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Synthesis of New Aza-*C*-disaccharides Linking 4-Deoxy-4-amino-β-L-*erythro*-furanose to C-2 of D-Glucose and D-Allose

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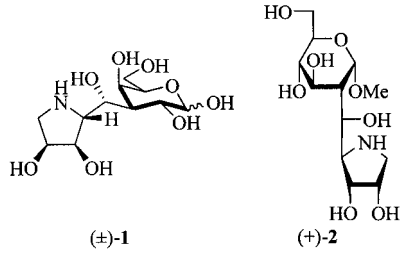
The cross-aldol condensation of *N*-benzyl-2,5-dideoxy-2,5-imino-3,4-*O*-isopropylidene-L-ribose with 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose (potassium enolate + HMPA) gave an aldol as the major product. DAST-induced water elimination gave two enones that were converted into the aza-*C*-disaccharides (+)-**4** [methyl 2-deoxy-2-(1,2,5-trideoxy-2,5-imino-L-ribitol-1*C*-yl)-α-D-glucopyranoside] and (+)-**5** (the α-D-allopyranoside analogue). Reduction of the aldol and deprotection provided aza-*C*-disaccharide (+)-**3** {methyl 2-deoxy-2-[(1*R* or 1*S*)-2,5-dideoxy-2,5-imino-L-ribitol-1*C*-yl]-α-D-allopyranoside} with a hydroxymethano linker.

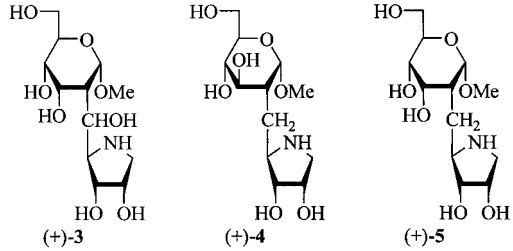
Introduction

The cell-surface oligosaccharides are the "words" used by cells to communicate with the outside world.[1–4] They guide social behaviour such as cell–cell and cell–invader interactions.[5] Carbohydrate mimetics such as *C*-disaccharides and aza-*C*-disaccharides are potential tools with which to study the mechanisms of cellular interactions, the biosynthesis of glycoproteins, the catabolism of glycoconjugates[6,7] and the mechanisms of digestion.[8,9] Glycomimetics can also be glycosidase inhibitors. They have focused applications as therapeutic agents to treat type-II diabetes (e.g., miglitol,[10] acarbose[11]) and obesity,[12] lysosomal diseases such as Gaucher's disease,[13] or influenza[14] [e.g., zanamivir (Relenza®),[15] oseltamivir phosphate (Tamiflu®)[16]]. Inhibitors of α-D-glucosidase and α-L-fucosidase are potential antiviral agents,[17] including anti-HIV agents.[5,18] Inhibitors of α-mannosidases are potential anticancer drugs.[19,20]

Aza-*C*-linked-disaccharides have more recognition sites than their corresponding monosaccharide analogues and are resistant to acid- and glycosidase-catalyzed hydrolysis. They are expected to become more specific inhibitors of glycosidases than monosaccharide mimetics such as polyhydroxypyrrolidine and piperidine derivatives.[21] The first example of an aza-*C*-disaccharide (1,5-dideoxy-1,5-imino-D-mannitol linked to the C-6 position of D-galactose through a CH_2 linker) was prepared by Johnson and co-workers[22] in 1994. Since then several groups have proposed ingenious and efficient syntheses of all kinds of aza-*C*-disaccharides and their analogues.[23,24] Because we have found that (2*R*,3*R*,4*S*)-3,4-dihydroxypyrrolidin-2-yl derivatives can be selective and potent α-mannosidase inhibitors[25] with antitumour activity[20] we have searched for methods to generate aza-*C*-disaccharides that link the (2*R*,3*R*,4*S*)-3,4-dihydroxypyrrolidin-2-yl moiety to various positions of several hexoses through hydroxymethano linkers [e.g., (±)-**1**,[26] (+)-**2**[27]].



In this report we disclose a very efficient approach to the synthesis of the new aza-*C*-disaccharides (+)-**3**, (+)-**4** and (+)-**5**.



Results and Discussion

Methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose [(+)-**6**] is readily available from D-man-

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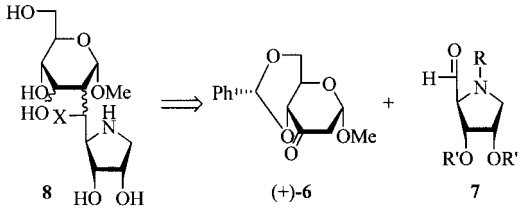
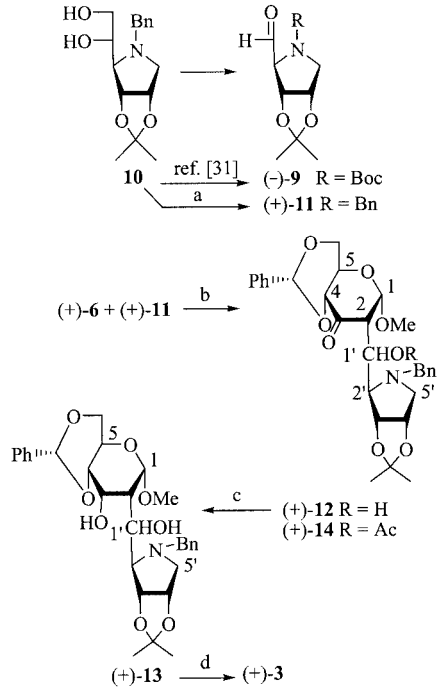
nose.[28] The groups of Fraser-Reid[29] and Chapleur[30] have established that β-elimination of a methoxide anion from enolates of **6** is a relatively slow reaction permitting the condensation of the latter with various electrophiles, without subsequent elimination. We thus envisaged a synthetic approach to the aza-*C*-disaccharides **8**, such as (+)-**3**, (+)-**4** and (+)-**5**, by cross-aldol condensation of ketone **6** with adequately protected 2,5-dideoxy-2,5-imino-L-ribose derivatives **7** (Scheme 1).



Scheme 1. Retrosynthesis plan to aza-*C*-disaccharides **8**.

We chose first the known aldehyde (–)-**9** derived from 1,4-(benzylimino)-1,4-dideoxy-2,3-*O*-isopropylidene-D-allitol (**10**)[31] for cross-aldol condensation with (+)-**6**. As related Boc-protected pyrrolidine-2-carbaldehyde derivatives could be coupled successfully with isolevoglucosenone-derived ketones via their dichlorozinc enolates,[32] we applied the same method to the reaction of (+)-**6** and (–)-**9** [(+)-**6** + KHMDS, then + $ZnCl_2$/THF, then + (–)-**9**]. However, none of our attempts met with success. We thus explored all kinds of other conditions [Et_3N/(c-$C_6H_{11})_2BCl$/Et_2O; iPr_2NH/$TiCl_4$, CH_2Cl_2, KHMDS alone/THF], but without better results as aldehyde (–)-**9** decomposed too readily (Scheme 2).

As the carbamate moiety of (–)-**9** is electrophilic and can compete with the aldehyde in reactions with the various enolates of (+)-**6**, we prepared the *N*-benzyl derivative (+)-**11**. Various conditions [$Pb(OAc)_4$/CH_2Cl_2, $NaIO_4$/H_2O/EtOH] for the oxidative cleavage of diol **10** were applied leading to low yields of impure aldehyde (+)-**11**. We finally found that pure (+)-**11** could be obtained in 90% yield when the oxidation with $NaIO_4$ involved a two-phase system with silica gel/H_2O and CH_2Cl_2. The aldehyde so-obtained, an unstable compound at room temperature and in the presence of light, underwent smooth cross-aldol condensation with (+)-**6**. The potassium enolate of (+)-**6** was prepared at –40 °C in THF by reaction with KHMDS. After cooling to –85 °C, HMPA (30% with respect to THF) was added and freshly obtained (+)-**11** was mixed with this solution. After 15 h at –85 °C, 95% conversion of (+)-**6** was observed by ^{1}H NMR spectroscopy. After aqueous work up, aldol (+)-**12** was obtained as the major product and isolated (purification by flash chromatography on silica gel) in 81% yield. Without HMPA the yield of (+)-**12** never surpassed 35%. No aldol was formed by using KHMDS and $ZnCl_2$ (–78 to –40 °C), LiHMDS or LDA. ^{1}H NMR analysis of the crude reaction mixture before chromatographic purification showed the presence of 2–4% of a diastereomeric aldol. The D-*ribo* configuration of the methyl



Scheme 2. Synthesis of aza-*C*-disaccharide (+)-**3**. Reagents and conditions: (a) SiO_2/CH_2Cl_2 + $NaIO_4$/H_2O, **10**/CH_2Cl_2 (90%); (b) 0.5 M KHMDS in toluene added to (+)-**6** in THF at –40 °C, 30 min, then addition of HMPA, –85 °C, addition of (+)-**11**/THF, –85 °C/15 h (81%); (c) $NaBH_4$/EtOH, 0 °C (68%); (d) H_2, PtO_2·H_2O (catalyst), H_2SO_4 (cat.)/MeOH, 20 °C, 24 h (60%).

pyranoside moiety of (+)-**12** was suggested by the ^3J(1-H,2-H) = 3.4 Hz coupling constant and was confirmed by the transformation described below. The absolute configuration of the hydroxymethano linker has not been determined. Assuming the validity of the Zimmerman–Traxler model[33] (steric factors and cyclic structure) for the cross-aldol reaction between (+)-**6** and (+)-**11**, it is expected to be (1′*S*) (Figure 1).

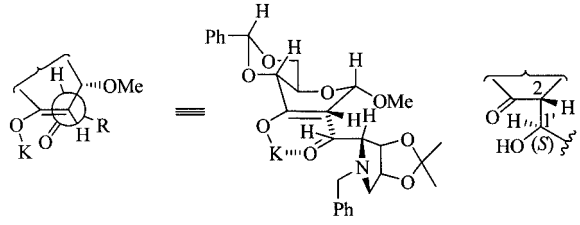


Figure 1. Hypothetical transition state of the aldol reaction: K enolate of (+)-**6** + (+)-**11** → (+)-**12**.

Reduction of (+)-**12** with $NaBH_4$ in EtOH furnished D-allopyranoside (+)-**13** (68%), the structure of which was confirmed by its ^{1}H NMR spectrum [^3J(2-H,3-H) = 3.4 Hz] and by the observation of an NOE between 3-OH and 5-H and between 2-H and 4-H in its 2D NOESY ^{1}H NMR spectrum. Hydrogenolysis of (+)-**13** in the presence of Adams' catalyst and H_2SO_4 gave (+)-**3** in 60% yield. Its structure (except for the absolute configuration of C-1′) was confirmed by its ^{1}H and ^{13}C NMR spectra and by its 2D COSY-45, ^{1}H NMR and HMQC (^{13}C/^{1}H) spectra.

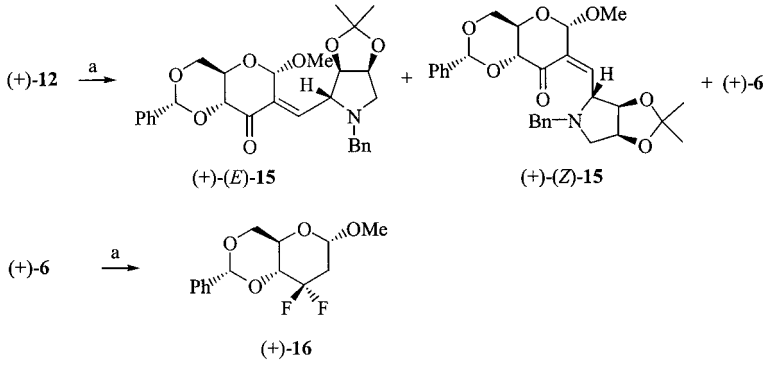
Attempts to convert aldol (+)-**12** into the corresponding enones via the corresponding methanesulfonic acid or acetic esters all failed. Treatment of (+)-**12** with Ac_2O/pyridine with or without DMAP catalyst led to complex mixtures containing less than 10% of the desired enones. Similarly, attempts to promote water elimination from (+)-**12** by treatment with I_2/Ph_3P,[34] $CuSO_4/SiO_2$ (20 °C, 2 Torr),[35] $BF_3{\cdot}Et_2O$,[36] camphorsulfonic acid/toluene (heating) or with HF/pyridine did not meet with success. We finally found that treatment of aldol (+)-**12** with DAST (Et_2NSF_3) under suitable conditions (3 equiv. of DAST, CH_2Cl_2, –78 to +20 °C in 4 h, quenching with H_2O and neutralization with $NaHCO_3$) provided a mixture of enones from which (+)-(*E*)-**15** and (+)-(*Z*)-**15** could be separated by flash chromatography on silica gel in 34 and 49% yields, respectively. By using a larger excess of DAST and longer reaction times at lower temperatures (–90 °C) lower yields of enones (+)-(*E*)-**15** and (+)-(*Z*)-**15** were obtained and the retro-aldol reaction competed generating ketone (+)-**6**, which was partially converted (Scheme 3) into difluoro derivative (+)-**16**, a known compound.[37]

The proportion of (*E*)-**15**/(*Z*)-**15** decreased from 34:49 to 10:34 (44% yield) on reducing the excess of DAST to 2 equiv. A possible mechanism for the smooth DAST-promoted β-elimination reaction (+)-**12** → (+)-(*E*)-**15** + (+)-(*Z*)-**15** involves the intermediate **17**, which is expected to undergo fast *syn* elimination (Scheme 4).[38]

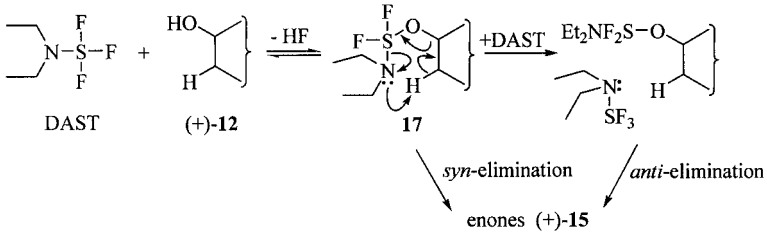
If this mechanism was unique, it would generate either (+)-(*E*)-**15** or (+)-(*Z*)-**15** since aldol (+)-**12** is a single compound. As the selectivity varies with the excess (concentration) of DAST, we propose that *anti* elimination also competes, the latter type of elimination being favoured at higher concentrations of DAST. We have observed that (+)-(*E*)-**15** and (+)-(*Z*)-**15** do not equilibrate on prolonged standing in the reaction mixture, but that both are destroyed. Alternatively, competition of an E1 mechanism (formation of cationic species by ionization of **17** assisted by the benzylamino moiety) cannot be rejected. DAST-induced eliminations from alcohols have been reported.[39]

Attempts to hydrogenate enone (+)-(*E*)-**15** with H_2/$PtO_2{\cdot}H_2O$ or Pd/charcoal led to complex mixtures of products. Under Luche and Gemal's conditions,[40] (+)-(*E*)-**15** was reduced stereoselectively into the allylic alcohol (–)-(*Z*)-**18** in 87% yield (Scheme 5). The ^1H NMR spectrum of the crude reaction mixture did not show any other product in addition to (–)-(*Z*)-**18**. Its structure was identified by the observation of an NOE between 3-H and 5-H in its 2D NOESY ^1H NMR spectrum.

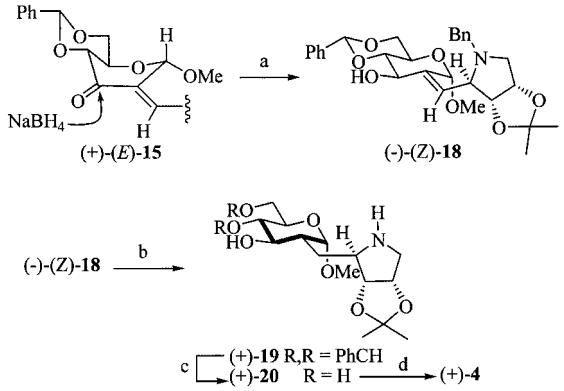
The high diastereoselectivity of the reduction (+)-(*E*)-**15** → (–)-(*Z*)-**18** can be interpreted in terms of the favoured boat conformation of the enone, rendering attack on the α-face highly preferred. Treatment of (–)-(*Z*)-**18** with H_2 (1 atm) and 10% palladium on charcoal in EtOAc gave a mixture of two products from which pure debenzylated amine (+)-**19** was isolated in 82% yield. Under these conditions, removal of the benzylidene group was a very slow process. This latter hydrogenolysis reaction required H_2 with $PtO_2{\cdot}H_2O$ as catalyst in methanol and (+)-**20** was obtained in 76% yield. Selective hydrolysis of the acetonide (+)-**20** with aqueous CF_3COOH provided the targeted aza-*C*-disaccharide (+)-**4** in 89% yield. The spectroscopic data of (+)-**19** and (+)-**20** (see Exp. Sect.) proved their structures.



Scheme 3. DAST-promoted β-elimination. Reagents and conditions: (a) 3 equiv. of DAST/CH_2Cl_2, –78 to 25 °C (83%).



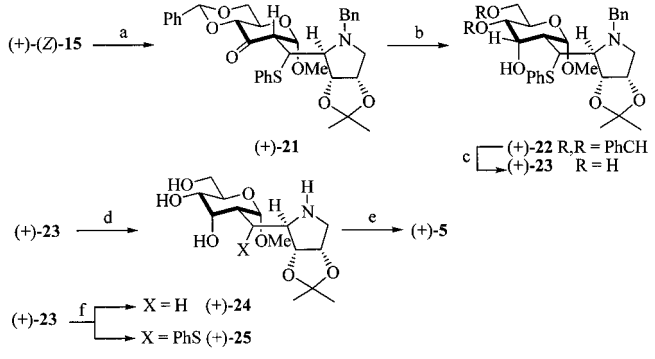
Scheme 4. Possible mechanism for the nonstereoselective β-elimination reaction (+)-**12** → (+)-(*E*)-**15** + (+)-(*Z*)-**15**.



Scheme 5. Preparation of aza-*C*-disaccharide (+)-**4**. Reagents and conditions: (a) $NaBH_4/CeCl_3$/MeOH, 20 °C (87%); (b) H_2 (1 atm), 10% Pd/charcoal/EtOAc, 20 °C, 6 h (82%); (c) H_2, $PtO_2{\cdot}H_2O$ (catalyst), H_2SO_4 (cat.), MeOH, 20 °C, 3 h (76%); (d) CF_3COOH/H_2O (4:1), 20 °C, 1 h (89%).

The high β-face hydrogenation of alkene (–)-(*Z*)-**18** and the preferred chair conformation adopted by the pyranoside moiety of this compound can be attributed to steric factors.

Under Luche and Gemal's conditions ($NaBH_4/CeCl_3$), reduction of enone (+)-(*Z*)-**15** gave the corresponding allylic alcohol (+)-(*E*)-**18** in low yield (< 20%). Steric hindrance to attack at the α-face of the ketone moiety of (+)-(*Z*)-**15** is probably the origin of this sluggish reaction. We thus explored another route to convert this enone into an aza-*C*-disaccharide. Conjugate addition of thiophenol[41] to (+)-(*Z*)-**15** in the presence of a catalytic amount of Et_3N furnished a single adduct (+)-**21** in 91% yield (Scheme 6). Then, reduction of ketone (+)-**21** with $NaBH_4$ in MeOH gave a single alcohol (+)-**22** in 95% yield. The absolute configuration of C-1′ in (+)-**21** and (+)-**22** has not been established. The relative *allo* configuration of the pyranoside moiety of (+)-**22** was deduced from its ^1H NMR spectrum [typical ^3J(2-H,3-H) = 3.0 Hz, ^3J(3-H,4-H) = 2.6 Hz].



Scheme 6. Synthesis of aza-*C*-disaccharide (+)-**5**. Reagents and conditions: (a) PhSH/CH_2Cl_2/Et_3N, 0 °C, 1 h (91%); (b) $NaBH_4$/EtOH, 0 °C, 1 h (95%); (c) H_2 (1 atm), 10% $PtO_2{\cdot}H_2O$, H_2SO_4 (cat.), MeOH, 20 °C, 15 h (80%); (d) Raney Ni (excess)/MeOH, 20 °C, 75 min (71%); (e) CF_3COOH/H_2O (4:1), 20 °C, 30 min (95%); (f) H_2 (1 atm), 10% Pd/charcoal, EtOAc, 20 °C, 6 h [54% of (+)-**23**, 29% of (+)-**24**, 4% of (+)-**25**].

On treatment of (+)-**22** with H_2 (1 atm) in the presence of $PtO_2{\cdot}H_2O$ as catalyst, smooth and selective hydrogenolysis of the benzylidene moiety occurred, leaving the thioether and the benzylamine intact. The triol (+)-**23** so-obtained was then hydrogenolysed with Raney nickel in methanol giving (+)-**24** in 71% yield. Selective hydrolysis of the acetonide moiety of (+)-**24** with aqueous CF_3COOH provided the aza-*C*-disaccharide (+)-**5** in 95% yield. The relative *allo* configuration of (+)-**24** and (+)-**5** was confirmed by their ^1H NMR and 2D ^1H NMR spectra. Attempts to carry out the hydrogenolysis of (+)-**23** with H_2 and Pd/charcoal gave mixtures of several products from which (+)-**25** was isolated in low yield in addition to (+)-**24** (≤ 29% yield).

Conclusions

Aldol condensation of *N*-benzyl-2,5-dideoxy-2,5-imino-3,4-*O*-isopropylidene-L-ribose with methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose gives an aldol as the major product which has been converted into three aza-*C*-disaccharides linking 4-deoxy-4-amino-β-L-*erythro*-furanose to C-2 of methyl α-D-glucopyranoside [(+)-**4**], to C-2 of α-D-allopyranoside [(+)-**5**] through a methano linker and to C-2 of α-D-allopyranoside [(+)-**3**] through a hydroxymethano linker. Exploration of the biological activities of these aza-*C*-disaccharides is in progress and will be reported in due course.

Experimental Section

General: Commercial reagents (Fluka, Aldrich) were used without further purification. Solvents were distilled prior to use: MeOH from Mg and I_2, DMF from P_2O_5 and CH_2Cl_2 from CaH_2. Light petroleum ether used refers to the fraction boiling at 40–60 °C. Solutions after reactions and extractions were concentrated in a rotary evaporator under reduced pressure. Liquid/solid flash chromatography (FC): columns of silica gel (0.040–0.63 mm, Merck No. 9385 silica gel 60, 240–400 mesh). TLC for reaction monitoring: Merck silica gel $60F_{254}$ plates; detection by UV light; Pancaldi reagent [$(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O], vanillin or $KMnO_4$. IR: Perkin–Elmer 1420 spectrometer. ^1H NMR: Bruker ARX 400 spectrometer (400 MHz); δ(H) in ppm relative to the solvent's residual ^1H signal ($CDCl_3$: δ = 7.27 ppm; CD_3OD: δ = 3.34 ppm) as internal reference; coupling constants *J* in Hz; all ^1H assignments were confirmed by 2D COSY-45 and 2D NOESY spectra. ^{13}C NMR: same instrument as above (100.6 MHz); δ(C) in ppm relative to the solvent's residual ^{13}C signal ($CDCl_3$: δ = 77.0 ppm; CD_3OD: δ = 48.5 ppm) as internal reference; coupling constants *J* in Hz. MS: chemical ionization (NH_3), fast atom bombardment (FAB) or electronic ionization (EI) mode; *m/z* (amu) (% relative to the base peak). MALDI-TOF mass spectra were obtained either from the Swiss Institute of Technology or from the University of Auckland Mass Spectral Facility. Elemental analyses: Ilse Beetz, 96301 Kronach, Germany. NMR spectra of the compounds described below are given in the Supporting Information.

***N*-Benzyl-2,5-dideoxy-2,5-imino-3,4-*O*-isopropylidene-L-ribose [(+)-11]:** A solution of $NaIO_4$ (94 mg, 0.44 mmol) in H_2O (0.68 mL) was added dropwise to a vigorously stirred suspension of chroma-

tographic grade silica gel (0.68 g) in CH_2Cl_2 (6 mL) in an Erlenmeyer flask and a flaky suspension was formed. Diol **10**[31] (100 mg, 0.34 mmol) in CH_2Cl_2 (0.68 mL) was then added. The reaction was monitored by TLC until disappearance of the starting material (10 min). The mixture was filtered under vacuum and the silica gel was washed with CH_2Cl_2. Evaporation of the solvent afforded the unstable product (+)-**11** (80 mg, 90%) as a colourless oil. $[\alpha]_{589}^{20}$ = +83 (*c* = 0.45, $CHCl_3$). IR (NaCl): $\tilde{\nu}$ = 3060, 3030, 2985, 2935, 2830, 2720, 2360, 1940, 1870, 1790, 1730, 1605, 1495, 1455, 1375, 1210, 1150, 1080, 1050, 860, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.53 (d, $^3J_{H,H}$ = 2.4 Hz, 1 H, 1-H), 7.34–7.30 (m, 5 H, Ar*H*), 4.79 (dd, $^3J_{H,H}$ = 5.9, $^3J_{H,H}$ = 2.4 Hz, 1 H, 3-H), 4.72 (dt, $^3J_{H,H}$ = 5.9, $^3J_{H,H}$ = 2.8 Hz, 1 H, 4-H), 4.01 (d, $^2J_{H,H}$ = 13.1 Hz, 1 H, CH_2Ph), 3.88 (d, $^2J_{H,H}$ = 13.1 Hz, 1 H, CH_2Ph), 3.44 (t, $^3J_{H,H}$ = 2.4 Hz, 1 H, 2-H), 3.17 (dd, $^2J_{H,H}$ = 11.2, $^3J_{H,H}$ = 5.9 Hz, 1 H, 5-H), 2.84 (dd, $^2J_{H,H}$ = 11.2, $^3J_{H,H}$ = 2.8 Hz, 1 H, 5-H), 1.57 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 201.0 (d, $^1J_{C,H}$ = 175 Hz, C-1), 138.0, 128.8, 128.4, 127.4 (Ar*C*), 113.1 [s, $C(CH_3)_2$], 80.5 (d, $^1J_{C,H}$ = 154 Hz, C-4), 79.6 (d, $^1J_{C,H}$ = 158 Hz, C-3), 76.1 (d, $^1J_{C,H}$ = 155 Hz, C-2), 58.5 (t, $^1J_{C,H}$ = 145 Hz, C-5), 58.1 (t, $^1J_{C,H}$ = 135 Hz, CH_2Ph), 27.0 (q, $^1J_{C,H}$ = 126 Hz, CH_3), 24.7 (q, $^1J_{C,H}$ = 126 Hz, CH_3) ppm. UV (MeCN): λ_{max} (ε) = 217 nm (2200 $dm^3 mol^{-1} cm^{-1}$). HRMS (MALDI-TOF): calcd. for $C_{15}H_{20}NO_3$ 262.1443 $[M + H]^+$; found 262.1467.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-[(1*R* or 1*S*)-2,5-(benzylimino)-2,5-dideoxy-3,4-*O*-isopropylidene-L-ribitol-1*C*-yl]-α-D-*ribo*-hexopyranosid-3-ulose [(+)-12]: KHMDS (0.5 M in toluene, 3.93 mL, 1.96 mmol) was added to a solution of ketone (+)-**6**[28] (400 mg, 1.51 mmol) in THF (8 mL) at –40 °C and the solution was stirred for 30 min. After cooling to –85 °C, HMPA (2.4 mL) was added. The mixture was allowed to settle for 1 h and then a solution of freshly synthesised aldehyde (+)-**11** (512 mg, 1.96 mmol) in THF (2 mL) was added. The resulting mixture was stirred at –85 °C overnight. Quenching was carried out at –85 °C by addition of an aq. satd. solution of NH_4Cl (5 mL). The mixture was extracted with EtOAc (10 mL, 3 times), the combined organic layers were dried with $MgSO_4$ and the solvent was evaporated. FC (hexane/EtOAc, 1:1) yielded the unstable adduct (+)-**12** (640 mg, 81%) as a white solid, m.p. 81–82 °C. $[\alpha]_{589}^{20}$ = +7 (*c* = 3.4, $CHCl_3$). IR (NaCl): $\tilde{\nu}$ = 3460, 3065, 2985, 2935, 2860, 1955, 1895, 1820, 1740, 1695, 1615, 1495, 1455, 1410, 1380, 1310, 1265, 1210, 1175, 1155, 1140, 1085, 1075, 1020, 970, 915 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.55–7.28 (m, 10 H, Ar*H*), 5.61 (s, 1 H, PhCH), 5.32 (d, $^3J_{H,H}$ = 3.4 Hz, 1 H, 1-H), 4.60 (dd, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 5.0 Hz, 1 H, 3-H), 4.51 (m, 1 H, 4′-H), 4.40 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4-H), 4.39 (dd, $^3J_{H,H}$ = 10.2, $^3J_{H,H}$ = 2.6 Hz, 1 H, 1′-H), 4.33 (dd, $^2J_{H,H}$ = 10.2, $^3J_{H,H}$ = 1.1 Hz, 1 H, 6-H), 4.19–4.08 (m, 1 H, 5-H), 4.10 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, CH_2Ph), 3.97 (t, $^2J_{H,H}$ = $^3J_{H,H}$ = 10.2 Hz, 1 H, 6-H), 3.46 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, CH_2Ph), 3.44 (s, 3 H, OCH_3), 3.25 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 5.8 Hz, 1 H, 5′-H), 3.13 (br. dd, $^3J_{H,H}$ = 10.2, $^3J_{H,H}$ = 3.4 Hz, 1 H, 2-H), 3.06 (dd, $^3J_{H,H}$ = 5.0, $^3J_{H,H}$ = 2.6 Hz, 1 H, 2′-H), 2.50 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 4.7 Hz, 1 H, 5′-H), 1.40 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 197.4 (s, C-3), 138.9 (s, Ar*C*), 138.5 (s, Ar*C*), 136.6 (s, Ar*C*), 129.3 (d, $^1J_{C,H}$ = 161 Hz, Ar*C*), 128.6 (d, $^1J_{C,H}$ = 160 Hz, Ar*C*), 128.3 (d, $^1J_{C,H}$ = 160 Hz, Ar*C*), 128.2 (d, $^1J_{C,H}$ = 160 Hz, Ar*C*), 126.9 (d, $^1J_{C,H}$ = 162 Hz, Ar*C*), 126.4 (d, $^1J_{C,H}$ = 157 Hz, Ar*C*), 113.3 [s, $C(CH_3)_2$], 102.7 (d, $^1J_{C,H}$ = 174 Hz, C-1), 101.7 (d, $^1J_{C,H}$ = 163 Hz, PhCH), 83.2 (d, $^1J_{C,H}$ = 134 Hz, C-4), 79.5 (d, $^1J_{C,H}$ = 154 Hz, C-3′), 77.3 (d, $^1J_{C,H}$ = 157 Hz, C-4′), 69.8 (t, $^1J_{C,H}$ = 140 Hz, C-6), 69.2 (d, $^1J_{C,H}$ = 143 Hz, C-2′), 66.7 (d, $^1J_{C,H}$ = 142 Hz, C-5), 62.9 (d, $^1J_{C,H}$ = 151 Hz, C-1′), 58.8 (t, $^1J_{C,H}$ = 142 Hz, C-5′), 57.0 (t, $^1J_{C,H}$ = 136 Hz, CH_2Ph), 55.5 (d, $^1J_{C,H}$ = 140 Hz, C-2), 55.4 (q, $^1J_{C,H}$ = 143 Hz, OCH_3), 27.4 (q, $^1J_{C,H}$ = 127 Hz, CH_3), 25.5 (q, $^1J_{C,H}$ = 126 Hz, CH_3) ppm. UV (MeCN): λ_{max} (ε) = 267 (3000), 214 nm (8200 $dm^3 mol^{-1} cm^{-1}$). MS (FAB): *m*/*z* (%) = 526 (5) $[M]^+$, 494 (12), 390 (2), 262 (4), 233 (15), 232 (100), 174 (4), 149 (6), 91 (100). HRMS (FAB): calcd. for $C_{29}H_{36}NO_8$ 526.24409 $[M + H]^+$; found 526.24319.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-[(1*R* or 1*S*)-2,5-(benzylimino)-2,5-dideoxy-3,4-*O*-isopropylidene-L-ribitol-1*C*-yl]-α-D-allopyranoside [(+)-13]: $NaBH_4$ (5 mg, 0.14 mmol) was added to a solution of crude (+)-**12** (75 mg, ca. 0.14 mmol) in EtOH (3 mL) at 0 °C. The mixture was stirred for 10 min and then quenched by addition of an aq. satd. solution of NH_4Cl (3 mL). The EtOH was evaporated and the residue extracted with EtOAc. The organic layer was dried with $MgSO_4$ and the solvent evaporated. FC (EtOAc/light petroleum ether, 1:1) yielded (+)-**13** (50 mg, 68%) as a white foam. $[\alpha]_{589}^{20}$ = +6 (*c* = 0.11, $CHCl_3$). IR (NaCl): $\tilde{\nu}$ = 3495, 3065, 3030, 2935, 2860, 2245, 1735, 1605, 1495, 1455, 1380, 1285, 1250, 1210, 1120, 1100, 1055, 1005, 910 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.56–7.26 (m, 10 H, Ar*H*), 5.67 (s, 1 H, PhCH), 5.03 (d, $^3J_{H,H}$ = 3.4 Hz, 1 H, 1-H), 4.65 (dd, $^3J_{H,H}$ = 6.5, ^3J = 5.0 Hz, 1 H, 3′-H), 4.53 (q, $^3J_{H,H}$ = 6.5 Hz, 1 H, 4′-H), 4.38 (dd, $^2J_{H,H}$ = 10.0, ^3J = 4.9 Hz, 1 H, 6-H), 4.36–4.33 (m, 2 H, 1′-H, 3-H), 4.20 (dt, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 4.9 Hz, 1 H, 5-H), 4.05 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, CH_2Ph), 3.83 (t, $^2J_{H,H}$ = $^3J_{H,H}$ = 10.0 Hz, 1 H, 6-H), 3.62 (dd, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 2.9 Hz, 1 H, 4-H), 3.49 (s, 3 H, OCH_3), 3.43 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, CH_2Ph), 3.43 (d, $^3J_{H,H}$ = 1.0 Hz, 1 H, 1′-OH), 3.30 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 6.5 Hz, 1 H, 5′-H), 3.02 (dd, $^3J_{H,H}$ = 4.7, $^3J_{H,H}$ = 2.0 Hz, 1 H, 2′-H), 2.92 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, 3-OH), 2.49 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 6.5 Hz, 1 H, 5′-H), 2.15 (dt, $^3J_{H,H}$ = 10.4, $^3J_{H,H}$ = 3.4 Hz, 1 H, 2-H), 1.47 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 137.4, 129.1, 128.9, 128.4, 128.2, 127.3, 126.3 (Ar*C*), 113.5 [s, $C(CH_3)_2$], 102.0 (d, $^1J_{C,H}$ = 163 Hz, PhCH), 99.8 (d, $^1J_{C,H}$ = 170 Hz, C-1), 79.6 (d, $^1J_{C,H}$ = 146 Hz, C-4), 78.9 (d, $^1J_{C,H}$ = 156 Hz, C-3′), 77.2 (d, $^1J_{C,H}$ = 155 Hz, C-4′), 69.4 (d, $^1J_{C,H}$ = 137 Hz, C-2′), 69.4 (t, $^1J_{C,H}$ = 148 Hz, C-6), 66.5 (d, $^1J_{C,H}$ = 152 Hz, C-3), 64.4 (d, $^1J_{C,H}$ = 150 Hz, C-1′), 59.0 (t, $^1J_{C,H}$ = 140 Hz, C-5′), 58.1 (d, $^1J_{C,H}$ = 149 Hz, C-5), 56.9 (t, $^1J_{C,H}$ = 143 Hz, CH_2Ph), 55.9 (q, $^1J_{C,H}$ = 143 Hz, OCH_3), 45.6 (d, $^1J_{C,H}$ = 127 Hz, C-2), 27.4 (q, $^1J_{C,H}$ = 127 Hz, CH_3), 25.4 (q, $^1J_{C,H}$ = 126 Hz, CH_3) ppm. UV (MeCN): λ_{max} (ε) = 203 (11600), 196 nm (13300 $dm^3 mol^{-1} cm^{-1}$). MS (CI): *m*/*z* (%) = 528 (4) $[M + H]^+$, 495 (5), 417 (3), 318 (7), 265 (38), 262 (30), 235 (85), 233 (54), 174 (53), 158 (40), 105 (59), 91 (100), 78 (31). HRMS (CI): calcd. for $C_{29}H_{38}NO_8$ 528.25974 $[M + H]^+$; found 528.26062.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-[(1*R* or 1*S*)-1-*O*-acetyl-2,5-benzylimino-2,5-dideoxy-3,4-*O*-isopropylidene-L-ribitol-1*C*-yl]-α-D-*ribo*-hexopyranosid-3-ulose [(+)-14]: Ac_2O (19.4 mg, 0.19 mmol) was added to a solution of (+)-**12** (50 mg, 0.095 mmol) in pyridine (2 mL) at 20 °C . The resulting mixture was stirred for 45 min. Pyridine was evaporated and the residue was diluted in EtOAc (10 mL) and in an aq. satd. solution of $NaHCO_3$ (10 mL) and extracted. The organic phase was dried with $MgSO_4$ and the solvent was evaporated. FC (light petroleum ether/EtOAc, gradient from 8:2 to 1:1) gave (+)-**14** (7.0 mg, 13%) and (+)-(*E*)-**15** (2.7 mg, 5%) as yellow solids. Data for (+)-(*E*)-**15**: see below. Data for (+)-**14**: M.p. 80–81 °C. $[\alpha]_{589}^{20}$ = +20 (*c* = 0.66, $CHCl_3$). IR (NaCl): $\tilde{\nu}$ = 2930, 2850, 1730, 1605, 1495, 1455, 1405, 1370, 1220, 1130, 1090, 1050, 1030, 910, 850 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.57–7.55 (m, 2 H, Ar*H*), 7.41–7.40 (m, 3 H, Ar*H*), 7.34–7.32 (m, 5 H, Ar*H*), 5.95 (dd, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 5.5 Hz, 1 H, 1′-H), 5.65 (s, 1 H,

PhCH), 5.55 (s, 1 H, 1-H), 4.89 (dd, $^3J_{H,H}$ = 6.3, ^3J = 4.8 Hz, 1 H, 3′-H), 4.62 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4-H), 4.59 (dd, $^3J_{H,H}$ = 6.3, $^3J_{H,H}$ = 5.1 Hz, 1 H, 4′-H), 4.42 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 4.5 Hz, 1 H, 6-H), 4.30 (d, $^2J_{H,H}$ = 13.4 Hz, 1 H, CH_2Ph), 4.19 (dt, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 4.5 Hz, 1 H, 5-H), 3.88 (t, $^2J_{H,H}$ = $^3J_{H,H}$ = 10.0 Hz, 1 H, 6-H), 3.61 (d, $^3J_{H,H}$ = 5.5 Hz, 1 H, 2-H), 3.41 (s, 3 H, OCH_3), 3.15 (d, $^2J_{H,H}$ = 13.4 Hz, 1 H, CH_2Ph), 3.06 (d, $^2J_{H,H}$ = 11.5 Hz, 1 H, 5′-H), 2.49 (dd, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 4.8 Hz, 1 H, 2′-H), 2.09 (dd, $^2J_{H,H}$ = 11.5, $^3J_{H,H}$ = 5.1 Hz, 1 H, 5′-H), 2.08 (s, 3 H, $OCOCH_3$), 1.57 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 199.4 (s, C-3), 169.8 (s, $OCOCH_3$), 138.6, 136.5, 129.4, 128.4, 128.3, 128.2, 127.0, 126.4 (Ar*C*), 111.5 [s, $C(CH_3)_2$], 102.4 (d, $^1J_{C,H}$ = 162 Hz, PhCH), 102.2 (d, $^1J_{C,H}$ = 174 Hz, C-1), 82.8 (d, $^1J_{C,H}$ = 145 Hz, C-4), 80.4 (d, $^1J_{C,H}$ = 155 Hz, C-3′), 77.4 (d, $^1J_{C,H}$ = 156 Hz, C-4′), 71.4, (d, $^1J_{C,H}$ = 154 Hz, C-1′), 69.9 (t, $^1J_{C,H}$ = 145 Hz, C-6), 67.7 (d, $^1J_{C,H}$ = 142 Hz, C-2′), 64.7 (d, $^1J_{C,H}$ = 152 Hz, C-5), 60.2 (t, $^1J_{C,H}$ = 135 Hz, C-5′), 58.9 (t, $^1J_{C,H}$ = 132 Hz, CH_2Ph), 58.8 (d, $^1J_{C,H}$ = 136 Hz, C-2), 54.8 (q, $^1J_{C,H}$ = 143 Hz, OCH_3), 26.3 (q, $^1J_{C,H}$ = 126 Hz, CH_3), 25.0 (q, $^1J_{C,H}$ = 127 Hz, CH_3), 21.4 (q, $^1J_{C,H}$ = 130 Hz, $OCOCH_3$) ppm. UV (MeCN): λ_{max} (ε) = 241 nm (1800 $dm^3 mol^{-1} cm^{-1}$). MS (FAB): *m*/*z* (%) = 568 (13) $[M]^+$, 508 (7), 308 (6), 232 (9), 219 (4), 154 (100), 136 (66), 120 (13), 91 (22), 89 (16). HRMS (FAB): calcd. for $C_{31}H_{38}NO_9$ 568.25466 $[M + H]^+$; found 568.25489.

Methyl 2-Deoxy-2-[(1*R* or 1*S*)-2,5-dideoxy-2,5-imino-L-ribitol-1*C*-yl]-α-D-allopyranoside [(+)-3]: A degassed mixture of (+)-**13** (40 mg, 0.076 mmol), $PtO_2 \cdot H_2O$ (2 mg, 10 mol%), one drop of H_2SO_4 and MeOH (2 mL) was stirred under H_2 (1 atm) at 20 °C for 24 h. After evaporation of the solvent, FC ($MeCN/NH_4OH$, 4:1) gave (+)-**3** (14 mg, 60%) as a yellowish oil. $[\alpha]_{589}^{25}$ = +41, $[\alpha]_{577}^{25}$ = +43, $[\alpha]_{435}^{25}$ = +52 (*c* = 0.4, MeOH). IR (NaCl): $\tilde{\nu}$ = 3350, 2930, 2360, 1590, 1410, 1115, 1045 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 4.90 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H, 1-H), 4.14–4.09 (m, 1 H, 1′-H), 4.10 (br. s, 1 H, 3-H), 3.98 (q, $^3J_{H,H}$ = 5.5 Hz, 1 H, 3′-H), 3.93 (q, $^3J_{H,H}$ = 5.5 Hz, 1 H, 4′-H), 3.80 (dd, $^2J_{H,H}$ = 9.6, $^3J_{H,H}$ = 4.7 Hz, 1 H, 6-H), 3.72–3.64 (m, 2 H, 5-H, 6-H), 3.37 (s, 3 H, OCH_3), 3.37–3.35 (m, 1 H, 4-H) 3.20 (dd, $^3J_{H,H}$ = 5.5, $^3J_{H,H}$ = 2.2 Hz, 1 H, 2′-H), 3.14 (dd, $^2J_{H,H}$ = 12.0, $^3J_{H,H}$ = 5.5 Hz, 1 H, 5′-H), 2.71 (dd, $^2J_{H,H}$ = 12.0, $^3J_{H,H}$ = 5.5 Hz, 1 H, 5′-H), 2.04 (dt, $^2J_{H,H}$ = 10.6, $^3J_{H,H}$ = 3.2 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, 25 °C): δ = 100.5 (d, $^1J_{C,H}$ = 168 Hz, C-1), 73.6 (d, $^1J_{C,H}$ = 149 Hz, C-3′), 71.8 (d, $^1J_{C,H}$ = 145 Hz, C-4′), 69.7 (d, $^1J_{C,H}$ = 148 Hz, C-3), 69.3 (d, $^1J_{C,H}$ = 145 Hz, C-5), 69.0 (d, $^1J_{C,H}$ = 144 Hz, C-1′), 68.8 (d, $^1J_{C,H}$ = 142 Hz, C-4), 64.7 (d, $^1J_{C,H}$ = 140 Hz, C-2′), 63.1 (t, $^1J_{C,H}$ = 143 Hz, C-6), 55.8 (q, $^1J_{C,H}$ = 142 Hz, OCH_3), 52.7 (t, $^1J_{C,H}$ = 139 Hz, C-5′), 47.4 (d, $^1J_{C,H}$ = 125 Hz, C-2) ppm. UV (MeOH): λ_{max} (ε) = 207 nm (1000 $dm^3 mol^{-1} cm^{-1}$). MS (FAB): *m*/*z* (%) = 310 (6) $[M + H]^+$, 309 (2) $[M]^+$, 308 (3), 273 (2), 219 (5), 176 (18), 152 (9), 124 (10), 120 (12), 89 (24). HRMS (FAB): calcd. for $C_{12}H_{24}NO_8$ 310.15019 $[M + H]^+$; found 310.14969. $C_{12}H_{23}NO_8 \cdot 3/2H_2O$ (322.16): calcd. C 42.85, H 7.79; found C 43.21, H 7.46.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-[(1*E*)-2,5-(benzylimino)-1,2,5-trideoxy-3,4-*O*-isopropylidene-L-ribitol-1*C*-ylidene]-α-D-*erythro*-hexopyranosid-3-ulose [(+)-(*E*)-15] and Methyl 4,6-*O*-Benzylidene-2-deoxy-2-[(1*Z*)-2,5-(benzylimino)-1,2,5-trideoxy-3,4-*O*-isopropylidene-L-ribitol-1*C*-ylidene]-α-D-*erythro*-hexopyranosid-3-ulose [(+)-(*Z*)-15]: Compound (+)-**12** (640 mg, 1.22 mmol) in CH_2Cl_2 (8 mL) was added to a solution of Et_2NSF_3 (DAST, 480 μL, 3.66 mmol) in CH_2Cl_2 (2 mL) at –78 °C. The resulting mixture was warmed to 25 °C over a period of 4 h. Quenching was carried out by addition of H_2O (4 mL) and then dropwise addition of an aq. satd. solution of $NaHCO_3$ (6 mL). The resulting mixture was extracted with CH_2Cl_2 (20 mL, 3 times) and after drying the collected organic fractions with $MgSO_4$, the solvent was evaporated. FC (light petroleum ether/EtOAc, 7:3) gave (+)-(*E*)-**15** (210 mg, 34%) and (+)-(*Z*)-**15** (303 mg, 49%), both as yellow solids. Data for (+)-(*E*)-**15**: M.p. 58–59 °C. $[\alpha]_{589}^{20}$ = +58 (*c* = 2.5, $CHCl_3$). IR (NaCl): $\tilde{\nu}$ = 2985, 2930, 2830, 1715, 1630, 1495, 1455, 1400, 1380, 1255, 1210, 1150, 1120, 1085, 1050, 1030, 1010, 915 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.53–7.28 (m, 10 H, Ar*H*), 6.75 (br. d, $^3J_{H,H}$ = 10.2 Hz, 1 H, 1′-H), 5.59 (s, 1 H, PhCH), 5.22 (br. s, 1 H, 1-H), 4.72 (dt, $^3J_{H,H}$ = 6.0, $^3J_{H,H}$ = 3.3 Hz, 1 H, 4′-H), 4.46 (dd, $^3J_{H,H}$ = 6.0, $^3J_{H,H}$ = 3.4 Hz, 1 H, 3′-H), 4.41 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 5.0 Hz, 1 H, 6-H), 4.30 (dt, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 5.0 Hz, 1 H, 5-H), 4.18 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4-H), 3.85 (t, $^2J_{H,H}$ = $^3J_{H,H}$ = 10.0 Hz, 1 H, 6-H), 3.77 (d, $^2J_{H,H}$ = 13.1 Hz, 1 H, CH_2Ph), 3.45 (d, $^2J_{H,H}$ = 13.1 Hz, 1 H, CH_2Ph), 3.43–3.40 (m, 1 H, 2′-H), 3.40 (s, 3 H, OCH_3), 3.21 (dd, $^2J_{H,H}$ = 10.6, $^3J_{H,H}$ = 6.0 Hz, 1 H, 5′-H), 2.69 (dd, $^2J_{H,H}$ = 10.6, $^3J_{H,H}$ = 3.3 Hz, 1 H, 5′-H), 1.57 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 189.6 (s, C-3), 142.6 (d, $^1J_{C,H}$ = 158 Hz, C-1′), 138.0 (s, Ar*C*), 136.6 (s, C-2), 136.5 (s, Ar*C*), 129.3 (d, $^1J_{C,H}$ = 159 Hz, Ar*C*), 128.5 (d, $^1J_{C,H}$ = 159 Hz, Ar*C*), 128.3 (d, $^1J_{C,H}$ = 160 Hz, Ar*C*), 128.2 (d, $^1J_{C,H}$ = 160 Hz, Ar*C*), 127.3 (d, $^1J_{C,H}$ = 160 Hz, Ar*C*), 126.4 (d, $^1J_{C,H}$ = 161 Hz, Ar*C*), 113.0 [s, $C(CH_3)_2$], 102.4 (d, $^1J_{C,H}$ = 163 Hz, PhCH), 98.2 (d, $^1J_{C,H}$ = 170 Hz, C-1), 84.4 (d, $^1J_{C,H}$ = 158 Hz, C-3′), 81.8 (d, $^1J_{C,H}$ = 140 Hz, C-4), 78.5 (d, $^1J_{C,H}$ = 156 Hz, C-4′), 69.2 (t, $^1J_{C,H}$ = 147 Hz, C-6), 66.4 (d, $^1J_{C,H}$ = 139 Hz, C-2′), 62.2 (d, $^1J_{C,H}$ = 152 Hz, C-5), 58.1 (t, $^1J_{C,H}$ = 140 Hz, C-5′), 57.0 (t, $^1J_{C,H}$ = 130 Hz, CH_2Ph), 54.9 (q, $^1J_{C,H}$ = 143 Hz, OCH_3), 27.2 (q, $^1J_{C,H}$ = 127 Hz, CH_3), 25.0 (q, $^1J_{C,H}$ = 126 Hz, CH_3) ppm. UV (MeCN): λ_{max} (ε) = 245 nm (8600 $dm^3 mol^{-1} cm^{-1}$). MS (EI): *m*/*z* (%) = 507 (8) $[M]^+$, 476 (11), 475 (10), 404 (8), 372 (4), 264 (3), 232 (28), 105 (23), 91 (100), 77 (13), 43 (14). HRMS (EI): calcd. for $C_{29}H_{33}NO_7$ 507.22570 $[M]^+$; found 507.22624. $C_{29}H_{33}NO_7$ (507.57): calcd. C 68.62, H 6.55; found C 68.57, H 6.56. Data for (+)-(*Z*)-**15**: M.p. 64–65 °C. $[\alpha]_{589}^{20}$ = +93 (*c* = 0.3, $CHCl_3$). IR (NaCl): $\tilde{\nu}$ = 2980, 2925, 2855, 1955, 1720, 1660, 1605, 1495, 1455, 1405, 1380, 1300, 1265, 1210, 1155, 1120, 1085, 1045, 1030, 1010, 970, 920 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.55–7.27 (m, 10 H, Ar*H*), 5.85 (d, ^3J = 9.7 Hz, 1 H, 1′-H), 5.58 (s, 1 H, PhCH), 5.21 (s, 1 H, 1-H), 4.65 (dt, $^3J_{H,H}$ = 6.4, $^3J_{H,H}$ = 4.4 Hz, 1 H, 4′-H), 4.40 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 4.6 Hz, 1 H, 6-H), 4.36–4.29 (m, 2 H, 3′-H, 4-H), 4.26 (dt, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 4.6 Hz, 1 H, 5-H), 3.93 (d, $^2J_{H,H}$ = 13.5 Hz, 1 H, CH_2Ph), 3.92–3.85 (m, 2 H, 6-H, 2′-H), 3.51 (d, $^2J_{H,H}$ = 13.5 Hz, 1 H, CH_2Ph), 3.40 (s, 3 H, OCH_3), 3.23 (dd, $^2J_{H,H}$ = 10.2, $^3J_{H,H}$ = 6.4 Hz, 1 H, 5′-H), 2.43 (dd, $^2J_{H,H}$ = 10.2, $^3J_{H,H}$ = 4.4 Hz, 1 H, 5′-H), 1.48 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 192.0 (s, C-3), 141.4 (d, $^1J_{C,H}$ = 154 Hz, C-1′), 138.9 (s, Ar*C*), 138.5 (s, Ar*C*), 136.6 (s, C-2), 129.3 (d, $^1J_{C,H}$ = 161 Hz, Ar*C*), 128.6 (d, $^1J_{C,H}$ = 160 Hz, Ar*C*), 128.3 (d, $^1J_{C,H}$ = 160 Hz, Ar*C*), 128.2 (d, $^1J_{C,H}$ = 160 Hz, Ar*C*), 126.9 (d, $^1J_{C,H}$ = 162 Hz, Ar*C*), 126.4 (d, $^1J_{C,H}$ = 157 Hz, Ar*C*), 113.8 [s, $C(CH_3)_2$], 104.0 (d, $^1J_{C,H}$ = 170 Hz, C-1), 102.0 (d, $^1J_{C,H}$ = 163 Hz, PhCH), 85.5 (d, $^1J_{C,H}$ = 157 Hz, C-3′), 83.8 (d, $^1J_{C,H}$ = 144 Hz, C-4), 78.1 (d, C-4′), 69.4 (t, $^1J_{C,H}$ = 140 Hz, C-6), 66.5 (d, $^1J_{C,H}$ = 142 Hz, C-2′), 64.0 (d, $^1J_{C,H}$ = 151 Hz, C-5), 58.2 (t, $^1J_{C,H}$ = 142 Hz, C-5′), 57.7 (t, $^1J_{C,H}$ = 136 Hz, CH_2Ph), 54.8 (q, $^1J_{C,H}$ = 143 Hz, OCH_3), 27.3 (q, $^1J_{C,H}$ = 128 Hz, CH_3), 25.5 (q, $^1J_{C,H}$ = 127 Hz, CH_3) ppm. UV (MeCN): λ_{max} (ε) = 243 nm(6800 $dm^3 mol^{-1} cm^{-1}$). MS (EI): *m*/*z* (%) = 507 (7) $[M]^+$, 475 (33), 430 (3), 398 (4), 340 (5), 245 (7), 232 (20), 105 (22), 91 (100), 77 (16), 57 (22), 43 (23). HRMS (EI): calcd. for $C_{29}H_{33}NO_7$ 507.22570 $[M]^+$; found 507.22559. $C_{29}H_{33}NO_7$ (507.57): calcd. C 68.62, H 6.55; found C 68.44, H 6.58.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-[(1*Z*)-2,5-(benzylimino)-1,2,5-trideoxy-3,4-*O*-isopropylidene-L-ribitol-1*C*-ylidene]-α-D-*arabino*-hexopyranoside [(–)-(*Z*)-18]: $NaBH_4$ (1.0 mg, 0.027 mmol) was added to a solution of $CeCl_3$ (6.7 mg, 0.027 mmol) and (+)-(*E*)-**15** (14 mg, 0.027 mmol) in MeOH (0.75 mL). After 10 min, the reaction was quenched with an aq. satd. solution of NH_4Cl (10 mL) and the resulting mixture extracted with Et_2O (10 mL, 3 times). The organic phases were dried with $MgSO_4$ and the solvents evaporated. FC (light petroleum ether/EtOAc, 1:1) gave (–)-(*Z*)-**18** (12 mg, 87%) as a colourless oil. $[\alpha]_{589}^{20} = -19$ (*c* = 0.21, $CHCl_3$). IR (NaCl): $\tilde{\nu}$ = 3435, 2985, 2930, 2860, 1640, 1495, 1455, 1375, 1255, 1210, 1160, 1105, 1090, 1060, 1035, 970 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.53–7.30 (m, 10 H, Ar*H*), 5.85 (dd, $^3J_{H,H}$ = 9.5, $^4J_{H,H}$ = 1.8 Hz, 1 H, 1′-H), 5.56 (s, 1 H, PhCH), 5.39 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H, 1-H), 4.70–4.61 (m, 2 H, 4′-H, 3-H), 4.37 (dd, $^3J_{H,H}$ = 7.0, $^3J_{H,H}$ = 4.8 Hz, 1 H, 3′-H), 4.31 (dd, $^3J_{H,H}$ = 10.2, ^3J = 4.8 Hz, 1 H, 6-H), 4.02 (dt, $^3J_{H,H}$ = 10.2, $^3J_{H,H}$ = 4.8 Hz, 1 H, 5-H), 3.87 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, CH_2Ph), 3.75 (t, $^2J_{H,H}$ = $^3J_{H,H}$ = 10.2 Hz, 1 H, 6-H), 3.47–3.40 (m, 2 H, 2′-H, 4-H), 3.42 (s, 3 H, OCH_3), 3.35 (d, 1 H, $^2J_{H,H}$ = 13.2 Hz, CH_2Ph), 3.20 (dd, $^2J_{H,H}$ = 10.3, $^3J_{H,H}$ = 6.2 Hz, 1 H, 5′-H), 2.48 (dd, $^2J_{H,H}$ = 10.3, $^3J_{H,H}$ = 4.0 Hz, 1 H, 5′-H), 1.54 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.3 (s, Ar*C*), 137.5 (s, C-2), 137.2 (s, Ar*C*), 129.8 (d, $^1J_{C,H}$ = 161 Hz, Ar*C*), 128.8 (d, $^1J_{C,H}$ = 162 Hz, Ar*C*), 128.4 (d, $^1J_{C,H}$ = 159 Hz, Ar*C*), 128.2 (d, $^1J_{C,H}$ = 159 Hz, Ar*C*), 127.1 (d, $^1J_{C,H}$ = 159 Hz, Ar*C*), 126.2 (d, $^1J_{C,H}$ = 161 Hz, Ar*C*), 124.9 (d, $^1J_{C,H}$ = 140 Hz, C-1′), 113.0 [s, $C(CH_3)_2$], 101.9 (d, $^1J_{C,H}$ = 158 Hz, PhCH), 97.7 (d, $^1J_{C,H}$ = 169 Hz, C-1), 85.0 (d, $^1J_{C,H}$ = 155 Hz, C-3′), 84.1 (d, $^1J_{C,H}$ = 145 Hz, C-4), 77.9 (C-3), 69.4 (d, $^1J_{C,H}$ = 149 Hz, C-4′), 69.0 (t, $^1J_{C,H}$ = 145 Hz, C-6), 66.3 (d, $^1J_{C,H}$ = 135 Hz, C-2′), 62.9 (d, $^1J_{C,H}$ = 147 Hz, C-5), 58.0 (t, $^1J_{C,H}$ = 137 Hz, C-5′), 56.9 (t, $^1J_{C,H}$ = 135 Hz, CH_2Ph), 54.7 (q, $^1J_{C,H}$ = 143 Hz, OCH_3), 27.3 (q, $^1J_{C,H}$ = 127 Hz, CH_3), 25.3 (q, $^1J_{C,H}$ = 126 Hz, CH_3) ppm. UV (MeCN): λ_{max} (ε) = 206 nm (23000 $dm^3 mol^{-1} cm^{-1}$). MS (FAB): *m*/*z* (%) = 510 (77) $[M + H]^+$, 509 (18) $[M]^+$, 508 (20), 494 (17), 478 (33), 391 (13), 360 (5), 232 (10), 120 (16), 91 (100). HRMS (FAB): calcd. for $C_{29}H_{36}NO_7$ 510.24918 $[M + H]^+$; found 510.24725.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-[(1*E*)-2,5-(benzylimino)-1,2,5-trideoxy-3,4-*O*-isopropylidene-L-ribitol-1*C*-ylidene]-α-D-*arabino*-hexopyranoside [(+)-(*E*)-18]: $NaBH_4$ (0.5 mg, 0.013 mmol) was added to a solution of $CeCl_3$ (3.2 mg, 0.013 mmol) and (+)-(*Z*)-**15** (6.7 mg, 0.013 mmol) in MeOH (0.5 mL). After 10 min, the reaction was quenched with an aq. satd. solution of NH_4Cl (10 mL) and the resulting mixture extracted with Et_2O (10 mL, 3 times). The organic phases were dried with $MgSO_4$ and the solvents evaporated. FC (light petroleum ether/EtOAc, 1:1) gave (+)-(*E*)-**18** (1.5 mg, 20%) as a colourless oil. $[\alpha]_{589}^{20} = +22$ (*c* = 0.15, $CHCl_3$). IR (NaCl): $\tilde{\nu}$ = 3435, 2925, 2850, 1725, 1650, 1495, 1455, 1375, 1335, 1260, 1210, 1175, 1155, 1125, 1090, 1060, 970 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.56–7.26 (m, 10 H, Ar*H*), 5.80 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.8 Hz, 1 H, 1′-H), 5.53 (s, 1 H, PhCH), 4.90 (s, 1 H, 1-H), 4.76–4.70 (m, 2 H, 4′-H, 3-H), 4.64 (dd, $^3J_{H,H}$ = 6.9, $^3J_{H,H}$ = 5.5 Hz, 1 H, 3′-H), 4.29 (dd, $^3J_{H,H}$ = 10.1, $^3J_{H,H}$ = 4.8 Hz, 1 H, 6-H), 4.04 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, CH_2Ph), 3.98 (dt, $^3J_{H,H}$ = 10.1, $^3J_{H,H}$ = 4.8 Hz, 1 H, 5-H), 3.72 (t, $^2J_{H,H}$ = $^3J_{H,H}$ = 10.1 Hz, 1 H, 6-H), 3.51 (dd, $^3J_{H,H}$ = 8.0, $^3J_{H,H}$ = 5.5 Hz, 1 H, 2′-H), 3.46 (t, $^3J_{H,H}$ = 10.1 Hz, 1 H, 4-H), 3.40 (s, 3 H, OCH_3), 3.39 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, CH_2Ph), 3.25 (dd, $^2J_{H,H}$ = 10.3, $^3J_{H,H}$ = 6.2 Hz, 1 H, 5′-H), 2.38 (dd, $^2J_{H,H}$ = 10.3, $^3J_{H,H}$ = 4.9 Hz, 1 H, 5′-H), 1.51 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 141.7 (s, Ar*C*), 136.9 (s, C-2), 129.0 (d, $^1J_{C,H}$ = 161 Hz, Ar*C*), 128.8 (d, $^1J_{C,H}$ = 162 Hz, Ar*C*), 128.5 (d, $^1J_{C,H}$ = 159 Hz, Ar*C*), 128.2 (d, $^1J_{C,H}$ = 159 Hz, Ar*C*), 127.5 (d, $^1J_{C,H}$ = 152 Hz, C-1′), 126.4 (d, $^1J_{C,H}$ = 159 Hz, Ar*C*), 114.0 [s, $C(CH_3)_2$], 105.3 (d, $^1J_{C,H}$ = 170 Hz, C-1), 102.1 (d, $^1J_{C,H}$ = 160 Hz, PhCH), 85.9 (d, $^1J_{C,H}$ = 157 Hz, C-3′), 84.7 (d, $^1J_{C,H}$ = 146 Hz, C-4), 77.2 (C-3), 70.6 (d, $^1J_{C,H}$ = 150 Hz, C-4′), 69.1 (t, $^1J_{C,H}$ = 147 Hz, C-6), 66.8 (d, $^1J_{C,H}$ = 139 Hz, C-2′), 64.0 (d, $^1J_{C,H}$ = 149 Hz, C-5), 57.9 (t, $^1J_{C,H}$ = 140 Hz, C-5′), 57.5 (t, $^1J_{C,H}$ = 135 Hz, CH_2Ph), 54.8 (q, $^1J_{C,H}$ = 145 Hz, OCH_3), 27.1 (q, $^1J_{C,H}$ = 128 Hz, CH_3), 25.2 (q, $^1J_{C,H}$ = 127 Hz, CH_3) ppm. UV (MeCN): λ_{max} (ε) = 257 (1300), 241 nm (1800 $dm^3 mol^{-1} cm^{-1}$). MS (FAB): *m*/*z* (%) = 510 (80) $[M + H]^+$, 509 (14) $[M]^+$, 508 (15), 494 (3), 478 (12), 391 (13), 360 (3), 232 (12), 219 (5), 120 (16), 167 (9), 149 (28), 120 (20), 91 (100). HRMS (FAB): calcd. for $C_{29}H_{36}NO_7$ 510.24918 $[M + H]^+$; found 510.24884.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-(1,2,5-trideoxy-2,5-imino-3,4-*O*-isopropylidene-L-ribitol-1*C*-yl)-α-D-glucopyranoside [(+)-19]: A degassed suspension of (–)-(*Z*)-**18** (75 mg, 0.15 mmol), 10% Pd on charcoal (156 mg) and EtOAc (15 mL) was stirred under H_2 (1 atm) at 20 °C for 6 h. The mixture was filtered through Celite and the solvent evaporated. FC (EtOAc) gave (+)-**19** (51 mg, 82%) as a white solid, m.p. 76–77 °C. $[\alpha]_{589}^{25} = +5$, $[\alpha]_{577}^{25} = +5$, $[\alpha]_{435}^{25} = +9$, $[\alpha]_{405}^{25} = +11$ (*c* = 1.35, MeOH). IR (NaCl): $\tilde{\nu}$ = 3415, 2930, 2360, 1640, 1375, 1060 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.48–7.46 (m, 2 H, Ar*H*), 7.31–7.29 (m, 3 H, Ar*H*), 5.56 (s, 1 H, PhCH), 4.71 (t, $^3J_{H,H}$ = 5.0 Hz, 1 H, 4′-H), 4.66 (d, $^3J_{H,H}$ = 3.5 Hz, 1 H, 1-H), 4.38 (br. d, $^3J_{H,H}$ = 5.0 Hz, 1 H, 3′-H), 4.16 (dd, $^2J_{H,H}$ = 10.2, $^3J_{H,H}$ = 4.8 Hz, 1 H, 6-H), 3.76–3.63 (m, 3 H, 5-H, 6-H, 3-H), 3.43 (t, $^3J_{H,H}$ = 9.0 Hz, 1 H, 4-H), 3.43 (s, 3 H, OCH_3), 3.14 (dd, $^3J_{H,H}$ = 12.0, $^3J_{H,H}$ = 4.0 Hz, 1 H, 2′-H), 2.97 (br. d, $^2J_{H,H}$ = 13.3 Hz, 1 H, 5′-H), 2.93 (dd, $^2J_{H,H}$ = 13.3, $^3J_{H,H}$ = 5.0 Hz, 1 H, 5′-H), 1.83 (m, 1 H, 2-H), 1.61 (ddd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 12.0, $^3J_{H,H}$ = 7.0 Hz, 1 H, 1′-H), 1.47 (dt, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 4.0 Hz, 1 H, 1′-H), 1.40 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 139.4 (s, Ar*C*), 129.9 (d, $^1J_{C,H}$ = 160 Hz, Ar*C*), 129.1 (d, $^1J_{C,H}$ = 160 Hz, Ar*C*), 127.6 (d, $^1J_{C,H}$ = 162 Hz, Ar*C*), 112.3 [s, $C(CH_3)_2$], 103.2 (d, $^1J_{C,H}$ = 163 Hz, PhCH), 102.8 (d, $^1J_{C,H}$ = 170 Hz, C-1), 87.7 (d, $^1J_{C,H}$ = 154 Hz, C-3′), 84.8 (d, $^1J_{C,H}$ = 142 Hz, C-4), 82.8 (d, $^1J_{C,H}$ = 158 Hz, C-4′), 71.2 (d, $^1J_{C,H}$ = 142 Hz, C-3), 70.2 (t, $^1J_{C,H}$ = 145 Hz, C-6), 64.9 (d, $^1J_{C,H}$ = 143 Hz, C-2′), 63.9 (d, $^1J_{C,H}$ = 148 Hz, C-5), 55.5 (q, $^1J_{C,H}$ = 142 Hz, OCH_3), 51.4 (t, $^1J_{C,H}$ = 140 Hz, C-5′), 47.4 (d, $^1J_{C,H}$ = 128 Hz, C-2), 31.2 (t, $^1J_{C,H}$ = 126 Hz, C-1′), 26.5 (q, $^1J_{C,H}$ = 127 Hz, CH_3), 24.2 (q, $^1J_{C,H}$ = 126 Hz, CH_3) ppm. UV (MeCN): λ_{max} (ε) = 204 (3600), 194 nm (3800 $dm^3 mol^{-1} cm^{-1}$). HRMS (MALDI-TOF): calcd. for $C_{22}H_{31}NNaO_7$ 444.1998 $[M + Na]^+$; found 444.1947.

Methyl 2-Deoxy-2-(1,2,5-trideoxy-2,5-imino-3,4-*O*-isopropylidene-L-ribitol-1*C*-yl)-α-D-glucopyranoside [(+)-20]: A degassed mixture of (+)-**19** (20 mg, 0.047 mmol), $PtO_2 \cdot H_2O$ (2 mg, 15 mol%) and MeOH (3 mL) was stirred under H_2 (1 atm) at 20 °C for 3 h. The resulting suspension was filtered through Celite and the solution evaporated. FC ($MeCN/NH_4OH$, 9:1) gave (+)-**20** (12 mg, 76%) as a white solid, m.p. 71–72 °C. $[\alpha]_{589}^{25} = +26$, $[\alpha]_{577}^{25} = +27$, $[\alpha]_{435}^{25} = +48$, $[\alpha]_{405}^{25} = +58$ (*c* = 0.5, MeOH). IR (NaCl): $\tilde{\nu}$ = 3400, 3110, 3040, 2360, 1405, 1055 cm^{-1}. ^1H NMR (400 MHz, CD_3OD, 25 °C): δ = 4.96 (br. t, $^3J_{H,H}$ = 6.0 Hz, 1 H, 4′-H), 4.67 (br. s, 1 H, 1-H), 4.66 (br. d, $^3J_{H,H}$ = 6.0 Hz, 1 H, 3′-H), 3.87 (br. dd, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 6.0 Hz, 1 H, 3-H), 3.79 (dd, $^2J_{H,H}$ = 11.0, $^3J_{H,H}$ = 2.2 Hz, 1 H, 6-H), 3.67 (dd, $^2J_{H,H}$ = 11.0, $^3J_{H,H}$ = 5.4 Hz, 1 H, 6-H), 3.57 (br. t, $^3J_{H,H}$ = 9.5 Hz, 1 H, 2′-H), 3.52–3.40 (m, 3 H, 5′-H, 5′-H, 5-H), 3.23 (s, 3 H, OCH_3), 3.24 (dd, $^3J_{H,H}$ = 11.0, $^3J_{H,H}$ = 6.0 Hz, 1 H, 4-H), 1.80–1.76 (m, 3 H, 2-H, 1′-H, 1′-H), 1.49 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, 25 °C):

δ = 113.2 [s, $C(CH_3)_2$], 102.2 (d, $^1J_{C,H}$ = 170 Hz, C-1), 84.7 (d, $^1J_{C,H}$ = 161 Hz, C-3′), 79.2 (d, $^1J_{C,H}$ = 161 Hz, C-4′), 74.8 (d, $^1J_{C,H}$ = 140 Hz, C-3), 73.7 (d, $^1J_{C,H}$ = 139 Hz, C-5), 72.7 (d, $^1J_{C,H}$ = 143 Hz, C-4), 66.2 (d, $^1J_{C,H}$ = 147 Hz, C-2′), 62.6 (t, $^1J_{C,H}$ = 144 Hz, C-6), 55.4 (q, $^1J_{C,H}$ = 141 Hz, OCH_3), 50.2 (t, $^1J_{C,H}$ = 149 Hz, C-5′), 45.6 (d, $^1J_{C,H}$ = 127 Hz, C-2), 29.8 (t, $^1J_{C,H}$ = 133 Hz, C-1′), 26.1 (q, $^1J_{C,H}$ = 128 Hz, CH_3), 24.0 (q, $^1J_{C,H}$ = 127 Hz, CH_3) ppm. UV (MeCN): λ_{max} (ε) = 197 nm (1400 $dm^3 mol^{-1} cm^{-1}$). HRMS (MALDI-TOF): calcd. for $C_{15}H_{28}NO_7$ 334.1866 $[M + H]^+$; found 334.1864.

Methyl 2-Deoxy-2-(1,2,5-trideoxy-2,5-imino-L-ribitol-1*C*-yl)-α-D-glucopyranoside [(+)-4]: Acetonide (+)-**20** (10 mg, 0.033 mmol) was dissolved in CF_3COOH/H_2O (4:1, 9.0 mL) at 20 °C. The reaction was monitored by TLC and after 1 h, the solvent was evaporated. FC (MeCN/NH_4OH, 4:1) yielded (+)-**4** (8.6 mg, 89%) as a white solid, m.p. 65–66 °C. $[\alpha]_{589}^{25}$ = +48, $[\alpha]_{577}^{25}$ = +53, $[\alpha]_{435}^{25}$ = +96, $[\alpha]_{405}^{25}$ = +117 (*c* = 0.21, MeOH). IR (NaCl): $\tilde{\nu}$ = 3150, 2360, 1405, 1055 cm^{-1}. ^1H NMR (400 MHz, CD_3OD, 25 °C): δ = 4.69 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H, 1-H), 4.20 (br. dd, $^3J_{H,H}$ = 4.8, $^3J_{H,H}$ = 3.9 Hz, 1 H, 4′-H), 3.84 (dd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 3.9 Hz, 1 H, 3′-H), 3.79 (dd, $^2J_{H,H}$ = 11.8, $^3J_{H,H}$ = 2.2 Hz, 1 H, 6-H), 3.68 (dd, $^2J_{H,H}$ = 11.8, $^3J_{H,H}$ = 5.4 Hz, 1 H, 6-H), 3.54 (br. dd, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 9.2 Hz, 1 H, 3-H), 3.51–3.41 (m, 3 H, 5-H, 5′-H, 2′-H), 3.34 (s, 3 H, OCH_3), 3.25 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4-H), 3.20 (br. d, $^2J_{H,H}$ = 11.8 Hz, 1 H, 5′-H), 2.01 (ddd, $^2J_{H,H}$ = 15.1, $^3J_{H,H}$ = 5.5, $^3J_{H,H}$ = 3.2 Hz, 1 H, 1′-H), 1.90–1.82 (m, 1 H, 1′-H), 1.78 (dq, $^3J_{H,H}$ = 9.2, $^3J_{H,H}$ = 3.2 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, 25 °C): δ = 101.5 (d, $^1J_{C,H}$ = 167 Hz, C-1), 77.4 (d, $^1J_{C,H}$ = 143 Hz, C-3′), 74.3 (d, $^1J_{C,H}$ = 139 Hz, C-3), 73.8 (d, $^1J_{C,H}$ = 138 Hz, C-5), 72.9 (d, $^1J_{C,H}$ = 141 Hz, C-4), 70.8 (d, $^1J_{C,H}$ = 153 Hz, C-4′), 62.7 (t, $^1J_{C,H}$ = 145 Hz, C-6), 61.4 (d, $^1J_{C,H}$ = 140 Hz, C-2′), 55.4 (q, $^1J_{C,H}$ = 142 Hz, OCH_3), 50.5 (t, $^1J_{C,H}$ = 146 Hz, C-5′), 45.5 (d, $^1J_{C,H}$ = 124 Hz, C-2), 30.9 (t, $^1J_{C,H}$ = 129 Hz, C-1′) ppm. UV (MeOH): λ_{max} (ε) = 205 nm (900 $dm^3 mol^{-1} cm^{-1}$). HRMS (MALDI-TOF): calcd. for $C_{12}H_{23}NNaO_7$ 316.1372 $[M + Na]^+$; found 316.1381.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-[(1*R* or 1*S*)-2,5-(benzylimino)-1,2,5-trideoxy-3,4-*O*-isopropylidene-1-(phenylthio)-L-ribitol-1*C*-yl]-α-D-*ribo*-hexopyranosid-3-ulose [(+)-21]: Et_3N (14 μL, 0.10 mmol) was added to a solution of (+)-(*Z*)-**15** (115 mg, 0.23 mmol) and thiophenol (30 μL, 0.29 mmol) in CH_2Cl_2 (5 mL) at 0 °C and the resulting solution was stirred at 0 °C for 1 h. The reaction was quenched by addition of an aq. satd. solution of NH_4Cl (10 mL) and extracted with CH_2Cl_2 (10 mL, 3 times). The combined organic layers were dried with $MgSO_4$ and after evaporation FC (light petroleum ether/EtOAc, 8:2) gave (+)-**21** (127 mg, 91%) as a white solid, m.p. 92–93 °C. $[\alpha]_{589}^{25}$ = +74, $[\alpha]_{577}^{25}$ = +78, $[\alpha]_{435}^{25}$ = +158 (*c* = 1.56, $CHCl_3$). IR (NaCl): $\tilde{\nu}$ = 2935, 2870, 1740, 1580, 1450, 1375, 1255, 1210, 1110, 1075, 1030, 965, 865 cm^{-1}.^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.56–7.54 (m, 2 H, Ar*H*), 7.50 (br. d, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar*H*), 7.40–7.38 (m, 3 H, Ar*H*), 7.30–7.18 (m, 6 H, Ar*H*), 6.97 (br. t, $^3J_{H,H}$ = 3.4 Hz, 2 H, Ar*H*), 5.62 (br. d, $^3J_{H,H}$ = 4.3 Hz, 1 H, 1-H), 5.61 (br. s, 1 H, PhCH), 4.66 (q, $^3J_{H,H}$ = 4.5 Hz, 1 H, 4′-H), 4.58 (dd, $^3J_{H,H}$ = 6.5, $^3J_{H,H}$ = 4.5 Hz, 1 H, 3′-H), 4.39 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 4.4 Hz, 1 H, 6-H), 4.34 (d, $^3J_{H,H}$ = 9.5 Hz, 1 H, 4-H), 4.14–4.00 (m, 3 H, 1′-H, 5-H, CH_2Ph), 3.99 (t, $^2J_{H,H}$ = $^3J_{H,H}$ = 10.0 Hz, 1 H, 6-H), 3.44 (d, $^3J_{H,H}$ = 13.3 Hz, 1 H, CH_2Ph), 3.20–3.10 (m, 3 H, 2-H, 5′-H, 2′-H), 3.09 (s, 3 H, OCH_3), 2.37 (dd, $^2J_{H,H}$ = 10.4, $^3J_{H,H}$ = 4.5 Hz, 1 H, 5′-H), 1.45 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 197.8 (s, C-3), 138.9, 136.9, 136.5, 129.8, 129.3, 129.0, 128.5, 128.3, 128.0, 126.7, 126.4, 126.3 (Ar*C*), 112.8 [s, $C(CH_3)_2$], 104.1 (d, $^1J_{C,H}$ = 176 Hz, C-1), 101.9 (d, $^1J_{C,H}$ = 162 Hz, PhCH), 83.7 (d, $^1J_{C,H}$ = 149 Hz, C-4), 82.7 (d, $^1J_{C,H}$ = 157 Hz, C-3′), 78.8 (d, $^1J_{C,H}$ = 157 Hz, C-4′), 72.1, (d, $^1J_{C,H}$ = 137 Hz, C-2), 69.7 (t, $^1J_{C,H}$ = 145 Hz, C-6), 67.5 (d, $^1J_{C,H}$ = 146 Hz, C-5), 58.6 (t, $^1J_{C,H}$ = 141 Hz, CH_2Ph), 58.3 (t, $^1J_{C,H}$ = 137 Hz, C-5′), 56.2 (q, $^1J_{C,H}$ = 143 Hz, OCH_3), 54.7 (*d*, $^1J_{C,H}$ = 142 Hz, C-2′), 46.2 (d, $^1J_{C,H}$ = 145 Hz, C-1′), 27.4 (q, $^1J_{C,H}$ = 127 Hz, CH_3), 25.3 (q, $^1J_{C,H}$ = 126 Hz, CH_3) ppm. UV (MeCN): λ_{max} (ε) = 257 (12500), 207 (32800), 202 nm (30300 $dm^3 mol^{-1} cm^{-1}$). HRMS (MALDI-TOF): calcd. for $C_{35}H_{40}NO_7S$ 618.2525 $[M + H]^+$; found 618.2589. $C_{35}H_{39}NO_7S \cdot 3/2H_2O$: calcd. C 65.20, H 6.57, N 2.17; found C 65.10, H 6.37, N 1.93.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-[(1*R* or 1*S*)-2,5-(benzylimino)-1,2,5-trideoxy-3,4-*O*-isopropylidene-1-(phenylthio)-L-ribitol-1*C*-yl]-α-D-allopyranoside [(+)-22]: $NaBH_4$ (15 mg, 0.40 mmol) was added portionwise to a solution of (+)-**21** (125 mg, 0.20 mmol) in EtOH (5 mL) at 0 °C. After 1 h at 0 °C, an aq. satd. solution of NH_4Cl (10 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (15 mL, 3 times). The organic phases were combined, dried with $MgSO_4$ and the solvent was evaporated. FC (pentane/EtOAc, 8:2) gave (+)-**22** (119 mg, 95%) as a white solid, m.p. 98–99 °C. $[\alpha]_{589}^{25}$ = +49, $[\alpha]_{577}^{25}$ = +53, $[\alpha]_{435}^{25}$ = +112, $[\alpha]_{405}^{25}$ = +142 (*c* = 0.55, $CHCl_3$). IR (NaCl): $\tilde{\nu}$ = 3455, 3060, 2930, 1950, 1010, 1735, 1580, 1450, 1375, 1210, 1100, 865 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.53 (dd, $^3J_{H,H}$ = 7.9, ^2J = 2.8 Hz, 2 H, Ar*H*), 7.51 (br. d, $^3J_{H,H}$ = 8.2 Hz, 2 H, Ar*H*), 7.41–7.38 (m, 3 H, Ar*H*), 7.29–7.26 (m, 2 H, Ar*H*), 7.21–7.16 (m, 4 H, Ar*H*), 6.90–6.87 (m, 2 H, Ar*H*), 5.67 (s, 1 H, PhCH), 5.37 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, 1-H), 4.69 (q, $^3J_{H,H}$ = 6.1 Hz, 1 H, 4′-H), 4.62 (dd, $^3J_{H,H}$ = 6.1, $^3J_{H,H}$ = 3.5 Hz, 1 H, 3′-H), 4.53 (br. s, 1 H, 3-H), 4.39 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 5.0 Hz, 1 H, 6-H), 4.20 (dt, $^3J_{H,H}$ = 10.0, ^3J = 5.0 Hz, 1 H, 5-H), 4.06 (dd, $^3J_{H,H}$ = 11.9, $^3J_{H,H}$ = 2.1 Hz, 1 H, 1′-H), 3.94 (d, $^2J_{H,H}$ = 13.1 Hz, 1 H, CH_2Ph), 3.83 (t, $^2J_{H,H}$ = $^3J_{H,H}$ = 10.0 Hz, 1 H, 6-H), 3.65 (dd, $^3J_{H,H}$ = 2.6, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4-H), 3.41 (br. s, 1 H, 2′-H), 3.30 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, CH_2Ph), 3.21 (s, 3 H, OCH_3), 3.19 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 6.1 Hz, 1 H, 5′-H), 2.93 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 3-OH), 2.34 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 6.1 Hz, 1 H, 5′-H), 2.25 (dt, $^3J_{H,H}$ = 11.9, $^3J_{H,H}$ = 3.0 Hz, 1 H, 2-H), 1.48 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.3, 137.4, 137.3, 130.3, 129.2, 129.0, 128.6, 128.3, 128.0, 126.7, 126.3 (Ar*C*), 113.1 [s, $C(CH_3)_2$], 102.1 (d, ^1J = 165 Hz, PhCH), 100.3 (d, $^1J_{C,H}$ = 174 Hz, C-1), 82.1 (d, $^1J_{C,H}$ = 153 Hz, C-3′), 79.6 (d, $^1J_{C,H}$ = 138 Hz, C-4), 78.6 (d, $^1J_{C,H}$ = 156 Hz, C-4′), 69.8 (d, $^1J_{C,H}$ = 137 Hz, C-2′) 69.4 (t, $^1J_{C,H}$ = 143 Hz, C-6), 66.4 (d, $^1J_{C,H}$ = 152 Hz, C-3), 58.5 (t, $^1J_{C,H}$ = 138 Hz, C-5′), 58.3 (t, $^1J_{C,H}$ = 139 Hz, CH_2Ph), 58.1 (d, $^1J_{C,H}$ = 146 Hz, C-5), 55.3 (q, $^1J_{C,H}$ = 143 Hz, OCH_3), 48.9 (d, $^1J_{C,H}$ = 143 Hz, C-1′), 46.2 (d, $^1J_{C,H}$ = 127 Hz, C-2), 27.6 (q, $^1J_{C,H}$ = 127 Hz, CH_3), 25.5 (q, $^1J_{C,H}$ = 126 Hz, CH_3) ppm. UV (MeOH): λ_{max} (ε) = 260 (5100), 212 nm (8800 $dm^3 mol^{-1} cm^{-1}$). HRMS (MALDI-TOF): calcd. for $C_{35}H_{42}NO_7S$ 620.2682 $[M + H]^+$; found 620.2645.

Methyl 2-Deoxy-2-[(1*R* or 1*S*)-2,5-(benzylimino)-1,2,5-trideoxy-3,4-*O*-isopropylidene-1-(phenylthio)-L-ribitol-1*C*-yl]-α-D-allopyranoside [(+)-23]: $PtO_2 \cdot H_2O$ (5 mg, 10 mol%) and a drop of H_2SO_4 were added to a solution of (+)-**22** (100 mg, 0.19 mmol) in MeOH (10 mL). The resulting suspension was stirred under H_2 (1 atm) at 20 °C overnight. The catalyst was filtered off (Celite) and the solution concentrated. FC (EtOAc) gave (+)-**23** (69 mg, 80%) as a white solid, m.p. 79–80 °C. $[\alpha]_{589}^{25}$ = +50, $[\alpha]_{577}^{25}$ = +60, $[\alpha]_{435}^{25}$ = +118, $[\alpha]_{405}^{25}$ = +145 (*c* = 0.15, MeOH). IR (NaCl): $\tilde{\nu}$ = 3455, 3060, 2925, 2855, 1645, 1580, 1450, 1375, 1250, 1210, 1150, 1110, 1045, 980, 860 cm^{-1}. ^1H NMR (400 MHz, CD_3OD, 25 °C): δ = 7.49 (br. d, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar*H*), 7.24 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar*H*),

7.15 (m, 1 H, Ar*H*), 7.09–7.07 (m, 3 H, Ar*H*), 6.78 (dd, $^3J_{H,H}$ = 6.3, $^4J_{H,H}$ = 2.6 Hz, 2 H, Ar*H*), 5.27 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, 1-H), 4.62–4.60 (m, 2 H, 3′-H, 4′-H), 4.25 (br. t, $^3J_{H,H}$ = 3.0 Hz, 1 H, 3-H), 4.03 (dd, $^3J_{H,H}$ = 11.8, $^3J_{H,H}$ = 3.0 Hz, 1 H, 1′-H), 3.86–3.69 (m, 4 H, 5-H, 6-H, CH_2Ph), 3.43 (dd, $^3J_{H,H}$ = 10.0, $^3J_{H,H}$ = 3.0 Hz, 1 H, 4-H), 3.32 (t, $^3J_{H,H}$ = 3.0 Hz, 1 H, 2′-H), 3.19 (*s*, 3 H, OCH_3), 3.18 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, CH_2Ph), 3.07–3.03 (m, 1 H, 5′-H), 2.24 (dd, $^2J_{H,H}$ = 9.7, $^3J_{H,H}$ = 4.6 Hz, 1 H, 5′-H), 2.07 (dt, $^3J_{H,H}$ = 11.8, $^3J_{H,H}$ = 3.0 Hz, 1 H, 2-H), 1.47 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, 25 °C): δ = 139.6, 139.2, 131.4, 130.1, 129.8, 129.0, 127.9, 127.3 (Ar*C*), 114.4 [s, $C(CH_3)_2$], 100.9 (d, $^1J_{C,H}$ = 169 Hz, C-1), 83.4 (d, $^1J_{C,H}$ = 154 Hz, C-3′), 79.7 (d, $^1J_{C,H}$ = 157 Hz, C-4′), 71.2 (d, $^1J_{C,H}$ = 132 Hz, C-2′), 69.9 (d, $^1J_{C,H}$ = 145 Hz, C-3), 69.3 (d, $^1J_{C,H}$ = 138 Hz, C-5), 69.0 (d, $^1J_{C,H}$ = 140 Hz, C-4), 63.0 (t, $^1J_{C,H}$ = 142 Hz, C-6), 59.7 (t, $^1J_{C,H}$ = 139 Hz, C-5′), 59.2 (t, $^1J_{C,H}$ = 130 Hz, CH_2Ph), 55.5 (q, $^1J_{C,H}$ = 143 Hz, OCH_3), 49.8 (d, $^1J_{C,H}$ = 144 Hz, C-1′), 47.1 (d, $^1J_{C,H}$ = 126 Hz, C-2), 27.9 (q, $^1J_{C,H}$ = 127 Hz, CH_3), 25.6 (q, $^1J_{C,H}$ = 126 Hz, CH_3) ppm. UV (MeOH): λ_{max} (ε) = 260 (13800), 212 nm (20900 $dm^3 mol^{-1} cm^{-1}$). HRMS (MALDI-TOF): calcd. for $C_{28}H_{37}NNaO_7S$ 554.2188 [M + Na]$^+$; found 554.2190.

Methyl 2-Deoxy-2-(1,2,5-trideoxy-2,5-imino-3,4-*O*-isopropylidene-L-ribitol-1*C*-yl)-α-D-allopyranoside [(+)-24]: A solution of (+)-**23** (17 mg, 0.032 mmol) in MeOH (3 mL) was treated with Raney Ni (200 mg) and stirred at 20 °C for 75 min. The resulting suspension was filtered through Celite and the solid was washed with MeOH. The solvent was evaporated. FC (MeCN/NH_4OH, 9:1) gave (+)-**24** (7.5 mg, 71%) as a white solid, m.p. 69–70 °C. $[\alpha]^{25}_{589}$ = +20, $[\alpha]^{25}_{577}$ = +22, $[\alpha]^{25}_{435}$ = +40, $[\alpha]^{25}_{405}$ = +48 (*c* = 0.6, MeOH). IR (NaCl): $\tilde{\nu}$ = 3140, 3040, 2360, 1405, 1050, 980 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 4.97 (br. t, $^3J_{H,H}$ = 5.0 Hz, 1 H, 4′-H), 4.69 (br. d, $^3J_{H,H}$ = 5.0 Hz, 1 H, 3′-H), 4.63 (d, $^3J_{H,H}$ = 3.4 Hz, 1 H, 1-H), 3.90 (br. t, $^3J_{H,H}$ = 2.5 Hz, 1 H, 3-H), 3.85–3.81 (m, 2 H, 2′-H, 6-H), 3.76–3.69 (m, 2 H, 5-H, 6-H), 3.52 (dd, $^2J_{H,H}$ = 13.3, ^3J = 5.0 Hz, 1 H, 5′-H), 3.49 (br. d, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4-H), 3.45 (br. d, $^2J_{H,H}$ = 13.3 Hz, 1 H, 5′-H), 3.37 (s, 3 H, OCH_3), 2.07–2.01 (m, 1 H, 2-H), 1.98–1.90 (m, 1 H, 1′-H), 1.80 (ddd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 9.8, $^3J_{H,H}$ = 6.0 Hz, 1 H, 1′-H), 1.50 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, 25 °C): δ = 113.6 [s, $C(CH_3)_2$], 101.3 (d, $^1J_{C,H}$ = 169 Hz, C-1), 83.8 (d, $^1J_{C,H}$ = 161 Hz, C-3′), 79.4 (d, $^1J_{C,H}$ = 160 Hz, C-4′), 70.0 (d, $^1J_{C,H}$ = 147 Hz, C-3), 69.3 (d, $^1J_{C,H}$ = 148 Hz, C-5), 68.8 (d, $^1J_{C,H}$ = 142 Hz, C-4), 63.9 (d, $^1J_{C,H}$ = 149 Hz, C-2′), 62.9 (t, $^1J_{C,H}$ = 141 Hz, C-6), 55.8 (q, $^1J_{C,H}$ = 142 Hz, OCH_3), 50.5 (t, $^1J_{C,H}$ = 141 Hz, C-5′), 40.9 (d, $^1J_{C,H}$ = 126 Hz, C-2), 26.8 (t, $^1J_{C,H}$ = 128 Hz, C-1′), 26.2 (q, $^1J_{C,H}$ = 127 Hz, CH_3), 24.1 (q, $^1J_{C,H}$ = 126 Hz, CH_3) ppm. UV (MeOH): λ_{max} (ε) = 205 nm (1000 $dm^3 mol^{-1} cm^{-1}$). HRMS (MALDI-TOF): calcd. for $C_{15}H_{28}NO_7$ 334.1866 [M + H]$^+$; found 334.1848.

Methyl 2-Deoxy-2-(2,5-imino-1,2,5-trideoxy-L-ribitol-1*C*-yl)-α-D-allopyranoside [(+)-(5)]: Compound (+)-**24** (13 mg, 0.039 mmol) was dissolved in CF_3COOH/H_2O (4:1, 10.0 mL) and the solution was stirred at 20 °C for 30 min. The solvent was evaporated. FC (MeCN/NH_4OH, 4:1) gave (+)-**5** (10.8 mg, 95%) as a white solid, m.p. 58–59 °C. $[\alpha]^{25}_{589}$ = +23, $[\alpha]^{25}_{577}$ = +24, $[\alpha]^{25}_{435}$ = +45, $[\alpha]^{25}_{405}$ = +55 (*c* = 0.5, MeOH). IR (NaCl): $\tilde{\nu}$ = 3355, 2925, 2360, 1665, 1420, 1130, 1045 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 4.68 (d, $^3J_{H,H}$ = 3.1 Hz, 1 H, 1-H), 4.07 (dd, $^3J_{H,H}$ = 6.5, $^3J_{H,H}$ = 5.0 Hz, 1 H, 4′-H), 3.85 (br. t, $^3J_{H,H}$ = 2.7 Hz, 1 H, 3-H), 3.82 (dd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 5.2 Hz, 1 H, 6-H), 3.72–3.67 (m, 2 H, 5-H, 6-H), 3.63 (dd, $^3J_{H,H}$ = 7.0, $^3J_{H,H}$ = 5.0 Hz, 1 H, 3′-H), 3.43 (dd, $^3J_{H,H}$ = 9.4, $^3J_{H,H}$ = 2.7 Hz, 1 H, 4-H), 3.36 (s, 3 H, OCH_3), 3.24 (dd, $^2J_{H,H}$ = 12.0, $^3J_{H,H}$ = 6.5 Hz, 1 H, 5′-H), 3.09 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, 2′-H), 2.89 (br. d, $^3J_{H,H}$ = 12.0 Hz, 1 H, 5′-H), 2.00 (ddd, ^3J = 13.6, $^3J_{H,H}$ = 7.0, $^3J_{H,H}$ = 3.1 Hz, 1 H, 2-H), 1.97–1.91 (m, 1 H, 1′-H), 1.69 (dt, $^2J_{H,H}$ = 14.7, $^3J_{H,H}$ = 7.0 Hz, 1 H, 1′-H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, 25 °C): δ = 101.5 (d, $^1J_{C,H}$ = 168 Hz, C-1), 78.7 (d, $^1J_{C,H}$ = 145 Hz, C-3′), 72.1 (d, $^1J_{C,H}$ = 148 Hz, C-4′), 71.8 (d, $^1J_{C,H}$ = 147 Hz, C-3), 69.4 (d, $^1J_{C,H}$ = 144 Hz, C-5), 69.0 (d, $^1J_{C,H}$ = 143 Hz, C-4), 63.0 (t, $^1J_{C,H}$ = 142 Hz, C-6), 60.2 (d, $^1J_{C,H}$ = 140 Hz, C-2′), 55.8 (q, $^1J_{C,H}$ = 142 Hz, OCH_3), 52.0 (t, $^1J_{C,H}$ = 142 Hz, C-5′), 41.7 (d, $^1J_{C,H}$ = 124 Hz, C-2), 32.0 (t, $^1J_{C,H}$ = 125 Hz, C-1′) ppm. UV (MeOH): λ_{max} (ε) = 206 nm (600 $dm^3 mol^{-1} cm^{-1}$). HRMS (MALDI-TOF): calcd. for $C_{12}H_{24}NO_7$ [M + H]$^+$ 294.1553; found 294.1562. $C_{12}H_{23}NO_7 \cdot 2H_2O$: calcd. C 43.76, H 8.26; found C 43.28, H 8.00.

Methyl 2-Deoxy-2-[(1*R* or 1*S*)-1,2,5-trideoxy-2,5-imino-3,4-*O*-isopropylidene-1-(phenylthio)-L-ribitol-1*C*-yl]-α-D-allopyranoside [(+)-25]: A degassed mixture of (+)-**23** (60 mg, 0.11 mmol), Pd on charcoal (100 mg) and EtOAc was stirred under H_2 (1 atm) at 20 °C. The reaction was monitored by TLC and after 6 h, only starting material was observed. More Pd on charcoal (300 mg) was added and the suspension was left at 20 °C overnight. The catalyst was filtered off (Celite) and the solvent evaporated. FC (MeCN/NH_4OH, 10:1) yielded (+)-**23** (32.4 mg, 54%), (+)-**25** (1.9 mg, 4%) and (+)-**24** (11 mg, 29%). Data for (+)-**25**: White solid, m.p. 64–65 °C. $[\alpha]^{25}_{589}$ = +41, $[\alpha]^{25}_{577}$ = +50 (*c* = 0.07, MeOH). IR (NaCl): $\tilde{\nu}$ = 3385, 2925, 2360, 1450, 1410, 1210, 1045, 980 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 7.48 (br. d, ^3J = 7.5 Hz, 2 H, Ar*H*), 7.30 (br. t, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar*H*), 7.20 (br. t, $^3J_{H,H}$ = 7.5 Hz, 1 H, Ar*H*), 5.12 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, 1-H), 4.67 (dt, $^3J_{H,H}$ = 6.1, $^3J_{H,H}$ = 3.5 Hz, 1 H, 4′-H), 4.59 (dd, $^3J_{H,H}$ = 6.1, $^3J_{H,H}$ = 3.5 Hz, 1 H, 3′-H), 4.21 (br. t, $^3J_{H,H}$ = 3.0 Hz, 1 H, 3-H), 3.82–3.77 (m, 2 H, 1′-H, 6-H), 3.70–3.68 (m, 2 H, 5-H, 6-H), 3.63 (t, $^3J_{H,H}$ = 3.5 Hz, 1 H, 2′-H), 3.40 (dd, $^3J_{H,H}$ = 9.6, ^3J = 3.0 Hz, 1 H, 4-H), 3.34 (dd, $^2J_{H,H}$ = 12.5, ^3J = 6.1 Hz, 1 H, 5′-H), 2.95 (s, 3 H, OCH_3), 2.86 (dd, $^2J_{H,H}$ = 12.5, $^3J_{H,H}$ = 3.5 Hz, 1 H, 5′-H), 2.07 (dt, $^3J_{H,H}$ = 11.5, $^3J_{H,H}$ = 3.0 Hz, 1 H, 2-H), 1.46 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, 25 °C): δ = 137.6 (s, Ar*C*), 131.5 (d, $^1J_{C,H}$ = 163 Hz, Ar*C*), 130.3 (d, $^1J_{C,H}$ = 162 Hz, Ar*C*), 128.0 (d, $^1J_{C,H}$ = 162 Hz, Ar*C*), 115.2 [s, $C(CH_3)_2$], 100.7 (d, $^1J_{C,H}$ = 170 Hz, C-1), 84.3 (d, $^1J_{C,H}$ = 155 Hz, C-3′), 83.2 (d, $^1J_{C,H}$ = 152 Hz, C-4′), 69.5 (d, $^1J_{C,H}$ = 150 Hz, C-3), 69.3 (d, $^1J_{C,H}$ = 142 Hz, C-5), 68.8 (d, $^1J_{C,H}$ = 140 Hz, C-4), 66.2 (d, $^1J_{C,H}$ = 140 Hz, C-2′), 63.0 (t, $^1J_{C,H}$ = 157 Hz, C-6), 55.2 (q, $^1J_{C,H}$ = 143 Hz, OCH_3), 53.1 (t, $^1J_{C,H}$ = 143 Hz, C-5′), 51.8 (d, $^1J_{C,H}$ = 140 Hz, C-1′), 48.5 (C-2), 27.4 (q, $^1J_{C,H}$ = 126 Hz, CH_3), 25.1 (q, $^1J_{C,H}$ = 127 Hz, CH_3) ppm. UV (MeOH): λ_{max} (ε) = 255 (11400), 207 nm (15100 $dm^3 mol^{-1} cm^{-1}$). HRMS (MALDI-TOF): calcd. for $C_{21}H_{31}NNaO_7S$ 464.1719 [M + Na]$^+$; found 464.1700.

Supporting Information (see footnote on the first page of the article): ^{1}H NMR (400 MHz) spectra of (+)-**11**, (+)-**12**, (+)-**13**, (+)-**14**, (+)-(*Z*)-**15**, (+)-(*E*)-**15**, (–)-(*Z*)-**18**, (+)-(*E*)-**18**, (+)-**19**, (+)-**20**, (+)-**21**, (+)-**22**, (+)-**23**, (+)-**24**, (+)-**25**, (+)-**3**, (+)-**4**, (+)-**5**; ^{13}C NMR (100.6 MHz) spectra of (+)-**3**, (+)-**4**, (+)-**5**, (+)-**25**, (+)-**13**, (+)-**14**, (+)-(*Z*)-**18**, (–)-(*E*)-**18**, (+)-**19**, (+)-**20**, (+)-**22**, (+)-**23**, (+)-**24**.

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