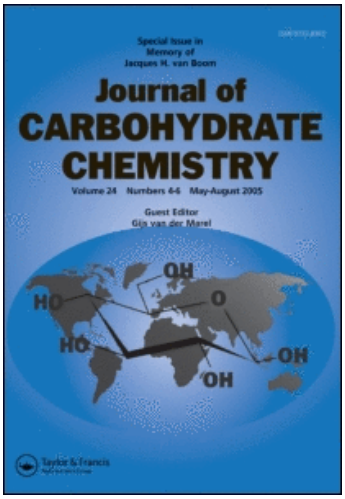

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PALLADIUM-CATALYZED SYNTHESIS OF BIS-GLYCOSIDES OF BUT-2-ENE-1,4-DIOL, BUTANE-1,4-DIOL AND 1,2-BIS(PROPENYL)BENZENE

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ABSTRACT

Palladium(0)-catalyzed reaction of various carbohydrates derived from glucofuranose, mannofuranose, ribofuranose, glucopyranose, and glucosamine, bearing a free hydroxyl group, with 1,4-bis-(methoxycarbonyloxy)but-2-ene afforded the corresponding bis-glycosides of butene-1,4-diol. Hydrogenation in the presence of palladium on charcoal of these unsaturated compounds led to the formation of the bis-glycosides of butane-1,4-diol. The condensation was successfully extended to the bis-carbonate of 1,2-bis-[(1-hydroxy)propen-2-yl]benzene and derivatives of glucofuranose, ribofuranose and glucosamine.

Key Words: Spacer-linked disaccharides; Palladium; Butene-1,2-diol; 1,2-bis-[(1-Hydroxy)propen-2-yl]benzene

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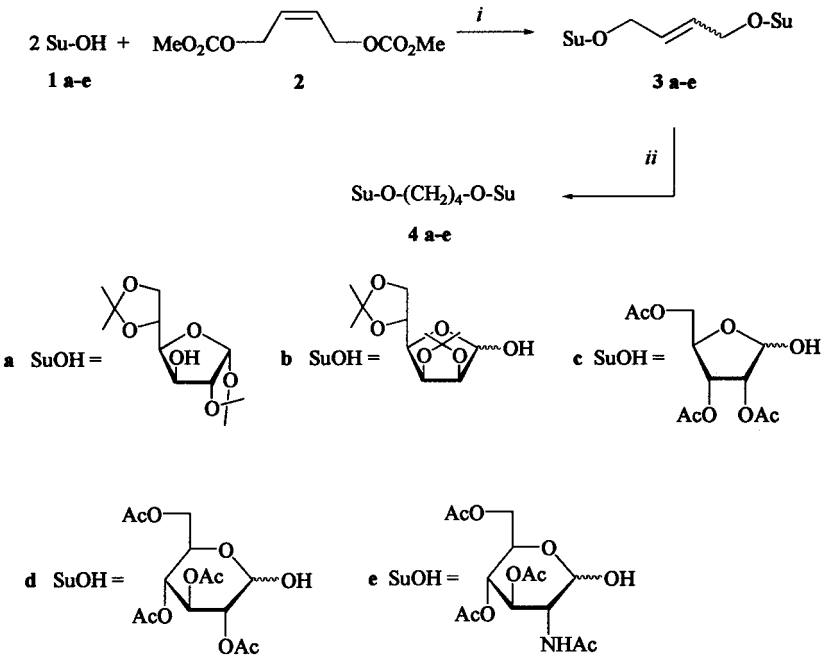
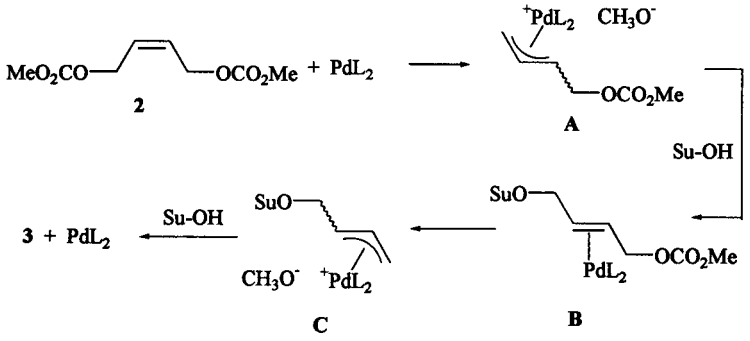
INTRODUCTION

Synthesis of spacer-modified disaccharides has attracted considerable attention during the last years.[1] This interest is mainly due to the biological importance of carbohydrates in mediating a host of biological responses. This implication of carbohydrates in molecular recognition processes has prompted researchers to prepare complex oligosaccharides as tools for the study of the binding modes of various protein–carbohydrate interactions. Another alternative is the synthesis of oligosaccharide mimics which may offer a more flexible access to potential biological compounds. For example, a homologous series of 1,10-bis(2-acetamido-2-deoxy-β-glucopyranosyloxy)alkanes were prepared by Lehmann's group[2,3] in order to study the mechanism of galactosylation of β-galactosyltransferase. An access to various spacer-linked 1,1′-bis-and 1,1′,1″-tris-β-glycosides was described by Patch et al.,[4] and to anomeric dimaltosides of alkanediols by Tsuzuki and Tsuchiya.[5] More recently, various *O*- and *C*-allyl and *O*-pentenyl D-galactopyranoside and lactoside homodimers were obtained by using ruthenium catalyzed olefin metathesis.[6–8] These spacer-linked carbohydrates are also precursors of gemini surfactants[9,10] or of various carbohydrate-based macrocycles.[11,12]

We have previously shown that palladium-catalyzed *O*-alkylation of unsaturated carbohydrates by various glycosides with free hydroxyl groups provided an easy access to various disaccharides. Following our continuing interest in the use of organometallic catalysis in the carbohydrate field, we report here the application of this palladium-catalyzed methodology for the synthesis of various spacer-linked disaccharides.[13–17]



Scheme 1. Palladium-catalyzed synthesis of bis-glycosides of butene-1,4-diol. Reagents: ***i***: $Pd_2(dba)_3$, dppb, THF, 25 °C; ***ii***: H_2, Pd/C 10%, AcOEt, 25 °C.



Scheme 2. Mechanism of the formation of the disaccharides.

RESULTS AND DISCUSSION

In our previous studies, we performed the palladium-catalyzed reaction between the bis-allylic carbonate **2** and various carbohydrates **1a–e** having a free hydroxyl group on the tetrahydrofuran ring at 60°C in the presence of a catalytic amount of tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$] and 1,4-bis(diphenylphosphino)butane (dppb) (Scheme 1).

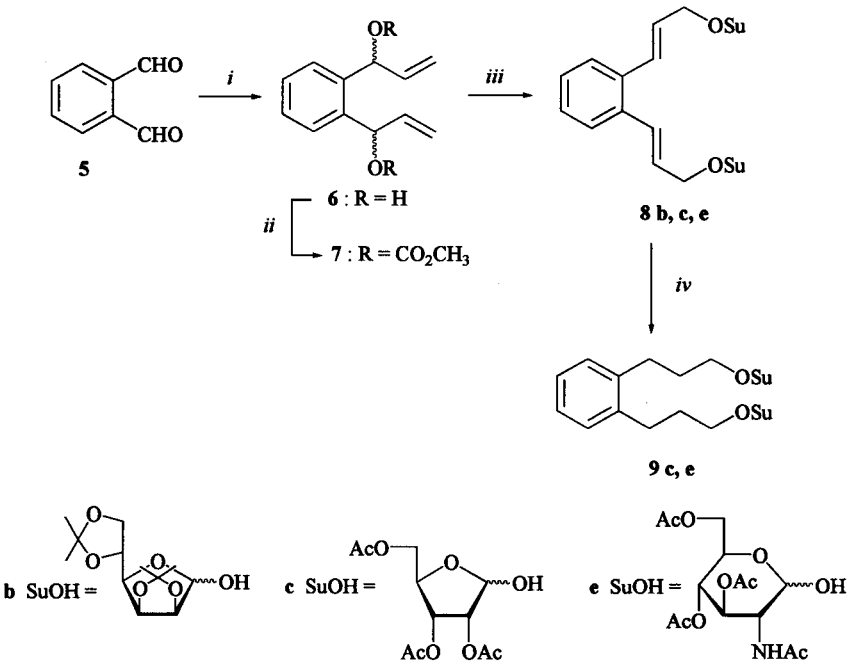
The proposed mechanism of formation of the disaccharides **3** is described in Scheme 2. Oxidative addition of the bis-carbonate **2** to the palladium complex would give the π-allyl palladium intermediate **A**. Hydrogen exchange between methoxide ion and the hydroxyl group of the carbohydrate, followed by attack of the new oxo-anion formed, is thought to afford the π-palladium complex **B**. A second oxidative addition on the palladium would give the new π-allyl palladium complex **C**, whose attack by a second molecule of carbohydrate then would lead to the unsaturated bis-saccharide **3**.

We first used the bis-carbonate **2** derived from butene-1,2-diol as the π-allyl precursor and as oxygen nucleophiles various carbohydrates **1a–e** (Scheme 1). The results obtained in these condensations are summarized in Table 1.

1,2;5,6-Di-*O*-isopropylidene-α-D-glucofuranose (**1a**) reacted with the bis-carbonate **2** under the standard conditions to give the unsaturated disaccharide **3a** in 29% yield after column chromatography as a 9:1 mixture of the two stereoisomers *E*/*Z*. The

Table 1. Palladium-Catalyzed Condensation of Carbonates **2** and **7** with Various Carbohydrates

Carbonate	Carbohydrate	Yield (%)	Anomers (%)
2	**1a**	26	–
	1b	38	α,α (100)
	1c	52	β,β/α,β (80/20)
	1d	56	α,α/α,β (50/50)
	1e	54	α,α/α,β (90/10)
7	**1b**	38	α,α (100)
	1c	63	β,β/α,β (75/25)
	1e	59	α,α/α,β (70/30)



Scheme 3. Palladium-catalyzed synthesis of bis-glycosides of 1,2-bis-[(1-hydroxy)propen-2-yl] benzene. Reagents: ***i***: CH_2 = $CHMgBr$, Et_2O, then H_2O; ***ii***: $ClCO_2CH_3$, C_5H_5N, CH_2Cl_2, 25 °C; ***iii***: SuOH, $Pd_2(dba)_3$, dppb, THF, 25 °C; ***iv***: H_2, Pd/C 10%, AcOEt, 25 °C.

presence of *E*/*Z* isomers was confirmed from the ^{13}C NMR data; we observed two signals for the allylic carbon atom, the signal of the *E*-isomer (δ 70.2 ppm) being at lower field than the signal of the *Z*-isomer (δ 66.0 ppm). Reduction of the double bond of compound **3a** in the presence of palladium on charcoal as the catalyst gave the saturated disaccharide **4a** quantitatively.

Reaction of the furanoses **1b** and **1c**, namely 2,3;5,6-di-*O*-isopropylidene-D-mannofuranose and 2,3,5-tri-*O*-acetyl-D-ribofuranose, having a free hydroxyl group at the anomeric position, with bis-carbonate **2** gave the corresponding disaccharides **3b** and **3c** in 38% and 52% yield, respectively. While bis-saccharide **3b** was obtained as the single α,α anomer and as an *E*/*Z* mixture (83:17), bis-saccharide **3c** was an α,β/β,β mixture in a 1:4 ratio.

When the reaction was performed using the pyranoses **1d** and **1e**, namely 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose and 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranose, bis-saccharides **3d** and **3e** were obtained in 56% and 59% yields, respectively. Disaccharide **3d** was a 1:1 mixture of the α,α and α,β anomers, while disaccharide **3e** was a 9:1 mixture of the two α,α and α,β anomers.

We then extended this coupling reaction to another allylic bis-carbonate **7** obtained by reaction of the corresponding diol **6** with methyl chloroformate in the presence of pyridine, in order to obtain potentially complexing molecules (Scheme 3). Coupling of bis-carbonate **7** with 2,3;5,6-di-*O*-isopropylidene-D-mannofuranose gave the bis-saccharide **8b** in 38% yield as the unique α,α anomer having the *E* stereochemistry. On the

other hand, when the coupling was performed with 2,3,5-tri-*O*-acetyl-D-ribofuranose and 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranose as the carbohydrates, bis-saccharides **8c** and **8e** were obtained in 63 and 59% yield, respectively. Compound **8c** was a 3:1 mixture of the β,β and α,β anomers with the *E* stereochemistry, while compound **8e** was a 7:3 mixture of α,α and α,β anomers, also with the *E* stereochemistry.

The determination of the anomeric configuration of the disaccharides was mainly based on ^{1}H and ^{13}C NMR spectroscopic data, in some cases after hydrogenation of the corresponding unsaturated disaccharides.

The α-anomeric configuration of compounds **3b** and **8b** was readily derived from the ^{1}H NMR data; the coupling constants $J_{1,2} \approx 0$ Hz for the anomeric proton at δ 5.00, 5.02, and 5.10 ppm, for (*Z*)-**3b**, (*E*)-**3b**, and **8b**, respectively, are characteristic of the α configuration in the mannofuranose series.[18,19] The α,α configuration was also confirmed from the ^{1}H NMR data of the saturated compound **4b**, exhibiting again a unique broad singlet for the anomeric proton at δ 4.97 ppm.

Compound **3b** was an 83:17 mixture of *E*/*Z* stereoisomers, as deduced from the ^{1}H NMR spectrum, the major isomer exhibiting two signals for the H-1 and H-2 protons at δ 5.02 and 4.61 ppm, respectively, while the minor one exhibited two signals at δ 5.00 and 4.58 ppm, respectively. The *E*/*Z* stereochemistry was assigned from the ^{13}C NMR data; the signal of the allylic carbon atom of the major isomer *E* is at lower field (δ 66.9 ppm) than the signal of the minor isomer *Z* (δ 62.6 ppm). For disaccharide **8b**, the stereochemistry at the double bond was *E*, according to the coupling constant $J = 15.7$ Hz observed for the ethylenic proton at δ 6.87 ppm.

For disaccharide **3c**, the signals of the anomeric protons appeared at δ 5.00 and 5.04 ppm in a 8:1 ratio as two broad singlets, characteristic of a cis arrangement of H-1 and H-2, thus indicating a β configuration in the ribofuranoside series;[20,21] the signal of the minor isomer corresponding to the α configuration appeared together with the H-2 and H-3 signals. We proposed for compound **3c** an 8:2 mixture of β,β and β,α anomers, this assignment being also in agreement with the stereoselectivity previously observed in quite similar alkylation reactions.[15] These assignments were confirmed by the ^{1}H NMR data of the saturated compound **4c**. We observed two broad singlets for H-1 at δ 4.96 and 4.99 ppm in a ratio 8:1, and a sole doublet at δ 5.23 ppm with a coupling constant $J_{1,2} = 5.6$ Hz in a ratio 1:8 compared to the signal at δ 4.96 ppm, characteristic of a β,β and β,α configuration in the ribofuranose series,[20,21] respectively. It is to be noticed that the relative chemical shifts for C-1 at δ 104.9, 105.2, and 105.4 for anomers α, β, and β, respectively, are in agreement with the literature data for such compounds, as well as the chemical shifts for C-5 and OCH_2.[22] The *E* stereochemistry was assigned at the double bond of compound **3c** since only one stereoisomer was detected.

For disaccharide **8c**, the signal of the anomeric proton appeared at δ 5.11 ppm for the major anomer as a broad singlet, characteristic of a β configuration, and at δ 5.26 as a doublet ($J_{1,2} = 4.4$ Hz) for the minor anomer, characteristic of an α configuration.[20,21] These assignments were confirmed from the ^{13}C NMR spectra, with the signal of the anomeric carbon at δ 99.6 ppm for the minor isomer, and at δ 104.3 ppm for the major one, characteristic of an α and β configuration, respectively.[22] The *E* stereochemistry of the double bond was assigned from the coupling constant $J = 15.8$ Hz of the ethylenic protons. The ^{13}C NMR spectrum of the saturated compound **4c** also confirmed these assignments, the signal for the anomeric carbon appearing at δ 100.6 and 105.3 ppm for the α and the β configuration, respectively.

Bis-carbohydrate **3d** was a 1:1 mixture of α,α and α,β anomers. The signal in the ^{1}H NMR spectrum of the anomeric proton for the anomer β appeared as a doublet at δ 4.56 ppm with a coupling constant $J_{1,2}=7.7$ Hz. When the anomeric proton for the anomer α appeared together with the H-4 signal of anomer α and the H-2 signal of anomer β, the H-2 signal for the α anomer appeared as a doublet of doublets at δ 4.89 ppm, with a coupling constant $J_{1,2}=3.7$ Hz.[20,23] The same values were observed for the reduced product **4d**, with a coupling constant $J_{1,2}=7.4$ Hz, and 3.7 Hz, for the β and α anomers, respectively.

The ^{13}C spectrum of **3d** is in agreement with this assignment. The signals corresponding to the anomeric carbon for **3d** were observed at δ 99.7 ppm for the β anomer, and at δ 94.8 and 95.1 ppm for the α anomer, the last one being the major signal. The signal of C-5 appeared at δ 67.4 and 71.8 ppm for the α and β anomers, respectively. The same trends were also observed for the saturated bis-carbohydrate **4d**; the minor signals, corresponding to the β anomer, appeared at higher field (δ 71.7 and 100.7 ppm for C-5 and C-1, respectively), than those of the major one corresponding to the α anomer (δ 67.2 and 95.8 ppm for C-5 and C-1, respectively).

Unsaturated bis-saccharide **3e** is a 9:1 mixture of α,α/β,β anomers. This assignment was mainly based on ^{1}H NMR spectral data; the signal of the anomeric proton appeared at δ 4.90 ppm as a doublet ($J_{1,2}=3.5$ Hz) for the major isomer, and as two doublets at δ 4.86 ($J_{1,2}=10.0$ Hz) and 4.92 ppm ($J_{1,2}=3.5$ Hz) for the minor one.[24] This assignment was confirmed by reduction of **3e** to the saturated bis-carbohydrate **4e**; the ^{1}H NMR spectrum of **4e** exhibited a unique doublet at δ 4.87 ppm with a coupling constant $J_{1,2}=3.7$ Hz for the major isomer, characteristic of the α,α configuration, while the minor isomer exhibited two doublets at δ 4.77 ppm ($J_{1,2}=9.2$ Hz) and 4.82 ppm ($J_{1,2}=3.7$ Hz), characteristic of a β and α configuration, respectively.

The α,α and α,β configuration for bis-saccharide **8e** was also based on the signal of the anomeric proton, as well as for the saturated disaccharide **9e**. The major isomer exhibited a doublet for the anomeric proton at δ 4.96 ppm with a coupling constant $J_{1,2}=3.3$ Hz, characteristic of an α configuration, whereas the minor isomer exhibited two doublets at δ 4.76 ppm ($J_{1,2}=9.2$ Hz) and δ 4.96 ppm ($J_{1,2}=3.3$ Hz), characteristic of a β and α configuration, respectively.[24] The anomeric signal for the saturated product **9e** appeared at δ 4.84 ppm ($J_{1,2}=3.3$ Hz) and 4.70 ppm ($J_{1,2}=9.2$ Hz) for the α and β anomers, respectively. The *E* configuration was assigned to the double bond of compound **8e** based on the coupling constant observed for the ethylenic proton ($J=15.4$ Hz).

CONCLUSION

In this paper, we have shown that diglycosides of butene-1,4-diol and butane-1,4-diol could be obtained in moderate to good yields starting from the bis-carbonate of butene-1,4-diol and various carbohydrates bearing a free hydroxyl group, such as 1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1a**), 2,3;5,6-di-*O*-isopropylidene-α-D-mannofuranose (**1b**), 2,3,5-tri-*O*-acetyl-D-ribofuranose (**1c**), 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**1d**), and 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranose (**1e**). Reduction of the double bond afforded disaccharides bearing a butyl moiety as a spacer. This methodology was successfully extended to the bis-carbonate of 1,2-bis-[(1-hydroxy)propen-2-yl]benzene and 2,3;5,6-di-*O*-isopropylidene-α-D-mannofuranose, 2,3,5-tri-*O*-acetyl-D-ribofuranose, and 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyra-

nose. Work is in progress in order to use this methodology for the introduction of longer spacers.

EXPERIMENTAL

General Methods. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel plates (60 F-254, Merck). Compounds were visualized under UV light (254 nm) or by spraying with an H_2SO_4 solution and heating. Column chromatography was performed on silica gel 60 (40–63 mesh, Merck). NMR spectra were recorded on Bruker AC 200 and AM 300 spectrometers, and chemical shifts are given in ppm on the δ scale from internal tetramethylsilane. Reactions involving palladium complexes were carried out in a Schlenk tube under a nitrogen atmosphere. THF was distilled from sodium/benzophenone and stored under a nitrogen atmosphere. $Pd_2(dba)_3$, 1,4-bis(diphenylphosphino)butane, 1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1a**), 2,3;5,6-di-*O*-isopropylidene-α-D-mannofuranose (**1b**) are from commercial sources. 2,3,5-Tri-*O*-acetyl-D-ribofuranose (**1c**), 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**1d**) and 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranose (**1e**) were prepared from the corresponding acetates according to the literature procedure.[25]

1,2-Bis-[1-(methoxycarbonyloxy)propen-2-yl]benzene (7). To a 1.0 M solution of vinylmagnesium bromide in tetrahydrofuran (60 mL, 60 mmol) was added slowly phthalic dicarboxaldehyde (**5**) (2.7 g, 20 mmol) dissolved in tetrahydrofuran (7 mL). After being stirred for 16 h, the solution was treated with cold water (10 mL), and the organic product was extracted with diethyl ether (2 × 20 mL). Evaporation of the solvent followed by flash chromatography of the residue using petroleum ether/ethyl acetate (1:1) as the eluent gave 1.33 g of diol **6** as a 3:2 mixture of the diastereoisomers (yield 35%). Oil; R_f 0.55; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.97 (bs, 2H, OH), 5.25 (dm, J = 10.5 Hz, 2H, $=CH_2$), 5.37 (dm, J = 17.4 Hz, 2H, $=CH_2$), 5.55 (bd, 2H, OCH<), 6.01–6.25 (m, 2H, —CH=), 7.30–7.50 (m, 4H, C_6H_4); ^{13}C (50 MHz, $CDCl_3$) δ 70.3 (CHO_{min}), 72.5 (CHO_{maj}), 115.0 ($=CH_{2maj}$), 115.4 ($=CH_{2min}$), 127.4, 128.3, 128.5, 139.2, 139.5, 140.1, and 140.3 (C_6H_4, —CH=). To a solution of this crude diol **6** (1.2 g, 6.3 mmol) and pyridine (1.25 g, 15.8 mmol) in CH_2Cl_2 (100 mL) was added slowly methyl chloroformiate (1.5 g, 15.8 mmol) at 0°C. After stirring at room temperature for 4 h the solution was filtered and washed with an aqueous solution of copper sulfate (2 × 100 mL). Evaporation of the solvent followed by flash-chromatography of the residual oil on silica using a mixture of ethyl acetate/petroleum ether (2:7) as the eluent gave the bis-carbonate **7** as a 3:2 mixture of two diastereoisomers (950 mg, 55% yield). R_f 0.54; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.76 (s, 2.4H, CH_3), 3.78 (s, 3.6H, CH_3), 5.23–5.39 (m, 4H, $=CH_2$), 5.99–6.18 (m, 2H, =CH—), 6.43–6.47(m, 2H, OCH<), 7.33–7.48 (m, 4H, C_6H_4); ^{13}C (50 MHz, $CDCl_3$) δ 54.8 (CH_3), 76.1 (CHO_{min}), 76.5 (CHO_{maj}), 117.4 ($=CH_{2min}$), 117.8 ($=CH_{2maj}$), 127.9 (m), 128.0 (maj), 128.8 (maj), 128.8 (min), 135.3 (min), 135.6 (min), 136.0 (maj) and 136.1 (min) (C_6H_4, —CH=), 154.9 (CO).

Anal. Calcd for $C_{16}H_{18}O_6$ (306.32): C, 62.74; H, 5.92. Found: C, 62.56; H, 5.85.

General procedure for palladium-catalyzed *O*-alkylation Reaction. The catalyst was prepared by stirring for 1 h $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol) and dppb (42.6 mg, 0.1 mmol) in tetrahydrofuran (5 mL) in a Schlenk tube under argon. This

solution was added under argon to a Schlenk tube containing the biscarbonate **2** (102 mg, 0.5 mmol), or **7** (153 mg, 0.5 mmol), and the carbohydrate derivative **1** (1.44 mmol) in tetrahydrofuran (5 mL). The solution was stirred at 60°C, and the reaction was followed by TLC. After disappearance of the starting biscarbonate, the solvent was evaporated, and the residue was purified by silica gel chromatography to give the bis-saccharides **3** or **8**.

(*E*/*Z*)-1,4-Bis-*O*-(1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranosid-3-yl)but-2-enediol (3a). Yield: 83 mg (29%); oil; R_f 0.22 (CH_2Cl_2/petroleum ether/diethyl ether 4:3:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (s, 6H, CH_3), 1.36 (s, 6H, CH_3), 1.42 (s, 6H, CH_3), 1.50 (s, 6H, CH_3), 3.93 (d, 2H, J = 2.9 Hz, H-3), 4.00 (dd, 2H, J = 8.7, 5.8 Hz, H-6), 3.90–4.25 (m, 8H, H-4, H-6, OCH_2CH═), 4.31 (ddd, 2H, J = 7.8, 5.9, 5.9 Hz, H-5), 4.54 (d, 2H, J = 3.6 Hz, H-2), 5.74 (t, 0.2 H, J = 3.6 Hz, ═CH (*Z*)), 5.81 (t, 1.8H, J = 2.8 Hz, ═CH (*E*)), 5.87 (d, 2H, J = 3.6 Hz, H-1); ^{13}C (50 MHz, $CDCl_3$) δ 25.4 (CH_3), 26.2 (CH_3), 26.8 (2 × CH_3), 66.0 (O*C*H_2CH═(*Z*)), 67.3 (C-6), 70.2 (O*C*H_2CH═(*E*)), 72.4 (C-5), 81.1 and 81.4 (C-3, C-4), 82.7 (C-2), 105.2 (C-1), 108.9 (*C*Me_2), 111.7 (*C*Me_2), 128.8 (═CH-(*Z*)), 129.2 (═CH-(*E*)).

Anal. Calcd for $C_{28}H_{44}O_{12}$ (572.65): C, 58.73; H, 7.74. Found: C, 58.79; H, 7.90.

(*E*/*Z*)-1,4-Bis(2,3;5,6-di-*O*-isopropylidene-α-D-mannofuranosyloxy)but-2-ene (3b). Yield: 163 mg (57%); oil; R_f 0.55 (ethyl acetate/petroleum ether 2:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 6H, CH_3), 1.38 (s, 6H, CH_3), 1.46 (s, 6H, CH_3), 1.47 (s, 6H, CH_3), 3.71 (dd, 2H, J = 7.8, 3.6 Hz, H-4), 4.03 (dd, 2H, J = 8.7, 4.3 Hz, H-6), 4.11 (dd, 2H, J = 8.7, 6.3 Hz, H-6), 3.80–4.20 (m, 4H, OCH_2CH═), 4.40 (ddd, 2H, J = 7.8, 6.3, 4.3 Hz, H-5), 4.58 (d, 0.17 × 2H, J = 5.9 Hz, H-2 (*Z*)), 4.61 (d, 0.83 × 2H, J = 5.9 Hz, H-2 (*E*)), 4.77 (dd, 2H, J = 5.9, 3.6 Hz, H-3), 5.00 (s, 0.17 × 2H, H-1 (*Z*)), 5.02 (s, 0.83 × 2H, H-1 (*E*)), 5.71 (dd, 0.17 × 2H, J = 4.0, 4.0 Hz, = CH-(*Z*)), 5.78 (dd, 0.83 × 2H, J = 2.9, 2.9 Hz,═CH-(*E*)); ^{13}C (50 MHz, $CDCl_3$) δ 24.5 (CH_3), 25.2 (CH_3), 25.9 (CH_3), 26.9 (CH_3), 62.6 (O*C*H_2CH═(*Z*)), 66.8 (C-6), 66.9 (O*C*H_2CH═(*E*)), 73.1 (C-5), 79.5 and 80.4 (C-2, C-3), 85.1 (C-4), 105.7 (C-1), 109.2 (*C*Me_2), 112.6 (*C*Me_2), 128.9 (═CH-(*E*)), 129.0 (═CH-(*Z*)).

Anal. Calcd for $C_{28}H_{44}O_{12}$ (572.65): C, 58.73; H, 7.74. Found: C, 58.79; H, 7.90.

(*E*)-1,4-Bis[2,3,5-tri-*O*-acetyl-D-ribofuranosyloxy)but-2-ene (3c). Yield: 157 mg (52%) (as a 1:4 mixture of the α,β/β,β anomers); oil; R_f 0.51 (ethyl acetate/petroleum ether 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03 (s, 6H, CH_3), 2.06 (s, 4.8H, CH_3), 2.07 (s, 1.2H, CH_3), 2.08 (s, 6H, CH_3), 3.65–3.80 (m, 2H, OCH_2), 3.90–4.01 (m, 2H, OCH_2), 4.08 (dd, 2H, J = 11.0, 4.8 Hz, H-5), 4.10–4.35 (m, 4H, H-4, H-5), 5.00 (s, 1.6H, H-1β_{maj}), 5.04 (s, 0.2H, H-1β_{min}) 5.15–5.38 (m, 4.2H, H-1α, H-2, H-3), 5.75 (dd, 2H, J = 2.9, 2.6 Hz,═CH—); ^{13}C (75 MHz, $CDCl_3$) δ 20.4 (CH_3), 20.5 (CH_3), 20.7 (CH_3), 64.4 (C-5β), 64.6 (C-5α), 67.3 (OCH_2-β_{maj}), 67.9 (OCH_2-β_{min}), 69.8 (OCH_2-α), 71.5 (C-4β), 71.9 (C-4α), 74.6 and 78.5 (C-2α, C-3α), 74.8 and 78.6 (C-2β, C-3β), 102.1 (C-1α), 104.4 (C-1β_{maj}), 105.3 (C-1β_{min}), 128.6 (═CH-β), 128.8 (═CH-α), 169.5, 169.6, and 170.6 (CO).

Anal. Calcd for $C_{26}H_{36}O_{16}$ (604.57): C, 51.66; H, 6.00. Found: C, 51.69; H, 6.17.

(*E*)-1,4-Bis[2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyloxy)but-2-ene (3d). Yield: 209 mg (56%) (as a 1:1 mixture of the α,α/α,β anomers); white solid; R_f 0.13 (ethyl

acetate/petroleum ether 2:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, CH_3), 2.02 (s, CH_3), 2.08 (s, CH_3), 2.09 (s, CH_3), 2.16 (s, CH_3), 3.65–3.73 (m, H-5β), 3.95–4.35 (m, OCH_2CH, H-5α, H-6), 4.56 (d, 0.5H, J = 7.7 Hz, H-1β), 4.89 (dd, 1.5H, J = 3.7, 10.0 Hz, H-2α), 4.95–5.15 (m, H-1α, H-4α, H-2β), 5.23 (dd, 0.5H, J = 9.6, 9.6 Hz, H-4β), 5.48 (dd, 0.5H, J = 9.9, 9.7 Hz, H-3β), 5.50 (dd, 1.5H, J = 9.7, 9.7 Hz, H-3α), 5.77 (dd, J = 6.6, 4.0 Hz, —CH═), 5.81 (dd, J = 4.0, 4.0 Hz, —CH═); ^{13}C (75 MHz, $CDCl_3$) δ 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 61.9 (C-6), 67.6 (OCH_2α), 68.6 (OCH_2β), 67.4 (C-5α), 68.5 (C-4β), 68.6 (C-4α), 70.1 (C-3α), 70.7 (C-2α), 71.3 (C-2β), 71.8 (C-5β), 72.8 (C-3β), 94.8 (C-1α_{min}), 95.1 (C-1α_{maj}), 99.7 (C-1β), 127.7 (═CH-β), 128.5 (═CH-α), 129.2 (═CH-α), 169.4, 169.6, 170.0, 170.1, 170.2, and 170.6 (CO).

Anal. Calcd for $C_{32}H_{44}O_{20}$ (748.12): C, 51.37; H, 5.88. Found: C, 51.45; H, 6.12.

(*E*)-1,4-Bis[2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranosyloxy)but-2-ene (3e). Yield: 201 mg (54%) (as a 9:1 mixture of the α,α/α,β anomers); oil; R_f 0.36 (ethyl acetate/petroleum ether/CH_3OH 8:1:1); αα anomer (in the mixture) ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95 (s, 6H, CH_3), 2.00 (s, 6H, CH_3), 2.01 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 3.95 (ddd, 2H, J = 9.8, 4.1, 2.3 Hz, H-5), 4.01 (dd, 2H, J = 13.0, 3.1 Hz, CH_2-CH═), 4.11 (dd, 2H, J = 12.3, 2.3 Hz, H-6), 4.19 (dd, 2H, J = 13.0, 2.8 Hz, CH_2-CH═), 4.23 (dd, 2H, J = 12.3, 4.1 Hz, H-6), 4.34 (ddd, 2H, J = 10.4, 9.3, 3.5 Hz, H-2), 4.90 (d, 2H, J = 3.5 Hz, H-1), 5.12 (dd, 2H, J = 9.8, 9.8 Hz, H-3), 5.22 (dd, 2H, J = 10.4, 9.8 Hz, H-4), 5.80 (dd, 2H, J = 3.2, 2.8 Hz, —CH═), 5.88 (d, 2H, J = 9.3 Hz, NH); ^{13}C (75 MHz, $CDCl_3$) δ 19.6 (CH_3), 19.7 (CH_3), 19.8 (CH_3), 22.1 (NHCOCH_3), 50.9 (C-2), 60.9 (C-6), 66.7 (OCH_2), 66.9 (C-5), 67.2, 70.1 (C-3, C-4), 95.7 (C-1), 128.1 (═CH—), 168.3, 169.1, 169.7, and 170.4 (CO); α,β anomer (in the mixture) ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93 (s, CH_3), 1.96 (s, CH_3), 2.00 (s, CH_3), 2.05 (s, CH_3), 4.86 (d, J = 10.0 Hz, H-1β), 4.92 (d, J = 3.5 Hz, H-1α), 4.24–4.30 (ddd, J = 9.4, 9.3, 3.5 Hz, H-2α), 5.26 (dd, J = 9.8, 9.5 Hz, H-3α), 5.73–5.76 (m, —CH═), 5.94 (d, J = 9.5 Hz, NH); ^{13}C (75 MHz, $CDCl_3$) δ 19.7 (CH_3), 20.1 (CH_3), 22.1 (NHCOCH_3), 51.3 (C-2), 61.2 (C-6), 66.7 (OCH_2), 66.4, 67.4, 69.9 (C-3, C-4, C-5), 90.6 (C-1α), 95.6 (C-1β), 127.9 (═CH—), 168.4, 169.3, 169.9, and 170.3 (CO).

Anal. Calcd for $C_{32}H_{46}O_{18}N_2$ (746.73): C, 51.47; H, 6.21; N, 3.75. Found: C, 51.22; H, 6.17; N, 3.65.

1,2-Bis[3-(2,3;5,6-di-*O*-isopropylidene-α-D-mannofuranosyloxy)-(*E*)-propenyl]-benzene (8b). Yield: 128 mg (38%); oil; R_f 0.44 (ethyl acetate/petroleum ether 1:4); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33 (s, 6H, CH_3), 1.39 (s, 6H, CH_3), 1.47 (s, 12H, CH_3), 4.00–4.41 (m, 12H, H-4, H-5, H-6, OCH_2—CH═), 4.65 (d, 2H, J = 5.9 Hz, H-2), 4.82 (dd, 2H, J = 5.9, 3.5 Hz, H-3), 5.1 (s, 2H, H-1), 6.05–6.19 (m, 2H, CH_2CH═), 6.87 (d, 2H, J = 15.7 Hz, ═CH—), 7.30–7.40 (m, 4H, C_6H_4); ^{13}C (50 MHz, $CDCl_3$) δ 24.6 (CH_3), 25.3 (CH_3), 26.0 (CH_3), 27.0 (CH_3), 67.0 (C-6), 68.0 (OCH_2), 73.3 (C-5), 79.6 (C-3), 80.5 (C-2, 85.2 (C-4), 105.8 (C-1), 109.3, 112.7, 127.9, 130.7, and 135.0 (C_6H_4), 126.8 (═CH), 127.7 (═CH).

Anal. Calcd for $C_{36}H_{50}O_{12}$ (674.79): C, 64.08; H, 7.47. Found: C, 64.25; H, 7.40.

1,2-Bis[3-(2,3,5-tri-*O*-acetyl-D-ribofuranosyloxy)-(*E*)-propenyl]benzene (8c). Yield: 223 mg (63%) (as a 3:1 mixture of the β,β/α,β anomers); oil; R_f 0.61 (ethyl acetate/petroleum ether 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.04 (s, CH_{3min}), 2.06 (s, CH_3), 2.07 (s, CH_3), 2.11 (s, CH_3), 2.13 (s, CH_{3min}), 4.02–4.28 (m, 4H, H-4, H-5), 4.28–

4.50 (m, 6H, H-5, OCH_2), 5.00 (m, 0.25H, H-2α), 5.11 (bs, 1.75H, H-1β), 5.18 (m, 0.25H, H-3α), 5.26 (d, 0.25H, J = 4.4 Hz, H-1α), 5.28 (d, 1.75H, J = 4.4 Hz, H-2β), 5.38 (dd, 1.75H, J = 6.0, 4.4 Hz, H-3β), 6.11 (dt, 4H, J = 15.8, 6.0 Hz, -CH_2CH═), 6.88 (d, 2H, J = 15.8 Hz, ═CH—), 7.20–7.28 (m, 2H, C_6H_4), 7.38–7.48 (m, 2H, C_6H_4); ^{13}C (75 MHz, $CDCl_3$) δ 20.5 (CH_3), 20.6 (CH_3), 20.8 (CH_3), 63.5 (C-5α), 64.4 (C-5β), 68.4 (OCH_2α), 68.7 (OCH_2β), 69.9 (C-4α), 70.8 (C-3α), 71.6 (C-4β), 74.9 (C-3β), 78.6 (C-2β), 79.3 (C-2α), 99.6 (C-1α), 104.3 (C-1β), 126.7, 130.7, and 134.9 (C_6H_4), 127.4, 127.9 (═CH—), 169.6 (CO-β), 169.7 (CO-β), 169.9 (CO-α), 170.6 (CO-β).

Anal. Calcd for $C_{34}H_{44}O_{16}$ (708.26): C, 57.61; H, 6.26. Found: C, 57.26; H, 5.95.

1,2-Bis[3-(2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranosyloxy)-(*E*)-propenyl]benzene (8e). Yield: 250 mg (59%) (as a 7:3 mixture of the α,α/α,β anomers); yellow solid; R_f 0.51 (ethyl acetate/methanol 8:2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92 (s, 6H, CH_3), 2.00 (s, 6H, CH_3), 2.01 (s, 6H, CH_3), 2.06 (s, 6H, CH_3), 3.90–4.40 (m, 12H, H-2, H-5, H-6, OCH_2), 4.76 (d, 0.3H, J = 9.2 Hz, H-1β), 4.96 (d, 1.7 Hz, J = 3.3 Hz, H-1α), 5.13 (dd, 2H, J = 9.9, 9.2 Hz, H-4), 5.24 (dd, 2H, J = 10.3, 9.9 Hz, H-3), 5.91 (d, 2H, J = 9.6 Hz, NH), 6.12 (dt, 2H, J = 15.4, 6.5 Hz, -CH_2—CH═), 6.87 (d, 2H, J = 15.4 Hz, ═CH—), 7.26 (dd, 2H, J = 5.1, 3.3 Hz, C_6H_4), 7.42 (d, 2H, J = 3.3 Hz, C_6H_4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6 (CH_3), 20.7 (2 × CH_3), 23.1 (CH_3), 51.9 (C-2α), 52.3 (C-2β), 62.1 (C-6), 67.4 (C-5β), 68.0, 68.3, and 71.2 (C-3, C-4, C-5), 68.8 (OCH_2CH═), 91.5 (C-1β), 96.6 (C-1α), 127.1, and 131.5 (═CH—), 126.8, 128.3, and 134.6 (C_6H_4), 169.3 (CO-α), 170.2 (CO-α), 170.3 (CO-β), 170.7 (CO-α), 170.9 (CO-β), 171.4 (CO-α).

Anal. Calcd for $C_{40}H_{52}O_{18}N_2$ (848.86): C, 56.60; H, 6.17. Found: C, 56.70; H, 6.17.

Hydrogenation of compounds 3 and 8. A solution of the unsaturated bis-saccharide **3** or **8** (0.11 mmol) in ethyl acetate (15 mL) was stirred under a hydrogen atmosphere at room temperature in the presence of Pd/C 10% (9 mg) for 24 h. The solvent was evaporated, and the residue was purified by column chromatography on silica gel to give the saturated bis-saccharide **4** or **9**.

1,4-Bis-*O*-(1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranosid-3-yl)butanediol (4a). Yield: 63 mg (100%); oil; R_f 0.28 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D^{25}$ − 33.5 (*c* 0.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 6H, CH_3), 1.34 (s, 6H, CH_3), 1.42 (s, 6H, CH_3), 1.50 (s, 6H, CH_3), 1.55–1.70 (m, 4H, CH_2), 3.45–3.70 (m, 4H, OCH_2), 3.85 (d, 2H, J = 2.9 Hz, H-3), 3.98 (dd, 2H, J = 8.5, 5.9 Hz, H-6), 4.08 (dd, 4H, J = 8.5, 5.9 Hz, H-6), 4.10 (dd, 2H, J = 7.5, 2.9 Hz, H-4), 4.29 (ddd, 2H, J = 7.5, 5.9, 5.9 Hz, H-5), 4.52 (d, 2H, J = 3.7 Hz, H-2), 5.86 (d, 2H, J = 3.7 Hz, H-1); ^{13}C (50 MHz, $CDCl_3$) δ 25.4 (CH_3), 26.3 (CH_3), 26.8 (CH_2), 26.8 (CH_3), 67.3 (C-6), 70.2 (OCH_2), 72.5 (C-5), 81.2 and 82.1 (C-3, C-4), 82.6 (C-2), 105.2 (C-1), 108.9 (*C*Me_2), 111.8 (*C*Me_2).

Anal. Calcd for $C_{28}H_{46}O_{12}$ (574.67): C, 58.52; H, 8.07. Found: C, 58.58; H, 8.15.

1,4-Bis(2,3;5,6-di-*O*-isopropylidene-α-D-mannofuranosyloxy)butane (4b). Yield: 63 mg (100%); oil; R_f 0.38 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D^{25}$ + 51.7 (*c* 0.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 6H, CH_3), 1.38 (s, 6H, CH_3), 1.46 (s, 6H, CH_3), 1.47 (s, 6H, CH_3), 1.57–1.63 (m, 4H, CH_2), 3.34–3.42 (m, 2H, OCH_2), 3.59–3.67 (m, 2H, OCH_2), 3.91 (dd, 2H, J = 7.7, 3.6 Hz, H-4), 4.03 (dd, 2H, J = 8.7, 4.4 Hz, H-6), 4.12 (dd, 2H, J = 8.7, 6.2 Hz, H-6), 4.40 (ddd, 2H, J = 7.7, 6.2, 4.4

Hz, H-5), 4.58 (d, 2H, $J = 5.9$ Hz, H-2), 4.78 (dd, 2H, $J = 5.9$, 3.6 Hz, H-3), 4.97 (s, 2H, H-1); ^{13}C (50 MHz, $CDCl_3$) δ 24.5 (CH_3), 25.2 (CH_3), 25.9 (CH_3), 26.1 (CH_2), 66.9 (OCH_2), 67.0 (C-6), 73.2 (C-5), 79.5 and 80.4 (C-2, C-3), 85.1 (C-4), 106.3 (C-1), 109.2 (CMe_2), 112.6 (CMe_2).

Anal. Calcd for $C_{28}H_{46}O_{12}$ (574.67): C, 58.52; H, 8.07. Found: C, 58.73; H, 8.17.

1,4-Bis(2,3,5-tri-*O*-acetyl-D-ribofuranosyloxy)butane (4c). Yield: 66 mg (100%) (as a 1:4 mixture of the α,β/β,β anomers); oil; R_f 0.51 (ethyl acetate/petroleum ether 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55–1.63 (m, 4H, CH_2), 2.02 (s, 6H, CH_3), 2.06 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 3.30–3.45 (m, 2H, OCH_2), 3.60–3.80 (m, 2H, OCH_2), 4.03–4.15 (m, 2H, H-4), 4.20–4.35 (m, 4H, H-5), 4.75–4.95 (m, 0.2H, H-2α), 4.96 (s, 1.60H, H-1β_{maj}), 4.99 (s, 0.2H, H-1β_{min}), 5.19 (bd, 1.8H, $J = 4.4$ Hz, H-2β), 5.23 (d, 0.2H, J = 5.9 Hz, H-1α), 5.29 (dd, 2H, $J = 7.6$, 4.4 Hz, H-3),); ^{13}C (75 MHz, $CDCl_3$) δ 20.5 (CH_3), 20.6 (CH_3), 20.8 (CH_3), 23.9 (CH_2α), 26.1 (CH_2-β), 63.2 (C-5α), 64.7 (C-5β), 67.9 (OCH_2-β), 69.5 (OCH_2α), 71.5 (C-4α), 71.6 (C-4β), 74.7 and 75.0 (C-2α, C-3α), 74.8 and 78.4 (C-2β, C-3β), 104.9 (C-1α_{min}), 105.2 (C-1β_{maj}), 105.4 (C-1β_{min}), 169.6, 169.7, and 170.5 (CO).

Anal. Calcd for $C_{26}H_{38}O_{16}$ (606.58): C, 51.48; H, 6.31. Found: C, 51.35; H, 6.48.

1,4-Bis[2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyloxy)butane (4d). Yield: 82 mg (100%) (as a 1:1 mixture of the α,α/α,β anomers); oil; R_f 0.13 (ethyl acetate/petroleum ether 3:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55–1.80 (m, 4H, CH_2), 1.98 (s, CH_3), 1.99 (s, CH_3), 2.00 (s, CH_3), 2.01 (s, CH_3), 2.02 (s, CH_3), 2.04 (s, CH_3), 2.06 (s, CH_3), 2.07 (s, CH_3), 3.35–3.45 (m, 2H, OCH_2), 3.65–3.75 (m, 2H, OCH_2), 3.95–4.25 (m, 6H, H-5, H-6), 4.49 (d, 0.5H, $J = 7.4$ Hz, H-1β), 4.84 (dd, 1.5H, $J = 10.3$, 3.7 Hz, H-2α), 4.93–5.10 (m, H-4, H-2β, H-1α), 5.19 (dd, 0.5H, $J = 9.5$, 8.8 Hz, H-3β), 5.43 (dd, 1H, $J = 9.5$, 9.6 Hz, H-3α_{maj}), 5.44 (dd, 0.5H, $J = 10.3$, 9.6 Hz, H-3α_{min}); ^{13}C (75 MHz, $CDCl_3$) δ 20.5 (CH_3), 20.6 ($2 \times CH_3$), 20.7 (CH_3), 25.8 (CH_{2min}), 26.1 (CH_2), 26.2 (CH_{2min}), 61.9 (C-6), 67.2 (C-5α), 68.2, 68.3 and 69.5 (OCH_2), 68.4 (C-4β), 68.6 (C-4α), 70.1 (C-3α), 70.9 (C-2α), 71.3 (C-2β), 71.7 (C-5β), 72.8 (C-3β), 95.7 (C-1α), 95.8 (C-1α), 100.7 (C-1β), 169.2, 169.5, 169.4, 170.1, 170.2, and 170.6 (CO).

Anal. Calcd for $C_{32}H_{46}O_{20}$ (750.12): C, 51.23; H, 6.13. Found: C, 51.10; H, 6.19.

1,4-Bis[2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranosyloxy)butane (4e). Yield: 82 mg (100%) (as a 9:1 mixture of the α,α/α,β anomers); oil; R_f 0.36 (ethyl acetate/petroleum ether/CH_3OH 8:1:1); anomer α,α (in the mixture) ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50–1.80 (m, 4H, CH_2), 1.91 (s, 6H, CH_3), 1.96 (s, 6H, CH_3), 1.97 (s, 6H, CH_3), 2.03 (s, 6H, CH_3), 3.40–3.50 (m, 2H, OCH_2), 3.63–3.74 (m, 2H, OCH_2), 3.92 (ddd, 2H, $J = 10.3$, 4.4, 2.3 Hz, H-5), 4.07 (dd, 2H, $J = 12.2$, 2.3 Hz, H-6), 4.23 (dd, 2H, $J = 12.2$, 4.5 Hz, H-6), 4.34 (ddd, 2H, $J = 10.3$, 8.8, 3.7 Hz, H-2), 4.87 (d, 2H, $J = 3.7$ Hz, H-1), 5.09 (dd, 2H, $J = 9.5$, 9.5 Hz, H-4), 5.19 (dd, 2H, $J = 10.3$, 10.3 Hz, H-3), 5.90 (d, 2H, $J = 8.8$ Hz, NH); ^{13}C (75 MHz, $CDCl_3$) δ 20.6 (CH_3), 20.7 ($2 \times CH_3$), 23.0 ($NHCOCH_3$), 26.0 (CH_2), 52.0 (C-2), 62.1 (C-6), 67.8, 68.4 and 71.1 (C-3, C-4, C-5), 67.8 (OCH_2), 97.0 (C-1), 169.3, 170.1, 170.6, and 171.4 (CO); signals corresponding to the anomer α,β (in the mixture): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.90, 1.96, 2.02 (CH_3), 4.77 (d, $J = 9.2$ Hz, H-1β), 4.82 (d, $J = 3.7$ Hz, H-1α); ^{13}C (75 MHz, $CDCl_3$) δ 52.6 (C-2), 91.9 (C-1), 170.2 (CO).

Anal. Calcd for $C_{32}H_{46}O_{18}N_2$ (746.73): C, 51.47; H, 6.21; N, 3.75. Found: C, 51.22; H, 6.17; N, 3.65.

1,2-Bis[3-(2,3,5-tri-*O*-acetyl-D-ribofuranosyloxy)propyl]benzene (9c). Yield: 78 mg (100%) (as a 7:3 mixture of the β,β/α,β anomers); oil; R_f 0.61 (ethyl acetate/petroleum ether 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78–1.90 (m, 4H, CH_2), 2.05 (s, 6H, CH_3), 2.06 (s, 6H, CH_3), 2.10 (s, 6H, CH_3), 2.66 (t, 4H, J = 7.5 Hz, CH_2), 3.42 (dt, 2H, J = 9.2, 6.6 Hz, OCH_2), 3.76 (dt, 2H, J = 9.2, 5.9 Hz, OCH_2), 4.11 (dd, 2H, J = 11.4, 5.5 Hz, H-5), 4.22–4.40 (m, 4H, H-4, H-5), 4.95–5.05 (bs, 1.7H, H-1β), 5.17 (dd, 0.3H, J = 7.4, 4.4 Hz, H-2α), 5.20–5.30 (m, 0.6H, H-3α, H-1α), 5.23 (d, 0.3H, J = 4.4 Hz, H-2β), 5.33 (dd, 2H, J = 6.6, 4.4 Hz, H-3), 7.10–7.15 (m, 4H, C_6H_4); ^{13}C (75 MHz, $CDCl_3$) δ 20.5 (CH_3), 20.6 (CH_3), 20.8 (CH_3), 28.8 (CH_2), 30;7 (CH_2), 63.5 (C-5α), 64.7 (C-5β), 67.6 (OCH_2β), 68.0 (OCH_2α), 70.0 (C-4α), 70.8 (C-3α), 71.7 (C-4β), 74.8 (C-3β), 78.4 (C-2β), 78.9 (C-2α), 100.6 (C-1α), 105.3 (C-1β), 126.2, 129.3, and 139.3 (C_6H_4), 169.6, 169.7, and 170.6 (CO).

Anal. Calcd for $C_{34}H_{48}O_{16}$ (712.75): C, 57.28; H, 6.79. Found: C, 57.39; H, 6.40.

1,2-Bis[3-(2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranosyloxy)propyl]benzene (9e). Yield: 94 mg (100%) (as a 7:3 mixture of the α,α/α,β anomers); white solid; R_f 0.51 (ethyl acetate/petroleum ether/methanol 8:2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75–1.90 (m, 4H, CH_2), 1.93 (s, 6H, CH_3), 2.00 (s, 6H, CH_3), 2.02 (s, 6H, CH_3), 2.03 (s, 6H, CH_3), 2.60–2.80 (m, 4H, CH_2), 3.50 (dt, 2H, J = 10.0, 6.6 Hz, OCH_2CH_2), 3.71 (dt, 2H, J = 10.0, 6.6 Hz, OCH_2CH_2), 3.86 (ddd, 2H, J = 9.5, 4.5, 2.2 Hz, H-5), 4.02 (dd, 2H, J = 12.5, 2.2, Hz, H-6), 4.17 (dd, 2H, J = 12.5, 4.5 Hz, H-6), 4.31 (ddd, 2H, J = 9.5, 9.3, 3.3 Hz, H-2), 4.70 (d, J = 9.2 Hz, 0.3H, H-1β), 4.84 (d, J = 3.3 Hz, 1.7H, H-1α), 5.09 (dd, 2H, J = 9.5, 9.5 Hz, H-4), 5.22 (dd, 2H, J = 9.5, 9.5 Hz, H-3), 5.89 (d, 2H, J = 9.2 Hz, NH), 7.00–7.20 (m, 4H, C_6H_4); ^{13}C (75 MHz, $CDCl_3$) δ 20.6 (CH_3), 20.7 (2 × CH_3), 20.8 (CH_3), 23.1 (CH_3α), 23.2 (CH_3β), 25.6 (2 × CH_2), 28.9 ($CH_2C_6H_4$), 30.3 ($CH_2C_6H_4$), 51.9 (C-2α), 52.3 (C-2β), 61.9 (C-6), 67.7, 68.3, and 71.2 (C-3, C-4, C-5), 67.9 (OCH_2α), 67.8 (OCH_2β), 93.4 (C-1β), 97.3 (C-1α), 126.5, 129.2, and 138.8 (C_6H_4), 169.3, 170.0, 170.6, and 171.4 (CO).

Anal. Calcd for $C_{40}H_{56}O_{18}$N2 (852.89): C, 56.33; H, 6.62. Found: C, 56.82; H, 6.35.

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