Selenium-Containing Glycosides and Glycosyl Phosphates as Precursors of Glycosyl Epoxides: New Approaches to the Synthesis of (5-Fluoro) and (5-Cyano) Glycosides

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry) in The University of Michigan 2008

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“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 synthesis.**”

To My Family

For all of your love and support over the years
ACKNOWLEDGMENTS

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<thead>
<tr>
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<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5-F)-GalNAcOR</td>
<td>(5-Fluoro) N-Acetylgalactosamine-O-glycoside</td>
</tr>
<tr>
<td>(5-F)-GlcNAcOR</td>
<td>(5-Fluoro) N-Acetylglucosamine-O-glycoside</td>
</tr>
<tr>
<td>AcBr</td>
<td>Acetyl bromide</td>
</tr>
<tr>
<td>Ac₂O</td>
<td>Acetic Anhydride</td>
</tr>
<tr>
<td>BF₃·OEt₂</td>
<td>Boron trifluoride etherate</td>
</tr>
<tr>
<td>Bn</td>
<td>Benzyl</td>
</tr>
<tr>
<td>BOM</td>
<td>Benzyloxymethyl</td>
</tr>
<tr>
<td>Bz</td>
<td>Benzoyl</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>Methylene Chloride</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>DAST</td>
<td>Diethylamino sulfurtrifluoride</td>
</tr>
<tr>
<td>DHP</td>
<td>3, 4-Dihydro-2H-pyran</td>
</tr>
<tr>
<td>DIEA</td>
<td>N, N-Diisopropylethylamine</td>
</tr>
<tr>
<td>DMDO</td>
<td>Dimethyldioxirane</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray Ionization</td>
</tr>
<tr>
<td>FucT III</td>
<td>α-1, 3/1,4-Fucosyltransferase</td>
</tr>
<tr>
<td>Gal</td>
<td>Galactose</td>
</tr>
<tr>
<td>GalNAc</td>
<td>N-Acetylgalactosamine</td>
</tr>
<tr>
<td>GalNAcOR</td>
<td>N-Acetylgalactosamine-O-glycoside</td>
</tr>
<tr>
<td>GalNAcT</td>
<td>N-Acetylgalactosaminyltransferase</td>
</tr>
<tr>
<td>GalT</td>
<td>Galactosyltransferase</td>
</tr>
<tr>
<td>GDP-Fuc</td>
<td>Guanidine 5’-diphospho-fucose</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Name</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Tol</td>
<td>Toluene</td>
</tr>
<tr>
<td>Troc</td>
<td>Trichloroethoxycarbonyl</td>
</tr>
<tr>
<td>TsOH</td>
<td>p-Toluenesulfonic Acid</td>
</tr>
<tr>
<td>TTBP</td>
<td>Tetrabenzylpyrophosphate</td>
</tr>
<tr>
<td>UDP</td>
<td>Uridine 5’-diphospho</td>
</tr>
<tr>
<td>UDP-Gal</td>
<td>Uridine 5’-diphospho-galactose</td>
</tr>
<tr>
<td>UDP-GalNAc</td>
<td>Uridine 5’-diphospho-(N)-Acetyl-galactosamine</td>
</tr>
<tr>
<td>UDP-(5-F)-GalNAc</td>
<td>Uridine 5’-diphospho-(5-Fluoro) (N)-Acetyl-galactosamine</td>
</tr>
<tr>
<td>UDP-GlcNAc</td>
<td>Uridine 5’-diphospho-(N)-Acetyl-glucosamine</td>
</tr>
<tr>
<td>UDP-(5-F)-GlcNAc</td>
<td>Uridine 5’-diphospho-(5-Fluoro) (N)-Acetyl-glucosamine</td>
</tr>
</tbody>
</table>
Enzyme-catalyzed transformations of carbohydrates proceed through different transition states, which may be studied by altering the electron density at various positions of the carbohydrate ring. By placing fluorine near a developing partial charge of a donor substrate, the reaction may be inhibited due to destabilization of the transition state. The pKₐ of an acceptor alcohol is also lowered by fluorine, possibly affecting its nucleophilicity. Epoxide fluoridolysis has been previously used in our lab to synthesize (5-F) GlcNAc glycosides and glycosyl phosphates. This methodology involves a two-step process of oxidation of a phenylselenide to a selenoxide and thermal elimination with DHP. This thesis extends this fluoridolysis methodology to (5-F) isoLacNAc and (5-F) LacNAc glycosides and also investigates fluorination in the GalNAc series. Results from attempts at fluorination of the GalNAc glycosides have resulted in a premature epoxide opening hypothesis. This hypothesis was derived from differences in fluorination of glycosyl epoxides containing different neighboring protecting groups.

In the pursuit of the (iso)LacNAc glycosides, selenium-containing monosaccharide acceptor substrates were unsuccessful in glycoside formation. In contrast, glycosylation of non-selenium containing monosaccharide acceptor substrates were successful in glycoside formation and were converted to selenium-containing disaccharides after glycosylation. The resulting selenium-containing disaccharides were then transformed into their corresponding epoxides and eventually into (5-F) isoLacNAc and (5-F) LacNAc glycosides.
In addition to studying fluorinated glycosides, formation of a new stable C-C bond has been investigated. This new transformation would increase functionality on the carbohydrate ring by installing a CN group at C-5. The CN group was installed using a Lewis acid activator and TMS-CN in cyanosilylation of glycosyl epoxides. This new method allows for subsequent reduction of the CN functional group to an amine, which could then be transformed into a probe of carbohydrate metabolizing enzymes.
CHAPTER 1

INTRODUCTION

Complex carbohydrates are important components of biological pathways and systems, such as blood group antigens, cellular metabolism, intercellular communication, and other processes.\(^1\) These carbohydrates are involved in glycoconjugates, such as glycoproteins and glycolipids, which are found in cell walls of bacteria, in cellular adhesion and other sites in various biological systems. The numbering system established for hexopyranoses is shown in Figure 1.1 for D-glucose. Carbon 1 is referred to as the anomeric position, and in the reducing sugar form (as shown in Figure 1.1), the carbohydrate exists in both the open (aldohexose) and closed (hexopyranose or hexofuranose) forms of the carbohydrate ring. C-1 of hexopyranosides determines the type of linkage in a glycosidic bond, where the C-1 substituent below the plane of the pyranose is an \(\alpha\)-linkage and a substituent above the plane the pyranose is a \(\beta\)-linkage.\(^2\)

![Figure 1.1: Numbering for Hexopyranoses](image-url)
Biosynthesis of complex carbohydrates involves several classes of enzymes, such as transferases, epimerases, dehydrogenases, oxidases and pyrophosphorylases. A glycosylation reaction between two carbohydrates involves an acceptor, which serves as the nucleophile, and the anomeric position of a donor, which serves as the electrophile. An example of an enzyme-catalyzed glycosylation reaction of glucose by UDP-galactose catalyzed by lactose synthase (E.C. 2.4.1.22) is shown in Figure 1.2.\(^3\)

![Figure 1.2: Example of a Glycosyltransferase Reaction](image)

Enzyme-catalyzed transformations of carbohydrates proceed through transition states, which may be studied by altering the electron density at various positions of the carbohydrate ring. A glycosylation reaction may be considered a nucleophilic substitution reaction in that loss of a leaving group and subsequent replacement by the nucleophile is observed. The degree of bond formation and bond breaking in the transition state is represented in Figure 1.3. A dissociative (exploded) transition state is characterized by formation of an oxocarbenium ion resulting from loss of the leaving group on the donor substrate and then nucleophilic attack by the acceptor substrate (Figure 1.3A). In an associative transition state, there are shorter bonds associated with the loss of the leaving group and new bond formation by the nucleophile (Figure 1.3B).
By placing fluorine near a developing partial positive charge in the transition state, the reaction may be inhibited due to destabilization of the transition state. The \( \text{pK}_a \) of the proximal alcohol in the acceptor substrate is also lowered, possibly affecting its nucleophilicity (Figure 1.4). The amount of inhibition by fluorine on the glycosylation reactions of interest will provide data towards the mechanism of action (dissociative vs. associative) of the enzyme.

**Figure 1.3: Dissociative vs. Associative Transition States**

**Figure 1.4: Proposed Transition States**

\( X = \text{H, F} \)
\( Y = \text{OH, NHAc} \)
Fluorine is an attractive choice for probing the transition state because of its strong electron-withdrawing characteristic, yet minimal steric effect (Table 1.1). The size of a C-F bond is similar to a C-OH bond and fluorine is a common choice for replacing C-OH groups to study carbohydrate metabolizing enzymes. These fluorinated deoxy sugars have been used to evaluate enzyme recognition of substrates by changing the hydrogen-bonding network from a donor (OH) to an acceptor (F). Replacement of a hydroxyl group with fluorine can be accomplished in one-step using DAST (diethylaminosulfur trifluoride) or Selectflour.

Table 1.1: Comparison of Fluorine with Hydrogen and OH Bonds

<table>
<thead>
<tr>
<th>Element</th>
<th>Bond Length CH₃-X (Å)</th>
<th>Van der Waals Radius (Å)</th>
<th>Total (Bond Length and Van der Waals Radius) (Å)</th>
<th>Electronegativity of H, F, and O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.09</td>
<td>1.20</td>
<td>2.29</td>
<td>2.1</td>
</tr>
<tr>
<td>F</td>
<td>1.39</td>
<td>1.35</td>
<td>2.74</td>
<td>4.0</td>
</tr>
<tr>
<td>O (in OH)</td>
<td>1.43</td>
<td>1.40</td>
<td>2.83</td>
<td>3.5</td>
</tr>
</tbody>
</table>

A more difficult transformation to obtain is the replacement of a C-H bond with a C-F bond. Fluoridolysis usually requires multiple synthetic transformations (as described later). Additionally, having fluorine at C-5 may lead instability because it is adjacent to the carbohydrate ring oxygen. Donation of the lone pair of the ring oxygen may lead to loss of fluoride ion and formation of an oxocarbenium ion (Figure 1.5).
Previous attempts at forming C-5 carbon-fluorine bonds in carbohydrates have resulted in poor yields (Figure 1.6). In the radical halogen exchange method developed by Withers and coworkers,\textsuperscript{9} compound 1 was brominated with NBS to form a C-5 bromide. The bromide was then displaced and epimerized with silver fluoride to give 2 in a poor yield of 8% (2 steps). Compound 2 had its remaining protecting groups removed using methanolic ammonia to form 3. The (5-F) glycoside was then used as a mechanistic probe of carbohydrate metabolizing enzymes.\textsuperscript{9,10}

![Diagram](image.png)

Figure 1.5: Formation of Oxocarbenium Ion from Loss of Fluoride

Figure 1.6: Radical Halogenation at C-5 by Withers and Coworkers

In addition to the displacement of bromide with AgF (Figure 1.5), White and coworkers improved the radical halogenation method by using AgBF\textsubscript{4} to form the C-F bond at C-5 (Figure 1.7).\textsuperscript{11} The known compound 4\textsuperscript{12} was fluorinated with AgBF\textsubscript{4} to give 5 in 61% yield.
Substitution of fluorine at the C-5 position in the synthesis of 5-fluoro derivatives of N-acetylglucosamine (GlcNAc) is also achieved using the epoxide fluoridolysis methodology previously developed in our lab (Figure 1.8).\(^8\) A 5, 6-epoxide (8 or 10) is opened with HF-pyridine to install the desired C-F bond at C-5. A phenylselenide at C-6 (6) is oxidized and eliminated in a two-step process to form an olefin (7 or 9), which is oxidized to yield the desired 5, 6-epoxide. Fluoridolysis in the GlcNAc series proceeds in good yields (72-83\%) and the epoxide intermediates are useful substrates for other nucleophilic reactions at C-5. However, epoxide fluoridolysis has not been reported in the GalNAc or (iso)LacNAc series and will be applied to these carbohydrates. In addition to fluoridolysis, acid-catalyzed reactions of hindered 2, 3 glycosyl epoxides are attained with TMS-CN or HCN and a Lewis acid.\(^{13-16}\) Acid-catalyzed “C-glycosylation” has not been applied to the 5, 6 GlcNAc epoxide 8 (X = OH, Y = H, Z = OH) and will be attempted in the GlcNAc series. The epoxides 8 and 10 are key intermediates because of the various possibilities of glycosylation reactions available.
Epoxide fluoridolysis has proven successful in the GlcNAc series (X = OH, Y = H, Z = OH). (5-F)-GlcNAc-β-octyl glycoside was synthesized and evaluated as an alternate acceptor substrate for β-1, 4 GalT (EC 2.4.1.38) from bovine milk. Results shows there was minimal effect on the $k_{cat}$ of the reaction for the fluorinated versus non-fluorinated substrates, suggesting little bond formation between the acceptor and the UDP-Gal donor (Table 1.2 and Figure 1.9). This result supports a dissociative transition state, which contains minimal bond formation between an acceptor and a donor. If negligible bond formation between an acceptor and the donor is observed, an oxocarbenium ion intermediate resulting from a more significant bond dissociation of the leaving group (UDP) similar to an $S_N$1 type reaction is suggested.
Table 1.2: Comparison of β-1, 4 GalT octyl-GlcNAc Glycoside versus (5-F) Octyl-GlcNAc Kinetic Data

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$K_M^{app}$ (μM)</th>
<th>$k_{cat}^{app}$ (s⁻¹)</th>
<th>$k_{cat}/K_M$ (M⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>octylGlcNAc</td>
<td>52 ± 4</td>
<td>9.1 ± 0.5</td>
<td>175,000</td>
</tr>
<tr>
<td>Octyl(5-F)GlcNAc</td>
<td>295 ± 65</td>
<td>6.5 ± 0.6</td>
<td>21,700</td>
</tr>
</tbody>
</table>

In addition, the epoxide fluoridolysis methodology was successful in the synthesis of the donor UDP-(5-F)-GlcNAc. UDP-(5-F)-GlcNAc was studied with CLS (UDP-GlcNAc:GlcNAc-P-P-Dol N-acetylglucosaminyltransferase, EC 2.4.1.141). UDP-GlcNAc had a $K_m$ of 392 ± 83 μM and a $V_{max}$ of 27.5 ± 1.9 cpm/min/μg. However, UDP-(5-F)-GlcNAc was inactive as a donor for CLS, suggesting UDP-(5-F)-GlcNAc to be an inhibitor. Figure 1.10 indicates that UDP-(5-F)-GlcNAc at 1.5 mM and 0.25 mM concentrations acted as an inhibitor when increasing the amount of UDP-GlcNAc. For both concentrations, increasing the concentration of UDP-GlcNAc lowers the inhibition of UDP-(5-F)-GlcNAc. The data suggests that the fluorinated donor served as a competitive inhibitor of UDP-GlcNAc and not as a substrate (Figure 1.10).
inactivating effect gives evidence that the electron-withdrawing fluorine is destabilizing a forming oxocarbenium ion-like transition state.

\[
\begin{align*}
\text{UDP} & \stackrel{\text{CLS}}{\rightarrow} \text{UDP} \\
\text{UDP}_{-}\text{UDPAc} & \quad \text{UDP}_{-}\text{UDPAc}
\end{align*}
\]

Figure 1.10: Inhibition Studies of CLS by UDP-(5-F)-GlcNAc

The UDP-(5-F)-GlcNAc alternate substrate was also evaluated as a mechanistic probe with UDP-GlcNAc C-4 epimerase. UDP-GlcNAc C-4 epimerase is found within the biosynthetic pathway of an unusual carbohydrate found in the lipopolysaccharide of the waterborne pathogen, *Plesiomonas shigelloides*. The enzyme catalyzes the
epimerization of the C-4 hydroxyl group of UDP-GlcNAc to UDP-GalNAc resulting in a 70:30 equilibrium, favoring UDP-GlcNAc (Figure 1.11). UDP-(5-F)-GlcNAc was shown to be an alternate substrate for the epimerase with a 270-fold decrease in $k_{cat}$ (Table 1.3). The decrease in $k_{cat}/K_m$ may be due to the 5-fluoro group hindering the rotation about the C-O-P bond during catalysis or due to the 5-fluoro group destabilizing the putative positive charge formation during hydride abstraction (Figure 1.11). More experimental data are needed in order to determine which mode of inhibition is occurring.

Table 1.3: Comparison of UDP-C-4-Epimerase UDP-GlcNAc versus UDP (5-F) GlcNAc Kinetic Data

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$K_M$ (µM)</th>
<th>$k_{cat}$ (min⁻¹)</th>
<th>$k_{cat}/K_M$ (M⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UDP-GlcNAc</td>
<td>137 ± 17</td>
<td>461 ± 33</td>
<td>56100 ± 403</td>
</tr>
<tr>
<td>UDP-(5-F)-GlcNAc</td>
<td>5.6 ± 1.7</td>
<td>1.73 ± 0.12</td>
<td>5100</td>
</tr>
</tbody>
</table>

Figure 1.11: Reaction Catalyzed by UDP-GlcNAc C-4 Epimerase: Proposed Mechanism

An extension of the epoxide fluoridolysis methodology is to study the effects of fluorine in the galactosamine (GalNAc) series (Figure 1.8). Since there was no genuine
sample of the UDP-(5-F)-GalNAc, 11, available at the time of the C-4 epimerase research described above, 11 was selected as a synthetic target. This sugar nucleotide could also be evaluated as a substrate for the C-4 epimerase and used as a mechanistic probe for GalNAcT in O-glycan biosynthesis (Figure 1.12A).

The biosynthesis of O-glycans, such as, Core 1 and Core 2, plays an important role in cellular adhesion, differentiation, invasion and metathesis of tumors. Recently, a positive correlation between increased GalNAcT activity and invasion and metathesis in early stages of gastric cancer has been reported (Figure 1.12A). Compound 11 could be used to determine the effects of fluorine on the donor substrate of GalNAcT and could potentially inhibit the formation of the Core 1 and Core 2 biosynthetic products involved in tumor progression of gastric cancer. Additionally, the effects of fluorine on an acceptor substrate in O-glycan biosynthesis, could also be investigated by synthesizing 12 as a possible β-1, 4 GalT substrate (Figure 1.12B). β-1, 4 GalT utilizes the acceptor O-linked glycopeptide, 12, and the donor GDP-Gal in order to form the Core 1 and Core 2 products. By inhibiting the β-1, 4 GalT enzymatic reaction, the Core products may be decreased and therefore result in a reduction of tumor progression. Based upon previous results, it is expected that the donor UDP-(5-F)-GalNAc should have a greater effect on O-glycan biosynthesis than the acceptor (5-F)-GlcNAc-β-octyl glycoside.
As well as studying the effects of fluorine on both donor and acceptor substrates in the O-glycan biosynthetic pathway, the proximity effect of fluorine could be investigated. FucT III (E.C. 2.4.1.65), involved in Lewis B blood group antigens, fucosylates the free C-4 or C-3 hydroxyl groups of the two disaccharides type 1 (isoLacNAc) and type 2 (LacNAc), respectively (Figure 1.13). FucT III has been linked to an increase in tumor size in prostate cancer cell line PC-3 due to an increase in cellular adhesion in the stromal cells. Therefore, work towards the inhibition of this enzyme could potentially impede prostate cancer progression. Two fluorinated analogs, 13a and 14a, could aid in investigating the effects of fluorine on FucT III glycosyl acceptor substrates by differentially affecting the pK\textsubscript{a} of the C-4 hydroxyl versus the C-3 hydroxyl and potentially affect their ability to act as acceptor substrates. It is also necessary to synthesize 13b and 14b in order to have non-fluorinated control substrates as the octyl glycoside (R = (CH\textsubscript{2})\textsubscript{7}CH\textsubscript{3}) is not the natural substrate for the enzyme. The octyl chain is
necessary for the binding to a reverse-phase solid support in the Sep-Pak assay used to evaluate the enzymatic reaction. The octyl side chain adheres to the reverse-phase C-18 column and elution with water results in water-soluble impurities in the column fractions. The desired octyl glycosides remain on the column, as they are not water soluble. The resulting glycosides are then eluted using MeOH. The effect of fluorine on FucT III could be analyzed by comparing the rates of $13a$ and $14a$ to $13b$ and $14b$, respectively. If FucT III follows a dissociative transition state similar to the $\beta$-1, 4 GalT, then there should be minimal difference between $13a$ and $14a$ as there should be little bond formation between the acceptor substrate and the GDP-Fuc donor. The ability of $13a$ and/or $14a$ to act as substrates in FucT III catalyzed glycosylation would permit the incorporation of fluorine in semisynthetic neoglycoconjugates.

Figure 1.13: Proposed Transition States for FucT III
In addition to epoxide fluoridolysis, it is possible that 5, 6 epoxides (Figure 1.8) could be used to form novel C-glycosides (Figure 1.14). It is known that 2, 3 epoxides can be converted to cyanodeoxy sugars. Regioisomers 16 and 17 can be formed from the 2, 3 epoxide 15 with either HCN\textsuperscript{16} or TMS-CN\textsuperscript{14} and a Lewis acid. Currently, there are no 5, 6 glycosyl epoxides reported using this type of acid-catalyzed “C-glycosylation”. The reaction conditions effective for acid-catalyzed C-glycosylation of 2, 3 epoxides 15 and 18 will be attempted on the 5, 6 epoxides, 19 (Figure 1.15). Formation of the (5-cyano) sugars would broaden the ability to functionalize carbohydrates. A stable C-C bond C-5 could be reduced to an amine, leading to branching of sugars or greater functionalization of glycosides (Figure 1.15). In addition, formation of the free amine 22 could be useful as a probe for carbohydrate metabolizing enzymes. A biotin molecule may be attached to the amine and used in a biotin/avidin capture assay\textsuperscript{25} as a new method for evaluating glycosyltransferase reactions.

Figure 1.14: 2, 3-C Cyanodeoxy Sugars
In order to evaluate the enzymes UDP-C-4-GlcNAc epimerase, GalNAcT, β-1, 4 GalT, and FucT III as described above, compounds 11, 12 (X = F), 13a, 13b, 14a and 14b have been selected as (5-fluoro) synthetic targets for use with the epoxide fluoridolysis methodology (Figure 1.16). The (5-fluoro) glycosides could be compared to their corresponding non-fluorinated, control, substrates in order to determine the effect fluorine has on the transition state of the glycosyltransferase reaction of interest. These GalNAc and (iso)LacNAc glycosides may be accessed through the GalNAc epoxide 8 (X = H, Y = OH, Z = OH) and the (iso)LacNAc epoxides 10 as described in Figure 1.8.

In addition to the GalNAc derivatives (11 and 12) and (iso)LacNAc glycosides (13 and 14), a new C-C bond formation utilizing an acid-catalyzed “C-glycosylation”
reaction will be attempted on the GlcNAc epoxide 8 (Figure 1.8, X = OH, Y = H, Z = OH). As shown in Figure 1.17, this may form a stable C-C bond at the C-5 position, 20, allowing for greater functionalization of carbohydrates or, alternatively the regioisomer, 21, a reducing sugar. In addition, it will be important to understand the functional group tolerance of the new cyanosilylation reaction in order to determine the scope of this methodology. As a result, both electron-withdrawing and electron-donating protecting groups will be evaluated with cyanosilylation.

![Chemical Structure](image)

**Figure 1.17: Synthetic Targets for (5-Cyano) Carbohydrates**
CHAPTER 2

REVIEW OF CURRENT DISCUSSIONS OF GALACTO AND GLUCO REACTIVITIES AND CURRENT GLYCOSYLATION METHODOLOGIES

2.1 Discussion of gluco versus galacto reactivities

Glucose and galactose sugars are structurally very similar; the only difference being the position of the C-4 hydroxyl group. However, this seemingly modest distinction imparts a variety of fundamental property changes between the two sugars. It will be of interest to see how the epoxide fluoridolysis reaction may be affected by the C-4 hydroxyl position, as this has not been reported in the literature.

Studies have indicated that the electronegativity of the C-4 substituent plays a role in the rate of acetolysis of galactopyranosides (Figure 2.1). The results show compound 24 acetolyses approximately 10 times faster than 25, which is approximately 5 times faster than 26. In contrast, the glucopyranoside series is not as influenced by the electronegative nature of the C-4 substituent. Compound 27 is approximately 2.9 times faster than 28 and 3.3 times faster than 29. The result of the glucopyranoside acetolysis rates is hypothesized to be due to a small “through-bond” interaction with the ring oxygen. In the case of the galacto configuration, there is a strong through-space interaction between the electronegative C-4 axial substituent and the forming oxocarbenium ion. In neutral galactopyranoside derivatives, the effect is destabilizing.
due to electrostatic repulsion. During oxocarbenium ion formation, the through-space effect is stabilizing.

![Figure 2.1: Glycopyranoside Acetolysis Substrates](image)

**2.2 Discussion of reactivity differences of carbohydrate ring positions**

In addition to differences between gluco versus galacto configurations, each of the 6 positions of the carbohydrate ring have different reactivities. The α:β selectivity at C-1 may be influenced by the neighboring C-2 position.\(^\text{27,28}\) In a gluco configuration, neighboring group participation on a donor substrate occurs with a participatory group at C-2 that can attack the α-face of the C-1 position. As a result, glycosylation with an acceptor preferentially forms a β-linkage. The C-3 hydroxyl is known to be a good nucleophile, but an electron-withdrawing N-phthalimido group at the C-2 position lowers the reactivity of the C-3 hydroxyl.\(^\text{29}\) The C-4 position is known to be in general a poor nucleophile.\(^\text{30}\) However, a C-3 and C-4 diol acceptor substrate with C-2 N-phthalimido or C-2 N-Troc will regioselectively form a 1-4 linkage.\(^\text{29,31}\) As a result, it is important to manipulate the reactivity of each position on donor and acceptor substrates of glycosylation reactions in order to attain the desired α:β-selectivity and 1, 3 or 1, 4 regiochemistry. In order to synthesize the desired (5-fluoro) (iso)LacNAc octyl glycosides 13 and 14, it will be necessary to perform a glycosylation reaction to form the
desired β-1, 3 and β-1, 4 disaccharides. Therefore, it will be important to design specific donors and acceptors to give the desired α:β selectivity and regiochemistry of the (iso)LacNAc derivatives. In addition to manipulating reactivities of the carbohydrate positions, the α:β-selectivity may also be influenced by the technique used to promote glycosylation.

2.3 Discussion of current glycosylation methodologies

Promotion of glycosylation reactions are widely reported in the literature. The earliest glycosylation techniques include the Koenigs-Knorr, Fisher-Raske, or Helfrich methods. The Koenigs-Knorr method involves a glycosyl halide donor and either a silver or a mercury salt as a promoter (Scheme 2.1).\textsuperscript{32,33}

![Scheme 2.1](image.png)

Additionally, Emil Fisher and Karl Raske developed a glycosylation reaction involving a glycosyl halide donor and an alkoxide base.\textsuperscript{34} A caustic solution was added to the donor halide with the acceptor alcohol resulting in a mixture of α:β glycosides (Scheme 2.2).
Helfrich glycosylation utilizes a Lewis acid promoter and a peracetylated glycoside donor substrate. This method forms the α- or β-glycosides in modest yields (Scheme 2.3).\textsuperscript{35,36}

Improved α:β selectivity in glycosylation reactions are observed with phenylthioglycoside donor substrates (Scheme 2.4).\textsuperscript{37} Thioglycoside promotion is similar to the Koenigs-Knorr promotion methods in that a mercury salt promoter used. Stereocontrol at the anomeric position for simple acceptors is readily accessible.
Enhanced thioglycoside activation include the promoters NIS\textsuperscript{28}, BSP\textsuperscript{30} and PhSCI\textsuperscript{38} (Scheme 2.5). These conditions generally proceed in good yields, allowing for good stereocontrol at C-1. A glycosyl triflate salt is formed in situ, along with formation of a disulfide leaving group upon activation from a sulfur-containing promoter. The acceptor alcohol then displaces the triflate to form the desired glycoside.\textsuperscript{39,40}
In general, good to excellent yields and stereoselectivity in glycosylation reactions may be attained using a trichloroacetimidate donor developed by Schmidt and co-workers.\textsuperscript{41} This method uses a strong Lewis-acid promoter with improved yields compared to the previous methods described above (Scheme 2.6).\textsuperscript{42}

Scheme 2.6

The trichloroacetimidate methodology also allows greater flexibility of selectivity at the anomeric position. This is achieved by controlling the temperature of activation of the glycosylation reaction.\textsuperscript{43} The use of an N-trichloroacetylcarbamate group which is analogous to a trichloroacetimidate, resulted in a dramatic difference in $\alpha$:$\beta$-selectivity due to the temperature of glycosylation activation (Table 2.1). A lower temperature of activation increases $\beta$-selectivity. A higher temperature of activation predominantly yields an $\alpha$-glycoside.
Table 2.1: Temperature Effects of α/β-Selectivity in Glycosylation Reactions

<table>
<thead>
<tr>
<th>Acceptor (ROH)</th>
<th>α-Selective glycosylation&lt;sup&gt;a&lt;/sup&gt;</th>
<th>β-Selective glycosylation&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO OH Bn O Bn O</td>
<td>0 °C, 5h 93%, α/β = 90/10</td>
<td>-40 °C, 1.5h then -23 °C, 16h, 83%, α/β = 15/85</td>
</tr>
<tr>
<td>Ph OH OH Bn O Bn O OMe</td>
<td>0 °C, 3h 86%, α/β = 96/4</td>
<td>-20 °C, 1h 74%, α/β = 17/83</td>
</tr>
</tbody>
</table>

<sup>a</sup> Me<sub>3</sub>SiClO<sub>4</sub> (20 mol %) in Et<sub>2</sub>O

<sup>b</sup> Me<sub>3</sub>SiOTf (20 mol %) in EtCN

The thioglycoside method previously described has been used to synthesize compound 13b (Scheme 2.7)<sup>44</sup>. The benzylidene acceptor and thioglycoside donor formed the desired disaccharide in modest yield and removal of the Troc at N-2 allowed for a library of different N-substituted β-1, 3 octyl glycosides (lacto-N-biose).

Scheme 2.7
The Koenigs-Knorr method was employed in the synthesis of the β-1, 4 octyl glycoside 14b \(^{45}\) (Scheme 2.8). This procedure proceeded in good yields to form 14b. The disadvantage of this synthesis is that the acceptor substrate is highly specific. A more divergent acceptor substrate allowing for access to multiple acceptor substrates for different regioisomers would be more useful. Chapter 4 describes syntheses for accessing both (5-fluoro) (iso)LacNAc and non-fluorinated (iso)LacNAc-octyl glycosides 13 and 14 from one readily available starting material.

Scheme 2.8
CHAPTER 3

SYNTHESIS OF C-6 PHENYLSELENIDE-GalNAc-OCTYL GLYCOSIDES AND C-6-PHENYLSELENIDE-GalNAc-GLYCOSYL PHOSPHATES

3.1 Introduction

In order to synthesize the desired (5-fluoro) and (5-cyano) GalNAc and GlcNAc glycosides\textsuperscript{11, 12, 20, 21}, it is necessary to synthesize C-6 phenylselenide-containing glycosides (Figure 1.8). These monosaccharide selenium-containing substrates will then be transformed to their corresponding 5, 6 epoxides and subjected to either epoxide fluoridolysis or cyanosilylation. The C-6 phenylselenide-containing GalNAc glycoside synthetic targets are shown in Figure 3.1. Protecting group flexibility at C-4 is desired because of the axial –OH substituent in the galacto configuration (Figure 3.1A). It is unknown what affect the axial C-4 –OH substituent will have on fluoridolysis or cyanosilylation. Therefore, it is important to explore electron-withdrawing versus electron-donating protecting groups at C-4, as well as the potential for neighboring group participation of different protecting groups. In terms of the cyanosilylation reaction, it is unknown what the functional group tolerance of the reaction conditions will be. As a result, it will also be important to investigate the role of electron-withdrawing versus electron-donating in cyanosilylation (Figure 3.1B).
Introduction of the phenylselenide (Chapter 1, Figure 1.8) can be achieved by two different methods (Figure 3.2). One approach involves displacement of a bromide with phenylselenol (Figure 3.2A), whereas an alternative route, developed by Nicolaou and Grieco, converts a free alcohol to a phenylselenide using N-phenylseleno phthalimide (N-PSP) and PBu$_3$ (Figure 3.2B).\(^{46}\)

Both methods have been investigated and applied in the syntheses of the glycosyl phenylselenides.
3.2 Synthesis of the β-octyl C-4–OH glycosides

In the case of the GalNAc-β-octyl glycosides, the phenylselenide has been installed via the halide displacement method (Figure 3.2A). Beginning with the known compounds 32a and 32b, the benzylidene intermediates were opened using Hanessian-Hullar conditions that produced a C-6 bromide and resulted in selective protection of the C-4 position as a benzoylester (Scheme 3.1). A non-amide group, e.g. phthaloyl, at the C-2 nitrogen is necessary for Hanessian-Hullar conditions, which proceeds through radical abstraction of the benzylidene hydrogen by Br· during the reaction. Instead of abstracting the benzylic hydrogen, the radical could abstract the amide hydrogen on the nitrogen, resulting in undesired reaction(s) and/or decomposition. The bromide was then displaced using PhSeH, NEt₃ and Bu₄NI (as a phase-transfer catalyst) to form the phenylselenides, 33a and 33b. The addition of Bu₄NI dramatically decreased the reaction time from 5 days to overnight. The free C-3 –OH groups were protected with a benzyloxyethyl (BOM) ether group to form 34a and 34b. Compound 34c was synthesized as reported by Matt Hartman. The order of the reaction sequence is important to avoid formation of an undesired C-6 chloro by-product (Scheme 3.2). The C-6 bromide must be displaced first by PhSeH before the C-3 protection, otherwise the release of chloride from the BOM-Cl reagent will displace the bromide and result in a 3:1 mixture of C-6 Br and C-6 Cl glycoside (Table 3.1). Attempts at sequestering the released chloride with silver salts proved unsuccessful. The resulting differentially protected glycosides 34a, 34b and 34c were transformed to 35a, 35b, and 35c by removal of the C-4 benzoyl protecting group with NaOMe.
Scheme 3.1

1. NBS, BaCO₃, CCl₄, Δ
2. PhSeH, NEt₃, Bu₄NI, THF, Δ

32 → 36

a. R₁ = (CH₂)₇CH₃, 83% (2 steps)
b. R₁ = TBS, 71% (2 steps)

36 → 39

BOM-Cl, DIEA, THF, Δ

a. R₁ = (CH₂)₇CH₃, 75%
b. R₁ = TBS, 88%
c. R₁ = PMP, 76%

Scheme 3.2

1. NBS, BaCO₃, CCl₄, Δ
2. PhSeH, NEt₃, Bu₄NI, THF, Δ

32 → 36

36 → 39

34b → 39

NaOMe, MeOH

Table 3.1: Attempts at Sequestering Released Chloride During C-3 BOM Protection

<table>
<thead>
<tr>
<th>BOM-Cl</th>
<th>DIEA</th>
<th>Silver Salt</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 (eq.)</td>
<td>5.5 (eq.)</td>
<td>None</td>
<td>34b/39 (3:1)</td>
</tr>
<tr>
<td>2 (eq.)</td>
<td>2.5 (eq.)</td>
<td>None</td>
<td>34b/39 (15:1)</td>
</tr>
<tr>
<td>5 (eq.)</td>
<td>5.5 (eq.)</td>
<td>AgCO₃</td>
<td>Decomposed</td>
</tr>
<tr>
<td>3 (eq.)</td>
<td>3.5 (eq.)</td>
<td>Ag₂O</td>
<td>Decomposed</td>
</tr>
</tbody>
</table>
3.3 Inversion of configuration from gluco to galacto

The inversion of configuration was accomplished via triflate formation and the SN2 displacement of the triflate by Et4NOAc (Scheme 3.3). Synthesis of 40c was performed once and not optimized, but 40a and 40b proceeded in good yields to form the desired GalNAc glycosides.

Scheme 3.3

![Scheme 3.3](image)

3.4 Synthesis of 6-SePh-GalNAc-β-octyl glycoside

Protecting group flexibility at the C-4 position was desired since this position would be adjacent to the 5, 6 epoxides (as described in 3.1). The role of an electron-withdrawing versus electron-donating protecting groups is of interest at C-4 as it is unknown how it will affect fluoridolysis and cyanosilylation. For the C-4 acetate (electron-withdrawing) derivative, the phthaloyl and acetyl groups of 40a were removed and the resulting 2-amino, 4-hydroxy glycoside was N- and O-acetylated to give 42a (Scheme 3.4). Alternatively, the C-4 acetate was removed by NaOMe and protected as a benzyl ether (electron-donating protecting group) using the method developed by Karst and coworkers. The phthaloyl group was then removed and acetylated to form 42b.
3.5 **Synthesis of 6-SePh-GalNAc-α-octyl glycoside**

Installing the phenylselenide on the GalNAc-α-octyl glycoside was investigated using both the halide displacement and the N-PSP methods. First, the α-linkage needed to be in place and several methods were investigated.

Initially, a thioglycoside was used because of the reported high α-selectivity in the literature (Scheme 3.5). Beginning with the glycoside 43, the phenylthio glycoside was formed using BF$_3$·OEt$_2$ and PhSH to form 44. The benzylidene 45 was then formed based on the procedure of Miyajima and coworkers by removing the acetyl protecting groups to form the triol and then using PhCH(OMe)$_2$ and pTsOH. After formation of the oxazolidinone, 46, glycosylation to form the α-linkage was attempted using AgOTf, PhSCl, DTBMP and 1-octanol. However, in contrast to the literature reports, the reaction failed to produce the desired α-octyl glycoside and starting materials were recovered (Table 3.2, entry 1). Other methods of thioglycoside activation were attempted,
but also failed to produce the desired $\alpha$-linkage (Table 3.2, entries 2-4). Starting materials were recovered in each of the methods described in Table 3.2.

Scheme 3.5

Table 3.2: Attempts at Formation of the $\alpha$-Octyl Glycoside

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AgOTf, PhSCI, DTBMP, 1-octanol Tol:1,4 dioxane, -78°C</td>
<td>No Product Formed</td>
</tr>
<tr>
<td>2</td>
<td>AgOTf, PhSCI, TTBMP, 1-octanol Tol:1,4 dioxane, -78°C</td>
<td>No Product Formed</td>
</tr>
<tr>
<td>3</td>
<td>BSP, DTBMP, TfO, 1-octanol CH$_2$Cl$_2$, -60 °C</td>
<td>No Product Formed</td>
</tr>
<tr>
<td>4</td>
<td>NIS, DTBMP, TMSOTf, 1-octanol CH$_2$Cl$_2$, rt</td>
<td>No Product Formed</td>
</tr>
</tbody>
</table>

An alternative to thioglycoside activation involved installing the octyl side chain at the beginning of the synthesis by Lewis acid activation of $N$-acetyl-D-glucosamine, 48,
in neat 1-octanol (Scheme 3.6).\textsuperscript{29,53} The α-glycoside 49, was then converted to the benzylidene and the free C-3 alcohol acetylated to yield compound 50. The 4, 6-benzylidene of compound 50 was opened with acid catalysis to give the diol and the C-6 position was selectively protected as a TBS ether to form 51. The gluco configuration was converted to the galacto configuration via triflate formation at the C-4 position and displacement of the triflate by Et\textsubscript{4}NOAc. The TBS silyl ether was then removed to give the free C-6 alcohol, 53. However, attempts at formation of the phenylselenide with the N-PSP method did not form the desired phenylselenide glycoside, 54. Perhaps the reaction failed due to neighboring group participation from the axial C-4 acetate group next to the C-6 alcohol. Compound 54 was recovered with no decomposition detected.

Scheme 3.6
In addition to 53, diol 50 was also subjected to the same N-PSP conditions (Scheme 3.7). However, only starting material was recovered. Alternatively, formation of a C-6 Br, 57, was attempted using NBS or CBr₄ with PPh₃.³⁴ Compound 49 was recovered and the desired bromide, 57, was not observed (Scheme 3.7). The α-linkage was not pursued further.

Scheme 3.7

3.6 Synthesis of 6-SePh-GalNAc phosphate

In pursuit of the 6-SePh-GalNAc phosphate glycosides, the BOM group at C-3 of 40c, was removed with BF₃·OEt₂ and the resulting hydroxyl group selectively acetylated with AcBr in a one-pot procedure to afford 58 (Scheme 3.8). However, attempts at deprotection of the PMP group failed with AcBr, ZnI₂ and BF₃·OEt₂. Following literature procedures, PMP deprotection and conversion to the glycosyl bromide was successful in a model reaction.³⁵ However, compound 58 could not be converted to 59 under identical conditions.
Consequently, the TBS ether was used because of its ease of deprotection (Scheme 3.9). The phthaloyl and acetyl protecting groups on compound 40b were removed via hydrazinolysis. The free C-2 amine was N-trifluoroacetylated with trifluoroacetic anhydride (TFAA) and pyridine forming the C-2 trifluoroacetamide as well as the TFA ester at C-4. The C-4 TFA ester was removed with a sodium bicarbonate wash to give the free C-4 –OH, 60. The resulting C-4 –OH group was protected with acetic anhydride and pyridine to yield 61a. Alternatively, the C-4 –OH group was protected as a benzyl ether to give 61b. The TBS silyl ether was removed to form the reducing sugar, which was then phosphorylated with tetrabenzyl pyrophosphate (TBPP) to give compound 62a. The C-2 trifluoroacetamide is critical for the stability of the glycosyl phosphate at C-1. The electron-withdrawing effects of fluorine stabilize the phosphate, allowing it to be purified by flash column chromatography and withstand multiple synthetic organic reaction conditions. When an acetamido group is at C-2, the glycosyl phosphate is unstable and cannot be purified via flash column chromatography. The same sequence of phosphorylation conditions used to form 62a was unsuccessful in forming 62b. Since flexibility was again desired at the C-4 position, attempts at removal of the acetate protecting group to form 63 failed using the mild conditions of guanidine/guanidinium nitrate.
It is proposed that the failed phosphorylation with O-Bn at C-4 is due to the fact that the O-Bn group cannot participate in the reaction at C-1 of the reducing sugar. A C-4 acetate in a galactose derivative can participate across the ring\textsuperscript{59} and possibly is coordinating with the Li\textsuperscript{+} ion generated from the LDA deprotonation (Figure 3.3, A). The coordination helps pull the Li\textsuperscript{+} ion away from the oxyanion at C-1, allowing for nucleophilic attack of the TTBP. The C-4 Bn ether cannot coordinate to the Li\textsuperscript{+} ion and the oxyanion is not as exposed and is unable attack the TTBP (Figure 3.3, B). A better leaving group on the phosphorylating agent, such as a phosphoramidite, may be needed to form the desired C-4 Bn glycosyl phosphate.

Figure 3.3: C-4 Ac vs. C-4 Bn Phosphorylation
As a result of the failure to obtain 62b as described above, a new method was attempted following the work of Thiem and Lazarevic (Scheme 3.10), in which the reducing sugar 64 was converted to a phosphite using dibenzyl-N, N'-diisopropylphosphoramidite (iPr)2NP(OBn)2 and 1-H-tetrazole and then oxidized with mCPBA to form the phosphate 65 in a one-pot procedure.

Scheme 3.10

The C-4 Bn ether protection described in Scheme 3.9 was optimized and a new route was developed and is shown in Scheme 3.11. The C-4 acetate was removed with NaOMe and the resulting free alcohol protected with a benzyl ether to give 67. The phthaloyl group was removed and trifluoroacetylated to give 61b, in a higher yielding sequence than previously described in Scheme 3.9. The TBS silyl ether was then removed to form the reducing sugar 68.

Scheme 3.11
Following the Thiem procedure, phosphorylation of 68 was achieved by formation of the phosphite followed by subsequent oxidation of the phosphite to the phosphate (Scheme 3.12). The oxidation conditions (NaIO₄ and NaHCO₃) resulted in the oxidation of both the phenylselenide and phosphite moieties to give the glycosyl phosphate 69.

Scheme 3.12

3.7 Synthesis of cyanosilylation precursor phenylselenides

Acid-catalyzed glycosylation of 2, 3 epoxides has been achieved using a strong Lewis acid with TMS-CN as described in Chapter 1, Figure 1.14. In order to test acid-catalyzed glycosylation on 5, 6 epoxides, the phenylselenides 71a and 71b were synthesized (Scheme 3.13). These precursors were designed to incorporate electron-withdrawing and electron-donating protecting groups in order to explore functional group tolerance of cyanosilylation.

Scheme 3.13
3.8 Conclusions

Formation of the C-6 selenium-containing GalNAc-β-octyl glycosides 42a and 42b with either electron-withdrawing (42a) or electron-donating (42b) protecting groups at C-4 proceeded in good yields. However, installation of the C-6 phenylselenide α-glycoside was unsuccessful with either thioglycoside activation (Table 3.2), N-PSP conversion of a C-6 OH to the C-6 SePh (Scheme 3.6), or formation of a C-6 Br (Scheme 3.7). In pursuit of the glycosyl phosphate, the electron-withdrawing C-4 acetate GalNAc α-phosphate 63 was formed in good yields from 62a in a 2-step process of deprotonation of the C-1 –OH with LDA and phosphorylation with TBPP. In contrast, attempts at phosphorylation of the C-4 Bn ether reducing sugar 68 with TBPP were not successful in forming the desired α-phosphate. Phosphitylation of 68 was successful using (iPr)_2NP(OBn)_2, followed by oxidation of the phosphite to the phosphate. Synthesis of the GlcNAc phenylselenides 71a and 71b was formed in good yields with both electron-withdrawing and electron-donating protecting groups at C-3 and C-4.

With the C-6 phenylselenide-containing GalNAc and GlcNAc glycosides (42a, 42b, 71a and 71b) and glycosyl phosphates (63 and 69) in hand, the phenylselenides will be transformed into their corresponding 5, 6 epoxides by a two-step process of oxidation of the selenide to the selenoxide and thermal elimination to an olefin (Chapter 5). Epoxidation of the resulting olefin with DMDO (Figure 1.8) should yield the desired GalNAc and GlcNAc epoxides 8. Epoxide fluoridolysis and cyanosilylation will be attempted on the epoxides to form the target compounds 11, 12, 20 and 21.
CHAPTER 4

SYNTHESIS OF C-6-PHENYLSELENIDE LacNAc DISACCHARIDES AND

(iso)LacNAc DISACCHARIDES

4.1 Introduction

In order to evaluate the (5-fluoro) (iso)LacNAc glycosides (13a and 14a) as mechanistic probes of FucT III-catalyzed glycosylation described in Chapter 1, it is necessary to synthesize the C-6 phenylselenide-containing β-1, 3 and β-1, 4 octyl glycosides (Figure 4.1). Formation of these target compounds proves synthetically challenging as glycosylation has not been reported using selenium-containing glycosides. Once installed, the phenylselenide glycosides may be transformed to the desired epoxides 10, which can undergo epoxide fluoridolysis to form the desired (5-fluoro) glycosides 13a and 14a.

![Figure 4.1: isoLacNAc and LacNAc C-6 Phenylselenide Synthetic Targets](image-url)
In addition to an octyl glycoside, an 8-methoxycarbonyloctyl (8-Mco) group could also be used at the C-1 position. The advantages of 8-Mco are the increase glycoside solubility when exposed to enzymatic buffer conditions. The disadvantages of 8-Mco are it cannot withstand several reaction conditions and 8-methoxycarbonyl octanol is costly. The octyl side chain is a known substrate for glycosyl transferase enzymes and can withstand broad synthetic reaction conditions. An octyl glycoside is necessary for the Sep-Pak assay used to evaluate the enzyme as described in Chapter 1.

There are two possibilities for forming the C-6 selenium-containing disaccharides with either an 8-Mco or octyl glycoside (Figure 4.2). Either phenylselenide monosaccharide acceptors (33 or 35), discussed in Chapter 3, are coupled with a galactosyl donor, or the phenylselenide is introduced after formation of the desired disaccharide linkage using the non-seleno precursors (32 or 72).

![Figure 4.2: Retrosynthetic Analysis for C-6 Phenylselenide Glycosides as Precursors of 5-(Fluoro) (iso)LacNAc Glycosides](image)

R₁ = TBS, (CH₂)₇Y, Y = CH₃ or CH₂CO₂Me
R₂ = Pht or HAc
X = Br or OCCCl₃
NH
4.2 Attempts at the synthesis of 6-SePh-(iso)LacNAc-β-octyl glycoside with selenium-containing acceptor substrates

The phenylselenide monosaccharide acceptors 73 and 33b were evaluated first as they were readily available (Table 4.1). Using Koenigs-Knorr and trichloroacetimidate glycosylation reactions discussed in Chapter 2, no disaccharide formation was observed. Compounds 73 and 33b were recovered, along with the hydrolysis products derived from the donors 74 and 75.

Table 4.1: β-1, 3 Glycosylation Attempts with Phenylselenide Monosaccharide Acceptor Substrates

<table>
<thead>
<tr>
<th>Entry</th>
<th>Donor</th>
<th>Acceptor</th>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X = Br (74)</td>
<td>R₁ = (CH₂)₆CO₂Me (73)</td>
<td>Hg(CN)₂ CaSO₄, 40 °C CH₂Cl₂/CH₃NO₂</td>
<td>No Product Formed</td>
</tr>
<tr>
<td>2</td>
<td>X = Br (74)</td>
<td>R₁ = TBS (33b)</td>
<td>Hg(CN)₂ 3Å sieves, 40 °C CH₂Cl₂/CH₃NO₂</td>
<td>No Product Formed</td>
</tr>
<tr>
<td>3</td>
<td>X = Cl (75)</td>
<td>R₁ = TBS (33b)</td>
<td>TMS-OTf 3Å sieves, CH₂Cl₂, 0°C</td>
<td>No Product Formed</td>
</tr>
</tbody>
</table>

Following the β-1, 3 glycosylation reactions previously attempted in Table 4.1, the phenylselenide-containing monosaccharide acceptor substrate 35b was used to attempt formation of the desired β-1, 4 disaccharides (Table 4.2). The results were

---

1 Compound 73 was isolated as a by-product of a reaction previously performed in our lab by Esther Joo.
identical to the isoLacNAc results and are shown in Table 4.1. The phenylselenide monosaccharide acceptors as well as the donor hydrolysis product were fully recovered.

Table 4.2: β-1, 4 Glycosylation Attempts with Phenylselenide Containing Monosaccharide Acceptor Substrates

<table>
<thead>
<tr>
<th>Entry</th>
<th>Donor</th>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X = Br</td>
<td>AgOTf, 3Å sieves, CH₂Cl₂, 0°C to rt</td>
<td>No Product Formed</td>
</tr>
<tr>
<td>2</td>
<td>X = Br</td>
<td>AgOTf, TMU, 3Å sieves, CH₂Cl₂, 0°C to rt</td>
<td>No Product Formed</td>
</tr>
<tr>
<td>3</td>
<td>X = Br</td>
<td>Hg(CN)₂, CaSO₄, 40 °C, CH₂Cl₂/CH₃NO₂, 0°C</td>
<td>No Product Formed</td>
</tr>
<tr>
<td>4</td>
<td>X = Cl</td>
<td>TMS-OTf, 3Å sieves, CH₂Cl₂, 0°C</td>
<td>No Product Formed</td>
</tr>
</tbody>
</table>

A proposed hypothesis as to why the phenylselenide monosaccharide acceptors are unable to form the desired disaccharide linkages is shown in Figure 4.3. It is presumed that the nucleophilic nature of C-6 selenium is greater than that of the C-3 or C-4 –OH acceptors and consumes the donor substrates in a non-productive manner.
4.3 Synthesis of 6-SePh-(iso)LacNAc-β-octyl glycoside with non-selenium-containing acceptor substrates

Given that the C-6 phenylselenide monosaccharide acceptors were unable to form the desired disaccharides, attention was turned toward the non-seleno-containing acceptors. The synthesis of the β-1, 3 glycoside with an 8-Mco side chain at C-1 was investigated. This approach utilized a trichloroacetimidate donor substrate, 77. In order to direct glycosylation towards the β configuration, a Troc group was used at C-2, due to its high β selectivity. After installation of the β-8-Mco side chain at C-1, the Troc group was then removed to form the free amine and N-acetylated to give 79. The benzylidene 80 was formed using benzaldehyde dimethyl acetal (PhCH(OMe)_2) and tosic acid monohydrate (pTsOH·H₂O) from a modified Schmidt procedure.
The Koenigs-Knorr and trichloroacetimidate methodologies (as described in Chapter 2) were applied in the formation of the desired β-1, 3 linkage. The Koenigs-Knorr method utilized either Hg(CN)$_2$ or AgOTf as an activator with a glycosyl bromide donor (Table 4.3). The best Koenigs-Knorr activator proved to be Hg(CN)$_2$. However the reaction required two days with mild heating. The trichloroacetimidate donor 75 and TMS-OTf activator (Table 4.3, entries 4 and 5) produced the desired β-1, 3 disaccharides in the highest yields and lowest reaction times. These reactions were temperature sensitive, with a lower activation temperature yielding the desired β-linkage$^{66}$ (82) versus a warmer temperature, which gives the α-linkage (83).$^{43}$
Table 4.3: β-1, 3 Glycosylation Attempts with Non-selenium Containing Monosaccharide Acceptor Substrates

<table>
<thead>
<tr>
<th>Entry</th>
<th>Donor Conditions</th>
<th>Acceptor Conditions</th>
<th>Disaccharide Conditions</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(X = \text{Br}) (74)</td>
<td>R1 = (CH(_2))(_6)CO(_2)Me (\text{R2 = NHAc (80)})</td>
<td>AgOTf, 3Å sieves, CH(_2)Cl(_2), 0°C to rt</td>
<td>45%</td>
</tr>
<tr>
<td>2</td>
<td>(X = \text{Br}) (74)</td>
<td>R1 = (CH(_2))(_6)CO(_2)Me (\text{R2 = NHAc (80)})</td>
<td>Hg((\text{CN})_2), CaSO(_4), 40°C CH(_2)Cl(_2)/CH(_3)NO(_2)</td>
<td>75%</td>
</tr>
<tr>
<td>3</td>
<td>(X = \text{Br}) (74)</td>
<td>R1 = (CH(_2))(_7)CH(_3) (\text{R2 = NPht (32)})</td>
<td>Hg((\text{CN})_2), CaSO(_4), 40°C CH(_2)Cl(_2)/CH(_3)NO(_2)</td>
<td>30%</td>
</tr>
<tr>
<td>4</td>
<td>(X = \text{CCl}_3) (\text{NH (75)})</td>
<td>R1 = (CH(_2))(_6)CO(_2)Me (\text{R2 = NHAc (80)})</td>
<td>TMS-OTf, 3Å sieves, CH(_2)Cl(_2), 0°C</td>
<td>81%</td>
</tr>
<tr>
<td>5</td>
<td>(X = \text{CCl}_3) (\text{NH (75)})</td>
<td>R1 = (CH(_2))(_7)CH(_3) (\text{R2 = NPht (32)})</td>
<td>TMS-OTf, 3Å sieves, CH(_2)Cl(_2), -20°C to rt</td>
<td>83%</td>
</tr>
</tbody>
</table>

The non-selenium containing disaccharide **82** was converted to the C-6 phenylselenide with Hannessian-Hullar conditions and displacement of the C-6 bromide with PhSeH and NEt\(_3\) to give **84** (Scheme 4.2). The addition of Bu\(_4\)NI resulted in a significant formation of a C-6 methyl by-product, and was avoided during bromide displacement. The N-phthaloyl, O-benzoyl and O-acetyl protecting groups were removed by H\(_2\)NNH\(_2\)·H\(_2\)O and a global N- and O-acetylation were performed to yield the desired C-6 phenylselenide-containing disaccharide glycoside **85**.
The β-1, 4 non-seleno acceptor substrates were synthesized using the precursors, 32 and 80, employed in the synthesis of β-1, 3 acceptor substrates. In order to manipulate the C-6 position and introduce a phenylselenide after disaccharide formation, a strategy was developed to isolate the C-6 –OH (Scheme 4.3). Either a reduction of the benzylidene 80 to a C-6 benzyl ether or acid-catalyzed opening of the benzylidene 32 followed by selective protection with a TBS group would differently protect the C-6 position. Reduction of the benzylidene using either HCl in ether with NaCNBH$_3$ or TES and TFA to form the C-6 Bn ether, 89, proved unreliable and low yielding. Opening of the benzylidene with AcOH/H$_2$O and selective protection of the free C-6 alcohol as a TBS ether to give, 87 or 90, proved to be better yielding and more reliable than the benzylidene reduction.
In comparison to the β-1, 3 reactions (Table 4.3), similar results were observed with the non-selenium containing monosaccharide acceptors for the β-1, 4 glycosylation conditions (Table 4.4). The Koenigs-Knorr method produced the desired β-linked disaccharide but in poor yields, even with the addition of 1, 1, 3, 3-tetramethylurea (TMU) \(^72\) (Table 4.4, entry 1). The trichloroacetimidate method was again superior to the Koenigs-Knorr method in terms of yields and reaction time. In the case of Table 4.4 entry 4, the TBS glycoside was removed with BF\(_3\)·OEt\(_2\) with an extended reaction time of 1 ½ hours. In the case of Table 4.4 entries 2 and 5, the acceptors 91 and 87 and TMS-OTf promoter successfully retained the TBS ether at C-6 to give compounds 93 and 95.\(^73\)
Table 4.4: β-1, 4 Glycosylation Attempts with Non-selenium Containing Monosaccharide Acceptor Substrates

<table>
<thead>
<tr>
<th>Entry</th>
<th>Donor</th>
<th>Acceptor</th>
<th>Conditions</th>
<th>Disaccharide</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$X = \text{Br}$</td>
<td>$R_1 = (\text{CH}_2)_8\text{CO}_2\text{CH}_3$</td>
<td>AgOTf, TMU, 3Å sieves, CH$_2$Cl$_2$, 0°C to rt</td>
<td>$R_1 = (\text{CH}_2)_8\text{CO}_2\text{CH}_3$</td>
<td>Trace</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R_2 = \text{NHAc}$</td>
<td></td>
<td>$R_2 = \text{NHAc}$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$X = \text{OCCl}_3$</td>
<td>$R_1 = (\text{CH}_2)_7\text{CH}_3$</td>
<td>TMS-OTf, 3Å sieves, CH$_2$Cl$_2$, -20°C</td>
<td>$R_1 = (\text{CH}_2)_7\text{CH}_3$</td>
<td>37%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R_2 = \text{NHAc}$</td>
<td></td>
<td>$R_2 = \text{NHAc}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$X = \text{OCCl}_3$</td>
<td>$R_1 = (\text{CH}_2)_7\text{CH}_3$</td>
<td>TMS-OTf, 3Å sieves, CH$_2$Cl$_2$, -20°C</td>
<td>$R_1 = (\text{CH}_2)_7\text{CH}_3$</td>
<td>Trace</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R_2 = \text{NPht}$</td>
<td></td>
<td>$R_2 = \text{NPht}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$X = \text{OCCl}_3$</td>
<td>$R_1 = (\text{CH}_2)_7\text{CH}_3$</td>
<td>1. BF$_3$OEt$_2$, 3Å sieves, CH$_2$Cl$_2$, -50°C 2. Ac$_2$O, pyr.</td>
<td>$R_1 = (\text{CH}_2)_7\text{CH}_3$</td>
<td>55% (2 steps)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R_2 = \text{NPht}$</td>
<td></td>
<td>$R_2 = \text{NPht}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$X = \text{OCCl}_3$</td>
<td>$R_1 = (\text{CH}_2)_7\text{CH}_3$</td>
<td>1. TMS-OTf, 3Å sieves, CH$_2$Cl$_2$, -20°C 2. Ac$_2$O, pyr.</td>
<td>$R_1 = (\text{CH}_2)_7\text{CH}_3$</td>
<td>22% (2 steps)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R_2 = \text{NPht}$</td>
<td></td>
<td>$R_2 = \text{NPht}$</td>
<td></td>
</tr>
</tbody>
</table>

In order to evaluate the N-PSP reagent for installation of the C-6 phenylselenide, a model reaction was performed on a simple C-6 alcohol (Scheme 4.4). The octyl glycoside 87 was O-acetylated to form 96 and the C-6 TBS ether removed with HF·pyridine to give the C-6 alcohol, 97. The C-6 phenylselenide, 98, was successfully formed in moderate yield using N-PSP and PBU$_3$ conditions. 46
The β-1, 4 C-6 phenylselenide glycoside was then formed using the same conditions (Scheme 4.5) as described in Scheme 4.4. The C-6 –OH, 99, was formed in a 92% yield, but its conversion to the selenide 100 proceeded in poor yield. Removal of the phthaloyl and acetyl protecting groups, followed by N- and O-acetylation produced 101.

**4.4 Synthesis of non-fluorinated (iso)LacNAc-octyl glycosides**

After formation of the desired β glycosidic linkages 82 and 95, the remaining protecting groups were removed in order to provide the non-fluorinated alternate substrates 13b and 14b (Scheme 4.6). The TBS ether at C-6 of 95 was removed during...
hydrazinolysis. This has not been previously reported in the literature and is a new method for removing primary TBS ethers.

Scheme 4.6

β-1,3 Disaccharide

1. AcOH/H₂O, Δ
2. H₂NNH₂·H₂O, EtOH, Δ
3. Ac₂O, pyr.

41% (3 steps)

β-1,4 Disaccharide

1. H₂NNH₂·H₂O, EtOH, Δ
2. Ac₂O, pyr.

70% (2 steps)

The non-fluorinated substrates were synthesized in order to compare the fluorinated versus non-fluorinated substrates with the FucT III enzyme. The octyl side chain was installed for the Sep-Pak assay used to evaluate the FucT III enzymatic reaction (Figure 4.4). The glycosides with the octyl side chain adhere to the reverse-phase column when eluted with water, washing away water-soluble impurities. Methanol is then used to remove the octyl glycosides from the column, allowing recovery and analysis of the trisaccharide product. Compounds 13b and 14b have been submitted to our collaborator, Hans Lin, for evaluation with the FucT III enzyme.
4.5 Conclusions

Both the β-1,3 and β-1,4 C-6 phenylselenide containing glycosides 85 and 101 were successfully synthesized by converting the non-selenium containing glycosides 82 and 95 to the C-6 selenium-containing glycosides. In contrast, attempts at glycosylation with phenylselenide-containing monosaccharide acceptor substrates were unsuccessful in disaccharide formation. Glycosylation reactions containing a C-6 phenylselenide containing acceptor have not been reported in the literature and Table 4.1 and Error! Reference source not found. provide the first evidence that C-6 phenylselenide monosaccharide acceptor substrates are not synthetically viable as acceptor substrates for glycosylation reactions. This problem can be overcome by converting the non-selenium containing glycosides to the C-6 phenylselenide glycosides as shown in Table 4.3 and Table 4.4.

In addition to the C-6 phenylselenide glycosides, the non-fluorinated alternate substrates 13b and 14b were also synthesized. Although these glycosides have been
previously reported in the literature, the new strategy presented in Section 4.4 is accessed from the readily available non-selenium containing disaccharides and is divergent to the C-6 phenylselenide-containing glycosides.
CHAPTER 5

SYNTHESIS OF 5, 6 EPOXY GLY COSIDES AND GLY COSYL PHOSPHATES

5.1 Introduction

5, 6 Epoxide installation is performed in a three-step process from the C-6 phenylselenides 42a, 42b, 71a, 71b, 63, 69, 85 and 101. The role of the axial C-4 substituent on the stability of 5, 6 epoxy GalNAc glycosides is of interest as this substituent will be adjacent to the 5, 6 epoxide. Both electron-withdrawing and electron-donating protecting groups have been investigated at the C-4 position to understand the role of the C-4 substituent on epoxide stability.

Oxidation of the phenylselenide to the selenoxide and thermal elimination in the presence of dihydropyran (DHP) provides the corresponding olefin (Figure 1.8). Epoxidation will be achieved using dimethyldioxirane (DMDO) because of the ease of removal of the by-product, acetone (Figure 5.1). Purification should be simplified because DMDO and acetone are easily removed by concentration in vacuo. The oxidant DMDO is synthesized from its parent ketone, acetone, and oxone in a NaHCO₃ solution. This reaction is pH-sensitive because of the peroxymonosulfate dianion generated during the course of the reaction. If the pH is too low, the peroxymonosulfate dianion concentration falls, causing the reaction to slow. If the pH is too high, the
peroxymonosulfate dianion will attack the dioxirane to yield the parent ketone, O₂, and sulfate.⁷₆

\[
\begin{align*}
\text{GlcNAc, X = OR, Y = H, Z = OR} \\
\text{GalNAc, X = H, Y = OR, Z = OR}
\end{align*}
\]

Figure 5.1: DMDO Epoxidation Reaction

5.2 Synthesis of 5, 6 GalNAc-β-octyl glycoside epoxides

The phenylselenide-containing compounds 42a and 42b were oxidized to the selenoxide and thermally eliminated to give 104a or 104b (Scheme 5.1). Alternatively, the BOM group was selectively removed and the resulting free alcohol protected as an acetate using BF₃·OEt₂ and AcBr to give 105. The oxidation and elimination were performed for both R⁴ = Ac and Bn. When R⁴ = Ac, the olefin, 106a, was found to be more stable than R⁴ = Bn, 106b and 106c. (The same trend was observed with the 5, 6 epoxides 107a-c, where R⁴ = Ac stabilized the epoxide.) When R⁴ = Bn, a yellow color was observed with both the olefin and epoxide after standing a few hours in a NMR tube. Therefore the reaction sequence was performed quickly to avoid decomposition. Use of R⁴ as an acetyl protecting group was theorized to help stabilize the olefin due to its electron-withdrawing nature. A 3:2 ratio of epoxide glycosides was observed for the C-4
OAc epoxide 107a, but the ratio was not determined for the C-4 benzyl ether glycosides, 107b and 107c.

Scheme 5.1

Submission of the epoxides for HRMS analysis resulted in decomposition of the epoxides. As a result, the formation of the olefins and epoxides in the reaction sequences were performed quickly to avoid formation of any potential decomposition products.

5.3 Synthesis of 5, 6 GalNAc phosphate epoxides

The glycosyl phenylselenide phosphate, 62a, was oxidized to the selenoxide and eliminated to form the olefin 108 (Scheme 5.2). The olefin was transformed to the epoxide, 109, with DMDO. The C-4 acetate glycosyl phosphate epoxide was formed in a 3:2 ratio of epoxides, similar to the β-octyl glycoside epoxide 107a.
In contrast, attempts at formation of the C-4 Bn galactosyl phosphate olefin 110 were not successful (Scheme 5.3). Loss of the $^{31}$P NMR signal was observed after elimination of the selenoxide was attempted. Given the instability of the C-4 Bn octyl glycosides 106b and 106c, it is not surprising that the olefin 110 was not stable since the phosphate is a better leaving group than octanol.

It is proposed that the electron-donating benzyl ether enhanced nucleophilicity of the putative vinyl ether 110, resulting in protonation of the olefin and formation of a carbocation at C-5, which could be stabilized by the ring oxygen. Quenching of the carbocation with $\text{H}_2\text{O}$ upon aqueous work-up could result in opening of the carbohydrate,
leading to loss of the phosphate leaving group at C-1 and decomposition (Figure 5.2).

Synthesis of the the C-4 Bn glycosyl phosphate, 110, was not pursued further.

![Chemical structure](image1)

**Figure 5.2: Hypothesis for Decomposition of 110**

### 5.4 Synthesis of isoLacNAc-octyl glycoside epoxide

In the case of the β-1, 3 isoLacNAc-octyl glycoside alternate substrate, spontaneous loss of the selenoxide to the olefin was observed during the course of the oxidation (Scheme 5.4). If the reaction time was extended, complete elimination to the olefin was observed eventually giving an 87% yield. If the reaction was stopped before complete oxidation to give the selenoxides, DHP elimination of the selenoxides resulted in a 63%, 2-step yield. If the elimination went longer than necessary (over 1 hour), removal of the acetates was observed. The resulting free alcohols could then be re-protected with acetic anhydride and pyridine to form 111 without causing decomposition. The epoxide 112 was formed in excellent yield with a 1:1 diastereomeric ratio. Though the epoxides would decompose upon submission of HRMS, nominal mass spectra could be obtained on the epoxides if obtained immediately upon work-up.
5.5 **Synthesis of LacNAc-octyl glycoside epoxide**

The same spontaneous loss of the selenoxides with direct formation of the olefin that was described in the previous section was also observed in the β-1, 4 disaccharide. However, complete conversion to the olefin was not observed. Therefore, the remaining selenoxides were thermally eliminated with DHP to afford the olefin 113 (Scheme 5.5). The epoxidation proceeded in good yield to give 114 as one diastereomer.

5.6 **Synthesis of glucosaminyl epoxides for attempts at cyanosilylation**

The phenylselenides 71a and 71b were oxidized using NaIO₄ to form their corresponding selenoxides (Scheme 5.6). The resulting selenoxides were then converted
to the olefins $115a$ and $115b$ by thermal elimination with DHP. The olefins were then treated with DMDO to afford their corresponding epoxides, $116a$ and $116b$, both in a 3:2 diastereomeric ratio.

Scheme 5.6

5.7 Synthesis of galactosaminyl epoxides for attempts at cyanosilylation

In addition to synthesizing the epoxides $116a$ and $116b$, the epoxide $118$ was also investigated. The galactosyl phenylselenide, $67$, used was previously described in Chapter 3, Scheme 3.10. The phenylselenide was oxidized to its corresponding selenoxide and then thermally eliminated with DHP to form the olefin $117$ (Scheme 5.7). Glycoside $117$ was transformed to the epoxide $118$ in good yield; however the diastereomeric ratio was undeterminable.
5.8 Conclusions

The GalNAc, GlcNAc and (iso)LAcNAc C-6 phenylselenide-containing glycosides were successfully transformed to their corresponding epoxides 107, 109, 112, 114, 116 and 118. In the case of the GalNAc-octyl glycosides and GalNAc-α-phosphates, an electron-withdrawing C-4 substituent formed a stable olefin and epoxide in a 3:2 diastereomeric ratio. Use of an electron-donating protecting group at C-4 led to an unstable olefin and epoxide, resulting in the need to proceed quickly through the reaction sequence.
6.1 Introduction

Epoxide fluoridolysis is achieved by using HF·pyridine which protonates the epoxide, and then allows the nucleophilic fluoride to attack, opening the epoxide\textsuperscript{77}. It is uncertain what effect an axial C-4 substituent will have on the GalNAc epoxide fluoridolysis. (5-fluoro) GalNAc glycosides have not been reported in the literature and our epoxide fluoridolysis methodology will be attempted on the GalNAc epoxides (8) previously described. (5-fluoro) (iso)LacNAc glycosides have not been described in the literature and this thesis presents the first attempts at epoxide fluoridolysis on β-1, 3 and β1-, 4 glycoosides. After fluoridolysis, the protecting groups can then be removed to form the desired 5-fluoro glycosides (Figure 6.1).\textsuperscript{8}

![Figure 6.1: Epoxide Fluoridolysis](image-url)
6.2 Attempts at synthesis of (5-F) GalNAc-β-octyl glycosides

When epoxide fluoridolysis was completed on 107a, 107b and 107c, decomposition was observed when R₄ = Ac (Scheme 6.1). When R₄ = Bn, as in 107b and 107c, fluoridolysis was successful and formed the desired C-F bond at C-5. However, the (5-F) GalNAc glycosides were unstable and decomposed upon purification on silica gel. Attempts at neutralizing the silica gel with 2% NEt₃ in the column eluent did not improve the stability of the (5-F) glycosides.

![Scheme 6.1](image)

6.3 Attempts at the synthesis of UDP (5-F) GalNAc

When epoxide fluoridolysis was attempted on 109 using HF-pyridine, loss of the C-1 phosphate peak was observed according to ³¹P NMR (Scheme 6.2). There was also only one fluorine peak according to ¹⁹F NMR, corresponding to the N-TFA group. As described above, the same results as the GalNAc-β-octyl glycoside was observed when there was a C-4 acetate protecting group, 107a to 119a.
6.4  Premature epoxide opening hypothesis

The hypothesis for the decomposition observed with the C-4 aceto-glycoside, 107a, and glycosyl phosphate, 109, is that premature epoxide opening occurred via anchiomeric assistance of the axial C-4 aceto substituent (Figure 6.2).

This decomposition seemingly can be avoided by having a non-participatory protecting group at the C-4 position, such as benzyl, as observed with the glycosyl epoxides 118b and 118c. However, the electron-donating benzyl ether does not seem to be able to stabilize the epoxide as well as the electron-withdrawing C-4 acetate. Perhaps use of an electron-withdrawing and non-participatory protecting group may help stabilize
the epoxide and allow for fluoridolysis. Repeated attempts of using a p-nitrobenzylbromide and a silver salt promoter\textsuperscript{78} resulted in decomposition of the model substrate 121, perhaps due to the nucleophilic nature of the selenium (Scheme 6.3). An alternative to the p-nitrobenzylbromide would be to use ClAc at C-4. ClAc is an electron-withdrawing protecting group, but potentially would not be involved in premature epoxide opening due to its reduced nucleophilicity of the electron-withdrawing Cl.

\textbf{Scheme 6.3}

![Scheme 6.3](image)

\textbf{6.5 Synthesis of (5-F) isoLacNAc-octyl glycoside}

Since the $\beta$-1, 3 and $\beta$-1, 4 disaccharides do not have an axial C-4 substituent, there should not be any neighboring group participation and epoxide fluoridolysis should proceed similarly to the GlcNAc series. In the case of the (5-F) isoLacNAc-octyl glycoside, epoxide fluoridolysis on 112 was achieved using HF-pyridine and the remaining acetate protecting groups were removed with methanolic ammonia to give 13a, X = F (Scheme 6.4).
6.6 Synthesis of (5-F) LacNAc-octyl glycoside

Synthesis of the (5-F) β-1, 4 octyl glycoside proceeded similarly as the β-1, 3 octyl glycoside (Scheme 6.5). After epoxide fluoridolysis on the epoxide 114, the O-Ac protecting groups were removed to afford 14a, X = F.

6.7 Synthesis of 5, 6 glucosaminyl cyano sugars

The glucosaminyl epoxides 116a, 116b and 123, 6-(OH) sugars, 124a, 124b and 124c, and 5-(OH), 6-(CN) sugars, 125a, 125b and 125c, using either AlCl₃ or BF₃·OEt₂ as the Lewis acid activator (Scheme 6.6). Both Lewis acids produced the desired cyano glycosides, however use of AlCl₃ in general proceeded with fewer undesired side products.
The regiochemistry of this reaction has been determined qualitatively using a 2, 4 dinitrophenylhydrazine (DNP) TLC spray (Figure 6.3). If there is a free alcohol at the C-5 position, then the glycoside exists as a reducing sugar in the open and closed forms of the carbohydrate. As a result, the glycoside has a ketone and is DNP-positive. If there is a cyano group at C-5, there is no ketone and therefore should be DNP-negative. The DNP results show that the major product formed was not DNP-positive. A minor product visible by TLC produced a faint DNP-positive stain, indicating formation of the (5-hydroxyl) glycoside in trace amounts.
Figure 6.3: Determination of C-5 Regioselectivity of (5-Cyano) Glycosides

After formation of the (5-cyano) glycosides, the CN group of 124c was reduced using H₂ and PtO₂ in MeOH to give the free amine 126 (Scheme 6.7). The amino group could then be potentially coupled to biotin or other compounds useful for assaying carbohydrates. These new glycosides could be useful as mechanistic probes of carbohydrate metabolizing enzymes.

Scheme 6.7

6.8 Attempted synthesis of 5, 6 galactosaminyl cyano sugars

In the case of the TBS glycoside 118, use of AlCl₃ resulted in a small amount of product formed by mass spectrum analysis, but mostly resulted in undesired side products (Scheme 6.8). Use of BF₃·OEt₂ on 118 resulted only in formation of undesired side products.
6.9 Conclusions

The GalNAc glycoside epoxides 107b and 107c successfully underwent epoxide fluoridolysis to form the (5-fluoro) GalNAc glycosides 119b and 119c. However, use of the C-4 acetate epoxide 107a, resulted in premature epoxide opening of the glycoside, presumably by neighboring group participation (Figure 6.2). This same trend was observed with the GalNAc glycosyl phosphate 120. It is noteworthy that the electron-withdrawing C-4 acetate had a stabilizing effect on the epoxide, whereas the electron-donating C-4 benzyl ether did not produce a stable epoxide.

Neighboring group participation was not observed in the (iso)LacNAc series as there is no axial C-4 substituent. The (5-fluoro) (iso)LacNac glycosides 13a and 14a were successfully synthesized.

In addition to epoxide fluoridolysis, attempts at a new C-C bond formation at C-5 were attempted using the GlcNAc and GalNAc epoxides 116a, 116b, 118 and 123. The cyanosilylation successfully produced the desired (5-cyano) GleNAc glycosides. The new method was amenable with electron-withdrawing and electron-donating protecting groups such as acetate and benzyl ethers. However, use of the GalNAc epoxide 118

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resulted in decomposition of the glycoside, perhaps due to the reactivity of the TBS ether and the strong Lewis acids AlCl$_3$ and BF$_3$·OEt$_2$. A more stable group at C-1, such as a GalNAc-octyl glycoside could be used. This would allow for comparison of the more labile C-F bond at C-5 to a more stable C-C bond at C-5.
CHAPTER 7

CONCLUSIONS

7.1 Synthesis of C-6 phenylselenide-containing monosaccharides and disaccharides

In conclusion, the C-6 phenylselenide monosaccharide glycosides were synthesized from the key benzylidene intermediate, 32. Several orthogonally protected phenylselenide glycosides were obtained in order to investigate the effect of electron-withdrawing versus electron-donating protecting groups at C-2, C-3 and C-4 during glycosylation reactions, epoxide fluoridolysis, and cyanosilylation reactions. Phenylselenide-containing β-octyl-glycosides and α-phosphates were synthesized as precursors to the fluorinated acceptor and donor substrates for the glycosyltransferases of interest.

In pursuit of the β-1, 3 and β-1, 4 disaccharides, the C-6 phenylselenide-containing monosaccharide glycosides were not acceptor substrates for formation of the selenium-containing glycosides (Table 4.1 and Error! Reference source not found.), presumably due to the selenium acting as a competitive nucleophile (Error! Reference source not found.). Fortunately, the C-6 phenylselenide-containing (iso)LacNAc-octyl glycosides were readily obtained by installing the selenium after disaccharide formation.

7.2 Synthesis of 5, 6 GalNAc, GlcNAc and (iso)LacNAc epoxides

Oxidation of the C-6 phenylselenide-containing glycosides to their corresponding selenoxides, followed by thermal elimination in the presence of DHP
produced the desired GalNAc, GlcNAc and (iso)LacNAc olefins. Epoxidation proceeded in good to excellent yields. In general, the GalNAc epoxides were formed in a 3:2 diastereomeric ratio. The GlcNAc and isoLAcNAc epoxides were formed in a 1:1 diastereomeric ratio, whereas the LacNAc epoxide was a single diastereomer. The role of electron-withdrawing versus electron-donating protecting groups was investigated in the stability of the olefins and epoxides. Stability of the olefins and epoxides was enhanced with the use of an electron-withdrawing protecting group at C-4. In contrast, an electron-donating protecting group at C-4 resulted in a more labile olefin and epoxide. In the case of the C-4 Ac GalNAc α-phosphate, formation of the olefin and epoxides proceeded in good yields. However, the C-4 Bn GalNAc α-phosphate olefin was unstable and resulted in decomposition.

7.3 Attempts at epoxide fluoridolysis and cyanosilylation

The role of participating versus non-participating protecting groups was investigated during attempts at epoxide fluoridolysis. In the GalNAc series, an axial electron-withdrawing C-4 acetate resulted in premature epoxide opening from neighboring group participation of the axial C-4 acetate (Figure 6.2). With a non-participatory protecting group at C-4, such as benzyl ether, the fluoridolysis was successful. However, the (5-fluoro) GalNAc glycosides were unable to be purified due to instability. In the future, an electron-withdrawing, non-participatory protecting group at C-4 may allow for stable C-F bond formation at C-5.

In pursuit of the β-1, 3 and β-1, 4 disaccharides, epoxide fluoridolysis was successful, allowing for potential evaluation of the FucT III glycosyltransferase. Since there was no axial C-4 substituent adjacent to the 5, 6 epoxides, therefore no premature epoxide opening was observed. Compounds 13a, 13b, 14a and 14b will be sent to our
collaborator Hans Lin at the Academia Sinica, Taiwan for biochemical evaluation with the FucT III enzyme. It will be interest to see if 13a and 14a will be substrates for FucT III and what effect fluorine has on glycosylation catalyzed by FucT III.

In addition to the formation of (5-fluoro) glycosides, the GlcNAc 5, 6 epoxides were subjected cyanosilylation conditions to form predominantly give the (5-cyano) glycosides. In the GalNAc series, only trace amounts of a cyano glycoside was detected by mass spectrum analysis. It is proposed that the TBS ether is not compatible with the strong Lewis acid conditions and resulted in decomposition. Perhaps use of an octyl glycoside at C-1 would allow for formation of a (5-cyano) GalNAc glycoside.

The CN group allowed access to the free amine, which may be coupled to biotin, fluorocene, KLH, peptides and other synthons used in evaluating glycosyltransferase reactions. Additional future work on the (5-cyano) glycosides should include optimization of the reaction conditions to improve yields, as well as further investigation of functional group tolerance. Overall, the cyanosilylation reaction is a promising new method for installing a carbon substituent at the C-5 position of carbohydrates.
CHAPTER 8

EXPERIMENTAL

**General Experimental:** All chemicals used were from Aldrich or Acros, except for BOM-Cl from TCI America and 8-methoxycarbonyl octanol from TRC. Water-sensitive reactions were conducted under an argon atmosphere and used oven-dried glassware, syringes and needles. Solvents were freshly distilled for moisture-sensitive reactions: THF from benzophenone ketyl, MeOH, NEt₃, CH₂Cl₂ and pyridine from CaH₂. CHCl₃ was purified by passing through a column of activated Al₂O₃. AgOTf was purified by azeotropic removal of impurities with toluene. Flash column chromatography used 230-400 mesh Whatman silica gel. TLC was run on Whatman 250 μm silica plates with UV fluorescence detected by short wave UV. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DRX-500 or 300 spectrometers or Varian 300 or 400 spectrometers. ¹H NMR chemical shifts (δ) for CDCl₃ or CD₂OD are in ppm using TMS as the reference at 0.00 ppm. ¹H NMR chemical shifts (δ) for spectra obtained in D₂O were referenced to HOD at 4.79 ppm. ¹³C NMR chemical shifts (δ) for CDCl₃ or CD₂OD are in ppm using the center solvent peak of CDCl₃ at 77.00 ppm as the reference and CD₂OD at 49.00 ppm as the reference. ¹⁹F NMR chemical shifts were referenced to TFA at 0 ppm as an external standard to TFA in CDCl₃. NMR assignments were based upon ¹H J values, ¹H COSY and HETCOR. Diastereomeric ratio of 5, 6 epoxides were determined by ¹H
NMR analysis. Mass spectra were recorded on a Micromass LCT Time-of-Flight mass spectrometer by electrospray ionization using sodium as the ion. Tetrabenzylpyrophosphate (TTBP) was prepared as described.\textsuperscript{79} Dimethyldioxirane was prepared as described.\textsuperscript{75} Compounds 43,\textsuperscript{80} 44,\textsuperscript{51} 46,\textsuperscript{38} 74,\textsuperscript{81} 75,\textsuperscript{81} 86,\textsuperscript{47} 91,\textsuperscript{73} were synthesized according to the literature procedures. Compound 32\textsuperscript{47} to 34\textsuperscript{8} was synthesized following modified procedures based upon the work of Matt Hartman, where the bromide was displaced first with phenylselenol before BOM protection at C-3. Compound 48 was purchased from Aldrich. Compound 76 and 77 were in spectral agreement with the literature.\textsuperscript{82} Compounds 76-80 were synthesized from modified literature procedures. Compound 78 was in spectral agreement with the literature.\textsuperscript{80} Compound 80 was in spectral agreement with the literature.\textsuperscript{83} Compound 102 was in spectral agreement with the literature.\textsuperscript{83}

Octyl 3-O-[(benzyloxy)methyl]-2,6-dideoxy-2-phthalamido-6-phenylseleno-D-glucopyranoside (35a).

![Chemical Structure](image)

To a stirred solution of 34a\textsuperscript{8} (1.90 g, 2.42 mmol) in 100 mL of THF:MeOH (1:1) was added 0.5M NaOMe solution (0.28 mL, 5.32 mmol). An additional portion (0.28 mL, 5.32 mmol) of the NaOMe solution was added after 17 h. After 45 h, the reaction was quenched with 2.0 g of Dowex 50W H\textsuperscript{+} form resin (2.1 meq/mL) and stirred gently for 30 min. The mixture was filtered and the filtrate concentrated. The resulting oil was
purified by flash column chromatography (hexanes:EtOAc, 3:1) to afford 35a as a colorless oil (1.47 g, 89%). $^1$H NMR (CDCl$_3$) $\delta$ 7.71 (d, 2H, NPh), 7.60 (m, 2H, NPh), 7.14 (m, 5H, SePh), 7.08 (m, 3H, ArH of BOM), 7.00 (m, 2H, ArH of BOM), 5.07 (d, 1H, $J = 8.3$ Hz, H1), 4.74 (d, 1H, $J = 7.1$ Hz, O-CH$_2$-Ph/Bn), 4.58 (d, 1H, $J = 7.1$ Hz, O-CH$_2$-Ph/Bn), 4.50 (d, 1H, $J = 12.0$ Hz, -OH), 4.33 (s, 2H, O-CH$_2$-O-Bn), 4.25 (d, 1H, $J = 10.8$ Hz, H4), 4.18 (dd, 1H, $J = 8.3$ Hz, H3), 3.69-3.62 (dd, 2H, H2/OCH$_2$-octyl), 3.49-3.42 (dd, 2H, H5/OCH$_2$-octyl), 3.31 (m, 1H, $J = 13.2$, 6.6 Hz, H6), 3.11 (m, 1H, $J = 12.8$, 8.3 Hz, H6), 1.32-1.31 (bs, 2H, CH$_3$-octyl), 1.16-0.97 (bs, 10H, CH$_3$-octyl), 0.88 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) $\delta$ 171.00, 136.30, 133.93, 132.03, 131.52, 130.99, 128.87, 128.41, 127.92, 127.72, 126.45, 123.47, 123.01, 98.11, 96.06, 82.53, 75.46, 74.00, 70.31, 69.50, 60.26, 55.15, 31.54, 31.47, 29.68, 29.01, 25.70, 22.53, 22.48, 20.92, 14.09, 13.95. MS (ES, Na$^+$): m/z (relative intensity) 704.2 (100). HRMS (M + Na$^+$) calcd for C$_{36}$H$_{43}$NO$_7$SeNa, 704.2102; found 704.2103.

$t$-Butyldimethylsilyl- 3-0-[(benzyloxy)methyl]- 2, 6-dideoxy-2-phthalamido-6-phenylseleno-3-D-glucopyranoside (35b).

To a stirred solution of 34b$^8$ (0.27 g, 0.340 mmol) in 10 mL of THF:MeOH (1:1) was added 1M NaOMe solution (0.35 mL, 0.35 mmol). After 6 h, the reaction was quenched with 0.75 g of Dowex 50W H$^+$ form resin (2.1 meq/mL) and stirred gently for 15 min. The mixture was filtered and the filtrate concentrated. The resulting oil was
purified by flash column chromatography (hexanes:EtOAc, 3:1) to afford 35b as a
colorless oil (0.20 g, 87%): $^1$H NMR (CDCl$_3$) $\delta$ 7.89 (d, 2H, NPh), 7.79 (m, 2H, NPh),
7.62 (m, 2H, SePh), 7.37-2.28 (m, 8H, SePh/ArH of BOM), 5.42 (d, 1H, J = 7.8 Hz, H1),
4.93 (d, 1H, J = 6.0 Hz, O-CH$_3$-Ph/Bn), 4.73 (d, 2H, O-CH$_3$-Ph/Bn/ O-CH$_2$-O-Bn), 4.33
(s, 1H, O-CH$_2$-O-Bn), 4.47 (d, 1H, J = 1.4 Hz, -OH), 4.40 (d, 1H, J = 10.9, 8.0 Hz, H3),
4.31 (dd, 1H, J = 10.8, 7.8 Hz, H2), 3.79 (dd, 1H, J = 9.0, 2.4 Hz, H4), 3.62 (m, 2H, J =
5.7, 3.0, 2.0 Hz, H5/H6), 3.24 (m, 1H, J = 12.6, 8.8 Hz, H6), 0.75-0.71 (bs, 9H, TBS),
0.13 (m, 3H, TBS) 0.08 (m, 3H, TBS). $^{13}$C NMR (CDCl$_3$) $\delta$ 168.80, 167.99, 136.53,
134.25, 132.11, 131.32, 129.17, 128.65, 128.16, 127.96, 127.86, 126.97, 123.58, 123.22,
96.29, 93.63, 82.48, 75.60, 74.38, 70.51, 57.43, 60.26, 30.07, -3.89, -5.57. MS (ES,
Na$^+$): m/z (relative intensity) 706.1 (100). HRMS (M + Na$^+$) calcd for
C$_{34}$H$_{41}$NO$_7$SeSiNa, 706.1715; found 706.1723.

$p$-Methoxyphenyl- 3-O-[(benzyloxy)methyl]- 2, 6-dideoxy-2-phthalamido-6-
phenylseleno-3-D-glucopyranoside (35c).

![Chemical Structure](image)

To a stirred solution of 34c (0.83 g, 1.23 mmol) in 100 mL of THF:MeOH (1:1)
was added 1M NaOMe solution (0.35 mL, 0.35 mmol). After 21 h, the reaction was
quenched with 1.75 g of Dowex 50W H$^+$ form resin (2.1 meq/mL) and stirred gently for
15 min. The mixture was filtered and the filtrate concentrated. The resulting oil was
purified by flash column chromatography (hexanes:EtOAc, 2:1) to afford 35c as a
colorless oil (0.53 g, 76%): $^1$H NMR (CDCl$_3$) $\delta$ 8.01 (d, 2H, NPh), 7.75 (m, 2H, NPh), 7.63-7.48 (m, 5H, ArH of BOM), 7.29 (m, 2H, SePh), 7.10 (m, 3H, SePh), 6.84 (m, 2H, PMP), 6.72 (m, 2H, PMP), 5.58 (dd, 1H, J = 8.5 Hz, H1), 4.79 (d, 1H, O-CH$_2$-Ph/Bn), 4.70-4.61 (m, 3H, H3/H4/ O-CH$_2$-Ph/Bn), 4.49 (s, 2H, O-CH$_2$-O-Bn), 4.33 (m, 1H, H2), 3.77 (dd, 1H, J = 9.0, 2.5 Hz, H5), 3.75 (s, 3H, OMe), 3.58 (dd, 1H, J = 8.5 Hz, H6), 3.16 (dd, 1H, J = 13.0, 8.5 Hz, H6). $^{13}$C NMR (CDCl$_3$) $\delta$ 155.35, 150.78, 136.25, 134.17, 132.15, 129.10, 129.02, 128.53, 128.42, 128.09, 127.93, 127.86, 126.67, 118.65, 118.51, 114.35, 97.58, 96.14, 82.51, 75.60, 73.81, 70.48, 55.57, 55.03, 29.61. MS (ES, Na$^+$): m/z (relative intensity) 698.1 (100). HRMS (M + Na$^+$) calcd for C$_{35}$H$_{33}$NO$_8$SeNa, 698.1269; found 698.1264.

Octyl 4-O-acetyl-3-O-[(benzyloxy)methyl]-2, 6-dideoxy-2-phthalamido-6-phenylseleno-3-O-galactopyranoside (40a).

To a stirred -5 °C solution of 35a (1.40 g, 2.06 mmol) in 60 mL of CH$_2$Cl$_2$ and pyridine (0.75 mL, 9.27 mmol) was added a freshly prepared solution of Tf$_2$O (0.69mL, 4.12 mmol) in 5 mL of CH$_2$Cl$_2$. The reaction solution turned a yellow-orange color with time and the temperature was maintained between -5 °C and +10 °C. After 2.25 h, the reaction was warmed to room temperature and diluted to 150 mL of CH$_2$Cl$_2$ and washed with 150 mL of satd. Cu$_2$SO$_4$, H$_2$O, and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The resulting oil (1.60 g) was taken on without any purification: $^1$H NMR (CDCl$_3$) $\delta$ 7.75 (d, 2H, NPh), 7.54 (m, 2H,
NPh), 7.24 (m, 2H, SePh), 7.08 (m, 3H, SePh), 6.85 (m, 5H, ArH of BOM), 5.11 (d, 1H, J = 8.4 Hz, H1), 4.83-4.76 (m, 2H, H3/H4), 4.72 (d, 1H, O-CH$_2$-Ph/Bn), 4.62 (d, 1H, O-CH$_2$-Ph/Bn), 4.32 (dd, 1H, J = 10.2, 8.4, Hz, H2), 4.15 (s, 2H, O-CH$_2$-O-Bn), 4.92 (dd, 1H, J = 9.3, 3.0 Hz, H5), 3.70 (m, 1H, J = 9.9, 6.0 Hz, CH$_2$-octyl), 3.38 (m, 1H, CH$_3$-octyl), 3.29 (dd, 1H, J = 12.9, 2.7 Hz, H6), 3.15 (dd, 1H, J = 13.2, 9.3 Hz, H6), 1.43 (bs, 2H, CH$_2$-octyl), 1.22-0.96 (bs, 10H, CH$_2$-octyl), 0.80 (t, 3H, CH$_3$-octyl).

$^{19}$F NMR (CDCl$_3$) $\delta$ 2.10. To the triflate glycoside was added a solution of Et$_4$NOAc (2.5 g, 9.85 mmol) in 25 mL of DMF. After 1 h, the reaction was concentrated to remove the DMF. The resulting red oil dissolved in 250 mL of CH$_2$Cl$_2$ and washed twice with 100 mL of H$_2$O and once with satd. NaCl solution. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude product was purified with flash column chromatography (hexanes:EtOAc, 3:1) to afford compound 40a (1.25 g, 85%, 2 steps) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.83 (d, 1H, NPh), 7.64 (m, 1H, NPh), 7.60 (s, 2H, NPh), 7.54 (m, 2H, SePh), 7.27 (m, 3H, SePh), 7.20 (m, 3H, ArH of BOM), 6.98 (m, 2H, ArH of BOM), 5.57 (d, 1H, J = 3.0 Hz, H4), 5.18 (d, 1H, J = 8.5 Hz, H1), 4.78 (d, 1H, J = 7.4 Hz, O-CH$_2$-Ph/Bn), 4.71 (dd, 1H, J = 11.0, 2.9 Hz, H3), 4.17 (s, 2H, J = 7.8 Hz, O-CH$_2$-O-Bn), 4.11 (dd, 1H, J = 6.9 Hz, H2), 3.87 (dd, 1H, J = 7.0 Hz, H5), 3.81 (m, 1H, CH$_2$-octyl), 3.40 (m, 1H, CH$_2$-octyl), 3.19 (dd, 1H, J = 12.9, 7.7 Hz, H6), 3.00 (dd, 1H, J = 12.8, 5.9 Hz, H6), 2.18 (s, 3H, OAc), 1.26-1.23 (bs, 2H, CH$_2$-octyl), 1.16-0.93 (bs, 10H, CH$_2$-octyl), 0.81 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) $\delta$ 170.57, 168.46, 167.63, 136.97, 133.95, 133.91, 132.85, 131.40, 131.34, 129.60, 129.18, 128.11, 127.35, 127.26, 127.09, 123.36, 122.98, 98.45, 92.82, 73.31, 71.56, 69.82, 69.49, 68.19, 60.28, 52.56, 31.53, 29.11, 29.00, 27.78, 25.68, 22.48, 20.95, 20.85, 14.10, 13.96, -0.92. MS (ES,
Na⁺): m/z (relative intensity) 746.2 (100). HRMS (M + Na⁺) calcd for C₃₈H₄₅NO₈SeNa, 746.2208; found 746.2232.

τ-Butyldimethylsilyl, 4-O-acetyl, 3-O-[(benzyloxy)methyl], 2, 6-dideoxy-6-phenylseleno-2-phthlamido-β-D-galactopyranoside (40b).

To a stirred -5 °C solution of 35b (0.065 g, 0.095 mmol) in 1.5 mL of CH₂Cl₂ and pyridine (0.030 mL, 0.428 mmol) was added a freshly prepared solution of Tf₂O (0.03 mL, 0.190 mmol) in 0.14 mL of CH₂Cl₂. The reaction solution turned a light pink color with time and the temperature was maintained between -5 °C and +10 °C. After 1 h, the reaction was diluted to 5 mL of CH₂Cl₂ and washed with 5 mL of satd. NaHCO₃ solution. The aqueous extract was washed with 5 mL of CH₂Cl₂ and the combined organic extracts washed with 10 mL of satd. NaCl solution. The resulting oil (0.074 g) was taken on without any purification: ¹H NMR (CDCl₃) δ 7.88 (d, 2H, NPht), 7.59 (m, 2H, NPht), 7.35 (m, 2H, SePh), 7.15 (m, 3H, SePh), 6.91 (m, 5H, ArH of BOM), 5.40 (dd, 1H, J = 8.0 Hz, H1), 4.86-4.69 (m, 3H, H3/H4/H2), 4.67 (d, 2H, O-CH₂-Ph/Bn), 4.23 (s, 2H, O-CH₂-O-Bn), 3.98 (dd, 1H, J = 9.0 Hz, H5), 3.32 (dd, 1H, J = 12.7 Hz, H6), 3.19 (dd, 1H, J = 9.6 Hz, H6), 0.71 (s, 9H, tBu), 0.15 (s, 3H, Me), 0.06 (a, 3H, Me). ¹⁹F NMR (CDCl₃) δ 1.78. To the triflate glycoside was added a solution of Et₄NOAc (0.18 g, 0.681 mmol) in 3 mL of DMF. After 15 min, the reaction was concentrated to remove the DMF. The crude product was dissolved in 50 mL of CH₂Cl₂ and washed twice with 25 mL of H₂O and once with satd. NaCl solution. The organic extract was dried with Na₂SO₄, filtered and the filtrate
concentrated. The crude product was purified with flash column chromatography (hexanes:EtOAc, 3:1) to afford 40b (0.08 g, 87%, 2 steps) as a colorless oil: \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.86 (d, 1H, NPh), 7.70 (m, 1H, NPh), 7.65 (m, 2H, NPh), 7.53 (m, 2H, SePh), 7.31 (m, 3H, SePh), 7.22 (m, 3H, ArH of BOM), 7.02 (m, 2H, ArH of BOM), 5.54 (d, 1H, J = 3.2 Hz, H4), 5.42 (d, 1H, J = 8.1 Hz, H1), 4.79 (d, J = 7.6 Hz, O-CH\(_2\)-Ph/Bn), 4.68 (dd, 1H, J = 11.2, 3.4 Hz, H3), 4.52 (d, 1H, J = 7.5 Hz, O-CH\(_2\)-O-Bn), 4.46 (d, 1H, J = 11.3, 8.1 Hz, H2), 4.20 (s, 2H, O-CH\(_2\)-Ph/BOM), 3.89 (dd, 1H, J = 8.1, 5.2 Hz, H5), 3.20 (dd, 1H, J = 12.8, 8.4 Hz, H6), 2.96 (dd, 1H, J = 12.8, 5.1 Hz, H6), 2.23 (s, 3H, OAc), 0.71 (s, 9H, tBu), 0.13 (s, 3H, Me), 0.02 (s, 3H, Me). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 171.20, 169.01, 168.43, 137.53, 134.46, 133.12, 131.89, 129.69, 128.61, 127.84, 127.67, 127.61, 123.77, 123.42, 109.98, 94.15, 93.38, 73.70, 71.80, 70.01, 68.89, 55.09, 30.10, 28.46, 25.77, 21.342, 17.95. MS (ES, Na\(^+\)): m/z (relative intensity) 748.1 (100). HRMS (M + Na\(^+\)) calcd for C\(_{36}\)H\(_{43}\)NO\(_8\)SeSiNa, 748.1821; found 748.1819.

\(p\)-Methoxyphenyl, 4-\(O\)-acetyl, 3-\(O\)-[(benzyloxy)methyl], 2, 6-dideoxy, 6-phenylseleno-2-phthlamido-\(\beta\)-D-galactopyranoside (40c).

To a stirred -5 °C solution of 35c (0.027 g, 0.040 mmol) in 0.5 mL of CH\(_2\)Cl\(_2\) and pyridine (0.01 mL, 0.18 mmol) was added 0.07 mL of a freshly prepared solution of Tf\(_2\)O (0.01 mL, 0.08 mmol) in 0.6 mL of CH\(_2\)Cl\(_2\). The reaction solution turned a yellow-orange color with time and the temperature was maintained between -5 °C and +10 °C. After 2 h, the reaction was diluted to 5 mL of CH\(_2\)Cl\(_2\) and washed with 5 mL of satd. NaHCO\(_3\) solution. The aqueous extract was washed with 5 mL of CH\(_2\)Cl\(_2\) and the combined
organic extracts washed with 10 mL of satd. NaCl solution, dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The resulting oil (0.029 g) was taken on without any purification: $^1$H NMR (CDCl$_3$) $\delta$ 7.54 (d, 2H, NPh), 7.51 (m, 2H, NPh), 7.28 (m, 2H, SePh), 7.14 (m, 3H, SePh), 6.88 (m, 2H, PMP), 6.85 (m, 2H, PMP), 5.63 (dd, 1H, $J$ = 8.4 Hz, H1), 4.91-4.69 (m, 3H, H3/H4/H2), 4.63 (d, 2H, $J$ = 8.3 Hz, O-CH$_2$-Ph/Bn), 4.19 (s, 2H, O-CH$_2$-O-Bn), 4.02 (dd, 1H, $J$ = 9.2, 2.3 Hz, H5), 3.74 (s, 3H, OMe), 3.36 (dd, 1H, $J$ = 13.3, 2.5 Hz, H6), 3.15 (dd, 1H, $J$ = 13.2, 9.2 Hz, H6). $^{19}$F NMR (CDCl$_3$) $\delta$ 1.69. To the triflate glycoside was added a solution of Et$_4$NOAc (0.07 g, 0.269 mmol) in 1 mL of DMF. After 15 min, the reaction was concentrated to remove the DMF. The crude product was dissolved in 5 mL of CH$_2$Cl$_2$ and washed twice with 5 mL of H$_2$O and once with satd. NaCl solution. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude product was purified with preparatory thin layer chromatography (hexanes:EtOAc, 2:1) to afford 40c (0.014 g, 49%, 2 steps) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.87 (d, 1H, $J$ = 7.3 Hz, NPh), 7.67 (m, 1H, NPh), 7.61 (s, 2H, NPh), 7.52 (m, 2H, SePh), 7.27 (m, 3H, SePh), 7.19 (m, 3H, ArH of BOM), 6.98 (m, 2H, ArH of BOM), 6.90 (dd, 2H, $J$ = 7.0, 2.0 Hz, PMP), 6.72 (dd, 2H, $J$ = 7.0, 3.6 Hz, PMP), 5.86 (d, 1H, $J$ = 8.0 Hz, H1), 5.58 (d, 1H, $J$ = 2.9 Hz, H4), 4.77 (dd, 1H, $J$ = 9.9, 7.6 Hz, H2), 4.72 (dd, 1H, $J$ = 11.0, 8.0 Hz, H3), 4.50 (d, 2H, $J$ = 7.5 Hz, O-CH$_2$-Ph/Bn), 4.17 (s, 2H, O-CH$_2$-O-Bn), 3.95 (dd, 1H, $J$ = 8.1, 5.3 Hz, H5), 3.72 (s, 3H, OMe), 3.17 (dd, 1H, $J$ = 12.9, 4.6 Hz, H6), 3.00 (dd, 1H, $J$ = 12.9, 5.3 Hz, H6), 2.21 (s, 3H, OAc). $^{13}$C NMR (CDCl$_3$) $\delta$ 171.07, 168.94, 168.12, 155.85, 151.26, 137.41, 134.56, 133.53, 131.77, 129.86, 129.75, 128.64, 127.92, 127.59, 123.99, 123.69, 118.98, 114.80, 98.28, 93.39, 73.98, 71.97, 70.07, 68.64, 56.00, 52.85, 28.36, 21.35. MS (ES, Na$^+$): m/z
Octyl 4-O-benzyl-3-O-[(benzyloxy)methyl]-2,6-dideoxy-6-phenylseleno-2-phthalamido-3-D-galactopyranoside (41).

To a stirred solution of 40a (1.25 g, 1.73 mmol) in 50 mL of THF:MeOH (1:1) was added 0.5M NaOMe solution (0.03mL, 0.553 mmol). After 21 h, the reaction solution was quenched with 2.00 g of Dowex 50W H⁺ form resin (2.1 meq/mL) and gently stirred for 15 min. The suspension was filtered and the filtrate concentrated. The resulting oil was purified using flash column chromatography (hexanes:EtOAc, 3:1) to afford the free C-4 OH glycoside (1.11 g, 95%) as a colorless oil: ¹H NMR (CDCl₃) δ 7.81 (m, 1H, Pht), 7.66 (m, 3H, Pht), 7.55 (m, 2H, ArH of BOM), 7.27 (m, 3H, ArH of BOM), 7.23 (m, 5H, PhSe), 7.21 (m, 3H, Bn), 7.08 (m, 2H, Bn), 5.10 (d, 1H, J = 8.0 Hz, H1), 4.77 (d, 1H, J = 7.3 Hz, -O-CH₂-O-Bn), 4.65 (d, 1H, J = 11.8 Hz, CH₂-Ph), 4.53 (m, 1H, Hz, H3), 4.39-31 (m, 2H, -O-CH₃-Ph), 4.27 (m, 1H, H2), 3.82-3.73 (m, 3H, CH₃-octyl/H4/H5), 3.40-3.31 (m, 2H, CH₃-octyl, H6), 3.23 (m, 1H, H6), 2.49 (d, 1H, J = 2.9 Hz, -OH), 1.39-1.32 (bs, 2H, CH₃-octyl), 1.18-0.95 (bs, 10H, CH₃-octyl), 0.82 (t, 3H, CH₃-octyl). ¹³C NMR (CDCl₃) δ 170.92, 168.58, 167.65, 136.81, 133.84, 133.79, 132.29, 131.39, 129.87, 128.99, 128.14, 127.43, 127.21, 126.83, 123.28, 122.85, 98.24, 93.69, 75.00, 74.13, 69.67, 69.27, 67.60, 60.18, 51.94, 31.45, 29.05, 28.92, 27.44, 25.62, 22.39, 20.83, 14.01, 13.87, -0.843. MS (ES, Na⁺): m/z (relative intensity) calcd for
C_{33}H_{43}NO_{7}SeNa, 706.2; found 706.2 (100). To a stirred 0 °C solution of the C-4 OH glycoside (0.22 g, 0.322 mmol) in 10mL of THF was added NaH (80% in oil, 0.015 g, 0.645 mmol). The resulting mixture was stirred for 30 min and had BnBr (0.08 mL, 0.645 mmol) and NBu$_4$I (0.60 g, 1.610 mmol) added to it. After 20.5 h, the reaction mixture was diluted with 50 mL of EtOAc and washed with 50 mL of H$_2$O, satd. NaHCO$_3$ and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The resulting oil was purified using flash column chromatography (hexanes:EtOAc, 5:1) to afford 41 (0.23 g, 92%; 87%, 2 steps) as a colorless oil: $^1$H NMR (CDCl$_3$) δ 7.64 (m, 1H, Pht), 7.47 (m, 3H, Pht), 7.37 (m, 2H, ArH of BOM), 7.34 (m, 3H, ArH of BOM), 7.29 (m, 5H, PhSe), 7.22 (m, 3H, Bn), 7.04 (m, 2H, Bn/Ph), 5.12 (d, 1H, J = 8.4 Hz, H1), 5.00 (d, 1H, J = 11.5 Hz, -O-CH$_2$-O-Bn), 4.75 (d, 1H, J = 6.9 Hz, CH$_2$-Ph), 4.72 (dd, 1H, J = 10.3, 2.6 Hz, H3), 4.62 (m, 1H, CH$_2$-Ph), 4.58 (dd, 1H, J = 11.2, 8.4 Hz, H2), 4.55 (d, 1H, J = 11.6 Hz, -O-CH$_2$-Ph), 4.28 (d, 2H, J = 12.1, 6.1 Hz, -O-CH$_2$-Ph), 4.10 (d, 1H, J = 2.4 Hz, H4), 3.77 (m, 1H, CH$_2$-octyl), 3.67 (m, 1H, CH$_2$-octyl), 3.35 (m, 1H, H5), 3.23 (dd, 1H, J = 12.6, 6.3 Hz, H6), 3.02 (dd, 1H, J = 12.6, 7.6 Hz, H6), 1.25-1.16 (bs, 2H, CH$_2$-octyl), 1.12-0.97 (bs, 10H, CH$_2$-octyl), 0.81 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) δ 168.86, 167.76, 138.26, 137.14, 133.08, 132.51, 131.67, 129.97, 128.16, 128.26, 128.24, 128.22, 127.61, 127.46, 127.17, 127.04, 123.35, 122.87, 98.50, 93.94, 76.36, 74.72, 73.59, 74.35, 69.73, 69.40, 52.69, 31.59, 29.20, 29.07, 29.03, 27.98, 25.76, 22.52. MS (ES, Na$^+$): m/z (relative intensity) 794.2 (100). HRMS (M + Na$^+$) calcd for C$_{43}$H$_{47}$NO$_7$SeNa, 794.2572; found 794.2604.
Octyl 2-acetamido-4-\(O\)-acetyl-3-\(O\)-[(benzyloxy)methyl]-2, 6-dideoxy-6-phenylseleno-3-\(D\)-galactopyranoside (42a).

To a stirred solution of 40a (0.150 g, 0.207 mmol) in 10 mL of EtOH in a Schlenk tube was added \(\text{H}_2\text{NNH}_2\cdot\text{H}_2\text{O}\) (1.00 mL, 19.7 mmol). The reaction was placed under a gentle vacuum, the tube sealed and heated to 100 °C. After 43 h, the reaction was cooled, the tube opened and the reaction mixture concentrated. The resulting oil/solid was dissolved in 20 mL of EtOAc and washed with 20 mL of satd. NaHCO\(_3\) solution. The aqueous extract was washed with 20 mL of EtOAc and the combined organic extracts washed with 50 mL of satd. NaCl solution, dried with Na\(_2\)SO\(_4\), filtered and the filtrate concentrated. The resulting colorless oil (0.110 g) was taken on without any purification. The resulting oil (0.110 g, 0.200 mmol) was dissolved in 3 mL of pyridine and 3 mL of Ac\(_2\)O. After 25.5 h, the reaction was diluted with 40 mL of EtOAc and washed with 40 mL of satd. CuSO\(_4\), H\(_2\)O, satd. NaHCO\(_3\), and satd. NaCl solutions. The organic extract was dried with Na\(_2\)SO\(_4\), filtered and the filtrate concentrated. The crude oil was purified using flash column chromatography (hexanes:EtOAc, 1:1) to afford 42a (0.100 g, 76%, 2 steps) as a colorless oil: \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.51 (m, 3H, ArH of BOM), 7.49 (m, 2H, ArH of BOM), 7.33 (m, 5H, PhSe), 5.61 (d, 1H, \(J = 7.5\) Hz, N-H), 5.49 (d, 1H, \(J = 3.1\) Hz, H4), 4.93 (d, 1H, \(J = 8.4\) Hz, H1), 4.83 (d, 1H, \(J = 7.2\) Hz, -O-CH\(_2\)-O-Bn), 4.67 (m, 1H, -O-CH\(_2\)-OBn), 4.57-4.54 (d, 2H, -O-CH\(_2\)-Ph), 4.50 (dd, 1H, \(J = 10.8, 3.2\) Hz, H3), 3.87 (dd, 1H, \(J = 9.5, 6.5\) Hz, H2), 3.74 (m, 2H, CH\(_2\), octyl), 3.45 (m, 1H, H5), 3.11 (dd, 1H, \(J = 12.8, 7.9\) Hz, H6), 2.89 (dd, 1H, \(J = 12.8, 5.7\) Hz, H6), 2.05 (s, 3H, NHAc), 1.89
Octyl 2-acetamido-4-O-benzyl-3-O-[(benzyloxy)methyl]-2, 6-dideoxy-6-phenylseleno-3-D-galactopyranoside (42b).

To a stirred solution of 41 (0.080 g, 0.103 mmol) in 4 mL of EtOH in a Schlenk tube was added H₂NNH₂·H₂O (0.45 mL, 9.323 mmol). The reaction placed under a gentle vacuum, the tube sealed and heated to 100 °C. After 44 h, the reaction was cooled, the tube opened and the reaction mixture concentrated. The resulting oil/solid was dissolved in 30 mL of EtOAc and washed with 15 mL of satd. NaHCO₃ solution. The aqueous extract was washed with 25 mL of EtOAc and the combined organic extracts washed with 40 mL of satd. NaCl solution, dried with Na₂SO₄, filtered and the filtrate concentrated. The resulting oil was purified using a short silica gel plug (hexanes:EtOAc, 1:1) to afford the free amine (0.060 g) as a colorless oil: ¹H NMR (CDCl₃) δ 7.45 (m, 2H, ArH of BOM), 7.36 (m, 3H, ArH of BOM), 7.30 (m, 5H, PhSe), 7.25 (m, 5H, Bn), 4.90 (d, 1H, J = 6.6 Hz, CH₂-Ph), 4.88 (d, 1H, J = 11.0 Hz, -O-CH₂-O-Bn), 4.81 (d, 1H, J = 6.8 Hz, O-CH₂-Ph), 4.72 (m, 1H, -O-CH₂-OBn), 4.63 (d, 1H, J = 11.8 Hz, -O-CH₂-Ph), 4.53 (d, 1H, J = 11.6 Hz, -O-CH₂-Ph), 4.09 (d, 1H, J = 7.8 Hz, H1),

(s, 3H, OAc), 1.25 (bs, 12H, CH₂-octyl), 0.88 (bs, 3H, CH₃). ¹³C NMR (CDCl₃) δ 170.46, 170.38, 137.37, 132.86, 129.61, 129.14, 128.37, 127.69, 127.60, 127.42, 127.22, 99.67, 93.04, 73.00, 72.35, 69.99, 69.66, 68.67, 54.45, 31.72, 29.36, 29.24, 29.18, 27.85, 25.82, 23.44, 22.55, 20.78, 13.99. MS (ES, Na⁺): m/z (relative intensity) 658.2 (100). HRMS (M + Na⁺) calcd for C₃₂H₄₅NO₇SeNa, 658.2259; found 658.2266.
3.92 (d, 1H, J = 2.3 Hz, H4), 3.87 (m, 1H, CH$_2$-octyl), 3.54 (dd, 1H, J = 10.3, 2.6 Hz, H3), 3.47 (m, 1H, H5), 3.87 (m, 1H, CH$_2$-octyl), 3.27 (dd, 1H, J = 10.2, 7.7 Hz, H2), 3.20 (dd, 1H, J = 12.5, 6.6 Hz, H6), 2.97 (dd, 1H, J = 12.5, 7.3 Hz, H6), 1.60 (bs, 2H, CH$_2$-octyl), 1.25 (bs, 10H, CH$_2$-octyl), 0.85 (s, 3H, CH$_3$-octyl). $^1$H NMR (CDCl$_3$) δ 138.36, 137.38, 132.59, 130.01, 129.11, 128.49, 128.22, 128.12, 127.85, 127.80, 127.58, 127.00, 104.49, 93.96, 81.45, 74.55, 73.76, 70.08, 69.89, 52.51, 31.78, 29.53, 29.36, 29.18, 28.19, 25.99, 22.61. The amine (0.060 g, 0.093 mmol) was immediately dissolved in 3 mL of Ac$_2$O and 3 mL of pyridine and had 10 mg of DMAP added to it. After 47 h, the reaction was diluted to 40 mL of EtOAc and washed with 40 mL of satd. CuSO$_4$, H$_2$O, satd. NaHCO$_3$, and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The resulting oil was purified using flash column chromatography (hexanes:EtOAc, 1:1) to afford 42b (0.043 g, 61%, 2 steps): $^1$H NMR (CDCl$_3$) δ 7.43 (m, 2H, ArH of BOM), 7.33 (m, 3H, ArH of BOM), 7.29 (m, 5H, PhSe), 7.25 (m, 5H, Bn), 5.87 (d, 1H, J = 6.9 Hz, NH), 4.92 (d, 1H, J = 3.6 Hz, H4), 4.91 (d, 1H, J = 7.7 Hz, H1), 4.86 (d, 1H, J = 6.3 Hz, CH$_2$-Ph), 4.76 (d, 1H, J = 6.5 Hz, -O-CH$_2$-Ph), 4.66 (d, 2H, -O-CH$_2$-OBn), 4.11 (dd, 1H, J = 7.0, 4.0 Hz, H3), 4.00 (d, 1H, -O-CH$_2$-Ph), 4.48 (d, 1H, J = 10.7 Hz, -O-CH$_2$-Ph), 3.82 (m, 1H, CH$_2$ octyl), 3.57-3.53 (dd, 2H, J = 12.6, 7.6 Hz, H5/H2), 3.43 (m, 1H, CH$_2$ octyl), 3.19 (dd, 1H, J = 12.4 Hz, H6), 2.93 (dd, 1H, J = 12.4, 7.6 Hz, H6), 1.90 (s, 3H, NHAc), 1.54 (bs, 2H, CH$_2$-octyl), 1.25 (bs, 10H, CH$_2$-octyl), 0.86 (s, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) δ 170.65, 138.22, 137.44, 132.44, 129.89, 129.07, 128.42, 128.28, 128.18, 128.09, 127.89, 127.72, 127.56, 127.49, 126.95, 99.35, 94.22, 76.45, 74.86, 74.62, 74.17, 69.82, 69.61, 60.29, 54.73, 31.72, 29.37, 29.25, 29.19, 27.99, 25.82, 23.50, 22.55, 20.94, 14.09, 14.00. MS (ES, Na$^+$): m/z
(relative intensity) 706.3 (100). HRMS (M + Na\(^+\)) calcd for C\(_{37}\)H\(_{49}\)NO\(_6\)SeNa, 706.2623; found 706.2628.

**Phenylthio 4, 6-\(\text{O}\)-benzylidene-2-deoxy-2-(2, 2, 2-trichloroethoxycarbonyl) amido-\(\text{\(\beta\)}\)-D-glucopyranoside (45).**

To a stirred 0 °C solution of 44 (3.55 g, 6.20 mmol) in 100 mL of MeOH and was added NaOMe powder (0.33 g, 6.197 mmol). After 2 h, 1.8 g of Dowex 50W H\(^+\) form resin (2.1 meq/mL) was added and the reaction mixture was gently stirred for 20 min. The reaction mixture was filtered and the filtrate concentrated. To a suspension of the resulting triol in 75 mL of dry CH\(_3\)CN was added PhCH(OMe)\(_2\) (1.58 mL, 10.5 mmol) and pTsOH (0.29 g, 1.55 mmol). After 20 h, the reaction was placed under a gentle vacuum. After 1 h, the reaction had 1 g of K\(_2\)CO\(_3\) added to it and was stirred for 30 min. The mixture was filtered and the filtrate concentrated. The crude product was purified with flash column chromatography (EtOAc) to afford compound 45 (3.00 g, 90%, 2 steps) as a colorless oil/solid: \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.45 (m, 5H, Ph), 7.35 (m, 5H, Ph), 5.54 (s, 1H, benzylidene), 5.25 (d, 1H, H1), 4.83 (d, 1H, \(J = 7.2, \text{CH}_2\)-Troc), 4.83 (d, 1H, \(J = 7.2, \text{CH}_2\)-Troc), 4.70 (m, 1H, CH\(_2\)-Troc), 4.36 (m, 1H, H3), 3.76 (m, 1H, H4), 3.54-3.45 (m, 4H, H2/H5/H6/H6). MS (ES, Na\(^+\)): m/z (relative intensity) calcd for C\(_{22}\)H\(_{23}\)NO\(_6\)SCl\(_3\)Na, 566.0; found 566.0 (100).

**Octyl 2-acetamido-2-deoxy-\(\alpha\)-D-glucopyranoside (49).**
To a stirred 0 °C suspension of N-acetyl D-glucosamine, 48, (2.00 g, 9.04 mmol) in 1-octanol (14 mL, 90.04 mmol) was added BF$_3$·OEt$_2$ (1.14 mL, 9.04 mmol). The reaction mixture was heated to 70 °C. After 3.5 h, the reaction was concentrated and the desired product crystallized with EtOH and ether to afford 49 (0.700 g, 23%) as a white powder: mp 103-106 °C. $^1$H NMR (CDCl$_3$) $\delta$ 4.78 (d, 1H, J = 3.5 Hz, H1), 4.38 (d, 1H, J = 8.3 Hz, N-H), 3.86 (dd, 1H, J = 10.6, 3.6 Hz, H2), 3.79 (dd, J = 9.7 Hz, H3), 3.71-3.65 (m, 3H, H4/H6/H6), 3.56 (m, 1H, H5), 3.53 (m, 1H, CH$_2$-octyl), 3.34 (m, 1H, CH$_2$-octyl), 1.97 (s, 3H, NHAc), 1.57 (bs, 2H, CH$_2$-octyl), 1.30-1.19 (bs, 10H, CH$_2$-octyl), 0.88 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) $\delta$ 96.88, 72.22, 71.24, 70.86, 67.40, 61.50, 61.20, 54.05, 32.14, 31.52, 29.04, 28.95, 25.79, 25.44, 22.22, 21.04, 12.91. MS (ES, Na$^+$): m/z (relative intensity) 356.2 (100). HRMS (M + Na$^+$) calcd for C$_{16}$H$_{31}$NO$_6$Na, 356.2049; found 356.2058.

Octyl 2-acetamido-3-O-acetyl-4, 6-O-benzylidene-2-deoxy-α-D-glucopyranoside (50).

To a stirred solution of 49 (0.50 g, 1.50 mmol) in 5 mL of DMF were added PhCH(OMe)$_2$ (0.31 mL, 2.099 mmol) and pTsOH·H$_2$O (0.028 mg, 0.150 mmol). After 19 h, the reaction was concentrated to remove the DMF. The crude product was crystallized by adding 50 mL of CH$_2$Cl$_2$:MeOH (6:1) and approximately 2 mL of H$_2$O. The product was precipitated by slowly adding hexanes to the solution to afford the
benzylidene (0.60 g, 95 %) as a white powder: $^1$H NMR (CDCl$_3$) $\delta$ 7.49 (bs, 2H, Ph), 7.35 (bs, 3H, Ph), 5.83 (d, 1H, $J = 7.5$ Hz, N-H), 5.56 (s, 1H, benzylidene), 4.81 (d, 1H, $J = 3.5$ Hz, H1), 4.27-4.20 (m, 2H, H3/H2), 3.89 (d, 1H, H4), 3.78 (d, 2H, H6/H6), 3.58 (dd, 1H, H5), 3.48 (m, 1H, CH$_2$-octyl), 3.39 (m, 1H, CH$_2$-octyl), 2.06 (s, 3H, NHAc), 1.58-1.55 (bs, 2H, CH$_2$-octyl), 1.28 (bs, 10H, CH$_2$-octyl), 0.88 (s, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) $\delta$ 134.46, 129.74, 129.19, 128.28, 126.29, 101.89, 97.64, 82.12, 70.79, 68.85, 68.28, 62.42, 54.12, 31.80, 29.35, 29.25, 26.17, 22.64, 14.08, 0.01. MS (ES, Na$^+$): m/z (relative intensity) calcd for C$_{37}$H$_{35}$NO$_9$SeNa, 444.2; found 444.2 (100). The resulting benzylidene (0.60 g, 1.423 mmol) was dissolved in pyridine (2.30 mL, 28.5 mmol) and Ac$_2$O (2.68 mL, 28.467 mmol). After 19 h, the reaction was diluted with 25 mL of EtOAc and washed with 25 mL of satd. CuSO$_4$, H$_2$O, satd. NaHCO$_3$ and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude product was purified with flash column chromatography (hexanes:EtOAc, 1:2) to afford 50 (0.44 g, 68%; 65%, 2 steps) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.41 (bs, 2H, Ph), 7.31 (bs, 3H, Ph), 5.86 (d, 1H, $J = 9.5$ Hz, N-H), 5.49 (s, 1H, benzylidene), 5.27 (d, 1H, $J = 10.2$ Hz, H3), 4.78 (d, 1H, $J = 3.6$ Hz, H1), 4.28 (dd, 1H, $J = 9.8$, 3.8 Hz, H2), 4.24 (d, 1H, $J = 10.3$, 4.8 Hz, H6), 3.76 (d, 1H, $J = 10.3$, 6.2 Hz, H6), 3.74 (m, 1H, H4), 3.68-3.63 (dd, 2H, H5/CH$_2$-octyl), 3.36 (m, 1H, CH$_2$-octyl), 2.04 (s, 3H, OAc), 1.93 (s, 3H, NHAc), 1.58-1.55 (bs, 2H, CH$_2$-octyl), 1.28-1.21 (bs, 10H, CH$_3$-octyl), 0.85 (s, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) $\delta$ 171.29, 169.96, 136.92, 128.95, 128.08, 126.04, 101.39, 97.72, 78.93, 70.30, 68.77, 68.31, 62.68, 60.25, 52.49, 31.68, 29.31, 29.19, 26.14, 26.00, 23.04, 22.51, 20.89, 20.78, 14.05, 13.95. MS (ES, Na$^+$): m/z (relative intensity) calcd for C$_{25}$H$_{37}$NO$_7$Na, 486.3; found 486.3 (100).
Octyl 2-acetamido-3-O-acetyl-6-O-t-butyldimethylsilyl-2-deoxy-α-D-glucopyranoside (51).

A solution of 50 (0.44 g, 0.95 mmol) in 15 mL of H₂O and AcOH (1:1) was heated to reflux. After 2 h, the reaction was cooled and concentrated. The crude product was diluted with 30 mL of EtOAc and washed with 20 mL of satd. NaHCO₃ and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified with flash column chromatography (EtOAc) to afford the diol (0.24 g, 73 %) as a colorless oil: ¹H NMR (CDCl₃) δ 5.96 (d, 1H, J = 9.2 Hz, N-H), 4.97 (d, 1H, J = 9.7 Hz, H3), 4.68 (d, 1H, H1), 4.08 (dd, 1H, J = 8.5 Hz, H2), 3.71 (d, 2H, H6/H6), 3.71 (d, 1H, H4), 3.55 (d, 1H, -OH), 3.45 (dd, 1H, H5), 3.32-3.26 (dd, 2H, CH₂-octyl), 1.98 (s, 3H, NHAc), 1.82 (s, 3H, OAc), 1.47-1.42 (bs, 2H, CH₂-octyl), 1.13 (bs, 10H, CH₂-octyl), 0.77 (s, 3H, CH₃-octyl). To a stirred solution of the diol in 5 mL of DMF were added imidazole (0.13g, 1.917 mmol) and TBS-Cl (0.12g, 0.799 mmol). After 18 h, the reaction was concentrated to remove the DMF. The crude product was dissolved in 20 mL of EtOAc and washed with 10 mL of H₂O and satd. NaCl solution. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified with flash column chromatography (EtOAc) to afford 51 (0.14 g, 45%; 32%, 2 steps) as a colorless oil: ¹H NMR (CDCl₃) δ 5.73 (d, 1H, J = 9.5 Hz, N-H), 5.08 (d, 1H, J = 10.6, 9.1 Hz, H3), 4.72 (d, 1H, J = 3.6 Hz, H1), 4.16 (dd, 1H, J = 9.8, 3.6 Hz, H2), 3.87 (d, 1H, J = 10.5, 4.6 Hz, H6), 3.79 (d, 1H, J
Octyl 2-acetamido-3, 4-di-O-acetyl-6-O-t-butyldimethylsilyl-2-deoxy-α-D-galactopyranoside (52).

To a stirred -5 °C solution of 51 (0.140 g, 0.285 mmol) in 5 mL of CH₂Cl₂ and pyridine (0.10 mL, 1.28 mmol) was added a freshly prepared solution of Tf₂O (0.09 mL, 0.571 mmol) in 0.85 mL of CH₂Cl₂. The reaction solution turned a yellow-orange color with time and the temperature was maintained between -5 °C and +10 °C. After 2.5 h, the reaction was warmed to room temperature and diluted to 10 mL of CH₂Cl₂ and washed with 10 mL of satd. Cu₂SO₄, H₂O, satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The resulting oil (0.156 g) was taken on without any purification: ¹H NMR (CDCl₃) δ 5.71 (d, 1H, 9.5 Hz, N-H), 5.34 (d, 1H, J = 9.9 Hz, H4), 4.77 (d, 1H, J = 3.6 Hz, H1), 4.24 (dd, 1H, J = 10.1, 3.6 Hz, H2), 3.85-3.80 (m, 2H, H3/H5), 3.79 (d, 2H, J = 2.5 Hz, H6/H6), 3.65 (m, 1H, CH₂-octyl), 3.39 (m, 1H, CH₂-octyl), 2.09 (s, 3H, NHAc), 1.86 (s, 3H, OAc), 1.57-1.55 (bs, 2H, CH₂-
octyl), 1.27-1.25 (bs, 10H, CH₃-octyl), 0.87 (s, 12H, tBu, CH₃-octyl), 0.06 (s, 6H, Me).

$^{13}$C NMR (CDCl₃) δ 171.16, 169.86, 96.72, 79.05, 70.59, 69.22, 68.50, 60.77, 52.48, 31.72, 29.23, 29.16, 26.04, 25.65, 23.09, 22.56, 20.55, 18.21, 13.99, -5.51, -5.67. $^{19}$F NMR (CDCl₃) δ 1.58. To the crude triflate glycoside was added a solution of Et₄NOAc (0.33 g, 1.25 mmol) in 5 mL of DMF. After 40 min, the reaction was concentrated and the crude red oil dissolved in 50 mL of EtOAc and washed twice with 25 mL of H₂O and once with satd. NaCl solution. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified with flash column chromatography (hexanes:EtOAc, 2:1) to afford 52 (0.050 g, 35%, 2 steps) as an oil: $^1$H NMR (CDCl₃) δ 5.59 (d, 1H, J = 10.0 Hz, N-H), 5.39 (d, 1H, J = 2.9 Hz, H4), 5.14 (dd, 1H, J = 14.4, 3.2 Hz, H3), 4.80 (d, 1H, J = 3.7 Hz, H1), 4.52 (dd, 1H, J = 8.5, 3.6 Hz, H2), 3.94 (dd, 1H, J = 12.9, 6.6 Hz, H5), 3.68 (m, 1H, CH₂-octyl), 3.59-3.53 (dd, 2H, J = 10.1, 2.9 Hz, H6), 3.36 (m, 1H, CH₂-octyl), 2.12 (s, 3H, NHAc), 2.02 (s, 3H, OAc), 1.95 (s, 3H, OAc), 1.56-1.55 (bs, 2H, CH₂-octyl), 1.26-1.19 (bs, 10H, CH₂-octyl), 0.87 (s, 12H, tBu, CH₃-octyl), 0.01 (s, 6H, Me). $^{13}$C NMR (CDCl₃) δ 171.06, 170.96, 170.12, 169.84, 97.39, 69.33, 68.92, 68.15, 67.39, 61.12, 60.31, 48.01, 31.73, 29.27, 29.20, 26.14, 25.67, 23.28, 22.57, 20.97, 20.75, 18.06, 14.12, 14.10, -5.64, -5.71. MS (ES, Na⁺): m/z (relative intensity) 554.4 (100). MS (ES, Na⁺): m/z (relative intensity) 554.3 (100). HRMS (M + Na⁺) calcd for C₂₆H₄₆NO₈SiNa, 554.3125; found 554.3128.

Octyl 2-acetamido-3, 4-di-O-acetyl-2-deoxy-α-D-galactopyranoside (53).

![Chemical Structure Diagram](image.png)
To a stirred 0 °C solution of 52 (0.050 g, 0.094 mmol) in 3 mL of CH₃CN and pyridine (0.25 mL, 3.10 mmol) in a Nalgene bottle was added 0.25 mL of HF-pyridine. The reaction was allowed to warm to room temperature. After 3.5 h, the reaction was diluted to 5 mL of CH₂Cl₂ and washed with 5 mL of satd. CuSO₄, H₂O, satd. NaHCO₃ and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified by preparatory thin layer chromatography (hexanes:EtOAc, 1:1) to afford 53 (0.03 g, 77%) as a colorless oil: ¹H NMR (CDCl₃) δ 5.65 (d, 1H, N-H), 5.30 (d, 1H, J = 2.8 Hz, H4), 5.16 (dd, 1H, J = 11.2, 3.1 Hz, H3), 4.82 (d, 1H, J = 3.6 Hz, H1), 4.53 (dd, 1H, J = 10.0, 3.6 Hz, H2), 3.97 (dd, 1H, J = 6.3 Hz, H5), 3.72-3.60 (m, 2H, H6/CH₃-octyl), 3.45 (m, 1H, H6), 3.36 (m, 1H, C₆H₅-octyl), 2.08 (s, 3H, NHAc), 2.02 (s, 3H, OAc), 1.93 (s, 3H, OAc), 1.52 (bs, 2H, CH₃-octyl), 1.26 (bs, 10H, C₆H₅-octyl), 0.85 (s, 3H, CH₃-octyl). ¹³C NMR (CDCl₃) δ 97.56, 71.12, 68.46, 68.34, 67.86, 67.51, 63.09, 47.65, 31.82, 29.71, 29.34, 29.28, 26.24, 23.36, 22.65, 21.01, 20.84, 14.10, 0.00. MS (ES, Na⁺): m/z (relative intensity) calcd for C₂₀H₃₅NO₈SeNa, 440.2; found 440.2 (100).

p-Methoxyphenyl, 3, 4-di-O-acetyl, 3-O-[(benzyloxy)methyl], 2, 6-dideoxy, 6-phenylseleno-2-phthlamido-β-D-galactopyranoside (58).

To a stirred 0 °C solution of 40c (0.150 g, 0.209 mmol) in 2 mL of CH₂Cl₂ were added AcBr (0.006 mL, 0.413 mmol) and BF₃·OEt₂ (0.0015 mL, 0.0209 mmol). After 20 min, the reaction was warmed to room temperature. After 5 h, the reaction was diluted to 5 mL of CH₂Cl₂ and washed three times with 5 mL of H₂O and once with satd. NaCl
solution. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified by flash column chromatography (hexanes:EtOAc, 2.5:1) to afford 58 (0.106 g, 80%) as a colorless oil: ¹H NMR (CDCl₃) δ 7.82 (d, 2H, NPh), 7.75 (m, 2H, NPh), 7.53 (m, 2H, SePh), 7.29 (m, 3H, SePh), 6.92 (m, 2H, PMP), 6.75 (m, 2H, PMP), 5.86 (dd, 1H, J = 11.4, 3.3 Hz, H₃), 5.77 (d, 1H, J = 8.5 Hz, H₁), 5.60 (d, 1H, J = 5.3 Hz, H₄), 4.81 (dd, 1H, J = 11.5, 8.5 Hz, H₂), 4.03 (dd, 1H, J = 8.0, 6.0 Hz, H₅), 3.74 (s, 3H, OMe), 3.19 (dd, 1H, J = 12.9, 8.3 Hz, H₆), 3.00 (dd, 1H, J = 12.9, 7.5 Hz, H₆), 2.22 (s, 3H, OAc), 1.89 (s, 3H, OAc). MS (ES, Na⁺): m/z (relative intensity) 662.0 (100). HRMS (M + Na⁺) calcd for C₃₁H₂₉NO₉SeNa, 662.0905; found 662.0901.

⁻Butyldimethylsilyl, 4-O-acetyl, 3-O-[(benzyloxy)methyl], 2, 6-dideoxy-6-phenylseleno-2-trifluoroacetamido-β-D-galactopyranoside (60).

To a suspension of 40b (0.125 g, 0.170 mmol) in 25 mL of EtOH in a Schlenk tube was added H₂NNH₂·H₂O (0.79 mL, 16.2 mmol). The reaction was placed under a gentle vacuum, the tube sealed and heated to 100 °C. After 68 h, the reaction was cooled, the tube opened and the reaction mixture concentrated. The resulting oil/solid was dissolved in 100 mL of EtOAc and washed with 75 mL of satd. NaHCO₃ solution. The aqueous extract was washed with 75 mL of EtOAc and the combined organic extracts washed with 150 mL of satd. NaCl solution, dried with Na₂SO₄, filtered and the filtrate concentrated. The resulting oil was purified using a short silica gel plug (hexanes:EtOAc, 1:1) to afford the free amino alcohol (0.080g, 85%) as a colorless oil:
$^1$H NMR (CDCl$_3$) $\delta$ 7.48 (m, 2H, SePh), 7.33 (m, 5H, ArH of BOM), 7.24 (m, 3H, SePh), 4.93 (d, 1H, $J$ = 7.0 Hz, O-CH$_2$-O-Bn), 4.86 (d, 1H, $J$ = 7.0 Hz, O-CH$_2$-Ph/Bn), 4.69 (s, 1H, $J$ = 11.7 Hz, O-CH$_2$-Ph/BOM), 4.65 (s, 1H, $J$ = 11.7 Hz, O-CH$_2$-Ph/BOM), 4.37 (d, 1H, $J$ = 7.6 Hz, H1), 4.03 (d, 1H, $J$ = 2.9 Hz, H4), 3.55 (dd, 1H, $J$ = 6.8 Hz, H5), 3.45 (dd, 1H, $J$ = 10.1, 3.1 Hz, H3), 3.28 (dd, 1H, $J$ = 12.7, 7.3 Hz, H6), 3.14 (dd, 1H, $J$ = 12.7, 6.4 Hz, H6), 3.02 (dd, 1H, $J$ = 10.1, 7.7 Hz, H2), 0.92 (s, 9H, tBu), 0.17 (s, 3H, Me), 0.01 (s, 3H, Me).

$^{13}$C NMR (CDCl$_3$) $\delta$ 207.32, 137.51, 132.62, 132.27, 130.53, 129.48, 128.90, 128.31, 127.26, 99.56, 94.78, 81.59, 76.93, 74.61, 70.57, 67.93, 54.33, 31.27, 28.14, 26.13, 18.34, -3.48, -4.95. MS (ES, Na$^+$): m/z (relative intensity) 576.1 (100). HRMS (M + Na$^+$) calcd for C$_{26}$H$_{40}$NO$_5$SeSiNa, 576.1660; found 576.1653. To a stirred 0 °C solution of the free amino alcohol in pyridine (0.50 mL, 6.46 mmol) was added TFAA (0.09 mL, 0.63 mmol). After 45 min, the solution was diluted with 25 mL of CH$_2$Cl$_2$ and washed with 25 mL of satd. CuSO$_4$, H$_2$O, satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The resulting oil was dissolved in 5 mL of EtOH, 10 mL of H$_2$O and 1 mL of satd. NaHCO$_3$ solution. After 4 h, the solution was neutralized with AcOH to pH = 6 and concentrated to leave the H$_2$O. The aqueous extract was washed with 10 mL of EtOAc two times and the combined organic extracts were washed with 20 mL of satd. NaCl solution, dried with Na$_2$SO$_4$, filtered and the filtrate concentrated to afford 60 (0.078 g, 95%; 80%, 2 steps) and taken on without any purification: $^1$H NMR (CDCl$_3$) $\delta$ 7.49 (m, 2H, SePh), 7.30 (m, 3H, SePh), 7.25 (m, 5H, ArH of BOM), 6.67 (d, 1H $J$ = 8.1 Hz, N-H), 4.88 (d, 1H, $J$ = 7.9 Hz, H1), 4.81 (d, 1H, $J$ = 7.0 Hz, O-CH$_2$-Ph/Bn), 4.72 (d, 1H, $J$ = 7.0 Hz, O-CH$_2$-Ph/Bn), 4.57 (m, 2H, O-CH$_2$-O-Bn), 4.08-4.04 (m, 2H, H5/H4), 3.83 (dd, 1H, $J$ = 9.9 Hz, H2), 3.60 (d, 1H, $J$ =
6.8 Hz, H3), 3.27 (dd, 1H, J = 12.7, 7.2 Hz, H6), 3.13 (dd, 1H, J = 12.7, 6.5 Hz, H6), 0.86 (s, 9H, tBu), 0.13 (s, 3H, Me), 0.07 (s, 3H, Me). $^{19}$F NMR (CDCl$_3$) $\delta$ 0.23.

$t$-Butyldimethylsilyl, 4-$O$-acetyl, 3-$O$-[(benzyloxy)methyl], 2, 6-dideoxy-6-phenylseleno-2-trifluoroacetamido-$\beta$-$D$-galactopyranoside (61a).

Compound 60 (0.077 g, 0.118 mmol) was dissolved in pyridine (0.60 mL, 7.42 mmol) and Ac$_2$O (0.6 mL, 6.36 mmol). After 15 h, the reaction was diluted to 25 mL of EtOAc and washed with 25 mL of satd. CuSO$_4$, H$_2$O, and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude oil was purified using flash column chromatography to afford 61a (0.076 g, 92%) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.47 (m, 2H, SePh), 7.33 (m, 3H, SePh), 7.27 (m, 5H, ArH of BOM), 6.39 (d, J = 8.3 Hz, N-H), 5.44 (d, 1H, J = 2.9 Hz, H4), 4.90 (d, 1H, J = 7.9 Hz, H1), 4.79 (d, 2H, J = 7.4 Hz, O-CH$_3$-Ph/Bn), 4.57 (m, 2H, O-CH$_3$-O-Bn), 4.49 (s, 2H, J = 12.1 Hz, O-CH$_3$-Ph/BOM), 4.15 (dd, 1H, J = 11.1, 3.2 Hz, H3), 3.85 (d, 1H, H2), 3.68 (m, 1H, H5), 3.10 (dd, 1H, J = 12.8, 8.3 Hz, H6), 2.86 (dd, 1H, J = 12.8, 5.2 Hz, H6), 2.14 (s, 3H, OAc), 0.87 (s, 9H, tBu), 0.15 (s, 3H, Me), 0.07 (s, 3H, Me). $^{13}$C NMR (CDCl$_3$) $\delta$ 170.97, 157.85, 157.56, 137.47, 133.13, 130.12, 129.73, 128.93, 128.35, 128.15, 127.77, 117.24, 95.67, 92.96, 76.31, 72.74, 70.30, 68.32, 55.92, 30.12, 28.19, 25.93, 21.27, 18.22, 1.44, -3.55, -5.08. $^{19}$F NMR (CDCl$_3$) $\delta$ 0.34. MS (ES, Na$^+$): m/z (relative intensity) 714.1 (100). HRMS (M + Na$^+$) calcd for C$_{30}$H$_{40}$F$_3$NO$_7$SeSiNa, 714.1589; found 714.1595.
*t*-butyldimethylsilyl 4-*O*-benzyl- 3-*O*-*([benzyl]oxy)methyl*, 2,6-dideoxy-6-phenylseleno-2-trifluoroacetamide-*ß*-D-glucopyranoside (61b).

To a stirred 0 °C solution of 60 (0.027 g, 0.040 mmol) in 0.7 mL of THF was added NaH (80% in oil, 0.003 g, 0.100 mmol). After 30 min., BnBr (0.0095 mL, 0.08 mmol) and NBu₄I (0.003 g, 0.008 mmol) were added and the temperature maintained at 0 °C for 1 h. The reaction was then warmed to room temperature. After 4 h, 0.05 mL of AcOH was slowly added at 0 °C and the reaction mixture was diluted with 5 mL of EtOAc and washed with 5 mL of H₂O, 5 mL of satd. NaHCO₃ and 5 mL of satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified by preparative thin layer chromatography (hexanes:EtOAc, 4:1) to afford 61b (0.020 g, 67%) as a colorless oil: ¹H NMR (CDCl₃) δ 7.37 (m, 10H, Bn/ ArH of BOM), 7.25 (m, 5H, SePh), 5.40 (dd, 1H, J = 6.4, 3.1 Hz, H1), 4.74 (d, 1H, J = 7.0 Hz, O-CH₂-Ph), 4.59 (m, 1H, O-CH₂-Ph), 4.53 (m, 4H, CH₂-Ph), 4.68 (s, 2H, O-CH₂-O-Bn), 4.67 (m, 1H, H3), 3.90 (d, 1H, J= 2.1 Hz, H4), 3.61 (dd, 1H, J= 10.9, 7.9, Hz, H2), 3.54 (m, 1H, H5), 3.12 (dd, 1H, J= 12.6, 6.8 Hz, H6), 2.89 (dd, 1H, J= 12.4, 6.7 Hz, H6), 0.86 (s, 9H, tBu), 0.12 (s, 3H, Me), 0.08 (s, 3H, Me). ¹³C NMR (CDCl₃) δ 157.84, 157.55, 138.44, 137.59, 132.61, 130.46, 129.64, 128.96, 128.79, 128.72, 128.35, 128.26, 128.06, 127.45, 117.27, 114.98, 95.43, 94.03, 76.73, 75.26, 74.92, 74.55, 70.42, 60.82, 56.38, 28.32, 25.96, 18.23, -3.60, -5.02. MS (ES, Na⁺): m/z (relative intensity) 762.1 (100). HRMS (M + Na⁺) calcd for C₃₅H₄₄NO₆SeSiF₃Na, 762.1953; found 762.1951.
4-O-Acetyl, 3-O-[(benzyloxy)methyl]-2, 6-dideoxy-6-phenylseleno-2-trifluoracetamido-∀-D-galactopyranosyl-1-dibenzyl phosphate (62).

To a stirred 0 °C solution of 61a (0.075 g, 0.108 mmol) in 1.5 mL of CH₃CN and pyridine (0.4 mL, 5.193 mmol) in a Nalgene bottle was added 0.15 mL HF-pyridine and the temperature maintained for 1 h. The reaction was allowed to warm to room temperature. After 5 h, the reaction was diluted with 20 mL of CH₂Cl₂ and extracted with 20 mL of satd. CuSO₄, H₂O, satd. NaHCO₃ and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified by flash column chromatography (hexanes:EtOAc, 3:1) to afford the free C-1 alcohol (0.061 g, 86%) as a colorless oil: ¹H NMR (CDCl₃) δ 7.50 (m, 2H, SePh), 7.34-7.26 (m, 18H, SePh/ ArH of BOM/Bn), 6.87 (d, 1H, N-H), 5.50 (dd, 1H, J = 2.4 Hz, H1), 5.28 (d, 1H, J = 3.4 Hz, H4), 4.80 (m, 1H, O-CH₃-Ph/Bn), 4.61-4.53 (d, 3H, O-CH₃-Ph/Bn/O-CH₂-O-Bn), 4.44 (m, 1H, H2), 4.20 (m, 1H, H5), 4.08 (dd, 1H, J = 3.0 Hz, H3), 3.68 (d, 1H, J = 2.0 Hz, -OH), 3.02 (dd, 1H, J = 12.7, 8.1 Hz, H6), 2.83 (dd, 1H, J = 12.7, 5.8 Hz, H6), 2.14 (s, 3H, OAc). To a stirred -78°C solution of the free alcohol (0.135 g, 0.23 mmol) in 8 mL of THF was added a freshly prepared solution of 0.21M LDA (1.68 mL, 0.35 mmol). After 15 min, a -78°C solution of TBPP (0.164 g, 0.300 mmol) in 4 mL of THF was added to the free alcohol solution. After 15 min, the reaction was warmed to 0°C. After 2.5 h, the reaction was warmed to room temperature and diluted with 100 mL of CH₂Cl₂ and washed with 100 mL of satd. NaHCO₃ twice and once with 100 mL of
satd. NaCl solution. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude product was purified with flash column chromatography (hexanes:EtOAc, 3:1) to afford 62 (0.161 g, 82%; 70%, 2 steps) as a colorless oil: \(^1\)H NMR (CDCl$_3$) $\delta$ 7.44 (m, 2H, SePh), 7.31 (m, 5H, ArH of BOM), 7.27 (m, 10H, Bn), 7.20 (m, 3H, SePh), 6.87 (d, 1H, J = 8.5 Hz, N-H), 5.79 (dd, 1H, J = 6.0, 3.2 Hz, H1), 5.52 (d, 1H, J = 2.3 Hz, H4), 4.49 (m, 4H, O-CH$_2$-Ph/Bn), 4.75 (d, 1H, J = 7.2 Hz, O-CH$_2$-O-Bn), 4.58 (m, 2H, O-CH$_2$-Ph/BOM), 4.51 (d, 1H, O-CH$_2$-O-Bn), 4.45 (m, 1H, H3), 4.11 (m, 1H, J = 6.9 Hz, H5), 3.91 (dd, 1H, J = 11.0, 3.1 Hz, H2), 2.99 (dd, 1H, J = 12.9, 7.2 Hz, H6), 2.81 (dd, 1H, J = 12.9, 6.9 Hz, H6), 2.12 (s, 3H, OAc). \(^{13}\)C NMR (CDCl$_3$) $\delta$ 170.76, 158.32, 158.02, 137.46, 135.80, 135.68, 133.64, 133.32, 130.32, 129.92, 129.47, 129.30, 129.15, 128.77, 128.68, 128.63, 128.30, 128.03, 117.32, 115.03, 96.67, 93.27, 71.87, 71.38, 70.64, 70.49, 68.17, 49.83, 30.29, 27.56, 21.33, 0.59. \(^{19}\)F NMR $\delta$ 0.43. \(^{31}\)P NMR $\delta$ -1.23. MS (ES, Na$^+$): m/z (relative intensity) 860.1 (100). HRMS (M + Na$^+$) calcd for C$_{38}$H$_{39}$F$_3$NO$_{10}$PSeNa, 860.1327; found 860.1329.

\(\alpha\)-Butyldimethylsilyl 3-\(\text{O}-\)\((\text{benzyloxy})\text{methyl}\)-2,6-dideoxy-6-phenylseleno-2-trifluoroacetamide-\(\text{\(\beta\)}\)-\(\text{D}\)-glucopyranoside (66).

To a stirred solution of 40b (0.09 g, 0.12 mmol) in 2 mL of dry THF was added 1M NaOMe solution (0.12 mL, 0.120 mmol). After 1 h, 0.35 g of Dowex 50W H$^+$ form resin (2.1 meq/mL) was added and gently stirred for 20 min. The mixture was filtered and the filtrate concentrated. The crude product was purified by flash column...
chromatography (hexanes:EtOAc, 4:1) to afford 66 (0.06 g, 71%) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.81 (d, 1H, Pht), 7.67 (m, 3H, Pht), 7.51 (m, 2H, ArH of BOM), 7.36 (m, 1H, ArH of BOM), 7.28 (m, 2H, SePh), 7.25 (m, 3H, SePh), 7.09 (m, 2H, ArH of BOM), 5.31 (dd, 1H, J = 7.9 Hz, H1), 4.76 (d, 1H, J = 7.1 Hz, O-CH$_2$-Ph), 4.66 (m, 1H, O-CH$_2$-Ph), 4.58 (dd, 1H, J = 11.1, 3.1 Hz, H3), 4.45 (dd, 1H, J= 11.1, 7.9, Hz, H2), 4.41 (s, 1H, O-CH$_2$-O-Bn), 4.32 (s, 1H, O-CH$_2$-O-Bn), 4.18 (d, 1H, H4), 3.76 (m, 1H, H5), 3.35 (dd, 1H, J= 12.7, 7.3 Hz, H6), 3.21 (dd, 1H, J= 12.7, 6.4 Hz, H6), 2.47 (d, 1H, J = 2.5 Hz, -OH), 0.66 (s, 9H, tBu), 0.08 (s, 3H, Me), 0.01 (s, 3H, Me). $^{13}$C NMR (CDCl$_3$) $\delta$ 168.80, 167.90, 136.90, 133.97, 132.21, 131.52, 130.18, 129.16, 128.51, 128.32, 127.65, 127.40, 126.93, 123.33, 122.92, 93.97, 93.60, 74.93, 74.17, 69.91, 68.02, 65.30, 54.15, 27.71, 25.29, 17.45, -4.07, -5.68. MS (ES, Na$^+$): m/z (relative intensity) 706.1 (100). HRMS (M + Na$^+$) calcd for C$_{34}$H$_{41}$NO$_7$SeSiNa, 706.1715; found 706.1719.

$t$-Butyldimethylsilyl 4-O-benzyl-3-O-[(benzyloxy)methyl]-2,6-dideoxy-6-phenylseleno-2-phthalimido-$\alpha$-D-glucopyranoside (67).

To a stirred 0 °C solution of 66 (1.24 g, 1.82 mmol) in 50 mL of THF was added NaH (80% in oil, 0.065 g, 2.728 mmol). After 30 min, BnBr (0.43 mL, 3.64 mmol) and NBu$_4$I (0.130 g, 0.364 mmol) were added and the solution was warmed to room temperature. After 22 h, the reaction was diluted with 100 mL of EtOAc and washed with 75 mL of H$_2$O, satd. NaHCO$_3$ and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude product was purified by flash column chromatography (hexanes:EtOAc, 5:1) to afford 67 (1.06 g, 76%) as a
colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.70 (m, 2H, Pht), 7.46-7.21 (m, 15H, Pht/SePh/Bn/ArH of BOM), 7.00 (m, 2H, PhSe), 5.33 (dd, 1H, J = 7.3 Hz, H1), 4.98 (d, 1H, J = 11.3 Hz, O-CH$_2$-Ph), 4.78 (m, 1H, O-CH$_2$-Ph), 4.70-4.59 (m, 3H, H3/H2/H5), 4.55 (m, 4H, CH$_2$-Ph), 4.33 (s, 2H, O-CH$_2$-O-Bn), 3.16 (m, 1H, H6), 4.03 (d, 1H, J= 1.9 Hz, H4), 3.24 (dd, 1H, J= 12.5, 6.9 Hz, H6), 2.92 (dd, 1H, J= 12.5, 6.7 Hz, H6), 0.86 (s, 9H, tBu), 0.12 (s, 3H, Me), 0.08 (s, 3H, Me). $^{13}$C NMR (CDCl$_3$) $\delta$ 168.93, 167.94, 138.22, 137.16, 133.86, 132.23, 132.10, 131.66, 130.27, 129.18, 128.55, 128.40, 128.33, 128.24, 128.14, 128.07, 128.01, 127.83, 127.72, 127.47, 127.18, 126.89, 123.27, 122.82, 93.98, 93.74, 76.04, 74.76, 74.53, 74.42, 69.75, 54.74, 53.40, 28.11, 26.18, 17.50, -4.03, -5.58. MS (ES, Na$^+$): m/z (relative intensity) 796.2 (100). HRMS (M + Na$^+$) calcd for C$_{39}$H$_{45}$NO$_7$SeSiNa, 796.2185; found 796.2181.

$t$-Butyldimethylsilyl 4-O-benzyl- 3-O-[(benzyloxy)methyl]-2,6-dideoxy-6-phenylseleno-2-trifluoroacetamide-$\exists$-D-glucopyranoside (61b).

To a stirred suspension of 67 (0.125 g, 0.161 mmol) in 5 mL of EtOH in a Schlenk tube was added H$_2$NNH$_2$·H$_2$O (0.73 mL, 15.2 mmol). The tube was placed under a gentle vacuum, the tube sealed, and heated to 100 °C. After 35 h, the reaction was cooled and the tube opened. The reaction mixture was diluted with 40 mL of EtOAc and washed with 20 mL of satd. NaHCO$_3$ solution and the aqueous extract washed with 20 mL of EtOAc. The combined organic extracts were washed with 50 mL of satd. NaCl solution, dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The resulting free amine was purified using a short silica gel plug (hexanes:EtOAc, 1:1) to afford the free
amino alcohol (0.094 g) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.41 (m, 2H, Bn), 7.35-7.25 (m, 13H, Bn/ ArH of BOM/SePh), 4.90 (d, 2H, O-CH$_2$-Ph), 4.82 (m, 1H, O-CH$_2$-Ph), 4.72 (d, 1H, CH$_2$-Ph), 4.64 (s, 2H, O-CH$_2$-O-Bn), 4.57 (s, 2H, O-CH$_2$-O-Bn), 4.35 (d, 1H, J = 7.5 Hz, H1), 3.87 (d, 1H, J= 2.1 Hz, H4), 3.51 (dd, 1H, J = 10.8, 2.6 Hz, H3), 3.48 (m, 1H, H5), 3.22 (m, 1H, H2), 3.20 (dd, 1H, J= 12.5, 6.9 Hz, H6), 2.90 (dd, 1H, J= 12.5, 6.6 Hz, H6), 1.57 (bs, 3H, NH$_2$), 0.92 (s, 9H, tBu), 0.16 (s, 3H, Me), 0.08 (s, 3H, Me). $^{13}$C NMR (CDCl$_3$) $\delta$ 137.38, 136.42, 131.10, 129.31, 128.25, 128.11, 127.67, 127.47, 127.26, 127.18, 127.06, 126.82, 126.77, 126.64, 126.55, 126.27, 125.91, 125.82, 98.54, 93.13, 80.36, 73.58, 73.04, 69.02, 64.21, 59.34, 52.38, 28.66, 27.22, 24.82, 17.01, -4.76, -6.21. MS (ES, Na$^+$): m/z (relative intensity) 644.2 (100). HRMS (M + Na$^+$) calcd for C$_{39}$H$_{45}$NO$_5$SeSiNa, 644.2305; found 644.2310. To a stirred 0 °C solution of the free amino alcohol (0.094 g, 0.146 mmol) in 1.0 mL of pyridine was added TFAA (0.10 mL, 0.731 mmol) and the temperature maintained at 0 °C. After 1 h, the reaction was diluted to 25 mL of EtOAc and washed with 25 mL of satd. CuSO$_4$, H$_2$O, satd. NaHCO$_3$, and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude product was purified by flash column chromatography (hexanes:EtOAc, 3:1) to afford 61b (0.100 g, 83%, 2 steps) as a colorless oil with identical $^1$H NMR, $^{13}$C NMR and Mass Spectrum data as previously described (60 to 61b).

4-O-benzyl-3-O-[(benzyloxy)methyl]-2, 6-dideoxy-6-phenylseleno-2-phthalimido-$\exists$-D-glucopyranoside (68).
To a stirred 0 °C solution of 61b (0.020 g, 0.027 mmol) in 0.4 mL of dry CH₃CN and 0.15 mL of pyridine in a Nalgene bottle was added 0.05 mL of HF pyridine. After 1 h, the reaction was warmed to room temperature. After 3.5 h, the reaction was diluted with 5 mL of CH₂Cl₂ and washed with 5 mL of satd. CuSO₄, satd. NaHCO₃, H₂O and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate evaporated. The crude product was purified by flash column chromatography (hexanes:EtOAc, 3:1) to afford 3.10C (0.015 g, 89%) as a colorless oil: ¹H NMR (CDCl₃) δ 7.44 (m, 3H, Bn/Ph), 7.32 (m, 12H, Bn/Ph), 7.25 (m, 5H, SePh), 6.77 (d, 1H, J= 8.5 Hz, N-H), 5.35 (d, 1H, J= 2.1 Hz, H4), 4.95 (d, 1H, J = 11.3 Hz, O-CH₂-Ph), 4.82 (m, 1H, O-CH₂-Ph), 4.75 (m, 1H, O-CH₂-Ph), 4.65 (m, 3H, CH₂-Ph), 4.59 (m, 1H, H1), 4.47 (d, 1H, J= 11.4, CH₂-Bn), 4.06-4.00 (m, 3H, H5/H2/CH₂-Ph), 3.61 (dd, 1H, J= 10.9, 7.9 Hz, H2), 3.54 (m, 1H, H5), 3.11 (dd, 1H, J = 12.6, 6.4 Hz, H6), 3.05 (m, 1H, H3), 2.95 (dd, 1H, J= 12.6, 7.8 Hz, H6). ¹³C NMR (CDCl₃) δ 157.73, 157.44, 138.24, 137.24, 132.88, 130.06, 129.56, 129.06, 128.95, 128.78, 128.61, 128.40, 128.23, 128.16, 127.98, 127.55, 117.29, 115.00, 93.79, 91.79, 75.92, 75.19, 74.72, 71.13, 70.26, 49.91, 28.10. MS (ES, Na⁺): m/z (relative intensity) 648.2 (100). HRMS (M + Na⁺) calcd for C₂₉H₃₀NO₆SeF₃Na, 648.1088; found 648.1095.

4-O-Benzyl, 3-O-[(benzyloxy)methyl]-2, 6-dideoxy-6-phenylselenoxo-2-trifluoracetamido-∀-D-galactopyranosyl-1-dibenzyl phosphate (69).
To a stirred suspension of 1-\textit{H}-tetrazole (0.006 mg, 0.080 mmol) in 0.25 mL of CH\textsubscript{2}Cl\textsubscript{2} was added (\textit{i}Pr\textsubscript{2})\textsubscript{NP(OBn)}\textsubscript{2} (0.014 mL, 0.044 mmol). After 15 min, the reducing sugar 68 (0.025 g, 0.040 mmol) in 0.25 mL of CH\textsubscript{2}Cl\textsubscript{2} was added to the stirred solution. After 7 h, the reaction was diluted to 3 mL of CH\textsubscript{2}Cl\textsubscript{2} and washed with 3 mL of satd. NaHCO\textsubscript{3}, H\textsubscript{2}O, and satd. NaCl solutions. The organic extract was dried with Na\textsubscript{2}SO\textsubscript{4}, filtered and the filtrate concentrated. The crude product was purified by flash column chromatography (hexanes:EtOAc, 3:1, 1% NEt\textsubscript{3}) to afford the phosphite (0.02 g, 59%) as a colorless oil/solid: \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \(\delta\) 7.64-7.20 (m, 25H, SePh/ ArH of BOM/Bn), 6.74 (d, 1H, \(J = 8.1\) Hz, N-H), 5.69 (dd, 1H, \(J = 7.7, 3.2\) Hz, H1), 4.96 (d, 1H, \(J = 5.1\) Hz, H4), 4.87-4.60 (m, 10H, O-CH\textsubscript{2}-Ph-Bn/O-CH\textsubscript{2}-O-Bn/O-CH\textsubscript{2}-Ph-BOM), 4.45 (m, 1H, H3), 4.09 (m, 1H, H5), 3.91 (dd, 1H, \(J = 6.0\) Hz, H2), 3.01 (dd, 1H, \(J = 12.2, 5.4\) Hz, H6), 2.73 (dd, 1H, H6). \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \(\delta\) 137.55, 132.14, 129.17, 128.55, 128.47, 128.37, 128.15, 128.00, 127.87, 127.57, 127.38, 127.34, 127.03, 93.58, 75.91, 74.87, 74.04, 71.88, 69.80, 64.47, 50.73, 49.68, 45.91, 27.07, 0.95. \textsuperscript{19}F NMR \(\delta\) 0.74. \textsuperscript{31}P NMR \(\delta\) 141.03. MS (ES, Na\textsuperscript{+}): m/z (relative intensity) 892.1 (100). HRMS (M + Na\textsuperscript{+}) calcd for C\textsubscript{43}H\textsubscript{43}NO\textsubscript{8}SePF\textsubscript{3}Na, 892.1741; found 892.1753. To a stirred solution of the phosphite (0.020 g, 0.023 mmol) in 3.5 mL of MeOH:H\textsubscript{2}O (6:1) were added NaHCO\textsubscript{3} (0.004 g, 0.050 mmol) and NaIO\textsubscript{4} (0.014 g, 0.069 mmol). A white precipitate formed during the course of the reaction. After 1.5 h, the reaction was filtered and the filtrate concentrated to leave the H\textsubscript{2}O. An additional 3 mL of H\textsubscript{2}O was added to the filtrate and the aqueous extract was washed 2 times with 5 mL of CH\textsubscript{2}Cl\textsubscript{2}. The combined organic layers were washed with satd. 10 mL of satd. NaCl solution and dried with Na\textsubscript{2}SO\textsubscript{4}, filtered and the filtrate concentrated to afford 69 (0.018 g, 90%; 53%, 2 steps) as a colorless oil/solid: \textsuperscript{1}H
NMR (CDCl$_3$) $\delta$ 7.54-7.17 (m, 25H, SePh/ ArH of BOM/Bn), 6.95 (d, 1H, N-H), 5.84 (dd, 1H, $J = 9.4$, 5.8 Hz, H1), 4.98 (d, 1H, H4), 5.06-4.63 (m, 10H, O-CH$_2$-Ph-Bn/O-CH$_2$-O-Bn/O-CH$_2$-Ph-BOM), 4.42 (m, 1H, H3), 4.03 (m, 1H, H5), 3.71 (dd, 1H, H2), 3.00 (dd, 1H, H6), 2.52 (dd, 1H, H6). $^{13}$C NMR (CDCl$_3$) $\delta$ 137.22, 132.04, 132.30, 130.06, 129.25, 128.50, 127.89, 127.56, 93.82, 91.72, 75.82, 75.54, 74.79, 73.91, 72.98, 69.82, 69.29, 68.11, 53.37, 49.71, 0.98. $^{19}$F NMR $\delta$ 0.77. $^{31}$P NMR $\delta$ -1.05. MS (ES, Na$^+$): m/z (relative intensity) calcd for C$_{43}$H$_{43}$NO$_{10}$SePF$_3$Na; found 922.4 (100).

**Octyl 2, 6-dideoxy-2-phthalamido-6-phenylseleno-$\alpha$-D-glucopyranoside (70).**

To a stirred solution of 33 (0.42 g, 0.63 mmol) in 12 mL of THF:MeOH (1:1) was added 0.5M NaOMe solution (0.07 mL, 1.26 mmol). After 16 h, the reaction was quenched with 0.50 g of Dowex 50W H$^+$ form resin (2.1 meq/mL) and stirred gently for 15 min. The mixture was filtered and the filtrate concentrated. The resulting oil was purified by flash column chromatography (hexanes:EtOAc, 1:1) to afford 70 as a colorless oil (0.23 g, 66%): $^1$H NMR (CDCl$_3$) $\delta$ 7.73 (d, 2H, NPh), 7.62 (m, 2H, NPh), 7.51 (m, 2H, SePh), 7.20 (m, 3H, SePh), 5.09 (d, 1H, $J = 8.4$ Hz, H1), 4.23 (m, 1H, H3), 4.06 (dd, 1H, $J = 10.8$, 8.4 Hz, H2), 3.67 (d, 2H, $J = 5.6$ Hz, -OH), 3.64 (m, 1H, CH$_3$-octyl), 3.62 (d, 1H, $J = 8.9$, 2.7 Hz, H4), 3.40 (ddd, 1H, $J = 8.9$, 3.7 Hz, H5), 3.33 (dd, 2H, $J = 12.9$, 2.7 Hz, H6), 3.30 (m, 1H, CH$_3$-octyl), 1.36-1.32 (bs, 2H, CH$_2$-octyl), 1.23-0.96 (bs, 10H, CH$_2$-octyl), 0.92 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) $\delta$ 171.31, 168.42,
Octyl 3, 4,-di-O-acetyl-2, 6-dideoxy-6-phenylseleno-2-phthalimido-β-D-glucopyranoside (71a).

Compound 70 (0.09 g, 0.16 mmol) was dissolved in 0.3 mL of Ac₂O and 0.3 mL of pyridine. After 5 h, the reaction was diluted with 25 mL of EtOAc and washed with satd. NaHCO₃, H₂O, and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using a short silica gel plug (hexanes:EtOAc, 1:1) to afford 71a (0.10 g, 99%) as a white powder. ¹H NMR (CDCl₃) δ 7.90-7.83 (m, 5H, Pht/SePh), 7.79-7.76 (m, 3H, SePh), 7.72 (m, 2H, Pht), 5.75 (dd, 1H, J = 10.6, 9.1 Hz, H4), 5.30 (d, 1H, J = 8.5 Hz, H1), 5.05 (m, 1H, H3), 4.30 (dd, 1H, J= 10.7, 8.6 Hz, H2), 3.87 (m, 1H, H5), 3.73 (m, 1H, CH₂-octyl), 3.39 (m, 1H, CH₂-octyl), 3.12-3.08 (dd, 1H, J = 12.9, 8.3 Hz, H6), 3.08-3.04 (m, 1H, H6), 2.00 (s, 3H, OAc), 1.85 (s, 3H, OAc), 1.40 (bs, 2H, CH₂-octyl), 1.24-0.95 (bs, 10H, CH₂-octyl), 0.96 (bs, 3H, CH₃). ¹³C NMR (CDCl₃) δ 170.23, 169.74, 134.35, 132.66, 129.14, 127.11, 123.64, 97.94, 73.79, 73.14, 70.73, 69.99, 54.88, 31.66, 29.32, 29.22, 29.13, 25.80, 22.61, 20.77, 20.52, 14.07. MS (ES, Na⁺): m/z (relative intensity) 666.1 (100). HRMS (M + Na⁺) calcd for C₃₂H₃₉NO₈Na, 668.1739; found 668.1740.
Octyl 3, 4, -di-O-benzyl-2, 6-dideoxy-6-phenylseleno-2-phthalimido-β-D-glucopyranoside (71b).

To a stirred 0 °C solution of 70 (0.135 g, 0.242 mmol) in 8 mL of THF was added NaH (0.023 g, 0.970 mmol). After 30 min, the reaction had BnBr (0.11 mL, 0.97 mmol) and Bu₄NI (0.44 g, 1.21 mmol) added to it. The solution was warmed to room temperature. After 17 h, the reaction was diluted with 40 mL of EtOAc and washed with 20 mL of satd. NaHCO₃, H₂O, and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using flash column chromatography (hex anes:EtOAc, 5:1) to afford 71b (0.110 g, 63%) as a colorless oil: ¹H NMR (CDCl₃) δ 7.65-7.48 (m, 2H, Pht), 7.32 (m, 2H, Pht), 7.30-7.21 (m, 10H, Bn), 7.00 (m, 2H, SePh), 6.87 (m, 2H, SePh), 5.09 (d, 1H, J = 8.5 Hz, H1), 4.90 (d, 1H, J= 11.0, CH₃-Bn), 4.79 (d, 1H, J= 12.0, CH₃-Bn), 4.65 (d, 1H, J= 11.1, CH₃-Bn), 4.42 (d, 1H, J= 12.0, CH₂-Bn), 4.33 (dd, 1H, J = 10.7, 8.6 Hz, H4), 4.15 (dd, 1H, J = 10.7 8.5, Hz, H4), 3.72 (dd, 1H, J= 9.4, 2.5 Hz, H5), 3.56 (m, 1H, CH₂-octyl), 3.56 (m, 1H, H2), 3.34-3.30 (m, 2H, H6/CH₂-octyl), 3.04 (dd, 1H, J = 12.6, 8.4 Hz, H6), 1.56 (bs, 2H, CH₂-octyl), 1.14-0.90 (bs, 10H, CH₂-octyl), 0.80 (bs, 3H, CH₃). ¹³C NMR (CDCl₃) δ 137.81, 137.70, 132.08, 131.03, 128.95, 128.48, 128.00, 127.93, 127.82, 127.29, 126.59, 97.99, 83.21, 79.34, 75.16, 74.94, 74.79, 69.55, 56.00, 31.57, 29.62, 29.15, 29.03, 25.72, 22.51, 13.98. MS (ES, Na⁺): m/z (relative intensity) 764.2 (100). HRMS (M + Na⁺) calcd for C₄₀H₄₃NO₆SeNa, 764.2466; found 764.2462.
3, 4, 6-tri-O-Acetyl-2-deoxy-2-(2, 2, 2-trichloroethoxycarbonyl) amido-β-D-glucopyranoside (76).

To a stirred solution of (H₂NCH₂)₂ (0.21 mL, 3.44 mmol) and AcOH (0.23 mL, 4.01 mmol) in 100 mL of THF was added 43 (1.50 g, 2.87 mmol). After 25 h, the solution was diluted with 60 mL of H₂O and the aqueous extract was washed three times with 120 mL of CH₂Cl₂. The combined organic extracts were washed with 360 mL of 0.1M HCl solution, 360 mL of satd. NaHCO₃ and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered, and the filtrate concentrated. The crude product was purified with flash column chromatography (hexanes:EtOAc, 1:1) to afford 76 (1.28 g, 92 %) as a colorless oil: ¹H NMR (CDCl₃) δ 5.50 (dd, 1H, J= 9.8 Hz, NH), 5.33-5.26 (m, 3H, H1/H3/H4), 5.09 (dd, 1H, J = 9.5 Hz, H2), 4.77 (d, 1H, J= 12.0 Hz, CH₂-Troc), 4.62 (s, 1H, CH₂-Troc), 4.58 (m, 1H, H5), 4.22-4.19 (m, 2H, H6/H6), 3.98 (m, 1H, OH), 2.09-1.97 (s, 9H, Ac). ¹³C NMR (CDCl₃) δ 169.92, 154.66, 95.75, 92.06, 74.91, 71.25, 68.71, 67.89, 62.45, 54.58, 14.54.

Trichloroacetimido 3, 4, 6-tri-O-acetyl-2-deoxy-2-(2, 2, 2-trichloroethoxycarbonyl) amido-α, β-D-glucopyranoside (77).
To a stirred solution of 76 (0.183 g, 3.800 mmol) in 20 mL of CH₂Cl₂ were added CCl₃CN (9.50 mL, 95.2 mmol) and K₂CO₃ (0.79 mg, 5.70 mmol). After 48 h, the reaction was filtered and the filtrate concentrated. The crude product was purified with flash column chromatography (hexanes:EtOAc, 1.5:1) to afford 77 (0.22 g, 96%) as a colorless oil: ¹H NMR (CDCl₃) δ 8.83 (s, 1H, NH), 5.79 (d, 1H, J = 3.6 Hz, H1), 5.40-5.20 (m, 3H, H3, H4, H2), 4.66 (m, 2H, CH₂-Troc), 4.31-4.11 (m, 3H, H5, H6, H6) 1.94-1.78 (m, 9H, OAc). ¹³C NMR (CDCl₃) δ 171.29, 170.75, 169.56, 160.54, 154.55, 109.99, 95.64, 94.74, 90.95, 78.01, 77.15, 74.84, 70.45, 67.87, 61.69, 60.60, 54.04, 21.25, 20.90, 20.83, 14.46. MS (ES, Na⁺): m/z (relative intensity) HRMS (M + Na⁺) calcd for C₁₇H₂₂NO₁₀Cl₆Na, 646.9; found 646.9 (100).

(8-Methoxycarbonyloctyl) 3, 4, 6-tri-O-acetyl-2-deoxy-2-(2, 2, 2-trichloroethoxycarbonyl) amido-β-D-glucopyranoside (78).

To a stirred 0°C solution of 77 (0.45 g, 0.72 mmol) in 10 mL of THF, 8-methoxycarbonyloctanol (0.13 mL, 0.55 mmol) and 0.45 g of 4Å powdered sieves was added freshly distilled TMS-OTf (0.013 mL, 0.072 mmol). After 1 hr, the reaction was quenched with 5 drops of NEt₃, filtered and the filtrate concentrated. The resulting residue was dissolved in 40 mL of EtOAc and washed with 40 mL of satd. NaHCO₃ and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified with flash column chromatography (CHCl₃:EtOAc, 7:1) to afford 78 (0.38 g, 92%) as an oil: ¹H NMR (CDCl₃) δ 5.75 (s,
1H, J = 9.0 Hz, H1), 5.24 (m, 1H, H4), 4.98 (m, 1H, H3), 4.70 (d, 1H, J = 11.9 Hz, NH), 4.60-4.57 (m, 2H, CH2-Troc), 4.22 (m, 2H, H2), 4.04 (m, 1H, H5), 3.79 (m, 1H, H6), 3.59 (s, 3H, OMe), 3.41 (m, 1H, H6), 2.23 (s, 3H, OAc), 2.20-2.01 (m, 6H, OAc), 1.51 (bs, 7H, octyl), 1.18 (bs, 9H, octyl). 13C NMR (CDCl3) δ 174.81, 171.15, 170.98, 169.92, 164.13, 154.60, 101.13, 95.92, 92.44, 74.74, 72.70, 72.46, 71.97, 70.54, 69.25, 63.15, 62.55, 60.79, 56.55, 51.87, 34.36, 33.01, 29.71, 29.53, 29.39-29.18, 28.56, 26.01, 25.77, 25.16, 21.39, 21.11, 21.01, 14.52. MS (ES, Na+): m/z (relative intensity) calcd for C37H35NO9SeNa, 740.1375; found 672.0 (100).

(8-Methoxycarbonyloctyl)-2-acetamido-3, 4, 6-tri-O-acetyl-2-deoxy-β-D-glucopyranoside (79).

To a stirred solution of 78 (0.15 g, 0.23 mmol) in 3 mL of AcOH was added Zn dust (1.01 g, 15.43 mmol). After 54 hours, Chelex 100 resin was added and the reaction was stirred for 1 h, filtered and the filtrate concentrated. The resulting oil was dissolved in 30 mL of EtOAc and washed with 15 mL of satd. NaHCO3 and NaCl solutions. The organic extract was dried with Na2SO4, filtered and the filtrate concentrated. The crude product (0.105 g) was taken on without purification as a colorless oil: 1H NMR (CDCl3) δ 7.46 (bs, 3H, NH3), 5.38 (m, 1H, H4), 4.97 (m, 1H, H3), 4.73 (d, 1H, J = 7.7 Hz, H1), 4.24 (dd, 1H, J = 12.3, 4.5 Hz, H6), 4.09 (s, 1H, CH2-octyl), 4.04 (m, 1H, H6), 3.86-3.68 (m, 2H, H5/H2), 3.62 (s, 3H, OMe), 2.26 (bs, 6H, OAc), 2.06 (s, 3H, OAc), 1.54 (bs, 10H, octyl), 1.21 (bs, 5H, octyl). The free amine (0.105 g, 0.22 mmol) was dissolved in 3
mL of dry pyridine and 3 mL of Ac₂O. After 20 h, the reaction was diluted with 25 mL of EtOAc and washed with 25 mL of satd. CuSO₄, satd. NaHCO₃, and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified with flash column chromatography (hexanes:EtOAc, 5:1) to afford 79 (0.095 g, 78%, 2 steps) as a colorless oil: ¹H NMR (CDCl₃) δ 5.82 (d, 1H, J = 8.6 Hz, NH), 5.29, (m, 1H, H3), 5.02 (m, 1H, H4), 4.68 (d, 1H, J = 8.3 Hz, H1), 4.23 (dd, 1H, J = 12.3, 4.7 Hz, H6), 4.12-4.05 (m, 2H, H6, CH₂-octyl), 3.83-3.79 (m, 2H, H5/H2), 3.63 (s, 3H, OMe), 3.42 (m, 1H, CH₂-octyl), 2.26 (s, 3H, OAc). 2.01-1.98 (bs, 10H, OAc), 1.54 (bs, 5H, octyl), 1.22 (bs, 5H, OAc). ¹³C NMR (CDCl₃) δ 174, 29, 171.10, 170.74, 170.14, 169.38, 100.58, 72.27, 71.62, 69.78, 68.68, 62.12, 60.32, 54.79, 51.40, 33.94, 29.26, 29.02-28.87, 25.63, 24.75, 23.21, 20.97, 20.68-20.57, 14.10.

(8-Methoxycarbonyloctyl) 2-Acetamido-4, 6-O-benzylidene-2-deoxy-β-D-glucopyranoside (80).

To a stirred solution of 79 (0.25 g, 0.48 mmol) in 4 mL of MeOH and 1.5 mL of THF was added 1M NaOMe solution (0.48 mmol). After 1.25 h, 1.40 g of Dowex 50W H⁺ form resin (2.1 meq/mL) was added and gently stirred for 20 minutes. The reaction mixture was filtered and the filtrate concentrated. To a suspension of the resulting triol in 5 mL of CH₃CN were added PhCH(OMe)₂ (0.12 mL, 0.82 mmol) and pTsOH (0.001 g, 0.048 mmol). After 21 h, the reaction was placed under a gentle vacuum. After 1 hour,
the reaction had 25 mg of K$_2$CO$_3$ and was stirred for 0.5 hours. The mixture was filtered and the filtrate concentrated. The crude product was purified with flash column chromatography (CH$_2$Cl$_2$:MeOH, 15:1) to afford **80** (0.08 g, 85%, 2 steps) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.48 (m, 2H, Ph), 7.35 (m, 3H, Ph), 6.02 (d, 1H, J = 6.5 Hz, N-H), 5.50 (s, 1H, benzylidene), 4.65 (d, 1H, J = 8.3 Hz, H1), 4.30 (dd, 1H, J = 10.4, 5.0 Hz, H3), 4.08 (m, 1H, octyl), 3.83 (m, 1H, H6), 3.75 (m, 1H, H4), 3.65 (s, 3H, OMe), 3.52 (m, 1H, octyl), 3.47-3.42 (m, 3H, H2/H5/H6), 2.29 (s, 3H, OAc), 1.57 (bs, 5H, octyl), 1.28 (bs, 9H, octyl). $^{13}$C NMR (CDCl$_3$) $\delta$ 174.29, 171.75, 137.09, 129.11, 128.21, 126.30, 101.79, 100.68, 81.63, 71.09, 69.97, 68.58, 66.20, 58.80, 51.43, 33.99, 29.38, 29.07-28.93, 25.74, 24.80, 23.52. MS (ES, Na$^+$): m/z (relative intensity) HRMS (M + Na$^+$) calcd for C$_{25}$H$_{40}$NO$_8$Na, 502.1; found 502.1 (100).

**(8-Methoxycarbonyloctyl) 2-acetamido-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-4, 6-O-benzylidene-2-deoxy-β-D-glucopyranoside (81).**

![Chemical Structure](image)

To a stirred solution of acceptor **80** (0.012 g, 0.026 mmol) in 1.0 mL of toluene:CH$_3$NO$_2$ (1:1) were added Hg(CN)$_2$ (0.02 g, 0.078 mmol) and 35 mg of CaSO$_4$. Donor **74**$^{81}$ (0.017 g, 0.041 mmol) was dissolved in 1.0 mL toluene:CH$_3$NO$_2$ (1:1) and added to the acceptor mixture and the reaction heated to 40 °C. After 47 h, the reaction was cooled and diluted with 15 mL of CH$_2$Cl$_2$ and washed with 15 mL of satd. NaHCO$_3$ solution, H$_2$O and satd. NaCl solution. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude oil was purified using flash column
chromatography (CH$_2$Cl$_2$:MeOH, 15:1) to afford 81 (0.015 g, 75%) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 5.80 (d, 1H, J=5.6 Hz, N-H), 5.54 (s, 1H, benzylidene), 5.18 (d, 1H, J = 8.6 Hz, H1), 4.71 (d, 1H, J = 8.2 Hz, H1’), 3.66 (s, 3H, OMe). $^{13}$C NMR (CDCl$_3$) $\delta$ 229.59, 174.29, 171.73, 137.05, 129.16, 128.25, 126.32, 101.91, 100.55, 81.71, 71.15, 70.00, 68.62, 66.27, 59.28, 51.45, 34.01, 29.42, 29.09, 29.01, 28.95, 25.80, 24.82, 23.62, 23.62, 20.80, 20.63. MS (ES, Na$^+$): m/z (relative intensity) 832.3 (100). HRMS (M + Na$^+$) calcd for C$_{40}$H$_{57}$NO$_{17}$Na, 832.3368; found 832.3375.

Octyl 3-O-(2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl)-4, 6-O-benzylidene-2-deoxy-2-phthalimido-α-D-glucopyranoside (82).

To a stirred solution of acceptor 32$^{47}$ (0.60 g, 1.22 mmol) and donor 75$^{81}$ (0.684 g, 1.34 mmol) in 20 mL of CH$_2$Cl$_2$ at -20 °C were added 1.0 g 3Å molecular sieves and freshly distilled TMS-OTf (0.05 mL, 0.304 mmol). The reaction was allowed to warm to 0 °C for 3 h and then to room temperature. After 24 h, the reaction was quenched with 0.05 mL of NEt$_3$ and filtered. The filtrate was washed with 20 mL of satd. NaHCO$_3$ and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude oil was purified using flash column chromatography (hexanes:EtOAc, 2:1) to afford 82 (0.840 g, 83%) as a colorless foam: $^1$H NMR (CDCl$_3$) $\delta$ 7.88 (s, 2H, Pht), 7.77 (s, 2H, Pht), 7.49 (s, 2H, Ph), 7.38 (s, 3H, Ph), 5.58 (s, 1H, benzylidene), 5.19 (d, 1H, J = 3.1 Hz, H4’), 5.14 (d, 1H, J = 8.5 Hz, H1), 4.99 (dd, 1H, J = 10.3, 8.0 Hz, H2’), 4.76-4.71 (m, 2H, H3/H3’), 4.55 (d, 1H, J = 8.0Hz, H1’), 4.37 (dd,
1H, J = 10.5, 4.8 Hz, H4), 4.30 (dd, 1H, J = 10.4, 8.6 Hz, H2), 4.03 (dd, 1H, J = 11.0, 8.3 Hz, H6’), 3.86 (m, 1H, H6’), 3.82-3.77 (m, 3H, H6/H6/C8-octyl), 3.63 (m, 1H, H5), 3.49 (m, 1H, H5’), 3.38 (m, 1H, C8-octyl), 2.08 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.92 (s, 3H, OAc), 1.26-1.13 (bs, 3H, C8-octyl), 1.03-0.96 (bs, 9H, C8-octyl), 0.82 (t, 3H, C3-octyl). 13C NMR (CDCl3) δ 170.23, 170.01, 169.98, 168.82, 137.05, 134.18, 129.22, 128.31, 126.00, 101.43, 100.48, 98.74, 81.08, 75.69, 70.99, 70.28, 70.01, 69.19, 68.74, 66.63, 66.31, 60.76, 56.38, 31.60, 29.20, 29.03, 29.01, 25.70, 22.53, 20.56, 20.49, 20.39, 20.06, 14.15, 13.99. MS (ES, Na+): m/z (relative intensity) 861.9 (100). HRMS (M + Na+) calcd for C43H53NO16Na, 862.3262; found 862.3259.

(8-Methoxycarbonyloctyl) 2-acetamido-3-O-(2,3,4,6-tetra-O-acetyl-3-D-galactopyranosyl)-4, 6-O-benzylidene-2-deoxy-α-D-glucopyranoside (83).

To a stirred solution of acceptor 80 (0.011 g, 0.023 mmol) in 0.75 mL of CH2Cl2 was added 15 mg of 4Å molecular sieves. Donor 75 (0.015 g, 0.030 mmol) was dissolved in 0.75 mL of CH2Cl2 and added to the acceptor mixture and the reaction cooled to 0 °C. Freshly distilled TMS-OTf (0.005 mL) was added. After 3 h, the reaction was quenched with 0.01 mL NEt3, filtered and the filtrate diluted with 5.0 mL of CH2Cl2 and washed with 5 mL of satd. NaHCO3 solution, H2O and satd. NaCl solution. The organic extract was dried with Na2SO4, filtered and the filtrate concentrated. The crude oil was purified using flash column chromatography (CH2Cl2:MeOH, 15:1) to afford 83 (0.020 g, 81%) as a colorless oil: 1H NMR (CDCl3) δ 7.48 (m, 2H, Ph), 7.34
Octyl 3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-4-O-benzoyl-6-phenylseleno-2-phthalamido-2-deoxy-β-D-glucopyranoside (84).

To a stirred solution of 82 (0.70 g, 0.83 mmol) in 35 mL of CCl₄ were added NBS (0.162 g, 0.916 mmol) and BaCO₃ (0.493 mg, 2.449 mmol). The reaction was heated to reflux and after a few minutes turned an orange color. As the reaction progressed, it became white. After 45 min, the reaction was cooled, filtered and the filtrated concentrated. The crude product was dissolved in 50 mL of CH₂Cl₂ and washed with 25 mL of H₂O 3 times and once with 25 mL of satd. NaCl solution. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated to yield the bromide (0.75 g) as a white powder and taken on without any purification: ¹H NMR (CDCl₃) δ 8.04 (m, 2H, m, 3H, Ph), 5.82 (d, 1H, J = 7.5 Hz, N-H), 5.75 (d, 1H, J = 4.7 Hz, H1’), 5.50 (s, 1H, benzylidene), 5.8 (d, 1H, J = 3.1 Hz, H4’), 5.07 (d, 1H, J = 8.3 Hz, H1), 5.01 (dd, 1H, J = 6.4, 3.4 Hz, H3’), 4.50 (m, 1H, H3), 4.32 (m, 1H), 4.34 (m, 1H, H5), 4.24 (m, 2H, H5’/H2’), 4.06 (m, 2H, H6’/H6’), 3.84 (m, 1H, CH₂-Mco), 3.76 (m, 1H, H6), 3.66 (s, 3H, OMe), 3.52 (m, 3H, CH₂-Mco/H4/H6), 3.11 (m, 1H, H2), 2.10 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.97 (s, 3H, NHAc), 1.64 (m, 14H, CH₂-Mco). ¹³C NMR (CDCl₃) δ 172.20, 171.05, 169.91, 164.39, 163.25, 129.26, 128.12, 126.05, 123.52, 109.75, 104.24, 90.69, 84.26, 70.71, 68.88, 67.50, 66.35, 61.30, 59.46, 51.43, 33.98, 29.38, 28.47, 25.94, 23.64, 20.66. MS (ES, Na⁺): m/z (relative intensity) 832.3 (100). HRMS (M + Na⁺) calcd for C₄₀H₅₇NO₁₇Na, 832.3368; found 832.3389.
Bz), 7.85 (d, 2H, NPh), 7.77 (m, 2H, NPh), 7.57 (m, 2H, Bz), 7.44 (m, 3H, Bz), 5.14 (m, 1H, H3), 5.11 (d, 1H, J = 8.5 Hz, H1), 4.97 (d, 1H, J = 4.2 Hz, H4'), 4.83 (dd, 1H, J = 10.5, 3.7 Hz, H3'), 4.54 (dd, 1H, J = 10.5, 3.5 Hz, H2'), 4.32 (m, 1H, H5'), 4.18 (d, 1H, J = 7.8 Hz, H1'), 4.09 (dd, 1H, J = 4.1 Hz, H2), 3.94 (m, 1H, H4), 3.77 (m, 1H, CH$_2$-octyl), 3.53 (m, 2H, H6'/H6'), 3.49-3.31 (m, 4H, H5/H6/H6/CH$_2$-octyl), 2.09-1.75 (s, 12H, OAc), 1.41 (bs, 3H, CH$_2$-octyl), 1.14-0.98 (bs, 9H, CH$_2$-octyl), 0.80 (t, 3H, CH$_3$-octyl).

$^{13}$C NMR (CDCl$_3$) δ 169.92, 168.88, 164.58, 134.40, 133.32, 131.32, 129.91, 129.68, 128.25, 123.44, 100.09, 97.84, 74.64, 73.68, 72.43, 71.05, 70.65, 70.13, 66.77, 68.76, 66.09, 60.03, 55.54, 53.30, 31.46, 31.15, 28.99, 28.89, 25.58, 22.40, 20.22, 13.87. MS (ES, Na$^+$): m/z (relative intensity) calcd for C$_{43}$H$_{52}$NO$_1$BrNa, 940.2; found 940.2 (100).

To a stirred solution of the bromide (0.75 g, 0.816 mmol) in 30 mL of THF were added NEt$_3$ (0.37 mL, 2.692), PhSeH (0.24 mL, 2.448 mmol) and Bu$_4$NI (0.075 g, 0.204 mmol). The reaction was brought to reflux at 65 °C. After 16 h, the reaction was cooled and diluted to 100 mL of CH$_2$Cl$_2$ and washed with 100 mL of satd. NaHCO$_3$, H$_2$O and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The resulting yellow oil was purified using flash column chromatography (hexanes:EtOAc, 2:1) to afford 84 (0.70 g, 82%, 2 steps) as a colorless oil: $^1$H NMR (CDCl$_3$) δ 8.03 (m, 2H, Bz), 7.87 (d, 2H, NPh), 7.79 (m, 2H, NPh), 7.58 (m, 2H, Bz), 7.46 (m, 4H, Bz/SePh), 7.19 (m, 2H, SePh), 5.23 (m, 1H, H3'), 5.07 (d, 1H, J = 8.5 Hz, H1), 5.00 (d, 1H, J = 2.9 Hz, H4'), 4.86 (dd, 1H, J = 10.3, 7.8 Hz, H2'), 4.79 (dd, 1H, J = 10.7, 8.9 Hz, H3), 4.56 (m, 1H, H5'), 4.34 (dd, 1H, J = 10.7, 8.5 Hz, H2), 4.09 (d, 1H, J = 7.8 Hz, H1'), 3.94 (m, 1H, H4), 3.72 (m, 2H, H6'/H6'), 3.52 (m, 1H, H5), 3.44 (m, 1H, H6), 3.33 (m, 2H, CH$_2$-octyl), 3.13 (m, 1H, H6), 2.08 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.16
1.95 (s, 3H, OAc), 1.87 (s, 3H, OAc), 1.27-1.17 (bs, 3H, CH₂-octyl), 1.06-1.00 (bs, 9H, CH₂-octyl), 0.83 (t, 3H, CH₃-octyl). ¹³C NMR (CDCl₃) δ 170.12, 170.04, 169.97, 169.00, 164.76, 134.49, 133.32, 132.19, 129.74, 128.99, 128.32, 126.79, 123.52, 100.23, 97.91, 74.97, 74.21, 70.81, 70.13, 69.65, 68.84, 66.18, 60.08, 55.74, 31.61, 29.05, 25.73, 22.56, 20.58, 20.36, 20.29, 14.03.  MS (ES, Na⁺): m/z (relative intensity) 1018.2 (100).

HRMS (M + Na⁺) calcld for C₄₉H₅₇NO₁₆SeNa, 1018.2740; found 1018.2745.

Octyl 2-acetamido-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)- 4-O-acetyl-6-phenylseleno-2-deoxy-β-D-glucopyranoside (85).

To a stirred solution of 84 (0.045 mg, 0.045 mmol) in 1.0 mL of EtOH in a Schlenk tube was added H₂NNH₂·H₂O (0.19 mL, 4.070 mmol). The reaction was placed under a gentle vacuum, the tube sealed and heated to 100 °C. After 18.5 h, the reaction was cooled, the tube opened and the reaction mixture concentrated and placed under vacuum for 6 h to afford the free amino alcohol (0.026 g) as a colorless oil. The product was taken on to the next step without any purification. The resulting free amino alcohol (0.026 g, 0.045 mmol) was dissolved in 3.0 mL of pyridine and 3.0 mL of Ac₂O. After 20.5 h, the reaction was diluted with 10 mL of EtOAc and washed with 10 mL of satd. CuSO₄, H₂O, satd. NaHCO₃, and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The resulting light yellow oil was purified using flash column chromatography (hexanes:EtOAc, 1:4) to afford 85 (0.030 g, 78%, 2 steps) as a colorless oil/solid: ¹H NMR (CDCl₃) δ 7.48 (m, 3H, SePh), 7.26 (m,
2H, SePh), 5.89 (d, 1H, J = 7.1 Hz, NH), 5.33 (d, 1H, J = 2.5 Hz, H4′), 5.04 (dd, 1H, J = 10.1 Hz, H2′), 4.96-4.90 (m, 2H, H3′/H1), 4.80 (dd, 1H, J = 9.1 Hz, H3), 4.55-4.48 (m, 3H, H1′/H4/H5′), 3.86 (dd, 1H, J = 12.9, 6.4 Hz, H6′), 3.66 (dd, 1H, J = 8.9, 6.1 Hz, H6′), 3.74 (m, 1H, H2), 3.42 (m, 1H, CH₂-octyl), 3.12 (m, 1H, CH₂-octyl), 3.03-2.97 (m, 3H, H5/H6/H6), 2.16 (s, 3H, OAc), 2.13 (bs, 15H, OAc/NHAc), 1.52 (bs, 3H, CH₂-octyl), 1.25 (bs, 9H, CH₂-octyl), 0.86 (t, 3H, CH₃-octyl). ¹³C NMR (CDCl₃) δ 175.13, 171.13, 170.88, 170.39, 170.11, 169.01, 169.01, 132.57, 129.01, 126.91, 100.53, 98.78, 73.73, 73.04, 71.06, 70.54, 69.87, 69.39, 66.92, 61.05, 60.36, 58.39, 31.79, 29.50, 29.44, 29.29, 25.89, 23.57, 22.61, 20.99, 20.89, 20.77, 20.60, 20.49, 14.15. MS (ES, Na⁺): m/z (relative intensity) 868.2 (100). HRMS (M + Na⁺) calcd for C₃₈H₅₅NO₁₇SeNa, 868.2635; found 868.2645.

Octyl 6-O-ter-butyldimethylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (87).

To a stirred solution of compound 86⁴⁷ (0.150 g, 0.356 mmol) in 1.5 mL of DMF were added imidazole (0.072 g, 1.068 mmol) and TBS-Cl (0.067 g, 0.445 mmol). After 39 h, the reaction was diluted with 10 mL of EtOAc and washed with 10 mL of H₂O and saturated NaCl solution. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using a short silica gel plug (EtOAc) to afford 87 (0.140 g, 74%) as a colorless oil. ¹H NMR (CDCl₃) δ 7.82 (m, 2H, Pht), 7.69 (m, 2H, Pht), 5.17 (d, 1H, J = 8.4 Hz, H1), 4.32 (dd, 1H, J = 8.1 Hz, H4), 4.08 (dd, 1H, J = 8.5, 3.5 Hz, H2), 3.97 (dd, 1H, J = 10.3, 5.0 Hz, H3), 3.87 (m, 1H, H5), 3.75
(8-Methoxylcarbonyloctyl)-2-acetamido-3-O-acetyl-4, 6-O-benzylidene-2-deoxy-β-D-glucopyranoside (88a).

Compound 80 (0.018 g, 0.370 mmol) was dissolved in pyridine (1.00 mL, 0.77 mmol) and Ac₂O (1.00 mL, 1.10 mmol). After 27 h, the reaction was diluted with 5 mL of EtOAc and washed with 5 mL of satd. CuSO₄, H₂O, satd. NaHCO₃ and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The resulting white oil/solid 88a (0.016 g, 84%) was taken on without any purification: ¹H NMR (CDCl₃) δ 7.43 (m, 2H, Ph), 7.34 (m, 3H, Ph), 5.74 (d, 1H, J = 9.3 Hz, NH), 5.50 (s, 1H, benzylidene), 5.27 (m, 1H, H4), 4.50 (d, 1H, J = 8.3 Hz, H1), 4.33 (dd, 1H, J = 10.5, 4.9 Hz, H3), 4.08 (m, 1H, H2), 3.81 (m, 2H, H5/CH₂-octyl), 3.69 (m, 1H, CH₂-octyl), 3.67 (s, 3H, OMe), 3.52 (dd, 1H, J = 9.8, 4.9 Hz, H6), 3.39 (dd, 1H, J = 6.8, 2.8 Hz, H6), 2.07 (s, 3H, OAc), 1.95 (s, 3H, OAc), 1.59 (bs, 5H, CH₂-octyl), 1.28 (bs, 10H, CH₂-octyl). ¹³C NMR (CDCl₃) δ 229.59, 174.27, 171.24, 170.00, 136.97, 129.05, 128.19, 126.08, 102.00, 101.36, 78.71, 71.87, 69.95, 66.38, 54.70, 51.42, 34.02,

Compound 32\textsuperscript{47} (2.25 g, 2.45 mmol) was dissolved in 10 mL of Ac\textsubscript{2}O and 10 mL of pyridine. After 19 h, the reaction was diluted to 75 mL of EtOAc and washed with 50 mL of satd. CuSO\textsubscript{4}, H\textsubscript{2}O, satd. NaHCO\textsubscript{3}, and satd. NaCl solutions. The organic extract was dried with Na\textsubscript{2}SO\textsubscript{4}, filtered and the filtrate concentrated. The crude product was purified by flash column chromatography (hexanes:EtOAc, 3:1) to afford 88b (1.12 g, 83\%) as a colorless oil: \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \(\delta\) 7.81 (bs, 2H, NPht), 7.66 (bs, 2H, NPht), 7.43 (bs, 2H, Ph), 7.30 (bs, 3H, Ph), 5.89 (d, 1H, \(J = 9.8\) Hz, H4), 5.51 (s, 1H, benzylidene), 5.43 (d, 1H, \(J = 8.4\) Hz, H1), 4.37 (d, 1H, \(J = 10.2, 4.1\) Hz, H3), 4.29 (dd, 1H, \(J = 9.1\) Hz, H2), 3.83-3.74 (m, 3H, H6/H6/H5), 3.71 (m, 1H, CH\textsubscript{2}-octyl), 3.42 (m, 1H, CH\textsubscript{3}-octyl), 2.04 (s, 3H, OAc), 1.93 (s, 3H, NHAc), 1.58-1.55 (bs, 2H, CH\textsubscript{2}-octyl), 1.28-1.21 (bs, 10H, CH\textsubscript{3}-octyl), 0.85 (s, 3H, CH\textsubscript{3}-octyl). \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \(\delta\) 170.03, 136.99, 134.28, 134.14, 128.14, 126.22, 123.44, 101.49, 98.65, 79.28, 77.50, 77.25, 76.99, 70.13, 69.76, 68.59, 66.18, 55.39, 31.55, 29.19, 29.14, 29.10, 29.01, 25.70, 22.50, 20.47, 14.01. MS (ES, Na\textsuperscript{+}): m/z (relative intensity) 574.2 (100). HRMS (M + Na\textsuperscript{+}) calcd for C\textsubscript{31}H\textsubscript{37}NO\textsubscript{8}Na, 574.2417; found 574.2415.
(8-Methoxycarbonyloctyl)-2-acetamido-3-O-acetyl; -6-O-benzyl-2-deoxy-3-D-glucopyranoside (89). Method (a).

To a stirred solution of 88a (0.022g, 0.042 mmol) in 1.0 mL of THF:CH₂Cl₂ (1:1) were added 0.02 g of 3Å molecular sieves and NaCNBH₃ (23mg, 0.379 mmol). Freshly prepared HCl (g) in ether was added at 0 °C until no gas was evolved. After 5 h, the reaction was filtered and the filtrate diluted to 10 mL of CH₂Cl₂ and washed with 10 mL of H₂O, satd. NaHCO₃, and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using preparatory thin layer chromatography (CH₂Cl₂:MeOH, 15:1) to afford 89 (0.004 g, 25%) as a colorless oil: ¹H NMR (CDCl₃) δ 7.33 (m, 5H, Ph), 5.52 (d, 1H, J = 9.1 Hz, NH), 5.05 (dd, 1H, J = 10.5, 9.1 Hz, H3), 4.59 (q, 2H, J = 11.9 Hz, CH₂-Ph), 4.48 (d, 1H, J = 8.3 Hz, H1), 3.89 (m, 1H, H2), 3.82 (m, 2H, H5/CH₂-octyl), 3.76 (m, 2H, H4/CH₂-octyl), 3.66 (s, 3H, OMe), 3.53 (m, 1H, H6), 3.42 (m, 1H, H6), 2.30 (d, 1H, J = 3.0 Hz, -OH), 2.30 (bs, 2H, CH₂-octyl), 2.10 (s, 3H, OAc), 1.93 (s, 3H, OAc), 1.58 (bs, 5H, CH₂-octyl), 1.27 (bs, 10H, CH₂-octyl). ¹³C NMR (CDCl₃) δ 174.29, 171.88, 169.99, 137.50, 128.50, 127.90, 127.74, 101.12, 75.40, 73.81, 73.77, 71.17, 70.64, 69.53, 54.70, 51.11, 51.43, 34.03, 29.39, 29.11, 29.03, 28.98, 25.75, 24.85, 23.33, 20.92. MS (ES, Na⁺): m/z (relative intensity) 546.2 (100). HRMS (M + Na⁺) calcd for C₂₇H₄₁NO₉Na, 546.2679; found 546.2679.
Method (b).

To a stirred 0 °C solution of 88a (0.01 g, 0.06 mmol) in 0.25 mL of CH₂Cl₂ were added dropwise TES (0.0091 mL, 0.113 mmol) followed by drop wise addition of TFA (0.0087 mL, 0.114 mmol). The reaction was allowed to stir overnight at 4 °C. After 30 h, the reaction was filtered and the filtrate diluted to 5 mL of CH₂Cl₂. The filtrate had 5 mL of satd. NaHCO₃ solution slowly added to neutralize the TFA. The aqueous extract was washed with 5 mL of CH₂Cl₂ and the combined organic extracts washed with sat NaCl solution. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using preparatory thin layer chromatography (CH₂Cl₂:MeOH, 15:1) to afford 89 (0.005 g, 50%) as a colorless oil with identical ¹H NMR, ¹³C NMR and mass spectrum data as identical to those reported for 89 prepared by Method (a).

Octyl 3-O-acetyl-6-O-tert-butyldimethylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (90).

Compound 88b (1.10 g, 1.99 mmol) was suspended in 50 mL of AcOH:H₂O (1:1) and heated to 100 °C. After 4.5 h, the reaction was cooled and concentrated. The crude product was diluted in 75 mL of EtOAc and washed with 50 mL of satd. NaHCO₃ and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated to afford the diol (0.89 g) as a colorless oil and taken on without any
purification. To a stirred solution of the crude diol (0.10 g, 0.22 mmol) in 2.0 mL of DMF were added TBS-Cl (0.040 g, 0.269 mmol) and imidazole (0.044 mg, 0.645 mmol). After 20 h, the DMF was concentrated. The crude product was diluted to 20 mL of EtOAc and washed with 10 mL of H₂O, and satd. NaCl solution. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using a short silica gel plug (EtOAc) to afford 90 (0.105 g, 81%, 2 steps) as a colorless oil: 

$$\text{H NMR (CDCl}_3\text{) } \delta 7.86 \text{ (bs, 2H, NPht), 7.74 \text{ (bs, 2H, NPht), 5.65 \text{ (d, 1H), J = 10.6, 8.9 Hz, H4), 5.35 \text{ (d, 1H, J = 8.5 Hz, H1), 4.21 \text{ (dd, 1H, J = 10.6, 8.5 Hz, H3), 3.97-3.83 \text{ (m, 2H, H5/H2), 3.78 \text{ (m, 2H, H6/H6), 3.61 \text{ (m, 1H, CH}_2\text{-octyl), 3.42 \text{ (m, 1H, CH}_2\text{-octyl), 2.94 \text{ (d, J = 4.9 Hz, OH), 2.04 \text{ (s, 3H, OAc), 1.93 \text{ (s, 3H, NHAac), 1.58-1.55 \text{ (bs, 2H, CH}_2\text{-octyl), 1.28-1.21 \text{ (bs, 10H, CH}_2\text{-octyl), 0.85 \text{ (s, 3H, CH}_3\text{-octyl).}}}}}}

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$$\text{C NMR (CDCl}_3\text{) } \delta 171.40, 170.32, 168.18, 167.78, 134.18, 134.11, 133.87, 131.37, 123.47, 123.41, 123.30, 98.09, 97.46, 76.23, 75.37, 73.77, 70.30, 70.07, 69.25, 69.04, 60.35, 55.42, 31.60, 29.29, 29.09, 25.87, 25.60, 22.52, 20.66, 17.94, 14.13. \text{ MS (ES, Na}^+\text{): m/z (relative intensity) calcd for C}_{30}\text{H}_{47}\text{NO}_8\text{Na, 512.3; found 512.3 (100).}}

Octyl 4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-acetamido-3-O-acetyl-6-O-t-butyldimethylsilyl-2-deoxy-β-D-glucopyranoside (93).

To a stirred solution of acceptor 91\textsuperscript{73} (0.028 g, 0.057 mmol) and donor 75\textsuperscript{81} (0.03 g, 0.06 mmol) in 3 mL of CH₂Cl₂ was added 0.10 g 3Å molecular sieves. The reaction was cooled to -30°C and freshly distilled TMS-OTf (0.002 mL, 0.045 mmol) was added
and the reaction allowed to warm to room temperature. After 24 h, the reaction was quenched with 2 drops of NEt₃, filtered and diluted to 20 mL of CH₂Cl₂. The filtrate was washed with 20 mL of satd. NaHCO₃ and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude oil was purified using flash column chromatography (hexanes:EtOAc, 2:1) to afford 93 (0.017 g, 37%) as a colorless oil/solid: ¹H NMR (CDCl₃) δ 5.74 (bs, 1H, N-H), 5.47-5.39 (m, 2H, H4’/H1), 4.99-4.92 (m, 3H, H2’/H3/H3’), 4.38-4.30 (m, 3H, H1’/H4/H2), 4.18-4.08 (m, 2H, H6’/H6’), 3.85-3.73 (m, 3H, H6/H6/CH₂-octyl), 3.51-3.41 (m, 3H, H5/H5’/CH₂-octyl), 2.13-1.95 (s, 18H, NHAc/OAc), 1.23 (bs, 3H, CH₂-octyl), 1.03-0.92 (bs, 9H, CH₂-octyl), 0.82 (t, 3H, CH₃-octyl). MS (ES, Na⁺): m/z (relative intensity) HRMS (M + Na⁺) calcd for C₄₇H₆₅NO₁₆Na, 842.3; found 842.3 (100).

Octyl 4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-3, 6-di-O-acetyl-2-deoxy-2-phthalamido-β-D-glucopyranoside (94).

To a stirred solution of acceptor 87 (0.01 g, 0.018 mmol) and donor 75 (0.05 g, 0.10 mmol) in 6.0 mL of CH₂Cl₂ was added 0.06 g of 3Å powdered molecular sieves and the mixture heated to reflux. After 1h, the reaction was cooled to -50 °C and BF₃·OEt₂ (0.0012 mL, 0.010 mmol) was added. After 1.5h, the reaction was quenched with 2 drops of NEt₃, the reaction solution was filtered and the filtrate concentrated. The resulting oil was diluted with 5mL of EtOAc and washed with 5mL of satd. NaHCO₃ and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate
concentrated. The crude oil was purified using preparative thin layer chromatography (hexanes:EtOAc, 1:1) to afford a partially deprotected disaccharide with complete loss of TBS group and partial loss of OAc groups (0.01 g) as a colorless oil. The resulting crude product was dissolved in 0.5 mL of pyridine and 0.5 mL of Ac₂O. After 20 h, the reaction was diluted with 5.0 mL EtOAc and washed with 5.0 mL of satd. CuSO₄, satd. NaHCO₃, H₂O, and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude oil was purified using preparative thin layer chromatography (hexanes:EtOAc, 1:1) to afford 94 (0.008 g, 55%, 2 steps) as a colorless oil: \(^1\)H NMR (CDCl₃) δ 7.80 (bs, 2H, Pht), 7.76 (s, 2H, Pht), 5.22 (d, 1H, J = 3.7 Hz, H4’), 5.20 (d, 1H, J = 9.0 Hz, H1), 5.17 (dd, 1H, J = 9.8 Hz, H2’), 5.15 (d, 1H, J = 8.5 Hz, H1’), 5.10 (dd, 1H, J = 9.2, 3.2 Hz, H5’), 5.03 (dd, 1H, J = 10.7, 3.8 Hz, H3’), 4.71 (dd, 1H, J = 10.6, 9.1 Hz, H3), 4.33 (dd, 1H, J = 10.5, 8.6 Hz, H2), 4.21 (dd, 1H, J = 12.3, 4.9 Hz, H6’), 4.10 (dd, 1H, J = 12.3, 2.6 Hz, H6’), 3.78 (m, 1H, CH₂-octyl), 3.74-3.69 (m, 3H, H4/H5/H6), 3.40-3.33 (m, 2H, CH₂-octyl/H6), 2.15-2.00 (bs, 12H, OAc), 1.91 (bs, 3H, OAc), 1.81 (bs, 3H, OAc), 1.37-1.30 (bs, 12H, CH₂-octyl), 0.89 (t, 3H, CH₂-octyl). \(^{13}\)C NMR (CDCl₃) δ 171.00, 170.73, 169.73, 169.53, 169.42, 134.36, 131.41, 98.11, 96.44, 74.42, 71.92, 69.95, 67.43, 67.13, 66.77, 66.59, 62.26, 55.36, 31.62, 29.18, 29.04, 25.76, 22.55, 20.88, 20.78, 20.49, 14.00, -0.03. MS (ES, Na⁺): m/z (relative intensity) 859.2 (100). HRMS (M + Na⁺) calcd for C₄₂H₅₅NO₁₈Na, 574.2417; found 574.2415.

Octyl 4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-3-O-acetyl-6-O-t-butyldimethylsilyl-2-deoxy-2-phthalamido-β-D-glucopyranoside (95).
To a stirred solution of donor 75\textsuperscript{x1} (0.15 g, 0.304 mmol) and acceptor 87 (0.10 g, 0.19 mmol) in 20 mL of CH\textsubscript{2}Cl\textsubscript{2} was added 0.25 g 3Å molecular sieves. The reaction was refluxed for 1h and then cooled to -50\(^\circ\)C and freshly distilled TMS-OTf (0.0099 mL, 0.045 mmol) was added. After 20 min, the reaction was quenched with 0.1 mL of NEt\textsubscript{3} and filtered. The filtrate was washed with 20 mL of satd. NaHCO\textsubscript{3} and satd. NaCl solutions. The organic extract was dried with Na\textsubscript{2}SO\textsubscript{4}, filtered and the filtrate concentrated. The crude oil was purified using flash column chromatography (hexanes:EtOAc, 2:1) to afford a disaccharide, with partial deprotection of acetates, as a colorless oil/solid (0.10 g): MS (ES, Na\textsuperscript{+}): m/z (relative intensity) 846.2 (100). The partially deprotected glycoside (0.59 g, 0.682 mmol) was dissolved in 10 mL of pyridine and 10 mL of Ac\textsubscript{2}O. After 20 h, the reaction was diluted to 50 mL of EtOAc and washed with 50 ml of satd. CuSO\textsubscript{4}, H\textsubscript{2}O, satd. NaHCO\textsubscript{3} and satd. NaCl solutions. The organic extract was dried with Na\textsubscript{2}SO\textsubscript{4}, filtered and the filtrate concentrated. The crude oil was purified using flash column chromatography (hexanes:EtOAc, 2:1) to afford 95 (0.21 g, 36%; 22%, 2 steps) as a colorless oil/solid: \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \(\delta\) 7.79 (bs, 2H, Pht), 7.69 (s, 2H, Pht), 5.67 (dd, 1H, J = 10.7, 9.0 Hz, H3’), 5.31 (d, 1H, J = 3.1 Hz, H4’), 5.26 (d, 1H, J = 8.4 Hz, H1), 5.07 (dd, 1H, J = 10.3, 8.0 Hz, H2’), 4.91 (dd, 1H, J = 10.4, 3.5 Hz, H3), 4.69 (d, 1H, J = 7.9 Hz, H1’), 4.13-4.02 (m, 4H, H4/H2/H6/H6’), 3.94-3.89 (m, 2H, H6’/H6’), 3.84 (m, 1H, H2), 3.81 (m, 1H, H5’), 3.71 (m, 1H, CH\textsubscript{3}-octyl), 3.47 (m, 1H, Hz, H5), 3.36 (m, 1H, CH\textsubscript{2}-octyl), 2.13-1.86 (s, 18H, NHAc, OAc), 1.67 (bs, 2H, CH\textsubscript{2}-octyl), 1.24-1.00 (bs, 12H, CH\textsubscript{3}-octyl), 0.87 (s, 12H, tBu, CH\textsubscript{3}-octyl), 0.06 (s, 6H, Me).
\(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 171.08, 170.30, 170.17, 170.08, 170.05, 168.85, 167.93, 167.93, 167.57, 134.11, 133.94, 131.33, 123.38, 100.32, 97.61, 75.13, 75.08, 71.10, 70.96, 70.49, 69.40, 69.13, 68.67, 66.79, 66.35, 61.02, 60.95, 60.31, 54.99, 31.57, 29.23, 29.04, 25.84, 25.79, 22.50, 20.96, 20.66, 20.57, 20.49, 18.24, 14.11, 13.97, -4.97, -5.33. MS (ES, Na\(^+\)): m/z (relative intensity) 930.3 (100). HRMS (M + Na\(^+\)) calcd for C\(_{38}\)H\(_{65}\)NO\(_{17}\)SiNa, 930.3919; found 930.3926.

**Octyl 3, 4, -di-O-acetyl-6-O-t-butyldimethylsilyl-2-deoxy-2-phthalimido-\(\beta\)-D-glucopyranoside (96).**

![Structure of compound 96](image)

Compound 87 (0.03 g, 0.06 mmol) was dissolved in Ac\(_2\)O (1.00 mL) and pyridine (1.00 mL). After 11 h, the reaction was diluted with 10 mL of EtOAc and washed with 10 mL of satd. CuSO\(_4\), H\(_2\)O, satd. NaHCO\(_3\), and satd. NaCl solutions. The organic extract was dried with Na\(_2\)SO\(_4\), filtered and the filtrate concentrated. The crude product was purified using a short silica gel plug (hexanes:EtOAc, 1:1) to afford 96 (0.034 g, 100%) as a colorless oil: \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.83 (m, 2H, Pht), 7.71 (m, 2H, Pht), 5.77 (dd, 1H, J = 10.8, 9.0 Hz, H4), 5.29 (d, 1H, J = 8.4 Hz, H1), 5.05 (m, 1H, H3), 4.24 (dd, 1H, J= 10.7, 8.4 Hz, H2), 3.79 (m, 1H, CH\(_2\)-octyl), 3.72 (m, 2H, H6/H6), 3.67 (m, 1H, H5), 3.40 (m, 1H, CH\(_2\)-octyl), 2.01 (s, 3H, OAc), 1.88 (s, 3H, OAc), 1.23 (bs, 2H, CH\(_2\)-octyl), 1.16-1.01 (bs, 13H, CH\(_3\)-octyl), 0.96-0.79 (s, 12H, tBu, CH\(_3\)-octyl), 0.06 (s, 6H, Me). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 170.29, 169.46, 134.82, 133.51, 131.44, 124.15, 122.79, 98.48, 75.28, 74.13, 71.73, 69.16, 62.67, 55.37, 30.21, 29.22, 28.22, 26.34, 25.78, 25.34,
21.26, 21.03, 20.23, 19.99, 13.52, -4.88, -5.82. MS (ES, Na\(^+\)): m/z (relative intensity) 642.3 (100). HRMS (M + Na\(^+\)) calcd for C\(_{32}\)H\(_{49}\)NO\(_9\)Na, 642.3074; found 642.3074.


To a stirred 0 °C solution of compound 96 in 1.00 mL of CH\(_3\)CN and pyridine (0.30 mL) was added HF-pyridine (0.30 mL). The reaction was allowed to warm to room temperature. After 4.5 h, the reaction was diluted to 5 mL of EtOAc and washed with 5 mL of satd. CuSO\(_4\), H\(_2\)O, satd. NaHCO\(_3\) and satd. NaCl solutions. The organic extract was dried with Na\(_2\)SO\(_4\), filtered and the filtrate concentrated. The crude product was purified using preparative thin layer chromatography (hexanes:EtOAc, 1:2) to afford 97 (0.025 g, 92%) as a colorless oil: \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.84 (m, 2H, Pht), 7.71 (m, 2H, Pht), 5.82 (dd, 1H, \(J = 10.6, 9.2\) Hz, H4), 5.36 (d, 1H, \(J = 8.5\) Hz, H1), 5.09 (m, 1H, H3), 4.27 (dd, 1H, J = 10.7, 8.5 Hz, H2), 3.85-3.76 (m, 2H, H5/OH), 3.70-3.62 (m, 3H, C\(_2\)H\(_8\)-octyl/H6/H6), 3.41 (m, 1H, CH\(_2\)-octyl), 2.11 (s, 3H, OAc), 1.92 (s, 3H, OAc), 1.37 (bs, 2H, CH\(_2\)-octyl), 1.11-0.99 (bs, 10H, CH\(_2\)-octyl), 0.81 (bs, 3H, CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 170.18, 134.30, 131.43, 123.60, 98.20, 74.07, 70.66, 70.13, 69.42, 61.49, 54.84, 31.69, 29.20, 25.81, 22.65, 22.53, 20.75, 20.45, 14.08. MS (ES, Na\(^+\)): m/z (relative intensity) 528.2 (100). HRMS (M + Na\(^+\)) calcd for C\(_{26}\)H\(_{35}\)NO\(_9\)Na, 528.2210; found 528.2224.

Octyl 3, 4, -di-O-acetyl-2, 6-dideoxy-6-phenylseleno-2-phthalimido-\(\beta\)-D-glucopyranoside (98).
To a stirred -20 °C solution of 97 (0.025 g, 0.049 mmol) in 0.01 mL of CH₂Cl₂ at were added N-PSP (0.029 g, 0.098 mmol) and PBu₃ (0.024 mL, 0.098 mmol). The solution was warmed to 0 °C and the temperature maintained. After 24 h, the reaction was diluted with 3 mL of CH₂Cl₂ and washed with satd. NaHCO₃, H₂O, and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using preparative thin layer chromatography (hexanes:EtOAc, 2:1) to afford 98 (0.019 g, 60%) as a white powder:

$^{1}$H NMR (CDCl₃) $\delta$ 7.90-7.83 (m, 5H, Pht/SePh), 7.79-7.76 (m, 3H, SePh), 7.72 (m, 2H, Pht), 5.75 (dd, 1H, J = 10.6, 9.1 Hz, H4), 5.30 (d, 1H, J = 8.5 Hz, H1), 5.05 (m, 1H, H3), 4.30 (dd, 1H, J = 10.7, 8.6 Hz, H2), 3.87 (m, 1H, H5), 3.73 (m, 1H, CH₂-octyl), 3.39 (m, 1H, CH₂-octyl), 3.12-3.08 (dd, 1H, J = 12.9, 8.3 Hz, H6), 3.08-3.04 (m, 1H, H6), 2.00 (s, 3H, OAc), 1.85 (s, 3H, OAc), 1.40 (bs, 2H, CH₂-octyl), 1.24-0.95 (bs, 10H, CH₂-octyl), 0.96 (bs, 3H, CH₃). $^{13}$C NMR (CDCl₃) $\delta$ 170.23, 169.74, 134.35, 132.66, 129.14, 127.11, 123.64, 97.94, 73.79, 73.14, 70.73, 69.99, 54.88, 31.66, 29.32, 29.22, 29.13, 25.80, 22.61, 20.77, 20.52, 14.07. MS (ES, Na$^+$): m/z (relative intensity) 666.1 (100). HRMS (M + Na$^+$) calcd for C₃₂H₃₉NO₈Na, 668.1739; found 668.1740.

Octyl 4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-3-O-acetyl-2-deoxy-2-phthalamido-β-D-glucopyranoside (99).
To a stirred 0 °C solution of 95 (0.22 g, 0.24 mmol) in 8.0 mL of CH₃CN and pyridine (1.0 mL) in a Nalgene bottle was added 1.0 mL HF·pyridine. The reaction was allowed to warm to room temperature. After 2.5 h, the reaction was diluted to 25 mL of CH₂Cl₂ and washed with 25 mL of satd. CuSO₄, H₂O, satd. NaHCO₃, and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrated concentrated. The crude oil was purified using a short silica gel plug (EtOAc) to afford 99 (0.177 g, 92%) as a colorless oil: ¹H NMR (CDCl₃) δ 7.80 (bs, 2H, Pht), 7.76 (s, 2H, Pht), 5.47 (m, 1H, H3’), 5.36 (d, J = 8.3 Hz, H1), 5.32 (d, 1H, H4’), 5.28 (m, 2H, H3/H2’), 5.11 (m, 1H, H3), 4.99 (m, 1H, H4), 4.66 (d, 1H, J = 7.7 Hz, H1’), 4.16 (dd, 1H, J = 10.0 Hz, H2), 4.10-3.98 (m, 3H, H6/H6/CH₂-octyl), 3.94-3.88 (m, 2H, H6’/H6’), 3.78 (m, 2H, H5/H5’), 3.58 (m, 1H, CH₂-octyl), 3.40 (d, 1H, J = 8.0 Hz, -OH), 2.12-1.89 (s, 18H, NHAc, OAc), 1.67 (bs, 2H, CH₂-octyl), 1.24-1.12 (m, 10H, CH₂-octyl), 0.80 (t, 3H, CH₃-octyl). ¹³C NMR (CDCl₃) δ 170.35, 170.21, 170.11, 169.87, 169.21, 167.97, 134.27, 132.65, 123.56, 100.97, 98.11, 75.61, 74.68, 71.36, 70.97, 70.48, 70.26, 69.21, 66.69, 60.76, 60.50, 55.03, 53.40, 31.59, 29.22, 29.06, 25.75, 22.54, 20.69, 20.64, 20.60, 20.58, 20.52, 14.01, 13.60. MS (ES, Na⁺): m/z (relative intensity) 816.3 (100). HRMS (M + Na⁺) calcd for C₃₈H₅₀NO₁₇Na, 816.3055; found 816.3079.

Octyl 4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-3-O-acetyl-2, 6-dideoxy-6-phenylseleno-2-phthalamido-β-D-glucopyranoside (100).
To a stirred -20 °C solution of 99 (0.030 g, 0.037 mmol) in 0.10 mL of CH$_2$Cl$_2$ was added N-PSP (0.022 g, 0.075 mmol) and PBU$_3$ (0.018 mL, 0.075 mmol). The reaction was warmed to 0 °C and the temperature maintained at 0 °C. After 41 h, the reaction was diluted to 5 mL of CH$_2$Cl$_2$ and washed with 5 mL of H$_2$O and satd. NaCl solution. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrated concentrated. The crude oil was purified using preparative thin layer chromatography (hexanes:EtOAc, 2:1) to afford 100 (0.014 g, 40%) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.83 (bs, 2H, Pht), 7.71 (m, 2H, Pht), 7.57 (m, 2H, SePh), 7.27 (m, 3H, SePh), 5.71 (dd, 1H, J = 10.6, 8.0 Hz, H2’), 5.33 (d, J = 8.4 Hz, H1), 5.27 (d, 1H, J = 3.4 Hz, H4’), 5.07 (dd, 1H, J = 10.4, 8.4 Hz, H2), 4.81 (dd, 1H, J = 10.4, 3.5 Hz, H3’), 4.46 (d, 1H, J = 8.0 Hz, H1’), 4.20 (dd, 1H, J = 10.6, 8.5 Hz, H3), 4.08 (m, 2H, H6’/H6’), 3.83 (m, 2H, H4/H5’), 3.75 (m, 1H, H5), 3.71 (m, 1H, CH$_2$-octyl), 3.43 (d, 1H, J = 12.4, 2.4 Hz, H6), 3.37 (m, 1H, CH$_2$-octyl), 3.14 (d, 1H, J = 12.3, 6.7 Hz, H6), 2.14-1.90 (s, 18H, NHAc, OAc), 1.41 (bs, 3H, CH$_2$-octyl), 1.24-1.03 (m, 9H, CH$_2$-octyl), 0.82 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) $\delta$ 170.35, 170.18, 170.03, 169.84, 168.92, 132.93, 129.24, 127.27, 101.01, 97.79, 80.16, 74.13, 71.06, 70.92, 70.53, 69.91, 69.16, 66.61, 60.78, 55.14, 53.41, 31.64, 29.39, 29.22, 25.79, 22.58, 20.63, 20.57, 20.51, 14.04, 13.62. MS (ES, Na$^+$): m/z (relative intensity) 956.2 (100). HRMS (M + Na$^+$) calcd for C$_{44}$H$_{55}$NO$_{16}$SeNa, 956.2584; found 956.2607.

Octyl 2-acetamido-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-3-O-acetyl-6-phenylseleno-2-deoxy-β-D-glucopyranoside (101).
To a stirred solution of 100 (0.050 g, 0.053 mmol) in 1 mL of EtOH in a Schlenk tube was added H$_2$NNH$_2$·H$_2$O (0.23 mL, 4.823 mmol). The reaction was placed under a gentle vacuum, the tube sealed and heated to 100 °C. After 15 h, the reaction was cooled, the tube opened and the reaction mixture concentrated and placed under vacuum for 6 h to afford the free amine as an oil/solid. The product was taken on to the next step without any purification. The crude product was dissolved in 1.0 mL of pyridine and 1.0 mL of Ac$_2$O. After 17.5 h, the reaction was diluted with 10 mL of EtOAc and washed with 10 mL of satd. CuSO$_4$, H$_2$O, satd. NaHCO$_3$, and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The resulting light yellow oil was purified using flash column chromatography (hexanes:EtOAc, 1:2) to afford 101 (0.040 g, 88%, 2 steps) as a colorless oil/solid: $^1$H NMR (CDCl$_3$) δ 7.58 (m, 3H, SePh), 7.35 (m, 2H, SePh), 5.60 (d, 1H, J = 9.5 Hz, NH), 5.29 (d, 1H, H4’), 5.04 (dd, 1H, J = 9.0 Hz, H2’), 4.82 (dd, 1H, J = 10.4, 3.3, Hz, H3’), 4.42 (d, 1H, J = 7.5 Hz, H1’), 4.37 (d, 1H, J = 8.0 Hz, H1), 4.08 (m, 2H, H6’/H6’), 4.04 (m, 1H, H5’), 3.81 (m, 1H, H3), 3.78-3.72 (m, 3H, H4/H2/H5), 3.64 (m, 1H, CH$_2$-octyl), 3.38 (m, 2H, H6/H6), 3.14 (m, 1H, CH$_2$-octyl), 2.17 (s, 3H, OAc), 2.13-1.91 (bs, 15H, OAc/NHAc), 1.52 (bs, 3H, CH$_2$-octyl), 1.25 (bs, 9H, CH$_3$-octyl), 0.87 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) δ 170.67, 170.03, 169.21, 133.48, 132.19, 130.24, 129.19, 128.60, 127.95, 126.67, 100.44, 100.16, 74.77, 73.66, 72.88, 71.19, 70.19, 69.69, 68.45, 67.25, 66.05, 60.87, 53.73, 52.58, 29.39, 25.90, 23.75, 22.73, 21.36, 21.14, 21.02, 20.32, 20.10, 19.99. MS (ES, Na$^+$): m/z (relative
Octyl 2-acetamido-3-O-(2,3,4,6-tetra-O-acetyl)-β-D-galactopyranosyl-4, 6-O-diacytetyl-2-deoxy-β-D-glucopyranoside (102).

A solution of 82 (0.022 g, 0.026 mmol) in 1.0 mL of H₂O and AcOH (1:1) was heated to reflux. After 2 h, the reaction was cooled and concentrated. The crude product was diluted with 30 mL of EtOAc and washed with 20 mL of satd. NaHCO₃ and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified with a short silica gel plug (EtOAc) to afford the diol (0.020 g) as a colorless oil. To a stirred solution of the diol (0.020 g, 0.026 mmol) in 0.5 mL of EtOH in a Schlenk tube was added H₂NNH₂·H₂O (0.11 mL, 2.35 mmol). The reaction was placed under a gentle vacuum, the tube sealed and heated to 100 °C. After 41 h, the reaction was cooled, the tube opened and the reaction mixture concentrated and placed under vacuum for 6.5 h to afford the free amino alcohol (0.01 g) as a colorless oil. The product was immediately taken on to the next step without any purification. The crude product (0.0.1 g, 0.022 mmol) was dissolved in 1.0 mL of pyridine and 1.0 mL of Ac₂O. After 18.5 h, the reaction was diluted with 5 mL EtOAc and washed with 5 mL of satd. CuSO₄, H₂O, satd. NaHCO₃, and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The resulting light yellow oil was purified using preparative thin layer chromatography to
afford \textbf{102} (0.008 g, 41\%, 3 steps) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 5.65 (d, 1H, J = 7.1 Hz, NH), 5.33 (d, 1H, J = 3.3 Hz, H4$'$), 5.06 (dd, 1H, J = 10.3, 7.9 Hz, H2$'$), 4.98-4.91 (m, 3H, H1/H3/H3$'$), 4.56-4.52 (m, 2H, H4/H1$'$), 4.13-4.06 (m, 4H, H2/H5'/H6'/H6$'$), 3.87-3.81 (m, 2H, H6/H6), 3.66 (m, 1H, H5), 3.46 (m, 1H, CH$_2$-octyl), 3.13 (m, 1H, CH$_2$-octyl), 2.14 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.96 (s, 3H, NHAc), 1.55 (bs, 3H, CH$_2$-octyl), 1.25 (bs, 9H, CH$_2$-octyl), 0.85 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) $\delta$ 170.73, 170.37, 170.27, 169.50, 168.90, 100.49, 98.96, 71.75, 71.03, 70.62, 70.05, 69.47, 69.11, 66.90, 62.55, 61.04, 60.35, 58.23, 53.37, 31.77, 29.44, 29.28, 25.87, 23.62, 22.60, 20.80, 20.61, 14.03. MS (ES, Na$^+$): m/z (relative intensity) 770.1 (100). HRMS (M + Na$^+$) calcd for C$_{34}$H$_{53}$NO$_{17}$Na, 770.3229; found 770.3211.

Octyl 2-acetamido-3-$\beta$-D-galactopyranosyl-2-deoxy-$\beta$-D-glucopyranoside (13b).

![Structure](image)

To a stirred solution of \textbf{102} (0.005 g, 0.0066 mmol) in 0.5 mL of MeOH:THF (1:1) was added 0.5M NaOMe solution (0.0028 mL, 0.0535 mmol). After 4 d, the reaction was quenched with 0.050 g of Dowex 50W H$^+$ form resin (2.1 meq/mL) and stirred gently for 20 min. The mixture was filtered and the filtrate concentrated. The resulting white powder was purified using a short silica gel plug with CHCl$_3$:MeOH (4:1) to afford \textbf{13b} (0.003 g, 100\%) as a white powder: $^1$H NMR (D$_2$O) $\delta$ 4.40 (d, 1H, J = 7.7 Hz, H1), 4.29 (d, 1H, J = 7.7 Hz, H1$'$), 3.79-3.74 (m, 3H, H2'/H3/H3$'$), 3.67-3.62 (m,
6H, H4'/H4/H2/H5/H6'/H6’), 3.57-3.43 (m, 2H, H6/H6), 3.41-3.34 (m, 3H, H5/-CH2-octyl), 1.90 (s, 3H, NHAc), 1.40 (bs, 3H, CH2-octyl), 1.14 (bs, 9H, CH3-octyl), 0.72 (t, 3H, CH3-octyl). \(^{13}\)C NMR (D\(_2\)O) δ 174.48, 103.51, 100.87, 82.49, 75.35, 75.27, 72.49, 70.68, 70.59, 68.75, 68.53, 61.01, 60.77, 54.62, 31.08, 28.55, 28.47, 28.32, 25.07, 22.27, 22.00, 13.37. MS (ES, Na\(^+\)): m/z (relative intensity) 518.3 (100). HRMS (M + Na\(^+\)) calcd for C\(_{22}\)H\(_{41}\)NO\(_{11}\)Na, 518.2577; found 518.2576.

**Octyl 2-acetamido-4-O-(2,3,4,6-tetra-O-acetyl-\(\beta\)-d-galactopyranosyl)-3,6-O-acetyl-2-deoxy-\(\beta\)-d-glucopyranoside (103).**

![Structural formula of the compound](image)

To a stirred solution of **95** (0.10 g, 0.12 mmol) in 4.0 mL of EtOH in a Schlenk tube was added H\(_2\)NNH\(_2\)·H\(_2\)O (0.53 mL, 10.4 mmol). The reaction was placed under a gentle vacuum, the tube sealed and heated to 100 °C. After 15 h, the reaction was cooled, the tube opened and the reaction mixture concentrated and placed under vacuum for 6 h to afford the free amino alcohol (0.026 g) as a colorless oil. The product was taken on to the next step without any purification. The crude product was dissolved in 3 mL of pyridine and 3 mL of Ac\(_2\)O. After 30 h, the reaction was diluted with 20 mL of EtOAc and washed with 20 mL of satd. CuSO\(_4\), H\(_2\)O, satd. NaHCO\(_3\), and satd. NaCl solutions. The organic extract was dried with Na\(_2\)SO\(_4\), filtered and the filtrate concentrated. The resulting yellow oil was purified using flash column chromatography (hexanes:EtOAc, 1:1) to afford **103** (0.06 g, 70%, 2 steps) as a colorless oil/solid: \(^1\)H NMR (CDCl\(_3\)) δ 5.63 (d, 1H, N-H), 5.35 (d, 1H, H4’), 5.23 (dd, 1H, J = 10.2 Hz, H2’), 5.19 (m, 1H, H3’), 5.04
(dd, 1H, J = 10.8, 7.8 Hz, H3), 4.82 (dd, 1H, J = 9.6 Hz, H4), 4.57 (d, 1H, J = 8.3 Hz, H1), 4.53 (dd, 1H, H2), 4.42 (d, 1H, J = 7.4 Hz, H1’), 4.10 (dd, 1H, H6’), 4.00 (m, 1H, H6’), 3.83-3.73 (m, 3H, H6/H6/CH2-octyl), 3.64 (m, 1H, H5), 3.57 (m, 1H, H6, H5’), 3.40 (m, 1H, CH2-octyl), 2.07-1.88 (s, 21H, NHAc, OAc), 1.53-1.51 (bs, 3H, CH2-octyl), 1.30-1.10 (bs, 9H, CH2-octyl), 0.85 (t, 3H, CH3-octyl). MS (ES, Na+): m/z (relative intensity) 770.3 (100). HRMS (M + Na+) calcd for C32H53NO17Na, 770.3211; found 770.3220.

**Octyl 2-acetamido-4-O-3-D-galactopyranosyl-2-deoxy-3-D-glucopyranoside (14b).**

To a stirred solution of 103 (0.055 g, 0.073 mmol) in 3.0 mL of MeOH was added NaOMe powder (0.008 g, 0.148 mmol). After 3 d, the reaction was quenched with 0.10 g of Dowex 50W H+ form resin (2.1 meq/mL) and stirred gently for 20 min. The mixture was filtered and the filtrate concentrated. The resulting white powder was purified using a short silica gel plug (CHCl3:MeOH, 4:1) to afford 14b (0.015 g, 42%) as a white powder: 1H NMR (D2O) δ 4.70-4.60 (m, 2H, H1/H1’), 3.95-3.92 (m, 3H, H2’/H3/H3’), 3.79 (m, 6H, H4’/H4/H2/H5’/H6’/H6’), 3.54-3.45 (m, 5H, H6/H6/H5/-CH2-octyl), 2.07 (s, 3H, NHAc), 1.63 (bs, 3H, CH2-octyl), 1.32 (bs, 9H, CH2-octyl), 0.89 (t, 3H, CH3-octyl). 13C NMR (D2O) δ 133.86, 126.09, 101.71, 75.14, 72.53, 71.75, 70.86, 70.70, 68.86, 66.01, 62.66, 60.98, 56.79, 47.68, 31.10, 28.37, 25.25, 25.07, 22.00, 21.87, 19.95, 13.38. MS (ES, Na+): m/z (relative intensity) 518.2 (100). HRMS (M + Na+) calcd for C22H41NO17Na, 518.2577; found 518.2582.
Octyl 2-acetamido-3-Ο-acetyl-4-Ο-benzyl-2, 6-dideoxy-6-phenylseleno-3-D-galactopyranoside (105).

To a stirred 0 °C solution of 42b (0.145 g, 0.212 mmol) in 3.0 mL of CH₂Cl₂ were added AcBr (0.076 mL, 1.061 mmol) and BF₃·OEt₂ (0.013 mL, 0.106 mmol). After 3.5 h, the reaction was dissolved in 30 mL of CH₂Cl₂ and washed with 30 mL of satd. NaHCO₃, H₂O, satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The resulting oil was purified using flash column chromatography (hexanes:EtOAc, 1:1) to afford 105 (0.09 g, 70%) as a colorless oil: ¹H NMR (CDCl₃) δ 7.48 (m, 2H, PhSe), 7.29 (m, 3H, PhSe), 7.24 (m, 5H, Bn), 5.39 (d, 1H, J = 8.4 Hz, NH), 5.24 (d, 1H, J = 9.2, 2.9 Hz, H4), 4.79 (d, 1H, J = 11.5 Hz, -O-CH₂-Ph.), 4.60 (d, 1H, J = 8.3 Hz, H1), 4.49 (d, 1H, J = 11.5 Hz, -O-CH₂-Ph), 4.06-4.03 (m, 2H, H3/H2), 3.82 (m, 1H, CH₃-octyl), 3.58 (m, 1H, H5), 3.42 (m, 1H, CH₃-octyl), 3.18 (dd, 1H, J = 12.6, 6.5 Hz, H6), 2.94 (dd, 1H, J = 12.6, 7.4 Hz, H6), 2.00 (s, 3H, OAc), 1.93 (s, 3H, NHAc), 1.53 (bs, 2H, CH₂-octyl), 1.25 (bs, 10H, CH₂-octyl), 0.87 (t, 3H, CH₃-octyl). ¹³C NMR (CDCl₃) δ 170.75, 170.06, 137.84, 132.66, 129.70, 129.19, 128.36, 128.23, 127.82, 127.15, 100.59, 75.06, 74.50, 74.28, 73.24, 69.46, 53.37, 52.10, 31.78, 29.41, 29.30, 29.24, 27.68, 25.87, 23.46, 22.61, 20.87, 14.05. MS (ES, Na⁺): m/z (relative intensity) 628.2 (100). HRMS (M + Na⁺) calcd for C₃₇H₄₉NO₆SeNa, 628.2153; found 628.2159.
Octyl 2-acetamido-3-O-[(benzyloxy)methyl]-5,6-dehydro-2,6-dideoxy-\textalpha-\textbeta-D-glucopyranoside (106a).

To a stirred solution of 42a (0.100 g, 0.157 mmol) in 21 mL of MeOH:H2O (6:1) were added NaHCO3 (0.014 g, 0.173 mmol) and NaIO4 (0.050 g, 0.235 mmol). A white precipitate formed during the course of the reaction. After 2.5 h, the reaction was filtered and the filtrate concentrated to leave the H2O. The H2O had an additional 30 mL of H2O added and the aqueous extract was washed 3 times with 30 mL of CH2Cl2. The combined organic extracts were washed with 90 mL of satd. NaCl solution and dried with Na2SO4, filtered and the filtrate concentrated to afford the selenoxide as a white oil/solid and taken on without any purification (0.100 g): $^1$H NMR (CDCl3) $\delta$ 7.68 (m, 3H, SePh), 7.54 (m, 2H, SePh), 7.33 (m, 5H, ArH of BOM), 5.98 (d, 1H, N-H), 5.28 (d, 1H, J = 3.1 Hz, H4), 4.91 (d, 1H, J = 8.5 Hz, H1), 4.83-4.77 (m, 2H, BOM), 3.64 (m, 1H, H3), 4.55 (m, 1H, H2), 4.32 (m, 1H, H5), 3.94 (m, 1H, H6), 3.80 (m, 1H, H6), 3.57 (m, 2H, CH2-octyl), 2.15 (s, 3H, NHAc), 1.92 (s, 3H, OAc), 1.27 (bs, 12H, CH2-octyl), 0.86 (bs, 3H, CH3-octyl). The crude product (0.100 g, 0.153 mmol) was then dissolved in 5 mL of DHP and heated to reflux at 100 °C. After 1.5 h, the reaction was cooled and diluted with 15 mL CH2Cl2 and washed with 15 mL of H2O, satd. NaHCO3, and satd. NaCl solutions. The organic extract was dried with Na2SO4, filtered and the filtrate concentrated. The crude product was purified using flash column chromatography (hexanes:EtOAc, 1:2) to afford 106a (0.042 g, 60%, 2 steps) as a colorless oil: $^1$H NMR (CDCl3) $\delta$ 7.59 (m, 3H, ArH of BOM), 7.36 (m, 2H, ArH of BOM), 4.88 (d, 1H, J=7.4
Hz, N-H), 4.80 (m, 1H, H1), 4.00 (m, 2H, H6), 3.63-3.54 (m, 3H, H4/H3/H5), 3.37 (m, 2H, CH₂-octyl), 3.14 (m, 1H, H2), 2.05 (s, 3H, NHAc), 1.76 (s, 3H, OAc), 1.29 (bs, 12H, CH₂-octyl), 0.92 (bs, 3H, CH₃-octyl). ¹³C NMR (CDCl₃) δ 135.50, 134.00, 129.45, 129.17, 120.01, 127.87, 127.62, 97.83, 93.74, 78.09, 63.25, 45.58, 28.83, 28.43, 25.57, 24.15.

Octyl 4-O-benzyl-3-O-[(benzyloxy)methyl]-5, 6-dehydro-2, 6-dideoxy-β-D-glucopyranoside (106b).

To a stirred solution of 42b (0.14 g, 0.20 mmol) in 28 mL of MeOH:H₂O (6:1) were added NaHCO₃ (0.019 g, 0.225 mmol) and NaIO₄ (0.065 g, 0.307 mmol). A white precipitate formed during the course of the reaction. After 1 h, the reaction was filtered and the filtrate concentrated to leave the H₂O. An additional 30 mL of H₂O was added to the filtrate and the aqueous extract was washed 3 times with 30 mL of CH₂Cl₂. The combined organic extracts were washed with 75 mL of NaCl saturated solution and dried with Na₂SO₄, filtered and the filtrate concentrated to afford a 4:1 diastereomeric mixture of selenoxides as a white oil/solid (0.135 g) and taken on without any purification: ¹H NMR (CDCl₃) δ 7.62 (m, 3H, SePh), 7.59 (m, 2H, SePh), 7.33 (m, 5H, ArH of BOM), 7.13 (m, 5H, Bn), 6.06 (d, 1H, J = 7.9 Hz, NH), 5.86 (d, 1H, J = 7.5 Hz, NH), 5.35 (d, 1H, J = 2.9 Hz, H4), 5.22 (d, 1H, J = 2.2 Hz, H4), 4.98-4.72, (m, 5H, H1/-O-CH₂-OBn/-O-CH₂-Ph), 4.63 (m, 2H, -O-CH₂-Ph), 4.35 (m, 1H, H3), 3.92 (m, 1H, H2), 3.69-3.43 (m, 5H, H5, H6, H6, CH₂-octyl), 2.14 (s, 3H, NHAc), 1.56 (bs, 2H, CH₂-octyl), 1.27 (bs, 9H,
CH$_2$-octyl), 0.84 (bs, 3H, CH$_3$-octyl). The crude selenoxides (0.135 g, 0.193 mmol) were dissolved in 10 mL of DHP and heated to reflux at 100 °C. After 2 h, the reaction was cooled and diluted with 25 mL of CH$_2$Cl$_2$ and washed with 25 mL of H$_2$O, satd. NaHCO$_3$, and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude product was purified using flash column chromatography (hexanes:EtOAc, 1:2) to afford 106b (0.060 g, 56%, 2 steps) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.54 (m, 1H, ArH of BOM), 7.32-7.20 (m, 9H, ArH of BOM, Bn), 5.86 (d, 1H, J=7.2 Hz, NH), 5.25 (d, 1H, J = 7.6 Hz, H1), 4.86-4.65 (m, 5H, -O-CH$_2$-OBn/-O-CH$_2$-Ph), 4.51 (m, 2H, H6), 4.59 (dd, 3H, J = 10.3, 3.1 Hz, H3), 4.34 (m, 1H, -O-CH$_2$-Ph), 4.11 (m, 1H, H4), 3.92 (m, 1H, CH$_2$-octyl), 3.79 (m, 1H, H2), 3.92 (m, 1H, CH$_2$-octyl), 1.88 (s, 3H, NHAc), 1.58 (bs, 2H, CH$_2$-octyl), 1.25 (bs, 10H, CH$_3$-octyl), 0.87 (bs, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) $\delta$ 170.52, 169.32, 152.05, 137.80, 137.61, 133.02, 131.96, 128.98, 128.38, 128.34, 128.27, 127.94, 127.83, 127.76, 127.71, 127.64, 127.50, 127.14, 100.70, 97.73, 93.79, 74.42, 73.76, 73.32, 71.02, 70.01, 69.62, 69.48, 69.40, 50.06, 43.86, 31.79, 29.46, 29.30, 29.25, 25.88, 23.50, 22.62, 14.06. MS (ES, Na$^+$): m/z (relative intensity) 548.3 (100). HRMS (M + Na$^+$) calcd for C$_{31}$H$_{43}$NO$_6$Na, 548.2988; found 548.2998.

**Octyl 3-O-acetyl-4-O-benzyl-5, 6-dehydro-2, 6-dideoxy-3-D-glucopyranoside (106c).**

To a stirred solution of 105 (0.090 g, 0.148 mmol) in 21 mL of MeOH:H$_2$O (6:1) were added NaHCO$_3$ (0.013 g, 0.163 mmol) and NaIO$_4$ (0.047 g, 0.223 mmol). A white
precipitate formed during the course of the reaction. After 1 h, the reaction was filtered and the filtrate concentrated to leave the H$_2$O. An additional 20 mL of H$_2$O was added to the filtrate and the aqueous extract was washed 3 times with 20 mL of CH$_2$Cl$_2$. The combined organic layers were washed with 50 mL of satd. NaCl solution and dried with Na$_2$SO$_4$, filtered and the filtrate concentrated to afford a 3:1 diastereomeric mixture of selenoxides as a colorless oil/solid (0.070 g) and taken on without any purification: $^1$H NMR (CDCl$_3$) δ 7.61 (m, 3H, SePh), 7.52 (m, 2H, SePh), 7.35 (m, 5H, Bn), 6.79 (d, 1H, J = 9.1 Hz, NH), 6.07 (d, 1H, J = 8.6 Hz, NH), 5.16 (d, 1H, J = 7.9, 2.8 Hz, H4), 4.74, (d, 1H, J = 11.7 Hz, -O-CH$_2$-Ph), 4.65 (d, 1H, J = 8.3 Hz, H1), 4.38 (m, 1H, -O-CH$_2$-Ph), 4.12 (m, 1H, H3), 3.88 (dd, 1H, J = 9.6, 6.4 Hz, H2), 3.78-3.71 (m, 2H, H5/C$_2$H$_5$-octyl), 3.24 (m, 1H, H6), 2.49 (d, 1H, J = 9.8 Hz, H6), 2.03 (s, 3H, OAc), 1.93 (s, 3H, NHAc), 1.58 (bs, 2H, CH$_2$-octyl), 1.27 (bs, 10H, CH$_2$-octyl), 0.84 (bs, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) δ 170.81, 170.22, 140.67, 137.40, 131.33, 129.67, 128.55, 128.30, 128.26, 127.90, 126.02, 125.77, 102.05, 100.84, 75.19, 75.08, 73.75, 70.05, 68.77, 55.09, 50.35, 31.80, 29.51, 29.34, 29.26, 25.87, 23.33, 22.61, 20.68, 14.04. The crude selenoxides (0.070 g, 0.112 mmol) were dissolved in 8 mL of DHP and heated to reflux at 100 °C. After 2.5 h, the reaction was cooled and diluted with 10 mL of CH$_2$Cl$_2$ and washed with 10 mL of H$_2$O, satd. NaHCO$_3$, and satd. NaCl solutions. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude product was purified using flash column chromatography (hexanes:EtOAc, 1:2, 1% NEt$_3$) to afford 106c (0.045 g, 70%, 2 steps) as a colorless oil: $^1$H NMR (CDCl$_3$) δ 7.34-7.25 (m, 5H, Bn), 5.57 (d, 1H, J=8.5 Hz, NH), 5.19 (dd, 1H, J = 10.1, 3.3 Hz, H4), 4.74 (s, 1H, J = 7.4 Hz, -O-CH$_2$-Ph), 4.69 (d, 1H, J = 8.7 Hz, H1), 4.39 (m, 1H, -O-CH$_2$-Ph), 4.28 (m, 1H, H3), 4.08 (m, 1H,
H6), 3.91 (m, 1H, CH2-octyl), 3.49 (m, 1H, CH3-octyl), 3.08 (m, 1H, H2), 2.07 (s, 3H, OAc), 1.94 (s, 3H, NHAc), 1.59 (bs, 2H, CH2-octyl), 1.26 (bs, 10H, CH2-octyl), 0.87 (bs, 3H, CH3-octyl). 13C NMR (CDCl3) δ 170.71, 169.97, 151.55, 137.71, 128.26, 127.68, 127.61, 101.64, 100.61, 73.39, 70.16, 69.68, 69.54, 53.37, 51.27, 45.81, 31.78, 29.43, 29.29, 29.22, 25.86, 23.38, 22.60, 20.98, 20.87, 14.03. MS (ES, Na+): m/z (relative intensity) 470.2 (100). HRMS (M + Na+): calcd for C31H43NO6Na, 470.2519; found 470.2516.

Octyl 2-acetamido-4-O-acetyl-3-O-[(benzyloxy)methyl]-2, deoxy-5, 6-epoxy-3-D-glucopyranoside (107a).

To a stirred 0 °C solution of 106a (0.030 g, 0.062 mmol) in 1.5mL of CH2Cl2 was added DMDO (approximately 15 mL). The reaction was placed in the cold box overnight at 4 °C. After 21 h, the solution was dried with Na2SO4, filtered and the filtrate concentrated to afford 107a (0.03 g, 96%) as a colorless oil: 1H NMR (CDCl3) δ 7.62-7.57 (m, 5H, ArH of BOM), 5.74 (bs, 1H, N-H), 5.67 (d, 1H, J = 2.4 Hz, H4), 5.14 (d, 1H, J = 8.0 Hz, H1), 4.63 (s, 2H, -O-CH2-O-Bn), 4.24 (s, 2H, CH2-Ph), 3.98-3.88 (m, 4H, H3/H5/CH2-octyl), 3.68 (dd, 1H, J = 7.9, 4.3 Hz, H2), 3.58-3.52 (m, 2H, H6/H6'), 2.07 (s, 3H, OAc), 1.97 (s, 3H, NHAc), 1.92-1.88 (bs, 3H, CH3-octyl), 1.76-1.66 (bs, 9H, CH3-octyl), 1.23 (t, 3H, CH3-octyl). 13C NMR (CDCl3) δ 140.16, 134.18, 129.97, 129.90, 128.58, 128.29, 127.70, 126.20, 93.38, 88.14, 73.62, 73.46, 68.63, 68.26, 65.37, 59.10, 25.99, 25.49, 25.20, 25.14, 22.90, 20.41, 19.14, -0.05.
Octyl 4-\(O\)-benzyl-3-\(O\)-\{(benzyloxy)methyl\}-2, deoxy-5, 6-epoxy-\(\beta\)-D-glucopyranoside (107b).

To a stirred 0 °C solution of 106b (0.035 g, 0.066 mmol) in 1.0 mL of \(\text{CH}_2\text{Cl}_2\) was added DMDO (approximately 10 mL). The reaction was placed in the cold box overnight at 4 °C. After 21 h, the solution was dried with \(\text{Na}_2\text{SO}_4\), filtered and the filtrate concentrated to afford 107b (0.035 g, 97%) as a colorless oil: \(^1\text{H} \text{NMR} \ (\text{CDCl}_3) \delta \ 7.32-7.23 \ (m, 10H, \text{ArH of BOM/Bn}), \ 4.90-4.32 \ (m, 14H, \text{NH}/H_4/H_1/O-\text{CH}_2-\text{O-Bn/CH}_2-\text{Ph/H}_3/\text{CH}_2-\text{octyl/H}_2/\text{H}_6/\text{H}_6), \ 1.75 \ (s, 3H, \text{NHAc}), \ 1.60 \ (bs, 3H, \text{CH}_2-\text{octyl}), \ 1.24 \ (bs, 9H, \text{CH}_2-\text{octyl}), \ 0.87 \ (t, 3H, \text{CH}_3-\text{octyl}). \ \ ^{13}\text{C} \text{NMR} \ (\text{CDCl}_3) \delta \ 177.99, \ 133.48, \ 130.13, \ 129.79, \ 129.02, \ 128.50, \ 127.87, \ 127.39, \ 126.53, \ 96.27, \ 94.03, \ 84.24, \ 75.09, \ 69.66, \ 68.62, \ 63.03, \ 58.14, \ 33.88, \ 32.73, \ 31.82, \ 29.28, \ 25.73, \ 25.30, \ 24.73, \ 22.86, \ 14.13.

Octyl 3-\(O\)-acetyl-4-\(O\)-benzyl-2, deoxy-5, 6-epoxy-\(\beta\)-D-glucopyranoside (107c).

To a stirred 0 °C solution of 106c (0.045 g, 0.100 mmol) in 2.0 mL of \(\text{CH}_2\text{Cl}_2\) was added DMDO (approximately 10 mL). The reaction was placed in the cold box overnight at 4 °C. After 17 h, the solution was dried with \(\text{Na}_2\text{SO}_4\), filtered and the filtrate concentrated to afford 107c (0.045 g, 97%) as a colorless oil: \(^1\text{H} \text{NMR} \ (\text{CDCl}_3) \delta \ 7.49-7.32 \ (m, 5H, \text{Bn}), \ 5.72-5.80 \ (m, 7H, \text{NH}/H_4/H_1/O-\text{CH}_2\text{Ph/CH}_2\text{-Ph}), \ 4.86-4.76 \ (m, 2H,
H3/H5), 4.07-3.73 (m, 5H, CH$_2$-octyl/H2/H6/H6), 2.03 (s, 3H, OAc), 1.75 (s, 3H, NHAc), 1.59 (bs, 3H, CH$_2$-octyl), 1.24 (bs, 9H, CH$_2$-octyl), 0.86 (t, 3H, CH$_3$-octyl).

4-O-Acetyl, 3-O-[(benzyloxy)methyl]-5, 6-dehydro, 2, 6-dideoxy-2-
trifluoracetamido-∀-D-galactopyranosyl-1-dibenzyl phosphate (108).

To a stirred solution of 62a (0.10 g, 0.120 mmol) in 25 mL of MeOH:H$_2$O (6:1) were added NaHCO$_3$ (0.011 g, 0.132 mmol) and NaIO$_4$ (0.038 g, 0.180 mmol). A white precipitate formed during the course of the reaction. After 3.5 h, the reaction was filtered and the filtrate concentrated to leave the H$_2$O. The filtrate had 20 mL of H$_2$O added and the aqueous extract was washed 3 times with 20 mL of CH$_2$Cl$_2$. The combined organic extracts were washed with 60 mL of satd. NaCl solution and dried with Na$_2$SO$_4$, filtered and the filtrate concentrated to afford a 3:2 diastereomeric mixture of selenoxides a white oil/solid (0.085 g) and taken on without any purification: $^1$H NMR (CDCl$_3$) $\delta$ 7.68 (m, 1H, SePh), 7.51 (m, 1H, SePh), 7.47 (m, 3H, SePh), 7.30 (m, 5H, ArH of BOM), 7.27 (m, 10H, Bn/Ph), 5.84 (m, 1H, H1), 5.40 (d, 1H, J = 2.2 Hz, H4), 5.15 (m, 4H, O-CH$_2$-Ph/Bn), 5.07 (dd, 1H, J = 9.3, 1.9 Hz, H3), 4.73-4.62 (d, 2H, O-CH$_2$-O-Bn/ O-CH$_2$-Ph/ArH of BOM), 4.12 (dd, 1H, J = 11.0, 2.9 Hz, H2), 3.93 (m, 1H, H5), 2.97 (dd, 1H, J = 12.3, 7.8 Hz, H6), 2.79 (dd, 1H, J = 12.3, 4.2 Hz, H6), 2.09 (s, 3H, OAc). $^{13}$C NMR (CDCl$_3$) $\delta$ 170.72, 170.54, 141.13, 137.34, 137.15, 135.89, 135.80, 135.48, 131.90, 130.22, 129.48, 129.20, 129.14, 129.06, 128.99, 128.92, 128.83, 128.68, 128.62, 128.54, 128.48, 128.36, 128.17, 128.14, 126.45, 126.11, 95.89, 95.80, 93.50, 93.39, 71.05, 70.82,
70.63, 70.56, 70.35, 70.25, 69.49, 68.78, 67.53, 66.90, 55.04, 53.84, 49.54, 21.23, 21.16.

\[ \delta = -75.94 \]  

\[ \delta = -1.20 \]

The crude selenoxides (0.085 g, 0.10 mmol) were dissolved in 3.0 mL of DHP and heated to reflux at 100 °C. After 4.5 h, the reaction was cooled and diluted with 25 mL of \( \text{CH}_2\text{Cl}_2 \) and washed with 25 mL of \( \text{H}_2\text{O} \), satd. \( \text{NaHCO}_3 \), and satd. \( \text{NaCl} \) solutions. The organic extract was dried with \( \text{Na}_2\text{SO}_4 \), filtered and the filtrate concentrated. The crude product was purified using preparative thin layer chromatography (hexanes:EtOAc, 1:2) to afford 108 (0.053 g, 67 %, 2 steps) as a colorless oil: \[ \delta = 7.34 \] (m, 5H, ArH of BOM), 7.28 (m, 10H, Bn/Ph), 5.88 (dd, 1H, \( J = 6.4, 3.1 \) Hz, H1), 5.73 (d, 1H, \( J = 3.4 \) Hz, H4), 5.02 (m, 4H, O-CH\(_2\)-Ph/Bn), 4.76 (s, 2H, O-CH\(_2\)-O-Bn), 4.74 (d, 1H, \( J = 7.0 \) Hz, O-CH\(_2\)-O-Bn), 4.70 (d, 1H, \( J = 7.0 \) Hz, O-CH\(_2\)-Ph/BOM), 4.67 (m, 1H, H2), 4.55 (m, 2H, H6), 4.07 (dd, 1H, \( J = 11.0, 3.4 \) Hz, H3), 2.12 (s, 3H, OAc). \[ \delta = 170.16, 157.89, 149.76, 137.09, 135.36, 129.22, 129.17, 129.02, 128.91, 128.83, 128.42, 128.39, 128.29, 128.16, 128.09, 117.07, 114.78, 105.17, 95.58, 93.95, 71.13, 70.36, 70.30, 69.07, 49.52, 21.36. \] \[ \delta = 0.48 \]  

\[ \delta = -1.67 \]

MS (ES, Na\(^+\)): m/z (relative intensity) 702.1 (100). HRMS (M + Na\(^+\)) calcd for C\(_{32}\)H\(_{33}\)F\(_3\)NO\(_{10}\)PNa, 702.1692; found 702.1703.

4-\(O\)-Acetyl, 3-\(O\)-[(benzyloxy)methyl]-2-deoxy, 5, 6-epoxy-2-trifluoracetamido-\(\forall\)-D-galactopyranosyl-1-dibenzyl phosphate (109).

\[
\begin{align*}
\text{AcO} & \quad \text{BOM} & \quad \text{TFA} \\
\text{NH} & \quad \text{O} & \quad \text{O} \\
\text{P} & \quad \text{OBn} & \quad \text{OBn}
\end{align*}
\]

To a stirred 0 °C solution of 108 (0.05 g, 0.07 mmol) in 0.5 mL of \( \text{CH}_2\text{Cl}_2 \) was added DMDO (approximately 11 mL). After 7.5 h, an additional 10 mL of DMDO was

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added to the reaction mixture. After 23 h, the solution was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated to afford a 1:0.7 ratio of epoxides 109 (0.049 g, 85%) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.17 (m, 5H, ArH of BOM), 7.06 (m, 10H, Bn/Ph), 6.15 (dd, 1H, H1), 5.98 (dd, 1H, J = 7.5, 3.3 Hz, H1), 5.41 (d, 1H, J = 3.2 Hz, H4), 5.38 (d, 1H, J = 3.3 Hz, H4), 5.04-4.92 (m, 8H, O-C$_2$H$_5$-Ph/Bn/ O-C$_2$-O-Bn/ O-C$_2$-Ph/ ArH of BOM), 4.67 (dd, 1H, J = 11.9, 6.8 Hz, H2), 4.40 (m, 1H, H3), 2.45 (m, 2H, H6), 2.41 (dd, 2H, J = 8.7, 4.5 Hz, H6), 1.74 (s, 3H, OAc). $^{13}$C NMR (CDCl$_3$) $\delta$ 168.98, 158.85, 158.56, 137.99, 129.14, 129.01, 128.99, 128.93, 128.90, 128.43, 128.61, 128.56, 128.50, 128.40, 128.31, 128.26, 128.21, 128.12, 128.02, 115.85, 97.01, 95.18, 81.73, 81.44, 73.36, 72.06, 70.68, 70.52, 70.28, 70.21, 68.19, 50.24, 49.50, 25.33, 20.47, 20.40, 20.16.

Octyl 2-acetamido-3-O-(2,3,4,6-tetra-O-acetyl-\(\beta\)-D-galactopyranosyl)- 4-O-acetyl-5, 6-dehydro-2, 6-dideoxy-\(\beta\)-D-glucopyranoside (111).

To a stirred solution of 85 (0.010 g, 0.012 mmol) in 1.75 mL of MeOH:H$_2$O (6:1) were added NaHCO$_3$ (0.001 g, 0.0129 mmol) and NaIO$_4$ (0.004 mg, 0.018 mmol). A white precipitate formed during the course of the reaction. After 2 h, the reaction was filtered and the filtrate concentrated to leave the H$_2$O. The filtrate had 5 mL of H$_2$O added and the aqueous extract was washed 3 times with 5 mL of EtOAc. The combined organic extracts were washed with 10 mL of satd. NaCl solution and dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude product was purified using flash column
chromatography (hexanes: EtOAc, 1:1) to afford 111 (0.007 g, 87%) as a white oil/solid:

\(^1H\) NMR (CDCl\(_3\)) \(\delta\) 6.03 (d, 1H, J = 9.8 Hz, N-H), 5.88 (d, 1H, J = 8.1 Hz, H1), 5.64 (m, 1H, H3), 5.37 (d, 1H, J = 3.2 Hz, H4'), 5.14 (dd, 1H, J = 10.3, 8.0 Hz, H2'), 5.01 (dd, 1H, J = 10.4, 3.4 Hz, H3'), 4.92 (dd, 2H, J = 3.1 Hz, H6/H6'), 4.81 (d, 1H, J = 7.9 Hz, H1'), 4.65 (m, 1H, H4), 4.43-4.40 (m, 3H, J = 6.5 Hz, H5'/H6'/H6'), 3.92 (m, 1H, H2), 3.78 (m, 1H, CH\(_2\)-octyl), 3.45 (m, 1H, CH\(_2\)-octyl), 2.10 (s, 3H, OAc), 2.07-1.98 (bs, 15H, OAc/NHAc), 1.55 (bs, 3H, CH\(_2\)-octyl), 1.19 (bs, 9H, CH\(_2\)-octyl), 0.85 (t, 3H, CH\(_3\)-octyl).

\(^13C\) NMR (CDCl\(_3\)) \(\delta\) 171.12, 170.37, 170.27, 170.06, 169.54, 169.09, 168.88, 150.88, 145.59, 121.66, 99.74, 95.28, 77.91, 70.98, 70.59, 69.84, 68.96, 68.62, 66.95, 66.42, 60.96, 60.34, 52.72, 31.77, 29.22, 29.13, 25.87, 23.97, 23.30, 22.58, 21.00, 20.93, 20.72, 20.64, 20.60, 20.53, 14.14, 14.05. MS (ES, Na\(^+\)): m/z (relative intensity) 710.3 (100). HRMS (M + Na\(^+\)) calcd for C\(_{32}\)H\(_{49}\)NO\(_{15}\)Na, 710.3000; found 710.2993.

Octyl 2-Acetamido-3-O-(2,3,4,6-tetra-O-acetyl-\(\alpha\)-D-galactopyranosyl)-4-O-acetyl-2-deoxy-5, 6-epoxy-\(\alpha\)-D-glucopyranoside (112).

![Chemical Structure](image)

To a stirred 0 °C solution of 111 (0.045 g, 0.065 mmol) in 2.0 mL of CH\(_2\)Cl\(_2\) was added DMDO (approximately 8 mL). After 13 h, the reaction was dried with Na\(_2\)SO\(_4\), filtered and the filtrate was concentrated to afford 112 (0.044 g, 95%) as a colorless oil:

\(^1H\) NMR (CD\(_3\)OD) \(\delta\) 5.78 (m, 1H, H3'), 5.56 (d, 1H, H4'), 5.50 (dd, 1H, H2'), 5.31 (d, 1H, H1), 5.02 (m, 1H, H3), 4.44 (d, 1H, H1'), 4.30 (m, 1H, H4), 4.18 (m, 1H, H5'), 3.75 (m, 2H, Hz, H6'/H6'), 3.43 (m, 1H, H2), 3.43 (m, 1H, CH\(_2\)-octyl), 3.13 (m, 1H, CH\(_2\)-octyl), 2.10 (s, 3H, OAc), 2.07-1.98 (bs, 15H, OAc/NHAc), 1.55 (bs, 3H, CH\(_2\)-octyl), 1.19 (bs, 9H, CH\(_2\)-octyl), 0.85 (t, 3H, CH\(_3\)-octyl).
2.78 (d, 1H, H6), 2.53 (d, 1H, H6), 2.12-1.69 (bs, 18H, OAc/NHAc), 1.62 (bs, 3H, CH3-octyl), 1.25 (bs, 9H, CH2-octyl), 0.90 (t, 3H, CH3-octyl). 13C NMR (C6D6) δ 170.61, 170.44, 170.23, 78.43, 71.66, 69.93, 69.58, 68.09, 67.64, 63.07, 61.58, 33.56, 32.55, 30.44, 30.17, 30.05, 26.65, 26.54, 23.39, 21.20, 21.12, 21.02, 20.64, 20.41, 20.28, 20.21, 14.67, -1.71. MS (ES, Na+): m/z (relative intensity) HRMS (M + Na+) calcd for C32H49NO16Na, 726.3; found 726.3 (100).

Octyl 2-acetamido-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-3-O-acetyl-5,6-dehydro-2,6-dideoxy-β-D-glucopyranoside (113).

To a stirred solution of 101 (0.04 g, 0.05 mmol) in 7.0 mL of MeOH:H2O (6:1) were added NaHCO3 (0.005 g, 0.058 mmol) and NaIO4 (0.017 g, 0.080 mmol). A white precipitate formed during the course of the reaction. After 2.5 h, the reaction was filtered and the filtrate concentrated to leave the H2O. The filtrate had 5.0 mL of H2O added and the aqueous extract was washed 3 times with 5.0 mL of EtOAc. The combined organic extracts were washed with 10 mL of satd. NaCl solution and dried with Na2SO4, filtered and the filtrate concentrated. The resulting mixture of olefin and selenoxides (0.031 g) was taken on without any purification. The crude selenoxides (0.031 g) was dissolved in 3.0 mL of DHP and heated to reflux at 100 °C. After 45 min, the reaction was cooled and diluted with 5.0 mL of CH2Cl2 and washed with 5.0 mL of H2O, satd. NaHCO3, and satd. NaCl solutions. The organic extract was dried with Na2SO4, filtered and the filtrate
concentrated. The crude product was purified using flash column chromatography (hexanes:EtOAc, 2:1) to afford 113 (0.012 g, 40%, 2 steps) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 6.55 (d, 1H, J = 9.6 Hz, N-H), 5.37 (d, 1H, J = 3.0 Hz, H4’), 5.29 (d, 1H, H1), 5.20 (dd, 1H, J = 8.0 Hz, H2’), 5.06 (dd, 1H, J = 10.5, 3.4 Hz, H3’), 4.92 (s, 1H, H6’), 4.88 (s, 1H, H6’), 4.68 (s, 1H, H6), 4.63 (s, 1H, H6), 4.54 (d, 1H, J = 7.9 Hz, H1’), 4.30 (m, 1H, H4), 4.21 (dd, 1H, J = 4.9 Hz, H3), 4.13 (m, 1H, H5’), 3.89 (m, 1H, H2), 3.75 (m, 1H, CH$_2$-octyl), 3.36 (m, 1H, CH$_2$-octyl), 2.17 (s, 3H, OAc), 2.09-1.96 (bs, 15H, OAc/NHAc), 1.53 (bs, 3H, CH$_2$-octyl), 1.35 (bs, 9H, CH$_2$-octyl), 0.86 (t, 3H, CH$_3$-octyl).

$^{13}$C NMR (CDCl$_3$) $\delta$ 171.13, 170.17, 170.09, 169.95, 169.33, 149.46, 103.87, 101.85, 97.76, 73.29, 70.86, 70.28, 69.44, 68.59, 68.05, 66.57, 60.88, 46.82, 31.82, 29.42, 29.32, 29.29, 26.10, 22.88, 22.63, 21.04, 20.85, 20.64, 14.18. MS (ES, Na$^+$): m/z (relative intensity) 710.3 (100). HRMS (M + Na$^+$) calcd for C$_{32}$H$_{49}$NO$_{15}$Na, 710.3000; found 710.3006.

**Octyl 2-acetamido-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)- 3-O-acetyl-2-deoxy-5, 6-epoxy-β-D-glucopyranoside (114).**

![Chemical Structure](image)

To a stirred 0 °C solution of 113 (0.011 g, 0.016mmol) in .01 mL of CH$_2$Cl$_2$ was added DMDO (approximately 8 mL). After 1 h, the reaction was dried with Na$_2$SO$_4$, filtered and the filtrate was concentrated to afford 114 (0.044 g, 95%) as a colorless oil: $^1$H NMR (C$_6$D$_6$) $\delta$ 6.37 (d, 1H, J = 9.7 Hz, N-H), 5.60 (m, 1H, H3), 5.49 (d, 1H, J = 3.0 Hz, H4’), 5.27 (d, 1H, J = 8.7 Hz, H1), 5.25 (dd, 1H, J = 10.6, 3.4 Hz, H3’), 4.82 (dd, 1H,
J = 2.8 Hz, H2'), 4.79 (m, 1H, H5'), 4.74 (d, 1H, J = 7.9 Hz, H1'), 4.12 (m, 2H, Hz, H6'/H6'), 3.85 (m, 1H, H4), 3.54 (m, 1H, CH2-octyl), 3.36 (m, 1H, H2), 3.18 (m, 1H, CH2-octyl), 2.82 (d, 1H, J = 4.7 Hz, H6), 2.43 (d, 1H, J = 4.7 Hz, H6), 2.01-1.61 (bs, 18H, OAc/NHAc), 1.53 (bs, 3H, CH2-octyl), 1.28 (bs, 9H, CH3-octyl), 0.91 (t, 3H, CH3-octyl). 13C NMR (C6D6) δ 171.06, 170.41, 170.00, 169.56, 169.22, 103.69, 101.62, 79.06, 74.08, 71.96, 71.49, 71.08, 69.91, 69.73, 67.49, 61.45, 51.45, 49.24, 32.51, 30.11, 30.06, 30.01, 26.64, 23.39, 23.20, 21.04, 20.76, 20.56, 20.48, 20.23, 14.67, -1.73. MS (ES, Na+): m/z (relative intensity) calcd for C32H49NO16Na, 726.3; found 726.3 (100).

Octyl 3, 4-O-di acetyl 5, 6-dehydro-2, 6-dideoxy-2-phthalamido-3-D-glucopyranoside (115a).

To a stirred solution of 71a (0.052 g, 0.008 mmol) in 7 mL of MeOH:H2O (6:1) were added NaHCO3 (0.007 g, 0.088 mmol) and NaIO4 (0.025 g, 0.121 mmol). A white precipitate formed during the course of the reaction. After 2 h, the reaction was filtered and the filtrate concentrated to leave the H2O. An additional 10 mL of H2O was added to the filtrate and the aqueous extract was washed 3 times with 15 mL of CH2Cl2. The combined organic extracts were washed with 50 mL of satd. NaCl solution and dried with Na2SO4, filtered and the filtrate concentrated to afford a 3:1 diastereomeric mixture of selenoxides as a white oil/solid (0.047 g) and taken on without any purification: 1H NMR (CDCl3) δ 7.84 (m, 2H, NPht), 7.72 (m, 2H, NPht), 7.54 (m, 5H, SePh), 5.78 (d, 1H, J = 10.3 Hz, H4), 5.65 (d, 1H, J = 10.3 Hz, H4), 5.53 (d, 1H, J = 8.5 Hz, H1), 5.35 (d, 1H, J = 8.5 Hz, H1), 4.97 (m, 1H, H3), 4.28 (m, 1H, H2), 3.89-3.83 (m, 2H, H5/H5), 3.55 (m,
1H, CH₂-octyl), 3.29 (m, 1H, CH₂-octyl), 3.09 (m, 1H, H6), 2.93 (m, 1H, H6), 1.98 (s, 3H, OAc), 1.84 (s, 3H, OAc), 1.43 (bs, 2H, CH₂-octyl), 1.24-0.94 (bs, 9H, CH₂-octyl), 0.85 (bs, 3H, CH₃-octyl). ¹³C NMR (CHCl₃) δ 169.94, 168.36, 167.68, 134.91, 134.79, 133.48, 132.78, 131.34, 130.50, 129.22, 126.45, 124.23, 122.77, 98.86, 72.85, 71.70, 70.95, 70.64, 69.75, 69.01, 55.32, 54.19, 31.66, 30.08, 29.11, 28.05, 26.75, 25.75, 22.61, 21.17, 20.89, 20.13, 19.85, 13.50. The crude selenoxides (0.047 g, 0.071 mmol) was dissolved in 3.0 mL of DHP and heated to reflux at 100 °C. After 1.25 h, the reaction was cooled and diluted with 5 mL of CH₂Cl₂ and washed with 5 mL of H₂O, satd. NaHCO₃, and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using preparative thin layer chromatography (hexanes:EtOAc, 2:1) to afford 115a (0.022 g, 65%, 2 steps) as a colorless oil: ¹H NMR (CDCl₃) δ 7.85 (m, 2H, NPht), 7.32-7.73 (m, 2H, NPht), 5.69 (dd, 1H, J = 10.2, 8.6 Hz, H3), 5.52 (m, 1H, H4), 5.37 (d, 1H, J = 8.3 Hz, H1), 4.88 (m, 1H, H6), 4.64 (m, 1H, H6), 4.42 (dd, 1H, J = 10.2, 8.3 Hz, H2), 3.87 (m, 1H, CH₂-octyl), 3.46 (m, 1H, CH₂-octyl), 2.12 (s, 3H, OAc), 1.88 (s, 3H, OAc), 1.44 (bs, 1H, CH₂-octyl), 1.18-0.95 (bs, 12H, CH₂-octyl), 0.80 (bs, 3H, CH₃-octyl). ¹³C NMR (CDCl₃) δ 169.94, 169.34, 167.54, 150.75, 134.94, 134.88, 133.58, 131.39, 124.24, 122.89, 99.71, 98.32, 97.55, 71.37, 70.89, 70.46, 70.24, 69.69, 69.19, 55.22, 54.09, 30.20, 29.20, 21.28, 21.02, 20.25, 19.98, 14.53. MS (ES, Na⁺): m/z (relative intensity) 510.2 (100). HRMS (M + Na⁺) calcd for C₂₆H₃₃NO₈Na, 510.2104; found 510.2098.

Octyl 3, 4-O-di benzyl 5, 6-dehydro-2, 6-dideoxy-2-phthalamido-∃-D-glucopyranoside (115b).
To a stirred solution of 71b (0.030 g, 0.040 mmol) in 3.5 mL of MeOH: H2O (6:1) were added NaHCO3 (0.004 mg, 0.044 mmol) and NaIO4 (0.013 g, 0.060 mmol). A white precipitate formed during the course of the reaction. After 4 h, the reaction was filtered and the filtrate concentrated to leave the H2O. An additional 5 mL of H2O was added to the filtrate and the aqueous extract was washed 3 times with 10 mL of EtOAc. The combined organic extracts were washed with 30 mL of satd. NaCl solution and dried with Na2SO4, filtered and the filtrate concentrated to afford a 2:1 diastereomeric mixture of selenoxides as a white oil/solid (0.025 g) and taken on without any purification: 1H NMR (CDCl3) δ 7.71 (m, 2H, NPht), 7.65 (m, 2H, NPht), 7.32 (m, 5H, SePh), 6.90 (m, 5H, Bn), 6.86 (m, 5H, Bn), 5.27 (d, 1H, J = 8.5 Hz, H1), 5.14 (d, 1H, CH2-Bn), 5.09 (d, 1H, CH2-Bn), 5.01 (d, 1H, CH2-Bn), 4.91 (d, 1H, CH2-Bn), 4.33 (d, 1H, CH2-octyl), 3.54 (m, 1H, H2), 3.44 (m, 1H, CH2-octyl), 3.39-3.30 (m, 2H, H5/H5), 2.97 (dd, 1H, J = 12.0, 2.9 Hz, H6), 2.65 (m, 1H, H6), 1.26 (bs, 2H, CH2-octyl), 1.14-0.90 (bs, 9H, CH2-octyl), 0.80 (bs, 3H, CH3-octyl). 13C NMR (CHCl3) δ 137.76, 133.78, 132.16, 131.19, 129.78, 129.67, 129.03, 128.64, 128.55, 128.40, 128.31, 128.24, 128.12, 128.07, 127.97, 127.89, 127.46, 127.38, 126.67, 126.21, 125.85, 123.29, 98.41, 98.25, 83.29, 82.68, 77.41, 75.27, 75.04, 73.93, 70.31, 69.85, 69.62, 57.02, 55.98, 32.58, 31.70, 29.08, 25.80, 22.74, 20.99, 14.05. The crude selenoxides (0.025 g, 0.033 mmol) was dissolved in 2.0 mL of DHP and heated to reflux at 100 °C. After 1 h, the reaction was cooled and diluted with 5 mL of CH2Cl2 and washed with 5 mL H2O, satd. NaHCO3, and satd. NaCl solutions. The organic extract was dried with Na2SO4, filtered and the filtrate concentrated. The crude product was
purified using preparative thin layer chromatography (hexanes:EtOAc, 5:1) to afford 115b (0.013 g, 68%, 2 steps) as a colorless oil: \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.68 (m, 4H, NPht), 7.40-7.25 (m, 5H, Bn), 6.98 (m, 2H, Bn), 6.86 (m, 3H, Bn), 5.18 (d, 1H, J = 7.9 Hz, H1), 4.87 (bs, 2H, H6/H6), 4.83 (d, 2H, J = 11.4 Hz, CH\(_2\)-Bn), 4.73 (d, 2H, J = 11.4 Hz, CH\(_2\)-Bn), 4.44 (d, 1H, J = 12.2 Hz, H3), 4.24 (dd, 1H, J = 10.4, 8.2 Hz, H2), 4.06 (m, 1H, H4), 3.81 (m, 1H, CH\(_2\)-octyl), 3.40 (m, 1H, CH\(_2\)-octyl), 1.39 (bs, 2H, CH\(_2\)-octyl), 1.16-0.98 (bs, 10H, CH\(_2\)-octyl), 0.80 (bs, 3H, CH\(_3\)-octyl). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 167.72, 153.72, 137.98, 133.75, 131.63, 128.51, 128.03, 127.95, 127.93, 127.89, 127.33, 123.27, 99.33, 97.19, 80.98, 77.03, 74.27, 73.51, 69.95, 55.69, 54.09, 31.22, 29.20, 24.28, 21.53, 20.35, 14.05. MS (ES, Na\(^{+}\)): m/z (relative intensity) 606.2 (100). HRMS (M + Na\(^{+}\)) calcd for C\(_{34}\)H\(_{37}\)NO\(_6\)Na, 606.2832; found 606.2844.

**Octyl 3, 4-O-di-acetyl-2-deoxy-5, 6-epoxy-phthalamido-β-D-glucopyranoside (116a).**

![Chemical Structure](image)

To a stirred 0 °C solution of 115a (0.022 g, 0.045 mmol) in 1.0 mL of CH\(_2\)Cl\(_2\) was added DMDO (approximately 10 mL). The reaction was placed in the cold box overnight at 4 °C. After 19 h, the solution was dried with Na\(_2\)SO\(_4\), filtered and the filtrate concentrated to afford 116a (0.021 g, 95%) as a colorless oil: \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.62-7.59-7.46 (m, 4H, Ph), 6.22 (d, 1H, H3), 5.67 (d, 1H, J = 8.4 Hz, H1), 5.18 (m, 1H, H4), 3.94 (dd, 1H, J = 8.9, 5.0 Hz, H2), 3.53 (m, 1H, CH\(_2\)-octyl), 3.43 (m, 1H, CH\(_2\)-octyl), 2.82 (m, 1H, H6), 2.44 (m, 1H, H6), 1.75 (s, 3H, OAc), 1.66 (s, 3H, OAc), 1.58 (bs, 3H,
CH$_3$-octyl), 1.27-0.99 (bs, 9H, CH$_3$-octyl), 0.88 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) δ 169.91, 168.82, 167.52, 133.53, 131.79, 128.11, 123.31, 123.08, 98.26, 79.73, 73.42, 72.11, 71.02, 69.93, 67.54, 55.34, 33.77, 31.15, 29.41, 26.14, 22.87, 20.04, 14.16. MS (ES, Na$^+$): m/z (relative intensity) calcd for C$_{26}$H$_{33}$NO$_9$Na, 526.1; found 526.1 (100).

**Octyl 4-O-benzyl-2-deoxy-5, 6-epoxy-2-phthalamido-$\beta$-D-glucopyranoside (116b).**

\[ \text{NPht} \quad \text{BnO} \quad \text{BnO} \quad \text{O} \quad \text{O} \quad \text{C-H$_2$-octyl} \quad \text{C-H$_2$-octyl} \quad \text{C-H$_2$-octyl} \]

To a stirred 0 °C solution of 115b (0.013 g, 0.022 mmol) in 0.75 mL of CH$_2$Cl$_2$ was added DMDO (approximately 5 mL). The reaction was placed in the cold box overnight at 4 °C. After 19 h, the solution was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated to afford a 1:1 diastereomeric ratio 116b (0.011 g, 85%) as a colorless oil:

$^1$H NMR (CDCl$_3$) δ 7.59-7.44 (m, 4H, Pht), 7.19-6.93 (m, 10H, Bn), 6.18 (d, 1H, J = 9.3 Hz, H1), 6.12 (d, 1H, J = 9.1 Hz, H1), 5.14 (d, 2H, J = 9.7 Hz, H4/H4), 4.92-4.71 (d, 4H, CH$_2$-Bn), 4.60-4.47 (m, 2H, H3/H2), 4.08 (m, 1H, CH$_3$-octyl), 3.87 (m, 1H, CH$_3$-octyl), 3.44 (m, 1H, H6), 3.33 (m, 1H, H6), 1.58 (bs, 2H, CH$_2$-octyl), 1.25-1.03 (bs, 10H, CH$_3$-octyl), 0.93 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) δ 133.34, 128.11, 127.23, 123.10, 123.08, 96.54, 81.23, 75.38, 69.93, 56.21, 32.02, 29.41, 26.14, 22.87, 14.16. MS (ES, Na$^+$): m/z (relative intensity) calcd for C$_{36}$H$_{41}$NO$_7$Na, 546.2679; found 622.2 (100).

$\tau$-Butyldimethylsilyl 4-O-benzyl-3-O-[(benzyl oxy)methyl]- 5, 6-dehydro-2, 6-dideoxy-$\beta$-d-glucopyranoside (117).
To a stirred solution of 67 (0.055 g, 0.071 mmol) in 7 mL of MeOH:H₂O (6:1) were added NaHCO₃ (0.007 g, 0.078 mmol) and NaIO₄ (0.022 g, 0.106 mmol). A white precipitate formed during the course of the reaction. After 5 h, the reaction was filtered and the filtrate concentrated to leave the H₂O. An additional 10 mL of H₂O was added to the filtrate and the aqueous extract was washed 2 times with 10 mL of CH₂Cl₂. The combined organic extracts were washed with 20 mL of satd. NaCl solution and dried with Na₂SO₄, filtered and the filtrate concentrated to afford a 1:1 diastereomeric mixture of selenoxides as a white oil/solid (0.052 g) and taken on without any purification: ¹H NMR (CDCl₃) δ 7.82 (m, 2H, NPht), 7.65 (m, 2H, NPht), 7.53 (m, 3H, SePh), 7.40-7.03 (m, 12H, SePh/ArH of BOM/Bn), 5.52 (d, 1H, H1), 5.38 (d, 1H, H1), 4.99 (d, 1H, -O-CH₂-OBn), 4.96 (d, 1H, -O-CH₂-OBn), 4.76-4.61, (m, 11H, -O-CH₂-OBn/-O-CH₂-Ph/H4/H4/H3/H3), 4.49 (m, 1H, -O-CH₂-Ph), 4.29 (m, 2H, -O-CH₂-Ph), 4.12 (m, 1H, H2), 4.07 (m, 1H, H2), 3.76 (m, 1H, H5), 3.73 (m, 1H, H5), 3.60 (m, 1H, H6), 3.22 (m, 1H, H6), 0.71 (bs, 18H, tBu), 0.11 (s, 3H, tBu), 0.09 (s, 3H, tBu), 0.06 (s, 3H, tBu), 0.03 (s, 3H, tBu). ¹³C NMR (CDCl₃) δ 133.93, 129.60, 128.61, 128.36, 128.31, 128.29, 128.24, 128.22, 127.47, 127.15, 125.60, 94.63, 93.96, 93.79, 76.14, 75.64, 75.25, 74.96, 74.78, 73.12, 69.78, 68.85, 55.93, 54.71, 54.50, 42.09, 25.29, 17.47, -3.95, -4.16, -5.61. The crude selenoxides (0.052 g, 0.066 mmol) were dissolved in 5 mL of DHP and heated to reflux at 100 °C. After 2 h, the reaction was cooled and diluted with 20 mL of EtOAc and washed with 20 mL of H₂O, satd. NaHCO₃, and satd. NaCl solutions. The organic extract was dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using preparative thin layer chromatography (hexanes:EtOAc, 3:1) to afford 117 (0.03 g, 75 %, 2 steps) as a colorless oil: ¹H NMR (CDCl₃) δ 8.82 (bs, 2H, NPht),
7.66 (m, 2H, NPht), 7.40-7.20 (m, 8H, ArH of BOM/Bn), 7.06 (m, 2H, Bn), 5.39 (d, 1H, J = 8.0 Hz, H1), 4.89 (d, 1H, -O-CH2-Ph), 4.85 (dd, 1H, J = 11.2, 3.1 Hz, H4), 4.76 (d, 1H, J = 10.5 Hz, -O-CH2-Ph/CH2-Bn), 4.74 (d, 1H, -O-CH2-Bn), 4.70 (dd, 1H, J = 11.2, 3.2 Hz, H3), 4.65 (m, 1H, H2), 4.60 (s, 2H, H6/H6), 4.55 (d, 1H, CH2-Bn), 1.25 (bs, 9H, tBu), 0.71 (bs, 3H, tBu, 0.65 (bs, 3H, tBu). 13C NMR (CDCl3) δ 171.12, 152.14, 137.97, 137.37, 133.98, 131.65, 128.34, 128.26, 127.88, 127.51, 127.47, 127.20, 102.06, 94.68, 93.46, 75.01, 74.21, 70.40, 69.81, 69.42, 69.34, 60.37, 54.75, 54.09, 25.33, 22.63, 21.03, 17.57, 14.18, -4.28, -5.47. MS (ES, Na+): m/z (relative intensity) 638.2 (100). HRMS (M + Na+) calcd for C35H41NO7Na, 638.2550; found 638.2562.

1,2-Butyldimethylsilyl 4-O-benzyl-3-O-[(benzyl oxy)methyl]-2-deoxy-5, 6-epoxy-2-phthalamido-3-D-galactopyranoside (118).

To a stirred 0 °C solution of 117 (0.03 g, 0.05 mmol) in 1.5 mL of CH2Cl2 was added DMDO (approximately 8 mL). After 1 h, the solution was dried with Na2SO4, filtered and the filtrate concentrated to afford a 1:1 diastereomeric ratio 118 (0.027 g, 90%) as a colorless oil: 1H NMR (CDCl3) δ 7.48 (m, 4H, Pht), 7.31-7.09 (m, 8H, ArH of ArH of BOM/Bn), 6.84 (d, 2H, Bn), 6.20 (d, 1H, J = 8.3 Hz, H1), 5.65 (d, 1H, J = 8.1 Hz, H1), 5.52 (dd, 1H, J = 11.3, 8.3 Hz, H3), 5.33 (dd, 1H, 11.3, 3.0 Hz, H4), 5.16 (dd, 1H, 11.3, 8.1 Hz, H3), 4.88 (d, 1H, -O-CH2-Ph), 4.70-4.41 (m, 8H, -O-CH2-Ph/CH2-Bn/H2/H2), 3.50 (m, 1H, H6), 3.34 (m, 1H, H6), 2.77 (m, 1H, H6), 2.16 (m, 1H, H6), 0.82 (bs, 18H, tBu), 0.21 (bs, 3H, tBu), 0.15 (s, 3H, tBu), 0.09 (s, 3H, tBu), 0.00 (s, 3H,
$^{13}$C NMR (CDCl$_3$) $\delta$ 139.01, 138.53, 138.29, 134.12, 132.64, 128.94, 128.88, 128.83, 128.76, 128.29, 128.12, 127.98, 127.81, 123.50, 95.09, 94.73, 94.42, 93.63, 79.93, 77.62, 76.57, 75.66, 75.62, 74.70, 74.31, 72.52, 70.19, 70.01, 55.78, 55.11, 52.56, 43.33, 26.01, 25.91, 18.18, -3.42, -3.83, -4.75, -4.92. MS (ES, Na$^+$): m/z (relative intensity) calcd for C$_{35}$H$_{37}$NO$_8$Na, 654.2; found 654.2 (100).

Octyl 4-O-benzyl-3-O-[(benzyloxy)methyl]-2, deoxy-5-fluoro-$\beta$-D-glucopyranoside (119b).

To a stirred -78 °C solution of 107b (0.035 g, 0.064 mmol) in a Schlenk tube in 1 mL of CH$_2$Cl$_2$ was added HF·pyridine (7 drops). After 40 min, the reaction was quenched with 5 drops of NEt$_3$ and the resulting light yellow solution was concentrated to afford 119b: $^1$H NMR (CDCl$_3$) $\delta$ 7.37-7.26 (m, 10H, ArH of BOM/Bn), 5.82 (d, 1H, J = 8.3 Hz, NH), 5.10 (s, 1H, O-CH$_2$-O-Bn), 4.75 (d, 1H, J = 7.1 Hz, CH$_2$-Ph), 4.65 (d, 1H, J = 7.0 Hz, CH$_2$-Ph), 4.57-4.48 (m, 5H, H4/H1/H3/H2/ CH$_2$-Ph), 4.42 (d, 1H, J = 10.6 Hz, CH$_2$-Ph), 4.18 (s, 1H, O-CH$_2$-O-Bn), 3.79 (m, 2H, CH$_2$-octyl), 3.53 (m, 2H, CH$_2$-octyl), 3.53 (m, 2H, CH$_2$-octyl), 2.90 (bs, 1H, -OH), 1.74 (s, 3H, NHAc), 1.56 (bs, 3H, CH$_2$-octyl), 1.24 (bs, 9H, CH$_2$-octyl), 0.85 (t, 3H, CH$_3$-octyl). $^{19}$F NMR (CDCl$_3$) $\delta$ 52.47. MS (ES, Na$^+$): m/z (relative intensity) calcd for C$_{31}$H$_{44}$NO$_7$FNa, 585.0; found 585.0 (100).

Octyl 3-O-acetyl-4-O-benzyl-2-deoxy-5-fluoro-$\beta$-D-glucopyranoside (119c).
To a stirred -78 °C solution of **107c** (0.021 g, 0.043 mmol) in a Schlenk tube in 1 mL of CH$_2$Cl$_2$ was added HF-pyridine (5 drops). After 30 min, the reaction was quenched with 5 drops of NEt$_3$ and the resulting light yellow solution was concentrated to afford **119c** (0.002 g, 9%) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.37-7.26 (m, 5H, Bn), 6.25 (d, 1H, NH), 5.21 (s, 1H, O-CH$_2$Ph), 4.90 (dd, 1H, H4), 4.70 (d, 1H, -O-CH$_2$Ph), 4.57-4.28 (m, 3H, H1/H3/H2), 3.79 (m, 2H, CH$_3$-octyl), 3.27 (m, 2H, H6/H6), 1.99 (s, 1H, OAc), 1.74 (s, 3H, NHAc), 1.56 (bs, 3H, CH$_2$-octyl), 1.24 (bs, 9H, CH$_2$-octyl), 0.85 (t, 3H, CH$_3$-octyl). $^{19}$F NMR (CDCl$_3$) $\delta$ 52.58. MS (ES, Na$^+$): m/z (relative intensity) calcd for C$_{25}$H$_{38}$NO$_7$Na, 506.2; found 506.2 (100).

**Octyl 2-acetamido-3-O-3-D-galactopyranosyl-2-deoxy-5-fluoro-3-D-glucopyranoside (13a).**

![Diagram of the molecule](image)

To a -78 °C stirred solution of **112** (0.018 g, 0.025 mmol) in 1.0 mL of CH$_2$Cl$_2$ was added HF-pyridine (0.01 mL). After 1.75 h, the reaction was quenched with 0.01 mL of NEt$_3$ and the resulting light yellow solution was diluted to 5 mL of CH$_2$Cl$_2$ and washed with 5 mL of H$_2$O and satd. NaCl solution. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated to afford the (5-F) glycoside (0.030 g) which was taken on without any purification. NH$_3$ was bubbled through a stirred methanolic solution (2 mL) of the resulting (5-F) glycoside at 0 °C. After 10 min, the flask was sealed and warmed to room temperature. After 1.5 h, the solvent and NH$_3$ were removed.
with a stream of nitrogen. The resulting product was purified using flash column chromatography (EtOAc MeOH, 5:1) to afford 13a (0.003 g, 25% 2 steps) as a white powder: $^1$H NMR (D$_2$O) $\delta$ 3.92 (m, 1H, H1), 3.76-3.58 (d, 4H, H1’/H2’/H3/H3’), 3.42-3.28 (m, 6H, H4’/H4/H2/H5’/H6’/H6’), 3.41-3.34 (m, 2H, $-CH_2$-octyl), 2.19-2.06 (m, 2H, H6/H6’), 1.86 (s, 3H, NHAc), 1.48 (bs, 3H, $CH_2$-octyl), 1.29 (bs, 9H, $CH_2$-octyl), 0.91 (t, 3H, $CH_3$-octyl). $^{13}$C NMR (D$_2$O) $\delta$ 174.73, 105.84, 90.69, 77.37, 72.32, 69.80, 61.53, 60.38, 55.56, 46.61, 40.64, 35.13, 29.38, 25.71, 21.58, 10.79. $^{19}$F NMR (D$_2$O) $\delta$ 89.6. MS (ES, Na$^+$): m/z (relative intensity) calcd for; found 536.2 (100). HRMS (M + Na$^+$) calcd for C$_{22}$H$_{40}$NO$_{11}$FNa, 536.2483; found 536.2457.

**Octyl 2-acetamido-4-Ø-D-galactopyranosyl-2-deoxy-5-fluoro-Ø-D-glucopyranoside (14a).**

To a -78 °C stirred solution of 114 (0.011 g, 0.015 mmol) in 1.0 mL of CH$_2$Cl$_2$ was added HF·pyridine (0.01 mL). After 2 h, the reaction was quenched with 0.01 mL of NEt$_3$ and the resulting light yellow solution was washed with 5 mL of H$_2$O and satd. NaCl solution. The organic extract was dried with Na$_2$SO$_4$, filtered and the filtrate concentrated to afford the (5-F) glycoside (0.020 g) and taken on without any purification. NH$_3$ was bubbled through a stirred methanolic solution (2 mL) of the resulting (5-F) glycoside at 0 °C. After 10 min, the flask was sealed and warmed to room temperature. After 1.5 h, the solvent and NH$_3$ were removed with a stream of nitrogen. The resulting product was purified using flash column chromatography (EtOAc MeOH,
5:1) to afford 14a (0.003 g, 37% 2 steps) as a white powder: $^1$H NMR (D$_2$O) $\delta$ 4.12 (d, 1H, J = 7.1 Hz, H1), 3.91 (m, 1H, H1’), 3.73-3.57 (m, 3H, H2’/H3/H3’), 3.44-2.93 (m, 8H, H4’/H4/H2/H5’/H6’/-C$_2$H$_5$-octyl), 2.00-1.95 (m, 2H, H6/H6’), 2.00 (s, 3H, NHaC), 1.47 (bs, 3H, CH$_2$-octyl), 1.32 (bs, 9H, CH$_2$-octyl), 0.84 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (D$_2$O) $\delta$ 173.64, 103.26, 90.68, 75.41, 72.49, 71.01, 69.31, 68.61, 61.94, 61.06, 56.48, 42.26, 31.11, 28.49, 25.05, 22.03, 21.31, 13.42, 10.55. $^{19}$F NMR (D$_2$O) $\delta$ 69.5. MS (ES, Na$^+$): m/z (relative intensity) calcd for; found 536.2 (100). HRMS (M + Na$^+$) calcd for C$_{22}$H$_{40}$NO$_{11}$FNa, 536.2483; found 536.2485.

Octyl 3, 4-O-diacetyl-5-cyano-2-deoxy-2-phthalimido-,$\alpha$-D-glucopyranoside (124a).

Method (a)

To a stirred 0 °C solution of 116a (0.014 g, 0.027 mmol) in 1.0 mL of CH$_2$Cl$_2$ were added TMS-CN (0.017 mL, 0.139 mmol) and AlCl$_3$ (5.4 mg, 0.040 mmol). The reaction was brought to reflux at 45 °C. After 6.5 h, the reaction was quenched with 1 mL of H$_2$O and stirred for 5 min. The organic extract was diluted to 5 mL of CH$_2$Cl$_2$ and washed with 5 mL of satd. NaCl solution, dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude product was purified using preparatory thin layer chromatography (hexanes:EtOAc, 1:1) to afford 124a (0.003 g, 21%) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.85 (m, 2H, NPh), 7.74 (m, 2H, NPh), 6.13 (d, 1H, H3), 5.97 (d, 1H, J = 8.7 Hz, H1), 5.30 (d, 1H, J = 9.4 Hz, H4), 4.68 (d, 1H, OH), 4.37 (dd, 1H, J = 8.6, 4.7 Hz, H2), 4.18 (m, 1H, H6), 4.04 (d, 1H, J = 10.3 Hz, H6), 3.85 (m, 1H, CH$_2$-octyl),
3.75 (m, 1H, CH₃-octyl), 2.02 (s, 3H, OAc), 1.95 (s, 3H, OAc), 1.40 (bs, 2H, CH₂-octyl), 1.24-0.95 (bs, 10H, CH₂-octyl), 0.82 (t, 3H, CH₃-octyl). ¹³C NMR (CDCl₃) δ 167.82, 158.83, 134.32, 123.52, 133.65, 93.90, 73.01, 71.86, 70.26, 68.88, 55.10, 53.49, 31.68, 29.84, 25.71, 22.50, 14.00, 0.91. MS (ES, Na⁺) m/z (relative intensity) 553.2 (100). HRMS (M + Na⁺) calcd for C₂₇H₃₄N₂O₉Na, 553.2162; found 553.2168. The resulting product did not stain with DNP.

**Method (b)**
To a stirred 0 °C solution of 116a (0.010 g, 0.019 mmol) in 1.0 mL of CH₂Cl₂ were added TMS-CN (0.012 mL, 0.099 mmol) and BF₃·OEt₂ (0.0036 mL, 0.028 mmol). The reaction was stirred at room temperature. After 6.5 h, the reaction was quenched with 1 mL of H₂O and stirred for 5 min. The organic extract was diluted to 5 mL of CH₂Cl₂ and washed with 5 mL of satd. NaCl solution, dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using preparatory thin layer chromatography (hexanes:EtOAc, 1:1) to afford 124a (0.003 g, 27%) as a colorless oil with identical ¹H NMR, ¹³C NMR and mass spectrum data as identical to those reported for 6.4Aa prepared by Method (a). The resulting product did not stain with DNP.

**Octyl 3, 4- O-dibenzyl-5-cyano-2-deoxy-2-phthalimido-D-glucopyranoside (124b).**

To a stirred 0 °C solution of 116b (0.014 g, 0.023 mmol) in 1.0 mL of CH₂Cl₂ were added TMS-CN (0.014 mL, 0.116 mmol) and AlCl₃ (4.6 mg, 0.034 mmol). The reaction was brought to reflux at 45 °C. After 6.5 h, the reaction was quenched with 1.0
mL of H₂O and stirred for 5 min. The organic extract was diluted to 5 mL of CH₂Cl₂ and washed with 5 mL of satd. NaCl solution, dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using preparatory thin layer chromatography (hexanes:EtOAc, 5:1) to afford 124b (0.005 g, 35%) as a colorless oil:

\[ ^1H \text{ NMR (CDCl}_3 \delta \text{ 7.65 (m, 4H, NPht), 7.36-7.20 (m, 6H, Bn), 7.09-6.84 (m, 4H, Bn), 6.35 (d, 1H, H4), 5.70 (d, 1H, J = 8.8 Hz, H1), 4.97 (d, 1H, O-CH}_2\text{Ph), 4.77 (d, 2H, -O-CH}_2\text{Ph/H3), 4.65 (d, 1H, O-CH}_2\text{Ph), 4.42 (d, 1H, O-CH}_2\text{Ph), 4.21 (dd, 1H, J = 10.9, 8.8 Hz, H2), 3.96 (m, 1H, H6), 3.81 (d, 1H, H6), 3.64 (m, 1H, CH}_2\text{-octyl), 3.64 (m, 1H, CH}_3\text{-octyl), 1.54 (bs, 2H, CH}_3\text{-octyl), 1.25-1.13 (bs, 10H, CH}_2\text{-octyl), 0.86 (t, 3H, CH}_3\text{-octyl).} \]

\[ ^13C \text{ NMR (CDCl}_3 \delta \text{ 167.89, 158.13, 137.61, 133.87, 133.65, 128.55, 128.20, 127.82, 127.34, 123.23, 100.20, 94.58, 81.42, 75.02, 74.95, 73.03, 69.88, 56.14, 31.62, 29.30, 29.04, 25.71, 22.55, 14.03, 0.01.} \]

MS (ES, Na⁺): m/z (relative intensity) 649.2 (100). HRMS (M + Na⁺) calcd for C₃₇H₄₂N₂O₇Na, 649.2890; found 649.2885. The resulting product did not stain with DNP.

**Method (b)**

To a stirred 0 °C solution of 116b (0.010 g, 0.016 mmol) in 1.0 mL of CH₂Cl₂ were added TMS-CN (0.010 mL, 0.083 mmol) and BF₃·OEt₂ (0.0034 mL, 0.024 mmol). The reaction was stirred at room temperature. After 6.5 h, the reaction was quenched with 1 mL of H₂O and stirred for 5 min. The organic extract was diluted to 5 mL of CH₂Cl₂ and washed with 5 mL of satd. NaCl solution, dried with Na₂SO₄, filtered and the filtrate concentrated. The crude product was purified using preparatory thin layer chromatography (hexanes:EtOAc, 5:1) to afford 124b (0.001 g, 10%) as a colorless oil.
with identical $^1$H NMR, $^{13}$C NMR and mass spectrum data as identical to those reported for 6.4Ab prepared by Method (a). The resulting product did not stain with DNP.

Octyl 3, 4-\textit{O}-diacetyl-2-acetamido-5-cyano-2-deoxy-\textit{\textbeta}-\textit{D}-glucopyranoside (124c).

Method (a)

To a stirred 0 °C solution of 123$^8$ (0.037 g, 0.089 mmol) in 2.0 mL of CH$_2$Cl$_2$ were added TMS-CN (0.050 mL, 0.445 mmol) and AlCl$_3$ (17 mg, 0.133 mmol). The reaction was brought to reflux at 45 °C. After 15.5 h, the reaction was quenched with 5 mL of H$_2$O and stirred for 5 min. The organic extract was diluted to 5 mL of CH$_2$Cl$_2$ and washed with 5 mL of satd. NaCl solution, dried with Na$_2$SO$_4$, filtered and the filtrate concentrated. The crude product was purified using preparatory thin layer chromatography (hexanes:EtOAc, 1:1) to afford 124c (0.013 g, 33%) as a colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 6.77 (d, 1H, J = 9.4 Hz, N-H), 4.94 (d, 1H, H3), 4.79-4.65 (d, 3H, H1/H4/OH), 4.33 (m, 1H, H2), 4.18 (m, 1H, H6), 3.94 (d, 1H, H6), 3.23 (m, 2H, C$_\text{H}_2$-octyl), 2.20 (s, 3H, OAc), 2.12 (s, 3H, OAc), 1.96 (s, 3H, NAc), 1.63 (bs, 2H, CH$_2$-octyl), 1.26 (bs, 10H, CH$_2$-octyl), 0.87 (t, 3H, CH$_3$-octyl). $^{13}$C NMR (CDCl$_3$) $\delta$ 170.46, 170.15, 100.45, 69.70, 67.90, 65.85, 64.32, 50.99, 46.63, 31.77, 29.46, 25.88, 22.80, 21.01, 14.09. MS (ES, Na$^+$): m/z (relative intensity) calcd for; found 465.2 (100). HRMS (M + Na$^+$) calcd for C$_{21}$H$_{34}$N$_2$O$_8$Na, 465.2213; found 465.2204. The resulting product did not stain with DNP.
Octyl 3, 4-O-diacetyl-2-acetamido-5-methyleneamino-2-deoxy-β-D-glucopyranoside (126).

To a solution of 124c (0.010 g, 0.022 mmol) in 10 mL of MeOH was added PtO₂ (50 mg, 0.180 mmol). The mixture was hydrogenated at 40 PSI. After 25 h, the reaction mixture was filtered through Celite and concentrated. The crude product purified using flash column chromatography (hexanes:EtOAc, 2:1) to afford 126 (0.09 g, 90%) as a colorless oil: ¹H NMR (CDCl₃) δ 5.99 (d, 1H, H3), 5.73 (d, 1H, J = 9.1 Hz, N-H), 5.22 (m, 1H, H4), 4.85 (d, 1H, J = 4.0 Hz, OH), 4.23-4.17 (m, 2H, H1/H2/CH₂), 3.90 (m, 2H, H5/CH₂), 3.65 (d, 1H, CH₂-octyl/NH₂), 3.61-3.49 (m, 3H, H6/H6/CH₂-octyl), 2.12 (s, 3H, OAc), 2.06 (s, 3H, OAc), 1.94 (s, 3H, NAc), 1.59 (bs, 2H, CH₂-octyl), 1.26 (bs, 10H, CH₂-octyl), 0.86 (t, 3H, CH₃-octyl). ¹³C NMR (CDCl₃) δ 172.43, 170.13, 166.46, 98.50, 79.21, 73.24, 70.48, 69.34, 66.58, 52.35, 40.64, 31.68, 29.61, 26.17, 22.73, 21.12, 14.00. MS (ES, Na⁺): m/z (relative intensity) calcd for; found 469.2 (100). HRMS (M + Na⁺) calcd for C₂₁H₃₈N₂O₈Na, 469.2526; found 469.2514.


