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Synthesis of disaccharides containing α-linked GlcNAc or β-linked ManNAc units

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Abstract—The synthesis of disaccharides containing α-linked GlcNAc or β-linked ManNAc units from shelf-stable, and yet highly reactive, 2-oximinoglycosyl donors is described. Access to a preponderance of the disaccharides containing either the α-linked GlcNAc or β-linked ManNAc unit can be obtained by careful choice of solvent and glycosidation conditions.

1. Introduction

β-Linked ManNAc units are integral parts of a number of bacterial capsular polysaccharides and lipopolysaccharides[1] and α-linked GlcNAc units are common structural features of glycoproteins and proteoglycans.[2] However, since both units contain *cis*-1,2 linkages, which are sterically less favoured than *trans*-1,2 linkages, they are generally difficult to synthesise.[3] Moreover, traditional neighbouring group participation strategies, which are commonly employed for the synthesis of β-linked gluco and galactopyranoside structures, cannot be used for the synthesis of these units since they favour formation of the epimeric α-ManNAc and β-GlcNAc units. New, efficient methods for synthesising these units are therefore required. One useful method for synthesising β-ManNAc units, as outlined by Lichtenthaler and co-workers is of particular relevance to our work.[4] 2-Oximinoglycosyl halide donors are used in this strategy and are typically activated with silver catalysts under Koenigs–Knorr conditions. However, often prolonged reaction times of 1–2 days are required for optimum yields, and the method has so far only been exploited for the synthesis of oligosaccharides containing β-ManNAc units. We now wish to report in full[5] our recent investigations in this area which have utilised 2-oximinothioglycosides as highly reactive, and yet shelf stable β-D-mannosaminyl or α-D-glucosaminyl donors.

2. Results and discussion

The ultimate aim of this current research programme is to develop methods for the synthesis of branched oligosaccharides containing β-ManNAc and α-GlcNAc residues. Orthogonally protected 2-oximino thioethyl and phenyl selenide donors were selected as key intermediates for this strategy since it was envisaged that the C-2 acetamido functionality could be introduced by a stereoselective reduction of the oxime functionality. Moreover, literature precedence suggested that the thioethyl and phenyl selenide donors would be stable to a range of reaction conditions, but would be readily activated to generate reactive intermediates when glycosidation was required.[6] A cyclic benzylidene acetal was selected to protect both the C-4 secondary alcohol and the C-6 primary alcohol in a rigid chair conformation. This is because the benzylidene group gives stable protection throughout the synthesis and yet should allow subsequent selective access to either the C-4 or C-6 acceptors using sodium cyanoborohydride–HCl[7] or a borane–THF complex, with a suitable Lewis acid[8] respectively.

In theory, a whole range of oxime donors could be utilised in our protocol. Initial attention focussed on the synthesis and use of benzyl oxime (**1**). This was synthesised from diol (**2**)[9] via a series of standard, high yielding transformations (Scheme 1). Thus regioselective protection of the C-2, C-3 diol (**2**) to afford the C-3 acetylated alcohol (**3**) was achieved chemically, using sodium hydride, acetyl chloride and copper chloride,[10] or enzymically, using vinyl acetate and a Lipase enzyme.[11] Oxidation of alcohol (**3**) to the corresponding ulose (**4**) proceeded smoothly via a Swern-type oxidation[12] and subsequent reaction of (**4**) with *O*-benzylhydroxylamine[13] (Scheme 1) afforded the required

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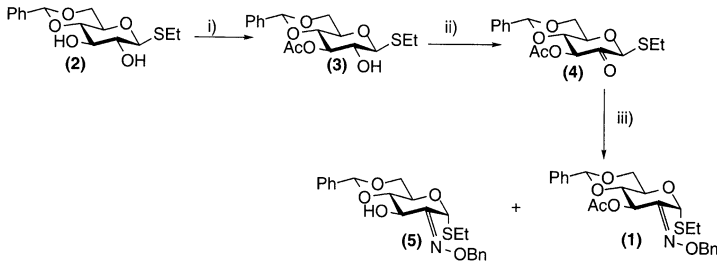


Scheme 1. (i) NaH, $CuCl_2$, AcCl, THF, 76% or vinyl acetate, *candida cylindracea* lipase (CCL), THF, 45°C, 96%; (ii) DMSO, TFAA, TEA, DCM; (iii) NH_2OBn, EtOH, 50°C, (**1**) 12% over 2 steps, (**5**) 10% over 2 steps.

oxime (**1**), together with some of the C-3 deprotected oxime (**5**).

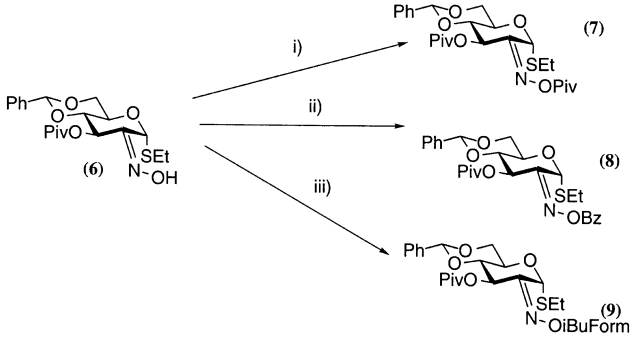
Initially, isolation of the ulose (**4**) was attempted prior to oxime formation. However, literature reports suggested similar ulose derivatives were unstable[14] and in fact we were unable to isolate (**4**), or anything of consequence following column chromatography on silica gel. In subsequent approaches (**4**) was not purified but added as an ethanolic solution to *O*-benzylhydroxylamine and allowed to stir at ambient temperature for 21 h. Since the reaction was sluggish, the reaction temperature was raised to 50°C for 3 h then allowed to cool to room temperature overnight. Although heating appeared to slightly aid progress, under these forcing conditions two product spots arose by TLC. Chromatography allowed isolation of the two products and ^{1}H NMR showed them to be the required oxime (**1**) and the C-3 deacetylated oxime (**5**), in yields of 12 and 10%, respectively, with no other sugar material isolated. The latter product is a result of the acetate being susceptible to base hydrolysis with *O*-benzylhydroxylamine. The anomeric stereochemistry and *Z*-oxime bond geometry of (**1**) were initially tentatively assigned through nOe NMR studies, the results of which are shown in Table 1.

Table 1.

Irradiated proton(s) in (**1**)	nOe
H-1	SCH_2CH_3 (vs), SCH_2CH_3 (vs), H-4 (s), H-5 (m), $PhCH_2$ (m), H-3 (w)
H-3	H-4 (vs), H-5 (vs), H-1 (w)

The very weak nOe between H-1 and H-3 compared with the very strong nOe between H-3 and H-4 and H-5 suggests the anomeric centre displays α-stereochemistry. The lack of nOe between H-3 and $PhCH_2$–ON, along with the nOe seen between H-1 and $PhCH_2$–ON suggests the oxime lies in the *Z*-geometry. There is further literature precedence to suggest that the *Z*-configuration is displayed by the oximes. Thus Beynon et al.[13] and Lemieux et al.[15] have reported that an equatorial hydrogen at C-1 will be deshielded by a *Z*-oxime at C-2, resulting in a downfield shift in the ^{1}H NMR for the proton at C-1. Comparisons with further oxime derivatives (**6**)–(**12**) (vide infra) (for which, in the majority of cases, X-ray data have unambiguously allowed assignments of the oximes as existing in the α-*Z*-conformations), also showed similar nOe and deshielding characteristics for H-1.

Considering the lability of the acetate protecting group in (**4**) and (**1**) to the oxime formation conditions, a range of alternative derivatives were prepared. The more robust C-3 *O*-Piv oxime (**6**) was prepared in 68% using a similar selective protection/oxidation/derivatisation strategy from diol (**2**). The oxime (**6**) was then protected using trimethylacetyl chloride (PivCl), BzCl or isobutyl chloroformate (IBCF) to give the pivaloate (**7**) (94%), benzoate (**8**) (82%) or isobutyl formate (**9**) (68%) derivatives respectively (Scheme 2).



Scheme 2. (i) PivCl, Pyr., DCM, 0–40°C, 94%; (ii) BzCl, Pyr., DCM, 0°C–rt, 82%; (iii) IBCF, Pyr., DCM, 0°C–rt, 68%.

The assignments of oxime bond geometry and anomeric stereochemistry were made in the same fashion as for (**1**) and (**5**). X-ray analysis confirmed that (**7**) and (**8**) displayed the α-*Z*-oxime conformation, and, in addition, a large positive $[\alpha]_D$ was noted in each case (Fig. 1)

Following the success of preparing oxime (**6**) in good yield by treating the ketone (**13**) with hydroxylamine hydrochloride and sodium acetate, the possibility of preparing benzyl oxime (**10**) and alkyl oximes (**11**) and (**12**) from ketone (**13**) using the hydrochloride salt of the protected hydroxylamines was investigated. To our delight we were successfully able to synthesise the benzyl (**10**) (43%), ethyl (**11**) (54%) and methyl (**12**) (66%) protected oximes in good yield as crystalline compounds (Scheme 3).

X-Ray analysis again confirmed the α-*Z*-oxime structure to be present for (11) and (12) (Fig. 2).

Thus from these results it appears that the oximes are consistently formed as the α-*Z*-conformers. Presumably, the steric bulk of the equatorial protecting group at C-3 influences formation of the *Z*-oximes in preference to the *E*-oximes. Epimerisation of the anomeric centre is likely to

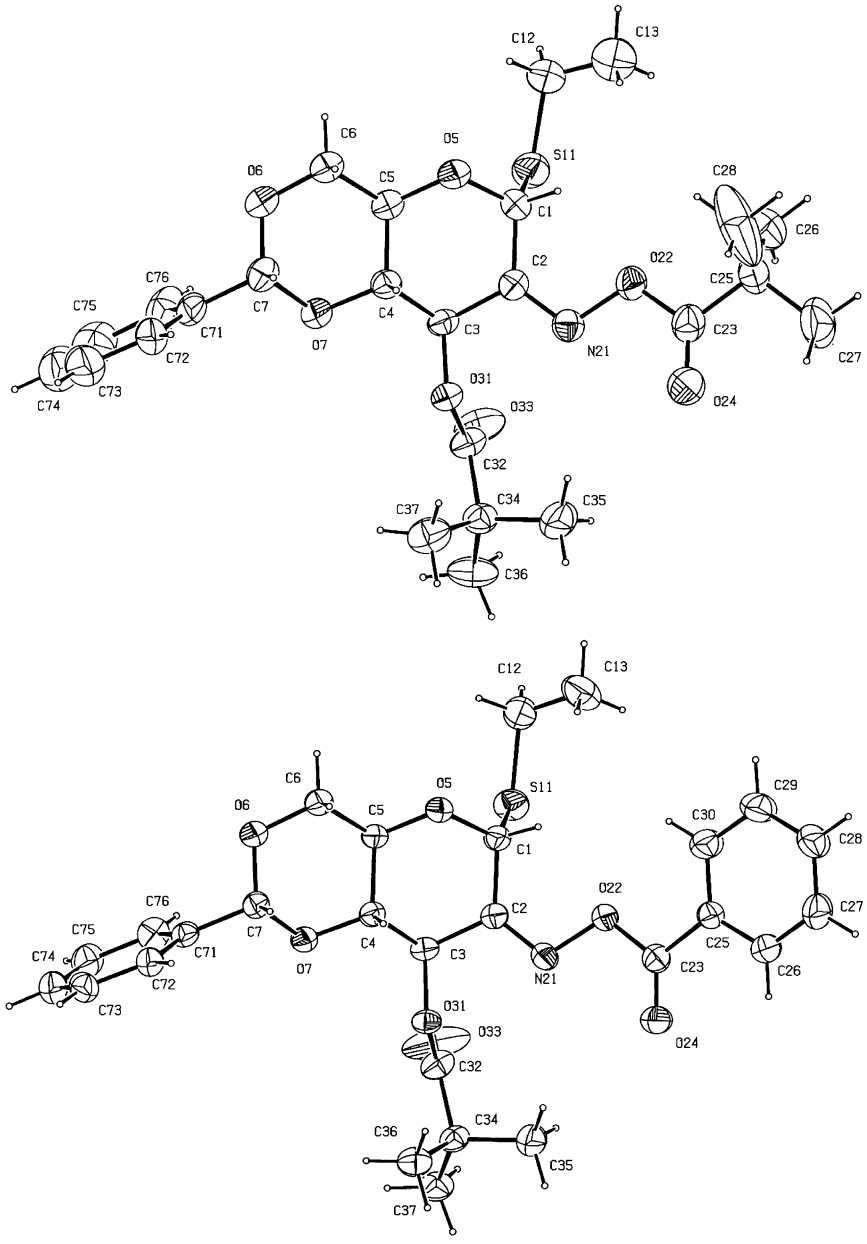
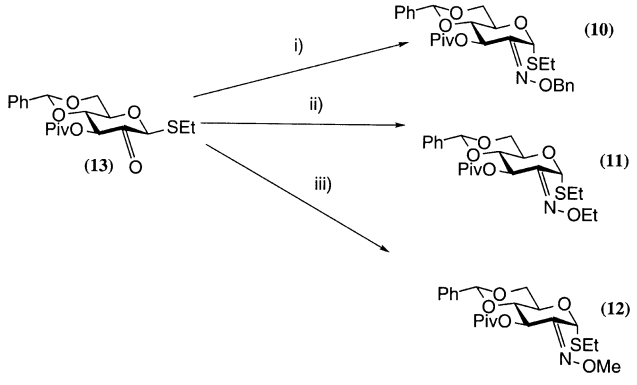


Figure 1. The structure of **7** and **8** with ellipsoids shown at 20% probability.



Scheme 3. (i) $BnONH_2$·HCl, NaOAc, H_2O, EtOH, 50°C, 43%; (ii) $EtONH_2$·HCl, NaOAc, H_2O, EtOH, 50°C, 54%; (iii) $MeONH_2$·HCl, NaOAc, H_2O, EtOH, 50°C, 66%.

take place under the moderately high temperature and strongly acidic conditions (50°C, pH 1–3) used for the oxime preparation step.

Reaction of ulose (**13**) with an instant ylid reagent ($MePPh_3Br$, $NaNH_2$, 3 equiv.) under refluxing conditions in anhydrous THF followed by column chromatography and recrystallisation yielded alkene (**14**) (Scheme 4). The α-anomeric stereochemistry was presumed from the large positive $[\alpha]_D$ (+160.0) and characteristic coupling constant for H-3/H-4 of 10.0 Hz. The α-stereochemistry was later confirmed by X-ray analysis. Epimerisation of the anomeric centre is presumably a result of the instant ylid reagent mediating the ketone–enol tautomerism process under refluxing conditions (Fig. 3).

The feasability of synthesising orthogonally protected

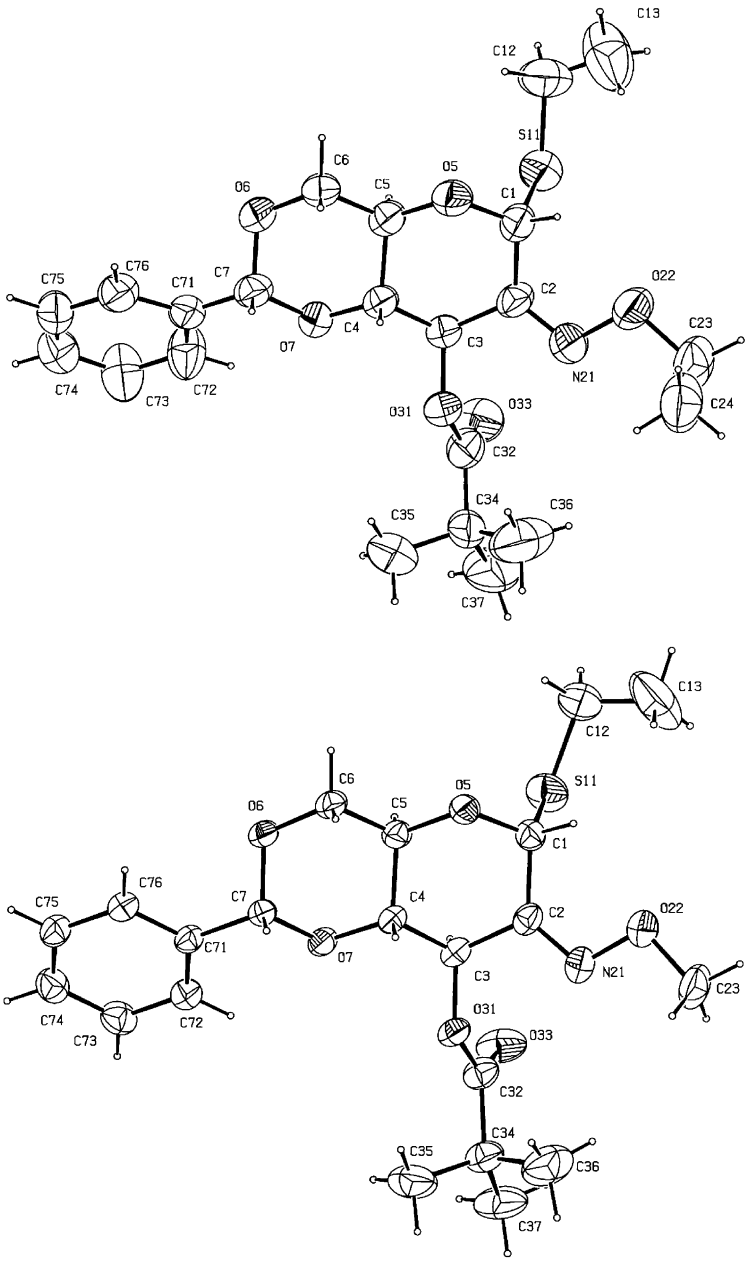
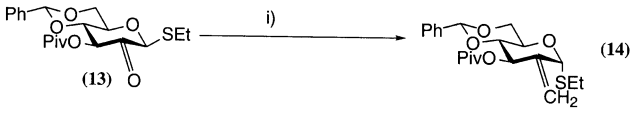


Figure 2. The structure of **11** and **12** with ellipsoids shown at 20% probability.

2-oximino phenylselenyl donors was also investigated. Thus, treatment of the diol (**15**) with sodium hydride, copper chloride and pivaloyl chloride afforded the regioselective protected C-3 *O*-Piv alcohol (**16**) in 44% yield.[11] However, subsequent oxidation under Swern conditions[12] followed by oxime formation with hydroxylamine hydrochloride and sodium acetate, resulted in an unexpected competitive reduction at the anomeric position. This afforded only 14% of the desired 2-oximino phenylselenyl donor (**17**) together with 50% of the anhydro oxime (**18**) (Scheme 5).



Scheme 4. (i) $MePPh_3Br$, $NaNH_2$, THF, heat, 48%.

Having prepared a range of 2-oximino donors, their utility in a range of glycosidation reactions was investigated. It was hoped that by altering reaction conditions, stereoselective entry to 2-oximino disaccharides would prove possible, and that such compounds would serve as useful precursors to disaccharides containing either α-linked GlcNAc or β-linked ManNAc units.

2.1. Investigation of the utility of oximino donors in glycosidation reactions

2.1.1. Glycosidation studies using NIS/TfOH and a range of sugar acceptors.[15] Initial attention focused upon the use of 2-oximino thioethyl donors (**7**), (**8**), (**11**) and (**14**) and monosaccharide acceptors (**19**)–(**22**) in the glycosidation reactions (Fig. 4).

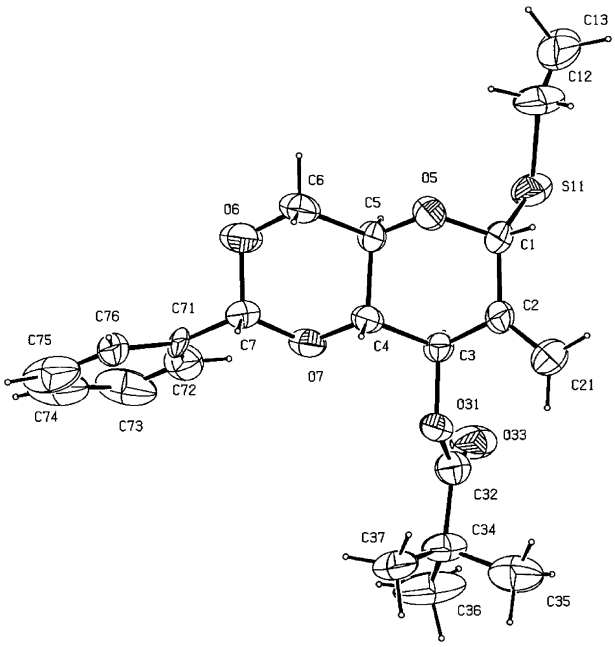


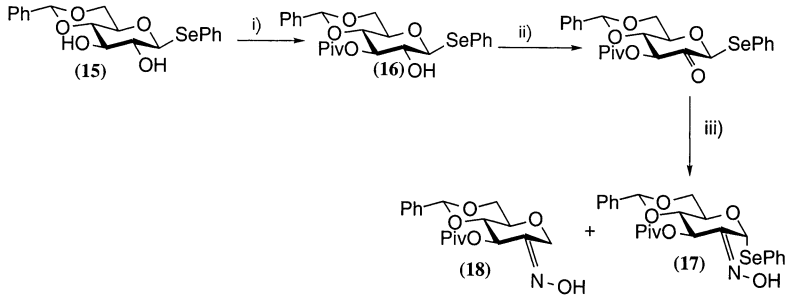
Figure 3. The structure of **14** with ellipsoids shown at 20% probability.

The C-6 acceptor (**19**) and C-4 acceptor (**21**) were both prepared from methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside, according to a literature procedure.[17] The C-3 acceptor (**20**) was synthesised from phenyl 4,6-*O*-benzylidene-α-D-glucopyranoside, using a Lipase-mediated regioselective protection.[10] The C-4 acceptor (**22**) was kindly donated by Dextra Laboratories for use in our studies. The glycosyl donors were activated at low temperature (−30°C) with the well documented reagent combination of NIS/TfOH, using anhydrous DCM as solvent.[16] The results obtained from the glycosidation reactions are highlighted in Fig. 5 and Table 2.

Table 2.

Donor	Acceptor	Disaccharide	Yield	α:β
(**7**)	(**19**)	(**23**)	51	6:1
(**7**)	(**20**)	(**24**)	57	5:1
(**7**)	(**21**)	(**25**)	64	1:1.5[a]
(**7**)	(**22**)	(**26**)	57	2.5:1
(**8**)	(**19**)	(**27**)	72	25:1
(**8**)	(**20**)	(**28**)	45	2:1
(**11**)	(**20**)	(**29**)	73	1.7:1

[a] Anomers remained inseparable by column chromatography.



Scheme 5. (i) NaH, $CuCl_2$, PivCl, THF, 44%; (ii) DMSO, TFAA, TEA, DCM; (iii) $NH_2OH{\cdot}HCl$, NaOAc, EtOH, H_2O, 60°C (**17**) 14%, (**18**) 50% over 2 steps.

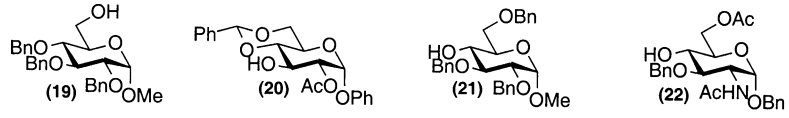


Figure 4.

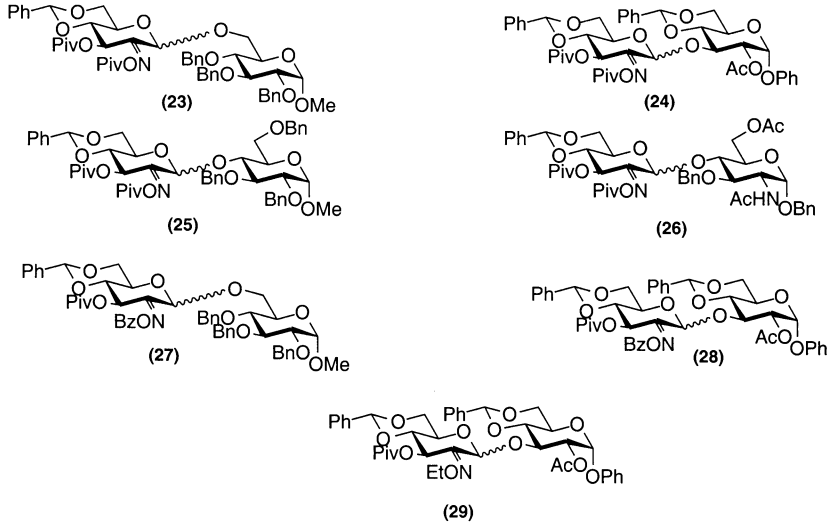


Figure 5.

In most cases the anomeric disaccharide products were separable by careful column chromatography on silica gel. An indication of the stereochemistry of the separated oxime disaccharides was obtained by reference to the literature. Thus for similar oxime disaccharides, it has been reported that H-1 for the α-anomers generally occur at lower field than for the β-anomers. This is due to the greater deshielding effect of the adjacent *Z*-oxime's oxygen.[13,15] It has also been reported by Lichtenthaler et al.[4] that β-oximinoglycosides show distinctly lower $J_{H\text{-}3/H\text{-}4}$ values ($J_{H\text{-}3/H\text{-}4}$=3–6 Hz) than their α-oximinoglycoside counterparts. This phenomenon is attributed to substantial flattening of the $^4C_1$ conformation around the anomeric centre of the β-anomer so that the pyranose ring can accommodate both the aglycone and the bulky oximino substituent. Although $J_{H\text{-}3/H\text{-}4}$ values for β-linked disacharides prepared in this work were higher than for values reported by Lichtenthaler ($J_{H\text{-}3/H\text{-}4}$=8–8.5 Hz), the coupling constants showed the same general trend to that reported in the literature, with β-linked disaccharides having smaller coupling constants than their isomeric α-linked disaccharides. Additional support for the assignment of stereochemistry is provided by a less positive and sometime negative $[\alpha]_D$ value generally being recorded for the β-oximinoglycosides compared to the α-oximinoglycosides. This phenomenon has been reported by Lemieux et al.[15] and Lichtenthaler et al.[4] Moreover, further evidence for stereochemistry assignment and *Z*-geometry could sometimes be gained from nOe data (Table 3).

Table 3.

Disaccharide	Irradiated proton	nOe
26α	H-1	(CH_3)$_3$CCO–ON (s), H-4 (s)
26α	H-3	H-4 (w), H-5 (m)
26β	H-1	(CH_3)$_3$CCO–ON (m), H-5 (m), H-3 (w)
26β	H-3	H-5 (m), H-4 (m) H-1 (w)
27α	H-1	CH_3O (w), H-4′ (w), H-6′ (s/w), H-4 (w), H-5 (w), H-1′ (w), H-3 (w), *Ph*CO–ON (s)
27α	H-3	CH_3O (w), H-4′ (w), H-4 (s), H-5 (s), ArCH_2 (w), H-1 (w),
27β	H-1	H-3 (m)
27β	H-3	H-5 (m), H-4 (w)

Examination of all of the analytical data indicated that formation of the α-disaccharides was generally favoured under the NIS/TfOH conditions, in DCM, as previously outlined in Table 2. Whilst little difference in yield and stereoselectivity was seen with the pivaloyl and benzoyl oximes (**7**) and (**8**), the ethyl oxime (**11**) yielded a slightly lower ratio of α-linked disaccharide, but in an enhanced yield. Disappointingly, the C-2 alkene oxime (**14**) afforded a complex mixture of products for which no positive identification of disaccharide products could be made from the ^{1}H NMR of the crude mixture. In order to investigate the utility of phenyl selenyl donors in our strategy, the 2-oximino phenyl selenyl donor (**17**) was converted to the respective pivaloyl oxime by treatment with pivaloyl chloride and pyridine, in 80% yield. This donor was then utilised in a NIS/TfOH mediated glycosidation reaction with acceptor (**19**). In this case the anomeric disaccharides (**23**α,β) were formed in 57% but as a 1:1 mixture of epimers. Considering the low yielding synthesis of the phenyl selenyl donor (**17**) and the lack of selectivity in the glycosidation reaction, the phenyl selenyl donors were abandoned in favour of the thioethyl donors.

That α-linked products are generally favoured upon activation of oximes (**7**) and (**8**) in DCM is in agreement with the involvement of an oxonium ion intermediate, and the influence of the anomeric effect. It is known that 'participating solvents' such as MeCN can greatly influence the stereoselectivity of such glycosidation reactions.[18] Therefore a range of the NIS/TfOH activated reactions were repeated at low temperature (−30°C) but using MeCN as solvent (Table 4).

Table 4.

Donor	Acceptor	Disaccharide	Yield (%)	α:β
(**7**)	(**19**)	(**23**)	75	1:1.4
(**7**)	(**20**)	(**24**)	88	1:3
(**7**)	(**21**)	(**25**)	54	1:3

Pleasingly, in all investigated cases, it proved possible to alter the stereoselectivity of the reaction in favour of the β-anomer. The isolated yields of disaccharides remained good to excellent.

2.1.2. Glycosidation studies using phenylsulfenyl triflate, S_N2 displacement with inversion of configuration of α-oximino triflate donors.[18] We were also interested to see whether Crich's excellent method[19] for synthesising β-linked saccharides, using α-mannosyl triflate donors, was compatible with our thioethyl oxime donors. Again, a range of donors (**7**), (**8**), (**12**) and (**14**) with varying electronic and steric properties were selected to react with monosaccharide acceptors (**19**)–(**21**). Reactions were performed at −55°C in a solvent mixture of DCM/Et_2O (1:1). In this way, entry to the oxime disaccharides (**23**)–(**25**), (**27**), (**28**) and (**30**) was achieved, the structures of which are depicted in Figs. 5 and 6. Yields and selectivities of disaccharides obtained in this way are displayed in Table 5.

The results gained showed that in situ generation of phenylsulfenyl triflate (PhSOTf) from silver triflate (AgOTf) and

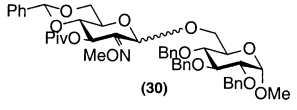
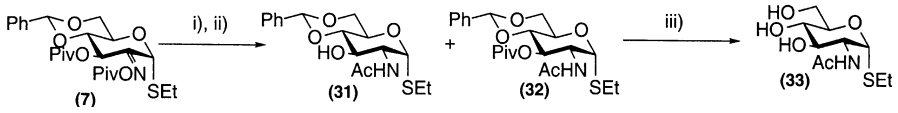


Figure 6.

Table 5.

Donor	Acceptor	Disaccharide	Yield	α:β
(**7**)	(**19**)	(**23**)	72	5:1
(**7**)	(**20**)	(**24**)	71	1:3
(**7**)	(**21**)	(**25**)	0	–
(**8**)	(**19**)	(**28**)	16	5:1
(**8**)	(**20**)	(**27**)	50	20:1
(**12**)	(**19**)	(**30**)	29	1:2.5



Scheme 6. (i) BH_3–DMS; (ii) Ac_2O, MeOH (**31**) 83%, (**32**) 8%; (iii) Recrystallisation MeOH/$CHCl_3$.

phenylsulfenyl chloride[20] (PhSCl) allowed activation of the oximino donors (**7**), (**8**) and (**12**). The reactions of donors (**7**) and (**8**) with acceptor (**20**) provided an interesting difference in selectivity. When using NIS/TfOH they had shown similar selectivities, but under the α-oximino triflate method, oxime (**7**) showed a distinctly superior β:α ratio. This pleasing reversal in ratio of disaccharide products was seen again with the methyl oxime (**12**), however the yield was lower and a number of impurities were formed which were difficult to remove. For the remaining reactions, yields were generally lower than for the NIS/TfOH reactions, and selectivities less easy to rationalise. Again, alkene (**14**) and phenyl selenyl donor (**17**) proved of little use in these reactions.

Although it may be possible to further optimise the yields and selectivities of the glycosidation reactions described thus far, we were keen to determine whether the oxime disaccharides prepared in our programme could be converted to α-GlcNAc or β-ManNAc containing disaccharides. Thus we next examined the stereoselective reduction of some of the oxime disaccharides.

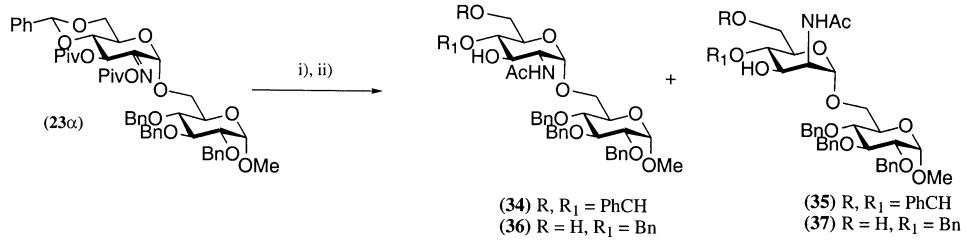
2.1.3. Stereoselective reduction of oximino derivatives. In order to create β-ManNAc or α-GlcNAc derivatives the stereoselective reduction of the oximino function must be achieved. Moreover, an examination of the coupling constants between H-1/H-2 in the ^1H NMRs of the reduced compounds, would provide further confirmation of the stereochemistry of the glycosidic bonds in the oxime disaccharide precursors. The stereoselective reduction of α-oximino and β-oximino benzoyl oxime disaccharide derivatives with a THF–BH_3 (12 equiv.) complex has been reported by Lichtenthaler et al.[4] In these cases the α-oximino derivatives were stereoselectively reduced to give the α-GlcNAc disaccharides and the β-oximino disaccharides were stereoselectively reduced to give the β-ManNAc disaccharides. In order to determine the suitability of this method for our system Piv-oxime (**7**) was treated with THF–BH_3 complex (12 equiv.) but the reaction was found to progress poorly. However when using a BH_3–DMS complex the reaction progressed more efficiently and with high stereoselectively at room temperature overnight.

The highly reactive nature of BH_3–DMS was shown in its ability to simultaneously remove the pivaloate group from the C-3 position, yielding (**31**) as the major product in 83% yield, along with 8% of (**32**) in which the pivaloate protecting group remained in-tact at C-3. Attempts to recrystallise (**31**) from methanol/chloroform were only successful in yielding a third product, (**33**), in which the benzylidene group had been removed (Scheme 6).

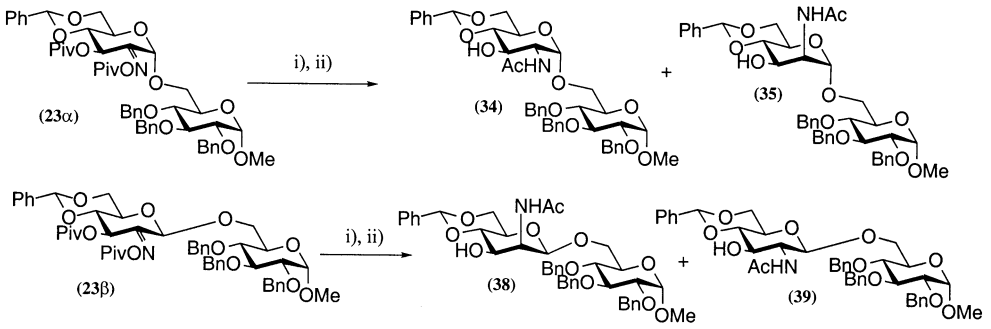
The fact that the sterically hindered pivaloate group had proven susceptible to cleavage with BH_3–DMS was particularly pleasing since the possibility of achieving a one-pot reduction/deprotection step was evident.

We next applied this reduction method to the α- and β-oximino disaccharides (**23**α) and (**23**β). For (**23**β) the reaction made only partial progress and afforded a complex mixture of products. Column chromatography and preparative TLC proved futile in isolating any pure material. However, with (**23**α) the reaction proceeded with a high degree of stereoselectivity and in acceptable yield. Isolation and analysis of the major products revealed a mixture of GlcNAc-α-(1, 3)-Glc (**34**)/ManNAc-α-(1, 3)-Glc (**35**) to have formed in a ratio of ~8:1 in 48% yield. The more polar products were isolated as an ~4.7:1 mixture of GlcNAc-α-(1, 3)-Glc (**36**)/ManNAc-α-(1, 3)-Glc (**37**) (37%) in which the benzylidene protecting group had been reductively ring opened to give the 4-*O*-benzyl ether (Scheme 7).

Considering the complexity of the product mixture obtained with this reduction method, the use of alternative reducing agents was investigated. Two alternative methods which have been utilised in the literature for the stereoselective reduction of saccharide oximes employ $LiAlH_4$[21] or $LiBH_4$, TMSCl.[22] The compatability of these reducing agents with our oxime disaccharides was next investigated. Thus the epimeric 1,6-linked disacharides (**23**α,β) were seperately treated with $LiAlH_4$ in dry Et_2O at 40°C. After careful quenching of the reactions with an aqueous solution of Rochelle's salt, the amines thus produced were acetylated using methanol in acetic anhydride. In this way both the α- and β-linked oxime disaacharides (**23**α,β) were efficiently



Scheme 7. (i) BH_3–DMS; (ii) Ac_2O (**34**)/(**35**) (8:1) 48% over 2 steps, (**36**)/(**37**) (4.7:1) 37% over 2 steps.



Scheme 8. (i) $LiAlH_4$; (ii) Ac_2O, MeOH, 43% (6:1 for (**34**)/(**35**)) over 2 steps from (**23**α); 42% (4:1 for (**38**)/(**39**)) over 2 steps from (**23**β).

reduced to predominantly afford the GlcNAc-α-(1,6)-Glc and ManNAc-β-(1,6)-Glc disaccharides (**34**) and (**38**), respectively (Scheme 8).

Although small quantities of the epimeric ManNAc-α-(1,6)-Glc and GlcNAc-β-(1,6)-Glc disaccharides (**35**) and (**39**) were formed in these reactions, α-GlcNAc and β-ManNAc linkages were successfully formed using this method. The predominance of these particular isomers is a result of hydride attack at the least hindered face of the oxime. In all cases, one-pot removal of the C-3 pivaloate group was also observed to afford alcohol acceptors ready for subsequent glycosidation reactions. This is potentially of use for access to branched oligosaccharides containing the α-GlcNAc or β-ManNAc unit.

The final reducing agent which has been studied within our group to date is $LiBH_4$/TMSCl,[22] which was employed for the reduction of the (1,6) linked disaccharides (**23**α) and (**23**β) (Scheme 9). This reducing agent has the advantage of requiring lower temperatures for reduction, compared with $LiAlH_4$ (−20°C vs 40°C). When the α-linked disaccharide (**23**α) was exposed to $LiBH_4$ and TMSCl, and the amine thus produced protected with MeOH/Ac_2O, only the GlcNAc-α-(1,6)-Glc disaccharide (**34**) was formed in 47% over two steps. In contrast with the results obtained using $LiAlH_4$, no epimeric α-ManNAc-α-(1,6)-Glc disaccharide could be detected. Less selective reduction resulted when the β-linked disaccharide (**23**β) was exposed to the same reducing conditions. In this case only 25% of reduced ManNAc-β-(1,6)-Glc and GlcNAc-β-(1,6)-Glc compounds (**40**) and (**41**) respectively could be isolated, in a ratio of 2:1 (**40**):(**41**). Interestingly, the acceptor component (**19**) was also isolated in 25% yield, suggesting that in this case some degradation of the glycosidic bond must be occurring. However, for reduction of (**23**β), the C-3–OPiv group remained in-tact within (**40**) and (**41**) under these reducing conditions, which is in contrast to the results obtained with $LiAlH_4$.

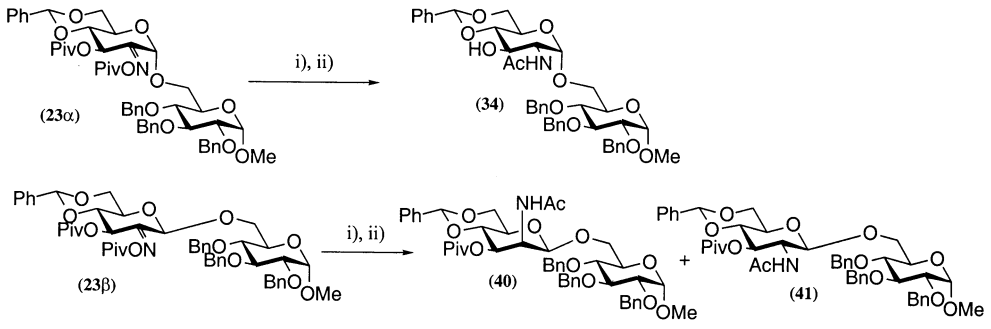
3. Conclusion

High yielding protocols are in place which allow expedient entry into a range of α-*Z*-oxime donors. X-Ray, nOe and ^1H NMR studies have confirmed that the oxime donors display the α-*Z*-oxime conformation. Two glycosidation methods have been shown to be compatible with the reactive, yet shelf stable, thioethyl oximino donors. Entry to disaccharides containing either α-linked GlcNAc or β-linked ManNAc units is generally possible using a two step glycosidation/reduction protocol. The disaccharides thus produced are useful precursors to branched oligosaccharides, by virtue of the orthogonal protecting groups incorporated within the α-GlcNAc and β-ManNAc units. Application of this methodology to targets of particular biological interest is now in progress within our laboratories.

4. Experimental

4.1. General methods

All reactions were monitored by thin layer chromatography (TLC) on Merck silica gel $60F_{254}$ 0.2 mm aluminium-backed plates. Column chromatography was conducted using Merck 70–230 mesh (standard) silica gel and 230–400 mesh (fine) silica gel. Visulization of tlc plates was by 254 nm UV light and by spray-head development using an



Scheme 9. (i) $LiBH_4$, TMSCl; (ii) Ac_2O, MeOH, 47% over 2 steps for (**34**), 25% over 2 steps for (**40**) and (**41**) in a ratio 2:1 (**40**)/(**41**).

Table 6.

Compound	(**7**)	(**8**)	(**11**)	(**12**)	(**14**)
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1$	Orthorhombic, $P2_12_12_1$
Unit cell dimension (Å, °)					
a	6.006(9)	5.996(9)	8.710(9)	8.946(10)	5.675(7)
b	19.007(17)	17.529(17)	9.832(12)	9.882(10)	11.263(14)
c	23.82(2)	25.22(3)	28.75(3)	13.026(14)	34.98(4)
β	(90)	(90)	(90)	98.14(1)	(90)
Volume (Å^3)	2720	2651	2462	1140	1610
Z, calc. density (mg m^{-3})	4, 1.206	4, 1.287	4, 1.181	2, 1.234	2, 1.658
Reflections collected	6759	6629	4235	4005	5198
Unique reflections/*R* (int)	4259/0.0376	4201/0.0203	2556/0.0761	2336/0.0301	5198
Data/restraints/parameters	4259/0/315	4201/0/330	2556/0/277	2336/0/268	4198/2/428
Final *R* indices [$I > 2s(I)$]					
*R*1	0.0741	0.0471	0.0747	0.0516	0.0296
*wR*2	0.2145	0.1432	0.1952	0.1481	0.0712
R indices (all data)					
*R*1	0.1489	0.0715	0.2071	0.0681	0.0367
*wR*2	0.2951	0.1655	0.2666	0.1637	0.0755
Largest diff. peak and hole (eÅ^{-3})	0.321, −0.213	0.263, −0.187	0.195, −0.242	0.240, −0.318	0.203, −0.153

ethanol–sulfuric acid reagent (25:1 EtOH/H_2SO_4). Anhydrous solvents were prepared as follows: dichloromethane (DCM) was distilled from calcium hydride; ethanol was distilled from iodine and magnesium filings; tetrahydrofuran (THF) was distilled over sodium wire from benzophenone; dimethylformamide (DMF) was dried over activated 4 Å molecular sieves for 24 h; miscellaneous anhydrous solvents were supplied as 'sure seal' bottles by Aldrich. When denoted in the general method preparations, reactions were carried out under an inert atmosphere of argon (Ar) or nitrogen (N_2). Solvents were evaporated under aspirator vacuum (ca. 20 mmHg) at about 35°C unless otherwise stated. Melting point analyses were carried out using an electrothermal digital melting point apparatus and are uncorrected. Specific rotation measurements were carried out using a Perkin–Elmer 341 polarimeter, elemental analyses were furnished by Medac Ltd., Brunel Science Centre, Surrey. ^{1}H NMR spectra were recorded at 600, 400 and 250 MHz and ^{13}C NMR spectra were recorded at 150, 100 and 62.5 MHz on Bruker instruments. DEPT NMR experiments were recorded at 150, 100 and 62.5 MHz on Bruker instruments. Mass spectral analyses were obtained in chemical ionization mode using a Fisons VG Autospec. Infra red spectra were recorded using a Perkin–Elmer paragon 1000 FTIR spectrophotometer. Crystal data and refinement details are provided in Table 6. Intensity data were collected with MoKa radiation using the MARresearch Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 100 Frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[23] The structures were solved using direct methods with the Shelx86 program.[24] In all five structures the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structures were then refined on F^2 using Shelxl.[25] The data have been deposited at the Cambridge Crystallographic Database reference numbers CCDC 165449-CCDC 165453 inclusive.

4.1.1. Ethyl 2-deoxy-2-(*O*-benzyl)oximino-3-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (1) and ethyl 2-deoxy-2-(*O*-benzyl)oximino-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (5). To dimethyl sulfoxide (20 μl, 0.52 mmol, 2 equiv.) in anhydrous dichloromethane (0.5 cm^3) at −50→−70°C under argon gas was added trifluoroacetic anhydride (60 μl, 0.39 mmol, 1.5 equiv.) in anhydrous dichloromethane (1 cm^3) dropwise. Alcohol (**3**)[10,11] (87 mg, 0.26 mmol) in anhydrous dichloromethane (1.25 cm^3) was added dropwise and the solution was stirred at −50→−70°C for 10 min and then allowed to warm to room temperature for 40 min prior to the addition of anhydrous TEA (115 μl, 0.83 mmol, 3 equiv.) dropwise. The reaction was washed with distilled water (15 cm^3), extracted with ethyl acetate (3×15 cm^3), dried with $MgSO_4$, filtered and the solvent removed in vacuo to afford the ulose intermediate (**4**), which was not purified. A solution of crude (**4**) in dry ethanol (7.5 cm^3) was added to *O*-benzylhydroxylamine (210 mg, 1.7 mmol, 6.5 equiv.) and the reaction was allowed to stir at room temperature for one day. In order to force the reaction to completion the temperature was raised to 50°C for 3 h and then allowed to cool to room temperature overnight. The reaction was concentrated and submitted to column chromatography using gradient elution (9:1→6:1 hexane/ethyl acetate, with 1% TEA). Concentration of the pure fractions afforded oxime (**1**) (13 mg, 12%) and the C-3 deacetylated oxime product (**5**) (10 mg, 10%). *For* (**1**). ν_{max} (film)/cm^{-1} 3108 m, 3051 s, 2985 s and 2895 s (C–H), 1738 s (C=O), 1660 w, 1513 m and 1502 s (C=C), 1483 s, 1445 s, 1370 s (C–H), 1290 s, 1218 s, 1145, 1100 br, 1080 br and 1020 br (C–O), 758 s and 700 s (Ar); δ_H (400 MHz; $CDCl_3$) 1.27 (3H, t, *J*=7.5 Hz, SCH_2CH_3), 2.10 (3H, s, CH_3CO), 2.57–2.75 (2H, m, SCH_2CH_3), 3.77 (1H, t, *J*=10.5 Hz, H-6), 3.84 (1H, t, *J*=10.0 Hz, H-4), 4.28 (1H, dd, *J*=5.0, 10.5 Hz, H-6), 4.35–4.41 (1H, m, H-5), 5.09–5.18 (2H, m, $PhCH_2O$), 5.54 (1H, s, PhCH), 5.72 (1H, d, *J*=10.0 Hz, H-3), 6.37 (1H, s, H-1) 7.29–7.48 (10H, m, Ar); δ_C (100 MHz; $CDCl_3$) 14.96 (SCH_2CH_3), 20.63 (CH_3CO), 25.72 (SCH_2CH_3), 63.72 ($PhCH_2O$) 68.55 (C-6), 69.08, 76.23, 77.09, 79.28, (C-1, C-3, C-4, C-5), 101.63 (PhCH),

126.28, 128.00, 128.09, 128.28, 128.31, 129.21, 136.89, 136.98, (Ar, $ArCH_2${C-2, C-6, C-3, C-5, C-4, C-1}), 148.50 (C-2), 169.59 (CH_3CO); (CI: Found $[M+H]^+$, 458.1639. $C_{24}H_{28}NO_6S$ requires $[M+H]^+$, 458.1637); *m/z* (CI) 458 ($[M+H]^+$, 3%), 396 (29), 352 (4), 290 (12), 200 (9), 148 (19), 105 (100), 91 (93), 77 (32), 43 (23). *For* (**5**) ν_{max} (film)/cm^{-1} 3350 br (O–H), 3026 s, 2985 s, 2918 s and 2890 s (C–H), 1740 s (C=O), 1502 s (C=C), 1480 s, 1445 s, 1370 s (C–H), 1270 s, 1218 s, 1080 br and 1020 br (C–O), 754 s and 710 s (Ar); δ_H (400 MHz; $CDCl_3$) 1.30 (3H, t, *J*=7.5 Hz, SCH_2CH_3), 2.65–2.75 (2H, m, SCH_2CH_3), 3.67 (1H, t, *J*=9.5 Hz, H-4), 3.76 (1H, m, H-6), 4.27–4.29 (2H, m, H-5, H-6), 4.59 (1H, d, *J*=10.0 Hz, H-3), 5.18–5.25 (2H, m, $PhCH_2O$), 5.58 (1H, s, PhC*H*), 6.36 (1H, s, H-1), 7.35–7.52 (10H, m, Ar); (CI: Found $[M+H]^+$, 416.1538. $C_{22}H_{25}NO_5S$ requires $[M+H]^+$, 416.1531); *m/z* (CI) 416 ($[M+H]^+$, 7%), 354 (8), 328 (23), 266 (12), 248 (7), 157 (16), 105 (53), 91 (100), 77 (24), 55 (12), 39 (10).

4.1.2. Ethyl 2-deoxy-2-oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (6). To dimethyl sulfoxide (514 μl, 7.24 mmol, 2 equiv.) in anhydrous dichloromethane (3.0 cm^3) at −78°C under argon gas was added trifluoroacetic anhydride (767 μl, 5.42 mmol, 1.5 equiv.) in anhydrous dichloromethane (233 μl). A thick white suspension was formed to which was added anhydrous dichloromethane (7 cm^3). Ethyl-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[10b] (1.437 g, 3.62 mmol) in anhydrous dichloromethane (5 cm^3) was added and the solution was stirred at −78°C for 50 min. Following the dropwise addition of anhydrous TEA (1.91 cm^3, 13.7 mmol, 3.8 equiv.) the reaction was allowed to warm to room temperature and stirred for 40 min. The reaction was diluted with ethyl acetate (25 cm^3), washed with distilled water (15 cm^3), extracted with ethyl acetate (3× 15 cm^3), dried with $MgSO_4$, filtered and the solvent removed in vacuo to afford the corresponding ketone which was not purified. A solution of the crude ketone in ethanol (50 cm^3) was added to a solution of sodium acetate (0.871 g, 10.86 mmol, 3 equiv.) and hydroxylamine hydrochloride (0.755 g, 10.86 mmol, 3 equiv.) in distilled water (5 cm^3) at 52°C. The reaction was stirred for 2 hours 30 min at which point the reaction was allowed to cool to room temperature then washed with distilled water (15 cm^3), extracted with dichloromethane (3×15 cm^3), dried with $MgSO_4$, filtered and the solvent removed in vacuo to afforded crude oxime (**6**). This procedure was repeated with 3.71 g (9.06 mmol) of alcohol and the crude portions of material (**6**) were combined and submitted to column chromatography (5.5:1 hexane/ethyl acetate, with 1% TEA). Concentration of the pure fractions afforded oxime (**6**) as white foam (3.62 g, 68%). $[\alpha]_D^{20}$=137.6 (*c* 0.5 in $CHCl_3$); ν_{max} (film)/cm^{-1} 3400 br (O–H), 3110 m, 3080 s, 3043 s, 2985 s, 2925 s and 2895 s (C–H), 1740 s (C=O), 1660 w 1530 m and 1502 s (C=C), 1480 s, 1455 s, 1370 s and 1320 s (C–H), 1290 s, 1218 s, 1180 br, 1145 br, 1100 br, 1080 br and 1020 br (C–O), 758 s and 700 s (Ar), 641 (C–S); δ_H (400 MHz; $CDCl_3$) 1.15 (9H, s, $(CH_3)_3CO$) 1.25 (3H, t, *J*=7.5 Hz, SCH_2CH_3), 2.55–2.71 (2H, m, SCH_2CH_3), 3.72 (1H, t, *J*=10.5 Hz, H-6), 3.80 (1H, app. t, *J*=10.5, 10.0 Hz, H-4), 4.23 (1H, dd, *J*=5.0, 10.5 Hz, H-6), 4.29–4.35 (1H, m, H-5), 5.49 (1H, s, PhC*H*), 5.66 (1H, d, *J*=10.5 Hz, H-3), 6.42 (1H, s, H-1) 7.27–7.37 (5H, m, Ar); δ_C (100 MHz; $CDCl_3$) 15.00 (SCH_2CH_3), 25.73 (SCH_2CH_3), 27.12 ($(CH_3)_3CCO$) 38.89 ($(CH_3)_3CCO$), 63.73 (C-5), 68.57 (C-6), 68.82 (C-3), 75.76 (C-1), 79.62 (C-4), 101.10 (PhCH), 125.96, 128.22, (Ar{C-2, C-6, C-3, C-5}), 129.00 (Ar{C-4}), 136.99 (Ar{C-1}), 149.78 (C-2), 177.14 ($(CH_3)_3CCO$); (CI: Found $[M+H]^+$, 410.1635. $C_{20}H_{28}NO_6S$ requires $[M+H]^+$, 410.1637); *m/z* (CI) 410 ($[M+H]^+$, 8%), 345 (12), 348 (100), 303 (52), 282 (6), 242 (70), 202 (12), 149 (74), 105 (75), 91 (33), 85 (36), 57 (73), 41 (26) 39 (27).

4.2. General procedure for forming acylated oximes

To a solution of oxime (**6**) (1 equiv.) in anhydrous dichloromethane at 0°C was added anhydrous pyridine (2 equiv.). To this solution was added the acylating or alkylating agent (3 equiv.) dropwise over 10 min. The reaction was warmed to room temperature, heated to 40°C then stirred overnight. The reaction was cooled to room temperature, washed with distilled water, then sodium bicarbonate, extracted with dichloromethane, dried with $MgSO_4$, filtered and the solvent removed in vacuo. Azeotropic removal of pyridine was achieved using toluene. The crude material was submitted to column chromatography (7:1 hexane/ethyl acetate, with 1% TEA).

4.2.1. Ethyl 2-deoxy-2-(*O*-pivaloyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (7). By following the general procedure above, oxime (**6**) (0.75 g, 1.83 mmol), anhydrous pyridine (295 μl, 3.66 mmol, 2 equiv.) and trimethylacetyl chloride (TMAC) (677 μl, 5.49 mmol, 3 equiv.) were reacted to afford oxime (**7**) (825 mg, 94%) as a white solid. Mp 165–166°C; $[\alpha]_D^{24}$=100.9 (*c* 0.45 in $CHCl_3$); (Found: C, 60.30; H, 6.97; N, 2.72; S, 6.23. $C_{25}H_{35}O_7NS$ requires C, 60.83; H, 7.15; N, 2.84; S, 6.49%); ν_{max} (KBr)/cm^{-1} 2968 s, 2932 s, 2910 s and 2872 s (C–H), 1768 vs and 1742 vs (C=O), 1639 w (C=C), 1480 s, 1458 s, 1399 w and 1370 s (C–H), 1282 s, 1270 s, 1179 s, 1152 vs, 1137 vs, 1097 br, 1023 s, 995 s and 972 s (C–O), 763 s and 700 s (Ar), 643 s (C–S); δ_H (400 MHz; $CDCl_3$) 1.21 (9H, s, $(CH_3)_3CCO$) 1.21 (9H, s, $(CH_3)_3CCO$) 1.28 (3H, app. t, *J*=7.0, 7.5 Hz, SCH_2CH_3), 2.55–2.75 (2H, m, SCH_2CH_3), 3.74 (1H, t, *J*=10.5 Hz, H-6), 3.91 (1H, t, *J*=10.0 Hz, H-4), 4.24 (1H, dd, *J*=5.0, 10.5 Hz, H-6), 4.32–4.38 (1H, m, H-5), 5.51 (1H, s, PhC*H*), 5.76 (1H, d, *J*=10.0 Hz, H-3), 6.24 (1H, s, H-1) 7.29–7.38 (5H, m, Ar); δ_C (100 MHz; $CDCl_3$) 14.91 (SCH_2CH_3), 25.53 (SCH_2CH_3), 27.01 ($(CH_3)_3CCO$) 27.18 ($(CH_3)_3CCO$), 38.68 ($(CH_3)_3CCO$), 38.87 ($(CH_3)_3CCO$), 63.70 (C-5), 68.35 (C-6), 68.56 (C-3), 76.52 (C-1), 79.06 (C-4), 101.25 (PhCH), 125.97, 128.22, (Ar{C-2, C-6, C-3, C-5}), 128.97 (Ar{C-4}), 136.76 (Ar{C-1}), 156.37 (C-2), 177.12 (2×$(CH_3)_3CCO$); (CI: Found $[M+H]^+$, 494.2223. $C_{25}H_{36}NO_7S$ requires $[M+H]^+$, 494.2212); *m/z* (CI) 511 ($[M+NH_4]^+$, 7%) 494 ($[M+H]^+$, 17), 432 (6), 392 (64), 347 (100), 302 (57), 285 (61), 242 (16), 196 (12), 150 (32), 105 (10), 85 (27), 57 (37), 41 (8) 39 (6).

4.2.2. Ethyl 2-deoxy-2-(*O*-benzoyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (8). By following the general procedure above, oxime (**6**) (0.70 g, 1.70 mmol), anhydrous pyridine (275 μl, 3.41 mmol, 2 equiv.) and benzoyl chloride (593 μl, 5.11 mmol,

3 equiv.) were reacted to afford oxime (**8**) (720 mg, 82%) as a white solid. Mp 109.6–110.6°C; $[\alpha]_D^{20}$=122.6 (*c* 0.5 in $CHCl_3$); (Found: C, 63.00; H, 6.08; N, 2.71; S, 6.14. $C_{27}H_{31}NO_7S$ requires C, 63.02; H, 6.27; N, 2.72; S, 6.23%); ν_{max} (KBr)/cm^{-1} 3091 w, 3070 w, 3042 w, 2986 s, 2964 s, 2914 s and 2859 s (C–H), 1765 vs and 1735 vs (C═O), 1638 w and 1602 w (C═C), 1480 s, 1460 s, 1416 s and 1385 s (C–H), 1263 s, 1248 vs, 1235 s, 1133 vs, 1095 vs, 1054 vs and 1021 s (C–O), 773 s and 696 vs (Ar), 670 w (C–S); δ_H (400 MHz; $CDCl_3$) 1.24 (9H, s, $(CH_3)_3COO$) 1.32 (3H, t, *J*=7.5 Hz, SCH_2CH_3), 2.60–2.80 (2H, m, SCH_2CH_3), 3.75 (1H, t, *J*=10.5 Hz, H-6), 3.97 (1H, t, *J*=10.0 Hz, H-4), 4.26 (1H, dd, *J*=5.0, 10.5 Hz, H-6), 4.35–4.41 (1H, m, H-5), 5.53 (1H, s, PhC*H*), 5.83 (1H, d, *J*=10.5 Hz, H-3), 6.39 (1H, s, H-1) 7.29–8.09 (10H, m, Ar); δ_C (100 MHz; $CDCl_3$) 14.93 (SCH_2CH_3), 25.55 (SCH_2CH_3), 27.01 ($(CH_3)_3CCO$) 38.87 ($(CH_3)_3CCO$), 63.75 (C-5), 68.31 (C-6), 68.64 (C-3), 76.54 (C-1), 78.99 (C-4), 101.21 (PhCH), 125.95, 128.20, (Ar{C-2, C-6, C-3, C-5}), 128.37 (PhCO{C-4}), 128.64, 129.61 (PhCO{C-2, C-6, C-3, C-5}) 129.04 (Ar{C-4}), 133.62 (PhCO{C-1}), 136.72 (Ar{C-1}), 157.15 (C-2), 162.33 (PhCO), 177.12 ($(CH_3)_3CCO$); (CI: Found $[M+H]^+$, 514.1924 $C_{27}H_{32}NO_7S$ requires $[M+H]^+$, 514.1899); *m/z* (CI) 531 ($[M+NH_4]^+$, 18%) 514 ($[M+H]^+$, 26), 452 (6), 408 (8), 392 (41), 347 (47), 302 (30), 286 (19), 122 (24), 105 (100), 77 (23), 57 (18).

4.2.3. Ethyl 2-deoxy-2-(*O*-isobutylformyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (9). By following the general procedure above, oxime (**6**) (0.20 g, 0.48 mmol), anhydrous pyridine (97 μl, 0.97 mmol, 2 equiv.) and isobutylchloroformate (IBCF) (190 μl, 1.46 mmol, 3 equiv.) were reacted to afford oxime (**9**) (168 mg, 68%) as a clear yellow oil. $[\alpha]_D^{25}$=109.2 (*c* 0.66 in $CHCl_3$); ν_{max} (nujol)/cm^{-1} 3100 w, 3075 w, 2990 s and 2895 s (C–H), 1795 vs and 1753 vs (C═O), 1660 w (C═C), 1495 m, 1482 m and 1410 m (C–H), 1290 s, 1275 m, 1230 vs, 1195 s, 1142 s, 1105 vs, 1085 s, 1005 s and 980 s (C–O), 760 s and 710 vs (Ar), 658 w (C–S); δ_H (400 MHz; $CDCl_3$) 0.87 (6H, d, *J*=6.5 Hz, $(CH_3)_2CHCH_2O$) 1.19 (9H, s, $(CH_3)_3COO$) 1.28 (3H, t, *J*=7.5 Hz, SCH_2CH_3), 1.89–1.99 (1H, m, $(CH_3)_2CHCH_2O$) 2.60–2.75 (2H, m, SCH_2CH_3), 3.75 (1H, app. t, *J*=10.0, 10.5 Hz, H-6), 3.89 (1H, t, *J*=10.0 Hz, H-4), 3.93 (2H, d, *J*=7.0 Hz, $(CH_3)_2CHCH_2O$), 4.24 (1H, dd, *J*=5.0, 10.5 Hz, H-6), 4.29–4.35 (1H, m, H-5), 5.50 (1H, s, PhC*H*), 5.75 (1H, d, *J*=10.5 Hz, H-3), 6.28 (1H, s, H-1) 7.27–7.39 (5H, m, Ar); δ_C (100 MHz; $CDCl_3$) 14.94 (SCH_2CH_3), 18.77 ($(CH_3)_2CHCH_2O$), 26.12 (SCH_2CH_3), 26.98 ($(CH_3)_3CCO$) 27.65 ($(CH_3)_2CHCH_2O$), 38.79 ($(CH_3)_3CCO$), 63.96 (C-5), 68.33, 68.42 (C-3, C-6), 74.93 ($(CH_3)_2CHCH_2O$), 76.59 (C-1), 79.12 (C-4), 101.21 (PhCH), 125.93, 128.20, (Ar{C-2, C-6, C-3, C-5}), 129.04 (Ar{C-4}), 136.74 (Ar{C-1}), 152.73 ($(CH_3)_2CHCH_2OCO$) 156.02 (C-2), 176.94 ($(CH_3)_3CCO$); (CI: Found $[M+NH_4]^+$, 527.2408. $C_{25}H_{39}N_2O_8S$ requires $[M+NH_4]^+$, 527.2427); *m/z* (CI) 527 ($[M+NH_4]^+$, 6%) 510 ($[M+H]^+$, 3), 448 (7), 404 (18), 392 (20), 348 (12), 302 (37), 286 (65), 242 (33), 150 (100), 105 (14), 85 (38), 57 (48).

4.3. General procedure for forming alkylated oximes

To an aqueous solution of *O*-alkylhydroxylamine hydrochloride (3 equiv.) and sodium acetate (3 equiv.) at 50°C was added a portion of crude ketone (1 equiv.) in ethanol. The reaction was stirred at 50–55°C for 5 h and 30 min at which point the reaction was cooled, diluted with dichloromethane, washed with distilled water, extracted with dichloromethane, dried ($MgSO_4$), filtered and the solvent removed in vacuo. The crude product was submitted to column chromatography using gradient elution (12:1→11:1 hexane/ethyl acetate, with 1% TEA).

4.3.1. Ethyl 2-deoxy-2-(*O*-benzyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (10). By following the general procedure outlined above, an aqueous solution (2.5 cm^3) of *O*-benzylhydroxylamine hydrochloride (302 mg, 1.89 mmol, 3 equiv.), sodium acetate (155 mg, 1.89 mmol, 3 equiv.) and crude ulose (**13**) (~250 mg, 0.63 mmol) in ethanol (4.5 cm^3) were combined to afford pure oxime (**10**) (136 mg, 43%) as a white solid. $[\alpha]_D^{22}$=116.4 (*c* 0.36 in $CHCl_3$); ν_{max} (nujol)/cm^{-1} 3115 w and 3085 w, (C–H), 1760 vs (C═O), 1330 w and 1298 s (C–H), 1255 m, 1115 s, 1085 m 1058 m, 1020 m, 1000 m and 980 s (C–O), 740 s and 710 m (Ar), 638 m (C–S); δ_H (250 MHz; $CDCl_3$) 1.13 (9H, s, $(CH_3)_3COO$), 1.20 (3H, t, *J*=7.5 Hz, SCH_2CH_3), 2.49–2.67 (2H, m, SCH_2CH_3), 3.65–3.84 (2H, m, H-6, H-4), 4.19–4.31 (2H, m, H-6, H-5), 4.97–5.10 (2H, m, $PhCH_2ON$), 5.48 (1H, s, PhC*H*), 5.63 (1H, dd, *J*=10.5, 1.0 Hz, H-3), 6.31 (1H, s, H-1) 7.21–7.38 (10H, m, Ar); δ_C (62.5 MHz; $CDCl_3$); 15.43 (SCH_2CH_3), 26.13 (SCH_2CH_3), 27.51 ($(CH_3)_3CCO$), 39.16 ($(CH_3)_3CCO$), 64.13 (C-5), 68.95 (C-6), 69.04 (C-3), 76.63 (C-1), 77.34 ($PhCH_2$), 79.80 (C-4), 101.51 (PhCH), 126.40, 128.53, 128.63, 128.73 (2×Ar{C-2, C-6, C-3, C-5}), 128.35, 129.41 (2×Ar{C-4}), 137.41, 137.56 (2×Ar{C-1}), 149.13 (C-2), 177.33 ($(CH_3)_3CCO$); (CI: Found $[M+H]^+$, 500.2087. $C_{27}H_{34}NO_6S$ requires $[M+H]^+$, 500.2106); *m/z* (CI) 500 ($[M+H]^+$, 5%) 438 ($[M-SEt]^+$, 65), 394 (6), 332 (20), 149 (21), 105 (9), 91 (100), 57 (15), 49 (27).

4.3.2. Ethyl 2-deoxy-2-(*O*-ethyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (11). By following the general procedure outlined above, an aqueous solution (2.5 cm^3) of *O*-ethylhydroxylamine hydrochloride (184 mg, 1.89 mmol, 3 equiv.), sodium acetate (155 mg, 1.89 mmol, 3 equiv.) and crude ulose (**13**) (~250 mg, 0.63 mmol) in ethanol (4.5 cm^3) were combined and purified by column chromatography. Concentration of the relevant fractions followed by hot recrystallisation from hexanes afforded pure oxime (**11**) (149 mg, 54%) as clear crystal cubes. Mp 86.1–87.0°C; $[\alpha]_D^{27}$=146.9 (*c* 0.25 in $CHCl_3$); (Found: C, 60.20; H, 7.07; N, 3.18; S, 7.16. $C_{22}H_{31}NO_6S$ requires C, 60.39; H, 7.14; N, 3.20; S, 7.33%); ν_{max} (nujol)/cm^{-1} 2998 w, 2980 w and 2924 vs (C–H), 1740 s (C═O), 1459m and 1364 m (C–H), 1283 m, 1178 m, 1153 m, 1140 m, 1098 m and 1035 s (C–O), 746 s and 696 s (Ar), 639 s (C–S); δ_H (250 MHz; $CDCl_3$) 1.12–1.19 (12H, m, ($(CH_3)_3CCO$), CH_3CH_2ON), 1.25 (3H, t, *J*=7.5 Hz, SCH_2CH_3), 2.54–2.67 (2H, m, SCH_2CH_3), 3.67–3.86 (2H, m, H-4, H-6), 4.01–4.10 (2H, m, CH_3CH_2ON), 4.20–4.32 (2H, m, H-5, H-6), 5.50 (1H, s, PhC*H*), 5.65 (1H, d, *J*=10.0 Hz, H-3), 6.27 (1H, s, H-1) 7.26–7.40 (5H, m, Ar); δ_C (250 MHz; $CDCl_3$); 14.86 (SCH_2CH_3), 15.42 (CH_3CH_2ON), 26.08 (SCH_2CH_3), 27.52 ($(CH_3)_3CCO$), 39.17 ($(CH_3)_3CCO$), 64.08 (C-5), 68.98 (C-6), 69.10 (C-3), 70.93

(CH_3CH_2ON), 76.50 (C-1), 79.87 (C-4), 101.52 (PhCH), 126.40, 128.62, (Ar{C-2, C-6, C-3, C-5}), 129.40 (Ar{C-4}), 137.42 (Ar{C-1}), 148.05 (C-2), 177.39 ($(CH_3)_3CCO$); (CI: Found $[M+H]^+$, 438.1954. $C_{22}H_{32}NO_6S$ requires $[M+H]^+$, 438.1950); *m/z* (CI) 438 ($[M+H]^+$, 5%), 393 (7), 376 (100), 332 (18), 270 (44), 149 (32), 105 (14), 85 (8), 57 (11).

4.3.3. Ethyl 2-deoxy-2-(*O*-methyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (12). By following the general procedure outlined above, an aqueous solution (2.5 cm^3) of *O*-methylhydroxylamine hydrochloride (157 mg, 1.87 mmol, 3 equiv.), sodium acetate (155 mg, 1.89 mmol, 3 equiv.) and crude ulose (**13**) (~250 mg, 0.63 mmol) in ethanol (4.5 cm^3) were combined to afford pure oxime (**12**) (164 mg, 66%) as clear crystal cubes. Mp 125.4–126.0°C; $[\alpha]_D^{25}$=156.9 (*c* 0.39 in $CHCl_3$); (Found: C, 59.69; H, 6.78; N, 3.32; S, 7.53. $C_{21}H_{29}NO_6S$ requires C, 59.56; H, 6.98; N, 3.31; S, 7.57%); ν_{max} (film)/cm^{-1} 3120 w, 3100 w, 2970 w, 2995 m, 2960 m and 2900 m (C–H), 1745 s (C=O), 1492 m, 1465 m and 1380 m (C–H), 1290 m, 1184 m, 1142 s, 1100 s, 1085 m, 1050 s and 1000 m (C–O), 760 w and 702 m (Ar), 650 w (C–S); δ_H (250 MHz; $CDCl_3$) 1.24 (9H, s, $(CH_3)_3CCO$), 1.31 (3H, t, *J*=7.5 Hz, SCH_2CH_3), 2.62–2.74 (2H, m, SCH_2CH_3), 3.74–3.93 (5H, m, H-4, H-6, CH_3O), 4.27–4.41 (2H, m, H-5, H-6), 5.57 (1H, s, PhCH), 5.73 (1H, d, *J*=10.0 Hz, H-3), 6.33 (1H, s, H-1) 7.33–7.45 (5H, m, Ar); δ_C (250 MHz; $CDCl_3$) 14.97 (SCH_2CH_3), 25.73 (SCH_2CH_3), 27.11 ($(CH_3)_3CCO$), 38.75 ($(CH_3)_3CCO$), 62.69 (CH_3O), 63.59 (C-5), 68.55 (C-6), 68.55 (C-3), 76.03 (C-1), 79.45 (C-4), 101.13 (PhCH), 125.99, 128.21, (Ar{C-2, C-6, C-3, C-5}), 129.00 (Ar{C-4}), 136.99 (Ar{C-1}), 148.04 (C-2), 176.98 ($(CH_3)_3CCO$); (CI: Found $[M+H]^+$, 424.1712. $C_{21}H_{30}NO_6S$ requires $[M+H]^+$, 424.1793); *m/z* (CI) 424 ($[M+H]^+$, 4%), 362 (100), 318 (26), 274 (43), 256 (64), 242 (27), 172 (46), 149 (43), 105 (38), 85 (35), 57 (100), 41 (23) 39 (14).

4.3.4. Ethyl 2-deoxy-2-methylene-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (14). To a stirred suspension of instant ylid (CH_3PPh_3Br, NH_2Na) (633 mg, 1.52 mmol, 3 equiv.) in anhydrous THF (5 cm^3), was added ulose (**13**) (200 mg, 0.50 mmol) dropwise as a solution in anhydrous THF (5 cm^3). The reaction was refluxed until tlc analysis showed the reaction to be complete (ca 15 min) at which point the reaction was cooled, diluted with dichloromethane, filtered through Celite®, concentrated and submitted to flash column chromatography, repeatedly (hexanes, with 1% TEA). Concentration of the pure fractions followed by recrystallisation from hexane afforded olefin (**14**) (96 mg, 48%) as white needles. Mp 122.2–122.9°C; $[\alpha]_D^{22}$=160.0 (*c* 0.15 in $CHCl_3$); ν_{max}/cm^{-1} 3095 m and 3060 m (CH_2=C), 3000 s, 2990 m, 2955 m, 2928 m and 2890 m (C–H), 1738 vs (C=O), 1680 m (C=C), 1490 m, 1478 m, 1465 m, 1420 m, 1395 m and 1380 s (C–H), 1295 s, 1220 br, 1185 s, 1160 s, 1100 vs, 1080 m, 1030 m (C–O), 975 s and 922 s (C–H), 763 s and 700 s (Ar), 622 s (C–S); δ_H (250 MHz; $CDCl_3$) 1.25 (9H, s, $(CH_3)_3CCO$), 1.30 (3H, t, *J*=7.5 Hz, SCH_2CH_3), 2.52–2.71 (2H, m, SCH_2CH_3), 3.64 (1H, t, *J*=10.0 Hz, H-4), 3.78 (1H, t, *J*=10.5 Hz, H-6), 4.27 (1H, dd, *J*=5.0, 10.5 Hz, H-6), 4.41–4.47 (1H, m, H-5), 5.03 (1H, d *J*=2.5 Hz, C=CH_2), 5.15 (1H, d *J*=2.5 Hz, C=CH_2), 5.53 (1H, s, PhCH), 5.75 (1H, s, H-1), 5.86 (1H, dd, *J*=0.5, 10.0 Hz, H-3), 7.25–7.45 (5H, m, Ar); δ_C (250 MHz; $CDCl_3$) 15.10 (SCH_2CH_3), 25.33 (SCH_2CH_3), 27.40 ($(CH_3)_3CCO$), 39.25 ($(CH_3)_3CCO$), 64.19 (C-5), 69.05 (C-6), 70.24 (C-3), 81.59, 85.56 (C-1, C-4), 101.28 (PhCH), 111.06 (C=CH_2), 126.13, 128.41, (Ar{C-2, C-6, C-3, C-5}), 129.10 (Ar{C-4}), 137.40, 140.87 (Ar{C-1}), C-2), 177.28 ($(CH_3)_3CCO$); (CI: Found $[M+H]^+$, 393.5753. $C_{21}H_{29}O_5S$ requires $[M+H]^+$, 393.5092); *m/z* (CI) 393 ($[M+H]^+$, 3%) 391 (2), 331 (43), 291 (20), 287 (41), 263 (10), 231 (15), 229 (20), 225 (27), 185 (42), 151 (26), 149 (100), 123 (65), 105 (30), 91 (37), 57 (57), 41 (18) 39 (10).

4.3.5. Phenyl 2-deoxy-2-oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-seleno-α-D-glucopyranoside (17) and 1-anhydro-1,2-dideoxy-2-oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-glucopyranoside (18). To dimethyl sulfoxide (200 μl, 2.8 mmol, 2 equiv.) in anhydrous dichloromethane (10.0 cm^3) at −78°C under argon gas was added trifluoroacetic anhydride (300 μl, 2.1 mmol, 1.5 equiv.) in anhydrous dichloromethane (233 μl). A solution of alcohol (**16**) (0.70 g, 1.4 mmol) in anhydrous dichloromethane (10 cm^3) was added and the solution was stirred at −78°C for 50 min. Following the dropwise addition of anhydrous TEA (1.0 cm^3, 3.8 equiv.) the reaction was allowed to warm to room temperature and stirred for 40 min. The reaction was diluted with dichloromethane (15 cm^3), washed with distilled water (15 cm^3), extracted with dichloromethane (3×15 cm^3), dried with $MgSO_4$, filtered and the solvent removed in vacuo to afford the corresponding ketone which was not purified. A solution of the crude ketone in ethanol (50 cm^3) was added to a solution of sodium acetate (0.344 g, 4.2 mmol, 3 equiv.) and hydroxylamine hydrochloride (0.29 g, 4.2 mmol, 3 equiv.) in distilled water (5 cm^3) at 60°C. The reaction was stirred for 3 hours at which point the reaction was allowed to cool to room temperature then washed with distilled water (15 cm^3), extracted with dichloromethane (3×15 cm^3), dried with $MgSO_4$, filtered and the solvent removed in vacuo. The crude mixture was submitted to column chromatography (hexane: ethyl acetate, 4:1 with 1% TEA). Concentration of the pure fractions afforded oxime (**17**) as a colourless oil (0.112 g, 14%). ν_{max} (film)/cm^{-1} 3365 br (O–H), 1734 (C=O); δ_H (400 MHz; $CDCl_3$) 1.42 (9H, s, $(CH_3)_3CO$) 3.71 (1H, app. t, *J*=10.0 Hz, H-6), 3.84 (1H, app. t, *J*=10.0 Hz, H-4), 4.20–4.36 (2H, m, H-5, H-6), 5.50 (1H, s, PhCH), 5.71 (1H, d, *J*=10.0 Hz, H-3), 6.78 (1H, s, H-1), 7.17–7.60 (10H, m, Ar), 8.97 (1H, s, OH); δ_C (63 MHz; $CDCl_3$) 27.5 ($(CH_3)_3CCO$) 39.4 ($(CH_3)_3CCO$), 65.9, 69.2, 76.0, 79.4 (C-1, C-3, C-4, C-5), 68.7 (C-6), 101.5 (PhCH), 126.3, 128.6, 128.9, 129.4, 135.6 (ArC–H), 128.8, 137.2 (ArC) (C-2), 150.6 (C=N), 177.7 (C=O); (CI: Found $[M+H]^+$, 506.1092. $C_{24}H_{28}NO_6Se$ requires $[M+H]^+$, 506.1082); *m/z* (CI) 506 ($[M+H]^+$, 10%), 348 (50), 314 (30), 246 (25), 158 (45), 105 (80), 78 (100). *Anhydro oxime* (**18**) was also isolated as a white crystalline compound (240 mg, 50%). mp 144°C (hexane/ether); $[\alpha]_D^{20}$=−77.3 (*c* 0.7, $CHCl_3$); ν_{max} (film)/cm^{-1} 3368 br (O–H), 1733(C=O); δ_H (400 MHz; $CDCl_3$) 1.44 (9H, s, $(CH_3)_3CO$) 3.48 (1H, ddd, *J*=5.0, 9.5 Hz, H-5), 3.69 (1H, app. t, *J*=10.0 Hz, H-6), 3.80 (1H, app. t, *J*=10.0 Hz, H-4), 3.83 (1H, d, *J*=15.0 Hz, H-1), 4.28 (1H, dd, *J*=5.0, 10.5 Hz, H-6), 5.19 (1H, d, *J*=15.0 Hz, H-1), 5.48 (1H, s, PhCH), 5.59 (1H, d, *J*=10.0 Hz, H-3), 7.16–7.38 (5H, m, Ar), 9.13 (1H, s, OH); δ_C (63 MHz;

$CDCl_3$) 27.5 ((CH_3)$_3$CCO) 39.4 ((CH_3)$_3$CCO), 62.7, 69.0 (C-1, C-6), 70.7, 70.8, 80.0 (C-3, C-4, C-5), 101.4 (PhCH), 126.3, 128.7, 129.4 (ArC–H), 137.3 (ArC) 151.1 (C=N), 178.2 (C=O); (CI: Found $[M+H]^+$, 350.1621. $C_{18}H_{23}NO_6$ requires $[M+H]^+$, 350.1604); *m/z* (CI) 350 ($[M+H]^+$, 10%), 248 (100), 144 (30), 105 (45).

4.4. Glycosidation methods

NIS/TfOH, method A.[16] To a flame dried flask containing freshly ground activated 3 Å molecular sieves were added the donor sugar and acceptor sugar (1.25 equiv.) in anhydrous dichloromethane or anhydrous acetonitrile. The solution was allowed to stir for 2 h under an inert atmosphere of N_2, at which point it was cooled to −30°C and a solution of NIS (1.2 equiv.)/TfOH (0.5 equiv.) in anhydrous Et_2O/$ClCH_2CH_2Cl$ (1:1) or anhydrous acetonitrile was added dropwise. The reaction was monitored by tlc until completion then quenched by addition of bisodium dithiosulfate ($Na_2S_2O_{3.5}H_2O$), washed with sodium bicarbonate and allowed to stir to room temperature. The reaction was diluted with dichloromethane, filtered through Celite® and extracted with dichloromethane. The organic liquor was dried with magnesium sulfate ($MgSO_4$), filtered and the solvent removed in vacuo. The residue was then submitted to column chromatography.

Anomeric α-triflate, method B.[19] To a flame dried flask containing freshly ground activated 3 Å molecular sieves was added a solution of anhydrous Et_2O/CH_2Cl_2 (1:1) and silver triflate (AgOTf, 3 equiv.), under an inert atmosphere of N_2. The reaction was then cooled to −78°C and a solution of phenylsulfenyl chloride in anhydrous dichloromethane was added in a dropwise manner. A solution of the donor sugar and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) in anhydrous Et_2O/CH_2Cl_2 (1:2) was added in a dropwise manner. The reaction was allowed to warm to −55°C over 30 min and then the acceptor sugar (1.25 equiv.) in anhydrous Et_2O/CH_2Cl_2 (1:2) was added. The reaction was monitored by TLC until completion at which point it was quenched with sodium bicarbonate and allowed to stir to room temperature. The reaction was diluted with dichloromethane, washed with brine, filtered through Celite® and extracted with dichloromethane. The organic liquor was dried with magnesium sulfate ($MgSO_4$), filtered and the solvent removed in vacuo. The residue was then submitted to column chromatography.

Preparation of phenylsulfenyl chloride.[20] To a solution of thiophenol (21.56 cm^3, 0.21 mol) in anhydrous pentane (100 cm^3) at 0°C was added sulfuryl chloride (19.4 cm^3, 0.24 mol) dropwise over 1 h, under an inert atmosphere of Argon gas. The reaction was allowed to warm to room temperature and stir overnight. The residual pentane was removed in vacuo and ~75% of the red/orange liquor was distilled at 0.2 mbar at 86–90°C, affording phenylsulfenyl chloride (17.51 g, 57%) as a red liquid.

4.4.1. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[2-deoxy-2-(*O*-pivaloyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-α/β-D-glucopyranoside]-1-*O*-α-D-glucopyranoside (23α,23β). Following method B detailed above an anhydrous solution of Et_2O/CH_2Cl_2 (1:1, 2 cm^3), silver triflate (156 mg, 0.60 mmol, 3 equiv.), phenylsulfenyl chloride (73 mg, 0.50 mmol, 2.5 equiv.) in anhydrous dichloromethane (1 cm^3), donor (**7**) (100 mg, 2.0 mmol) and DTBMP (125 mg, 0.61 mmol, 3 equiv.) in anhydrous Et_2O/CH_2Cl_2 (1:2, 1.5 cm^3), acceptor (**19**) (117 mg, 0.25 mmol, 1.25 equiv.) in anhydrous Et_2O/CH_2Cl_2 (1:2, 1.5 cm^3) were reacted and worked up as outlined above. ^{1}H NMR of the crude mixture showed ~5:1 ratio of (**23**α,**23**β). The mixture was submitted to column chromatography using fine grade silica (4:1 hexane: ethyl acetate then 3.5:1 hexane: ethyl acetate, with 1% TEA) afforded the major α-disaccharide product (**23**α) (112 mg, 62%) as a clear oil. and the minor β-disaccharide product (**23**β) (39 mg, 10%) as a clear oil. *For* (**23**α) $[\alpha]_D^{23}$=45.2 (*c* 0.5 in $CHCl_3$); ν_{max} (nujol)/cm^{-1} 3120 w, 3085 w and 3050 m (C–H), 1778 s, 1750 s (C=O), 1620 w, 1600 w, 1505 m and 1490 s (C=C), 1405 m and 1340 w (C–H), 1295 s, 1220 s, 1180 br, 1140 br, 1095 br, 1055 br and 1035 br (C–O), 760 s and 705 s (Ar); δ_H (250 MHz; $CDCl_3$) 1.11 (9H, s, (CH_3)$_3$CCO), 1.20 (9H, s, (CH_3)$_3$CCO), 3.29 (3H, s, CH_3O), 3.38 (1H, app. t, *J*=9.5, 9.0 Hz, H-4′), 3.47 (1H, dd, *J*=3.5, 9.5 Hz, H-2′), 3.57–4.08 (7H, m, H-5′, H-6′, H-6, H-6′, H-4, H-3′, H-5), 4.14 (1H, dd, *J*=5.0, 10.0 Hz, H-6), 4.47 (1H, d, *J*=3.5 Hz, H-1′), 4.48–4.94 (6H, m, PhCH_2), 5.47 (1H, s, PhC*H*), 5.75 (1H, s, H-1), 5.79 (1H, d, *J*=10.0 Hz, H-3), 7.16–7.35 (20H, m, Ar); δ_C (62.5 MHz; $CDCl_3$) 27.50 (2×((CH_3)$_3$CCO)), 38.99 ((CH_3)$_3$CCO), 39.32 ((CH_3)$_3$CCO), 55.70 (CH_3O), 63.60 (C-5), 67.84 (C-6′), 68.83 (C-3), 68.90 (C-6), 70.15, (C-5′), 73.81, 75.43, 76.06 (3×(PhCH_2)), 77.89 (C-4′), 80.09 (C-4), 80.29 (C-2′), 82.56 (C-3′), 93.04 (C-1), 98.40 (C-1′), 101.65 (PhCH), 126.37, 127.97, 128.24, 128.28, 128.36, 128.48. 128.67, 128.79, 128.89, 129.51, 137.19, 138.50, 138.52, 139.11 ((4×Ar{C-2, C-6}), (4×Ar{C-3, C-5}) (3×Ar{C-1}), (4×Ar{C-4})), 156.18 (C-2, PhO{C-1}), 173.81, 177.61 (2×((CH_3)$_3$CCO)); (CI: Found $[M+NH_4]^+$, 913.4462, $C_{51}H_{65}N_2O_{13}$ requires $[M+NH_4]^+$, 913.4486); *m/z* (CI) 913 ($[M+NH_4]^+$, 7%), 253, (10), 105 (18), 91 (100), 57 (31). *For* (**23**β). $[\alpha]_D^{23}$=−37.6 (*c* 0.45 in $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 1.11 (9H, s, (CH_3)$_3$CCO), 1.12 (9H, s, (CH_3)$_3$CCO), 3.29 (3H, s, CH_3O), 3.38–3.48 (2H, m, H-2′, H-4′), 3.55–3.75 (4H, m, H-5, H-6, H-6′, H-5′), 3.90–3.97 (2H, m, H-6′, H-3′), 4.15–4.27 (1H, m, H-6), 4.39–4.59 (4H, m, H-4, H-1′, PhCH_2), 4.69–4.94 (4H, m, PhCH_2), 5.33 (1H, s, PhC*H*), 5.75 (1H, s, H-1), 5.88 (1H, d, *J*=8.5 Hz, H-3), 7.16–7.33 (20H, m, Ar); δ_C (62.5 MHz; $CDCl_3$) 27.39, ((CH_3)$_3$CCO), 27.44 ((CH_3)$_3$CCO), 39.04 ((CH_3)$_3$CCO), 39.16 (C(CH_3)$_3$CCO), 55.55 (CH_3O), 66.42 (C-5), 67.33 (C-6′), 68.48 (C-3), 69.93 (C-6), 70.20, (C-5′), 73.82, 75.49, 76.10 (3×(PhCH_2)), 77.62, 78.27 (C-4, C-4′), 80.27 (C-2′), 82.29 (C-3′), 91.67 (C-1), 98.36 (C-1′), 101.55 (PhCH), 126.38, 128.06, 128.23, 128.48, 128.66, 128.80. 128.89, 129.49, 137.14, 138.35, 138.44, 139.06 ((4×Ar{C-2, C-6}), (4×Ar{C-3, C-5}) (4×Ar{C-1}), (4×Ar{C-4})), 155.95 (C-2), 173.86, 176.95 (2×((CH_3)$_3$CCO)); (CI: Found $[M+NH_4]^+$, 913.4462, $C_{51}H_{65}N_2O_{13}$ requires $[M+NH_4]^+$, 913.4486); *m/z* (CI) 913 ($[M+NH_4]^+$, 3%), 794 (2), 346 (5), 302 (8), 253, (11), 243 (7), 181 (12), 105 (24), 91 (100), 85 (22), 57 (41), 41 (10), 39 (9).

4.4.2. Phenyl 2-*O*-acetyl-3-*O*-[2-deoxy-2-(*O*-pivaloyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-α/β-D-glucopyranoside]-4,6-*O*-benzylidene-1-*O*-α-D-glucopyranoside (24α,24β). Following method B detailed above, an

anhydrous solution of Et_2O/CH_2Cl_2 (1:1, 4 cm^3), silver triflate (156 mg, 0.60 mmol, 3 equiv.), phenylsulfenyl chloride (73 mg, 0.50 mmol, 2.5 equiv.) in anhydrous dichloromethane (2 cm^3), donor (**7**) (100 mg, 2.0 mmol) and DTBMP (124 mg, 0.61 mmol, 3 equiv.) in anhydrous Et_2O/CH_2Cl_2 (1:2, 2 cm^3), acceptor (20) (98 mg, 0.25 mmol, 1.25 equiv.) in anhydrous Et_2O/CH_2Cl_2 (1:2, 1.5 cm^3) were reacted and worked up as outlined above. ^1H NMR of the crude mixture showed ~1:3 (**24**α,**24**β). The mixture was submitted to column chromatography, using fine grade silica gel (5:1 hexane/ethyl acetate then 3.5:1 hexane/ethyl acetate, with 1% TEA). Evaporation of pure fractions of the minor product afforded α-disaccharide (**24**α). (25 mg, 17%) as a foam. Evaporation of the remaining fractions containing disaccharide products afforded a mixture of ≥11:1 of disaccharides (**24**β,**24**α). (75 mg, 54%) as a foam. *For* (**24**α). $[\alpha]_D^{20}$=61.3 (*c* 0.15 in $CHCl_3$); ν_{max} (nujol)/cm^{-1} 3120 w, 3085 m and 3060 m (C–H), 1782 s, and 1755 s (C═O), 1615 s, 1602 m and 1500 m (C═C), 1325 s and 1295 m (C–H), 1240 s, 1222 s, 1180 m, 1138 s, 1105 s, 1090 s and 1038 s (C–O), 745 s and 705 s (Ar); δ_H (250 MHz; $CDCl_3$) 0.80 (9H, s, (CH_3)$_3$CCO), 1.21 (9H, s, (CH_3)$_3$CCO), 2.10 (3H, s, CH_3CO), 3.66–3.85 (3H, m, H-5, H-4′, H-6′), 3.89–4.05 (2H, m, H-6, H-4), 4.10 (1H, dd, *J*=5.0, 10.0 Hz, H-6), 4.32–4.46 (2H, m, H-6′, H-5′), 4.56 (1H, t, *J*=9.5 Hz, H-3′), 4.94 (1H, dd, *J*=4.0, 9.5 Hz, H-2′), 5.48 (1H, s, PhC*H*), 5.53 (1H, s, PhC*H*), 5.69 (1H, d, *J*=4.0 Hz, H-1′), 5.78 (1H, d, *J*=10.5 Hz, H-3), 6.26 (1H, s, H-1), 6.94–7.36 (15H, m, Ar); δ_C (62.5 MHz; $CDCl_3$) 21.23 (*C*H_3CO), 27.11 ((*C*H_3)$_3$CCO), 27.46 ((*C*H_3)$_3$CCO), 38.52 ((CH_3)$_3$*C*CO), 39.31 ((CH_3)$_3$*C*CO), 63.30, 63.82 (C-5′, C-5), 68.79, 68.94, 69.01 (C-3, C-6, C-6′), 72.04, 72.15 (C-2′, C-3′), 80.09, 81.82 (C-4′, C-4), 92.29 (C-1), 95.47 (C-1′), 101.76, 102.02 (Ph*C*H′, Ph*C*H), 117.19, 123.49, 126.28, 126.65, 128.69, 128.76, 129.52, 129.61, 130.11, 137.20 ((2×Ar{C-1}), (3×Ar{C-4}), (3×Ar{C-2, C-6}), (3×Ar{C-3, C-5})), 155.12, 156.57 (C-2, PhO{C-1}), 170.44 (CH_3*C*O), 173.91, ((CH_3)$_3$C*C*O) 177.65, ((CH_3)$_3$C*C*O); (CI: Found $[M+NH_4]^+$, 835.3616, $C_{44}H_{55}N_2O_{14}$ requires $[M+NH_4]^+$, 835.3653); *m/z* (CI) 835 ($[M+NH_4]^+$, 8%), 724 (14), 711 (8), 415 (15), 321 (18), 263 (23), 149 (25), 105 (100), 93 (51), 85 (33), 77 (27), 57 (65), 43 (15), 41 (22), 39 (32). *For* (**24**β). $[\alpha]_D^{20}$=49.0 (*c* 0.6 in $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 1.19 (9H, s, (CH_3)$_3$CCO), 1.24 (9H, s, (CH_3)$_3$CCO), 1.98 (3H, s, CH_3CO), 3.48–3.76 (4H, m, H-6, H-5, H-4′, H-6′), 3.98–4.16 (2H, m, H-5′, H-6), 4.17 (1H, dd, *J*=5.0, 10.0 Hz, H-6′), 4.45–4.59 (2H, m, H-4, H-3′), 4.62 (1H, s, PhC*H*), 4.89 (1H, dd, *J*=3.5, 9.5 Hz, H-2′), 5.52 (1H, s, PhC*H*), 5.72 (1H, d, *J*=3.5 Hz, H-1′), 5.81 (1H, d, *J*=8.5 Hz, H-3), 6.09 (1H, s, H-1), 6.94–7.46 (15H, m, Ar); δ_C (62.5 MHz; $CDCl_3$) 21.46 (*C*H_3CO), 27.45 ((*C*H_3)$_3$CCO), 27.66 ((*C*H_3)$_3$CCO), 39.11 ((CH_3)$_3$*C*CO), 39.21 ((CH_3)$_3$*C*CO), 63.69 (C-5′), 67.00 (C-5), 68.92 (C-3), 69.16, 69.41 (C-6, C-6′), 73.84 (C-2′), 74.33 (C-3′), 76.74 (C-4), 80.61 (C-4′), 91.96 (C-1), 95.15 (C-1′), 100.77, 102.74 (Ph*C*H′, Ph*C*H), 116.96, 123.50, 126.33, 126.62, 128.40, 128.83, 129.21, 130.16, 137.20 ((2×Ar{C-1}), (3×Ar{C-4}), (3×Ar{C-2, C-6}), (3×Ar{C-3, C-5})), 156.55, 157.44 (C-2, PhO{C-1}), 170.47 (CH_3*C*O), 173.97, ((CH_3)$_3$C *C*O) 177.03, ((CH_3)$_3$C*C*O); (CI: Found $[M]^+$, 817.3316, $C_{44}H_{51}NO_{14}$ requires $[M]^+$, 817.3309); *m/z* (CI) 817 ($[M]^+$, 1%), 724 ($[M-OPh]^+$, 2), 716 (5), 622 (3), 415 (13), 348 (20), 241 (28), 321 (16), 241 (28), 149 (22), 131 (19), 105 (100), 93 (44), 91 (19), 85 (21), 77 (26), 57 (39), 43 (15), 41 (21), 39 (31).

4.4.3. Benzyl 2-deoxy-*N*-acetyl-3-*O*-benzyl-4-[2-deoxy-2-(*O*-pivaloyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-α/β-D-glucopyranoside]-1-*O*-α-D-glucopyranoside (26α, 26β). Following method A detailed above, and using anhydrous dichloromethane as solvent, donor (**7**) (75 mg, 0.152 mmol), acceptor (**22**) (68 mg, 0.152 mmol, 1.0 equiv.), NIS (47 mg, 0.192 mmol, 1.26 equiv.), TfOH (6.7 μl, 0.08 mmol, 0.5 equiv.) were reacted and quenched and worked up as outlined above then submitted to column chromatography (1:1 cyclohexane/ethyl acetate, with 1% TEA as co-solvent). Evaporation of pure fractions of the major product afforded α-disaccharide (**26**α) (40 mg, 30%) as a clear oil. Evaporation of the fractions containing both disaccharide anomers afforded a 1:1 ratio of (**26**α/**26**β) (25 mg, 19%,) as a clear oil. Finally, evaporation of the following fractions afforded β-disaccharide (**26**β) (9 mg, 7%, total yield 74 mg, 57%,) as a clear oil. *For* (**26**α). $[\alpha]_D^{20}$=124.9 (*c* 0.45 in $CHCl_3$); ν_{max} (nujol)/cm^{-1} 3115 w, 3085 m and 3050 m (C–H), 1740 s, and 1680 s (C═O), 1620 w, 1595 m and 1507 m (C═C), 1460 s and 1445 m (C–H), 1375 s, 1340 m, 1270 br, 1145 s, 1120 s, 1040 br and 920 s (C–O), 740 s and 700 s (Ar); δ_H (600 MHz; $CDCl_3$) 1.05 (9H, s, (CH_3)$_3$CCO), 1.30 (9H, s, (CH_3)$_3$CCO), 1.79 (3H, s, CH_3CO), 2.10 (3H, s, CH_3CO), 3.68 (1H, dd, *J*=9.0, 10.5 Hz, H-3′), 3.77 (1H, t, *J*=10.5 Hz, H-6), 3.81 (1H, app. t, *J*=9.0, 9.5 Hz, H-4′), 3.92 (1H, dd, *J*=3.0, 10.0 Hz, H-5′), 4.01 (1H, t, *J*=10.0 Hz, H-4), 4.20–4.24 (3H, m, H-6′, H-2, H-5), 4.40–4.47 (4H, m, H-6′, H-6, PhCH_2), 4.68 (2H, dd, *J*=9.5, 11.5 Hz, PhCH_2), 4.88 (1H, d, *J*=3.5 Hz, H-1′), 5.22 (1H, d, *J*=9.0 Hz, NH), 5.59 (1H, s, PhC*H*), 5.97 (1H, d, *J*=10.5 Hz, H-3), 6.09 (1H, s, H-1), 7.22–7.48 (15H, m, Ar); δ_C (150 MHz; $CDCl_3$) 20.71 (*C*H_3CO), 23.26 (*C*H_3CO), 26.94 ((*C*H_3)$_3$CCO), 27.09 ((*C*H_3)$_3$CCO), 38.50 ((CH_3)$_3$*C*CO), 38.93 ((CH_3)$_3$*C*CO), 52.36 (C-2′), 63.14 (C-6′), 64.59 (C-5), 68.25 (C-6), 68.48 (C-3), 69.00 (C-5′), 70.05 (Ph*C*H$_2$), 74.97 (Ph*C*H$_2$), 78.50, (C-3′), 79.71 (C-4), 83.71 (C-4′), 95.42 (C-1), 96.88 (C-1′), 101.34 (Ph*C*H), 125.98, 127.62, 128.02, 128.24, 128.31, 128.46, 128.67, 129.11, 136.74, 136.77 138.20 ((3×Ar{C-1}), (3×Ar{C-4}), (3×Ar{C-2, C-6}), (3×Ar{C-3, C-5})), 155.16 (C-2), 169.80 (CH_3*C*O), 170.51 (CH_3*C*O), 173.24, ((CH_3)$_3$C*C*O) 177.31, ((CH_3)$_3$C*C*O); (CI: Found $[M]^+$, 874.3852, $C_{47}H_{58}N_2O_{14}$ requires $[M]^+$, 874.3888); *m/z* (CI) 874 ($[M]^+$, 1%), 773 (1), 528 (16), 444 (100), 336 (32), 228 (11), 105 (14), 91 (80), 85 (16), 57 (23), 41 (10), 39 (10). *For* (**26**β). $[\alpha]_D^{25}$=24.7 (*c* 0.45 in $CHCl_3$); ν_{max} (nujol)/cm^{-1} 3310 w (N–H), 3110 w, 3085 w and 3060 m (C–H), 1780 s, 1750 s and 1675 s (C═O), 1550 m and 1510 m (C═C), 1490 s (C–H), 1320 m, 1285 m, 1240 s, 1120 s, 1090 br and 1045 br (C–O), 760 m and 710 m (Ar); δ_H (600 MHz; $CDCl_3$) 1.23 (9H, s, (CH_3)$_3$CCO), 1.24 (9H, s, (CH_3)$_3$CCO), 1.83 (3H, s, CH_3CO), 2.06 (3H, s, CH_3CO), 3.64–3.72 (2H, m, H-5, H-6), 3.76–3.80 (1H, m, H-3′), 3.89–3.92 (2H, m, H-4′, H-5′), 4.12–4.15 (1H, m, H-6′), 4.27 (1H, dd, *J*=4.0, 9.0 Hz, H-6) 4.35 (1H, dt, *J*=3.5, 10.0 Hz, H-2′), 4.44–4.49 (2H, m, H-4, PhCH_2), 4.54 (1H, d, *J*=11.5 Hz, H-6′), 4.68–4.72 (2H, m, PhCH_2), 4.84 (1H, d, *J*=3.5 Hz, H-1′), 4.84 (1H, d, *J*=10.5 Hz, PhCH_2), 5.25 (1H, s, PhC*H*), 5.42 (1H, d, *J*=9.5 Hz, NH), 5.98 (1H, d, *J*=9.0 Hz, H-3), 6.23 (1H, s, H-1), 7.29–7.42 (15H,

m, Ar); δ_C (150 MHz; $CDCl_3$) 20.72 (CH_3CO), 23.31 (CH_3CO), 26.97 (($CH_3)_3CCO$), 27.09 (($CH_3)_3CCO$), 38.58 (($CH_3)_3CCO$), 38.73 (($CH_3)_3CCO$), 52.55 (C-2′), 62.27 (C-6′), 66.16 (C-5), 68.10 (C-3), 69.01 (C-5′), 69.33 (C-6), 69.92 (PhCH_2), 75.05 (PhCH_2), 75.69, (C-4′), 76.77 (C-4), 79.86 (C-3′), 91.85 (C-1), 96.91 (C-1′), 100.88 (PhCH), 125.95, 127.71, 127.93, 128.16, 128.23, 128.51, 128.69, 128.96, 136.71, 136.74 137.74 ((3×Ar{C-1}), (3×Ar{C-4}), (3×Ar{C-2, C-6}), (3×Ar{C-3, C-5})), 156.80 (C-2), 169.63 (CH_3CO), 170.26 (CH_3CO), 173.53 (($CH_3)_3CCO$), 176.40 (($CH_3)_3CCO$); (CI: Found $[M+H]^+$, 875.3988, $C_{47}H_{59}N_2O_{14}$ requires $[M+H]^+$, 875.3966); *m/z* (CI) 875 ($[M+H]^+$, 5%), 767 (6), 474 (23), 444 (5), 364 (23), 348 (19), 336 (17), 320 (10), 319 (9), 242 (30), 211 (17), 124 (14), 105 (33), 91 (100), 85 (9), 57 (13), 43 (5), 41 (5), 39 (7).

4.4.4. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[2-deoxy-2-(*O*-benzoyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-α/β-D-glucopyranoside]-1-*O*-α-D-glucopyranoside (27α,27β). Following method A detailed above, and using anhydrous dichloromethane as solvent, donor (**8**) (75 mg, 0.146 mmol), acceptor (**19**) (82 mg, 0.175 mmol, 1.2 equiv.), NIS (43 mg, 0.175 mmol, 1.2 equiv.) and TfOH (6.5 μl, 0.073 mmol, 0.5 equiv.) were reacted and quenched and worked up as outlined above. ^{1}H NMR of the crude mixture showed ≥25:1, α/β ratio of disaccharide products. The crude mixture was submitted to column chromatography (4:1 hexane/ethyl acetate then 3.5:1 hexane/ethyl acetate, with 1% TEA). Evaporation of pure fractions of major product afforded α-disaccharide (**27**α) (97 mg, 72%) as a colourless oil. $[\alpha]_D^{25}$=56.3 (*c* 0.4 in $CHCl_3$); ν_{max} (nujol)/cm^{-1} 3120 w, 3090 m and 3065 m (C–H), 1760 br (C=O), 1618 w, 1600 m and 1515 m (C=C), 1325 m and 1300 m (C–H), 1263 br, 1165 br, 1115 br, 1060 br and 1038 br (C–O), 740 m and 715 m (Ar); δ_H (600 MHz; $CDCl_3$) 1.35 (9H, s, ($CH_3)_3CCO$), 3.36 (3H, s, CH_3O), 3.46 (1H, dd, *J*=3.5, 9.5 Hz, H-2′), 3.54 (1H, app. t, *J*=9.0, 10.0 Hz, H-4′), 3.78–3.84 (3H, m, H-6′, H-5′, H-6), 3.91 (1H, dd, *J*=4.5, 11.5 Hz, H-6′), 3.98 (1H, app. t, *J*=9.0, 9.5 Hz, H-3′), 4.01 (1H, t, *J*=10.5 Hz, H-4), 4.14 (1H, m, H-5), 4.31 (1H, dd, *J*=5.0, 11.5 Hz, H-6), 4.49 (1H, d, *J*=12.0 Hz, PhCH_2), 4.52 (1H, d, *J*=3.5 Hz, H-1′), 4.61 (1H, d, *J*=12.0 Hz, PhCH_2), 4.66 (1H, d, *J*=11.5 Hz, PhCH_2), 4.82 (1H, d, *J*=11.0 Hz, PhCH_2), 4.97 (2H, dd, *J*=11.0, 15.0 Hz, PhCH_2), 5.60 (1H, s, PhCH), 5.98 (1H, d, *J*=10.5 Hz, H-3), 6.11 (1H, s, H-1), 7.25–7.61 (23H, m, Ar), 8.01–8.03 (2H, m, Ar); δ_C (150 MHz; $CDCl_3$) 27.10 (($CH_3)_3CCO$), 38.95 (($CH_3)_3CCO$), 55.26 (CH_3O), 63.20 (C-5), 67.20 (C-6′), 68.48 (C-3), 68.54 (C-6), 70.05, (C-5′), 73.34, 75.03, 75.58 (3×(PhCH_2)), 77.21 (C-4′), 79.87 (C-4), 80.16 (C-2′), 81.93 (C-3′), 92.74 (C-1), 97.96 (C-1′), 101.29 (PhCH), 125.97, 127.50, 127.80, 127.82, 127.87, 127.92. 127.95, 128.25, 128.33, 128.37, 128.41, 128.47, 128.65, 129.09, 129.66, 133.58, 136.81, 138.01, 138.12, 138.70 ((5×Ar{C-1}), (5×Ar{C-4}), (5×Ar{C-2, C-6}), (5× Ar{C-3, C-5})), 156.57 (C-2), 162.41 (PhCO), 177.13, (($CH_3)_3CCO$); (EI: Found $[M-CH_2C_6H_5]^+$, 824.3303, $C_{46}H_{50}NO_{13}$ requires $[M-CH_2C_6H_5]^+$, 824.3282); *m/z* (CI) 934 ($[M+NH_4]^+$, 5%), 348 (8), 304 (18), 242, (9), 198 (9), 131 (8), 122 (13), 105 (100), 91 (96), 77 (20), 57 (19). *For* β-disaccharide (**27**β). ν_{max} (nujol)/cm^{-1} 3120 w, 3095 m and 3060 m (C–H), 1780 s, 1760 s (C=O), 1620 w, 1600 w, 1510 m and 1490 s (C=C), 1410 m and 1340 m (C–H), 1285 s, 1160 br, 1140 br, 1090 br, 1055 br and 1035 br (C–O), 760 s and 705 s (Ar); δ_H (400 MHz; $CDCl_3$) 1.23 (9H, s, ($CH_3)_3CCO$), 3.37 (3H, s, CH_3O), 3.48–3.57 (2H, m, H-2′, H4′), 3.72–3.87 (5H, m, H-6′, H-6′, H-5′, H-6, H-4), 4.00 (1H, t, *J*=9.5 Hz, H-3′), 4.08–4.13 (1H, m, H-5), 4.27 (1H, dd, *J*=5.0, 10.5 Hz, H-6), 4.58 (1H, d, *J*=3.5 Hz, H-1′) 4.58 (1H, d, *J*=11.0 Hz, PhCH_2), 4.68 (1H, d, *J*=12.0 Hz, PhCH_2), 4.76 (1H, d, *J*=12.0 Hz, PhCH_2), 4.83 (1H, d, *J*= 11.0 Hz, PhCH_2), 4.89 (1H, d, *J*=11.0 Hz, PhCH_2), 4.96 (1H, d, *J*=11.0 Hz, PhCH_2), 5.55 (1H, s, PhCH), 5.78 (1H, d, *J*=10.0 Hz, H-3), 6.11 (1H, s, H-1), 7.26–7.41 (25H, m, Ar); δ_C (100 MHz; $CDCl_3$) 27.1 (($CH_3)_3CCO$), 38.9 (($CH_3)_3CCO$), 55.3 (CH_3O), 91.0 (C-1), 98.0 (C-1′), 101.1 (PhCH), 149.9 (C-2), 167.8 (PhCO), 177.1 (($CH_3)_3CCO$).

4.4.5. Phenyl 2-*O*-acetyl-3-*O*-[2-deoxy-2-(*O*-benzoyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-α/β-D-glucopyranoside]-4,6-*O*-benzylidene-1-*O*-α-D-glucopyranoside (28α,28β). Following method A detailed above, and using anhydrous dichloromethane as solvent, donor (**8**) (50 mg, 0.097 mmol), acceptor (**20**) (39 mg, 0.10 mmol, 1.1 equiv.), NIS (30 mg, 0.12 mmol, 1.25 equiv.), TfOH (4.5 μl, 0.05 mmol, 0.5 equiv.) were reacted and quenched and worked up as outlined above. ^{1}H NMR of the crude mixture showed ~2:1, (**28**α,**28**β). The mixture was submitted to column chromatography (20:1 toluene/ethyl acetate, with 1% TEA) and evaporation of fractions containing the major product afforded α-disaccharide (**28**α) (≥20:1, (**28**α,**28**β), 18 mg, 22%) as a white solid. Evaporation of the remaining fractions containing both disaccharide anomers afforded a mixture of disaccharides (**28**α,**28**β) in a ratio of 1.6:1 (19 mg, 23%, 45% total yield) as an opaque oil. *For* (**28**α). $[\alpha]_D^{20}$=58.8 (*c* 0.48 in $CHCl_3$); ν_{max} (nujol)/cm^{-1} 3085 m and 3040 m (C–H), 1750 br, and 1710 s (C=O), 1605 s, 1600 m and 1500 m (C=C), 1490 s, 1460 s, 1375 s and 1320 m (C–H), 1290 s, 1245 s, 1180 br, 1150 br, 1100 br, 1060 br and 1025 br (C–O), 760 s and 705 s (Ar); δ_H (400 MHz; $CDCl_3$) 1.24 (9H, s, ($CH_3)_3CCO$), 2.09 (3H, s, CH_3CO), 3.70 (1H, t, *J*=10.0 Hz, H-6′), 3.78–3.86 (2H, m, H-4′, H-6), 3.96–4.01 (2H, m, H-4, H-5′), 4.16 (1H, dd, *J*=5.0, 10.0 Hz, H-6′), 4.30–4.45 (2H, m, H-5, H-6), 4.60 (1H, t, *J*=9.5 Hz, H-3′), 4.96 (1H, dd, *J*=4.0, 10.0 Hz, H-2′), 5.42 (1H, s, PhCH'), 5.55 (1H, s, PhCH), 5.74 (1H, d, *J*=4.0 Hz, H-1′), 5.88 (1H, d, *J*=10.5 Hz, H-3), 6.44 (1H, s, H-1), 6.96–7.69 (20H, m, Ar); δ_C (62.5 MHz; $CDCl_3$) 21.20 (CH_3CO), 27.50 (($CH_3)_3CCO$), 39.37 (($CH_3)_3CCO$), 63.25 (C-5′), 63.84 (C-5), 68.98 (C-3, C-6, C-6′), 72.13 (C-2′), 72.44 (C-3′), 80.06 (C-4), 81.93 (C-4′), 92.58 (C-1), 95.37 (C-1′), 101.52 (PhCH'), 101.83 (PhCH), 117.18, 123.48, 126.04, 126.34, 128.39, 128.70, 129.98, 130.11, 133.73, 134.96, 137.16 ((3×Ar{C-1}), (4×Ar{C-4}), (4×Ar{C-2, C-6}), (4×Ar{C-3, C-5})), 156.55 (C-2, PhO{C-1}), 163.54 (PhCO), 170.49 (CH_3CO), 177.13, (($CH_3)_3CO$); (CI: Found $[M]^+$, 837.2976, $C_{46}H_{47}NO_{14}$ requires $[M]^+$, 837.2996); *m/z* (CI) 837 ($[M]^+$, 1%), 744 ($[M-OPh]^+$, 5), 732 (3), 149 (14), 123 (20), 105 (100), 91 (11), 85 (13), 77 (25), 57 (36), 43 (11), 41 (8). *For* (**28**β). δ_H (250 MHz; $CDCl_3$) 1.22 (9H, s, ($CH_3)_3CCO$), 1.69 (3H, s, CH_3CO), 4.26 (1H, s, PhCH), 4.85 (1H, dd, *J*=3.5, 9.5 Hz, H-2′), 5.51 (1H, s, PhCH), 5.70 (1H, d, *J*=4.0 Hz, H-1′), 5.86 (1H, d, *J*=8.0 Hz, H-3), 6.28 (1H, s, H-1).

4.4.6. Phenyl 2-*O*-acetyl-3-*O*-[2-deoxy-2-(*O*-ethyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-α/β-D-glucopyranoside]-4,6-*O*-benzylidene-1-*O*-α-D-glucopyranoside (29α,29β). Following method A detailed above, and using anhydrous dichloromethane as solvent, donor (**11**) (30 mg, 0.069 mmol), acceptor (**20**) (33 mg, 0.085 mmol, 1.25 equiv.), NIS (20 mg, 0.082 mmol, 1.2 equiv.) and TfOH (3 μl, 0.034 mmol, 0.5 equiv.) in $Et_2O/ClCH_2CH_2Cl$ (1:1, 1.45 cm^3) were reacted and quenched and worked up as outlined above. ^1H NMR of the crude mixture showed ~1.7:1 ratio of (**29**α,**29**β). The mixture was submitted to column chromatography (5.5:1 hexane/ethyl acetate→5:1 hexane/ethyl acetate→4.5:1 hexane/ethyl acetate, with 1% TEA as co-solvent). Evaporation of pure fractions containing the major product afforded α-disaccharide (**29**α) (18 mg, 35%) as a foam. Evaporation of the remaining fractions containing both disaccharide anomers afforded a ratio of ~1:2 of (**29**α,**29**β) (20 mg, 38 and 73% total yield) as an opaque oil. *For* (**29**α). $[\alpha]_D^{20}$=63.3 (*c* 0.15 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 1748 s (C=O), 1545 m (C=C), 1490 s, 1459 s, 1320 m (C–H), 1290 s, 1244 s, 760 s and 705 s (Ar); δ_H (250 MHz; $CDCl_3$) 0.87 (3H, t, *J*=7.0 Hz, CH_3CH_2ON) 1.16 (9H, s, $(CH_3)_3CCO$), 2.03 (3H, s, CH_3CO), 3.66–3.87 (6H, CH_3CH_2ON, H-6′, H-6, H-4, H-4′), 3.97 (1H, m, H-5′), 4.12 (1H, dd, *J*=5.0, 10.0 Hz, H-6′), 4.23–4.39 (2H, m, H-5, H-6), 4.55 (1H, t, *J*=9.5 Hz, H-3′), 4.83 (1H, dd, *J*=4.0, 10.0 Hz, H-2′), 5.49 (1H, s, PhC*H*), 5.55 (1H, s, PhC*H*), 5.64 (1H, d, *J*=10.0 Hz, H-3), 5.74 (1H, d, *J*=4.0 Hz, H-1′), 6.39 (1H, s, H-1), 6.94-7.40 (15H, m, Ar); δ_C (62.5 MHz; $CDCl_3$) 14.82 (CH_3CH_2ON), 21.21 (CH_3CO), 27.53 ($(CH_3)_3CCO$), 39.16 ($(CH_3)_3CCO$), 63.22, 63.36 (C-5′, C-5), 69.15, 70.57 (C-3, C-6, C-6′, CH_3CH_2ON), 71.14, 72.39 (C-2′, C-3′), 80.18, 82.21 (C-4, C-4′), 91.75 (C-1), 95.31 (C-1′), 101.70, 101.84 (PhCH′, PhCH), 117.26, 123.37, 126.36, 126.52, 128.48, 128.63, 129.37, 129.42, 130.06, 137.45 ((2×Ar{C-1}), (3×Ar{C-4}), (3×Ar{C-2, C-6}), (3×Ar{C-3, C-5})), 147.10 (C-2), 156.63 (PhO{C-1}), 170.67 (CH_3CO), 177.45, ($(CH_3)_3CC$=O); (CI: Found $[M+H]^+$, 762.3146, $C_{41}H_{48}NO_{14}$ requires $[M+H]^+$, 762.3125); *m/z* (CI) 837 ($[M+NH_4]^+$, 1%), 762 ($[M+H]^+$, 5%), 668 ($[M-OPh]^+$, 11), 415 (29), 376 (69), 348 (20), 321 (20), 270 (29), 242 (23), 149 (42), 131 (50), 105 (100), 93 (57), 91 (21), 85 (20), 77 (22), 68 (34), 65 (35), 57 (24), 55 (19), 43 (14), 41 (13), 39 (33). *For* (**29**β). δ_H (250 MHz; $CDCl_3$) 1.06 (3H, app. t, *J*=7.0, 7.5 Hz, CH_3CH_2O) 1.18 (9H, s, $(CH_3)_3CCO$), 2.03 (3H, s, CH_3CO), 4.55 (1H, t, *J*=9.5 Hz, H-3′), 4.83 (1H, dd, *J*=3.5, 9.5 Hz, H-2′), 5.48 (1H, s, PhC*H*), 5.58 (1H, d, *J*=8.0 Hz, H-3), 5.66 (1H, d, *J*=4.0 Hz, H-1′), 5.67 (1H, s, PhC*H*), 6.20 (1H, s, H-1).

4.4.7. Phenyl 2-*O*-acetyl-3-*O*-[2-deoxy-2-(*O*-methyl)oximino-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-α/β-D-glucopyranoside]-4,6-*O*-benzylidene-1-*O*-α-D-glucopyranoside (30α,30β). Following method B detailed above, silver triflate (46 mg, 0.18 mmol, 3 equiv.), phenylsulfenyl chloride (21 mg, 0.15 mmol, 2.5 equiv.), donor (**12**) (25 mg, 0.06 mmol) and DTBMP (36 mg, 0.18 mmol, 3 equiv.) in anhydrous Et_2O:CH_2Cl_2 (1:2, 1 cm^3), acceptor (**20**) (29 mg, 0.08 mmol, 1.25 equiv.) in anhydrous Et_2O/CH_2Cl_2 (1:2, 1 cm^3) were reacted and quenched and worked up as outlined above. ^1H NMR of the crude reaction mixture showed it to contain a ~2.5:1, (**30**β,**30**α. The crude mixture was submitted to column chromatography (6.5:1 hexane/ethyl acetate→6:1 hexane/ethyl acetate→5.5:1 hexane/ethyl acetate, with 1% TEA). Evaporation of fractions containing the less polar eluting product afforded α-disaccharide (**30**α), contaminated with an unidentified but possibly related product (5 mg, 11%), as a clear oil. Evaporation of the pure fractions of the second eluting product afforded β-disaccharide (**30**β) (5 mg, 11%) as a clear oil. Finally, the remaining fractions afforded β-disaccharide (**30**β) as a clear oil containing a minor impurity (3 mg, 7%). *For* (**30**α). δ_H (250 MHz; $CDCl_3$) 1.16 (9H, s, $(CH_3)_3CCO$), 2.08 (3H, s, CH_3CO), 3.45 (3H, s, CH_3ON), 4.53 (1H, t, *J*=9.5 Hz, H-3′), 4.83 (1H, dd, *J*=4.0, 10.0 Hz, H-2′), 5.49 (1H, s, PhC*H*), 5.50 (1H, s, PhC*H*), 5.64 (1H, d, *J*=10.0 Hz, H-3), 5.78 (1H, d, *J*=4.0 Hz, H-1′), 6.36 (1H, s, H-1); δ_C (62.5 MHz; $CDCl_3$) 21.22 (CH_3CO), 27.54 (($CH_3)_3CCO$), 62.54, 63.42, 66.42, 69.02, 69.08 (C-5′, C-5, CH_3ON, C-3, C-6, C-6′), 71.51, 72.38 (C-2′, C-3′), 80.10 82.22 (C-4, C-4′), 91.70 (C-1), 95.52 (C-1′), 101.72, 101.88 (PhCH′, PhCH), 117.23, 123.37, 126.47, 126.52, 128.50, 128.65, 129.46, 130.07 ((3×Ar{C-4}), (3×Ar{C-2, C-6}), (3×Ar{C-3, C-5})); *For* (30β). $[\alpha]_D^{20}$=24.5 (*c* 0.2 in $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 1.18 (9H, s, $(CH_3)_3CCO$), 2.03 (3H, s, CH_3CO), 3.33–3.46 (2H, m, H-6, H-5), 3.61 (1H, t, *J*=9.5 Hz, H-4′), 3.70 (1H, app. t, *J*=10.0, 10.5 Hz, H-6′), 3.81 (3H, s, CH_3ON), 3.92–4.03 (2H, m, H-6, H-5′), 4.09 (1H, s, PhC*H*), 4.17 (1H, dd, *J*=5.0, 10.0 Hz, H-6′), 4.30 (1H, dd, *J*=8.5, 10.0 Hz, H-4), 4.56 (1H, t, *J*=9.5 Hz, H-3′), 4.91 (1H, dd, *J*=3.5, 10.0 Hz, H-2′), 5.48 (1H, s, PhC*H*), 5.58 (1H, d, *J*=8.5 Hz, H-3), 5.67 (1H, d, *J*=3.5 Hz, H-1′), 6.18 (1H, s, H-1) 7.00–7.46 (15H, m, Ar); δ_C (62.5 MHz; $CDCl_3$) 21.16 (CH_3CO), 27.45 (($CH_3)_3CCO$), 63.22, 66.60, 68.97, 69.29, 69.34 70.42, 74.72 (C-5′, C-5, CH_3ON, C-3, C-6, C-6′, C-2′, C-3′), 76.85 80.16 (C-4′, C-4), 89.65 (C-1), 95.35 (C-1′), 100.14, 103.79 (PhCH′, PhCH), 117.08, 123.37, 126.27, 127.12, 128.25, 128.97, 130.10 ((3×Ar{C-4}), (3×Ar{C-2, C-6}), (3×Ar{C-3, C-5})); (CI: Found $[M]^+$, 747.2881, $C_{40}H_{45}NO_{13}$ requires $[M]^+$, 747.2890); *m/z* (CI) 837 ($[M]^+$, 10%), 654 ($[M-OPh]^+$, 16), 415 (16), 362 (72), 348 (13), 321 (21), 256 (24), 242 (18), 149 (44), 105 (100), 93 (50), 91 (22), 85 (16), 77 (27), 57 (31), 55 (14), 43 (18), 41 (13), 39 (27).

4.5. Reduction of oximino derivatives

4.5.1. Ethyl 2-deoxy-2-*N*-acetyl-3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (32) and ethyl 2-deoxy-2-*N*-acetyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (31) and ethyl 2-deoxy-2-*N*-acetyl-1-thio-α-D-glucopyranoside (33). To a solution of oxime (**7**) (0.100 g, 0.20 mmol) in anhydrous THF (2.5 cm^3) at −8°C was added, in a dropwise manner, an anhydrous solution of 2 M BH_3–DMS (2.4 cm^3, 2.4 mmol, 12 equiv.) in THF. The reaction was stirred at −8°C for 30 min then allowed to warm up to room temperature and left stirring over night. The reaction was quenched by careful addition of methanol then excess acetic anhydride (3 cm^3) was added and the reaction was stirred for 3 h. The reaction was then quenched with basic amberlite (^-OH) resin, filtered and concentrated to dryness. The crude material was submitted to column chromatography (5:1 hexane/ethyl acetate, 1% TEA→4:1→3:1→ethyl acetate). Concentration of less polar

product afforded acetamide (**32**) (7 mg, 8%) as a white solid. Concentration of fractions containing the more polar product afforded acetamide (**31**) (60 mg, 83%), as a white solid. Attempted recrystallisation of (**31**) (methanol/chloroform) yielded a third compound (**33**) which proved to be ethyl 2-deoxy-2-*N*-acetyl-1-thio-α-D-glucopyranoside. *For* (**32**). δ_H (400 MHz; $CDCl_3$) 1.21 (9H, s, $(CH_3)_3CCO$), 1.31 (3H, t, J=7.5 Hz, SCH_2CH_3), 2.09 (3H, s, CH_3CO), 2.58–2.68 (2H, m, SCH_2CH_3), 3.60 (1H, dt, J=5.5, 11.0 Hz, H-2), 3.67 (1H, J=9.5 Hz, H-4), 3.79 (1H, t, J=10.0 Hz, H-6), 4.26–4.38 (2H, m, H-5, H-6), 5.32 (1H, app. t, J=9.5, 10.5 Hz, H-3), 5.52 (1H, s, PhC*H*), 5.54 (1H, d, J=5.5 Hz, H-1), 7.33–7.46 (5H, m, Ar), 7.75 (1H, d, J=5.5 Hz, N*H*); δ_C (100 MHz; $CDCl_3$); 14.81 (SCH_2CH_3), 19.14 (CH_3CO), 24.87 (SCH_2CH_3), 27.04 ($(CH_3)_3CCO$) 38.92 ($(CH_3)_3CCO$), 63.21, 63.69, 67.77 (C-5, C-2, C-3), 68.75 (C-6), 80.26 (C-4), 84.57 (C-1), 101.25 (PhCH), 125.87, 128.22, (Ar{C-2, C-6, C-3, C-5}), 128.90 (Ar{C-4}), 136.96 (Ar{C-1}), 170.21 (CH_3CO), 177.54 ($(CH_3)_3CCO$). *For* (**31**). ν_{max} (film)/cm^{-1} 3440 br (O–H), 3300 s (N–H), 3100 w, 3080 w, 2970 s, 2960 s and 2870 s (C–H), 1665 m (CH_2=C), 1643 m (C=O), 1548 m (N–H), 1460 s and 1382 m (C–H), 1298 m, 1267 m, 1240 s, 1137 s, 1083 s and 1060 br (C–O), 760 m and 702 m (Ar), 640 m (C–S); δ_H (250 MHz; $CDCl_3$) 1.22 (3H, t, J=7.5 Hz, SCH_2CH_3), 1.99 (3H, s, CH_3CO), 2.53–2.59 (2H, m, SCH_2CH_3), 3.51 (1H, t, J=9.0 Hz, H-4), 3.67–3.77 (2H, m, H-6, H-3), 4.08–4.22 (2H, m, H-6, H-5), 4.31 (1H, ddd, J=5.5, 8.0, 10.5 Hz, H-2), 5.35 (1H, d, J=5.5 Hz, H-1), 5.49 (1H, s, PhC*H*), 5.82 (1H, d, J=8.5 Hz, N*H*) 7.27–7.61 (5H, m, Ar); δ_C (62.5 MHz; $CDCl_3$); 15.63 (SCH_2CH_3), 23.81 (CH_3CO), 26.31 (SCH_2CH_3), 54.58 (C-2), 63.84, 70.61 (C-5, C-3), 69.10 (C-6), 82.82 (C-4), 85.64 (C-1), 102.46 (PhCH), 126.73, 128.75, (Ar{C-2, C-6, C-3, C-5}), 129.71 (Ar{C-4}), 137.39 (Ar{C-1}), 171.61 (CH_3CO); (CI: Found $[M+H]^+$, 354.1386. $C_{17}H_{24}NO_5S$ requires $[M+H]^+$, 354.1375); *m*/*z* (CI) 354 ($[M+H]^+$, 100%), 294 (52), 292 (51), 168 (9), 149 (12), 126 (12), 105 (17). *For* (**33**). $[\alpha]_D^{25}$=176 (*c* 0.05 in MeOH) {Lit.[1] $[\alpha]_D^{25}$=175 (*c* 0.8 in H_2O)}; ν_{max} (film)/cm^{-1} 3370 br (O–H, N–H), 2980 w and 2950 w (C–H), 1678 w and 1665 w (CH_2=C), 1638 vs (C=O), 1475 m, 1470 m and 1435 m (C–H), 1142 w, 1105 m, 1080 s 1045 m and 1040 m (C–O), 640 w (C–S); δ_H (250 MHz; CD_3OD) 1.27 (3H, t, J=7.5 Hz, SCH_2CH_3), 1.99 (3H, s, CH_3CO), 2.57–2.63 (2H, m, SCH_2CH_3), 3.30–3.33 (1H, m, 4-O*H*), 3.36 (1H, dd, J=9.0, 10.0 Hz, H-4), 3.59 (1H, dd, J=9.0, 11.0 Hz, H-3), 3.68–3.85 (2H, m, H-6, H-6), 3.97–4.00 (1H, m, H-5), 4.02 (1H, dd, J=5.5, 11.0 Hz, H-2), 5.47 (1H, d, J=5.5 Hz, H-1); δ_C (62.5 MHz; CD_3OD); 15.74 (SCH_2CH_3), 22.93 (CH_3CO), 25.90 (SCH_2CH_3), 56.23 (C-2), 63.01, 73.03, 74.60 (C-5, C-6, C-3, C-4), 85.02 (C-1); (CI: Found $[M+H]^+$, 266.1064. $C_{10}H_{20}NO_5S$ requires $[M+H]^+$, 266.1062); *m*/*z* (CI) 266 ($[M+H]^+$, 75%), 236 (17), 206 (34), 204 (100), 186 (34), 168 (20), 146 (20), 144 (22), 138 (26), 134 (20), 126 (27), 114 (17), 102 (51) 84 (27), 60 (54), 59 (23), 43 (25).

4.5.2. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[2-deoxy-2-*N*-acetal-4,6-*O*-benzylidene-1-α-D-glucopyranoside]-1-*O*-α-D-glucopyranoside (34). To a solution of oxime (**23**α) (70 mg, 0.074 mmol) in anhydrous THF (1.5 cm^3) at −12°C was added, in a dropwise manner, an anhydrous solution of 2 M BH_3–DMS (459 μl, 0.92 mmol, 12 equiv.) in THF. The reaction was stirred at −10°C for 30 min then allowed to warm up to room temperature, followed by heating at 45°C overnight. The reaction was allowed to cool to room temperature before quenching by careful addition of methanol. Excess acetic anhydride (2 cm^3) was added to the reaction. After 3–4 h of stirring the reaction was neutralized with basic Amberlite ($^-$OH) resin, filtered and concentrated to dryness. ^{1}H NMR of the crude mixture showed one major and three minor components. The crude material was submitted to column chromatography (3: 1 dichloromethane/ethyl acetate, 1% TEA→2:1→1:1→ethyl acetate). Evaporation of fractions containing the major product afforded a mixture of disaccharide diastereoisomers (**34**)/(**35**) (~8:1, 27 mg, 48%). Additional reduction products from which the benzylidene protecting group had been partially removed from the donor were also isolated as mixtures (~4.7:1, (**36**)/(**37**), 21.5 mg, 37%). *For* (**34**). δ_H (400 MHz; $CDCl_3$) 1.82 (3H, s, CH_3CO), 3.39 (3H, s, CH_3O), 3.49 (1H, dd, J=3.5, 9.5 Hz, H-2′), 3.49 (1H, app. t, J=9.0, 9.5 Hz, H-4′), 3.57 (1H, t, J=9.5 Hz, H-4), 3.60 (1H, dd, J=2.0, 11.5 Hz, H-6′), 3.72 (1H, t, J=10.0 Hz, H-6), 3.74–3.85 (2H, m, H-5′, H-5), 3.89 (1H, app. t, J=9.5, 10.0 Hz, H-3), 3.91 (1H, dd, J=4.0, 11.5 Hz, H-6′), 4.02 (1H, app. t, J=9.0, 9.5 Hz, H-3′), 4.12 (1H, ddd, J=4.0, 8.0, 10.0 Hz, H-2), 4.19 (1H, dd, J=4.5, 10.0 Hz, H-6), 4.58 (1H, d, J=3.5 Hz, H-1′), 4.64 (1H, d, J=11.0 Hz, PhCH_2), 4.70 (1H, d, J=12.0 Hz, PhCH_2), 4.80–4.86 (2H, m, PhCH_2), 4.85 (1H, d, J=4.0 Hz, H-1), 4.93 (1H, d, J=11.0 Hz, PhCH_2), 5.02 (1H, d, J=11.0 Hz, PhCH_2), 5.45 (1H, s, PhC*H*), 6.17 (1H, d, J=8.0 Hz, N*H*), 7.19–7.41 (20H, m, Ar); δ_C (62.5 MHz; $CDCl_3$) 23.58 (CH_3CO), 55.16 (C-2), 55.80 (CH_3O), 63.20 (C-5), 67.67, 69.18 (C-6′, C-6), 70.17, 70.77 (C-5′, C-3), 73.78, 75.44, 76.20 (3×(PhCH_2)), 77.74, 80.29, 82.34, 82.40 (C-4′, C-2′, C-3′, C-4), 98.51, 99.12, 102.39 (C-1′, C-1, PhCH), 126.81, 128.13, 128.32, 128.37, 128.44, 128.50, 128.67, 128.86, 128.95, 129.60, ((4×Ar{C-4}), (4×Ar{C-2, C-6}), (4×Ar{C-3, C-5}); (CI: Found $[M+H]^+$, 756.3351, $C_{43}H_{50}NO_{11}$ requires $[M+H]^+$, 756.3383); *m*/*z* (CI) 756 ($[M+H]^+$, 10%), 616 (10), 382 (8), 292, (58), 130 (23), 105 (23), 91 (100), 74 (21), 57 (11), 35 (12). *For* (**35**). δ_H (400 MHz; $CDCl_3$) 4.45 (1H, ddd, J=1.5, 7.5, 5.0 Hz, H-2), 6.25 (1H, d, J=7.5 Hz, N*H*); *For* (**37**). δ_H (400 MHz; $CDCl_3$) 4.42 (1H, ddd, J=1.5, 4.5, 8.0 Hz, H-2), 6.20 (1H, d, J=8.0 Hz, NH).

4.5.3. Typical method for reduction of the oxime disaccharides with $LiAlH_4$.[21] $LiAlH_4$ (6 equiv.) was added portionwise to a stirred solution of oxime disaccharide (1 equiv.) in dry diethyl ether. The resulting reaction mixture was then heated at reflux and after 1 h the reaction had gone to completion as indicated by tlc analysis. Saturated potassium sodium tartrate (Rochelle's salt) was added dropwise to the reaction mixture, followed by EtOAc. The resulting mixture was filtered through Celite®, dried ($MgSO_4$) and concentrated in vacuo. The resulting residue was dissolved in MeOH and acetic anhydride and stirred at room temperature. After TLC analysis indicated the reaction had reached completion the reaction mixture was co-evaporated with toluene and the resulting residue was purified by column chromatography (ethyl acetate) to afford the *N*Ac disaccharides.

For (**38**). Clear oil. δ_H (400 MHz; $CDCl_3$) 1.97 (3H, s, CH_3CO), 3.27–3.24 (2H, m, H-4′, H-5), 3.28 (3H, s, CH_3O), 3.40 (1H, dd, J=3.5, 9.5 Hz, H-2′), 3.50 (1H, dd, J=5.5, 11.0 Hz, H-6′), 3.56 (1H, app. t, J=9.5 Hz, H-4), 3.66–3.73 (2H, m, H-5′, H-6), 3.83 (1H, dd, J=4.0, 9.5 Hz, H-3), 3.90–3.95 (2H, m, H-3′, H-6′), 4.20 (1H, dd, J=5.0, 10.5 Hz, H-6), 4.29 (1H, dd, J=1.5, 4.4 Hz, H-2), 4.38 (1H, d, J=1.5 Hz, H-1), 4.46–4.51 (2H, m, H-1′, O–CH_2Ph), 4.59 (1H, d, J=12.0 Hz, O–CH_2Ph), 4.73 (1H, d, J=12.5 Hz, O–CH_2Ph), 4.74 (1H, d, J=11.0 Hz, O–CH_2Ph), 4.83 (1H, d, J=11.5 Hz, O–CH_2Ph), 4.92 (1H, d, J=11.0 Hz, O–CH_2Ph), 5.46 (1H, s, PhC*H*), 5.90 (1H, d, J=6.5 Hz, N*H*), 7.19–7.42 (20 H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$): 22.1 (*C*H_3CO) 55.6 (*C*H_3O), 66.3, 67.4, 70.6, 76.2, 78.6, 78.7, 80.5, 81.0 (C-2, C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′), 68.7, 72.4, 73.9, 74.8 (C-6, C-6′, 3× Ph*C*H_2), 97.0, 98.4, 101.2 (C-1, C-1′, Ph*C*H), 125.2, 125.3, 126.7, 126.9, 127.0, 127.2, 127.3, 127.5, 127.6, 128.2 (Ar*C*H), 135.9, 136.9, 137.2, 137.5 (Ar*C*), 172.5 (*C*=O); *m*/*z* (CI): Found $[M+H]^+$ 756.3385. $C_{43}H_{50}NO_{11}$ requires $[M+H]^+$ 756.3383; *For* (**39**) δ_H (400 MHz; $CDCl_3$) 3.30 (3H, s, OCH_3), 4.63 (1H, d, J=8.5 Hz, H-1), 5.45 (1H, s, PhC*H*), 5.71 (1H, d, J=5.5 Hz, NH).

4.6. Typical method for reduction of the oxime disaccharides with $LiBH_4$, TMSCl[22]

To a solution of $LiBH_4$ (5 equiv.) in dry THF was added TMSCl (12.5 equiv.) at −20°C under N_2 and the mixture was stirred for a further 2 h at room temperature. The mixture was recooled to −20°C and a solution of the oxime disacharide (1 equiv.) in THF was added dropwise. The resulting reaction mixture was stirred at room temperature until tlc analysis indicated the reaction to be complete (ca. 12–24 h). Upon completion, MeOH was added dropwise, followed by neutralisation of the reaction mixture with TEA. Evaporation of the mixture in vacuo resulted in a residue which was dissolved in MeOH and acetic anhydride and stirred at room temperature. After TLC analysis indicated the reaction had reached completion the reaction mixture was co-evaporated with toluene and the resulting residue was purified by column chromatography (ethyl acetate) to afford the *N*Ac disaccharides.

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