CHAPTER 3

A Ring Expansion-Glycosylation Strategy toward the Synthesis of Septano-oligosaccharides

ABSTRACT: A one-pot ring expansion-glycosylation reaction was performed using 1,2-cyclopropanated sugars as glycosyl donors and carbohydrate O-nucleophiles as acceptors to provide septano-hexose mimics of pyranose and furanose derivatives. The methodology was extended to synthesize septano-oligosaccharides by adopting a divergent strategy as well as an iterative protocol.

3.1 Introduction

Mimicking natural glycans is one of the intellectual ways of misleading microorganisms and enzymes that are responsible for a variety of diseases. An important method of mimicking natural carbohydrates is by expanding or contracting the ring size. The ring-expanded versions of hexoses are the so-called septanoses/carbohydrate-based oxepanes, which have been shown to be very important mimics of carbohydrates. Structure-activity studies on oral antithrombotic beciparcil derivatives revealed that ring-expansion to a seven-membered thio
sugar exhibited a 10-fold increase in activity relative to the reference compound, beciparcil.\(^3\) Protein-carbohydrate interaction studies by Peczuh et al., involving concanavalin A and methyl septanosides, provided preliminary evidence that septanosides can resemble pyranosides.\(^4\) Septanose mimics of nucleosides\(^5\) and nucleic acids\(^6\) have also been synthesized and evaluated for their antiviral and RNA-cleavage\(^7\) properties.

Even though several methods are available for the synthesis of septanose monosaccharides,\(^8\) not many reports have been published on the preparation of septanose containing oligo- and polysaccharides.\(^9,8b\) \(1,2\)-cyclopropanated sugars also serve as versatile synthons for the synthesis of carbohydrate-based oxepanes by adopting the standard Ferrier rearrangement conditions.\(^10\) In addition, the base-mediated ring-expansion of geminal dihalocyclopropanated sugar derivatives with various nucleophiles including sugar alcohols provides septanose containing mono and oligosaccharides.\(^11\) These interesting methods are discussed in chapter 1 of this thesis (section 1.4).

We envisaged that incorporating an electron-withdrawing functionality at the C-3 position of \(1,2\)-cyclopropanated sugar derivatives would provide access to cyclic donor acceptor cyclopropanes, which might undergo a regioselective electrophilic ring-opening reactions assisted by the endocyclic oxygen, to give oxepane derivatives. Based on this protocol, we herein present stereoselective ring-opening of 3-oxo-\(1,2\)-cyclopropanated sugar derivatives with carbohydrate \(O\)-nucleophilic glycosyl acceptors. Even though this kind of donor-acceptor cyclopropanes have been shown to undergo Lewis acid promoted ring-expansion with silyl enolates,\(^12\) to the best of our knowledge, this is the first report of using these sugar derivatives as glycosyl donors in oligosaccharide synthesis. Further, an iterative glycosylation technology has been developed and utilized for the synthesis of a diseptanohexose oligosaccharide.

In this chapter, we describe the stereoselective synthesis of 2,3-dideoxyseptano-hexoses by TMSOTf-mediated one-step ring-expansion glycosylation of sugar-derived \(1,2\)-cyclopropanated donors with a series of carbohydrate acceptors. To the best of our knowledge, no reports are available for the synthesis of di- and oligoseptanosides from this type of glycosyl donor.
3.2 Results and Discussion

The 3-oxo-1,2-cyclopropanated glycosyl donors were prepared from the benzyl-protected glycals in four steps. Oxidation of C3-OBn group followed by selective reduction of ketone provided the sugar-derived enol, which upon sequential syn-cyclopropanation and Swern oxidation gave the 3-oxo-1,2-cyclopropanated sugar derivatives in good yield. Initially, oxidation of 3,4,6-tri-0-benzyl-D-glucal 1 with [hydroxy(tosyloxy)iodo]benzene (HTIB or Koser’s reagent) in acetonitrile gave the sugar-derived enone 2 in moderate yield. Luche reduction of 2 produced the allal derivative 3 as a single diastereomer. Hydroxyl-directed cyclopropanation of 3 using CH2I2 and Et2Zn under Simmons-Smith reaction conditions produced 1,2-cyclopropanated allose derivative 4, which upon Swern oxidation provided the 1,2-cyclopropan-3-pyranone 5 in excellent yield (Scheme 3.1).

Reagents and Conditions: (i) PhIOH(OTs), 4 Å MS, CH3CN, 0 °C to rt, 75 min; (ii) NaBH4, CeCl3.7H2O, MeOH, -78 °C, 1 h; (iii) CH2I2, Et2Zn, Et2O, 0 °C, 5 h; (iv) (COCl)2, DMSO, Et3N, CH2Cl2, -78 °C, 1 h.

Scheme 3.1: Synthesis of D-glucose-derived 1,2-cyclopropanated donor

3.2.1 Discovery and Optimization of the Ring-Expansion–Glycosylation Reaction

Our preliminary investigations focused on optimization of the glycosylation reaction conditions using 5 as the glycosyl donor and sugar-derived O-nucleophiles as glycosyl acceptors. The sugar acceptor possessing free OH at 6th position was used as a model acceptor for the glycosylation reaction. The preparation of these glycosyl acceptors is discussed in chapter 2 of this thesis (section 2.2). Toward this, 5 (1 mmol) was glycosylated with 2,3,4,5-di-O-isopropylidene-α-D-fructopyranose 6 (1.1 mmol) as an acceptor in CH2Cl2.
at -78 °C using catalytic BF₃·Et₂O (0.2 equiv) as Lewis acid. The glycosylation reaction proceeded smoothly and provided the septanohexose disaccharide 7 in 65% yield, respectively (Table 1, entry 1). A slight improvement that favored the α-glycoside formation was observed by using (CF₃SO₂)₂O or InCl₃ as Lewis acids under similar reaction conditions (Table 3.1, entries 2 and 4). Interestingly, when TMSOTf was used as a catalyst, the ring-expansion glycosylation proceeded fruitfully, with excellent α-selectivity, providing the disaccharide 7 with 1:0.11 (α:β) selectivity in excellent yield (Table 3.1, entry 5). Carrying out the reaction either at -78 °C or from -10 to 0 °C did not improve the stereoselectivity of the glycosylation reaction (Table 3.1, entries 6 and 7).

**Table 3.1**: Optimization of reaction conditions for one-step ring-expansion-glycosylation reaction using 1,2-cyclopropanated sugar donor 5.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst (0.2 equiv)</th>
<th>temperature conditions (°C)</th>
<th>yield</th>
<th>α:β&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BF₃·OEt₂</td>
<td>-78 to +25</td>
<td>65%</td>
<td>1.0:71</td>
</tr>
<tr>
<td>2</td>
<td>(CF₃SO₂)₂O</td>
<td>-78 to +25</td>
<td>60%</td>
<td>1.0:57</td>
</tr>
<tr>
<td>3</td>
<td>InCl₃</td>
<td>-78 to +25</td>
<td>&lt;5</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>InCl₃&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-78 to +25</td>
<td>50%</td>
<td>1.0:45</td>
</tr>
<tr>
<td>5</td>
<td>TMSOTf</td>
<td>-78 to +25</td>
<td>89%</td>
<td>1.0:11</td>
</tr>
<tr>
<td>6</td>
<td>TMSOTf</td>
<td>-78</td>
<td>72%</td>
<td>1.0:71</td>
</tr>
<tr>
<td>7</td>
<td>TMSOTf</td>
<td>-10 to 0</td>
<td>82%</td>
<td>1.0:42</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yield represents pure and isolated products. <sup>b</sup>1 equiv of catalyst was used. <sup>c</sup>Based on septanosyl anomeric proton ratio

### 3.2.2 Plausible Mechanistic Pathway

The major α-glycosylated product can be envisaged arising by a preferential approach of the nucleophile along an axial trajectory toward the oxocarboxonium ion intermediate.¹⁸ As shown in Scheme 3.2, activation of the glycosyl donor 5 with TMSOTf would generate the oxocarbenium ion intermediate 8 via the cleavage of C1-C2 bond. The trimethylsilyl enolate
8 would react with acceptor 6, preferentially in the axial direction, due to the anomeric effect,\(^{19}\) provide the α-selective septanohexose 7 as the major product.

\[ \text{Scheme 3.2: Proposed mechanism for the stereoselective formation of } \alpha\text{-glycoside} \]

### 3.2.3 Scope of the Reaction

After optimizing the reaction conditions, the aforementioned ring expansion-glycosylation was extended to the various sugar derived 1,2-cyclopropa-3-pyranone donors and carbohydrate-derived \(O\)-nucleophilic glycosyl bond acceptors.

**Synthesis of sugar-derived 1,2-cyclopropa-3-pyranone donors**

Like D-glucose-derived 1,2-cyclopropanone 5, three more glycosyl donors were efficiently synthesized from the benzyl-protected glycals in good to excellent yield.

\[ \text{Scheme 3.3: Synthesis of D-galactose-derived 1,2-cyclopropanated donor} \]

**Reagents and Conditions:** (i) PhIOH(OTs), 4 Å MS, CH\(_2\)CN, 0 °C to rt, 75 min; (ii) NaBH\(_4\), CeCl\(_3\).7H\(_2\)O, MeOH, -78 °C, 1 h; (iii) CH\(_3\)I\(_2\), Et\(_2\)Zn, Et\(_2\)O, 0 °C, 5 h; (iv) (COCl\(_2\)), DMSO, Et\(_3\)N, CH\(_3\)Cl\(_2\), -78 °C, 1 h.
The oxidation of 3,4,6-tri-\(O\)-benzyl D-galactal 9 with Koser’s reagent in CH\(_3\)CN gave the D-galactose-based enone 10 which upon Luche reduction at -78 °C provided the 4,6-di-\(O\)-benzyl D-galactal 11 as a single diastereomer. Selective benzylation of D-galactal using sodium hydride and benzyl bromide in DMF also provide 11 but with moderate yield. Simmons-Smith cyclopropantion of 11 with CH\(_2\)I\(_2\)/Et\(_2\)Zn produced exclusive syn-cyclopropanated sugar derivative 12 which gave the D-galactose-derived 1,2-cyclopropa-3-pyranone 13 under the Swern oxidation conditions in excellent yield (Scheme 3.3).

Similarly, 3,4-di-\(O\)-benzyl D-arabinal 14 was oxidized with Koser’s reagent to give the D-arabinose-derived enone 15 which upon Luche reduction with NaBH\(_4\) in presence of CeCl\(_3\).7H\(_2\)O provided the 4-\(O\)-benzyl D-arabinal 16. Hydroxyl directed cyclopropantaion of 16 with CH\(_2\)I\(_2\)/Et\(_2\)Zn in ether at 0 °C afforded the cyclopropane adduct 17 as a single diastereomer. Swern oxidation of 17 gave the D-arabinose-derived 1,2-cyclopropa-3-pyranone 18 in excellent yield (Scheme 3.4). The 18 could also be synthesized from 3,4-di-\(O\)-benzyl D-xylal using the same series of reactions.

Reagents and Conditions: (i) PhIOH(OTs), 4 Å MS, CH\(_3\)CN, 0 °C to rt, 75 min; (ii) NaBH\(_4\), CeCl\(_3\).7H\(_2\)O, MeOH, -78 °C, 1 h; (iii) CH\(_2\)I\(_2\), Et\(_2\)Zn, Et\(_2\)O, 0 °C, 5 h; (iv) (COCl)\(_2\), DMSO, Et\(_3\)N, CH\(_2\)Cl\(_2\), -78 °C, 1 h.

Scheme 3.4: Synthesis of D-arabinose-derived 1,2-cyclopropanated donor

In addition to this, we also prepared 6-deoxy 1,2-cyclopropanated sugar donor for the ring-expansion glycosylation reaction. The treatment of 3,4-di-\(O\)-benzyl D-rhamnal 19, which was synthesized using a well known procedure\(^{20}\) from the D-glucal in three steps, with Koser’s reagent gave the D-rhamnose-derived enone 20. Luche reduction of 20 provided enol 21 which on cyclopropanation under the Simmons-Smith reaction conditions furnished the
cyclopropyl adduct 22. Swern oxidation of 22 gave the D-rhamnose-derived cyclopropane 23 in good yield (Scheme 3.5).

**Scheme 3.5**: Synthesis of D-rhamnose-derived 1,2-cyclopropanated donor

**Synthesis of Glycosyl Acceptors**

In chapter 2 (section 2.2), we have discussed the synthesis of 2,3;4,5-di-O-isopropylidene-α-D-fructopyranose 6 and 1,2;3,4-di-O-isopropylidene-α-D-galactose 24, which were prepared from D-fructose and D-galactose respectively in one-step. In order to prepare the other carbohydrate derived O-nucleophiles, we used methyl 4,6-O-benzylidene-α-D-glucopyranoside 25 (vide supra see chapter 2, section 2.2) for the synthesis of sugar acceptors possessing the hydroxyl group at C2 and C3. The selective benzylation of 25 with sodium hydride and benzyl bromide in presence of copper (II) chloride at reflux conditions provided the methyl 3-O-benzyl 4,6-O-benzylidene-α-D-glucopyranoside 26 in 70% yield.

**Scheme 3.5**: Synthesis of glycosyl acceptors
On the other hand, benzylation of 24 with 1 equivalent of sodium hydride and 1 equivalent of benzyl bromide in DMF gave the methyl 2-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside 27 in 55% yield as isolated product (Scheme 3.5).

Furthermore, enone-based glycosyl acceptors were prepared and evaluated their reactivity toward the glycosylation process. Protection of 6-OH in D-glucal 28 with tert-butyldimethylsilyl (TBS) group using TBDMS chloride in presence of imidazole gave the 6-O-tet-butyldimethylsilyl D-glucal 29, which upon oxidation with pyridinium dichromate (PDC) in dichloromethane provided the glycosyl acceptor 30 in good yield. Similarly, D-rhamnal 31 was oxidized with PDC in dichloromethane to give the 6-deoxy sugar acceptor 32 in excellent yield. By utilizing the enone functionality, 32 has been used in the iterative process for the synthesis of septano-oligosaccharides.

![Scheme 3.6: Synthesis of enone-based glycosyl acceptors](image)

*Reagents and Conditions:* (i) TBSCl (1 eq), Imidazole, 0°C to rt, 10 h; (ii) PDC, CH2Cl2, 0°C to rt, 3 h.

The glycosyl donors and acceptors in hand, we intended to synthesize various septanose containing di- and oligosaccharides. Thus, the reaction of acceptor 24 with 1,2-cyclopropanated donors 5 and 13 gave rise to septanohexose derivatives 33 and 34, respectively, with modest diastereoselectivity at the newly formed C1' anomeric center (α:β (7:3)) in excellent yield (Table 3.2, entries 1 and 2). The methodology was also applied to the sugar acceptors possessing less reactive secondary alcohols. Thus, different 1,2-cyclopropan-3-pyranone donors 5, 13, and 18 were glycosylated with the sugar acceptor 26, possessing a free hydroxyl group at the C2 position (Table 3.2, entries 3, 4 and 5). Interestingly, donors 5 and 18, upon glycosylation with 26, provided selectively the α-glycosylated septanohexoses 35 and 37, whereas donor 13 with acceptor 26 provided a diastereomeric mixture of 36a and
Table 3.2: Stereoselective synthesis of septanohexoses

<table>
<thead>
<tr>
<th>entry</th>
<th>donor cyclopropane</th>
<th>acceptor</th>
<th>septano-hexose derivatives (%)</th>
<th>α:β ratio</th>
</tr>
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<tr>
<td>1</td>
<td><img src="image1.png" alt="image" /></td>
<td><img src="image2.png" alt="image" /></td>
<td><img src="image3.png" alt="image" /></td>
<td>7:3</td>
</tr>
<tr>
<td>2</td>
<td><img src="image4.png" alt="image" /></td>
<td><img src="image5.png" alt="image" /></td>
<td><img src="image6.png" alt="image" /></td>
<td>7:3</td>
</tr>
<tr>
<td>3</td>
<td><img src="image7.png" alt="image" /></td>
<td><img src="image8.png" alt="image" /></td>
<td><img src="image9.png" alt="image" /></td>
<td>Only α</td>
</tr>
<tr>
<td>4</td>
<td><img src="image10.png" alt="image" /></td>
<td><img src="image11.png" alt="image" /></td>
<td><img src="image12.png" alt="image" /></td>
<td>7:3</td>
</tr>
<tr>
<td>5</td>
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<td><img src="image14.png" alt="image" /></td>
<td><img src="image15.png" alt="image" /></td>
<td>Only α</td>
</tr>
<tr>
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<td><img src="image16.png" alt="image" /></td>
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<td><img src="image18.png" alt="image" /></td>
<td>Only α</td>
</tr>
<tr>
<td>7</td>
<td><img src="image19.png" alt="image" /></td>
<td><img src="image20.png" alt="image" /></td>
<td><img src="image21.png" alt="image" /></td>
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</tr>
<tr>
<td>8</td>
<td><img src="image22.png" alt="image" /></td>
<td><img src="image23.png" alt="image" /></td>
<td><img src="image24.png" alt="image" /></td>
<td>Only α</td>
</tr>
<tr>
<td>9</td>
<td><img src="image25.png" alt="image" /></td>
<td><img src="image26.png" alt="image" /></td>
<td><img src="image27.png" alt="image" /></td>
<td>Only α</td>
</tr>
</tbody>
</table>
\( \text{36}\beta \) in 7:3 ratio, respectively (Table 3.2, entry 4). The structure of the minor diastereomer \( \text{36}\beta \) was confirmed by X-ray crystallography (Figure 3.1).\(^{26}\)

![Figure 3.1: ORTEP diagrams of septanohexose \( \text{36}\beta \)](image)

Glycosylation of donors 5, 18, and 23 with acceptor 27, in which the free hydroxyl is at C3, provided the corresponding septanohexoses 38, 39, and 40 as single diastereomers with the \( \alpha \)-configuration at the newly formed glycosidic center (Table 3.2, entries 6, 7 and 8). The stereochemistry at C1' for all the disaccharide derivatives was assigned based on the chemical shift value of the anomeric carbon\(^{27}\) (\( \delta_{C1'} \) for \( \alpha \)-septanosides ranges from 99 to 104 ppm while for \( \beta \)-septanosides it ranges from \( \delta \) 104-111 ppm) as well as two-dimensional NMR experiments. For the septanohexoses possessing a \( \beta \)-glycosidic bond, a strong NOE was observed between the 1,3-diaxial hydrogens at C1' and C6' which was absent in the case of septanosides with \( \alpha \)-glycosidic linkage.

The sugar-derived enone acceptor 30 was also very reactive toward the one-step ring-expansion-glycosylation reaction with donor 23 and produced the disaccharide derivative 41 as a single diastereomer in excellent yield (Table 3.2, entry 9). It is well-known that the stereoselectivity in the glycosylation of hexose derived oxocarbenium ions is dictated by stereoelectronic effects in the glycosyl donor and the nonbonding steric interactions from the glycosyl acceptors.\(^{18,28}\) The above experimental results provide an ample evidence that similar effects play a role in the glycosylation of septanosides as well.
3.2.4 Synthesis of Diseptano-hexose Trisaccharides

After successful synthesis of a series of septanohexose disaccharide derivatives, we focused our attention on the synthesis of diseptanohexose trisaccharides. Thus, stereoselective reduction of disaccharide 38 with lithium tri-tert-butoxyaluminum hydride in ethanol at -78 °C provided the acceptor alcohol 42 (Scheme 3.7). However, the glycosylation of donor 5 with acceptor 42 did not happen under the optimized reaction conditions. The orientation of hydroxyl group at C4’ was deduced based on 1H and COSY NMR analysis.

Reagents and Conditions: (i) LiAl(OtBu)₃H, EtOH, -78 °C, 1 h; (ii) TMSOTf, CH₂Cl₂, -78 °C to rt, 3 h.

Scheme 3.7: Attempts to synthesis of diseptanohexose trisaccharide

We reasoned that the very low reactivity of the acceptor 42 might be due to the axial orientation of hydroxyl group. Therefore, inversion of the axial hydroxyl in 42 via Mitsunobu

Reagents and Conditions: (i) PNB-OH, DIAD, Ph₃P, THF, rt, 8 h; (ii) NaOMe/MeOH, rt, 1 h; (iii) TMSOTf, 4 Å MS, CH₂Cl₂, -78 °C to rt, 3 h; (iv) LiAl(OtBu)₃H, EtOH, -78 °C, 1 h.

Scheme 3.8: Synthesis of diseptanohexose trisaccharide
reaction provided disaccharide-based benzoate 43. The deprotection of benzoate 43 with NaOMe/MeOH gave the disaccharide acceptor 44. Gratifyingly, glycosylation of 5 with acceptor disaccharide 44 proceeded smoothly, generating the diagnostanohexose trisaccharide derivative 45 as a single diastereomer (Scheme 3.8). Stereoselective reduction of ketone 45 provided the trisaccharide acceptor 46-α,α which can be used further for the synthesis of septano-oligosaccharides. The stereochemistry of trisaccharides was deduced based on the chemical shift value of anomeric carbons of septanose residues.

3.2.5 Iterative protocol for the synthesis of septano-oligosaccharides

Finally, an iterative protocol for the synthesis of septano-oligosaccharides was investigated. Many biologically active natural products possess deoxysugar subunits in their structures. Therefore, we planned to use 6-deoxy glucal derived 1,2-cyclopropanated sugar 23 as a glycosyl donor and alcohol 32 as an acceptor. Thus, glycosylation of 23 with 32 provided disaccharide 47 as a single diastereomer in good yield. Reduction of diketone 47 to the corresponding diol, followed by Simmons-Smith cyclopropanation and subsequent Swern oxidation of the diol provided the donor 48 as a mixture of α- and β-cyclopropanated products in 2:1 ratio, respectively, in 75% yield after three steps. Glycosidation of 48 with acceptor 32, using TMSOTf in CH2Cl2 at -78 °C, provided the trisaccharide derivative 49 as a single diastereomer in which the second glycosylation was also α selective (Scheme 3.9).

![Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH2Cl2, -78 °C, 3 h; (ii) CeCl3·7H2O, NaBH4, MeOH, -78 °C, 1 h; (iii) CH3I, Et2Zn, Et2O, 0 °C, 5 h; (iv) (COCl)2, DMSO, Et3N, CH2Cl2, -78 °C, 1 h; (v) TMSOTf, 4 Å MS, CH2Cl2, -78 °C, 3 h.](attachment:image.png)

Scheme 3.9: Iterative protocol for the synthesis of septano-oligosaccharides.
3.3 Summary and Conclusion

A novel ring expansion-glycosylation reaction has been developed for the synthesis of septanose derivatives which uses sugar-derived 1,2-cyclopropa-3-pyranones as glycosyl donors and carbohydrate-derived O-nucleophiles as acceptors. The generality of the reaction was evaluated by performing a number of glycosylation reactions and synthesizing several septanohexose derivatives. Two different methods (a divergent synthesis and an iterative technique) for the synthesis of septanose-derived oligosaccharides were successfully performed. Ligation of these ring-expanded sugar mimics to natural products and evaluation of their biological properties are presently under investigation.

3.4 Experimental Section

3.4.1 Materials and Methods

Chemicals and solvents were purchased from the local suppliers and Sigma-Aldrich® chemical company. Solvents were used in the reactions after distilled over the dehydrated agents. 4 Å Molecular sieves, used in the reactions, were crushed and activated at 400 °C for 1 h. All the reactions were carried out under N₂ or Ar conditions and monitored by the thin layer chromatography (TLC) using silica-gel on aluminum plates (GF₂₅₄) by charring with 5% (v/v) H₂SO₄ in methanol or by phosphomolybdic acid (PMA) stain or by ultra violet (UV) detection. Silica-gel (100-200 mesh) was used for column chromatography to purify the all the compounds. ¹H, ¹³C, DEPT spectra were recorded on Bruker® 400 MHz and 500 MHz spectrometers in CDCl₃. ¹H NMR chemical shifts were reported in parts per million (ppm) (δ) with TMS as internal standard (δ 0.00) and ¹³C NMR were reported in chemical shifts with solvent reference (CDCl₃, δ 77.00). High resolution mass spectra (HRMS) were recorded on Bruker® maXis spectrometer.

3.4.2 Experimental Procedures and Spectral Data

(3.4.2.1) 4,6-di-O-benzyl-1,5-anhydro-2-deoxy-α-1,2-C-methylene-D-allo-pyranose 4:

Reagents and Conditions: (i) CH₂I₂, Et₂Zn, Et₂O, 0 °C, 5 h.
To a solution of 3 (1.5 g, 4.6 mmol) in ether (15 mL) at 0 °C was added 1 M Et₂Zn in hexane (13.7 mL, 13.7 mmol) and CH₂I₂ (1.2 mL, 13.7 mmol). The mixture was stirred for 5 h at the same temperature, then quenched with saturated NH₄Cl solution (75 mL) and extracted with ether (75 mL x 2). The combined organic layers were washed with water (50 mL), brine (50 mL) and dried over anhydrous Na₂SO₄. Purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (3:7) provided 4 (1.4 g, 90%) as a colorless solid. Rᵣ = 0.32 (2:3 ethyl acetate/hexane).

**Rᵣ** = 0.32 (2:3 ethyl acetate/hexane).

1H NMR (400 MHz, CDCl₃): δ 7.22 - 7.32 (m, 10H), 4.69 (d, 1H, J = 12.0 Hz), 4.60 (d, 1H, J = 12.0 Hz), 4.58 (d, 1H, J = 12.0 Hz), 4.53 (d, 1H, J = 12.0 Hz), 4.26 (t, 1H, J = 7.2 Hz), 3.74 – 3.78 (m, 1H), 3.68 (dd, 1H, J = 2.0 Hz, J = 10.8 Hz), 3.56 (dd, 1H, J = 4.8 Hz, J = 10.4 Hz), 3.41 – 3.45 (m, 1H), 3.23 (dd, 1H, J = 7.6 Hz, J = 9.2 Hz), 1.34 – 1.42 (m, 1H), 0.66 – 0.76 (m, 2H).

13C NMR (100 MHz, CDCl₃): δ 138.2, 137.9, 128.4, 128.2, 127.8, 127.7, 127.5, 79.7, 77.5, 74.0, 73.5, 71.3, 69.1, 53.9, 18.3, 11.4.

HRMS (ESI) calcd for C₂₁H₂₄O₄+Na 363.1573, found 363.1573.

**(3.4.2.2) Compound 5:**

Reagents and Conditions: (i) (COCl)₂, DMSO, Et₃N, CH₂Cl₂, -78 °C, 1 h.

To a solution of (COCl)₂ (380 µL, 4.4 mmol) in CH₂Cl₂ (12 mL) at -78 °C was added DMSO (520 µL, 7.3 mmol) dropwise. After 10 min of stirring at the same temperature, 4 (1 g, 2.9 mmol) in CH₂Cl₂ (12 mL) was added dropwise for a period of 15 min. After stirring for 30 min at -78 °C, Et₃N (1.47 mL, 14.5 mmol) was added and allowed to warm to room temperature. The reaction mixture was diluted with CH₂Cl₂ (75 mL), washed with water (50 mL x 2), brine (50 mL) and dried over anhydrous Na₂SO₄. Removal of solvent gave the crude residue which upon purification by silica-gel column chromatography with ethyl acetate/hexane (3:7) provided D-glucose-derived 1,2-cyclopropa-3-pyranone 5 (980 mg, 99%) as a colorless solid. Rᵣ = 0.58 (2:3 ethyl acetate/hexane).
1H NMR (400 MHz, CDCl₃): δ 7.26 - 7.35 (m, 10H), 4.97 (d, 1H, J = 11.2 Hz), 4.59 (d, 1H, J = 12.0 Hz), 4.53 (d, 1H, J = 12.0 Hz), 4.50 (d, 1H, J = 11.2 Hz), 4.17 – 4.20 (m, 1H), 4.00 (ddd, 1H, J = 2.0 Hz, J = 4.4 Hz, J = 10.0 Hz), 3.91 (d, 1H, J = 10.0 Hz), 3.72 (dd, 1H, J = 4.4 Hz, J = 10.8 Hz), 3.62 (dd, 1H, J = 4.4 Hz, J = 10.8 Hz), 1.92 (dt, 1H, J = 6.0 Hz, J = 10.8 Hz), 1.27 – 1.37 (m, 2H).

13C NMR (100 MHz, CDCl₃): δ 205.0, 137.8, 137.4, 128.3, 128.3, 128.1, 127.8, 127.7, 127.6, 81.5, 77.6, 74.1, 73.6, 68.8, 57.8, 25.7, 19.8.

HRMS (ESI) calcd for C₂₁H₂₂O₄+Na 361.1416, found 361.1416.

(3.4.2.3) General procedure for ring expansion-glycosylation reaction:
A suspension of 1,2-cyclopropanated sugar ketone (0.3 mmol), glycosyl acceptor (0.33 mmol) and 4 Å MS powder in dry CH₂Cl₂ (5 mL) was stirred at room temperature for 30 min under argon. After cooling the reaction mixture to -78 °C, TMSOTf (0.06 mmol) was added dropwise and the solution was warmed slowly to 25 °C for a period of 1 h and stirred for 3 h at the same temperature. After completion of reaction (by TLC), the reaction mixture was quenched with saturated NaHCO₃ solution (5 mL), filtered through celite and the filter cake was washed with CH₂Cl₂ (20 mL x 2). The organic phase was separated and washed with aq. NaHCO₃ (10 mL x 2), water (10 mL) and brine (5 mL). Removal of CH₂Cl₂ under reduced pressure provided the crude disaccharide which upon purification by silica-gel column chromatography (ethyl acetate/hexane) afforded pure septanosyl disaccharide.

(3.4.2.4) Compound 7:

Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH₂Cl₂, -78 °C to rt, 4 h

Compound 7 was synthesized using D-glucose-derived 1,2-cyclopropanated 1,2-cyclopropa-3-pyranone 5 (100 mg, 0.29 mmol), glycosyl acceptor 6 (84 mg, 0.32 mmol), TMSOTf (10 µL, 0.05 mmol) and 4 Å MS power in CH₂Cl₂ (5 mL) according to the general procedure for ring expansion-glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 1 h and at 25 °C for 3 h. The crude product was purified by silica-gel column chromatography (ethyl
acetate/hexane 3:7) to afford septanosyl disaccharide 7 (156 mg, 89%) as a colorless oil. R_f = 0.53 (2:3 ethyl acetate/hexane).

^1^H NMR (400 MHz, CDCl_3): δ 7.26 - 7.31 (m, 10H), 4.96 (dd, 1H, J = 4.4 Hz, J = 8.0 Hz), 4.58 - 4.64 (m, 3H), 4.49 (d, 1H, J = 12.0 Hz), 4.41 (d, 1H, J = 12.0 Hz), 4.34 (d, 1H, J = 2.8 Hz), 4.22 - 4.27 (m, 2H), 4.01 (d, 1H, J = 7.2 Hz), 3.96 (d, 1H, J = 10.4 Hz), 3.90 (d, 1H, J = 12.8 Hz), 3.73 (d, 1H, J = 12.8 Hz), 3.67 (dd, 1H, J = 4.0 Hz, J = 10.0 Hz), 3.57 (dd, 1H, J = 4.0 Hz, J = 10.0 Hz), 3.52 (d, 1H, J = 10.4 Hz), 2.58 (dd, 1H, J = 2.8 Hz, J = 6.4 Hz, J = 14.4 Hz), 2.44 (td, 1H, J = 2.8 Hz, J = 14.4 Hz), 2.25 - 2.32 (m, 1H), 2.05 - 2.10 (m, 1H), 1.52 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.31 (s, 3H).

^13^C NMR (100 MHz, CDCl_3): δ 208.4, 137.9, 137.3, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 108.9, 108.5, 105.8, 104.5, 100.5, 84.1, 73.4, 73.0, 70.9, 70.4, 70.1, 70.0, 69.1, 68.5, 61.0, 35.6, 28.0, 26.5, 25.9, 25.3, 24.0.

HRMS (ESI) calcd for C_{33}H_{42}O_{10}^+Na 621.2676, found 621.2686.

(3.4.2.5) 4,6-di-O-benzyl-1,5-anhydro-2-deoxy-α-1,2-C-methylene-D-galacto-pyranose 12:

\[ \begin{align*}
11 & \xrightarrow{0 \text{h}} 12 \\
\text{Reagents and Conditions: (i) CH}_2\text{I}_2, \text{Et}_2\text{Zn, Et}_2\text{O, 0 °C, 5 h.}
\end{align*} \]

To a solution of 4,6-di-O-benzyl-D-galactal 11 (1 g, 3.06 mmol) in ether (10 mL) at 0 °C was added 1 M Et_2Zn in hexane (9.2 mL, 9.2 mmol) and CH_2I_2 (0.74 mL, 9.19 mmol). The mixture was stirred for 5 h at same temperature, then quenched with saturated NH_4Cl solution (75 mL) and extracted with ether (50 mL x 2). The combined organic layers were washed with water (30 mL), brine (30 mL) and dried over anhydrous Na_2SO_4. Purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (2:3) provided 4,6-di-O-benzyl-1,5-anhydro-2-deoxy-α-1,2-C-methylene-D-galacto-pyranose 12 (0.92 g, 89%) as a colorless oil. R_f = 0.32 (2:3 ethyl acetate/hexane).

^1^H NMR (400 MHz, CDCl_3): δ 7.23 - 7.31 (m, 10H), 4.61 (d, 1H, J = 11.6 Hz), 4.53 (d, 1H, J = 11.6 Hz), 4.51 (d, 1H, J = 11.6 Hz), 4.40 (d, 1H, J = 11.6 Hz), 4.16 (t, 1H, J = 6.0 Hz), 3.73 - 3.79 (m, 2H), 3.50 - 3.56 (m, 2H), 3.38 - 3.41 (m, 1H), 1.19 - 1.25 (m, 1H), 1.09
-1.10 (m, 1H), 0.58 – 0.61 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.0, 137.6, 128.3, 127.8, 127.6, 127.5, 76.4, 75.6, 75.5, 73.3, 68.8, 65.3, 54.0, 16.9, 11.1.

**HRMS (ESI)** calcd for C\(_{21}\)H\(_{24}\)O\(_4\)+Na 363.1573, found 363.1573.

**Chapter 3**

**(3.4.2.6) Compound 13:**

\[
\begin{align*}
\text{Reagents and Conditions:} & \quad (i) (\text{COCl})_2, \text{DMSO, Et}_3\text{N, CH}_2\text{Cl}_2, -78 ^\circ\text{C, 1 h.} \\
\end{align*}
\]

To a solution of oxaloyl chloride (342 µL, 3.96 mmol) in CH\(_2\)Cl\(_2\) (10 mL) at -78 °C was added DMSO (468 µL, 6.6 mmol) dropwise. After 10 min of stirring at the same temperature, 4,6-di-O-benzyl-1,5-anhydro-2-deoxy-\(\alpha\)-1,2-C-methylene-D-galacto-pyranose 12 (0.9 g, 2.64 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added dropwise for a period of 15 min. After stirring for 30 min at -78 °C, Et\(_3\)N (1.8 mL, 13.0 mmol) was added and allowed to warm to room temperature. The reaction mixture was diluted with CH\(_2\)Cl\(_2\) (75 mL), washed with water (50 mL x 2), brine (50 mL) and dried over anhydrous Na\(_2\)SO\(_4\). Removal of solvent gave the crude residue which upon purification by silica-gel column chromatography with ethyl acetate/hexane (3:7) provided D-galactose-derived 1,2-cyclopropa-3-pyranone 13 (885 mg, 99%) as a colorless liquid. \(R_f = 0.64\) (2:3 ethyl acetate/hexane).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.23 – 7.32 (m, 10H), 4.61 (d, 1H, \(J = 11.6\) Hz), 4.52 (d, 1H, \(J = 11.6\) Hz), 4.40 (d, 1H, \(J = 12.0\) Hz), 4.38 (d, 1H, \(J = 12.0\) Hz), 4.16 – 4.19 (m, 1H), 4.03 (t, 1H, \(J = 6.0\) Hz), 3.62 – 3.66 (m, 2H), 3.48 (dd, 1H, \(J = 6.0\) Hz, \(J = 9.6\) Hz), 1.83 – 1.87 (m, 1H), 1.72 – 1.78 (m, 1H), 1.23 – 1.28 (m, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 201.9, 137.6, 136.8, 128.2, 128.0, 128.0, 127.8, 127.6, 80.0, 79.5, 73.4, 71.5, 68.3, 58.0, 23.8, 19.0.

**HRMS (ESI)** calcd for C\(_{21}\)H\(_{22}\)O\(_4\)+Na 361.1416, found 361.1416.

**(3.4.2.7) 4-O-benzyl-D-arabinal 16:**

\[
\begin{align*}
\text{Reagents and Conditions:} & \quad \text{CeCl}_3.7\text{H}_2\text{O, NaBH}_4, \text{MeOH, -78 °C, 1 h.}
\end{align*}
\]
To a solution of sugar enone 15 (2 g, 9.8 mmol) and CeCl₃·7H₂O (5.47 g, 14.7 mmol) in MeOH (30 mL) at -78 °C was added cooled (-10 °C) solution of NaBH₄ (556 mg, 14.7 mmol) in MeOH (12 mL) dropwise for a period of 10 min. The solution was stirred for 1 h at -78 °C, then quenched with saturated NH₄Cl and extracted twice with ethyl acetate (100 mL x 2). The combined organic layers were washed with water (75 mL), brine (75 mL) and dried (Na₂SO₄). Removal of solvent and purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (1:4) gave 4-O-benzyl-D-arabinal 16 (1.8 g, 90%) as a colorless oil. R_f = 0.6 (3:7 ethyl acetate/hexane).

**1H NMR (400 MHz, CDCl₃):** δ 7.29 – 7.35 (m, 5H), 6.38 (d, 1H, J = 6.0 Hz), 4.86 (dd, 1H, J = 5.2 Hz, J = 6.0 Hz), 4.65 (s, 1H), 4.64 (s, 1H), 4.21 (t, 1H, J = 4.4 Hz), 3.92 (s, 1H), 3.90 (s, 1H), 3.70 (dd, 1H, J = 4.0 Hz, J = 6.0 Hz), 3.68 (dd, 1H, J = 4.0 Hz, J = 6.0 Hz), 2.59 (bs, 1H).

**13C NMR (100 MHz, CDCl₃):** δ 146.2, 137.4, 128.4, 128.0, 127.7, 100.9, 73.1, 71.3, 62.3, 60.6. HRMS (ESI) calcd for C₂₁H₂₄O₄⁺Na 229.0841, found 229.0841.

(3.4.2.8) 4-O-benzyl-1,5-anhydro-2-deoxy-α-1,2-C-methylene-d-arabino-pyranose 17:

![Chemical Structure](image)

**Reagents and Conditions:** (i) CH₂I₂, Et₂Zn, Et₂O, 0 °C, 5 h.

To a solution of 4-O-benzyl-D-arabinal 16 (700 mg, 3.39 mmol) in ether (10 mL) at 0 °C was added 1 M Et₂Zn in hexane (10.2 mL, 10.2 mmol) and CH₂I₂ (0.81 mL, 10.18 mmol). The mixture was stirred for 5 h at same temperature, then quenched with saturated NH₄Cl solution (75 mL) and extracted with ether (50 mL x 2). The combined organic layers were washed with water (50 mL), brine (50 mL) and dried over anhydrous Na₂SO₄. Removal of solvent followed by purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (3:7 to 2:3) provided 4-O-benzyl-1,5-anhydro-2-deoxy-α-1,2-C-methylene-d-arabino-pyranose 17 (672 mg, 90%) as a colorless liquid. R_f = 0.27 (3:7 ethyl acetate/hexane).

**1H NMR (400 MHz, CDCl₃):** δ 7.26 – 7.33 (m, 5H), 4.64 (d, 1H, J = 11.6 Hz), 4.37 (d, 1H, J = 11.6 Hz), 4.17 (bs, 1H), 3.83 (dd, 1H, J = 3.2 Hz, J = 12.4 Hz), 3.70 –
3.74 (m, 1H), 3.57 – 3.59 (m, 1H), 3.25 (d, 1H, J = 12.4 Hz), 2.79 (d, 1H, J = 9.6 Hz), 1.14 – 1.25 (m, 2H), 0.57 – 0.62 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.6, 128.2, 127.6, 127.5, 74.9, 71.1, 64.1, 63.9, 53.9, 16.4, 10.8.

HRMS (ESI) calcd for C$_{13}$H$_{16}$O$_3$+Na 243.0997, found 243.0997.

(3.4.2.9) Compound 18:

![Diagram of compounds 17 and 18](image)

Reagents and Conditions: (i) (COCl)$_2$, DMSO, Et$_3$N, CH$_2$Cl$_2$, -78 °C, 1 h.

To a solution of (COCl)$_2$ (293 µL, 3.40 mmol) in CH$_2$Cl$_2$ (8 mL) at -78 °C was added DMSO (403 µL, 5.67 mmol) dropwise. After 10 min of stirring at the same temperature, the above 4-O-benzyl-1,5-anhydro-2-deoxy-α-1,2-C-methylene-D-arabino-pyranose 17 (500 mg, 2.27 mmol) in CH$_2$Cl$_2$ (8 mL) was added dropwise for a period of 15 min. After stirring for 30 min at -78 °C, Et$_3$N (1.5 mL, 11.2 mmol) was added and allowed to warm to room temperature. The reaction mixture was diluted with CH$_2$Cl$_2$ (50 mL), washed with water (25 mL x 2), brine (25 mL) and dried over anhydrous Na$_2$SO$_4$. Removal of solvent gave the crude residue which upon purification by silica-gel column chromatography with ethyl acetate/hexane (1:4) provided compound 18 (490 mg, 99%) as a colorless oil. $R_f$ = 0.48 (3:7 ethyl acetate/hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.26 – 7.34 (m, 5H), 4.90 (d, 1H, J = 12.0 Hz), 4.59 (d, 1H, J = 12.0 Hz), 4.13 (dd, 1H, J = 4.0 Hz, J = 9.6 Hz), 3.94 (dd, 1H, J = 5.2 Hz, J = 10.0 Hz), 3.85 (dd, 1H, J = 5.6 Hz, J = 10.4 Hz), 3.74 (t, 1H, J = 10.4 Hz), 1.85 – 1.91 (m, 1H), 1.25 – 1.29 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 204.0, 137.3, 128.3, 127.8, 127.7, 76.3, 73.0, 71.0, 59.1, 25.7, 19.5.

HRMS (ESI) calcd for C$_{13}$H$_{14}$O$_3$+Na 241.0841, found 241.0841.

(3.4.2.10) 6-deoxy-4-O-benzyl-D-allal 21:

![Diagram of compounds 20 and 21](image)

Reagents and Conditions: CeCl$_3$.7H$_2$O, NaBH$_4$, MeOH, -78 °C, 1 h
To a solution of D-rhamnose derived enone 20 (1 g, 4.58 mmol) and CeCl₃.7H₂O (2.56 g, 6.87 mmol) in MeOH (20 mL) at -78 °C was added cooled (-10 °C) solution of NaBH₄ (260 mg, 6.87 mmol) in MeOH (7 mL) dropwise for a period of 10 min. The solution was stirred for 1 h at -78 °C, then quenched with saturated NH₄Cl solution (30 mL) and extracted twice with ethyl acetate (50 mL x 2). The combined organic layers were washed with water (25 mL), brine (25 mL) and dried (Na₂SO₄). Removal of solvent and purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (3:7 to 2:3) provided 6-deoxy-4-O-benzyl-D-allal 21 (0.9 g, 90%) as crystalline needles. Rᵢ = 0.61 (3:7 ethyl acetate/hexane).

**¹H NMR (400 MHz, CDCl₃):** δ 7.24 – 7.35 (m, 5H), 6.30 (dd, 1H, J= 1.2 Hz, J = 6.0 Hz), 4.83 (d, 1H, J = 11.6 Hz), 4.77 (d, 1H, J = 11.6 Hz), 4.68 (dd, 1H, J = 2.4 Hz, J= 6.0 Hz), 4.33 (bs, 1H, 3.86 – 3.93 (m, 1H), 3.26 (dd, 1H, J = 6.8 Hz, J = 9.6 Hz), 1.86 (d, 1H, J = 5.2 Hz), 1.39 (d, 3H, J = 6.4 Hz).

**¹³C NMR (100 MHz, CDCl₃):** δ 144.6, 138.2, 128.5, 127.9, 103.2, 82.4, 74.2, 74.1, 69.9, 17.6.

**HRMS (ESI) calcd for C₁₃H₁₆O₃+Na 243.0997, found 243.0997.**

(3.4.2.11) 4-O-benzyl-1,5-anhydro-2,6-dideoxy-α-1,2-C-methylene-D-allo-pyranose 22:

![Chemical Structure](image)

**Reagents and Conditions:** (i) CH₂I₂, Et₂Zn, Et₂O, 0 °C, 5 h.

To a solution of 6-deoxy-4-O-benzyl-D-allal 21 (800 mg, 3.63 mmol) in ether (15 mL) at 0 °C was added 1 M Et₂Zn in hexane (10.8 mL, 10.8 mmol) and CH₂I₂ (0.87 mL, 10.8 mmmol). The mixture was stirred for 5 h at same temperature, then quenched with saturated NH₄Cl solution (75 mL) and extracted with ether (50 mL x 2). The combined organic layers were washed with water (50 mL), brine (50 mL) and dried over anhydrous Na₂SO₄. Removal of solvent followed by purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (3:7 to 2:3) provided 4-O-benzyl-1,5-anhydro-2,6-dideoxy-α-1,2-
C-methylene-D-allo-pyranose 22 (680 mg, 80%) as a white solid. \( R_f = 0.38 \) (3:7 ethyl acetate/hexane).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.26 – 7.34 (m, 5H), 4.75 (d, 1H, \( J = 12.0 \) Hz), 4.67 (d, 1H, \( J = 12.0 \) Hz), 4.21 (t, 1H, \( J = 7.6 \) Hz), 3.69 – 3.72 (m, 1H), 3.35 (dd, 1H, \( J = 6.4 \) Hz, \( J = 9.6 \) Hz), 2.84 (dd, 1H, \( J = 7.6 \) Hz, \( J = 9.2 \) Hz), 1.34 – 1.38 (m, 1H), 1.22 (d, 3H, \( J = 6.4 \) Hz), 0.64 – 0.69 (m, 2H).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 138.2, 128.6, 127.7, 84.7, 74.4, 74.2, 71.5, 54.0, 18.7, 17.5, 11.6.

HRMS (ESI) calcd for C\(_{14}\)H\(_{18}\)O\(_3\)+Na 257.1154, found 257.1154.

(3.4.2.12) Compound 23:

Reagents and Conditions: (i) (COCl\(_2\), DMSO, Et\(_3\)N, CH\(_2\)Cl\(_2\), -78 °C, 1 h.

To a solution of (COCl\(_2\)) (331 µL, 3.84 mmol) in CH\(_2\)Cl\(_2\) (8 mL) at -78 °C was added DMSO (454 µL, 6.4 mmol) dropwise. After 10 min of stirring at the same temperature, the above 4-\( O \)-benzyl-1,5-anhydro-2,6-dideoxy-\( \alpha \)-1,2-C-methylene-D-allo-pyranose 22 (600 mg, 2.56 mmol) in CH\(_2\)Cl\(_2\) (8 mL) was added dropwise for a period of 15 min. After stirring for 30 min at -78 °C, Et\(_3\)N (1.76 mL, 12.6 mmol) was added and allowed to warm to room temperature. The reaction mixture was diluted with CH\(_2\)Cl\(_2\) (50 mL), washed with water (25 mL x 2), brine (25 mL) and dried over anhydrous Na\(_2\)SO\(_4\). Removal of solvent gave the crude residue which upon purification by silica-gel column chromatography with ethyl acetate/hexane (1:4) provided D-rhamnose-derived 1,2-cyclopropa-3-pyranone 23 (588 mg, 99%) as a colorless solid. \( R_f = 0.62 \) (3:7 ethyl acetate/hexane).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.26 – 7.33 (m, 5H), 4.99 (d, 1H, \( J = 11.6 \) Hz), 4.53 (d, 1H, \( J = 11.6 \) Hz), 4.10 (dd, 1H, \( J = 4.4 \) Hz, \( J = 9.2 \) Hz), 3.89 – 3.96 (m, 1H), 3.45 (d, 1H, \( J = 9.6 \) Hz), 1.86 – 1.91 (m, 1H), 1.26 (d, 3H, \( J = 6.0 \) Hz), 1.25 – 1.28 (m, 2H).

\(^1\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 204.8, 137.4, 128.2, 128.1, 127.8, 82.0, 78.7, 73.8, 57.6, 25.8, 19.8, 18.1.

HRMS (ESI) calcd for C\(_{14}\)H\(_{16}\)O\(_3\)+Na 255.0997, found 255.0997.
(3.4.2.13) Compounds 33α and 33β:

Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH₂Cl₂, -78 °C to rt, 3 h.

Compound 33 was synthesized using D-glucose-derived 1,2-cyclopropa-3-pyranone 5 (120 mg, 0.35 mmol), sugar acceptor 24 (100 mg, 0.38 mmol), TMSOTf (12 µL, 0.07 mmol) and 4 Å MS powder in CH₂Cl₂ (6 mL) according to the general procedure for ring expansion-glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 1 h and room temperature for 2 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 3:7) to afford septanosyl disaccharides 33α and 33β (180 mg, 85%) as an inseparable mixture.

(3.4.2.14) Compounds 34α and 34β:

Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH₂Cl₂, -78 °C to rt, 6 h.

Compound 34 was synthesized using D-galactose-derived 1,2-cyclopropa-3-pyranone 13 (150 mg, 0.44 mmol), sugar acceptor 24 (126 mg, 0.48 mmol), TMSOTf (15 µL, 0.08 mmol) and 4 Å MS powder in CH₂Cl₂ (8 mL) according to the general procedure for ring expansion-glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 1 h and then at room temperature for 5 h. The obtained crude product was purified and separated by silica-gel column chromatography (ethyl acetate/hexane 3:7 to 2:3) to give septanosyl disaccharides 34α (156 mg) and 34β (66 mg) (85% combined yield).

34α: colorless oil. Rf = 0.66 (2:3 ethyl acetate/hexane).

1H NMR (400 MHz, CDCl₃): δ 7.22 - 7.32 (m, 10H), 5.47 (d, 1H, J = 5.2 Hz), 5.02 (dd, 1H, J = 4.4 Hz, J = 6.4 Hz), 4.67 (d, 1H, J = 11.6 Hz), 4.59 (dd, 1H, J = 2.4 Hz, J = 8.0 Hz),
4.45 (d, 1H, J = 12.0 Hz), 4.40 (d, 1H, J = 12.0 Hz), 4.37 (d, 1H, J = 12.0 Hz), 4.29 (dd, 1H, J = 2.4 Hz, J = 5.2 Hz), 4.19 – 4.23 (m, 1H), 4.18 (dd, 1H, J = 1.6 Hz, J = 8.0 Hz), 3.95 (d, 1H, J = 1.2 Hz), 3.92 (dd, 1H, J = 1.6 Hz, J = 6.4 Hz), 3.86 (dd, 1H, J = 6.4 Hz, J = 10.0 Hz), 3.69 (dd, 1H, J = 6.4 Hz, J = 10.0 Hz), 3.58 – 3.64 (m, 2H), 2.66 (ddd, 1H, J = 2.4 Hz, J = 5.6 Hz, J = 13.6 Hz), 2.46 (ddd, 1H, J = 2.4 Hz, J = 5.6 Hz, J = 13.6 Hz), 2.19 – 2.27 (m, 1H), 1.73 – 1.81 (m, 1H), 1.51 (s, 3H), 1.41 (s, 3H), 1.32 (bs, 6H).

\( \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\): } \delta \text{ 209.3, 137.9, 137.1, 128.4, 128.3, 128.3, 127.9, 127.6, 127.5, 109.2, 108.5, 99.3, 96.2, 82.8, 73.1, 73.0, 70.9, 70.6, 70.5, 68.7, 66.2, 66.0, 65.9, 34.9, 28.6, 26.0, 25.9, 24.8, 24.5.}

\( \text{HRMS (ESI) calcd for C}_{33}\text{H}_{42}\text{O}_{10}^+\text{Na 621.2676, found 621.2693.} \\)

\( \beta: \) colorless oil. \( R_f = 0.33 \) (2:3 ethyl acetate/hexane). \( \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\): } \delta \text{ 7.25 - 7.34 (m, 10H), 5.51 (d, 1H, J = 5.2 Hz), 4.74 (d, 1H, J = 11.6 Hz), 4.53 – 4.57 (m, 2H), 4.48 (d, 1H, J = 11.6 Hz), 4.45 (d, 1H, J = 11.6 Hz), 4.43 (d, 1H, J = 11.6 Hz), 4.27 (dd, 1H, J = 2.4 Hz, J = 4.8 Hz), 4.10 (dd, 1H, J = 1.2 Hz, J = 8.0 Hz), 4.03 (d, 1H, J = 2.4 Hz), 3.92 – 3.98 (m, 3H), 3.70 (dd, 1H, J = 6.4 Hz, J = 8.8 Hz), 3.62 (dd, 1H, J = 8.8 Hz, J = 12.4 Hz), 2.70 (dt, 1H, J = 6.0 Hz, J = 13.2 Hz), 2.39 (dt, 1H, J = 7.2 Hz, J = 13.2 Hz), 2.01 – 2.06 (m, 2H), 1.51 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H).

\( \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\): } \delta \text{ 210.6, 137.9, 137.2, 128.3, 128.1, 128.1, 127.8, 127.6, 127.6, 109.2, 108.6, 106.2, 96.2, 85.3, 76.0, 73.4, 73.3, 71.4, 70.6, 70.4, 69.1, 67.8, 67.7, 34.8, 30.6, 26.0, 25.9, 24.9, 24.4.}

\( \text{HRMS (ESI) calcd for C}_{33}\text{H}_{42}\text{O}_{10}^+\text{Na 621.2676, found 621.2686.} \)

(3.4.2.15) Compound 35:

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\): } \delta \text{ 210.6, 137.9, 137.2, 128.3, 128.1, 128.1, 127.8, 127.6, 127.6, 109.2, 108.6, 106.2, 96.2, 85.3, 76.0, 73.4, 73.3, 71.4, 70.6, 70.4, 69.1, 67.8, 67.7, 34.8, 30.6, 26.0, 25.9, 24.9, 24.4.}

\( \text{HRMS (ESI) calcd for C}_{33}\text{H}_{42}\text{O}_{10}^+\text{Na 621.2676, found 621.2686.} \)

\( \text{Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH}_2\text{Cl}_2, \text{-78 °C, 5 h.} \)

Compound 35 was synthesized using D-glucose-derived 1,2-cyclopropa-3-pyranone 5 (100 mg, 0.29 mmol), sugar acceptor 26 (118 mg, 0.32 mmol), TMSOTf (10 µL, 0.05 mmol) and 4 Å MS power in CH\(_2\)Cl\(_2\) (5 mL) according to the general procedure for ring expansion-glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 5 h. The crude
product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to afford septanosyl disaccharide 35 (195 mg, 93%) as a thick gum. Rf = 0.7 (3:7 ethyl acetate/hexane). ^1H NMR (400 MHz, CDCl3): δ 7.46 – 7.48 (m, 2H), 7.24 - 7.38 (m, 18H), 5.47 (s, 1H), 4.97 (dd, 1H, J = 2.8 Hz, J = 9.2 Hz), 4.87 (d, 1H, J = 11.6 Hz), 4.84 (d, 1H, J = 3.6 Hz), 4.67 (d, 1H, J = 11.6 Hz), 4.51 – 4.54 (m, 3H), 4.34 (d, 1H, J = 11.6 Hz), 4.24 (dd, 1H, J = 4.8 Hz, J = 10.4 Hz), 3.97 (t, 1H, J = 9.2 Hz), 3.75 – 3.87 (m, 3H), 3.61 – 3.65 (m, 2H), 3.52 – 3.59 (m, 2H), 3.43 (t, 1H, J = 9.2 Hz), 3.38 (s, 3H), 2.80 (td, 1H, J = 4.4 Hz, J = 12.4 Hz), 2.26 (dt, 1H, J = 4.8 Hz, J = 12.0 Hz), 2.02 – 2.07 (m, 1H), 1.85 – 1.95 (m, 1H).

^13C NMR (100 MHz, CDCl3): δ 208.7, 138.6, 137.8, 137.3, 136.7, 128.8, 128.4, 128.3, 128.2, 128.1, 128.1, 127.6, 127.5, 125.9, 108.2, 101.0, 100.1, 84.6, 82.2, 78.3, 77.9, 77.8, 75.1, 73.2, 72.3, 70.8, 68.9, 62.0, 55.1, 33.7, 33.0. HRMS (ESI) calcd for C_{42}H_{46}O_{10}+Na^+ 733.2989, found 733.2989.

(3.4.2.16) Compound 36α and 36β:

Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH2Cl2, -78 °C to rt, 4 h.

Compounds 36 were synthesized using D-galactose-derived 1,2-cyclopropa-3-pyranone 13 (135 mg, 0.39 mmol), sugar acceptor 26 (163 mg, 0.43 mmol), TMSOTf (14 µL, 0.07 mmol) and 4 Å MS powder in CH2Cl2 (7 mL) according to the general procedure for ring expansion-glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 1 h and at room temperature for 3 h. The obtained crude product was purified and separated by silica-gel column chromatography (ethyl acetate/hexane 3:7 to 2:3) as clean septanosyl disaccharides 36α (176 mg) and 36β (75 mg) (89% combined yield).

36α: colorless oil. Rf = 0.3 (3:7 ethyl acetate/hexane). ^1H NMR (400 MHz, CDCl3): δ 7.17 – 7.46 (m, 20H), 5.49 (s, 1H), 5.11 – 5.12 (m, 1H), 4.89 (d, 1H, J = 3.6 Hz), 4.79 (d, 1H, J = 11.6 Hz), 4.72 (d, 1H, J = 11.6 Hz), 4.65 (1H, J = 12.0 Hz), 4.34 – 4.41 (m, 2H), 4.21 – 4.29...
(m, 3H), 4.02 (dd, 1H, $J = 3.6$ Hz, $J = 9.6$ Hz), 3.87 – 3.92 (m, 2H), 3.73 – 3.78 (m, 1H), 3.61 – 3.69 (m, 2H), 3.52 (t, 1H, $J = 8.4$ Hz), 3.42 – 3.47 (m, 1H), 3.39 (s, 3H), 2.62 – 2.66 (m, 1H), 2.52 – 2.56 (m, 1H), 2.27 – 2.34 (m, 1H), 1.80 – 1.83 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 208.9, 138.7, 138.2, 137.3, 137.0, 128.8, 128.4, 128.3, 128.1, 128.0, 127.5, 127.3, 125.9, 123.9, 101.1, 97.1, 95.6, 82.7, 81.8, 75.2, 73.6, 73.1, 72.8, 68.8, 68.7, 66.1, 62.2, 55.1, 34.7, 31.4.

HRMS (ESI) calcd for C$_{42}$H$_{46}$O$_{10}$+Na 733.2989, found 733.2989.

36β: colorless solid. $R_f = 0.45$ (3:7 ethyl acetate/hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45 – 7.48 (m, 2H), 7.24 – 7.37 (m, 18H), 5.44 (s, 1H), 4.77 – 4.88 (m, 4H), 4.65 (d, 1H, $J = 11.6$ Hz), 4.52 (d, 1H, $J = 11.6$ Hz), 4.44 (d, 1H, $J = 11.6$ Hz), 4.42 (d, 1H, $J = 11.6$ Hz), 4.22 (dd, 1H, $J = 4.8$ Hz, $J = 10.0$ Hz), 4.01 – 4.05 (m, 2H), 3.96 (t, 1H, $J = 9.2$ Hz), 3.82 (dd, 1H, $J = 3.6$ Hz, $J = 9.6$ Hz), 3.71 – 3.79 (m, 2H), 3.56 – 3.61 (m, 2H), 3.39 – 3.41 (m, 4H), 2.55 – 2.60 (m, 1H), 2.33 – 2.40 (m, 1H), 1.98 – 2.03 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 209.5, 138.7, 138.0, 137.3, 137.0, 128.8, 128.3, 128.2, 128.1, 128.0, 127.6, 127.6, 127.9, 108.4, 101.0, 100.2, 85.3, 82.3, 78.4, 77.6, 75.1, 73.5, 73.3, 70.0, 68.9, 62.0, 55.1, 34.8, 31.6.

HRMS (ESI) calcd for C$_{42}$H$_{46}$O$_{10}$+Na 733.2989, found 733.2989.

(3.4.2.17) Compound 36:

![Diagram of a compound](image)

Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH$_2$Cl$_2$, -78 °C to rt, 4 h.

Compound 36 was synthesized using D-arabinose-derived 1,2-cyclopropa-3-pyranone 18 (100 mg, 0.45 mmol), sugar acceptor 26 (187 mg, 0.5 mmol), TMSOTf (16 µL, 0.09 mmol) and 4 Å MS powder in CH$_2$Cl$_2$ (5 mL) according to the general procedure for ring expansion-glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 5 h. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to give septanosyl disaccharide 36 (216 mg, 80%) as a semi solid. $R_f = 0.46$ (3:7 ethyl acetate/hexane).
$^1$H NMR (400 MHz, CDCl$_3$): δ 7.47 – 7.49 (m, 2H), 7.25 - 7.39 (m, 13H), 5.57 (s, 1H), 5.00 (dd, 1H, $J = 4$ Hz, 8.8 Hz), 4.88 (d, 1H, $J = 11.6$ Hz), 4.79 (d, 1H, $J = 3.6$ Hz), 4.72 (d, 1H, $J = 12.0$ Hz), 4.68 (d, 1H, $J = 12.0$ Hz), 4.37 (d, 1H, $J = 12.0$ Hz), 4.27 – 4.33 (m, 2H), 4.18 (dd, 1H, $J = 4.8$ Hz, $J = 6.0$ Hz), 3.95 (t, 1H, $J = 9.6$ Hz), 3.82 (td, 1H, $J = 4.4$ Hz, $J = 9.6$ Hz), 3.75 (dd, 1H, $J = 9.6$ Hz, $J = 10.4$ Hz), 3.69 (dd, 1H, $J = 3.6$ Hz, $J = 9.6$ Hz), 3.62 (dd, 1H, $J = 9.2$ Hz, $J = 8.4$ Hz), 3.58 (dd, 1H, $J = 4.4$ Hz, $J = 13.2$ Hz), 3.41 (s, 3H), 2.49 (tdt, 1H, $J = 3.2$ Hz, $J = 12.4$ Hz, $J = 16.0$ Hz), 2.34 (dd, 1H, $J = 3.6$ Hz, $J = 5.2$ Hz, $J = 16.0$ Hz), 1.92 – 2.09 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 207.6, 138.6, 137.6, 137.2, 128.9, 128.5, 128.3, 128.2, 128.1, 127.7, 126.0, 103.7, 101.2, 99.9, 82.2, 82.2, 79.0, 78.1, 75.2, 72.2, 69.0, 62.1, 61.5, 55.3, 35.5, 28.3.

HRMS (ESI) calcd for C$_{34}$H$_{38}$O$_9$+Na 613.2414, found 613.2414.

(3.4.2.18) Compound 38:

Compound 38 was synthesized using D-glucose-derived 1,2-cyclopropa-3-pyranone 5 (250 mg, 0.73 mmol), glycosyl acceptor 27 (302 mg, 0.81 mmol), TMSOTf (26 µL, 0.14 mmol) and 4 Å MS powder in CH$_2$Cl$_2$ (13 mL) according to the general procedure for ring expansion-glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 1 h and at 25 °C for 3 h. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 3:7) to afford septanosyl disaccharide 38 (498 mg, 95%) as a thick gum. $R_f$ = 0.6 (2:3 ethyl acetate/hexane).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.46 – 7.48 (m, 2H), 7.20 - 7.36 (m, 18H), 5.48 (s, 1H), 5.09 (dd, 1H, $J = 2.0$ Hz, 8.8 Hz), 4.72 (d, 1H, $J = 12.0$ Hz), 4.62 (d, 1H, $J = 12.0$ Hz), 4.55 (d, 1H, $J = 3.6$ Hz), 4.46 (d, 1H, $J = 12.0$ Hz), 4.33 (bs, 2H), 4.29 (d, 1H, $J = 12.0$ Hz), 4.20 (dd, 1H, $J = 4.4$ Hz, $J = 6.0$ Hz), 4.11 (t, 1H, $J = 9.6$ Hz), 3.78 – 3.84 (m, 2H), 3.73 (td, 1H, $J = 4.4$ Hz, $J = 10.0$ Hz), 3.65 (t, 1H, $J = 10.4$ Hz), 3.49 – 3.54 (m, 2H), 3.37 – 3.41 (m,
2H), 3.34 (s, 3H), 2.80 (td, 1H, \( J = 4.8 \) Hz, \( J = 12.0 \) Hz), 2.26 (dt, 1H, \( J = 5.2 \) Hz, \( J = 12.0 \) Hz), 2.02 – 2.06 (m, 1H), 1.83 – 1.92 (m, 1H).

\( ^{13} \text{C NMR (100 MHz, CDCl}_3 \):} \( \delta 209.5, 138.2, 137.8, 137.4, 137.0, 128.8, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.3, 126.3, 106.1, 101.3, 98.7, 85.4, 79.8, 79.6, 78.1, 76.7, 73.4, 73.2, 72.2, 70.3, 68.8, 62.5, 55.2, 33.9, 32.1. 

\( \text{HRMS (ESI) calecd for C}_42\text{H}_46\text{O}_{10}\text{+Na 733.2989, found 733.3007.} \)

**(3.4.2.19) Compound 39:**

![Chemical Structure of Compound 39](image)

Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH\(_2\)Cl\(_2\), -78 °C to rt, 4 h.

Compound 39 was synthesized using D-arabinose-derived 1,2-cyclopropa-3-pyranone 18 (80 mg, 0.36 mmol), glycosyl acceptor 27 (150 mg, 0.4 mmol), TMSOTf (13 µL, 0.07 mmol) and 4 Å MS powder in CH\(_2\)Cl\(_2\) (5 mL) according to the general procedure for ring expansion-glycosylation reaction **(3.4.2.3)**. The reaction mixture was stirred at -78 °C for 1 h and at 25 °C for 3 h. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 3:7) to afford septanosyl disaccharide 39 (197 mg, 91%) as white solid. \( R_f = 0.37 \) (3:7 ethyl acetate/hexane).

\( ^{1} \text{H NMR (400 MHz, CDCl}_3 \):} \( \delta 7.17 – 7.45 \) (m, 15H), 5.49 (s, 1H), 5.20 (dd, 1H, \( J = 4.0 \) Hz, \( J = 8.0 \) Hz), 4.67 (d, 1H, \( J = 12.4 \) Hz), 4.59 -4.63 (m, 2H), 4.55 (d, 1H, \( J = 12.4 \) Hz), 4.32 (d, 1H, \( J = 12.4 \) Hz), 4.27 (dd, 1H, \( J = 5.6 \) Hz, \( J = 14.4 \) Hz), 4.24 (dd, 1H, \( J = 4.8 \) Hz, \( J = 10.0 \) Hz), 4.21 (dd, 1H, \( J =9.6 \) Hz, \( J = 18.8 \) Hz), 3.94 (dd, 1H, \( J = 4.4 \) Hz, \( J = 5.6 \) Hz), 3.81 (td, 1H, \( J = 4.4 \) Hz, \( J = 9.6 \) Hz), 3.68 (t, 1H, \( J = 10.0 \) Hz), 3.50 (dd, 1H, \( J = 3.6 \) Hz, \( J = 9.6 \) Hz), 3.45 (t, 1H, \( J = 9.6 \) Hz), 3.32 – 3.38 (m, 4H), 2.43 (ddt, 1H, \( J = 3.6 \) Hz, \( J = 11.6 \) Hz, \( J = 16.4 \) Hz), 2.33 (ddd, 1H, \( J = 3.6 \) Hz, \( J = 6.8 \) Hz, \( J = 16.4 \) Hz), 2.00 – 2.08 (m, 1H), 1.76 – 1.85 (m, 1H).

\( ^{13} \text{C NMR (100 MHz, CDCl}_3 \):} \( \delta 208.2, 137.7, 137.4, 137.2, 129.1, 128.5, 128.3, 128.2, 127.9, 127.6, 126.2, 101.7, 100.7, 98.5, 82.5, 80.3, 80.0, 74.1, 73.1, 71.4, 69.0, 62.5, 60.5, 55.3, 35.5, 28.2. \text{HRMS (ESI) calecd for C}_{34}\text{H}_{38}\text{O}_{9}\text{+Na 613.2414, found 613.2414.} \)
(3.4.2.20) Compound 40:

Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH₂Cl₂, -78 °C to rt, 4 h.

Compound 40 was synthesized using D-rhamnose-derived 1,2-cyclopropa-3-pyranone 23 (85 mg, 0.36 mmol), glycosyl acceptor 27 (150 mg, 0.4 mmol), TMSOTf (13 µL, 0.07 mmol) and 4 Å MS powder in CH₂Cl₂ (5 mL) according to the general procedure for ring expansion-glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 3 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to give septanosyl disaccharide 40 (205 mg, 93%) as a colorless solid. R<sub>f</sub> = 0.7 (3:7 ethyl acetate/hexane).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.25 – 7.41 (m, 15H), 5.47 (s, 1H), 5.29 (dd, 1H, J = 4.8 Hz, J = 8.4 Hz), 4.77 (d, 1H, J = 12.0 Hz), 4.65 (d, 1H, J = 11.6 Hz), 4.59 (d, 1H, J = 12.0 Hz), 4.55 (d, 1H, J = 3.6 Hz), 4.39 (d, 1H, J = 11.6 Hz), 4.33 (t, 1H, J = 9.6 Hz), 4.26 (t, 1H, J = 6.8 Hz), 4.22 (dd, 1H, J = 4.8 Hz, J = 10.4 Hz), 3.78 (td, 1H, J = 4.8 Hz, J = 10.4 Hz), 3.66 (t, 1H, J = 10.0 Hz), 3.58 (d, 1H, J = 10.8 Hz), 3.52 (t, 1H, J = 9.6 Hz), 3.43 (dd, 1H, J = 3.6 Hz, J = 9.6 Hz), 3.36 (s, 3H), 2.49 (ddd, 1H, J = 3.2 Hz, J = 6.4 Hz, J = 15.2 Hz), 2.32 – 2.40 (m, 1H), 2.17 – 2.27 (m, 1H), 1.96 – 2.04 (m, 1H), 1.23 (d, 3H, J = 6.4 Hz).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 209.0, 138.0, 137.5, 137.3, 129.0, 128.4, 128.4, 128.3, 128.0, 127.9, 125.9, 101.4, 100.1, 99.0, 89.1, 83.0, 77.8, 73.7, 72.9, 72.9, 69.1, 66.1, 61.8, 55.3, 35.9, 28.1, 20.6.

HRMS (ESI) calcd for C<sub>35</sub>H<sub>40</sub>O<sub>9</sub>Na 627.2570, found 627.2570.

(3.4.2.21) Compound 41:

Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH₂Cl₂, -78 °C, 3 h.
Compound 41 was synthesized using D-rhamnose-derived 1,2-cyclopropa-3-pyranone 23 (70 mg, 0.3 mmol), glycosyl acceptor 30 (85 mg, 0.33 mmol), TMSOTf (10 µL, 0.06 mmol) and 4 Å MS powder in CH₂Cl₂ (5 mL) according to the general procedure for ring expansion-glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 3 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to give septanosyl disaccharide 41 (141 mg, 96%) as a colorless solid. 

R_f = 0.67 (3:7 ethyl acetate/hexane).

**1H NMR (400 MHz, CDCl₃):** δ 7.31 – 7.37 (m, 6H), 5.41 (dd, 1H, J = 4.4 Hz, J = 8.4 Hz), 5.35 (d, 1H, J = 6.0 Hz), 4.69 (d, 1H, J = 11.2 Hz), 4.44 (d, 1H, J = 11.2 Hz), 4.42 (d, 1H, J = 11.6 Hz), 4.31 (ddd, 1H, J = 3.2 Hz, J = 4.4 Hz, J = 11.2 Hz), 4.12 (t, 1H, J = 6.4 Hz), 3.00 (dd, 1H, J = 3.2 Hz, J = 11.6 Hz), 3.92 (dd, 1H, J = 4.4 Hz, J = 11.6 Hz), 3.65 (d, 1H, J = 6.4 Hz), 2.41 – 2.49 (m, 2H), 2.30 – 2.38 (m, 1H), 2.19 – 2.29 (m, 1H), 1.31 (d, 3H, J = 6.4 Hz), 0.97 (s, 9H), 0.10 (s, 6H).

**13C NMR (100 MHz, CDCl₃):** δ 208.4, 192.6, 162.3, 137.2, 128.4, 128.0, 128.0, 104.7, 100.6, 89.1, 82.0, 73.0, 70.2, 67.0, 61.6, 35.9, 27.1, 25.8, 20.8, 18.4, -5.2, -5.2.

**HRMS (ESI) calcld for C₂₆H₃₈O₇Si+Na 513.2285, found 513.2285.**

(3.4.2.22) Compound 42:

A solution of ketone 38 (350 mg, 0.49 mmol) in EtOH (10 mL) was added dropwise to a solution of LiAlH(OC(CH₃)₃)₃ (250 mg, 0.98 mmol) in EtOH (10 mL) at -78 °C. The mixture was stirred for 1 h at same temperature, then slowly quenched with saturated NH₄Cl solution (20 mL) and allowed to warm to room temperature. Ethanol was evaporated under reduced pressure and the obtained thick syrup was extracted twice with ethyl acetate (20 mL x 2). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried (MgSO₄). Purification of crude residue by silica-gel column chromatography with ethyl
acetate/hexane (3:7 to 2:3) provided septano-hexose disaccharide 42 (343 mg, 98%) as a colorless oil. R_f = 0.38 (3:7 ethyl acetate/hexane).

^1H NMR (500 MHz, CDCl_3): \( \delta \) 7.47 – 7.49 (m, 2H), 7.18 – 7.36 (m, 18H), 5.47 (s, 1H), 5.03 (dd, 1H, \( J = 2.8 \) Hz, \( J = 8.0 \) Hz), 4.75 (d, 1H, \( J = 12.0 \) Hz), 4.61 (d, 1H, \( J = 12.0 \) Hz), 4.55 (d, 1H, \( J = 3.2 \) Hz), 4.32 – 4.45 (m, 6H), 4.19 (dd, 1H, \( J = 4.4 \) Hz, \( J = 10.0 \) Hz), 4.08 (d, 1H, \( J = 9.2 \) Hz), 3.99 – 4.01 (m, 1H), 3.73 – 3.80 (m, 2H), 3.61 – 3.67 (m, 2H), 3.51 (dt, 1H, \( J = 2.8 \) Hz, \( J = 6.8 \) Hz, \( J = 9.2 \) Hz), 3.38 – 3.45 (m, 2H), 3.34 (s, 3H), 1.92 – 2.07 (m, 3H), 1.73 – 1.79 (m, 1H), 1.60 – 1.66 (m, 1H).

^13C NMR (125 MHz, CDCl_3): \( \delta \) 138.4, 138.2, 138.0, 137.5, 128.8, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.3, 126.4, 105.4, 101.5, 98.9, 82.6, 80.3, 79.4, 77.0, 76.4, 73.6, 73.3, 72.0, 71.2, 69.7, 68.9, 62.4, 55.2, 30.9, 25.4.

HRMS (ESI) calcd for C_{42}H_{48}O_{18}Na 735.3145, found 735.3145.

(3.4.2.23) compound 43:

Reagents and Conditions: (i) PNB-OH, DIAD, Ph_3P, THF, rt, 8 h.

A solution of alcohol 42 (300 mg, 0.42 mmol), triphenylphosphine (441 mg, 1.68 mmol) and \( p \)-nitrobenzoic acid (281 mg, 1.68 mmol) in THF (10 mL) at 0 °C was added DIAD (330 \( \mu \)L, 1.68 mmol) dropwise. Upon completion of the addition, the solution was allowed to stir at room temperature for over night. Removal the solvent under reduced pressure followed by purification of crude mixture by silica-gel column chromatography with ethyl acetate/hexane (1:4) gave diaccharide-based \( p \)-nitrobenzoate 43 (358 mg, 99% yield) as light yellow oil. R_f = 0.61 (3:7 ethyl acetate/hexane).

^1H NMR (400 MHz, CDCl_3): \( \delta \) 8.10 (d, 2H, \( J = 9.2 \) Hz), 8.01 (d, 2H, \( J = 9.2 \) Hz), 7.16 – 7.35 (m, 20H), 5.53 (s, 1H), 5.35 (dd, 1H, \( J = 4.4 \) Hz, \( J = 7.2 \) Hz), 4.74 (d, 1H, \( J = 12.0 \) Hz), 4.65 (d, 1H, \( J = 12.0 \) Hz), 5.59 (d, 1H, \( J = 12.0 \) Hz), 4.58 (d, 1H, \( J = 4.0 \) Hz), 4.47 (d, 1H, \( J = 12.0 \) Hz), 4.36 (s, 2H), 4.21 – 4.27 (m, 2H), 3.74 – 3.79 (m, 2H), 3.65 – 3.72 (m, 2H), 3.54
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- 3.59 (m, 2H), 3.43 – 3.50 (m, 2H), 3.36 (s, 3H), 2.03 – 2.09 (m, 1H), 1.89 – 1.99 (m, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 163.8, 150.3, 138.3, 137.9, 137.7, 137.5, 135.6, 130.7, 128.8, 128.5, 128.3, 128.1, 128.0, 127.7, 127.6, 127.3, 126.3, 123.4, 106.2, 101.4, 98.8, 79.9, 79.8, 79.7, 78.0, 75.4, 74.8, 73.5, 73.3, 72.7, 71.1, 69.0, 62.6, 55.3, 30.3, 22.7.

HRMS (ESI) calcd for C\(_{49}\)H\(_{51}\)NO\(_{13}\)+Na 884.3258, found 884.3258.

(3.4.2.24) Compound 44:

\begin{align*}
\text{OBn} & \\
\text{O} & \\
\text{MeO} & \\
\text{OBn} & \\
\text{OO} & \\
\text{Ph} & \\
\text{O} & \\
\text{OBn} & \\
\text{BnO} & \\
\text{PNBO} & \\
\text{HO} & \\
\end{align*}

Reagents and Conditions: (i) NaOMe, MeOH, rt, 1 h.

To a solution of above \(p\)-nitrobenzoate sugar derivative 43 (250 mg, 0.29 mmol) in MeOH (2.3 mL) at room temperature was added methanolic solution of NaOMe (330 \(\mu\)L) (freshly prepared from 100 mg of Na in 20 mL of MeOH) and stirred for 1 h. The solution was neutralised with amberlite IR120 (acedic resin) and filtered. Removal of solvent under reduced pressure followed by purification of the crude residue by silica-gel chromatography with ethyl acetate/hexane (2:3) gave disaccharide 44 (203 mg, 99%) as a colorless gum. \(R_f\) = 0.36 (3:7 ethyl acetate/hexane).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.47 – 7.49 (m, 2H), 7.18 – 7.35 (m, 18H), 5.49 (s, 1H), 4.91 (dd, 1H, \(J = 3.0\) Hz, \(J = 9.0\) Hz), 4.74 (d, 1H, \(J = 12.0\) Hz), 4.63 (d, 1H, \(J = 12.0\) Hz), 4.55 (d, 1H, \(J = 3.5\) Hz), 4.42 (d, 1H, \(J = 12.0\) Hz), 4.39 (d, 1H, \(J = 12.0\) Hz), 4.38 (d, 1H, \(J = 12.0\) Hz), 4.34 (d, 1H, \(J = 12.0\) Hz), 4.20 (dd, 1H, \(J = 4.5\) Hz, \(J = 10.0\) Hz), 4.13 (t, 1H, \(J = 9.5\) Hz), 3.88 – 3.91 (m, 1H), 3.68 – 3.76 (m, 2H), 3.66 (t, 1H, \(J = 10.0\) Hz), 3.55 (t, 1H, \(J = 5.5\) Hz), 3.54 (dd 1H, \(J = 3.5\) Hz, \(J = 9.5\) Hz), 3.51 (t, 1H, \(J = 9.0\) Hz), 3.38 – 3.44 (m, 2H), 3.34 (s, 3H), 1.93 – 2.01 (m, 1H), 1.80 – 1.91 (m, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.2, 138.0, 137.8, 137.4, 128.8, 128.4, 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 127.2, 126.2, 107.1, 101.3, 98.6, 81.6, 80.1, 79.8, 79.6, 75.9, 73.4, 73.2, 72.1, 71.7, 70.7, 68.8, 62.4, 55.2, 29.7, 24.0.

HRMS (ESI) calcd for C\(_{42}\)H\(_{48}\)O\(_{18}\)+Na 735.3145, found 735.3145.
(3.4.2.25) Compound 45:

Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH2Cl2, -78 °C to rt, 4 h.

Disceptano-hexose trisaccharide derivative 45 was synthesized using D-glucose-derived 1,2-cyclopropa-3-pyranone 5 (65 mg, 0.19 mmol), glycosyl acceptor 44 (150 mg, 0.21 mmol), TMSOTf (5.4 µL, 0.03 mmol) and 4 Å MS powder in CH2Cl2 (5 mL) according to the general procedure for ring expansion-glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 1 h and then at 25 °C for 3 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 3:7) to give disceptano-hexose trisaccharide derivative 45 (160 mg, 79%) as colorless oil. Rf = 0.77 (2:3 ethyl acetate/hexane).

1H NMR (500 MHz, CDCl3): δ 7.47 – 7.49 (m, 2H), 7.14 – 7.36 (m, 30H), 5.47 (s, 1H), 4.95 - 5.00 (m, 1H), 4.88 (dd, 1H, J = 3.0 Hz, J = 7.5 Hz), 4.77 (1H, J = 12.0 Hz), 4.75 (dd, 1H, J = 2.5 Hz, J = 9.0 Hz), 4.67 (d, 1H, J = 12.5 Hz), 4.52 – 4.54 (m, 3H), 4.38 – 4.40 (m, 2H), 4.35 (d, 1H, J = 3.5 Hz), 4.32 (d, 1H, J = 12.0 Hz), 4.28 (d, 1H, J = 12.5 Hz), 4.12 – 4.19 (m, 3H), 3.71 – 3.80 (m, 3H), m3.65 (d, 1H, J = 9.0 Hz), 3.61 (dd, 1H, J = 3.0 Hz, J = 13.0 Hz), 3.57 (dd, 1H, J = 4.0 Hz, J = 5.5 Hz), 3.51 – 3.53 (m, 2H), 3.47 – 3.50 (m, 2H), 3.43 – 3.46 (m, 1H), 3.33 – 3.36 (m, 4H), 2.84 (td, 1H, J = 5.0 Hz, J = 11.5 Hz), 2.29 – 2.35 (m, 1H), 2.03 – 2.06 (m, 1H), 1.81 – 1.91 (m, 3H), 1.67 – 1.71 (m, 2H).

13C NMR (100 MHz, CDCl3): δ 209.3, 138.7, 138.5, 138.3, 137.9, 137.5, 136.8, 128.7, 128.4, 128.3, 128.1, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 127.6, 127.5, 127.3, 127.1, 126.3, 105.0, 103.0, 101.1, 99.2, 85.2, 81.1, 79.6, 78.9, 78.2, 77.3, 76.3, 76.1, 73.5, 73.2, 73.1, 72.4, 72.2, 71.6, 70.6, 68.9, 62.5, 55.2, 34.0, 32.9, 30.2, 21.3.

HRMS (ESI) calcd for C63H70O14+Na 1073.4663, found 1073.4664.
A solution of ketone 45 (155 mg, 0.14 mmol) in EtOH (5 mL) was added dropwise to a solution of LiAlH(OtBu)₃ (71 mg, 0.28 mmol) in EtOH (5 mL) at -78 °C. The mixture was stirred for 1 h at same temperature, then slowly quenched with saturated NH₄Cl solution (10 mL) and allowed to warm to room temperature. Ethanol was evaporated under reduced pressure and the obtained thick syrup was extracted twice with ethyl acetate (20 mL x 2). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried (MgSO₄). Purification of crude residue by silica-gel column chromatography with ethyl acetate/hexane (2:3) provided disepano-hexose trisaccharide 46 (153 mg, over all 76% for two steps) as a colorless oil. R_f = 0.5 (2:3 ethyl acetate/hexane).

**1H NMR (500 MHz, CDCl₃):** δ 7.48 – 7.50 (m, 2H), 7.18 – 7.38 (m, 28H), 5.48 (s, 1H), 4.89 (dd, 1H, J = 3.0Hz, J = 8.0 Hz), 4.78 (d, 1H, J = 12.0 Hz), 4.75 (dd, 1H, J = 3.5 Hz, J = 7.0 Hz), 4.69 (d, 1H, J = 12.0Hz), 4.53 (d, 1H, J = 12.0 Hz), 4.52 (d, 1H, J = 3.5 Hz), 4.50 (d, 1H, J = 12.0 Hz), 4.45 (d, 1H, J = 12.0 Hz), 4.41 (d, 1H, J = 12.0 Hz), 4.37 (d, 1H, J = 12.0 Hz), 4.35 (d, 1H, J = 12.0 Hz), 4.29 (d, 1H, J = 12.0 Hz), 4.17 (dd, 1H, J = 2.0 Hz, J = 10.0 Hz), 4.07 – 4.11 (m, 2H), 3.74 (dd, 1H, J = 4.5 Hz, J = 9.0 Hz), 3.68 – 3.72 (m, 1H), 3.66 (t, 1H, J = 7.5 Hz), 3.60 (dd, 1H, J= 4.5 Hz, J = 9.0 Hz), 3.57 - 3.59 (m, 1H), 3.55 – 3.56 (m, 2), 3.53 – 3.54 (m, 2H), 3.49 – 3.50 (m, 1H), 3.45- 2.46 (m, 1H), 3.36 – 3.91 (m, 1H), 3.34 (s, 3H), 1.92 – 2.06 (m, 2H), 1.82 - 1.87 (m, 1H), 1.64 – 1.75 (m, 6H).

**13C NMR (100 MHz, CDCl₃):** δ 138.7, 138.7, 138.4, 138.1, 137.9, 137.6, 128.7,128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3, 127.1, 126.3, 105.3, 101.8, 101.2, 82.3, 81.5, 79.5, 78.8, 77.5, 76.8, 76.2, 75.9, 73.5, 73.2, 73.1, 72.6, 72.2, 71.7, 71.2, 69.4, 68.9, 62.6, 55.3, 30.6, 30.3, 25.3, 21.6.
HRMS (ESI) calcd for C₆₃H₇₂O₁₄⁺Na 1075.4820, found 1075.4820.

(3.4.2.27) Compound 47:

Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH₂Cl₂, -78 °C, 3 h.

Septano-hexose disaccharide derivative 47 was synthesized using D-rhamnose-derived 1,2-cyclopropa-3-pyranone 23 (200 mg, 0.86 mmol), glycosyl acceptor 32 (120 mg, 0.94 mmol), TMSOTf (31 µL, 0.17 mmol) and 4 Å MS powder in CH₂Cl₂ (15 mL) according to the general procedure for ring expansion-glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 3 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to give septano-hexose disaccharide derivative 47 (217 mg, 70%) as a colorless solid. R<sub>f</sub> = 0.5 (3:7 ethyl acetate/hexane).

¹H NMR (500 MHz, CDCl₃): δ 7.28 – 7.38 (m, 6H), 5.35 – 5.38 (m, 2H), 4.69 (d, 1H, J = 11.5 Hz), 5.41 (4.42 (d, 1H, J = 11.5 Hz), 4.34 (dd, 1H, J = 6.0 Hz, J = 11.5 Hz), 4.12 – 4.18 (m, 2H), 3.65 (d, 1H, J = 6.5 Hz), 2.53 (ddd, 1H, J = 3.6 Hz, J = 5.6 Hz, J = 15.6 Hz), 2.41 – 2.49 (m, 1H), 2.31 – 2.39 (m, 1H), 2.22 – 2.27 (m, 1H), 1.50 (d, 3H, J = 6.5 Hz), 1.30 (d, 3H, J = 6.5 Hz).

¹³C NMR (125 MHz, CDCl₃): δ 208.3, 193.3, 162.6, 137.1, 128.4, 128.1, 128.0, 105.1, 100.8, 89.1, 78.2, 74.8, 73.0, 66.8, 35.8, 27.0, 20.9, 17.5.

HRMS (ESI) calcd for C₂₀H₂₄O₆⁺Na 383.1471, found 383.1471.

(3.4.2.28) Compound 48:

Reagents and Conditions: (i) CeCl₃·7H₂O, NaBH₄, MeOH, -78 °C, 1 h; (ii) CH₂J₂, Et₂Zn, Et₂O, 0 °C, 5 h; (iii) (COCl)₂, DMSO, Et₃N, CH₂Cl₂, -78 °C, 1 h.

To a solution of septano-hexose disaccharide derivative 47 (150 mg, 0.41 mmol) and CeCl₃·7H₂O (458 mg, 1.23 mmol) in MeOH (6 mL) at -78 °C, was added cooled (-10 °C)
solution of NaBH₄ (46 mg, 1.23 mmol) in MeOH (2 mL) dropwise for a period of 10 min. The solution was stirred for 1 h at same temperature and slowly quenched with saturated NH₄Cl solution (15 mL). The mixture was extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried (Na₂SO₄). Removal of solvent provided the crude diol (148 mg, 0.4 mmol) as colorless gum. This crude diol mixture was dissolved in ether (5 mL), and subsequently 1 M Et₂Zn in hexane (1.2 mL, 1.21 mmol) and CH₂I₂ (98 µL, 1.21 mmol) were added at 0 °C and stirred for 5 h at the same temperature. After completion of reaction (TLC), saturated NH₄Cl (15 mL) was added and extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried (Na₂SO₄). Removal of solvent gave crude 1,2-cyclopropanated disaccharide diol mixture (130 mg, 0.34 mmol) which was used for next step without purification. For oxidation of diol, DMSO (120 µL, 1.7 mmol) was added dropwise to a solution of (COCl)₂ (88 µL, 1.02 mmol) in CH₂Cl₂ (3 mL) at -78 °C. After stirring for 10 min at the same temperature, the above 1,2-cyclopropanated disaccharide diol mixture (130 mg, 0.34 mmol) in CH₂Cl₂ (3 mL) was added dropwise for a period of 15 min. After stirring for 30 min at -78 °C, Et₃N (468 µL, 3.36 mmol) was added and allowed to warm to room temperature. The reaction mixture was diluted with CH₂Cl₂ (20 mL), washed with water (10 mL x 2), brine (10 mL) and dried over anhydrous Na₂SO₄. The crude residue was purified by silica-gel column chromatography (ethyl acetate/hexane 3:7) provided 1,2-cyclopropanated-septanosyl disaccharide-derivative 48 (115 mg, 75% after three steps) as a mixture (α:β = 2:1).

(3.4.2.29) Compound 49:

\[
\text{Reagents and Conditions: (i) TMSOTf, 4 Å MS, CH₂Cl₂, -78 °C, 3 h.}
\]

Diseptano-hexose trisaccharide derivative 49 was synthesized using glycosyl donor 48 (100 mg, 0.26 mmol), glycosyl acceptor 32 (37 mg, 0.29 mmol), TMSOTf (9.4 µL, 0.05 mmol) and 4 Å MS powder in CH₂Cl₂ (5 mL) according to the general procedure for ring expansion-
glycosylation reaction (3.4.2.3). The reaction mixture was stirred at -78 °C for 3 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to give disepano-hexose trisaccharide derivative 49 (87 mg, 65%) as a colorless oil. Rf = 0.32 (3:7 ethyl acetate/hexane).

1H NMR (500 MHz, CDCl3): δ 7.29 – 7.37 (m, 6H), 5.44 (dd, 1H, J = 5.0 Hz, J = 8.5 Hz), 5.36 (d, 1H, J = 6.0 Hz), 4.86 (dd, 1H, J = 5.0 Hz, J = 8.5 Hz), 4.67 (d, 1H, J = 11.5 Hz), 4.40 (d, 1H, J = 11.5 Hz), 4.36 (dd, 1H, J = 6.5 Hz, J = 12.0 Hz), 4.18 (d, 1H, J = 12.0 Hz), 4.13 (t, 1H, J = 6.5 Hz), 4.05 (d, 1H, J = 8.5 Hz), 4.03 (dd, 1H, J = 5.5 Hz, J = 11.5 Hz), 3.62 (d, 1H, J = 7.0 Hz), 2.51 – 2.55 (m, 1H), 2.44 – 2.50 (m, 2H), 2.38 – 2.43 (m, 1H), 2.28 – 2.37 (m, 2H), 2.15 – 2.20 (m, 1H), 1.90 – 1.97 (m, 1H), 1.49 (d, 3H, J = 6.0 Hz), 1.33 (d, 3H, J = 5.5 Hz), 1.29 (d, 3H, J = 6.5 Hz).

13C NMR (100 MHz, CDCl3): δ 208.2, 207.6, 193.3, 162.7, 137.1, 128.5, 128.1, 128.1, 105.1, 100.3, 99.8, 89.1, 83.6, 78.2, 74.7, 73.1, 66.9, 65.3, 35.8, 35.7, 27.2, 27.0, 20.9, 20.2, 17.6.

HRMS (ESI) calcd for C27H34O9+Na 525.2101, found 525.2101.

3.5 References


26. CCDC deposition no. 903373.

3.6 NMR Spectra
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\[ \text{\textit{1}H NMR, 400 MHz, CDCl}_3 \]

\[ \text{\textit{13}C NMR, 100 MHz, CDCl}_3 \]
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![NMR spectra](image)

1H NMR, 400 MHz, CDCl$_3$

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- 13C NMR, 100 MHz, CDCl$_3$

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1H NMR, 400 MHz, CDCl3

13C NMR, 100 MHz, CDCl3
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1H NMR, 400 MHz, CDCl3

13C NMR, 100 MHz, CDCl3
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A Ring Expansion-Glycosylation Strategy toward…

\[ \text{1H-1H COSY NMR, 400 MHz, CDCl}_3 \]

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NOE observed between \( H^1 \) and \( H^6 \)
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\[ \text{1H NMR, 400 MHz, CDCl}_3 \]

\[ \text{13C NMR, 100 MHz, CDCl}_3 \]
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$\text{H NMR, 400 MHz, CDCl}_3$

$\text{13C NMR, 100 MHz, CDCl}_3$
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$^1$H NMR, 400 MHz, CDCl$_3$

192.66, 208.41

$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$

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$^{1}H$ NMR, 500 MHz, CDCl$_3$,

$^{13}C$ NMR, 125 MHz, CDCl$_3$. 

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$\text{H NMR, 500 MHz, CDCl}_3$

$\text{C NMR, 100 MHz, CDCl}_3$

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$\text{H NMR, 500 MHz, CDCl}_3$
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\[ \text{1}^\text{H NMR, 500 MHz, CDCl}_3 \]

\[ \text{1}^\text{C NMR, 100 MHz, CDCl}_3 \]
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