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Double diastereoselective SuperQuat glycolate aldol reactions: Application to the asymmetric synthesis of polyfunctionalised lactones

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Received 30th July 2004, Accepted 13th September 2004
First published as an Advance Article on the web 11th October 2004

Polyfunctionalised lactones with up to five contiguous stereocentres may be prepared with high stereocontrol by a double diastereoselective aldol protocol with protected homochiral α,β-dihydroxy- or α,β-γ-trihydroxyaldehydes and a chiral glycolate oxazolidinone, followed by subsequent *O*-desilylation and lactonisation.

Introduction

The aldol reaction is one of the most powerful transformations for the stereocontrolled formation of C–C bonds available to the synthetic chemist today. Stereocontrol in these reactions may be achieved through the application of chiral catalysts,[1] chiral Lewis acids[2] and chiral auxiliaries,[3] with the relationship between enolate geometry and product configuration generally well defined and understood.[4] Within this context, the glycolate aldol reaction represents a powerful transformation for the stereocontrolled formation of 1,2-diol units and has found numerous applications in total synthesis and the preparation of natural product fragments.[5] Stereocontrol in these reactions has been achieved through the use of chiral catalysts, reagents or auxiliaries. While examples of catalytic and chiral reagent controlled asymmetric glycolate aldol reactions are somewhat limited, the use of tin(II)[6] and zinc[7] catalysts and, more recently, proline organocatalysis[8] have been reported, although the use of chiral reagents has been largely confined to the use of chiral enol borinates.[9] In contrast, a number of chiral auxiliaries have been used in glycolate aldol reactions including the boron enolates of norephedrine ester,[10] 4-oxapyrone[11] and selone[12] auxilaries. The most widely used auxiliary for these reactions is arguably Evans' oxazolidinone[13] and its thio-oxazolidinethione derivatives, with highly stereoselective routes to *syn*- and *anti*-stereoisomers available by judicious choice of the Lewis acid used to generate the enolate. For example, *syn*-aldol products **2** are observed for the boron[14] and titanium[15] enolate aldol additions of glycolate oxazolidinones **1**, while conversely, the titanium[16] enolates of glycolate oxazolidinethiones and the tin(II)[17] enolates of glycolate oxazolidinones generate the corresponding *anti*- aldol products such as **3** (Fig. 1).

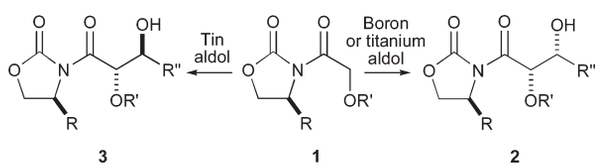


Fig. 1 Asymmetric glycolate aldol reactions using chiral oxazolidinones.

Building on this literature precedent, previous investigations from this laboratory have shown that the glycolate[18] SuperQuat derivative (*S*)-*N*-α-benzyloxyacetyl-4-benzyl-5,5-dimethyloxazolidin-2-one (*S*)-**4** readily undergoes highly stereoselective boron mediated *syn*-aldol reactions with a range of aromatic and aliphatic aldehydes, generating the corresponding *syn*-aldol products **5** in good to excellent yields as single diastereoisomers after purification. Subsequent *O*-silyl protection of the aldol products, and DIBAL reduction gives stereoselectively the corresponding *N*-1′-hydroxyalkyloxazolidin-2-ones **6**, which undergo base promoted fragmentation (K_2CO_3/MeOH) to give the highly functionalised and differentially protected α,β-dihydroxyaldehydes **7** in good yield and without loss of stereochemical integrity (Fig. 2).[19]

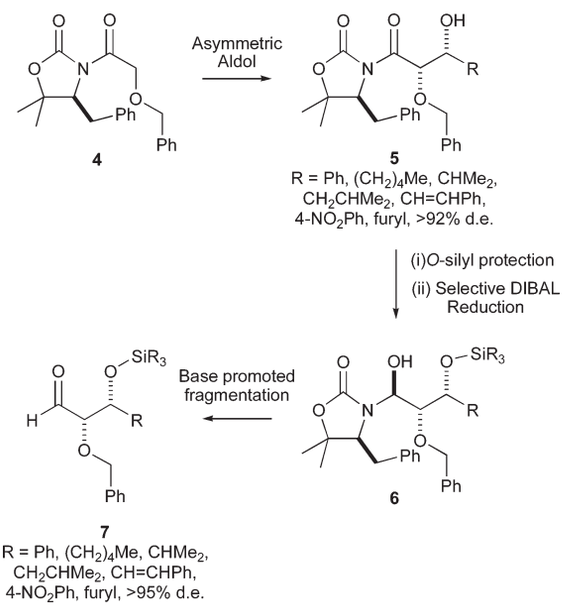


Fig. 2 Asymmetric synthesis of differentially protected α,β-dihydroxyaldehydes.

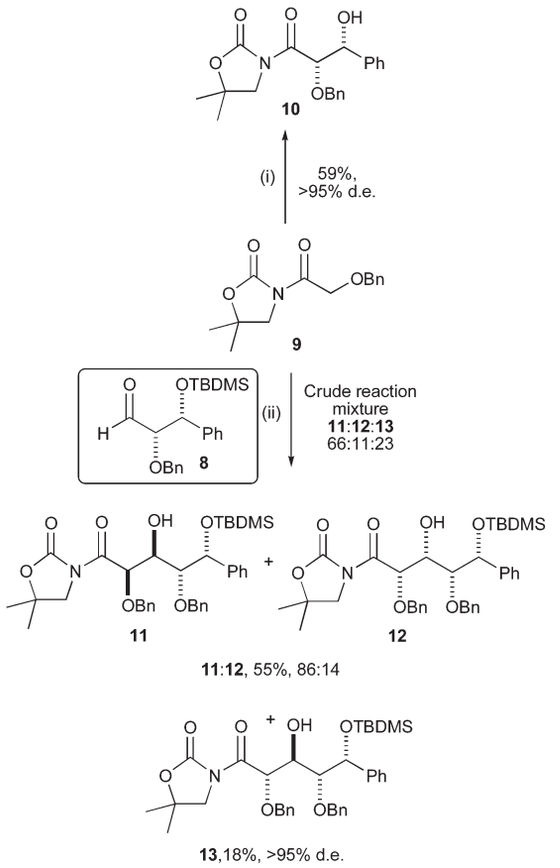
As part of our ongoing research directed toward the asymmetric synthesis of carbohydrates and highly functionalised building blocks,[20] the iteration of this asymmetric aldol strategy was investigated. The high and predictable levels of selectivity observed using oxazolidinone aldol reactions has facilitated their previous limited use in double diastereoselective aldol reactions.[21] For instance, boron mediated oxazolidinone aldol reactions with chiral aldehydes that have inherently low levels of facial control proceed under the stereocontrol of the chiral auxiliary and over-ride the low facial control of the aldehyde, giving the expected *syn*-aldol products.[22] However, if the aldehyde has a high diastereofacial bias, the oxazolidinone auxiliary may control the configuration of the newly formed α-stereocentre, while the aldehyde controls the β-stereocentre, which can result in the formation of the *anti*-aldol product.[23] We report herein that marked double asymmetric induction is found in the aldol reaction of homochiral α,β-dihydroxyaldehydes such as **7** with chiral glycolate oxazolidinones, give a rationale for the asymmetric induction observed in these systems, and demonstrate that highly functionalised and stereodefined lactones may be readily prepared from the aldol products.

DOI: 10.1039/b411724g

Results and discussion

The development of a double diastereoselective iterative aldol strategy; evaluation of the stereodirecting capability of oxazolidinone and aldehyde components

Initial studies were directed towards the development of an iterative aldol strategy, with (2*S*,3*R*)-2-benzyloxy-3-(*tert*-butyldimethylsilanyloxy)-3-phenyl–propionaldehyde **8**[19] used as a model homochiral aldehyde for this protocol. In an attempt to understand fully and predict the stereochemical outcome of the aldol reaction between a chiral aldehyde and a chiral glycolate oxazolidinone, it was necessary to quantify the diastereofacial bias of each reaction component. The inherent diastereocontrol that chiral aldehyde **8** exerts upon the aldol reaction in the formation of both the α- and β-stereogenic centres was first assessed through an aldol reaction with an achiral oxazolidinone. The desired substrate for this model study, *N*-α-benzyloxyacetyl–oxazolidin-2-one **9**, was readily prepared by treatment of 5,5-dimethyl–oxazolidin-2-one with *n*-BuLi and benzyloxyacetyl chloride in 86% yield. The diastereocontrol in the boron mediated aldol reaction with an achiral aldehyde was first assessed, with treatment of oxazolidinone **9** with Et_2BOTf followed by Hünig's base and subsequent addition of benzaldehyde giving the aldol product **10** as single diastereoisomer (>98% de) in 59% isolated yield. The relative *syn*-configuration within **10** was assigned by ^1H NMR ($J_{C(2')H–C(3')H}$ 4.5 Hz),[24] consistent with the reaction proceeding *via* the (*Z*)-boron enolate, controlling the relative configuration of the α- and β-stereogenic centres *via* a Zimmerman–Traxler transition state. With this information in hand, quantification of the asymmetric induction offered by homochiral α,β-dihydroxyaldehyde **8** in the aldol reaction with achiral oxazolidinone **9** was investigated. Boron mediated aldol reaction between aldehyde **8** and *N*-acyl–oxazolidin-2-one **9** initially proved unreliable, with incomplete conversion being observed. Storage of the hygroscopic aldehyde as a solution in DCM over 4 Å molecular sieves allowed the reaction to be driven to completion, furnishing a 66 : 11 : 23 mixture of three components **11** : **12** : **13**, with purification by chromatography affording the *anti*-aldol (2′*S*,3′*S*,4′*R*,5′*R*)-**13** in 18% yield and in >95% de, and an inseparable 86 : 14 mixture of *syn*-aldols (2′*R*,3′*S*,4′*R*,5′*R*)-**11** and (2′*S*,3′*R*,4′*R*,5′*R*)-**12** in 55% yield. Analysis of this product distribution indicates that the (*Z*)-boron enolate of **9** preferentially adds to the *Si* face of aldehyde **8** with high (89 : 11) selectivity, indicating that the chiral aldehyde exerts high levels of stereocontrol in the formation of the β-centre, while the aldehyde exercises only low stereocontrol (66 : 34) over the formation of the α-stereocentre, with addition to the *Re* face of the enolate being favoured (Scheme 1).[25]



Scheme 1 Reagents and conditions: (i) Et_2BOTf, *i*-Pr_2NEt, CH_2Cl_2, then PhCHO, −78 to 0 °C; (ii) Et_2BOTf, *i*-Pr_2NEt, CH_2Cl_2, then **8**, −78 to 0 °C.

Double diastereoselective aldol reactions for the asymmetric synthesis of polyfunctionalised lactones

With this information in hand, double asymmetric induction was anticipated for the aldol reactions between aldehyde **8** and the chiral glycolate oxazolidin-2-ones (*S*)-**4** and (*R*)-**4**.[26] As the chiral aldehyde exerts only a small (66 : 34) bias over the preferred configuration of the α-centre in the aldol reaction with achiral oxazolidinone **9**, it was predicted that the chiral oxazolidinone would exert dominant control over the preferred absolute configuration at this centre upon reaction with the chiral aldehyde. However, as both the aldehyde and the oxazolidinone exert high stereocontrol in the formation of the β-centre of the aldol products, matched and mismatched reactions with the products differing in configuration at the β-centre of the aldol products, may be expected. Furthermore, the sense of the matched and mismatched pairings could be predicted. In the reaction of the (*Z*)-boron enolate of (*R*)-glycolate oxazolidinone **4** with chiral aldehyde **8** with an inherent *Si* facial bias, the stereochemical elements controlling the formation of the β-centre are predicted to be mutually reinforcing, furnishing a single diastereoisomeric product **14**. In contrast, the reaction of the (*Z*)-boron enolate of (*S*)-glycolate oxazolidinone **4** with aldehyde **8**, the diastereofacial elements controlling the formation of the β-centre would be opposed, and a mixture of aldol products **15** and **16** would be expected (Fig. 3).

To investigate this hypothesis, homochiral aldehyde **8** was used in an aldol reaction with the (*Z*)-boron enolate of glycolate oxazolidin-2-one (*S*)-**4**,[27] affording a 57 : 43 mixture of the separable diastereoisomeric aldol products (2′*S*,3′*R*,4*S*,4′*R*,5′*R*)-**15** and (2′*S*,3′*S*,4*S*,4′*R*,5′*R*)-**16**, isolated in 35% and 34% yield respectively as single diastereoisomers after chromatographic purification. This mismatched addition is consistent with the (*Z*)-boron enolate providing the dominant stereochemical control in the aldol reaction, with addition to aldehyde **8** occurring exclusively on the *Si* face of the enolate, giving the aldol products that only differ in configuration at the β-centre. In contrast, the aldol addition between (*R*)-**4** and aldehyde **8** furnished (2′*R*,3′*S*,4*R*,4′*R*,5′*R*)-**14** as the sole aldol product in >98% de, giving **14** in 54% isolated yield and as a single diastereoisomer after chromatography (Scheme 2).

The generality of this double diastereoselective aldol protocol was next investigated, with (2*S*,3*S*)-2-benzyloxy-3-(*tert*-butyldimethylsilanyloxy)-3-furyl–propionaldehyde **17** (>95% de)[19] used in the boron mediated aldol reaction with (*R*)- and (*S*)-glycolate oxazolidinones **4**. Generation of the (*Z*)-boron enolate of (*R*)-glycolate oxazolidinone **4** and treatment with aldehyde **17** gave aldol product **18** as a single diastereoisomer.[28] In contrast, addition of the (*Z*)-boron enolate of (*S*)-glycolate oxazolidinone **4** to aldehyde **17** gave a 58 : 42 mixture of the separable diastereoisomeric aldol products **19** and **20**, which were isolated in 39% and 32% yield respectively as single diastereoisomers after chromatographic purification (Scheme 3).[28]

In order to determine the relative configurations within the aldol products arising from these double diastereoselective aldol

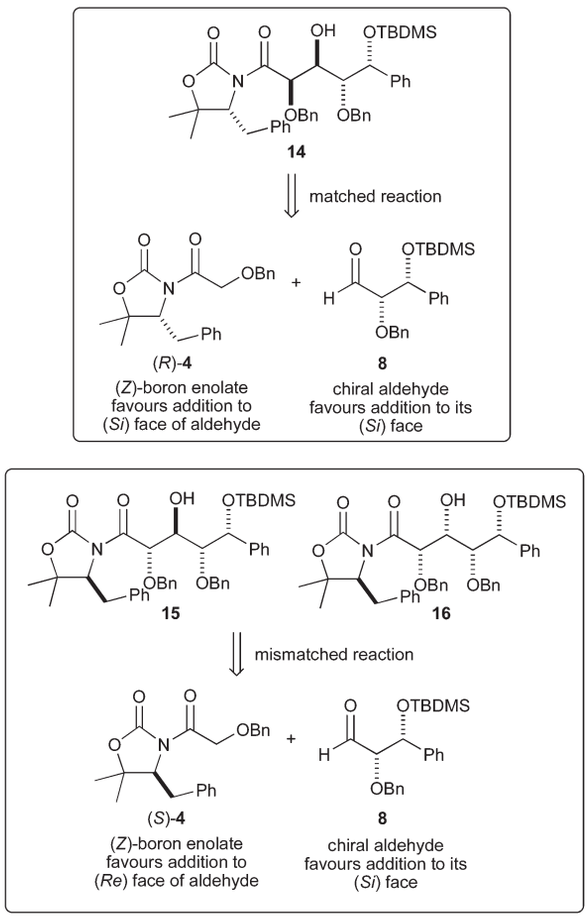
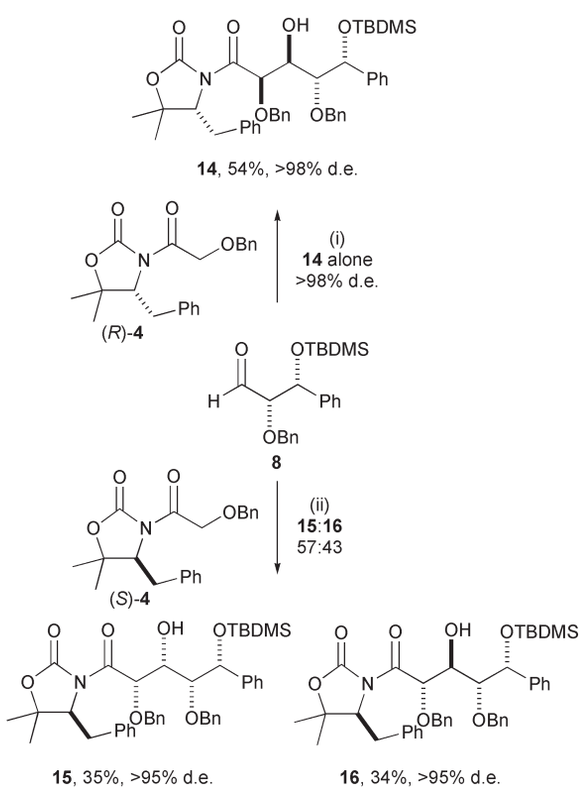
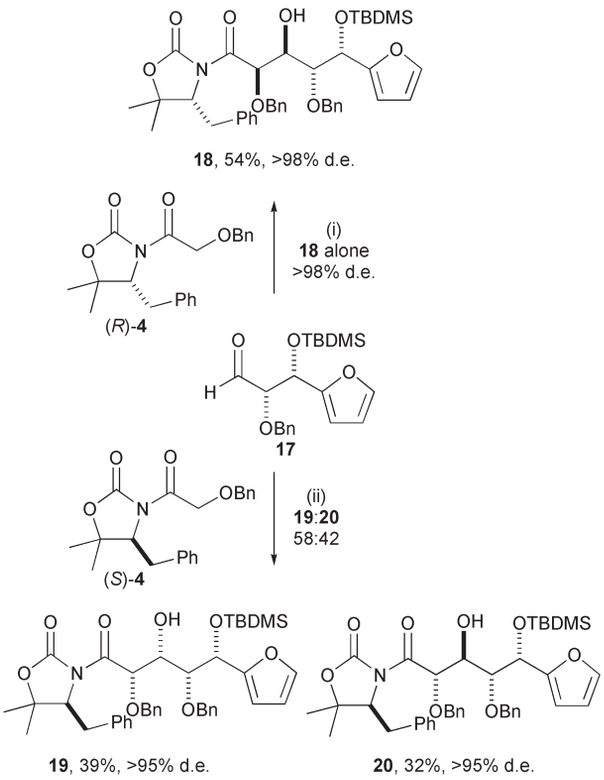


Fig. 3 Proposed matched and mismatched reaction pairings in the double asymmetric aldol reaction.



Scheme 2 Reagents and conditions: (i) (*R*)-**4**, Et_2BOTf, *i*-Pr_2NEt, CH_2Cl_2, −78 °C to 0 °C (ii) (*S*)-**4**, Et_2BOTf, *i*-Pr_2NEt, CH_2Cl_2, −78 °C to 0 °C.

reactions, it was envisaged that treatment of the aldol products with a fluoride source would induce *O*-desilylation and concomitant lactonisation, giving homochiral poly-substituted lactones

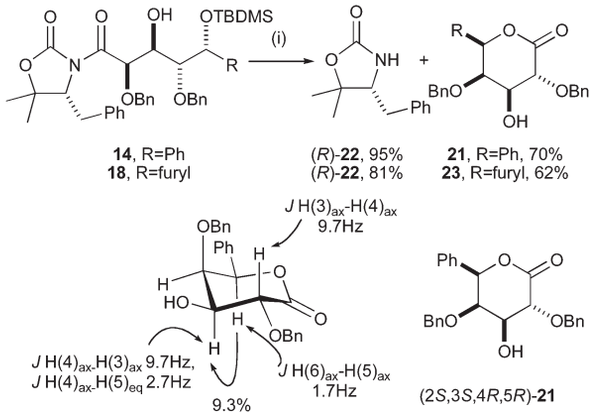


Scheme 3 Reagents and conditions: (i) (*R*)-**4**, Et_2BOTf, *i*-Pr_2NEt, CH_2Cl_2, −78 °C to 0 °C (ii) (*S*)-**4**, Et_2BOTf, *i*-Pr_2NEt, CH_2Cl_2, −78 °C to 0 °C.

that would be amenable to configurational analysis by NMR spectroscopy. Initial studies concentrated upon deprotection and lactonisation within the "matched" reaction series, with model studies conducted on aldol product **14**. Treatment of aldol **14** with TBAF in THF at both 0 °C and rt resulted in a complex mixture of products, presumably due to decomposition upon attempted deprotection due to the highly basic nature of the fluoride ion. Buffering the solution with acetic acid proved successful,[29] giving the desired lactone (2*R*,3*S*,4*R*,5*R*)-**21** as a single diastereoisomer in 70% yield, and returning the auxiliary (*R*)-**22** in 95% yield, after chromatography. The relative configuration within lactone **21** was assigned on the basis of ^1H NMR spectroscopy, which indicated that lactone **21** adopts a chairlike conformation in solution. Analysis of ^1H–^1H coupling constants was used to indicate the typical axial and equatorial relationships between the C(2)H, C(3)H, C(4)H and C(5)H ring protons, with NOE difference analysis confirming the 1,3 diaxial relationship between C(3)H and C(5)H. The absolute (2*R*,3*S*,4*R*,5*R*)-configuration within lactone **21** was then assigned upon the known stereodirecting preference of oxazolidinone auxiliaries in simple glycolate aldol reactions.[30] Similarly, treatment of C(5′)-furyl aldol **18** with TBAF in AcOH generated the corresponding lactone **23** in 62% isolated yield as a single stereoisomer and returned the oxazolidinone auxiliary in 81% yield, with the relative configuration within lactone **23** assigned by analogy to that within **21** (Scheme 4).

Having developed a protocol for desilyation and lactonisation in the matched aldol series, this methodology was extended to the mismatched aldol products. Treatment of the major diastereoisomers **15** and **19** arising from the mismatched reactions with TBAF in AcOH gave the corresponding lactones **24** and **25** in 85% and 80% yield respectively, and returned the auxiliary in 83% and 90% yield. The relative configuration within lactone **24** was determined by a combination of ^1H NMR and NOE difference analysis, with the absolute configuration assigned relative to the known configuration at C(5) and C(6). The relative and absolute configuration within lactone **25** was assigned by analogy (Scheme 5).

In an attempt to prepare a crystalline derivative of lactones **24** and **25** for X-ray crystallographic analysis, derivatisation of the free hydroxyl functionality within lactones **24** and **25** by treatment



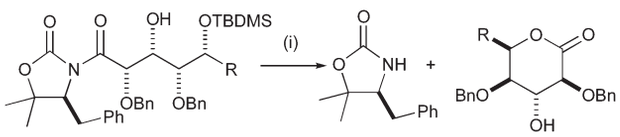
14, R=Ph
18, R=furyl

(*R*)-**22**, 95%
(*R*)-**22**, 81%

21, R=Ph, 70%
23, R=furyl, 62%

(2*S*,3*S*,4*R*,5*R*)-**21**

Scheme 4 Reagents and conditions: (i) TBAF, AcOH, THF, rt.



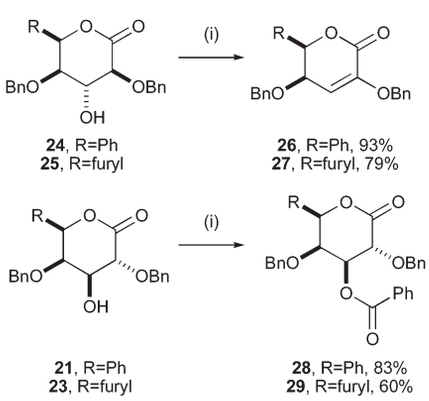
15, R=Ph
19, R=furyl

(*S*)-**22**, 83%
(*S*)-**22**, 90%

24, R=Ph, 85%
25, R=furyl, 80%

Scheme 5 Reagents and conditions: (i) TBAF, AcOH, THF, rt.

with benzoyl chloride, as previously described by Clive *et al.* was investigated.[31] However, treatment of both lactones **24** and **25** with benzoyl chloride resulted in elimination, furnishing the corresponding αβ-unsaturated lactones **26** and **27** in good yield after chromatography. In order to ascertain whether elimination under these conditions was general to all lactones, or a consequence of the relative configuration within them, treatment of the lactones **21** and **23** under identical conditions gave selectively the corresponding *O*-benzoyl lactones **28** and **29** in 83% and 60% yield, with no evidence of elimination, confirming that the relative configuration within each of the pairs of aldol diastereoisomers **14** and **18** and **15** and **19** is identical, but that the relative configuration between the pairs differs (Scheme 6).



24, R=Ph
25, R=furyl

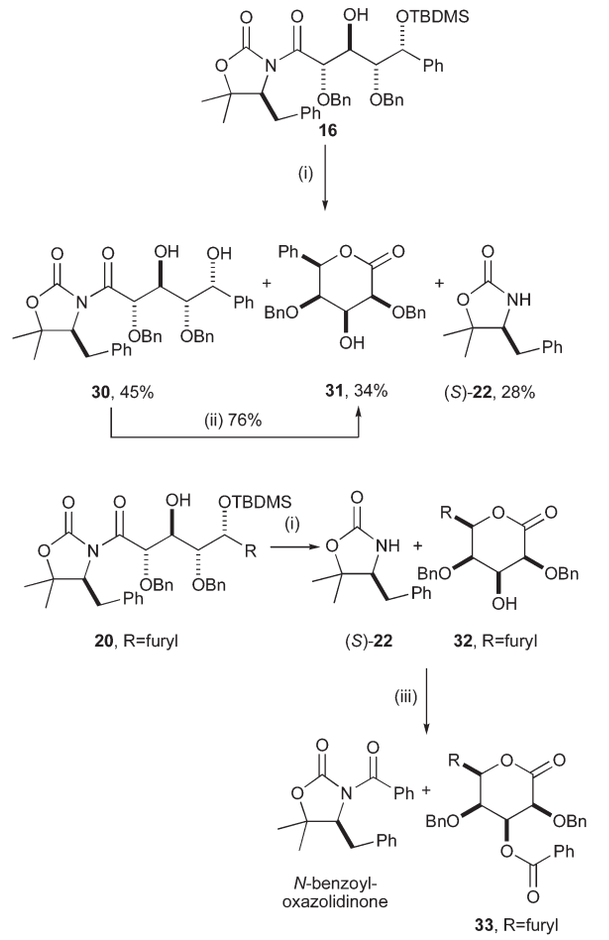
26, R=Ph, 93%
27, R=furyl, 79%

21, R=Ph
23, R=furyl

28, R=Ph, 83%
29, R=furyl, 60%

Scheme 6 Reagents and conditions: (i) PhCOCl, NEt_3, DMAP, CH_2Cl_2.

Treatment of the minor diastereoisomer **16** from the mismatched aldol reaction of aldehyde **8** with TBAF in AcOH gave a mixture of the corresponding lactone (2*S*,3*S*,4*R*,5*R*)-**31** in 34% isolated yield, the *O*-deprotected aldol product **30** in 45% yield and auxiliary (*S*)-**22** in 28% yield after chromatographic purification. Further conversion of the desilylated aldol adduct **30** to the lactone **31** was achieved by refluxing in toluene, giving lactone **31** in 76% yield and returning oxazolidinone (*S*)-**22** in 99% yield. The relative configuration within lactone **31** was determined by ^{1}H NMR and NOE difference analysis, with the absolute configuration assigned relative to the known configuration at C(5) and C(6). Treatment of the minor diastereoisomer **20** with TBAF under identical conditions furnished an inseparable mixture of the desired lactone **32** and the auxiliary (*S*)-**22**, which upon treatment with benzoyl chloride furnished a partially separable mixture of (*S*)-3-benzoyl-4-benzyl-5,5-dimethyl–oxazolidin-2-one and *O*-benzoylated lactone **33** which proved amenable to NOE difference studies, allowing determination of the relative configuration within (2*S*,3*S*,4*R*,5*S*)-**33** (Scheme 7).

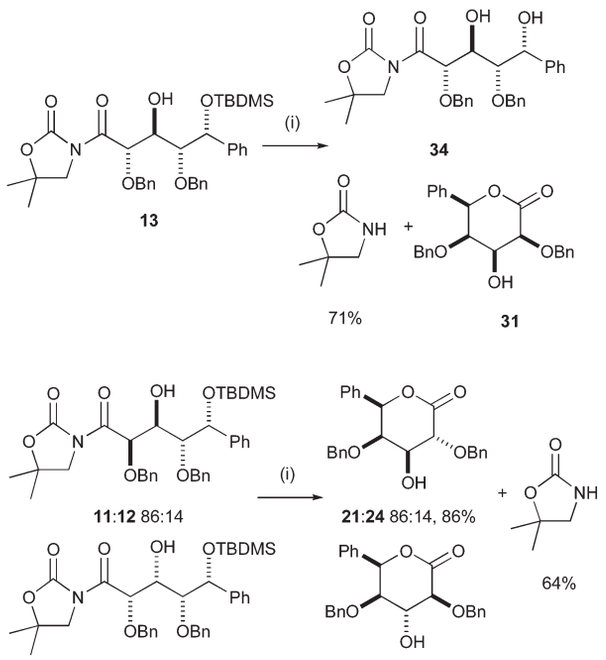


Scheme 7 Reagents and conditions: (i) TBAF, AcOH, THF, rt; (ii) toluene, Δ; (iii) PhCOCl, NEt_3, DMAP, CH_2Cl_2.

Having demonstrated that the preparation of lactones **24**–**33** facilitated their configurational analysis, the relative configuration within the aldol products derived from reaction of the achiral oxazolidinone **9** with the chiral aldehyde **8** were established by chemical correlation. Treatment of the 86 : 14 mixture of *syn*-aldols (2′*R*,3′*S*,4′*R*,5′*R*)-**11** and (2′*S*,3′*R*,4′*R*,5′*R*)-**12** with TBAF in AcOH gave an inseparable 86 : 14 mixture of the lactones (2*R*,3*S*,4*R*,5*R*)-**21** and (2*S*,3*R*,4*R*,5*R*)-**24** in 86% yield. Treatment of the *anti*-aldol **13** with TBAF and acetic acid gave an inseparable 66 : 34 mixture of the desilylated aldol **34** and the corresponding lactone **31**, consistent with the relative configuration within the *anti*-aldol **13** disfavouring the intramolecular cyclisation (Scheme 8).

Models for double diastereoselective aldol reactions

The prediction of the stereochemical course of nucleophilic addition to chiral α-substituted carbonyl components has been much studied, with the seminal contributions of Cram and Elhafez,[32] Cornforth *et al.*,[33] Karabatsos,[34] Felkin *et al.*[35] and Anh and Eisenstein[36] having been used extensively to delineate the contributing factors to stereocontrol in these reactions.[37] While these models are usually used to rationalise the inherent diastereofacial bias of the aldehyde, a range of groups have investigated the aldol reactions of α-oxygen substituted aldehydes with either boron, lithium or titanium enolates derived from achiral donors, and have shown that high levels of *syn*-C(2)–C(3)- and *anti*-C(3)–C(4)-selectivity is usually noted.[38] Recent reports by Evans *et al.*[39] have studied extensively the origin of this asymmetric induction, with the modi-



Scheme 8 Reagents and conditions: (i) TBAF, AcOH, THF, rt.

fied Cornforth dipolar model receiving increasing attention over the previously accepted polar Felkin–Anh model for the reaction of (*Z*)-enolates, due to destabilising *syn*-pentane interactions in the reactive conformer of the Felkin–Anh model (Fig. 4).[40]

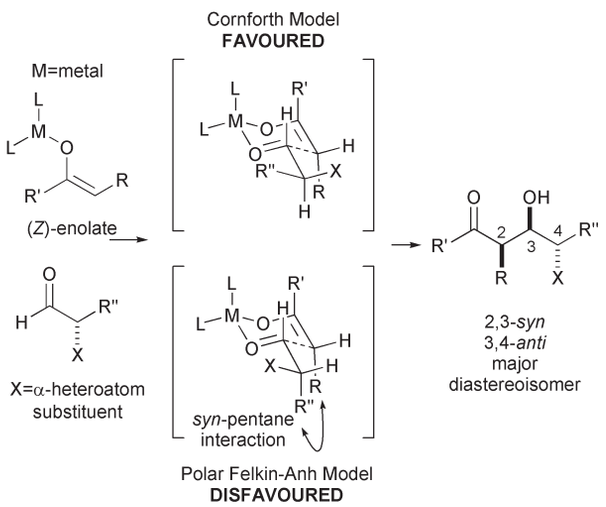


Fig. 4 Comparison of Cornforth and Felkin–Anh models for the reaction of a metallated (*Z*)-enolate and an α-heteroatom substituted aldehyde.

While these models consider the predominant effect of the α-heteroatom substituted stereogenic centre upon the preferred facial selectivity upon addition to the aldehyde, a β-stereocentre may also have an effect upon the preferred aldehyde facial selectivity, and the stereochemical mutually reinforcing potential of combinations of α- and β-stereocentres has also been explored.[41] With these precedents in mind, simple models that account for the stereochemical outcome of these double diastereoselective asymmetric aldol reactions may be rationalised. In the matched case, the formation of a single diastereoisomeric product with *syn*-selectivity between the newly formed α- and β-sterogenic centres is consistent with the reaction proceeding *via* a chelated transition state between the (*Z*)-boron enolate of the glycolate oxazolidinone and the aldehyde. Upon the assumption that addition to the aldehyde proceeds under the predominant influence of the α-stereocentre *via* the preferred Cornforth conformation, a distinct preference for nucleophilic addition to its *Si* face can be predicted, consistent with the results of the aldol reaction of aldehyde **8** and achiral oxazolidinone **9**. In this transition state, the stereocontrol of the enolate (high stereocontrol at both α- and β-stereocentres) and the aldehyde (high stereocontrol at β-stereocentre) are therefore additive, with addition of the *Re* face of the enolate to the *Si* face of the aldehyde giving a single diastereoisomeric product (Fig. 5).[42]

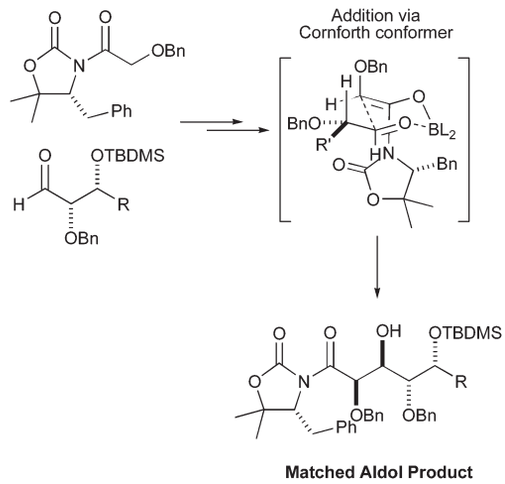


Fig. 5 Proposed transition state for the matched double diastereoselective aldol reactions.

In the mismatched reaction manifold, the formation of two diastereoisomeric products is consistent with the reaction proceeding *via* two competing transition states, in which the stereochemical elements controlling the stereoselective formation of the β-centre are opposed. Assuming that the reaction occurs *via* the (*Z*)-boron enolate and a chelated transition state, the formation of the major diastereoisomer in the mismatched case is consistent with the reaction proceeding under the predominant control of the oxazolidinone *via* the Zimmerman–Traxler chair-type transition state **35**, with addition of the *Si* face of the enolate to the *Re* face of the aldehyde (contrary to that expected under Cornforth control) giving the *syn*-C(2)–C(3) and *syn*-C(3)–C(4) configuration. The formation of the minor *anti*-C(2)–C(3) and *anti*-C(3)–C(4) diastereoisomer is consistent with addition of the *Si* face of the oxazolidinone enolate to the Cornforth favoured *Si* face of the aldehyde. While aldol reaction *via* chair transition state **37** is disfavoured by 1,3 diaxial interactions between the oxazolidinone and aldehyde alkyl substituents, addition *via* the boat transition state **36** is preferred, and competes effectively with the alternative chair transition state **35**, resulting in low diastereoselectivity (Fig. 6).

Double diastereoselective aldol reactions: application to the asymmetric synthesis of a differentially protected polyhydroxylated lactone

Having shown that double diastereoselection is observed in the aldol reaction of aldehydes such as **8** and **17** with chiral glycolate oxazolidinones, a demonstration of the versatility of this protocol was undertaken. It was envisaged that aldol reaction of glycolate oxazolidinones (*S*)-**4** and (*R*)-**4** with the aldehyde **38** prepared from mannitol[43] would exhibit double asymmetric induction, with subsequent formation of the aldehyde from the 'matched' reaction, and iteration of the aldol protocol, giving rise to a polyhydroxylated lactone after deprotection. Upon the assumption that addition to aldehyde **38** proceeds under Cornforth control, it was predicted that the aldehyde would inherently prefer enolate addition to its *Si* face, and should therefore be "matched" upon reaction with the (*Z*)-boron enolate of (*S*)-**4**, and mismatched upon reaction with the (*Z*)-boron enolate of (*R*)-**4**. In practice, boron mediated aldol addition of (*S*)-**4** to aldehyde **38** afforded the *syn*-product (1′*R*,2′*S*,3′*S*,4*S*)-**39** in 93% de, with chromatographic purification giving **39** as a single diastereoisomer in 73% yield. The absolute configuration within aldol **39** was established by conversion to the known triol **41**. Reduction of **39** with lithium borohydride afforded the cor-

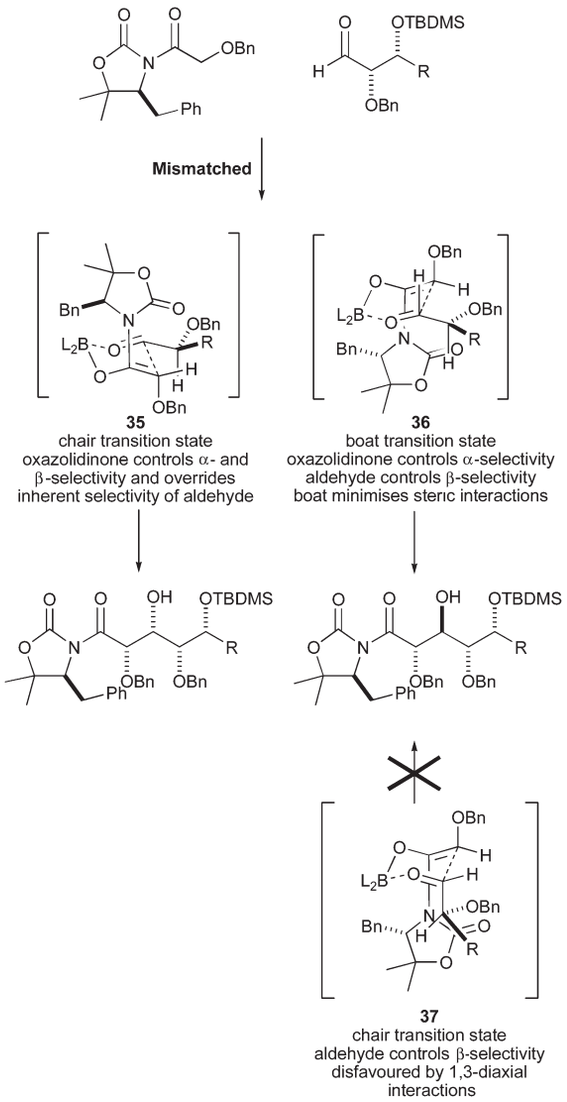
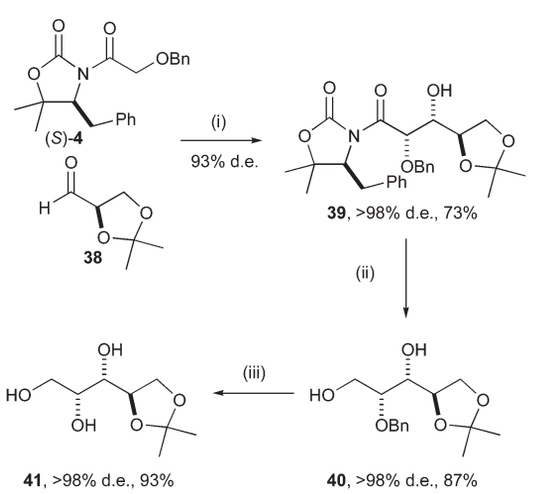


Fig. 6 Proposed transition states for the mismatched double diastereoselective aldol reactions.

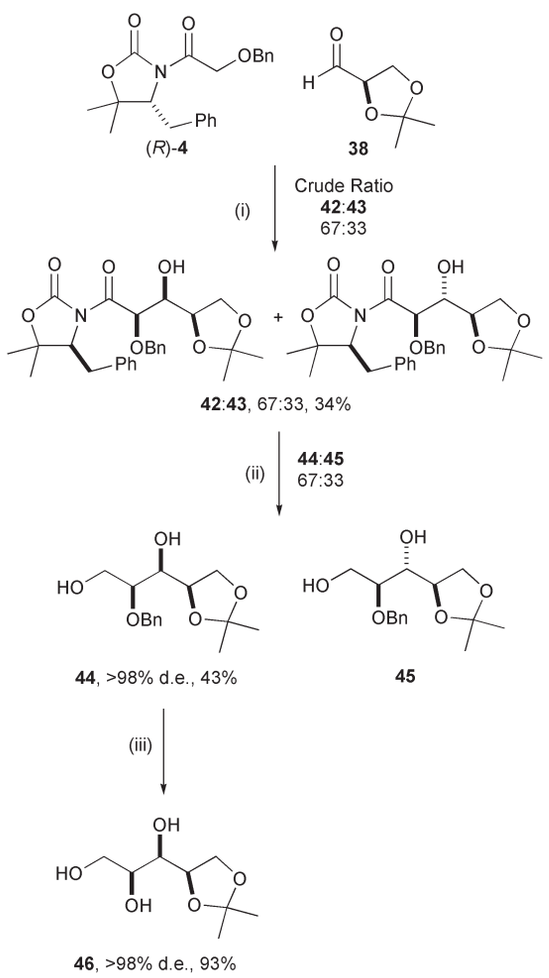
responding diol **40** in 87% yield, with subsequent hydrogenolysis giving the known triol **41** in 93% yield with comparable spectroscopic properties to the literature {$[a]_D^{25}$ −0.69 (c = 1.2, EtOH), lit.[44] $[a]_D^{25}$ −0.63 (c = 2.35, EtOH)} (Scheme 9).

In contrast, the mismatched aldol reaction of (*R*)-**4** and **38** proved to be highly capricious, and did not proceed to completion (with respect to the enolate) even in the presence of a large excess



Scheme 9 Reagents and conditions: (i) Et_2BOTf, *i*-Pr_2NEt, **38**, CH_2Cl_2, −78–0 °C; (ii) $LiBH_4$, H_2O, Et_2O; (iii) Pd/C, AcOH, MeOH, H_2 (1 atm).

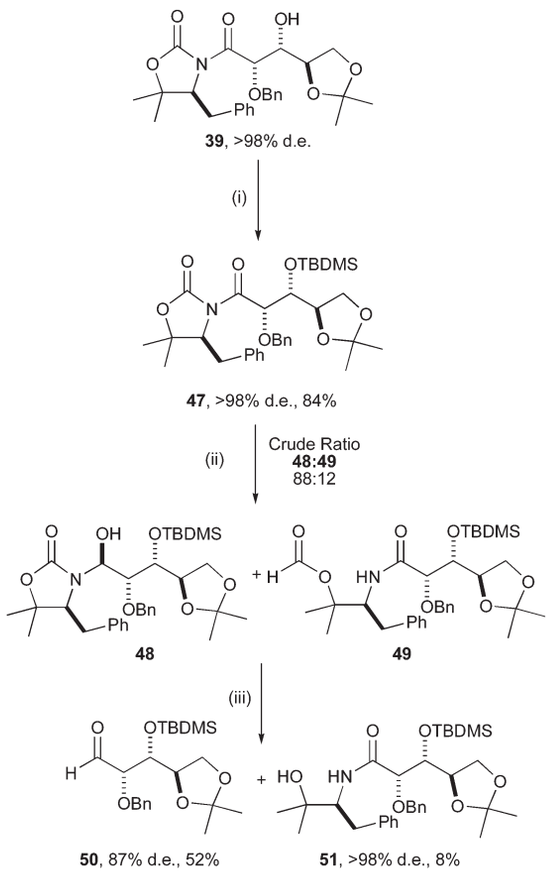
of the aldehyde, giving a 67 : 33 mixture of two diastereoisomers in ~40% conversion.[45] Chromatographic purification furnished an inseparable 67 : 33 mixture of **42** and **43** in 34% combined yield. Reduction of the 67 : 33 mixture of **42** and **43** with lithium borohydride gave a 67 : 33 mixture of diols **44** and **45**, with subsequent purification furnishing the diol **44** as a single diastereoisomer in 43% yield, and a mixture of **44** and **45** in 44% yield. Hydrogenolysis of the homogenous diol **44** afforded the known triol **46** in 93% yield with comparable spectroscopic properties to the literature {$[a]_D^{25}$ +8.2 (c = 0.9, EtOH), lit.[44] $[a]_D^{25}$ +8.31 (c = 3.05, EtOH)}, allowing unambiguous assignment of the configuration within the major diastereoisomeric aldol adduct. Repeated chromatography of the mixture of the diols **44** and **45** failed to isolate a homogenous sample of the minor diastereoisomeric diol **45**. The *anti*-relative configuration within **45** was therefore assigned by analogy to the minor diastereoisomer formed in the previously observed mismatched aldol reactions, upon the assumption that the oxazolidinone controls the configuration at the α-centre and the aldehyde in the β-centre in the aldol reaction (Scheme 10).



Scheme 10 Reagents and conditions: (i) Et_2BOTf, *i*-Pr_2NEt, RCHO, CH_2Cl_2: (ii) $LiBH_4$, H_2O, Et_2O; (iii) Pd/C, AcOH, MeOH, H_2 (1 atm).

Given the unreliable nature, and low stereoselectivity, of the mismatched aldol reaction of (*R*)-**4** and **38**, no further studies were carried out on this system. However, iteration of the aldol reaction with the aldehyde derived from the matched aldol reaction was investigated. Attempted silylation of **39** with TBDMSOTf led to decomposition, while treatment with TBDMSCl at rt returned only starting material. However, treatment of **39** with TDBMSCl in the presence of 4 Å molecular sieves followed by warming to 60 °C resulted in the formation of the desired TBDMS ether **47** in 84% yield. Treatment of **47** with DIBAL furnished a 88 : 12 mixture of the stable 1′-hydroxyalkyloxazolidin-2-one **48**[46,47] and the formate ester **49** (the product of endocyclic cleavage), which after chromatographic purification gave an inseparable 88 : 12 mixture

of **48** (>98% de) and **49** in 68% combined yield. Treatment of the inseparable mixture of **48**–**49** with K_2CO_3 in MeOH–H_2O resulted in fragmentation of **48** to the desired aldehyde **50** and hydrolysis of the formate ester **49** to the corresponding alcohol **51**, with purification affording the aldehyde **50** in 52% yield and 87% de, and the alcohol **51** in 8% yield (Scheme 11).



Scheme 11 Reagents and conditions: (i) TBDMSCl, imidazole, DMAP, DMF, 60 °C; (ii) DIBAL, CH_2Cl_2, −78 °C; (iii) K_2CO_3, MeOH, H_2O, rt.

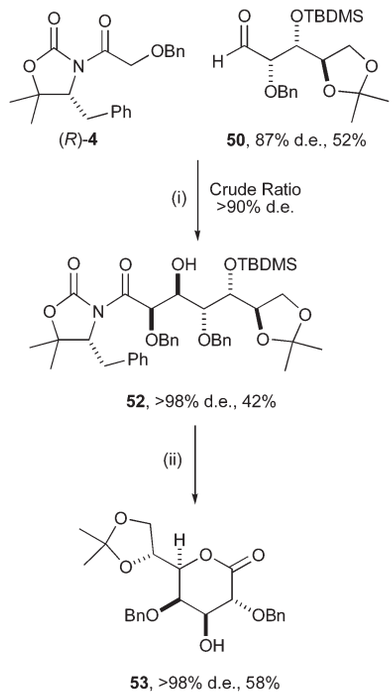
With aldehyde **50** (87% de) in hand, its iterative aldol reaction in the predicted matched series was investigated, with addition of the (*Z*)-boron enolate of (*R*)-glycolate oxazolidinone **4** to aldehyde **50** evaluated, giving **52** as a single diastereoisomer in 42% yield after purification.[48] Treatment of **52** with TBAF in AcOH gave, after *O*-desilylation and concomitant lactonisation, the polyfunctionalised lactone **53** that contains five contiguous stereocentres as a single diastereoisomer in 58% yield (Scheme 12).

In conclusion, we have shown that polyfunctionalised lactones with up to five contiguous stereocentres may be prepared with high stereocontrol by a double diastereoselective aldol protocol with protected homochiral α,β-dihydroxy- or α,β,γ-trihydroxy-aldehydes and a homochiral glycolate oxazolidinone, followed by subsequent *O*-desilylation and lactonisation. The further application of this methodology for the asymmetric total synthesis of carbohydrates and derivatives thereof is currently underway within our laboratory.

Experimental

General experimental

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



Scheme 12 Reagents and conditions: (i) Et_2BOTf, *i*-Pr_2NEt, **50**, CH_2Cl_2: (ii) TBAF, AcOH, THF, rt.

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 (δ_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 the Bruker DPX-200 (200 MHz), the Bruker AVANCE AV-400 (400 MHz) or the 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 (δ_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 the 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 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. Specific 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 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 a *N*-acyl-oxazolidin-2-one to an aldehyde. 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*-acyl–oxazolidin-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 (*v*:*v* 1:1), 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 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*-acyl–oxazolidin-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 3 for the acylation of lactones with PhCOCl. Et_3N (2.5 eq), PhCOCl (1.3 eq) and DMAP (0.1 eq) were added sequentially to a solution of lactone (1 eq) in CH_2Cl_2 at ambient temperature. After stirring for 18 h, the reaction mixture was quenched with saturated, aqueous NH_4Cl solution, extracted with CH_2Cl_2, washed with dilute aqueous $NaHCO_3$ and brine and dried. The crude product was purified by column chromatography.

Preparation of 3-(2′-benzyloxyacetyl)-5,5-dimethyl-oxazolidin-2-one 9. *n*-BuLi (5.74 mL, 14.35 mmol) was added to a stirred solution of 5,5-dimethyl–oxazolidin-2-one (1.50 g, 13.04 mmol) in THF at −78 °C. After 15 min, $PhCH_2OCH_2COCl$ (2.70 mL, 16.95 mmol) was added dropwise *via* syringe and stirred at −78 °C for 15 min before being warmed to ambient temperature. After 2 h, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and acetic acid, extracted with EtOAc, washed sequentially with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo.* Purification by column chromatography furnished **9** as a white solid (2.95 g, 11.22 mmol, 86%).

9: R_f 0.2 [2:1 pentane–Et_2O]; mp 63–64 °C [pentane–Et_2O]; δ_H (200 MHz, $CDCl_3$) 1.50 [6H, s, $C(CH_3)_2$], 3.75 [2H, s, NCH_2], 4.67 [2H, s, CH_2OCH_2Ph], 4.70 [2H, s, CH_2OCH_2Ph], 7.27–7.40 [5H, m, Ph*H*]; δ_C (50 MHz, $CDCl_3$) 27.3 [$C(CH_3)_2$], 53.8 [NCH_2], 69.5 [CH_2OCH_2Ph], 73.4 [CH_2OCH_2Ph], 80.1 [$C(CH_3)_2$], 127.9 [*p-Ph*], 128.0, 128.5 [*m*/*o-Ph*], 137.2 [*i-Ph*], 152.6 [*C*=O endocyclic], 170.5 [*C*=O exocyclic]; ν_{max}(KBr disc, cm^{-1}) 1773 [C=O endocyclic], 1717 [C=O exocyclic]; $C_{14}H_{17}NO_4$ requires C 63.9, H 6.5, N 5.3%; found C 63.9, H 6.5, N 5.3%; *m*/*z* APCI+ 116 [100%, SQH^+], 264 [2%, MH^+].

Preparation of 3-(2′-benzyloxy-3′-hydroxy-3′-phenyl)-propionyl)-5,5-dimethyl-oxazolidin-2one 10. Following representative procedure 1, CF_3SO_3H (0.15 mL, 1.71 mmol), Et_3B (1.71 mL, 1.71 mmol), **9** (300 mg, 1.14 mmol), *i*-Pr_2NEt (0.28 mL, 1.80 mmol) and PhCHO (0.14 mL, 1.37 mmol) in CH_2Cl_2 (20 mL) furnished **10** (248 mg, 0.67 mmol, 59%) as a white solid after column chromatography.

10: R_f 0.23 [1:2 30–40 °C petrol–Et_2O]; mp 59–60 °C [30–40 °C petrol–Et_2O]; δ_H (400 MHz, $CDCl_3$) 1.25 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.43 [3H, s, $C(CH_3)_A(CH_3)_B$], 3.49–3.59 [2H, ABq, *J* 11.0, NCH_2], 4.49–4.60 [2H, ABq, *J* 11.6, $CHOCH_2Ph$], 5.03 [1H, d, *J* 4.5, CH(OH)], 5.51 [1H, d, *J* 4.5, $CHOCH_2Ph$], 7.16–7.47 [10H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 27.0, 27.1 [$C(CH_3)_2$], 54.1 [NCH_2], 73.3 [$CHOCH_2Ph$], 75.0 [*C*H(OH)], 79.3 [$C(CH_3)_2$], 80.9 [*C*HOCH_2Ph], 128.0, 128.1 [*p-Ph*], 126.6, 128.2, 128.3, 128.4 [*m*/*o-Ph*], 139.0, 136.74 [*i-Ph*], 152.2 [*C*=O endocyclic], 171.1 [*C*=O exocyclic]; ν_{max}(KBr disc, cm^{-1}) 1764 [C=O endocyclic], 1709 [C=O exocyclic]; HRMS $C_{21}H_{24}NO_5$ [MH^+] requires 370.1654, found 370.1654; *m*/*z* ES+ 352 [100%, MH^+–H_2O], 370 [25%, MH^+], 387 [75%, MNH_4^+], 392 [97%, MNa^+].

Preparation of (2′*S*,3′*S*,4′*R*,5′*R*)-3-[2′,4′-bis-benzyloxy-5′-(tert-butyl-dimethyl-silanyloxy)-3′-hydroxy-5′-phenyl-pentanoyl]-5,5-dimethyl-oxazolidin-2-one (2′*S*,3′*S*,4′*R*,5′*R*)-13, (2′*R*,3′*S*,4′*R*,5′*R*)-3-[2′,4′-bis-benzyloxy-5′-(*tert*-butyl-dimethyl-silanyloxy)-3′-hydroxy-5′-phenyl-pentanoyl]-5,5-dimethyl-oxazolidin-2-one (2′*R*,3′*S*,4′*R*,5′*R*)-11 and (2′*S*,3′*R*,4′*R*,5′*R*)-3-[2′,4′-bis-benzyloxy-5′-(*tert*-butyl-dimethyl-silanyloxy)-3′-hydroxy-5′-phenyl-pentanoyl]-5,5-dimethyl-oxazolidin-2-one (2′*S*,3′*R*,4′*R*,5′*R*)-12. Following representative procedure 1, CF_3SO_3H (0.15 mL, 1.70 mmol), Et_3B (1.70 mL, 1.70 mmol), **9** (370 mg, 1.42 mmol), *i*-Pr_2NEt (0.35 mL, 1.99 mmol) and **8** (537 mg, 1.45 mmol) in CH_2Cl_2 (30 mL) furnished a 23:66:11 mixture of **13**:**11**:**12** which after purification by column chromatography gave **13** (165 mg, 0.26 mmol, 18%) as a pale yellow oil and a 86:14 mixture of **11**:**12** (495 mg, 0.78 mmol, 55%) as a clear colourless oil.

13: R_f 0.33 [3:1 40–60 °C petrol–Et_2O]; δ_H (400 MHz, $CDCl_3$) −0.17 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.07 [3H, s, $Si(CH_3)_A(CH_3)_B$], 0.92 [9H, s, $SiC(CH_3)_3$], 1.06 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.32 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.78 [1H, d, *J* 10.7, NCH_AH_B], 3.30 [1H, d, *J* 10.7, NCH_AH_B], 3.31 [1H, d, *J* 7.8, CH(O*H*)], 3.77 [1H, dd, *J* 7.0, 4.5, C*H*OCH_2Ph.CH(OTBDMS)], 4.02–4.07 [1H, m, C*H*(OH)], 4.20 [1H, d, *J* 10.5, $CHOCH_AH_BPh$], 4.39 [1H, d, *J* 10.5, $CHOCH_AH_BPh$], 4.51 [1H, d, *J* 11.5, $CHOCH_CH_DPh$], 4.73 [1H, d, *J* 11.5, $CHOCH_CH_DPh$], 5.05 [1H, d, *J* 4.5, C*H*(OTBDMS)], 5.34 [1H, d, *J* 3.4, CO.C*H*OCH_2Ph], 7.20–7.43 [15H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) −5.2, −4.6 [$Si(CH_3)_2$], 18.1 [$SiC(CH_3)_3$], 25.8 [$SiC(CH_3)_3$], 26.7 [$C(CH_3)_2$], 53.7 [NCH_2], 72.6 [*C*H(OH)], 73.2, 73.9 [2 × $CHOCH_2Ph$], 74.2 [*C*H(OTBDMS)], 77.9 [CO.*C*$HOCH_2Ph$], 79.2 [$C(CH_3)_2$], 82.8 [$CHOCH_2Ph$.CH(OTBDMS)], 126.9, 127.7, 128.0, 128.2, 128.3, 128.4 [*m*/*o-Ph*], 127.3, 127.4 [*p-Ph*], 137.6, 138.5, 141.4 [*i-Ph*], 152.5 [*C*=O endocyclic], 170.5 [*C*=O exocyclic]; ν_{max}(thin film, cm^{-1}) 3450 [O–H], 1774 [C=O endocyclic], 1711 [C=O exocyclic]; $C_{36}H_{47}NO_7Si$ requires C 68.2, H 7.5, N 2.2%, found C 68.3, H 7.5, N 2.2%; $[\alpha]_D^{25}$ −51.0 (*c* = 1.25, $CHCl_3$); *m*/*z* LD+ (MALDI) 656, 657 [100%, 40%, MNa^+].

11–**12**: R_f 0.22 [3:1 30–40 °C petrol–Et_2O]; δ_H (400 MHz, $CDCl_3$) −0.23 [3H, s, $Si(CH_3)_A(CH_3)_B$ (**12**)], −0.136 [3H, s, $Si(CH_3)_A(CH_3)_B$ (**11**)], −0.01 [3H, s, $Si(CH_3)_A(CH_3)_B$ (**12**)], 0.02 [3H, s, $Si(CH_3)_A(CH_3)_B$ (**11**)], 0.82 [9H, s, $SiC(CH_3)_3$ (**12**)], 0.89 [9H, s, $SiC(CH_3)_3$ (**11**)], 1.26 [3H, s, $C(CH_3)_A(CH_3)_B$ (**12**)], 1.36 [3H, s, $C(CH_3)_A(CH_3)_B$ (**11**)], 1.40 [3H, s, $C(CH_3)_A(CH_3)_B$ (**12**)], 1.45 [3H, s, $C(CH_3)_A(CH_3)_B$ (**11**)], 3.34 [1H, d, *J* 10.9, NCH_AH_B (**12**)], 3.55 [1H, d, *J* 10.9, NCH_AH_B (**12**)], 3.59–3.66 [2H, ABq, *J* 10.9, NCH_2 (**11**)], 3.72 [1H, dd, *J* 8.9, 2.9, C*H*OCH_2Ph.CHPh (**11**)], 3.84–3.86 [1H, m, C*H*OCH_2Ph.CHPh (**12**)], 4.11 [1H, dd, *J* 2.4, 8.9, C*H*(OH) (**11**)], 4.17 [1H, d, *J* 11.8, $CHOCH_AH_BPh$ (**11**)], 4.27 [2H, d, *J* 11.3, $CHOCH_AH_BPh$ and $CHOCH_CH_DPh$ (**11**)], 4.29 [1H, d, *J* 11.0, $CHOCH_AH_BPh$ (**12**)], 4.57 [1H, d, *J* 11.0, $CHOCH_CH_DPh$ (**11**)], 4.59–4.62 [1H, m, C*H*(OH) (**12**)], 4.70 [2H, d, *J* 11.0, $CHOCH_2Ph$ (**12**)], 4.89 [1H, d, *J* 7.1, COC*H*OCH_2Ph (**12**)], 4.96 [1H, d, *J* 11.0, $CHOCH_AH_BPh$ (**12**)], 5.06 [1H, d, *J* 2.8, C*H*(OTBDMS) (**11**)], 5.18 [1H, d, *J* 3.7, C*H*(OTBDMS) (**12**)], 5.54 [1H, d, *J* 2.7, CO.C*H*OCH_2Ph (**11**)], 7.21–7.48 [30H, m, Ph*H* (**11** and **12**)]; δ_C (100 MHz, $CDCl_3$) −5.2, −4.7 [$Si(CH_3)_2$ (**11** and **12**)], 18.1 [$SiC(CH_3)_3$ (**12**)], 18.3 [$SiC(CH_3)_3$ (**11**)], 25.9 [$SiC(CH_3)_3$ (**12**)], 25.9 [$SiC(CH_3)_3$ (**11**)], 26.9 and 27.4

[C(CH_3)$_2$ (**12**)], 27.0, 27.1 [C(CH_3)$_2$ (**11**)], 54.1 [NCH_2 (**12**)], 54.2 [NCH_2 (**11**)], 70.7 [*C*H(OH) (**12**)], 71.7 [*C*H(OH) (**11**)], 72.6 and 73.1 [2 × CHOCH_2Ph (**11**)], 72.8 and 74.3 [2 × CHOCH_2Ph (**12**)], 74.1 [*C*H(OTBDMS) (**11**)], 77.0 [*C*H(OTBDMS) (**12**)], 77.7 [CO.*C*HOCH$_2$Ph (**11**)], 78.5 [CO.*C*HOCH$_2$Ph (**12**)], 79.2 [*C*(CH$_3$)$_2$ (**11**)], 79.3 [*C*(CH$_3$)$_2$ (**12**)], 82.0 [*C*HOCH$_2$Ph.CHPh (**11**)], 82.4 [*C*HOCH$_2$Ph.CHPh (**12**)], 127.3, 128.0 [*p-Ph* (**11**)], 127.1, 127.9, 128.2, 128.3 [*m*/*o-Ph* (**11**)], 127.6, 127.7, 128.1, 128.2 [*p*- and *m*/*o-Ph* (**12**)], 137.3, 138.5, 141.2 [*i-Ph* (**11**)], 137.2, 138.7, 141.6 [*i-Ph* (**12**)], 152.1 [*C*=O endocyclic (**11**)], 152.6 [*C*=O endocyclic (**12**)], 171.0 [*C*=O exocyclic (**12**)], 171.7 [*C*=O exocyclic (**11**)]; ν_{max}(thin film, cm^{-1}) 3471 [O–H], 1780 [C=O endocyclic], 1711 [C=O exocyclic]; HRMS $C_{36}H_{51}N_2O_7Si$ [MNH_4^+] requires 651.3466, found 651.3471; *m*/*z* LD+ (MALDI) 656, 657, 658 [100%, 40%, 15%, MNa^+].

Preparation of (2′*S*,3′*R*,4*S*,4′*R*,5′*R*)-4-benzyl-3-[2′,4′-bis-benzyloxy-5′-(*tert*-butyl-dimethyl-silanyloxy)-3′-hydroxy-5′-phenyl-pentanoyl]-5,5-dimethyl-oxazolidin-2-one (2′*S*,3′*R*, 4*S*,4′*R*,5′*R*)-15 and (2′*S*,3′*S*,4*S*,4′*R*, 5′*R*)-4-benzyl-3-[2′, 4′-bis-benzyloxy-5′-(*tert*-butyl-dimethyl-silanyloxy)-3′-hydroxy-5′-phenyl-pentanoyl]-5,5-dimethyl-oxazolidin-2-one (2′*S*,3′*S*,4*S*,4′*R*,5′*R*)-16. Following representative procedure 1, CF_3SO_3H (0.29 mL, 3.24 mmol), Et_3B (3.24 mL, 3.24 mmol), (*S*)-**4** (950 mg, 2.70 mmol), *i*-Pr_2NEt (0.61 mL, 3.51 mmol) and **8** (1.00 g, 2.70 mmol) in CH_2Cl_2 (20 mL) furnished a 57 : 43 ratio of **15** : **16** which after purification by column chromatography gave **15** (690 mg, 0.95 mmol, 35%) and **16** (667 mg, 0.92 mmol, 34%) as white solids.

15: R_f 0.14 [5 : 1 pentane–Et_2O]; mp 124–125 °C [pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) −0.16 [3H, s, Si(CH_3)$_A$(CH$_3$)$_B$], 0.077 [3H, s, Si(CH$_3$)$_A$(CH_3)$_B$], 0.92 [9H, s, SiC(CH_3)$_3$], 0.94 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.12 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$], 2.70 [1H, dd, *J* 14.4, 9.6, CHCH_AH$_B$Ph], 3.09 [1H, dd, *J* 14.4, 2.5, CHCH$_A$$H_B$Ph], 3.23 [1H, d, *J* 7.4, CH(O*H*)], 3.74–3.78 [2H, m, C*H*OCH$_2$Ph.CH(OTBDMS) and C*H*CH$_2$Ph], 4.04–4.10 [2H, m, C*H*(OH) and CHOCH_AH$_B$Ph], 4.47 [2H, app. t, *J* 11.9, CHOCH_2Ph], 4.76 [1H, d, *J* 11.4, CHOCH$_A$$H_B$Ph], 5.07 [1H, d, *J* 3.7, C*H*(OTBDMS)], 5.31 [1H, d, *J* 1.7, CO.C*H*OCH$_2$Ph], 7.01–7.45 [20H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) −5.2 and −4.7 [Si(*C*H$_3$)$_2$], 18.1 [Si*C*(CH$_3$)$_3$], 22.0 and 27.8 [C(*C*H$_3$)$_2$], 25.8 [SiC(*C*H$_3$)$_3$], 34.8 [CH*C*H$_2$Ph], 63.4 [*C*HCH$_2$Ph], 72.2 [*C*H(OH)], 73.1 and 73.7 [2 × CHO*C*H$_2$Ph], 74.1 [*C*H(OTBDMS)], 79.1 [CO.*C*HOCH$_2$Ph], 81.9 [*C*H(OCH$_2$Ph).CH(OTBDMS)], 83.3 [*C*(CH$_3$)$_2$], 126.5, 127.0, 127.1, 127.4 [*p-Ph*], 127.4, 127.8, 128.1 128.4, 128.5, 128.6, 128.7, 128.9 [*m*/*o-Ph*], 137.1, 137.8, 138.5, 141.2 [*i-Ph*], 152.7 [*C*=O endocyclic], 169.7 [*C*=O exocyclic]; ν_{max}(KBr disc, cm^{-1}) 1768 [C=O endocyclic], 1712 [C=O exocyclic]; HRMS $C_{43}H_{57}N_2O_7Si$ [MNH_4^+] requires 741.3935, found 741.3937; $[\alpha]_D^{25}$ −12.0 (*c* = 1, $CHCl_3$); *m*/*z* LD+ (MALDI) 746 [100%, MNa^+], 762 [50%, MK^+].

16: R_f 0.11 [5 : 1 pentane–Et_2O]; mp 116–117 °C [pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) −0.21 [3H, s, Si(CH_3)$_A$(CH$_3$)$_B$], 0.01 [3H, s, Si(CH$_3$)$_A$(CH_3)$_B$], 0.84 [9H, s, SiC(CH_3)$_3$], 1.04 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.23 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$], 2.73 [1H, d, *J* 7.6, CH(O*H*)], 2.79 [1H, dd, *J* 14.5, 9.8, CHCH_AH$_B$Ph], 3.08 [1H, dd, *J* 14.5, 3.5, CHCH$_A$$H_B$Ph], 3.79–3.83 [1H, m, C*H*(OH)], 3.92 [1H, dd, *J* 6.9, 1.7, C*H*OCH$_2$Ph.CH(OTBDMS)], 4.16 [1H, dd, *J* 9.8, 3.5, C*H*CH$_2$Ph], 4.26 [1H, d, *J* 11.2, CHOCH_AH$_B$Ph], 4.49 [1H, d, *J* 11.2, CHOCH$_A$$H_B$Ph], 4.63 [1H, d, *J* 10.8, CHOCH_CH$_D$Ph], 4.91 [1H, d, *J* 6.9, C*H*(OTBDMS)], 4.94 [1H, d, *J* 10.8, CHOCH$_C$$H_D$Ph], 5.25 [1H, d, *J* 4.0, CO.C*H*OCH$_2$Ph], 7.18–7.42 [20H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) −4.9, −4.7 [Si(*C*H$_3$)$_2$], 18.0 [Si*C*(CH$_3$)$_3$], 22.0, 27.8 [C(*C*H$_3$)$_2$], 25.8 [SiC(*C*H$_3$)$_3$], 35.1 [CH*C*H$_2$Ph], 63.8 [*C*HCH$_2$Ph], 70.5 [*C*H(OH)], 72.6, 74.3 [2 × CHO*C*H$_2$Ph], 76.7 [*C*H(OTBDMS)], 77.8 [CO.*C*HOCH$_2$Ph], 82.2 [*C*HOCH$_2$Ph.CH(OTBDMS)], 83.1 [*C*(CH$_3$)$_2$], 126.7, 127.3, 127.3, 127.4 [*p-Ph*], 127.7, 127.8, 128.0, 128.1, 128.3, 128.5, 128.8, 129.1 [*m*/*o-Ph*], 137.0, 137.2, 138.7, 141.6 [*i-Ph*], 152.7 [*C*=O endocyclic], 170.6 [*C*=O exocyclic]; ν_{max}(thin film, cm^{-1}) 1776 [C=O endocyclic], 1710 [C=O exocyclic]; HRMS $C_{43}H_{57}N_2O_7Si$ [MNH_4^+] requires 741.3935, found 741.3934; $[\alpha]_D^{25}$ +130.4 (*c* = 1.05, $CHCl_3$); *m*/*z* LD+ (MALDI) 746.29, 747.25, 748.21 [100%, 50%, 15%, MNa^+].

Preparation of (2′*R*,3′*S*,4*R*,4′*R*,5′*R*)-4-benzyl-3-[2′,4′-bis-benzyloxy-5′-(*tert*-butyl-dimethyl-silanyloxy)-3′-hydroxy-5′-phenyl–pentanoyl]-5,5-dimethyl–oxazolidin-2-one (2′*R*,3′*S*,4*R*,4′*R*,5′*R*)-14. Following representative procedure 1, CF_3SO_3H (0.12 mL, 1.36 mmol), Et_3B (1.36 mL, 1.36 mmol), (*R*)-**4** (400 mg, 1.13 mmol), *i*-Pr_2NEt (0.28 mL, 1.58 mmol) and **8** (400 mg, 1.14 mmol) in CH_2Cl_2 (15 mL) furnished **14** (442 mg, 0.61 mmol, 54%) as a white solid after column chromatography.

14: R_f 0.25 [1 : 1 pentane–Et_2O]; mp 142–144 °C [pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) −0.15 [3H, s, Si(CH_3)$_A$(CH$_3$)$_B$], 0.01 [3H, s, Si(CH$_3$)$_A$(CH_3)$_B$], 0.890 [9H, s, SiC(CH_3)$_3$], 1.31 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.343 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$], 2.86 [1H, dd, *J* 14.4, 9.6, CHCH_AH$_B$Ph], 2.89 [1H, d, *J* 7.3, CH(O*H*)], 3.14 [1H, dd, *J* 14.4, 3.8, CHCH$_A$$H_B$Ph], 3.69 [1H, dd, *J* 8.9, 2.6, C*H*(OCH$_2$Ph).CH(OTBDMS)], 4.00–4.05 [1H, m, C*H*(OH)], 4.09 [1H, d, *J* 11.7, CHOCH_AH$_B$Ph], 4.16 [1H, d, *J* 11.0, CHOCH_CH$_D$Ph], 4.25 [1H, d, *J* 11.7, CHOCH$_A$$H_B$Ph], 4.44 [1H, d, *J* 11.0, CHOCH$_C$$H_D$Ph], 4.47 [1H, dd, *J* 9.6, 3.8, C*H*CH$_2$Ph], 5.05 [1H, d, *J* 2.6, C*H*(OTBDMS)], 5.55 [1H, d, *J* 2.0, CO.C*H*OCH$_2$Ph], 7.19–7.42 [20H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) −4.9, −4.7 [Si(*C*H$_3$)$_2$], 18.2 [*C*(CH$_3$)$_3$], 22.1, 28.1 [C(*C*H$_3$)$_2$], 25.9 [C(*C*H$_3$)$_3$], 35.3 [CH*C*H$_2$Ph], 64.0 [*C*HCH$_2$Ph], 71.5 [*C*H(OH)], 72.3, 73.3 [2 × CHO*C*H$_2$Ph], 74.1 [*C*H(OTBDMS)], 77.6 [CO.*C*HOCH$_2$Ph], 81.9 [*C*HOCH$_2$Ph.CH(OTBDMS)], 83.1 [*C*(CH$_3$)$_2$], 126.7, 127.0, 127.2, 127.4, 127.6, 127.8, 128.1, 128.3, 128.4, 128.5, 128.6, 129.1 [*p*- and *m*/*o-Ph*], 137.0, 137.3, 138.5, 141.3 [*i-Ph*], 152.1 [*C*=O endocyclic], 171.2 [*C*=O exocyclic]; ν_{max}(KBr disc, cm^{-1}) 1782 [C=O endocyclic], 1702 [C=O exocyclic]; $C_{43}H_{53}NO_7Si$ requires C 71.3, H 7.4, N 1.9%, found C 71.3, H 7.4, N 2.0%; $[\alpha]_D^{20}$ +14.6 (*c* = 1.0, $CHCl_3$); *m*/*z* LD+ (MALDI) 746, 747, 748 [100%, 45%, 15%, MNa^+].

Preparation of (2′*R*,3*S*′,4*R*,4′*R*,5′*S*)-4-benzyl-3-[2′,4′-bis-benzyloxy-5′-(*tert*-butyl-dimethyl-silanyloxy)-5′-furan-2″-yl-3′-hydroxy-pentanoyl]-5,5-dimethyl–oxazolidin-2-one (2′*R*,3*S*′,4*R*,4′*R*,5′*S*)-18. Following representative procedure 1, CF_3SO_3H (0.24 mL, 2.72 mmol), Et_3B (2.72 mL, 2.72 mmol), (*R*)-**4** (800 mg, 2.27 mmol), *i*-Pr_2NEt (0.55 mL, 3.18 mmol) and **17** (817 mg, 2.27 mmol) in CH_2Cl_2 (20 mL) furnished **18** (565 mg, ~0.91 mmol, ~40%) as a white solid contaminated with <10% of (*R*)-**4** after column chromatography.

18: R_f 0.1 [1 : 1 pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) −0.08 [3H, s, Si(CH_3)$_A$(CH$_3$)$_B$], 0.01 [3H, s, SiC(CH$_3$)$_A$(CH_3)$_B$], 0.87 [9H, s, SiC(CH_3)$_3$], 1.34 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.35 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$], 2.83–2.94 [2H, m, CHCH_AH$_B$Ph and CH(O*H*)], 3.14 [1H, dd, *J* 14.4, 3.7, CHCH$_A$$H_B$Ph], 3.86 [1H, dd, *J* 8.8, 3.3, C*H*OCH$_2$Ph.CH(OTBDMS)], 4.20 [2H, app. d, *J* 11.0, C*H*(OH) and CHOCH_AH$_B$Ph], 4.39 [2H, s, CHOCH_2Ph], 4.45 [1H, d, *J* 11.0, CHOCH$_A$$H_B$Ph], 4.48 [1H, dd, *J* 11.6, 3.8, C*H*CH$_2$Ph], 5.06 [1H, d, *J* 3.3, C*H*(OTBDMS)], 5.56 [1H, d, *J* 2.2, CO.C*H*OCH$_2$Ph], 6.30–6.34 [2H, m, C*H*(furan)], 7.20–7.42 [16H, m, Ar*H*]; δ_C (100 MHz, $CDCl_3$) −5.4, −5.1 [SiC(*C*H$_3$)$_2$], 18.2 [Si*C*(CH$_3$)$_3$], 22.1, 28.2 [C(*C*H$_3$)$_2$], 25.8 [SiC(*C*H$_3$)$_3$], 35.2 [CH*C*H$_2$Ph], 64.0 [*C*HCH$_2$Ph], 69.1 [*C*H(OTBDMS)], 71.3 [*C*H(OH)], 72.4, 72.7 [2 × CHO*C*H$_2$Ph], 77.7 [CO.*C*HOCH$_2$Ph], 80.1 [*C*HOCH$_2$Ph.CH(OTBDMS)], 83.7 [*C*(CH$_3$)$_2$], 107.8, 110.4, 141.3 [*C*H(furan)], 126.7, 126.9, 127.2 [*p-Ph*], 127.5, 127.9, 128.0, 128.3, 128.6, 129.1 [*m*/*o-Ph*], 137.0, 137.3, 138.7 [*i-Ph*], 152.5 [*i-Ar* furan], 154.4 [*C*=O endocyclic], 171.1 [*C*=O exocyclic]; ν_{max}(KBr disc, cm^{-1}) 3531 [O–H], 1779 [C=O endocyclic], 1708 [C=O endocyclic]; HRMS $C_{41}H_{55}N_2O_8Si$ [MNH_4^+] requires 731.3728, found 731.3727; *m*/*z* LD+ (MALDI) 736, 737, 738, 739 [100%, 60%, 20%, 5%, MNa^+], 752, 753, 754, 755 [80%, 30%, 20%, 5%, MK^+].

Preparation of (2′*S*,3′*R*,4*S*,4′*R*,5′*S*)-4-benzyl-3-[2′,4′-bis-benzyloxy-5′-(*tert*-butyl-dimethyl-silanyloxy)-5′-furan-2″-yl-3′-hydroxy-pentanoyl]-5,5-dimethyl-oxazolidin-2-one (2′*S*,3′*R*,4*S*,4′*R*,5′*S*)-19 and (2′*S*,3′*S*,4*S*,4′*R*,5′*S*)-4-benzyl-3-[2′,4′-bis-benzyloxy-5′-(*tert*-butyl-dimethyl-silanyloxy)-5′-furan-2″-yl-3′-hydroxy-pentanoyl]-5,5-dimethyl-oxazolidin-2-one (2′*S*,3′*S*,4*S*,4′*R*,5′*S*)-20. Following representative procedure 1, CF_3SO_3H (0.28 mL, 3.23 mmol), Et_3B (3.23 mL, 3.23 mmol), (*S*)-**4** (950 mg, 2.69 mmol), *i*-Pr_2NEt (0.66 mL, 3.77 mmol) and **17** (1 g, 2.78 mmol) in CH_2Cl_2 (30 mL) furnished a 58 : 42 mixture of **19** : **20** which after purification by column chromatography gave **19** (651 mg, ~1.05 mmol, ~39%) as a yellow oil contaminated with <10% of (*S*)-**4** and **20** (531 mg, 0.85 mmol, 32%) as a pale yellow oil after column chromatography.

19: R_f 0.12 [3 : 1 pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) −0.14 [3H, s, Si(CH_3)$_A$(CH$_3$)$_B$], 0.01 [3H, s, Si(CH$_3$)$_A$(CH_3)$_B$], 0.83 [9H, s, SiC(CH_3)$_3$], 1.11 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.27 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$], 2.77–2.86 [2H, m, CHCH_AH$_B$Ph and CH(OH)], 3.09 [1H, dd, *J* 14.4, 3.4, CHCH$_A$$H_B$Ph], 3.80–3.83 [1H, m, C$H$(OH)], 4.08 [1H, dd, *J* 7.8, 1.7, CHOCH$_2$Ph.CH(OTBDMS)], 4.22 [1H, dd, *J* 3.5, 9.8, CHCH$_2$Ph], 4.34 [1H, d, *J* 11.1, CHOCH_AH$_B$Ph], 4.53 [1H, d, *J* 11.4, CHOCH_CH$_D$Ph], 4.53 [1H, d, *J* 11.1, CHOCH$_A$$H_B$Ph], 4.94–4.97 [2H, m, CHOCH$_C$$H_D$Ph and C$H$(OTBDMS)], 5.31 [1H, d, *J* 3.9, CO.CHOCH$_2$Ph], 6.27–6.33 [2H, m, CH furan], 7.20–7.41 [16H, m, ArH]; δ_C (100 MHz, $CDCl_3$) −5.2, −5.0 [Si(*C*H$_3$)$_2$], 18.1 [Si*C*(CH$_3$)$_3$], 22.0, 27.8 [C(*C*H$_3$)$_2$], 25.7 [SiC(*C*H$_3$)$_3$], 35.2 [CH*C*H$_2$Ph], 63.9 [*C*HCH$_2$Ph], 70.4 [*C*H(OTBDMS)], 70.7 [*C*H(OH)], 72.7, 74.3 [2 × CHO*C*H$_2$Ph], 78.1 [CO.*C*HOCH$_2$Ph], 80.4 [*C*HOCH$_2$Ph.CH(OTBDMS)], 83.7 [*C*(CH$_3$)$_2$], 108.3, 110.2, 142.0 [*C*H furan], 126.7, 126.9, 127.3 [*p-Ph*], 127.9, 128.1, 128.2, 128.5, 128.6, 129.1 [*m/o-Ph*], 136.6, 137.0, 137.2 [*i-Ph*], 152.5 [*i-Ar* furan], 152.7 [*C*=O endocyclic], 170.3 [*C*=O exocyclic]; ν_{max}(thin film, cm^{-1}) 3535 [O–H], 1777 [C=O endocyclic], 1713 [C=O endocyclic]; HRMS $C_{41}H_{55}N_2O_8Si$ [MNH_4^+] requires 731.3728, found 731.3722; *m/z* LD+ (MALDI) 736, 737, 738 [35%, 20%, 3%, MNa$^+$], 752, 753, 754, 755 [100%, 45%, 15%, 3%, MK$^+$].

20: R_f 0.23 [3 : 1 pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) −0.62 [3H, s, Si(CH_3)$_A$(CH$_3$)$_B$], 0.08 [3H, s, Si(CH$_3$)$_A$(CH_3)$_B$], 0.86 [9H, s, SiC(CH_3)$_3$], 0.91 [9H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.11 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$], 2.72 [1H, dd, *J* 14.6, 10.4, CHCH_AH$_B$Ph], 3.11 [1H, dd, *J* 14.6, 2.7, CHCH$_A$$H_B$Ph], 3.16 [1H, d, *J* 8.0, CH(OH)], 3.80 [1H, dd, *J* 10.4, 3.0, CHCH$_2$Ph], 3.92 [1H, dd, *J* 7.7, 3.9, CHOCH$_2$Ph.CH(OTBDMS)], 4.09–4.14 [1H, m, CH(OH)], 4.17 [1H, d, *J* 10.2, CHOCH_AH$_B$Ph], 4.47–4.50 [2H, m, CHO-CH$_A$$H_B$Ph and CHOC$H_CH_D$Ph], 4.75 [1H, d, *J* 11.4, CHO-CH$_C$$H_D$Ph], 5.12 [1H, d, *J* 3.9, CH(OTBDMS)], 5.33 [1H, d, *J* 3.6, CO.CHOCH$_2$Ph], 6.30–6.32 [2H, m, CH(furan)], 7.07–7.45 [16H, m, ArH]; δ_C (100 MHz, $CDCl_3$) −5.2, −5.0 [Si(*C*H$_3$)$_2$], 18.1 [Si*C*(CH$_3$)$_3$], 22.0, 27.7 [C(*C*H$_3$)$_2$], 25.7 [SiC(*C*H$_3$)$_3$], 34.8 [CH*C*H$_2$Ph], 63.4 [*C*HCH$_2$Ph], 68.5 [*C*H(OTBDMS)], 72.1 [*C*H(OH)], 73.1, 73.3 [2 × CHO*C*H$_2$Ph], 79.3 [CO.*C*HOCH$_2$Ph], 80.1 [*C*HOCH$_2$Ph.CH(OTBDMS)], 83.3 [*C*(CH$_3$)$_2$], 107.8, 110.4, 141.4 [*C*H furan], 126.5, 127.5, 127.9 [*p-Ph*], 128.0, 128.2, 128.3, 128.4, 128.6, 128.9 [*m/o-Ph*], 137.1, 137.7, 138.5 [*i-Ph*], 152.8 [*C*=O endocyclic], 154.2 [*i-Ar* furan], 169.8 [*C*=O exocyclic]; ν_{max}(thin film, cm^{-1}) 3527 [O–H], 1774 [C=O endocyclic], 1707 [C=O endocyclic]; HRMS $C_{41}H_{55}N_2O_8Si$ [MNH_4^+] requires 731.3728, found 731.3721; $[\alpha]_D^{26}$ −12.4 (*c* = 1.0, $CHCl_3$); *m/z* LD+ (MALDI) 736, 737, 738, 739 [100%, 60%, 25%, 3%, MNa$^+$], 752, 753, 754 [50%, 30%, 10%, MK$^+$].

Preparation of (2*R*,3*S*,4*S*,5*R*)-2,4-bis-benzyloxy-3-hydroxy-5-phenyl-tetrahydro-pyran-2-one (2*R*,3*S*,4*S*,5*R*)-21 and (*R*)-4-benzyl-5,5-dimethyl-oxazolidin-2-one (*R*)-22. Following representative procedure 2, **14** (230 mg, 0.32 mmol), TBAF (0.48 mL, 0.48 mmol) and AcOH (0.02 mL, 0.32 mmol) in THF (30 mL) furnished **21** (90 mg, 0.22 mmol, 70%) as a white solid and (*R*)-**22** (62 mg, 0.301 mmol, 95%) as a white solid after column chromatography.

21: R_f 0.19 [1 : 1 pentane–Et_2O]; mp 142–144 °C [pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) 4.05 [1H, d, *J* 11.1, CH(OCH_AH$_B$Ph).CHPh], 4.08 [1H, t, *J* 2.3, CH(OCH$_2$Ph).CHPh], 4.25 [1H, dd, *J* 9.7, 2.7, CH(OH)], 4.32 [1H, d, *J* 11.1, CH(OCH$_A$$H_B$Ph).CHPh], 4.41 [1H, *J* 9.7, CO.CHOCH$_2$Ph], 4.76 [1H, d, *J* 11.1, CO.CHOCH_CH$_D$Ph], 5.24 [1H, d, *J* 11.1, CO.CHOCH$_C$$H_D$Ph], 5.39 [1H, d, *J* 1.7, CHPh], 6.89–6.91 [2H, m, PhH], 7.20–7.26 [4H, m, PhH], 7.33–7.47 [9H, m, PhH]; δ_C (100 MHz, $CDCl_3$) 72.2 [*C*H(OH)], 74.8 [CO.CHO*C*H$_2$Ph], 75.2 [CHO*C*H$_2$Ph.CHPh], 77.0 [CO.*C*HOCH$_2$Ph], 78.4 [*C*HOCH$_2$Ph.CHPh], 80.4 [*C*HPh], 126.3, 127.9, 128.0, 128.3, 128.4, 128.6 [*p-* and *m/o-Ph*], 135.7, 137.1, 137.2 [*i-Ph*], 170.3 [*C*=O]; ν_{max}(KBr disc, cm^{-1}) 3528 [O–H], 1727 [C=O]; HRMS $C_{25}H_{28}NO_5$ [MNH_4^+] requires 422.1967, found 422.1973; $[\alpha]_D^{26}$ +80.4 (*c* = 0.55, $CHCl_3$); *m/z* ES+ 422 [100%, MNH_4^+].

Preparation of (2*R*,3*S*,4*R*,5*S*)-2,4-bis-benzyloxy-3-hydroxy-5-furan-2′-yl-tetrahydro-pyran-2-one (2*R*,3*S*,4*R*,5*S*)-23 and (*R*)-4-benzyl-5,5-dimethyl-oxazolidin-2-one (*R*)-22. Following representative procedure 2, **18** (200 mg, ~0.28 mmol), TBAF (0.42 mL, 0.42 mmol) and AcOH (0.02 mL, 0.28 mmol) in THF (10 mL) furnished **23** (66 mg, 0.17 mmol) as a clear colourless oil and (*R*)-**22** (47 mg, 0.22 mmol) as a white solid and returned (*R*)-**4** (18 mg, 0.05 mmol) as a pale yellow oil after column chromatography.

23: R_f 0.08 [2 : 1 pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) 4.18 [1H, dd, *J* 9.5, 2.8, CH(OH)], 4.25 [1H, d, *J* 2.6, CH(OCH$_2$Ph).CH(C$_4$H$_3$O)], 4.35 [1H, d, *J* 11.2, CHOCH_AH$_B$Ph], 4.39 [1H, d, *J* 9.5, CO.CHOCH$_2$Ph], 4.52 [1H, d, *J* 11.2, CHO-CH$_A$$H_B$Ph], 4.74 [1H, d, *J* 11.1, CHOCH_CH$_D$Ph], 5.20 [1H, d, *J* 11.1, CHOCH$_C$$H_D$Ph], 5.40 [1H, d, *J* 0.9, CH(OCH$_2$Ph).CH(C$_4$H$_3$O)], 6.42–6.44 [1H, m, CH furan], 6.51–6.99 [1H, m, CH furan], 7.09–7.45 [11H, m, ArH]; δ_C (100 MHz, $CDCl_3$) 71.8 [*C*H(OH)], 74.7, 74.8 [2 × CHO*C*H$_2$Ph], 75.1 [CHOCH$_2$Ph.*C*H(C$_4$H$_3$O)], 76.2 [*C*HOCH$_2$Ph.CH(C$_4$H$_3$O)], 77.0 [CO.*C*HOCH$_2$Ph], 109.0, 110.9, 142.3 [*C*H furan], 127.9, 128.0, 128.3, 128.4, 128.5, 128.6 [*p-* and *m/o-Ph*], 137.1, 137.2 [*i-Ph*], 148.4 [*i-Ar* furan], 169.5 [*C*=O]; ν_{max}(thin film, cm^{-1}) 3436 [O–H], 1743 [C=O]; HRMS $C_{23}H_{23}O_6$ requires 395.1495, found 395.1489; $[\alpha]_D^{25}$ +61.0 (*c* = 1.35, $CHCl_3$); *m/z* APCI+ 395 [25%, MH$^+$].

Preparation of (2*S*,3*R*,4*S*,5*R*)-2,4-bis-benzyloxy-3-hydroxy-5-phenyl-tetrahydro-pyran-2-one (2*S*,3*R*,4*S*,5*R*)-24 and (*S*)-4-benzyl-5,5-dimethyl-oxazolidin-2-one (*S*)-22. Following representative procedure 2, **15** (500 mg, ~0.70 mmol), TBAF (1.05 mL, 1.05 mmol) and AcOH (0.04 mL, 0.70 mmol) in THF (10 mL) furnished **24** (184 mg, 0.46 mmol) as a white solid, (*S*)-**22** (93 mg, 0.45 mmol) as a white solid and (*S*)-**4** (27 mg, 0.08 mmol) as a pale yellow oil after column chromatography.

24: R_f 0.18 [1 : 1 pentane–Et_2O]; mp 132–134 °C [pentane–Et_2O]; δ_H (500 MHz, $CDCl_3$) 2.81 [1H, br s, OH], 3.76 [1H, t, *J* 1.6, CH(OCH$_2$Ph).CHPh], 4.15 [1H, dd, *J* 7.7, 1.2, CH(OH)], 4.20 [1H, *J* 7.7, CO.CHOCH$_2$Ph], 4.22 [1H, d, *J* 12.2, CH(OCH_AH$_B$Ph).CHPh], 4.44 [1H, d, *J* 12.2, CH(OCH$_A$$H_B$Ph).CHPh], 4.66 [1H, d, *J* 11.5, CO.CHOCH_CH$_D$Ph], 5.15 [1H, d, *J* 11.5, CO.CHOCH$_C$$H_D$Ph], 5.47 [1H, d, *J* 1.8, CHPh], 6.89–6.90 [2H, m, PhH], 7.15–7.22 [3H, m, PhH], 7.34–7.47 [10H, m, PhH]; δ_C (125 MHz, $CDCl_3$) 71.6 [CH(O*C*H$_2$Ph).CHPh], 73.3 [CO.CHO*C*H$_2$Ph], 74.3 [CO.*C*HOCH$_2$Ph], 78.12 [*C*HPh], 78.8 [*C*H(OH)], 80.4 [*C*H(OCH$_2$Ph).CHPh], 126.7, 127.7, 127.8, 128.1, 128.2, 128.3, 128.4, 128.5, 128.7 [*p-* and *m/o-Ph*], 134.9, 136.7, 136.9 [*i-Ph*], 169.4 [*C*=O]; ν_{max}(KBr disc, cm^{-1}) 3436 [O–H], 1756 [C=O]; $C_{25}H_{24}O_5$ requires C 74.2, H 6.0%, found C 74.1, H 5.7%; $[\alpha]_D^{20}$ −109.6 (*c* = 0.25, $CHCl_3$); *m/z* ES+ 422 [100%, MNH_4^+].

Preparation of (2*S*,3*R*,4*R*,5*S*)-2,4-bis-benzyloxy-3-hydroxy-5-furan-2′-yl-tetrahydro–pyran-2-one (2*S*,3*R*,4*R*,5*S*)-25 and (*S*)-4-benzyl-5,5-dimethyl-oxazolidin-2-one (*S*)-22. Following representative procedure 2, **19** (120 mg, 0.168 mmol), TBAF

(0.25 mL, 0.25 mmol) and AcOH (0.01 mL, 0.17 mmol) in THF (10 mL) furnished **25** (50 mg, 0.14 mmol, 80%) as a pale yellow oil and (*S*)-**22** (31 mg, 0.15 mmol, 90%) after column chromatography.

25: R_f 0.24 [1 : 1 pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) 3.93 [1H, t, *J* 3.0, C*H*(OCH$_2$Ph).CH(C$_4$H$_3$O)], 4.10 [1H, d, *J* 7.9, CO.C*H*OCH$_2$Ph], 4.20–4.25 [1H, m, C*H*(OH)], 4.48 [1H, d, *J* 11.9, CHOCH_AH$_B$Ph], 4.62 [1H, d, *J* 11.9, CHOCH$_A$$H_B$Ph], 4.67 [1H, d, *J* 11.4, CHOCH_CH$_D$Ph], 5.13 [1H, d, *J* 11.4, CHOCH$_C$$H_D$Ph], 5.47 [1H, d, *J* 2.7, CH(OCH$_2$Ph).C*H*(C$_4$H$_3$O)], 6.33–6.40 [1H, m, C*H* furan], 6.50 [1H, m, C*H* furan], 7.17–7.46 [11H, m, Ar*H*]; δ_C (100 MHz, $CDCl_3$) 72.4, 74.0 [2 × CHO*C*H$_2$Ph], 73.2 [CHOCH$_2$Ph.*C*H(C$_4$H$_3$O)], 73.9 [*C*H(OH)], 78.7 [*C*HOCH$_2$Ph.CH(C$_4$H$_3$O)], 79.0 [CO.*C*HOCH$_2$Ph], 110.6, 111.2, 143.1 [*C*H(furan)], 128.4, 128.8, 128.9, 129.0, 129.1, 129.2 [*p*- and *m*/*o*-*Ph*], 137.2, 137.3 [*i*-*Ph*], 148.4 [C^4(furan)], 169.3 [*C*=O]; ν_{max}(thin film, cm^{-1}) 3431 [O–H], 1761 [C=O]; HRMS $C_{23}H_{22}O_6Na$ [MNa$^+$] requires 417.1314, found 417.1306; $[\alpha]_D^{25}$ −33.7 (*c* = 0.3, $CHCl_3$); *m*/*z* ES+ 395 [35%, MH$^+$], 412 [45%, MNH$_4^+$], 417 [85%, MNa$^+$].

Preparation of (4*R*,5*R*)-2,4-bis-benzyloxy-5-phenyl-3,4-dihydro-pyran-2-one 26. Following representative procedure 3, Et_3N (0.02 mL, 0.12 mmol), PhCOCl (0.01 mL, 0.10 mmol), DMAP (1 mg, 0.001 mmol) and **24** (20 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) furnished **26** (18 mg, 0.05 mmol, 93%) after column chromatography.

26: R_f 0.25 [1 : 1 pentane–Et_2O]; mp 105–106 °C [pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) 4.08 [2H, s, OCH_2Ph], 4.16 [1H, dd, *J* 6.5, 2.6, C*H*OCH$_2$Ph], 4.97 [2H, ABq, *J* 12.7, OCH_2Ph], 5.50 [1H, d, *J* 2.5, C*H*Ph], 5.80 [1H, d, *J* 6.5, *C*H=COCH$_2$Ph], 6.91–6.93 [2H, m, Ph*H*], 7.22–7.69 [13H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 70.4, 71.2 [O*C*H$_2$Ph], 70.8 [*C*HOCH$_2$Ph], 81.5 [*C*HPh], 109.2 [*C*H=COCH$_2$Ph], 126.6, 127.3, 127.5, 128.3, 128.4, 128.8, 130.5, 134.5 [*m*/*o*-*Ph*], 127.7, 128.7, 128.8 [*p*-*Ph*], 135.1, 135.1, 137.4 [*i*-*Ph*], 146.0 [CH=*C*OCH$_2$Ph], 160.3 [*C*=O]; ν_{max}(KBr disc, cm^{-1}) 1723 [C=O], 1641 [C=C]; HRMS $C_{25}H_{26}NO_4$ [MH$^+$] requires 404.1861, found 404.1857; $[\alpha]_D^{25}$ −106.3 (*c* = 1.5, $CHCl_3$); *m*/*z* APCI+ (NH_3) 108.9 [PhCH$_2$OH$_2^+$, 38%], 387.1 [MH$^+$, 13%], 404.1 [MNH$_4^+$, 11%].

Preparation of (4*R*,5*S*)-2,4-bis-benzyloxy-5-furan-2-yl-3, 4-dihydro-pyran-2-one 27. Following representative procedure 3, Et_3N (0.014 mL, 0.10 mmol), PhCOCl (0.006 mL, 0.05 mmol), DMAP (1 mg, 0.001 mmol) and **25** (16 mg, 0.04 mmol) in CH_2Cl_2 (5 mL) furnished **27** (12 mg, 0.03 mmol, 79%) as a pale yellow oil after column chromatography.

27: R_f 0.24 [1 : 1 pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) 4.31 [2H, ABq, *J* 11.9, CHOCH_2Ph], 4.39 [1H, dd, *J* 6.2, 3.0, C*H*OCH$_2$Ph], 4.94 [2H, ABq, *J* 12.2, CH=COCH_2Ph], 5.53 [1H, d, *J* 2.8, C*H*C$_4$H$_4$O], 5.77 [1H, d, *J* 6.2, C*H*=COCH$_2$Ph], 6.43–6.44 [1H, m, C*H*(furan)], 6.62–6.63 [1H, m, C*H*(furan)], 7.12–7.45 [11H, m, Ar*H*]; δ_C (100 MHz, $CDCl_3$) 69.2 [*C*HOCH$_2$Ph], 70.4 [CH=CO*C*H$_2$Ph], 70.9 [CHO*C*H$_2$Ph], 76.0 [*C*HC$_4$H$_4$O], 109.2 [*C*H=COCH$_2$Ph], 109.6, 110.8, 142.4 [*C*H(furan)], 127.8, 128.0 [*p*-*Ph*], 127.4, 128.3, 128.4, 128.7, 128.8 [*m*/*o*-*Ph*], 135.0, 137.1 [*i*-*Ph*], 145.8 [C^4 furan], 148.1 [*C*=O]; ν_{max}(thin film, cm^{-1}) 1725 [C=O]; HRMS $C_{23}H_{21}O_3$ [MH$^+$] requires 377.1389, found 377.1388; $[\alpha]_D^{25}$ −101.2 (*c* = 1.1, $CHCl_3$); *m*/*z* ES+ 398 [70%, MNa$^+$].

Preparation of (2*R*,3*S*,4*R*,5*R*)-2,4-bis-benzyloxy-3-benzoyl-5-phenyl-tetrahydro-pyran-2-one (2*R*,3*S*,4*R*,5*R*)-28. Following representative procedure 3, Et_3N (0.02 mL, 0.12 mmol), PhCOCl (0.01 mL, 0.10 mmol), DMAP (1 mg, 0.005 mmol) and **21** (20 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) furnished **28** (21 mg, 0.041 mmol, 83%) as a pale yellow oil after column chromatography [3 : 1 pentane–Et_2O].

28: δ_H (400 MHz, $CDCl_3$) 4.00 [2H, ABq, *J* 11.2, CHOCH_2Ph.CHPh], 4.30 [1H, d, *J* 2.0, C*H*OCH$_2$Ph.CHPh], 4.73 [1H, *J* 10.2, CO.C*H*OCH$_2$Ph], 4.94 [1H, d, *J* 11.8, CO.CHOCH_AH$_B$Ph], 5.15 [1H, d, *J* 11.8, CO.CHOCH$_A$$H_B$Ph], 5.56 [1H, d, *J* 0.61, C*H*Ph], 5.61 [1H, dd, *J* 10.2, 2.4, C*H*(OBz)], 6.78–8.19 [20H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 73.3 [CO.*C*HOCH$_2$Ph], 74.0 [*C*H(OBz)], 74.5 [CO.CHO*C*H$_2$Ph], 75.0 [CHO*C*H$_2$Ph.CHPh], 77.0 [*C*HOCH$_2$Ph.CHPh], 79.9 [*C*HPh], 126.3, 127.5, 127.8, 127.9, 128.1, 128.3, 128.3, 128.4, 128.5, 128.6, 128.8, 129.0, 129.2, 129.8, 130.0, 130.5 [*p*- and *m*/*o*-*Ph*], 135.4, 136.4, 137.0 [*i*-*Ph*], 165.6 [CH(*C*OBz)], 169.8 [*C*=O lactone]; ν_{max}(thin film, cm^{-1}) 1753, 1722 [C=O]; HRMS $C_{32}H_{30}O_6$ [MH$^+$] requires 509.1886, found 509.1887; $[\alpha]_D^{25}$ −17.7 (*c* = 1.0, $CHCl_3$); *m*/*z* CI+ 491 [40%, MH$^+$–H$_2$O], 509 [30%, MH$^+$].

Preparation of (2*R*,3*S*,4*R*,5*S*)-2,4-bis-benzyloxy-3-benzoyl-5-furan-2-yl-tetrahydro-pyran-2-one (2*R*,3*S*,4*R*,5*S*)-29. Following representative procedure 3, Et_3N (0.02 mL, 0.16 mmol), PhCOCl (0.02 mL, 0.12 mmol), DMAP (2 mg, 0.01 mmol) and **23** (25 mg, 0.06 mmol) in CH_2Cl_2 (10 mL) furnished **29** (18 mg, 0.036 mmol, 60%) as a pale yellow oil after column chromatography.

29: R_f 0.23 [3 : 1 pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) 4.18 [1H, d, *J* 11.4, CHOCH_AH$_B$Ph], 4.30 [1H, d, *J* 11.4, CHOCH$_A$$H_B$Ph], 4.49 [1H, t, *J* 2.0, C*H*(OBz)], 4.71 [1H, d, *J* 10.2, C*H*C$_4$H$_4$O], 4.91 [1H, d, *J* 11.8, OCH_CH$_D$Ph], 5.13 [1H, d, *J* 11.7, OCH$_C$$H_D$Ph], 5.55 [1H, dd, J 10.2, 2.5, C*H*OCH$_2$Ph.CHC$_4$H$_4$O], 5.58 [1H, s, CO.C*H*OCH$_2$Ph], 6.44–6.45 [1H, m, C*H*(furan)], 6.54–6.55 [1H, m, C*H*(furan)], 6.97–7.34 [6H, m, Ar*H*], 7.44–7.65 [9H, m, Ar*H*], 7.89–7.91 [1H, m, Ar*H*]; δ_C (100 MHz, $CDCl_3$) 73.4, 73.5 [CO.*C*HOCH$_2$Ph and *C*HC$_4$H$_4$O], 74.5, 74.6 [CHO*C*H$_2$Ph], 74.8, 74.9 [*C*H(OBz) and *C*HOCH$_2$Ph.CHC$_4$H$_4$O], 109.1, 111.0, 142.3 [*C*H(furan)], 127.9, 128.0, 128.2, 128.4, 128.5, 128.8, 128.9, 129.3, 129.9 [*p*- and *m*/*o*-*Ph*], 133.6, 136.6, 136.8 [*i*-*Ph*], 148.0 [CH(*C*OBz)], 165.5 [C^4 furan], 169.2 [*C*=O lactone]; ν_{max}(thin film, cm^{-1}) 1726 [C=O]; HRMS $C_{30}H_{27}O_7$ [MH$^+$] requires 499.1757, found 499.1759; $[\alpha]_D^{26}$ +26.7 (*c* = 0.3, $CHCl_3$); *m*/*z* CI+ 377 [MH$^+$–PhCO$_2$H and H$_2$O, 20%], 394 [MH$^+$–PhCO$_2$H, 100%], 499 [MH$^+$, 5%].

Preparation of (2′*S*,3′*S*,4*S*,4′*S*,5′*R*)-4-benzyl-3-(2′,4′-bis-benzyloxy-3′,5′-dihydroxy-5′-phenyl–pentanoyl)-5,5-dimethyl–oxazolidin-2-one 30, (2*S*,3*S*,4*R*,5*R*)-2,4-bis-benzyloxy-3-hydroxy-5-phenyl-tetrahydro-pyran-2-one (2*S*,3*S*,4*R*,5*R*)-31 and (*S*)-4-benzyl-5,5-dimethyl-oxazolidin-2-one (*S*)-22. Following representative procedure 2, **16** (220 mg, 0.3 mmol), TBAF (0.46 mL, 0.46 mmol) and AcOH (0.02 mL, 0.30 mmol) in THF (20 mL) furnished a 66 : 34 mixture of **30** : **31** which after purification by column chromatography gave **30** (82 mg, 0.13 mmol, 45%) as a pale yellow oil, **31** (41 mg, 0.10 mmol, 34%) as a white solid and (*S*)-**22** (17 mg, 0.08 mmol, 28%) as a white solid.

30: R_f 0.09 [1 : 1 30–40 °C petrol–Et_2O]; δ_H (400 MHz, $CDCl_3$) 1.10 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.27 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$], 2.84 [1H, dd, *J* 14.4, 9.5, CHCH_AH$_B$Ph], 3.052[1H, dd, *J* 14.4, 4.2, CHCH$_A$$H_B$Ph], 3.1 [1H, br s, CH(O*H*)Ph], 3.43 [1H, d, *J* 7.1, CO.CH(OCH$_2$Ph).CH(O*H*)], 3.86 [1H, dd, *J* 5.4, 2.5, C*H*(OCH$_2$Ph).CH(OH)Ph], 4.13 [1H, d, *J* 10.7, CH(OCH_AH$_B$Ph).CH(OH)Ph], 4.17 [1H, d, *J* 5.6, CO.CH(OCH$_2$Ph).C*H*(OH)], 4.23 [1H, dd, *J* 9.5, 4.2, C*H*CH$_2$Ph], 4.32 [1H, d, *J* 11.5, CO.CH(OCH_CH$_D$Ph).CH(OH)], 4.46 [1H, d, *J* 10.7, CH(OCH$_A$$H_B$Ph).CH(OH)Ph], 4.59 [1H, d, *J* 11.5, CO.CH(OCH$_C$$H_D$Ph).CH(OH)], 5.10 [1H, s, C*H*(OH)Ph], 5.47 [1H, d, *J* 6.2, CO.C*H*OCH$_2$Ph], 7.15–7.40 [20H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 21.9, 27.7 [C(*C*H$_3$)$_2$], 35.4 [CH*C*H$_2$Ph], 63.5 [*C*HCH$_2$Ph], 72.3 [CO.CH(OCH$_2$Ph).*C*H(OH)], 72.6, 72.8 [2 × CHO*C*H$_2$Ph], 72.9 [CO.*C*HOCH$_2$Ph], 77.3 [*C*H(OH)Ph], 80.4 [*C*H(OCH$_2$Ph).CH(OH)Ph], 83.4 [*C*(CH$_3$)$_2$], 126.8, 127.4, 127.7, 128.2 [*p*-*Ph*], 126.1, 128.2, 128.5, 128.6, 128.7, 129.1 [*m*/*o*-*Ph*], 136.8, 137.1, 137.5, 141.3 [*i*-*Ph*], 153.1 [*C*=O endocyclic], 170.6 [*C*=O exocyclic]; ν_{max}(thin film, cm^{-1}) 1771 [C=O endocyclic], 1709 [C=O exocyclic]; HRMS $C_{37}H_{39}NO_7Na$ [MNa$^+$] requires 632.2624, found 632.2626; $[\alpha]_D^{23}$ −24.5 (*c* = 1.0, $CHCl_3$); *m*/*z* ES+ 632 [100%, MNa$^+$].

31: R_f 0.07 [1 : 1 30–40 °C petrol–Et_2O]; mp 164–165 °C [pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) 3.98

[1H, dd, *J* 3.1, 5.9, C*H*(OCH$_2$Ph).CHPh], 4.09 [1H, d, *J* 11.5, CH(OC*H*$_A$H$_B$Ph).CHPh], 4.18 [1H, d, *J* 11.5, CH(OCH$_A$*H*$_B$Ph).CHPh], 4.21 [1H, *J* 4.8, CO.C*H*OCH$_2$Ph], 4.41 [1H, dd, *J* 4.9, 5.8, C*H*(OH)], 4.76 [1H, d, *J* 12.2, CO.CHOC*H*$_C$H$_D$Ph], 5.13 [1H, d, *J* 12.2, CO.CHOCH$_C$*H*$_D$Ph], 5.28 [1H, d, *J* 3.1, C*H*Ph], 6.89–6.92 [2H, m, Ph*H*], 7.17–7.42 [13H, m, Ph*H*]; δ_C (125 MHz, $CDCl_3$) 67.4 [*C*H(OH)], 73.1 [CO.CHO*C*H$_2$Ph], 73.8 [CO.*C*HOCH$_2$Ph], 74.2 [CHO*C*H$_2$Ph.CHPh], 75.2 [*C*HOCH$_2$Ph.CHPh], 79.1 [*C*HPh], 127.9, 128.0, 128.2 [*p-Ph*], 126.7, 127.7, 128.1, 128.2, 128.4, 128.5 [*m*/*o-Ph*], 134.6, 136.3, 136.8 [*i-Ph*], 169.1 [*C*=O]; ν_{max}(KBr disc, cm^{-1}) 3444 [O–H], 1764 [C=O]; HRMS $C_{25}H_{24}O_5Na$ [MNa$^+$] requires 427.1521, found 427.1535; $[\alpha]_D^{25}$ +64.0 (*c* = 0.28, $CHCl_3$); *m*/*z* ES+ 427 [100%, MNa$^+$].

Preparation of (2*S*,3*S*,4*R*,5*R*)-2,4-bis-benzyloxy-3-hydroxy-5-phenyl-tetrahydro-pyran-2-one (2*S*,3*S*,4*R*,5*R*)-31 and (*S*)-4-benzyl-5,5-dimethyl-oxazolidin-2-one (*S*)-22. A solution of **30** (75 mg, 0.12 mmol) in PhMe (5 mL) was refluxed for 16 h, then cooled to ambient temperature and concentrated *in vacuo*. Purification by column column chromatography gave **31** (37 mg, 0.09 mmol, 76%) as a white solid and (*S*)-**22** (24 mg, 0.12 mmol, 99%) as a white solid.

Preparation of (2*S*,3*S*,4*R*,5*S*)-2,4-bis-benzyloxy-3-hydroxy-5-furan-2′-yl-tetrahydro-pyran-2-one (2*S*,3*S*,4*R*,5*S*)-32 and (*S*)-4-benzyl-5,5-dimethyl-oxazolidin-2-one (*S*)-22. Following representative procedure 2, **20** (300 mg, 0.42 mmol), TBAF (0.63 mL, 0.63 mmol) and AcOH (0.02 mL, 0.42 mmol) in THF (10 mL) furnished a 50 : 50 inseparable mixture of **32** and (*S*)-**22** (131 mg) as a pale yellow oil after column chromatography.

32: R_f 0.14 [2 : 1 Et$_2$O–pentane]; δ_H (400 MHz, $CDCl_3$) 4.05–4.09 [2H, m, C*H*(OH) and CO.C*H*OCH$_2$Ph], 4.14 [1H, d, *J* 10.3, CHOC*H*$_A$H$_B$Ph], 4.21–4.26 [1H, m, C*H*(OCH$_2$Ph).CH(C$_4$H$_3$O)], 4.41 [1H, d, *J* 11.4, CHOC*H*$_C$H$_D$Ph], 4.49 [1H, d, *J* 10.3, CHOCH$_A$*H*$_B$Ph], 4.67 [1H, d, *J* 11.4, CHOCH$_C$*H*$_D$Ph], 5.36 [1H, d, *J* 5.0, CH(OCH$_2$Ph).C*H*(C$_4$H$_3$O)], 6.34–6.36 [2H, m, C*H* furan], 7.18–7.42 [11H, m, Ar*H*]; δ_C (100 MHz, $CDCl_3$) 63.5 [*C*H(OH)], 72.2 [*C*HOCH$_2$Ph.CH(C$_4$H$_3$O)], 72.6, 72.9 [2 × CHO*C*H$_2$Ph], 78.2 [CO.*C*HOCH$_2$Ph and CH(OCH$_2$Ph).*C*H(C$_4$H$_3$O)], 107.0, 110.5, 141.6 [*C*H furan], 127.8, 127.9 [*p-Ph*], 128.1, 128.3, 128.5, 128.9 [*m*/*o-Ph*], 136.9, 137.7 [*i-Ph*], 152.9 [*i-Ar* furan], 169.9 [*C*=O]; ν_{max}(thin film, cm^{-1}) 3400 [O–H], 1770 [C=O]; HRMS $C_{23}H_{23}O_6$ [MH$^+$] requires 395.1495, found 395.1491; *m*/*z* CI+ 377 [25%, MH$^+$–H$_2$O], 395 [15%, MH$^+$].

Preparation of (2*S*,3*S*,4*R*,5*S*)-2,4-bis-benzyloxy-3-benzoyl-5-furan-2-yl-tetrahydro-pyran-2-one (2*S*,3*S*,4*R*,5*S*)-33 and (*S*)-3-benzoyl-4-benzyl-5,5-dimethyl-oxazolidin-2-one. Following representative procedure 3, Et$_3$N (0.04 mL, 0.32 mmol), PhCOCl (0.03 mL, 0.25 mmol), DMAP (2 mg, 0.01 mmol) and a 50 : 50 mixture of **32** and (*S*)-**22** (50 mg, 0.127 mmol) in CH_2Cl_2 (10 mL) furnished **33** (63 mg) as a pale yellow oil contaminated with (*S*)-3-benzoyl-4-benzyl-5,5-dimethyl–oxazolidin-2-one and (*S*)-3-benzoyl-4-benzyl-5,5-dimethyl–oxazolidin-2-one (12 mg, 0.04 mmol) as a white foam after column chromatography.

33: R_f 0.26 [1 : 1 pentane–Et$_2$O]; δ_H (400 MHz, $CDCl_3$) 4.52 [1H, d, *J* 10.4, CHOC*H*$_A$H$_B$Ph.CHC$_4$H$_4$O], 4.65 [1H, dd, *J* 7.4, 4.5, C*H*(OBz)], 4.70 [2H, s, CO.CHOC*H*$_2$Ph], 4.87 [1H, d, *J* 10.4, CHOCH$_A$*H*$_B$Ph.CHC$_4$H$_4$O], 5.58 [1H, dd, *J* 6.5, 4.5, C*H*OCH$_2$Ph.CHC$_4$H$_4$O], 5.88 [1H, d, *J* 6.6, C*H*C$_4$H$_4$O], 6.33–6.34 [1H, m, C*H*(furan)], 6.48–6.49 [1H, m, C*H*(furan)], 6.56 [1H, d, *J* 6.6, CO.C*H*OCH$_2$Ph], 7.12–7.63 [16H, m, Ar*H*]; δ_C (100 MHz, $CDCl_3$) 69.1 [*C*HC$_4$H$_4$O], 73.1 [*C*H(OBz)], 73.5 [CO.*C*HOCH$_2$Ph], 74.4 [CHO*C*H$_2$Ph.CHC$_4$H$_4$O], 75.2 [CO.*C*HOCH$_2$Ph], 78.8 [*C*HOCH$_2$Ph.CHC$_4$H$_4$O], 110.2, 110.6, 142.8 [*C*H (furan)], 126.6, 127.5, 128.0 [*p-Ph*], 128.0, 128.2, 128.3, 128.4, 128.4, 128.5, 128.5, 128.7, 128.8, 129.8, 129.9, 130.0, 130.1 [*m*/*o-Ph*], 136.9, 137.2, 137.7 [*i-Ph*], 152.1 [C^4 furan], 164.2 [CH(*C*OBz)], 170.2 [*C*=O lactone]; ν_{max}(thin film, cm^{-1}) 1777, 1728 [C=O]; HRMS $C_{30}H_{27}O_7$ [MH$^+$] requires 499.1757, found 499.1748; *m*/*z* CI+ 377.24 [MH$^+$–PhCO$_2$H and H$_2$O, 40%], 394.45 [MH$^+$–PhCO$_2$H, 70%], 499.27 [MH$^+$, 7%].

(*S*)-3-benzoyl-4-benzyl-5,5-dimethyl–oxazolidin-2-one: R_f 0.2 [3 : 1 pentane–Et$_2$O]; δ_H (400 MHz, $CDCl_3$) 1.30 [3H, s, C(C*H*$_3$)$_A$(CH$_3$)$_B$], 1.52 [3H, s, C(CH$_3$)$_A$(C*H*$_3$)$_B$], 2.87 [1H, dd, *J* 14.0, 9.8, CHC*H*$_A$H$_B$Ph], 3.50 [1H, dd, *J* 14.0, 4.3, CHCH$_A$*H*$_B$Ph], 4.68 [1H, dd, C*H*CH$_2$Ph], 7.22–7.42 [5H, m, Ph*H*], 7.43–7.50 [2H, m, Ph*H*], 7.52–7.58 [1H, m, Ph*H*], 7.63–7.71 [5H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 22.6, 28.1 [C(*C*H$_3$)$_2$], 34.5 [CH*C*H$_2$Ph], 64.6 [*C*HCH$_2$Ph], 82.3 [*C*(CH$_3$)$_2$], 127.0, 130.6 [*p-Ph*], 127.9, 128.8, 129.2, 129.3 [*m*/*o-Ph*], 133.4, 136.5 [*i-Ph*], 152.6 [*C*=O endocyclic], 170.4 [*C*=O exocyclic]; ν_{max}(KBr disc, cm^{-1}) 1776 [C=O endocyclic], 1687 [C–O exocyclic]; HRMS $C_{19}H_{20}NO_3$ [MH$^+$] requires 310.1443, found 310.1456; $[\alpha]_D^{25}$ +36.4 (*c* = 1.25, $CHCl_3$); *m*/*z* CI+ (NH_3) 105 [100%, MH$^+$-SQ], 310 [60%, MH$^+$].

Preparation of (2*R*,3*S*,4*R*,5*R*)-2,4-bis-benzyloxy-3-hydroxy-5-phenyl-tetrahydro-pyran-2-one (2*R*,3*S*,4*R*,5*R*)-21, (2*S*,3*R*,4*R*,5*R*)-2,4-bis-benzyloxy-3-hydroxy-5-phenyl-tetrahydro–pyran-2-one (2*S*,3*R*,4*R*,5*R*)-24 and 5,5-dimethyl-oxazolidin-2-one. Following representative procedure 2, a mixture of **11**–**12** (190 mg, 0.30 mmol), TBAF (0.45 mL, 0.45 mmol) and AcOH (0.02 mL, 0.30 mmol) in THF (10 mL) furnished an inseparable mixture of **21**–**24** (81 mg, 0.26 mmol, 86%) as a white solid and 5,5-dimethyl–oxazolidin-2-one (30 mg, 0.19 mmol, 64%) as a white solid after column chromatography.

Preparation of (2′*S*,3′*S*,4′*S*,5′*R*)-4-benzyl-3-(2′,4′-bis-benzyloxy-3′,5′-dihydroxy-5′-phenyl-pentanoyl)-5,5-dimethyl-oxazolidin-2-one 34, (2*S*,3*S*,4*R*,5*R*)-2,4-bis-benzyloxy-3-hydroxy-5-phenyl-tetrahydro-pyran-2-one (2*S*,3*S*,4*R*,5*R*)-31 and 5,5-dimethyl-oxazolidin-2-one. Following representative procedure 2, **13** (70 mg, 0.11 mmol), TBAF (0.16 mL, 0.16 mmol) and AcOH (0.006 mL, 0.11 mmol) in THF (10 mL) furnished a 66 : 34 mixture of **34** : **31** which after purification by column chromatography furnished an inseparable 66 : 34 mixture of **34** : **31** (48 mg) as a pale yellow oil and 5,5-dimethyl-oxazolidin-2-one (9 mg, 0.08 mmol, 71%) as a pale peach solid.

34: R_f 0.12 [1 : 1 pentane–Et$_2$O; double eluted]; δ_H (400 MHz, $CDCl_3$) 1.20 [3H, s, C(C*H*$_3$)$_A$(CH$_3$)$_B$], 1.40 [3H, s, C(CH$_3$)$_A$(C*H*$_3$)$_B$], 3.19 [1H, d, *J* 10.8, NC*H*$_A$H$_B$], 3.49 [1H, d, *J* 10.8, NCH$_A$*H*$_B$], 3.89 [1H, dd, *J* 5.6, 3.0, C*H*(OCH$_2$Ph).CHPh], 4.13 [1H, d, *J* 10.8, CHOC*H*$_A$H$_B$Ph], 4.21–4.23 [2H, m, 2 × C*H*(OH)], 4.40 [1H, d, *J* 10.8, CHOCH$_A$*H*$_B$Ph], 4.47 [1H, d, *J* 11.5, CHOC*H*$_C$H$_D$Ph], 4.70 [1H, d, *J* 11.5, CHOCH$_C$*H*$_D$Ph], 5.46 [1H, d, *J* 5.6, CO.C*H*OCH$_2$Ph], 7.14–7.43 [15H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 26.7, 26.8 [C(*C*H$_3$)$_2$], 53.9 [N*C*H$_2$], 72.4, 72.8 [2 × *C*H(OH)], 73.0, 73.1 [2 × CHO*C*H$_2$Ph], 76.7 [CO.*C*HOCH$_2$Ph], 79.4 [*C*(CH$_3$)$_2$], 81.3 [*C*H(OCH$_2$Ph).CHPh], 127.4, 127.7, 127.8 [*p-Ph*], 128.1, 128.2, 128.3, 128.4, 128.5, 128.6 [*m*/*o-Ph*], 137.0, 137.6, 141.4 [*i-Ph*], 152.7 [*C*=O endocyclic], 170.9 [*C*=O exocyclic]; ν_{max}(thin film, cm^{-1}) 3438 [O–H], 1769 [C=O endocyclic], 1708 [C=O exocyclic]; $C_{30}H_{33}NO_7Na$ [MNa$^+$] requires 542.2155, found 542.2167; *m*/*z* ES+ 542 [100%, MNa$^+$].

Preparation of (1″*R*,2′*S*,3′*S*,4*S*)-4-benzyl-3-(2′-benzyloxy-3′-(2″,2″-dimethyl-[1″,3″]dioxolan-4″-yl)-3-hydroxy-propionyl)-5,5-dimethyl-oxazolidin-2-one (1″*R*,2′*S*,3′*S*,4*S*)-39. Following representative procedure 1, CF_3SO_3H (0.90 mL, 10.19 mmol), Et$_3$B (10.20 mL, 10.20 mmol), (*S*)-**4** (3.00 g, 8.50 mmol), *i*-Pr$_2$NEt (2.07 mL, 11.90 mmol) and **38** (1.43 g, 11.01 mmol) in CH_2Cl_2 (70 mL) furnished **39** (3.00 g, 6.20 mmol, 73%) as a white solid after column chromatography.

39: R_f 0.15 [2 : 1 pentane–Et$_2$O]; m.p 100–101 °C [pentane–Et$_2$O]; δ_H (400 MHz, $CDCl_3$) 1.33 [3H, s, C(C*H*$_3$)$_A$(CH$_3$)$_B$ (acetonide)], 1.37 [3H, s, C(C*H*$_3$)$_A$(CH$_3$)$_B$ (auxiliary)], 1.39 [3H, s, C(CH$_3$)$_A$(C*H*$_3$)$_B$ (auxiliary)], 1.44 [3H, s, C(CH$_3$)$_A$(C*H*$_3$)$_B$ (acetonide)], 2.50 [1H, d, *J* 7.4, CH(O*H*)], 2.84 [1H, dd, *J* 14.4, 9.4, CHC*H*$_A$H$_B$Ph], 3.06 [1H, dd, *J* 14.4, 4.0, CHCH$_A$*H*$_B$Ph], 3.82–3.87 [1H, m, C*H*(OH)], 4.06 [2H, d, *J* 5.4, OCHC*H*$_2$O],

4.16–4.21 [1H, m, OC*H*CH_2O], 4.46–4.52 [3H, m, C*H*CH_2Ph and CHOC*H*$_2$Ph], 5.49 [1H, d, *J* 3.8, C*H*OCH_2Ph], 7.20–7.38 [15H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 22.2, 28.5 [C(*C*H_3)$_2$ (auxiliary)], 25.3, 26.6 [C(*C*H_3)$_2$ (acetonide)], 35.3 [CH*C*H_2Ph], 63.8 [*C*HCH_2Ph], 66.7 [OCH*C*H_2O], 73.0 [CHO*C*H_2Ph], 73.2 [*C*H(OH)], 75.6 [O*C*HCH_2O], 77.9 [*C*HOCH_2Ph], 83.2 [*C*(CH_3)$_2$ (auxiliary)], 109.5 [*C*(CH_3)$_2$ (acetonide)], 126.8, 128.1 [*p-Ph*], 128.4, 128.7, 129.1 [*m*/*o-Ph*], 136.8, 137.1 [*i-Ph*], 152.4 [*C*=O endocyclic], 170.7 [*C*=O exocyclic]; ν_{max}(KBr disc, cm^{-1}) 3456 [O–H], 1775 [C=O endocyclic], 1707 [C=O exocyclic]; $C_{27}H_{33}NO_7$ requires C 67.1, H 6.9, N 2.9%, found C 66.8, H 6.9, N 3.0%; [*a*] −43.1 (*c* = 1.4, $CHCl_3$); *m*/*z* ES+ 426 [20%, MH^+–Me_2CO], 506 [100%, MNa^+].

Preparation of (1′*R*,2*R*,3*S*)-2-benzyloxy-1-(2′,2′-dimethyl-[1′,3′]dioxolan-4′-yl)-propane-1,3-diol (1′*R*,2*R*,3*S*)-40 and (*S*)-4-benzyl-5,5-dimethyl-oxazolidin-2-one (*S*)-22. $LiBH_4$ (0.52 mL, 1.04 mmol) was added to a solution of **39** (500 mg, 1.04 mmol) in THF (20 mL) and H_2O (0.19 mL, 1.04 mmol) at 0 °C. After stirring for 20 min, the reaction mixture was quenched with 0.5 M NaOH solution, warmed to ambient temperature and stirred for a further 45 min. The layers were separated and the aqueous layer extracted with Et_2O, washed with brine, dried and concentrated *in vacuo*. The crude product was purified by column chromatography to afford **40** (256 mg, 0.91 mmol, 87%) as a white gum and (*S*)-**22** (209 mg, 1.02 mmol, 98%).

40: R_f 0.05 [35:1 $CHCl_3$–MeOH]; δ_H (400 MHz, $CDCl_3$) 1.35 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.40 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 3.61–3.66 [1H, m, C*H*(OH)], 3.67–3.69 [1H, m, OC*H*CH_2O], 3.76 [1H, dd, *J* 11.8, 4.3, OCHCH_AH$_B$O], 3.82 [1H, dd, *J* 11.8, 5.4, OCHCH$_A$$H_B$O], 3.96–4.02 [1H, m, C$H_AH_B$OH], 4.03–4.12 [2H, m, CH$_A$$H_B$OH and C*H*OCH$_2$Ph], 4.63 [1H, d, *J* 11.4, CHOCH_AH$_B$Ph], 4.73 [1H, d, *J* 11.4, CHOCH$_A$$H_B$Ph], 7.29–7.40 [5H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 25.3, 26.7 [C(*C*H_3)$_2$], 62.3 [OCH*C*H_2O], 67.4 [*C*H_2OH], 73.0 [CHO*C*H_2Ph], 73.7 [*C*H(OH)], 75.5 [*C*HOCH_2Ph], 78.6 [O*C*HCH_2O], 109.3 [*C*(CH_3)$_2$], 128.0 [*p-Ph*], 128.0, 128.5 [*m*/*o-Ph*], 137.9 [*i-Ph*]; ν_{max} (thin film, cm^{-1}) 3391 [O–H]; HRMS $C_{15}H_{22}O_5Na$ [MNa^+] requires 305.1389, found 305.1392; [*a*] −19.3 (*c* = 1.5, $CHCl_3$); *m*/*z* ES+ 305 [100%, MNa^+].

Preparation of (1′*R*,2*R*,3*S*)-1-(2′,2′-dimethyl-[1′,3′]dioxolan-4′-yl)-propane-1,2,3-triol (1′*R*,2*R*,3*S*)-41. Pd/C (25 mg) was added to a solution of **40** (50 mg, 0.18 mmol) in MeOH (4 mL) and AcOH (0.32 mL) at ambient temperature. After stirring under a hydrogen atmosphere for 16 h, the reaction was filtered through Celite® (eluent: MeOH) and concentrated *in vacuo*. The crude product was purified by trituration with Et_2O to afford **41** (32 mg, 0.17 mmol, 93%) as a white oil.

41: δ_H (200 MHz, MeOD) 1.38 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.41 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 3.55–3.72 [2H, m], 3.77–3.82 [2H, m], 3.86–4.02 [2H,m], 4.08–4.25 [1H, m]; $[a]_D^{25}$ −0.69 (*c* = 1.2, EtOH), {lit.[44] $[a]_D^{25}$ −0.63 (*c* = 2.35, EtOH).

Preparation of (1″*R*,2′*R*,3′*R*,4*R*)-4-benzyl-3-(2′-benzyloxy-3′-(2,2-dimethyl-[1,3]dioxolan-4-yl)-3-hydroxy-propionyl)-5,5-dimethyl–oxazolidin-2-one (1″*R*,2′*R*,3′*R*,4*R*)-42 and (1″*R*,2′*R*,3′*S*,4*R*)-4-benzyl-3-(2′-benzyloxy-3′-(2,2-dimethyl-[1,3]dioxolan-4-yl)-3-hydroxy–propionyl)-5,5-dimethyl-oxazolidin-2-one (1″*R*,2′*R*,3′*S*,4*R*)-43. Following representative procedure 1, CF_3SO_3H (0.15 mL, 1.70 mmol), Et_3B (1.70 mL, 1.70 mmol), (*R*)-**4** (500 mg, 1.42 mmol), *i*-Pr_2NEt (0.35 mL, 1.99 mmol) and **35** (203 mg, 1.56 mmol) in CH_2Cl_2 (40 mL) furnished an inseparable 66:34 mixture of **42**:**43** (230 mg, 0.48 mmol, 34%) as a clear colourless oil and returned (*R*)-**4** (222 mg, 0.63 mmol, 44%) as a pale yellow solid after column chromatography.

42:**43**: R_f 0.09 [1:1 30–40 °C petrol–Et_2O]; δ_H (400 MHz, $CDCl_3$) 1.38–1.43 [24H, m, C(CH_3)$_2$(auxiliary and acetonide; **42** and **43**)], 2.69 [2H, d, *J* 8.4, CH(O*H*) (**42** and **43**)], 2.85 [1H, dd, *J* 14.4, 9.5, CHCH_AH$_B$Ph (**43**)], 2.93 [1H, dd, *J* 14.4, 9.1, CHCH_AH$_B$Ph (**42**)], 3.03 [1H, dd, *J* 14.4, 3.9, CHCH$_A$$H_B$Ph (**43**)], 3.10 [1H, dd, *J* 14.4, 4.4, CHCH$_A$$H_B$Ph (**42**)], 3.64–3.70 [1H, m, OCHCH_AH$_B$O (**43**)], 3.74–3.79 [1H, m, OCHCH$_A$$H_B$O (**43**)], 3.77 [1H, dd, *J* 5.0, 3.9, OCHCH_AH$_B$O (**42**)], 3.82–3.89 [1H, m, C*H*(OH) (**42**)], 3.84 [1H, dd, *J* 5.0, 6.4, OCHCH$_A$$H_B$O (**42**)], 4.21–4.24 [2H, m, OC*H*CH_2O (**42**) and C*H*(OH) (**43**)], 4.27 [1H, d, *J* 11.5, CHOCH_AH$_B$Ph (**42**)], 4.31–4.35 [1H, m, OC*H*CH_2O (**43**)], 4.41 [1H, d, *J* 11.5, CHOCH_AH$_B$Ph (**43**)], 4.49–4.58 [6H, m, C*H*OCH$_A$$H_B$Ph (**42** and **43**) and C*H*CH$_2$Ph (**42** and **43**)], 5.22 [1H, d, *J* 3.1, C*H*OCH$_2$Ph (**42**)], 5.50 [1H, d, *J* 4.2, C*H*OCH$_2$Ph (**43**)], 7.17–7.38 [20H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 22.0, 22.1, 25.6, 26.6, 26.8, 27.1, 28.3, 28.4 [C(*C*H_3)$_2$(acetonide and auxiliary; **42** and **43**)], 35.3 [CH*C*H_2Ph (**43**)], 35.4 [CH*C*H_2Ph (**42**)], 62.3 [OCH*C*H_2O (**43**)], 63.9 [*C*HCH$_2$Ph (**42** and **43**)], 65.9 [OCH*C*H_2O (**42**)], 72.7 [CHO*C*H_2Ph (**43**)], 72.8 [CHO*C*H_2Ph (**42**)], 73.1 [*C*H(OH) (**42**)], 75.2 [*C*HOCH$_2$Ph (**43**)], 76.5 [*C*HOCH$_2$Ph (**42**)], 76.8, 77.1, 77.2 [O*C*HCH_2O (**42** and **43**) and *C*H(OH) (**43**)], 83.3 [*C*(CH_3)$_2$ (auxiliary; **43**)], 83.7 [*C*(CH_3)$_2$ (auxiliary; **42**)], 109.4 [*C*(CH_3)$_2$ (acetonide; **42**)], 109.9 [*C*(CH_3)$_2$ (acetonide; **43**)], 126.9, 127.2, 128.1 [*p-Ph* (**42** and **43**)], 128.2, 128.3, 128.4, 128.5, 128.7, 129.1, 129.2 [*m*/*o-Ph* (**42** and **43**)], 136.6, 136.7, 126.8, 136.9 [*i-Ph* (**42** and **43**)], 152.7 [*C*=O endocyclic (**43**)], 152.8 [*C*=O endocyclic (**42**)], 169.8 [*C*=O exocyclic (**42**)], 170.1 [*C*=O exocyclic (**43**)]; ν_{max}(KBr disc, cm^{-1}) 1772 [C=O endocyclic], 1713 [C=O exocyclic]; HRMS $C_{27}H_{33}NO_7Na$ [MNa^+] requires 506.2155, found 506.2152; *m*/*z* ES+ 501 [50%, MNH_4^+], 506 [100%, MNa^+].

Preparation of (1′*R*,2*S*,3*R*)-2-benzyloxy-1-(2′,2′-dimethyl-[1′,3′]dioxolan-4′-yl)-propane-1,3-diol(1′*R*,2*S*,3*R*)-44,(1′*R*,2*S*,3*S*)-2-benzyloxy-1-(2′,2′-dimethyl-[1′,3′]dioxolan-4′-yl)-propane-1,3-diol(1′*R*,2*S*,3*S*)-45and(*R*)-4-benzyl-5,5-dimethyl-oxazolidin-2-one (*R*)-22. $LiBH_4$ (0.16 mL, 0.31 mmol) was added to a solution of **42** and **43** (150 mg, 0.31 mmol) in THF (20 mL) and H_2O (0.02 mL, 0.31 mmol) at 0 °C. After stirring for 20 min, the reaction mixture was quenched with 0.5 M NaOH solution, warmed to ambient temperature and stirred for a further 45 min. The layers were separated and the aqueous layer extracted with Et_2O, washed with brine, dried and concentrated *in vacuo*. The crude product was purified by column chromatography to afford **44** (38 mg, 0.13 mmol, 43%) as a clear colourless oil, an 84:16 mixture of **44**:**45** (17 mg, 0.06 mmol, 19%) and a 28:72 mixture of **44**:**45** (22 mg, 0.08 mmol, 25%) and (*R*)-**22** (53 mg, 0.26 mmol, 83%).

44: R_f 0.14 [80:1 CH_2Cl_2–MeOH]; δ_H (400 MHz, $CDCl_3$) 1.37 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.43 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 2.42 [1H, br s, CH$_2$O*H*], 2.66 [1H, d, *J* 6.0, CH(O*H*)], 3.52–3.56 [1H, m, C*H*(OH)], 3.65–3.74 [1H, m, OC*H*CH_2O], 3.74–3.80 [1H, m, CH_AH$_B$OH], 3.78 [1H, dd, *J* 8.2, 7.0, OCHCH_AH$_B$O], 3.86–3.91 [1H, m, CH$_A$$H_B$OH], 3.91 [1H, dd, *J* 8.2, 6.5, OCHCH$_A$$H_B$O], 4.26–4.30 [1H, m, C*H*OCH$_2$Ph], 4.61 [1H, d, *J* 11.7, CHOCH_AH$_B$Ph], 4.70 [1H, d, *J* 11.7, CHOCH$_A$$H_B$Ph], 7.29–7.40 [5H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 25.4, 26.5 [C(*C*H_3)$_2$], 61.3 [*C*H_2OH], 66.1 [OCH*C*H_2O], 71.6 [O*C*HCH$_2$O], 72.4 [CHO*C*H_2Ph], 75.7 [*C*HOCH$_2$Ph], 78.9 [*C*H(OH)], 109.5 [*C*(CH_3)$_2$], 128.6 [*p-Ph*], 128.1, 128.6 [*m*/*o-Ph*], 137.8 [*i-Ph*]; ν_{max} (thin film, cm^{-1}) 3414.5 [O–H]; HRMS $C_{15}H_{21}O_5$ [M–H^+] requires 281.1389, found 281.1390; $[a]_D^{22}$ +13.2 (*c* = 0.85, $CHCl_3$); *m*/*z* ES− 223 [100%, M–Me_2C=O^+], 281 [95%, M–H^+].

45: R_f 0.09 [80:1 CH_2Cl_2–MeOH]; δ_H (400 MHz, $CDCl_3$) 1.42 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.43 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 3.60–3.69 [2H, m, OCHCH_AH$_B$O and CH_AH$_B$OH], 3.72–3.87 [2H, m, OCHCH$_A$$H_B$O and CH$_A$$H_B$OH], 3.89–3.94 [1H, m, C*H*OCH$_2$Ph], 4.09–4.14 [2H, m, C*H*(OH) and OC*H*CH$_2$O], 4.67–4.76 [2H, ABq, *J* 11.7, CHOCH_2Ph], 7.26–7.41 [5H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 26.8, 27.0 [C(CH_3)$_2$], 61.6 [*C*H_2OH], 62.4 [OCH*C*H_2O], 72.4 [CHO*C*H_2Ph], 77.0 [O*C*HCH$_2$O], 77.1 [*C*H(OH)], 78.3 [*C*HOCH$_2$Ph], 109.2 [*C*(CH_3)$_2$], 128.0 [*p-Ph*], 128.0, 128.6 [*m*/*o-Ph*], 137.5 [*i-Ph*]; ν_{max} (thin film, cm^{-1}) 3387 [O–H]; HRMS $C_{15}H_{21}O_5$ [M–H^+] requires 281.1389, found 281.1392; *m*/*z* ES− 223 [100%, M–Me_2C=O], 281 [85%, M–H^+].

Preparation of (1′*R*,2*S*,3*R*)-1-(2′,2′-dimethyl-[1′,3′]dioxolan-4′-yl)-propane-1,2,3-triol (1′*R*,2*S*,3*R*)-46. Pd/C (10 mg) was added to a solution of **44** (35 mg, 0.12 mmol) in MeOH (4 mL) and AcOH (0.32 mL) at ambient temperature. After stirring under a hydrogen atmosphere for 16 h, the reaction was filtered through Celite® (eluent: MeOH) and concentrated *in vacuo*. The crude product was purified by trituration with Et_2O to afford **46** (21 mg, 0.11 mmol, 93%) as a clear colourless oil.

46: δ_H (200 MHz, MeOD) 1.37 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.43 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$], 3.51–3.73 [5H, m], 3.72–3.82 [2H, m]; $[\alpha]_D^{22}$ +8.2 (c = 0.9, EtOH), {lit.[44] $[\alpha]_D^{25}$ +8.31 (c = 3.05, EtOH).

Preparation of (1″*R*,2′*S*,3′*S*,4*S*)-benzyl-3-[2′-benzyloxy-3′-(2″,2″-dimethyl-[1″,3″]dioxolan-4″-yl)-3′-(*tert*-butyl-dimethyl-silanyloxy)-propionyl]-5,5-dimethyl-oxazolidin-2-one 47. Imidazole (1.47 g, 21.55 mmol), TBDMSCl (1.63 g, 10.78 mmol) and DMAP (56 mg, 0.43 mmol) were added sequentially to a solution of **39** (2.08 g, 4.31 mmol) in DMF (15 mL) at ambient temperature. The reaction mixture was then warmed to 60 °C. After stirring for 18 h, the reaction mixture was quenched with MeOH, diluted with Et_2O, washed with water, dried and concentrated *in vacuo*. Purification by column chromatography furnished **47** (2.16 g, 3.62 mmol, 84%) as a white solid.

47: R_f 0.2 [5 : 1 30–40 °C petrol–Et_2O]; mp 70–71 °C [30–40 °C petrol–Et_2O]; δ_H (400 MHz, $CDCl_3$) 0.73 [3H, s, Si(CH_3)$_A$(CH$_3$)$_B$], 0.88 [9H, s, SiC(CH_3)$_3$], 0.12 [3H, s, Si(CH$_3$)$_A$(CH_3)$_B$], 1.26 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$ (acetonide)], 1.31 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$ (auxiliary)], 1.33 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$ (auxiliary)], 1.38 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$ (acetonide)], 2.58 [1H, dd, J 14.5, 10.4, CHCH_AH$_B$Ph], 2.96 [1H, dd, J 14.5, 4.0, CHCH$_A$$H_B$Ph], 3.93–4.01 [2H, m, OCHCH_2O], 4.07 [1H, t, J 6.8, CH(OTBDMS)], 4.20–4.23 [1H, m, OCHCH$_2$O], 4.35 [1H, dd, J 10.4, 4.0, CHCH$_2$Ph], 4.47 [1H, d, J 11.6, CHOCH_AH$_B$Ph], 4.61 [1H, d, J 11.6, CHOCH$_A$$H_B$Ph], 5.42 [1H, d, J 6.7, CHOCH$_2$Ph], 7.21–7.38 [10H, m, PhH]; δ_C (100 MHz, $CDCl_3$) −4.7, −3.7 [Si(CH$_3$)$_2$], 18.3 [SiC(CH$_3$)$_3$], 22.6, 28.8 [C(CH$_3$)$_2$(auxiliary)], 25.2, 26.5 [C(CH$_3$)$_2$(acetonide)], 26.0 [SiC(CH$_3$)$_3$], 34.7 [CHCH$_2$Ph], 64.2 [CHCH$_2$Ph], 66.5 [OCHCH$_2$O], 73.2 [CHOCH$_2$Ph], 74.8 [CH(OTBDMS)], 76.3 [OCHCH$_2$O], 79.1 [CHOCH$_2$Ph], 82.2 [C(CH$_3$)$_2$ (auxiliary)], 109.2 [C(CH$_3$)$_2$ (acetonide)], 126.7, 127.9 [*p-Ph*], 128.3, 128.6, 128.7, 128.9 [*m*/*o-Ph*], 137.1, 127.5 [*i-Ph*], 152.5 [C=O endocyclic], 171.6 [C=O exocyclic]; ν_{max}(KBr disc, cm^{-1}) 1776 [C=O endocyclic], 1706 [C=O exocyclic]; $C_{33}H_{47}NO_7Si$ requires C 66.3, H 7.9, N 2.3%, found C 66.4, H 7.7, 2.3%; [α] +3.4 (c = 0.5, $CHCl_3$); m/z ES+ 540 [100%, MH$^+$–Me$_2$CO], 620 [75%, MNa$^+$].

Preparation of (1″*R*,2′*S*,3′*S*,4*S*)-4-benzyl-3-[2′-benzyloxy-3′-(*tert*-butyl-dimethyl-silanyloxy)-3′-{2″,2″-dimethyl-[1″,3″]dioxolan-4″-yl}-1′-hydroxy–propyl]-5,5-dimethyl-oxazolidin-2-one 48 and (1″*R*,2*S*,2′*S*,3′*S*)-2-[2′-benzyloxy-3′-(*tert*-butyl-dimethyl-silanyloxy)-3′-{2″,2″-dimethyl-[1″,3″]dioxolan-4″-yl}-propionylamino]-1,1-dimethyl-3-phenyl-propyl formate 49. DIBAL (1.68 mL, 1.68 mmol) was added dropwise to a stirred solution of **47** (500 mg, 0.84 mmol) in CH_2Cl_2 (10 mL) at −78 °C. The reaction was quenched at −78 °C after 30 min with saturated, aqueous NH_4Cl solution, warmed to ambient temperature and stirred for a further 30 min. The reaction mixture was filtered through Celite® (eluent: CH_2Cl_2), the layers separated, dried and concentrated *in vacuo*. Purification by column chromatography furnished an inseparable 88 : 12 mixture of **48** and **49** (342 mg, 0.57 mmol, 68%) as a pale yellow oil.

48 : **49**: R_f 0.28 [1 : 1 30–40 °C petrol–Et_2O]; δ_H (400 MHz, $CDCl_3$) −0.02 [3H, s, Si(CH_3)$_A$(CH$_3$)$_B$ (**49**)], 0.079 [3H, s, Si(CH$_3$)$_A$(CH_3)$_B$ (**49**)], 0.11 [6H, s, Si(CH_3)$_2$(**48**)], 0.87 [9H, s, SiC(CH_3)$_3$ (**49**)], 0.90 [9H, s, SiC(CH_3)$_3$ (**48**)], 1.11 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$ (auxiliary, **48**)], 1.25 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$ (acetonide, **48**)], 1.26 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$ (auxiliary, **49**)], 1.31 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$ (acetonide, **48**)], 1.39 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$ (acetonide, **49**)], 1.42 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$ (auxiliary, **48**)], 1.45 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$ (acetonide, **49**)], 1.78 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$ (auxiliary, **49**)], 2.60–2.66 [1H, m, CHCH_AH$_B$Ph (**49**)], 2.63 [1H, dd, J 14.7, 9.4, CHCH_AH$_B$Ph (**48**)], 3.08 [1H, dd, J 14.7, 5.1, CHCH$_A$$H_B$Ph (**48**)], 3.14 [1H, dd, J 14.4, 4.8, CHCH$_A$$H_B$Ph (**49**)], 3.54–3.58 [2H, m, OCHCH_AH$_B$O and CH(OTBDMS) (**49**)], 3.66 [1H, dd, J 6.8, 3.2, OCHCH$_A$$H_B$O (**49**)], 3.77–3.81 [1H, m, OCHCH_AH$_B$O (**48**)], 3.84–3.87 [2H, m, OCHCH$_A$$H_B$O (**48**) and OC$HCH_2$O (**49**)], 4.05 [1H, dd, J 9.4, 5.1, CHCH$_2$Ph (**48**)], 4.09 [1H, d, J 9.1, CH(OH) (**48**)], 4.15–4.20 [2H, m, OCHCH$_2$O (**48**) and CHOCH$_2$Ph (**49**)], 4.30 [1H, dd, J 9.2, 2.1, CH(OTBDMS) (**48**)], 4.32–4.39 [1H, m, CHCH$_2$Ph (**49**)], 4.44 [1H, d, J 11.6, CHOCH_AH$_B$Ph (**49**)], 4.54 [1H, d, J 11.6, CHOCH$_A$$H_B$Ph (**49**)], 4.68 [1H, app. t, J 9.1, CHOCH$_2$Ph (**48**)], 4.72–4.80 [2H, ABq, J 11.8, CHOCH_2Ph (**48**)], 7.08–7.41 [20H, m, PhH (**48** and **49**)], 7.88 [1H, s, CHO (**49**)]; δ_C (100 MHz, $CDCl_3$) −4.6, −4.5 [Si(CH$_3$)$_2$ (**48**)], −4.2, −4.1 [Si(CH$_3$)$_2$ (**49**)], 18.1 [SiC(CH$_3$)$_3$ (**49**)], 18.2 [SiC(CH$_3$)$_3$ (**48**)], 22.1, 27.5 [C(CH$_3$)$_2$ (auxiliary, **48**)], 23.8, 24.6 [C(CH$_3$)$_2$ (auxiliary, **49**)], 25.2, 26.5 [C(CH$_3$)$_2$ (acetonide, **48**)], 25.2, 26.4 [C(CH$_3$)$_2$ (acetonide, **49**)], 25.9 [SiC(CH$_3$)$_3$ (**48**)], 26.0 [SiC(CH$_3$)$_3$ (**49**)], 35.3 [CHCH$_2$Ph (**48**)], 35.8 [CHCH$_2$Ph (**49**)], 57.0 [CHCH$_2$Ph (**49**)], 64.4 [OCHCH$_2$O (**49**)], 65.9 [CHCH$_2$Ph (**48**)], 65.9 [OCHCH$_2$O (**48**)], 72.2 [OCHCH$_2$O (**49**)], 72.8 [CH(OH) (**48**)], 73.4 [CHOCH$_2$Ph (**48**)], 73.8 [CHOCH$_2$Ph (**49**)], 75.2 [CH(OTBDMS) (**49**)], 75.6 [CH(OTBDMS) (**48**)], 77.3 [OCHCH$_2$O (**48**)], 79.3 [CHOCH$_2$Ph (**48**)], 81.9 [C(CH$_3$)$_2$ (auxiliary, **48**)], 82.4 [C(CH$_3$)$_2$ (auxiliary, **49**)], 84.8 [CHOCH$_2$Ph (**49**)], 108.1 [C(CH$_3$)$_2$ (acetonide, **48**)], 108.2 C(CH$_3$)$_2$ (acetonide, **49**)], 126.8, 127.6 [*p-Ph* (**48**)], 127.0, 128.1 [*p-Ph* (**49**)], 127.4, 128.5, 128.7, 128.9 [*m*/*o-Ph* (**48**)], 127.8, 128.4, 128.6, 129.1 [*m*/*o*-Ph (**49**)], 136.6, 138.3 [*i-Ph* (**48**)], 137.0, 137.6 [*i-Ph* (**49**)], 157.4 [C=O (**48**)], 160.0 [C=O ester (**49**)], 169.9 [C=O amide (**49**)]; ν_{max}(thin film, cm^{-1}) 3406 [O–H (**48**)], 1730 [C=O (**48**)]; HRMS $C_{33}H_{50}NO_7Si$ [MH$^+$] requires 600.3357, found 600.3359; m/z APCI+ 206 [70%, SQH$^+$], 600 [5%, MH$^+$].

Preparation of (1′*R*,2*S*,3*S*)-2-benzyloxy-3-(*tert*-butyl-dimethyl-silanyloxy)-3-(2′,2′-dimethyl-[1′,3′]dioxolan-4′-yl)-propionaldehyde 50, (1″*R*,2*S*,2′*S*,3*S*)-*N*-(1′-benzyl-2′-hydroxy-2′-methyl-propyl)-2-benzyloxy-3-(*tert*-butyl-dimethyl-silanyloxy)-3-(2″,2″-dimethyl-[1″,3″]dioxolan-4″-yl)-propionamide 51 and (*S*)-4-benzyl-5,5-dimethyl-oxazolidn-2-one (*S*)-22. K_2CO_3 (81 mg, 0.58 mmol) was added to a suspension of **48** and **49** (250 mg, 0.42 mmol) in MeOH–H_2O (v : v 4 : 1; 10 mL) at ambient temperature. After stirring for 15 min, the reaction mixture was diluted with CH_2Cl_2, washed with water and brine and dried. Purification by column chromatography furnished **50** (86 mg, 0.22 mmol, 52%, 87% de) as a clear colourless oil, **51** (20 mg, 0.03 mmol, 8%) as a pale yellow oil and (*S*)-**22** (50 mg, 0.24 mmol, 58%) as a white solid.

50: δ_H (400 MHz, $CDCl_3$) 0.000 [3H, s, Si(CH_3)$_A$(CH$_3$)$_B$], 0.07 [3H, s, Si(CH$_3$)$_A$(CH_3)$_B$], 0.87 [9H, s, SiC(CH_3)$_3$], 1.32 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.36 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$], 3.87 [1H, dd, J 8.1, 6.6, OCHCH_AH$_B$O], 3.90 [1H, dd, J 3.8, 1.5, CHOCH$_2$Ph], 3.98 [1H, dd, J 8.1, 6.3, OCHCH$_A$$H_B$O], 4.12–4.14 [1H, m, OC$HCH_2$O], 4.18–4.22 [1H, m, C$H$(OTBDMS)], 4.60 [1H, d, J 11.8, CHOCH_AH$_B$Ph], 4.74 [1H, d, J 11.8, CHOCH$_A$$H_B$Ph], 7.27–7.38 [5H, m, PhH], 9.71 [1H, d, J 1.5, CHO]; δ_C (100 MHz, $CDCl_3$) −4.8, −4.4 [Si(CH$_3$)$_2$], 18.2 [SiC(CH$_3$)$_3$], 25.2, 26.5 [C(CH$_3$)$_2$], 25.8 [SiC(CH$_3$)$_3$], 66.2 [OCHCH$_2$O], 73.2 [CHOCH$_2$Ph], 73.6 [OCHCH$_2$O], 75.6 [CHOCH$_2$Ph], 84.8 [CH(OTBDMS)], 108.9 [C(CH$_3$)$_2$], 128.1, 128.5 [*p*- and *m*/*o-Ph*], 137.2 [*i-Ph*], 203.2 [CHO]; ν_{max}(thin film, cm^{-1}) 1734 [C=O]; HRMS $C_{21}H_{34}O_5NaSi$ [MNa$^+$] requires 417.2073, found 417.2083; $[\alpha]_D^{25}$ −15.3 (c = 0.75, $CHCl_3$); m/z ES+ 337 [35%, MH$^+$–Me$_2$CO], 417 [100%, MNa$^+$].

51: δ_H (400 MHz, $CDCl_3$) −0.12 [3H, s, Si(CH_3)$_A$(CH$_3$)$_B$], 0.03 [3H, s, Si(CH$_3$)$_A$(CH_3)$_B$], 0.83 [9H, s, SiC(CH_3)$_3$], 1.19 [6H, s, C(CH_3)$_2$ (auxiliary)], 1.28 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$ (acetonide)], 1.39 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$ (acetonide)], 2.60 [1H, dd, J 14.1, 10.5, CHCH_AH$_B$Ph], 2.81 [1H, s, OH], 3.08 [1H, dd, J 14.1, 4.3, CHCH$_A$$H_B$Ph], 3.72–3.81 [4H, m, OCHCH_AH$_B$O, OCHCH$_2$O, CHOCH$_2$Ph and CH(OTBDMS)], 3.92 [1H, dd, J 7.3, 6.2,

OCHCH$_A$H$_B$O], 4.01–4.07 [1H, m, C*H*CH$_2$Ph], 4.44 [1H, d, *J* 11.5, CHOC*H$_A$*H$_B$Ph], 4.56 [1H, d, *J* 11.5, CHOCH$_A$*H$_B$*Ph], 6.70 [1H, d, *J* 8.7, N*H*], 7.14–7.39 [10H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) −4.4, −4.1 [Si(*C*H$_3$)$_2$], 18.1 [Si*C*(CH$_3$)$_3$], 25.3, 26.5 [C(*C*H$_3$)$_2$ (acetonide)], 25.8, 28.2 [C(*C*H$_3$)$_2$ (auxiliary)], 25.9 [SiC(*C*H$_3$)$_3$], 36.1 [CH*C*H$_2$Ph], 59.4 [*C*HCH$_2$Ph], 65.3 [OCH*C*H$_2$O], 72.6 [O*C*HCH$_2$O], 73.2 [*C*(CH$_3$)$_2$ (auxiliary)], 74.0 [CHO*C*H$_2$Ph], 75.3 [*C*H(OTBDMS)], 82.0 [*C*HOCH$_2$Ph], 108.5 [*C*(CH$_3$)$_2$ (acetonide)], 126.9, 128.2 [*p-Ph*], 128.1, 128.6, 128.7, 129.0 [*m/o-Ph*], 137.1, 138.1 [*i-Ph*], 171.2 [*C*=O]; ν_{max}(thin film, cm^{-1}) 3408 [O–H], 1660 [C=O]; $C_{32}H_{49}NO_6Si$ requires C 67.2, H 8.6, N 2.45%, found C 67.0, H 8.7, N 2.4%; $[\alpha]_D^{24}$ −33.2 (*c* = 1.3, $CHCl_3$); *m/z* APCI+ 513 [50%, MH$^+$–Me$_2$CO], 571 [20%, MH$^+$].

Preparation of (1″*R*,2′*R*,3′*S*,4*R*,4′*R*,5′*S*)-4-benzyl-3-[2′,4′-bis-benzyloxy-5′-(2″, 2″-dimethyl-[1″, 3″]dioxolan-4″-yl)-5′-(*tert*-butyl–dimethyl-silanyloxy)-3′-hydroxy-pentanoyl]-5,5-dimethyl-oxazolidin-2-one (1″*R*,2′*R*,3′*S*,4*R*,4′*R*,5′*S*)-52. Following representative procedure 1, CF_3SO_3H (0.11 mL, 1.27 mmol), Et_3B (1.27 mL, 1.27 mmol), (*R*)-**4** (375 mg, 1.06 mmol), *i*-Pr$_2$NEt (0.26 mL, 1.48 mmol) and **50** (424 mg, 1.07 mmol) in CH_2Cl_2 (20 mL) furnished **52** (333 mg, ~0.45 mmol, ~42%) as a clear colourless oil contaminated with <8% of (*R*)-**4** after column chromatography.

52: R_f 0.16 [1 : 1 pentane–Et_2O]; δ_H (400 MHz, $CDCl_3$) 0.06 [3H, s, Si(CH$_3$)$_A$(C*H*$_3$)$_B$], 0.08 [3H, s, Si(CH$_3$)$_A$(C*H*$_3$)$_B$], 0.87 [9H, s, SiC(C*H*$_3$)$_3$], 1.35 [3H, s, C(C*H*$_3$)$_A$(CH$_3$)$_B$ (acetonide)], 1.37 [3H, s, C(C*H*$_3$)$_A$(CH$_3$)$_B$ (auxiliary)], 1.38 [3H, s, C(CH$_3$)$_A$(C*H*$_3$)$_B$ (auxiliary)], 1.41 [3H, s, C(CH$_3$)$_A$(C*H*$_3$)$_B$ (acetonide)], 2.84–2.92 [2H, m, CH(O*H*) and CHC*H$_A$*H$_B$Ph], 3.14 [1H, dd, *J* 14.4, 3.7, CHCH$_A$-*H$_B$*Ph], 3.836 [1H, dd, *J* 9.4, 2.2, C*H*OCH$_2$Ph.CH(OTBDMS)], 3.91 [1H, t, *J* 7.6, OCHC*H$_A$*H$_B$O], 3.96–4.03 [2H, m, C*H*(OH) and OCHCH$_A$*H$_B$*O], 4.17–4.21 [1H, m, C*H*(OTBDMS)], 4.19 [1H, d, *J* 11.1, CHOC*H$_A$*H$_B$Ph], 4.29–4.33 [1H, m, OC*H*CH$_2$O], 4.46 [1H, d, *J* 11.1, CHOCH$_A$*H$_B$*Ph], 4.50–4.54 [2H, m, CHOC*H$_C$*H$_D$Ph and C*H*CH$_2$Ph], 4.66 [1H, d, *J* 12.0, CHOCH$_C$*H$_D$*Ph], 5.50 [1H, app. s, CO.C*H*OCH$_2$Ph], 7.20–7.38 [15H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) −4.5, −4.3 [Si(*C*H$_3$)$_2$], 18.2 [Si*C*(CH$_3$)$_3$], 22.1, 28.3 [C(*C*H$_3$)$_2$ (auxiliary)], 25.2, 26.5 [C(*C*H$_3$)$_2$ (acetonide)], 26.0 [SiC(*C*H$_3$)$_3$], 35.3 [CH*C*H$_2$Ph], 64.0 [*C*HCH$_2$Ph], 66.0 [OCH*C*H$_2$O], 71.6 [*C*H(OH)], 72.2, 72.7 [2 × CHO*C*H$_2$Ph], 72.7 [*C*H(OTBDMS)], 75.6 [O*C*HCH$_2$O], 77.4 [*C*HOCH$_2$Ph.CH(OTBDMS)], 77.8 [CO.*C*HOCH$_2$Ph], 83.7 [*C*(CH$_3$)$_2$ (auxiliary)], 108.0 [*C*(CH$_3$)$_2$ (acetonide)], 126.8, 127.3, 127.8 [*p-Ph*], 127.3, 128.2, 128.3, 128.4, 128.6, 129.1 [*m/o-Ph*], 136.9, 137.2, 138.5 [*i-Ph*], 152.3 [*C*=O endocyclic], 170.8 [*C*=O exocyclic]; ν_{max}(thin film, cm^{-1}) 3462 [O–H], 1779 [C=O endocyclic], 1708 [C=O endocyclic]; HRMS $C_{42}H_{57}NO_9NaSi$ [MNa$^+$] requires 770.3700, found 770.3689; $[\alpha]_D^{26}$ +43.4 (*c* = 0.55, $CHCl_3$); *m/z* ES+ 748 [50%, MH$^+$], 770 [100%, MNa$^+$].

Preparation of (1′*R*,2*R*,3*S*,4*R*,5*S*)-2,4-bis-benzyloxy-5-(2′,2′-dimethyl-[1′,3′]dioxolan-4-yl)-4-hydroxy-tetrahydro-pyran-2-one (1′*R*,2*R*,3*S*,4*R*,5*S*)-53 and (*R*)-4-benzyl-5,5-dimethyl-oxazolidin-2-one (*R*)-22. Following representative procedure 2, **52** (330 mg, ~0.44 mmol), TBAF (0.66 mL, 0.66 mmol) and AcOH (0.03 mL, 0.44 mmol) in THF (20 mL) furnished (*R*)-**4** (81 mg, 0.23 mmol) as a pale yellow oil, **53** (82 mg, 0.19 mmol) as a clear colourless oil and (*R*)-**22** (50 mg, 0.24 mmol) after column chromatography.

53: R_f 0.17 [1 : 1 30–40 °C petrol–Et_2O]; δ_H (400 MHz, $CDCl_3$) 1.37 [3H, s, C(C*H*$_3$)$_A$(CH$_3$)$_B$], 1.43 [3H, s, C(CH$_3$)$_A$(C*H*$_3$)$_B$], 4.04–4.09 [3H, m, OCHC*H$_A$*H$_B$O, C*H*OCHCH$_2$O and C*H*(OCH$_2$Ph).CHOCHCH$_2$O], 4.15 [1H, dd, *J* 9.1, 6.0, OCHCH$_A$*H$_B$*O], 4.23 [1H, t, *J* 2.2, C*H*(OH)], 4.31–4.38 [1H, m, CHOC*H*CH$_2$O], 4.32 [1H, d, *J* 10.0, CO.C*H*OCH$_2$Ph], 4.72 [1H, d, *J* 11.2, CHOC*H$_A$*H$_B$Ph], 4.76 [1H, d, *J* 11.0, CHOC*H$_C$*H$_D$Ph], 4.87 [1H, d, *J* 11.0, CHOCH$_C$*H$_D$*Ph], 5.19 [1H, d, *J* 11.2, CHOCH$_A$*H$_B$*Ph], 7.25–7.44 [10H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 25.1, 27.0 [C(*C*H$_3$)$_2$], 67.1 [CHOCH*C*H$_2$O], 72.0 [*C*H(OCH$_2$Ph).CHOCHCH$_2$O], 72.6 [CHO*C*HCH$_2$O], 74.4 [*C*H(OH)], 74.7, 75.4 [2 × CHO*C*H$_2$Ph], 76.6 [CO.*C*HOCH$_2$Ph], 79.8 [*C*HOCHCH$_2$O], 109.7 [*C*(CH$_3$)$_2$], 128.0, 128.3 [*p-Ph*], 128.0, 128.4, 128.6, 128.7 [*m/o-Ph*], 137.1, 137.8 [*i-Ph*], 169.6 [*C*=O]; ν_{max}(thin film, cm^{-1}) 3446 [O–H], 1751 [C=O]; $C_{24}H_{28}O_7$ requires C 67.3, H 6.6%, found C 67.4, H 6.6%; $[\alpha]_D^{24}$ +72.0 (*c* = 0.25, $CHCl_3$); *m/z* ES+ 429 [40%, MH$^+$], 446 [100%, MNH$_4^+$].

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.).

References and Notes

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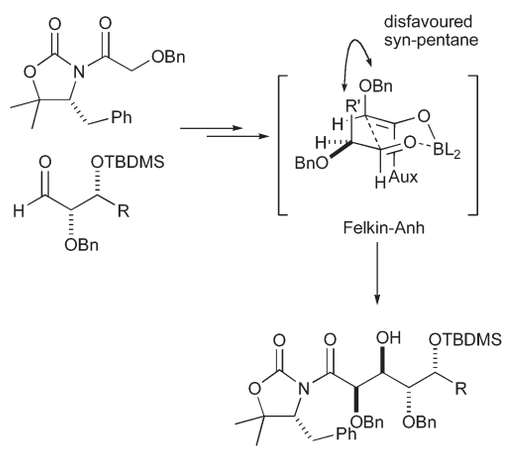

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