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Synthesis of Linear-B Saccharopeptides via Enzymatic Galactosylation of Non-natural Glucosamide Acceptors

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Abstract—A series of D- and L-glycopyranuronic acids are coupled to glucosamines to give saccharopeptides. These 'disaccharides', in which the acetyl moiety of the natural *N*-acetyl-glucosamine is replaced by various sugar acids, turned out to be surprisingly good substrates for β(1-4)-galactosyl-transferase and α(1-3)-galactosyl-transferase. The enzymes transfer successively two galactose units from the donor UDP-galactose onto these acceptor substrates, despite the far reaching alterations, regio- and stereospecifically in the expected manner to give linear-B saccharopeptides.

Introduction

Besides peptides, cell-surface oligosaccharides are involved in a variety of physiologically important adhesion and recognition phenomena,[1,2] thus attracting the attention of the pharmaceutical industry recently.[3–5] Immunologically active carbohydrates evoked increased interest[3,6] because of their relevance in the xenotransplantation area.[7–9] Sugar amides (e.g., uronamides) have been designed and integrated into synthetic concepts to serve as oligosaccharide[10–12] or peptide mimetics.[13–15] These 'saccharopeptides' or 'peptidosaccharides' combine features of oligosaccharides, for example the glycosidic linkage, and peptides, for example the conformationally restricted amide-bonds.

Our interest in this quite unusual hybrid class of compounds results from the search for analogues of the natural linear-B trisaccharide **8** ($R' = CH_3$, R = glycoprotein).[16] This sugar is one of the most important xenoantigens discovered so far. The substance is able to bind to preformed human IgG and IgM. This prevents the attack of those antibodies to the α-gal epitopes on the cell surface of a non-primate xenograft and therefore reduces hyperacute rejection to a certain amount.[16] Though it is known that carbohydrates show an improved binding towards their receptors if presented in a polyvalent manner,[17–20] there is still an ongoing search for low molecular weight carbohydrate analogues and mimetics. The most attractive pathway for the synthesis of oligovalent carbohydrate ligands[17,21–23] and non-natural carbohydrate analogues[19,23–26] is a combined use of chemical and enzymatic methods in vitro. Moreover, we were interested if the glycosyltransferase methodology can be applied to design highly altered oligosaccharide structures predictably resulting in new linear-B mimetics with improved and/or altered physiological properties.

Results and Discussion

The pathway for the synthesis of novel linear-B saccharopeptides, which have the natural *N*-acetyl moiety of the glcNAc-subunit replaced by a number of glycuronamides is shown in Scheme 1. These building blocks contain additional non-natural functionalities, which allow further synthetic manipulations succeeding the enzymatic assemblage.

The known precursors **1** and **2** were prepared according to published procedures.[27] A series of D- and L-glycuronic acids **3**,[28] including C-glycosidic structures, were obtained from a TEMPO-catalyzed oxidation[29] of the corresponding sugars or aminosugars. These acids **3** were then coupled to the glucosamines **1** or **2** using HBPyU [*O*-(benzotriazole-1-yl)-*N*,*N*,*N*′,*N*′-bis(tetramethylene)-uronium hexafluorophosphate] according to general peptide coupling protocols[30,31] to give the saccharopeptides **4/5** after a subsequent saponification of

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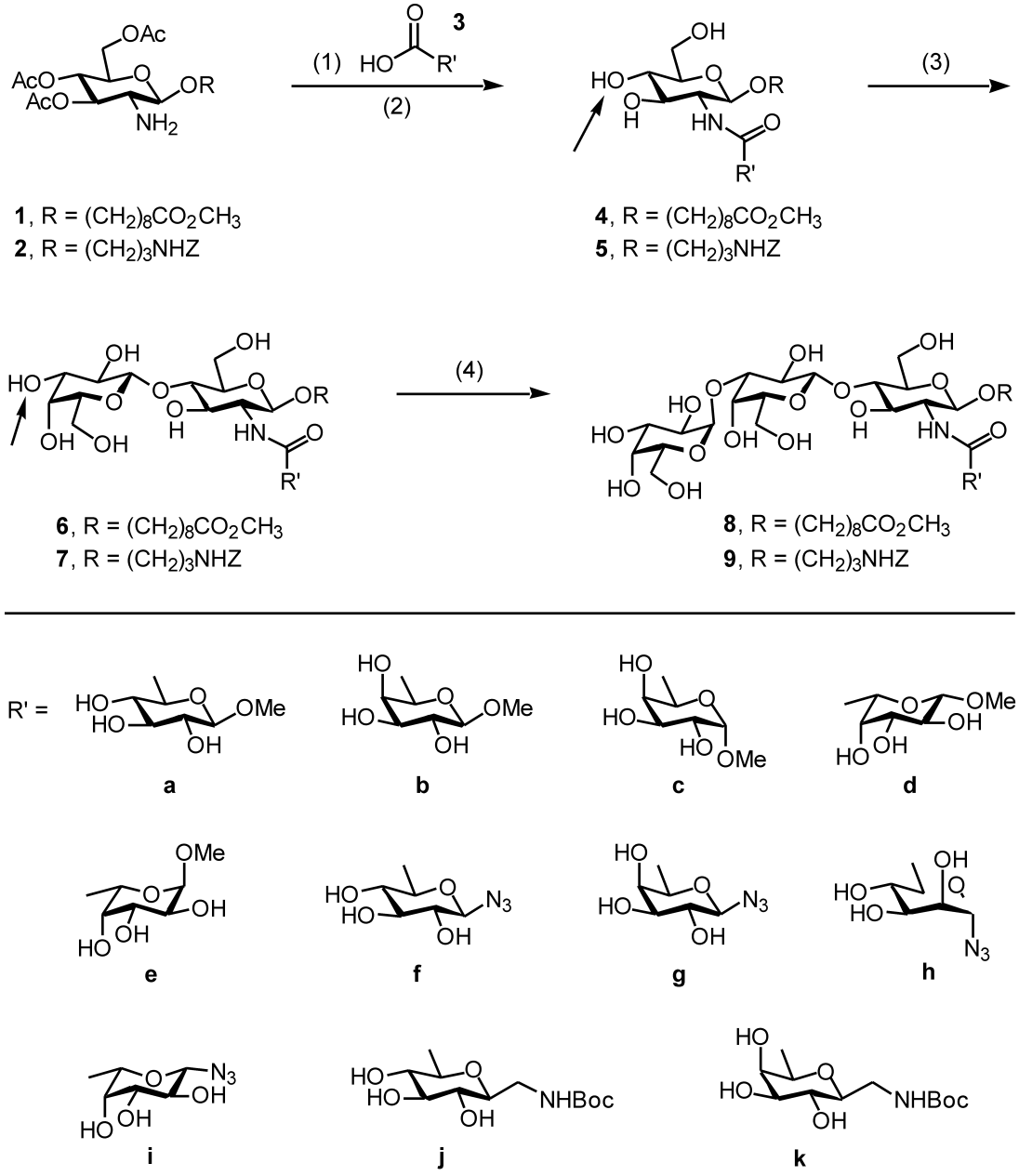
the *O*-acetyl groups. We employed several other coupling reagents (DIC/HOBt, EDC/HOBt, TBTU) but HBPyU was the only one to give satisfying and reproducible results.

Although numerous glycosylation methods are known, the chemical synthesis of complex oligosaccharides is still not a routine procedure.[32] Difficulties often occur from tedious protecting group manipulations and cumbersome separations of the desired product from the glycosylation mixture. A modern and convenient approach is to apply glycosyl-transferases.[24,33] These enzymes transfer a monosaccharide moiety from nucleotide-activated donor substrates highly regio- and stereospecifically onto a hydroxyl group of a growing oligosaccharide chain in vivo and in vitro.

We could recently show that a number of recombinant glycosyl-transferases can be successfully used to glycosylate a wide range of non-natural acceptors very efficiently.[27,34] Consequently, we incubated the non-natural saccharopeptides **4/5** first with commercial β(1-4)-galactosyl-transferase and the donor UDP-galactose (Table 1). Comparative NMR investigations (COSY, TOCSY, and HSQC) of the starting sugars **4/5** and the isolated products **6/7** confirm the attachment of an additional galactose unit in all cases. Indicative for a β-linked galactose in **6/7** (Table 2) are signals at about 104 ppm in the ^{13}C NMR spectra for the galactose C-1 atoms corresponding to additional doublets in the ^{1}H NMR spectra at about 4.5 ppm ($J \sim 6.8$ Hz) for galactose H-1 atoms. The large downfield shift of the C-4 signal of the glucosamide moiety from about 72 ppm in

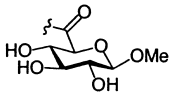
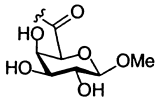
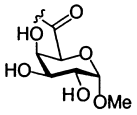
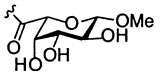
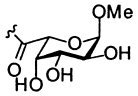
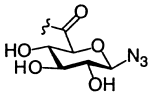
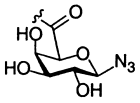
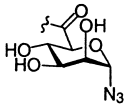
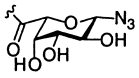
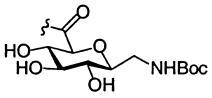
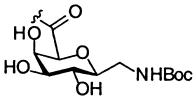


Scheme 1. (1) HBPyU, NEt_3, DMF; (2) MeONa, MeOH; (3) β(1-4)gal-t, UDP-gal; (4) α(1-3)gal-t, UDP-gal (for yields see Table 1).

4/5 to about 79–81 ppm in **6/7** proves that galactose is linked to the 4-OH group.[27]

The saccharopeptides **6/7** were subsequently incubated with UDP-gal and recombinant α(1-3)-gal-t. This enzyme transfers a galactose unit from UDP-gal onto the 3-OH group of a terminal galactose in an α-mode in vivo.[35] The same mode of reaction is observed with the non-natural substrates **6** and **7** to give the linear-B derivatives **8** and **9** selectively. The α-attachment of a second galactose moiety in **8/9** is corroborated by an additional proton signal at about 5.1 ppm with a small axial–equatorial coupling ($J = \sim 3.5$ Hz; see selected NMR data in Table 2). A new carbon signal at about 96–98 ppm further confirms a new α-linkage. A comparison of the product spectra and those of the starting sugars **6/7** clearly indicates that the additional galactose has been transferred onto the 3-OH group of the terminal galactose. The C-3 signals of these sugars are shifted down-field from about 73–75 ppm in the starting

Table 1. Yields of couplings and enzymatic galactosylations

Acid **3**	Acyl R′-C=O	Glucosamine	Amides **4**, **5**		β-Galactosides **6**, **7**			α-Galactosides **8**, **9**		
			Entry	(%)[a]	Entry	(%)	(mg)	Entry	(%)	(mg)
3a (β-D-glc)		**1**	**4a**	31	**6a**	53	10.7	**8a**	67	27.9
3b (β-D-gal)		**1**	**4b**	49	**6b**	61	16.2	**8b**	61	22.6
3c (α-D-gal)		**1**	**4c**	38	**6c**	58	16.5	**8c**	73	13.3
3d (β-L-gal)		**1**	**4d**	26	**6d**	96	36.5	**8d**	80	19.9
3e (α-L-gal)		**1**	**4e**	12	**6e**	40	12.1	**8e**	80	14.9
3f (β-D-glc)		**1** **2**	**4f** **5f**	51 58	**6f** **7f**	56 46	14.5 5	**8f** **9f**	41,[b] 41[c] 41	5.0,[b] 4.9[c] 9.2
3g (β-D-gal)		**1** **2**	**4g** **5g**	37 31	**6g** **7g**	58 49	14.9 12.6	**8g** **9g**	53,[b] 28[c] 96	6.5,[b] 3.4[c] 11.7
3h (α-D-man)		**1**	**4h**	15	**6h**	62	13.7	**8h**	83	10.1
3i (β-L-gal)		**1** **2**	**4i** **5i**	75 32	**6i** **7i**	65 52	16.8 133	**8i** **9i**	94 98	11.5 11.9
3j (β-D-glc)		**1** **2**	**4j** **5j**	20 21	**6j** **7j**	63 43	15.9 161	**8j** **9j**	80 80	9.6 9.6
3k (β-D-gal)		**1** **2**	**4k** **5k**	73 56	**6k** **7k**	59 34	14.8 212	**8k** **9k**	77 92	9.3 10.0

[a]Combined yield of coupling step and deacetylation.
[b]Yield for 'Lemieux ester'.
[c]Yield for 'Lemieux acid'.

Table 2. Selected NMR data of saccharopeptides

Entry	α-Galactose		β-Galactose				Glucosamide			Sugar acid		
	H-1[a]	C-1	H-1[b]	C-1	C-3	C-4	H-4	C-1	C-4	H-4	C-1	C-4
6a			4.51	104.0	73.5	69.5	3.75	101.7	79.7	3.62	104.4	72.3
6b			4.39	104.8	74.6	70.2	3.62	102.0	80.8	4.16	105.8	70.7
6c			4.39	105.1	74.9	70.2	3.61	102.2	81.2	4.23	101.8	71.2
6d			4.40	104.8	74.8	70.1	3.65	102.3	80.4	4.16	105.8	70.7
6e			4.45	104.5	73.7	69.2	3.66	101.7	79.5	4.29	101.1	70.4
6f			4.50	103.8	73.0	68.8	3.75	101.1	79.1	3.62	90.3	71.7
7f			4.49	103.6	73.1	68.8	3.73	101.1	79.2	3.61	90.5	71.6
6g			4.50	103.7	73.0	68.8	3.74	100.7	79.1	4.29	90.7	69.4
7g			4.49	103.7	73.1	68.8	3.72	101.0	79.1	4.29	90.8	69.2
6h			4.50	103.7	72.9	68.8	3.74	101.0	79.1	3.90	90.3	68.0
6i			4.50	103.7	73.0	68.8	3.74	101.2	79.0	4.30	90.7	69.2
7i			4.48	103.7	72.8	68.7	3.71	101.1	79.0	4.24	90.8	69.2
6j			4.49	103.7	73.0	68.8	3.73	100.9	79.3	3.56	78.7	72.3
7j			4.47	103.5	73.0	68.8	3.71	101.3	79.1	3.56	78.7	72.6
6k			4.50	103.7	72.9	68.7	3.71	100.4	79.4	4.30	79.6	69.9
7k			4.47	103.7	73.0	68.7	3.69	100.9	79.1	4.28	79.2	69.8
7k			4.47	103.7	73.0	68,.7	3.69	100.9	79.1	4.28	79.2	69.8
8a	5.06	97.7	4.47	105.1	79.7	66.9	3.69	102.6	81.3	3.53	105.6	74.2
8b	5.05	97.7	4.46	105.2	79.5	66.0	3.62	102.2	81.2	4.17	106.1	70.3
8c	4.99	96.7	4.39	104.1	79.0	65.6	3.55	101.1	80.4	4.13	100.8	70.3
8d	5.08	96.9	4.49	104.1	78.6	65.7	3.66	101.8	80.2	4.19	105.1	70.0
8e	5.07	96.4	4.49	103.7	78.5	65.6	3.64	101.6	79.7	4.27	100.6	70.4
8f	5.17	95.8	4.58	103.7	77.8	65.4	3.77	101.1	79.6	3.62	90.3	71.5
9f	5.16	95.9	4.55	103.5	77.7	65.3	3.73	101.2	79.4	3.61	90.3	71.4
8g	5.17	95.8	4.57	103.5	77.6	65.4	3.74	100.6	79.4	4.30	90.7	69.5
9g	5.16	96.0	4.55	103.5	77.6	65.2	3.72	100.7	79.2	4.28	90.8	69.2
8h	5.16	96.0	4.58	103.5	77.5	65.3	3.76	101.0	79.3	3.90	90.3	68.0
8i	5.16	96.0	4.57	103.6	77.5	65.3	3.75	101.3	79.3	4.30	90.7	69.3
9i	5.16	95.9	4.57	103.5	77.6	65.2	3.72	101.2	79.2	4.24	90.8	69.1
8j	5.17	95.9	4.57	103.6	77.6	65.3	3.72	100.9	79.6	3.54	78.7	72.1
9j	5.17	95.9	4.55	103.6	77.7	65.2	3.72	101.2	79.4	3.51	78.6	72.1
8k	5.17	95.9	4.56	103.6	77.4	65.2	3.75	100.2	79.6	4.29	79.4	69.9
9k	5.17	96.1	4.58	103.5	77.8	65.3	3.70	100.9	79.6	4.27	79.1	69.8

[a]Doublet ($J = \sim 3.5$ Hz).
[b]Doublet ($J = \sim 6.8$ Hz).

materials **6/7** to 77.4–79.7 ppm in the product sugars **8/9**. This is in agreement with a glycosylation at the 3-OH group. In addition, the neighboring C-4 signals are slightly shifted upfield by about 3–4 ppm (Table 2). For the remaining C and H signals of the compounds **8** and **9**, only minor changes are observed compared to the starting material. These data are in excellent agreement with the NMR data obtained for the natural linear-B[36] and confirm the structure of all sugars **8** and **9**.

The results discussed above are not trivial[37] because it could not have been predicted in advance that both galactosyl-transferases accept all the non-natural saccharopeptides **4/5** and **6/7** as substrates. The changes, which have been introduced by replacing the natural *N*-acetyl group with a glycuronamide, are significant; nevertheless enzymatic galactosylations work as expected for the parent acceptors. Although some glycuronides show a D-gluco (**a**, **f**, **j**) or D-galacto (**b**, **c**, **g**, **k**) configuration, none of these substituents is glycosylated. Furthermore, none of the non-natural substrates **4/5** and **6/7** inhibits the investigated transferases. On the contrary, all saccharopeptides **4/5** and **6/7** are good substrates. The additional, non-natural azido (**f**–**i**) and C-glycoside (**j**, **k**) structures do not impair the transferases and the azido functions are stable during the enzymatic transformations.

Conclusion

These investigations show, in addition to previous reports,[24,27,31] an unexpected high substrate promiscuity of β(1-4)gal-t and recombinant α(1-3)gal-t. Both enzymes tolerate the replacement of the stereochemically modest *N*-acetyl moiety of the natural acceptor substrates by bulky, highly polar D- and L-glycuronamides (→ saccharopeptides). Those rigid compounds are unambiguously processed to linear-B saccharopeptides after two sequential incubations with β(1-4)gal-t and α(1-3)gal-t and their natural donor substrate UDP-galactose. Thus, the preparative applicability of the investigated transferases has been substantially extended. They proved to be useful tools to get an easy and unexpected access to a new class of compounds with a high and predictable regio- and stereochemical potential. Therefore, galactosyl-transferases have become an indispensable tool for glycochemists, especially if future genetic engineering of the enzymes is taken into account. This may further enhance the synthetic value of glycosyl-transferases.

Experimental

All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 400 spectrometer with multi-probe head.

COSY, TOCSY, and HSQC experiments were performed using the manufacturers software. Proton and carbon signals were assigned by the combined use of these spectra.[38,39] ^{1}H NMR shifts were measured in CD_3OD or D_2O and referenced to internal D_2O (4.80 ppm), and ^{13}C NMR shifts are referenced to CD_3OD (49.0 ppm) unless otherwise stated. ^{1}H NMR and ^{13}C NMR shift assignments are tentative.

TLC was performed on silica gel $60F_{254}$ glass sheets (Merck), and sugars were stained with *p*-anisaldehyde/sulfuric acid (Pernod mixture). Flash chromatography was done using silica gel 60, 0.040–0.063 mm (Merck).

Solvents and chemicals used were of commercial quality unless otherwise stated. Commercial UDP-galactose was used (Yamasa Corp., Japan). Bovine serum albumine (BSA, no. 28031) and calf intestine alkaline phosphatase (CIAP, E.C.3.1.3.1, no. 108146, 7500 U/498 μL) were obtained from Boehringer/Roche Diagnostics. Bovine β(1-4)galactosyl-transferase (E.C.2.4.1.22) was purchased from Yamasa or Merck. Recombinant α(1-3)galactosyl-transferase (E.C.2.4.1.90, ~2 U/mL) was obtained from transfected insect cells.[35] For the preparation of compounds **1**, **2**, **4a**–**e**, and **6a**–**e** see ref 27. Missing MS and $[\alpha]_D$ data are due to urgent need of the compounds in biological assays.

General procedures A–C

General procedure A (GP A). Coupling of glycopyranuronic acids 3 to glucosamines 1 and 2. According to general peptide coupling protocols,[30,31] 0.30 mmol of the amine **1** or **2**, 0.33 mmol of the glycopyranuronic acid **3**, and 0.33 mmol triethyl amine are dissolved at room temperature under argon in 5 mL dry DMF. The clear solution is treated with 0.33 mmol HBPyU [*O*-(benzotriazole-1-yl)-*N*,*N*,*N*′,*N*′-bis(tetramethylene)uronium hexafluorophosphate] and stirred for 1–3 days at room temperature. The mixture is then evaporated to dryness and the residue chromatographed over silica gel (eluent: CH_2Cl_2/MeOH, 10/1) to yield an acetylated saccharopeptide intermediate. This compound is dissolved in 5 mL dry methanol containing 0.1% sodium methanolate and stirred at room temperature for 1–5 h until TLC (CH_2Cl_2/MeOH, 10/3) shows complete consumption of the starting material. Evaporation gives saccharopeptides **4/5** as solids which are crystallized from MeOH/ether or purified over silica gel (eluent: CH_2Cl_2/MeOH/H_2O, 10/2/0.2).

General procedure B (GP B). Enzymatic β-galactosylation of saccharopeptides 4 and 5. Following standard β-galactosylation protocols,[27,40] compound **4** or **5** (36.3 μmol) is dissolved in 170 μL DMSO and 1.4 mL HEPES-buffer (0.1 M, pH 7.0). To this solution are added 1.6 mg BSA, 7.1 mg (35.9 μmol) $MnCl_2\times4H_2O$, and 43.6 μmol UDP-gal. This mixture is briefly vortexed and then incubated at 37 °C with 2 μL CIAP and 300 μL β(1-4)gal-t (1.5 U). When TLC (CH_2Cl_2/MeOH/H_2O, 10/4/0.8) indicates that the reaction has stopped, usually after 2–6 days, the turbid solution is centrifugated and the supernatant passed over a C-18 reversed-phase column, washed with water and eluted with methanol. The solvent is evaporated and the residue chromatographed over silica gel (eluent: CH_2Cl_2/MeOH/H_2O, 10/2/0.2→6/4/1) to give the pure unreacted starting material **4/5** and β-galactosylated sugars **6/7** as white powders after lyophilization from water.

General procedure C (GP C). Enzymatic α-galactosylation of saccharopeptides 6 and 7. According to general α-galactosylation protocols,[35,40] 13.6 μmol of saccharide **6** or **7**, 35.8 μmol UDP-gal, and 0.7 mg BSA are added to a mixture of 450 μL sodium cacodylate-buffer (0.5 M, pH 6.5) containing 11.3 mg (57.1 μmol) $MnCl_2\times4H_2O$. This mixture is briefly vortexed and then incubated at 37 °C with 150 μL of an α(1-3)gal-t solution (300 mU) and 2 μL CIAP for 1–3 days. The turbid mixture is then centrifugated, passed over a short C-18 reversed phase column, washed with water, and eluted with methanol. After evaporation of the solvents, the residue is chromatographed over silica gel (eluent: CH_2Cl_2/MeOH/H_2O, 10/4/0.8→6/4/1) to give the pure oligosaccharides **8/9** as white powders after a final lyophilization from water.

Individual protocols and data

8-Methoxycarbonyloctyl 2-deoxy-2-(1-deoxy-1-azido-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 4f. According to GP A, 200 mg (0.913 mmol) of 1-deoxy-1-azido-β-D-glucohexopyranosiduronic acid **3f** were coupled to 398 mg (0.837 mmol) of glucosamine **1**, using 394 mg (0.913 mmol) HBPyU, 127 μL NEt_3, and 12 mL DMF. After work-up, 335 mg (59%) acetylated intermediate was obtained, which was deacetylated to give 239 mg (87%) of the title sugar after crystallization from MeOH/ether. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.51, 3.76, 3.58, 3.37, 3.32, 3.74 and 3.92; glcA-unit (H-1 to H-5) δ 4.64, 3.25, 3.48, 3.58, 3.87; aglycon (H-2 to H-9, OCH_3) δ 2.36, 1.63, 1.35, 1.36, 1.58, 3.52 and 3.91, 3.69. ^{13}C NMR (CD_3OD) glcN-unit (C-1–C-6) δ 101.6, 56.4, 74.8, 71.3, 77.2, 61.8; glcA-unit (C-1–C-5) δ 91.4, 73.2, 76.5, 72.0, 76.9; aglycon (C-2–C-9, OCH_3) δ 34.1, 25.3, 29.4, 26.1, 29.5, 69.8, 50.9. HRMS calcd for $C_{22}H_{38}N_4O_{12}$ + Na 573.2384: found MS + Na 573.2383.

3-Benzoxycarbonylaminopropyl 2-deoxy-2-(1-deoxy-1-azido-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 5f. Following GP A, 200 mg (0.913 mmol) of 1-deoxy-1-azido-β-D-glucohexopyranosiduronic acid **3f** were coupled to 416 mg (0.837 mmol) of glucosamine **2**, using 394 mg (0.913 mmol) HBPyU, 127 μL NEt_3, and 12 mL DMF. After work-up, 501 mg (86%) acetylated intermediate was obtained. Deacetylation gave 271 mg (67%) of sugar **5f** after crystallization from MeOH/Et_2O. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.47, 3.76, 3.55, 3.37, 3.29, 3.71 and 3.91; glcA-unit (H-1 to H-5) δ 4.63, 3.24, 3.47, 3.59, 3.88; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.55 and 3.94, 1.75, 3.18 and 3.34, 5.12, 7.37–7.43. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 101.6, 56.5, 74.8, 71.5, 76.7, 61.8; glcA-unit (C-1 to C-5) δ 91.1, 73.3, 76.6, 72.2, 77.2; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ

66.7, 29.8, 37.6, 66.3, 127.4-129.6. HRMS calcd for $C_{23}H_{33}N_5O_{12}$ + Na 594.2023: found MS + Na 594.2018.

8-Methoxycarbonyloctyl 2-deoxy-2-(1-deoxy-1-azido-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 4g. According to GP A, 193 mg (0.880 mmol) of 1-deoxy-1-azido-β-D-galactohexopyranosiduronic acid **3g** were coupled to 380 mg (0.800 mmol) of glucosamine **1**, using 380 mg (0.880 mmol) HBPyU, 122 μL NEt_3, and 11.5 mL DMF. After work-up, 358 mg (66%) acetylated intermediate was obtained, which was deacetylated to give 155 mg (56%) of sugar **4g** after chromatographic purification. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.68, 3.63, 3.70, 3.35, 3.33, 3.72 and 3.92; galA-unit (H-1 to H-5) δ 4.58, 3.60, 3.60, 4.24, 4.18; aglycon (H-2 to H-9, OCH_3) δ 2.36, 1.64, 1.35, 1.37, 1.60, 3.55 and 3.86, 3.69. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 100.8, 57.3, 74.3, 71.5, 76.9, 61.9; galA-unit (C-1 to C-5) δ 91.6, 70.9, 73.7, 69.7, 77.6; aglycon (C-2 to C-9, OCH_3) δ 33.9, 25.4, 29.2, 26.1, 29.4, 70.0, 50.7. HRMS calcd for $C_{22}H_{38}N_4O_{12}$ + Na 573.2384: found MS + Na 573.2382.

3-Benzoxycarbonylaminopropyl 2-deoxy-2-(1-deoxy-1-azido-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 5g. Following GP A, 72.3 mg (0.330 mmol) of 1-deoxy-1-azido-β-D-galactohexopyranosiduronic acid **3g** were coupled to 149 mg (0.300 mmol) of glucosamine **2**, using 142 mg (0.330 mmol) HBPyU, 45.8 μL NEt_3, and 5 mL DMF. After work-up, 68.9 mg (33%) acetylated intermediate was obtained. Deacetylation gave 53 mg (95%) of sugar **5g** after chromatographic purification. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.57, 3.74, 3.62, 3.36, 3.31, 3.71 and 3.92; galA-unit (H-1 to H-5) δ 4.60, 3.60, 3.60, 4.25, 4.21; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.57 and 3.92, 1.76, 3.22 and 3.30, 5.12, 7.31–7.45. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 101.3, 56.7, 74.8, 71.7, 76.9, 61.9; galA-unit (C-1 to C-5) δ 91.7, 70.9, 73.7, 69.8, 77.5; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 66.8, 29.6, 37.7, 66.3, 127.2–129.8. HRMS calcd for $C_{23}H_{33}N_5O_{12}$ + Na 594.2023: found MS + Na 594.2019.

8-Methoxycarbonyloctyl 2-deoxy-2-(1-deoxy-1-azido-α-D-mannohexopyranosyluronamide)-β-D-glucopyranoside 4h. According to GP A, 193mg (0.880 mmol) of 1-deoxy-1-azido-α-D-mannohexopyranosiduronic acid **3h** were coupled to 380 mg (0.800 mmol) of glucosamine **1**, using 380 mg (0.880 mmol) HBPyU, 121 μL NEt_3, and 11.5 mL DMF. After work-up, 450 mg (83%) acetylated intermediate was obtained, which was deacetylated to give 18.9 mg (5.3%) of sugar **4h** after chromatographic purification. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.54, 3.73, 3.60, 3.37, 3.34, 3.83 and 3.92; manA-unit (H-1 to H-5) δ 5.51, 3.91, 3.68, 3.79, 4.11; aglycon (H-2 to H-9, OCH_3) δ 2.35, 1.64, 1.35, 1.37, 1.60, 3.55 and 3.92, 3.68. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 101.6, 56.7, 74.6, 71.4, 76.9, 61.8; manA-unit (C-1 to C-5) δ 91.2, 69.8, 70.6, 70.5, 74.1; aglycon (C-2 to C-9, OCH_3) δ 34.1, 25.3, 29.0, 26.1, 29.6, 69.8, 50.7. HRMS calcd for $C_{22}H_{38}N_4O_{12}$ + Na 573.2384: found MS + Na 573.2385.

8-Methoxycarbonyloctyl 2-deoxy-2-(1-deoxy-1-azido-β-L-galactohexopyranosyluronamide)-β-D-glucopyranoside 4i. According to GP A, 73.3 mg (0.330 mmol) of 1-deoxy-1-azido-β-L-galactohexopyranosiduronic acid **3i** were coupled to 143 mg (0.300 mmol) of glucosamine **1**, using 142 mg (0.330 mmol) HBPyU, 45.8 μL NEt_3, and 5 mL DMF. After work-up, 168 mg (83%) acetylated intermediate was obtained, which was deacetylated to give 123 mg (90%) of sugar **4i** after crystallization from MeOH/Et_2O. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.53, 3.81, 3.63, 3.38, 3.35, 3.73 and 3.92; galA-unit (H-1–H-5) δ 4.61, 3.61, 3.64, 4.25, 4.20; aglycon (H-2 to H-9, OCH_3) δ 2.36, 1.65, 1.36, 1.37, 1.59, 3.53 and 3.92, 3.69. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 101.5, 56.7, 74.6, 71.1, 77.1, 61.9; galA-unit (C-1 to C-5) δ 91.5, 70.6, 73.4, 69.8, 77.6; aglycon (C-2 to C-9, OCH_3) δ 34.0, 25.3, 29.0, 26.0, 29.5, 69.6, 50.8. HRMS calcd for $C_{22}H_{38}N_4O_{12}$ + Na 573.2384: found MS + Na 573.2385.

3-Benzoxycarbonylaminopropyl 2-deoxy-2-(1-deoxy-1-azido-β-L-galactohexopyranosyluronamide)-β-D-glucopyranoside 5i. Following GP A, 72.3 mg (0.330 mmol) of 1-azido-β-L-galactohexopyranosiduronic acid **3i** were coupled to 149 mg (0.300 mmol) of glucosamine **2**, using 142 mg (0.330 mmol) HBPyU, 45.8 μL NEt_3, and 5 mL DMF. After work-up, 139 mg (66%) acetylated intermediate was obtained, which was deacetylated to give 69.0 mg (62%) of sugar **5i** after chromatographic purification. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.52, 3.80, 3.64, 3.37, 3.34, 3.72 and 3.92; galA-unit (H-1 to H-5) δ 4.62, 3.57, 3.60, 4.25, 4.27; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.56 and 3.93, 1.76, 3.20 and 3.29, 5.11, 7.31–7.40. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 101.5, 56.8, 74.6, 71.3, 76.9, 61.9; galA-unit (C-1 to C-5) δ 91.6, 70.8, 73.4, 69.8, 77.6; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 66.8, 29.6, 37.8, 66.3, 127.2–129.6. HRMS calcd for $C_{23}H_{33}N_5O_{12}$−H 570.2047: found MS−H 570.2054.

8-Methoxycarbonyloctyl 2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 4j. Following GP A, 111 mg (0.360 mmol) of 1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-glucohexopyranosiduronic acid **3j** were coupled to 157 mg (0.330 mmol) of glucosamine **1**, using 155 mg (0.360 mmol) HBPyU, 50.0 μL NEt_3, and 5 mL DMF. After work-up, 116 mg (46%) acetylated intermediate was obtained. Deacetylation gave 42.4 mg (44%) of sugar **4j** after crystallization from MeOH/Et_2O. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.54, 3.73, 3.60, 3.35, 3.32, 3.74 and 3.93; glcA-unit [H-1 to H-5, H-1′, C(CH_3)$_3$] δ 3.34, 3.24, 3.45, 3.47, 3.75, 3.32 and 3.62, 1.49; aglycon (H-2 to H-9, OCH_3) δ 2.36, 1.64, 1.35, 1.36, 1.57, 3.53 and 3.93, 3.69. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 101.3, 56.4, 74.6, 71.5, 76.9, 61.9; glcA-unit [C-1 to C-5, C-1′, C(CH$_3$)$_3$] δ 79.7, 71.4, 77.8, 73.1, 78.1, 41.5, 27.7; aglycon (C-2 to C-9, OCH_3) δ 33.9, 25.4, 29.2, 26.1, 29.5, 69.8, 50.7. HRMS calcd for $C_{28}H_{50}N_2O_{14}$ + Na 661.3160: found MS + Na 661.3161.

3-Benzoxycarbonylaminopropyl 2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-glucohexopyrano-

syluronamide)-β-D-glucopyranoside 5j. Following GP A, 101 mg (0.330 mmol) of 1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-glucohexopyranosiduronic acid **3j** were coupled to 149 mg (0.300 mmol) of glucosamine **2**, using 142 mg (0.330 mmol) HBPyU, 45.8 μL NEt_3, and 5 mL DMF. After work-up, 72.0 mg (31%) acetylated intermediate was obtained. Deacetylation gave 40.4 mg (67%) of sugar **5j** after chromatographic purification. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.46, 3.76, 3.54, 3.37, 3.28, 3.72 and 3.92; glcA-unit [H-1 to H-5, H-1′, C(CH_3)$_3$] δ 3.34, 3.22, 3.45, 3.48, 3.78, 3.30 and 3.58, 1.48; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.54 and 3.95, 1.75, 3.19 and 3.35, 5.12, 7.31–7.43. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 101.6, 56.4, 74.8, 71.5, 77.2, 61.8; glcA-unit [C-1 to C-5, C-1′, C(CH_3)$_3$] δ 79.7, 71.4, 77.8, 72.9, 78.2, 41.6, 27.6; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 66.7, 29.8, 37.6, 66.3, 127.2-129.5. HRMS calcd for $C_{29}H_{45}N_3O_{14}$ + Na 682.2799: found MS + Na 682.2795.

8-Methoxycarbonyloctyl 2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 4k. According to GP A, 101 mg (0.330 mmol) of 1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-galactohexopyranosiduronic acid **3k** were coupled to 143 mg (0.300 mmol) of glucosamine **1**, using 142 mg (0.330 mmol) HBPyU, 45.8 μL NEt_3, and 5 mL DMF. After work-up, 170 mg (74%) acetylated intermediate was obtained which was deacetylated to give 140 mg (99%) of sugar **4k** after crystallization from MeOH/Et_2O. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.76, 3.52, 3.56, 3.36, 3.35, 3.74 and 3.93; galA-unit [H-1 to H-5, H-1′, C(CH_3)$_3$] δ 3.28, 3.55, 3.79, 4.26, 4.01, 3.34 and 3.66, 1.50; aglycon (H-2 to H-9, OCH_3) δ 2.36, 1.65, 1.35, 1.36, 1.61, 3.57 and 3.90, 3.70. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 100.6, 57.6, 74.6, 71.5, 77.2, 61.9; galA-unit [C-1 to C-5, C-1′, C(CH_3)$_3$] δ 80.2, 68.1, 74.0, 70.6, 79.0, 41.6, 27.7; aglycon (C-2 to C-9, OCH_3) δ 34.0, 25.4, 29.4, 26.0, 29.5, 69.8, 50.7. MS calcd for $C_{28}H_{50}N_2O_{14}$−H 637 638.709: found MS−H 637.

3-Benzoxycarbonylaminopropyl 2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 5k. Following GP A, 101 mg (0.330 mmol) of 1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-galactohexopyranosiduronic acid **3k** were coupled to 149 mg (0.300 mmol) of glucosamine **2**, using 142 mg (0.330 mmol) HBPyU, 45.8 μL NEt_3, and 5 mL DMF. After work-up, 171 mg (73%) acetylated intermediate was obtained. Deacetylation gave 111 mg (77%) of sugar **5k** after crystallization from MeOH/Et_2O. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.55, 3.71, 3.56, 3.36, 3.28, 3.72 and 3.92; galA-unit [H-1 to H-5, H-1′, C(CH_3)$_3$] δ 3.28, 3.56, 3.62, 4.27, 4.06, 3.37 and 3.63, 1.49; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.57 and 3.94, 1.75, 3.32 and 3.41, 5.13, 7.38–7.46. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 101.1, 56.8, 74.6, 71.5, 76.9, 61.8; galA-unit [C-1 to C-5, C-1′, C(CH_3)$_3$] δ 80.1, 68.3, 74.7, 70.3, 79.0, 41.6, 27.7; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 66.6, 29.6, 37.4, 66.3, 127.2-129.2. MS calcd for $C_{29}H_{45}N_3O_{14}$ + Na 682: found MS + Na 682.

8-Methoxycarbonyloctyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 6f. According to GP B, 20.0 mg (36.3 μmol) of sugar **4f** were dissolved in 170 μL DMSO and 1.4 mL HEPES-buffer and incubated with 26.6 mg (43.6 μmol) UDP-gal, 1.6 mg BSA, 7.1 mg (35.9 μmol) $MnCl_2 \times 4H_2O$, 2 μL CIAP, and 300 μL β(1-4)gal-t (1.5 U) for 6 days After work-up, 8.3 mg (42%) of starting material **4f** and 14.5 mg (56%) of sugar **6f** were isolated. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1–H-6,6′) δ 4.64, 3.83, 3.83, 3.75, 3.63, 3.87 and 4.03; β-gal-unit (H-1 to H-6,6′) δ 4.50, 3.55, 3.72, 3.96, 3.77, 3.77 and 3.81; glcA-unit (H-1 to H-5) δ 4.82, 3.33, 3.59, 3.62, 4.00; aglycon (H-2 to H-9, OCH_3) δ 2.43, 1.63, 1.35, 1.34, 1.58, 3.65 and 3.93, 3.72. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.1, 55.7, 72.8, 79.1, 75.5, 60.4; β-gal-unit (C-1 to C-6) δ 103.8, 71.5, 73.0, 68.8, 75.8, 61.6; glcA-unit (C-1 to C-5) δ 90.3, 73.0, 75.4, 71.7, 76.9; aglycon (C-2 to C-9, OCH_3) δ 34.1, 25.0, 28.8, 25.6, 28.6, 71.4, 52.1. HRMS calcd for $C_{28}H_{48}N_4O_{17}$−H 711.2936: found MS−H 711.2944.

3-Benzoxycarbonylaminopropyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 7f. According to GP B, 20.0 mg (35.0 μmol) of sugar **5f** were dissolved in 170 μL DMSO and 1.4 mL HEPES-buffer and incubated with 25.6 mg (42.0 μmol) UDP-gal, 1.5 mg BSA, 6.8 mg (34.4 μmol) $MnCl_2 \times 4H_2O$, 2 μL CIAP, and 300 μL β(1-4)gal-t (1.5 U) for 4 days. After work-up, 10.8 mg (54%) of starting material **5f** and 11.8 mg (46%) of sugar **7f** were isolated. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.55, 3.83, 3.79, 3.73, 3.60, 3.85 and 4.01; β-gal-unit (H-1 to H-6,6′) δ 4.49, 3.58, 3.69, 3.95, 3.76, 3.76 and 3.79; glcA-unit (H-1 to H-5) δ 4.73, 3.30, 3.54, 3.61, 3.97; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.62 and 3.94, 1.75, 3.17 and 3.23, 5.13, 7.41–7.52. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.1, 55.8, 72.6, 79.2, 75.0, 60.4; β-gal-unit (C-1 to C-6) δ 103.6, 71.7, 73.1, 68.8, 75.6, 61.5; glcA-unit (C-1 to C-5) δ 90.5, 72.8, 75.5, 71.6, 77.4; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 67.8, 29.2, 37.6, 67.0, 127.0–129.6. MS calcd for $C_{29}H_{43}N_5O_{17}$−H 732 733.684: found MS−H 732.

8-Methoxycarbonyloctyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 6g. According to GP B, 20.0 mg (36.3 μmol) of sugar **4g** were dissolved in 170 μL DMSO and 1.4 mL HEPES-buffer and incubated with 26.6 mg (43.6 μmol) UDP-gal, 1.6 mg BSA, 7.1 mg (35.9 μmol) $MnCl_2 \times 4H_2O$, 2 μL CIAP, and 300 μL β(1-4)gal-t (1.5 U) for 6 days. After work-up, 8.4 mg (42%) of starting material **4g** and 14.9 mg (58%) of sugar **6g** were isolated. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.70, 3.81, 3.87, 3.74, 3.62, 3.85 and 4.01; β-gal-unit (H-1 to H-6,6′) δ 4.50, 3.58, 3.68, 3.94, 3.75, 3.76 and 3.79; galA-unit (H-1 to H-5) δ 4.74, 3.60, 3.77, 4.29, 4.33; aglycon (H-2 to H-9, OCH_3) δ 2.41, 1.62, 1.32, 1.31, 1.57, 3.63 and 3.85, 3.70. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 100.7, 56.0, 72.6, 79.1, 74.9, 60.3; β-gal-unit (C-1 to C-6) δ 103.7, 71.5, 73.0, 68.8, 75.6, 61.5; galA-unit (C-1 to C-5) δ 90.7, 70.7, 72.8, 69.4, 76.9; aglycon (C-2 to C-9, OCH_3) δ 34.3, 25.0,

28.5, 25.4, 28.9, 71.4, 52.1. HRMS calcd for $C_{28}H_{48}N_4O_{17}$ + Na 735.2912: found MS + Na 735.2911.

3-Benzoxycarbonylaminopropyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 7g. According to GP B, 20.0 mg (35.0 μmol) of sugar **5g** were dissolved in 170 μL DMSO and 1.4 mL HEPES-buffer and incubated with 25.6 mg (42.0 μmol) UDP-gal, 1.5 mg BSA, 6.8 mg (34.4 μmol) $MnCl_2 \times 4H_2O$, 2 μL CIAP, and 300 μL β(1-4)gal-t (1.5 U) for 5 days. After work-up, 10.1 mg (50%) of starting material **5g** and 12.6 mg (49%) of sugar **7g** were isolated. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.61, 3.83, 3.82, 3.72, 3.59, 3.83 and 3.99; β-gal-unit (H-1 to H-6,6′) δ 4.49, 3.56, 3.69, 3.95, 3.75, 3.75 and 3.78; galA-unit (H-1 to H-5) δ 4.72, 3.58, 3.74, 4.29, 4.34; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.63 and 3.92, 1.77, 3.23 and 3.30, 5.13, 7.40–7.49. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.0, 55.8, 72.8, 79.1, 74.8, 60.4; β-gal-unit (C-1 to C-6) δ 103.7, 71.7, 73.1, 68.8, 75.6, 61.3; galA-unit (C-1 to C-5) δ 90.8, 70.4, 72.8, 69.2, 76.9; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 68.0, 29.0, 37.8, 66.9, 127.4–130.1. MS calcd for $C_{29}H_{43}N_5O_{17}$−H 732: found MS−H 732.

8-Methoxycarbonyloctyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-α-D-mannohexopyranosyluronamide)-β-D-glucopyranoside 6h. According to GP B, 17.0 mg (30.9 μmol) of sugar **4h** were dissolved in 170 μL DMSO and 1.4 mL HEPES-buffer and incubated with 22.7 mg (37.1 μmol) UDP-gal, 1.4 mg BSA, 6.0 mg (30.3 μmol) $MnCl_2 \times 4H_2O$, 2 μL CIAP, and 300 μL β(1-4)gal-t (1.5 U) for 4 days. After work-up, 3.4 mg (20%) of starting material **4h** and 13.7 mg (62%) of sugar **6h** were isolated. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.63, 3.80, 3.81, 3.74, 3.61, 3.85 and 4.01; β-gal-unit (H-1 to H-6,6′) δ 4.50, 3.56, 3.68, 3.94, 3.75, 3.76 and 3.78; manA-unit (H-1 to H-5) δ 5.55, 3.93, 3.79, 3.90, 4.02; aglycon (H-2 to H-9, OCH_3) δ 2.40, 1.61, 1.32, 1.32, 1.58, 3.62 and 3.91, 3.70. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.0, 55.7, 72.8, 79.1, 75.0, 60.3; β-gal-unit (C-1 to C-6) δ 103.7, 71.5, 72.9, 68.8, 75.6, 61.4; manA-unit (C-1 to C-5) δ 90.3, 69.9, 70.0, 68.0, 74.1; aglycon (C-2 to C-9, OCH_3) δ 34.1, 24.8, 28.5, 25.4, 28.8, 71.4, 52.2. MS calcd for $C_{28}H_{48}N_4O_{17}$ + Na 735: found MS + Na 735.

8-Methoxycarbonyloctyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-L-galactohexopyranosyluronamide)-β-D-glucopyranoside 6i. According to GP B, 20.0 mg (36.3 μmol) of sugar **4i** were dissolved in 170 μL DMSO and 1.4 mL HEPES-buffer and incubated with 26.6 mg (43.6 μmol) UDP-gal, 1.6 mg BSA, 7.1 mg (35.9 μmol) $MnCl_2 \times 4H_2O$, 2 μL CIAP, and 300 μL β(1-4)gal-t (1.5 U) for 3 days. After work-up, 6.9 mg (35%) of starting material **4i** and 16.8 mg (65%) of sugar **6i** were isolated. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.63, 3.86, 3.93, 3.74, 3.61, 3.85 and 4.01; β-gal-unit (H-1 to H-6,6′) δ 4.50, 3.56, 3.68, 3.94, 3.75, 3.75 and 3.79; galA-unit (H-1 to H-5) δ 4.71, 3.59, 3.78, 4.30, 4.29; aglycon (H-2 to H-9, OCH_3) δ 2.41, 1.62, 1.32, 1.31, 1.56, 3.62 and 3.91, 3.71. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.2, 55.8, 72.5, 79.0, 75.0, 60.4; β-gal-unit (C-1 to C-6) δ 103.7, 71.7, 73.0, 68.8, 75.6, 61.2; galA-unit (C-1 to C-5) δ 90.7, 70.6, 72.8, 69.2, 77.2; aglycon (C-2 to C-9, OCH_3) δ 34.1, 25.0, 28.3, 25.4, 28.7, 71.3, 52.3. MS calcd for $C_{28}H_{48}N_4O_{17}$ 712.705: found MS−H 711.

3-Benzoxycarbonylaminopropyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-L-galactohexopyranosyluronamide)-β-D-glucopyranoside 7i. According to GP B, 20.0 mg (35.0 μmol) of sugar **5i** were dissolved in 170 μL DMSO and 1.4 mL HEPES-buffer and incubated with 25.6 mg (42.0 μmol) UDP-gal, 1.5 mg BSA, 6.8 mg (34.4 μmol) $MnCl_2 \times 4H_2O$, 2 μL CIAP, and 300 μL β(1-4)gal-t (1.5 U) for 3 days. After work-up, 9.5 mg (48%) of starting material **5i** and 13.3 mg (52%) of sugar **7i** were isolated. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.59, 3.82, 3.81, 3.71, 3.57, 3.83 and 3.99; β-gal-unit (H-1 to H-6,6′) δ 4.48, 3.53, 3.65, 3.94, 3.72, 3.71 and 3.74; galA-unit (H-1 to H-5) δ 4.62, 3.50, 3.71, 4.24, 4.27; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.60 and 3.96, 1.75, 3.19 and 3.22, 5.13, 7.44–7.51. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.1, 55.8, 72.6, 79.0, 75.0, 60.2; β-gal-unit (C-1 to C-6) δ 103.7, 72.1, 72.8, 68.7, 75.5, 61.3; galA-unit (C-1 to C-5) δ 90.8, 70.5, 72.5, 69.2, 77.2; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 68.1, 28.9, 37.9, 67.0, 127.0–129.6. HRMS calcd for $C_{29}H_{43}N_5O_{17}$−H 732.2576: found MS−H 732.2573.

8-Methoxycarbonyloctyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 6j. According to GP B, 20.0 mg (31.3 μmol) of sugar **4j** were dissolved in 170 μL DMSO and 1.4 mL HEPES-buffer and incubated with 22.9 mg (37.6 μmol) UDP-gal, 1.4 mg BSA, 6.1 mg (30.8 μmol) $MnCl_2 \times 4H_2O$, 2 μL CIAP, and 300 μL β(1-4)gal-t (1.5 U) for 3 days. After work-up, 7.3 mg (37%) of starting material **4j** and 15.9 mg (63%) of sugar **6j** were isolated. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.63, 3.80, 3.81, 3.73, 3.61, 3.85 and 4.00; β-gal-unit (H-1 to H-6,6′) δ 4.49, 3.54, 3.68, 3.95, 3.75, 3.76 and 3.78; glcA-unit [H-1–H-5, H-1′, C(CH_3)$_3$] δ 3.44, 3.34, 3.53, 3.56, 3.84, 3.32 and 3.55, 1.46; aglycon (H-2 to H-9, OCH_3) δ 2.40, 1.61, 1.32, 1.33, 1.56, 3.62 and 3.91, 3.70. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 100.9, 55.8, 73.0, 79.3, 74.9, 60.3; β-gal-unit (C-1 to C-6) δ 103.7, 72.1, 73.0, 68.8, 75.6, 61.5; glcA-unit [C-1 to C-5, C-1′, C(CH_3)$_3$] δ 78.7, 71.1, 76.9, 72.3, 78.7, 41.3, 27.9; aglycon (C-2 to C-9, OCH_3) δ 34.2, 25.0, 28.6, 25.7, 28.6, 71.3, 52.1. MS calcd for $C_{34}H_{60}N_2O_{19}$ 801: found MS + Na 823.

3-Benzoxycarbonylaminopropyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 7j. According to GP B, 30.0 mg (45.5 μmol) of sugar **5j** were dissolved in 240 μL DMSO and 2.0 mL HEPES-buffer and incubated with 33.3 mg (54.7 μmol) UDP-gal, 2.0 mg BSA, 8.9 mg (44.9 μmol) $MnCl_2 \times 4H_2O$, 3 μL CIAP, and 450 μL β(1-4)gal-t (2.25 U) for 5 days. After work-up, 17.1 mg (57%) of starting material **5j** and 16.1 mg (43%) of sugar **7j** were isolated. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.52, 3.79, 3.77, 3.71, 3.55, 3.84 and 3.99; β-gal-unit (H-1 to H-6,6′) δ 4.47, 3.52, 3.69, 3.94, 3.75, 3.76 and 3.78;

glcA-unit [H-1 to H-5, H-1′, C(CH_3)$_3$] δ 3.39, 3.29, 3.51, 3.56, 3.84, 3.23 and 3.44, 1.42; aglycon (H-1 to H-3, OCH_2Ph, C$_6H_5$) δ 3.59 and 3.94, 1.74, 3.17 and 3.22, 5.12, 7.37–7.51. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.3, 55.6, 72.8, 79.1, 74.9, 60.4; β-gal-unit (C-1 to C-6) δ 103.5, 72.0, 73.0, 68.8, 75.6, 61.5; glcA-unit [C-1 to C-5, C-1′, C(CH_3)$_3$] δ 78.7, 71.1, 77.2, 72.6, 79.0, 41.3, 27.9; aglycon (C-1 to C-3, OCH_2Ph, C$_6H_5$) δ 67.6, 28.9, 37.4, 67.0, 127.0-130.1. MS calcd for $C_{35}H_{55}N_3O_{19}$ 821: found MS−H 820.

8-Methoxycarbonyloctyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 6k. According to GP B, 20.0 mg (31.3 μmol) of sugar **4k** were dissolved in 170 μL DMSO and 1.4 mL HEPES-buffer and incubated with 22.9 mg (37.6 μmol) UDP-gal, 1.4 mg BSA, 6.1 mg (30.8 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 300 μL β(1-4)gal-t (1.5 U) for 3 days. After work-up, 7.9 mg (40%) of starting material **4k** and 14.8 mg (59%) of sugar **6k** were isolated. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.78, 3.65, 3.95, 3.71, 3.61, 3.85 and 4.01; β-gal-unit (H-1 to H-6,6′) δ 4.50, 3.55, 3.68, 3.94, 3.74, 3.74 and 3.78; galA-unit [H-1 to H-5, H-1′, C(CH_3)$_3$] δ 3.36, 3.55, 3.72, 4.30, 4.14, 3.28 and 3.63, 1.46; aglycon (H-2 to H-9, OCH_3) δ 2.39, 1.61, 1.30, 1.31, 1.57, 3.62 and 3.86, 3.70. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 100.4, 56.5, 72.6, 79.4, 75.0, 60.4; β-gal-unit (C-1 to C-6) δ 103.7, 71.7, 72.9, 68.7, 75.6, 61.5; galA-unit [C-1 to C-5, C-1′, C(CH_3)$_3$] δ 79.6, 67.9, 73.8, 69.9, 78.4, 41.6, 27.9; aglycon (C-2 to C-9, OCH_3) δ 34.1, 25.1, 28.6, 25.7, 28.3, 71.6, 52.3. HRMS calcd for $C_{34}H_{60}N_2O_{19}$ + Cl 835.3479: found MS + Cl 835.3480.

3-Benzoxycarbonylaminopropyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 7k. According to GP B, 50.0 mg (75.8 μmol) of sugar **5k** were dissolved in 400 μL DMSO and 3.4 mL HEPES-buffer and incubated with 55.5 mg (91.1 μmol) UDP-gal, 3.4 mg BSA, 14.8 mg (74.7 μmol) $MnCl_2\times4H_2O$, 4 μL CIAP, and 550 μL β(1-4)gal-t (2.75 U) for 6 days. After work-up, 20.7 mg (42%) of starting material **5k** and 21.2 mg (34%) of sugar **7k** were isolated. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.57, 3.79, 3.80, 3.69, 3.52, 3.83 and 3.99; β-gal-unit (H-1 to H-6,6′) δ 4.47, 3.54, 3.57, 3.94, 3.75, 3.73 and 3.76; galA-unit [H-1 to H-5, H-1′, C(CH_3)$_3$] δ 3.37, 3.53, 3.66, 4.28, 4.17, 3.28 and 3.53, 1.45; aglycon (H-1 to H-3, OCH_2Ph, C$_6H_5$) δ 3.60 and 3.91, 1.73, 3.17 and 3.27, 5.14, 7.38–7.50. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 100.9, 55.8, 72.8, 79.1, 74.9, 60.4; β-gal-unit (C-1 to C-6) δ 103.7, 71.2, 73.0, 68.7, 75.6, 61.3; galA-unit [C-1 to C-5, C-1′, C(CH_3)$_3$] δ 79.2, 67.9, 73.4, 69.8, 78.3, 41.3, 27.9; aglycon (C-1 to C-3, OCH_2Ph, C$_6H_5$) δ 67.4, 28.8, 37.2, 67.0, 126.6–129.8. MS calcd for $C_{35}H_{55}N_3O_{19}$−H 820: found MS−H 820.

8-Methoxycarbonyloctyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(methyl-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 8a. According to GP C, 33.8 mg (48.2 μmol) of sugar **6a** were dissolved in 1.5 mL cacodylate-buffer and incubated with 77.5 mg (127 μmol) UDP-gal, 2.5 mg BSA, 40.0 mg (202 μmol) $MnCl_2\times4H_2O$, 5 μL CIAP, and 500 μL α(1-3)gal-t (1 U) for 3 days to give 27.9 mg (67%) of the title sugar. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.54, 3.74, 3.65, 3.69, 3.46, 3.85 and 3.88; β-gal-unit (H-1 to H-6,6′) δ 4.47, 3.65, 3.71, 4.07, 3.65, 3.68 and 3.74; α-gal-unit (H-1 to H-6,6′) δ 5.06, 3.81, 3.82, 3.94, 4.16, 3.68 (2 H); glcA-unit (H-1 to H-5, OCH_3) δ 4.29, 3.29, 3.47, 3.53, 3.76, 3.55; aglycon (H-2 to H-9, OCH_3) δ 2.32, 1.58, 1.29, 1.29, 1.58, 3.48 and 3.86, 3.67. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 102.6, 57.1, 77.0, 81.3, 77.4, 62.2; β-gal-unit (C-1 to C-6) δ 105.1, 71.2, 79.7, 66.9, 76.8, 63.0; α-gal-unit (C-1 to C-6) δ 97.7, 70.3, 71.3, 71.3, 73.6, 62.9; glcA-unit (C-1 to C-5, OCH_3) δ 105.6, 74.7, 77.4, 74.2, 76.6, 58.8; aglycon (C-2 to C-9, OCH_3) δ 35.7, 26.5, 30.8, 27.3, 31.3, 72.7, 53.2.

8-Methoxycarbonyloctyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(methyl-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 8b. According to GP C, 30.1 mg (42.9 μmol) of sugar **6b** were dissolved in 1.5 mL cacodylate-buffer and incubated with 69.0 mg (113 μmol) UDP-gal, 2.5 mg BSA, 35.6 mg (180 μmol) $MnCl_2\times4H_2O$, 5 μL CIAP, and 500 μL α(1-3)gal-t (1 U) for 3 days to give 22.6 mg (61%) of the title sugar. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.64, 3.71, 3.82, 3.62, 3.45, 3.87 and 3.94; β-gal-unit (H-1 to H-6,6′) δ 4.46, 3.67, 3.68, 4.07, 3.71, 3.84 and 3.91; α-gal-unit (H-1 to H-6,6′) δ 5.05, 3.84, 3.83, 3.93, 4.21, 3.71 and 3.78; galA-unit (H-1 to H-5, OCH_3) δ 4.23, 3.56, 3.56, 4.17, 4.04, 3.60; aglycon (H-2 to H-9, OCH_3) δ 2.32, 1.59, 1.30, 1.30, 1.58, 3.54 and 3.80, 3.65. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 102.2, 56.6, 73.7, 81.2, 75.9, 61.5; β-gal-unit (C-1 to C-6) δ 105.2, 70.5, 79.5, 66.0, 76.2, 61.5; α-gal-unit (C-1 to C-6) δ 97.7, 70.2, 70.2, 70.5, 71.8, 61.8; galA-unit (C-1 to C-5, OCH_3) δ 106.1, 71.3, 74.3, 70.3, 76.3, 57.1; aglycon (C-2–C-9, OCH_3) δ 33.8, 25.0, 29.6, 25.1, 29.6, 70.6, 51.4.

8-Methoxycarbonyloctyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(methyl-α-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 8c. According to GP C, 14.8 mg (21.1 μmol) of sugar **6c** were dissolved in 700 μL cacodylate-buffer and incubated with 33.9 mg (55.6 μmol) UDP-gal, 1.1 mg BSA, 17.5 mg (88.5 μmol) $MnCl_2\times4H_2O$, 3 μL CIAP, and 200 μL α(1-3)gal-t (400 mU) for 3 days to give 13.3 mg (73%) of the title sugar. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.54, 3.64, 3.74, 3.55, 3.37, 3.79 and 3.83; β-gal-unit (H-1 to H-6,6′) δ 4.39, 3.60, 3.69, 3.95, 3.61, 3.63 and 3.72; α-gal-unit (H-1 to H-6,6′) δ 4.99, 3.75, 3.75, 3.82, 4.13, 3.62 and 3.63; galA-unit (H-1 to H-5, OCH_3) δ 4.80, 3.74, 3.64, 4.13, 4.13, 3.37; aglycon (H-2 to H-9, OCH_3) δ 2.26, 1.53, 1.25, 1.25, 1.52, 3.54 and 3.75, 3.60. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 101.1, 56.0, 72.9, 80.4, 75.5, 61.1; β-gal-unit (C-1 to C-6) δ 104.1, 70.0, 79.0, 65.6, 75.7, 61.4; α-gal-unit (C-1 to C-6) δ 96.7, 70.1, 68.8, 70.1, 71.8, 61.7; galA-unit (C-1 to C-5, OCH_3) δ 100.8, 69.2, 70.1, 70.3, 71.2, 55.3; aglycon (C-2 to C-9, OCH_3) δ 33.8, 25.0, 29.3, 25.9, 29.6, 69.9, 51.0.

8-Methoxycarbonyloctyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(methyl-β-L-galactohexopyranosyluronamide)-β-D-glucopyranoside 8d. According to GP C, 10.0 mg (14.3 μmol) of sugar **6d** were dissolved in 450 μL cacodylate-buffer and incubated with 23.0 mg (37.7 μmol) UDP-gal, 0.7 mg BSA, 11.9 mg (60.1 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 150 μL α(1-3)gal-t (300 mU) for 3 days to give 9.9 mg (80%) of the title sugar. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.55, 3.86, 3.81, 3.66, 3.49, 3.86 and 3.93; β-gal-unit (H-1 to H-6,6′) δ 4.49, 3.67, 3.72, 4.08, 3.64, 3.71 and 3.78; α-gal-unit (H-1 to H-6,6′) δ 5.08, 3.84, 3.86, 3.95, 4.21, 3.63 and 3.71; galA-unit (H-1 to H-5, OCH_3) δ 4.25, 3.57, 3.60, 4.19, 4.05, 3.61; aglycon (H-2 to H-9, OCH_3) δ 2.34, 1.59, 1.30, 1.30, 1.59, 3.51 and 3.84, 3.67. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 101.8, 56.0, 73.0, 80.2, 75.3, 60.6; β-gal-unit (C-1 to C-6) δ 104.1, 70.2, 78.6, 65.7, 75.1, 61.6; α-gal-unit (C-1 to C-6) δ 96.9, 68.6, 70.4, 70.2, 71.8, 61.6; galA-unit (C-1 to C-5, O*C*H_3) δ 105.0, 72.3, 73.4, 70.0, 76.0, 57.2; aglycon (C-2 to C-9, O*C*H_3) δ 33.8, 25.8, 29.3, 25.0, 29.4, 70.1, 51.3.

8-Methoxycarbonyloctyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(methyl-α-L-galactohexopyranosyluronamide)-β-D-glucopyranoside 8e. According to GP C, 15.1 mg (21.6 μmol) of sugar **6e** were dissolved in 650 μL cacodylate-buffer and incubated with 34.7 mg (56.8 μmol) UDP-gal, 1.0 mg BSA, 17.9 mg (90.6 μmol) $MnCl_2\times4H_2O$, 3 μL CIAP, and 200 μL α(1-3)gal-t (400 mU) for 3 days to give 14.9 mg (80%) of the title sugar. ^{1}H NMR (CD_3OD, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.51, 3.86, 3.79, 3.64, 3.49, 3.88 and 3.96; β-gal-unit (H-1 to H-6,6′) δ 4.49, 3.67, 3.74, 4.08, 3.68, 3.72 and 3.80; α-gal-unit (H-1 to H-6,6′) δ 5.07, 3.84, 3.86, 3.95, 4.19, 3.68 and 3.72; galA-unit (H-1 to H-5, OCH_3) δ 4.91, 3.83, 3.80, 4.27, 4.22, 3.43; aglycon (H-2 to H-9, OCH_3) δ 2.33, 1.58, 1.29, 1.29, 1.58, 3.48 and 3.88, 3.67. ^{13}C NMR (CD_3OD) glcN-unit (C-1 to C-6) δ 101.6, 55.4, 72.8, 79.7, 75.4, 60.8; β-gal-unit (C-1 to C-6) δ 103.7, 70.4, 78.5, 65.6, 75.6, 61.6; α-gal-unit (C-1 to C-6) δ 96.4, 68.3, 68.5, 70.0, 71.7, 61.6; galA-unit (C-1 to C-5, O*C*H_3) δ 100.6, 68.3, 70.0, 70.4, 71.8, 55.5; aglycon (C-2 to C-9, O*C*H_3) δ 33.9, 25.9, 29.2, 25.0, 29.5, 70.6, 51.5.

8-Methoxycarbonyloctyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 8f. According to GP C, 10.0 mg (14.0 μmol) of sugar **6f** were dissolved in 300 μL cacodylate-buffer and incubated with 22.5 mg (36.9 μmol) UDP-gal, 0.7 mg BSA, 11.6 mg (58.6 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 300 μL α(1-3) gal-t (0.6 U/mL; 180 mU) for 3 days to give 5.0 mg (41%) of 'Lemieux ester' **8f** and 4.9 mg (41%) of the corresponding 'Lemieux acid'. Data of **8f**: ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.63, 3.83, 3.82, 3.77, 3.64, 3.87 and 4.03; β-gal-unit (H-1 to H-6,6′) δ 4.58, 3.70, 3.81, 4.21, 3.75, 3.79 and 3.81; α-gal-unit (H-1 to H-6,6′) δ 5.17, 3.89, 3.98, 4.06, 4.23, 3.77 (2H); glcA-unit (H-1 to H-5) δ 4.82, 3.35, 3.60, 3.62, 4.01; aglycon (H-2 to H-9, OCH_3) δ 2.42, 1.63, 1.34, 1.35, 1.59, 3.65 and 3.93, 3.72. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.1, 55.9, 73.0, 79.6, 75.2, 60.4; β-gal-unit (C-1 to C-6) δ 103.7, 70.2, 77.8, 65.4, 75.3, 61.5; α-gal-unit (C-1 to C-6) δ 95.8, 68.5, 69.6, 69.8, 71.7, 61.3; glcA-unit (C-1 to C-5) δ 90.3, 72.8, 75.4, 71.5, 77.0; aglycon (C-2 to C-9, O*C*H_3) δ 34.1, 25.0, 28.3, 25.4, 28.8, 71.3, 52.1. $[\alpha]_D$ +41 (*c* 0.25, H_2O). HRMS calcd for $C_{34}H_{58}N_4O_{22}$ + Na 897.3440: found MS + Na 897.3436.

3-Benzoxycarbonylaminopropyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 9f. According to GP C, 10.0 mg (13.6 μmol) of sugar **7f** were dissolved in 450 μL cacodylate-buffer and incubated with 21.9 mg (35.8 μmol) UDP-gal, 0.7 mg BSA, 11.3 mg (57.1 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 150 μL α(1-3)gal-t (300 mU) for 1 day to give 9.2 mg (76%) of the title sugar. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.54, 3.82, 3.76, 3.73, 3.57, 3.84 and 4.01; β-gal-unit (H-1 to H-6,6′) δ 4.55, 3.69, 3.79, 4.19, 3.74, 3.78 and 3.80; α-gal-unit (H-1 to H-6,6′) δ 5.16, 3.88, 3.97, 4.04, 4.21, 3.76 and 3.77; glcA-unit (H-1 to H-5) δ 4.72, 3.30, 3.55, 3.61, 3.97; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.60 and 3.94, 1.75, 3.15 and 3.21, 5.13, 7.38–7.48. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.2, 55.6, 72.8, 79.4, 75.0, 60.4; β-gal-unit (C-1 to C-6) δ 103.5, 70.1, 77.7, 65.3, 75.3, 61.2; α-gal-unit (C-1 to C-6) δ 95.9, 68.3, 69.7, 69.5, 71.5, 61.3; glcA-unit (C-1 to C-5) δ 90.3, 72.8, 75.4, 71.4, 77.4; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 67.8, 28.9, 37.6, 67.1, 131.8-134.4. $[\alpha]_D$ +29 (*c* 0.60, H_2O). HRMS calcd for $C_{35}H_{53}N_5O_{22}$ + H 896.3259: found MS + H 896.3272.

8-Methoxycarbonyloctyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 8g. According to GP C, 10.0 mg (14.0 μmol) of sugar **6g** were dissolved in 300 μL cacodylate-buffer and incubated with 22.5 mg (36.9 μmol) UDP-gal, 0.7 mg BSA, 11.6 mg (58.6 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 300 μL α(1-3) gal-t (0.6 U/ml; 180 mU) for 1 day to give 6.5 mg (53%) of 'Lemieux ester' **8g** and 3.4 mg (28%) of the corresponding 'Lemieux acid'. Data of **8g**: ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.70, 3.79, 3.89, 3.74, 3.63, 3.86 and 4.02; β-gal-unit (H-1 to H-6,6′) δ 4.57, 3.70, 3.79, 4.20, 3.74, 3.78 and 3.80; α-gal-unit (H-1 to H-6,6′) δ 5.17, 3.88, 3.97, 4.04, 4.22, 3.75 (2 H); galA-unit (H-1 to H-5) δ 4.76, 3.59, 3.79, 4.30, 4.33; aglycon (H-2 to H-9, OCH_3) δ 2.40, 1.61, 1.31, 1.31, 1.57, 3.64 and 3.85, 3.70. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 100.6, 55.8, 72.8, 79.4, 74.9, 60.4; β-gal-unit (C-1 to C-6) δ 103.5, 70.4, 77.6, 65.4, 75.3, 61.3; α-gal-unit (C-1 to C-6) δ 95.8, 68.3, 69.8, 69.5, 71.7, 61.3; galA-unit (C-1 to C-5) δ 90.7, 70.6, 73.0, 69.5, 76.9; aglycon (C-2 to C-9, O*C*H_3) δ 34.3, 25.1, 28.3, 25.4, 28.9, 71.7, 52.3. $[\alpha]_D$ +29 (*c* 0.33, H_2O). HRMS calcd for $C_{34}H_{58}N_4O_{22}$ + H 875.3623: found MS + H 875.3607.

3-Benzoxycarbonylaminopropyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 9g. According to GP C, 10.0 mg (13.6 μmol) of sugar **7g** were dissolved in 450 μL cacodylate-buffer and incubated with 21.9 mg (35.8 μmol) UDP-gal, 0.7 mg BSA, 11.3 mg (57.1 μmol) $MnCl_2\times4H_2O$, 2 μL

CIAP, and 150 μL α(1-3)gal-t (300 mU) for 1 day to give 11.7 mg (96%) of the title sugar. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.60, 3.82, 3.82, 3.72, 3.58, 3.82 and 4.00; β-gal-unit (H-1 to H-6,6′) δ 4.55, 3.68, 3.79, 4.20, 3.73, 3.74 and 3.77; α-gal-unit (H-1 to H-6,6′) δ 5.16, 3.87, 3.97, 4.04, 4.19, 3.75 (2 H); galA-unit (H-1 to H-5) δ 4.73, 3.58, 3.74, 4.28, 4.34; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.63 and 3.91, 1.75, 3.21 and 3.27, 5.13, 7.42–7.52. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 100.7, 55.6, 72.9, 79.2, 75.0, 60.4; β-gal-unit (C-1 to C-6) δ 103.5, 70.2, 77.6, 65.2, 75.3, 61.4; α-gal-unit (C-1 to C-6) δ 96.0, 68.3, 69.7, 69.5, 71.5, 61.4; galA-unit (C-1 to C-5) δ 90.8, 70.5, 72.9, 69.2, 76.8; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 68.0, 29.2, 37.8, 67.0, 127.4–129.6. $[\alpha]_D$ +31 (*c* 0.59, H_2O). HRMS calcd for $C_{35}H_{53}N_5O_{22}$ +H 896.3259: found MS+H 896.3274.

8-Methoxycarbonyloctyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-α-D-mannohexopyranosyluronamide)-β-D-glucopyranoside 8h. According to GP C, 10.0 mg (14.0 μmol) of sugar **6h** were dissolved in 450 μL cacodylate-buffer and incubated with 22.5 mg (36.8 μmol) UDP-gal, 0.7 mg BSA, 11.6 mg (58.7 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 150 μL α(1-3) gal-t (300 mU) for 1 day to give 10.1 mg (83%) of the title sugar. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.64, 3.81, 3.81, 3.76, 3.62, 3.85 and 4.02; β-gal-unit (H-1 to H-6,6′) δ 4.58, 3.69, 3.80, 4.20, 3.74, 3.78 and 3.80; α-gal-unit (H-1 to H-6,6′) δ 5.16, 3.88, 3.97, 4.04, 4.21, 3.76 (2 H); manA-unit (H-1 to H-5) δ 5.55, 3.93, 3.79, 3.90, 4.22; aglycon (H-2 to H-9, OCH_3) δ 2.40, 1.62, 1.31, 1.32, 1.59, 3.62 and 3.91, 3.70. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.0, 55.7, 72.9, 79.3, 75.0, 60.4; β-gal-unit (C-1 to C-6) δ 103.5, 70.1, 77.5, 65.3, 75.2, 61.3; α-gal-unit (C-1 to C-6) δ 96.0, 68.5, 69.7, 69.5, 71.6, 61.2; manA-unit (C-1 to C-5) δ 90.3, 69.9, 70.0, 68.0, 74.1; aglycon (C-2 to C-9, O*C*H_3) δ 34.3, 24.8, 28.3, 25.4, 28.8, 71.3, 52.1. $[\alpha]_D$ +104 (*c* 0.59, H_2O). HRMS calcd for $C_{34}H_{58}N_4O_{22}$−H 873.3464: found MS−H 873.3480.

8-Methoxycarbonyloctyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-L-galactohexopyranosyluronamide)-β-D-glucopyranoside 8i. According to GP C, 10.0 mg (14.0 μmol) of sugar **6i** were dissolved in 450 μL cacodylate-buffer and incubated with 22.5 mg (36.9 μmol) UDP-gal, 0.7 mg BSA, 11.6 mg (58.6 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 150 μL α(1-3) gal-t (300 mU) for 1 day to give 11.5 mg (94%) of the title sugar. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.63, 3.86, 3.86, 3.75, 3.62, 3.86 and 4.02; β-gal-unit (H-1 to H-6,6′) δ 4.57, 3.68, 3.80, 4.20, 3.74, 3.78 and 3.81; α-gal-unit (H-1 to H-6,6′) δ 5.16, 3.87, 3.97, 4.04, 4.21, 3.76 (2 H); galA-unit (H-1 to H-5) δ 4.71, 3.58, 3.78, 4.30, 4.29; aglycon (H-2 to H-9, OCH_3) δ 2.41, 1.62, 1.32, 1.32, 1.56, 3.62 and 3.91, 3.71. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.3, 55.6, 72.6, 79.3, 75.0, 60.4; β-gal-unit (C-1 to C-6) δ 103.6, 70.1, 77.5, 65.3, 75.3, 61.2; α-gal-unit (C-1 to C-6) δ 96.0, 68.4, 69.7, 69.5, 71.7, 61.3; galA-unit (C-1 to C-5) δ 90.7, 70.4, 72.7, 69.3, 77.1; aglycon (C-2 to C-9, O*C*H_3) δ 34.2, 25.0, 28.2, 25.7, 28.5, 71.2, 52.3. $[\alpha]_D$ +67 (*c* 0.73, H_2O). HRMS calcd for $C_{34}H_{58}N_4O_{22}+NH_4$ 897.3440: found MS+NH_4 897.3441.

3-Benzoxycarbonylaminopropyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-azido-β-L-galactohexopyranosyluronamide)-β-D-glucopyranoside 9i. According to GP C, 10.0 mg (13.6 μmol) of sugar **7i** were dissolved in 450 μL cacodylate-buffer and incubated with 21.9 mg (35.8 μmol) UDP-gal, 0.7 mg BSA, 11.3 mg (57.1 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 150 μL α(1-3)gal-t (300 mU) for 1 day to give 11.9 mg (98%) of the title sugar. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.57, 3.83, 3.83, 3.72, 3.57, 3.84 and 4.00; β-gal-unit (H-1 to H-6,6′) δ 4.55, 3.68, 3.79, 4.19, 3.73, 3.78 and 3.80; α-gal-unit (H-1 to H-6,6′) δ 5.16, 3.87, 3.97, 4.04, 4.20, 3.75 (2 H); galA-unit (H-1 to H-5) δ 4.63, 3.53, 3.65, 4.24, 4.27; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.62 and 3.97, 1.76, 3.19 and 3.23, 5.13, 7.39–7.50. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.2, 55.6, 72.6, 79.2, 75.0, 60.4; β-gal-unit (C-1 to C-6) δ 103.5, 70.2, 77.6, 65.2, 75.2, 61.4; α-gal-unit (C-1 to C-6) δ 95.9, 68.3, 69.8, 69.5, 71.5, 61.3; galA-unit (C-1 to C-5) δ 90.8, 70.3, 72.7, 69.1, 77.0; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 67.9, 28.9, 37.8, 67.0, 127.0–130.1. $[\alpha]_D$ +71 (*c* 0.79, H_2O). HRMS calcd for $C_{35}H_{53}N_5O_{22}$+Na 918.3080: found MS+Na 918.3080.

8-Methoxycarbonyloctyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 8j. According to GP C, 10.0 mg (12.5 μmol) of sugar **6j** were dissolved in 400 μL cacodylate-buffer and incubated with 20.1 mg (32.9 μmol) UDP-gal, 0.6 mg BSA, 10.4 mg (52.6 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 200 μL α(1-3)gal-t (400 mU) for 1 day to give 9.6 mg (80%) of the title sugar. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.63, 3.82, 3.82, 3.72, 3.61, 3.85 and 4.02; β-gal-unit (H-1 to H-6,6′) δ 4.57, 3.68, 3.79, 4.20, 3.74, 3.78 and 3.80; α-gal-unit (H-1 to H-6,6′) δ 5.17, 3.88, 3.97, 4.04, 4.22, 3.76 (2 H); glcA-unit [H-1 to H-5, H-1′, C(CH_3)$_3$] δ 3.44, 3.32, 3.53, 3.54, 3.84, 3.40 and 3.55, 1.46; aglycon (H-2 to H-9, OCH_3) δ 2.40, 1.60, 1.32, 1.32, 1.56, 3.62 and 3.93, 3.70. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 100.9, 55.7, 72.8, 79.6, 75.0, 60.4; β-gal-unit (C-1 to C-6) δ 103.6, 70.2, 77.6, 65.3, 75.3, 61.3; α-gal-unit (C-1 to C-6) δ 95.9, 68.5, 69.9, 69.6, 71.5, 61.3; glcA-unit [C-1 to C-5, C-1′, C(*C*H_3)$_3$] δ 78.7, 71.1, 77.2, 72.1, 78.9, 41.3, 27.9; aglycon (C-2 to C-9, O*C*H_3) δ 34.2, 25.0, 28.5, 25.3, 28.5, 71.1, 52.3. $[\alpha]_D$ +37 (*c* 0.64, H_2O). HRMS calcd for $C_{40}H_{70}N_2O_{24}$+Na 985.4215: found MS+Na 985.4262.

3-Benzoxycarbonylaminopropyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-glucohexopyranosyluronamide)-β-D-glucopyranoside 9j. According to GP C, 10.0 mg (12.2 μmol) of sugar **7j** were dissolved in 450 μL cacodylate-buffer and incubated with 19.6 mg (32.1 μmol) UDP-gal, 0.6 mg BSA, 10.1 mg (51.1 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 150 μL α(1-3)gal-t (300 mU) for 1 day to give 9.6 mg (80%) of the title sugar. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1

to H-6,6′) δ 4.51, 3.80, 3.75, 3.72, 3.54, 3.83 and 4.01; β-gal-unit (H-1 to H-6,6′) δ 4.55, 3.69, 3.79, 4.20, 3.74, 3.77 and 3.78; α-gal-unit (H-1 to H-6,6′) δ 5.17, 3.88, 3.98, 4.04, 4.22, 3.70 and 3.72; glcA-unit [H-1 to H-5, H-1′, C(CH_3)$_3$] δ 3.40, 3.29, 3.51, 3.51, 3.84, 3.24 and 3.44, 1.43; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.59 and 3.95, 1.73, 3.16 and 3.22, 5.13, 7.39–7.51. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 101.2, 55.5, 72.8, 79.4, 74.9, 60.4; β-gal-unit (C-1 to C-6) δ 103.6, 70.1, 77.7, 65.2, 75.3, 61.3; α-gal-unit (C-1 to C-6) δ 95.9, 68.3, 69.7, 69.5, 71.6, 61.4; glcA-unit [C-1 to C-5, C-1′, C(CH_3)$_3$] δ 78.6, 71.1, 77.0, 72.1, 78.9, 41.1, 27.7; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 67.6, 28.9, 37.2, 67.1, 127.0-129.8. $[\alpha]_D$ +39 (*c* 0.53, H_2O). HRMS calcd for $C_{41}H_{65}N_3O_{24}$−H 982.3880: found MS−H 982.3881.

8-Methoxycarbonyloctyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 8k. According to GP C, 10.0 mg (12.5 μmol) of sugar **6k** were dissolved in 450 μL cacodylate-buffer and incubated with 20.1 mg (32.9 μmol) UDP-gal, 0.6 mg BSA, 10.4 mg (52.6 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 150 μL α(1-3)gal-t (300 mU) for 1 day to give 9.3 mg (77%) of the title sugar. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.78, 3.68, 3.98, 3.75, 3.64, 3.87 and 4.03; β-gal-unit (H-1 to H-6,6′) δ 4.56, 3.69, 3.81, 4.20, 3.76, 3.81 and 3.84; α-gal-unit (H-1 to H-6,6′) δ 5.17, 3.90, 3.98, 4.04, 4.22, 3.75 and 3.76; galA-unit [H-1 to H-5, H-1′, C(CH_3)$_3$] δ 3.39, 3.58, 3.73, 4.29, 4.14, 3.31 and 3.65, 1.46; aglycon (H-2 to H-9, OCH_3) δ 2.40, 1.62, 1.31, 1.32, 1.57, 3.66 and 3.89, 3.70. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 100.2, 56.4, 72.5, 79.6, 74.9, 60.5; β-gal-unit (C-1 to C-6) δ 103.6, 70.1, 77.4, 65.2, 75.3, 61.3; α-gal-unit (C-1 to C-6) δ 95.9, 68.3, 69.7, 69.5, 71.5, 61.3; glcA-unit [C-1 to C-5, C-1′, C(CH_3)$_3$] δ 79.4, 68.2, 73.9, 69.9, 78.5, 41.5, 27.9; aglycon (C-2 to C-9, OCH_3) δ 34.3, 25.0, 28.6, 25.4, 28.3, 71.3, 52.3. $[\alpha]_D$ +36 (*c* 0.52, H_2O). HRMS calcd for $C_{40}H_{70}N_2O_{24}$+Na 985.4216: found MS+Na 985.4213.

3-Benzoxycarbonylaminopropyl α-D-galactopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-deoxy-2-(1-deoxy-1-*tert*-butoxycarbonylaminomethyl-β-D-galactohexopyranosyluronamide)-β-D-glucopyranoside 9k. According to GP C, 9.0 mg (11.0 μmol) of sugar **7k** were dissolved in 400 μL cacodylate-buffer and incubated with 17.7 mg (29.0 μmol) UDP-gal, 0.5 mg BSA, 9.2 mg (46.5 μmol) $MnCl_2\times4H_2O$, 2 μL CIAP, and 200 μL α(1-3)gal-t (400 mU) for 1 day to give 10.0 mg (92%) of the title sugar. ^{1}H NMR (D_2O, 400.1 MHz) glcN-unit (H-1 to H-6,6′) δ 4.59, 3.74, 3.82, 3.70, 3.54, 3.80 and 3.99; β-gal-unit (H-1 to H-6,6′) δ 4.58, 3.69, 3.81, 4.21, 3.72, 3.75 (2 H); α-gal-unit (H-1 to H-6,6′) δ 5.17, 3.86, 3.99, 4.05, 4.22, 3.75 (2 H); galA-unit [H-1 to H-5, H-1′, C(CH_3)$_3$] δ 3.40, 3.56, 3.69, 4.27, 4.18, 3.29 and 3.53, 1.45; aglycon (H-1 to H-3, OCH_2Ph, C_6H_5) δ 3.62 and 3.86, 1.75, 3.18 and 3.27, 5.13, 7.35–7.48. ^{13}C NMR (D_2O) glcN-unit (C-1 to C-6) δ 100.9, 55.9, 73.0, 79.6, 75.0, 60.4; β-gal-unit (C-1 to C-6) δ 103.5, 70.1, 77.8, 65.3, 75.2, 61.2; α-gal-unit (C-1 to C-6) δ 96.1, 68.3, 69.6, 69.6, 71.7, 61.2; galA-unit [C-1 to C-5, C-1′, C(CH_3)$_3$] δ 79.1, 67.9, 73.9, 69.8, 78.4, 41.3, 27.9; aglycon (C-1 to C-3, OCH_2Ph, C_6H_5) δ 67.8, 28.9, 37.4, 67.0, 127.4–130.1. $[\alpha]_D$ +31 (*c* 0.50, H_2O). HRMS calcd for $C_{41}H_{65}N_3O_{24}$+Na 1006.3856: found MS+Na 1006.3868.

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