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Role of the 4,6-*O*-acetal in the regio- and stereoselective conversion of 2,3-di-*O*-sulfonyl-β-D-galactopyranosides to D-idopyranosides

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ABSTRACT

The recently reported conversion of 2,3-di-*O*-sulfonyl-D-galactopyranosides to D-idopyranosides has provided an efficient route to obtaining orthogonally-protected idopyranoside building blocks with a β-1,2-*cis* glycosidic linkage. In an effort to expand the scope of this process and better understand the regio- and stereoselectivity observed in the key di-inversion step of the method, a small library of 4,6-*O*-acetal protected galactopyranosides has been synthesized and used as substrates in the process, together with a number of substrates that lack the acetal functionality. The results suggest that although the substituent at the acetal center does not contribute to the observed selectivity of the process, the acetal group is indeed required for efficient conversion by reducing the conformational flexibility of the substrate, resulting in enhanced reaction rates at both the O-transsulfonylation and epoxide ring-opening steps.

1. Introduction

D- and L-idopyranosides are conformationally unique hexopyranosides abundant in nature. For example, they present as D-*ido*-heptopyranosides in the capsular polysaccharide (CPS) structure of *Campylobacter jejuni*,[1] or as the oxidized L-iduronic acids found in glycosaminoglycans (GAGs) such as heparin, heparan, and dermatan sulfates. Idopyranosides can display significant conformational flexibility due to the relative high energy of their $^4C_1$ and $^1C_4$ chair conformations, which results in a lower energy barrier between the chair and twist boat conformations.[2] Since the idopyranosides found in nature are often functionalized with O-substitutions such as partial sulfation in the GAGs (various patterns at all positions) and 7-*O*-phosphoramidation in the *C. jejuni* D-*ido*-heptopyranoside-antigen,[1] accessing orthogonally-protected idopyranoside building blocks are key to streamlining their syntheses in sufficient quantities for biological and pharmacological testing.

Recently, the development of efficient syntheses to obtain antigenic oligosaccharides related to *C. jejuni* CPS has drawn our interest, as this gastrointestinal pathogen also expresses lipopolysaccharides which have structural elements resembling human gangliosides.[3] Upon recovering from *C. jejuni* bacterial infection, some patients develop carbohydrate-specific antibodies against these lipopolysaccharides, leading to the development of Guillain–Barré Syndrome, an acute and severe autoimmune neurological disease resulting from the aforementioned molecular mimicry.[3,4] In an effort to potentially re-direct the immune response away from lipopolysaccharides, we have become interested in chemically synthesizing a carbohydrate-based conjugate vaccine against the unique 6-deoxy-β-D-*ido*-heptopyranoside present in the CPS of *C. jejuni* serotype HS:4 (Fig. 1).[1] Previously, it was shown that subcutaneous inoculation with conjugates containing the CPS extracted from natural sources elicited promising immunological results.[5]

The synthesis of the β-linked *ido*-heptopyranoside present in the *C. jejuni* CPS presents a significant challenge due to the unusual configuration and the β-1,2-*cis*-glycosidic linkage. Recently, our group has published a short, scalable method from D-galactose which could be used to obtain orthogonally protected D-idopyranoside (Scheme 1). The method relies on a di-inversion at C-2 and C-3 of 4,6-*O*-benzylidene-2,3-di-*O*-sulfonyl-β-D-galactopyranosides (**1**–**2**); the conversion proceeds with high regio- and stereoselectivity to give only the desired product (**4**), as detected in the crude ^{1}H NMR.[6] The method was compatible with a series of nucleophiles (MeO^-, $AllO^-$, BnO^-); more importantly, this methodology was also found to be applicable to the synthesis of β-linked idopyranoside-containing oligosaccharides. We also observed that in using the corresponding α-D-galactopyranosides, the conversion proceeds with reduced regio- and stereoselectivity.[6,7] A similar two-step approach using methyl 4,6-*O*-benzylidene-3-*O*-tosyl-β-D-galactopyranoside has also been reported, which upon treatment with base affords the intermediate 2,3-anhydro-gulopyranoside, and subsequent attack with a nucleophile in the presence of microwave irradiation provides the 2-O-substituted idopyranoside.[8]

The acetal protecting group is useful in orthogonal protection strategies, as it can be either fully hydrolyzed, or regioselectively

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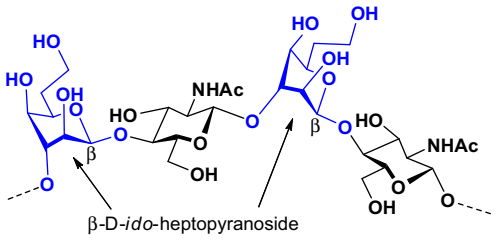


Figure 1. The β-D-*ido*-heptopyranoside present in capsular polysaccharide of *Campylobacter jejuni*.

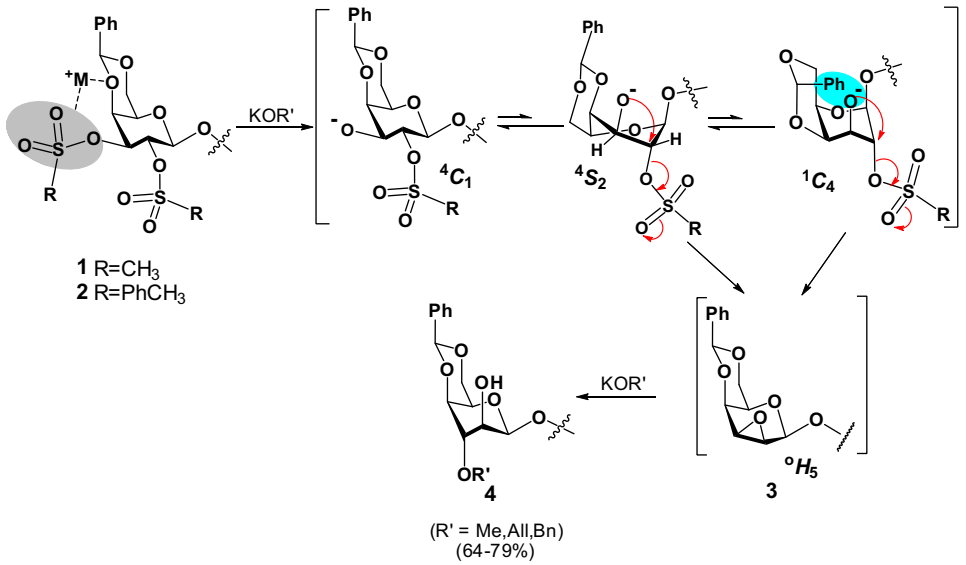
opened under reductive conditions by using a combination of hydride agent (such as $LiAlH_4$, $NaBH_3CN$, DIBAL-H, silane, and borane) and Lewis acid (TMSOTf, $AlCl_3$, $BF_3{\cdot}Et_2O$, metal triflate, etc.).[9–11] Applying the Hanessian–Hullar reaction conditions[12] or using substituted benzylidenes and other related acetals could offer further flexibility in orthogonal deprotections for our total synthesis of *C. jejuni ido*-heptopyranoside analogs.

We also probed the mechanism of the regio- and stereoselective di-inversion step of the 2,3-di-*O*-sulfonates and found that alkali cations play an important role in preferentially activating sulfonates that have a *cis*-oriented neighboring oxygen, leading to an O-transsulfonylation as a result of S–O bond scission. The alkali cation could coordinate with either the more electron rich oxygen of the S=O or the slightly less electron rich oxygen of the S–O.[13] After the 3-O-transsulfonylation step, a negatively charged 3-oxide is generated, which nucleophilically substitutes the C-2 sulfonate by attacking the backside of the stereocenter, resulting in an inversion of C-2 configuration. However, this step is not straightforward, as the molecule adopts predominantly the $^4C_1$ chair conformation, causing both C-2 and C-3 substituents to occupy a *trans*-diequatorial orientation; the formation of the 2,3-epoxide is not possible from such conformation. In order for the intramolecular S_N2 nucleophilic substitution to occur, the molecule needs to switch to another conformation so that the two substituents at C-2 and C-3 can achieve a *trans*-diaxial or pseudo-*trans*-diaxial orientation. This can be realized through conversion to the $^4S_2$ or $^1C_4$ conformation. In this work, we set out to probe the influence of conformational flexibility on the conversion of 4,6-*O*-benzylidene protected galactopyranoside systems to idopyranosides.

2. Results and discussion

Conformational flexibility of the substrates greatly affects the conversion of 4,6-*O*-acetal protected galactopyranosides to the corresponding idopyranosides. As discussed above, it is beneficial to have a more flexible substrate so that the ring-flip can occur to facilitate epoxide formation; however, for steps involving the O-desulfonylation and epoxide opening, a less conformationally flexible substrate should be favored, as this facilitates the intermolecular nucleophilic attacks. In 4,6-*O*-benzylidene protected β-galactopyranosides the $^4C_1$ chair is most stable, as in the $^4S_2$ or $^1C_4$ conformers more substituents will be forced to occupy an axial or pseudo-axial position, resulting in higher energy conformations. Through examination of a molecular model, we also observed that the phenyl group of the acetal may play a significant role in controlling the conformational flexibility; for example, if the pyranoside adopts a $^4C_1$ chair, the most stable conformation of the molecule should occur when the six-membered acetal ring also adopts a chair conformation placing the phenyl group in an equatorial position. However, when a ring-flip of the pyranoside to the $^1C_4$ chair occurs, if the six-membered acetal ring also flips to the opposite chair, this would place the phenyl ring in close proximity to the C-3 substituent, thus increasing unfavorable steric interactions; the introduction of additional substituents on the phenyl ring, especially at the *m*- and *o*-positions, would increase the steric hindrance further, thus decreasing the conformational flexibility. Thus, the *o*-, *m*-, and *p*-methoxybenzylidene protected galactopyranosides (**5**–**7**) and a *p*-nitrobenzylidene protected analog (**8**) were synthesized and compared to the less sterically hindered ethylidene analog (**9**), as well as the highly flexible methylidene analog (**10**) (Fig. 2). The placement of the electron-withdrawing nitro group on the phenyl ring could also affect the electron density of the acetal O-4 and O-6 centers compared to the other electron-donating methoxybenzylidene analogs; this could influence the alkali-coordination, thus affecting the reaction rate of the O-transsulfonylation step.

In order to synthesize the desired acetal derivatives **5**–**8**, the respective dimethyl acetal reagents **12**–**15** were synthesized from their corresponding aldehyde in near quantitative yields using the method described by Johnsson et al.[14] Camphorsulfonic acid (CSA)-catalyzed transacetalations of compounds **12**–**15** with methyl β-D-galactopyranoside (**11**) afforded the corresponding



Scheme 1. Key step involving the di-inversion of C-2 and C-3 in the regio- and stereoselective conversion of D-galactopyranosides to D-idopyranosides.

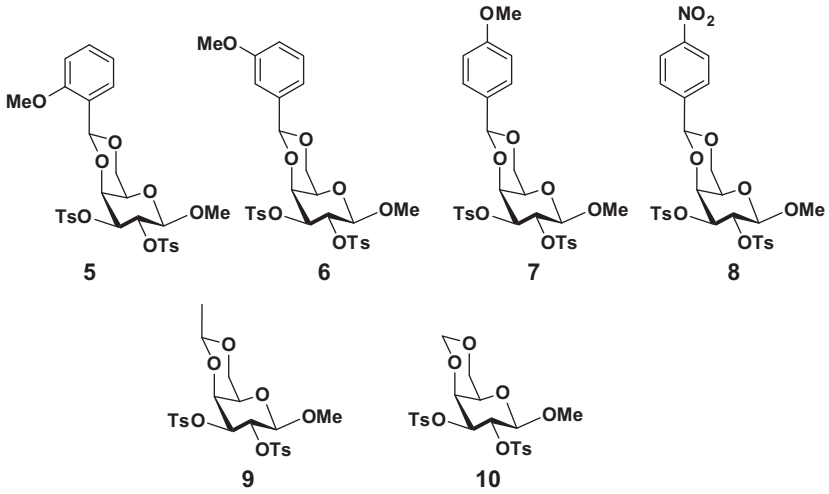
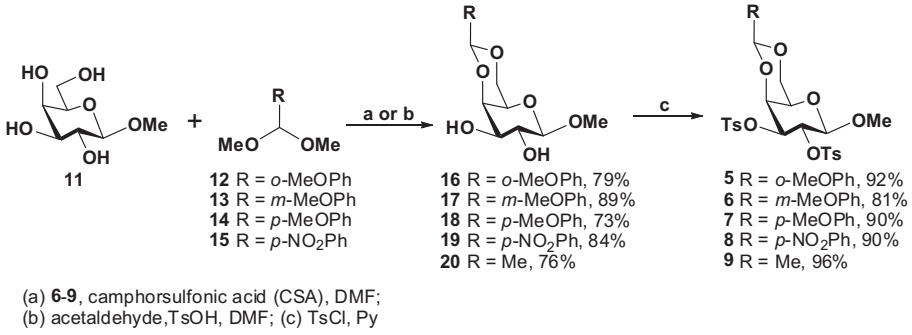


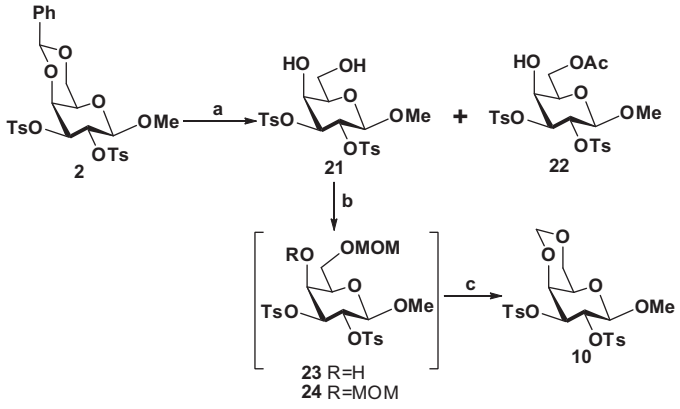
Figure 2. Different methyl 4,6-*O*-acetal-2,3-di-*O*-tosyl-β-D-galactopyranosides to probe the influence of conformational flexibility on the conversion of galactopyranosides to idopyranosides.



Scheme 2. Synthesis of a series of 2,3-di-*O*-toluenesulfonyl-β-D-galactopyranosides (**5**–**9**) from compound **11**.

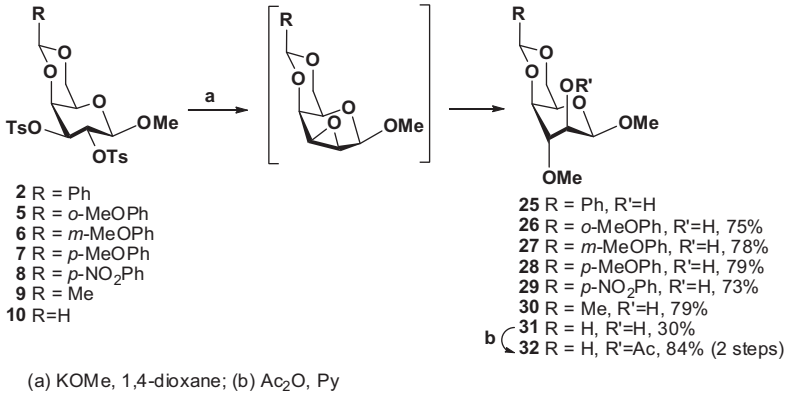
4,6-*O*-acetal protected derivatives **16**–**19** in 73–89% yields (Scheme 2).[15] For compound **20**, the synthesis was carried out using acetaldehyde/*p*-toluenesulfonic acid as a reagent (76%). The subsequent 2,3-di-O-sulfonylations. with *p*-toluenesulfonyl chloride (TsCl) in pyridine afforded the target substrates **5**–**9** in 81–96% yields.

To obtain a substrate containing the 4,6-*O*-methylidene acetal of galactopyranoside (**10**), the method described in Scheme 2 was attempted (not shown) using dimethoxymethane as a reagent with compound **11**; however, the desired compound 4,6-*O*-methylidene-β-D-galactopyranoside (not shown) was found to form in poor yield likely due to the formation of a mixture of non-cyclized mixed acetals (MOM) and cyclized acetals (both the 1,3-dioxolane and 1,3-dioxane forms).[16] An alternative route was pursued using the previously synthesized 4,6-*O*-benzylidene-2,3-di-*O*-tosyl-β-D-galactopyranoside **2** as a starting material (Scheme 3). Initial attempts at hydrolysis using aqueous acetic acid were sluggish, and resulted in concomitant acetylation of O-6 to afford **22** in substantial amounts (~40% as estimated by TLC); the latter was not desirable as subsequent conversion to **21** was considered to be difficult due to the sensitivity of the tosylate function to alkaline conditions. Alternatively, hydrolysis of **2** with 50% trifluoroacetic acid–water at room temperature proceeded smoothly to afford the 4,6-diol **21** in 94% yield. The subsequent treatment of **21** with neat dimethoxymethane under the catalysis of CSA was quite slow, and in an effort to drive the reaction to completion a Soxhlet apparatus containing molecular sieves (4 Å) was used to remove methanol from the reaction mixture, as the methanol could be



Scheme 3. The synthesis of methyl 4,6-*O*-methylidene-2,3-di-*O*-tosyl-β-D-galactopyranoside **10**.

azeotropically distilled with dimethoxymethane and then removed by passing over the bed of molecular sieves.[16] The reaction afforded primarily a mixture of the 6-*O*-MOM (**23**) and 4,6-di-*O*-MOM (**24**) protected compounds, and produced only trace amounts of the desired 4,6-*O*-methylidene acetal protected **10**; in order to drive the reaction to completion, dimethoxymethane was evaporated to dry, and then the reaction mixture redissolved into



Scheme 4. Conversion of 4,6-*O*-acetal-2,3-di-*O*-sulfonyl-β-D-galactopyranosides to 4,6-*O*-acetal-3-*O*-methyl-β-D-idopyranosides.

dichloromethane and further refluxed with CSA for several days, which upon column chromatography afforded the product **10** in 83% yield.

All synthesized 4,6-*O*-acetal-2,3-di-*O*-tosyl-β-D-galactopyranosides **5**–**10** were then reacted with potassium methoxide at room temperature (Scheme 4). It was found that in all cases, the reactions resulted in clean conversion to the 4,6-*O*-acetal-3-*O*-methyl-β-D-idopyranosides as detected by ^{1}H NMR; for substituted acetal derivatives **5**–**9**, the desired idopyranosides **26**–**30** were isolated in yields of 73–79%. This yield is comparable to the previously reported conversion of compound **2** to **25** (66%, not optimized).[6] For the unsubstituted methylidene acetal **10**, the desired idopyranoside **31** was isolated albeit in low yields (~30%), presumably due to a loss of product during work-up because of an increased water-solubility of the product. In order to increase the isolated yield, the crude reaction mixture was acetylated, and the 2-O-acetylated idopyranoside **32** was isolated in a much improved yield (84%).

The consistent high regio- and stereoselective conversion of all acetal-protected 2,3-di-*O*-sulfonyl D-galactopyranosides (**2**, **5**–**10**) to D-idopyranosides (**25**–**30**, **32**) indicated that although there are some degrees of difference in ring flexibility introduced by substituents attached to the acetal carbon center, this did not contribute to significant differences in the observed reactivity and regio/stereoselectivity. The $^4S_2$ conformer may be the main mediator of the intramolecular cyclization, and in this conformation the substituent placed at the acetal carbon center does not appear to interact significantly with the substituent at C-3, which could explain why all synthesized 4,6-*O*-acetal protected substrates gave similar yields of the corresponding D-idopyranoside.

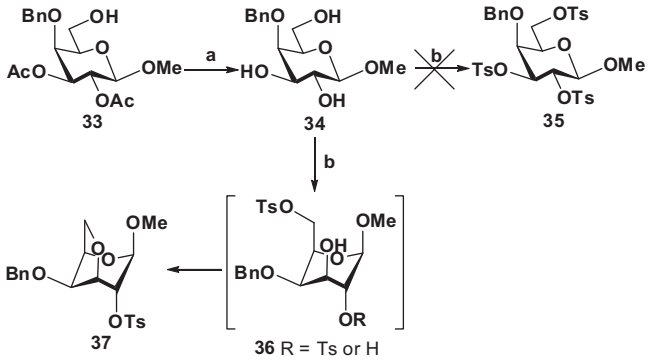
The reaction progression of **2**, **7**, and **8** with potassium methoxide was monitored by ^{1}H NMR; the results indicated that indeed the *p*-nitrobenzylidene acetal-containing substrate **8** reacted slowest (Table 1), likely due to weaker cation coordination at O-4 because of the aryl nitro-substituent. Contrary to expectations based on electron-donating ability, substrates **2** and **7** were observed to react at a similar rate, although both with the expected regioselectivity; this may be explained by the aryl methoxy substituent competing for cation coordination making it less available to activate the reaction.

We thus turned our attention to substrates lacking the 4,6-*O*-acetal functionality, as these compounds should be even more flexible than any of the 4,6-*O*-acetal-protected galactopyranosides. Compound **35** was chosen as a possible substrate, as it was thought to be readily obtained from triol **34**. Compound **34** was obtained via a Zemplén transesterification of methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-β-D-galactopyranoside **33**, which was prepared from methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranoside according to literature procedure (Scheme 5).[11,17] Unfortunately, attempts at tri-tosylation of the triol (**34**) using TsCl in anhydrous pyridine did not yield the desired 2,3,6-tri-*O*-tosylate (**35**); instead, 3,6-anhydro product **37** was isolated. Compound **37** was possibly formed via first a selective 6-O-tosylation (→**36**) followed by an intramolecular S_N2 nucleophilic attack from the 3-hydroxyl group to form the 3,6-anhydro functionality. The pyranoside may ring-flip from the $^4C_1$ to $^1C_4$ chair during the process, which affords a favorable anomeric effect for β-glycosides that helps to counterbalance the unfavorable axial orientations,

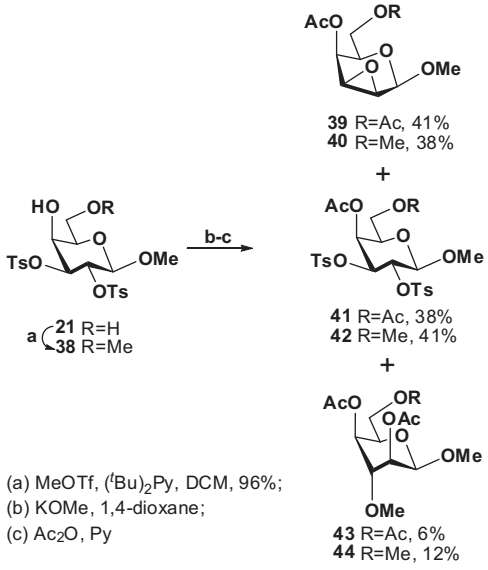
Table 1
^{1}H NMR monitoring of the reaction progression of di-sulfonates **2**, **7**, and **8**[a]

Time (h)	Ph			*p*-MeOPh			*p*-NO_2Ph		
	2	Int[b]	**25**	**7**	Int[b]	**28**	**8**	Int[b]	**29**
0	100	0	0	100	0	0	100	0	0
2	60	33	8	69	23	8	82	14	4
4	49	35	16	45	44	12	71	21	8
6	30	51	19	41	38	21	60	28	12
8	23	56	22	33	42	25	56	28	16
10	16	59	25	31	43	26	43	39	18

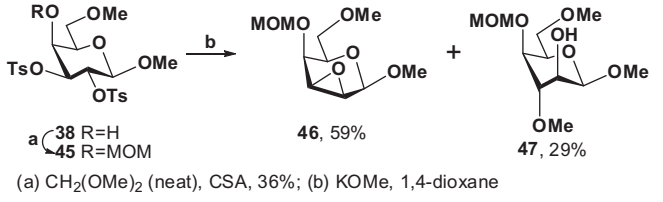
[a] Relative amounts of the starting material, intermediate epoxide, and *ido*-configured product were determined by periodically analyzing aliquots from the reaction mixtures; the relative amounts of each were determined by integration of the benzylic protons in the ^{1}H NMR.
[b] Refers to the 2,3-anhydro-talopyranoside intermediate.



Scheme 5. Initial attempts at obtaining a 2,3-di-*O*-tosyl-β-D-galactopyranoside which lacked the 4,6-*O*-acetal functionality were unsuccessful, and instead resulted in an intramolecular ring closure.



Scheme 6. 2,3-Di-*O*-tosyl-β-D-galactopyranosides **21** and **38** lacking the 4,6-*O*-acetal were subjected to a methoxide solution in order to probe the regio- and stereoselectivity of the resultant reaction.



Scheme 7. 4,6-O-Protected-2,3-di-*O*-tosyl-β-D-galactopyranoside **45** was reacted with methoxide solution to probe the regio- and stereoselectivity of the resultant reaction.

which enables the attack of O-3 at C-6; this is similar to the process observed by Crich et al. while studying the Hanessian–Hullar reaction in β-galactosides.[12]

Since compound **21** had already two tosylates at the C-2 and C-3 positions, another effort to obtain galactopyranosides that lack a 4,6-*O*-acetal functionality was carried out using the 4,6-diol **21** as a starting material. A 4,6-di-O-methylation was attempted on diol **21** using methyl triflate as a reagent in the presence of 2,6-di-*tert*-butylpyridine.[18] However, only trace amounts of 4,6-di-O-methylated compound were obtained (<1% isolated yield); instead, the 6-O-monomethylated compound (**38**) was obtained in near quantitative yield (96%) (Scheme 6). The axial OH-4 is seemingly too unreactive to be methylated under the methylating conditions that were used; more forceful attempts with stronger base or heating resulted in unidentified decomposition. Nevertheless, both substrates **21** and **38** were treated with a methoxide solution as before. However, both reactions were found to be sluggish, affording several compounds even after several days. To facilitate the purification, both crude reaction mixtures were acetylated, and subsequently purified by column chromatography on silica gel to afford the 2,3-anhydro-talopyranoside intermediate which was isolated in each case (**39**, 42%; **40**, 38%), along with an acetylated derivative resulting from the unreacted 2,3-di-*O*-tosylate (**41**, 38%, **42**, 41%); interestingly, the expected idopyranoside was only isolated in low yield (**43**, 6%; **44**, 12%). Attempts to improve the yield of idopyranoside by carrying out the reaction at higher temperatures (50–80 °C) were unsuccessful, as although more idopyranoside was observed to form, new by-products with elimination were also formed as evidenced by the crude ^{1}H NMR.

In order to confirm that the retardation of reaction rate was not due to the unprotected OH-4 position, compound **38** was protected with a methoxymethyl (MOM) ether (→**45**, 36% yield), and then exposed to methoxide solution. Similar to the observations made for the other substrates lacking a 4,6-*O*-acetal, the reaction rate was significantly slowed resulting in isolation of both the 2,3-anhydro-β-D-talopyranoside **46** and 3-*O*-methyl-idopyranoside **47** after 4 days (Scheme 7).

The above results are in sharp contrast with the use of conformationally less flexible 4,6-*O*-acetal analogs of galactopyranoside. The presence of the 4,6-*O*-acetals clearly enhanced the reactivity of all prepared 2,3-di-*O*-sulfonates of galactopyranosides (**2**, **5**–**10**), as all these compounds were smoothly converted to the corresponding idopyranosides. However, the observation of intermediate epoxides as well as poor yields for the desired idopyranosides in all non-acetal-protected cases confirmed the beneficial effect of using less flexible substrates in the nucleophilic opening of 2,3-epoxides. Furthermore, the observation of unreacted disulfonates in the cases of **21** and **38** also confirmed the putative reduced reactivity of the 3-*O*-sulfonate in the O-desulfonylation step for the non-acetal protected substrates; this is most likely due to the increased conformational flexibility which affects the cation-mediated polarization of the 3-*O*-sulfonate as well as the success rate of nucleophilic attack by the incoming nucleophile on the S-center.[13]

3. Conclusions

In conclusion, we have synthesized a small library of methyl 4,6-*O*-acetal-2,3-di-*O*-tosyl-β-D-galactopyranoside derivatives and then treated them with methoxide. Despite the conformational flexibility difference between the *o*-, *m*-, and *p*-methoxybenzylidene, *p*-nitrobenzylidene, ethylidene, and methylidene acetals, all 4,6-*O*-acetal-protected substrates resulted in a highly regio- and stereoselective conversion to the corresponding methyl 4,6-*O*-acetal-3-*O*-methyl-β-D-galactopyranoside derivatives, as was previously reported for the 4,6-*O*-benzylidene acetal; either the $^4S_2$ or $^1C_4$ conformer is likely responsible for mediating the intramolecular cyclization in the majority of cases. However, all non-4,6-*O*-acetal-protected substrates reacted at much reduced reaction rates at both the first O-transsulfonylation step and the subsequent *trans*-diaxial epoxide opening, indicating that the torsional strain afforded by the acetals assists in both mechanistic steps of the di-inversion transformation probably by reducing the conformational stability of the substrates.

4. Experimental data

4.1. General methods

All commercial reagents were used as supplied unless otherwise stated. Thin layer chromatography was performed on Silica Gel 60-F254 (E. Merck, Darmstadt) with detection by fluorescence, charring with 5% aqueous sulfuric acid, or a ceric ammonium molybdate solution. Column chromatography was performed on Silica Gel 60 (Silicycle, Ontario) and solvent gradients given refer to stepped gradients and concentrations are reported as % v/v. Organic solutions were concentrated and/or evaporated to dry 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 MeOH prior to use. Optical rotations were determined in a 5 cm cell at 20 ± 2 °C; $[\alpha]_D^{20}$ values are given in units of

10^{-1} deg cm^2/g. NMR spectra were recorded on Bruker spectrometers 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, δ_C 77.23, $CDCl_3$). ^{1}H and ^{13}C NMR spectra were assigned with the assistance of 2D gCOSY and 2D gHSQC experiments. High-resolution ESI-QTOF mass spectra were recorded on an Agilent 6520 Accurate Mass Quadrupole Time-of-Flight LC/MS spectrometer. All of the data were obtained with the assistance of the analytical services of the Department of Chemistry, University of Calgary.

4.2. General procedure for the synthesis of dimethyl acetals (12–15)

A solution of the aldehyde (3.5 mmol), trimethyl orthoformate (5.9 mmol), and acidic resin (Amberlite IR-120H, 15 mg) in dry MeOH (4.0 mL) was heated at 110 °C in a microwave reactor for 20 min, as reported previously for the synthesis of *p*-anisaldehyde dimethyl acetal.[14] Upon cooling back to room temperature, the solution was filtered and diluted with EtOAc (50 mL). The organic phase was washed with saturated $NaCl_{(aq)}$ solution (2 × 50 mL), and the combined aqueous layers further extracted with EtOAc (70 mL). The organic phases were combined, dried with Na_2SO_4, filtered, and evaporated to dry to afford the product (89–98% yields).

4.3. Methyl 4,6-*O*-(*o*-methoxybenzylidene)-β-D-galactopyranoside (16)

The glycoside starting material (**11**, 511 mg, 2.63 mmol) and *o*-anisaldehyde dimethyl acetal (**12**, 810 mg, 4.45 mmol) were dissolved into dry DMF (6.0 mL), camphorsulphonic acid (CSA; to pH 3) was added, and the reaction solution left mixing at room temperature under argon. After 18 h the solution was neutralized with Et_3N (to pH 8), and evaporated to dry via co-evaporation with toluene (3 × 5 mL). The crude mixture was purified by column chromatography on silica gel using 2→3% MeOH–CH_2Cl_2 to afford the desired product **16** as a white solid (649 mg, 2.08 mmol, 79% yield). R_f 0.46 (acetone:hexanes 7:3). $[\alpha]_D^{20}$: −46.4° (*c* 1.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.64 (dd, 1H, *J* = 7.6, 1.8 Hz, Ar), 7.30 (ddd, 1H, *J* = 8.3, 7.5, 1.8 Hz, Ar), 6.96 (ddd, 1H, *J* = 7.5, 7.5, 0.8 Hz, Ar), 6.85 (dd, 1H, *J* = 8.3, <1 Hz, Ar), 5.93 (s, 1H, ArC*H*), 4.31 (dd, 1H, *J* = 12.5, 1.4 Hz, H-6a), 4.19 (d, 1H, *J* = 7.5 Hz, H-1), 4.19 (dd, 1H, *J* = 3.9, 1.0 Hz, H-4), 4.09 (dd, 1H, *J* = 12.5, 1.9 Hz, H-6b), 3.81 (s, 3H, OMe), 3.74 (ddd, 1H, *J* = 9.5, 7.6, 1.7 Hz, H-2), 3.64 (ddd, 1H, *J* = 9.5, 9.5, 3.8 Hz, H-3), 3.58 (s, 3H, OMe), 3.45 (m, 1H, H-5), 2.52 (d, 1H, *J* = 9.4 Hz, 3-OH), 2.52 (d, 1H, *J* = 1.8 Hz, 2-OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 156.63 (Ar), 130.62 (Ar), 127.94 (Ar), 126.06 (Ar), 120.93 (Ar), 110.76 (Ar), 104.01 (C-1), 96.70 (ArCH), 75.68 (C-4), 73.07 (C-3), 72.20 (C-2), 69.54 (C-6), 67.12 (C-5), 57.36 (OMe), 55.80 (OMe). HRMS *m*/*z* calcd for $C_{15}H_{20}O_7$ $(M+Na)^+$: 335.1101; found: 335.1100.

4.4. Methyl 4,6-*O*-(*m*-methoxybenzylidene)-β-D-galactopyranoside (17)

The glycoside starting material (**11**, 988 mg, 5.09 mmol) and *m*-anisaldehyde dimethyl acetal (**13**, 1.470 g, 8.07 mmol) were dissolved into dry DMF (10 mL), and the procedure in Section 4.3 was followed to obtain the crude product, which was subsequently purified by column chromatography on silica gel using 1.5→2.5→3% MeOH–CH_2Cl_2 to afford the desired product **17** as a white solid (1.412 g, 4.52 mmol, 89% yield). R_f 0.29 (acetone:hexanes 1:1). $[\alpha]_D^{20}$: −39.0° (*c* 0.96, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.25 (dd, 1H, *J* = 8.0, 7.8 Hz, Ar), 7.05 (m, 2H, Ar), 6.88 (ddd, 1H, *J* = 8.2, 2.6, 1.0 Hz, Ar), 5.51 (s, 1H, ArC*H*), 4.33 (dd, 1H, *J* = 12.5, 1.5 Hz, H-6a), 4.19 (d, 1H, *J* = 7.4 Hz, H-1), 4.19 (dd, 1H, *J* = 3.6, 1.2 Hz, H-4), 4.06 (dd, 1H, *J* = 12.5, 1.9 Hz, H-6b), 3.79 (s, 3H, OMe), 3.75–3.71 (m, 1H, H-2), 3.66 (ddd, 1H, *J* = 9.5, 8.8, 3.6 Hz, H-3), 3.56 (s, 3H, OMe), 3.47 (m, 1H, H-5), 2.52 (m, 2H, 2-OH and 3-OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 159.81 (Ar), 139.12 (Ar), 129.53 (Ar), 119.03 (Ar), 115.29 (Ar), 112.00 (Ar), 104.02 (C-1), 101.57 (ArCH), 75.59 (C-4), 73.02 (C-3), 72.06 (C-2), 69.40 (C-6), 66.97 (C-5), 57.35 (OMe), 55.57 (OMe). HRMS *m*/*z* calcd for $C_{15}H_{20}O_7$ $(M+Na)^+$: 335.1101; found: 335.1090.

4.5. Methyl 4,6-*O*-(*p*-nitrobenzylidene)-β-D-galactopyranoside (19)

The glycoside starting material (**11**, 841 mg, 4.33 mmol) and *p*-nitrobenzaldehyde dimethyl acetal (**15**, 1.751 g, 8.88 mmol) were dissolved into dry DMF (10 mL), CSA (to pH 3) was added, and the reaction solution left mixing at 75 °C under argon. After 30 h the solution was neutralized with Et_3N (to pH 8), and evaporated to dry via co-evaporation with toluene (3 × 10 mL). The crude mixture was purified by column chromatography on silica gel using 2→2.5→3% MeOH–CH_2Cl_2 to afford the desired product **19** as a white solid (1.197 g, 3.66 mmol, 84% yield). R_f 0.38 (acetone:hexanes 7:3). $[\alpha]_D^{20}$: −18.0° (*c* 0.85, acetone). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.23–8.18 (m, 2H, Ar), 7.70–7.66 (m, 2H, Ar), 5.63 (s, 1H, ArC*H*), 4.37 (dd, 1H, *J* = 12.5, 1.5 Hz, H-6a), 4.26–4.25 (m, 1H, H-4), 4.22–4.19 (m, 1H, H-1), 4.11 (dd, 1H, *J* = 12.5, 1.9 Hz, H-6b), 3.76–3.68 (m, 2H, H-2 and H-3), 3.57 (s, 3H, OMe), 3.53–3.51 (m, 1H, H-5), 2.47–2.40 (m, 2H, 2-OH and 3-OH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 148.62 (Ar), 143.91 (Ar), 127.76 (Ar), 123.67 (Ar), 104.07 (C-1), 99.98 (ArCH), 75.66 (C-4), 72.79 (C-3), 71.91 (C-2), 69.45 (C-6), 66.78 (C-5), 57.58 (OMe). HRMS *m*/*z* calcd for $C_{14}H_{17}NO_8$ $(M+NH_4)^+$: 345.1292; found: 345.1295.

4.6. Methyl 4,6-*O*-ethylidene-β-D-galactopyranoside (20)

The glycoside starting material (**11**, 731 mg, 3.77 mmol) and acetaldehyde (0.25 mL, 4.5 mmol) were dissolved into dry MeCN (7.3 mL), *p*-toluenesulfonic acid (to pH 3) was added, and the reaction solution left mixing at room temperature under argon. After 21 h the solution was neutralized with Et_3N (to pH 7) and evaporated to dry. The crude mixture was purified by column chromatography on silica gel using 2→3→4→5% MeOH–CH_2Cl_2 to afford the desired product **20** as a white solid (628 mg, 2.85 mmol, 76% yield). R_f 0.39 (MeOH:CH_2Cl_2 7:93). $[\alpha]_D^{20}$: −24.7° (*c* 1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 4.71 (q, 1H, *J* = 5.1 Hz, CH_3CH), 4.13 (dd, 1H, *J* = 12.5, 1.5 Hz, H-6a), 4.12 (d, 1H, *J* = 7.6 Hz, H-1), 3.96 (dd, 1H, *J* = 3.8, 1.0 Hz, H-4), 3.84 (dd, 1H, *J* = 12.5, 1.9 Hz, H-6b), 3.67 (ddd, 1H, *J* = 9.7, 7.6, 2.3 Hz, H-2), 3.58 (ddd, 1H, *J* = 9.6, 8.0, 3.8 Hz, H-3), 3.52 (s, 3H, OMe), 3.33 (m, 1H, H-5), 3.10 (d, 1H, *J* = 2.4 Hz, 2-OH), 2.94 (d, 1H, *J* = 8.0 Hz, 3-OH), 1.35 (d, 3H, *J* = 5.1 Hz, CH_3CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 104.02 (C-1), 99.42 (CH_3CH), 74.97 (C-4), 72.75 (C-3), 71.70 (C-2), 68.82 (C-6), 66.80 (C-5), 57.31 (OMe), 20.96 (CH_3CH). HRMS *m*/*z* calcd for $C_9H_{16}O_6$ $(M+NH_4)^+$: 238.1285; found: 238.1288.

4.7. Methyl 4,6-*O*-(*o*-methoxybenzylidene)-2,3-di-*O*-tosyl-β-D-galactopyranoside (5)

The diol starting material (**16**, 545 mg, 1.75 mmol) and *p*-toluenesulfonyl chloride (TsCl; 1.390 g, 7.29 mmol) were dissolved into dry pyridine (5 mL) and left mixing at 45 °C for 36 h. The reaction was quenched with water (5 mL) and then concentrated and co-evaporated with toluene (2 × 20 mL). The crude product was redissolved into EtOAc (60 mL), washed with saturated $NaCl_{(aq)}$ solution (2 × 60 mL), water (60 mL), dried with Na_2SO_4, filtered, and evapo-

rated to dry. The crude mixture was purified by column chromatography on silica gel using 25→30% EtOAc–toluene to afford the desired product **5** as a white solid (996 mg, 1.60 mmol, 92% yield). R_f 0.64 (acetone:CH_2Cl_2 1:19). $[\alpha]_D^{20}$: +0.7° (*c* 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.79–7.74 (m, 2H, Ar), 7.73–7.69 (m, 2H, Ar), 7.59 (dd, 1H, *J* = 7.6, 1.7 Hz, Ar), 7.31 (ddd, 1H, *J* = 8.3, 7.5, 1.8 Hz, Ar), 7.28–7.25 (m, 2H, Ar), 7.19–7.15 (m, 2H, Ar), 6.98 (ddd, 1H, *J* = 7.5, 7.5, 0.8 Hz, Ar), 6.86 (dd, 1H, *J* = 8.3, <1 Hz, Ar), 5.66 (s, 1H, ArC*H*), 4.88 (dd, 1H, *J* = 9.9, 7.7 Hz, H-2), 4.58 (dd, 1H, *J* = 9.9, 3.7 Hz, H-3), 4.38 (dd, 1H, *J* = 3.7, <1 Hz, H-4), 4.25 (d, 1H, *J* = 7.7 Hz, H-1), 4.22 (dd, 1H, *J* = 12.5, 1.6 Hz, H-6a), 3.98 (dd, 1H, *J* = 12.5, 1.7 Hz, H-6b), 3.83 (s, 3H, OMe), 3.38–3.37 (m, 1H, H-5), 3.21 (s, 3H, OMe), 2.40 (s, 3H, Ts), 2.35 (s, 3H, Ts). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 156.73 (Ar), 145.09 (Ar), 144.56 (Ar), 134.84 (Ar), 133.56 (Ar), 130.50 (Ar), 129.77 (Ar), 129.53 (Ar), 128.45 (Ar), 128.31 (Ar), 127.87 (Ar), 125.82 (Ar), 120.97 (Ar), 110.92 (Ar), 101.66 (C-1), 96.84 (ArCH), 77.27 (C-3), 76.48 (C-2), 74.60 (C-4), 68.91 (C-6), 66.29 (C-5), 57.02 (OMe), 56.01 (OMe), 21.86 (Ts), 21.82 (Ts). HRMS *m*/*z* calcd for $C_{29}H_{32}O_{11}S_2$ $(M+NH_4)^+$: 638.1724; found: 638.1721.

4.8. Methyl 4,6-*O*-(*m*-methoxybenzylidene)-2,3-di-*O*-tosyl-β-D-galactopyranoside (6)

The diol starting material (**17**, 321 mg, 1.03 mmol) and TsCl (826 mg, 4.33 mmol) were dissolved into dry pyridine (3.5 mL) and the procedure in Section 4.7 was followed to afford the pure product **6** as a white solid (517 mg, 0.834 mmol, 81% yield). R_f 0.62 (acetone:CH_2Cl_2 1:19). $[\alpha]_D^{20}$: +17.6° (*c* 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.79–7.72 (m, 4H, Ar), 7.28–7.22 (m, 5H, Ar), 7.01–6.99 (m, 1H, Ar), 6.98–6.95 (m, 1H, Ar), 6.88 (ddd, 1H, *J* = 8.2, 2.6, 0.9 Hz, Ar), 5.30 (s, 1H, ArC*H*), 4.84 (dd, 1H, *J* = 9.9, 7.7 Hz, H-2), 4.62 (dd, 1H, *J* = 9.9, 3.7 Hz, H-3), 4.42 (dd, 1H, *J* = 3.7, 0.6 Hz, H-4), 4.27 (dd, 1H, *J* = 12.3, 1.5 Hz, H-6a), 4.24 (d, 1H, *J* = 7.7 Hz, H-1), 3.98 (dd, 1H, *J* = 12.5, 1.7 Hz, H-6b), 3.81 (s, 3H, OMe), 3.41–3.40 (m, 1H, H-5), 3.19 (s, 3H, OMe), 2.40 (s, 3H, Ts), 2.39 (s, 3H, Ts). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 159.69 (Ar), 145.29 (Ar), 144.57 (Ar), 138.71 (Ar), 134.79 (Ar), 133.60 (Ar), 129.93 (Ar), 129.53 (Ar), 129.39 (Ar), 128.48 (Ar), 128.30 (Ar), 118.88 (Ar), 115.16 (Ar), 111.87 (Ar), 101.67 (C-1), 101.08 (ArCH), 77.25 (C-3), 76.34 (C-2), 74.48 (C-4), 68.76 (C-6), 66.19 (C-5), 57.03 (OMe), 55.54 (OMe), 21.89 (Ts), 21.82 (Ts). HRMS *m*/*z* calcd for $C_{29}H_{32}O_{11}S_2$ $(M+NH_4)^+$: 638.1724; found: 638.1718.

4.9. Methyl 4,6-*O*-(*p*-methoxybenzylidene)-2,3-di-*O*-tosyl-β-D-galactopyranoside (7)

The diol starting material[15] (**18**, 919 mg, 2.94 mmol) and TsCl (2.019 g, 10.6 mmol) were dissolved into dry pyridine (20 mL) and the procedure in Section 4.7 was followed to obtain the crude product, which was subsequently purified by column chromatography on silica gel using 25% EtOAc–toluene to afford the desired product **7** as a white solid (1.643 g, 2.65 mmol, 90% yield). R_f 0.55 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: +26.0° (*c* 0.95, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.78–7.72 (m, 4H, Ar), 7.36–7.30 (m, 2H, Ar), 7.27–7.22 (m, 4H, Ar), 6.89–6.83 (m, 2H, Ar), 5.26 (s, 1H, ArC*H*), 4.84 (dd, 1H, *J* = 9.9, 7.8 Hz, H-2), 4.61 (dd, 1H, *J* = 9.9, 3.7 Hz, H-3), 4.39 (dd, 1H, *J* = 3.7, <1 Hz, H-4), 4.23 (d, 1H, *J* = 7.7 Hz, H-1), 4.25–4.21 (m, 1H, H-6a), 3.95 (dd, 1H, *J* = 12.5, 1.5 Hz, H-6b), 3.80 (s, 3H, OMe), 3.39 (m, 1H, H-5), 3.18 (s, 3H, OMe), 2.40 (s, 3H, Ts), 2.39 (s, 3H, Ts). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 160.36 (Ar), 145.23 (Ar), 144.55 (Ar), 134.81 (Ar), 133.60 (Ar), 129.90 (Ar), 129.52 (Ar), 128.44 (Ar), 128.30 (Ar), 127.81 (Ar), 113.67 (Ar), 101.62 (C-1), 101.15 (ArCH), 77.33 (C-3), 76.43 (C-2), 74.36 (C-4), 68.67 (C-6), 66.12 (C-5), 57.02 (OMe), 55.53 (OMe), 21.88 (Ts), 21.81 (Ts). HRMS *m*/*z* calcd for $C_{29}H_{32}O_{11}S_2$ $(M+NH_4)^+$: 638.1724; found: 638.1707.

4.10. Methyl 4,6-*O*-(*p*-nitrobenzylidene)-2,3-di-*O*-tosyl-β-D-galactopyranoside (8)

The diol starting material (**19**, 919 mg, 2.94 mmol) and TsCl (2.019 g, 10.6 mmol) were dissolved into dry pyridine (20 mL) and the procedure in Section 4.7 was followed to obtain the crude product, which was subsequently purified by column chromatography on silica gel using 25% EtOAc–toluene to afford the desired product **8** as a white solid (1.643 g, 2.65 mmol, 90% yield). R_f 0.31 (acetone:hexanes 3:2). $[\alpha]_D^{20}$: +14.4° (*c* 0.91, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.20–8.18 (m, 2H, Ar), 7.82–7.77 (m, 2H, Ar), 7.74–7.69 (m, 2H, Ar), 7.62–7.60 (m, 2H, Ar), 7.31–7.24 (m, 4H, Ar), 5.49 (s, 1H, ArC*H*), 4.78 (dd, 1H, *J* = 9.9, 7.7 Hz, H-2), 4.64 (dd, 1H, *J* = 9.9, 3.7 Hz, H-3), 4.56 (dd, 1H, *J* = 3.7, <1 Hz, H-4), 4.30 (dd, 1H, *J* = 12.5, <1 Hz, H-6a), 4.23 (d, 1H, *J* = 7.7 Hz, H-1), 4.04 (dd, 1H, *J* = 12.5, 1.6 Hz, H-6b), 3.48 (m, 1H, H-5), 3.11 (s, 3H, OMe), 2.40 (s, 6H, Ts). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 148.52 (Ar), 145.55 (Ar), 144.69 (Ar), 143.56 (Ar), 134.64 (Ar), 133.11 (Ar), 130.01 (Ar), 129.51 (Ar), 128.41 (Ar), 127.60 (Ar), 123.51 (Ar), 101.57 (C-1), 99.50 (ArCH), 76.94 (C-3), 76.35 (C-2), 74.73 (C-4), 68.79 (C-6), 65.97 (C-5), 57.18 (OMe), 21.91 (Ts), 21.81 (Ts). HRMS *m*/*z* calcd for $C_{28}H_{29}NO_{12}S_2$ $(M+NH_4)^+$: 653.1469; found: 653.1449.

4.11. Methyl 4,6-*O*-ethylidene-2,3-di-*O*-tosyl-β-D-galactopyranoside (9)

The diol starting material (**20**, 720 mg, 3.27 mmol) and TsCl (1.862 g, 9.77 mmol) were dissolved into dry pyridine (7.5 mL) and the procedure from Section 4.7 was followed to obtain the crude product, which was subsequently purified by column chromatography on silica gel using 30→35% EtOAc–toluene to afford the desired product **9** as a white solid (1.651 g, 3.12 mmol, 96% yield). R_f 0.62 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: +28.3° (*c* 1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.81–7.77 (m, 2H, Ar), 7.75–7.72 (m, 2H, Ar), 7.32–7.29 (m, 2H, Ar), 7.27–7.25 (m, 2H, Ar), 4.78 (dd, 1H, *J* = 10.0, 7.7 Hz, H-2), 4.52 (q, 1H, *J* = 5.1 Hz, CH_3CH), 4.52 (dd, 1H, *J* = 10.0, 3.6 Hz, H-3), 4.19 (dd, 1H, *J* = 3.7, 0.7 Hz, H-4), 4.17 (d, 1H, *J* = 7.8 Hz, H-1), 4.07 (dd, 1H, *J* = 12.5, 1.6 Hz, H-6a), 3.75 (dd, 1H, *J* = 12.5, 1.7 Hz, H-6b), 3.29 (m, 1H, H-5), 3.11 (s, 3H, OMe), 2.42 (s, 3H, Ts), 2.40 (s, 3H, Ts), 1.30 (d, 3H, *J* = 5.1 Hz, CH_3CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 145.34 (Ar), 144.57 (Ar), 134.73 (Ar), 133.40 (Ar), 129.91 (Ar), 129.49 (Ar), 128.48 (Ar), 128.44 (Ar), 101.57 (C-1), 99.45 (CH_3CH), 77.23 (C-3), 76.41 (C-2), 73.97 (C-1), 68.21 (C-6), 66.01 (C-5), 57.12 (OMe), 21.91 (Ts), 21.82 (Ts), 20.87 (CH_3CH). HRMS *m*/*z* calcd for $C_{23}H_{28}O_{10}S_2$ $(M+NH_4)^+$: 546.1462; found: 546.1452.

4.12. Methyl 2,3-di-*O*-tosyl-β-D-galactopyranoside (21)

The starting material (**2**, 838 mg, 1.42 mmol) was dissolved into a solution of trifluoroacetic acid (5.0 mL) and water (5.0 mL), and left mixing at room temperature. After 4 h, the reaction was diluted with water (50 mL), and then the product extracted with EtOAc (2 × 50 mL). The combined organic phases were neutralized with Et_3N (to pH 8), then washed with saturated $NaHCO_{3(aq)}$ solution (50 mL), saturated $NaCl_{(aq)}$ solution (50 mL), dried with Na_2SO_4, filtered, and then evaporated to dry. The crude mixture was purified by column chromatography on silica gel using 15→20% acetone–hexanes to afford the pure product **21** as a white solid (670 mg, 1.33 mmol, 94% yield). R_f 0.23 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: −4.4° (*c* 0.99, MeOH). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.83–7.80 (m, 2H, Ar), 7.72–7.69 (m, 2H, Ar), 7.34–7.31 (m, 2H, Ar), 7.27–7.24 (m, 2H, Ar), 4.73 (dd, 1H, *J* = 9.7, 7.7 Hz, H-2), 4.52 (dd, 1H, *J* = 9.8, 3.1 Hz, H-3), 4.40 (dd, 1H, *J* = 3.1, <1 Hz, H-4), 4.18 (d, 1H, *J* = 7.7 Hz, H-1), 3.91 (dd, 1H, *J* = 11.8, 5.9 Hz, H-6a), 3.82 (dd, 1H, *J* = 11.8, 4.8 Hz, H-6b), 3.51 (m, 1H, H-5), 3.08 (s, 3H, OMe),

2.43 (s, 3H, Ts), 2.40 (s, 3H, Ts). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 145.71 (Ar), 144.64 (Ar), 134.71 (Ar), 132.66 (Ar), 130.13 (Ar), 129.50 (Ar), 128.60 (Ar), 128.45 (Ar), 101.84 (C-1), 79.43 (C-3), 77.08 (C-2), 73.70 (C-5), 69.13 (C-4), 62.33 (C-6), 57.18 (OMe), 21.96 (Ts), 21.82 (Ts). HRMS *m*/*z* calcd for $C_{21}H_{26}O_{10}S_2$ $(M+Na)^+$: 525.0859; found: 525.0843.

4.13. Methyl 6-*O*-acetyl-2,3-di-*O*-tosyl-β-D-galactopyranoside (22)

Attempts at acetal hydrolysis using a combination of acetic acid/water at elevated temperatures resulted in the 6-O-acetylated by-product **22** isolated as a white solid. R_f 0.57 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: +15.8° (*c* 1.01, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.85–7.81 (m, 2H, Ar), 7.72–7.67 (m, 2H, Ar), 7.35–7.32 (m, 2H, Ar), 7.26–7.24 (m, 2H, Ar), 4.69 (dd, 1H, *J* = 9.8, 7.7 Hz, H-2), 4.53 (dd, 1H, *J* = 9.8, 3.1 Hz, H-3), 4.30 (dd, 1H, *J* = 3.1, 0.9 Hz, H-4), 4.27 (d, 2H, *J* = 6.4 Hz, H-6a and H-6b), 4.14 (d, 1H, *J* = 7.7 Hz, H-1), 3.64 (td, 1H, *J* = 6.4, 0.9 Hz, H-5), 3.05 (s, 3H, OMe), 2.43 (s, 3H, Ts), 2.40 (s, 3H, Ts), 2.04 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 170.94 (Ac), 145.74 (Ar), 144.64 (Ar), 134.64 (Ar), 132.64 (Ar), 130.12 (Ar), 129.47 (Ar), 128.59 (Ar), 128.45 (Ar), 101.59 (C-1), 79.21 (C-3), 76.93 (C-2), 71.57 (C-5), 68.16 (C-4), 62.30 (C-6), 56.97 (OMe), 21.94 (Ts), 21.80 (Ts), 20.96 (Ac). HRMS *m*/*z* calcd for $C_{23}H_{28}O_{11}S_2$ $(M+Na)^+$: 567.0965; found: 567.0947.

4.14. Methyl 6-*O*-methoxymethyl-2,3-di-*O*-tosyl-β-D-galactopyranoside (23), methyl 4,6-di-*O*-methoxymethyl-2,3-di-*O*-tosyl-β-D-galactopyranoside (24), and methyl 4,6-*O*-methylidene-2,3-di-*O*-tosyl-β-D-galactopyranoside (10)

A solution of the starting material (**21**, 406 mg, 0.805 mmol) and CSA (to pH 2) were refluxed in neat dimethoxy methane (20 mL) with a Soxhlet apparatus containing crushed molecular sieves (4 Å), in order to azeotropically distill and remove evolved MeOH from the reaction mixture. After 48 h, the reaction mixture was evaporated to dry (at 30 °C) and could be purified by column chromatography on silica gel using 15→20% EtOAc–toluene to afford a 3:1 mixture of **23** and **24** as white solids. Alternatively, the crude mixture could be redissolved into dry CH_2Cl_2 (20 mL), and further refluxed for 48 h. The reaction mixture was neutralized with Et_3N (to pH 8), diluted with CH_2Cl_2 (50 mL), washed with saturated $NaCl_{(aq)}$ solution (2 × 50 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude mixture was purified by column chromatography on silica gel using 20% EtOAc–toluene to afford the pure product **10** as a white solid (344 mg, 0.669 mmol, 83% yield). Data for **23**: R_f 0.52 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: +11.0° (c 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.85–7.80 (m, 2H, Ar), 7.73–7.68 (m, 2H, Ar), 7.34–7.31 (m, 2H, Ar), 7.26–7.23 (m, 2H, Ar), 4.72 (dd, 1H, *J* = 9.8, 7.7 Hz, H-2), 4.60 (s, 2H, CH_3OCH_2), 4.53 (dd, 1H, *J* = 9.8, 3.1 Hz, H-3), 4.40–4.39 (m, 1H, H-4), 4.16 (d, 1H, *J* = 7.7 Hz, H-1), 3.77 (dd, 1H, *J* = 10.5, 6.1 Hz, H-6a), 3.75 (dd, 1H, *J* = 10.5, 5.7 Hz, H-6b), 3.59 (ddd, 1H, *J* = 6.0, 5.7, <1 Hz, H-5), 3.33 (s, 3H, OMe), 3.06 (s, 3H, OMe), 2.66 (d, 1H, J = 3.2 Hz, 4-OH), 2.43 (s, 3H, Ts), 2.40 (s, 3H, Ts). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 145.63 (Ar), 144.58 (Ar), 134.74 (Ar), 132.80 (Ar), 130.09 (Ar), 129.46 (Ar), 128.59 (Ar), 128.47 (Ar), 101.73 (C-1), 97.15 (CH_3OCH_2), 79.48 (C-3), 77.15 (C-2), 72.74 (C-5), 68.66 (C-4), 66.53 (C-6), 56.98 (OMe), 55.69 (OMe), 21.95 (Ts), 21.81 (Ts). HRMS *m*/*z* calcd for $C_{23}H_{30}O_{11}S_2$ $(M+Na)^+$: 569.1122; found: 569.1097. Data for **24**: R_f 0.56 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: +0.6° (c 1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.86–7.82 (m, 2H, Ar), 7.73–7.69 (m, 2H, Ar), 7.34–7.31 (m, 2H, Ar), 7.27–7.25 (m, 2H, Ar), 4.87 (d, 1H, *J* = 6.7 Hz, $CH_3OCHaHb$), 4.71 (d, 1H, *J* = 6.6 Hz, $CH_3OCHaHb$), 4.69 (dd, 1H, *J* = 10.1, 7.6 Hz, H-2), 4.60 (s, 2H, CH_3OCH_2), 4.49 (dd, 1H, *J* = 10.1, 2.9 Hz, H-3), 4.30 (dd, 1H, *J* = 2.8, <1 Hz, H-4), 4.12 (d, 1H, *J* = 7.6 Hz, H-1), 3.70 (dd, 1H, *J* = 10.3, 6.6 Hz, H-6a), 3.66 (d, 1H, *J* = 10.3, 5.7 Hz, H-6b), 3.60–3.57 (m, 1H, H-5), 3.36 (s, 3H, OMe), 3.33 (s, 3H, OMe), 3.00 (s, 3H, OMe), 2.43 (s, 3H, Ts), 2.40 (s, 3H, Ts). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 145.49 (Ar), 144.53 (Ar), 134.81 (Ar), 132.70 (Ar), 130.02 (Ar), 129.41 (Ar), 128.79 (Ar), 128.54 (Ar), 101.66 (C-1), 98.50 (CH_3OCH_2), 97.20 (CH_3OCH_2), 78.18 (C-3), 77.42 (C-2), 74.69 (C-4), 73.33 (C-5), 66.56 (C-6), 56.93 (OMe), 56.72 (OMe), 55.69 (OMe), 21.95 (Ts), 21.80 (Ts). HRMS *m*/*z* calcd for $C_{25}H_{34}O_{12}S_2$ $(M+NH_4)^+$: 608.1830; found: 608.1817. Data for **10**: R_f 0.46 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: +17.4° (*c* 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.83–7.78 (m, 2H, Ar), 7.74–7.69 (m, 2H, Ar), 7.32–7.29 (m, 2H, Ar), 7.27–7.24 (m, 2H, Ar), 5.08 (d, 1H, *J* = 6.4 Hz, C*Ha*Hb), 4.77 (dd, 1H, *J* = 10.0, 7.7 Hz, H-2), 4.59 (d, 1H, *J* = 6.5 Hz, CHa*Hb*), 4.55 (dd, 1H, *J* = 10.0, 3.6 Hz, H-3), 4.23 (dd, 1H, *J* = 3.6, <1 Hz, H-4), 4.20 (d, 1H, *J* = 7.7 Hz, H-1), 4.09 (dd, 1H, *J* = 12.4, <1 Hz, H-6a), 3.74 (dd, 1H, *J* = 12.4, 1.6 Hz, H-6b), 3.39–3.38 (m, 1H, H-5), 3.09 (s, 3H, OMe), 2.42 (s, 3H, Ts), 2.39 (s, 3H, Ts). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 145.45 (Ar), 144.57 (Ar), 134.66 (Ar), 133.09 (Ar), 129.95 (Ar), 129.45 (Ar), 128.52 (Ar), 101.44 (C-1), 93.43 (CH_2), 76.90 (C-3), 76.33 (C-2), 74.15 (C-4), 68.13 (C-6), 66.80 (C-5), 56.95 (OMe), 21.91 (Ts), 21.79 (Ts). HRMS *m*/*z* calcd for $C_{22}H_{26}O_{10}S_2$ $(M+NH_4)^+$: 532.1306; found: 532.1286.

4.15. Methyl 4,6-*O*-(*o*-methoxybenzylidene)-3-*O*-methyl-β-D-idopyranoside (26)

A solution of KOBu-*t* in MeOH (2.27 M, 0.75 mL, 1.70 mmol) was added to a solution of the di-tosylate starting material (**5**, 211 mg, 0.340 mmol) in 1,4-dioxane (3.3 mL). After 3 days the reaction mixture was evaporated to dry, redissolved into EtOAc (30 mL), washed with saturated $NaCl_{(aq)}$ solution (2 × 30 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude mixture was purified by column chromatography on silica gel using 30% acetone–hexanes to afford the pure product **26** as a yellow solid (83 mg, 0.25 mmol, 75% yield). R_f 0.30 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: −62.7° (*c* 1.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.48 (dd, 1H, *J* = 7.6, 1.7 Hz, Ar), 7.29 (ddd, 1H, *J* = 8.3, 7.5, 1.7 Hz, Ar), 6.92 (ddd, 1H, *J* = 7.5, 7.5, 0.9 Hz, Ar), 6.85 (dd, 1H, *J* = 8.3, <1 Hz, Ar), 5.78 (s, 1H, ArC*H*), 4.59 (d, 1H, *J* = <1 Hz, H-1), 4.36 (dd, 1H, *J* = 12.5, 1.5 Hz, H-6a), 4.05 (dd, 1H, *J* = 12.5, 1.8 Hz, H-6b), 3.98 (ddd, 1H, *J* = 2.7, 1.1, 1.1 Hz, H-4), 3.82 (s, 3H, OMe), 3.72 (dddd, 1H, *J* = 11.8, 3.2, 1.0, 1.0 Hz, H-2), 3.66–3.64 (m, 1H, H-5), 3.60 (dd, 1H, *J* = 2.9, 2.9 Hz, H-3), 3.58 (s, 3H, OMe), 3.46 (d, 1H, *J* = 11.8 Hz, 2-OH), 3.43 (s, 3H, OMe). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 156.86 (Ar), 130.74 (Ar), 128.11 (Ar), 125.69 (Ar), 120.91 (Ar), 111.15 (Ar), 100.44 (C-1), 98.54 (ArCH), 78.93 (C-3), 73.45 (C-4), 70.06 (C-6), 66.96 (C-5), 66.91 (C-2), 58.45 (OMe), 57.19 (OMe), 55.83 (OMe). HRMS *m*/*z* calcd for $C_{16}H_{22}O_7$ $(M+Na)^+$: 349.1258; found: 349.1255.

4.16. Methyl 4,6-*O*-(*m*-methoxybenzylidene)-3-*O*-methyl-β-D-idopyranoside (27)

A solution of KOBu-*t* in MeOH (2.39 M, 0.70 mL, 1.67 mmol) was added to a solution of the di-tosylate starting material (**6**, 210 mg, 0.339 mmol) in 1,4-dioxane (3.3 mL), and the procedure in Section 4.15 was followed to obtain the pure product **27** as a white solid (86 mg, 0.26 mmol, 78% yield). R_f 0.38 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: −51.3° (*c* 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.27–7.21 (m, 1H, Ar), 7.05–7.03 (m, 1H, Ar), 7.01–6.98 (m, 1H, Ar), 6.86 (ddd, 1H, *J* = 8.2, 2.6, 0.8 Hz, Ar), 5.47 (s, 1H, ArC*H*), 4.59 (d, 1H, *J* = <1 Hz, H-1), 4.39 (dd, 1H, *J* = 12.5, 1.3 Hz, H-6a), 4.07 (dd, 1H, *J* = 12.5, 1.8 Hz, H-6b), 4.00 (ddd, 1H, *J* = 2.7, <1, <1 Hz, H-4), 3.78 (s, 3H, OMe), 3.74 (dddd, 1H, *J* = 11.8, 3.1, <1, <1 Hz, H-

2), 3.69–3.68 (m, 1H, H-5), 3.66 (dd, 1H, J = 2.9, 2.9 Hz, H-3), 3.58 (s, 3H, OMe), 3.46 (s, 3H, OMe), 3.14 (d, 1H, J = 11.8 Hz, 2-OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 159.80 (Ar), 138.89 (Ar), 129.60 (Ar), 118.66 (Ar), 115.53 (Ar), 111.30 (Ar), 101.63 (ArCH), 100.47 (C-1), 78.83 (C-3), 73.50 (C-4), 69.91 (C-6), 66.92 (C-5), 66.84 (C-2), 58.58 (OMe), 57.28 (OMe), 55.54 (OMe). HRMS m/z calcd for $C_{16}H_{22}O_7$ $(M+NH_4)^+$: 344.1704; found: 344.1702.

4.17. Methyl 4,6-*O*-(*p*-methoxybenzylidene)-3-*O*-methyl-β-D-idopyranoside (28)

A solution of KOBu-*t* in MeOH (2.59 M, 0.65 mL, 1.69 mmol) was added to a solution of the di-tosylate starting material (**7**, 210 mg, 0.338 mmol) in 1,4-dioxane (2.3 mL), and the procedure in Section 4.15 was followed to obtain the pure product **28** as a yellow syrup (88 mg, 0.27 mmol, 79% yield). R_f 0.40 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: −49.6° (c 0.98, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.41–7.35 (m, 2H, Ar), 6.87–6.82 (m, 2H, Ar), 5.45 (s, 1H, ArC*H*), 4.58 (d, 1H, J = 1.0 Hz, H-1), 4.36 (dd, 1H, J = 12.5, 1.5 Hz, H-6a), 4.05 (dd, 1H, J = 12.5, 1.9 Hz, H-6b), 3.98 (ddd, 1H, J = 2.8, 1.2, 1.2 Hz, H-4), 3.78 (s, 3H, OMe), 3.73 (dddd, 1H, J = 11.7, 3.1, 1.1, 1.1 Hz, H-2), 3.67–3.66 (m, 1H, H-5), 3.64 (dd, 1H, J = 2.9, 2.9 Hz, H-3), 3.58 (s, 3H, OMe), 3.45 (s, 3H, OMe), 3.16 (d, 1H, J = 11.7 Hz, 2-OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 160.44 (Ar), 130.05 (Ar), 127.63 (Ar), 113.85 (Ar), 101.73 (ArCH), 100.48 (C-1), 78.86 (C-3), 73.44 (C-4), 69.86 (C-6), 66.89 (C-5), 66.87 (C-2), 58.55 (OMe), 57.26 (OMe), 55.51 (OMe). HRMS m/z calcd for $C_{16}H_{22}O_7$ $(M+H)^+$: 327.1438; found: 327.1432.

4.18. Methyl 3-*O*-methyl-4,6-*O*-(*p*-nitrobenzylidene)-β-D-idopyranoside (29)

A solution of KOBu-*t* in MeOH (2.02 M, 0.90 mL, 1.82 mmol) was added to a solution of the di-tosylate starting material (**8**, 234 mg, 0.368 mmol) in 1,4-dioxane (3.7 mL), and the procedure in Section 4.15 was followed to obtain the pure product **29** as a yellow solid (92 mg, 0.27 mmol, 73% yield). R_f 0.36 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: −45.8° (c 1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.22–8.17 (m, 2H, Ar), 7.68–7.63 (m, 2H, Ar), 5.58 (s, 1H, ArC*H*), 4.60 (d, 1H, J = 1.1 Hz, H-1), 4.42 (dd, 1H, J = 12.5, 1.4 Hz, H-6a), 4.11 (dd, 1H, J = 12.5, 1.9 Hz, H-6b), 4.03 (ddd, 1H, J = 2.8, 1.2, 1.2 Hz, H-4), 3.75 (dddd, 1H, J = 11.4, 3.1, 1.1, 1.1 Hz, H-2), 3.73–3.71 (m, 1H, H-5), 3.68 (dd, 1H, J = 2.9, 2.9 Hz, H-3), 3.58 (s, 3H, OMe), 3.48 (s, 3H, OMe), 2.90 (d, 1H, J = 11.4 Hz, 2-OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 148.54 (Ar), 143.81 (Ar), 127.39 (Ar), 123.66 (Ar), 100.45 (C-1), 99.85 (ArCH), 78.76 (C-3), 73.56 (C-4), 69.92 (C-6), 66.76 (C-2 and C-5), 58.64 (OMe), 57.28 (OMe). HRMS m/z calcd for $C_{15}H_{19}NO_8$ $(M+NH_4)^+$: 359.1449; found: 359.1446.

4.19. Methyl 4,6-*O*-ethylidene-3-*O*-methyl-β-D-idopyranoside (30)

A solution of KOBu-*t* in MeOH (2.0 M, 4.5 mL, 8.9 mmol) was added to a solution of the di-tosylate starting material (**9**, 947 mg, 1.79 mmol) in 1,4-dioxane (15 mL), and the procedure in Section 4.15 was followed to obtain the crude product, which was subsequently purified by column chromatography on silica gel using 20→25% acetone–hexanes to afford the pure product **30** as a white solid (331 mg, 1.41 mmol, 79% yield). R_f 0.19 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: −104° (c 1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 4.66 (q, 1H, J = 5.1 Hz, C*H*CH_3), 4.52 (d, 1H, J = <1 Hz, H-1), 4.17 (dd, 1H, J = 12.5, 1.4 Hz, H-6a), 3.83 (dd, 1H, J = 12.6, 1.9 Hz, H-6b), 3.75 (ddd, 1H, J = 2.8, 1.1, <1 Hz, H-4), 3.68 (dddd, 1H, J = 11.7, 3.1, 1.1, <1 Hz, H-2), 3.56–3.52 (m, 5H, H-5, OMe, and H-3), 3.41 (s, 3H, OMe), 3.16 (d, 1H, J = 11.7 Hz, 2-OH), 1.32 (d, 3H, J = 5.1 Hz, CHC*H*$_3$). ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 100.37 (C-1), 99.60 (*C*HCH$_3$), 78.68 (C-3), 72.82 (C-4), 69.26 (C-6), 66.84 (C-2), 66.68 (C-5), 58.44 (OMe), 57.16 (OMe), 21.16 (CH*C*H$_3$). HRMS m/z calcd for $C_{10}H_{18}O_6$ $(M+NH_4)^+$: 252.1442; found: 252.1441.

4.20. Methyl 3-*O*-methyl-4,6-*O*-methylidene-β-D-idopyranoside (31) and methyl 2-*O*-acetyl-3-*O*-methyl-4,6-*O*-methylidene-β-D-idopyranoside (32)

A solution of KOBu-*t* in MeOH (2.63 M, 0.70 mL, 1.8 mmol) was added to a solution of the di-tosylate starting material (**10**, 185 mg, 0.360 mmol) in 1,4-dioxane (2.7 mL). After 3 days the reaction mixture was concentrated, and then redissolved into dry pyridine (1.50 mL) and acetic anhydride (Ac_2O; 1.50 mL) and left heating at 65 °C. After 2 h the reaction mixture was evaporated to dry via co-evaporation with toluene (2 × 3 mL), then redissolved into EtOAc (30 mL), washed with saturated $NaCl_{(aq)}$ solution (2 × 30 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude mixture was purified by column chromatography on silica gel using 20→30% acetone–hexanes to afford the pure product **32** as a white solid (79 mg, 0.30 mmol, 84% yield). R_f 0.58 (acetone:hexanes 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 5.06 (d, 1H, J = 6.2 Hz, C*Ha*Hb), 4.88 (ddd, 1H, J = 2.9, 1.5, <1 Hz, H-2), 4.67 (d, 1H, J = 6.2 Hz, CHa*Hb*), 4.65 (d, 1H, J = 1.5 Hz, H-1), 4.23–4.20 (m, 1H, H-6a), 3.83 (dd, 1H, J = 12.4, 2.1 Hz, H-6b), 3.65–3.64 (m, 1H, H-4), 3.61–3.60 (m, 1H, H-5), 3.58 (dd, 1H, J = 2.8, 2.8 Hz, H-3), 3.51 (s, 3H, OMe), 3.48 (s, 3H, OMe), 2.11 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 171.25 (Ac), 98.68 (C-1), 93.38 (CH_2), 76.95 (C-3), 71.92 (C-4), 69.03 (C-6), 67.65 (C-5), 66.73 (C-2), 58.80 (OMe), 56.94 (OMe), 21.39 (Ac). HRMS m/z calcd for $C_{11}H_{18}O_7$ $(M+Na)^+$: 285.0945; found: 285.0944. An initial attempt at isolating the *ido*-pyranoside product prior to acetylation afforded **31** as a white solid but in a significantly lower yield (~30%). R_f 0.41 (acetone:hexanes 1:1). $[\alpha]_D^{20}$: −80.8° (c 1.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 5.08 (d, 1H, J = 6.3 Hz, C*Ha*Hb), 4.66 (d, 1H, J = 6.3 Hz, CHa*Hb*), 4.55 (d, 1H, J = <1 Hz, H-1), 4.21–4.17 (m, 1H, H-6a), 3.81 (dd, 1H, J = 12.5, 1.8 Hz, H-6b), 3.73–3.69 (m, 2H, H-4 and H-2), 3.62–3.60 (m, 1H, H-5), 3.57–3.55 (m, 4H, H-3 and OMe), 3.42 (s, 3H, OMe), 3.09 (d, 1H, J = 11.2 Hz, 2-OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 100.38 (C-1), 93.75 (CH_2), 78.66 (C-3), 72.78 (C-4), 69.28 (C-6), 67.62 (C-5), 66.86 (C-2), 58.52 (OMe), 57.08 (OMe). HRMS m/z calcd for $C_9H_{16}O_6$ $(M+Na)^+$: 243.0839; found: 243.0836.

4.21. General procedure for studying the di-inversion reaction rate

A solution of KOBu-*t* in MeOH (2.3 M, 1.0 mmol) was added to a solution of the di-tosylate starting material (**2**, **7**, or **8**, 0.20 mmol) in 1,4-dioxane (2.0 mL). The reaction progress was monitored over time by removing an aliquot, which was extracted with EtOAc (1 mL) in water (1 mL), evaporated to dry, and analyzed by ^{1}H NMR to quantify the reaction progression.

4.22. Methyl 4-*O*-benzyl-β-D-galactopyranoside (34)

A NaOMe solution was added dropwise (1.5 M NaOMe/MeOH, to pH 10) to a solution of the starting material (**33**, 246 mg, 0.668 mmol) in dry MeOH (3.0 mL) and left mixing at room temperature for 2 h. The reaction was then neutralized to pH 6 using ion exchange resin (Amberlite IR-120H), filtered, and evaporated to dry to obtain the product **34** as a white solid (190 mg, 0.667 mmol, quantitative yield). R_f 0.54 (MeOH:CH_2Cl_2 1:9). $[\alpha]_D^{20}$: −29.1° (c 1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.37–7.26 (m, 5H, Ar), 4.78 (d, 1H, J = 11.7 Hz, PhC*Ha*Hb), 4.71 (d, 1H, J = 11.7 Hz, PhCHa*Hb*), 4.14 (d, 1H, J = 7.3 Hz, H-1), 3.83 (m, 1H,

H-6a), 3.78 (dd, 1H, J = 3.1, 1.1 Hz, H-4), 3.71–3.57 (m, 3H, H-2, H-3, and H-6b), 3.53 (s, 3H, OMe), 3.51 (ddd, 1H, J = 6.9, 5.4, 1.1 Hz, H-5), 2.61 (broad, 1H, 2-OH), 2.46 (d, 1H, J = 5.7 Hz, 3-OH), 1.68 (broad, 6-OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 138.14 (Ar), 128.83 (Ar), 128.60 (Ar), 128.37 (Ar), 104.26 (C-1), 75.57 (C-4), 75.38 (C-5), 75.28 ($PhCH_2$), 74.56 (C-3), 72.70 (C-2), 62.16 (C-6), 57.36 (OMe). HRMS m/z calcd for $C_{14}H_{20}O_6$ $(M+Na)^+$: 307.1152; found: 307.1154.

4.23. Methyl 3,6-anhydro-4-*O*-benzyl-2-*O*-tosyl-β-D-galactopyranoside (37)

The starting material (**34**, 133 mg, 0.467 mmol) and TsCl (539 mg, 2.83 mmol) were dissolved into dry pyridine (1.50 mL) and the procedure in Section 4.7 was followed to obtain the crude product, which was subsequently purified by column chromatography on silica gel using 10% acetone–hexanes to afford the desired product **37** as a white solid (160 mg, 0.381 mmol, 82% yield). R_f 0.73 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: −38.7° (c 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.78–7.73 (m, 2H, Ar), 7.36–7.26 (m, 7H, Ar), 4.56 (d, 1H, J = 11.8 Hz, PhC*Ha*Hb), 4.54 (dd, 1H, J = 4.9, <1 Hz, H-2), 4.48 (d, 1H, J = 11.8 Hz, PhCHa*Hb*), 4.42 (d, 1H, J = <1 Hz, H-1), 4.27–4.24 (m, 1H, H-5), 4.22 (dd, 1H, J = 4.9, <1 Hz, H-3), 4.10 (dd, 1H, J = 9.5, <1 Hz, H-6a), 4.10 (dd, 1H, J = 1.7, <1 Hz, H-4), 3.90 (dd, 1H, J = 9.5, 3.1 Hz, H-6b), 3.26 (s, 3H, OMe), 2.44 (s, 3H, Ts). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 145.73 (Ar), 137.66 (Ar), 133.09 (Ar), 130.33 (Ar), 128.76 (Ar), 128.25 (Ar), 128.23 (Ar), 128.00 (Ar), 100.49 (C-1), 79.22 (C-2), 77.77 (C-4), 76.51 (C-3), 75.99 (C-5), 71.48 ($PhCH_2$), 71.21 (C-6), 56.24 (OMe), 21.89 (Ts). HRMS m/z calcd for $C_{21}H_{24}O_7S$ $(M+NH_4)^+$: 438.1581; found: 438.1582.

4.24. Methyl 6-*O*-methyl-2,3-di-*O*-tosyl-β-D-galactopyranoside (38)

A solution of the starting material (**21**, 406 mg, 0.807 mmol) and 2,6-di-*tert*-butylpyridine (0.53 mL, 2.5 mmol) in dry CH_2Cl_2 (5.0 mL) was cooled to 0 °C under argon, then methyl triflate (0.24 mL, 2.2 mmol) was added dropwise and the mixture warmed back up to room temperature. After 8 h, the flask was cooled back to 0 °C and second aliquots of 2,6-di-*tert*-butylpyridine (0.53 mL, 2.5 mmol) and methyl triflate (0.24 mL, 2.2 mmol) were added and the reaction mixture warmed back to room temperature. After another 12 h, the reaction was quenched with water (50 mL) and the product extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with saturated $NaHCO_{3(aq)}$ solution (50 mL), saturated $NaCl_{(aq)}$ solution (50 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude mixture was purified by column chromatography on silica gel using 20% acetone–hexanes to afford the pure product **38** as a white solid (399 mg, 0.772 mmol, 96% yield). R_f 0.47 (acetone:hexanes 1:1). $[\alpha]_D^{20}$: +6.3° (c 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.84–7.79 (m, 2H, Ar), 7.71–7.68 (m, 2H, Ar), 7.34–7.30 (m, 2H, Ar), 7.27–7.22 (m, 2H, Ar), 4.72 (dd, 1H, J = 9.7, 7.7 Hz, H-2), 4.51 (dd, 1H, J = 9.7, 3.1 Hz, H-3), 4.38–4.36 (m, 1H, H-4), 4.15 (d, 1H, J = 7.7 Hz, H-1), 3.65 (dd, 1H, J = 10.0, 5.2 Hz, H-6a), 3.60 (dd, 1H, J = 10.0, 5.3 Hz, H-6b), 3.56–3.53 (m, 1H, H-5), 3.35 (s, 3H, OMe), 3.06 (s, 3H, OMe), 2.83 (d, 1H, J = 3.6 Hz, 4-OH), 2.42 (s, 3H, Ts), 2.39 (s, 3H, Ts). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 145.56 (Ar), 144.54 (Ar), 134.75 (Ar), 132.80 (Ar), 130.06 (Ar), 129.44 (Ar), 128.58 (Ar), 128.45 (Ar), 101.73 (C-1), 79.42 (C-3), 77.17 (C-2), 72.74 (C-5), 71.66 (C-6), 68.98 (C-4), 59.72 (OMe), 57.03 (OMe), 21.93 (Ts), 21.80 (Ts). HRMS m/z calcd for $C_{22}H_{28}O_{10}S_2$ $(M+Na)^+$: 539.1016; found: 539.1001.

4.25. Methyl 4,6-di-*O*-acetyl-2,3-anhydro-β-D-talopyranoside (39), methyl 4,6-di-*O*-acetyl-2,3-di-*O*-tosyl-β-D-galactopyranoside (41), and methyl 2,4,6-tri-*O*-acetyl-3-*O*-methyl-β-D-idopyranoside (43)

A solution of KOBu-*t* in MeOH (2.3 M, 1.00 mL, 2.3 mmol) was added to a solution of the di-tosylate starting material (**21**, 225 mg, 0.447 mmol) in 1,4-dioxane (4.0 mL). After 4 days the reaction mixture was diluted with Ac_2O (3.0 mL) and dry pyridine (3.0 mL) and then left heating at 65 °C. After 2 h the reaction mixture was evaporated to dry via co-evaporation with toluene (3 × 5 mL), redissolved into EtOAc (50 mL), washed with saturated $NaCl_{(aq)}$ solution (2 × 50 mL), and then the combined aqueous phases extracted with EtOAc (2 × 50 mL). The combined organic layers were then dried with Na_2SO_4, filtered, and evaporated to dry. The crude mixture was purified by column chromatography on silica gel using 10→15→20% EtOAc–toluene to afford acetylated starting material **41** as a white solid (101 mg, 0.171 mmol, 38% yield), the idopyranoside product **43** as a colorless syrup (9 mg, 0.03 mmol, 6% yield), and then the acetylated talopyranoside intermediate **39** as a white solid (48 mg, 0.18 mmol, 41% yield). Data for **41**: R_f 0.65 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: +2.4° (c 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.80–7.72 (m, 4H, Ar), 7.32–7.27 (m, 4H, Ar), 5.55 (dd, 1H, J = 2.9, 0.9 Hz, H-4), 4.70–4.62 (m, 2H, H-2 and H-3), 4.21 (d, 1H, J = 7.5 Hz, H-1), 4.06 (dd, 1H, J = 11.5, 6.6 Hz, H-6a), 4.03 (dd, 1H, J = 11.5, 6.4 Hz, H-6b), 3.77 (ddd, 1H, J = 6.5, 6.5, 0.9 Hz, H-5), 3.11 (s, 3H, Me), 2.43 (s, 3H, Ts), 2.42 (s, 3H, Ts), 2.09 (s, 3H, Ac), 2.02 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 170.55 (Ac), 169.48 (Ac), 145.59 (Ar), 144.73 (Ar), 134.69 (Ar), 132.79 (Ar), 130.04 (Ar), 129.54 (Ar), 128.66 (Ar), 128.49 (Ar), 101.84 (C-1), 76.84 (C-2), 75.85 (C-3), 71.02 (C-5), 68.37 (C-4), 61.57 (C-6), 57.33 (Me), 21.96 (Ts), 21.85 (Ts), 20.86 (Ac), 20.74 (Ac). HRMS m/z calcd for $C_{25}H_{30}O_{12}S_2$ $(M+Na)^+$: 609.1071; found: 609.1047. Data for **43**: R_f 0.55 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: −48.2° (c 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 4.94 (ddd, 1H, J = 3.3, 1.7, <1 Hz, H-2), 4.79 (ddd, 1H, J = 3.0, 2.0, <1 Hz, H-4), 4.69 (d, 1H, J = 1.7 Hz, H-1), 4.25 (dd, 1H, J = 11.2, 7.2 Hz, H-6a), 4.21 (dd, 1H, J = 11.2, 5.8 Hz, H-6b), 4.15 (ddd, 1H, J = 7.1, 5.9, 1.9 Hz, H-5), 3.60 (dd, 1H, J = 3.3, 3.3 Hz, H-3), 3.52 (s, 3H, OMe), 3.49 (s, 3H, OMe), 2.09 (s, 3H, Ac), 2.06 (s, 3H, Ac), 2.04 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 170.76 (Ac), 170.38 (Ac), 170.31 (Ac), 98.92 (C-1), 75.71 (C-3), 70.89 (C-5), 67.35 (C-2), 66.52 (C-4), 62.56 (C-6), 59.06 (OMe), 57.35 (OMe), 21.17 (Ac), 21.00 (Ac), 20.94 (Ac). HRMS m/z calcd for $C_{14}H_{22}O_9$ $(M+Na)^+$: 357.1156; found: 357.1151. Data for **39**: R_f 0.51 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: −79.0° (c 0.96, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 4.98 (dd, 1H, J = 4.3, 3.9 Hz, H-4), 4.77 (d, 1H, J = <1, H-1), 4.27 (dd, 1H, J = 11.6, 7.2 Hz, H-6a), 4.21 (dd, 1H, J = 11.6, 5.6 Hz, H-6b), 3.80 (ddd, 1H, J = 7.2, 5.6, 3.8 Hz, H-5), 3.64 (dd, 1H, J = 4.3, 4.0 Hz, H-3), 3.56 (s, 3H, OMe), 3.28 (dd, 1H, J = 3.9, <1 Hz, H-2), 2.14 (s, 3H, Ac), 2.04 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 170.83 (Ac), 170.80 (Ac), 98.72 (C-1), 72.70 (C-5), 64.62 (C-4), 62.22 (C-6), 57.01 (OMe), 51.41 (C-2), 51.24 (C-3), 20.96 (Ac), 20.87 (Ac). HRMS m/z calcd for $C_{11}H_{16}O_7$ $(M+Na)^+$: 283.0788; found: 283.0782.

4.26. Methyl 4-*O*-acetyl-2,3-anhydro-6-*O*-methyl-β-D-talopyranoside (40), methyl 4-*O*-acetyl-6-*O*-methyl-2,3-di-*O*-tosyl-β-D-galactopyranoside (42), and methyl 2,4-di-*O*-acetyl-3,6-di-*O*-methyl-β-D-idopyranoside (44)

A solution of KOBu-*t* in MeOH (2.3 M, 0.60 mL, 1.4 mmol) was added to a solution of the di-tosylate starting material (**38**, 143 mg, 0.277 mmol) in 1,4-dioxane (2.1 mL). After 3 days the reaction mixture was quenched with Ac_2O (1 mL), concentrated, and then redissolved into dry pyridine (1.50 mL) and additional Ac_2O

(1.00 mL) and left heating at 65 °C. After 2 h the reaction mixture was evaporated to dry via co-evaporation with toluene (3 × 3 mL), redissolved into EtOAc (30 mL), washed with saturated $NaCl_{(aq)}$ solution (2 × 30 mL), and then the combined aqueous phases extracted with EtOAc (2 × 30 mL). The combined organic layers were then dried with Na_2SO_4, filtered, and evaporated to dry. The crude mixture was purified by column chromatography on silica gel using 20→25→30% acetone–hexanes to afford acetylated starting material **42** as a white solid (64 mg, 0.11 mmol, 41% yield), the idopyranoside product **44** as a colorless syrup (10 mg, 0.033 mmol, 12% yield), and then the acetylated talopyranoside intermediate **40** as a white solid (25 mg, 0.11 mmol, 38% yield). Data for **42**: R_f 0.46 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: +5.4° (*c* 1.00, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ_H 7.81–7.71 (m, 4H, Ar), 7.34–7.25 (m, 4H, Ar), 5.54 (dd, 1H, *J* = 3.3, <1 Hz, H-4), 4.68 (dd, 1H, *J* = 9.9, 7.5 Hz, H-2), 4.61 (dd, 1H, *J* = 9.9, 3.3 Hz, H-3), 4.19 (d, 1H, *J* = 7.5 Hz, H-1), 3.65 (ddd, 1H, *J* = 6.3, 5.0, <1 Hz, H-5), 3.40 (dd, 1H, *J* = 10.3, 5.0 Hz, H-6a), 3.39 (dd, 1H, *J* = 10.3, 6.3 Hz, H-6b), 3.28 (s, 3H, OMe), 3.11 (s, 3H, OMe), 2.43 (s, 3H, Ts), 2.41 (s, 3H, Ts), 2.09 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 169.65 (Ac), 145.52 (Ar), 144.67 (Ar), 134.71 (Ar), 132.83 (Ar), 130.02 (Ar), 129.51 (Ar), 128.62 (Ar), 128.49 (Ar), 101.87 (C-1), 77.08 (C-2), 76.14 (C-3), 72.80 (C-5), 71.06 (C-6), 69.15 (C-4), 59.66 (OMe), 57.41 (OMe), 21.96 (Ts), 21.85 (Ts), 20.81 (Ac). HRMS *m*/*z* calcd for $C_{24}H_{30}O_{11}S_2$ $(M+Na)^+$: 581.1122; found: 581.1115. Data for **44**: R_f 0.33 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: −45.0° (*c* 1.01, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ_H 4.93–4.92 (m, 1H, H-2), 4.81–4.80 (m, 1H, H-4), 4.67 (d, 1H, *J* = 1.7 Hz, H-1), 4.08 (ddd, 1H, *J* = 6.1, 6.1, 2.0 Hz, H-5), 3.58 (dd, 1H, *J* = 3.3, 3.3 Hz, H-3), 3.57 (dd, 1H, *J* = 10.1, 6.3 Hz, H-6a), 3.52 (dd, 1H, *J* = 10.1, 6.0 Hz, H-6b), 3.52 (s, 3H, Me), 3.48 (s, 3H, Me), 3.34 (s, 3H, Me), 2.09 (s, 3H, Ac), 2.05 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 170.40 (Ac), 170.34 (Ac), 98.89 (C-1), 75.79 (C-3), 72.18 (C-5), 71.32 (C-6), 67.51 (C-2), 66.78 (C-4), 59.51 (Me), 58.91 (Me), 57.33 (Me), 21.20 (Ac), 21.00 (Ac). HRMS *m*/*z* calcd for $C_{13}H_{22}O_8$ $(M+Na)^+$: 329.1207; found: 329.1198. Data for **40**: R_f 0.24 (EtOAc:toluene 1:1). $[\alpha]_D^{20}$: −119.9° (*c* 1.03, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ_H 4.93 (dd, 1H, *J* = 4.7, 3.5 Hz, H-4), 4.75 (d, 1H, *J* = <1 Hz, H-1), 3.69 (ddd, 1H, *J* = 6.3, 5.9, 3.5 Hz, H-5), 3.64 (dd, 1H, *J* = 4.7, 3.9 Hz, H-3), 3.56 (s, 3H, OMe), 3.55 (dd, 1H, *J* = 10.2, 6.4 Hz, H-6a), 3.51 (dd, 1H, *J* = 10.2, 5.8 Hz, H-6b), 3.33 (s, 3H, OMe), 3.24 (dd, 1H, *J* = 3.9, <1 Hz, H-2), 2.13 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 170.86 (Ac), 98.99 (C-1), 74.38 (C-5), 70.57 (C-6), 64.84 (C-4), 59.62 (OMe), 57.09 (OMe), 51.41 and 51.35 (C-2 and C-3), 20.85 (Ac). HRMS *m*/*z* calcd for $C_{10}H_{16}O_6$ $(M+Na)^+$: 255.0839; found: 255.0841.

4.27. Methyl 4-*O*-methoxymethyl-6-*O*-methyl-2,3-di-*O*-tosyl-β-D-galactopyranoside (45)

A solution of the starting material (**38**, 309 mg, 0.598 mmol) and CSA (to pH 3) in neat dimethoxymethane (10 mL) was left mixing at reflux with a Soxhlet apparatus containing crushed molecular sieves (4 Å). After 7 days, the reaction mixture was neutralized with Et_3N (to pH 8), evaporated to dry, and then purified by column chromatography on silica gel using 15→20% acetone–hexanes to afford both the desired product **45** as a white solid (121 mg, 0.216 mmol, 36% yield) and unreacted starting material (161 mg, 0.311 mmol, 52% recovered). R_f 0.56 (acetone:hexanes 2:3). $[\alpha]_D^{20}$: −3.6° (c 1.02, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ_H 7.86–7.80 (m, 2H, Ar), 7.73–7.68 (m, 2H, Ar), 7.33–7.30 (m, 2H, Ar), 7.27–7.24 (m, 2H, Ar), 4.85 (d, 1H, *J* = 6.7 Hz, $CH_3OCHaHb$), 4.69 (d, 1H, *J* = 6.7 Hz, $CH_3OCHaHb$), 4.68 (dd, 1H, *J* = 9.9, 7.7 Hz, H-2), 4.47 (dd, 1H, *J* = 10.0, 3.0 Hz, H-3), 4.27 (dd, 1H, *J* = 2.9, <1 Hz, H-4), 4.10 (d, 1H, *J* = 7.6 Hz, H-1), 3.57–3.53 (m, 1H, H-5), 3.55 (dd, 1H, *J* = 11.2, 5.4 Hz, H-6a), 3.49 (dd, 1H, *J* = 11.2, 8.2 Hz, H-6b), 3.37 (s, 3H, OMe), 3.33 (s, 3H, OMe), 2.99 (s, 3H, OMe), 2.43 (s, 3H, Ts), 2.40 (s, 3H, Ts). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 145.48 (Ar), 144.53 (Ar), 134.75 (Ar), 132.63 (Ar), 130.01 (Ar), 129.40 (Ar), 128.78 (Ar), 128.52 (Ar), 101.61 (C-1), 98.42 (CH_3OCH_2), 78.15 (C-3), 77.43 (C-2), 74.57 (C-4), 73.18 (C-5), 70.88 (C-6), 59.40 (OMe), 56.98 (OMe), 56.70 (OMe), 21.95 (Ts), 21.80 (Ts). HRMS *m*/*z* calcd for $C_{24}H_{32}O_{11}S_2$ $(M+NH_4)^+$: 578.1724; found: 578.1725.

4.28. Methyl 2,3-anhydro-4-*O*-methoxymethyl-6-*O*-methyl-β-D-talopyranoside (46) and methyl 4-*O*-methoxymethyl-3,6-di-*O*-methyl-β-D-idopyranoside (47)

A solution of KOBu-*t* in MeOH (2.3 M, 0.40 mL, 0.92 mmol) was added to a solution of the di-tosylate starting material (**45**, 102 mg, 0.183 mmol) in 1,4-dioxane (2.0 mL), and the procedure from Section 4.15 was followed to obtain the crude mixture, which was subsequently purified by column chromatography on silica gel using 10% acetone–hexanes to afford the talopyranoside intermediate **46** as a white solid (25 mg, 0.11 mmol, 59% yield) and the idopyranoside product **47** as a colorless syrup (14 mg, 0.053 mmol, 29% yield). Data for **46**: R_f 0.43 (acetone:hexanes 2:3). $[\alpha]_D^{20}$: −27.7° (c 0.92, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ_H 4.85 (d, 1H, *J* = 6.9 Hz, $CH_3OCHaHb$), 4.74 (d, 1H, *J* = <1 Hz, H-1), 4.69 (d, 1H, *J* = 6.9 Hz, $CH_3OCHaHb$), 3.89 (dd, 1H, *J* = 4.3, 3.2 Hz, H-4), 3.65–3.58 (m, 3H, H-5, H-6a, and H-6b), 3.54 (s, 3H, OMe), 3.51 (dd, 1H, *J* = 4.2, 4.2 Hz, H-3), 3.44 (s, 3H, OMe), 3.36 (s, 3H, OMe), 3.24 (dd, 1H, *J* = 4.0, <1 Hz, H-2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 98.89 (C-1), 96.30 (CH_3OCH_2), 75.73 (C-5), 70.98 (C-6), 67.42 (C-4), 59.50 (OMe), 56.66 (OMe), 56.12 (OMe), 52.32 (C-3), 51.34 (C-2). HRMS *m*/*z* calcd for $C_{10}H_{18}O_6$ $(M+NH_4)^+$: 252.1442; found: 252.1435. Data for **47**: R_f 0.38 (acetone:hexanes 2:3). $[\alpha]_D^{20}$: −13.5° (c 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ_H 4.73 (d, 1H, *J* = 6.8 Hz, $CH_3OCHaHb$), 4.63 (d, 1H, *J* = 6.8 Hz, $CH_3OCHaHb$), 4.56 (d, 1H, *J* = 1.3 Hz, H-1), 4.00 (ddd, 1H, *J* = 6.5, 6.5, 1.7 Hz, H-5), 3.73 (dddd, 1H, *J* = 10.5, 3.3, 1.3, 1.3 Hz, H-2), 3.69 (ddd, 1H, *J* = 3.3, 1.5, 1.5 Hz, H-4), 3.65 (dd, 1H, *J* = 3.3, 3.3 Hz, H-3), 3.62 (dd, 1H, *J* = 9.8, 6.5 Hz, H-6a), 3.58 (dd, 1H, *J* = 9.8, 6.6 Hz, H-6b), 3.55 (s, 3H, OMe), 3.42 (s, 3H, OMe), 3.42 (s, 3H, OMe), 3.38 (s, 3H, OMe), 3.06 (d, 1H, *J* = 10.5 Hz, 2-OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 100.64 (C-1), 96.96 (CH_3OCH_2), 77.81 (C-3), 73.07 (C-5), 71.82 (C-4), 71.31 (C-6), 68.25 (C-2), 59.39 (OMe), 58.49 (OMe), 57.11 (OMe), 56.53 (OMe). HRMS *m*/*z* calcd for $C_{11}H_{22}O_7$ $(M+Na)^+$: 289.1258; found: 289.1249.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2013.05.001.

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