Introduction

Stereoelectronic effects dictate the shape and behaviour of molecules. Understanding and harnessing these effects enables the conception of effective and stereoselective synthetic chemistry. Carbohydrates are densely decorated molecules bearing a variety of different functional groups in numerous configurational and stereochemical constellations. The decoration pattern of carbohydrates plays an all-important role during furanosylation reactions. During a glycosylation reaction a donor glycoside is generally activated to give an electrophilic species bearing significant oxocarbenium ion character. Although steric effects are often decisive in determining the overall shape of a neutral molecule, in charged molecules electronic effects become more important and they may in fact outweigh steric effects. For example, protonated iminosugars, that is, carbohydrates having the endocyclic oxygen replaced by a nitrogen, may change their configuration to place their ring substituents in a sterically unfavourable (pseudo)-axial orientation to stabilise the positive charge on the ring nitrogen. In line with these stereoelectronic effects, glycosyl donors that feature an “axial-rich” substitution pattern, are generally more reactive than glycosyl donors equipped with equatorially disposed functional groups. However, it is extremely challenging to understand—let alone predict—what the overall effect of multiple ring substituents is on the reactivity of a particular glycosyl donor and as a result the effect on the stereoselectivity in a glycosylation reaction. Based on a computational strategy of Rhoad and co-workers, we have recently introduced a method to determine the conformational behaviour of furanosyl oxocarbenium ions. By calculating the relative energy of a large number of fixed furanosyl oxocarbenium ion conformers and mapping these in energy contour plots we could determine, which conformations played an important role during furanosylation reactions and we were able to relate the population of the different conformational states to the stereoselectivity of the reactions. The introduced conformational energy landscape mapping method provided detailed insight into how the ring substituents—as stand-alone entities but also collectively—influenced the shape, stability and reactivity of the furanosyl oxocarbenium ions. In this initial study, only ether substituents were assessed. We here present an in-depth study on the stereoelectronic substituent effects of different functional groups that are all...
highly relevant in oligosaccharide synthesis. Understanding these effects will enable the development of effective glycosylation methodologies and aid in the interpretation of the outcome of glycosylation reactions. We have studied the effect of C2-fluoride and C2-azide substituents, as well as C4-carboxylic acid ester groups, as these functionalities are commonly employed in the assembly of fluorinated, cis-linked glycosamine-containing or glycuronic acid- featuring oligosaccharides, respectively.1–25

Herein, we describe the synthesis of a panel of twelve structurally varying furanosyl imidate donors, comprising all possible pentofuranosyl diastereoisomers (Figure 1, 1–12), their glycosylation properties were studied by experimental chemical glycosylations as well as by a computational investigation on the reactive intermediates active during the glycosylation and responsible for the stereoselective outcome of the reaction, that is, the furanosyl oxocarbenium ions.

Results and Discussion

Synthesis

The set of d-ribo-, d-arabinof-, d-lyxo- and d-xyro-configured furanosyl donors 1–12 (Figure 1) that was needed for this study was prepared as depicted in Scheme 1. All donors studied here were equipped with an N-phenyl trifluoroacetimidate anomeric leaving group.26–29 The uronic acid methyl esters were prepared as depicted in Scheme 1. All donors studied here ranosyl donors were prepared as depicted in Scheme 1. Aqueous TFA-mediated hydrolysis of the donor 1 was prepared as depicted in Scheme 1. All donors studied here were equipped with an anomeric methyl group and installation of the trifluoro-N-phenyl imidate group with Cs2CO3 proceeded uneventfully to give donors 1–4.

For the functionalisation on C2 we first investigated the inversion of the C2-triflates 29–32, generated from the corresponding C2-alcohols 25–2832–35 with a suitable azide or fluoride nucleophile (Scheme 1 B).36 Inversion of the ribosyl C2-OTf group in 29 by using an excess of NaN3 in DMF at 80 °C proceeded smoothly to give the 2-azidoarabinoside 34 in high yield (see Table 1, entry 1, conditions A). The inversion of 29 by using tetrabutylammonium fluoride as the source of the fluoride nucleophile in THF at ambient temperature gave 38 in good yield (71%, Table 1, entry 2, conditions B). This yield could be further improved to 86% by employing CsF in tert-amiyl alcohol at 90 °C (Table 1, entry 3, conditions C).37

When the arabinoside C2-triflate 30 (a mixture of anomers) was treated under conditions A to install the C2 azide group and provide 33, a mixture of products resulted consisting of the desired C2-azide 33 and the anomeric azide 51 (Figure 2 A, 86%, 33/51 = 4:1, Table 1, entry 4). The stereospecific formation of the β-azide 51 (Figure 2 A) can be explained by the generation of a transient methyl oxiranium ion intermediate, that is substituted in an S2-like fashion by the azide anion on the anomeric centre (see Figure 2 B, path A).38

The fluoride substitution on 30 also comes along with side reactions. When 30 was subjected to conditions B by using TBAF, only the β-anomer of 30 reacted to provide 37, leaving the α-anomer untouched (Table 1, entry 5).39 At higher temperatures, by using CsF (conditions C), both anomers reacted to provide the corresponding C2-fluorides. However, reaction of the α-anomer of 30 also provided the anomic tert-amiyl product 52 (Figure 2 A), resulting from a migration of the anomic methoxime by substitution of the C2-triflate and subsequent solvolysis of the formed oxocarbenium ion (Figure 2 B, paths A, B and/or C). The weaker nucleophilicity of tert-amiyl alcohol with respect to the azide anion likely leads to more S2 character in the substitution reaction of the methyl oxiranium ion and generation of an anomic mixture of 52, where the azide stereospecifically provided the β-azide 51.

The xylosyl C2-alcohols 28a and 28b could be readily separated and their C2-triflates 32α and 32β could therefore be in-

Figure 1. Target donors 1–12 and the subsequent stereoselectivity investigation by glycosylations and computational analysis (Bn = benzyl)
dividually investigated in the substitution reactions (Scheme 1B, Table 1, entries 7–12). The inversion of the α-anomer 32a with NaN₃ provided the 2-azidolylxoside 35a (67 %, Table 1, entry 7), alongside two side products, that is, the 5-azidolylxoside 53a and the bicycle 55 (Figure 2A), which were formed in 12 and 7 % yield, respectively. The generation of these side products stems from the participation of the primary C5-OBn group, which is capable of substituting the C2-OTf group. Nucleophilic attack at C5 provides 53a, whereas substitution at the benzylic position generates the bicycle 55 (see Figure 2C, paths A and B). When the substitution of the C2-triflate 32a was tried under conditions B to furnish the desired C2-fluoro lyxose 39a (Table 1, entry 8), no conversion was observed and therefore, the reaction was heated to 70 °C. Under these conditions, the 2-triflyllyxose 39a was formed in 44 % yield, whereas alcohol 28 was regenerated through hydrolysis of the triflate. Application of conditions C (Table 1, entry 9) only resulted in the formation of products originating from C5-OBn participation: the 5-fluoroxyloside 54a and the bicycle 55 (Figure 2A and D) were obtained in 57 and 21 % yield, respectively.

Inversion of the C2-OTf group of the β-xyloside 32b with either the azide or fluoride nucleophiles did not lead to any desired inversion products (Table 1, entries 10–12). Conditions A only provided the C5-azido product 53b (Figure 2A), whereas conditions B led to the formation of 54b, through the participation of the C5-OBn group (Figure 2C, path A). Elimination to give furan 56 was also observed under conditions B (Table 1, entry 11). Interestingly, the use of CsF (conditions C, Table 1, entry 12) provided, besides the side product 54b, the 2-fluoroxyloside 40b in low yield, apparently through a double-displacement mechanism (Figure 2D, path C). Generation of product 40b through this route proved advantageous because its generation from lyxo-triflate 31 was ineffective (see below).

All conditions examined to transform lyxo-triflate 31 to one of the inverted products (i.e., 36/40) were ineffective (Table 1, entry 13) and furan 56 was formed exclusively within minutes. We therefore took a different approach to generate the 2-azidoxyloside (Scheme 1C). Thus, glycal 49 was functionalised by azidophenylselenation with TMSN₃ and N-(phenylseleno)phthalimide to give the desired 2-azidoxyloside 50 with good diastereoselectivity (xylo/lyxo 9:1).[41,42] Oxidative hydrolysis of the selenophenyl group by aqueous NIS then gave lactol 44. Acidolysis of the anomeric methyl ethers 33–35 and 37–40 by using aqueous formic acid provided the other lactols 41–43.

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Scheme 1. a) i) 2,2,6,6-Tetramethylpiperidine N-oxyl (TEMPO), diacetoxyiodobenzene (BAIB), dichloromethane, H₂O; ii) MeI, K₂CO₃, DMF; b) trifluoroacetic acid (TFA)/H₂O (9/1); c) 2,2,2-trifluoro-N-phenylacetimidoyl chloride, C₅H₅N, acetonitrile, H₂O; d) trifluoromethanesulfonic anhydride (Tf₂O), pyridine, dichloromethane; e) NaN₃, DMF, see Table 1; f) tetrabutylammonium fluoride (TBAF), THF; or CsF, tert-amyl alcohol, see Table 1; g) HCOOH, H₂O; h) 2,2,2-trifluoro-N-phenylacetimidoyl chloride, 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU), dichloromethane; i) TFA, H₂O, THF; j) 4-dimethylaminopyridine (DMAP), diisopropylethylamine (DIPEA), thiophosgene, dichloromethane; k) 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine, toluene; l) N-(phenylseleno)phthalimide, azidotrimethylsilane (TMSN₃), TBAF, dichloromethane; m) N-iodosuccinimide (NIS), H₂O, acetonitrile, THF.
and 45–48, respectively (Scheme 1B). Finally, all eight lactols were transformed into the corresponding N-phenyl trifluoracetimidates 5–12 to complete the set of donor furanosides.

Glycosylations

With the complete set of functionalised furanosyl imidate donors 1–12 in hand, the stereoselectivity of the glycosylation reactions by using allyltrimethylsilane (allyl-TMS) or [D]triethylsilane ([D]TES) as acceptors, were examined. Allyl-TMS and [D]TES are poor nucleophiles and are ideal acceptors to study the results of these glycosylations together with the corresponding N-phenyl trifluoracetimidates 5–12 to complete the set of donor furanosides.

Table 1. Synthesis of C2-modified methyl glycosides 33–40 through C2-triflate inversion.

| Entry | Triflate | Cond. | Substitution product | Yield [a] | Side products [yield [%]] |
|-------|----------|-------|----------------------|----------|--------------------------|
| from α-ribo- to α-arabino-configured | | | | | |
| 1 | 29 | A (N2) | 34 | 93 | – |
| 2 | 29 | B (TBAF) | 38 | 71 | – |
| 3 | 29 | C (CsF) | 38 | 86 | – |
| from α-arabino- to α-ribo-configured | | | | | |
| 4 | 30 | A | 33 | 80[b] | 51[b] |
| 5 | 30 | B | 37 | β only | 42 | 30[c](17) |
| 6 | 30 | C | 37 | 63 | 52[c](17) |

[α] Reagents and conditions: A) 0.2 M solution in DMF, NaN₃ (5 equiv), 80 °C, 2 h; B) 0.2 M solution in THF, TBAF (2.5 equiv), 0–20 °C, overnight; C) 0.35 M solution in tert-amyl alcohol, CsF (4 equiv), 90 °C, overnight.
[b] Combined yield of 33 and 51 as a 4:1 mixture. [c] Overnight; [d] 70 °C, 5 h for entry 8, overnight for entry 11; [e] 110 °C overnight. [f] α/β = 88:12; [g] Yield not determined.

Table 2. Glycosylation reactions of donors 1–12 and 57–60 with the acceptors [D]TES and allyl-TMS.[b]

| Entry | Donor | Acceptor | Product | Yield [%] |
|-------|-------|----------|---------|-----------|
| 57 | allyl-TMS | 61 | > 98.2 | 50[c] |
| 58 | allyl-TMS | 62 | < 2.98 | 62[c] |
| 59 | allyl-TMS | 63 | < 2.98 | 100[c] |
| 60 | allyl-TMS | 64 | 85:15 | 40[c] |
| 61 | allyl-TMS | 65 | 85:15 | 68[c] |
| 62 | allyl-TMS | 66 | 85:15 | 68[c] |
| 63 | allyl-TMS | 67 | 85:15 | 68[c] |
| 64 | allyl-TMS | 68 | 85:15 | 68[c] |
| 65 | allyl-TMS | 69 | 85:15 | 68[c] |
| 66 | allyl-TMS | 70 | 85:15 | 68[c] |
| 67 | allyl-TMS | 71 | 85:15 | 68[c] |
| 68 | allyl-TMS | 72 | 85:15 | 68[c] |
| 69 | allyl-TMS | 73 | 85:15 | 68[c] |
| 70 | allyl-TMS | 74 | 85:15 | 68[c] |
| 71 | allyl-TMS | 75 | 85:15 | 68[c] |
| 72 | allyl-TMS | 76 | 85:15 | 68[c] |

[a] Anomeric configuration established by HSQC-HECADE and NOESY NMR spectroscopy.[48–50] Detailed experimental conditions are provided in the Experimental Section. [b] Literature values, see reference [15]. [c] Calculated yields from isolated mixed fractions.

Figure 2. A) Observed side products 51–56 and 40[b]. B) Proposed reaction pathways for the formation of 51 and 52. C) Proposed reaction pathways for the formation of 53a and 54a (path A) as well as 55 (path B). D) Proposed reaction pathways for the formation of 53b and 54b (path A) as well as 40[b] (path C).
ribo-, arabinob- and lyxo-configured donors [57, 58 and 59] provided exclusively the 1,2-cis-substitution products, whereas the xylose donor [60] gave the anomeric deuterium α and β products in a 85:15 α/β ratio (Table 2, entry 1, 5, 9 and 13). Strikingly, the 1,2-cis selectivity in the glycosylation reactions was also observed for the reactions of the C2- and C5-modified furanosyl donors. All reactions performed with the ribose donors [1, 5 and 9] (Table 2, entries 2–4), the arabinose donors [2, 6 and 10] (Table 2, entries 6–8) and the lyxose donors [3, 7 and 11] (Table 2, entries 10–12) proceeded with excellent 1,2-cis stereoselectivity. The reactions of the xylose donors [4, 8 and 12] (Table 2, entries 14–16) proceed with poorer stereoselectivity. The 2-azidoxyloside donor [8] gives a 85:15 mixture of anomers (product 72), which is in line with the outcome of the reaction of the corresponding tri-O-benzyl donor [60] (Table 2, entries 13 and 15). The 2-fluoroxyllose [76] is formed in a 70:30 α/β ratio (Table 2, entry 16) and the uronic acid xylosyl donor 4 provided the least selective reaction giving roughly equal amounts of both the α and the β product [68, Table 2, entry 14]. The reactions of the xylosyl donors also provided significant quantities of side products. In all reactions, the anomeric N-phenyl-trifluoracetimide donors, [47] to our knowledge they have never been reported for N-phenyl trifluoracetimides. In the reaction of the xyluronic acid ester 4, the tricyclic compound 81 (Figure 3) was also formed, originating from an intramolecular electrophilic aromatic substitution reaction of the C2-O-benzyl group.

Overall it can be concluded that—quite surprisingly—the nature of the substituents on the furanosyl donors has relatively little effect on the stereochemical outcome of the glycosylation reactions.

Computations
To rationalise the stereochemical outcome of the glycosylations described above, we next assessed the structure of the oxocarbenium ions involved. Woerpel and co-workers have described above, we next assessed the structure of the C2- and C5-modified furanosyl oxocarbenium ions. To rationalise the stereochemical outcome of the glycosylation reactions. We therefore adopted this method here, to probe the effect of the C2 and C5 modifications on the stability of the oxocarbenium ion conformers and we have calculated the relative energy of the C4-CO2Me, C2-N3 and C2-F furanosyl ions as a function of their shape to deliver the CEL maps shown in Figure 5. To generate these maps the benzyl ethers in the substrates used in the experiments described above, have been replaced for methyl ethers (see Figure 5, [82–97]), to minimise computational costs. [16] For the C2-N3 and C2-F ions, three maps were generated for each of the C4–C5 gg, gt and tg rotamers (Figure 4D), and these were combined to provide the overall CEL map shown in Figure 5. A similar approach was taken for the bisected and eclipsed structures of the C4-CO2Me oxocarbenium ions. The most important conformations for each ion are given next to the CEL map of each oxocarbenium ion in Figure 5 (see the Supporting Information for the corresponding energies).

From the CEL maps of the ribo-configured furanosyl oxocarbenium ions [82–85] (Figure 5, top row) it becomes clear that the overall shape of the energy landscape is comparable for all four ions, with the energy minima centred on the E1 conformera
This indicates that a fluoride or azide at C2 is best positioned in a pseudo-equatorial orientation to allow for stabilisation of the ion by hyperconjugation of the C2–H bond, which is in line with the effect of a C2-ether functionality. 

From the CEL map of the C2-F ion it does become apparent that there is a stronger tendency of the fluorine atom to occupy a pseudo-equatorial orientation. The E3 conformer of 85 is 5.2 kcal mol⁻¹ higher in energy than the lowest-energy E₁ conformer, whereas this difference is only 1.9 kcal mol⁻¹ for 82 and around 2.5 kcal mol⁻¹ for 83 and 84. The preference of the C4-CO₂Me to take up an axial orientation becomes apparent from the CEL map of ion 83. Interestingly, there is only a marginal difference between the eclipsed and bisected orientation of the carboxylic acid ester and both orientations seem to be equally capable of stabilising the electron-depleted anomeric centre when the C4-CO₂Me takes up a pseudo-axial orientation (see Supporting Information). By using the lowest-energy E₃ conformers as product-forming intermediates, the formation of the 1,2-cis products can be readily accounted for by using the inside attack model for all of the examined ribofuranosides.

The CEL maps for the arabino-configured furanosyl oxocarbenium ions 86–89 (Figure 5, second row) also show great similarity, with each map showing an energy minimum around the E₃ conformation. Thus, the hyperconjugative stabilisation of the C2–H bond, in combination with a sterically favourable pseudo-equatorial orientation for all substituents seems decisive for these ions. Inside attack on the E₃ conformers leads to the formation of the 1,2-cis products as found experimentally. Of note, the CEL map of the C2-N₃ shows a second energy minimum for the T₄/E₁ conformer with minimal ring puckering. From the stereochemical outcome of the glycosylation reactions it seems that this conformer does not play a major role.

Figure 4. A) The two-conformer model, visualising the preferential nucleophilic attack from the inside face. Important rotations are denoted by dashed arrows. B) The two principal conformations of the two-conformer model (E₃–E₂) shown for every carbohydrate configuration, examples taken as their tri-O-benzyl-protected form. The colours indicate the relative preferential orientations for H2 and O3: green is relatively stabilising whereas red is relatively destabilising. C) Pseudo-rotational circle showing the twenty canonical furanoside structures, with phase-angles (P) and puckering amplitudes (τₘ). D) Possible C₄–C₅ rotamers: gg, gt and tg for the C5-OMe oxocarbenium ions, and two rotamers, eclipsed and bisected, for the C4-CO₂Me oxocarbenium ions.
Figure 5. Conformational energy landscape maps for the four diastereoisomeric pentofuranosides and their C5 and C2 modifications. Energies are expressed as $\Delta G^{\text{CH}_2 \text{Cl}_2}$ in [kcal mol$^{-1}$].
in the addition reaction. This could indicate that attack on this almost flat conformation is significantly less favourable than the inside attack of the $\text{E}^1$ envelope, which leads to the favourable C1–C2 staggered product.

The CEL maps of the lyxo-configured oxocarbenium ions 90–93 (Figure 5, third row) show a single energy minimum on the $\text{E}^1$ side of the CEL maps and the difference in energy between these structures and the other conformers appears to be even larger than the energy differences observed for the ribosyl oxocarbenium ions. This can be understood by realising that the $E_1$ envelope not only loses the stabilising interactions of the C2 and C3 substituents, present in the $\text{E}^1$ conformer, but also experiences severe 1,3-diaxial interactions between the C2 and C4 groups, especially for the electronically most favourable gg rotamer. Again, the CEL maps show great similarity for all substitution patterns, indicating analogous behaviour of the lyxofuranosides in the glycosylation reaction. This is indeed borne out in the experimental glycosylations that all proceed in a completely stereoselective fashion to provide the all-lyxofuranosides in the glycosylation reaction. This is indeed all substitution patterns, indicating analogous behaviour of the $E$ prepared to the sterically unfavourable situation in the $S_N1$-type glycosylation reactions. An exclusive 1,2-cis-selective, whereas the xyluronic acid donor reacted in a non-stereoselective manner. The experimental results have been complemented by computational studies, generating conformational energy landscape (CEL) maps for the intermediate oxocarbenium ions. These maps have shown that the stereoelectronic effects of the C2 and C5 modifications are, across the board, similar to a C2-ether substituent. These groups therefore have a similar effect on the stereoechemical outcome of glycosylation reactions taking place through an $S_N1$-like mechanism and the lowest-energy oxocarbenium ion conformers, revealed by the CEL maps, have, in combination with the inside attack model, provide a suitable explanation for the experimentally observed cis stereoselectivity. The maps have revealed that for most of the studied furanosyl oxocarbenium ions the canonical $\text{E}^1$ and $E_1$ envelopes represent the lowest-energy structures. However, for the xyluronic acid ions other low-energy structures can be found, taking up $T_2$ and $\text{E}^1$ conformations. The occurrence of these structures coincides with a relatively poor selectivity in the addition reactions. For these ions it appears that the “two-conformer model” falls short in providing an adequate explanation to account for the (lack of) stereoselectivity and that more oxocarbenium ion conformations have to be taken into account as product-forming intermediates. Further insight into the structure of glycosyl oxocarbenium ions and the trajectories of nucleophiles that attack these will lead to a better understanding of the $S_N1$ side of the glycosylation reaction mechanism continuum and this can eventually pave the way to a new stereoselective glycosylation methodology. 

Conclusions

In summary, we have disclosed synthetic routes to access all diastereoisomeric C2-azido and C2-fluoro furanosides as well as all furanosyl uronic acid esters. In total, a set of twelve different functionalised furanosyl donors has been synthesised and these have been glycosylated with allytrimethylsilane and [(D)trimethylsilyl] to establish the stereoselectivity of these donors in $S_N1$-type glycosylation reactions. An exclusive 1,2-cis selectivity was observed for all ribo-, arabinono- and lyxo-configured donors, despite the structural modifications made on the C2- and C5-positions. The 2-azido and 2-fluoro xylose donors were moderately 1,2-cis-selective, whereas the xyluronic acid donor reacted in a non-stereoselective manner. The experimental results have been complemented by computational studies, generating conformational energy landscape (CEL) maps for the intermediate oxocarbenium ions. These maps have shown that the stereoelectronic effects of the C2 and C5 modifications are, across the board, similar to a C2-ether substituent. These groups therefore have a similar effect on the stereoechemical outcome of glycosylation reactions taking place through an $S_N1$-like mechanism and the lowest-energy oxocarbenium ion conformers, revealed by the CEL maps, have, in combination with the inside attack model, provide a suitable explanation for the experimentally observed cis stereoselectivity. The maps have revealed that for most of the studied furanosyl oxocarbenium ions the canonical $\text{E}^1$ and $E_1$ envelopes represent the lowest-energy structures. However, for the xyluronic acid ions other low-energy structures can be found, taking up $T_2$ and $\text{E}^1$ conformations. The occurrence of these structures coincides with a relatively poor selectivity in the addition reactions. For these ions it appears that the “two-conformer model” falls short in providing an adequate explanation to account for the (lack of) stereoselectivity and that more oxocarbenium ion conformations have to be taken into account as product-forming intermediates. Further insight into the structure of glycosyl oxocarbenium ions and the trajectories of nucleophiles that attack these will lead to a better understanding of the $S_N1$ side of the glycosylation reaction mechanism continuum and this can eventually pave the way to a new stereoselective glycosylation methodology. 

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Conflict of interest

The authors declare no conflict of interest.

Keywords: conformation analysis · energy landscape maps · glycosylation · oxocarbenium ions · substituent effect

[1] P. Deslongchamps, Stereoelectronic Effects in Organic Chemistry, Pergamon, Oxford, 1983.
[2] M. Sinnott, Carbohydrate Chemistry and Biochemistry: Structure and Mechanism, RSC, London, 2007.
[3] H. A. Taha, M. R. Richards, T. L. Lowary, Chem. Rev. 2013, 113, 1851–1876.
[4] P. O. Adero, H. Amarasekara, P. Wen, L. Bohé, D. Crich, Chem. Rev. 2018, 118, 8242 – 8284.
[5] E. van Rijsset, A. P. A. Janssen, A. Males, G. J. Davies, G. A. van der Marck, H. S. Overkleeft, J. D. C. Codée, ChemBioChem 2017, 18, 1297 – 1304.

These are not the final page numbers!
For selected examples on donor reactivities, see: a) Reactivity Tuning in Oligosaccharide Assembly (Eds.: B. Fraser-Reid, J. C. López), Springer, Heidelberg, 2011, pp. 1–29; b) P. Grice, S. V. Ley, J. Pietruszka, H. W. M. Priepeke, E. P. E. Walther, Synlett 1995, 781–784; c) N. L. Douglas, S. V. Ley, U. Lucking, S. L. Warnerr, J. Chem. Soc. Perkin Trans. I 1998, 51–66; d) Z. Zhang, I. R. Ollmann, X. S. Ye, R. Wischnat, T. Baasov, C.-H. Wong, J. Am. Chem. Soc. 1999, 121, 734–753; e) K.-K. T. Mong, C.-H. Wong, Angew. Chem. Int. Ed. 2002, 41, 4087–4090; Angew. Chem. 2002, 114, 4261–4264; f) J. C. M. Pedersen, L. G. Marinescu, M. Bols, Chem. Commun., 2008, 2465–2467; g) M. Heuckendorff, C. M. Pedersen, M. Bols, J. Org. Chem. 2013, 78, 7234–7248.

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Stereoselectivity

Furanosyl Oxocarbenium Ion Conformational Energy Landscape Maps as a Tool to Study the Glycosylation Stereoselectivity of 2-Azidofuranoses, 2-Fluorofuranoses and Methyl Furanosyl Uronates

Explaining selectivity: A combined experimental and computational approach is used to investigate the stereoselective outcome of glycosylation reactions of differentially substituted furanoses. A high 1,2-cis selectivity was found for the ribo-, arabino- and lyxo-configured furanosides, whereas the xylosyl derivatives show a lack of selectivity (see figure).