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Neighbouring Group Participation During Glycosylation: Do 2-Substituted Ethyl Ethers Participate?

Daniel J. Cox,[a] Govind P. Singh,[b] Andrew J. A. Watson,[b] and Antony J. Fairbanks*[b]

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The development of new protecting groups that undergo neighbouring group participation (NGP) via six-membered ring intermediates to promote the formation of α-1,2-*cis* glycosidic linkages complements the established use of 5-ring NGP in terms of stereochemical outcome. A selection of glycosyl donors was synthesised that possessed novel 2-iodo- and 2-(phenylseleno)ethyl ether protecting groups in an attempt to promote highly α-selective glycosylation by 6-ring NGP. Although the fully armed donors produced α-glucosides as the predominant reaction products, low-temperature NMR studies did not show NGP by the observation of cyclised reaction intermediates. The corresponding disarmed glycosyl donors were unexpectedly less stereoselective. NMR spectroscopy revealed that the 2-iodoethyl ether did not participate in any of the glycosylation processes; however, the 2-(phenylseleno)ethyl ether did participate, and β-configured cyclic intermediates were observed. The fact that considerable amounts of β-glycoside product were formed in these latter cases indicated that the predominant reaction pathway to product did not occur through the observed cyclic species. Clearly, a fine balance exists during glycosylation reactions, and the reaction pathway to product depends on a variety of factors. Notably, the formation of cyclised intermediates by 6-ring NGP is not on its own sufficient to ensure high levels of α-stereoselectivity.

Introduction

The issue of control of anomeric stereochemistry during glycosylation reactions represents a challenge that has yet to be completely addressed by the synthetic chemist. Although 1,2-*trans* glycosidic linkages can usually be synthesised with high levels of stereocontrol through classical 5-ring neighbouring group participation (NGP) of 2-*O*-acyl-protected glycosyl donors,[1] the stereocontrolled synthesis of 1,2-*cis* glycosidic linkages is considerably more difficult.[2]

The use of new types of NGP, for example the intermediacy of a six-membered-ring intermediate, to enforce the formation of 1,2-*cis* glycosidic linkages, represents an attractive proposition which, in theory, could be applied generally to access all α-1,2-*cis* glycosides (e.g. α-*gluco*, α-*galacto* and so on). Boons has been a pioneer of this field, and in a series of seminal works[3] has described significant advances, such as the use of chiral auxiliaries at the 2-position of donors that operate through 6-ring NGP to control the diastereoselectivity of glycosylation. Turnbull[4] has also been active in a similar vein, and has reported both the control of stereochemistry of glycosylation by NGP of remote thioethers and by the use of cyclic β-configured donors to promote α-glycoside formation.

As can been seen in Figure 1 the situation for 6-ring NGP during a glycosylation process is complicated by the potential for two different configurations of any cyclic intermediate, and also the equilibria between a glycosyl cation (or other acyclic intermediate) and these cyclic species. It may be expected that a glycosyl cation should react with a glycosyl acceptor (ROH) in a predominantly non-selective fashion, whereas a *trans*-decalin cyclic intermediate should react to preferentially produce the α-glycoside product. Conversely, nucleophilic attack of an acceptor directly on the *cis*-decalin intermediate should lead to the β-glycoside. In the Boons[3] and Turnbull[4] systems the judicious placing of a substituent on the ethyl group, which adopts an equatorial position in the *trans*-decalin intermediate promotes the formation of this species, and results in high levels of α-selectivity. In contrast to this situation, Demchenko has reported the synthesis and use of 2-*O*-picolyl-protected glycosyl donors that are proposed to react through cyclic 6-ring intermediates, but which have been shown to preferentially produce the β-glycoside product through an α-configured *cis* decalin-type intermediate.[5]

Our work began by reasoning that any glycosyl donor possessing a 2-*O*-ethyl ether,[6] in which the 2-position was substituted by a heteroatom, could show a tendency to promote α-glucoside formation. Although the Boons and Turnbull approaches do produce high levels of α-selectivity,

[a] Department of Chemistry, Chemistry Research Laboratory, University of Oxford,
Mansfield Road, Oxford, OX1 3TA, UK
[b] Department of Chemistry, University of Canterbury,
Private Bag 4800, Christchurch 8140, New Zealand
E-mail: antony.fairbanks@canterbury.ac.nz
www.chem.canterbury.ac.nz

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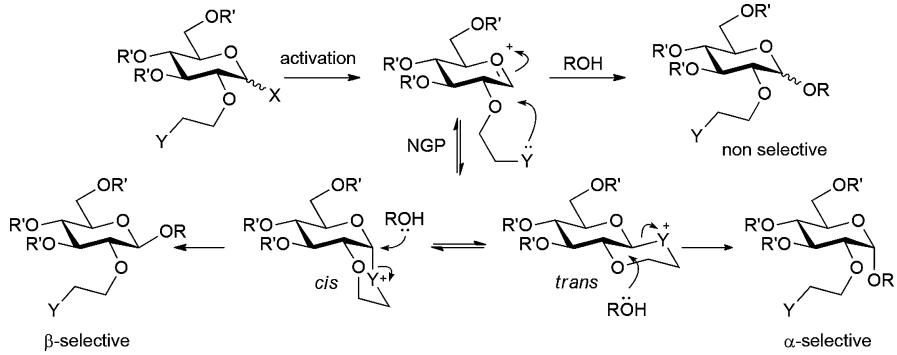


Figure 1. Postulated equilibria between the glycosyl cation and 6-ring intermediates arising from NGP of 2-substituted ethyl ethers, and the stereochemical consequences for the outcome of glycosylation.

the installation of the additional stereogenic centre that is required in the side chain does complicate the approach to an extent. We recently disclosed the synthesis and utility of a series of 2-*O*-(thiophen-2-yl)-methyl-protected glycosyl donors in stereoselective α-glycosylation reactions.[7] Following this report our attention turned to the use of softer atoms at the 2-position of an ethyl ether to increase the propensity for 6-ring NGP, and increase the levels of α-selectivity produced. This paper reports the synthesis and glycosylation reactions of a variety of differently protected glycosyl donors that possess 2-*O*-ethyl ethers, which are substituted with Se and I, and also includes NMR studies that reveal the extent to which NGP operates within these systems.

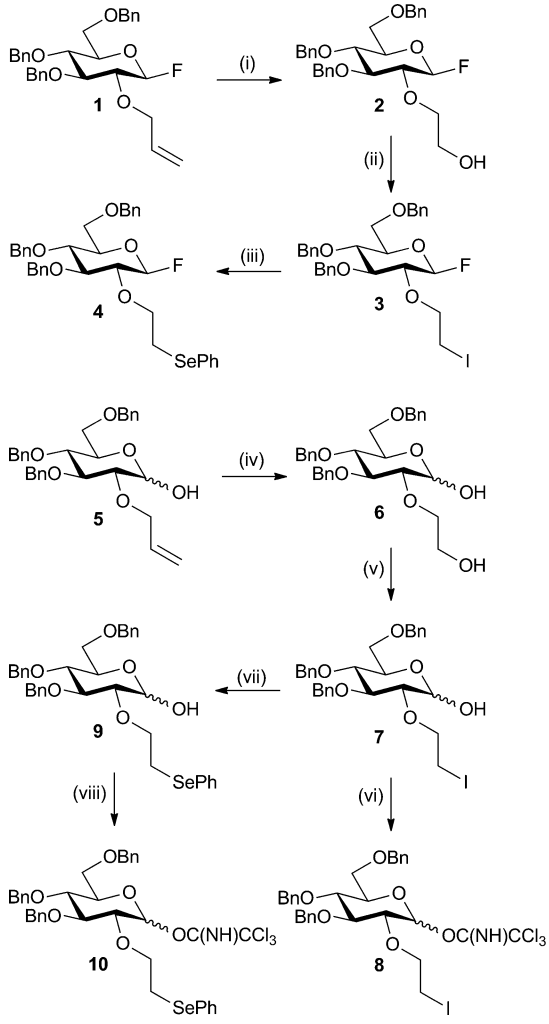
Results and Discussion

Studies on Fully Armed Donors

Both selenium and iodine are known to participate as neighbouring functional groups in a variety of substitution processes.[8] Moreover the 2-(phenylseleno) ethyl ether was reported as an alcohol protecting group back in 1975,[9] but has found little application since that point of time. A series of glycosyl donors possessing either Se or I at the 2-postion of a 2-*O*-ethyl ether were therefore targeted. Owing to the operational simplicity by which the 2-hydoxyl may be differentiated from the others through the intermediacy of a 1,2-orthoester, donors that possessed "arming" benzyl ether protection of the other three hydroxy groups were targeted for the first study (Scheme 1).

Synthesis of Donors

Direct conversion of glycosyl donors possessing a free OH group at position-2 into the corresponding substituted ethyl ethers proved more problematic than expected, and so more indirect routes were adopted that involved 2-*O*-allyl ethers as intermediates. Ozonolysis of known glycosyl fluoride **1**[10] with a reductive work-up gave alcohol **2** that underwent an Appel reaction[11] with I_2, PPh_3 and imidazole, to



Scheme 1. (i) O_3, CH_2Cl_2/MeOH, –78 °C, 15 min; then $NaBH_4$, –78 °C to room temp., 1 h, 81%; (ii) I_2, PPh_3, imidazole, THF, reflux, 16 h, 89%; (iii) PhSeH, NaH, THF, reflux, 16 h, 86%. (iv) O_3, CH_2Cl_2/MeOH, –78 °C, 15 min; then $NaBH_4$, –78 °C to room temp., 1 h, 85%; (v) I_2, PPh_3, imidazole, THF, reflux, 16 h, 76%; (vi) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 3 h, 84%; (vii) PhSeH, NaH, THF, reflux, 16 h, 81%; (viii) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 3 h, 88%.

give iodide **3**. Treatment of **3** with sodium phenylselenide, pre-formed by reaction of phenylselenol with NaH, gave donor **4** in excellent yield. Corresponding trichloroacetimidate donors **8** and **10** were made by an analogous route. Thus ozonolysis of known hemiacetal **5**[12] followed by reductive work-up gave diol **6**. Appel reaction of **6** was selective for the primary hydroxy group, and gave iodide **7** in 76% yield. Reaction of **7** with trichloroacetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave trichloroacetimidate donor **8**. Alternatively treatment of **7** with sodium phenyl selenide gave hemiacetal **9**, which was readily converted into trichloroacetimidate donor **10**.

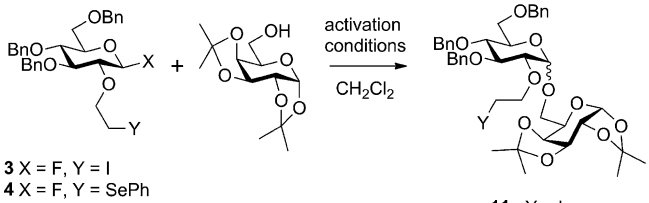
Glycosylation Reactions

Donors **3**, **4**, **8** and **10** were glycosylated with diacetone galactose as a model acceptor. The 2-(phenylseleno) ethyl ether protected donors **4** and **10** were investigated first. Glycosyl fluoride **4** was activated by using $BF_3{\cdot}OEt_2$ (1.5 equiv.). Unlike the case of the equivalent 2-*O*-(thiophen-2-yl) methyl protected glycosyl donor,[6] good yields of disaccharide **11b** were observed, and TLC analysis indicated that the reactions progressed cleanly. The preference for α-selectivity was also encouraging. This selectivity increased with a decrease in reaction temperature and the best results were obtained at –78 °C (α/β ratio, 4.5:1; Table 1, Entry 3). This selectivity was substantially better than the selectivity observed for the corresponding 2-*O*-(thiophen-2-yl) methyl protected glycosyl fluoride donor.[7] Glycosylation of corresponding trichloroacetimidate donor **10** with diacetone galactose with a catalytic amount of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as activator at 0 °C produced disaccharide **11b** in an excellent yield of 88%, but with low anomeric selectivity (α/β ratio, 1.5:1; Table 1, Entry 4). However, reduction of the reaction temperature to –78 °C increased the observed stereoselectivity (α/β ratio, 5:1; Table 1, Entry 6), without significantly altering the yield.

Attention then turned to the glycosylation of 2-iodoethyl protected glycosyl donors **3** and **8**. Glycosyl fluoride **3** was activated with supra-stoichiometric quantities of $BF_3{\cdot}OEt_2$, and produced disaccharide **11a** in good to moderate yields. The α-selectivity, though slightly lower than that observed with the corresponding 2-(phenylseleno) ethyl ether, again increased with a decrease in temperature. Reaction of trichloroacetimidate **8** with diacetone galactose gave a higher yield of **11a** than with the fluoride donor and again α-selectivity was also observed. Overall the results were marginally better than those observed for fluoride donor **3** (α/β ratio, 3.5:1; Table 1, Entry 12), though the level of stereocontrol still fell short of the α-selectivity observed with the corresponding 2-(phenylseleno)ethyl ether.

Se-containing trichloroacetimidate donor **10** was then glycosylated with a small selection of other acceptors (Table 2). Glycosylation with methanol as an acceptor produced methyl glycoside **14** in good yield, but without any stereocontrol (α/β ratio, 1:1; Table 2, Entry 1). This result was in line with the outcome of glycosylation of the corresponding 2-*O*-(thiophen-2-ylmethyl) protected trichloroacetimidate donor,[7] which had revealed that the stereoselectivity of the reaction was dependent upon the steric bulk of the glycosyl acceptor. Reaction with the *gluco* primary alcohol acceptor **12** produced disaccharide **15** in a reaction that was α-selective (α/β ratio, 2:1; Table 2, Entry 2). Likewise reaction with the secondary alcohol acceptor **13** produced the corresponding disaccharide **16** with a similar level of stereocontrol (α/β ratio, 2:1; Table 2, Entry 3).

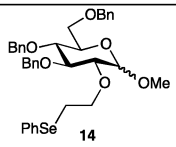
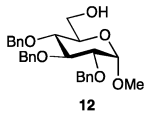
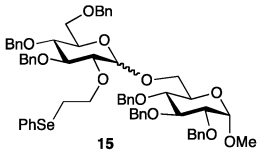
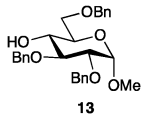
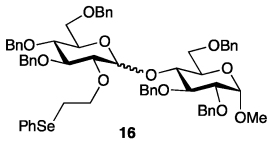
Table 1. Glycosylation of diacetone galactose (2 equiv.) with donors **3**, **4**, **8** and **10**.



Entry	Glycosyl donor	Activation conditions[a]	Time [h]	Temperature [°C]	Yield of **11** [%]	α/β ratio[b]
1	**4**	A	1.5	0	74	1:1
2	**4**	A	2.5	–40	70	2.25:1
3	**4**	A	5	–78	62	4.5:1
4	**10**	B	0.5	0	88	1.5:1
5	**10**	B	1	–40	83	3:1
6	**10**	B	1.5	–78	80	5:1
7	**3**	A	1.5	0	74	1:1
8	**3**	A	2.5	–40	70	2:1
9	**3**	A	5	–78	62	3:1
10	**8**	B	1	0	84	1:1
11	**8**	B	2	–40	78	2:1
12	**8**	B	4	–78	75	3.5:1

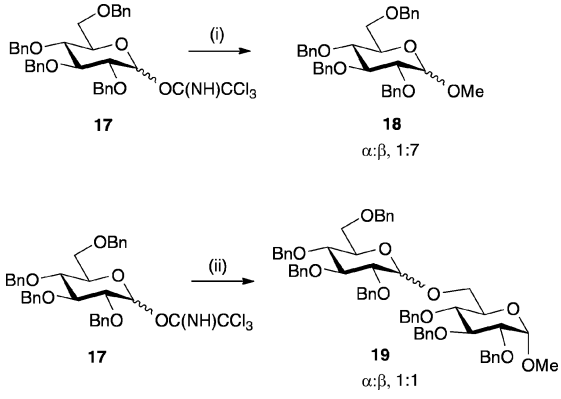
[a] Activation conditions: A: $BF_3{\cdot}OEt_2$ (1.5 equiv.). B: TMSOTf (0.1 equiv.). [b] Anomeric ratios were determined by integration of appropriate peaks in the ^1H NMR spectra.

Table 2. Glycosylation[a] of donor **10** with a variety of acceptors.

Entry	Acceptor	Product	Yield (%)	α:β ratio[b]
1	MeOH	 **14**	88	1:1
2	 **12**	 **15**	83	2:1
3	 **13**	 **16**	61	2:1

[a] Reaction conditions: acceptor (2.0 equiv.), TMSOTf (0.1 equiv.), –78 °C, CH_2Cl_2. [b] Anomeric ratios were determined by integration of appropriate peaks in the ^1H NMR spectra.

To place these observed stereoselectivities in context, control reactions were undertaken with the per-benzylated trichloroacetimidate donor **17** under identical reaction conditions (Scheme 2). These reactions ranged from being very *β-selective* to non-selective. When methanol was used as acceptor methyl glycoside **18** was formed as a mixture of anomers in an α:β ratio of 1:7, whereas when monosaccharide **12** was used as the acceptor disaccharide **19** was formed as a 1:1 mixture of anomers. These control reactions implied that the α-stereoselectivity observed by using **3**, **4**, **8** and **10** as glycosyl donors was a result of the presence of the 2-iodo and 2-(phenylseleno) ethyl ether protecting groups.



17 **18** α:β, 1:7

17 **19** α:β, 1:1

Scheme 2. (i) MeOH (2.0 equiv.) TMSOTf (0.1 equiv.), –78 °C, CH_2Cl_2; (ii) **12** (2.0 equiv.), TMSOTf (0.1 equiv.), –78 °C, CH_2Cl_2.

NMR Studies

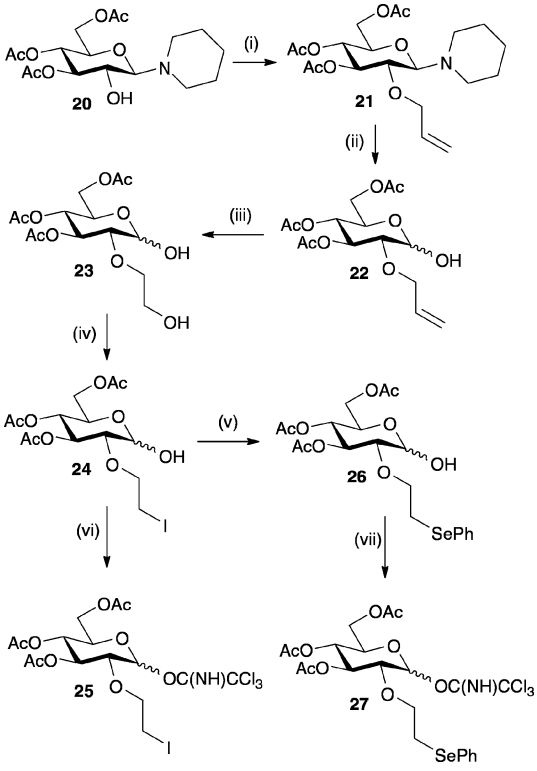
Whether the increased α-selectivity observed with the donors possessing substituted ethyl ethers (relative to their benzylated counterpart) was the direct result of 6-ring NGP, or whether it was a result of other possible effects, could be best revealed by NMR studies. Boons and Turnbull have performed low-temperature NMR spectroscopic experiments on activated glycosyl donors and demonstrated NGP through cross correlation between C-1 on the donor and the H-8a/b methylene protons on the substituted ethyl group, as well as significant changes in the chemical shifts of H1 and H8a/b. NMR spectroscopic studies were therefore performed on donors **8** and **10**. Both compounds were activated in the absence of acceptor at –78 °C in CD_2Cl_2 by addition of a stoichiometric amount of TMSOTf, and NMR spectra were obtained. For iodo-substituted donor **8** one major species[13] was observed by NMR spectroscopy, but there was no obvious shift in the signal for either H-8a/b or H-1 upon activation (see Supporting Information). In addition, no cross-correlation could be observed between C-1 and H8a/b. Studies then turned to 2-(phenylseleno) donor **10**. However, there was no obvious shift in the signal for either H-8a/b or H-1 upon activation. In addition, no cross-correlation was observed between C-1 and H-8a/b. These NMR spectroscopic studies provide strong supporting evidence that NGP is not responsible for the levels of α-selectivity observed when glycosylation reactions are performed with these fully armed donors. A combination of steric, electronic and/or ion pairing effects are probably responsible for the increased α-selectivity observed relative to corresponding per-benzylated donor **17**.

Studies on Disarmed Donors

Boons recently reported an interesting observation that the use of glycosyl donors that possessed disarming protecting groups resulted in more stereoselective glycosylation reactions.[3d] In this paper he postulated a dynamic equilibrium between cyclic intermediates and the acyclic glycosyl cation (Figure 1), and a Curtin–Hammett scenario in which electron-donating protecting groups on the donor led to increased reaction through the open chain form in a non-stereoselective process. If such an effect were general then all of the above donors, which possess only "arming" benzyl protecting groups, should in fact be the least stereoselective variants. Furthermore it was postulated that perhaps cyclic intermediates had not been observed in the NMR spectroscopic studies performed above because of the electron donating protecting groups, which favoured the acyclic cation. The corollary to this situation is that electron withdrawing "disarming" protecting groups on a donor will destabilise any glycosyl cation intermediate, and so should increase the preponderance of neighbouring groups to participate. Therefore the current study was extended to investigate the effects that both inductive and torsional disarming of the donors may have on the stereochemical outcome of the reaction, with the objective to obtain further enhancements in α-stereoselectivity and to observe NGP by NMR spectroscopy.

Synthesis of Donors

Because higher yields had been obtained for glycosylation of the trichloroacetimidates, attention focused solely on their use as donors. Initially, per-acetylated versions of the 2-iodoethyl and 2-(phenylseleno) ethyl donors were synthesised as shown in Scheme 3.

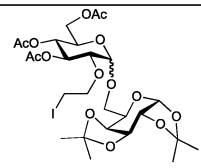
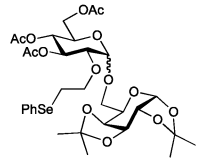
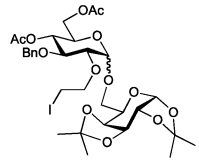
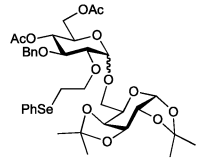
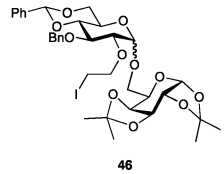
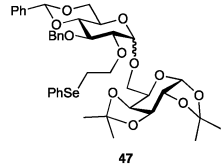


Scheme 3. (i) allyl iodide, Ag_2O, DMF, 45%; (ii) MeOH, HCl, 89%; (iii) (a) O_3, CH_2Cl_2, –78 °C, 15 min then add Me_2S; (b) $NaBH_3CN$, CH_2Cl_2, AcOH, 0 °C, 54%; (iv) I_2, PPh_3, imidazole, THF, reflux, 16 h, 78%; (v) PhSeH, *i*Pr_2NEt, DMF, room temp., 16 h, 90%; (vi) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 3 h, 81%; (vii) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 3 h, 92%.

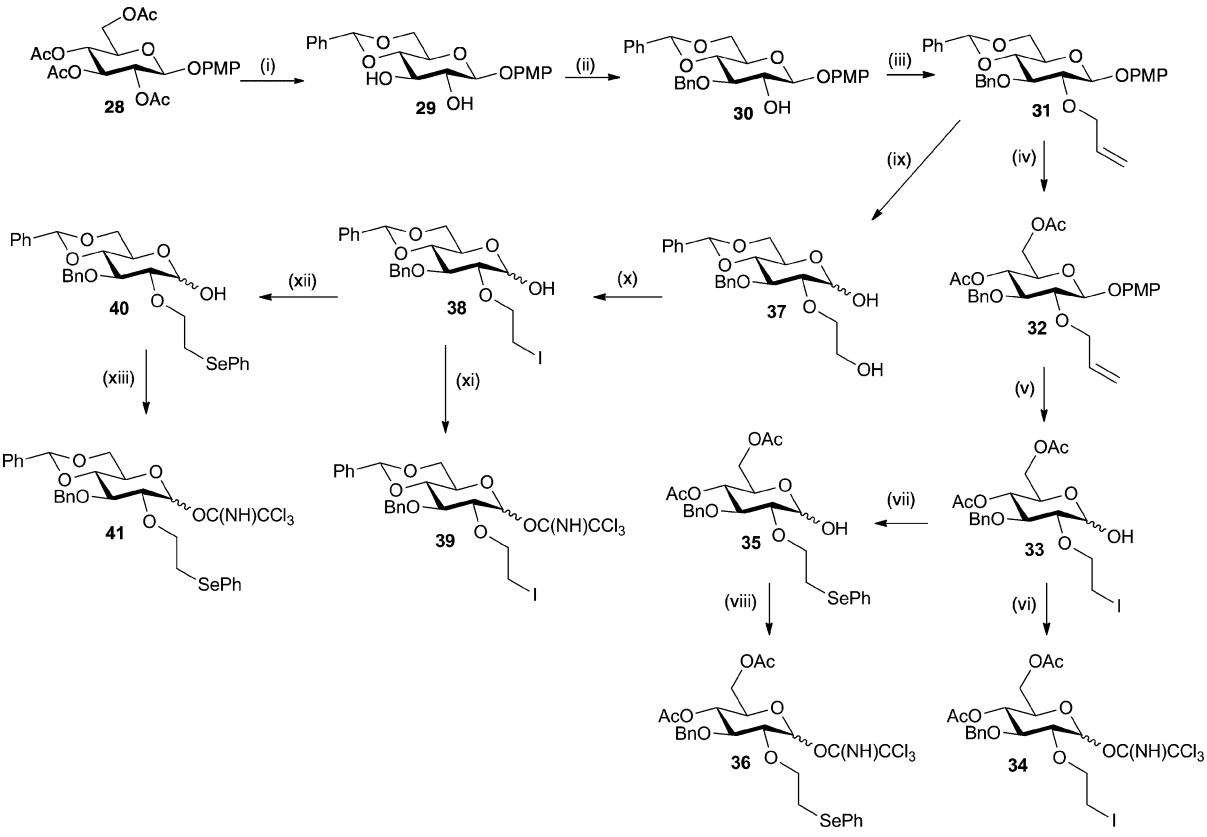
Several routes to selectively access the 2-hydroxy of glucose met with either failure or complications during purification, so piperidine derivative **20**, which is readily available from glucose penta-acetate in a single step, was used.[14] Allylation of the free hydroxy group of **20** with allyl iodide and silver oxide gave allyl ether **21**. Hydrolysis of the glycosyl piperidine gave hemiacetal **22**, which was subjected to a sequence of ozonolysis and reduction to give diol **23**. Particular care was required during the reduction step to avoid either reduction of the hemiacetal, or loss of acetate protection. The best yields were achieved by using sodium cyanoborohydride as the reducing agent. An Appel reaction allowed conversion of the primary hydroxy into an iodide to give **24**, the structure of which was confirmed by X-ray crystallography (see Supporting Information).[15] Attempted conversion to selenide **26** by using selenophenol and sodium hydride as base led to the formation of the corresponding cyclic ether as the sole reaction product. However, this transformation could be achieved in high yield by the use Hunig's base in conjunction with selenophenol. Finally, both **24** and **26** were converted into corresponding trichloroacetimidates **25** and **27** for use as glycosyl donors.

Next, several "partially disarmed" donors were synthesised (Scheme 4). Known *p*-methoxyphenyl (PMP) glycoside **28**[16] was converted into benzylidene derivative **29**, after which regioselective benzylation via an intermediate tin acetal gave benzyl ether **30**, in which the 2-hydroxy re-

Table 3. Glycosylation[a] of diacetone galactose with donors **25**, **27**, **34**, **36**, **39** and **41**.

Entry	Donor	Product	Yield (%)	α:β ratio[b]
1	**25**	 **42**	76	1:2
2	**27**	 **43**	75	2:3
3	**34**	 **44**	81	1:2
4	**36**	 **45**	94	1:4
5	**39**	 **46**	77	1:2
6	**41**	 **47**	93	1:3

[a] Reaction conditions: acceptor (2.0 equiv.), TMSOTf (0.1 equiv.), –78 °C, CH_2Cl_2. [b] Anomeric ratios were determined by integration of appropriate signals in the ^1H NMR spectra.



Scheme 4. (i) (a) NaOMe, MeOH, 1.5 h; (b) CSA, $PhCH(OMe)_2$, DMF, 8 h, 56% over two steps; (ii) (a) Bu_2SnO, MeOH, reflux, 24 h; (b) BnBr, CsF, DMF, 72 h, 43%; (iii) NaH, allyl bromide, DMF, 0 °C, 4 h, 72%; (iv) (a) AcOH, H_2O, 60 °C; (b) Ac_2O, pyridine, DMAP, 91%; (v) (a) O_3, CH_2Cl_2, –78 °C; (b) $NaBH_3CN$, CH_2Cl_2, AcOH; (c) I_2, PPh_3, imidazole, THF, reflux, 16 h, 20% over 3 steps; (vi) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 3 h, 89%; (vii) PhSeH, NaH, THF, reflux, 16 h, 75%; (viii) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 3 h, 74%; (ix) O_3, CH_2Cl_2/MeOH, –78 °C then add $NaBH_4$, 73%; (x) I_2, PPh_3, imidazole, THF, reflux, 24 h, 39%; (xi) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 8 h, 96%; (xii) PhSeH, NaH, THF, reflux, 16 h, 66%; (xiii) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 8 h, 92%.

mained free. Allylation of **30** then provided divergent allyl ether **31**. Hydrolysis of the 4,6-benzylidene and acetylation provided diacetate **32**. This was followed by ozonolysis and reduction, which also resulted in removal of the anomeric PMP protecting group, and immediate Appel reaction to yield iodide **33**, which was then converted into corresponding trichloroacetimidate donor **34**. Alternatively, nucleophilic substitution of the iodine in **33** by phenyl selenide gave phenylseleno hemiacetal **35**, which was then converted into trichloroacetimidate **36**. Alternatively, direct ozonolysis and reduction of **31** gave diol **37**, which was then converted into corresponding iodo- and 2-(phenylseleno)ethyl trichloroacetimidate donors **39** and **41** by using identical reaction sequences.

Glycosylation Reactions

A systematic study was undertaken into the glycosylation of donors **25**, **27**, **34**, **36**, **39** and **41** (Table 3). In contrast to initial expectations, all of these donors were considerably less α-stereoselective than their tri-benzylated counterparts **8** and **10**. Tri-acetylated "fully disarmed" donors **25** and **27** reacted to produce anomeric mixtures of products, in which the undesired β-anomer predominated. Corresponding diacetates **34** and **36**, which possessed a benzyl ether at the 3-position, were similarly non-stereoselective, and produced mixtures in which the β-anomer predominated. Finally, torsionally deactivated and conformationally restricted 4,6-benzylidene donors **39** and **41** also displayed low stereoselectivity, again in favour of the undesired β-anomer.

These results contrasted markedly with the expectation that the disarmed donors should result in more stereoselective glycosylation reactions than the fully armed ones, based on the premise that they should be more likely to undergo NGP. Furthermore the small preference for β-selectivity observed for these donors was the converse of the stereoselectivity with the corresponding tri-benzylated donors, which were predominantly α-selective.

NMR Studies

To try and rationalise these findings a second series of NMR studies was undertaken to investigate if NGP occurs for the disarmed donors. Compounds were activated in the absence of acceptor at –78 °C in CD_2Cl_2 by the addition of a stoichiometric amount of TMSOTf, and NMR spectra were recorded. For the three iodoethyl donors, **25**, **34** and **39**, no obvious NMR signal shifts in H8 or H-1 upon activation, nor were any cross correlations observed between

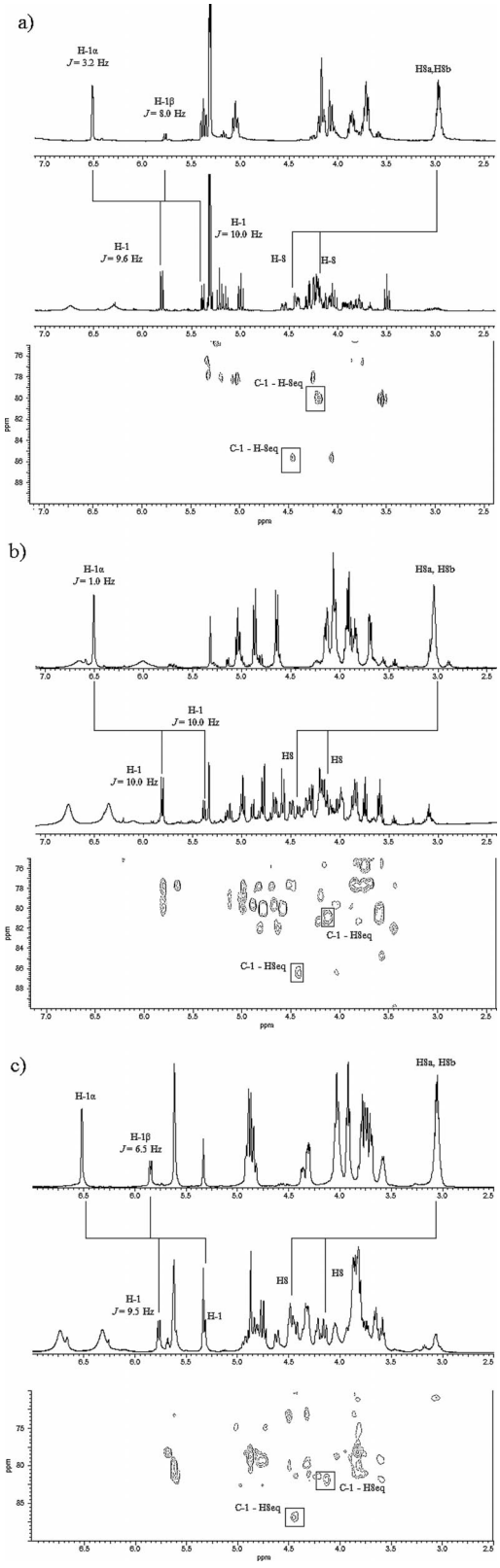


Figure 2. Low temperature NMR spectra of: (a) donor **27**; (b) donor **36** and (c) donor **41**, before and after activation at –78 °C in CD_2Cl_2. Changes in chemical shift were observed for H-1 and H-8a/b upon activation, and cross-correlations were seen between C-1 and H-8eq in the HMBC spectra. The observed $J_{H1,H2}$ (9–10 Hz) and $J_{H1,C1}$ (168 Hz) coupling constants indicated that cyclic species were β-configured.

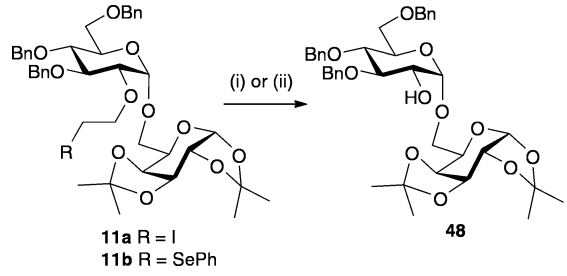
C-1 and H-8a/b in the HMBC spectra observed, which indicates that NGP did not occur for these disarmed iodo-substituted donors. For donor **25** two materials were observed by NMR spectroscopy in a ratio that corresponded to the ratio of stereoisomers formed in the product.

However, for the corresponding phenylseleno donors **27**, **36** and **41** evidence of NGP was observed in all cases (Figure 2). For per-acetylated donor **27** two compounds were formed upon activation (Figure 2, a), both of which were β-configured as confirmed by both the $J_{H1,H2}$ (9–10 Hz) and the $J_{H1,C1}$ coupling constants (168 Hz). Both materials showed cross correlation between C-1 and H-8eq in the HMBC spectrum, indicating that NGP occurs. The NMR spectroscopic data suggest that both materials are β-configured cyclised intermediates, but differ in that the Ph group attached to Se is either axial or equatorial.[17] For activation of donor **36**, which possesses two disarming acetate groups at positions-4 and 6 and an arming benzyl ether at position-3, two compounds were produced upon activation, which showed corresponding shifts in the signals for H-1 and H8a/b, and also cross correlation in the HMBC spectrum between C-1 and H8, indicating that NGP occurred (Figure 2, b). Similar evidence for cyclisation was observed for 4,6-benzylidene protected donor **41** (Figure 2, c); namely shifts in the signals for H-1 and H8a/b and cross-correlations between C-1 and H-8eq.

The NMR studies indicated that NGP did indeed occur for all of the disarmed phenylseleno donors, even though these compounds were less α-selective than fully armed benzylated donor **10**, which did not undergo NGP according to NMR spectroscopy. Evidence that a cyclic intermediate is formed upon activation of a donor does not mean necessarily that this is the reactive species through which glycosylation occurs. Notably, although all of the cyclic intermediates observed were β-configured, as indicated by NMR spectroscopic coupling constants, significant amounts of β-glycoside product were formed, indicating that most reaction must take place via intermediates not seen by NMR spectroscopy.

Deprotection

As a conclusion to this work the deprotection of two synthesised disaccharides was undertaken to demonstrate the ability of these substituted ethyl ethers to act as protecting groups.



Scheme 5. (i) H_2O_2, THF, 1 h; reflux 1 h; NIS, H_2O/THF, 16 h, 76%; (ii) KO*t*Bu, THF, reflux, 3 h; NIS, H_2O/THF, 16 h, 73%.

Since selenoxides readily undergo *syn* elimination, oxidation of a 2-(phenylseleno) ethyl ether can be followed by elimination to give a vinyl ether, which can then be removed hydrolytically. Accordingly, a sample of disaccharide **11b** was treated with hydrogen peroxide in tetrahydrofuran (THF). By heating the mixture to reflux the elimination step was affected, and subsequent treatment of the so-formed vinyl ether with *N*-iodosuccinimide (NIS) in THF/H_2O afforded deprotected disaccharide **48** in 76% yield (Scheme 5). The 2-iodoethyl ether was removed in a similar manner, again via an intermediate vinyl ether. Thus, treatment of **11a** with potassium *tert*-butoxide in THF at reflux temperatures affected elimination to give a vinyl ether, which was immediately treated with NIS in THF/H_2O to afford **48** in 73% yield.

Conclusions

In an attempt to promote highly stereoselective α-glycosylation by 6-ring NGP, a selection of glycosyl donors were synthesised that possess new 2-iodoethyl-ether and 2-(phenylseleno)ethyl-ether protecting groups at the 2-position. The "fully-armed" tri-benzylated donors produced α-glucosides as the predominant reaction products. However, low temperature NMR studies did not provide evidence of NGP by the observable formation of cyclised reaction intermediates. A subsequent investigation with corresponding disarmed glycosyl donors unexpectedly revealed them to be less stereoselective than their fully armed counterparts. For the disarmed donors low-temperature NMR studies revealed the 2-iodoethyl ether did not participate in any of the glycosylation processes. In contrast, the 2-(phenylseleno)-ethyl ether was shown to participate, and in all three cases β-configured cyclic intermediates were observed by NMR spectroscopy. However, the fact that considerable amounts of β-glycoside product were formed from glycosylation of the Se-containing donors indicated that the predominant reaction pathway to product did not occur via the observed cyclic species.

It can be concluded from these investigations that selenium is a better participating group than iodine, and is therefore more likely to form the basis of a useful achiral participating neighbouring group designed to promote α-glycoside formation. However this work demonstrates that formation of a cyclised intermediate alone is not sufficient to ensure a high level of selectivity during glycosylation. Likewise it shows that glycosylation of disarmed donors is not necessarily more stereoselective than that of the corresponding fully armed compounds, even if the latter do show a lower propensity to undergo NGP because of protecting group stabilisation of a glycosyl cation or other acyclic intermediate. An extremely subtle balance exists between alternative reaction pathways during glycosylation. Further fine-tuning of protecting group structure is required to develop a reliable achiral variant that affects high levels of α-selectivity through 6-ring NGP.

Experimental Section

General: All reactions involving moisture-sensitive reagents were performed under an atmosphere of argon or nitrogen by using standard vacuum Schlenk-line techniques. All glassware for such reactions was flame-dried and cooled under an atmosphere of argon. Reactions conducted at –78 °C were cooled by means of an acetone/dry-ice bath; those conducted at –40 °C by were cooled means of an acetonitrile/dry-ice bath; those conducted at 0 °C were cooled by means of an ice bath. Solvent was removed under reduced pressure by using a Büchi™ rotary evaporator. Diethyl ether, toluene, dichloromethane and acetonitrile were dried by passing them through a column of activated basic alumina. THF was distilled from sodium/benzophenone under an argon atmosphere prior to use. *N*,*N*-Dimethylformamide (DMF), pyridine and methanol were purchased from Aldrich in sure/seal™ bottles. All other solvents were used as supplied (analytical or HPLC grade) without purification. Petroleum ether refers to the fraction of light petroleum ether boiling in the range 40–60 °C. Reagents were used as supplied without further purification unless otherwise stated. Thin Layer Chromatography (TLC) was carried out on Merck Silica Gel $60F_{254}$ aluminium-backed plates. Visualisation of the plates was achieved by using a UV lamp (λ_{max} = 254 or 365 nm), ammonium molybdate (5% in 2 M H_2SO_4), sulfuric acid (5% in EtOH), iodine, vanillin, and/or potassium permanganate. Flash column chromatography was carried out with Sorbsil C60 40/60 silica. Melting points were recorded with a Kofler hot-block. Proton and carbon nuclear magnetic resonance spectra were recorded with Bruker DPX200 (200 MHz), Bruker DPX250 (250 MHz), Bruker DPX 400 (400 MHz), Bruker AV400 (400 MHz), and Bruker AV500 (500 MHz) spectrometers. All chemical shifts are quoted relative to the residual solvent as an internal standard. ^1H and ^{13}C spectra were assigned by using COSY, DEPT, HSQC, HMBC, TOCSY and DPFGSE-TOCSY techniques. Low-resolution mass spectra were recorded with a Micromass Platform 1 spectrometer or a Micromass LCT Premier spectrometer by using atmospheric pressure electrospray ionisation in either positive or negative polarity. High-resolution mass spectra were recorded by Mr Robin Procter, Dr Lingzhi Gong, or Mr Colin Sparrow with either a Walters 2790-Micromass LCT electrospray ionisation or a Bruker FT-ICR mass spectrometer by using electrospray ionisation or chemical ionisation techniques as stated. Optical rotations were measured with a Perkin–Elmer 241 polarimeter with a water-jacketed 1 cm^3 cell with a path length of 1 dm. Concentrations (*c*) are given in g/100 cm^3, solvent and temperature are recorded. Microanalyses were performed by the Inorganic Chemistry Laboratory Elemental Analysis service at the University of Oxford.

3,4,6-Tri-*O*-benzyl-2-*O*-(2-hydroxyethyl)-β-D-glucopyranosyl Fluoride (2): A solution of allyl ether **1**[10] (121 mg, 0.246 mmol) in CH_2Cl_2/methanol (3 mL, 1:1) was treated with ozone at –78 °C until the solution turned blue. The reaction was quenched by the addition of $NaBH_4$ (42 mg, 1.105 mmol) in small portions over 10 min. The reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 4:1) to afford alcohol **2** (101 mg, 81%) as a colourless oil. $[a]_D^{25}$ = +30.0 (*c* = 1.0 in $CHCl_3$). IR (KBr): $\tilde{\nu}_{max}$ = 3480 (br., OH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.40 (br. s, 1 H, -CH_2CH_2OH), 3.51 (m, 1 H, H-2), 3.60 (a dt, *J* = 9.6, *J* = 3.0 Hz, 1 H, C*H*H′CH_2OH), 3.63–3.84 (m, 7 H, H-3, H-4, H-6, H-6′, CH*H*′$_2CH_2OH$, CH_2CH_2OH), 3.91 (ddd, $J_{4,5}$ = 10.9, $J_{5,6}$ = 5.1, $J_{5,6'}$ = 3.0 Hz, 1 H, H-5) 4.57, 4.66 (ABq, J_{AB} = 12.1 Hz, 2 H, $PhCH_2$), 4.59, 4.84 (ABq, J_{AB} = 10.9 Hz, 2 H, $PhCH_2$), 4.91 (br. s, 2 H, $PhCH_2$), 5.19 (dd, $J_{1,2}$ =

7.1, $J_{1,F}$ 52.8 Hz, 1 H, H-1), 7.17–7.42 (m, 15 H, 15 × Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 62.3 (CH_2CH_2OH), 68.2 (t, C-6), 73.7, 73.9, 75.0 (3 x t, 3 × $PhCH_2$), 74.8 (d, C-5), 75.8 (t, CH_2CH_2OH), 77.2 (d, C-4), 81.9 (dd, $J_{2,F}$ = 22.4 Hz, C-2), 83.2 (d, C-3), 109.7 (dd, $J_{1,F}$ = 215.7 Hz, C-1), 127.8, 128.0, 128.0, 128.0, 128.5, 128.5, 128.6, 128.6 (8 × d, 8 × Ar-CH), 137.7, 137.8, 137.8 (3 × s, 3 × Ar-C) ppm. MS (ES^+): *m*/*z* (%) = 519 (90) [M + Na^+], 514 (100) [M + NH_4^+]. HRMS (ES^+): calcd. for $C_{29}H_{33}FO_6Na$ (M + Na^+) 519.2153; found 519.2148. $C_{29}H_{33}FO_6$ (496.57): calcd. C 70.14, H 6.70; found C 70.38, H 6.87.

3,4,6-Tri-*O*-benzyl-2-*O*-(2-iodoethyl)-β-D-glucopyranosyl Fluoride (3): Alcohol **2** (0.250 g, 0.504 mmol) was dissolved in freshly distilled THF (5 mL) under an atmosphere of argon. A mixture iodine (0.191 g, 0.756 mmol), imidazole (0.051 g, 0.756 mmol) and PPh_3 (0.147 g, 0.756 mmol) were added as a solution in THF (5 mL) and the reaction heated to reflux. After 16 h, TLC (petroleum ether/ethyl acetate, 4:1) indicated formation of a single major product (R_f 0.6) and complete consumption of starting material (R_f 0.2). The reaction was cooled to room temp. and concentrated in vacuo. The resulting residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 10:1) to afford iodide **3** (0.272 g, 89%) as a white crystalline solid, m.p. 61–63 °C (petroleum ether/ethyl acetate). $[\alpha]_D^{25}$ = –4.7 (*c* = 1.0 in $CHCl_3$). IR (KBr): $\tilde{\nu}_{max}$ = 3850 (br., C–I) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.12–3.16 (m, 2 H, OCH_2CH_2I), 3.35 (ddd, $J_{1,2}$ = 6.9, $J_{2,3}$ = 8.7, $J_{2,F}$ 12.4 Hz, 1 H, H-2), 3.46–3.50 (m, 1 H, H-5), 3.54 (at, *J* = 8.7 Hz, 1 H, H-3), 3.59–3.65 (m, 3 H, H-4, H-6, H-6'), 3.79–3.85 (m, 1 H, $OCHH'CH_2I$), 3.93–3.99 (m, 1 H, $OCHH'CH_2I$), 4.46, 4.54 (ABq, J_{AB} = 11.8 Hz, 2 H, $PhCH_2$), 4.46, 4.72 (ABq, J_{AB} = 11.2 Hz, 2 H, $PhCH_2$), 4.74, 4.88 (ABq, J_{AB} = 11.1 Hz, 2 H, $PhCH_2$), 5.09 (dd, $J_{1,2}$ = 6.9, $J_{1,F}$ 52.6 Hz, 1 H, H-1), 7.06–7.29 (m, 15 H, 15 × Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 2.5 (OCH_2CH_2I), 68.2 (C-6), 72.9 (OCH_2CH_2I), 73.6, 74.8, 75.0 (3 × $PhCH_2$), 74.8 (C-5), 76.9 (C-4), 82.2 (C-2, $J_{2,F}$ = 22.4 Hz), 83.3 (C-3), 109.5 (C-1, $J_{1,F}$ = 215.70 Hz), 127.8, 127.8, 127.9, 127.9 (4 × ArCH), 128.4, 128.5 (2 × ArC) ppm. MS (ES^+): *m*/*z* (%) = 629 (95) [M + Na^+], 624 (100) [M + NH_4^+]. HRMS (ES^+): calcd. for $C_{29}H_{32}O_5FINa$ [M + Na^+] 629.1176; found 629.1180. $C_{29}H_{32}FIO_5$ (606.47): calcd. C 57.43, H 5.32; found C 57.46, H 5.34.

3,4,6-Tri-*O*-benzyl-2-*O*-[2-(phenylselenyl)ethyl]-β-D-glucopyranosyl Fluoride (4): PhSeH (0.079 mL, 0.500 mmol) was added to a stirred suspension of NaH (0.012 g, 0.500 mmol) in THF (5 mL). After 30 min, iodide **3** (0.242 g, 0.400 mmol) was added as a solution in THF (5 mL) and the reaction heated to reflux. After 16 h, TLC (petroleum ether/ethyl acetate, 4:1) indicated formation of a single major product (R_f 0.5) and complete consumption of starting material (R_f 0.6). The reaction was diluted with CH_2Cl_2 (20 mL) and washed with water (20 mL). The aqueous layer was then extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic extracts were washed with saturated sodium hydrogen carbonate (20 mL) then brine (20 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 10:1) to afford selenide **4** (0.218 g, 86%) as a pale yellow oil. $[\alpha]_D^{25}$ = +2.5 (*c* = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.08 (m, 2 H, OCH_2CH_2SePh), 3.39–3.46 (m, 1 H, H-2), 3.56–3.63 (m, 2 H, H-3, H-5), 3.68–3.74 (m, 3 H, H-4, H-6, H-6'), 3.88–3.94 (m, 1 H, $OCHH'CH_2SePh$), 4.03–4.09 (m, 1 H, $OCHH'CH_2SePh$), 4.55, 4.64 (ABq, J_{AB} = 12.3 Hz, 2 H, $PhCH_2$), 4.55, 4.82 (ABq, J_{AB} = 10.6 Hz, 2 H, $PhCH_2$), 4.79, 4.94 (ABq, J_{AB} = 11.0 Hz, 2 H, $PhCH_2$), 5.09 (dd, $J_{1,2}$ = 6.6, $J_{1,F}$ 52.8 Hz, 1 H, H-1), 7.16–7.36 (m, 20 H, 20 × Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.0 (OCH_2CH_2SePh), 68.3 (C-6), 71.9 (OCH_2CH_2SePh), 73.6, 74.8, 75.0 (3 × $PhCH_2$), 75.0 (C-5), 75.5 (C-4), 82.2 (C-2, $J_{2,F}$ = 22.1 Hz), 83.3 (C-3), 109.5 (C-1, $J_{1,F}$ = 214.7 Hz), 127.0, 127.8, 127.8, 127.9, 127.9, 128.4, 128.5, 129.1, 129.7 (9 × ArCH), 137.8, 137.9, 138.3 (3 × ArC) ppm. MS (ES^+): *m*/*z* (%) = 659 (100) [M + Na^+]. HRMS (ES^+): calcd. for $C_{35}H_{37}O_5FSeNa$ (M + Na^+) 659.1685; found 659.1698. $C_{35}H_{37}FO_5Se$ (635.63): calcd. C 66.35, H 6.34; found C 66.40, H 6.45.

3,4,6-Tri-*O*-benzyl-2-*O*-(2-hydroxyethyl)-α/β-D-glucopyranose (6): A solution of allyl ether **5**[12] (121 mg, 0.246 mmol) in CH_2Cl_2/methanol (3 mL, 1:1) was treated with ozone at –78 °C until the solution turned blue. The reaction was quenched by the addition of $NaBH_4$ (42 mg, 1.105 mmol) in small portions over 10 min. The reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 4:1) to afford 3,4,6-tri-*O*-benzyl-2-*O*-(2-hydroxyethyl)ether-α/β-D-glucopyranose **6** (101 mg, 76%) as a colourless oil. IR (KBr): $\tilde{\nu}_{max}$ = 3470 (br., OH) cm^{-1}. ^{1}H NMR [400 MHz, $CDCl_3$, 5:1 mixture of α:β anomers observed, major α anomer quoted]: δ = 3.31 (m, 1 H, H-2), 3.50–3.75 (m, 8 H, H-3, H-4, H-6, H-6', OCH_2CH_2OH, OCH_2CH_2OH), 3.90 (m, 1 H, H-5) 4.57, 4.66 (ABq, J_{AB} = 12.1 Hz, 2 H, $PhCH_2$), 4.59, 4.84 (ABq, J_{AB} = 10.9 Hz, 2 H, $PhCH_2$), 4.91 (br. s, 2 H, $PhCH_2$), 5.38 (dd, $J_{1,2}$ = 3.3 Hz, 1 H, H-1), 7.14–7.35 (m, 15 H, 15 × Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 62.2 (OCH_2CH_2OH), 68.7 (C-6), 70.3 (C-5), 72.6, 73.5, 74.2 (3 × $PhCH_2$), 75.8 (OCH_2CH_2OH), 78.0, 80.9, 81.6 (C-2, C-3, C-4), 90.9 (C-1), 127.8, 127.9, 127.9, 128.0, 128.4, 128.4, 128.5, 128.5 (8 × Ar-CH), 137.7, 137.8, 137.8 (3 × Ar-C) ppm. MS (ES^+): *m*/*z* (%) = 517 (100) [M + Na^+]. HRMS (ES^+): calcd. for $C_{29}H_{34}O_7Na$ [M + Na^+] 517.2202; found 517.2210. $C_{29}H_{34}O_7$ (494.58): calcd. C 70.43, H 6.93; found C 70.55, H 6.99.

3,4,6-Tri-*O*-benzyl-2-*O*-(2-iodoethyl)-α/β-D-glucopyranose (7): Diol **6** (0.249 g, 0.504 mmol) was dissolved in freshly distilled THF (5 mL) under an atmosphere of argon. A mixture of iodine (0.191 g, 0.756 mmol), imidazole (0.051 g, 0.756 mmol) and PPh_3 (0.147 g, 0.756 mmol) were added as a solution in THF (5 mL) and the reaction heated to reflux. After 16 h, TLC (petroleum ether/ethyl acetate, 4:1) indicated formation of a single major product (R_f 0.4) and complete consumption of the starting material (R_f 0.1). The reaction was cooled to room temp. and concentrated in vacuo. The resulting residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 6:1) to afford iodide **7** (0.231 g, 76%) as a colourless oil. ^{1}H NMR [400 MHz, $CDCl_3$, 5:1 mixture of α:β anomers observed, major α anomer quoted]: δ = 3.12–3.16 (m, 2 H, OCH_2CH_2I), 3.35 (dd, $J_{1,2}$ = 3.3, $J_{2,3}$ = 8.2 Hz, 1 H, H-2), 3.46–3.55 (m, 2 H, H-4, H-5), 3.59–3.65 (m, 3 H, H-4, H-6, H-6'), 3.79–3.85 (m, 1 H, $OCHH'CH_2I$), 3.93–3.99 (m, 1 H, $OCHH'CH_2I$), 4.46, 4.54 (ABq, J_{AB} = 11.8 Hz, 2 H, $PhCH_2$), 4.46, 4.72 (ABq, J_{AB} = 11.2 Hz, 2 H, $PhCH_2$), 4.74, 4.88 (ABq, J_{AB} = 11.1 Hz, 2 H, $PhCH_2$), 5.35 (d, $J_{1,2}$ = 3.3 Hz, 1 H, H-1), 7.06–7.29 (m, 15 H, 15 × Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.0 (OCH_2CH_2I), 68.5 (C-6), 70.5 (OCH_2CH_2I), 72.0, 73.5, 75.0 (3 × $PhCH_2$), 74.8 (C-5), 76.9 (C-4), 82.2 (C-2), 83.3 (C-3), 91.5 (C-1), 127.8, 127.8, 127.9, 127.9 (4 × ArCH), 128.4, 128.5 (2 × ArC) ppm. MS (ES^+): *m*/*z* (%) = 627 (95) [M + Na^+], 622 (100) [M + NH_4^+]. HRMS (ES^+): calcd. for $C_{29}H_{33}O_6INa$ [M + Na^+] 627.1220; found 627.1210. $C_{29}H_{33}IO_6$ (604.48): calcd. C 57.62, H 5.50; found C 57.51, H 5.58.

***O*-[3,4,6-Tri-*O*-benzyl-2-*O*-(2-iodoethyl)-α/β-D-glucopyranosyl] Trichloroacetimidate (8):** Hemiacetal **7** (0.773 g, 1.28 mmol) was dissolved in freshly distilled CH_2Cl_2 (8 mL) at 0 °C under an argon atmosphere. DBU (0.078 mL, 0.51 mmol) was added followed by

trichloroacetonitrile (1.31 mL, 12.8 mmol). After 5 h, TLC (petroleum ether/ethyl acetate, 4:1, with 1% added triethylamine) indicated the formation of a single product (R_f 0.6) and complete consumption of the starting material (R_f 0.4). The reaction was concentrated in vacuo and the resulting residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 7:1, with 1% added triethylamine) to afford trichloroacetimidate **8** (0.835 g, 84%) as a colourless oil. IR (KBr): $\tilde{\nu}_{max}$ = 3345 (w, NH), 1659 (s, C=N) cm^{-1}. ^1H NMR [400 MHz, $CDCl_3$, 15:1 mixture of α:β anomers observed, major α anomer quoted]: δ = 3.14–3.17 (m, 2 H, OCH_2CH_2I), 3.60–4.04 (m, 8 H, H-2, H-3, H-4, H-5, H-6, H-6', OCH_2CH_2I), 4.49, 4.63 (ABq, J_{AB} = 12.0 Hz, 2 H, $PhCH_2$), 4.54, 4.87 (ABq, J_{AB} = 10.6 Hz, 2 H, $PhCH_2$), 4.83, 5.00 (ABq, J_{AB} = 10.8 Hz, 2 H, $PhCH_2$), 6.67 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H-1), 7.11–7.29 (m, 15 H, 15 × Ar-H), 8.61 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.0 (OCH_2CH_2I), 68.0 (C-6), 70.5 (OCH_2CH_2I), 73.5, 73.6, 75.0, 75.4 (3 × ArCH_2), 73.5, 78.8, 81.2, 84.4 (C-2, C-3, C-4, C-5), 94.4 [OC(NH)CCl_3], 97.6 (C-1), 126.2, 126.6, 126.9, 127.7, 127.8, 127.9, 128.1, 128.4, (8 × Ar-CH), 137.8, 138.0, 138.6 (3 × Ar-C), 163.8 (s, C=NH) ppm. MS (ES^+): *m/z* (%) = 765 (100) [M + NH_4^+]. HRMS (ES^+): calcd. for $C_{31}H_{33}Cl_3NO_6INa$ [M + Na^+] 770.0316; found 770.0319.

3,4,6-Tri-*O*-benzyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranose (9): PhSeH (0.079 mL, 0.500 mmol) was added to a stirred suspension of NaH (0.012 g, 0.500 mmol) in THF (5 mL). After 30 min, iodide **7** (0.242 g, 0.400 mmol) was added as a solution in THF (5 mL) and the reaction heated to reflux. After 16 h, TLC (petroleum ether/ethyl acetate, 4:1) indicated formation of a single product (R_f 0.3) and complete consumption of starting material (R_f 0.4). The reaction was diluted with CH_2Cl_2 (20 mL) and washed with water (20 mL). The aqueous layer was then extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic extracts were washed with saturated sodium hydrogen carbonate (20 mL) then brine (20 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 10:1) to afford selenide **9** (0.205 g, 81%) as a pale yellow oil. ^1H NMR [400 MHz, $CDCl_3$, 5:1 mixture of α:β anomers observed, major α anomer quoted]: δ = 3.02–3.07 (m, 2 H, OCH_2CH_2SePh), 3.35 (dd, $J_{1,2}$ = 3.3, $J_{2,3}$ = 8.2 Hz, 1 H, H-2), 3.41–3.55 (m, 2 H, H-4, H-5), 3.59–3.65 (m, 3 H, H-4, H-6, H-6'), 3.79–3.85 (m, 1 H, $OCHH'CH_2SePh$), 3.93–3.99 (m, 1 H, $OCHH'CH_2SePh$), 4.45, 4.53 (ABq, J_{AB} = 11.8 Hz, 2 H, $PhCH_2$), 4.46, 4.72 (ABq, J_{AB} = 11.2 Hz, 2 H, $PhCH_2$), 4.70, 4.83 (ABq, J_{AB} = 11.1 Hz, 2 H, $PhCH_2$), 5.25 (d, $J_{1,2}$ = 3.3 Hz, 1 H, H-1), 7.06–7.37 (m, 20 H, 20 × Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.9 (OCH_2CH_2SePh), 68.9 (C-6), 70.3 (OCH_2CH_2SePh), 72.0, 73.5, 75.0 (3 × $PhCH_2$), 74.8, 76.9, 82.2, 83.3 (C-2, C-3, C-4, C-5), 91.5 (C-1), 127.0, 127.2, 127.6, 127.7,127.7, 127.9, 127.9, 128.0, 128.3, 128.4 (10 × ArCH), 131.5, 132.6, 132.8, 133.3 (4 × ArC) ppm. MS (ES^+): *m/z* (%) = 657 (95) [M + Na^+], 652 (100) [M + NH_4^+]. HRMS (ES^+): calcd. for $C_{35}H_{38}O_6SeNa$ [M + Na^+] 657.1731; found 657.1719. $C_{35}H_{38}O_6Se$ (633.64): calcd. C 66.34, H 6.04; found C 66.51, H 6.23.

***O*-{3,4,6-Tri-*O*-benzyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranosyl} Trichloroacetimidate (10):** Hemiacetal **9** (0.812 g, 1.28 mmol) was dissolved in freshly distilled CH_2Cl_2 (8 mL) at 0 °C under an argon atmosphere. DBU (0.078 mL, 0.51 mmol) was added followed by trichloroacetonitrile (1.31 mL, 12.8 mmol). After 5 h, TLC (petroleum ether/ethyl acetate, 4:1, with 1% added triethylamine) indicated the formation of a single product (R_f 0.6) and complete consumption of the starting material (R_f 0.4). The reaction was concentrated in vacuo and the resulting residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 7:1, with 1% added triethylamine) to afford trichloroacetimidate **10** (0.901 g, 88%) as a colourless oil. IR (KBr): $\tilde{\nu}_{max}$ = 3345 (w, NH), 1662 (s, C=N) cm^{-1}. ^1H NMR [400 MHz, $CDCl_3$, 15:1 mixture of α:β anomers observed, major α anomer quoted]: δ = 3.02–3.09 (m, 2 H, OCH_2CH_2SePh), 3.60–4.04 (m, 8 H, H-2, H-3, H-4, H-5, H-6, H-6', OCH_2CH_2SePh), 4.48, 4.63 (ABq, J_{AB} = 11.3 Hz, 2 H, $PhCH_2$), 4.52, 4.84 (ABq, J_{AB} = 10.6 Hz, 2 H, $PhCH_2$), 4.83, 5.00 (ABq, J_{AB} = 12.0 Hz, 2 H, $PhCH_2$), 6.69 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H-1), 7.10–7.34 (m, 20 H, 29 × Ar-H), 8.54 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.9 (OCH_2CH_2SePh), 68.3 (C-6), 70.3 (OCH_2CH_2SePh), 73.5, 73.7, 75.1 (3 × ArCH_2), 73.1, 78.5, 81.0, 84.4 (C-2, C-3, C-4, C-5), 94.0 [OC(NH)CCl_3], 97.5 (C-1), 126.2, 126.6, 127.0, 127.1, 127.3, 127.7, 127.7, 127.9, 128.1, 128.4, (10 × Ar-CH), 137.8, 138.0, 138.6, 138.8 (4 × Ar-C), 164.0 (s, C=NH) ppm. MS (ES^+): *m/z* (%) = 795 (100) [M + NH_4^+]. HRMS (ES^+): calcd. for $C_{37}H_{38}Cl_3NO_6SeNa$ [M + Na^+] 800.0828; found 800.0821.

General Method A: To a flame-dried round-bottom flask containing activated 3 Å molecular sieves (0.100 g) was added a solution of the glycosyl fluoride donor (125 mM) and the glycosyl acceptor (2 equiv.) in freshly distilled CH_2Cl_2. The reaction mixture was cooled to the designated temperature under an argon atmosphere, then $BF_3{\cdot}OEt_2$ (1.5 equiv.) was added. The reaction was monitored by TLC (toluene/ethyl acetate, 9:1) until the formation of a major product (typically $R_f \approx 0.4$) and complete consumption of starting material (typically $R_f \approx 0.7$) was observed. The reaction was quenched with saturated sodium hydrogen carbonate solution and filtered through Celite®. The mixture was diluted with CH_2Cl_2, washed with saturated sodium hydrogen carbonate solution and the aqueous layer extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (typically toluene/ethyl acetate, 15:1).

General Method B: To a flame-dried round-bottom flask containing activated molecular sieves (3 Å) (0.100 g) was added a solution of the trichloroacetimidate donor (125 mM) and the glycosyl acceptor (2 equiv.) in freshly distilled CH_2Cl_2. The reaction mixture was cooled to the designated temperature under an argon atmosphere, then TMSOTf (0.1 equiv.) was added. The reaction was monitored by TLC (toluene/ethyl acetate, 9:1) until the formation of a major product (R_f typically about 0.4) and complete consumption of starting material (R_f typically about 0.6) was observed. The reaction was quenched with saturated sodium hydrogen carbonate solution and filtered through Celite®. The mixture was diluted with CH_2Cl_2, washed with saturated sodium hydrogen carbonate solution, and the aqueous layer extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (typically toluene/ethyl acetate, 15:1).

3,4,6-Tri-*O*-benzyl-2-*O*-(2-iodoethyl)-α/β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-α-D-galactopyranoside (11a): Disaccharide **11a**, a colourless oil. ^1H NMR [400 MHz, $CDCl_3$, 1:1 mixture of α:β anomers observed]: δ = 1.34 (br. s, 12 H, 2 × $CH_3\alpha$, 2 × $CH_3\beta$), 1.46, 1.47, 1.53, 1.55 (4 × s, 2 ×, 12 H $CH_3\alpha$, 2 × $CH_3\beta$), 3.12–3.16 (m, 4 H, $OCH_2CH_2I\alpha/\beta$), 3.40 (m, 1 H, H-$5_b\beta$), 3.46 (at, J = 8.0 Hz, 1 H, H-$2_b\beta$), 3.50–3.79 (m, 10 H, H-$2_a\alpha$, H-$5_a\alpha$, H-$2_a\beta$, H-$5_a\beta$, H-$2_b\alpha$, H-$5_b\alpha$, H-$6_b\alpha$, H-$6'_b\alpha$, H-$6_b\beta$, H-$6'_b\beta$), 3.97–4.63 (m, 20 H, H-$3_a\alpha$, H-$4_a\alpha$, H-$6_a\alpha$, H-$6'_a\alpha$, H-$3_a\beta$, H-$4_a\beta$, H-$4_b\beta$, H-$6_a\beta$, H-$6'_a\beta$, H-$3_b\alpha$, H-$4_b\alpha$, H-$1_a\beta$, H-$3_a\beta$, $OCH_2CH_2I\alpha/\beta$), 4.71–5.25 (m, 12 H, 6 × $PhCH_2\alpha$, 6 × $PhCH_2\beta$), 4.95 (d, $J_{1,2}$ = 4.1 Hz, 1 H, H-$1_b\alpha$), 5.55 (d, $J_{1,2}$ = 5.0 Hz, 1 H, H-$1_a\beta$), 5.60 (d, $J_{1,2}$ = 5.0 Hz,

1 H, H-1$_a$α), 7.07–7.29 (m, 30 H, 15 × Ar-CHα, 15 × Ar-CHβ) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 4.6, 4.7 (OCH$_2$-*C*H$_2$Iα/β), 66.3, 66.4 (C-6$_a$α, C-6$_a$β), 68.2, 68.7, (C-6$_b$α, C-6$_b$β), 70.1, 70.3 (O*C*H$_2$CH$_2$Iα/β), 73.2, 75.4, 75.3 (3 × Ar*C*H$_2$), 70.6, 70.9, 71.4, 71.5, 74.7, 77.6, 79.5, 81.0, 81.2, 84.3 (C-2$_a$-C-5$_a$α/β, C-2$_b$-C-5$_b$α/β), 94.9 (d, C-1$_a$β), 96.0 (d, C-1$_a$α), 97.0 (d, C-1$_b$α), 103.4 (d, C-1$_b$β), 126.0, 126.5, 126.6, 127.2, 127.6, 127.7, 127.9, 128.1, 128.2, 128.4 (10 × Ar-CH), 137.9, 138.1, 138.3, 138.7, 140.9, 141.2 (6 × Ar-C) ppm. MS (ES$^+$): *m*/*z* (%) = 869 (100) [M + Na$^+$]. HRMS (ES$^+$): calcd. for $C_{41}H_{51}O_{11}INa$ [M + Na$^+$] 869.2374; found 869.2381. $C_{41}H_{51}IO_{11}$ (846.75): calcd. C 58.16, H 6.07; found C 58.25, H 6.13.

3,4,6-Tri-*O*-benzyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-α-D-galactopyranoside (11b): Disaccharide **11b**, a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) [1:1 mixture of α:β anomers observed]: δ = 1.34 (br. s, 12 H, 2 × CH$_3$α, 2 × CH$_3$β), 1.46, 1.47, 1.53, 1.55 (4 × s, 2 ×, 12 HCH$_3$α, 2 × CH$_3$β), 3.10–3.14 (m, 4 H, OCH$_2$C*H*$_2$SePhα/β), 3.44 (m, 1 H, H-5$_b$β), 3.50 (at, *J* = 8.4 Hz, 1 H, H-2$_b$β), 3.54–3.86 (m, 10 H, H-2$_a$α, H-5$_a$α, H-2$_a$β, H-5$_a$β, H-2$_b$α, H-5$_b$α, H-6$_b$α, H-6′$_b$α, H-6$_b$β, H-6′$_b$β), 3.99 (at, *J* = 9.4 Hz, 1 H, H-4$_b$β), 4.04–4.65 (m, 20 H, H-3$_a$α, H-4$_a$α, H-6$_a$α, H-6′$_a$α, H-3$_a$β, H-4$_a$β, H-6$_a$β, H-6′$_a$β, H-3$_b$α, H-4$_b$α, H-1$_a$β, H-3$_a$β, O*C*H$_2$CH$_2$SePhα/β), 4.74–5.31 (m, 12 H, 6 × PhCH$_2$α, 6 × PhCH$_2$β), 4.98 (d, $J_{1,2}$ = 4.1 Hz, 1 H, H-1$_b$α), 5.52 (d, $J_{1,2}$ = 5.1 Hz, 1 H, H-1$_a$β), 5.57 (d, $J_{1,2}$ = 5.1 Hz, 1 H, H-1$_a$α), 7.08–7.38 (m, 40 H, 20 × Ar-CHα, 20 × Ar-CHβ) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.8, 26.9 (OCH$_2$*C*H$_2$SePhα/β), 66.3, 66.9 (C-6$_a$α, C-6$_a$β), 68.3, 68.7, (C-6$_b$α, C-6$_b$β), 70.5, 70.6 (O*C*H$_2$CH$_2$SePhα/β), 73.5, 75.1, 75.8 (3 × Ar*C*H$_2$), 70.7, 70.9, 71.2, 71.5, 74.7, 77.6, 79.5, 81.1, 81.6, 84.3 (C-2$_a$-C-5$_a$α/β, C-2$_b$-C-5$_b$α/β), 95.4 (d, C-1$_a$β), 96.2 (d, C-1$_a$α), 97.1 (d, C-1$_b$α), 104.4 (d, C-1$_b$β), 126.0, 126.5, 126.6, 127.2, 127.6, 127.7, 127.9, 128.1, 128.2, 128.4 (10 × Ar-CH), 137.9, 138.1, 138.3, 138.7, 140.9, 141.2 (6 × Ar-C) ppm. MS (ES$^+$): *m*/*z* (%) = 899 (100) [M + Na$^+$]. HRMS (ES$^+$): calcd. for $C_{47}H_{56}O_{11}SeNa$ [M + Na$^+$] 899.2886; found 899.2880. $C_{47}H_{56}O_{11}Se$ (875.91): calcd. C 64.45, H 6.44; found C 64.23, H 6.58.

Methyl 3,4,6-Tri-*O*-benzyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranoside (14): General Method B with trichloroacetimidate **10** (125 mM) and MeOH (2 equiv.) gave methyl glycoside **14** as a colourless oil. ^{1}H NMR [400 MHz, $CDCl_3$, 1:1 mixture of α:β anomers observed]: δ = 3.10–3.14 (m, 4 H, OCH$_2$C*H*$_2$SePhα/β), 3.38–3.50 (m, 4 H, H-2α, H-2β, H-5α, H-5β), 3.60 (br. s, 2 H, CH$_3$α/β), 3.61–3.65 (m, 4 H, H-3α, H-3β, H-4α, H-4β), 3.68–3.78 (m, 4 H, H-6α, H-6β, H-6′α, H-6′β), 4.02–4.05 (m, 4 H, O*C*H$_2$CH$_2$SePhα/β), 4.29 (d, $J_{1,2}$ = 7.8 Hz, 1 H, H-1β), 4.31 (d, $J_{1,2}$ = 3.0 Hz, 1 H, H-1α), 4.51–4.98 (m, 12 H, 3 × Ar-CHα, 3 × Ar-CHβ), 7.15–7.43 (m, 40 H, 20 × Ar-CHα, 20 × Ar-CHβ) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.8, 26.9 (OCH$_2$*C*H$_2$SePhα/β), 57.1 (*C*H$_3$), 68.8 (C-6), 70.5 (O*C*H$_2$CH$_2$SePhα/β), 75.1, 75.3, 75.8 (3 × Ar*C*H$_2$), 74.9 (C-5), 77.8 (C-3), 81.9 (d, C-2), 84.4 (d, C-4), 104.5 (d, C-1), 126.8, 127.6, 127.6, 127.7, 127.8, 127.9, 128.0, 128.4, 128.4, 129.3 (10 × d, 10 × Ar-CH), 138.0, 138.1, 138.5, 142.9 (4 × s, 4 × Ar-C) ppm. MS (ES$^+$): *m*/*z* = 666 [M + NH$_4^+$] (100). HRMS (ES$^+$): calcd. for $C_{36}H_{40}O_6SeNa$ [M + Na$^+$] 671.1888; found 671.1880. $C_{36}H_{40}O_6Se$ (647.67): calcd. C 66.76, H 6.23; found C 66.70, H 6.28.

3,4,6-Tri-*O*-benzyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranosyl-(1→6)-methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (15): General Method B with trichloroacetimidate **10** (125 mM) and acceptor **12** (2 equiv.) gave disaccharide **15** as a colourless oil. ^{1}H NMR[400 MHz, $CDCl_3$, 2:1 mixture of α:β anomers observed]: δ = 3.08–3.12 (m, 6 H, OCH$_2$C*H*$_2$SePhα/β), 3.14 (s, 6 H, OMeα), 3.16 (s, 3 H, OMeβ), 3.39 (dd, $J_{2,3}$ = 9.7, $J_{3,4}$ = 2.9 Hz, 1 H, H-3$_b$β), 3.43 (m, 1 H, H-3$_a$β), 3.50 (dd, $J_{1,2}$ = 3.4, $J_{2,3}$ = 9.6 Hz, 2 H, H-2$_a$α), 3.61–3.66 (m, 2 H, H-2$_a$β, H-6$_b$β), 3.73–3.87 (m, 10 H, H-6$_a$α, H-6$_b$α, H-6′$_b$α, H-4$_a$β, H-4$_b$β, H-6$_a$β, H-6′$_b$β), 3.88–3.94 (m, 4 H, H-4$_a$α, H-5$_a$α), 3.96–4.08 (m, 8 H, H-4$_b$α, H-6′$_a$α, H-5$_a$β, OC*H*$_2$CH$_2$SePhα/β), 4.11 (dd, $J_{2,3}$ = 10.2, $J_{3,4}$ = 2.7 Hz, 2 H, H-3$_b$α), 4.16 (dd, $J_{1,2}$ = 7.5, $J_{2,3}$ = 9.7 Hz, 1 H, H-2$_b$β), 4.21–4.32 (m, 10 H, H-2$_b$α, H-3$_a$α, H-5$_b$α, PhC*H*$_2$α, H-5$_b$β, PhC*H*$_2$β), 4.34–4.38 (m, 3 H, PhC*H*$_2$α, H-6′$_a$β), 4.44 (d, $J_{1,2}$ = 7.5 Hz, 2 H, H-1$_b$β), 4.46–5.13 (m, 28 H, H-1$_a$α, 8 × PhC*H*H′α, H-1$_a$β, 10 × PhC*H*H′β), 5.29 (d, $J_{1,2}$ = 3.4 Hz, 2 H, H-1$_b$α), 7.04–7.45 (m, 105 H, 35 × Ar-Hα, 35 × Ar-Hβ) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 54.9, 55.0, 68.7, 69.0, 70.0, 70.7, 71.3, 72.7, 72.8, 73.0, 73.5, 73.7, 74.7, 74.8, 75.1, 75.2, 75.3, 75.5, 76.2, 78.3, 78.6, 78.6, 79.9, 81.1, 81.2, 82.3, 82.4, 82.7, 98.2, 98.4, 104.6, 127.4, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.2, 128.4, 128.5, 128.5, 128.6, 128.6, 138.7, 139.2, 139.2, 139.5, 139.7, 139.8 ppm. MS (ES$^+$): *m*/*z* (%) = 1103 (100) [M + Na$^+$]. HRMS (ES$^+$): calcd. for $C_{63}H_{68}O_{11}SeNa$ [M + Na$^+$] 1103.3825; found 1103.3830. $C_{63}H_{68}O_{11}Se$ (1080.18): calcd. C 70.05, H 6.35; found C 70.12, H 6.39.

3,4,6-Tri-*O*-benzyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranosyl-(1→4)-methyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (16): General Method B with trichloroacetimidate **10** (125 mM) and acceptor **13** (2 equiv.) gave disaccharide **16** as a colourless oil. ^{1}H NMR [400 MHz, $CDCl_3$, 2:1 mixture of α:β anomers observed]: δ = 3.09–3.13 (m, 6 H, OCH$_2$C*H*$_2$SePhα/β), 3.16 (s, 6 H, OMeα), 3.18 (s, 3 H, OMeβ), 3.39 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 2.2 Hz, 1 H, H-3$_b$β), 3.43–3.47 (m, 2 H, H-3$_a$β, H-2$_a$α), 3.61–3.66 (m, 2 H, H-2$_a$β, H-6$_b$β), 3.70–3.84 (m, 10 H, H-6$_a$α, H-6$_b$α, H-6′$_b$α, H-4$_a$β, H-4$_b$β, H-6$_a$β, H-6′$_b$β), 3.88–3.94 (m, 4 H, H-4$_a$α, H-5$_a$α), 3.93–4.05 (m, 8 H, H-4$_b$α, H-6′$_a$α, H-5$_a$β, OC*H*$_2$CH$_2$SePhα/β), 4.09 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.0 Hz, 2 H, H-3$_b$α), 4.16 (dd, $J_{1,2}$ = 7.1, $J_{2,3}$ = 9.7 Hz, 1 H, H-2$_b$β), 4.21–4.32 (m, 10 H, H-2$_b$α, H-3$_a$α, H-5$_b$α, PhC*H*$_2$α, H-5$_b$β, PhC*H*$_2$β), 4.34–4.38 (m, 3 H, PhC*H*$_2$α, H-6′$_a$β), 4.47 (d, $J_{1,2}$ = 7.1 Hz, 2 H, H-1$_b$β), 4.53–5.10 (m, 28 H, H-1$_a$α, 8 × PhC*H*H′α, H-1$_a$β, 10 × PhC*H*H′β), 5.25 (d, $J_{1,2}$ = 3.4 Hz, 2 H, H-1$_b$α), 7.08–7.44 (m, 105 H, 35 × Ar-Hα, 35 × Ar-Hβ) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 54.8, 55.2, 68.6, 69.2, 70.1, 70.4, 71.6, 72.6, 72.9, 73.0, 73.5, 73.6, 74.7, 74.8, 75.1, 75.2, 75.4, 75.5, 76.0, 78.0, 78.6, 78.7, 79.4, 80.9, 81.1, 82.3, 82.5, 82.7, 98.2, 98.7, 104.5, 127.1, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128.3, 128.4, 128.5, 128.6, 128.8, 138.7, 139.0, 139.1, 139.3, 139.3, 139.4 ppm. MS (ES$^+$): *m*/*z* (%) = 1103 (100) [M + Na$^+$]. HRMS (ES$^+$): calcd. for $C_{63}H_{68}O_{11}SeNa$ [M + Na$^+$] 1103.3825; found 1103.3830]. $C_{63}H_{68}O_{11}Se$ (1080.18): calcd. C 70.05, H 6.35; found C 70.12, H 6.39.

***N*-(3,4,6-Tri-*O*-acetyl-2-*O*-allyl-β-D-glucopyranosyl)piperidine (21):**[18] Alcohol **20**[14] (18.67 g, 50 mmol) and Ag_2O (12.75 g, 1.1 equiv.) were mixed in anhydrous DMF (50 mL) and stirred under N_2. Allyl iodide (25 g, 3 equiv.) was then added dropwise to the reaction and the mixture was stirred for 16 h. Analysis by TLC (eluent; petroleum ether/EtOAc, 3:1) showed complete conversion to the product (R_f 0.3). The reaction was then filtered and concentrated under vacuum. The residue was then dissolved in $CHCl_3$ (100 mL) before washing with H_2O (150 mL). The organic layer was then dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude material was then purified by flash column chromatography (eluent; petroleum ether/EtOAc, 3:1). The product (9.34 g, 45% yield) was isolated as a colourless solid, m.p. 106–108 °C [ref. 103 °C].[18] [α]$_D$ = + 17.7 (*c* = 1.0 $CHCl_3$) [ref. [α]$_D$ = + 18 (*c* = 1.3 $CHCl_3$)].[18] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.46–1.59 [m, 6 H, N(CH$_2$C*H*$_2$)$_2$C*H*$_2$], 2.01 [s, 3 H, C(O)CH$_3$], 2.04 [s, 3 H, C(O)CH$_3$], 2.06 [s, 3 H, C(O)CH$_3$], 2.60–2.63 [m, 2 H, N(C*H*$_2$CH$_2$)$_2$CH$_2$], 2.85–2.89 [m, 2 H, N(C*H*$_2$CH$_2$)$_2$CH$_2$], 3.51–3.57 (m, 2 H, H-2 and

H-5), 3.94 (d, J = 9.5 Hz, 1 H, H-1), 4.05–4.09 (m, 2 H, H-6 and O-CH_2-CH=CH$_2$), 4.21 (dd, J = 12.0 5.0 Hz, 1 H, H-6′), 4.34 (dd, J = 12.5 5.0 Hz, 1 H, O-CH_2-CH=CH$_2$), 4.89 (t, J = 9.5 Hz, 1 H, H-4), 5.10 (t, J = 9.5 Hz, 1 H, H-3), 5.15 (dd, J = 10.5 0.5 Hz, 1 H, CH=CH_2), 5.22 (dd, J = 17.5 1.5 Hz, 1 H, CH=CH_2), 5.79–5.86 (m, 1 H, CH=CH$_2$) ppm. ^{13}C NMR (126 MHz, CDCl$_3$): δ = 20.8 [q, C(O)CH$_3$], 20.9 [q, C(O)CH$_3$], 21.0 [q, C(O)CH$_3$], 24.8 [t, N(CH$_2$CH$_2$)$_2$CH_2], 26.3 [t, N(CH$_2$CH_2)$_2$CH$_2$], 49.3 [t, N-(CH_2CH$_2$)$_2$CH$_2$], 62.7 (t, C-6), 69.2 (d, C-4), 72.5 (t, O-CH_2-CH=CH$_2$), 72.8 (d, C-2), 73.8 (d, C-5), 75.5 (d, C-3), 96.0 (d, C-1), 117.0 (t, CH=CH_2), 135.2 (d, CH=CH$_2$), 170.1 (s, C=O), 170.3 (s, C=O), 170.9 (s, C=O) ppm. HRMS (ESI-TOF): calcd. for C$_{20}$H$_{31}$NO$_8$H$^+$ [M + H$^+$] 414.2122; found 414.2138.

2-*O*-Allyl-3,4,6-tri-*O*-acetyl-α,β-D-glucopyranose (22): Piperidine **21** (500 mg, 1.2 mmol) was dissolved in MeOH (25 mL) and stirred under N$_2$. Aqueous HCl (1.0 M, 1.5 equiv.) was added and the reaction was stirred overnight. After 16 h, TLC [eluent; petroleum ether/EtOAc, 3:2) showed complete consumption of the starting material (R_f 0.7) and appearance of the product (R_f 0.2). The reaction was then diluted with toluene (50 mL) before concentrating under vacuum. The residue was then evaporated with toluene (2 × 50 mL). The crude material was then purified by flash column chromatography (eluent; petroleum ether/EtOAc, 3:2) to give hemiacetal **22** (374 mg, 89% yield) as a yellow oil. ^{1}H NMR [400 MHz, CDCl$_3$, mixture of α:β anomers observed]: δ = 2.02 [s, 3 H, C(O)-CH_3], 2.02 [s, 3 H, C(O)CH_3], 2.05 [s, 6 H, 2 × C(O)CH_3], 2.08 [s, 3 H, C(O)CH_3], 2.09 [s, 3 H, C(O)CH_3], 3.11 (br. s, 1 H, OH), 3.33 (dd, J = 9.6 7.6 Hz, 1 H, H-2$_\beta$), 3.57 (dd, J = 9.6 3.6 Hz, 1 H, H-2$_\alpha$), 3.69–3.74 (m, 1 H, H-5), 4.07–4.15 (m, 5 H, CH_2CH=CH$_2$, H-6, H-6 and H-6′), 4.20–4.35 (m, 4 H, H-5, CH_2CH=CH$_2$ and H-6′), 4.77 (dd, J = 7.6 4.8 Hz, 1 H, H-1$_\beta$), 4.98–5.03 (m, 2 H, H-4$_\alpha$ and H-4$_\beta$), 5.12–5.30 (m, 5 H, H-3$_\beta$ and CH$_2$CH=CH_2), 5.35–5.42 (m, 2 H, H-1$_\alpha$ and H-3$_\alpha$), 5.79–5.89 (m, 2 H, CH$_2$CH=CH$_2$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 20.8 [q, C(O)CH$_3$], 20.8 [q, C(O)CH$_3$], 20.9 [q, C(O)CH$_3$], 20.9 [q, C(O)CH$_3$], 21.0 [q, C(O)-CH$_3$], 62.2 (t, C-6), 62.4 (t, C-6), 67.5 (d, C-5), 68.5 (d, C-4), 68.7 (d, C-4), 71.9 (d, C-5 and C-3), 72.4 (t, CH$_2$CH=CH$_2$), 73.5 (t, CH$_2$CH=CH$_2$), 74.0 (d, C-3), 77.1 (d, C-2$_\alpha$), 79.8 (d, C-2$_\beta$), 91.2 (d, C-1$_\alpha$), 97.4 (d, C-1$_\beta$), 117.5 (t, CH$_2$CH=CH_2), 118.4 (t, CH$_2$CH=CH_2), 134.0 (d, CH$_2$CH=CH$_2$), 134.5 (d, CH$_2$CH=CH$_2$), 169.9 (s, C=O), 170.0 (s, C=O), 170.3 (s, C=O), 170.3 (s, C=O), 170.9 (s, C=O), 170.9 (s, C=O) ppm. HRMS (ESI-TOF): calcd. for C$_{15}$H$_{22}$O$_9$Na$^+$ [M + Na$^+$] 369.1156; found 369.1169.

3,4,6-Tri-*O*-acetyl-2-*O*-(2-hydroxyethyl)-α/β-D-glucopyranose (23): Allyl ether **22** (10.74 g, 31 mmol) was dissolved in CH$_2$Cl$_2$ (300 mL) under N$_2$ and cooled to –78 °C. Ozone was then bubbled through the solution for 90 min until it turned a deep blue. The excess ozone was then removed by bubbling N$_2$ through the solution until the colour had dissipated. Dimethyl sulfide (11.4 mL, 5 equiv.) was then added and the solution warmed to room temperature over an hour. The reaction was then concentrated under vacuum to remove the excess dimethyl sulfide before re-dissolving in CH$_2$Cl$_2$ (300 mL) and acetic acid (11.7 mL, 6.6 equiv.). The solution was then cooled to 0 °C and sodium cyanoborohydride (3.90 g, 2 equiv.) was added portion wise before the reaction was left to stir overnight. The next day the reaction was quenched by the addition of H$_2$O (50 mL). Brine (200 mL) was then added and the organic layer separated before the aqueous layer was extracted with CH$_2$Cl$_2$ (2 × 200 mL). The combined organic layers were then dried (MgSO$_4$), filtered, and concentrated under vacuum before purifying by flash column chromatography (eluent; EtOAc/petroleum ether, 5:1. R_f 0.35 and 0.26) to afford diol **23** (5.90 g, 54% yield) as a colourless oil. $\tilde{\nu}_{max}$ = (neat) 3446 (br. s, O-H), 1748 (s, C=O) cm^{-1}. ^{1}H NMR [400 MHz, CDCl$_3$, mixture of α:β anomers observed]: δ = 2.02 [s, 3 H, C(O)-CH_3], 2.03 [s, 3 H, C(O)CH_3], 2.04 [s, 3 H, C(O)CH_3], 2.06 [s, 3 H, C(O)CH_3], 2.07 [s, 3 H, C(O)CH_3], 2.08 [s, 3 H, C(O)CH_3], 3.36 (dd, J = 9.2 8.0 Hz, 1 H, H-2$_\beta$), 3.56 (dd, J = 9.6 3.6 Hz, 1 H, H-2$_\alpha$), 3.66–3.75 (m, 7 H, H-5$_\beta$, 2 × OCH$_2$CH_2OH and OCH_2-CH$_2$OH), 3.80–3.84 (m, 2 H, OCH_2CH$_2$OH), 4.09–4.15 (m, 2 H, H-6$_\alpha$ and H-6$_\beta$), 4.21–4.29 (m, 3 H, H-5$_\alpha$, H-6′$_\alpha$ and H-6′$_\beta$), 4.78 (d, J = 7.6 Hz, 1 H, H-1$_\beta$), 4.99–5.05 (m, 2 H, H-4$_\alpha$ and H-4$_\beta$), 5.14 (app. t, J = 9.6 9.2 Hz, 1 H, H-3$_\beta$), 5.40 (app. t, J = 9.6 Hz, 1 H, H-3$_\alpha$), 5.43 (d, J = 3.2 Hz, 1 H, H-1$_\alpha$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 20.8 [q, C(O)CH_3], 20.8 [q, C(O)CH_3], 20.9 [q, C(O)CH_3], 20.9 [q, C(O)CH_3], 21.0 [q, C(O)CH_3], 61.8 (t, OCH$_2$CH_2OH), 62.2 (t, OCH$_2$CH_2OH), 62.3 (t, C-6$_\alpha$), 62.3 (t, C-6$_\beta$), 67.5 (d, C-5$_\alpha$), 68.5 (d, C-4$_\alpha$), 68.7 (d, C-4$_\beta$), 71.9 (d, C-5$_\beta$), 72.0 (d, C-3$_\alpha$), 72.8 (t, OCH$_2$CH$_2$OH), 74.4 (t, OCH$_2$CH$_2$OH), 74.6 (d, C-3$_\beta$), 78.6 (d, C-2$_\alpha$), 81.5 (d, C-2$_\beta$), 90.8 (d, C-1$_\alpha$), 96.8 (d, C-1$_\beta$), 169.9 (s, C=O), 169.9 (s, C=O), 170.6 (s, C=O), 170.8 (s, C=O), 170.9 (s, C=O), 171.0 (s, C=O) ppm. HRMS (ESI-TOF): calcd. for C$_{14}$H$_{22}$Cl$_3$O$_{10}$Na$^+$ 373.1105; found 373.1102.

3,4,6-Tri-*O*-acetyl-2-*O*-(2-iodoethyl)-α/β-D-glucopyranose (24): Diol **23** (490 mg, 1.4 mmol) was dissolved in THF (30 mL) under N$_2$. To this was added imidazole (143 mg, 1.5 equiv.), triphenylphosphine (551 mg, 1.5 equiv.), and iodine (533 mg, 1.5 equiv.). Once the iodine had been added the reaction was purged with N$_2$ for 10 min before heating to reflux overnight. The next day the reaction was cooled to room temperature before filtering. The solution was then concentrated under vacuum before purifying by flash column chromatography (eluent; petroleum ether/EtOAc, 3:2. R_f 0.21) to afford iodide **24** (503 mg, 78% yield) as a colourless oil. $\tilde{\nu}_{max}$ = (neat) 3460 (br. s, O-H), 1748 (s, C=O) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) [mixture of α:β anomers observed]: δ = 2.02 [s, 3 H, C(O)-CH_3], 2.03 [s, 3 H, C(O)CH_3], 2.08 [s, 3 H, C(O)CH_3], 2.08 [s, 3 H, C(O)CH_3], 2.09 [s, 6 H, 2 × C(O)CH_3], 3.19–3.23 (m, 4 H, 2 × OCH$_2$CH_2I), 3.31 (dd, J = 9.6 7.6 Hz, 1 H, H-2$_\beta$), 3.57 (dd, J = 9.6 3.6 Hz, 1 H, H-2$_\alpha$), 3.70–3.74 (m, 1 H, H-5$_\beta$), 3.80–3.92 (m, 3 H, OCH_2CH$_2$I), 4.07–4.15 (m, 3 H, H-6$_\alpha$, H-6$_\beta$ and OCH_2CH$_2$I), 4.20–4.30 (m, 3 H, H-5$_\alpha$, H-6′$_\alpha$ 7 H-6′$_\beta$), 4.78 (d, J = 7.6 Hz, 1 H, H-1$_\beta$), 4.97–5.03 (m, 2 H, H-4$_\alpha$ and H-4$_\beta$), 5.16 (app. t, J = 9.6 Hz, 1 H, H-3$_\beta$), 5.39–5.44 (m, 2 H, H-1$_\alpha$ and H-3$_\alpha$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 2.7 (t, OCH$_2$CH_2I), 3.1 (t, OCH$_2$CH_2I), 20.7 [q, C(O)CH_3], 20.8 [q, C(O)CH_3], 20.9 [q, C(O)CH_3], 21.2 [q, C(O)CH_3], 21.2 [q, C(O)CH_3], 62.2 (t, C-6$_\alpha$), 62.3 (t, C-6$_\beta$), 67.5 (d, C-5$_\alpha$), 68.5 (d, C-4$_\alpha$), 68.7 (d, C-4$_\beta$), 71.7 (d, C-3$_\alpha$), 71.8 (d, C-5$_\beta$), 72.0 (t, OCH$_2$CH$_2$I), 73.2 (t, OCH$_2$CH$_2$I), 73.7 (d, C-3$_\beta$), 78.4 (d, C-2$_\alpha$), 80.8 (d, C-2$_\beta$), 91.0 (d, C-1$_\alpha$), 97.1 (d, C-1$_\beta$), 169.9 (s, C=O), 170.0 (s, C=O), 170.3 (s, C=O), 170.3 (s, C=O), 170.9 (s, C=O), 170.9 (s, C=O) ppm. HRMS (ESI-TOF): calcd. for C$_{14}$H$_{21}$IO$_9$Na$^+$ 483.0122; found 483.0133.

***O*-[3,4,6-Tri-*O*-acetyl-2-*O*-(2-iodoethyl)]-α/β-D-glucopyranose Trichloroacetimidate (25):** Hemiacetal **24** (503 mg, 1.1 mmol) was dissolved in was dissolved in CH$_2$Cl$_2$ (10 mL) under N$_2$. To this was added trichloroacetonitrile (1.1 mL, 10 equiv.) and DBU (0.07 mL, 0.4 equiv.). The reaction was then left to stir overnight. The next day the reaction was concentrated under vacuum and the residue purified by flash column chromatography (eluent; petroleum ether/EtOAc. R_f 0.42 and 0.19) to afford trichloroacetimidate **25** (535 mg, 81% yield) as a yellow oil. ^{1}H NMR [400 MHz, CDCl$_3$, 5.1:1 mixture of α:β anomers observed, major α anomer quoted]: δ = 2.04 [s, 3 H, C(O)CH$_3$], 2.07 [s, 3 H, C(O)CH$_3$], 2.09 [s, 3 H, C(O)CH$_3$], 3.15 (app. t, 2 H, CHCH_2I), 3.73–3.79 (m, 2 H, H-2 and CH_2CH$_2$I), 3.90–3.95 (m, 1 H, CH_2CH$_2$I), 4.09–4.15 (m, 1 H, H-6), 4.20 (ddd, J = 10.2 4.0 1.6 Hz, 1 H, H-5), 4.28 (dd, J = 12.6 4.2 Hz, 1 H, H-6′), 5.11 (app. t, J = 10.0 9.6 Hz, 1 H, H-4), 5.46

(app. t, J = 9.6 Hz, 1 H, H-3), 6.58 (d, J = 3.2 Hz, 1 H, H-1), 8.68 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 2.1 (t, CH_2CH_2I), 20.8 [q, C(O)CH_3], 20.8 [q, C(O)CH_3], 21.2 [q, C(O)CH_3], 61.7 (t, C-6), 68.0 (d, C-4), 70.1 (d, C-5), 71.5 (d, C-3), 72.1 (t, CH_2CH_2I), 77.3 (d, C-2), 97.6 [s, OC(NH)CCl_3], 93.5 (d, C-1), 161.2 (C=NH), 169.8 (s, C=O), 170.1 (s, C=O), 170.6 (s, C=O) ppm. HRMS (ESI-TOF): calcd. for $C_{16}H_{21}Cl_3INO_9Na^+$ [M + Na^+] 625.9219; found 625.9217.

3,4,6-Tri-*O*-acetyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranose (26): Iodide **24** (690 mg, 1.5 mmol) was dissolved in DMF (10 mL) under N_2. Hunig's base (0.32 mL, 1.2 equiv.) and benzeneselenol (0.19 mL, 1.2 equiv.) were added, and the mixture was stirred at room temp. After 16 h, the reaction was concentrated under vacuum and purified by flash column chromatography (eluent; petroleum ether/EtOAc, 3:2. R_f 0.2) to afford selenide **26** (664 mg, 90% yield) as a yellow oil. $\tilde{\nu}_{max}$ = (neat) 1748 (s, C=O) cm^{-1}. ^{1}H NMR [400 MHz, $CDCl_3$, mixture of α:β anomers observed]: δ = 2.02 and 2.03 [12 H, C(O)CH_3 × 4], 2.08 [6 H, C(O)CH_3 × 2], 2.95–3.06 (m, 4 H, OCH_2CH_2SePh), 3.15 (br. s, 1 H, OH), 3.26 (1 H, at, J = 8.8 8.4 Hz, H-2$_\beta$), 3.49–3.52 (m, 2 H, H-2$_\alpha$ and OH), 3.69–3.72 (m, 1 H, H-5$_\beta$), 3.79–3.86 (m, 3 H, OCH_2SePh), 4.00–4.14 (m, 3 H, OCH_2SePh, H-6$_\alpha$ and H-6$_\beta$), 4.20–4.30 (m, 3 H, H-5$_\alpha$, H-6′$_\alpha$ and H-6′$_\beta$), 4.74 (dd, 1 H, J = 7.6 4.8 Hz, H-1$_\beta$), 4.99 (2 H, at, J = 10.0 9.6 Hz, H-4$_\alpha$ and H-4$_\beta$), 5.13 (1 H, at, J = 9.6 Hz, H-3$_\beta$), 5.32 (br. s, 1 H, H-1$_\alpha$), 5.37 (1 H, at, J = 9.6 Hz, H-3$_\alpha$), 7.25–7.27 (m, 6 H, ArH), 7.49–7.50 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7 [q, C(O)CCH_3], 20.7 [q, C(O)CCH_3], 20.8 [q, C(O)CCH_3], 21.0 [q, C(O)CCH_3], 27.2 (t, OCH_2CH_2SePh), 27.4 (t, OCH_2CH_2SePh), 62.1, 62.3 (2 × t, C-6), 67.5 (d, C-5$_\alpha$), 68.5 (d, C-4$_\alpha$ and C-4$_\beta$), 68.7 (t, OCH_2CH_2SePh), 70.9 (d, C-3$_\alpha$), 71.8 (d, C-5$_\beta$), 71.8 (t, OCH_2CH_2SePh), 74.0 (d, C-3$_\beta$), 78.3 (d, C-2$_\alpha$), 80.9 (d, C-2$_\beta$), 90.9 (d, C-1$_\alpha$), 97.1 (d, C-1$_\beta$), 127.2, 127.4, 129.2, 129.3, 129.3, 129.7, 132.7, 132.9 (8 × ArC), 169.9 (s, C=O), 170.0 (s, C=O), 170.3 (s, C=O), 170.3 (s, C=O), 170.9 (s, C=O), 170.9 (s, C=O) ppm. HRMS (ESI-TOF): calcd. for $C_{20}H_{26}O_9SeNa^+$ 513.0635; found 513.0640.

***O*-{3,4,6-Tri-*O*-acetyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranosyl} Trichloroacetimidate (27):** Hemiacetal **26** (245 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (10 mL) under N_2. Trichloroacetonitrile (0.5 mL, 10 equiv.) and DBU (0.03 mL, 0.4 equiv.) were added, and the reaction was stirred at room temp. After 16 h, TLC (petroleum ether/EtOAc, 1:1) showed complete consumption of the starting material (R_f 0.3) and the formation of two new spots for the product (R_f 0.6 and 0.7). The reaction was then concentrated under vacuum and purified by flash column chromatography (eluent; petroleum ether/EtOAc, 3:1. R_f 0.30 and 0.18) to afford trichloroacetimidate **27** (291 mg, 92% yield) as a yellow oil. $\tilde{\nu}_{max}$ = (neat) 1748 (s, C=O) 1674 (s, C=N) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) [mixture of α:β anomers observed, major α anomer quoted]: δ = 2.03 and 2.04 [6 H, 2 × s, 2 × C(O)CH_3], 2.06 [s, 3 H, C(O)CH_3], 2.92–2.98 (m, 2 H, OCH_2CH_2SePh), 3.68–3.75 (m, 2 H, H-2 and OCH_2CH_2SePh), 3.85–3.91 (m, 1 H, OCH_2CH_2SePh), 4.09 (dd, 1 H, J = 12.4 1.6 Hz, H-6), 4.16–4.20 (m, 1 H, H-5), 4.27 (dd, 1 H, J = 12.4 4.4 Hz, H-6′), 5.09 (1 H, at, J = 10.0 9.6 Hz, H-4), 5.43 (1 H, at, J = 10.0 9.6 Hz, H-3), 6.54 (d, 1 H, J = 3.2 Hz, H-1), 7.24–7.26 (m, 3 H, ArH), 7.46–7.49 (m, 2 H, ArH), 8.63 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8 [q, C(O)CH_3], 20.8 [q, C(O)CH_3], 21.0 [q, C(O)CH_3], 26.9 (t, OCH_2CH_2SePh), 61.7 (t, C-6), 68.1 (d, C-4), 70.1 (d, C-5), 71.1 (t, OCH_2CH_2SePh), 71.6 (d, C-3), 77.2 (d, C-2), 93.5 (d, C-1), 97.6 [OC(NH)CCl_3], 127.3, 129.3, 129.7, 132.9 (4 × ArC), 161.2 (s, C=NH), 170.0 (s, C=O), 170.1 (s, C=O), 170.7 (s, C=O) ppm. HRMS (ESI-TOF): calcd. for $C_{22}H_{26}Cl_3NO_9SeNa^+$ 655.9702; found 655.9707.

***p*-Methoxyphenyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (29):** Sodium methoxide (0.250 g, 4.63 mmol) was dissolved in anhydrous methanol (150 mL) and the solution was stirred at room temp. PMP glycoside **28**[16] (21.0 g, 46.3 mmol) was added portionwise and the mixture was stirred at room temp. under a nitrogen atmosphere. After 90 min, TLC (petroleum ether/ethyl acetate, 1:1), indicated formation of a single product (R_f 0) and complete consumption of starting material (R_f 0.5). The mixture was concentrated in vacuo. DMF (75 mL), benzaldehydedimethylacetal (8.30 mL, 55.0 mmol) and camphor sulfonic acid (CSA; 2.20 g, 9.30 mmol) were added and the mixture was rotated in a round bottomed flask on a rotator evaporator at 60 °C under pressure of 240 mbar for 8 h. After this time TLC (petroleum ether/ethyl acetate, 3:2) showed formation of a major product (R_f 0.1) and complete consumption of starting material (R_f 0.5). The reaction was quenched by the addition of triethylamine (0.97 mL, 6.94 mmol) and then concentrated in vacuo. The residue was dissolved in ethyl acetate (1 L), then washed with water (2 × 300 mL), brine (100 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. Recrystallization (propanol/methanol) yielded diol **29** (10.0 g, 56%), m.p. 192–195 °C. $[\alpha]_D^{20}$ = – 51.3 (c = 1.0 in MeOH). IR (KBr): $\tilde{\nu}_{max}$ = 3560 (br., OH) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 3.52–3.56 (m, 3 H, H-2, H-3 and H-4), 3.72–3.84 (m, 5 H, H-5, H-6, -OCH_3), 4.28–4.32 (dd, $J_{6,6'}$ = 10.4, $J_{6'5}$ 5.0 Hz, 1 H, H-6′), 5.60 (s, 1 H, -CHPh), 4.91 (d, $J_{1,2}$ = 8 Hz, 1 H, H-1), 6.83–7.04 (m, 9 H, Aromatic-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): 155.8–114.7 (8 C, Ar-C), 102.2 (d, C-1), 101.8 (d, CHPh), 80.2 (d, C-4), 74.2 (d, C-3), 72.5 (d, C-2), 68.0 (d, C-5), 66.0 (t, C-6), 54.2 (q, -OMe) ppm. HRMS (ES^+): calcd. for $C_{20}H_{22}O_7Na$ [M + Na^+] 397.1263; found 397.1263.

***p*-Methoxyphenyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (30):** Diol **29** (6.50 g, 17.4 mmol) was dissolved in methanol (200 mL). Dibutyl tin oxide (5.20 g, 20.8 mmol) was added and the reaction was stirred at reflux temperatures for 24 h. The solvent was then removed and the residue was dissolved in DMF (200 mL), and the mixture was stirred at room temp. Benzyl bromide (2.47 mL, 20.8 mmol) and caesium fluoride (3.42 g, 34.7 mmol) were added and the solution was stirred for 72 h, after which TLC (petroleum ether/ethyl acetate, 2:1) showed the formation of a major product (R_f 0.5), but TLC (CH_2Cl_2/diethyl ether, 19:1) showed a major spot at R_f 0.8 and minor spots at R_f 0.9. The mixture was concentrated in vacuo, and the residue extracted with CH_2Cl_2 (400 mL), and the organic layer was treated with KF solution (400 mL, 1*M* conc.), dried ($MgSO_4$), filtered and concentrated in in vacuo. Recrystallization (methanol) yielded benzyl ether **30** (3.50 g, 43%) as white crystalline solid, m.p. 198–201 °C. $[\alpha]_D^{20}$ = –22.1 (c = 1.0 in $CHCl_3$). IR (KBr): $\tilde{\nu}_{max}$ = 3560 (br., OH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53 (br. s, 1 H, OH), 3.50–3.59 (m, 1 H, H-5), 3.71–3.86 (m, 7 H, H-2, H-3, H-4, H-6, -OCH_3), 4.37 (m, 1 H, H-6′), 4.90 (d, $J_{1,2}$ = 8 Hz, 1 H, H-1), 4.83, 5.00 (ABq, J_{AB} = 12 Hz, 2 H, -OCH_2Ph), 5.60 (s, 1 H, CHPh), 6.82–7.51 (14 H, 14 H, Aromatic-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): 55.6 (q, -OMe), 66.6 (t, C-6), 68.7 (d, C-5), 74.1 (d, C-2), 74.7 (t, CH_2Ph), 80.2 (d, C-4), 81.2 (d, C-3), 101.3 (d, CHPh), 102.5 (d, C-1), 159.2–114.6 (14 C, Ar-C) ppm. HRMS (ES^+): calcd. for $C_{27}H_{28}O_7Na$ [M + Na^+] 487.1733; found 487.1732.

***p*-Methoxyphenyl 2-*O*-Allyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (31):** Alcohol **30** (3.00 g, 6.40 mmol) was dissolved in anhydrous DMF (20 mL) and a suspension of sodium hydride (0.330 g, 13.7 mmol) in anhydrous DMF (20 mL) was added at

0 °C under a nitrogen atmosphere. Allyl bromide (1.17 mL, 13.7 mmol) was then added slowly. The reaction was warmed to room temp. and stirred. After 4 h TLC (petroleum ether/ethyl acetate, 4:1) showed complete consumption of starting material (R_f 0.1) and formation of a single product (R_f 0.3). The reaction was then quenched by the addition of methanol (20 mL) and concentrated in vacuo. The resulting residue was dissolved in CH_2Cl_2 (30 mL), washed with water (2 × 15 mL), brine (15 mL) and dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification by flash chromatography (petroleum ether/ethyl acetate, 6:1) yielded allyl ether **31** (2.33 g, 72%) as white crystalline solid, m.p. 177–180 °C. $[\alpha]_D^{20}$ = –34.6 (*c* = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56 (m, 1 H, H-5), 3.62 (m, 1 H, H-2), 4.98 (m, 2 H, -OC*H*H′Ph, H-1), 4.85 (d, J_{gem} = 11.2 Hz, 1 H, -OCH*H*′$_2$Ph), 4.49 (m, 2 H, -OCH_2CH=CH$_2$), 4.37 (m, 1 H, H-6′), 3.71–3.86 (m, 6 H, H-3, H-4, H-6, -OCH$_3$), 5.21 (d, J_Z = 10 Hz, 1 H, -OCH$_2$CH=C*H*zH$_E$), 5.35 (d, J_E = 16 Hz, 1 H, -OCH$_2$CH=CHz*H*$_E$), 5.59 (s, 1 H, CHPh), 6.00 (m, 1 H, -OCH$_2$C*H*=CH$_2$), 6.84–7.52 (m, 14 H, Aromatic-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): 55.6 (q, -OMe), 68.7 (d, C-5), 66.2 (t, C-6), 74.282 (d, C-2), 75.1 (t, CH$_2$Ph), 80.8 (d, C-4), 81.1 (d, C-3), 81.6 (t, -O*C*H$_2$CH=CH$_2$), 101.2 (d, CHPh), 103.3 (d, C-1), 114.6–155.6 (14C, Ar-C, -OCH$_2$*C*H=CH$_2$, -OCH$_2$CH=*C*H$_2$) ppm. HRMS (ES$^+$): calcd. for $C_{30}H_{32}O_7Na$ [M + Na$^+$] 527.2046; found 527.2051.

***p*-Methoxyphenyl 2-*O*-Allyl-3-*O*-benzyl-4,6-di-*O*-acetyl-β-D-glucopyranoside (32):** Acetic acid (aq. 80%, 6 mL) was added to a solution of benzylidene acetal **31** (100 mg, 0.200 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was then stirred at 60 °C. After 48 h, TLC (petroleum ether/ethyl acetate, 3:1) indicated formation of a major product (R_f 0.1) and complete consumption of starting material (R_f 0.8). The mixture was diluted with CH_2Cl_2 (10 mL) and washed with saturated aq. $NaHCO_3$ (2 × 15 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was dissolved in the mixture of Ac_2O/pyridine (1:1, 5 mL) and 4-dimethylaminopyridine (DMAP; 0.005 g, 0.040 mmol) was added, and the mixture was stirred at room temp. After 16 h, TLC (petroleum ether/ethyl acetate, 3:1) indicated the formation of a major product (R_f 0.3) and complete consumption of the starting material (R_f 0.1). The mixture was then co-evaporated with toluene (4 × 25 mL). The resulting residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 4:1) to afford diacetate **32** (0.091 g, 91%) as a white crystalline solid, m.p. 63–65 °C (petroleum ether/ethyl acetate). $[\alpha]_D^{20}$ = –62.8 (*c* = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93, 2.06 (2 × s, 6 H, 2 × COC*H*$_3$) 3.82 (m, 3 H, H-2, H-4, H-5), 3.78 (s, 3 H, -OCH$_3$), 4.07–4.11 (dd, $J_{6,6'}$ = 9.2, $J_{6,5}$ = 3.8 Hz, 1 H, H-6), 4.21–4.25 (dd, $J_{6',6}$ = 9.2, $J_{6',5}$ = 3.8 Hz, 1 H, H-6′), 4.29–4.33 (dd, J_{gem} = 9.2, J_{vic} 3.8 Hz, 1 H, -OC*H*H′CH=CH$_2$), 4.47–4.51 (dd, J_{gem} = 9.2, J_{vic} 3.8 Hz, 1 H, -OCH*H*′CH=CH$_2$), 4.67, 4.87 (ABq, J_{AB} = 11.2 Hz, 2 H, CH$_2$Ph), 4.81 (d, $J_{1,2}$ = 11.2 Hz, 1 H, H-1), 5.05 (at, *J* = 8 Hz, 1 H, H-3), 5.19 (d, J_z = 10 Hz, 1 H, -OCH$_2$CH=H$_E$*H*$_Z$), 5.86 (d, J_E = 16 Hz, 1 H, -OCH$_2$CH=*H*$_E$H$_Z$) 6.01 (m, 1 H, -OCH$_2$C*H*=CH$_2$), 6.79–7.52 (m, 9 H, Aromatic-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 20.7, 20.7 (2 × q, 2 × CO*C*H$_3$) 55.6 (q, -OMe), 62.5 (t, C-6), 69.6 (d, C-3), 73.8 (t, -O*C*H$_2$CH=CH$_2$) 75.2 (t, CH$_2$Ph) 72.0, 81.3, 81.4 (3 × d, C-2, C-4, C-5), 102.8 (d, H-1), 114.5 (t, -OCH$_2$CH=*C*H$_2$), 117.3–128.4 (5 × d, ArC-H), 134.7 (-OCH$_2$*C*H=CH$_2$), 138.2, 151.3, 155.5 (3 × s, Ar-C), 169.5, 170.7 (2 × s, 2 × *C*OCH$_3$) ppm. HRMS (ES$^+$): calcd. for $C_{27}H_{32}O_9Na$ [M + Na$^+$] 523.1944; found 523.1945.

3-*O*-Benzyl-4,6-di-*O*-acetyl-2-*O*-(2-iodoethyl)-α/β-D-glucopyranose (33): PMP glycoside **32** (5.00 g, 10.00 mmol) was dissolved in CH_2Cl_2 (150 mL) under N_2, and cooled to –78 °C. Ozone was then bubbled through the solution until it turned deep blue. The excess ozone was then removed by bubbling N_2 through the solution until the colour had dissipated. Dimethyl sulfide (3.7 mL, 50 mmol) was then added, and the solution was warmed to room temperature over an hour. The reaction was then concentrated under vacuum to remove the excess dimethyl sulfide before re-dissolving in a mixture of CH_2Cl_2 (150 mL) and acetic acid (4.0 mL, 66.0 mmol). The solution was then cooled to 0 °C and sodium cyanoborohydride (1.51 g, 24 mmol) was added portion wise, and the reaction was left to stir. After 16 h, TLC (petroleum ether/ethyl acetate, 1:4) showed the formation of a major product (R_f 0.2) and the complete disappearance of starting material (R_f 0.95). The reaction was then quenched by the addition of H_2O (25 mL). Brine (100 mL) was then added, the organic layer separated, and the aqueous layer was re-extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extracts were then dried ($MgSO_4$), filtered, concentrated in vacuo and purified by flash column chromatography (petroleum ether/ethyl acetate, 1:4) to afford 3-*O*-benzyl-4,6-diacetyl-2-*O*-(2-hydroxyethyl)-α/β-D-glucopyranose (2.00 g) as a colourless oil which was used directly in the next step. The residue was then dissolved in THF (100 mL) under a nitrogen atmosphere. I_2 (1.92 g, 7.55 mmol), imidazole (0.514 g, 7.55 mmol) and PPh_3 (1.98 g, 7.55 mmol) were added, and the reaction mixture was heated to reflux. After 16 h, TLC (petroleum ether/ethyl acetate, 2:1) indicated formation of a major product (R_f 0.3) and complete consumption of starting material (R_f 0.0). The reaction was cooled to room temp. and concentrated in vacuo. The resulting residue was purified by flash chromatography (petroleum ether/ethyl acetate, 5:2) to afford iodide **33** (1.00 g, 20%) as colourless oil. IR (KBr): $\tilde{\nu}_{max}$ = 1744 (s, C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) [1:1 mixture of α/β anomers observed]: δ = 1.92, 1.93, 2.06, 2.07 (12 H, 4 × s, 2 × COC*H*$_3$ α, 2 × COC*H*$_3$ β), 3.03 (br. s, 2 H, -OH α, -OH β), 3.22–3.30 (m, 6 H, -OH β, -OCH$_2$C*H*$_2$I α, OCH$_2$C*H*$_2$I β, H-2 α/β), 3.52–3.62 (m, 3 H, H-2 α/β, H-3 α, H-3 β), 3.87–4.22 (m, 10 H, H-6 α, H-6 β, H-6′ α, H-6′ β, -OC*H*$_2$CH$_2$I α, -OC*H*$_2$CH$_2$I β, H-4 α, H-4 β), 3.82–4.17 (m, 5 H, -OCH*H*′CH$_2$I β, -OC*H*H′CH$_2$I α, -OC*H*H′CH$_2$I β, H-6′ α, H-6′ β), 4.63–4.88 (m, 5 H, C*H*$_2$Ph α, C*H*$_2$Ph β, H-1 β), 4.98–5.03 (m, 2 H, H-5 α, H-5 β), 5.37 (d, $J_{1,2}$ = 2.8 Hz, 1 H, H-1 α), 7.25–7.35 (m, 10 H, 5 × Ar-CH α, 5 × Ar-CH β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 2.9, 3.3 (2 × t, -OCH$_2$-*C*H$_2$I α, -OCH$_2$*C*H$_2$I β), 20.7, 20.7, 20.7, 20.7 (4 × q, 2 × CO*C*H$_3$ α, 2 × CO*C*H$_3$ β), 62.2, 62.4 (2 × t, C-6 α, C-6 β), 68.0, 68.0 (2 × d, C-2 α, C-2 β), 69.5, 69.6 (2 × t, -O*C*H$_2$CH$_2$I α, -O*C*H$_2$CH$_2$I β), 75.4, 75.7 (2 × t, -*C*H$_2$Ph α, -*C*H$_2$Ph β), 72.1, 73.1, 78.6, 80.7, 81.3, 83.4 (6 × d, C-3 α, C-3 β, C-4 α, C-4 β, C-5 α, C-5 β), 91.2 (d, C-1 β), 97.4 (d, C-1 α), 127.7–128.4 (6 × d, 3 × Ar-CH α, 3 × Ar-CH β), 138.1, 138.1 (Ar-C α, Ar-C β), 169.6–171.4 (4C, 2 × CH$_3$*C*O α, 2 × CH$_3$*C*O β) ppm. HRMS (ES$^+$): calcd. for $C_{19}H_{25}O_8NaI$ [M + Na$^+$] 531.0492; found 531.0494.

3-[*O*-Benzyl-4,6-di-*O*-acetyl-2-*O*-(2-iodoethyl)-α/β-D-glucopyranosyl] Trichloroacetimidate (34): Hemiacetal **33** (0.144 g, 0.283 mmol) was dissolved in distilled CH_2Cl_2 (3 mL) under a nitrogen atmosphere and cooled to 0 °C. DBU (0.017 mL, 0.112 mmol), and trichloroacetonitrile (0.284 mL, 2.83 mmol), were added, and the reaction mixture was allowed to stir. After 8 h, TLC [petroleum ether/ethyl acetate, 2:1, with 1% triethanolamine (TEA)] indicated the formation of a major product (R_f 0.5), and the complete consumption of starting material (R_f 0.1). The reaction was cooled to room temp. and concentrated in vacuo. The resulting residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1, with 1% TEA) to afford trichloroacetimidate **34** (0.164 g, 89%) as colourless oil. IR (KBr): $\tilde{\nu}_{max}$ = 1740 (s, C=O), 1672 (s, C=N) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) [2:1 mixture of α/β anomers observed]: δ = 1.93, 1.95, 2.05 (12 H, 2 × s, 2 × COC*H*$_3$ α, 2 × COC*H*$_3$

β), 3.18 (m, 4 H, -OCH$_2$CH$_2$I α, OCH$_2$CH$_2$I β), 3.62–4.25 (m, 14 H, -OCH$_2$CH$_2$I α, OCH$_2$CH$_2$I β, H-5 α, H-5 β, H-3 α, H-3 β, H-6 α, H-6 β, H-6′ α, H-6′ β, H-4 α, H-4 β) 4.67, 4.90 (ABq, J_{AB} = 11.6 Hz, 4 H, CH$_2$Ph α, CH$_2$Ph β), 5.08 (m, 2 H, H-2 α, H-2 β), 5.73 (d, $J_{1,2}$ = 8 Hz, 1 H, H-1 β), 6.53 (d, $J_{1,2}$ = 3.2 Hz, 1 H, H-1 α), 7.25–7.35 (m, 10 H, 5×Ar-CH α, 5×Ar-CH β), 8.62, 8.71 (N-H α, N-H β) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): 2.1, 2.2 (2×t, -OCH$_2$CH$_2$I α, -OCH$_2$CH$_2$I β), 20.6, 20.6, 20.7, 20.7 (4×q, 2×COCH$_3$ α, 2×COCH$_3$ β), 61.8, 61.9 (2×t, C-6 α, C-6 β), 68.8, 69.3 (2×d, C-2 α, C-2 β), 70.5, 71.8 (2×t, -CH$_2$Ph α, -CH$_2$Ph β), 72.8, 73.3 (2×t, -OCH$_2$CH$_2$I α, -OCH$_2$CH$_2$I β), 70.5, 71.8, 75.3, 77.3, 77.9, 79.9 (6×d, C-3 α, C-3 β, C-4 α, C-4 β, C-5 α, C-5 β), 81.0, 81.3 (2×s, CCl$_3$ α, CCl$_3$ β) 93.7 (d, C-1 β), 97.6 (d, C-1 α), 127.7, 127.8, 127.9, 128.0, 128.3, 128.4 (6 C, 3×Ar-CH α, 3×Ar-CH β), 138.1, 138.1 (Ar-C α, Ar-C β), 160.8, 160.9 (2×s, C=NH α, C=NH β), 169.5, 169.5, 170.6, 170.6 (4×s, 4C, 2×CH$_3$CO α, 2×CH$_3$CO β) ppm. HRMS (ES$^+$): calcd. for C$_{21}$H$_{25}$NO$_8$Cl$_3$INa [M + Na$^+$] 673.9588; found 673.9589.

3-*O*-Benzyl-4,6-di-*O*-acetyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranose (35): Selenophenol (0.140 mL, 1.30 mmol) was added to a stirred suspension of sodium hydride (60% dispersion in mineral oil, 0.016 g, 0.650 mmol) in THF (5 mL). After 30 min, iodide **33** (0.240 g, 0.470 mmol) was added as a solution in THF (5 mL), and the reaction was then heated to reflux. After 16 h, TLC (toluene/ethyl acetate, 2:1) indicated the formation of a single major product (R_f 0.55) and the complete consumption of starting material (R_f 0.50). The reaction was cooled and diluted with CH$_2$Cl$_2$ (20 mL) and washed with water (20 mL). The aqueous layer was then extracted with CH$_2$Cl$_2$ (2×20 mL) and the combined organic extracts were washed with saturated aq. sodium hydrogen carbonate solution (20 mL) and brine (20 mL). The organic phase was dried (MgSO$_4$), filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 4:1) to afford selenide **35** (0.190 g, 75%) as colourless oil. IR (KBr): $\tilde{\nu}$ = 1740 (s, C=O), 1672 (s, C=N) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) [1:1 mixture of α/β anomers observed]: δ = 1.90–2.09 (m, 12 H, 2×COCH$_3$ α, 2×COCH$_3$ β), 3.03–3.08 (m, 4 H, OCH$_2$CH$_2$SePh α, OCH$_2$CH$_2$SePh β), 3.14 (br. s, 1 H, -OH α/-OH β) 3.26 (at, J = 5.0 Hz, 1 H, H-2 β), 3.46–3.58 (m, 3 H, H-2 α, H-3 α, H-3 β), 3.48–3.58 (m, 4 H, H-4 α, H-4 β, H-5 α, H-5 β), 3.80–4.23 (m, 12 H, OCH$_2$CH$_2$SePh α, OCH$_2$CH$_2$SePh β, H-6′ α, H-6′ β, H-6 α, H-6 β), 4.60–4.85 (m, 4 H, PhCH$_2$ α, PhCH$_2$ β), 4.97 (at, J = 9.2 Hz, 1 H, H-1 β), 5.29 (d, $J_{1,2}$ = 3.3 Hz, 1 H, H-1 α), 7.26–7.49 (m, 20 H, 10×Ar-CH α, 10×Ar-CH β) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): 20.7, 20.7, 20.7, 20.7 (4×q, 2×COCH$_3$ α, 2×COCH$_3$ β), 27.3, 27.6 (2×t, OCH$_2$CH$_2$SePh α, OCH$_2$CH$_2$SePh β), 62.2, 62.4 (2×t, C-6 α, C-6 β), 68.0, 69.4 (2×t, C-5 α, C-5 β), 69.6, 70.7 (2×t, OCH$_2$CH$_2$SePh α, OCH$_2$CH$_2$SePh β), 72.0, 72.1 (2×t, CH$_2$Ph α, CH$_2$Ph β), 75.2, 75.3, 78.6, 80.7, 81.4, 83.5 (6×d, C-2 α, C-2 β, C-3 α, C-3 β, C-4 α, C-4 β), 91.1 (d, C-1 β), 97.2 (d, C-1 α), 127.1, 127.2, 127.3, 127.5, 127.6, 127.7, 127.8, 127.9, 128.4, 129.1, 129.2, 129.3, 132.6, 132.8, 138.2, 138.3 (16×Ar-C), 169.5, 169.6, 170.8, 170.8 (4C, 2×CH$_3$CO α, 2×CH$_3$CO β) ppm. HRMS (ES$^+$): calcd. for C$_{25}$H$_{30}$O$_8$NaSe [M + Na$^+$] 561.1000; found 561.0998.

3-{*O*-Benzyl-4,6-diacetyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranosyl} Trichloroacetimidate (36): Hemiacetal **35** (0.190 g, 0.353 mmol) was dissolved in distilled CH$_2$Cl$_2$ (10 mL) and stirred under a nitrogen atmosphere. The solution was cooled to 0 °C, and DBU (0.018 mL, 0.118 mmol) and trichloroacetonitrile (0.354 mL, 3.53 mmol) were added sequentially. After 8 h, TLC (petroleum ether/ethyl acetate, 2:1, with 1% TEA) indicated the formation of a major product (R_f 0.7) and the complete consumption of starting material (R_f 0.2). The reaction was warmed to room temp. and concentrated in vacuo. The resulting residue was purified by flash chromatography (petroleum ether/ethyl acetate, 4:1, with 1% TEA) to afford trichloroacetimidate **36** (0.177 g, 74%) as colourless oil. IR (KBr): $\tilde{\nu}_{max}$ = 3319 (w, N–H), 1745 (s, C=O), 1673 (s, C=N) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) [50:1 mixture of α/β anomers observed, major α anomer quoted]: δ = 1.95, 2.04 (6 H, 2×s, 2×COCH$_3$) 3.01 (m, 2 H, -OCH$_2$CH$_2$SePh), 3.67 (dd, $J_{2,3}$ = 9.6, $J_{1,2}$ = 3.2 Hz, 1 H, H-2), 3.79–3.97 (m, 3 H, OCH$_2$CH$_2$SePh, H-3), 4.04–4.21 (m, 3 H, H-6, H-6′, H-4), 4.64, 4.87 (ABq, J_{AB} = 11.2 Hz, 2 H, -OCH$_2$Ph), 5.09 (at, J = 10 Hz, 1 H, H-5), 6.51 (d, $J_{1,2}$ = 3.6 Hz, 1 H, H-1), 7.23–7.48 (m, 10 H, Ar-CH), 8.60 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): 20.6, 20.7 (2×q, 2×COCH$_3$), 26.9 (t, -OCH$_2$CH$_2$SePh), 61.8 (t, C-6), 68.7 (d, C-5), 70.4, 70.6 (2×t, CH$_2$Ph, -OCH$_2$CH$_2$SePh), 75.2 (d, C-3), 77.9 (d, C-4), 93.07 (d, C-1), 127.1, 127.7, 127.9, 128.3, 129.1, 129.7, 132.7, 138.2 (8 C, 12×Ar-C), 161.0 (s, C=NH), 169.5, 170.6 (2×s, 2×COCH$_3$) ppm. HRMS (ES$^+$): calcd. for C$_{27}$H$_{30}$O$_8$NCl$_3$SeNa [M + Na$^+$] 704.0100; found 704.0098.

3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(2-hydroxyethyl)-α/β-D-glucopyranose (37): A solution of PMP glycoside **31** (0.200 g, 0.400 mmol) in CH$_2$Cl$_2$/MeOH (9 mL, 2:1) was treated with ozone at –78 °C until the solution turned blue. The reaction was quenched by the addition of NaBH$_4$ (27 mg, 0.72 mmol) in small portions over 10 min. At this point TLC (CH$_2$Cl$_2$/MeOH, 195:5) showed the formation of a major product (R_f 0.4) and complete disappearance of starting material (R_f 0.95). The reaction mixture was warmed to room temp. and then concentrated in vacuo. The residue was dissolved in ethyl acetate (20 mL), then washed with saturated sodium hydrogen carbonate solution (2×5 mL), brine (5 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. Purification by flash column chromatography (CH$_2$Cl$_2$/MeOH, 97:3) followed by recrystallization (petroleum ether/ethyl acetate) yielded diol **37** (0.117 g, 73%) as white crystalline solid, m.p. 148–151 °C (petroleum ether/ethyl acetate). IR (KBr): $\tilde{\nu}_{max}$ = 3400 (br., O–H) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) [1:1.4 mixture of α/β anomers observed]: δ = 3.34 (at, J = 8 Hz, 1 H, H-2 β), 4.46 (m, 1 H, -OCHH′CH$_2$OH α), 3.58 (dd, $J_{2,3}$ = 12, $J_{1,2}$ = 3.6 Hz, 1 H, H-2 α), 3.78–3.83 (m, 10 H, -OCH$_2$CH$_2$OH α, -OCH$_2$CH$_2$OH β, -OCHH′CH$_2$OH β, H-3 α, H-3 β, H-5 α, H-6 α, H-6 β), 3.84–3.93 (m, 2 H, -OCHH′CH$_2$OH α, -OCHH′CH$_2$OH β), 4.00 (at, J = 8 Hz, 1 H, H-4 α), 4.09 (m, 1 H, H-5 β), 4.29–4.36 (m, 2 H, H-6′ α, H-6′ β), 4.73 (d, $J_{1,2}$ = 8 Hz, 1 H, H-1 β), 4.77, 4.97 (ABq, J_{AB} = 12 Hz, 4 H, CH$_2$Ph α, CH$_2$Ph β), 5.34 (d, $J_{1,2}$ = 3.6 Hz, 1 H, H-1 α), 5.57 (s, 1 H, CHPh β), 5.58 (s, 1 H, CHPh α), 7.26–7.48 (m, 20 H, 10×Ar-CH α, 10×Ar-CH β) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): 62.2 (C-5 β), 62.3, 62.5 (-OCH$_2$CH$_2$OH α, -OCH$_2$CH$_2$OH β), 66.2 (-OCH$_2$CH$_2$OH α), 68.7 (C-6 β), 69.0 (C-6 α), 73.0 (C-5 α), 74.5 (-OCH$_2$CH$_2$OH β), 75.0, 75.2 (-CH$_2$Ph α, -CH$_2$Ph β), 77.8 (C-4 α), 80.5, 80.8 (C-3 α, C-3 β), 81.8 (C-4 β), 82.2, 83.4 (C-2 α, C-2 β), 91.7 (C-1 α), 97.4 (C-1 β), 101.2, 101.3 (-CHPh α, -CHPh β), 126.0–134.5 (16 C, 8×Ar-CH α, 8×Ar-CH β) ppm. HRMS (ES$^+$): calcd. for C$_{22}$H$_{26}$O$_7$Na [M + Na$^+$] 425.1576; found 425.1575.

3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(2-iodoethyl)-α/β-D-glucopyranose (38): Diol **37** (0.214 g, 0.500 mmol) was stirred in THF (10 mL) under a nitrogen atmosphere. I$_2$ (0.191 g, 0.760 mmol), imidazole (0.051 g, 0.760 mmol) and PPh$_3$ (0.200 g, 0.760 mmol) were added. The reaction mixture was then heated to reflux. After 24 h, TLC (petroleum ether/ethyl acetate, 2:1) indicated the formation of a major product (R_f 0.3), and complete consumption of starting material (R_f 0.1). The reaction was then cooled to room temp. and concentrated in vacuo. The resulting residue was purified

by flash chromatography (petroleum ether/ethyl acetate, 5:1) to afford iodide **38** (0.112 g, 39%) as white crystalline solid, m.p. 179–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) [1:1.6 mixture of α/β anomers observed]: δ = 3.08 (br. s, 1 H, -OH α), 3.27 (m, 7 H, -OH β, H-2 α, H-2 β, H-3 α, H-3 β, H-4 α, H-4 β), 3.50 (m, 1 H, H-5 α), 3.69 (m, 6 H, H-5 β, -OCH$_2$C*H*$_2$I α, -OCH$_2$C*H*$_2$I β, -OCH*H*′CH$_2$I α), 3.82–4.17 (m, 5 H, -OCH*H*′CH$_2$I β, -OC*H*H′CH$_2$I α, -OC*H*H′CH$_2$I β, H-6′ α, H-6′ β), 3.35 (m, 2 H, -OCH*H*′CH$_2$-OH α, -OCH*H*′CH$_2$OH β), 4.48 (d, $J_{1,2}$ = 8 Hz, 1 H, H-1 β), 4.81, 4.96 (ABq, J_{AB} = 12 Hz, 4 H, CH$_2$Ph α, CH$_2$Ph β), 5.36 (d, $J_{1,2}$ = 3.6 Hz, 1 H, H-1 α), 5.58 (s, 2 H, CHPh α, CHPh β), 7.27–7.50 (m, 20 H, 10 × Ar-CH α, 10 × Ar-CH β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 3.2, 3.6 (-OCH$_2$C*H*$_2$I α, -OCH$_2$C*H*$_2$I β), 62.5, 66.3 (C-6 α, C-6 β), 68.6, 69.0 (-OC*H*$_2$CH$_2$I α, -OC*H*$_2$CH$_2$I β), 72.5, 73.5 (C-5 α, C-5 β), 75.1, 75.2 (-CH$_2$Ph α, -CH$_2$Ph β), 78.1 (C-4 α), 80.5, 80.6 (C-3 α, C-3 β), 81.6 (C-4 β), 82.0, 83.6 (C-2 α, C-2 β), 92.1 (C-1 α), 97.4 (C-1 β), 101.2, 101.3 (-CHPh α, -CHPh β), 126.0–138.5 (16 C, 8 × Ar-CH α, 8 × Ar-CH β) ppm. HRMS (ES$^+$): calcd. for $C_{22}H_{25}O_6NaI$ [M + Na$^+$] 535.0590; found 535.0594.

3-[*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(2-iodoethyl)-α/β-D-glucopyranosyl] Trichloroacetimidate (39): Hemiacetal **38** (0.091 g, 0.178 mmol) was dissolved in distilled CH_2Cl_2 (3 mL) under a nitrogen atmosphere and stirred a 0 °C. DBU (0.011 mL, 0.071 mmol) and trichloroacetonitrile (0.182 mL, 1.78 mmol) were sequentially. After 8 h, TLC (petroleum ether/ethyl acetate, 3:1, with 1% TEA) indicated the formation of a major product (R_f 0.4) and complete consumption of starting material (R_f 0.2). The reaction was warmed to room temp. and concentrated in vacuo. The resulting residue was purified by flash chromatography (petroleum ether/ethyl acetate, 7:1, with 1% TEA) to afford trichloroacetimidate **39** (0.112 g, 96%) as colourless oil. IR (KBr): $\tilde{\nu}_{max}$ = 3451 (w, N–H), 1674 (s, C=N) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) [3.5:1 mixture of α/β anomers observed]: δ = 3.15 (m, 4 H, -OCH$_2$C*H*$_2$I α, -OCH$_2$C*H*$_2$I β), 3.56–3.87 (m, 6 H, H-3 α, H-3 β, -OC*H*$_2$CH$_2$I α, - OC*H*$_2$CH$_2$I β), 3.89–4.09 (m, 8 H, H-2 α, H-2 β, H-4 α, H-4 β, H-5 α, H-5 β, H-6′ α, H-6′ β), 4.32–4.36 (dd, $J_{6,6'}$ = 10.4, $J_{6,5}$ = 4.8 Hz, 1 H, H-6 α), 4.38–4.42 (dd, $J_{6,6'}$ = 10.4, $J_{6,5}$ = 4.8 Hz, 1 H, H-6 β), 4.85, 4.93 (ABq, J_{AB} = 12 Hz, 4 H, CH$_2$Ph α, CH$_2$Ph β), 5.57 (s, 1 H, CHPh β), 5.59 (s, 1 H, CHPh α), 5.84 (d, $J_{1,2}$ = 7.8 Hz, 1 H, H-1 β), 6.51 (d, $J_{1,2}$ = 3.6 Hz, 1 H, H-1 α), 7.26–7.51 (m, 20 H, 10 × Ar-CH α, 10 × Ar-CH β), 8.62 (s, 1 H, NH α), 8.73 (s, 1 H, NH β) ppm. ^{13}C (100 MHz, $CDCl_3$): 2.3, 2.4 (-OCH$_2$C*H*$_2$I α, -OCH$_2$C*H*$_2$I β), 65.1, 66.6 (C-6 α, C-6 β), 68.5, 68.7 (-OC*H*$_2$CH$_2$I α, -OC*H*$_2$CH$_2$I β), 72.4, 74.0 (C-5 α, C-5 β), 75.1, 75.2 (-CH$_2$Ph α, -CH$_2$Ph β), 77.3, 77.7, 79.6, 80.5, 81.1 (C-2 α, C-2 β, C-3 α, C-3 β, C-4 α, C-4 β), 81.2, 81.4 (*C*Cl$_3$ α, *C*Cl$_3$ β), 94.6 (C-1 α), 97.9 (C-1 β), 101.3, 101.3 (-CHPh α, -CHPh β), 125.9–138.4 (16 C, 8 × Ar-CH α, 8 × Ar-CH β), 161.3 (*C*=NH). HRMS (ES$^+$): calcd. for $C_{24}H_{25}NO_6Cl_3INa$ [M + Na$^+$] 677.9684; found 677.9694.

3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranose (40): Selenophenol (0.120 mL, 1.15 mmol) was added to a stirred suspension of sodium hydride (60% dispersion in mineral oil, 0.018 g, 0.750 mmol) in THF (5 mL). After 30 min, iodide **38** (0.300 g, 0.590 mmol) was added as a solution in THF (5 mL), and the reaction mixture was then heated to reflux. After 16 h, TLC (toluene/ethyl acetate, 2:1) indicated the formation of a single product (R_f 0.65), and complete consumption of starting material (R_f 0.60). The reaction mixture was cooled, diluted with CH_2Cl_2 (20 mL), and washed with water (20 mL). The aqueous layer was then extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic extracts were washed with saturated aq. sodium hydrogen carbonate solution (20 mL) and brine (20 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 4:1) to afford selenide **40** (0.210 g, 66%) as a white crystalline solid, m.p. 128–130 °C (petroleum ether/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) [1.4:1 mixture of α/β anomers observed]: δ = 3.05–3.08 (m, 4 H, OCH$_2$CH$_2$SePh α, OCH$_2$C*H*$_2$SePh β), 3.22 (at, J = 5.0 Hz, 1 H, H-2 β), 3.39–3.44 (m, 4 H, H-2 α, H-3 α, H-3 β), 3.49–3.97 (m, 8 H, H-4 α, H-4 β, H-5 α, H-5 β, H-6′ α, H-6′ β), 4.02–5.00 (m, 4 H, OC*H*$_2$CH$_2$SePh α, OC*H*$_2$CH$_2$SePh β), 4.29–4.36 (m, 2 H, H-6 α, H-6 β), 4.74–4.92 (m, 5 H, PhCH$_2$ α, PhCH$_2$ β, H-1 β), 4.26 (d, $J_{1,2}$ = 3.3 Hz, 1 H, H-1 α), 7.26–7.49 (m, 30 H, 15 × Ar-CH α, 15 × Ar-CH β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 27.4, 27.9 (2 × t, OCH$_2$C*H*$_2$SePh α, OCH$_2$C*H*$_2$SePh β), 62.5, 66.4 (2 × d, C-5 α, C-5 β), 68.7, 69.0 (2 × t, C-6 α, C-6 β), 71.2, 72.4 (2 × t, OCH$_2$CH$_2$SePh α, OC*H*$_2$CH$_2$SePh β), 75.0, 75.1 (2 × t, CH$_2$Ph α, CH$_2$Ph β), 78.1, 80.5, 80.7, 81.5, 81.8, 83.8 (6 × d, C-2 α, C-2 β, C-3 α, C-3 β, C-4 α, C-4 β), 91.9 (d, C-1 α), 97.5 (d, C-1 β), 101.2, 101.3 (2 × d, CHPh α, CHPh β), 126.0–132.8 (24 × Ar-C) ppm. HRMS (ES$^+$): calcd. for $C_{28}H_{30}O_6$-SeNa [M + Na$^+$] 565.1105; found 565.1105.

3-{*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranosyl} Trichloroacetimidate (41): Hemiacetal **40** (0.060 g, 0.111 mmol) was dissolved in distilled CH_2Cl_2 (2.5 mL) under a nitrogen atmosphere. The stirred solution was cooled to 0 °C, and to it were added sequentially DBU (0.005 mL, 0.044 mmol) and trichloroacetonitrile (0.143 mL, 1.11 mmol). After 8 h, TLC (petroleum ether/ethyl acetate, 3:1, with 1% TEA) indicated formation of a major product (R_f 0.5) and complete consumption of starting material (R_f 0.2). The reaction was warmed to room temp. and concentrated in vacuo. The resulting residue was purified by flash chromatography (petroleum ether/ethyl acetate, 8:1, with 1% TEA) to afford trichloroacetimidate **41** (0.072 g, 92%) as colourless oil. IR (KBr): $\tilde{\nu}_{max}$ = 3350 (w, N–H), 1673 (s, C=N) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) [1.6:1 mixture of α/β anomers observed]: δ = 2.99–3.04 (m, 5 H, -OCH$_2$C*H*$_2$SePh α, OCH$_2$C*H*$_2$SePh β, H-5 α/β), 3.49–3.79 (m, 7 H, H-2 α, H-2 β, H-3 α, H-3 β, H-4 α, H-4 β, H-5 α/β), 3.84–3.92 (m, 2 H, OC*H*$_2$CH$_2$SePh α/β), 3.94–4.08 (m, 4 H, OC*H*$_2$CH$_2$SePh α/β, H6′ α, H-6′ β), 4.33 (dd, $J_{6,6'}$ = 10.4, $J_{6,5}$ = 5.4 Hz, 1 H, H-6 α), 4.38 (dd, $J_{6,6'}$ = 10.4, $J_{6,5}$ = 5.4 Hz, 1 H, H-6 β), 4.79–4.93 (m, 4 H, CH$_2$Ph α, CH$_2$Ph β), 5.56 (s, 1 H, CHPh β), 5.58 (s, 1 H, CHPh α), 5.80 (d, $J_{1,2}$ = 7.8 Hz, 1 H, H-1 β), 6.48 (d, $J_{1,2}$ = 4.0 Hz, 1 H, H-1 α), 7.26–7.51 (m, 30 H, 15 × Ar-CH α, 15 × Ar-CH β), 8.57 (s, 1 H, NH α), 8.69 (s, 1 H, NH β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 26.7, 26.9 (-OCH$_2$C*H*$_2$SePh α, -OCH$_2$C*H*$_2$SePh β), 65.1, 66.6 (C-6 α, C-6 β), 68.6, 68.7 (-OC*H*$_2$CH$_2$SePh α, -OC*H*$_2$CH$_2$SePh β), 71.2, 72.8 (C-5 α, C-5 β), 75.0, 75.2 (-CH$_2$Ph α, -CH$_2$Ph β), 77.7, 79.7, 80.6, 81.0, 81.1, 81.3 (C-2 α, C-2 β, C-3 α, C-3 β, C-4 α, C-4 β), 94.5, 94.5 (*C*Cl$_3$ α, *C*Cl$_3$ β), 98.0, 98.0 (C-1 α, C-1 β), 101.3, 101.3 (-CHPh α, -CHPh β), 125.9–138.4 (24 C, 12 × Ar-CH α, 12 × Ar-CH β), 161.0, 161.2 (*C*=NH α, *C*=NH β) ppm. HRMS (ES$^+$): calcd. for $C_{30}H_{30}O_6NCl_3SeNa$ [M + Na$^+$] 708.0192; found 708.0198.

3,4,6-Tri-*O*-acetyl-2-*O*-(2-iodoethyl)-α/β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranoside (42): General Method B gave disaccharide **42** as a colourless oil (67 mg, 76% yield). $\tilde{\nu}_{max}$ = (neat) 1751 (s, C=O). ^{1}H NMR (400 MHz, $CDCl_3$) [mixture of α:β anomers observed]: δ = 1.32 [3 × s, 9 H, (C)C*H*$_3$], 1.33 [2 × s, 6 H, (C)C*H*$_3$], 1.43 [s, 3 H, (C)C*H*$_3$], 1.45 [s, 3 H, (C)C*H*$_3$], 1.51 [s, 3 H, (C)C*H*$_3$], 2.01 [s, 3 H, C(O)C*H*$_3$], 2.02 [s, 3 H, C(O)C*H*$_3$], 2.06 [s, 3 H, C(O)C*H*$_3$], 2.08 [s, 3 H, C(O)C*H*$_3$], 2.09 [2 × s, 6 H, C(O)C*H*$_3$], 3.18–3.23 (m, 4 H, OCH$_2$C*H*$_2$I), 3.32 (dd, J = 9.6 8.4 Hz, 1 H, H-2$_b$β), 3.54 (dd, J = 9.6 3.6 Hz, 1 H, H-2$_b$α), 3.62–3.84 (m, 6 H, 2 × OC*H*$_2$CH$_2$I, H-5$_b$α, H-5$_b$β, H-6$_a$α and H-6$_a$β), 3.87–3.93 (m, 1 H, OC*H*$_2$CH$_2$I), 3.98–4.10 (m, 6 H, H-5$_a$α,

H-5$_a$β, H-6′$_a$α, H-6′$_a$β, H-6$_b$α, H-6$_b$β), 4.16–4.21 (m, 3 H, OCH_2-CH$_2$I, H-2$_a$α and H-2$_a$β), 4.26–4.33 (m, 4 H, H-4$_a$α, H-4$_a$β, H-6′$_b$α and H-6′$_b$β), 4.48 (d, J = 7.6 Hz, 1 H, H-1$_b$β), 4.59–4.63 (m, 2 H, H-3$_a$α and H-3$_a$β), 4.97–5.03 (m, 2 H, H-4$_b$α and H-4$_b$β), 5.04 (d, J = 1.2 Hz, 1 H, H-1$_b$α), 5.14 (at, J = 9.6 9.2 Hz, 1 H, H-3$_b$β), 5.39 (at, J = 10.0 9.6 Hz, 1 H, H-3$_b$α), 5.50–5.52 (m, 2 H, H-1$_a$α and H-1$_a$β) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 2.6 (t, OCH$_2$-CH$_2$I), 3.9 (t, OCH$_2$$CH_2$I), 20.8 [q, C(O)$CH_3$], 20.8 [q, C(O)$CH_3$], 20.9 [2 × q, C(O)$CH_3$], 21.2 [q, C(O)$CH_3$], 21.3 [q, C(O)$CH_3$], 24.5 [q, (C)$CH_3$], 24.9 [q, (C)$CH_3$], 25.1 [q, (C)$CH_3$], 25.1 [q, (C)$CH_3$], 26.1 [q, (C)$CH_3$], 26.2 [q, (C)$CH_3$], 26.3 [q, (C)$CH_3$], 26.3 [q, (C)-$CH_3$], 62.1 (t, C-6$_b$α), 62.2 (t, C-6$_b$β), 67.5 (d, C-5$_a$α), 67.5 (d, C-5$_a$β), 67.7 (t, O$CH_2CH_2$I), 68.7 (d, C-4$_b$α), 68.7 (d, C-4$_b$β), 70.5 (d, C-4$_a$α), 70.6 (d, C-4$_a$β), 70.7 (t, C-6$_a$α), 70.8 (t, C-6$_a$β), 70.9 (d, C-3$_a$α), 71.0 (d, C-3$_a$β), 71.4 (d, C-2$_a$α), 71.5 (d, C-2$_a$β), 71.7 (2 × d, C-5$_b$β and C-5$_b$α), 71.7 (d, C-3$_b$α), 73.1 (t, O$CH_2CH_2$I), 73.7 (d, C-3$_b$β), 78.1 (d, C-2$_b$α), 79.6 (d, C-2$_b$β), 96.4 (d, C-1$_a$β), 96.5 (d, C-1$_a$α), 97.2 (d, C-1$_b$α), 104.0 (d, C-1$_b$β), 108.8 [s, ($C$)CH$_3$], 108.9 [s, ($C$)CH$_3$], 109.4 [s, ($C$)CH$_3$], 109.6 [s, ($C$)CH$_3$], 169.9 (s, C=O), 170.0 (s, C=O), 170.2 (s, C=O), 170.3 (s, C=O), 170.8 (s, C=O), 170.9 (s, C=O) ppm. HRMS (ESI-TOF): calcd. for $C_{26}H_{39}IO_{14}H^+$ [M + H$^+$] 703.1457; found 703.1463 and 725.1285 [M + Na$^+$].

3,4,6-Tri-*O*-acetyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranoside (43): General Method B gave disaccharide **43** as a yellow oil (69 mg, 75% yield). $\tilde{\nu}_{max}$ = (neat) 1749 (s, C=O). ^{1}H NMR (400 MHz, CDCl$_3$) [mixture of α:β anomers observed]: δ = 1.29 [s, 3 H, (C)CH_3], 1.30 [s, 3 H, (C)CH_3], 1.32 [s, 3 H, (C)CH_3], 1.33 [s, 3 H, (C)CH_3], 1.42 [s, 3 H, (C)CH_3], 1.44 [s, 3 H, (C)CH_3], 1.48 [s, 3 H, (C)CH_3], 1.56 [s, 3 H, (C)CH_3], 2.00 [s, 3 H, C(O)CH_3], 2.00 [s, 3 H, C(O)CH_3], 2.01 [s, 3 H, C(O)CH_3], 2.03 [s, 3 H, C(O)CH_3], 2.07 [s, 3 H, C(O)CH_3], 2.08 [s, 3 H, C(O)CH_3], 2.94–3.07 (m, 4 H, OCH$_2$CH_2SePh), 3.30 (dd, J = 9.2 7.6 Hz, 1 H, H-2$_b$β), 3.49 (dd, J = 10 3.6 Hz, 1 H, H-2$_b$α), 3.62–3.90 (m, 8 H, 3 × OCH_2CH$_2$SePh, H-5$_a$α, H-5$_a$β, H-5$_b$β, H-6$_a$α and H-6$_a$β), 3.98–4.11 (m, 7 H, H-5$_a$α, H-5$_a$β, H-5$_b$α, H-6′$_a$α, H-6′$_a$β, H-6$_b$α, H-6$_b$β), 4.15–4.21 (m, 3 H, OCH_2CH$_2$SePh, H-4$_a$α and H-4$_a$β), 4.25–4.32 (m, 4 H, H-2$_a$α and H-2$_a$β, H-6′$_b$α, H-6′$_b$β), 4.47 (d, J = 7.6 Hz, 1 H, H-1$_b$β), 4.57–4.61 (m, 2 H, H-3$_a$α and H-3$_a$β), 4.96–5.01 (m, 2 H, H-4$_b$α and H-4$_b$β), 5.02 (d, J = 3.6 Hz, 1 H, H-1$_b$α), 5.10 (at, J = 9.6 9.2 Hz, 1 H, H-3$_b$β), 5.36 (at, J = 9.6 Hz, 1 H, H-3$_b$α), 5.49–5.51 (m, 2 H, H-1$_a$α and H-1$_a$β), 7.23–7.26 (m, 6 H, ArH), 7.46–7.50 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 20.8 [q, C(O)CH$_3$], 20.8 [q, C(O)CH$_3$], 20.9 [q, C(O)CH$_3$], 21.0 [q, C(O)CH$_3$], 24.5 [q, (C)CH$_3$], 24.7 [q, (C)CH$_3$], 25.1 [q, (C)CH$_3$], 25.1 [q, (C)CH$_3$], 26.1 [q, (C)CH$_3$], 26.1 [q, (C)CH$_3$], 26.2 [q, (C)CH$_3$], 26.3 [q, (C)CH$_3$], 27.0 (t, OCH$_2$$CH_2$SePh), 27.3 (t, OCH$_2$$CH_2$SePh), 62.1 (t, C-6$_b$α), 62.2 (t, C-6$_b$β), 66.3 (d, C-5$_b$α), 67.4 (d, C-5$_a$α), 67.6 (d, C-5$_a$β), 68.1 (t, O$CH_2CH_2$SePh), 68.7 (d, C-4$_b$α), 68.7 (d, C-4$_b$β), 70.3 (t, C-6$_a$α), 70.5 (t, C-6$_a$β), 70.7 (d, C-2$_a$α), 70.7 (d, C-2$_a$β), 70.9 (d, C-3$_a$β), 70.9 (d, C-3$_a$α), 71.5 (2 × d, C-4$_a$α and C-4$_a$β), 71.7 (d, C-5$_b$β), 71.9 (d, C-3$_b$α), 72.1 (t, O$CH_2CH_2$SePh), 73.9 (d, C-3$_b$β), 78.1 (d, C-2$_b$α), 79.7 (d, C-2$_b$β), 96.4 (d, C-1$_a$α), 96.4 (d, C-1$_a$β), 97.2 (d, C-1$_b$α), 104.0 (d, C-1$_b$β), 108.8 [s, ($C$)CH$_3$], 108.9 [s, ($C$)CH$_3$], 109.4 [s, ($C$)CH$_3$], 109.6 [s, ($C$)CH$_3$], 126.9, 127.3, 129.2, 129.3, 129.7, 130.4, 132.5, 132.9 (8 × ArC), 169.9 (s, C=O), 170.0 (s, C=O), 170.3 (s, C=O), 170.3 (s, C=O), 170.8 (s, C=O), 170.9 (s, C=O) ppm. HRMS (ESI-TOF): calcd. for $C_{32}H_{44}O_{14}SeH^+$ [M + H$^+$] 733.1972; found 733.1972 and 755.1797 [M + Na$^+$].

3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(2-iodoethyl)-α/β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranoside (44): General Method B gave disaccharide **44** (0.130 g, 81%) as a colourless oil. ^{1}H NMR (400 MHz, [D$_6$]DMSO) [1:2 mixture of α/β anomers observed]: = 1.25–1.44 (m, 24 H, 4 × CH$_3$α, 4 × CH$_3$β), 1.91–1.96 (m, 12 H, 2 × COCH_3 α, 2 × COCH_3 β), 3.20–3.29 (m, 5 H, OCH$_2$-CH_2I α, OCH$_2$CH_2I β, H-5$_b$ α/β), 3.49–3.94 (m, 14 H, H-2$_a$ α, H-2$_a$ β, H-3$_a$ α, H-3$_a$ β, H-4$_a$ α, H-4$_a$ β, H-3$_b$ α, H-3$_b$ β, H-5$_b$ α/β, H-6$_b$ α, H-6$_b$ β, H-6′$_b$ α, H-6′$_b$ β, -OCHH'CH$_2$I α/β), 4.03–4.09 (m, 3 H, -OCHH′CH$_2$I α, -OCHH′CH$_2$I β, -OCHH'CH$_2$I α/β), 4.20–4.33 (m, 4 H, H-5$_a$ α, H-5$_a$ β, H-4$_b$ α, H-4$_b$ β), 4.33–4.47 (m, 4 H, H-6$_a$ α, H-6$_a$ β, H-6′$_a$ α, H-6′$_a$ β), 4.51 (d, 1 H, $J_{1,2}$ 8 Hz, H-1$_a$ β), 4.55–4.82 (m, 6 H, CH_2Ph α, CH_2Ph β, H-2$_b$ α, H-2$_b$ β), 5.01 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1$_a$ α), 5.43 (d, 2 H, $J_{1,2}$ = 4.8 Hz, H-1$_b$ α, H-1$_b$ β), 7.25–7.33 (m, 10 H, 5 × Ar-CHα, 5 × Ar-CHβ) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 5.7, 5.8 (2 × t, OCH$_2$$CH_2$I α, OCH$_2$-$CH_2$I β), 20.9, 20.9, 21.0, 21.0 (4 × q, 2 × COCH$_3$ α, 2 × COCH$_3$ β), 24.6, 24.7, 24.8, 25.1, 25.2, 25.3, 26.3, 26.4 (4 × q, CH$_3$ α, 4 × q, CH$_3$ β), 62.4, 62.5 (2 × t, C-6$_b$ α, C-6$_b$ β), 66.2, 66.5 (2 × t, C-6$_a$ α, C-6$_a$ β), 67.3, 67.4 (2 × t, OCH$_2$CH$_2$I α, OCH$_2$CH$_2$I β), 69.7, 69.8 (2 × t, ArCH$_2$ α, ArCH$_2$ β), 70.1, 70.2, 70.3, 70.4, 70.5, 70.6, 70.8, 70.9, 71.0, 72.8, 74.6, 74.8, 78.5, 79.8, 80.9, 82.1 (16 × d, C-2$_a$ α, C-3$_a$ α, C-4$_a$ α, C-5$_a$ α, C-2$_a$ β, C-3$_a$ β, C-4$_a$ β, C-5$_a$ β, C-2$_b$ α, C-3$_b$ α, C-4$_b$ α, C-5$_b$ α, C-2$_b$ β, C-3$_b$ β, C-4$_b$ β, C-5$_b$ β), 96.1, 96.1 (2 X d, C-1$_b$ α, C-1$_b$ β) 96.6 (d, C-1$_a$ β), 98.0 (d, C-1$_a$ α), 108.2, 108.3, 108.7, 108.8 [4 × s, C(CH$_3$)$_2$ × 2 α, C(CH$_3$)$_2$ × 2 β], 127.8, 127.9, 128.1, 128.2, 128.5, 128.6 (6 × d, Ar-CH), 138.9, 139.0 (2 × s, Ar-C), 169.8, 169.8, 170.5, 170.5 (4 × s, 4 C, 2 × CH$_3$$C$O α, 2 × CH$_3$$C$O β) ppm. HRMS (ES$^+$): calcd. for $C_{34}H_{43}O_{11}INa$ [M + Na$^+$] 777.1748; found 777.1752.

3-*O*-Benzyl-4,6-diacetyl-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranoside (45): General Method B gave disaccharide **45** (0.140 g, 94%) as a colourless oil. ^{1}H NMR (400 MHz, CD$_3$CN) [1:4 mixture of α/β anomers observed]: δ = 1.32–1.53 (m, 24 H, 4 × CH$_3$ α, 4 × CH$_3$ β), 1.96–2.03 (m, 12 H, 2 × COCH_3 α, 2 × COCH_3 β), 3.10–3.14 (m, 4 H, OCH$_2$CH_2SePh α, OCH$_2$CH_2SePh β), 3.24 (at, J = 6.8 Hz, 2 H, H-2$_a$ α, H-2$_a$ β), 3.93 (m, 10 H, H-5$_b$ α, H-5$_b$ β, H-6$_a$ α, H-6$_a$ β, H-6′$_a$ α, H-6′$_a$ β, H-6$_b$ α, H-6$_b$ β, H-6′$_b$ α, H-6′$_b$ β), 3.91–4.02 (m, 7 H, -OCH_2CH$_2$SePh α/β, H-3$_a$ α, H-3$_a$ β, H-4$_a$ α, H-4$_a$ β), 4.21–4.40 (m, 5 H, -OCH_2CH$_2$SePh α/β, H-5$_a$ β, H-5$_a$ β), 4.41–4.62 (m, 2 H, H-2$_b$ α, H-2$_b$ β), 4.71–4.78 (m, 2 H, H-3$_b$ α, H-3$_b$ β), 4.45 (d, $J_{1,2}$ = 8 Hz, 1 H, H-1$_a$ β), 4.58–4.89 (m, 8 H, CH_2Ph α, CH_2Ph β, H-4$_b$ α, H-4$_b$ β, H-5$_b$ α, H-5$_b$ β), 5.03 (d, $J_{1,2}$ = 3.5 Hz, 1 H, H-1$_a$ α), 5.49 (d, $J_{1,2}$ = 4 Hz, 2 H, H-1$_b$ α, H-1$_b$ β), 7.27–7.53 (m, 20 H, 10 × Ar-CHα, 10 × Ar-CHβ) ppm. ^{13}C NMR (100 MHz, CD$_3$CN): 19.9, 19.9, 20.1, 21.1 (4 × q, 2 × COCH$_3$ α, 2 × COCH$_3$ β), 23.7, 23.8 (2 × t, OCH$_2$$CH_2$SePh α, OCH$_2$$CH_2$SePh β), 24.2, 24.3, 24.4, 25.3, 25.3, 25.4, 25.4, 26.7 (8 × q, 4 × CH$_3$ α, 4 × CH$_3$ β), 62.2, 62.2 (2 × t, OCH$_2$CH$_2$SePh α, OCH$_2$CH$_2$SePh β), 66.3, 66.8, 67.3, 67.5 (4 × t, C-6$_a$ α, C-6$_a$ β, C-6$_b$ α, C-6$_b$ β), 69.4, 69.7 (2 × d, C-2$_b$ α, C-2$_b$ β), 70.3, 70.4, 70.5, 70.6, 70.7, 70.9, 71.0, 71.3, 71.4, 71.8 (8 × d, C-3$_a$ α, C-4$_a$ α, C-5$_a$ α, C-3$_a$ β, C-4$_a$ β, C-5$_a$ β, C-3$_b$ α, C-4$_b$ α, C-3$_b$ β, C-4$_b$ β), 74.7, 74.9 (2 × t, ArCH$_2$ α, ArCH$_2$ β), 80.3, 81.2 (2 × d, C-2$_a$ α, C-2$_a$ β), 78.4, 82.2 (2 × d, C-5$_b$ α, C-5$_b$ β), 96.2 (d, C-1$_a$ β), 96.5 (d, C-1$_a$ α), 103.7, 103.7 (2 × d, C-1$_b$ α, C-1$_b$ β), 108.4, 108.4, 108.9, 108.9 [4 × s, C(CH$_3$)$_2$ × 2 α, C(CH$_3$)$_2$ × 2 β], 126.6–131.7 (12 × d, Ar-CH), 131.8, 131.9, 138.7, 138.9 (4 × s, Ar-C), 169.6, 169.6, 170.3, 170.3 (4 C, 2 × CH$_3$$C$O α, 2 × CH$_3$$C$O β) ppm. HRMS (ES$^+$): calcd. for $C_{37}H_{48}O_{13}SeNa$ [M + Na$^+$] 803.2156; found 803.2168.

3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(2-iodoethyl)-α/β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranoside (46): General Method B gave disaccharide **46** (0.176 g, 77%) as a colourless oil; ^{1}H NMR (400 MHz, CDCl$_3$) [1:2 mixture of α/β anomers observed]: δ = 1.35, 1.37, 1.47, 1.56, 1.58, 1.61, 1.63 (8 × s, 24 H,

4×CH_3α, 4×CH_3β), 3.27–3.34 (m, 5 H, OCH_2CH_2I α, OCH_2CH_2I β, H-5b α), 3.40 (m, 1 H, H-5bβ), 3.53 (m, 1 H, H-5a α), 3.60–3.87 (m, 9 H, H-2a α, H-2a β, H-5a β, H-2b α, H-4 b α, H-4 b β, H-5b α, H-5b β, H-6′a α/β), 3.93–4.09 (m, 9 H, H-2a α, H-2a β, H-3a α, H-3a β, H-4a α, H-4b β, H-6b α, H-6b β, H-6′a α/β), 4.16–4.24 (m, 2 H, OCH_2CH_2I α/β), 4.33–4.47 (m, 4 H, OCH_2CH_2I α/β, H-6a α, $H\text{-}6_a$ β), 4.50 (d, $J_{1,2}$ = 8 Hz, 1 H, H-1a β), 4.61 (m, 2 H, H-6′b α, H-6′ b), 4.82–4.93 (m, 4 H, CH_2Ph α, CH_2Ph β), 5.05 (d, $J_{1,2}$ = 3.5 Hz, 1 H, H-1a α), 5.56 (s, 4 H, CHPh α, CHPh β, H-1b α, H-1b β), 7.27–7.50 (m, 20 H, 10×Ar-CHα, 10×Ar-CHβ) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 3.8, 3.9 (OCH_2CH_2I α, OCH_2CH_2I β), 24.5, 24.8, 24.9, 25.0, 25.9, 26.0, 26.1, 26.2 (4×q, CH_3 α, 4×q, CH_3 β), 62.5, 65.7 (2×t, C-6a α, C-6a β), 66.0, 66.8, (2×t, C-6b α, C-6b β), 67.4, 68.7 (2×t, OCH_2CH_2I α, OCH_2CH_2I β), 69.0, 70.4 (2×t, $ArCH_2$ α, $ArCH_2$ β), 70.6, 70.7, 70.8, 70.9, 71.4, 72.0, 73.6, 75.2, 76.7, 77.3, 78.2, 80.4, 80.6, 81.4, 82.1, 82.5 (16×d, C-2a–C-5a α, C-2a–C-5a β, C-2b–C-5b α, C-2b–C-5b β), 96.4 (d, C-1a β), 98.0 (d, C-1a α), 101.1 (d, C-1b α), 101.3 (d, C-1b β), 104.5, 104.5 (d, CHPh α, CHPh β), 108.7, 108.7, 109.4, 109.5 [s, $C(CH_3)_2$×2 α, $C(CH_3)_2$×2 β], 126.0, 126.5, 126.6, 127.2, 127.6, 127.7, 127.9, 128.1, 128.2, 128.3, 128.4, 129.0 (12×d, Ar-CH), 137.3, 137.4, 138.3, 138.6 (4×s, Ar-C) ppm. HRMS (ES^+): calcd. for $C_{34}H_{43}O_{11}INa$ [M + Na^+] 777.1748; found 777.1752.

3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-[2-(phenylselenyl)ethyl]-α/β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-D-galactopyranoside (47): General Method B gave disaccharide **47** (0.065 g, 93%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) [1:3 mixture of α/β anomers observed]: δ = 1.34 (br. s, 12 H, 2×CH_3 α, 2×CH_3 β), 1.46, 1.47, 1.53, 1.55 (14×s, 12 H, 2×CH_3 α, 2×CH_3 β), 3.06–3.18 (m, 4 H, OCH_2CH_2SePh α, OCH_2CH_2SePh β, $H\text{-}5_b$ α), 3.40 (m, 1 H, $H\text{-}5_b$ β), 3.53 (m, 1 H, $H\text{-}5_a$ α), 3.49 (dd, $J_{6,6'}$ = 8.2, $J_{5,6}$ = 3.2 Hz, 1 H, $H\text{-}6_b$ α), 3.58–3.82 (m, 8 H, $H\text{-}2_a$ α, $H\text{-}2_a$ β, $H\text{-}5_a$ β, $H\text{-}2_b$ α, $H\text{-}4_b$ α, $H\text{-}4_b$ β, $H\text{-}5_b$ α, $H\text{-}5_b$ β), 3.84–4.13 (m, 7 H, $H\text{-}2_a$ α, $H\text{-}2_a$ β, $H\text{-}3_a$ α, $H\text{-}3_a$ β, $H\text{-}4_a$ α, $H\text{-}4_b$ β, $H\text{-}6_b$ β), 4.16–4.24 (m, 4 H, OCH_2CH_2I α/β, $H\text{-}6_a$ α/β $H\text{-}6'_a$ α, $H\text{-}6'_a$ β), 4.33–4.47 (m, 3 H, OCH_2CH_2I α/β, $H\text{-}6_a$ α/β), 4.48 (d, $J_{1,2}$ = 8 Hz, 1 H, $H\text{-}1_a$ β), 4.61 (m, 2 H, $H\text{-}6'_b$ α, $H\text{-}6'_b$), 4.80–4.88 (m, 4 H, CH_2Ph α, CH_2Ph β), 5.02 (d, $J_{1,2}$ = 3.5 Hz, 1 H, $H\text{-}1_a$ α), 5.53 (s, 4 H, CHPh α, CHPh β, $H\text{-}1_b$ α, $H\text{-}1_b$ β), 7.27–7.50 (m, 30 H, 15×Ar-CHα, 15×Ar-CHβ) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 24.4, 24.6 (OCH_2CH_2I α, OCH_2CH_2I β), 24.9, 25.0, 25.9, 26.0, 26.1, 26.2, 27.0, 27.1 (4×q, CH_3 α, 4×q, CH_3 β), 62.5, 62.5 (2×t, $C\text{-}6_a$ α, $C\text{-}6_a$ β), 65.8, 66.0 (2×t, C-6b α, C-6b β), 66.9, 67.3 (2×t, OCH_2CH_2I α, OCH_2CH_2I β), 68.9, 69.0 (2×t, $ArCH_2$ α, $ArCH_2$ β), 70.2, 70.4, 70.6, 70.7, 70.8, 70.9, 71.3, 72.4, 75.0, 75.1, 78.2, 80.5, 80.6, 81.3, 82.0, 82.4 (16×d, $C\text{-}2_a$ α, $C\text{-}3_a$ α, $C\text{-}4_a$ α, $C\text{-}5_a$ α, $C\text{-}2_a$ β, $C\text{-}3_a$ β, $C\text{-}4_a$ β, $C\text{-}5_a$ β, $C\text{-}2_b$ α, $C\text{-}3_b$ α, $C\text{-}4_b$ α, $C\text{-}5_b$ α, $C\text{-}2_b$ β, $C\text{-}3_b$ β, $C\text{-}4_b$ β, $C\text{-}5_b$ β), 96.3 (d, $C\text{-}1_a$ β), 98.0 (d, $C\text{-}1_a$ α), 101.1 (d, $C\text{-}1_b$ α), 101.2 (d, $C\text{-}1_b$ β), 104.6, 104.6 (d, CHPh α, CHPh β), 108.6, 108.6, 109.2, 109.4 [s, $C(CH_3)_2$×2 α, $C(CH_3)_2$×2 β], 126.0, 126.5, 126.6,126.9, 127.2, 127.3 127.6, 127.7, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 129.0, 129.1, 129.2, 130.4 (18×d, Ar-CH), 132.2, 132.6, 137.3, 137.4, 138.3, 138.6 (6×s, Ar-C) ppm. HRMS (ES^+): calcd. for $C_{40}H_{48}O_{11}SeNa$ [M + Na^+] 807.2260; found 807.2258.

3,4,6-Tri-*O*-benzyl-α/β-D-glucopyranosyl-(1→6)-1:2,3:4-di-*O*-isopropylidene-α-D-galactopyranoside (48):[19,20] **Method 1:** Disaccharide **11b** (α:β ratio 5:1) (0.223 g, 0.254 mmol) was dissolved in freshly distilled THF (10 mL) under an atmosphere of argon. The reaction was cooled to 0 °C and H_2O_2 (1 mL, 30% solution in THF) was added. The reaction was warmed to room temp. and stirred for 1 h, then heated at reflux for a further 1 h, after which TLC (toluene/ethyl acetate, 9:1) indicated the formation of a major product (R_f 0.5) and complete consumption of starting material (R_f 0.4). The reaction was cooled to room temp. and then NIS (0.381 mmol) and water (1 mL) were added and the reaction stirred for 16 h, after which TLC indicated the formation of a single product (R_f 0.2) The reaction was diluted with CH_2Cl_2 (20 mL) and washed with water (20 mL). The aqueous layer was then extracted with CH_2Cl_2 (2×20 mL) and the combined organic extracts were washed with saturated sodium hydrogen carbonate (20 mL) then brine (20 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (toluene/ethyl acetate, 6:1) to afford alcohol **48** (0.137 g, 76%) as a colourless oil. These data are in agreement with those reported in the literature. ^1H NMR (400 MHz, $CDCl_3$) [5:1 mixture of α:β anomers observed, major α-anomer quoted]: δ = 1.34, 1.35, 1.45, 1.54 (4×s, 12 H, 4×CH_3), 3.63–3.79 (m, 6 H, $H\text{-}2_b$, $H\text{-}3_b$, $H\text{-}4_b$, $H\text{-}6_b$, $H\text{-}6'_b$, $H\text{-}6_a$), 3.85 (ddd, J = 9.9, J = 3.0, J = 2.2 Hz, 1 H, $H\text{-}5_b$), 3.91 (m, 1 H, $H\text{-}6'_a$), 3.99–4.01 (m, 1 H, $H\text{-}5_a$), 4.25 (dd, J = 7.9, J = 1.9 Hz, 1 H, $H\text{-}4_a$), 4.34 (dd, $J_{1,2}$ = 4.9, $J_{2,3}$ = 2.2 Hz, 1 H, $H\text{-}2_a$), 4.63 (dd, $J_{2,3}$ = 2.2, $J_{3,4}$ = 7.8 Hz, 1 H, $H\text{-}3_a$), 4.49, 4.83 (ABq, J = 10.3 Hz, 2 H, $PhCH_2$), 4.50, 4.64 (ABq, J = 11.7 Hz, 2 H, $PhCH_2$), 4.93 (d, $J_{1,2}$ = 3.2 Hz, 1 H, $H\text{-}1_b$), 4.82, 4.98 (ABq, J = 10.7 Hz, 2 H, $PhCH_2$), 5.53 (d, $J_{1,2}$ = 4.9 Hz, 1 H, $H\text{-}1_a$), 7.12–7.41 (m, 15 H, 15×Ar-H) ppm. MS (ES^+): *m/z* = 715 [M + Na^+] (100).

Method 2: Disaccharide **11a** (α:β ratio 3.5:1) (0.215 g, 0.254 mmol) was dissolved in freshly distilled THF (10 mL) under an atmosphere of argon. KO*t*Bu (0.5 mL, 1 M solution in THF) was added and the reaction was heated at reflux for 3 h, after which TLC (toluene/ethyl acetate, 9:1) indicated the formation of a major product (R_f 0.5) and complete consumption of starting material (R_f 0.4). The reaction was cooled to room temp. and then NIS (0.381 mmol) and water (1 mL) were added and the reaction stirred for 16 h, after which indicated the formation of a single product (R_f 0.2) The reaction was diluted with CH_2Cl_2 (20 mL) and washed with water (20 mL). The aqueous layer was then extracted with CH_2Cl_2 (2×20 mL) and the combined organic extracts were washed with saturated sodium hydrogen carbonate (20 mL) then brine (20 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (toluene/ethyl acetate, 6:1) to afford alcohol **48** (0.128 g, 73%) as a colourless oil identical to the material described above.

Supporting Information (see footnote on the first page of this article): X-ray crystallographic data, spectra for all compounds and low-temperature NMR studies.

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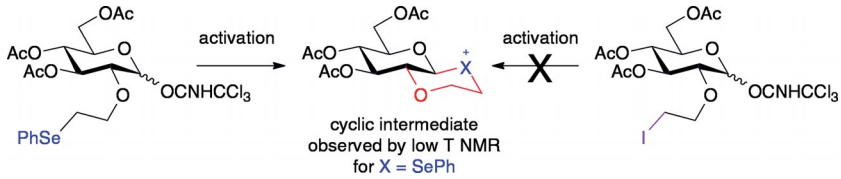
Glycosylation



The propensity of 2-iodo- or 2-(phenylseleno)ethyl ethers moieties at the 2-position of a glycosyl donor to participate in glycosylation reactions depends on both the nature of the nucleophile (Se >> I), and the protecting groups on the other hydroxys of the glycosyl donor. The formation of β-configured 6-ring cyclic intermediates is not alone sufficient to ensure high levels of α-selectivity.

Keywords: Synthetic methods / Carbohydrates / Glycosylation / Neighboring-group effects / Diastereoselectivity

