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Stereoselective synthesis of *C*-glycosides from carboxylic acids: the tandem Tebbe–Claisen approach †

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A variety of β- or α-*C*-glycosides may be readily accessed in an entirely stereoselective fashion from esters derived from the reaction of carboxylic acids and 3-hydroxy glycals, by way of a tandem reaction sequence of Tebbe methylenation and Claisen rearrangement. Though of wide scope, for example allowing the synthesis of 1–6 linked *C*-disaccharides, the methodology does not currently allow the synthesis of *C*-glycosyl α-amino acids.

Introduction

Over recent years *C*-glycosides[1] have become popular synthetic targets,[2,3] particularly as potential glycomimetics,[4] which may themselves have possible therapeutic applications in accordance with the well-established importance of carbohydrates in a plethora of biological process.[5] However despite considerable synthetic interest in this area, there is still currently some debate as to the potential general ability of *C*-glycosides to act as non-hydrolysable mimics of their natural *O*-linked counterparts.[6,7] In order to address this question directly it would seem appropriate to test the ability of a variety of *C*-glycosides to act generally as glycomimetics by high-throughput biological screening. Such a screening program would require synthetic access to a wide variety of *C*-glycosides in a parallel synthetic manner. However despite the large amount of previous work in this field, no one single synthetic approach to *C*-glycosides seems immediately amenable to parallel synthesis, suggesting that the development of new synthetic methodology is desirable.

When we considered how best to develop a new parallel synthetic approach to *C*-glycosides two important aspects became apparent. These were firstly stereochemical control of the *C*-glycosylation reaction, and secondly the potential generality of the overall reaction sequence. In order to avoid the tedious and often difficult separation of mixtures of anomeric products, it seemed that one could profitably use a thermal sigmatropic rearrangement for the construction of the new carbon–carbon bond at the anomeric centre with complete control of stereochemistry.[8] However rather than choosing to adopt the classic Claisen–Ireland approach, which can result in the formation of a mixture of diastereomers at the carbon atom attached to the anomeric centre due to lack of stereocontrol of enolate formation, it was envisaged that a tandem process involving Tebbe methylenation[9] and thermal sigmatropic rearrangement should allow stereoselective access to a wide range of *C*-glycosides. Thus esterification of a suitably protected glycal **1** with a chosen carboxylic acid would lead to the formation of a glycal ester **2**. Tebbe methylenation would then produce an enol ether **3**, which could in turn undergo a stereospecific sigmatropic rearrangement to yield the desired *C*-glycoside **4** (Fig. 1). The advantages of the approach were considered to be the potential generality of the reaction sequence, since in theory almost any carboxylic acid could be used for the esterification step (*vide infra*), and the stereospecificity of the anomeric C–C bond forming reaction: *gluco* derived glycals producing solely the β-*C*-glycosides, and *allo* derived glycals giving rise solely to the α-*C*-glycosides respectively.

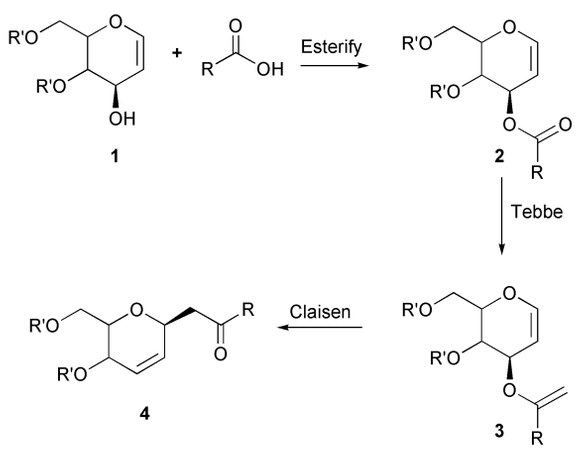

Fig. 1

Herein we report full details of this tandem Tebbe–Claisen approach[10,11] which allows synthetic access to a wide range of either α- or β-*C*-glycosides in an entirely stereoselective fashion.

Results and discussion

Synthesis of β-*C*-Glycosides

The tandem Tebbe–Claisen approach to *C*-glycosides requires access to selectively protected glycals in which the 3-hydroxy group is free for esterification, with a wide range of carboxylic acids to allow parallel synthesis. As an initial model system, the 4,6-*O*-silyl protected glucose-derived glycal **5**[12] was synthesised from glucose β-pentaacetate in 4 steps following literature procedures (72% overall yield). Esterification of **5** with either benzoic, octanoic, or palmitic acids was achieved by treatment of the glycal with the corresponding carboxylic acid and dicyclohexylcarbodiimide (DCC), with catalytic *N,N*-dimethylaminopyridine (DMAP), yielding esters **6a**–**c** in excellent yields. The two-step sequence of Tebbe methylenation and Claisen rearrangement was then undertaken. Tebbe reaction proceeded smoothly in a THF–pyridine mixture at −40 °C, to yield the corresponding enol ethers **7a**–**c**, which although moderately stable, were in general used for subsequent rearrangement after minimal purification on a short column of basic alumina. Thermal rearrangement of this set of enol ethers **7a**–**c** occurred upon heating to 180 °C, in either benzonitrile or tributylamine,[13] producing the corresponding β-*C*-glycosides **8a**–**c**[14] in

† This is one of a number of contributions from the current members of the Dyson Perrins Laboratory to mark the end of almost 90 years of organic chemistry research in that building, as all its current academic staff move across South Parks Road to a new purpose-built laboratory.

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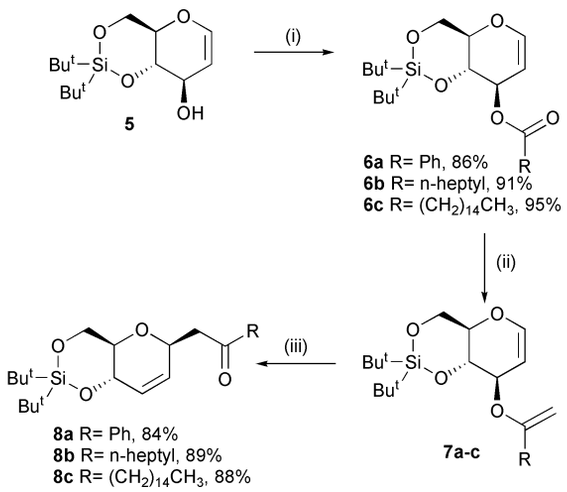
good to excellent yield (84–89%, Scheme 1, reaction yields quoted over two steps of methylenation and rearrangement). The structure of β-*C*-glycoside **8a** was confirmed by X-ray crystallography (Fig. 2)



Scheme 1 *Reagents and conditions*: (i) RCO_2H, DCC, DMAP, CH_2Cl_2, RT; (ii) Tebbe reagent, THF, pyridine, −40 °C; (iii) 180 °C, PhCN or Bu_3N.

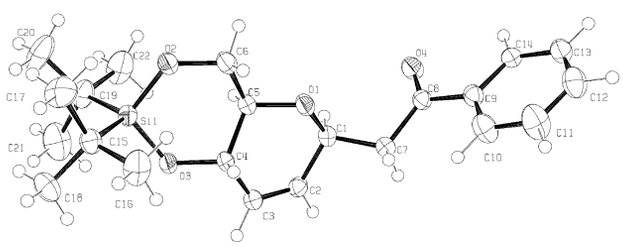
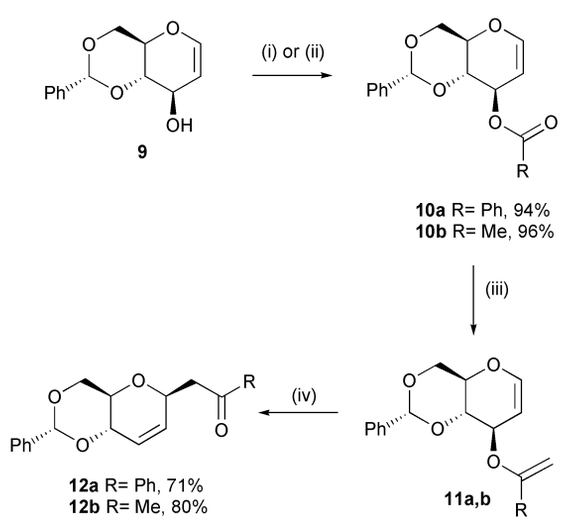


Fig. 2 X-Ray crystal structure of β-*C*-glycoside **8a** showing crystallographic numbering scheme [thermal ellipsoid plot (ORTEP-34) at 40% probability].

For further exemplification the corresponding 4,6-*O*-benzylidene protected glycal **9** was also synthesised as a starting material, by a synthetic route recently developed in our laboratory [15] which was significantly more efficient than the low yielding [16] or protracted previously reported procedures.[17] The corresponding benzoate **10a** and acetate **10b** were accessed from **9** by the use of benzoyl chloride or acetic anhydride respectively (94% and 96% yields, Scheme 2). Tebbe methylenation of these



Scheme 2 *Reagents and conditions*: (i) BzCl, DMAP, pyridine, 0 °C; (ii) Ac_2O, pyridine, RT; (iii) Tebbe reagent, THF, pyridine, −40 °C; (iv) 180 °C, Bu_3N.

glycal esters again yielded the desired intermediate enol ethers **11a** and **11b**. Thermal rearrangement proceeded rapidly upon heating to 180 °C in tributylamine to yield the β-*C*-glycosides **12a** and **12b** (71% and 80% yields over two steps, Scheme 2). The structure of *C*-glycoside **12b** was also confirmed by X-ray crystallography (Fig. 3).

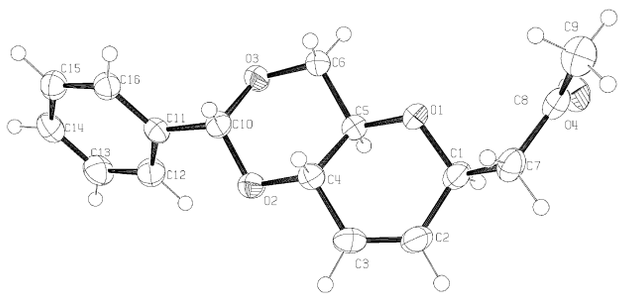


Fig. 3 X-Ray crystal structure of β-*C*-glycoside **12b** showing crystallographic numbering scheme [thermal ellipsoid plot (ORTEP-34) at 40% probability].

Synthesis of α-*C*-Glycosides

With the successful synthesis of a variety of β-*C*-glycosides in hand, attention then turned to the synthesis of the corresponding α-*C*-glycosides, which necessarily entailed the use of glycal esters epimeric at the 3-position as starting materials. The 4,6-*O*-silyl protected *allo*-alcohol **14** was therefore synthesised from allal **13** [18] by regioselective silylation with di-*tert*-butylsilyl ditriflate in DMF at low temperature (77% yield, Scheme 3). In addition as further substrates for investigation, the 4,6-*O*-benzylidene protected allal **15** and the corresponding C-2 methyl substituted derivative **16** were also synthesised following literature procedures.[19] The silyl protected glycal **14** was converted into the palmitic ester **17** by treatment with palmitic acid, DCC, and catalytic DMAP. Treatment of benzylidene protected glycal **15** with benzoyl chloride and catalytic DMAP in pyridine furnished the benzoate ester **18a**, whilst acetylation of **15** with acetic anhydride in pyridine, yielded the acetate **18b**, and finally treatment of **15** with palmitic acid, DCC, and catalytic DMAP, gave the palmitic ester **18c**. Similarly methyl substituted glycal **16** was converted into its benzoate ester **19** by treatment with benzoyl chloride. Methylenation of this selection of esters **17**, **18a**–**c**, **19** proceeded smoothly under standard reaction conditions (treatment with ~2 equivalents of Tebbe reagent at −40 °C, in a 4 : 1 mixture of THF and pyridine), to yield the corresponding enol ethers **20**–**22** (Scheme 3) in excellent yields. The structure of enol ether **21b** was confirmed by X-ray crystallography (Fig. 4).

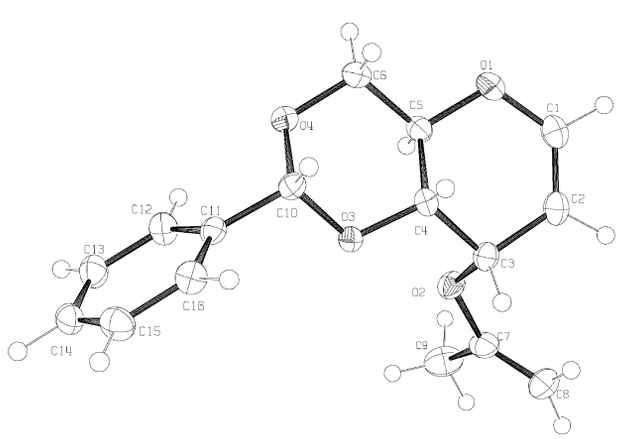
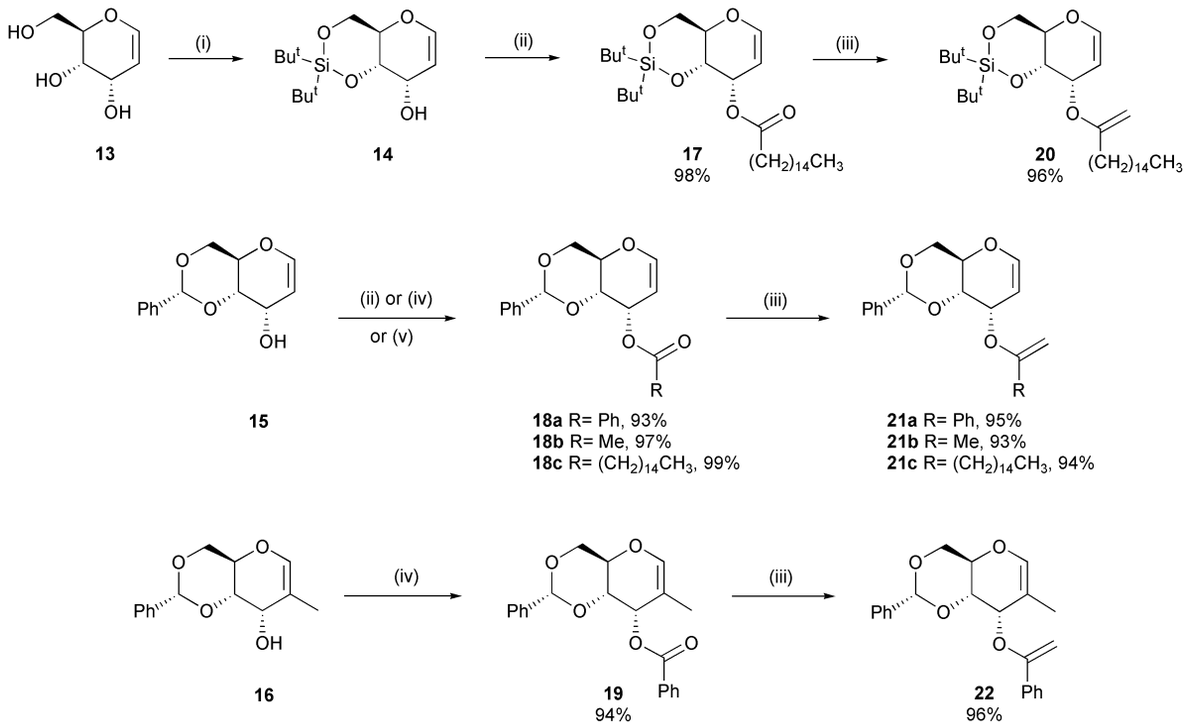


Fig. 4 X-Ray crystal structure of enol ether **21b** showing crystallographic numbering scheme [thermal ellipsoid plot (ORTEP-34) at 40% probability].

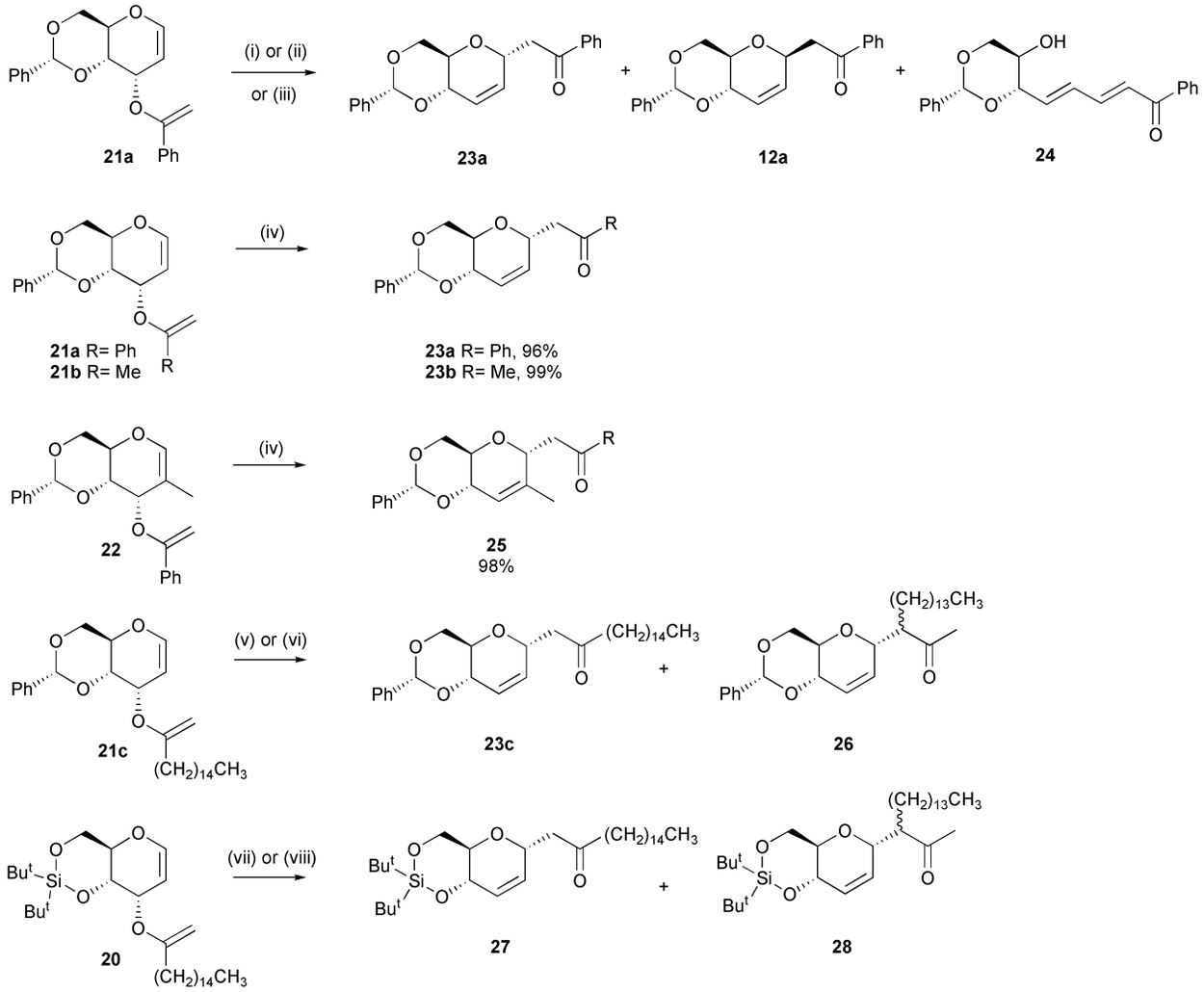


Scheme 3 *Reagents and conditions*: (i) $^{t}Bu_2Si(OTf)_2$, DMF, −40 °C to RT, 77%; (ii) RCO_2H, DCC, DMAP, CH_2Cl_2, RT; (iii) Tebbe, THF, pyridine, −40 °C; (iv) PhCOCl, DMAP, pyridine, 0 °C; (v) Ac_2O, pyridine, RT.

With this selection of enol ethers in hand attention turned to the subsequent Claisen rearrangement. Thermal rearrangement of enol ether **21a** was attempted following conditions that had successfully yielded the corresponding β-*C*-glycosides, but it was found that heating **21a** to 180 °C in benzonitrile as solvent produced a mixture of both α- and β-*C*–glycoside products, **23a** and **12a** (Scheme 4), albeit in a favourable ratio of α : β, 5 : 1. In addition small amounts of the open chain diene **24** were also observed, indicating the probable mechanism by which the α-*C*-glycosides are inter-converted to their thermodynamically more favoured β-counterparts.[20,21] Although in the β-series the formation of minor amounts of epimeric product that was occasionally observed during thermal rearrangement in benzonitrile could be suppressed by changing the solvent to tributylamine, in the α-series this proved not to be the case; once again anomeric mixtures of products were formed. In an attempt to avoid this epimerisation process a selection of Lewis acid catalysed reactions were investigated as an alternative to thermal rearrangement. However, reactions undertaken with a variety of different Lewis acid catalysts, including $NaBF_4$, $AlCl_3$, $BF_3{\cdot}OEt_2$, $Yb(OTf)_3$, and $TiCl_4$, under a variety of reaction conditions, perhaps not unsurprisingly[22] again resulted in the formation of mixtures of epimeric products, together with variable amounts of open chain diene **24**. Although in some cases the ratio of products was in favour of the desired α-anomer (*e.g.* α : β ratio of 16 : 1, for $BF_3{\cdot}OEt_2$), the yields for these reactions were at best modest (~60%). Moreover since the original synthetic objective was the development of methodology that allowed complete control of anomeric stereochemistry, the search for alternative reaction conditions continued.

In the face of the persistent anomerisation problem it was thought prudent to monitor the rate of formation of the undesired β-anomer relative to the Claisen rearrangement itself. The most expedient way to do this appeared to be *via in situ* reaction monitoring by NMR, importantly in a solvent where the characteristic proton resonances for the starting material and both the α- and β-*C*-glycoside products were well separated. Therefore a series of sealed tube reactions, which rather fortuitously revealed some interesting results, were undertaken in deuterated benzene as the solvent. When the thermal rearrangement of **21a** was performed in d_6-benzene in a sealed tube the reaction proceeded smoothly and *no formation of the undesired β-anomer was observed*. This unexpected observation pointed the way to the use of benzene as the solvent for the rearrangement reaction. Indeed a series of thermal rearrangements in benzene pleasingly produced pure α-*C*-glycosides. However mindful of the toxicity of benzene, a selection of alternative solvents were screened at a variety of temperatures. Thermal rearrangement in xylene at 195 °C proved to be optimum, and gratifyingly enol ethers **21a**, **21b** and **22** all rearranged smoothly in excellent yield and most importantly entirely stereoselectively to yield only the α-*C*-glycoside products **23a**, **23b** and **25** respectively. The anomeric stereochemistry of α-*C*-glycoside **23a** was confirmed by X-ray crystallography as previously detailed,[10] whilst the anomeric configurations of the other α-*C*-glycosides were confirmed by NOE difference experiments.[23]

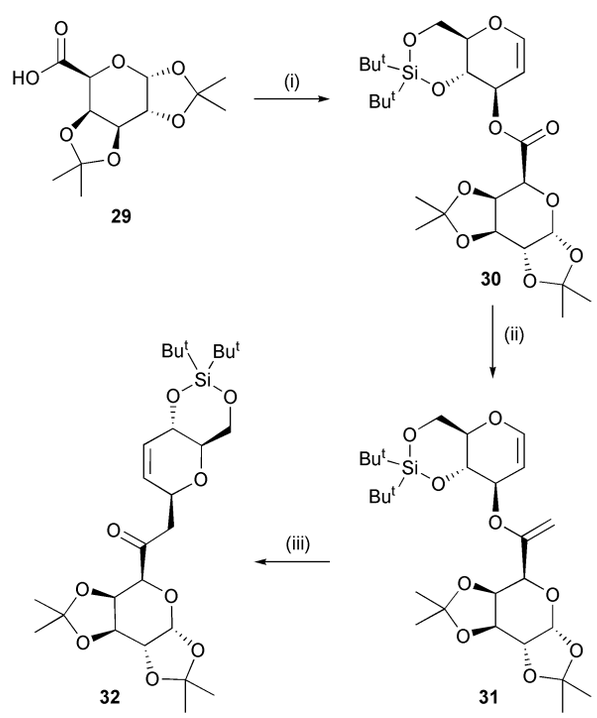
During rearrangement of the two palmitic esters **21c** and **20** in addition to the desired α-C-glycosides **23c** and **27** two side products were occasionally observed. These side products were identified as the α-*C*-glycosides **26** and **28**, and are presumably formed *via* partial isomerisation of the glycal enol ethers **21c** and **20** to the thermodynamically preferred more substituted tautomers before rearrangement. Frustratingly the relative amounts of these products formed appeared to be quite variable depending on the length of reaction and solvent. For example in one instance the use of xylene as solvent for the rearrangement of **20** completely suppressed the formation of **28**, but a similar experiment with d_6-benzene as solvent resulted in the formation of **28** in an almost equal amount to that of the desired product **27**. However the formation of **26** from **21c** was observed even in xylene as solvent. Unfortunately complete suppression of the formation of these side-products has not yet proved possible. Indeed it has subsequently been discovered that sealed tube rearrangement of palmitic ester **6b** in xylene at 195 °C also leads to the formation of this type of isomeric product, whereas none was previously observed during thermal rearrangement at 180 °C in either benzonitrile, or tributylamine.



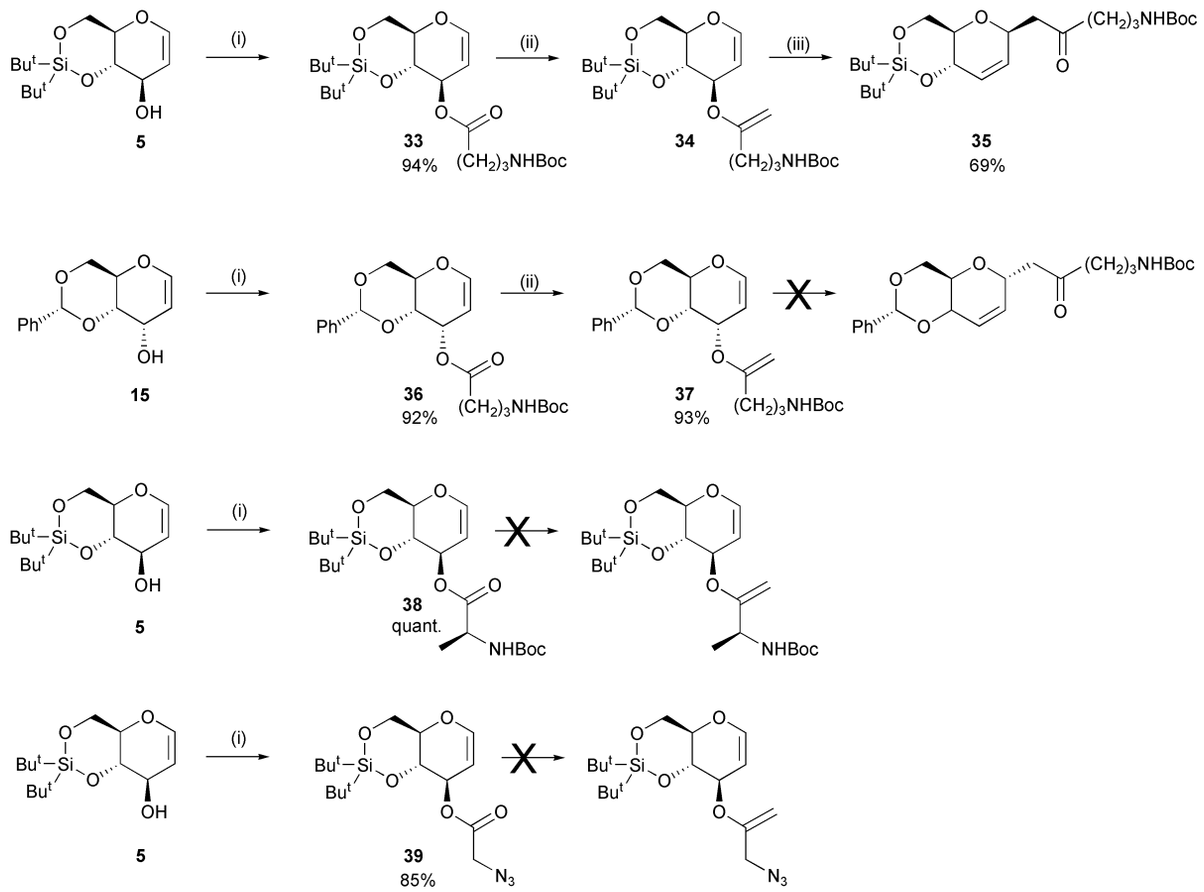
Scheme 4 *Reagents and conditions*: (i) Bu_3N, 180 °C; (ii) PhCN, 180 °C; (iii) various Lewis acids at low temperature; (iv) xylene, sealed tube, 195 °C; (v) xylene, sealed tube, 195 °C, ratio **23c** : **26**, 1.3 : 1, yield 85%; (vi) d_6-benzene, 195 °C, sealed tube, ratio **23c** : **26**, 1 : 1, yield 84%; (vii) xylene, sealed tube, 195 °C, **27** only, yield 85%; (viii) d_6-benzene, 195 °C, sealed tube, ratio **27** : **28**, 1.4 : 1, yield 94%.

Synthesis of *C*-disaccharides

One the most appealing features of this *C*-glycosylation strategy is the potential range of carboxylic acids which may be used for the esterification reaction. In particular the use of carboxylic acids derived from carbohydrates as coupling partners would allow the linking of one saccharide unit to the anomeric position of another *via* a methylene bridge. In order to test out the potential of this type of approach for the conjugation of carbohydrates, the synthesis of a β-*C*-linked disaccharide was undertaken. Thus the known galacturonic acid **29**,[24] (obtained in high yield by ruthenium mediated[25] oxidation of diacetone galactose), was coupled with glycal **5**, to yield the ester **30**. Tebbe methylenation of **30** was found to be much more sluggish than the previous examples, but by the use of an extended reaction time (24 h) and an excess of Tebbe reagent, a satisfactory yield of the desired enol ether **31** was obtained (72% yield based on recovered starting material; the reaction could not be driven to completion). Claisen rearrangement of enol ether **31** occurred rapidly at 180 °C in benzonitrile to yield the desired β-*C*-disaccharide **32** in a satisfactory 56% yield (Scheme 5). This reaction demonstrates the feasibility of the approach for the synthesis of (1–6) linked *C*-disaccharides. Moreover, since it should in principle be relatively straightforward to achieve access to the 6-hydroxy of compounds such as **32** one should be able to iterate such a process, by a sequence of oxidation, esterification and Tebbe–Claisen, in order to access *C*-trisaccharides and higher homologues.



Scheme 5 *Reagents and conditions*: (i) **5**, DCC, DMAP, CH_2Cl_2, 91%; (ii) Tebbe, THF, pyridine, −40 °C to RT, 72%; (iii) 180 °C, PhCN, 56%.



Scheme 6 *Reagents and conditions*: (i) RCO_2H, DCC, DMAP, CH_2Cl_2, RT; (ii) Tebbe, THF, pyridine, −40 °C; (iii) Bu_3N, 180 °C.

Attempted synthesis of *C*-glycosyl amino acids

There has recently been much interest in the synthesis of *C*-glycosyl amino acids, either as potential building blocks for the synthesis of *C*-glycopeptides of for other purposes.[26] In principle the tandem Tebbe–Claisen approach could provide facile access to a wide range of such materials directly from suitably protected forms of the parent amino acids. Moreover since any α-amino acid, or indeed the β- or γ-acid of aspartic or glutamic acids, could be used for esterification, a wide range of such materials could be accessed in a parallel manner through a short reaction sequence. In order to firstly test compatibility of a typical amino protecting group with the Tebbe–Claisen reaction sequence Boc protected 4-aminobutyric acid was investigated as a substrate. Thus both silyl protected glycal **5** and benzylidene protected glycal **15** were esterified by treatment with 4-aminobutyric acid and DCC in the presence of DMAP, to yield the two required esters **33** and **36** respectively (Scheme 6). Both esters underwent reaction with the Tebbe reagent to provide the two enol ethers **34** and **37** respectively, this transformation being notable in so far as that no side reaction of the Boc protecting group was observed. Thermal rearrangement of enol ether **34** was complete in 1 hour after heating at 180 °C in tributylamine and yielded the desired β-*C*-glycoside **35** in a respectable yield over two steps. However benzylidene protected enol ether **37** only reacted extremely slowly under similar conditions, and no appreciable amount of product was observed—the starting material being recovered in this case.

Encouraged by these initial studies, which in particular indicated the compatibility of Boc protection with the Tebbe reaction, two further esters were synthesised as substrates for methylenation and rearrangement in an attempt to access *C*-glycosyl amino acids. Thus glycal **5** was esterified with both *N*-Boc protected alanine, and α-azido acetic acid to yield esters **38** and **39** respectively. However unfortunately neither of these esters could be methylenated using the Tebbe reagent—in both cases reaction of ester **38** or **39** did occur, but the isolated product was simply the alcohol **5**. This inability of the Tebbe reagent to methylenate esters of α-amino acids[27] therefore appears to currently preclude the synthesis of *C*-glycosyl amino acids using this methodology.

Summary

It is clear that the combined use of Tebbe methylenation and thermal Claisen rearrangement provides a powerful and potentially rather general route to stereodefined α- or β-*C*-glycosides. However, although access to the β-compounds is facile, in order to obtain pure α-products careful control of reaction conditions is required in order to avoid competing formation of the thermodynamically more stable β-*C*-glycoside products. This is currently best achieved by performing the thermal reactions in either xylene or benzene in a sealed tube. By the use of carbohydrate derived carboxylic acids as coupling partners this methodology may be applied to the synthesis of (1–6) linked *C*-disaccharides. However the failure of the Tebbe reagent to methylenate glycal esters derived from α-amino acids currently precludes the use of this methodology for the synthesis of *C*-glycosyl amino acids. Further investigations into the use of the tandem Tebbe–Claisen approach for the synthesis of a wide variety of *C*-glycosides, and *C*-oligosaccharides, and into the use of alternative methylenation conditions to allow the synthesis of *C*-glycosyl amino acids, are currently in progress, and results will be reported in due course.

Experimental

General methods

Melting points were recorded on a Kofler hot block and are uncorrected. Proton nuclear magnetic resonance (δ_H) spectra were recorded on a Bruker DRX 500 (500 MHz), a Bruker DPX 400 (400 MHz) or on a Varian Gemini 200 (200 MHz)

spectrometer. Carbon nuclear magnetic resonance (δ_C) spectra were recorded on a Bruker DPX 400 (100.6 MHz) or on a Bruker AC 200 (50.3 MHz) spectrometer. Spectra were assigned using COSY, HMQC, APT or DEPT and/or HMBC and/or edited HSQC, and/or NOESY experiments. All chemical shifts are quoted on the δ-scale in parts per million (ppm). All NMR experiments were performed at a probe temperature of 30 °C. Infrared spectra were recorded on a Perkin-Elmer 150 Fourier Transform spectrophotometer. Low resolution mass spectra were recorded a VG Micromass Platform using either atmospheric pressure chemical ionisation (APCI), or negative ion electrospray (ES^-) or positive ion electrospray (ES^+), or on a Micromass GCT TOF spectrometer, using solid probe temperature programmed field ionisation (FI). High resolution mass spectra (electrospray) were performed on a Waters 2790-Micromass LCT electrospray ionisation mass spectrometer, or by the EPSRC Mass Spectrometry Service Centre, Department of Chemistry, University of Wales, Swansea on a MAT900 XLT electrospray ionisation mass spectrometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter with a path length of 1 dm. Concentrations are given in g per 100 ml. Microanalyses were performed by the microanalytical services of the Inorganic Chemistry Laboratory, Oxford. Thin layer chromatography (TLC) was carried out on Merck Kieselgel 0.22–0.25 mm thickness glass-backed sheets, precoated with $60F_{254}$ silica. Plates were developed using 5% w/v ammonium molybdate in 2 M sulfuric acid. Flash column chromatography was carried out using Sorbsil C60 40/60 silica. Solvents and reagents were dried and purified before use according to standard procedures under an atmosphere of argon; methanol was distilled from sodium hydride, dichloromethane and toluene were distilled from calcium hydride, pyridine was distilled from calcium hydride and stored over potassium hydroxide, and diethyl ether and tetrahydrofuran were distilled from a solution of sodium benzophenone ketyl immediately before use.

General crystallography

Single crystals were mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package. Examination of the systematic absences of the intensity data indicated the space group. The structure was solved using the direct-methods program SIR92, which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily.‡

General method A: DCC mediated esterification

Anhydrous dichloromethane was added to a mixture of the glycal (1 equiv.), the carboxylic acid (1.5 equiv.), dicyclohexylcarbodiimide (2 equiv.) and 4-dimethylaminopyridine (0.2 equiv.) under an atmosphere of argon. The resulting reaction mixture was stirred at room temperature for 15 h, after which time TLC (petrol : ethyl acetate) indicated the complete consumption of starting material and the formation of a major product. The mixture was filtered through a pad of Celite and the residue washed with dichloromethane. The resulting filtrate was then concentrated *in vacuo* and the residue purified by flash column chromatography (petrol : ethyl acetate, 12 : 1)

‡ CCDC reference numbers 212630–212632. See http://www.rsc.org/suppdata/ob/b3/b306675b/ for crystallographic data in .cif or other electronic format.

General method B : Tebbe methylenation

Tebbe reagent (2–4 equiv.) was added drop-wise to a stirred solution of glycal ester (1 equiv.) in tetrahydrofuran (2 ml) and pyridine (0.5 ml) at −40 °C, under an atmosphere of argon. After 1.5 h, TLC (petrol : diethyl ether, 8 : 1 + 2% triethylamine) indicated complete consumption of starting material and the formation of a major product. The reaction mixture was quenched by the drop-wise addition of sodium hydroxide solution (0.1 M, ~0.2 ml) until the effervescence ceased. The reaction mixture was diluted with petrol (10 ml) and stirred for a further 10 min. The mixture was then filtered through a short column of basic alumina and eluted with petrol : diethyl ether, 6 : 1 with 2% triethylamine to obtain the glycal enol ether. This unstable compound was typically used in the next step with out further purification.

General method C: thermal rearrangement in benzonitrile or tributylamine

The crude enol ether (~50 mg) was heated in benzonitrile (1 ml) or tributylamine (1 ml) at 180 °C for 25 min, after which time TLC (petrol : diethyl ether, 8 : 1 + 2% triethylamine) indicated the complete consumption of starting material and the formation of a major product. The reaction was concentrated *in vacuo* and the residue purified by flash column chromatography (petrol : diethyl ether, 6 : 1) to obtain the *C*-glycoside.

General method D: sealed tube thermal rearrangement

The enol ether (~50 mg) was dissolved in anhydrous xylene (1 ml) under an atmosphere of argon and heated in a sealed pressure tube at 195 °C. After 2 h 15 min, TLC (petrol : ethyl acetate, 3 : 1 +2% triethylamine) indicated the complete consumption of starting material and the formation of a major product. The reaction mixture was then concentrated *in vacuo* and the residue purified by flash column chromatography (petrol : ethyl acetate, 3 : 1) to obtain the *C*-glycoside.

1,5-Anhydro-3-*O*-benzoyl-2-deoxy-4,6-*O*-di(*tert*-butyl)silanediyl-D-*arabino*-hex-1-enitol 6a

General method A: Alcohol **5** (1.5 g, 5.25 mmol), benzoic acid (843 mg, 7.37 mmol), dicyclohexylcarbodiimide (2.17 g, 10.5 mmol) and 4-dimethylaminopyridine (129 mg, 1.06 mmol), gave ester **6a** (1.76 g, 86%) as a colourless oil; $[\alpha]_D^{23}$ −164.6 (*c*, 1 in $CHCl_3$); ν_{max} (thin film): 1723 (s, C=O), 1648 (m, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.99, 1.07 (18H, 2 × s, 2 × $C(CH_3)_3$), 4.00–4.07 (2H, m, H-5 and H-6), 4.23–4.25 (1H, m, H-6′), 4.37 (1H, dd, $J_{3,4}$ 7.6 Hz, $J_{4,5}$ 9.9 Hz, H-4), 4.88 (1H, dd, $J_{1,2}$ 6.1 Hz, $J_{2,3}$ 2.0 Hz, H-2), 5.60 (1H, double apparent triplet (dat), *J* 1.8 and 7.6 Hz, H-3), 6.37 (1H, dd, $J_{1,3}$ 1.5 Hz, H-1), 7.45–7.49 (2H, m, Ar–H_{meta}), 7.57–7.59 (1H, m, Ar–H_{para}), 8.07–8.09 (2H, m, Ar–H_{ortho}); δ_C (100.6 MHz, $CDCl_3$) 19.8, 22.7 (2 × s, 2 × $C(CH_3)_3$), 26.8, 27.4 (2 × q, 2 × $C(CH_3)_3$), 65.8 (t, C-6), 72.9, 73.0 (2 × d, C-3 and C-5), 73.6 (d, C-4), 100.6 (d, C-2), 128.4, 129.6 (2 × d, C_{meta} and $_{ortho}$ Ar), 130.3 (s, C_{ipso} Ar), 133.0 (d, C_{para} Ar), 145.1 (d, C-1), 166.5 (s, CO_2Ph); *m*/*z* (FI^+) 390 (M^+, 45%). (HRMS calcd. for $C_{21}H_{30}O_5Si$ (M) 390.1863. Found 390.1868) (Found: C, 64.53; H, 8.05. $C_{21}H_{30}O_5Si$ requires C, 64.58; H, 7.74%).

1,5-Anhydro-2-deoxy-3-*O*-octanoyl-4,6-*O*-di(*tert*-butyl)silanediyl-D-*arabino*-hex-1-enitol 6b

General method A: Octanoic acid (0.55 ml, 3.49 mmol), alcohol **5** (500 mg, 1.75 mmol), dicyclohexylcarbodiimide (720 mg, 3.49 mmol) and 4-dimethylaminopyridine (43 mg, 0.35 mmol), gave ester **6b** (658 mg, 91%) as a colourless oil; $[\alpha]_D^{23}$ −59.1 (*c*, 1 in

$CHCl_3$); ν_{max} (thin film): 1741 (s, C=O), 1647 (m, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.88 (3H, t, J 6.9 Hz, $O_2C(CH_2)_6CH_3$), 0.99, 1.06 (18H, 2 × s, 2 × $C(CH_3)_3$), 1.27–1.33 (8H, m, $O_2CCH_2CH_2(CH_2)_4CH_3$), 1.62–1.69 (2H, m, $O_2CCH_2CH_2(CH_2)_4CH_3$), 2.31–2.40 (2H, m, $O_2CCH_2(CH_2)_5CH_3$), 3.92 (1H, ddd, $J_{4,5}$ 10.2 Hz, $J_{5,6}$ 10.3 Hz, $J_{5,6'}$ 4.6 Hz, H-5), 3.99 (1H, at, J 10.1 Hz, H-6), 4.16 (1H, dd, $J_{3,4}$ 7.6 Hz, H-4), 4.19 (1H, dd, $J_{6,6'}$ 9.7 Hz, H-6′), 4.71 (1H, dd, $J_{1,2}$ 6.0 Hz, $J_{2,3}$ 2.0 Hz H-2), 5.41 (1H, dat, J 1.8 Hz and 7.6 Hz, H-3), 6.32 (1H, dd, $J_{1,3}$ 1.6 Hz, H-1); δ_C (100.6 MHz, $CDCl_3$) 13.9 (q, $O_2C(CH_2)_6CH_3$), 19.6, 22.5 (2 × s, 2 × $C(CH_3)_3$), 26.7, 27.2 (2 × q, 2 × $C(CH_3)_3$), 22.5, 25.0, 28.8, 28.8, 31.5 (5 × t, $O_2CCH_2(CH_2)_5CH_3$), 34.5 (t, $O_2CCH_2(CH_2)_5CH_3$), 65.7 (t, C-6), 71.8 (d, C-3), 72.9 (d, C-5), 73.7 (d, C-4), 100.8 (d, C-2), 145.0 (d, C-1), 173.9 (s, $O_2C(CH_2)_6CH_3$); m/z (FI^+) 412 (M^+, 68%). (HRMS calcd. for $C_{22}H_{40}O_5Si$ (M^+) 412.2645. Found 412.2645) (Found: C, 64.06; H, 9.72. $C_{22}H_{40}O_5Si$ requires C, 64.04; H, 9.77%).

1,5-Anhydro-2-deoxy-3-*O*-hexadecanoyl-4,6-*O*-di(*tert*-butyl)-silanediyl-D-*arabino*-hex-1-enitol 6c

General method A: Alcohol **2** (250 mg, 0.87 mmol), palmitic acid (448 mg, 1.75 mmol), dicyclohexylcarbodiimide (360 mg, 1.75 mmol) and 4-dimethylaminopyridine (21 mg, 0.17 mmol), gave ester **6c** (435 mg, 95%) as a colourless oil; $[\alpha]_D^{23}$ −49.3 (c, 1 in $CHCl_3$); ν_{max} (thin film) 1742 (C=O), 1647 (C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.88 (3H, t, J 6.8 Hz, $O_2C(CH_2)_{14}CH_3$), 0.99 and 1.06 (18H, 2 × s, 2 × $C(CH_3)_3$), 1.21–1.30 (24H, m, $O_2CCH_2CH_2(CH_2)_{12}CH_3$), 1.61–1.69 (2H, m, $O_2CCH_2CH_2(CH_2)_{12}CH_3$), 2.30–2.38 (2H, m, $O_2CCH_2(CH_2)_{13}CH_3$), 3.93 (1H, ddd, $J_{4,5}$ 9.8 Hz, $J_{5,6}$ 10.2 Hz, $J_{5,6'}$ 4.6 Hz, H-5), 3.99 (1H, at, J 10.0 Hz, H-6), 4.16 (1H, dd, $J_{3,4}$ 7.6 Hz, H-4), 4.19 (1H, dd, $J_{6,6'}$ 9.7 Hz, H-6′), 4.71 (1H, dd, $J_{1,2}$ 6.0 Hz, $J_{2,3}$ 2.0 Hz, H-2), 5.41 (1H, dat, J 1.8 Hz, J 7.6 Hz, H-3), 6.31 (1H, dd, $J_{1,3}$ 1.5 Hz, H-1); δ_C (100.6 MHz, $CDCl_3$) 14.1 (q, $O_2C(CH_2)_{14}CH_3$), 19.8, 22.5 (2 × s, 2 × $C(CH_3)_3$), 26.8, 27.3 (2 × q, 2 × $C(CH_3)_3$), 22.7, 24.9, 25.1, 29.0, 29.1, 29.3, 29.3, 29.4, 29.6, 29.6, 29.7, 29.7, 31.9 (13 × t, $O_2CCH_2(CH_2)_{13}CH_3$), 34.6 (t, $O_2CCH_2(CH_2)_{13}CH_3$), 65.7 (t, C-6), 71.8 (d, C-3), 72.9 (d, C-5), 73.6 (d, C-4), 100.7 (d, C-2), 144.8 (d, C-1), 173.7 (s, $O_2C(CH_2)_{14}CH_3$); m/z (FI^+) 524 (M^+, 34%). (HRMS calcd. for $C_{30}H_{56}O_5Si$ (M^+) 524.3897. Found 524.3892) (Found: C, 68.58; H, 10.71. $C_{30}H_{56}O_5Si$ requires C, 68.65; H, 10.75%).

1,5-Anhydro-2-deoxy-3-*O*-(1-phenylethenyl)-4,6-*O*-di(*tert*-butyl)-silanediyl-D-*arabino*-hex-1-enitol 7a

General method B: Tebbe reagent (1.02 ml, 0.51 mmol), glycal ester **6a** (50 mg, 0.13 mmol), tetrahydrofuran (2 ml) and pyridine (0.5 ml), gave enol ether **7a** (52 mg) as a colourless oil. This unstable compound was carried through to the next step without further purification; ν_{max} (thin film): 1645 (m, C=C), 1615 (w, C=C) cm^{-1}; δ_H (400 MHz, C_6D_6) 1.11, 1.16 (18H, 2 × s, 2 × $C(CH_3)_3$), 3.97 (1H, ddd, $J_{4,5}$ 10.4 Hz, $J_{5,6}$ 10.4 Hz, $J_{5,6'}$ 5.0 Hz, H-5), 4.08 (1H, at, J 10.4 Hz, H-6), 4.28 (1H, dd, $J_{6,6'}$ 10.3 Hz, H-6′), 4.52 (1H, d, J_{gem} 2.5 Hz, C=CHH′), 4.55 (1H, dd, $J_{3,4}$ 7.3 Hz, H-4), 4.85 (1H, d, C=CHH′), 4.91 (1H, dat, J 1.5 Hz, 7.2 Hz, H-3), 5.00 (1H, dd, $J_{1,2}$ 6.1 Hz, $J_{2,3}$ 1.8 Hz, H-2), 6.19 (1H, dd, $J_{1,3}$ 1.4 Hz, H-1), 7.20–7.30 (3H, m, Ar–H), 7.86–7.88 (2H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 20.1, 23.0 (2 × s, 2 × $C(CH_3)_3$), 27.3, 27.7 (2 × q, 2 × $C(CH_3)_3$), 66.5 (t, C-6), 73.3 (d, C-5), 75.4 (d, C-4), 76.5 (d, C-3), 85.7 (t, C=CH_2), 100.7 (d, C-2), 126.0, 128.5, 128.9 (5 × d, Ar), 136.2 (s, C_{ipso} Ar), 144.7 (d, C-1), 160.1 (s, C=CH_2); m/z ($APCI^+$) 389 (MH^+, 39%) (HRMS calcd. for $C_{22}H_{33}O_4Si$ (MH^+) 389.2148. Found 389.2142).

1,5-Anhydro-2-deoxy-4,6-*O*-di(*tert*-butyl)-3-*O*-(1-heptylethenyl)-silanediyl-D-*arabino*-hex-1-enitol 7b

General method B: Tebbe reagent (0.97 ml, 0.48 mmol), glycal ester **6b** (50 mg, 0.12 mmol), tetrahydrofuran (2 ml) and pyridine (0.5 ml), gave enol ether **7b** (56 mg) as a pale yellow oil. This unstable compound was used in the next step with out further purification; ν_{max} (thin film): 1652, 1645 (2 × C=C); δ_H (500 MHz, C_6D_6) 1.02 (3H, t, J 6.8 Hz, $(CH_2)_6CH_3$), 1.14, 1.18 (18H, 2 × s, 2 × $C(CH_3)_3$), 1.38–1.47 (8H, m, $(CH_2)_2(CH_2)_4CH_3$), 1.70–1.77 (2H, m, $CH_2CH_2(CH_2)_4CH_3$), 2.25–2.33 (2H, m, $CH_2(CH_2)_5CH_3$), 3.95 (1H, ddd, $J_{4,5}$ 10.4 Hz, $J_{5,6}$ 10.4 Hz, $J_{5,6'}$ 5.0 Hz, H-5), 4.06 (1H, at, J 10.4 Hz, H-6), 4.15 (1H, s, C=CHH′), 4.17 (1H, s, C=CHH′), 4.27 (1H, dd, $J_{6,6'}$ 10.3 Hz, H-6′), 4.45 (1H, dd, $J_{3,4}$ 7.3 Hz, H-4), 4.79 (1H, br d, J 7.3 Hz, H-3), 5.03 (1H, dd, $J_{1,2}$ 6.1 Hz, $J_{2,3}$ 0.9 Hz, H-2), 6.22 (1H, d, H-1); δ_C (100.6 MHz, C_6D_6) 14.5 (q, $(CH_2)_6CH_3$)), 20.1, 23.0 (2 × s, 2 × $C(CH_3)_3$), 27.3, 27.8 (2 × q, 2 × $C(CH_3)_3$), 23.3, 27.8, 29.5, 29.8, 32.4 (5 × t, $CH_2(CH_2)_5CH_3$), 36.0 (t, $CH_2(CH_2)_5CH_3$), 66.5 (t, C-6), 73.3 (d, C-5), 75.1 (d, C-4), 75.3 (d, C-3), 82.7 (t, C=CH_2), 100.7 (d, C-2), 144.5 (d, C-1), 162.7 (s, C=CH_2); m/z (CI^+) 411 (MH^+, 35%).

1,5-Anhydro-2-deoxy-4,6-*O*-di-(*tert*-butyl)-3-*O*-(1-pentadecyl-ethenyl)silanediyl-D-*arabino*-hex-1-enitol 7c

General method B: Tebbe reagent (0.76 ml, 0.38 mmol), glycal ester **6c** (50 mg, 0.10 mmol), tetrahydrofuran (2 ml) and pyridine (0.5 ml), gave enol ether **7c** (58 mg) as a pale yellow oil. This unstable compound was used in the next step with out further purification; ν_{max} (thin film): 1651, 1647 (s, 2 × C=C); δ_H (400 MHz, C_6D_6) 0.91 (3H, t, J 6.8 Hz, $(CH_2)_{14}CH_3$), 1.02 (9H, s, $C(CH_3)_3$), 1.06 (9H, s, $C(CH_3)_3$), 1.22–1.37 (24H, m, $(CH_2)_2(CH_2)_{12}CH_3$), 1.59–1.66 (2H, m, $CH_2CH_2(CH_2)_{12}CH_3$), 2.11–2.25 (2H, m, $CH_2(CH_2)_{13}CH_3$), 3.82 (1H, ddd, $J_{4,5}$ 10.3 Hz, $J_{5,6}$ 10.3 Hz, $J_{5,6'}$ 4.9 Hz, H-5), 3.93 (1H, at, J 10.3 Hz, H-6), 4.03 (1H, d, J_{gem} 1.6 Hz, C=CHH′), 4.04 (1H, d, C=CHH′), 4.14 (1H, dd, $J_{6,6'}$ 10.2 Hz, H-6′), 4.31 (1H, dd, $J_{3,4}$ 7.3 Hz, H-4), 4.65 (1H, br d, 7.3 Hz, H-3), 4.90 (1H, dd, $J_{1,2}$ 6.1 Hz, $J_{2,3}$ 1.7 Hz, H-2), 6.06 (1H, dd, $J_{1,3}$ 1.3 Hz, H-1); δ_C (100.6 MHz, C_6D_6) 14.6 (q, $(CH_2)_{14}CH_3$), 20.2, 23.1 (2 × s, 2 × $C(CH_3)_3$), 27.4, 27.9 (2 × q, 2 × $C(CH_3)_3$), 23.4, 27.9, 29.6, 30.1, 30.3, 30.4, 30.5, 30.7, 30.7, 30.7, 32.6 (11 × t, $CH_2(CH_2)_{13}CH_3$), 36.1 (t, $CH_2(CH_2)_{13}CH_3$), 66.6 (t, C-6), 73.4 (d, C-5), 75.2 (d, C-4), 75.3 (d, C-3), 82.7 (t, C=CH_2), 100.8 (d, C-2), 144.6 (d, C-1), 162.7 (s, C=CH_2); m/z ($APCI^+$) 524 (MH^+, 15%).

1-(1′,5′-Anhydro-4′,6′-*O*-di(*tert*-butyl)silanediyl-2′,3′-dideoxy-β-D-*erythro*-hex-2′-enopyranosyl)acetophenone 8a

General method C: Crude enol ether **7a** (52 mg), in benzonitrile (1 ml), gave the β-*C*-glycoside **8a** (42 mg, 84% over two steps) as a white crystalline solid; mp 130–131 °C (petrol); $[\alpha]_D^{22}$ +46.6 (c, 1 in $CHCl_3$); ν_{max} (KBr disc): 1682 (s, C=O) cm^{-1}; δ_H (400 MHz, C_6D_6) 1.20, 1.21 (18H, 2 × s, 2 × $C(CH_3)_3$), 2.68 (1H, dd, $J_{1',C(O)CHH'}$ 6.5 Hz, J_{gem} 16.7 Hz, C(O)CHH′), 3.17 (1H, dd, $J_{1',C(O)CHH'}$ 6.8 Hz, C(O)CHH′), 3.74 (1H, ddd, $J_{4',5'}$ 8.5 Hz, $J_{5',6'}$ 10.4 Hz, $J_{5',6''}$ 5.1 Hz, H-5′), 4.02 (1H, at, J 10.2 Hz, H-6′), 4.30 (1H, dd, $J_{6',6''}$ 10.0 Hz, H-6″), 4.64–4.68 (1H, m, H-4′), 4.99–5.01 (1H, m, H-1′), 5.68 (1H, dat, $J_{2',3'}$ 10.4 Hz, J 1.9 Hz, H-2′), 6.05 (1H, br d, J 10.4 Hz, H-3′), 7.06–7.12 (2H, m, Ar–H), 7.17–7.21 (1H, m, Ar–H), 7.87–7.90 (2H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 20.5, 23.1 (2 × s, 2 × $C(CH_3)_3$), 27.6, 27.8 (2 × q, 2 × $C(CH_3)_3$), 44.2 (t, CH_2COPh), 67.7 (t, C-6′), 71.0 (d, C-4′), 72.6 (d, C-1′), 75.4 (d, C-5′), 128.5, 128.8 (4 × d, $C_{ortho\ and\ meta}$ Ar), 129.9 (d, C-2′), 130.5 (d, C-3′), 133.1 (d, C_{para} Ar), 137.7 (s, C_{ipso} Ar), 196.5 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 5.00 (H-1′), enhancements: 2.68 (C(O)CHH′, 2.7%), 3.17 (C(O)CHH′, 2.7%), 3.74 (H-5′, 10.9%), 5.68 (H-2′, 5.3%). Irradiate δ 3.74 (H-5′), enhancements: 4.30 (H-6″, 4.6%), 4.66 (H-4′, 1.8%), 5.00 (H-1′, 12.2%); m/z ($APCI^+$) 389 (MH^+, 21), 411 (MNa^+, 7.5%). (HRMS calcd. for $C_{22}H_{33}O_4Si$ (MH^+) 389.2148. Found: 389.2139) (Found: C, 67.85; H, 8.33. $C_{22}H_{32}O_4Si$ requires: C, 68.00: H, 8.30%).

Crystal data for 8a

$C_{22}H_{33}O_4Si$, M = 388.58, monoclinic, a = 8.4698(2), b = 6.4952(2), c = 20.0695(4) Å, U = 1101.4 Å^3, T = 150 K, space group $P2_1$, Z = 2, μ(Mo–K$_\alpha$) 0.129 mm^{-1}, 10755 reflections measured, 2712 unique (R_{int} = 0.039, R = 0.0319. The final wR was 0.0373 (all data).

1-(1′,5′-Anhydro-4′,6′-*O*-di(*tert*-butyl)silanediyl-2′,3′-dideoxy-β-D-*erythro*-hex-2′-enopyranosyl)nonan-2-one 8b

General method C: Crude enol ether **7b** (56 mg), in benzonitrile (1 ml), gave the β-*C*-glycoside **8b** (44.5 mg, 89% over two steps) as a colourless oil; $[\alpha]_D^{22}$ +25.8 (*c*, 1 in $CHCl_3$); ν_{max} (thin film) 1715 (s, C=O) cm^{-1}; δ_H (500 MHz, C_6D_6) 0.88 (3H, t, *J* 7.1 Hz, C(O)(CH$_2$)$_6$CH$_3$), 1.09, 1.10 (18H, 2 × s, 2 × C(CH$_3$)$_3$), 1.14–1.26 (8H, m, C(O)CH$_2$CH$_2$(CH$_2$)$_4$CH$_3$), 1.48–1.51 (2H, m, C(O)CH$_2$CH$_2$(CH$_2$)$_4$CH$_3$), 2.01–2.08 (3H, m, C(O)C*H*H′ and C*H*$_2$C(O)CH$_2$(CH$_2$)$_5$CH$_3$), 2.41 (1H, dd, $J_{1',C(O)CHH'}$ 7.6 Hz, J_{gem} 16.0 Hz, C(O)CH*H*′), 3.59 (1H, ddd, $J_{4',5'}$ 8.5 Hz, $J_{5',6'}$ 10.3 Hz, $J_{5',6''}$ 5.1 Hz, H-5′), 3.94 (1H, at, *J* 10.2 Hz, H-6′), 4.21 (1H, dd, $J_{6',6''}$ 10.0 Hz, H-6″), 4.52–4.55 (1H, m, H-4′), 4.65–4.67 (1H, m, H-1′), 5.43 (1H, dat, $J_{2',3'}$ 10.4 Hz, *J* 1.8 Hz, H-2′), 5.91 (1H, br d, *J* 10.3 Hz, H-3′); δ_C (100.6 MHz, C_6D_6) 14.6 (q, C(O)-(CH$_2$)$_6$CH$_3$), 20.5, 23.2 (2 × s, 2 × *C*(CH$_3$)$_3$), 27.6, 27.9 (2 × q, 2 × C(*C*H$_3$)$_3$), 23.3, 24.0, 29.7, 29.8, 32.3 (5 × t, C(O)CH$_2$-(*C*H$_2$)$_5$CH$_3$), 43.9 (t, C(O)*C*H$_2$(CH$_2$)$_5$CH$_3$), 48.1 (t, *C*H$_2$CO-(CH$_2$)$_6$CH$_3$), 67.8 (t, C-6′), 71.1 (d, C-4′), 72.6 (d, C-1′), 75.5 (d, C-5′), 129.8 (d, C-2′), 130.6 (d, C-3′), 206.6 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 4.66 (H-1′), enhancements: 2.05 (C*H*$_2$CO(CH$_2$)$_5$CH$_3$, 3.3%), 3.59 (H-5′, 10.0%), 5.43 (H-2′, 4.9%). Irradiate δ 3.59 (H-5′), enhancements: 4.21 (H-6′, 3.9%), 4.66 (H-1′, 10.3%); *m*/*z* (APCI$^+$) 411 (MH$^+$, 34%) (HRMS calcd. for $C_{23}H_{43}O_4Si$ (MH$^+$) 411.2931. Found: 411.2940).

1-(1′,5′-Anhydro-4′,6′-*O*-di(*tert*-butyl)silanediyl-2′,3′-dideoxy-β-D-*erythro*-hex-2′-enopyranosyl)heptadecan-2-one 8c

General method C: Crude enol ether **7c** (58 mg), in tributylamine (1 ml), gave the β-*C*-glycoside **8c** (44 mg, 88% over two steps) as a white foam; $[\alpha]_D^{25}$ + 8.0 (*c*, 0.5 in $CHCl_3$); ν_{max} (thin film) 1716 (s, C=O) cm^{-1}; δ_H (400 MHz, C_6D_6) 0.91 (3H, t, *J* 6.8 Hz, C(O)(CH$_2$)$_{14}$C*H*$_3$), 1.09, 1.10 (18H, 2 × s, 2 × C(CH$_3$)$_3$), 1.17–1.32 (24H, m, C(O)CH$_2$CH$_2$(C*H*$_2$)$_{12}$CH$_3$), 1.49–1.56 (2H, m, C(O)CH$_2$C*H*$_2$(CH$_2$)$_{12}$CH$_3$), 2.02–2.08 (3H, m, C(O)C*H*H′ and CH$_2$C(O)C*H*$_2$(CH$_2$)$_{13}$CH$_3$), 2.41 (1H, dd, $J_{1',C(O)CHH'}$ 7.7 Hz, J_{gem} 16.0 Hz, C(O)CH*H*′), 3.59 (1H, ddd, $J_{4',5'}$ 8.5 Hz, $J_{5',6'}$ 10.4 Hz, $J_{5',6''}$ 5.1 Hz, H-5′), 3.94 (1H, at, *J* 10.2 Hz, H-6′), 4.22 (1H, dd, $J_{6',6''}$ 9.9 Hz, H-6″), 4.52–4.56 (1H, m, H-4′), 4.64–4.67 (1H, m, H-1′), 5.42 (1H, dat, $J_{2',3'}$ 10.4 Hz, *J* 1.9 Hz, H-2′), 5.91 (1H, br d, *J* 10.3 Hz, H-3′); δ_C (100.6 MHz, C_6D_6) 14.7 (q, C(O)(CH$_2$)$_{14}$*C*H$_3$), 20.6, 23.2 (2 × s, 2 × *C*(CH$_3$)$_3$), 27.6, 27.9 (2 × q, 2 × C(*C*H$_3$)$_3$), 23.4, 24.0, 29.8, 30.1, 30.2, 30.2, 30.4, 30.4, 30.4, 30.5, 30.5, 30.5, 32.6 (13 × t, C(O)CH$_2$(*C*H$_2$)$_{13}$CH$_3$), 43.9 (t, C(O)*C*H$_2$(CH$_2$)$_{13}$CH$_3$), 48.1 (t, *C*H$_2$CO(CH$_2$)$_{14}$CH$_3$), 67.8 (t, C-6′), 71.1 (d, C-4′), 72.6 (d, C-1′), 75.5 (d, C-5′), 129.8 (d, C-2′), 130.6 (d, C-3′), 206.6 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 4.66 (H-1′), enhancements: 2.05 (CH$_2$C(O)(CH$_2$)$_{14}$CH$_3$, 3.5%), 2.41 (C(O)CHH′, 1.9%), 3.59 (H-5′, 9.0%), 5.42 (H-2′, 5.0%). Irradiate δ 3.59 (H-5′), enhancements: 4.22 (H-6″, 4.1%), 4.54 (H-4′, 1.8%), 4.66 (H-1′, 9.7%), 5.91 (H-3′, 0.7%); *m*/*z* (ES$^+$) 523 (MH$^+$, 100), 540 (MNH$_4^+$, 48), 545 (MNa$^+$, 30), 561 (MK$^+$, 12%). (HRMS calcd. for $C_{31}H_{62}O_4$-SiN (MNH$_4^+$) 540.4448. Found: 540.4447) (Found: C, 71.07; H, 11.15. $C_{31}H_{58}O_4Si$ requires: C, 71.21: H, 11.18%).

1,5-Anhydro-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-D-*arabino*-hex-1-enitol 10a

Benzoyl chloride (0.20 ml, 1.71 mmol) was added drop-wise to a stirred solution of alcohol **9** (200 mg, 0.85 mmol) and 4-dimethylaminopyridine (21 mg, 0.17 mmol) in pyridine (6 ml) at 0 °C in an atmosphere of argon. The reaction mixture was stirred for 15 min, after which time TLC (petrol : ethyl acetate, 4 : 1) indicated the complete consumption of starting material (R_f 0.2) and the formation of a single product (R_f 0.6). Methanol (1 ml) was then added to the reaction mixture and the solvent was removed *in vacuo*. The resulting residue was dissolved in dichloromethane (30 ml), washed with water (2 × 30 ml), dried (magnesium sulfate), filtered and concentrated *in vacuo*. Purification of the product by recrystallisation (petrol–ethyl acetate) afforded the ester **10a** (272 mg, 94%) as white crystals; mp 147–149 °C [Lit.[28] 146–147 °C (ethanol)]; $[\alpha]_D^{22}$ −245 (*c*, 1 in $CHCl_3$) [Lit.[27] $[\alpha]_D^{23}$ −40.2 (*c*, 1 in $CHC1_3$)]; δ_H (400 MHz, $CDCl_3$) 3.92 (1H, at, *J* 10.4 Hz, H-6), 4.10 (1H, ddd, $J_{4,5}$ 10.3 Hz, $J_{5,6}$ 10.2 Hz, $J_{5,6'}$ 5.1 Hz, H-5), 4.24 (1H, dd, $J_{3,4}$ 7.8 Hz, H-4), 4.45 (1H, dd, $J_{6,6'}$ 10.6 Hz, H-6′), 4.94 (1H, dd, $J_{1,2}$ 6.1 Hz, $J_{2,3}$ 2.1 Hz, H-2), 5.66 (1H, s, CHPh), 5.83 (1H, dat, H-3), 6.46 (1H, dd, $J_{1,3}$ 1.3 Hz, H-1), 7.34–7.39 (3H, m, Ar–H), 7.43–7.51 (4H, m, Ar–H), 7.55–7.60 (1H, m, Ar–H), 8.06–8.09 (2H, m, Ar–H).

3-*O*-Acetyl-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*arabino*-hex-1-enitol 10b

A mixture of alcohol **9** (100 mg, 0.43 mmol) and acetic anhydride (0.40 ml, 4.27 mmol) in pyridine (0.35 ml, 4.27 mmol) was stirred at room temperature for 1 h, after which time TLC (petrol : ethyl acetate, 4 : 1) indicated the complete consumption of starting material (R_f 0.2) and the formation of a single product (R_f 0.6). Water (1 ml) was then added to the reaction mixture and the solvent was concentrated *in vacuo*. The resulting residue was dissolved in dichloromethane (20 ml), washed with water (2 × 20 ml), dried (magnesium sulfate), filtered and concentrated *in vacuo*. The product was purified by flash column chromatography (petrol : ethyl acetate, 8 : 1) to afford acetate **10b** (113 mg, 96%) as a white crystalline solid; mp 140–141 °C (petrol–ethyl acetate) [Lit.[15] mp 136–137 °C (acetone–hexane)]; $[\alpha]_D^{22}$ −102 (*c*, 1 in $CHCl_3$) [Lit.[15] $[\alpha]_D^{27}$ −85 (*c*, 1 in $CHC1_3$)]; δ_H (200 MHz, $CDCl_3$) 2.10 (3H, s, CH_3), 3.81–4.11 (3H, m, H-4, H-5 and H-6), 4.38–4.45 (1H, m, H-6′), 4.83 (1H, dd, $J_{1,2}$ 6.1 Hz, $J_{2,3}$ 2.0 Hz, H-2), 5.55 (1H, dd, $J_{3,4}$ 7.8 Hz, H-3), 5.62 (1H, s, CHPh), 6.41 (1H, dd, $J_{1,3}$ 1.4 Hz, H-1), 7.32–7.41 (3H, m, Ar–H), 7.45–7.54 (2H, m, Ar–H).

1,5-Anhydro-4,6-*O*-benzylidene-2-deoxy-3-*O*-(1-phenylethenyl)-D-*arabino*-hex-1-enitol 11a

General method B: Tebbe reagent (2.36 ml, 1.18 mmol), glycal ester **10a** (100 mg, 0.30 mmol) in tetrahydrofuran (4 ml) and pyridine (1 ml), gave enol ether **11a** (106 mg) as a white foam. This unstable compound was used in the next step with out further purification; ν_{max} (thin film): 1640 (C=C), 1594 (w, C=C) cm^{-1}; δ_H (400 MHz, C_6D_6) 3.49 (1H, at, *J* 10.4 Hz, H-6), 3.76 (1H, ddd, $J_{4,5}$ 10.3 Hz, $J_{5,6}$ 10.3 Hz, $J_{5,6'}$ 5.2 Hz, H-5), 4.05 (1H, dd, $J_{3,4}$ 7.6 Hz, H-4), 4.14 (1H, dd, $J_{6,6'}$ 10.5 Hz, H-6′), 4.32 (1H, d, J_{gem} 2.8 Hz, C=C*H*H′), 4.72 (1H, d, C=CH*H*′), 4.86 (1H, dd, $J_{1,2}$ 6.2 Hz, $J_{2,3}$ 1.7 Hz, H-2), 4.94 (1H, br d, *J* 7.6 Hz, H-3), 5.29 (1H, s, CHPh), 6.05 (1H, d, H-1), 7.04–7.15 (6H, m, Ar–H), 7.54–7.57 (2H, m, Ar–H), 7.72–7.75 (2H, m, Ar–H); δ_C (100.6 MHz,C_6D_6) 68.6 (t, C-6), 69.4 (d, C-5), 72.5 (d, C-3), 78.5 (d, C-4), 85.5 (t, C=CH$_2$), 100.6 (d, C-2), 101.9 (d, CHPh), 126.4, 126.9, 128.6, 128.7, 129.1, 129.3 (10 × d, $C_{ortho,\ meta}$ and $_{para}$ Ar), 137.4, 138.3 (2 × s, C_{ipso} Ar), 145.2 (d, C-1), 159.4 (s, C=CH$_2$); *m*/*z* (CI$^+$) 337 (MH$^+$, 10%).

1,5-Anhydro-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2-propenyl)-D-*arabino*-hex-1-enitol 11b

General method B: Tebbe reagent (1.74 ml, 0.87 mmol), glycal ester **10b** (120 mg, 0.43 mmol) in tetrahydrofuran (4 ml) and pyridine (1 ml), gave enol ether **11b** (130 mg) as a pale yellow crystalline solid. This unstable compound was used in the next

step with out further purification; ν_{max} (thin film): 1661, 1635 (m, 2 × C=C) cm^{-1}; δ_H (400 MHz, C_6D_6) 1.75 (3H, s, CH_3), 3.44 (1H, at, *J* 10.4 Hz, H-6), 3.74 (1H, ddd, $J_{4,5}$ 10.3 Hz, $J_{5,6}$ 10.3 Hz, $J_{5,6'}$ 5.2 Hz, H-5), 3.95 (1H, br s, C=C*H*H′), 3.96 (1H, d, J_{gem} 1.3 Hz, C=CH*H*′), 3.98 (1H, dd, $J_{3,4}$ 7.6 Hz, H-4), 4.11 (1H, dd, $J_{6,6'}$ 10.5 Hz, H-6′), 4.82 (1H, d, $J_{2,3}$ 1.7 Hz, H-3), 4.87 (1H, dd, $J_{1,2}$ 6.2 Hz, H-2), 5.28 (1H, s, C*H*Ph), 6.03 (1H, dd, H-1), 7.06–7.15 (3H, m, Ar–H), 7.53–7.56 (3H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 21.6 (q, CH_3), 68.6 (t, C-6), 69.4 (d, C-5), 71.6 (d, C-3), 78.4 (d, C-4), 83.6 (t, C=*C*H_2), 100.6 (d, C-2), 102.1 (d, *C*HPh), 127.1, 128.5, 129.3 (5 × d, $C_{ortho,\ meta}$ and *para* Ar), 138.3 (s, C_{ipso} Ar) 145.0 (d, C-1), 158.5 (s, *C*=CH_2); *m*/*z* (CI^+) 275 (MH^+, 6%).

1-(1′,5′-Anhydro-4′,6′-*O*-benzylidene-2′,3′-dideoxy-β-D-*erythro*-hex-2′-enopyranosyl)acetophenone 12a

General method C: Crude enol ether **11a** (106 mg), in tributylamine (2 ml), gave β-*C*-glycoside **12a** (70 mg, 71% over two steps) as a white crystalline solid, mp 99–100 °C (petrol–diethyl ether); $[\alpha]_D^{25}$ +57 (*c*, 0.5 in $CHCl_3$); ν_{max} (KBr disc): 1683 (s, C=O) cm^{-1}; δ_H (400 MHz, C_6D_6) 2.67 (1H, dd, $J_{1',C(O)CHH'}$ 6.5 Hz, J_{gem} 16.6 Hz, C(O)C*H*H′), 3.11 (1H, dd, $J_{1',C(O)CHH'}$ 6.7 Hz, C(O)CH*H*′), 3.57 (1H, at, *J* 10.0 Hz, H-6′), 3.61–3.67 (1H, m, H-5′), 4.04–4.07 (1H, m, H-4′), 4.19 (1H, dd, $J_{5',6''}$ 4.1 Hz, $J_{6',6''}$ 9.6 Hz, H-6″), 4.90–4.94 (1H, m, H-1′), 5.43 (1H, s, CHPh), 5.63 (1H, dat, $J_{2',3'}$ 10.4 Hz, *J* 2.1 Hz, H-2′), 5.99 (1H, br d, *J* 10.4 Hz, H-3′), 7.06–7.10 (2H, m, Ar–H), 7.14–7.20 (4H, m, Ar–H), 7.62–7.64 (2H, m, Ar–H), 7.76–7.79 (2H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 43.6 (t, *C*H_2COPh), 69.3 (t, C-6′), 71.1 (d, C-5′), 72.5 (d, C-1′), 75.2 (d, C-4′), 101.9 (d, CHPh), 126.6, 127.0, 127.5, 127.7, 127.8, 128.0, 128.0, 128.1, 128.3, 128.7, 130.7, 132.7 (12 × d, C-2′, C-3′ and $C_{ortho,\ meta}$ and *para* Ar), 137.2, 138.3 (2 × s, C_{ipso} Ar), 195.8 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 4.92 (H-1′), enhancements: 2.67 (C(O)C*H*H′, 1.9%), 3.11 (C(O)CH*H*′, 1.8%), 3.64 (H-5′, 11.3%), 5.63 (H-2′, 4.2%). Irradiate δ 3.64 (H-5′), enhancements: 4.06 (H-4′, 1.2%), 4.19 (H-6″, 3.9%), 4.92 (H-1′, 10.6%), 5.99 (H-3′, 0.9%); *m*/*z* (CI^+) 337 (MH^+, 25%). (HRMS calcd. for $C_{21}H_{21}O_4$ (MH^+) 337.1439. Found: 337.1434) (Found: C, 74.92; H, 6.01. $C_{21}H_{20}O_4$ requires: C, 74.98: H, 5.99%).

1-(1′,5′-Anhydro-4′,6′-*O*-benzylidene-2′,3′-dideoxy-β-D-*erythro*-hex-2′-enopyranosyl)propan-2-one 12b

General method C: Crude enol ether **11b** (130 mg), in tributylamine (2 ml), gave β-*C*-glycoside **12b** (94 mg, 80% over two steps) as a white crystalline solid; mp 67 °C (petrol); $[\alpha]_D^{25}$ +80 (*c*, 1 in $CHCl_3$); ν_{max} (KBr disc): 1708 (s, C=O) cm^{-1}; δ_H (500 MHz, C_6D_6) 1.71 (3H, s, CH_3), 2.02 (1H, dd, $J_{1',C(O)CHH'}$ 5.7 Hz, J_{gem} 16.1 Hz, C(O)C*H*H′), 2.35 (1H, dd, $J_{1',C(O)CHH'}$ 7.6 Hz, C(O)CH*H*′), 3.53–3.59 (2H, m, H-5′ and H-6′), 3.98–4.00 (1H, m, H-4′), 4.18 (1H, m, H-6″), 4.54–4.58 (1H, m, H-1′), 5.39 (1H, dat, $J_{2',3'}$ 10.4 Hz, *J* 2.1 Hz, H-2′), 5.41 (1H, s, C*H*Ph), 5.93 (1H, br d, *J* 10.4 Hz, H-3′), 7.15–7.25 (3H, m, Ar–H), 7.67–7.69 (2H, m, Ar–H); δ_C (125.7 MHz, C_6D_6) 28.8 (q, CH_3), 46.9 (t, *C*H_2COCH$_3$), 68.1 (t, C-6′), 70.0 (d, C-5′), 71.2 (d, C-1′), 73.9 (d, C-4′), 100.7 (d, *C*HPh), 125.5 (2 × d, Ar), 125.9 (d, C-3′), 126.9 (2 × d, Ar), 127.6 (d, C_{para} Ar), 129.2 (d, C-2′), 137.2 (s, C_{ipso} Ar), 204.0 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 4.56 (H-1′), enhancements: 2.02 (C(O)C*H*H′, 2.8%), 2.35 (C(O)CH*H*′, 2.8%), 3.56 (H-5′ and H-6″, 9.0%), 5.39 (H-2′, 4.4%). Irradiate δ 3.56 (H-5′ and H-6′), enhancements: 3.99 (H-4′, 1.9%), 4.18 (H-6″, 14.2%), 4.56 (H-1′, 6.3%), 5.41 (C*H*Ph, 3.8%); *m*/*z* (CI^+) 275 (MH^+, 15%), 292 (MNH_4^+, 12%). (Found: C, 70.05; H, 6.65. $C_{16}H_{18}O_4$ requires: C, 70.06; H, 6.61%).

Crystal data for 12b

$C_{16}H_{18}O_4$, *M* = 274.32, orthorhombic, *a* = 5.1126(5), *b* = 14.2991(2), *c* = 19.1347(8) Å, *U* = 1398.9 Å^3, *T* = 150 K, space group $P2_12_12_1$, *Z* = 4, μ(Mo–K_α) 0.093 mm^{-1}, 14624 reflections measured, 1883 unique (R_{int} = 0.051), *R* = 0.0315. The final *wR* was 0.0355 (all data).

1,5-Anhydro-2-deoxy-4,6-*O*-di(*tert*-butyl)silanediyl-D-*ribo*-hex-1-enitol 14

Di-*tert*-butylsilyl bistrifluoromethanesulfonate (0.96 ml, 2.63 mmol) was added drop-wise over 15 min to a stirred solution of allal **13** (350 mg, 2.39 mmol) in dimethylformamide (10 ml) at −40 °C in an atmosphere of argon. The resulting reaction mixture was stirred for 1 h, after which time TLC (ethyl acetate : methanol, 19 : 1) indicated the complete consumption of starting material (R_f 0.4) and the formation of a major product (R_f 0.9). Pyridine (0.23 ml, 2.87 mmol) was then added to the reaction mixture and stirred for a further 10 min. The mixture was diluted with diethyl ether (50 ml), washed with a solution of saturated sodium hydrogen carbonate (25 ml) and then with water (2 × 25 ml). The organic layer was dried (magnesium sulfate), filtered and concentrated *in vacuo*. The resultant residue was purified by flash column chromatography (petrol : ethyl acetate, 6 : 1) to afford the alcohol **14** (528 mg, 77%) as a white crystalline solid; mp 67–68 °C (petrol); $[\alpha]_D^{24}$ +117 (*c*, 1 in $CHCl_3$); ν_{max} (KBr disc): 3580 (br, OH), 1643 (s, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.04, 1.08 (18H, 2 × s, 2 × C(CH_3)$_3$), 2.69 (1H, s, OH), 3.94–4.06 (3H, m, H-4, H-5 and H-6), 4.15–4.17 (1H, m, H-3), 4.28 (1H, dd, $J_{5,6'}$ 3.5 Hz, $J_{6,6'}$ 9.3 Hz, H-6′), 5.00 (1H, at, *J* 5.9 Hz, H-2), 6.41 (1H, d, $J_{1,2}$ 6.0 Hz, H-1); δ_C (100.6 MHz, $CDCl_3$) 20.2, 22.8 (2 × s, 2 × *C*(CH_3)$_3$), 27.1, 27.4 (2 × q, 2 × C(*C*H_3)$_3$), 61.6 (d, C-3), 65.9 (t, C-6), 67.8 (d, C-5), 74.4 (d, C-4), 100.5 (d, C-2), 145.8 (d, C-1); *m*/*z* (FI^+) 286 (M^+, 100%). (HRMS calcd. for $C_{14}H_{26}O_4Si$ (M^+) 286.1600. Found 286.1613) (Found: C, 58.74; H, 9.13. $C_{14}H_{26}O_4Si$ requires C, 58.70; H, 9.15%).

1,5-Anhydro-2-deoxy-4,6-*O*-di(*tert*-butyl)silanediyl-3-*O*-hexadecanoyl-D-*ribo*-hex-1-enitol 17

General method A: Alcohol **14** (250 mg, 0.87 mmol), palmitic acid (448 mg, 1.75 mmol), dicyclohexylcarbodiimide (360 mg, 1.75 mmol) and 4-dimethylaminopyridine (21 mg, 0.17 mmol), in dichloromethane (8 ml), gave the ester **17** (447 mg, 98%) as a colourless oil; $[\alpha]_D^{25}$ +186 (*c*, 1 in $CHCl_3$); ν_{max} (thin film) 1738 (s, C=O), 1643 (m, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.88 (3H, t, *J* 6.8 Hz, $O_2C(CH_2)_{14}CH_3$), 1.02 and 1.05 (18H, 2 × s, 2 × C(CH_3)$_3$), 1.26–1.29 (24H, m, $O_2C.CH_2CH_2(CH_2)_{12}CH_3$), 1.62–1.65 (2H, m, $O_2C.CH_2CH_2(CH_2)_{12}CH_3$), 2.30–2.34 (2H, m, $O_2C.CH_2(CH_2)_{13}CH_3$), 3.96 (1H, at, *J* 10.2 Hz, H-6), 4.09 (1H, ddd, $J_{4,5}$ 10.5 Hz, $J_{5,6}$ 10.3 Hz, $J_{5,6'}$ 4.7 Hz, H-5), 4.19 (1H, dd, $J_{3,4}$ 3.9 Hz, H-4), 4.26 (1H, dd, $J_{6,6'}$ 10.1 Hz, H-6′), 4.97 (1H, at, *J* 6.0 Hz, H-2), 5.30 (1H, dd, $J_{2,3}$ 5.9 Hz, H-3), 6.40 (1H, d, $J_{1,2}$ 5.9 Hz, H-1); δ_C (100.6 MHz, $CDCl_3$) 14.1 (q, $O_2C(CH_2)_{14}CH_3$), 20.1, 22.7 (2 × s, 2 × *C*(CH_3)$_3$), 26.8, 27.3 (2 × q, 2 × C(*C*H_3)$_3$), 22.7, 24.8, 29.1, 29.2, 29.3, 29.4, 29.6, 29.6, 29.7, 29.7, 31.9 (11 × t, $O_2CCH_2(CH_2)_{13}CH_3$), 34.4 (t, $O_2CCH_2(CH_2)_{13}CH_3$), 64.1 (d, C-3), 65.9 (t, C-6), 68.9 (d, C-5), 72.7 (d, C-4), 98.4 (d, C-2), 146.6 (d, C-1), 173.3 (s, C=O); *m*/*z* (FI^+) 524 (M^+, 69%). (HRMS calcd. for $C_{30}H_{56}O_5Si$ (M^+) 524.3897. Found 524.3876) (Found: C, 68.83; H, 10.77. $C_{30}H_{56}O_5Si$ requires C, 68.65; H, 10.75%).

1,5-Anhydro-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hex-1-enitol 18a

Benzoyl chloride (0.8 ml, 6.8 mmol) was added drop-wise to a stirred solution of the alcohol **15** (400 mg, 1.71 mmol) and 4-dimethylaminopyridine (42 mg, 0.34 mmol) in pyridine (3 ml) at 0 °C in an atmosphere of argon. The reaction mixture was stirred for 15 min, after which time TLC (petrol : ethyl acetate; 3 : 1) indicated the complete consumption of starting material (R_f 0.3) and the formation of a single product (R_f 0.5).

Methanol (1.5 ml) was then added to quench the reaction mixture and the solvent was evaporated *in vacuo*. The resulting residue was dissolved in dichloromethane (50 ml), washed with water (2 × 50 ml), dried (magnesium sulfate), filtered and concentrated *in vacuo*. The purification of the product by flash column chromatography (petrol : ethyl acetate, 4 : 1) afforded the ester **18a** (537 mg, 93%) as colourless crystals; mp 77–78 °C (petrol–ethyl acetate); $[\alpha]_D^{25}$ +383.5 (*c*, 1 in $CHCl_3$); ν_{max} (KBr disc) 1717 (s, C=O), 1636 (m, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.91 (1H, at, *J* 10.4 Hz, H-6), 4.11 (1H, dd, $J_{3,4}$ 3.8 Hz, $J_{4,5}$ 10.4 Hz, H-4), 4.37 (1H, ddd, $J_{5,6}$ 10.3 Hz, $J_{5,6'}$ 5.2 Hz, H-5), 4.52 (1H, dd, $J_{6,6'}$ 10.6 Hz, H-6′), 5.19 (1H, at, *J* 6.0 Hz, H-2), 5.64–5.66 (1H, m, H-3), 5.66 (1H, s, CHPh), 6.56 (1H, d, $J_{1,2}$ 6.0 Hz, H-1), 7.28–7.32 (3H, m, Ar–H), 7.41–7.48 (4H, m, Ar–H), 7.56–7.60 (1H, m, Ar–H), 8.10–8.13 (2H, m, Ar–H); δ_C (100.6 MHz, $CDCl_3$) 62.8 (d, C-3), 65.2 (d, C-5), 68.7 (t, C-6), 76.1 (d, C-4), 98.5 (d, C-2), 101.7 (d, CHPh), 126.1, 128.2, 128.3, 129.7 (4 × d, $C_{ortho\ and\ meta}$ Ar), 129.1 (d, C_{para} Ar), 130.3 (s, C_{ipso} Ar), 133.0 (d, C_{para} Ar), 137.0 (s, C_{ipso} Ar), 147.5 (d, C-1), 166.1 (s, C=O); *m*/*z* (CI^+) 339 (MH^+, 8%), 356 (MNH_4^+, 11%). (Found C, 71.02; H, 5.36. $C_{20}H_{18}O_5$ requires C, 71.00; H, 5.36%).

3-*O*-Acetyl-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hex-1-enitol 18b

A mixture of the alcohol **15** (400 mg, 1.71 mmol) and acetic anhydride (0.8 ml, 8.5 mmol) in pyridine (0.7 ml, 8.5 mmol) was stirred at room temperature for 4 h, after which time TLC (petrol : ethyl acetate; 3 : 1) indicated the complete consumption of starting material (R_f 0.3) and the formation of a single product (R_f 0.5). Water (5 ml) was then added to the reaction mixture and the solvent was evaporated *in vacuo*. The resulting residue was dissolved in dichloromethane (50 ml), washed with water (3 × 50 ml), dried (magnesium sulfate), filtered and concentrated *in vacuo*. The product was purified by recrystallisation from petrol–ethyl acetate to afford the acetate **18b** (457 mg, 97%) as a colourless crystalline solid; mp 123 °C; $[\alpha]_D^{25}$ +271 (*c*, 1 in $CHCl_3$); ν_{max} (KBr disc) 1732 (s, C=O), 1633 (w, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.11 (3H, s, CH_3), 3.85 (1H, at, *J* 10.4 Hz, H-6), 3.99 (1H, dd, $J_{3,4}$ 3.9 Hz, $J_{4,5}$ 10.5 Hz, H-4), 4.20 (1H, ddd, $J_{5,6}$ 10.4 Hz, $J_{5,6'}$ 5.2 Hz, H-5), 4.48 (1H, dd, $J_{6,6'}$ 10.6 Hz, H-6′), 5.02 (1H, at, *J* 6.0 Hz, H-2), 5.45 (1H, dd, $J_{2,3}$ 5.9 Hz, H-3), 5.62 (1H, s, CHPh), 6.51 (1H, d, $J_{1,2}$ 6.0 Hz, H-1), 7.37–7.41 (3H, m, Ar–H), 7.46–7.49 (2H, m, Ar–H); δ_C (100.6 MHz, $CDCl_3$) 21.2 (q, CH_3), 62.0 (d, C-3), 64.9 (d, C-5), 68.6 (t, C-6), 76.0 (d, C-4), 98.4 (d, C-2), 101.5 (d, CHPh), 126.0, 128.3 (2 × d, $C_{ortho\ and\ meta}$ Ar), 129.1 (d, C_{para} Ar), 137.0 (s, C_{ipso} Ar), 147.3 (d, C-1), 170.6 (s, C=O); *m*/*z* (CI^+) 277 (MH^+, 11), 294 (MNH_4^+, 5%). (Found: C, 65.39; H, 5.86. $C_{15}H_{16}O_5$ requires C, 65.21; H, 5.84%).

1,5-Anhydro-4,6-*O*-benzylidene-2-deoxy-3-*O*-hexadecanoyl-D-*ribo*-hex-1-enitol 18c

General method A: Alcohol **15** (200 mg, 0.85 mmol), palmitic acid (438 mg, 1.71 mmol), dicyclohexylcarbodiimide (352 mg, 1.71 mmol) and 4-dimethylaminopyridine (21 mg, 0.17 mmol), in anhydrous dichloromethane (8 ml), gave the ester **18c** (401 mg, 99%) as a white crystalline solid; mp 62–63 °C (petrol); $[\alpha]_D^{25}$ +175 (*c*, 1 in $CHCl_3$); ν_{max} (KBr disc) 1742 (s, C=O), 1634 (m, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.90 (3H, t, *J* 6.7 Hz, $O_2C(CH_2)_{14}CH_3$), 1.24–1.30 (24H, m, $O_2C.CH_2CH_2(CH_2)_{12}CH_3$), 1.58–1.67 (2H, m, $O_2C.CH_2CH_2(CH_2)_{12}CH_3$), 2.35 (2H, t, *J* 7.5 Hz, $O_2C.CH_2(CH_2)_{13}CH_3$), 3.85 (1H, at, *J* 10.4 Hz, H-6), 3.99 (1H, dd, $J_{3,4}$ 4.0 Hz, $J_{4,5}$ 10.5 Hz, H-4), 4.19 (1H, ddd, $J_{5,6}$ 10.4 Hz, $J_{5,6'}$ 5.2 Hz, H-5), 4.47 (1H, dd, $J_{6,6'}$ 10.6 Hz, H-6′), 5.02 (1H, at, *J* 6.0 Hz, H-2), 5.47 (1H, dd, $J_{2,3}$ 5.8 Hz, H-3), 5.62 (1H, s, CHPh), 6.50 (1H, d, $J_{1,2}$ 6.0 Hz, H-1), 7.34–7.38 (3H, m, Ar–H), 7.45–7.48 (2H, m, Ar–H); δ_C (100.6 MHz, $CDCl_3$) 14.1 (q, $O_2C(CH_2)_{14}CH_3$), 22.7, 25.0, 29.1, 29.2, 29.3, 29.4, 29.6, 29.6, 29.7, 29.7, 31.9 (11 × t, $O_2CCH_2(CH_2)_{13}CH_3$), 34.5 (t, $O_2CCH_2(CH_2)_{13}CH_3$), 61.7 (d, C-3), 64.9 (d, C-5), 68.6 (t, C-6), 76.1 (d, C-4), 98.5 (d, C-2), 101.5 (d, CHPh), 126.1, 128.2 (2 × d, $C_{ortho\ and\ meta}$ Ar), 129.0 (d, C_{para} Ar), 137.1 (s, C_{ipso} Ar), 147.2 (d, C-1), 173.4 (s, C=O); *m*/*z* (FI^+) 472 (M^+, 100%). (HRMS calcd. for $C_{29}H_{44}O_5$ (M^+) 472.3189. Found 472.3188) (Found: C, 73.75; H, 9.41. $C_{29}H_{44}O_5$ requires C, 73.69; H, 9.38%).

1,5-Anhydro-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-2-methyl-D-*ribo*-hex-1-enitol 19

Benzoyl chloride (0.19 ml, 1.61 mmol) was added drop-wise to a stirred solution of the alcohol **16** (100 mg, 0.40 mmol) and 4-dimethylaminopyridine (9.8 mg, 0.08 mmol) in pyridine (1 ml) at 0 °C, under an atmosphere of argon. The reaction mixture was stirred for 15 min, after which time TLC (petrol : ethyl acetate; 3 : 1) indicated the complete consumption of starting material (R_f 0.4) and the formation of a single product (R_f 0.6). Methanol (1.0 ml) was then added to quench the reaction mixture and the solvent evaporated *in vacuo*. The resulting residue was dissolved in dichloromethane (15 ml), washed with water (2 × 15 ml), dried (magnesium sulfate), filtered and concentrated *in vacuo*. The purification of the product by flash column chromatography (petrol : ethyl acetate, 3 : 1) afforded the ester **19** (134 mg, 94%) as a white crystalline solid; mp 75–76 °C (petrol–diethyl ether); $[\alpha]_D^{25}$ +299 (*c*, 1 in $CHCl_3$); ν_{max} (KBr disc) 1721 (s, C=O), 1662 (w, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.73 (3H, s, CH_3), 3.88 (1H, at, *J* 10.4 Hz, H-6), 4.07 (1H, dd, $J_{3,4}$ 4.0 Hz, $J_{4,5}$ 10.5 Hz, H-4), 4.20 (1H, ddd, $J_{5,6}$ 10.3 Hz, $J_{5,6'}$ 5.2 Hz, H-5), 4.49 (1H, dd, $J_{6,6'}$ 10.6 Hz, H-6′), 5.63 (1H, s, C*H*Ph), 5.80 (1H, d, H-3), 6.41 (1H, s, H-1), 7.21–7.29 (3H, m, Ar–H), 7.31–7.33 (2H, m, Ar–H), 7.45–7.49 (2H, m, Ar–H), 7.57–7.60 (1H, m, Ar–H), 8.12–8.14 (2H, m, Ar–H); δ_C (100.6 MHz, $CDCl_3$) 15.7 (q, CH_3), 64.6 (d, C-5), 66.0 (d, C-3), 68.7 (t, C-6), 76.2 (d, C-4), 101.3 (d, *C*HPh), 106.6 (s, C-2), 126.0, 128.1, 128.3, 129.8 (4 × d, $C_{ortho\ and\ meta}$ Ar), 128.9 (d, C_{para} Ar), 130.2 (s, C_{ipso} Ar), 133.0 (d, C_{para} Ar), 137.0 (d, C_{ipso} Ar), 142.3 (d, C-1), 166.6 (s, C=O); *m*/*z* (EI^+) 352 (M^+, 9), 353 (MH^+, 1%). (HRMS calcd. for $C_{21}H_{20}O_5$ (M) 352.1311. Found: 352.1293) (Found: C, 71.75; H, 5.76. $C_{21}H_{20}O_5$ requires C, 71.58; H, 5.72%).

1,5-Anhydro-2-deoxy-4,6-*O*-di(*tert*-butyl)silanediyl-3-*O*-(hepta-dec-1-en-2-yl)-D-*ribo*-hex-1-enitol 20

General method B: Tebbe reagent (3.1 ml, 1.5 mmol), ester **17** (200 mg, 0.38 mmol) in tetrahydrofuran (8 ml) and pyridine (2 ml), gave the enol ether **20** (192 mg, 96%) as a colourless oil; $[\alpha]_D^{25}$ +166 (*c*, 1 in diethyl ether); ν_{max} (thin film): 1646, 1640 (w, 2 × C=C); δ_H (400 MHz, C_6D_6) 0.91 (3H, t, *J* 6.8 Hz, $(CH_2)_{14}CH_3$), 1.06, 1.16 (18H, 2 × s, 2 × $C(CH_3)_3$), 1.31–1.37 (24H, m, $(CH_2)_2(CH_2)_{12}CH_3$), 1.61–1.66 (2H, m, CH_2CH_2-$(CH_2)_{12}CH_3$), 2.15 (1H, m, *J* 7.3 Hz, C*H*H′$(CH_2)_{13}CH_3$), 2.26 (1H, m, CH*H*′$(CH_2)_{13}CH_3$), 3.93 (1H, at, *J* 10.4 Hz, H-6), 3.96 (1H, d, J_{gem} 1.8 Hz, C=C*H*H′), 4.03 (1H, d, C=CH*H*′), 4.08 (1H, dd, $J_{3,4}$ 3.8 Hz, $J_{4,5}$ 10.4 Hz, H-4), 4.24 (1H, dd, $J_{5,6'}$ 4.9 Hz, $J_{6,6'}$ 10.1 Hz, H-6′), 4.31 (1H, ddd, $J_{5,6}$ 10.4 Hz, H-5), 4.34 (1H, dd, $J_{2,3}$ 5.6 Hz, H-3), 4.91 (1H, at, *J* 5.8 Hz, H-2), 6.11 (1H, d, $J_{1,2}$ 6.0 Hz, H-1); δ_C (100.6 MHz, C_6D_6) 14.6 (q, $(CH_2)_{14}CH_3$), 20.8, 23.2 (2 × s, 2 × *C*$(CH_3)_3$), 27.5, 27.9 (2 × q, 2 × C(*C*$H_3)_3$), 23.4, 28.2, 29.9, 30.1, 30.2, 30.4, 30.4, 30.5, 30.5, 30.5, 32.6 (11 × t, $CH_2(CH_2)_{13}CH_3$), 36.2 (t, *C*$H_2(CH_2)_{13}CH_3$), 66.7 (t, C-6), 67.3 (d, C-3), 69.4 (d, C-5), 74.8 (d, C-4), 82.3 (t, C=*C*H_2), 99.2 (d, C-2), 146.0 (d, C-1), 162.6 (s, *C*=CH_2); *m*/*z* (FI^+) 522 (M^+, 100%), (CI^+). (HRMS calcd. for $C_{31}H_{58}O_4Si$ (M^+) 522.4104. Found: 522.4103) (Found: C, 71.39; H, 11.19. $C_{31}H_{58}O_4Si$ requires: C, 71.21: H, 11.18%).

1,5-Anhydro-4,6-*O*-benzylidene-2-deoxy-3-*O*-(1-phenylethenyl)-D-*ribo*-hex-1-enitol 21a

General method B: Tebbe reagent (14.2 ml, 7.1 mmol), ester **18a** (600 mg, 1.77 mmol) in tetrahydrofuran (24 ml) and pyridine

(6 ml), gave the enol ether **21a** (568 mg, 95%) as a white crystalline solid; mp 75–76 °C; $[\alpha]_D^{26}$ +334 (*c*, 1 in diethyl ether); ν_{max} (KBr disc): 1635 (C=C) cm^{-1}; δ_H (400 MHz, C_6D_6) 3.32 (1H, at, *J* 10.4 Hz, H-6), 3.38 (1H, dd, $J_{3,4}$ 3.7 Hz, $J_{4,5}$ 10.5 Hz, H-4), 4.04 (1H, dd, $J_{5,6'}$ 5.3 Hz, $J_{6,6'}$ 10.5 Hz, H-6′), 4.11 (1H, d, J_{gem} 2.1 Hz, C=C*H*H′), 4.23 (1H, ddd, $J_{5,6}$ 10.4 Hz, H-5), 4.31–4.33 (1H, m, H-3), 4.56 (1H, d, C=CH*H*′), 4.69 (1H, at, *J* 5.9 Hz, H-2), 5.13 (1H, s, CHPh), 5.94 (1H, d, $J_{1,2}$ 6.1 Hz, H-1), 6.85–6.97 (6H, m, Ar–H), 7.40–7.42 (2H, m, Ar–H), 7.60–7.62 (2H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 65.4 (d, C-5), 66.7 (d, C-3), 69.0 (t, C-6), 77.6 (d, C-4), 84.6 (t, C=*C*H_2), 99.2 (d, C-2), 102.1 (d, CHPh), 126.3, 126.9, 128.4, 128.6 (4 × d, C_{ortho} and *meta* Ar), 128.8, 129.2 (2 × d, C_{para} Ar), 137.5, 138.3 (2 × s, C_{ipso} Ar), 146.5 (d, C-1), 160.1 (s, *C*=CH_2); *m*/*z* (FI^+) 336 (M^+, 100%). (HRMS calcd. for $C_{21}H_{20}O_4$ (M^+) 336.1362. Found: 336.1354) (Found: C, 75.07; H, 6.03. $C_{21}H_{20}O_4$ requires: C, 74.98: H, 5.99%).

1,5-Anhydro-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2-propenyl)-D-*ribo*-hex-1-enitol 21b

General method B: Tebbe reagent (4.3 ml, 2.17 mmol), ester **18b** (150 mg, 0.54 mmol) in tetrahydrofuran (6 ml) and pyridine (1.5 ml), gave the enol ether **21b** (139 mg, 93%) as a white crystalline solid; mp 93–94 °C; $[\alpha]_D^{26}$ +241 (*c*, 1 in diethyl ether); ν_{max} (KBr disc): 1659, 1632 (2 × C=C) cm^{-1}; δ_H (500 MHz, C_6D_6) 1.75 (3H, s, CH_3), 3.49 (1H, at, *J* 10.3 Hz, H-6), 3.53 (1H, dd, $J_{3,4}$ 3.9 Hz, $J_{4,5}$ 10.4 Hz, H-4), 3.97 (2H, s, C=CH_2), 4.23 (1H, dd, $J_{5,6'}$ 5.4 Hz, $J_{6,6'}$ 10.5 Hz, H-6′), 4.37 (1H, ddd, $J_{5,6}$ 10.4 Hz, H-5), 4.41 (1H, dd, $J_{2,3}$ 5.6 Hz, H-3), 4.89 (1H, at, *J* 5.9 Hz, H-2), 5.29 (1H, s, C*H*Ph), 6.11 (1H, d, $J_{1,2}$ 6.1 Hz, H-1), 7.07–7.11 (1H, m, Ar–H), 7.14–7.17 (2H, m, Ar–H), 7.59–7.60 (2H, m, Ar–H); δ_C (125.7 MHz, C_6D_6) 21.8 (q, CH_3), 65.2, 65.4 (2 × d, C-3 and C-5), 69.2 (t, C-6), 77.7 (d, C-4), 83.1 (t, C=*C*H_2), 99.4 (d, C-2), 102.2 (d, *C*HPh), 127.1, 129.3 (2 × d, C_{ortho} and *meta* Ar), 128.5, (d, C_{para} Ar), 138.5 (s, C_{ipso} Ar), 146.4 (d, C-1), 159.4 (s, *C*=CH_2); *m*/*z* (FI^+) 274 (M^+, 100%). (HRMS calcd. for $C_{16}H_{18}O_4$ (M^+) 274.1205. Found: 274.1208) (Found: C, 70.15; H, 6.62. $C_{16}H_{18}O_4$ requires: C, 70.06: H, 6.61%).

Crystal data for 21b

$C_{16}H_{18}O_4$, *M* = 274.32, orthorhombic, *a* = 5.8009(2), *b* = 13.1214(4), *c* = 18.5666(5) Å, *U* = 1413.2 Å^3, *T* = 150 K, space group $P2_12_12_1$, *Z* = 4, μ(Mo–K_α) 0.092 mm^{-1}, 8918 reflections measured, 1887 unique (R_{int} = 0.031), *R* = 0.0289. The final *wR* was 0.0319 (all data).

1,5-Anhydro-4,6-*O*-benzylidene-2-deoxy-3-*O*-(heptadec-1-en-2-yl)-D-*ribo*-hex-1-enitol 21c

General method B: Tebbe reagent (4.2 ml, 2.12 mmol), ester **18c** (250 mg, 0.53 mmol) in tetrahydrofuran (10 ml) and pyridine (2.5 ml), gave the enol ether **21c** (234 mg, 94%) as a white crystalline solid; mp 61 °C; $[\alpha]_D^{25}$ +158 (*c*, 1 in diethyl ether); ν_{max} (thin film): 1646, 1625 (w, 2 × C=C); δ_H (400 MHz, C_6D_6) 0.91 (3H, t, *J* 6.7 Hz, $(CH_2)_{14}CH_3$), 1.24–1.30 (24H, m, $(CH_2)_2$-$(CH_2)_{12}CH_3$), 1.58–1.65 (2H, m, $CH_2CH_2(CH_2)_{12}CH_3$), 2.13–2.21 (2H, m, $CH_2(CH_2)_{13}CH_3$), 3.49 (1H, at, *J* 10.4 Hz, H-6), 3.52 (1H, dd, $J_{3,4}$ 3.8 Hz, $J_{4,5}$ 10.1 Hz, H-4), 4.00 (1H, d, J_{gem} 1.4 Hz, C=C*H*H′), 4.06 (1H, d, C=CH*H*′), 4.24 (1H, dd, $J_{5,6'}$ 5.4 Hz, $J_{6,6'}$ 10.4 Hz, H-6′), 4.39 (1H, ddd, $J_{5,6}$ 10.4 Hz, H-5), 4.42 (1H, dd, $J_{2,3}$ 5.8 Hz, H-3), 4.91 (1H, at, *J* 5.9 Hz, H-2), 5.28 (1H, s, CHPh), 6.12 (1H, d, $J_{1,2}$ 6.1 Hz, H-1), 7.10–7.15 (1H, m, Ar–H), 7.18–7.22 (2H, m, Ar–H), 7.61–7.63 (2H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 14.7 (q, $(CH_2)_{14}CH_3$), 23.4, 28.1, 29.7, 30.1, 30.2, 30.3, 30.4, 30.4, 30.5, 32.6 (10 × t, $CH_2(CH_2)_{13}CH_3$), 36.2 (t, $CH_2(CH_2)_{13}CH_3$), 65.3, 65.4 (2 × d, C-3 and C-5), 69.2 (t, C-6), 77.7 (d, C-4), 82.2 (t, C=*C*H_2), 99.5 (d, C-2), 102.2 (d, CHPh), 127.1, 128.5 (2 × d, C_{ortho} and *meta* Ar), 129.3 (d, C_{para} Ar), 138.6 (s, C_{ipso} Ar), 146.4 (d, C-1), 163.0 (s, *C*=CH_2); *m*/*z* (FI^+) 470 (M^+, 100%). (HRMS calcd. for $C_{30}H_{46}O_4$ (M^+) 470.3396. Found: 470.3387) (Found: C, 76.54; H, 9.88. $C_{30}H_{46}O_4$ requires: C, 76.55; H, 9.85%).

1,5-Anhydro-4,6-*O*-benzylidene-2-deoxy-2-methyl-3-*O*-(1-phenylethenyl)-D-*ribo*-hex-1-enitol 22

General method B: Tebbe reagent (3.4 ml, 1.70 mmol), the ester **19** (150 mg, 0.43 mmol) in tetrahydrofuran (6 ml) and pyridine (1.5 ml), gave the enol ether **22** (144 mg, 96%) as a colourless oil; $[\alpha]_D^{25}$ +181 (*c*, 1 in $CHCl_3$); ν_{max} (KBr disc): 1663, 1643 (w, 2 × C=C) cm^{-1}; δ_H (500 MHz, C_6D_6) 1.52 (3H, s, CH_3), 3.52–3.58 (2H, m, H-4 and H-6), 4.24–4.31 (2H, m, H-5 and H-6′), 4.50 (1H, d, $J_{3,4}$ 3.7 Hz, H-3), 4.59 (1H, d, J_{gem} 2.6 Hz, C=C*H*H′), 4.81 (1H, d, C=CH*H*′), 5.33 (1H, s, CHPh), 6.04 (1H, s, H-1), 7.03–7.15 (6H, m, Ar–H), 7.55–7.57 (2H, m, Ar–H), 7.77–7.79 (2H, m, Ar–H); δ_C (125.7 MHz, C_6D_6) 16.5 (q, CH_3), 64.7 (d, C-5), 69.3 (t, C-6), 72.0 (d, C-3), 78.5 (d, C-4), 86.1 (t, C=*C*H_2), 102.1 (d, CHPh), 108.2 (s, C-2), 126.6, 127.0, 128.5, 128.6 (4 × d, C_{ortho} and *meta* Ar), 128.9, 129.3 (2 × d, C_{para} Ar), 137.8, 138.5 (2 × s, C_{ipso} Ar), 141.5 (d, C-1), 162.4 (s, *C*=CH_2); *m*/*z* (FI^+) 350 (M^+, 100%). (HRMS calcd. for $C_{22}H_{22}O_4$ (M^+) 350.1518. Found: 350.1511) (Found: C, 75.42; H, 6.32. $C_{22}H_{22}O_4$ requires: C, 75.41: H, 6.33%).

1-(1′,5′-Anhydro-4′,6′-*O*-benzylidene-2′,3′-dideoxy-α-D-*erythro*-hex-2′-enopyranosyl)acetophenone 23a

General method D: Enol ether **21a** (40 mg, 0.12 mmol) in anhydrous xylene (1 ml), gave α-*C*-glycoside **23a** (38.4 mg, 96%) as a white crystalline solid; mp 130–131 °C (petrol–diethyl ether); $[\alpha]_D^{25}$ +32.5 (*c*, 1 in $CHCl_3$); ν_{max} (KBr disc): 1679 (s, C=O) cm^{-1}; δ_H (400 MHz, C_6D_6) 2.52 (1H, dd, $J_{1',C(O)CHH'}$ 6.0 Hz, J_{gem} 16.3 Hz, C(O)C*H*H′), 3.07 (1H, dd, $J_{1',C(O)CHH'}$ 7.6 Hz, C(O)CH*H*′), 3.51 (1H, at, *J* 10.1 Hz, H-6′), 3.60 (1H, ddd, $J_{4',5'}$ 8.0 Hz, $J_{5',6'}$ 10.2 Hz, $J_{5',6''}$ 4.3 Hz, H-5′), 3.90–3.93 (1H, m, H-4′), 4.07 (1H, dd, $J_{6',6''}$ 10.0 Hz, H-6″), 4.99–5.04 (1H, m, H-1′), 5.33 (1H, s, C*H*Ph), 5.53 (1H, dat, $J_{2',3'}$ 10.4 Hz, *J* 2.5 Hz, H-2′), 5.94 (1H, br d, *J* 10.4 Hz, H-3′), 7.00–7.04 (2H, m, Ar–H), 7.09–7.20 (4H, m, Ar–H), 7.63–7.65 (2H, m, Ar–H), 7.71–7.73 (2H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 42.2 (t, CH_2COPh), 66.6 (d, C-5′), 70.0 (t, C-6′), 71.3 (d, C-1′), 75.7 (d, C-4′), 102.2 (d, *C*HPh), 127.1, 127.8 (d, C-3′), 128.5, 128.7, 128.9 (4 × d, C_{ortho} and *meta* Ar), 129.2 (d, C_{para} Ar), 130.7 (d, C-2′) 133.3 (d, C_{para} Ar), 137.8, 138.9 (2 × s, C_{ipso} Ar), 196.7 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 5.01 (H-1′), enhancements: 2.52 (C(O)C*H*H′, 1.8%), 3.07 (C(O)CH*H*′, 1.4%), 3.60 (H-5′, 0.5%), 3.92 (H-4′, 0.9%), 5.53 (H-2′, 4.8%). Irradiate δ 3.60 (H-5′), enhancements: 2.52 (C(O)C*H*H′, 2.6%), 3.07 (C(O)CH*H*′, 4.9%), 3.92 (H-4′, 1.2%), 4.07 (H-6″, 4.8%), 5.01 (H-1′, 0.6%), 5.33 (C*H*Ph, 0.8%), 5.53 (H-2′, 0.3%), 5.94 (H-3′, 0.7%); *m*/*z* (FI^+) 336 (M^+, 100%). (HRMS calcd. for $C_{21}H_{20}O_4$ (M^+) 336.1362. Found: 336.1358) (Found: C, 74.69; H, 5.89. $C_{21}H_{20}O_4$ requires: C, 74.98: H, 5.99%).

Data for diene 24

A white crystalline solid; mp 146–147 °C (diethyl ether); $[\alpha]_D^{25}$ −32 (*c*, 0.5 in $CHCl_3$); ν_{max} (KBr disc): 3410 (br, OH), 1659 (C=C), 1628, 1590 (2 × C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.51 (1H, br s, OH), 3.67–3.74 (2H, m, H-7 and H-8), 4.26–4.30 (1H, m, H-6), 4.32–4.39 (1H, m, H-8′), 5.59 (1H, s, CHPh), 6.45 (1H, dd, $J_{4,5}$ 15.3 Hz, $J_{5,6}$ 5.5 Hz, H-5), 6.71 (1H, dd, $J_{3,4}$ 11.2 Hz, H-4), 7.04 (1H, d, $J_{2,3}$ 15.1 Hz, H-2), 7.33–7.60 (4H, m, H-3 and Ar–H), 7.89–7.95 (2H, m, Ar–H); δ_C (100.6 MHz, $CDCl_3$) 65.6 (d, C-7), 71.1 (t, C-8), 81.6 (d, C-6), 101.0 (d, CHPh), 126.4 (d, C-2), 126.2, 128.3, 128.4, 128.6 (4 × d, C_{ortho} and *meta* Ar), 129.1 (d, C_{para} Ar), 130.6 (d, C-4) 132.9 (d, C_{para} Ar), 137.4, 137.8 (2 × s, C_{ipso} Ar), 139.2 (d, C-5), 143.6 (d, C-3), 190.8 (s, C-1); *m*/*z* (FI^+) 336 (M^+, 100%). (HRMS calcd. for $C_{21}H_{20}O_4$ (M^+) 336.1362. Found: 336.1369) (Found: C, 74.97; H, 5.75. $C_{21}H_{20}O_4$ requires: C, 74.98: H, 5.99%).

1-(1′,5′-Anhydro-4′,6′-*O*-benzylidene-2′,3′-dideoxy-α-D-*erythro*-hex-2′-enopyranosyl)propan-2-one 23b

General method D: Enol ether **21b** (40 mg, 0.15 mmol), in anhydrous xylene (1 ml), gave α-*C*-glycoside **23b** (39.4 mg, 99%) as a white crystalline solid; mp 91–92 °C (petrol); $[\alpha]_D^{26}$ +58 (*c*, 1 in $CHCl_3$); ν_{max} (KBr disc) 1704 (s, C=O) cm^{-1}; δ_H (400 MHz, C_6D_6) 1.60 (3H, s, CH_3), 1.86 (1H, dd, $J_{1',C(O)CHH'}$ 5.6 Hz, J_{gem} 16.3 Hz, C(O)C*H*H′), 2.30 (1H, dd, $J_{1',C(O)CHH'}$ 8.2 Hz, C(O)CH*H*′), 3.46 (1H, ddd, $J_{4',5'}$ 7.8 Hz, $J_{5',6'}$ 10.2 Hz, $J_{5',6''}$ 4.1 Hz, H-5′), 3.53 (1H, at, *J* 10.0 Hz, H-6′), 3.87–3.90 (1H, m, H-4′), 4.14 (1H, dd, $J_{6',6''}$ 9.8 Hz, H-6″), 4.65–4.70 (1H, m, H-1′), 5.33 (1H, s, C*H*Ph), 5.35 (1H, dat, $J_{2',3'}$ 10.4 Hz, *J* 2.6 Hz, H-2′), 5.90 (1H, br d, *J* 10.4 Hz, H-3′), 7.10–7.21 (3H, m, Ar–H), 7.63–7.66 (2H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 30.4 (q, CH_3), 46.8 (t, CH_2COCH_3), 66.3 (d, C-5′), 70.0 (t, C-6′), 70.8 (d, C-1′), 75.6 (d, C-4′), 102.3 (d, *C*HPh), 127.1 (2 × d, C_{ortho} and $_{meta}$ Ar), 127.7 (d, C-3′), 128.5 (2 × d, C_{ortho} and $_{meta}$ Ar), 129.3 (d, C_{para} Ar), 130.4 (d, C-2′), 138.9 (s, C_{ipso} Ar), 204.7 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 4.68 (H-1′), enhancements: 1.86 (C(O)C*H*H′, 1.4%), 2.30 (C(O)CH*H*′, 0.8%), 5.35 (H-2′, 3.1%). Irradiate δ 3.46 (H-5′), enhancements: 1.86 (C(O)C*H*H′, 0.4%), 2.30 (C(O)CH*H*′, 1.2%), 4.14 (H-6″, 1.0%). Irradiate δ 2.30 (C(O)CH*H*′), enhancements: 1.60 (CH_3, 2.0%), 1.86 (C(O)C*H*H′, 21.1%), 3.46 (H-5′, 7.7%), 4.68 (H-1′, 1.9%). Irradiate δ 1.86 (C(O)C*H*H′), enhancements: 2.30 (C(O)CH*H*′, 20.3%), 3.46 (H-5′, 2.0%), 4.68 (H-1′, 2.8%), 5.35 (H-2′, 1.6%); *m*/*z* (FI^+) 274 (M^+, 100%). (HRMS calcd. for $C_{16}H_{18}O_4$ (M) 274.1205. Found: 274.1205) (Found: C, 69.93; H, 6.60. $C_{16}H_{18}O_4$ requires: C, 70.06: H, 6.61%).

1-(1′,5′-Anhydro-4′,6′-*O*-benzylidene-2′,3′-dideoxy-2′-methyl-α-D-*erythro*-hex-2′-enopyranosyl)acetophenone 25

General method D: Enol ether **22** (40 mg, 0.11 mmol) in anhydrous xylene (1 ml), gave α-*C*-glycoside **25** (39 mg, 98%) as a white crystalline solid; mp 117–118 °C (petrol–diethyl ether); $[\alpha]_D^{25}$ +43.8 (*c*, 0.5 in $CHCl_3$); ν_{max} (KBr disc): 1676 (s, C=O), 1598 (w, C=C) cm^{-1}; δ_H (400 MHz, C_6D_6) 1.39 (3H, s, CH_3), 2.58 (1H, dd, $J_{1',C(O)CHH'}$ 3.5 Hz, J_{gem} 15.7 Hz, C(O)C*H*H′), 3.25 (1H, dd, $J_{1',C(O)CHH'}$ 9.4 Hz, C(O)CH*H*′), 3.58 (1H, at, *J* 10.2 Hz, H-6′), 3.76 (1H, ddd, $J_{4',5'}$ 8.2 Hz, $J_{5',6'}$ 10.1 Hz, $J_{5',6''}$ 4.1 Hz, H-5′), 4.05–4.09 (1H, m, H-4′ and H-6″), 5.01–5.03 (1H, m, H-1′), 5.45 (1H, s, CHPh), 5.79 (1H, br s, H-3′), 7.12–7.16 (2H, m, Ar–H), 7.20–7.32 (4H, m, Ar–H), 7.77–7.78 (2H, m, Ar–H), 7.88–7.90 (2H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 19.3 (q, CH_3), 40.2 (t, CH_2COPh), 66.6 (d, C-5′), 69.8 (t, C-6′), 74.8 (d, C-1′), 76.2 (d, C-4′), 102.0 (d, CHPh), 123.5 (d, C-3′), 127.0, 128.5, 128.7, 128.9 (4 × d, C_{ortho} and $_{meta}$ Ar), 129.1, 133.1 (2 × d, C_{para} Ar), 137.6 (d, C-2′), 138.0, 139.0 (2 × s, C_{ipso} Ar), 197.1 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 5.02 (H-1′), enhancements: 1.39 (CH_3, 3.5%), 2.58 (C(O)CHH′, 3.1%), 3.76 (H-5′, 0.8%), 4.07 (H-4′ and H-6″, 0.9%), 5.79 (H-3′, 0.5%). Irradiate δ 3.76 (H-5′), enhancements: 3.25 (C(O)CHH′, 8.1%), 4.07 (H-4′ and H-6″, 5.1%), 5.02 (H-1′, 0.4%), 5.45 (CHPh, 0.2%), 5.79 (H-3′, 0.4%). Irradiate δ 3.25 (C(O)CH*H*′), enhancements: 2.58 (C(O)C*H*H′, 26.0%), 3.76 (H-5′, 13.8%), 5.02 (H-1′, 1.1%). Irradiate δ 2.58 (C(O)C*H*H′), enhancements: 1.39 (CH_3, 4.1%), 3.25 (C(O)CH*H*′, 23.7%), 5.02 (H-1′, 6.5%); *m*/*z* (FI^+) 350 (M^+, 100%). (HRMS calcd. for $C_{22}H_{22}O_4$ (M^+) 350.1518. Found: 350.1512) (Found: C, 75.25; H, 6.47. $C_{22}H_{22}O_4$ requires: C, 75.41: H, 6.33%).

1-(1′,5′-Anhydro-4′,6′-*O*-benzylidene-2′,3′-dideoxy-α-D-*erythro*-hex-2′-enopyranosyl)heptadecan-2-one 23c and 3-(1′,5′-anhydro-4′,6′-*O*-benzylidene-2′,3′-dideoxy-α-D-*erythro*-hex-2′-enopyranosyl)heptadecan-2-one 26

Enol ether **21c** (40 mg, 0.08 mmol) was heated in anhydrous xylene (1 ml), or benzene (1 ml), for 10 h, when TLC (petrol : diethyl ether, 4 : 1 +1% triethylamine) indicated the complete consumption of starting material (R_f 0.7) and the formation of a mixture of products (R_f 0.28 and 0.34). The reaction mixture was then concentrated *in vacuo* and the residue purified by flash column chromatography (petrol : diethyl ether, 4 : 1) to obtain two compounds (total yield 34 mg, 85%; ratio **23c** : **26** = 1.3 : 1); α-*C*-glycoside **23c** as a white crystalline solid; mp 88–89 °C (petrol); $[\alpha]_D^{25}$ +21 (*c*, 0.5 in $CHCl_3$); ν_{max} (KBr disc): 1709 (s, C=O) cm^{-1}; δ_H (400 MHz, C_6D_6) 1.02 (3H, t, *J* 6.8 Hz, C(O)-$(CH_2)_{14}CH_3$), 1.30–1.52 (24H, m, $C(O)CH_2CH_2(CH_2)_{12}CH_3$), 1.63 (2H, m, *J* 7.3 Hz, $C(O)CH_2CH_2(CH_2)_{12}CH_3$), 2.07 (1H, dd, $J_{1',CHH'C(O)}$ 5.7 Hz, J_{gem} 16.2 Hz, C*H*H′C(O)$(CH_2)_{14}CH_3$), 2.10 (2H, t, *J* 7.4 Hz, $CH_2C(O)CH_2(CH_2)_{13}CH_3$), 2.54 (1H, dd, $J_{1',CHH'C(O)}$ 8.3 Hz, CHH′C(O)$(CH_2)_{14}CH_3$), 3.62–3.70 (2H, m, H-5′ and H-6′), 4.01–4.04 (1H, m, H-4′), 4.26–4.34 (1H, m, H-6″), 4.89–4.94 (1H, m, H-1′), 5.46 (1H, s, CHPh), 5.52 (1H, dat, $J_{2',3'}$ 10.4 Hz, *J* 2.6 Hz, H-2′), 6.04 (1H, br d, *J* 10.4 Hz, H-3′), 7.21–7.32 (3H, m, Ar–H), 7.76–7.78 (2H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 14.5 (q, C(O)$(CH_2)_{14}CH_3$), 23.3, 24.0, 29.7, 30.0, 30.1, 30.1, 30.3, 30.4, 30.4, 30.4, 32.5 (11 × t, C(O)-$CH_2(CH_2)_{13}CH_3$), 43.8 (t, $C(O)CH_2(CH_2)_{13}CH_3$), 46.0 (t, CH_2C-(O)$(CH_2)_{14}CH_3$), 66.3 (d, C-5′), 70.0 (t, C-6′), 70.9 (d, C-1′), 75.5 (d, C-4′), 102.2 (d, *C*HPh), 127.0 (C_{ortho} and $_{meta}$ Ar), 127.6 (d, C-3′), 128.5 (C_{ortho} and $_{meta}$ Ar), 129.2 (d, C_{para} Ar), 130.5 (d, C-2′), 138.8 (s, C_{ipso} Ar), 206.5 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 4.92 (H-1′), enhancements: 2.07 (C(O)C*H*H′, 1.3%), 2.54 (C(O)CH*H*′, 0.4%), 5.52 (H-2′, 5.2%). Irradiate δ 4.02 (H-4′), enhancements: 3.66 (H-5′ and H-6′, 5.1%), 4.92 (H-1′, 1.3%), 5.46 (C*H*Ph, 15.9%), 6.04 (H-3′, 4.1%). Irradiate δ 2.54 (CH*H*′C(O)$(CH_2)_{14}CH_3$), enhancements: 2.08 ($CH_2C(O)CH_2(CH_2)_{13}CH_3$ and C(O)C*H*H′, 26.6%), 3.66 (H-5′ and H-6′, 6.5%), 4.92 (H-1′, 2.1%); *m*/*z* (FI^+) 470 (M^+, 100%). (HRMS calcd. for $C_{30}H_{46}O_4$ (M^+) 470.3396. Found: 470.3416).

Together with methyl ketone **26** as a white foam; $[\alpha]_D^{25}$ +5.8 (*c*, 0.5 in $CHCl_3$); ν_{max} (thin film): 1697 (s, C=O) cm^{-1}; δ_H (400 MHz, C_6D_6) 0.91 (3H, t, *J* 6.7 Hz, $(CH_2)_{13}CH_3$), 1.06–1.31 (24H, m, $CHCH_2(CH_2)_{12}CH_3$), 1.56–1.64 (1H, m, C*H*H′-$(CH_2)_{12}CH_3$), 1.68–1.75 (1H, m, CH*H*′$(CH_2)_{12}CH_3$), 1.78 (3H, s, CHC(O)CH_3), 2.57 (1H, m, C*H*C(O)CH_3), 3.52–3.59 (2H, m, H-5′ and H-6′), 3.88–3.90 (1H, m, H-4′), 4.18–4.24 (1H, m, H-6″), 4.45–4.49 (1H, m, H-1′), 5.34 (1H, s, C*H*Ph), 5.50 (1H, dat, $J_{2',3'}$ 10.5 Hz, *J* 2.5 Hz, H-2′), 5.93 (1H, br d, *J* 10.4 Hz, H-3′), 7.10–7.21 (3H, m, Ar–H), 7.64–7.66 (2H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 14.7 (q, $(CH_2)_{13}CH_3$), 23.4, 27.4, 30.0, 30.1, 30.3, 30.4, 30.5, 30.5, 30.7, 30.7 (10 × t, $CH_2(CH_2)_{12}CH_3$), 31.2 (q, CHC(O)CH_3), 32.6 (t, C(H)$CH_2(CH_2)_{12}CH_3$), 56.0 (d, *C*HC(O)CH_3), 66.8 (d, C-5′), 70.0 (t, C-6′), 74.7 (d, C-1′), 75.8 (d, C-4′), 102.4 (d, *C*HPh), 127.1 (C_{ortho} and $_{meta}$ Ar), 128.1 (d, C-3′), 128.6 (C_{ortho} and $_{meta}$ Ar), 129.3 (d, C_{para} Ar), 129.3 (d, C-2′), 138.8 (s, C_{ipso} Ar), 208.9 (s, C=O); NOE experiment (500 MHz, $CDCl_3$): Irradiate δ 4.47 (H-1′), enhancements: 2.57 (C*H*C(O)CH_3, 1.2%), 5.50 (H-2′, 6.5%). Irradiate δ 3.89 (H-4′), enhancements: 3.55 (H-5′ and H-6′, 5.4%), 4.47 (H-1′, 1.0%), 5.34 (C*H*Ph, 15.4%), 5.93 (H-3′, 5.0%). Irradiate δ 2.57 (C*H*C(O)CH_3), enhancements: 3.55 (H-5′ and H-6′, 6.7%), 4.47 (H-1′, 1.8%); *m*/*z* (FI^+) 470 (M^+, 100%). (HRMS calcd. for $C_{30}H_{46}O_4$ (M^+) 470.3396. Found: 470.3386) (Found: C, 76.43; H, 9.85. $C_{30}H_{46}O_4$ requires: C, 76.55: H, 9.85%).

1-(1′,5′-Anhydro-4′,6′-*O*-di(*tert*-butyl)silanediyl-2′,3′-dideoxy-α-D-*erythro*-hex-2′-enopyranosyl)heptadecan-2-one 27

General method D: Enol ether **20** (40 mg, 0.08 mmol) in anhydrous xylene (1 ml), after 4 h, gave α-*C*-glycoside **27** (39.2 mg, 98%) as a white foam; $[\alpha]_D^{25}$ +8 (*c*, 1.0 in $CHCl_3$); ν_{max} (thin film) 1717 (s, C=O) cm^{-1}; δ_H (400 MHz, C_6D_6) 0.91 (3H, t, *J* 6.7 Hz, C(O)$(CH_2)_{14}CH_3$), 1.09, 1.13 (18H, 2 × s, 2 × $C(CH_3)_3$), 1.20–1.33 (24H, m, $C(O)CH_2CH_2(CH_2)_{12}CH_3$), 1.50 (2H, m, $C(O)CH_2CH_2(CH_2)_{12}CH_3$), 1.98 (2H, t, *J* 7.3 Hz, C(O)CH_2-

$(CH_2)_{13}CH_3$), 2.07 (1H, dd, $J_{1',\ CHH'C(O)}$ 5.9 Hz, J_{gem} 15.9 Hz, C*H*H′C(O)$(CH_2)_{14}CH_3$), 2.50 (1H, dd, $J_{1',\ CHH'C(O)}$ 8.0 Hz, CH*H*′C(O)$(CH_2)_{14}CH_3$), 3.62 (1H, ddd, $J_{4',5'}$ 8.5 Hz, $J_{5',6'}$ 10.2 Hz, $J_{5',6''}$ 4.9 Hz, H-5′), 3.97 (1H, at, *J* 10.2 Hz, H-6′), 4.27 (1H, dd, $J_{6',6''}$ 10.0 Hz, H-6″), 4.44 (1H, dd, $J_{3',4'}$ 1.6 Hz, H-4′), 4.74–4.78 (1H, m, H-1′), 5.45 (1H, dat, $J_{2,'3'}$ 10.4 Hz, *J* 2.4 Hz, H-2′), 5.92 (1H, br d, *J* 10.4 Hz, H-3′); δ_C (100.6 MHz, C_6D_6) 14.7 (q, C(O)$(CH_2)_{14}CH_3$), 20.5, 23.2 (2 × s, 2 × *C*$(CH_3)_3$), 27.6, 28.0 (2 × q, 2 × C(*C*$H_3)_3$), 23.4, 24.1, 29.8, 30.1, 30.2, 30.2, 30.4, 30.4, 30.5, 30.5, 30.5, 32.6 (12 × t, C(O)CH_2(*C*$H_2)_{13}CH_3$), 43.6 (t, C(O)*C*$H_2(CH_2)_{13}CH_3$), 46.3 (t, *C*H_2C(O)$(CH_2)_{14}CH_3$), 68.1 (t, C-6′), 70.0 (d, C-5′), 70.6 (d, C-1′), 71.1 (d, C-4′), 129.2 (d, C-2′), 130.9 (d, C-3′), 206.6 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 4.76 (H-1′), enhancements: 1.98 (CH_2C(O)-*C*$H_2(CH_2)_{13}CH_3$, 1.3%), 2.07 (C*H*H′C(O)$(CH_2)_{14}CH_3$, 2.1%), 2.50 (CH*H*′C(O)$(CH_2)_{14}CH_3$, 1.6%), 3.62 (H-5′, 0.7%), 3.97 (H-6′, 0.3%), 4.44 (H-4′, 0.6%), 5.45 (H-2′, 5.9%). Irradiate δ 3.62 (H-5′), enhancements: 1.98 (CH_2C(O)*C*$H_2(CH_2)_{13}CH_3$, 0.5%), 2.07 (C*H*H′C(O)$(CH_2)_{14}CH_3$, 2.3%), 2.50 (CH*H*′C(O)$(CH_2)_{14}$-CH_3, 4.4%), 4.27 (H-6″, 4.2%), 4.44 (H-4′, 2.2%), 4.76 (H-1′, 0.9%), 5.45 (H-2′, 0.5%), 5.92 (H-3′, 1.1%). Irradiate δ 2.50 (CH*H*′C(O)$(CH_2)_{14}CH_3$), enhancements: 1.98 (CH_2C(O)C*H*$_2$-$(CH_2)_{13}CH_3$, 2.7%), 2.07 (C*H*H′C(O)$(CH_2)_{14}CH_3$, 23.1%), 3.62 (H-5′, 6.4%), 4.76 (H-1′, 2.9%), 5.45 (H-2′, 0.3%), 5.92 (H-3′, 0.3%). Irradiate δ 2.07 (C*H*H′C(O)$(CH_2)_{14}CH_3$), enhancements: 2.50 (CH*H*′C(O)$(CH_2)_{14}CH_3$, 22.6%), 3.62 (H-5′, 3.3%), 4.76 (H-1′, 4.6%), 5.45 (H-2′, 4.0%); *m*/*z* (FI^+) 522 (M^+, 100%). (HRMS calcd. for $C_{31}H_{58}O_4Si$ (M^+) 522.4104. Found: 522.4107) (Found: C, 71.32; H, 11.16. $C_{31}H_{58}O_4Si$ requires: C, 71.21: H, 11.18%).

3-(1′,5′-anhydro-4′,6′-*O*-di(*tert*-butyl)silanediyl-2′,3′-dideoxy-α-D-*erythro*-hex-2′-enopyranosyl)heptadecan-2-one 28

General method D: Enol ether **20** (40 mg, 0.08 mmol), in deuterated benzene (1 ml), after 7 h at 195 °C, gave a mixture of two products (R_f 0.51 and 0.46, 37.5 mg, 94%; **27** : **28** = 1.4 : 1); α-*C*-glycoside **27** as a white foam identical to the compound previously above, and methyl ketone **28** as a colourless oil; $[\alpha]_D^{25}$ −11 (*c*, 1.0 in $CHCl_3$); ν_{max} (thin film): 1713 (s, C=O) cm^{-1}; δ_H (400 MHz, C_6D_6) 1.03 (3H, t, *J* 6.8 Hz, $(CH_2)_{13}CH_3$), 1.20, 1.24 (18H, 2 × s, 2 × C$(CH_3)_3$), 1.26–1.43 (24H, m, $CHCH_2(CH_2)_{12}CH_3$), 1.71–1.79 (1H, m, C*H*H′$(CH_2)_{12}CH_3$), 1.84 (3H, s, CHC(O)CH_3), 1.83–1.98 (1H, m, CH*H*′$(CH_2)_{12}CH_3$), 2.84 (1H, ddd, *J* 3.8 and 8.8 Hz, C*H*C(O)CH_3), 3.75 (1H, ddd, $J_{4',5'}$ 8.2 Hz, $J_{5',6'}$ 10.2 Hz, $J_{5',6''}$ 4.9 Hz, H-5′), 4.09 (1H, at, *J* 10.2 Hz, H-6′), 4.42 (1H, dd, $J_{6',6''}$ 10.0 Hz, H-6″), 4.54–4.58 (2H, m, H-1′ and H-4′), 5.63 (1H, dat, $J_{2',3'}$ 10.5 Hz, *J* 2.0 Hz, H-2′), 6.05 (1H, br d, *J* 10.4 Hz, H-3′); δ_C (100.6 MHz, C_6D_6) 14.5 (q, $(CH_2)_{13}CH_3$), 20.4, 23.0 (2 × s, 2 × *C*$(CH_3)_3$), 27.5, 27.9 (2 × q, 2 × C(*C*$H_3)_3$), 23.3, 27.4, 29.7, 29.9, 30.0, 30.2, 30.3, 30.3 (8 × t, $CH_2(CH_2)_{12}CH_3$), 30.8 (q, CHC(O)*C*H_3), 32.5 (t, C(H)*C*$H_2(CH_2)_{12}CH_3$), 56.3 (d, *C*HC(O)-CH_3), 68.0 (t, C-6′), 70.4 (d, C-5′), 71.1 (d, C-4′), 74.2 (d, C-1′), 127.8 (d, C-2′), 131.3 (d, C-3′), 208.4 (s, C=O); NOE experiment (500 MHz, $CDCl_3$): Irradiate δ 4.40 (H-4′), enhancements: 2.25 (CHC(O)CH_3, 2.0%), 2.89 (C*H*C(O)CH_3, 0.9%), 3.45 (H-5′, 2.0%), 3.89 (H-6′, 3.9%), 5.97 (H-3′, 5.3%). Irradiate δ 4.35 (H-1′), enhancements: 2.25 (CHC(O)CH_3, 0.6%), 2.89 (C*H*C(O)-CH_3, 2.0%), 5.63 (H-2′, 8.4%). Irradiate δ 3.45 (H-5′), enhancements: 2.25 (CHC(O)CH_3, 0.7%), 2.89 (C*H*C(O)CH_3, 9.0%), 4.17 (H-6″, 4.8%), 4.40 (H-4′, 3.6%). Irradiate δ 2.89 (C*H*C(O)CH_3), enhancements: 2.25 (CHC(O)CH_3, 4.7%), 3.45 (H-5′, 10.6%), 5.63 (H-2′, 2.4%); *m*/*z* (FI^+) 522 (M^+, 100%). (HRMS calcd. for $C_{31}H_{58}O_4Si$ (M^+) 522.4104. Found: 522.4113).

6-*O*-(1′,5′-Anhydro-2′-deoxy-4′,6′-*O*-di(*tert*-butyl)silanediyl-D-*arabino*-hex-1′-en-3′-yl)-l,2:3,4-di-*O*-isopropylidene-α-D-galacturonic ester 30

General method A: Glycal **5** (500 mg, 1.74 mmol), galacturonic acid **29** (957 mg, 3.49 mmol), dicyclohexylcarbodiimide (720 mg, 3.49 mmol) and 4-dimethylaminopyridine (43 mg, 0.35 mmol), in anhydrous dichloromethane (15 ml), gave ester **30** (947 mg, 91%) as a colourless oil; $[\alpha]_D^{23}$ −133 (*c*, 1 in $CHCl_3$); ν_{max} (thin film) 1730 (s, C=O), 1648 (w, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.99, 1.04 (18H, 2 × s, 2 × C$(CH_3)_3$), 1.33, 1.35, 1.45, 1.53 (12 H, 4 × s, 2 × C$(CH_3)_2$), 3.92 (1H, ddd, $J_{4',5'}$ 9.9 Hz, $J_{5',6'}$ 10.3 Hz, $J_{5',6''}$ 4.6 Hz, H-5′), 3.98 (1H, at, *J* 10.0 Hz, H-6′), 4.19 (1H, dd, $J_{6',6''}$ 9.7 Hz, H-6″), 4.21 (1H, dd, $J_{3',4'}$ 8.0 Hz, H-4′), 4.39 (1H, dd, $J_{1,2}$ 5.0 Hz, $J_{2,3}$ 2.7 Hz, H-2), 4.48 (1H, d, $J_{4,5}$ 2.2 Hz, H-5), 4.58 (1H, dd, $J_{3,4}$ 7.7 Hz, H-4), 4.67 (1H, dd, H-3), 4.77 (1H, dd, $J_{1',2'}$ 6.0 Hz, $J_{2',3'}$ 2.1 Hz, H-2′), 5.53 (1H, dat, *J* 1.7 and 7.6 Hz, H-3′), 5.68 (1H, d, H-1), 6.32 (1H, dd, H-1′); δ_C (100.6 MHz, $CDCl_3$) 19.8, 22.6 (2 × s, 2 × *C*$(CH_3)_3$), 24.8, 24.9, 25.8, 26.0 (4 × q, 2 × C(*C*$H_3)_2$), 26.8, 27.3 (2 × q, 2 × C(*C*$H_3)_3$), 65.7 (t, C-6′), 68.5 (d, C-5), 70.2 (d, C-2), 70.7 (d, C-3), 72.1 (d, C-4), 72.8 (d, C-5′), 73.0 (d, C-3′), 73.4 (d, C-4′), 96.5 (d, C-1), 100.3 (d, C-2′), 109.0, 110.1 (2 × s, 2 × *C*$(CH_3)_2$), 144.9 (d, C-1′), 167.8 (s, C=O); *m*/*z* (FI^+) 542 (M^+, 100%). (HRMS calcd. for $C_{26}H_{42}O_{10}Si$ (M^+) 542.2547. Found 542.2568) (Found: C, 57.68; H, 7.73. $C_{26}H_{42}O_{10}Si$ requires C, 57.54; H, 7.80%).

6-*O*-(1′,5′-Anhydro-2′-deoxy-4′,6′-*O*-di(*tert*-butyl)silanediyl-D-*arabino*-hex-1′-en-3′-yl)-7-deoxy-l,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hept-6-enopyranose 31

General method B: Tebbe reagent (1.48 ml, 0.74 mmol), ester **30** (50 mg, 0.09 mmol) in tetrahydrofuran (2 ml) and pyridine (0.5 ml), after 48 h, gave enol ether **31** (27 mg, 54%, 72% yield over recovered starting material) as a colourless oil; $[\alpha]_D^{24}$ −105 (*c*, 1 in $CHCl_3$); ν_{max} (thin film): 1646 (m, C=C) cm^{-1}; δ_H (400 MHz, C_6D_6) 0.98, 1.02 (18H, 2 × s, 2 × C$(CH_3)_3$), 1.01, 1.20, 1.32, 1.52 (12H, 4 × s, 2 × C$(CH_3)_2$), 3.79 (1H, ddd, $J_{4',5'}$ 10.3 Hz, $J_{5',6'}$ 10.4 Hz, $J_{5',6''}$ 5.0 Hz, H-5′), 3.93 (1H, at, *J* 10.3 Hz, H-6′), 4.13 (1H, dd, $J_{6',6''}$ 10.3 Hz, H-6″), 4.19 (1H, dd, $J_{1,2}$ 5.0 Hz, $J_{2,3}$ 2.3 Hz, H-2), 4.34 (1H, dd, $J_{3',4'}$ 7.3 Hz, H-4′), 4.55 (1H, d, $J_{4,5}$ 2.0 Hz, H-5), 4.56 (1H, dd, $J_{3,4}$ 7.7 Hz, H-3), 4.60 (1H, dd, H-4), 4.62 (1H, d, J_{gem} 1.0 Hz, C=C*H*H′) 4.78 (1H, dat, *J* 2.0 and 7.3 Hz, H-3′), 4.97 (1H, d, C=CH*H*′) 5.02 (1H, dd, $J_{1',2'}$ 6.1 Hz, $J_{2',3'}$ 1.8 Hz, H-2′), 5.59 (1H, d, H-1), 6.06 (1H, dd, $J_{1',3'}$ 1.4 Hz, H-1′); δ_C (100.6 MHz, C_6D_6) 20.2, 23.1 (2 × s, 2 × *C*$(CH_3)_3$), 25.1, 25.2, 26.2, 26.7 (4 × q, 2 × C(*C*$H_3)_2$), 27.4, 27.8 (2 × q, 2 × C(*C*$H_3)_3$), 66.6 (t, C-6′), 68.3 (d, C-4), 71.6 (d, C-2), 71.8 (d, C-5), 72.3 (d, C-3), 73.5 (d, C-5′), 75.5 (d, C-4′), 76.7 (d, C-3′), 85.4 (t, C=*C*H_2), 97.5 (d, C-1), 101.6 (d, C-2′), 108.9, 109.7 (2 × s, 2 × *C*$(CH_3)_2$), 144.4 (d, C-1′), 158.4 (s, *C*=CH_2); *m*/*z* (CI^+) 541 (MH^+, 42%), (FI^+) 540 (M^+, 100%). (HRMS calcd. for $C_{27}H_{44}O_9Si$ (M^+) 540.2755. Found 540.2747) (Found C, 59.84; H, 8.31. $C_{27}H_{44}O_9Si$ requires C, 59.97; H, 8.20%).

7-(1′,5′-Anhydro-4′,6′-*O*-di(*tert*-butyl)silanediyl-2′,3′-dideoxy-β-D-*erythro*-hex-2′-enopyranosyl)-7-deoxy-l,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-heptanopyranos-6-ulose 32

General method C: Enol ether **31** (25 mg, 0.05 mmol), in tributylamine (0.5 ml), gave β-*C*-glycoside **32** (14 mg, 56%) as a white foam; $[\alpha]_D^{23}$ −46 (*c*, 1 in $CHCl_3$); ν_{max} (thin film): 1722 (m, C=O) cm^{-1}; δ_H (400 MHz, C_6D_6) 0.95, 1.02 (6H, 2 × s, C$(CH_3)_2$), 1.07, 1.07 (18H, 2 × s, 2 × C$(CH_3)_3$), 1.21, 1.37 (6H, 2 × s, C$(CH_3)_2$), 2.81 (1H, dd, $J_{1',CHH'C(O)}$ 6.7 Hz, J_{gem} 18.3 Hz, C*H*H′C(O)), 3.31 (1H, dd, $J_{1',\ CHH'C(O)}$ 6.6 Hz, CH*H*′C(O)), 3.60 (1H, ddd, $J_{4',5'}$ 8.5 Hz, $J_{5',6'}$ 10.5 Hz, $J_{5',6''}$ 5.1 Hz, H-5′), 3.89 (1H, at, *J* 10.2 Hz, H-6′), 4.06 (1H, dd, $J_{1,2}$ 5.0 Hz, $J_{2,3}$ 2.4 Hz, H-2), 4.19 (1H, dd, $J_{6',6''}$ 10.0 Hz, H-6″), 4.35 (1H, dd, $J_{3,4}$ 7.9 Hz, H-3), 4.35 (1H, d, $J_{4,5}$ 2.0 Hz, H-5), 4.46 (1H, dd, H-4), 4.48 (1H, m, *J* 1.9 Hz and 8.4 Hz, H-4′), 4.84–4.89 (1H, m, H-1′), 5.45 (1H, d, H-1) 5.62 (1H, dat, *J* 1.9 Hz, $J_{2',3'}$ 10.4 Hz, H-2′), 5.87 (1H, dat, *J* 1.9 and 10.4 Hz, H-3′); δ_C (100.6 MHz, C_6D_6) 20.5, 23.1 (2 × s, 2 × *C*$(CH_3)_3$), 24.3, 24.9, 26.2, 26.3 (4 × q, 2 × C(*C*$H_3)_2$), 27.7, 28.0 (2 × q, 2 × C(*C*$H_3)_3$), 46.1 (t, *C*HH′C(O)), 67.9 (t, C-6′), 71.1 (d, C-2), 71.1 (d, C-4′), 71.2 (d, C-3), 71.6 (d, C-1′), 73.2 (d, C-4), 74.5 (d, C-5), 75.5 (d, C-5′), 97.1 (d, C-1),

109.0, 109.7 (2 × s, 2 × $C(CH_3)_2$), 130.1 (d, C-2′), 130.3 (d, C-3′), 206.0 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 4.87 (H-1′), enhancements: 2.81 (C*H*H′C(O), 2.7%), 3.31 (CH*H*′C(O), 2.8%), 3.60 (H-5′, 9.6%), 5.62 (H-2′, 5.9%). Irradiate δ 3.60 (H-5′), enhancement 4.19 (H-6″, 4.5%), 4.48 (H-4′, 2.1%), 4.87 (H-1′, 10.8%); *m*/*z* (APCI$^+$) 541 (MH^+, 100%). (HRMS calcd. for $C_{27}H_{45}O_9Si$ (MH^+) 541.2831. Found 541.2832) (Found C, 60.20; H, 8.08. $C_{27}H_{44}O_9Si$ requires C, 59.97; H, 8.20%).

3-*O*-(4-*tert*-Butoxycarbonylaminobutanoyl)-1,5-anhydro-2-deoxy-4,6-*O*-di(*tert*-butyl)silanediyl-D-*arabino*-hex-1-enitol 33

General method A: Glycal **5** (250 mg, 0.87 mmol), 4-*tert*-butoxycarbonylaminobutyric acid (355 mg, 1.75 mmol), dicyclohexylcarbodiimide (360 mg, 1.75 mmol) and 4-dimethylaminopyridine (21 mg, 0.17 mmol), in anhydrous dichloromethane (8 ml), gave ester **33** (388 mg, 94%) as a colourless oil; $[a]_D^{22}$ −64 (*c*, 1 in $CHCl_3$); ν_{max} (thin film) 3374 (br, N–H), 1739, 1717 (s, 2 × C=O), 1648 (m, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.92, 1.00, 1.38 (27H, 3 × s, 3 × $C(CH_3)_3$), 1.76–1.83 (2H, m, $O_2CCH_2CH_2CH_2$-NHBoc), 2.29–2.41 (2H, m, $O_2CCH_2(CH_2)_2NHBoc$), 3.05–3.15 (2H, m, $O_2C(CH_2)_2CH_2NHBoc$), 3.86 (1H, ddd, $J_{4,5}$ 9.8 Hz, $J_{5,6}$ 10.3 Hz, $J_{5,6'}$ 4.6 Hz, H-5), 3.92 (1H, at, *J* 10.0 Hz, H-6), 4.10 (1H, dd, $J_{3,4}$ 7.8 Hz, H-4), 4.13 (1H, dd, $J_{6,6'}$ 9.7 Hz, H-6′), 4.67 (1H, dd, $J_{1,2}$ 6.1 Hz, $J_{2,3}$ 1.8 Hz, H-2), 4.80 (1H, br s, NH), 5.33 (1H, br d, *J* 7.6 Hz, H-3), 6.26 (1H, dd, $J_{1,3}$ 1.4 Hz, H-1); δ_C (100.6 MHz, $CDCl_3$) 19.7, 22.6 (2 × s, 2 × $C(CH_3)_3$), 25.3 (t, O_2CCH_2-CH_2CH_2NHBoc), 26.7, 27.3, 28.3 (3 × q, 3 × $C(CH_3)_3$), 31.7 (t, $O_2CCH_2(CH_2)_2NHBoc$), 39.6 (t, $O_2C(CH_2)_2CH_2NHBoc$), 65.6 (t, C-6), 72.1, 72.7, 73.6 (3 × d, C-3, C-4 and C-5), 79.0 (s, $OC(CH_3)_3$), 100.4 (d, C-2), 144.9 (d, C-1), 155.8 (s, NCO_2), 173.1 (s, $O_2C(CH_2)_3$); *m*/*z* (CI$^+$) 472 (MH^+, 4%). (Found C, 58.80; H, 8.66; N, 2.95. $C_{23}H_{41}N_1O_7Si_1$ requires C, 58.57; H, 8.76; N, 2.97%).

3-*O*-(5-*tert*-Butoxycarbonylaminopent-1-en-2-yl)-1,5-anhydro-2-deoxy-4,6-*O*-di(*tert*-butyl)silanediyl-D-*arabino*-hex-1-enitol 34

General method B: Tebbe reagent (0.85 ml, 0.42 mmol), ester **33** (50 mg, 0.11 mmol) in tetrahydrofuran (2 ml) and pyridine (0.5 ml), gave enol ether **34** (54 mg) as a yellow oil. This unstable compound was used in the next step with out further purification; ν_{max} (thin film) 3367 (br, N–H), 1716 (s, C=O), 1652, 1645 (w, 2 × C=C) cm^{-1}; δ_H (400 MHz, C_6D_6) 0.99, 1.04, 1.45 (27H, 3 × s, 3 × $C(CH_3)_3$), 1.48–1.66 (2H, m, CH_2CH_2-CH_2NHBoc), 2.00 (2H, t, *J* 7.1 Hz, $CH_2(CH_2)_2NHBoc$), 3.08–3.13 (2H, m, $(CH_2)_2CH_2NHBoc$), 3.79 (1H, ddd, $J_{4,5}$ 10.3 Hz, $J_{5,6}$ 10.4 Hz, $J_{5,6'}$ 5.0 Hz, H-5), 3.86–3.91 (1H, m, H-6), 3.92 (1H, s, C=C*H*H′), 3.94 (1H, s, C=CH*H*′), 4.12 (1H, dd, $J_{6,6'}$ 10.3 Hz, H-6′), 4.24 (1H, dd, $J_{3,4}$ 7.4 Hz, H-4), 4.37 (1H, br s, N–H), 4.57 (1H, br d, *J* 7.3 Hz, H-3), 4.83 (1H, dd, $J_{1,2}$ 6.1 Hz, $J_{2,3}$ 1.6 Hz, H-2), 6.03 (1H, dd, $J_{1,3}$ 0.9 Hz, H-1); δ_C (100.6 MHz, C_6D_6) 20.2, 23.1 (2 × s, 2 × $C(CH_3)_3$), 27.4, 27.9, (2 × q, 2 × $C(CH_3)_3$), 28.2 (t, $CH_2CH_2CH_2NHBoc$), 28.8 (q, $C(CH_3)_3$), 32.9 (t, $CH_2(CH_2)_2NHBoc$), 40.2 (t, $(CH_2)_2CH_2NHBoc$), 66.5 (t, C-6), 73.3, 75.1, 75.4 (3 × d, C-3, C-4 and C-5), 78.5 (s, $OC(CH_3)_3$), 83.3 (t, C=CH_2), 100.5 (d, C-2), 144.6 (d, C-1), 156.0 (s, NCO_2), 161.8 (s, C=CH_2); *m*/*z* (ES$^+$) 470 (MH^+, 2), 492 (MNa^+, 30), 508 (MK^+, 3%).

1-(1′,5′-Anhydro-2′,3′-dideoxy-4′,6′-*O*-di(*tert*-butyl)silanediyl-β-D-*erythro*-hex-2′-enopyranosyl)-5-*tert*-butoxycarbonylaminopentan-2-one 35

General method C: Crude enol ether **34** (54 mg), in tributylamine (1 ml), gave β-*C*-glycoside **35** (34 mg, 69% over two steps) as a colourless oil; $[a]_D^{25}$ +7.8 (*c*, 0.5 in $CHCl_3$); ν_{max} (thin film): 3370 (br, NH), 1715 (s, br, 2 × C=O) cm^{-1}; δ_H (400 MHz, C_6D_6) 1.09 (18H, s, 2 × $C(CH_3)_3$), 1.34–1.49 (2H, m, $CH_2CH_2CH_2$-NHBoc), 1.43 (9H, s, $C(CH_3)_3$), 1.92 (2H, t, *J* 7.2 Hz, CH_2-$(CH_2)_2NHBoc$), 2.00 (1H, dd, $J_{1',CHH'C(O)}$ 5.5 Hz, J_{gem} 16.0 Hz, C*H*H′C(O)), 2.33 (1H, dd, $J_{1',CHHC(O)'}$ 7.8 Hz, CH*H*′C(O)), 2.82–2.93 (2H, m, $(CH_2)_2CH_2NHBoc$), 3.56 (1H, ddd, $J_{4',5'}$ 8.5 Hz, $J_{5',6'}$ 10.4 Hz, $J_{5',6''}$ 5.0 Hz, H-5′), 3.92 (1H, at, $J_{6',6''}$ 10.2 Hz, H-6′), 4.10 (1H, br s, NH), 4.20 (1H, dd, $J_{6',6''}$ 9.9 Hz, H-6″), 4.51 (1H, dd, $J_{3',4'}$ 1.2 Hz, H-4′), 4.57–4.60 (1H, m, H-1′), 5.37 (1H, dat, *J* 1.8 Hz, $J_{2',3'}$ 10.4 Hz, H-2′), 5.89 (1H, br d, *J* 10.3 Hz, H-3′); δ_C (100.6 MHz, C_6D_6) 20.6, 23.2 (2 × s, 2 × $C(CH_3)_3$), 24.3 (t, $CH_2CH_2CH_2NHBoc$), 27.6, 28.0, 28.8 (3 × q, 3 × $C(CH_3)_3$), 40.2 (t, $(CH_2)_2CH_2NHBoc$), 40.7 (t, $CH_2(CH_2)_2$-NHBoc), 48.1 (t, $CH_2C(O)$), 67.8 (t, C-6′), 71.1 (d, C-4′), 72.6 (d, C-1′), 75.5 (d, C-5′), 78.8 (s, $OC(CH_3)_3$), 129.7 (d, C-2′), 130.6 (d, C-3′), 156.2 (s, $CO_2C(CH_3)_3$), 206.4 (s, C=O); NOE experiment (500 MHz, C_6D_6): Irradiate δ 4.59 (H-1′), enhancements: 2.00 (C*H*H′C(O), 2.9%), 2.33 (CH*H*′C(O), 2.0%), 3.56 (H-5′, 9.9%), 5.37 (H-2′, 5.2%). Irradiate δ 4.51 (H-4′), enhancements: 3.56 (H-5′, 1.9%), 3.92 (H-6′, 3.4%), 5.89 (H-3′, 4.2%). Irradiate δ 3.56 (H-5′), enhancements: 4.20 (H-6″, 4.1%), 4.51 (H-4′, 2.0%), 4.59 (H-1′, 10.1%). Irradiate 2.33 (CH*H*′C(O)), enhancements: 2.00 (C*H*H′C(O), 28.2%), 4.59 (H-1′, 3.1%); *m*/*z* (ES$^+$) 470 (MH^+, 90), 487 (MNH_4^+, 77), 492 (MNa^+, 100), 508 (MK^+, 30%). (HRMS calcd. for $C_{24}H_{44}$-O_6NSi (MH^+) 470.2938. Found 470.2938) (Found C, 61.37; H, 9.26; N, 3.00. $C_{24}H_{43}O_6NSi$ requires C, 61.37; H, 9.24; N, 2.98%).

3-*O*-(4-Butoxycarbonylaminobutanoyl)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hex-1-enitol 36

General method A: Glycal **15** (500 mg, 2.13 mmol), 4-*tert*-butoxycarbonylaminobutyric acid (868 mg, 4.27 mmol), dicyclohexylcarbodiimide (881 mg, 4.27 mmol) and 4-dimethylaminopyridine (52 mg, 0.43 mmol), in anhydrous dichloromethane (15 ml), gave ester **36** (826 mg, 92%) as a white crystalline solid; mp 106–107 °C (petrol–diethyl ether); $[a]_D^{24}$ +201 (*c*, 1 in $CHCl_3$); ν_{max} (thin film) 3379 (br, N–H), 1733, 1711 (s, 2 × C=O), 1637 (m, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.43 (9H, s, $C(CH_3)_3$), 1.75–1.81 (2H, m, $CH_2CH_2CH_2NHBoc$), 2.36–2.40 (2H, m, $CH_2(CH_2)_2NHBoc$), 3.06–3.11 (2H, m, $O_2C(CH_2)_2$-CH_2NHBoc), 3.85 (1H, at, *J* 10.4 Hz, H-6), 4.00 (1H, dd, $J_{3,4}$ 4.0 Hz, $J_{4,5}$ 10.5 Hz, H-4), 4.17 (1H, ddd, $J_{5,6}$ 10.4 Hz, $J_{5,6'}$ 5.2 Hz, H-5), 4.48 (1H, dd, $J_{6,6'}$ 10.6 Hz, H-6′), 4.52 (1H, br s, NH), 5.01 (1H, at, *J* 6.0 Hz, H-2), 5.46 (1H, dd, $J_{2,3}$ 5.8 Hz, H-3), 5.62 (1H, s, CHPh), 6.51 (1H, d, $J_{1,2}$ 6.0 Hz, H-1), 7.36–7.39 (3H, m, Ar–H), 7.45–7.47 (2H, m, Ar–H); δ_C (100.6 MHz, $CDCl_3$) 25.3 (t, $CH_2CH_2CH_2NHBoc$), 28.0 (q, $C(CH_3)_3$), 31.8 (t, $CH_2(CH_2)_2NHBoc$), 39.7 (t, $(CH_2)_2CH_2NHBoc$), 61.9 (d, C-3), 64.9 (d, C-5), 68.5 (t, C-6), 76.0 (d, C-4), 79.0 (s, $OC(CH_3)_3$), 98.3 (d, C-2), 101.4 (d, CHPh), 126.0, 128.3 (2 × d, C_{ortho} and $_{meta}$ Ar), 129.2 (d, C_{para} Ar), 136.9 (s, C_{ipso} Ar), 147.5 (d, C-1), 155.9 (s, NCO_2), 172.8 (s, $O_2C(CH_2)_3$); *m*/*z* (CI$^+$) 420 (MH^+, 21%), 437 (MNH_4^+, 6%). (Found C, 63.10; H, 6.98; N, 3.35. $C_{22}H_{29}O_7N$ requires C, 62.99; H, 6.97; N, 3.34%).

3-*O*-(5-*tert*-Butoxycarbonylaminopent-1-en-2-yl)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hex-1-enitol 37

General method B: Tebbe reagent (0.95 ml, 0.95 mmol), ester **36** (100 mg, 0.24 mmol), in tetrahydrofuran (4 ml) and pyridine (1 ml), gave enol ether **37** (93 mg, 93%) as a white crystalline solid; mp 88 °C; $[a]_D^{25}$ +187.5 (*c*, 1 in $CHCl_3$); ν_{max} (thin film): 3380 (br, NH), 1711 (s, C=O), 1634 (m, C=C) cm^{-1}; δ_H (400 MHz, C_6D_6) 1.41 (9H, s, $C(CH_3)_3$), 1.48–1.61 (2H, m, $CH_2CH_2CH_2NHBoc$), 1.92–2.01 (2H, m, $CH_2(CH_2)_2NHBoc$), 2.97–3.02 (2H, m, $(CH_2)_2CH_2NHBoc$), 3.46–3.53 (2H, m, H-4 and H-6), 3.90 (2H, d, *J* 5.7 Hz, C=CH_2), 4.21–4.33 (3H, m, H-3, H-5 and H-6′), 4.40 (1H, br s, NH), 4.86 (1H, at, *J* 5.8 Hz, H-2), 5.28 (1H, s, CHPh), 6.13 (1H, d, $J_{1,2}$ 6.1 Hz, H-1), 7.10–7.15 (1H, m, Ar–H), 7.18–7.22 (2H, m, Ar–H), 7.54–7.56 (2H, m, Ar–H); δ_C (100.6 MHz, C_6D_6) 28.1 (t, $CH_2CH_2CH_2NHBoc$), 28.8 (q, $C(CH_3)_3$), 33.2 (t, $CH_2(CH_2)_2NHBoc$), 40.3 (t, $(CH_2)_2CH_2NHBoc$), 65.3,

65.3 (2 × d, C-3 and C-5), 69.1 (t, C-6), 77.5 (d, C-4), 78.3 (s, O*C*$(CH_3)_3$), 82.8 (t, C=*C*H_2), 99.3 (d, C-2), 102.1 (d, CHPh), 127.0, 128.6 (2 × d, $C_{ortho\ and\ meta}$ Ar), 129.4 (d, C_{para} Ar), 138.4 (s, C_{ipso} Ar), 146.5 (d, C-1), 156.1 (s, NCO_2), 162.0 (s, *C*=CH_2); *m*/*z* (FI^+) 417 (M^+, 100%). (HRMS calcd. for $C_{23}H_{31}O_6N$ (M^+) 417.2151. Found 417.2157) (Found C, 65.99; H, 7.49; N, 3.35. $C_{23}H_{31}O_6N$ requires C, 66.17; H, 7.48; N, 3.35%).

3-*O*-(*N*-*tert*-Butoxycarbonyl-L-alanyl)-4,6-*O*-di-*tert*-butylsilanediyl-D-*arabino*-hex-1-enitol 38

General method A: Glycal **5** (1.011 g, 3.53 mmol), *N*-*tert*-butoxycarbonyl-L-alanine (0.868 g, 4.59 mmol), dimethylaminopyridine (86 mg, 0.71 mmol) and dicyclohexylcarbodiimide (1.46 g, 7.06 mmol), in dichloromethane (40 ml), gave ester **38** (1.6479 g, quant.) as a colourless oil; $[\alpha]_D^{25}$ −65.4 (*c*, 0.93 in $CHCl_3$); ν_{max} (thin film): 3371 (b, NH), 1721 (s, C=O), 1649 (s, C=C), 1504 (s, C=O) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.97, 1.05 (18H, 2 × s, 2 × C$(CH_3)_3$), 1.39 (3H, d, $J_{CH_3,CH}$ 7.0 Hz, CH_3), 1.44 (9H, s, OC$(CH_3)_3$), 3.88–4.01 (2H, m, H-5, H-6), 4.10–4.21 (2H, m, H-4, H-6′), 4.36–4.40 (1H, m, C*H*CH_3), 4.67 (1H, dd, $J_{1,2}$ 6.1 Hz, $J_{2,3}$ 2.1 Hz, H-2), 5.07–5.10 (1H, m, NH), 5.41–5.43 (1H, m, H-3), 6.32 (1H, dd, $J_{1,3}$ 1.4 Hz, H-1); δ_C (100.6 MHz, $CDCl_3$) 18.8 (q, CH_3), 19.8, 22.6 (2 × s, 3 × *C*$(CH_3)_3$), 26.8, 27.3 (2 × q, 6 × C(*C*$H_3)_3$), 28.3 (q, 3 × OC(*C*$H_3)_3$), 49.4 (d, *C*HCH_3), 65.6 (t, C-6), 72.8, 73.0, 73.5 (3 × d, C-3, C-4, C-5), 99.9 (d, C-2), 145.3 (d, C-1), 154.9 (s, CH*C*(O)O), 173.1 (s, O*C*(O)N); *m*/*z* (ES^+) 516 (MNH_4^+ + MeCN, 11), 480 (MNa^+, 5), 475 (MNH_4^+, 7), 458 (MH^+, 9%) (HRMS calcd. for $C_{22}H_{40}O_7NSi$ (MH^+) 458.2574. Found 458.2574).

3-*O*-(Azidoacetyl)-4,6-*O*-di-*tert*-butylsilanediyl-D-*arabino*-hex-1-enitol 39

General method A: Glycal **5** (1.346 g, 4.70 mmol), azidoacetic acid (605.7 mg, 5.99 mmol), dicyclohexylcarbodiimide (1.90 g, 9.22 mmol) and dimethylaminopyridine (113 mg, 0.922 mmol), in dichloromethane (20 ml), gave ester **39** (1.47 g, 85%) as a colourless oil; $[\alpha]_D^{19}$ −55.6 (*c*, 1.08 in $CHCl_3$); ν_{max} (thin film): 2109 (s, N_3), 1752 (s, C=O), 1648 (w, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.00, 1.06 (18H, 2 × s, 2 × C$(CH_3)_3$), 3.93 (2H, s, N_3CH_2), 3.94–4.03 (2H, m, H-5, H-6), 4.18–4.23 (2H, m, H-4, H-6′), 4.76 (1H, dd, $J_{1,2}$ 6.1 Hz, $J_{2,3}$ 1.9 Hz, H-2), 5.48–5.51 (1H, m, H-3), 6.36 (1H, dd, $J_{1,3}$ 1.7 Hz, H-1); δ_C (100.7 MHz, $CDCl_3$) 19.8, 22.7 (2 × s, 2 × *C*$(CH_3)_3$), 26.8, 27.3 (2 × q, 2 × C(*C*$H_3)_3$), 50.5 (t, N_3CH_2), 65.6 (t, C-6), 72.9, 73.5, 74.0 (3 × d, C-3, C-4, C-5), 99.7 (d, C-2), 145.6 (d, C-1), 181.3 (s, C=O); *m*/*z* (FI^+) 369 (100, M^+). (HRMS calcd. for $C_{16}H_{27}N_3O_5Si$ (M^+) 369.1720. Found, 369.1734).

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