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# Studies on the 6-homologation of β-D-idopyranosides

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ABSTRACT

β-D-Idopyranosides are interesting sugars because of their unusual conformational flexibility in the pyranosyl ring, and also their β-1,2-*cis*-anomeric configuration. Here we report our studies of the regioselective opening of 4,6-*O*-benzylidene-protected β-D-idopyranosides under reducing conditions, and the subsequent 6-homologation via Swern oxidation and Wittig olefination to afford a 6,7-dideoxy-β-D-*ido*-hept-6-enopyranoside. This olefination product was found to adopt predominantly $^{1}C_{4}$ conformation in solution by NMR experiments, which places the vinyl group at a more sterically hindered axial position and creates difficulty in subsequent hydroborations.



## 1. Introduction

Idoses are sugars with a limited distribution in nature, which play crucial roles in different biological processes. For example, L-idose is found in the repeating disaccharides of both heparin and heparan sulfate, which are part of glycosaminoglycans that play an important role in cell differentiation, viral infection, and cancer metastasis [1–4]. In both heparin and heparan sulfate, the L-idose exists in the α-pyranose form and is oxidized at the C6-position to form a uronic acid; extensive sulfation also occurs at the O2-positions (Fig. 1). Conversely, the D-idose is found in the repeating disaccharide of bacterial capsular polysaccharides (CPs) of *Campylobacter jejuni* HS:4, in the form of 6-deoxy-β-D-heptopyranose with partial *O*-phosphoramidation at O2 and O7 [5]. Compared to other monosaccharides, the pyranosyl forms of idoses are unique due to their enhanced conformational flexibility because both their $^{4}C_{1}$ and $^{1}C_{4}$ chair conformers experience extensive 1,3-diaxial interactions, resulting in relatively high energy chair conformations. This effectively lowers the energy barrier between the chair and half-chair conformers during ring flipping, making polysaccharides containing idopyranose units more flexible. Indeed, apart from the two chair conformers, idopyranose is also found to adopt other conformations, depending on its particular structural environment [6,7].

Recently, the development of an efficient synthesis for the 6-deoxy-β-D-*ido*-heptopyranose and related oligosaccharides of *Campylobacter jejuni* HS:4 CPs has drawn our interest due to its unique structure and potential immunological properties. The 6-deoxy-β-D-*ido*-heptopyranose is also a very challenging monosaccharide to synthesize due to its β-1,2-*cis*-glycosidic linkage and the presence of axial hydroxyl groups at each of the C2, C3, and C4 positions in the monosaccharide $^{4}C_{1}$ chair, and as well an unusual 7-carbon backbone with 6-deoxygenation. Previously, we published a short, scalable synthesis of β-D-idopyranosides from β-D-galactopyranosides by carrying out a double inversion at both C2 and C3 of 2,3-di-*O*-sulfonyl-β-D-galactopyranosides via 2,3-anhydro-β-D-talopyranoside intermediates (Scheme 1) [8,9]; the opening of the 2,3-anhydro-β-D-talopyranoside by an alkoxide was very regio- and stereoselective to afford the orthogonally protected β-D-idopyranoside typically with an O-alkyl group at O3 and a fused *O*-benzylidene at O4 and O6. The method was compatible with a series of nucleophilic alkoxides ($MeO^{-}$, $AllO^{-}$, $BnO^{-}$), and more importantly, this methodology was also found to be applicable to the synthesis of oligosaccharides containing β-linked idopyranosides. Here we report our initial studies on the 6-homologation of β-linked idopyranosides.

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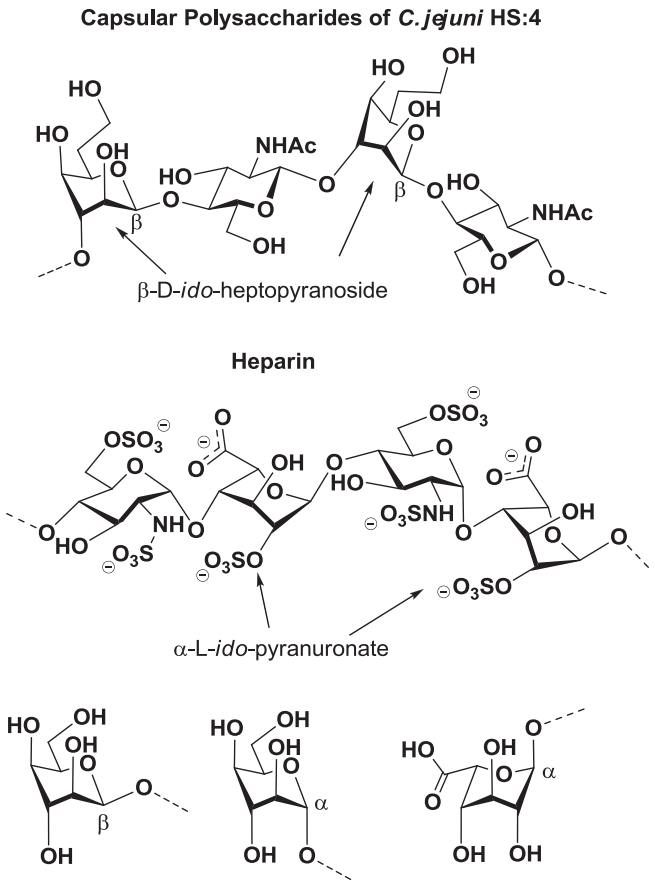


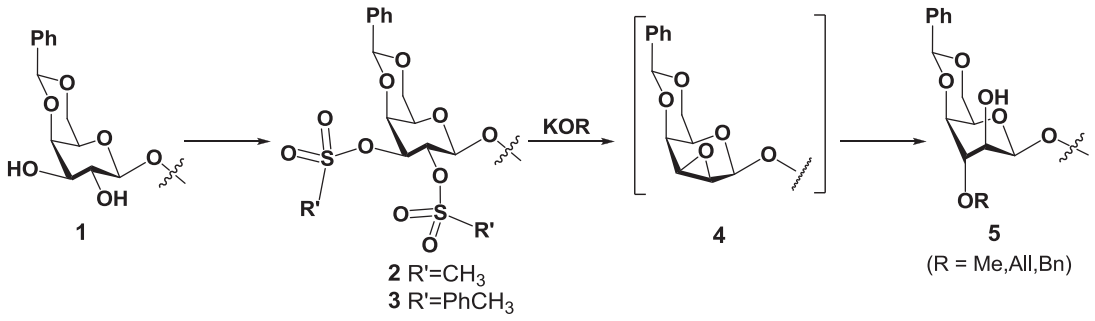

**Fig. 1.** Examples of D- and L-idopyranosides found in nature.

## 2. Results and discussion

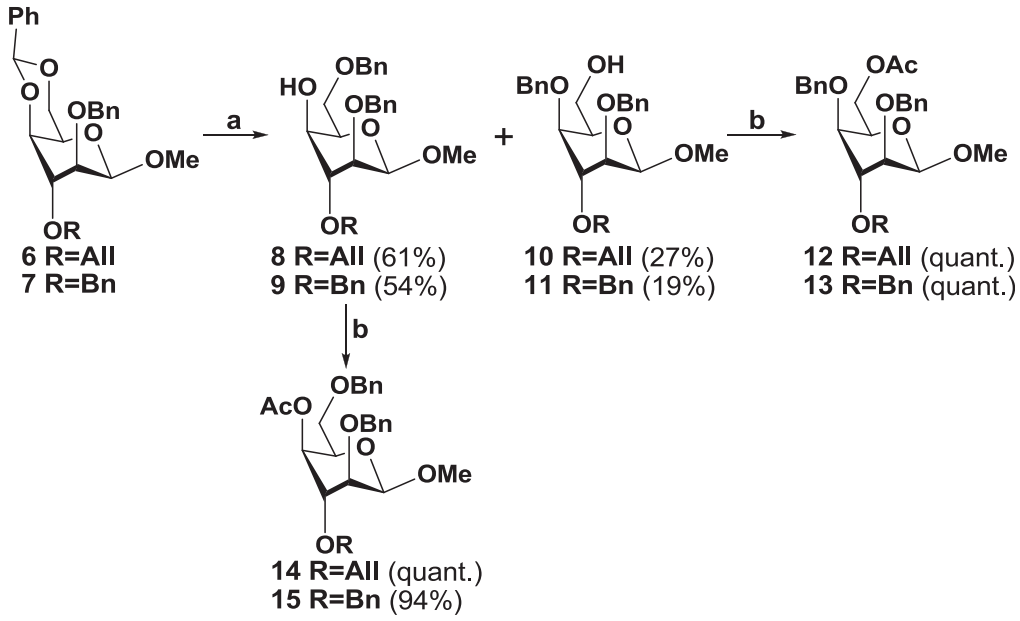
The studies on 6-homologation required the synthesis of idopyranoside substrates with a free 6-OH substituent. Since regioselective reductive acetal openings have been well studied in other hexose systems, it was envisaged that using methyl 3-*O*-alkyl-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-idopyranoside derivatives (**6** and **7**) [8] could afford the desired substrates. In the literature, DIBAL-H was reported to reductively open the 4,6-*O*-benzylidene of several hexopyranosides in toluene without the need for a Lewis acid, to afford the 6-OH-4-*O*-benzyl isomer as a major product in a regioselective manner [10]. Thus, both compounds **6** and **7** were subjected to reaction with DIBAL-H using anhydrous toluene as solvent (Scheme 2). The reactions afforded two products in a roughly 2:1 ratio yield in each case, as evidenced by TLC, and the compounds (**8**–**11**) were purified by chromatography on silica gel. Unfortunately, the significant overlapping of signals and weak correlations to OH peaks in the $^{1}$H-$^{1}$H COSY spectra prevented a full determination of the position (O4 or O6) of the benzyl group in each case. An acetylation was then performed for each isomer (**8**–**11**), and based on the significant deshielding of the proton at either C4 or C6 in the acetylated products (**12**–**15**). It was disappointing to discover that in fact the desired 4-*O*-benzylated regioisomer had been the one formed in only a minor amount in each case (**10**, 27%; **11**, 19%), and that the major product obtained was in fact the undesired 6-*O*-benzylated isomer (**8**, 61%; **9**, 54%). Similar regioselectivities were observed when the DIBAL-H reduction was performed in anhydrous hexanes. This is in sharp contrast with the literature reported on the reductive opening of 4,6-*O*-benzylidene derivatives of α-D-gluco- and α-D-mannopyranosides, which afforded the 4-*O*-benzylated regioisomers in high yields (>69%). However, our results were consistent with the 4,6-*O*-benzylidene-protected α-D-galactopyranoside, which gave the 6-*O*-benzylated regioisomer in 80% yield [10]. It is likely that the axially oriented O4 in both galacto- and idopyranosides (**6** and **7**) plays a crucial role in determining regioselectivity. This suggests that the O4 coordinates the aluminum centre of DIBAL-H preferentially, which selectively activates the O4-side of the acetal; a subsequent hydride is delivered to O4 to afford the observed 6-*O*-benzylated regioisomers (**8** and **9**).

Since O2 in both substrates **6** and **7** is also axially oriented and present at the same face of the pyranosyl ring as O4, it was postulated that a change in the regioselectivity of the DIBAL-H reaction may occur if an unprotected 2-OH substrate, such as 3-*O*-benzylated compound **16**, was utilized (Scheme 3). Unfortunately, formation of the undesired 6-*O*-benzylated isomer **17** (66% yield) was still observed as the major product upon reacting compound **16** with DIBAL-H under similar conditions, along with the desired 4-*O*-benzyl regioisomer (**18**, 19% yield) as a minor product. Respective acetylation of the formed products (→**19**, →**20**) helped to confirm the regiochemistry of the isomers unambiguously. Modification of the reaction temperatures (from −72 °C to rt) and solvent (hexanes, toluene) were again unsuccessful in altering the observed regioselectivity.

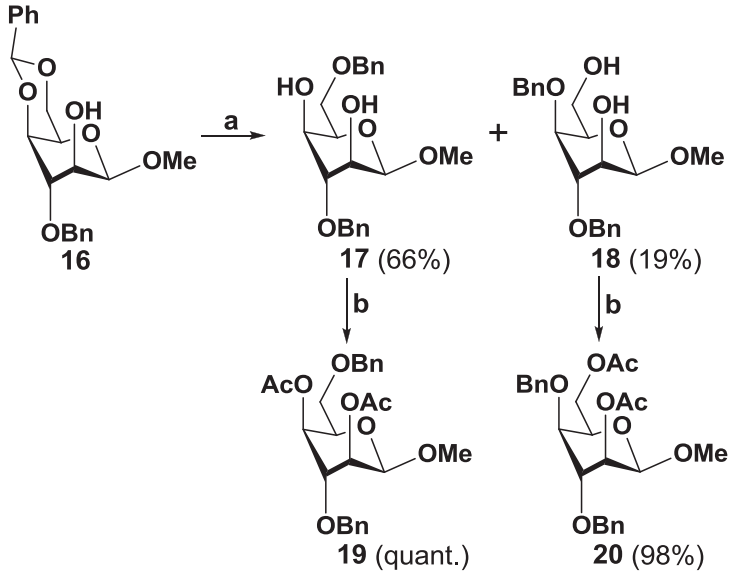
It was therefore decided to try switching from DIBAL-H as reagent, to borane as the source of hydride together with a Lewis acid activator. Using the 3-*O*-benzyl derivative **7** as a substrate and $BH_3$·THF/TMSOTf as reagents [11], the desired regioisomer **11** was obtained without the 4-OH regioisomer (as determined by TLC). However, the product formation was found to be very sensitive to the reaction conditions applied (Scheme 4): the desired product **11** was observed to easily undergo over-reduction to form the linear iditol **21**. Carrying out the reduction at lower temperatures (below 0 °C) was not helpful, as the initial reduction did not proceed. It was found that the reaction temperature needed to be monitored very



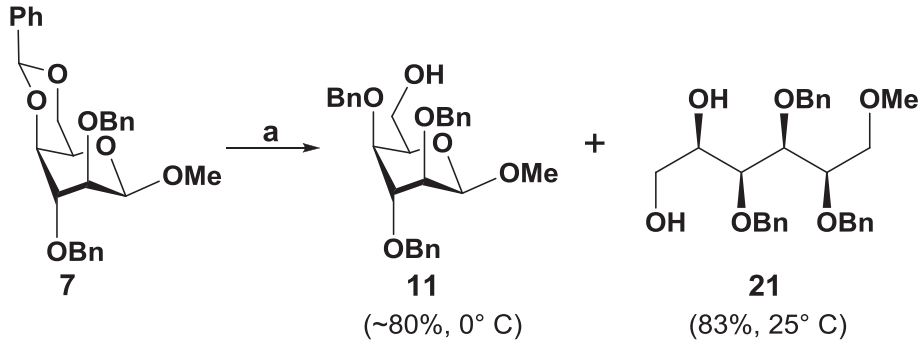

**Scheme 1.** Key step involving the di-inversion of C2 and C3 in the regio- and stereoselective conversion of D-galactopyranosides into D-idopyranosides.



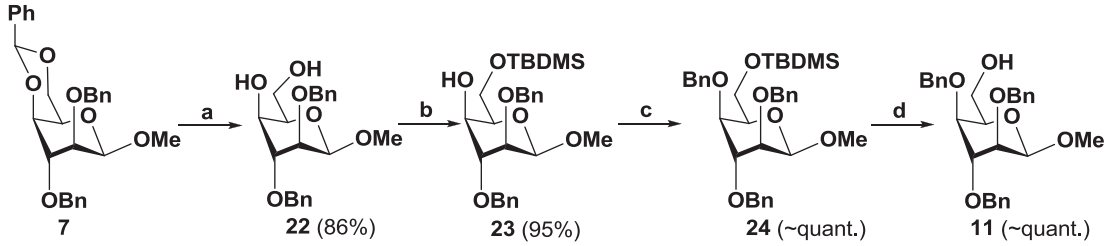

**Scheme 2.** Attempts at opening methyl 3-*O*-alkyl-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-idopyranosides **6** and **7** with DIBAL-H favoured formation of the undesired regioisomer. Reagents and Conditions: (a) DIBAL-H, hexanes or toluene; (b) $Ac_2O$/pyridine.




**Scheme 3.** Reduction of **16** with DIBAL-H again afforded the undesired 6-*O*-benzyl **17** as the major regioisomer and desired 4-*O*-benzyl **18** as the minor isomer. Reagents and Conditions: (a) DIBAL-H, toluene; (b) $Ac_2O$/pyridine.




**Scheme 4.** Reductive acetal openings of **7** using $BH_3$·THF. Reagents and conditions: (a) $BH_3$·THF, TMSOTf, $CH_2Cl_2$, ambient temperature or 0 °C.

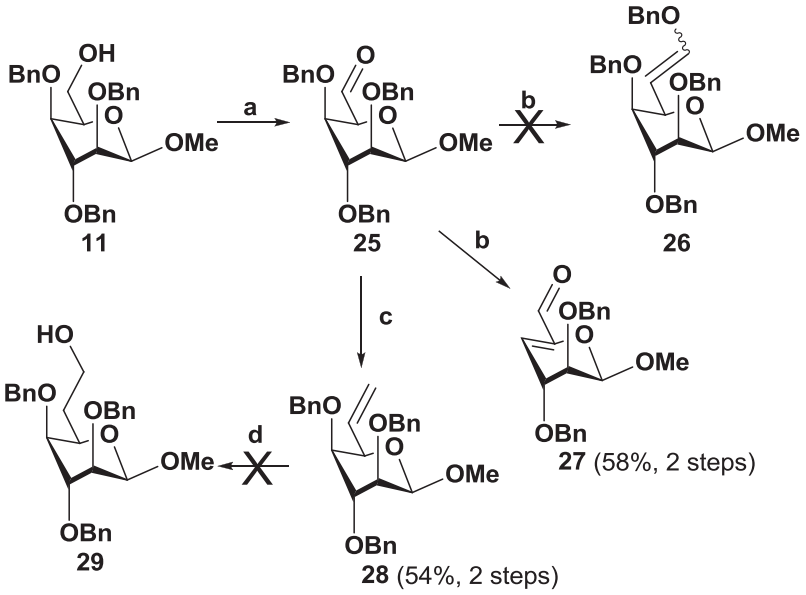



**Scheme 5.** A protection-deprotection sequence could be utilized to prepare methyl 2,3,4-tri-*O*-benzyl-β-D-idopyranoside **11** in excellent yield. Reagents and conditions: (a) 80% AcOH–$H_2O$, 60 °C, 3 h; (b) TBDMSCl, pyridine; (c) BnBr, NaH, THF; (d) TBAF, THF.

closely at 0 °C in order to obtain the desired product (**11**, ~80%); allowing the reaction to warm up above 5 °C resulted in over reduction, and after stirring at ambient temperature for 30 min afforded the undesired iditol **21** in 83% yield (isolated). Unfortunately, at larger scales the method was also found to be difficult to control and always afforded amounts of the undesired iditol, which in addition displayed very similar retention on silica to desired idopyranose **11** resulting in difficult separations, and thus the method was deemed unsuitable for larger scale synthesis.

In the face of significant challenge to prepare the desired 6-OH derivatives of β-D-idopyranosides directly from the 4,6-*O*-benzylidene-protected derivatives, a multi-step protection-deprotection strategy was attempted (Scheme 5). Using the 4,6-*O*-benzylidene acetal **7** as a starting material, a mild hydrolysis was carried out by heating a solution of compound **7** in 80% acetic acid-$H_2O$ for 3 h. The resulting 4,6-diol **22** was isolated in 86% yield. The primary hydroxyl group of compound **22** was then regioselectively protected using *tert*-butyldimethylsilyl chloride (TBDMSCl) in anhydrous pyridine to afford the desired compound **23** in excellent yield (95%). The O4 position was subsequently benzylated using standard conditions (BnBr/NaH) to afford fully protected compound **24** in quantitative yield. The 6-*O*-desilylation was finally carried out using tetra-*n*-butylammonium fluoride (TBAF) in THF to give the desired methyl 2,3,4-tri-*O*-benzyl-β-D-idopyranoside **11** in quantitative yield. This indirect reaction sequence worked very well and could be performed at gram-scale.

With the desired 6-hydroxyl **11** in hand, we attempted to carry out a 6-homologation via Wittig olefination (Scheme 6). Thus, a Swern oxidation was initially carried out. Compound **11** was treated with oxalyl chloride (2.1 equiv.) and DMSO (3.2 equiv.) in dichloromethane at −78 °C, followed by treatment with triethylamine for 15 min [12,13]; after warming to ambient temperature, the starting material was completely consumed. However, the crude $^1$H NMR spectrum showed the crude reaction mixture contained two major products in approximately 1:1 ratio. The desired aldehyde **25** was clearly observed to have formed as a signal at 9.86 ppm (aldehyde proton) was observed in the $^1$H NMR spectrum; however, a second product, presumably the hydrate form of compound **25** was also observed (this hydration might be due to contact with trace amounts of water in deuterated chloroform). Since the aldehyde functionality is known to be unstable, the crude aldehyde mixture was used directly without further purification. Crude mixture containing aldehyde **25** was reacted with an ylide derived from benzyloxymethyltriphenylphosphonium chloride by treatment with *n*-butyllithium [14]. However, the reaction afforded only a β-elimination product **27** (58% yield) which was formed via loss of the 4-benzyloxy group of aldehyde **25**, and disappointingly no desired benzyl enolether **26** was identified. It was thought that the $Ph_3P{=}CHOBn$ might be too bulky, thus presenting significant steric hindrance for the olefination; therefore, a less sterically




**Scheme 6.** Synthetic route for obtaining β-D-*ido*-heptopyranoside **28** from compound **11** using Wittig olefination, and another attempted olefination with a benzyloxy ylide. Reagents and conditions: (a) oxalyl chloride, DMSO, $Et_3N$, $CH_2Cl_2$; (b) $BnOCH_2PPh_3^+Cl^-$, *n*-BuLi, toluene; (c) $CH_3PPh_3^+Br^-$, *n*-BuLi, toluene; (d) (i) $BH_3$·THF or 9-BBN, (ii) $H_2O_2$, NaOH, MeOH.

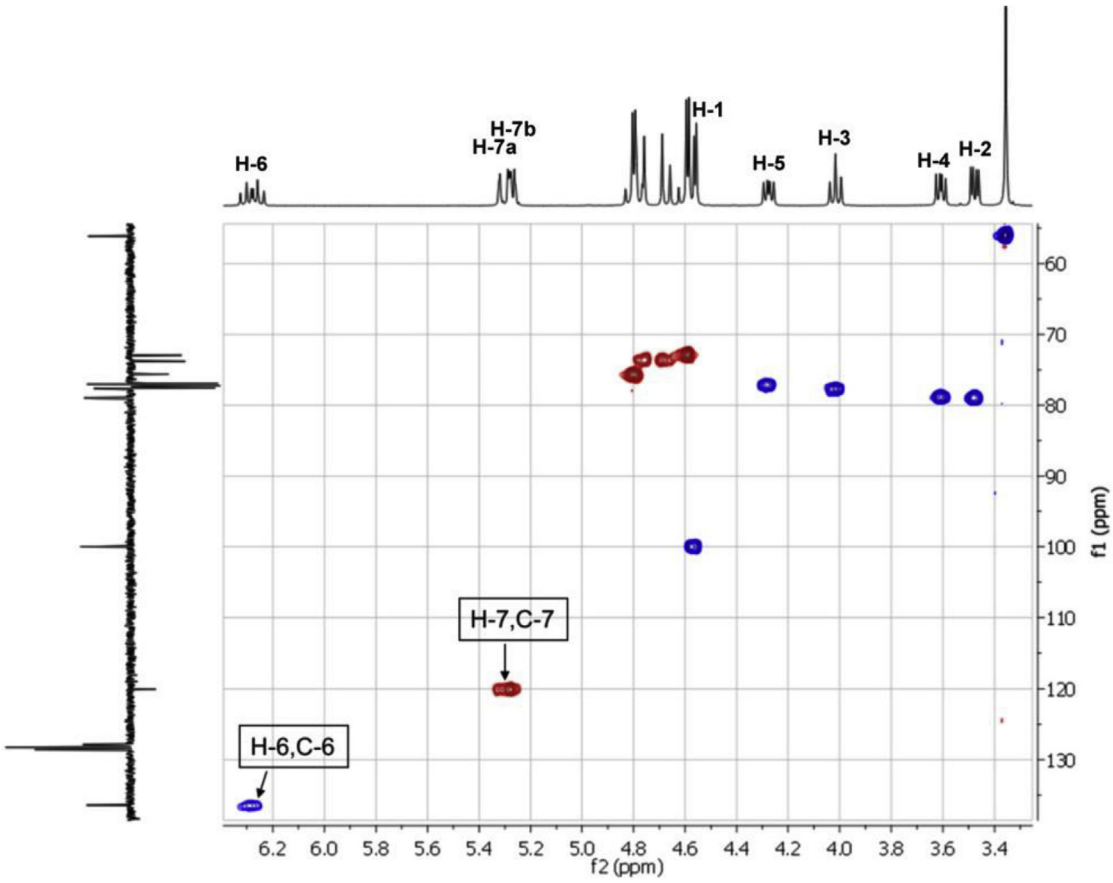



**Fig. 2.** $^{1}$H-$^{13}$C HSQC NMR correlation spectrum of methyl 2,3,4-tri-*O*-benzyl-6,7-dideoxy-β-D-*ido*-hept-6-enopyranoside **28** ($CDCl_3$, 400 MHz).

hindered ylide, the methylidenetriphenylphosphorane (generated *in situ* by reacting methyl triphenylphosphonium bromide and *n*-BuLi) was used to react with the crude aldehyde **25** in anhydrous toluene [15]. After one hour, the desired heptose **28** was successfully formed and isolated in moderate yield (54% yield over two steps from **11**) by column chromatography on silica gel (8 → 15% EtOAc − hexanes).

The structure of the vinylic derivative **28** was confirmed using NMR spectroscopy. In support of the structural assignment, the alkenic proton H-6 was observed at 6.28 ppm as ddd ($J$ = 17.0, 9.8, 9.8 Hz) while the other two alkenic protons H-7a and H-7b were observed in the 5.24–5.34 ppm region. In the $^{1}$H-$^{13}$C HSQC spectrum (Fig. 2), the above alkenic protons were found to correlate respectively with carbon signals at 136.43 ppm (C-6) and 120.05 ppm (C-7). Furthermore, electrospray high-resolution mass spectrometry also led further support to the identity of compound **28** (*m/z* for $(M+Na)^+$: expected: 483.2142; found: 483.2143).

Unfortunately, subsequent attempts at hydroboration-oxidation of the alkene functionality of **28** using $BH_3$·THF, followed by $H_2O_2$/$HO^-$ oxidation were unsuccessful. The reaction mixture was found to be a complex mixture which could not be further identified. Thus, no desired compound **29** was formed. Since one molecule of $BH_3$ reagent is capable of reacting with up to three molecules of substrate, we thought that a switch to 9-BBN could help resolve the problem, as it is only capable of hydroborating one substrate molecule at a time; in addition, 9-BBN has a larger size which could result in improved regioselectivity. Unfortunately, even with prolonged heating only unreacted starting material was recovered. These results contrast sharply with the hydroborations of similar substrates related to D-glucopyranosides [15–17]. For example, Zhang and co-workers reported the hydroboration of methyl 2,3,4-tri-*O*-benzyl-6,7-dideoxy-α-D-*gluco*-hept-6-enopyranoside with 9-BBN followed by conventional oxidation with hydrogen peroxide; this afforded the corresponding primary alcohol in 80% yield [17].

The significant difficulty observed during hydroboration of compound **28** might be due to unfavourable steric interactions as a result of ring flipping. Many idopyranosides prepared in this and other work were observed to exist predominantly in one chair conformer, depending on the nature and position of substituents on the idopyranosyl rings as well as the compound's ability to form intramolecular hydrogen bonds [8,18]. Table 1 summarizes the observed coupling constants of *ido*-heptopyranoside **28** and another two representative idopyranosides **9** and **11**. As can be seen for compound **9** that has a 4-hydroxyl group, we observed consistently small $^{3}J$ coupling constants (<3.0 Hz) for all $J_{H\text{-}1,H\text{-}2}$, $J_{H\text{-}2,H\text{-}3}$, $J_{H\text{-}3,H\text{-}4}$, and $J_{H\text{-}4,H\text{-}5}$, which suggests the presence of axial substituents at C2, C3, and C4, confirming that compound **9** exists predominantly in a $^{4}C_1$ chair conformation in solution. This preferred conformation is probably stabilized by an intramolecular hydrogen bond between OH-4…O2, as both O2 and OH-4 are occupying axial positions (Fig. 3). On the other hand, in the case of analogous compounds **11** and **28**, which have small $J_{H\text{-}1,H\text{-}2}$ (3.3–3.6 Hz) and intermediate $J_{H\text{-}4,H\text{-}5}$ (5.5–5.9 Hz), but large $J_{H\text{-}2,H\text{-}3}$, $J_{H\text{-}3,H\text{-}4}$ coupling constants (7.9–8.8 Hz), these coupling patterns suggest that both compounds exist predominantly in $^{1}C_4$ chair conformers in solution; thus, the substituents at C2, C3, and C4 occupy an equatorial position while the substituents at C1 and C5 occupy an axial position. This explains the lower reactivity of

**Table 1**
Typical conformations of β-D-idopyranosides **9**, **11**, and **28** based on observed $^{3}J_{H\text{-}1,H\text{-}2}$, $^{3}J_{H\text{-}2,H\text{-}3}$, $^{3}J_{H\text{-}3,H\text{-}4}$, $^{3}J_{H\text{-}4,H\text{-}5}$ coupling constants.

| Coupling Constants | Predominantly $^{4}C_1$ | Predominantly $^{1}C_4$ | |
|---|---|---|---|
| | Compound **9** | Compound **11** | Compound **28** |
| $^{3}J_{H\text{-}1,H\text{-}2}$ | 0.9 Hz | 3.3 Hz | 3.6 Hz |
| $^{3}J_{H\text{-}2,H\text{-}3}$ | 3.0 Hz | 7.9 Hz | 8.8 Hz |
| $^{3}J_{H\text{-}3,H\text{-}4}$ | 3.0 Hz | 7.9 Hz | 8.7 Hz |
| $^{3}J_{H\text{-}4,H\text{-}5}$ | <1 Hz | 5.5 Hz | 5.9 Hz |

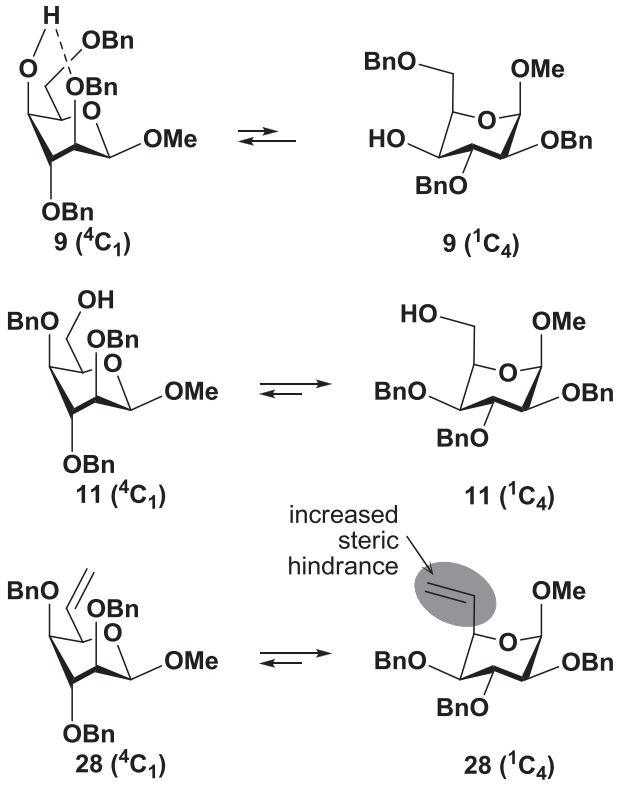



**Fig. 3.** Preferred solution conformations of exemplary β-D-idopyranosides **9**, **11**, and **28** based on $^{1}$H NMR spectra. Other compounds such as **8**, **14**, **15**, **17**, **18**, **19**, and **20** were also found to adopt a $^{4}C_1$ chair, while compounds **10**, **12**, and **13** were found to adopt the $^{1}C_4$ chair conformation (not shown, see Experimental section).

compound **28** during hydroborations, because it has an axial vinyl group that experiences increased steric hindrance.

## 3. Conclusions

We have studied the reductive acetal opening of 4,6-*O*-benzylidene-protected β-D-idopyranosides with DIBAL-H and borane/TMSOTf. It was found that the DIBAL-H-mediated reductive opening in toluene consistently favoured the formation of a secondary alcohol (4-OH), while the borane/TMSOTf-mediated reductive opening in dichloromethane favoured the formation of a primary alcohol (6-OH). However, the latter method was found to be difficult to control and thus, unsuitable for large scale synthesis. To prepare the desired regioisomer with a primary hydroxyl group (6-OH) of the β-D-idopyranosides, it was preferable to follow a more conventional method using a bulky silyl ether as a temporary protecting group of the primary hydroxyl position (6-OH). We were successful at 6-homologation of a β-D-idopyranoside using Wittig olefination, but the obtained β-D-*ido*-heptopyranoside was found to experience increased conformational flexibility in favour of the $^{1}C_4$ conformer, which places the 5-vinyl group at a more sterically hindered axial position. We are currently studying other 6-homologation methods. However, considering the inherent conformational flexibility issues associated with the β-D-idopyranosides, it is likely that alternative strategies will need to be developed in order to succeed with the total synthesis of the desired 6-deoxy-β-D-*ido*-heptopyranosides.

## 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 MHz or 600 MHz (as indicated), and the first-order proton chemical shifts $\delta_H$ and $\delta_C$ are reported in $\delta$ (ppm) and referenced to residual $CHCl_3$ ($\delta_H$ 7.24, $\delta_C$ 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. Methyl 3-O-allyl-2,6-di-O-benzyl-β-D-idopyranoside (*8*) and Methyl 3-O-allyl-2,4-di-O-benzyl-β-D-idopyranoside (*10*)

A solution of the starting material [8] (**6**, 1.677 g, 4.065 mmol) in dry toluene (20 mL) was cooled to −10 °C, and then DIBAL-H solution (1 M in toluene, 12 mL, 12 mmol) was added portionwise over 10 min. After 45 min, the reaction solution was diluted with $CH_2Cl_2$ (50 mL), quenched with MeOH (20 mL), and then evaporated to dry. The crude mixture was redissolved into EtOAc (100 mL), washed with 2 N $HCl_{(aq)}$ solution (3 × 100 mL), $H_2O$ (100 mL), dried with $Na_2SO_4$, filtered, and evaporated to dry. The crude mixture was purified via column chromatography on silica using 8 → 10 → 15% EtOAc − hexanes to afford first 6-*O*-benzyl regioisomer **8** as a colourless syrup (1.033 g, 2.492 mmol, 61% yield), unreacted starting material (134 mg, 0.324 mmol, 8% recovered), and 4-*O*-benzyl regioisomer **10** as a colourless syrup (456 mg, 1.10 mmol, 27% yield). Data for **8**: $R_f$ 0.77 (EtOAc: hexanes 2:3). $[\alpha]_D^{20}$: −81.5° (*c* 1.00, $CHCl_3$). $^{1}$H NMR ($CDCl_3$, 400 MHz) δH: 7.36–7.25 (m, 10H, Ar), 5.76 (dddd, 1H, *J* = 17.2, 10.5, 5.6, 5.6 Hz, $OCH_2CH{=}CH_2$), 5.16 (dddd, 1H, *J* = 17.5, 1.6, 1.6, 1.6 Hz, $OCH_2CH{=}CHaHb$), 5.12 (dddd, 1H, *J* = 10.6, 1.3, 1.3, 1.3 Hz, $OCH_2CH{=}CHa\mathit{Hb}$), 4.88 (d, 1H, *J* = 12.2 Hz, PhC*Ha*Hb), 4.64 (d, 1H, *J* = 0.6 Hz, H-1), 4.64 (d, 1H, *J* = 12.1 Hz, PhCHa*Hb*), 4.61 (d, 1H, *J* = 11.7 Hz, PhC*Ha*Hb), 4.56 (d, 1H, *J* = 12.0 Hz, PhCHa*Hb*), 4.01 (ddd, 1H, *J* = 6.4, 5.4, 1.0 Hz, H-5), 3.95 (dddd, 1H, *J* = 12.9, 5.5, 1.4, 1.4 Hz, OC*Ha*HbCH=$CH_2$), 3.90 (dddd, 1H, *J* = 12.9, 5.7, 1.4, 1.4 Hz, OCHa*Hb*CH=$CH_2$), 3.80 (dd, 1H, *J* = 10.2, 5.2 Hz, H-6a), 3.75 (dd, 1H, *J* = 10.2, 6.8 Hz, H-6b), 3.70 (dd, 1H, *J* = 3.1, 3.1 Hz, H-3), 3.59–3.58 (m, 2H, H-2 and H-4), 3.57 (s, 3H, OMe), 3.50 (d, 1H, *J* = 11.1 Hz, 4-OH). $^{13}$C NMR ($CDCl_3$, 100 MHz)

δC: 138.60 (Ar), 137.75 (Ar), 134.18 ($OCH_2CH{=}CH_2$), 128.59 (Ar), 128.51 (Ar), 128.26 (Ar), 128.12 (Ar), 127.86 (Ar), 127.72 (Ar), 117.69 ($OCH_2CH{=}CH_2$), 101.05 (C-1), 75.78 (C-3), 74.80 (C-2), 74.73 (C-5), 74.39 ($PhCH_2$), 73.77 ($PhCH_2$), 71.21 ($OCH_2CH{=}CH_2$), 70.14 (C-6), 67.11 (C-4), 57.18 (OMe). Anal. calc'd for $C_{24}H_{30}O_6$: C, 69.54; H, 7.30; found: C, 69.68; H, 7.46. HRMS *m/z* calc'd for $C_{24}H_{30}O_6$ $(M+Na)^+$: 437.1935; found: 437.1927.

Data for **10**: $R_f$ 0.22 (EtOAc: hexanes 2:3). $[\alpha]_D^{20}$: −39° (*c* 0.97, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHz) δH: 7.36–7.24 (m, 10H, Ar), 5.92 (dddd, 1H, *J* = 17.2, 10.6, 5.6, 5.6 Hz, $OCH_2CH{=}CH_2$), 5.25 (dddd, 1H, *J* = 17.2, 1.5, 1.5, 1.5 Hz, $OCH_2CH{=}CHaHb$), 5.15 (dddd, 1H, *J* = 10.4, 1.4, 1.4, 1.4 Hz, $OCH_2CH{=}CHaHb$), 4.76 (d, 1H, *J* = 11.7 Hz, $PhCHaHb$), 4.73 (d, 1H, *J* = 12.4 Hz, $PhCHaHb$), 4.68 (d, 1H, *J* = 12.3 Hz, $PhCHaHb$), 4.58 (d, 1H, *J* = 11.7 Hz, $PhCHaHb$), 4.52 (d, 1H, *J* = 3.3 Hz, H-1), 4.25 (dddd, 1H, *J* = 12.6, 5.6, 1.3, 1.3 Hz, $OCHaHbCH{=}CH_2$), 4.18 (dddd, 1H, *J* = 12.6, 5.7, 1.3, 1.3 Hz, $OCHaHbCH{=}CH_2$), 3.95 (ddd, 1H, *J* = 5.4, 5.4, 5.4 Hz, H-5), 3.89 (dd, 1H, *J* = 7.7, 7.7 Hz, H-3), 3.91–3.86 (m, 1H, H-6a), 3.81 (ddd, 1H, *J* = 12.0, 7.5, 5.6 Hz, H-6b), 3.58 (dd, 1H, *J* = 7.6, 5.5 Hz, H-4), 3.44 (s, 3H, OMe), 3.41 (dd, 1H, *J* = 7.9, 3.3 Hz, H-2), 2.82 (dd, 1H, *J* = 7.4, 5.1 Hz, 6-OH). $^{13}C$ NMR ($CDCl_3$, 100 MHz) δC: 138.29 (Ar), 137.90 (Ar), 134.90 ($OCH_2CH{=}CH_2$), 128.40 (Ar), 128.33 (Ar), 127.95 (Ar), 127.91 (Ar), 127.84 (Ar), 127.74 (Ar), 116.80 ($OCH_2CH{=}CH_2$), 99.93 (C-1), 77.90 (C-2), 77.53 (C-4), 76.44 (C-3), 75.06 (C-5), 73.66 ($PhCH_2$), 73.58 ($PhCH_2$), 73.32 ($OCH_2CH{=}CH_2$), 62.92 (C-6), 56.78 (OMe). HRMS *m/z* calc'd for $C_{24}H_{30}O_6$ $(M+Na)^+$: 437.1946; found: 437.1953.

### 4.3. Methyl 2,3,6-tri-O-benzyl-β-D-idopyranoside (**9**) and Methyl 2,3,4-tri-O-benzyl-β-D-idopyranoside (**11**)

A solution of the starting material [8] (**7**, 110 mg, 0.239 mmol) in dry toluene (1.0 mL) was cooled to −30 °C, and then DIBAL-H solution (1.5 M in toluene, 0.56 mL, 0.84 mmol) was added portionwise over 10 min. After 2 h, the reaction solution was diluted with $CH_2Cl_2$ (10 mL), quenched with $H_2O$ (2 mL), and then evaporated to dry. The crude mixture was redissolved into EtOAc (20 mL) and $H_2O$ (20 mL), washed with saturated $NaCl_{(aq)}$ solution (2 × 20 mL), dried with $Na_2SO_4$, filtered, and evaporated to dry. The crude mixture was purified via column chromatography on silica using 8 → 10→15% EtOAc − hexanes to afford 6-*O*-benzyl regioisomer **9** as a colourless syrup (60 mg, 0.13 mmol, 54% yield) and 4-*O*-benzyl regioisomer **11** as a colourless syrup (21 mg, 0.045 mmol, 19% yield). Data for **9**: $R_f$ 0.67 (EtOAc: hexanes 2:3). $[\alpha]_D^{20}$: −30° (*c* 0.94, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHz) δH: 7.35–7.28 (m, 13H, Ar), 7.23–7.20 (m, 2H, Ar), 4.84 (d, 1H, *J* = 12.2 Hz, $PhCHaHb$), 4.69 (d, 1H, *J* = 0.9 Hz, H-1), 4.63 (d, 1H, *J* = 11.9 Hz, $PhCHaHb$), 4.62 (d, 1H, *J* = 12.2 Hz, $PhCHaHb$), 4.57 (d, 1H, *J* = 12.0 Hz, $PhCHaHb$), 4.50 (d, 1H, *J* = 11.9 Hz, $PhCHaHb$), 4.45 (d, 1H, *J* = 11.9 Hz, $PhCHaHb$), 4.07 (ddd, 1H, *J* = 6.7, 5.5, <1.0 Hz, H-5), 3.82 (dd, 1H, *J* = 10.2, 5.2 Hz, H-6a), 3.78 (dd, 1H, *J* = 3.0, 3.0 Hz, H-3), 3.77 (dd, 1H, *J* = 10.1, 6.7 Hz, H-6b), 3.65 (dd, 1H, *J* = 2.6, <1.0 Hz, H-4), 3.62 (dd, 1H, *J* = 3.3, <1.0 Hz, H-2), 3.57 (s, 3H, OMe). $^{13}C$ NMR ($CDCl_3$, 100 MHz) δC: 138.61 (Ar), 137.70 (Ar), 137.68 (Ar), 128.66 (Ar), 128.59 (Ar), 128.52 (Ar), 128.25 (Ar), 128.12 (Ar), 127.86 (Ar), 127.73 (Ar), 101.02 (C-1), 75.93 (C-3), 74.76 (C-5), 74.72 (C-2), 74.33 ($PhCH_2$), 73.78 ($PhCH_2$), 72.23 ($PhCH_2$), 70.15 (C-6), 67.07 (C-4), 57.17 (OMe). Anal. calc'd for $C_{28}H_{32}O_6$: C, 72.39; H, 6.94; found: C, 72.28; H, 7.10. HRMS *m/z* calc'd for $C_{28}H_{32}O_6$ $(M+Na)^+$: 487.2091; found: 487.2084.

Data for **11**: $R_f$ 0.42 (acetone: hexanes 2:3). $[\alpha]_D^{20}$: −20.5° (*c* 1.03, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHz): δH 7.37–7.24 (m, 15H, Ar), 4.80 (d, 1H, *J* = 11.1 Hz, $PhCHaHb$), 4.76 (d, 1H, *J* = 11.7 Hz, $PhCHaHb$), 4.74 (d, 1H, *J* = 12.1 Hz, $PhCHaHb$), 4.71 (d, 1H, *J* = 11.0 Hz, $PhCHaHb$), 4.67 (d, 1H, *J* = 12.2 Hz, $PhCHaHb$), 4.55 (d, 1H, *J* = 11.6 Hz, $PhCHaHb$), 4.53 (d, 1H, *J* = 3.3 Hz, H-1), 4.03 (dd, 1H, *J* = 7.9, 7.9 Hz, H-3), 3.96 (ddd, 1H, *J* = 5.4, 5.4, 5.4 Hz, H-5), 3.90 (ddd, 1H, *J* = 12.0, 5.1, 5.1 Hz, H-6a), 3.82 (ddd, 1H, *J* = 12.0, 8.2, 5.3 Hz, H-6b), 3.63 (dd, 1H, *J* = 7.8, 5.5 Hz, H-4), 3.47 (dd, 1H, *J* = 7.9, 3.5 Hz, H-2), 3.47 (s, 3H, OMe), 2.68 (dd, 1H, *J* = 8.1, 5.0 Hz, 6-OH). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δC 138.63 (Ar), 138.47 (Ar), 138.04 (Ar), 128.71 (Ar), 128.65 (Ar), 128.64 (Ar), 128.30 (Ar), 128.24 (Ar), 128.16 (Ar), 128.09 (Ar), 127.96 (Ar), 100.16 (C-1), 78.45 (C-2), 78.08 (C-4), 77.17 (C-3), k75.30 (C-5), 75.11 ($PhCH_2$), 74.01 ($PhCH_2$), 73.95 ($PhCH_2$), 63.38 (C-6), 57.14 (OMe). HRMS *m/z* calc'd for $C_{28}H_{32}O_6$ $(M+Na)^+$: 487.2091; found: 487.2082.

### 4.4. Methyl 6-O-acetyl-3-O-allyl-2,4-di-O-benzyl-β-D-idopyranoside (**12**)

The starting material (**10**, 64 mg, 0.15 mmol) was dissolved into pyridine (0.50 mL) and $Ac_2O$ (0.50 mL) and left mixing at rt. After 18 h, the reaction mixture was heated at 60 °C. After 4 h of heating, the reaction mixture was concentrated and co-evaporated with toluene (3 × 0.5 mL). The crude product was purified via column chromatography on silica gel using 15% EtOAc − hexanes to afford the pure product **12** as a colourless syrup (69 mg, 0.15 mmol, quant. yield). $R_f$ 0.22 (EtOAc: hexanes 2:3). $[\alpha]_D^{20}$: −16° (*c* 0.99, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHz): δH 7.36–7.24 (m, 10H, Ar), 5.88 (dddd, 1H, *J* = 17.2, 10.4, 5.7, 5.7 Hz, $OCH_2CH{=}CH_2$), 5.21 (dddd, 1H, *J* = 17.2, 1.7, 1.6, 1.6 Hz, $OCH_2CH{=}CHaHb$), 5.13 (dddd, 1H, *J* = 10.4, 1.7, 1.2, 1.2 Hz, $OCH_2CH{=}CHaHb$), 4.72 (s, 2H, $PhCH_2$), 4.70 (d, 1H, *J* = 12.0 Hz, $PhCHaHb$), 4.59 (d, 1H, *J* = 11.9 Hz, $PhCHaHb$), 4.55 (d, 1H, *J* = 3.2 Hz, H-1), 4.48 (dd, 1H, *J* = 11.6, 4.8 Hz, H-6a), 4.35 (dd, 1H, *J* = 11.6, 8.4 Hz, H-6b), 4.17 (dddd, 1H, *J* = 12.6, 5.7, 1.4, 1.4 Hz, $OCHaHbCH{=}CH_2$), 4.12 (dddd, 1H, *J* = 12.6, 5.8, 1.3, 1.3 Hz, $OCHaHbCH{=}CH_2$), 4.10 (ddd, 1H, *J* = 8.4, 5.1, 4.9 Hz, H-5), 3.75 (dd, 1H, *J* = 7.4, 7.4 Hz, H-3), 3.52 (dd, 1H, *J* = 7.3, 5.2 Hz, H-4), 3.46 (s, 3H, OMe), 3.42 (dd, 1H, *J* = 7.4, 3.2 Hz, H-2), 2.01 (s, 3H, Ac). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δC 170.95 (Ac), 138.62 (Ar), 138.19 (Ar), 135.02 ($OCH_2CH{=}CH_2$), 128.52 (Ar), 128.19 (Ar), 128.04 (Ar), 127.92 (Ar), 117.19 ($OCH_2CH{=}CH_2$), 100.75 (C-1), 77.44 (C-2), 76.67 (C-4), 75.96 (C-3), 73.93 ($PhCH_2$), 73.43 ($OCH_2CH{=}CH_2$), 73.10 ($PhCH_2$), 72.77 (C-5), 64.43 (C-6), 56.73 (OMe), 21.10 (Ac). HRMS *m/z* calc'd for $C_{26}H_{32}O_7$ $(M+Na)^+$: 479.2040; found: 479.2042.

### 4.5. Methyl 2,3,4-tri-O-benzyl-6-O-acetyl-β-D-idopyranoside (**13**)

The starting material (**11**, 12 mg, 0.025 mmol) was dissolved into pyridine (0.30 mL) and $Ac_2O$ (0.30 mL) and left mixing at 60 °C. After 1 h, the reaction mixture was concentrated and co-evaporated with toluene (1 mL). The crude product was purified via column chromatography on silica gel using 15% acetone − hexanes to afford the pure product **13** as a colourless syrup (13 mg, 0.026 mmol, quant. yield). $R_f$ 0.55 (acetone: hexanes 2:3). $[\alpha]_D^{20}$: −5.4° (*c* 1.03, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHz): δH 7.34–7.24 (m, 15H, Ar), 4.72 (d, 1H, *J* = 12.4 Hz, $PhCHaHb$), 4.70 (d, 1H, *J* = 10.6 Hz, $PhCHaHb$), 4.69 (d, 1H, *J* = 12.4 Hz, $PhCHaHb$), 4.66 (d, 1H, *J* = 11.7 Hz, $PhCHaHb$), 4.63 (d, 1H, *J* = 10.9 Hz, $PhCHaHb$), 4.57 (d, 1H, *J* = 3.2 Hz, H-1), 4.55 (d, 1H, *J* = 11.8 Hz, $PhCHaHb$), 4.49 (dd, 1H, *J* = 11.7, 4.8 Hz, H-6a), 4.37 (dd, 1H, *J* = 11.7, 8.4 Hz, H-6b), 4.13 (ddd, 1H, *J* = 8.4, 4.9, 4.9 Hz, H-5), 3.86 (dd, 1H, *J* = 7.3, 7.3 Hz, H-3), 3.56 (dd, 1H, *J* = 7.2, 5.1 Hz, H-4), 3.48 (dd, 1H, *J* = 7.4, 3.1 Hz, H-2), 3.47 (s, 3H, OMe), 2.02 (s, 3H, Ac). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δC 171.01 (Ac), 138.61 (Ar), 138.51 (Ar), 138.14 (Ar), 128.62 (Ar), 128.60 (Ar), 128.57 (Ar), 128.27 (Ar), 128.18 (Ar), 128.15 (Ar), 128.00 (Ar), 127.98 (Ar), 100.77 (C-1), 77.61 (C-2), 76.76 (C-4), 76.29 (C-3), 74.80 ($PhCH_2$), 73.97 ($PhCH_2$), 73.07 ($PhCH_2$), 72.80 (C-5), 64.49 (C-6), 56.80 (OMe), 21.16 (Ac). HRMS *m/z* calc'd for $C_{30}H_{34}O_7$ $(M+Na)^+$: 529.2197; found: 529.2199.

### 4.6. Methyl 4-O-acetyl-3-O-allyl-2,6-di-O-benzyl-β-D-idopyranoside (**14**)

The starting material (**8**, 63 mg, 0.15 mmol) was dissolved into pyridine (0.50 mL) and $Ac_2O$ (0.50 mL) and left mixing at 45 °C. After 18 h, the reaction mixture was concentrated and co-evaporated with toluene (2 × 1 mL). The crude product was purified via column chromatography on silica gel using 10% acetone – hexanes to afford the pure product **14** as a colourless syrup (69 mg, 0.15 mmol, quant. yield). $R_f$ 0.38 (acetone: hexanes 1:4). $[\alpha]_D^{20}$: −66° (*c* 0.97, $CHCl_3$). $^1$H NMR ($CDCl_3$, 400 MHz): δH 7.34–7.22 (m, 10H, Ar), 5.77 (dddd, 1H, *J* = 17.2, 10.4, 5.5, 5.5 Hz, $OCH_2CH{=}CH_2$), 5.18 (dddd, 1H, *J* = 17.2, 1.5, 1.5, 1.5 Hz, $OCH_2CH{=}CHaHb$), 5.11 (dddd, 1H, *J* = 10.4, 1.4, 1.4, 1.4 Hz, $OCH_2CH{=}CHa\mathit{Hb}$), 4.79 (d, 1H, *J* = 12.5 Hz, PhC*Ha*Hb), 4.74–4.73 (m, 1H, H-4), 4.60 (d, 1H, *J* = 1.9 Hz, H-1), 4.59 (d, 1H, *J* = 12.0 Hz, PhC*Ha*Hb), 4.55 (d, 1H, *J* = 12.7 Hz, PhCHa*Hb*), 4.45 (d, 1H, *J* = 12.0 Hz, PhCHa*Hb*), 4.15 (ddd, 1H, *J* = 6.4, 6.4, 2.4 Hz, H-5), 4.04 (dddd, 1H, *J* = 12.9, 5.3, 1.4, 1.4 Hz, OC*Ha*HbCH=$CH_2$), 3.98 (dddd, 1H, *J* = 12.9, 5.7, 1.4, 1.4 Hz, OCHa*Hb*CH=$CH_2$), 3.73 (dd, 1H, *J* = 3.7, 3.7 Hz, H-3), 3.69 (dd, 1H, *J* = 9.8, 6.3 Hz, H-6a), 3.65 (dd, 1H, *J* = 9.8, 6.5 Hz, H-6b), 3.52 (s, 3H, OMe), 3.44 (ddd, 1H, *J* = 3.8, 1.7, <1 Hz, H-2), 1.94 (s, 3H, Ac). $^{13}$C NMR ($CDCl_3$, 100 MHz): δC 171.01 (Ac), 138.71 (Ar), 138.30 (Ar), 134.28 ($OCH_2CH{=}CH_2$), 128.61 (Ar), 128.48 (Ar), 128.02 (Ar), 127.99 (Ar), 127.90 (Ar), 127.84 (Ar), 117.71 ($OCH_2CH{=}CH_2$), 101.10 (C-1), 74.90 (C-2), 74.20 (Ph$CH_2$), 74.12 (C-3), 73.69 (Ph$CH_2$), 72.35 (C-5), 71.82 ($OCH_2CH{=}CH_2$), 68.97 (C-6), 68.00 (C-4), 57.04 (OMe), 21.18 (Ac). HRMS *m/z* calc'd for $C_{26}H_{32}O_7$ $(M+NH_4)^+$: 474.2486; found: 474.2493.

### 4.7. Methyl 4-O-acetyl-2,3,6-tri-O-benzyl-β-D-idopyranoside (**15**)

The starting material (**9**, 43 mg, 0.093 mmol) was dissolved into pyridine (0.50 mL) and $Ac_2O$ (0.50 mL) and left mixing at 60 °C. After 3 h, the reaction mixture was concentrated and co-evaporated with toluene (3 × 1 mL). The crude product was purified via column chromatography on silica gel using 10% acetone – hexanes to afford the pure product **15** as a colourless syrup (44 mg, 0.087 mmol, 94% yield). $R_f$ 0.72 (acetone: hexanes 2:3). $[\alpha]_D^{20}$: −54° (*c* 0.95, $CHCl_3$). $^1$H NMR ($CDCl_3$, 400 MHz): δH 7.34–7.20 (m, 15H, Ar), 4.82 (ddd, 1H, *J* = 3.6, 2.5, <1 Hz, H-4), 4.71 (d, 1H, *J* = 12.5 Hz, PhC*Ha*Hb), 4.63 (d, 1H, *J* = 1.8 Hz, H-1), 4.62 (d, 1H, *J* = 11.9 Hz, PhC*Ha*Hb), 4.59, (d, 1H, *J* = 12.2 Hz, PhC*Ha*Hb), 4.52 (d, 1H, *J* = 11.8 Hz, PhCHa*Hb*), 4.50 (d, 1H, *J* = 12.5 Hz, PhCHa*Hb*), 4.45 (d, 1H, *J* = 12.0 Hz, PhCHa*Hb*), 4.20 (ddd, 1H, *J* = 6.4, 6.4, 2.5 Hz, H-5), 3.83 (dd, 1H, *J* = 3.7, 3.7 Hz, H-3), 3.69, (dd, 1H, *J* = 9.9, 6.3 Hz, H-6a), 3.66 (dd, 1H, *J* = 9.9, 6.5 Hz, H-6b), 3.51 (s, 3H, OMe), 3.45 (ddd, 1H, *J* = 3.8, 1.8, <1 Hz, H-2), 1.92 (s, 3H, Ac). $^{13}$C NMR ($CDCl_3$, 100 MHz): δC 171.02 (Ac), 138.61 (Ar), 138.31 (Ar), 137.94 (Ar), 128.64 (Ar), 128.62 (Ar), 128.47 (Ar), 128.08 (Ar), 128.01 (Ar), 127.99 (Ar), 127.92 (Ar), 127.90 (Ar), 127.83 (Ar), 101.03 (C-1), 75.07 (C-2), 74.35 (C-3), 74.09 (Ph$CH_2$), 73.70 (Ph$CH_2$), 72.95 (Ph$CH_2$), 72.37 (C-5), 68.99 (C-6), 67.95 (C-4), 57.04 (OMe), 21.16 (Ac). HRMS *m/z* calc'd for $C_{30}H_{34}O_7$ $(M+Na)^+$: 529.2197; found: 529.2192.

### 4.8. Methyl 3,6-di-O-benzyl-β-D-idopyranoside (**17**) and Methyl 3,4-di-O-benzyl-β-D-idopyranoside (**18**)

A solution of the starting material [8] (**16**, 192 mg, 0.516 mmol) in dry toluene (2.0 mL) was flushed with Ar, cooled to 0 °C in an ice-$H_2O$ bath, and then DIBAL-H solution (1.5 M in toluene, 1.6 mL, 2.4 mmol) was added dropwise. The reaction flask was warmed to rt, and after 2 d diluted with $CH_2Cl_2$ (100 mL). The reaction was quenched with MeOH (5 mL), then washed with 2 N $HCl_{(aq)}$ solution (2 × 100 mL), $H_2O$ (2 × 100 mL), dried with $Na_2SO_4$, filtered, and evaporated to dry. The crude reaction mixture was purified via column chromatography on silica gel using 10 → 15% acetone – hexanes to afford both the 6-*O*-benzyl isomer **17** (127 mg, 0.340 mmol, 66% yield), followed by the 4-*O*-benzyl isomer **18** (38 mg, 0.10 mmol, 19% yield). Data for **17**: $R_f$ 0.39 (EtOAc: hexanes 1:1). $[\alpha]_D^{20}$: −12.9° (*c* 1.01, $CHCl_3$). $^1$H NMR ($CDCl_3$, 400 MHz): δH 7.37–7.25 (m, 10H, Ar), 4.65 (d, 1H, *J* = 0.8 Hz, H-1), 4.61 (d, 1H, *J* = 12.0 Hz, PhC*Ha*Hb), 4.59 (s, 2H, Ph$CH_2$), 4.57 (d, 1H, *J* = 11.9 Hz, PhCHa*Hb*), 4.02 (ddd, 1H, *J* = 5.9, 4.9, 0.9 Hz, H-5), 3.87 (dd, 1H, *J* = 3.0, 3.0 Hz, H-3), 3.82 (dd, 1H, *J* = 10.3, 4.8 Hz, H-6a), 3.83–3.81 (m, 1H, H-2), 3.77 (dd, 1H, *J* = 10.3, 6.0 Hz, H-6b), 3.74 (dddd, 1H, *J* = 9.0, 2.8, 1.1, 1.0 Hz, H-4), 3.69 (d, 1H, *J* = 9.0 Hz, 4-OH), 3.57 (s, 3H, OMe), 2.93 (d, 1H, *J* = 3.3 Hz, 2-OH). $^{13}$C NMR ($CDCl_3$, 100 MHz): δC 138.25 (Ar), 137.80 (Ar), 128.72 (Ar), 128.63 (Ar), 128.20 (Ar), 127.96 (Ar), 127.93 (Ar), 127.77 (Ar), 99.84 (C-1), 76.21 (C-3), 73.94 (Ph$CH_2$), 73.71 (C-5), 72.54 (Ph$CH_2$), 70.69 (C-6), 68.86 (C-2), 67.54 (C-4), 56.87 (OMe). HRMS *m/z* calc'd for $C_{21}H_{26}O_6$ $(M+Na)^+$: 397.1622; found: 397.1616.

Data for **18**: $R_f$ 0.27 (EtOAc: hexanes 1:1). $[\alpha]_D^{20}$: −36.2° (*c* 1.08, $CHCl_3$). $^1$H NMR ($CDCl_3$, 400 MHz): δH 7.39–7.26 (m, 8H, Ar), 7.24–7.19 (m, 2H, Ar), 4.65 (d, 1H, *J* = 1.4 Hz, H-1), 4.65–4.62 (m, 1H, PhC*Ha*Hb), 4.61 (d, 1H, *J* = 11.8 Hz, PhC*Ha*Hb), 4.53 (d, 1H, *J* = 11.9 Hz, PhCHa*Hb*), 4.35 (d, 1H, *J* = 11.7 Hz, PhCHa*Hb*), 3.96–3.92 (m, 1H, H-5), 3.93 (dd, 1H, *J* = 3.4, 3.4 Hz, H-3), 3.89 (ddd, 1H, *J* = 11.0, 7.2, 3.9 Hz, H-6a), 3.77 (dddd, 1H, *J* = 10.8, 3.6, 1.3, 1.3 Hz, H-2), 3.60 (ddd, 1H, *J* = 11.0, 8.6, 4.5 Hz, H-6b), 3.56 (s, 3H, OMe), 3.43–3.39 (m, 1H, H-4), 3.22 (d, 1H, *J* = 10.8 Hz, 2-OH), 1.80 (dd, 1H, *J* = 8.6, 3.9 Hz, 6-OH). $^{13}$C NMR ($CDCl_3$, 100 MHz): δC 137.70 (Ar), 136.90 (Ar), 128.86 (Ar), 128.82 (Ar), 128.63 (Ar), 128.59 (Ar), 128.36 (Ar), 127.97 (Ar), 100.82 (C-1), 74.85 (C-5), 73.97 (C-3), 73.65 (C-4), 72.76 (Ph$CH_2$), 68.78 (C-2), 62.56 (C-6), 57.21 (OMe). HRMS *m/z* calc'd for $C_{21}H_{26}O_6$ $(M+Na)^+$: 397.1622; found: 397.1624.

### 4.9. Methyl 2,4-di-O-acetyl-3,6-di-O-benzyl-β-D-idopyranoside (**19**)

The starting material (**17**, 82 mg, 0.22 mmol) was dissolved into pyridine (0.50 mL) and $Ac_2O$ (0.50 mL) and left mixing at 60 °C. After 3 h, the reaction mixture was evaporated to dry via co-evaporation with toluene (2 × 1 mL). The crude product was purified via column chromatography on silica gel using 15% acetone – hexanes to afford the pure product **19** as a colourless syrup (102 mg, 0.22 mmol, quant. yield). $R_f$ 0.59 (EtOAc: hexanes 1:1). $[\alpha]_D^{20}$: −37.2° (*c* 1.02, $CHCl_3$). $^1$H NMR ($CDCl_3$, 400 MHz): δH 7.38–7.24 (m, 10H, Ar), 4.98 (ddd, 1H, *J* = 3.1, 1.7, 0.9 Hz, H-2), 4.90 (ddd, 1H, *J* = 2.9, 2.0, 0.9 Hz, H-4), 4.75 (d, 1H, *J* = 1.7 Hz, H-1), 4.72 (d, 1H, *J* = 11.8 Hz, PhC*Ha*Hb), 4.68 (d, 1H, *J* = 11.8 Hz, PhCHa*Hb*), 4.59 (d, 1H, *J* = 12.0 Hz, PhC*Ha*Hb), 4.44 (d, 1H, *J* = 12.0 Hz, PhCHa*Hb*), 4.23 (ddd, 1H, *J* = 6.4, 6.4, 1.9 Hz, H-5), 3.83 (dd, 1H, *J* = 3.1, 3.1 Hz, H-3), 3.67 (dd, 1H, *J* = 9.8, 6.3 Hz, H-6a), 3.64 (dd, 1H, *J* = 9.8, 6.6 Hz, H-6b), 3.52 (s, 3H, OMe), 2.07 (s, 3H, Ac), 1.96 (s, 3H, Ac). $^{13}$C NMR ($CDCl_3$, 100 MHz): δC 170.33 (Ac), 170.29 (Ac), 138.15 (Ar), 137.51 (Ar), 128.69 (Ar), 128.64 (Ar), 128.23 (Ar), 128.03 (Ar), 127.97 (Ar), 127.89 (Ar), 98.98 (C-1), 73.86 (C-3), 73.76 (Ph$CH_2$), 73.05 (Ph$CH_2$), 72.32 (C-5), 68.62 (C-6), 67.88 (C-2), 66.99 (C-4), 57.30 (OMe), 21.18 (Ac), 20.97 (Ac). HRMS *m/z* calc'd for $C_{25}H_{30}O_8$ (M+Na)+: 481.1833; found: 481.1829.

### 4.10. Methyl 2,6-di-O-acetyl-3,4-di-O-benzyl-β-D-idopyranoside (**20**)

The starting material (**18**, 27 mg, 0.072 mol) was dissolved into pyridine (0.40 mL) and $Ac_2O$ (0.40 mL) and left mixing at 60 °C. After 3 h, the reaction mixture was concentrated and co-evaporated with toluene (2 × 1 mL). The crude product was purified via column chromatography on silica gel using 15% acetone – hexanes to afford

the pure product **20** as a colourless syrup (33 mg, 0.071 mmol, 98% yield). $R_f$ 0.60 (EtOAc: hexanes 1:1). $[\alpha]_D^{20}$: −19.6° (*c* 1.02, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHz): δH 7.38–7.24 (m, 8H, Ar), 7.23–7.18 (m, 2H, Ar), 4.90 (ddd, 1H, *J* = 4.8, 2.4, <1 Hz, H-2), 4.77 (d, 1H, *J* = 2.4 Hz, H-1), 4.70 (d, 1H, *J* = 11.8 Hz, PhC*Ha*Hb), 4.62 (d, 1H, *J* = 11.8 Hz, PhCHa*Hb*), 4.49 (d, 1H, *J* = 11.7 Hz, PhC*Ha*Hb), 4.38 (d, 1H, *J* = 11.8 Hz, PhCHa*Hb*), 4.37 (dd, 1H, *J* = 11.4, 7.4 Hz, H-6a), 4.33 (dd, 1H, *J* = 11.5, 5.6 Hz, H-6b), 4.11 (ddd, 1H, *J* = 7.3, 5.6, 3.2 Hz, H-5), 3.94 (dd, 1H, *J* = 4.8, 4.8 Hz, H-3), 3.50 (s, 3H, OMe), 3.43–3.40 (m, 1H, H-4), 2.02 (s, 3H, Ac), 2.00 (s, 3H, Ac). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δC 171.06 (Ac), 170.92 (Ac), 137.88 (Ar), 137.70 (Ar), 128.73 (Ar), 128.61 (Ar), 128.24 (Ar), 128.20 (Ar), 128.15 (Ar), 128.08 (Ar), 99.04 (C-1), 74.25 (C-4), 73.59 (Ph$CH_2$), 72.90 (C-3), 72.65 (C-5), 72.62 (Ph$CH_2$), 69.23 (C-2), 63.76 (C-6), 57.04 (OMe), 21.27 (Ac), 21.07 (Ac). HRMS *m/z* calc'd for $C_{25}H_{30}O_8$ $(M+Na)^+$: 481.1833; found: 481.1831.

### 4.11. Methyl 2,3,4-tri-O-benzyl-β-D-idopyranoside (**11**) and 2,3,4-tri-O-benzyl-1-O-methyl-D-iditol (**21**)

The starting material [8] (**7**, 103 mg, 0.222 mmol) was dissolved into dry $CH_2Cl_2$ (1.0 mL), cooled to 0 °C, and then $BH_3$·THF solution (1 M in THF, 1.00 mL, 1.00 mmol) and TMSOTf (6 μL, 0.03 mmol) were added dropwise. The solution was slowly warmed back to rt, and after 2 h was neutralized with $Et_3N$ (to pH 8), quenched with $H_2O$ (2 mL), and diluted with $CH_2Cl_2$ (30 mL). The organic phase was washed with saturated $NaCl_{(aq)}$ solution (2 × 30 mL), $H_2O$ (30 mL), dried with $Na_2SO_4$, filtered, and evaporated to dry. The crude mixture was purified via column chromatography on silica using 10 → 15 → 20% acetone − hexanes to afford by-product **21** as a colourless syrup (86 mg, 0.18 mmol, 83% yield). Alternatively, if the same reaction was left at 0 °C instead of warmed to rt, the desired product **11** was obtained in similar yields. Data for **21**: $R_f$ 0.50 (acetone: hexanes 2:3). $[\alpha]_D^{20}$: −20° (*c* 0.99, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHz): δH 7.34–7.24 (m, 15H, Ar), 4.79 (d, 1H, *J* = 11.2 Hz, PhC*Ha*Hb), 4.73 (d, 1H, *J* = 11.8 Hz, PhC*Ha*Hb), 4.70 (d, 1H, *J* = 11.6 Hz, PhC*Ha*Hb), 4.62 (d, 1H, *J* = 11.4 Hz, PhCHa*Hb*), 4.54 (d, 1H, *J* = 11.8 Hz, PhCHa*Hb*), 4.52 (d, 1H, *J* = 11.2 Hz, PhCHa*Hb*), 3.88 (dd, 1H, *J* = 7.2, 3.9 Hz, H-3), 3.77 (ddd, 1H, *J* = 5.1, 5.1, 4.0 Hz, H-2), 3.64 (dd, 1H, *J* = 7.2, 3.0 Hz, H-4), 3.59–3.51 (m, 3H, H-1a, H-1b, and H-5), 3.50 (ddd, 1H, *J* = 11.0, 6.2, 4.5 Hz, H-6a), 3.38 (ddd, 1H, *J* = 11.0, 8.4, 4.4, H-6b), 3.27 (s, 3H, OMe), 2.61 (d, 1H, *J* = 6.7 Hz, 5-OH), 1.85 (dd, 1H, *J* = 8.3, 4.4 Hz, 6-OH). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δC 138.35 (Ar), 138.33 (Ar), 138.16 (Ar), 128.73 (Ar), 128.67 (Ar), 128.63 (Ar), 128.58 (Ar), 128.57 (Ar), 128.51 (Ar), 128.21 (Ar), 128.08 (Ar), 128.05 (Ar), 79.50 (C-4), 78.97 (C-3), 76.83 (C-2), 75.02 (Ph$CH_2$), 74.83 (Ph$CH_2$), 72.98 (Ph$CH_2$), 72.45 (C-1), 71.24 (C-5), 64.52 (C-6), 59.24 (OMe). HRMS *m/z* calc'd for $C_{28}H_{34}O_6$ $(M+Na)^+$: 489.2248; found: 489.2264.

### 4.12. Methyl 2,3-di-O-benzyl-6-O-(tert-butyldimethylsilyl)-β-D-idopyranoside (**23**)

The starting material [8] (**22**, 323 mg, 0.864 mmol) and *tert*-butyldimethylsilyl chloride (219 mg, 1.45 mmol) in dry pyridine (3.0 mL) were left mixing at rt under Ar. After 12 h, the reaction mixture was quenched with MeOH (1 mL), and then evaporated to dry via co-evaporation with toluene (2 × 1 mL). The crude mixture was purified via column chromatography on silica using 10% acetone − hexanes to afford the pure product **23** as a colourless syrup (402 mg, 0.823 mmol, 95% yield). $R_f$ 0.79 (acetone: hexanes 2:3). $[\alpha]_D^{20}$: −77.2° (*c* 1.06, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHz): δH 7.36–7.20 (m, 10H, Ar), 4.82 (d, 1H, *J* = 12.2 Hz, PhC*Ha*Hb), 4.64 (d, 1H, *J* = 0.9 Hz, H-1), 4.60 (d, 1H, *J* = 12.2 Hz, PhCHa*Hb*), 4.49 (d, 1H, *J* = 11.9 Hz, PhC*Ha*Hb), 4.44 (d, 1H, *J* = 11.9 Hz, PhCHa*Hb*), 3.91 (dd, 1H, *J* = 8.9, 6.4 Hz, H-6a), 3.86 (ddd, 1H, *J* = 7.2, 6.3, 1.0 Hz, H-5), 3.81–3.76 (m, 2H, H-6b and H-3), 3.66 (dddd, 1H, *J* = 11.8, 2.9, 1.2, 1.2 Hz, H-4), 3.59 (ddd, 1H, *J* = 3.3, 1.1, 1.1 Hz, H-2), 3.54 (s, 3H, OMe), 3.42 (d, 1H, *J* = 11.8 Hz, 4-OH), 0.89 (s, 9H, $C(CH_3)_3$), 0.07 (s, 6H, SiMe). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δC 137.83 (Ar), 137.82 (Ar), 128.69 (Ar), 128.61 (Ar), 128.25 (Ar), 128.15 (Ar), 128.10 (Ar), 127.82 (Ar), 101.21 (C-1), 76.08 (C-3), 76.00 (C-5), 75.03 (C-2), 74.31 (Ph$CH_2$), 72.27 (Ph$CH_2$), 66.23 (C-4), 62.26 (C-6), 57.12 (OMe), 26.10 ($C(CH_3)_3$), 18.49 ($C(CH_3)_3$), −5.10 (SiMe), −5.17 (SiMe). HRMS *m/z* calc'd for $C_{27}H_{40}O_6Si$ $(M+Na)^+$: 511.2486; found: 511.2490.

### 4.13. Methyl 2,3,4-tri-O-benzyl-6-O-(tert-butyldimethylsilyl)-β-D-idopyranoside (**24**)

The starting material (**23**, 402 mg, 0.823 mmol), benzyl bromide (0.18 mL, 1.5 mmol), and NaH (57–63% oil dispersion, 85 mg, 2.1 mmol) in dry THF (5 mL) were left mixing at rt under Ar. After 14 h, the reaction mixture was quenched with MeOH (1 mL), evaporated to dry, and then redissolved into EtOAc (50 mL). The organic phase was washed with saturated $NaCl_{(aq)}$ solution (2 × 50 mL), dried with $Na_2SO_4$, filtered, and evaporated to dry. The crude material was purified via column chromatography on silica using 10% acetone − hexanes to afford the pure product **24** as a colourless syrup (495 mg, 0.856 mmol, quant. yield). $R_f$ 0.78 (acetone: hexanes 2:3). $[\alpha]_D^{20}$: −22.4° (*c* 1.02, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHz): δH 7.34–7.20 (m, 15H, Ar), 4.74 (d, 1H, *J* = 12.5 Hz, PhC*Ha*Hb), 4.66 (d, 1H, *J* = 12.5 Hz, PhCHa*Hb*), 4.61 (d, 1H, *J* = 11.9 Hz, PhC*Ha*Hb), 4.59 (d, 1H, *J* = 2.7 Hz, H-1), 4.56 (d, 1H, *J* = 11.5 Hz, PhC*Ha*Hb), 4.52 (d, 1H, *J* = 11.9 Hz, PhCHa*Hb*), 4.50 (d, 1H, *J* = 11.4 Hz, PhCHa*Hb*), 3.94–3.89 (m, 3H, H-5, H-6a, and H-6b), 3.77 (dd, 1H, *J* = 5.8, 5.8 Hz, H-3), 3.54–3.50 (m, 4H, H-4 and OMe), 3.48 (dd, 1H, *J* = 5.9, 2.7 Hz, H-2), 0.89 (s, 9H, $C(CH_3)_3$), 0.06 (s, 3H, SiMe), 0.05 (s, 3H, SiMe). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δC 138.90 (Ar), 138.60 (Ar), 138.46 (Ar), 128.58 (Ar), 128.48 (Ar), 128.46 (Ar), 128.24 (Ar), 128.20 (Ar), 128.06 (Ar), 127.93 (Ar), 127.80 (Ar), 127.79 (Ar), 100.84 (C-1), 76.76 (C-2), 76.21 (C-5), 75.94 (C-3), 75.64 (C-4), 73.88 (Ph$CH_2$), 73.00 (Ph$CH_2$), 62.57 (C-6), 56.79 (OMe), 26.16 ($C(CH_3)_3$), 18.50 ($C(CH_3)_3$), −5.06 (SiMe), −5.11 (SiMe). HRMS *m/z* calc'd for $C_{34}H_{46}O_6Si$ $(M+Na)^+$: 601.2956; found: 601.2951.

### 4.14. Methyl 2,3,4-tri-O-benzyl-β-D-idopyranoside (**11**)

The starting material (**24**, 508 mg, 0.877 mmol) and tetrabutyl ammonium fluoride solution (1 M in THF, 1.00 mL, 1.00 mmol) in dry THF (5.0 mL) were left mixing at rt under Ar. After 2 h the reaction mixture was evaporated to dry, and the crude material purified via column chromatography on silica using 14 → 20% acetone − hexanes to afford the pure product **11** as a colourless syrup (405 mg, 0.872 mmol, quant. yield); characterization of the product agreed with the previously published literature [12,13]. $R_f$ 0.42 (acetone: hexanes 2:3). $[\alpha]_D^{20}$: −20.5° (*c* 1.03, $CHCl_3$). $^1H$ NMR ($CDCl_3$, 400 MHz): δH 7.37–7.24 (m, 15H, Ar), 4.80 (d, 1H, *J* = 11.1 Hz, PhC*Ha*Hb), 4.76 (d, 1H, *J* = 11.7 Hz, PhC*Ha*Hb), 4.74 (d, 1H, *J* = 12.1 Hz, PhC*Ha*Hb), 4.71 (d, 1H, *J* = 11.0 Hz, PhCHa*Hb*), 4.67 (d, 1H, *J* = 12.2 Hz, PhCHa*Hb*), 4.55 (d, 1H, *J* = 11.6 Hz, PhCHa*Hb*), 4.53 (d, 1H, *J* = 3.3 Hz, H-1), 4.03 (dd, 1H, *J* = 7.9, 7.9 Hz, H-3), 3.96 (ddd, 1H, *J* = 5.4, 5.4, 5.4 Hz, H-5), 3.90 (ddd, 1H, *J* = 12.0, 5.1, 5.1 Hz, H-6a), 3.82 (ddd, 1H, *J* = 12.0, 8.2, 5.3 Hz, H-6b), 3.63 (dd, 1H, *J* = 7.8, 5.5 Hz, H-4), 3.47 (dd, 1H, *J* = 7.9, 3.5 Hz, H-2), 3.47 (s, 3H, OMe), 2.68 (dd, 1H, *J* = 8.1, 5.0 Hz, 6-OH). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δC 138.63 (Ar), 138.47 (Ar), 138.04 (Ar), 128.71 (Ar), 128.65 (Ar), 128.64 (Ar), 128.30 (Ar), 128.24 (Ar), 128.16 (Ar), 128.09 (Ar), 127.96 (Ar), 100.16 (C-1), 78.45 (C-2), 78.08 (C-4), 77.17 (C-3), k75.30 (C-5), 75.11 (Ph$CH_2$), 74.01 (Ph$CH_2$), 73.95 (Ph$CH_2$), 63.38 (C-6), 57.14 (OMe). HRMS *m/z* calc'd for $C_{28}H_{32}O_6$ $(M+Na)^+$: 487.2091; found:

487.2082.

### 4.15. Methyl 2,3,4-tri-O-benzyl-β-D-ido-hexodialdo-1,5-pyranoside (**25**)

A solution of oxalyl chloride (0.13 mL, 1.5 mmol) in dry $CH_2Cl_2$ (2.0 mL) was cooled to −78 °C, and then a solution of DMSO (0.16 mL, 2.3 mmol) in dry $CH_2Cl_2$ (1.0 mL) was slowly added. The mixture was left at −78 °C for 10 min, and then a solution of alcohol **11** (338 mg, 0.728 mmol) in dry $CH_2Cl_2$ (3.0 mL) was added to the reaction mixture, and the latter flask rinsed with $CH_2Cl_2$ (2 × 0.3 mL). After an additional 15 min at −78 °C, $Et_3N$ (0.60 mL, 4.3 mmol) was added, and then the reaction mixture warmed back to rt. Saturated $NaCl_{(aq)}$ solution (50 mL) was added to quench the reaction, the mixture diluted further with $CH_2Cl_2$ (50 mL), and then the aqueous layer drained. The organic phase was washed further with saturated $NaCl_{(aq)}$ solution (50 mL), $H_2O$ (50 mL), dried with $Na_2SO_4$, filtered, and evaporated to dry to obtain the crude product **25** as a colourless syrup, which was used directly for the subsequent step; characterization based on the crude $^1$H NMR agreed with the previously published literature [12,13].

### 4.16. Methyl 2,3-di-O-benzyl-4-deoxy-β-D-arabino-hex-4-en-dialdo-1,5-pyranoside (**27**)

A solution of the benzyloxymethyltriphenylphosphonium chloride salt (prepared by refluxing a solution of benzyl chloromethyl ether and $PPh_3$ in toluene, 423 mg, 1.01 mmol) and *n*-BuLi (1.6 M in hexanes, 0.67 mL, 1.1 mmol) in toluene (1.00 mL) was left under Ar for 30 min, and then a solution of the aldehyde (**25**, 95 mg, 0.21 mmol) in dry toluene (0.40 mL) was added. After 1 h, the reaction mixture was diluted with EtOAc (60 mL), washed with saturated $NaCl_{(aq)}$ solution (2 × 60 mL), water (60 mL), dried with $Na_2SO_4$, filtered, and evaporated to dry. The crude product was purified by column chromatography on silica gel using 10 → 15% acetone − hexanes to unexpectedly afford by-product **27** (67 mg, 0.12 mmol, 58% yield). Data for **27**: $R_f$ 0.93 (EtOAc: toluene 1:1). $[\alpha]_D^{20}$: $(1.3 \times 10^2)^\circ$ (*c* 1.1, $CHCl_3$). $^1$H NMR ($CDCl_3$, 600 MHz): δH 9.17 (s, 1H, H-6), 7.36–7.27 (m, 10H, Ar), 5.85 (d, 1H, $J$ = 2.7 Hz, H-4), 4.92 (d, 1H, $J$ = 2.6 Hz, H-1), 4.81 (d, 1H, $J$ = 12.1 Hz, PhC*Ha*Hb), 4.75 (d, 1H, $J$ = 11.6 Hz, PhC*Ha*Hb), 4.71 (d, 1H, $J$ = 12.1 Hz, PhCHa*Hb*), 4.70 (d, 1H, $J$ = 11.6 Hz, PhCHa*Hb*), 4.47 (dd, 1H, $J$ = 8.1, 2.7 Hz, H-3), 3.79 (dd, 1H, $J$ = 8.1, 2.6 Hz, H-2), 3.45 (s, 3H, OMe). $^{13}$C NMR ($CDCl_3$, 150 MHz): δC 186.23 (C-6), 148.60 (C-5), 138.08 (Ar), 137.94 (Ar), 128.79 (Ar), 128.78 (Ar), 128.35 (Ar), 128.20 (Ar), 128.06 (Ar), 120.57 (C-4), 100.05 (C-1), 76.56 (C-2), 73.72 (Ph*C*$H_2$), 73.51 (C-3), 72.85 (Ph*C*$H_2$), 57.18 (OMe). HRMS *m/z* calc'd for $C_{21}H_{22}O_5$ $(M+NH_4)^+$: 372.1806; found: 372.1806.

### 4.17. Methyl 2,3,4-tri-O-benzyl-6,7-dideoxy-β-D-ido-hept-6-enopyranoside (**28**)

A solution of the phosphonium salt (1092 mg, 3.06 mmol) and *n*-BuLi (1.5 M in hexanes, 1.8 mL, 2.7 mmol) in toluene (4.0 mL) was left under Ar for 30 min, and then a solution of the crude aldehyde (**25**, began previous step with 0.728 mmol) was added. After 1 h, the reaction mixture was diluted with EtOAc (60 mL), washed with saturated $NaCl_{(aq)}$ solution (2 × 60 mL), dried with $Na_2SO_4$, filtered, and evaporated to dry. The crude product was purified by column chromatography on silica gel using 8 → 10 → 15% EtOAc − hexanes to afford the desired product **28** as a colourless syrup (181 mg, 0.393 mmol, 54% yield over 2 steps); characterization agreed with the previously published literature [12,13]. $R_f$ 0.75 (acetone: hexanes 2:3). $[\alpha]_D^{20}$: −6.0° (*c* 0.98, $CHCl_3$). $^1$H NMR ($CDCl_3$, 400 MHz): δC 7.37–7.24 (m, 15H, Ar), 6.28 (ddd, 1H, $J$ = 17.0, 9.8, 9.8 Hz, H-6), 5.34–5.24 (m, 2H, H-7a and H-7b), 4.82 (d, 1H, $J$ = 10.9 Hz, PhC*Ha*Hb), 4.78 (d, 1H, $J$ = 10.9 Hz, PhCHa*Hb*), 4.77 (d, 1H, $J$ = 12.4 Hz, PhC*Ha*Hb), 4.67 (d, 1H, $J$ = 12.2 Hz, PhCHa*Hb*), 4.61 (d, 1H, $J$ = 11.7 Hz, PhC*Ha*Hb), 4.57 (d, 1H, $J$ = 11.5 Hz, PhCHa*Hb*), 4.56 (d, 1H, $J$ = 3.6 Hz, H-1), 4.27 (dd, 1H, $J$ = 9.6, 6.0 Hz, H-5), 4.02 (dd, 1H, $J$ = 8.7, 8.7 Hz, H-3), 3.61 (dd, 1H, $J$ = 8.7, 5.9 Hz, H-4), 3.48 (dd, 1H, $J$ = 8.8, 3.6 Hz, H-2), 3.36 (s, 3H, OMe). $^{13}$C NMR ($CDCl_3$, 100 MHz): δC 138.94 (Ar), 138.59 (Ar), 138.37 (Ar), 136.43 (C-6), 128.60 (Ar), 128.57 (Ar), 128.52 (Ar), 128.28 (Ar), 128.22 (Ar), 128.00 (Ar), 127.92 (Ar), 127.84 (Ar), 120.05 (C-7), 99.99 (C-1), 79.04 (C-2), 78.95 (C-4), 77.62 (C-3), 77.01 (C-5), 75.60 (Ph*C*$H_2$), 73.79 (Ph*C*$H_2$), 72.92 (Ph*C*$H_2$), 56.12 (OMe). HRMS *m/z* calc'd for $C_{16}H_{22}O_7$ $(M+Na)^+$: 483.2142; found: 483.2143.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carres.2017.04.007.

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