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<tr>
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<td>Farrell, Mark</td>
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The anomerisation of glycosidic linkages

By

Mark Farrell

A Thesis presented to

The National University of Ireland

For the degree of

Doctor of Philosophy

Based on the research carried out in the

School of Chemistry,

National University of Ireland,

Galway

Under the supervision and direction of

Prof. Paul V. Murphy

National University of Ireland,

Galway
Acknowledgements

I would like to express my special appreciation and thanks to my advisor Professor Murphy, you have been a tremendous mentor for me. I would like to thank you for encouraging my research and for allowing me to grow as a research scientist. Your advice on both research as well as on my career have been priceless. I would to thank all the Murphy group members who have been present during my time at NUI, Galway. In particular I would like to thank Ciarán O’Reilly and Carmela Napolitano who were both especially helpful during the early stages of my Ph.D. and so often pointed me in the right direction. I would like to thank Jenifer Hendel for being a great lab mate, truly helping with my chemistry and for keeping us downstairs boys in line. I would really like to thank Daniele Lo Re for making me ask questions I wouldn’t have previously asked and for being a great mentor in the lab.

To my parents, thank you for being always so supportive of everything I do. To my lovely Cheryl, thank you for putting up with my mood swings in the closing stages of my thesis, thank you for always being so supportive and always keeping my feet truly planted on the ground.

To my beautiful daughter Emilia, I dedicate this work to you.
Abstract

This thesis deals with the anomerisation of glycosidic linkages using TiCl$_4$ and SnCl$_4$. Methods involving the Lewis acid induced anomerisations of glycosides have been published over the past decade, however this methodology has not been widely utilised in carbohydrate chemistry due to low yields, large variations in selectivity, and the need for specific functional groups (e.g., carbamate). It is felt that a better understanding of the anomerisation reaction could be achieved by probing the effects of protecting groups and pushing the reaction to its limits.

Chapter 1 deals with the anomerisation of glycosyl azides. Previous work by Murphy et al. has led to reasonable but not high selectivity using SnCl$_4$. Since this work was carried out a seminal publication by Murphy et al. demonstrated the advantages of using TiCl$_4$ in anomerisation reactions. The application of TiCl$_4$ and varying the carboxylic functionality from acid to ester gave the desired high selectivities in good yields. Chapter 2 applies this successful approach to the anomerisation of disaccharide substrates, resulting in regioselective anomerisations and giving the desired α-products in high selectivities and yields.

Scheme 1: the anomerisation of glycosyl azides and disaccharides

Chapter 3 deals with the influence of protecting groups on the rate of the anomerisation reaction. The rate of anomerisation for has been quantified for 34 substrates in an attempt to elucidate the influence of the steric and electronic effects. It was evident from the results obtained that both steric and electronic effects have an influence on the rate of anomerisation.
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Symbols and Abbreviations

$\alpha$  \hspace{1cm} alpha

$\beta$  \hspace{1cm} beta

$\delta$  \hspace{1cm} chemical shift in ppm downfield from TMS

$[\alpha]_D$  \hspace{1cm} specific rotation

$^\circ C$  \hspace{1cm} degrees Celsius

2,2-DMP  \hspace{1cm} 2,2-dimethoxypropane

Å  \hspace{1cm} Ångstrom

Ac  \hspace{1cm} acetate

Ac$_2$O  \hspace{1cm} acetic anhydride

AcCl  \hspace{1cm} acetyl chloride

AcOH  \hspace{1cm} acetic acid

AgOTf  \hspace{1cm} silver triflate

BAIB  \hspace{1cm} (diacetoxyiodo)benzene

BF$_3$·OEt$_2$  \hspace{1cm} boron trifluoride diethyl etherate

Bn  \hspace{1cm} benzyl

BnBr  \hspace{1cm} benzyl bromide

Bu  \hspace{1cm} butyl

Bu$_4$NHSO$_4$  \hspace{1cm} tetrabutylammonium hydrogen sulfate

Bu$_4$NI  \hspace{1cm} tetrabutylammonium iodide

Bu$_4$NN$_3$  \hspace{1cm} tetrabutylammonium azide

Bz  \hspace{1cm} benzoate
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>BzCl</td>
<td>benzoyl chloride</td>
</tr>
<tr>
<td>COSY</td>
<td>Correlation Spectroscopy</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>D₂O</td>
<td>deuterium oxide</td>
</tr>
<tr>
<td>DBU</td>
<td>1,8-diazabicycloundec-7-ene</td>
</tr>
<tr>
<td>dd</td>
<td>Doublet of doublets</td>
</tr>
<tr>
<td>ddd</td>
<td>Doublet of doublets of doublets</td>
</tr>
<tr>
<td>DEPT</td>
<td>Distortionless Enhancement by Polarisation Transfer</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-dimethyaminopyridine</td>
</tr>
<tr>
<td>DMC</td>
<td>2-chloro-1,3-dimethylimidazolinium chloride</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMTST</td>
<td>N,N-dimethyl-N'-p-tolyl-sulfamide</td>
</tr>
<tr>
<td>dt</td>
<td>doublet of triplets</td>
</tr>
<tr>
<td>ES-HRMS</td>
<td>High-Resolution Mass Spectrometry - Electrospray Ionization</td>
</tr>
<tr>
<td>Et₃N</td>
<td>triethylamine</td>
</tr>
<tr>
<td>Et₃SiH</td>
<td>triethylsilane</td>
</tr>
<tr>
<td>EtOAc</td>
<td>ethylacetate</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared (spectroscopy)</td>
</tr>
<tr>
<td>gHMBCAD</td>
<td>Heteronuclear Multiple Bond Correlation</td>
</tr>
<tr>
<td>gHSQCAD</td>
<td>Heteronuclear Single Quantum Correlation</td>
</tr>
<tr>
<td>h</td>
<td>hours</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz</td>
</tr>
<tr>
<td>$J$</td>
<td>coupling constant, in Hz</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
<td>$M^+$</td>
<td>Mass of the molecular ion (mass spectrometry)</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>Me$_3$Si</td>
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</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>min</td>
<td>minutes</td>
</tr>
<tr>
<td>mL, µL</td>
<td>milliliter, microliter</td>
</tr>
<tr>
<td>mol, mmol</td>
<td>mole, milimole</td>
</tr>
<tr>
<td>MP</td>
<td>methoxyphenyl</td>
</tr>
<tr>
<td>NBS</td>
<td>$N$- bromosuccinimide</td>
</tr>
<tr>
<td>NIS</td>
<td>$N$- iodosuccinimide</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NOE</td>
<td>Nuclear Overhauser Effect</td>
</tr>
<tr>
<td>NOESY</td>
<td>Nuclear Overhauser Effect Spectroscopy</td>
</tr>
<tr>
<td>OTf</td>
<td>triflate</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>Piv</td>
<td>pivaloyl</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>Py</td>
<td>pyridine</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>S_N2</td>
<td>bimolecular nucleophilic substitution</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>TBAF</td>
<td>tetrabutylammoniumfluoride</td>
</tr>
<tr>
<td>TBDPS</td>
<td>tert-butyldiphenylsilyl</td>
</tr>
<tr>
<td>TBS</td>
<td>tert-butyldimethylsilyl</td>
</tr>
<tr>
<td>td</td>
<td>triplet of doublets</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-Tetramethyl-1-piperidinyloxy</td>
</tr>
<tr>
<td>TfOH</td>
<td>trifluoromethanesulfonic acid</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
<tr>
<td>TMSI</td>
<td>trimethylsilyl iodide</td>
</tr>
<tr>
<td>TMSN_3</td>
<td>trimethylsilyl azide</td>
</tr>
<tr>
<td>TMSOTf</td>
<td>trimethylsilyl trifluoromethanesulfonate</td>
</tr>
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</table>
Chapter 1: Introduction to carbohydrate chemistry and anomerisation

1.1 Introduction to carbohydrates

Previously looked upon as merely structural and energy storage biomolecules, carbohydrates are now seen clearly to be among the essential classes of biomolecules. Carbohydrates are the most abundant class of biomolecules found in nature and can be found in various forms, spanning from the simple monosaccharide to complex polysaccharides and glycoconjugates.\(^1\)\(^-\)\(^3\)

In the past 60 years carbohydrates have been implicated in many biological processes such as cellular proliferation, viral and bacterial infection, cell-cell recognition, fertilization, embryogenesis, neuronal development and hormone activities\(^4\)\(\)-\(^8\). The importance of carbohydrates has lead to an ever growing area of research, which is receiving more attention from the scientific community and the pharmaceutical industry, due to the potential to discover possible drug candidates. As it stands, over 50 synthetically prepared FDA approved drugs contain carbohydrates, while many more have evolved from carbohydrates with the use of medicinal chemistry\(^9\). In the case of some mono-, di- and trisaccharide conjugates, removal of the carbohydrate moiety greatly diminished the therapeutic value of the drug\(^9\).

One major issue is the availability of the biologically important glycans. Although they are the most abundant class of biomolecules, their diversity and complexity, which is taken advantage of in signalling systems, results in minute quantities of a single molecule forms being available for isolation\(^10\). It is at this point where synthetic carbohydrate chemistry enters the fray. Synthesis has been used as a tool to prepare adequate quantities of well defined natural glycans to probe their functional roles\(^1\). It is also a leading tool in the preparation of carbohydrate based therapeutics, due to the possibility of producing not just the natural glycans but various analogous glycans and glycojugates.
In nature oligosaccharide fragments are synthesised inside the cell, in the Golgi apparatus. Monosaccharides are taken up by the cell, converted into activated building blocks which can then be assembled by enzymatic means to form oligosaccharides and these oligosaccharides are then transported to their site of functionality.

Organic chemists have taken inspiration from nature for the chemical synthesis of oligosaccharides. However, differentiation between the various hydroxyl groups and the need to form stereoselective linkages, a feat which is achieved so elegantly in nature by enzymes, must now be achieved by chemical means. Although the majority of desired glycans are in theory accessible by chemical means, the synthesis of these complex structures is far from trivial. In 1982 Professor Hans Paulsen, declared: “Although we have now learned to synthesize oligosaccharides, it should be emphasized that each oligosaccharide synthesis remains an independent problem, whose resolution requires considerable systematic research and a good deal of know-how. There are no universal reaction conditions for oligosaccharide syntheses.” This is due in no small part to the issue of achieving stereoselectivity when preparing glycosidic linkages.

The following sections will introduce some carbohydrate terminology, as well as stereoelectronic effects, and will briefly discuss glycosidic bond formation including approaches towards stereoselective glycoside synthesis.

1.2 Carbohydrate terminology

The IUPAC nomenclature for carbohydrates is highly complex and for this reason it shall only be briefly addressed to help further understand the forthcoming concepts. The IUPAC nomenclature for carbohydrates has evolved away from the common systematic naming system used for organic compounds and in many cases trivial names are widely used and trivial names are often used. For example (2R,3S,4R,5R)-2,3,4,5,6-pentahydroxyhexanal is more commonly referred to as d-glucose. Carbohydrates can exist in cyclic and acyclic forms which can rapidly interconvert in solution, however cyclic forms tend to dominate (Scheme 2). For example an aqueous solution of solution d-glucose, the 5 membered furanose and the acyclic aldehyde, are collectively present to a level less than 1%.
Monosaccharides are numbered along the carbon chain of the Fischer projection (A) and this translates to the Haworth projection form (B).

**Scheme 2: Cyclisation and carbohydrate numbering**

Due to the aforementioned cyclisation of the open chain form, a stereogenic centre is formed which is referred to as the anomeric centre. The two resulting stereoisomers are referred to as α- and β-anomers. The orientation of the anomeric substituent in the Haworth projection determines which anomer is present. If the anomeric substituent is pointing in the Haworth projection then the β-anomer is present, while if it is pointing down the α-anomer is present. The cyclic hemiacetal form of both protected and non-protected carbohydrates can freely interconvert between the axial and equatorial orientations via its non-cyclic form (Scheme 3). It is relevant to note that such interconversions do not happen freely when dealing with glycosides and a greater energy barrier must be overcome to achieve anomerisation in such cases.

**Scheme 3: Interconversion between anomers of glucose**

### 1.2.1 The anomeric effect

During undergraduate chemistry courses, students are taught that substituents on a cyclohexane ring favour an equatorial orientation for steric reasons. However, it
has been shown that carbohydrates and similar systems, show preference for a conformation or configuration yielding an electron withdrawing substituent in an axial orientation at the anomeric centre, even in the case of bulky substituents (Scheme 4)\textsuperscript{17}. This phenomenon is due to a stereoelectronic effect known as the anomeric effect.

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\includegraphics[width=0.3\textwidth]{example.png}};
\node (b) at (2,0) {\includegraphics[width=0.3\textwidth]{example.png}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 4: Preference for an EWG to favour an axial conformation}\textsuperscript{17}

The anomeric effect does not only apply to carbohydrates, but also too many similar systems. The generalized anomeric effect applies to segments of the form $R-X-A-Y$, where $R$ represents a carbon atom in the ring, $X$ is a heteroatom in the ring which possesses lone pairs, $A$ is the anomeric carbon and $Y$ is an electronegative element or group. It is stated that there is a preference for an electron withdrawing substituent to lie in a gauche rather than in an anti position (Figure 1)\textsuperscript{18}. This preference has been explained by electrostatic and molecular orbital models.

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\includegraphics[width=0.3\textwidth]{example.png}};
\node (b) at (2,0) {\includegraphics[width=0.3\textwidth]{example.png}};
\end{tikzpicture}
\end{center}

\textbf{Figure 1: Newman projection depicting gauche and anti conformations}\textsuperscript{18}

Originally the anomeric effect was explained solely in terms of electrostatic interactions. This model postulated that a minimization of an unfavourable dipole interaction occurs when the electronegative substituent is in an axial orientation\textsuperscript{19}. In the axial orientation the dipoles are perpendicular and partially cancel each other out (Figure 2).
In studies carried out to further reinforce this model the effect of solvent polarity on the anomeric preference showed mixed results, further complicating the theory. It was predicted that a polar solvent would stabilize the more polar equatorial configuration thus driving the equilibrium to favour the equatorial anomer. Studies carried out on 2-methoxy tetrahydropyran followed this trend\textsuperscript{20}. However a study using 2-carbomethoxy-1,3-dithiane showed that the axial conformation was preferred in polar solvents at low temperatures\textsuperscript{21}. These experiments showed that the electrostatic model was not solely sufficient in explaining the anomeric effect.

The observation, involving the bond lengthening between the anomeric carbon and the aglycon atom, led to the explanation by a molecular orbital model\textsuperscript{22}. The stabilization and bond lengthening can be explained as being due to molecular orbital overlap, where the \textit{n}-molecular orbital of the endocyclic oxygen donates electrons into the $\sigma^*$ orbital of the C-X bond (Figure 3). This donation of electrons can only occur when the anomeric substituent is in an axial orientation due to the requirement of the oxygen orbital and the anti-bonding orbital’s to be anti-periplanar. The degree of stabilization is inversely proportional to the energy difference between the interacting orbitals. Greatest stabilization is achieved between two orbitals of similar energies\textsuperscript{17}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{Electrostatic model for the anomeric effect}
\end{figure}
For the purpose of this thesis it is also of interest to note factors which affect the magnitude of the anomeric effect, such as the nature of the aglycon and other ring substituents. The effect of the aglycon’s electron withdrawing character has been well studied\textsuperscript{17,23}. For example, variation of the anomeric substituent of tri-O-benzoate derivatives of xylopyranose, resulted in an increased preference for the $^{1}C_4$ conformation as the electron withdrawing character of the aglycon increases\textsuperscript{17}.

![Molecular orbital model](image)

**Figure 3: Molecular orbital model**

The magnitude of the anomeric effect has also been shown to be influenced by the electronegativity of the equatorial C-5 substituent\textsuperscript{18}. A study carried out by....

<table>
<thead>
<tr>
<th>X</th>
<th>% of $^{1}C_4$ conformer</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>19</td>
</tr>
<tr>
<td>MeO</td>
<td>26</td>
</tr>
<tr>
<td>AcO</td>
<td>47</td>
</tr>
<tr>
<td>BzO</td>
<td>50</td>
</tr>
<tr>
<td>F</td>
<td>90-100</td>
</tr>
<tr>
<td>Cl</td>
<td>98</td>
</tr>
<tr>
<td>Br</td>
<td>90-100</td>
</tr>
</tbody>
</table>

**Table 1: Conformational equilibria of xylose derivatives**\textsuperscript{17}
varying the equatorial C-5 substituent of tetra-O-acetate derivatives of glucose supports this theory, indicating that electron withdrawing groups increase the anomeric effect\textsuperscript{18}.

\[ \text{Table 2: Effect of substituent's at C-5}^{18} \]

<table>
<thead>
<tr>
<th>R</th>
<th>Anomeric effect, Kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.3</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>1.31</td>
</tr>
<tr>
<td>CH(_2)I</td>
<td>1.35</td>
</tr>
<tr>
<td>CH(_2)Cl</td>
<td>1.43</td>
</tr>
<tr>
<td>CH(_2)OAc</td>
<td>1.45</td>
</tr>
<tr>
<td>CH(_2)OTs</td>
<td>1.75</td>
</tr>
</tbody>
</table>

In compounds with an aglycon, where the atom bonded to the anomeric carbon possesses lone pairs, electron donation may occur in the opposite direction which is known as the exo-anomeric effect. This involves an interaction between the lone pairs of the aglycon and the antibonding orbital of the carbon-ring oxygen bond (Figure 4)\textsuperscript{24}. It has been stated that the exo anomeric effect is responsible for influencing glycoside conformation, which is a significant observation when one considers the importance of carbohydrate interactions\textsuperscript{25}.

\[ \text{Figure 4: The exo-anomeric effect}^{24} \]

Another related stereoelectronic effect, where a positively charged aglycon predominantly exists in an equatorial position, is known as the reverse anomeric
Introduction to carbohydrate chemistry and anomerisation

Section 1.2.2 Glycosidic bond formation

As previously stated, glycosidic linkages in nature are prepared in a regio- and stereospecific manner by nature’s enzymatic toolkit. Glycosyltransferases couple activated carbohydrates (donor) to a hydroxyl group of another carbohydrate (acceptor). The in vitro synthesis of glycosidic linkages has been inspired by this type of reaction. However, the lack of specificity in chemical synthesis, leads to the requirement of fully protected donors bearing a leaving group at the anomeric centre and a protected glycosyl acceptor bearing a free hydroxyl group (Scheme 6). The most common approach to chemical glycosidation involves the chemoselective activation of the leaving group on the donor molecule, leading to a highly reactive oxocarbenium intermediate. The planar nature of the oxocarbenium intermediate allows for attack from either face, leading to two possible diastereomeric products i.e., α- or β- anomers. It is important to note that although it is long assumed that glycosylation reactions go through an oxocarbenium ion, the intermediate has only been observed by mass spectrometry or in silico.

The nature of the anomeric leaving group has a great impact on a glycosylation reaction. Although various types of leaving groups can be found in the literature, three in particular dominate and shall be discussed briefly:
I. Glycosyl halides

Köenigs-Knorr type glycosylations were first introduced in 1901 and involve the activation of glycosyl bromides and chlorides using halophilic salts (e.g. AgOTf, Ag₂CO₃, HgBr, Hg(CN)₂)³³. The solubility of the salt largely controls the nature of the reaction. Soluble salts are believed to lead to the formation of an oxocarbenium intermediate, which can lead to the formation of either the α- or β-anomer (Scheme 7a). Insoluble salts give the reaction greater S_N₂ like character, resulting in an inversion of the stereochemistry at the anomeric centre (Scheme 7b)³⁴–³⁶.

![Scheme 7: Köenigs-Knorr glycosylations](image)

II. Thioglycosides.

Thioglycosides were first reported in 1909 by Fischer³⁷ and have received much attention, even to this day, with various methods of preparation and activation being reported³⁸. However it was not until the 1970s that they were utilized in polysaccharide synthesis³⁹. The stability, ease of preparation, the abundance of activation systems available and their tunable reactivity, has led to thioglycosides being used widely by the synthetic carbohydrate community¹¹,³⁸. The activation of thioglycosides can be carried out in a highly chemoselective manner, with thiophilic reagents being widely utilized (Scheme 8). The NIS/TfOH system introduced by van Boom⁴⁰ has been successful for a variety of systems and resulted in a trend towards a variety of halonium based systems¹¹,³⁸. Recently organosulfur compounds have been investigated as activating agents, with reagents such as DMTST, MeSOTf and PhSOTf receiving much attention¹¹. It has been observed that sulfinates and
Introduction to carbohydrate chemistry and anomerisation

Chapter 1

sulfoxides in the presence of Tf₂O can activate ‘disarmed’ donors, even at low temperatures\(^{41-43}\). One notable advantage of the variety of activation methods, particularly at lower temperatures, is the ability to preferentially activate donors, allowing for the further development of one pot strategies\(^{44}\).

![Scheme 8: Thioglycoside activation](image)

III. Trichloroacetimidates

The trichloroacetimidate method, introduced by Schmidt and co-workers in 1980\(^{45}\), was the first universal glycosylation method which avoided the use of heavy metals and where activation could be achieved with catalytic quantities of Lewis acid. Although primarily used in the synthesis of \(O\)-glycosides, examples of its use in the synthesis of \(S\)-, \(N\)-, \(P\)- and \(C\)-glycosides have been described in the literature\(^{46}\). Trichloroacetimidate donors are seen to be reasonably stable, but lack the stability associated with thioglycosides. Nonetheless, they are easily prepared from the corresponding hemiacetal with trichloroacetonitrile in the presence of base, with strong bases giving thermodynamically favoured \(\alpha\)-imidate and weak bases giving the kinetically favoured \(\beta\)-imidate (Scheme 9a). Mild Lewis acids, such as BF\(_3\).OEt\(_2\) and TMSOTf, have been shown to efficiently and catalytically activate anomic imidates at room temperature and at lower temperatures (Scheme 9b). Such mild conditions have resulted in trichloroacetimidate donors being successfully applied in solid phase carbohydrate synthesis\(^{11}\).
1.2.2 Factors effecting carbohydrate reactivity

The nature of the substituents about the pyranose ring has the largest effect on the carbohydrate reactivity. In 1908, Glover et al. reported that the rate of glycoside hydrolysis was directly related to the number of axial substituents about the ring\(^{47}\). It was initially proposed that this was a result of a decrease in steric strain, leading from the reactant to the planar oxocarbenium intermediate\(^{19}\). However, studies carried out by the group of Withers have shown that the rate of glycoside hydrolysis decreases when a hydroxyl group is replaced by a more electron withdrawing fluorine atom, while the corresponding deoxy derivative shows an increase in the rate of hydrolysis\(^{48,49}\). These results indicate that the reactivity of glycosides, at least towards hydrolysis, is mainly dependent on the electronic properties of the substituents.

**Figure 1: Effect of substituent orientation on the rate of hydrolysis\(^{48}\)**
Bols et al. further investigated this phenomenon using a variety of amino sugar model compounds, where they noted that the basicity of the endocyclic nitrogen was similarly dependent on the substituents about the ring. They then proposed that equatorial substituents have greater electron withdrawing power than the corresponding axial substituent, due to charge dipole interactions. This interaction, although not fully explained, is believed to be due to the dipole associated with the respective hydroxyl groups. This further explains the rate increase observed with an increasing number of axial substituents, as the more electron rich pyranose can better stabilise the positive charge build up leading to the oxocarbenium ion intermediate. Additional studies also showed that steric effects do not largely impact the reactivity of carbohydrates towards hydrolysis, thus disproving the Edwards hypothesis.

As one may imagine, protecting groups can further emphasize the reactivity dependence on electronic effects. The “armed-disarmed” terminology is widely used to depict the reactivity of protected carbohydrates. In 1982, Paulsen noted that “benzyl protected compounds are always more reactive than the acetylated or benzoylated derivatives”. Following this, Fraiser-Reid investigated the effect of protecting groups on the oxidative hydrolysis of \( n \)-pentenyl glycosides, which resulted in the benzyl derivative (armed) reaching completion six times faster than the corresponding acetate derivative (disarmed) (Scheme 10). The difference in reactivity is due to the inductive properties of the protecting groups. The electron inducing benzyl ethers accelerated activation of the leaving group and they are said

---

Figure 2a) Basicity of substituted amino sugars; b) Electron withdrawing ability based on dipole effects

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to be activating, whereas electron withdrawing esters, partially retard the activation and are said to be deactivating. In general the same rules apply for the protecting groups on glycosyl acceptors, where the greater electron density about the ring leads to a more reactive acceptor\textsuperscript{12,54}.

\begin{center}
\includegraphics[width=\textwidth]{scheme_10.png}
\end{center}

**Scheme 10: Effect of protecting groups on the hydrolysis pentenyl glycosides\textsuperscript{54}**

Conformational changes also influence the reactivity of carbohydrates. For example, glucose in the $^1\text{C}_4$ conformation has a greater number of axial substituents than glucose in the $^4\text{C}_1$ conformation and thus the $^1\text{C}_4$ conformation is more reactive towards hydrolysis. The relative rate of hydrolysis of the 3,6-anhydrosugar shown below exemplifies this\textsuperscript{55}.

\begin{center}
\includegraphics[width=\textwidth]{figure_7.png}
\end{center}

**Figure 7: Effects of conformational changes on reactivity\textsuperscript{55}**

Bulky silyl protecting groups have also been used to induce a ring flip to the more reactive $^1\text{C}_4$ conformation\textsuperscript{56–58}. Donors and acceptors of this sort are said to be “super armed” and can be selectively activated at low temperature and therefore such compounds are useful in one pot strategies (Scheme 11).
1.3 The stereoselective synthesis of glycosides

The formation of a stereoselective glycoside bond is possibly the biggest challenge in carbohydrate syntheses. Glycosides are classified according to the relative and absolute configuration at C-1 and C-2, namely 1,2-trans and 1,2-cis (Figure 8).

Although this area is well studied and many of the challenges have been overcome, there remains a need for a general method of stereoselective glycoside formation. The introduction of a desired stereochemistry is in the majority of cases carried out in the glycosidic bond forming step. An alternative method is to carry out an anomerisation reaction post-glycosidic bond formation.

1.3.1 Stereochemical control in glycosylation reactions

In section 1.2.2, a basic mechanism of glycosylation reactions is presented, however in reality the numerous possible intermediates can impact the stereochemical outcome of a glycosylation reaction (Scheme 12). The activated glycosyl donors can undergo SN2 type nucleophilic attack leading to inversion of the
anomeric stereochemistry. Partial dissociation results in contact ion pairs, in which the anion can block nucleophilic attack on the partially associated face, thus leading to an $S_N1$ with inversion. Upon full dissociation a solvent separated ion pair is thought to occur and the outcome of the reaction is dependent on the relative energy of the transition states leading the product(s). The figure below omits the influence of solvent and directing protecting groups which, in conjunction with the glycosyl donors and the method of activation, play important roles in the stereochemical outcome of a glycosylation reaction. A summary of methods utilized to control the anomeric selectivity in glycosylation reactions shall therefore be presented below.

![Scheme 12: Mechanism of glycosylation](image)

The synthesis of 1,2-trans glycosides can be trivial relative to the synthesis of 1,2-cis glycosides. The use of a participating protecting group (ester or amide) at position 2, allows for the preparation of a 1,2-trans linkage in a highly selective manner. The selectivity is derived from the attack of the carbonyl of the participating group on the oxocarbenium intermediate, giving rise to an acyloxonium intermediate. The $S_N2$ type nucleophilic attack on this intermediate leads to the 1,2-trans product (Scheme 13). An orthoester side product can result but can be rearranged to the desired glycoside under acidic conditions.

---

1 Recreated from ‘Stereoselective Glycosylation’ notes of Prof. David Crich.
Novel protecting group systems have also been utilized to induce anomeric selectivity. Boons et al. developed a method involving a (ethoxycarbonyl)benzyl ether at the 2-position where the stereochemical configuration of the protecting group determines the selectivity attained (Scheme 14)\textsuperscript{61}. The ethyl ester of the protecting group, can nucleophilically add to the oxocarbenium intermediate, forming an acyloxonium intermediate. The steric interactions of the phenyl group, determines the stereochemistry of this intermediate and subsequent S\textsubscript{N}2 type nucleophilic attack leads to the glycosidic bond formation. Similar approaches involving cyclic sulfonium donors\textsuperscript{62} and picolyl protecting groups\textsuperscript{63} have also been employed.

**Scheme 13: Neighbouring group participation**

**Scheme 14: Neighbouring group participation of (ethoxycarbonyl)benzyl ether protecting groups\textsuperscript{61}**
The choice of reaction solvent or co-solvent can help in achieving the desired stereoselectivity. Ethers, such as diethyl ether and THF, have been seen to increase the $\alpha$-selectivity of a reaction$^{64-66}$. The oxygen of the ether adds to the oxocarbenium ion, resulting in a beta oxonium intermediate, guided by a preference for ether to take an equatorial orientation. The reactive intermediate can be displaced leading to higher $\alpha$-selectivities. In contrast the use of acetonitrile as a solvent or co-solvent is seen to result in increased $\beta$-selectivity$^{65}$. In this case, an $\alpha$-nitrilium intermediate is believed to occur and inverse displacement results in high quantities of $\beta$-anomer$^{65,67,68}$.

![Scheme 15: Solvent effects on glycosylation reactions](image)

As previously mentioned, glycosyl halides activated with insoluble salts, can be displaced with anionic nucleophiles, inverting the stereochemistry$^{34-36}$. Anomeric halides preferentially exist as the $\alpha$-anomer which, will be displaced to give the $\beta$-glycoside. Addition of tetrabutyl ammonium halide leads to an anomerisation of the $\alpha$-halide. The more reactive $\beta$-halide is readily displaced by non anionic nucleophiles and thus can be used in O-glycoside synthesis using alcohols. Lemieux pioneered this system in 1975 using glycosyl bromides and Bu$_4$NBr$^{69}$. Similarly Gervay-Hague investigated the reactivity of glycosyl iodides in the presence of Bu$_4$NI, resulting in reasonable $\alpha$-selectivities$^{70,71}$.

![Scheme 16: In-situ $\beta$-halide formation$^{69}$](image)
Trichloroacetimidates have also been shown to undergo $S_N2$ type reactions. The relative ease with which $\alpha$- and $\beta$-trichloroacetimidates can be selectively prepared makes this an attractive procedure. Lewis acid activation at low temperatures has lead to imidate displacement, thus inverting the stereochemistry at the anomeric centre.$^{45,72,73}$

![Scheme 17](image1.png)

**Scheme 17: The $S_N2$ type displacement of trichloroacetimidates**$^{72,73}$

Preactivation in the presence of $\text{Tf}_2\text{O}$ results in high $\beta$-selectivities in the case of 4,6-benzylidene protected mannosyl thioglycosides and sulfoxides.$^{42,74}$ Crich and co-workers, with the aid of low temperature NMR studies, postulate that the acceptor reacts to give an $\alpha$-anomeric triflate(C) or the corresponding contact ion pair(D), rather than the free oxocarbenium ion(B) (Scheme 18)$^{75}$. It was thought that the benzylidene protecting group invokes torsional ring strain which disfavours the formation of the planar oxocarbenium ion.

![Scheme 18](image2.png)

**Scheme 18: Mechanism proposed by Crich.**

Schmidt showed that the activation of 4,6-benzylidene protected mannosyl trichloroacetimidates with $\text{TMSOTf}$ also resulted in high $\beta$-selectivity$^{76}$. He suggested a flattened twist boat conformer as the reactive intermediate, as this conformer would favour attack from the $\beta$-face for steric and electronic reasons.$^{76,77}$
Interestingly analogous glucose donors result in high $\alpha$-glycoside selectivity and it is thought they favour an SN1 like mechanism, with nucleophilic attack on a free oxocarbenium intermediate\textsuperscript{78}. This additionally questions the effect of the C-2 substituent and Schmidt proposed that in the case of the mannose type structures, the electron withdrawing C-2 substituent would further favour his proposed intermediate, due to a favourable dipole interaction\textsuperscript{77}. However it is also fair to suggest that an electron withdrawing group at C-2 may disfavour the formation of an oxocarbenium intermediate, thus favouring the anomeric triflate or corresponding contact ion pair\textsuperscript{79}. When investigating the kinetic isotope effect on the reaction, Crich showed that the reaction went through a SN1 type mechanism, suggesting that the anomeric triflate dissociates prior to nucleophilic attack\textsuperscript{80}. Whitfield \textit{et al.} have suggested that this may be the case in all types of glycosylations\textsuperscript{60}. He suggests that rather than SN2 type displacement of a covalently bonded leaving group, it is nucleophilic displacement of the corresponding contact ion intermediate pair which results in the stereochemical outcome of the reaction.

Thus far, the role of various leaving groups, additives and auxiliaries has been discussed, but what of the free oxocarbenium ion (assuming it is formed) and how can the resulting selectivities be rationalised? A free oxocarbenium ion can exist in a variety of conformations, however the $^4\text{H}_3$ and $^3\text{H}_4$ conformations dominate\textsuperscript{81,82}. Nucleophilic addition to these half chair conformers occurs in a pseudo axial fashion, with attack on the face leading to a favoured chair transition state rather than a twist boat transition state.

**Scheme 19: Mechanistic proposal of Schmidt\textsuperscript{76,77}**

![Scheme 19: Mechanistic proposal of Schmidt](image-url)
Introduction to carbohydrate chemistry and anomeration

Chapter 1

Scheme 20: Nucleophilic attack on free oxocarbenium ion conformers.

Much insight on the effect of substituents has emerged from the work carried out by the group of Woerpel, where they have extensively studied the effect of substituents about the pyranose ring and the resulting stereoselectivities\(^{83}\). It has been shown that electronegative substituents at C-3 and C-4 favour an axial orientation, electrostatically stabilising the oxocarbenium ion, thus favouring one conformer over the other\(^{81,82}\). It is somewhat of an assumption that these factors also stabilise the transition states, however studies on model substrates, investigating the effects individually exonerate these claims (Scheme 21 A & B)\(^{84,85}\). In the case of substituents at C-5 and C-2, steric interactions seem to be greater and influence the outcome as shown in Figure 29 examples C & D.

Scheme 21: Effect of electron withdrawing substituent’s at C-3 & C-4\(^{84,85}\)
Woerpel et al., also investigated pyranose rings bearing multiple substituents. The outcome of these reactions is less predictable, as steric interactions between the substituents and the incoming nucleophiles come into play. In such situations the product may not arise from the stereoelectronically stabilised conformation (A), as steric interactions result in a higher energy barrier leading to the associated transition state (TS A) for product formation. The energy barrier leading to the transition state for conformational interconversion (TS C) is relatively low, consequently conformational interconversion may readily occur. According to the Curtin Hammet principle, the product may therefore arise from an energetically less favoured conformation (B) in which the energy barrier leading to the associated transition state (TS B) for product formation is less.

![Energy diagram showing transitions between conformations](image)

**Figure 9: Curtin Hammet principle**

1.3.2 Anomerisation

The anomerisation of glycosides involves an acid or base induced reaction, which results in the formation of the thermodynamically favoured anomer. Anomerisation reactions have been studied for the best part of a century, with the first Lewis acid anomerisations being reporting by Pacsu in the late 1920s and early 1930s.
The mechanism of such Lewis acid induced anomerisations has been debated, with two alternative pathways being proposed. Lemieux proposed an exocyclic mechanism, where the anomeric substituent is activated by the Lewis acid, thus leading to a contact ion oxocarbenium intermediate. The cleaved aglycon can then attack the oxocarbenium leading to either the α- or β-glycoside. As this reaction is reversible, at reaching equilibrium the α-anomer is thermodynamically favoured (Scheme 23A) \(^{89,90}\). Lindberg proposed an alternative mechanism involving endocyclic cleavage. This involves Lewis acid coordination to the ring oxygen, leading to cleavage of the O5-C1 bond resulting in an open chain intermediate. Rotation about the C1-C2 bond and nucleophilic addition of O-5 leads to the thermodynamically favoured product (Scheme 23B) \(^{91}\).

Scheme 23: Suggested anomerisation pathways; A) Exocyclic cleavage; B) Endocyclic cleavage.

It is now widely accepted that both pathways can occur, but that Lewis acid induced anomerisations predominantly follow the endocyclic pathway. Crossover experiments have indicated that both pathways might operate but the exocyclic pathway seems much slower if it occurs\(^{92}\). Murphy et al. and Manabe et al. have also carried out trapping experiments, which resulted in the trapping of an open chain intermediate that arises from endocyclic cleavage (Scheme 24) \(^{93,94}\).
As with glycosylation reactions, work has been invested into understanding the factors which alter the rate and the selectivity in anomerisation reactions. The anomeric ratios resulting from an anomerisation reaction seem to be related to the magnitude of the anomeric effect in the compound. Factors influencing the anomeric effect have been previously outlined in section 1.1.2. The nature of the protecting group plays a key role in both the rate and stereochemical outcome of anomerisation reactions. Even somewhat slight variations have resulted in substantial reactivity differences. For example, replacing acetate protecting groups with benzoate protecting groups leads to an increase in the rate of the reaction and an increased amount of $\alpha$-anomer\textsuperscript{93,95}. Koto et al. investigated the effect of ether protecting groups relative to acetate protecting groups, observing a significant increase in the rate of reaction when the acetate of O-6 was replaced with a benzyl or methyl ether\textsuperscript{96}. This suggested that increasing the electron density at O-6 enhances the ability of the oxygen to chelate to the Lewis acid. Studying the anomerisation reactions of substrates lacking the functionality confirmed this hypothesis\textsuperscript{96}. Further studies investigating electronic effects, demonstrated that per-benzylated systems anomerised much faster than para-chlorobenzylated protected systems, indicating that increasing the electron density about the pyranose ring stabilises the transition state leading to the reaction intermediate resulting in a faster reaction\textsuperscript{97}. 

**Scheme 24: Trapping experiments: A) Manabe et al.\textsuperscript{94}; B) Murphy et al.\textsuperscript{93}**

![Scheme 24](image-url)
Protecting groups inducing ring strain such as 2,3-trans-carbamates and carbonates have been more recently employed in anomerisation reactions\textsuperscript{98–101}. Reactions carried out involving a 2,3-trans-carbamate glucosyl thiol donor, resulted in unusually high \( \alpha \)-selectivity\textsuperscript{102}. It is speculated that the carbamate protecting group locks the carbohydrate in a \( ^4C_1 \) conformation and the ring strain encourages endocyclic cleavage\textsuperscript{94}. Crich \textit{et al.} have recently disclosed their unsuccessful attempts to study the mutarotation of 4,5-trans-carbamate protected sialosyl hemiacetals, due to a preference for the open chain keto form, reflecting the strain imposed by the presence of the cyclic carbamate\textsuperscript{103}. Ye \textit{et al.} developed a one pot glycosylation-anomerisation utilizing a 2,3-trans-carbonate to great effect\textsuperscript{101}. More recently Manabe \textit{et al.} have demonstrated the anomerisation of multiple \( \beta \)-glycosidic linkages in a single reaction, where the nature of the substituent on the nitrogen of the carbamate is seen to have an important influence on the resulting anomeric ratio\textsuperscript{104}.

<table>
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<th>Entry</th>
<th>( R^1 )</th>
<th>( R^2 )</th>
<th>( R^3 )</th>
<th>( R^4 )</th>
<th>Time (s)</th>
<th>% of ( \alpha )-anomer</th>
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</thead>
<tbody>
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<td>OBn</td>
<td>OBn</td>
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<td>OAc</td>
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<tr>
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<td>OAc</td>
<td>OAc</td>
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<td>OBn</td>
<td>OBn</td>
<td>H</td>
<td>4</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 3: Effect of substituents at C-5 studied by Koto \textit{et al.}\textsuperscript{96}
The Murphy group have utilised a rate increase associated with having a carbonyl group at C-6 of the pyranose ring\textsuperscript{92,93,105–109}. While carrying out glycosylation reactions with glucuronic acid derivatives using SnCl\textsubscript{4} as the activating agent, it was noticed that an α-favourable mixture was achieved even in the presence of a participating group at C-2\textsuperscript{105,108}. Further investigations, involving a series of β-glycosides and treating them with SnCl\textsubscript{4} resulted in the formation of comparable anomeric mixtures, thus concluding that a glycosylation-anomerisation reaction was occurring (Scheme 26A) \textsuperscript{92}. A glycosylation-anomerisation reaction has also been disclosed by Hindsgaul and Lemieux in 1980\textsuperscript{110} where the presence of a carboxylic acid group in a group at the 2-position led to an increase in anomerisation rate.
The electronic nature of the aglycon has a large effect on the rate and the stereochemical outcome of the reaction, where $O$-cyclohexylglycosides (electron inducing) were seen to be faster than $O$-phenyl glycosides (electron withdrawing)\cite{105}. A similar effect has been demonstrated by Magnusson et al. in 1998\cite{111}. Altering the carboxyl functionality also has an effect on the reaction outcome. While carboxylic acids result in the greatest rate enhancement, esters gave rise to higher ratios in favour of the $\alpha$-product\cite{92,93}.

Scheme 26: Glycosylation anomerisation; A) Murphy et al.\cite{92}; B) Hindsgaul & Lemieux\cite{110}

Scheme 27: Glycolipid synthesis with anomerisation as the key step\cite{107}
The choice of Lewis acid is key and in some cases system specific. For example, TiCl$_4$ is not compatible with the carbonate or carbamate type systems while BF$_3$.OEt$_2$ has been applied successfully$^{101}$. Conversely SnCl$_4$ and TiCl$_4$ have led to anomerisation in simple per-acylated systems in dichloromethane, whereas BF$_3$.OEt$_2$ requires the use of MeNO$_2$ as a solvent, thus increasing its Lewis acidity$^{93,111}$. It has been shown that the concentration and stoichiometry of the Lewis acid does not only affect the rate of the reaction but the selectivity also$^{93,96}$. Increases in both concentration and stoichiometry have been demonstrated to further favour the $\alpha$-anomer, although the latter does not proceed in a linear fashion and is substrate specific$^{93}$. The reaction temperature also affects the anomeric ratio at equilibrium, with lower temperatures resulting in higher quantities of $\alpha$-anomer$^{93}$.

Main aim of this thesis work

Although anomerisation reactions have been studied for the best part of a century, the literature available relative to that of glycosylation based methodology is minimal. This is due to the anomerisation requiring somewhat specific structural features, which may not be straightforward to introduce. Low yields often resulted due to Lewis acid assisted ether cleavage and degradation in the presence of benzyl groups. It has been the primary aim of this thesis to further develop an understanding of SnCl$_4$ and TiCl$_4$ induced anomerisation reactions of substrates which have acyl protecting groups, with a view of expanding the applicability of the reaction in the synthesis of glycosides.
Chapter 2: The anomerisation of glycosyl azides

2.1 Introduction to glycosyl azides

Carbohydrates exist predominantly in biological systems as glycoconjugates and are omnipresent on cellular surfaces\(^1\). This being the case there is a need for straightforward methods to prepare both natural and unnatural structures to probe the functionality of these carbohydrates. Glycosyl azides serve as a useful class of intermediates in carbohydrate chemistry due to their stability and versatility, and are frequently used as precursors in the synthesis of natural and unnatural N-linked structures of biological importance (Scheme 28).

![Scheme 28: Glycosyl azide transformations\(^{112-123}\)](image)

The posttranslational N-glycosylation of proteins has a great impact on the functionality of the protein in its biological environment\(^{124,125}\). However, isolated N-linked glycopeptides and glycoproteins are usually heterogeneous, thus chemical synthesis can be used to elucidate the structural detail and biological activity\(^{126}\). One of the major difficulties associated with the synthesis of N-linked glycopeptides is the stereoselective preparation of the glycoside amide\(^{123}\). Preparation via a glycosyl azide using classical Staudinger conditions can result in anomic mixtures due to...
anomerisation of the iminophosphorane intermediate, however optimization has led to highly stereocontrolled reactions\textsuperscript{119–122}. Traceless Staudinger ligations were later applied, yielding much success, due to the intramolecular nature of the reaction (Scheme 29)\textsuperscript{127,128}.

Scheme 29: Traceless Staudinger ligations; A) Bernardi et al.\textsuperscript{127}; B) Kiessling et al.\textsuperscript{128}

The reinvigoration of the azide-alkyne Huisgen cycloaddition in the last ten years by click chemistry associated methodologies has led to the reaction being widely used in all branches of chemistry, with carbohydrate chemistry being no exception\textsuperscript{129–139}. A simple Reaxys\textsuperscript{®} search results in 1014 hits from 245 research articles where the starting material is a glycosyl azide and the product is a result of an azide-alkyne Huisgen cycloaddition. The robust nature of the triazole functionality makes it ideal for coupling sugars to solid surfaces and to incorporate carbohydrates into molecules with potential therapeutic value\textsuperscript{129}.

Scheme 30: Generalised Reaxys\textsuperscript{®} structure search March 2014

It has been shown that triazoles effectively mimic \textit{trans}-amide bonds\textsuperscript{140–146}, and due to this various neoglycopeptides containing carbohydrates appended to the peptide via a triazole have been synthesised\textsuperscript{147–155}. This linkage is prepared from a glycosyl azide and alkyne containing amino acid derivative or vice versa. These
The anomerisation of glycosyl azides

Triazole containing neoglycopeptides offer an alternative to C-linked derivatives which are tedious to prepare and are often low yielding\textsuperscript{147}. The increased stability of these neoglycopeptides to enzymatic cleavage can increase the half life of the molecule in biological systems and may possibly increase the biological activity\textsuperscript{156}.

![Scheme 3: Neoglycoconjugate synthesis\textsuperscript{157}]

Carbohydrates involved in signalling pathways can interact with carbohydrate binding proteins known as lectins. It has been shown that multivalency is important in such interactions and that individual carbohydrate structures show only low affinity\textsuperscript{158,159}. A variety of such multivalent structures showing biological activity have been prepared via glycosyl azides\textsuperscript{160–166}.

2.2 Synthesis of glycosyl azides.

The first glycosyl azide was synthesised by Bertho in 1930 with the displacement of a glycosyl bromide with NaN\textsubscript{3}\textsuperscript{167}. Procedures of this type usually require high temperatures, which is preferably avoidable with azides. Protocols utilizing phase transfer catalysis in a diphase system can be carried out at room temperature and...
result in comparable yields\textsuperscript{168}. Garvey-Hague \textit{et al.} have also shown the successful preparation of glycosyl azides via a glycosyl iodide intermediate in a one pot procedure\textsuperscript{169}. Lewis acid catalysed activation of an anomic acetate in the presence of TMSN\textsubscript{3} has been shown to prepare glycosyl azides in high yields with initial methods using SnCl\textsubscript{4}\textsuperscript{33}. More recently catalytic amounts of FeCl\textsubscript{3} have been applied, resulting in glycosyl azide formation in greater than 85% yield\textsuperscript{170}. The preparation of glycosyl azides from unprotected carbohydrates has recently been explored by Shoda \textit{et al.}, using DMC to selectively activate the anomic hydroxyl group in the presence of base and sodium azide, resulting in exclusively β-selectivity\textsuperscript{171}.

![Scheme 32: General procedures for the preparation of glycosyl azides](image)

### 2.2.1 The preparation of 1,2-\textit{cis} glycosyl azides.

Thus far the methodologies described above result in the formation of 1,2-\textit{trans} glycosyl azides, although some can be altered to invert the selectivity. For example 1,2-\textit{cis} glycosyl azides can be prepared from anomeric halides, where the nucleophilic azide source displaces the less stable β-halide which can be prepared directly or in situ from the α-halide using a tetrabutylammonium halide salt. Both methods have been utilized with a variety of azide sources, however selectivity and reaction yields vary dramatically\textsuperscript{172–177}. While attempting to prepare α-azides of L-fucose derivatives from the corresponding α-iodide in the presence of Bu\textsubscript{4}NI,
Bernardi et al. showed the influence of azide source on the selectivity of the reaction\textsuperscript{127}. Reactions carried out using Bu$_4$NN$_3$ resulted in β-azide formation while NaN$_3$ gave the desired α-product. The reaction outcome was attributed to the relative solubilities of the azide sources.

<table>
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<tr>
<td>Bu$_4$NN$_3$</td>
<td>β-anomer</td>
<td>36%</td>
</tr>
<tr>
<td>NaN$_3$</td>
<td>α-anomer</td>
<td>64%</td>
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</table>

Scheme 33: Effects of azide source on stereochemical outcome\textsuperscript{127}

The preparation of glycosyl azide via free radical chemistry has been documented by Renaud et al. in 2001\textsuperscript{178}. As with many radical reactions involving carbohydrates, complete α-selectivity was achieved\textsuperscript{179}. The reaction when carried out with 2-deoxy glucose dithiocarbonate derivative results in product formation in good yield, however the yield from the glucose dithiocarbonate derivative is poor as the 2-$O$-acetyl group impedes the reaction and it is proposed that this is due to β-alkoxy effect\textsuperscript{180}.

Scheme 34: α-azide preparation via free radical chemistry\textsuperscript{180}

More recently Compain et al. published the preparation of α-glycosyl azide via 1,6-Anhydro sugars\textsuperscript{181}. These reactions are catalysed by TMSOTf and selectivities ranging from 1:1 to >20:1 α:β are reported in moderate to good yields. Interestingly the stereochemical outcome of the reaction is rationalised based on preferential nucleophilic attack on the $^4$H$_3$ oxocarbenium intermediate.
The preparation of glycosyl azides via Lewis acid promoted glycosylation has been referred to above. These reactions are usually carried out with catalytic quantities of SnCl₄ for 2-10 hours. The stereochemical outcome of the reaction is dependent on the nature of the substituent at C-2. Under these conditions and the presence of a participating protecting group at C-2, 1,2-trans selectivity is observed. However, it has been seen that increasing the quantity of SnCl₄ and the reaction time can result in anomerisation and a mixture of the α- and β-glycosyl azides. The effects of substituents on such anomerisation reactions have been studied extensively by Murphy et al.

2.3 Objectives.

Although the reported method to prepare α-glycosyl azides by Murphy et al. results in respectable α-selectivity, it was envisioned that increasing the anomic
selectivity and the yield towards the synthesis of such compounds, would further enhance their synthetic utility. Recent studies have shown that TiCl₄ results in faster anomerisations and greater amounts of the α-anomer.²⁹,¹⁰⁶,¹⁰⁷ It was proposed that varying the carbonyl substituent at C-6 and opting for TiCl₄ rather than SnCl₄ may provide the desired result. It was also felt that carrying out the glycosylation and anomerisation reactions separately will lead to a greater understanding of the anomerisation reaction.

2.4 Results and discussion.

Initial studies were carried out on methyl 2,3,4-tri-O-acetyl-1-azido-1-deoxy-β-D-glucopyranuronate 3, which was prepared in 3 steps from D-glucurono-6,3-lactone 1 according to literature procedures.¹⁸⁷

**Scheme 37: Synthesis β-glucopyranuronate azide**

Carrying out the anomerisation reaction with 2.5 equivalents of TiCl₄ at room temperature overnight proved promising, with greater than 90% α-selectivity being observed. However the yield of the reaction was as low as 47%, this being mainly due to the presence of side products and the formation of a thick emulsion upon workup with saturated aqueous NaHCO₃. Lowering the reaction to -15 °C inhibited the formation of side products and resulted in an increase in the yield of reaction to 65%. This result indicated that to further increase the reaction yield, emulsion formation had to be prevented. A variety of aqueous quenches were investigated, such as a 1M KHSO₄ wash which prevents emulsion formation in reactions with SnCl₄, however it did not prove successful in this case. Washing with 1M HCl or brine, followed by a sat. aq. NaHCO₃ wash was also unsuccessful. Washing once with sat. aq. NH₄Cl reduced emulsion formation in the sat. aq. NaHCO₃ wash. Washing twice with sat. aq. NH₄Cl completely prevented emulsion formation, with the yield being increased to 91% and an α:β ratio of 95:5 being observed.
Following this work-up optimisation, the effect of the ester on the stereoselectivity was investigated. The allyl ester derivative 6 was prepared from 3, which underwent saponification with LiOH in a THF/H₂O/MeOH to give 5 in 93% yield. Treatment of 5 with allyl iodide in DMF, followed by the addition of Ac₂O and DMAP gave 6 in 71% yield. Treatment of the allyl ester under optimised anomerisation conditions gave 7 in 82% with an α:β ratio of 94:6. It has been reported that the presence of an allyl ester results in faster anomerisation and higher anomeric selectivities, however in this case the difference seemed negligible, hence the methyl ester was utilised from this point on in the study.

Scheme 39: A) Synthesis of allyl ester derivative 6; B) Anomerisation of 6

With the glucopyranuronate ester derivatives in hand, interest turned towards other monosaccharide substrates. The galactopyranuronate methyl ester was an obvious choice, however an analogous synthetic pathway to that utilised for the synthesis of 3 proved unsuccessful, as the SnCl₄ catalysed glycosylation resulted in an anomeric mixture of the glycosyl azide. Anomerisation studies with galactose substrates has shown them to undergo anomerisation at a faster rate than the corresponding glucose derivatives due to the greater electron density about the pyranose ring, hence even catalytic amounts of SnCl₄ and short reaction times resulted in undesired anomerisation. Attempts to prepare the β-galactopyranuronate
The anomerisation of glycosyl azides

azide via an \(\alpha\)-glycosyl bromide in DMF in the presence of NaN\(_3\) with conventional heating also resulted in anomeric mixtures, which may be due to the solubility of NaN\(_3\), as it is only partially soluble under such conditions. The slow nature of the reaction, allows the soluble NaBr side product to displace the \(\alpha\)-bromide resulting in the more reactive \(\beta\)-bromide, which can also be nucleophilically displaced by anionic azide, resulting in anomic mixtures (Scheme 40).

Scheme 40: Proposed mechanism for the formation of anomic mixtures under standard reaction conditions

Interestingly, carrying out the reaction in sealed Biotage microwave vial with the aid of sonication gave the \(\beta\)-azide 11 exclusively in 92% yield\(^{188}\). Anomerisation of 11 gave 12 in high yield and high selectivity.

Scheme 41: Synthesis and anomerisation of the galactopyranuronate ester derivative 11

The commercial unavailability of mannuronic acid led to the preparation of the mannospyranuronate methyl ester 18 derivative via D-mannose. Treatment of the peracetylated compound 13 with I\(_2\) and Et\(_3\)SiH in DCM, gave an intermediate
The anomerisation of glycosyl azides

glycosyl iodide which was immediately reacted with Bu₄NN₃ in DCM to give 14 in 64% yield\textsuperscript{169,189}. The resulting azide was then subjected to Zemplén deacetylation, followed by a one pot silylation-benzylation to give 16\textsuperscript{54}. Removal of the silyl protecting group with HF-pyridine gave 17 in 85% yield. TEMPO/BAIB mediated oxidation, followed by base catalysed esterification gave 18. The anomerisation of 18 gave 19 in high yield and high selectivity.

\[\text{Scheme 42: Synthesis and anomerisation of the mannopyranuronate ester derivative 18}\]

Attention then turned to the preparation of the 2-deoxy-\textit{N}-acetyl-glucuronides 30 and 31, which were prepared in a similar manner to 18. An analogous synthesis has also recently been published by Burn \textit{et al}\textsuperscript{190}. The peracetylated precursor was treated with HBr to give the glycosyl bromide which was treated directly with Bu₄NN₃ to give glycosyl azides 22 and 23\textsuperscript{157}. Deacetylation followed by one pot silylation and benzylation gave 24 and 25, both in good yield. The silyl group was then removed with HF-pyridine to reveal the primary hydroxyl group which was oxidised with TEMPO/BAIB. Esterification attempts under basic condition, resulted in low yield, hence acid catalysed esterification was utilized giving 30 and 31. Gratifyingly the \textit{N}-acetyl group did not affect the outcome of the anomerisation reaction and high selectivities and yields were achieved.
Scheme 43: Synthesis and anomerisation of 2-deoxy-N-acetyl-glycuronides 30 and 31

To probe the regioselectivity of the reaction, disaccharide 45 was prepared. The glycosyl acceptor 39 was prepared from 34 in 6 steps in 23% overall yield. The synthesis began with the preparation of the glycosyl azide 35 form pentaacetyl glucose via Lewis acid promoted glycosylation followed by Zemplén deacetylation to give 36 in 77% yield over the 2 steps. Treatment of 36 with TIPDSCl₂ gave the 4,6-disiloxane intermediate 37, which upon treatment with TsOH rearranged to give the 4,3-disiloxane 38\textsuperscript{191,192}. Selective TEMPO/BAIB mediated oxidation of the primary alcohol, followed by base catalysed esterification gave acceptor 39.
The anomerisation of glycosyl azides

Chapter 2

Scheme 4: Synthesis of glycosyl acceptor 39

Donor 43 was also prepared from pentaacetyl glucose. BF\textsubscript{3}·OEt\textsubscript{2} mediated O-allylation gave 40, which was then deacetylated and benzoylated to give 42 in 88% yield. Removal of the anomeric protecting group with PdCl\textsubscript{2} and subsequent treatment of the hemiacetal with trichloroacetonitrile in the presence of catalytic DBU gave trichloroacetimidate donor 43.

Scheme 45: Synthesis of glycosyl donor 43

The glycosylation reaction was carried out with catalytic TMSOTf and gave 44 in 67% yield. The disiloxane group was removed with methanolic HCl and the diol intermediate was benzoylated to give 45. The anomerisation of 45 went smoothly with only the anomeric azide being anomerised.
2.5 Conclusions.

In summary an optimised method for the anomerisation of azido glycopyranuronate esters has been developed. Seven substrates have been synthesised and the anomerisation of said substrates resulted in high yields and selectivities. This work has been published in Chemistry a European Journal in 2012\textsuperscript{109}.
Table 4: Summary of the anomerisation study

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>α:β</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure 3" /></td>
<td><img src="image2" alt="Chemical Structure 4" /></td>
<td>95:5</td>
<td>91%</td>
</tr>
<tr>
<td><img src="image3" alt="Chemical Structure 6" /></td>
<td><img src="image4" alt="Chemical Structure 7" /></td>
<td>94:6</td>
<td>82%</td>
</tr>
<tr>
<td><img src="image5" alt="Chemical Structure 11" /></td>
<td><img src="image6" alt="Chemical Structure 12" /></td>
<td>97:3</td>
<td>93%</td>
</tr>
<tr>
<td><img src="image7" alt="Chemical Structure 18" /></td>
<td><img src="image8" alt="Chemical Structure 19" /></td>
<td>95:5</td>
<td>90%</td>
</tr>
<tr>
<td><img src="image9" alt="Chemical Structure 30" /></td>
<td><img src="image10" alt="Chemical Structure 32" /></td>
<td>95:5</td>
<td>90%</td>
</tr>
<tr>
<td><img src="image11" alt="Chemical Structure 31" /></td>
<td><img src="image12" alt="Chemical Structure 33" /></td>
<td>9:1</td>
<td>87%</td>
</tr>
<tr>
<td><img src="image13" alt="Chemical Structure 45" /></td>
<td><img src="image14" alt="Chemical Structure 46" /></td>
<td>9:1</td>
<td>94%</td>
</tr>
</tbody>
</table>

Thus far the method has been applied in the Murphy group to prepare novel triazole linked glycolipids and a variety of multivalent compounds of biological interest. It is important to note the reduction of the uronic acid went smoothly to give...
the α-galactosyl azide. Such studies show the potential of this methodology to prepare compounds of biological interest. The versatility and the regioselectivity of the reaction further enhances the utility of this methodology.

Figure 10: Application of anomerisation methodology
Chapter 3: The regiospecific anomerisation of benzoylated disaccharides

3.1 Disaccharides as building blocks in oligosaccharide synthesis.

The efficient synthesis of both natural and analogous unnatural polysaccharides is essential to investigate applications for such structures. Although the majority of synthetic strategies begin from deprotected monosaccharides, the synthesis of polysaccharides where one sugar unit is added at a time is inefficient and can be synthetically risky especially where the introduction of a 1,2-cis glycosidic linkage is required. In the ideal situation, disaccharide building blocks can be prepared containing the desired selectivity and the polysaccharide synthesis is then carried out in a convergent manner. This approach is particularly useful in the synthesis of polysaccharides with repeating units\textsuperscript{194-197}. For example, a variety of publications can be found on the preparation of disaccharide building for the synthesis of heparin and heparin sulphate libraries\textsuperscript{194,196,198-200}.

The synthesis of such disaccharides does not always result in the desired selectivity. As the reactivity and selectivity of carbohydrates varies greatly depending on the monosaccharide in question and the protecting group strategy applied about the pyranose ring, slight differences in the structure can lead to big difference in selectivity and yield for the glycosylation reaction, as such no generalised method has yet been achieved\textsuperscript{59}. Although the yield of glycosylation reactions is important, it is sometimes sacrificed in order to achieve the desired selectivity. In cases where an $\alpha$-glycosidic linkage is desired and an anomeric mixture is achieved, anomerisation of the glycosidic linkage could be used to prepare the desired linkage and remove the need for tedious optimisation and/or separation of the resulting anomers.
3.2 Synthetic utility.

The methodology presented below involves the anomerisation of uronic acid derivitaves. Galcturonans are an interesting and important class of biopolymers which contain this functionality\textsuperscript{197}. It is envisioned that this methodology would allow for the synthesis of disaccharide building towards the preparation of defined molecules of this class and to prepare compounds to inhibit enzymatic hydrolysis of such compounds.
In the concluding remarks of Chapter 2 it is noted that the uronic acid building block was successfully reduced to the α-galactosyl azide. This broadens the utility of the methodology and allows it to be applied to the preparation of oligosaccharides without a uronic acid. Building blocks for the synthesis of interesting compounds could be prepared utilizing anomerisation to gain the desired selectivity, followed by reduction and protecting group manipulation.

**Figure 11: Possible galacturonan targets**

**Figure 12: Potential synthetic targets**
3.2 Objectives.

Encouraged by previous results discussed in Chapter 2, it was thought that applying the optimized conditions to disaccharide substrates may result in anomerisation in a regioselective manner. Previous attempts carried out on a disaccharide under similar conditions by Murphy et al. resulted in 36:64 α:β selectivity. This chapter looks at the anomerisation of a variety of disaccharide compounds, probing the utility of the reaction. While planning the study, it was proposed that having a glycosyl azide at the anomeric centre of the sugar lacking ester functionality could prove beneficial, as glycosyl azides of this type are often inert to anomerisation. This would deconvolute the outcome of the reaction as only one anomerisation would be observed, if the reaction was successful.

![Scheme 48: Proposed disaccharide anomerisation](image)

3.3 Results and Discussion.

The study began by preparing the 1,6-linked compound 53, via a glycosylation reaction with imidate donor 52 and acceptor 48. Acceptor 48 was synthesised form previously prepared 36, which underwent a one-pot silylation benzylation followed by removal of the TBDPS group with TBAF to give the acceptor in 43% yield over the 2 steps.

![Scheme 49: Synthesis of acceptor 48](image)

Donor 52 was prepared via a similar route from 41, resulting in intermediate 50 which was oxidized with TEMPO/BAIB and subsequent base mediated esterification gave 51. Removal of the anomeric allyl protecting group with PdCl₂, followed by DBU catalysed synthesis of trichloroacetimidate 52 in 28% yield from 41.
The regiospecific anomerisation of benzoylated disaccharides

Chapter 3

The glycosylation reaction went smoothly to give 53 in good yield. Treatment of 53 with the conditions optimised in Chapter 2, gratifyingly gave 54 in high yield and selectivity. No side products were observed in the $^1$H NMR following the workup and the mixture was merely passed through a silica plug to remove any remaining TiCl$_4$ associated residues.

Next the anomerisation of a secondary linkage was investigated. The oxygen atom in such linkages is less electron rich than the corresponding oxygen in a primary linkage, which should have a bearing on the anomerisation reaction. Taking intermediate 38 and treating it AcCl in collidine at -35 °C for 3 hours, resulted in selective acetylation at the primary alcohol in 70% yield$^{204}$. The TMSOTf mediated glycosylation of 55 and 52 gave disaccharide 56 in 89% yield. Compound 56 underwent anomerisation to give 57 in high selectivity and yield. This result not only showed the anomerisation of a secondary glycosyl linkage but also showed that the reaction could be carried out in the presence of disiloxane groups. Seeing as benzyl...
The regiospecific anomerisation of benzoylated disaccharides

Ethers and analogues protecting groups are labile under such Lewis acidic conditions, this is important as it expands the protecting group strategies which may be applied under these anomerisation conditions. It is also important to note that the siloxane protecting group may enhance the anomerisation reaction, as it would be less electron withdrawing than acyl protecting groups.

Attention then turned to the synthesis of the 1,4-linked disaccharides 61 and 63. The glycosyl acceptor was prepared from 36, beginning with the selective introduction of a 6,4-isopropylidene was achieved with 2,2-DMP and catalytic p-TsOH in DMF. Treatment of the 2,3-diol with TIPDSCl₂ in pyridine gave 58 in 71% yield over the two steps. Initial attempts to selectively remove the isopropylidene with catalytic p-TsOH or CSA or dowex® 50WX8 H+-resin in methanol resulted in mixtures of desired product, a compound lacking the isopropylidene with the disiloxane being partially cleaved and predominantly the fully deprotected compound. It has previously been shown that amberlyst® 15 hydrogen form can remove an isopropylidene from an acid sensitive substrate, however initial trials with amberlyst® 15 hydrogen form also resulted in a mixture of compounds. Both resins are strongly acidic however the amberlyst® resin can be dried by azeotropic removal of water with toluene. Further drying on high vacuum, followed by addition to a solution of 58 in MeOH gave the desired product in 46% yield as the major product along with other partially and fully deprotected compounds. It was found that newly purchased resin further increase the yield to 82%. With 59 in hand, a regioselective acylation was once again applied to give 60.

Scheme 52: Synthesis and anomerisation of 56
The regiospecific anomerisation of benzoylated disaccharides

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Scheme 53: Synthesis of acceptor 60

Disaccharide 61 was formed in 66% yield by reacting 60 with trichloroacetimidate 52 in the presence of TMSOTf. Anomerisation of 61 gave 62 in high yield and selectivity. The acetate and disiloxane protecting groups were then removed using methanolic HCl and the resulting triol intermediate was treated with benzoyl chloride in pyridine to give 63 in 54% yield. Subjecting 63 to the anomerisation conditions satisfyingly gave 64 in high yield and selectivity. This was a significant result as anomerisation reactions with such electronically deficient systems have not resulted in high stereoselectivities.

Scheme 54: Anomerisation of disaccharides 61 and 63

The synthesis of the 1,3-disaccharide involved the preparation of acceptor 65 from intermediate 37 where 2-OH was regioselectively protected using AcCl in collidine at -35 °C and allowing the reaction to come slowly to room temperature. The greater nucleophilicity of the 2-OH, as well as possible steric hindrance at the 3-
The regiospecific anomerisation of benzoylated disaccharides

OH due to the iso-propyl substituents of the disiloxane protecting group, result in the selective introduction of the acyl group. Subsequent glycosylation of acceptor 65 and donor 52 gave disaccharide 66 in good yield. Again the anomerisation went smoothly to give 67. The protecting groups on 66 were then manipulated to give 68 in 54% yield. Treating 68 with TiCl₄ as previously described gave 69 in high yield and selectivity. It is of interest to note that attempts to anomerise an acetylated derivative of 68 were unsuccessful.

Scheme 55: Synthesis and anomerisation of 66 and 68

The success of the anomerisations discussed above, led us to investigate the anomerisation of analogous compounds lacking the ester functionality. Compound 70 was prepared from acceptor 48 and donor 43 in the presence of catalytic TMSOTf. Although the anomerisation resulted in an α-favourable anomeric mixture, the selectivity was moderate relative to the selectivity achieved for the methyl ester containing derivative 53.
It was thought that the reactivity of the disaccharide towards anomerisation may be increased by adding the disiloxane protecting group. Coupling 59 and donor 43 followed by acetyl protection of 4-OH gave disaccharide 72. Gratifyingly 72 anomerised to give 73 in 89% yield with a $\alpha:\beta$ of 9:1. The higher selectivity seen here due to the addition of the disiloxane is intriguing and may be useful in future studies with similar substrates.

Disaccharide 74, which contains a secondary linkage, was prepared to investigate this effect further. Unfortunately no anomerisation occurred and the starting material was recovered when TiCl$_4$ was applied.
Figure 13: Secondary linked disaccharide

3.5 Summary and conclusions.

The results obtained from the disaccharide anomerisation study represent a novel method for the regioselective anomerisation of disaccharides with high selectivities and yields being achieved. The anomerisation of such deactivated substrates shows the potential of the method and its possible application in synthetic carbohydrate chemistry.
Table 5: Summary of disaccharide anomerisation study

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>α:β</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td></td>
<td>96:5</td>
<td>94 %</td>
</tr>
<tr>
<td>54</td>
<td>92 %</td>
<td></td>
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</tr>
<tr>
<td>55</td>
<td>91 %</td>
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<td></td>
</tr>
<tr>
<td>56</td>
<td>95:5</td>
<td>90 %</td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>95:5</td>
<td>90 %</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>95:5</td>
<td>87 %</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>91 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>83:17</td>
<td>91 %</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>91 %</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The ester functionality enhances the reactivity of such substrates towards anomerisation which is agreement with previous studies[^93][^106][^107]. The presence of this ester could potentially allow for site directed anomerisation in structures of greater complexity. While omission of this ester group would also further enhance this
methodology and although anomeration occurred with compounds 70 and 72, these compounds are 1,6-linked. The attempt to anomeration the analogous 1,4-linked compound was unsuccessful and even though this is disappointing, it reveals the boundaries of the current system, thus presenting a new challenge. Such challenges require the development of an improved promoter system and further studies to understand the effects of the protecting groups involved.
Chapter 4: The effects of acyl protecting groups on the rate of anomerisation

4.1 Introduction

In 1954, Reeves et al. observed a substantial rate increase in the anomerisation of substrates bearing benzoate protecting groups in comparison to the acetyl protected derivatives\(^{95}\). During the course of an investigation, probing the factors affecting the rate and the stereochemical outcome of anomerisation reactions, Murphy et al. quantified this difference in rate\(^{93}\). It was observed that the benzoate protected substrate anomerised at a rate five times greater than the corresponding acetyl protected compound. During the course of the investigation outlined in Chapter 3, the acetate protected derivative of compound 68 failed to anomerise, while compound 68, which is benzoate protected, underwent anomerisation smoothly.

![Figure 14: Trend observed by Murphy et al.](image)

Such observations are counterintuitive, as the study of Koto et al. showed a benzyl ether protected carbohydrate reacts faster than the corresponding acetate protected compounds, which is presumably due to the electronic nature of the protecting groups\(^{96}\). This was ratified with the study involving p-chlorobenzyl ether carried out by Mukaiyama et al.\(^{97}\). Therefore, the factors affecting the rate of anomeriation are analogous to those affecting the activation of glycosyl donors\(^{iii}\). However, studies carried out by Wong et al. have shown that acetate protected thioglycosides are activated at a faster rate than the corresponding benzoate protected thioglycosides\(^{207}\).

\(^{iii}\)Note: Changing the conformation from \(4\C_1\) to \(\C_4\) should in theory reverse the anomeric effect and therefore would not be useful in the anomerisation study discussed herein.
It is apparent from this that electronic effects, as usually described for carbohydrate systems, are likely not to be the cause of the rate increase seen with the benzoate protected compounds. Another possibility is that the effect is steric in nature. Although steric effects have been used to explain the stereochemical outcome of reactions (see Chapter 1), it is not evident from an extensive literature search that there are examples of steric effects increasing the rate of glycosyl donor activation or anomerisation reactions. However, this is a possible explanation for the rate increase in this case, as the steric interactions between the benzoate groups may reduce the entropy of the system. This could lead to preorganisation of chelating groups that are involved in chelation of the Lewis acid, and would lead to an increase in the rate of anomerisation\textsuperscript{208-211}.

4.2 Objectives

To examine this hypothesis, there was an objective to prepare a library of compounds to study in more detail how the protecting groups affect the rate of anomerisation. As the goal of this research is to improve the anomerisation reaction, where possible attempts were to be made to further increase the rate of the anomerisation reaction based on the findings. Finally, if successful, the improved protecting group strategy would be applied to the anomerisation of substrates, analogous to those which have previously been unsuccessful (e.g. compound 74).

4.3 Results and discussion

The study began with the synthesis of compounds 75β and 77β. Compound 75β was prepared as previously described by Murphy et al\textsuperscript{93}. Zemplén deacetylation of 75β gave intermediate 76 in quantitative yield. Benzoylation of 76 with benzoyl chloride in pyridine gave 77β in 78% yield.

\begin{equation}
\begin{align*}
\text{AcO} & \quad \text{NaOMe, MeOH} & \quad \text{RT, 1 h, 95\%} \\
\text{AcO} & \quad \text{HO} & \quad \text{BzCl, Py, 0 °C to RT, 78 \%} \\
\text{75β} & \quad \text{76} & \quad \text{77β}
\end{align*}
\end{equation}

Scheme 58: Preparation of 77β from 75β

Attention then turned the preparation of monobenzoylated compounds 80β, 81β, 86β and 87β. These compounds were prepared so as to investigate and compare
the effect of the benzoate protection on the rate of anomerisation at each of the positions about the pyranose ring. The four compounds were prepared from intermediate 78, which itself was prepared in 74% yield from 76. Acetylation of the 4,6-benzylidene protected compound gave compound 79 in 89% yield. The oxidative cleavage of the benzylidene using NaBrO3 and Na2S2O4, under bi-phasic conditions, followed by acetylation, resulted in the formation a separable mixture, giving 80β and 81β in 79% total yield, with the ratio being 32:68 in favour of compound 80β.

Scheme 59: Synthesis of compounds 80β and 81β

Benzylation of 78 under the biphasic alkali conditions previously reported by Oscarson et al. gave a mixture of compounds 82 and 83 (69:31 respectively) in 56% yield212. Benzoylation of the respective free hydroxyl groups gave compounds 84 and 85 in good yields. Hydrogenolysis of these intermediates, followed by acetylation with Ac2O in pyridine gave 86β and 87β in 91% and 87% yields respectively.

Scheme 60: Preparation of compound 86β and 87β
With these compounds in hand, attention turned to the quantification of the rate of anomerisation for each substrate. Murphy et al. have previously shown that Lewis acid catalysed anomerisations generated straight line plots with use of the equation\(^{93}\) which can be applied for equilibrium kinetics:

\[
\ln \left( \frac{[A]_0 - [A]_e}{[A]_t - [A]_e} \right) = -(k_f + k_r)t
\]

where \([A]_0\) is the initial concentration of the \(\beta\)-anomer, \([A]_e\) is the concentration of the \(\beta\) anomer at equilibrium, \([A]_t\) is the concentration of the \(\beta\)-anomer at a time \(t\), \(k_f\) is the rate constant of the forward reaction \((\beta \rightarrow \alpha)\) and \(K_r\) is the rate constant of the reverse reaction \((\alpha \rightarrow \beta)\). Herein, \(k\) is used to represent \((k_f + k_r)\). The reactions were monitored by NMR and data obtained were found to give straight line plots according to the equilibrium rate law. Each reaction was carried out in triplicate and all plots had \(r^2\) values of 0.97 or greater.

Examination of the relative rates showed a two fold rate increase for the fully benzoylated compound 77\(\beta\) when compared to 75\(\beta\)\(^{iv}\). Compound 80\(\beta\) was the slowest of all the monobenzooylated compounds, none of which showed a major rate increase compared to the peracetylated compound. The reduction in rate for 80\(\beta\) can be rationalised by the reduction of the electron density at saccharide C-6 position by the electron withdrawing benzoyl group thus reducing the rate of the anomerisation and it is in line with the study of Koto et al\(^{96}\). The rates obtained for compounds 81\(\beta\) and 86\(\beta\) are higher than 80\(\beta\), but less than the peracetylated compound. This may be due to the proximity of the benzoate groups to the site of chelation and/or the reaction centre and thus the reaction is less sensitive to the electron withdrawing effect of the benzoate groups in these derivatives.

The rate of anomerisation observed for compound 87\(\beta\) conflicted this proposal as it anomerises the fastest of the monobenzooylated compounds, although it cannot alone be declared as the cause of the rate increase seen for 77\(\beta\). The rate observed for 87\(\beta\) could be due to a number of phenomena, however two rational

\(^{iv}\) Note: This anomerisation study was carried out using 1 equivalent of SnCl\(_4\) rather than with the 0.5 equivalent of the promoter as carried out previously by Murphy et al. As a result the relative rates will vary as the rate of anomerisation does not have a linear relationship to the concentration of SnCl\(_4\) used and the relationship also varies from substrate to substrate.
explanations can be proposed. Stabilisation by an acyl group has previously been proposed by Manabe et al.\textsuperscript{104} and although acetate and benzoate groups both contain the required carbonyl functionality, the steric difference between the group may result in the carbonyl being orientated in a conformation which further enhances the this stabilisation, thus resulting in a faster anomerisation reaction.

<table>
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<th>$10^4(k_f + k_r)$ (s$^{-1}$)</th>
<th>Relative Rate</th>
<th>$\alpha$:$\beta$ (Yield)</th>
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<tr>
<td><img src="image2" alt="Structure 2" /></td>
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<td>2.07</td>
<td>95:5 (72%)</td>
</tr>
<tr>
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<td>6.0</td>
<td>0.79</td>
<td>92:8 (81%)</td>
</tr>
<tr>
<td><img src="image4" alt="Structure 4" /></td>
<td>7.1</td>
<td>0.93</td>
<td>89:11 (76%)</td>
</tr>
<tr>
<td><img src="image5" alt="Structure 5" /></td>
<td>7.2</td>
<td>0.95</td>
<td>93.7 (73%)</td>
</tr>
<tr>
<td><img src="image6" alt="Structure 6" /></td>
<td>8.6</td>
<td>1.13</td>
<td>9:1 (61%)</td>
</tr>
</tbody>
</table>

Table 6: Rate of anomerisation for series I compounds

Although this type of stabilisation has not been previously proposed in synthetic carbohydrate chemistry, cation-$\pi$ interactions have been used to rationalise the
stabilisation of the transition state leading to the oxocarbenium ion in glycosyl hydrolases\textsuperscript{213–218}. These interactions may not only be involved in anomerisation reactions but also in glycosylation reactions. The work of Wong et al. showed the relative rate of glycosylation of the 2-\textit{O}-acetyl and 2-\textit{O}-benzoyl protected compounds (\textbf{C} and \textbf{D}) to be faster for the 2-\textit{O}-benzoyl compound, which could also be explained by a greater stabilisation of the transition state by the benzoate group\textsuperscript{219}.

\begin{figure}
\centering
\includegraphics[width=0.7\textwidth]{oxocarbenium_stabilisation}
\caption{Oxocarbenium stabilisation by acyl groups}
\end{figure}

Attention next turned to the preparation of compounds bearing two or three benzoate groups. Compound \textbf{88\textbeta} was prepared from intermediate \textbf{79}, by applying the previously outlined oxidative benzylidene cleavage followed by benzoylation to give \textbf{88\textbeta} in 62\% yield.

\begin{scheme}
\centering
\includegraphics[width=0.5\textwidth]{scheme_61}
\caption{Preparation of compound \textbf{88\textbeta}}
\end{scheme}

Compound \textbf{91\textbeta} was prepared from benzylidene intermediate \textbf{78} in 3 steps. Benzoylation of \textbf{78} with benzoyl chloride in pyridine gave intermediate \textbf{89}. Acid catalysed cleavage of the benzylidene acetal in a DCM/MeOH gave intermediate \textbf{90}.
which was taken crude to the next step and was acetylated to give $91\beta$ in 40% yield from 78.

![Scheme 62: Synthesis of compound 91β](image)

The synthesis of compounds $98\beta$ and $99\beta$ was carried out in a similar manner from compounds 82 and 83 respectively. Acid catalysed cleavage of the benzylidene acetal as previously described followed by benzylation gave compounds 94 and 95. Oxidative cleavage of the benzyl ether protecting groups with NaBrO$_3$ and Na$_2$S$_2$O$_4$ went smoothly to give the monohydroxylated intermediates which were acetylated to give the desired substrates in good yield.

![Scheme 63: Synthetic route to compounds 98β and 99β](image)
Compounds $102\beta$ and $103\beta$ were prepared from benzylidene acetal 89 using the biphasic oxidative ring opening procedure previously described. Acetylation of intermediates 100 and 101 gave compounds $102\beta$ and $103\beta$ in moderate yield.

\[
\begin{array}{c}
\text{Ph} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{BzO} \quad \text{OBu} \quad \text{1} \quad \text{NaBrO}_3, \text{Na}_2\text{S}_2\text{O}_4, \quad \text{EtOAc/H}_2\text{O}, \quad \text{Rt, 4 h} \\
\text{89} \quad \text{100: } R^1 = \text{Bz}, R^2 = \text{H} \\
\quad \text{101: } R^1 = \text{H}, R^2 = \text{Bz} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Ac}_2\text{O, Py,} \quad 0^\circ\text{C to rt, 16 h} \\
\text{102}: R^1 = \text{Bz}; R^2 = \text{Ac}; 24\% \\
\quad \text{103}: R^1 = \text{Ac}; R^2 = \text{Bz}; 48\%
\end{array}
\]

**Scheme 64: Preparation of compounds $102\beta$ and $103\beta$**

Kinetic studies on the di- and tri benzoylated compounds did not result in any compound having a rate comparable or better than that of the fully benzoylated $77\beta$ and as before only one compound anomerised at a faster rate than compound $75\beta$. The rate of anomerisation for compound $88\beta$ is relatively slow. This was not surprising and the rationalisation applied to the rate observed for compound $80\beta$ can also be applied here. Contrary to this compound $91\beta$ has a less electron withdrawing acetate at C-6 but has the benzoate at C-2 that may be involved in the cation-π interaction and this was the only dibenzoylated derivative to be faster than $77\beta$. Compound $98\beta$ was the slowest in this series; the effect of the electron withdrawing benzoates at C-3, C-4 and C-6 seems to be additive and deactivate the saccharide towards anomerisation.

When comparing rates of anomerisation of $98\beta$ and $99\beta$, the proposal for a greater stabilisation by the benzoate group at C-2 can be again supported as $99\beta$ shows a rate increase. The rate of anomerisation for compound $99\beta$, exemplified the effect of the benzoate at C-2 and although the rate increase is modest, in relative terms it is substantial. Compounds $102\beta$ and $103\beta$ elucidate the importance of the electronic nature of the protecting groups at C-4 and C-6. When compared with $91\beta$, which has acetate groups at these positions, it is evident that the electron
The effects of acyl protecting groups on the rate of anomeration

withdrawing nature of the benzoate groups result in a decrease in the rate of anomeration.
The effects of acyl protecting groups on the rate of anomerisation

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Table 7: Anomerisation of series II compounds

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$10^4(k_f + k_r)$ (s$^{-1}$)</th>
<th>Relative Rate</th>
<th>$\alpha:\beta$ (Yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcO</td>
<td>OAc</td>
<td>7.6</td>
<td>1</td>
</tr>
<tr>
<td>BzO</td>
<td>OBz</td>
<td>15.7</td>
<td>2.07</td>
</tr>
<tr>
<td>BzO</td>
<td>OAc</td>
<td>4.6</td>
<td>0.61</td>
</tr>
<tr>
<td>AcO</td>
<td>OBz</td>
<td>8.5</td>
<td>1.12</td>
</tr>
<tr>
<td>BzO</td>
<td>OAc</td>
<td>3.7</td>
<td>0.49</td>
</tr>
<tr>
<td>BzO</td>
<td>OBz</td>
<td>6.2</td>
<td>0.82</td>
</tr>
<tr>
<td>AcO</td>
<td>OBz</td>
<td>6.6</td>
<td>0.87</td>
</tr>
<tr>
<td>AcO</td>
<td>OBz</td>
<td>5.6</td>
<td>0.74</td>
</tr>
</tbody>
</table>
The twelve compounds which were thus far kinetically analysed have shown consistently a rate enhancement by the benzoate group at C-2, but rate reductions for benzoates at C-3, C-4, C-6. On the basis of all the data, one might expect a rate reduction for 77β but this compound is faster than expected. To further probe the cause of this rate increase for 77β conformational analysis was carried out using NOE experiments and computational modeling.

The NOE experiments were used to calculate the distances between the protons at C-6 and the proton at C-4 for different compounds 75β, 77β and 98β. The conformation about the C-5–C-6 bond is of particular interest in this instance, as it has been previously published that the oxygen bonded to C-6 and/or the oxygen of the carbonyl present in the protecting group may have a role to play in the chelation of the Lewis acid93,96.

![Figure 16: Possible sites of Lewis acid chelation](image)

The gauche-gauche (gg), trans-gauche (tg) and gauche-trans (gt) conformations are depicted below (Figure ) and it is evident from simple conformational analysis that the gg and the gt conformations will allow chelation occur, however the tg conformation will not. It has been shown that in the case where R= H, there was not a strong preference for one of these conformational isomers220. However increasing steric interactions have been shown to result in one or more of the conformers being disfavoured221,222. It is of interest to note that the effect of constraining these conformers have been carried out for glycoside hydrolysis223,224, however the results cannot be correlated directly to the anomerisation, of interest herein, as hydrolysis and anomerisation have different mechanisms (i.e. endocyclic vs. exocyclic cleavage), hence a separate study would have to be carried out to investigate the effect of conformation between C-5 and C-6 on the rate of anomerisation.

It is important to note that due to rotation about the C-5–C-6 bond, the results obtained may reflect an average distance rather than actual distance between the proton at C-4 and the protons at C-6 The 2-D NOE spectra were acquired with
mixing times varying from 200 ms to 700 ms, thus allowing for a build up curve to be obtained by plotting the mixing times against the absolute NOE build-up (i.e., the peak areas of the cross peaks). A build up curve corresponding to the cross peak between H-1 and H-3 was also constructed, as this distance would be expected to be fixed if the $^4$C$_1$ conformation is fixed for each of the compounds; this distance was used as a reference distance.

Figure 17: Possible conformations about the C-5–C-6 bond.

Figure 13: Build up curve for compound 75β

---

v The method to carry out this study was obtained from the PhD thesis of Dr. Jenifer Hendel.  
vii For the build up curves of other compounds see appendix 2.
The data points of the build up curve were then fitted to the following equation\(^{225,226}\):

\[
A_{\text{cross}}(\tau_m) = k_1(-e^{-k_2\tau_m} + e^{-k_3\tau_m})
\]

In this equation \(A_{\text{cross}}\) is the area of the cross-peak, \(\tau_m\) is the mixing time (milliseconds, ms) and \(k_{1-3}\) represent constants. The lines on the graphs were extrapolated to zero and the initial slope (at \(\tau_m = 0\)) was obtained. The distance between the hydrogen atoms was then calculated using the isolated spin-pair approximation, where the initial slope is proportional to the inverse distance (\(r^6\)). Using a known distance between the two reference protons and the initial slope from the corresponding build-up curve, the distance between the protons at protons at C-6 and the proton at H-4 could be calculated using the following equation\(^{225,226}\):

\[
r_{\text{unknown}}^6 = \text{slope}_{\text{reference}} \times (r_{\text{reference}}^6/\text{slope}_{\text{unknown}})
\]

The calculated distances provide evidence that conformation about the C-5–C-6 bond was different for compounds bearing a benzoate at position six compared to the compounds which had an acetate at this position. These distances suggested that compound 75\(\beta\) is in \(gg\) conformation, while compounds 77\(\beta\) and 98\(\beta\) are in the \(gt\) conformation. In the \(gt\) conformation, the ring oxygen is in close proximity to O-6 and the oxygen of the benzoate group. Although this may have an effect on the rate of anomerisation it was not in agreement with the experimental findings for compound 98\(\beta\), hence computational studies were carried out to investigate the energy differences between each conformation for the three compounds studied.
Computational studies were carried out using Macromodel™ as part of the Schroedinger Programme™ in an attempt to rationalise the results obtained from the NOE experiments. The force field used was OPLS-AA (Optimized Potentials for Liquid Simulations-All Atom) and the calculations were carried out under solvent free conditions. Compounds were first minimized and subsequently conformational searches were carried out where structures with a ΔE of >10 kcal mol⁻¹ relative to the lowest energy minimized structure being retained in the search.

Each of the compounds investigated showed a preference for the gt conformation, with the gg conformation being the next lowest energy conformation. It is interesting to note the tg conformation was not observed within the energy parameter where structures were retained in the search. Although the distances calculated by the NOE experiments and the molecular modelling to not correlate, the distances observed in the NOE experiments for compound 77β and 98β could only occur in a gt conformation.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Dist. H⁶α to H₄</th>
<th>Dist. H⁷α to H₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>75β</td>
<td>3.45 Å</td>
<td>2.62 Å</td>
</tr>
<tr>
<td>77β</td>
<td>2.78 Å</td>
<td>2.70 Å</td>
</tr>
<tr>
<td>98β</td>
<td>2.80 Å</td>
<td>2.89 Å</td>
</tr>
</tbody>
</table>

Figure 19: Distances calculated by NOE experiments
Further computational analysis of the conformations about the C5-C-6 bond were carried out using dihedral driving, in an attempt to evaluate the rotational restrictions present for each compound. Comparing the two compounds of similar structure $77\beta$ and $98\beta$ gives an interesting insight into the conformational differences. The two compounds have a similar profiles going between the $gg$ and $gt$ conformations, showing a preference for the $gt$ conformation, while it is evident that compound $77\beta$ disfavours the $tg$ conformation. Compound $75\beta$ shows little preference for the $gg$ or $gt$ conformation and as expected from previous calculations the $tg$ conformation occurs at a higher energy and although the energy barrier to this conformation is higher than that calculated going from the $gg$ to the $gt$ or vice versa, it is not substantial when compared to the barrier observed for compound $77\beta$. 

![Conformations](image.png)

**Figure 20: Computational conformational studies and distances determined by modelling and NOE experiments**
Leading on from these conformational analysis studies, it was considered that having four benzoyl groups on the saccharide could lead to enhanced steric interaction that could influence preorganisation about the C-5 to C-6 bond and increase in anomerisation rate. It was decided to vary the nature of the acyl group at C-2 to try to gain insight as to whether a steric effect was involved in the reaction. Compounds 105β, 106β and 107β were thus prepared from compound 94, using the previously outlined for oxidative removal of the benzyl ether, giving intermediate 104 which was used directly in the next step and reacted with the three corresponding acid chlorides.
Kinetic studies on these compounds proved to be revealing, as the rate of anomerisation increased as the electron withdrawing ability of the substituents decreased and as the size of the protecting group increased. Although it is interesting to note that compound 77β does not follow this electronic trend. It was attempted to correlate the data to the Taft equation, however due to the small sample size and the slight variation in the functionality of the substrates, it was felt the results obtained may not truly reflect the effect of sterics and electronics on the rate of anomerisation.
The effects of acyl protecting groups on the rate of anomerisation

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Table 8: Rate of anomerisation for series III compounds

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$10^4(\kappa_f + \kappa_r)$ (s$^{-1}$)</th>
<th>Relative Rate</th>
<th>$\alpha:\beta$ (Yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Diagram" /></td>
<td>15.7</td>
<td>2.07</td>
<td>95:5 (72%)</td>
</tr>
<tr>
<td><img src="image" alt="Diagram" /></td>
<td>3.7</td>
<td>0.49</td>
<td>9:1 (84%)</td>
</tr>
<tr>
<td><img src="image" alt="Diagram" /></td>
<td>4.1</td>
<td>0.53</td>
<td>94:6 (66%)</td>
</tr>
<tr>
<td><img src="image" alt="Diagram" /></td>
<td>5.5</td>
<td>0.72</td>
<td>92:8 (48%)</td>
</tr>
<tr>
<td><img src="image" alt="Diagram" /></td>
<td>9.9</td>
<td>1.3</td>
<td>95:5 (89%)</td>
</tr>
</tbody>
</table>

In an attempt to investigate further the other factors which may be in play, such as the proposed cation-π interaction, compounds 108β, 111β, 112β, 113β and 114β were prepared so as to vary the cation-π-interactions and effects due to protecting groups other than position C-2. Compound 108 was prepared as previously described by Murphy et al. from compound 76$^{93}$. The 2-O-acyl compounds were prepared from intermediate 92, which was treated with NaH and methyl iodide to give compound 109. As previously described, the benzyl ether was removed and acylation of the hydroxyl-containing intermediate gave the desired compounds in good yields, after purification by chromatography.
Anomerisation studies on these compounds resulted in compound 113β being faster than its acetylated counterpart 112β. Interestingly compound 114β is faster than 113β showing that electronics could also play an important role at the C-2 position, where the pivalate is more electron donating and leads to an increase in rate compared to the benzoate. This comparison does not however correlate to the rates observed for previously discussed compounds 77β and 107β where the 2-O-benzooyl protected compound is seen to be faster than the 2-O-pivoyl protected compound indicating that the benzoate at C-3, 4 and 6 play a role in the difference observed.

Compound 111β was prepared in order to try to directly investigate the proposed cation-π interaction. Dougherty et al. have previously published that a fluorine substituted benzene has a lesser cation-π interaction than benzene. It is also important to note that according to the Taft polar substituent constant and Hammet σ and σ+ vaules a p-fluorophenyl substituent and a phenyl substituent are electronically comparable. Interesting the rate observed for compound 111β was the lowest in this series of compounds by a significant amount and provides further evidence that a cation-π interaction plays a role in the stabilisation of a carbocation in the transition state for the anomerisation reaction.
Next attention was turned to studying the effect of modification at the C-6 position as it was felt that decreasing the electron withdrawing ability of the ester protecting group would further increase the rate of anomerisation. A series of compounds were prepared which had benzoate protecting groups at C-2, 3 and 4 and a variety of substituted benzoates at C-6. The compounds were prepared from compound 89 which was treated with MSA and NaBH₃CN, resulting in the regioselective opening of the benzylidene acetal to give 115. Benzoylation of the resulting monohydroxy intermediate gave 116. Oxidative removal of the benzyl ether followed by acylation with a variety of acid chlorides in pyridine gave the desired library of compounds in good yields.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$10^4(k_f + k_i)$ (s⁻¹)</th>
<th>Relative Rate</th>
<th>$\alpha: \beta$ (Yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Substrate" /></td>
<td>4676.0</td>
<td>615.3</td>
<td>96:4 (72%)</td>
</tr>
<tr>
<td><img src="image2" alt="Substrate" /></td>
<td>3088.3</td>
<td>406.4</td>
<td>92:8 (74%)</td>
</tr>
<tr>
<td><img src="image3" alt="Substrate" /></td>
<td>4088.4</td>
<td>537.9</td>
<td>95:5 (71%)</td>
</tr>
<tr>
<td><img src="image4" alt="Substrate" /></td>
<td>4386.0</td>
<td>577.1</td>
<td>94:6 (86%)</td>
</tr>
<tr>
<td><img src="image5" alt="Substrate" /></td>
<td>1854.7</td>
<td>244.0</td>
<td>95:5 (52%)</td>
</tr>
</tbody>
</table>

Table 9: Rate of anomerisation for series IV compounds
The effects of acyl protecting groups on the rate of anomerisation

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Scheme 67: Synthesis of compound 117β to 120β

The anomerisation studies carried out under these compounds gave interesting results. All of these compounds anomerised more slowly than perbenzoylated 77β and no trend was clear for this series of compounds. It could be the case that there may be an interaction between the phenyl rings of the benzoate groups and that by changing the electrostatics of a single benzoate this interaction is disrupted. NOE experiments and computational studies carried out on compounds 119β and 120β give analogous results to the results obtained for compound 77β. Interestingly, overlapping these three structures resulted in a slight variation in the conformation of the benzoate groups at positions four and six and the change can be correlated to the rates observed. Conformational calculation for compounds 117β and 118β were then carried out and the lowest energy conformations found were also overlayed, further illustrating this conformational difference.
Figure 22: A) conformational change at C-6; B) overall conformational change
Table 10: Rate of anomerisation for series V compounds

It was thought that the reduction in rate observed with the substituted benzoyl compound could be overcome by changing the protecting groups so that all positions have the same protecting group, as is the case with compound \(77\beta\). Aromatic and aliphatic protecting groups were investigated and were prepared from intermediate \(76\) under similar conditions to those used to prepared compound \(77\beta\).
The effects of acyl protecting groups on the rate of anomerisation

Scheme 68: Synthesis of compound 121β to 130β

The anomerisation of the aliphatic ester protecting groups gave results which followed the trends seen for the compounds in series III (compounds 105β to 107β). The rates obtained for compounds 121β to 123β do not compare to the rate obtained for compound 77β, thus once again indicating that both steric and electronic effects impact the rate of anomerisation.
The effects of acyl protecting groups on the rate of anomerisation

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Table 11: Rates of anomerisation for series VI compounds

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>$10^4(k_f + k_i)$ (s$^{-1}$)</th>
<th>Relative Rate</th>
<th>α:β (Yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>121β</td>
<td><img src="image1" alt="Image" /></td>
<td>8.3</td>
<td>1.09</td>
<td>90:10 (66%)</td>
</tr>
<tr>
<td>122β</td>
<td><img src="image2" alt="Image" /></td>
<td>9.4</td>
<td>1.24</td>
<td>92:8 (76%)</td>
</tr>
<tr>
<td>123β</td>
<td><img src="image3" alt="Image" /></td>
<td>10.1</td>
<td>1.33</td>
<td>95:5 (81%)</td>
</tr>
</tbody>
</table>

The anomerisation studies carried out on the compounds bearing aromatic ester groups provided interesting results. The two $p$-halogen substituted compounds were particularly slow and this may be due to the ability of the halogen atoms to weaken cation-π interactions$^{230}$. The rate of anomerisation for compounds 126β, 127β and 128β was high and this is the first time a rate faster than that observed for 77β has been achieved. It is evident that the rate increase observed is largely due to electronics, although attempts to graph the logarithm of the relative rates (i.e. $\log(k_f/k_i)$) against the Taft electronic parameters and Hammett values (both $\sigma$ and $\sigma^+$ values) did not result in a straight line plots (include in the table Taft and Hammett parameters).
The effects of acyl protecting groups on the rate of anomerisation

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Table 12: Rates of anomerisation for series VII compounds

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>$10^4(k_f + k_r)$ (s$^{-1}$)</th>
<th>Relative Rate</th>
<th>$\alpha:\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>124β</td>
<td>O</td>
<td>6.2</td>
<td>0.82</td>
<td>95:5</td>
</tr>
<tr>
<td>125β</td>
<td>O</td>
<td>7.2</td>
<td>0.95</td>
<td>90:10</td>
</tr>
<tr>
<td>126β</td>
<td>O</td>
<td>31.1</td>
<td>4.09</td>
<td>95:5</td>
</tr>
<tr>
<td>127β</td>
<td>O</td>
<td>27.9</td>
<td>3.67</td>
<td>92:8</td>
</tr>
<tr>
<td>128β</td>
<td>O</td>
<td>27.0</td>
<td>3.55</td>
<td>94:6</td>
</tr>
<tr>
<td>129β</td>
<td>O</td>
<td>12.5</td>
<td>1.64</td>
<td>90:1</td>
</tr>
<tr>
<td>130β</td>
<td>O</td>
<td>21.6</td>
<td>2.84</td>
<td>95:5</td>
</tr>
</tbody>
</table>
Compounds $129\beta$ and $130\beta$ gave conflicting results, however the pKa value for the corresponding carboxylic acids also vary substantially\(^{viii}\). The pKa for 1-napthanoic acid would suggest that the 1-napthoyl group is electron withdrawing and hence the rate of anomerisation should be extremely slow for compound $129\beta$, however the relative rate is still greater than 1. This can be attributed to steric interactions and the cation-$\pi$ interaction at C-2 which stabilises the transition state leading to the endocyclic intermediate. The pKa value for 2-napthanoic acid is slightly lower than that of benzoic acid, thus one would expect the rate to be faster than that observed for $130\beta$ and $77\beta$ and this is the case. This result further illustrates the importance of steric interaction in anomerisation reactions of this type.

Having observed a substantial rate increase with the $p$-methoxybenzoate protecting groups, it was deemed worthwhile preparing a disaccharide analogous to compound 74, which had $p$-methoxybenzoate protecting groups instead of benzoate protecting groups. It was thought that rate enhancement could occur in this case, as previous studies with compound 74 starting material was fully recovered. Disaccharide 133 was prepared from known compound 131 using $p$-methoxybenzoyl chloride in pyridine. The coupling of donor 132 with acceptor 65 was carried out with NIS and TfOH and gave the desired disaccharide in 84% yield. The anomerisation of compound $133\beta$ did not result in an $\alpha$-favourable mixture. However it is promising that the anomerisation occurs to some extent.

Scheme 69: Synthesis and anomerisation of compound $133\beta$

\(^{viii}\) pKa value: 1-napthanoic acid = 3.7; 2-napthanoic acid = 4.17; benzoic acid = 4.19; acetic acid = 4.76.
4.4 Conclusions

In conclusion the rate of anomerisation has been quantified for 34 substrates in a attempt to elucidate the effect of benzoate protecting groups and to try expand the anomerisation of disaccharide substrates to non-uronic acid derivatives. The data obtained shows that the rate of anomerisation is affected by both the steric and electronic properties of the protecting groups. It is also evident that the rate observed for compound 77β is due to a steric effect and the benzoate groups must be present at all positions for this to occur. There is also an unexpected rate increase for a benzoate at C-2, which was further investigated using a 4-fluorobenzate. The involvement of this effect in the rate observed for compound 77β is however unclear and further investigations need to be carried out to elucidate this effect. It is again clear from the study carried out with the substituted benzoate and napthoyl protected compounds (124β – 130β) that the anomerisation reaction is affected by both the steric and electronic properties of the protecting groups. The attempt to apply the 4-methoxybenzoate groups to disaccharide anomerisation did not result in the desired outcome, however it shows the limitations of the system and the need to find a better protecting group strategy and/or an improved promoter system. It is evident from this study that further alterations to the protecting group strategy may be enough to bring about the desired α-selectivity.
Chapter 5: Experimental data

General Experimental Conditions:

Optical rotations were determined at the sodium D line at 20°C using a Schmidt and Haensch UniPol L1000. NMR spectra were recorded with a 500 MHz or 600 MHz Varian spectrometer. Chemical shifts are reported relative to internal Me₄Si in CDCl₃ (δ 0.0) or HOD in D₂O (δ 4.79) for ¹H and Me₄Si in CDCl₃ (δ 0.0) or CDCl₃ (δ 77.0) for ¹³C. ¹H NMR signals were assigned with the aid of COSY and ¹³C NMR signals were assigned with the aid of DEPT, gHSQCAD and/or gHMBCAD. Coupling constants are reported in hertz. The IR spectra were recorded as thin films using a PerkinElmer Spectrum 100 FT-IR Spectrometer with an ATR attachment. High resolution mass spectra were recorded using a Waters LCT Premier XE (ESI-TOF instrument). Silica gel (pore size 60 Å, particle size 40-60 μm 230-400 mesh particle size) was purchased from Sigma-Aldrich. Dichloromethane, THF and DMF reaction solvents were obtained from a Pure Solv™ Solvent Purification System. Acetone and acetonitrile solvents (Chromatsolv for HPLC grade, >99.9%) and anhydrous pyridine were obtained from Sigma-Aldrich. 1M TiCl₄ in CH₂Cl₂ was purchased from Sigma Aldrich.

Chapter 2 experimental procedures:

![Chemical structure](image)

**Methyl 1,2,3,4-tetra-O-acetyl-β-D-glucopyranopyranuronate (2)**

Triethylamine (0.15 mL) was added to a suspension of D-Glucurono-6,3-lactone (10 g, 56.8 mmol) in anhydrous methanol (150 mL). The reaction was stirred overnight. The solvent was evaporated and the resulting foam was used without further purification. The foam was taken up in acetic anhydride (50 mL) and sodium acetate (5 g, 61 mmol) was added. The resulting suspension was stirred for 4 days at room temperature. The reaction was poured onto ice water (300 mL) and stirred overnight. The resulting precipitate was filtered, washed with water and recrystallised with
ethanol to give 2 as a white solid (8.1 g, 38%); \([\alpha]_D +9.31\) (c 1.5, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.76 (d, \(3^J\) (H,H) = 7.8, 1H; H-1), 5.30 (apt. t, \(3^J\) (H,H) = 9.2, 1H; H-3), 5.23 (apt. t, \(3^J\) (H,H) = 9.5, 1H; H-4), 5.13 (apt. t, \(3^J\) (H,H) = 8.4, 1H; H-2), 4.17 (d, \(3^J\) (H,H) = 9.6, 1H; H-5), 3.73 (s, 3H; CO\(_2\)CH\(_3\)), 2.11 (s, 3H; CO\(_2\)CH\(_3\)), 2.03 (s, 6H; 2 x CO\(_2\)CH\(_3\), overlapping peaks), 2.02 (s, 3H; CO\(_2\)CH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 169.9 (C\(_O\)2CH\(_3\)), 169.4, 169.1, 168.8, 166.8 (4 x C\(_O\)CH\(_3\)), 91.3 (C-1), 73.0 (C-5), 71.8 (C-3), 70.1 (C-2), 68.9 (C-4), 53.0 (CO\(_2\)CH\(_3\)), 20.7, 20.5, 20.5, 20.4 (4 x COCH\(_3\)). [\(\alpha\)]\(_D\) +9.31° (c 1.5, CHCl\(_3\)); IR (film) cm\(^{-1}\): 2956, 1752, 1443, 1372, 1203, 1038; ESI-HRMS calcd for C\(_{15}\)H\(_{20}\)O\(_{11}\)Na 399.0903, found m/z 399.0887 [M+Na]\(^+\).

**Methyl 2,3,4-tri-O-acetyl-\(\beta\)-D-glucopyranosyluronate azide (3)**

Compound 2 (4g, 10.6 mmol) was dissolved in DCM (25 mL) and cooled using an ice bath. TMSN\(_3\) (4.18 mL, 31.8 mmol) and SnCl\(_4\) (0.62 mL, 5.3 mmol) were added and the resulting solution was stirred overnight at room temperature. The reaction mixture was diluted with CH\(_2\)Cl\(_2\) (25 mL) and was washed twice with 1M KHSO\(_4\) (50 mL x 2), satd Aq. NaHCO\(_3\) (50 mL), brine (50 mL), dried over anhydrous NaSO\(_4\), filtered and the solvent was removed under reduced pressure. This residue was recrystallised from ethanol to yield 3 as a white solid (2.6 g, 69 %); [\(\alpha\)]\(_D\) -39.5 (c 1.0, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.31 – 5.19 (m, 2H; H-2, H-4, overlapping peaks), 4.96 (apt. t, \(3^J\) (H,H) = 9.0 Hz, 1H; H-3), 4.71 (d, \(3^J\) (H,H) = 8.7 Hz, 1H; H-1), 4.12 (d, \(3^J\) (H,H) = 9.5 Hz, 1H; H-5), 3.78 (s, 3H; CO\(_2\)CH\(_3\)), 2.07 (s, 3H; COCH\(_3\)), 2.03 (s, 3H; COCH\(_3\)), 2.02 (s, 3H; COCH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 170.1, 169.4, 169.2 (3 x COCH\(_3\)), 166.6 (COOCH\(_3\)), 88.2 (C-1), 74.4 (C-5), 72.0 (C-4), 70.6 (C-3), 69.1 (C-2), 53.2 (CO\(_2\)CH\(_3\)), 20.7 (2 x COCH\(_3\)), 20.6 (COCH\(_3\)). IR (film) cm\(^{-1}\): 2956, 2123, 1755, 1439, 1371, 1241, 1038; ES-HRMS calcd for C\(_{13}\)H\(_{20}\)O\(_3\)N\(_4\) 377.1309, found m/z 377.1326 [M+NH\(_4\)]\(^+\).
Methyl 1-azido-1-deoxy-β-D-glucopyranosyluronate (5)\textsuperscript{108}

Azide 3 (1 g, 2.8 mmol) was added to LiOH (100 mL, 0.1 M) in MeOH-H\textsubscript{2}O-THF (5:2:1) and cooled to 0 °C and stirred for 16 h and allowed to attain room temp. Dowex\textsuperscript{®} 50WX8 H\textsuperscript{+}-resin was then added and then filtration and evaporation gave the unprotected azide (0.57 g, 93%) which was used in the next step without further purification; [α]\textsubscript{D} +9.3 (c 0.2, CH\textsubscript{3}OH); \textsuperscript{1}H NMR (500 MHz, D\textsubscript{2}O) δ 4.76 (d, 1H; \textsuperscript{3}J (H,H) = 8.8 Hz; H-1), 3.81 (d, \textsuperscript{3}J (H,H) = 9.4 Hz, 1H; H-5), 3.58 – 3.48 (m, 2H; H-3, H-4, overlapping signals), 3.31 (apt t, \textsuperscript{3}J (H,H) = 8.7 Hz, 1H; H-2); \textsuperscript{13}C NMR (126 MHz, D\textsubscript{2}O):  δ 175.2 (C\textsubscript{O2H}), 89.9 (C-1), 77.6 (C-5), 75.5 (C-4), 72.5 (C-2), 71.4 (C-3); IR (film) cm\textsuperscript{-1}: 3239 (OH), 2120 (N\textsubscript{3}), 1607 (C=O), 1419, 11243, 1056, 1027; ESI-HRMS calcd for C\textsubscript{6}H\textsubscript{9}N\textsubscript{3}O\textsubscript{6}Na 242.0389, found m/z 242.0394 [M+Na]\textsuperscript{+}.

Allyl 2,3,4-tri-O-acetyl-1-azido-1-deoxy-β-D-glucopyranuronate (6)\textsuperscript{234}

Sodium hydrogen carbonate (0.23 g, 2.7 mmol) and allyl iodide (0.25 mL, 2.7 mmol) were, respectively, added to intermediate 5 (0.5 g, 2.3 mmol) in DMF (5 mL). The mixture was then stirred for 16 h at room temp and then cooled to 0 °C. DMAP (0.03 g, 0.2 mmol) and Ac\textsubscript{2}O (1.1 mL, 11.5 mmol) were added and the resulting mixture was stirred for 16 h. The resulting suspension was diluted with EtOAc (30 mL), washed with 1M HCl (2 x 30 mL), NaHCO\textsubscript{3} (30 mL), brine (30 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 1:1) gave 6 (0.74 g, 71%) as a white solid; [α]\textsubscript{D} -18.8 (c 2.85, CH\textsubscript{2}Cl\textsubscript{2}); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 5.90 (ddt, \textsuperscript{3}J (H,H) = 16.8, 10.2, 6.0 Hz, 1H; -CH\textsubscript{2}CH=CH\textsubscript{2}), 5.36 (dq, \textsuperscript{3}J (H,H) = 16.8 Hz, \textsuperscript{2}J (H,H) = 1.2 Hz, 1H; CH\textsubscript{2}CH=CH\textsubscript{2}), 5.31–5.22 (m, 3H; overlapping peaks; -CH\textsubscript{2}CH=CH\textsubscript{2}, H-3, H-4), 4.99–4.93 (m, 1H; H-2), 4.71 (d, \textsuperscript{3}J (H,H) = 8.7, 1H Hz; H-1), 4.64 (qd, \textsuperscript{2}J (H,H) = -13.0 Hz, \textsuperscript{3}J (H,H) = 6.0 Hz, 2H; CH\textsubscript{2}CHCH\textsubscript{2}), 2.07 (s, 3H; COCH\textsubscript{3}), 2.02 (s, 3H; COCH\textsubscript{3}), 2.00 (s, 3H; COCH\textsubscript{3}); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): δ = 169.9, 169.2, 169.1 (each COCH\textsubscript{3}), 165.7 (CO\textsubscript{2}CH\textsubscript{2}CHCH\textsubscript{2}), 130.9 (-CH\textsubscript{2}CH=CH\textsubscript{2}), 119.6 (-CH\textsubscript{2}CH=CH\textsubscript{2}), 88.0 (C-1), 74.3 (C-5), 71.9 (C-3), 70.4 (C-2), 69.0 (C-4), 66.8 (-CH\textsubscript{2}CHCH\textsubscript{2}), 20.5 (2s, each COCH\textsubscript{3}, overlapping peaks); IR
Experimental data

Chapter 5

Methyl 1,2,3,4-tetra-O-acetyl-β-D-galactopyranuronate (9)

Perchloric acid (0.05 mL) was added slowly to Ac₂O (15 mL) at 0 °C. D-Galacturonic acid (2.5 g, 11.8 mmol) was then added and the mixture was stirred at 0 °C for 30 min and at room temp for a further 3 h. At this point the reaction was cooled to 0 °C and MeOH was slowly added. The mixture was partitioned between CH₂Cl₂ (50 mL) and H₂O (50 mL). The layers were separated and the aq layer was extracted with CH₂CH₂ (2 x 25 mL). The combined organic portions were washed with water (50 mL), brine (50 mL), dried over Na₂SO₄, filtered and the solvent was removed under diminished pressure. The resulting residue was taken up in DMF (25 mL) and then NaHCO₃ (1.2 g, 14.2 mmol) and methyl iodide (0.88 mL, 14.2 mmol) were added and the mixture was stirred for 16 h before being diluted with EtOAc (50 mL) and H₂O (50 mL). The layers were separated and the aq layer was extracted with EtOAc ( 2 x 25 mL). The combined organic layer were washed with 1M aq HCl (50 mL), NaHCO₃ (50 mL), brine (50 mL), dried over Na₂SO₄, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 1:1) gave the acetylated intermediate (3.0 g, 71%) as a white solid; [α]D +137.9 (c 0.5, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 6.51 (d, 3 J (H,H) = 2.6 Hz, 1H; H-1), 5.84 – 5.78 (m, 1H; H-4), 5.41 – 5.35 (m, 2H; H-3, H-2, overlapping peaks), 4.74 (d, 3 J (H,H) = 1.4 Hz, 1H; H-5), 3.75 (s, 3H; CO₂CH₃), 2.14 (s, 3H; COCH₃), 2.11 (s, 3H; COCH₃), 2.01 (s, 6H; 2 x COCH₃, overlapping peaks); ¹³C NMR (126 MHz, CDCl₃) δ 170.0, 169.7, 168.4 (4 x C=OCH₃, overlapping peaks), 166.5 (CO₂CH₃), 89.6 (C-1), 70.7 (C-5), 68.6 (C-4), 67.0 (C-2), 66.0 (C-3), 52.8 (CO₂CH₃), 20.8, 20.6, 20.5 (2s) (4 x (COCH₃); IR (film) cm⁻¹: 2984, 1770, 1746, 1440, 137, 1252, 1207. ESI-HRMS calcd for C₁₅H₂₀O₁₁Na 399.0903, found m/z 399.0897 [M+Na]⁺.
Methyl 2,3,4-tri-O-acetyl-1-bromo-1-deoxy-α-D-galactopyranuronate (10)\textsuperscript{93}

Compound 9 (2.5 g, 6.6 mmol) was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (25 mL) and the mixture was cooled using an ice bath. To this was added 33% HBr in AcOH (25 mL) and the mixture was allowed to attain room temp and stirred overnight. The mixture was then diluted with CH\textsubscript{2}Cl\textsubscript{2} (50 mL), poured onto iced water (50 mL), the layers were separated and the aq layer washed with further CH\textsubscript{2}Cl\textsubscript{2} (25 mL). The combined organic extracts were washed with ice water (100 mL), satd aq NaHCO\textsubscript{3} (50 mL), brine (50 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and the solvent was removed under diminished pressure. The title compound 10 was obtained as a white foam (2.14 g, 81%) and was used in the next step without further purification; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 6.76 (d, \textsuperscript{3}J (H,H) = 3.9 Hz, 1H; H-1), 5.82 (dd, \textsuperscript{3}J (H,H) = 3.4, 1.7 Hz, 1H; H-4), 5.47 - 5.41 (m, 1H; H-3), 5.09 (dd, \textsuperscript{3}J (H,H) = 10.7, 3.8 Hz, 1H; H-2), 4.87 (1H; d, \textsuperscript{3}J (H,H) = 1.2 Hz; H-5), 3.76 (s, 3H; CO\textsubscript{2}CH\textsubscript{3}), 2.10 (s, 7H; 2 x COCH\textsubscript{3}), 2.01 (s, 3H; COCH\textsubscript{3}); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): δ 169.8, 169.6, 169.4 (3 x COCH\textsubscript{3}), 165.8 (CO\textsubscript{2}CH\textsubscript{3}), 87.2 (C-1), 72.4 (C-5), 67.9 (C-4), 67.6 (C-3), 67.2 (C-2), 53.0 (CO\textsubscript{2}CH\textsubscript{3}), 20.7, 20.5, 20.4 (3 x COCH\textsubscript{3}); IR (film) cm\textsuperscript{-1}: 2992, 2957, 1755, 1372, 1220, 1093, 1013.

Methyl 2,3,4-tri-O-acetyl-1-azido-1-deoxy-β-D-galactopyranuronate (11)\textsuperscript{187}

The bromide 10 (0.25 g, 0.63 mmol) and NaN\textsubscript{3} (0.41 g, 6.3 mmol) were placed in a Biotage microwave vial and then DMF (2.5 mL) was added and the vial sealed and the resulting suspension was placed in an ultrasonic bath and then sonicated for 15-20 min. The vial was opened and the solution was poured on H\textsubscript{2}O (15 mL) and extracted twice with EtOAc (15 mL). The combined organic extracts were washed with H\textsubscript{2}O (40 mL), brine (40 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 1:1) gave 11 (0.21 g, 92%) as a white solid; [α]D \textsubscript{16.3} (c 0.6, CH\textsubscript{2}Cl\textsubscript{2}); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 5.74 (dd, \textsuperscript{3}J (H,H) = 3.5, 1.4 Hz, 1H; H-4), 5.19 (dd,
Experimental data

\[ ^3J(H,H) = 10.4, 8.8 \text{ Hz}, 1H; H-2), 5.09 \text{ (dd, } ^3J(H,H) = 10.4, 3.5 \text{ Hz, 1H; H-3), 4.67 (d, } ^3J(H,H) = 8.8 \text{ Hz, 1H; H-1), 4.39 \text{ (d, } ^3J(H,H) = 1.4 \text{ Hz, 1H; H-5), 3.78 (s, 3H; CO}_2CH_3), 2.13 \text{ (s, 3H; COCH}_3), 2.09 \text{ (s, 3H; COCH}_3), 2.00 \text{ (s, 3H; COCH}_3). \]

\[ ^{13}C \text{ NMR (126 MHz, CDCl}_3): \delta 170.1 \text{ (CO}_2CH_3), 169.8, 169.4, 165.9 \text{ (3 x COCH}_3), 88.6 \text{ (C-1), 74.2 (C-5), 70.5 (C-3), 68.1 (C-4), 67.8 (C-2), 53.1 (CO}_2CH_3), 20.8, 20.7 (2s (3 x COCH}_3); IR (film) cm}^{-1}: 2980, 2119, 1771, 1737, 1273, 1239, 1210, 1051; ESI-HRMS calcd for C_{13}H_{17}O_9N_3Na 382.0862, found m/z 382.0866 [M+Na]^+ \]

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\[ ^2,^3,^4,^6\text{-Tetra-}O\text{-acetyl-}\beta\text{-D-mannopyranosyl azide (14)} \]

Penta-\( O\)-acetyl-\( \alpha \)-D-mannose (3 g, 7.7 mmol) was dissolved in CH\(_2\)Cl\(_2\) (80 mL), I\(_2\) (2.74 g, 10.8 mmol) was added followed by the slow addition of Et\(_3\)SiH (1.72 mL, 10.8 mmol; warning exothermic). The reaction was heated at reflux for 20 min and was then cooled to room temp, diluted with CH\(_2\)Cl\(_2\) (80 mL) and washed with satd aq NaHCO\(_3\) (150 mL) containing 10% Na\(_2\)S\(_2\)O\(_3\). The aq phase was further extracted with CH\(_2\)Cl\(_2\) (50 mL) and the combined organic extracts were dried over Na\(_2\)SO\(_4\), filtered and the solvent was removed under diminished pressure. The residual glycosyl iodide was taken up in CH\(_2\)Cl\(_2\) (60 mL) and tetrabutylammonium azide (3.3 g, 11.6 mmol) was added. The reaction mixture was stirred overnight before diluting with CH\(_2\)Cl\(_2\) (50 mL) and extracting with 1M HCl (100 mL). The aq phase was further washed with CH\(_2\)Cl\(_2\) (30 mL) and the combined organic extracts were dried over Na\(_2\)SO\(_4\), filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 1:1) gave 14 (2.1 g, 64%) as a white solid; [\(\alpha\)]\(_D\) -70.6 (c 0.3, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.44 (dd, \(^3J\) (H,H) = 3.3, 1.3 Hz, 1H; H-2), 5.26 (apt t, \(^3J\) (H,H) = 10.0 Hz, 1H; H-4), 5.04 (dd, \(^3J\) (H,H) = 10.1, 3.3 Hz, 1H; H-3), 4.73 (d, \(^3J\) (H,H) = 1.3 Hz, 1H; H-1), 4.28 (dd, \(^2J\) (H,H) = -12.4 Hz, \(^3J\) (H,H) = 5.7 Hz, 1H; H-6a), 4.20 (dd, \(^2J\) (H, H) = -12.4 Hz, \(^3J\) (H,H) = 2.5 Hz, 1H; H-6b), 3.76 (ddd, \(^3J\) (H,H) = 10.0, 5.7, 2.5 Hz, 1H; H-5), 2.20 (s, 3H; COCH\(_3\)), 2.11 (s, 3H; COCH\(_3\)), 2.05 (s, 3H; COCH\(_3\)), 1.99 (s, 3H; COCH\(_3\)); \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 170.6, 169.9 (2s), 169.5 (each COCH\(_3\)), 85.1 (C-1), 74.6 (C-5), 70.9 (C-3), 69.2 (C-2), 65.3 (C-4), 62.3 (C-6), 20.7, 20.6, 20.5 (each
Experimental data

COCH₃); IR (film) cm⁻¹: 2115, 1744, 1366, 1238, 1209, 1038; ESI-HRMS calcd for C₆H₁₅N₄O₅ 391.1465, found m/z 391.1469 [M+NH₄]⁺.

β-D-mannopyranosyl azide (15)

Azide 14 (1.8 g, 4.8 mmol) was taken up in MeOH (20 mL) and NaOMe (0.05 g, 0.96 mmol) was added and the mixture stirred for 1 h. Dowex® 50WX8 H⁺-resin (500 mg) was then added and the resulting suspension was stirred until the solution was neutral. This was then filtered and the solvent was removed to give the deprotected intermediate (0.93 g, 94%) as a white solid; [α]D -42.6 (c 0.2, CH₃OH);

¹H NMR (500 MHz, D₂O) δ 4.87 (d, ³J (H,H) = 1.1 Hz, 1H; H-1), 3.03 (dd, ³J (H,H) = 3.2, 1.1 Hz, 1H; H-2), 3.96 (dd, ²J (H,H) = -12.3 Hz, ³J (H,H) = 2.2 Hz, 1H; H-6a), 3.77 (dd, ²J (H,H) = -12.3 Hz, ³J (H,H) = 6.4 Hz, 1H; H-6b), 3.67 (dd, ³J (H,H) = 9.7, 3.2 Hz, 1H; H-3), 3.61 (apt t, ³J (H,H) = 9.6 Hz, 1H; H-4), 3.49 (ddd, ³J (H,H) = 9.5, 6.4, 2.2 Hz, 1H; H-5); ¹³C NMR (126 MHz, D₂O) δ 87.2 (C-1), 78.3 (C-5), 72.7 (C-3), 71.0 (C-2), 66.4 (C-4), 60.9 (C-6); IR (film) cm⁻¹: 3332, 2886, 2113, 1739, 1370, 1243, 1053, 1008; ESI-HRMS calcd for C₈H₁₃N₃O₆Na 228.0596, found m/z 228.0600 [M+Na]⁺.

6-O-tert-Butyldiphenylsilyl-2,3,4-tri-O-benzoyl-β-D-mannopyranosyl azide (16)

Compound 15 (0.9 g, 4.4 mmol) was dissolved in pyridine (50 mL) and the resulting solution was cooled over an ice bath. TBDPSCl (1.36 mL, 5.3 mmol) was then added in a drop-wise manner and the reaction mixture was allowed to attain room temp and was stirred overnight. The resulting suspension was again cooled using an ice bath and benzoyl chloride (1.12 mL, 9.7 mmol) was added slowly and the mixture was allowed to warm to room temp and was stirred overnight. Methanol (5 mL) was then added and the resulting slurry was diluted with EtOAc (50 mL), washed twice with 1M HCl (50 mL), satd aq NaHCO₃ (50 mL), brine (50 mL), dried over Na₂SO₄, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc, 7:3) gave 16 (2.53 g, 76%)
as a foam; \([\alpha]_D -19.5\ (c\ 0.1, \text{CH}_2\text{Cl}_2)\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\ 8.15-7.13\) (ms, 25H; Ar-H), 6.26 (apt t, \(^3\)J (H,H) = 10.0 Hz, 1H; H-4), 5.96 (dd, \(^3\)J (H,H) = 3.2, 1.3 Hz, 1H; H-2), 5.56 (dd, \(^3\)J (H,H) = 10.3, 3.2 Hz, 1H; H-3), 5.00 (d, \(^3\)J (H,H) = 1.3 Hz, 1H; H-1), 3.99–3.88 (m, 3H; H-6a, H-6b, H-5, overlapping peaks), 1.12 (s, 9H; C(CH\(_3\))\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\ 165.7, 165.4, 164.9\) (each C OPPh), 135.7, 135.5 (5 x Ar-CH, overlapping peaks), 133.5 133.3 (2s), 132.6 (5 x Ar-C), 130.2, 129.8, 129.7 (2s), 129.6, 129.3, 129.0, 128.8, 128.6, 128.5, 128.3, 127.8, 127.6 (20 x Ar-CH, overlapping peaks), 85.4 (C-1), 77.4 (C-5), 72.4 (C-3), 70.3 (C-2), 65.4 (C-4), 61.8 (C-6), 26.5 (C(CH\(_3\))\(_3\), overlapping peaks), 19.2 (C(CH\(_3\))\(_3\)); IR (film) cm\(^{-1}\): 2931, 2119, 1729, 1452, 1259, 1092, 1025; ESI-HRMS calcd for C\(_{43}\)H\(_{41}\)N\(_3\)O\(_8\)SiNa \(m/z\) 778.2561, found \(m/z\) 778.2553 [M+Na]\(^+\).

2,3,4-tri-O-benzoyl- \(\beta\)-D-mannopyranosyl azide (17)

The TPDPS derivative 16 (2.5 g, 3.3 mmol) was dissolved in THF (25 mL) and the mixture cooled over an ice bath. Acetic acid (0.38 mL, 6.6 mmol) was added followed by 1M TBAF in THF (6.6 mL, 6.6 mmol). The mixture was allowed to attain room temp and stirred for 16 h. Silica was then added and the solvent was removed to adsorb the residue onto silica gel. This was directly subjected to flash chromatography (petroleum ether-EtOAc 3:2) to give the primary alcohol intermediate (1.38 g, 81%) as a white solid; \([\alpha]_D -6.2\ (c\ 0.06, \text{CH}_2\text{Cl}_2)\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\ 8.14–7.14\) (m, 15H; aromatic H), 5.81 (apt t, \(^3\)J (H,H) = 9.9 Hz, 1H; H-4), 5.68 (dd, \(^3\)J (H,H) = 10.1, 3.3 Hz, 1H; H-3), 5.07 (d, \(^3\)J (H,H) = 1.3 Hz, 1H; H-1), 4.02–3.80 (m, 3H; overlapping H-6a, H-6b, H-5); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\ 166.1, 165.5, 165.3\) (3 x COPh), 133.8, 133.7, 133.4, 130.1, 129.8, 129.7 (9 x Ar-CH, overlapping peaks), 128.9 (Ar-C), 128.7 (2s) (2 x Ar-CH, Ar-C, overlapping peaks), 128.6 (2 x Ar-CH, overlapping peaks), 128.5 (2s) (2 x Ar-CH, Ar-C, overlapping peaks), 128.3 (2 x Ar-CH, overlapping peaks), 85.7 (C-1), 77.2 (C-5), 71.5 (C-3), 70.0 (C-2), 66.4 (C-4), 61.4 (C-6); IR (film) cm\(^{-1}\): 3514, 2118, 1721, 1452, 1248, 1090, 1026; ESI-HRMS calcd for C\(_{27}\)H\(_{25}\)N\(_3\)O\(_8\)SiNa 660.1389, found \(m/z\) 660.1397 [M+Na]\(^+\).
**Methyl 1-azido-2,3,4-tri-O-benzoyl-1-deoxy-β-D-mannopyranuronate (18)**

Alcohol 17 (1.3 g, 2.5 mmol) was taken up in MeCN-H$_2$O (3:1, 50 mL) and then BAIB (8.05 g, 25.0 mmol) and TEMPO (0.04 g, 0.25 mmol) were added and the mixture stirred for 5 h and the solvent was then evaporated under diminished pressure. The resulting residue was taken up in CH$_2$Cl$_2$ (50 mL) and washed with 10% Na$_2$S$_2$O$_3$ (50 mL), 1M HCl (50 mL), brine (50 mL), dried over Na$_2$SO$_4$, filtered and the solvent was removed under diminished pressure. The residue was dissolved in DMF (50 mL), NaHCO$_3$ (0.32 g, 3.75 mmol) and methyl iodide (0.23 mL, 3.75 mmol) were added. The mixture was stirred overnight before being diluted with EtOAc (50 mL) and H$_2$O (50 mL). The layers were separated and the aq layer was extracted with further EtOAc (2 x 20 mL). The combined organic extracts were washed with 1M HCl (50 mL), H$_2$O (50 mL), brine (50 mL), dried over Na$_2$SO$_4$, filtered and the solvent removed. Flash chromatography of the residue (petroleum ether-EtOAc 7:3) gave 18 (0.33 g, 24%) as a white solid; [α]$_D$ 144.2 (c 0.85, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): δ = 8.10 (dd, $^3$J (H,H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.95 (dd, $^3$J (H,H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.65 – 7.61 (m, 1H; Ar-H), 7.57 – 7.44 (m, 4H; Ar-H, overlapping peaks), 7.39 (t, $^3$J (H,H) = 7.9 Hz, 2H; Ar-H), 7.29 (t, $^3$J (H,H) = 7.8 Hz, 2H; Ar-H), 5.97 (apt t, $^3$J (H,H) = 9.3 Hz, 1H; H-4), 5.92 (dd, $^3$J (H,H) = 3.3, 1.6 Hz, 1H; H-2), 5.67 (dd, $^3$J (H,H) = 9.6, 3.3 Hz, 1H; H-3), 5.18 (d, $^3$J (H,H) = 1.6 Hz, 1H; H-1), 4.45 (d, $^3$J (H,H) = 9.2 Hz, 1H; H-5), 3.74 (s, 3H; CO$_2$CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 167.0 (CO$_2$CH$_3$), 165.5 (2s), 165.3 (3 x COPh), 133.9, 133.7, 133.6, 130.3, 130.0 (2s) (12 x Ar-CH, overlapping peaks), 128.9 (2s) (2 x Ar-C), 128.8 (2 x Ar-CH, overlapping peaks), 128.7 (2s) (Ar-C, 2 xAr-CH, overlapping peaks), 128.5 (2 x Ar-CH, overlapping peaks), 86.0 (C-1), 74.8 (C-5), 70.8 (C-3), 69.2 (C-2), 67.3 (C-4), 53.2 (CO$_2$CH$_3$); IR (film) cm$^{-1}$: 2954, 2125, 1731, 1455, 1376, 1259, 1104, 998; ESI-HRMS calcld for C$_{28}$H$_{33}$O$_9$N$_3$Na 568.1332, found m/z 568.1339 [M+Na]$^+$.
2-Acetamido-3,4,6-tri-O-Acetyl-2-deoxy-β-D-glucopyranosyl azide (22)<sup>235</sup>
Pentaacetyl-D-glucosamine (3 g, 7.7 mmol) was suspended in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and cooled to 0 °C. A 33% solution of HBr in AcOH (30 mL) was added and the reaction mixture was stirred for 5 h, keeping the reaction on ice. The reaction was then diluted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and poured onto ice (100 mL). The layers were separated and the aq layer was washed with a further portion of CH<sub>2</sub>Cl<sub>2</sub> (30 mL). The combined organic extracts were washed with ice (100 mL), satd aq NaHCO<sub>3</sub> (100 mL), brine (100 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under diminished pressure to give 9. Freshly prepared 9 was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and tetrabutylammonium azide (4.38 g, 15.4 mmol) was added. The reaction mixture was stirred overnight and the solvent was removed under diminished pressure. Flash chromatography of the residue (EtOAc) gave the intermediate azide (1.55 g, 54%) as a white solid; <sup>[α]</sup><sub>D</sub> -49.8 (c 0.15, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 5.66 (d, <sup>3</sup>J (H,H) = 8.9 Hz, 1H; NHCOCH<sub>3</sub>), 5.24 (dd, <sup>3</sup>J (H,H) = 10.6, 9.4 Hz, 1H; H-3), 5.10 (dd, <sup>3</sup>J (H,H) = 10.1, 9.4 Hz, 1H; H-4), 4.76 (d, <sup>3</sup>J (H,H) = 9.2 Hz, 1H; H-1), 4.27 (dd, <sup>2</sup>J (H,H) = -12.4 Hz, <sup>3</sup>J (H,H) = 4.9 Hz, 1H; H-6a), 4.16 (dd, <sup>2</sup>J (H,H) = -12.4 Hz, <sup>3</sup>J (H,H) = 2.3 Hz, 1H; H-6b), 3.91 (apt dt, <sup>3</sup>J (H,H) = 10.6, 9.2 Hz, 1H; H-2), 3.79 (ddd, <sup>3</sup>J (H,H) = 10.1, 4.9, 2.3 Hz, 1H; H-5), 2.10 (s, 3H; COCH<sub>3</sub>), 2.04 (s, 3H; COCH<sub>3</sub>), 2.03 (s, 3H; NHCOC<sub>2</sub>H<sub>5</sub>), 1.98 (s, 3H; COCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 171.0, 170.6, 170.3 (each COCH<sub>3</sub>), 169.2 (NHCOC<sub>2</sub>H<sub>5</sub>), 88.4 (C-1), 74.0 (C-5), 72.1 (C-3), 68.0 (C-4), 61.8 (C-6), 54.2 (C-2), 23.2 (NHCOC<sub>2</sub>H<sub>5</sub>), 20.7, 20.6 (2s) (3 x COCH<sub>3</sub>); IR (film) cm<sup>-1</sup>: 3334, 2959, 2141, 2105, 1740, 1659, 1371, 1224, 1034; ESI-HRMS calcd for C<sub>14</sub>H<sub>20</sub>N<sub>4</sub>O<sub>8</sub>Na 395.1179, found m/z 395.1187 [M+Na]<sup>+</sup>.

**2-Acetamido-3,4,6-tri-O-Acetyl-2-deoxy-β-D-galactopyranosyl azide (23)<sup>157</sup>**

Reaction of pentaacetyl-D-galactosamine (3 g, 7.7 mmol) as described above for the corresponding glucosamine 22, gave the intermediate azide 23 (1.7 g, 59%) as a white solid; <sup>[α]</sup><sub>D</sub> -30.5 (c 0.04, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 5.56 (d, <sup>3</sup>J (H,H) = 8.8 Hz, 1H; NHCOC<sub>2</sub>H<sub>5</sub>), 5.38 (dd, <sup>3</sup>J (H,H) = 3.3, 1.1 Hz, 1H; H-4), 5.24 (dd, <sup>3</sup>J (H,H) = 11.1, 3.3 Hz, 1H; H-3), 4.79 (d, <sup>3</sup>J (H,H) = 9.2 Hz, 1H; H-1), 4.19 –
4.13 (m, 2H; H-6a, H-6b, overlapping peaks), 4.07 – 3.97 (m, 2H; H-5, H-2, overlapping peaks), 2.16 (s, 3H; NHCOCH₃), 2.06 (s, 3H; COCH₃), 2.01 (s, 3H; COCH₃), 1.99 (s, 3H; COCH₃); ¹³C NMR (126 MHz, CDCl₃) δ 170.5, 170.4 (3 x COCH₃), 170.1 (NHCOCH₃), 88.7 (C-1), 72.8 (C-5), 69.7 (C-3), 66.5 (C-4), 61.4 (C-6), 50.8 (C-2), 23.4 (NHCOCH₃), 20.7, 20.6 (2s) (3 x COCH₃); IR (film) cm⁻¹: 3267, 2932, 2113, 1723, 1549, 1315, 1240, 1061; ESI-HRMS calcd for C₁₄H₂₀N₄O₈Na 395.1179, found m/z 395.1184 [M+Na]⁺.

2-Acetamido-2-deoxy-β-D-glucopyranosyl azide (24)²³⁶

This intermediate (1.5 g, 4.0 mmol) was dissolved in MeOH (20 mL) and NaOMe (0.04 g, 0.8 mmol) was added. The reaction was quenched after 1 h by the addition of Dowex® 50WX8 H⁺-resin (50 mg). The reaction was filtered and the solvent was removed to give the unprotected GlcNAc derivative (0.89 g, 91%) as a white solid; [α]D -21.9 (c 0.07, CH₃OH); ¹H NMR (500 MHz, D₂O): δ 4.78 (d, ³J (H,H) = 9.4 Hz, 1H; H-1), 3.95 (dd, ²J (H, H) = -12.5 Hz, ³J (H,H) = 2.2 Hz, 1H; H-6a), 3.79 (dd, ²J (H,H) = -12.5 Hz, ³J (H,H) = 5.5 Hz, 1H; H-6b), 3.73 (dd, ³J (H,H) = 10.2, 9.4 Hz, 1H; H-2), 3.62 – 3.57 (m, 1H; H-3), 3.57 – 3.34 (m, 1H; H-5), 3.50 (dd, ³J (H,H) = 9.8, 8.7 Hz, 1H; H-4), 2.08 (s, 3H; NHCOCH₃); ¹³C NMR (126 MHz, D₂O) δ 174.7 (NHCOCH₃), 88.6 (C-1), 77.8 (C-5), 73.6 (C-3), 69.4 (C-4), 60.5 (C-6), 55.0 (C-2), 22.0 (NHCOCH₃); IR (film) cm⁻¹: 3266, 2920, 2112, 1737, 1544, 1373, 1235, 1034; ESI-HRMS calcd for C₈H₁₅N₄O₅ 233.1012, found m/z 233.1019[M+H]⁺.

2-Acetamido-2-deoxy-β-D-galactopyranosyl azide (25)¹⁵⁷

Treatment of this azide (1.65 g, 4.4 mmol) as described above for the corresponding GlcNAc derivative with MeOH (20 mL) and NaOMe (0.05 g, 0.9 mmol) gave the unprotected GalNAc azide (25) (0.93 g, 86%) as a white solid; [α]D -145.2 (c 0.04, CH₃OH); ¹H NMR (500 MHz, D₂O): δ 4.68 (d, ³J (H,H) = 9.3 Hz, 1H; H-1), 3.99 (dd, ³J (H,H) = 3.1, 0.8 Hz, 1H; H-4), 3.94 (dd, ³J (H,H) = 10.7, 9.3 Hz, 1H; H-2),
3.85 – 3.75 (m, 4H; H-6a, H-6b, H-5, H-3, overlapping peaks), 2.07 (s, 3H; NHCOC\(\text{H}_3\)); \(^{13}\)C NMR (126 MHz, D\(_2\)O): \(\delta\) 174.9 (NHC\(\text{O}\)C\(\text{H}_3\)), 89.0 (C-1), 77.2 (C-5), 70.7 (C-3), 67.6 (C-4), 60.9 (C-6), 51.7 (C-2), 22.1 (NHCOC\(\text{H}_3\)); IR (film) cm\(^{-1}\): 3329, 2907, 2095, 1639, 1553, 1429, 1326, 1226, 1018; ESI-HRMS calcd for C\(_8\)H\(_{14}\)N\(_4\)O\(_5\)Na 269.0862, found m/z 269.0851 [M+Na].

**2-Acetamido-6-O-tert-butyldiphenylsilyl-3,4-di-O-benzoyl-2-deoxy-\beta-D-glucopyranosyl azide (26)**

This polyhydroxylated intermediate (0.84 g, 3.4 mmol) was taken up in pyridine (15 mL) and the resulting solution was cooled using an ice bath. TBDPSCl (1.1 mL, 4.1 mmol) was added dropwise and the mixture was allowed to attain room temp and stirred for 16 h. The resulting suspension was cooled using an ice bath and benzoyl chloride (0.87 mL, 7.5 mmol) was added slowly. The reaction mixture was allowed to warm to room temp and then stirred for 16 h after which time MeOH (~5 mL) was added. The resulting slurry was diluted with EtOAc (50 mL), washed with 1M HCl (2 x 25 mL), satd aq NaHCO\(_3\) (50 mL), brine (50 mL), dried over Na\(_2\)SO\(_4\), filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 6:4) gave 11 (1.8 g, 76%) as a white foam; \([\alpha]_D\) -51.2 (c 0.13, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.98 – 7.91 (m, 2H; Ar-H), 7.90 – 7.83 (m, 2H; Ar-H), 7.75 – 7.68 (m, 2H; Ar-H), 7.61 – 7.45 (m, 4H; Ar-H), 7.42 – 7.32 (m, 6H; Ar-H), 7.18 (dd, \(^3\)J (H,H) = 8.1, 7.0 Hz, 2H; Ar-H), 5.82 – 5.70 (m, 2H; H-4, NHCOC\(\text{H}_3\), overlapping peaks), 5.59 (dd, \(^3\)J (H,H) = 10.7, 9.6 Hz, 1H; H-3), 4.76 (d, \(^3\)J (H,H) = 9.2 Hz, 1H; H-1), 4.25 (apt dt, \(^3\)J (H,H) = 10.7, 9.2 Hz, 1H; H-2), 3.91–3.78 (m, 3H; H-6a, H-6b, H-5, overlapping peaks), 1.91 (s, 3H; NHCOC\(\text{H}_3\)), 1.04 (s, 9H; C(CH\(_3\))\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 170.5 (NHC\(\text{O}\)C\(\text{H}_3\)), 167.1, 164.8 (2 x COPh), 135.6, 135.5, 133.6, 133.5, 133.3 (6 x Ar-CH, overlapping peaks), 132.9, 132.8 (2 x Ar-C), 130.0, 129.7 (2s), 129.6, 128.5 (2s) (6 x Ar-CH, overlapping peaks) (Ar-C, 2 x Ar-CH, overlapping peaks), 128.4 (2s) (Ar-C, 2 x Ar-CH, overlapping peaks), 127.7, 127.6 (4 x Ar-CH, overlapping peaks), 88.6 (C-1), 77.1 (C-5), 73.2 (C-3), 68.3 (C-4), 62.2 (C-6), 54.6 (C-2), 26.6 (C(CH\(_3\))\(_3\), overlapping peaks), 23.3 (NHCOC\(\text{H}_3\)), 19.2 (C(CH\(_3\))\(_3\)); IR (film) cm\(^{-1}\):
Experimental data

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3268, 2931, 2113, 1725, 1657, 1548, 1240, 1061; ESI-HRMS calcd for C_{38}H_{40}N_{4}O_{7}SiNa 701.2533, found m/z 701.2540 [M+Na]^+.

2-Acetamido-6-O-tert-butyldiphenylsilyl-3,4-di-O-benzoyl-2-deoxy-β-D-galactopyranosyl azide (27)

Intermediate 25 (0.9 g, 3.7 mmol) was reacted with pyridine (15 mL) and TBDPSCl (1.14 mL, 4.4 mmol) and then benzoyl chloride (0.93 mL, 8.0 mmol) as described above gave after chromatography (petroleum ether-EtOAc, 6:4) the title compound 27 (1.79 g, 70%) as a white foam; [α]_D +32.7 (c 0.1, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.07 – 8.02 (m, 2H; Ar-H), 7.87 – 7.83 (m, 2H; Ar-H), 7.66 – 7.60 (m, 3H; Ar-H), 7.54 – 7.47 (m, 5H; Ar-H), 7.42 – 7.28 (m, 5H; Ar-H), 7.11 (t, ^3J (H,H) = 7.6 Hz, 2H; Ar-H), 6.00 – 5.94 (m, 1H; H-3), 5.64 – 5.57 (m, 2H; H-4, NHCOCH_3, overlapping peaks), 4.80 (d, ^3J (H,H) = 9.2 Hz, 1H; H-1), 4.33 (apt dt, ^3J (H,H) = 11.1, 9.0 Hz, 1H; H-2), 4.06 (ddd, ^3J (H,H) = 7.4, 6.1, 1.2 Hz, 1H; H-5), 3.86 – 3.75 (m, 2H; H-6a, H-6b, overlapping peaks), 1.89 (s, 3H; NHCOCH_3), 0.99 (s, 9H; C(CH_3)_3); ^13C NMR (126 MHz, CDCl_3): δ 170.5 (NHCOCH_3), 166.4, 165.3 (2 x COPh), 135.5, 135.4, 133.5 (2s), 133.4 (6 x Ar-CH, overlapping peaks), 132.7, 132.5 (2 x Ar-C), 129.9 (2s), 129.8, 129.7 (6 x Ar-CH, overlapping peaks), 129.4, 128.8 (2 x Ar-C), 128.6, 128.4, 127.8, 127.6 (8 x Ar-CH, overlapping peaks), 89.0 (C-1), 75.7 (C-5), 71.0 (C-4), 67.1 (C-3), 51.1 (C-6), 51.4 (C-2), 26.6 (C(CH_3)_3, overlapping peaks), 23.3 (NHCOCH_3), 19.0 (C(CH_3)_3); IR (film): cm⁻¹: 3994, 2860, 2115, 1722, 1657, 1272, 1106, 1068; ESI-HRMS calcd for C_{38}H_{40}N_{4}O_{7}SiNa 701.2533, found m/z 701.2525[M+Na]^+.

2-Acetamido-3,4-di-O-benzoyl-2-deoxy-β-D-glucopyranosyl azide (28)

The TPDPS derivative 26 (0.75 g, 1.1 mmol) was dissolved in THF (15 mL) and HF-pyridine (5 mL) was added slowly. The reaction mixture was then stirred overnight before dilution with EtOAc (50 mL) and careful addition of the mixture to
satd aq NaHCO₃ (100 mL). The resulting biphasic mixture was separated and the organic phase washed with further satd aq NaHCO₃ (50 mL), 1M HCl (50 mL), brine (50 mL), dried over Na₂SO₄, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 3:7) gave the intermediate alcohol (0.45 g, 89%) as a white foam; [α]D -22.7 (c 0.05, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 7.91 (ddd, 3 J (H,H) = 8.5, 3.9, 1.4 Hz, 1H; Ar-H), 7.56 – 7.44 (m, 2H; Ar-H), 7.35 (ddd, 3 J (H,H) = 8.8, 7.5, 1.5 Hz, 1H; Ar-H), 5.94 (d, 3 J (H,H) = 8.9 Hz, 1H; NHCOCH₃), 5.78 (dd, 3 J (H,H) = 10.7, 9.4 Hz, 1H; H-3), 5.51 (apt t, 3 J (H,H) = 9.7 Hz, 1H; H-4), 4.97 (d, 3 J (H,H) = 9.3 Hz, 1H; H-1), 4.16 (apt dt, 3 J (H,H) = 10.7, 8.9 Hz, 1H; H-2), 3.93 – 3.81 (m, 2H; H-5, H-6a, overlapping peaks), 3.80 – 3.64 (m, 1H; H-6b), 1.89 (s, 3H; NHCOCH₃); ¹³C NMR (126 MHz, CDCl₃): δ 170.6 (NHCOCH₃), 166.7, 165.9 (2 x COPh), 133.7 (2s) (2 x Ar-CH), 129.8 (4 x Ar-CH, overlapping peaks), 128.5 (2s) (4 x Ar-CH, Ar-C, overlapping peaks), 128.4 (Ar-C), 88.7 (C-1), 76.7 (C-5), 72.4 (C-3), 69.0 (C-4), 61.2 (C-6), 54.6 (C-2), 23.2 (NHCOCH₃); IR (film) cm⁻¹: 3274, 2965, 2115, 1720, 1451, 1260, 1069, 1024; ESI-HRMS calcd for C₂₂H₂₂N₄O₇Na 477.1386, found m/z 477.1384 [M+Na]+.

2-Acetamido-3,4-di-O-benzoyl-2-deoxy-β-D-galactopyranosyl azide (29)

Treatment of the TBDPS derivative 27 (0.75 g, 1.1 mmol) in THF (15 mL) with HF-pyridine (5 mL) as described for 26 gave the primary alcohol intermediate (0.46 g, 93%) as a white foam; [α]D +68.2 (c 0.2, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.14 – 7.28 (m, 10H; Ar-H), 5.80 (d, 3 J (H,H) = 9.0 Hz, 1H; NHCOCH₃), 5.77 – 5.73 (m, 1H; H-4), 5.58 (dd, 3 J (H,H) = 11.1, 3.3 Hz, 1H; H-3), 4.86 (d, 3 J (H,H) = 9.2 Hz, 1H; H-1), 4.51 (apt dt, 3 J (H,H) = 11.1, 9.0 Hz, 1H; H-2), 4.05 (td, 3 J (H,H) = 6.7, 1.0 Hz, 1H; H-5), 3.84 (apt dt, 2 J (H,H) = -11.5 Hz, 3 J (H,H) 5.3 Hz, 1H; H-6a), 3.69 – 3.61 (m, 1H; H-6b), 1.92 (s, 3H; NHCOCH₃); ¹³C NMR (126 MHz, CDCl₃): δ 170.6 (NHCOCH₃), 166.7, 166.2 (2 x COPh), 134.0, 133.7, 130.1, 129.8, 128.8 (6 x Ar-CH, overlapping peaks), 128.6 (2s) (2 x Ar-C), 128.5 (4 x Ar-CH, overlapping peaks), 89.1 (C-1), 76.0 (C-5), 70.8 (C-3), 68.2 (C-4), 60.5 (C-6), 51.2 (C-2), 23.3
(NHCOCH$_3$); IR (film) cm$^{-1}$: 3286, 2929, 2114, 1722, 1660, 1249, 1093, 1025; ESI-HRMS calcd for C$_{22}$H$_{22}$N$_4$O$_7$Na 477.1386, found m/z 477.1392 [M+Na]$^+$. 

![Chemical structure](image)

**Methyl 2-acetamido-1-azido-1,2-dideoxy-3,4-di-O-benzoyl-β-D-glucopyranuronate (30)**

Compound 28 (0.4 g, 0.9 mmol) was dissolved in MeCN-H$_2$O (10 mL, 3:1) and TEMPO (0.14 g, 0.09 mmol) and BAIB (0.72 g, 2.3 mmol) were added. The mixture was stirred for 5 h at which point 10% Na$_2$S$_2$O$_3$ (5 mL) was added and the mixture concentrated. The resulting slurry was dissolved in EtOAc (25 mL) and extracted with 1M HCl (25 mL), dried over Na$_2$SO$_4$, filtered and the solvent was removed under diminished pressure. The residue was taken up in MeOH (10 mL) and p-TsOH.H$_2$O (0.35 g, 0.2 mmol) was added. The mixture was stirred for 16 h and triethylamine (0.5 mL) was added and the the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 6:4) gave 30 (0.2 g, 47%) as a white foam; [α]D 58.7 (c 0.9, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 7.94 (dd, $^3$J(H,H) = 8.2, 1.4 Hz, 2H; Ar-H), 7.88 (dd, $^3$J(H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.55 – 7.47 (m, 2H; Ar-H), 7.40 – 7.36 (m, 2H; Ar-H), 7.33 (dd, $^3$J(H,H) = 8.5, 7.1 Hz, 2H; Ar-H), 7.30 – 7.27 (m, 2H; Ar-H), 5.89 (d, $^3$J(H,H) = 8.7 Hz, 1H; NHCOCH$_3$), 5.83 (dd, $^3$J(H,H) = 10.3, 9.3 Hz, 1H; H-3), 5.66 (apt t, $^3$J(H,H) = 9.5 Hz, 1H; H-4), 5.12 (d, $^3$J(H,H) = 8.9 Hz, 1H; H-1), 4.41 (d, $^3$J(H,H) = 9.7 Hz, 1H; H-5), 4.09 (apt dt, $^3$J(H,H) = 10.3, 8.7 Hz, 1H; H-2), 3.68 (s, 3H; CO$_2$CH$_3$), 1.92 (s, 3H; NHCOCH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 170.6 (NHCOCH$_3$), 166.8 (CO$_2$CH$_3$), 166.4, 165.1 (2 x COPh), 133.7, 133.5 (2 x Ar-CH), 129.9, 129.7 (4 x Ar-CH, overlapping peaks), 128.6 (Ar-C), 128.5 (2 x Ar-CH, overlapping peaks), 128.4 (2 x Ar-CH, Ar-C, overlapping peaks), 88.6 (C-1), 74.4 (C-5), 71.5 (C-3), 69.7 (C-4), 54.4 (C-2), 53.0 (CO$_2$CH$_3$), 23.2 (COCH$_3$); IR (film) cm$^{-1}$: 2954, 2113, 1721, 1451, 1247, 1096, 1069, 1026; ESI-HRMS calcd for C$_{23}$H$_{23}$O$_8$N$_4$Na 505.1335, found m/z 505.1354 [M+Na]$^+$. 

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Methyl 2-acetamido-1-azido-1,2-dideoxy-3,4-di-O-benzoyl-β-D-glucopyranuronate (31)

Intermediate 29 (0.4 g, 0.9 mmol) was taken up in MeCN-H₂O (10 mL, 3:1) was reacted with TEMPO (0.14 g, 0.09 mmol) and BAIB (0.72 g, 2.3 mmol) and the resulting carboxylic acid treated with p-TsOH.H₂O (0.35 g, 0.2 mmol) in MeOH (10 mL) as described above to give 31 (0.22 g, 51%) as a white foam; [α]D 39.3 (c 0.6, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ = 7.92 - 7.37 (ms, 10H; Ar-H), 6.11 (dd, 3J (H,H) = 3.5, 1.4 Hz, 1H; H-4), 5.82 – 5.76 (m, 2H; NHCOCH₃, H-3, overlapping peaks), 5.14 (d, 3J (H,H) = 9.0 Hz, 1H; H-1), 4.67 (d, 3J (H,H) = 1.4 Hz, 1H; H-5), 4.23 (dt, 3J (H,H) = 11.0, 9.0 Hz, 1H; H-2), 3.72 (s, 3H; CO₂CH₃), 1.91 (s, 3H; NHCOCH₃); ¹³C-NMR (126 MHz, CDCl₃): δ 170.7 (NHCOCH₃), 166.2, 165.9 (2 x COPh), 165.1 (CO₂CH₃), 133.7, 133.6, 130.0, 129.8 (6 x Ar-CH, overlapping peaks), 128.8 (Ar-C), 128.6 (2 x Ar-CH, Ar-C, overlapping peaks), 128.5 (2 x Ar-CH, overlapping peaks), 88.7 (C-1), 74.4 (C-5), 69.8 (C-3), 68.6 (C-4), 52.9 (CO₂CH₃), 51.3 (C-2), 23.3 (NHCOCH₃); IR (film) cm⁻¹: 2956, 2117, 1725, 1665, 1451, 1248, 1092, 1067, 1025; ESI-HRMS calcd for C₂₃H₂₂O₈N₄Na 505.1335, found m/z 505.1340 [M+Na]⁺.

2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl azide (35)

Glucose pentaacetate (10 g, 25.6 mmole) was taken up in CH₂Cl₂ (80 ml) and cooled using an ice bath. TMSN₃ (5.1 ml, 38.4 mmole) was added, followed by drop wise addition of SnCl₄ (1.5 ml, 12.8 mmole). The reaction mixture was allowed to come slowly to room temperature overnight. The resulting solution was diluted with CH₂Cl₂ (100 ml) and washed twice with 1M KHSO₄ (100 ml), satd Aq NaHCO₃ (100 ml), brine (100 ml), dried over anhydrous NaSO₄, filtered and the solvent was removed under reduced pressure. This residue was recrystallised from ethanol to yield 35 (7.7 g, 81 %) as a white solid; [α]D -31.9 (c 0.28, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 5.22 (apt. t, 3J (H,H) = 9.5 Hz, 1H; H-3), 5.11 (apt. t, 3J (H,H) = 9.7 Hz, 1H; H-2).
Hz, 1H; H-4), 4.96 (dd, $^3J(H,H) = 9.5$, 8.8 Hz, 1H; H-2), 4.65 (d, $^3J(H,H) = 8.8$ Hz, 1H; H-1), 4.27 (dd, $^2J(H,H) = -12.5$, $^3J(H,H) = 4.8$ Hz, 1H; H-6a), 4.17 (dd, $^2J(H,H) = -12.5$, $^3J(H,H) = 10.1$, 4.8, 2.3 Hz, 1H; H-5), 2.10 (s, 3H; COCH$_3$), 2.08 (s, 3H; COCH$_3$), 2.03 (s, 3H; COCH$_3$), 2.01 (s, 3H; COCH$_3$). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.6, 170.1, 169.3, 169.2 (4 x COCH$_3$), 87.9 (C-1), 74.0 (C-5), 72.6 (C-3), 70.6 (C-2), 67.9 (C-4), 61.6 (C-6), 20.7, 20.6, 20.5 (4 x COCH$_3$, overlapping peaks); IR (film) cm$^{-1}$: 2909, 2117, 1753, 1368, 1209, 1036; ESI-HRMS calcd for C$_{14}$H$_{19}$N$_3$O$_9$Na 396.1019, found m/z 396.1023 [M+Na]$^+$.  

\[ \beta\text{-D-glucopyranosyl azide (36)}^{237} \]

Sodium methoxide (0.2 g, 4.0 mmol) was added to the azide 35 (7.5 g, 20.1 mmol) in MeOH (50 mL) and the mixture was stirred for 1 h and then Dowex® 50WX8 H$^+$-resin (500 mg) was added and the resulting suspension stirred until the pH was 7. This mixture was then filtered and the solvent was removed under diminished pressure to give β-D-glucopyranosyl azide (3.92 g, 95%) as a white solid; [α]$_D$ -31.0 (c 0.3, CH$_3$OH); $^1$H-NMR (500 MHz, D$_2$O): δ 4.75 (d, $^3J(H,H) = 8.8$ Hz, 1H; H-1), 3.93 (dd, $^2J(H,H) = -12.4$ Hz, $^3J(H,H) = 2.2$ Hz, 1H; H-6a), 3.75 (dd, $^2J(H,H) = -12.4$ Hz, $^3J(H,H) = 5.7$ Hz, 1H; H-6b), 3.57 – 3.49 (m, 2H; H-5, H-3, overlapping peaks), 3.41 (apt t, $^3J(H,H) = 9.0$ Hz, 1H; H-4 ), 3.27 (apt t, $^3J(H,H) = 9.0$ Hz, 1H; H-2), $^{13}$C-NMR (126 MHz, D$_2$O): δ 90.9 (C-1), 79.0 (C-5), 76.9 (C-3), 73.6 (C-2), 69.9 (C-4), 61.4 (C-6); IR (film) cm$^{-1}$: 3303, 2881, 2125, 1742, 1377, 1263, 1064; ESI-HRMS calcd for C$_6$H$_{12}$N$_3$O$_5$ 206.0777, found m/z 206.0772 [M+H]$^+$.  

\[ 4,6\text{-O-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-} \beta\text{-D-glucopyranosyl azide (37).} \]

To a solution of 36 (3.5 g, 17.1 mmol) in pyridine (50 mL) at 0°C was added 1,3-
dichloro-1,1,3,3-tetraisopropylidisiloxane (0.99 mL, 20.5 mmol) and the mixture was allowed to warm to room temp and was then stirred for 5 h at which point MeOH (1 mL) was added and the solvent removed under diminished pressure. The resulting residue was taken up in EtOAc (50 mL) and washed with 1M HCl (50 mL), NaHCO₃ (50 mL), brine (50 mL), then dried over Na₂SO₄, filtered and the solvent removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc, 7:3) gave 37 (4.7 g, 61%) as a white solid; [α]D -80.7 (c 0.20, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 4.58 (d, ³J (H,H) = 8.6 Hz, 1H; H-1), 4.09 (dd, ²J (H,H) = 12.7 Hz, ³J (H,H) = 2.1 Hz, 1H; H-6a), 4.00 (dd, ²J (H,H) = 12.7 Hz, ³J (H,H) = 1.5 Hz, 1H; H-6b), 3.83 (apt t, ³J (H,H) = 9.1 Hz, 1H; H-4), 3.60 (apt t, ³J (H,H) = 9.1 Hz, 1H; H-3), 3.34 – 3.26 (m, 2H; H-5, H-2, overlapping peaks), 2.56 (s, 2H; 2 x OH), 1.25 – 0.89 (m, 28H; 4 x CH(CH₃)₂, overlapping peaks); ¹³C NMR (126 MHz, CDCl₃): δ 90.8 (C-1), 78.7 (C-5), 76.5 (C-3), 73.5 (C-2), 68.8 (C-4), 60.6 (C-6), 17.4, 17.3, 17.2 (3s), 17.1 (2s) (8 x CH(CH₃)₂, overlapping peaks), 13.6, 13.2, 12.5 (2s) (4 x CH(CH₃)₂, overlapping peaks); IR (film) cm⁻¹: 3420, 2868, 2115, 1465, 1248, 1025; ESI-HRMS calcd for C₁₈H₃₇N₃O₆Si₂Na 442.2349, found m/z 442.2352 [M+Na⁺].

![Diol 37](image)

3,4-O-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranosyl azide (38)

To a solution of diol 37 (2 g, 4.45 mmol), in DMF (25 mL), p-TsOH.H₂O (0.17 g, 0.9 mmol) was added and the mixture stirred at room temp for 5 h and it was then diluted with EtOAc (50 mL), washed with H₂O (2 x 25 mL), satd aq NaHCO₃ (50 mL), brine (50 mL), dried over Na₂SO₄, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 8:2) gave the 3,4-protected intermediate (1.87 g, 94%) as a clear oil; [α]D -4.8 (c 0.17, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ = 4.60 (d, ³J (H,H) = 8.6 Hz, 1H; H-1), 3.93 (ddd, ²J (H,H) = -12.0 Hz, ³J (H,H) = 6.3, 2.2 Hz, 1H; H-6a), 3.77 (ddd, ²J (H,H) = -12.0 Hz, ³J (H,H) = 7.2, 4.9 Hz, 1H; H-6b), 3.73 – 3.64 (m, 2H; H-4, H-3, overlapping peaks), 3.45 (ddd, ³J (H,H) = 8.9, 4.9, 2.8 Hz, 1H; H-5), 3.38 (apt td, ³J (H,H) = 8.6, 2.2 Hz, 1H; H-2), 2.44 (d, ³J (H,H) = 2.3 Hz, 1H; OH), 1.93 (apt t, ³J (H,H) = 8.6, 2.2 Hz, 1H; H-2).
Experimental data

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(H,H) = 6.8 Hz, 1H; OH), 1.16 – 0.86 (m, 28H; 4 x CH(CH₃)₂, overlapping peaks);
¹³C NMR (126 MHz, CDCl₃) δ 89.5 (C-1), 79.8 (C-3), 78.4 (C-5), 73.9 (C-2), 72.1 (C-4), 61.9 (C-6), 17.3 (3s), 17.2 (2s), 17.1 (8 x CH(CH₃)₂, overlapping peaks), 12.9, 12.8, 12.1 (2s) (4 x CH(CH₃)₂, overlapping peaks); IR (film) cm⁻¹: 3349, 2868, 2114, 1464, 1248, 1052, 987; ESI-HRMS calcd for C₁₈H₃₇N₃O₆Si₂Na 442.2349, found m/z 442.2356 [M+Na]⁺.

Methyl 1-azido-1-deoxy-3,4-O-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranuronate (39)

Intermediate 38 (1.8 g, 4.0 mmol) was dissolved in MeCN-H₂O (60 mL, 3:1) and BAIB (3.24 g, 10.1 mmol) and TEMPO (0.06 g, 0.4 mmol) were added and the mixture was stirred for 5 h. Work-up as described above for the TEMPO-BAIB oxidation gave the carboxylic acid, which when treated in DMF (25 mL) with NaHCO₃ (0.5 g, 6.0 mmol) and methyl iodide (0.37 mL, 6.0 mmol) as described above gave 39 (0.97 g, 51%) as a clear oil after chromatography (petroleum ether-EtOAc 9:1); [α]D -3.6° (c 0.06, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ = 4.61 (d, 3 J (H,H) = 8.7 Hz, 1H; H-1), 3.96 – 3.90 (m, 2H; H-5, H-4, overlapping peaks), 3.78 (s, 3H; OCH₃), 3.68 (ddd, 3 J (H,H) = 8.5, 6.4, 1.9 Hz, 1H; H-3), 3.45 (td, 3 J (H,H) = 8.7, 1.9 Hz, 1H; H-2), 2.43 (d, 3 J (H,H) = 2.4 Hz, 1H; OH), 1.29–0.46 (m, 28H; 4 x CH(CH₃)₂, overlapping peaks); ¹³C NMR (126 MHz, CDCl₃): δ 168.2 (CO₂CH₃), 89.9 (C-1), 79.3 (C-3), 77.4 (C-5), 73.7 (C-4), 73.4 (C-2), 52.4 (CO₂CH₃), 17.3, 17.2 (4s), 17.1, 17.0 (2s) (8 x CH(CH₃)₂, overlapping peaks), 12.9, 12.8, 12.2, 12.1 (4 x CH(CH₃)₂, overlapping peaks); IR (film) cm⁻¹: 3441, 2867, 2125, 1785, 1736, 1464, 1251, 1081, 987; ESI-HRMS calcd for C₁₉H₃₇N₃O₆Si₂Na 498.2068, found m/z 498.2074 [M+Na]⁺.

Allyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (40)
Glucose pentaacetate (15 g, 38.4 mmol) was taken up in CH₂Cl₂ (80 ml) and cooled using an ice bath. To the resulting solution was added allyl alcohol (6.5 ml, 96.0 mmol) and BF₃·OEt₂ (23.7 ml, 192.0 mmol) and the reaction mixture was allowed to come to room temperature and stir overnight. The solution was diluted with CH₂Cl₂ (150 ml) and poured slowly onto satd aq NaHCO₃ (250 ml). The biphasic mixture was separated and the organic layer washed with a further portion of satd aq NaHCO₃ (250 ml), brine (250 ml), dried over Na₂SO₄, filtered and concentrated. The crude product was purified via flash chromatography (petroleum ether-EtOAc 6:4) to 40 (9.1 g, 61%) as a white solid; [α]D -28.3° (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 5.84 (dddd, ³J (H,H) = 17.3, 10.4, 6.1, 4.9 Hz, 1H, CH₂CH₂), 5.27 (dq, ⁴J (H,H) = 1.7 Hz, 1H; CH₂CHCH₂), 5.24 – 5.16 (m, 2H, H-3; CH₂CH₂, overlapping peaks), 5.09 (dd, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 4.55 (d, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 5.09 (dd, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 4.55 (d, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 5.09 (dd, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 4.55 (d, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 5.09 (dd, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 4.55 (d, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 5.09 (dd, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 4.55 (d, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 5.09 (dd, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 4.55 (d, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 5.09 (dd, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 4.55 (d, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 5.09 (dd, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4), 4.55 (d, ³J (H,H) = 10.0, 9.3 Hz, 1H; H-4). ¹H NMR (500 MHz, CDCl₃) δ 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), 170.6, 170.3, 169.4, 169.3 (4 x COCH₃), IR (film) cm⁻¹: 2951, 1738, 1445, 1369, 1208, 1031; ES-HRMS calcd for C₁₇H₂₅O₁₀ 389.1448, found m/z 389.1456 [M+H]⁺.

Allyl β-D-glucopyranoside (41) ³²³⁸

Compound 40 (9 g, 23.2 mmole) was taken up in MeOH (50 ml) and NaOMe (0.25 g, 4.6 mmole) was added. The reaction was followed by TLC and upon completion dowex® 50WX8 H⁺-resin (500mg) was added and the resulting suspension was stirred until the solution was neutralised. This was then filtered and evaporated to give 41 (4.4 g, 87%) as a white solid; [α]D -35.0 (c 0.2, CH₃OH); ¹H NMR (500
MHZ, D₂O) δ 5.85 (dddd, 3J (H,H) =17.0, 10.5, 6.3, 5.5 Hz, 1H; CH₂CHCH₂), 5.25 (dq, 3J (H,H) =17.0, 1H; CH₂CHCH₂), 5.15 (dq, 3J (H,H) =10.5, 4J (H,H) = 1.5 Hz, 1H; CH₂CHCH₂), 4.73 (d, 3J (H,H) = 8.0 Hz, 1H; H-1), 4.26 (ddt, 2J (H,H) = 12.7, 3J (H,H) = 5.5, 4J (H,H) = 1.4 Hz, 1H; CH₂CHCH₂), 4.09 (ddt, 2J (H,H) = -12.7, 3J (H,H) =6.3, 4J (H,H) = 1.4 Hz, 1H; CH₂CHCH₂), 3.78 (dd, 2J (H,H) = -12.3, 3J (H,H) =2.2 Hz, 1H; H-6a), 3.58 (dd, 2J (H,H) = -12.3, 3J (H,H) = 6.0 Hz, 1H; H-6b), 3.35 (apt. t, 3J (H,H) = 9.2 Hz, 1H; H-3), 3.33 – 3.29 (m, 1H; H-5), 3.25 (dd, 3J (H,H) = 9.9, 8.9 Hz, 1H; H-4), 3.15 (dd, 3J (H,H) = 9.3, 8.0 Hz, 1H; H-2);¹³C NMR (126 MHz, D₂O) δ 133.2 (CH₂CHCH₂), 118.7 (CH₂CHCH₂), 101.1 (C-1), 75.8 (C-5), 75.7 (C-3), 73.0 (C-2), 70.5 (CH₂CHCH₂), 69.6 (C-4), 60.7 (C-6); IR (film) cm⁻¹: 3295, 2915, 1664, 1458, 1365, 1109, 1073, 1022; ES-HRMS calcd for C₉H₁₆O₅Na 243.0845, found m/z 243.0852 [M+Na]⁺.

**Allyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranoside (42)**

Intermediate 41 (4.4 g, 20.0 mmole) was taken up in pyridine and cooled using an ice bath. BzCl (20.43 ml, 175.8 mmole) was added slowly via a dropping funnel. The reaction mixture was allowed to attain room temperature and stir over night, before quenching with MeOH. The resulting slurry was diluted with EtOAc (100 ml), washed twice with 1M HCl (100 ml), satd aq NaHCO₃ (100 ml), brine (100 ml), dried over Na₂SO₄, filtered and concentrated. The resulting residue was purified via flash chromatography (petroleum ether-EtOAc 8:2) to 42 (10.3 g, 81%) as a white solid; [α]₀ +19.4 (c 0.2, CH₂Cl₂);¹H NMR (500 MHz, CDCl₃) δ 8.04 – 8.01 (m, 2H; Ar-H), 7.98 – 7.95 (m, 2H; Ar-H), 7.91 – 7.88 (m, 2H; Ar-H), 7.85 – 7.81 (m, 2H; Ar-H), 7.57 – 7.47 (m, 3H; Ar-H), 7.43 – 7.38 (m, 4H; Ar-H), 7.37 – 7.32 (m, 2H; Ar-H), 7.30 – 7.26 (m, 2H; Ar-H), 5.91 (apt. t, 3J (H,H) = 9.6 Hz, 1H; H-3), 5.80 (dddd, 3J (H,H) = 17.0, 10.4, 6.3, 4.9 Hz, 1H; CH₂CHCH₂), 5.68 (apt. t, 3J (H,H) = 9.7 Hz, 1H; H-4), 5.56 (dd, 3J (H,H) = 9.7, 7.8 Hz, 1H; H-2), 5.22 (dq, 3J (H,H) =17.0, 4J (H,H) = 1.6 Hz, 1H; CH₂CHCH₂), 5.12 (dq, 3J (H,H) =10.4, 4J (H,H) = 1.6 Hz, 1H; CH₂CHCH₂), 4.90 (d, 3J (H,H) = 7.8 Hz, 1H; H-1), 4.64 (dd, 2J (H,H) = -12.1, 3J (H,H) = 3.2 Hz, 1H; H-6a), 4.51 (dd, 2J (H,H) = -12.1, 3J (H,H) = 5.4 Hz,
1H; H-6b), 4.38 – 4.33 (m, 1H; CH$_2$CHCH$_2$), 4.20 – 4.13 (m, 2H; CH$_2$CHCH$_2$, H-5, overlapping peaks); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 166.1, 165.8, 165.2, 165.1 (4 x COPh), 133.4 (Ar-CH), 133.3 (CH$_2$CHCH$_2$), 133.2, 133.2, 133.1, 129.8, 129.8, 129.7, 129.6 (14 x Ar-CH, overlapping peaks), 129.3, 128.8, 128.8, 128.4 (4 x Ar-C), 128.4, 128.3, 128.3 (5 x Ar-CH, overlapping peaks), 117.9 (CH$_2$CHCH$_2$), 99.8 (C-1), 72.9 (C-3), 72.2 (C-5), 71.9 (C-2), 70.1 (CH$_2$CHCH$_2$), 69.8 (C-4), 63.2 (C-6); IR (film) cm$^{-1}$: 3072, 1729, 1451 1249, 1090, 1026; ES-HRMS calcd for C$_{37}$H$_{36}$NO$_{10}$ 653.2261, found m/z 653.22644 [M+NH$_4$]$.^+$

\[ \text{2,3,4,6-tetra-O-benzoyl-1-(2,2,2-trichloro-1-iminoethoxy)-\(\alpha\)-D-glucopyranoside (43)}^{93} \]

Compound 42 (10 g, 15.7 mmole) was taken up in MeOH/ CH$_2$Cl$_2$ (50 ml, 3:1) and PdCl$_2$ (0.56 g, 3.1 mmole) was added. The reaction mixture was stirred over night, before filtration through celite and concentration to give the crude product which was purified via flash chromatography (petroleum ether-EtOAc 6:4). The resulting hemiacetal (6.4 g, 10.7 mmole) was taken up in CH$_2$Cl$_2$ (50 ml) and cooled using an ice bath. To this was added trichloroacetonitrile (10.75 ml, 107.3 mmole) and catalytic DBU (0.25 ml). The reaction was followed by TLC and upon consumption of the starting material the solution was concentrated to ~10 ml. This was directly purified via flash chromatography (petroleum ether-EtOAc 7:3, 0.1% Et$_3$N) to 43 (6.7 g, 76 % over 2 steps) as a white solid; [$\alpha$]$_D$ +78.8 (c 0.2, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.64 (s, 1H; NH), 8.07 – 8.00 (m, 2H; Ar-H), 7.96 (ddd, $^3$J (H,H) = 8.5, 4.9, 1.6 Hz, 4H; Ar-H), 7.87 (dd, $^3$J (H,H) = 7.9, 1.7 Hz, 2H; Ar-H), 7.59 – 7.47 (m, 3H; Ar-H), 7.43 (td, $^3$J (H,H) = 7.4, 5.5 Hz, 3H; Ar-H), 7.37 (d, $^3$J (H,H) = 7.8 Hz, 4H; Ar-H), 7.30 (t, $^3$J (H,H) = 7.8 Hz, 2H; Ar-H), 6.84 (d, $^3$J (H,H) = 3.7 Hz, 1H; H-1), 6.28 (apt. t, $^3$J (H,H) = 10.0 Hz, 1H; H-3), 5.82 (apt. t, $^3$J (H,H) = 10.0 Hz, 1H; H-4), 5.63 (dd $^3$J (H,H) = 10.2, 3.7 Hz, 1H; H-2), 4.67 – 4.60 (m, 2H; H-5, H-6a, overlapping peaks), 4.49 (dd, $^2$J (H,H) = -12.5, $^3$J (H,H) = 5.2 Hz, 1H; H-6b); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 166.0, 165.6, 165.4, 165.2 (4 x COPh), 160.5
Experimental data

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(C(NH)CCl₃) 133.5, 133.3, 133.1, 129.9, 129.8, 129.7 (14 x Ar-CH, overlapping peaks), 129.6, 128.8, 128.6 (4 x ArC, overlapping peaks), 128.5, 128.4, 128.4, 128.3 (6 x Ar-CH, overlapping peaks), 93.1 (C-1), 70.7 (C-2, C-5, overlapping peaks), 70.2 (C-3), 68.7 (C-4), 62.5 (C-6); IR (film) cm⁻¹: 334, 1723, 1452, 1248, 1091, 1025, 931.

Methyl 2-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-1-azido-1-deoxy-3,4-O-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranuronate (44)

To a flame dried flask, containing freshly activated 4 Å molecular sieves (0.6 g), was added 39 (0.25 g, 0.5 mmol), 43 (0.58 g, 0.8 mmol) and CH₂Cl₂ (6 mL). The resulting suspension was stirred at room temp for 30 min before cooling to 0 °C using an ice bath. TMSOTf (0.029 mL, 0.16 mmol) was then added and the reaction mixture was allowed to attain room temp over 1 h. Triethylamine (0.25 mL) was added, the mixture filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 8:2) gave 44 (0.35 g, 67%) as a white foam; [α]D -22.6 (c 0.07, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.06 – 8.01 (m, 2H; Ar-H), 7.91 (dd, ³J (H,H) = 8.5, 4.0, 1.3 Hz, 4H; Ar-H), 7.82 – 7.71 (m, 2H; Ar-H), 7.57 – 7.52 (m, 1H; Ar-H), 7.50 (dd, ³J (H,H) = 8.3, 6.7 Hz, 2H; Ar-H), 7.41 (apt q, ³J (H,H) = 7.8 Hz, 3H; Ar-H), 7.35 (td, ³J (H,H) = 7.7, 4.2 Hz, 4H; Ar-H), 7.28 – 7.22 (m, 1H; Ar-H), 5.85 (apt t, ³J (H,H) = 9.5 Hz, 1H; H-3), 5.73 (apt t, ³J (H,H) = 9.6 Hz, 1H; H-4), 5.58 (dd, ³J (H,H) = 9.6, 7.7 Hz, 1H; H-2), 5.35 (d, ³J (H,H) = 7.7 Hz, 1H; H-1), 4.71 (dd, ²J (H,H) = -12.1 Hz, ³J (H,H) = 3.2 Hz, 1H; H-6a), 4.57 – 4.47 (m, 2H; H-1’, H6-b, overlapping peaks), 4.11 (ddd, ³J (H,H) = 10.0, 5.2, 3.2 Hz, 1H; H-5), 3.93 (apt t, ³J (H,H) = 8.5 Hz, 1H; H-2’), 3.89 – 3.79 (m, 3H; H-3’, H-4’, H-5’, overlapping peaks), 3.75 (s, 3H; OCH₃), 1.06-0.68 (m, 28H; 4 x CH(CH₃)₂, overlapping peaks); ¹³C-NMR (126 MHz, CDCl₃): δ 168.1 (CO₂CH₃), 166.1, 165.8, 165.1 (2s) (4 x COPh), 133.4, 133.2 (2s), 133.1, 129.9, 129.8, 129.7 (12 x Ar-CH, overlapping peaks), 129.6, 129.2, 128.8, 128.0 (4 x Ar-
Experimental data

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C), 128.4 (2s), 128.3, 128.2 (8 x Ar-CH, overlapping peaks), 100.0 (C-1), 88.4 (C-1'), 79.7 (C-3'), 77.2 (C-5'), 76.4 (C-2'), 74.0 (C-4'), 73.1 (C-3), 72.5 (C-2), 72.3 (C-5), 69.6 (C-4), 62.9 (C-6), 52.4 (CO2CH3), 17.5, 17.4, 17.2 (2s), 17.1, 17.0 (2s) (8 x CH(CH3)2, overlapping peaks), 12.8, 12.7, 12.3, 12.2 (4 x CH(CH3)2, overlapping peaks); IR (film) cm⁻¹: 2946, 2119, 1728, 1452, 1249, 1089, 986. ESI-HRMS calcd for C53H63N3O16S2Na 1076.3645, found m/z 1076.3652 [M+Na]^+.

Methyl 1-azoido-1-deoxy-2-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-3,4-di-O-benzoyl-β-D-glucopyranosuronate (45)

Disaccharide 44 (0.2 g, 0.19 mmol) was added to 1.25 M HCl in methanol (10 mL) at 0 °C and the resulting solution was allowed to attain room temp and stirred for 16 h. The mixture was cooled using an ice bath, diluted with MeOH (20 mL) and NaHCO₃ was then added. The resulting slurry was concentrated to dryness and the residue suspended in pyridine and cooled using an ice bath. Benzoyl chloride (0.13 mL, 1.1 mmol) was then added and the mixture allowed to warm to room temp and was stirred for a further 16 h. Methanol (0.5 mL) was added and the mixture diluted with EtOAc (10 mL). This was washed with 1M HCl (2 x 5 mL), satd aq NaHCO₃ (10 mL), brine (10 mL), and then dried over Na₂SO₄, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc, 6:4) gave 45 (0.12 g, 63%) as a glassy solid; [α]D -12.2 (c 0.35, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.11 (dd, J = 8.3, 1.5 Hz, 2H; Ar-H), 8.06 (dd, J = 8.4, 1.4 Hz, 2H; Ar-H), 7.86 (dd, J = 8.4, 1.4 Hz, 2H; Ar-H), 7.78 (dd, J = 8.3, 1.4 Hz, 2H; Ar-H), 7.71 (dd, J (H,H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.65 (dd, J (H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.60 (dd, J (H,H) = 8.2, 1.4 Hz, 2H; Ar-H), 7.58 – 7.41 (m, 6H; Ar-H), 7.40 – 7.36 (m, 1H; Ar-H), 7.35 – 7.28 (m, 5H; Ar-H), 7.21 (td, J (H,H) = 7.9, 6.4 Hz, 4H; Ar-H), 5.76 – 5.64 (m, 3H; H-3, H-3', H-4, overlapping peaks), 5.55–5.48 (m, 2H; H-4', H-2', overlapping peaks), 5.07 (d, J (H,H) = 7.8 Hz, 1H; H-1'), 4.90 (d, J (H,H) = 7.7 Hz, 1H; H-1), 4.71 (dd, J (H,H) = -12.2 Hz, J (H,H) = 3.1Hz, 1H; H-6a), 4.54 (dd, J (H,H) = -12.2 Hz, J (H,H) = 4.6Hz, 1H; H-
Experimental data

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6b), 4.26 (d, $^3J(H,H) = 9.2$ Hz, 1H; H-5'), 4.16 (ddd, $^3J(H,H) = 9.5$, 4.6, 3.1 Hz, 1H; H-5), 4.10 (apt t, $^3J(H,H) = 8.2$ Hz, 1H; H-2), 3.66 (s, 3H; OCH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 166.9 (CO$_2$CH$_3$), 166.1, 165.7, 165.0, 165.0, 164.8 (6 x COPh, overlapping peaks), 133.7, 133.4 (2s), 133.2 (2s), 132.9 , 130.2, 129.8, 129.7 (2s), 129.6 (18 x Ar-CH, overlapping peaks), 129.5, 129.2, 128.9, 128.8 128.7, 128.6 (6 x Ar-C, overlapping peaks) 128.5 (2s), 128.4 (2s) 128.2, 128.1 (12 x Ar-CH, overlapping peaks), 100.9 (C-1'), 88.8 (C-1), 77.1 (C-2), 74.7 (C-5'), 73.6 (C-3), 72.8 (C-3'), 72.3 (C-5), 71.9 (C-2'), 69.6 (C-4), 69.3 (C-4'), 62.7 (C-6), 52.9 (CO$_2$CH$_3$); IR (film) cm$^{-1}$: 2953, 2120, 1726, 1684, 1452, 1248, 1091, 1067, 1026; ESI-HRMS calcd for C$_{55}$H$_{45}$O$_{17}$N$_3$Na 1042.2647, found m/z 1042.2671 [M+Na]$^+$. 

General procedure for the anomerisation reactions using TiCl$_4$:

The β-anomer (1 eq) was added to a flame dried round bottomed flask and anhydrous CH$_2$Cl$_2$ (10 mL per g of substrate) was added. The flask was then cooled on an ice bath and 2.5 eq TiCl$_4$ (1.0 M in CH$_2$Cl$_2$) was added dropwise. The flask was then left to stand in a freezer (-15 to -18 °C) for 48-72 h. The mixture was diluted with CH$_2$Cl$_2$ and washed with NH$_4$Cl (1.0 M, 10 mL). The aq layer was extracted with CH$_2$Cl$_2$ and the combined organic layers were washed with satd aq NaHCO$_3$ and brine. The organic layer was dried over Na$_2$SO$_4$, filtered through silica gel and the solvent removed to give the products.

Methyl 2,3,4-tri-O-acetyl-α-D-glucopyranosyuronate azide (4) 

[α]$_D$ -129.0 (c 1.15, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$) δ 5.67 (d, $^3J(H,H) = 4.2$, 1H; H-1), 5.42 (apt t, $^3J(H,H) = 9.6$, 1H; H-3), 5.15 (apt t, $^3J(H,H) = 9.6$, 1H; H-4), 4.96 (ddd, $^3J(H,H) = 9.9$, 4.2, 1H; H-2), 4.48 (d, $^3J(H,H) = 9.9$, 1H; H-5), 3.76 (s, 3H, CO$_2$CH$_3$), 2.10 (s, 3H; COCH$_3$), 2.04 (s, 3H; COCH$_3$), 2.03 (s, 3H; COCH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 169.8, 169.6, 169.4 (3 x COCH$_3$), 167.4 (CO$_2$CH$_3$), 86.1 (C-1), 69.9 (C-3), 69.7 (C-4), 69.0 (C-2), 68.6 (C-5), 53.0 (CO$_2$CH$_3$), 20.6, 20.5, 20.5 (3 x COCH$_3$); IR (film) cm$^{-1}$: 2956, 2120, 1728, 1687, 1452, 1246, 1091, 1067, 1026; ESI-HRMS calcd for C$_{13}$H$_{17}$O$_9$N$_3$Na 382.0862, found m/z 382.0867 [M+Na]$^+$. 

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Allyl 2,3,4-tri-O-acetyl-1-azido-1-deoxy-α-D-glucopyranuronate (7)

[α]D 127.8 (c 1.2, CH2Cl2); 1H-NMR (500 MHz, CDCl3) δ 5.90 (ddt, 3J (H,H) = 17.0, 10.4, 6.0 Hz, 1H; -CH2CH2H), 5.68 (d, 3J (H,H) = 4.2 Hz, 1H; H-1), 5.42 (apt t, 3J (H,H) = 9.6 Hz, 1H; H-3), 5.36 (dd, 3J (H,H) = 17.0 Hz, 2J (H,H) = -1.4 Hz, 1H; -CH2CH=CH2), 5.30 (dd, 3J (H,H) = 10.4 Hz, 2J (H,H) = -1.4 Hz 1H; -CH2CHCH2), 5.16 (apt t, 3J (H,H) = 9.6 Hz, 1H; H-4), 4.96 (dd, 3J (H,H) = 10.2, 4.2 Hz, 1H; H-2), 4.70–4.56 (m, 2H; -CH2CHCH2), 4.50 (d, 3J (H,H) = 9.9 Hz, 1H; H-5), 2.10 (s, 3H; COCH3), 2.02 (s, 3H; COCH3), 2.01 (s, 3H; COCH3); 13C NMR (126 MHz, CDCl3) δ 169.9, 169.8, 169.6 (3 x COCH3), 166.8 (C O2CH2CHCH2), 131.1 (-CH2CHCH2), 119.9 (-CH2CHCH2), 86.3 (C-1), 70.1 (C-5), 69.8 (C-2), 69.1 (C-4), 68.9 (C-3), 67.0 (-CH2CHCH2), 20.8, 20.7, 20.7 (3 x COCH3); IR (film) cm⁻¹: 2955, 2113, 1721, 1451, 1247, 1093, 1069, 1026. ESI-HRMS calcd for C15H19O9N3Na 408.1019, found m/z 408.1031 [M+Na]+.

Methyl 2,3,4-tri-O-acetyl-1-azido-1-deoxy-α-D-galactopyranuronate (12)

[α]D 178.3 (c 3.3, CH2Cl2); 1H NMR (500 MHz, CDCl3) δ 5.77 (d, 3J (H,H) = 3.8 Hz, 1H; H-1), 5.76 (dd, 3J (H,H) = 3.1, 1.6 Hz, 1H; H-4), 5.40 – 5.13 (m, 2H; H-2, H-3, overlapping peaks), 4.77 (d, 3J (H,H) = 1.6 Hz, 1H; H-5), 3.77 (s, 3H; CO2Me), 2.11 (s, 3H; COCH3), 2.10 (s, 3H; COCH3), 2.00 (s, 3H; COCH3); 13C NMR (126 MHz, CDCl3) δ 170.0, 169.7, 169.6 (3 x COCH3), 166.6 (CO2CH3), 87.0 (C-1), 70.1 (C-5), 68.6 (C-4), 66.9, 66.8 (C-2, C-3), 52.8 (CO2CH3), 20.6 (2s) 20.5 (3 x COCH3); [α]D 178.3 (c 3.3, CH2Cl2); IR (film) cm⁻¹: 2962, 2114, 1767, 1743, 1368, 1250, 1211, 1173, 1056; ESI-HRMS calcd for C13H17O9N3Na 382.0862, found m/z 382.0863 [M+Na]+.
Methyl 1-azido-2,3,4-tri-O-benzoyl-1-deoxy-α-D-mannopyranuronate (19)

[α]_D - 48.5 (c 0.8, CH₂Cl₂); \(^1^H\) NMR (500 MHz, CDCl₃) \(\delta = 8.04\) (td, \(^3^J\) (H,H) = 8.2, 1.4 Hz, 4H; Ar-H), 7.91 (dd, \(^3^J\) (H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.62 - 7.56 (m, 2H; Ar-H), 7.53 (dd, \(^3^J\) (H,H) = 7.6, 6.7, 1.4 Hz, 1H; Ar-H), 7.45 (td, \(^3^J\) (H,H) = 7.9, 2.4 Hz, 4H; Ar-H), 7.38 (t, \(^3^J\) (H,H) = 7.9 Hz, 2H; Ar-H), 5.96 - 5.91 (m, 1H; H-4), 5.89 - 5.84 (m, 2H; H-1, H-3, overlapping peaks), 5.59 (dd, \(^3^J\) (H,H) = 4.8, 3.2 Hz, 1H; H-2), 4.84 (d, \(^3^J\) (H,H) = 6.6 Hz, 1H; H-5), 3.64 (s, 3H; CO₂CH₃); \(^{13}\)C NMR (126 MHz, CDCl₃): \(\delta = 167.8\) (CO₂CH₃), 165.2, 165.2, 164.9 (3 x COPh), 133.7, 133.7, 129.9, 129.9, 129.8 (9 x Ar-CH, overlapping peaks), 128.8, 128.7 (2 x Ar-C), 128.6 (2s) (Ar-C, 4 x Ar-CH, overlapping peaks), 128.5 (2 x Ar-CH, overlapping peaks), 86.0 (C-1), 72.1 (C-5), 69.0 (C-2), 68.4 (H-3), 68.1 (C-4), 52.8 (CO₂CH₃); IR (film) cm\(^{-1}\): 2955, 2120, 1726, 1452, 1244, 1091, 1069, 1026; ESI-HRMS calcd for C₂₈H₂₃O₉N₃Na 568.1332, found m/z 568.1327 [M+Na]⁺.

Methyl 2-acetamido-1-azido-3,4-di-O-benzoyl-1,2-dideoxy-α-D-glucopyranuronate azide (32)

[α]_D 75.6 (c 1.7, CH₂Cl₂); \(^1^H\) NMR (500 MHz, CDCl₃): \(\delta = 7.92\) (ddd, \(^3^J\) (H,H) = 8.5, 5.1, 1.4 Hz, 4H; Ar-H), 7.55 - 7.49 (m, 2H; Ar-H), 7.37 (td, \(^3^J\) (H,H) = 7.7, 3.9 Hz, 4H; Ar-H), 6.03 (d, \(^3^J\) (H,H) = 8.5 Hz, 1H; NHCOCH₃), 5.74 (d, \(^3^J\) (H,H) = 3.9 Hz, 1H; H-1), 5.66 - 5.61 (apt t, \(^3^J\) (H,H) = 9.3 Hz, 1H; H-4), 5.60 - 5.55 (apt t, \(^3^J\) (H,H) = 10.3 Hz, 1H; H-3), 4.70 (d, \(^3^J\) (H,H) = 9.5 Hz, 1H; H-5), 4.60 (ddd, \(^3^J\) (H,H) = 10.3, 8.5, 4.1 Hz, 1H; H-2), 3.67 (s, 3H; CO₂CH₃), 1.91 (s, 3H; NHCOCH₃); \(^{13}\)C NMR (126 MHz, CDCl₃): \(\delta = 170.1\) (NHCOCH₃), 167.4 (CO₂CH₃), 167.0, 165.1 (2 x COPh), 133.8, 133.6, 129.9, 129.7 (6 x Ar-CH, overlapping peaks), 128.7 (Ar-C) 128.5 (2s) (4 x Ar-CH, overlapping peaks) 128.34 (Ar-C), 88.0 (C-1), 70.5 (C-5), 70.0 (C-4), 69.3 (C-2), 53.0 (CO₂CH₃), 51.5 (C-2), 23.0 (NHCOCH₃); IR...
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Methyl 2-acetamido-1-azido-3,4-di-\(\text{O}\)-benzoyl-1,2-dideoxy-\(\alpha\)-D-galactopyranuronate (33)

\(\alpha\)_D 64.1 (c 1.15, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)); \(\delta = 8.05\) (dd, \(^3\)J (H, H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.84 (dd, \(^3\)J (H, H) = 8.3, 1.3 Hz, 2H; Ar-H), 7.63 – 7.58 (m, 1H; Ar-H), 7.55 – 7.50 (m, 1H; Ar-H), 7.49 – 7.45 (m, 2H, Ar-H), 7.34 (t, \(^3\)J (H, H) = 7.8 Hz, 2H; Ar-H), 6.11 (dd, \(^3\)J (H, H) = 3.4, 1.5 Hz, 1H; H-4), 5.84 (d, \(^3\)J (H, H) = 4.0 Hz, 1H; H-1), 5.73 (d, \(^3\)J (H, H) = 8.7 Hz, 1H; NHCOCH\(_3\)), 5.48 (dd, \(^3\)J (H, H) = 11.3, 3.4 Hz, 1H; H-3), 4.94 (d, \(^3\)J (H, H) = 1.5 Hz, 1H; H-5), 4.89 (ddd, \(^3\)J (H, H) = 11.3, 8.7, 4.1 Hz, 1H; H-2), 3.72 (s, 3H; CO\(_2\)CH\(_3\)), 1.92 (s, 3H; NHCOCH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 170.2\) (NHCOCH\(_3\)), 166.7 (C\(_{O2}\)CH\(_3\)), 166.5, 165.2 (2 x COPh), 133.7 (2s), 130.0, 129.9 (6 x Ar-CH, overlapping peaks), 128.8 (Ar-C), 128.6 (2s) (2 x Ar-CH, Ar-C, overlapping peaks), 128.5 (Ar-C, overlapping peaks), 88.9 (C-1), 70.6 (C-5), 68.7 (C-4), 68.1 (C-3), 52.9 (C\(_{O2}\)CH\(_3\)), 47.7 (C-2), 23.2 (NHCOCH\(_3\)); IR (film) cm\(^{-1}\): 2923, 2123, 1755, 1451, 1247, 1093, 1024; ESI-HRMS calcd for C\(_{23}\)H\(_{22}\)O\(_8\)N\(_4\)Na 505.1335, found m/z 505.1346 [M+Na]\(^+\).

Methyl 1-azido-1-deoxy-2-\(\text{O}\)-(2,3,4,6-tetra-\(\text{O}\)-benzoyl-\(\beta\)-D-glucopyranosyl)-3,4-di-\(\text{O}\)-benzoyl-\(\alpha\)-D-glucopyranuronate (46)

\(\alpha\)_D 61.1 (c 0.6, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)); \(\delta = 8.09\) (dt, \(^3\)J (H, H) = 7.0, 1.4 Hz, 2H; Ar-H), 7.90 (dd, \(^3\)J (H, H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.83 (dd, \(^3\)J (H, H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.73 (dd, \(^3\)J (H, H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.60 (t, \(^3\)J (H, H) = 7.5 Hz, 1H; Ar-H), 7.55 (dd, \(^3\)J (H, H) = 8.3, 1.5 Hz, 2H; Ar-H), 7.49 (qd, \(^3\)J (H, H) = 8.7, 7.4 Hz, 4H; Ar-H), 7.42 (dd, \(^3\)J (H, H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.41 – 7.28
Experimental data

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(m, 7H; Ar-H), 7.22 (t, $^3J(H,H) = 7.9$ Hz, 2H; Ar-H), 7.12 (t, $^3J(H,H) = 7.8$ Hz, 2H; Ar-H), 7.05 (t, $^3J(H,H) = 7.8$ Hz, 2H; Ar-H), 5.93 (d, $^3J(H,H) = 4.1$ Hz, 1H; H-1’), 5.87 – 5.78 (m, 2H; H-2’, H-3, overlapping peaks), 5.68 (apt t, $^3J(H,H) = 9.7$ Hz, 1H; H-3’), 5.52 (dd, $^3J(H,H) = 9.9$, 7.8 Hz, 1H; H-2), 5.41 (apt t, $^3J(H,H) = 9.9$ Hz, 1H; H-4’), 5.00 (d, $^3J(H,H) = 7.9$ Hz, 1H; H-1), 4.82 (dd, $^2J(H,H) = -12.3$ Hz, $^3J(H,H) = 2.8$ Hz, 1H; H-6a), 4.60 (d, $^3J(H,H) J = 10.1$ Hz, 1H; H-5’), 4.41 (dd, $^2J(H,H) J = -12.3$ Hz, $^3J(H,H) = 4.8$ Hz, 1H; H-6b), 4.21 – 4.12 (m, 2H; H-4, H-5, overlapping peaks), 3.63 (s, 3H; CO$_2$CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 167.9 (CO$_2$CH$_3$), 166.2, 165.8, 165.4, 165.2, 164.8, 164.7 (6 x COPh, overlapping peaks), 133.7, 133.5, 133.4, 133.0, 132.8, 130.0 (2s), 129.9, 129.8, 129.6 (18 x Ar-CH, overlapping peaks), 129.5 (2s) (2 x Ar-CH, Ar-C, overlapping peaks), 128.8 (2s) (2 x Ar-C, 128.7 (4s) (2 x Ar-CH, 3 x Ar-C, overlapping peaks), 128.6, 128.5, 128.4, 128.3, 128.2 (10 x Ar-CH, overlapping peaks), 102.4 (C-1), 88.6 (C-1’), 78.3 (C-5), 72.9 (C-4), 72.6 (C-3), 71.7 (C-2), 70.2 (C-4’), 70.1 (C-2’), 70.0 (C-5’), 69.2 (C-3’), 62.3 (C-6’), 53.0 (CO$_2$CH$_3$); IR (film) cm$^{-1}$: 2925, 2124, 1725, 1452, 1258, 1089, 1067, 1025; ESI-HRMS calcd for C$_{55}$H$_{48}$O$_7$N$_3$Na 1042.2647, found m/z 1042.2658 [M+Na]$^+$. 
Chapter 3 experimental procedures:

6-O-tert-Butyldiphenylsilyl-2,3,4-tri-O-benzoyl-β-D-mannopyranosyl azide (47)
Azide 36 (1 g, 4.87 mmol) was reacted with TBDPSCl (1.5 mL, 5.85 mmol) in pyridine and then benzoyl chloride (3.73 mL, 32.14 mmol) as described above to give the silylated intermediate (1.99 g, 54%) as a foam; [α]D -25.9 (c 0.41, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 7.99 – 7.94 (m, 2H; Ar-H), 7.91 – 7.86 (m, 2H; Ar-H), 7.86 – 7.81 (m, 2H; Ar-H), 7.74 – 7.69 (m, 2H; Ar-H), 7.61 – 7.56 (m, 2H; Ar-H), 7.56 – 7.50 (m, 2H; Ar-H), 7.45 – 7.34 (m, 7H; Ar-H), 7.34 – 7.27 (m, 3H; Ar-H), 7.23 – 7.18 (m, 2H; Ar-H), 5.86 (apt t, 3J (H,H) = 9.7 Hz, 1H; H-3), 5.75 (apt t, 3J (H,H) = 9.7 Hz, 1H; H-3), 5.47 (dd, 3J (H,H) = 9.7, 8.8 Hz, 1H; H-2), 4.87 (d, 3J (H,H) = 8.8 Hz, 1H; H-1), 3.96 – 3.84 (m, 3H; H-6a, H-6b, H-5, overlapping peaks), 1.06 (s, 9H; C(CH3)3); 13C NMR (126 MHz, CDCl3): δ 165.8, 165.1, 164.8 (3 x COPh), 135.6, 135.5, 133.4, 133.3, 133.2 (7 x Ar-CH, overlapping peaks), 132.9, 132.8 (2 x Ar-C), 129.9, 129.8, 129.8, 129.7, 129.6 (8 x Ar-CH, overlapping peaks), 129.0, 128.8, 128.7 (3 x Ar-C), 128.4, 128.4, 128.3, 127.7, 127.6 (10 x Ar-CH, overlapping peaks), 88.1 (C-1), 77.3 (C-5), 73.1 (C-3), 71.5 (C-2), 68.5 (C-4), 62.3 (C-6), 26.6 (C(CH3)3), 19.2 (C(CH3)3); IR (film) cm⁻¹: 3071, 2858, 2116, 1731, 1451, 1245, 1088, 1068; ESI-HRMS calcd for C43H42N3O8Si 756.2736, found m/z 756.2742 [M+H]+.

2,3,4-Tri-O-benzoyl-β-D-glucopyranosyl azide (48)
Compound 47 (1.89 g, 2.50 mmol) was taken up in THF (50 mL) was cooled over ice and AcOH (0.29 mL, 5.03 mmol) and 1.0 M TBAF in THF (5.03 mL, 5.03 mmol) added and the mixture stirred for 16 h. The product was adsorbed onto silica gel and flash chromatography (petroleum ether-EtOAc 3:2) gave 29 (1.02 g, 79%) as
a white solid; $\left[\alpha\right]_D^{20} +88.1$ (c 0.2, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 7.95 (td, $^3$$J$(H,H) = 8.2, 1.4 Hz, 4H; Ar-H), 7.83 (dd, $^3$$J$(H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.54 (tt, $^3$$J$(H,H) = 6.7, 4.8, 1.3 Hz, 2H; Ar-H), 7.45 – 7.35 (m, 5H; Ar-H), 7.28 (t, $^3$$J$(H,H) = 7.8 Hz, 2H; Ar-H), 5.96 (apt t, $^3$$J$(H,H) = 9.8 Hz, 1H; H-3), 5.54 (apt t, $^3$$J$(H,H) = 9.8, 8.8 Hz, 1H; H-2), 4.96 (d, $^3$$J$(H,H) = 8.8 Hz, 1H; H-1), 3.96 – 3.86 (m, 2H; H-5, H-6a, overlapping peaks), 3.77 (dt, $^3$$J$(H,H) = -13.2 Hz, $^3$$J$(H,H) = 4.8 Hz, 1H; H-6b), 2.60 (dd, $^3$$J$(H,H) = 8.8, 5.6 Hz, 1H; OH); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 166.0, 165.7, 165.0 (3 x COPh), 133.8, 133.5, 133.4, 130.0, 129.9, 129.7 (9 x Ar-CH, overlapping peaks), 128.7, 128.6 (2 x Ar-C), 128.5, 128.4 (4 x Ar-CH, overlapping peaks), 128.3 (2s) (Ar-C, 2 x Ar-CH, overlapping peaks), 88.4 (C-1), 77.0 (C-5), 72.6 (C-3), 71.2 (C-2), 69.0 (C-4), 61.1 (C-6); IR (film) cm$^{-1}$: 3491, 2122, 1723, 1450, 1244, 1088; ESI-HRMS calcd for C$_{27}$H$_{27}$NO$_{8}$Na 399.0903, found m/z 399.0887 [M+Na]$^+$.

**Allyl 6-O-tert-butylidiphenylsilyl-2,3,4-tri-O-benzoyl-β-D-glucopyranoside (49)**

Intermediate 41 (10 g, 45.4 mmol) was reacted with pyridine (100 mL), TBDPSCl (14.1 mL, 54.5 mmol) and benzoyl chloride (34.82 mL, 299.7 mmol) as described previously to give 49 (27.3 g, 78%) as a foam; $\left[\alpha\right]_D^{20} -21.1$ (c 0.1, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.99 – 7.94 (m, 1H), 7.88 – 7.81 (m, 2H; Ar-H), 7.71 – 7.67 (m, 4H; Ar-H), 7.62 – 7.58 (m, 2H; Ar-H), 7.54 – 7.48 (m, 2H; Ar-H), 7.44 – 7.27 (m, 9H; Ar-H), 7.25 – 7.21 (m, 2H; Ar-H), 5.88 – 5.78 (m, 2H; CH$_2$CHCH$_2$, C-3, overlapping peaks ), 5.62 (apt t, $^3$$J$(H,H) = 9.2 Hz, 1H; H-4), 5.53 (dd, $^3$$J$(H,H) = 9.7, 7.9 Hz, 1H; H-2), 5.25 (dq, $^3$$J$(H,H) = 17.3 Hz, $^2$$J$(H,H) = 1.7 Hz, 1H; CH$_2$CHCH$_2$), 5.15 (dq, $^3$$J$(H,H) = 10.5 Hz, $^2$$J$(H,H) = 1.4 Hz, 1H; CH$_2$CH=C(H$_2$)), 4.85 (d, $^3$$J$(H,H) = 7.9 Hz, 1H; H-1), 4.38 (ddt, $^2$$J$(H,H) = -13.3 Hz, $^3$$J$(H,H) = 4.8, 1.7 Hz, 1H; CH$_2$CH=CH$_2$), 4.17 (ddt, $^2$$J$(H,H) = -13.3 Hz, $^3$$J$(H,H) = 6.3, 1.4 Hz, 1H; CH$_2$CH=CH$_2$), 3.90 – 3.82 (m, 2H; H-5, H-6a, H-6b, overlapping peaks), 1.04 (s, 9H; C(CH$_3$)$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 165.9, 165.0 (3 x COPh, overlapping peaks), 135.6, 135.5 (4 x Ar-CH, overlapping peaks), 133.6 (CH$_2$CH=CH$_2$), 133.2 (2 x Ar-CH), 133.1 (2s) (Ar-C, 2 x Ar-CH, overlapping peaks), 133.0 (Ar-C), 129.8
(2s), 129.7, 129.6 (2s) (6 x Ar-CH, overlapping peaks), 129.5, 129.2, 129.0 (3 x Ar-C), 128.3 (2s), 128.2, 127.6 (2s) (11 x Ar-CH, overlapping peaks), 117.6 (CH₂CHCH₂), 99.7 (C-1), 75.2 (C-5), 73.4 (C-3), 72.0 (C-2), 69.6 (CH₂CH=CH₂), 69.3 (C-4), 62.8 (C-6), 26.6 (C(CH₃)₃, overlapping peaks), 19.2 (C(CH₃)₃); IR (film) cm⁻¹: 3071, 2857, 1729, 1451, 1259, 1091, 1026; ESI-HRMS calcd for C₄₆H₄₆O₉SiNa 793.2809, found m/z 793.2798 [M+Na]⁺.

**Allyl 2,3,4-tri-O-benzoyl-β-D-glucopyranoside (50)**

The TBDPS derivative 49 (27.0 g, 35.0 mmol) was dissolved in THF (250 mL) and the resulting solution was cooled using an ice bath. To this AcOH (4 mL, 70.0 mmol) and 1M TBAF in THF (70 mL, 70.0 mmol) were added. The mixture was allowed to attain room temp and was stirred for 16 h and the product adsorbed on silica gel. Flash chromatography (petroleum ether-EtOAc 3:2) gave the intermediate alcohol (14.4 g, 77%) as a white solid; [α]D₂₃.0 (c 0.2, CH₂Cl₂); 1H NMR (500 MHz, CDCl₃) δ 7.95 (apt tt, 3J (H,H) = 7.3, 1.4 Hz, 4H; Ar-H), 7.89 – 7.81 (m, 2H; Ar-H), 7.59 – 7.47 (m, 2H; Ar-H), 7.46 – 7.35 (m, 5H; Ar-H), 7.31 – 7.26 (m, 2H; Ar-H), 5.93 (apt t, 3J (H,H) = 9.7 Hz, 1H; H-3), 5.81 (dddd, 3J (H,H) = 17.0, 10.7, 6.1, 5.0 Hz, 1H; CH₂CHCH₂), 5.60 – 5.39 (m, 2H; H-2, H-4, overlapping peaks), 5.26 (dq, 3J (H,H) = 17.0 Hz, 2J (H,H) = -1.4 Hz, 1H; CH₂CHCH₂), 5.15 (dq, 3J (H,H) = 10.7 Hz, 2J (H,H) = -1.4 Hz, 1H; CH₂CHCH₂), 4.89 (d, 3J (H,H) = 7.9 Hz, 1H; H-1), 4.39 (ddt, 2J (H,H) = -13.3 Hz, 3J (H,H) = 5.0, 1.6 Hz, 1H; CH₂CHCH₂), 4.19 (ddt, 2J (H,H) = -13.3 Hz, 3J (H,H) = 6.1, 1.4 Hz, 1H; CH₂CHCH₂), 3.86 (dd, 2J (H,H) = -12.4 Hz, 3J (H,H) = 8.8, 1.9 Hz, 1H; H-6a), 3.83 – 3.68 (m, 2H; H-6b, H-5), 2.55 (dd, 3J (H,H) = 8.8, 5.3 Hz, 1H; OH); 13C NMR (126 MHz, CDCl₃) δ 166.0, 165.8, 165.0 (3 x COPh), 133.7 (Ar-CH, overlapping peaks), 133.4 (CH₂CHCH₂), 133.2 (2s) (2 x Ar-CH), 129.9, 129.8, 129.7 (6 x Ar-CH, overlapping peaks), 129.3, 128.8, 128.6 (3 x Ar-C), 128.5, 128.3 (2s) (6 x Ar-CH), 117.7 (CH₂CHCH₂), 100.0 (C-1), 74.6 (C-5), 72.8 (C-3), 71.8 (C-4), 70.2 (CH₂CHCH₂), 69.6 (C-2), 61.4 (C-6); IR (film) cm⁻¹: 3380, 2955, 1722, 1451, 1259, 1066, 1026; ESI-HRMS calcd for C₃₀H₂₈O₉Na 555.1631, found m/z 555.1637 [M+Na]⁺.
Experimental data

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1-O-allyl-2,3,4-tri-O-benzoyl-β-D-glucopyranosiduronic acid, methyl ester (51)

Intermediate 50 (14 g, 26.3 mmol) in MeCN-H2O (100 mL, 3:1) was oxidised, using BAIB (21.17 g, 65.7 mmol) and TEMPO (0.4 g, 2.6 mmol), and the resulting acid was esterified in DMF (80 mL) using NaHCO3 (3.3 g, 39.5 mmol) and methyl iodide (2.5 mL, 39.5 mmol) as described above to give 51 (8.7 g, 59%) as a foam; [α]D -40.0 (c 0.07, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 7.98 – 7.92 (m, 4H; Ar-H), 7.90 – 7.83 (m, 2H; Ar-H), 7.52 (ddd, 3J (H,H) = 7.6, 4.9, 2.4, 1.3 Hz, 2H; Ar-H), 7.47 – 7.43 (m, 1H; Ar-H), 7.38 (ddd, 3J (H,H) = 8.2, 6.2, 3.5, 1.7 Hz, 4H; Ar-H), 7.33 – 7.28 (m, 2H; Ar-H), 5.90 (apt t, 3J (H,H) = 9.3 Hz, 1H; H-3), 5.80 (ddd, 3J (H,H) = 17.0, 10.5, 6.4, 4.7 Hz, 1H; CH2CHCH2), 5.71 (apt t, 3J (H,H) = 9.4 Hz, 1H; H-4), 5.57 (dd, 3J (H,H) = 9.3, 7.3 Hz, 1H; H-2), 5.26 (dq, 3J (H,H) = 17.0 Hz, 2J (H,H) = -1.6 Hz, 1H; CH2CHCH2), 5.16 (dq, 3J (H,H) = 10.5 Hz, 2J (H,H) = 1.4 Hz, 1H; CH2CHCH2), 4.92 (d, 3J (H,H) = 7.3 Hz, 1H; H-1), 4.42 (ddt, 2J (H,H) = -13.2 Hz, 3J (H,H) = 4.8, 1.6 Hz, 1H; CH2CH=CH2), 4.35 (d, 3J (H,H) = 9.4 Hz, 1H), 4.17 (ddt, 2J (H,H) = -13.2 Hz), 3J (H,H) = 6.4, 1.4 Hz, 1H; CH2CH=CH2), 3.70 (s, 3H; CO2CH3); 13C NMR (126 MHz, CDCl3): δ 167.4 (CO2CH3), 165.6, 165.2, 165.0 (3 x COPh), 133.4, 133.3, 133.2 (3 x Ar-CH), 133.1 (CH2CH=CH2), 129.8 (3s) (6 x Ar-CH, overlapping peaks), 129.2, 128.7, 128.5 (3 x Ar-C), 128.4 (2s), 128.3 (6 x Ar-CH, overlapping peaks), 118.0 (CH2CH=CH2), 99.6 (C-1), 72.9 (C-5), 72.0 (C-3), 71.5 (C-2), 70.2 (CH2CHCH2), 70.1 (C-4), 52.9 (CO2CH3); IR (film) cm⁻¹: 3068, 1761, 1726, 1451, 1250, 1088; ESI-HRMS calcd for C31H32NO10 578.2026, found m/z 578.2031 [M+NH4]+.
**2,3,4-Tri-O-benzoyl-1-deoxy-1-(2,2,2-trichloro-1-iminoethoxy)-D-glucopyranuronate, methyl ester (52)**

The allyl glycoside 51 (8.5 g, 15.1 mmol) was dissolved in MeOH-CH₂Cl₂ (60 mL, 3:1) and PdCl₂ (0.54 g, 3.0 mmol) was added and the mixture was stirred for 16 h at room temp. The resulting suspension was filtered through celite and the solvent was removed to give a foam. Flash chromatography (petroleum ether-EtOAc 6:4) gave the hemiacetal (5.6 g, 10.8 mmol). This intermediate was dissolved in CH₂Cl₂ (50 mL) and cooled on an ice bath and trichloroacetonitrile (10.8 mL, 107.6 mmol) and DBU (0.5 mL) were added. The mixture was stirred for 5 h and was directly subjected to flash chromatography (petroleum ether-EtOAc 7:3, 0.1% Et₃N) to give 52 (6.95 g, 69%) as a white foam; [α]₀ +44.4 (c 0.18, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.68 (s, 1H; NH), 8.00 – 7.93 (m, 4H; Ar-H), 7.92 – 7.85 (m, 2H; Ar-H), 7.58 – 7.49 (m, 2H; Ar-H), 7.46 (ddt, 3J (H,H) = 8.7, 7.2, 1.3 Hz, 1H; Ar-H), 7.42 – 7.30 (m, 5H; Ar-H), 6.91 (d, 3J (H,H) = 3.6 Hz, 1H; H-1), 6.29 (apt t, 3J (H,H) = 9.9 Hz, 1H; H-3), 5.76 (apt t, 3J (H,H) = 9.9 Hz, 1H; H-4), 5.63 (dd, 3J (H,H) = 10.1, 3.6 Hz, 1H; H-2), 4.77 (d, 3J (H,H) = 10.5 Hz, 1H; H-5), 3.69 (s, 3H; CO₂CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 167.2 (CO₂CH₃), 165.5, 165.2 (3 x COPh, overlapping peaks), 160.3 (OC(NH)CCl₃), 133.6 (2s), 133.4, 129.9 (2s), 129.7 (9 x Ar-CH, overlapping peaks), 128.7, 128.6 (2 x Ar-C), 128.5 (2 x Ar-CH, overlapping peaks), 128.4 (2s) (4 x Ar-CH, Ar-C, overlapping peaks), 92.9 (C-1), 70.9 (C-5), 70.2 (C-2), 69.6 (C-4), 69.3 (C-3), 53.0 (CO₂CH₃); IR (film) cm⁻¹: 3068, 1728, 1451, 1278, 1092, 1025.

**2,3,4-Tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-5-S-(methoxycarbonyl)-β-D-xylopyranosyl)-β-D-glucopyranosyl azide (53)**

The glycosidation of acceptor 48 (0.2 g, 0.39 mmol) and donor 52 (0.43 g, 0.58 mmol) was carried out as previously described to give 53 (0.33 g, 84%) as a white solid; [α]₀ -10.1 (c 0.75, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ = 8.06 – 7.97 (m, 2H), 7.98 – 7.90 (m, 4H), 7.90 – 7.85 (m, 4H), 7.79 – 7.74 (m, 2H), 7.52 (t, 3J (H,H)
Experimental data

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6-O-acetyl-3,4-O-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranosyl azide (55)

A solution of 38 (0.75 g, 1.7 mmol) in collidine (5 mL) was cooled to -35 °C. To this was added freshly distilled AcCl (0.13 mL, 1.84 mmol) and the reaction mixture was allowed to attain room temp. Methanol was added and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 9:1) gave 26 (0.58 g, 70%) as a white solid; [α]D -23.0 (c 0.18, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ = 4.56 (d, 3J (H,H) = 8.7 Hz, 1H; H-1), 4.44 (dd, 2J (H,H) = 12.0 Hz, 3J (H,H) = 2.1 Hz, 1H; H-6a), 4.20 (dd, 2J (H,H) = 12.0 Hz, 3J (H,H) = 5.2 Hz, 1H; H-6b), 3.74 – 3.67 (m, 1H; H-4), 3.67 – 3.62 (m, 1H; H-3), 3.56 (ddd, 3J (H,H) = 9.3, 5.3, 2.1 Hz, 1H; H-5), 3.40 (apt t, 3J (H,H) = 8.7 Hz, 1H; H-2), 2.44 (d, 3J (H,H) = 2.6 Hz, 1H; OH), 2.09 (s, 3H; COCH3), 1.12 – 0.93 (m, 28H; 4 x CH(CH3)2, overlapping peaks); 13C NMR (126 MHz, CDCl3): δ 170.7 (OCOCH3),
89.6 (C-1), 79.7 (C-3), 76.1 (C-5), 73.7 (C-2), 72.2 (C-4), 62.9 (C-6), 20.9, 17.3 (3s), 17.2 (3s), 17.1 (8 x CH(CH₃)₂, overlapping peaks), 12.8, 12.7, 12.1 (2s) (4 x CH(CH₃)₂, overlapping peaks); IR (film) cm⁻¹: 3504, 2947, 2868, 2911, 1725, 1463, 1250, 1028, 980; ESI-HRMS calcd for C₂₀H₃₉N₃O₇Si₂Na 512.224, found m/z 512.2229 [M+Na]⁺.

2-0-(2,3,4-Tri-O-benzoyl-5-S-(methoxycarbonyl)-β-D-xylopyranosyl)-3,4-O-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-6-O-acetyl-β-D-glucopyranosyl azide (56)

Glycosidation with acceptor 55 (0.5 g, 1.0 mmol) and donor 52 (0.91 g, 1.2 mmol) as described above gave 56 (0.88 g, 89%) as a foam; [α]D -4.0 (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ = 7.91 (ddt, 3J (H,H) = 17.1, 7.0, 1.4 Hz, 4H; Ar-H), 7.81 (dd, 3J (H,H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.54 – 7.48 (m, 2H; Ar-H), 7.44 – 7.33 (m, 5H; Ar-H), 7.28 (d, 3J (H,H) = 7.8 Hz, 2H; Ar-H), 5.84 (apt t, 3J (H,H) = 9.2 Hz, 1H; H-3'), 5.78 (apt t, 3J (H,H) = 9.5 Hz, 1H; H-4’), 5.58 (dd, 3J (H,H) = 9.0, 7.6 Hz, 1H; H-2’), 5.34 (d, 3J (H,H) = 7.5 Hz, 1H; H-1’), 4.54 (d, 3J (H,H) = 8.1 Hz, 1H; H-1), 4.44 (dd, 2J (H,H) = -12.0 Hz, 3J (H,H) = 2.2 Hz, 1H; H-6a), 4.33 (d, 3J (H,H) = 9.6 Hz, 1H; H-5’), 4.14 (dd, 2J (H,H) = -12.0 Hz, 3J (H,H) = 5.1 Hz, 1H; H-6b), 3.87 – 3.82 (m, 1H; H-2), 3.79 (apt t, 3J (H,H) = 8.5 Hz, 1H; H-3), 3.73 (s, 3H; CO₂CH₃), 3.71 – 3.63 (m, 1H; H-4), 3.49 (ddd, 3J (H,H) = 9.5, 5.1, 2.1 H-z, 1H; H-5), 2.08 (s, 3H; COCH₃), 1.08 – 0.72 (m, 28H; 4 x CH(CH₃)₂, overlapping peaks); ¹³C NMR (126 MHz, CDCl₃): δ 170.7 (COCH₃), 167.0 (CO₂CH₃), 165.7, 165.0 (2s), (3 x COPh), 133.4, 133.3 (2s)129.9, 129.8, 129.7 (9 x Ar-CH, overlapping peaks), 129.2, 128.8, 128.6 (3 x Ar-C), 128.4, 128.3, 128.2 (6 x Ar-CH, overlapping peaks), 100.2 (C-1’), 88.4 (C-1), 79.8 (C-3), 78.0 (C-2), 75.6 (C-5), 73.1 (C-5’), 72.6 (C-3’), 72.5 (C-4), 72.1 (C-2’), 70.1 (C-4’), 62.8 (C-6), 53.0 (CO₂CH₃), 20.9 (COCH₃), 17.5 (2s) 17.4, 17.3, 17.2 (3s)17.1 (8 x CH(CH₃)₂, overlapping peaks), 12.8, 12.7, 12.3 (2s) (4
Experimental data

4,6-O-isopropylidene-2,3-O-(1,1,2,2-tetraisopropyl-1,3-disiloxanediyl)-2-O-acetyl-β-D-glucopyranosyl azide (58)

Azide 36 (1.5 g, 7.3 mmol) was dissolved in DMF (15 mL) and 2,2-dimethoxypropane (1.78 mL, 14.6 mmol) and p-toluenesulfonic acid (0.14 g, 0.73 mmol) were added and the reaction mixture was stirred at room temp for 3 h. Triethylamine (1 mL) was added and the solvent was removed and the residue dissolved in pyridine (15 mL) and the mixture cooled over ice. 1,3-Dichloro-1,1,2,2-tetraisopropyl disiloxane (2.88 g, 9.13 mmol) was added and the mixture stirred for 16 h at room temp. Methanol (1 mL) was added followed by EtOAc (50 mL) and this layer was washed with 1M HCl (2 x 50 mL), satd aq NaHCO₃ (50 mL), brine (50 mL), dried over Na₂SO₄, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 95:5) gave the protected intermediate (2.53 g, 71%) as a clear oil; [α]D +78.8 (c 0.25, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 4.57 (d, J(H,H) = 8.2 Hz, 1H; H-1), 3.95 (dd, J(H,H) = 10.8 Hz, 3J(H,H) = 5.3 Hz, 1H; H-6a), 3.75 (apat t, J(H,H) = 10.5 Hz, 1H; H-6b), 3.68 (dd, J(H,H) = 8.9, 7.9 Hz, 1H; H-3), 3.55 – 3.49 (m, 2H; H-2, H-4, overlapping peaks), 3.32 (td, J(H,H) = 10.0, 5.3 Hz, 1H; H-5), 1.47 (s, 3H; C(CH₃)₂), 1.38 (s, 3H; C(CH₃)₂), 1.13–0.99 (m, 28H; 4 x CH(CH₃)₂), overlapping peaks); ¹³C NMR (126 MHz, CDCl₃) δ 99.5 (C(CH₃)₂), 91.3 (C-1), 78.1 (C-2), 76.6 (C-3), 72.7 (C-4), 69.5 (C-5), 62.0 (C-6), 28.9, 19.0 (C(CH₃)₂), 17.3, 17.2, 17.1 (2s), 17.0, 16.8 (8 x CH(CH₃)₂, overlapping peaks), 12.9, 12.8, 12.2, 12.0 (4 x CH(CH₃)₂, overlapping peaks); IR (film) cm⁻¹: 2945, 2867, 2115, 1738, 1465, 1064, 983; ESI-HRMS calcd for C₂₁H₄₂N₃O₆Si₂ 488.7451, found m/z 488.7458 [M+H]⁺.
Experimental data

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2,3-O-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranosyl azide (59)
Intermediate 58 (2.5 g, 5.1 mmol) was dissolved in MeOH and amberlyst® 15 H+ (3.0 g) was added and the mixture stirred for 5 h. The resin was filtered off and the solvent was removed and flash chromatography of the residue (petroleum ether-EtOAc, 8:2) gave the required 2,3-O-silylated intermediate (1.88 g, 82%) as a wax; [α]D -18.0 (c 0.11, CH2Cl2); 1H NMR (500 MHz, CDCl3) δ 4.61 (d, J(H,H) = 8.1 Hz, 1H; H-1), 3.95 (dd, J(H,H) = -12.1 Hz, J(H,H) = 3.1 Hz, 1H; H-6a), 3.81 (dd, J(H,H) = -12.1 Hz, J(H,H) = 3.1 Hz, 1H; H-6b), 3.66 (apt t, J(H,H) = 8.5 Hz, 1H; H-3), 3.55 (apt td, J(H,H) = 9.2, 8.6, 1.4 Hz, 1H; H-4), 3.51 – 3.45 (m, 2H; H-5, H-2, overlapping peaks), 2.45 (d, J(H,H) = 2.2 Hz, 1H; OH), 2.04 (s, 1H; OH), 1.12 – 0.99 (m, 28H; 4 x C(CH3)2, overlapping peaks); 13C NMR (126 MHz, CDCl3) δ 90.8 (C-1), 80.1 (C-3), 76.9 (C-5) 76.5 (C-2), 70.6 (C-4), 62.3 (C-6), 17.4, 17.2 (3s) 17.1, 17.0 (8 x CH(CH3)2, overlapping peaks), 12.8 (2s), 12.1, 12.4 (4 x CH(CH3)2, overlapping peaks); IR (film) cm⁻¹: 3372, 2945, 2868, 2117, 1738, 1464, 1143, 1036, 986; ESI-HRMS calcd for C18H37N3O6Si2Na 442.2349, found m/z 442.2354 [M+Na]+.

2,3-O-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-6-O-acetyl-β-D-glucopyranosyl azide (60)
Compound 59 (1.5 g, 3.35 mmol) was reacted with freshly distilled AcCl (0.26 mL, 3.69 mmol) in collidine (7.5 mL) as previously described and gave 60 (0.97 g, 59%) after flash chromatography (petroleum ether-EtOAc 9:1); [α]D -25.6 (c 0.25, CH2Cl2); 1H NMR (500 MHz, CDCl3) δ 4.57 (d, J(H,H) = 8.2 Hz, 1H; H-1), 4.42 (dd, J(H,H) = -12.2 Hz, J(H,H) = 2.2 Hz, 1H; H-6a), 4.30 (dd, J(H,H) = -12.2 Hz, J(H,H) = 5.4 Hz, 1H; H-6b), 3.64 (apt t, J(H,H) = 8.6 Hz, 1H; H-3), 3.59
Experimental data

2,3-O-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-4-O-(2,3,4-tri-O-benzoyl-5-S-(methoxycarbonyl)-β-D-xylopyranosyl)-6-O-acetyl-β-D-glucopyranosyl azide (61)

Glycosidation of 60 (0.5 g, 1.02 mmol) with donor 52 (1.13 g, 1.53 mmol) as previously described gave 61 (0.67 g, 66%) after chromatography (petroleum ether-EtOAc 8:2) as a glass; [α]D -75.3 (c 0.3, CH2Cl2); 1H NMR (500 MHz, CDCl3) δ = 7.98 – 7.90 (m, 4H; Ar-H), 7.86 – 7.81 (m, 2H; Ar-H), 7.58 – 7.51 (m, 2H; Ar-H), 7.48 – 7.36 (m, 6H; Ar-H), 7.30 (t, 3J (H,H) = 7.8 Hz, 2H; Ar-H), 5.84 (apt t, 3J (H,H) = 9.5 Hz, 1H; H-3”), 5.69 (apt t, 3J (H,H) = 9.6 Hz, 1H; H-4”), 5.50 (dd, 3J (H,H) = 9.6, 7.8 Hz, 1H; H-2”), 4.92 (d, 3J (H,H) = 7.8 Hz, 1H; H-1”), 4.47 (d, 3J (H,H) = 8.3 Hz, 1H; H-1), 4.35 (dd, 2J (H,H) = -12.2 Hz, 3J (H,H) = 2.0 Hz, 1H; H-6a), 4.28 (d, 3J (H,H) = 9.7 Hz, 1H; H-5”), 4.14 (dd, 3J (H,H) = -12.2 Hz, 3J (H,H) = 4.9 Hz, 1H; H-6b), 3.80 (apt t, 3J (H,H) = 8.4 Hz, 1H; H-3), 3.76 – 3.69 (m, 4H; CO2CH3, H-4, overlapping peaks), 3.49 (apt t, 3J (H,H) = 8.3 Hz, 1H; H-2), 3.42 (dd, 3J (H,H) = 10.0, 4.9, 2.0 Hz, 1H; H-5), 2.03 (s, 3H; COCH3), 1.23 – 1.04 (m, 28H; 4 x CH(CH3)2, overlapping peaks); 13C NMR (126 MHz, CDCl3): δ 170.3 (COCH3), 166.5 (COCH3), 165.5, 164.9, 164.6 (3 x COPh), 133.5, 133.4, 133.3, 129.8 (2s) (9 x Ar-CH, overlapping peaks), 128.7, 128.6 (3 x Ar-C, overlapping peaks), 128.5, 128.4, 128.3 (6 x Ar-CH, overlapping peaks), 100.9 (C-1’), 90.5 (C-1), 77.8 (C-3), 77.1 (C-4), 74.6 (C-5), 73.7 (C-5”), 72.3 (C-3”), 71.8 (C-2”), 70.2 (C-
2,3,6-Tri-O-benzoyl-4-O-(2,3,4-tri-O-benzoyl-5-S-(methoxycarbonyl)-β-D-xylopyranosyl)-β-D-glucopyranosyl azide (63)

Disaccharide 31 (0.3 g, 0.3 mmol) was added to 1.25 M HCl in methanol (10 mL) at 0 °C and the resulting solution was allowed to attain room temp and stirred for 16 h. The reaction mixture was cooled over an ice bath, diluted with MeOH (20 mL) and NaHCO$_3$ was added. The resulting slurry was concentrated to dryness and the residue suspended in pyridine and cooled over an ice bath. BzCl (0.21 mL, 1.8 mmol) was then added and the reaction mixture was allowed to warm to room temp and was stirred overnight. Methanol (0.5 mL) was added and the mixture diluted with EtOAc (10 mL). This layer was washed with 1M HCl (2 x 5 mL), satd aq NaHCO$_3$ (10 mL), brine (10 mL), dried over Na$_2$SO$_4$, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 6:4) gave 63 (0.17 g, 63%) as a glass; $[\alpha]_D$ 56.6 ($c$ 1.15, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 8.02 – 7.98 (m, 2H; Ar-H), 7.89 (dd, $^3$J (H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.76 – 7.72 (m, 4H; Ar-H), 7.62 (dd, $^3$J (H,H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.58 (dd, $^3$J (H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.5 – 7.45 (m, 6H; Ar-H), 7.45 – 7.33 (m, 7H; Ar-H), 7.29 – 7.17 (m, 8H; Ar-H), 5.78 – 5.67 (m, 3H, Ar-H, 3’, overlapping peaks), 5.54 – 5.48 (m, 2H; H-2’, H4’, overlapping peaks), 5.07 (d, $^3$J (H,H) = 7.6 Hz, 1H; H-1’), 4.87 (d, $^3$J (H,H) = 8.0 Hz, 1H; H-1), 4.57 (dd, $^2$J (H,H) = -12.4 Hz, $^3$J (H,H) = 3.0 Hz, 1H; H-6a), 4.41 (dd, $^2$J (H,H) = -12.4 Hz, $^3$J (H,H) = 5.1 Hz, 1H; H-6b), 4.35 (d, $^3$J (H,H) = 9.1 Hz, 1H; H-5’), 4.12 – 4.07 (m, 2H; H-5, H-2, overlapping peaks), 3.73 (s, 3H; CO$_2$CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 166.7 (CO$_2$CH$_3$), 166.0, 165.5, 165.1, 165.0, 164.9, 164.7 (6 x COPh), 133.4 (2s), 133.3, 133.1, 132.9, 129.8 (2s), 129.7 (3s), 129.6 (18 x Ar-CH, overlapping peaks), 129.5, 128.8, 128.7, 128.5 (3s) (6 x Ar-C), 128.4 (2s), 128.3
Experimental data

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(2s), 128.2, 128.1 (12 x Ar-CH, overlapping peaks), 100.8 (C-1'), 88.8 (C-1), 77.7 (C-2), 73.9 (C-5 & C-3, overlapping peaks), 73.0 (C-5'), 72.2 (C-3'), 71.6 (C-2'), 70.0 (C-4'), 69.0 (C-4), 62.8 C-6), 53.0 (CO₂CH₃); IR (film) cm⁻¹: 2945, 2867, 2120, 1724, 1452, 1248, 1092, 1066, 1027, 986, 702; ESI-HRMS calcd for C₅₅H₄₅O₁₇N₃Na 1042.2647, found m/z 1042.2631 [M+Na]⁺.

2-O-Acetyl-4,6-O-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranosyl azide (65)

A solution of 37 (0.5 g, 1.1 mmol) in collidine (2.5 mL) was cooled to -35 °C. To this was added freshly distilled AcCl (0.087 mL, 1.23 mmol) and the reaction mixture was allowed to attain room temp and stirred for 16 h. MeOH was added and the solvent was removed and flash chromatography of the residue (petroleum ether-EtOAc 9:1) gave the 2-O-acetylated intermediate (0.42 g, 78%); [α]D -21.8 (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 4.92 – 4.84 (m, 1H; H-2), 4.53 (d, ³J (H,H) = 9.0 Hz, 1H; H-1), 3.99 – 3.91 (m, 1H; H-6a), 3.82 – 3.71 (m, 3H; H-6b, H-4, H-3, overlapping peaks), 3.45 (dddd, ³J (H,H) = 7.9, 5.2, 2.8, 1.3 Hz, 1H; H-5), 2.09 (s, 3H; COCH₃), 1.98 – 1.91 (m, 1H; OH), 1.13 – 0.89 (m, 28H; 4 x CH(CH₃)₂, overlapping peaks); ¹³C NMR (126 MHz, CDCl₃): δ 169.2 (COCH₃), 87.9 (C-1), 78.4 (C-5), 77.3 (C-4), 72.7 (C-3), 72.5 (C-2), 61.9 (C-6), 20.6 (COCH₃), 17.2 (2s), 17.1 (4s) (8 x CH(CH₃)₂, overlapping peaks), 12.8 (2s), 12.1, 12.0 (4 x CH(CH₃)₂, overlapping peaks); IR (film) cm⁻¹: 3533, 2943, 2866, 2121, 1729, 1462, 1243, 980; ESI-HRMS calcd for C₂₀H₃₉N₃O₇Si₂Na 512.224, found m/z 512.2232 [M+Na]⁺.
2-O-Acetyl-3-O-(2,3,4-tri-O-benzoyl-5-S-(methoxycarbonyl)-β-D-xylopyranosyl)-4,6-O-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranosyl azide (66)

Glycosidation of intermediate 65 (0.4 g, 0.8 mmol) with 52 (0.91 g, 1.2 mmol) gave 66 (0.65 g, 82%) after chromatography (petroleum ether-EtOAc 8:2) as a foam; [α]D -24.1 (c 0.1, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ = 7.98 (dd, 3J (H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.93 (dd, 3J (H,H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.86 (dd, 3J (H,H) = 8.3, 1.4 Hz, 2H; Ar-H), 7.51 (dd, 3J (H,H) = 7.5, 3.6 Hz, 2H; Ar-H), 7.47 – 7.42 (m, 1H), 7.38 (q, 3J (H,H) = 7.9 Hz, 4H; Ar-H), 7.30 (t, 3J (H,H) = 7.8 Hz, 2H; Ar-H), 5.89 (apt t, 3J (H,H) = 9.3 Hz, 1H; H-3’), 5.71 (apt t, 3J (H,H) = 9.4 Hz, 1H; H-4’), 5.53 (dd, 3J (H,H) = 9.3, 7.4 Hz, 1H; H-2’), 5.09 (d, 3J (H,H) = 7.4 Hz, 1H; H-1’), 4.83 (t, 3J (H,H) = 9.0 Hz, 1H; H-2), 4.36 (d, 3J (H,H) = 9.5 Hz, 1H; H-5), 4.28 – 4.19 (m, 2H; H-6a, H-1, overlapping peaks), 3.85 (dd, 2J (H,H) = 12.2 Hz, 3J (H,H) = 7.3 Hz, 1H; H-6b), 3.70 (s, 3H; CO2CH3), 3.63 (dd, 3J (H,H)= 9.1, 7.7 Hz, 1H; H-3), 3.59 – 3.49 (m, 2H; H-5, H-4, overlapping peaks), 2.06 (s, 3H; COCH3), 1.09 – 0.94 (m, 28H; 4 x CH(CH3)2, overlapping peaks); 13C NMR (126 MHz, CDCl3) δ 169.3 (COCH3), 167.5 (CO2CH3), 165.7, 165.3, 165.2 (3 x COPh), 133.6, 133.4, 130.0, 129.9 (9 x Ar-CH, overlapping peaks), 129.4, 129.0, 128.9 (3 x Ar-C), 128.6 (2s), 128.5 (6 x Ar-CH, overlapping peaks), 101.7 (C-1’), 87.6 (C-1), 79.0 (C-5), 77.4 (C-3), 73.3 (C-4), 73.0 (C-5’), 72.6 (C-2), 72.3 (C-3’), 71.8 (C-2’), 70.3 (C-4’), 69.0 (C-6), 53.0 (CO2CH3), 20.8 (COCH3), 17.6, 17.5, 17.3 (4s), 17.2 (8 x CH(CH3)2, overlapping peaks), 12.9, 12.8, 12.3, 12.2 (4 x CH(CH3)2, overlapping peaks); IR (film) cm⁻¹: 2948, 2868, 2118, 1732, 1452, 1248, 1223, 1092, 1068, 1041, 1027, 984; ESI-HRMS calcd for C₄₈H₆₁O₁₆N₃SbNa 1014.3488, found m/z 1014.3533 [M+Na]^+.

2,4,6-Tri-O-benzoyl-3-O-(2,3,4-tri-O-benzoyl-5-S-(methoxycarbonyl)-β-D-xylopyranosyl)-β-D-glucopyranosyl azide (68)
Disaccharide 66 (0.25 g, 0.252 mmol) was added to 1.25 M HCl in methanol (10 mL) at 0 °C and the resulting solution was allowed to attain room temp and stirred for 16 h. The reaction mixture was cooled over an ice bath, diluted with MeOH (20 mL) and NaHCO₃ was added. The resulting slurry was concentrated to dryness and the residue suspended in pyridine and cooled over an ice bath. BzCl (0.18 mL, 1.5 mmol) was then added and the reaction mixture was allowed to warm to room temp and was stirred overnight. Methanol (0.5 mL) was added and the mixture diluted with EtOAc (10 mL). This layer was washed with 1M HCl (2 x 5 mL), satd aq NaHCO₃ (10 mL), brine (10 mL), dried over Na₂SO₄, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (petroleum ether-EtOAc 6:4) gave 68 (0.15 g, 63%) as a glass; [α]D -15.6 (c 1.25, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ = 8.00 (dd, 3J (H,H) = 8.4, 1.4 Hz, 2H; Ar-H), 7.95 – 7.90 (m, 4H; Ar-H), 7.88 (ddd, 3J (H,H) = 8.4, 3.0, 1.4 Hz, 4H; Ar-H), 7.79 – 7.75 (m, 2H; Ar-H), 7.55 – 7.50 (m, 4H; Ar-H), 7.48 – 7.27 (m, 14H; Ar-H), 5.91 (apt t, 3J (H,H) = 9.3 Hz, 1H; H-3'), 5.79 (apt t, 3J (H,H) = 9.6 Hz, 1H; H-3), 5.68 (apt t, 3J (H,H) = 9.3 Hz, 1H; H-4'), 5.54 (dd, 3J (H,H) = 9.2, 7.3 Hz, 1H; H-2'), 5.38 (apt t, 3J (H,H) = 7.3 Hz, 1H; H-1'), 4.65 (d, 3J (H,H) = 8.8 Hz, 1H; H-1), 4.35 (d, 3J (H,H) = 9.4 Hz, 1H; H-5'), 4.13 (dd, 2J (H,H) = -12.0 Hz, 3J (H,H) = 1.9 Hz, 1H; H-6a), 4.06 (ddd, 3J (H,H) = 9.7, 7.6, 1.9 Hz, 1H; H-5), 3.90 (dd, 2J (H,H) = -12.0 Hz, 3J (H,H) = 7.6 Hz, 1H; H-6b), 3.66 (s, 3H; CO₂CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 167.2 (CO₂CH₃), 165.6, 165.5, 165.3, 165.2, 165.0, 164.9 (6 x COPh), 133.6, 133.5, 133.4, 133.3, 129.9 (2s), 129.8 (2s), 129.7 (18 x Ar-CH, overlapping peaks), 129.1, 128.8, 128.7 (2s), 128.6 (5 x Ar-C, overlapping peaks), 128.5, 128.4 (2s) (8 x Ar-CH, Ar-C, overlapping peaks), 128.3 (2s) (4 x Ar-CH, overlapping peaks), 101.5 (C-1'), 87.8 (C-1), 76.5 (C-5), 72.8 (C-5'), 72.6 (C-3), 71.8 (C-3'), 71.5 (C-2'), 71.2 (C-2), 70.0 (C-4'), 69.1 (C-4), 68.6 (C-6), 52.9 (CO₂CH₃); IR (film) cm⁻¹: 2956, 2120, 1714, 1451, 1247, 1088, 1068, 1026; ESI-HRMS calcd for C₅₅H₄₅O₁₇N₃Na 1042.2647, found m/z 1042.2646 [M+Na]⁺.
2,3,4-Tri-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl azide (70)

Glycosidation of intermediate 43 (0.5 g, 0.67 mmol) with 48 (0.23 g, 0.45 mmol) gave 70 (0.42 g, 86%) after chromatography (Cyclohexane-EtOAc 8:2) as a foam; [α]D 8.0 (c 0.1, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.01 (t, J(H,H) = 8.4, 4H; Ar-H), 7.90 (dd, J(H,H) = 14.7, 7.7, 4H; Ar-H), 7.86 – 7.79 (m, 4H; Ar-H), 7.76 (d, J(H,H) = 7.4, 2H; Ar-H), 7.57 – 7.46 (m, 5H; Ar-H), 7.46 – 7.34 (m, 11H; Ar-H), 7.32 – 7.22 (m, 5H; Ar-H), 5.90 (apt. t, J(H,H) = 9.6, 1H; H-3’), 5.78 (apt. t, J(H,H) = 9.6, 1H; H-3), 5.64 (apt. t, J(H,H) = 9.7, 1H; H-4’), 5.52 (dd, J(H,H) = 9.8, 7.8, 1H; H-2’), 5.38 – 5.30 (m, 2H; H-2, H-4, overlapping peaks), 5.00 (d, J(H,H) = 7.9, 1H; H-1’), 4.66 – 4.56 (m, 2H; H-6aa’, H-1, overlapping peaks) 4.44 (dd, J(H,H) = -12.1, J(H,H) = 4.9, 1H; H-6bb’), 4.13 (ddd, J(H,H) = 9.6, 4.7, 2.9, 1H; H-5’), 4.09 – 4.00 (m, 2H; H-6a, H-5, overlapping peaks), 3.90 (dd, J(H,H) = 11.8, J(H,H) = 7.2, 1H; H-6b); 13C NMR (126 MHz, CDCl3): δ 166.1, 165.7, 165.5, 165.2, 165.1, 164.9 (7 x COPh, overlapping peaks), 133.6, 133.5, 133.4, 133.3, 133.2, 133.1, 129.9, 129.8, 129.7 (14 x Ar-CH, overlapping peaks), 129.5, 129.2, 128.8, 128.7, 128.6 (7 x Ar-C, overlapping peaks), 128.4, 128.3 (14 x Ar-CH, overlapping peaks), 101.6 (C-1’), 87.8 (C-1), 76.5 (C-5), 72.7 (C-3’), 72.6 (C-3), 72.3 (C-5’), 71.8 (C-2’), 71.2 (C-2), 69.5 (C-4’), 69.2 (C-4), 68.3 (C-6), 62.9 (C-6’); ESI-HRMS calcd for C55H45O17N3Na 1042.2647, found m/z 1042.2653 [M+Na]+.

2,3-O-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-4-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl azide (72)
Glycosidation of intermediate 43 (0.5 g, 0.67 mmol) with 59 (0.3 g, 0.67 mmol) followed by acetylation of the crude product with Ac₂O (250 μl) in pyridine (5 ml) gave 72 (0.5 g, 69%) after chromatography (cyclohexane-EtOAc 8:2) as a glassy solid; [α]D 6.7 (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.07 – 7.93 (m, 4H; Ar-H), 7.90 (d, ³J (H, H) = 7.6, 2H; Ar-H), 7.83 (d, ³J (H, H) = 7.6, 2H; Ar-H), 7.59 – 7.45 (m, 4H; Ar-H), 7.41 (dt, ³J (H, H) = 10.1, 7.6, 4H; Ar-H), 7.34 (t, ³J (H, H) = 7.7, 2H; Ar-H), 7.31 – 7.24 (m, 2H; Ar-H), 5.90 (apt. t, ³J (H, H) = 9.6, 1H; H-3’), 5.67 (apt. t, ³J (H, H) = 9.7, 1H; H-4’), 5.51 (dd, ³J (H, H) = 9.8, 7.9, 1H; H-2’), 4.99 (d, ³J (H, H) = 7.9, 1H; H-1’), 4.72 (apt. t, ³J (H, H) = 9.7, 1H; H-4), 4.64 (dd, ³J (H, H) = 12.2, ³J (H, H) = 3.1, 1H; H-6a’), 4.47 (dd, ³J (H, H) = 12.2, ³J (H, H) = 5.0, 1H; H-6b’), 4.25 (d, ³J (H, H) = 8.2, 1H; H-1), 4.14 (ddd, ³J (H, H) = 10.0, 5.1, 3.1, 1H; H-5’), 3.89 (dd, ³J (H, H) = 11.9, ³J (H, H) = 2.0, 1H; H-6), 3.71 (dd, ³J (H, H) = 12.0, ³J (H, H) = 7.8, 1H; H-6), 3.65 – 3.52 (m, 2H; H-3,H-5, overlapping peaks), 3.43 (apt. t, ³J (H, H) = 8.4, 1H; H-2), 1.99 (s, 3H; COCH₃), 1.24 – 0.83 (m, 28H; 4 x CH(CH₃)₂, overlapping peaks); ¹³C NMR (126 MHz, CDCl₃): δ 169.5 (COCH₃), 166.1, 165.7, 165.2 (4 x COPh, overlapping peaks), 133.4, 133.2, 133.1, 129.8, 129.7 (12 x Ar-CH, overlapping peaks), 129.6, 129.3, 128.8 (4 x Ar-C, overlapping peaks), 128.4, 128.3 (8 x Ar-CH, overlapping peaks), 101.5 (C-1’), 89.9 (C-1), 77.2 (C-3), 76.9 (C-2), 76.0 (C-5), 72.8 (C-3’), 72.3 (C-5’), 71.8 (C-2), 70.3 (C-4), 69.6 (C-4’), 68.6 (C-6), 63.0 (C-6’), 20.6 (COCH₃), 17.1, 16.9 (8 x CH(CH₃)₂, overlapping peaks), 12.8, 12.7, 12.0 (4 x CH(CH₃)₂, overlapping peaks); ESI-HRMS calcd for C₅₉H₇₀O₇N₃Na 1129.4060, found m/z 1129.4068 [M+Na]⁺.

2-O-acetyl-3-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-4,6-O-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranosyl azide (74)

[α]D 6.1 (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.03 (d, ³J (H, H) = 7.7, 2H; Ar-H), 7.98 (d, ³J (H, H) = 7.7, 2H; Ar-H), 7.90 (d, ³J (H, H) = 7.7, 2H; Ar-H), 7.83 (d, ³J (H, H) = 7.6, 2H; Ar-H), 7.52 (dq, ³J (H, H) = 21.7, 7.5, 4H; Ar-H), 7.44 – 7.27 (m, 8H; Ar-H), 5.94 (apt. t, ³J (H, H) = 9.6, 1H; H-3’), 5.69 (apt. t, ³J (H, H) = 9.7, 1H; H-
Experimental data

Chapter 5

4’), 5.53 (dd, 3 J (H,H) = 9.7, 7.8, 1H; H-2’), 5.07 (d, 3 J (H,H) = 7.8, 1H; H-1’), 4.81 (apt. t, 3 J (H,H) = 9.1, 1H; H-2), 4.63 (dd, 3 J (H,H) = -12.1, 3 J (H,H) = 3.2, 1H; H-6a’), 4.52 (dd, 3 J (H,H) = -12.2, 3 J (H,H) = 5.0, 1H; H-6b’), 4.24 – 4.06 (m, 3H; H-1, H-6a, H-5’, overlapping peaks), 3.79 (dd, 3 J (H,H) = -12.0, 3 J (H,H) = 7.8, 1H; H-6b), 3.61 (t, 3 J (H,H) = 8.7, 1H; H-3), 3.52 (dd, 3 J (H,H) = 9.6, 7.8, 1H; H-5), 3.48 – 3.43 (m, 1H; H-4), 2.06 (s, 3H; COCH3), 1.18 – 0.82 (m, 28H; 4 x CH(CH3)2, overlapping peaks); 13C NMR (126 MHz, CDCl3): δ 169.1 (COCH3), 166.1, 165.2, 165.1 (4 x COPh, overlapping peaks), 133.4, 133.2, 133.1, 129.8, 129.7 (12 x Ar-CH, overlapping peaks), 129.6, 129.3, 128.8 (4 x Ar-C, overlapping peaks), 128.4, 128.3 (8 x Ar-CH, overlapping peaks), 101.5 (C-1’), 87.3 (C-1), 78.7 (C-4), 77.2 (C-3), 73.3 (C-5), 72.9 (C-3’), 72.4 (C-2), 72.2 (C-2’), 71.9 (C-5’), 69.6 (C-4’), 68.5 (C-6), 63.1 (C-6’), 20.6 (COCH3), 17.3, 17.2, 17.1, 17.0 (8 x CH(CH3)2, overlapping peaks), 12.7, 12.1, 12.0 (4 x CH(CH3)2, overlapping peaks); ESI-HRMS calcd for C54H65N3O16Si2Na 1090.3801, found m/z 1090.3811 [M+Na]+.

General procedure for the anomerisation reactions using TiCl4:
The β-anomer (1 eq) was added to a flame dried round bottomed flask and anhydrous CH2Cl2 (10 mL per g of substrate) was added. The flask was then cooled on an ice bath and 2.5 eq TiCl4 (1.0 M in CH2Cl2) was added dropwise. The flask was then left to stand in a freezer (-15 to -18 °C) for 48-72 h. The mixture was diluted with CH2Cl2 and washed with NH4Cl (1.0 M, 10 mL). The aq layer was extracted with CH2Cl2 and the combined organic layers were washed with satd aq NaHCO3 and brine. The organic layer was dried over Na2SO4, filtered through silica gel and the solvent removed to give the products.

![2,3,4-Tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-5-S-(methoxycarbonyl)-α-D-xylopyranosyl)-β-D-glucopyranosyl azide](image)

2,3,4-Tri-O-benzoyl-6-O-(2,3,4-tri-O-benzoyl-5-S-(methoxycarbonyl)-α-D-xylopyranosyl)-β-D-glucopyranosyl azide (54)
[α]D 44.9 (c 1.1, CH2Cl2); 1H NMR (500 MHz, CDCl3) δ = 8.13 – 8.02 (m, 2H; Ar-H), 8.00 (dd, 3J (H,H) = 8.5, 1.5 Hz, 2H; Ar-H), 7.96 (d, 3J (H,H) = 6.9 Hz, 2H; Ar-H), 7.91 (ddd, 3J (H,H) = 8.2, 3.7, 1.4 Hz, 4H; Ar-H), 7.81 (dd, 3J (H,H) = 8.3, 1.5 Hz, 2H; Ar-H), 7.55 – 7.27 (m, 17H; Ar-H), 6.29 (apt t, 3J (H,H) = 9.8 Hz, 1H; H-3’), 5.88 (apt t, 3J (H,H) = 9.7 Hz, 1H; H-3), 5.68 (apt t, 3J (H,H) = 9.8 Hz, 1H; H-4’), 5.60 (apt t, 3J (H,H) = 9.8 Hz, 1H; H-4), 5.51 (d, 3J (H,H) = 3.6 Hz, 1H; H-1’), 5.40 – 5.31 (m, 2H; H-2, H-2’, overlapping peaks), 4.90 (d, 3J (H,H) = 8.8 Hz, 1H; H-1), 4.74 (d, 3J (H,H) = 10.1 Hz, 1H; H-5’), 4.16 – 4.02 (m, 2H; H-5, H-6a, overlapping peaks), 3.80 (dd, 2J (H,H) = -11.5 Hz, 3J (H,H) = 1.9 Hz, 1H; H-6b), 3.60 (s, 3H; CO2CH3); 13C NMR (126 MHz, CDCl3): δ 168.3 (CO2CH3), 165.9, 165.8, 165.7, 165.5, 165.2, 165.0 (6 x COPh), 133.7 (2s), 133.6, 133.5, 133.3, 130.1 (2s), 130.0, 129.9 (2s) (18 x Ar-CH, overlapping peaks), 129.2, 129.1, 129.0, 128.9 (4 x Ar-C), 128.7 (2s) (2 x Ar-CH, Ar-C, overlapping peaks), 128.6 (2s) (4 x Ar-CH, Ar-C, overlapping peaks), 128.5 (2s), 128.4 (6 x Ar-CH, overlapping peaks), 96.4 (C-1’), 88.2 (C-1), 75.5 (C-5), 72.9 (C-3), 71.5 (C-2), 71.3 (C-2’), 70.2 (C-4’), 69.9 (C-3’), 68.9 (C-4), 68.6 (C-5’), 67.0 (C-6), 52.9 (CO2CH3); IR (film) cm⁻¹: 2955, 2924, 2118, 1726, 1451, 1248, 1090, 1067, 1025; ESI-HRMS calcd for C55H45O17N3Na 1042.2647, found m/z 1042.2649 [M+Na]+.

2-O-(2,3,4-Tri-O-benzoyl-5-S-(methoxycarbonyl)-α-D-xylopyranosyl)-3,4-O-((1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-6-O-acetyl-β-D-glucopyranosyl azide (57)

[α]D 48.0 (c 0.35, CH2Cl2); 1H-NMR (500 MHz, CDCl3) δ = 8.00 (dd, 3J (H,H) = 8.3, 1.5 Hz, 2H; Ar-H), 7.96 – 7.91 (m, 2H; Ar-H), 7.88 (dd, 3J (H,H) = 8.3, 1.5 Hz, 2H; Ar-H), 7.57 – 7.49 (m, 1H; Ar-H), 7.46 – 7.37 (m, 5H; Ar-H), 7.30 (t, 3J (H,H) = 7.7 Hz, 2H; Ar-H), 6.21 (apt t, 3J (H,H) = 10.1 Hz, 1H; H-3’), 6.08 (d, 3J (H,H) = 3.7 Hz, 1H; H-1’), 5.65 (apt t, 3J (H,H) = 10.0 Hz, 1H; H-4’), 5.35 (dd, 3J (H,H) = 10.4, 3.7 Hz, 1H; H-2’), 4.94 (d, 3J (H,H) = 10.3 Hz, 1H; H-5’), 4.49 (d, 3J (H,H) = 8.7 Hz, 1H; H-1), 4.40 (dd, 2J (H,H) = -12.0 Hz, 3J (H,H) = 2.2 Hz, 1H; H-6a), 4.15
(dd, $^2J (H,H) = -12.0$ Hz, $^3J (H,H) = 5.0$ Hz, 1H; H-6b), 3.87 (apat t, $^3J (H,H) = 8.7$ Hz, 1H; H-3), 3.73 (apat t, $^3J (H,H) = 8.9$ Hz, 1H; H-4), 3.64 (s, 3H; CO$_2$CH$_3$), 3.56 (apat t, $^3J (H,H) = 8.8$ Hz, 1H; H-2), 3.51 (dq, $^3J (H,H) = 7.3$, 3.0, 2.5 Hz, 1H; H-5), 2.05 (s, 3H; COCH$_3$), 1.45 – 0.75 (m, 28H; 4 x CH(CH$_3$)$_2$, overlapping peaks); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 170.7 (COCH$_3$), 168.2 (CO$_2$CH$_3$), 165.6, 165.4, 165.3 (3 x COPh), 133.4 (2s), 133.2, 129.8, 129.7 (9 x Ar-CH, overlapping peaks), 94.9 (C-1'), 89.7 (C-1), 78.0 (C-3), 76.9 (C-2), 75.7 (C-5), 72.7 (C-4), 71.0 (C-2'), 70.0 (C-4'), 69.0 (C-3'), 68.6 (C-5'), 62.7 (C-6), 52.7 (CO$_2$CH$_3$), 29.7 (COCH$_3$), 20.8, 17.5 (2s), 17.4, 17.3, 17.2 (2s), 17.1 (2s) (8 x CH(CH$_3$)$_2$, overlapping peaks), 12.9, 12.7, 12.2, 11.4 (4 x CH(CH$_3$)$_2$, overlapping peaks); IR (film) cm$^{-1}$: 3072, 2953, 2120, 1727, 1452, 1248, 1091, 1067, 1026; ESI-HRMS calcd for C$_{48}$H$_{61}$O$_{16}$N$_{4}$Si$_{3}$Na 1014.3488, found m/z 1014.3494 [M+Na]$^+$. 

2,3-O-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-4-O-(2,3,4-tri-O-benzoyl-5-S-(methoxycarbonyl)-α-D-xylopyranosyl)-6-O-acetyl-β-D-glucopyranosyl azide (62) 

[$\alpha$]$D$ 29.0 (c 0.2, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.05 (dd, $^3J (H,H) = 8.2$, 1.4 Hz, 2H; Ar-H), 7.94 – 7.89 (m, 4H; Ar-H), 7.58 – 7.53 (m, 2H; Ar-H), 7.51 – 7.46 (m, 1H; Ar-H), 7.43 – 7.36 (m, 4H; Ar-H), 7.26 (m, 2H; Ar-H), 5.99 (d, $^3J (H,H) = 2.4$ Hz, 1H; H-1’), 5.81 (apat t, $^3J (H,H) = 5.5$ Hz, 1H; H-3’), 5.65 (apat t, $^3J (H,H) = 4.9$ Hz, 1H; H-4’), 5.46 (dd, $^3J (H,H) = 5.9$, 2.4 Hz, 1H; H-2’), 4.77 (d, $^3J (H,H) = 4.7$ Hz, 1H; H-5’), 4.60 (dd, $^3J (H,H) = -12.2$ Hz, $^3J (H,H) = 2.3$ Hz, 1H; H-6a), 4.53 (d, $^3J (H,H) = 8.2$ Hz, 1H; H-1), 4.40 (dd, $^3J (H,H) = -12.2$ Hz, $^3J (H,H) = 5.0$ Hz, 1H; H-6b), 4.04 (dd, $^3J (H,H) = 9.9$, 8.6 Hz, 1H; H-4), 3.87 (apat t, $^3J (H,H) = 8.6$ Hz, 1H; H-3), 3.65 – 3.59 (m, 4H; CO$_2$CH$_3$; H-5, overlapping peaks), 3.53 (apat t, $^3J (H,H) = 8.4$ Hz, 1H; H-2), 2.06 (s, 3H; COCH$_3$), 1.17 – 0.83 (m, 28H; 4 x CH(CH$_3$)$_2$, overlapping peaks); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 170.7 (COCH$_3$), 168.4 (COCH$_3$), 165.4, 165.2 (3 x COPh, overlapping peaks), 133.7, 133.4, 130.1,
130.0, 129.8 (9 x Ar-CH, overlapping peaks), 199.3 128.8, 128.6 (3 x Ar-C) 128.4, 128.3 (6 x Ar-CH, overlapping peaks), 94.6 (C-1’), 90.5 (C-1), 80.3 (C-3), 76.7 (C-2), 74.4 (C-5), 74.2 (C-4) 72.3 (C-5’), 68.6 (H-3’), 68.2 (H-4’), 67.4 (H-2’) 63.0 (C-6), 52.6 (COCH3), 20.8 (COCH3), 17.3 (2s), 17.2 (2s), 17.1, 16.9 (8 x CH(CH3)2, overlapping peaks), 12.9, 12.7, 12.1, 12.0 (4 x CH(CH3)2, overlapping peaks); IR (film) cm⁻¹: 2927, 2868, 2118, 1729, 1452, 1246, 1091, 1068, 1026, 988; ESI-HRMS calcd for C48H61O16N3Si2Na 1014.3488, found m/z 1014.3467 [M+Na]⁺.

\[\text{2,3,6-Tri-O-benzoyl-4-O-(2,3,4-tri-O-benzoyl-5-S-(methoxycarbonyl)-a-D-xylopyranosyl)-b-D-glucopyranosyl azide (64)\]  
\[\delta \text{CDCl}_3 \delta = 8.07 – 8.02 (m, 2H; Ar-H), 8.01 – 7.98 (m, 2H; Ar-H), 7.97 – 7.94 (m, 2H; Ar-H), 7.91 (ddd, 3J (H,H) = 8.5, 3.9, 1.4 Hz, 4H; Ar-H), 7.83 – 7.79 (m, 2H; Ar-H), 7.55 – 7.27 (m, 17H; Ar-H), 6.28 (apt t, 3J (H,H) = 9.8 Hz, 1H; H-3’), 5.87 (apt t, 3J (H,H) = 9.7 Hz, 1H; H-3), 5.67 (apt t, 3J (H,H) = 9.7 Hz, 1H; H-4’), 5.59 (apt t, 3J (H,H) = 9.7 Hz, 1H; H-4), 5.50 (d, 3J (H,H) = 3.7 Hz, 1H; H-1’), 5.38 – 5.32 (m, 2H; H-2, H-2’; overlapping peaks), 4.89 (d, 3J (H,H) = 8.8 Hz, 1H; H-1), 4.73 (d, 3J (H,H) = 10.1 Hz, 1H; H-5’), 4.10 (ddd, 3J (H,H) = 9.8, 6.3, 1.7 Hz, 1H; H-5), 4.05 (dd, 2J (H,H) = -11.3 Hz, 3J (H,H) = 6.4 Hz, 1H; H-6a), 3.79 (dd, 2J (H,H) = -11.3 Hz, 3J (H,H) = 1.7 Hz, 1H; H-6b), 3.60 (s, 3H; COCH3); 13C NMR (126 MHz, CDCl3): δ 168.1 (COCH3), 165.7 (2s) 165.6, 165.4, 165.0, 164.8 (6 x COPh), 133.6, 133.5 (2s), 133.3, 133.2, 130.0, 129.9 (2s), 129.8 (2s) (18 x Ar-CH, overlapping peaks), 129.1, 128.9, 128.8 (2s), 128.6 (5 x Ar-C), 128.5 (2s) (2x Ar-CH, Ar-C, overlapping peaks), 128.4(2s), 128.3 (2s) (10 x Ar-CH, overlapping peaks), 96.3 (C-1’), 88.1 (C-1), 75.4 (C-5), 72.8 (C-3), 71.3 (C-2), 71.2 (C-2’), 70.0 (C4’), 69.8 (C-3’), 68.8 (C-4), 68.4 (C-5’), 66.8 (C-6), 52.8 (COCH3); IR (film) cm⁻¹: 2952, 2119, 1725, 1452, 1247, 1091, 1067, 1026, 704; ESI-HRMS calcd for C55H45O17N3Si2Na 1042.2647, found m/z 1042.2665 [M+Na]⁺.
2-O-Acetyl-3-O-(2,3,4-tri-O-benzoyl-5-S-(methoxycarbonyl)-α-D-xylopyranosyl)-4,6-O-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-β-D-glucopyranosyl azide (67)

$[\alpha]_D -9.7 \text{(c 0.35, CH}_2\text{Cl}_2)$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 8.00$ (dd, $^3J (H,H) = 8.2, 1.4$ Hz, 2H; Ar-H), 7.95 (dd, $^3J (H,H) = 8.3, 1.4$ Hz, 2H; Ar-H), 7.90 (dd, $^3J (H,H) = 8.3, 1.4$ Hz, 2H; Ar-H), 7.54 – 7.49 (m, 2H; Ar-H), 7.46 – 7.36 (m, 5H; Ar-H), 7.31 (t, $^3J (H,H) = 7.7$ Hz, 2H; Ar-H), 6.19 (apt t, $^3J (H,H) = 9.9$ Hz, 1H; H-3’), 5.68 – 5.62 (m, 2H; H-1’, H-4’, overlapping peaks), 5.32 (dd, $^3J (H,H) = 10.1, 3.7$ Hz, 1H; H-2), 4.68 (d, $^3J (H,H) = 10.1$ Hz, 1H; H-5’), 4.56 (apt t, $^3J (H,H) = 8.8$ Hz, 1H; H-2), 4.43 (d, $^3J (H,H) = 9.0$ Hz, 1H; H-1), 4.01 – 3.98 (m, 2H; H-6a, H-6b, overlapping peaks), 3.71 – 3.63 (m, 5H; CO$_2$CH$_3$, H-3, H-4, overlapping peaks), 3.53 – 3.46 (m, 1H; H-5) 2.05 (s, 3H; COCH$_3$), 1.22 – 0.94 (m, 28H; 4 x CH(CH$_3$)$_2$, overlapping peaks); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta 168.9$ (COCH$_3$), 168.4 (CO$_2$CH$_3$), 165.7 (2s), 165.5 (3 x COPh), 133.6, 133.5, 133.3, 130.0, 129.9 (9 x Ar-CH, overlapping peaks), 129.2, 129.0, 128.9 (3 x Ar-C), 128.7, 128.5 (2s) (6 x Ar-CH, overlapping peaks), 96.6 (C-1’), 87.9 (C-1), 77.9 (C-5), 77.6 (C-4), 72.5 (C-2), 72.4 (C-3), 71.6 (C-2’), 70.3 (C-4), 69.8 (C-3’), 68.7 (C-5), 65.9 (C-6), 53.0 (CO$_2$CH$_3$), 20.8 (COCH$_3$), 17.4 (4s), 17.3 (2s) (8 x CH(CH$_3$)$_2$, overlapping peaks), 12.9, 12.8, 12.3, 12.2 (4 x CH(CH$_3$)$_2$, overlapping peaks); IR (film) cm$^{-1}$: 2925, 2867, 2117, 1731, 1452, 1260, 1095, 1067, 1041, 983; ESI-HRMS calcd for C$_{48}$H$_{61}$O$_{16}$N$_3$Si$_2$Na 1014.3488, found m/z 1014.3492 [M+Na]$^+$. 

![Chemical structure image](image-url)
2,4,6-Tri-O-benzoyl-3-O-(2,3,4-tri-O-benzoyl-5-S-(methoxycarbonyl)-α-D-xylopyranosyl)-β-D-glucopyranosyl azide (69)

[α]D 40.2 (c 0.95, CH2Cl2); 1H NMR (500 MHz, CDC13): δ 8.15 – 8.10 (m, 2H; Ar-H), 8.08 – 8.03 (m, 2H; Ar-H), 8.02 – 7.98 (m, 2H; Ar-H), 7.97 – 7.94 (m, 2H; Ar-H), 7.94 – 7.89 (m, 3H Ar-H), 7.83 – 7.77 (m, 2H; Ar-H), 7.64 – 7.60 (m, 1H; Ar-H), 7.56 – 7.27 (m, 19H; Ar-H), 6.29 (apt t, 3J (H,H) = 9.8 Hz, 1H; H-3’), 5.88 (apt t, 3J (H,H) = 9.7 Hz, 1H; H-3’), 5.68 (apt t, 3J (H,H) = 9.8 Hz, 1H; H-4’), 5.59 (apt t, 3J (H,H) = 9.8 Hz, 1H; H-5’), 5.51 (d, 3J (H,H) = 3.7 Hz, 1H; H-1’), 5.40 – 5.30 (m, 2H; H-2, H-2’, overlapping peaks), 4.90 (d, 3J (H,H) = 8.8 Hz, 1H; H-1), 4.74 (d, 3J (H,H) = 10.1 Hz, 1H; H-5’), 4.11 (ddd, 3J (H,H) = 9.6, 6.4, 1.7 Hz, 1H; H-5), 4.05 (dd, 2J (H,H) = -11.3 Hz, 3J (H,H) = 6.4 Hz, 1H; H-6a), 3.79 (d, 2J (H,H) = -11.3 Hz, 3J (H,H) = 1.7 Hz, 1H; H-6b), 3.60 (s, 3H; CO2CH3); 13C NMR (126 MHz, CDCl3): δ 168.1 (CO2CH3), 165.7 (2s), 165.6, 165.4, 165.0, 164.8 (6 x COPh), 133.7, 133.6, 133.5 (2s), 133.3, 133.2, 130.2, 130.0 (2s), 129.9, 129.8 (2s) (18 x Ar-CH, overlapping peaks), 129.1, 128.9, 128.8 (2s), 128.6 (5 x Ar-C), 128.5 (3s) (4 x Ar-CH, Ar-C, overlapping peaks), 128.4 (2s), 128.3 (2s) (8 x Ar-CH, overlapping peaks), 96.3 (C-1’), 88.1 (C-1), 75.4 (C-5), 72.8 (C-3), 71.3 (C-3’), 71.2 (C-4’), 70.0 (C-2’), 69.8 (C-2), 68.8 (C-4), 68.4 (C-5’), 66.8 (C-6), 52.8 (CO2CH3); IR (film) cm⁻¹: 2957, 2924, 2119, 1724, 1452, 1248, 1090, 1067, 1025; ESI-HRMS calcd for C55H47O17N3Na 1042.2647, found m/z 1042.2653 [M+Na]+.

2,3,4-Tri-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzoyl-α-D-glucopyranosyl)-β-D-glucopyranosyl azide (71)

[α]D 27.7 (c 0.8, CH2Cl2); 1H NMR (500 MHz, CDC13): δ 8.09 (d, 3J (H,H) = 7.7, 2H; Ar-H), 8.04 (d, 3J (H,H) = 7.4, 2H; Ar-H), 7.99 – 7.94 (m, 2H; Ar-H), 7.93 – 7.88 (m, 4H; Ar-H), 7.80 (d, 3J (H,H) = 8.0, 1H; Ar-H), 7.55 – 7.27 (m, 24H; Ar-H), 6.26 (apt t, 3J (H,H) = 9.8, 1H; H-3’), 5.84 (apt t, 3J (H,H) = 9.6, 1H; H-3), 5.68 (apt t, 3J (H,H) = 9.8, 1H; H-4’), 5.45 – 5.39 (m, 2H; H-4, H-1’, overlapping peaks), 5.35 (dd, 3J
Overlapping peaks; 3.73 (dd, J = 3, 1H; H-5', overlapping peaks), 4.17 – 3.99 (m, 2H; H-6a, H-5, overlapping peaks), 3.73 (dd, J (H, H) = -11.5, 1H; H-6b'); 13C NMR (126 MHz, CDCl3): δ 166.0, 165.8, 165.7, 165.1, 164.8 (7 x COPh, overlapping peaks), 133.6, 133.4, 133.1, 130.0, 129.9, 129.8, 129.7 (21 x Ar-CH, overlapping peaks), 129.2, 128.9, 128.8, 128.6 (7 x Ar-C, overlapping peaks), 128.5, 128.4, 128.3, 128.3 (14 x Ar-CH, overlapping peaks), 95.8 (C-1'), 87.9 (C-1), 75.4 (C-5), 72.8 (C-3), 71.8 (C-2'), 71.2 (C-2), 70.6 (C-3'), 69.2 (C-4'), 68.9 (C-4), 68.1 (C-5'), 66.2 (C-6), 62.7 (C-6'); ESI-HRMS calcd for C55H45O17N3Na 1042.2647, found m/z 1042.2653 [M+Na]+.

2,3-O-(1,1,3,3-tetraisopropyl-1,3-disiloxanediyl)-4-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzoyl-α-D-glucopyranosyl)-β-D-glucopyranosyl azide (73)

[α]D 31.2 (c 0.6, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.08 (d, J (H, H) = 7.7, 2H; Ar-H), 8.02 (d, J (H, H) = 7.8, 2H; Ar-H), 7.95 (d, J (H, H) = 7.7, 2H; Ar-H), 7.87 (d, J (H, H) = 7.8, 2H; Ar-H), 7.59 – 7.26 (m, 12H; Ar-H), 6.21 (apt. t, J (H, H) = 9.8, 1H; H-3'), 5.67 (apt. t, J (H, H) = 9.9, 1H; H-4'), 5.37 (d, J (H, H) = 3.8, 1H; H-1'), 5.30 (dd, J (H, H) = 10.1, 3.8, 1H; H-2), 4.81 (apt. t, J (H, H) = 9.7, 1H; H-4), 4.70 – 4.53 (m, 3H; H-6a', H-5', H-1, overlapping peaks), 4.41 (dd, J (H, H) = -11.9, 1H; H-6b'), 3.90 (dd, J (H, H) = -11.1, 1H; H-6b), 3.78 – 3.64 (m, 2H; H-5, H-3), 3.58 (dd, J (H, H) = -11.1, 1H; H-6b), 3.29 (apt. t, J (H, H) = 8.4, 1H; H-2), 2.03 (s, 3H; COCH3), 1.16 – 0.91 (m, 28H; 4 x CH(CH3)2, overlapping peaks), 13C NMR (126 MHz, CDCl3): δ 169.3 (COCH3), 166.0, 165.8, 165.7, 165.3 (4 x COPh), 133.4, 133.3, 133.1, 133.0, 130.0, 129.9 (8 x Ar-CH, overlapping peaks), 129.8 (Ar-C, 2 x Ar-CH, overlapping peaks), 129.7 (4 x Ar-CH,
overlapping peaks), 129.2, 129.0, 128.8 (3 x Ar-C), 128.4, 128.3 (4 x Ar-CH, overlapping peaks), 95.4 (C-1’), 89.9 (C-1), 77.5 (C-5), 76.5 (C-2), 74.5 (C-3), 72.0 (C-2’), 70.6 (C-3’), 70.3 (C-4), 69.2 (C-4’), 67.9 (C-5’), 66.8 (C-6), 62.8 (C-6’), 20.7 (COCH₃), 17.2, 17.1, 16.9 (8 x CH(CH₃)₂, overlapping peaks), 12.8, 12.6, 12.0 (4 x CH(CH₃)₂, overlapping peaks); ESI-HRMS calcd for C₅₉H₆₇O₁₇N₃Na 1129.4060, found m/z 1129.4062 [M+Na]⁺.
Chapter 4 experimental procedures:

General Procedures:

1. Acylation

A solution of the substrate (1 eq) in pyridine (5 mL/0.25 g) was cooled using an ice bath and to this was added DMAP\(^9\) (0.1 eq) followed by the slow addition of the acylation agent. The reaction mixture was allowed to attain room temperature and was stirred overnight before being quenched by the addition of MeOH. The resulting solution was concentrated, diluted with EtOAc, washed twice with 1M HCl, satd aq NaHCO\(_3\), brine, dried over Na\(_2\)SO\(_4\), filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (cyclohexane-EtOAc 8:2 to 6:4) gave the desired compound.

2. Oxidative removal of benzyl ethers or opening of benzylidene acetals followed by acylation.

To a solution of the substrate in EtOAc (1 mL per 0.05 g) was added a solution of NaBrO\(_3\) (3 eq) in H\(_2\)O (1 mL per 0.05 g). The biphasic mixture was stirred vigorously and to this was added a solution of 85\% Na\(_2\)S\(_2\)O\(_4\) (3 eq) in H\(_2\)O (1 mL per 20 mg) in a dropwise manner. The reaction was followed by TLC and upon consumption of the starting material, the reaction was quenched with a 1M aq Na\(_2\)S\(_2\)O\(_3\) (0.5 mL) was added. The layers were separated and the organic layer was dried over Na\(_2\)SO\(_4\), filtered and solvent was removed under diminished pressure. The resulting residue was taken up in pyridine and cooled using an ice bath. To this solution was added DMAP (0.1 eq) followed by the slow addition of the acylating agent (2.5 eq). The reaction was allowed to attain room temperature and was stirred overnight before being quenched by the addition of MeOH. The resulting solution was diluted with EtOAc, washed twice with 1M HCl, satd aq NaHCO\(_3\), brine, dried over Na\(_2\)SO\(_4\), filtered and solvent was removed under diminished pressure. Flash chromatography of the residue (cyclohexane-EtOAc 8:2 to 6:4) gave the desired compound(s).

\(^9\) The addition of DMAP is optional and in some cases was omitted.
Butyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (75β) \(^{93}\)

\([\alpha]_D -23.6 \text{ (c 0.2, CH}_2\text{Cl}_2)\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.19 (apt. t, \(^3\)J (H,H) = 9.5, 1H; H-3), 5.07 (apt. t, \(^3\)J (H,H) = 9.8, 1H; H-4), 4.97 (dd, \(^3\)J (H,H) = 9.7, 7.9, 1H; H-2), 4.48 (d, \(^3\)J (H,H) = 8.0, 1H; H-1), 4.25 (dd, \(^2\)J (H,H) = -12.2, \(^3\)J (H,H) = 4.8, 1H; H-6a), 4.12 (dd, \(^2\)J (H,H) = -12.2, \(^3\)J (H,H) = 2.4, 1H; H-6b), 3.87 (dt, \(^2\)J (H,H) = -12.2, \(^3\)J (H,H) = 2.4, 1H; H-6b), 3.68 (ddd, \(^3\)J (H,H) = 10.0, 4.7, 2.5, 1H; H-6a), 3.47 (dt, \(^2\)J (H,H) = -9.7, \(^3\)J (H,H) = 6.3, 1H; CHH), 3.68 (ddd, \(^3\)J (H,H) = 10.0, 4.7, 2.5, 1H; H-5), 3.47 (dt, \(^2\)J (H,H) = -9.7, \(^3\)J (H,H) = 6.8, 1H; CHH), 2.07 (s, 3H; COCH\(_3\)), 2.03 (s, 3H; COCH\(_3\)), 2.01 (s, 3H; COCH\(_3\)), 1.99 (s, 3H; COCH\(_3\)), 1.60 – 1.45 (m, 2H; CH\(_2\)), 1.43 – 1.27 (m, 2H; CH\(_2\)), 0.89 (t, \(^3\)J (H,H) = 7.4, 3H; CH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 170.7, 170.3, 169.4, 169.3 (4 x COCH\(_3\)), 100.8 (C-1), 72.8 (C-5), 71.7 (C-2), 71.3 (C-2), 69.9 (CH\(_2\)), 68.5 (C-4), 62.0 (C-6), 31.4 (CH\(_2\)), 20.7, 20.6 (4 x COCH\(_3\), overlapping peaks), 18.9 (CH\(_2\)), 13.7 (CH\(_3\)); IR (film) cm\(^{-1}\): 2961, 2875, 1747, 1725, 1374, 1265, 1238, 1224, 1097, 1029, 903, 716, 612; ESI-HRMS calcd for C\(_{18}\)H\(_{32}\)O\(_{10}\)N 422.2024, found m/z 422.2024 [M+NH\(_4\)]\(^+\).

Butyl β-D-glucopyranoside (76) \(^{93}\)

75β (11.4 g, 28.2 mmole) was taken up in anhydrous MeOH (150 mL) and NaOMe was added. The reaction was followed by TLC and upon consumption of the starting material Dowex® 50WX8 H\(^+\)-resin (1 g) was added and the mixture was stirred until the solution was neutralised. The resulting mixture was then filtered and solvent was evaporated under diminished pressure to give 76 (6.33 g) in 96 % yield; \([\alpha]_D -5.3 \text{ (c 0.2, CH}_2\text{Cl}_2)\); \(^1\)H NMR (500 MHz, D\(_2\)O): \(\delta\) 4.32 (d, \(^3\)J (H,H) = 8.0, 1H; H-1), 3.86 – 3.69 (m, 2H; H-6a, CHH, overlapping peaks), 3.64 – 3.49 (m, 2H; H-6a, CHH, overlapping peaks), 3.41 – 3.27 (m, 2H; H-3, H-5, overlapping peaks), 3.28 – 3.17 (m, 1H, H-4), 3.12 (dd, \(^3\)J (H,H) = 9.4, 7.9, 1H; H-2), 1.56 – 1.39 (m, 2H; CH\(_2\)), 1.31 – 1.13 (m, 2H; CH\(_2\)), 0.77 (t, \(^3\)J (H,H) = 7.4, 3H; CH\(_3\)); \(^{13}\)C NMR (126 MHz, D\(_2\)O): \(\delta\) 102.1 (C-1), 75.8 (C-3, C-5, overlapping peaks), 73.1 (C-2), 70.3 (CH\(_2\)), 69.6 (C-4), 60.7 (C-6), 30.8 (CH\(_2\)), 18.4 (CH\(_2\)), 13.0 (CH\(_3\)); IR (film) cm\(^{-1}\): 3368, 3243, 2966,
2871, 1754, 178, 1376, 1209, 1066, 1034, 749; ESI-HRMS calcd for $C_{10}H_{20}O_6Na$ 259.1158, found $m/z$ 259.1151 [M+Na]$^+$.  

**Butyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranoside (77β)**

76 (1 g, 4.23 mmol) was subjected to general procedure 1, using Benzoyl chloride as the acylating agent. Purification by flash chromatography (cyclohexane-EtOAc 8:2) gave 77β (2.15 g, 78%) as a foam; $[\alpha]_D$ 14.6 (c 0.5, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.01 (d, $^3J(H,H) = 7.7$, 1H; Ar-H), 7.95 (d, $^3J(H,H) = 7.7$, 1H; Ar-H), 7.90 (d, $^3J(H,H) = 7.8$, 1H; Ar-H), 7.83 (d, $^3J(H,H) = 7.7$, 1H; Ar-H), 7.51 (dq, $^3J(H,H) = 21.4$, 7.5, 2H; Ar-H), 7.40 (dq, $^3J(H,H) = 15.9$, 7.8, 3H; Ar-H), 7.34 (t, $^3J(H,H) = 7.7$, 1H; Ar-H), 7.28 (t, $^3J(H,H) = 7.1$, 1H; Ar-H), 5.90 (apt. t, $^3J(H,H) = 9.6$, 1H; H-3), 5.67 (apt. t, $^3J(H,H) = 9.7$, 1H; H-4), 5.52 (dd, 9.7, 7.9, 1H; H-2), 4.83 (d, $^3J(H,H) = 7.8$, 1H; H-1), 4.63 (dd, $^3J(H,H) = -12.2$, 3J(H,H) = 3.3, 1H; H-6a), 4.50 (dd, $^3J(H,H) = -12.1$, 3J(H,H) = 5.2, 1H; H-6b), 4.15 (ddd, $^3J(H,H) = 9.3$, 5.2, 3.4, 1H; H-5), 3.91 (dt, $^3J(H,H) = -9.7$, 3J(H,H) = 6.3, 1H; CHH), 3.55 (dt, $^3J(H,H) = -9.7$, 3J(H,H) = 6.8, 1H; CHH), 1.56 – 1.45 (m, 2H; CH$_2$), 1.23 (m, 2H; CH$_2$), 0.74 (t, $^3J(H,H) = 7.4$, 1H; CH$_3$); $^3$C NMR (126 MHz, CDCl$_3$): $\delta$ 166.1, 165.8, 165.2, 165.1 (4 x COPh), 133.4, 133.2, 133.1, 129.8, 129.7 (8 x Ar-CH, overlapping peaks), 129.6, 129.4, 128.8 (4 x Ar-C, overlapping peaks), 128.3, 128.2 (4 x Ar-CH, overlapping peaks), 102.3 (C-1), 72.9 (C-3), 72.1 (C-5), 71.9 (C-2), 70.0 (CH$_2$), 69.9 (C-4), 63.2 (C-6), 31.4 (CH$_2$), 18.9 (CH$_3$), 13.5 (CH$_3$); IR (film) cm$^{-1}$: 3337, 2960, 2875, 1724, 1602, 1451, 1260, 1118, 1091, 1066, 1026, 952, 704; ESI-HRMS calcd for $C_{38}H_{40}O_{10}N$ 670.2652, found $m/z$ 670.2668 [M+NH$_4^+$]$^+$.  

**Butyl 4,6-O-benzylidene-β-D-glucopyranoside (78)**

Compound 76 (13.2 g, 55.87 mmol) was taken up in MeCN (100 mL) and to this was added benzyledehyde dimethyl actel and catalytic $p$-TsOH.H$_2$O (0.5 g, 2.63 mmol). The reaction was stirred for 2 h, before triethylamine (0.22 mL, 3 mmol) was added. The resulting suspension was evaporated to dryness under diminished
pressure and purified by flash chromatography (CH$_2$Cl$_2$-MeOH 95:5) to give 78 (13.41 g, 74%) as a white solid; [α]$_D$ -35.7 (c 0.2, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CD$_2$OD): δ 7.49 (dd, $^2$J (H,H) = 6.7, 2.8, 2H; Ar-H), 7.33 (dd, $^2$J (H,H) = 5.1, 2.0, 3H; Ar-H), 5.57 (s, 1H; CHPh), 4.27 (dd, $^3$J (H,H) = 10.4, 4.4, 1H; H-1), 4.27 (dd, $^3$J (H,H) = -10.4, $^3$J (H,H) = 4.4, 1H; H-6a), 3.84 (dt, $^2$J (H,H) = -9.6, $^3$J (H,H) = 6.7, 1H; CHH), 3.76 (apt. t, $^3$J (H,H) = 9.8, 1H, H-6b), 3.62 (apt. t, $^3$J (H,H) = 8.8, 1H; H-3), 3.57 (dt, $^2$J (H,H) = -9.6, $^3$J (H,H) = 6.6, 1H; CHH), 3.49 – 3.39 (m, 2H, H-5, overlapping peaks), 3.27 (d, $^3$J (H,H) = 8.6, 1H; H-2), 1.67 – 1.53 (m, 2H; CH$_2$), 1.47 – 1.36 (m, 2H; CH$_2$), 0.93 (t, $^3$J (H,H) = 7.4, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CD$_2$OD): δ 137.7 (Ar-C) 128.5, 127.6, 126.1 (5 x Ar-CH, overlapping peaks), 103.6 (C-1), 101.5 (CHPh), 80.9 (C-4), 74.6 (C-2), 73.3 (C-3), 69.4 (CH$_2$), 68.3 (C-6), 66.1 (C-5), 31.5 (CH$_2$), 18.8 (CH$_2$), 12.7 (CH$_3$); IR (film) cm$^{-1}$: 3995, 3370, 2931, 2875, 1725, 1695, 1452, 1262, 1177, 1088, 1067, 980, 950, 751, 701; ESI-HRMS calcd for C$_{17}$H$_{25}$O$_{10}$ 325.1621, found m/z 325.1657 [M+H]$^+$.

Butyl 2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranoside (79)

78 (1 g, 3.08 mmol) was subjected to general procedure 1, using acetic anhydride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 8:2) gave 79 (1.12 g, 89%) as a white solid; [α]$_D$ 6.7 (c 0.3, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.50 – 7.38 (m, 2H; Ar-H), 7.39 – 7.32 (m, 3H; Ar-H), 5.50 (s, 1H; CHPh), 5.31 (apt. t, $^3$J (H,H) = 9.3, 1H; H-3), 4.99 (dd, $^3$J (H,H) = 9.4, 7.9, 1H; H-2), 4.57 (d, $^3$J (H,H) = 8.0, 1H; H-1), 4.36 (dd, $^2$J (H,H) = -10.6, $^3$J (H,H) = 5.0, 1H; H-6a), 3.87 (dt, $^2$J (H,H) = -9.6, $^3$J (H,H) = 6.3, 1H; CHH), 3.80 (apt. t, $^3$J (H,H) = 10.3, 1H; H-6b), 3.69 (apt. t, $^3$J (H,H) = 9.6, 1H; H-4), 3.58 – 3.46 (m, 2H; CHH, H-5, overlapping peaks), 2.05 (s, 3H; COCH$_3$), 2.04 (s, 3H; COCH$_3$), 1.64 – 1.50 (m, 2H; CH$_2$), 1.42 – 1.29 (m, 2H; CH$_2$), 0.90 (t, $^3$J (H,H) = 7.4, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 170.2, 169.5 (2 x COCH$_3$), 136.8 (Ar-C), 129.1, 128.2, 126.1 (5 x Ar-CH, overlapping peaks), 101.4 (C-1, CHPh, overlapping peaks), 78.4 (C-4), 72.3 (C-2), 71.8 (C-2), 70.1 (C-3), 68.6 (CH$_2$), 66.3 (C-5), 31.4 (CH$_2$), 20.8, 20.7 (2 x COCH$_3$), 18.9 (CH$_3$), 13.7 (CH$_3$); IR (film) cm$^{-1}$: 2961, 2876, 1733, 1371, 1240,
Experimental data

1177, 1087, 1057, 1027, 992, 966, 904, 762, 696; ESI-HRMS calcd for C_{21}H_{38}O_{8}Na 431.1682, found m/z 431.1667 [M+Na]^+.

Preparation of compounds 80β and 81β.

79 (1g, 2.45 mmol) was subjected to the conditions outlined in general procedure 2, using acetic anhydride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 8:2) gave compounds 80β (0.617 g, 54%) and 81β (0.285 g, 25%).

Butyl 2,3,4-tri-O-acetyl-6-O-benzoyl-β-D-glucopyranoside (80β)

[α]_D -12.5 (c 1.6, CH3C2); 1H NMR (500 MHz, CDCl3): δ 8.05 (dd, 3J (H,H) = 8.5, 1.3, 2H; Ar-H), 7.63 – 7.53 (m, 1H; Ar-H), 7.48 – 7.42 (m, 2H; Ar-H), 5.18 (apt. t, 3J (H,H) = 9.4, 1H; H-3), 4.53 (d, 3J (H,H) = 8.0, 1H; H-4), 5.01 (dd, 3J (H,H) = 9.4, 8.0, 1H; H-2), 4.38 (dd, 3J (H,H) = -12.0, 3J (H,H) = 4.8, 1H; H-6b), 3.77 (m, 2H; H-5, CHH, overlapping peaks), 3.49 (dt, 3J (H,H) = 9.6, 3J (H,H) = 6.7, 1H; CHH), 2.04 (s, 3H; COCH3), 2.01 (s, 6H; 2 x COCH3, overlapping peaks), 1.61 – 1.47 (m, 2H; CH2), 1.39 – 1.19 (m, 2H; CH2), 0.88 (t, 3J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 170.3, 169.3 (3 x COCH3, overlapping peaks), 166.2 (COPh), 133.2, 129.7 (3 x Ar-CH, overlapping peaks), 129.6 (Ar-C), 128.4 (Ar-CH, overlapping peaks), 100.8 (C-1), 72.9 (C-3), 71.7 (C-5), 71.4 (C-2), 69.9 (CH2), 68.9 (C-4), 62.7 (C-6), 31.4 (CH2), 20.6 (3 x COCH3), 18.9 (CH2), 13.7 (CH3). IR (film) cm⁻¹: 2963, 2874, 1731, 1368, 1241, 1175, 1089, 1060, 1025, 1001, 950, 901, 759; ESI-HRMS calcd for C_{23}H_{34}O_{10}N 484.2183, found m/z 484.2189 [M+NH4]^+.

Butyl 2,3,6-tri-O-acetyl-4-O-benzoyl-β-D-glucopyranoside (81β)
Experimental data

[α]D -64.3 (c 0.9, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 7.99 – 7.94 (m, 2H, Ar-H), 7.59 – 7.55 (m, 1H; Ar-H), 7.47 – 7.41 (m, 2H; Ar-H), 5.41 (apt. t, 3J (H,H) = 9.5 Hz, 1H; H-3), 5.34 (apt. t, 3J (H,H) = 9.6 Hz, 1H; H-4), 5.05 (dd, 3J (H,H) = 9.5, 7.9 Hz, 1H; H-2), 4.57 (d, 3J (H,H) = 7.9 Hz, 1H; H-1), 4.25 (dd, 3J (H,H) = 9.5, 7.9 Hz, 1H; H-2), 4.19 (dd, 2J (H,H) = 12.2 Hz, 1H; H-6a), 3.90 (dt, 2J (H,H) = -9.6 Hz, 1H; H-4), 3.83 (ddd, J = 9.5, 5.0, 3.2 Hz, 1H; CH3). 13C NMR (126 MHz, CDCl3): δ 170.6, 170.2, 169.3 (3 x COCH3), 165.1 (COPh), 133.6, 129.8 (2s, 3 x Ar-C), 128.8 (Ar-C), 128.6 (Ar-CH, overlapping peaks), 100.92 (C-1), 72.6 (C-3), 71.8 (C-5), 71.5 (C-2), 69.9 (CH2), 69.4 (C-4), 62.5 (C-6), 31.4(CH2), 20.6, 20.5 (3 x COCH3, overlapping peaks), 19.0 (CH2), 13.7 (CH3); IR (film) cm⁻¹: 2964, 2880, 1735, 1373, 1241, 1178, 1083, 1059, 1031, 987, 962, 900, 761; ESI-HRMS calcld for C23H34O8N 484.2183, found m/z 484.2184 [M+NH4]⁺.

Preparation of compounds 82 and 83.

Compound 78 (5.6 g, 17.26 mmole) was taken up in CH2Cl2 (90 mL) and to this was added TBAHS (0.586 g, 1.73 mmole) and a 5% aq solution of NaOH (45 mL). The mixture was refluxed for 48 h, allowed to cool to room temperature and the reaction was quenched by the addition of a 1 M HCl solution. The biphasic mixture was extracted with CH2Cl2 twice and the resulting organic solution was dried over Na2SO4, filtered and solvent was removed under diminished pressure. The resulting residue was purified by flash chromatography (toluene-acetone 9:1) allowing for separation of the products to give compounds 82 (2.75 g, 39%) and 83 (1.21 g, 17%).

![Butyl 3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (82)](image)

Butyl 3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (82)

[α]D -18.7 (c 0.1, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 7.51 – 7.46 (m, 2H; Ar-H), 7.42 – 7.34 (m, 5H; Ar-H), 7.34 – 7.27 (m, 3H; Ar-H), 5.57 (s, 1H; CHPh), 4.96 (d, 2J (H,H) = -11.7 Hz, 1H; CHPh), 4.81 (d, 2J (H,H) = -11.7 Hz, 1H; CHPh), 4.39 (d,
$^{3}J$ (H,H) = 7.7, 1H; H-1), 4.35 (dd, $^{2}J$ (H,H) = -10.5, $^{3}J$ (H,H) = 4.9, 1H; H-6a), 3.90 (dt, $^{2}J$ (H,H) = -9.5, $^{3}J$ (H,H) = 6.8, 1H; CHH), 3.80 (apt. t, $^{3}J$ (H,H) = 10.3, 1H; H-6b), 3.71 (apt. t, $^{3}J$ (H,H) = 9.1, 1H; H-4), 3.66 (apt. t, $^{3}J$ (H,H) = 8.8, 1H; H-3), 3.59 – 3.54 (m, 2H; CHH, H-2), 3.44 (td, $^{3}J$ (H,H) = 9.4, 5.0, 1H; H-5), 2.40 (d, $^{3}J$ (H,H) = 2.2, 1H; OH), 1.63 (dq, $^{3}J$ (H,H) = 9.0, 6.9, 2H; CH2), 1.39 (h, $^{3}J$ (H,H) = 7.4, 2H; CH2), 0.93 (t, $^{3}J$ (H,H) = 7.4, 3H; CH3); $^{13}$C NMR (126 MHz, CDCl3): $\delta$ 138.4, 137.3 (2 x Ar-C), 129.0, 128.4, 128.2, 128.0, 127.7, 126.0 (10 x Ar-CH, overlapping peaks), 103.3 (C-1), 101.2 (CHPh), 81.4 (C-4), 80.2 (C-3), 74.5 (CH2Ph), 74.4 (C-2), 70.2 (CH2), 68.7 (C-6), 66.4 (C-5), 31.6 (CH2), 19.1(CH2), 13.8 (CH3); IR (film) cm$^{-1}$: 3065, 2961, 1723, 1452, 1260, 1088, 1067, 1026, 1002, 853, 706; ESI-HRMS calcd for C$_{24}$H$_{31}$O$_{6}$ 415.2121, found m/z 415.2122 [M+H$^+$].

Butyl 2-O-benzyl-4,6-O-benzylidene- $\beta$ -D-glucopyranoside (83)

$[\alpha]_{D}$ -12.1 (c 0.1, CH$_{2}$Cl$_{2}$); $^{1}$H NMR (500 MHz, CDCl$_{3}$): $\delta$ 7.52 – 7.45 (m, 2H; Ar-H), 7.41 – 7.33 (m, 6H; Ar-H), 7.33 – 7.29 (m, 1H; Ar-H), 5.52 (s, 1H; CHPh), 4.96 (d, $^{2}J$ (H,H) = -11.4, 1H; CHPh), 4.73 (d, $^{2}J$ (H,H) = -11.4, 1H; CHPh), 4.51 (d, $^{3}J$ (H,H) = 7.7, 1H; H-1), 4.34 (dd, $^{2}J$ (H,H) = -10.5, $^{3}J$ (H,H) = 5.0, 1H; H-6a), 3.94 (dt, $^{3}J$ (H,H) = 9.5, $^{3}J$ (H,H) = 6.6, 1H; CHH), 3.83 (td, $^{3}J$ (H,H) = 9.1, 2.2, 1H; H-3), 3.78 (apt. t, $^{3}J$ (H,H) = 10.3, 1H; H-6b), 3.61 – 3.51 (m, 2H; CHH, H-4, overlapping peaks), 3.42 (td, $^{3}J$ (H,H) = 9.7, 5.0, 1H; H-5), 3.37 – 3.31 (m, 1H; H-2), 2.47 (d, $^{3}J$ (H,H) = 2.2, 1H; OH), 1.65 (dq, $^{3}J$ (H,H) = 15.3, 6.9, 2H; CH2), 1.43 (dq, $^{3}J$ (H,H) = 15.0, 7.3, 2H; CH2), 0.94 (t, $^{3}J$ (H,H) = 7.4, 3H; CH3); $^{13}$C NMR (126 MHz, CDCl$_{3}$): $\delta$ 138.2, 137.0 (2 x Ar-C), 129.2, 128.5, 128.3, 128.1, 127.9, 126.3 (10 x Ar-CH, overlapping peaks), 103.8 (C-1), 101.7 (CHPh), 81.8 (C-2), 80.4 (C-4), 74.7 (CH$_{2}$Ph), 73.1 (C-3), 70.2 (CH2), 68.7 (C-6), 66.1 (C-5), 31.6 (CH2), 19.3(CH2), 13.8 (CH3); IR (film) cm$^{-1}$: 3498, 3065, 2958, 2931, 2875, 1457, 1386, 1375, 1274, 1180, 1101, 1085, 1051, 981, 965, 909, 920, 851, 794, 731, 695; ESI-HRMS calcd for C$_{24}$H$_{31}$O$_{6}$ 415.2121, found m/z 415.2126 [M+H$^+$].
**Butyl 2-Ο-benzoyl-3-Ο-benzyl-4,6-Ο-benzylidene-β-D-glucopyranoside (84)**

82 (2.5 g, 6.03 mmol) was subjected to the conditions outlined in general procedure 1, using benzoyl chloride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 9:1) gave 84 (2.28 g, 73%) as a white solid; [α]D -31.5. (c 1.3, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.00 (dd, 3J (H,H) = 8.3, 1.4, 2H; Ar-H), 7.64 – 7.54 (m, 1H; Ar-H), 7.54 – 7.49 (m, 2H; Ar-H), 7.46 (d, 3J (H,H) = 6.8, 1H; Ar-H), 7.43 – 7.37 (m, 3H; Ar-H), 7.19 – 7.12 (m, 3H; Ar-H), 7.11 – 7.04 (m, 2H; Ar-H), 5.62 (s, 1H; CCHPh), 5.32 – 5.22 (m, 1H; H-2), 4.83 (d, 3J (H,H) = -12.1, 1H; CHHPh), 4.70 (d, 2J (H,H) = -9.7, 4.7, 1H; H-5), 3.45 (dt, 2J (H,H) = -9.8, 3J (H,H) = 6.8, 1H; CHH), 1.53 – 1.37 (m, 2H; CH2), 1.27 – 1.12 (m, 2H; CH2), 0.71 (t, 3J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 165.1 (COPh), 137.9, 137.2 (2 x Ar-C), 133.0 (Ar-CH), 129.9 (Ar-C), 129.8, 129.0, 128.3, 128.1, 128.0, 127.5, 126.0 (14 x Ar-CH, overlapping peaks), 101.8 (C-1), 101.3 (CPh), 81.7 (C-4), 77.9 (C-3), 73.9 (C2HPh), 73.5 (C-2), 70.0 (C2H), 68.8 (C-6), 66.3 (C-5), 31.4 (C2H), 18.8 (C2H), 13.5 (CH2); IR (film) cm⁻¹: 3493, 3065, 2958, 2875, 1498, 1457, 1374, 1274, 1180, 1101, 1085, 1051, 981, 965, 909, 920, 696; ESI-HRMS calcd for C31H38O7 536.2648, found m/z 536.2643 [M+NH₄]⁺.

![Butyl 2-Ο-benzoyl-3-Ο-benzyl-4,6-Ο-benzylidene-β-D-glucopyranoside (85)](image)

**Butyl 2-Ο-benzoyl-3-Ο-benzyl-4,6-Ο-benzylidene-β-D-glucopyranoside (85)**

To a solution of 83 (1 g, 2.4 mmol) was subjected to the conditions outlined in general procedure 1, using benzoyl chloride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 9:1) gave 85 (1.0 g, 80%) as a white solid; [α]D -33.3. (c 1.6, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 7.98 (d, 3J (H,H) = 7.6, 2H; Ar-H), 7.56 (t, 3J (H,H) = 7.4, 1H; Ar-H), 7.50 – 7.39 (m, 3H; Ar-H), 7.35 – 7.26 (m, 3H; Ar-H), 7.20 – 7.05 (m, 4H; Ar-H), 5.58 (apt. t, 3J (H,H) = 9.4, 1H), 5.47 (s, 1H; CHHPh), 4.82 (d, 2J (H,H) = -11.5, 1H; CHHPh), 4.71 – 4.63 (m, 1H; CHHPh, H-1, overlapping peaks), 4.38 (dd, 2J (H,H) = -10.5, 3J (H,H) = 4.9, 1H; H-6a), 3.98 (dt, 2J (H,H) = -9.5, 3J (H,H) = 6.5, 1H; CHH), 3.81 (apt. t, 3J (H,H) = 10.3,
Butyl 2-O-benzoyl-4,6,3-tri-O-acetyl-β-D-glucopyranoside (86β)

84 (0.5 g, 0.96 mmol) was taken up in CH₂Cl₂/MeOH (1:1, 20 mL) and placed under a N₂ atmosphere before adding catalytic 20% Pd-C. H₂ gas was then bubbled through the system and the resulting mixture was stirred overnight under an atmosphere of H₂ (balloon). The H₂ atmosphere was then replaced with N₂, filtered and solvent was evaporated under diminished pressure. The resulting residue was taken up in pyridine (5 mL) and cooled using an ice bath. To this was added Ac₂O (0.225 mL, 2.4 mmol) and the solution was stirred overnight before being diluted with EtOAc (30 mL), washed twice with 1M HCl (50 mL), satd aq NaHCO₃ (50 mL), brine (50 mL), dried over Na₂SO₄, filtered and the solvent was removed under diminished pressure. Flash chromatography of the residue (cyclohexane-EtOAc 7:3) gave 86β (0.41 g, 91%) as a white solid; [α]D -9.5 (c 2.5 CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃); δ 8.07 – 7.91 (m, 2H; Ar-H), 7.65 – 7.53 (m, 1H; Ar-H), 7.50 – 7.39 (m, 1H; Ar-H), 5.40 (apt. t, ³J (H,H) = 9.6 Hz, 1H; H-3), 5.26 (dd, ³J (H,H) = 9.8, 7.9 Hz, 1H; H-2), 5.17 (apt. t, ³J (H,H) = 9.7 Hz, 1H; H-4), 4.63 (d, ³J (H,H) = 7.9 Hz, 1H; H-1), 4.31 (dd, ²J (H,H) = -12.2, ³J (H,H) = 4.8 Hz, 1H; H6a), 4.18 (dd, ²J (H,H) = -12.2, ³J (H,H) = 2.5 Hz, 1H; H-6b), 3.88 (dt, ²J (H,H) = -9.7, ³J (H,H) = 6.3 Hz, 1H; CHH), 3.77 (dd, J = 10.0, 4.8, 2.5 Hz, 1H; H-5), 3.49 (dt, ²J (H,H) = 9.7, ³J (H,H) = 6.7 Hz, 1H; CHH), 2.11 (s, 3H; COCH₃), 2.04 (s, 3H; COCH₃), 1.93 (s, 3H; COCH₃), 1.56 – 1.41 (m, 2H; CH₂), 1.31 – 1.14 (m, 2H; CH₂), 0.74 (t, ³J (H,H) = 7.4 Hz, 3H; CH₃); ¹³C NMR (126 MHz, CDCl₃); δ 170.7, 170.3, 169.4 (3 x COCH₃), 165.0 (COPh), 133.3, 129.7 (Ar-CH, overlapping peaks), 129.4 (Ar-C), 128.4 (Ar-CH), 144
Experimental data

101.1 (C-1), 72.7 (C-3), 71.9 (C-5), 71.7 (C-2), 70.0 (CH₂), 68.6 (C-4), 62.1 (C-6), 31.3 (CH₂), 20.8, 20.6, 20.6 (3 x COCH₃), 18.8 (CH₂), 13.5 (CH₃); IR (film) cm⁻¹: 2961, 1746, 1237, 1029, 715, 612; ESI-HRMS calcd for C₂₃H₄₃O₈N 484.2183, found m/z 484.2185 [M+NH₄]^+.

**Butyl 2,4,6-tri-O-acetyl-3-O-benzoyl-β-D-glucopyranoside (87β)**

Prepared using the procedure previously described to prepare compound 86β starting with 85 (0.5 g, 0.96 mmol) to give 87β (0.39 g, 87%) as a viscous oil; [α]D 27.22 (c 1.2, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.04 – 7.83 (m, 2H; Ar-H), 7.60 – 7.52 (m, 1H; Ar-H), 7.43 (apt. t, ³J (H,H) = 7.8, 2H; Ar-H), 5.47 (d, ³J (H,H) = 9.6, 1H; H-3), 5.26 (apt.t, ³J (H,H) = 9.8, 1H; H-4), 5.15 (dd, ³J (H,H) = 9.8, 8.0, 1H; H-2), 4.58 (d, ³J (H,H) = 8.0, 1H; H-1), 4.30 (dd, ³J (H,H) = -12.3, ³J (H,H) = 4.8, 1H; H-6a), 4.17 (dd, ³J (H,H) = -12.3, ³J (H,H) = 2.4, 1H; H-6b), 3.90 (dt, ³J (H,H) = -9.7, ³J (H,H) = 6.3, 1H; CHH), 3.78 (ddd, ³J (H,H) = 9.9, 4.8, 2.5, 1H; H-5), 3.52 (dt, ³J (H,H) = -9.6, ³J (H,H) = 6.8, 1H; CHH), 2.10 (s, 3H; COCH₃), 1.95 (s, 3H; COCH₃), 1.92 (s, 3H; COCH₃), 1.64 – 1.48 (m, 2H; CH₂), 1.44 – 1.26 (m, 2H; CH₂), 0.91 (t, ³J (H,H) = 7.4, 3H; CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 170.7, 169.3, 169.2 (3 x COCH₃), 165.9 (COPh), 133.5, 129.8 (3 x Ar-CH, overlapping peaks), 128.9 (Ar-C), 128.5 (Ar-CH, overlapping peaks), 100.9 (C-1), 73.3 (C-3), 71.8 (C-5), 71.3 (C-2), 69.9 (CH₂), 68.4 (C-4), 62.0 (C-6), 31.4 (CH₂), 20.8, 20.6, 20.5 (3 x COCH₃), 18.9 (CH₂), 13.7 (CH₃). IR (film) cm⁻¹: 2962, 1742, 1267, 1092, 1028, 896, 708, 522; ESI-HRMS calcd for C₂₃H₃₀O₁₀Na 489.1737, found m/z 489.1741 [M+Na]^+.

**Butyl 2,3-di-O-acetyl-4,6-di-O-benzoyl-β-D-glucopyranoside (88β)**

79 (0.5g, 1.22 mmole) was subjected to the conditions outlined in general procedure 2, using benzoyle chloride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 7:3) gave 88β (0.40 g, 62%) as a foam; [α]D 11.7 (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.01 – 7.90 (m, 4H; Ar-H), 7.43 – 7.37 (m, 2H; Ar-H), 7.33 (d, ³J (H,H) = 7.8, 2H; Ar-H), 5.42 (d, ³J (H,H) = 9.6, 1H; H-3), 5.18 (dd, ³J (H,H) = 9.8, 8.0, 1H; H-2), 4.62 (d, ³J (H,H) = 8.0, 1H; H-1), 4.34 (dd, ³J (H,H) = -12.3, ³J (H,H) = 4.8, 1H; H-6a), 4.19 (dd, ³J (H,H) = -12.3, ³J (H,H) = 2.4, 1H; H-6b), 3.86 (dt, ³J (H,H) = -9.7, ³J (H,H) = 6.3, 1H; CHH), 3.78 (ddd, ³J (H,H) = 9.9, 4.8, 2.5, 1H; H-5), 3.52 (dt, ³J (H,H) = -9.6, ³J (H,H) = 6.8, 1H; CHH), 2.10 (s, 3H; COCH₃), 1.95 (s, 3H; COCH₃), 1.92 (s, 3H; COCH₃), 1.64 – 1.48 (m, 2H; CH₂), 1.44 – 1.26 (m, 2H; CH₂), 0.91 (t, ³J (H,H) = 7.4, 3H; CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 170.7, 169.3, 169.2 (3 x COCH₃), 165.9 (COPh), 133.5, 129.8 (3 x Ar-CH, overlapping peaks), 128.9 (Ar-C), 128.5 (Ar-CH, overlapping peaks), 100.9 (C-1), 73.3 (C-3), 71.8 (C-5), 71.3 (C-2), 69.9 (CH₂), 68.4 (C-4), 62.0 (C-6), 31.4 (CH₂), 20.8, 20.6, 20.5 (3 x COCH₃), 18.9 (CH₂), 13.7 (CH₃). IR (film) cm⁻¹: 2962, 1742, 1267, 1092, 1028, 896, 708, 522; ESI-HRMS calcd for C₂₃H₃₀O₁₀Na 489.1737, found m/z 489.1741 [M+Na]^+. 145
Experimental data

7.64 – 7.50 (m, 2H; Ar-H), 7.44 – 7.35 (m, 4H; Ar-H), 5.51 – 5.41 (m, 2H; H-3,H-4, overlapping peaks), 5.15 – 5.00 (m, 1H; H-3), 4.61 (d, \( ^3J(H,H) = 8.0, 1H; H-1 \)), 4.56 (dd, \( ^2J(H,H) = -12.1, ^2J(H,H) = 3.3, 1H; H-6a \)), 4.42 (dd, \( ^2J(H,H) = -12.1, ^2J(H,H) = 5.2, 1H; H-6b \)), 4.04 – 3.94 (m, 1H; H-5), 3.88 (dt, \( ^2J(H,H) = -9.7, ^2J(H,H) = 6.3, 1H; CH(H) \)), 3.51 (dt, \( ^2J(H,H) = -9.6, ^2J(H,H) = 6.7, 1H; CHH \)), 2.06 (s, 3H; COCH3), 1.91 (s, 3H; COCH3), 1.61 – 1.53 (m, 2H; CH2), 1.44 – 1.26 (m, 2H; CH2), 0.89 (t, \( ^3J(H,H) = 7.4, 3H; CH3 \)); \(^{13}\)C NMR (126 MHz, CDCl3): \( \delta \) 170.2, 169.4 (2 x COCH3), 166.1, 165.1 (2 x COPh), 133.5, 133.1, 129.8, 129.7 (6 x Ar-CH, overlapping peaks), 129.6, 128.8 (2 x Ar-C), 128.5, 128.3 (4 x Ar-CH, overlapping peaks), 100.9 (C-1), 72.6 (C-3), 71.9 (C-5), 71.5 (C-2), 69.9 (CH2), 69.7 (C-4), 63.1 (C-6), 31.4 (CH2), 20.7, 20.5 (2 x COCH3), 18.9 (CH2), 13.7 (CH3). IR (film) cm\(^{-1}\): 2967, 1754, 1277, 1213, 1071, 764, 706; ESI-HRMS calcd for C\(_{28}\)H\(_{38}\)O\(_{10}\)N 546.2339, found \( m/z \) 546.2343 [M+NH\(_4\)]\(^+\).

\[ \text{Butyl 2,3-di-O-benzyl-4,6-O-benzylidene-\( \beta \)-D-glucopyranoside (89)} \]

78 (1.22 g, 5.16 mmole) was subjected to the conditions outlined in general procedure 1, using benzoyl as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 8:2) gave 89 (2.12 g, 77%) as a foam; \([\alpha]\)\(_D\) 39.6 (c 0.6, CH\(_2\)Cl\(_2\); \(^1\)H NMR (500 MHz, CDCl3): \( \delta \) 7.96 (d, \( ^3J(H,H) = 7.6, 3H; Ar-H \)), 7.49 (dd, \( ^3J(H,H) = 12.9, 7.1, 2H; Ar-H \)), 7.44 – 7.28 (m, 10H; Ar-H), 5.78 (apt. t, \( ^3J(H,H) = 9.6, 1H; H-3 \)), 5.55 (s, 1H; CHPh), 5.49 – 5.43 (m, 1H; H-2), 4.79 (d, \( ^3J(H,H) = 7.8, 1H; H-1 \)), 4.44 (dd, \( ^2J(H,H) = -10.6, ^2J(H,H) = 4.9, 1H; H-6a \)), 3.97 – 3.83 (m, 3H; H-6b, H-4, CHH), 3.70 (td, \( ^2J(H,H) = 9.7, 4.9, 1H; H-5 \)), 3.53 (dt, \( ^2J(H,H) = -9.7, ^2J(H,H) = 6.7, 1H; CHH \)), 1.49 – 1.42 (m, 1H; CH2), 1.33 – 1.17 (m, 2H; CH2), 0.74 (t, \( ^3J(H,H) = 7.4, 3H; CH3 \)); \(^{13}\)C NMR (126 MHz, CDCl3): \( \delta \) 165.6, 165.2 (2 x COPh), 136.8, 133.1, 133.0, 129.8, 129.7 (7 x Ar-CH, overlapping peaks), 129.4, 129.0, (3 x Ar-C, overlapping peaks), 128.3, 128.2, 126.1 (8x Ar-CH, overlapping peaks), 101.8 (C-1), 101.4 (CHPh), 78.9 (C-4), 72.5 (C-2), 72.1 (C-3), 70.2 (CH2), 68.7 (C-6), 66.6 (C-5), 31.4 (CH2), 18.8 (CH2), 13.5 (CH3). IR (film) cm\(^{-1}\): 336, 2966, 2880, 1733, 1717, 1451, 1290, 1259, 1092, 1071, 1028, 987, 954,

Butyl 2,3-di-O-benzoyl-4,6-di-O-acetyl-β-D-glucopyranoside (91β)

To a solution of 89 (2.0 g, 3.76 mmole) in CH₂Cl₂/MeOH (1:1, 10 mL) was added p-TsOH·H₂O (0.71 g, 3.76 mmol) and the reaction was stirred at room temperature until the starting material had been consumed, at which point the reaction was neutralised by the addition of triethylamine (0.75 mL, 5.6 mmole). The resulting solution was evaporated to dryness and the residue was taken up in pyridine (10 mL) and cooled using an ice bath. To this was added Ac₂O (1.3 mL, 15.04 mmol) and the reaction was allowed to attain room temperature and stir over night before being diluted with diluted with EtOAc (30 mL), washed twice with 1M HCl (50 mL), satd aq NaHCO₃ (50 mL), brine (50 mL), dried over Na₂SO₄, filtered and solvent was removed under diminished pressure. The resulting residue was purified by flash chromatography (cyclohexane-EtOAc 6:4) to give 91β (1.03 g, 52 %) as a white solid; [α]D₂.7 (c 0.2, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 7.92 (dd, 3J (H,H) = 12.6, 7.7, 4H; Ar-H), 7.50 (td, 3J (H,H) = 7.3, 4.1, 2H; Ar-H), 7.37 (q, 3J (H,H) = 7.5, 4H; Ar-H), 5.65 (apt. t, 3J (H,H) = 9.7, 1H; H-3), 5.53 – 5.37 (m, 1H; H-2), 5.34 (apt. t, 3J (H,H) = 9.7, 1H; H-3), 4.71 (d, 3J (H,H) = 7.9, 1H; H-1), 4.34 (dd, 3J (H,H) = -12.4, 3J (H,H) = 4.5, 1H; H-6a), 4.21 (dd, 3J (H,H) = -12.3, 3J (H,H) = 2.5, 1H; H-6b), 3.96 – 3.77 (m, 2H; H-5, CHH, overlapping peaks), 3.51 (dt, 3J (H,H) = -9.7, 3J (H,H) = 6.7, 1H; CHH), 2.12 (s, 3H; COCH₃), 1.94 (s, 3H; COCH₃), 1.49 (ddd, 3J (H,H) = 21.9, 10.6, 6.4, 2H; CH₂), 1.32 – 1.02 (m, 2H; CH₂), 0.74 (t, 3J (H,H) = 7.4, 3H; CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 170.7, 169.4 (2x COCH₃), 165.8, 165.0 (2 x COPh), 133.3, 133.1, 129.8, 129.7 (6 x Ar-CH, overlapping peaks), 129.4, 128.8 (2 x Ar-C), 128.4, 128.3 (4 x Ar-CH, overlapping peaks), 101.2 (C-1), 73.1 (C-3), 71.9 (C-4), 71.7 (C-5), 70.0 (CH₂), 68.6 (C-4), 62.1 (C-6), 31.3 (CH₂), 20.8, 20.5 (2 x COCH₃), 18.8 (CH₂), 13.5 (CH₃); IR (film) cm⁻¹: 2965, 1721, 1369, 1277, 1089, 1055, 1028, 973, 707, 617; ESI-HRMS calcd for C₂₈H₅₆O₁₀N 546.2339, found m/z 546.2337[M+NH₄]⁺.
Butyl 2-O-benzyl-3,4,6-tri-O-benzoyl-β-D-glucopyranoside (94)

To a solution of 82 (1.7 g, 4.10 mmol) in CH₂Cl₂/MeOH (1:1, 20 mL) was added p-TsOH.H₂O (0.78 g, 4.10 mmol) and the reaction was stirred at room temperature until the starting material had been consumed, at which point the reaction was neutralised by the addition of triethylamine (0.7 mL, 4.92 mmol). The resulting solution was evaporated to dryness and the residue was taken up in pyridine and cooled using an ice bath. To this was added BzCl (0.95 mL, 8.20 mmol) and the reaction was allowed to attain room temperature and stir overnight before being diluted with dilute with EtOAc (50 mL), washed twice with 1M HCl (100 mL), satd aq NaHCO₃ (100 mL), brine (100 mL), dried over Na₂SO₄, filtered and solvent was removed under diminished pressure. The resulting residue was purified via flash chromatography (cyclohexane-EtOAc 8:3) to give 94 (1.60 g, 61%) as a foam.

δ 8.01 – 7.94 (m, 2H; Ar-H), 7.59 – 7.43 (m, 3H; Ar-H), 7.34 (dt, J(H,H) = 25.1, 7.9, 6H; Ar-H), 7.19 – 7.03 (m, 5H; Ar-H), 7.05 (d, J = 8.9, 1H; H-1), 4.83 (pH, δ = 11.7, 1H; CH₂Ph), 4.67 (dd, J(H,H) = 11.7, 1H; CH₃), 4.56 (dd, J(H,H) = 12.0, 3J(H,H) = 5.7, 1H; H-6b), 4.05 – 3.95 (m, 2H; H-5, CH₃, overlapping peaks), 3.67 – 3.56 (m, 2H; CH₂, overlapping peaks), 1.74 – 1.59 (m, 2H; CH₂), 1.50 – 1.37 (m, 2H; CH₂), 0.94 (t, J(H,H) = 7.4, 3H; CH₃), 13C NMR (126 MHz, CDCl₃): δ 166.1, 165.7, 165.4 (3 x COPh), 137.6 (Ar-C), 133.3, 133.0, 129.8, 129.8, 129.7 (9 x Ar-CH, overlapping peaks), 129.5, 128.9, (3 x Ar-C, overlapping peaks), 128.3, 128.2, 128.1, 127.6 (11 x Ar-CH, overlapping peaks), 103.8 (C-1), 78.5 (C-4), 74.1 (CH₂Ph), 73.9 (C-3), 71.8 (C-5), 70.1 (C-2), 70.0 (CH₂), 63.5 (C-6), 31.7 (CH₂), 19.2 (CH₂), 13.8 (CH₃); IR (film) cm⁻¹: 3341, 2974, 2876, 1724, 1263, 1117, 1091, 1068, 1028, 705 ESI-HRMS calcd for C₃₈H₃₈O₉Na 661.2414, found m/z 661.2408 [M+Na⁺].
Butyl 2,4,6-tri-O-benzyol-3-O-benzyl- β-D-glucopyranoside (95β)

Prepared using the procedure for the preparation of compound 94, starting from 82 (2.0 g, 4.82 mmol) giving 95β (1.66 g, 54%) as a foam; [α]D 6.1 (c 0.3, CH₂Cl₂); 1H NMR (500 MHz, CDCl₃): δ 8.05 – 7.97 (m, 2H; Ar-H), 7.60 – 7.55 (m, 4H; Ar-H), 7.54 – 7.50 (m, 2H; Ar-H), 7.47 – 7.44 (m, 1H; Ar-H), 7.44 – 7.40 (m, 2H; Ar-H), 7.37 (t, 3J (H,H) = 7.7, 2H; Ar-H), 7.07 – 7.01 (m, 1H; Ar-H), 6.98 (m, 4H; Ar-H), 5.57 (apt. t, 3J (H,H) = 9.5, 1H; H-4), 5.43 – 5.33 (m, 1H; H-2), 4.67 (d, 3J (H,H) = 7.8, 1H; H-1), 4.62 – 4.55 (m, 3H; H-6a, CH₂Ph, overlapping peaks), 4.42 (dd, 2J (H,H) = -12.0, 3J (H,H) = 5.5, 1H; H-6b), 4.07 (apt.t, 2J (H,H) = 9.1, 1H; H-3), 3.99 (dd, 3J (H,H) = 9.3, 5.5, 3.4, 1H; H-5), 3.86 (dt, 2J (H,H) = -9.8, 3J (H,H) = 6.7, 1H; CH₃H), 3.48 (dt, 2J (H,H) = -9.8, 3J (H,H) = 6.7, 1H; CH₂H), 0.72 (t, 3J (H,H) = 7.5, 1H; CH₃₃); 13C NMR (126 MHz, CDCl₃): δ 166.2, 165.0, 164.9 (COph), 137.2 (Ar-C), 133.4, 133.1, 133.0 (3 x Ar-CH), 129.8 (Ar-C, 2 x Ar-CH, overlapping peaks), 129.7, 129.7 (Ar-C, 4 x Ar-CH, overlapping peaks) 129.3 (Ar-C), 128.4, 128.3, 128.1, 128.0, 127.6 (11 x Ar-CH, overlapping peaks), 101.2 (C-1), 79.4 (C-3), 73.8 (CH₂Ph), 73.5 (C-2), 72.1 (C-5), 71.2 (C-4), 69.7 (CH₃), 63.5 (C-6), 31.4 (CH₂), 18.9(CH₃), 13.5(CH₃); IR (film) cm⁻¹: 3336, 2960, 2875, 1724, 1260, 1118, 1090, 1065, 1026, 703; ESI-HRMS calcd for C₃₈H₅₆O₇Na 661.2414, found m/z 661.2435 [M+Na]+.

Butyl 2-O-acetyl-3,4,6-tri-O-benzyol- β-D-glucopyranoside (98β)

94 (1.5g, 2.35 mmol) was subjected to the conditions outlined in general procedure 2, using acetic anhydride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 7:3) gave 98β (0.81 g, 59%) as a foam; [α]D 5.2 (c 0.1, CH₂Cl₂); 1H NMR (500 MHz, CDCl₃): δ 8.00 (dd, 3J (H,H) =8.1, 1.4, 2H; Ar-H), 7.89 (td, 3J (H,H) =8.1, 1.4, 4H; Ar-H), 7.57 – 7.45 (m, 3H; Ar-H), 7.42 – 7.30 (m, 7H; Ar-H), 5.70 (apt. t, 3J (H,H) = 9.6, 1H; H-3), 5.59 (apt. t, 3J (H,H) = 9.7, 1H; H-4), 5.25 (dd, 3J (H,H) = 9.7, 7.9, 1H; H-2), 4.70 (d, 2J (H,H) = 7.9, 1H; H-1), 4.60 (dd, 2J (H,H) =12.1, 3J (H,H) =3.3, 1H; H-6a), 4.46 (dd, 2J (H,H) =12.1, 3J (H,H) = 5.3, 1H; H-6b), 4.07 (dd, 3J (H,H) = 9.8, 5.3, 3.3, 1H; H-5), 3.91 (dt, 2J (H,H) = -9.6, 3J (H,H) = 6.4, 1H; CH₃H), 3.55 (dt, 2J (H,H) = -9.6, 3J (H,H) = 6.7, 1H;
CHH), 1.97 (s, 3H; COCH₃), 1.67 – 1.49 (m, 2H; CH₂), 1.44 – 1.28 (m, 2H; CH₂), 0.90 (t, 3J (H,H) = 7.4, 3H; CH₂O); ¹³C NMR (126 MHz, CDCl₃): δ 169.3 (COCH₃), 166.1, 165.8, 165.2 (3 x COPh), 133.4, 133.3, 133.1, 129.8, 129.7 (9 x Ar-CH, overlapping peak), 129.6, 128.9, 128.8 (3 x Ar-C), 128.4, 128.3 (6 x Ar-CH, overlapping peaks), 101.0 (C-1), 73.1 (C-3), 72.0 (C-5), 71.5 (C-2), 69.9 (C-4), 69.8 (CH₂), 63.2 (C-6), 31.4 (CH₂), 20.6 (COCH₃), 19.0 (CH₂), 13.7 (CH₃); IR (film) cm⁻¹: 2963, 1714, 1265, 1218, 1091, 1026, 706; ESI-HRMS calcd for C₃₃H₃₈O₁₀N 608.2496, found m/z 608.2490 [M+NH₄]⁺.

Preparation of compound 99β: Butyl 2,4,6-tri-O-benzoyl-3-O-acetyl-β-D-glucopyranoside (99β)

95 (1.5g, 2.35 mmol) was subjected to the conditions outlined in general procedure 2, using acetic anhydride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 7:3) gave 98β (0.97 g, 72%) as a foam; [α]D12.71 (c 0.2, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.04 – 7.91 (m, 5H; Ar-H), 7.64 – 7.47 (m, 4H; Ar-H), 7.51 – 7.27 (m, 6H; Ar-H), 5.65 (apt. t, 3J (H,H) = 9.6, 1H; H-3), 5.51 (apt. t, 3J (H,H) = 9.7, 1H; H-4), 5.36 (dd, 3J (H,H) = 9.7, 7.9, 1H; H-2), 4.74 (d, 3J (H,H) = 7.9, 1H; H-1), 4.60 (dd, 3J (H,H) = -12.0, 3J (H,H) = 3.3, 1H; H-6a), 4.46 (dd, 3J (H,H) = -12.1, 3J (H,H) = 5.3, 1H; H-6b), 4.06 (ddd, 3J (H,H) = 10.0, 5.2, 3.3, 1H; H-5), 3.88 (dt, 3J (H,H) = -9.6, 3J (H,H) = 6.3, 1H; CHH), 3.51 (dt, 3J (H,H) = -9.8, 3J (H,H) = 6.7, 1H; CHH), 1.83 (s, 3H; COCH₃), 1.59 – 1.39 (m, 2H; CH₂), 1.34 – 1.16 (m, 2H; CH₂), 0.74 (t, 3J (H,H) = 7.4, 3H; CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 170.1 (COCH₃), 166.1, 165.2, 165.0 (3 x COPh), 133.5, 133.3, 133.1, 129.8, 129.7 (9 x Ar-CH, overlapping peaks), 129.6 129.4, 128.8 (3 x Ar-C), 128.5, 128.4, 128.3 (6 x Ar-CH₂, overlapping peaks), 101.2 (C-1), 72.4 (C-3), 72.1 (C-5), 71.9 (C-2), 70.0 (CH₂), 69.8 (C-4), 63.2 (C-6), 31.3 (CH₂), 20.5 (COCH₃), 18.8 (CH₂), 13.5 (CH₃); IR (film) cm⁻¹: 2960, 1716, 1452, 1263, 1215, 1090, 1068, 1026, 974, 706; ESI-HRMS calcd for C₃₃H₃₈O₁₀N 608.2496, found m/z 608.2495 [M+NH₄]⁺.
To a solution of \textbf{89} (1.5 g, 2.8 mmol) was subjected to the conditions outlined in general procedure 2, using acetic anhydride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 8:2) gave compounds \textbf{102β} (0.4 g, 24\%) and \textbf{103β} (0.8 g, 48\%);

**Butyl 2,3,4-tri-O-benzoyl-6-O-acetyl-β-D-glucopyranoside (102β)**

\([\alpha]_D\) 15.9 (c 0.2, \(\text{CH}_2\text{Cl}_2\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.95 (dd, \(^3\)J (H,H) = 7.8, 1.7, 2H; Ar-H), 7.91 (dd, \(^3\)J (H,H) = 8.0, 1.5, 2H; Ar-H), 7.86 – 7.80 (m, 2H; Ar-H), 7.55 – 7.48 (m, 2H; Ar-H), 7.45 – 7.40 (m, 1H; Ar-H), 7.37 (td, \(^3\)J (H,H) = 7.7, 4.5, 5H; Ar-H), 7.28 (apt. t, \(^3\)J (H,H) = 7.9, 2H; Ar-H), 5.86 (apt. t, \(^3\)J (H,H) = 9.6, 1H; H-3), 5.58 (apt. t, \(^3\)J (H,H) = 9.7, 1H; H-4), 5.49 (dd, \(^3\)J (H,H) = 9.7, 7.8, 1H; H-2), 4.79 (d, \(^3\)J (H,H) = 7.8, 1H; H-1), 4.33 (dd, \(^2\)J (H,H) = -12.1, \(^3\)J (H,H) = 4.9, 1H; H-6a), 4.27 (dd, \(^2\)J (H,H) = 12.1, \(^3\)J (H,H) = 3.1, 1H; H-6b), 4.00 (ddd, \(^3\)J (H,H) = 9.8, 5.0, 3.1, 1H; H-5), 3.93 (dt, \(^2\)J (H,H) = -9.7, \(^3\)J (H,H) = 6.4, 1H; CHH), 3.55 (dt, \(^2\)J (H,H) = -9.7, \(^3\)J (H,H) = 6.7, 1H; CHH), 2.04 (s, 2H; COCH\(_3\)), 1.59 – 1.45 (m, 2H; CH\(_2\)), 1.32 – 1.17 (m, 2H; CH\(_2\)), 0.76 (t, \(^3\)J (H,H) = 7.4, 3H; CH\(_3\)); \(^13\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 170.6 (COCH\(_3\)), 165.8, 165.2 (3 x COPh, overlapping peaks), 133.4, 133.2, 133.1, 129.8, 129.7, 129.7 (9 x Ar-CH, overlapping peaks), 129.4, 128.8 (3 x Ar-C, overlapping peaks), 128.4, 128.3, 128.3 (6 x Ar-CH, overlapping peaks), 101.3 (C-1), 72.9 (C-3), 72.0 (C-5), 71.9 (C-2), 70.1 (CH\(_2\)), 69.5 (C-4), 62.6 (C-6), 31.4 (CH\(_2\)), 20.7 (COCH\(_3\)). 18.9 (CH\(_2\)), 13.6 (CH\(_3\)); IR (film) cm\(^{-1}\): 2945, 1730, 1226, 1067, 1025, 705; ESI-HRMS calcd for C\(_{33}\)H\(_{34}\)O\(_{10}\)Na 613.2050, found \(m/z\) 613.2048 [M+Na]\(^{+}\).

**Butyl 2,3,6-tri-O-benzoyl-4-O-acetyl-β-D-glucopyranoside (103β)**

\([\alpha]_D\) 9.4 (c 0.4, \(\text{CH}_2\text{Cl}_2\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.16 – 8.01 (m, 2H; Ar-H), 7.93 (ddd, \(^3\)J (H,H) = 13.6, 8.4, 1.4, 4H; Ar-H), 7.67 – 7.55 (m, 1H; Ar-H), 7.56 – 7.44 (m, 4H; Ar-H), 7.44 – 7.30 (m, 4H; Ar-H), 5.69 (apt. t, \(^3\)J (H,H) = 9.6, 1H; H-
Experimental data

3H; C (dp, [H,H] = 12.1, 3J (H,H) = 2.7, 1H; H-6a), 4.46 (dd, 2J (H,H) = -12.1, 3J (H,H) = 5.1, 1H; H-6b), 4.01 (dd, 3J (H,H) = 10.0, 5.1, 2.8, 1H; H-5), 3.89 (dt, 2J (H,H) = -9.7, 3J (H,H) = 6.3, 1H; CHH), 3.52 (dt, 2J (H,H) = -9.7, 3J (H,H) = 6.7, 1H; CHH), 1.93 (s, 3H; COCH3), 1.58 – 1.40 (m, 2H; CH2), 1.43 – 1.12 (m, 2H; CH2), 0.73 (t, 3J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 169.4 (COCH3), 166.2, 165.8, 165.0 (3 x COPh), 133.3, 133.2, 133.1, 129.8, 129.7 (9 x Ar-CH, overlapping peaks), 129.6, 129.4, 128.9 (3 x Ar-C), 128.4, 128.4, 128.3 (6 x Ar-CH, overlapping peaks), 101.2 (C-1), 73.2 (C-3), 72.0 (C-5), 71.8 (C-2), 70.0 (CH2) 69.0 (C-4), 62.9 (C-6), 31.3 (CH2), 20.6 (COCH3), 18.8 (CH2), 13.5 (CH3); IR (film) cm⁻¹: 2960, 1730, 1450, 1286, 1101, 981, 661; ESI-HRMS calcld for C33H38O10N 608.2496, found m/z 608.2496 [M+NH₄]⁺.

Butyl 2-propionyl-3,4,6-tri-O-benzoyl-β-D-glucopyranoside (105β)

94 (0.25 g, 0.39 mmol) was subjected to the conditions outlined in general procedure 3, using propionyl chloride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 7:2) gave 105β (0.175 g, 74%) as a foam; [α]D 37.8 (c 0.1, CH2C2); 1H NMR (500 MHz, CDCl3): δ 8.00 (d, 3J (H,H) = 7.7, 2H; Ar-H), 7.90 (dd, 3J (H,H) = 7.5, 2.0, 4H; Ar-H), 7.51 (dt, 3J (H,H) = 21.8, 7.5, 3H; Ar-H), 7.45 – 7.32 (m, 6H; Ar-H), 5.71 (apt. t, 7J (H,H) = 9.7, 1H; H-3), 5.60 (apt. t, 7J (H,H) = 9.7, 1H; H-4), 5.38 – 5.22 (m, 1H; H-2), 4.71 (d, 3J (H,H) = 7.9, 1H; H-1), 4.60 (dd, 2J (H,H) = -12.2, 3J (H,H) = 3.3, 1H; H-6a), 4.47 (dd, 2J (H,H) = -12.2, 3J (H,H) = 5.2, 1H; H-6b), 4.08 (dd, 3J (H,H) = 9.3, 5.3, 3.4, 1H; H-5), 3.91 (dt, 2J (H,H) = -9.6, 3J (H,H) = 6.4, 1H; CHH), 3.55 (dt, 2J (H,H) = -9.7, 3J (H,H) = 6.9, 1H; CHH), 2.24 (qd, 3J (H,H) = 7.8, 5.7, 2H, CH2), 1.67 – 1.50 (m, 2H; CH2), 1.35 (dp, J=13.7, 6.8, 2H; CH2), 0.99 (t, 3J (H,H) = 7.6, 3H; CH3), 0.90 (t, 3J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 172.8 (COCH2CH3), 166.1, 165.8, 165.2 (3 x COPh), 133.4, 133.3, 133.1, 129.8, 129.7 (9 x Ar-CH, overlapping peaks), 129.6, 128.9, 128.8 (3 x Ar-C), 128.4, 128.3 (6 x Ar-C, overlapping peaks), 101.0
(C-1), 73.1 (C-3), 72.1 (C-5), 71.3 (C-2), 69.9 (CH2), 69.8 (C-4), 63.2 (C-6), 31.4 (CH2), 27.4 (CH2), 19.0 (CH2), 13.7 (CH3), 9.0 (CH3). ESI-HRMS calcd for C34H35O10Na 627.2206, found m/z 627.2214[M+Na]⁺.

**Butyl 2-O-isobutyryl-3,4,6-tri-O-benzoyl-β-D-glucopyranoside (106β)**

94 (0.25 g, 0.39 mmol) was subjected to the conditions outlined in general procedure 3, using isobutyryl chloride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 7:2) gave 106β (0.195 g, 81%) as a foam; [α]D 2.8 (c 0.2, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.08 – 7.98 (m, 2H; Ar -H), 7.89 (ddd, 3J (H,H) =8.1, 1H; Ar-H), 7.59 – 7.47 (m, 3H; Ar-H), 7.41 – 7.32 (m, 6H; Ar-H), 5.73 (apt. t, 3J (H,H) = 9.7, 1H; H-3), 5.60 (apt. t, 3J (H,H) = 9.7, 1H; H-4), 5.28 (dd, 3J (H,H) = 9.8, 1H; H-2), 4.71 (d, 3J (H,H) = 9.7, 1H; H-1), 4.60 (dd, 2J (H,H) = -12.1, 3J (H,H) = 3.3, 1H; H-6a), 4.48 (dd, 2J (H,H) = -12.0, 3J (H,H) = 5.3, 1H; H-6b), 4.08 (ddd, 3J (H,H) = 5.3, 3J (H,H) = 3.3, 1H; H-5), 3.91 (dt, 2J (H,H) = -9.6, 3J (H,H) = 6.3, 1H; CHH), 3.54 (dt, 2J (H,H) = -9.6, 3J (H,H) = 6.8, 1H; CHH), 2.47 (p, 3J (H,H) = 7.0, 1H; CH(CH3)2), 1.62 – 1.49 (m, 2H; CH2), 1.35 (ddt, 3J (H,H) = 14.1, 8.9, 7.0, 2H; CH2), 1.05 (d, 3J (H,H) = 7.0, 3H; CH3), 0.96 (d, 3J (H,H) = 7.0, 3H; CH3), 0.89 (t, 3J (H,H) = 7.4, 3H; CH3). 13C NMR (126 MHz, CDCl3): δ 175.4 (COCH(CH3)2), 166.1, 165.8, 165.2 (3 x COPh), 133.4, 133.3, 133.0, 129.8, 129.8, 129.7 (9 x Ar-CH, overlapping peaks), 129.6, 128.9, 128.8 (3 x Ar-C), 128.4, 128.3 (6 x Ar-CH, overlapping peaks), 101.1 (C-1), 73.0 (C-3), 72.1 (C-5), 71.0 (C-2), 69.9 (CH2), 69.8 (C-4), 63.3 (C-6), 33.9 (CH(CH3)2), 31.5 (CH2), 19.0 (CH2), 18.7 (2 x CH3, overlapping peaks), 13.7 (CH3); IR (film) cm⁻¹: 33336, 2971, 2933, 2875, 1741, 1727, 1716, 1453, 1273, 1100, 1070, 1049, 1055, 975, 951, 708; ESI-HRMS calcd for C35H38O10Na 641.2363, found m/z 641.2333 [M+Na]⁺.
Butyl 2-O-pivaloyl-3,4,6-tri-O-benzoyl-β-D-glucopyranoside (107β)

94 (0.25 g, 0.39 mmol) was subjected to the conditions outlined in general procedure 3, using trimethyl acetyl chloride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 7:2) gave 106β (0.172 g, 70%) as a foam; [α]₀⁺ 8.43 (c 0.2, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.10 – 7.95 (m, 2H; Ar-H), 7.89 (t, J (H,H) =7.6, 4H; Ar-H), 7.67 – 7.37 (m, 3H; Ar-H), 7.42 – 7.33 (m, 6H; Ar-H), 5.75 (apt. t, J (H,H) =9.7, 1H; H-3), 5.59 (apt. t, J (H,H) =9.7, 1H; H-4), 5.27 (dd, J (H,H) =9.9, 1H; H-2), 4.71 (d, J (H,H) =7.9, 1H; H-1), 4.60 (dd, J (H,H) =12.1, 3J (H,H) =3.3, 1H; H-6a), 4.48 (dd, J (H,H) =12.1, 3J (H,H) =5.3, 1H; H-6b), 4.08 (ddd, J (H,H) =9.2, 5.3, 3.3, 1H; H-5), 3.91 (dt, J (H,H) =-9.6, 3J (H,H) =6.4, 1H; CHH), 3.54 (dt, J (H,H) =-9.7, 3J (H,H) =6.8, 1H; CHH), 1.66 – 1.51 (m, 2H, CH₂), 1.44 – 1.26 (m, 2H; CH₂), 1.05 (s, 9H; 3 x CH₃, overlapping peaks), 0.89 (t, J (H,H) =7.4, 1H; CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 176.6 (COC(CH₃)₃), 166.1, 165.8, 165.2 (3 x COPh), 133.4, 133.3, 133.0, 129.8, 129.7 (9 x Ar-CH, overlapping peaks), 128.9, 128.8 (3 x Ar-C, overlapping peaks), 128.4, 128.3 (6 x Ar-CH, overlapping peaks), 101.2 (C-1), 73.0 (C-3), 72.1 (C-5), 71.0 (C-2), 69.9 (C-4), 69.8 (CH₂), 63.3 (C-6), 38.7 (C(CH₃)₃), 31.5 (CH₂), 26.8 (3 x CH₃, overlapping peaks), 19.0 (CH₂), 13.7 (CH₃); ESI-HRMS calcd for C₃₆H₄₀O₁₀Na 655.2519, found m/z 655.2529 [M+Na]+.

Butyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside (108β)₉₅

76 (0.5 g, 2.11 mmol) was taken up in DMF (10 mL) and cooled using an ice bath. To this was added 60% NaH (0.65 g, 16.93 mmol) and the reaction mixture was stirred for 1 h, at which point Mel (1.05 mL, 16.93 mmol) was added. The resulting suspension was stirred overnight before being diluted with Et₂O (10 mL) washed twice with 1M HCl (20 mL), satd aq NaHCO₃ (20 mL), brine (20 mL), dried over Na₂SO₄, filtered and the solvent was evaporated under diminished pressure. The resulting residue was purified via flash chromatography (cyclohexane-EtOAc 1:1) to give 108β (0.32 g, 53%) as clear oil; [α]₀⁻ -18.7 (c 0.3, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 4.20 (d, J (H,H) =7.5, 1H; H-1), 3.90 (dt, J (H,H) =9.5, 3J (H,H) =6.4, 1H; CHH), 3.65 – 3.59 (m, 4H; H-6a, OCH₃, overlapping peaks) 3.56 (s, 3H; OCH₃), 154
3.54 (dd, $^2J(\text{H}, \text{H}) = 10.7$, $^3J(\text{H}, \text{H}) = 4.9$, 1H; H-6b), 3.51 (s, 3H; OCH$_3$), 3.46 (dt, $^2J(\text{H}, \text{H}) = 9.5$, $^3J(\text{H}, \text{H}) = 6.8$, 1H; CHH), 3.25 (ddd, $^3J(\text{H}, \text{H}) = 9.4$, 4.9, 2.0, 1H; H-5), 3.18 – 3.09 (m, 2H; H-3, H-4, overlapping peaks), 2.97 (td, $^3J(\text{H}, \text{H}) = 7.7$, 1.4, 1H; H-2), 1.65 – 1.51 (m, 2H; CH$_2$), 1.45 – 1.31 (m, 2H; CH$_2$), 0.91 (t, $^3J(\text{H}, \text{H}) = 7.4$, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 103.4 (C-1), 86.4 (C-3), 83.8 (C-2), 79.5 (C-4), 74.6 (C-5), 71.4 (C-6), 69.7 (CH$_2$), 60.8, 60.4, 59.3 (4 x OCH$_3$), 31.7 (C$_2$), 19.2 (CH$_3$), 13.8 (CH$_3$); IR (film) cm$^{-1}$: 3935, 2834, 1461, 1372, 1098; ESI-HRMS calcd for C$_{14}$H$_{28}$O$_6$Na 315.1784, found m/z 345.1791 [M+Na]$^+$.

**Butyl 2-O-benzyl-3,4,6-tri-O-methyl-\(\beta\)-D-glucopyranoside (109)**

92 (1.5 g, 4.6 mmol) was subjected to the procedure used to prepare compound 108. The resulting crude product was purified via flash chromatography (cyclohexane-EtOAc 7:3) to give 109 (1.05 g, 62%) as clear oil; [$\alpha$]$_D$ -4.6 (c 0.1, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.39 – 7.29 (m, 4H; Ar-H), 7.30 – 7.21 (m, 1H; Ar-\(H\)), 4.89 (d, $^2J(\text{H}, \text{H}) = -11.0$, 1H; CHHPh), 4.68 (d, $^2J(\text{H}, \text{H}) = -11.1$, 1H; CHHPh), 4.31 (d, $^3J(\text{H}, \text{H}) = 7.3$, 1H; H-1), 3.93 (dt, $^2J(\text{H}, \text{H}) = -9.5$, $^3J(\text{H}, \text{H}) = 6.4$, 1H; CHH), 3.68 – 3.61 (m, 4H; H-6a, OCH$_3$, overlapping peaks), 3.59 – 3.47 (m, 4H; H-6b, CHH, OCH$_3$, overlapping peaks), 3.40 (s, 3H; OCH$_3$), 3.29 – 3.21 (m, 3H, 3 x CH), 3.14 (dd, $^3J(\text{H}, \text{H}) = 9.8$, 8.3, 1H; CH), 1.69 – 1.56 (m, 2H; CH$_2$), 1.46 – 1.30 (m, 2H; CH$_2$), 0.92 (t, $^3J(\text{H}, \text{H}) = 7.4$, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 138.6 (Ar-C), 128.3, 128.1, 127.6 (5 x Ar-CH, overlapping peaks), 103.5 (C-1), 86.5 (CH), 81.9 (CH), 79.6 (CH), 74.7 (CH$_2$Ph), 74.6 (CH), 71.4 (C-6), 69.7 (CH$_2$), 61.1, 60.4, 59.3 (3 x OCH$_3$), 31.8 (CH$_2$), 19.3 (CH$_2$), 13.9 (CH$_3$); IR (film) cm$^{-1}$: 3961, 2846, 1420, 1381, 1088, 710; ESI-HRMS calcd for C$_{20}$H$_{35}$O$_6$Na 386.2543, found m/z 386.2548[M+NH$_4$]$^+$. 

![Butyl 2-O-benzyl-3,4,6-tri-O-methyl-\(\beta\)-D-glucopyranoside (109)](image-url)
Butyl 2-O-(4-fluorobenzoyl)-3,4,6-tri-O-methyl-β-D-glucopyranoside (111β)

109 (0.15 g, 0.41 mmol) was subjected to the conditions outlined in general procedure 3, using 4-fluorobenzoyl chloride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 6:4) gave 111β (0.121 g, 74%) as a white solid; [α]D -33.7 (c 0.5, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.13 – 8.00 (m, 2H; Ar-H), 7.15 – 7.05 (m, 2H; Ar-H), 5.09 (dd, 3J (H,H) =9.5, 8.0, 1H; H-2), 4.45 (d, 3J (H,H) =7.9, 1H; H-1), 3.85 (dt, 3J (H,H) = -9.7, 3J (H,H) = 6.3, 1H; CHH), 3.67 (dd, 3J (H,H) = -10.7, 3J (H,H) =2.0, 1H; H-6a), 3.61 (dd, 3J (H,H) =10.7, 3J (H,H) =4.7, 1H; H-6b), 3.55 (s, 3H; OCH3) 3.48 (s, 3H; OCH3), 3.45 – 3.36 (m, 6H; OCH3, H-5, H-2, CHH), 3.35 – 3.21 (m, 1H; H-4), 1.43 – 1.33 (m, 2H; CH2), 1.27 – 1.11 (m, 2H; CH2), 0.71 (t, 3J (H,H) =7.4, 3H; CH3). 13C NMR (126 MHz, CDCl3): δ 165.78(d, 1J (C,F) = 254.0; Ar-C-F), 164.2 (COC6H4F) 132.2(d, 3J (C,F) = 9.0; 2 x Ar-CH, overlapping peaks), 126.4 (d, 3J (C,F) =3.1; Ar-C), 115.5 (d, 3J (C,F) =21.9; 2 x Ar-CH, overlapping peaks), 101.0 (C-1), 84.8 (C-3), 79.3 (C-4), 75.1 (C-5), 73.7 (C-2), 71.3 (C-6), 69.4 (CH2), 60.5, 60.3, 59.4 (3 x OCH3), 31.4 (CH2), 18.9 (CH2), 13.6 (CH3); IR (film) cm\(^{-1}\) 3517, 1260, 1088, 1055, 720; ESI-HRMS calcd for C\(_{20}\)H\(_{29}\)O\(_{7}\)FNa 423.1795, found m/z 423.1799 [M+Na]\(^+\).

Butyl 2-O-acetyl-3,4,6-tri-O-methyl-β-D-glucopyranoside (112β)

109 (0.15 g, 0.41 mmol) was subjected to the conditions outlined in general procedure 3, using acetic anhydride as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 6:4) gave 112β (0.106 g, 81%) as a clear oil; [α]D -194 (c 0.6, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 4.84 (dd, 3J (H,H) =9.3, 7.9, 1H; H-2), 4.30 (d, 3J (H,H) =8.0, 1H; H-1), 3.85 (dt, 3J (H,H) =9.7, 3J (H,H) =6.2, 1H; CHH), 3.64 (dd, 3J (H,H) = -10.8, 3J (H,H) = 2.0, 1H; H-6a), 3.57 (dd, 3J
Experimental data

Chapter 5

\[(H,H) = -10.8, \quad ^3J(H,H) = 4.8, \quad 1H; \quad \text{H-6b}, 3.53 \text{ (s, 3H; OCH}_3\text{), 3.51 \text{ (s, 3H; OCH}_3\text{),}}
\]

\[3.45 - 3.39 \text{ (m, 4H; OCH}_3\text{), CHH, overlapping peaks), 3.36 - 3.19 \text{ (m, 3H; H-3, H-4, H-5, overlapping peaks), 2.08 \text{ (s, 3H; COCH}_3\text{), 1.58 - 1.43 \text{ (m, 2H; CH}_2\text{), 1.39 - 1.27 \text{ (m, 2H; CH}_2\text{), 0.88 \text{ (t, } ^3J(H,H) = 7.4, \quad 3H; CH}_3\text{);}}
\]

\[^{13}C \text{ NMR (126 MHz, CDCl}_3\text{: } \delta \quad 169.5 \quad \text{(COCH}_3\text{), 100.9 \quad \text{(C-1), 84.6 \quad \text{(C-3), 79.3 \quad \text{(C-4), 75.0 \quad \text{(C-4), 73.0 \quad \text{(C-2), 71.3 \quad (CH}_2\text{), 69.3 \quad \text{(C-6), 60.4, 60.1, 59.4 \quad (3 x OCH}_3\text{, overlapping peaks), 31.4 \quad \text{(COCH}_3\text{), 20.9 \quad \text{(CH}_2\text{), 19.0 \quad \text{(CH}_2\text{), 13.7 \quad \text{(CH}_3\text{); IR (film) cm}^{-1} \quad 3511, 3256, 2928, 1725, 1268, 1091, 1062, 712, 520; \quad \text{ESI-HRMS calcd for C}_{15}H_{28}O_{7}Na 343.1733, found m/z 343.1741[M+Na]^+}.\]

Butyl 2-O-benzoyl-3,4,6-tri-O-methyl-β-D-glucopyranoside (113β)

109 (0.15 g, 0.41 mmol) was subjected to the conditions outlined in general procedure 3 with benzoyl chloride being used as the acylating reagent. Purification by flash chromatography (cyclohexane-EtOAc 6:4) gave 113β (0.110 g, 70%) as a clear oil; [α]D -23.3 (c 0.1, CH2Cl2); ^1H NMR (500 MHz, CDCl3): \( \delta \quad 8.11 - 7.92 \text{ (m, 2H; Ar-H), 7.57 \quad \text{(tt, } ^3J(H,H) = 7.0, 1.4, 1H; \quad \text{Ar-H), 7.45 \quad \text{(t, } ^3J(H,H) = 7.8, 2H; \quad \text{Ar-H),}}
\]

\[5.12 \quad \text{(dd, } ^3J(H,H) = 9.5, 8.0, 1H; \quad \text{H-2), 4.46 \quad \text{(d, } ^3J(H,H) = 8.0, 1H; \quad \text{H-1), 3.85 \quad \text{(dt, } ^2J(H,H) = -9.7, ^3J(H,H) = 6.3, 1H; \quad \text{CHH), 3.68 \quad \text{(dd, } ^2J(H,H) = -10.7, ^3J(H,H) = 2.0, 1H; \quad \text{H-6a), 3.61 \quad \text{(dd, } ^2J(H,H) = -10.7, ^3J(H,H) = 4.8, 1H; \quad \text{H-6b), 3.55 \quad \text{(s, 3H; OCH}_3\text{),}}
\]

\[3.49 \quad \text{(s, 3H; OCH}_3\text{), 3.47 - 3.37 \text{ (m, 6H; OCH}_3\text{, H-5, H-3, CHH, overlapping peaks), 3.35 - 3.28 \text{ (m, 1H; H-4), 1.51 - 1.34 \text{ (m, 2H; CH}_2\text{), 1.27 - 1.10 \text{ (m, 2H; CH}_2\text{), 0.71 \quad \text{(t, } ^3J(H,H) = 7.4, 3H; \quad \text{CH}_3\text{);}}
\]

\[^{13}C \text{ NMR (126 MHz, CDCl}_3\text{: } \delta \quad 165.2 \quad \text{(COPh), 132.9 \quad \text{(Ar-CH), 132.9 \quad \text{(Ar-C) 129.7, 128.3 \quad (4 x Ar-CH, overlapping peaks), 101.1 \quad \text{(C-1),}}
\]

\[84.9 \quad \text{(C-3), 79.3 \quad \text{(C-4), 75.1 \quad \text{(C-5), 73.7 \quad \text{(C-2), 71.4 \quad \text{(C-6), 69.5 \quad \text{(CH}_2\text{), 60.5, 60.3, 59.4 \quad (3 x OCH}_3\text{), 31.4 \quad \text{(CH}_2\text{), 18.9 \quad \text{(CH}_2\text{), 13.6 \quad \text{(CH}_3\text{); IR (film) cm}^{-1} \quad 3515, 2933, 1726, 1266, 1059, 710, 519; \quad \text{ESI-HRMS calcd for C}_{20}H_{30}O_{7}Na 405.1889, found m/z 405.1892 [M+Na]^+}.\]
Butyl 2-O-pivaloyl-3,4,6-tri-O-methyl-β-D-glucopyranoside (114β)

109 (0.15 g, 0.41 mmol) was subjected to the conditions outlined in general procedure 3, using trimethyl acetyl chloride as the acylating reagent. Purification via flash chromatography (cyclohexane-EtOAc 6:4) gave 114β (0.104 g, 70%) as a waxy solid; [α]D -25.6 (c 0.2, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 4.84 (appt, 3J (H,H) = 8.5, 1H; H-2), 4.31 (d, 3J (H,H) = 8.0, 1H; H-1), 3.83 (dt, 2J (H,H) = 9.4, 3J (H,H) = 6.4, 1H; CHH) 3.64 (dd, 2J (H,H) = -10.7, 3J (H,H) = -10.7, 3J (H,H) = 4.8, 1H; H-6b), 3.53 (s, 3H; OCH3), 3.50 (s, 3H; OCH3), 3.43 – 3.36 (m, 4H; OH3, CHH, overlapping peaks), 3.35 – 3.31 (m, 1H; H-5), 3.30 – 3.20 (m, 2H; H-3, H-4, overlapping peaks), 1.56 – 1.42 (m, 2H; CH2), 1.37 – 1.25 (m, 1H, CH2), 1.22 (s, 9H; 3 x CH3, overlapping peaks), 0.90 – 0.84 (m, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 176.7 (COC(CH3)3), 101.1 (C-1), 84.8 (C-3), 79.6 (C-4), 74.9 (C-5), 72.5 (C-2), 71.3 (C-6), 69.3 (CH2), 60.4, 60.2, 59.4 (3 x OCH3), 38.7 (C(CH3)3), 31.6 (CH2), 27.1 (3 x CH3, overlapping peaks), 19.1 (CH2), 13.8 (CH2); IR (film) cm⁻¹ 3516, 2940, 1727, 1267, 1089, 1060, 711, 540; ESI-HRMS calcd for C18H34O7Na 385.2202, found m/z 385.2209[M+Na]+.

Butyl 2,3-di-O-benzoyl-6-O-benzyl-β-D-glucopyranoside (115)

89 (10g, 18.8 mmole) was taken up in anhydrous THF (150 mL) and to this was added 4 Å molecular sieves (10 g) and NaBH3CN (8.26 g, 131.44 mmole). The resulting suspension was stirred for 30 min before MSA (8.53 mL, 131.44 mmole) was slowly added (WARNING: gas evolution). After 5 h the reaction was quenched with triethylamine (25 mL). The suspension was filtered and evaporated before being taken up in EtOAc, washed satd aq NaHCO3 (200 mL), brine (200 mL), dried over Na2SO4, filtered and the solvent was removed under deminised pressure. Flash chromatography of the residue (cyclohexane-EtOAc 8:2) gave 115 (8.04 g, 82%) as white solid; [α]D 14.4 (c 0.6, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 7.96 (dd, 3J (H,H) = 15.5, 7.8, 4H; Ar-H), 7.50 (td, 3J (H,H) = 7.4, 5.4, 2H; Ar-H), 7.48 – 7.27 (m, 7H; Ar-H), 5.55 – 5.25 (m, 2H; H-2, H-3, overlapping peaks), 4.87 – 4.49 (m, 2H; C-1, CHHPh, overlapping peaks), 3.95 (appt, 3J (H,H) = 9.1, 1H; H-4), 3.89 (dt, 2J (H,H) = -10.1, 3J (H,H) = 6.4, 1H; CHH), 3.87 – 3.84 (m, 1H; H-6a, H-6b,
overlapping peaks), 3.69 (dt, $^3J$ (H,H) = 9.5, 4.7, 1H; H-5), 3.50 (dt, $^2J$ (H,H) = -9.7, $^3J$ (H,H) = 6.7, 1H; CHH), 1.49 (dddt, $J$ = 25.8, 13.9, 7.3, 1.6, 2H; CH$_2$), 1.27 – 1.05 (m, 2H; CH$_2$), 0.79 – 0.66 (m, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 167.2, 165.2 (2 x COPh), 137.6 (Ar-C), 133.4, 133.0, 130.0, 129.9 (6 x Ar-CH, overlapping peaks) 129.7, 129.5 (2 x Ar-C), 129.1, 128.5, 128.4, 128.3, 127.8 (9 x Ar-CH, overlapping peaks), 101.1 (C-1), 76.7 (C-3), 74.5 (C-5), 73.8 (CH$_2$Ph), 71.5 (C-2), 71.3 (C-4), 70.2 (C-6), 69.8 (CH$_2$), 31.4 (CH$_2$), 18.9 (CH$_2$), 13.6 (CH$_3$) IR (film) cm$^{-1}$: 3494, 2951, 1760, 1585, 1451, 1266, 1089, 1059, 1027, 999, 710; ESI-HRMS calcd for C$_{31}$H$_{34}$O$_8$Na 557.2151, found m/z 557.2150 [M+Na]$^+$.

**Butyl 2,3,4-tri-O-benzoyl-6-O-benzyl-β-D-glucopyranoside (116)**

115 (8.0 g, 14.96 mmol) was acylated with benzoyl chloride using the conditions outlined in general procedure 1. Purification by flash chromatography (cyclohexane-EtOAc 8:2) gave 116 (7.166 g, 75%) as a foam; [α]$_D$ 6.1 (c 0.1, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): δ 8.16 – 8.03 (m, 2H; Ar-H), 8.02 – 7.89 (m, 4H; Ar-H), 7.60 (t, $^3J$ (H,H) = 7.5, 1H; Ar-H), 7.49 (q, $^3J$ (H,H) = 7.3, 4H; Ar-H), 7.42 – 7.33 (m, 4H; Ar-H), 7.13 – 7.05 (m, 5H; Ar-H), 5.77 (apt. t, $^3J$ (H,H) = 9.4, 1H; H-4), 5.38 (dd, $^3J$ (H,H) = 9.9, 7.9, 1H; H-2), 4.71 (d, $^3J$ (H,H) = 7.9, 1H; H-1), 4.65 (dd, $^2J$ (H,H) = -11.9, $^3J$ (H,H) = 2.2, 1H; H-6a), 4.62 – 4.51 (m, 3H; H-6b, CHHPh, overlapping peaks), 3.96 (apt. t, $^3J$ (H,H) = 9.3, 1H; H-3), 3.91 – 3.80 (m, 2H; H-5, CHH, overlapping peaks), 3.49 (dt, $^2J$ (H,H) = -9.7, $^3J$ (H,H) = 6.8, 1H; CHH), 1.56 – 1.36 (m, 2H; CH$_2$), 1.29 – 1.00 (m, 2H; CH$_2$), 0.88 – 0.60 (m, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 166.2, 165.7, 165.3 (3 x COPh), 136.7 (Ar-C), 133.2, 133.2, 133.0 (3 x Ar-CH), 129.8 (Ar-C, 3 x Ar-CH, overlapping peaks), 129.7 (2 x Ar-CH, overlapping peaks), 129.5, 129.3 (2 x Ar-C), 128.4, 128.4, 128.3, 128.0 (12 x Ar-CH, overlapping peaks), 101.2 (C-1), 76.0 (C-3), 75.2 (C-4), 74.8 (CH$_2$Ph), 73.3 (C-5), 72.1 (C-2), 69.9 (CH$_2$), 63.2 (C-6), 31.4 (CH$_2$), 18.8 (CH$_2$), 13.5 (CH$_3$); IR (film) cm$^{-1}$: 3490, 3066, 2959, 2874, 1725, 1602, 1452, 1258, 1088, 1067, 1026, 981, 910, 704; ESI-HRMS calcd for C$_{38}$H$_{38}$O$_{8}$Na 661.2414, found m/z 608.2417 [M+Na]$^+$. 
Butyl 2,3,4-tri-O-benzoyl-6-O-(4-fluorobenzoyl)-β-D-glucopyranoside (117β)

116 (0.25 g, 0.39 mmol) was subjected to the conditions outlined in general procedure 3, using 4-fluorobenzoyl chloride as the acylating reagent. Purification via flash chromatography (cyclohexane-EtOAc 8:2) gave 117β (0.22 g, 84%) as a foam; [α]D 9.2 (c 0.2, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.05 – 8.00 (m, 2H; Ar-H), 7.99 – 7.93 (m, 2H; Ar-H), 7.91 – 7.86 (m, 2H; Ar-H), 7.86 – 7.80 (m, 2H; Ar-H), 7.54 – 7.47 (m, 2H; Ar-H), 7.46 – 7.27 (m, 7H; Ar-H), 7.19 – 6.88 (m, 2H, Ar-H), 5.89 (apt. t, 3J (H,H) = 9.6, 1H; H-3), 5.67 (apt. t, 3J (H,H) = 9.7, 1H; H-4), 5.51 (dd, 3J (H,H) = 9.8, 7.8, 1H; H-2), 4.83 (d, 3J (H,H) = 7.8, 1H; H-1), 4.62 (dd, 3J (H,H) = -12.1, 3J (H,H) = 3.4, 1H; H-6a), 4.50 (dd, 3J (H,H) = -12.0, 3J (H,H) = 4.9, 1H; H-6b), 4.14 (ddd, 3J (H,H) = 9.9, 4.9, 3.4, 1H; H-5), 3.91 (dt, 3J (H,H) = -9.7, 3J (H,H) = 6.4, 1H; CHH), 3.55 (dt, 3J (H,H) = -9.7, 3J (H,H) = 6.7, 1H; CHH), 1.62 – 1.35 (m, 2H; CH2), 1.30 – 1.16 (m, 2H; CH2), 0.74 (t, 3J (H,H) = 7.4, 1H; CH3); 13C NMR (126 MHz, CDCl3): δ 166.49 (d, 1J (C,F) = 128.5; Ar-CF), 165.8, 165.1 (3 x COPh, overlapping peaks) 164.8 (COOC6H4F), 133.4, 133.2, 133.1 (3 x Ar-CH), 132.29 (d, 3J (C,F) = 9.5; 2 Ar-CH, overlapping peaks), 129.8, 129.7, 129.7 (6 x Ar-CH, overlapping peaks), 129.4, 128.8, (3 x Ar-C, overlapping peaks). 128.4, 128.3 (6 Ar-CH, overlapping peaks), 125.84 (d, 4J (C,F) = 3.0; Ar-C), 115.49 (d, 2J (C,F) = 22.0; 2 x Ar-CH, overlapping peaks), 101.3 (C-1), 72.9 (C-3), 72.0 (C-2), 71.9 (C-5), 70.1 (CH2), 69.8 (C-4), 63.3 (C-6), 31.4 (CH2), 18.9 (CH2), 13.5 (CH3); IR (film) cm−1: 2959, 1722, 1451, 1260, 1091, 1066, 1026, 704; ESI-HRMS calcd for C38H35O10NaF 693.2112, found m/z 693.2113 [M+Na]+.

Butyl 2,3,4-tri-O-benzoyl-6-O-(4-chlorobenzoyl)-β-D-glucopyranoside (118β)
116 (0.25 g, 0.39 mmol) was subjected to the conditions outlined in general procedure 3, using 4-chlorobenzoyl chloride as the acylating agent. Purification by flash chromatography (cyclohexane-EtOAc 8:2) gave 118β (0.180 g, 67%) as a foam; [α]D 11.8 (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 7.99 – 7.92 (m, 4H; Ar-H), 7.89 (dd, ³J(H,H) = 8.3, 1.3, 2H; Ar-H), 7.83 (dd, ³J(H,H) = 8.3, 1.4, 2H; Ar-H), 7.51 (dt, ³J(H,H) = 8.9, 7.4, 2H; Ar-H), 7.46 – 7.32 (m, 7H; Ar-H), 7.29 (t, ³J(H,H) = 7.9, 2H; Ar-H), 5.90 (apt. t, ³J(H,H) = 9.7, 1H; H-3), 5.67 (apt. t, ³J(H,H) = 9.7, 1H; H-4), 5.52 (dd, ³J(H,H) = 9.8, 7.8, 1H; H-2), 4.84 (d, ³J(H,H) = 7.8, 1H; H-1), 4.63 (dd, ³J(H,H) = -12.1, ³J(H,H) = 3.5, 1H; H-6a), 4.51 (dd, ³J(H,H) = -12.1, ³J(H,H) = 5.0, 1H; H-6b), 4.14 (dd, ³J(H,H) = 9.9, 4.9, 3.4, 1H; H-5), 3.91 (dt, ³J(H,H) = -9.7, ³J(H,H) = 6.3, 1H; CHH), 3.55 (dt, ³J(H,H) = -9.7, ³J(H,H) = 6.7, 1H; CHH), 1.60 – 1.44 (m, 2H; CH₂), 1.29 – 1.19 (m, 2H; CH₂), 0.75 (t, ³J(H,H) = 7.4, 3H; CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 165.8 (COCl₃), 165.3, 165.2, 165.1 (3 x COPh), 139.6 (Ar-Cl), 133.4, 133.2, 133.1, 131.1, 129.8, 129.7 (11 x ArCH, overlapping peaks), 129.4, 128.8 (3 x Ar-C), 128.7, 128.4, 128.3, 128.3 (8 x Ar-CH, overlapping peaks), 128.0 (Ar-CH), 101.3 (C-1), 72.9 (C-3), 72.0 (C-2), 71.9 (C-5), 70.1 (CH₂), 69.8 (C-4), 63.4 (C-6), 31.4 (CH₂), 18.9 (CH₃), 13.5 (CH₃); IR (film) cm⁻¹: 2961, 1708, 1604, 1249, 1166, 1088, 1025, 845, 766; ESI-HRMS calcd for C₃₈H₅₀O₁₀NaCl 709.1816, found m/z 709.1822 [M+Na]⁺.

Butyl 2,3,4-tri-O-benzoyl-6-O-(4-methylbenzoyl)-β-D-glucopyranoside (119β)

116 (0.25 g, 0.39 mmol) was subjected to the conditions outlined in general procedure 3, using 4-methylbenzoyl chloride as the acylating reagent. Purification via flash chromatography (cyclohexane-EtOAc 8:2) gave 119β (0.185 g, 71%) as a foam; [α]D 2.1 (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 7.96 (dd, ³J(H,H) = 8.1, 1.4, 2H; Ar-H), 7.90 (dd, ³J(H,H) = 7.9, 3.6, 4H; Ar-H), 7.86 – 7.79 (m, 2H; Ar-H), 7.56 – 7.47 (m, 2H; Ar-H), 7.44 – 7.29 (m, 7H; Ar-H), 7.19 (d, ³J(H,H) = 7.9, 2H; Ar-H), 5.90 (apt. t, ³J(H,H) = 9.7, 1H; H-3), 5.66 (apt. t, ³J(H,H) = 9.7, 1H; H-4), 5.52 (dd, ³J(H,H) = 9.8, 7.8, 1H; H-2), 4.83 (d, ³J(H,H) = 7.8, 1H; H-1), 4.62
(dd, $^2J (H, H) = -12.0$, $^3J (H, H) = 3.3$, 1H; H-6a), 4.49 (dd, $^2J (H, H) = -12.1$, $^3J (H, H) = 5.4$, 1H; H-6b), 4.15 (dd, $^3J (H, H) = 9.2$, 5.4, 3.4, 1H; H-5), 3.92 (dt, $^3J (H, H) = -9.8$, $^3J (H, H) = 6.3$, 1H; CHH), 3.55 (dt, $^2J (H, H) = -9.8$, $^3J (H, H) = 6.7$, 1H; CHH), 2.40 (s, 3H; CH$_3$), 1.64 – 1.38 (m, 2H; CH$_2$), 1.34 – 1.18 (m, 2H; CH$_2$), 0.75 (t, $^3J (H, H) = 7.4$, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 166.2 (COCH$_3$), 165.8, 165.2, 165.1 (3 x COPh), 143.8 (Ar-C(CH$_3$)), 133.3, 133.2, 133.1, 129.8, 129.7 (11 x Ar-CH, overlapping peaks), 129.4 (Ar-C), 129.0 (2 x Ar-CH, overlapping peaks), 128.9, 128.8 (2 x ArC), 128.4, 128.3, 128.3 (6 x ArCH, overlapping peaks), 126.9 (Ar-C), 101.3 (C-1), 73.0 (C-3), 72.2 (C-5), 72.0 (C-2), 70.0 (CH$_2$), 69.9 (C-4), 63.1 (C-6), 31.4 (CH$_2$), 18.9 (CH$_2$), 13.5 (CH$_3$); IR (film) cm$^{-1}$: 2978, 1187, 1649, 1501, 1212, 1166, 1069, 1045, 1012, 751; ESI- HRMS calcd for C$_{39}$H$_{38}$O$_{10}$Na $m/z$ 689.2363, found $m/z$ 689.2361 [M+Na]$^+$. 

![Butyl 2,3,4-tri-O-benzoyl-6-O-(4-methoxybenzoyl)-β-D-glucopyranoside (120β)](image)

Butyl 2,3,4-tri-O-benzoyl-6-O-(4-methoxybenzoyl)-β-D-glucopyranoside (120β)  

116 (0.25 g, 0.39 mmol) was subjected to the conditions outlined in general procedure 3 using 4-methoxybenzoyl chloride as the acylating reagent. Purification via flash chromatography (cyclohexane-EtOAc 8:2) gave 120β (0.234 g, 88%) as a foam; $[\alpha]_D$ 12.1 (c 0.2, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.00 – 7.94 (m, 4H; Ar-H), 7.89 (dd, $^2J (H, H) = 8.4$, 1.4, 2H; Ar-H), 7.83 (dd, $^3J (H, H) = 8.2$, 1.4, 2H; Ar-H), 7.54 – 7.45 (m, 2H; Ar-H), 7.44 – 7.24 (m, 7H; Ar-H), 6.86 (d, $^3J (H, H) = 8.8$, 2H; Ar-H), 5.89 (apt. t, $^3J (H, H) = 9.6$, 1H; H-3), 5.67 (apt. t, $^3J (H, H) = 9.7$, 1H; H-4), 5.51 (dd, $^3J (H, H) = 9.7$, 7.9, 1H; H-2), 4.83 (d, $^3J (H, H) = 7.8$, 1H; H-1), 4.61 (dd, $^3J (H, H) = -12.0$, $^2J (H, H) = 3.3$, 1H; H-6a), 4.47 (dd, $^2J (H, H) = -12.0$, $^3J (H, H) = 5.2$, 1H; H-6b), 4.14 (dd, $^3J (H, H) = 9.9$, 5.2, 3.3, 1H; H-5), 3.91 (dt, $^3J (H, H) = 9.7$, 6.3, 1H; CHH), 3.85 (s, 3H; OCH$_3$), 3.55 (dt, $^3J (H, H) = 9.8$, $^3J (H, H) = 6.7$, 1H; CHH), 1.51 (qdd, $^3J (H, H) = 13.7$, 8.5, 6.7, 2H; CH$_2$), 1.32 – 1.13 (m, 2H; CH$_2$), 0.74 (t, $^3J (H, H) = 7.4$, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 165.8 (COPh, COCH$_3$(OCH$_3$), overlapping peaks), 165.2, 165.1 (2 x COPh), 163.4 (Ar-C(OCH$_3$), 133.3, 133.2, 133.1, 131.8, 129.8, 129.7 (11 x Ar-CH, overlapping peaks), 129.4,
Experimental data

128.9 (3 x Ar-C, overlapping peaks), 128.4, 128.3, 128.3 (6 x Ar-CH, overlapping peaks), 122.0 (Ar-C), 113.6 (2 x Ar-CH, overlapping peaks), 101.3 (C-1), 73.0 (C-3), 72.2 (C-5), 72.0 (C-2), 70.0 (C-4), 69.9 (CH2), 63.0 (C-5), 55.4 (OCH3), 31.4 (CH2), 18.9 (CH2), 13.5 (CH3); IR (film) cm⁻¹: 2961, 1718, 1604, 1551, 1248, 1166, 1088, 1025, 844, 764, 695; ESI-HRMS calcd for C₃₀H₃₈O₁₁Na 705.2312, found m/z 705.2310 [M+Na]+.

Butyl 2,3,4,6-tetra-O-propionyl-β-D-glucopyranoside (121β)

76 (0.25g, 1.06 mmol) was acylated using propionyl chloride under the conditions outlined in general procedure 1. Purified via flash chromatography (cyclohexane-EtOAc 7:3) to give 121β (0.283 g, 58%) as a clear oil; [α]D -8.7 (c 0.1, CH2Cl2); ¹H NMR (500 MHz, CDCl3): δ 5.22 (apt. t, 3J (H,H) = 9.5, 1H; H-3), 5.10 (apt. t, 3J (H,H) = 9.7, 1H; H-4), 5.00 (dd, 3J (H,H) = 9.6, 8.0, 1H; H-2), 4.49 (d, 3J (H,H) = 7.9, 1H; H-1), 4.25 (dd, 3J (H,H) = -12.3, 3J (H,H) = 5.0, 1H; H-6a), 4.14 (dd, 3J (H,H) = -12.2, 3J (H,H) = 2.4, 1H; H-6b), 3.86 (dt, 3J (H,H) = 9.6, 3J (H,H) = 6.3, 1H; CHH), 3.69 (ddd, J=9.9, 4.9, 2.4, 1H; H-5), 3.47 (dt, 3J (H,H) = -9.7, 3J (H,H) = 6.8, 1H; CHH), 2.43 – 2.32 (m, 2H; CH₂), 2.32 – 2.18 (m, 6H; 6 x CH₂, overlapping peaks), 1.54 (dddd, 3J (H,H) = 19.8, 15.1, 11.2, 7.0, 2H; CH₂), 1.32 (dq, 3J (H,H) = 15.2, 6.8, 6.4, 2H; CH₂), 1.16 – 1.02 (m, 12H; 4 x CH₃, overlapping peaks), 0.89 (t, 3J (H,H) =7.4, 3H; CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 174.1, 173.7, 172.8, 172.7 (4 x COCH₂CH₃), 100.9 (C-1), 72.7 (C-3), 71.9 (C-5), 71.2 (C-2), 69.8 (CH₂), 68.3 (C-4), 61.9 (C-6), 31.4 (CH₂), 27.4 (4 x CH₂, overlapping peaks), 18.9 (CH₂), 13.7 (CH₃),9.1, 9.0, 8.9 (4 x CH₃, overlapping peaks); IR (film) cm⁻¹: 2964, 1724, 1604, 1511, 1251, 1166, 1092, 1068, 1026, 845, 765, 707; ESI-HRMS calcd for C₂₂H₃₆O₁₀Na 483.2206, found m/z 483.2209 [M+Na]⁺.
Butyl 2,3,4,6-tetra-O-isobutyryl-β-D-glucopyranoside (122β)

76 (0.25 g, 1.06 mmol) was acylated using isobutyryl chloride under the conditions outlined in general procedure 1. Purification via flash chromatography (cyclohexane-EtOAc 7:3) gave 122β (0.41 g, 75%) as a clear oil; [α]D -9.2 (c 0.2, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 5.25 (apt. t, 3 J (H,H) = 9.6, 1H; H-3), 5.10 (apt. t, 3 J (H,H) = 9.7, 1H; H-4), 5.00 (dd, 3 J (H,H) = 9.7, 8.0, 1H; H-2), 4.49 (d, 3 J (H,H) = 8.0, 1H; H-1), 4.26 - 4.10 (m, 2H; H-6), 3.85 (dt, 2 J (H,H) = -9.5, 3 J (H,H) = 6.3, 1H; CHH), 3.75 - 3.63 (m, 1H; H-5), 3.46 (dt, 2 J (H,H) = -9.7, 3 J (H,H) = 6.8, 1H; CHH), 2.59 (p, 3 J (H,H) = 7.0, 1H; CH(CH3)2), 2.55 - 2.39 (m, 3H; 3 x CH(CH3)2, overlapping peaks), 1.59 - 1.45 (m, 2H; CH2), 1.41 - 1.26 (m, 2H; CH2), 1.17 (d, 3 J (H,H) = 2.7, 3H; CH3), 1.16 (d, 3 J (H,H) = 2.6, 3H; CH3), 1.14 - 1.00 (m, 18H; 6 x CH3, overlapping peaks), 0.88 (t, 3 J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 176.7, 176.1, 175.2, 175.2 (4 x COCH(CH3)2), 101.0 (C-1), 72.3 (C-3), 72.1 (C-5), 71.0 (C-2), 69.7 (CH2), 68.1 (C-4), 61.9 (C-6), 33.9, 33.8 (4 x CH(CH3)2, overlapping peaks), 31.4 (CH2), 19.0, 18.9, 18.8, 18.7 (CH2, 8 x CH3, overlapping peaks), 13.7 (CH3); IR (film) cm⁻¹: 2970, 1726, 1256, 1091, 1027, 847, 709; ESI-HRMS calcd for C26H44O10Na 539.2832, found m/z 539.2825 [M+Na]⁺.

Butyl 2,3,4,6-tetra-O-pivaloyl-β-D-glucopyranoside (123β)

76 (0.25 g, 1.06 mmol) was acylated using trimethyl acetyl chloride under the conditions outlined in general procedure 1. Purification via flash chromatography (cyclohexane-EtOAc 7:3) gave 123β (0.43 g, 71%) as a clear oil; [α]D -4.6 (c 0.1, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 5.30 (apt. t, 3 J (H,H) = 9.5, 1H; H-3), 5.08 (apt. t, 3 J (H,H) = 9.7, 1H; H-3), 5.00 (dd, 3 J (H,H) = 9.6, 8.0, 1H; H-2), 4.48 (d, 3 J
Butyl 2,3,4,6-tetra-O-(4-chlorobenzoyl)-β-D-glucopyranoside (124β)

76 (0.25g, 1.06 mmol) was acylated using 4-chlorobenzoyl chloride under the conditions outlined in general procedure 1. Purification via flash chromatography (cyclohexane-EtOAc 7:3) gave 124β (0.695 g, 83%) as a clear oil; [α]_D^2 4.9 (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 7.96 – 7.90 (m, 2H; Ar-H), 7.79 (dd, ^3^J (H,H) = 7.7, 1.0, 2H; Ar-H), 7.77 – 7.71 (m, 2H; Ar-H), 7.41 – 7.33 (m, 2H; Ar-H), 7.34 – 7.30 (m, 2H; Ar-H), 7.30 – 7.21 (m, 2H; Ar-H), 5.81 (apt. t, ^3^J (H,H) = 9.7, 1H; H-3), 5.61 (apt.t, ^3^J (H,H) = 9.7, 1H; H-4), 5.46 (dd, ^3^J (H,H) = 9.8, 7.8, 1H; H-2), 4.81 (d, ^3^J (H,H) = 7.8, 1H; H-1), 4.60 (dd, ^3^J (H,H) = -12.2, ^3^J (H,H) = 3.4, 1H; H-6a), 4.49 (dd, ^2^J (H,H) = -12.1, ^3^J (H,H) = 4.9, 1H; H-6b), 4.12 (ddd, ^3^J (H,H) = 9.9, 4.9, 3.4, 1H; H-5), 3.91 (dt, ^2^J (H,H) = -9.8, ^3^J (H,H) = 6.4, 1H; CH₂), 3.54 (dt, ^2^J (H,H) = -9.7, ^3^J (H,H) = 6.7, 1H; CH₂), 1.32 – 1.17 (m, 2H; CH₂), 0.76 (t, ^3^J (H,H) = 7.4, 3H; CH₂); ^13^C NMR (126 MHz, CDCl₃): δ 165.2, 164.9, 164.3, 164.2 (4 x COC₆H₄Cl), 140.2, 140.0,
139.8, 139.7 (4 x Ar-CCl), 131.1 (8 x Ar-CH, overlapping peaks), 128.8, 128.7 (8 x Ar-CH, overlapping peaks), 127.9, 127.6, 127.0 (4 x Ar-C, overlapping peaks), 101.1 (C-1), 73.2 (C-3), 72.0 (C-2), 71.8 (C-5), 70.1 (CH₂), 69.9 (C-4), 63.2 (C-6), 31.3 (CH₂), 18.8 (CH₂), 13.5 (CH₃); IR (film) cm⁻¹: 2964, 1722, 1604, 1511, 1250, 1166, 1068, 1091, 1026, 845, 765; ESI-HRMS calcd for C₃₈H₃₂O₁₀Cl₄Na 811.0647, found m/z 811.0653 [M+Na]⁺.

**Butyl 2,3,4,6-tetra-O-(4-flourobenzoyl)-β-D-glucopyranoside (125β)**

76 (0.25g, 1.06 mmol) was acylated using 4 flurorbenzoyl chloride under the conditions outlined in general procedure 1. Purification via flash chromatography (cyclohexane-EtOAc 7:3) gave 125β (0.32g, 42%) as a clear oil; [α]D 26.8 (c 0.4, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.06 – 8.00 (m, 2H; Ar-CH), 8.00 – 7.93 (m, 2H; Ar-CH), 7.93 – 7.87 (m, 2H; Ar-H), 7.87 – 7.80 (m, 2H; Ar-H), 7.12 – 6.90 (m, 8H; Ar-H), 5.82 (apt. t, ³J (H,H) =9.7, 1H; H-3), 5.62 (apt. t, ³J (H,H) =9.7, 1H; H-4), 5.47 (dd, ³J (H,H) =9.8, 7.8, 1H; H-2), 4.81 (d, ³J (H,H) =7.9, 1H; H-1), 4.62 (dd, ³J (H,H) = -12.1, ³J (H,H) = 3.2, 1H; H-6a), 4.48 (dd, ³J (H,H) = -12.1, ³J (H,H) = 5.0, 1H; H-6b), 4.12 (ddd, ³J (H,H) =9.9, 5.0, 3.3, 1H; H-5), 3.91 (dt, ³J (H,H) = -9.7, ³J (H,H) =6.3, 1H; CH₃), 3.54 (dt, ³J (H,H) = -9.7, ³J (H,H) =6.7, 1H; C₃H₃), 1.60 – 1.41 (m, 2H; CH₂), 1.31 – 1.12 (m, 2H; CH₂), 0.75 (t, ³J (H,H) =7.4, 1H; CH₃). ¹³C NMR (126 MHz, CDCl₃): δ 167.8 – 164.6 (m; 4 x Ar-CF, 2 x COC₆H₄F, overlapping peaks), 164.2, 164.1 (2 x COC₆H₄F), 132.44 – 132.2 (m; 4 x Ar-CH, overlapping peaks), 125.7 (d, ⁴J (C,F) =2.9; Ar-C), 125.5(d, ⁴J (C,F) =3.0; Ar-C), 124.9 (d, ⁴J (C,F) =2.9; Ar-C), 124.9 (d, ⁴J (C,F) =2.8; Ar-C), 124.8 (d, ⁴J (C,F) =2.9; Ar-C), 115.7 (m; 4 x Ar-CH, overlapping peaks), 101.2 (C-1), 73.1 (C-3), 71.9 (C-5, C-2, overlapping peaks), 70.1 (CH₂), 69.8 (C-4), 63.1 (C-6), 31.3 (CH₂), 18.8 (CH₂), 13.5
Experimental data

Chapter 5

Butyl 2,3,4,6-tetra-O-(4-methoxybenzoyl)-β-D-glucopyranoside (126β)

76 (0.25 g, 1.06 mmol) was acylated using 4-methoxybenzoyl chloride under the conditions outlined in general procedure 1. Purification by flash chromatography (cyclohexane-EtOAc 7:3) gave 126β (0.655 g, 80%) as a clear oil; [α]D 17.1 (c 0.2, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 7.95 (d, 3J (H,H) = 8.7, 2H; Ar-H), 7.93 – 7.90 (m, 2H; Ar-H), 7.86 – 7.82 (m, 2H; Ar-H), 7.81 – 7.76 (m, 2H; Ar-H), 6.87 – 6.82 (m, 4H; Ar-H), 6.81 – 6.78 (m, 2H; Ar-H), 6.77 – 6.70 (m, 2H; Ar-H), 5.81 (apt. t, 3J (H,H) = 9.7, 1H; H-3), 5.59 (apt.t, 3J (H,H) = 9.7, 1H; H-4), 5.45 (dd, 2J (H,H) = 9.8, 7.8, 1H; H-2), 4.79 (d, 2J (H,H) = 7.7, 1H; H-1), 4.58 (dd, 2J (H,H) = -11.9, 3J (H,H) = 3.4, 1H; H-6a), 4.45 (dd, 2J (H,H) = -12.1, 3J (H,H) = 5.3, 1H; H-6b), 4.10 (ddd, 3J (H,H) = 9.3, 5.3, 3.4, 1H; H-5), 3.89 (dt, 2J (H,H) = -9.7, 3J (H,H) = 6.3, 1H; C/H), 3.84 (s, 3H; OCH3), 3.81 (s, 3H; OCH3), 3.79 (s, 3H; OCH3), 3.75 (s, 3H; OCH3), 3.53 (dt, 2J (H,H) = -9.8, 3J (H,H) = 6.8, 1H; C/H), 1.57 – 1.43 (m, 2H; CH2), 1.29 – 1.17 (m, 2H; CH2), 0.75 (t, 3J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 165.9, 165.4, 164.8 (4 x COC6H4(OCH3), overlapping peaks), 163.6, 163.4 (4 x Ar-C(OCH3), 131.9, 131.8 (8 x Ar-CH, overlapping peaks), 122.1, 121.8, 121.3 (4 x Ar-C, overlapping peaks), 113.6, 113.5 (8 x Ar-CH, overlapping peaks), 101.4 (C-1), 72.7 (C-3), 72.2 (C-2), 71.7 (C-5), 69.9 (CH2), 69.7 (C-4), 63.2 (C-6), 55.4, 55.3 (4 x OCH3, overlapping peaks), 31.4 (CH3), 18.9 (CH2), 13.6 (CH3); IR (film) cm⁻¹: 2960, 1717, 1604, 1511, 1248, 1087, 1025, 844, 764; ESI-HRMS calcd for C42H48O44N 790.3075, found m/z 790.3080 [M+NH4]⁺.
Butyl 2,3,4,6-tetra-O-(4-methylbenzoyl)-β-D-glucopyranoside (127β)

76 (0.25g, 1.06 mmol) was acylated using 4-methylbenzoyl chloride under the conditions outlined in general procedure 1. Purification via flash chromatography (cyclohexane-EtOAc 7:3) gave 127β (0.571 g, 76%) as a clear oil; \([\alpha]_D \text{35.2} (c 1.2, \text{CH}_2\text{Cl}_2) \text{; } ^1\text{H NMR} (500 \text{ MHz, CDCl}_3): \delta 7.92 - 7.87 \text{ (m, 2H; Ar-H)}, 7.86 - 7.83 \text{ (m, 2H; Ar-H)}, 7.78 \text{ (d, } ^3\text{J (H,H) = 8.2, 2H; Ar-H)}, 7.74 - 7.70 \text{ (m, 2H; Ar-H)}, 7.17 \text{ (t, } ^2\text{J (H,H) = 8.7, 4H; Ar-H)}, 7.12 \text{ (d, } ^2\text{J (H,H) = 8.0, 2H; Ar-H)}, 7.06 \text{ (d, } ^2\text{J (H,H) = 8.0, 2H; Ar-H)}, 5.87 \text{ (apt.t, } ^2\text{J (H,H) = 9.7, 1H; H-3)}, 5.62 \text{ (apt.t, } ^2\text{J (H,H) = 9.7, 1H; H-4)}, 5.49 \text{ (dd, } ^2\text{J (H,H) = 9.8, 7.9, 1H; H-2)}, 4.81 \text{ (d, } ^2\text{J (H,H) = 7.8, 1H; H-1)}, 4.60 \text{ (dd, } ^2\text{J (H,H) = -12.1, 3J (H,H) = 3.3, 1H; H-6a)}, 4.47 \text{ (dd, } ^2\text{J (H,H) = -12.1, 3J (H,H) = 5.5, 1H; H-6b)}, 4.13 \text{ (ddd, } ^2\text{J (H,H) = 9.3, 5.5, 3.3, 1H; H-5)}, 3.90 \text{ (dt, } ^2\text{J (H,H) = -9.7, 3J (H,H) = 6.4, 1H; CHH)}, 3.54 \text{ (dt, } ^2\text{J (H,H) = -9.8, 3J (H,H) = 6.8, 1H; CHH)}, 2.39 \text{ (s, 3H; CH$_3$)}, 2.35 \text{ (s, 3H; CH$_3$)}, 2.33 \text{ (s, 3H; CH$_3$)}, 2.28 \text{ (s, 3H; CH$_3$)}, 1.50 \text{ (dddt, } ^2\text{J (H,H) = 24.6, 13.9, 8.5, 6.8, 2H; CH$_2$)}, 1.29 - 1.13 \text{ (m, 2H; CH$_2$)}, 0.75 \text{ (d, } ^2\text{J (H,H) = 7.4, 2H; CH$_3$)}; ^13\text{C NMR} (126 \text{ MHz, CDCl}_3): \delta 166.2, 165.8, 165.2, 165.1 \text{ (4 x COC$_6$H$_4$(CH$_3$)), 144.1, 143.8, 143.7 (4 x Ar-C(CH$_3$) overlapping peaks), 129.9, 129.8, 129.7 (8 x Ar-CH, overlapping peaks), 129.0, 128.9 (8 x Ar-CH, overlapping peaks), 126.9, 126.7, 126.2, 126.1 (4 x ArC), 101.3 (C-1), 72.7 (C-3), 72.2 (C-5), 71.8 (C-2), 70.0 (CH$_2$), 69.7 (C-4), 63.2 (C-6), 31.4 (CH$_2$), 21.7, 21.6 (4 x CH$_3$, overlapping peaks), 18.9(CH$_3$), 13.6 (CH$_3$); IR (film) cm$^{-1}$: 2966, 1722, 1609, 1582, 11376, 1231, 1061, 1021, 789, 695; ESI-HRMS calcd for C$_{42}$H$_{44}$O$_{10}$Na 731.2832, found m/z 731.2820 [M+Na]$^+$. 

Experimental data
Butyl 2,3,4,6-tetra-O-(4-tert-butylbenzoyl)-β-D-glucopyranoside (128β)

76 (0.25g, 1.06 mmol) was acylated using 4-tert-butylbenzoyl chloride under the conditions outlined in general procedure 1. Purification via flash chromatography (cyclohexane-EtOAc 7:3) gave 128β (0.595 g, 64%) as a clear oil; [α]D 34.2 (c 0.4, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 7.99 – 7.92 (m, 2H; Ar-H), 7.91 – 7.83 (m, 4H; Ar-H), 7.82 – 7.74 (m, 2H; Ar-H), 7.45 – 7.35 (m, 6H; Ar-H), 7.33 – 7.28 (m, 2H; Ar-H), 5.87 (apt. t, 3J (H,H) =9.6, 1H; H-3), 5.63 (apt. t, 3J (H,H) =9.7, 1H; H-4), 5.49 (dd, 3J (H,H) =9.7, 7.8, 1H; H-2), 4.80 (d, 3J (H,H) =7.8, 1H; H-1), 4.62 (dd, 2J (H,H) =-12.1, 3J (H,H) = 2.9, 1H; H-6a), 4.44 (dd, 2J (H,H) = -12.1, 3J (H,H) = 5.5, 1H; H-6b), 4.11 (dd, 3J (H,H) =9.9, 5.5, 3.0, 1H; H-5), 3.88 (dt, 2J (H,H) = -9.8, 3J (H,H) = 6.4, 1H; C(CH3), 3.53 (dt, 2J (H,H) = -9.8, 3J (H,H) = 6.8, 1H; C(CH3), 1.59 – 1.42 (m, 2H, CH2), 1.33 (s, 9H; C(CH3)3), 1.31 – 1.28 (m, 18H; C(CH3)3), 1.28 – 1.13 (m, 11H; C(CH3)2, CH2, overlapping peaks), 0.73 (t, 3J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 166.2, 165.8, 165.2, 165.0 (4 x COC6H4(tBu)), 157.0, 156.7 (4 x Ar-C(tBu), overlapping peaks), 129.8, 129.7, 129.6 (8 x Ar-CH, overlapping peaks), 126.9, 126.7, 126.2, 126.1 (4 x Ar-C), 125.3, 125.2 (8 x Ar-CH, overlapping peaks), 101.3 (C-1), 72.8 (C-3), 72.4 (C-5), 71.8 (C-2), 69.9 (CH2), 69.6 (C-4), 63.1 (C-6), 35.1, 35.0 (4 x C(CH3)3, overlapping peaks), 31.4 (CH2), 31.1, 31.0 (12 x CH3, overlapping peaks), 18.9 (CH2), 13.6 (CH3); ESI-HRMS calcd for C54H68O10Na 899.4710, found m/z 899.4714 [M+Na]⁺.
Butyl 2,3,4,6-tetra-O-(1-naphthoyl)-β-D-glucopyranoside (129β)

76 (0.25 g, 1.06 mmol) was acylated using 1-naphthoyl chloride under the conditions outlined in general procedure 1. Purification via flash chromatography (cyclohexane-EtOAc 7:3) gave 129β (0.6 g, 67%) as a clear oil; [α]D 25.8 (c 0.7, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.92 (d, 3J (H,H) = 8.6, 1H; Ar-H), 8.70 – 8.61 (m, 2H; Ar-H), 8.46 (d, 3J (H,H) = 8.7, 1H; Ar-H), 8.25 (dd, 3J (H,H) = 7.3, 1.3, 1H; Ar-H), 8.19 (dd, 3J (H,H) = 7.3, 1.2, 1H; Ar-H), 8.13 – 8.07 (m, 2H; Ar-H), 7.97 (d, 3J (H,H) = 8.2, 2H; Ar-H), 7.93 (d, 3J (H,H) = 8.2, 1H; Ar-H), 7.90 – 7.81 (m, 3H; Ar-H), 7.77 (dd, 3J (H,H) = 7.9, 1.3, 1H; Ar-H), 7.71 (d, 3J (H,H) = 8.2, 1H; Ar-H), 7.59 (ddd, 3J (H,H) = 8.5, 6.8, 1.4, 1H; Ar-H), 7.52 (ddd, 3J (H,H) = 8.4, 7.0, 1.3, 1H; Ar-H), 7.49 – 7.29 (m, 9H; Ar-H), 7.19 (ddd, 3J (H,H) = 8.3, 6.9, 1.4, 1H; Ar-H), 6.18 (apt. t, 3J (H,H) = 9.6, 1H; H-3), 5.92 (apt. t, 3J (H,H) = 9.7, 1H; H-4), 5.76 (dd, 3J (H,H) = 9.8, 7.9, 1H; H-2), 4.99 (d, 3J (H,H) = 7.9, 1H; H-1), 4.78 (d, 3J (H,H) = 4.3, 2H; H-6), 4.33 (dt, 3J (H,H) = 9.2, 4.3, 1H; H-5), 4.04 (dt, 3J (H,H) = -9.5, 6.4, 1H; CHH), 3.63 (dt, 3J (H,H) = -9.5, 3J (H,H) = 6.7, 1H; CHH), 1.69 – 1.47 (m, 2H; CH2), 1.31 (ddd, 3J (H,H) = 16.3, 14.2, 11.0, 6.9, 2H; CH2), 0.76 (t, 3J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 167.0, 166.7, 166.0, 165.8 (4 x COAr), 133.9 (Ar-CH, overlapping peaks), 133.7, 133.6 (4 x Ar-C, overlapping peaks), 133.5, 133.4, (3 x Ar-CH, overlapping peaks), 131.3, 131.1 (4 x Ar-C, overlapping peaks), 130.7, 130.5, 129.8, 128.5, 128.3, 127.9, 127.7, 127.5 (12 x Ar-CH, overlapping peaks), 126.7, 126.4 (3x Ar-C, overlapping peaks), 126.2, 126.1, 126.0, 125.8, 125.7, 125.6 (6 x Ar-CH), 125.5 (Ar-C), 125.4, 125.1, 124.6, 124.4, 124.3 (6 x Ar-CH, overlapping peaks), 101.4 (C-1), 73.0 (C-3), 72.3 (C-5), 72.1 (C-2), 70.1 (CH2), 69.9 (C-4), 63.4 (C-6), 31.5 (CH2), 19.0 (CH2), 13.6 (CH3); ESI-HRMS calcd for C54H44O10Na 875.2832, found m/z 875.2859 [M+Na]+.
Butyl 2,3,4,6-tetra-O-(2-napthoyl)-β-D-glucopyranoside (130β)

76 (0.25 g, 1.06 mmol) was acylated using 2-napthoyl chloride under the conditions outlined in general procedure 1. Purification via flash chromatography (cyclohexane-EtOAc 7:3) gave 130β (0.68 g, 75%) as a clear oil; [α]D 18.4 (c 0.5, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.54 (dd, 3J (H,H) =8.3, 1.6, 2H; Ar-H), 8.44 (dd, 3J (H,H) =25.0, 1.6, 2H; Ar-H), 7.99 (ddd, 3J (H,H) =15.5, 8.6, 1.7, 2H; Ar-H), 7.92 – 7.85 (m, 2H; Ar-H), 7.85 – 7.76 (m, 6H; Ar-H), 7.75 – 7.62 (m, 6H), 7.59 – 7.38 (m, 8H; Ar-H), 6.11 (apt. t, 3J (H,H) =9.6, 1H; H-3), 5.85 (apt. t, 3J (H,H) =9.6, 1H; H-4), 5.69 (dd, 3J (H,H) =9.7, 7.8, 1H; H-2), 4.99 (d, 3J (H,H) =7.8, 1H; H-1), 4.75 (dd, 3J (H,H) =-11.9, 3J (H,H) = 3.9, 1H; H-6a), 4.69 (dd, 3J (H,H) =-11.9, 3J (H,H) = 5.1, 1H; H-6b), 4.34 (dt, 3J (H,H) =9.5, 4.6, 1H; H-5), 3.99 (dt, 3J (H,H) =-9.8, 3J (H,H) = 6.4, 1H; CHH), 3.62 (dt, 3J (H,H) =-9.9, 3J (H,H) = 6.8, 1H; CHH), 1.65 – 1.47 (m, 2H; CH2), 1.32 – 1.18 (m, 2H; CH2), 0.73 (t, 3J (H,H) =7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 166.3, 166.1, 165.4, 165.3 (4 x COAr), 135.6, 135.5, 135.5, 132.3, 132.3, 132.2, 132.2 (8 x Ar-C, overlapping peaks), 131.6, 131.6, 131.4, 131.3, 129.4, 129.4, 129.3, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 127.7, 127.6, 127.6, 127.5 (22 x Ar-CH, overlapping peaks), 126.8 (Ar-C), 126.6 (Ar-C, 2 x Ar-CH, overlapping peaks), 126.5, 126.0 (2 x Ar-C, overlapping peaks), 125.2, 125.1, 125.0 (4 x Ar-CH, overlapping peaks), 101.4 (C-1), 73.2 (C-3), 72.2 (C-2), 72.1 (C-5), 70.5 (C-4), 70.1 (CH2), 63.8 (C-6), 31.4 (CH2), 18.9 (CH2), 13.6 (CH3); IR (film) cm⁻¹: 2961, 1718, 1604, 1511, 1248, 1167, 1068, 1025, 766, 706; ESI-HRMS calcd for C54H44O10Na 875.2832, found m/z 875.2841[M+Na]+.
2-O-acetyl-3-O-(2,3,4,6-tetra-O-(4-methoxybenzoyl)-β-D-glucopyranosyl)-4-O-(1,1,3,3-tetraisopropyl-1,3-disiloxyanediyl)-β-D-glucopyranosyl azide (133β).

[α]D 29.0 (c 0.2, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 7.95 (dd, 3J (H,H) = 14.8, 8.6, 4H; Ar-2H), 7.84 (d, 3J (H,H) = 8.6, 2H; Ar-H), 7.79 (d, 3J (H,H) = 8.6, 2H; Ar-H), 6.87 (t, 3J (H,H) = 7.9, 4H; Ar-H), 7.84 (d, 3J (H,H) = 8.6, 2H; Ar-H), 6.79 (d, 3J (H,H) = 8.6, 2H; Ar-H), 6.74 (d, 3J (H,H) = 8.6, 2H; Ar-H), 5.82 (apt. t, 3J (H,H) = 9.7, 1H; H-3'), 5.61  (apt. t, 3J (H,H) = 9.7, 1H; H-4'), 5.49 – 5.42 (m, 1H; H-2'), 5.03 (d, 3J (H,H) = 7.8, 1H; H-1'), 4.80 (d, 3J (H,H) = 9.2, 1H; H-2), 4.58 (dd, 3J (H,H) = 12.2, 3J (H,H) = 3.3, 1H; H-6a'), 4.47 (dd, 3J (H,H) = 12.1, 3J (H,H) = 5.1, 1H; H-6b'), 4.23 (d, 3J (H,H) = 9.0, 1H; H-1), 4.19 (d, 3J (H,H) = 11.9, 1H; H-6a), 4.12 (dt, 3J (H,H) = 9.1, 4.1, 1H; H-5'), 3.85 (s, 3H; OC6H4), 3.82 (s, 3H; OCH3), 3.80 (s, 3H; OCH3), 3.79 – 3.74 (m, 4H, OCH3, H-6b, overlapping peaks), 3.61 (apt. t, 3J (H,H) = 8.7, 1H; H-3), 3.52 (apt. t, 3J (H,H) = 8.7, 1H; H-5), 3.44 (apt. t, 3J (H,H) = 8.9, 1H; H-4), 2.06 (s, 3H, COCH3), 1.07 – 0.85 (m, 28H; 4 x CH(CH3)2, overlapping peaks); 13C NMR (126 MHz, CDCl3): δ 169.1 (COCH3), 165.8, 165.3, 164.8 (4 x COC6H4(OCH3), overlapping peaks), 163.6, 163.5, 163.4 (4 x Ar-C(OCH3), overlapping peaks), 131.9, 131.8 (4 x Ar-CH, overlapping peaks), 122.1, 121.8, 121.3, 121.2 (4 x Ar-C, overlapping peaks), 113.6, 113.5 (4 x Ar-CH, overlapping peaks), 101.6 (C-1’), 87.3 (C-1), 78.8 (C-5), 77.2 (C-3), 73.3 (C-4), 72.6 (C-3), 72.5 (C-2), 72.3 (C-5’), 71.7 (C-2’), 69.5 (C-4’), 68.4 (C-6), 63.0 (C-6’), 55.3 (4 x OCH3, overlapping peaks), 20.6 (COCH3), 17.3, 17.1 (8 x CH(CH3)2, overlapping peaks), 12.6, 12.1, 12.0 (4 x CH(CH3)2, overlapping peaks)
General procedure for the anomerisation of kinetic substrates.
To a solution of the substrate (0.064 mmol) in CDCl$_3$ (0.65 mL) in an NMR tube, was added a freshly prepared solution of SnCl$_4$ in CDCl$_3$ (0.2 mL of 0.32M, 0.064 mmol). The solution was mixed thoroughly and the reaction was then monitored by $^1$H NMR at 25 °C. Once equilibrium had been reached the solution was diluted with DCM (1 mL) and washed twice with 1M KHSO$_4$ (1 mL), satd aq NaHCO$_3$ (1 mL), brine (1 mL), dried over anhydrous Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure. The resulting residue was taken up in CH$_2$Cl$_2$ and passed through a short column of silica for further purification, followed by evaporation of the solvent under diminished pressure which gave the desired compound. (Note: All glass wear (NMR tube, volumetrics, syringes etc) were oven dried before use. The samples where dried on a high vacuum line for at least 24 hr prior to use. CDC$_3$ was distilled using phosphorus pentoxide and was analyzed before use for water content. $^{31}$P NMR was also run to insure there was no phosphoric acid present. A fresh solution of SnCl$_4$ was prepared for each kinetic run. As regards the plots themselves the same three peaks were integrated at each time interval. Each substrate was run at least three times. In some cases (e.g. compounds 75$\beta$ and 77$\beta$) the substrate was run multiple times at random intervals during the study to ensure the quality of the solvent and the SnCl$_4$ solutions were consistent).

Butyl 2,3,4,6-tetra-O-acetyl-$\alpha$-D-glucopyranoside (75$\alpha$)$^{93}$
$[\alpha]_D$ 49.1 (c 0.5, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.48 (d, $^3J$ (H,H) =10.0, 1H; H-3), 5.12 – 4.96 (m, 2H; H-1, H-4, overlapping peaks), 4.84 (dd, $^3J$ (H,H) =10.2, 3.7, 1H; H-2), 4.25 (dd, $^2J$ (H,H) = -12.3, $^3J$ (H,H) = 4.6, 1H; H-6a), 4.09 (dd, $^2J$ (H,H) = -12.3, $^3J$ (H,H) = 2.4, 1H; H-6b), 4.01 (ddd, $^3J$ (H,H) =10.3, 4.7, 2.3, 1H; H-5), 3.68 (dt, $^2J$ (H,H) = -9.9, $^3J$ (H,H) =6.5, 1H; CHH), 3.43 (dt, $^2J$ (H,H) = -9.9, $^3J$ (H,H) =6.5, 1H; CHH), 2.09 (s, 3H; COCH$_3$), 2.02 (s, 3H; COCH$_3$), 2.01 (s, 6H; 2 x COCH$_3$, overlapping peaks), 1.58 (dq, $^3J$ (H,H) = 8.1, 6.3, 2H; CH$_2$), 1.43 – 1.34 (m, 2H; CH$_2$), 0.93 (t, $^3J$ (H,H) =7.4, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 170.6, 170.2, 170.1 169.6 (4 x COCH$_3$), 95.6 (C-1), 70.9 (C-2), 70.2 (c-3), 68.6 (C-4), 68.4
Butyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranoside (77α)

$\left[\alpha\right]_D^{10} 11.7$ (c 0.8, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.05 (dd, $^3J$(H,H) = 8.0, 1.5, 2H; Ar-H), 8.00 – 7.97 (m, 2H; Ar-H), 7.95 – 7.92 (m, 2H; Ar-H), 7.87 (dd, $^3J$(H,H) = 8.3, 1.4, 2H; Ar-H), 7.57 – 7.54 (m, 1H; Ar-H), 7.53 – 7.48 (m, 2H; Ar-H), 7.45 – 7.34 (m, 8H; Ar-H), 7.29 (t, $^2J$(H,H) = 7.8, 2H; Ar-H), 6.19 (t, $^2J$(H,H) = 9.8, 1H; H-3), 5.67 (t, $^2J$(H,H) = 9.7, 1H; H-4), 5.34 (d, $^2J$(H,H) = 3.7, 1H; H-1), 5.30 (dd, $^2J$(H,H) = 10.1, 3.7, 1H; H-2), 4.72 – 4.54 (m, 1H; H-6a), 4.52 – 4.41 (m, 2H; H-6a, H-5, overlapping peaks), 3.80 (dt, $^2J$(H,H) = -9.9, $^3J$(H,H) = 6.5, 1H; CHH), 3.49 (dt, $^2J$(H,H) = -9.9, $^3J$(H,H) = 6.6, 1H; CHH), 1.60 (ddd, $^2J$(H,H) = 13.6, 6.9, 4.2, 2H; CH$_2$), 1.34 (m, 2H; CH$_2$), 0.83 (t, $^2J$(H,H) = 7.4, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 166.2, 165.8, 165.3 (4 x COPh, overlapping peaks), 133.4, 133.3, 133.1, 129.9, 129.7 (8 x Ar-CH, overlapping peaks), 129.2, 129.1, 128.9 (4 x Ar-C, overlapping peaks), 128.4, 128.2 (4 x Ar-CH, overlapping peaks), 96.0 (C-1), 72.0 (C-2), 70.6 (C-3), 69.6 (C-4), 68.7 (CH$_2$), 67.7 (C-5), 63.1 (C-6), 31.3 (CH$_2$), 19.2 (CH$_2$), 13.7 (CH$_3$); IR (film) cm$^{-1}$: 3369, 2958, 1720, 1384, 1057, 1026, 705; ESI-HRMS calcd for C$_{38}$H$_{40}$O$_{10}$N 670.2652, found m/z 670.2651 [M+NH$_4$]$^+$. 

Butyl 2,3,4-tri-O-acetyl-6-O-benzoyl-α-D-glucopyranoside (80α)

$\left[\alpha\right]_D^{10} 10.0$ (c 0.3, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.05 (d, $^3J$(H,H) = 7.6, 1H; Ar-H), 7.57 (t, $^3J$(H,H) = 7.4, 1H; Ar-H), 7.45 (apt. t, $^3J$(H,H) = 7.7, 1H; Ar-H), 5.52 (apt. t, $^3J$(H,H) = 9.8, 1H; H-3), 5.15 (apt. t, $^3J$(H,H) = 9.8, 1H; H-4), 5.07 (d, $^3J$(H,H) = 3.7, 1H; H-1), 4.87 (dd, $^3J$(H,H) = 10.2, 3.8, 1H; H-2), 4.47 (dd, $^3J$(H,H) = 12.2, $^3J$(H,H) = 2.4, 1H; H-6a), 4.37 (dd, $^3J$(H,H) = 12.2, $^3J$(H,H) = 5.1, 1H; H-
6b), 4.16 (ddd, 3J (H,H) = 10.2, 5.1, 2.4, 1H; H-5), 3.71 (dt, 2J (H,H) = -9.8, 3J (H,H) = 6.6, 1H; CHH), 3.44 (dt, 2J (H,H) = -9.8, 3J (H,H) = 6.6, 1H; CHH), 2.06 (s, 3H; COCH\textsubscript{3}), 2.03 (s, 3H; COCH\textsubscript{3}), 2.02 (s, 2H; COCH\textsubscript{3}), 1.64 – 1.54 (m, 2H; CH\textsubscript{2}), 1.43 – 1.30 (m, 2H; CH\textsubscript{2}), 0.91 (t, 3J (H,H) = 7.4, 1H; CH\textsubscript{3}); 13\textsuperscript{C} NMR (126 MHz, CDCl\textsubscript{3}): δ 170.2, 170.1, 169.6 (3 x COCH\textsubscript{3}), 166.2 (COPh), 133.2, 129.7 (3 x Ar-CH, overlapping peaks), 129.6 (Ar-C), 128.4 (2 x Ar-CH, overlapping peaks), 95.6 (C-1), 71.0 (C-2), 70.3 (C-3), 69.0(C-4), 68.4 (CH\textsubscript{2}), 67.2 (C-5), 62.6 (C-6), 31.3 (CH\textsubscript{3}), 20.7, 20.6 (COCH\textsubscript{3}, overlapping peaks), 19.2 (CH\textsubscript{2}), 13.7 (CH\textsubscript{3}); IR (film) cm\textsuperscript{-1}: 2959, 2880, 1735, 1374, 1239, 1181, 1084, 1055, 1030, 990, 976, 906, 763, 697; ESI-HRMS calcd for C\textsubscript{23}H\textsubscript{30}O\textsubscript{10}Na 489.1737, found m/z 489.1740 [M+Na]\textsuperscript{+}.

**Butyl 2,3,6-tri-O-acetyl-4-O-benzoyl-\alpha-D-glucopyranoside (81α)**

[α]\textsubscript{D} 5.9 (c 0.6, CH\textsubscript{2}Cl\textsubscript{2}); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 7.99 (dd, 3J (H,H) = 8.2, 1.4, 2H; Ar-H), 7.66 – 7.56 (m, 1H; Ar-H), 7.46 (t, 3J (H,H) = 7.8, 2H; Ar-H), 5.72 (apt.t, 3J (H,H) = 9.8, 1H; H-3), 5.30 (apt.t, 3J (H,H) = 9.8, 1H; H-4), 5.15 (d, 3J (H,H) = 3.7, 1H; H-1), 4.92 (dd, 3J (H,H) = 10.2, 3.7, 1H; H-2), 4.29 (dd, 3J (H,H) = -12.3, 3J (H,H) = 4.8, 1H; H-6a), 4.22 (dd, 3J (H,H) = -12.3, 3J (H,H) = 2.8, 1H; H-6b), 4.16 (dd, J=10.1, 4.8, 2.7, 1H; H-5), 3.74 (dt, 2J (H,H) = -9.9, 3J (H,H) = 6.5, 1H; CHH), 3.49 (dt, 2J (H,H) = -9.9, 3J (H,H) = 6.6, 1H; CHH), 2.16 (s, 3H; COCH\textsubscript{3}), 2.12 (s, 3H; COCH\textsubscript{3}), 1.97 (s, 3H; COCH\textsubscript{3}), 1.67 – 1.58 (m, 2H; CH\textsubscript{2}), 1.46 – 1.34 (m, 2H; CH\textsubscript{2}), 0.96 (t, 3J (H,H) = 7.4, 3H; CH\textsubscript{3}); 13\textsuperscript{C} NMR (126 MHz, CDCl\textsubscript{3}): δ 173.1 , 171.4, 171.2 (3 x COCH\textsubscript{3}), 165.5 (COPh), 133.9, 130.0, 128.7 (5 x Ar-CH, overlapping peaks), 128.5 (Ar-C), 95.5 (C-1), 71.4 (C-2), 70.5 (C-3), 69.3 (C-4), 68.7 (CH\textsubscript{2}), 67.1 (C-5), 63.5 (C-6), 31.3 (CH\textsubscript{3}), 20.9, 20.8 (3 x COCH\textsubscript{3}), 19.2 (CH\textsubscript{2}), 13.8 (CH\textsubscript{3}); IR (film) cm\textsuperscript{-1}: 2963, 2880, 1730, 1367, 1241, 1173, 1084, 1054, 1026, 990, 969, 901, 761, 699; ESI-HRMS calcd for C\textsubscript{23}H\textsubscript{34}O\textsubscript{9}N 484.2183, found m/z 484.2191[M+NH\textsubscript{4}]\textsuperscript{+}.
Butyl 2-O-benzoyl-4,6,3-tri-O-acetyl-α-D-glucopyranoside (86a)

\[\alpha\]D 11.5 (c 0.5, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.08 – 7.95 (m, 2H; Ar-H), 7.59 – 7.53 (m, 1H; Ar-H), 7.44 (t, 3J (H,H) = 7.8, 2H; Ar-H), 5.77 – 5.60 (m, 1H; H-3), 5.21 (d, 3J (H,H) = 3.8, 1H, H-1), 5.14 (apt t, 3J (H,H) = 9.8, 1H; H-4), 5.05 (dd, 3J (H,H) = 10.4, 4.0, 1H; H-2), 4.29 (dd, 3J (H,H) = -12.3, 3J (H,H) = 4.6, 1H; H-6a), 4.15 – 4.11 (m, 1H, H-6b), 4.08 (ddd, 3J (H,H) = 10.1, 4.6, 2.3, 1H; H-5), 3.70 (dt, 3J (H,H) = -9.8, 3J (H,H) = 6.4, 1H; CHH), 3.42 (dt, 3J (H,H) = -9.9, 3J (H,H) = 6.4, 1H; CHH), 2.11 (s, 3H; COCH3), 2.05 (s, 3H; COCH3), 1.95 (s, 3H; COCH3), 1.56 – 1.49 (m, 2H; CH2), 1.31 (h, 3J (H,H) = 7.4, 2H; CH2), 0.82 (t, 3J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 170.7, 170.2, 169.6 (3 x COCH3), 165.7 (COPh), 133.4, 129.8 (3 x Ar-CH, overlapping peaks), 129.1 (Ar-C), 128.5 (2 x Ar-CH, overlapping peaks), 95.8 (C-1), 71.6 (C-2), 70.2 (C-3), 68.6 (C-4), 68.5 (CH2), 67.3 (C-5), 62.0 (C-6), 31.3 (CH2), 20.7 (3 x COCH3), overlapping peaks), 19.1 (CH2), 13.6 (CH3); IR (film) cm⁻¹: 2874, 1725, 1229, 1116, 704; ESI-HRMS calcd for C23H30O10Na 489.1737, found m/z 489.1735 [M+Na]⁺.

Butyl 2,4,6-tri-O-acetyl-3-O-benzoyl-α-D-glucopyranoside (87a)

\[\alpha\]D 2.6 (c 0.1, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 7.98 (d, 3J (H,H) = 7.3, 2H; Ar-H), 7.61 – 7.54 (m, 1H; Ar-H), 7.43 (apt t, 3J (H,H) = 7.8, 2H; Ar-H), 5.75 (apt t, 3J (H,H) = 9.9, 1H; H-3), 5.29 – 5.16 (m, 1H; H-4), 5.10 (d, 3J (H,H) = 3.7, 1H; H-1), 5.04 (dd, 3J (H,H) = 10.2, 3.7, 1H; H-2), 4.28 (dd, 3J (H,H) = 12.2, 3J (H,H) = 4.6, 1H; H-6a), 4.17 – 4.02 (m, 2H; H-6b, H-5 , overlapping peaks), 3.73 (dt, 3J (H,H) = -9.8, 3J (H,H) = 6.6, 1H; CHH), 3.47 (dt, 3J (H,H) = -9.7, 3J (H,H) = 6.5, 1H; CHH), 2.11 (s, 3H; COCH3), 1.97 (s, 3H; COCH3), 1.93 (s, 3H; COCH3), 1.68 – 1.56 (m, 2H; CH2), 1.41 (qd, 3J (H,H) = 7.2, 2.4, 2H; CH2), 0.94 (t, 3J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 170.7, 169.5 (3 x COCH3, overlapping peaks), 165.9 (COPh), 133.4, 129.8 (3 x Ar-CH, overlapping peaks), 129.1 (Ar-C), 128.5 (2 x Ar-CH, overlapping peaks), 95.9 (C-1), 71.0 (C-2), 70.7 (C-3), 68.5 (C-4, CH2, overlapping peaks), 67.4 (C-5), 62.0 (C-6), 31.3 (CH2), 20.8, 20.6, 20.5 (3 x COCH3), 19.2 (CH2), 13.8(CH3); IR (film) cm⁻¹: 2875, 1723, 1451, 1369, 1213,
Experimental data

Chapter 5

1069, 686, 547; ESI-HRMS calcd for C\textsubscript{23}H\textsubscript{34}O\textsubscript{8}N 484.2183, found m/z 484.2189 [M+NH\textsubscript{4}]\textsuperscript{+}.

![Butyl 2,3-di-O-acetyl-4,6-di-O-benzoyl-β-D-glucopyranoside (88α)]

[α]D 60.6 (c 0.3, CH\textsubscript{2}Cl\textsubscript{2}); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 8.00 (ddd, J=7.7, 6.0, 1.5, 4H; Ar-H), 7.64 – 7.49 (m, 2H; Ar-H), 7.41 (dd, \textsuperscript{3}J (H,H) =14.9, 7.5, 4H; Ar-H), 5.75 (apt. t, \textsuperscript{3}J (H,H) =9.9, 1H; H-3), 5.41 (apt.t, \textsuperscript{3}J (H,H) =9.8, 1H; H-4), 5.16 (d, \textsuperscript{3}J (H,H) =3.7, 1H; H-1), 4.95 (dd, \textsuperscript{3}J (H,H) =10.2, 3.7, 1H; H-2), 4.54 (dd, \textsuperscript{2}J (H,H) = -12.2, \textsuperscript{3}J (H,H) = 3.0, 1H; H-6a), 4.42 (dd, \textsuperscript{2}J (H,H) = -12.2, \textsuperscript{3}J (H,H) = 5.4, 1H; H-6b), 4.31 (ddd, \textsuperscript{2}J (H,H) =10.1, 5.3, 2.9, 1H; H-5), 3.76 (dt, \textsuperscript{2}J (H,H) = -9.9, \textsuperscript{3}J (H,H) = 6.6, 1H; C\textsubscript{17}H\textsubscript{3}), 3.49 (dt, \textsuperscript{2}J (H,H) = -9.8, \textsuperscript{3}J (H,H) = 6.7, 1H; C\textsubscript{17}H\textsubscript{3}), 2.13 (s, 3H; COCH\textsubscript{3}), 1.97 (s, 2H; COCH\textsubscript{3}), 1.69 – 1.57 (m, 2H; CH\textsubscript{2}), 1.39 (dt, \textsuperscript{3}J (H,H) =15.0, 7.4, 2H; CH\textsubscript{2}), 0.93 (t, \textsuperscript{3}J (H,H) =7.4, 3H; CH\textsubscript{3}); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): δ 171.4 (2 x COCH\textsubscript{3}, overlapping peaks), 166.5, 165.6 ( 2 x COPh), 133.8, 133.3, 130.0, 129.8 (5 x Ar-CH, overlapping peaks), 129.3 (Ar-C), 128.6 (2 x Ar-CH overlapping peaks), 128.5 (Ar-C), 128.4 (2 x Ar-CH, overlapping peaks), 95.5 (C-1), 71.5 (C-2), 70.6 (C-3), 69.7 (C-4), 68.6 (CH\textsubscript{2}), 67.4 (C-5), 63.3 (C-6), 31.3 (CH\textsubscript{2}), 20.8 (2 x COCH\textsubscript{3}, overlapping peaks), 19.2 (CH\textsubscript{2}), 13.8 (CH\textsubscript{3}); IR (film) cm\textsuperscript{-1}: 2878, 1716, 1232, 1182, 1034, 999, 750, 680 ;ESI-HRMS calcd for C\textsubscript{28}H\textsubscript{36}O\textsubscript{10}N 546.2339, found m/z 546.2341[M+NH\textsubscript{4}]\textsuperscript{+}.

![Butyl 2,3-di-O-benzoyl-4,6-di-O-acetyl-α-D-glucopyranoside (91α)]

[α]D 15.2 (c 0.2, CH\textsubscript{2}Cl\textsubscript{2}); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 7.95 (td, \textsuperscript{3}J (H,H) =8.1, 1.4, 4H; Ar-H), 7.55 – 7.47 (m, 2H; Ar-H), 7.38 (t, \textsuperscript{3}J (H,H) =7.6, 4H; Ar-H), 5.99 (apt. t, \textsuperscript{3}J (H,H) =9.8, 1H; H-3), 5.34 (apt. t, \textsuperscript{3}J (H,H) =9.9, 1H; H-3), 5.29 (d, \textsuperscript{3}J (H,H) =3.6, 1H; H-1), 5.23 (dd, \textsuperscript{3}J (H,H) =10.2, 3.7, 1H; H-2), 4.39 (dd, \textsuperscript{2}J (H,H) = -12.4, \textsuperscript{3}J (H,H) = 4.5, 1H; H-6a), 4.26 (dd, \textsuperscript{2}J (H,H) = -12.3, \textsuperscript{3}J (H,H) = 2.3, 1H; H-
Experimental data

6b), 4.20 (dd, $^3J$ (H,H) =10.3, 4.4, 2.4, 1H; H-5), 3.75 (dt, $^2J$ (H,H) = -9.8, $^3J$ (H,H) = 6.4, 1H; CHH), 3.48 (dt, $^2J$ (H,H) = -9.8, $^3J$ (H,H) = 6.5, 1H; CHH), 2.27 (s, 3H; COCH$_3$), 2.02 (s, 3H; COCH$_3$), 1.63 – 1.51 (m, 2H; CH$_2$), 1.35 (q, $^3J$ (H,H) =7.4, 2H; CH$_2$), 0.84 (t, $^3J$ (H,H) =7.4, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 173.8, 171.2 (2 x COCH$_3$), 166.1, 166.0 (2 x COPh), 133.6, 129.9, 129.8 (6 x Ar-C, overlapping peaks), 128.8, 128.7 (2 x Ar-C), 128.5, 128.4 (2 x Ar-CH), 96.0 (C-1), 71.8 (C-2), 70.7 (C-3), 69.0 (C-4), 68.9 (CH$_2$), 67.1 (C-5), 63.4 (C-6), 31.3 (CH$_3$), 21.1, 20.8 (2 x COCH$_3$), 19.2 (CH$_2$), 13.7 (CH$_3$); IR (film) cm$^{-1}$: 2932, 1717, 1265, 1171, 1069, 1037, 918, 856, 685; ESI-HRMS calcd for C$_{28}$H$_{36}$O$_{10}$N 546.2339, found m/z 546.2352 [M+NH$_4$]$^+$. 

Butyl 2-0-acetyl-3,4,6-tri-O-benzoyl-β-D-glucopyranoside (98a)

[α]$_D$ 36.42 (c 0.1, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): δ 8.03 (dd, $^3J$ (H,H) =8.2, 1.3, 2H; Ar-H), 7.91 (td, $^3J$ (H,H) =8.1, 1.4, 4H; Ar-H), 7.59 – 7.52 (m, 1H; Ar-H), 7.52 – 7.46 (m, H; Ar-H), 7.43 – 7.39 (m, 2H; Ar-H), 7.35 (td, $^3J$ (H,H) =7.8, 2.9, 4H; Ar-H), 5.99 (apt. t, $^3J$ (H,H) =9.8, 1H; H-3), 5.57 (apt. t, $^3J$ (H,H) =9.8, 1H; H-4), 5.21 – 5.02 (m, 2H; H-1, H-2, overlapping peaks), 4.56 (dd, $^2J$ (H,H) = -12.0, $^3J$ (H,H) = 2.8, 1H; H-6a), 4.43 (dd, $^2J$ (H,H) = -12.0, $^3J$ (H,H) = 5.3, 1H; H-6b), 4.38 (ddd, $^3J$ (H,H) =10.2, 5.3, 2.7, 1H; H-5), 3.79 (dt, $^2J$ (H,H) = -9.8, $^3J$ (H,H) = 6.6, 1H; CHH), 3.51 (dt, $^2J$ (H,H) = -9.8, $^3J$ (H,H) = 6.6, 1H; CHH), 1.98 (s, 3H; COCH$_3$), 1.64 (dt, $^3J$ (H,H) =8.7, 6.7, 2H; CH$_2$), 1.42 (p, $^3J$ (H,H) =7.5, 2H; CH$_2$), 0.94 (t, $^3J$ (H,H) =7.4, 2H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 170.3 (COCH$_3$), 166.1, 165.6, 165.3 (3 x COPh), 133.3, 133.2, 133.1, 129.9, 129.7, 129.7 (9 xAr-CH, overlapping peaks), 129.2, 128.9, 128.4 (3 x Ar-C), 128.3 (6 x Ar-CH, overlapping peaks), 95.8 (C-1), 71.2 (C-2), 70.5 (C-3), 69.7 (C-4), 68.5 (CH$_2$), 67.7 (C-5), 63.0 (C-6), 31.3 (CH$_3$), 20.6 (COCH$_3$), 19.2 (CH$_2$), 13.8 (CH$_3$); IR (film) cm$^{-1}$: 2875, 1757, 1492, 1265, 1178, 1068, 964 686; ESI-HRMS calcd for C$_{33}$H$_{38}$O$_{10}$N 608.2496, found m/z 608.2500 [M+NH$_4$]$^+$. 

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Butyl 2,4,6-tri-O-benzoyl-3-O-acetyl-α-D-glucopyranoside (99a)

[α]D 25.4 (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.08 – 7.88 (m, 5H; Ar-H), 7.62 – 7.51 (m, 3H; Ar-H), 7.50 – 7.37 (m, 7H; Ar-H), 5.94 (apt. t, ³J (H,H) = 9.9, 1H; H-3), 5.49 (apt. t, ³J (H,H) = 9.8, 1H; H-4), 5.28 (d, ³J (H,H) = 3.8, 1H; H-1), 5.14 (dd, ²J (H,H) = 10.2, ³J (H,H) = 3.8, 1H; H-2), 4.56 (dd, ²J (H,H) = 7.4, 1H; H-6a), 4.47 – 4.40 (m, 1H; H-6b), 4.37 (dd, ³J (H,H) = 10.2, 5.3, 2.8, 1H; H-5), 3.76 (dt, ²J (H,H) = 9.8, ³J (H,H) = 6.5, 1H; CHH), 3.46 (dt, ²J (H,H) = 9.8, ³J (H,H) = 6.5, 1H; CHH), 1.86 (s, 3H; COCH₂), 1.66 – 1.50 (m, 2H; CH₂), 1.32 (m, 2H; CH₂), 0.81 (t, ³J (H,H) = 7.4, 1H; CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 170.1 (COCH₃), 166.1, 165.7, 165.3 (3 x COPh), 133.5, 133.4, 133.1, 129.9, 129.9, 129.7 (9 x Ar-CH, overlapping peaks), 129.1, 128.9 (3 x Ar-C, overlapping peaks), 128.5, 128.3 (6 x ArCH, overlapping peaks), 95.8 (C-1), 71.8 (C-2), 70.0 (C-3), 69.7 (C-4), 68.6 (CH₂), 67.6 (C-5), 63.1 (C-6), 31.3 (CH₂), 20.6 (COCH₃), 19.2 (CH₂), 13.6 (CH₃); IR (film) cm⁻¹: 2874, 1757, 1584, 1376, 1176, 1010, 892, 617; ESI-HRMS calcd for C₃₅H₃₈O₁₀N 608.2496, found m/z 608.2491[M+NH₄⁺].

Butyl 2,3,4-tri-O-benzoyl-6-O-acetyl-α-D-glucopyranoside (102a)

[α]D 24.8 (c 0.3, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.01 – 7.90 (m, 4H; Ar-H), 7.90 – 7.82 (m, 2H; Ar-H), 7.51 (t, ³J (H,H) = 7.4, 2H; Ar-H), 7.44 – 7.35 (m, 4H; Ar-H), 7.29 (t, ³J (H,H) = 7.8, 2H; Ar-H), 6.15 (apt. t, ³J (H,H) = 9.8, 1H; H-3), 5.58 (apt. t, ³J (H,H) = 9.5, 1H; H-3), 5.33 (d, ³J (H,H) = 3.8, 1H; H-1), 5.27 (dd, ³J (H,H) = 10.2, 3.8, 1H; H-2), 4.34 – 4.28 (CHH), 2.08 (s, 3H; COCH₂), 1.62 – 1.52 (m, 2H, CH₂), 1.37 (q, ³J (H,H) = 7.5, 1H; CH₂), 0.86 (t, ³J (H,H) = 7.4, 4H; CH₂); ¹³C NMR (126 MHz, CDCl₃): δ 170.3 (COCH₃), 166.1, 165.6, 165.3 (3 x COPh), 133.3, 133.2, 133.1, 129.9, 129.7, 129.7 (9 x Ar-CH, overlapping peaks), 129.2, 128.8, 128.6 (3 x Ar-C), 128.3 (6 x Ar-CH, overlapping peaks), 95.8 (C-1), 71.2 (C-3), 70.5 (C-4), 69.7 (C-2), 68.5 (CH₂), 67.7 (C-5), 63.0 (C-6), 31.3 (CH₂), 20.6 (COCH₃), 19.2
Experimental data

Butyl 2,3,6-tri-O-benzoyl-α-D-glucopyranoside (103α)

[α]D 23.3 (c 0.1, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.10 (dd, J(H,H) = 8.3, 1.4, 2H; Ar-H), 8.01 – 7.89 (m, 4H; Ar-H), 7.62 – 7.57 (m, 1H; Ar-H), 7.55 – 7.45 (m, 4H; Ar-H), 7.45 – 7.33 (m, 4H; Ar-H), 6.00 (apt. t, J(H,H) = 9.8, 1H; H-3), 5.42 (apt. t, J(H,H) = 9.9, 1H; H-4), 5.29 (d, J = 3.7, 1H; H-1), 5.22 (dd, J(H,H) = 10.2, 3.7, 1H; H-2), 4.54 (dd, J(H,H) = -12.2, J(H,H) = 5.0, H1; H-6a), 4.45 (dd, J(H,H) = -12.2, J(H,H) = 5.0, H1; H-6b), 4.31 (ddd, J(H,H) = 10.3, 5.0, 2.4, 1H; H-5), 3.76 (dt, J(H,H) = -9.8, J(H,H) = 6.5, 1H; CHH), 3.47 (dt, J(H,H) = -9.8, J(H,H) = 6.5, 1H; CHH), 1.96 (s, 3H; COCH3), 1.62 – 1.51 (m, 2H; CH2), 1.33 (s, 3H; COCH3), 0.82 (t, J(H,H) = 7.4, 1H; CH2); 13C NMR (126 MHz, CDCl3): δ 169.5 (COCH3), 166.2, 165.8 (3 x COPh, overlapping peaks), 133.3, 133.2, 129.9 (5 x Ar-CH, overlapping peaks), 129.2 (4 x Ar-CH, overlapping peaks), 129.2, 129.1 (2 x Ar-C), 128.4 (6 x Ar-CH, overlapping peaks) 95.9 (CH2), 71.9 (C-2), 70.8 (C-3), 68.8 (C-4), 68.6 (CH2), 67.6 (C-5), 62.8 (C-6), 31.3 (CH2), 20.6 (COCH3), 19.2 (CH2), 13.6 (CH3); IR (film) cm⁻¹: 2964, 1721, 1447, 1277, 1087, 983, 670; ESI-HRMS calc for C33H34O10Na 613.2050, found m/z 613.2045 [M+Na]+.

Butyl 2-O-propionyl-3,4,6-tri-O-benzyloxy-D-glucopyranoside (105α)

[α]D 97.7 (c 0.5, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.06 – 7.94 (m, 2H; Ar-H), 7.95 – 7.87 (m, 4H; Ar-H), 7.54 (t, J(H,H) = 7.5, 1H; Ar-H), 7.49 (td, J(H,H) = 7.4, 4.6, 2H; Ar-H), 7.41 (t, J(H,H) = 7.6, 2H; Ar-H), 7.35 (t, J(H,H) = 7.7, 4H; Ar-H), 5.99 (apt. t, J(H,H) = 9.8, 1H; H-3), 5.57 (apt. t, J(H,H) = 9.9, 1H; C-4),
Experimental data

Butyl 2-\textit{O}-isobutyryl-3,4,6-tri-\textit{O}-benzoyl-\textbeta-D-glucopyranoside (106a)

$[\alpha]_D$ 24.7 (c 0.4, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.06 – 8.01 (m, 2H; Ar-H), 7.91 (ddd, $^3$J (H,H) = 18.3, 8.4, 1.4, 4H; Ar-H), 7.57 – 7.52 (m, 1H; Ar-H), 7.52 – 7.45 (m, 2H; Ar-H), 7.45 – 7.36 (m, 2H; Ar-H), 7.37 – 7.33 (m, 4H; Ar-H), 6.01 (apt. t, $^3$J (H,H) = 9.8, 1H; H-3), 5.58 (apt. t, $^3$J (H,H) = 9.8, 1H; H-4), 5.15 (d, $^3$J (H,H) = 3.8, 1H; H-1), 5.11 (ddd, $^3$J (H,H) = 10.1, 3.7, 1H; H-2), 4.56 (dd, $^2$J (H,H) = 12.1, $^2$J (H,H) = 2.8, 1H; H-6a), 4.44 (dd, $^2$J (H,H) = 12.1, $^2$J (H,H) = 5.3, 1H; H-6b), 4.38 (ddd, $^3$J (H,H) = 10.2, 5.4, 2.8, 1H; H-5), 3.78 (dt, $^2$J (H,H) = 9.8, $^3$J (H,H) = 6.7, 1H; CHH), 2.48 (dt, $^2$J (H,H) = 14.0, $^3$J (H,H) = 7.0, 1H; CH(CH$_3$)$_2$), 1.68 – 1.60 (m, 2H; CH$_2$), 1.46 – 1.38 (m, 2H; CH$_2$), 1.04 (dt, $^3$J (H,H) = 7.0, 3H; CH$_3$), 0.97 (d, $^3$J (H,H) = 7.0, 3H; CH$_3$), 0.93 (t, $^3$J (H,H) = 7.4, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 176.4 (COCH(CH$_3$)$_2$), 166.1, 165.6, 165.3 (3 x COPh), 133.3, 133.1, 133.0, 129.9, 129.7 (9 x Ar-CH, overlapping peaks), 129.2, 128.9 (3 x Ar-C, overlapping peaks), 128.4, 128.3 (6 x Ar-CH, overlapping peaks), 95.9 (C-1), 71.1 (C-2), 70.6 (C-3), 69.7 (C-4), 68.5 (CH$_2$), 67.7 (C-5), 63.1 (C-6), 33.8 (CH(CH$_3$)$_2$), 31.4 (CH$_2$), 19.2 (CH$_2$), 18.7 (CH$_2$), 18.6(CH$_3$), 181
13.8(CH₃); IR (film) cm⁻¹: 3294, 3001, 2920, 2865, 1758, 1731, 1709, 1443, 1268, 1093, 1065, 1038, 932, 754; ESI-HRMS calcd for C₃₅H₃₈O₁₀Na 641.2363, found m/z 641.2360 [M+Na].

**Butyl 2-O-pivaloyl-3,4,6-tri-O-benzoyl-α-D-glucopyranoside (107α)**

[α]D 34.4 (c 0.5, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃):  δ 8.03 (d, ³J (H,H) =7.5, 2H; Ar-H), 7.93 (d, ³J (H,H) =8.0, 2H; Ar-H), 7.89 (d, ³J (H,H) =8.1, 4H; Ar-H), 7.48 (td, ³J (H,H) =7.5, 7.0, 2.8, 2H; Ar-H), 7.40 – 7.34 (m, 5H; Ar-H), 6.04 (apt. t, ³J (H,H) =9.9, 1H; H-3), 5.59 (apt. t, ³J (H,H) =9.9, 1H; H-4), 5.16 (d, ³J (H,H) =3.7, 1H; H-1), 5.06 (dd, ³J (H,H) =10.2, 3.8, 1H; H-2), 4.57 (dd, ³J (H,H) =-12.1, ³J (H,H) =2.9, 1H; H-6a), 4.44 (dd, ³J (H,H) =-12.1, ³J (H,H) =5.4, 1H; H-6b), 4.39 (dd, ³J (H,H) =10.3, 5.3, 2.9, 1H; H-5), 3.78 (dt, ³J (H,H) =-9.8, ³J (H,H) =6.4, 1H; CΗΗ), 3.47 (dt, ³J (H,H) =-9.9, ³J (H,H) =6.7, 1H; CΗΗ), 1.66 – 1.52 (m, 2H; CH₂), 1.46 – 1.34 (m, 2H; CH₂), 1.05 (s, 9H; 3 x CH₃, overlapping peaks), 0.93 (t, ³J (H,H) =7.4, 3H; CH₃); ¹³C NMR (126 MHz, CDCl₃): δ  178.1 (COO(CH₃)₃), 165.8, 165.1 (3 x C=O, overlapping peaks), 133.4, 133.2, 133.1, 129.8, 129.7, 129.7 (9 x Ar-C, overlapping peaks), 129.4, 128.8 (3 x Ar-C, overlapping peaks), 128.4, 128.3 (6 x Ar-C, overlapping peaks), 101.2 (C-1), 73.0 (C-3), 72.3 (C-4), 71.9 (C-2), 69.8 (CH₂), 69.6 (C-5), 62.6 (C-6), 38.8 (COOC(CH₃)₃), 31.4 (CH₂), 27.1 (COOC(CH₃)₃, overlapping peaks), 18.9 (CH₂), 13.5 (CH₃); ESI-HRMS calcd for C₃₅H₄₄O₁₀Na 650.2960, found m/z 650.2951 [M+NH₄].

**Butyl 2,3,4,6-tetra-O-methyl-α-D-glucopyranoside (108α)**

[α]D 53.9 (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃):  δ 4.91 (d, ³J (H,H) =3.6, 1H; H-1), 3.68 – 3.55 (m, 6H; H-6, CH, OCH₃, CΗΗ overlapping peaks), 3.55 – 3.49 (m, 4H; CΗΗ, OCH₃, overlapping peaks), 3.49 – 3.45 (m, 5H; C-6b, CH OCH₃, overlapping peaks), 3.40 (s, 3H; OCH₃, overlapping peaks), 3.21 – 3.16 (m, 2H; C-2, CH, overlapping peaks), 1.69 – 1.50 (m, 2H; CH₂), 1.46 – 1.22 (m, 2H; CH₂), 0.90
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$t, J (H,H) = 7.4, 3H; CH_3$; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 96.2 (C-1), 83.3 (C-2), 81.7 (CH), 79.6 (CH), 71.1 (CH$_2$), 69.8(CH), 67.7 (C-6), 60.8, 60.4, 59.2, 58.7 (4 x OCH$_3$), 31.4 (CH$_2$), 19.4 (CH$_2$), 13.8(CH$_3$). IR (film) cm$^{-1}$ : 3937, 2843, 1450, 1381, 1092; ESI-HRMS calcd for C$_{14}$H$_{29}$O$_6$ 385.2202, found m/z 385.2209 [M+H]$^+$. 

Butyl 2-$O$-(4-flourobenzoyl)-3,4,6-tri-$O$-methyl-$\alpha$-D-glucopyranoside (111$\alpha$)  
$[\alpha]_D$ 22.0 (c 0.2, CH$_2$Cl$_2$); 8.10 (dd, $^3J (H,H) = 8.4, 1.2, 2H; Ar-H), 7.60 - 7.53 (m, 2H; Ar-H), 5.11 (d, $^3J (H,H) = 3.6, 1H; H-1), 4.90 - 4.84 (m, 1H; H-2), 3.77 - 3.70 (m, 2H, 2 x CH$_2$ overlapping peaks), 3.69 - 3.60 (m, 3H; H-6a, H-6b, CHH, overlapping peaks), 3.61 (s, 3H; OCH$_3$), 3.54 (s, 3H; OCH$_3$), 3.43 (s, 3H; OCH$_3$), 3.40 (dt, $^3J (H,H) = 10.0, ^2J (H,H) = 6.8, 1H; CHH), 3.6 (apt t, $^3J (H,H) = 9.8, 1H; CH) 1.49 (dq, $^2J (H,H) = 8.2, ^3J (H,H) = 6.6, 2H; CH$_2$), 1.34 - 1.27 (m, 2H; CH$_2$), 0.84 (t, $^3J (H,H) = 7.3, 3H; CH$_2$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 167.1 (d, $^1J (C,F) = 254.0; ArCF), 165.6 (COCl$_3$H$_4$F) 135.1(d, $^3J (C,F) = 9.0; 2 x ArCH, overlapping peaks), 128.1 (d, $^4J (C,F) = 3.1; ArC), 114.9 (d, $^2J (C,F) = 21.9; 2 x Ar-CH, overlapping peaks). 96.4 (C-1), 85.1 (C-2), 80.2 (C-3), 75.1 (C-5), 74.7 (C-4), 71.8 (C-6), 70.4 (CH$_2$), 60.8, 60.6, 59.9 (3 x OCH$_3$), 31.3 (CH$_2$), 18.9 (CH$_2$), 13.6 (CH$_3$); ESI-HRMS calcd for C$_{20}$H$_{31}$O$_7$F 401.1976, found m/z 401.1970 [M+H]$^+$. 

Butyl 2-$O$-acetyl-3,4,6-tri-$O$-methyl-$\alpha$-D-glucopyranoside (112$\alpha$)  
$[\alpha]_D$ 13.3 (c 0.1, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.97 (d, $^3J (H,H) = 3.8, 1H; H-1), 4.69 (dd, $^3J (H,H) = 10.0, 3.7, 1H; H-2), 3.72 - 3.46 (m, 10H; H-6a, H-6b, 2 x CH, CHH, 2 x OCH$_3$, overlapping peaks), 3.47 - 3.36 (m, 4H; CHH, OCH$_3$, overlapping peaks), 3.25 (apt t, $^3J (H,H) = 9.5, 1H; CH), 2.10 (s, 3H; COCH$_3$), 1.54 (d, $^3J (H,H) = 8.2, 2H; CH$_2$), 1.36 (ddt, $^3J (H,H) = 10.6, 7.7, 4.2, 2H; CH$_2$), 0.91 (t, $^3J
(H,H) = 7.3, 3H; CH₃);¹³C NMR (126 MHz, CDCl₃): δ 170.3 (COCH₃), 95.8 (C-1), 81.4 (CH), 79.5 (CH), 73.5 (CH), 71. (C-6), 70.0 (C-H), 67.8 (CH₂), 60.7, 60.5, 59.2 (3 x OCH₃), 31.4 (CH₂), 21.0 (COCH₃), 19.3 (CH₃), 13.8 (CH₃); IR (film) cm⁻¹ 3511, 3260, 2940, 1730, 1268, 1089, 1057, 708; ESI-HRMS calcd for C_{15}H_{28}O_{7}Na 343.1733, found m/z 343.1730[M+Na]⁺.

Butyl 2-O-benzoyl-3,4,6-tri-O-methyl-α-D-glucopyranoside (113α)
[α]D 4.8 (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 8.08 (dd, ᵃJ (H,H) = 8.2, 1.4, 2H; Ar-H), 7.60 – 7.53 (m, 1H; Ar-H), 7.45 (t, ᵃJ (H,H) = 7.7, 2H; Ar-H), 5.09 (d, ᵃJ (H,H) = 3.7, 1H; H-1), 4.95 (dd, ᵃJ (H,H) = 10.0, 3.8, 1H; H-2), 3.77 (apt. t, ᵃJ (H,H) = 9.5, 1H; H-3), 3.73 (ddd, ᵃJ (H,H) = 10.1, 4.0, 2.1, 1H; H-5), 3.69 – 3.60 (m, 4H; H-6a, H-6b, CHHH, overlapping peaks), 3.58 (s, 3H; OCH₃), 3.57 (s, 3H; OCH₃), 3.43 (s, 3H; OCH₃), 3.37 (dt, ᵃJ (H,H) = 10.1, ᵃJ (H,H) = 6.6, 1H; CHH), 3.33 (apt t, ᵃJ (H,H) = 9.6, 1H; H-4) 1.51 (dq, ᵃJ (H,H) = 8.2, ᵃJ (H,H) = 6.6, 2H; CH₂), 1.36 – 1.29 (m, 2H; CH₂), 0.82 (t, ᵃJ (H,H) = 7.4, 3H; CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 165.9 (COPh), 133.1 (Ar-CH), 130.0 (Ar-C), 129.7, 128.4 (4 x Ar-CH, overlapping peaks), 96.1 (C-1), 81.7 (C-3), 79.5 (C-4), 73.9 (C-2), 71.1 (C-6), 70.0 (C-5), 67.9 (CH₂), 60.8, 60.6, 59.3 (3 x OCH₃), 31.4 (CH₂), 19.2 (CH₂), 13.7 (CH₃); IR (film) cm⁻¹ 3254, 2930, 1728, 1314, 1179, 1088, 1027, 960, 687, 547; ESI-HRMS calcd for C_{20}H_{30}O_{7}Na 405.1889, found m/z 405.1898[M+Na]⁺.

Butyl 2-O-pivaloyl-3,4,6-tri-O-methyl-α-D-glucopyranoside (114α)
[α]D 15.8 (c 0.1, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ 4.96 (d, ᵃJ (H,H) = 4.2, 1H; H-1), 4.65 – 4.53 (m, 1H; H-2), 3.67 – 3.57 (m, 5H; 2 x CH, H-6a, H-6b, CHHH, overlapping peaks), 3.56 (s, 3H; OCH₃), 3.54 (s, 3H; OCH₃), 3.40 (s, 3H; OCH₃), 3.37 – 3.29 (m, 1H; CHH), 3.27 – 3.22 (m, 1H; CH), 1.51 (dt, ᵃJ (H,H) = 8.1, 6.7, 2H; CH₂), 1.35 (qd, ᵃJ (H,H) = 7.5, 1.5, 2H; CH₂), 1.22 (s, 9H; 3 x CH₃, overlapping peaks), 0.89 (td, ᵃJ (H,H) = 7.3, 1.5, 3H; CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 177.8
Experimental data

Chapter 5

Butyl 2,3,4-tri-O-benzoyl-6-O-(4-fluorobenzoyl)-α-D-glucopyranoside (117α)

$[\alpha]_D$ 23.3 (c 0.1, CH₂Cl₂); $^1$H NMR (500 MHz, CDCl₃): δ $8.09 - 8.02$ (m, 2H; Ar-H), $8.00 - 7.97$ (m, 2H; Ar-H), $7.94$ (d, $^3J$(H,H) = 7.7, 2H; Ar-H), $7.46 - 7.33$ (m, 5H; Ar-H), $7.29$ (t, $^3J$(H,H) = 7.7, 2H; Ar-H), $7.09$ (t, $^3J$(H,H) = 8.6, 2H; Ar-H), $6.19$ (apt. t, $^3J$(H,H) = 9.8, 1H; H-3), $5.67$ (apt. t, $^3J$(H,H) = 9.8, 1H; H-3), $5.34$ (d, $^3J$(H,H) = 3.8, 1H; H-1), $5.30$ (dd, $^3J$(H,H) = 10.1, 3.7, 1H; H-2), $4.67 - 4.56$ (m, 1H; H-6a), $4.52 - 4.40$ (m, 2H; H-6b, H-5), $3.79$ (dt, $^3J$(H,H) = -9.9, $^3J$(H,H) = 6.5, 1H; CHH), $3.50$ (dt, $^3J$(H,H) = -9.9, $^3J$(H,H) = 6.6, 1H; CHH), $1.66 - 1.56$ (m, 2H; CH₂), $1.35$ (h, $^3J$(H,H) = 7.4, 2H; CH₂), $0.84$ (t, 7.4, 2H); $^{13}$C NMR (126 MHz, CDCl₃): δ $166.3$ (d, $^1J$(C,F) = 131.6; Ar-CF), $165.8$, $165.3$, $165.2$ (3 x COPh), $164.8$ (COC₆H₄F), $133.4$, $133.3$, $133.1$ (3 x Ar-CH), $132.3$ (d, $^3J$(C,F) = 9.5; 2 x ArCH, overlapping peaks), $129.9$, $129.8$, $129.7$ (6 x Ar-CH, overlapping peaks), $129.2$, $129.0$, $128.9$ (3 x Ar-C), $128.4$, $128.3$ (6 x Ar-CH, overlapping peaks), $125.9$ (d, $^4J$(C,F) = 2.8; Ar-C), $115.5$ (d, $^2J$(C,F) = 22.0; 2 x Ar-CH, overlapping peaks), $96.0$ (C-1), $72.0$ (C-2), $70.5$ (C-3), $69.6$ (C-4), $68.7$ (CH₂), $67.6$ (C-5), $63.2$ (C-6), $31.3$ (CH₂), $19.2$ (CH₂), $13.7$ (CH₃); IR (film) cm⁻¹: 2960, 1721, 1602, 1259, 1089, 1067, 1026, 706; ESI-HRMS calcd for C₁₈H₁₄O₇NaF 693.2112, found m/z 693.2124 [M+Na]+.

Butyl 2,3,4-tri-O-benzoyl-6-O-(4-chlorobenzoyl)-α-D-glucopyranoside (118α)

$[\alpha]_D$ 23.3 (c 0.1, CH₂Cl₂); $^1$H NMR (500 MHz, CDCl₃): δ $8.09 - 8.02$ (m, 2H; Ar-H), $8.00 - 7.97$ (m, 2H; Ar-H), $7.94$ (d, $^3J$(H,H) = 7.7, 2H; Ar-H), $7.87$ (d, $^3J$(H,H) = 7.8, 2H; Ar-H), $7.51$ (td, $^3J$(H,H) = 7.3, 5.3, 2H; Ar-H), $7.46 - 7.33$ (m, 5H; Ar-H), $7.29$ (t, $^3J$(H,H) = 7.7, 2H; Ar-H), $7.09$ (t, $^3J$(H,H) = 8.6, 2H; Ar-H), $6.19$ (apt. t, $^3J$(H,H) = 9.8, 1H; H-3), $5.67$ (apt. t, $^3J$(H,H) = 9.8, 1H; H-3), $5.34$ (d, $^3J$(H,H) = 3.8, 1H; H-1), $5.30$ (dd, $^3J$(H,H) = 10.1, 3.7, 1H; H-2), $4.67 - 4.56$ (m, 1H; H-6a), $4.52 - 4.40$ (m, 2H; H-6b, H-5), $3.79$ (dt, $^3J$(H,H) = -9.9, $^3J$(H,H) = 6.5, 1H; CHH), $3.50$ (dt, $^3J$(H,H) = -9.9, $^3J$(H,H) = 6.6, 1H; CHH), $1.66 - 1.56$ (m, 2H; CH₂), $1.35$ (h, $^3J$(H,H) = 7.4, 2H; CH₂), $0.84$ (t, 7.4, 2H); $^{13}$C NMR (126 MHz, CDCl₃): δ $166.3$ (d, $^1J$(C,F) = 131.6; Ar-CF), $165.8$, $165.3$, $165.2$ (3 x COPh), $164.8$ (COC₆H₄Cl), $133.4$, $133.3$, $133.1$ (3 x Ar-CH), $132.3$ (d, $^3J$(C,F) = 9.5; 2 x ArCH, overlapping peaks), $129.9$, $129.8$, $129.7$ (6 x Ar-CH, overlapping peaks), $129.2$, $129.0$, $128.9$ (3 x Ar-C), $128.4$, $128.3$ (6 x Ar-CH, overlapping peaks), $125.9$ (d, $^4J$(C,F) = 2.8; Ar-C), $115.5$ (d, $^2J$(C,F) = 22.0; 2 x Ar-CH, overlapping peaks), $96.0$ (C-1), $72.0$ (C-2), $70.5$ (C-3), $69.6$ (C-4), $68.7$ (CH₂), $67.6$ (C-5), $63.2$ (C-6), $31.3$ (CH₂), $19.2$ (CH₂), $13.7$ (CH₃); IR (film) cm⁻¹: 2960, 1721, 1602, 1259, 1089, 1067, 1026, 706; ESI-HRMS calcd for C₁₈H₁₄O₇NaCl 679.1622, found m/z 679.1632 [M+Na]+.

Butyl 2,3,4-tri-O-benzoyl-6-O-(4-chlorobenzoyl)-α-D-glucopyranoside (118α)
[α]D 37.8 (c 0.1, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.01 – 7.96 (m, 3H; Ar-H), 7.95 – 7.91 (m, 2H; Ar-H), 7.91 – 7.81 (m, 2H; Ar-H), 7.50 (dd, J = 7.4, 5.2, 2H; Ar-H), 7.45 – 7.33 (m, 10H; ArH), 6.20 (apt. t, 3J (H, H) = 9.8, 1H; H-3), 5.68 (apt. t, 2J (H, H) = 9.6, 1H; H-4), 5.34 (d, 3J (H, H) = 3.7, 1H; H-1), 5.30 (dd, 2J (H, H) = 10.1, 3.7, 1H; H-2), 4.60 (dd, 2J (H, H) = -11.7, 3J (H, H) = 2.5, 1H; H-6a), 4.53 – 4.35 (m, 2H; H-6b, H-5, overlapping peaks), 3.80 (dt, 2J (H, H) = -10.0, 3J (H, H) = 6.5, 1H; CHH), 3.50 (dt, 2J (H, H) = -9.9, 3J (H, H) = 6.6, 1H; CHH), 1.71 – 1.52 (m, 2H; CH2), 1.35 (q, 3J (H,H) = 7.5, 1H; CH2), 0.84 (t, 3J (H,H) = 7.4, 3H; CH3). 13C NMR (126 MHz, CDCl3): δ 165.8 (COC6H4Cl, COPh, overlapping peaks), 165.8, 165.3 (2 x COPh), 139.6, 133.4, 133.3, 133.1, 129.1, 129.8, 129.7 (11 x Ar-CH, overlapping peaks), 129.2, 129.0, 128.8 (3 x Ar-C), 128.7, 128.4, 128.3 (8 x Ar-CH, overlapping peaks), 128.1 (Ar-C), 96.0 (C-1), 72.0 (C-2), 70.5 (C-3), 69.6 (C-4), 68.7 (CH2), 67.6 (C-5), 63.3 (C-6), 31.3 (CH2), 19.2 (CH2), 13.7 (CH3); IR (film) cm^−1: 2973, 1743, 1582, 1511, 1421, 1269, 1034, 1011, 789; ESI-HRMS cale d for C38H35O10NaCl 709.1816, found m/z 709.1817 [M+Na]^+.

Butyl 2,3,4-tri-O-benzoyl-6-O-(4-methoxybenzoyl)-α-D-glucopyranoside (120a)

[α]D 35.1 (c 0.1, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.03 – 7.96 (m, 4H; Ar-H), 7.96 – 7.90 (m, 2H; Ar-H), 7.89 – 7.83 (m, 2H; Ar-H), 7.50 (q, 3J (H, H) = 7.6, 2H; Ar-H), 7.46 – 7.40 (m, 1H; Ar-H), 7.37 (dd, 2J (H, H) = 14.8, 7.5, 4H; Ar-H), 7.29 (t, 3J (H, H) = 7.7, 2H; Ar-H), 6.93 – 6.69 (m, 2H; Ar-H), 6.18 (apt. t, 3J (H, H) = 9.9, 1H; H-3), 5.67 (apt. t, 3J (H, H) = 9.7, 1H; H-4), 5.34 (d, 3J (H, H) = 3.7, 1H; H-1), 5.29 (dd, 2J (H, H) = 10.1, 3.7, 1H; H-2), 4.62 – 4.51 (m, 1H; H-6a), 4.47 – 4.38 (m, 2H; H-6b, H-5, overlapping peaks), 3.85 (s, 3H; OCH3), 3.80 (dt, 2J (H, H) = -9.9, 3J (H, H) = -9.9, 3J (H, H) = 6.6, 1H; CHH), 1.67 – 1.53 (m, 2H; CH2), 1.35 (q, 3J (H, H) = 7.5, 2H; CH2), 0.83 (t, 3J (H, H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 165.9 (COPh), 165.8 (COPh, COC6H4(OCH3), overlapping peaks), 165.3 (COPh), 163.5 (Ar-C(OCH3)), 133.1, 133.3, 131.8, 129.9, 129.7 (11 x Ar-CH, overlapping peaks), 129.2, 129.1, 128.9 (3 x ArC), 128.4, 128.2 (6 x Ar-CH, overlapping peaks), 122.1 (Ar-C), 113.6 (2 x Ar-CH,
Experimental data

overlapping peaks), 96.0 (C-1), 72.1 (C-2), 70.6 (C-3), 69.6 (C-4), 68.6 (CH$_2$), 67.8 (C-5), 62.8 (C-6), 55.4 (OCH$_3$), 31.3 (CH$_2$), 19.2 (CH$_2$), 13.7 (CH$_3$); IR (film) cm$^{-1}$: 2962, 1117, 1604, 1511, 1248, 1166, 1088, 1069, 1025, 845, 765, 694; ESI-HRMS calcd for C$_{39}$H$_{38}$O$_{11}$Na 705.2312, found m/z 705.2318 [M+Na]$^+$.  

Butyl 2,3,4-tri-O-benzoyl-6-O-(4-methylbenzoyl)-α-D-glucopyranoside (119α)

[α]$_D$ 19.6 (c 0.1, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): δ 8.02 – 7.95 (m, 2H; Ar-H), 7.96 – 7.90 (m, 4H; Ar-H), 7.87 (dd, $^3$J (H,H) = 8.3, 1.4, 2H; Ar-H), 7.55 – 7.47 (m, 2H; Ar-H), 7.39 (ddt, $^3$J (H,H) = 20.6, 13.0, 7.6, 5H; Ar-H), 7.29 (t, $^3$J (H,H) = 7.7, 2H; Ar-H), 7.21 (d, $^3$J (H,H) = 7.9, 2H; Ar-H), 6.18 (apt. t, $^3$J (H,H) = 9.8, 1H; H-3), 5.66 (apt. t, $^3$J (H,H) = 9.6, 1H; H-4), 5.34 (d, $^3$J (H,H) = 3.7, 1H; H-1), 5.29 (dd, $^3$J (H,H) = 10.1, 3.8, 1H; H-2), 4.60 – 4.55 (m, 1H; H-6a), 4.49 – 4.40 (m, 2H; H-6b, H-5, overlapping peaks), 3.80 (dt, $^3$J (H,H) = 9.9, $^3$J (H,H) = 6.5, 1H; CHH), 3.49 (dt, $^3$J (H,H) = 9.9, $^3$J (H,H) = 6.6, 1H; CHH), 2.40 (s, 3H; CH$_3$), 1.64 – 1.55 (m, 2H; CH$_2$), 1.35 (p, $^3$J (H,H) = 7.4, 2H; CH$_2$), 0.83 (t, $^3$J (H,H) = 7.4, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 166.2 (COC$_6$H$_4$(CH$_3$)$_2$), 165.8, 165.3 (3 x COPh, overlapping peaks), 143.8 (Ar-C(CH$_3$)$_2$), 133.3, 133.3, 133.0, 129.9, 129.7, 129.7 (11 x Ar-CH, overlapping peaks), 129.2 (Ar-C), 129.1 (2 x Ar-CH, Ar-C, overlapping peaks), 128.9 (Ar-C), 128.4, 128.2 (6 x Ar-CH, overlapping peaks), 127.0 (Ar-C), 95.9 (C-1), 72.1 (C-2), 70.6 (C-3), 69.6 (C-4), 68.6 (CH$_2$), 67.8 (C-5), 62.9 (C-6), 31.3 (CH$_2$), 21.7 (CH$_3$), 19.2 (CH$_2$), 13.7 (CH$_3$); IR (film) cm$^{-1}$: 3007, 1725, 1594, 1538, 1217, 1141, 1037, 1020, 864, 786, 681; ESI-HRMS calcd for C$_{39}$H$_{38}$O$_{10}$Na 689.2363, found m/z 689.2374 [M+Na]$^+$.  

Butyl 2,3,4,6-tetra-O-propionyl-α-D-glucopyranoside (121α)
Butyl 2,3,4,6-tetra-O-isobutyryl-α-D-glucopyranoside (122a)

[α]D 19.8 (c 0.3, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 5.54 (apt. t, 3J (H,H) = 9.8, 1H; H-3), 5.08 (apt. t, 3J (H,H) = 9.9, 1H; H-3), 5.05 (d, 3J (H,H) = 3.8, 1H; H-1), 4.84 (dd, 3J (H,H) = 10.2, 3.8, 1H; H-2), 4.17 (dd, 3J (H,H) = -12.2, 3J (H,H) = 5.1, 1H; H-6a), 4.11 (dd, 3J (H,H) = -12.4, 3J (H,H) = 2.1, 1H; H-6b), 4.02 (dd, 3J (H,H) = 10.3, 5.0, 2.1, 1H; H-5), 3.68 (dt, 3J (H,H) = -9.8, 3J (H,H) = 6.5, 1H; CHH), 3.40 (dt, 3J (H,H) = -9.8, 3J (H,H) = 6.6, 1H; CHH), 2.59 (p, 3J (H,H) = 7.0, 1H; CH), 2.55 – 2.42 (m, 3H; 3 x CH, overlapping peaks), 1.62 – 1.32 (m, 2H; CH2), 1.43 – 1.15 (m, 2H; CH2), 1.23 – 1.15 (m, 6H, 2 x CH2, overlapping peaks), 1.15 – 1.03 (m, 18H; 6 x CH3, overlapping peaks), 0.92 (t, 3J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 176.7, 176.2, 175.9, 175.4 (4 x COCH(CH3)2), 95.6 (C-1), 71.0 (C-2), 69.7 (C-3), 68.3 (C-4), 68.0 (CH2), 67.5 (C-5), 61.8 (C-6), 33.9, 33.8 (4 x COCH(CH3)2, overlapping peaks), 31.3 (CH2), 19.2 (4 x CH3, overlapping peaks), 18.9 (CH2, 2 x CH3, overlapping peaks), 18.8 (2 x CH3, overlapping peaks), 13.7 (CH3); IR (film) cm⁻¹: 2987, 1768, 1606, m 1453, 1167, 1068, 891, 759, 636; ESI-HRMS calcd for C26H44O10Na 539.2836, found m/z 539.2836 [M+Na]+.

\[\text{Butyl 2,3,4,6-tetra-O-isobutyryl-}\alpha-\text{D-glucopyranoside (122a)}\]
Butyl 2,3,4,6-tetra-O-pivaloyl-α-D-glucopyranoside (123α)

[α]D 11.8 (c 0.1, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 5.55 (apt. t, 3J (H,H) = 9.7, 1H; H-3), 5.11 – 4.98 (m, 2H; H-1, H-4, overlapping peaks), 4.78 (dd, 2J (H,H) = 10.0, 3.8, 1H; H-2), 4.14 (dd, 2J (H,H) = -12.2, 3J (H,H) = 1.9, 1H; H-6a), 4.08 – 3.99 (m, 2H; H-6b, H-5, overlapping peaks), 3.67 (dt, 2J (H,H) = -9.7, 3J (H,H) = 6.4, 1H, C\H\H), 3.36 (dt, 2J (H,H) = -9.8, 3J (H,H) = 6.7, 1H; C(CH3)3), 1.62 – 1.49 (m, 2H; C\H\2), 1.42 – 1.31 (m, 2H; CH2), 1.21 (s, 9H; C(CH3)3), 1.15 (s, 19H; 2 x C(CH3)3), 0.91 (t, 3J (H,H) = 7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 178.0, 177.7, 177.0, 176.6 (4 x COC(CH3)3), 95.4 (C-1), 71.3 (C-2), 69.7 (C-3), 68.1 (CH2), 68.0 (C-4), 67.5 (C-5), 62.0 (C-6), 38.8, 38.7 (4 x C(CH3)3, overlapping peaks), 31.4(CH2)2, 27.2, 27.1, 27.0 (12 x CH3, overlapping peaks), 19.2 (CH2), 13.7 (CH3); IR (film) cm-1: 2961, 1718, 1600, 1514, 1253, 1169, 1094, 1070, 891, 788; ESI-HRMS calcd for C30H52O10Na 595.3458, found m/z 595.3459 [M+Na]⁺.

Butyl 2,3,4,6-tetra-O-(4-chlorobenzoyl)-α-D-glucopyranoside (124α)

[α]D 56.3 (c 0.8, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.00 – 7.93 (m, 2H; Ar-H), 7.93 – 7.88 (m, 2H; Ar-H), 7.87 – 7.81 (m, 2H; Ar-H), 7.81 – 7.75 (m, 2H; Ar-H), 7.42 – 7.22 (m, 8H; Ar-H), 6.10 (apt. t, 3J (H,H) =9.8, 1H; H-3), 5.61 (apt. t, 3J (H,H) =9.7, 1H; H-4), 5.39 – 5.16 (m, 2H; H-1, H-2, overlapping peaks), 4.57 (dd, 2J (H,H) = -11.8, 3J (H,H) = 2.6, 1H; H-6a), 4.52 – 4.35 (m, 2H; H-6b, H-5), 3.79 (dt, 2J (H,H) = -9.8, 3J (H,H) = 6.4, 1H; C\H\H), 3.49 (dt, 2J (H,H) = -9.9, 3J (H,H) = 6.6, 1H; C\H\H), 1.67 – 1.56 (m, 2H; CH2), 1.35 (h, 3J (H,H) = 7.4, 2H; CH2), 0.85 (t, 3J (H,H) =7.3, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 165.2, 164.9, 164.8, 164.4 (4 x
Butyl 2,3,4,6-tetra-O-(4-flourobenzoyl)-α-D-glucopyranoside (125a)

[α]D 78.9 (c 0.5, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.09 – 8.03 (m, 2H; Ar-H), 8.02 – 7.96 (m, 2H; Ar-H), 7.94 (dd, 3J (H,H) = 8.6, 5.4, 2H; Ar-H), 7.87 (dd, 2J (H,H) = 8.7, 5.5, 2H; Ar-H), 7.14 – 7.00 (m, 6H; Ar-H), 6.96 (t, 3J (H,H) = 8.5, 2H; Ar-H), 6.12 (apt. t, 3J (H,H) = 9.8, 1H; H-3), 5.63 (apt. t, 3J (H,H) = 9.7, 1H; H-4), 5.35 – 5.24 (m, 2H; H-1, H-2), 4.63 – 4.53 (m, 1H; H-6a), 4.51 – 4.37 (m, 2H; H-6b, H-5, overlapping peaks), 3.79 (dt, 2J (H,H) = -9.9, 3J (H,H) = 6.5, 1H; C(HH), 3.50 (dt, 2J (H,H) = -9.8, 3J (H,H) = 6.6, 1H; C(HH), 1.68 – 1.42 (m, 2H; C(H2), 1.35 (h, 3J (H,H) = 7.4, 2H; C(H2), 0.84 (t, 3J (H,H) = 7.4, 3H; C(H3)); 13C NMR (126 MHz, CDCl3): δ 167.40 – 164.53 (m; 4 x Ar-CF, 2 x COC6H4F, overlapping peaks), 164.3 (COC6H4F), 133.30 – 131.33 (m; 4 x Ar-CH, overlapping peaks), 115.78 – 115.35 (m; 4 x Ar-CH, overlapping peaks), 96.0 (C-1), 71.9 (C-2), 70.8 (C-3), 69.6 (C-4), 68.7 (CH2), 67.6 (C-5), 63.0 (C-6), 31.3 (CH2), 19.2 (CH2), 13.6 (CH3); IR (film) cm⁻¹: 2974, 1724, 1603, 1267, 1153, 1068, 759; ESI-HRMS calcd for C38H32O10Cl4Na 747.1829, found m/z 747.1838 [M+Na]^+. 
Butyl 2,3,4,6-tetra-O-(4-methoxybenzoyl)-α-D-glucopyranoside (126α)

$[\alpha]_D$ 101.9 (c 1.8, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDC$_3$): $\delta$ 8.02 – 7.97 (m, 2H; Ar-H), 7.96 – 7.92 (m, 2H; Ar-H), 7.90 – 7.87 (m, 2H; Ar-H), 7.86 – 7.80 (m, 2H; Ar-H), 6.92 – 6.87 (m, 2H; Ar-H), 6.86 – 6.83 (m, 2H; Ar-H), 6.83 – 6.80 (m, 2H; Ar-H), 6.78 – 6.73 (m, 2H; Ar-H), 6.11 (apt. t, $^3$J (H,H) = 9.8, 1H; H-3), 5.60 (apt. t, $^3$J (H,H) = 9.5, 1H; H-4), 5.31 (d, $^3$J (H,H) = 3.7, 1H; H-1), 5.23 (dd, $^3$J (H,H) = 10.2, 3.7, 1H; H-2), 4.59 – 4.53 (m, 1H; H-6a), 4.45 – 4.38 (m, 2H; H-6b, H-5, overlapping peaks), 3.85 (s, 3H; OCH$_3$), 3.81 (s, 3H; OCH$_3$), 3.80 (s, 3H; OCH$_3$), 3.80 – 3.77 (m, 1H; CHH), 3.75 (s, 3H; OCH$_3$), 3.48 (dt, $^2$J (H,H) = -9.8, $^3$J (H,H) = 6.6, 1H; CHH), 1.65 – 1.54 (m, 2H; CH$_2$), 1.34 (h, $^3$J (H,H) = 7.4, 2H; CH$_2$), 0.84 (t, $^3$J (H,H) = 7.4, 3H; CH$_3$); $^{13}$C NMR (126 MHz, CDC$_3$): $\delta$ 165.9, 165.6, 165.4, 165.0 (4 x COC-$_4$H$_4$(OCH$_3$) 163.6, 163.4 (4 X Ar-C(OCH$_3$), overlapping peaks), 132.0, 131.8 (8 x Ar-CH$_3$, overlapping peaks), 122.2, 121.7, 121.5, 121.4 (4 x Ar-C, overlapping peaks), 113.6, 113.5 (8 x Ar-CH$_3$, overlapping peaks), 96.1 (C-1), 71.9 (C-2), 70.3 (C-3), 69.5 (C-4), 68.5 (C$_2$H$_2$), 67.8 (C-5), 63.0 (C-6), 55.4, 55.3 (4 x OCH$_3$, overlapping peaks), 31.3 (CH$_2$), 19.2 (CH$_2$), 13.7 (CH$_3$); IR (film) cm$^{-1}$: 2987, 1691, 1615, 1524, 1256, 1060, 1021, 857, 766; ESI-HRMS calcd for C$_{42}$H$_{44}$O$_{14}$Na 795.2629, found m/z 795.2633 [M+Na]$^+$. 

Experimental data

Chapter 5
Butyl 2,3,4,6-tetra-O-(4-methylbenzoyl)-\(\alpha\)-D-glucopyranoside (127a)

\([\alpha]_D\) 98.1 (c 0.9, CH\(_2\)Cl\(_2\); \(^1\)H NMR (500 MHz, CDC\(_3\)): \(\delta\) 7.99 – 7.89 (m, 2H; Ar-H), 7.90 – 7.83 (m, 2H; Ar-H), 7.84 – 7.80 (m, 2H; Ar-H), 7.78 – 7.74 (m, 2H; Ar-H), 7.24 – 7.20 (m, 2H; Ar-H), 7.18 – 7.12 (m, 4H; Ar-H), 7.11 – 7.06 (m, 2H; Ar-H)

6.15 (apt. t, \(^3\)J (H,H) = 9.9, 1H; H-3), 5.61 (apt. t, \(^3\)J (H,H) = 9.7, 1H; H-4), 5.32 (d, \(^3\)J (H,H) = 3.8, 1H; H-1), 5.25 (dd, \(^3\)J (H,H) = 10.1, 3.7, 1H; H-2), 4.63 – 4.53 (m, 1H; H-6a), 4.50 – 4.37 (m, 2H; H-6b, H-5, overlapping peaks), 3.78 (dt, \(^3\)J (H,H) = -9.8, \(^2\)J (H,H) = 6.5, 1H; CHH), 3.47 (dt, \(^3\)J (H,H) = -9.9, \(^3\)J (H,H) = 6.6, 1H; CHH), 2.40 (s, 3H; C\(_3\)H), 2.35 (s, 3H; C\(_3\)H), 2.35 (s, 3H; C\(_3\)H), 2.29 (s, 3H; C\(_3\)H), 1.67 – 1.52 (m, 2H; CH\(_2\)), 1.34 (q, \(^3\)J (H,H) = 7.4, 2H; CH\(_2\)), 0.83 (t, \(^3\)J (H,H) = 7.4, 1H; CHH)

\(^1\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 166.2, 165.9, 165.8, 165.3 (4 x COC\(_6\)H\(_4\)(CH\(_3\))), 144.0, 143.7 (4 x Ar-C(CH\(_3\)) overlapping peaks), 129.9, 129.7, 129.1, 129.0, 128.9 (16 x Ar-CH, overlapping peaks), 127.0, 126.5, 126.4, 126.2 (4 x Ar-C), 96.0 (C-1), 72.0 (C-2), 70.3 (C-3), 69.5 (C-4), 68.6 (CH\(_2\)), 67.8 (C-5), 63.0 (C-6), 31.3 (CH\(_2\)), 21.7, 21.6 (4 x CH\(_3\), overlapping peaks), 19.2 (CH\(_2\)), 13.7 (CH\(_3\)); IR (film) cm\(^{-1}\): 2962, 1718, 1604, 1511, 1249, 1167, 1088, 1068, 1025, 845, 766; ESI-HRMS calcd for C\(_{42}\)H\(_{44}\)O\(_{10}\)Na 731.2832, found m/z 731.2830 [M+Na]\(^+\).

Butyl 2,3,4,6-tetra-O-(4-tert-butylbenzoyl)-\(\alpha\)-D-glucopyranoside (128a)

\([\alpha]_D\) 133.4 (c 1.2, CH\(_2\)Cl\(_2\); \(^1\)H NMR (500 MHz, CDC\(_3\)): \(\delta\) 8.02 – 7.93 (m, 2H; Ar-H), 7.94 – 7.87 (m, 4H; Ar-H), 7.83 (d, \(^3\)J (H,H) = 8.5, 2H; Ar-H), 7.47 – 7.43 (m, 2H; Ar-H), 7.43 – 7.36 (m, 4H; Ar-H), 7.34 – 7.29 (m, 2H; Ar-H), 6.17 (apt. t, \(^3\)J (H,H) = 9.8, 1H; H-3), 5.66 (apt. t, \(^3\)J (H,H) = 9.4, 1H; H-4), 5.32 (d, \(^3\)J (H,H) = 3.7, 1H; H-1), 5.27 (dd, \(^3\)J (H,H) = 10.2, 3.8, 1H; H-2), 4.64 – 4.53 (m, 1H; H-6a), 4.48 – 4.35 (m, 2H; H-6b, H-5, overlapping peaks), 3.78 (dt, \(^3\)J (H,H) = -9.8, \(^3\)J (H,H) = 6.6, 1H; CHH), 3.48 (dt, \(^3\)J (H,H) = -9.8, \(^3\)J (H,H) = 6.6, 1H; CHH), 1.65 – 1.54 (m, 2H; CH\(_2\)), 1.37 – 1.32 (m, 11H; C(CH\(_3\))\(_3\), CH\(_2\), overlapping peaks), 1.30 (s, 18H; 2 x
C(CH$_3$)$_3$, overlapping peaks), 1.25 (s, 9H; C(CH$_3$)$_3$), 0.83 (t, $^3J$ (H,H) = 7.4, 1H; CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 166.2, 165.8, 165.7, 165.3 (4 x COC$_6$H$_4$Bu), 157.0, 156.9, 156.7, 156.6 (4 x Ar-C(Bu), overlapping peaks), 129.8, 129.6 (8 x Ar-CH, overlapping peaks), 127.0, 126.6, 126.4, 126.2 (4 x Ar-C), 125.3, 125.2 (8 x Ar-CH, overlapping peaks), 96.0 (C-1), 72.0 (C-2), 70.4 (C-3), 69.4 (C-4), 68.6 (CH$_2$), 67.9 (C-5), 62.9 (C-6), 35.1, 35.0 (4 x C(CH$_3$)$_3$, overlapping peaks), 31.4 (CH$_2$), 31.1, 31.0 (12 x CH$_3$, overlapping peaks), 19.2 (CH$_2$), 13.7 (CH$_3$); ESI-HRMS calcd for C$_{54}$H$_{68}$O$_{10}$Na 899.4710, found m/z 899.4719[M+Na]$^+$.

Butyl 2,3,4,6-tetra-O-(1-napthoyl)-$\alpha$-D-glucopyranoside (129a)

$[\alpha]_D$ 18.4 (c 0.5, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.97 (d, $^3J$ (H,H) = 8.6, 1H; Ar-H), 8.93 (d, $^3J$ (H,H) = 8.5, 1H; Ar-H), 8.73 (d, $^3J$ (H,H) = 8.3, 1H; Ar-H), 8.51 (d, $^3J$ (H,H) = 8.7, 1H; Ar-H), 8.37 – 8.19 (m, 2H; Ar-H), 8.07 – 7.92 (m, 4H; Ar-H), 7.92 – 7.78 (m, 3H; Ar-H), 7.71 (d, $^3J$ (H,H) = 8.1, 1H; Ar-H), 7.65 – 7.59 (m, 1H; Ar-H), 7.58 – 7.14 (m, 12H; Ar-H), 6.49 (ddd, $^3J$ (H,H) = 11.2, 9.6, 1.6, 1H; H-4), 5.95 (apt. t, $J$=9.9, 1H; H-3), 5.61 – 5.46 (m, 2H; H-1, H-2, overlapping peaks), 4.78 – 4.73 (m, 2H; H-6), 4.65 (dt, $^3J$ (H,H) = 10.2, 4.0, 1H; H-5), 3.96 – 3.84 (m, 1H; CHH), 3.60 (dt, $^5J$ (H,H) = 9.8, $^3J$ (H,H) = 6.6, 1H; CHH), 1.66 (dt, $^3J$ (H,H) = 8.9, 6.5, 2H; CH$_2$), 1.43 – 1.33 (m, 2H; CH$_2$), 0.84 (t, $^3J$ (H,H) = 7.4, H; CH$_2$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 167.0, 166.7, 166.6, 166.0 (4 x COAr), 134.0, 133.9 (2 x Ar-CH), 133.8, 133.7 (3 x Ar-C, overlapping peaks), 133.6 (Ar-CH), 133.5 (Ar-C), 133.3 (Ar-CH), 131.4, 131.3, 131.2, 131.0 (4 x Ar-C), 130.6, 130.6, 129.9, 128.5, 128.4, 128.3, 127.9, 127.8, 127.5 (10 x Ar-CH, overlapping peaks), 126.5, 126.4 (3 x Ar-C), 126.2, 126.2, 126.0, 125.8, 125.6 (6 x Ar-CH, overlapping peaks), 125.6 (2 x
Experimental data

Chapter 5

Ar-C, Ar-CH, overlapping peaks), 125.5, 125.2, 124.5, 124.5, 124.4 (6 x Ar-CH, overlapping peaks), 96.2 (C-1), 72.1 (C-2), 70.6 (C-3), 69.7 (C-4), 68.8 (CH2), 67.9 (C-5), 63.3 (C-6), 31.5 (CH2), 19.3 (CH2), 13.7 (CH3); ESI-HRMS calcd for C54H44O10Na 875.2832, found m/z 875.2838 [M+Na]+.

Butyl 2,3,4,6-tetra-O-(2-napthoyl)-α-D-glucopyranoside (130a)

[α]D 164.2 (c 1.6, CH2Cl2); 1H NMR (500 MHz, CDCl3): δ 8.57 (dd, 3J (H,H) =11.3, 2.9, 2H; Ar-H), 8.01 (dddd, 3J (H,H) =16.2, 8.5, 1.7, 2H; Ar-H), 7.94 (dd, 3J (H,H) =8.7, 1.8, 1H; Ar-H), 7.92 - 7.86 (m, 2H; Ar-I), 7.82 (dd, 3J (H,H) =10.5, 8.2, 2H; Ar-H), 7.76 (td, 3J (H,H) =8.9, 8.4, 3.3, 4H; Ar-H), 7.69 (t, 3J (H,H) =8.1, 3H; Ar-H), 7.62 (dd, 3J (H,H) =8.4, 4.6, 3H; Ar-H), 7.55 – 7.35 (m, 9; Ar-H), 6.46 (apt. t, 3J (H,H) =9.8, 1H; H-3), 5.91 (apt. t, 3J (H,H) =9.6, 1H; H-4), 5.57 (dd, 3J (H,H) =10.2, 3.7, 1H; H-2), 5.51 (d, 3J (H,H) =3.8, 1H; H-1), 4.86 - 4.60 (m, 3H; H-6a, H-6b, H-5, overlapping peaks), 3.93 (dt, 2J (H,H) = -9.9, 3J (H,H) = 6.5, 1H; CHH), 3.61 (dt, 2J (H,H) = -9.9, 3J (H,H) = 6.6, 1H; CHH), 1.78 – 1.61 (m, 2H; CH2), 1.41 (q, 2J (H,H) =7.4, 2H; CH2), 0.86 (t, 2J (H,H) =7.4, 3H; CH3); 13C NMR (126 MHz, CDCl3): δ 167.1, 166.5, 166.4, 166.2 (4 x COAr), 135.6, 132.3, 132.2, 132.0, 131.9, 131.6 (12 x Ar-C, overlapping peaks), 129.5, 129.4, 128.6, 128.4, 128.3, 128.2, 127.6, 127.5, 126.7, 126.6, 126.5, 126.4, 126.0, 125.7, 125.1, 125.0 (28 x Ar-CH, overlapping peaks), 96.1 (C-1), 72.3 (C-2), 71.1 (C-3), 70.5 (C-4), 68.9 (CH2), 67.8 (C-5), 64.1 (C-6), 31.4 (CH2), 19.3 (CH2), 13.7 (CH3); IR (film) cm⁻¹: 2967, 1718, 1605, 1582, 1510, 1376, 1239, 1168, 1088, 1021, 802, 695; ESI-HRMS calcd for C54H44O10Na 875.2832, found m/z 875.2830 [M+Na]⁺.
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(239) Hendel, J. L. The synthesis of a Lewis X trisaccharide analogue, University of Guelph, 2008. (PhD thesis)
Appendix 1: NOE build up curves

![Diagram showing NOE build up curves](image)

### Cross peak integrations

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Appendix

\[ \text{Cross peak integrations} \]

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