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Synthesis and ^{13}C NMR Spectroscopy of Model Compounds for the Microstructure Analysis of Poly(Vinyl Glycoside)s

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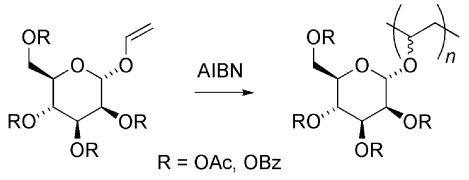
A series of glycosylated diol and triol derivatives was synthesized in order to serve as model compounds for the analysis of the stereochemistry, regiochemistry, and defect structures of poly(vinyl glycoside)s. ^{13}C NMR spectroscopic analysis of these compounds revealed that the attached chiral carbohydrate substituents induced a strong correlation of the chemical shifts of both the anomeric C and the α-C atom of the aglycon with the absolute configuration of the latter. The influence of the stereoconfiguration of β- and γ-C atoms as well as the regiochemistry of the aglycon on the chemical shifts of the α-C and the anomeric C atom was also investigated.

Introduction

Synthetic glycopolymers, i.e., hybrid materials of carbohydrates and synthetic polymers, are attracting increasing interest as potentially biomimetic materials, because carbohydrates play an important role in biomaterials and cell signaling.[1–6] While most of these investigations have dealt with carbohydrate-functionalized standard monomers such as styrenes, acrylates, methacrylates, or acrylamides, we have recently reported the preparation of glycosylated poly(vinyl alcohol) via free radical polymerization of 1-*O*-vinyl glycosides (Scheme 1).[7,8] The obtained poly(vinyl glycoside)s represent the structurally simplest glycosylated polymers with an all-carbon backbone; they may exhibit a defined tacticity and secondary structure formation; and they may be regarded as interesting candidates for both biocompatible and biodegradable materials.

While the free radical polymerization of the 1-*O*-vinyl mannopyranosides has worked acceptably well,[7,8] some details of the reaction mechanism remained inscrutable because the vinyl glycosides represent an entirely new class of radically polymerizable monomers (Scheme 2). Other examples of simple vinyl acetals had been reported to be non-polymerizable,[9] and divinyl acetals had been found to produce complex mixtures of microstructures.[10]

It was, hence, not obvious (*i*) that the polymerization would work regioselectively in the sense of a 1,2-polyaddition, (*ii*) what kinds of regiochemical defects (head-head, tail-tail connectivity) would be present in the polymer, (*iii*) which kinds of termination or transfer reactions were encountered, (*iv*) and to which extent the polymerization proceeded in a stereoselective fashion, furnishing polymers with a controlled tacticity (relative stereochemistry of the repeating units). Moreover, the analysis of the microstructure by means of ^{1}H and ^{13}C NMR spectroscopy turned out to be less straightforward than in the case of poly(vinyl ether)s and poly(vinyl acetate),[11–16] probably due to the inherent rigidity of the obtained poly(vinyl glycoside)s and the presence of the chiral carbohydrate substituents.



Scheme 1. Synthesis of poly(vinyl glycoside)s via free radical polymerization of 1-*O*-vinyl glycosides; R = OAc, OBz.[7,8]

We report here the preparation of a series of D-mannosylated diol and triol derivatives which are to serve as low molecular weight model compounds for the regiochemical and stereochemical analysis of poly(vinyl mannopyranoside)s. Furthermore, the ^{13}C NMR spectra of the obtained derivatives were investigated. The influence of the absolute and relative stereoconfigurations of the α-, β-, and γ-C atoms of the aglycon residue on the chemical shifts of both the anomeric carbon and the α-C atom of the aglycon itself was analyzed, which may give a useful handle for the interpretation of the microstructural details of poly(vinyl glycoside)s.

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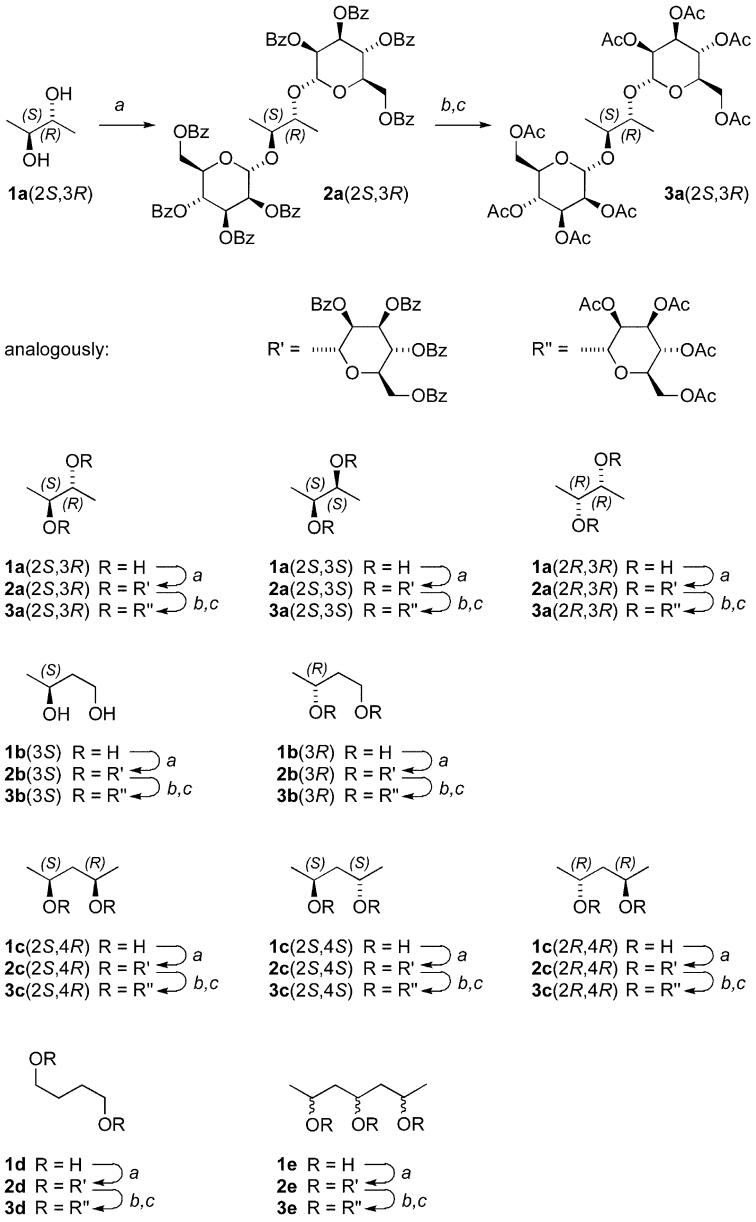
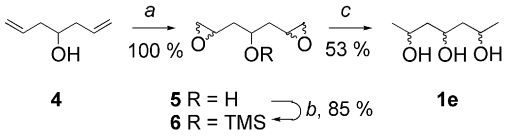


Scheme 2. Synthesis of D-mannosylated diol and triol derivatives as model compounds for the regio- and stereochemical analysis of analogous poly(vinyl mannopyranoside)s. *Reagents and reaction conditions*, *a*: phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside (**7**), NIS, TfOH, DCM, 0 °C; *b*: NaOMe/MeOH, room temp.; *c*: Ac_2O/pyridine. Yields see Table 1.

Results and Discussion

The diols **1a**, **1b**, **1c**(2*R*,4*R*), **1c**(2*S*,4*S*), and **1d** were commercially available in their diastereomerically and enantiomerically pure forms and were applied in the synthesis of the corresponding D-mannosylated model compounds **2** or **3** without further purification. The *meso* diastereomer of alcohol **1c**(2*R*,4*S*) was obtained by separating it from the *rac* diastereomers **1c**(2*R*,4*R*) and **1c**(2*S*,4*S*) by means of silica gel column chromatography.[17] Finally, heptane-2,4,6-triol (**1e**),[18,19] which had previously been prepared by high pressure hydrogenation of diacetylacetone in Et_2O at 100 °C,[20] by reduction of diacetylacetone with sodium borohydride,[21] as well as stereoselectively in a multi-step synthesis,[22] was straightforwardly prepared in four simple steps starting from the commercially available 3-hydroxyhepta-1,6-diene (**4**) (Scheme 3).



Scheme 3. Synthesis of heptane-2,4,6-triol. *Reagents and reaction conditions*, *a*: *m*CPBA/DCM; *b*: TMS-Cl, NEt_3, THF, 0 °C; *c*: DiBAl-H, toluene, 0 °C, silica gel column chromatography.

Thus, the oxidation of **4** with *m*CPBA furnished 1,2:6,7-diepoxyheptan-4-ol (**5**) in quantitative yield. The product was then converted into the corresponding silyl ether **6**. Finally, the epoxide functions of **6** were regioselectively opened by using DiBAl-H, and the TMS-group was quantitatively removed during the purification of the crude product using silica gel column chromatography. As none of the preceding steps had been performed in a stereoselective manner, the desired triol **1e** was obtained as an inseparable mixture of all different diastereomers which was used in the following glycosylation reaction without further purification.

The different diols **1a**–**d** as well as triol **1e** were then glycosylated with phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside (**7**)[23] as the glycosyl donor and activation with NIS/TfOH (Scheme 2). All benzoylated glycosides were purified by silica gel column chromatography followed by recrystallization from ethyl acetate/hexane. The isolated yields of the glycosylation reactions were generally good (Table 1), although the glycosylation of the *syn* diols **1a**(*R*,*R*) and **1a**(*S*,*S*) was noticeably less efficient than the reaction of either its *anti* diastereomer **1a**(*S*,*R*) as well as any of the other diol substrates **1b**–**d** containing either primary hydroxy groups or 1,3-diol functions, indicating that steric hindrance may be an issue. Even the threefold glycosylation of the triol **1e** was accomplished in 70% isolated yield, furnishing a mixture of different stereoisomers.

Table 1. Isolated yields of the perbenzolyated D-mannopyranosides **2a**–**e** synthesized from the corresponding alcohols **1a**–**e**, and isolated yields of the peracetylated D-mannopyranosides **3a**–**e** over two steps starting from **2a**–**e**.

R–OH		% Yield		% Yield
1a(2*S*,3*R*)	**2a**(2*S*,3*R*)	84	**3a**(2*S*,3*R*)	75
1a(2*R*,3*R*)	**2a**(2*R*,3*R*)	66	**3a**(2*R*,3*R*)	81
1a(2*S*,3*S*)	**2a**(2*S*,3*S*)	56	**3a**(2*S*,3*S*)	82
1b(3*R*)	**2b**(3*R*)	85	**3b**(3*R*)	76
1b(3*S*)	**2b**(3*S*)	70	**3b**(3*S*)	71
1c(2*S*,4*R*)	**2c**(2*S*,4*R*)	75	**3c**(2*S*,4*R*)	79
1c(2*R*,4*R*)	**2c**(2*R*,4*R*)	86	**3c**(2*R*,4*R*)	82
1c(2*S*,4*S*)	**2c**(2*S*,4*S*)	80	**3c**(2*S*,4*S*)	80
1d	**2d**	88	**3d**	72
1e	**2e**	70	**3e**	75

The attempted analogous glycosylation of the alcohols **1a**–**e** with **7** as the glycosyl donor turned out to be significantly less efficient in all cases due to side reactions. The peracetylated mannopyranosides **3a**–**e** were, instead, prepared by debenzoylation of the corresponding mannopyranosides **2a**–**e** followed by acetylation in situ. As a recrystallization of the peracetylated compounds failed in all cases, they were purified by silica gel column chromatography and obtained in yields of 71–82% over two steps (Table 1).

As far as their molecular structure is concerned, the obtained di- and triglycosylated derivatives are appropriate model compounds for the stereochemical and regiochemical analysis of the corresponding perbenzoylated and peracetylated poly(vinyl mannopyranoside)s via ^{13}C NMR spectroscopy. Thus, the 2,4-diglycosides **2c** and **3c** (as well as the 2,4,6-triglycosides **2e** and **3e**) are representative for the typical repeating units of the corresponding polymers resulting from a 1,2-polyaddition (head–tail connectivity) with different tacticity, i.e., relative and absolute stereoconfiguration. Likewise, the diglycosides **2b** and **3b** are models for the typical end groups resulting from hydrogen addition to the radical chain end, as is the case for either chain transfer reactions or termination via disproportionation. Finally, the 2,3-diglycosides **2a** and **3a** as well as **2d** and **3d** mimic regiochemical defect structures resulting from 2,1-misinsertions with head–head and tail–tail connectivity, respectively.

In order to be useful as model compounds for the microstructure analysis of poly(vinyl glycoside)s, however, the ^{13}C NMR spectra of **2a**–**e** and **3a**–**e** must show significant chemical shift changes as a result of the stereo- and regiochemical differences.

The ^{13}C NMR spectra of the perbenzoylated model compounds **2a**–**e** as well as the peracetylated derivatives **3a**–**e**, indeed, proved that both their stereoconfiguration and their regiochemistry had a significant effect on the chemical shifts of the respective α-C atoms of the aglycon (which will uniformly be referred to as C7 in the following discussion for the sake of simplicity; compare Figure 1) and the anomeric carbons of the attached carbohydrate substituent (C1). The trends observed in the two different series of perbenzoylated and peracetylated derivatives were exactly the same; just the absolute chemical shift values of C7 and C1 were higher in the perbenzoylated molecules, and the chemical shift differences tended to be, on average, a little larger, as

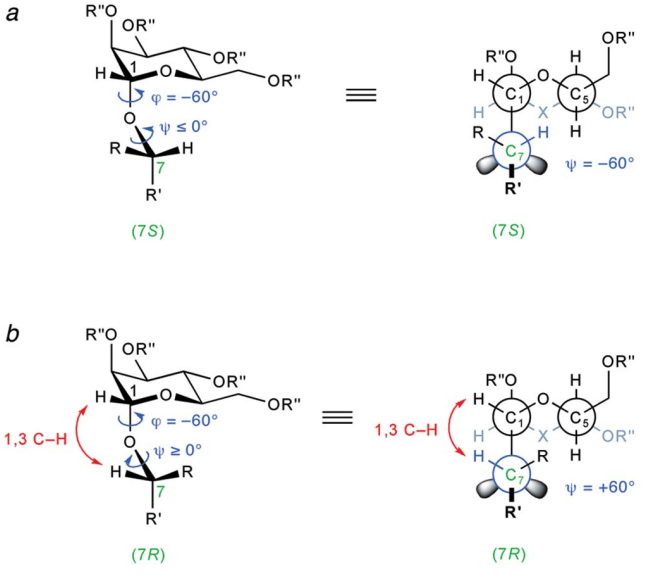


Figure 1. Preferred conformations of the α-D-mannopyranosides with (*a*) 7*R* configuration and (*b*) 7*S* configuration, i.e., R′ > R in both cases; R′′ = OBz; X = CH(OR′′).[34] With a preferred staggered conformation of the C1–O bond ($\phi \approx -60°$) in both cases and a staggered conformation of the O–C7 bond with $\psi \approx -60°$ and $\psi \approx +60°$ for the 7*S*- and the 7*R*-epimer, respectively, only the latter would exhibit C–H 1,3-interactions between C1–H1 and C7–H7 responsible for the observed downfield shifts in the ^{13}C NMR chemical shifts of the anomeric carbon (C1) and the α-C atom of the aglycon (C7).

well. Most importantly, the chemical shifts of C7 and C1 showed a strong dependence on the absolute stereoconfiguration of C7 itself (columns Δ_α in Tables 2 and 3). Notably, the chemical shifts of C7 with an (*R*) configuration were always observed to experience a 2.2–4.9 ppm downfield shift with respect to the C7 with an (*S*) configuration (given the same constitution). The same trend was observed for the anomeric carbons which, when the carbohydrate residue was attached to a C7 with (*R*) configuration, were shifted by 1.8–4.1 ppm downfield as compared to the anomeric carbons of a carbohydrate residue attached to a C7 with (*S*) configuration.

Table 2. Influence of the stereoconfiguration of the α-, β-, and γ-C atom of the aglycon on the chemical shifts (in ppm) of the α-C (C7) itself as well as the anomeric C atom (C1) of the attached carbohydrate substituent in the different diastereomers of the perbenzoylated compounds **2a**–**e**.

	C7(*R*)	C7(*S*)	Δ_α[a]	$C1_{7R}$[b]	$C1_{7S}$[b]	Δ_α[a]
2a(2*R*,3*R*)	79.4	–		98.9	–	
			+4.9			+4.2
2a(2*S*,3*S*)	–	74.5		–	94.7	
2a(2*S*,3*R*)	79.4	74.6	+4.8	99.1	95.2	+3.9
Δ_β[a]	±0.0	–0.1	–	–0.2	–0.5	–
2b(3*R*)	74.7	–		98.2	–	
			+2.8			+2.1
2b(3*S*)	–	71.9		–	96.1	
2c(2*R*,4*R*)	75.5	–		99.1	–	
			+3.3			+3.5
2c(2*S*,4*S*)	–	72.2		–	95.6	
2c(2*S*,4*R*)	74.7	71.8	+2.9	97.9	95.7	+2.2
Δ_γ[a]	+0.8	+0.4	–	+1.2	–0.1	–
2d	67.1	–		97.9	–	
2e	78.3–72.7	–		100.6–96.3	–	

[a] Differences in chemical shifts of C7 or C1 depending on the stereoconfiguration of the α-, β-, and γ-C atom of the aglycon, respectively. [b] Anomeric carbon C1 of the α-D-mannopyranosyl residue attached to C7(*R*) and C7(*S*), respectively.

Table 3. Influence of the stereoconfiguration of the α-, β-, and γ-C atom of the aglycon on the chemical shifts (in ppm) of the α-carbon (C7) itself as well as the anomeric carbon (C1) of the attached carbohydrate substituent in the different diastereomers of the peracetylated compounds **3a**–**e**.

	C7(*R*)	C7(*S*)	Δ_α[a]	$C1_{7R}$[b]	$C1_{7S}$[b]	Δ_α[a]
3a(2*R*,3*R*)	77.3	–		97.4	–	
			+4.1			+3.9
3a(2*S*,3*S*)	–	73.2		–	93.5	
3a(2*S*,3*R*)	77.3	73.0	+4.3	97.2	93.1	+4.1
Δ_β[a]	±0.0	+0.2	–	+0.2	+0.4	–
3b(3*R*)	72.9	–		96.9	–	
			+3.1			+2.8
3b(3*S*)	–	69.8		–	94.1	
3c(2*R*,4*R*)	74.4	–		97.9	–	
			+3.2			+3.3
3c(2*S*,4*S*)	–	71.2		–	94.6	
3c(2*S*,4*R*)	72.5	70.3	+2.2	96.2	94.4	+1.8
Δ_γ[a]	+1.9	+0.9	–	+1.7	+0.2	–
3d	67.3	–		96.7	–	
3e	78.0–70.2	–		98.3–95.4	–	

[a] Differences in chemical shifts of C7 or C1 depending on the stereoconfiguration of the α-, β-, and γ-C atoms of the aglycon, respectively. [b] Anomeric carbon C1 of the α-D-mannopyranosyl residue attached to C7(*R*) and C7(*S*), respectively.

In contrast to the strong influence of the stereoconfiguration of the α-C atom itself, a closer inspection of the NMR spectroscopic data of the different diastereomers of **2a** and **3a**, respectively, revealed that, in general, the chemical shifts of the C7 and C1 carbons were only marginally affected by the stereoconfiguration of the β-C atoms (rows Δ_β in Table 2 and Table 3). Both the absolute and the relative stereoconfiguration of the γ-C atom, on the other hand, had a more pronounced effect in most cases (rows Δ_γ in Tables 2 and 3). Thus, a detailed comparison of the chemical shifts of the respective C7 and C1 carbons of the different diastereomers of **2c** and **3c** showed downfield shifts of up to 1.9 ppm for γ-C atoms with (*R*) configuration. Moreover, the chemical shift differences with respect to the (*R*,*S*) diastereomer were, in all cases, substantially larger for the (*R*,*R*) diastereomers as compared to the (*S*,*S*) diastereomers. The significant downfield shifts of C7 and C1 in the (*R*,*R*) diastereomers of **3c** appear to be even more relevant taking into account that the diastereomeric mixtures of **2e** and **3e** exhibited C7 and C1 carbons at chemical shifts of up to 78.3 and 100.6 ppm as well as 78.0 and 98.3 ppm (**3e**), respectively. In the latter case, these were the highest values observed for all derivatives **3a**–**e**. Presumably, the effect of the stereoconfiguration of the two γ-C atoms on the central C7 and C1 carbons in the (*R,r,R*) diastereomer present in the mixture is cumulative in this case, which appears to make the peracetylated compounds the most suitable model compounds for the microstructure analysis of, likewise, peracetylated poly(vinyl mannopyranoside)s.

Finally, the regiochemistry constituted another important parameter determining the chemical shifts of C7, whereas the anomeric carbons C1 remained more or less unaffected. Thus, a comparison of the chemical shifts of the α-C atoms of the 1,2-diglycosylated derivatives **2a** and **3a** with those of the respective 1,3-diglycosylated compounds **2b**, **2c**, **3b**, and **3c** as well as the 1,4-diglycosylated molecules **2d** and **3d** revealed a systematic trend to higher fields, spanning a large chemical shift range of more than 12 and 10 ppm in total within the two series. It must be acknowledged, however, that this effect can, apparently, be (over) compensated by the observed stereochemical effects, since the highest overall chemical shifts were, presumably, observed for the (*R,r,R*) diastereomers of **2e** and **3e**, as already mentioned above.

In summary, the preceding experimental data proved that the ^{13}C NMR chemical shifts of the α-C atoms of the aglycon (C7) and the anomeric carbons (C1) were correlated to the regiochemistry of the compounds, the absolute stereoconfiguration of C7 itself, as well as the absolute and relative stereoconfiguration of the γ-C atoms of the aglycon. While the chemical shift differences as such are, of course, not surprising because (due to the carbohydrate substituents' chirality) a change of the absolute configuration of C7

gives rise to different diastereomers, the large chemical shift range of 10–12 ppm covered deserves a closer inspection.

The conformation at the glycosidic linkage is described by the dihedral angles ϕ(H1–C1–O–C7) and ψ(C1–O–C7–H7).[24] As the α-glycosides have been shown to exhibit a strong preference for staggered conformation with a dihedral angle $\phi \approx -60°$ (Figure 1),[25,26] the stereochemistry of the aglycon mainly affects the dihedral angle ψ which, in turn, strongly influences the ^{1}H and ^{13}C NMR chemical shifts of the anomeric carbon (C1) and the α-C atom of the aglycon (C7), as has been amply demonstrated.[25–31] For 2-methylcyclohexyl α-D-glycosides, for example, dihedral angles of $\psi \leq 0°$ and $\psi \geq 0°$ have been observed for the derivatives with 7*S* and 7*R* configuration of the α-C atoms, respectively. The latter exhibited downfield shifts of +6.1 and +5.1 ppm for the ^{13}C NMR chemical shifts of C1 and C7 (i.e., the C1′ of the 2-methylcyclohexyl substituent).[25,26] Similarly, downfield shifts of +5.0 and +5.4 ppm were, more recently, observed for the C1 and C7 carbons of enantiomerically pure menthyl α-D-mannopyranosides with 7*R* configuration (compared to those with 7*S* configuration).[32]

Interestingly, these downfield shifts for the ^{13}C NMR chemical shifts of the anomeric carbon (C1) and the α-C atom of the aglycon (C7) for derivatives with a 7*R*-configuration are in absolute agreement with our own observations and have been attributed[25,26] to the effect of spatial C–H interactions on the ^{13}C NMR chemical shifts,[33] as they are also observed for the typical 1,3-interactions in polycyclic systems.[34] By analogy, it may be expected that α-D-mannopyranosides with two (large) substituents R and R′ with different steric demand (R′ > R)[35] attached to C7 would favor a staggered conformation of the O–C7 bond with $\psi \approx -60°$ for the 7*S*-epimer and $\psi \approx +60°$ for the 7*R*-epimer, placing the largest residue R′ into an *antiperiplanar* orientation with respect to the carbohadrate residue in both cases (Figure 1). These conformations would, consequently, lead to a strong 1,3-interaction of C7–H7 with C1–H1 only in the case of the 7*R*-epimer. This 1,3-interaction, accordingly, induces a downfield shift in the ^{13}C NMR chemical shifts of both the anomeric carbon C1 and C7 (α-C atom) simultaneously. Likewise, the only marginal influence of the β-C atoms in the case of the α-mannopyranosides investigated here is well in line with previous examples.[25,26] This is also true for the observed stronger effect of the γ-C atoms which may be explained by C–H 1,5-interactions (γ-*gauche* effect).[25,26] It is interesting to note, however, that the latter effect and its observed cumulative nature also imply the presence of a preferred backbone conformation which may lead to defined secondary structures of the corresponding poly(vinyl glycoside)s.

Conclusions

In conclusion, a series of perbenzoylated and peracetylated glycosides of enantiomerically pure diols as well as a diastereomeric mixture of one triol derivative have been prepared. The chemical shifts of the α-C atom of the aglycon and the anomeric carbon were found to be strongly dependent on the absolute configuration of the α-C atom itself, the absolute and the relative stereoconfiguration of the γ-C atom of the aglycon, as well as the regiochemistry. As a result, chemical shift differences of more than 10 ppm were observed for the α-C atom. These features make the glycosides **2a**–**e** and **3a**–**e** useful as model compounds for an investigation of both the mechanism of the novel free radical polymerization of vinyl glycosides and a detailed analysis of the microstructure and tacticity of the obtained poly(vinyl glycoside)s.

Experimental Section

All experiments were carried out in dried Schlenk glassware in an inert N_2 atmosphere, unless noted otherwise. All reagents were purchased as reagent grade from commercial sources and used without further purification. Solvents were purchased as reagent grade and distilled once prior to use. Anhydrous solvents were freshly distilled and stored over molecular sieves prior to use. DCM was refluxed and distilled from CaH_2. The commercially available derivatives **1a**(2*R*,3*R*), **1a**(2*S*,3*S*), **1a**(2*S*,4*R*), **1b**(3*S*), **1b**(3*R*), **1c**(2*R*,4*R*), **1c**(2*S*,4*S*), and **1d**, as well as hepta-1,6-dien-4-ol **4** were used without further purification. Phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside (**7**) was prepared according to a published procedure.[23]

General Procedure for the Glycosylation Reactions (Procedure A): The alcohol (typically 0.2 mmol), pyranoside **7** (typically 4 equiv.), 4 Å molecular sieves, and DCM (50 mL/g of **7**) were placed in a dried Schlenk flask under nitrogen. The mixture was cooled to 0 °C, and *N*-iodosuccinimide (5 equiv.) as well as TfOH (4 equiv.) were added. After 3 min, the reaction was quenched with triethylamine (large excess). The solution was diluted with Et_2O (about 500 mL/g of substrate), washed with 1 M HCl, saturated aqueous $NaHCO_3$ solution, and saturated aqueous NaCl solution, dried with $MgSO_4$, filtered, and the solvents evaporated to dryness. The pure products were obtained by flash column chromatography, followed by recrystallization in some cases.

General Procedure for the Debenzoylation and Acetylation Reactions (Procedure B): The benzoylated compound (typically 0.1–0.2 mmol) and NaOMe (typically 0.37 mmol) were added into a flask containing MeOH (20 mL), and the reaction mixture was stirred at room temperature for about 2 h until the conversion was complete. Amberlite IR-120 (H^+; typically 0.37 mmol) was added into the reaction mixture. After about 3 min, when the pH of the reaction mixture reached pH 7–8, the Amberlite was filtered off. The solution was concentrated and dried in high vacuum for 12 h. The residue was dissolved in pyridine (20 mL), and Ac_2O (3 mL, large excess) was added slowly via a syringe over a time period of 3 h. The reaction mixture was stirred at room temperature for 1 h and then diluted with Et_2O. The organic phase was washed with 1 M HCl, saturated aqueous $NaHCO_3$ solution as well as saturated aqueous NaCl solution, and dried with $MgSO_4$. The pure products were obtained by flash column chromatography.

(2*S*,4*R*)-Pentane-2,4-diol [1c(2*S*,4*R*)]: The compound was separated from commercially available mixture of pentane-2,4-diols using silica gel chromatography (ethyl acetate/hexane, 1:2); **1a**(*S*,*R*) was obtained as the first fraction. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.08 (s, 2 H, OH), 4.00–3.91 (m, 2 H, 2-H, 4-H), 1.51–

1.43 (m, 2 H, 3-H), 1.12 (d, $^3J_{H,H}$ = 6.3 Hz, 6 H, 1-H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 68.7 (2 C, 2-C, 4-C), 46.3 (3-C), 24.0 (2 C, 1-C, 5-C) ppm.

Heptane-2,4,6-triol (1e): 1,2:6,7-Diepoxy-4-(trimethylsilyloxy)heptane (**6**) (100 mg, 0.46 mmol) was added to a flask containing toluene (30 mL). The solution was cooled to 0 °C, and DiBAl-H (2.0 mL, 2.4 mmol) was added. After stirring at room temperature for 12 h, the reaction mixture was evaporated to dryness. After repeated purification by flash column chromatography (silica gel, ethyl acetate/hexane, 1:2, ethyl acetate/methanol, 5:1, then methanol); **1e** (36 mg, 53%, mixture of diastereomers) was obtained as a colorless syrup. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 4.53 (s, 3 H, OH), 4.00–3.12 (m, 3 H, 2-H, 4-H, 6-H), 2.00–1.23 (m, 4 H, 3-H, 5-H), 1.13–1.05 (m, 6 H, 1-H, 7-H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 68.1, 66.3, 65.2, 65.2, 63.4, 63.2 (2-C, 4-C, 6-C), 47.6, 47.3, 47.0 (3-C, 5-C), 24.8, 24.2, 24.1 (1-C, 7-C) ppm. MS (EI): *m*/*z* calcd. for $C_7H_{16}O_3$ ([M – $2C_2H_5O$]$^+$) 58.04, found 58.05.

(2*S*,3*R*)-2,3-Bis(2′,3′,4′,6-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)butane [2a (2*S*,3*R*)]: The product was prepared according to procedure A, using (2*S*,3*R*)-butane-2,3-diol [**1a** (2*S*,3*R*)] (0.033 mL, 0.37 mmol), thioglycoside **7** (1 g, 1.5 mmol), *N*-iodosuccinimide (405 mg, 1.8 mmol), and TfOH (0.11 mL, 1.2 mmol). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:6) and recrystallization from ethanol; **2a** (2*S*,3*R*) (386 mg, 84%) was obtained as a white solid, $[a]_D^{25}$ = –43.17 (*c* = 1.04, CH_3Cl). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.13–6.99 (m, 40 H, H_{Ar}), 6.23 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4′-H), 6.21 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4′-H), 6.03 (dd, $^3J_{H,H}$ = 10.0, 3.0 Hz, 1 H, 3′-H), 5.95 (dd, $^3J_{H,H}$ = 10.0, 3.0 Hz, 1 H, 3′-H), 5.78–5.75 (m, 2 H, 2′-H), 5.44 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, 1′-H), 5.31 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, 1′-H), 4.82 (dd, $^3J_{H,H}$ = 13.5, $^2J_{H,H}$ = 3.5 Hz, 1 H, 6′-H), 4.73 (dd, $^3J_{H,H}$ = 12.0, $^2J_{H,H}$ = 2.5 Hz, 1 H, 6′-H), 4.69–4.63 (m, 3 H, 5′-H, 5′-H, 6′-H), 4.58 (dd, $^3J_{H,H}$ = 12.0, 4.5 Hz, 1 H, 6′-H), 4.17–4.11 (m, 1 H, 2-H), 4.09–4.03 (m, 1 H, 3-H), 1.48 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H), 1.32 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, 1-H, 4-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]acetone, 25 °C): δ = 166.4–165.8 (8 C, Ph*C*O), 134.4–129.1 (48 C, C_{Ar}), 99.1 (1′-C), 95.2 (1′-C), 79.4 (3-C), 74.6 (2-C), 71.9 (5′-C), 71.8 (5′-C), 71.5 (3′-C), 71.4 (3′-C), 70.4 (2′-C), 70.2 (2′-C), 67.5 (4′-C), 67.3 (4′-C), 63.6 (6′-C), 63.5 (6′-C), 16.3, 13.8 (1-C, 4-C) ppm. $C_{72}H_{62}O_{20}$ (1246.38): calcd. C 69.33, H 5.01; found C 69.14, H 4.99. HRMS (MALDI): *m*/*z* calcd. for $C_{72}H_{62}O_{20}$ ([M + Na]$^+$) 1269.3727, found 1269.3716.

(2*R*,3*R*)-2,3-Bis(2′,3′,4′6′-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)butane [2a (2*R*,3*R*)]: This product was prepared according to procedure A, using (2*R*,3*R*)-butane-2,3-diol [**1a** (2*R*,3*R*)] (0.083 mL, 0.093 mmol), thioglycoside **7** (0.25 g, 0.38 mmol), *N*-iodosuccinimide (101 mg, 0.45 mmol), and TfOH (0.028 mL, 0.3 mmol). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:6) and recrystallization from ethanol; **2a** (2*R*,3*R*) (76 mg, 66%) was obtained as a white solid, $[a]_D^{25}$ = –53.07 (*c* = 1.41, CH_3Cl). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.15–7.19 (m, 40 H, H_{Ar}), 6.12 (t, $^3J_{H,H}$ = 10.0 Hz, 2 H, 4′-H), 6.00 (dd, $^3J_{H,H}$ = 10.0, 3.5 Hz, 2 H, 3′-H), 5.81 (dd, $^3J_{H,H}$ = 3.0, 1.5 Hz, 2 H, 2′-H), 5.8 (d, $^3J_{H,H}$ = 1.5 Hz, 2 H, 1′-H), 4.69 (dd, $^3J_{H,H}$ = 12.0, 2.0 Hz, 2 H, 6′-H), 4.60–4.56 (m, 2 H, 5′-H), 4.53 (dd, $^3J_{H,H}$ = 12.0, $^2J_{H,H}$ = 4.5 Hz, 2 H, 6′-H), 4.00–3.93 (m 2 H, 2-H, 3-H), 1.41 (d, $^3J_{H,H}$ = 5.5 Hz, 6 H, 1-H, 4-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 166.3–165.5 (8 C, Ph*C*O), 133.4–128.3 (48 C, C_{Ar}), 98.9 (2 C, 1′-C), 79.4 (2 C, 2-C, 3-C), 71.2 (2 C, 5′-C), 70.0 (2 C, 3′-C), 69.5 (2 C, 2′-C), 67.5 (2 C, 4′-C), 63.3 (2 C, 6′-C), 17.3 (2 C, 1-C, 4-C) ppm. $C_{72}H_{62}O_{20}$ (1246.38): calcd. C 69.33, H 5.01; found C 69.08, H 5.05. HRMS (MALDI): *m*/*z* calcd. for $C_{72}H_{62}O_{20}$ ([M + Na]$^+$) 1269.3727, found 1269.3706.

(2*S*,3*S*)-2,3-Bis(2′,3′,4′6′-*O*-benzoyl-α-D-mannopyranosyloxy)butane [2a (2*S*,3*S*)]: The product was prepared according to procedure A, using (2*S*,3*S*)-butane-2,3-diol [**1a** (2*S*,3*S*)] (0.046 mL, 0.5 mmol), thioglycoside **7** (1.3 g, 1.9 mmol), *N*-iodosuccinimide (675 mg, 3.0 mmol), and TfOH (0.18 mL, 2.0 mmol). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:6) and recrystallization from ethanol; **2a** (2*S*,3*S*) (350 mg, 56%) was obtained as a white solid, $[a]_D^{25}$ = –35.46 (*c* = 0.65, CH_3Cl). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.19–6.65 (m, 40 H, H_{Ar}), 6.31 (t, $^3J_{H,H}$ = 10.0 Hz, 2 H, 4′-H), 5.98 (dd, $^3J_{H,H}$ = 10.0, 3.0 Hz, 2 H, 3′-H), 5.76 (dd, $^3J_{H,H}$ = 3.0, 1.5 Hz, 2 H, 2′-H), 5.32 (d, $^3J_{H,H}$ = 1.5 Hz, 2 H, 1′-H), 4.89 (dd, $^3J_{H,H}$ = 12.5, $^2J_{H,H}$ = 2.0 Hz, 2 H, 6′-H), 4.83–4.79 (m, 2 H, 5′-H), 4.72 (dd, $^3J_{H,H}$ = 12.0, $^2J_{H,H}$ = 4.0 Hz, 2 H, 6′-H), 4.15–4.08 (m, 2 H, 2-H, 3-H), 1.29 (d, $^3J_{H,H}$ = 5.5 Hz, 6 H, 1-H, 4-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 166.3–165.7 (8 C, Ph*C*O), 133.6–128.1 (48 C, C_{Ar}), 94.7 (2 C, 1′-C), 74.5 (2 C, 2-C, 3-C), 71.1 (2 C, 5′-C), 70.7 (2 C, 3′-C), 70.0 (2 C, 2′-C), 66.4 (2 C, 4′-C), 63.0 (2 C, 6′-C) 14.5 (2 C, 1-C, 4-C) ppm. HRMS (MALDI): *m*/*z* calcd. for $C_{72}H_{62}O_{20}$ ([M + Na]$^+$) 1269.3727, found 1269.3721.

(3*R*)-1,3-Bis(2′,3′,4′6′-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)butane [2b (3*R*)]: The product was prepared according to procedure A, using (3*R*)-butane-1,3-diol [**1b** (3*R*)] (18 mg, 0.2 mmol), thioglycoside **7** (550 mg, 0.8 mmol), *N*-iodosuccinimide (247 mg, 1.1 mmol), TfOH (0.055 mL, 0.8 mmol). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:6) and recrystallization from ethanol; **2b** (3*R*) (215 mg, 85%) was obtained as a white solid, $[a]_D^{25}$ = –63.92 (*c* = 1.80, CH_3Cl). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.20–7.22 (m, 40 H, H_{Ar}), 6.17 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4′-H), 6.16 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4′-H), 5.99 (2dd, $^3J_{H,H}$ = 10.0, 3.0 Hz, 2 H, 3′-H), 5.79 (dd, $^3J_{H,H}$ = 3.0, 1.7 Hz, 1 H, 2′-H), 5.67 (dd, $^3J_{H,H}$ = 3.0, 1.7 Hz, 1 H, 2′-H), 5.34 (d, $^3J_{H,H}$ = 1.7 Hz, 1 H, 1′-H), 5.32 (d, $^3J_{H,H}$ = 1.7 Hz, 1 H, 1′-H), 4.80 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 2.3 Hz, 1 H, 6′-H), 4.73 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 2.3 Hz, 1 H, 6′-H), 4.65–4.48 (m, 4 H, 5′-H, 6′-H), 4.20 (m, 1 H), 4.08 (m, 1 H), 3.85 (m, 1 H), (1-H, 3-H), 2.02 (m, 2 H, 2-H), 1.49 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, 4-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 166.3–165.2 (8 C, Ph*C*O), 133.5–128.3 (48 C, C_{Ar}), 98.6 (1′-C), 98.2 (1′-C), 74.7 (3-C), 71.1 (5′-C), 70.4 (5′-C), 70.2 (3′-C), 70.1 (3′-C), 69.1 (2′-C), 68.9 (2′-C), 67.1 (4′-C), 67.0 (4′-C), 65.0 (1-C), 63.2 (6′-C), 63.0 (6′-C), 36.8 (2-C), 22.1 (4-C) ppm. $C_{72}H_{62}O_{20}$ (1246.38): calcd. C 69.33, H 5.01; found C 69.06, H 4.96. HRMS (MALDI): *m*/*z* calcd. for $C_{72}H_{62}O_{20}$ ([M + Na]$^+$) 1269.3727, found 1269.3721.

(3*S*)-1,3-Bis(2′,3′,4′6′-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)butane [2b (3*S*)]: The product was prepared according to procedure A, using (3*S*)-butane-1,3-diol [**1b** (3*S*)] (18 mg, 0.2 mmol), thioglycoside **7** (550 mg, 0.8 mmol), *N*-iodosuccinimide (247 mg, 1.1 mmol), TfOH (0.055 mL, 0.8 mmol). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:6) and recrystallization from ethanol; **2b** (3*S*) (174 mg, 70%) was obtained as a white solid, $[a]_D^{25}$ = –43.37 (*c* = 1.78, CH_3Cl). ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 8.20–7.25 (m, 40 H, H_{Ar}), 6.30 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4′-H), 6.28 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4′-H), 6.04 (dd, $^3J_{H,H}$ = 10.0, 3.2 Hz, 1 H, 3′-H), 6.01 (dd, $^3J_{H,H}$ = 10.0, 3.2 Hz, 1 H, 3′-H), 5.88 (dd, $^3J_{H,H}$ = 3.2, 1.7 Hz, 1 H, 2′-H), 5.83 (dd, $^3J_{H,H}$ = 3.2, 1.7 Hz, 1 H, 2′-H), 5.49 (d, $^3J_{H,H}$ = 1.7 Hz, 1 H, 1′-H), 5.37 (d, $^3J_{H,H}$ = 1.7 Hz, 1 H, 1′-H), 4.93–4.64 (m, 6 H, 5′-H, 6′-H), 4.35 (m, 1 H, 3-H), 4.26 (dt, $^3J_{H,H}$ = 10.0, $^2J_{H,H}$ = 7.0 Hz, 1 H, 1-H), 4.03 (dt, $^3J_{H,H}$ = 10.0, $^2J_{H,H}$ = 6.4 Hz, 1 H, 1-

H), 2.23 (m, 2 H, 2-H), 1.42 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, 4-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]acetone, 25 °C): δ = 166.4–165.8 (8 C, Ph*C*O), 134.4–129.2 (48 C, C_{Ar}), 98.4 (1′-C), 96.1 (1′-C), 71.90 (3-C), 71.85 (5′-C), 71.64 (5′-C), 71.56 (3′-C), 71.3 (3′-C), 70.2 (2′-C), 69.9 (2′-C), 67.55 (4′-C), 67.46 (4′-C), 66.1 (1-C), 63.6 (6′-C), 63.4 (6′-C), 37.3 (2-C), 19.5 (4-C) ppm. $C_{72}H_{62}O_{20}$ (1246.38): calcd. C 69.33, H 5.01; found C 69.07, H 5.00. HRMS (MALDI): *m*/*z* calcd. for $C_{72}H_{62}O_{20}$ ([M + Na]$^+$) 1269.3727, found 1269.3703.

(2*S*,4*R*)-2,4-Bis(2′,3′,4′6′-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)pentane [2c(2*S*,4*R*)]: The product was prepared according to procedure A, using (2*S*,4*R*)-pentane-2,4-diol [**1c**(2*S*,4*R*)] (13 mg, 0.12 mmol), thioglycoside **7** (325 mg, 0.47 mmol), *N*-iodosuccinimide (160 mg, 0.71 mmol), TfOH (0.062 mL, 0.71 mmol). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:6) and recrystallization from ethanol; **2c**(2*S*,4*R*) (113 mg, 75%) was obtained as a white solid, $[\alpha]_D^{25}$ = –49.59 (*c* = 2.27, CH_3Cl). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.20–7.24 (m, 40 H, H_{Ar}), 6.21 (t, $^3J_{H,H}$ = 10.2 Hz, 1 H, 4′-H), 6.18 (t, $^3J_{H,H}$ = 9.9 Hz, 1 H, 4′-H), 5.98 (dd, $^3J_{H,H}$ = 10.2, 3.0 Hz, 2 H, 3′-H), 5.71 (dd, $^3J_{H,H}$ = 3.2, 1.7 Hz, 1 H, 2′-H), 5.68 (dd, $^3J_{H,H}$ = 3.2, 1.7 Hz, 1 H, 2′-H), 5.34 (m, 2 H, 1′-H), 4.81–4.52 (m, 6 H, 5′-H, 6′-H), 4.24–4.11 (m, 2 H, 2-H, 4-H), 2.34–2.24 (m, 1 H, 3-H), 1.86–1.77 (m, 1 H, 3-H), 1.49 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H), 1.42 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, 1-H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.3–165.6 (8 C, Ph*C*O), 133.5–128.4 (48 C, C_{Ar}), 97.9 (1′-C), 95.7 (1′-C), 74.7 (4-C), 71.8 (2-C), 71.4 (5′-C), 71.2 (5′-C), 70.3 (3′-C), 70.2 (3′-C), 69.6 (2′-C), 69.3 (2′-C), 67.2 (4′-C), 67.1 (4′-C), 63.2 (6′-C), 63.1 (6′-C), 44.0 (3-C), 21.7, 19.5 (1-C, 5-C) ppm. $C_{73}H_{64}O_{20}$ (1260.40): calcd. C 69.52, H 5.11; found C 69.24, H 5.08. HRMS (ESI): *m*/*z* calcd. for $C_{73}H_{64}O_{20}$ ([M + Na]$^+$) 1283.3883, found 1283.3886.

(2*R*,4*R*)-2,4-Bis(2′,3′,4′6′-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)pentane 2c(2*R*,4*R*): The product was prepared according to procedure A, using (2*R*,4*R*)-pentane-2,4-diol [**1c**(2*R*,4*R*)] (52 mg, 0.5 mmol), thioglycoside **7** (1.3 g, 1.9 mmol), *N*-iodosuccinimide (675 mg, 3.0 mmol), TfOH (0.18 mL, 2.0 mmol). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:6) and recrystallization from ethanol; **2c**(2*R*,4*R*) (540 mg, 86%) was obtained as a white solid, $[\alpha]_D^{25}$ = –77.32 (*c* = 0.76, CH_3Cl). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.07–7.21 (m, 40 H, H_{Ar}), 6.06 (t, $^3J_{H,H}$ = 10.0 Hz, 2 H, 4′-H), 5.94 (dd, $^3J_{H,H}$ = 10.0, 3.0 Hz, 2 H, 3′-H), 5.58 (dd, $^3J_{H,H}$ = 3.0, 1.7 Hz, 2 H, 2′-H), 5.36 (m, 2 H, 1′-H), 4.65 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 2.4 Hz, 2 H, 6′-H), 4.58–4.54 (m, 2 H, 5′-H), 4.50 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 4.9 Hz, 2 H, 6′-H), 4.20–4.12 (m, 2 H, 2-H, 4-H), 1.81–1.76 (m, 2 H, 3-H), 1.45 (d, $^3J_{H,H}$ = 6.0 Hz, 6 H, 1-H, 5-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 166.3–165.3 (8 C, Ph*C*O), 133.4–128.3 (48 C, C_{Ar}), 99.1 (2 C, 1′-C), 75.5 (2 C, 2-C, 4-C), 71.1 (2 C, 5′-C), 70.1 (2 C, 3′-C), 69.1 (2 C, 2′-C), 67.4 (2 C, 4′-C), 63.4 (2 C, 6′-C), 45.7 (3-C), 22.4 (2 C, 1-C, 5-C) ppm. $C_{73}H_{64}O_{20}$ (1260.40): calcd. C 69.52, H 5.11; found C 69.24, H 5.09. HRMS (MALDI): *m*/*z* calcd. for $C_{73}H_{64}O_{20}$ ([M + Na]$^+$) 1283.3883, found 1283.3878.

(2*S*,4*S*)-2,4-Bis(2′,3′,4′6′-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)pentane [2c(2*S*,4*S*)]: The product was prepared according to procedure A, using (2*S*,4*S*)-pentane-2,4-diol [**1c**(2*S*,4*S*)] (13 mg, 0.12 mmol), thioglycoside **7** (325 mg, 0.47 mmol), *N*-iodosuccinimide (160 mg, 0.71 mmol), and TfOH (0.062 mL, 0.71 mmol). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:6) and recrystallization from ethanol; **2c**(2*S*,4*S*) (121 mg, 80%) was obtained as a white solid, $[\alpha]_D^{25}$ = –51.10 (*c* = 1.04, CH_3Cl). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.07–7.23 (m, 40 H, H_{Ar}), 6.15 (t, $^3J_{H,H}$ = 10.0 Hz, 2 H, 4′-H), 5.93 (dd, $^3J_{H,H}$ = 10.0, 3.0 Hz, 2 H, 3′-H), 5.64 (dd, $^3J_{H,H}$ = 3.0, 1.7 Hz, 2 H, 2′-H), 5.25 (d, $^3J_{H,H}$ = 1.7 Hz, 2 H, 1′-H), 4.72 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 2.3 Hz, 2 H, 6′-H), 4.59–4.53 (m, 4 H, 5′-H, 6′-H), 4.12–4.04 (m, 2 H, 2-H, 4-H), 2.05 (m, 2 H, 3-H), 1.32 (d, $^3J_{H,H}$ = 6.0 Hz, 6 H, 1-H, 5-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 166.2–165.6 (8 C, Ph*C*O), 133.6–128.4 (48 C, C_{Ar}), 95.6 (2 C, 1′-C), 72.2 (2 C, 2-C, 4-C), 71.5 (2 C, 5′-C), 70.3 (2 C, 3′-C), 69.6 (2 C, 2′-C), 67.0 (2 C, 4′-C), 63.1 (2 C, 6′-C), 44.6 (3-C), 19.8 (2 C, 1-C, 5-C) ppm. $C_{73}H_{64}O_{20}$ (1260.40): calcd. C 69.52, H 5.11; found C 69.28, H 5.17. HRMS (ESI): *m*/*z* calcd. for $C_{73}H_{64}O_{20}$ ([M + Na]$^+$) 1283.3883, found 1283.3883.

1,4-Bis(2′,3′,4′6′-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)butane (2d): The product was prepared according to general procedure A, using butane-1,4-diol **1d** (34 mg, 0.38 mmol), thioglycoside **7** (1.1 g, 1.6 mmol), *N*-iodosuccinimide (405 mg, 1.8 mmol), and TfOH (0.11 mL, 1.2 mmol). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:6) and recrystallization from ethanol; **2d** (412 mg, 88%) was obtained as a white solid, $[\alpha]_D^{25}$ = –59.64 (*c* = 0.89, CH_3Cl). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.18–7.24 (m, 40 H, H_{Ar}), 6.18 (t, $^3J_{H,H}$ = 10.0 Hz, 2 H, 4′-H), 5.99 (dd, $^3J_{H,H}$ = 10.2, 3.3 Hz, 2 H, 3′-H), 5.78 (dd, $^3J_{H,H}$ = 3.3, 1.5 Hz, 2 H, 2′-H), 5.18 (d, *J* = 1.5 Hz, 2 H, 1′-H), 4.77 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 2.3 Hz, 2 H, 6′-H), 4.61–4.48 (m, 4 H, 5′-H, 6′-H), 4.03–3.91 (m, 2 H, 1-H 4-H), 3.74–3.64 (m, 2 H, 1-H 4-H), 1.97–1.85 (m, 4 H, 2-H 3-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 166.3–165.5 (8 C, Ph*C*O), 133.5–128.4 (48 C, C_{Ar}), 97.9 (2 C, 1′-C), 70.7 (2 C, 5′-C), 70.3 (2 C, 3′-C), 69.1 (2 C, 2′-C), 68.5 (2 C, 4′-C), 67.1 (2 C, 1-C, 4-C), 63.1 (2 C, 6′-C), 26.4 (2 C, 2-C, 3-C) ppm. $C_{72}H_{62}O_{20}$ (1260.40): calcd. C 69.33, H 5.01; found C 69.07, H 5.26. HRMS (ESI): *m*/*z* calcd. for $C_{72}H_{62}O_{20}$ ([M + Na]$^+$) 1269.3727, found 1269.3722.

2,4,6-Tris(2′,3′,4′6′-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)-heptane (2e): The product was prepared according to procedure A, using the diastereomeric mixture of heptane-2,4,6-triol (**1e**) (9 mg, 0.06 mmol, mixture of diastereomers), thioglycoside **7** (324 mg, 0.47 mmol), *N*-iodosuccinimide (115 mg, 0.51 mmol), TfOH (0.044 mL, 0.5 mmol). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:6) and recrystallization from ethanol; **2e** (80 mg, 70%, mixture of diastereomers) was obtained as a white solid. ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 8.18–7.08 (m, H_{Ar}), 6.34–5.32 (m), 5.00–3.76 (m, 1′-H-6′-H, 2-H, 4-H, 6-H), 2.58–1.98 (m, 3-H, 5-H), 1.68–1.45 (m, 1-H, 7-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]acetone, 25 °C): δ = 166.4–165.9 (Ph*C*O), 134.3–129.1 (C_{Ar}), 100.6–96.3 (1′-C), 78.3–75.3, 72.7–69.1, (2-C, 4-C, 6-C, 2′-C, 3′-C, 5′-C) 68.0–67.6 (4′-C), 64.3–63.5 (6′-C), 44.3–42.5 (3-C, 5-C), 22.8–19.6 (1-C, 7-C) ppm. HRMS (MALDI): *m*/*z* calcd. for $C_{109}H_{94}O_{30}$ ([M + Na]$^+$) 1905.5722, found 1905.5681.

(2*S*,3*R*)-2,3-Bis(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-butane [3a(2*S*,3*R*)]: The product was prepared according to procedure B, using **2a**(2*S*,3*R*) (250 mg, 0.2 mmol), NaOMe (20 mg, 0.37 mmol), Amberlite IR-120 (H$^+$; 85 mg, 0.37 mmol), and Ac_2O (3 mL, large excess). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:2); **3a**(2*S*,3*R*) (113 mg, 75%) was obtained as a colorless solid, $[\alpha]_D^{25}$ = +52.70 (*c* = 0.74, CH_3Cl). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.32–5.17 (m, 6 H, 2′-H, 3′-H, 4′-H), 4.99 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, 1′-H), 4.93 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, 1′-H), 4.31–4.04 (m, 6 H, 5′-H, 6′-H), 3.82–3.78 (m, 2 H, 2-H, 3-H), 2.13 (s, 3 H, CH_3), 2.12 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.02 (m, 6 H, CH_3), 1.96 (m, 6 H, CH_3), 1.24 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H), 1.14 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, 1-H, 4-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 170.0–169.5 (8 C, CH_3CO), 97.2 (1′-C), 93.1 (1′-C), 77.3 (3-C), 73.0 (2-C), 69.1

(5′-C), 68.9 (5′-C), 68.7 (3′-C), 68.6 (3′-C), 68.3 (2′-C), 68.0 (2′-C), 65.7 (4′-C), 65.3 (4′-C), 62.2 (6′-C), 62.0 (6′-C), 20.6–20.3 (8 C, *C*H$_3$CO), 15.5, 13.2 (1-C, 4-C) ppm. $C_{32}H_{46}O_{20}$ (750.26): calcd. C 51.20, H 6.18; found C 51.16, H 6.20. HRMS (ESI): *m*/*z* calcd. for $C_{32}H_{46}O_{20}$ ([M + Na]$^+$) 773.2475, found 773.2479.

(2*R*,3*R*)-2,3-Bis(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-butane 3a(2*R*,3*R*): The product was prepared according to procedure B, using **2a**(2*R*,3*R*) (180 mg, 0.14 mmol), NaOMe (20 mg, 0.37 mmol), Amberlite IR-120 (H$^+$; 85 mg, 0.37 mmol), and Ac_2O (3 mL, large excess). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:2); **3a**(2*R*,3*R*) (85 mg, 81%) was obtained as a colorless syrup, $[\alpha]_D^{25}$ = +53.30 (*c* = 0.86, CH_3Cl). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.32–5.23 (m, 4 H, 3′-H, 4′-H), 5.20 (dd, $^3J_{H,H}$ = 3.0, 1.5 Hz, 2 H, 2′-H), 4.96 (d, $^3J_{H,H}$ = 1.5 Hz, 2 H, 1′-H), 4.24 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 5.8 Hz, 2 H, 6′-H), 4.12 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 2.6 Hz, 2 H, 6′-H), 4.08–4.04 (m, 2 H, 5′-H), 3.76–3.71 (m, 2 H, 2-H, 3-H), 2.13 (s, 6 H, C*H*$_3$), 2.09 (s, 6 H, C*H*$_3$), 2.04 (s, 6 H, C*H*$_3$), 1.97 (s, 6 H, C*H*$_3$), 1.21 (d, $^3J_{H,H}$ = 6.0 Hz, 6 H, 1-H, 4-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 170.0–169.5 (8 C, CH$_3$*C*O), 97.4 (2 C, 1′-C), 77.3 (2 C, 2-C, 3-C), 69.1 (2 C, 5′-C), 68.4 (2 C, 3′-C), 68.3 (2 C, 2′-C), 65.7 (2 C, 4′-C), 62.2 (2 C, 6′-C), 20.5–20.3 (8 C, *C*H$_3$CO), 16.1 (2 C, 1-C, 4-C) ppm. $C_{32}H_{46}O_{20}$ (750.26): calcd. C 51.20, H 6.18; found C 50.99, H 6.12. HRMS (ESI): *m*/*z* calcd. for $C_{32}H_{46}O_{20}$ ([M + Na]$^+$) 773.2475, found 773.2473.

(2*S*,3*S*)-2,3-Bis(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-butane [3a(2*S*,3*S*)]: The product was prepared according to procedure B, using **2a**(2*S*,3*S*) (160 mg, 0.13 mmol), NaOMe (20 mg, 0.37 mmol), Amberlite IR-120 (H$^+$; 85 mg, 0.37 mmol), and Ac_2O (3 mL, large excess). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:2); **3a**(2*S*,3*S*) (80 mg, 82%) was obtained as a colorless solid, $[\alpha]_D^{25}$ = +54.94 (*c* = 0.46, CH_3Cl). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.35–5.26 (m, 4 H, 3′-H, 4′-H), 5.22 (dd, $^3J_{H,H}$ = 3.2, 1.7 Hz, 2 H, 2′-H), 4.97 (d, $^3J_{H,H}$ = 1.7 Hz, 2 H, 1′-H), 4.36 (dd, $^3J_{H,H}$ = 12.6, $^2J_{H,H}$ = 5.3 Hz, 2 H, 6′-H), 4.13–4.08 (m, 4 H, 5′-H, 6′-H), 3.90–3.82 (m, 2 H, 2-H, 3-H), 2.16 (s, 6 H, C*H*$_3$), 2.09 (s, 6 H, C*H*$_3$), 1.99 (s, 6 H, C*H*$_3$), 1.97 (s, 6 H, C*H*$_3$), 1.16 (d, $^3J_{H,H}$ = 5.8 Hz, 6 H, 1-H, 4-H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO, 25 °C): δ = 170.0–169.2 (8 C, CH$_3$*C*O), 93.5 (2 C, 1′-C), 73.2 (2 C, 2-C, 3-C), 69.1 (2 C, 5′-C), 68.8 (2 C, 3′-C), 68.1 (2 C, 2′-C), 65.0 (2 C, 4′-C), 61.7 (2 C, 6′-C), 20.6–20.2 (8 C, *C*H$_3$CO), 13.8 (2 C, 1-C, 4-C) ppm. $C_{32}H_{46}O_{20}$ (750.26): calcd. C 51.20, H 6.18; found C 50.92, H 6.32. HRMS (ESI): *m*/*z* calcd. for $C_{32}H_{46}O_{20}$ ([M + Na]$^+$) 773.2475, found 773.2474.

(3*R*)-1,3-Bis(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-butane [3b(3*R*)]: The product was prepared according to procedure B, using **2b**(3*R*) (510 mg, 0.41 mmol), NaOMe (50 mg, 0.93 mmol), Amberlite IR-120 (H$^+$; 215 mg, 0.95 mmol), and Ac_2O (3 mL, large excess). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:2); **3b**(3*R*) (230 mg, 76%) was obtained as a colorless syrup, $[\alpha]_D^{25}$ = +32.72 (*c* = 1.68, CH_3Cl). ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 5.12–5.00 (m, 6 H, 2′-H, 3′-H, 4′-H), 4.90 (m, 1 H, 1′-H), 4.81 (m, 1 H, 1′-H), 4.15–4.10 (m, 2 H, 6′-H), 4.03–3.99 (m, 3 H, 5′-H, 6′-H), 3.93–3.89 (m, 1 H, 5′-H), 3.87–3.82 (m, 1 H), 3.72–3.67 (m, 1 H), 3.49–3.44 (m, 1 H), (1-H, 3-H), 2.08–1.91 (m, 24 H, C*H*$_3$), 1.79–1.73 (m, 2 H, 2-H), 1.22 (d, $^3J_{H,H}$ = 6.1 Hz, 3 H, 4-H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO, 25 °C): δ = 170.0–169.4 (8 C, CH$_3$*C*O), 96.94 (1′-C), 96.90 (1′-C), 72.9 (3-C), 69.2 (5′-C), 68.8 (5′-C), 68.7 (3′-C), 68.5 (3′-C), 68.1 (2′-C), 67.9 (2′-C), 65.7 (4′-C), 65.5 (4′-C), 64.1 (1-C), 62.2 (6′-C), 62.0 (6′-C), 35.6 (2-C), 21.1–20.4 (9 C, *C*H$_3$CO, 4-C) ppm. $C_{32}H_{46}O_{20}$ (750.26): calcd. C 51.20, H 6.18; found C 50.95, H 6.19. HRMS (ESI): *m*/*z* calcd. for $C_{32}H_{46}O_{20}$ ([M + Na]$^+$) 773.2475, found 773.2480.

(3*S*)-1,3-Bis(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-butane [3b(3*S*)]: The product was prepared according to procedure B, using **2b**(3*S*) (180 mg, 0.14 mmol), NaOMe (20 mg, 0.37 mmol), Amberlite IR-120 (H$^+$; 84 mg, 0.37 mmol), and Ac_2O (3 mL, large excess). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:2); **3b**(3*S*) (75 mg, 71%) was obtained as a colorless syrup, $[\alpha]_D^{25}$ = +74.06 (*c* = 2.7, CH_3Cl). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.31–5.24 (m, 4 H, 3′-H, 4′-H), 5.18 (dd, $^3J_{H,H}$ = 3.2, 1.5 Hz, 1 H, 2′-H), 5.15 (dd, $^3J_{H,H}$ = 3.2, 1.5 Hz, 1 H, 2′-H), 4.93 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, 1′-H), 4.81 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, 1′-H), 4.31 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 5.2 Hz, 1 H, 6′-H), 4.28 (dd, *J* = 12.1, 5.2 Hz, 1 H, 6′-H), 4.08 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 2.6 Hz, 1 H, 6′-H), 4.06 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 2.6 Hz, 1 H, 6′-H), 4.01–3.94 (m, 2 H, 5′-H), 3.93–3.88 (m, 1 H), 3.81–3.76 (m, 1 H), 3.59–3.54 (m, 1 H), (1-H, 3-H), 2.14 (m, 6 H, C*H*$_3$), 2.08 (s, 3 H, C*H*$_3$), 2.07 (s, 3 H, C*H*$_3$), 2.03 (s, 3 H, C*H*$_3$), 2.02 (s, 3 H, C*H*$_3$), 1.97 (s, 3 H, C*H*$_3$), 1.96 (s, 3 H, C*H*$_3$), 1.93–1.87 (m, 1 H, 2-H), 1.84–1.77 (m, 1 H, 2-H), 1.18 (d, $^3J_{H,H}$ = 6.1 Hz, 3 H, 4-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 170.0–169.4 (8 C, CH$_3$*C*O), 96.4 (1′-C), 94.1 (1′-C), 69.8 (3-C), 69.3 (2 C, 5′-C), 68.8 (3′-C), 68.7 (3′-C), 68.2 (2′-C), 67.9 (2′-C), 65.5 (2 C, 4′-C), 64.1 (1-C), 62.0 (6′-C), 61.96 (6′-C), 35.7 (2-C), 20.6–20.3 (8 C, *C*H$_3$CO), 18.7 (4-C) ppm. $C_{32}H_{46}O_{20}$ (750.26): calcd. C 51.20, H 6.18; found C 50.92, H 6.21. HRMS (ESI): *m*/*z* calcd. for $C_{32}H_{46}O_{20}$ ([M + Na]$^+$) 773.2475, found 773.2473.

(2*S*,4*R*)-2,4-Bis(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-pentane [3c(2*S*,4*R*)]: The product was prepared according to procedure B, using **2c**(2*S*,4*R*) (180 mg, 0.14 mmol), NaOMe (20 mg, 0.37 mmol), Amberlite IR-120 (H$^+$; 84 mg, 0.37 mmol), and Ac_2O (3 mL, large excess). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:2); **3c**(2*S*,4*R*) (86 mg, 79%) was obtained as a colorless syrup, $[\alpha]_D^{25}$ = +45.53 (*c* = 1.51, CH_3Cl). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.32–5.23 (m, 4 H, 3′-H, 4′-H), 5.13 (dd, $^3J_{H,H}$ = 3.2, 1.5 Hz, 1 H, 2′-H), 5.10 (dd, $^3J_{H,H}$ = 3.2, 1.5 Hz, 1 H, 2′-H), 4.92 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, 1′-H), 4.90 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, 1′-H), 4.28 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 5.2 Hz, 1 H, 6′-H), 4.24 (dd, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 5.2 Hz, 1 H, 6′-H), 4.10–4.04 (m, 3 H, 5′-H, 6′-H), 3.97–3.93 (m, 1 H, 5′-H), 3.91–3.82 (m, 2 H, 2-H, 4-H), 2.13 (s, 3 H, C*H*$_3$), 2.13 (s, 3 H, C*H*$_3$), 2.07 (s, 3 H, C*H*$_3$), 2.06 (s, 3 H, C*H*$_3$), 2.03 (s, 3 H, C*H*$_3$), 2.02 (s, 3 H, C*H*$_3$), 1.97 (s, 3 H, C*H*$_3$), 1.97 (s, 3 H, C*H*$_3$), 1.97–1.93 (m, 1 H, 3-H), 1.58–1.53 (m, 1 H, 3-H), 1.29 (d, $^3J_{H,H}$ = 6.1 Hz, 3 H), 1.18 (d, $^3J_{H,H}$ = 6.1 Hz, 3 H), (1-H, 5-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO, 25 °C): δ = 170.0–169.6 (8 C, CH$_3$*C*O), 96.2 (1′-C), 94.4 (1′-C), 72.5 (4-C), 70.3 (2-C), 69.3 (5′-C), 69.2 (5′-C), 68.7 (3′-C), 68.6 (3′-C), 68.4 (2′-C), 68.1 (2′-C), 65.7 (4′-C), 65.5 (4′-C), 62.2 (2 C, 6′-C), 42.7 (3-C), 20.8–20.4 (8 C, *C*H$_3$CO), 19.0 (2 C, 1-C, 5-C) ppm. $C_{33}H_{48}O_{20}$ (764.27): calcd. C 51.83, H 6.33; found C 51.87, H 6.39. HRMS (ESI): *m*/*z* calcd. for $C_{33}H_{48}O_{20}$ ([M + Na]$^+$) 787.2631, found 787.2630.

(2*R*,4*R*)-2,4-Bis(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-pentane [3c(2*R*,4*R*)]: The product was prepared according to procedure B, using **2c**(2*R*,4*R*) (210 mg, 0.17 mmol), NaOMe (20 mg, 0.37 mmol), Amberlite IR-120 (H$^+$; 84 mg, 0.37 mmol), and Ac_2O (3 mL, large excess). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:2); **3c**(2*R*,4*R*) (107 mg, 82%) was obtained as a colorless solid, $[\alpha]_D^{25}$ = +10.29 (*c* = 0.89, CH_3Cl). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.33 (dd, $^3J_{H,H}$ = 10.1, 3.2 Hz, 2 H, 3′-H), 5.23 (t, $^3J_{H,H}$ = 10.1 Hz, 2 H, 4′-H), 5.03 (dd, $^3J_{H,H}$ = 3.2, 1.7 Hz, 2 H, 2′-H), 4.89 (d, $^3J_{H,H}$ = 1.7 Hz, 2 H, 1′-H), 4.23 (dd,

$^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 6.1 Hz, 2 H, 6′-H), 4.12–4.07 (m, 4 H, 5′-H, 6′-H), 3.89–3.85 (m, 2 H, 2-H, 4-H), 2.11 (s, 6 H, CH_3), 2.07 (s, 6 H, CH_3), 2.03 (s, 6 H, CH_3), 1.99 (s, 6 H, CH_3), 1.59–1.56 (m, 2 H, 3-H), 1.27 (d, $^3J_{H,H}$ = 6.1 Hz, 6 H, 1-H, 5-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 170.0–169.5 (8 C, CH_3CO), 97.9 (2 C, 1′-C), 74.4 (2 C, 2-C, 4-C), 69.3 (2 C, 5′-C), 68.4 (2 C, 3′-C), 68.2 (2 C, 2′-C), 65.8 (2 C, 4′-C), 62.2 (2 C, 6′-C), 44.4 (3-C), 21.5 (2 C, 1-C, 5-C), 20.6–20.4 (8 C, CH_3CO) ppm. $C_{33}H_{48}O_{20}$ (764.27): calcd. C 51.83, H 6.33; found C 51.90, H 6.40. HRMS (MALDI): *m*/*z* calcd. for $C_{33}H_{48}O_{20}$ ([M + Na]$^+$) 787.2631, found 787.2636.

(2*S*,4*S*)-2,4-Bis(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-pentane [3c(2*S*,4*S*)]: The product was prepared according to procedure B, using **2c**(2*S*,4*S*) (190 mg, 0.15 mmol), NaOMe (20 mg, 0.37 mmol), Amberlite IR-120 (H$^+$; 84 mg, 0.37 mmol), and Ac_2O (3 mL, large excess). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:2); **3c**(*S*,*S*) (90 mg, 80%) was obtained as colorless solid, $[\alpha]_D^{25}$ = +73.03 (*c* = 1.16, CH_3Cl). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.34–5.24 (m, 4 H, 3′-H, 4′-H), 5.14 (dd, $^3J_{H,H}$ = 3.2, 1.5 Hz, 2 H, 2′-H), 4.93 (d, $^3J_{H,H}$ = 1.5 Hz, 2 H, 1′-H), 4.29 (dd, $^3J_{H,H}$ = 12.3, $^2J_{H,H}$ = 5.1 Hz, 2 H, 6′-H), 4.09 (dd, *J* = 12.3, $^2J_{H,H}$ = 2.1 Hz, 2 H, 6′-H), 4.07–4.00 (m, 2 H, 5′-H), 3.91–3.81 (m, 2 H, 2-H, 4-H), 2.16 (s, 6 H, CH_3), 2.09 (s, 6 H, CH_3), 2.05 (s, 6 H, CH_3), 1.99 (s, 6 H, CH_3), 1.82 (m, 2 H, 3-H), 1.21 (d, $^3J_{H,H}$ = 6.0 Hz, 6 H, 1-H, 5-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 170.1–169.5 (8 C, CH_3CO), 94.6 (2 C, 1′-C), 71.2 (2 C, 2-C, 4-C), 69.4 (2 C, 5′-C), 68.6 (2 C, 3′-C), 68.2 (2 C, 2′-C), 65.5 (2 C, 4′-C), 62.1 (2 C, 6′-C), 43.6 (3-C), 20.6–20.4 (8 C, CH_3CO), 19.4 (2 C, 1-C, 5-C) ppm. $C_{33}H_{48}O_{20}$ (764.27): calcd. C 51.83, H 6.33; found C 51.78, H 6.39. HRMS (ESI): *m*/*z* calcd. for $C_{33}H_{48}O_{20}$ ([M + Na]$^+$) 787.2631, found 787.2635.

1,4-Bis(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyloxy)butane (3d): The product was prepared according to procedure B, using **2d** (230 mg, 0.18 mmol), NaOMe (20 mg, 0.37 mmol), Amberlite IR-120 (H$^+$; 84 mg, 0.37 mmol), and Ac_2O (3 mL, large excess). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:2); **3d** (96 mg, 72%) was obtained as white solid, $[\alpha]_D^{25}$ = +57.56 (*c* = 2.44, CH_3Cl). ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 5.10–5.05 (m, 6 H, 2′-H, 3′-H, 4′-H), 4.85 (m, 2 H, 1′-H), 4.15–4.00 (m, 4 H, 6′-H), 3.92–3.89 (m, 2 H, 5′-H), 3.66–3.62 (m, 2 H, 1-H, 4-H) 3.50–3.45 (m, 2 H, 1-H, 4-H), 2.08–1.91 (m, 24 H, CH_3), 1.64–1.59 (m, 4 H, 2-H, 3-H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 170.1–169.6 (8 C, CH_3CO), 96.7 (2 C, 1′-C), 68.83 (2 C, 5′-C), 68.76 (2 C, 3′-C), 67.9 (2 C, 2′-C), 67.3 (2 C, 1-C, 4-C), 65.5 (2 C, 4′-C), 62.1 (2 C, 6′-C), 25.6 (2 C, 2-C, 3-C), 20.6–20.5 (8 C, CH_3CO) ppm. $C_{32}H_{46}O_{20}$ (750.26): calcd. C 51.20, H 6.18; found C 50.92, H 6.21. HRMS (ESI): *m*/*z* calcd. for $C_{32}H_{46}O_{20}$ ([M + Na]$^+$) 773.2475, found 773.2473.

2,4,6-Tris(2′,3′,4′6′-tetra-*O*-acetyl-α-D-mannopyranosyloxy)-heptane (3e): The product was prepared according to procedure B, using **2e** (775 mg, 0.41 mmol, mixture of diastereomers), NaOMe (200 mg, 0.37 mmol), Amberlite IR-120 (H$^+$; 1 g, 4.4 mmol), and Ac_2O (3 mL, large excess). After flash column chromatography (silica gel, ethyl acetate/hexane, 1:1); **3e** (350 mg, 75%, mixture of diastereomers) was obtained as white solid. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 5.32–4.76 (m), 4.29–3.72 (m, 1′-H–6′-H, 2-H, 4-H, 6-H), 2.11–1.61 (m, 3-H, 5-H), 1.30–1.15 (m, CH_3, 1-H, 7-H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 170.0–169.5 (CH_3CO), 98.3–95.4 (1′-C), 78.0–70.2 (2-C, 4-C, 6-C), 69.3–68.2 (2′-C, 3′-C, 5′-C), 65.7–65.4 (4′-C), 62.4–61.7 (6′-C), 42.0–40.8 (3-C, 5-C), 21.5–18.4 (CH_3CO, 1-C, 7-C) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{49}H_{70}O_{30}$ ([M + Na]$^+$) 1161.3844, found 1161.3849.

Heptan-1,2:6,7-diepoxy-4-ol (5): Hepta-1,6-dien-4-ol (**4**) (0.6 mL, 4.6 mmol) and mCPBA (3 g, 13 mmol, 2.9 equiv.) were added to a flask containing DCM (100 mL). The reaction mixture was stirred overnight at room temperature. The reaction mixture was evaporated to dryness. After purification by flash column chromatography (silica gel, ethyl acetate/hexane, 1:3); **5** (660 mg, 100%) was obtained as a colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.43–4.04 (m, 1 H, 4-H), 3.62–3.55 (m, 1 H, OH), 3.16–3.05 (m, 2 H, 2-H, 6-H), 2.81–2.74 (m, 2 H, 1-H, 7-H), 2.58–2.47 (m, 2 H, 1-H, 7-H), 1.96–1.83 (m, 2 H, 3-H, 5-H), 1.62–1.50 (m, 2 H, 3-H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 68.7, 67.9, (4-C), 50.3, 50.1, 50.0, (2-C, 6-C), 47.0, 46.6, (1-C, 7-C), 39.9, 39.5, 39.4, (3-C, 5-C) ppm. HRMS (EI): *m*/*z* calcd. for $C_7H_{12}O_3$ ([M – C_3H_5O]$^+$) 87.0441, found 87.0441.

1,2:6,7-Diexpoxy-4-(trimethylsilyloxy)heptane (6): Heptan-1,2:6,7-diepoxy-4-ol **5** (700 mg, 4.9 mmol), and triethylamine (1.6 g, 15.8 mmol, 3.3 equiv.) were added to a flask containing THF (50 mL). The solution was cooled to 0 °C, and TMS-Cl (1.3 mL, 10.2 mmol, 2.1 equiv.) was added dropwise. The reaction mixture was stirred for 6 h, and the reaction was followed by TLC. Then, the reaction mixture was evaporated to dryness. After purification by flash column chromatography (silica gel, ethyl acetate/hexane, 1:5); **6** (890 mg, 85%) was obtained as a colorless syrup. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 4.03–3.94 (m, 1 H, 4-H), 2.93–2.82 (m, 2 H, 2-H, 6-H), 2.68–2.57 (m, 2 H, 1-H, 7-H), 2.39–2.27 (m, 2 H, 1-H, 7-H), 1.77–1.36 (m, 4 H, 3-H, 5-H), 0.00 (m, 9 H, SiCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 68.3, 68.1, 68.0, (4-C), 49.4, 49.2, 49.0, 48.9, (2-C, 6-C), 47.3, 47.2, 46.33, 46.27, (1-C, 7-C), 41.0, 40.8, 40.4, 39.9, (3-C, 5-C), 0.1, 0.03, –0.01 (SiCH_3) ppm. HRMS (EI): *m*/*z* calcd. for $C_{10}H_{20}O_2Si$ ([M – C_3H_5O]$^+$) 159.0836, found 159.0832.

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of **1c**(2*S*,4*R*), **1e**, **2a**–**e**, **3a**–**e**, **5** and **6**.

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