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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.0c01170 • Publication Date (Web): 26 Jun 2020

Selective Synthesis of Some Aminosugars *via* Catalytic Aminohydroxylation of Protected 2,3-Unsaturated D-Gluco- and D-Galacto-2-hexenopyranosides

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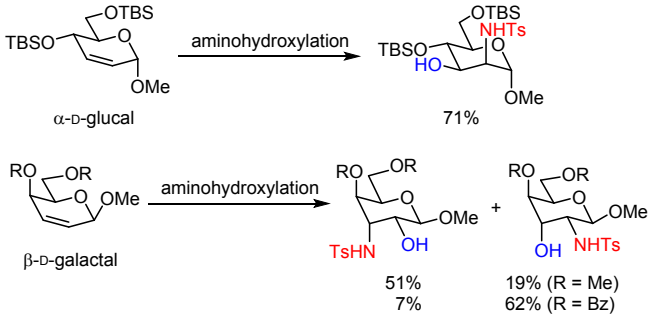
Supporting Information Placeholder



ABSTRACT: The aminohydroxylation of methyl 4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-unsaturated α-D-glucopyranoside proceeds in the presence of chloramine-T, OsO_4 (4 mol%), $(DHQ)_2PHAL$ (5 mol%), and TEBAC (triethylbenzylammonium chloride) in both a stereo- and regioselective manner to produce protected methyl α-D-mannosamide as the sole product. In contrast, the reaction of methyl 2,3-unsaturated β-D-galactopyranoside under the same conditions produced a mixture of regioisomers, although the stereochemistry was perfectly controlled. The regioisomeric ratio was dependent on the nature of the protecting group and ligand used.

INTRODUCTION

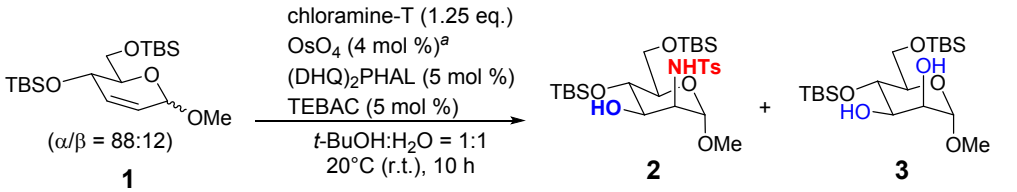
Aminosugar moieties are often found in natural and unnatural compounds.[1,2] For example, D-glucosamine is a main constitutent of bacterial peptidoglycan, fungal and insect chithin, and mammalian glycoproteins.

Furthermore, a few carbohydrates containing aminosugars, such as sialyl acids,[3] anthracycline antibiotics,[4] kanamycin,[5] and pyranmycins[6] have been also reported. In contrast, rare sugars have been recognized as functional biological compounds because of their application as low-calorie sweeteners, antioxidants, inhibitors of various glycosidases, and so on.[7,8] In 2016, we reported the selective synthesis of D-talopyranosides and D-gulopyranosides using asymmetric dihydroxylation. In these reactions, a complete reversal of the diastereoselectivity was observed in the reaction using protected 2,3-unsaturated D-galactopyranoside due to the protecting group selected, which led to the selective formation of D-talopyranoside and D-gulopyranoside.[9] When *O*-benzoyl-protected 2,3-unsaturated D-galactopyranoside was used as a substrate, D-talopyranoside was obtained as the predominant product. In contrast to the dihydroxylation of 2,3-unsaturated sugars, aminohydroxylation requires control over not only the stereoselectivity, but also the regioselectivity of the reaction.[10] In 1977, Dyong and co-workers reported reaction of 3,4,6-tri-*O*-acetyl-D-glucal (1,2-unsaturated) with chroramine-T, the sodium salt of *N*-chloro-*p*-toluenesulfonamide in the presence of OsO_4 to afford to mixture of four products, those were regio- and stereoisomers of 1-amino-2-hydroxy and 1-hydroxy-2-amino sugars.[11] In 1995, Matsumoto et al. reported the aminohydroxylation of 3,4-unsaturated sugars to afford a regioisomeric mixture of 3-amino-4-hydroxy and 3-hydroxy-4-amino sugars using OsO_4 and chroramine-T.[12] However, the authors did not examine the reaction in the presence of a chiral ligand. In 2015, Cadona and Goti reported the tethered aminohydroxylation of D-glycals. The reaction included the $K_2OsO_2(OH)_4$ oxidation of carbamate to give oxazolidinone, followed by hydrolysis using $LiOH/H_2O$ to afford the target 2- and 3-aminosugars.[13] This paper reports the synthesis of D-aminosugars including *rare* aminosugars using asymmetric catalytic aminohydroxylation[14-16] of 2,3-unsaturated D-gluco- and D-galacto-2-hexenopyranosides (2,3-unsaturated D-glucopyranoside and 2,3-unsaturated D-galactopyranoside). Most of the reported methods use 1,2-unsaturated D-glucopyranoside (D-glucal) as a substrate, whereas, in our case, 2,3-unsaturated D-glucopyranoside and 2,3-unsaturated D-galactopyranoside were used those led high regio- and stereoselective synthesis of aminosugars.

RESULTS AND DISCUSSION

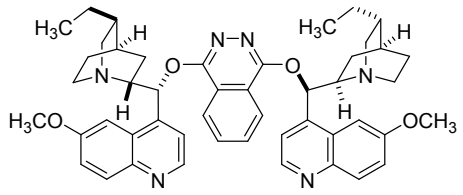
Initially, we attempted the reaction of methyl 4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-unsaturated D-glucopyranoside (α/β = 88:12) using chloramine-T (1.25 eq.), OsO_4 (4 mol%), $(DHQ)_2PHAL$ (5 mol%), and TEBAC (triethylbenzylammonium chloride), which serve as a phase transfer (PT) catalyst. The results of our optimization study are summarized in Table 1.

Table 1. Catalytic Aminohydroxylation of Methyl 4,6-di-*O*-(*tert*-Butyldimethylsilyl)-2,3-Unsaturated D-Glucopyranoside

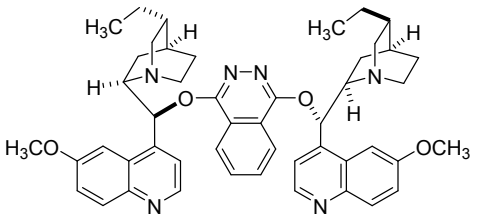


entry	variation from above	yield (%)[b] 2	3
1	—	72	11
2	at 58 °C	43	24
3	at 0 °C	56	5
4	$K_2OsO_4{\cdot}2H_2O$ instead of OsO_4	30	31
5	no TEBAC	73	11
6	Only α isomer of substrate **1** was used.	71	6
7	Only α isomer of substrate **1** was used. $(DHQD)_2PHAL$ instead of $(DHQ)_2PHAL$	67	11
8	Only α isomer of substrate **1** was used. quinuclidine instead of $(DHQ)_2PHAL$	33	60

[a] 1% OsO_4 in *tert*-butyl alcohol solution containing 0.35% of *tert*-butyl hydroperoxide.
[b] Isolated yield. The ratio of **2** and **3** was determined by ^1H NMR analysis.



$(DHQ)_2PHAL$

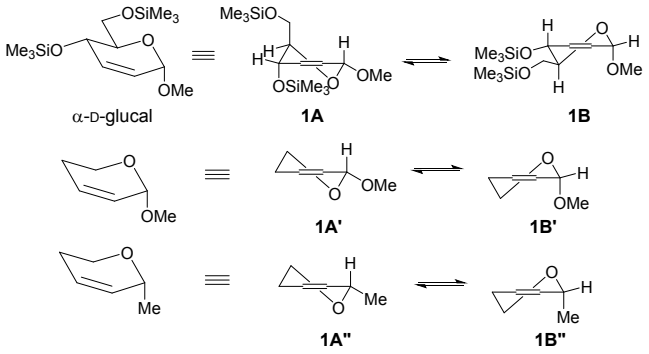


$(DHQD)_2PHAL$

The reaction proceeds via an imidotorioxoosmium (VIII) species, followed by a [3+2] cylcoaddition reaction and hydrolysis to afford the aminohydroxylated product.[17,18] In most cases, protected methyl-D-mannosamide **2** was predominantly accompanied by the formation of protected methyl α-D-mannopyranoside **3**.The best result was obtained under the conditions shown in entry 6. In all cases, both the stereoselectivity and regioselectivity were controlled perfectly in the aminohydroxylation reaction.[19] As for the effect of reaction temperature, we found room temperature (20 ^{O}C) was the best choice to obtain desired amino sugar **2** (entry 1–3). As an osmium source, the use of OsO_4 solution (see Experimental Section) afforded higher yield than the use of $K_2OsO_4.2H_2O$ (entry 4). The effect of the addition of phase transfer catalyst (PTC) such as TEBAC was proved to suppress the formation of undesired diol product (entery 5). Judging from the results from entries 6-8, the use of only α-isomer as a substrate gave higher yield. The use of $(DHQ)_2PHAL$ as a ligand afforded the best result, this may be because of the matching effect of substrate control and catalyst control.

The obtained region- and stereoselectivity may be explained by considering the conformation of substrate **1**. We calculated the difference in the stability of the two possible conformations of methyl 2,3-unsaturated α-D-glucopyranoside and its derivatives (Table 2). The $^{0}H_5$ conformer of trimethylsilyl-protected 2,3-unsaturated methyl-D-glucopyranoside was found to be 6 kcal/mol more stable than its corresponding $^{5}H_0$ conformer. In addition, for the compound possessing only a methoxy group at the anomeric position, the $^{0}H_5$ conformer was 2 kcal/mol more stable than the $^{5}H_0$ conformer, whereas for the compound possessing a methyl group at the anomeric position, the $^{0}H_5$ conformer was 1.2 kcal/mol less stable than its $^{5}H_0$ conformer (See, Supporting Information). We notice that we should give cation to discuss the relationship between the difference of calculated ground state energy and distribution of products. However, the values shown in Table 2 would support the explanation of regio- and stereoselectivity of the results in Table 1. It should be noted in the case of methyl group instead of methoxy group at anomeric position, the stabilization by anomeric effect was not observed.

Table 2. Conformations of 2,3-Unsaturated D-Glucopyranoside Derivatives



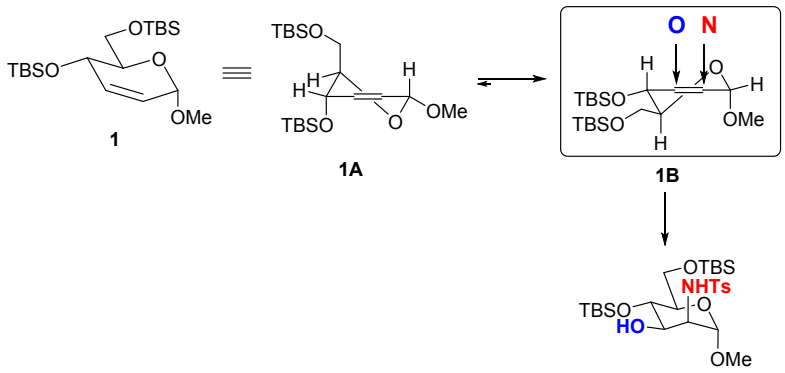
substrate	**A**	**B**
2,3-unsaturated-α-D-glucopyranoside (**1A**, **1B**)	0.0	–6.0
2-α-methoxy-3,4-dihydropyran (**1A'**, **1B'**)	0.0	–2.6
2-α-methyl-3,4-dihydropyran (**1A"**, **1B"**)	0.0	+1.2

kcal/mol

LC-BLYP/6-31G(d) (in gas phase)

Our conformational analysis showed that both "N (NTs)" and "O" approach from the less hindered top-side of the double bond (Scheme 1). Concerning the perfect regioselectivity, it may be explained the bulky "N (NTs)" favored less hindered C2-position.[20] As for the generation of dihydroxylated diol **3**, another catalytic cycle (cycle AD) accompanies cycle AA, as shown in Scheme 2, which shows the catalytic cycle for the reaction of methyl 4,6-di-*O*-protected-2,3-unsaturated β-D-galactopyranoside (Table 3).

Scheme 1. Origin of the Regio- and Stereoselectivity of the Aminohydroxylation Reaction



Subsequently, we examined the reaction of methyl 4,6-di-*O*-(*t*-butyldimethylsilyl)-2,3-unsaturated α-D-galactopyranoside. However, the reactivity of α-D-galactopyranoside in the aminohydroxylation reaction was lower when compared with α-D-glucopyranoside, and starting material **4** remained unreacted even upon increasing the amounts of OsO_4 and $(DHQ)_2PHAL$ used in the reaction. In addition, the formation of the diol product was observed when using α-D-galactopyranoside derivatives in the reaction, particularly for the benzoyl protected substrates (SI Table 1). Therefore, we changed the substrate from 4,6-protected α-D-galactopyranoside to β-D-galactopyranoside.[21] The results are summarized in Table 3.

Scheme 2. Catalytic Cycle for the Formation of the *N*-Tosyl Amino Alcohol (5βa–5βf and 6βa–6βf) and Diol (7βa–7βf)

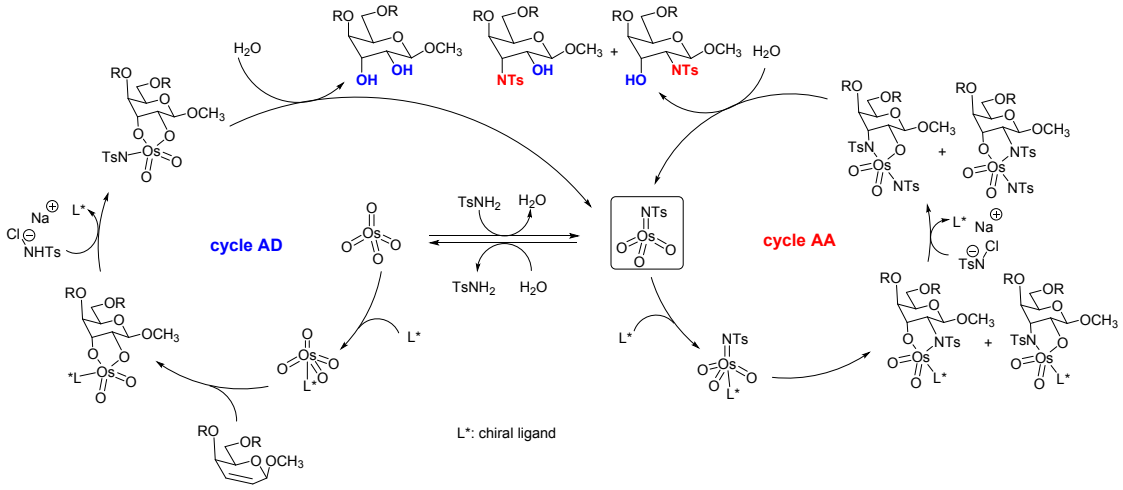
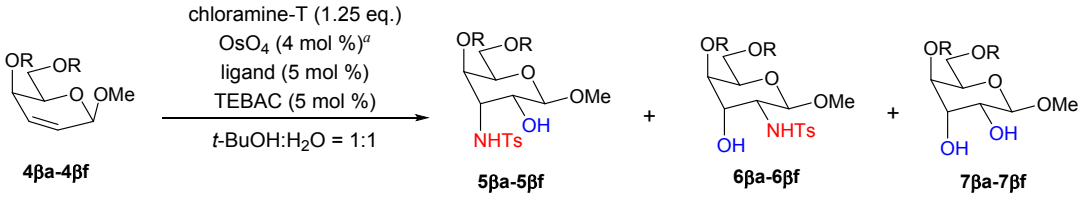


Table 3. Aminohydroxylation of Methyl 4,6-di-*O*-Protected 2,3-Unsaturated β-D-Galactopyranosides



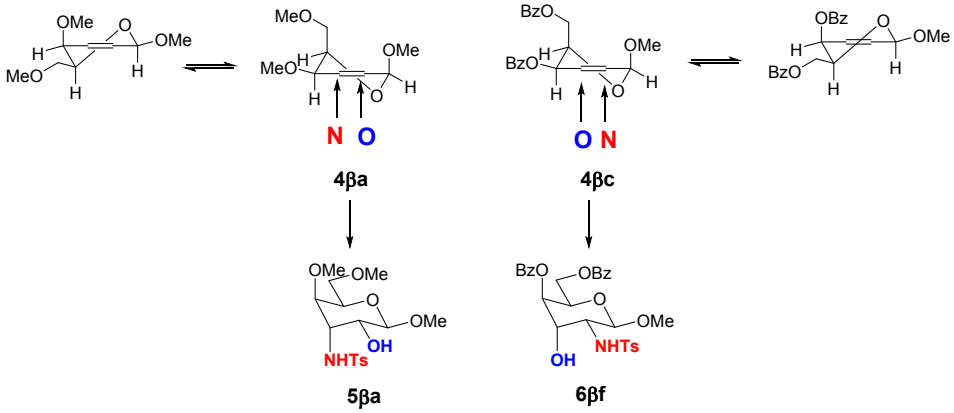
entry	ligand (5 mol %)	R	time/h	yield[b] 5βa-5βf	6βa-6βf	7βa-7βf
1	none	Me (**4βa**)	6	14	15	2
2	none	Bn (**4βb**)	4	22	19	35
3	none	Bz (**4βc**)	24	4	14	67
4	none	Piv (**4βd**)	24	5	16	62
5	none	TBS (**4βe**)	3	30	25	13
6	none	TBDPS (**4βf**)	24	16	41	13
7	quinuclidine	Me (**4βa**)	4	21	16	0
8	quinuclidine	Bn (**4βb**)	6	30	19	17
9	quinuclidine	Bz (**4βc**)	6	6	20	43
10	quinuclidine	Piv (**4βd**)	9	12	31	37
11	quinuclidine	TBS (**4βe**)	12	35	25	16
12	quinuclidine	TBDPS (**4βf**)	6	7	22	11
13	$(DHQ)_2PHAL$	Me (**4βa**)	4	51	19	0
14	$(DHQ)_2PHAL$	Bn (**4βb**)	3	47	24	6
15	$(DHQ)_2PHAL$	Bz (**4βc**)	6	37	28	19
16	$(DHQ)_2PHAL$	Piv (**4βd**)	6	34	42	11
17	$(DHQ)_2PHAL$	TBS (**4βe**)	24	52	23	4
18	$(DHQ)_2PHAL$	TBDPS (**4βf**)	48	16	41	12
19	$(DHQD)_2PHAL$	Me (**4βa**)	7	20	27	0
20	$(DHQD)_2PHAL$	Bn (**4βb**)	5	29	31	5
21	$(DHQD)_2PHAL$	Bz (**4βc**)	8	7	62	17
22	$(DHQD)_2PHAL$	Piv (**4βd**)	5	7	56	14
23	$(DHQD)_2PHAL$	TBS (**4βe**)	24	48	25	2
24	$(DHQD)_2PHAL$	TBDPS (**4βf**)	24	7	26	4

[a] 1% OsO_4 in *tert*-butyl alcohol solution containing 0.35% of *tert*-butyl hydroperoxide. [b] Yield was determined by ^1H NMR analysis for each product based on starting materials, then each product (**5**, **6**, and **7**) was separated by silica-gel column chromatography.

The results show the nature of the protecting group R influences the regioselectivity of the reaction.[19] The regioselectivity may be controlled by the synergistic effect between the stereo- and electronic effects of the substrate[19a] and the nature of the ligand used in the reaction. The highest selectivity observed for 3-*N*-tosyl-2-hydroxy product **5βa** was obtained in the case of the smallest protecting group

(R = Me). The reaction may proceed via conformer of **4A**,[22] whereas the highest selectivity observed for 2-*N*-tosyl-3-hydroxy product **6βf** was obtained when R = Bz (Scheme 3). Upon comparing the reaction performed in the presence and absence of the ligand, it is clear that the use of a ligand remarkably increases the yield of the aminohydroxylated product obtained. Among the ligands studied (quinuclidine, $(DHQ)_2PHAL$, and $(DHQD)_2PHAL$), the chiral $(DHQ)_2PHAL$ and $(DHQD)_2PHAL$ ligands enhance both the reactivity and selectivity. For example, when methoxy-protected 2,3-unsaturated α-D-galactopyranoside **4βa** was used as the substrate, the use of quinuclidine afforded the 3-*N*-tosyl-2-hydroxy product **5βa** and 2-*N*-tosyl-3-hydroxy product **6βa** in 21 and 16% yield, respectively. When $(DHQ)_2PHAL$ was used instead of quinuclidine, **5βa** and **6βa** were obtained in 51 and 19% yield, respectively (The ratio of **5βa**/**6βa** was 73:27). The use of $(DHQD)_2PHAL$ gave **5βa** and **6βa** in 7 and 62% yield, respectively for benzoyl-protected 2,3-unsaturated α-D-galactopyranoside **6βc** (The ratio of **5βa**/**6βc** was 10:90).

Scheme 3. Origin of the Stereo- and Regioselectivity in the Aminohydroxylation Reaction



In summary, the aminohydroxylation of methyl 4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-unsaturated α-D-glucopyranoside proceeded in both a stereo- and regioselective manner to afford protected methyl α-D-

mannopyranoside. In contrast, methyl 2,3-unsaturated α-D-galactopyranoside was inert to the conditions considered for the aminohydroxylation reaction. Therefore, by changing the stereochemistry of the anomeric position from α to β, the use of methyl 2,3-unsaturated β-D-galactopyranoside gave a mixture of regioisomers, although the stereochemistry was perfectly controlled. The regioisomer was dependent on the nature of the protecting group and ligand used. The highest selectivity of the 3-*N*-tosyl-2-hydroxy product (73:27) was obtained using a combination of the methyl protected substrate and $(DHQ)_2PHAL$ ligand. In contrast, the highest selectivity of the 2-*N*-tosyl-3-hydroxy product (10:90) was obtained using a combination of the benzoyl-protected substrate and $(DHQD)_2PHAL$ ligand. D-Glucosamine, D-mannosamine, and D-galactosamine are common aminosugars. Thus, the aminosugars obtained from methyl 2,3-unsaturated β-D-galactopyranoside are classified as *rare* aminosugars. Further studies on the synthesis of other aminosugars based on this strategy are ongoing in our laboratory.

Experimental section

General Section. All reactions were carried out in well-cleaned and oven-dried glassware under magnetic stirring. All starting materials were obtained from commercial sources or were synthesized using standard procedures. Melting points were measured on a Yanaco MP-500D instrument and were not corrected. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra (400 and 100 MHz, respectively) were recorded on a Bruker Avance III HD 400 spectrometer; TMS (0 ppm) and $CDCl_3$ (77.0 ppm) were used as internal standards, respectively. The following abbreviations are used to describe NMR peak multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Mass spectra were measured on a Thermo Auest LCQ DECA Plus instrument with GL Sciences Inc. Inert Cap5 as a column (70–310 °C) or JEOL The AccuTOF LC-plus JMS-T 100LP. Mass spectra were measured using a JEOL JMS-T100LP (DART method, ambient ionization) or a LTQ Orbitrap Elite (Thermo Fisher Scientific, Brehmen, Germany) with an electrospray ionization (ESI) ion source. Elemental analyses were performed using Yanaco CHN Corder MT-5. Optical rotations were measured by HORIBA SEPA-500 Polarimeter using 10 cm cell. Preparative column chromatography was performed with Fuji Silysia BW-4:10MH silica gel or YMC_GEL Silica (6

nm I-40-63 μm). Thin layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F254 aluminum sheets.

Preparation of OsO_4 solution.[23] Commercially available OsO_4 (1 g) was solved in 39.8 mL of *tert*-butyl alcohol and 0.20 mL of 70% (or 90%) *tert*-butyl peroxide. The mixture was stirred to provide 25 mg (ca. 0.1 mmol)/1 mL stock solution.

Synthesis of Starting Materials

***Methyl 2,3-dideoxy-4,6-di-O-(tert-butyldimethylsilyl)-α-D-erythro-hex-2-enopyranoside* (1α)**. In the two-necked flask were added 3,4,6-tri-*O*-acetyl-D-glucal (6.0 g, 22 mmol), MeOH (1.8 mL, 44 mmol), and $ClCH_2CH_2Cl$ (80 mL). Then 1 M $SnCl_4$ in CH_2Cl_2 (6.6 mL, 6.6 mmol) was dropped slowly at 0 ºC. After confirmation of the complete consumption of 3,4,6-tri-*O*-acetyl-D-glucall by ^1H NMR, satd. $NaHCO_3$ was added for quenching of the reaction. Extraction with CH_2Cl_2, followed by washing with brine and dried with anhydrous Na_2SO_4. After evaporation, the obtained residue was silica-gel column chromatographed using hexane and ethyl acetate (4:1) as an eluent to give methyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (4.4 g, 17.2 mmol, 78%). Then, NaOMe (378 mg, 7 mmol) and MeOH (10 mL) were added to the CH_2Cl_2 (15 mL) solution of 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (2.44 g, 10 mmol). After stirring for 2 h at room temperature, the mixture was concentrated to remove solvent. To the residue, were added imidazole (5.4 g, 80 mmol) and *tert*-butyldimethylsilyl chloride (7.5 g, 50 mmol) and DMF (20 mL). After stirring 20 h, methanol was added for quenching. Extraction with diethyl ether, followed by washing with brine and dried with anhydrous Na_2SO_4. After evaporation, the obtained residue was silica-gel column chromatographed using hexane and ethyl acetate (50:1) as an eluent to give methyl 2,3-dideoxy-4,6-di-*O*-(*tert*-butyldimethylsilyl)-α-D-*erythro*-hex-2-enopyranoside (**1α**) (3.4 g, 8.6 mmol, 86%). Colorless liquid; $[\alpha]_D^{19}$ = +108.4 (*c* = 1.0, $CHCl_3$); IR (neat) 2954, 2928, 2885, 2857, 1472, 1463, 1390, 1361, 1312, 1252, 1187, 1126, 1094, 1070, 1015, 967, 884, 833, 812, 774, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.68 (ddd, *J* = 10.2, 2.6, 2.0 Hz, 1H), 4.85 (s, 1H), 4.12 (dq, *J* = 8.9, 1.6 Hz, 1H) 3.87 (dd, *J* = 11.1, 1.7 Hz, 1H), 3.62–3.77 (m, 2H),

3.43 (s, 3H), 0.91 (s, 9H), 0.88 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 134.6, 125.5, 95.3, 72.7, 64.3, 62.9, 55.6, 26.1, 25.8, 18.6, 18.0, -4.1, -4.7, -5.0, -5.2; HRMS [ESI$^+$]. m/z calcd for $C_{19}H_{40}NaO_4Si_2$: 411.2357 $[M+Na]^+$, Found: 411.2353 $[M+Na]^+$.

Synthesis of Methyl 4,6-di-O-Acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranoside (S1).[9] In the two-necked flask were added 3,4,6-tri-*O*-acetyl-D-galactal (1.5 g, 5.5 mmol), MeOH (0.45 mL, 11 mmol), and $ClCH_2CH_2Cl$ (40 mL). Then 1 M $SnCl_4$ in CH_2Cl_2 (1.65 mL, 1.65 mmol) was dropped slowly at 0 ºC. After confirmation of the complete consumption of 3,4,6-tri-*O*-acetyl-D-galactal by ^1H NMR, satd. $NaHCO_3$ was added for quenching of the reaction. Extraction with CH_2Cl_2, followed by washing with brine and dried with anhydrous Na_2SO_4. After evaporation, the obtained residue was silica-gel column chromatographed using hexane and ethyl acetate (4:1) as an eluent to give methyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (**S1**) (926 mg, 3.8 mmol, 69%). White solid; mp = 55.1—56.0 °C; $[\alpha]_D^{27}$ = -159.7 (*c* = 0.43, $CHCl_3$); IR (neat) 2957, 2897, 2825, 1730, 1437, 1365, 1220, 1183, 1103, 1042, 959, 906, 750, 648, 600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.12 (ddd, *J* = 0.8, 5.2, 10.0 Hz, 1H), 6.04 (dd, *J* = 2.8, 10.0 Hz, 1H), 5.02 (dd, *J* = 2.8, 5.6 Hz, 1H), 4.97 (d, *J* = 2.8 Hz, 1H), 4.33 (dt, *J* = 2.8, 6.0 Hz,1H), 4.24 (d, *J* = 6.4 Hz, 2H), 3.45 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 170.6, 170.3, 130.5, 125.2, 94.8, 66.7, 62.8, 55.6, 20.8; HRMS [DART$^+$]. m/z calcd for $C_{10}H_{13}O_5$: 213.0763 $[M\text{-}OMe]^+$, Found: 213.0769 $[M\text{-}OMe]^+$.

Synthesis of Methyl 4,6-di-O-Benzoyl-2,3-dideoxy-α-D-threo-hex-2-enopyranoside (4αc). In the two-necked flask were added methyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*threo*- hex-2-enopyranoside (**S1**) (2.2 g, 9.0 mmol), NaOMe (194 mg, 3.6 mmol), MeOH (5 mL), and CH_2Cl_2 (7.5 mL). After stirring for 2 h at room temperature, the mixture was concentrated to remove solvent. To the residue, were added pyridine (13 mmol) and benzoyl chloride (5.2 mL, 45 mmol). After stirring 20 h, methanol was added for quenching. Extraction with ethyl acetate, followed by washing with brine and dried with anhydrous

Na_2SO_4. After evaporation, the obtained residue was silica-gel column chromatographed using hexane and ethyl acetate (10:1) as an eluent to give methyl 4,6-di-*O*-benzoyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (**4αc**) (3.3 g, 8.8 mmol, 98%). White solid; mp = 94.4–98.7 °C; $[\alpha]_D^{26}$ = -197.6 (*c* = 0.35, $CHCl_3$); IR (neat) 2800–3000, 1712, 1601, 1584, 1490, 1449, 1417, 1331, 1312, 1290, 1261, 1175, 1128, 1096, 1069, 1048, 1026, 964, 879, 859, 804, 754, 707, 686, 617 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.01–8.07 (m, 4H), 7.54–7.60 (m, 2H), 7.41–7.46 (m, 4H), 6.28 (ddd, *J* = 1.2, 5.6, 10.0 Hz, 1H), 6.10 (dd, *J* = 2.8, 10.0 Hz, 1H), 5.35 (dd, *J* = 2.4, 5.6 Hz, 1H), 5.05 (d, *J* = 2.4 Hz, 1H), 4.67 (dd, *J* = 7.6, 10.8 Hz), 4.60 (ddd, *J* = 1.6, 2.0, 10.4 Hz, 1H), 4.52(dd, *J* = 4.4, 10.8 Hz, 1H), 3.48 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 133.3, 130.7, 129.8, 129.6, 128.4, 125.3, 95.0, 67.2, 63.5, 55.7; HRMS [DART$^+$]. m/z calcd for $C_{20}H_{17}O_5$: 337.1076 $[M\text{-}OMe]^+$, Found:337.1055 $[M\text{-}OMe]^+$

Synthesis of Methyl 4,6-di-O-(tert-Butyldimethylsilyl)-2,3-dideoxy-α-D-threo-hex-2-enopyranoside (4αe). In the two-necked flask were added methyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (**S1**) (2.2 g, 9.0 mmol), NaOMe (194 mg, 3.6 mmol), MeOH (5 mL), and CH_2Cl_2 (7.5 mL). After stirring for 2 h at room temperature, the mixture was concentrated to remove solvent. To the residue, were added imidazole (4.9 g, 72 mmol) and *tert*-butyldimethylsilyl chloride (6.8 g, 45 mmol) and DMF (20 mL). After stirring 20 h, methanol was added for quenching. Extraction with diethyl ether, followed by washing with brine and dried with anhydrous Na_2SO_4. After evaporation, the obtained residue was silica-gel column chromatographed using hexane and ethyl acetate (50:1) as an eluent to give methyl 4,6-di-*O*-(*tert*-butyldimethylsiloxy)-2,3-dideoxy-α-D-threo-hex-2-enopyranoside (**4αe**) (3.0 g, 7.6 mmol,

85%). Colorless liquid; $[\alpha]_D^{27}$ = -95.4 (*c* = 0.35, $CHCl_3$); IR (neat) 2950, 2924, 2891, 2854, 1470, 1408, 1359, 1251, 1188, 1142, 1109, 1096, 1045, 1020, 1004, 959, 936, 872, 832, 772, 731, 687, 664 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.01 (ddd, *J* = 0.8, 5.2, 10.0 Hz, 1H), 5.87 (dd, *J* = 3.2, 12.5 Hz, 1H), 4.92 (d, *J* = 2.8 Hz, 1H), 3.93 (ddd, *J* = 2.4, 6.4, 7.2 Hz, 1H), 3.89 (dd, *J* = 2.4, 5.2 Hz, 1H), 3.82 (dd, *J* = 5.2, 10.4 Hz, 1H), 3.76 (dd, *J* = 6.8, 10.8 Hz, 1H), 3.43 (s, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.07—0.08 (m, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 129.8, 127.7, 95.0, 71.8, 62.8, 62.0, 55.2, 25.9, 25.8, 18.3, 18.2, -4.0, -4.7, -5.3, -5.4; HRMS [$DART^+$]. m/z calcd for $C_{18}H_{37}O_3Si_2$:357.2281 $[M\text{-}OMe]^+$, Found: 357.2253 $[M\text{-}OMe]^+$.

Synthesis of 1,5-Anhydro-6-O-(tert-butyldimethylsilyl)-3,4-O-carbonate-2-deoxy-D-lyxo-hex-1-enopyranose (S2).[21] In the two-necked flask were added 3,4,6-tri-*O*-acetyl-D-galactal (0.27 g, 1 mmol), CH_2Cl_2 (0.83 mL), MeOH (0.56 mL), and NaOMe (0.022 g, 0.4 mmol) and the mixture was stirred at 29 °C for 2 h. After removal of solvent under reduced pressure, CH_2Cl_2 (2.2 mL) and imidazole (0.15 g, 2.2 mmol) were added then *tert*-butylchlorodimethylsilane (0.17 g, 1.1 mmol) was added at 0 °C. After stirring at room temperature, the mixture was quenched with MeOH. After usual work-up, the mixture of imidazole (6.8 mg, 0.1 mmol) and 1,1'-carbonyldiimidazole (0.24 g, 1.5 mmol) in THF (0.45 mL) solution was added to the above mixture at 0 °C. After stirring at room temperature for 20 h and usual work-up. The obtained residue was purified by silica-gel column chromatography (benzene:CH_2Cl_2 = 2:1) to give 1,5-anhydro-6-*O*-(*tert*-butyldimethylsilyl)-3,4-*O*-carbonate-2-deoxy-D-*lyxo*-hex-1-enopyranose (**S2**) (0.15 g, 0.51 mmol, 51%). White solid; mp = 52.0–54.0 °C; $[\alpha]_D^{17}$ = -74.6 (*c* = 1.0, $CHCl_3$); IR (neat) 2948, 2928, 2885, 2857, 1786, 1647, 1470, 1463, 1367, 1316, 1242, 1166, 1115, 1086, 1069, 1017, 995, 898, 833, 778, 768, 697, 668, 645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.66 (d, *J* = 6.7 Hz, 1H), 5.18 (dd, *J* = 7.6, 3.2 Hz, 1H), 4.99–4.91 (m, 2H), 3.98–3.83 (m, 3H), 0.90 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 154.3, 149.3, 98.2, 74.1, 72.9, 69.0, 61.2, 25.9, 18.4, -5.3, -5.4; HRMS [DART]. m/z calcd for $C_{13}H_{23}O_5Si_1$: 287.1315 $[M\text{-}OMe]^+$, Found:287.1304 $[M\text{-}OMe]^+$.

Synthesis of Methyl 2,3-Dideoxy-6-O-(tert-butyldimethylsilyl)-β-D-threo-hex-2-enopyranoside (S3).[21]

In the two-necked flask were added 1,5-anhydro-6-*O*-(*tert*-butyldimethylsilyl)-3,4-*O*-carbonate-2-deoxy-D-lyxo-hex-1-enopyranose **S2** (0.29 g, 1 mmol), THF (6 mL), MeOH (0.08 mL, 2 mmol), PPh_3 (0.079 g, 0.3 mmol), and $Pd(OAc)_2$ (0.022 g, 0.1 mmol), and the mixture was stirred at room temperature for 17 h. After filtration, the residue was washed with ethyl acetate, and solvent was removed under reduced pressure. The obtained crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 4:1) to afford methyl 2,3-dideoxy-6-*O*-(*tert*-butyldimethylsilyl)-β-D-*threo*-hex-2-enopyranoside (**S3**) (0.23 g, 0.84 mmol, 84%). Colorless liquid; $[\alpha]_D^{21}$ = -120.3 (*c* = 1.0, $CHCl_3$); IR(neat) 3426, 2948, 2928, 2883, 2855, 1471, 1389, 1252, 1206, 1121, 1091, 1049, 995, 953, 834, 776, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.11–6.02 (m, 1H), 5.73 (d, *J* = 10.1 Hz, 1H), 4.90 (s, 1H), 3.91–3.80 (m, 2H), 3.74 (ddd, *J* = 10.5, 6.0, 2.3 Hz, 1H), 3.60 (tt, *J* = 6.1, 2.5 Hz, 1H), 3.47–3.40 (m, 3H), 2.5 (br s, 1H), 0.88–0.82 (m, 9H), 0.03 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 131.1, 130.3, 98.7, 75.7, 62.7, 62.4, 55.8, 25.9, 18.3, -5.3, -5.4; HRMS [DART]. m/z calcd for $C_{13}H_{27}O_4Si_1$: 275.1679 $[M\text{-}OMe]^+$, Found:275.1659 $[M\text{-}OMe]^+$.

Synthesis of Methyl 2,3-Dideoxy-β-D-threo-hex-2-enopyranoside (S4). In the two-necked flask were added methyl 2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (**S3**) (2.7 g, 9.54 mmol) and THF (95 mL). Tetrabutylammonium fluoride in THF 1 mol/L (19 mL, 19 mmol) was added to the mixture at 0 °C, and the mixture was stirred at room temperature for 2 h. After removal of solvent, the obtained residue was purified by silica-gel column chromatography (hexane:ethyl acetate = 4:1) to afford methyl 2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (**S4**) (1.5 g, 9.32 mmol, 94%). White solid; mp: 73.5-74.0 °C; $[\alpha]_D^{20}$ = -183.0 (*c* = 1.0, $CHCl_3$); IR(neat) 3252 br, 3047, 3001, 2969, 2927, 2838, 1395, 1339, 1203, 1147, 1117, 1051, 1037, 1002, 991, 953, 856, 785, 622, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.14 (ddd, *J* = 10.1, 4.8, 1.4 Hz, 1H), 5.85 (dt, *J* = 10.1, 1.1 Hz, 1H), 5.01 (q, *J* = 1.5 Hz, 1H), 4.08–4.01 (m, 1H), 3.96 (dt, *J* = 12.2, 6.0 Hz, 1H), 3.87 (ddd, *J* = 12.0, 7.4, 4.5 Hz, 1H), 3.79 (ddd, *J* = 7.4, 4.4, 3.1 Hz, 1H), 3.55 (s,

3H), 2.27 (br, 1H), 2.0 (br s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 130.9, 130.1, 98.4, 75.1, 62.8, 62.4, 56.1; HRMS [DART]. m/z calcd for $C_6H_9O_3$:129.0552 $[M\text{-}OMe]^+$, Found:129.0555 $[M\text{-}OMe]^+$.

Synthesis of methyl 2,3-dideoxy-4,6-di-O-methyl-β-D-threo-hex-2-enopyranoside (4βa). In the two-necked flask were added methyl 2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (0.48 g, 3 mmol) and DMF (7.2 mL). NaH (60%, dispersion in paraffin liquid, 0.48 g, 3 mmol) was added at 0 ºC, and the mixture was stirred for 1 h at 0 ºC. Iodomethane (0.75 mL, 12 mmol) was added at this temperature, and the reaction was stirred at room temperature for 21 h. After the confirmation of completion of the reaction, the mixture was quenched with methanol. After usual work-up, the obtained crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 2:1) to afford methyl 2,3-dideoxy-4,6-di-*O*-methyl-β-D-*threo*-hex-2-enopyranoside (**4βa**) (0. 47g, 2.5 mmol, 83%). Colorless liquid; $[\alpha]_D^{19}$ = -223.6 (*c* = 0.40, $CHCl_3$); IR(neat) 2897, 2824, 1446, 1394, 1324, 1202, 1118, 1097, 1056, 1000, 961, 881, 831, 795, 665, 622 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.18–6.09 (m, 1H), 5.91 (d, *J* = 10.3 Hz, 1H), 5.01 (s, 1H), 3.88 (tt, *J* = 5.7, 2.4 Hz, 1H), 3.71–3.62 (m, 3H), 3.53–3.48 (m, 3H), 3.45–3.41 (m, 3H), 3.41– 3.39 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 131.4, 127.9, 97.9, 73.9, 72.0, 70.2, 59.3, 56.6, 55.4; HRMS [DART]. m/z calcd for $C_8H_{13}O_3$: 157.0865 $[M\text{-}OMe]^+$, Found: 157.0890 $[M\text{-}OMe]^+$.

Synthesis of Methyl 2,3-Dideoxy-4,6-di-O-benzyl-β-D-threo-hex-2-enopyranoside (4βb). In the two-necked flask were added methyl 2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (**S4**) (0.56 g, 3.5 mmol) and DMF (17 mL). NaH (60%, dispersion in paraffin liquid, 0.56 g, 14 mmol) was added at 0 ºC, and the mixture was stirred for 1 h at 0 ºC. Benzyl bromide (1.66 mL, 14 mmol) was added at this temperature, and the reaction was stirred at room temperature for 21 h. After the confirmation of completion of the reaction, the mixture was quenched with methanol. After usual work-up, the obtained crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 5:1) to afford methyl 2,3-dideoxy-4,6-di-*O*-benzyl-β-D-*threo*-hex-2-enopyranoside **(4βb)** (1.2 g, 3.5 mmol, 100%). Colorless liquid; $[\alpha]_D^{20}$ = -146.2 (*c* = 1.0, $CHCl_3$); IR (neat) 3028, 2862, 1496, 1453, 1206, 1109, 1096, 1055, 1027, 1002, 960,

792, 733, 696, 608 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.38–7.23 (m, 10H) , 6.06 (ddd, *J* = 10.2, 4.4, 1.5 Hz, 1H), 5.88 (dt, *J* = 10.3, 1.0 Hz, 1H) , 5.01 (q, *J* = 1.5 Hz, 1H), 4.68–4.51 (m, 4H) , 4.00–3.92 (m, 1H), 3.92–3.86, (m, 1H), 3.80 (s, 1H), 3.51 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 138.5, 138.3, 131.1, 128.4, 128.3, 127.8, 127.6, 98.0, 74.1, 73.6, 70.8, 69.6, 68.5, 55.6; HRMS [DART]. m/z calcd for $C_{20}H_{21}O_3$: 309.1491 $[M\text{-}OMe]^+$, Found: 309.1499 $[M\text{-}OMe]^+$.

Synthesis of Methyl 2,3-Dideoxy-4,6-di-O-benzoyl-β-D-threo-hex-2-enopyranoside (4βc). In the two-necked flask were added methyl 2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (1.44 g, 9.0 mmol), CH_2Cl_2 (20 mL), and pyridine (5.81 mL, 72 mmol). Benzoyl chloride (4.2 mL, 36 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 24 h. After the confirmation of completion of the reaction, the mixture was quenched with methanol. After usual work-up, the obtained crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1→hexane:ethyl acetate = 5:1) to give methyl 2,3-dideoxy-4,6-di-*O*-benzoyl-β-D-*threo*-hex-2-enopyranoside **(4βc)** (3.3 g, 9 mmol, 100%). White solid; mp: 70.0–70.5 ºC; $[\alpha]_D^{20}$ = -223.1 (*c* = 1.0, $CHCl_3$); IR(neat) 2926, 2382, 1718, 1450, 1251, 1176, 1106, 1057, 1028, 902, 706, 687, 676, 642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.03–7.97 (m, 2H), 7.61–7.50 (m, 2H), 6.24 (ddd, *J* = 10.2, 4.7, 1.5 Hz, 1H), 6.07–5.99 (m, 1H), 5.54–5.48 (m, 1H), 5.15 (q, *J* = 1.5 Hz, 1H), 4.70 (dd, *J* = 11.4, 7.2 Hz, 1H), 4.54 (dd, *J* = 11.5, 5.7 Hz, 1H), 4.34 (ddd, *J* = 7.1, 5.7, 3.1 Hz, 1H), 3.55 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 133.4, 133.2, 132.5, 129.9, 129.8, 129.7, 129.6, 128.5, 126.8, 97.9, 71.3, 64.6, 63.4, 55.6; HRMS [DART]. m/z calcd for $C_{20}H_{17}O_5$: 337.1076 $[M\text{-}OMe]^+$, Found: 337.1087 $[M\text{-}OMe]^+$.

Synthesis of methyl 2,3-dideoxy-4,6-di-O-pivaloyl-β-D-threo-hex-2-enopyranoside (4βl). In the two-necked flask were added methyl 2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (0.56 g, 3.5 mmol), CH_2Cl_2 (7.7 mL), pyridine (2.8 mL, 35 mmol), and *N*,*N*-dimethyl-4-aminopyridine (0.043 g, 0.35 mmol). Pivaloyl chloride (2.13 mL, 17.5 mmol) was added at 0 ºC, and the mixture was stirred at room temperature for 21 h. After the confirmation of completion of the reaction, the mixture was quenched with methanol. After

usual work-up, the obtained crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 6:1) to afford methyl 2,3-dideoxy-4,6-di-*O*-pivaloyl-β-D-*threo*-hex-2-enopyranoside **(4βd)** (1.14 g, 3.5 mmol, 100%). Colorless liquid; $[\alpha]_D^{20}$ = -167.5 (*c* = 1.0, $CHCl_3$); IR(neat) 2971, 2936, 2907, 2869, 1727, 1480, 1462, 1397, 1280, 1209, 1142, 1056, 952, 768, 752, 533 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.10–6.04 (m, 1H), 5.94 (d, *J* = 10.1 Hz, 1H), 5.10–5.04 (m, 2H), 4.31 (dd, *J* = 11.1, 7.1 Hz, 1H), 4.19 (dd, *J* = 11.1, 6.4 Hz, 1H), 4.06 (td, *J* = 6.7, 2.8 Hz, 1H), 3.50 (s, 3H), 1.21 (s, 9H), 1.12 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 27.1, 27.1, 38.8, 39.0, 55.2, 62.3, 63.2, 71.2, 98.0, 126.8, 132.5, 177.7, 178.1; HRMS [DART]. m/z calcd for $C_{16}H_{25}O_5$: 297.1702 $[M\text{-}OMe]^+$, Found: 297.1711$[M\text{-}OMe]^+$.

Synthesis of Methyl 2,3-Dideoxy-4,6-di-O-(tert-butyldimethylsilyl)-β-D-threo-hex-2-enopyranoside (4βe). In the two-necked flask were added methyl 2,3-dideoxy-6-*O*-[(1,1-dimethyl)silyl]-β-D-*threo*-hex-2-enopyranoside (1.82 g, 6.6 mmol), CH_2Cl_2 (15 mL) and imidazole (1.08 g, 15.9 mmol). *tert*-Butylchlorodimethylsilane (1.2 g, 7.9 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 17 h. After the confirmation of completion of the reaction, the mixture was quenched with methanol. After usual work-up, the obtained crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 1:30) to give methyl 2,3-dideoxy-4,6-di-*O*-(*tert*-butyldimethylsilyl)-β-D-*threo*-hex-2-enopyranoside **(4βe)** (2.36 g, 6.1 mmol, 92%). Colorless liquid; $[\alpha]_D^{20}$ = -99.2 (*c* = 1.0, $CHCl_3$); IR(neat) 2954, 2928, 2883, 2856, 1471, 1389, 1252, 1095, 1059, 1005, 833, 773, 667, 538 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.97 (ddd, *J* = 10.2, 4.5, 1.5 Hz, 1H), 5.75 (dt, *J* = 10.2, 1.0 Hz, 1H), 5.01 (q, *J* = 1.5 Hz, 1H), 4.10–4.05 (m, 1H), 3.83 (s, 1H), 3.81 (s, 1H), 3.63 (dt, *J* = 6.2, 3.0 Hz, 1H), 3.47 (s, 3H), 0.90 (s, 9H) 0.88 (s, 9H), 0.07 (s, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 131.5, 129.5, 97.7, 76.6, 63.0, 62.6, 55.0, 26.1, 26.0, 18.5, 18.3, -4.0, -4.6, -5.1; HRMS [DART]. m/z calcd for $C_{18}H_{37}O_3Si_2$: 357.2281 $[M\text{-}OMe]^+$, Found:357.2294 $[M\text{-}OMe]^+$.

Synthesis of methyl 2,3-dideoxy-4,6-di-O-(tert-butyldiphenylsilyl)-β-D-threo-hex-2-enopyranoside (4βf). In the two-necked flask were added methyl 2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (0.48 g, 3 mmol), CH_2Cl_2 (6.7 mL), and imidazole (0.98 g, 14.4 mmol) were added. *tert*-Butyldiphenylsilyl chloride (1.85 mL, 7.2 mmol) was added at 0 ºC, and the mixture was stirred at room temperature for 21 h. After the confirmation of completion of the reaction, the mixture was quenched with methanol. After usual work-up, the obtained crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 12:1) to afford methyl 2,3-dideoxy-4,6-di-*O*-(*tert*-butyldiphenylsilyl)-β-D-*threo*-hex-2-enopyranoside **(4βf)** (1.61 g, 2.4 mmol, 84%). Colorless liquid; $[\alpha]_D^{20}$ = -72.6 (*c* = 1.0, $CHCl_3$); IR (neat) 2958, 2930, 2893, 2856, 1427, 1390, 1111, 1055, 998, 822, 738, 699, 610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.68 (ddd, *J* = 12.8, 8.0, 1.5 Hz, 4H), 7.60 (ddd, *J* = 11.6, 8.0, 1.3 Hz, 4H),0.91 (s, 9H), 7.43–7.27 (m, 12H) , 5.65 – 5.55 (m, 2H), 4.89 (s, 1H), 4.10 (dd, *J* = 11.0, 7.7 Hz 1H) , 4.07–4.03 (m, 1H), 3.94 (dd, *J* = 11.0, 4.2 Hz 1H), 3.64 (dt, *J* = 7.6, 4.1 Hz 1H), 3.52 (s, 3H), 1.07 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.2, 135.9, 135.8, 135.7, 134.1, 134.0, 133.9, 133.4, 131.2, 129.9, 129.7, 129.5, 127.8, 127.7, 127.5, 97.7, 76.6, 64.4, 64.0, 55.4, 27.1, 27.0,19.4; HRMS [DART]. m/z calcd for $C_{38}H_{45}O_3Si_2$: 605.2907 $[M\text{-}OMe]^+$, Found: 605.2935 $[M\text{-}OMe]^+$.

General procedure for the catalytic asymmetric aminohydroxylation. In the Schlenk flask were added protected 2,3-unsaturated D-gluco- or D-galacto-2-hexenopyranoside (0.5 mmol), benzyltriethylammonium chloride (0.025 mmol), $(DHQ)_2PHAL$ (0.025 mmol), *tert*-BuOH (0.5 mL), H_2O (0.5 mL), chloramine T · $3H_2O$ (0.625 mmol), and OsO_4 solution (0.2 mL, 0.02 mmol). The reaction mixture was stirred at room temperature. After the confirmation of completion of the reaction, Na_2SO_3 (0.5 mmol) was added at room temperature for quenching. The mixture was stirred at room temperature for 3 h. Extraction with $CHCl_3$ followed by evaporation afforded crude product. The ratio was determined

by ^{1}H NMR analysis using an internal standard at this stage. For purification silica-gel column chromatography was used.

Typical procedure for the catalytic asymmetric aminohydroxylation. In the Schlenk flask were added 2,3-dideoxy-4,6-di-*O*-(*tert*-butyldimethylsilyl)-β-D-*threo*-hex-2-enopyranoside (0.19 g, 0.5 mmol), benzyltriethylammonium chloride (5.7 mg, 0.025 mmol), $(DHQ)_2PHAL$ (0.019 g, 0.025 mmol), *tert*-BuOH (0.5 mL), H_2O (0.5 mL), chloramine T·$3H_2O$ (0.176 g, 0.625 mmol), and OsO_4 solution (0.2 mL, 0.02 mmol). The reaction mixture was stirred at room temperature. After the confirmation of completion of the reaction, Na_2SO_3 (0.071 g, 0.5 mmol) was added at room temperature for quenching. The mixture was stirred at room temperature for 3 h. Extraction with $CHCl_3$ followed by evaporation afforded crude product. The ratio was determined by ^{1}H NMR analysis using an internal standard at this stage. For purification silica-gel column chromatography (hexane:ethyl acetate = 2:1) was used.

Methyl 4,6-di-O-(tert-Butyldimethylsilyl)-2-deoxy-2-(p-toluenesulfonamido)-α-D-mannopyranoside (2). White solid; mp: 93.0–94.0°C; $[\alpha]_D^{20}$ = +28.3 (*c* = 1.0, $CHCl_3$); IR (neat) 3498, 3278, 2954, 2927, 2899, 2856, 1471, 1456, 1440, 1359, 1316, 1307, 1273, 1251, 1165, 1092, 1073, 1057, 1004, 965, 939, 835, 814, 803, 777, 662, 552 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.74 (d, *J* = 8.5 Hz, 1H), 4.30 (d, *J* = 1.6 Hz, 1H), 3.67–3.85 (m, 3H), 3.53 (dq, *J* = 2.7, 2.2 Hz, 1H), 3.48 (t, *J* = 9.1 Hz, 1H), 3.40 (ddd, *J* = 9.3, 4.8, 1.9 Hz, 1H), 3.22 (s, 3H), 2.44 (s, 3H), 2.13 (d, *J* = 8.2 Hz, 1H), 0.91 (s, 9H), 0.87 (s, 9H), 0.11 (s, 3H), 0.08 (s, 6H), 0.07 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 144.0, 136.8, 129.9, 127.3, 99.2, 73.3, 69.7, 62.4, 56.9, 54.8, 26.0, 21.6, 18.3, -3.9, -4.9, -5.0, -5.2; HRMS [DART]. m/z calcd for $C_{25}H_{46}NO_6SSi_2$: 544.2584 $[M\text{-}OMe]^+$, Found: 544.2594$[M\text{-}OMe]^+$.

Methyl 4,6-di-O-(tert-Butyldimethylsilyl)-α-D-mannopyranoside (3). Colorless liquid; $[\alpha]_D^{21}$ = +59.8 (*c* = 1.0, $CHCl_3$); IR(neat) 3445, 2952, 2928, 2895, 2856, 1472, 1463, 1388, 1360, 1251, 1100, 1071, 1057,

968, 879, 833, 807, 776, 676 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.70 (d, *J* = 1.4 Hz, 1H), 3.82–3.90 (m, 2H), 3.63–3.79 (m, 3H), 3.50 (dt, *J* = 8.8, 6.3 Hz, 1H), 3.37 (s, 3H), 2.24 (br s, 1H), 2.14 (br s, 1H), 0.89 (s, 9H), 0.89 (s, 9H), 0.14 (s, 3H), 0.10 (s, 3H), 0.07 (s, 3H), 0.07 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 100.5, 73.3, 72.4, 71.3, 69.5, 62.7, 54.8, 26.0, 18.5, 18.4, -3.9, -4.7, -5.0, -5.2; HRMS [ESI^+]. m/z calcd for $C_{19}H_{42}NaO_6Si_2$: 445.2412 $[M+Na]^+$, Found: 445.2405 $[M+Na]^+$.

Methyl 4,6-di-O-(tert-butyldimethylsilyl)-3-deoxy-3-(p-toluenesulfonamido)-α-D-gulopyranoside (5αe). White solid; mp: 99.0–99.9 °C; $[\alpha]_D^{20}$ = + 19.5 (*c* = 0.18, $CHCl_3$); IR (neat) 3509, 3274, 2953, 2929, 2856, 1462, 1427, 1355, 1328, 1254, 1164, 1110, 1096, 1088, 1056, 1021, 899, 833, 778, 666, 578 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.82 (d, *J* = 9.0 Hz, 1H) , 4.67 (d, *J* = 3.5 Hz, 1H), 3.97 (dt, *J* = 10.4, 4.7 Hz, 1H), 3.84 (d, *J* = 3.4 Hz, 1H), 3.79 (t, *J* = 6.3 Hz, 1H), 3.56–3.68 (m, 2H), 3.50 (dt, *J* = 8.5, 3.9 Hz, 1H), 3.43 (s, 3H), 2.42 (s, 3H), 1.82 (d, *J* = 10.5 Hz, 1H) , 0.89 (s, 9H), 0.86 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H), 0.01 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 143.7, 137.6, 129.9, 127.3, 100.3, 70.3, 67.2, 63.4, 62.5, 56.7, 55.8, 26.0, 25.8, 21.7, 18.4, 18.0, -4.6, -5.1, -5.2, -5.3; HRMS [ESI^+]. m/z calcd for $C_{26}H_{49}NNaO_7SSi_2$: 598.2660 $[M+Na]^+$, Found: 598.2640.

Methyl 4,6-di-O-(tert-Butyldimethylsilyl)-2-deoxy-2-(p-toluenesulfonamido)-α-D-gulopyranoside (6αe). White solid; mp: 74.5–75.3 °C; $[\alpha]_D^{20}$ = +41.7 (*c* = 0.33, $CHCl_3$); IR (neat) 3506, 3435, 3274, 3144, 2950, 2928, 2884, 2855, 2360, 2341, 1598, 1470, 1462, 1416, 1356, 1321, 1253, 1152, 1113, 1092, 1053, 1021, 940, 859, 833, 813, 778, 666, 650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 5.50 (d, *J* = 10.1 Hz, 1H), 4.77 (d, *J* = 3.2 Hz, 1H), 3.93 (t, *J* = 6.3 Hz, 1H), 3.87 (d, *J* = 3.8 Hz, 1H), 3.85–3.72 (m, 3H) 0.13 (s, 3H), 3.54–3.61 (m, 1H), 3.48 (s, 3H), 3.45 (s, 1H), 2.54 (s, 3H), 1.00 (s, 9H), 0.95 (s, 9H), 0.17 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 143.5, 137.9, 129.8, 127.1, 100.2, 71.7, 69.6, 66.6, 62.2, 55.8, 49.5, 25.8, 25.7, 21.5, 18.2, 17.9, -5.0, -5.2, -5.3, -5.4; HRMS [ESI^+]. m/z calcd for $C_{26}H_{49}NNaO_7SSi_2$: 598.2660 $[M+Na]^+$, Found: 598.2645.

Methyl 4,6-di-O-Methyl-3-deoxy-3-(p-toluenesulfonamido)-β-D-gulopyranoside (5βa). Colorless liquid; $[\alpha]_D^{19}$ = -72.0 (*c* = 0.48, $CHCl_3$); IR (neat) 3474, 3271, 2929, 2830, 1598, 1448, 1409, 1372, 1329, 1205, 1158, 1082, 1055, 998, 948, 911, 814, 752, 730, 673, 551 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.31 (br s, 1H), 4.38 (d, *J* = 8.1 Hz, 1H), 4.13 (t, *J* = 6.1 Hz, 1H), 3.73 (s, 1H), 3.72–3.65 (m, 1H), 3.55 (d, *J* = 6.2 Hz, 2H), 3.51–3.46 (m, 4H), 3.37 (t, *J* = 1.8 Hz, 6H), 2.8 (br s, 1H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.0, 135.0, 129.9, 127.6, 101.0, 76.9, 71.8, 71.3, 66.6, 59.2, 58.7, 56.7, 52.7, 21.6; HRMS [DART]. m/z calcd for $C_{16}H_{26}N_1O_7S$: 376.1430 $[M+H]^+$, Found: 376.1421 $[M+H]^+$.

Methyl 4,6-di-O-Methyl-2-deoxy-2-(p-toluenesulfonamido)-β-D-gulopyranoside (6βa). Colorless liquid; $[\alpha]_D^{19}$ = -94.6 (*c* = 0.22, $CHCl_3$); IR (neat) 3458, 3282, 2929, 2824, 1598, 1446, 1404, 1324, 1200, 1152, 1078, 1038, 948, 908, 814, 752, 730, 671, 551 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 5.1 (br s, 1H), 4.46 (d, *J* = 8.3 Hz, 1H), 4.43 (s, 1H), 4.04 (td, *J* = 7.3, 5.9, 0.8 Hz, 1H) , 3.60–3.44 (m, 2H), 3.37 (s, 3H), 3.36 (s, 3H), 3.33–3.29 (m, 1H) 3.29–3.22 (m, 3H), 3.17–3.06 (m, 2H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.7, 136.0, 129.6, 127.5, 99.3, 77.3, 71.9, 71.2, 66.5, 59.3, 58.5, 56.3, 55.0, 21.6; HRMS [DART]. m/z calcd for $C_{16}H_{26}N_1O_7S$: 376.1430 $[M+H]^+$, Found: 376.1415 $[M+H]^+$.

Methyl 4,6-di-O-Methyl-β-D-gulopyranoside (7βa). Colorless liquid; $[\alpha]_D^{19}$ = -36.7 (*c* = 0.02, $CHCl_3$); IR (neat) 3426, 2918, 2848, 1726, 1448, 1201, 1100, 1072, 1030, 955, 911, 750, 672, 620, 593, 566, 536 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.51 (d, *J* = 7.9 Hz, 1H), 4.26 (t, *J* = 3.4 Hz, 1H), 4.08 (dt, *J* = 6.3, 1.4 Hz, 1H) 3.69–3.57 (m, 3H), 3.54 (s, 3H), 3.44 (s, 3H), 3.41 (s, 3H) 3.37 (dd, *J* = 3.4, 1.6 Hz, 1H) , 2.5 (br s, 1H), 2.4 (br s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 101.2, 78.0, 72.1, 69.5, 67.5, 59.3, 58.9, 56.7; HRMS [DART]. m/z calcd for $C_9H_{19}O_6$: 223.1182 $[M+H]^+$, Found: 223.1199 $[M+H]^+$.

Methyl 4,6-di-O-Benzyl-3-deoxy-3-(p-toluenesulfonamido)-β-D-gulopyranoside (5βb). Colorless liquid; $[\alpha]_D^{20}$ = -76.5 (*c* = 0.64, $CHCl_3$); IR (neat) 3468, 3269, 2928, 2868, 1453, 1358, 1159, 1088, 1066, 942, 814, 698, 673, 596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.3 Hz, 2H), 7.38–7.25 (m, 12H)

, 5.1 (br s, 1H), 4.58–4.32 (m, 5H), 4.15 (t, *J* = 5.9 Hz, 1H), 4.04–3.98 (m, 1H), 3.77 (ddd, *J* = 7.5, 5.0, 1.7 Hz, 1H), 3.61 (dd, *J* = 10.0, 6.6 Hz, 1H), 3.48 (m, 5H) , 2.4 (br s, 1H), 2.39 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 143.9, 138.1, 137.8, 135.2, 129.8, 128.4, 128.3, 127.9, 127.7, 127.6, 127.5, 101.1, 74.5, 73.3, 72.9, 72.0, 69.0, 66.8, 56.8, 53.6, 21.6; HRMS [DART]. m/z calcd for $C_{27}H_{30}N_1O_6S$: 496.1794 $[M\text{-}OMe]^+$, Found: 496.1799 $[M\text{-}OMe]^+$.

Methyl 4,6-di-O-Benzyl-2-deoxy-2-(p-toluenesulfonamido)-β-D-gulopyranoside (6βb). Colorless liquid; $[\alpha]_D^{13}$ = -100.7 (*c* = 0.34, $CHCl_3$); IR (neat) 3026, 2916, 2862, 1454, 1323, 1154, 1076, 1038, 747, 666, 551 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.36–7.16 (m, 12H), 4.79 (s, 1H), 4.56–4.47 (m, 3H), 4.47–4.41 (m, 3H), 4.10 (td, *J* = 6.4, 1.4 Hz, 1H), 3.63–3.53 (m, 3H), 3.33 (s, 3H), 3.09 (dt, *J* = 8.1, 2.7 Hz, 1H), 2.6 (br s, 1H), 2.39 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 143.8, 138.0, 137.7, 135.4, 129.8, 128.4, 128.3, 128.0, 127.9, 127.7, 127.5, 99.2, 74.7, 73.4, 72.6, 72.2, 68.8, 66.6, 56.5, 55.4, 21.6; HRMS [DART]. m/z calcd for $C_{27}H_{30}N_1O_6S$: 496.1794 $[M\text{-}OMe]^+$, Found: 496.1809 $[M\text{-}OMe]^+$.

Methyl 4,6-di-O-Benzyl-β-D-gulopyranoside (7βb). Colorless liquid; $[\alpha]_D^{13}$ = -55.5 (*c* = 0.28, $CHCl_3$); IR (neat) 3393, 2914, 1716, 1586, 1453, 1314, 1268, 1205, 1071, 1026, 747, 697, 666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38–7.20 (m, 10H), 4.67–4.41 (m, 5H), 4.18 (t, *J* = 3.4 Hz, 1H), 4.13 (dt, *J* = 6.3, 1.3 Hz, 1H), 3.76–3.60 (m, 4H), 3.53 (s, 3H), 2.6 (br s, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 138.1, 137.9, 128.4, 128.0, 127.9, 127.7, 101.3, 75.7, 73.4, 72.9, 72.2, 69.5, 68.9, 68.3, 56.8; HRMS [DART]. m/z calcd for $C_{21}H_{27}O_6$: 375.1808 $[M+H]^+$, Found: 375.1803 $[M+H]^+$.

Methyl 4,6-di-O-Benzoyl-3-deoxy-3-(p-toluenesulfonamido)-β-D-gulopyranoside (5βc). White solid; mp: 82.0–84.0 ºC; $[\alpha]_D^{13}$ = -120.7 (*c* = 0.30, $CHCl_3$); IR (neat) 3462, 3272, 2292, 1721, 1600, 1451, 1317, 1265, 1159, 1092, 1026, 942, 814, 708, 669, 550 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 7.8 Hz, 4H) 7.88 (d, *J* = 7.0 Hz, 2H) 7.61–7.50 (m, 2H), 7.46–7.36 (m, 4H), 7.29 (dd, *J* = 8.2, 2.7 Hz, 2H) , 5.92 (t, *J* = 3.8 Hz, 1H), 5.24 (d, *J* = 3.6 Hz, 1H), 4.70–4.56 (m, 3H), 4.37 (dd, *J* = 11.0, 5.6 Hz, 1H) , 3.88–3.79 (m, 1H), 3.58 (s, 3H), 3.57 (s, 1H), 2.57 (brs, 1H), 2.37 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz,

$CDCl_3$) δ 133.5, 133.1, 129.9, 129.7, 129.6, 129.0, 128.5, 128.4, 127.9, 101.2, 70.2, 68.6, 67.4, 62.8, 57.2, 53.7, 21.6; HRMS [DART]. m/z calcd for $C_{27}H_{26}N_1O_8S$: 524.1379 $[M\text{-}OMe]^+$, Found: 524.1394 $[M+H]^+$.

Methyl 4,6-di-O-Benzoyl-2-deoxy-2-(p-toluenesulfonamido)-β-D-gulopyranoside (6βc). White solid; mp: 66.0–72.0 ºC; $[\alpha]_D^{13}$ = -97.3 (*c* = 0.23, $CHCl_3$); IR (neat) 3464, 3276, 2959, 1720, 1600, 1451, 1327, 1264, 1156, 1112, 1026, 814, 709, 670, 551 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 8.4, 1.3 Hz, 4H), 7.67–7.59 (m, 3H), 7.57–7.51 (m, 1H), 7.49–7.37 (m, 4H), 7.04 (d, *J* = 7.9 Hz, 2H), 5.27 (dd, *J* = 3.7, 1.2 Hz, 1H), 4.98 (d, *J* = 4.0 Hz, 1H), 4.64 (d, *J* = 8.2 Hz, 1H), 4.54 (dd, *J* = 10.7, 6.9 Hz, 1H), 4.51–4.43 (m, 1H), 4.40 (t, *J* = 3.2 Hz, 1H), 4.34 (dd, *J* = 10.7, 5.5 Hz, 1H), 3.39 (s, 3H), 3.13–3.08 (m, 1H), 3.0 (br s, 1H), 2.26 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.0, 165.1, 143.8, 135.4, 133.6, 133.2, 129.9, 129.7, 129.6, 129.0, 128.5, 128.4, 127.3, 99.7, 70.1, 69.6, 62.5, 57.2, 56.9, 55.2, 21.4; HRMS [DART]. m/z calcd for $C_{28}H_{30}N_1O_9S$: 556.1641 $[M+H]^+$, Found: 556.1651 $[M+H]^+$.

Methyl 4,6-di-O-benzoyl-β-D-gulopyranoside (7βc). White solid; mp: 50.0–52.0 ºC; $[\alpha]_D^{20}$ = -65.5 (*c* = 1.0, $CHCl_3$); IR (neat) 3445, 2913, 1716, 1601, 1451, 1263, 1110, 1070, 1024, 707, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.11–8.04 (m, 2H) , 8.04–7.97 (m, 2H) , 7.62–7.50 (m, 2H) , 7.48–7.37 (m, 4H) , 5.38 (dd, *J* = 3.6, 1.3 Hz, 1H), 4.69 (d, *J* = 8.0 Hz, 1H), 4.61 (dd, *J* = 10.9, 6.9 Hz, 1H), 4.52 (td, *J* = 12.6, 1.2 Hz, 1H), 4.41 (dd, *J* = 10.9, 5.8 Hz, 1H), 4.30 (q, *J* = 3.3 Hz, 1H), 3.81–3.73 (m, 1H), 3.61 (s, 3H), 3.05 (s, 1H), 2.74 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.1, 165.4, 133.6, 133.1, 129.9, 129.7, 129.1, 128.5, 128.4, 101.6, 70.5, 70.2, 69.4, 68.8, 62.6, 57.2; HRMS [DART]. m/z calcd for $C_{21}H_{23}O_8$: 403.1393 $[M+H]^+$, Found: 403.1404 $[M+H]^+$.

Methyl 4,6-di-O-Pivaloyl-3-deoxy-3-(p-toluenesulfonamido)-β-D-gulopyranoside (5βd). Colorless liquid; $[\alpha]_D^{20}$ = -64.9 (*c* = 0.53, $CHCl_3$); IR (neat) 3473, 3280, 2972, 2866, 1732, 1480, 1281, 1155, 1136, 1091, 1043, 944, 752, 667, 551 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 5.51 (dd, *J* = 3.4, 1.1 Hz, 1H), 5.20–5.10 (m, 1H), 4.53 (d, *J* = 8.0 Hz, 1H), 4.44 (td, *J* = 6.9, 1.2 Hz 1H), 4.25 (dd, *J* = 11.0, 7.1 Hz 1H), 4.03 (dd, *J* = 11.0, 6.9 Hz, 1H), 3.62 (dd, *J* = 7.6, 5.0 Hz, 1H), 3.54 (s, 3H), 3.33 (t, *J* = 3.6 Hz 1H), 2.6 (br s, 1H), 2.43 (s, 3H), 1.28 (s, 9H), 1.20 (s, 9H); $^{13}C\{^1H\}$

NMR (100 MHz, $CDCl_3$) δ 177.9, 176.8, 144.1, 134.3, 129.8, 127.9, 101.0, 69.6, 67.5, 67.0, 61.4, 57.2, 53.7, 39.0, 38.7, 27.1, 21.6; HRMS [DART]. m/z calcd for $C_{23}H_{34}N_1O_8S$: 484.2005 $[M\text{-}OMe]^+$, Found: 484.2010 $[M\text{-}OMe]^+$.

Methyl 4,6-di-O-Benzyl-2-deoxy-2-(p-toluenesulfonamido)-β-D-gulopyranoside (6βd). Colorless liquid; $[\alpha]_D^{16}$ = -70.9 (*c* = 0.14, $CHCl_3$); IR (neat) 3479, 3277, 2972, 1732, 1480, 1282, 1141, 1083, 1042, 754, 732, 667, 551 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.0 (br s, 1H), 4.89 (dd, *J* = 3.6, 1.4 Hz, 1H), 4.53 (d, *J* = 8.3 Hz, 1H), 4.30–4.22 (m, 1H), 4.21–4.10 (m, 2H), 4.02 (dd, *J* = 11.1, 6.4 Hz, 1H), 3.35 (s, 3H), 3.01 (dt, *J* = 7.8, 3.5 Hz, 1H), 2.92 (br, 1H), 2.42 (s, 3H), 1.17 (s, 9H), 1.13 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.0, 177.2, 143.8, 136.1, 129.7, 127.4, 99.6, 69.9, 68.8, 67.7, 61.7, 56.9, 55.0, 39.0, 38.7, 27.1, 26.9, 21.5; HRMS [DART]. m/z calcd for $C_{23}H_{34}N_1O_8S$: 484.2005 $[M\text{-}OMe]^+$, Found: 484.1996 $[M\text{-}OMe]^+$.

Methyl 4,6-di-O-Pivaloyl-β-D-gulopyranoside (7βd). Colorless crystal; mp = 116.0–117.0 ˚ C; $[\alpha]_D^{21}$ = -48.9 ˚(*c* = 0.11, $CHCl_3$); IR (neat) 3495, 2975, 2907, 2845, 1716, 1480, 1284, 1164, 1122, 1061, 966, 768, 741, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.0 (br s, 1H), 4.58 (d, *J* = 8.1 Hz, 1H), 4.30 (t, *J* = 6.9 Hz, 1H), 4.22 (dd, *J* = 10.9, 7.3 Hz, 1H), 4.14–4.05 (m, 2H), 3.61–3.55 (m, 1H), 3.57 (s, 3H), 3.0 (br s, 1H), 2.7 (br s, 1H), 1.22 (s, 9H), 1.19 (s, 9H)); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.1, 177.6, 101.4, 70.0, 69.9, 69.3, 68.7, 61.9, 57.2, 39.1, 38.8, 27.1; HRMS [DART]. m/z calcd for $C_{17}H_{31}O_8$: 363.2019 $[M+H]^+$, Found:363.2014 $[M+H]^+$.

Methyl 4,6-di-O-(tert-Butyldimethylsilyl)-3-deoxy-3-(p-toluenesulfonamido)-β-D-gulopyranoside (5βe). Colorless crystal; mp: 119.0–121.0 ºC; $[\alpha]_D^{17}$ = -73.2 (*c* = 0.38, $CHCl_3$); IR (neat) 3496, 3214, 2961, 2927, 2855, 1462, 1254, 1161, 1117, 1078, 1052, 937, 833, 775, 674, 578 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.2 (br, 1H), 4.33 (d, *J* = 8.3 Hz, 1H), 4.18 (d, *J* = 2.7 Hz, 1H), 3.93 (t, *J* = 6.4 Hz, 1H), 3.79–3.60 (m, 3H), 3.50 (s, 3H), 3.31–3.25 (m, 1H), 2.42 (s, 3H), 0.90 (s, 9H), 0.82 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H), 0.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.0, 135.3, 129.9, 127.8, 101.4, 74.2, 68.5, 66.7, 62.3, 57.2, 56.8, 26.0, 25.9, 21.7, 18.4,

18.1, -4.7, -4.8, -5.0, -5.2; HRMS [DART]. m/z calcd for $C_{25}H_{46}N_1O_6SSi_2$: 544.2584 $[M\text{-}OMe]^+$, Found: 544.2594 $[M\text{-}OMe]^+$.

Methyl 4,6-di-O-(tert-Butyldimethylsilyl)-2-deoxy-2-(p-toluenesulfonamido)-β-D-gulopyranoside (6βe). White solid; mp: 187.0–188.0 ºC; $[\alpha]_D^{17}$ = -88.8 (*c* = 0.22 , $CHCl_3$); IR (neat) 3525 br, 3270, 2952, 2928, 2886, 2855, 1470, 1407, 1331, 1249, 1159, 1118, 1075, 1048, 942, 881, 835, 780, 670, 532 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 8.0 Hz, 2H), 4.82 (d, *J* = 2.7 Hz, 1H), 4.47 (d, *J* = 8.2 Hz, 1H), 4.17 (q, *J* = 3.1 Hz, 1H), 3.85–3.79 (m, 1H), 3.76 (d, *J* = 3.6 Hz, 1H), 3.65 (s, 1H), 3.12 (dt, *J* = 8.2, 2.8 Hz, 1H) , 2.69 (d, *J* = 3.1 Hz, 1H) , 2.41 (s, 3H) , 3.63 (s, 1H), 3.36 (s, 3H) 0.87 (s, 9H), 0.80 (s, 9H), 0.04 (s, 9H), 0.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.9, 135.8, 129.9, 127.6, 99.6, 74.5, 70.4, 68.7, 61.9, 56.7, 55.0, 26.0, 25.9, 21.7, 18.4, 18.1, -4.6, -4.9, -5.1, -5.2; HRMS [DART]. m/z calcd for $C_{25}H_{46}N_1O_6SSi_2$: 544.2584 $[M\text{-}OMe]^+$, Found: 544.2611 $[M\text{-}OMe]^+$.

Methyl 4,6-di-O-(tert-butyldimethylsilyl)-β-D-gulopyranoside (7βe). Colorless liquid; $[\alpha]_D^{19}$ = -42.6 °(*c* = 0.17, $CHCl_3$); IR (neat) 3439 br, 2950, 2928, 2881, 2856, 1472, 1389, 1361, 1253, 1076, 1046, 1022, 1005, 939, 833, 774, 731, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.49 (d, *J* = 8.0 Hz, 1H), 4.02 (t, *J* = 3.2 Hz, 1H), 3.89–3.82 (m, 2H), 3.75–3.68 (m, 3H), 2.5 (br s, 1H), 2.5 (br s, 1H), 0.90 (s, 9H), 0.89 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 101.7, 74.5, 71.8, 69.5, 69.4, 61.9, 57.2, 26.1, 25.9, 18.4, 18.2, -4.6, -4.8, -5.1, -5.2; HRMS [DART]. m/z calcd for $C_{19}H_{43}O_6Si_2$: 423.2598 $[M+H]^+$, Found: 423.2623 $[M+H]^+$.

Methyl 4,6-di-O-(tert-Butyldiphenylsilyl)-3-deoxy-3-(p-toluenesulfonamido)-β-D-gulopyranoside (5βf). Colorless liquid; $[\alpha]_D^{20}$ = -45.1 (*c* = 1.0, $CHCl_3$); IR (neat) 3046, 2930, 2857, 1427, 1160, 1104, 1091, 1055, 936, 908, 755, 734, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.54–7.29 (m, 16H), 7.25–7.11 (m, 6H), 4.9 (br s, 1H), 4.33 (d, *J* = 8.2 Hz, 1H), 4.20 (d, *J* = 3.3 Hz, 1H), 3.94–3.82 (m, 2H), 3.74 (dd, *J* = 10.8, 8.1 Hz, 1H), 3.55 (s, 3H), 3.44–3.39 (m, 1H), 3.10 (dd, *J* = 10.9, 3.2 Hz, 1H), 2.40 (s, 3H), 2.2 (br s, 1H), 0.98 (s, 9H), 0.89 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.6, 136.1, 135.9, 135.6, 135.2, 133.8, 133.6, 133.0, 132.4, 129.9, 129.7, 129.6, 127.8, 127.7, 127.6,

101.4, 75.1, 70.1, 66.8, 64.5, 56.9, 56.5, 27.1, 26.8, 21.7, 19.4, 19.2; Anal. Calcd for $C_{45}H_{57}NO_7SSi_2$: C, 67.04; H, 6.97; N, 1.70. Found: C, 66.77; H, 7.01; N, 1.90.

Methyl 4,6-di-O-(tert-Butyldiphenylsilyl)-2-deoxy-2-(p-toluenesulfonamido)-β-D-gulopyranoside (6βf). Colorless liquid; $[\alpha]_D^{20}$ = -41.4 (*c* = 1.0, $CHCl_3$); IR (neat) 2950, 2940, 2893, 2857, 1427, 1324, 1111, 1053, 998, 821, 755, 736, 700, 607 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.73 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.60–7.51 (m, 2H), 7.48–7.21 (m, 18H), 7.10 (t, *J* = 7.6 Hz, 2H), 5.34 (d, *J* = 4.8 Hz, 1H), 4.44 (d, *J* = 8.3 Hz, 1H), 4.17 (q, *J* = 3.2 Hz, 1H), 3.84 (dd, *J* = 8.3, 2.2 Hz, 1H), 3.75 (dd, *J* = 10.8, 8.2 Hz, 1H), 3.58 (d, *J* = 3.5 Hz, 1H), 3.44 (ddd, *J* = 8.0, 4.7, 3.0 Hz, 1H), 3.36 (s, 3H), 3.13 (dd, *J* = 10.8, 2.8 Hz, 1H), 2.6 (br s, 1H), 2.40 (s, 3H) 0.94 (s, 9H), 0.89 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.5, 136.6, 136.1, 135.9, 135.7, 135.5, 133.8, 133.6, 132.7, 132.5, 130.0, 129.8, 129.7, 127.8, 127.6, 127.5, 99.9, 75.4, 70.8, 64.6, 56.5, 54.6, 27.0, 26.8, 21.7, 19.4.19.1; Anal. Calcd for $C_{45}H_{57}NO_7SSi_2$: C, 67.04; H, 6.97; N, 1.70. Found: C, 66.67; H, 7.01; N, 1.70.

Methyl 4,6-di-O-(tert-Butyldiphenylsilyl)-β-D-gulopyranoside (7βf). Colorless liquid; $[\alpha]_D^{16}$ = -12.1 (*c* = 0.44, $CHCl_3$); IR (neat) 3417, 2952, 2930, 2893, 2857, 1427, 1104, 1069, 1046, 755, 735, 700, 614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.57–7.48 (m, 6H), 7.47–7.23 (m, 14H), 7.19 (t, *J* = 7.5 Hz, 2H), 4.46 (d, *J* = 8.0 Hz, 1H), 3.94–3.78 (m, 4H), 3.76 (d, *J* = 3.4 Hz, 1H), 3.58 (s, 3H), 3.50–3.40 (m, 1H), 2.28 (d, *J* = 2.7 Hz, 1H), 2.21 (d, *J* = 1.3 Hz, 1H), 1.00 (s, 9H), 0.96 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.0, 135.8, 135.7, 133.9, 133.7, 133.3, 132.9, 130.0, 129.9, 129.6, 127.8, 127.7, 101.7, 75.4, 71.4, 71.3, 69.4, 64.4, 57.0, 27.1, 26.9, 19.5, 19.3; HRMS [DART]. m/z calcd for $C_{38}H_{47}O_5Si_2$: 639.2962 $[M\text{-}OMe]^+$, Found: 639.2962 $[M\text{-}OMe]^+$.

DFT calculations

All calculations were performed with the Gaussian 09 package.[24] The geometry was optimized by the LC-BLYP[25] DFT method with 6-31G* basis set in gas phase. Frequency analyses were also carried out to identify the stationary points (no imaginary frequency) and to estimate thermodynamic properties at

298.15 K and 1 atm and Gibbs free energies. The molecular structures were depicted by using the CYLview v1.0.561 β.[26]

Supporting Information

The supporting information is available free of charge at

Procedure for the synthesis of starting materials **1α** and **4βa**-**4βf**, typical procedure for aminohydroxylation, characterization of products, ^{1}H and ^{13}C NMR spectral data for all compounds, and DFT calculations.

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Notes

The authors declare no competing financial interest.

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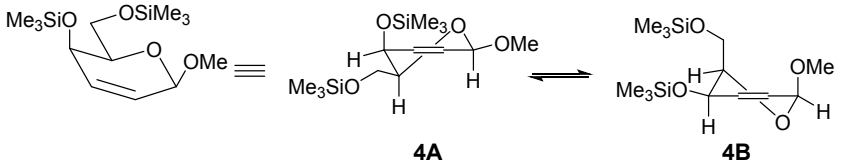

4A **4B**

	4A	**4B**
2,3-unsaturated-β-D-galactopyranoside	0	-1.7

kcal/mol

LC-BLYP/6-31G(d) (in gas phase)

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