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# A SuperQuat glycolate aldol approach to the asymmetric synthesis of hexose monosaccharides

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***Received 15th October 2004, Accepted 16th November 2004***
***First published as an Advance Article on the web 15th December 2004***

A stereoselective two-carbon homologation protocol has been developed and applied to the asymmetric synthesis of the hexose monosaccharides D-galactose, D-fucose, D-idose, D-6-deoxyidose, D-talose and D-6-deoxytalose.

## Introduction

Monosaccharides play an essential part in biochemical processes. The traditional route for the preparation of bespoke monosaccharides typically involves chemical manipulation of pre-existing functionality in common, readily available sugars.[1] Although versatile, this approach is inherently limited to the elaboration of common chiral pool building blocks and typically involves laborious protecting group manipulation. As a result, a wide variety of asymmetric approaches to these valuable synthetic targets have been developed, including the use of asymmetric Diels–Alder reactions,[2] alkene dihydroxylation,[3] chemoenzymatic approaches,[4] diastereoselective additions of nucleophiles to alkoxyaldehydes[5] and chiral Lewis acid catalysis.[6] Perhaps the most general and widely recognised asymmetric approach to a diverse range of monosaccharides is that employed by Sharpless *et al.* for the synthesis of the L-hexoses, utilising asymmetric epoxidation from a four-carbon starting unit.[7]

An alternative strategy for the synthesis of monosaccharides and their derivatives is the use of the aldol reaction,[8,9] as elegantly demonstrated by Kobayashi *et al.* who have combined the catalytic asymmetric aldol reaction with asymmetric dihydroxylation for the asymmetric synthesis of L-fucose.[10] The asymmetric aldol reaction is arguably the most reliable synthetic protocol available to organic chemists, capable of the selective formation of a C–C bond and two stereogenic centres in a predictable fashion, with the relationship between enolate geometry and product configuration generally well defined.[11] The glycolate aldol reaction represents an important sub-class of this powerful transformation that allows the stereocontrolled formation of 1,2-diol units and has found numerous applications in total synthesis and the preparation of natural product fragments.[12] Iterative aldol strategies have been used for the synthesis of molecular fragments containing multiple stereogenic centres,[13] notably for the synthesis of polypropionates,[14] with only limited examples of this approach being directed toward the synthesis of monosaccharides.[15] A recent advance within this area has been reported by MacMillan *et al.*, who have shown that proline can catalyse the direct aldol reaction of α-hydroxyaldehydes enantioselectively,[16] and that subsequent tandem Mukaiyama aldol–cyclisation catalysed by a Lewis acid allows the asymmetric synthesis of a variety of monosaccharides.[17]

Previous investigations from this laboratory have demonstrated that reduction of *N*-acyl 5,5-dimethyloxazolidinones with DIBAL-H allows direct access to highly enantiomerically enriched aldehydes.[18] Our recent studies have also shown that (*S*)-*N*-α-benzyloxyacetyl-4-benzyl-5,5-dimethyloxazolidin-2-one **1** undergoes highly stereoselective boron-mediated *syn*-glycolate aldol reactions, with *O*-silyl protection giving the protected aldols **2**. Subsequent DIBAL-H reduction furnishes the corresponding *N*-1′-hydroxyalkyloxazolidin-2-ones, with base promoted fragmentation ($K_2CO_3$/MeOH) giving the highly functionalised and differentially protected α,β-dihydroxyaldehydes **3** in good yield and with high diastereoselectivity.[19] These aldehydes readily undergo double diastereoselective aldol reactions with glycolate oxazolidinones (*S*)-**1** and (*R*)-**1**, an approach that has previously been used for the synthesis of polyfunctionalised lactones with multiple contiguous stereocentres.[20] The application of this double diastereoselective glycolate aldol methodology for the asymmetric synthesis of a range of monosaccharides is described herein, part of which has been communicated previously.[21] In this approach, each iteration of the aldol protocol accomplishes a stereoselective two-carbon chain extension, furnishing hexose monosaccharides after two iterations of the aldol protocol (Fig. 1).

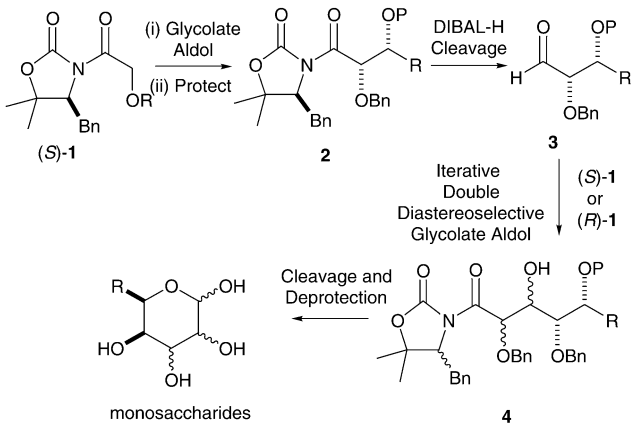



**Fig. 1** Proposed iterative aldol protocol for the asymmetric synthesis of monosaccharides.

## Results and discussion

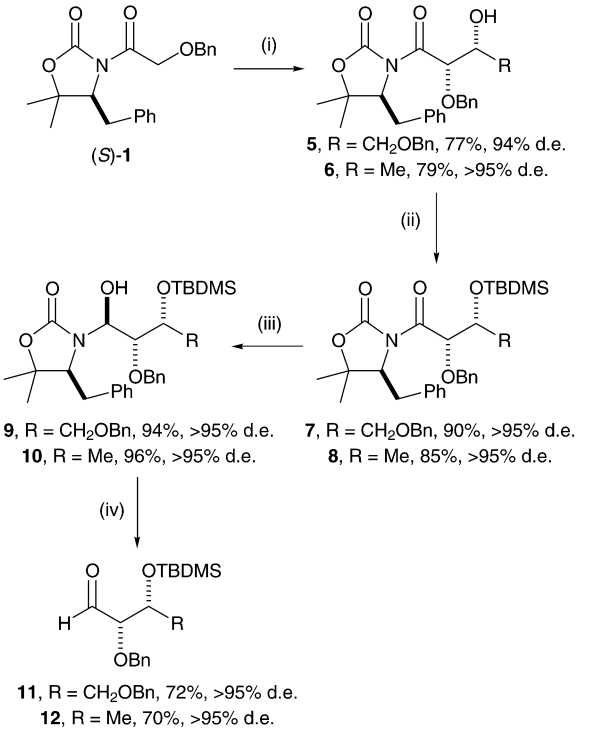
### Asymmetric synthesis of protected tetroses

Initial investigations concentrated upon the asymmetric synthesis of homochiral tetroses, following the reported procedure from the known chiral glycolate oxazolidinone **1**,[22] with acetaldehyde and benzyloxyacetaldehyde used as the two-carbon chain extension components in this reaction manifold. Boron-mediated aldol reactions with the (*Z*)-enolate of glycolate oxazolidinone **1** with both benzyloxyacetaldehyde and acetaldehyde gave the expected *syn*-aldol products (4*S*,2′*S*,3′*R*)-**5** and (4*S*,2′*S*,3′*R*)-**6** in 94% and >95% d.e. respectively, as shown by $^1$H NMR spectroscopic analysis of the crude reaction product mixtures. Chromatographic purification on silica gave *syn*-aldol products (4*S*,2′*S*,3′*R*)-**5** (*J* 3.6 Hz) and (4*S*,2′*S*,3′*R*)-**6** (*J* 3.3 Hz) as single diastereoisomers in 77% and 79% yield

DOI: 10.1039/b415943h

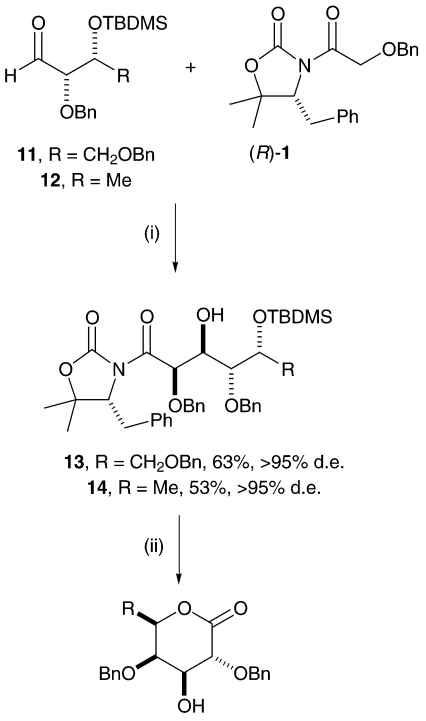
respectively.[23] To facilitate formation of the corresponding *N*-1′-hydroxyoxazolidinones upon reduction,[24] the single hydroxyl functionalities within aldol produts **5** and **6** were protected as their silyl ethers by treatment with TBDMSCl and imidazole, giving *O*-silyl protected (4*S*,2′*S*,3′*R*)-**7** and (4*S*,2′*S*,3′*R*)-**8** in 90% and 85% yield respectively. DIBAL-H reduction of **7** and **8** gave the stable *N*-1′-hydroxy species[25] **9** and **10** as single diastereoisomers in 94% and 96% isolated yield respectively.[26] Fragmentation of *N*-1′-hydroxy species **9** and **10** to the required tetrose was efficiently promoted by treatment with $K_2CO_3$ (1.4 eq.) in MeOH–$H_2O$ (4 : 1) for fifteen minutes, giving the 3-*O*-silyloxy-D-threose derivative (2*S*,3*R*)-**11** and the 3-*O*-silyloxy-4-deoxythreose derivative (2*S*,3*R*)-**12** in good yield and in >95% d.e. in each case (Scheme 1).




**Scheme 1** *Reagents and conditions:* (i). $Et_2BOTf$, $^iPr_2NEt$, benzyloxyacetaldehyde or acetaldehyde, THF, −78 °C; (ii). TBDMSCl, imidazole, DMAP, DMF, rt; (iii). DIBAL-H, DCM, −78 °C; (iv). $K_2CO_3$ (1.4 eq.), MeOH–$H_2O$ (4 : 1), rt.

**Double diastereoselective iterative aldol reactions and monosaccharide synthesis**

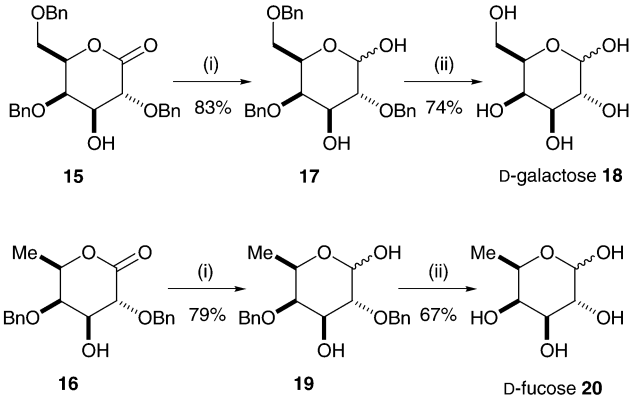
**(i) Matched aldol series – asymmetric synthesis of D-fucose and D-galactose.** Our previous investigations concerned with the double diastereoselective[27] aldol reaction of aldehydes such as **11** and **12** with homochiral glycolate oxazolidinones (*R*)-**1** or (*S*)-**1** have demonstrated that the (*Z*)-boron enolate of the oxazolidinone **1** shows high levels of stereocontrol at both the newly formed α- and β-stereogenic centres of the aldol product.[20] In contrast, aldehydes such as **11** and **12** show high stereocontrol upon the formation of the β-stereogenic centre, but only low control in the formation of the α-stereocentre. Upon their mutual reaction, aldehydes such as **11** and **12** and the boron enolates of homochiral glycolate oxazolidinones (*R*)-**1** or (*S*)-**1** result in matched and mismatched combinations, giving a matched *syn*-aldol configuration, and mismatched *syn*- and *anti*-combinations with the products differing in configuration at the β-centre of the aldol products.[28] With these results in hand, it was expected that the matched combination for the iteration of the aldol protocol with homochiral tetrose derivatives **11** and **12** would be with the (*Z*)-boron enolate of the oxazolidinone (*R*)-**1**. Thus, reaction of (*R*)-*N*-glycolate oxazolidinone **1** and tetroses **11** and **12** furnished in each case the corresponding *syn*-aldol products (4*R*,2′*R*,3′*S*,4′*R*,5′*R*)-**13** and (4*R*,2′*R*,3′*S*,4′*R*,5′*R*)-**14** in >95% d.e., with purification furnishing the desired aldol products **13** and **14** as single diastereoisomers in 63% and 53% yield respectively. Treatment of both **13** and **14** with TBAF in AcOH–THF[29] promoted desilylation of the C(4′)-*O*-TBDMS protected hydroxyl group and concomitant *in situ* cyclisation, giving the lactones (2*R*,3*S*,4*R*,5*R*)-**15** and (2*R*,3*S*,4*R*,5*R*)-**16** in 81% and 73% yield respectively (Scheme 2). Both lactones **15** and **16** showed well dispersed $^1H$ NMR spectra, allowing the relative configurations within them to be readily determined by $^1H$ NMR NOE difference spectroscopy, with the absolute configurations following from the known stereodirecting preference of oxazolidinone auxiliaries in simple glycolate aldol reactions.




**Scheme 2** *Reagents and conditions:* (i). $Et_2BOTf$, $^iPr_2NEt$, THF, −78 °C; (ii). TBAF, AcOH, THF, rt.

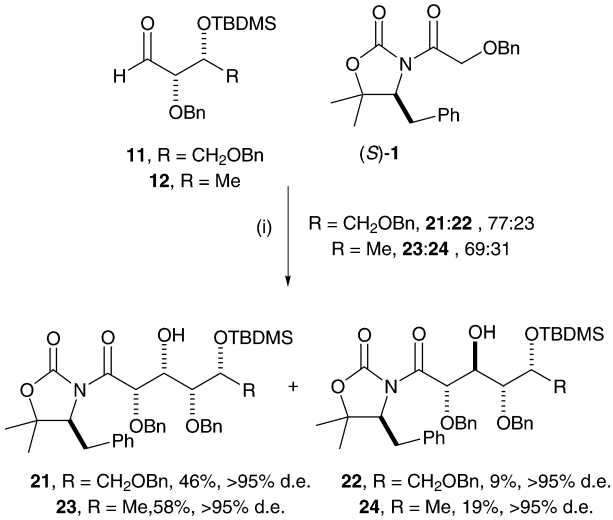
Conclusive proof of the configurational assignment within lactones **15** and **16** was achieved by their selective conversion to the monosaccharides D-galactose and D-fucose respectively *via* reduction and hydrogenolytic *O*-benzyl deprotection. Treatment of lactone **15** with DIBAL in DCM and quenching of the reaction with a minimal quantity of saturated aqueous ammonium chloride solution allowed efficient reduction and product isolation, giving 2,4,6-tris(*O*-benzyl)-D-galactose (2*R*,3*S*,4*R*,5*R*)-**17** in 73% yield as a 67 : 33 mixture of anomers after purification by chromatography. Further treatment of lactol **17** in an EtOAc–EtOH mixture with palladium on carbon under a hydrogen atmosphere furnished D-galactose (2*R*,3*S*,4*R*,5*R*)-**18** in 74% yield as a 67 : 33 mixture of anomers {$[\alpha]_D^{25}$ +79.8 (*c* 0.5, $H_2O$, 10 min), lit.[30] $[\alpha]_D^{25}$ +80.2 (*c* 0.5, $H_2O$, 10 min)} after recrystallisation. The $^1H$ (400 MHz) spectroscopic properties of synthetic **18** were identical to those of a commercially available sample of D-galactose by mixed $^1H$ (400 MHz) spectroscopy and mixed melting point. Repetition of this protocol with lactone **16** similarly gave 2,4-bis(*O*-benzyl)-D-fucose (2*R*,3*S*,4*R*,5*R*)-**19** as an inseparable 67 : 33 mixture of anomers in 79% yield, with debenzylation furnishing D-fucose **20** in 67% yield as a 67 : 33 mixture of anomers {$[\alpha]_D^{25}$ +38.4 (*c* 0.25, $H_2O$, 10 min), lit.[31] $[\alpha]_D^{25}$ +39.1 (*c* 0.25, $H_2O$, 10 min)} after recrystallisation, with

$^1$H (400 MHz) spectroscopic properties identical to those of a commercial sample (Scheme 3).



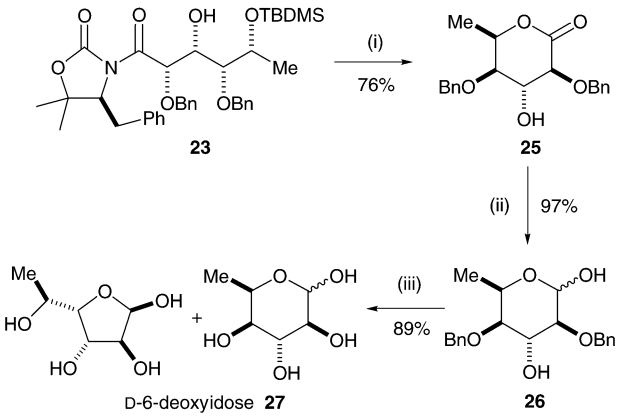

**Scheme 3** *Reagents and conditions*: (i). DIBAL, $CH_2Cl_2$, −78 °C; (ii). Pd/C, EtOH–EtOAc (1 : 5), $H_2$ (1 atm).

**(ii) Mismatched double diastereoselective aldol series – asymmetric synthesis of D-idose, D-6-deoxyidose, D-6-deoxytalose and D-talose.** Having demonstrated the utility of the matched iterative aldol approach for the synthesis of D-galactose and D-fucose, it was predicted that the stereochemically mismatched aldol reaction of tetroses (2*S*,3*R*)-**11** and (2*S*,3*R*)-**12** with the (*Z*)-boron enolate of (*S*)-glycolate **1** would result in a diastereoisomeric mixture of *syn*-(2′*S*,3′*R*,4*S*,4′*R*,5′*R*)- and *anti*-(2′*S*,3′*S*,4*S*,4′*R*,5′*R*)-aldol products. In practice, boron-mediated aldol reaction of (*S*)-**1** with the 3-*O*-silyloxy-D-threose derivative (2*S*,3*R*)-**11** proceeded to completion to give a 77 : 23 mixture of *syn*-(2′*S*,3′*R*,4*S*,4′*R*,5′*R*)-**21** and *anti*-(2′*S*,3′*S*,4*S*,4′*R*,5′*R*)-**22**. Chromatographic purification gave **21** and **22** in 46% and 9% yield respectively, and in >95% d.e. in each case. The 3-*O*-silyloxy-4-deoxythreose derivative (2*S*,3*R*)-**12** similarly gave a separable 69 : 31 mixture of *syn*-(2′*S*,3′*R*,4*S*,4′*R*,5′*R*)-**23** and *anti*-(2′*S*,3′*S*,4*S*,4′*R*,5′*R*)-**24** upon reaction with (*S*)-**1**, giving **23** and **24** in 58% and 19% yield respectively, and in >95% d.e. in each case after purification (Scheme 4).



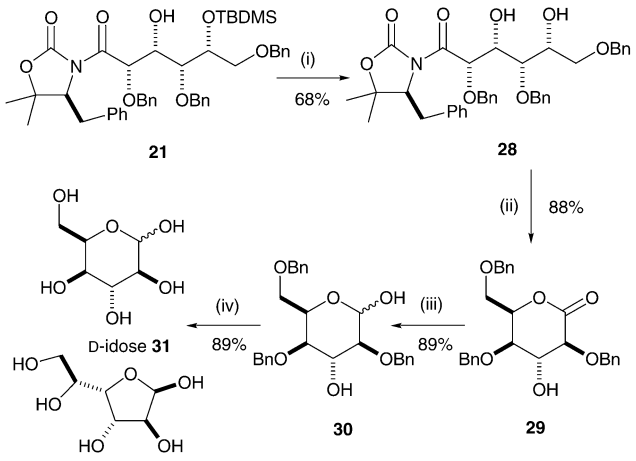

**Scheme 4** *Reagents and conditions:* (i). $Et_2BOTf$, $^iPr_2NEt$, THF, −78 °C.

With homogenous samples of the each aldol product arising from the mismatched aldol protocol in hand, the *syn*-diastereoisomers **21** and **23** were deprotected to their corresponding monosaccharides. Following the standard protocol, AcOH–THF promoted desilylation of aldol product **23** proved efficient, furnishing the desired lactone (2*S*,3*R*,4*R*,5*R*)-**25** in 76% yield, with subsequent DIBAL reduction affording an inseparable 80 : 20 anomeric mixture of 2,4-bis(*O*-benzyl)-D-6-deoxyidose **26** in 97% yield. Hydrogenation furnished D-6-deoxyidose **27** as a mixture of pyranose and furanose species in 88% yield {$[a]_D^{25}$ +12.0 (*c* 1.5, $H_2O$, 24 h), lit.[32] $[a]_D^{25}$ +12.0 (*c* 2.67, $H_2O$)} after trituration with $Et_2O$ (Scheme 5).



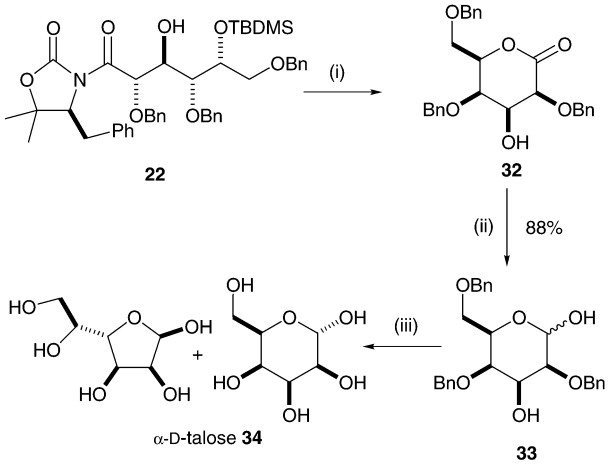

**Scheme 5** *Reagents and conditions:* (i). TBAF, AcOH, THF, rt; (ii). DIBAL, $CH_2Cl_2$, −78 °C; (iii). Pd/C, EtOH–EtOAc (1 : 5), $H_2$ (1 atm).

Attempted deprotection of *syn*-aldol product **21** with AcOH–THF proved unsuccessful, necessitating the development of an alternative desilylation protocol in this series. Treatment of **21** with 1.5 equivalents of HF–pyridine in THF resulted in partial desilylation, although the reaction could not be forced to completion even after addition of 5 equivalents of HF–pyridine. A range of alternative methods for *O*-silyl deprotection were also investigated, with CAN in MeOH,[33] a mixture of formic acid, THF and water,[34] trimethylsilyl triflate and neutral alumina[35] and $(PhCN)_2PdCl_2$ in acetone and water[36] all resulting in less than 10% desilylation. However, treatment of aldol **21** with a 1% solution of iodine in MeOH at 70 °C promoted smooth desilylation,[37] giving the desilylated aldol adduct **28** in 68% yield, which after refluxing in toluene for 16 hours furnished the desired lactone (2*S*,3*R*,4*R*,5*R*)-**29** as a single diastereoisomer in 88% yield. Subsequent reduction of lactone **29** gave 2,4,6-tris(*O*-benzyl)-D-idose (2*S*,3*R*,4*R*,5*R*)-**30** as an inseparable 67 : 33 mixture of anomers in 89% yield, with hydrogenation giving D-idose as a mixture of pyranose and furanose species in 89% yield {$[a]_D^{25}$ +7.7 (*c* 0.3, $H_2O$, 10 min), lit.[38] *ent*-$[a]_D^{25}$ −9.8 (*c* 0.45, $H_2O$, 10 min)} after trituration with $Et_2O$. The $^1$H (400 MHz) spectroscopic properties of synthetic **31** were identical with those of a commercially available sample of L-idose (Scheme 6).



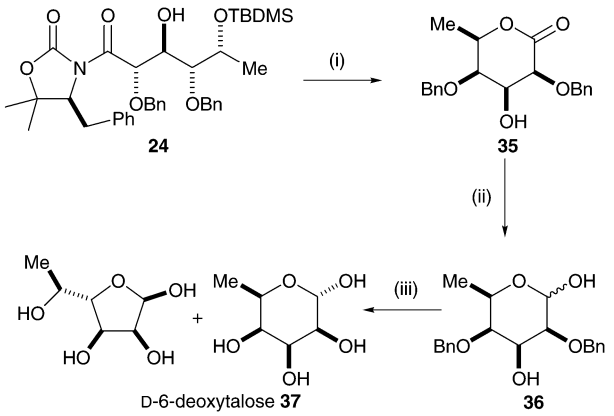

**Scheme 6** *Reagents and conditions:* (i). 1% solution of $I_2$ in MeOH, 70 °C; (ii). toluene, Δ; (iii). DIBAL, $CH_2Cl_2$, −78 °C; (iv). Pd/C, EtOH–EtOAc (1 : 5), $H_2$ (1 atm).

The minor *anti*-diastereoisomers from the mismatched aldol protocol **22** and **24** were next submitted to a similar protocol for the synthesis of D-talose and D-6-deoxytalose respectively. Treatment of aldol **22** with TBAF/AcOH furnished an inseparable 67 : 33 mixture of the desired lactone (2*S*,3*S*,4*R*,5*S*)-**32** and the SuperQuat auxiliary in 50% yield, with DIBAL-H reduction of the mixture giving the desired lactol (2*S*,3*S*,4*R*,5*R*)-**33** as a single diastereoisomer of unknown anomeric configuration, as an inseparable mixture with the SuperQuat auxiliary. Hydrogenolysis of the mixture of the lactol **33** and oxazolidin-2-one, and subsequent trituration of the crude reaction mixture with $Et_2O$, afforded D-talose **34** as a mixture of pyranose and furanose species and facilitated separation from the auxiliary. The $^1H$ (400 MHz) spectrum and specific rotation of synthetic D-talose **34** were consistent with those of commercially available α-D-talose {$[a]_D^{25}$ +19.4 (*c* 0.25, $H_2O$, 24 h), lit.[39] $[a]_D^{25}$ +19.8 (*c* 0.35, $H_2O$, 24 h)} (Scheme 7).




**Scheme 7** *Reagents and conditions:* (i). TBAF, AcOH, THF, rt; (ii). DIBAL, $CH_2Cl_2$, −78 °C; (iii). Pd/C, EtOH–EtOAc (1 : 5), $H_2$ (1 atm).

In a similar fashion, treatment of aldol-**24** with TBAF/AcOH gave an inseparable 58 : 42 mixture of the desired lactone (2*S*,3*S*,4*R*,5*S*)-**35** and the SuperQuat auxiliary in 89% yield, with reduction to the lactol **36** and hydrogenation affording a mixture of D-6-deoxytalose **37** and the oxazolidin-2-one. Trituration of the crude reaction product with $Et_2O$ enabled the isolation of D-6-deoxytalose **37** as a mixture of pyranose and furanose species {$[a]_D^{25}$ +17.7 (*c* 0.35, $H_2O$, 24 h), lit.[40] *ent*-$[a]_D^{25}$ −17.3 (*c* 0.35, $H_2O$, 24 h)} with spectroscopic properties consistent with that of the literature (Scheme 8).




**Scheme 8** *Reagents and conditions:* (i). TBAF, AcOH, THF, rt; (ii). DIBAL, $CH_2Cl_2$, −78 °C; (iii). Pd/C, EtOH–EtOAc (1 : 5), $H_2$ (1 atm).

In conclusion, we have demonstrated that iterative glycolate aldol reactions may be used to prepare a range of monosaccharides. As both (*R*)- and (*S*)-enantiomers of the SuperQuat oxazolidinone auxiliary are used in this strategy, this protocol is equally applicable to the synthesis of the enantiomeric L-series of monosaccharides. Further work is currently being directed toward the extension of this strategy to allow the incorporation of both *syn*- and *anti*-aldol combinations and the use of amino aldehydes in this iterative, three-stage, two-carbon homologation protocol for the asymmetric synthesis of natural product fragments.

## Experimental

### General

All reactions were carried out under nitrogen or argon using standard vacuum line techniques, using glassware that was flame dried and cooled under nitrogen. Reactions described as being performed at −78 °C were cooled by means of an acetone–dry ice bath and those at 0 °C by an ice bath. THF and $Et_2O$ were distilled from sodium–benzophenone ketyl under nitrogen prior to use. $CH_2Cl_2$ was distilled from calcium hydride under nitrogen prior to use. Toluene was distilled from sodium under nitrogen prior to use. *n*-Butyllithium was used as a solution in hexanes and was titrated against diphenylacetic acid prior to use. DIBAL was used as supplied (Aldrich) as a 1 M solution in hexanes. All other reagents were used as supplied without further purification. Column chromatography was performed on silica gel (Kieselgel 60). TLC was performed on Merck aluminium sheets coated with 0.2 mm silica gel 60 $F_{254}$. Plates were visualised either by UV light (254 nm), iodine, ammonium molybdate (7% solution in ethanol) or potassium permanganate (1% in 2% aqueous acetic acid, containing 7% potassium carbonate). Infra-red spectra were recorded as thin films or KBr discs using a Perkin–Elmer PARAGON 1000 FT-IR spectrometer. Selected peaks are reported in $cm^{-1}$. $^1H$ NMR spectra were recorded on Bruker DPX-400 (400 MHz), Bruker DQX-400 (400 MHz) or Bruker AM-500 (500 MHz) spectrometers. Chemical shifts ($\delta_H$) are reported in parts per million (ppm) and are referenced to the residual solvent peak. Coupling constants (*J*) are measured in hertz. Two-dimensional COSY spectra were recorded on Bruker DPX-200 (200 MHz), Bruker AVANCE AV-400 (400 MHz) or Bruker DPX-400 (400 MHz) spectrometers. $^{13}C$ spectra were recorded at 50.31 MHz on the Varian Gemini 200 or the Bruker DPX-200 spectrometers, at 100.62 MHz on the Bruker AVANCE AV-400 or the Bruker DPX-400 spectrometers and at 125.77 MHz on the Bruker AM-500 spectrometer. Chemical shifts ($\delta_C$) are quoted in ppm and referenced using residual solvent peaks. Two-dimensional HMQC and HMBC spectra were recorded on the Bruker DQX-400 (400 MHz) or the Bruker DPX-400 (400 MHz) spectrometers. NOE difference and NOESY spectra were recorded on a Bruker AM-500 spectrometer. $^{19}F$ spectra were recorded on a Bruker DPX-250 (235 MHz). Low resolution mass spectra (*m*/*z*) were recorded on either a VG Masslab 20–250 instrument (CI, $NH_3$) or a Platform instrument (APCI). MALDI spectra were recorded on a Micromass MALDI TOF SPEC 2E spectrometer. Major peaks are listed with intensities quoted as percentages of the base peak. Accurate mass measurements were recorded on a VG Autospec and a Waters 2790-Micromass LCT electrospray ionisation mass spectrometer operating at a resolution of 5000 full width half height. Positive ion spectra were calibrated relative to PEG with tetraoctylammonium bromide as the internal lock mass. Negative ion spectra were calibrated relative to poly-DL-alanine with leucine enkephalin as the internal lock mass. Optical rotations were recorded on a Perkin–Elmer 241 polarimeter, using a path length of 10 cm, in spectroscopic grade solvents (Aldrich), with concentrations (*c*) given in g per 100 $cm^3$, solvent and temperature as recorded. Elemental analyses were obtained by Mrs A. Douglas of the Inorganic Chemistry Analytical Department using an Elementar Vario EL combustion elemental analyser. Melting points were recorded on a Gallenkamp hot stage apparatus and are uncorrected.

**Representative procedure 1 for the aldol addition of *N*-acyloxazolidin-2-one to aldehydes**

$CF_3SO_3H$ (1.2 eq.) was added to $Et_3B$ (1 M in hexanes; 1.2 eq.) at ambient temperature then warmed to 40 °C. After stirring for 10 min, the resultant solution was cooled to 0 °C and added to a solution of *N*-acyloxazolidin-2-one (1.0 eq.) in $CH_2Cl_2$ *via* cannula. After stirring for 10 min, $^{i}Pr_2NEt$ (1.4 eq.) was added and the reaction mixture was stirred for a further 20 min. The reaction was then cooled to −78 °C and freshly distilled aldehyde (1.1 eq.) was added either *via* syringe or *via* cannula as a solution in $CH_2Cl_2$. After stirring for 30 min, the resultant mixture was warmed to 0 °C and stirred for a further hour. The reaction was quenched with MeOH–$H_2O_2$ (1 : 1 v/v), extracted with $CH_2Cl_2$, washed with brine, dried and concentrated *in vacuo*. The crude product was purified by column chromatography.

**Representative procedure 2 for the protection of aldol adducts with TBDMSCl**

Imidazole (5.0 eq.), TBDMSCl (2.5 eq.) and DMAP (0.1 eq.) were added sequentially to a solution of *N*-acyloxazolidin-2-one (1.0 eq.) in DMF at ambient temperature. After stirring for 18 h, the reaction was quenched with MeOH, diluted with $Et_2O$, washed with water, dried and concentrated *in vacuo*. The crude product was purified by column chromatography.

**Representative procedure 3 for the DIBAL reduction of aldol adducts and lactones**

DIBAL (2.0 eq.) was added dropwise to a stirred solution of *N*-acyloxazolidin-2-one (1.0 eq.) in $CH_2Cl_2$ at −78 °C. The reaction was quenched at −78 °C after 20 min with saturated aqueous $NH_4Cl$ solution, warmed to room temperature and stirred for a further 20 min. The resultant mixture was filtered through Celite® (eluent: $CH_2Cl_2$), dried over $MgSO_4$. The organic extracts were concentrated *in vacuo* and purified by column chromatography on silica gel to give the desired product.

**Representative procedure 4 for the fragmentation of aminols with $K_2CO_3$**

$K_2CO_3$ (1.4 eq.) was added to a suspension of aminol (1.0 eq.) in MeOH–$H_2O$ (4 : 1 v/v) at ambient temperature. After stirring for 15 min, the reaction mixture was diluted with $CH_2Cl_2$, washed with water and brine and dried. The crude product was purified by column chromatography.

**Representative procedure 5 for the formation of lactones**

A mixture of TBAF (1 M in THF; 1.5 eq.) and AcOH (1.0 eq.) was added to a stirred solution of *N*-acyloxazolidin-2-one (1.0 eq.) in THF at ambient temperature. After stirring for 16 h, the reaction mixture was diluted with $CH_2Cl_2$, washed with dilute aqueous $NaHCO_3$ and brine, dried and concentrated *in vacuo*. The crude product was purified by column chromatography.

**Representative procedure 6 for the hydrogenolysis of lactols**

10% Pd/C was added to a solution of lactol in EtOAc–EtOH (5 : 1 v/v) at ambient temperature. After stirring under a hydrogen atmosphere for 54 h, the reaction mixture was filtered through Celite® (eluent: MeOH) and concentrated *in vacuo*. The crude product was purified by recrystallisation or column chromatography.

**Preparation of (2′*S*,3′*R*,4*S*)-4-benzyl-3-(2′,4′-bis(benzyloxy)-3-hydroxybutyryl)-5,5-dimethyloxazolidin-2-one 5**

Following **Representative procedure 1**, $CF_3SO_3H$ (0.40 mL, 4.52 mmol), $Et_3B$ (4.52 mL, 4.52 mmol), (*S*)-**1** (1.33 g, 3.77 mmol), $^{i}Pr_2NEt$ (0.92 mL, 5.28 mmol) and benzyloxyacetaldehyde (625 mg, 4.15 mmol) in $CH_2Cl_2$ (50 mL) furnished **5** (1.46 g, 2.90 mmol, 77%) as a white solid after column chromatography. $R_f$ 0.09 [1 : 1 pentane–$Et_2O$]; mp 83–84 °C [30–40 °C petrol–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 1.29 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.35 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.84 [1H, dd, *J* 14.4, 9.5, $CHCH_AH_BPh$], 3.09 [1H, dd, *J* 14.4, 4.0, $CHCH_AH_BPh$], 3.63 [1H, dd, *J* 10.0, 6.7, $CH_AH_BOCH_2Ph$], 3.69 [1H, dd, *J* 10.0, 5.6, $CH_AH_BOCH_2Ph$], 4.20–4.22 [1H, m, C*H*(OH)], 4.41 [1H, d, *J* 11.4, $CHOCH_AH_BPh$], 4.45 [1H, dd, *J* 9.5, 4.0, C*H*$CH_2Ph$], 4.50 [1H, d, *J* 11.8, $CH_2OCH_AH_BPh$], 4.55 [1H, d, *J* 11.4, $CHOCH_AH_BPh$], 4.59 [1H, d, *J* 11.8, $CH_2OCH_AH_BPh$], 5.41 [1H, d, *J* 3.6, C*H*O$CH_2Ph$], 7.21–7.38 [15H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) 22.1, 28.2 [$C(CH_3)_2$], 35.2 [$CHCH_2Ph$], 63.8 [*C*H$CH_2Ph$], 70.8 [*C*H(OH)], 70.9 [$CH_2OCH_2Ph$], 72.9 [$CHOCH_2Ph$], 73.4 [$CH_2OCH_2Ph$], 77.5 [*C*H$OCH_2Ph$], 83.4 [$C(CH_3)_2$], 126.8, 127.7, 128.1 [*p-Ph*], 127.9, 128.3, 128.4, 128.7, 128.8, 129.1 [*m*/*o-Ph*], 136.8, 137.1, 138.0 [*i-Ph*], 152.7 [*C*=O endocyclic], 170.6 [*C*=O exocyclic]; $\nu_{max}$ (thin film, $cm^{-1}$) 3745 [O–H], 1775 [C =O endocyclic], 1707 [C=O exocyclic]; $C_{30}H_{47}NO_6Si$ requires C 71.55, H 6.61, N 2.78%, found C 71.23, H 6.54, N 2.81%; $[\alpha]_D^{25}$ −37.1 (*c* 1.0, $CHCl_3$); *m*/*z* ES+ 504 [10%, $MH^+$], 525 [100%, $MNa^+$].

**Preparation of (2′*S*,3*R*,4*S*)-4-benzyl-3-(2′-benzyloxy-3-hydroxybutyryl)-5,5-dimethyloxazolidin-2-one 6**

Following **Representative procedure 1**, $CF_3SO_3H$ (0.75 mL, 8.5 mmol), $Et_3B$ (8.50 mL, 8.50 mmol), (*S*)-**1** (2.50 g, 7.08 mmol), $^{i}Pr_2NEt$ (1.73 mL, 9.91 mmol) and MeCHO (0.43 mL, 7.79 mmol) in $CH_2Cl_2$ (40 mL) furnished **6** (2.23 g, 5.62 mmol, 79%) as a white solid after column chromatography. $R_f$ 0.11 [1 : 1 pentane–$Et_2O$]; mp 92–94 °C [pentane–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 1.30 [3H, d, *J* 6.4, CH(OH)C$H_3$], 1.38 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.39 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.37 [1H, d, *J* 8.3, CH(O*H*)], 2.86 [1H, dd, *J* 14.4, 4.0, $CHCH_AH_BPh$], 3.06 [1H, dd, *J* 14.4, 9.4, $CHCH_AH_BPh$], 4.05–4.01 [1H, m, C*H*(OH)], 4.43 [1H, d, *J* 11.4, $CHOCH_AH_BPh$], 4.52 [1H, dd, *J* 9.4, 4.0, C*H*$CH_2Ph$], 4.57 [1H, d, *J* 11.4, $CHOCH_AH_BPh$], 5.16 [1H, d, *J* 3.3, C*H*O$CH_2Ph$], 7.21–7.37 [10H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) 19.5 [CH(OH)*C*$H_3$], 22.1, 28.4 [$C(CH_3)_2$], 35.3 [$CHCH_2Ph$], 63.8 [*C*H(OH)], 68.8 [*C*H$CH_2Ph$], 72.9 [$CHOCH_2Ph$], 80.2 [*C*H$OCH_2Ph$], 83.4 [$C(CH_3)_2$], 126.9, 128.1 [*p-Ph*], 128.3, 128.4, 128.7, 129.1 [*m*/*o-Ph*], 136.7, 137.1 [*i-Ph*], 152.8 [*C*=O endocyclic], 170.8 [*C*=O exocyclic]; $\nu_{max}$ (KBr disc, $cm^{-1}$) 1761 [C=O endocyclic], 1715 [C=O exocyclic]; $C_{23}H_{27}NO_5$ requires C 69.50, H 6.85, N 3.52%, found C 69.54, H 6.81, N 3.50%; $[\alpha]_D^{24}$ −89.9 (*c* 1.0, $CHCl_3$); *m*/*z* APCI+ 206 [75%, $SQH^+$], 398 [100%, $MH^+$].

**Preparation of (2′*S*,3′*R*,4*S*)-4-benzyl-3-(2′,4′-bis(benzyloxy)-3′-(*tert*-butyldimethylsilanyloxy)butyryl)-5,5-dimethyloxazolidin-2-one 7**

Following **Representative procedure 2**, **5** (1.57 g, 3.12 mmol), TBDMSCl (1.18 g, 7.80 mmol), imidazole (1.06 g, 15.6 mmol) and DMAP (40 mg, 0.3 mmol) in DMF (10 mL) furnished **7** (1.73 g, 2.80 mmol, 90%) as a pale yellow oil after column chromatography. $R_f$ 0.22 [10 : 1 pentane–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 0.08 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.09 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.89 [9H, s, $SiC(CH_3)_3$], 1.02 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.22 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.59 [1H, dd, *J* 14.5, 10.3, $CHCH_AH_BPh$], 3.00 [1H, dd, *J* 14.5, 2.8, $CHCH_AH_BPh$], 3.52 [1H, dd, *J* 10.7, 5.2, $CH_AH_BOCH_2Ph$], 3.76 [1H, dd, *J* 10.7, 6.2, $CH_AH_BOCH_2Ph$], 4.19 [1H, dd, *J* 10.3, 2.8, C*H*$CH_2Ph$], 4.27–4.31 [1H, m, C*H*(OTBDMS)], 4.41–4.53 [2H, ABq, *J* 11.4, $CH_2OCH_2Ph$], 4.55–4.66 [2H, ABq, *J* 11.8, $CHOCH_2Ph$], 5.47 [1H, d, *J* 6.0, C*H*O$CH_2Ph$], 7.20–7.38 [15H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) −4.9, −4.6 [$Si(CH_3)_2$], 18.2 [$SiC(CH_3)_3$], 22.4, 28.0 [$C(CH_3)_2$], 25.8 [$SiC(CH_3)_3$], 34.7 [$CHCH_2Ph$], 63.9 [*C*H$CH_2Ph$], 71.7 [$CH_2OCH_2Ph$], 72.4 [*C*H(OTBDMS)], 73.2, 73.3 [$CHOCH_2Ph$ and $CH_2OCH_2Ph$], 78.6 [*C*H$OCH_2Ph$], 82.4 [$C(CH_3)_2$], 126.6,

127.5, 127.8 [*p-Ph*], 128.0, 128.2, 128.3, 128.4, 128.6, 129.0 [*m/o-Ph*], 137.2, 137.8, 138.0 [*i-Ph*], 152.4 [*C*=O endocyclic], 171.4 [*C*=O exocyclic]; $\nu_{max}$ (thin film, $cm^{-1}$) 1776 [C=O endocyclic], 1704 [C=O exocyclic]; HRMS $C_{36}H_{47}NO_6NaSi$ [$MNa^+$] requires 640.3070, found 640.3055; $[\alpha]_D^{24}$ +2.0 (*c* 0.65, $CHCl_3$); *m/z* ES+ 618 [30%, $MH^+$], 634 [100%, $MNH_4^+$], 663 [100%, $MNa_2^+$].

**Preparation of (2′*S*,3′*R*,4*S*)-4-benzyl-3-[2′-benzyloxy-3′-(*tert*-butyldimethylsilanyloxy)butyryl]-5,5-dimethyloxazolidin-2-one 8**

Following **Representative procedure 7**, **6** (2.00 g, 3.91 mmol), TBDMSCl (1.48 g, 9.78 mmol), imidazole (1.33 g,19.55 mmol) and DMAP (47 mg, 0.39 mmol) in DMF (10 mL) furnished **8** (1.70 g, 3.33 mmol, 85%) as a white solid after flash column chromatography. $R_f$ 0.15 [10 : 1 pentane–$Et_2O$]; mp 62–63 °C [pentane–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 0.05 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.07 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.88 [9H, s, $SiC(CH_3)_3$], 1.20 [3H, d, *J* 10.2, $CHCH_3$], 1.34 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.36 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.77 [1H, dd, *J* 14.5, 9.7, $CHCH_AH_BPh$], 2.97 [1H, dd, *J* 14.5, 3.4, $CHCH_AH_BPh$], 4.13–4.16 [1H, m, C*H*(OTBDMS)], 4.43 [1H, dd, *J* 9.7, 3.4, $CHCH_2Ph$], 4.54 [2H, s, $CHOCH_2Ph$], 5.42 [1H, d, *J* 5.4, $CHOCH_2Ph$], 7.20–7.38 [10H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) −4.7 [$Si(CH_3)_2$], 18.3 [$SiC(CH_3)_3$], 19.0, 22.2 [$C(CH_3)_2$], 25.9 [$SiC(CH_3)_3$], 28.4 [$CHCH_3$], 35.1 [$CHCH_2Ph$], 64.1 [$CHCH_2Ph$], 70.0 [$CHOCH_2Ph$], 73.1 [$CHOCH_2Ph$], 79.5 [*C*H(OTBDMS)], 82.6 [$C(CH_3)_2$], 126.7, 127.8 [*p-Ph*], 128.3, 128.4, 128.6, 129.1 [*m/o-Ph*], 137.0, 137.7 [*i-Ph*], 152.3 [*C*=O endocyclic], 171.4 [*C*=O exocyclic]; $\nu_{max}$ (KBr disc, $cm^{-1}$) 1778 [C=O endocyclic], 1702 [C=O exocyclic]; $C_{29}H_{41}NO_5Si$ requires C 68.07, H 8.08, N 2.74%, found C 68.28, H 8.08, N 2.69%; $[\alpha]_D^{23}$ −10.1 (*c* 1.1, $CHCl_3$); *m/z* APCI+ 206 [70%, $SQH^+$], 380 [100%, $MH^+$ − OTBDMS], 512 [35%, $MH^+$].

**Preparation of (2′*S*,3′*R*,4*S*)-benzyl-3-[2′,4′-bis(benzyloxy)-3′-(*tert*-butyldimethylsilanyloxy)-1′-hydroxybutyl]-5,5-dimethyloxazolidin-2-one 9**

Following **Representative procedure 3**, DIBAL (5.5 mL, 5.51 mmol) and **7** (1.70 g, 2.75 mmol) in $CH_2Cl_2$ (50 mL) furnished **9** (1.59 g, 2.58 mmol, 94%) as a very viscous oil. $\delta_H$ (400 MHz, $CDCl_3$) 0.08 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.09 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.89 [9H, s, $SiC(CH_3)_3$], 1.07 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.26 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.67 [1H, dd, *J* 14.8, 10.1, $CHCH_AH_BPh$], 3.19 [1H, dd, *J* 14.8, 4.5, $CHCH_AH_BPh$], 3.54 [1H, dd, *J* 9.6, 6.6, $CH_AH_BOCH_2Ph$], 3.66 [1H, dd, *J* 9.6, 4.5, $CH_AH_BOCH_2Ph$], 4.01 [1H, dd, *J* 10.1, 4.5, $CHCH_2Ph$], 4.18–4.21 [1H, m, C*H*(OTBDMS)], 4.24 [1H, dd, *J* 8.8, 3.4, $CHOCH_2Ph$], 4.31 [1H, br s, O*H*], 4.49 [2H, ABq, *J* 12.0, $CH_2OCH_2Ph$], 4.70 [2H, ABq, *J* 11.8, $CHOCH_2Ph$], 4.97 [1H, d, *J* 8.7, C*H*(OH)], 7.06–7.36 [15H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) −4.8, −4.6 [$Si(CH_3)_2$], 18.0 [$SiC(CH_3)_3$], 22.1, 27.6 [$C(CH_3)_2$], 25.8 [$SiC(CH_3)_3$], 35.4 [$CHCH_2Ph$], 65.4 [$CHCH_2Ph$], 70.9 [$CH_2OCH_2Ph$], 71.4 [*C*H(OTBDMS)], 73.2, 73.3 [2 × $OCH_2Ph$], 76.8 [$CHOCH_2Ph$], 79.2 [*C*H(OH)], 81.6 [$C(CH_3)_2$], 126. 7, 127.6, 127.7 [*p-Ph*], 127.8, 128.3, 128.4, 128.6, 128.8 [*m/o-Ph*], 136.8, 138.1, 138.1 [*i-Ph*], 157.1 [*C*=O endocyclic]; $\nu_{max}$ (thin film, $cm^{-1}$) 3401 [O–H], 1728 [C=O]; HRMS $C_{37}H_{46}N_2O_6Si$ [$MNH_4^+$] requires 642.3125, found 642.3136; $[\alpha]_D^{24}$ +1.25 (*c* 1.6, $CHCl_3$); *m/z* ES+ 607 [100%, $MH^+ - H_2O$], 642 [100%, $MNH_4^+$].

**Preparation of (2′*S*,3′*R*,4*S*)-4-benzyl-3-[2′-benzyloxy-3′-(*tert*-butyldimethylsilanyloxy)-1′-hydroxypropyl]-5,5-dimethyloxazolidin-2-one 10**

Following **Representative procedure 3**, DIBAL (6.7 mL, 6.66 mmol) and **8** (1.70 g, 3.33 mmol) in $CH_2Cl_2$ (40 mL) furnished **10** (1.65 g, 3.21 mmol, 96%) as a very viscous oil. $\delta_H$ (400 MHz, $CDCl_3$) 0.07 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.08 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.88 [9H, s, $SiC(CH_3)_3$], 1.09 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.23 [3H, d, *J* 6.3, $CHCH_3$], 1.27 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.72 [1H, dd, *J* 14.8, 9.9, $CHCH_AH_BPh$], 3.24 [1H, dd, *J* 14.8, 4.6, $CHCH_AH_BPh$], 4.00 [1H, dd, *J* 9.9, 4.6, $CHCH_2Ph$], 4.08–4.15 [2H, m, C*H*(OTBDMS) and CH(O*H*)], 4.48 [1H, d, *J* 4.9, C*H*(OH)], 4.69 [2H, s, $CHOCH_2Ph$], 5.05 [1H, dd, *J* 8.3, 4.9, $CHOCH_2Ph$], 7.09–7.37 [10H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) −4.8, −5.3 [$Si(CH_3)_2$], 17.4 [$CHCH_3$], 17.9 [$SiC(CH_3)_3$], 22.1, 27.6 [$C(CH_3)_2$], 25.7 [$SiC(CH_3)_3$], 35.5 [$CHCH_2Ph$], 65.2 [$CHCH_2Ph$], 68.6 [*C*H(OTBDMS)], 73.1 [$CHOCH_2Ph$], 77.8 [$CHOCH_2Ph$], 79.2 [*C*H(OH)], 81.2 [$C(CH_3)_2$], 126.6, 127.9 [*p-Ph*], 127.9, 128.5, 128.6, 128.8 [*m/o-Ph*], 137.0, 138.0 [*i-Ph*], 157.0 [*C*=O endocyclic]; $\nu_{max}$ (KBr disc, $cm^{-1}$) 3328 [O–H broad], 1725 [C=O]; $C_{29}H_{43}NO_5Si$ requires C 67.80, H 8.44, N 2.73%, found C 67.84, H 8.49, N 2.91%; $[\alpha]_D^{20}$ +9.1 (*c* 1.0, $CHCl_3$); *m/z* ES+ 496 [35%, $MH^+ - H_2O$], 536 [100%, $MNa^+$].

**Preparation of (2*S*,3*R*)-2,4-bis(benzyloxy)-3-(*tert*-butyldimethylsilanyloxy)butrylaldehyde 11**

Following **Representative procedure 4**, **9** (1.60 g, 2.58 mmol) and $K_2CO_3$ (500 mg, 3.62 mmol) in MeOH–$H_2O$ (4 : 1 v/v; 50 mL) furnished **11** (764 mg, 1.84 mmol, 72%) as a clear colourless oil. $\delta_H$ (400 MHz, $CDCl_3$) 0.01 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.03 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.86 [9H, s, $SiC(CH_3)_3$], 3.53 [1H, dd, *J* 9.8, 4.9, $CH_AH_BOCH_2Ph$], 3.61 [1H, dd, *J* 9.8, 5.6, $CH_AH_BOCH_2Ph$], 3.87 [1H, dd, *J* 4.5, 1.3, $CHOCH_2Ph$], 4.15–4.19 [1H, m, C*H*(OTBDMS)], 4.48 [2H, q, *J* 12.2, $CH_2OCH_2Ph$], 4.56 [1H, d, *J* 12.0, $CHOCH_AH_BPh$], 4.76 [1H, d, *J* 12.0, $CHOCH_AH_BPh$], 7.27–7.37 [10H, m, Ph*H*], 9.75 [1H, d, *J* 1.3, C*H*O]; $\delta_C$ (100 MHz, $CDCl_3$) −4.8, −4.6 [$Si(CH_3)_2$], 18.0 [$SiC(CH_3)_3$], 25.7 [$SiC(CH_3)_3$], 70.4 [$CH_2OCH_2Ph$], 72.5 [*C*H(OTBDMS)], 73.1, 73.3 [2 × $OCH_2Ph$], 84.1 [$CHOCH_2Ph$], 127.6, 128.0, 128.1, 128.3, 128.5 [*p*- and *m/o-Ph*], 137.4, 137.9 [*i-Ph*], 202.7 [*C*HO]; $\nu_{max}$ (thin film, $cm^{-1}$) 1733 [C=O]; HRMS $C_{24}H_{35}O_4Si$ requires 415.2305, found 415.2311; $[\alpha]_D^{24}$ −18.5 (*c* 1.05, $CHCl_3$); *m/z* ES+ 415 [100%, $MH^+$].

**Preparation of (2*S*,3*R*)-2-benzyloxy-3-(*tert*-butyldimethylsilanyloxy)butyraldehyde 12**

Following **Representative procedure 4**, **10** (1.60 g, 3.12 mmol) and $K_2CO_3$ (603 mg, 4.37 mmol) in MeOH–$H_2O$ (4 : 1 v/v; 50 mL) furnished **12** (672 mg, 2.18 mmol, 70%) as a clear colourless oil and the auxiliary (556 mg, 2.71 mmol, 87%) as a white solid after column chromatography. $\delta_H$ (400 MHz, $CDCl_3$) 0.04 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.06 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.87 [9H, s, $SiC(CH_3)_3$], 1.21 [3H, d, *J* 6.3, $CHCH_3$], 3.73 [1H, dd, *J* 5.0, 1.4, $CHOCH_2Ph$], 4.12–4.18 [1H, m, C*H*(OTBDMS)], 4.54 [1H, d, *J* 12.0, $CHOCH_AH_BPh$], 4.77 [1H, d, *J* 12.0, $CHOCH_AH_BPh$], 7.27–7.36 [5H, m, Ph*H*], 9.77 [1H, d, *J* 1.4, C*H*O]; $\delta_C$ (100 MHz, $CDCl_3$) −4.6 [$Si(CH_3)_2$], 18.0 [$SiC(CH_3)_3$], 19.5 [$CHCH_3$], 25.7 [$SiC(CH_3)_3$], 69.1 [$CHOCH_2Ph$], 72.8 [$CHOCH_2Ph$], 86.4 [*C*H(OTBDMS)], 128.0 [*p-Ph*], 128.0, 128.4 [*m/o-Ph*], 137.4 [*i-Ph*], 203.6 [*C*HO]; $\nu_{max}$ (thin film, $cm^{-1}$) 1735 [C=O]; HRMS $C_{17}H_{29}O_3Si$ [$MH^+$] requires 309.1886, found 309.1899; $[\alpha]_D^{25}$ −48.4 (*c* 0.5, $CHCl_3$); *m/z* ES+ 279 [40%, $MH^+$ − CHO], 291 [35%, $MH^+ - H_2O$], 309 [100%, $MH^+$], 331 [15%, $MNa^+$].

**Preparation of (2′*R*,3′*S*,4*R*,4′*R*,5′*R*)-4-benzyl-3-[2′,4′,6-tris(benzyloxy)-5′-(*tert*-butyldimethylsilanyloxy)-3′-hydroxyhexanoyl]-5,5-dimethyloxazolidin-2-one 13**

Following **Representative procedure 1**, $CF_3SO_3H$ (0.16 mL, 1.87 mmol), $Et_3B$ (1.90 mL, 1.87 mmol), (*R*)-**1** (550 mg, 1.56 mmol), $^iPr_2NEt$ (0.38 mL, 2.18 mmol) and **11** (700 mg, 1.69 mmol) in $CH_2Cl_2$ (30 mL) furnished **13** (751 mg, 0.98 mmol, 63%) as a clear colourless oil after column chromatography. $R_f$ 0.09 [5 : 1 pentane–$Et_2O$; double eluted];

$\delta_H$ (400 MHz, $CDCl_3$) 0.04 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.05 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.88 [9H, s, $SiC(CH_3)_3$], 1.34 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.37 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.89 [1H, dd, *J* 14.4, 9.6, $CHCH_AH_BPh$], 1.37 [1H, d, *J* 7.1, CH(O*H*)], 3.17 [1H, dd, *J* 14.4, 3.7, $CHCH_AH_BPh$], 3.62 [1H, dd, *J* 9.6, 6.5, $CH_AH_BOCH_2Ph$], 3.73 [1H, dd, *J* 9.6, 4.9, $CH_AH_BOCH_2Ph$], 3.83 [1H, dd, *J* 9.2, 3.0, C*H*OCH$_2$Ph.CH(OTBDMS)], 4.18–4.22 [3H, m, C*H*(OH), C*H*(OTBDMS) and 1 × $CHOCH_2Ph$], 4.49–4.59 [6H, m, C*H*CH$_2$Ph and 5 × $CHOCH_2Ph$], 5.51 [1H, d, *J* 2.0, CO.C*H*OCH$_2$Ph], 7.21–7.40 [20H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) −4.8, −4.6 [$Si(CH_3)_2$], 18.1 [$SiC(CH_3)_3$], 22.1, 28.2 [$C(CH_3)_2$], 25.9 [$SiC(CH_3)_3$], 35.3 [CH*C*H$_2$Ph], 64.1 [*C*HCH$_2$Ph], 71.2 [*C*H$_2$OCH$_2$Ph], 71.4, 71.5 [*C*H(OTBDMS) and *C*H(OH)], 72.3, 72.5, 73.2 [$CH_2OCH_2Ph$ and 2 × $CHOCH_2Ph$], 77.4 [*C*HOCH$_2$Ph.CH(OTBDMS)], 78.0 [CO.*C*HOCH$_2$Ph], 83.3 [$C(CH_3)_2$], 126.8, 127.4, 127.5, 127.8 [*p-Ph*], 127.3, 127.6, 128.3, 128.5, 128.6, 128.7, 128.0, 129.1 [*m/o-Ph*], 137.0, 137.4, 138.2, 138.7 [*i-Ph*], 152.4 [*C*=O endocyclic], 170.9 [*C*=O exocyclic]; $\nu_{max}$ (thin film, $cm^{-1}$) 3455 [O–H], 1778 [C=O endocyclic], 1708 [C=O endocyclic]; $C_{45}H_{57}NO_8Si$ requires C 70.37, H 7.48, N 1.82%, found C 70.26, H 7.53, N 1.81%; $[\alpha]_D^{26}$ +32.9 (*c* 0.65, $CHCl_3$); *m/z* LD+ (MALDI) 790, 791, 792 [100%, 50%, 20%, $MNa^+$].

### Preparation of (2′*R*,3′*S*,4*R*,4′*R*,5′*R*)-4-benzyl-3-[2′,4′-bis(benzyloxy)-5′-(*tert*-butyldimethylsilanyloxy)-3′-hydroxypentanoyl]-5,5-dimethyloxazolidin-2-one 14

Following **Representative procedure 1**, $CF_3SO_3H$ (0.12 mL, 1.36 mmol), $Et_3B$ (1.36 mL, 1.36 mmol), (*R*)-**1** (400 mg, 1.13 mmol), $^iPr_2NEt$ (0.28 mL, 1.58 mmol) and **12** (375 mg, 1.22 mmol) in $CH_2Cl_2$ (15 mL) furnished **14** (395 mg, 0.60 mmol, 53%) as a pale yellow oil after column chromatography. $R_f$ 0.08 [1 : 1 pentane–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 0.02 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.03 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.86 [9H, s, $SiC(CH_3)_3$], 1.35 [3H, d, *J* 5.1, $CHCH_3$], 1.37 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.40 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.86 [1H, dd, *J* 14.4, 9.8, $CHCH_AH_BPh$], 3.18 [1H, dd, *J* 14.4, 3.4, $CHCH_AH_BPh$], 3.68 [1H, dd, *J* 9.0, 3.6, C*H*OCH$_2$Ph.CH(OTBDMS)], 4.09–4.12 [1H, m, C*H*(OTBDMS)], 4.25–4.29 [1H, m, C*H*CH$_2$Ph], 4.28 [1H, d, *J* 11.2, $CHOCH_AH_BPh$], 4.49–4.55 [3H, m, C*H*(OH) and $CHOCH_2Ph$], 4.57 [1H, d, *J* 11.3, $CHOCH_AH_BPh$], 5.50 [1H, d, *J* 2.2, CO.C*H*OCH$_2$Ph], 7.20–7.39 [15H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) −4.7, −4.6 [$Si(CH_3)_2$], 17.6 [$CHCH_3$], 18.0 [$SiC(CH_3)_3$], 22.1, 28.2 [$C(CH_3)_2$], 25.8 [$SiC(CH_3)_3$], 35.2 [CH*C*H$_2$Ph], 64.2 [*C*H(OH)], 69.0 [*C*H(OTBDMS)], 71.3 [*C*HCH$_2$Ph], 72.4, 72.5 [2 × $CHOCH_2Ph$], 78.2, 78.3 [2 × *C*HOCH$_2$Ph], 83.3 [$C(CH_3)_2$], 126.7, 127.7, 127.4 [*p-Ph*], 128.3, 128.5, 128.6, 128.7, 129.0, 129.1 [*m/o-Ph*], 137.1, 137.6, 1386, [*i-Ph*], 152.5 [*C*=O endocyclic], 171.0 [*C*=O exocyclic]; $\nu_{max}$ (thin film, $cm^{-1}$) 3460 [O–H], 1778 [C=O endocyclic], 1712 [C=O exocyclic]; $C_{38}H_{51}NO_7Si$ requires C 68.95, H 7.77, N 2.12%, found C 68.67, H 7.70, N 2.27%; $[\alpha]_D^{26}$ +27.6 (*c* 1.15, $CHCl_3$); *m/z* LD+ (MALDI) 684, 685, 686 [100%, 40%, 15%, $MNa^+$], 700, 701, 702 [60%, 25%, 10%, $MK^+$].

### Preparation of (2*R*,3*S*,4*R*,5*R*)-2,4-bis(benzyloxy)-5-benzyloxymethyl-3-hydroxytetrahydropyran-2-one 15

Following **Representative procedure 5**, **13** (130 mg, 0.17 mmol), TBAF (0.26 mL, 0.26 mmol) and AcOH (0.01 mL, 0.17 mmol) in THF (7 mL) furnished **15** (62 mg, 0.14 mmol, 81%) as a pale yellow oil after column chromatography. $R_f$ 0.14 [1 : 1 pentane–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 2.55 [1H, d, *J* 2.3, CH(O*H*)], 3.67–3.75 [2H, m, C$H_2$OCH$_2$Ph], 4.08 [1H, d, *J* 9.8, C*H*(OH)], 4.16 [1H, t, *J* 2.3, C*H*(OCH$_2$Ph).CHCH$_2$OCH$_2$Ph], 4.31 [1H, d, *J* 9.8, CO.C*H*OCH$_2$Ph], 4.43–4.46 [1H, m, C*H*CH$_2$OCH$_2$Ph], 4.47–4.56 [2H, ABq, *J* 11.7, $CH_2OCH_2Ph$], 4.61 [1H, d, *J* 11.2, CH(O$CH_AH_B$Ph).CH$_2$OCH$_2$Ph], 4.71 [1H, d, *J* 11.2, CO.CHO$CH_CH_D$Ph], 4.85 [1H, d, *J* 11.2, $CHOCH_AH_BPh.CH_2OCH_2Ph$], 5.19 [1H, d, *J* 11.2, CO.CHO$CH_CH_D$Ph], 7.21–7.43 [15H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) 67.5 [$CH_2OCH_2Ph$], 72.0 [*C*H(OH)], 73.6 [$CH_2OCH_2Ph$], 74.0 [*C*H(OCH$_2$Ph).CHCH$_2$OCH$_2$Ph], 74.7 [CH(O*C*H$_2$Ph).CHCH$_2$OCH$_2$Ph], 75.1 [CO.CHO*C*H$_2$Ph], 76.7 [CO.*C*HOCH$_2$Ph], 77.8 [CH(OCH$_2$Ph).*C*HCH$_2$OCH$_2$Ph], 127.8, 127.9, 128.0, 128.3, 128.4, 128.5, 128.6, 128.7 [*p-* and *m/o-Ph*], 137.1, 137.3, 137.7 [*i-Ph*], 169.7 [*C*=O]; $\nu_{max}$ (thin film, $cm^{-1}$) 3457 [O–H], 1743 [C=O]; $C_{27}H_{28}O_6$ requires C 72.30, H 6.29%, found C 72.33, H 6.30%; $[\alpha]_D^{26}$ +41.5 (*c* 0.55, $CHCl_3$); *m/z* ES+ 467 [60%, $MNH_4^+$], 471 [100%, $MNa^+$].

### Preparation of (2*R*,3*S*,4*R*,5*R*)-2,4-bis(benzyloxy)-3-hydroxy-5-methyltetrahydropyran-2-one 16

Following **Representative procedure 5**, **14** (200 mg, 0.30 mmol), TBAF (0.45 mL, 0.45 mmol) and AcOH (0.02 mL, 0.30 mmol) in THF (10 mL) furnished **16** (75 mg, 0.22 mmol, 73%) as a white solid after column chromatography. $R_f$ 0.25 [2 : 1 pentane–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 1.37 [3H, d, *J* 6.5, $CHCH_3$], 2.51 [1H, br s, O*H*], 3.83 [1H, t, *J* 2.2, C*H*OCH$_2$Ph.CHCH$_3$], 4.09 [1H, dd, *J* 10.0, 2.5, C*H*(OH)], 4.31 [1H, d, *J* 10.0, CO.C*H*OCH$_2$Ph], 4.42 [1H, qd, *J* 6.5, 1.9, C*H*CH$_3$], 4.68 [1H, d, *J* 11.4, $CHOCH_AH_BPh$], 4.71 [1H, d, *J* 11.2, $CHOCH_CH_DPh$], 4.89 [1H, d, *J* 11.4, $CHOCH_AH_BPh$], 5.22 [1H, d, *J* 11.2, $CHOCH_CH_DPh$], 7.16–7.44 [10H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) 17.0 [CH*C*H$_3$], 72.4 [*C*H(OH)], 74.7, 75.2 [2 × $CHOCH_2Ph$], 76.2 [*C*HCH$_3$], 76.3 [CO.*C*HCH$_2$Ph], 76.7 [*C*HOCH$_2$Ph.CHCH$_3$], 128.0, 128.1, 128.3, 128.6, 128.8, 129.1 [*p-* and *m/o-Ph*], 137.2, 137.6 [*i-Ph*], 170.4 [*C*=O]; $\nu_{max}$ (thin film, $cm^{-1}$) 3443 [O–H], 1732 [C=O]; HRMS $C_{20}H_{23}O_5Na$ [$MNa^+$] requires 343.1544, found 343.1545; $[\alpha]_D^{25}$ +130.2 (*c* 2.5, $CHCl_3$); *m/z* ES+ 365 [90%, $MNa^+$].

### Preparation of 2,4,6-tris(*O*-benzyl)-D-galactose 17

Following **Representative procedure 3**, DIBAL (0.50 mL, 0.50 mmol), **15** (114 mg, 0.25 mmol) in $CH_2Cl_2$ (5 mL) furnished **17**[41] (89 mg, 83%, 2 : 1 mixture of anomers) as a white solid after column chromatography. $R_f$ 0.12 and 0.05 [1 : 1 30–40 °C petrol–$Et_2O$]; mp 104–106 °C [MeOH–$Et_2O$] {lit.[41b] mp 126–128 °C [MeOH]}; $\delta_H$ (400 MHz, $CDCl_3$) 2.30 [1H, d, *J* 5.2, $C^3HO$*H* (major)], 2.33 [1H, d, *J* 5.0, $C^3HO$*H* (minor)], 3.24 [1H, s, $C^1HO$*H* (major)], 3.48–3.67 [6H, m, $CHCH_2OCH_2Ph$ (major and minor), $C^3HOH$ (minor) and $C^4HOCH_2Ph$ (major)], 3.79 [1H, dd, *J* 3.5, 9.9, $C^2HOCH_2Ph$ (major)], 3.83 [1H, d, *J* 3.2, $C^2HOCH_2Ph$ (minor)], 3.89 [1H, dd, *J* 0.9, 3.1, $C^4HOCH_2Ph$ (minor)], 4.03–4.07 [1H, m, $C^3HOH$], 4.21 [1H, dt, *J* 0.7, 6.3, $C^5HCH_2OCH_2Ph$ (major)], 4.43 [1H, d, *J* 11.9, $CHOCH_AH_BPh$ (minor)], 4.44 [1H, d, *J* 12.0, $CHOCH_AH_BPh$ (major)], 4.52 [1H, d, *J* 12.0, $CHOCH_AH_BPh$ (major)], 4.61–4.73 [7H, m, $C^5HCH_2OCH_2Ph$ (minor), $CH_2OCH_2Ph$ (major), $CHOCH_CH_DPh$ (major) $CH_2OCH_2Ph$ (minor) and $CHOCH_AH_BPh$ (minor)], 4.98 [1H, d, *J* 11.5, $CHOCH_CH_DPh$ (minor)], 4.79 [1H, d, *J* 11.6, $CHOCH_CH_DPh$ (major)], 4.80 [1H, d, *J* 11.5, $CHOCH_CH_DPh$ (minor)], 5.30 [2H, br s, $C^1HOH$ (major and minor)], 7.27–7.41 [30H, m, Ph*H* (major and minor)]; $\delta_C$ (100 MHz, $CDCl_3$) 68.9 [$CH_2OCH_2Ph$ (minor)], 69.0 [$CH_2OCH_2Ph$ (major)], 69.2 [$C^5HCH_2OCH_2Ph$ (major)], 69.9 [$C^3H$(OH) (major)], 72.8 [$CH_2OCH_2Ph$ (major and minor)], 73.5, 75.0 [$CHOCH_2Ph$ (major)], 73.5, 74.6 [$CHOCH_2Ph$ (minor)], 73.7, 73.9 [$C^5HCH_2OCH_2Ph$ (minor) and $C^3H$(OH) (minor)], 75.60 [$C^2HOCH_2Ph$ (minor)], 76.6 [$C^4HOCH_2Ph$ (major)], 77.4 [$C^2HOCH_2Ph$ (major)], 80.8 [$C^4HOCH_2Ph$ (minor)], 91.1 [$C^1H$(OH) (major)], 97.6 [$C^1H$(OH) (minor)], 127.9, 128.1, 128.2, 128.4, 128.6 [*p-* and *m/o-Ph* (major)], 127.7, 127.8, 128.2, 128.4, 128.5 [*p-* and *m/o-Ph* (minor)], 137.6, 137.7, 137.8, 138.3, 138.3 [*i-Ph* (major and minor)]; $\nu_{max}$ (KBr disc, $cm^{-1}$) 3435 [O–H], 1105, 1027, 1167 [C–O]; HRMS $C_{28}H_{31}O_8$ [$MCO_2H^-$] requires 495.2019, found 495.2032; $[\alpha]_D^{25}$ +21.7 (*c* 0.3, $CHCl_3$, 15 min), $[\alpha]_D^{25}$ +21.0 (*c* 0.3, $CHCl_3$, 22 h) {lit.[41] $[\alpha]_D^{25}$ +40.4 (*c* 1.0, $CHCl_3$,

2 min), $[\alpha]_D^{25}$ +36.3 (*c* 1, $CHCl_3$, 20 h)}; *m/z* ES− 449 [20%, M − $H^+$], 495 [100%, $MCO_2H^-$].

### Preparation of D-galactose 18

Following **Representative procedure 6**, Pd/C (30 mg) and **17** (83 mg, 0.18 mmol) in EtOAc–EtOH (6 mL) furnished **18** (24 mg, 0.13 mmol, 78%) after recrystallisation. Mp 158–159 °C [MeOH–$Et_2O$] {lit.[30] mp 159–162 °C [MeOH–$Et_2O$]}; $\delta_H$ (400 MHz, $D_2O$) 3.35 [1H, dd, *J* 7.9, 9.9, $C^2HOH$ (major)], 3.51 [1H, dd, *J* 3.4, 9.9, $C^3HOH$ (major)], 3.56–3.67 [6H, m, $C^5HCH_2OH$ (major and minor), $C^3HOH$ (minor) and $C^5HOH$ (major)], 3.69 [1H, dd, *J* 3.4, 11.4, $C^2HOH$ (minor)], 3.79 [1H, d, *J* 3.2, $C^4HOH$ (major)], 3.84 [1H, d, *J* 7.4, $C^4HOH$ (minor)], 3.95 [1H, t, *J* 6.2, $C^5HCH_2OH$ (minor)], 4.44 [1H, d, *J* 7.8, $C^1HOH$ (major)], 5.13 [1H, d, *J* 3.6, $C^1HOH$ (minor)]; $[\alpha]_D^{25}$ +79.8 (*c* 0.25, $H_2O$, 15 min), $[\alpha]_D^{25}$ +76.8 (*c* 0.25, $H_2O$, 24 h), {lit.[30] $[\alpha]_D^{25}$ +80.2 (*c* 0.25, $H_2O$, 15 min), $[\alpha]_D^{25}$ +75.6 (*c* 0.25, $H_2O$, 24 h)}.

### Preparation of 2,4-bis(*O*-benzyl)-D-fucose 19

Following **Representative procedure 3**, DIBAL (0.53 mL, 0.26 mmol), (2*R*,3*S*,4*R*,5*R*)-**16** (90 mg, 0.26 mmol) in $CH_2Cl_2$ (5 mL) furnished (2*R*,3*S*,4*R*,5*R*)-**19**[42] (71 mg, 0.21 mmol, 79%, 2 : 1 mixture of anomers) as a white solid after column chromatography. $R_f$ 0.11 and 0.04 [1 : 1 30–40 °C petrol–$Et_2O$]; mp 126–127 °C [petrol/$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 1.20 [3H, d, *J* 6.6, $CHCH_3$ (major)], 1.25 [3H, d, *J* 6.4, $CHCH_3$ (minor)], 2.30 [1H, br s, $C^3H(OH)$ (major)], 2.41 [1H, br s, $C^3H(OH)$ (minor)], 3.00 [1H, br s, $C^1H(OH)$], 3.49–3.53 [2H, m, $C^1H(OH)$ (minor) and $C^2HOCH_2Ph$ (minor)], 3.58 [1H, app. d, *J* 3.2, $C^4HOCH_2Ph$ (minor)], 3.60–3.69 [2H, m, $C^5HCH_3$ (minor) and $C^3H(OH)$ (minor)], 3.65 [1H, app. d, *J* 2.6, $C^4HOCH_2Ph$ (major)], 3.78 [1H, dd, *J* 3.5, 9.9, $C^2HOCH_2Ph$ (major)], 4.05 [1H, dd, *J* 2.6, 9.9, $C^3H(OH)$ (major)], 4.16 [1H, q, *J* 6.6, $C^5HCH_3$ (major)], 4.61 [1H, t, *J* 6.8, $C^1H(OH)$ (minor)], 4.64–4.83 [5H, m, $CHOCH_AH_BPh$, $CHOCH_2Ph$ (major and minor) and $CHOCH_AH_BPh$, $CHOCH_CH_DPh$ (minor)], 4.85 [1H, d, *J* 11.7, $CHOCH_AH_BPh$ (major)], 4.90 [1H, d, *J* 11.4, $CHOCH_AH_BPh$ (minor)], 4.99 [1H, d, *J* 11.3, $CHOCH_CH_DPh$ (minor)], 5.30 [1H, d, *J* 3.2, $C^1HOH$ (major)], 7.26–7.44 [20H, m, Ph*H* (major and minor)]; $[\alpha]_D^{25}$ +64.0 (*c* 0.35, $CHCl_3$,10 min), $[\alpha]_D^{25}$ +62.6 (*c* 0.2, $CHCl_3$, 24 h) {lit.[42] *ent*-$[\alpha]_D^{25}$ −75.5 (*c* 1.16, $CHCl_3$}.

### Preparation of D-fucose 20

Following **Representative procedure 6**, Pd/C (15 mg) and **19** (65 mg, 0.19 mmol) in EtOAc–EtOH (6 mL) furnished **20** (21 mg, 0.13 mmol, 67%, 2 : 1 mixture of anomers) after recrystallisation. Mp 144–146 °C [MeOH–$Et_2O$], {lit.[31] mp 145–146 °C [MeOH–$Et_2O$]}; $\delta_H$ (400 MHz, $D_2O$) 1.07 [3H, d, *J* 6.6, $C^5HCH_3$ (major)], 1.11 [3H, d, *J* 6.4, $C^5HCH_3$ (minor)], 3.31 [1H, dd, *J* 7.9, 10.0, $C^2HOH$ (major)], 3.50 [1H, dd, *J* 3.4, 10.0, $C^3HOH$ (major)], 3.60 [1H, app. d, *J* 2.8, $C^4HOH$ (major)], 3.63–3.73 [4H, m, $C^2HOH$ (minor), $C^3HOH$ (minor), $C^4HOH$ (minor) and $C^5HCH_3$ (major)], 4.06 [1H, q, J 6.6, $C^5HCH_3$ (minor)], 4.41 [1H, d, *J* 7.8, $C^1HOH$ (major)], 5.06 [1H, d, *J* 3.7, $C^1HOH$ (minor)]; $[\alpha]_D^{25}$ +38.4 (*c* 0.25, $H_2O$, 15 min), $[\alpha]_D^{25}$ +74.8 (*c* 0.25, $H_2O$, 24 h), {lit.[31] $[\alpha]_D^{25}$ +39.1 (*c* 0.25, $H_2O$, 15 min), $[\alpha]_D^{25}$ +76.0 (*c* 0.25, $H_2O$, 24 h)}.

### Preparation of (2′*S*,3′*R*,4*S*,4′*R*,5′*R*)-4-benzyl-3-[2′,4′,6-tris(benzyloxy)-5′-(*tert*-butyldimethylsilanyloxy)-3′-hydroxyhexanoyl]-5,5-dimethyloxazolidin-2-one 21 and (2′*S*,3′*S*,4*S*,4′*R*,5′*R*)-4-benzyl-3-[2′,4′,6-tris(benzyloxy)-5′-(*tert*-butyldimethylsilanyloxy)-3′-hydroxyhexanoyl]-5,5-dimethyloxazolidin-2-one 22

Following **Representative procedure 1**, $CF_3SO_3H$ (0.16 mL, 1.87 mmol), $Et_3B$ (1.90 mL, 1.87 mmol), (*S*)-**1** (550 mg, 1.56 mmol), $^iPr_2NEt$ (0.38 mL, 2.18 mmol) and **11** (700 mg, 1.69 mmol) in $CH_2Cl_2$ (30 mL) furnished a 3.3 : 1 mixture of **21** and **22** which after purification by column chromatography gave **21** (553 mg, 0.72 mmol, 46%) as a pale yellow oil and **22** (107 mg, 0.14 mmol, 9%) as a pale yellow oil. **21**: $R_f$ 0.17 [3 : 1 pentane–$Et_2O$, double eluted]; $\delta_H$ (400 MHz, $CDCl_3$) 0.03 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.04 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.87 [9H, s, $SiC(CH_3)_3$], 1.07 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.26 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.83 [1H, dd, *J* 14.5, 9.8, $CHCH_AH_BPh$], 3.11 [1H, dd, *J* 14.5, 3.4, $CHCH_AH_BPh$], 3.21 [1H, d, *J* 6.9, CH(O*H*)], 3.61 [1H, dd, *J* 10.3, 6.1, $CH_AH_BOCH_2Ph$], 3.73 [1H, dd, *J* 9.6, 4.9, $CH_AH_BOCH_2Ph$], 3.80 [1H, d, *J* 5.1, $CHOCH_2Ph.CH(OTBDMS)$], 4.08–4.12 [1H, m, C*H*(OTBDMS)], 4.19 [1H, dd, *J* 9.7, 3.5, $CHCH_2Ph$], 4.33–4.36 [1H, m, C*H*(OH)], 4.41 [1H, d, *J* 11.3, $CHOCH_AH_BPh$], 4.52 [2H, s, $CH_2OCH_2Ph$], 4.53–4.56 [1H, m, $CHOCH_CH_DPh$], 4.60 [1H, d, *J* 11.3, $CHOCH_AH_BPh$], 4.61 [1H, d, *J* 10.8, $CHOCH_CH_DPh$], 5.46 [1H, d, *J* 4.3, $CO.CHOCH_2Ph$], 7.21–7.37 [20H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) −4.9, −4.6 [$Si(CH_3)_2$], 18.1 [$SiC(CH_3)_3$], 22.0, 27.7 [$C(CH_3)_2$], 25.8 [$SiC(CH_3)_3$], 35.2 [$CHCH_2Ph$], 64.0 [$CHCH_2Ph$], 69.6 [CH(OH)], 70.7 [CH(OTBDMS)], 71.8 [$CH_2OCH_2Ph$], 72.7, 72.7, 73.3 [$CH_2OCH_2Ph$ and 2 × $CHOCH_2Ph$], 77.7 [$CHOCH_2Ph.CH(OTBDMS)$], 77.9 [$CO.CHOCH_2Ph$], 83.1 [$C(CH_3)_2$], 126.6, 127.4, 127.5, 127.9 [*p-Ph*], 127.6, 128.1, 128.2, 128.3, 128.5, 129.1 [*m/o-Ph*], 137.1, 137.3, 138.2 [*i-Ph*], 153.0 [C=O endocyclic], 171.0 [C=O exocyclic]; $\nu_{max}$ (thin film, $cm^{-1}$) 3419 [O–H], 1775 [C=O endocyclic], 1707.9 [C=O endocyclic]; $C_{45}H_{57}NO_8$ requires C 70.37, H 7.48, N 1.82%, found C 70.83, H 7.48, N 2.04%; $[\alpha]_D^{26}$ +9.3 (*c* 0.30, $CHCl_3$); *m/z* LD+ (MALDI) 790, 791, 792 [100%, 60%, 20%, $MNa^+$]. **22**: $R_f$ 0.26 [3 : 1 pentane–$Et_2O$; double eluted]; $\delta_H$ (400 MHz, $CDCl_3$) 0.09 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.11 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.85 [3H, s, $C(CH_3)_A(CH_3)_B$], 0.89 [9H, s, $SiC(CH_3)_3$], 1.14 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.76 [1H, dd, *J* 14.5, 10.1, $CHCH_AH_BPh$], 3.11 [1H, dd, *J* 14.5, 3.0, $CHCH_AH_BPh$], 3.63–3.67 [1H, m, $CH_AH_BOCH_2Ph$], 3.67 [1H, d, *J* 6.4, CH(O*H*)], 3.74 [1H, dd, *J* 9.7, 4.4, $CH_AH_BOCH_2Ph$], 3.86–3.90 [2H, m, $CHOCH_2Ph.CH(OTBDMS)$ and $CHCH_2Ph$], 4.10–4.14 [1H, m, C*H*(OH)], 4.25–4.28 [1H, m, C*H*(OTBDMS)], 4.45–4.57 [5H, m, $CO.CHOCH_AH_BPh$, $CHOCH_2Ph.CH(OTBDMS)$ and $CH_2OCH_2Ph$], 4.72 [1H, d, *J* 11.5, $CO.CHOCH_AH_BPh$], 5.27 [1H, d, *J* 3.4, $CO.CHOCH_2Ph$], 7.11–7.42 [20H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) −4.6 [$Si(CH_3)_2$], 18.0 [$SiC(CH_3)_3$], 22.0, 27.6 [$C(CH_3)_2$], 25.8 [$SiC(CH_3)_3$], 35.0 [$CHCH_2Ph$], 63.5 [$CHCH_2Ph$], 70.9 [$CH_2OCH_2Ph$], 71.6 [CH(OTBDMS)], 72.3 [$CH_2OCH_2Ph$], 72.9 [CH(OH)], 73.2, 73.2 [2 × $CHOCH_2Ph$], 76.2 [$CHOCH_2Ph.CH(OTBDMS)$], 79.9 [$CO.CHOCH_2Ph$], 83.3 [$C(CH_3)_2$], 126.5, 127.5, 127.6, 127.6, 127.7, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 129.0 [*p-Ph* and *m/o-Ph*], 137.2, 137.9, 138.1, 138.3 [*i-Ph*], 152.7 [C=O endocyclic], 169.7 [C=O exocyclic]; $\nu_{max}$ (thin film, $cm^{-1}$) 3458 [O–H], 1774 [C=O endocyclic], 1707 [C=O endocyclic]; HRMS $C_{45}H_{57}NO_8NaSi$ [$MNa^+$] requires 790.3751, found 790.3773; $[\alpha]_D^{26}$ +18.3 (*c* 0.80, $CHCl_3$); *m/z* LD+ (MALDI) 790, 791, 792, 793 [100%, 65%, 30%, 10%, $MNa^+$].

### Preparation of (2′*S*,3′*R*,4*S*,4′*R*,5′*R*)-4-benzyl-3-[2′,4′-bis(benzyloxy)-5′-(*tert*-butyldimethylsilanyloxy)-3′-hydroxypentanoyl]-5,5-dimethyloxazolidin-2-one 23 and (2′*S*,3′*S*,4*S*,4′*R*,5′*R*)-4-benzyl-3-[2′,4′-bis(benzyloxy)-5′-(*tert*-butyldimethylsilanyloxy)-3′-hydroxypentanoyl]-5,5-dimethyloxazolidin-2-one 24

Following **Representative procedure 1**, $CF_3SO_3H$ (0.19 mL, 2.20 mmol), $Et_3B$ (2.20 mL, 2.20 mmol), (*S*)-**1** (650 mg, 1.84 mmol), $^iPr_2NEt$ (0.45 mL, 2.58 mmol) and **12** (600 mg, 1.95 mmol) in $CH_2Cl_2$ (20 mL) furnished a 2.2 : 1 ratio of **23** and **24** which after purification by column chromatography gave **23** (226 mg, 0.34 mmol, 19%) as a pale yellow oil and **24** (677 mg, ∼1.02 mmol, ∼56%) as a white solid contaminated

with <5% of (*S*)-**1** after column chromatography. **23**: $R_f$ 0.12 [5 : 1 pentane–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 0.01 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.04 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.88 [9H, s, $SiC(CH_3)_3$], 1.19 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.21 [3H, d, *J* 6.3, $CHCH_3$], 1.30 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.86 [1H, dd, *J* 14.5, 9.7, $CHCH_AH_BPh$], 3.00 [1H, d, *J* 8.1, CH(O*H*)], 3.13 [1H, dd, *J* 14.4, 3.6, $CHCH_AH_BPh$], 3.62 [1H, dd, *J* 5.4, 1.7, C*H*O$CH_2$Ph.CH(OTBDMS)], 3.97–4.00 [1H, m, C*H*(OTBDMS)], 4.24–4.27 [1H, m, C*H*(OH)], 4.33 [1H, dd, *J* 9.7, 3.6, C*H*$CH_2$Ph], 4.41 [1H, d, *J* 11.2, $CHOCH_AH_BPh$], 4.56–4.67 [3H, m, $CHOCH_AH_BPh$ and $CHOCH_2Ph$], 5.39 [1H, d, *J* 3.9, CO.C*H*O$CH_2$Ph], 7.21–7.40 [15H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) −4.8, −4.7 [$Si(CH_3)_2$], 18.1 [$SiC(CH_3)_3$], 19.0 [$CHCH_3$], 22.1, 27.9 [$C(CH_3)_2$], 25.9 [$SiC(CH_3)_3$], 35.2 [$CHCH_2Ph$], 64.0 [*C*H$CH_2$Ph], 68.2 [*C*H(OTBDMS)], 69.5 [*C*H(OH)], 72.8, 73.3 [2 × $CHOCH_2Ph$], 78.9 [CO.*C*H$OCH_2$Ph], 79.9 [*C*H$OCH_2$Ph.CH(OTBDMS)], 83.1 [$C(CH_3)_2$], 126.7, 127.1, 127.5, [*p-Ph*], 127.9, 128.0, 128.2, 128.3, 128.7, 129.1 [*m/o-Ph*], 137.0, 137.2, 138.3 [*i-Ph*], 152.7 [*C*=O endocyclic], 170.8 [*C*=O exocyclic]; $\nu_{max}$ (KBr disc, $cm^{-1}$) 3435 [O–H], 1765 [C=O endocyclic], 1705 [C=O exocyclic]; HRMS $C_{38}H_{55}N_2O_7Si$ [$MNH_4^+$] requires 679.3779, found 679.3769; *m/z* LD+ (MALDI) 684, 685, 686, 687 [100%, 50%, 20%, 5%, $MNa^+$], 700, 701, 702 [40%, 30%, 10%, $MK^+$]. **24**: $R_f$ 0.19 [5 : 1 pentane: $Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 0.09 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.10 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.89 [9H, s, $C(CH_3)_3$], 0.92 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.17 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.30 [3H, d, *J* 6.4, $CHCH_3$], 2.79 [1H, dd, *J* 14.5, 10.0, $CHCH_AH_BPh$], 3.11 [1H, dd, *J* 14.5, 3.3, $CHCH_AH_BPh$], 3.75 [1H, dd, *J* 7.8, 3.6, C*H*O$CH_2$Ph.CH(OTBDMS)], 3.97 [1H, dd, *J* 10.0, 3.3, C*H*$CH_2$Ph], 4.14–4.20 [2H, m, C*H*(OTBDMS) and C*H*(OH)], 4.47–4.56 [3H, m, $CHOCH_AH_BPh$ and $CHOCH_2Ph$], 4.72 [1H, d, *J* 11.6, $CHOCH_AH_BPh$], 5.31 [1H, d, *J* 3.3, CO.C*H*O$CH_2$Ph], 7.15–7.44 [15H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) −4.9, −4.7 [$Si(CH_3)_2$], 17.7 [$CHCH_3$], 17.9 [$C(CH_3)_3$], 22.0, 27.5 [$C(CH_3)_2$], 25.7 [$C(CH_3)_3$], 35.1 [$CHCH_2Ph$], 63.6 [*C*H$CH_2$Ph], 68.6 [*C*H(OTBDMS)], 72.3, 73.3 [2 × $CHOCH_2Ph$], 73.2 [*C*H(OH)], 77.5 [*C*H$OCH_2$Ph.CH(OTBDMS)], 79.9 [CO.*C*H$OCH_2$Ph], 83.2 [$C(CH_3)_2$], 126.6, 127.5, 127.7 [*p-Ph*], 127.9, 128.1, 128.3, 128.5, 129.0, 129.1 [*m/o-Ph*], 137.2, 138.1, 138.2 [*i-Ph*], 152.8 [*C*=O endocyclic], 170.2 [*C*=O exocyclic]; $\nu_{max}$ (thin film, $cm^{-1}$) 3459 [O–H], 1777 [C=O endocyclic], 1706 [C=O exocyclic]; HRMS $C_{38}H_{55}N_2O_7Si$ [$MNH_4^+$] requires 679.3779, found 679.3774; $[\alpha]_D^{26}$ +9.6 (*c* 1.5, $CHCl_3$); *m/z* LD+ (MALDI) 684, 685, 686, 687 [100%, 40%, 15%, 5%, $MNa^+$], 700, 701, 702 [50%, 20%, 10%, $MK^+$].

### Preparation of (2*S*,3*R*,4*R*,5*R*)-2,4-bis(benzyloxy)-3-hydroxy-5-methyltetrahydropyran-2-one 25

Following **Representative procedure 5**, **23** (200 mg, 0.30 mmol), TBAF (0.45 mL, 0.45 mmol) and AcOH (0.02 mL, 0.30 mmol) in THF (10 mL) furnished **25** (78 mg, 0.228 mmol, 76%) as a white solid after column chromatography. $R_f$ 0.12 [1 : 1 pentane–$Et_2O$]; mp 84–85 °C [pentane–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 1.39 [3H, d, *J* 6.5, $CHCH_3$], 3.56 [1H, t, *J* 2.1, C*H*($OCH_2Ph$).$CHCH_3$], 4.03–4.08 [2H, m, C*H*(OH) and CO.C*H*O$CH_2$Ph], 4.51 [1H, d, *J* 12.0, $CHOCH_AH_BPh$], 4.53–4.57 [1H, m, C*H*$CH_3$], 4.60 [1H, d, *J* 11.4, $CHOCH_CH_DPh$], 4.76 [1H, d, *J* 12.0, $CHOCH_AH_BPh$], 5.12 [1H, d, *J* 11.4, $CHOCH_CH_DPh$], 7.27–7.43 [10H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) 15.7 [$CHCH_3$], 71.1, 73.2 [2 × $CHOCH_2Ph$], 73.7 [$CHCH_3$], 74.1 [CO.*C*H$CH_2$Ph], 77.9 [*C*H(OH)], 79.3 [*C*H$OCH_2$Ph.$CHCH_3$], 127.9, 127.9 [*p-Ph*], 128.2, 128.3, 128.4, 128.6 [*m/o-Ph*], 136.8, 137.0 [*i-Ph*], 169.6 [*C*=O]; $\nu_{max}$ (thin film, $cm^{-1}$) 3447 [O–H], 1717 [C=O]; HRMS $C_{20}H_{22}O_5Na$ [$MNa^+$] requires 365.1365, found 365.1352; $[\alpha]_D^{26}$ −95.8 (*c* 1.5, $CHCl_3$); *m/z* ES+ 365 [$MNa^+$, 100%].

### Preparation of 2,4-di-*O*-benzyl-D-6-deoxyidose 26

Following **Representative procedure 3**, DIBAL (0.76 mL, 0.76 mmol), **25** (130 mg, 0.38 mmol) in $CH_2Cl_2$ (5 mL) furnished **26** (127 mg, 0.37 mmol, 97%, 4 : 1 mixture of anomers) as a white solid after column chromatography. $R_f$ 0.12 and 0.04 [1 : 1 30–40 °C petrol–$Et_2O$]; mp 108–109 °C [MeOH–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$)[43] 1.27 [3H, d, *J* 6.9, $C^5HCH_3$ (α-p)], 1.39 [3H, d, *J* 6.5, $C^5HCH_3$ (β-p)], 2.10 [1H, d, *J* 3.2, $C^3H$(O*H*) (β-p)], 2.75 [1H, d, *J* 3.7, $C^3H$(O*H*) (α-p)], 3.22–3.23 [1H, m, $C^4HOCH_2Ph$ (β-p)], 3.31 [1H, dd, *J* 7.9, 5.7, $C^2HOCH_2Ph$ (α-p)], 3.38 [1H, dd, *J* 4.5, 2.6, $C^2HOCH_2Ph$ (β-p)], 3.48 [1H, dd, *J* 7.0, 4.5, $C^4HOCH_2Ph$ (α-p)], 3.74 [1H, d. *J* 9.6, $C^1H$(O*H*) (β-p)], 3.94 [1H, app. td, $C^3H$(OH) (α-p)], 4.05 [1H, qd, *J* 6.8, 3.2, $C^5HCH_3$ (β-p)], 4.15–4.18 [1H, m, $C^3H$(OH) (β-p)], 4.29 [1H, qd, *J* 6.9, 4.6, $C^5HCH_3$ (α-p)], 4.57 [1H, d, *J* 12.0, $CHOCH_AH_BPh$ (β-p)], 4.61 [1H, d, *J* 11.8, $CHOCH_AH_BPh$ (α-p)], 4.64 [1H, d, *J* 2.6, $CHOCH_CH_DPh$ (β-p)], 4.67 [1H, d, *J* 2.6, $CHOCH_CH_DPh$ (β-p)], 4.68–4.73 [2H, ABq, J 5.4, $CHOCH_2Ph$ (α-p)], 4.74 [1H, d, *J* 12.0, $CHOCH_AH_BPh$ (β-p)], 4.84 [1H, d, *J* 11.8, $CHOCH_AH_BPh$ (α-p)], 5.02 [1H, dd, *J* 9.4, 2.6, $C^1HOH$ (β-p)], 5.04–5.06 [1H, m, $C^1H$(OH) (α-p)], 7.27–7.42 [20H, m, Ph*H* (α-p and β-p)]; $\delta_C$ (100 MHz, $CDCl_3$) 14.3 [$C^5HCH_3$ (α-p)], 16.9 [$C^5HCH_3$ (β-p)], 66.5 [$C^3HOH$ (β-p)], 66.9 [$C^5HCH_3$ (α-p)], 69.8 [$C^5HCH_3$(β-p)], 70.6 [$C^3H$(OH) (α-p)], 72.7, 73.6 [2 × $CHOCH_2Ph$ (α-p)], 72.8, 73.1 [2 × $CHOCH_2Ph$ (β-p)], 77.5 [$C^2HOCH_2Ph$ and $C^4HOCH_2Ph$ (β-p)], 78.8 [$C^4HOCH_2Ph$ (α-p)], 80.3 [$C^2HOCH_2Ph$ (α-p)], 92.0 [$C^1H$(OH) (β-p)], 93.6 [$C^1H$(OH) (α-p)], 127.8, 127.9 [*p-Ph* (α-p)], 127.9, 128.1, 128.4, 128.5 [*m/o-Ph* (α-p)], 128.0, 128.2, 128.4, 128.6 [*p*- and *m/o-Ph* (β-p)], 138.1 [*i-Ph* (α-p and β-p)]; $\nu_{max}$ (KBr disc, $cm^{-1}$) 3427 [O–H], 1095 [C–O]; $C_{28}H_{31}O_8$ [$MNa^+$] requires 367.1521, found 367.1525; $[\alpha]_D^{25}$ +2.0 (*c* 0.2, $CHCl_3$, 15 min), $[\alpha]_D^{25}$ +2.1 (*c* 0.2, $CHCl_3$, 24 h); *m/z* ES+ 367 [100%, $MNa^+$].

### Preparation of D-6-deoxyidose 27

Following **Representative procedure 6**, Pd/C (25 mg) and **26** (150 mg, 0.43 mmol) in EtOAc–EtOH (12 mL) furnished **27**[44] (62 mg, 0.38 mmol, 89%) as a viscous oil after titration with $Et_2O$. $\delta_H$ (400 MHz, $D_2O$, selected peaks) 1.14–1.22 [12H, m, α-p, α-f, β-p, β-p $C^5HCH_3$], 3.22–3.26 [3H, m, α-p, β-p, α-f $C^3HOH$], 3.39 [1H, s, β-f $C^3HOH$], 3.57–3.67 [4H, m, α-p, β-p, α-f, β-f $C^4HOH$], 3.85–3.89 [1H, m, f, $C^5HCH_3$], 3.91–3.99 [1H, m, f, $C^5HCH_3$], 4.01–4.09 [1H, m, p, $C^5HCH_3$], 4.12–4.18 [1H, m, p, $C^5HCH_3$], 4.44 [1H, s, α-p, $C^1HOH$], 4.79 [1H, d, *J* 6.9, β-p, $C^1HOH$], 5.00 [1H, s, α-f, $C^1HOH$], 5.13 [1H, s, β-f, $C^1HOH$]; $\delta_C$ (100 MHz, $D_2O$) 12.9, 16.0 [α-p, β-p $C^5HCH_3$], 18.2, 18.6 [α-f, β-f $C^5HCH_3$], 64.4, 66.6, 67.5, 75.2, 75.8, 76.6, 82.6, 86.2 [α-f, β-f], 69.9, 70.0, 70.5, 70.7 [β-p], 70.2, 71.9, 72.1, 74.2 [α-p], 92.5 [α-p $C^1HOH$], 92.7 [β-p $C^1HOH$], 96.3 [β-f $C^1HOH$], 102.4 [α-f $C^1HOH$]; $\nu_{max}$ (thin film, $cm^{-1}$) 3423 [O–H], 1495, 1457 [C–O]; HRMS $C_6H_{11}O_5$ [$M–H^+$] requires 163.0606, found 163.0607; $[\alpha]_D^{25}$ +9.0 (*c* 1.5, $H_2O$; 15 min), $[\alpha]_D^{25}$ +12.0 (*c* 1.5, $H_2O$; 24 h) {lit.[44] $[\alpha]_D^{25}$ +12.0 (*c* 2.67, $H_2O$), lit.[32] $[\alpha]_D^{25}$ +14.7 (*c* 0.7, $H_2O$); *m/z* ES− 163.0 [100%, M − $H^+$].

### Preparation of (2′*S*,3′*R*,4*S*,4′*S*,5′*R*)-4-benzyl-3-(2′,4′,5′-tris(benzyloxy)-3′,5′-dihydroxyhexanoyl)-5,5-dimethyloxazolidin-2-one 28

A solution of iodine in methanol (1% m/v; 30 mL) was added to **21** (280 mg, 0.36 mmol) at ambient temperature and the resultant mixture refluxed at 85 °C for 6 h. After cooling to ambient temperature, the reaction mixture was quenched with a saturated aqueous sodium thiosulfate solution, diluted with $CH_2Cl_2$, washed with brine, dried and concentrated *in vacuo*. Purification by column chromatography furnished **28** (159 mg, 0.24 mmol, 68%) as a clear colourless oil. $R_f$ 0.07 [1 : 1 30–40 °C petrol–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 1.26 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.32 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.87 [1H, dd, *J* 14.4, 9.5, $CHCH_AH_BPh$], 3.13 [1H, dd, *J* 14.4, 3.8, $CHCH_AH_BPh$], 3.54 [1H, dd, *J* 9.5, 6.0, $CH_AH_BOCH_2Ph$], 3.59 [1H, dd, *J* 9.5, 3.8, $CH_AH_BOCH_2Ph$], 3.87 [1H, dd, *J* 5.9, 2.9, C*H*($OCH_2Ph$).CH(OH)$CH_2OCH_2Ph$], 3.97–4.01 [1H, m,

C*H*(OH)$CH_2OCH_2$Ph], 4.27 [1H, dd, *J* 5.9, 3.4, CO.CH-($OCH_2$Ph).C*H*(OH)], 4.38–4.43 [2H, m, C*H*$CH_2$Ph and 1 × O$CH_2$*H*Ph], 4.72–4.47 [4H, m, 4 × O$CH_2$*H*Ph], 4.82 [1H, d, *J* 11.2, 1 × O$CH_2$*H*Ph], 5.39 [1H, d, *J* 3.4, CO.C*H*O$CH_2$Ph], 7.18–7.45 [20H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) 22.0, 28.1 [C(*C*$H_3$)$_2$], 35.2 [CH*C*$H_2$Ph], 63.9 [*C*H$CH_2$Ph], 69.6 [*C*H(OH)$CH_2OCH_2$Ph], 71.0 [*C*$H_2OCH_2$Ph], 71.5 [CO.CHO$CH_2$Ph.*C*H(OH)], 72.8, 73.3, 74.7 [$CH_2OCH_2$Ph and 2 × CHO*C*$H_2$Ph], 77.5 [CO.*C*HO$CH_2$Ph], 78.8 [*C*H($OCH_2$Ph).CH(OH)$CH_2OCH_2$Ph], 83.7 [*C*$(CH_3)_2$], 126.8, 127.7, 128.1, 128.9 [*p-Ph*], 127.8, 128.3, 128.4, 128.4, 128.6, 128.7, 129.1 [*m/o-Ph*], 136.8, 137.0, 137.9 [*i-Ph*], 152.5 [*C*=O endocyclic], 170.1 [*C*=O exocyclic]; $\nu_{max}$ (thin film, $cm^{-1}$) 3482 [O–H], 1773 [C=O endocyclic], 1706 [C=O exocyclic]; HRMS $C_{39}H_{43}NO_8Na$ [$MNa^+$] requires 676.2886, found 676.2877; $[\alpha]_D^{26}$ +18.2 (*c* 0.3, $CHCl_3$); *m/z* ES+ 676 [100%, $MNa^+$].

### Preparation of (2*S*,3*R*,4*R*,5*R*)-2,4-bis(benzyloxy)-3-hydroxy-5-(benzyloxymethyl)tetrahydropyran-2-one 29

A solution of **28** (263 mg, 0.40 mmol) in PhMe (20 mL) was refluxed for 16 h, then cooled to ambient temperature and concentrated *in vacuo*. Purification by column column chromatography gave (2*S*,3*R*,4*R*,5*R*)-**29** (158 mg, 0.35 mmol, 88%) as a clear colourless oil. $R_f$ 0.17 [1 : 1 30–40 °C petrol–$Et_2O$]; $\delta_H$ (400 MHz, $C_6D_6$) 2.37 [1H, d, *J* 2.8, O*H*], 3.60 [1H, dd, *J* 10.0, 5.2, C$H_A$$H_B$O$CH_2$Ph], 3.66 [1H, t, *J* 2.9, C*H*($OCH_2$-Ph).C$HCH_2OCH_2$Ph], 3.79 [1H, dd, *J* 10.0, 6.0, C$H_A$$H_B$-O$CH_2$Ph], 3.81 [1H, d, *J* 8.7, CO.C*H*O$CH_2$Ph], 4.08 [1H, dt, *J* 8.7, 2.8, C*H*(OH)], 4.25–4.33 [3H, m, C*H*$CH_2$O$CH_A$$H_B$Ph and CHOC$H_A$$H_B$Ph], 4.36 [1H, d, *J* 13.9, $CHCH_2OCH_A$$H_B$Ph], 4.55 [1H, d, *J* 11.3, CHOC$H_C$$H_D$Ph], 4.62 [1H, d, *J* 11.8, $CHOCH_A$$H_B$Ph], 5.19 [1H, d, *J* 11.3, $CHOCH_C$$H_D$Ph], 7.04–7.31 [13H, m, Ph*H*], 7.42–7.48 [2H, m, Ph*H*]; $\delta_C$ (100 MHz, $C_6D_6$) 68.5 [*C*$H_2OCH_2$Ph], 71.6 [$CH_2OCH_2$Ph], 73.6, 73.7 [2 × CHO*C*$H_2$Ph], 74.4 [*C*H(OH)], 76.2 [*C*H$CH_2OCH_2$Ph], 78.1 [*C*H($OCH_2$Ph).C$HCH_2OCH_2$Ph], 78.9 [CO.*C*HO$CH_2$Ph], 128.0, 128.2, 128.5, 128.1 [*m/o-Ph*], 128.1, 128.4, 128.6 [*p-Ph*], 138.1, 138.3, 138.5 [*i-Ph*], 169.2 [*C*=O]; $\nu_{max}$ (thin film, $cm^{-1}$) 3445 [O–H], 1749 [C=O]; HRMS $C_{27}H_{32}NO_6$ [$MNH_4^+$] requires 466.2230, found 466.2226; $[\alpha]_D^{25}$ −73.0 (*c* 0.5, $CHCl_3$); *m/z* ES+ 466 [100%, $MNH_4^+$], 471 [40%, $MNa^+$].

### Preparation of 2,4,6-tri-*O*-benzyl-D-idose 30

Following **Representative procedure 3**, DIBAL (0.36 mL, 0.36 mmol), **29** (80 mg, 0.17 mmol) in $CH_2Cl_2$ (10 mL) furnished **30** (72 mg, 0.16 mmol, 89%, 2 : 1 mixture of anomers) as a clear colourless oil after column chromatography. $R_f$ 0.1 [1 : 1 30–40 °C petrol–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 1.71 [1H, br s, $C^1$H(O*H*) (major)], 2.20 [1H, br s, $C^1$H(O*H*) (minor)], 2.86 [1H, d, *J* 5.2, $C^3$H(O*H*) (major)], 3.35–3.39 [2H, m, $C^2$*H*O$CH_2$Ph (major and minor)], 3.51–3.54 [2H, m, $C^4$*H*O$CH_2$Ph (major and minor)], 3.59 [1H, dd, *J* 10.6, 3.7, C$H_A$$H_B$O$CH_2$Ph (major)], 3.70 [1H, dd, *J* 10.5, 5.2, C$H_A$$H_B$O$CH_2$Ph (minor)], 3.78–3.82 [2H, m, $C^6$H$_A$$H_B$O$CH_2$Ph (major and minor)], 3.99 [1H, q, *J* 5.8, $C^3$*H*(OH) (major)], 3.99 [1H, br s, $C^3$H(O*H*) (minor)], 4.12 [1H, q, *J* 4.8, $C^5$*H*$CH_2$O$CH_2$Ph (minor)], 4.16–4.21 [1H, m, $C^3$*H*(OH) (minor)], 4.32–4.36 [1H, m, $C^5$*H*$CH_2$O$CH_2$Ph (major)], 4.48–4.79 [12H, m, 6 × O$CH_2$*H*Ph (major and minor)], 5.07 [1H, dd, *J* 10.2, 3.1, $C^1$*H*(OH) (minor)], 5.22 [1H, t, *J* 4.1, $C^1$*H*(OH) (major)], 7.19–7.42 [30H, m, Ph*H* (major and minor)]; $\delta_C$ (100 MHz, $CDCl_3$) 69.2 [$C^5$HCH$_2$OCH$_2$Ph (minor)], 68.4 [$C^5$HCH$_2$OCH$_2$Ph (major)], 69.0, 69.1 [*C*$H_2OCH_2$Ph (major and minor)], 72.5, 73.3, 73.5 [$CH_2OCH_2$Ph and 2 × CHO*C*$H_2$Ph (major)], 72.6, 72.8 [$C^3$H(OH) (major and minor)], 73.0, 73.4, 73.6 [$CH_2OCH_2$Ph and 2 × CHO*C*$H_2$Ph (minor)], 76.6, 76.7 [$C^4$HOCH$_2$Ph (major and minor)], 78.0, 78.2 [$C^2$HOCH$_2$Ph (major and minor)], 94.3 [$C^1$H(OH) (major)], 95.7 [$C^1$H(OH) (minor)], 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6 [*p*- and *m/o-Ph* (major and minor)], 137.8, 137.9, 138.0, 138.1 [*i-Ph* (major and minor)]; $\nu_{max}$ (thin film, $cm^{-1}$) 3419 [O–H], 1496, 1454 [C–O]; HRMS $C_{27}H_{34}O_6N$ [$MNH_4^+$] requires 468.2386, found 468.2386; $[\alpha]_D^{25}$ −3.5 (*c* 0.2, $CHCl_3$, 15 min), $[\alpha]_D^{25}$ −3.7 (*c* 0.2, $CHCl_3$, 24 h); *m/z* ES+ 473 [100%, $MNa^+$].

### Preparation of D-idose 31

Following **Representative procedure 6**, Pd/C (25 mg) and **30** (70 mg, 0.15 mmol) in EtOAc–EtOH (6 mL) furnished **31**[38] (24 mg, 0.13 mmol, 89%) as an oil after trituration with $Et_2O$. $\delta_H$ (400 MHz) 3.30 [1H, dd, *J* 8.1, 6.1, α-p $C^6$$H_A$$H_B$OH], 3.37 [1H, dd, *J* 9.3, 4.7, α-f $C^6$$H_A$$H_B$OH], 3.46–3.51 [1H, m], 3.55–3.61 [5H, m], 3.62–3.80 [6H, m], 3.87–3.91 [3H, m], 3.96 [1H, t, *J* 3.7], 3.99–4.06 [3H, m], 4.09 [1H, t, *J* 4.8], 4.87 [1H, d, *J* 6.1, β-p $C^1$*H*OH], 4.96 [1H, d, *J* 1.5, α-p $C^1$*H*OH], 5.10 [1H, d, *J* 1.2, β-f $C^1$*H*OH], 5.31 [1H, d, *J* 4.3, α-f $C^1$*H*OH]; $[\alpha]_D^{25}$ +7.7 (*c* 0.3, $H_2O$; 15 min), $[\alpha]_D^{25}$ +6.3 (*c* 0.3, $H_2O$; 24 h) {lit.[38] *ent*-$[\alpha]_D^{25}$ −9.8 (*c* 0.45, $H_2O$; 15 min), $[\alpha]_D^{25}$ −8.0 (*c* 0.45, $H_2O$; 24 h)}.

### Preparation of (2*S*,3*S*,4*R*,5*R*)-2,4-bis(benzyloxy)-3-hydroxy-5-(benzyloxymethyl)tetrahydropyran-2-one 32

Following **Representative procedure 5**, **22** (100 mg, 0.13 mmol), TBAF (0.2 mL, 0.20 mmol) and AcOH (0.007 mL, 0.13 mmol) in THF (5 mL) furnished a 1 : 2 mixture of **32** and (*S*)-4-benzyl-5,5-dimethyloxazolidin-2-one (55 mg) as a pale yellow oil after column chromatography. **32**: $R_f$ 0.09 [1 : 1 pentane–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 3.45 [1H, d, *J* 4.8, O*H*], 3.75–3.77 [2H, m, C$H_2$O$CH_2$Ph], 3.97–4.00 [2H, m, C*H*($OCH_2$Ph).C$H_2OCH_2$Ph and CO.C*H*O$CH_2$Ph], 4.33–4.37 [1H, m, C*H*(OH)], 4.43–4.48 [1H, m, C*H*$CH_2$O$CH_2$Ph], 4.51–4.57 [3H, m, CHOC$H_A$$H_B$Ph, CHOC$H_C$$H_D$Ph and $CH_2OCH_A$$H_B$Ph], 4.69–4.96 [2H, m, $CHOCH_A$$H_B$Ph and $CHOCH_C$$H_D$Ph], 5.07 [1H, d, *J* 12.1, $CH_2OCH_A$$H_B$Ph], 7.17–7.39 [15H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) 67.2 [*C*H(OH)], 67.9 [*C*$H_2OCH_2$Ph], 72.1 [*C*H($OCH_2$Ph).C$HCH_2OCH_2$Ph], 73.1, 73.5, 73.7 [$CH_2OCH_2$Ph and 2 × CHO*C*$H_2$Ph], 74.1 [CO.*C*HO$CH_2$Ph], 77.3 [*C*H$CH_2OCH_2$Ph], 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 129.1 [*p*- and *m/o-Ph*], 136.6, 136.8, 137.2 [*i-Ph*], 168.9 [*C*=O]; $\nu_{max}$ (thin film, $cm^{-1}$) 3328 [O–H], 1751 [C=O]; HRMS $C_{27}H_{28}O_6Na$ [$MNa^+$] requires 471.1784, found 471.1778; *m/z* ES+ 466 [60%, $MNH_4^+$], 471 [100%, $MNa^+$].

### Preparation of 2,4,6-tri-*O*-benzyl-D-talose 33

Following **Representative procedure 3**, DIBAL (0.58 mL, 0.58 mmol), **32** (130 mg, 1 : 2 mixture of **32** and (*S*)-4-benzyl-5,5-dimethyloxazolidin-2-one) in $CH_2Cl_2$ (5 mL) furnished a mixture of **33** and (*S*)-4-benzyl-5,5-dimethyloxazolidin-2-one (120 mg, one anomer, 1 : 2 mixture of **33** and (*S*)-4-benzyl-5,5-dimethyloxazolidin-2-one) as a clear colourless oil after column chromatography. **33**: $R_f$ 0.22 [1 : 2 30–40 °C petrol–$Et_2O$]; $\delta_H$ (400 MHz, $C_6D_6$) 3.17 [1H, d, *J* 11.2, $C^3$HO*H*], 3.58–3.62 [2H, m, C$H_A$$H_B$O$CH_2$Ph and $C^4$*H*O$CH_2$Ph], 3.72 [1H, dd, *J* 1.6, 4.1, $C^2$*H*O$CH_2$Ph], 3.76 [1H, dd, *J* 7.3, 9.6, $CH_A$$H_B$O$CH_2$Ph], 4.10 [1H, br s, $C^1$HO*H*], 4.18–4.22 [1H, m, $C^3$*H*OH], 4.23 [1H, d, *J* 11.8, CHOC$H_A$$H_B$Ph], 4.29 [1H, d, *J* 11.8, $CHOCH_A$$H_B$Ph], 4.31 [1H, d, *J* 11.8, CHOC$H_C$$H_D$Ph], 4.39–4.43 [1H, m, $C^5$*H*$CH_2$O$CH_2$Ph], 4.52 [1H, d, *J* 11.8, $CHOCH_C$$H_D$Ph], 4.56 [1H, d, *J* 11.8, $CH_2CHOCH_A$$H_B$Ph], 4.72 [1H, d, *J* 11.8, $CH_2CHOCH_A$$H_B$Ph], 5.46 [1H, app. s, $C^1$*H*OH], 7.11–7.43 [15H, m, Ph*H*]; $\delta_C$ (100 MHz, $C_6D_6$) 66.8 [$C^3$H(OH)], 69.4 [$C^5$HCH$_2$OCH$_2$Ph], 70.5 [*C*$H_2OCH_2$Ph], 73.1 [$CH_2OCH_2$Ph and CHO*C*$H_2$Ph], 75.5 [CHO*C*$H_2$Ph], 77.4 [$C^4$HOCH$_2$Ph], 78.5 [$C^2$HOCH$_2$Ph], 92.4 [$C^1$H(OH)], 127.6, 127.9 [*p-Ph*], 127.6, 127.7, 128.8, 129.2 [*m/o-Ph*], 139.0, 139.3, 139.7 [*i-Ph*]; $\nu_{max}$ (thin film, $cm^{-1}$) 3411 [O–H], 1644, 1604 [C–O]; HRMS $C_{27}H_{30}O_6Na$ [$MNa^+$] requires 473.1940, found 473.1944; *m/z* ES+ 473 [100%, $MNa^+$].

**Preparation of D-talose 34**

Following **Representative procedure 6**, Pd/C (20 mg) and an inseparable 1 : 2 mixture of **33** and (*S*)-4-benzyl-5,5-dimethyloxazolidin-2-one (130 mg) in EtOAc–EtOH (6 mL) furnished **34**[39] (11 mg, 0.06 mmol) after titration with $Et_2O$. Mp 131–134 °C [$Et_2O$]; $\delta_H$ (400 MHz, $D_2O$) 3.51–3.55 [2H, m], 3.61 [1H, d, *J* 4.2], 3.65–3.70 [6H, m], 3.71–3.76 [6H, m], 3.80–3.82 [4H, m], 3.86–3.90 [1H, m], 3.97–4.01 [2H, m], 4.09 [1H, t, *J* 3.5], 4.22–4.23 [1H, m], 4.72 [1H, d, *J* 1.1, β-p C$^1$*H*OH], 5.15 [1H, s, α-f C$^1$*H*OH], 5.18 [1H, d, *J* 1.8, α-p C$^1$*H*OH], 5.27 [1H, d, *J* 3.5, β-f C$^1$*H*OH]; $[\alpha]_D^{25}$ +18.6 (*c* 0.35, $H_2O$; 15 min), $[\alpha]_D^{25}$ +19.4 (*c* 0.35, $H_2O$; 24 h) {lit.[39] $[\alpha]_D^{25}$ +22.0 (*c* 0.5, $H_2O$; 15 min), $[\alpha]_D^{25}$ +19.8 (*c* 0.5, $H_2O$; 24 h)}.

**Preparation of (2*S*,3*S*,4*R*,5*R*)-2,4-bis(benzyloxy)-3-hydroxy-5-methyltetrahydropyran-2-one 35**

Following **Representative procedure 5**, **24** (140 mg, 0.21 mmol), TBAF (0.32 mL, 0.32 mmol) and AcOH (0.012 mL, 0.21 mmol) in THF (10 mL) furnished an inseparable 1.4 : 1 mixture of **35** and (*S*)-4-benzyl-5,5-dimethyloxazolidin-2-one (128 mg) as a pale yellow oil after column chromatography. **35**: $R_f$ 0.15 [1 : 2 40–60 °C petrol–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 1.41 [3H, d, *J* 6.6, CHC*H*$_3$], 3.21 [1H, d, *J* 3.5, CH(O*H*)], 3.76 [1H, dd, *J* 5.8, 4.2, C*H*(OCH$_2$Ph).CHCH$_3$], 4.04 [1H, d, *J* 3.7, CO.C*H*OCH$_2$Ph], 4.36–4.43 [2H, m, C*H*CH$_3$ and C*H*(OH)], 4.59 [1H, d, *J* 11.8, CHOC*H*$_A$H$_B$Ph], 4.71 [1H, d, *J* 12.1, CHOC*H*$_C$H$_D$Ph], 4.75 [1H, d, *J* 11.8, CHOCH$_A$*H*$_B$Ph], 5.09 [1H, d, *J* 12.1, CHOCH$_C$*H*$_D$Ph], 7.17–7.40 [10H, m, Ph*H*]; $\delta_C$ (100 MHz, $CDCl_3$) 16.1 [CH*C*H$_3$], 67.6 [*C*H(OH)], 72.9, 73.7 [2 × CHO*C*H$_2$Ph], 73.8 [*C*HOCH$_2$Ph.CHCH$_3$], 74.2 [CO.*C*HCH$_2$Ph], 74.8 [*C*HCH$_3$], 127.2, 128.0, 128.1, 128.4, 128.7, 129.1 [*p*- and *m*/*o*-*Ph*], 136.8, 136.9 [*i*-*Ph*], 157.9 [*C*=O]; $\nu_{max}$ (thin film, cm$^{-1}$) 1748 [C=O]; HRMS $C_{20}H_{22}O_5Na$ [MNa$^+$] requires 365.1365, found 365.1372; *m*/*z* ES+ 343 [12%, MH$^+$], 360 [100%, MNH$_4^+$], 365 [35%, MNa$^+$].

**Preparation of 2,4-bis(*O*-benzyl)-D-talose 36**

Following **Representative procedure 3**, DIBAL (0.32 mL, 0.32 mmol), **35** (55 mg, 1 : 1 mixture of **35** and (*S*)-4-benzyl-5,5-dimethyloxazolidin-2-one) in $CH_2Cl_2$ (5 mL) furnished **36** (46 mg, single anomer, 1 : 2 mixture of **36** and (*S*)-4-benzyl-5,5-dimethyloxazolidin-2-one) as a pale yellow oil after column chromatography. **36**: $R_f$0.12 [1 : 1 30–40 °C petrol–$Et_2O$]; $\delta_H$ (400 MHz, $CDCl_3$) 1.27 [3H, d, *J* 6.7, C$^5$HC*H*$_3$], 3.39 [1H, d, *J* 3.0, C$^1$H(O*H*)], 3.49 [1H, dd, *J* 3.8, 1.8, C$^4$*H*OCH$_2$Ph], 3.52–3.55 [1H, m, C$^2$*H*OCH$_2$Ph], 3.90–3.95 [1H, m, C$^3$*H*(OH)], 4.12–4.17 [1H, m, C$^5$*H*CH$_3$], 4.49 [1H, d, *J* 12.0, CHOC*H*$_A$H$_B$Ph], 4.63 [1H, d, *J* 11.8, CHOC*H*$_C$H$_D$Ph], 4.77 [1H, d, *J* 11.8, CHOCH$_C$*H*$_D$Ph], 4.81 [1H, d, *J* 12.0, CHOCH$_A$*H*$_B$Ph], 5.37 [1H, app. s, C$^1$*H*(OH)]; $\delta_C$ (100 MHz, $CDCl_3$) 16.8 [C$^5$HC*H*$_3$], 66.2, 66.3 [C$^3$H(OH) and *C*$^5$HCH$_3$], 73.5, 75.8 [2 × CHO*C*H$_2$Ph], 79.1, 78.4 [2 × *C*HOCH$_2$Ph], 92.3 [*C*$^1$H(OH)], 127.6, 127.7 [*p*-*Ph*], 127.8, 127.9, 128.3, 128.4 [*m*/*o*-*Ph*], 138.0, 138.5 [*i*-*Ph*]; $\nu_{max}$ (thin film, cm$^{-1}$) 2929 [O–H], 1496, 1455 [C–O]; HRMS $C_{20}H_{24}O_5Na$ [MNa$^+$] requires 367.1521, found 367.1522; *m*/*z* ES+ 367 [100%, MNa$^+$].

**Preparation of D-6-deoxytalose 37**

Following **Representative procedure 6**, Pd/C (15 mg) and **36** (45 mg, 1 : 2 mixture of **36** and (*S*)-4-benzyl-5,5-dimethyloxazolidin-2-one in EtOAc–EtOH (6 mL) furnished**37**[40] (16 mg, 0.10 mmol) as a white solid after recrystallisation. Mp 118–120 °C [MeOH–$Et_2O$], {lit.[40] mp 119–120 °C [EtOH]}; $\delta_H$ (400 MHz, $D_2O$) 1.10–1.16 [12H, m, α-p, α-f, β-p, β-f C$^5$HC*H*$_3$], 3.49–3.60 [2H, m], 3.61–3.63 [4H, m], 3.64 [1H, t, *J* 3.3], 3.68 [1H, t, *J* 1.5], 3.71–3.73 [2H, m], 3.73 [1H, d, *J* 3.0], 3.79 [1H, t, *J* 3.2], 3.85 [1H, dd, *J* 4.7, 1.3], 3.96 [1H, d, *J* 1.5], 4.03–4.10 [2H, m], 4.65 [1H, s, β-p C$^1$*H*OH], 5.09 [1H, d, *J* 0.9, α-p C$^1$*H*OH], 5.11 [1H, d, *J* 1.4, α-f C$^1$*H*OH], 5.23 [1H, s, β-f C$^1$*H*OH]; $\delta_C$ (125 MHz, $D_2O$) 15.9 [β-p C$^5$HC*H*$_3$], 16.1 [α-p C$^5$HC*H*$_3$], 18.3 [α-f C$^5$HC*H*$_3$], 18.7 [β-f C$^5$HC*H*$_3$], 61.6 [α-f *C*$^5$HCH$_3$], 65.6 [α-p *C*$^3$H(OH)], 67.3 [α-p *C*$^5$HCH$_3$], 67.5 [β-f *C*$^5$HCH$_3$],69.0 [β-p *C*$^3$H(OH)], 69.3 [α-f *C*$^3$H(OH)], 70.7 [α-p *C*$^2$H(OH)], 70.8 [β-f *C*$^2$H(OH)], 71.4 [β-f *C*$^3$H(OH)], 71.5 [β-p *C*$^5$HCH$_3$], 71.6 [β-p *C*$^4$H(OH) and *C*$^2$H(OH)], 72.5 [α-p *C*$^4$H(OH)], 75.7 [α-f *C*$^2$H(OH)], 86.1 [α-f *C*$^4$H(OH)], 86.8 [β-f *C*$^4$H(OH)], 94.2 [α-p *C*$^1$H(OH)], 94.9 [β-p *C*$^1$H(OH)], 96.3 [β-f *C*$^1$H(OH)], 100.9 [α-f *C*$^1$H(OH)]; $[\alpha]_D^{25}$ +19.1 (*c* 0.35, $H_2O$; 15 min), $[\alpha]_D^{25}$ +17.7 (*c* 0.35, $H_2O$; 24 h), {lit.[40]*ent*-$[\alpha]_D^{25}$ −17.3 (*c* 0.35, $H_2O$; 24 h)}.


## Acknowledgements

The authors wish to thank Astra-Zeneca for a studentship (R. L. N.) and New College, Oxford for a Junior Research Fellowship (A. D. S.).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