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Preparation and reactivity of imino glycals: stereocontrolled, divergent approach to imino sugars

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The synthesis of 3,4,6-tri-*O*-acetyl imino D-glucal **2** from D-glucal is reported. This imino glycal participates in a variety of Lewis acid mediated carbon–carbon bond forming reactions by allylic displacement of the C-3 acetate group by added nucleophiles. Allyl silanes, trimethylsilyl enol ethers, alkenes and dialkyl zinc reagents serve as suitable reaction partners. In all the cases studied, the β-anomer is predominant. Using imino glycal **8**, epimeric at C-5, it is established that the configuration at C-5 of the piperidine ring plays a major role in controlling the stereochemical outcome. These results are rationalised by invoking the intermediacy of a conjugated *N*-acyliminium ion. A short stereocontrolled synthesis of (+)-deoxoprosophylline is achieved using this chemistry. Additionally, imino glucal **2** is transformed into bromo piperidine **16**, whose X-ray crystal structure is determined. Bromide **16** participates in palladium catalysed Stille and Suzuki cross-couplings allowing access to C-2 substituted imino sugars **17** and **18**. In other studies, imino sugar *C*-glycosides **21** and **22** are made by combining the Lewis acid mediated carbon–carbon bond forming reactions with stereospecific dihydroxylations.

Introduction

Glycals, carbohydrates incorporating a double bond between C-1 and C-2, are extremely useful starting materials for the preparation of monosaccharides, oligosaccharides and other enantiomerically enriched organic molecules.[1,2] For example, 3,4,6-tri-*O*-acetyl D-glucal **1** undergoes a variety of useful addition reactions across the glycal double bond (Fig. 1).[2] Moreover, the presence of a good leaving group at C-3 facilitates S_N' reactions allowing the introduction of a wide variety of nucleophiles at C-1 of the sugar nucleus with concomitant migration of the double bond.[2] As the development of general methods for the assembly of imino sugars, important inhibitors of the glycosidase enzymes, remains an intense area of current activity,[3,4] we reasoned that an aza analogue of **1** such as tri-*O*-acetyl imino glucal **2** might serve as a versatile intermediate on route to a wide range of imino sugars. Prior to systematic studies undertaken independently by ourselves,[5,6] and by Comins,[7] imino glycals appear to have received rather scant attention.[8,9] In this paper, we describe the preparation of imino glycal **2**, demonstrate that it can be used in a wide variety of stereoselective C–C bond forming reactions at C-1 of the piperidine nucleus, and after further manipulation, palladium catalysed cross-coupling reactions at C-2.[6]

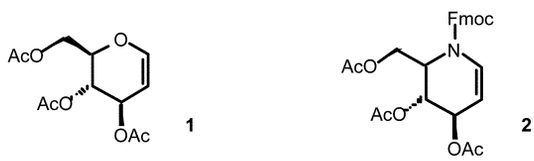

Fig. 1 3,4,6-Tri-*O*-acetyl D-glucal and 3,4,6-tri-*O*-acetyl imino D-glucal.

Results and discussion

Synthesis of imino glycals

Imino glucal **2** was made from D-glucal as outlined in Scheme 1. Protection of the hydroxy groups as *p*-methoxybenzyl ethers followed by hydration of the double bond gave hemiacetal **3**. Wittig olefination with methylenetriphenylphosphorane followed by TPAP oxidation of the resulting secondary alcohol furnished ketone **4**, which was converted into amine **5** by reduction of the corresponding oxime and further Fmoc protection. Using lithium aluminium hydride as reducing agent, this provided **5** as an inseparable 77 : 23 mixture of isomers in favour of the required (6*R*)-diastereoisomer. Whilst stereocontrolled reduction in favour of this diastereomer was expected on the basis of close precedent,[5,10] this assignment was confirmed by two X-ray crystal structures later obtained on derived imino sugars (*vide infra*). After the PMB ether protecting groups had been switched to acetates, triacetate **6** could be separated from its C-6 epimer **7** by preparative MPLC. Completion of the synthesis of **2** was achieved by ozonolytic cleavage of the terminal double bond of diastereomerically pure **6**,† followed by dehydration of the resulting hemiacetal using oxalyl chloride.‡ The characterisation of imino glucal **2**, and many of the synthetic intermediates, by NMR spectroscopy was hampered by the presence of rotamers about the *N*–Fmoc bond. This necessitated the use of variable temperature NMR spectroscopy to complete structural assignments (see Experimental).

An identical sequence was used to complete the synthesis of imino glycal **8**, epimeric at C-5, from alkene **7**, a side-product of the sequence depicted in Scheme 1. Ozonolysis of the terminal double bond provided the hemiacetal (69%) which upon dehydration using oxalyl chloride gave imino glycal **8** in 70% yield (Scheme 2).

† The use of dimethyl sulfide as the reducing agent in the ozonolysis proved crucial. Attempts to effect this transformation using triphenylphosphine triggered elimination of acetic acid from the intermediate aldehyde resulting in the formation of the corresponding (*E*)-α,β-unsaturated aldehyde.

‡ Other dehydrating agents ($SOBr_2$, Ac_2O, MsCl, *p*-TSA and Martin sulfurane {$[PhC(CF_3)_2O]_2SPh_2$}) proved less effective for this elimination.

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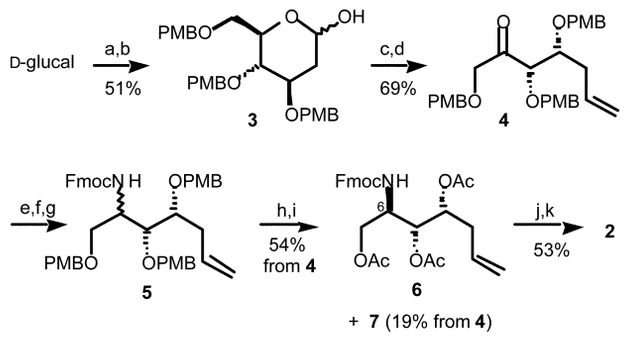
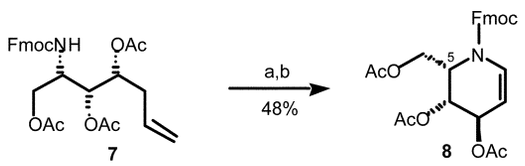
Table 1 Lewis acid mediated additions to imino glucal **2**

Entry	Conditions[a,b]	β : α[c]	Products (% yield)[d]
1	$H_2C{=}CHCH_2SiMe_3$, $BF_3{\cdot}Et_2O$	79 : 21	**9a** (78); **10a** (18)
2	Et_2Zn, $BF_3{\cdot}Et_2O$	67 : 33	**9b** (63); **10b** (27)
3	$H_2C{=}C(OSiMe_3)Ph$, $BF_3{\cdot}Et_2O$	62 : 38	**9c** (64); **10c** (31)
4	Methylenecyclohexane, $SnBr_4$	86 : 14	**9d** (80); **10d** (10)

[a] All reactions performed using 1.0–1.5 equiv of Lewis acid and 1.2–1.5 equiv of nucleophile in CH_2Cl_2 at the temperature indicated in the text. Reactions warmed to rt or 0 °C and quenched by addition of aq $NaHCO_3$. [b] Crude products treated with piperidine in CH_2Cl_2 for 1–2 h to remove the Fmoc group. [c] Ratio determined by ^1H NMR analysis prior to purification. [d] Isolated yields after silica gel chromatography.



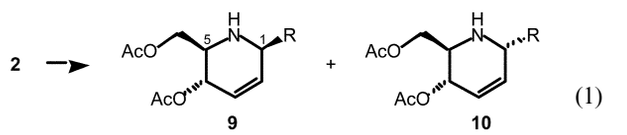
Scheme 1 *Reagents and conditions:* (a) NaH, PMBCl, DMF; (b) $Hg(OAc)_2$, THF–H_2O then $NaBH_4$; (c) $Ph_3P{=}CH_2$, toluene; (d) TPAP, NMO, 4 Å sieves, CH_2Cl_2; (e) $HONH_2{\cdot}HCl$, pyridine, EtOH, 60 °C; (f) $LiAlH_4$, Et_2O, rt; (g) FmocCl, K_2CO_3, THF : H_2O (3 : 1); (h) CF_3CO_2H, CH_2Cl_2; (i) Ac_2O, pyridine, rt; (j) O_3, −78 °C, CH_2Cl_2 then Me_2S, rt; (k) $(COCl)_2$, Et_3N, DMF, CH_2Cl_2.



Scheme 2 *Reagents and conditions:* (a) O_3, −78 °C, CH_2Cl_2 then Me_2S, rt; (b) $(COCl)_2$, Et_3N, DMF, CH_2Cl_2.

Lewis acid mediated additions to imino glycals 2 and 8

Imino glucal **2** participates in a wide variety of Lewis acid mediated C–C bond forming reactions by allylic displacement of the C-3 acetate group. Treatment of **2** with allyl trimethylsilane and $BF_3{\cdot}Et_2O$ at −50 °C provides, after Fmoc deprotection, piperidine **9a** in 78% yield along with small amount of the readily separable α-anomer **10a** [eqn. (1) and Table 1]. Similarly, $BF_3{\cdot}Et_2O$ promoted addition of diethyl zinc at −20 °C, and 1-phenyl-1-(trimethylsiloxy)ethylene at −45 °C, yield **9b** and **9c** respectively as the major products. Furthermore, Prins-type addition of methylenecyclohexane mediated by $SnBr_4$ at room temperature gives **9d** in excellent yield. In all these examples, the 1,5-*cis* piperidine **9** was produced as the major product. Interestingly, this stereochemical outcome is the reverse of that observed when the same nucleophiles are added to 3,4,6-tri-*O*-acetyl D-glucal **1** under comparable conditions, wherein the 1,5-*trans* product is predominant.[11]



a: R = $CH_2CH{=}CH_2$; **b**: R = Et;
c: R = CH_2COPh; **d**: R = CH_2(1-cyclohexenyl)

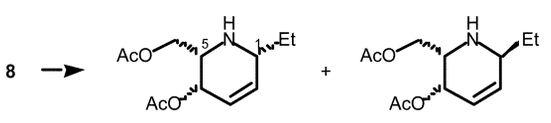
Reaction of imino glycal **8** (which is epimeric at C-5 compared to **2**) with diethyl zinc in the presence of $BF_3{\cdot}OEt_2$ yielded two tetrahydropyridines in a 58 : 42 ratio as determined by ^1H NMR analysis. Again, removal of the Fmoc group with piperidine proceeded uneventfully to give a 1.4 : 1 mixture of **11** and **12** in 80% yield. Partial separation of the diastereomers was possible using MPLC to give **11** (40%) and **12** (27%). Comparison of the ^1H NMR spectrum of **11**, with that of the crude reaction mixture confirmed it to be the major product.

Table 2 Selected NOE data for **9**–**12** determined at 400 MHz

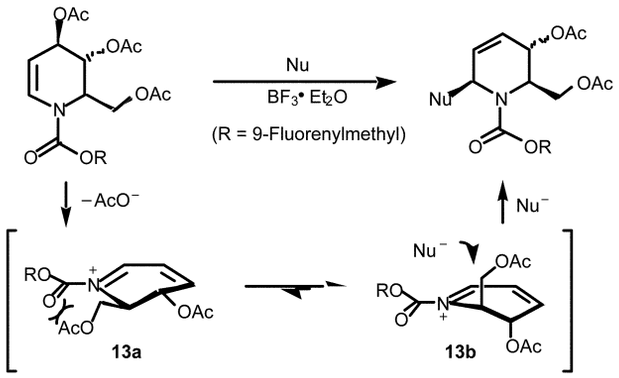
Compound	Observed NOE enhancements
9a	H-1 ⟶ H-5 (7.1%); H-5 ⟶ H-1 (6.3%)
9b	H-1 ⟶ H-5 (6.4%); H-5 ⟶ H-1 (6.1%)
9c	H-1 ⟶ H-5 (7.1%); H-5 ⟶ H-1 (6.7%)
9d	H-1 ⟶ H-5 (8.6%); H-5 ⟶ H-1 (6.9%)
10a	H-5 ⟶ CH_2CH=CH_3 (3.9%)
10b	CH_2CH_3 ⟶ H-1 and H-5 (5.9%)
10c	CHCOPh ⟶ H-5 (6.6%); CHCOPh ⟶ H-5 (4.7%)
10d	H-1 ⟶ H-5 (0%); H-5 ⟶ H-1 (0%)
11	H-1 ⟶ H-5 (2.1%); H-5 ⟶ H-1 (2.8%)
12	CH_2CH_3 ⟶ H-1 (3.8%), CH_2CH_3 ⟶ H-5 (3.4%)

The stereochemical assignments for **9**–**12** were deduced using NOE experiments. Large reciprocal enhancements were observed between H-1 and H-5 in **9a**–**d** and **11** indicating a *cis* relationship between these hydrogens (Table 2). Consistent with these assignments, NOE's were observed for **10a**–**c** and **12** between H-5 and the methylene hydrogens of the newly introduced C-1 substituent.

Piperidine systems structurally related to imino glucal **2** are known to produce conjugated iminium ions upon addition of Lewis acids.[12–15] Based upon these observations, we suggest that *N*-acyliminium ion **13** is a key intermediate in the carbon–carbon bond forming reactions of imino glucal **2** (Scheme 4). In all the additions studied, nucleophilic attack occurs regiospecifically at C-1 of iminium ion **13** and we were unable to isolate any products derived from attack at C-3 (Table 1). In simpler systems, Kozikowski rationalised this regiochemical outcome on the basis of kinetic preference for attack at the site of lowest electron density in the conjugated *N*-acyliminium ion.[12] Further support for the intermediacy of **13** comes from analysing the diastereoselectivity of the reactions. Conjugated iminium ions bearing a C-5 substituent favour the formation of 1,5-*cis* piperidines.[13–15] Such findings are fully consistent with our own experimental results [eqn. (1) and Scheme 3]. Arguments similar to those used by earlier workers can be used to rationalise the addition of the nucleophile to the seemingly more hindered face. Thus, we propose that two conformations of the intermediate *N*-acyliminium ion **13a** and **13b** exist in solution. Steric repulsion between the C-5 acetoxymethyl group and the *N*-Fmoc group disfavours **13a** relative to **13b**. Stereoelectronically controlled axial attack of the nucleophile to the top face of **13b** then leads to the observed major product.

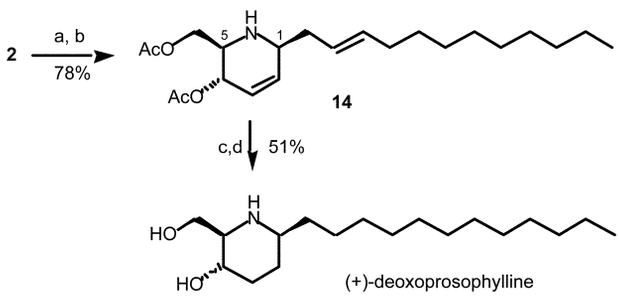


Scheme 3 *Reagents and conditions:* (a) Et_2Zn, $BF_3{\cdot}Et_2O$, CH_2Cl_2, −20 °C; (b) piperidine, CH_2Cl_2, rt, 1 h.



Scheme 4 Proposed origin of stereoselectivity.

To test the utility of this methodology, we examined its application to a natural product synthesis. (+)-Deoxoprosophylline is a derivative (Wolff–Kishner reduction product) of (+)-prosophylline, itself isolated from *Prosopis africana*.[16] Based on the smooth C-1 allylation of imino glycal **2**, we felt that we would be able to devise a stereocontrolled approach to (+)-deoxoprosophylline.[17] Addition of trimethyl-(1-nonyl-allyl)-silane[17e] to imino glycal **2** using $BF_3{\cdot}OEt_2$ at −60 °C, proceeded smoothly to give a mixture of Fmoc protected piperidines (9 : 1 ratio by ^{1}H NMR spectroscopy). Diastereomerically pure **14** was isolated in 78% overall yield after Fmoc removal (Scheme 5). The stereochemical assignments of **14** and its C-1 epimer were confirmed by NOE studies [**14**: H-1 ⟶ H-5 (8.5%); H-5 ⟶ H-1 (7.6%); C-1 epimer: no NOE's observed between H-1 and H-5]. This addition proceeded with higher levels of stereocontrol than that observed using allyltrimethylsilane. The greater steric bulk of the silane in this instance may account for the enhanced facial selectivity. Hydrogenation of **14** using Pt/C in ethanol (60%) and further removal of the acetate groups with lithium hydroxide (85%) readily gave (+)-deoxoprosophylline after recrystallisation from acetone.§ ^{1}H and ^{13}C NMR spectra obtained for the synthetic material were in good agreement with those reported, as were physical data {$[a]_D^{24}$ +12.5 (*c* 0.24, $CHCl_3$); Lit.[17f] $[a]_D^{20}$ +13 (*c* 0.22, $CHCl_3$); mp 84–85 °C; Lit.[17f] mp 83 °C}.

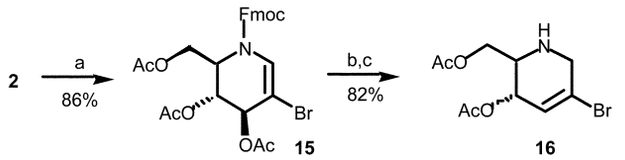


Scheme 5 *Reagents and conditions*: (a) $BF_3{\cdot}Et_2O$, CH_2Cl_2, $H_2C{=}CHCH(SiMe_3)(CH_2)_8CH_3$, −60 ⟶ 0 °C, 3 h; (b) piperidine, CH_2Cl_2, rt, 1 h; (c) H_2, Pt/C, EtOH, 1.5 h; (d) LiOH, THF–H_2O, 2.5 h.

Bromination of imino glycal 2 and further palladium catalysed cross-coupling reactions

Hayashi has shown that 3,4,6-tri-*O*-acetyl-2-bromo-D-glucal undergoes Stille and Heck reactions with a wide range of vinylic coupling partners.[18] By analogy, we imagined that a C-2 brominated derivative of imino glycal **2** might undergo similarly useful cross-coupling reactions and provide access to imino sugars bearing carbon substituents at C-2. To this end, imino glucal **2** was reacted with bromine at −78 °C then Hünig's base to give bromide **15** in 86% yield (Scheme 6).

§ Pt/C was found to be superior to Pd/C for this hydrogenation.



Scheme 6 *Reagents and conditions*: (a) Br_2, CH_2Cl_2, −78 °C, then ^{i}Pr$_2$EtN; (b) Et_3SiH, $BF_3{\cdot}Et_2O$, CH_2Cl_2, −50 °C; (c) piperidine, CH_2Cl_2, rt, 1 h.

Preliminary studies revealed that this bromide does undergo palladium catalysed coupling reactions (*e.g.* $CH_2{=}CHSnBu_3$, $Pd(dba)_2$, P(*o*-PhMe)$_3$, 80 °C, MeCN, 85%) although the products were themselves not well suited for further manipulation. It proved more convenient to cleave the Fmoc group and reductively migrate the double bond before undertaking the palladium mediated cross-couplings. Thus, treatment of **15** with triethylsilane and boron trifluoride yielded vinyl bromide **16** in good yield after Fmoc deprotection (Scheme 6). The structure of **16** was unambiguously established by X-ray crystallography after the preparation and crystallisation of its hydrochloride salt (Fig. 2). In addition to verifying the site of bromination in the conversion of **2** into **15**, this structure also confirms our earlier expectation that the reduction of the oxime derived from ketone **4** produced the (6*R*)-diastereomer as the major product (*vide supra*).

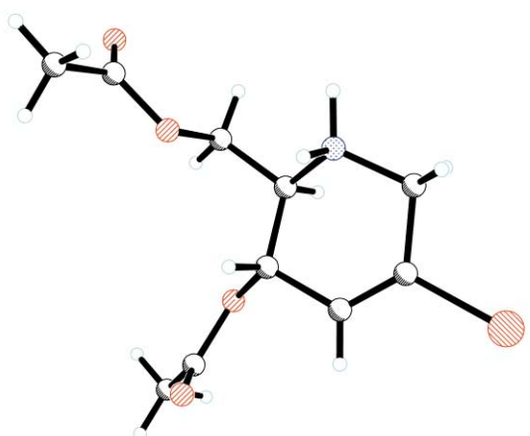
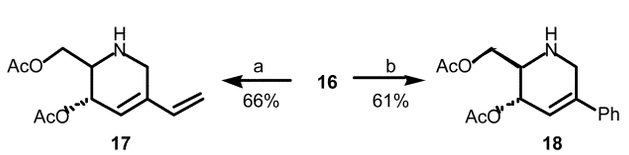


Fig. 2 X-Ray crystal structure of one of the independent molecules of **16**·HCl (chloride ion omitted for clarity).

Reaction of bromide **16** with vinyl tributyltin, and separately with phenylboronic acid[19] provided tetrahydropyridines **17** and **18** respectively in reasonable yields (Scheme 7). The conditions for these Stille and Suzuki cross-couplings have not been optimised. These results establish that C-2 substituted imino sugar derivatives are accessible from the corresponding imino glycal.



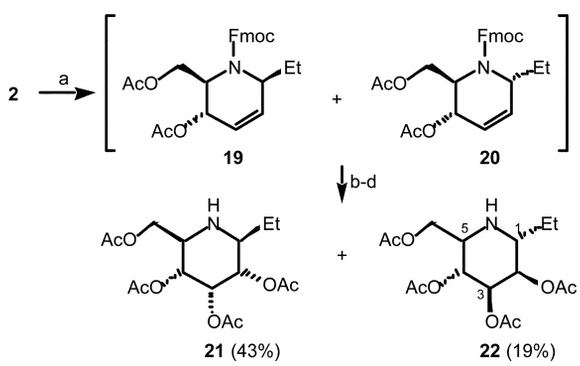
Scheme 7 *Reagents and conditions:* (a) $Bu_3SnCH{=}CH_2$, $Pd(dba)_2$, P(*o*-MePh)$_3$, MeCN, sealed tube, 80 °C; (b) $PhB(OH)_2$, $Pd(dppf)Cl_2$, K_3PO_4, THF, 70 °C.

Synthesis of imino sugar *C*-glycosides

We anticipated that C-1 substituted piperidines **9**–**12** could readily be transformed into imino sugar *C*-glycosides by further stereocontrolled dihydroxylation of the carbon–carbon double bond. Importantly, compounds of this type are known to be potent inhibitors of the glycosidase enzymes. For example, β-1-*C*-ethyl deoxymannonojirimycin has been shown by Fleet

to be a powerful inhibitor of human liver α-l-fucosidase (K_i = 0.07 μM).[20] To explore this approach to imino sugar *C*-glycosides, glucal **2** was treated with diethylzinc and $BF_3{\cdot}OEt_2$ to give Fmoc-protected tetrahydropyridines **19** and **20** in accordance with our earlier observations (Table 1). Dihydroxylation of the crude mixture with OsO_4 and NMO, acetylation and subsequent Fmoc cleavage produced readily separable **21** and **22** in 43% and 19% yields respectively over the 4 steps. The product ratio reflects the stereoselectivity of the initial ethylation reaction (Table 1). The structure of **21** was conclusively proved by X-ray crystallography, the details of which have been reported elsewhere.[6] The structure of minor adduct **22** was solved by NMR methods. NOE enhancements [CH_2CH_3 ⟶ H-5 (1.7%); H-5 ⟶ CH_2CH_3 (2.8%)] confirmed that it was the expected α-anomer. Additional NOE's revealed that H-3 and H-5 reside on the same face of the piperidine ring [H-5 ⟶ H-3 (4.3%)]. Furthermore, large ^1H–^1H coupling constants were observed $J_{4,5}$ 9.2 and $J_{3,4}$ 9.5 indicating that H-3, H-4 and H-5 are *trans*-diaxially disposed. All other data were consistent with the proposed structure.

Interestingly, just two of the four possible diastereomeric products were isolated from the sequence depicted in Scheme 8 indicating that both **19** and **20** undergo stereospecific dihydroxylation. The formation of **21** involves 'anti-Kishi' osmylation[21] from the bottom face of **19** presumably because the top face is blocked by the equatorially positioned ethyl group. Dihydroxylation of **20** occurs from the sterically accessible top face to give **22**. To our surprise, from experiments undertaken on separated **19** and **20**, we have observed that dihydroxylation of the seemingly more hindered β-anomer **19** requires just 20 hours whereas α-anomer **20**, with an apparently more accessible top-face, osmylated more slowly and took 5 days for complete conversion.



Scheme 8 *Reagents and conditions*: (a) $BF_3{\cdot}Et_2O$, Et_2Zn, CH_2Cl_2, −20 °C ⟶ rt; 2 h; (b) OsO_4 (cat.), *N*-methylmorpholine-*N*-oxide, acetone–H_2O, 5 d; (c) Ac_2O, pyridine, 2 h; (d) piperidine, CH_2Cl_2, 1 h.

Conclusions

To summarise, we have devised an 11 step synthesis of imino glucal **2** from D-glucal which proceeds in 10% overall yield. By analogy with 3,4,6-tri-*O*-acetyl D-glucal, we hoped that **2** could be a useful entry point into a diverse range of imino sugar derivatives. Based on the work reported herein, this initial optimism is well founded. Imino glucal **2** undergoes Lewis acid mediated carbon–carbon bond forming reactions by allylic displacement of the C-3 acetate group. The reactions are stereoselective and favour the formation of the β-anomer. This stereochemical outcome is best rationalised by invoking the intermediacy of a conjugated *N*-acyliminium ion. By combining this methodology with further dihydroxylations, imino sugar *C*-glycosides, important inhibitors of the glycosidase enzymes, can be produced in a stereocontrolled manner. Since a wide variety of carbon substituents can be added to C-1 of imino glycals **2** and **8**, this could provide a rather divergent approach to this class of compounds. Finally, we have established that the double bond of imino glucal **2** reacts with electrophilic species such as bromine. The resulting bromide **15** can be used to introduce carbon substituents into C-2 of the piperidine ring using traditional palladium catalysed cross-coupling reactions. Future work will focus on developing a more concise synthesis of imino glucal **2**, and further exemplifying its use in the preparation of biologically relevant imino sugars.

Experimental

General

'Light petroleum' refers to the fraction boiling between 40 °C and 60 °C. Dichloromethane was distilled over calcium hydride, diethyl ether and THF were distilled over sodium and benzophenone. All other solvents were obtained anhydrous from Aldrich. Reactions were carried out under an atmosphere of nitrogen unless otherwise stated. Flash chromatography was carried out using Matrex silica 60, 230–400 mesh. Infrared spectra were recorded in the 4000–600 cm^{-1} range using a Nicolet Magna IR 550 spectrometer with internal calibration. Spectra were recorded as KBr discs, Nujol mulls or as thin films. ^1H and ^{13}C NMR spectra were recorded using Bruker Avance 300 or 400 MHz instruments in deuterated solvents. NMR chemical shifts are quoted in ppm and *J* values are given in Hz. Spectroscopic data is annotated with the following abbreviations: br broad, s singlet; d doublet; t triplet; q quartet and m multiplet. ^1H and ^{13}C NMR assignments were made using COSY (^1H–^1H correlation) and HMQC (^1H–^{13}C correlation) techniques. High and low resolution mass spectra were recorded on a Micromass Quattro II instrument (EPSRC Mass Spectrometry Service, Swansea). Melting Points were determined using a Gallenkamp melting point apparatus. Optical rotations were measured on an Optical Activity Ltd. AA-1000 polarimeter, values are quoted in 10^{-1} cm^2 g^{-1}.

1,5-Anhydro-2-deoxy-3,4,6-tri-*O*-(4-methoxybenzyl)-D-*arabino*-hex-1-enitol 23

To a stirred solution of D-glucal (5.00 g, 34.2 mmol) in DMF (250 cm^3) was added 4-methoxybenzyl chloride (15.3 cm^3, 113 mmol), followed by portionwise addition of NaH (60% dispersion in oil, 8.21 g, 205 mmol) at 0 °C. Stirring was continued for 30 min at 0 °C and then for 5 h at 60 °C. The resulting solution was cooled to 0 °C, methanol (50 cm^3) then water (200 cm^3) added, and the resulting mixture extracted with diethyl ether (3 × 250 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided **23** (16.2 g, 93%) as a colourless solid; mp 45–47 °C; $[\alpha]_D^{22}$ 0.0 (*c* 1.0, $CHCl_3$); ν_{max} (KBr)/cm^{-1} 2999, 2935, 2908, 2865, 2836, 1513; δ_H (400 MHz; $CDCl_3$) 7.27 (4H, d, *J* 8.6, ArH), 7.17 (2H, d, *J* 8.6, ArH), 6.86 (6H, m, ArH), 6.42 (1H, d, $J_{1,2}$ 6.2, H-1), 4.85 (1H, dd, $J_{2,1}$ 6.2, $J_{2,3}$ 2.6, H-2), 4.75 (1H, d, *J* 10.8, OCH*H*Ar), 4.60–4.49 (5H, m, 5 × OCH*H*Ar), 4.18 (1H, m, H-3), 4.03 (1H, m, H-5), 3.81 (10H, m, H-4, 3 × OCH_3), 3.80–3.71 (2H, m, H-6, H-6′); δ_C (100 MHz; $CDCl_3$) 159.3 (ArC), 159.3 (ArC), 159.2 (ArC), 144.6 (C-1), 130.6 (ArC), 130.4 (ArC), 130.2 (ArC), 129.5 (ArCH), 129.4 (ArCH), 129.3 (ArCH), 113.8 (ArCH), 113.8 (ArCH), 100.1 (C-2), 76.9 (C-5), 75.5 (C-3), 74.2 (C-4), 73.3 (OCH_2Ar), 73.1 (OCH_2Ar), 70.2 (OCH_2Ar), 68.3 (C-6), 55.3 (OCH_3), 55.2 (OCH_3); *m*/*z* (ES^+) 529 (M + Na^+), 524 (M + NH_4^+), 121. HRMS (ES^+); calcd for $C_{30}H_{38}NO_7$ (M + NH_4^+) 524.2648, found 524.2652.

2-Deoxy-3,4,6-tri-*O*-(4-methoxybenzyl)-D-*arabino*-hexopyranose 3

To a stirred solution of **23** (15.8 g, 31.2 mmol) in THF (370 cm^3) at 0 °C was added a solution of $Hg(OAc)_2$ (14.9 g, 46.8

mmol) in water (130 cm^3). The resulting solution was stirred at room temperature for 45 min, then water (60 cm^3) was added. To this solution was added portionwise, $NaBH_4$ (7.10 g, 188 mmol) at 0 °C, and after a further 15 min, the mixture was extracted with ethyl acetate (3 × 500 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 3) provided **3** (9.0 g, 55%) as a 7 : 3 mixture of α- and β-isomers and as a colourless solid; mp 96–98 °C; ν_{max} (KBr)/cm^{-1} 3425 (OH), 2935 (CH), 2837 (CH), 1612, 1515; δ_H (400 MHz; $CDCl_3$) 7.28–7.24 (4H, m, ArH), 7.11–7.05 (2H, m, ArH), 6.88–6.81 (6H, m, ArH), 5.39 (0.7H, br s, H-1_{maj}), 4.81–4.41 (6.3H, m, 6 × OCH*H*Ar, H-1_{min}), 4.04–3.38 (14.3H, m, 2 × H-6, 3 × OCH_3, H-5, H-3, H-4, OH_{min}), 2.81 (0.7H, t, *J* 2.3, OH_{maj}), 2.32 (0.3H, ddd, *J* 12.6, 5.0, 2.0, H-2_{min}), 2.25 (0.7H, ddd, *J* 13.1, 5.0, 1.2, H-2_{maj}), 1.71–1.49 (1H, m, H-2′); *m*/*z* (ES^+) 547 (M + Na^+), 542 (M + NH_4^+) 279, 119. HRMS (ES^+); calcd for $C_{30}H_{40}NO_8$ (M + NH_4^+) 542.2754, found 542.2751.

1,2,3-Trideoxy-4,5,7-tri-*O*-(4-methoxybenzyl)-D-*arabino*-hept-1-enitol 24

To a stirred solution of **3** (17.4 g, 33.2 mmol) in toluene (250 cm^3) at 0 °C was added dropwise ^{n}BuLi (1.6 M in hexanes, 20.7 cm^3, 33.1 mmol). After 10 min at 0 °C, the solution was warmed to room temperature and stirred for 40 min. To a stirred solution of $MePPh_3Br$ (35.6 g, 99.7 mmol) in toluene (250 cm^3) at 0 °C was added dropwise ^{n}BuLi (1.6 M in hexanes, 62.2 cm^3, 99.5 mmol). After 10 min at 0 °C, the solution was warmed to room temperature and stirred for 40 min. The yellow ylide solution was added dropwise to the anion of **3**. The mixture was stirred for 15 min, then heated at 85 °C for 45 min. On cooling to room temperature, acetone (100 cm^3) was added then the mixture concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided **24** (13.3 g, 77%) as colourless oil; $[\alpha]_D^{22}$ −3.0 (*c* 1.0, $CHCl_3$); ν_{max} (film)/cm^{-1} 3481 (OH), 3000, 2935, 2909, 2864, 1612; δ_H (400 MHz; $CDCl_3$) 7.28–7.17 (6H, m, ArH), 6.90–6.84 (6H, m, ArH), 5.82–5.71 (1H, m, H-2), 5.12–5.03 (2H, m, 2 × H-1), 4.57–4.43 (6H, m, 6 × OCH*H*Ar), 4.00 (1H, m, H-6), 3.81 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 3.79 (3H, s, OCH_3), 3.69 (1H, td, *J* 6.1, 3.4, H-4), 3.59 (3H, m, H-5, 2 × H-7), 3.10 (1H, d, *J* 4.5, OH), 2.50–2.35 (2H, m, 2 × H-3); δ_C (100 MHz; $CDCl_3$) 159.3 (ArC), 159.2 (ArC), 135.2 (C-2), 130.4 (ArC), 130.2 (ArC), 130.1 (ArC), 129.9 (ArCH), 129.7 (ArCH), 129.6 (ArCH), 117.2 (C-1), 113.8 (ArCH), 113.8 (ArCH), 113.7 (ArCH), 78.6 (C-4), 77.5 (C-5), 73.1 (O*C*H_2Ar), 73.0 (O*C*H_2Ar), 72.0 (O*C*H_2Ar), 70.9 (C-7), 70.5 (C-6), 55.3 (OCH_3), 34.5 (C-3); *m*/*z* (ES^+) 545 (M + Na^+), 540 (M + NH_4^+). HRMS (ES^+); calcd for $C_{31}H_{42}NO_7$ (M + NH_4^+) 540.2961, found 540.2958.

1,2,3-Trideoxy-4,5,7-tri-*O*-(4-methoxybenzyl)-D-*arabino*-hept-1-en-6-ulose 4

To a stirred solution of **24** (2.64 g, 5.05 mmol) in dichloromethane (50 cm^3) at 0 °C was added 4 Å molecular sieves (2.50 g), NMO (888 mg, 7.58 mmol) and finally TPAP (89.0 mg, 0.253 mmol). The resulting mixture was stirred for 10 min at 0 °C, then 2 h at room temperature. The mixture was filtered through a plug of silica and concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided **4** (2.34 g, 89%) as a colourless oil; $[\alpha]_D^{23}$ −22.0 (*c* 1.0, $CHCl_3$); ν_{max} (film)/cm^{-1} 3001, 2936, 2908, 2866, 2837, 1731 (C=O); δ_H (400 MHz; $CDCl_3$) 7.20–7.13 (6H, m, ArH), 6.86–6.80 (6H, m, ArH), 5.65 (1H, m, H-2), 5.04–5.01 (2H, m, 2 × H-1), 4.52–4.19 (8H, m, 2 × H-7, 6 × OCH*H*Ar), 3.95 (1H, br s, H-5), 3.76–3.72 (10H, m, H-4, 3 × OCH_3), 2.39 (2H, t, *J* 6.8, H-3); δ_C (100 MHz; $CDCl_3$) 209.3 (C=O), 159.7 (ArC), 159.4 (ArC), 159.3 (ArC), 134.0 (C-2), 130.2 (ArCH), 129.8 (ArCH), 129.75 (ArCH), 129.7 (ArC), 129.4 (ArC), 128.9 (ArC), 118.1 (C-1), 113.9 (ArCH), 113.8 (ArCH), 113.7 (ArCH), 83.8 (C-5), 79.6 (C-4), 74.3 (CH_2), 73.7 (CH_2), 72.9 (CH_2), 72.2 (CH_2), 55.2 (OCH_3), 55.2 (OCH_3), 55.2 (OCH_3), 34.4 (C-3); *m*/*z* (ES^+) 543 (M + Na^+), 538 (M + NH_4^+), 152. HRMS (ES^+); calcd for $C_{31}H_{40}NO_7$ (M + NH_4^+) 538.2805, found 538.2801.

1,2,3-Trideoxy-4,5,7-tri-*O*-(4-methoxybenzyl)-D-*arabino*-hept-1-en-6-ulose oxime 25

To a stirred solution of **4** (2.14 g, 4.11 mmol) in ethanol (60 cm^3) was added $NH_2OH{\cdot}HCl$ (859 mg, 12.36 mmol) and pyridine (1.0 cm^3, 12.36 mmol) at room temperature. The resulting mixture was stirred for 30 min at 60 °C. Upon cooling to room temperature, the mixture was concentrated *in vacuo*. Diethyl ether (40 cm^3) was added and the mixture washed with water (3 × 30 cm^3). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 3) provided **25** (2.14 g, 97%) as a 1 : 1 mixture of *E* and *Z* isomers and as a colourless oil; ν_{max} (film)/cm^{-1} 3331 (OH), 2935, 2909, 2865, 2837, 1612, 1514; δ_H (400 MHz; $CDCl_3$) 9.30 (1H, br s, OH), 7.27–7.20 (6H, m, ArH), 6.87–6.82 (6H, m, ArH), 5.75 (1H, m, H-2), 5.12–4.93 (2.5H, m, 2 × H-1, 0.5H × H-5), 4.65–4.10 (8.5H, m, 0.5 × H-5, 2 × H-7, 6 × OCH*H*Ar), 3.90–3.78 (10H, m, H-4, 3 × OCH_3), 2.38–2.18 (2H, m, H-3); δ_C (100 MHz; $CDCl_3$) 159.4 (ArC), 159.3 (ArC), 159.2 (ArC), 159.2 (ArC), 159.1 (ArC), 159.1 (ArC), 157.3 (C-6), 156.3 (C-6), 134.8 (C-2), 134.75 (C-2), 130.9 (ArC), 130.6 (ArC), 130.2 (ArC), 130.0 (ArCH), 129.9 (ArC), 129.8 (ArC), 129.8 (ArCH), 129.7 (ArCH), 129.7 (ArCH), 129.7 (ArCH), 129.5 (ArCH), 129.4 (ArCH), 117.2 (C-1), 117.15 (C-1), 113.8 (ArCH), 113.7 (ArCH), 113.6 (ArCH), 81.0 (CH), 79.5 (CH), 79.2 (CH), 75.3 (CH), 73.3 (CH_2), 73.2 (CH_2), 73.0 (CH_2), 72.7 (CH_2), 72.65 (CH_2), 71.6 (CH_2), 67.7 (CH_2), 62.2 (CH_2), 55.3 (OCH_3), 55.25 (OCH_3), 35.8 (C-3), 35.3 (C-3); *m*/*z* (ES^+) 558 (M + Na^+), 536 (M + H^+). HRMS (ES^+); calcd for $C_{31}H_{38}NO_7$ (M + H^+) 536.2648, found 536.2654.

1,2,3,6-Tetradeoxy-6-[[(9-fluorenylmethyloxy)carbonyl]-amino]-4,5,7-tri-*O*-(4-methoxybenzyl)-D-hept-1-enitol 5

To a stirred solution of **25** (1.90 g, 3.55 mmol) in diethyl ether (20 cm^3) at room temperature was added lithium aluminium hydride (1.0 M in diethyl ether, 10.6 cm^3, 10.6 mmol) dropwise. After stirring for 16 h, ethyl acetate (30 cm^3) and sodium hydroxide (5M, 30 cm^3) were added to quench the reaction (CAUTION). Water (50 cm^3) was then added, and the mixture extracted with diethyl ether (3 × 50 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. To the resulting amine in tetrahydrofuran–water (40 cm^3, 2.5 : 1) at 0 °C was added portionwise potassium carbonate (1.70 g, 12.3 mmol) followed by 9-fluorenylmethyl chloroformate (2.41 g, 9.32 mmol). The mixture was stirred for 45 min at 0 °C. Water (50 cm^3) was added and the mixture extracted with dichloromethane (3 × 50 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided **5** (2.29 g, 87%) as a colourless oil and as a 77 : 23 mixture of diastereomers; ν_{max} (film)/cm^{-1} 3426 (NH), 3053, 2937, 2838, 1720 (C=O), 1612, 1513; δ_H (400 MHz; d_6-DMSO at 110 °C) 7.82 (2H, d, *J* 7.6, ArH), 7.64 (2H, t, *J* 8.6, ArH), 7.38 (2H, t, *J* 7.6, ArH), 7.26 (2H, t, *J* 7.5, ArH), 7.23–7.16 (6H, m, ArH), 6.87–6.81 (6H, m, ArH), 6.51 (0.77H, br d, *J* 7.6, NH), 6.25 (0.23H, br s, NH), 5.86–5.75 (1H, m, H-2), 5.09–4.97 (2H, m, 2 × H-1), 4.58–4.27 (8H, m, 8 × OCH*H*), 4.20–4.14 (1H, m, OCH_2CH), 4.05–3.95 (1H, m, H-5), 3.735 (3H, s, OCH_3), 3.730 (3H, s, OCH_3), 3.70 (3H, s, OCH_3), 3.70–3.35 (4H, m, H-4, H-6, 2 × H-7), 2.45–2.20 (2H, m, 2 × H-3); *m*/*z*(ES^+) 766 (M + Na^+), 761 (M + NH_4^+), 166. HRMS (ES^+); calcd for $C_{46}H_{53}N_2O_8$ (M + NH_4^+) 761.3802, found 761.3776.

1,2,3,6-Tetradeoxy-6-[[(9-fluorenylmethyloxy)-carbonyl]-amino]-4,5,7-tri-*O*-acetyl-D-*arabino*-hept-1-enitol 6 and 1,2,3,6-tetradeoxy-6-[[(9-fluorenylmethyloxy)-carbonyl]amino]-4,5,7-tri-*O*-acetyl-D-*xylo*-hept-1-enitol 7

To a stirred solution of **5** (1.70 g, 2.29 mmol) in dichloromethane (40 cm^3) was added a 10% solution of TFA (6.20 cm^3, 80.5 mmol) in dichloromethane (50 cm^3) at room temperature dropwise. After 10 min, a deep purple colouration persisted. Toluene (30 cm^3) was added then the mixture concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 3 : 1 ⟶ 1 : 0) provided a colourless solid. This solid was dissolved in pyridine (10.0 cm^3, 123 mmol) at 0 °C and acetic anhydride (10.0 cm^3, 106 mmol) was added dropwise. After stirring for 12 h at room temperature, the mixture was concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided a 77 : 23 mixture of diastereomers. Separation by MPLC on a Merck Lobar Lichroprep Si60 column gave **6** (750 mg, 64%) as a colourless foam; mp 41–42 °C; $[\alpha]_D^{23}$ −7.00 (*c* 1.0, $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3343 (NH), 3068, 2957, 1745 (C=O), 1533, 1224; δ_H (400 MHz; $CDCl_3$) 7.76 (2H, d, *J* 7.5, ArH), 7.64–7.56 (2H, m, ArH), 7.40 (2H, t, *J* 7.3, ArH), 7.35–7.29 (2H, m, ArH), 5.78–5.65 (1H, m, H-2), 5.20–5.05 (5H, m, 2 × H-1, H-4, H-5, NH), 4.45 (1H, dd, *J* 10.6, 6.5, OCH*H*), 4.35 (1H, dd, *J* 10.6, 7.4, OCH*H*), 4.30–4.20 (3H, m, OC*H*H, OCH_2CH, H-6), 4.02–3.96 (1H, m, OCH*H*), 2.35–2.25 (2H, m, 2 × H-3), 2.14 (3H, s, CH_3), 2.10 (3H, s, CH_3), 2.06 (3H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 170.7 (C=O), 170.3 (C=O), 170.1 (C=O), 155.7 (C=O), 144.1 (ArC), 143.6 (ArC), 141.4 (ArC), 141.3 (ArC), 132.4 (C-2), 127.75 (ArCH), 127.7 (ArCH), 127.1 (ArCH), 125.1 (ArCH), 125.0 (ArCH), 120.0 (ArCH), 118.7 (C-1), 71.3 (C-5), 70.5 (C-4), 67.1 (OCH_2), 63.0 (OCH_2), 49.6 (CH), 47.1 (CH), 35.5 (C-3), 21.1 (CH_3), 20.8 (CH_3), 20.7 (CH_3); *m*/*z*(ES^+) 527 (M + NH_4^+) 510 (M + H^+) 358, 179. HRMS (ES^+); calcd for $C_{28}H_{35}N_2O_8$ (M + NH_4^+) 527.2393, found 527.2395. Further elution gave **7** (250 mg, 22%) as a colourless foam; $[\alpha]_D^{22}$ −4.00 (*c* 1.0, $CHCl_3$); mp 37–41 °C; ν_{max} (KBr)/cm^{-1} 3348 (NH), 2953, 2836, 1745 (C=O), 1511, 1225; δ_H (400 MHz; d_6-DMSO at 110 °C) 7.84 (2H, d, *J* 7.5, ArH), 7.68 (2H, d, *J* 7.5, ArH), 7.40 (2H, t, *J* 7.5, ArH), 7.35–7.29 (2H, m, ArH), 5.75–5.63 (1H, m, H-2), 5.17–5.03 (4H, m, 2 × H-1, H-4, H-5), 4.40–3.60 (6H, m, 4 × OCH*H*, OCH_2CH, H-6), 2.45–2.25 (2H, m, 2 × H-3), 2.03 (3H, s, CH_3), 1.98 (3H, s, CH_3), 1.96 (3H, s, CH_3); *m*/*z*(ES^+) 532 (M + Na^+), 527 (M + NH_4^+). HRMS (ES^+); calcd for $C_{28}H_{31}N_2O_8Na$ (M + Na^+) 532.1947, found 532.1948.

2-Deoxy-1,5-[[(9-fluorenylmethyloxy)-carbonyl]imino]-3,4,6-tri-*O*-acetyl-D-*arabino*-hexopyranose 26

A stirred solution of **6** (600 mg, 1.18 mmol) in dichloromethane (6 cm^3) at −78 °C, was treated with a stream of ozone for 6 min. Dimethyl sulfide (1.0 cm^3, 13.6 mmol) was added, and after 30 min, the mixture was warmed to room temperature and stirred for 1 h. Concentration of the mixture *in vacuo* and subsequent column chromatography (ethyl acetate–light petroleum; 1 : 3) provided **26** (439 mg, 73%) as a colourless solid; mp 42–45 °C; ν_{max} (KBr)/cm^{-1} 3447 (OH), 3369 (OH), 3058, 2961, 1745 (C=O), 1225; δ_H (300 MHz; $CDCl_3$) 7.80 (2H, d, *J* 7.5, ArH), 7.70–7.60 (2H, m, ArH), 7.45 (2H, t, *J* 7.5, ArH), 7.35 (2H, t, *J* 7.5, ArH), 5.48–5.05 (5H, m, H-1, H-3, H-4, OCH_2CH), 4.55–3.94 (5H, m, H-5, 2 × H-6, OCH_2CH, OH), 2.25–1.90 (11H, m, 2 × H-2, 3 × CH_3); *m*/*z*(ES^+) 534 (M + Na^+), 529 (M + NH_4^+) 474, 119. HRMS (ES^+); calcd for $C_{27}H_{33}N_2O_9$ (M + NH_4^+) 529.2186, found 529.2187.

1,5-Anhydro-2-deoxy-1,5-[[(9-fluorenylmethyloxy)carbonyl]-imino]-3,4,6-tri-*O*-acetyl-D-*arabino*-hex-1-enitol 2

To a stirred solution of **26** (500 mg, 9.77 mmol) in DMF (2 cm^3), dichloromethane (10 cm^3) and triethylamine (136 µl, 0.976 mmol) at 0 °C was added oxalyl chloride (94 µl, 1.10 mmol) in dichloromethane (1 cm^3) dropwise. After 30 min at 0 °C, a saturated solution of sodium hydrogen carbonate (5 cm^3) was added. On warming to room temperature, the mixture was extracted with dichloromethane (3 × 10 cm^3). The combined organic layers were dried over $MgSO_4$, filtered, then concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided **2** (348 mg, 72%) as a colourless foam; mp 47–50 °C; $[\alpha]_D^{24}$ −131 (*c* 1.0, $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3066, 3019, 2958, 1726 (C=O), 1652, 1240; δ_H (400 MHz; d_6-DMSO at 100 °C) 7.84 (2H, d, *J* 7.5, ArH), 7.60 (2H, d, *J* 7.5, ArH), 7.41 (2H, t, *J* 7.5, ArH), 7.32 (2H, dt, *J* 1.2, 7.5, ArH), 6.90 (1H, d, $J_{1,2}$ 8.4, H-1), 5.13 (1H, m, H-4), 5.06–5.00 (1H, m, H-2), 4.94–4.90 (1H, m, H-3), 4.61 (1H, dd, *J* 10.7, 6.3, OCH*H*CH), 4.53 (1H, dd, *J* 10.7, 6.0, OCH*H*CH), 4.46 (1H, m, H-5), 4.33 (1H, t, *J* 6.3, OCH_2CH), 4.15 (1H, dd, *J* 11.2, 7.3, H-6), 4.02 (1H, m, H-6′), 1.98 (3H, s, CH_3), 1.97 (3H, s, CH_3), 1.96 (3H, s, CH_3); δ_C (100 MHz; d_6-DMSO at 100 °C) 170.0 (C=O), 169.3 (C=O), 169.2 (C=O), 153.1 (C=O), 144.0 (ArC), 143.9 (ArC), 141.40 (ArC), 141.35 (ArC), 128.2 (ArCH), 127.7 (C-1), 127.55 (ArCH), 127.50 (ArCH), 125.2 (ArCH), 120.5 (ArCH), 101.6 (C-2), 68.3 (OCH_2CH), 67.1 (C-4), 64.2 (C-3), 60.0 (C-6), 52.1 (C-5), 47.2 (OCH_2CH), 20.9 (CH_3), 20.8 (CH_3), 20.7 (CH_3); *m*/*z*(ES^+) 511 (M + NH_4^+) 434, 152, 94. HRMS (ES^+); calcd for $C_{27}H_{31}N_2O_8$ (M + NH_4^+) 511.2080, found 511.2078. $C_{27}H_{27}NO_8$ requires C, 65.4; H, 5.4; N, 2.8%. Found: C, 65.7; H, 5.5; N, 2.8%.

2-Deoxy-1,5-[[(9-fluorenylmethyloxy)carbonyl]imino]-3,4,6-tri-*O*-acetyl-D-*xylo*-hexopyranose 27

A stirred solution of **7** (180 mg, 0.353 mmol) in dichloromethane (6 cm^3) at −78 °C, was treated with a stream of ozone for 3 min. Dimethyl sulfide (500 µl, 6.81 mmol) was added and the mixture stirred at −78 °C for 30 min, then warmed to room temperature and stirred for 1 h. Concentration *in vacuo* and subsequent column chromatography (ethyl acetate–light petroleum; 1 : 3) provided **27** (125 mg, 69%) as a colourless oil; ν_{max} (neat)/cm^{-1} 3456 (OH), 2968, 1744 (C=O), 1711 (C=O), 1231; δ_H (400 MHz; d_6-DMSO at 110 °C) 7.83 (2H, dd, *J* 7.5, 2.6, ArH), 7.62 (2H, d, *J* 7.5, ArH), 7.41 (2H, t, *J* 7.5, ArH), 7.32 (2H, m, ArH), 5.88 (1H, br s, OH), 5.76 (1H, br s, H-1), 5.44 (1H, td, *J* 11.2, 5.0, H-3), 4.88 (1H, dd, *J* 10.3, 6.5, H-4), 4.78–4.72 (1H, m, H-5), 4.47–4.40 (3H, m, H-6, OCH_2CH), 4.31–4.21 (2H, m, H-6′, OCH_2CH), 2.19–2.12 (1H, m, H-2), 2.04 (3H, s, CH_3), 2.00 (3H, s, CH_3), 1.94 (3H, s, CH_3), 1.73–1.65 (1H, m, H-2′); δ_C (100 MHz; d_6-DMSO at 110 °C) 170.0 (C=O), 169.9 (C=O), 169.8 (C=O), 154.7 (C=O), 144.3 (ArC), 144.2 (ArC), 141.3 (ArC), 128.1 (ArCH), 128.05 (ArCH), 127.5 (ArCH), 125.5 (ArCH), 125.4 (ArCH), 120.45 (ArCH), 120.4 (ArCH), 75.0 (C-1), 71.7 (C-4), 68.0 (t), 65.8 (C-3), 64.0 (t), 51.7 (d), 47.4 (d), 36.6 (C-2), 20.9 (CH_3), 20.8 (CH_3), 20.7 (CH_3); *m*/*z*(ES^+) 534 (M + Na^+), 529 (M + NH_4^+), 409. HRMS (ES^+); calcd for $C_{27}H_{33}N_2O_9$ (M + NH_4^+) 529.2186, found 529.2193.

1,5-Anhydro-2-deoxy-1,5-[[(9-fluorenylmethyloxy)carbonyl]-imino]-3,4,6-tri-*O*-acetyl-D-*xylo*-hex-2-enopyranose 8

To a stirred solution of **27** (500 mg, 9.77 mmol) in DMF (2 cm^3), dichloromethane (5 cm^3) and triethylamine (136 µl, 0.976 mmol) at 0 °C was added oxalyl chloride (94 µl, 1.10 mmol) in dichloromethane (1 cm^3) dropwise. After 30 min at 0 °C, saturated sodium hydrogen carbonate solution (5 cm^3) was added and the mixture extracted with dichloromethane (3 × 10 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided **8** (338 mg, 70%) as a colourless foam; $[\alpha]_D^{23}$ −88 (*c* 1.0, $CHCl_3$); mp 45–47 °C; ν_{max} (KBr)/cm^{-1} 3066, 2958, 1744 (C=O), 1655, 1228; δ_H (400 MHz; d_6-DMSO at 110 °C) 7.84 (2H, d, *J* 7.6, ArH), 7.64–7.59 (2H, m, ArH), 7.40 (2H, t, *J* 7.5, ArH), 7.35–7.29 (2H, m,

ArH), 6.70 (1H, br d, $J_{1,2}$ 8.3, H-1), 5.51 (1H, dt, J 8.9, 2.1, H-3), 5.08 (1H, dd, $J_{4,3}$ 8.9, $J_{4,5}$ 5.7, H-4), 4.81 (1H, dd, $J_{2,1}$ 8.3, $J_{2,3}$ 2.2, H-2), 4.58 (1H, dd, J 10.6, 6.3, OCH*H*CH), 4.53–4.46 (2H, m, OCH*H*CH, H-5), 4.37–4.31 (2H, m, OCH_2CH, H-6), 4.07 (1H, dd, J 11.8, 6.0, H-6′), 2.07 (3H, s, CH_3), 2.00 (3H, s, CH_3), 1.92 (3H, s, CH_3); δ_C (100 MHz; d_6-DMSO at 110 °C) 170.2 (C=O), 170.0 (C=O), 169.6 (C=O), 152.5 (C=O), 144.1 (ArC), 144.0 (ArC), 141.4 (ArC), 128.1 (ArCH), 127.6 (ArCH), 127.5 (ArCH), 126.6 (C-1), 125.3 (ArCH), 120.4 (ArCH), 103.5 (C-2), 69.6 (C-4), 68.5 (OCH_2CH), 68.0 (C-3), 60.0 (C-6), 52.3 (C-5), 47.3 (OCH_2CH), 20.9 (CH_3), 20.75 (CH_3), 20.70 (CH_3); m/z(ES^+) 516 ($M + Na^+$), 511 ($M + NH_4^+$). HRMS (ES^+); calcd for $C_{27}H_{31}N_2O_8$ ($M + NH_4^+$) 511.2080, found 511.2079.

3-β-(1,5-Anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-β-D-*erythro*-hex-2-eno-pyranosyl)-1-propene 9a and 3-α-(1,5-anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-α-D-*erythro*-hex-2-eno-pyranosyl)-1-propene 10a

To a stirred solution of **2** (100 mg, 0.203 mmol) in dichloromethane (2 cm^3) at −50 °C was added allyl trimethylsilane (48 µl, 0.302 mmol), followed by boron trifluoride diethyl etherate (25 µl, 0.197 mmol). The resulting solution was stirred for 1.5 h at −50 °C then allowed to warm to 0 °C over 1.5 h. Saturated sodium hydrogen carbonate solution (5 cm^3) was added, then the mixture extracted with dichloromethane (3 × 10 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was redissolved in dichloromethane (2 cm^3) and piperidine (250 µl, 2.52 mmol) added. After stirring for 2 h at room temperature, the solution was concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided **9a** (40 mg, 78%) as a colourless oil; $[\alpha]_D^{23}$ +140 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3460 (NH), 3336 (NH), 3078, 2980, 2936, 1740 (C=O), 1244; δ_H (400 MHz; $CDCl_3$) 5.80–5.67 (2H, m, H-2, CH_2CH=CH_2), 5.63 (1H, m, H-3), 5.16–5.06 (3H, m, H-4, CH_2CH=CH_2), 4.18 (1H, dd, $J_{6,6'}$ 11.4, $J_{6,5}$ 2.9, H-6), 4.01 (1H, dd, $J_{6,'6}$ 11.4, $J_{6',5}$ 6.1, H-6′), 3.46 (1H, m, H-1), 3.00 (1H, ddd, $J_{5,4}$ 9.1, $J_{5,6'}$ 6.1, $J_{5,6}$ 2.9, H-5), 2.41 (1H, br s, NH), 2.20 (2H, t, J 6.8, CH_2CH=CH_2), 2.04 (3H, s, CH_3), 2.02 (3H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 170.8 (C=O), 170.6 (C=O), 134.0 (=CH), 133.7 (=CH), 125.9 (C-3), 118.4 (CH=CH_2), 67.7 (C-4), 64.6 (C-6), 55.6 (C-5), 53.3 (C-1), 40.0 (CH_2CH=CH_2), 21.1 (CH_3), 20.8 (CH_3); m/z(ES^+) 529 (2M + Na^+), 276 ($M + Na^+$), 254 ($M + H^+$). HRMS (ES^+); calcd for $C_{13}H_{20}NO_4$ ($M + H^+$) 254.1392, found 254.1386. Further elution gave **10a** (9 mg, 18%) as a colourless oil; $[\alpha]_D^{23}$ +63.0 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3447 (NH), 3338 (NH), 3076, 2931, 1740 (C=O), 1233; δ_H (400 MHz; $CDCl_3$) 5.90 (1H, m, H-2), 5.85–5.72 (2H, m, H-3, C*H*=CH_2), 5.16–5.09 (2H, m, CH=CH_2), 5.08–5.03 (1H, m, H-4), 4.14 (1H, dd, $J_{6,6'}$ 11.3, $J_{6,5}$ 4.5, H-6), 4.06 (1H, dd, $J_{6',6}$ 11.3, $J_{6',5}$ 7.2, H-6′), 3.43–3.36 (1H, m, H-1), 3.23–3.18 (1H, m, H-5), 2.28 (2H, t, J 7.0, CH_2CH=CH_2), 2.19 (1H, br s, NH), 2.07 (3H, s, CH_3), 2.06 (3H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 170.8 (C=O), 170.6 (C=O), 135.1 (*C*H=CH_2), 134.4 (C-2), 124.2 (C-3), 118.0 (CH=CH_2), 66.9 (C-4), 63.8 (C-6), 51.6 (C-5), 50.4 (C-1), 38.7 (CH_2CH=CH_2), 21.2 (CH_3), 20.8 (CH_3); m/z(ES^+) 529 (2M + Na^+), 507 (2M + H^+), 276 ($M + Na^+$), 254 ($M + H^+$). HRMS (ES^+); calcd for $C_{13}H_{20}NO_4$ ($M + H^+$) 254.1392, found 254.1395.

β-(1,5-Anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-β-D-*erythro*-hex-2-eno-pyranosyl)ethane 9b and α-(1,5-anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-α-D-*erythro*-hex-2-eno-pyranosyl)ethane 10b

To a stirred solution of **2** (100 mg, 0.203 mmol) in dichloromethane (2 cm^3) at −20 °C was added diethylzinc (1.0 M in hexanes, 304 µl, 0.304 mmol), followed by boron trifluoride diethyl etherate (25 µl, 0.197 mmol). The mixture was slowly warmed to room temperature over 1 h. Saturated sodium hydrogen carbonate solution (5 cm^3) was added and the resulting mixture extracted with dichloromethane (3 × 10 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was redissolved in dichloromethane (2 cm^3) and piperidine (250 µl, 2.52 mmol) added at room temperature. After stirring for 1 h, the solution was concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided **9b** (31 mg, 63%) as a colourless oil; $[\alpha]_D^{23}$ +139 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3462 (NH), 3337 (NH), 3036, 2964, 2936, 1740 (C=O); δ_H (400 MHz; $CDCl_3$) 5.81 (1H, m, H-2), 5.65 (1H, m, H-3), 5.16 (1H, m, H-4), 4.23 (1H, dd, $J_{6,6'}$ 11.3, $J_{6,5}$ 2.8, H-6), 4.06 (1H, dd, $J_{6',6}$ 11.3, $J_{6',5}$ 6.3, H-6′), 3.34 (1H, br m, H-1), 3.02 (1H, ddd, $J_{5,4}$ 9.1, $J_{5,6'}$ 6.3, $J_{5,6}$ 2.8, H-5), 2.27 (1H, br s, NH), 2.08 (3H, s, CH_3), 2.06 (3H, s, CH_3), 1.47 (2H, m, CH_2CH_3), 0.95 (3H, t, J 7.5, CH_2CH_3); δ_C (100 MHz; $CDCl_3$) 170.9 (C=O), 170.6 (C=O), 134.2 (C-2), 125.4 (C-3), 67.9 (C-4), 64.8 (C-6), 55.7 (C-5), 55.4 (C-1), 28.8 (CH_2CH_3), 21.1 (CH_3), 20.9 (CH_3), 9.8 (CH_2CH_3); m/z(ES^+) 242 ($M + H^+$), 184. HRMS (ES^+); calcd for $C_{12}H_{20}NO_4$ ($M + H^+$) 242.1392, found 242.1388. Further elution gave **10b** (13 mg, 27%) as a colourless oil; $[\alpha]_D^{26}$ +69.0 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3457 (NH), 3345 (NH), 2963, 2934, 2876, 1741 (C=O); δ_H (400 MHz; $CDCl_3$) 5.93 (1H, m, H-2), 5.72 (1H, m, H-3), 5.04 (1H, m, H-4), 4.15–4.07 (2H, m, 2 × H-6), 3.25–3.16 (2H, m, H-1, H-5), 2.08 (3H, s, CH_3), 2.07 (3H, s, CH_3), 1.95 (1H, br s, NH), 1.53 (2H, m, CH_2CH_3), 0.97 (3H, t, J 7.5, CH_2CH_3); δ_C (100 MHz; $CDCl_3$) 170.9 (C=O), 170.7 (C=O), 135.4 (C-2), 123.5 (C-3), 66.8 (C-4), 63.7 (C-6), 52.3 (CH), 51.9 (CH), 27.6 (CH_2CH_3), 21.2 (CH_3), 20.9 (CH_3), 10.9 (CH_2CH_3); m/z(ES^+) 242 ($M + H^+$), 184, 122. HRMS (ES^+); calcd for $C_{12}H_{20}NO_4$ ($M + H^+$) 242.1392, found 242.1394.

β-(1,5-Anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-β-D-*erythro*-hex-2-eno-pyranosyl)acetophenone 9c and α-(1,5-anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-α-D-*erythro*-hex-2-eno-pyranosyl)acetophenone 10c

To a stirred solution of **2** (100 mg, 0.203 mmol) in dichloromethane (2 cm^3) at −40 °C was added 1-phenyl-1-(trimethylsilyloxy)ethylene (62 µl, 0.302 mmol), followed by boron trifluoride diethyl etherate (35 µl, 0.280 mmol). The solution was slowly warmed to 0 °C over 45 min, during which time the solution turned bright green. Saturated sodium hydrogen carbonate solution (5 cm^3) was added, and the resulting mixture extracted with dichloromethane (3 × 10 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was redissolved in dichloromethane (2 cm^3) and piperidine (250 µl, 2.52 mmol) added. After stirring for 1 h at room temperature, the solution was concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided **9c** (43 mg, 64%) as a yellow oil; $[\alpha]_D^{21}$ +121.0 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3456 (NH), 3346 (NH), 3063, 3040, 2950, 2937, 1733 (C=O), 1683 (C=O); δ_H (400 MHz; C_6D_6) 7.83–7.79 (2H, m, ArH), 7.21 (1H, t, J 7.3, ArH), 7.12 (2H, t, J 7.5, ArH), 5.89–5.78 (1H, m, H-3), 5.58–5.52 (2H, m, H-2, H-4), 4.47 (1H, dd, $J_{6,6'}$ 11.4, $J_{6,5}$ 2.6, H-6), 4.13 (1H, dd, $J_{6',6}$ 11.4, $J_{6',5}$ 7.5, H-6′), 4.10–4.03 (1H, m, H-1), 3.31–3.25 (1H, m, H-5), 2.82 (1H, dd, J 17.7, 9.1, C*H*HCOPh), 2.58 (1H, dd, J 17.7, 3.8, CH*H*COPh), 2.58 (1H, br s, NH), 1.75 (3H, s, CH_3), 1.73 (3H, s, CH_3); δ_C (100 MHz; C_6D_6) 197.7 (C=O), 169.9 (C=O), 169.8 (C=O), 136.9 (ArC), 133.0 (ArCH), 132.9 (C-2), 128.4 (ArCH), 128.0 (ArCH), 126.5 (C-3), 68.5 (C-4), 64.8 (C-6), 56.2 (C-5), 50.4 (C-1), 44.5 (CH_2COPh), 20.4 (CH_3), 20.0 (CH_3); m/z(CI) 332 ($M + H^+$), 212, 152, 138, 94. HRMS (ES^+); calcd for $C_{18}H_{22}NO_5$ ($M + H^+$) 332.1498, found 332.1503. Further elution gave **10c** (21 mg, 31%) as a yellow oil; $[\alpha]_D^{22}$ +35.0 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3344 (NH), 3038, 2935, 1739 (C=O), 1682 (C=O), 1241; δ_H (400 MHz; C_6D_6) 7.83–7.79 (2H, m, ArH), 7.23–7.18 (1H, m, ArH), 7.12 (2H, t, J 7.5, ArH), 5.87–5.83 (1H, m, H-3), 5.70–5.66 (1H, m, H-2), 5.29

(1H, m, H-4), 4.27 (1H, dd, $J_{6,6'}$ 11.1, $J_{6,5}$ 7.0, H-6), 4.15 (1H, dd, $J_{6',6}$ 11.1, $J_{6',5}$ 4.1, H-6′), 4.00 (1H, m, H-1), 3.27 (1H, dt, $J_{5,6'}$ 4.1, $J_{5,6} = J_{5,4}$ 7.0, H-5), 2.98 (1H, dd, *J* 17.0, 9.1, C*H*HCOPh), 2.56 (1H, dd, *J* 17.0, 4.4, CH*H*COPh), 1.95 (1H, br s, NH), 1.77 (6H, s, 2 × CH_3); δ_C (100 MHz; C_6D_6) 197.7 (C=O), 169.9 (C=O), 169.7 (C=O), 137.2 (ArC), 134.2 (C-2), 132.7 (ArCH), 128.4 (ArCH), 128.0 (ArCH), 125.1 (C-3), 66.9 (C-4), 63.4 (C-6), 51.9 (C-5), 47.6 (C-1), 42.5 (CH_2), 20.4 (CH_3), 20.1 (CH_3); *m*/*z* (CI) 332 (M + H^+), 212, 154, 152. HRMS (ES^+); calcd for $C_{18}H_{22}NO_5$ (M + H^+) 332.1498, found 332.1502.

β-(1,5-Anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-β-D-*erythro*-hex-2-eno-pyranosyl)methylcyclohexene 9d and α-(1,5-anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-α-D-*erythro*-hex-2-eno-pyranosyl)methylcyclohexene 10d

To a stirred solution of **2** (100 mg, 0.203 mmol) in dichloromethane (2 cm^3) at room temperature was added methylenecyclohexane (29 µl, 0.241 mmol), followed by tin (IV) bromide (133 mg, 0.31 mmol) in dichloromethane (2 cm^3). The resulting solution was stirred for 5 min, then saturated sodium hydrogen carbonate solution (5 cm^3) was added and the mixture extracted with dichloromethane (3 × 10 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was redissolved in dichloromethane (2 cm^3) and piperidine (250 µl, 2.52 mmol) added at room temperature. After stirring for 1 h, the solution was concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided **9d** (50 mg, 80%) as a colourless oil; $[a]_D^{24}$ +117 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3340 (NH), 2930, 2857, 2836, 1740 (C=O), 1238; δ_H (400 MHz; $CDCl_3$) 5.82–5.77 (1H, m, H-2), 5.63–5.58 (1H, m, H-3), 5.48 (1H, br s, =C*H*), 5.18–5.13 (1H, m, H-4), 4.21 (1H, dd, $J_{6,6'}$ 11.3, $J_{6,5}$ 2.9, H-6), 4.01 (1H, dd, $J_{6',6}$ 11.3, $J_{6',5}$ 6.7, H-6′), 3.51–3.45 (1H, m, H-1), 3.01 (1H, ddd, $J_{5,4}$ 9.3, $J_{5,6'}$ 6.7, $J_{5,6}$ 2.9, H-5), 2.04 (3H, s, CH_3), 2.03 (3H, s, CH_3), 2.05–1.75 (6H, m, 3 × CH_2), 1.81 (1H, br s, NH), 1.62–1.51 (4H, m, 2 × CH_2); δ_C (100 MHz; $CDCl_3$) 170.8 (C=O), 170.6 (C=O), 134.5 (C-2), 133.6 (C), 125.1 (C-3), 124.8 (=*C*H), 68.1 (C-4), 64.9 (C-6), 55.9 (C-5), 51.9 (C-1), 44.5 (NCH*C*H_2), 28.5 (CH_2), 25.3 (CH_2), 22.9 (CH_2), 22.4 (CH_2), 21.1 (CH_3), 20.8 (CH_3); *m*/*z*(ES^+) 637 (2M + Na^+), 330 (M + Na^+), 308 (M + H^+), 264. HRMS (ES^+); calcd for $C_{17}H_{26}NO_4$ (M + H^+) 308.1862, found 308.1854. Further elution gave **10d** (6.0 mg, 10%) as a colourless oil; ν_{max} (neat)/cm^{-1} 3329 (NH), 2928, 2856, 2838, 1743 (C=O), 1235; δ_H (400 MHz; $CDCl_3$) 5.90–5.85 (1H, m, H-2), 5.70 (1H, dt, *J* 10.2, 2.3, H-3), 5.51 (1H, br s, =C*H*), 5.09–5.05 (1H, m, H-4), 4.18 (1H, dd, $J_{6,6'}$ 11.1, $J_{6,5}$ 4.0, H-6), 4.01 (1H, dd, $J_{6',6}$ 11.1, $J_{6',5}$ 7.9, H-6′), 3.48–3.42 (1H, m, H-1), 3.24–3.19 (1H, m, H-5), 2.18–1.95 (6H, m, 3 × CH_2), 2.08 (3H, s, CH_3), 2.07 (3H, s, CH_3), 1.80–1.44 (5H, m, NH, 2 × CH_2); δ_C (100 MHz; $CDCl_3$) 170.8 (C=O), 170.7 (C=O), 134.7 (C-2), 134.6 (C), 124.9 (=*C*H), 123.9 (C-3), 67.5 (C-4), 64.2 (C-6), 51.2 (C-5), 48.9 (C-1), 42.5 (NCH*C*H_2), 28.2 (CH_2), 25.4 (CH_2), 22.9 (CH_2), 22.4 (CH_2), 21.2 (CH_3), 20.8 (CH_3); *m*/*z*(ES^+) 637 (2M + Na^+), 330 (M + Na^+), 308 (M + H^+). HRMS (ES^+); calcd for $C_{17}H_{26}NO_4$ (M + H^+) 308.1862, found 308.1859.

β-(1,5-Anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-β-D-*threo*-hex-2-eno-pyranosyl)ethane 12 and α-(1,5-anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-α-D-*threo*-hex-2-eno-pyranosyl)ethane 11

To a stirred solution of **8** (150 mg, 0.304 mmol) in dichloromethane (2 cm^3) at −20 °C was added diethylzinc (1.0 M in hexane, 456 µl, 0.456 mmol), followed by boron trifluoride diethyl etherate (43 µl, 0.339 mmol). The resulting solution was allowed to warm to room temperature over 1 h, then stirred for a further 1 h. Saturated sodium hydrogen carbonate solution (5 cm^3) was added, and the mixture extracted with dichloromethane (3 × 10 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was redissolved in dichloromethane (2 cm^3) at room temperature and piperidine (250 µl, 2.52 mmol) added. After stirring for 1 h, the solution was concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4) provided a 1 : 1.4 mixture of **12** and **11** respectively as judged by ^1H NMR spectroscopy (59 mg, 80%). Partial separation of the two diastereomers was carried out using MPLC on a Merck Lobar Lichroprep Si60 column to give **12** (20 mg, 27%) as a colourless oil; $[a]_D^{25}$ +191 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3458 (NH), 3343 (NH), 3035, 2963, 2929, 2876, 1743 (C=O), 1233; δ_H (400 MHz; $CDCl_3$) 6.02 (1H, dd, $J_{2,3}$ 10.2, *J* 3.4, H-2), 5.84 (1H, ddd, $J_{3,2}$ 10.2, $J_{3,4}$ 4.5, 2.0, H-3), 5.13 (1H, m, H-4), 4.14 (1H, dd, $J_{6,6'}$ 11.1, $J_{6,5}$ 5.9, H-6), 4.06 (1H, dd, $J_{6',6}$ 11.1, $J_{6',5}$ 8.0, H-6′), 3.36 (1H, ddd, $J_{5,6'}$ 8.0, $J_{5,6}$ 5.9, $J_{5,4}$ 3.5, H-5), 3.30–3.25 (1H, m, H-1), 2.07 (3H, s, CH_3), 2.06 (3H, s, CH_3), 1.75 (1H, br s, NH), 1.55–1.43 (2H, m, C$H_2$$CH_3$), 0.97 (3H, t, *J* 7.4, CH_2CH_3); δ_C (100 MHz; $CDCl_3$) 170.9 (C=O), 170.6 (C=O), 136.5 (C-2), 122.7 (C-3), 65.4 (C-4), 63.6 (C-6), 53.3 (C-1), 49.9 (C-5), 26.6 (*C*$H_2$$CH_3$), 21.1 ($CH_3$), 20.9 ($CH_3$), 10.9 ($CH_2$*C*$H_3$); *m*/*z*($ES^+$) 264 (M + Na^+), 242 (M + H^+). HRMS (ES^+); calcd for $C_{12}H_{20}NO_4$ (M + H^+) 242.1392, found 242.1394. Further elution gave **11** (29 mg, 40%) as a colourless oil; $[a]_D^{23}$ +161.0 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3456 (NH), 3330 (NH), 3033, 2964, 2936, 2878, 1740 (C=O), 1240; δ_H (400 MHz; $CDCl_3$) 5.99 (1H, dd, $J_{2,3}$ 10.0, 1.2, H-2), 5.94 (1H, ddd, $J_{3,2}$ 10.0, 4.8, 2.0, H-3), 5.11–5.07 (1H, m, H-4), 4.17 (1H, dd, $J_{6,6'}$ 11.1, $J_{6,5}$ 6.3, H-6), 4.06 (1H, dd, $J_{6',6}$ 11.1, $J_{6',5}$ 7.5, H-6′), 3.30–3.24 (1H, m, H-1), 3.21–3.15 (1H, m, H-5), 2.07 (3H, s, CH_3), 2.06 (3H, s, CH_3), 1.61 (1H, br s, NH), 1.55 (2H, quintet, *J* 7.4, C$H_2$$CH_3$), 0.97 (3H, t, *J* 7.4, CH_2CH_3); δ_C (100 MHz; $CDCl_3$) 170.8 (C=O), 170.7 (C=O), 137.5 (C-2), 123.1 (C-3), 65.2 (C-4), 64.3 (C-6), 56.2 (C-1), 54.9 (C-5), 28.4 (*C*$H_2$$CH_3$), 21.1 ($CH_3$), 20.9 ($CH_3$), 10.0 ($CH_2$*C*$H_3$); *m*/*z*($ES^+$) 264 (M + Na^+), 242 (M + H^+). HRMS (ES^+); calcd for $C_{12}H_{20}NO_4$ (M + H^+) 242.1392, found 242.1395.

12-β-(1,5-Anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-β-D-*erythro*-hex-2-eno-pyranosyl)dodec-2-ene 14 and 12-α-(1,5-anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-α-D-*erythro*-hex-2-eno-pyranosyl)dodec-2-ene 28

To a stirred solution of trimethyl-(1-nonyl-allyl)-silane[17c] (110 mg, 0.457 mmol) in dichloromethane (3 ml) at −60 °C was added **2** (150 mg, 0.304 mmol) dropwise followed by boron trifluoride diethyl etherate (37.0 µl, 0.292 mmol). The resulting mixture was stirred at −50 °C for 1.5 h then allowed to warm to 0 °C over 1.5 h. Saturated sodium hydrogen carbonate solution (5 ml) was added, and the resulting mixture extracted with dichloromethane (3 × 10 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo.* The residue was redissolved in dichloromethane (3 ml) and piperidine (400 µl, 4.04 mmol) at room temperature and stirred for 1 h, then concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 40 increasing to 1 : 9) provided **14** (90 mg, 78%) as a colourless oil; $[a]_D^{26}$ +110.0 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3462 (NH), 3338 (NH), 3037, 2924, 2854, 1740 (C=O), 1457, 1233; δ_H (400 MHz; $CDCl_3$) 5.80 (1H, br d, $J_{2,3}$ 10.1, H-2), 5.65 (1H, br d, $J_{3,2}$ 10.1, H-3), 5.53 (1H, m, CH_2C*H*=CH), 5.33 (1H, m, CH_2CH=C*H*), 5.15 (1H, dd, $J_{4,5}$ 9.0, $J_{4,3}$ 1.8, H-4), 4.20 (1H, dd, $J_{6,6'}$ 11.3, $J_{6,5}$ 2.6, H-6), 4.03 (1H, dd, $J_{6',6}$ 11.3, $J_{6',5}$ 6.1, H-6′), 3.41 (1H, br s, H-1), 3.01 (1H, ddd, $J_{5,4}$ 8.9, $J_{5,6'}$ 6.1, $J_{5,6}$ 2.6, H-5), 2.14 (2H, t, *J* 6.6, CHCH_2CH=CH), 2.06 (3H, s, CH_3), 2.05 (3H, s, CH_3), 1.99 (2H, m, =CHC$H_2$$CH_2$), 1.89 (1H, br s, NH), 1.40–1.20 (14H, m, 7 × CH_2), 0.86 (3H, t, *J* 7.2, CH_3); δ_C (100 MHz; $CDCl_3$) 170.8 (C=O), 170.6 (C=O), 134.9 (CH_2*C*H=CH), 134.1 (C-2), 125.6 (C-3), 124.9 (CH_2CH=*C*H), 67.8 (C-4), 64.8 (C-6), 55.6 (C-5), 53.7 (C-1), 38.9 (*C*H_2CH=), 32.7 (*C*H_2CH=), 31.9 (CH_2), 29.6

(CH_2), 29.55 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 22.7 (CH_2), 21.1 (CH_3), 20.8 (CH_3), 14.1 (CH_3); *m/z*(ES^+) 781 (2M + Na^+), 759 (2M + H^+), 402 (M + Na^+), 380 (M + H^+), 264, 119. HRMS (ES^+); calcd for $C_{22}H_{38}NO_4$ (M + H^+) 380.2801, found 380.2790. Further elution gave **28** (10 mg, 9%) as a colourless oil; $[\alpha]_D^{26}$ +10.0 (*c* 0.5, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3457 (NH), 3339 (NH), 2950, 2925, 2854, 1744 (C=O), 1237; δ_H (400 MHz; $CDCl_3$) 5.94–5.88 (1H, m, H-2), 5.77–5.71 (1H, m, H-3), 5.58–5.49 (1H, m, CH_2CH=CH), 5.42–5.33 (1H, m, CH_2CH=C*H*), 5.08–5.03 (1H, m, H-4), 4.17–4.04 (2H, m, 2 × H-6), 3.40–3.30 (1H, m, H-1), 3.25–3.18 (1H, m, H-5), 2.21 (2H, m, CH_2CH=CH), 2.08 (6H, s, 2 × CH_3), 2.07–1.98 (4H, m, 2 × CH_2), 1.78 (1H, br s, NH), 1.40–1.20 (12H, m, 6 × CH_2), 0.87 (3H, t, *J* 7.2, CH_3); δ_C (100 MHz; $CDCl_3$) 170.9 (C=O), 170.6 (C=O), 134.7 (C-2), 134.6 (CH_2*C*H=CH), 126.0 (CH_2CH=*C*H), 123.8 (C-3), 67.0 (C-4), 63.9 (C-6), 51.7 (C-5), 50.8 (C-1), 37.6 (*C*H_2CH=), 32.7 (*C*H_2CH=), 31.9 (CH_2), 29.65 (CH_2), 29.60 (CH_2), 29.55 (CH_2), 29.50 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 21.2 (CH_3), 20.9 (CH_3), 14.1 (CH_3); *m/z*(ES^+) 781 (2M + Na^+), 759 (2M + H^+), 402 (M + Na^+), 380 (M + H^+). HRMS (ES^+); calcd for $C_{22}H_{38}NO_4$ (M + H^+) 380.2801, found 380.2801.

12-β-(1,5-Anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-β-D-*erythro*-hexo-pyranosyl)dodecane 29

To a stirred solution of **14** (23 mg, 0.06 mmol) in ethanol (2 ml) at room temperature was added a spatula tip of Pt/C. The solution was placed under an atmosphere of hydrogen and stirred for 1.5 h. Filtration through a plug of Celite, concentration *in vacuo*, and subsequent column chromatography (ethyl acetate–light petroleum; 1 : 5) provided **29** (14 mg, 60%) as a colourless solid; mp 44–45 °C; $[\alpha]_D^{32}$ +27.0 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3333 (NH), 2953, 2922, 2851, 1742 (C=O), 1723 (C=O), 1253, 1230; δ_H (400 MHz; $CDCl_3$) 4.52 (1H, td, *J* 10.6, 4.5, H-4), 4.18 (1H, dd, $J_{6,6'}$ 11.1, $J_{6,5}$ 2.8, H-6), 4.01 (1H, dd, $J_{6',6}$ 11.1, $J_{6',5}$ 7.0, H-6′), 2.91–2.85 (1H, m, H-5), 2.55–2.48 (1H, m, H-1), 2.20–2.13 (1H, m, H-3), 2.07 (3H, s, CH_3), 2.03 (3H, s, CH_3), 1.83–1.72 (3H, m, 3 × CH*H*), 1.38–1.15 (23H, m, H-3′, NH, 21 × CH*H*), 0.87 (3H, t, *J* 6.8, CH_3); δ_C (100 MHz; $CDCl_3$) 170.9 (C=O), 170.3 (C=O), 71.1 (C-4), 65.2 (C-6), 58.6 (C-5), 55.9 (C-1), 36.5 (CH_2), 31.9 (CH_2), 31.1 (CH_2), 30.3 (CH_2), 29.8 (C-3), 29.7 (CH_2), 29.65 (CH_2), 29.6 (CH_2), 29.55 (CH_2), 29.4 (CH_2), 26.2 (CH_2), 22.7 (CH_2), 21.2 (CH_3) 20.9 (CH_3), 14.1 (CH_3); *m/z*(ES^+) 789 (2M + Na^+), 767 (2M + H^+), 406 (M + Na^+), 384 (M + H^+). HRMS (ES^+); calcd for $C_{22}H_{41}NO_4Na$ (M + Na^+) 406.2933, found 406.2931.

(+)-Deoxoprosophylline

To a stirred solution of **29** (30 mg, 0.077 mmol) in THF–water (3 : 1, 2 ml) at room temperature was added lithium hydroxide (9.0 mg, 0.377 mmol). The solution was stirred for 2.5 h, then the THF removed on a rotary evaporator, and the resulting aqueous solution extracted with dichloromethane (3 × 10 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (dichloromethane–methanol; 9 : 1) provided an off-white solid which was recrystallised (acetone) to give (+)-deoxoprosophylline (20 mg, 85%) as a colourless solid; mp 84–85 °C (lit.[17f] mp 83 °C); $[\alpha]_D^{24}$ +12.5 (*c* 0.24, $CHCl_3$) {lit.[17f] $[\alpha]_D^{20}$ +13.0 (*c* 0.22, $CHCl_3$)}; ν_{max} (KBr)/cm^{-1} 3314 (OH, NH), 2925, 2854, 1457; δ_H (400 MHz; $CDCl_3$), 3.82 (1H, dd, $J_{6,6'}$ 11.1, $J_{6,5}$ 4.5, H-6), 3.76 (1H, dd, $J_{6',6}$ 11.1, $J_{6',5}$ 4.9, H-6′), 3.50 (1H, m, H-4), 2.75–2.55 (3H, br s, NH, 2 × OH), 2.60–2.53 (3H, m, H-1, H-5, 1 × CH*H*), 2.10–2.01 (1H, m, 1 × CH*H*), 1.80–1.73 (1H, m, 1 × CH*H*), 1.45–1.13 (23H, m, 23 × CH*H*), 0.87 (3H, t, *J* 6.8, CH_3); δ_C (100 MHz; $CDCl_3$) 70.0 (C-4), 64.0 (C-6), 63.3 (C-5), 56.2 (C-1), 36.2 (CH_2), 33.7 (CH_2), 31.9 (CH_2), 30.8 (CH_2), 29.75 (CH_2), 29.7 (CH_2), 29.65 (CH_2), 29.6 (CH_2), 29.55 (CH_2), 29.4 (CH_2), 26.2 (CH_2), 22.7 (CH_2), 14.1 (CH_3); *m/z*(ES^+) 300 (M + H^+), 119. HRMS (ES^+); calcd for $C_{18}H_{38}NO_2$ (M + H^+) 300.2902, found 300.2903.

1,5-Anhydro-2-bromo-2-deoxy-1,5-[[(9-fluorenylmethyloxy)-carbonyl]imino]-3,4,6-tri-*O*-acetyl-D-*arabino*-hex-1-enitol 15

To a stirred solution of **2** (250 mg, 0.507 mmol) in dichloromethane (6 cm^3) at −78 °C was added bromine (29 µl, 0.566 mmol) dropwise until an orange colour persisted. Diisopropylethylamine (97 µl, 0.557 mmol) was added and the reaction was left to warm to room temperature, then stirred for a further 45 min. Aqueous $Na_2S_2O_3$ solution (5 cm^3) was added, then the mixture extracted with dichloromethane (3 × 10 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 5) provided **15** (250 mg, 86%) as a colourless foam; mp 55–57 °C; $[\alpha]_D^{25}$ −100.0 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 2955, 1752 (C=O), 1652, 1215; δ_H (400 MHz; d_6-DMSO at 110 °C) 7.86 (2H, d, *J* 7.5, ArH), 7.60 (2H, d, *J* 7.5, ArH), 7.41 (2H, t, *J* 7.5, ArH), 7.32 (2H, t, *J* 7.5, ArH), 7.10 (1H, br s, H-1), 5.19–5.16 (2H, m, H-3, H-4), 4.66 (1H, dd, *J* 10.5, 6.0, OCH*H*CH), 4.57 (1H, dd, *J* 10.5, 5.7, OCH*H*CH), 4.41 (1H, br s, H-5), 4.35 (1H, t, *J* 5.7, OCH_2CH), 4.12 (1H, dd, *J* 11.4, 6.9, H-6), 4.05–3.96 (1H, m, H-6), 2.04 (3H, s, CH_3), 1.99 (3H, s, CH_3), 1.95 (3H, s, CH_3); δ_C (100 MHz; d_6-DMSO at 110 °C) 170.1 (C=O), 169.2 (C=O), 169.0 (C=O), 152.3 (C=O), 144.0 (ArC), 143.8 (ArC), 141.4 (ArC), 141.3 (ArC), 128.6 (C-1), 128.2 (ArCH), 127.6 (ArCH), 127.55 (ArCH), 125.2 (ArCH), 120.5 (ArCH), 68.6 (OCH_2CH), 68.4 (CH), 67.4 (CH), 59.7 (C-6), 51.7 (C-5), 47.1 (OCH_2CH), 20.9 (CH_3), 20.7 (CH_3), 20.65 (CH_3); *m/z*(CI^+) 591 and 589 (M + NH_4^+), 514, 512. HRMS (ES^+); calcd for $C_{27}H_{30}N_2O_8{}^{79}Br$ (M + NH_4^+) 589.1186, found 589.1177.

1,5-Anhydro-2-bromo-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-β-D-*erythro*-hex-2-eno-pyranosyl 16

To a stirred solution of **15** (100 mg, 0.175 mmol) in dichloromethane (2 cm^3) at −50 °C was added triethylsilane (62 µl, 0.388 mmol), followed by boron trifluoride diethyl etherate (28 µl, 0.221 mmol). The resulting solution was stirred for 1 h, then allowed to warm to room temperature. After stirring for a further 12 h, saturated sodium hydrogen carbonate solution (5 cm^3) was added, and the mixture extracted with dichloromethane (3 × 10 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. This residue was redissolved in dichloromethane (2 cm^3) at room temperature then piperidine (250 µl, 2.52 mmol) added. After stirring for 1 h, the solution was concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 1 : 4 ⟶ 1 : 2) provided **16** (42 mg, 82%) as a colourless solid; mp 69–71 °C; $[\alpha]_D^{21}$ +110 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3328 (NH), 2961, 2935, 2848, 1740 (C=O), 1651 (C=C), 1234; δ_H (400 MHz; $CDCl_3$) 6.11 (1H, m, H-3), 5.19–5.14 (1H, m, H-4), 4.19–4.09 (2H, m, 2 × H-6), 3.62 (1H, dt, $J_{1,1'}$ 18.1, 2.3, H-1), 3.49 (1H, d, $J_{1',1}$ 18.1, H-1′), 3.08–3.03 (1H, m, H-5), 2.08 (3H, s, CH_3), 2.075 (3H, s, CH_3), 1.98 (1H, br s, NH); δ_C (100 MHz; $CDCl_3$) 170.8 (C=O), 170.3 (C=O), 126.7 (C-2), 126.5 (C-3), 68.2 (C-4), 63.2 (C-6), 53.8 (C-5), 50.8 (C-1), 21.0 (CH_3), 20.8 (CH_3); *m/z*(CI^+) 294 and 292 (M + H^+). HRMS (ES^+); calcd for $C_{10}H_{15}NO_4Br$ (M + H^+) 292.0184, found 292.0186.

Preparation and X-ray crystallographic data for 16·HCl

To a stirred solution of **16** (30 mg, 0.103 mmol) in diethyl ether (2 cm^3) was added 1 M HCl in diethyl ether (0.21 cm^3). After 1 h, the solvent was removed under reduced pressure. X-ray diffraction studies were performed on a colourless crystal grown from diethyl ether–light petroleum at 298 K using a Bruker SMART diffractometer with graphite-monochromated Mo–Kα radiation (λ = 0.71073 Å). The structure was solved by

direct methods. $C_{10}H_{15}NO_4BrCl$, M = 328.59, orthorhombic, space group $P2_12_12_1$, a = 6.9448(5), b = 20.840(2), c = 30.325(2) Å, U = 4388.9(5) Å^3, Z = 12 (3 crystallographically independent molecules), D_c = 1.492 Mg m^{-3}, μ = 2.994 mm^{-1}, $F(000)$ = 1992, crystal size = 0.1 × 0.05 × 0.05 mm, Flack parameter −0.002(8). Of 22127 measured data, 6429 were unique (R_{int} = 0.0656) and 3699 observed ($I > 2\sigma(I)$]) to give R_1 = 0.0349 and wR_2 = 0.0530. All non-hydrogen atoms were refined with anisotropic displacement parameters; The NH_2 protons were located from a ΔF map and allowed to refine isotropically subject to a distance constraint (N–H = 0.98 Å). All remaining hydrogen atoms bound to carbon were idealised. Structural refinements were by the full-matrix least-squares method on F^2.¶

1,5-Anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-2-vinyl-D-*erythro*-hex-2-eno-pyranosyl 17

$Pd(dba)_2$ (16 mg, 17.5 μmol) and tri-*o*-tolylphosphine (10 mg, 32.9 μmol) in acetonitrile (3 cm^3) were stirred at 80 °C in a sealed tube for 1 h. The mixture was cooled to room temperature, then a solution of **16** (50 mg, 0.171 mmol) in acetonitrile (1 cm^3) was added followed by tributyl(vinyl)tin (100 μl, 0.342 mmol). The tube was sealed and the mixture stirred for 4 h at 80 °C. On cooling to room temperature, the mixture was filtered through a pad of silica then concentrated *in vacuo*. Column chromatography (ethyl acetate–methanol; 99 : 1) provided **17** (27 mg, 66%) as a colourless oil; $[\alpha]_D^{25}$ +153 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3440 (NH), 2929, 2854, 1736 (C=O), 1655 (C=C), 1625 (C=C), 1237; δ_H (400 MHz; $CDCl_3$) 6.26 (1H, dd, *J* 17.7, 11.0, C*H*=CH_2), 5.70 (1H, br s, H-3), 5.27–5.21 (1H, m, H-4), 5.17–5.06 (2H, m, CH=CH_2), 4.18 (1H, dd, $J_{6,6'}$ 11.4, $J_{6,5}$ 3.5, H-6), 4.09 (1H, dd, $J_{6',6}$ 11.4, $J_{6',5}$ 6.0, H-6′), 3.60–3.49 (2H, m, H-1), 3.03 (1H, ddd, $J_{5,4}$ 7.8, $J_{5,6'}$ 6.0, $J_{5,6}$ 3.5, H-5), 2.08 (3H, s, CH_3), 2.07 (3H, s, CH_3), 1.94 (1H, br s, NH); δ_C (100 MHz; $CDCl_3$) 170.9 (C=O), 170.7 (C=O), 139.6 (C-2), 136.0 (*C*H=CH_2), 124.9 (C-3), 114.0 (CH=*C*H_2), 67.6 (C-4), 63.9 (C-6), 55.1 (C-5), 43.1 (C-1), 21.2 (CH_3), 20.9 (CH_3); *m*/*z*(ES$^+$) 501 (2M + Na$^+$), 479 (2M + H$^+$), 240 (M + H$^+$). HRMS (ES$^+$); calcd for $C_{12}H_{18}NO_4$ (M + H$^+$) 240.1236, found 240.1238.

1,5-Anhydro-2,3-dideoxy-4,6-di-*O*-acetyl-1,5-imino-2-phenyl-D-*erythro*-hex-2-eno-pyranosyl 18

To a stirred solution of **16** (50 mg, 0.171 mmol) in THF (3 cm^3) was added phenylboronic acid (23 mg, 0.187 mmol), potassium phosphate (55 mg, 0.259 mmol) then dichloro[1,1′-bis-(diphenylphosphino)ferrocene]palladium(II) dichloromethane adduct (3 mg, 3.67 μmol). The resulting mixture was stirred at 70 °C for 26 h. On cooling to room temperature, water (5 cm^3) was added. The mixture was extracted with dichloromethane (3 × 10 cm^3), the combined organic layers dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (ethyl acetate–light petroleum; 3 : 2) provided **18** (30 mg, 61%) as a colourless oil; $[\alpha]_D^{24}$ +108 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3338 (NH), 3057, 3032, 2931, 1734 (C=O), 1235; δ_H (300 MHz; $CDCl_3$) 7.37–7.27 (5H, m, ArH), 6.05 (1H, m, H-3), 5.37–5.31 (1H, m, H-4), 4.24 (1H, dd, $J_{6,6'}$ 11.3, $J_{6,5}$ 3.6, H-6), 4.14 (1H, dd, $J_{6',6}$ 11.3, $J_{6',5}$ 6.1, H-6′), 3.85 (1H, dt, $J_{1,1'}$ 17.3, 2.5, H-1), 3.74 (1H, d, $J_{1',1}$ 17.3, H-1′), 3.12 (1H, ddd, $J_{5,4}$ 7.7, $J_{5,6'}$ 6.1, $J_{5,6}$ 3.6, H-5), 2.10 (3H, s, CH_3), 2.09 (3H, s, CH_3), 1.99 (1H, br s, NH); δ_C (75 MHz; $CDCl_3$) 171.3 (C=O), 171.1 (C=O), 141.5 (C), 138.5 (C), 128.9 (CH), 128.5 (CH), 125.6 (CH), 121.5 (CH), 68.1 (C-4), 64.4 (C-6), 55.2 (C-5), 46.2 (C-1), 21.6 (CH_3), 21.3 (CH_3); *m*/*z*(ES$^+$) 579 (2M + H$^+$), 290 (M + H$^+$), 230. HRMS (ES$^+$); calcd for $C_{16}H_{20}NO_4$ (M + H$^+$) 290.1392, found 290.1394.

¶ CCDC reference number 208078. See http://www.rsc.org/suppdata/ob/b3/b303817c/ for crystallographic data in .cif or other electronic format.

β-(1,5-Anhydro-1,5-imino-2,3,4,6-tetra-*O*-acetyl-D-allopyranosyl)ethane 21 and α-(1,5-anhydro-1,5-imino-2,3,4,6-tetra-*O*-acetyl-D-mannopyranosyl)ethane 22

To a stirred solution of **2** (100 mg, 0.203 mmol) in dichloromethane (2 cm^3) at −20 °C was added diethylzinc (1.0 M in hexane, 304 μl, 0.304 mmol), followed by boron trifluoride diethyl etherate (25 μl, 0.197 mmol). The resulting solution was allowed to warm to room temperature over 2 h. Saturated sodium hydrogen carbonate solution (5 cm^3) was added, then extracted with dichloromethane (3 × 10 cm^3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was dissolved in acetone/water (2 : 1, 3 cm^3), 4-methylmorpholine *N*-oxide (48.0 mg, 0.410 mmol) added, followed by osmium tetraoxide (2.10 mg, 8.26 μmol) in water (1 cm^3). After stirring for 5 days, the solution was cooled to 0 °C, saturated $NaHSO_3$ solution (4 cm^3) added, and the mixture warmed to room temperature. After 30 min, the mixture was extracted with ethyl acetate (3 × 10 cm^3), the combined organic layers dried over $MgSO_4$, filtered and concentrated *in vacuo*. To this residue in pyridine (1.0 cm^3, 12.4 mmol) at room temperature was added acetic anhydride (1.0 cm^3, 10.6 mmol). After 2 h, the mixture was concentrated *in vacuo*, then redissolved in dichloromethane (2 cm^3). Piperidine (300 μl, 3.03 mmol) was added and the mixture stirred for 1 h. Concentration *in vacuo* followed by column chromatography (ethyl acetate–light petroleum; 1 : 4) provided **21** (31 mg, 43%) as a colourless solid; mp 113–114 °C; $[\alpha]_D^{26}$ +9.0 (*c* 1.0, $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3458 (NH), 3318 (NH), 2966, 2921, 2897, 2876, 1751 (C=O), 1227; δ_H (400 MHz; $CDCl_3$) 5.56 (1H, *J* 2.7, H-3), 4.77 (1H, dd, $J_{4,5}$ 10.5, $J_{4,3}$ 2.7, H-4), 4.60 (1H, dd, $J_{2,1}$ 10.2, $J_{2,3}$ 2.7, H-2), 4.11 (2H, d, *J* 6.8, 2 × H-6), 3.24 (1H, dt, $J_{5,4}$ 10.5, *J* 3.8, H-5), 2.98–2.92 (1H, m, H-1), 2.13 (3H, s, CH_3), 2.07 (3H, s, CH_3), 2.00 (3H, s, CH_3), 1.98 (3H, s, CH_3), 1.66–1.56 (1H, m, CH*H*CH_3), 1.32 (1H, br s, NH), 1.26–1.15 (1H, m, CH*H*CH_3), 0.95 (3H, t, *J* 7.4, CH_3); δ_C (100 MHz; $CDCl_3$) 170.8 (C=O), 170.2 (C=O), 169.8 (C=O), 169.5 (C=O), 72.0 (C-2), 69.1 (C-3), 68.7 (C-4), 63.7 (C-6), 53.9 (C-1), 52.2 (C-5), 24.4 (*C*H_2CH$_3$), 20.85 (CH_3), 20.8 (CH_3), 20.75 (CH_3), 20.7 (CH_3), 9.7 (CH_2*C*H$_3$); *m*/*z*(ES$^+$) 741 (2M + Na$^+$), 382 (M +Na$^+$), 360 (M + H$^+$). HRMS (ES$^+$); calcd for $C_{16}H_{26}NO_8$ (M + H$^+$) 360.1658, found 360.1658. Further elution gave **22** (14 mg, 19%) as a colourless oil; $[\alpha]_D^{23}$ −5.0 (*c* 1.0, $CHCl_3$); ν_{max} (neat)/cm^{-1} 3470 (NH), 3339 (NH), 2966, 2938, 2878, 1754 (C=O), 1254; δ_H (400 MHz; C_6D_6) 5.50 (1H, t, *J* 9.5, H-4), 5.46 (1H, t, *J* 3.0, H-2), 5.41 (1H, dd, $J_{3,4}$ 9.5, $J_{3,2}$ 3.0, H-3), 4.41 (1H, dd, $J_{6,6'}$ 11.4, $J_{6,5}$ 4.7, H-6), 4.04 (1H, dd, $J_{6',6}$ 11.4, $J_{6',5}$ 3.2, H-6′), 2.89–2.82 (1H, m, H-5), 2.73–2.67 (1H, m, H-1), 1.83 (3H, s, CH_3), 1.82 (3H, s, CH_3), 1.75 (6H, s, 2 × CH_3), 1.37–1.24 (3H, m, NH, CH_2CH$_3$), 0.87 (3H, t, *J* 7.3, CH_2C*H*$_3$); δ_C (100 MHz; $CDCl_3$) 169.7 (C=O), 169.6 (C=O), 169.35 (C=O), 169.3 (C=O), 72.5 (C-2), 70.6 (C-3), 68.4 (C-4), 63.1 (C-6), 56.9 (C-1), 52.1 (C-5), 22.1 (*C*H_2CH$_3$), 20.3 (CH_3), 20.2 (CH_3), 20.1 (CH_3), 20.05 (CH_3), 10.8 (CH_2*C*H$_3$); *m*/*z*(ES$^+$) 741 (2M + Na$^+$), 382 (M + Na$^+$), 360 (M + H$^+$). HRMS (ES$^+$); calcd for $C_{16}H_{26}NO_8$ (M + H$^+$) 360.1658, found 360.1654.

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