A Scalable Approach to Obtaining Orthogonally Protected β-D-Idopyranosides

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Ⓢ *Supporting Information*

ABSTRACT: A practical method to obtain orthogonally protected D-idopyranose from D-galactose has been developed, which is the first method to enable synthesis of the challenging β-D-idopyranoside linkage. The method relies on a key double inversion at O-2 and O-3 in an easily prepared D-galactose derivative, which proceeds regio- and stereoselectively through a 2,3-anhydrotalopyranoside; reaction using a selection of alkoxides affords exclusively the 3-O-alkylidopyranoside, which can be used to generate an orthogonally protected monosaccharide. The process is scalable and requires minimal purification, so it could be used to produce building blocks to aid in the synthesis of various β-idopyranose-containing oligosaccharide targets to further probe their biological functions.
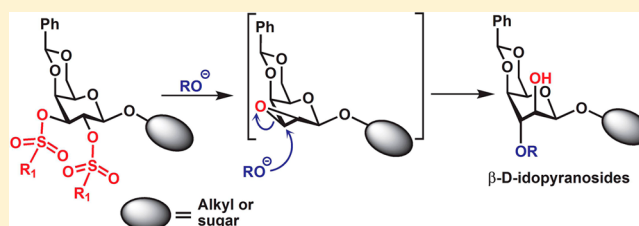
■ INTRODUCTION

Ido-configured sugars have unique conformational properties due to the high energy chair conformation which most other sugars adopt because the 2-, 3-, and 4-O-substituents are forced to adopt an axial orientation. As a result, the L-iduronic acids (Figure 1a), naturally abundant in heparin, heparan, and
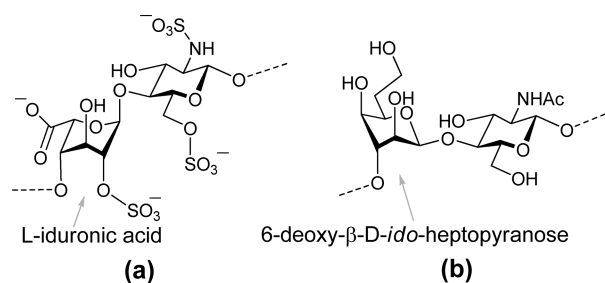

Figure 1. Examples of L-iduronic acid and 6-deoxy-D-*ido*-heptopyranoside found in heparin (a) and *C. jejuni* capsular polysaccharides (b).

dermatan sulfates, often interconvert rapidly between $^1C_4$, $^4C_1$, and ^2S_O because of the low energy barrier between conformational isomers.[1] These glycosaminoglycans (GAGs) have generated interest because of their bioactivity and mediation of various physiological processes such as cell growth and differentiation and blood coagulation.[2] Because of the diversity of GAG oligosaccharides obtained from natural sources, it is often difficult to determine which fragments are responsible for mediating activity; therefore, the synthesis of well-defined derivatives has been pursued in order to better understand the structure–activity relationship. As a result, a method to control the sulfation through chemical synthesis is necessary; this can be achieved with orthogonal protection of the five hydroxyl groups on the sugar ring. Upon deprotection, these sites can be further modified to yield the desired product. The generation of orthogonally protected monosaccharide units also allows for the same building blocks to be used in the syntheses of various oligosaccharide targets with improved efficiency.[3]

Although the ability to obtain orthogonally protected idose units has been recognized as a significant synthetic challenge because of its unique conformational and chemical properties, efforts to obtain the L-series of orthogonally protected building blocks has recently seen some progress.[4−10] An early method beginning from D-glucuronolactone was developed by Wong et al. that produced orthogonally protected L-iduronic acid in eight steps; the method relied on a key inversion at C-5 that was achieved via radical bromination of methyl 1,2,3,4-tetra-O-acetyl-α- or β-D-glucopyranuronate and a subsequent stereoselective reduction using tributyltin hydride to afford the desired L-*ido* configuration over the D-*gluco* in a 2:1 ratio for the α-anomer and a 3:1 ratio for the β-anomer;[9] the isolated tetraacetates of methyl α- or β-L-idopyranuronates were both converted to the 1,2-acetal-protected derivative on the basis of previous work done by the Seeberger group;[11] the 3,4-di-O-acetate was selectively deprotected at O-3 and then reprotected with a benzoyl or pivaloyl group to give the orthogonally protected methyl L-idopyranuronates.

An alternate route was published by Whitfield et al. involving a seven-step synthesis beginning from 1,2-O-isopropylidene-6,3-D-glucuronolactone,[7,8] which is an expensive starting material; the synthesis involved the activation of OH-5 via 5-triflate followed by a C-5 inversion with pivalate, and the obtained 1,2-O-isopropylidene-6,3-L-iduronolactone was then
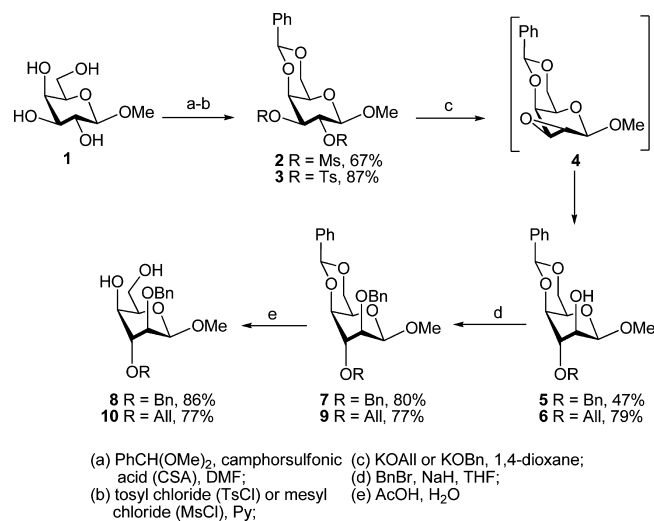
converted to the methyl ester, which was accompanied by a concomitant pivaloyl migration from O-5 to O-3; unfortunately, multiple low-yielding reactions (a 13% yield four-step sequence) were followed during the subsequent transformation of furanose to the pyranose, and a 2,4-di-O-acetyl-3-O-pivaloyl-protected imidate glycosyl donor was eventually obtained as an α/β mixture (73%), which showed good glycosylation properties to provide α-linked disaccharides in 64−85% yields; the neighboring-group participation at O-2 (Ac) provided excellent stereocontrol during glycosylations. A third method of obtaining orthogonally protected L-idose from Hung et al. utilizes diacetone α-D-glucose and involves seven steps but involves a low-yielding inversion step at a late stage of the synthesis.[4,5,12] In addition, the protecting group at O-3 is restricted to a benzyl ether, and the groups at O-2 and O-6 are restricted to ester linkages.

While efforts to obtain the L-idose and derivatives through chemical synthesis have progressed over the past decade, the exploration of routes to obtain orthogonally protected D-idose has been extremely limited. Although much less prevalent, D-ido-configured sugars have garnered interest in library screening studies for bioactivity,[13−15] and their potential utility arguably remains underexplored. The recently identified capsular polysaccharide (CPS) structure of *Campylobacter jejuni* (serotype HS:4, strain CG8486) contains a 6-deoxy-β-D-ido-heptopyranose (Figure 1b, partially modified by O-methyl phosphoramidate at O-2/O-7) as part of a repeating disaccharide unit,[16] which could potentially elicit an important immunological response owing to its unique nature; it could potentially redirect the immune response and subsequently decrease the risk of Guillain−Barré syndrome, which has been associated with antibody production against *C. jejuni* lipopolysaccharide.[17−19] The characteristic feature in the repeating disaccharide unit of the CPS is the presence of a β-linked idose glycosyl unit which presents a considerable synthetic challenge. Unfortunately, all above-mentioned methods for L-idose are designed to form α-glycosidic linkages thus no method has yet been able to accommodate a β-glycosidic bond formation in idose chemistry. It is also difficult to take advantage of the anchimeric assistance strategy or the anomeric effect to prepare such glycosidic linkage. The development of orthogonally protected D-idose units is the key to facilitate subsequent O-3 glycosylation and C-6 chain extension for the 6-deoxy-β-D-ido-heptopyranose synthesis, and the obtained results would enable access to a variety of D-idose-containing oligosaccharides that could be used in conjugate vaccines to better probe the potential immune response generated by this unique *C. jejuni* CPS structure. In addition, the developed orthogonal protecting strategy could allow for a selective modification with the phosphoramidate group at O-2 or O-7 position of the generated 6-deoxy-β-D-ido-heptopyranose.

■ RESULTS AND DISCUSSION

Although a few efforts have been designed to obtain the unusual D-ido-pyranose configuration, a general and widely applicable method to synthesize β-D-idopyranosides is not available. Wiggins et al. briefly investigated the synthesis of a methyl 3-O-methyl-β-D-idopyranoside in 1944:[20] methyl 4,6-O-benzylidene-2,3-di-O-tosyl-β-D-galactopyranoside (**3**, Scheme 1) was treated with sodium methoxide in refluxing methanol to obtain a complex mixture containing methyl 3-O-methyl-β-D-idopyranoside (32% yield) and methyl 2,3-anhydro-4,6-O-benzylidene-β-D-talopyranoside (**4**, 4.1% yield), together with

Scheme 1. Efficient, Scalable Method To Obtain Orthogonally Protected D-Idose from D-Galactose

(a) PhCH(OMe)$_2$, camphorsulfonic acid (CSA), DMF;
(b) tosyl chloride (TsCl) or mesyl chloride (MsCl), Py;
(c) KOAll or KOBn, 1,4-dioxane;
(d) BnBr, NaH, THF;
(e) AcOH, H$_2$O

several other side products. To improve the yield, they followed an alternate route by starting from the methyl 4,6-O-benzylidene-2-O-tosylgalactopyranoside (prepared from the methyl galactoside via a five step protection−deprotection sequence[21]) and carried out a base-catalyzed detosylation. The epoxide **4** was then converted to the desired methyl 3-O-methyl-β-D-idopyranoside in a separate treatment with sodium methoxide in hot methanol (49% yield over 2 steps); the reaction also afforded a tiny amount of methyl 2-O-methyl-β-D-galactopyranoside as a side product (<0.01%). Recently, Frahn[22] reported that when the 2,3-di-O-tosylate **3** was treated with sodium methoxide in dioxane, the *talo*-epoxide **4** was isolated in 66% yield after 4 h at room temperature, while the methyl 3-O-methyl-β-D-idopyranoside was isolated in 12% yield. By thin layer chromatography (TLC) the author also observed that the amount of the idopyranoside increased progressively over time, but no further information was provided.

The synthesis of oligosaccharide analogues related to the CPS of *C. jejuni* requires access to orthogonally protected β-D-idopyranosides. It appears that the only route which would easily allow for such protected products is the approach established by Wiggins,[20] although their limited study only examined the formation of di-O-methyl protected idopyranosides, and unfortunately the lack of selectivity and harsh conditions required for cleavage of these methyl ethers severely limits the use of these compounds for subsequent chemical modifications. However, the general scope and applicability of the approach to other nucleophiles and substrates was not known, so we decided to examine the feasibility of developing such an approach to become a general method for synthesizing D-idopyranoside-containing oligosaccharides (Scheme 1). Indeed, preliminary results indicated that under optimized reaction conditions, the 4,6-O-benzylidene-3-O-methyl-β-D-idopyranoside could be directly obtained in a much improved yield (66%) from either 2,3-di-O-tosylate (**3**) or 2,3-di-O-mesylate (**2**, Scheme 1).

Reaction of the disulfonates with benzyloxide in benzyl alcohol-dioxane at room temperature provided directly the desired methyl 3-O-benzyl-4,6-O-benzylidene-β-D-idopyranoside **5** as the only product isolated in modest yields (47%); no 2-O-benzyl substituted galactopyranoside byproduct was

Scheme 2. Proposed Mechanism of Diinversion To Afford D-Idose from D-Galactose
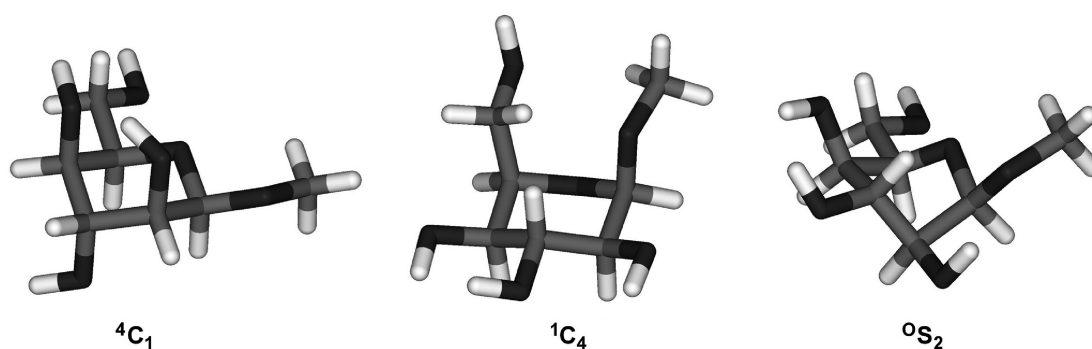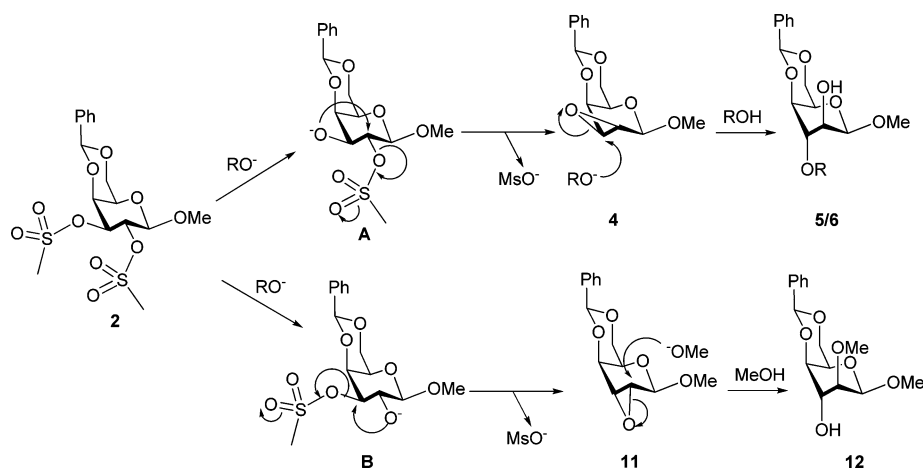
Figure 2. $^4C_1$, $^1C_4$, and $^OS_2$ conformations of methyl β-D-idopyranoside.

detected. Although TLC indicated that only a single product had formed during the reaction, difficulty in removing the excess benzyl alcohol resulted in a lower purified yield than what had been observed previously for the reaction with methoxide. In switching to a more volatile alcohol, treatment of the sulfonates with allyloxide in either allyl alcohol-dioxane or allyl alcohol-benzene also afforded the desired 3-O-allylated β-D-idopyranoside analogue 6 exclusively which was isolated in a greatly improved yield (79%). Although isomerization of allyl ethers has often been reported to occur in strong base, this was not observed under the described reaction conditions, likely a result of the above reaction proceeding at room temperature. This method is highly desirable because it is easily scalable; we were able to perform all steps toward the preparation of 5 and 6 in greater than 10 g quantities, and in addition, the reaction sequence could be carried through from 1 to ido-configured 5 or 6 with only a single column chromatography purification required after the final di-inversion step. The subsequent 2-O-benzylation of 5 afforded the 2,3-di-O-benzylated compound 7 in 80% yield, and the 4,6-benzylidene was subsequently removed in 80% acetic acid−water to provide the corresponding diol 8 (86% yield).

Furthermore, this method also provides an opportunity to introduce orthogonal protecting groups onto the β-D-idopyranoside. For example, starting from compound 6 which has a 3-O-allyl protecting group, O-benzylation at the O-2 position was carried out; compound 9 which has the O-2 and O-3 differentially protected was obtained in 77% yield, and we subsequently removed the 4,6-benzylidene protecting group in a similar manner as 7 to afford the corresponding 4,6-diol 10 in

77% yield. The primary 6-OH group could be further regioselectively modified, which should provide an intermediate that has the remaining three secondary positions orthogonally protected; through protecting group manipulations, each position can be accessed selectively.

The interesting regio- and stereoselectivity observed in the key di-inversion reaction results from selective attack of the alkoxide at the sulfur center of the 3-sulfonate to effectively cleave the S−O bond and produce the O-3 anionic sugar A, which can then undergo an intramolecular attack to afford the 2,3-anhydro-taloside 4 (Scheme 2); this type of S−O cleavage has been previously observed and confirmed through ^{18}O-labeling base-catalyzed hydrolysis reactions.[23−26] Upon oxirane formation, selective attack at C-3 by the nucleophile results in the diaxial products 5/6, which are preferred over the diequatorial products because of their lower energy transition states (a consequence of the Fürst-Plattner rule). Our improved regioselectivity in epoxide opening as compared to the previous attempt discussed earlier by Wiggins et al.[20] likely results from performing the reaction at room temperature instead of at reflux, to afford a better yield of the kinetic product.

Although no galactoside byproduct was observed in any of our reactions, in a few attempts a trace amount of the methyl 2,3-anhydro-4,6-O-benzylidene-β-D-guloside (11) was isolated (2% yield); this could result from attack of the 2-sulfonate (→ B) to produce the diastereomeric epoxide (11). Theoretically, the alkoxide could attack this regioisomer to afford the 2-O-alkyl-idopyranoside; however, this byproduct was never observed in the crude ^{1}H NMR. This was likely a result of 2,3-anhydro-D-gulo- and talopyranosides preferring to adopt an

Scheme 3. Reaction of Sodium Methoxide with Methyl 4,6-*O*-Benzylidene-2,3-di-*O*-mesylgalactopyranoside 14

(a) MsCl, Py, DCM; (b) NaOMe, MeOH, dioxane

2   :   5
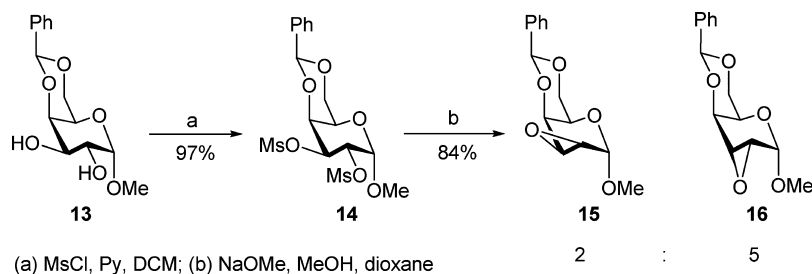
$^O H_5$ half-chair conformation; the $^O H_5$ conformation can be confirmed via ^1H NMR coupling constants between vicinal H-1 and H-4 protons: a very small coupling constant (<1.5 Hz) when the relationship is trans, and a slightly larger coupling constant (<5.6 Hz) when the relationship is cis.[27,28] It was previously demonstrated that in this preferred $^O H_5$ conformation, the approach of a nucleophile to attack the epoxide ring is significantly more sterically hindered in the *gulo*- as compared to the *talo*-stereoisomer;[27−30] this interference of approach of the nucleophile could prevent the *gulo*-epoxide from reacting at room temperature. This decreased reactivity was confirmed by reacting the *gulo*-epoxide (**11**) with sodium methoxide: after several days at room temperature and even heating at 70 °C for 18 h, it was found that the reaction did not go to completion. Upon workup, the crude ^1H NMR indicated only partial conversion to the methyl 4,6-*O*-benzylidene-2-*O*-methylidopyranoside **12** as the exclusive new product, present with the remaining starting material (1:2 ratio of *gulo*-:*ido*-).

Success in obtaining the idose structure was confirmed using NMR methods, since its unique $^3J_{H,H}$ coupling constants can be used to infer its conformational preferences. Small coupling constants observed for $^3J_{H-1,H-2}$, $^3J_{H-2,H-3}$, and $^3J_{H-3,H-4}$ indicate small dihedral angles which suggests that the β-idopyranoside prefers to adopt a $^4C_1$ chair over a $^1C_4$ chair, although in some compounds coupling has been observed between H-2 and H-4 which suggests that these structures likely fluctuate from $^4C_1$ to other nonchair conformations, such as $^O S_2$ (Figure 2).[1,28,29] Although methyl 4,6-*O*-benzylidene-α-D-idopyranose has been observed to prefer the $^4C_1$ conformation, which is stabilized by intramolecular H-bonding between OH-2 and O-4 and likely also between OH-3 and O-1, the β-epimer has a large $^3J_{H-2,OH-2}$ coupling constant (11.5−12.1 Hz) which suggests an antiperiplanar orientation (based on the Karplus curve) between OH-2 and H-2.[28] This also supports the preference for adopting a skew conformation in which H-bonding to O-4 would be unfavorable, although the possibility of OH-2 and O-1 H-bonding exists instead, as previously discussed by Perlin et al.[28]

In an effort to better understand the scope of the reaction, a study of which types of nucleophiles were appropriate for the transformation was undertaken. Simple alkoxides appear most successful (methoxide, allyloxide, benzyloxide), and the use of a thiolate (thiomethoxide, thioethoxide) resulted in a quantitative recovery of starting material after several days at room temperature. This suggests that an anionic oxygen is more effective at cleaving the S−O bond, although the cleavage of a sulfonate linkage via attack on the sulfur center by thiophenoxide has been reported in literature.[23]

Next, the effect of the anomeric linkage was probed by first studying its stereochemical requirements. Synthesis of methyl 4,6-*O*-benzylidene-2,3-di-*O*-mesyl-α-D-galactopyranoside **14**
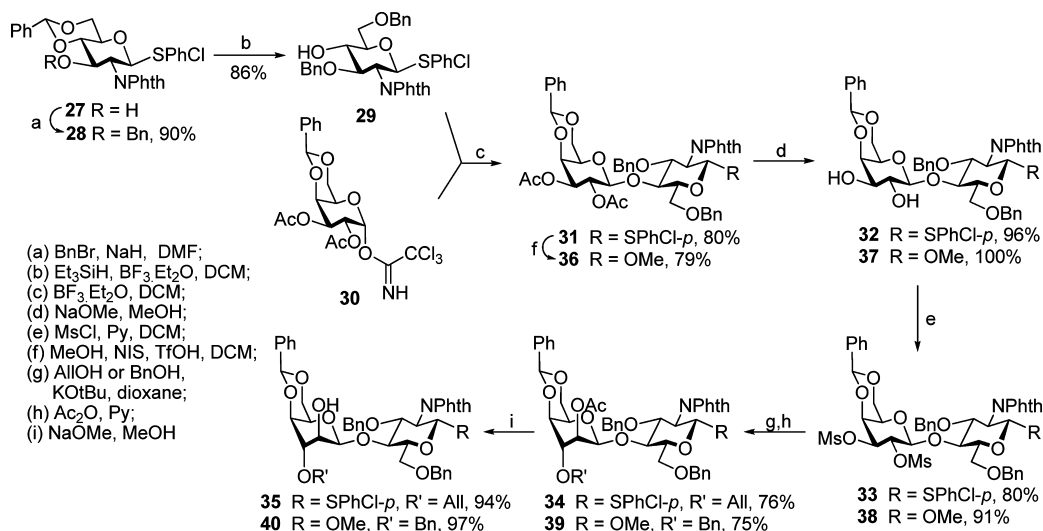
was obtained in two steps from methyl α-D-galactopyranoside,[31,32] and then reacted with sodium methoxide solution at room temperature (Scheme 3). After several days a mixture of *talo*- (**15**) and *gulo*-epoxides (**16**) were isolated; the lack of further nucleophilic attack to open the epoxide could be explained by the unfavorable 1,3-diaxial-type interactions that prevent approach of the nucleophile at both the C-2 and C-3 positions. A previous attempt to form epoxides from similar conditions also resulted in a mixture of *gulo*- and *talo*-epoxides,[24] suggesting that although nucleophilic attack on these isomers has been observed to be stereospecific (at elevated temperatures) to give the expected diaxial products,[29] the poor stereoselectivity observed for epoxide formation from the dimesylate suggests that using our approach in α-galactoside will not be as successful as in the β-isomers.

To further probe the requirements of the anomeric center, several other *O*-glycosides and *S*-glycosides were synthesized (Scheme 4). For example, 4,6-*O*-benzylidenated allyl β-D-

Scheme 4. Formation of a D-Idose Derivative from Allyl 4,6-*O*-Benzylidene-2,3-di-*O*-mesylgalactoside 18 and β-D-Thiogalactosides 21 and 25

(a) MsCl, DCM, Py; (b) KOtBu, BnOH, dioxane
(c) KOtBu, AllOH, dioxane
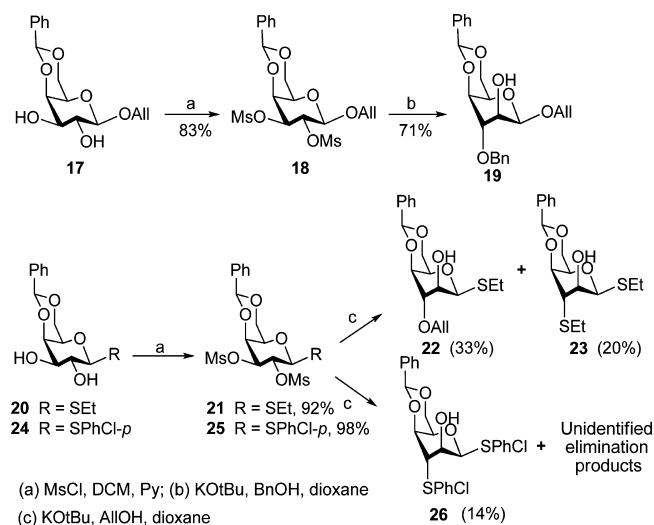
galactopyranoside (**17**)[33] was mesylated to obtain the desired target **18**, which upon reaction with potassium benzyloxide, afforded exclusively the desired allyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-idopyranoside **19** in 71% yield. On the other hand, reactions with β-D-thioglycoside analogues **20**[34] and **24**[35] were much less successful (Scheme 4). When the dimesylate (**21**) of ethyl thioglycoside **20** was treated with allyloxide in an allyl alcohol−dioxane mixture, the desired 3-*O*-allyl β-D-thioidopyranoside **22** was obtained in 33% yield together with **23** (20% yield) which bears a 3-thioethyl group; alternatively, when the

Scheme 5. Synthesis of Two D-Idose-Containing Disaccharides

(a) BnBr, NaH, DMF;
(b) Et₃SiH, BF₃.Et₂O, DCM;
(c) BF₃.Et₂O, DCM;
(d) NaOMe, MeOH;
(e) MsCl, Py, DCM;
(f) MeOH, NIS, TfOH, DCM;
(g) AllOH or BnOH, KOtBu, dioxane;
(h) Ac₂O, Py;
(i) NaOMe, MeOH

Scheme 6. Deprotection Scheme for Disaccharide 39

(a) H₂, Pd, AcOH, MeOH;
(b) NH₂NH₂.H₂O, EtOH;
(c) Ac₂O, Pyr;
(d) NaOMe, MeOH, 62% (4 steps)
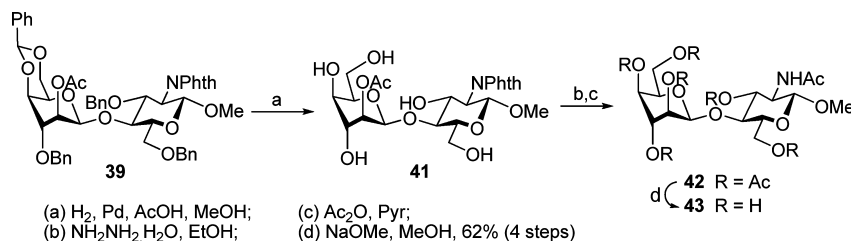
dimesylate (**25**) from *p*-chlorophenyl thioanalogue **24** was subjected to the same reaction conditions, no desired product was obtained, but the reaction indeed afforded an analogous 3-thio-*p*-chlorophenyl-substituted byproduct (**26**) and other unidentified elimination products. Clearly the byproducts **23** and **26** must be obtained via an interesting intermolecular attack by thioethyl or thio-*p*-chlorophenyl on the intermediate 2,3-anhydrotaloside in each case; the increased nucleophilicity of the anomeric sulfur atom over negatively charged allyloxide is likely to account for the observed byproduct formation.

To further appreciate the scope of the reaction and also demonstrate that this indeed was a suitable method for installing β-*ido*-glycosidic linkages, we prepared two β-D-*ido*-(1→4)-β-D-GlcNAc disaccharide analogues related to *C. jejuni* CPS (Scheme 5). Thus, starting from the previously known D-glucosamine thioglycoside **27**,[35] we protected the O-3 position with benzyl (→**28**, 90% yield). After regioselective opening of the 4,6-O-benzylidene acetal group using triethylsilane, the alcohol **29** was obtained (86% yield). Boron trifluoride etherate-mediated activation of the imidate donor **30**[36] enabled the glycosylation reaction with **29** to afford the desired thiodisaccharide **31** in 80% yield (based on recovered glycosyl acceptor). The thioglycoside was then deacetylated via Zemplén transesterification to afford intermediate diol **32** which was directly di-O-mesylated to afford compound **33**. The reaction of the dimesylate with allyloxide afforded a disaccharide with the expected 3′-O-allyl-substituted β-D-idopyranosyl unit. Interestingly, due to the sensitivity of the phthalimido-protecting group to strong bases, partial cleavage of this N-protecting group occurred upon alkoxide treatment to produce the corresponding carboxylic acid derivative, which became evident by the significant increase in polarity observed

for this intermediate compound. Fortunately, heating the product in acetic anhydride and pyridine restored the phthalimido group to afford the desired acetylated product **34** in 76% yield, with a few minor byproducts indicated by thin layer chromatography. Based on the previous observations made for the monosaccharides, one of the byproducts observed for this transformation may have been due to the nucleophilic thioglycoside, although the effect of the thio-linkage in this latter instance was much less detrimental to the di-inversion reaction than what had been observed previously. A subsequent deacetylation of the OH-2′ position provided alcohol **35** which was fully characterized by 1D ¹H, ¹³C, and 2D GCOSY, GHSQC NMR experiments as well as high-resolution mass spectrometry.

Alternatively, the thioglycoside **31** was converted to an O-methyl glycoside **36** via a subsequent N-iodosuccinimide/triflic acid-mediated glycosylation reaction with methanol. Deacetylation of the methyl glycoside afforded diol intermediate **37**, which gave the target compound **38** after a dimesylation; treatment of **38** with benzyloxide afforded the desired β-D-idopyranosyl substituted disaccharide, which had the phthalimido group partially opened as before; again, acetylation was necessary to restore the integrity of the phthalimido-protecting group to afford the desired product **39** in 75% yield over two steps; in this instance with the O-glycoside, no other byproducts were observed in these 2 reactions. Interestingly, the half-width of the phthalimido peaks in the ¹³C NMR varied greatly between the O-glycoside and the S-glycoside analogues. The half-widths were observed to be significantly greater for the O-glycosides, indicating that in these compounds the phthalimido carbons were more sterically restrained resulting in their faster relaxation times.[37] This could be a result of the

shorter anomeric C—O bond which results in a more restricted C—N bond rotation for the phthalimido group.

The O-linked disaccharide **39** was then deprotected (Scheme 6) via hydrogenation to concomitantly remove both the benzylidene acetal and benzyl groups (→**41**). This intermediate was then subjected to hydrazine hydrate which simultaneously removed the phthalimido and acetyl groups;[38] the product was not isolated but instead fully acetylated to afford **42**, which upon a selective de-O-acetylation provided the final deprotected product **43** in 62% yield over the four-step deprotection sequence. It was found that the β-D-idopyranosyl linkage is somewhat sensitive to acidic conditions, thus full acetylation in pyridine (basic) was performed instead of using more direct Ac$_2$O—MeOH condition (acidic) for selective N-acetylation.

■ CONCLUSIONS

In conclusion, we have developed a practical method to obtain D-idopyranose from D-galactose, which is the first approach that enables access to orthogonally protected D-idose. In addition, it is the first method to allow for the synthesis of oligosaccharides containing the challenging β-1,2-cis-linked idopyranosides. The key double inversions of galactose at O-2 and O-3 were achieved through the regio- and stereoselective opening of 2,3-anhydro talopyranosides using a selection of alkoxides, and the process is scalable and requires minimal purification, so could be used to produce building blocks to aid in the synthesis of various β-idopyranose-containing oligosaccharide targets to further probe their biological functions.

■ EXPERIMENTAL SECTION

General Methods. All commercial reagents were used as supplied unless otherwise stated. Thin-layer chromatography was performed on silica gel 60-F254 with detection by fluorescence, charring with 5% aqueous sulfuric acid, or a ceric ammonium molybdate solution. Column chromatography was performed on silica gel 60, and solvent gradients given refer to stepped gradients and concentrations are reported as % v/v. Organic solutions were concentrated and/or evaporated to dryness under vacuum in a water bath (<60 °C). Molecular sieves were stored in an oven at 100 °C and flame-dried under vacuum before use. Amberlite IR-120H ion-exchange resin was washed multiple times with methanol prior to use. Optical rotations were determined in a 5 cm cell at 20 ± 2 °C; $[\alpha]^{20}_D$ values are given in units of 10^{-1} deg·cm^2/g. NMR spectra were recorded at either 400 or 600 MHz (as indicated), and the first-order proton chemical shifts δ_H and δ_C are reported in δ (ppm) and referenced to residual CHCl$_3$ (δ_H 7.24 and δ_C 77.23, CDCl$_3$) or CD$_2$HOD (δ_H 3.31, δ_C 49.15, CD$_3$OD). ^{1}H and ^{13}C NMR spectra were assigned with the assistance of 2D GCOSY, 2D GTOCSY, 2D GHSQC, 2D GHMBC, 1D TOCSY, and/or 1D HMBC experiments. High-resolution mass spectra were recorded using ESI-QTOF LC/MS mass spectrometry.

Methyl 3-O-Benzyl-4,6-O-benzylidene-β-D-idopyranoside (5). A solution of potassium *tert*-butoxide in benzyl alcohol (2.07 M, 5.0 mL, 10.3 mmol) was added to a solution of the ditosylate starting material **3** (1.099 g, 1.86 mmol) in 1,4-dioxane (15 mL). After 2 days, the reaction mixture was evaporated to dryness via coevaporation with water (2 × 20 mL), redissolved in ethyl acetate (100 mL), washed with water (3 × 100 mL), dried with sodium sulfate, filtered, and concentrated under reduced pressure to a viscous syrup. The crude mixture was purified by column chromatography on silica gel using 10→15→18% ethyl acetate—hexanes to afford the pure product as a yellow syrup (323 mg, 0.868 mmol, 47% yield). R_f = 0.82 (ethyl acetate/toluene 1:1). $[\alpha]^{20}_D$: −35.0 (c 1.04, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.47 − 7.44 (m, 2H, Ph), 7.37−7.29 (m, 8H, Ph), 5.48 (s, 1H, PhCH), 4.69 (d, 1H, J = <1 Hz, H-1), 4.66 (d, 1H, J = 11.8 Hz, PhCH$_2$), 4.62 (d, 1H, J = 11.8 Hz, PhCH$_2$), 4.38 (dd, 1H, J = 12.5, 1.4 Hz, H-6a), 4.07 (dd, 1H, J = 12.5, 1.9 Hz, H-6b), 4.01 (m,

1H, H-4), 3.89 (dd, 1H, J = 2.9, 2.9 Hz, H-3), 3.77 (m, 1H, H-2), 3.75 (m, 1H, H-5), 3.59 (s, 3H, CH$_3$), 3.16 (d, 1H, J = 11.7 Hz, 2-OH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.6 (Ph), 137.5 (Ph), 129.4 (Ph), 128.8 (Ph), 128.5 (Ph), 128.4 (Ph), 127.8 (Ph), 126.3 (Ph), 101.7 (PhCH), 100.5 (C-1), 76.8 (C-3), 73.8 (C-4), 72.8 (PhCH$_2$), 69.9 (C-6), 67.3 (C-2), 67.0 (C-5), 57.2 (CH$_3$). HRMS (ESI): calcd m/z for C$_{21}$H$_{24}$O$_6$ (M + Na)$^+$ 395.1465, found 395.1464.

Methyl 3-O-Allyl-4,6-O-benzylidene-β-D-idopyranoside (6). A solution of potassium *tert*-butoxide in allyl alcohol (3.23 M, 52 mL, 0.17 mmol) was added to a solution of the ditosylate starting material **3** (11.06 g, 18.72 mmol) in benzene (150 mL). After 4 days, the reaction mixture was evaporated to dryness, redissolved in ethyl acetate (200 mL), washed with saturated sodium chloride solution (2 × 200 mL) and water (1 × 200 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 25% ethyl acetate—hexanes to afford the pure product as a white solid (4.77 g, 14.8 mmol, 79% yield). R_f = 0.49 (ethyl acetate/toluene 1:1). $[\alpha]^{20}_D$: −55.5° (c 1.01, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46−7.41 (m, 2H, Ph), 7.32−7.27 (m, 3H, Ph), 5.84 (dddd, 1H, J = 17.1, 10.5, 5.6, 5.6 Hz, CH$_2$CH=CH$_2$), 5.46 (s, 1H, PhCH), 5.25 (dddd, 1H, J = 17.2, 1.5, 1.5, 1.5 Hz, CH$_2$CH=CH$_2$), 5.18 (dddd, 1H, J = 10.4, 1.3, 1.3, 1.3 Hz, CH$_2$CH=CH$_2$), 4.62 (d, 1H, J = 0.6 Hz, H-1), 4.33 (dd, 1H, J = 12.5, 1.3 Hz, H-6a), 4.08 (dddd, 1H, J = 12.8, 5.6, 1.4, 1.4 Hz, CH$_2$CH=CH$_2$), 4.04 (dddd, 1H, J = 12.9, 5.4, 1.4, 1.4 Hz, CH$_2$CH=CH$_2$), 4.04 (dd, 1H, J = 12.6, 1.6 Hz, H-6b), 3.95 (m, 1H, H-4), 3.77 (dd, 1H, J = 2.9, 2.9 Hz, H-3), 3.69 (m, 2H, H-2 and H-5), 3.55 (s, 3H, OCH$_3$), 3.14 (d, 1H, J = 11.7 Hz, 2-OH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.4 (Ph), 133.9 (CH$_2$CH=CH$_2$), 129.2 (Ph), 128.3 (Ph), 126.1 (Ph), 117.9 (CH$_2$CH=CH$_2$), 101.5 (PhCH), 100.4 (C-1), 76.3 (C-3), 73.7 (C-4), 71.5 (CH$_2$CH=CH$_2$), 69.7 (C-6), 67.2 (C-2 or C-5), 66.8 (C-2 or C-5), 57.0 (OCH$_3$). HRMS (ESI): calcd m/z for C$_{17}$H$_{22}$O$_6$ (M + Na)$^+$ 345.1309, found 345.1306. Anal. Calcd for C$_{17}$H$_{22}$O$_6$: C, 63.34; H, 6.88. Found: C, 63.26; H, 6.87.

Methyl 2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-idopyranoside (7). The starting material **5** (1.000 g, 2.68 mmol) was dissolved in dry tetrahydrofuran (10.0 mL), and then the solution was cooled to 0 °C using an ice—water bath. Sodium hydride (57–63% oil dispersion, 225 mg, 5.62 mmol) was added in a portionwise fashion, followed by benzyl bromide (0.42 mL, 3.5 mmol) which was also added portionwise over 10 min. The mixture was warmed to room temperature and then allowed to mix under argon overnight. The reaction was quenched via the addition of methanol (3 mL), evaporated to dryness, and then redissolved in ethyl acetate (120 mL). The organic phase was washed with saturated aqueous sodium chloride solution (2 × 120 mL) and water (1 × 120 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 20% ethyl acetate—hexanes to afford the desired product as a yellow syrup (990 mg, 2.14 mmol, 80% yield). R_f = 0.66 (acetone/hexanes 4:6). $[\alpha]^{20}_D$: −24.1 (c 0.99, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 7.61 (dd, 2H, J = 7.6, 1.8 Hz, PhCH), 7.45−7.29 (m, 13H, Ph), 5.55 (s, 1H, PhCH), 4.90 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.80 (d, 1H, J = 1.4 Hz, H-1), 4.71 (d, 1H, J = 12.1 Hz, PhCH$_2$), 4.65 (d, 1H, J = 12.3 Hz, PhCH$_2$), 4.62 (d, 1H, J = 12.2 Hz, PhCH$_2$), 4.41 (dd, 1H, J = 12.5, 0.9 Hz, H-6a), 4.10 (dd, 1H, J = 12.5, 2.0 Hz, H-6b), 4.02−3.99 (m, 2H, H-3 and H-4), 3.73 (m, 1H, H-5), 3.70 (m, 1H, H-2), 3.64 (s, 3H, OMe). ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 138.7 (Ph), 138.2 (Ph), 137.6 (Ph), 128.8 (Ph), 128.5 (Ph), 128.03 (Ph), 127.96 (Ph), 127.93 (Ph), 127.65 (Ph), 127.59 (Ph), 127.2 (Ph), 126.8 (Ph), 101.2 (PhCH), 100.6 (C-1), 76.5 (C-3), 73.8 (C-2), 73.2 (C-4), 72.9 (PhCH$_2$), 72.3 (PhCH$_2$), 69.6 (C-6), 66.6 (C-5), 56.6 (OMe). HRMS (ESI): calcd m/z for C$_{28}$H$_{30}$O$_6$ (M + Na)$^+$ 485.1935, found 485.1934.

Methyl 2,3-Di-O-benzyl-β-D-idopyranoside (8). The starting material **7** (243 mg, 0.526 mmol) was dissolved in acetic acid (2.0 mL) and water (0.5 mL) and heated at 60 °C. After 3 h, the mixture was concentrated and coevaporated with toluene (3 × 2 mL). The crude mixture was purified by column chromatography on silica gel using 15→20% acetone—hexanes to afford the desired product as a yellow syrup (169 mg, 0.451 mmol, 86% yield). R_f = 0.37 (acetone/hexanes

4:6). $[\alpha]^{20}_D$: −71.0 (c 1.04, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.34−7.26 (m, 8H, Ph), 7.22−7.18 (m, 2H, Ph), 4.83 (d, 1H, J = 12.1 Hz, PhCH$_2$), 4.68 (d, 1H, J = 0.7 Hz, H-1), 4.61 (d, 1H, J = 12.1 Hz, PhCH$_2$), 4.49 (d, 1H, J = 11.9 Hz, PhCH$_2$), 4.46 (d, 1H, J = 11.9 Hz, PhCH$_2$), 3.98 (ddd, 1H, J = 11.1, 7.2, 3.4 Hz, H-6a), 3.92 (ddd, 1H, J = 7.2, 3.9, 1.0 Hz, H-5), 3.79 (ddd, 1H, J = 11.1, 8.8, 3.9 Hz, H-6b), 3.75 (dd, 1H, J = 3.3, 3.3 Hz, H-3), 3.63 (m, 1H, H-4), 3.61 (m, 1H, H-2), 3.56 (d, 1H, J = 11.4 Hz, 4-OH), 3.56 (s, 3H, Me), 2.24 (dd, 1H, J = 8.8, 3.5 Hz, 6-OH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.61 (Ph), 137.58 (Ph), 128.74 (Ph), 128.66 (Ph), 128.3 (Ph), 128.2 (Ph), 127.8 (Ph), 101.2 (C-1), 76.0 (C-3), 75.5 (C-5), 74.8 (C-2), 74.5 (PhCH$_2$), 72.4 (PhCH$_2$), 67.5 (C-4), 63.1 (C-6), 57.3 (Me). HRMS (ESI): calcd m/z for C$_{21}$H$_{26}$O$_6$ (M + Na)$^+$ 397.1622, found 397.1631.

Methyl 3-O-Allyl-2-O-benzyl-4,6-O-benzylidene-β-D-idopyranoside (9). The starting material **6** (325 mg, 1.01 mmol) was dissolved in dry tetrahydrofuran (3.5 mL) and then the solution was cooled to 0 °C using an ice−water bath. Sodium hydride (57−63% oil dispersion, 65 mg, 1.6 mmol) was added in a portionwise fashion, followed by benzyl bromide (0.32 mL, 2.7 mmol) dropwise over several minutes. The mixture was warmed to room temperature and then allowed to mix under argon overnight. The reaction was quenched via the addition of methanol (1 mL), evaporated to dryness, and then redissolved in ethyl acetate (60 mL). The organic phase was washed with saturated aqueous sodium chloride solution (2 × 60 mL) and water (1 × 60 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 20% ethyl acetate−hexanes to afford the desired product as a clear, colorless syrup (322 mg, 0.781 mmol, 77% yield). R_f = 0.64 (ethyl acetate/toluene 6:4). $[\alpha]^{20}_D$: −31.0 (c 0.93, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.55−7.51 (m, 2H, PhCH), 7.41−7.36 (m, 2H, PhCH$_2$), 7.33−7.23 (m, 6H, Ph), 5.86 (dddd, 1H, J = 17.2, 10.4, 5.6, 5.6 Hz, CH$_2$=CHCH$_2$), 5.50 (s, 1H, PhCH), 5.25 (dddd, 1H, J = 17.2, 1.6, 1.6, 1.6 Hz, CH$_2$=CHCH$_2$), 5.19 (dddd, 1H, J = 10.4, 1.4, 1.4, 1.4 Hz, CH$_2$=CHCH$_2$), 4.88 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.69 (d, 1H, J = 1.4 Hz, H-1), 4.68 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.36 (dd, 1H, J = 12.5, 1.1 Hz, H-6a), 4.07 (dd, 1H, J = 12.5, 2.0 Hz, H-6b), 4.05 (m, 2H, CH$_2$=CHCH$_2$), 3.91 (ddd, 1H, J = 1.6, 1.6, <1 Hz, H-4), 3.85 (dd, 1H, J = 3.3, 2.2 Hz, H-3), 3.66 (m, 1H, H-5), 3.59 (m, 1H, H-2), 3.58 (s, 3H, OMe). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 138.9 (Ph), 138.2 (Ph), 134.2 (CH$_2$=CHCH$_2$), 129.0 (Ph), 128.2 (Ph), 128.1 (Ph), 127.8 (Ph), 127.3 (Ph), 126.9 (Ph), 117.7 (CH$_2$=CHCH$_2$), 101.4 (PhCH), 100.8 (C-1), 76.4 (C-3), 73.9 (C-2), 73.4 (C-4), 73.2 (PhCH$_2$), 71.4 (CH$_2$=CHCH$_2$), 69.8 (C-6), 66.7 (C-5), 56.8 (OMe). HRMS (ESI): calcd m/z for C$_{24}$H$_{28}$O$_6$ (M + Na)$^+$ 435.1778, found 435.1774.

Methyl 3-O-Allyl-2-O-benzyl-β-D-idopyranoside (10). A solution of the starting material **9** (3.45 g, 8.36 mmol) in aqueous acetic acid (50 mL; acetic acid/water 4:1) was allowed to mix at 80 °C. After 16 h, the reaction mixture was evaporated to dryness via coevaporation with toluene (3 × 20 mL) and then redissolved in methanol (40 mL). A sodium methoxide solution was added (1.5 M NaOMe in MeOH, to pH 8), and the solution was allowed to mix at room temperature for 1 h. The mixture was then neutralized with ion-exchange resin (Amberlite IR-120H, to pH 6), filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 20% acetone−hexanes to afford the desired product as a yellow syrup (2.09 g, 6.44 mmol, 77% yield). R_f = 0.18 (ethyl acetate/toluene 6:4). $[\alpha]^{20}_D$: −86.9° (c 0.93, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.34−7.27 (m, 5H, Ph), 5.76 (dddd, 1H, J = 17.2, 10.4, 5.6, 5.6 Hz, CH$_2$CH=CH$_2$), 5.16 (dddd, 1H, J = 17.2, 1.6, 1.6, 1.6 Hz, CH$_2$CH=CH$_2$), 5.12 (dddd, 1H, J = 10.4, 1.3, 1.3, 1.3 Hz, CH$_2$CH=CH$_2$), 4.87 (d, 1H, J = 12.1 Hz, PhCH$_2$), 4.64 (d, 1H, J = 0.9 Hz, H-1), 4.63 (d, 1H, J = 12.1 Hz, PhCH$_2$), 3.97 (ddd, 1H, J = 11.4, 7.1, <1 Hz, H-6a), 3.93 (dddd, 2H, J = 5.7, 1.2, 1.2, 1.2 Hz, CH$_2$CH=CH$_2$), 3.87 (ddd, 1H, J = 7.1, 4.3, <1 Hz, H-5), 3.78 (ddd, 1H, J = 11.4, 4.2, <1 Hz, H-6b), 3.68 (m, 1H, H-3), 3.59−3.58 (m, 3H, H-2, H4, and 4-OH), 3.56 (s, 3H, CH$_3$), 2.29 (broad, 1H, 6-OH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.6 (Ph), 134.1 (CH$_2$CH=CH$_2$), 128.6 (Ph), 128.3 (Ph), 128.2 (Ph), 117.9 (CH$_2$CH=CH$_2$), 101.2 (C-1), 75.8 (C-3), 75.4 (C-5), 74.9 (C-2), 74.5 (PhCH$_2$), 71.4 (CH$_2$CH=CH$_2$), 67.6

(C-4), 63.0 (C-6), 57.3 (CH$_3$). HRMS (ESI): calcd m/z for C$_{17}$H$_{24}$O$_6$ (M + Na)$^+$ 347.1465, found 347.1464.

Methyl 2,3-Anhydro-4,6-O-benzylidene-β-D-gulopyranoside (11). The byproduct **11** was isolated as a white solid in trace amounts (2%) in a few instances during the synthesis of **6**; the data collected agrees with published literature.[30,39]

Methyl 4,6-O-Benzylidene-2-O-methyl-β-D-idopyranoside (12). The starting material **11** and sodium methoxide solution (1.5 M NaOMe in MeOH; 0.4 mmol) were dissolved in dioxane (0.3 mL) and allowed to mix at room temperature. After 3 days no significant change was evident on TLC, so the reaction mixture was heated at 70 °C for 18 h and then evaporated to dryness. The crude material was redissolved in ethyl acetate (5 mL), washed with water (5 mL), and then evaporated to dryness to obtain the crude product (as a mixture with unreacted **11**) which was directly analyzed by ^{1}H NMR and GCOSY. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.52−7.50 (m, 2H, Ph), 7.36−7.30 (m, 3H, Ph), 5.45 (s, 1H, PhCH), 4.77 (d, 1H, J = 1.5 Hz, H-1), 4.33−4.28 (m, 1H, H-6a), 4.24 (m, 1H, H-3), 4.03 (dd, 1H, J = 12.6, 2.1 Hz, H-6b), 3.87 (dd, 1H, J = 1.5, 1.5 Hz, H-4), 3.69 (m, 1H, H-5), 3.54 (s, 3H, OMe), 3.50 (s, 3H, OMe), 3.34 (dd, 1H, J = 4.3, 1.3 Hz, H-2), 2.15 (broad, 1H, 3-OH).

Methyl 4,6-O-Benzylidene-2,3-di-O-mesyl-α-D-galactopyranoside (14). The starting material **13** (152 mg, 0.539 mmol) and methanesulfonyl chloride (0.19 mL, 2.4 mmol) were dissolved in dry dichloromethane (1.0 mL) and pyridine (0.5 mL) and allowed to mix at room temperature under argon. After 24 h, the reaction was quenched via the addition of methanol (0.5 mL), evaporated to dryness, and then redissolved in ethyl acetate (20 mL). The organic phase was washed with saturated sodium chloride solution (3 × 20 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude material was purified by column chromatography on silica gel using 20% ethyl acetate−toluene to afford the pure product as a white solid (206 mg, 0.523 mmol, 97% yield). R_f = 0.47 (ethyl acetate/toluene 1:1). $[\alpha]^{20}_D$: +152 (c 0.98, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.51−7.46 (m, 2H, Ph), 7.39−7.33 (m, 3H, Ph), 5.55 (s, 1H, PhCH), 5.09 (d, 1H, J = 3.4 Hz, H-1), 5.08 (dd, 1H, J = 10.4, 3.6 Hz, H-3), 4.99 (dd, 1H, J = 10.2, 3.6 Hz, H-2), 4.53 (dd, 1H, J = 3.6, <1 Hz, H-4), 4.24 (dd, 1H, J = 12.7, 1.5 Hz, H-6a), 4.04 (dd, 1H, J = 12.7, 1.6 Hz, H-6b), 3.71 (m, 1H, H-5), 3.44 (s, 3H, OCH$_3$), 3.06 (s, 3H, SO$_2$CH$_3$), 3.04 (s, 3H, SO$_2$CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.2 (Ph), 129.4 (Ph), 128.4 (Ph), 126.3 (Ph), 101.0 (PhCH), 98.5 (C-1), 75.2 (C-4), 74.5 (C-3), 73.7 (C-2), 68.8 (C-6), 62.2 (C-5), 56.1 (OCH$_3$), 39.1 (CH$_3$), 38.7 (CH$_3$). HRMS (ESI): calcd m/z for C$_{16}$H$_{22}$O$_{10}$S$_2$ (M + NH$_4$)$^+$ 456.0993, found 456.0980.

Methyl 2,3-Anhydro-4,6-O-benzylidene-α-D-talopyranoside (15) and Methyl 2,3-Anhydro-4,6-O-benzylidene-α-D-gulopyranoside (16). A solution of sodium methoxide (1.5 M sodium methoxide in methanol, 1.4 mL, 2.1 mmol) was added to a solution of **14** (175 mg, 0.399 mmol) in dioxane (3.5 mL) and allowed to mix at room temperature under argon. After 3 days, the reaction mixture was evaporated to dryness, redissolved in ethyl acetate (20 mL), washed with saturated sodium chloride solution (3 × 20 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude material was purified by column chromatography on silica gel using 20→30→50% ethyl acetate−hexanes to afford **15** (27 mg, 0.10 mmol, 25% yield) and **16** (62 mg, 0.23 mmol, 59% yield) as white solids; their full characterization agrees with those previously published in literature.[22,30,40]

Allyl 4,6-O-benzylidene-2,3-di-O-mesyl-α-D-galactopyranoside (18). Methanesulfonyl chloride (2.8 mL, 36 mmol) was added to a solution of the starting material **17** (153 mg, 49.6 mmol) in dry dichloromethane (30 mL) and dry pyridine (15 mL). The reaction was allowed to mix for 24 h at room temperature, quenched via the addition of methanol (10 mL), concentrated and then redissolved in ethyl acetate (60 mL). The organic phase was washed with saturated aqueous sodium chloride solution (3 × 60 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 10% ethyl acetate−toluene to afford the desired product as a white solid (192 mg, 41.3 mmol, 83% yield). R_f = 0.53 (acetone/toluene 2:8). $[\alpha]^{20}_D$:

+23.5 (c 1.06, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.48 (m, 2H, Ph), 7.37−7.29 (m, 3H, Ph), 5.87 (dddd, 1H, J = 17.2, 10.4, 6.6, 5.3 Hz, CH$_2$CH=CH$_2$), 5.51 (s, 1H, PhCH), 5.30 (dddd, 1H, J = 17.2, 1.5, 1.5, 1.5 Hz, CH$_2$CH=CH$_2$), 5.21 (dddd, 1H, J = 10.4, 1.2, 1.2, 1.2 Hz, CH$_2$CH=CH$_2$), 4.83 (dd, 1H, J = 10.0, 7.7 Hz, H-2), 4.75 (dd, 1H, J = 10.0, 3.6 Hz, H-3), 4.56 (d, 1H, J = 7.7 Hz, H-1), 4.45 (dd, 1H, J = 3.6, 0.5 Hz, H-4), 4.41 (dddd, 1H, J = 12.5, 5.3, 1.4, 1.4 Hz, CH$_2$CH=CH$_2$), 4.24 (dd, 1H, J = 12.6, 1.4 Hz, H-6a), 4.09 (dddd, 1H, J = 12.5, 6.6, 1.1, 1.1 Hz, CH$_2$CH=CH$_2$), 4.02 (dd, 1H, J = 12.6, 1.6 Hz, H-6b), 3.46 (m, 1H, H-5), 3.12 (s, 3H, CH$_3$), 3.09 (s, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.3 (Ph), 133.0 (CH$_2$CH=CH$_2$), 129.2 (Ph), 128.3 (Ph), 126.4 (Ph), 118.9 (CH$_2$CH=CH$_2$), 100.9 (PhCH), 98.9 (C-1), 77.1 (C-3), 76.8 (C-2), 75.0 (C-4), 70.3 (CH$_2$CH=CH$_2$), 68.5 (C-6), 66.1 (C-5), 39.5 (CH$_3$), 39.1 (CH$_3$). HRMS (ESI): calcd m/z for C$_{18}$H$_{24}$O$_{10}$S$_2$ (M + Na)$^+$ 487.0703, found 487.0705. Anal. Calcd for C$_{18}$H$_{24}$O$_{10}$S$_2$: C, 46.54; H, 5.21. Found: C, 46.85; H, 4.75.

Allyl 3-O-Benzyl-4,6-O-benzylidene-β-D-idopyranoside (19). A solution of potassium *tert*-butoxide (286 mg, 2.55 mmol) in benzyl alcohol (1.00 mL, 9.65 mmol) was left for 30 min and then added to a solution of the dimesylate starting material **18** (139 mg, 0.300 mmol) in benzene (2.0 mL), and the contents of the flask were allowed to mix at room temperature. After 2 days, the reaction mixture was evaporated to dryness, and the crude contents were redissolved in ethyl acetate (60 mL). The organic phase was washed with saturated aqueous sodium chloride solution (3 × 60 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 20% ethyl acetate−hexanes to afford the desired product as a pale yellow syrup (85 mg, 0.21 mmol, 71% yield). R_f = 0.75 (ethyl acetate/toluene 1:1). [α]^{20}$_D$: −35.1 (c 1.01, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.47−7.42 (m, 2H, Ph), 7.38−7.28 (m, 8H, Ph), 5.96 (dddd, 1H, J = 17.2, 10.4, 6.5, 5.1 Hz, CH$_2$CH=CH$_2$), 5.48 (s, 1H, PhCH), 5.29 (dddd, 1H, J = 17.2, 1.6, 1.6, 1.6 Hz, CH$_2$CH=CH$_2$), 5.19 (dddd, 1H, J = 10.4, 1.7, 1.2, 1.2 Hz, CH$_2$CH=CH$_2$), 4.82 (d, 1H, J = 0.9 Hz, H-1), 4.66 (d, 1H, J = 11.8 Hz, PhCH$_2$), 4.61 (d, 1H, J = 11.8 Hz, PhCH$_2$), 4.45 (dddd, 1H, J = 12.8, 5.1, 1.5, 1.5 Hz, CH$_2$CH=CH$_2$), 4.37 (dd, 1H, J = 12.5, 1.5 Hz, H-6a), 4.15 (dddd, 1H, J = 12.8, 6.5, 1.3, 1.3 Hz, CH$_2$CH=CH$_2$), 4.06 (dd, 1H, J = 12.5, 1.9 Hz, H-6b), 4.00 (ddd, 1H, J = 2.8, 1.1, 1.1 Hz, H-4), 3.89 (dd, 1H, J = 2.9, 2.9 Hz, H-3), 3.77 (dddd, 1H, J = 11.6, 3.1, 1.0, 1.0 Hz, H-2), 3.74 (m, 1H, H-5), 3.16 (d, 1H, J = 11.7 Hz, 2-OH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.6 (Ph), 137.5 (Ph), 134.5 (CH$_2$CH=CH$_2$), 129.4 (Ph), 128.8 (Ph), 128.5 (Ph), 128.4 (Ph), 127.9 (Ph), 126.3 (Ph), 117.8 (CH$_2$CH=CH$_2$), 101.7 (PhCH), 98.3 (C-1), 76.8 (C-3), 73.9 (C-4), 72.8 (PhCH$_2$), 70.2 (CH$_2$CH=CH$_2$), 69.9 (C-6), 67.5 (C-2), 67.0 (C-5). HRMS (ESI): calcd m/z for C$_{23}$H$_{26}$O$_6$ (M + Na)$^+$ 421.1622, found 421.1627.

Ethyl 4,6-O-Benzylidene-2,3-di-O-mesyl-1-thio-β-D-galactopyranoside (21). The starting material **20** (195 mg, 0.625 mmol) and methanesulfonyl chloride (0.50 mL, 6.5 mmol) were dissolved in dry dichloromethane (6.0 mL) and dry pyridine (3.0 mL) and allowed to mix at room temperature. After 16 h, excess reagent was quenched by the addition of methanol (5 mL), and then the reaction mixture was concentrated to a viscous syrup via coevaporation with toluene (2 × 5 mL). The crude product was redissolved in ethyl acetate (50 mL), washed with saturated sodium chloride solution (2 × 50 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 25% ethyl acetate−toluene to afford the desired product as a white solid (270 mg, 0.577 mmol, 92% yield). R_f = 0.60 (ethyl acetate/toluene 1:1). [α]^{20}$_D$: −2.1 (c 0.97, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.55−7.51 (m, 2H, Ph), 7.45−7.39 (m, 3H, Ph), 5.58 (s, 1H, PhCH), 5.08 (dd, 1H, J = 9.6, 9.6 Hz, H-2), 4.84 (dd, 1H, J = 9.6, 3.6 Hz, H-3), 4.59 (dd, 1H, J = 3.6, <1 Hz, H-4), 4.57 (d, 1H, J = 9.7 Hz, H-1), 4.33 (dd, 1H, J = 12.6, 1.5 Hz, H-6a), 4.03 (dd, 1H, J = 12.6, 1.6 Hz, H-6b), 3.58 (m, 1H, H-5), 3.25 (s, 3H, SO$_2$CH$_3$), 3.18 (s, 3H, SO$_2$CH$_3$), 2.92 (dq, 1H, J = 12.3, 7.5 Hz, CH$_2$CH$_3$), 2.81 (dq, 1H, J = 12.3, 7.5 Hz, CH$_2$CH$_3$), 1.36 (dd, 3H, J = 7.5, 7.5 Hz, CH$_2$CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.4 (Ph), 129.4 (Ph), 128.4 (Ph), 126.4 (Ph), 101.2 (PhCH), 82.3 (C-1), 78.0 (C-3), 75.0 (C-4), 74.5

(C-2), 69.6 (C-5), 68.8 (C-6), 39.9 (SO$_2$CH$_3$), 39.2 (SO$_2$CH$_3$), 23.2 (CH$_2$CH$_3$), 14.9 (CH$_2$CH$_3$). HRMS (ESI): calcd m/z for C$_{17}$H$_{24}$O$_9$S$_3$ (M + NH$_4$)$^+$ 486.0921, found 486.0906.

Ethyl 3-O-Allyl-4,6-O-benzylidene-1-thio-β-D-idopyranoside (22) and Ethyl 4,6-O-Benzylidene-3-deoxy-3-S-ethyl-1-thio-β-D-idopyranoside (23). A solution of potassium *tert*-butoxide in allyl alcohol (4.9 M, 1.36 mL, 20 mmol) was added to a solution of the dimesylate starting material **21** (312 mg, 0.666 mmol) in dioxane (10 mL). After 24 h, the reaction mixture was evaporated to dryness, redissolved in ethyl acetate (50 mL), washed with saturated sodium chloride solution (2 × 50 mL), water (50 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 7→10→15% ethyl acetate−hexanes to afford **22** as a white solid (76 mg, 0.22 mmol, 33% yield) and the byproduct **23** as a white solid (47 mg, 0.13 mmol, 20% yield). **Data for 22.** R_f 0.74 (ethyl acetate/toluene 1:1). [α]^{20}$_D$: −80.4 (c 1.08, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.48−7.43 (m, 2H, Ar), 7.36−7.31 (m, 3H, Ar), 5.88 (dddd, 1H, J = 17.2, 10.4, 5.6, 5.6 Hz, CH$_2$CH=CH$_2$), 5.48 (s, 1H, PhCH), 5.28 (dddd, 1H, J = 17.2, 1.5, 1.5, 1.5 Hz, CH$_2$CH=CH$_2$), 5.21 (dddd, 1H, J = 10.4, 1.4, 1.2, 1.2 Hz, CH$_2$CH=CH$_2$), 4.94 (d, 1H, J = <1 Hz, H-1), 4.36 (dd, 1H, J = 12.5, 1.4 Hz, H-6a), 4.12 (dddd, 1H, J = 12.8, 5.6, 1.4, 1.3 Hz, CH$_2$CH=CH$_2$), 4.08 (dddd, 1H, J = 12.9, 5.7, 1.4, 1.4 Hz, CH$_2$CH=CH$_2$), 4.03 (dd, 1H, J = 12.6, 1.8 Hz, H-6b), 4.00 (ddd, 1H, J = 2.6, 1.4, 1.2 Hz, H-4), 3.75 (m, 1H, H-3), 3.72 (m, 1H, H-2), 3.69 (m, 1H, H-5), 3.34 (d, 1H, J = 11.8 Hz, 2-OH), 2.76 (q, 2H, J = 7.4 Hz, CH$_2$CH$_3$), 1.31 (t, 3H, J = 7.4 Hz, CH$_2$CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.6 (Ar), 134.1 (CH2CHCH$_3$), 129.4 (Ar), 128.5 (Ar), 126.3 (Ar), 118.1 (CH$_2$CH=CH$_2$), 101.8 (PhCH), 83.2 (C-1), 75.4 (C-3), 73.8 (C-4), 71.6 (CH$_2$CH=CH$_2$), 70.1 (C-6), 69.1 (C-2), 68.6 (C-5), 25.4 (CH$_2$CH$_3$), 15.3 (CH$_2$CH$_3$). HRMS (ESI): calcd m/z for C$_{18}$H$_{24}$O$_5$S (M + NH$_4$)$^+$ 370.1683, found 370.1679. **Data for 23.** R_f = 0.63 (ethyl acetate/hexanes 1:4). [α]^{20}$_D$: −37.7 (c 0.88, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.49−7.44 (m, 2H, Ar), 7.36−7.32 (m, 3H, Ar), 5.46 (s, 1H, PhCH), 5.00 (d, 1H, J = <1 Hz, H-1), 4.36 (dd, 1H, J = 12.5, 1.5 Hz, H-6a), 4.05 (m, 1H, H-4), 4.02 (dd, 1H, J = 12.5, 1.8 Hz, H-6b), 3.78 (dddd, 1H, J = 12.1, 2.4, 1.2, 1.2 Hz, H-2), 3.72 (m, 1H, H-5), 3.64 (d, 1H, J = 12.1 Hz, 2-OH), 3.28 (dd, 1H, J = 2.4, 2.4 Hz, H-3), 2.76 (q, 2H, J = 7.4 Hz, CH$_2$CH$_3$), 2.67 (q, 2H, J = 7.4 Hz, CH$_2$CH$_3$), 1.31 (q, 3H, J = 7.4 Hz, CH$_2$CH$_3$), 1.30 (q, 3H, J = 7.4 Hz, CH$_2$CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.5 (Ar), 129.5 (Ar), 128.6 (Ar), 126.4 (Ar), 101.9 (PhCH), 83.3 (C-1), 75.8 (C-4), 71.2 (C-2), 70.3 (C-6), 68.4 (C-5), 47.6 (C-3), 27.2 (CH$_2$CH$_3$), 25.5 (CH$_2$CH$_3$), 15.3 (CH$_2$CH$_3$), 15.1 (CH$_2$CH$_3$). HRMS (ESI): calcd m/z for C$_{17}$H$_{24}$O$_4$S$_2$ (M + NH$_4$)$^+$ 374.1454, found 374.1454.

p-Chlorophenyl 4,6-O-Benzylidene-2,3-di-O-mesyl-1-thio-β-D-galactopyranoside (25). The starting material **24** (0.79 g, 2.0 mmol) and methanesulfonyl chloride (1.00 mL, 12.9 mmol) were dissolved in dry dichloromethane (10 mL) and dry pyridine (5 mL) and allowed to mix at room temperature. After 16 h, excess reagent was quenched by the addition of methanol (10 mL), and then the reaction mixture was evaporated to dryness. The crude product was redissolved in ethyl acetate (60 mL), washed with saturated sodium chloride solution (2 × 60 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 25% ethyl acetate−toluene to afford the desired product as a white solid (1.08 g, 1.96 mmol, 98% yield). R_f = 0.55 (ethyl acetate/toluene 1:1). [α]^{20}$_D$: −28.3 (c 1.06, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.63−7.58 (m, 2H, SPhCl), 7.41−7.36 (m, 3H, PhCH), 7.33−7.29 (m, 2H, PhCH), 7.19−7.14 (m, 2H, SPhCl), 5.52 (s, 1H, PhCH), 4.93 (dd, 1H, J = 9.5, 9.5 Hz, H-2), 4.79 (dd, 1H, J = 9.5, 3.5 Hz, H-3), 4.65 (d, 1H, J = 9.5 Hz, H-1), 4.55 (dd, 1H, J = 3.5, 0.8 Hz, H-4), 4.35 (dd, 1H, J = 12.5, 1.7 Hz, H-6a), 4.02 (dd, 1H, J = 12.5, 1.6 Hz, H-6b), 3.59 (m, 1H, H-5), 3.21 (s, 3H, CH$_3$), 3.11 (s, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.1 (Ar), 135.9 (SPhCl), 135.4 (Ar), 129.7 (PhCH), 129.4 (SPhCl), 128.6 (PhCH), 128.1 (Ar), 126.5 (PhCH), 101.4 (PhCH), 84.1 (C-1), 78.0 (C-3), 74.6 (C-4), 74.0 (C-2), 69.7 (C-5), 68.9 (C-6), 40.1 (CH$_3$), 39.4 (CH$_3$). HRMS (ESI): calcd m/z for C$_{21}$H$_{23}$ClO$_9$S$_3$ (M + NH$_4$)$^+$ 568.0531, found 568.0524.

p-Chlorophenyl 4,6-*O*-Benzylidene-3-*S*-*p*-chlorophenyl-3-deoxy-1-thio-β-D-idopyranoside (**26**). A solution of potassium *tert*-butoxide in allyl alcohol (4.89 M, 1.61 mL, 23.6 mmol) was added to a solution of the starting material **25** (433 mg, 0.786 mmol) in dioxane (10 mL). After 3 days, the reaction mixture was evaporated to dryness, redissolved in ethyl acetate (100 mL), washed with saturated sodium chloride solution (2 × 100 mL) and water (100 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 7→10→16→40% ethyl acetate−hexanes to afford a number of products, none of which was the desired 3-*O*-allyl-substituted idose compound; instead, byproduct **26** was obtained as a white solid (57 mg, 0.11 mmol, 14% yield) along with a few unidentified elimination products. R_f = 0.90 (ethyl acetate/toluene 1:1). $[\alpha]^{20}_D$: +8.9 (*c* 1.01, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.50−7.44 (m, 4H, Ar), 7.38−7.26 (m, 9H, Ar), 5.46 (s, 1H, PhC*H*), 5.23 (d, 1H, *J* = <1 Hz, H-1), 4.40 (dd, 1H, *J* = 12.6, 1.3 Hz, H-6a), 4.06 (m, 1H, H-4), 4.04 (dd, 1H, *J* = 12.6, 1.7 Hz, H-6b), 3.93 (m, 1H, H-2), 3.85 (m, 1H, H-5), 3.77 (d, 1H, *J* = 12.2 Hz, 2-OH), 3.76 (dd, 1H, *J* = 2.3, 2.3 Hz, H-3). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.2 (Ar), 133.8 (Ar), 133.0 (Ar), 132.84 (Ar), 132.79 (Ar), 131.1 (Ar), 130.0 (Ar), 129.6 (Ar), 129.3 (Ar), 128.6 (Ar), 126.3 (Ar), 102.0 (PhCH), 86.6 (C-1), 74.3 (C-4), 70.2 (C-6), 70.0 (C-2), 68.3 (C-5), 50.6 (C-3). HRMS (ESI): calcd *m/z* for C$_{25}$H$_{22}$Cl$_2$O$_4$S$_2$ (M + NH$_4$)$^+$ 538.0675, found 538.0661.

p-Chlorophenyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-1-thio-β-D-glucopyranoside (**28**). Starting material **27** (294 mg, 0.561 mmol) was dissolved in dry *N*,*N*-dimethylformamide (3.0 mL), sodium hydride (57−63% oil dispersion, 36 mg, 0.91 mmol) was added , and then benzyl bromide (0.08 mL, 0.7 mmol) was slowly added. After 30 min, the reaction was quenched via the addition of methanol (1 mL), and then the reaction solution was evaporated to dryness, redissolved in ethyl acetate (60 mL), washed with saturated aqueous sodium chloride solution (2 × 60 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 15% ethyl acetate−hexanes to afford the desired product as a white solid (310 mg, 0.505 mmol, 90% yield). R_f = 0.90 (acetone: toluene 1:4). $[\alpha]^{20}_D$: +71.0 (*c* 1.01, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.86−7.61 (m, 4H, Ar), 7.52−7.49 (m, 2H, Ar), 7.41−7.36 (m, 3H, Ar), 7.32−7.27 (m, 2H, Ar), 7.23−7.19 (m, 2H, Ar), 6.98−6.83 (m, 5H, Ar), 5.61 (s, 1H, PhCH), 5.56 (d, 1H, *J* = 10.5 Hz, H-1), 4.76 (d, 1H, *J* = 12.3 Hz, PhCH$_2$), 4.48 (d, 1H, *J* = 12.3 Hz, PhCH$_2$), 4.41 (dd, 1H, *J* = 9.8, 8.9 Hz, H-3), 4.41 (dd, 1H, *J* = 10.3, 4.5 Hz, H-6a), 4.25 (dd, 1H, *J* = 10.4, 10.1 Hz, H-2), 3.82 (dd, 1H, *J* = 9.9, 9.9 Hz, H-6b), 3.77 (dd, 1H, *J* = 9.6, 8.9 Hz, H-4), 3.70 (ddd, 1H, *J* = 9.6, 9.6, 4.6 Hz, H-5). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 168.0 (Phth), 167.4 (Phth), 137.8 (Ar), 137.4 (Ar), 134.8 (Ar), 134.7 (Ar), 134.2 (Ar), 134.1 (Ar), 131.7 (Ar), 129.9 (Ar), 129.2 (Ar), 128.5 (Ar), 128.3 (Ar), 128.2 (Ar), 127.6 (Ar), 126.2 (Ar), 123.7 (Ar), 123.6 (Ar), 101.5 (PhCH), 83.9 (C-1), 82.9 (C-4), 75.6 (C-3), 74.4 (PhCH$_2$), 70.6 (C-5), 68.8 (C-6), 54.9 (C-2). HRMS (ESI): calcd *m/z* for C$_{34}$H$_{28}$ClNO$_6$S (M + Na)$^+$ 636.1218, found 636.1218.

p-Chlorophenyl 3,6-Di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**29**). The starting material **28** (1.93 g, 3.14 mmol) was dissolved in dry dichloromethane (20 mL), cooled to 0 °C in an ice−water bath, and triethylsilane (2.5 mL, 16 mmol) was added followed by the slow addition of boron trifluoride diethyl etherate (0.80 mL, 6.4 mmol). After 3.5 h, the reaction was quenched via neutralization with triethylamine (to pH 8) and concentrated to a syrup. The crude mixture was purified by column chromatography on silica gel using 15→20% acetone−hexanes to afford the desired product as a white solid (1.66 g, 2.69 mmol, 86% yield) as well as a small amount of recovered starting material (87 mg, 0.14 mmol, 5% recovered yield). R_f = 0.69 (acetone/toluene 1:4). $[\alpha]^{20}_D$: +61.4 (*c* 1.05, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.81 (d, 1H, *J* = 6.2 Hz, Ar), 7.70−7.67 (m, 3H, Ar), 7.39−7.27 (m, 7H, Ar), 7.15−7.11 (m, 2H, Ar), 7.04−6.99 (m, 2H, Ar), 6.96−6.90 (m, 3H, Ar), 5.49 (d, 1H, *J* = 10.0 Hz, H-1), 4.71 (d, 1H, *J* = 12.2 Hz, PhCH$_2$), 4.60 (d, 1H, *J* = 11.8 Hz, PhCH$_2$), 4.55 (d, 1H, *J* = 11.8 Hz, PhCH$_2$), 4.51 (d, 1H, *J* = 12.2 Hz, PhCH$_2$), 4.24 (dd, 1H, *J* = 10.1, 8.3 Hz, H-3), 4.20 (dd, 1H, *J*

= 10.1, 10.1 Hz, H-2), 3.82 (dd, 1H, *J* = 10.4, 5.1 Hz, H-6a), 3.79 (m, 1H, H-4), 3.78 (dd, 1H, *J* = 10.4, 4.5 Hz, H-6b), 3.67 (ddd, 1H, *J* = 9.5, 4.8, 4.6 Hz, H-5), 2.91 (d, 1H, *J* = 2.9 Hz, 4-OH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 168.3 (Phth), 167.5 (Phth), 138.1 (Ar), 137.8 (Ar), 134.4 (Ar), 134.3 (Ar), 134.2 (Ar), 134.1 (Ar), 131.8 (Ar), 130.6 (Ar), 129.1 (Ar), 128.7 (Ar), 128.4 (Ar), 128.12 (Ar), 128.10 (Ar), 127.9 (Ar), 127.7 (Ar), 123.7 (Ar), 123.5 (Ar), 83.5 (C-1), 79.9 (C-3), 78.2 (C-5), 74.8 (PhCH$_2$), 74.0 (C-4), 73.9 (PhCH$_2$), 70.7 (C-6), 54.6 (C-2). HRMS (ESI): calcd *m/z* for C$_{34}$H$_{30}$ClNO$_6$S (M + NH$_4$)$^+$ 633.1821, found 633.1817.

p-Chlorophenyl 2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-β-D-galacto-pyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**31**). A solution of glycosyl donor **30** (1.457 g, 2.932 mmol), glycosyl acceptor **29** (1.166 g, 1.893 mmol), and molecular sieves (4 Å, crushed, 1.858 g) was prepared in dry dichloromethane (24 mL), and then the contents were divided in roughly equal amounts into two flasks. After being mixed at room temperature under argon for 2 h, the mixtures were cooled to −72 °C, boron trifluoride diethyl etherate was added (to pH 3), and the mixtures were warmed slowly to room temperature. After 16 h, the reactions were quenched via addition of triethylamine (to pH 8), filtered, and then evaporated to dryness. The crude material was combined and redissolved in ethyl acetate (120 mL), washed with saturated sodium bicarbonate solution (100 mL), saturated sodium chloride solution (100 mL), and water (100 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 20→30% ethyl acetate−hexanes to afford recovered starting material (310 mg, 0.503 mmol) and the desired product as a white solid (1.571 g, 1.653 mmol, 80% yield based on recovered starting material). R_f = 0.48 (ethyl acetate/toluene 3:7). $[\alpha]^{20}_D$: +44.5 (*c* 0.97, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.78 (d, 1H, *J* = 7.1 Hz, Phth), 7.70−7.64 (m, 2H, Phth), 7.59 (d, 1H, *J* = 7.2 Hz, Phth), 7.41−7.37 (m, 2H, Ar), 7.36−7.29 (m, 7H, Ar), 7.22−7.16 (m, 3H, Ar), 7.13−7.10 (m, 2H, Ar), 6.96−6.93 (m, 2H, Ar), 6.75−6.71 (m, 3H, Ar), 5.42 (d, 1H, *J* = 10.6 Hz, GlcN_H1), 5.40 (s, 1H, PhCH), 5.34 (dd, 1H, *J* = 10.4, 7.9 Hz, Gal_H2), 4.94 (d, 1H, *J* = 12.6 Hz, PhCH$_2$), 4.80 (dd, 1H, *J* = 10.4, 3.6 Hz, Gal_H3), 4.71 (d, 1H, *J* = 11.8 Hz, PhCH$_2$), 4.63 (d, 1H, *J* = 7.9 Hz, Gal_H1), 4.53 (d, 1H, *J* = 12.6 Hz, PhCH$_2$), 4.50 (d, 1H, *J* = 11.8 Hz, PhCH$_2$), 4.26 (dd, 1H, *J* = 3.8, <1 Hz, Gal_H4), 4.26 (dd, 1H, *J* = 12.3, 1.4 Hz, Gal_H6a), 4.25 (dd, 1H, *J* = 10.0, 8.4 Hz, GlcN_H3), 4.16 (dd, 1H, *J* = 10.5, 10.2 Hz, GlcN_H2), 4.05 (dd, 1H, *J* = 10.0, 8.5 Hz, GlcN_H4), 3.90 (dd, 1H, *J* = 12.4, 1.7 Hz, Gal_H6b), 3.81 (dd, 2H, *J* = 2.6, <1 Hz, GlcN_H6a and GlcN_H6b), 3.57 (ddd, 1H, *J* = 10.0, 2.6, 2.4 Hz, GlcN_H5), 3.25 (m, 1H, Gal_H5), 2.03 (s, 3H, Ac), 2.03 (s, 3H, Ac). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 170.9 (Ac), 169.2 (Ac), 168.0 (Phth), 167.5 (Phth), 138.6 (Ar), 138.2 (Ar), 137.8 (Ar), 134.7 (Ar), 134.5 (Ar), 134.1 (Ar), 133.9 (Ar), 131.9 (Ar), 131.8 (Ar), 130.3 (Ar), 129.2 (Ar), 129.1 (Ar), 128.7 (Ar), 128.6 (Ar), 128.3 (Ar), 128.1 (Ar), 128.01 (Ar), 127.98 (Ar), 127.1 (Ar), 126.6 (Ar), 123.62 (Ar), 123.56 (Ar), 101.3 (PhCH), 100.7 (Gal_C1), 83.2 (GlcN_C1), 79.4 (GlcN_C5), 78.2 (GlcN_C4), 75.5 (PhCH$_2$), 73.7 (PhCH$_2$), 73.5 (GlcN_C3), 72.3 (Gal_C3), 69.5 (Gal_C2), 68.9 (Gal_C6), 68.1 (GlcN_C6), 66.4 (Gal_C5), 55.0 (GlcN_C2), 21.09 (Ac), 21.08 (Ac). HRMS (ESI): calcd *m/z* for C$_{51}$H$_{48}$ClNO$_{13}$S (M + Na)$^+$ 972.2427, found 972.2426.

p-Chlorophenyl 4,6-*O*-Benzylidene-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**32**). A sodium methoxide solution was added dropwise (1.5 M NaOMe/MeOH, to pH 10) to a solution of the starting material **31** (910 mg, 957 mmol) in dry methanol (0.5 mL) and dry dichloromethane (0.5 mL) and allowed to mix at room temperature for 1 h. The reaction was then neutralized using ion-exchange resin (Amberlite IR-120H, to pH 6), filtered, and evaporated to dryness to obtain the pure product as a white solid (796 mg, 919 mmol, 96% yield). R_f = 0.40 (ethyl acetate/toluene 1:1). $[\alpha]^{20}_D$: +17.8 (*c* 0.98, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.85−7.64 (m, 4H, Ar), 7.44−7.34 (m, 9H, Ar), 7.30−7.25 (m, 3H, Ar), 7.20−7.15 (m, 2H, Ar), 7.05−7.03 (m, 2H, Ar), 6.90−6.82 (m, 3H, Ar), 5.49 (d, 1H, *J* = 10.5 Hz, GlcN_H1), 5.48 (s, 1H, PhCH), 4.99 (d, 1H, *J* = 12.3 Hz,

PhCH$_2$), 4.72 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.62 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.58 (d, 1H, J = 7.0 Hz, Gal_H1), 4.57 (d, 1H, J = 12.4 Hz, PhCH$_2$), 4.44 (dd, 1H, J = 10.1, 8.7 Hz, GlcN_H3), 4.25 (dd, 1H, J = 10.4, 10.3 Hz, GlcN_H2), 4.22 (dd, 1H, J = 12.3, 1.2 Hz, Gal_H6a), 4.14 (dd, 1H, J = 9.8, 9.0 Hz, GlcN_H4), 4.10 (dd, 1H, J = 11.3, 3.7 Hz, GlcN_H6a), 4.09 (dd, 1H, J = 3.8, <1 Hz, Gal_H4), 3.91 (m, 1H, Gal_H6b), 3.90 (m, 1H, GlcN_H6b), 3.74 (m, 1H, Gal_H2), 3.73 (m, 1H, GlcN_H5), 3.53 (ddd, 1H, J = 9.4, 9.1, 3.7 Hz, Gal_H3), 3.30 (d, 1H, J = 2.3 Hz, Gal_2OH), 3.16 (m, 1H, Gal_H5), 2.61 (d, 1H, J = 8.8 Hz, Gal_3OH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 168.2 (Phth), 167.4 (Phth), 138.6 (Ar), 138.1 (Ar), 137.9 (Ar), 134.8 (Ar), 134.6 (Ar), 134.1 (Ar), 134.0 (Ar), 131.8 (Ar), 130.1 (Ar), 129.3 (Ar), 129.1 (Ar), 128.6 (Ar), 128.3 (Ar), 128.07 (Ar), 128.06 (Ar), 128.0 (Ar), 127.2 (Ar), 126.6 (Ar), 123.6 (Ar), 123.5 (Ar), 103.2 (Gal_C1), 101.5 (PhCH), 83.2 (GlcN_C1), 79.3 (GlcN_C5), 79.2 (GlcN_C3), 78.6 (GlcN_C4), 75.3 (PhCH$_2$), 75.2 (Gal_C4), 73.6 (PhCH$_2$), 73.0 (Gal_C3), 72.6 (Gal_C2), 69.1 (Gal_C6), 68.5 (GlcN_C6), 66.7 (Gal_C5), 55.1 (GlcN_C2). HRMS (ESI): calcd m/z for C$_{47}$H$_{44}$ClNO$_{11}$S (M + Na)$^+$ 888.2216, found 888.2213.

p-Chlorophenyl 4,6-O-Benzylidene-2,3-di-O-mesyl-β-D-galacto-pyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (33). The starting material **32** (724 mg, 0.835 mmol) and methanesulfonyl chloride (0.32 mL, 4.1 mmol) were dissolved in dry dichloromethane (3.5 mL) and dry pyridine (3.5 mL) and then allowed to mix at 45 °C. After 16 h, the reaction was quenched via the addition of water (1 mL) and concentrated via coevaporation with toluene (2 × 2 mL). The crude mixture was redissolved in ethyl acetate (60 mL), washed with saturated sodium chloride solution (2 × 60 mL) and water (60 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel using 0.5→0.7% methanol–dichloromethane to afford the desired product as a white solid (683 mg, 0.668 mmol, 80% yield). R_f = 0.75 (ethyl acetate/toluene 1:1). $[\alpha]^{20}_D$: +21.7 (c 0.96, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.79 (d, 1H, J = 7.1 Hz, Phth), 7.71−7.65 (m, 2H, Phth), 7.60 (d, 1H, J = 7.8 Hz, Phth), 7.42−7.35 (m, 6H, Ar), 7.32−7.29 (m, 4H, Ar), 7.31−7.29 (m, 4H, Ar), 6.96−6.93 (m, 2H, Ar), 6.78−6.71 (m, 3H, Ar), 5.45 (s, 1H, PhCH), 5.45 (d, 1H, J = 10.0 Hz, GlcN_H1), 4.91 (d, 1H, J = 12.4 Hz, PhCH$_2$), 4.77 (d, 1H, J = 11.8 Hz, PhCH$_2$), 4.77 (dd, 1H, J = 10.0, 7.8 Hz, Gal_H2), 4.55 (d, 1H, J = 7.8 Hz, Gal_H1), 4.49 (dd, 1H, J = 10.0, 3.8 Hz, Gal_H3), 4.47 (d, 1H, J = 12.4 Hz, PhCH$_2$), 4.43 (d, 1H, J = 11.9 Hz, PhCH$_2$), 4.38 (dd, 1H, J = 3.8, <1 Hz, Gal_H4), 4.29 (dd, 1H, J = 12.5, 1.4 Hz, Gal_H6a), 4.26 (dd, 1H, J = 10.2, 8.6 Hz, GlcN_H3), 4.18 (dd, 1H, J = 10.2, 10.2 Hz, GlcN_H2), 4.15 (dd, 1H, J = 9.9, 8.6 Hz, GlcN_H4), 4.01 (dd, 1H, J = 11.3, 2.9 Hz, GlcN_H6a), 3.91 (dd, 1H, J = 12.5, 1.7 Hz, Gal_H6b), 3.80 (dd, 1H, J = 11.3, 1.4 Hz, GlcN_H6b), 3.64 (ddd, 1H, J = 10.0, 2.7, 1.4 Hz, GlcN_H5), 3.12 (m, 1H, Gal_H5), 3.08 (s, 3H, CH$_3$), 3.07 (s, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 168.1 (Phth), 167.5 (Phth), 138.4 (Ar), 138.3 (Ar), 137.3 (Ar), 134.51 (Ar), 134.46 (Ar), 134.1 (Ar), 134.0 (Ar), 131.85 (Ar), 131.75 (Ar), 130.4 (Ar), 130.0 (Ar), 129.4 (Ar), 129.2 (Ar), 128.8 (Ar), 128.7 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.0 (Ar), 127.3 (Ar), 126.4 (Ar), 123.65 (Ar), 123.57 (Ar), 101.4 (PhCH), 99.4 (Gal_C1), 83.3 (GlcN_C1), 79.0 (GlcN_C5), 78.2 (GlcN_C4), 77.9 (GlcN_C3), 77.1 (Gal_C3), 76.6 (Gal_C2), 75.5 (PhCH$_2$), 74.3 (Gal_C4), 73.7 (PhCH$_2$), 68.5 (Gal_C6), 68.1 (GlcN_C6), 65.8 (Gal_C5), 55.0 (GlcN_C2), 39.8 (CH$_3$), 39.7 (CH$_3$). HRMS (ESI): calcd m/z for C$_{49}$H$_{48}$ClNO$_{15}$S$_3$ (M + Na)$^+$ 1044.1767, found 1044.1768.

p-Chlorophenyl 2-O-Acetyl-3-O-allyl-4,6-O-benzylidene-β-D-ido-pyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (34). A solution of potassium *tert*-butoxide in allyl alcohol (4.35 M, 1.00 mL, 14.7 mmol) was added to a solution of the starting material **33** (564 mg, 0.551 mmol) in dioxane (10.0 mL). After 6 days, the reaction mixture was evaporated to dryness to afford the partially hydrolyzed phthalimido intermediate **33B**: R_f 0.06 (ethyl acetate/toluene 1:1). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.96 (d, 1H, J = 7.9 Hz, Ar), 7.46−7.10 (m, 22H, Ar), 6.81 (d, 1H, J = 8.6 Hz, NH), 5.81 (dddd, 1H, J = 17.1, 10.4, 5.6, 5.6 Hz, CH$_2$CH=CH$_2$), 5.44 (s, 1H, PhCH), 5.24 (dddd, 1H, J = 17.2, 1.5, 1.5, 1.5 Hz, CH$_2$CH=

CH$_2$), 5.19 (dddd, 1H, J = 10.4, 1.4, 1.2, 1.2 Hz, CH$_2$CH=CH$_2$), 4.98 (d, 1H, J = 11.5 Hz, PhCH$_2$), 4.98 (d, 1H, J = 8.2 Hz, GlcN_H1), 4.90 (d, 1H, J = <1 Hz, Ido_H1), 4.71 (d, 1H, J = 11.4 Hz, PhCH$_2$), 4.56 (d, 1H, J = 11.8 Hz, PhCH$_2$), 4.52 (d, 1H, J = 11.8 Hz, PhCH$_2$), 4.17 (dd, 1H, J = 12.6, <1 Hz, Ido_H6a), 4.12 (m, 1H, GlcN_H2), 4.10 (m, 1H, GlcN_H3), 4.05 (m, 1H, GlcN_H4), 4.05 (dddd, 1H, J = 12.8, 5.6, 1.4, 1.4 Hz, CH$_2$CH=CH$_2$), 4.01 (dddd, 1H, J = 12.9, 5.7, 1.4, 1.3 Hz, CH$_2$CH=CH$_2$), 3.92 (m, 1H, Ido_H4), 3.90 (dd, 1H, J = 12.6, 1.6 Hz, Ido_H6b), 3.82 (dd, 1H, J = 11.8, 5.3 Hz, GlcN_H6a), 3.75 (m, 1H, GlcN_H6b), 3.75 (m, 1H, GlcN_H5), 3.75 (m, 1H, Ido_H3), 3.67 (m, 1H, Ido_H2), 3.53 (m, 1H, Ido_H5). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 182.1 (Ac), 170.7 (Phth), 145.9 (Ar), 138.4 (Ar), 134.3 (CH$_2$CH=CH$_2$), 134.0 (Ar), 132.2 (Ar), 131.1 (Ar), 129.2 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 127.9 (Ar), 127.6 (Ar), 126.2 (Ar), 118.3 (CH$_2$CH=CH$_2$), 101.7 (PhCH), 99.4 (Ido_C1), 85.0 (GlcN_C1), 79.5 (GlcN_C4), 79.2 (GlcN_C5), 76.9 (GlcN_C3), 76.2 (Ido_C3), 74.3 (PhCH$_2$), 73.6 (Ido_C4), 73.4 (PhCH$_2$), 71.8 (CH$_2$CH=CH$_2$), 69.7 and 69.5 (Ido_C6 and GlcN_C6), 67.7 (Ido_C2), 67.3 (Ido_C5), 54.2 (GlcN_C2). HRMS (ESI): calcd m/z for C$_{50}$H$_{50}$ClNO$_{12}$S (M + Na)$^+$ 946.2634, found 946.2592. The crude material was then redissolved in dry pyridine (1.0 mL) and acetic anhydride (1.0 mL) and allowed to mix at 65 °C. After 16 h, the reaction mixture was evaporated to dryness via coevaporation with toluene (2 × 1 mL), redissolved in ethyl acetate (40 mL), washed with saturated sodium chloride solution (2 × 40 mL) and water (40 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude material was then purified via column chromatography on silica using 10→20% acetone−hexanes to afford the pure product as a white solid (398 mg, 0.420 mmol, 76% yield). R_f = 0.33 (acetone/hexanes 3:7). $[\alpha]^{20}_D$: +14.9° (c 1.03, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.80 (d, 1H, J = 7.0 Hz, Phth), 7.70−7.66 (m, 2H, Phth), 7.61 (d, 1H, J = 7.1 Hz, Phth), 7.42−7.40 (m, 2H, Ar), 7.36−7.30 (m, 7H, Ar), 7.24−7.20 (m, 3H, Ar), 7.13−7.10 (m, 2H, Ar), 6.99−6.97 (m, 2H, Ar), 6.79−6.74 (m, 3H, Ar), 5.82 (dddd, 1H, J = 17.1, 10.5, 5.6, 5.6 Hz, CH$_2$CH=CH$_2$), 5.43 (d, 1H, J = 10.5 Hz, GlcN_H1), 5.39 (s, 1H, PhCH), 5.25 (dddd, 1H, J = 17.2, 1.5, 1.5, 1.5 Hz, CH$_2$CH=CH$_2$), 5.18 (dddd, 1H, J = 10.4, 1.3, 1.3, 1.3 Hz, CH$_2$CH=CH$_2$), 5.07 (d, 1H, J = 1.2 Hz, Ido_H1), 4.99 (d, 1H, J = 12.3 Hz, PhCH$_2$), 4.89 (ddd, 1H, J = 3.4, 1.4, 1.4 Hz, Ido_H2), 4.61 (d, 1H, J = 12.3 Hz, PhCH$_2$), 4.57 (m, 2H, PhCH$_2$), 4.32 (dd, 1H, J = 10.2, 8.7 Hz, GlcN_H3), 4.24 (dd, 1H, J = 12.5, 1.2 Hz, Ido_H6a), 4.15 (dd, 1H, J = 10.4, 10.4 Hz, GlcN_H2), 4.13 (dd, 1H, J = 9.8, 8.8 Hz, GlcN_H4), 4.10 (dddd, 1H, J = 12.8, 5.4, 1.4, 1.4 Hz, CH$_2$CH=CH$_2$), 4.05 (dddd, 1H, J = 12.8, 5.8, 1.4, 1.4 Hz, CH$_2$CH=CH$_2$), 3.89 (dd, 1H, J = 12.5, 1.9 Hz, Ido_H6b), 3.82 (dd, 1H, J = 11.0, 1.7 Hz, GlcN_H6a), 3.78 (m, 1H, Ido_H4), 3.78 (m, 1H, Ido_H3), 3.75 (dd, 1H, J = 11.0, 3.4 Hz, GlcN_H6b), 3.65 (ddd, 1H, J = 9.9, 3.4, 1.7 Hz, GlcN_H5), 3.48 (m, 1H, Ido_H5), 1.98 (s, 3H, Ac). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 171.0 (Ac), 168.2 (Phth), 167.4 (Phth), 138.8 (Ar), 138.6 (Ar), 138.4 (Ar), 134.9 (Ar), 134.6 (Ar), 134.1 (CH$_2$CH=CH$_2$), 134.0 (Ar), 131.9 (Ar), 131.8 (Ar), 130.0 (Ar), 129.2 (Ar), 129.1 (Ar), 128.5 (Ar), 128.2 (Ar), 128.1 (Ar), 127.8 (Ar), 127.5 (Ar), 127.3 (Ar), 126.7 (Ar), 123.7 (Ar), 123.5 (Ar), 118.2 (CH$_2$CH=CH$_2$), 101.3 (PhCH), 98.0 (Ido_C1), 82.8 (GlcN_C1), 79.1 (GlcN_C5), 78.2 (GlcN_C3), 78.2 (GlcN_C4), 75.1 (PhCH$_2$), 74.8 (Ido_C3), 73.3 (PhCH$_2$), 72.0 (Ido_C4), 71.7 (CH$_2$CH=CH$_2$), 69.5 (Ido_C6), 68.9 (GlcN_C6), 67.4 (Ido_C2), 67.0 (Ido_C5), 54.9 (GlcN_C2), 21.3 (Ac). HRMS (ESI): calcd m/z for C$_{52}$H$_{50}$ClNO$_{12}$S (M + Na)$^+$ 970.2634, found 970.2634.

p-Chlorophenyl 3-O-Allyl-4,6-O-benzylidene-β-D-idopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (35). A sodium methoxide solution was added dropwise (1.5 M NaOMe/MeOH, to pH 10) to a solution of the starting material **34** (170 mg, 0.179 mmol) in dry methanol (1.0 mL) and dry dichloromethane (1.0 mL) and allowed to mix at room temperature. After 20 min, the reaction was then neutralized using ion-exchange resin (Amberlite IR-120H, to pH 6), filtered, and evaporated to dryness. The crude material was then purified via column chromatography using 20% acetone - hexanes to afford the pure product as a white solid (152 mg, 0.168 mmol 94% yield). R_f = 0.44

(acetone/hexanes 3:7). $[\alpha]^{20}_D$: +2.4° (c 0.98, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.78 (d, 1H, J = 7.0 Hz, Phth), 7.69–7.65 (m, 2H, Phth), 7.61 (d, 1H, J = 7.1 Hz, Phth), 7.34–7.24 (m, 12H, Ar), 7.13–7.10 (m, 2H, Ar), 7.01–6.99 (m, 2H, Ar), 6.81–6.75 (m, 3H, Ar), 5.80 (dddd, 1H, J = 17.2, 10.4, 5.6, 5.6 Hz, CH$_2$CH=CH$_2$), 5.45 (d, 1H, J = 10.5 Hz, GlcN_H1), 5.42 (s, 1H, PhCH), 5.23 (dddd, 1H, J = 17.2, 1.5, 1.5, 1.5 Hz, CH$_2$CH=CH$_2$), 5.17 (dddd, 1H, J = 10.4, 1.3, 1.3, 1.3 Hz, CH$_2$CH=CH$_2$), 4.98 (d, 1H, J = <1 Hz, Ido_H1), 4.98 (d, 1H, J = 12.3 Hz, PhCH$_2$), 4.59 (d, 1H, J = 11.9 Hz, PhCH$_2$), 4.57 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.54 (d, 1H, J = 12.3 Hz, PhCH$_2$), 4.43 (dd, 1H, J = 10.2, 8.7 Hz, GlcN_H3), 4.27 (dd, 1H, J = 12.4, 1.1 Hz, Ido_H6a), 4.16 (dd, 1H, J = 10.4, 10.3 Hz, GlcN_H2), 4.09 (dd, 1H, J = 9.8, 8.8 Hz, GlcN_H4), 4.04 (dddd, 1H, J = 12.8, 5.6, 1.4, 1.4 Hz, CH$_2$CH=CH$_2$), 4.00 (dddd, 1H, J = 12.8, 5.7, 1.4, 1.4 Hz, CH$_2$CH=CH$_2$), 3.92 (m, 1H, Ido_H4), 3.92 (dd, 1H, J = 12.4, 1.8 Hz, Ido_H6b), 3.84 (dd, 1H, J = 11.0, 1.8 Hz, GlcN_H6a), 3.81 (dd, 1H, J = 11.0, 3.3 Hz, GlcN_H6b), 3.79 (dd, 1H, J = 3.0, 2.9 Hz, Ido_H3), 3.73 (m, 1H, Ido_H2), 3.73 (m, 1H, GlcN_H5), 3.58 (m, 1H, Ido_H5), 3.27 (d, 1H, J = 11.9 Hz, Ido_2OH). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 168.1 (Phth), 167.5 (Phth), 138.8 (Ar), 138.5 (Ar), 137.6 (Ar), 135.0 (Ar), 134.6 (Ar), 134.1 (CH$_2$CH=CH$_2$), 134.05 (Ar), 133.96 (Ar), 131.9 (Ar), 131.8 (Ar), 129.9 (Ar), 129.4 (Ar), 129.1 (Ar), 128.5 (Ar), 128.4 (Ar), 128.1 (Ar), 127.8 (Ar), 127.5 (Ar), 127.2 (Ar), 126.2 (Ar), 123.6 (Ar), 123.5 (Ar), 118.1 (CH$_2$CH=CH$_2$), 101.7 (PhCH), 100.1 (Ido_C1), 82.8 (GlcN_C1), 79.2 (GlcN_C5), 79.0 (GlcN_C4), 78.5 (GlcN_C3), 76.4 (Ido_C3), 75.4 (PhCH$_2$), 73.5 (Ido_C4), 73.3 (PhCH$_2$), 71.6 (CH$_2$CH=CH$_2$), 69.8 (Ido_C6), 68.8 (GlcN_C6), 67.7 (Ido_C2), 67.2 (Ido_C5), 55.0 (GlcN_C2). HRMS (ESI): calcd m/z for C$_{50}$H$_{48}$ClNO$_{11}$S (M + Na)$^+$ 928.2529, found 928.2524.

Methyl 2,3-Di-O-acetyl-4,6-O-benzylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (36). The disaccharide donor **31** (859 mg, 0.903 mmol), dry methanol (0.30 mL, 7.4 mmol), and molecular sieves (4 Å crushed, 1.148 g) were added to dry dichloromethane (9.0 mL) and allowed to mix under argon at room temperature. After 1.5 h, the flask was cooled to −75 °C, and then N-iodosuccinimide (422 mg, 1.88 mmol) and triflic acid (100 μL) were added. The flask was warmed up to room temperature, allowed to mix for 16 h, and then neutralized with triethylamine (to pH 8). The reaction contents were filtered through Celite and the molecular sieves washed with dichloromethane (2 × 25 mL). The organic phase was washed with saturated sodium bicarbonate solution (60 mL), saturated sodium chloride solution (60 mL), water (60 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude material was then purified via column chromatography using 20→25% acetone - hexanes to afford the pure product as a white solid (522 mg, 0.623 mmol, 79% yield based on recovered starting material) and recovered starting material (102 mg, 0.118 mmol, 13% yield). R_f = 0.54 (ethyl acetate/toluene 3:7). $[\alpha]^{20}_D$: +39.6 (c 0.97, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.78–7.56 (m, 4H, Ar), 7.39–7.30 (m, 7H, Ar), 7.24–7.17 (m, 3H, Ar), 6.97 (m, 2H, Ar), 6.78–6.71 (m, 3H, Ar), 5.40 (s, 1H, PhCH), 5.34 (dd, 1H, J = 10.4, 8.0 Hz, Gal_H2), 5.00 (d, 1H, J = 8.5 Hz, GlcN_H1), 4.98 (d, 1H, J = 12.6 Hz, PhCH$_2$), 4.80 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.77 (dd, 1H, J = 10.4, 3.7 Hz, Gal_H3), 4.62 (d, 1H, J = 8.0 Hz, Gal_H1), 4.53 (d, 1H, J = 12.6 Hz, PhCH$_2$), 4.50 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.26 (m, 1H, Gal_H6a), 4.25 (m, 1H, GlcN_H3), 4.25 (m, 1H, Gal_H4), 4.13 (dd, 1H, J = 10.8, 8.6 Hz, GlcN_H2), 4.10 (dd, 1H, J = 9.8, 8.5 Hz, GlcN_H4), 3.90 (dd, 1H, J = 12.3, 1.7 Hz, Gal_H6b), 3.84 (dd, 1H, J = 10.9, 3.3 Hz, GlcN_H6a), 3.80 (dd, 1H, J = 10.9, 1.7 Hz, GlcN_H6b), 3.52 (ddd, 1H, J = 9.9, 3.2, 1.7 Hz, GlcN_H5), 3.36 (s, 3H, OCH$_3$), 3.22 (m, 1H, Gal_H5), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 170.9 (Ac), 169.2 (Ac), 168.3 (Phth), 167.9 (Phth), 138.9 (Ar), 138.3 (Ar), 137.9 (Ar), 133.8 (Phth), 132.1 (Phth), 131.9 (Phth), 129.2 (Ar), 128.7 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 127.9 (Ar), 127.1 (Ar), 126.6 (Ar), 123.4 (Phth), 101.3 (PhCH), 100.6 (Gal_C1), 99.4 (GlcN_C1), 78.5 (GlcN_C4), 77.2 (GlcN_C3), 75.3 (PhCH$_2$), 75.2 (GlcN_C5), 73.8 (PhCH$_2$), 73.5 (Gal_C4), 72.3 (Gal_C3), 69.5 (Gal_C2), 68.9 (Gal_C6), 67.9 (GlcN_C6), 66.3 (Gal_C5), 56.8

(OCH$_3$), 55.9 (GlcN_C2), 21.09 (Ac), 21.06 (Ac). HRMS (ESI): calcd m/z for C$_{46}$H$_{47}$NO$_{14}$ (M + NH$_4$)$^+$ 855.3335, found 855.3313.

Methyl 4,6-O-Benzylidene-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (37). A sodium methoxide solution was added dropwise (1.5 M NaOMe in MeOH, to pH 10) to a solution of the starting material **36** (382 mg, 0.456 mmol) in dry methanol (2.0 mL) and dry dichloromethane (2.0 mL) and the solution allowed to mix at room temperature. After 15 min, the reaction was then neutralized using ion-exchange resin (Amberlite IR-120H, to pH 6), filtered, and evaporated to dryness to obtain the pure product as a white solid (345 mg, 0.458 mmol, quantitative yield). R_f = 0.17 (ethyl acetate/toluene 3:7). $[\alpha]^{20}_D$: +26.8 (c 1.05, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.74–7.65 (m, 4H, Phth), 7.39–7.33 (m, 6H, Ar), 7.30–7.22 (m, 4H, Ar), 7.04–7.00 (m, 2H, Ar), 6.86–6.79 (m, 3H, Ar), 5.44 (s, 1H, PhCH), 5.02 (d, 1H, J = 8.5 Hz, GlcN_H1), 4.96 (d, 1H, J = 12.4 Hz, PhCH$_2$), 4.75 (d, 1H, J = 12.2 Hz, PhCH$_2$), 4.58 (d, 1H, J = 12.2 Hz, PhCH$_2$), 4.55 (d, 1H, J = 8.0 Hz, Gal_H1), 4.53 (d, 1H, J = 12.4 Hz, PhCH$_2$), 4.40 (dd, 1H, J = 10.7, 8.6 Hz, GlcN_H3), 4.18 (dd, 1H, J = 10.6, 8.5 Hz, GlcN_H2), 4.18 (dd, 1H, J = 12.7, 1.1 Hz, Gal_H6a), 4.16 (m, 1H, GlcN_H4), 4.07 (dd, 1H, J = 11.3, 3.2 Hz, GlcN_H6a), 4.05 (dd, 1H, J = 3.7, <1 Hz, Gal_H4), 3.85 (dd, 1H, J = 12.7, 1.6 Hz, Gal_H6b), 3.83 (dd, 1H, J = 11.5, 1.9 Hz, GlcN_H6b), 3.69 (ddd, 1H, J = 9.6, 7.9, 2.0 Hz, Gal_H2), 3.65 (ddd, 1H, J = 9.9, 3.0, 2.0 Hz, GlcN_H5), 3.47 (ddd, 1H, J = 9.2, 9.2, 3.8 Hz, Gal_H3), 3.37 (s, 3H, OCH$_3$), 3.32 (broad, 1H, Gal_2OH), 3.08 (m, 1H, Gal_H5), 2.50 (broad, 1H, Gal_3OH). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 168.4 (Phth), 167.8 (Phth), 138.8 (Ar), 138.1 (Ar), 137.9 (Ar), 133.9 (Ar), 131.9 (Ar), 129.3 (Ar), 128.6 (Ar), 128.4 (Ar), 128.13 (Ar), 128.07 (Ar), 127.92 (Ar), 127.90 (Ar), 127.2 (Ar), 126.6 (Ar), 123.5 (Ar), 103.2 (Gal_C1), 101.5 (PhCH), 99.5 (GlcN_C1), 78.9 (GlcN_C4), 78.4 (GlcN_C3), 75.2 (Gal_C4), 75.0 (PhCH$_2$), 74.9 (GlcN_C5), 73.6 (PhCH$_2$), 73.0 (Gal_C3), 72.7 (Gal_C2), 69.2 (Gal_C6), 68.4 (GlcN_C6), 66.7 (Gal_C5), 56.8 (OCH$_3$), 56.0 (GlcN_C2). HRMS (ESI): calcd m/z for C$_{42}$H$_{43}$NO$_{12}$ (M + NH$_4$)$^+$ 771.3123, found 771.3094.

Methyl 4,6-O-Benzylidene-2,3-di-O-mesyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (38). The starting material **37** (237 mg, 0.314 mmol) and methanesulfonyl chloride (0.08 mL, 1 mmol) were dissolved in dry pyridine (1.4 mL) and dry dichloromethane (1.5 mL) and allowed to mix at 45 °C. After 16 h, the reaction was quenched via the addition of water (0.5 mL), the crude mixture evaporated to dryness via coevaporation with toluene (2 × 1 mL) and then redissolved in ethyl acetate (30 mL). The organic phase was washed with saturated sodium chloride solution (2 × 30 mL), water (30 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude material was then purified via column chromatography on silica using 0.4 → 0.7% methanol–dichloromethane to afford the pure product as a white solid (261 mg, 0.287 mmol, 91% yield). R_f = 0.42 (methanol/dichloromethane 1:49). $[\alpha]^{20}_D$: +6.0 (c 0.95, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.79–7.57 (m, 4H, Phth), 7.42–7.35 (m, 5H, Ar), 7.33–7.30 (m, 2H, Ar), 7.24–7.23 (m, 1H, Ar), 7.22–7.18 (m, 2H, Ar), 6.98–6.94 (m, 2H, Ar), 6.79–6.73 (m, 3H, Ar), 5.45 (s, 1H, PhCH), 5.02 (d, 1H, J = 8.5 Hz, GlcN_H1), 4.92 (d, 1H, J = 12.4 Hz, PhCH$_2$), 4.85 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.75 (dd, 1H, J = 9.9, 7.9 Hz, Gal_H2), 4.49 (d, 1H, J = 7.8 Hz, Gal_H1), 4.46 (d, 1H, J = 12.4 Hz, PhCH$_2$), 4.44 (dd, 1H, J = 10.0, 3.9 Hz, Gal_H3), 4.40 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.36 (dd, 1H, J = 3.8, <1 Hz, Gal_H4), 4.29 (dd, 1H, J = 12.5, 1.4 Hz, Gal_H6a), 4.25 (dd, 1H, J = 10.7, 8.5 Hz, GlcN_H3), 4.18 (dd, 1H, J = 9.7, 8.5 Hz, GlcN_H4), 4.14 (dd, 1H, J = 10.7, 8.5 Hz, GlcN_H2), 4.03 (dd, 1H, J = 11.1, 2.8 Hz, GlcN_H6a), 3.91 (dd, 1H, J = 12.5, 1.7 Hz, Gal_H6b), 3.80 (dd, 1H, J = 11.1, 1.5 Hz, GlcN_H6b), 3.61 (ddd, 1H, J = 9.9, 2.6, 1.6 Hz, GlcN_H5), 3.37 (s, 3H, OCH$_3$), 3.08 (s, 3H, SO$_2$CH$_3$), 4.08 (m, 1H, Gal_H5), 3.07 (s, 3H, SO$_2$CH$_3$). 13C NMR (CDCl3, 150 MHz): δ 168.3 (Phth), 167.9 (Phth), 138.7 (Ar), 138.4 (Ar), 137.3 (Ar), 133.9 (Ar), 132.0 (Ar), 129.4 (Ar), 128.8 (Ar), 128.6 (Ar), 128.44 (Ar), 128.35 (Ar), 128.0 (Ar), 127.2 (Ar), 126.4 (Ar), 123.5 (Ar), 101.4 (PhCH), 99.5 (GlcN_C1), 99.3 (Gal_C1), 78.6 (GlcN_C4), 77.2 (Gal_C3), 77.1 (GlcN_C3), 76.6 (Gal_C2), 75.3 (PhCH$_2$), 74.7

(GlcN_C5), 74.3 (Gal_C4), 73.7 (PhCH$_2$), 68.6 (Gal_C6), 67.9 (GlcN_C6), 65.8 (Gal_C5), 57.0 (OCH$_3$), 55.9 (GlcN_C2), 39.8 (SO$_2$CH$_3$), 39.7 (SO$_2$CH$_3$). HRMS (ESI): calcd m/z for C$_{44}$H$_{47}$NO$_{16}$S$_2$ (M + Na)$^+$ 932.2229, found 932.2202.

Methyl 2-O-Acetyl-3-O-benzyl-4,6-O-benzylidene-β-D-idopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (39). A solution of potassium *tert*-butoxide in benzyl alcohol (4.01 M, 0.54 mL, 2.2 mmol) in dioxane (0.5 mL) was added to a solution of the starting material **38** (261 mg, 0.287 mmol) in dioxane (5.0 mL). After 6 days, the reaction mixture was evaporated to dryness via coevaporation with water (3 × 5 mL) and then redissolved in dry pyridine (2 mL) and acetic anhydride (2 mL) and allowed to mix at 70 °C. After 16 h, the reaction mixture was evaporated to dryness via coevaporation with toluene (3 × 2 mL), redissolved in ethyl acetate (30 mL), washed with saturated sodium chloride solution (2 × 30 mL) and water (30 mL), dried with sodium sulfate, filtered, and evaporated to dryness. The crude material was then purified via column chromatography on silica using 20% acetone−hexanes to afford the pure product as a white solid (189 mg, 0.214 mmol, 75% yield). R_f = 0.45 (acetone/hexanes 3:7). $[\alpha]^{20}_D$: +32.3° (c 0.99, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.81−7.69 (m, 4H, Phth), 7.46−7.45 (m, 2H, Ar), 7.37−7.31 (m, 9H, Ar), 7.30−7.24 (m, 4H, Ar), 7.08−7.04 (m, 2H, Ar), 6.87−6.80 (m, 3H, Ar), 5.41 (s, 1H, PhCH), 5.18 (d, 1H, J = 0.8 Hz, Ido_H1), 5.09 (d, 1H, J = 12.2 Hz, PhCH$_2$), 5.07 (d, 1H, J = 8.5 Hz, GlcN_H1), 5.02 (m, 1H, Ido_H2), 4.70 (d, 1H, J = 11.8 Hz, PhCH$_2$), 4.66 (d, 1H, J = 12.2 Hz, PhCH$_2$), 4.61 (d, 1H, J = 11.7 Hz, PhCH$_2$), 4.59 (d, 1H, J = 11.9 Hz, PhCH$_2$), 4.55 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.39 (dd, 1H, J = 10.7, 8.6 Hz, GlcN_H3), 4.29 (dd, 1H, J = 12.4, <1 Hz, Ido_H6a), 4.25 (dd, 1H, J = 9.8, 8.7 Hz, GlcN_H4), 4.21 (dd, 1H, J = 10.7, 8.5 Hz, GlcN_H2), 3.92 (dd, 1H, J = 12.3, 1.9 Hz, Ido_H6b), 3.91 (m, 1H, Ido_H3), 3.84 (dd, 1H, J = 10.9, 1.6 Hz, GlcN_H6a), 3.83 (m, 1H, Ido_H4), 3.77 (dd, 1H, J = 11.0, 3.4 Hz, GlcN_H6b), 3.65 (ddd, 1H, J = 9.8, 3.2, 1.6 Hz, GlcN_H5), 3.53 (m, 1H, Ido_H5), 3.41 (s, 3H, OCH$_3$), 2.03 (s, 3H, OAc). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 171.0 (OAc), 168.6 (Phth), 167.5 (Phth), 139.0 (Ar), 138.6 (Ar), 138.4 (Ar), 137.5 (Ar), 133.8 (Ar), 132.0 (Ar), 129.2 (Ar), 128.7 (Ar), 128.40 (Ar), 128.39 (Ar), 128.3 (Ar), 128.2 (Ar), 128.03 (Ar), 127.96 (Ar), 127.6 (Ar), 127.4 (Ar), 127.2 (Ar), 126.6 (Ar), 123.4 (Ar), 101.3 (PhCH), 99.5 (GlcN_C1), 97.7 (Ido_C1), 78.4 (GlcN_C4), 77.3 (GlcN_C3), 75.1 (Ido_C3), 74.85 (GlcN_C5), 74.84 (PhCH$_2$), 73.2 (PhCH$_2$), 72.8 (PhCH$_2$), 72.1 (Ido_C4), 69.5 (Ido_C6), 68.7 (GlcN_C6), 67.2 (Ido_C2), 66.9 (Ido_C5), 56.7 (OCH$_3$), 55.8 (GlcN_C2), 21.3 (OAc). HRMS (ESI): calcd m/z for C$_{51}$H$_{51}$NO$_{13}$ (M + Na)$^+$ 908.3253, found 908.3225.

Methyl 3-O-Benzyl-4,6-O-benzylidene-β-D-idopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (40). A sodium methoxide solution was added dropwise (1.5 M NaOMe/MeOH, to pH 10) to a solution of the starting material **39** (34 mg, 0.039 mmol) in dry methanol (0.2 mL) and dry dichloromethane (0.2 mL) and the solution allowed to mix at room temperature. After 15 min, the reaction was neutralized using ion-exchange resin (Amberlite IR-120H, to pH 6), filtered, and evaporated to dryness to afford the pure product as a white solid (32 mg, 0.037 mmol, 97% yield). R_f = 0.29 (acetone/hexanes 3:7). $[\alpha]^{20}_D$: +3.1 (c 1.08, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.77−7.64 (m, 4H, Phth), 7.36−7.35 (m, 2H, Ar), 7.31−7.23 (m, 13H, Ar), 7.04−7.02 (m, 2H, Ar), 6.82−6.78 (m, 3H, Ar), 5.40 (s, 1H, PhCH), 5.05 (d, 1H, J = <1 Hz, Ido_H1), 5.03 (d, 1H, J = 8.6 Hz, GlcN_H1), 5.02 (d, 1H, J = 12.3 Hz, PhCH$_2$), 4.56 (d, 1H, J = 11.8 Hz, PhCH$_2$), 4.56 (d, 1H, J = 12.0 Hz, PhCH$_2$), 4.56 (d, 1H, J = 12.3 Hz, PhCH$_2$), 4.53 (d, 1H, J = 12.1 Hz, PhCH$_2$), 4.52 (d, 1H, J = 11.8 Hz, PhCH$_2$), 4.44 (dd, 1H, J = 10.7, 8.6 Hz, GlcN_H3), 4.27 (dd, 1H, J = 12.5, 1.1 Hz, Ido_H6a), 4.16 (m, 1H, GlcN_H2), 4.16 (m, 1H, GlcN_H4), 3.92 (m, 1H, Ido_H4), 3.90 (dd, 1H, J = 12.5, 1.7 Hz, Ido_H6b), 3.86 (dd, 1H, J = 2.9, 2.9 Hz, Ido_H3), 3.82 (dd, 1H, J = 11.0, 1.8 Hz, GlcN_H6a), 3.79 (dd, 1H, J = 11.0, 3.3 Hz, GlcN_H6b), 3.77 (m, 1H, Ido_H2), 3.68 (ddd, 1H, J = 9.9, 3.1, 2.0 Hz, GlcN_H5), 3.60 (m, 1H, Ido_H5), 3.37 (s, 3H, OCH$_3$), 3.28 (d, 1H, J = 11.9 Hz, Ido_2OH). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 168.1 (Phth), 139.0 (Ar), 138.5 (Ar), 137.64 (Ar), 137.56 (Ar), 133.8 (Ar), 132.0 (Ar), 129.4 (Ar), 128.8 (Ar), 128.5 (Ar),

128.43 (Ar), 128.37 (Ar), 128.3 (Ar), 128.0 (Ar), 127.9 (Ar), 127.6 (Ar), 127.5 (Ar), 127.1 (Ar), 126.2 (Ar), 101.7 (PhCH), 100.0 (Ido_C1), 99.5 (GlcN_C1), 79.4 (GlcN_C4), 77.7 (GlcN_C3), 76.7 (Ido_C3), 75.2 (PhCH$_2$), 75.0 (GlcN_C5), 73.6 (Ido_C4), 73.3 (PhCH$_2$), 72.8 (PhCH$_2$), 69.8 (Ido_C6), 68.7 (GlcN_C6), 67.7 (Ido_C2), 67.2 (Ido_C5), 56.8 (OCH$_3$), 56.0 (GlcN_C2). HRMS (ESI): calcd m/z for C$_{49}$H$_{49}$NO$_{12}$ (M + NH$_4$)$^+$ 861.3593, found 861.3656.

Methyl 2-O-Acetyl-β-D-idopyranosyl-(1→4)-2-deoxy-2-phthalimido-β-D-glucopyranoside (41). The protected disaccharide **39** (75 mg, 0.085 mmol), palladium(0) (10% Pd on charcoal; 33 mg), and acetic acid (2 drops) were added to dry methanol (3.0 mL), and the solution was allowed to mix under positive pressure hydrogen gas. After 2 days, the mixture was filtered and evaporated to dryness. The crude material was then purified via column chromatography on silica using 8% methanol−dichloromethane to afford the pure product as a white solid (46 mg, 0.087 mmol, quantitative yield). R_f = 0.45 (methanol/dichloromethane 1:9). $[\alpha]^{20}_D$: −24.8 (c 0.77, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.82−7.78 (m, 2H, Phth), 7.71−7.67 (m, 2H, Phth), 5.08 (d, 1H, J = 8.5 Hz, GlcN_H1), 5.06 (dd, 1H, J = 2.8, <1 Hz, Ido_H2), 5.03 (d, 1H, J = <1 Hz, Ido_H1), 4.80 (broad, 1H, GlcN_3OH), 4.52 (broad, 1H, Ido_3OH), 4.38 (ddd, 1H, J = 10.5, 8.9, <1 Hz, GlcN_H3), 4.09 (m, 1H, Ido_H5), 4.04 (dd, 1H, J = 10.7, 8.5 Hz, GlcN_H2), 4.01 (m, 1H, Ido_H3), 3.90 (m, 1H, GlcN_H6a), 3.83−3.76 (m, 4H, GlcN_H4, GlcN_H6b, Ido_H6a, and Ido_H6b), 3.64−3.59 (m, 3H, Ido_H4, GlcN_6OH, and Ido_6OH), 3.45 (m, 1H, GlcN_H5), 3.36 (s, 3H, OCH$_3$), 3.10 (broad, 1H, J = 8.7 Hz, Ido_4OH), 2.09 (s, 3H, Ac). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 170.2 (Ac), 168.65 (Phth), 168.62 (Phth), 134.4 (Ar), 132.0 (Ar), 124.0 (Ar), 123.4 (Ar), 99.6 (GlcN_C1), 99.1 (Ido_C1), 81.5 (GlcN_C4), 76.0 (Ido_C5), 74.6 (GlcN_C5), 70.4 (Ido_C2), 70.2 (GlcN_C3), 69.5 (Ido_C3), 68.5 (Ido_C4), 62.1 (Ido_C6), 60.9 (GlcN_C6), 57.3 (OCH$_3$), 56.2 (GlcN_C2), 21.2 (Ac). HRMS (ESI): calcd m/z for C$_{23}$H$_{29}$NO$_{13}$ (M + NH$_4$)$^+$ 545.1977, found 545.1965.

Methyl 2,3,4,6-Tetra-O-acetyl-β-D-idopyranosyl-(1→4)-2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranoside (42). The starting material **41** (46 mg, 0.087 mmol) and hydrazine monohydrate (15 μL, 0.30 mmol) were refluxed in 95% ethanol (1.0 mL) for 24 h to afford the free amine (R_f 0.53 in water: methanol 1:3). The reaction mixture was evaporated to dryness and then redissolved in dry pyridine (0.5 mL) and acetic anhydride (0.5 mL). After the mixture was heated at 70 °C for 14 h, it was evaporated to dryness via coevaporation with toluene (2 × 1 mL) and then purified via column chromatography on silica using 1→ 3% methanol−dichloromethane to afford the pure product as a white solid (35 mg, 0.054 mmol, 62% yield over two steps). R_f = 0.29 (methanol/dichloromethane 3:97). $[\alpha]^{20}_D$: −21.3 (c 1.05, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.58 (d, 1H, J = 9.2 Hz, NHAc), 5.15 (dd, 1H, J = 4.8, 4.8 Hz, Ido_H3), 5.09 (dd, 1H, J = 10.3, 8.7 Hz, GlcN_H3), 4.88 (dd, 1H, J = 5.0, 2.2 Hz, Ido_H2), 4.83 (d, 1H, J = 2.2 Hz, Ido_H1), 4.79 (dd, 1H, J = 4.5, 2.6 Hz, Ido_H4), 4.39 (dd, 1H, J = 11.8, 2.7 Hz, GlcN_H6a), 4.39 (d, 1H, J = 8.1 Hz, Ido_H1), 4.27 (dd, 1H, J = 12.0, 4.8 Hz, GlcN_H6b), 4.21−4.14 (m, 3H, Ido_H5, Ido_H6a, and Ido_H6b), 3.92 (ddd, 1H, J = 10.3, 9.2, 8.2 Hz, GlcN_H2), 3.73 (dd, 1H, J = 9.4, 8.8 Hz, GlcN_H4), 3.60 (ddd, 1H, J = 9.5, 4.7, 2.6 Hz, GlcN_H5), 3.44 (s, 3H, OMe), 2.09 (s, 3H, Ac), 2.08 (s, 3H, Ac), 2.06 (s, 3H, Ac), 2.06 (s, 3H, Ac), 2.06 (s, 3H, Ac), 2.05 (s, 3H, Ac), 1.93 (s, 3H, Ac). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 171.3 (Ac), 170.74 (Ac), 170.69 (Ac), 170.5 (Ac), 169.82 (Ac), 169.75 (Ac), 168.8 (Ac), 102.0 (GlcN_C1), 97.6 (Ido_C1), 76.0 (GlcN_C4), 72.9 (GlcN_C3), 72.6 (GlcN_C5), 71.5 (Ido_C5), 67.5 (Ido_C3), 67.2 (Ido_C2), 66.7 (Ido_C4), 63.0 (GlcN_C6), 62.6 (Ido_C6), 56.9 (OMe), 54.0 (GlcN_C2), 23.5 (Ac), 21.01 (Ac), 20.96 (Ac), 20.9 (Ac), 20.8 (Ac). HRMS (ESI): calcd m/z for C$_{27}$H$_{39}$NO$_{17}$ (M + H)$^+$ 650.2291, found 650.2285.

Methyl β-D-Idopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (43). A sodium methoxide solution was added dropwise (1.5 M NaOMe in MeOH, to pH 10) to a solution of the starting material **42** (18 mg, 0.028 mmol) in dry methanol (0.20 mL), and the solution was allowed to mix at room temperature. After 12 h, the reaction was then neutralized using ion-exchange resin (Amberlite IR-

120H, to pH 6), filtered, and evaporated to dryness to afford the pure product as a colorless syrup (11 mg, 0.028 mmol, quantitative yield). $[\alpha]^{20}_D$: −9.9 (c 0.95, MeOH). ^{1}H NMR (CD$_3$OD, 400 MHz): δ 4.89 (d, 1H, J = <1 Hz, Ido_H1), 4.33 (d, 1H, J = 8.1 Hz, GlcN_H1), 4.00−3.95 (m, 2H, Ido_H5 and Ido_H3), 3.84 (dd, 1H, J = 12.1, 2.2 Hz, GlcN_H6a), 3.81 (dd, 1H, J = 11.5, 7.6 Hz, Ido_H6a), 3.76−3.64 (m, 6H, GlcN_H6b, GlcN_H2, Ido_H6b, Ido_H2, GlcN_H4, and GlcN_H3), 3.53 (m, 1H, Ido_H4), 3.46 (s, 3H, OMe), 3.40 (ddd, 1H, J = 9.1, 4.3, 2.1 Hz, GlcN_H5), 1.97 (s, 3H, Ac). ^{13}C NMR (CD$_3$OD, 100 MHz): δ 173.8 (Ac), 103.8 (GlcN_C1), 101.1 (Ido_C1), 81.1 (GlcN_C4), 77.2 (Ido_C5), 76.7 (GlcN_C5), 74.3 (GlcN_C3), 72.0 (Ido_C2), 71.5 (Ido_C3), 70.4 (Ido_C4), 62.9 (Ido_C6), 62.1 (GlcN_C6), 57.2 (OMe), 56.8 (GlcN_C2), 23.1 (Ac). HRMS (ESI): calcd m/z for C$_{15}$H$_{27}$NO$_{11}$ (M + Na)$^+$ 420.1476, found 420.1478.

ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all compounds and ^{1}H_^{1}H GCOSY spectra for all synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Kurihara, Y.; Ueda, K. *Carbohydr. Res.* **2006**, *341*, 2565.

(2) Capila, I.; Linhardt, R. J. *Angew. Chem. Int. Ed.* **2002**, *41*, 391.

(3) Boltje, T. J.; Buskas, T.; Boons, G.-J. *Nat. Chem.* **2009**, *1*, 611.

(4) Hung, S. C.; Thopate, S. R.; Chi, F. C.; Chang, S. W.; Lee, J. C.; Wang, C. C.; Wen, Y. S. *J. Am. Chem. Soc.* **2001**, *123*, 3153.

(5) Lu, N.-D. L.; Shie, C.-R.; Kulkarni, S. S.; Pan, G.-R.; Lu, X.-A.; Hung, S.-C. *Org. Lett.* **2006**, *8*, 5995.

(6) Ke, W. J.; Whitfield, D. M. *Carbohydr. Res.* **2004**, *339*, 2841.

(7) Ke, W.; Whitfield, D. M.; Gill, M.; Larocque, S.; Yu, S. H. *Tetrahedron Lett.* **2003**, *44*, 7767.

(8) Ke, W. J.; Whitfield, D. M.; Brisson, J. R.; Enright, G.; Jarrell, H. C.; Wu, W. G. *Carbohydr. Res.* **2005**, *340*, 355.

(9) Yu, H. N.; Furukawa, J.; Ikeda, T.; Wong, C. H. *Org. Lett.* **2004**, *6*, 723.

(10) Lohman, G. J. S.; Hunt, D. K.; Hogermeier, J. A.; Seeberger, P. H. *J. Org. Chem.* **2003**, *68*, 7559.

(11) Orgueira, H. A.; Bartolozzi, A.; Schell, P.; Litjens, R.; Palmacci, E. R.; Seeberger, P. H. *Chem.—Eur. J.* **2003**, *9*, 140.

(12) Lee, J. C.; Lu, X. A.; Kulkarni, S. S.; Wen, Y. S.; Hung, S. C. *J. Am. Chem. Soc.* **2004**, *126*, 476.

(13) Hakamata, W.; Muroi, M.; Kadokura, K.; Nishio, T.; Oku, T.; Kimura, A.; Chiba, S.; Takatsuki, A. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1489.

(14) Hakamata, W.; Muroi, M.; Nishio, T.; Oku, T.; Takatsuki, A. *J. Carbohydr. Chem.* **2004**, *23*, 27.

(15) Aoshima, H.; Yokoyama, T.; Tanizaki, J.; Izu, H.; Yamada, M. *Biosci. Biotechnol. Biochem.* **1997**, *61*, 979.

(16) Chen, Y. H.; Poly, F.; Pakulski, Z.; Guerry, P.; Monteiro, M. A. *Carbohydr. Res.* **2008**, *343*, 1034.

(17) Yu, R. K.; Usuki, S.; Ariga, T. *Infect. Immun.* **2006**, *74*, 6517.

(18) Galanis, E. *Can. Med. Assoc. J.* **2007**, *177*, 570.

(19) Monteiro, M. A.; Baqar, S.; Hall, E. R.; Chen, Y.-H.; Porter, C. K.; Bentzel, D. E.; Applebee, L.; Guerry, P. *Infect. Immun.* **2009**, *77*, 1128.

(20) Wiggins, L. F. *J. Chem. Soc.* **1944**, 522.

(21) Bacon, J. S. D.; Bell, D. J.; Kosterlitz, H. W. *J. Chem. Soc.* **1939**, 1248.

(22) Frahn, J. L. *Aust. J. Chem.* **1980**, *33*, 1021.

(23) Tagaki, W.; Kurusu, T.; Oae, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2894.

(24) Szeja, W. *Carbohydr. Res.* **1988**, *183*, 135.

(25) Bunton, C. A.; Frei, Y. F. *J. Chem. Soc.* **1951**, 1872.

(26) Bunton, C. A.; Welch, V. A. *J. Chem. Soc.* **1956**, 3240.

(27) Jesudason, M. V.; Owen, L. N. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2019.

(28) Abdel-Malik, M. M.; Peng, Q. J.; Perlin, A. S. *Carbohydr. Res.* **1987**, *159*, 11.

(29) Jesudason, M. V.; Owen, L. N. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2024.

(30) Cunningham, D.; Gavin, N.; Lee, E.; McArdle, P.; Ocallaghan, J.; Higgins, T. *Carbohydr. Res.* **1988**, *177*, 1.

(31) Sadeghi-Khomami, A.; Forcada, T. J.; Wilson, C.; Sanders, D. A. R.; Thomas, N. R. *Org. Biomol. Chem.* **2010**, *8*, 1596.

(32) Paulsen, H.; Stoye, D. *Chem. Ber. Recl.* **1969**, *102*, 3824.

(33) Lassaletta, J. M.; Carlsson, K.; Garegg, P. J.; Schmidt, R. R. *J. Org. Chem.* **1996**, *61*, 6873.

(34) Gridley, J. J.; Hacking, A. J.; Osborn, H. M. I.; Spackman, D. G. *Tetrahedron* **1998**, *54*, 14925.

(35) Zhang, P.; Ng, K.; Ling, C.-C. *Org. Biomol. Chem.* **2010**, *8*, 128.

(36) Figueroa-Perez, S.; Verez-Bencomo, V. *Carbohydr. Res.* **1999**, *317*, 29.

(37) Jarymowycz, V. A.; Stone, M. J. *Chem. Rev.* **2006**, *106*, 1624.

(38) Tsvetkov, Y. E.; Backinowsky, L. V. *Carbohydr. Res.* **1985**, *135*, 312.

(39) Wang, Y.; Li, Q.; Cheng, S. H.; Wu, Y. F.; Guo, D. J.; Fan, Q. H.; Wang, X. F.; Zhang, L. H.; Ye, X. S. *Org. Lett.* **2005**, *7*, 5577.

(40) Abdel-Malik, M. M.; Perlin, A. S. *Carbohydr. Res.* **1989**, *190*, 39.