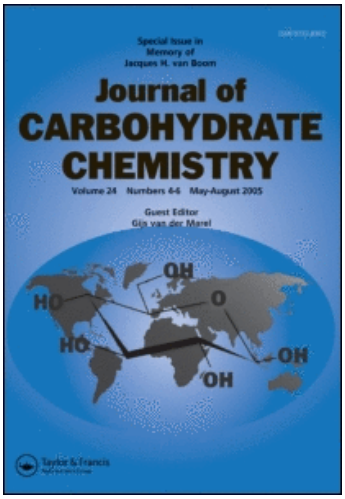

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SYNTHESIS OF GLYCOSIDE DERIVATIVES EMPLOYING THE FERRIER REARRANGEMENT[1]

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ABSTRACT

Various glycals underwent smooth Lewis acid-catalysed allylic rearrangement reactions with *O*-nucleophiles to yield 2,3-unsaturated glycoside derivatives. In the hexose series predominantly α-D-, and in the pentose series β-D-anomers resulted. Among others ω-cyano- as well as ω-benzyloxycarbonylamino functionalised alcohols could be used successfully. With diols the corresponding 1,1'-bridged disaccharides could be obtained.

INTRODUCTION

The *O*-glycosides of 2,3-dideoxy-2,3-unsaturated aldoses can be obtained from glycals by allylic rearrangement in the presence of *O*-nucleophiles and a Lewis or Brønsted acid. Among different glycosylation procedures this method, commonly known as the Ferrier reaction,[2-4] offers several unique features. Even comparatively weak nucleophiles are suiTable for this reaction and usually the corresponding glycosides are obtained in high yields under simple conditions. For glycals of the hexose series the formation of α-anomers prevails.

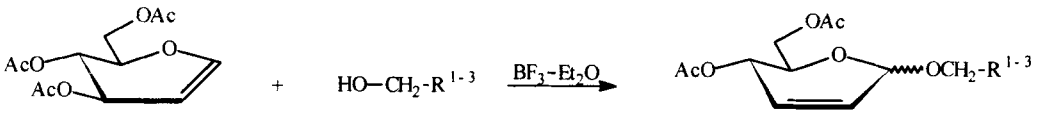
With the unsaturated glycosides a variety of reactions such as the vicinal one-step Sharpless *cis*-oxyamination,[5,6] epoxidations or hydroxylations can be performed.[7] A number of Lewis acid catalysts of various strength such as BF_3-Et_2O,[2] $SnBr_4$, $ZnCl_2$[8] or a non-acid catalyst like iodonium dicollidinium perchlorate have been employed for Ferrier reactions. Also, the use of iodine[9] and cation exchange resin[10] was reported. The application of this method is also attractive because a great number of glycals are easily available as reported.[11-19]

In this paper we present the employment of the Ferrier reaction for the facile formation of functionalised glycosides from various alcohols, alcohols carrying functional groups, hydroxy acid esters, and diols.

RESULTS AND DISCUSSION

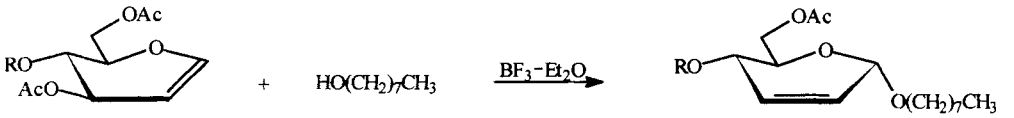
The reaction of 3,4,6-tri-*O*-acetyl-D-glucal **(1)** with various unsaturated alcohols, such as allyl alcohol, 1-pentenol and farnesol in dichloromethane performed at -30 °C under boron trifluoride catalysis led to alkyl 4,6-di-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosides **(2, 3, 4)** in very good yields. Only by reaction with 4-penten-1-ol was an anomeric mixture of α:β = 5:1 obtained, whereas the other alcohols reacted to give the α-anomers exclusively. Compound **3** could be used in turn as glycosyl donor for preparation of 2',3'-dideoxyoligosaccharides. This alternative is of particular interest in cases in which the required acid medium for Ferrier reactions cannot be employed due to concommitant glycoside cleavage.[20,21] In the case of the acyclic sesquiterpene farnesol, several by-products were obtained. Therefore, the labile major product **4** could be isolated only in maximally 47 % yield depending strongly on the amount and the addition rate of Lewis acid (Scheme 1).

Further studies were performed to compare the reactivity of mono- and disaccharide glycals in the Ferrier reaction, and 1-octanol was chosen as a model nucleophile. These reactions were carried out in dry dichloromethane with BF_3-Et_2O and the peracetylated glucal **1**, maltal **5** and cellobial **6**. The results are presented in Scheme 2

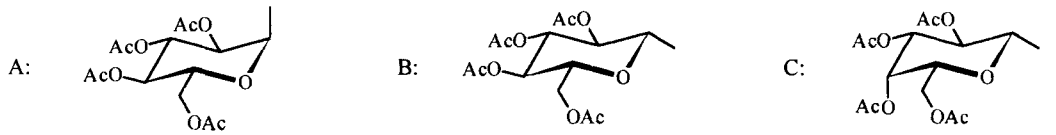


1	R^1: $CH=CH_2$	(91 %)	**2**
	R^2: $CH_2CH_2CH=CH_2$	(89 %)	**3**
	R^3: $CH=C(CH_3)CH_2CH_2CH=C(CH_3)CH_2CH_2CH=C(CH_3)_2$	(47 %)	**4**

Scheme 1



1	R: Ac	**7**	R: Ac
5	R: A	**8**	R: A
6	R: B	**9**	R: B
13	R: C		

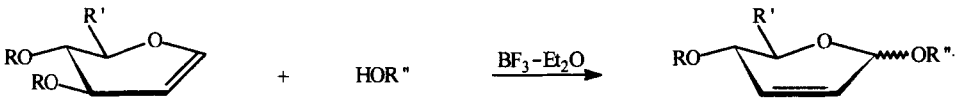


Scheme 2

Table 1

glycal	temperature	time	product	yield
1	-30 °C→-10 °C	10 min	**7**	82 %
5	-20 °C→0 °C	40 min	**8**	85 %
6	-20 °C→0 °C	60 min	**9**	55 %

and Table 1. All compounds are α-anomers, which was additionally confirmed by NMR spectroscopy of the corresponding hydrogenated products.[22] Generally, in order to reach



1, 10-13 **14-18** R": $(CH_2)_2CN$
19-21 R": $(CH_2)_6NHZ$

a good yield in Ferrier reactions with disaccharide glycals higher temperatures, longer reaction times and excess of Lewis acid were required.

Next, an examination of the Ferrier reaction of various glycals with 3-hydroxy propionic acid nitrile and 6-benzyloxycarbonylaminohexan-1-ol was performed. Following reaction with 3-hydroxypropionic acid nitrile, the CN-group could be converted into the corresponding amine, amide or acid. From the products with an NHZ group, the free amine could be isolated after hydrogenation using palladium on carbon in methanol. All glycals reacted with 3-hydroxy propionic acid nitrile under BF_3-Et_2O catalysis to give the corresponding 2,3-unsaturated compounds with good to excellent yields (see Table 2, entries 1-5). Only in the reaction of glycal **10** with a poor leaving-group (OTBDMS) at C-3 was a markedly lower yield observed. This result indicated that a suiTable leaving group at C-3 was essential to realize Ferrier reactions in accepTable yields.[23]

By analogous reaction with 3,4-di-*O*-acetyl-D-xylal (**12**) a mixture of α- and β-*glycero*-pent-2-enopyranosides was obtained with the β-isomer (see Table 2, entry 4). These two anomers could be easily separated by column chromatography on silica gel, and as the major product, the β-anomer was isolated in 64 % yield. The α-anomer **17a** (19 % yield) showed large vicinal coupling between H-4 and both H-5a and H-5e ($J_{4,5a}$ = 8.1, $J_{4,5e}$ = 5.6 Hz) in accord with a favorable $^{O}H_5$(D) conformation.[24] The conformation of the β-anomer **17b** was identified from its ^{1}H NMR-spectrum as ^5H_O(D), because of the characteristic small coupling constants ($J_{4,5a}$ = 2.5 and $J_{4,5e}$ = 1.5 Hz). The position of the H-4 signals of these compounds differed considerably; for compound **17a** this signal appeared as a centered muliplet at δ = 5.23 ppm, whereas for compound **17b** it formed a ddd system at δ = 4.90 ppm.

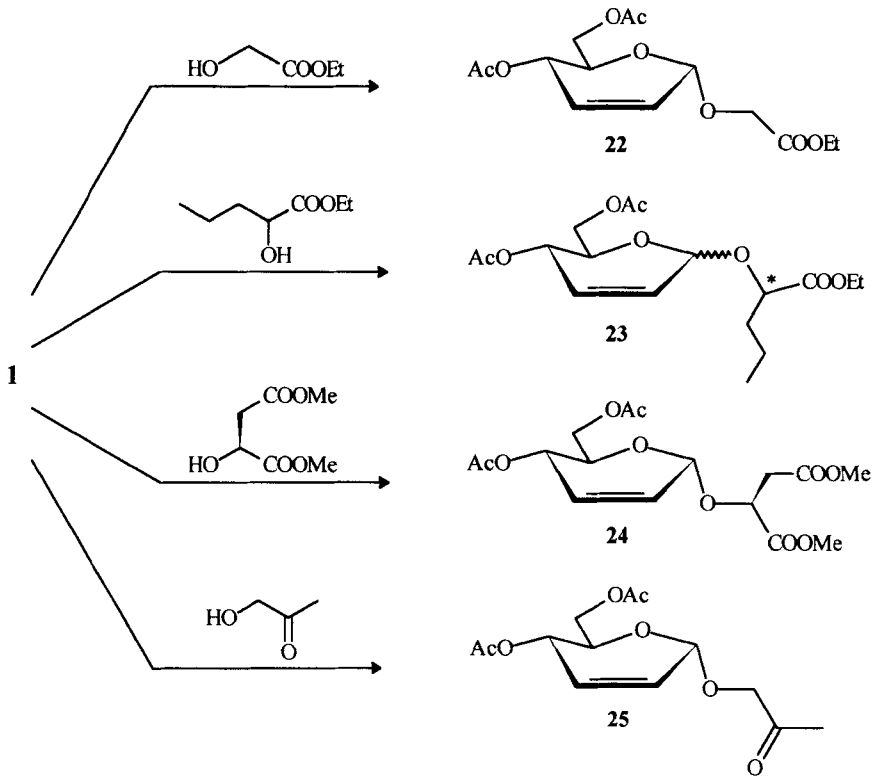
Table 2

entry	R	R'	glycal	temp.[°C]	yield [%]	anomer	product
1	Ac	CH_2OAc	**1**	-20	91	α	**14**
2	OTBDMS H	$CH_2OTBDMS$	**10**	-45	38	α	**15**
3	Ac	CH_3	**11**	-40	80	α	**16**
4	Ac	H	**12**	-30	19 64	α β	**17a** **17b**
5	cf. Scheme 2		**13**	-35	90	α	**18**
6	Ac	CH_2OAc	**1**	-30	75	α	**19**
7	Ac	CH_3	**11**	-40	82	β	**20**
8	cf. Scheme 2		**13**	-20	90	α	**21**

Nucleophile HOR": entry 1-5: HO-$(CH_2)_2$-CN;
entry 6-8: HO-$(CH_2)_6$-NHZ

For Ferrier glycosylation with 6-benzyloxycarbonylaminohexan-1-ol as nucleophile, an excess of catalyst was required because apparently a complex is formed which does not show any reactivity. The results of these reaction are presented in Table 2 (entries 6-8). Optimum yields were obtained in all three cases if boron trifluoride-diethyl etherate was added in small portions at low temperature and the reaction was stopped after about 30 min at 0 °C. In contrast to other glycals which gave α-anomers, the reaction of 3,4-di-*O*-acetyl-D-xylal **(12)** led exclusively to the corresponding β-product **20** in 82 % yield.This result is in accord with previous findings in the pentose series,[25,26] which was justified by the missing influence of the large substituted 5-hydroxymethyl group. Again, the ^1H NMR spectrum of this derivative showed small couplings between H-4 and H-5a or H-5e which indicate the energetically favoured ^5H_O(D)-conformation of the β-D-*glycero*-system.

The only examples of hydroxy acid esters studied as nucleophiles in Ferrier reactions were hydroxyamino acid esters[27] and ethyl 3-hydroxybutyrate.[9] It was decided



Scheme 3

to revisit this reaction (see Scheme 3), and our experiments showed high yields and stereoselecivities in contrast to the previous report.

All the reactions of glycal **1** with various hydroxy acid esters or hydroxy acetone in the presence of boron trifluoride-diethyl etherate in dichloromethane led to the expected alkyl 2,3-dideoxy-α-derivatives. In the case of DL-2-hydroxyvaleric acid ethyl ester an inseparable mixture of diastereoisomeric α,β-anomers **23** (1:1) was obtained, which however, could be identified by ^{1}H NMR spectroscopy.

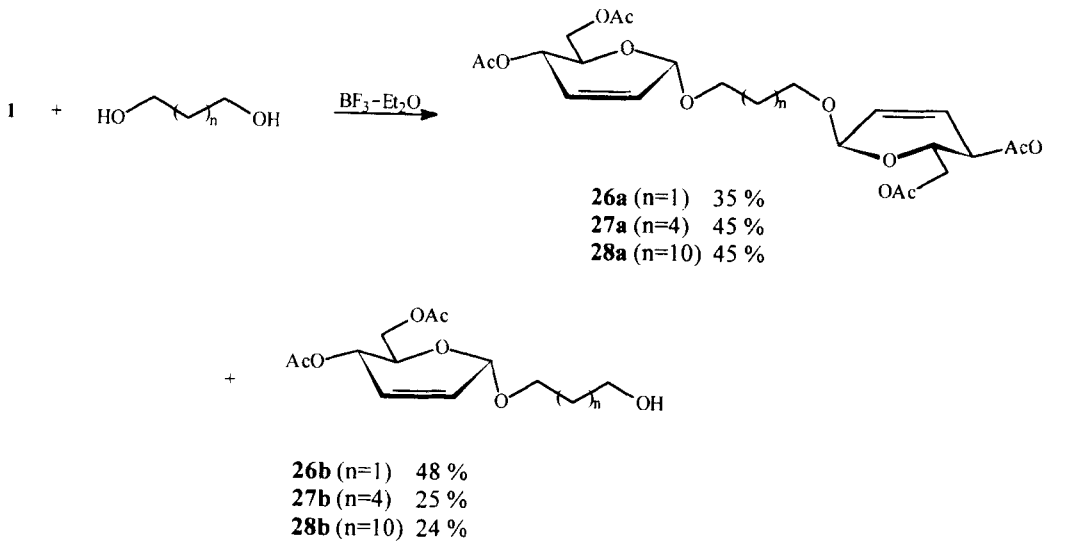
Finally, the Ferrier reaction was studied with diols and diolamines . In the case of diols as model compounds 1,3-propanediol, 1,6-hexanediol and 1,12-dodecanediol were chosen. Treatment of 3,4,6-tri-*O*-acetyl-D-glucal **(1)** with these diols in dry dichloromethane under BF_3-Et_2O catalysis at -20 °C for 30 min and at 0 °C for a few

minutes afforded, after work up, a mixture of two compounds. These were the corresponding 1,1'-bridged disaccharides **(26a, 27a, 28a)** and as a minor products the monosubstituted derivatives **(26b, 27b, 28b)**, which could be easily separated by column chromatography on silica gel (Scheme 4). The yields seem to improve with the increasing length of the carbon chain of these diols. Due to their symmetry, compounds **26a**, **27a** and **28a** showed only a single set of signals for the saccharide part in the NMR spectrum. To confirm the anomeric configuration, one compound was hydrogenated with Pd/C in methanol to furnish a saturated product, which by NMR spectrosopy clearly proved to be the α-anomer.[22]

As final model compounds diethanolamine and 2-amino-1,3-propanediol were chosen. In both compounds the amino functions were protected with Fmoc-groups[28] to give **29** and **30** in 56 and 69 % yield, respectively. This protection was necessary in order to enable a clean reaction without formation of a non-reactive complex between the amine and the Lewis acid. The use of the Fmoc-group is advantageous in this case, because of its acid stability and its easy removal under basic conditions or by hydrogenation. These protected amines **29** and **30** reacted with glycal **1** in the presence of BF_3-Et_2O at low temperature to give 1,1'-bridged disaccharides **31a** and **32a** in 15 and 65 % yield, respectively. As second products, in analogy to the diols, the mono derivatives **31b** and **32b** were identified and isolated in 72 and 26% yield (Scheme 5). The structures of all these new compounds were established by ^1H NMR spectroscopy. For compound **32a** a pure α-configuration was proved, whereas product **31b** was obtained as an anomeric mixture (α:β = 1:1).

EXPERIMENTAL

General methods. All reactions were carried out using dried solvents and were monitored by TLC (Merck, silica gel plates GF_{245}). The products were purified by flash chromatography (Merck, silica gel 60, 230-400 mesh) with distilled solvents. Melting points were determined using a Reichert heating table microscope and are uncorrected. Optical rotations were measured using a Perkin-Elmer 243 polarimeter (sodium D line: 589 nm) in a 10-cm polarimeter cuvette at 20 °C. NMR spectra were recorded with a

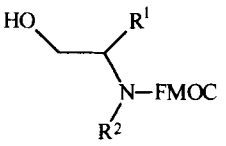


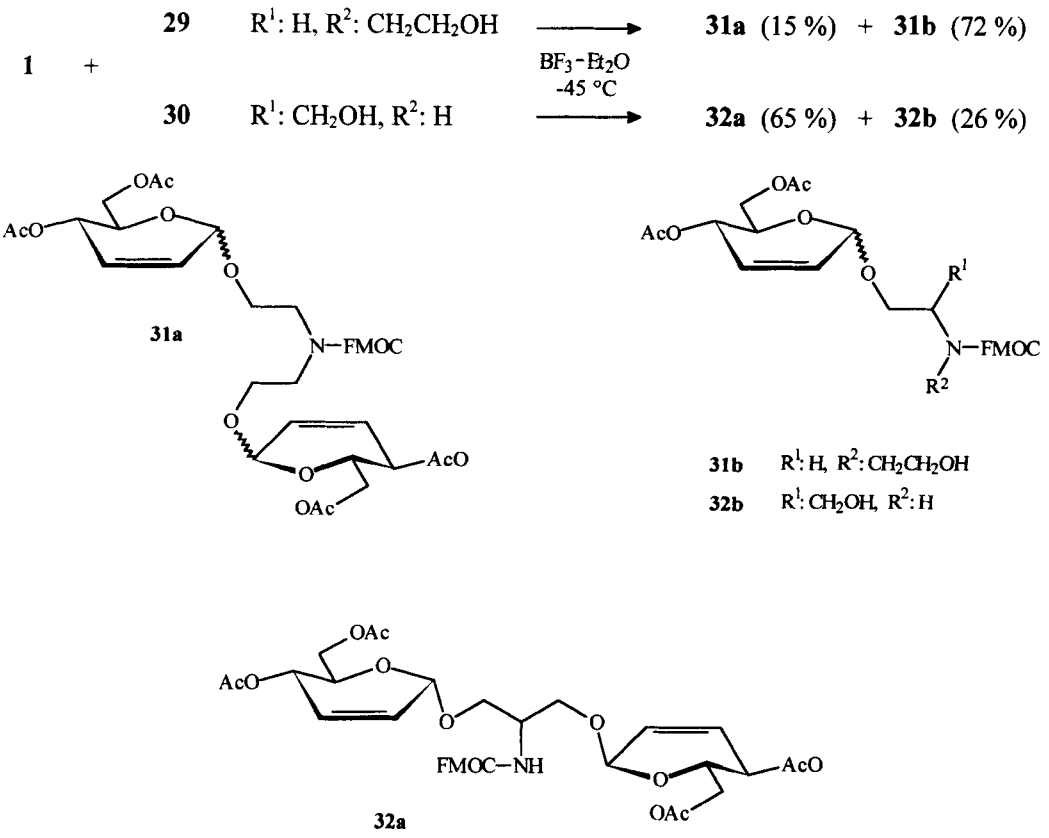
Scheme 4

Bruker AMX-400 spectrometer (400 MHz for ^1H and 100.67 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard.

General procedure for Ferrier reaction. To a solution of glycal and aglycone in anhydrous dichloromethane the catalyst was introduced in one portion at the given temperature. The mixture was stirred until the reaction was complete according to TLC. Then, the reaction mixture was neutralized with saturated sodium hydrogen carbonate solution, washed with water, and the organic phase was dried over $MgSO_4$. After filtration the solvent was evaporated under reduced pressure and the crude product was purified on silica gel.

Allyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2). Tri-*O*-acetyl-D-glucal **(1)** (300 mg, 1.1 mmol), allyl alcohol (90 μL, 1.32 mmol) and BF_3-Et_2O (50 μL) in dichloromethane (10 mL) were converted as described above at -25 °C. The reaction was quenched at -5 °C. Purification by flash chromatography (petroleum ether/EtOAc, 3:1) afforded compound **2** (271 mg, 91 %) as colourless syrup: [α]$^{20}_D$ +108° (*c* 0.5, $CHCl_3$); [lit.[29] [α]$^{20}_D$ +111.5° (*c* 1.2, $CHCl_3$)]; ^1H NMR (400 MHz, $CDCl_3$) δ 5.95 (m, 1H, H-2'-allyl), 5.90 (ddd~brd, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$=10.2 Hz,





Scheme 5

$J_{2,4}$=1.5 Hz,H-2), 5.84 (dd, 1H, $J_{3,4}$=2.5 Hz, H-3), 5.31 (m, 2H, H-1a', H-1b'-allyl), 5.21 (ddd~dd, 1H, $J_{4,5}$ = 10.7 Hz, H-4), 5.08 (bs, 1H, H-1), 4.26 (m, 1H, H-5), 4.25 (dd, 1H, $J_{5,6a}$=5.1 Hz, $J_{6a,6b}$=12.2 Hz, H-6a), 4.19 (dd, 1H, $J_{5,6b}$=2.5 Hz, H-6b), 4.11 (m, 2H, H-3a', H-3b'-allyl), 2.09, 2.07 (each s, each 3H, OAc) ppm.

Pent-4-enyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α,β-D-*erythro*-hex-2-enopyranoside (3). Tri-*O*-acetyl-D-glucal **1** (1.0 g, 3.7 mmol) and 4-penten-1-ol (575 μL, 5.55 mmol)

were treated under BF_3-Et_2O catalysis at -30 °C following the general procedure. The reaction was stopped at 0 °C and the crude product was purified by flash chromatography (petroleum ether/EtOAc, 4:1). 975 mg (89 %) of **3** was obtained as a colourless syrup. $[\alpha]^{20}_D$ +173° (*c* 0.5, $CHCl_3$); α : β = 5 : 1 (according to ^1H NMR); (α-anomer): ^1H NMR (400 MHz, $CDCl_3$) δ 5.88 (ddd~brd, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, $J_{2,4}$ = 1.5 Hz, H-2), 5.83 (dd, 1H, $J_{3,4}$ = 2.5 Hz, H-3), 5.84 (m, 1H, H-2'-pentenyl), 5.31 (ddd~dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.04 (dd, 1H, H-1a'-pentenyl), 5.02 (bs, 1H, H-1), 4.98 (dd, 1H, H-1b'-pentenyl), 4.24 (dd, 1H, $J_{5,6a}$ = 5.6 Hz, $J_{6a,6b}$ = 12.2 Hz; H-6a), 4.18 (dd, 1H, $J_{5,6b}$ = 2.5 Hz, H-6b), 4.11 (ddd, 1H, H-5), 3.79 (m, 1H, H-5a'-pentenyl), 3.53 (m, 1H, H-5b'-pentenyl), 2.14 (m, 2H, H-3a', H-3b'-pentenyl), 2.09, 2.08 (each s, each 3H, OAc), 1.72 (m, 2H, H-4a', H-4b'-pentenyl) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.33, 169.84 (2 C=O), 137.56 (C-4'-pentenyl), 128.58, 127.47 (C-2, C-3), 114.49 (C-5'-pentenyl), 94.02 (C-1), 67.81 (C-6), 66.49, 64.89 (C-4, C-5), 62.62 (C-1'-pentenyl), 29.75, 28.47 (C-2', C-3'-pentenyl), 20.51, 20.34 (2 OAc) ppm.

Anal. Calcd for $C_{15}H_{22}O_6$ (298.3): C, 60.39; H, 7.43. Found: C, 60.11; H, 7.51.

Farnesyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (4). Starting from **1** (1.0 g, 3.7 mmol) and farnesol (1.38 mL, 5.55 mmol) and using the same procedure as for **3**, product **4** was isolated after flash chromatography (petroleum ether/EtOAc, 6:1) as a yellow syrup in 47 % yield (750 mg): $[\alpha]^{20}_D$ +89° (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.88 (dd~d, 1H, $J_{1,2}$ < 1.0 Hz, $J_{2,3}$ = 10.7 Hz, H-2), 5.82 (dt~dd ,1H, $J_{3,4}$=1.5 Hz, H-3), 5.38 (t, 1H, H-2'-farnesyl), 5.30 (dd, 1H, $J_{4,5}$=9.7 Hz, H-4), 5.11 (m, 2H, H-6', H-10'-farnesyl), 5.07 (bs, 1H, H-1), 4.25 (dd, 1H, $J_{5,6a}$=5.6 Hz, $J_{6a,6b}$=12.2 Hz, H-6a), 4.19 (dd, 1H, $J_{5,6b}$=2.5 Hz, H-6b), 4.15 (ddd, 1H, H-5), 4.11 (m, 2H, H-1a', H-1b'-farnesyl), 2.11, 2.08 (each s, each 3H, OAc), 2.05 (m, 8H, 4 CH_2-farnesyl), 1.70, 1.68, 1.60, 1.55 (each s, 3H, CH_3-farnesyl) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.67, 170.17 (2 C=O), 135.39, 135.23, 131.16, 128.85, 127.88, 124.36, 124.13, 119.59 (C-2, C-3, C-2', C-3', C-6', C-7', C-10', C-11'-farnesyl), 93.06 (C-1), 66.71, 65.23 (C-4, C-5), 64.49, 62.97 (C-6, C-1'-farnesyl), 39.52, 39.45, 26.54, 26.41 (C-4', C-5', C-8', C-9'), 25.52, 23.21, 17.46, 15.84 (4 Me-farnesyl), 20.81, 20.64 (2 OAc) ppm.

Anal. Calcd for $C_{25}H_{38}O_6$ (434.6): C, 69.10; H, 8.81. Found: C, 69.01; H, 8.89.

Octyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (7). Tri-*O*-acetyl-D-glucal **1** (200 mg, 0.73 mmol) and 1-octanol (175 μL, 1.1 mmol) were treated at -30 °C in the presence of BF_3-Et_2O according to the general procedure. After purification by flash chromatography (petroleum ether/EtOAc, 2:1) the colourless syrup **7** (206 mg, 82 %) was obtained; [α]$^{20}_D$ -87.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (dd, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.83 (ddd, 1H, $J_{1,3}$ = 1.5 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 5.31 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.02 (brd, 1H, H-1), 4.25 (dd, 1H, $J_{5,6a}$ = 5.1 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.18 (dd, 1H, $J_{5,6b}$=2.0 Hz, H-6b), 4.11 (ddd, 1H, H-5), 3.77 (dt, 1H, H-1a'-octyl), 3.51 (dt, 1H, H-1b'-octyl), 2.11, 2.09 (each s, each 3H, OAc), 1.64-1.52 and 1.40-1.21 (2 m, 12H, H-2' to H-7'-octyl), 0.88 (t, 3H, CH_3) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.43, 169.84 (2 C=O), 129.07, 128.06 (C-2, C-3), 94.49 (C-1), 66.94, 65.39 (C-4, C-5), 69.12, 63.13 (C-6, C-1'-octyl), 31.91, 29.82, 29.47, 29.35, 26.33, 22.74 (C-2'-C-7'-octyl), 21.08, 20.91 (2 OAc), 14.19 (CH_3) ppm.

Anal. Calcd for $C_{18}H_{30}O_6$ (342.4): C, 63.14; H, 8.83. Found: C, 63.12; H, 8.79.

Octyl 6-*O*-Acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (8). Maltal hexaacetate **5** (300 mg, 0.54 mmol) and 1-octanol (130 μL, 0.81 mmol) were treated at -20 °C with of BF_3-Et_2O according to the general procedure. After purification by flash chromatography (petroleum ether/EtOAc, 2:1) compound **8** (287 mg, 85 %) was obtained as white crystals; mp 98 °C; [α]$^{20}_D$ = -115.6° (*c*=1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (m, 2H, H-2, H-3), 5.35 (dd~t, 1H, H-3'), 5.24 (d, 1H, $J_{1',2'}$=4.1 Hz, H-1'), 5.01 (t, 1H, $J_{3',4'}$ = 9.9 Hz, $J_{4',5'}$ = 9.7 Hz, H-4'), 4.91 (bs, 1H, $J_{1,2}$ < 1.0 Hz, H-1), 4.78 (dd, 1H, $J_{2',3'}$ = 10.2 Hz, H-2'), 4.26 (dd, 1H, $J_{5',6a'}$ = 4.0 Hz, $J_{6a',6b'}$ = 12.2 Hz, H-6a'), 4.23-3.95 (m, 6H, H-4, H-5, H-6a, H-6b, H-5', H-6b'), 3.69 (dt, 1H, H-1a'-octyl), 3.43 (dt, 1H, H-1b'-octyl), 2.09, 2.07, 2.03, 1.99, 1.97 (each s, each 3H, OAc), 1.59-1.49 und 1.35-1.17 (2 m, 12H, H-2' to H-7'-octyl), 0.81 (t, 3H, CH_3) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 169.64, 169.56, 169.25, 168.97, 168.54 (5 C=O), 127.32, 127.03 (C-2, C-3), 93.27, 93.09 (C-1, C-1'), 76.02, 75.69, 69.76, 68.84, 67.20, 66.32 (C-4, C-5, C-2', C-3', C-4', C-5'), 68.06 (C-1'-octyl), 60.69, 59.37 (C-6, C-6'), 30.83, 28.74, 28.39, 28.23, 25.25, 21.63 (C-2'-C-7'-octyl), 20.38, 20.02, 19.81, 19.65, 19.58 (5 OAc), 13.07 (CH_3) ppm.

Anal. Calcd for $C_{30}H_{46}O_{14}$ (630.7): C, 57.13; H, 7.35. Found: C, 57.42; H, 7.41.

Octyl 6-*O*-Acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (9). Cellobial hexaacetate **6** (300 mg, 0.54 mmol) and 1-octanol (130 µL, 0.81 mmol) were treated at -20 °C in the presence of BF_3-Et_2O as described above. After purification by flash chromatography (petroleum ether/EtOAc, 2:1) compound **9** (187 mg, 55 %) was obtained as white crystals; mp 102 °C; [α]$^{20}_D$ -75.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (d, 1H, $J_{1,2}$<1.0 Hz, $J_{2,3}$=10.2 Hz, H-2), 5.69 (dt, 1H, $J_{1,3}$ = 1.5 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 5.12 (dd~t, 1H, H-4'), 4.99 (t, 1H, $J_{3',4'}$ = 9.7 Hz, $J_{4',5'}$ = 9.2 Hz, H-3'), 4.91 (dd, 1H, $J_{1',2'}$ = 8.1 Hz, $J_{2',3'}$ = 9.7 Hz, H-2'), 4.89 (brd, 1H, H-1), 4.54 (d, 1H, H-1'), 4.21 (dd, 1H, $J_{5',6b'}$ = 2.0 Hz, $J_{6a',6b'}$ = 12.2 Hz; H-6b'), 4.15 (dd, 1H, $J_{5,6a}$ = 4.6 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.13-4.04 (m, 3H, H-4, H-6b, H-6a'), 3.94 (ddd, 1H, $J_{5',6'}$ = 5.1 Hz, H-5'), 3.69-3.61 (m, 2H, H-5, H-1a'-octyl), 3.39 (dt, 1H, H-1b'-octyl), 2.09, 2.07, 2.01, 1.96, 1.92 (each s, each 3H, OAc), 1.66-1.48 und 1.33-1.15 (2 m, 12H, H-2'-H to 7'-octyl), 0.81 (t, 3H, CH_3) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.11, 169.68, 169.55, 169.21, 168.34 (5 C=O), 130.17, 126.29 (C-2, C-3), 100.72, 93.39 (C-1, C-1'), 72.47, 71.77, 70.82, 70.40, 67.37, 66.39 (C-4, C-5, C-2', C-3', C-4', C-5'), 67.90 (C-1'-octyl), 62.14, 60.93 (C-6, C-6'), 30.81, 28.71, 28.37, 28.24, 25.22, 21.63 (C-2'-C-7'-octyl), 20.01, 19.82, 19.66, 19.55, 19.51 (5 OAc), 13.18 (CH_3) ppm.

Anal. Calcd for $C_{30}H_{46}O_{14}$ (630.7): C, 57.13; H, 7.35. Found: C, 57.33; H, 7.45.

2-Cyanoethyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (14). Tri-*O*-acetyl-D-glucal **1** (500 mg, 1.84 mmol) und 3-hydroxypropionic acid nitrile (200 µL, 2.76 mmol) dissolved in dichloromethane (50 mL), were treated in the presence of BF_3-Et_2O at -20 °C according to the general procedure. The reaction was stopped at 0 °C and after purification by flash chromatography (petroleum ether/EtOAc, 3:1) the yellow syrup **14** (473 mg, 91 %) was obtained; [α]$^{20}_D$ +28.5° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (dd ~ d,1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.77 (dt, 1H, $J_{1,3}$ = 2.0 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 5.25 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.01 (brs, 1H, H-1), 4.16 (m, 2H, H-6a, H-6b), 4.07 (m, 1H, H-5), 3.90 (m, 1H, H-1a'-nitrile), 3.73 (m, 1H, H-1b'-nitrile), 2.62 (m, 2H, H-2a', H-2b'-nitrile), 2.05, 2.02 (each s, each 3H, OAc) ppm.

Anal. Calcd for $C_{13}H_{17}O_6N$ (283.3): C, 55.12; H, 6.05; N, 4.94. Found: C, 55.07; H, 6.09; N, 4.86.

2-Cyanoethyl 6-*O*-*tert*-Butyldimethylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (15). 1,5-Anhydro-2-deoxy-3,6-di-*O*-*tert*-butyldimethylsilyl-D-*arabino*-hex-1-enitol (**10**)[28] (250 mg, 0.66 mmol) and 3-hydroxypropionic acid nitrile (70 μL, 1.0 mmol) were treated in the presence of $SnBr_4$ (100 μL 1M solution) in dichloromethane (15 mL) at -45 °C according to the general procedure. Flash chromatography (toluene/EtOAc, 3:1) of the residue gave compound **15** (79 mg, 38 %) as colourless syrup; [α]$^{20}_D$ +32.6° (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (dd~d, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.62 (dt, 1H, $J_{1,3}$ = 1.0 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 4.88 (d~brs, 1H, H-1), 4.06 (ddd, 1H, $J_{4,OH}$ = 4.1 Hz, $J_{4,5}$ = 8.6 Hz, H-4), 3.83 (dd, 1H, $J_{5,6a}$ = 6.1 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 3.81 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, H-6b), 3.72-3.60 (m, 3H, H-5, H-1a', H-1b'-nitrile), 2.62-2.52 (m, 2H, H-2a', H-2b'-nitrile), 0.79 (s, 9H, CMe_3), 0.02 (s, 6H, Si-Me) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 133.61, 125.12 (C-2, C-3), 117.79 (CN), 94.79 (C-1), 70.78, 66.69 (C-4, C-5), 65.18, 63.34 (C-6, C-1a'-nitrile), 25.99 (3C, *tert*-butyl), 19.34 (C-2'-nitrile), 18.41 (q, Si-C), -5.34, -5.41 (2C, Si-Me) ppm.

Anal. Calcd for $C_{15}H_{27}O_4NSi$ (313.5): C, 57.47; H, 8.68; N, 4.47. Found: C, 57.23; H, 8.77; N, 4.41.

2-Cyanoethyl 4-*O*-Acetyl-2,3,6-trideoxy-α-D-*erythro*-hex-2-enopyranoside (16). 3,4-Di-*O*-acetyl-D-rhamnal (**11**) (150 mg, 0.7 mmol) and 3-hydroxypropionic acid nitrile (80 μL, 1.11 mmol) dissolved in dichloromethane (10 mL), were treated in the presence of BF_3-Et_2O at -40 °C according to the general procedure. The reaction was stopped of at -15 °C and after purification by flash chromatography (petroleum ether/EtOAc, 3:1) the yellow syrup **16** (126 mg, 80 %) was obtained; [α]$^{20}_D$ +136.8° (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd~dd,1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, $J_{2,4}$ = 1.5 Hz, H-2), 5.77 (ddd~dd, 1H, $J_{1,3}$ = 2.0 Hz, $J_{3,4}$ = 3.0 Hz, H-3), 5.03 (ddd, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 4.98 (bs, 1H, H-1), 3.97 (dd, 1H, $J_{5,6}$ = 6.1 Hz, H-5), 3.93 (m, 1H, H-1a'-nitrile), 3.73 (m, 1H, H-1b'-nitrile), 2.63 (m, 2H, H-2a', H-2b'-nitrile), 2.06 (s, 3H, OAc), 1.21 (d, 3H, H-6) ppm.

Anal. Calcd for $C_{11}H_{15}O_4N$ (225.2): C, 58.66; H, 6.71; N, 6.22. Found: C, 58.49; H, 6.69; N, 6.11.

2-Cyanoethyl 4-*O*-Acetyl-2,3-dideoxy-α-D-*glycero*-pent-2-enopyranoside (17a) and **2-Cyanoethyl 4-*O*-acetyl-2,3-dideoxy-β-D-*glycero*-pent-2-enopyranoside (17b).** Di-*O*-acetyl-D-xylal (**11**) (400 mg, 2.0 mmol) and 3-hydroxypropionic acid nitrile (205 μL, 3.0 mmol) dissolved in dichloromethane (20 mL) were treated in the presence of BF_3-Et_2O at -30 °C according to the general procedure. The reaction was stopped after 5 min at -20 °C and the anomers were separated by flash chromatography (petroleum ether/EtOAc, 3:1). Products **17a** and **17b** were isolated as colourless syrups in 19 % (80 mg) and 64 % yield (270 mg), respectively; **17a**: $[\alpha]^{20}_D$ +113.2° (*c* 1.5, $CHCl_3$). **17b**: $[\alpha]^{20}_D$ +39.4° (*c* 0.5, $CHCl_3$); α:β = 1 : 3.5; **17a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (dd, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.80 (ddd~dt, 1H, $J_{1,3}$ = 2.0 Hz, $J_{3,4}$ = 2.0 Hz, H-3), 5.23 (m, 1H, H-4), 4.94 (bs, 1H, H-1), 3.90 (m, 1H, H-1a'-nitrile), 3.82 (dd, 1H, $J_{4,5e}$ = 5.6 Hz, $J_{5a,5e}$ = 11.2 Hz; H-5e), 3.74 (dd, 1H, $J_{4,5a}$ = 8.1 Hz, H-5a), 3.68 (m, 1H, H-1b'-nitrile), 2.59 (m, 2H, H-2a', H-2b'-nitrile), 1.98 (s, 3H, OAc) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.39 (C=O), 129.57, 128.07 (C-2, C-3),117.57 (CN), 94.45 (C-1), 64.61 (C-4), 63.00, 60.18 (C-5, C-1'-nitrile), 20.85 (OAc), 19.11 (C-2'-nitrile) ppm. **17b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (ddd~dd, 1H, $J_{1,3}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 5.1 Hz, H-3), 5.96 (dd, 1H, $J_{1,2}$ = 2.5 Hz, H-2), 4.94 (d, 1H, H-1), 4.90 (ddd, 1H, $J_{4,5a}$ = 2.5 Hz, $J_{4,5e}$ = 1.5 Hz, H-4), 4.11 (dd, 1H, $J_{5a,5e}$ = 13.7 Hz, H-5a), 3.90 (m, 1H, H-1a'-nitrile), 3.80 (dd, 1H, H-5e), 3.69 (m, 1H, H-1b'-nitrile), 2.59 (m, 2H, H-2a', H-2b'-nitrile), 2.02 (s, 3H, OAc) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.46 (C=O), 129.82, 125.49 (C-2, C-3),117.55 (CN), 93.34 (C-1), 62.89 (C-4), 62.86, 61.50 (C-5, C-1'-nitrile), 20.98 (OAc), 19.07 (C-2'-nitrile) ppm.

Anal. Calcd for $C_{10}H_{13}O_4N$ (211.2): C, 56.87; H, 6.20; N, 6.63. Found: **17a**: C, 56.78; H, 6.09; N, 6.51; **17b**: C, 56.94; H, 6.24; N, 6.59.

2-Cyanoethyl 6-*O*-Acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (18). Hexaacetyl lactal **13** (1.0 g, 1.78 mmol) and 3-hydroxypropionic acid nitrile (190 μL, 2.67 mmol) were treated as described above under BF_3-Et_2O catalysis at -35 °C. The reaction was stopped at -20 °C. Flash chromatography (petroleum ether/EtOAc, 3:1) gave **18** (918 mg, 90 %) as crystalline solid: mp 122 °C; $[\alpha]^{20}_D$ +44.4° (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14

(dd~d, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.76 (dt, 1H, $J_{1,3}$ = 2.0 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 5.39 (dd, 1H, $J_{3',4'}$ = 3.6 Hz, $J_{4',5'}$ = 1.0 Hz, H-4'), 5.21 (dd, 1H, $J_{1',2'}$ = 8.1 Hz, $J_{2',3'}$ = 10.2 Hz, H-2'), 5.03 (brs, 1H, H-1), 5.01 (dd, 1H, H-3'), 4.58 (d, 1H, H-1'), 4.33 (dd, 1H, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 11.7 Hz, H-6a), 4.19 (dd, 1H, $J_{5',6a'}$ = 6.6 Hz, $J_{6a',6b'}$ = 11.2 Hz, H-6a'), 4.17-4.08 (m, 3H, H-4, H-6b, H-6b'), 4.04 (ddd, 1H, $J_{4,5}$ = 9.7 Hz, $J_{5,6b}$ = 5.1 Hz, H-5), 3.96-3.90 (m, 2H, H-5', H-1a"-nitrile), 3.78 (m, 1H, H-1b"-nitrile), 3.68 (m, 2H, H-2a", H-2b"-nitrile), 2.16, 2.12, 2.08, 2.05, 1.98 (each s, each 3H, OAc)ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.61, 170.36, 170.23, 170.08, 169.39 (5 C=O), 132.12, 126.12 (C-2, C-3), 117.53 (CN), 102.29 (C-1'), 94.84 (C-1), 73.09, 70.84, 79.79, 68.82, 67.88, 66.86 (C-4, C-5, C-2', C-3', C-4', C-5'), 63.39, 62.94, 61.19 (C-6, C-6', C-1"-nitrile), 20.85, 20.67, 20.64, 20.54, 20.49 (5 OAc), 19.11 (C-2"-nitrile) ppm.

Anal. Calcd for $C_{25}H_{33}O_{14}N$ (571.5): C, 52.54; H, 5.82; N, 2.45. Found: C, 52.20; H, 5.89; N, 2.41.

***N*-Benzyloxycarbonyl-6-aminohexyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (19).** Tri-*O*-acetyl-D-glucal **1** (355 mg, 1.30 mmol) and 6-benzyloxycarbonylaminohexan-1-ol (490 mg, 1.95 mmol), dissolved in dichloromethane (20 mL) were treated in the presence of BF_3-Et_2O (350 μL, 2.8 mmol) at -30 °C analogous to the general procedure. Within 1 h the reaction mixture was warmed to 0 °C and stirred until the reaction was complete according to TLC. After purification by flash chromatography (toluene/EtOAc, 3:1→2:1) a slightly yellow syrup **19** (589 mg, 75 %) was obtained; [α]$^{20}_D$ +94.5° (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.13 (m, 5H, H-Ar), 5.88 (dd~d, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.82 (ddd ~ dt, 1H, $J_{1,3}$ = 1.5 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 5.31 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.09 (s, 2H, CH_2-Ph), 5.01 (brs, 1H, H-1), 4.74 (brs, 1H, N-H), 4.25 (dd, 1H, $J_{5,6a}$ = 5.1 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.17 (dd, 1H, $J_{5,6b}$ = 2.5 Hz, H-6b), 4.09 (ddd, 1H, H-5), 3.76 (dt, 1H, H-1a'-hexyl), 3.49 (dt, 1H, H-1b'-hexyl), 3.19 (m, 2H, H-6a', H-6b'-hexyl), 2.10, 2.08 (each s, each 3H, OAc), 1.65-1.27 (m, 8H, H-2ab', H-3ab', H-4ab', H-5ab'-hexyl) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.32, 170.11, 169.84 (2 C=O), 136.21-124.85 (C-2, C-3, Ph-C), 93.97 (C-1), 68.34 (CH_2 -Ph), 66.45 (C-4), 66.16 (C-1'-hexyl), 64.92 (C-5), 62.61

(C-6), 40.56 (C-6'-hexyl), 29.50, 29.18, 26.08, 25.49 (C-2', C-3', C-4', C-5'-hexyl), 20.52, 20.34 (2 OAc) ppm.

Anal. Calcd for $C_{23}H_{33}O_8N$ (451.5): C, 61.18; H, 7.37; N, 3.10. Found: C, 61.11; H, 7.32; N, 3.06.

***N*-Benzyloxycarbonyl-6-aminohexyl 4-*O*-Acetyl-2,3-dideoxy-β-D-*glycero*-pent-2-enopyranoside (20).** Starting from di-*O*-acetyl-D-xylal **(12)** (265 mg, 1.33 mmol) and 6-benzyloxycarbonylaminohexan-1-ol (500 mg, 2.00 mmol) the corresponding experiment as described above at -40 °C and under BF_3-Et_2O catalysis (350 µL, 2.8 mmol) afforded after flash chromatography (toluene/EtOAc, 3:1) product **20** (425 mg, 82 %) as yellow syrup; [α]$^{20}_D$ +69.7° (*c* 0.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.26 (m, 5H, H-Ar), 6.06 (dd, 1H, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 5.1 Hz, H-3), 6.02 (dd, 1H, $J_{1,2}$ = 2.5 Hz, H-2), 5.09 (s, 2H, CH_2-Ph), 4.98 (d, 1H, H-1), 4.94 (m, 1H, H-4), 4.71 (bs, 1H, N-H), 4.15 (dd, 1H, $J_{4,5a}$ = 3.1 Hz, $J_{5a,5e}$ = 13.2 Hz, H-5a), 3.82 (dd~d, 1H, $J_{4,5e}$<1.0 Hz, H-5e), 3.76 (dt, 1H, H-1a'-hexyl), 3.47 (dt, 1H, H-1b'-hexyl), 3.19 (m, 2H, H-6a', H-6b'-hexyl), 2.08 (s, OAc), 1.64-1.31 (m, 8H, H-2ab', H-3ab', H-4ab', H-5ab'-hexyl) ppm.

Anal. Calcd for $C_{21}H_{29}O_6N$ (391.5): C, 64.43; H, 7.47; N, 3.58. Found: C, 64.32; H, 7.51; N, 3.49.

***N*-Benzyloxycarbonyl-6-aminohexyl 4-*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-galacto-pyranosyl)-6-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (21).** Hexa-*O*-acetyl lactal **13** (1.5 g, 2.68 mmol) and 6-benzyloxycarbonylaminohexan-1-ol (1.02 g, 4.02 mmol), dissolved in dichloromethane (40 mL) were treated in the presence of BF_3-Et_2O (700 µL, 5.6 mmol) at -20 °C according to the general procedure. Within 1 h the reaction mixture was warmed to 0 °C and stirred until the reaction was complete according to TLC. After purification by flash chromatography (toluene/EtOAc, 3:1) the crystalline solid **21** (1.82g, 90 %) was obtained; mp 62 °C; [α]$^{20}_D$ +54.4° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.13 (m, 5H, H-Ar), 6.08 (dd~d, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.74 (ddd~dt, 1H, $J_{1,3}$ = 2.0 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 5.38 (dd, 1H, $J_{3',4'}$ = 3.1 Hz, $J_{4',5'}$ = 1.0 Hz, H-4'), 5.20 (dd, 1H, $J_{1',2'}$ = 7.6 Hz, $J_{2',3'}$ = 10.2 Hz, H-2'), 5.09 (s, 2H, CH_2-Ph), 5.01 (dd, 1H, H-3'), 4.95 (dd~d, 1H, H-1), 4.57 (d, 1H,

H-1'), 4.27 (dd, 1H, $J_{6a,6b}$ = 11.7 Hz, H-6a), 4.21-4.08 (m, 4H, H-4, H-6b, H-6a', H-6b'), 4.00 (ddd, 1H, $J_{4,5}$ = 9.2 Hz, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 5.1 Hz, H-5), 3.92 (ddd, 1H, $J_{5',6a'}$ = 6.6 Hz, $J_{5',6b'}$ = 7.1 Hz, H-5'), 3.72 (dt, 1H, H-1a"-hexyl), 3.45 (dt, 1H, H-1b"-hexyl), 3.19 (m, 2H, H-6a", H-6b"-hexyl), 2.15, 2.11, 2.08, 2.05, 1.99 (each s, each 3H, OAc), 1.63-1.24 (m, 8H, H-2ab', H-3ab', H-4ab', H-5ab'-hexyl) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.89, 170.73, 170.55, 170.41, 170.25, 169.62 (5 C=O, C=O-amide), 131.39, 129.19, 128.67, 128.38, 128.26, 128.24, 127.35, 125.46 (C-2, C-3, C-Ar), 102.49 (C-1'), 94.55 (C-1), 73.65, 71.02, 70.88, 68.99, 67.54, 67.03 (C-4, C-5, C-2', C-3', C-4', C-5'), 68.78 (CH_2-Z), 63.30, 62.89, 61.44 (C-6, C-6', C-1"-hexyl), 41.19 (C-6"-hexyl), 32.72, 29.75, 26.68, 26.09 (C-2", C-3", C-4", C-5"-hexyl), 21.62, 21.04, 20.83, 20.81, 20.71 (5 OAc) ppm.

Anal. Calcd for $C_{36}H_{54}O_{16}N$ (756.8): C, 57.13; H, 7.19; N, 1.85. Found: C, 57.04; H, 7.02; N, 1.80.

Carboxyethylmethyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (22). Tri-*O*-acetyl-D-glucal **1** (1.0 g, 3.7 mmol) and ethyl hydroxyacetate (700 μL, 7.4 mmol) were treated under BF_3-Et_2O catalysis at -35 °C according to the general procedure. The crude product was purified on silica gel with petroleum ether/EtOAc (3:1) to give **22** (1.05 g, 91 %) as colourless syrup; [α]$^{20}_D$ +255° (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (dd~d, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.91 (ddd~dt, 1H, $J_{1,3}$ = 1.5 Hz, $J_{3,4}$ = 2.0 Hz, H-3), 5.35 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.14 (brs, 1H, H-1), 4.32-4.12 (m, 7H, H-5, H-6a, H-6b, H-2a', H-2b'-acid, CH_2-ester), 2.10, 2.08 (each s, each 3H, OAc), 1.29 (t, 3H, CH_3-ester) ppm.

Anal. Calcd for $C_{14}H_{20}O_8$ (316.3): C, 53.16; H, 6.33. Found: C, 52.98; H, 6.33.

1-Carboxyethylbutyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α,β-D-*erythro*-hex-2-enopyranoside (23). Tri-*O*-acetyl-D-glucal **1** (200 mg, 0.73 mmol) and ethyl D,L-2-hydroxyvalerate (220 μL, 1.46 mmol) were treated in the presence of BF_3-Et_2O at -30 °C according to the general procedure. The crude product was purified on silica gel with petroleum ether/EtOAc (4:1) to give a mixture of α- and β-pyranosides (1:1) of **23** (245 mg, 93 %) as colourless syrup; [α]$^{20}_D$ +99.8° (*c* 1.0, $CHCl_3$); (α-anomer): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (dd~d, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 10.7 Hz, H-2), 5.85 (ddd~dt, 1H, $J_{1,3}$ = 1.5 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 5.39 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.05 (d~brs,

1H, H-1), 4.37-4.14 (m, 4H, H-6a, H-6b, CH_2-ester), 4.09 (ddd, 1H, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 5.6 Hz, H-5), 4.03 (H-2'-acid), 2.08, 2.07 (each s, each 3H, OAc), 1.75 (m, 2H, H-3a', H-3b'-acid), 1.45 (m, 2H, H-4a', H-4b'-acid), 1.29 (t, 3H, CH_3-ester), 0.95 (t, 3H, CH_3-acid) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 172.03, 170.85 (2 C=O), 170.55 (COOEt), 128.78, 127.09 (C-2, C-3), 92.82 (C-1), 74.61 (C-2'-acid), 66.97, 64.77 (C-4, C-5), 62.59, 60.52 (C-6, CH_2-ester), 34.59 (C-3'-acid), 20.50, 20.29 (2 OAc), 18.59 (C-4'-acid), 13.79, 13.75 (2 CH_3) ppm.

Anal. Calcd for $C_{17}H_{25}O_8$ (357.4): C, 57.13; H, 7.05. Found: C, 56.99; H, 7.45.

Dimethyl *O*-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-L-(-)-malate (24). Tri-*O*-acetyl-D-glucal **1** (220 mg, 0.81 mmol) and dimethyl-L-malate (160 µL, 1.20 mmol) were treated in the presence of BF_3-Et_2O at -45 °C according to the general procedure. The crude product was purified on silica gel with toluene/EtOAc (3:1) to give **24** (255 mg, 84 %) as colourless syrup; [α]$^{20}_D$ +55.6° (*c* 0.75, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.94 (dd~d, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.79 (ddd~dt, 1H, $J_{1,3}$ = 1.5 Hz, $J_{3,4}$ = 2.0 Hz, H-3), 5.38 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.20 (brs,1H, H-1), 4.51 (dd, 1H, J_{gem} = 16.8 Hz, CH), 4.30-4.17 (m, 3H, H-5, H-6a, H-6b), 3.77, 3.71 (each s, each 3H, COOMe), 2.88 (dd, 1H, CH_2-eq), 2.79 (dd, 1H, $J_{4,5}$ = 9.7 Hz, $J_{CH,CHeq}$ = 4.6 Hz, $J_{CH,CHax}$ =6.1 Hz, CH_2-ax), 2.09, 2.07 (each s, each 3H, OAc) ppm.

Anal. Calcd for $C_{16}H_{22}O_{10}$ (374.4): C, 51.34; H, 5.92. Found: C, 51.07; H, 5.92.

2-Oxopropyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranside (25). Tri-*O*-acetyl-D-glucal **1** (1.0 g, 3.7 mmol) and hydroxyacetone (555 µL, 7.4 mmol) were treated in the presence of BF_3-Et_2O at -30 °C according to the general procedure. Purification by flash chromatography (petroleum ether/EtOAc,3:1) afforded **25** (862 mg, 82 %) as colourless syrup; [α]$^{20}_D$ +87° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.95 (dd~d, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.91 (ddd~dt, 1H, $J_{1,3}$ = 1.5 Hz, $J_{3,4}$ = 2.0 Hz, H-3), 5.33 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.07 (brs, 1H, H-1), 4.27 (d, 2H, H-1a', H-1b'-propanone), 4.25-4.12 (m, 3H, H-5, H-6a, H-6b), 2.18 (s, 3H, Me-propanone), 2.09, 2.08 (each s, each 3H, OAc) ppm.

Anal. Calcd for $C_{13}H_{18}O_7$ (286.3): C, 54.54; H, 6.34. Found: C, 54.60; H, 6.30.

Bis - 1,3 - (4,6 -di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyloxy)-pro-pane (26a) and **3-Hydroxypropyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-**

enopyranoside (26b). Tri-*O*-acetyl-D-glucal **1** (600 mg, 2.2 mmol) and 1,3-propanediol (80 μL, 1.1 mmol) were treated in the presence of BF_3-Et_2O at -20 °C according to the general procedure. After 3 min the reaction was stopped at -10 °C. The crude product was fractioned on silica gel with petroleum ether/EtOAc (2:1) to give **26a** (184 mg, 35 %) and **26b** (145 mg, 48 %) as colourless syrups. **26a**: [α]$^{20}_D$ +169.4° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd~d, 2H, $J_{1,2}$ = 0.8 Hz, $J_{2,3}$ = 10.2 Hz, $J_{2,4}$ = 1.5 Hz, H-2,2'), 5.81 (dd, 2H, $J_{3,4}$ = 2.0 Hz, H-3,3') 5.31 (dd, 2H, $J_{4,5}$ = 9.6 Hz, H-4,4'), 5.02 (brs, 2H, H-1,1'), 4.25 (dd, 2H, $J_{5,6a}$ = 5.1 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a,6a'), 4.16 (dd, 2H, $J_{5,6b}$ = 2.5 Hz, H-6b,6b'), 4.09 (ddd, 2H, H-5,5'), 3.87 (m, 2H, H-1a",1a'"-propane), 3.61 (m, 2H, H-1b",1b'"), 2.11, 2.09 (each s, each 3H, OAc), 1.93 (m, 2H, H-2"-propane) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.29, 169.81 (4 C=O), 128.67, 127.35 (C-2,2', C-3,3'), 94.16 (C-1,1'), 66.49 (C-5,5'), 65.33 (C-1",1'"-propane), 64.84 (C-4,4'), 62.54 (C-6,6'), 29.69 (C-2"-propane), 20.49, 20.35 (4 OAc) ppm.

Anal. Calcd for $C_{23}H_{32}O_{12}$ (500.5): C, 54.16; H, 6.99. Found: C, 54.11; H, 6.84.

26b: [α]$^{20}_D$ +45.5° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (dd, 1H, $J_{1,2}$ = 0.8 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.83 (ddd~dt, 1H, $J_{1,3}$ = 2.0 Hz, $J_{3,4}$ = 3.0 Hz, H-3), 5.31 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.03 (brs, 1H, H-1), 4.24 (dd, 1H, $J_{5,6a}$ = 5.6 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.19 (dd, 1H, $J_{5,6b}$ = 2.5 Hz,H-6b), 4.09 (ddd, 1H, H-5), 3.97 (m, 1H, H-1a'-propane), 3.78 (m~brs, 2H, H-3a', H-3b'-propane), 3.68 (m, 1H, H-1b'), 2.11, 2.09 (each s, each 3H, OAc), 1.89 (m, 2H, H-2a', H-2b'-propane), 1.59 (bs, 1H, OH) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.28, 169.80 (2 C=O), 128.87, 127.16 (C-2, C-3), 94.02 (C-1), 66.65, 64.91 (C-4, C-5), 66.42, 62.69, 60.51 (C-6, C-1', C-3'-propane), 31.82 (C-2'-propane), 20.49, 20.31 (2 OAc) ppm.

Anal. Calcd for $C_{13}H_{20}O_7$ (288.3): C, 55.20; H, 6.44. Found: C, 55.02; H, 6.51.

Bis-1,6-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyloxy)-hexane (27a) and **6-Hydroxyhexyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (27b).** Tri-*O*-acetyl-D-glucal **1** (463 mg, 1.7 mmol) and 1,6-hexanediol (100 mg, 0.85 mmol) were treated in the presence of BF_3-Et_2O at -20 °C according to the general procedure. The reaction was stopped at 0 °C. The crude product was fractioned on silica gel with petroleum ether/EtOAc(2:1) to give **27a** (207 mg, 45 %) and **27b** (70 mg, 25 %) as colourless syrups. **27a**: [α]$^{20}_D$ +64.2° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400

MHz, $CDCl_3$) δ 5.81 (ddd~d, 2H, $J_{1,2}$ = 0.8 Hz, $J_{2,3}$ = 10.7 Hz, $J_{2,4}$ = 1.0 Hz, H-2,2'), 5.76 (dd, 2H, $J_{3,4}$ = 2.0 Hz, H-3,3'), 5.24 (dd, 2H, $J_{4,5}$ = 9.7 Hz, H-4,4'), 4.95 (brs, 2H, H-1,1'), 4.19 (dd, 2H, $J_{5,6a}$ = 5.6 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a,6a'), 4.10 (dd, 2H, $J_{5,6b}$ = 2.5 Hz, H-6b,6b'), 4.02 (m, 2H, H-5,5'), 3.70 (m, 2H, H-1a",1a'"-hexane), 3.44 (m, 2H, H-1b",1b'"-hexane), 2.04, 2.01 (each s, each 3H, OAc), 1.54 (m, 4H, H-2a",2a'", H-2b",2b'"-hexane), 1.30 (m, 4H, H-3a",3a'", H-3b",3b'"-hexane) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.29, 169.82 (4 C=O), 128.60, 127.47 (C-2,2', C-3,3'), 93.98 (C-1,1'), 68.39 (C-1",1'"-hexane), 66.46, 64.88 (C-4,4', C-5,5'), 62.58 (C-6,6'), 29.25, 25.66 (C-2",2'", C-3"3'"-hexane), 20.52, 20.25 (4 OAc) ppm.

Anal. Calcd for $C_{26}H_{38}O_{12}$ (542.6): C, 57.56; H, 7.06. Found: C, 57.58; H, 7.15.

27b: [α]$^{20}_D$ +29.7° (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddd~d, 1H, $J_{1,2}$ = 0.8 Hz, $J_{2,3}$ = 10.7 Hz, $J_{2,4}$ = 1.0 Hz, H-2), 5.72 (dd, 1H, $J_{3,4}$ = 2.0 Hz, H-3), 5.21 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 4.92 (brs, 1H, H-1), 4.16 (dd, 1H, $J_{5,6a}$ = 5.6 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.08 (dd, 1H, $J_{5,6b}$ = 2.5 Hz, H-6b), 3.99 (ddd, 1H, H-5), 3.67 (1H, H-1a'-hexane), 3.55 (t, 2H, H-6a', H-6b'-hexane), 3.41 (m, 1H, H-1b'-hexane), 2.02, 1.99 (each s,each 3H, OAc), 1.61-1.24 (m, 8H, H-2a', H-2b', H-3'a, H-3b', H-4a', H-4b', H-5a', H-5b'-hexane) ppm.

Anal. Calcd for $C_{16}H_{26}O_7$ (330.4): C, 58.17; H, 7.93. Found: C, 58.19; H, 7.97.

Bis-1,12-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro* - hex - 2-enopyranosyloxy)-dodecane (28a) and **12-Hydroxydodecyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-eno-pyranoside (28b).** Tri-*O*-acetyl-D-glucal **1** (850 mg, 3.12 mmol) and 1,12-dodecanediol (300 mg, 1.48 mmol) were treated in the presence of BF_3-Et_2O at -20 °C according to the general procedure. After 30 min the reaction was stopped at 0 °C. The crude product was fractioned on silica gel with petroleum ether/EtOAc (4:1) to give **28a** (418 mg, 45 %) and **28b** (147 mg, 24 %) as colourless syrups. **28a**: [α]$^{20}_D$ +73.5° (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.04 (ddd~d, 2H, $J_{1,2}$ = 0.8 Hz, $J_{2,3}$ = 10.2 Hz, $J_{2,4}$ = 1.0 Hz, H-2,2'), 6.00 (dd, 2H, $J_{3,4}$ = 2.0 Hz, H-3,3'), 5.48 (dd, 2H, $J_{4,5}$ = 9.7 Hz, H-4,4'), 5.19 (d~brs, 2H, H-1,1'), 4.42 (dd, 2H, $J_{5,6a}$ = 5.6 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a,6a'), 4.33 (dd, 2H, $J_{5,6b}$ = 2.0 Hz, H-6b,6b'), 4.27 (ddd, 2H, H-5,5'), 3.93 (m, 2H, H-

1a",1a'"-dodecane), 3.67 (m, 2H, H-1b",1b'"-dodecane), 2.24, 2.22 (each s, each 3H, 4 OAc), 1.76 (m, 4H, H-2a",2a'", H-2b",2b'"-dodecane), 1.46 (m, 16H, H-3ab",3ab'", H-4ab",4ab'", H-5ab",5ab'", H-6ab",6ab'"-dodecane) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.32, 169.84 (4 C=O), 128.55, 127.54 (C-2,2', C-3,3'), 93.97 (C-1,1'), 68.57 (C-1",1'"-dodecane), 66.45, 64.91 (C-4,4', C-5,5'), 62.61 (C-6,6'), 29.29, 29.15, 29.08, 28.99, 25.81 (C-2",2'", C-3",3'", C-4",4'", C-5",5'", C-6",6'"-dodecane), 20.52, 20.34 (4 OAc) ppm.

Anal. Calcd for $C_{32}H_{50}O_{12}$ (636.2): C, 61.37; H, 7.98. Found: C, 60.95; H, 7.93.

28b: [α]$^{20}_D$ +34.3° (*c* 0.5; $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddd~d, 1H, $J_{1,2}$ = 0.8 Hz, $J_{2,3}$ = 10.2 Hz, $J_{2,4}$ = 1.5 Hz, H-2), 5.77 (ddd, 1H, $J_{1,3}$ = 1.5 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 5.25 (ddd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 4.96 (d~brs, 1H, H-1), 4.19 (dd, 1H, $J_{5,6a}$ = 5.6 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.11 (dd, 1H, $J_{5,6b}$ = 2.5 Hz, H-6b), 4.04 (ddd, 1H, H-5), 3.70 (m, 1H, H-1a'-dodecane), 3.57 (t, 2H, H-12a', H-12b'-dodecane), 3.43 (m, 1H, H-1b'-dodecane), 2.04, 2.01 (each s, each 3H, OAc), 1.60-1.18 (m, 20H, H-2ab', H-3ab', H-4ab', H-5ab', H-6ab', H-7ab', H-8ab', H-9ab', H-10ab', H-11ab'-dodecane) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.37, 169.85 (2 C=O), 128.54, 127.54 (C-2, C-3), 93.96 (C-1), 68.57 (C-1'-dodecane), 66.44, 64.90 (C-4, C-5), 62.61 (C-6), 32.35 (C-12'-dodecane), 29.28, 29.15, 29.11, 29.08, 29.01, 28.99, 28.95, 25.79, 25.66, 25.28 (C-2', C -3', C-4', C-5', C-6', C-7', C-8', C-9', C-10', C-11'-dodecane), 20.52, 20.34 (2 OAc) ppm.

Anal. Calcd for $C_{22}H_{38}O_7$ (414.5): C, 63.74; H, 9.24. Found: C, 63.71; H, 9.20.

***N*-9-Fluorenylmethoxycarbonyl diethanolamine (29).** A solution of 9-fluorenylmethoxycarbonyl chloride (2.16 g, 8.35 mmol) in ether (20 mL) was cooled in an ice bath and a suspension of diethanolamine (0.8 mL, 8.35 mmol) in ether/dioxane was added slowly. The mixture was stirred under cooling for 20 min and another 3 hours at room temperature. After filtration the ether solution was washed with water, dried over $MgSO_4$ and concentrated. The crude product was purified by chromatography (CH_2Cl_2/MeOH) to give **29** (1.53 g, 56 %) as syrup; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H, H-Ar), 7.56 (d, 2H, H-Ar), 7.39 (t, 2H, H-Ar), 7.31 (t, 2H, H-Ar), 4.58 (d, 2H, CH_2-Fmoc), 4.21 (t, 1H, CH-Fmoc), 3.76 (bs, 2H, aliphat.-H), 3.41 (bs, 4H, aliphat.-H), 3.18 (bs, 2H, aliphat.-H), 2.58 (bs, 2H, 2 OH) ppm.

2-*N*-(9-Fluorenylmethoxycarbonylamino) 1,3-propanediol (30). 2-Amino-1,3-propanediol (1.0 g, 11.0 mmol) was treated with 9-fluorenylmethoxycarbonyl chloride (2.84 g, 11.0 mmol) using the same procedure as for **29** to give **30** (2.37 g, 69 %) as slightly yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H, H-Ar), 7.63 (d, 2H, H-Ar), 7.36 (t, 2H, H-Ar), 7.28 (t, 2H, H-Ar), 4.36 (d, 2H, CH_2-Fmoc), 4.19 (t, 1H, CH-Fmoc), 3.63 (m, 1H, H-2-propanediol), 3.58 (bs, 4H, H-1a, H-1b, H-3a, H-3b-propanediol), 3.28 (bs, 2H, 2 OH) ppm.

***N,N*-Bis-[2-(4,6-di-*O*-acetyl-2,3-dideoxy - α,β -D-*erythro*-hex-2-enopyranosyl-oxy)-ethyl-]-9-fluorenylmethoxycarbonylamine (31a)** and **[*N*-(9-Fluorenyl-methoxycarbonyl)-*N*-(2-hydroxyethyl)-2-aminoethyl] 4,6-Di-*O*-acetyl-2,3-dideoxy-α, β-D-*erythro*-hex-2-enopyranoside (31b).** Tri-*O*-acetyl-D-glucal **1** (175 mg, 0.64 mmol) and **29** (100 mg, 0.31 mmol) were treated in the presence of BF_3-Et_2O at -45 °C according to the general procedure. The reaction was stopped at -25 °C. The crude product was fractioned on silica gel with toluene/EtOAc (3:1→1:1) to give **31a** (34 mg, 15 %) and **31b** (116 mg, 72 %) as yellow syrups. **31a**: [α]$^{20}_D$ +30.4° (*c* 0.25, $CHCl_3$); (α-anomer): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, 2H, H-Ar), 7.56 (d, 2H, H-Ar), 7.39 (t, 2H, H-Ar), 7.31 (t, 2H, H-Ar), 5.87 (dd~d, 2H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 10.2 Hz, H-2,2'), 5.78 (dd, 2H, $J_{3,4}$ = 2.5 Hz, H-3,3'), 5.31 (dd, 2H, $J_{4,5}$ = 9.2 Hz, H-4,4'), 5.00 (brs, 2H, H-1,1'), 4.52 (d, 2H, CH_2-Fmoc), 4.24 (dd, 2H, $J_{5,6a}$ = 6.6 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a,6a'), 4.21 (t, CH-Fmoc), 4.13 (dd, 2H, $J_{5,6b}$ = 2.5 Hz, 2 H-6b), 4.02 (m, 2H, 2 H-5), 3.89-3.27 (m, 8H, aliphat.-H), 2.09, 2.07 (each s, each 3H, 4 OAc) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.23, 169.91 (4 C=O), 155.50 (C=O-Fmoc), 128.82-119.51 (C-2', C-3', C-Ar), 93.96 (C-1,1'), 66.88, 64.79 (C-4.4', C-5,5'), 66.55, 66.32, 66.17 (2 C-2'-ethyl, CH_2-Fmoc), 62.45 (C-6,6'), 47.22, 47.13 (2 C-1'-ethyl), 46.97 (CH-Fmoc), 20.48, 20.30 (2 OAc) ppm.

Anal. Calcd for $C_{39}H_{45}O_{13}N$ (735.8): C, 63.66; H, 6.16; N, 1.90. Found: C, 62.97; H, 6.06; N, 1.94.

31b: [α]$^{20}_D$ +32.3° (*c* 0.3, $CHCl_3$); (α-anomer): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, 2H, H-Ar), 7.57 (d, 2H, H-Ar), 7.40 (t, 2H, H-Ar), 7.32 (t, 2H, H-Ar), 5.89 (m, 1H, H-2), 5.75 (m, 1H, H-3), 5.30 (m, 1H, H-4), 5.01 (d~brs, 1H, H-1), 4.53 (d, 2H, CH_2-

Fmoc), 4.26-4.17 (m, 2H, H-6a, CH-Fmoc), 4.13 (dd, 1H, $J_{5,6b}$ = 2.5 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6b), 3.98 (m, 1H, H-5), 3.77-3.14 (m, 8H, aliphat.-H), 2.10, 2.08 (each s, each 3H, OAc) ppm.

Anal. Calcd for $C_{29}H_{33}O_8N$ (523.6): C, 66.53; H, 6.35; N, 2.68. Found: C, 66.39; H, 6.29; N, 2.42.

2-[*N*-(9 - Fluorenylmethoxycarbonylamino)]-bis-[1,3-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyloxy)]propane (32a) and **2-[*N*-(9-Fluorenylmethoxycarbonylamino)] - 3 - (4,6 - di - *O* - acetyl - 2,3 - dideoxy -α - D - *erythro* - hex-2-enopyranosyloxy)propanol (32b).** Tri-*O*-acetyl-D-glucal **1** (417 mg, 1.53 mmol) and **30** (230 mg, 0.73 mmol) were treated in the presence of BF_3-Et_2O at -45 °C according to the general procedure. After 30 min the reaction was stopped at -20 °C. The crude product was fractioned on silica gel with toluene/EtOAc (3:1) to give **32a** (344 mg, 65 %) and **32b** (100 mg, 26 %) as yellow syrups. **32a**: [α]$^{20}_D$ +67.2° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H, H-Ar), 7.59 (d, 2H, H-Ar), 7.39 (t, 2H, H-Ar), 7.29 (t, 2H, H-Ar), 5.89 (dd~d, 2H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 10.2 Hz, H-2,2'), 5.82 (dd, 2H, $J_{3,4}$ = 3.0 Hz, H-3,3'), 5.30 (dd, 2H, $J_{4,5}$ = 9.7 Hz, H-4,4'), 5.03 (d~brs, 2H, H-1,1'), 4.44 (d, 2H, CH_2-Fmoc), 4.28-4.18 (m, 3H, H-6a,6a', CH-Fmoc), 4.13 (dd, 2H, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6b,6b'), 4.06 (m, 2H, H-5,5'), 3.95-3.53 (m, 5H, aliphat.-H), 2.09, 2.08, 2.07, 2.06 (each s, each 3H, 4 OAc) ppm. ^{13}C NMR (100.67 MHz, $CDCl_3$) δ 170.67, 170.19 (4 C=O), 143.87 (C=O-Fmoc), 129.52-120.04 (C-2,2', C-3.3', C-Ar), 94.28 (C-1,1'), 67.23, 65.25 (C-4.4', C-5,5'), 66.78, 66.73 (C-1", C-3"-propane), 62.99, 62.87 (C-6,6', CH_2-Fmoc), 47.29 (CH-Fmoc), 30.95 (C-2"-propane), 20.79, 20.76 (4 OAc) ppm.

Anal. Calcd for $C_{38}H_{43}O_{14}N$ (721.8): C, 61.87; H, 5.87; N, 1.90. Found: C, 62.08; H, 6.02; N, 1.93.

32b: [α]$^{20}_D$ +62.8° (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H, H-Ar), 7.58 (d, 2H, H-Ar), 7.39 (t, 2H, H-Ar), 7.29 (t, 2H, H-Ar), 5.91 (d, 1H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.81 (dd, 1H, $J_{3,4}$ = 2.5 Hz, H-3), 5.27 (dd, 1H, $J_{4,5}$ = 9.5 Hz,, H-4), 5.02 (brs, 1H, H-1), 4.44 (d~brs, 2H, CH_2-Fmoc), 4.25-4.18 (m, 2H, H-6a, CH-Fmoc), 4.12 (dd, 1H, $J_{5,6b}$ = 7.2 Hz, $J_{6a,6b}$ = 12.7 Hz, H-6b), 4.04 (m, 1H, H-5), 3.95-3.64 (m, 5H, aliphat-H), 2.09, 2.07 (each s, each 3H, 2 OAc) ppm. ^{13}C NMR (100.67

MHz, $CDCl_3$) δ 170.78, 170.19 (2 C=O), 143.86 (C=O-Fmoc), 129.69-120.02 (C-2, C-3, C-Ar), 95.08 (C-1), 67.31, 65.36 (C-4, C-5), 68.18, 66.75 (C-1', C-3'-propane), 63.19, 61.71 (C-6, CH_2-Fmoc), 47.26 (CH-Fmoc), 30.93 (C-2'-propane), 20.95, 20.73 (OAc) ppm.

Anal. Calcd for $C_{28}H_{31}O_9N$ (525.6): C, 63.99; H, 5.95; N, 2.67. Found: C, 63.97; H, 6.03; N, 2.65.

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REFERENCES AND NOTES

1. Dedicated to the memory of Prof. Akira Hasegawa.
2. R. J. Ferrier and N. J. Prasad, *J. Chem. Soc. C,* 570 (1969).
3. R. J. Ferrier, *Adv. Carbohydr. Chem.,* **20**, 67 (1965).
4. R. J. Ferrier, *Adv. Carbohydr. Chem. Biochem.,* **24**, 199 (1969).
5. K. B. Sharpless, A. O. Chong and K. Oshima, *J. Org. Chem.,* **41**, 177 (1976).
6. I. Dyong, G. Schulte, Q. Lam-Chi and H. Friege, *Carbohydr. Res.,* **68**, 257 (1979).
7. R. J. Ferrier and N. J. Prasad, *J. Chem. Soc. C*, 575 (1969).
8. B. Fraser-Reid, D. R. Kelly, D. B. Tulshian and P. S. Ravi, *J. Carbohydr. Chem.,* **2**, 105 (1983).
9. M. Koreeda, T. A. Houston, B. K. Shull, E. Klemke and R. J. Tuinman, *Synlett,* 90 (1995).
10. A. F. Hadfield and A. C. Sartorelli, *Carbohydr. Res.,* **101**, 197 (1982).
11. E. Fischer and K. Zach, *Sitzber. Kgl. Preuss. Akad. Wiss.,* **16**, 311 (1913).
12. W. Roth and W. Pigman, *Methods Carbohydr. Chem.,* **2**, 405 (1963).
13. R. Csuk, A. Fürstner, B. I. Glänzer and H. Weidmann, *J. Chem. Soc., Chem. Commun.,* 1149 (1986).
14. L. Somsak and I. Nemeth, *J. Carbohydr. Chem.,* **12**, 679 (1993).
15. J. H. P. Pollon, G. Llewellyn and J. M. Williams, *Synthesis,* 758 (1989).
16. G. Kovacs, J. Gyarmati, L. Somsak and K. Micskei, *Tetrahedron Lett.,* **37**, 1293 (1996).
17. S. J. Eitelman, R. H. Hall and A. Jordan, *J. Chem. Soc., Perkin Trans. 1,* 595 (1978).
18. A. Fernandez-Mayoralas, A. Marra, M. Trumtel, A. Veyrières and P. Sinaÿ, *Carbohydr. Res.,* **188**, 81 (1989).
19. N. Sakairi and H. Kuzuhara, *J. Chem. Soc., Chem. Commun.,* 1874 (1993).

20. D. R. Mootoo, P. Konradsson, U. E. Udodong and B. Fraser-Reid, *J. Am. Chem. Soc.*, **110**, 5583 (1988).
21. B. Fraser-Reid, U. E. Udodong, Z. Wu, H. Ottosson, J. R. Merritt, C. S. Rao, C. Roberts and R. Madsen, *Synlett*, 927 (1992).
22. E. Wieczorek, Dissertation, Univ. Hamburg 1997.
23. P. Bhate, D. Horton and W. Priebe, *Carbohydr. Res.*, **144**, 331 (1985).
24. B. Doboszewski, N. Blaton and P. Herdewijn, *J. Org. Chem.*, **60**, 7909 (1995).
25. R.J. Ferrier and G.H. Sankey, *J. Chem. Soc. C*, 974 (1969).
26. K. Bock, I. Lundt and C. Pedersen, *Acta Chem. Scand.*, **23**, 2083 (1969).
27. L. P. Egan, J. R. Vercellotti and W. T. Lowry, *Carbohydr. Res.*, **23**, 261 (1972).
28. L. A. Carpino and G. Y. Han, *J. Org. Chem.*, **37**, 3404 (1972).
29. K. Heyns and R. Hohlweg, *Chem. Ber.*, **111**, 1632 (1978).
30. W. Kinzy and R. R. Schmidt, *Tetrahedron Lett.*, **28**, 1981 (1987).