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Note

A D-ribofuranosylenamine as glycosyl acceptor †

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Monosaccharide glycosylamines are widely known carbohydrate derivatives of interest as building blocks in the syntheses of complex glycoconjugates and *neo*glycoconjugates and have also been used in the preparations of *N*-nucleosides, glycosyl isothiocyanates, glycosylthioureas, and glycosylaminoheterocycles [1–9]. The data on oligosaccharide glycosylamines are limited. Disaccharide glycosylamines can be prepared from reducing disaccharides, under mild conditions, by reaction with aqueous ammonium hydrogencarbonate [3,10,11], but this procedure depends on the availability of the starting material. The synthesis of oligosaccharide glycosylamines can also be carried out by building the molecule from monosaccharide derivatives. In this way, we have recently reported the synthesis of *O*-protected gentiobiosylenamines through glycosylation reactions using 6-*O*-tritylglucosylenamines as glycosyl acceptors [12]. On the other hand, the D-ribofuranosyl configuration is, together with 2-deoxy-D-ribofuranosyl, the most frequent in natural nucleosides and many efforts have been devoted to synthetic [13,14] and structural [15–17] studies of different D-ribofuranosylamine derivatives. We now describe the preparation of *N*-alkenyl-α- (**1**) and -β-D-ribofuranosylamine (**2**) and the use of **1**, which is crystalline and the major reaction product, as glycosyl acceptor in glycosylation reactions. In this way, the *O*-protected [β-D-Glc*p*-(1 → 5)-α-D-Rib*f*] (**4** and **5**), [β-D-Gal*p*-(1 → 5)-α-D-Rib*f*] (**6** and **7**), and [β-D-Gal*f*-(1 → 5)-α-D-Rib*f*] (**9**) disaccharide and [α-D-Glc*p*-(1 → 4)-β-D-Glc*p*-(1 → 5)-α-D-Rib*f*] (**8**) trisaccharide *N*-alkenylglycosylamines have been obtained. The *N*-pro-

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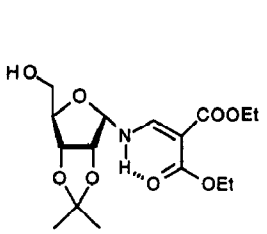
Table 1
Selected NMR spectral parameters (δ) and J (Hz) of compounds **1**, **2**, and **4–11**

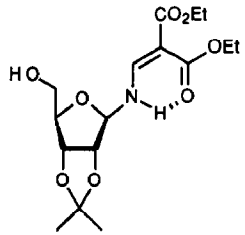
Compd. [a]	Ring A [b]				Ring B [b]					
	δ H-1	$J_{1,2}$	δ C-1	δ C-5	$J_{1',2'}$	δ H-4′	δ H-5′	δ C-1′	δ C-5′	δ CO_3
1	5.34dd	4.5	89.9	63.8						
2	5.15d	0.0	97.6	63.7						
4	5.27dd	3.7	90.1	71.3	7.6	5.10t	3.71ddd	100.3	71.7	
5	5.31dd	4.4	90.4	71.8	7.9	5.71t	4.20m	101.4	72.4	
6	5.29dd	4.1	90.2	71.6	7.9	5.40dd	3.92td	101.2	70.8	
7	5.37dd	3.9	90.4	69.7	7.9	6.01dd	4.36td	101.9	72.5	
8	5.22dd	4.2	90.3	71.3	8.0	4.00t	3.70dd	100.3	72.5	
9	5.17dd	4.4	90.2	69.9	0.0	4.69dd	6.39ddd	105.8	69.4	
10	5.11dd	4.1	90.1	72.5	5.2	5.39d	3.97m	97.6	65.4	121.2
11	5.20dd	4.1	90.4	69.7	5.5	4.10–3.98m	4.30–4.17m	96.9	72.8	121.8

[a] For solvents and frequencies, see Experimental.
[b] Rings A and B(′) refer to the α-D-ribofuranosyl and β-D-gluco(galacto)pyranosyl (α-D-galactofuranosyl for **8**) rings, respectively.

tecting diethoxycarbonylvinyl group is easy to remove under mild conditions which do not affect the glycosidic bonds in oligosaccharides [7,18].



1



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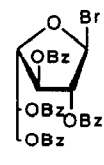

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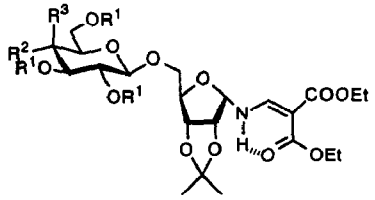
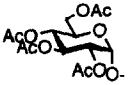
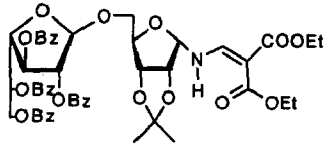
The *N*-protected 2,3-*O*-isopropylidene-D-ribofuranosylamines **1** and **2** were obtained from 2,3-*O*-isopropylidene-D-ribofuranosylamine *p*-toluenesulfonate [14] by reaction with diethyl ethoxymethylenemalonate. Both alkenylribofuranosylamines were isolated by column chromatography and their structures assigned based on spectroscopic data. The anomeric configuration was evident from δ H-1, $J_{1,2}$, δ C-1, and $\Delta\delta_{CH_3}$ values (Table 1 and Experimental). In furanoid rings, only when $J_{1,2}$ is less than 3 Hz can a trans-relationship between the corresponding protons be assigned [14,19]; additionally, a cis anomeric proton resonates at lower field than a trans anomeric proton, so that assignments can be made if the δ values for both anomers are available. For **1** and **2**, both methods can be applied. The anomeric proton of **1** resonates as a double doublet at 5.34 ppm, and the signal for the same proton in **2** appears at 5.15 ppm as a doublet ($J_{1,2} = 0.0$ Hz), in agreement with the cis H-1,H-2 disposition (**1**) and trans H-1,H-2 disposition (**2**) respectively. Moreover, the ^{13}C NMR chemical shifts for the furanoid rings of **1** and **2**, and the $\Delta\delta_{CH_3}$ for the isopropylidene methyl groups (< 1.5 ppm for **1** and > 1.5 ppm for **2**) were in good agreement with those reported for related



	4	5	6	7	8
R^1	Ac	Bz	Ac	Bz	Ac
R^2	OAc	OBz	H	H	
R^3	H	H	OAc	OBz	H

D-ribofuranosylamines [15]. The enamino moiety of **1** and **2** had the hydrogen bond shown in the structure, as is deduced from the two ^{13}C NMR signals at ~ 168.0 (C=O chelated) and 165.8 ppm (C=O free) [12]. The HRMS of **1** showed losses of EtO· and the enamino group, and the peaks at m/z 216, 187, and 142 described for other glycosylenamines [12,20].

The per-*O*-acylglycosyl bromides used as glycosyl donors were prepared by conventional methods [21,22]. In the case of the benzoylated D-*galacto* derivative, treatment of D-galactose with benzoyl chloride and pyridine yielded a mixture of pyranoid and furanoid perbenzoates, which, when treated with HBr (33%) in



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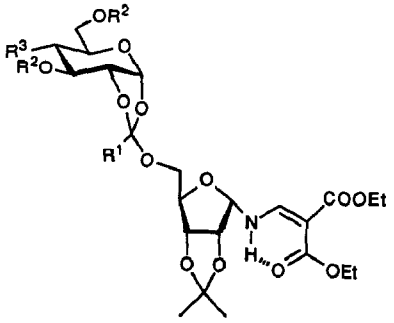


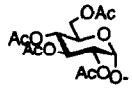
	10	11
R^1	Ph	Me
R^2	Bz	Ac
R^3	OBz	

Table 2
Glycosylations of **1**

Entry	Glycosyl bromide	Promoter	Solvent	Oligosaccharide (yield %) [b]	Orthoester (yield %) [b]
1	Acetobromoglucose	$AgClO_4$	$MeNO_2$	**4** (20)	
2	Acetobromoglucose	AgOTf	CH_2Cl_2	**4** (22)	
3	Benzobromoglucose	AgOTf	CH_2Cl_2	**5** (29)	
6	Acetobromogalactose	Ag_2CO_3	CH_2Cl_2	**6** (31)	Detected
7	Pyranoid and furanoid benzobromogalactose [a]	$AgClO_4$	CH_3NO_2	**7** (14), **9** (28)	
8	Acetobromomaltose	$AgClO_4$	CH_3NO_2	**8** (30)	
9	Benzobromoglucose	Ag_2CO_3	CH_2Cl_2	Detected	**10** (50)
10	Acetobromomaltose	Ag_2CO_3	CH_2Cl_2	**8** (22)	**11** (44)

[a] See discussion.
[b] On pure isolated product.

acetic acid, led to a 1:0.7 mixture of 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide and 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl bromide (**3**). This mixture was a hygroscopic syrup which could be kept at low temperatures (< −20°) for three months and was characterised from its NMR data (see Experimental). It was used directly in the corresponding glycosylation reaction. The structure of **3** was based on ^1H–^1H COSY and ^1H–^{13}C HETCOR NMR experiments; the $J_{1,2}$ and $J_{2,3}$ values were 0.0 Hz in agreement with the trans relationship between the corresponding protons [14,19], and were similar to those for other galactofuranosyl derivatives [23]. The ring size of **3** was also confirmed by the chemical shift of the resonance for H-4 (4.98 ppm) [18] corresponding to a C*H*–O– group, whereas the resonance for H-5 appears at 6.20 ppm corresponding to a C*H*OBz group. For 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide, the same protons resonated at 6.14 (H-4, C*H*OBz) and 4.92 ppm (H-5, C*H*–O–). The chemical shift (88.3 ppm) for the resonance of C-1 in **3** is similar to that for a β-ribofuranosyl bromide previously described [24].

Table 2 summarises the results of the glycosylation reactions of **1**, using different per-*O*-acylglycosyl bromides as glycosyl donors, and also different promoters and solvents. The yields, as in the synthesis of gentiobiosylenamines [12], are not high and there were no large differences when different promoters were used. The disaccharide (**4–7**) and trisaccharide (**8**) glycosylamines had the β configuration in ring B (see footnote b of Table 1) as is deduced from the corresponding $J_{1',2'}$ (7.6–8.0 Hz) and δ C-1′ (~ 101 ppm) values. The structures of **4–8** were consistent with NMR data (Table 1 and Experimental). The resonance of C-5 of the D-*ribo* ring (ring A) in **4–8** underwent a strong deshielding (~ 7.5 ppm) compared with that for **1**, corresponding to a glycosylated position [25]. Compounds **4–8** do not fulfil the Imbach rules for the assignment of the 2,3-*O*-isopropylidene-D-ribofuranosylamine anomeric configuration based on $\Delta\delta_{CH_3}$ [17] and $\Delta\delta_{CH_3}$ [15–17] of the isopropylidene group. However, the acetyl derivatives **4**, **6**, and **8** have the same $\Delta\delta_{CH_3}$ values (1.5 ppm), and this value is different to that for benzoyl derivatives **5** and **7** (2.1 ppm).

When the preparation of **7** was carried out, the mixture of galactopyranosyl bromides described above was used as glycosyl donor. Besides **7**, the 5-*O*-β-D-galactofuranosyl-α-D-ribofuranosylamine **9** was isolated after chromatography. The structure of **9** was based on NMR ^1H–^1H COSY and ^1H–^{13}C HETCOR experiments. When the NMR data were compared with those for **1**, there were no significant changes for the ribofuranosyl moiety, except the expected downfield shift of the resonance of C-5. The $^3J_{H,H}$ values for the galactofuranosyloxy moiety (ring B) were indicative of furanoid structure and β configuration [14,19] ($J_{1',2'}$ 0.0 Hz). The furanoid ring was also supported by the chemical shifts of H-4′ (4.69 ppm), H-5′ (6.39 ppm), and C-1′–C-5′ (ring B) [26]. Compound **9** is formed by glycosylation of **1** with **3**. This glycosylation occurred with retention of the anomeric configuration in ring B. There are bibliographic data [24,27] on Koenigs–Knorr glycosylation reactions in the presence of silver salts, which occur with retention and inversion of the anomeric configuration, although inversion predominates. In the formation of **9**, other products were detected chromatographically but could not be isolated.

It has been reported that orthoesters are intermediates in Koenigs–Knorr reactions employing soluble mercury or silver salts [27]. We have detected or isolated (Table 2) orthoester intermediates (**10** and **11**) when the glycosylation reactions were carried out with silver carbonate as promoter in dichloromethane. The resonances of the nucleus of ring A in **10** and **11** had practically the same δ (^1H and ^{13}C) and *J* values as the corresponding resonances for **1** and **4–9**. However, the chemical shifts and coupling constants for the resonances of the protons of ring B in **10** and **11** are different from those for the D-*gluco* derivatives **4** and **5** and correspond very closely with those of the corresponding protons of previously described D-*gluco* orthoester derivatives [28]. These similarities, and its bulky nature, make it probable that the ribofuranosylenamino group has the exo orientation.

The orthoester structure is also supported by the presence in the ^{13}C NMR spectra of a signal at ~ 121.5 ppm (Table 1) characteristic of the orthoester carbon (CO_3) [28,29]. In the preparation of **6** (Table 2, entry 6), an orthoester could be detected (δ_{CO_3} 121.8) but could not be purified.

The $J_{1,NH}$ values observed for compounds **1**, **2**, and **4–11** are indicative of an anti relationship between the corresponding protons. This conformation is similar to that described for *N*-acyl-α-D-ribofuranosylamines [17].

1. Experimental

General methods.—Melting points are uncorrected. Optical rotations were measured at 22 ± 1°C for solutions in CH_2Cl_2 or $CHCl_3$, and UV spectra were obtained for solutions in CH_2Cl_2. FTIR spectra were recorded for KBr discs. ^1H NMR spectra (200, 300, and 500 MHz) were obtained for solutions in $CDCl_3$ or benzene-d_6; *J* values are given in Hz. Assignments were confirmed by decoupling, H–D exchange, and homonuclear 2D COSY experiments. ^{13}C NMR spectra were

recorded at 50.3, 75.4, and 125.7 MHz. Proton-decoupled attached proton test [30] (APT), DEPT, and heteronuclear 2D correlated spectra were obtained in order to assist in carbon resonance assignments. For nomenclature of the different rings, see footnote b of Table 1. Ring C (″) is the α-D-glucopyranosyl ring in **8** and **11**. EI-mass spectra (70 eV) were measured with a KRATOS MS-80RFA instrument, with an ionising current of 100 μA, an accelerating voltage of 4 kV, and a resolution of 1000 (10% valley definition). The elemental composition of the ions was determined with a resolution of 10000 (10% valley definition). The FABMS spectra were measured with the same instrument. Ions were produced by a beam of Xe atoms (6–7 keV), using a matrix consisting of glycerol or thioglycerol and NaI as salt. TLC was performed on Silica Gel HF_{254} (Merck), with detection by UV light or charring with H_2SO_4. Silica Gel 60 (Merck, 230 mesh) was used for preparative chromatography.

N-(2,2-Diethoxycarbonylvinyl)-2,3-O-isopropylidene-α- (**1**) *and -β-D-ribofuranosylamine* (**2**).—A solution of 2,3-*O*-isopropylidene-D-ribofuranosylamine *p*-toluenesulfonate [14] (5.4 g, 0.015 mmol) in MeOH (50 mL) was treated with 2 M methanolic NaOMe (8 mL). The mixture was stirred for 1 h and diethyl ethoxymethylenemalonate (3 mL, 0.015 mmol) was added. The reaction was left overnight. The solvent was evaporated, and the residue was dissolved in water, extracted with CH_2Cl_2, washed with water, and dried ($MgSO_4$). Column chromatography (5:1 ether–hexane) gave **1** (eluted second; 2.8 g, 51%) and **2** (eluted first; 2.2 g, 40%).

Compound **1** had mp 126–128°C (from 1:1 EtOAc–hexane), $[\alpha]_D$ −9.0° (*c* 1.0, $CHCl_3$); λ_{max} (CH_2Cl_2) 279 nm (ε_{mM} 22.0); ν_{max} 3518 (OH), 3312 (NH), 1720 (C=O free) [31], 1634 (C=O chelated), 1610 (C=C and NH) [12,31], and 1230 cm^{-1} (C–O–C). NMR data ($CDCl_3$): ^1H (500 MHz), Table 1, and also δ 9.42 (dd, 1 H, $J_{NH,=CH}$ 13.6, $J_{1,NH}$ 8.9 Hz, NH), 8.07 (d, 1 H, =CH), 4.83 (dd, 1 H, $J_{2,3}$ 6.2, $J_{3,4}$ 1.3 Hz, H-3), 4.75 (dd, 1 H, H-2), 4.25 (m, 2 H, CH_3CH_2), 4.18 (m, 3 H, H-4 and CH_3CH_2), 3.80 (dt, 1 H, $J_{5a,5b}$ 11.5, $J_{4,5a}$ 1.3, $J_{5a,OH}$ 1.3 Hz, H-5a), 3.70 (dt, 1 H, $J_{4,5b}$ 1.3, $J_{5b,OH}$ 1.3 Hz, H-5b), 2.58 (t, 1 H, OH), 1.63, 1.39 (2 s, each 3 H, 2 CH_3; Δδ CH_3 0.24), 1.31 and 1.27 (2 t, each 3 H, *J* 7.1 Hz, 2 CH_3CH_2); ^{13}C (125.7 MHz), Table 1 and also δ 167.6 (C=O chelated), 165.9 (C=O free), 157.4 (=CH), 113.6 (CMe_2), 92.9 (=C), 82.3 (C-4), 81.9 (C-3), 79.5 (C-2), 59.8, 59.7 (2 CH_2CH_3), 26.0, 24.6 (2 CH_3, Δδ CH_3 1.4), 14.2 and 14.1 (2 CH_2CH_3). Mass spectrum: *m/z* 359.1600 (50%, M^+), 344 (15, $M^+ - Me$), 328.1442 (10, $M^+ - CH_2OH$), 314.1268 (38, $M^+ - EtO^·$), 298.0925 (10, 328 − H_2CO), 216.0869 (40, $C_9H_{14}O_5N^+$) [12], 187.0745 (35, $C_8H_{13}O_4N^+$) [12], 186.0415 [4, $M^+ - NHCH{=}C(CO_2Et)_2$], 173.0726 (10, $C_8H_{13}O_4^+$), 170 (91), and 142.0073 (100, $C_6H_8O_3N^+$) [12]. Anal. Calcd for $C_{16}H_{25}NO_8$: C, 53.47; H, 7.01; N, 3.90. Found: C, 53.41; H, 7.29; N, 3.96.

Compound **2** was a white amorphous solid; $[\alpha]_D$ −56.0° (*c* 0.4, $CHCl_3$); ν_{max} 3500 (OH), 3252 (NH), 1715 (C=O free), 1650 (C=O chelated), 1610 (C=C and NH), and 1260 cm^{-1} (C–O–C). NMR data ($CDCl_3$): ^1H (500 MHz), Table 1 and also δ 9.83 (dd, 1 H, $J_{NH,=CH}$ 13.8, $J_{1,NH}$ 10.0 Hz, NH), 8.04 (d, 1 H, =CH), 4.88 (d, 1 H, $J_{2,3}$ 5.9, $J_{3,4}$ 0.0 Hz, H-3), 4.71 (d, 1 H, H-2), 4.37 (bs, 1 H, H-4), 4.23 (dd, 1 H, $J_{5a,5b}$ 11.5, $J_{4,5a}$ 0.8 Hz, H-5a), 4.22, 4.20 (2 q, each 2 H, *J* 7.1 Hz, 2 CH_3CH_2), 4.18 (dd,

1 H, $J_{4,5b}$ 0.8 Hz, H-5b), 2.38 (bs, 1 H, OH), 1.55, 1.35 (2 s, each 3 H, 2 CH_3; $\Delta\delta$ CH_3 0.20), 1.33 and 1.29 (2 t, each 3 H, 2 CH_3CH_2); ^{13}C (125.7 MHz), Table 1 and also δ 168.0 (C=O chelated), 165.8 (C=O free), 157.5 (=CH), 112.9 (CMe_2), 93.2 (=C), 86.6 (C-2), 86.3 (C-4), 82.2 (C-3), 59.9, 59.7 (2 CH_2CH_3), 26.6, 24.9 (2 CH_3, $\Delta\delta$ CH_3 1.7), 14.3 and 14.2 ($2CH_2CH_3$). Anal. Calcd for $C_{16}H_{25}NO_8$: C, 53.47; H, 7.01; N, 3.90. Found: C, 53.73; H, 7.27; N, 3.92.

*2,3,4,6-Tetra-*O*-acetyl-α-*D*-gluco(galacto)pyranosyl bromides, 2,3,4,6-tetra-*O*-benzoyl-α-*D*-glucopyranosyl bromide, and 2,3,6,2',3',4',6'-hepta-*O*-acetylmaltosyl bromide.*—These compounds were prepared by described methods [21,22].

*2,3,4,6-Tetra-*O*-benzoyl-α-*D*-galactopyranosyl bromide and 2,3,5,6-tetra-*O*-benzoyl-β-*D*-galactofuranosyl bromide* (**3**).—Conventional [22] treatment of D-galactose (5 g, 27.7 mmol) with benzoyl chloride (19.3 mL, 166.6 mmol) and pyridine (25 mL) yielded a mixture of tetra-*O*-benzoyl-D-galactopyranosyl and tetra-*O*-benzoyl-D-galactofuranosyl bromides (19.0 g, 98%). A solution of this mixture in CH_2Cl_2 (13 mL) was treated with HBr (33%) in AcOH (28 mL), and stirred at room temperature until disappearance of the starting material (TLC). Toluene (330 mL) was added and the solution was repeatedly evaporated to dryness, to give a syrup (16.9 g, 95%) that was a 1:0.7 (^1H NMR integral) mixture of the title compounds, which was used without further purification. Selected NMR data for 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide: ^1H (500 MHz, $CDCl_3$), δ 6.99 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 6.14 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 1.1 Hz, H-4), 6.07 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-3), 5.69 (dd, 1 H, H-2), 4.92 (td, 1 H, $J_{5,6a} = J_{5,6b} = 6.4$ Hz, H-5), 4.66 (dd, 1 H, $J_{6a,6b}$ 11.6 Hz, H-6a), and 4.48 (dd, 1 H, H-6b); ^{13}C (125.7 MHz), δ 88.2 (C-1), 71.7 (C-5), 68.8 (C-3), 68.5 (C-2), 68.0 (C-4), and 61.6 (C-6). Selected NMR data for **3**: ^1H (500 MHz, $CDCl_3$), δ 6.66 (s, 1 H, $J_{1,2}$ 0.0 Hz, H-1), 6.20 (m, 1 H, H-5), 5.91 (s, 1 H, $J_{2,3}$ 0.0 Hz, H-2), 5.70 (d, 1 H, $J_{3,4}$ 4.5 Hz, H-3), 4.98 (t, 1 H, $J_{4,5}$ 4.5 Hz, H-4), and 4.75 (m, 2 H, H-6a,6b); ^{13}C (125.7 MHz), δ 88.3 (C-1), 85.5 (C-2), 84.7 (C-4), 76.4 (C-3), 69.4 (C-5), and 63.3 (C-6).

Glycosylations of N-*(2,2-diethoxycarbonylvinyl)-2,3-*O*-isopropylidene-α-*D*-ribofuranosylamine* (**1**).—To a stirred mixture of **1** (0.3 g, 0.83 mmol), promoter (1.24 mmol), molecular sieves (3 or 4 Å), and dry solvent (4 mL) was added the corresponding glycosyl halide (1.24 mmol). The mixture was stirred for 2–3 h under N_2, then diluted with the corresponding solvent and filtered through Celite. The insoluble material was washed with CH_2Cl_2, and the combined filtrates and washings were washed with satd aq $NaHCO_3$ (2 × 15 mL) and water (2 × 15 mL), dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography. The following compounds were prepared in this manner.

N-*(2,2-Diethoxycarbonylvinyl)-2,3-*O*-isopropylidene-5-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-α-*D*-ribofuranosylamine* (**4**). 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide in nitromethane with silver perchlorate as promoter. Column chromatography (4:1 ether–hexane) gave **4** (112 mg, 20%) as a white amorphous solid; $[\alpha]_D$ −9.5° (*c* 1.0, $CHCl_3$); λ_{max} (CH_2Cl_2) 276 nm (ϵ_{mM} 21.0); ν_{max} 3313 (NH), 1760 (C=O acetate), 1727 (C=O free), 1666 (C=O chelated), 1609 (C=C and NH), and 1230 cm^{-1} (C–O–C). NMR data ($CDCl_3$): ^1H (200 MHz), Table 1 and also δ 9.45 (dd, 1 H, $J_{NH,=CH}$ 13.6, $J_{1,NH}$ 8.8 Hz, NH), 8.09 (d, 1 H, =CH), 5.22 (t, 1

H, $J_{2',3'} = J_{3',4'} = 9.5$ Hz, H-3'), 5.10 (t, 1 H, $J_{4',5'}$ 9.5 Hz, H-4'), 5.01 (dd, 1 H, H-2'), 4.75–4.60 (m, 2 H, H-2,3), 4.47 (d, 1 H, H-1'), 4.31 (dd, 1 H, $J_{6'a,6'b}$ 10.1, $J_{5',6'a}$ 4.7 Hz, H-6'a), 4.25, 4.20 (2 q, each 2 H, J 7.0 Hz, 2 CH_3CH_2), 4.20–4.05 (m, 2 H, H-4,5a), 4.14 (dd, 1 H, $J_{5',6'b}$ 2.4 Hz, H-6'b), 3.57 (dd, 1 H, $J_{5a,5b}$ 10.2, $J_{4,5b}$ 2.6 Hz, H-5b), 2.10, 2.07, 2.04, 2.02 (4 s, each 3 H, 4 Ac), 1.64, 1.28 (2 s, each 3 H, 2 CH_3; $\Delta\delta$ CH_3 0.36), and 1.26 (t, 6 H, 2 CH_3CH_2); ^{13}C (50.3 MHz), Table 1 and also δ 170.3, 169.8, 169.1, 168.9 (4 $COCH_3$), 167.6 (C=O chelated), 165.4 (C=O free), 157.3 (=CH), 113.2 (CMe_2), 92.9 (=C), 81.9 (C-3), 80.1 (C-4), 79.2 (C-2), 72.1 (C-3'), 71.0 (C-2'), 67.9 (C-4'), 61.5 (C-6'), 59.7, 59.5 (2 CH_2CH_3), 25.8, 24.3 (2 CH_3, $\Delta\delta$ CH_3 1.5), 20.5, 20.4 (2 C), 20.3 (4 $COCH_3$), 14.2 and 14.1 (2 CH_2CH_3). FAB-mass spectrum: m/z 712 (100%, $[M + Na]^+$), and 690 (30, $[M + H]^+$). Anal. Calcd for $C_{30}H_{43}NO_{17}$: C, 52.25; H, 6.28; N, 2.03. Found: C, 52.23; H, 6.67; N, 1.92.

Compound **4** (140 mg, 22%) was also obtained by using CH_2Cl_2 as solvent and silver triflate as promoter.

N-*(2,2-Diethoxycarbonylvinyl)-2,3-O-isopropylidene-5-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-α-D-ribofuranosylamine* (**5**). 2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl bromide as glycosyl donor in CH_2Cl_2 with silver triflate. Column chromatography (toluene–EtOAc 4 : 1) gave **5** (230 mg, 29%) as a white amorphous solid; $[\alpha]_D$ −87.5° (*c* 0.9, CH_2Cl_2); λ_{max} (CH_2Cl_2) 276 and 232 nm (ϵ_{mM} 21.5 and 42.9); ν_{max} 3304 (NH), 1736 (C=O benzoate), 1729 (C=O free), 1665 (C=O chelated), 1601 (C=C and NH), and 1269 cm^{-1} (C–O–C). NMR data ($CDCl_3$): ^1H (500 MHz), Table 1 and also δ 9.42 (dd, 1 H, $J_{NH,=CH}$ 13.7, $J_{1,NH}$ 9.4 Hz, NH), 8.15–7.26 (m, 20 H, 4 Ph), 8.13 (d, 1 H, =CH), 5.92 (t, 1 H, $J_{2',3'} = J_{3',4'} = 9.8$ Hz, H-3'), 5.71 (t, 1 H, $J_{4',5'}$ 9.8 Hz, H-4'), 5.58 (dd, 1 H, H-2'), 4.77 (d, 1 H, H-1'), 4.66 (dd, 1 H, $J_{6'a,6'b}$ 12.2, $J_{5',6'a}$ 3.2 Hz, H-6'a), 4.53 (dd, 1 H, $J_{5',6'b}$ 5.6 Hz, H-6'b), 4.52 (dd, 1 H, $J_{2,3}$ 6.1 Hz, H-2), 4.45 (d, 1 H, $J_{3,4}$ 0.0 Hz, H-3), 4.30–4.15 (m, 6 H, H-4,5a, 2 CH_3CH_2), 3.54 (dd, 1 H $J_{5a,5b}$ 10.2, $J_{4,5b}$ 2.0 Hz, H-5b), 1.51, 0.93 (2 s, each 3 H, 2 CH_3; $\Delta\delta$ CH_3 0.58), 1.33 and 1.29 (2 t, each 3 H, J 7.1 Hz, 2 CH_3CH_2); ^{13}C (75.5 MHz), Table 1 and also δ 167.9, 166.0, 165.6 (2 C), 165.0 (2 C) (4 COPh, C=O chelated, and C=O free), 157.6 (=CH), 133.6–128.2 (24 C, aromatic), 113.0 (CMe_2), 92.9 (=C), 81.9 (C-3), 80.3 (C-4), 79.3 (C-2), 72.3 (C-3'), 71.8 (C-2'), 69.5 (C-4'), 62.9 (C-6'), 59.8, 59.6 (2 CH_2CH_3), 25.8, 23.7 (2 CH_3, $\Delta\delta$ CH_3 2.1), 14.3 and 14.2 (2 CH_2CH_3). FAB-mass spectrum: m/z 960 (40%, $[M + Na]^+$). Anal. Calcd for $C_{50}H_{51}NO_{17}$: C, 64.03; H, 5.48; N, 1.49. Found: C, 63.94; H, 5.42; N, 1.05.

N-*(2,2-Diethoxycarbonylvinyl)-2,3-O-isopropylidene-5-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-ribofuranosylamine* (**6**). 2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl bromide as glycosyl donor in CH_2Cl_2 with silver carbonate. Column chromatography (EtOAc–hexane 1 : 1) gave **6** (213 mg, 31%) as a white amorphous solid; $[\alpha]_D$ −93.0° (*c* 1.0, $CHCl_3$); λ_{max} ($CHCl_3$) 277 nm (ϵ_{mM} 20.7); ν_{max} 3306 (NH), 1750 (C=O acetate), 1725 (C=O free), 1663 (C=O chelated), 1605 (C=C and NH), and 1225 cm^{-1} (C–O–C). NMR data ($CDCl_3$): ^1H (500 MHz), Table 1 and also δ 9.44 (dd, 1 H, $J_{NH,=CH}$ 12.6, $J_{1,NH}$ 9.3 Hz, NH), 8.12 (d, 1 H, =CH), 5.40 (dd, 1 H, $J_{4',5'}$ 1.1 Hz, H-4'), 5.18 (dd, 1 H, $J_{2',3'}$ 10.5 Hz, H-2'), 5.02 (dd, 1 H, $J_{3',4'}$ 3.4

Hz, H-3′), 4.70 (d, 1 H, $J_{2,3}$ 6.1, $J_{3,4}$ 0.0 Hz, H-3), 4.67 (dd, 1 H, H-2), 4.43 (d, 1 H, H-1′), 4.26–4.19 (m, 2 H, H-6′a,6′b), 4.25, 4.24 (2 q, each 2 H, J 6.8 Hz, 2 CH_3CH_2), 4.19–4.12 (m, 2 H, H-4,5a), 3.92 (td, 1 H, $J_{5',6'a}$ 6.6, $J_{5',6'b}$ 6.6 Hz, H-5′), 3.57 (dd, 1 H, $J_{5a,5b}$ 10.4, $J_{4,5b}$ 2.6 Hz, H-5b), 2.19, 2.09, 2.07, 2.00 (4 s, each 3 H, 4 Ac), 1.61, 1.40 (2 s, each 3 H, 2 CH_3, $\Delta\delta$ CH_3 0.21), 1.34 and 1.31 (2 t, each 3 H, 2 CH_3CH_2); ^{13}C (75.5 MHz), Table 1 and also δ 170.3 170.1, 169.9, 169.3 (4 $COCH_3$), 167.8 (C=O chelated), 165.8 (C=O free), 157.5 (=CH), 113.4 (CMe_2), 93.1 (=C), 82.0 (C-3), 80.3 (C-4), 79.4 (C-2), 70.4 (C-3′), 68.7 (C-2′), 66.6 (C-4′), 61.0 (C-6′), 59.9, 59.7 (2 CH_2CH_3), 26.0, 24.5 (2 CH_3; $\Delta\delta CH_3$ 1.5), 20.6, 20.4 (each 2 C, 4 $COCH_3$), 14.3 and 14.2 (2 CH_2CH_3). FAB-mass spectrum: m/z 712 (100%, $[M + Na]^+$). Anal. Calcd for $C_{30}H_{43}NO_{17}$: C, 52.25; H, 6.28; N, 2.03. Found: C, 52.25; H, 6.03; N, 2.03.

N-(2,2-Diethoxycarbonylvinyl)-2,3-O-isopropylidene-5-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-α-D-ribofuranosylamine (**7**) *and N-(2,2-Diethoxycarbonylvinyl)-2,3-O-isopropylidene-5-O-(2,3,5,6-tetra-O-benzoyl-β-D-galactofuranosyl)-α-D-ribofuranosylamine* (**9**). The glycosyl donor was the 1:0.7 mixture of 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide and **3** described above. Silver perchlorate was used as promoter and nitromethane as solvent. Column chromatography (1:1 hexane–EtOAc) gave **7** (eluted second; 110 mg, 14%) and **9** (eluted first; 220 mg, 28%). Compound **7** was a white amorphous solid which had $[\alpha]_D$ −57.0° (*c* 0.6, CH_2Cl_2); λ_{max} (CH_2Cl_2) 277 and 241 nm (ϵ_{mM} 19.4 and 25.9); ν_{max} 3320 (NH), 1742 (C=O benzoate), 1720 (C=O free), 1656 (C=O chelated), 1599 (C=C and NH), and 1260 cm^{-1} (C–O–C). NMR data ($CDCl_3$): ^1H (500 MHz), Table 1 and also δ 9.42 (dd, 1 H, $J_{NH,=CH}$ 13.5, $J_{1,NH}$ 9.2 Hz, NH), 8.15–7.20 (m, 20 H, 4 Ph), 8.18 (d, 1 H, =CH), 6.01 (dd, 1 H, $J_{4',5'}$ 1.0 Hz, H-4′), 5.79 (dd, 1 H, $J_{2',3'}$ 10.4 Hz, H-2′), 5.66 (dd, 1 H, $J_{3',4'}$ 3.6, H-3′), 4.77 (d, 1 H, H-1′), 4.73 (dd, 1 H, $J_{6'a,6'b}$ 11.4, $J_{5',6'a}$ 6.7 Hz, H-6′a), 4.52 (dd, 1 H, $J_{2,3}$ 6.1 Hz, H-2), 4.48 (d, 1 H, $J_{3,4}$ 0.0 Hz, H-3), 4.47 (d, 1 H, $J_{5',6'b}$ 6.7 Hz, H-6′b), 4.31–4.25 (m, 2 H, H-4,5a), 4.25–4.20 (m, 4 H, 2 CH_3CH_2), 3.59 (dd, $J_{5a,5b}$ 10.3, $J_{4,5b}$ 2.2 Hz, H-5b), 1.52, 0.91 (2 s, each 3 H, 2 CH_3; $\Delta\delta$ CH_3 0.61), 1.34 and 1.32 (2 t, each 3 H, J 7.1 Hz, 2 CH_3CH_2); ^{13}C (50.3 MHz), Table 1 and also δ 167.8, 165.8, 165.6, 165.4, 165.3, 165.2 (4 $COPh$, C=O chelated, and C=O free), 157.5 (=CH), 133.6–128.2 (24 C, aromatic), 113.1 (CMe_2), 93.0 (=C), 82.0 (C-3), 80.4 (C-4), 79.3 (C-2), 71.5 (C-3′), 70.9 (C-2′), 67.7 (C-4′), 61.6 (C-6′), 59.8, 59.7 (2 CH_2CH_3), 25.8, 23.7 (2 CH_3; $\Delta\delta$ CH_3 2.1), 14.4 and 14.2 (2 CH_2CH_3). FAB-mass spectrum: m/z 961 (100%, $[M + H + Na]^+$) Anal. Calcd for $C_{50}H_{51}NO_{17}$: C, 64.03; H, 5.48; N, 1.49. Found: C, 64.06; H, 5.50; N, 1.47.

Compound **9** (220 mg, 28%) was a white amorphous solid, $[\alpha]_D$ −95.0° (*c* 0.6, CH_2Cl_2); λ_{max} (CH_2Cl_2) 276 and 242 nm (ϵ_{mM} 24.4 and 34.5); ν_{max} 3330 (NH), 1740 (C=O benzoate), 1722 (C=O free), 1650 (C=O chelated), 1590 (C=C and NH), and 1270 cm^{-1} (C–O–C). NMR data: ^1H (500 MHz, benzene-d_6), Table 1 and also δ 10.00 (dd, 1 H, $J_{NH,=CH}$ 13.6, $J_{1,NH}$ 9.0 Hz, NH), 8.10–7.20 (m, 20 H, 4 Ph), 8.07 (d, 1 H, =CH), 5.81 (dd, 1 H, $J_{3',4'}$ 4.6, $J_{2',3'}$ 0.7 Hz, H-3′), 5.50 (d, 1 H, H-2′), 4.96 (s, 1 H, H-1′), 4.85 (dd, 1 H, $J_{6'a,6'b}$ 11.7, $J_{5',6'a}$ 7.1 Hz, H-6′a), 4.73 (dd, 1 H, $J_{5',6'b}$ 4.8 Hz, H-6′b), 4.69 (dd, 1 H, $J_{4',5'}$ 4.2 Hz, H-4′), 4.60 (d, 1 H, $J_{2,3}$ 6.2, $J_{3,4}$ 0.0 Hz, H-3), 4.51 (dd, 1 H, H-2), 4.18 (q, 2 H, J 7.1 Hz, CH_3CH_2), 4.11–4.03 (m, 3 H,

CH_3CH_2, H-4), 3.61 (dd, 1 H, $J_{5a,5b}$ 10.5, $J_{4,5a}$ 2.9 Hz, H-5a), 2.83 (dd, 1 H, $J_{4,5b}$ 2.6 Hz, H-5b), 1.65, 1.21 (2 s, each 3 H, 2 CH_3; $\Delta\delta$ CH_3 0.44), 1.10 and 1.03 (2 t, each 3 H, 2 CH_3CH_2); ^{13}C (50.3 MHz, $CDCl_3$) Table 1 and also δ 167.7, 165.9, 165.5, 165.4 (2 C), 165.2 (4 *C*OPh, C=O chelated, and C=O free), 157.1 (=CH), 133.8–128.3 (24 C, aromatic), 113.5 (CMe_2), 93.0 (=C), 81.9 (C-3), 80.3 (2 C, C-2′,4), 79.4 (2 C, C-2,4′), 77.4 (C-3′), 62.9 (C-6′), 59.9, 59.6 (2 CH_2CH_3), 26.0, 24.6 (2 CH_3; $\Delta\delta$ CH_3 1.4), 14.2 and 14.1 (2 CH_2CH_3). FAB-mass spectrum: *m/z* 961 (100%, $[M + H + Na]^+$). Anal. Calcd for $C_{50}H_{51}NO_{17}$: C, 64.03; H, 5.48; N, 1.49. Found: C, 64.03; H, 5.52; N, 1.40.

N-*(2,2-Diethoxycarbonylvinyl)-2,3-*O*-isopropylidene-5-*O*-[2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranosyl]-α-*D*-ribofuranosylamine* (**8**). 2,3,6,2′,3′,4′,6′-Hepta-*O*-acetylmaltosyl bromide was used as glycosyl donor in nitromethane with silver perchlorate as promoter. Column chromatography (3:2 EtOAc–hexane) gave **8** (240 mg, 30%) as a white amorphous solid; $[\alpha]_D$ −2.0° (*c* 1.0, $CHCl_3$); λ_{max} (CH_2Cl_2) 276 nm (ε_{mM} 12.1); ν_{max} 3334 (NH), 1753 (C=O acetate), 1705 (C=O free), 1663 (C=O chelated), 1605 (C=C and NH), and 1235 cm^{-1} (C–O–C). NMR data ($CDCl_3$): ^1H (500 MHz), Table 1 and also δ 9.43 (dd, 1 H, $J_{NH,=CH}$ 13.8, $J_{1,NH}$ 9.1 Hz, NH), 8.07 (d, 1 H, =CH), 5.40 (d, 1 H, $J_{1'',2''}$ 4.0 Hz, H-1″), 5.36 (t, 1 H, $J_{2'',3''}$ 10.2, $J_{3'',4''}$ 10.2 Hz, H-3″), 5.27 (t, 1 H, $J_{2',3'}$ 9.5, $J_{3',4'}$ 9.5 Hz, H-3′), 5.06 (t, 1 H, $J_{4'',5''}$ 10.2 Hz, H-4″), 4.86 (dd, 1 H, H-2″), 4.84 (dd, 1 H, H-2′), 4.69 (d, 1 H, $J_{2,3}$ 6.0, $J_{3,4}$ 0.0 Hz, H-3), 4.61 (dd, 1 H, H-2), 4.51 (d, 1 H, H-1′), 4.48 (dd, 1 H, $J_{6'a,6'b}$ 12.4, $J_{5',6'a}$ 2.6 Hz, H-6′a), 4.30–4.26 (m, 4 H, H-6′b,6″a, CH_3CH_2), 4.26–4.21 (m, 1 H, H-4), 4.19 (q, 2 H, *J* 7.1 Hz, CH_3CH_2), 4.07 (dd, 1 H, $J_{6''a,6''b}$ 12.3, $J_{5'',6''b}$ 2.5 Hz, H-6″b), 4.05 (dd, 1 H, $J_{5a,5b}$ 10.4, $J_{4,5a}$ 2.8 Hz, H-5a), 4.00 (t, 1 H, $J_{4',5'}$ 9.5 Hz, H-4′), 3.96 (m, 1 H, H-5″), 3.70 (dd, 1 H, $J_{5',6'a}$ 4.2 Hz, H-5′), 3.58 (dd, 1 H, $J_{4,5b}$ 2.7 Hz, H-5b), 2.16, 2.11, 2.03, 2.02, 2.01 (5 s, each 3 H, 5 Ac), 2.05 (s, 6 H, 2 Ac), 1.60, 1.35 (2 s, each 3 H, 2 CH_3, $\Delta\delta$ CH_3 0.25), 1.33 and 1.30 (2 t, each 3 H, 2 CH_3CH_2); ^{13}C (125.7 MHz), Table 1 and also δ 170.5 (2 $COCH_3$), 170.3, 170.0, 169.9, 169.4, 169.3 (5 $COCH_3$), 167.8 (C=O chelated), 165.9 (C=O free), 157.5 (=CH), 113.6 (CMe_2), 95.7 (C-1″), 93.4 (=C), 82.1 (C-3), 80.4 (C-4), 79.5 (C-2), 74.9 (C-3′), 72.8 (C-4′), 72.1 (C-2′), 70.0 (C-2″), 69.3 (C-3″), 68.6 (C-5″), 68.0 (C-4″), 62.6 (C-6′), 61.6 (C-6″), 59.9, 59.8 (2 CH_2CH_3), 26.1, 24.6 (2 CH_3; $\Delta\delta$ CH_3 1.5), 20.8 (2 $COCH_3$), 20.7, 20.5 (2 $COCH_3$), 20.6 (3 $COCH_3$), 14.4 and 14.3 (2 CH_2CH_3). FAB-mass spectrum: *m/z* 1000 (30%, $[M + Na]^+$), 978 (20, $[M + H]^+$). Anal. Calcd for $C_{42}H_{59}NO_{25}$: C, 51.58; H, 6.08; N, 1.43. Found: C, 51.24; H, 6.04; N, 1.34.

*3,4,6-Tri-*O*-benzoyl-α-*D*-glucose 1,2-[*N*-(2,2-diethoxycarbonylvinyl)-2,3-*O*-isopropylidene-α-*D*-ribofuranosylamine-5-yl orthobenzoate]* (**10**). The glycosyl donor was 2,3,4,6-tetra-*O*-benzoyl-α-*D*-glucopyranosyl bromide in CH_2Cl_2 with silver carbonate as promoter. Column chromatography (4:1 toluene–EtOAc) gave **10** (394 mg, 50%) as a white amorphous solid; $[\alpha]_D$ −23.0° (*c* 0.7, $CHCl_3$); λ_{max} (CH_2Cl_2) 276 and 241 nm (ε_{mM} 28.1 and 31.7); ν_{max} 3304 (NH), 1738 (C=O benzoate), 1729 (C=O free), 1684 (C=O chelated), 1601 (C=C and NH), and 1260 cm^{-1} (C–O–C). NMR data ($CDCl_3$): ^1H (500 MHz), Table 1 and also δ 9.36 (dd, 1 H, $J_{NH,=CH}$ 13.8, $J_{1,NH}$ 9.4 Hz, NH), 8.10–7.15 (m, 20 H, 4 Ph), 7.96 (d, 1 H, =CH), 6.00 (d, 1 H, H-1′), 5.67

(dd, 1 H, $J_{2',3'}$ 4.3, $J_{3',4'}$ 0.8 Hz, H-3'), 5.39 (dd, 1 H, $J_{4',5'}$ 8.8 Hz, H-4'), 4.69 (dd, 1 H, H-2'), 4.59 (dd, 1 H, $J_{2,3}$ 6.2 Hz, H-2), 4.55 (d, 1 H, $J_{3,4}$ 0.0 Hz, H-3), 4.43 (dd, 1 H, $J_{6'a,6'b}$ 12.2, $J_{5',6'a}$ 2.7 Hz, H-6'a), 4.28 (dd, 1 H, $J_{5',6'b}$ 5.1 Hz, H-6'b), 4.18 (m, 2 H, CH_3CH_2), 4.16 (t, 1 H, $J_{4,5a}$ 3.2 Hz, H-4), 4.15 (q, 2 H, J 7.1 Hz, CH_3CH_2), 3.44 (dd, 1 H, $J_{5a,5b}$ 10.5 Hz, H-5a), 3.38 (dd, 1 H, $J_{4,5b}$ 3.2 Hz, H-5b), 1.51, 1.27 (2 s, each 3 H, 2 CH_3; $\Delta\delta$ CH_3 0.24), 1.21 and 1.19 (2 t, each 3 H, 2 CH_3CH_2); ^{13}C (75.5 MHz), Table 1 and also δ 167.8, 165.8 (2 C), 165.7, 165.0, 164.5 (4 COPh, C=O chelated, and C=O free), 157.3 (=CH), 134.8–125.9 (24 C, aromatic), 113.7 (CMe_2), 93.2 (=C), 82.2 (C-3), 80.3 (C-4), 79.4 (C-2), 69.0 (C-2'), 68.2 (C-3'), 67.7 (C-4'), 63.7 (C-6'), 59.8 (2 CH_2CH_3), 26.0, 24.7 (2 CH_3; $\Delta\delta$ CH_3 1.3), 14.3 and 14.2 (2 CH_2CH_3). FAB-mass spectrum: m/z 960 (85%, $[M + Na]^+$). Anal. Calcd for $C_{50}H_{51}NO_{17}$: C, 64.03; H, 5.48; N, 1.49. Found: C, 64.08; H, 5.27; N, 1.34.

3,6,2',3',4',6'-Hexa-O-acetyl-α-maltose 1,2-[N-(2,2-diethoxycarbonylvinyl)-2,3-O-isopropylidene-α-D-ribofuranosylamine-5-yl orthoacetate] (**11**). 2,3,6,2',3',4',6'-Hepta-O-acetylmaltosyl bromide was used as glycosyl donor in CH_2Cl_2 with silver carbonate. Column chromatography (3 : 1 ether–hexane) gave **8** (eluted second, 176 mg, 22%) and **11** (eluted first, 352 mg, 44%) as a white amorphous solid; $[\alpha]_D$ +0.3° (*c* 1.0, $CHCl_3$); λ_{max} (CH_2Cl_2) 276 nm (ε_{mM} 21.1); ν_{max} 3455 (NH), 1758 (C=O acetate), 1705 (C=O free), 1670 (C=O chelated), 1605 (C=C and NH), and 1233 cm^{-1} (C–O–C). NMR data ($CDCl_3$): ^1H (500 MHz) Table 1 and also δ 9.47 (dd, 1 H, $J_{NH,=CH}$ 13.9, $J_{1,NH}$ 9.0 Hz, NH), 8.04 (d, 1 H, =CH), 5.75 (d, 1 H, H-1'), 5.46 (d, 1 H, $J_{1'',2''}$ 3.1 Hz, H-1''), 5.40 (t, 1 H, $J_{2'',3''}$ 10.0, $J_{3'',4''}$ 10.0 Hz, H-3''), 5.07 (d, 1 H, $J_{4'',5''}$ 10.0 Hz, H-4''), 5.04 (dd, 1 H, $J_{2',3'}$ 2.8, $J_{3',4'}$ 1.3 Hz, H-3'), 4.83 (dd, 1 H, H-2''), 4.72 (d, 1 H, $J_{2,3}$ 6.2, $J_{3,4}$ 0.0 Hz, H-3), 4.69 (dd, 1 H, H-2), 4.36 (dd, 1 H, H-2'), 4.35–4.17 (m, 8 H, H-4,5',6'a,6''a, 2 CH_3CH_2), 4.10–3.98 (m, 3 H, H-4',5'',6''b), 3.89 (m, 1 H, H-6'b), 3.66 (dd, 1 H, $J_{5a,5b}$ 10.2, $J_{4,5a}$ 3.0 Hz, H-5a), 3.53 (dd, 1 H, $J_{4,5b}$ 3.0 Hz, H-5b), 2.12, 2.11, 2.10, 2.09, 2.04, 2.02 (6 s, each 3 H, 6 Ac), 1.77 (s, 3 H, Me orthoester), 1.62, 1.39 (2 s, each 3 H, 2 CH_3; $\Delta\delta$ CH_3 0.23), 1.33 and 1.29 (2 t, each 3 H, J 7.1 Hz, 2 CH_3CH_2); ^{13}C (125.7 MHz), Table 1 and also δ 170.4 (2 C), 170.0 (2 C), 169.3, 169.2 (6 $COCH_3$), 167.7 (C=O chelated), 165.7 (C=O free), 157.3 (=CH), 113.9 (CMe_2), 95.3 (C-1''), 93.2 (=C), 82.3 (C-3), 80.6 (C-4), 79.6 (C-2), 70.3 (C-2''), 69.7 (C-3''), 68.8 (C-5''), 68.3 (C-3'), 68.2 (C-4''), 68.0 (C-4'), 67.9 (C-2'), 63.7 (C-6'), 61.8 (C-6''), 59.8, 59.7 (2 CH_2CH_3), 26.2, 24.8 (2 CH_3; $\Delta\delta$ CH_3 1.4), 21.0, 20.8, 20.7, 20.6 (2 C), 20.5 (6 $COCH_3$), 14.3 and 14.2 (2 CH_2CH_3). FAB-mass spectrum: m/z 1000 (15%, $[M + Na]^+$), 978 (12, $[M + H]^+$). Anal. Calcd for $C_{42}H_{59}NO_{25}$: C, 51.58; H, 6.08; N, 1.43. Found: C, 51.02; H, 5.98; N, 1.29.

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