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Efficient stereocontrolled synthesis of *C*-glycosides using glycosyl donors substituted by propane 1,3-diyl phosphate as the leaving group

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Abstract—α- and β-Glycosyl cyanides, per-*O*-acetyl-1,2-*O*-1-cyanoethylidenes and *C*-allyl glycopyranosides were efficiently prepared by treatment of 2,3,4-tri-*O*-acetyl-α,β-L-rhamno-, L-fuco- and 2,3,4,6-tetra-*O*-acetyl-α,β-D-galactopyranosyl propane-1,3-diyl phosphates with trimethylsilyl cyanide (TMSCN) and allyltrimethylsilane in the presence of trimethylsilyl triflate (TMSOTf). Similarly 2,3,4,6-tetra-*O*-benzyl-α,β-D-manno- and D-glucopyranosyl propane-1,3-diyl phosphates were employed in the synthesis of *C*-glycosides.

1. Introduction

The fact that cell–cell interactions are dependant on the interaction of oligosaccharides at the cell surface has recently been accepted by the chemical and biological communities. Binding of these oligosaccharides by receptor proteins leads to cell adhesion[1] and the biological consequences of these events can be beneficial, as in fertilisation, or detrimental, as in the case of bacterial[2] or viral adhesion[3] and inflammation.[4] The development of structures that can interrupt the binding of the receptors of specific carbohydrates or that can be used as probes becomes important in therapeutic regimes and has been the impetus behind these areas of research. However, the use of glycosides has been hampered by the fact that the glycosidic bond is susceptible towards hydrolysis and a plethora of enzymes exist to accomplish such tasks in vivo. This liability has led to the design and synthesis of glycomimetics with the aim that the biological properties of naturally occurring glycosides would be retained while being resistant towards hydrolysis.

The *C*-glycosides constitute such a class of compounds and there are a number of reports of such naturally occurring structures.[5] Central among this class are glycosyl cyanides and *C*-allyl glycosides, which are regarded as being synthetically useful for the preparation of biologically important carbohydrate analogues.

Glycosyl cyanides are versatile intermediates as the cyano group can be easily transformed into a variety of other functionalities.[5c] Early methods for the preparation of cyanides involved the use of peracylated glycosyl halides with mercury(II)[6a] or silver cyanides,[6b] and more recently via radical cyanation reactions.[6c] Other approaches for the synthesis of these compounds involve the cyanation of fluoroglycosides with Me_2AlCN and the reduction of *C*-glycopyranosyl nitromethanes with PCl_3 and pyridine.[7]

The allyl group can be simply converted to epoxypropyl functions that are recognised as active site-directed irreversible inhibitors of sugar processing enzymes.[8] Furthermore, the double bond of the allyl group allows a wide range of transformations that are centred on its cleavage to an active aldehyde group that can be readily elaborated.[9] This strategy has been extended to incorporate the synthetic potential of *C*-vinyl and *C*-alkynyl glycosides.[10]

The main approaches used for the synthesis of *C*-allyl glycosides have involved the treatment of benzylated glycolactones with allylmagnesium bromide followed by stereoselective reduction of the resulting hemiketal product with triethylsilane in the presence of boron trifluoride etherate.[11]

The Keck reaction has also been employed using either tri-*n*-butylallyltin or allylic sulphides or sulphones.[12] Access to these *C*-allyl glycosides is most commonly

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achieved using protected glycosyl fluorides, 1-*O*-acetyl glycopyranoses and other sugar derivatives with allyltrimethylsilane[13] in the presence of Lewis acids. More recently there has been an approach that uses the Keck radical allylation of protected sugar dihalides.[14] One of the drawbacks of these approaches is that with the exception of the Kishi method[11] the reactions invariably proceed in moderate yields and the stereoselectivity is usually in favour of the α-anomer.

2. Results and discussion

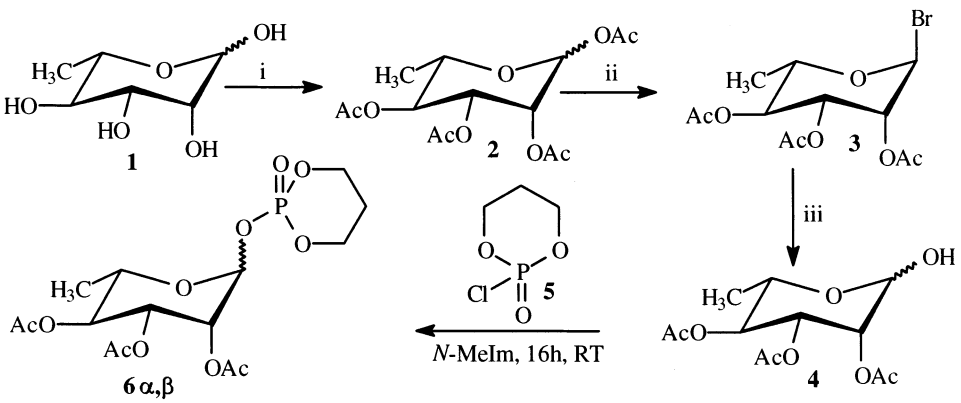
In our recent investigations we have introduced the propane-1,3-diyl phosphate as the anomeric leaving group at the anomeric centre of 2,3,4,6-tetra-*O*-benzyl-α,-D-gluco-, D-mannopyranoses,[15] 2,3,4-tri-*O*-acetyl-α,β-L-fuco- and 2,3,4,6-tetra-*O*-acetyl-α,β-galactopyranoses and successfully prepared α,β-*O*-glycosides and fucosidase substrates.[16] Herein, we report on our findings targeted at the synthesis of *C*-glycosides employing L-rhamno-, L-fuco-, D-galacto-, D-manno- and D-glucosyl donors having propane-1,3-diyl phosphate as an anomeric leaving group.

The requisite *O*-acetyl and *O*-benzyl protected glycosyl donors were readily prepared by means of phosphorylation of the anomeric hydroxyl group with propane-1,3-diyldioxyphosphoryl chloride **5** in the presence of *N*-methyl imidazole in excellent yields.[15,16] Similarly acetylation of L-rhamnopyranose **1** with acetic anhydride and pyridine solvent gave 1,2,3,4-tetra-*O*-acetyl-α,β-L-rhamnopyranose **2**, which was converted to the α-rhamnopyranosyl bromide **3** by treatment with 33% HBr–AcOH. Oxidation of **3** with Ag_2CO_3 gave 2,3,4-tri-*O*-acetyl-α,β-L-rhamnopyranose **4** in 86% overall yield. Reaction of **4** with propane-1,3-diyldioxyphosphoryl chloride **5** gave phosphates **6α** and **6β** as a hygroscopic mixture in a 5:1 ratio (Scheme 1).

In all of the cases examined it was found that the α-anomer was the major product based on the ^{1}H NMR spectral data. The ^{1}H NMR spectrum of **6α** showed a quartet (J 1.3 Hz) for C(1)H at δ 5.64 and a multiplet ($J_{P\text{-}H}$ 15.2 Hz) for the C(5_{ax}) and C(5_{eq}) protons at δ 1.86–1.93 and δ 2.32–2.38 respectively. In contrast, the ^{1}H NMR spectrum of **6β** showed a doublet (J 8.6 Hz) for C(1)H at δ 5.49. The ^{13}C NMR spectra showed C(1) signals of **6a** and **6β** δ 94.81 with $J_{C\text{-}H}$ 183.8 Hz and δ 93.46 with $J_{C\text{-}H}$ 162.3, respectively.

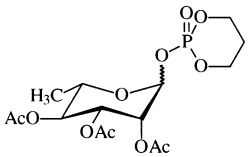
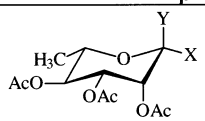
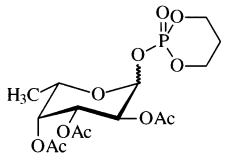
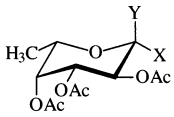
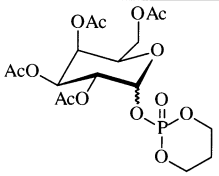
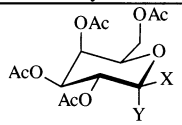
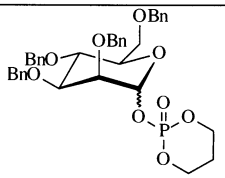
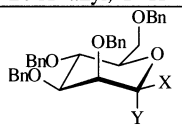
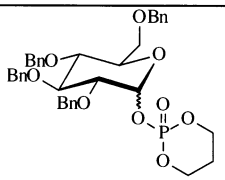
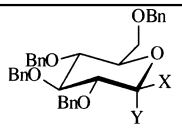
With these phosphates in hand we investigated their displacement reaction with TMSCN and allyltrimethyl silane in the presence of TMSOTf[17] as an anomeric activator, the findings are detailed in the Table 1. In the case of *O*-acetyl glycosyl donors of L-rhamno-, L-fuco- and D-galactopyranoses **6**, **10** and **16** (Table 1) with TMSCN and TMSOTf in CH_2Cl_2 solvent at −78°C, to our surprise we obtained 1,2-*O*-(1-cyanoethylidene)-glycoses as *exo*/*endo* mixture of **9a**/**9b**, **15a**/**15b** and **21a**/**21b** in yields of 79, 73 and 76%, respectively (Schemes 2 and 3).[18]

In the case of the L-fucopyranosyl donor **10** we obtained *exo* isomer **15a** as the major product (72% yield) and its *endo* isomer **15b** obtained in low yield of 1%. Prior to these findings similar compounds were prepared by Meyers[19] in poor yields ranging from 8–14% using mercury cyanide as the cyanide source. The formation of these products can be readily explained by trapping of the intermediate acetoxonium ion by cyanide ion. The ^{1}H and ^{13}C NMR spectral data of the α-cyanoacetals were consistent with the structures. The ^{13}C NMR data were most informative for assignment of the *exo*/*endo* isomers and exhibit the –C≡N resonance in the region between 116 to 117 ppm.[19] These α-cyanoacetals were stereoselectively converted to the corresponding per-*O*-acetyl glycopyranosyl cyanides (Schemes 2 and 3) by treatment with 1 equiv. of TMSOTf at room temperature for 24 h. Both the L-fuco-, and D-galactopyranosyl 1,2-*O*-(1-cyanoethylidene) derivatives **15a**/**15b** and **21a**/**21b** were readily rearranged to the corresponding *C*-cyano glycosides in good yields (Table 1). Thus, the propane-1,3-diyl 2,3,4-tri-*O*-acetyl-α,β-L-fucopyranosyl phosphate **10** with TMSCN in the presence of 1 equiv. of TMSOTf gave a mixture of compounds **11** and **12**[5c,19] in 63 and 15% yields, respectively, with the α-isomer predominant (ratio = 4:1). In the case of glycosyl donor **16** we obtained 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl cyanide **18** as the major product in 45%



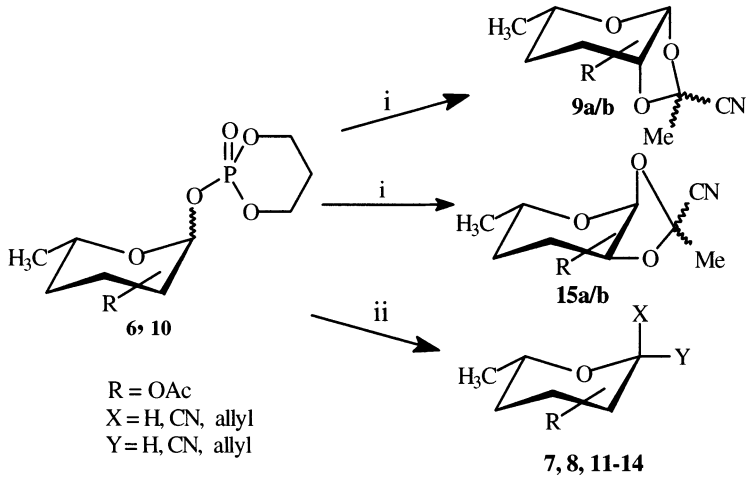
Scheme 1. (i) Ac_2O, Py, rt, 12 h; (ii) 33% HBr–AcOH, rt, 15 min; (iii) Ag_2CO_3, acetone, 0.5 h.

Table 1. Reactions of *O*-acetyl and *O*-benzyl protected glycosyl donors with TMSCN and allyltrimethylsilane in presence of with TMSOTf

Glycoside Donor	Product	Yield	α:β	^{1}H and ^{13}C NMR data δ C(1)H	δ C≡N
 6α:6β 5:1	 **7α** X=H, Y=CN	37%	α only	δ 4.58 (α)	113.90 (α)
	7β X=CN, Y=H	0% + 46%	**9a**	δ 4.00 (α)	
	8α X=H, Y=allyl	76%	4:1	δ 3.59 (β)	
	8β X=allyl, Y=H	0%			
 10α:10β 20:1	 **11** X=H, Y=CN	63%	4:1	δ 5.27 (α)	114.50 (α)
				δ 4.28 (β)	114.70 (β)
	12 X=CN, Y=H	15%		δ 4.25 (α)	
	13 X=H, Y=allyl	49%	3:2	δ 3.66 (β)	
	14 X=allyl, Y=H	31%			
 16α:16β 20:1	 **17** X=H, Y=CN	31%	2:3	δ 5.18 (α)	113.89 (α)
				δ 4.31 (β)	114.31 (β)
	18 X=CN, Y=H	45%		δ 4.10 (α)	
	19 X=H, Y=allyl	12%	1:5	δ 3.36 (β)	
	20 X=allyl, Y=H	61%			
 22α:22β 10:1	 **23** X=H, Y=CN	49%	3:2	δ 4.76 (α)	115.36 (α)
				δ 4.10 (β)	116.02 (β)
	24 X=CN, Y=H	32%		δ 4.02 (α)	
	25 X=H, Y=allyl	39%	1:1	δ 3.81 (β)	
	26 X=allyl, Y=H	39%			
 27α:27β 19:1	 **28** X=H, Y=CN	48%	3:2	δ 4.60 (α)	115.33 (α)
				δ 4.06 (β)	116.00 (β)
	29 X=CN, Y=H	32%		δ 5.04 (α)	
	30α X=H, Y=allyl	79%	1:12	δ 4.28 (β)	
	30β X=allyl, Y=H	0%			

yield.[7b,7c,19] The L-rhamanose analogue **9a**/**9b** was more resistant to conversion using these conditions in that only 37% of **7**α was obtained after 24 hours along with recovered α-cyanoacetal **9a** in 46% yield, reflecting the increased stability of the *cis*-fused 6,5-ring system towards Lewis acids. The ^{13}C NMR spectral data of these α,β-*C*-glycosyl cyanides exhibit a resonance between 113 and 114 ppm and consistent with the data of reported compounds.[7b,19]

Similarly, the *O*-benzylated D-manno- and D-glucopyranosyl donors **22** and **27** were employed in the preparation of *C*-cyano glycosides. In the case of glycosyl donor **22** on treatment with TMSCN in presence of TMSOTf at −78°C afforded a mixture of α,β-D-mannopyranosyl cyanides **23** and **24** (Scheme 3) in 49 and 32% and the α:β ratio is 3:2. The stereochemistry at the anomeric centre was assigned on the basis of ^{1}H and ^{13}C NMR spectral data. In particular the resonance for the cyanide carbon at δ 116.02 (α-anomer) and 115.36 (β-anomer) was particularly informative and this was in agreement with the data reported by Ichikawa,[20] however, this was not consistent with the data reported by Gervay.[20b,21] In the case of the D-



Scheme 2. (i) 1 equiv. of TMSCN, cat. TMSOTf, −78 to 0°C, CH_2Cl_2, 0.5 h; (ii) 1 equiv. of allyltrimethylsilane, TMSCN, cat. to 1 equiv. of TMSOTf, −78 to 0°C, CH_2Cl_2, 0.5–24 h.

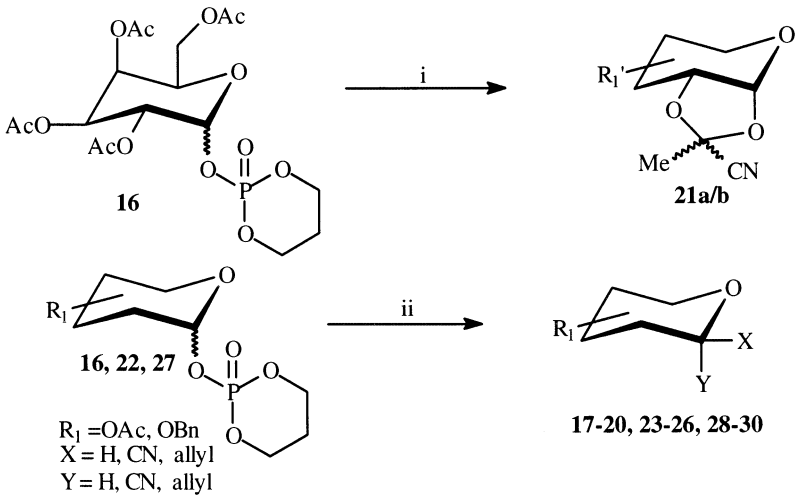
glucopyranosyl donor **27** under similar reaction conditions we obtained α,β-D-glucopyranosyl cyanides **28** and **29** with selectivity in favour of the α-isomer (α:β ratio, 3:2).

Under similar conditions, treatment of *O*-acetyl protected glycosyl donors **6** and **10** (Table 1) with allyltrimethyl silane in presence of TMSOTf at −78°C resulted in the formation of the *C*-allyl glycosides (Scheme 2). Initially 3-(tri-*O*-acetyl-α-L-rhamnopyranosyl)-1-propene **8α**[9b] was obtained in 76% yield and its β-isomer was identified in TLC, but we were unable to isolate the compound **8β** (ratio α,β = 4:1). Reaction of glycosyl donor **10** with allyltrimethylsilane gave mixture of 3-(tri-*O*-acetyl-α,β-L-fucopyranosyl)-1-propene **13** and **14**[22] in yields of 49 and 31%, respectively. Allylation of glycosyl donor **16** with allyltrimethylsilane, the α,β-D-galactoyranosyl-1-propene **19**[12c] and **20**[14,22] was obtained (Scheme 3) in 12 and 61% yield with high β-selectivity (α,β = 1:5). In the examples wherein **6**, **10** and **16** were the glycosyl donors we did not observe the analogous orthoesters, reflecting the increased nucleophilicity of the allyltrimethyl silane function in comparison to trimethylsilyl cyanide.

We have performed further allylation experiments with allyltrimethylsilane on *O*-benzyl protected glycosyl donors **22** and **27**. Thus, *C*-glycosidation of D-mannopyranosyl phosphate **22** with TMSOTf at −78°C afforded the α,β-*C*-allyl mannopyranosides[9a,b,13b] **25** and **26** (Scheme 3) in good yield (α:β anomers 1:1) (Scheme 3). When glycosyl donor **27** was reacted with allyltrimethylsilane in presence of TMSOTf under similar conditions we obtained higher stereoselectivity in that β-*C*-allyl-D-glucoside **30β** (Scheme 3) was the major isomer, (ratio α:β 1:12) in 79% yield. We were unable to isolate the α-isomer by silica gel column chromatography.

3. Conclusion

We have demonstrated that the treatment of a range of *O*-acetyl and *O*-benzyl protected glycosyl donors with



Scheme 3. (i) 1 equiv. of TMSCN, cat. TMSOTf, −78 to 0°C, CH_2Cl_2, 0.5 h; (ii) 1 equiv. of allyltrimethylsilane, TMSCN, cat. to 1 equiv. of TMSOTf, −78 to 0°C, CH_2Cl_2, 0.5–4 h.

TMSCN and allyltrimethylsilane in the presence of TMSOTf as an anomeric activator proceeds in good yields, high stereoselectivity and provides ready access to *C*-glycosides.

4. Experimental

Melting points were determined on a GallenKamp capillary melting-point apparatus and are uncorrected. Optical rotations were determined on a Bellingham & Stanley ADP 220 polarimeter. $[\alpha]_D$ values are in units of 10^{-1} deg cm^2 g^{-1}. All reactions were monitored by TLC on Silica Gel 60 F-254 plated (Merck) with detection by UV, phosphomolybdic acid or basic aq. potassium permanganate solutions. Flash chromatography was performed on a Silica Gel 60 (230–400 mesh, Merck). All reactions were carried out under argon or nitrogen atmosphere in oven-dried glassware unless otherwise stated. CH_2Cl_2 was distilled from calcium hydride and stored over 4 Å molecular sieves. Organic solutions were dried over Na_2SO_4 and evaporations were carried out under reduced pressure at 40°C. 'Petrol' refers to petroleum spirit (distillation range 40–60°C), which was distilled prior to use, and 'ether' refers to diethyl ether.

The ^{1}H NMR and ^{13}C NMR spectra were recorded with JEOL GSX 270 NMR spectrometer, for solutions in $CDCl_3$ (unless stated otherwise) [residual $CHCl_3$ (δ_H 7.26 ppm) or $CDCl_3$ (δ_C 77.0 ppm) as internal standard] at 300 K. ^{31}P NMR spectra were recorded in $CDCl_3$, at 109.25 MHz on a JEOL GSX 270 NMR spectrometer, using trimethyl phosphate as the external reference. IR spectra were recorded on a UNICAM series FTIR spectrometer. Mass spectra were obtained on an AEI MS 902 or VG ZAB-E spectrometer. Microanalysis were performed by MEDAC Ltd, Surrey, UK.

4.1. 2′,3′,4′-Tri-*O*-acetyl-α,β-L-rhamnopyranosyl-[1,3,2]-dioxaphosphinane 2-oxide 6α and 6β

2,3,4-Tri-*O*-acetyl-α,β-L-rhamnopyranose **4** (3 g, 10.34 mmol) was dissolved in CH_2Cl_2 (30 mL) and the solution was cooled to 0°C. To this solution was added 2-chloro-[1,3,2]-dioxaphosphinane-2-oxide **5** (4.84 g, 31.03 mmol) and 1-methylimidazole (2.5 g, 30.44 mmol) dropwise over 5 min. Stirring was continued for 16 h, with gradual warming to room temperature. The solvent was removed, the residue was re-dissolved in CH_2Cl_2 (30 mL) and the resulting solution was evaporated to remove traces of 1-methylimidazole. The resulting residue was dissolved in CH_2Cl_2 (30 mL) and washed successively with ice-water (30 mL), aq. $NaHCO_3$ (2×30 mL) and water (30 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The oily residue was purified by silica gel column chromatography (EtOAc–'petrol' 7:3) to afford the phosphates **6α** and **6β** (ratio 5:1) as an inseparable hygroscopic mixture (2.70 g, 63%). For isomer **6α** (major): $[\alpha]^{19}_{Dmix} = -35.7$ (*c* 2.9, $CHCl_3$); IR (film) ν_{max} 1749, 1373, 1216 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.27 (3H, d, $J = 6.6$ Hz), 1.86–1.93 (1H, m, $J_{P\text{-}H} = 15.2$ Hz, H-5$_{ax}$), 2.01 (3H, s), 2.08 (3H, s), 2.17 (3H, s), 2.32–2.38 (1H, m, $J_{P\text{-}H} = 15.2$ Hz, H-5$_{eq}$), 4.03–4.16 (1H, m), 4.38–4.59 (4H, m), 5.13 (1H, d, $J = 9.2$ Hz), 5.29–5.36 (2H, m), 5.64 (1H, q, $J = 1.3$ Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 17.17, 20.37, 20.49 (2C), 25.67, 68.31, 68.59, 68.91, 69.05, 69.09, 70.03, 94.81 ($J_{C\text{-}H} = 183.8$ Hz), 169.63, 169.97 (2C); ^{31}P NMR (109.25 MHz, $CDCl_3$) δ −11.63; *m*/*z* (CI, NH_3) calcd for $C_{15}H_{27}NO_{11}P$: 428.1322. Found: 428.1322 [M+NH_4]$^+$; anal. calcd for $C_{15}H_{27}NO_{11}P$: C, 43.91; H, 5.65; P, 7.55. Found: C, 43.34; H, 5.31; P, 7.68. For isomer **6β** (minor): ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.49 (d, $J = 8.6$ Hz), ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 93.46 (d, $J = 3.9$, $J_{C\text{-}H} = 162.3$ Hz); ^{31}P NMR (109.25 MHz, $CDCl_3$) δ −10.90.

4.2. 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl cyanide 7α

To a stirred solution of propane-1,3-diyl 2,3,4-tri-*O*-acetyl-α,β-L-rhamnopyranosyl phosphate **6** (1 g, 2.44 mmol) and TMSOTf (540 mg, 2.44 mmol) in dry CH_2Cl_2 (10 mL) at 0°C was added trimethylsilyl cyanide (240 mg, 2.42 mmol) over 5 min and the reaction mixture stirred for 24 h at rt. After quenching with aq. $NaHCO_3$ (10 mL), the mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (15 mL). The organic phase was dried over Na_2SO_4. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (EtOAc–'petrol' 7:3) to give **7α** as a white solid (0.270 g, 37%): mp 117–119°C; $[\alpha]^{22}_D = +19.7$ (*c* 1.5, $CHCl_3$); ν_{max} (KBr) 3023, 2980, 1754, 1430, 1373, 1216 cm^{-1};^{1}H NMR (270 MHz, $CDCl_3$) δ 1.29 (3H, d, $J = 5.9$ Hz), 2.00 (3H, s), 2.06 (3H, s), 2.25 (3H, s), 3.51 (1H, dq, $J = 5.9$, 3.3 Hz), 4.58 (1H, d, $J = 1.3$ Hz), 4.97 (1H, dd, $J = 3.3$, 2.6 Hz), 5.04 (1H, d, $J = 9.2$ Hz), 5.59 (1H, dd, $J = 3.3$, 1.3 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 17.33, 20.38, 20.41, 20.55, 66.43, 67.80, 69.35, 70.47, 75.52, 113.90, 169.53, 169.66, 169.94; *m*/*z* (CI, NH_3) calcd for $C_{13}H_{21}N_2O_7$: 317.3196. Found: 317.2361 [M+NH_4]$^+$.

4.3. 3-(2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-1-propene 8α

A solution of **6** (1 g, 2.44 mmol) in CH_2Cl_2 (10 mL) was cooled to −78°C under an N_2 gas atmosphere was added TMSOTf (catalytic). After 2 min allyltrimethylsilane (280 mg, 2.45 mmol) in CH_2Cl_2 (2 mL) was added, and the reaction mixture was stirred for 30 min at −78°C and then allowed to warm to 0°C. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed successively with aq. $NaHCO_3$ (15 mL) and water (15 mL) followed by drying over Na_2SO_4. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (EtOAc–'petrol' 2:8) to yield the title compound **8α** as a colourless oil (580 mg, 76%): $[\alpha]^{22}_D = -1.8$ (*c* 2.2, $CHCl_3$); ν_{max} (film) 1745, 1643, 1228 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.23 (3H, d, $J = 5.9$ Hz), 2.01 (3H, s), 2.07 (3H, s), 2.13 (3H, s), 2.55–2.61 (2H, m), 3.73 (1H, dq, $J = 6.6$, 2.0 Hz), 4.00 (1H, dt, $J = 9.2$, 2.6 Hz), 5.00 (1H, dd, $J = 9.9$, 2.0 Hz), 5.07 (1H, dd, $J = 9.2$, 5.3 Hz), 5.20–5.33 (3H, m), 5.71 (1H, ddt, $J = 9.9$, 6.6, 3.3 Hz); ^{13}C NMR (67.8 MHz,

$CDCl_3$) δ 17.46, 20.56, 20.66, 20.82, 33.50, 68.01, 68.92, 70.21, 71.35, 74.29, 118.05, 132.76, 169.74, 169.98, 170.16; m/z (CI, NH_3) calcd for $C_{15}H_{26}NO_7$: 332.1709. Found: 332.1710 $[M+NH_4]^+$.

4.4. 3,4-Di-*O*-acetyl-1,2-*O*-[1-(*exo*-,*endo*-cyano)-ethylidene]-α-L-rhamnopyranose 9a and 9b[18a]

The title compounds were prepared using a similar procedure to that employed for compound **7α**, by treating compound **6** (1 g, 2.44 mmol) with TMSOTf (67 mg, 0.30 mmol) and trimethylsilyl cyanide (240 mg, 2.44 mmol) in CH_2Cl_2 (10 mL) at −78°C over 0.5 h. Chromatographic purification of the resulting residue (EtOAc–'petrol' 3:7) gave a mixture of *exo*-**9a** (331 mg, 46%) and *endo*-**9b** (245 mg, 33%) isomers (ratio *exo*/*endo* 3.8:2.2). For *exo* isomer **9a**: mp 143–145°C; $[\alpha]_D^{22}=-2.4$ (c 5.0, $CHCl_3$); ν_{max} (KBr) 3019, 1754, 1373, 1216 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.21 (3H, d, $J=5.9$ Hz), 1.93 (3H, s), 2.07 (3H, s), 2.13 (3H, s), 3.51 (1H, dddd, $J=9.9$, 6.6, 5.9, 2.6 Hz), 4.57 (1H, dd, $J=4.6$, 2.0 Hz), 5.02 (1H, dd, $J=10.6$, 9.9 Hz), 5.21 (1H, dd, $J=9.9$, 4.0 Hz), 5.41 (1H, d, $J=2.0$ Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 17.28, 20.60, 20.63, 26.44, 69.31, 69.71, 69.74, 78.27, 96.54, 101.57, 116.61, 169.71, 170.08. For *endo* isomer **9b**: $[\alpha]_D^{22}=+61.06$ (c 2.2, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.21 (3H, d, $J=6.6$ Hz), 1.92 (3H, s), 2.07 (3H, s), 2.13 (3H, s), 3.49 (1H, dddd, $J=9.2$, 6.6, 5.9, 2.6 Hz), 4.57 (1H, dd, $J=4.0$, 2.6 Hz), 4.83 (1H, d, $J=2.0$ Hz), 5.21 (1H, dd, $J=9.9$, 4.0 Hz), 5.41 (1H, dd, $J=3.3$, 2.6 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 17.23, 20.43, 20.59, 26.44, 65.45, 68.93, 69.80, 72.36, 96.62, 101.57, 116.61, 169.64, 169.70.

4.5. 2,3,4-Tri-*O*-acetyl-α,β-L-fucopyranosyl cyanide 11 and 12[19]

The title compounds were prepared using similar procedure to that detailed for **7α**. Thus, to the propane-1,3-diyl 2,3,4-tri-*O*-acetyl-α,β-L-fucopyranosyl phosphate **10** (1 g, 2.44 mmol) in CH_2Cl_2 (10 mL) was added TMSOTf (540 mg, 2.44 mmol) and trimethylsilyl cyanide (240 mg, 2.44 mmol) at 0°C and the reaction mixture was stirred at rt for 24 h. Chromatographic purification of the obtained residue (Et_2O–'petrol' 7:3) gave **11** (460 mg, 63%) and **12** (115 mg, 15%) as a mixture (ratio α:β, 4:1). For isomer **11**: mp 98°C (lit.:[19] 97–98°C); $[\alpha]_D^{22}=-112.3$ (c 3.3, $CHCl_3$); ν_{max} (KBr) 3023, 1752, 1430, 1373, 1216 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.21 (3H, d, $J=6.59$ Hz), 2.02 (3H, s), 2.14 (3H, s), 2.17 (3H, s), 4.20 (1H, dq, $J=7.28$, 5.28 Hz), 5.12 (1H, d, $J=5.27$ Hz), 5.19 (1H, dd, $J=10.56$, 5.28 Hz), 5.27 (1H, dd, $J=2.64$, 1.97 Hz), 5.36 (1H, q, $J=1.32$ Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 15.91, 20.39, 20.49, 20.55, 64.96, 65.55, 68.77, 69.77, 70. 85, 114.40, 169.56, 169.88, 170.15; m/z (CI, NH_3) calcd for $C_{13}H_{21}N_2O7$: 317.3196. Found: 317.2349 $[M+NH_4]^+$. For isomer **12**: mp 124–126°C (lit.:[19] 123–125°C); $[\alpha]_D^{22}=-39.7$ (c 3.5, $CHCl_3$); ν_{max} (KBr) 3023, 1752, 1430, 1371, 1216 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.21 (3H, d, $J=6.6$ Hz), 2.00 (3H, s), 2.12 (3H, s), 2.21 (3H, s), 3.82 (1H, dq, $J=6.6$, 6.0 Hz), 4.28 (1H, d, $J=9.9$ Hz), 4.99 (1H, q, $J=3.3$ Hz), 5.27 (1H, dd, $J=3.3$, 3.3 Hz), 5.46 (1H, t, $J=9.9$ Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 15.89, 20.35, 20.42 (2C), 66.01, 66.55, 69.65, 71.08, 74.21, 114.70, 168.81, 169.79, 170.28; m/z (CI, NH_3) calcd for $C_{13}H_{21}N_2O_7$: 317.3196. Found: 317.2349 $[M+NH_4]^+$.

4.6. 3-(2′,3′,4′-Tri-*O*-acetyl-α,β-L-fucopyranosyl)-1-propene 13 and 14[22]

To a solution of propane-1,3-diyl 2,3,4-tri-*O*-acetyl-α,β-L-fucopyranosyl phosphate **10** (1 g, 2.44 mmol) in CH_2Cl_2 (10 mL) at −78°C was reacted with TMSOTf (33 mg, 0.15 mmol) and allyltrimethylsilane (0.278 g, 2.39 mmol) similar to that detailed in the preparation of compound **8α**. Flash chromatographic purification of the resulting residue (EtOAc–'petrol' 3:7) gave a mixture of anomers **13** (370 mg, 49%) and **14** (240 mg, 31%) in the ratio 3:2. For isomer **13**: ν_{max} (film) 1749, 1640, 1216 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.06 (3H, d, $J=6.0$ Hz), 1.94 (3H, s), 1.98 (3H, s), 2.09 (3H, s), 2.17 (1H, ddd, $J=15.2$, 6.6, 5.3 Hz), 2.39 (1H, ddd, $J=15.2$, 7.3, 3.3 Hz), 3.87 (1H, dq, $J=6.6$, 2.0 Hz), 4.17 (1H, dt, $J=10.6$, 5.3 Hz), 5.01 (1H, dd, $J=9.9$, 2.6 Hz), 5.03 (1H, dd, $J=15.2$, 1.3 Hz), 5.12 (1H, dd, $J=9.9$, 3.3 Hz), 5.19 (1H, dd, $J=4.0$, 2.0 Hz), 5.24 (1H, dd, $J=9.9$, 5.3 Hz), 5.63 (1H, ddt, $J=16.4$, 9.9, 6.6 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 15.84, 20.60, 20.64, 20.71, 30.53, 65.53, 68.12, 68.43, 70.66, 71.93, 117.30, 133.78, 169.88, 170.13, 170.54. For isomer **14**: ^1H NMR (270 MHz, $CDCl_3$), δ 1.08 (3H, d, $J=6.6$ Hz), 1.94 (3H, s), 1.95 (3H, s), 2.08 (3H, s), 2.18 (1H, ddd, $J=15.2$, 7.9, 3.3 Hz), 2.39 (1H, ddd, $J=15.2$, 6.0, 2.6 Hz), 3.48–3.66 (1H, m), 3.86 (1H, dq, $J=6.6$, 1.3 Hz), 4.19 (1H, dt, $J=6.6$, 5.3 Hz), 4.98 (1H, dd, $J=10.6$, 3.3 Hz), 5.05–5.17 (1H, m), 5.12 (1H, dd, $J=9.9$, 3.3 Hz), 5.23–5.26 (1H, m), 5.60 (1H, ddt, $J=16.5$, 8.6, 6.6 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 15.93, 20.57, 20.60, 20.65, 29.65, 65.52, 66.44, 67.79, 68.20, 70.60, 117.37, 133.82, 169.94, 170.19, 170.54.

4.7. 3,4-Di-*O*-acetyl-1,2-*O*-[1-(*exo*,endo-cyano)-ethylidene]-α-L-fucopyranose 15a and 15b[18c]

The title compounds were prepared using a similar procedure to that employed for compound **7α**, by treating compound **10** (1 g, 2.44 mmol) with TMSOTf (0.068 g, 0.30 mmol) and trimethylsilyl cyanide (240 mg, 2.44 mmol) in CH_2Cl_2 (10 mL) at −78°C over 0.5 h. Flash chromatographic purification of the resulting residue (Et_2O–'petrol' 3:7) gave mixture of *exo* **15a** (522 mg, 72%) and *endo* **15b** (8 mg, 1%) isomers. For isomer **15a**: $[\alpha]_D^{22}=+1.3$ (c, 1.0, $CHCl_3$); ν_{max} (film) 3021, 1752, 1430, 1371, 1216 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.21 (3H, d, $J=6.6$ Hz), 1.85 (3H, s), 2.07 (3H, s), 2.15 (3H, s), 4.23 (1H, dd, $J=4.6$, 3.3 Hz), 4.91 (1H, dd, $J=7.3$, 3.3 Hz), 5.21 (1H, dd, $J=3.3$, 1.3 Hz), 5.30–5.37 (1H, m), 5.84 (1H, d, $J=5.3$ Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 16.06, 20.46, 20.61, 25.94, 68.18, 68.29, 71.55, 72,14, 96.60, 99.62, 116.95, 169.97, 170.10. For isomer **15b**: mp 100–102°C (lit.:[18c] 103–105°C); $[\alpha]_D^{22}=+134.6$ (c, 0.3, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.22 (3H, d, $J=6.6$ Hz), 1.78 (3H, s), 2.02 (3H, s), 2.17 (3H, s), 4.27 (1H, dd, $J=4.2$, 2.6 Hz), 5.02–5.13 (1H, m), 5.25 (1H, dd, $J=2.6$, 2.0 Hz), 5.43 (1H, dd, $J=7.9$, 3.3 Hz), 5.69 1H, d, $J=5.3$ Hz).

4.8. 2,3,4,6-Tetra-*O*-acetyl-α,β-D-galactopyranosyl cyanide 17 and 18[19]

The title compounds were prepared using a similar procedure to that employed for compound **7α**, by treating propane-1,3-diyl 2,3,4,6-tetra-*O*-acetyl-α-β-D-galactopyranosyl phosphate **16** (1 g, 2.14 mmol) with TMSOTf (475 mg, 2.14 mmol) and trimethylsilyl cyanide (220 mg, 2.14 mmol) in CH_2Cl_2 (10 mL) at 0°C. The reaction mixture was stirred at rt for 24 h. Flash chromatographic purification of the obtained residue (EtOAc–'petrol' 3:7) gave a mixture of isomers **17** (230 mg, 31%) and **18** (340 mg, 45%) (ratio 2:3). For isomer **17**: mp 94–96°C (lit.:[19,22] 93–94°C); $[\alpha]_D^{22}=+122.0$ (*c* 2.0, $CHCl_3$); ν_{max} (KBr) 3023, 2980, 2930, 1754, 1430, 1371, 1216 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.02 (3H, s), 2.07 (3H, s), 2.15 (6H, s), 4.10–4.16 (2H, m), 4.30 (1H, dt, $J=6.6$, 4.6 Hz), 5.18 (1H, appt, $J=5.9$, 4.0 Hz), 5.25 (1H, d, $J=5.3$ Hz), 5.28 (1H, dd, $J=2.0$, 1.3 Hz), 5.52 (1H, q, $J=1.3$, Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.35 (2C), 20.45 (2C), 60.99, 64.93, 65.61, 66.78, 68.30, 72.33, 113.89, 169.43, 169.72, 169.76, 170.14; *m*/*z* (CI, NH_3) calcd for $C_{15}H_{23}N_2O9$: 375.3562. Found: 375.3606 $[M+NH_4]^+$. For isomer **18**: mp 166–168°C (lit.:[22] 168–169°C); $[\alpha]_D^{28}=+67.7$ (*c* 1.6, $CHCl_3$); ν_{max} (KBr) 3025, 2981, 2927, 1754, 1430, 1371, 1216 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.01 (3H, s), 2.03 (3H, s), 2.05 (3H, s), 2.07 (3H, s), 3.95 (1H, dt, $J=6.6$, 1.3 Hz), 4.07–4.30 (2H, m), 4.31 (1H, d, $J=10.6$ Hz), 5.00 (1H, q, $J=3.3$, Hz), 5.32 (1H, q, $J=1.3$, Hz), 5.49 (1H, t, $J=10.6$ Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.32, 20.41, 20.44, 20.47, 61.14, 65.97, 66.67, 66.69, 70.71, 75.31, 114.31, 169.87, 170.00, 170.03, 170.19; *m*/*z* (CI, NH_3) calcd for $C_{15}H_{23}N_2O_9$: 375.3562. Found: 375.3606 $[M+NH_4]^+$.

4.9. 3-(2′,3′,4′,6′-Tetra-*O*-acetyl-α,β-D-galactopyranosyl)-1-propene 19 and 20[12c,14,22]

To a solution of propane-1,3-diyl 2,3,4,6-tetra-*O*-acetyl-α,β-D-galactopyranosyl phosphate **16** (500 mg, 1.06 mmol) in CH_2Cl_2 (5 mL) at −78°C was added TMSOTf (59 mg, 0.26 mmol) and allyltrimethylsilane (130 mg, 1.06 mmol) as detailed in the preparation of compound **8α**. Flash chromatographic purification of the resulting residue (EtOAc–'petrol' 2:8) gave a mixture of anomers **19** (46 mg, 12%) and **20** (238 mg, 61%) in the ratio 1:5. For isomer **19**: $[\alpha]_D^{27}=+20.8$ (*c* 1.8, $CHCl_3$); ν_{max} (film) 1752, 1642, 1218 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.03 (3H, s), 2.04 (3H, s), 2.08 (3H, s), 2.12 (3H, s), 2.28 (1H, dddt, $J=9.9$, 6.0, 2.6, 1.3 Hz), 2.45 (1H, dddt, $J=9.9$, 8.6, 2.6, 1.3 Hz), 4.06–4.13 (2H, m), 4.18 (1H, dd, $J=8.6$, 3.3 Hz), 4.25 (1H, ddd, $J=5.3$, 4.6, 4.0 Hz), 5.09 (2H, m), 5.18 (2H, m), 5.41 (1H, dt, $J=3.3$, 2.6 Hz), 5.69 (1H, dddd, $J=17.2$, 9.2, 6.6, 3.2 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$), δ 20.50, 20.57 (2C), 20.62, 30.84, 61.33, 67.51, 67.85, 68.21 (2C), 71.34, 117.27, 133.30, 169.70, 169.80, 169.97, 170.43; HRMS (EI) calcd for $C_{17}H_{25}O_9$: 373.1498. Found: 373.1501[M+H]. For isomer **20**: mp 103–105°C. $[\alpha]_D^{23}=+15.3$ (*c* 3.7, $CHCl_3$); ν_{max} (KBr) 1752, 1643, 1226 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.95 (3H, s), 1.96 (3H, s), 1.99 (3H, s), 2.04 (3H, s), 2.15 (1H, ddddd, $J=15.2$, 8.6, 6.6, 1.3, 1.3 Hz), 2.34 (1H, ddddd, $J=15.2$, 7.3, 2.6, 1.3, 1.3 Hz), 3.36 (1H, ddd, $J=9.2$, 5.9, 2.6 Hz), 3.76 (1H, dd, $J=6.6$, 1.3, Hz), 3.95–4.05 (3H, m), 4.07 (1H, dt, $J=9.2$, 3.3 Hz), 5.01–5.22 (1H, m), 5.11–5.22 (1H, m), 5.33 (1H, dd, $J=3.3$, 2.6 Hz), 5.61 (1H, dddd, $J=17.2$, 10.6, 7.3, 3.3 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.44, 20.51 (2C), 20.56, 30.80, 61.28, 67.49, 67.82, 68.20 (2C), 71.31, 117.45, 133.29, 169.62, 169.72, 169.91, 170.35; HRMS (EI) calcd for $C_{17}H_{25}O_9$: 373.1498. Found: 373.1504 [M+H].

4.10. 3,4,6-Tri-*O*-acetyl-1,2-*O*-[1(-*exo*,*endo*-cyano)-ethylidene]-α-D-galactopyranose 21a and 21b

The title compounds were prepared using a similar procedure to that employed for compound **7α**, by treating compound **16** (500 mg, 1.06 mmol) with TMSOTf (46 mg, 0.20 mmol) and trimethylsilyl cyanide (105 mg, 1.06) in CH_2Cl_2 (5 mL) at −78°C over 0.5 h. Chromatographic purification of the resulting residue (Et_2O–'petrol' 3:7) gave *exo*-**21a** (203 mg, 53%) and *endo*-**21b** (87 mg, 23%) isomers (ratio *exo*/*endo* 7:3). For *exo* isomer **21a**: $[\alpha]_D^{20}=+74.3$ (*c* 1.8, $CHCl_3$); ν_{max} (film) 3025, 2962, 1754, 1430, 1371, 1226 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.76 (3H, s), 1.95 (3H, s), 1.96 (3H, s), 2.01 (3H, s), 4.02 (1H, d, $J=1.3$ Hz), 4.05 (1H, d, $J=1.3$ Hz), 4.20 (1H, d, $J=5.3$ Hz), 4.23 (1H, d, $J=4.6$ Hz), 4.86 (1H, dd, $J=6.6$, 4.0 Hz), 5.27 (1H, dd, $J=3.3$, 2.0 Hz), 5.76 (1H, d, $J=4.6$ Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.13, 20.20, 20.29, 25.57, 61.12, 65.17, 69.60, 70.87, 72.53, 97.06, 98.74, 116.58, 169.41, 169.53, 170.04. For *endo* isomer **21b**: $[\alpha]_D^{20}=+13.2$ (*c*, 2.4, $CHCl_3$); ν_{max} (film) 3019, 1752, 1371, 1214 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$), δ 1.87 (3H, s), 2.04 (3H, s), 2.07 (6H, s), 4.08–4.21 (2H, m), 4.24–4.46 (2H, m), 4.96 (1H, dd, $J=6.6$, 3.3 Hz), 5.42 (1H, dd, $J=7.3$, 2.6 Hz), 5.86 (1H, d, $J=5.3$ Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.38, 20.43, 20.54, 25.80, 61.20, 65.34, 69.82, 71.11, 72.70, 98.54, 98.93, 117.48, 169.43, 169.48, 170.31.

4.11. 2,3,4,6-Tetra-*O*-benzyl-α,β-D-mannopyranosyl cyanide 23 and 24[20]

The title compounds were prepared using a similar procedure to that employed for compound **7α**, by treating propane-1,3-diyl 2,3,4,6-tetra-*O*-benzyl-α-β-D-mannopyranosyl phosphate **22** (500 mg, 0.75 mmol) with TMSOTf (21 mg, 0.094 mmol) and trimethylsilyl cyanide (75 mg, 0.75 mmol) in CH_2Cl_2 (10 mL) at −78°C. Flash chromatographic purification of the obtained residue (Et_2O–'petrol' 4:6) gave a mixture of **23** (204 mg, 49%) and **24** (136 mg, 32%) isomers (ratio 3:2). For isomer **23**: $[\alpha]_D=+30.6$ (*c*, 6.7, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 3.67–3.86 (4H, m), 3.89 (1H, dd, $J=9.2$, 3.3 Hz), 3.98 (1H, t, $J=8.6$ Hz), 4.46 (1H, d, $J=11.9$ Hz), 4.50 (1H, d, $J=10.6$ Hz), 4.54 (1H, d, $J=11.2$ Hz), 4.59 (1H, d, $J=9.2$ Hz), 4.62 (1H, d, $J=11.2$ Hz), 4.64 (2H, m), 4.76 (1H, d, $J=2.6$ Hz), 4.82 (1H, d, $J=10.6$ Hz), 7.14–7.35 (20H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 65.19, 68.36, 72.54, 72.66, 73.31, 73.73, 74.71, 74.98, 77.00, 79.71, 115.36, 127.52, 127.62, 127.70, 127.75, 127.78, 127.81, 128.00, 128.25, 128.40, 128.46, 136.99, 137.66, 137.88, 137.99. For iso-

mer **24**: $[\alpha]_D = -12.5$ (*c*, 3.7, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 3.36 (1H, ddd, $J = 9.9$, 4.0, 3.3 Hz), 3.46 (1H, dd, $J = 9.2$, 2.6 Hz), 3.69–3.70 (2H, m), 3.86 (1H, d, $J = 9.2$ Hz), 3.94 (1H, s), 4.10 (1H, s), 4.48 (1H, d, $J = 11.9$ Hz), 4.49 (1H, d, $J = 9.2$ Hz), 4.52 (1H, m), 4.61 (2H, m), 4.79 (1H, d, $J = 10.6$ Hz), 4.86 (1H, d, $J = 11.9$ Hz), 4.93 (1H, d, $J = 11.9$ Hz), 7.13–7.46 (20H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 67.28, 68.80, 72.42, 73.45, 73.93, 74.14, 74.54, 75.15, 80.32, 82.25, 116.02, 127.48, 127.69, 127.77, 127.80, 127.92, 128.17, 128.23 (2C), 128.26, 128.42, 137.45, 137.62, 137.85, 137.95.

4.12. 3-(2′,3′,4′,6′-Tetra-*O*-benzyl-α,β-D-mannopyranosyl)-1-propene 25 and 26[9]

To a solution of propane-1,3-diyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-mannopyranosyl phosphate **22** (796 mg, 1.19 mmol) in CH_2Cl_2 (10 mL) at −78°C was reacted with TMSOTf (33 mg, 0.15 mmol) and allyltrimethylsilane (136 mg, 1.20 mmol) similar to that detailed in the preparation of compound **8α**. Flash chromatographic purification of the resulting residue (Et_2O–'petrol' 2:8) gave a mixture of anomers **25**[20a] (265 mg, 39%) and **26**[20a] (265 mg, 39%) in the ratio 1:1. For isomer **25**: $[\alpha]_D^{25} = +10.9$ (*c*, 2.2, CHC_3); ^1H NMR (270 MHz, $CDCl_3$) δ 2.25–2.32 (2H, m), 3.38 (1H, q, $J = 6.60$, Hz), 3.56 (1H, dd, $J = 4.6$, 2.6 Hz), 3.66 (1H, d, $J = 3.3$ Hz), 3.69–3.75 (2H, m), 3.77 (1H, dd, $J = 7.3$, 4.6 Hz), 3.96–4.02 (1H, m), 4.45 (1H, d, $J = 11.2$ Hz), 4.48 (1H, d, $J = 12.5$ Hz +1H, unresolved), 4.49 (1H, d, $J = 11.9$ Hz+1H, d, $J = 11.9$ Hz), 4.51 (1H, d, $J = 12.5$ Hz), 4.53 (1H, m), 4.63 (1H, d, $J = 11.2$ Hz), 4.93 (1H, dd, $J = 14.5$, 1.3 Hz), 4.94 (1H, dd, $J = 13.2$, 1.3 Hz), 5.62–5.78 (1H, m), 7.10–7.35 (20H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 34.65, 65.77, 69.17, 71.53, 72.07, 72.30, 73.25, 73.73 (2C), 74.93, 75.28, 76.88, 117.10, 127.42, 127.58, 127.65, 127.67, 127.84, 127.93, 127.95, 128.19, 128.28, 128.33 (2C), 134.34, 138.20, 138.30, 138.31, 138.47; *m*/*z* (CI, NH_3) calcd for $C_{37}H_{44}NO_5$: 582.3219. Found: 582.3224 $[M+NH_4]^+$. For isomer **26**: $[\alpha]_D^{25} = -4.62$ (*c*, 0.43, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 2.21–2.32 (1H, m), 2.40–2.51 (1H, m), 3.25 (1H, dd, $J = 7.3$, 6.6 Hz), 3.37 (1H, q, $J = 6.6$ Hz), 3.53–3.61 (2H, m), 3.63 (1H, d, $J = 6.0$ Hz), 3.69 (1H, dd, $J = 2.6$, 1.3 Hz), 3.81 (1H, appt, $J = 9.9$ Hz), 4.45 (1H, d, $J = 11.9$ Hz) 4.47 (1H, d, $J = 10.6$ Hz+1H, unresolved), 4.49 (1H, d, $J = 11.9$ Hz), 4.55 (1H, d, $J = 11.9$ Hz), 4.63 (1H, d, $J = 12.5$ Hz), 4.71 (1H, d, $J = 11.9$ Hz), 4.79 (1H, d, $J = 10.6$ Hz), 4.93–5.00 (2H, m), 5.56–5.72 (1H, m), 7.10–7.34 20H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 35.69, 65.82, 69.77, 72.47, 73.45, 74.34, 74.83, 75.18, 75.49, 78.26, 79.92, 85.49, 117.21, 127.40, 127.46, 127.51, 127.61, 127.64, 127.67, 127.89, 128.01, 128.08, 128.22, 128.26, 128.3228.37, 134.72, 138.42, 138.45, 138.59, 138.90; *m*/*z* (CI, NH_3) calcd for $C_{37}H_{44}NO_5$: 582.3219. Found: 582.3227 $[M+NH_4]^+$.

4.13. 2,3,4,6-Tetra-*O*-benzyl-α,β-D-glucopyranosyl cyanide 28 and 29[20a]

The title compounds were prepared using similar procedure to that employed for compound **7α**, by treating propane-1,3-diyl 2,3,4,6-tetra-*O*-benzyl-α-β-D-glucopyranosyl phosphate **27** (500 mg, 0.75 mmol) with TMSOTf (21 mg, 0.094 mmol) and trimethylsilyl cyanide (75 mg, 0.75 mmol) in CH_2Cl_2 (10 mL) at −78°C and the reaction mixture was stirred for 0.5 h. Flash chromatographic purification of the obtained residue (Et_2O–'petrol' 3:7) gave a mixture of isomers **28** (198 mg, 48%) and **29** (132 mg, 32%) (ratio 3:2). For isomer **28**: $[\alpha]_D^{28} = +37.3$ (*c*, 1.6, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 3.62–3.68 (2H, m), 3.71 (1H, dd, $J = 3.3$, 2.6 Hz), 3.79 (1H, dd, $J = 3.3$, 2.0 Hz), 3.83 (1H, dd, $J = 3.3$, 2.6 Hz), 3.89 (1H, d, $J = 9.2$ Hz), 4.41 (1H, d, $J = 12.5$ Hz), 4.48 (1H, d, $J = 10.6$ Hz), 4.53 (1H, d, $J = 11.9$ Hz), 4.59 (1H, d, $J = 11.9$ Hz), 4.60 (1H, d, $J = 6.6$ Hz), 4.77 (1H, d, $J = 11.9$ Hz), 4.80 (1H, d, $J = 10.6$ Hz), 4.82 (1H, d, $J = 10.6$ Hz), 4.93 (1H, d, $J = 10.6$ Hz), 7.11–7.38 (20H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 66.87, 67.81, 73.48, 73.83, 75.10, 75.89, 76.14, 76.28, 77.47, 83.08, 115.33, 127.60, 127.71, 127.74, 127.80, 128.03, 128.23, 128.25, 128.36 (2C), 128.29 (2C), 128.68, 137.15, 137.49, 137.89, 138.22; *m*/*z* (CI, NH_3) calcd for $C_{35}H_{39}N_2O_5$: 567.7073. Found: 567.3861 $[M+NH_4]^+$ For isomer **29**: $[\alpha]_D^{28} = +16.7$ (*c*, 1.3, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 3.32–3.38 (1H, m), 3.42 (1H, dd, $J = 9.2$, 2.6 Hz), 3.54–3.63 (2H, m), 3.80 (1H, d, $J = 8.6$ Hz), 3.91 (1H, d, $J = 1.3$ Hz), 4.10 (1H, bs), 4.33 (1H, d, $J = 12.5$ Hz), 4.43 (1H, d, $J = 11.2$ Hz), 4.47 (1H, d, $J = 11.2$ Hz+1H, unresolved), 4.51 (1H, d, $J = 12.5$ Hz), 4.73 (1H, d, $J = 11.9$ Hz), 4.85 (1H, 1H, d, $J = 11.2$ Hz), 4.88 (1H, m), 7.12–7.39 (20H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 67.39, 68.81, 72.56, 73.56, 73.96, 74.61, 75.27, 80.45, 82.33, 83.07, 116.00, 127.59, 127.72, 127.76, 127.79, 127.90, 128.00, 128.04, 128.31, 128.36, 128.40, 128.51, 128.68, 137.43, 137.62, 137.83, 138.20; *m*/*z* (CI, NH_3) calcd for $C_{35}H_{39}N_2O_5$: 567.7073 Found: 567.3861 $[M+NH_4]^+$.

4.14. 3-(2′,3′,4′,6′-Tetra-*O*-benzyl-β-D-glucopyranosyl)-1-propene 30β

To a solution of propane-1,3-diyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranosyl phosphate **27** (792 mg, 1.20 mmol) in CH_2Cl_2 (10 mL) at −78°C was reacted with TMSOTf (33 mg, 0.15 mmol) and allyltrimethylsilane (137 mg, 1.20 mmol) similar to that detailed in the preparation of compound **8α**. Flash chromatographic purification of the resulting residue (Et_2O–'petrol' 3:7) gave **30β** (530 mg, 79%) as the major isomer: $[\alpha]_D^{26} = +20.7$ (*c* 0.9, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.67–1.77 (1H, m), 2.46–2.52 (1H, m), 3.60–3.63 (2H, m), 3.68 (1H, dd, $J = 7.3$, 3.3 Hz), 3.75–3.79 (2H, m), 4.09–4.16 (1H, m), 4.28 (1H, appt, 6.6 Hz), 4.44 (1H, d, $J = 12.5$ Hz), 4.46 (1H, d, $J = 10.6$ Hz), 4.59 (1H, d, $J = 11.9$ Hz), 4.64 (1H, m), 4.67 (1H, d, $J = 11.9$ Hz), 4.78 (1H, d, $J = 10.6$ Hz), 4.79 (1H, d, $J = 10.6$ Hz), 4.91 (1H, d, $J = 10.6$ Hz), 5.04 (1H, dd, $J = 9.2$, 2.0 Hz), 5.08 (1H, dd, $J = 14.5$, 2.0 Hz), 5.74–5.89 (1H, m), 7.11–7.73 (20H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 29.66, 69.05, 71.22, 73.08, 73.48 (2C), 73.73, 75.02, 75.38, 78.18, 80.11, 82.41, 116.82, 127.55, 127.58, 127.68, 127.76, 127.81, 127.86, 127.89, 127.94, 128.31, 128.37, 128.42, 134.28, 138.29 (2C), 138.82 (2C); *m*/*z* (CI, NH_3) calcd for $C_{37}H_{44}NO_5$: 582.3219. Found: 582.3216. $[M+NH_4]$.

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21. Closer examination of Gervay's data suggested that the resonance for the nitrile carbon of compound **24** was absent as were the resonances for the some of the aromatic carbons. In addition the $[\alpha]_D$ [−12.5 (*c*, 3.7); lit.:[20a] −14.9 (*c*, 1.0); lit.:[20b] −51.2 (*c*, 6.6)] was found to be at variance with our findings and with those of Ichikawa, at higher concentrations we found little variance.
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