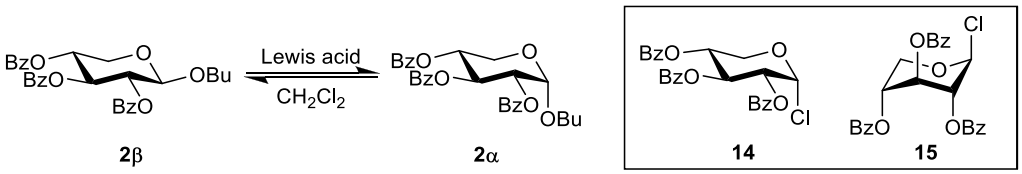
2.2 Behaviour of O- and S-glycosides towards $TiCl_4$, $SnCl_4$ and BF_3OEt_2.

The $TiCl_4$ promoted reaction of xylopyranoside **2β** (Table 1) led only to the formation of a mixture of glycosyl chlorides **14** and **15**[23] (entry 1). Carrying out this reaction at lower temperature led to only **2β** being recovered (entry 2), while reducing the reaction time (entry 3) to 2 h at room temperature also led to mostly recovered **2β**. In contrast, the use of $SnCl_4$ (2.5 equiv) at room temperature gave a mixture of anomers where **2α** (entry 4) predominated after 24 h. Decreasing the temperature reduced glycosyl chloride formation while still giving **2α** (entry 6).

The $SnCl_4$ (2.5 equiv) promoted reactions of equatorial *O*-glycosides **1** and **3-6** also gave the axial *O*-glycoside as the major product, as determined by ^{1}H-NMR spectroscopic analysis of the product mixture after work-up (>85% yield), with the original reactant being the other main component (Table 2). For $SnCl_4$ and **1**β, the use of reaction temperatures of -30 °C and 4 °C, like that of **2β**, gave slightly higher axial:equatorial ratios when compared to reaction at 20 °C. In contrast, reaction of arabinopyranosides and fucopyranosides **3-6** led to lower amounts of the axial anomer on lowering the reaction temperature to 4 °C or -30 °C. This

is likely due to reduced reaction rates for **3-6** compared to **1** or **2** (vide infra). In contrast with the findings for **2β** (Table 1) the use of $TiCl_4$ did give axial anomers for **1β** and **3β, 4β** and **6β**. However the stereoselectivities/yields were generally lower than that observed for $SnCl_4$ and, in the case of **4** and **6**, glycosyl chloride formation predominated at 20 °C.

Table 1 Effect of Lewis acid and temperature on reactions of xylopyranoside **2β**[a]



2β 2α 14 15

Entry	Time	Temp.	Lewis acid	Equivalents	%2α	%2β	%14	%15
1	24 h	20 °C	$TiCl_4$	2.5	<2	4	35	60
2	24 h	4 °C	$TiCl_4$	2.5	<2	>94	<2	<4
3	2 h	20 °C	$TiCl_4$	2.5	<2	80	<2	20
4	24 h	20 °C	$SnCl_4$	2.5	74	22	<2	4
5	24 h	4 °C	$SnCl_4$	2.5	68	24	<2	6
6	24 h	-30 °C	$SnCl_4$	2.5	80	20	<2	<4
7	24 h	20 °C	$SnCl_4$	5	78	18	2	<4

[a]Product ratios were determined by ^{1}H-NMR spectroscopic analysis of product mixtures after work-up.

Table 2 $SnCl_4$ (0.5 equiv) promoted anomerisation reactions of **1β-6β** in CH_2Cl_2[a]

Entry	Reactant	Temp.	α:β
1	**1β**	-30 °C	88:12
2	**1β**	4 °C	84:16
3	**1β**	20 °C	77:23
4	**2β**	-30 °C	80:20
5	**2β**	4 °C	78:22
6	**2β**	20 °C	75:25
7	**3β**	-30 °C	41:59
8	**3β**	4 °C	75:25
9	**3β**	20 °C	79:21
10	**4β**	-30 °C	56:44
11	**4β**	4 °C	72:28
12	**4β**	20 °C	79:21
13	**5β**	-30 °C	8:92
14	**5β**	4 °C	48:52
15	**5β**	20 °C	78:22
16	**6β**	-30 °C	4:96
17	**6β**	4 °C	28:72
18	**6β**	20 °C	80:20

[a]The proportion of α-anomer was determined after 24 h by ^1H NMR spectroscopy. These experiments reported were carried out once.

The anomerisation of *S*-glycosides **8-10** was next investigated. $SnCl_4$ was found to work best at 20 °C, whereas at this temperature, the use of $TiCl_4$ led to formation of glycosyl chlorides. The stereoselectivity after 24 h, was generally lower in *S*-glycoside anomerisation than for the corresponding *O*-glycoside (see Table 3). This is related to factors which influence relative stability of anomers such as the endo-anomeric effect as well as intramolecular steric and repulsive and Coulombic interactions. Unlike the glycosyl thiols, which epimerised to the equatorial thiol with $SnCl_4$, these *S*-glycosides gave the axial anomer preferentially.

Boron trifluoride etherate was investigated as an alternative Lewis acid, but was unable to promote useful anomerisation for butyl glycosides. In the reaction of **6β** it gave a complex mixture with a trace of **6α** detected by NMR spectroscopy. Only in the case of isopropyl glycosides, which are more significantly reactive than butyl glycosides (see Table 3), could useful anomerisation be observed with $BF_3{\cdot}OEt_2$ (0.5 equiv); thus the reaction of this Lewis acid with **13β** gave a 4:1 mixture of **13α** and **13β** after 24 h.

2.3 Conformational analysis

The conformations of the pyranosides may be expected to influence reactivity. Ellervik and colleagues have reviewed xylopyranosides, including their conformational preferences. In the case of methyl β-D-xylopyranoside the $^3J_{H1,H2}$ = 7.8 Hz and was regarded as being consistent with adoption of the $^4C_1$ conformation exclusively. Deviation from this and other couplings, towards lower values is diagnostic of conformational change. The observed J-values for ring protons on the xylopyranosides were measured in the ^{1}H-NMR spectra recorded at 500 MHz in $CDCl_3$ (see experimental section or Table S1 in the supporting information). For the β-anomers of the *O*-xylopyranosides, the $^3J_{H1,H2}$ value was consistently less than 7.8 Hz, which indicates that the $^1C_4$ conformation is populated.[24] This population of $^1C_4$ is higher for benzoylated *O*-xylopyranosides (for **2β** $^3J_{H1,H2}$ = 5.3 Hz; for **13β** $^3J_{H1,H2}$ = 5.5 Hz) than for

acetylated counterparts (for **1β** $^3J_{H1,H2}$ = 6.8 Hz; for **12β** $^3J_{H1,H2}$ = 7.0 Hz). Comparison of J-values for **1β** with those reported for methyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside in $CDCl_3$ show they are in excellent agreement and consistent with a population of the $^4C_1$ conformer of >80%, with $^1C_4$ conformer at <20%.[25] In contrast, the J values for the benzoylated **2β** indicates there is a population of ~60% of $^4C_1$ conformer and ~40% $^1C_4$. While the $^3J_{H1,H2}$ for the *S*-glycosides is higher than the corresponding *O*-glycoside, the examination of the other ring coupling constants indicate that their $^1C_4$ conformer is also populated, with evidence of a higher population again for the benzoylated structure **8β** compared to the acetylated **7β**. All the α-xylopyranosides have higher preferences for the $^4C_1$ conformer compared to the β-anomers. Examination of the J values for the arabinopyranosides (see experimental section or Table S2 in supporting information) and comparison with a published conformational analysis for methyl arabinopyranosides[26] indicate that their α-anomers can also adopt the $^1C_4$ conformer with the $^4C_1$ population decreasing from ~80% for **3α** compared to <70% for the benzoylated **4**. In contrast, the β-L-fucosides adopt predominantly the $^1C_4$ conformers, supported, for example, by $^3J_{H1,H2}$ values which are consistently ~8.0 Hz.

2.3 Kinetics of $SnCl_4$ promoted anomerisation and mechanistic considerations

The reactivity of **1**-**11** towards $SnCl_4$ (0.5 equiv) in $CDCl_3$ was established by NMR spectroscopy as previously described.[3] Concentrations of equatorial glycosides and the products were monitored with time and the data obtained was fitted with the equation[27] for equilibrium kinetics:

$$\ln\left(\frac{[\mathrm{A}]_0 - [\mathrm{A}]_\mathrm{e}}{[\mathrm{A}]_\mathrm{t} - [\mathrm{A}]_\mathrm{e}}\right) = -(k_\mathrm{f} + k_\mathrm{r})\mathrm{t}$$

The isolated yields of the products after work-up, and before chromatographic separations were carried out, varied between 85-96%. The $k_f + k_r$ values obtained from linear plots generated

using the equation above are given in Table 3; the coefficients of determination (R^2) values varied from 0.929 to 0.999. The relative $k_f + k_r$ values, where comparisons are made to the slowest reactant, i.e. the fucopyranoside **5β**, is provided in Table 3. Also included in the study was glucopyranoside **11β**, so that comparisons could be made with it. The $k_f + k_r$ for **11β** measured herein (14.5 x 10^{-6} s^{-1}) in $CDCl_3$ pre-distilled from P_2O_5, when using 0.5 equivalent of $SnCl_4$ is comparable that observed previously under similar conditions (19 x 10^{-6} s^{-1}) reported by Pilgrim and Murphy.[3]

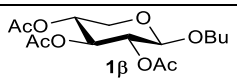
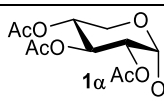
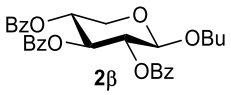
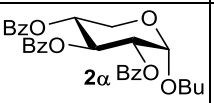
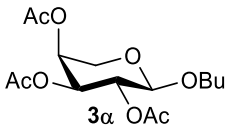
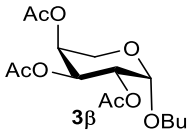
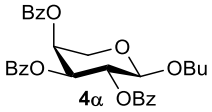
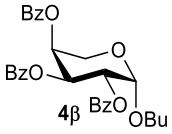
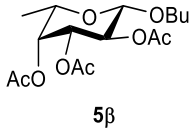
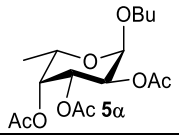
The α:β ratios (Table 3) in the final product mixtures were not as high for reactions of **1**-**10** compared to reaction of the *O*-glucopyranoside **11β** (16:1).[16] The highest stereoselectivity was 5.6:1 in favour of the axial anomer of the benzoylated *O*-fucopyranoside **6**. Hence, the absence of an electron withdrawing oxygen atom on the substituent at C-5 leads to a reduction in axial anomer preference. Recent work with uronic acids, for example, comparing them with glucopyranose or galactopyranose, shows that a more electron withdrawing C-5 substituent gives rise to increased axial anomer preference when equilibration is possible.[4, 28]

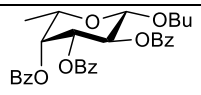
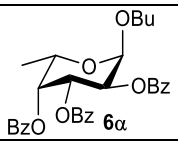
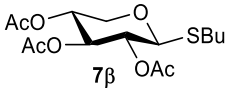
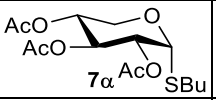
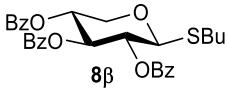
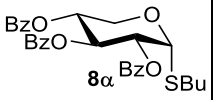
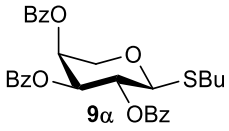
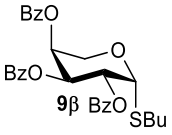
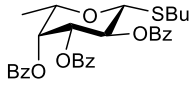
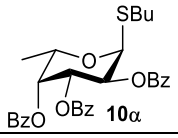
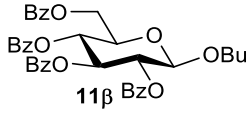
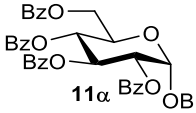
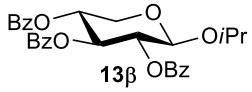
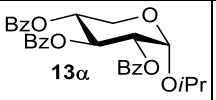
Benzoylated glycosides underwent anomerisation ~1.3 to 3.3 times faster than their acetylated counterparts (c.f. entries 2 *vs* 1, 4 *vs* 3, 6 *vs* 5, 8 *vs* 7). This is consistent with data acquired for **11β** when compared to the reactivity of its acetylated counterpart, although it is not clear if this is for similar reasons.[3] From work on glucopyranosides, which are conformationally rigid, there is a benefit from having a benzoyl group at C-2, compared to an acetyl group.[21] This may indicate there is a role for the 2-*O*-benzoyl group in stabilising a carbocation intermediate, generated during the course of the reaction, through resonance. Benzoyl groups may normally be expected to reduce reactivity towards anomerisation through inductive or field effects as they are more electron withdrawing than acetates (*p*Ka benzoic acid = 4.20 *vs* *p*Ka acetic acid = 4.76). In the case of xylopyranoside and arabinopyranoside, the presence of benzoyl groups

increase the population of the axial rich conformer ($^1C_4$) but there is no evidence for similar behaviour for the fucopyranosides.

One interesting observation is that the xylopyranoside **2β** (entry 2) was about 1.6 fold faster than glucopyranoside **11β** (entry 11) even though the xylopyranoside lacks the chelating substituent at C-5, present in glucopyranoside. This questions the necessity of chelation, involving the ring oxygen and C-5 substituent. However, the C-5 substituent in glucopyranose is electron withdrawing and its absence leads to a more electron rich pyranose ring, which could partially explain the increased reactivity of xylopyranoside, compensating for any benefit that would arise from having a chelating substituent. That the isopropyl glycoside **13β** was faster than the corresponding butyl glycoside **2** is consistent with greater electron releasing properties of the isopropyl group, compared to the butyl group.

Table 3 Kinetic data and product ratios for $SnCl_4$-promoted anomerisation. Yields were >85% in each reaction.

Entry	Reactant	Axial Product	$10^6(k_f + k_r)$ (s^{-1})	Relative $k_f + k_r$	Anomeric ratio (axial:equatorial)
1			17	8.9	3.4:1
2			23.5	12.4	3.5:1
3			3.7	1.9	3.6:1
4			11.3	5.9	3.7:1
5			1.9	1.0	4.3:1

6	 **6β**	 **6α**	2.8	1.5	5.6:1
7	 **7β**	 **7α**	17.3	9.1	1.4:1
8	 **8β**	 **8α**	20.4	10.7	1.7:1
9	 **9α**	 **9β**	41.4	21.8	2:1
10	 **10β**	 **10α**	33.2	17.5	2:1
11	 **11β**	 **11α**	14.5	7.6	16:1
12	 **13β**	 **13α**	555	292	7.5:1

The *O*-fucopyranosides with an axial C-4 substituent in their $^4C_1$ conformers, but with a methyl substituent instead of hydrogen at C-5, underwent anomerisation more slowly than arabinopyranosides (c.f. entries 3 with 5 and 4 with 6). The higher stereoselectivity found for fucopyranosides (c.f. entries 5 vs 3/1; c.f. 6 vs 4/2) compared to xylopyranosides and arabinopyranosides may be due to the C-5 methyl substituent, being more electron donating than a hydrogen atom, increasing electron density on the pyranose oxygen atom and increasing the endoanomeric effect. Interestingly, the D-xylopyranosides, if considering all equatorial substituents in their $^4C_1$ conformer, are more reactive than the corresponding L-arabinopyranosides, the latter having one axial C-4 substituent in their $^4C_1$ conformers (c.f. entries 1 with 3 and 2 with 4).

In the earlier study based on glucopyranosides/galactopyranosides and related uronic acids the *S*-glycosides were generally faster than the corresponding *O*-glycosides. Herein, the *S*-

fucopyranoside **10β** was an order of magnitude faster than *O*-fucopyranoside **6β** whereas *S*-arabinopyranoside **9α** was ~ 3fold faster than *O*-arabinopyranoside **4**α. This can be explained due to sulfur being more electron releasing than oxygen and hence better able to stabilise the carbocation generated by endocyclic cleavage. In the acid catalysed hydrolysis of S- and O-glycosides, which proceed by exocyclic cleavage, the O-glycosides cleave faster.[29] Here, the *S*-xylopyranoside **8β** reacted slightly more slowly than its *O*-glycoside counterpart **2β** (compare entries 1 vs 8) whereas the *O*-xylopyranoside **7β** had a similar reaction rate as the thioglycoside **1β**.

The kinetic data could indicate that anomerisation in the xylopyranosides involves exocyclic cleavage whereas those of fucopyranosides and arabinopyranosides involve endocyclic cleavage. To investigate this in xylopyranoside, a crossover experiment was attempted. Thus, the xylosides **1β** and **13β** were mixed at the same concentrations as investigated for the kinetics experiments in an NMR tube and $SnCl_4$ (0.5 equiv) was added in $CDCl_3$ and the reaction monitored by NMR. While anomerisation of the mixture of **1β** and **13β** gave both **1α** and **13α** after a few hours, as well as remaining reactants, it was only after 24 h that the crossover products **2α** and **12α** (each ~ 5%) could be seen; these were evidenced by the appearance of broad signals at δ 5.14 for **12α** and at δ 5.27 for **2α** in accordance with those signals observed in standard samples of **2α/12α** prepared herein. At 24 h, the ratios of **1α** : **13α** : **1β** : **13β** : **2α** : **12α** in the crossover reaction mixture was 30 : 30 : 12.5 : 12.5 : 5 : 5. The relative amount of crossover product did continue to increase after 24 h. It was found to be much higher if 10-fold higher concentrations of $SnCl_4$ was used. But the latter experiment also gave a more complex mixture and the conditions are very different to those where the kinetics were measured. Thus, anomerisation via crossover can take place, possibly via exocyclic cleavage, but it is slow relative to the intramolecular anomerisation. However, slow crossover or lack of crossover can still be explained by an exocyclic cleavage pathway which gives anomerisation

predominantly via intimate ion pairs and thus results from the crossover could not conclusively rule out exocyclic cleavage.[30] In previous work from our laboratory on glucopyranosides and galactopyranosides,[4] the outcome of trapping experiments[31] supported also the occurrence of endocyclic cleavage for the $SnCl_4$ catalysed anomerisation, although it was not possible to get such evidence as part of this study.

2.7 Conclusions

The Lewis acid catalyzed anomerization reactions of D-xylo-, L-arabino- and L-fucopyranosides have been studied, providing a basis for investigating new applications of the reaction. The reactivity order is xylopyranoside > arabinopyranoside > fucopyranoside and this coincides with the relative conformational flexibility of these pyranosides. This correspondence could be interpreted as the $^1C_4$ conformers of xylopyranosides and arabinopyranosides being more susceptible to $SnCl_4$ promoted endocyclic cleavage, than fucopyranosides. This hypothesis would need to be supported by more extensive study. However, it has been shown both in glycoside hydrolysis[1a] and glycosylation[32] that saccharide reactivity is increased when axial rich conformers have increased population. It is clear that chelation of $SnCl_4$ to a substituent at C-5 of a pyranoside is not required for anomerisation to proceed.

Experimental Section

General Experimental Procedures NMR spectra were recorded (25 °C) with a 500 MHz Agilent spectrometer. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (J) given in Hertz (Hz). Chemical shifts are reported relative to internal standard Me_4Si in $CDCl_3$ (d 0.0) for ^1H and $CDCl_3$ (d 77.0) for ^{13}C. ^1H NMR spectral signals were

assigned with the aid of COSY, ^{13}C NMR spectral signals using DEPT, gHSQCAD and/or gHMBCAD. NMR data for known compounds was in good agreement with previously published data. High resolution mass spectra were measured in positive and/or negative mode as indicated using a Waters LCT Mass Spectrometer. TLC was performed on aluminium sheets precoated with silica gel and spots visualized by UV and charring with H_2SO_4-EtOH (1:20) or cerium molybdate, unless otherwise stated. Chromatography was carried out with silica gel 60 (0.040-0.630 mm) and using a stepwise solvent polarity gradient correlated with TLC mobility, unless otherwise stated. CH_2Cl_2, MeOH, toluene and THF reaction solvents were used as obtained from a Pure Solv™ Solvent Purification System. Optical rotations were determined at the sodium D line at 20°C using a Schmidt and Haensch UniPol L1000. The IR spectra were recorded using thin film with a PerkinElmer Spectrum 100 FT-IR Spectrometer with an ATR attachment. Unless otherwise noted, all commercially available compounds were used as obtained from suppliers without further purification.

Butyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside 1β 2,3,4-Tri-*O*-acetyl-β-xylopyranosyl bromide[33] (7.1 g, 20.9 mmol) was added, under nitrogen, to I_2 (5.31 g, 20.9 mmol), DDQ (2.37 g, 10.5 mmol), n-butanol (3.83 mL, 41.9 mmol) and 4Å molecular sieves in anhydrous CH_2Cl_2 (12 mL). The mixture was stirred at room temperature for 4.5 h, and it was then filtered through celite, washed with $Na_2S_2O_3$ (2% w/v), satd aq $NaHCO_3$ and then brine. The colourless organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. Chromatography (cyclohexane-EtOAc, 4:1) gave the title compound (white solid, 2.62 g, 38%); R_f 0.32 (cyclohexane-EtOAc, 4:1); $[\alpha]_D^{20}$ -56 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.16 (t, *J* = 8.6 Hz, 1H, H-3), 4.98-4.89 (overlapping signals, 2H, H-2 and H-4), 4.46 (d, *J* = 6.8 Hz, 1H, H-1), 4.12 (dd, *J* = 11.8, 5.1 Hz, 1H, H-5a), 3.82 (dt, *J* = 9.6, 6.4 Hz, 1H, OC*H*H), 3.46 (dt, *J* = 9.6, 6.6 Hz, 1H, OCH*H*), 3.36 (dd, *J* = 11.8, 8.8 Hz, 1H, H-5b), 2.05 (s,

3H, C(O)CH_3), 2.05 (s, 3H, C(O)CH_3), 2.04 (s, 3H, C(O)CH_3), 1.59–1.51 (overlapping signals, 2H, OCH_2CH_2), 1.40–1.30 (overlapping signals, 2H, $O(CH_2)CH_2$), 0.91 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 169.8, 169.4 (each C=O), 100.7 (C-1), 71.5 (C-3), 70.9 (C-4), 69.4 (C-5), 68.9 (C-2), 62.0 (OCH_2), 31.4 (OCH_2CH_2), 20.8, 20.7, 20.7 (each C(O)CH_3), 19.0 ($O(CH_2)CH_2$), 13.7 (CH_3); IR (ATR) cm^{-1}: 2937, 1737, 1368, 1222, 1077, 1056; ESI-HRMS calcd for $C_{15}H_{24}O_8Na$ 355.1369, found *m/z* 355.1370 $[M+Na]^+$.

Butyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranoside 2β The reaction of 2,3,4-tri-*O*-benzoyl-α-D-xylopyranosyl bromide[13] (1.14 g, 2.17 mmol), I_2 (0.55 g, 2.17 mmol), DDQ (0.25 g, 1.09 mmol) and n-butanol (0.39 mL, 4.34 mmol) as described for the preparation of **1β**, gave, after chromatography (cyclohexane-EtOAc 7:1), the title compound as a crystalline solid. Recrystallization from ethanol gave white crystals (0.49 g, 44%); R_f 0.32 (cyclohexane-EtOAc 7:1); $[\alpha]_D^{20}$ -29.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03-7.97 (overlapping signals, 6H, Ar-H), 7.56-7.49 (overlapping signals, 3H, Ar-H), 7.41-7.33 (overlapping signals, 6H, Ar-H), 5.74 (t, *J* = 7.1 Hz, 1H, H-3), 5.36 (dd, *J* = 7.1, 5.3 Hz, 1H, H-2), 5.29 (td, *J* = 6.9, 4.2 Hz, 1H, H-4), 4.82 (d, *J* = 5.2 Hz, 1H, H-1), 4.43 (dd, *J* = 12.1, 4.2 Hz, 1H, H-5a), 3.88 (dt, *J* = 9.5, 6.3 Hz, 1H, OC*H*H), 3.71 (dd, *J* = 12.2, 6.9 Hz, 1H, H-5b), 3.53 (dt, *J* = 9.5, 6.5 Hz, 1H, OCH*H*), 1.61-1.55 (overlapping signals, 2H, OCH_2CH_2), 1.33 (dt, *J* = 14.8, 7.4 Hz, 2H, $O(CH_2)_2CH_2$), 0.83 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.3, 133.3, 133.2 (each C=O), 129.9, 129.8, 128.4, 128.3, 128.3 (Ar-C and CH), 100.0 (C-1), 70.3 (C-2), 70.2 (C-3), 69.2 (C-4), 69.1 (C-5), 61.1 (OCH_2), 31.6 (OCH_2CH_2), 19.1 ($O(CH_2)_2CH_2$), 13.7 (CH_3); IR (ATR) cm^{-1}: 1708, 1604, 1457, 1256, 1072, 1030, 712, 688; ESI-HRMS calcd for $C_{30}H_{30}O_8Na$ 541.1838, found *m/z* 541.1833 $[M+Na]^+$.

Butyl 2,3,4-tri-*O*-acetyl-α-L-arabinopyranoside 3α Reaction of 2,3,4-tri-O-acetyl-β-L-arabinopyranosyl bromide[34] (1.2 g, 3.5 mmol), I_2 (0.90 g, 3.35 mmol), DDQ (0.40 g, 1.8 mmol) and n-butanol (0.65 mL, 7.08 mmol) in dry CH_2Cl_2 (11.0 mL) as described for the preparation of **1β**, gave, after chromatography (cyclohexane-EtOAc 3:2), the title compound as a yellow oil (0.45 g, 61%); R_f 0.29 (cyclohexane-EtOAc 3:2); $[\alpha]_D^{20}$ +4.93 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26 (td, J = 3.4, 1.8 Hz, 1H, H-4), 5.18 (dd, J = 9.4, 6.9 Hz, 1H, H-2), 5.04 (dd, J = 9.4, 3.5 Hz, 1H, H-3), 4.40 (d, J = 6.8 Hz, 1H, H-1), 4.03 (dd, J = 13.0, 3.4 Hz, 1H, H-5a), 3.86 (dt, J = 9.6, 6.3 Hz, 1H, OC*H*H), 3.62 (dd, J = 13.0, 1.8 Hz, 1H, H-5b), 3.46 (dt, J = 9.6, 6.7 Hz, 1H. OCH*H*), 2.13 (s, 3H, C(O)CH_3), 2.06 (s, 3H, C(O)CH_3), 2.03 (s, 3H, C(O)CH_3), 1.58-1.52 (overlapping signals, 2H, OCH_2CH_2), 1.41-1.33 (overlapping signals, 2H, $O(CH_2)CH_2$), 0.91 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 170.2, 169.4 (C=O), 101.0 (C-1), 70.2 (C-3), 69.5 (C-2), 69.3 (C-5), 67.7 (C-4), 63.1 (OCH_2), 31.5 (OCH_2CH_2), 21.0, 20.8, 20.7 (each C(O)CH_3), 19.1 ($O(CH_2)CH_2$), 13.8 (CH_3); IR cm^{-1}: 2960, 1741, 1369, 1222, 1048, 1020; ES-HRMS calcd for $C_{15}H_{24}O_8Na$ 355.1369, found m/z 355.1368 $[M+Na]^+$.

Butyl 2,3,4-tri-*O*-benzoyl-α-L-arabinopyranoside 4α Reaction of 2,3,4-tri-*O*-benzoyl-α-L-arabinopyranosyl bromide[13] (0.13 g, 0.03 mmol) was added to I_2 (0.06 g, 0.25 mmol), DDQ (0.025g, 0.125 mmol) and n-butanol (0.045 mL, 0.125 mmol) in dry CH_2Cl_2 (0.5 mL) as described for the preparation of **1β**, gave, after chromatography (cyclohexane-EtOAc 4:1), the title compound (0.09 g, 72%) as a white powder: R_f 0.26 (cyclohexane-EtOAc 4:1); $[\alpha]_D^{20}$ +155.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06-8.00 (overlapping signals, 4H, Ar-H), 7.96-7.93 (overlapping signals, 2H, Ar-H), 7.59-7.52 (overlapping signals, 2H, Ar-H), 7.51-7.47 (m, 1H, Ar-H), 7.46-7.40 (overlapping signals, 4H, Ar-H), 7.36-7.31 (overlapping signals, 3H, Ar-H), 5.72-5.67 (overlapping signals, 2H, H-2 and H-4), 5.61 (dd, *J* = 8.4, 3.4

Hz, 1H, H-3), 4.74 (d, *J* = 5.9 Hz, 1H, H-1), 4.32 (dd, *J* = 12.7, 4.5 Hz, 1H, H-5a), 3.96-3.87 (overlapping signals, 2H, H-5b and OC*H*H), 3.54 (dt, *J* = 9.6, 6.6 Hz, 1H, OCH*H*), 1.64-1.55 (overlapping signals, 2H, OCH_2CH_2), 1.35-1.27 (overlapping signals, 2H, $O(CH_2)_2CH_2$), 0.80 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 165.6, 165.2 (each C=O), 133.3, 133.3, 133.2, 129.9, 129.8, 129.8, 129.4, 129.2, 128.4, 128.4, 128.3, 110.0 (each Ar-C and CH), 77.2 (C-1), 70.4 (C-3), 70.0 (C-2), 69.5 (OCH_2), 68.3 (C-4), 62.2 (C-5), 31.5 (OCH_2CH_2), 19.1 ($O(CH_2)_2CH_2$), 13.7 (CH_3); IR (ATR) cm^{-1}: 1719, 1604, 1457, 1256, 1071, 1030, 712, 688; ES-HRMS calcd for $C_{30}H_{30}O_8Na$ 541.1838, found *m/z* 541.1849 $[M+Na]^+$.

Butyl 2,3,4-tri-*O*-acetyl-β-L-fucopyranoside 5β Reaction of 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide[35] (1.44 g, 4.08 mmol), I_2 (1.0 g, 4.08 mmol), DDQ (0.46 g, 2.04 mmol) and n-butanol (0.75 mL, 8.15 mmol) in dry CH_2Cl_2 (13 mL) as described for the preparation of **1β**, gave, after chromatography (cyclohexane-EtOAc 2:1), the title compound as a colourless oil (0.63 g; 45 %); R_f 0.17 (cyclohexane-EtOAc 3:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.23 (dd, J = 3.5, 1.1 Hz, 1H, H-4), 5.18 (dd, J = 10.5, 7.9 Hz, 1H. H-2), 5.02 (dd, J = 10.5, 3.5 Hz, 1H, H-3), 4.42 (d, J = 7.9 Hz, 1H, H-1), 3.91 (dt, J = 9.6, 6.2 Hz, 1H, OC*H*H), 3.79 (qd, J = 6.4, 1.1 Hz, 1H, H-5), 3.46 (dt, J = 6.9, 4.1, 2.7 Hz, 1H, OCH*H*), 2.17 (s, 3H, CO)CH_3), 2.04 (s, 3H, C(O)CH_3), 1.98 (s, 3H, C(O)CH_3), 1.64-1.48 (overlapping signals, 2H, OCH_2CH_2), 1.40-1.30 (overlapping signals, 2H, $O(CH_2)_2CH_2$), 1.23 (d, J = 6.4 Hz, 3H, CH_3), 0.90 (t, J = 7.4 Hz, 3H, CH_2CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 170.3, 169.5 (each C=O), 101.2 (C-1), 71.4 (C-3), 70.4 (C-4), 69.8 (OCH_2), 69.1 (C-2), 69.1 (C-5), 31.4 (OCH_2CH_2), 20.8, 20.7, 20.7 (each C(O)CH_3), 19.0 ($O(CH_2)_2CH_2$), 16.1 (CH_3), 13.8 (CH_2CH_3); IR cm^{-1}: 3707, 2966, 1744, 1367, 1215, 1174, 1033, 1017; ES-HRMS calcd for $C_{16}H_{26}O_8Na$ 369.1525, found *m/z* 369.1522 $[M+Na]^+$.

Butyl 2,3,4-tri-*O*-benzoyl-β-L-fucopyranoside 6β Reaction of 2,3,4-tri-*O*-benzoyl-β-L-fucopyranosyl bromide[36] (1.10 g, 2.04 mmol), I_2 (0.71 g, 2.79 mmol), DDQ (0.32g, 1.39 mmol) and n-butanol (0.51 mL, 5.57 mmol) in dry CH_2Cl_2 (14 mL), as described for the preparation of **1β**, gave, after chromatography (cyclohexane-EtOAc 3:2), the title compound (0.57 g, 57%) as a white solid: R_f 0.29 (2:3 EtOAc-cyclohexane); $[\alpha]_D^{20}$ -180 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13-8.08 (overlapping signals, 2H, Ar-H), 7.98-7.94 (overlapping signals, 2H, Ar-H), 7.82-7.77 (overlapping signals, 2H, Ar-H), 7.63-7.58 (m, 1H, Ar-H), 7.53-7.45 (overlapping signals, 3H, Ar-H), 7.44-7.40 (m, 1H, Ar-H), 7.38 (t, *J* = 7.7 Hz, 2H, Ar-H), 7.25-7.21 (overlapping signals, 2H, Ar-H), 5.74 (dd, *J* = 10.5, 8.0 Hz, 1H, H-2), 5.71 (d, *J* = 3.6 Hz, 1H, H-4), 5.55 (dd, *J* = 10.4, 3.5 Hz, 1H, H-3), 4.74 (d, *J* = 8.0 Hz, 1H, H-1), 4.07 (q, *J* = 6.4 Hz, 1H, H-5), 3.97 (dt, *J* = 9.8, 6.3 Hz, 1H, OC*H*H), 3.55 (dt, *J* = 9.8, 6.8 Hz, 1H, OCH*H*), 1.60-1.47 (overlapping signals, 2H, OCH_2CH_2), 1.36 (d, *J* = 6.4 Hz, 3H, CH_3), 1.30-1.18 (overlapping signals, 2H, $O(CH_2)_2CH_2$), 0.75 (t, *J* = 7.4 Hz, 3H, $O(CH_2)_3CH_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 165.7, 165.3 (each C=O), 133.4, 133.2, 133.0, 130.0, 129.8, 129.7, 129.3, 129.0, 128.5, 128.3, 128.2 (Ar-C and CH), 101.5 (C-1), 72.2 (C-3), 71.2 (C-2), 70.0 (OCH_2), 69.9 (C-4), 69.7 (C-5), 31.4 (OCH_2CH_2), 18.9 ($O(CH_2)_2CH_2$), 16.4 (CH_3), 13.6 (CH_2CH_3); IR (ATR) cm^{-1}: 1722, 1602, 1452, 1259, 1066, 1026, 705; ES-HRMS calcd for $C_{31}H_{32}O_8Na$ 555.1995, found *m/z* 555.1996 $[M+Na]^+$.

Butyl 2,3,4-tri-*O*-acetyl-1-D-thioxylopyranoside 7 2,3,4-Tri-*O*-acetyl-1-thio-D-xylopyranose[37] (0.3 g, 1.0 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL). To this, DIPEA (0.38 mL, 2.16 mmol) and iodobutane (0.53 mL, 4.62 mmol) were added at room temp. The mixture was stirred for 3 h and the solvent was removed under reduced pressure. Chromatography of the residue (4:1 cyclohexane-EtOAc) gave the two anomers of **7** (α-anomer: 0.05 g, 14%; β-anomer: 0.19 g, 53%) as pale yellow solids. Analytical data for **7α**: R_f

0.3 (cyclohexane-EtOAc 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (d, *J* = 5.4 Hz, 1H, H-1), 5.34 (t, *J* = 9.4 Hz, 1H, H-3), 4.98-4.87 (overlapping signals, 2H, H-2 and H-4), 4.03 (t, *J* = 10.8 Hz, 1H, H-5a), 3.79 (dd, *J* = 11.3, 5.7 Hz, 1H, H-5b), 2.59-2.47 (overlapping signals, 2H, SCH_2), 2.07 (s, 3H, $C(O)CH_3$), 2.04 (s, 6H, 2 x $C(O)CH_3$), 1.62-1.52 (overlapping signals, 2H, SCH_2CH_2), 1.45-1.34 (overlapping signals, 2H, $S(CH_2)_2CH_2$), 0.91 (t, *J* = 7.3 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0 (2s), 169.7 (each C=O), 82.2 (C-1), 70.8 (C-2), 69.6 (C-3), 69.2 (C-4), 59.2 (C-5), 31.5 (SCH_2CH_2), 30.0 (SCH_2), 21.9 ($S(CH_2)_2CH_2$), 20.8, 20.7 (overlapping signals, each $C(O)CH_3$), 13.6 (CH_3); IR (ATR) cm^{-1}: 2931, 1747, 1367, 1211, 1068, 1038; ESI-HRMS calcd for $C_{15}H_{28}O_7NS$ 366.1586, found *m/z* 366.1587 $[M+NH_4]^+$. Analytical data for **7β** : R_f 0.24 (cyclohexane-EtOAc 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.18 (t, *J* = 8.5 Hz, 1H, H-3), 4.99-4.93 (overlapping signals, 2H, H-2 and H-4), 4.51 (d, *J* = 8.7 Hz, 1H, H-1), 4.22 (dd, *J* = 11.6, 5.1 Hz, 1H, H-5a), 3.38 (dd, *J* = 11.6, 9.1 Hz, 1H, H-5b), 2.73-2.60 (overlapping signals, 2H, SCH_2), 2.07 (s, 3H, $C(O)CH_3$), 2.05 (s, 6H, 2 x $C(O)CH_3$), 1.61-1.53 (overlapping signals, 2H, SCH_2CH_2), 1.44-1.36 (overlapping signals, 2H, $S(CH_2)_2CH_2$), 0.91 (t, *J* = 7.3 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 169.8, 169.4 (each C=O), 83.8 (C-1), 72.3 (C-3), 69.8 (C-2), 68.7 (C-4), 65.6 (C-5), 31.6 (SCH_2CH_2), 29.7 (SCH_2), 21.9 ($S(CH_2)_2CH_2$), 20.7, 20.7, 20.7 (each $C(O)CH_3$), 13.6 (CH_3); IR (ATR) cm^{-1}: 2957, 1748, 1366, 1207, 1063, 1051; ESI-HRMS calcd for $C_{15}H_{28}O_7NS$ 366.1586, found *m/z* 366.1582 $[M+NH_4]^+$.

Butyl 2,3,4-tri-*O*-benzoyl-1-D-thioxylopyranoside 8 2,3,4-Tri-*O*-benzoyl-1-thio-D-xylopyranose[13] (0.5 g, 1.05 mmol), was dissolved in anhydrous CH_2Cl_2 (10 mL). Then DIPEA (0.36 mL, 2.09 mmol) and iodobutane (0.53 mL, 4.75 mmol) were added at room temp and the mixture was stirred for 3 h. The solvent was removed under reduced pressure. Chromatography of the residue (13:1 cyclohexane-EtOAc) gave the two anomers of **8** (0.21 g,

38%) and the β-anomer (0.24 g, 43%), each as a white solid. Analytical data for **8α**: R_f 0.3 (cyclohexane-EtOAc, 12:1); $[\alpha]_D^{20}$ +73 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03-7.90 (overlapping signals, 6H, Ar-H), 7.54-7.49 (overlapping signals, 2H, Ar-H), 7.49-7.44 (m, 1H, Ar-H), 7.43-7.29 (overlapping signals, 6H, Ar-H), 5.99 (t, *J* = 9.2 Hz, 1H, H-3), 5.77 (d, *J* = 5.3 Hz, 1H, H-1), 5.43 (dd, *J* = 9.6, 5.3 Hz, 1H, H-2), 5.37 (td, *J* = 9.4, 5.5 Hz, 1H, H-4), 4.28 (t, *J* = 10.7 Hz, 1H, H-5a), 4.10 (dd, *J* = 11.3, 5.4 Hz, 1H, H-5b), 2.65-2.53 (overlapping signals, 2H, SCH_2), 1.63-1.53 (overlapping signals, 2H, SCH_2CH_2), 1.42-1.31 (overlapping signals, 2H, $S(CH_2)_2CH_2$), 0.87 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 165.5, 165.5 (each C=O), 133.4, 133.4, 133.2, 130.0, 129.8, 129.7, 129.2, 129.1, 129.0, 128.4, 128.4, 128.3 (Ar-C and CH), 82.8 (C-1), 71.5 (C-2), 70.1 (C-3), 69.9 (C-4), 59.7 (C-5), 31.6 (SCH_2CH_2), 30.2 (SCH_2), 21.9 ($S(CH_2)_2CH_2$), 13.6 (CH_3); IR (ATR) cm^{-1}: 2958, 1720, 1452, 1251, 1093, 1068, 704, 687; ESI-HRMS calcd for $C_{30}H_{34}O_7SN$ 552.2056, found *m/z* 552.2047 $[M+NH_4]^+$. Analytical data for **8β** R_f 0.21 (cyclohexane -EtOAc 12:1); $[\alpha]_D^{20}$ +35.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03-7.95 (overlapping signals, 6H, Ar-H), 7.56-7.47 (overlapping signals, 3H, Ar-H), 7.41-7.31 (overlapping signals, 6H, Ar-H), 5.77 (t, *J* = 7.2 Hz, 1H, H-3), 5.44 (t, *J* = 7.0 Hz, 1H, H-2), 5.31 (td, *J* = 7.3, 4.3 Hz, 1H, H-4), 4.96 (d, *J* = 7.1 Hz, 1H, H-1), 4.60 (dd, *J* = 11.9, 4.4 Hz, 1H, H-5a), 3.72 (dd, *J* = 12.0, 7.4 Hz, 1H, H-5b), 2.81-2.67 (overlapping signals, 2H, SCH_2), 1.67-1.56 (overlapping signals, 2H, SCH_2CH_2), 1.46-1.35 (overlapping signals, 2H, , $S(CH_2)_2CH_2$), 0.90 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 165.3, 165.2 (each C=O), 133.4, 133.3, 129.9, 129.9, 129.0, 128.4, 128.4, 128.3 (Ar-C and CH), 83.7 (C-1), 71.1 (C-3), 70.2 (C-2), 69.1 (C-4), 64.1 (C-5), 31.7 (SCH_2CH_2), 30.4 (SCH_2), 21.9 ($S(CH_2)_2CH_2$), 13.6 (CH_3); IR (ATR) cm^{-1}: 1717, 1453, 1246, 1094, 1067, 1028, 704; ESI-HRMS calcd for $C_{30}H_{30}O_7SNa$ 557.1610, found *m/z* 557.1611 $[M+Na]^+$.

Butyl 2,3,4-tri-*O*-benzoyl-1-thio-α-L-arabinopyranoside 9α 2,3,4-Tri-*O*-benzoyl-1-thio-α-L-arabinopyranose (0.50 g, 1.05 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL). DIPEA (0.36 mL, 2.09 mmol) and iodobutane (0.53 mL, 4.75 mmol) were added at room temp and the mixture was stirred for 15 h. The solvent was then removed and chromatography of the residue (12:1 cyclohexane-EtOAc) gave the title compound (0.47 g, 83%), as a white solid: R_f 0.43 (cyclohexane-EtOAc, 5:1); $[\alpha]_D^{20}$ +132.2 (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.06-7.99 (overlapping signals, 4H, Ar-H), 8.00-7.92 (overlapping signals, 2H, Ar-H), 7.60-7.52 (overlapping signals, 2H, Ar-H), 7.52-7.47 (m, 1H, Ar-H), 7.47-7.38 (overlapping signals, 4H, Ar-H), 7.39-7.31 (overlapping signals, 2H, Ar-H), 5.79 (t, *J* = 7.9 Hz, 1H, H-2), 5.72 (apparent q, *J* = 3.4 Hz, 1H, H-4), 5.64 (dd, *J* = 8.2, 3.4 Hz, 1H, H-3), 4.88 (d, *J* = 7.7 Hz, 1H, H-1), 4.43 (dd, *J* = 12.7, 4.3 Hz, 1H, H-5a), 3.93 (dd, *J* = 12.8, 2.2 Hz, 1H, H-5b), 2.81 (ddd, *J* = 12.8, 8.3, 6.3 Hz, 1H, SC*H*H), 2.74 (dt, *J* = 12.6, 7.5 Hz, 1H, SCH*H*), 1.69-1.57 (overlapping signals, *J* = 6.7 Hz, 2H, SCH_2CH_2), 1.41 (h, *J* = 7.3 Hz, 2H, $S(CH_2)_2CH_2$), 0.90 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 165.5, 165.3 (each C=O), 133.4, 133.4, 133.3, 129.9, 129.9, 129.8, 129.4, 129.0, 128.5, 128.4, 128.4 (Ar-C and CH), 83.92 (C-1), 71.2 (C-3), 69.3 (C-2), 68.7 (C-4), 31.9 (SCH_2), 30.3 (SCH_2CH_2), 22.0 ($S(CH_2)_2CH_2$), 13.6 (CH_3); IR (ATR) cm^{-1}: 2960, 1727, 1451, 1251, 1082, 1067, 1026, 704; ES-HRMS calcd for $C_{26}H_{22}O_7SNa$ 557.1610, found *m/z* 557.1605 $[M+Na]^+$.

Butyl 2,3,4-Tri-*O*-benzoyl-1-thio-β-L-fucopyranoside 10β 2,3,4-Tri-*O*-benzoyl-1-thio-β-L-fucopyranoside (0.5 g, 1.02 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL). DIPEA (0.36 mL, 2.09 mmol) and iodobutane (0.53 mL, 4.75 mmol) were then added and the mixture was stirred for 6 h at room temp. The solvent was removed and then chromatography of the residue (cyclohexane-EtOAc 10:1) gave the title compound (0.452 g, 81%), as a white solid; R_f 0.34 (cyclohexane-EtOAc 10:1); $[\alpha]_D^{20}$ -191.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz,

$CDCl_3$) δ 8.12-8.07 (overlapping signals, 2H, Ar-H), 8.00-7.93 (overlapping signals, 2H, Ar-H), 7.80-7.76 (overlapping signals, 2H, Ar-H), 7.64-7.57 (m, 1H, Ar-H), 7.52-7.46 (overlapping signals, 3H, Ar-H), 7.44-7.34 (overlapping signals, 3H, Ar-H), 7.26-7.20 (overlapping signals, 2H, Ar-H), 5.82 (t, *J* = 9.9 Hz, 1H, H-2), 5.76 (d, *J* = 3.5 Hz, 1H, H-4), 5.59 (dd, *J* = 9.9, 3.4 Hz, 1H, H-3), 4.77 (d, *J* = 9.8 Hz, 1H, H-1), 4.11 (q, *J* = 6.4 Hz, 1H, H-5), 2.87 (ddd, *J* = 12.3, 8.7, 6.2 Hz, 1H, SC*H*H), 2.78 (ddd, *J* = 12.3, 8.7, 6.8 Hz, 1H, SCH*H*), 1.71-1.58 (overlapping signals, 2H, SCH_2CH_2), 1.49-1.37 (overlapping signals, 2H, $S(CH_2)_2CH_2$), 1.35 (d, *J* = 6.4 Hz, 3H, CH_3), 0.91 (t, *J* = 7.3 Hz, 3H, $S(CH_2)_3CH_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 165.6, 165.4 (each C=O), 133.4, 133.2, 133.2, 129.9, 129.7, 129.7, 129.4, 129.3, 128.5, 128.3, 128.2 (Ar-C and CH), 83.7 (C-1), 73.8 (C-5), 73.2 (C-3), 71.3 (C-4), 68.1 (C-2), 31.8 (SCH_2CH_2), 29.5 (SCH_2), 22.0 ($S(CH_2)_2CH_2$), 16.7 (CH_3), 13.6 ($S(CH_2)_3CH_3$); IR (ATR) cm^{-1}: 2960, 1721, 1451,1256, 1094, 1067, 1026, 703; ES-HRMS calcd for $C_{31}H_{32}O_7SNa$ 571.1766, found *m/z* 571.1744 $[M+Na]^+$.

Isopropyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside 12β Glycosylation reaction with 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (0.92 g, 3.12 mmol), I_2 (0.8 g, 3.13 mmol), DDQ (0.36 g, 1.57 mmol) and isopropanol (0.48 mL, 6.26 mmol) in anhydrous CH_2Cl_2 (15.65 mL) as described above, gave after chromatography (cyclohexane-EtOAc 2:1), the title compound (0.27 g, 27%) as a white solid; R_f 0.32 (cyclohexane-EtOAc 3:2); $[\alpha]_D^{20}$ -54.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (t, *J* = 8.9 Hz, 1H, H-3), 4.95 (td, *J* = 9.0, 5.3 Hz, 1H, H-4), 4.88 (dd, *J* = 9.0, 7.0 Hz, 1H, H-2), 4.52 (d, *J* = 7.1 Hz, 1H, H-1), 4.11 (dd, *J* = 11.7, 5.3 Hz, 1H, H-5a), 3.90 (hept, *J* = 6.0 Hz, 1H, $CH(CH_3)_2$), 3.33 (dd, *J* = 11.7, 9.2 Hz, 1H, H-5b), 2.05 (s, 3H, $C(O)CH_3$), 2.04 (s, 3H, $C(O)CH_3$), 2.03 (s, 3H, $C(O)CH_3$), 1.22 (d, *J* = 6.2 Hz, 3H, CH_3), 1.13 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 169.8, 169.4 (each C=O), 99.5 (C-1), 72.2 ($CH(CH_3)_2$), 71.8 (C-3), 71.2 (C-2), 69.0 (C-4), 62.1 (C-5), 23.3, 21.8

(each CH_3), 20.7 (3s) (each C(O)*C*H_3); IR (ATR) cm^{-1}: 2983, 1749, 1366, 1217, 1072, 1060; ESI-HRMS calcd for $C_{14}H_{22}O_8Na$ 341.1212, found *m/z* 341.1212 $[M+Na]^+$.

Isopropyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranoside 13β Glycosylation using 2,3,4-tetra-*O*-benzoyl-α-D-xylopyranosyl bromide (1.19 g, 2.26 mmol), I_2 (0.58 g, 2.26 mmol), DDQ (0.26 g, 1.13 mmol) and isopropanol (0.35 mL, 4.53 mmol) as described for the preparation of **1β**, gave, after chromatography (cyclohexane-EtOAc 6:1), the title compound (0.47 g, 41%) as a white solid. R_f 0.28 (cyclohexane-EtOAc 6:1); $[\alpha]_D^{20}$ -32.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-7.96 (overlapping signals, 6H, Ar-H), 7.56-7.47 (overlapping signals, 3H, Ar-H), 7.39-7.33 (overlapping signals, 6H, Ar-H), 5.76 (t, *J* = 7.3 Hz, 1H, H-3), 5.35-5.26 (overlapping signals, 2H, H-2 and H-4), 4.90 (d, *J* = 5.5 Hz, 1H, H-1), 4.44 (dd, *J* = 12.1, 4.3 Hz, 1H, H-5a), 4.00 (hept, *J* = 6.2 Hz, 1H, C*H*$(CH_3)_2$), 3.69 (dd, *J* = 12.1, 7.2 Hz, 1H, H-5b), 1.27 (d, *J* = 6.2 Hz, 3H, CH_3), 1.12 (d, *J* = 6.1 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 165.4, 165.1 (each C=O), 133.3, 133.2, 133.1, 129.9, 129.8, 129.8, 129.5, 129.3, 129.2, 128.4, 128.3 (Ar-C and CH), 98.6 (C-1), 71.7 (*C*H$(CH_3)_2$), 70.7 (C-2), 70.75 (C-3), 69.3 (C-4), 61.3 (C-5), 23.3 (CH_3), 21.7 (CH_3); IR (ATR) cm^{-1}: 2975, 1720, 1602, 1452, 1249, 1089, 1068, 1026, 705, 686; ESI-HRMS calcd for $C_{29}H_{28}O_8Na$ 527.1682, found *m/z* 527.1685 $[M+Na]^+$.

Anomerisation Reactions including Kinetics Experiments. Typically, the reactant (~30 mg) was dissolved in anhydrous CH_2Cl_2 to generate a 0.2 M solution which was then placed under nitrogen or argon. $SnCl_4$ (1.0 M in CH_2Cl_2) or $TiCl_4$ (1.0 M in CH_2Cl_2) was added at room temp, and the mixture was cooled to 4 °C or -30 °C or left to stir at room temperature (~20 °C). The mixture was left for 24 h before diluting with EtOAc and washing with 1.0 M $KHSO_4$ (for $SnCl_4$) or 1.0 M NH_4Cl (for $TiCl_4$). The aqueous layer was extracted with EtOAc

and the combined organic layers were washed with satd $NaHCO_3$ and brine, dried over Na_2SO_4 and then the solvent was removed under reduced pressure. For kinetics experiments, the reactant (0.068 mmol) was dried prior to the reaction, before dissolving in freshly distilled $CDCl_3$ (0.75 mL) and then placed in a 5 mm NMR tube. $SnCl_4$ (0.1 mL of an 0.34 M solution in $CDCl_3$) was then added and the concentration of the anomers was measured by ^{1}H-NMR spectroscopy at 25°C , usually over several days until equilibrium was attained. The reaction mixture was then diluted with EtOAc, washed with $KHSO_4$, satd. $NaHCO_3$, brine and dried over Na_2SO_4. This product was analysed by ^{1}H-NMR spectroscopy to obtain the ratio of products. The solvent was removed under reduced pressure and the resulting residue was subjected to column chromatography providing a sample of the axial anomer for analytical purposes, and also for determination of the isolated yield. The $CDCl_3$ used in the kinetic experiments was pre-distilled over phosphorus pentoxide and analysed for water content before use; usually the presence of H_2O can be detected by ^{1}H-NMR due to it having a signal at ~ δ 1.60 ppm. NMR tubes were dried in an oven before use. A fresh solution of $SnCl_4$ was prepared for each sample. The average integration of 2-3 signals in the NMR spectrums was used to determine the concentration of the α- and β-anomers during monitoring. The kinetics experiments were carried out in triplicate for each reactant and average *k*f+*k*r values and average ratios are reported in the manuscript.

Butyl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside 1α R_f 0.38 (cyclohexane- EtOAc 4:1); $[\alpha]_D^{20}$ -51.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (t, *J* = 9.8 Hz, 1H, H-3), 4.99 (d, *J* = 3.7 Hz, 1H, H-1), 4.99-4.91 (m, 1H, H-4), 4.79 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2), 3.77 (dd, *J* = 10.9, 5.9 Hz, 1H, H-5a), 3.69 (dt, *J* = 9.8, 6.5 Hz, 1H, OC*H*H), 3.62 (t, *J* = 10.8 Hz, 1H, H-5b), 3.39 (dt, *J* = 9.8, 6.5 Hz, 1H, OCH*H*), 2.17 (s, 3H, C(O)*C*H$_3$), 2.06 (s, 3H, C(O)*C*H$_3$), 2.03 (s, 3H, C(O)*C*H$_3$), 1.62-1.54 (overlapping signals, 2H, OCH$_2$C*H*$_2$), 1.44-1.34 (overlapping

signals, 2H, O(CH_2)CH_2), 0.93 (t, *J* = 7.4 Hz, 3H, CH_3);^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 170.1, 170.0 (each C=O), 95.6 (C-1), 71.2(C-2), 69.7 (C-3), 69.5 (C-4), 68.2 (C-5), 58.2 (OCH_2), 30.9 (OCH_2CH_2), 20.8, 20.7, 20.7 (each C(O)CH_3), 19.2 ($O(CH_2)_2CH_2$), 13.8 (CH_3); IR (ATR) cm^{-1}: 2922, 1741, 1369, 1223, 1078, 1058. 1030; ESI-HRMS calcd for $C_{15}H_{24}O_8Na$ 355.1369, found *m/z* 355.1368 $[M+Na]^+$.

Butyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranoside 2α R_f 0.27 (cyclohexane-EtOAc 7:1); $[\alpha]_D^{20}$ +71.13 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-7.95 (overlapping signals, 4H, Ar-H), 7.95-7.89 (overlapping signals, 2H, Ar-H), 7.55-7.49 (overlapping signals, 2H, Ar-H), 7.47-7.42 (m, 1H, Ar-H), 7.42-7.35 (overlapping signals, 4H, Ar-H), 7.34-7.28 (overlapping signals, 2H, Ar-H), 6.16 (t, *J* = 9.8 Hz, 1H, H-3), 5.39 (td, *J* = 10.1, 5.8 Hz, 1H, H-4), 5.28-5.23 (overlapping signals, 2H, H-1 and H-2), 4.07 (dd, *J* = 10.8, 5.9 Hz, 1H, H-5a), 3.87 (t, *J* = 10.8 Hz, 1H, H-5b), 3.78 (dt, *J* = 9.9, 6.4 Hz, 1H, OC*H*H), 3.45 (dt, *J* = 9.8, 6.5 Hz, 1H, OCH*H*), 1.65-1.51 (overlapping signals, 2H, OCH_2CH_2), 1.41-1.30 (overlapping signals, 2H, $O(CH_2)_2CH_2$), 0.84 (t, *J* = 7.3 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.85, 165.80, 165.63 (each C=O), 133.33, 133.28, 133.09, 129.85, 129.82, 129.68, 129.39, 129.16, 129.13, 128.41, 128.29, 128.28 (Ar-C and CH), 96.07 (C-1), 71.98 (C-2), 70.34 (C-4), 70.07 (C-3), 68.46 (OCH_2), 58.59 (C-5), 31.38 (OCH_2CH_2), 19.19 ($O(CH_2)_2CH_2$), 13.68 (CH_3); IR (ATR) cm^{-1}: 2951, 1719, 1252, 1094, 1043, 705, 687; ESI-HRMS calcd for $C_{30}H_{30}O_8Na$ 548.1838, found *m/z* 548.1833 $[M+Na]^+$.

Butyl 2,3,4-tri-*O*-acetyl-β-L-arabinopyranoside 3α R_f 0.48 (2:3 EtOAc-cyclohexane); $[\alpha]_D^{20}$ +150.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.37-5.33 (overlapping signals, 2H, H-3 and H-4), 5.15 (dd, *J* = 9.9, 3.5 Hz, 1H, H-2), 5.07 (d, *J* = 3.6 Hz, 1H, H-1), 3.96 (dd, *J* = 13.2, 1.2 Hz, 1H, H5a), 3.72-3.64 (overlapping signals, 2H, H-5b and OC*H*H), 3.40 (dt, *J* = 9.7, 6.5 Hz, 1H, OCH*H*), 2.14 (s, 3H, C(O)CH_3), 2.07 (s, 3H, C(O)CH_3), 2.01 (s, 3H, C(O)CH_3), 1.61-1.53 (overlapping signals, 2H, OCH_2CH_2), 1.44-1.34 (overlapping signals,

2H, O(CH_2)CH_2), 0.93 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 170.4, 170.1 (each C=O), 96.3 (C-1), 69.2 (C-3), 68.5 (C-5), 68.2 (C-2), 67.3 (C-4), 60.3 (O*C*H_2), 31.4 (OCH_2*C*H_2), 20.9, 20.8, 20.7 (each C(O)CH_3), 19.2 (O(CH_2)*C*H_2), 13.7 (CH_3); IR (ATR) cm^{-1}: 2961, 1740, 1371, 1217, 1062; ESI-HRMS calcd for $C_{15}H_{28}O_8N$ 350.1815, found *m/z* 350.1820 $[M+NH_4]^+$.

Butyl 2,3,4-tri-*O*-benzoyl-β-L-arabinopyranoside 4α R_f 0.31 (cyclohexane-EtOAc 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12-8.08 (overlapping signals, 2H, Ar-H), 8.00-7.97 (m, 1H, Ar-H), 7.89-7.82 (overlapping signals, 2H, Ar-H), 7.62-7.57 (m, 1H, Ar-H), 7.54-7.42 (overlapping signals, 4H, Ar-H), 7.41-7.36 (overlapping signals, 2H, Ar-H), 7.29-7.25 (overlapping signals, 3H, Ar-H), 5.94 (dd, *J* = 10.7, 3.6 Hz, 1H, H-3), 5.75 (dt, *J* = 3.5, 1.6 Hz, 1H, H-4), 5.71 (dd, *J* = 10.7, 3.6 Hz, 1H, H-2), 5.32 (d, *J* = 3.5 Hz, 1H, H-1), 4.21 (dd, *J* = 13.2, 1.4 Hz, 1H, H-5a), 3.95 (dd, *J* = 13.1, 2.0 Hz, 1H, H-5b), 3.79 (dt, *J* = 9.8, 6.4 Hz, 1H, OC*H*H), 3.47 (dt, *J* = 9.8, 6.5 Hz, 1H, OCH*H*), 1.63-1.56 (overlapping signals, 2H, OCH_2CH_2), 1.44-1.34 (overlapping signals, 2H, O(CH_2)$_2$CH_2), 0.86 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 165.8, 165.6 (each C=O), 133.3, 133.3, 133.1, 129.8, 129.8, 129.7, 129.3, 129.3, 128.5, 128.5, 128.4, 128.3, 128.3 (Ar-C and CH), 96.8 (C-1), 70.3 (C-4), 69.5 (C-2), 68.4 (OCH_2), 68.1 (C-3), 60.5 (C-5), 31.4 (OCH_2*C*H_2), 19.2 (O(CH_2)$_2$*C*H_2), 13.7 (CH_3); IR (ATR) cm^{-1}: 2959, 1719, 1451, 1248, 1092, 1068, 1026, 705, 686; ESI-HRMS calcd for $C_{30}H_{34}O_8N$ 536.2284, found *m/z* 536.2285 $[M+NH_4]^+$.

Butyl 2,3,4-tri-*O*-acetyl-α-L-fucopyranoside 5α *Rf* 0.41 (cyclohexane-EtOAc 2:1); $[\alpha]_D^{20}$ -134.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.36 (dd, *J* = 10.7, 3.4 Hz, 1H, H-3), 5.30 (d, *J* = 3.3 Hz, 1H, H-4), 5.10 (dd, *J* = 10.8, 3.8 Hz, 1H, H-2), 5.05 (d, *J* = 3.6 Hz, 1H, H-1), 4.16 (q, *J* = 6.5 Hz, 1H, H-5), 3.68 (dt, *J* = 9.8, 6.5 Hz, 1H, OC*H*H), 3.41 (dt, *J* = 9.8, 6.5 Hz, 1H, OCH*H*), 2.16 (s, 3H, C(O)CH_3), 2.07 (s, 3H, C(O)CH_3), 1.99 (s, 3H, C(O)CH_3), 1.61-1.52 (overlapping signals, 2H, OCH_2CH_2), 1.43-1.33 (overlapping signals, 2H, O(CH_2)$_2$CH_2), 1.14

(d, *J* = 6.6 Hz, 3H, CH_3), 0.93 (t, *J* = 7.4 Hz, 3H, CH_2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 170.5, 170.1 (each C=O), 96.0 (C-1), 71.2 (C-4), 68.4 (C-2), 68.2, 68.1 (overlapping signals, C-3 and OCH_2), 64.2 (C-5), 31.4 (OCH_2CH_2), 20.8, 20.7, 20.7 (each $C(O)CH_3$), 19.2 ($O(CH_2)_2CH_2$), 15.9 (CH_3), 13.7 (CH_2CH_3); IR (ATR) cm^{-1}: 2917, 1743, 1371, 1220, 1048; ESI-HRMS calcd for $C_{16}H_{26}O_8Na$ 369.1525, found *m/z* 369.1522 $[M+Na]^+$.

Butyl 2,3,4-tri-*O*-benzoyl-α-L-fucopyranoside 6α R_f 0.41 (cyclohexane-EtOAc 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13-8.08 (overlapping signals, 2H, Ar-H), 8.01-7.96 (overlapping signals, 2H, Ar-H), 7.82-7.77 (overlapping signals, 2H, Ar-H), 7.65-7.59 (m, 1H, Ar-H), 7.50 (overlapping signals, 3H, Ar-H), 7.45-7.40 (m, 1H, Ar-H), 7.40-7.35 (overlapping signals, 2H, Ar-H), 7.26-7.21 (overlapping signals, 2H, Ar-H), 5.96 (dd, J = 10.7, 3.5 Hz, 1H, H-3), 5.76 (dd, J = 3.5, 1.3 Hz, 1H, H-4), 5.64 (dd, J = 10.7, 3.7 Hz, 1H, H-2), 5.32 (d, J = 3.7 Hz, 1H, H-1), 4.43 (qd, J = 6.5, 1.2 Hz, 1H, H-5), 3.78 (dt, J = 9.8, 6.4 Hz, 1H, OC*H*H), 3.48 (dt, J = 9.9, 6.5 Hz, 1H, OCH*H*), 1.62-1.56 (overlapping signals, 2H, OCH_2CH_2), 1.44-1.33 (overlapping signals, 2H, $O(CH_2)_2CH_2$), 1.28 (d, J = 6.6 Hz, 3H, CH_3), 0.86 (t, J = 7.4 Hz, 3H, CH_2CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 166.0, 165.7 (each C=O), 133.3, 133.2, 133.0, 129.9, 129.8, 129.6, 129.6, 129.5, 129.4, 129.4, 128.5, 128.5, 128.3, 128.2 (each Ar-C and CH), 96.5 (C-1), 72.1 (C-4), 69.4 (C-2), 68.9 (C-3), 68.4 (OCH_2), 64.8 (C-5), 31.5 (OCH_2CH_2), 19.2 ($O(CH_2)_2CH_2$), 16.1 (CH_3), 13.7 (CH_2CH_3); IR (ATR) cm^{-1}: 2959, 1721, 1452, 1261, 1095, 1026, 706, 686; ESI-HRMS calcd for $C_{31}H_{36}O_8N$ 550.2441, found *m/z* 550.2443 $[M+NH_4]^+$.

Butyl 2,3,4-tri-*O*-benzoyl-1-thio-β-L-arabinopyranoside 9α R_f 0.23 (cyclohexane-EtOAc 12:1); $[\alpha]_D^{20}$ +239.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12-8.06 (overlapping signals, 2H, Ar-H), 7.64-7.57 (m, 1H, Ar-H), 7.56-7.43 (overlapping signals, 4H, Ar-H), 7.43-7.36 (overlapping signals, 2H, Ar-H), 7.32-7.23 (overlapping signals, 2H, Ar-H), 5.90-5.85 (overlapping signals, 2H, H-1 and H-2), 5.80 (dd, *J* = 10.1, 3.1 Hz, 1H, H-3), 5.74 (dt, *J* = 3.5, 1.9 Hz, 1H, H-4), 4.57 (dd, *J* = 13.2, 1.5 Hz, 1H, H-5a), 3.98 (dd, *J* = 13.2, 2.5 Hz,

1H, H-5b), 2.66-2.54 (overlapping signals, 2H, SCH_2), 1.65-1.52 (overlapping signals, 2H, SCH_2CH_2), 1.45-1.32 (overlapping signals, 2H, $S(CH_2)_2CH_2$), 0.88 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 165.7, 165.4 (each C=O), 133.4, 133.4, 133.2, 129.9, 129.9, 129.7, 129.6, 129.2, 129.1, 128.5, 128.5, 128.3 (each C=O), 83.2 (C-1), 69.8 (C-4), 69.3 (C-2), 68.5 (C-3), 60.9 (C-5), 31.6 (SCH_2CH_2), 30.0 (SCH_2), 21.9 ($S(CH_2)_2CH_2$), 13.6 (CH_3); IR (ATR) cm^{-1}: 2958, 1720, 1451, 1249, 1068, 1025, 703, 686; ESI-HRMS calcd for $C_{30}H_{34}O_7SN$ 552.2056, found *m/z* 552.2057 $[M+NH_4]^+$.

Butyl 2,3,4-Tri-*O*-benzoyl-1-thio-α-L-fucopyranoside 10α R_f 0.28 (cyclohexane-EtOAc 10:1); $[\alpha]_D^{20}$ -212.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15-8.08 (overlapping signals, 2H, Ar-H), 8.02-7.94 (overlapping signals, 2H, Ar-H), 7.84-7.75 (overlapping signals, 2H, Ar-H), 7.63-7.59 (m, 1H, Ar-H), 7.54-7.46 (overlapping signals, 3H, Ar-H), 7.45-7.34 (overlapping signals, 3H, Ar-H), 7.26-7.21 (overlapping signals, 2H, Ar-H), 5.93 (d, *J* = 3.9 Hz, 1H, H-1), 5.85-5.78 (overlapping signals, 2H, H-2 and H-3), 5.78-5.71 (m, 1H, H-4), 4.77 (q, *J* = 6.4 Hz, 1H, H-5), 2.68-2.59 (m, 1H, SC*H*H), 2.56 (dt, *J* = 12.9, 7.4 Hz, 1H, SCH*H*), 1.68-1.56 (overlapping signals, 2H, SCH_2CH_2), 1.42-1.34 (overlapping signals, 2H, $S(CH_2)CH_2$), 1.30 (d, *J* = 6.6 Hz, 3H, CH_3), 0.88 (t, *J* = 7.4 Hz, 3H, $S(CH_2)_3CH_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 165.8, 165.5 (each C=O), 133.4, 133.3, 133.1, 129.9, 129.7, 129.4, 129.2, 129.2, 128.6, 128.4, 128.2 (Ar-C and CH), 82.9 (C-1), 71.8 (C-4), 69.4, 69.0 (C-2 and C-3), 65.3 (C-5), 31.7 (SCH_2CH_2), 30.1 (SCH_2), 21.9 ($S(CH_2)_2CH_2$), 16.1 (CH_3), 13.6 $S(CH_2)_3CH_3$); IR (ATR) cm^{-1}: 2957, 1721, 1451, 1257, 1095, 1068, 1026, 704, 686; ESI-HRMS calcd for $C_{31}H_{32}O_7SNa$ 571.1766, found *m/z* 571.1767 $[M+Na]^+$.

Isopropyl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside 12α R_f 0.46 (cyclohexane-EtOAc 2:1); $[\alpha]_D^{20}$ +132.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (t, *J* = 9.8 Hz, 1H, H-3), 5.11 (d, *J* = 3.6 Hz, 1H, H-1), 4.95 (td, *J* = 10.0, 6.1 Hz, 1H, H-4), 4.74 (dd, *J* = 10.2, 3.7 Hz, 1H, H-2), 3.84 (hept, *J* = 6.3 Hz, 1H, $CH(CH_3)_2$), 3.78-3.67 (overlapping signals, 2H, H-5a and H-

5b), 2.06 (s, 3H, C(O)CH_3), 2.03 (s, 6H, 2 x C(O)CH_3), 1.24 (d, *J* = 6.3 Hz, 3H, CH_3), 1.11 (d, *J* = 6.3 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 170.1, 170.0 (each C=O), 93.9 (C-1), 71.2 (C-2), 70.7 (C*H*(CH_3)$_2$), 69.7, 69.6 (C-3 and C-4), 58.2 (C-5), 23.1, 21.4 (each CH_3), 20.8, 20.7, 20.7 (each C(O)*C*H_3); IR (ATR) cm^{-1}: 2976, 1743, 1367, 1214, 1038; ESI-HRMS calcd for $C_{14}H_{26}O_8N$ 336.1658, found *m/z* 336.1660 $[M+NH_4]^+$.

Isopropyl 2,3,4-tri-*O*-benzoyl- α-D-xylopyranoside 13α R_f 0.35 (cyclohexane-EtOAc 6:1); $[\alpha]_D^{20}$ +77.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.96 (overlapping signals, 4H, Ar-H), 7.95-7.92 (overlapping signals, 2H, Ar-H), 7.54-7.49 (overlapping signals, 2H, Ar-H), 7.47-7.43 (m, 1H, Ar-H), 7.41-7.36 (overlapping signals, 4H, Ar-H), 7.34-7.30 (overlapping signals, 2H, At-H), 6.15 (t, *J* = 9.9 Hz, 1H, H-3), 5.39 (dd, *J* = 10.2, 6.0 Hz, 1H, H-4), 5.37 (d, *J* = 3.8 Hz, 1H, H-1), 5.21 (dd, *J* = 10.1, 3.8 Hz, 1H, H-2), 4.06 (dd, *J* = 10.8, 5.9 Hz, 1H, H-5a), 3.98-3.87 (overlapping signals, 2H, H-5a and C*H*(CH_3)$_2$), 1.28 (d, *J* = 6.2 Hz, 3H, CH_3), 1.07 (d, *J* = 6.1 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 165.8, 165.7 (each C=O), 133.3, 133.3, 133.1, 129.8, 129.8, 129.7, 129.4, 129.2, 129.2, 128.4, 128.4, 128.3 (Ar-C and CH), 94.6 (C-1), 72.0 (C-2), 71.4 (*C*H(CH_3)$_2$), 70.4 (C-4), 70.1 (C-3), 58.7 (C-5), 23.3, 21.7 (each CH_3); IR (ATR) cm^{-1}: 2980, 1719, 1602, 1454, 1275, 1253, 1096, 1038, 705, 688; ESI-HRMS calcd for $C_{29}H_{32}O_8N$ 522.2128, found *m/z* 522.2128 $[M+NH_4]^+$.

Acknowledgements

This publication has emanated from research supported by Science Foundation Ireland (SFI, grant number 12/IA/1398) and is co-funded under the European Regional Development Fund under Grant Number 14/SP/2710.

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