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An Improvement in the Bending Ability of a Hinged Trisaccharide with the Assistance of a Sugar—Sugar Interaction

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Abstract: Hinged di- and trisaccharides incorporating 2,4-diamino-β-D-xylopyranoside as a hinge unit (Hin) were synthesized. Bridging of the diamino group of Hin by carbonylation or chelation to a metal ion results in a conformational change from $^4C_1$ to $^1C_4$, which in turn causes a bending of the oligosaccharides. In this study, the bending abilities of the hinged oligosaccharides were compared, in terms of the reactivities toward carbonylation and chelation. Di- or trisaccharides containing a 6-*O*-glycosylated mannopyranoside or galactopyranoside at their reducing ends had bending abilities similar to that of the Hin monosaccharide, probably because there were neither attractive nor repulsive interactions between the reducing and nonreducing ends. However, when Hin was attached at O2 of methyl mannopyranoside (ManαMe), the bending ability was dependent on the nonreducing sugar and the reaction conditions. Typically, a disaccharide—Hinβ(1,2)ManαMe—was difficult to bend under all the tested reaction conditions, and the bent population in the presence of Zn^{II} was only 4%. On the other hand, a trisaccharide—Manα(1,3)Hinβ(1,2)ManαMe—was bent immediately after the addition of Zn^{II} or Hg^{II}, and the bent population reached 75%, much larger than those of all the other hinged trisaccharides ever tested (<40%). This excellent bending ability suggests an attractive interaction between the reducing and nonreducing ends. The extended conformation was recovered by the addition of triethylenetetramine, a metal ion chelator. Reversible, quick, and efficient bending of the hinged trisaccharide was thus achieved.

Keywords: bioorganic chemistry · carbohydrates · hinged oligosaccharides · molecular recognition · oligosaccharides

Introduction

A substantial number of natural poly- and oligosaccharides function as reinforcing elements in biological systems, providing proteins, cells, organs, and even whole organisms with mechanical stability.[1] Some oligosaccharides are ligands of lectins and antibodies, through which they participate in cell–cell recognition events, bacterial infections, or immune systems.[2] Although the poly- and oligosaccharides are flexible polymers, the conformational variation of these polymers[3] seems to be less than that of polypeptides, the polymers permitting the complicated folding processes involved in building proteins. Moreover, unlike poly- and oligosaccharides, polypeptides can act as the movable components of molecular machines, such as allosteric enzymes, motor proteins, and chaperones.[4] On the other hand, recent studies revealed that hyaluronan, a glycosaminoglycan, is flexible enough to assume kink, fold, or bent structures through a combination of glycosidic bond rotations (φ, ϕ, ω), and a biological function was ascribed to this flexibility.[5] However, the movements of this glycosaminoglycan would be as modest as those of the other oligosaccharides inasmuch as only the glycosidic bonds are the sources of the flexibility, and so its impact on these functions might be insufficient for it to serve as a movable component of a molecular machine.

A lot of natural poly- and oligosaccharides are composed of pyranosides fixed in the $^4C_1$ conformation. The rigidity of the pyranosides restricts the movement of oligosaccharides to a great extent, so biological systems might have selected peptides for the movable components of the molecular ma-

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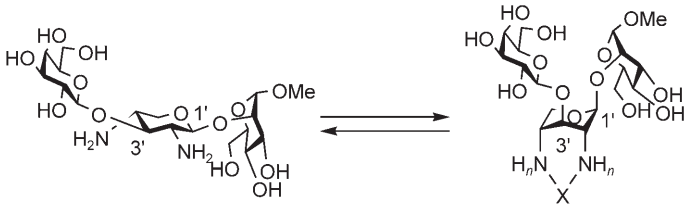
chines. To make the poly- and oligosaccharides more flexible and thereby more useful for the construction of artificial architectures, the ring flip of a monosaccharide unit is prerequisite. In this context, xylopyranosides are useful monosaccharides, since the ring flip is easy and the $^1C_4$ conformation could be fixed as, for example, a 2,4-boronate derivative.[6] In this connection, the authors have succeeded in bending a trisaccharide—Galβ(1,3)Hinβ(1,2)ManαMe (**1**; Scheme 1)—through a $^4C_1$–$^1C_4$ ring flip of the hinge sugar



Scheme 1. The extended and bent states of a hinged trisaccharide.

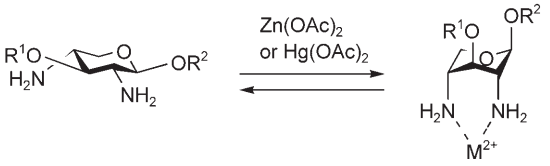
unit: 2,4-diamino-2,4-dideoxy-β-D-xylopyranoside (Hin). In solution, Hin assumes the $^4C_1$ conformation, the extended conformation with regard to C1−O1 and C3−O3 bonds, and it falls into a $^4C_1$–$^1C_4$ equilibrium in the presence of Zn^{II} or Hg^{II}, due to chelation by the diaxial amino groups of the bent $^1C_4$ conformers **2** and **3** (Scheme 1).[7] The bent structure was transient in the exchanging metal complex formation, but was isolable as an *N*,*N*′-carbonyl derivative **4** or a Pt^{II} complex **5** at the expense of long reaction times.[8] Such a sharply bent structure had been unachievable with any combinations of glycosidic bond rotations or heparin-like conformational changes of the pyranosides. This unusual bent structure, which is switchable from and to the extended counterpart through chelation and dechelation, would thus extend the scope of oligosaccharides as raw materials for functional polymers and molecular devices. In practice, we have synthesized a metal fluorosensor through the use of this hinge sugar as a pivot for the tongs-like movement of this molecular device.[9]

Previously it had been demonstrated that the $^1C_4$ population of xylose in the presence of Hg^{II} was 17% in the case of the trisaccharide **1** and 39% in that of the trisaccharide Galβ(1,3)Hinβ(1,6)ManαMe (**6**).[7] The difference between the bent-state stabilities of the two hinged trisaccharides **1** and **6** suggests that the bending ability is influenced by the interaction between the reducing and nonreducing ends. In this report we investigate the bending abilities of several hinged di- and trisaccharides, to assess the compatibility between the two end sugars and ultimately to find a better combination.

Results and Discussion

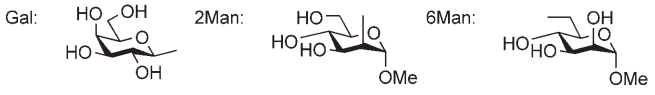
We synthesized three new hinged disaccharides (**10**, **13**, **19**) and four new hinged trisaccharides (**17**, **23**, **31**) as shown in Scheme 2. The disaccharide **10** was synthesized by glycosylation of methyl 2,4-diazido-2,4-dideoxy-β-D-xylopyranoside (**8**) with per-*O*-acetylated galactopyranosyl trichloroacetimidate (**7**) as a glycosyl donor to give the protected disaccharide **9**, followed by deacetylation and reduction of the azide groups. The disaccharides **13** and **19** were prepared by reduction of the azide groups and the benzyloxy groups of the reported precursors **12** and **18**.[7] The disaccharide precursor **27** for the synthesis of the trisaccharide **31** was obtained by the stereoselective glycosylation of methyl 2,3,6-tri-*O*-benzyl-α-D-galactopyranoside (**25**) with 2,4-diazido-2,4-dideoxy-β-D-xylopyranosyl trichloroacetimidate (**24**) as a glycosyl donor, with subsequent deacetylation. The trisaccharides (**17**, **23**, **31**) were synthesized in the same manner from the disaccharide precursors (**12**, **18**, **27**). Glycosylation of the disaccharides (**12**, **18**, **27**) with 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl trichloroacetimidate (**11**) gave the protected trisaccharides (**14**, **20**, **28**), which were then subjected to deacetylation (**15**, **21**, **29**), reduction at the azido groups (**16**, **22**, **30**), and reductive debenzylation to give the desired trisaccharides (**17**, **23**, **31**). Large ^3J values were observed for the ring protons of the hinge units in all the synthesized di- and trisaccharides, indicating the assumption of a $^4C_1$ conformation by the corresponding hinge unit in solution.

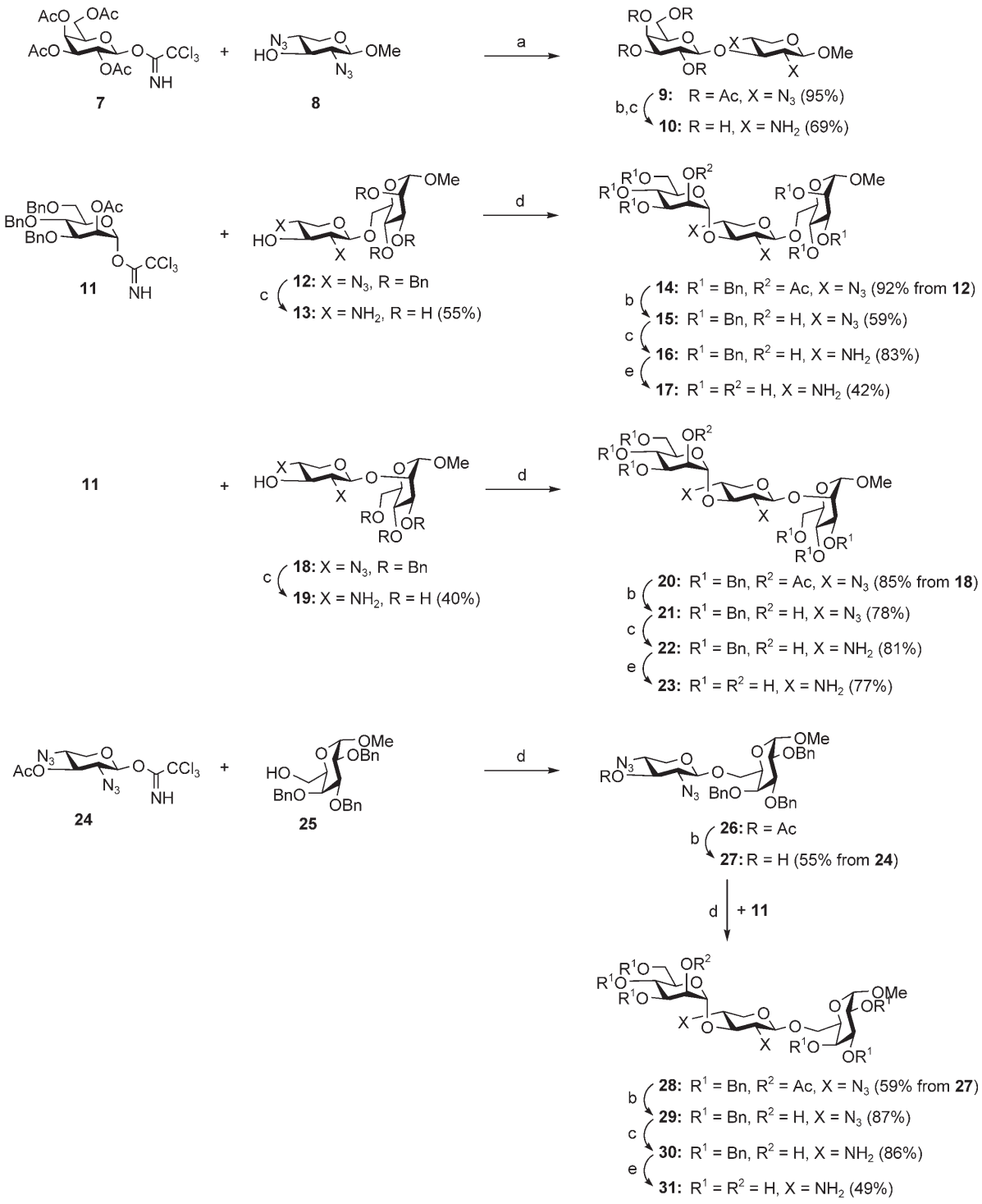
Table 1. Comparison of the bending abilities of the hinged mono-, di-, and trisaccharides in the presence of $Zn(OAc)_2$ or $Hg(OAc)_2$, in terms of the $^1C_4$ population of the hinge unit.



Compd	R^1	R^2	Metal ion	Equiv	$^1C_4$ (%)
	monosaccharide				
32	H	Me	Zn^{II}	2.9	33[a]
32	H	Me	Hg^{II}	0.5	41[a]
	disaccharide				
10	Gal[b]	Me	Zn^{II}	1.3	37
10	Gal	Me	Hg^{II}	0.5	42
13	H	6Man	Zn^{II}	2.1	30
13	H	6Man	Hg^{II}	0.5	35
19	H	2Man	Zn^{II}	2.0	4
19	H	2Man	Hg^{II}	0.5	5
	trisaccharide				
1	Gal	2Man	Zn^{II}	3.1	23[a]
1	Gal	2Man	Hg^{II}	0.5	17[a]
6	Gal	6Man	Zn^{II}	2.0	21[a]
6	Gal	6Man	Hg^{II}	0.5	39[a]
23	Man	2Man	Zn^{II}	1.5	75
23	Man	2Man	Hg^{II}	0.5	≈75

[a] Data from reference [7]. [b] The abbreviations are as follows:





Scheme 2. The syntheses of hinged di- and trisaccharides: a) $BF_3{\cdot}OEt_2$, MS (4 Å), CH_2Cl_2; b) NaOMe, MeOH; c) H_2S, Py/H_2O; d) TMSOTf, MS (4 Å), CH_2Cl_2, −40 °C to RT; e) Na, liq. NH_3/THF, RT.

First of all we examined the effects of $Zn(OAc)_2$ and $Hg(OAc)_2$ additions to the selected di- and trisaccharides (**10**, **13**, **19**, **23**) in $[D_3]$AcONa buffer (Table 1). As in the previous studies, the addition of the metal ions caused signal broadenings in the ^1H NMR at 25 °C, due to the relatively slow exchange between $^4C_1$ and $^1C_4$ structures of the hinge unit. All the measurements were therefore performed at temperatures between 70 and 80 °C, at which the signals were sharp enough for J values to be read. ^1H NMR spectra of compound **23** in the absence and in the presence of $Zn(OAc)_2$ are shown in Figure 1. The signal splittings of the hinge sugar unit became smaller after the addition of Zn-

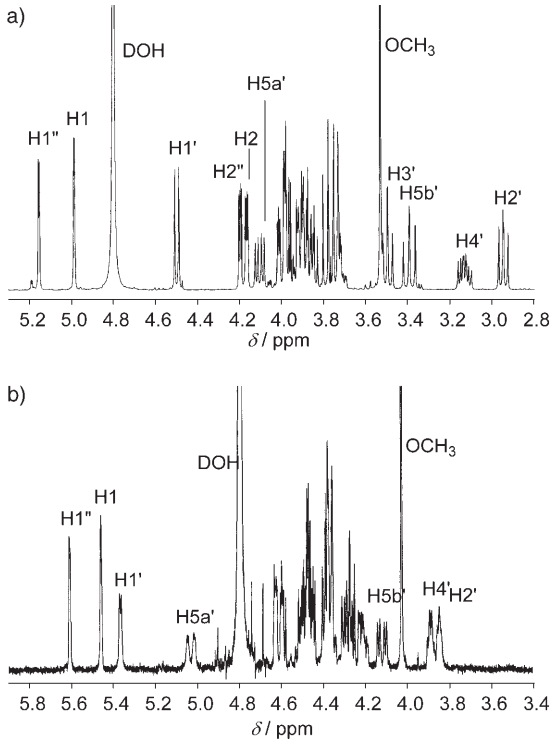
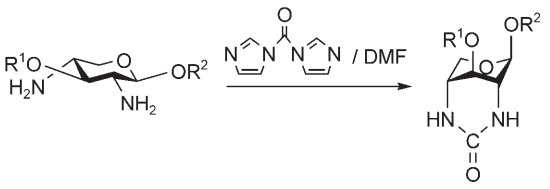


Figure 1. ^{1}H NMR spectra (400 MHz) of compound **23** (26 mM) in the absence and in the presence of $Zn(OAc)_2$ (1.5 equiv) in [D_3]AcONa buffer (pH 7.0, 50 mM). a) **23** at 25 °C; b) **23** with $Zn(OAc)_2$ at 80 °C.

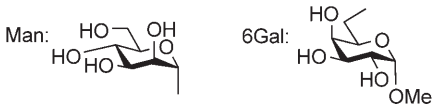
$(OAc)_2$, as has been observed for the other hinge sugars. Populations (%) of the $^1C_4$ conformation were computed by a multiple regression analysis with a least-squares fitting of the ^3J values calculated for model structures to the observed ones. The calculated ^3J values were derived by the generalized Karplus equation[10] from the dihedral angles of the computed $^4C_1$, $^1C_4$, $^2S_0$, $^3S_1$, and ^{03}B structures optimized with PC Spartan Plus software (Wavefunction Inc.) by use of the SYBYL force field. The populations of the skew and boat conformations were negligible. As a result, the disaccharides **10** and **13**, with nonreducing galactose (Gal) and with 6-*O*-glycosylated mannose (6Man), respectively, at their reducing ends, were comparable to the monosaccharide **32** and the trisaccharide **6** with regard to their bending ability, and the populations of the $^1C_4$ conformations in the presence of a metal ion were between 30% and 42% (Table 1). However, a significant loss of bending ability was found in the case of the disaccharide **19**, with a 2-*O*-glycosylated mannose (2Man) at the reducing end: the addition of $Zn(OAc)_2$ and $Hg(OAc)_2$ afforded only 4% and 5% $^1C_4$ conformations of the hinge unit, respectively. In contrast, the bending ability of the trisaccharide **23**, with a nonreducing Man and a 2Man at the reducing end, was overwhelmingly efficient: a $^1C_4$ population of 75% was achieved when 1.5 equivalents of Zn^{II} were added, as shown by the ^{1}H NMR spectral change (Figure 1). The extended conformation of **23** was quickly recovered by the addition of 1.5 equivalents of triethylenetetramine, a chelator of Zn^{II}. The same trends were observed in the experiments with 0.5 equivalent Hg^{II} and about the same degree of the bent population was obtained (≈75%), though the slight signal broadenings in the ^{1}H NMR spectrum hampered the full conformation analysis by ^3J values. The chelation of the hinge sugars to Zn^{II} and Hg^{II} was a reversible process, so the $^1C_4$ populations reflect the thermodynamic stabilities of the bent conformation in water.

Table 2. Comparison of the bending abilities of the hinged mono-, di-, and trisaccharides in terms of the reactivity toward the carbonylation of the hinge unit.



Compd.	R^1	R^2	Product	Temp.	Time [h]	Yield [%]
	monosaccharide					
32	H	Me	**33**	RT	2	77[a]
	disaccharide					
19	H	2Man[b]	**34**	120 °C	24	46
	trisaccharide					
1	Gal	2Man	**4**	120 °C	40	36[a]
6	Gal	6Man	**35**	RT	5	87
17	Man	6Man	**36**	RT	5	86
23	Man	2Man	**37**	RT	5	75
31	Man	6Gal	**38**	RT	5	68

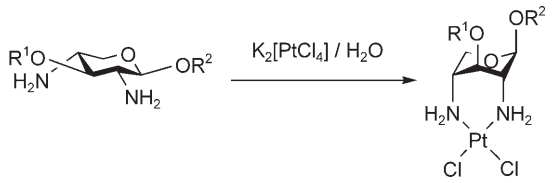
[a] Data from reference [8]. [b] The same abbreviations are used as those in Table 1, except for the following:



We next examined the *N,N'*-carbonylation of the hinged di- and trisaccharides in DMF (Table 2). We had previously reported that the carbonylation of the trisaccharide **1** was sluggish and required harsh conditions relative to those used for the monosaccharide **32**. Similarly poor reactivity was observed for the disaccharide **19**: heating for 24 h afforded only a 46% yield of the product **34**. However, the trisaccharides **6**, **17**, **23**, and **31** showed as good a reactivity as the monosaccharide **32** toward the carbonylation, with the reactions proceeding in room temperature within 5 h and giving 70% to 90% yields of the products **35**, **36**, **37**, and **38**, respectively. The carbonylated products **34–38** were isolated and characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.

Third, we examined Pt^{II} complex formation by the same di- and trisaccharides as used for the carbonylation. The Pt^{II} complex formations were carried out through the addition of $K_2[PtCl_4]$ to the buffered solutions of the hinged oligosaccharides and were monitored through optical rotation changes to calculate the first-order rate constants (Table 3). Previously, the monosaccharide **32** and trisaccharide **1** had shown similar reactivity toward Pt^{II} complex formation. In this study, the Pt^{II} complex formation rate for the disaccharide **19** was elucidated as about 50% of that of the trisacchar-

Table 3. Comparison of the bending abilities of the hinged mono-, di-, and trisaccharides in terms of reactivity toward the complexation of the hinge unit with Pt^{II}.



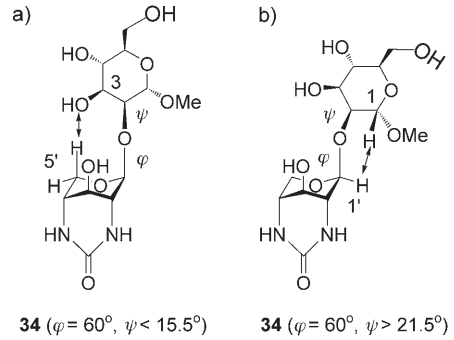
Compd	R^1	R^2	Product	Yield [%]	k [$\times 10^{-4}$ s^{-1}][a]
	monosaccharide				
32	H	Me	**39**	46[b]	1.30[b]
	disaccharide				
19	H	2Man[c]	**40**	43	0.79
	trisaccharide				
1	Gal	2Man	**5**	46[b]	1.68[b]
6	Gal	6Man	**41**	46	1.11
17	Man	6Man	**42**	21	1.15
23	Man	2Man	**43**	49	1.17
31	Man	6Gal	**44**	60	1.23

[a] First-order rate constants determined by optical rotation changes. [b] Data from reference [8]. [c] The same abbreviations are used as in Table 2.

ide **1**. On the other hand, Pt^{II} complex formation by the trisaccharides **6**, **17**, **23**, and **31** proceeded smoothly at rates slightly slower than that of the monosaccharide **32**. The Pt^{II} complex products **40**–**44** were isolated and characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry.

From the three bending processes of the hinge sugars, it is now possible to discuss and anticipate the factors influencing the bending abilities of the hinged oligosaccharides. Both the nonreducing Gal and the 6Man and 6Gal at the reducing ends have small influences on the bending abilities of the di- and trisaccharides **10**, **13**, **6**, **17**, and **31**. In particular, the observations for the trisaccharides **6**, **17**, and **31** were contrary to our expectations that the two end sugars would clash with each other to result in much less bent formations, suggesting that there is neither attractive nor repulsive sugar–sugar interaction when the trisaccharides **6**, **17**, and **31** are bent with the assistance of the chelation. Perhaps the 6Man or 6Gal units can escape these interactions through C5–C–6 rotation.

The disaccharide **19**, with 2Man at the reducing end, showed the weakest bending abilities for each of the three reactions tested above. This low bending ability is attributable to the constrained structure of the bent state, as illustrated by the carbonylated derivative **34** (Figure 2). If we assume the usual *exo* anomeric torsion angle (60°)[11] for O5′-C1′-O-C2 (φ) of **34**, the stress-free range for another glycosidic torsion angle, H2-C2-O-C1′ (ψ), is extremely small, between 15.5° and 21.5°, as demonstrated by manual variation of the torsion angle of the minimized structure on computer. For ψ with more than 21.5° and less than 15.5°, the H1′–H1 and H5a′–O3 distances are less than 2.4 Å and 2.6 Å, respectively, each within the van der Waals distance. Therefore, the bending process accompanies a loss in the freedom of motion to a great extent.



34 (φ = 60°, ψ < 15.5°) **34** (φ = 60°, ψ > 21.5°)

Figure 2. The predicted repulsive interactions in compound **34**. The structure was minimized by use of PC Spartan Plus software (Wavefunction Inc.) with the SYBYL force field, and the glycosidic torsion angles φ and ψ were manually varied. a) The distance between O3 and H5a′ is less than 2.6 Å when φ = 60° and ψ > 21.5°. b) The distance between H1 and H1′ is less than 2.4 Å when φ = 60° and ψ < 15.5°.

Since the trisaccharide **1** is the 3′-*O*-β-galactosylated derivative of disaccharide **19**, this trisaccharide is likely to have as low a bending ability as its counterpart **19**. Indeed, the *N*,*N*′-carbonylation of **1** proceeded as slowly as that of **19**. However, as has been demonstrated in previous papers, all the chelation reactions of **1** were comparable to those of the monosaccharide **32**, showing a fair bending ability. The better bending ability of the trisaccharide **1** than of the disaccharide **19** in the chelation reactions is explicable in terms of an attractive interaction between Gal and 2Man, which compensates for the repulsive interactions in the disaccharide counterpart at the reducing end. Our previous NOESY study on the conformation of the bent trisaccharide **4** revealed a close contact of OH2″ and O5,[8] suggesting hydrogen bonding between Gal and 2Man. This single hydrogen bond is not strong enough to exceed the intrinsic bending difficulty in the disaccharide counterpart, and this is perhaps the reason why the bending ability of the trisaccharide **1** is slightly less than that of the monosaccharide **32**. The sluggish carbonylation of **1** may be due to weakening of the single hydrogen bond in the polar DMF. The above explanations are tentative, because the solvent polarity may influence both the interresidual conformations and the reactivity of the hinge sugars through stereoelectronic effects. The contradictory behaviors of the hinge sugars toward the three bending processes will be uncovered only after thorough examinations are performed.

The trisaccharide **23** bent very efficiently in the presence of Zn^{II} or Hg^{II}. The $^1C_4$ population of 75% is much larger than those of all the other hinged trisaccharides ever tested (<40%). Moreover, the extended conformation of **23** was completely recovered through the addition of triethylenetetramine, so we have improved the efficiency of a stretch–bent switch of a hinged trisaccharide to a great extent. This result indicates that the bent conformation of **23** is thermodynamically more stable than the extended conformation in the presence of metal ions. The rapid and perfect bend formation has been demonstrated with a dipyrene derivative of hinge sugar, in which the bent structure was assisted by π–π

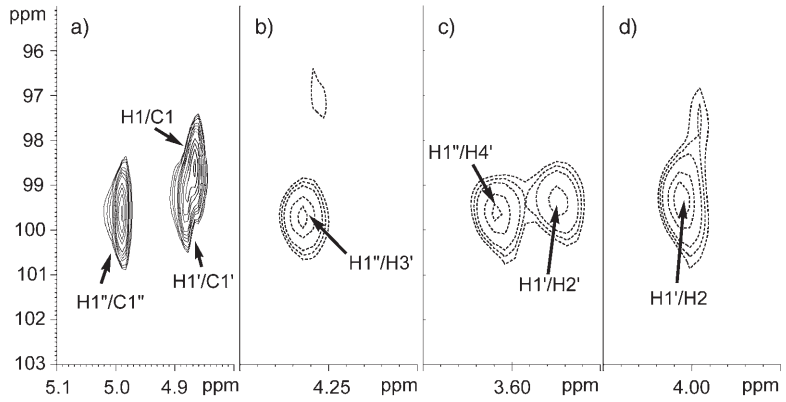


Figure 3. Selected signals from the 2D HMQC-NOESY spectrum of the compound **37**. The contours for positive and negative signals are represented by solid and dotted lines, respectively. The ordinates and abscissas scale the chemical shifts in δ (ppm) for ^{13}C and ^{1}H NMR, respectively. a) HMQC signals for H1″/C1″, H1′/C1′, and H1/C1; b) NOESY signals for H1″/H3′; c) NOESY signals for H-1″/H-4′ and H-1″/H-2′; d) NOESY signals for H-1′/H-2.

stacking of the pyrene groups.[9] It is therefore obvious that Man and 2Man in **23** have an attractive interaction. Although we found no NOE cross-peaks between the nonreducing and reducing ends of the bent trisaccharide **37** in a 2D HMQC-NOESY experiment (Figure 3), NOEs for H-1″/H-3′, H-1″/H-4′, and H-1′/H-2 were observed. We also carried out an AMBER* conformation search for **37** by generating the various conformations by the Monte-Carlo method, in which the distances between NOE hydrogen atoms are restricted to 1.5 to 2.0 Å. The simulation found ten stable conformations within 2.0 kcal mol^{-1} of the lowest conformational energy. The most stable conformer was found three times and has (φ, ψ) of (80.7, −35.8) and (−76.7, 1.3) for the nonreducing and reducing glycosidic bonds, respectively, while the other nine stable conformers have similar (φ, ψ) angles. These results provide support for the U-shape structure of **37**, in which the 3OH″ and 6C of the mannose residues point upward and their hydrophobic faces are almost in parallel (Figure 4). Although these

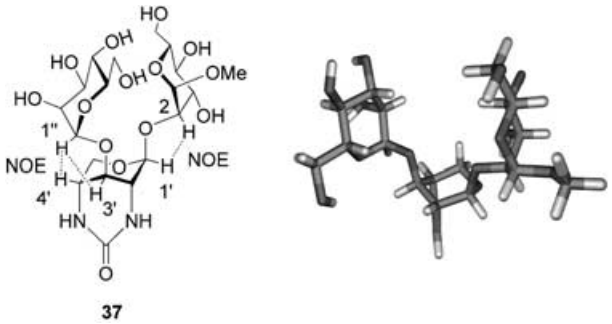


Figure 4. The global minimum conformation of the *N*,*N*′-carbonylated trisaccharide **37** from NOEs and the conformation search.

model structures exhibited no hydrogen bonds between Man and 2Man, the possibility of hydrogen bonding-assisted bending could not be abandoned. The hydrophobic effects in stabilizing the Man–2Man stacking are another potential driving force.

In contrast to the Zn^{II} and Hg^{II} chelation reactions, the carbonylation and Pt^{II} complex formation of **23** proceeded at nearly the same rates as those of the monosaccharide **32**. Both the carbonylation and the Pt^{II} complex formation are irreversible and first-order reactions, and the cyclization through the second N–C or N–metal bond formation is rate-determining.[8] The reactivity is thus determined both by the nucleophilicity of the second amino group undergoing the cyclization and by the stability of the $^{1}C_4$ conformation (i.e., the effective concentration of the reactive species). The effective concentration of the cyclizing amino group of **23** in water, on the basis of the $^{1}C_4$ populations in the presence of Zn^{II}, is twice that of **32**. Therefore, in the case of the Pt^{II} complex formations, the nucleophilicity of the cyclizing amino group is lower for **23** than for **32**, probably due to steric repulsion between the nonreducing Man and Pt^{II}. This was also the case for the carbonylation, and the low nucleophilicity of the second amino group of **23** resulted in the same rate of carbonylation as for **32**.

If the compatibilities of the two end sugars are responsible for the bending abilities of the hinged trisaccharides, this relationship should also hold in the trisaccharide counterparts of longer oligosaccharides. To find the best combination of the reducing and nonreducing ends, we investigated the bending abilities of various hinged trisaccharides. As a result, we found that the bent structure of the trisaccharide **23** was more stable than the extended structure in the presence of Zn^{II} or Hg^{II}, despite the apparent crowdedness. This trisaccharide counterpart should therefore be an important component of functional oligosaccharides.

The above discussions relate closely to specific sugar–sugar interactions[12] such as Le^{X}–Le^{X}[13] and GM3–Gg3,[14] through which cell–cell adhesion is mediated. These interactions usually require Ca^{II} to "glue" the sugars strongly with ionic bonds, but the specificity of the binding obviously originates from the integrated weak interactions such as hydrogen bonds and hydrophobic contacts between the sugars. Furthermore, (KDN)GM3–Gg3 interaction does not require Ca^{II} in the binding of rainbow trout sperm to egg,[15] so the understanding of these sugar–sugar interactions is becoming increasingly important.[16] However, these interactions are too weak to be investigated as thoroughly as sugar–protein or sugar–DNA interactions. Polyvalent or tethered model systems have therefore been employed for the studies of sugar–sugar interactions.[17] Our hinged trisaccharides are different from polyvalent or tethered model systems in that

two sugars are forced into contact with each other with the assistance of chelation, so the very weak interactions, usually unmeasurable, might be evaluated with this system, whereas the interactions between large oligosaccharides will still be difficult.

This study is also relevant to molecular switches.[18] When a certain signal, such as a small molecule or light, is applied to a molecular switch, the switch's conformation changes concomitantly with certain of its physical properties, such as conductivity and fluorescence. Though the hinge trisaccharide **23** does not generate any striking physical property changes in its current form, it might serve as part of a molecular switch if appropriate components were attached, as has been demonstrated by the hinge-based metal ion sensor,[9] conformational changes in which generate an excimer fluorescence with the addition of a metal ion.

Conclusion

Hinge sugars—2,4-diamino-2,4-dideoxy-β-D-xylopyranosides—are potential components for molecular devices, since the $^4C_1$–$^1C_4$ conformational change induced by chelation of the diamino group with a metal ion generates a transition between the extended and bent conformations with regard to the 1-*O*- and 3-*O*-substituents. In previous studies the conformational change of the hinge sugar has been unsatisfactory, giving at most 40% $^1C_4$ population. One exception was the 1,3-di-*O*-pyrenylmethyl hinge sugar, which permitted nearly a 100% $^1C_4$ population in the presence of Zn^{II}, probably because a π–π stacking of the pyrene groups assists the bent structure formation. This study has demonstrated the presence of sugar–sugar attractive interactions that assist the formation of bent trisaccharides. To this end we have examined three hinged disaccharides and five hinged trisaccharides for their bending abilities in terms of $^1C_4$ populations in the presence of Zn^{II} or Hg^{II}, reactivity toward an *N*,*N*′-carbonylation to afford the locked bent structures, and/or rates of chelation to Pt^{II}. The bending ability of a hinged disaccharide—Hinβ(1,2)ManαMe—was very low: it afforded at most a 5% $^1C_4$ population in the presence of a metal ion, required harsh conditions to bridge the diamino group with a carbonyl group, and underwent a sluggish chelation to Pt^{II}. However, the hinged trisaccharide Manα(1,3)Hinβ(1,2)ManαMe with the common reducing disaccharide had a bending ability better than that of the hinge monosaccharide, affording a bent population of 75% in the presence of Zn^{II}. This high $^1C_4$ population should extend the scope for using the hinged trisaccharide in molecular devices and functional polysaccharides.

Experimental Section

General: All solvents and reagents used were reagent grade and, in cases in which further purification was required, standard procedures[19] were followed. Solution transfers when anhydrous conditions were required were performed under dry argon with use of syringes. Thin-layer chromatograms (TLCs) were performed on precoated silica gel Merck 60-F254 plates (Art 5715) and visualized by quenching of fluorescence and/or by charring after spraying with $CeSO_4$ (1%)/$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1.5%)/H_2SO_4 (10%). Column chromatography was performed on Merck Kieselgel 60 (Art 7734), Wako gel C-300, or Kanto Silica gel 60N (spherical, neutral) with the solvent systems specified. Optical rotations were determined with a Horiba SEPA-200 or a JASCO DIP-4 polarimeter in 1 dm or 0.1 dm length cells. ^{1}H NMR (1D, COSY, HMQC, and HMBC) spectra were recorded at 400 MHz (Varian Unity-400) or 270 MHz (JEOL EX-270). Internal tetramethylsilane ($\delta = 0$ ppm) was used as a standard in $CDCl_3$, or solvent peaks were used as standards. Chemical shifts are expressed in ppm referenced to the solvent as an internal standard. The multiplicities of signals are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, ddd = doublet of doublets of doublets, br = broad signal, m = multiplet. ^{13}C NMR spectra were recorded at 67.8 MHz (JEOL JNM-EX-270) or 100.6 MHz (Varian Unity-400) and a solvent peak ($\delta = 77.0$ ppm of $CDCl_3$) or acetone ($\delta = 30.89$ ppm in D_2O) was used as a standard. High-resolution mass spectra (HRMS) were recorded on a Mariner Biospectrometry Workstation ESI-TOF MS.

NOE study: For the NOE study, the trisaccharide **37** (15 mg) was dissolved in D_2O (0.3 mL) and examined in a Bruker AVANCE 400 instrument. The sample was set to 298 K. Two-dimensional ^{1}H–^{13}C HMQC, HMQC-TOCSY, and HMQC-NOESY spectra were measured by use of pulse programs in the Bruker standard library (invbtp, invbmltp, and invbnotp, respectively). During acquisition, GARP decoupling was performed toward ^{13}C (F1 dimension). For HMQC-TOCSY experiments, the MLEV-17 pulse sequence was used and its mixing time was varied from 20 ms to 80 ms. For HMQC-NOESY experiments, the mixing time was also varied (100 ms to 800 ms). A total of 256 *t*1 data points were collected with 64 transients per *t*1. The data were transformed as a 2 K and 1 K matrix.

Computational methods: Molecular mechanics calculations were performed with MacroModel 5.5[20] and the force field used was AMBER*. Conformational analysis of the trisaccharide **37** was performed in GB/SA water[21] by a Monte-Carlo procedure. We searched for the lowest-energy conformations satisfying two distances (H-1′/H2, H1″/H3′ and H1″/H4′) within 1.5–2 Å as suggested by NOE experiments. These distance constraints were applied with the force constant of 250 kJ mol^{-1} Å^{-2}. The Monte-Carlo search was conducted with a total of 10000 search steps with use of TNCG minimization to gradient convergence (< 0.05 kJ mol^{-1}). A total of 2539 unique conformations were saved. The lowest-energy conformer was found three times and there were nine additional conformers within 2.0 kcal mol^{-1}. The lowest-energy conformer is shown in Figure 4.

Methyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→3)-2,4-diazido-2,4-dideoxy-3-*O*-β-D-xylopyranoside (9): A solution of 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl trichloroacetimidate (**7**; 2.634 g, 5.35 mmol) in dichloromethane (15 mL) was slowly added at −75 °C to a stirred mixture of methyl 2,4-diazido-2,4-dideoxy-3-*O*-β-D-xylopyranoside (**8**; 712 mg, 3.32 mmol), $BF_3\cdot OEt_2$ (100 μL, 813 μmol), and molecular sieves (4 Å, 0.80 g) in dichloromethane (15 mL). The temperature was allowed to increase slowly to room temperature over 2 h. After the addition of triethylamine (200 μL, 1.44 mmol), the mixture was evaporated and chromatographed on silica gel (hexane/ethyl acetate 2:1) to give **9** (1.715 g, 95%) as a foam: $R_f = 0.29$ (hexane/ethyl acetate 2:1); $[\alpha]_D^{25} = +8.3$ ($c = 1.23$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 5.38$ (dd, $^3J_{3,4} = 3.5$, $^3J_{4,5} = 1.0$ Hz, 1H; H4′), 5.23 (dd, $^3J_{1,2} = 7.9$, $^3J_{2,3} = 10.5$ Hz, 1H; H2′), 5.04 (dd, 1H; H3′), 4.85 (d, 1H; H1′), 4.23 (dd, $^3J_{5,6a} = 6.3$, $^2J_{6a,6b} = 11.1$ Hz, 1H; H6a′), 4.11 (dd, $^3J_{5,6b} = 7.2$ Hz, 1H; H6b′), 4.09 (d, $^3J_{1,2} = 7.9$ Hz, 1H; H-1), 3.97 (dd, $^3J_{4,5a} = 5.5$, $^2J_{5a,5b} = 12.1$ Hz, 1H; H5a), 3.93 (ddd, 1H; H5′), 3.54 (s, 3H; OCH_3), 3.52 (ddd, $^3J_{3,4} = 9.3$, $^3J_{4,5b} = 10.7$ Hz, 1H; H4), 3.43 (dd, $^3J_{2,3} = 9.6$ Hz, 1H; H3), 3.24 (dd, 1H; H2), 3.04 (dd, 1H; H5b), 2.13, 2.10, 2.04, 1.99 (4×s, 3H each; $COCH_3$) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$, 25 °C): $\delta = 170.3$, 170.3, 170.1, 169.5 (CH_3CO), 103.6, 101.1 (C1, C1′), 80.0, 70.9, 70.5, 69.0, 66.8, 66.0, 63.9, 61.0, 59.5, 57.1 (C2, C3, C4, C5, C2′, C3′, C4′, C5′, C6′, OCH_3),

20.7, 20.6, 20.5 (CH_3CO) ppm; elemental analysis calcd (%) for $C_{20}H_{28}N_6O_{12}$ (544.5): C 44.12, H 5.18, N 15.44; found: C 44.09, H 5.19, N 15.18.

Methyl (β-D-galactopyranosyl)-(1→3)-2,4-diamino-2,4-dideoxy-3-*O*-β-D-xylopyranoside (10): A solution of **9** (1.542 g, 2.83 mmol) in NaOMe (50 mM, 20 mL) was kept at room temperature for 4 h. The mixture was evaporated and chromatographed on silica gel (ethyl acetate/MeOH 20:1) to give a product (815 mg) with an R_f value of 0.26 (ethyl acetate/MeOH 20:1). The product was dissolved in pyridine/H_2O (1:1, 50 mL), and H_2S gas was bubbled for 10 min at 0 °C. The solution was kept for 15 h, evaporated, and chromatographed on spherical silica gel (*i*PrOH/H_2O/28% NH_3 8:1:1) to give **10** (638 mg, 69%) as white solid: R_f = 0.47 (*i*PrOH/H_2O/28% NH_3 7:3:1); m.p. 235 °C (decomp); $[\alpha]_D^{24} = -26.2$ (c = 1.03 in H_2O); ^{1}H NMR (400 MHz, D_2O, 70 °C, DOH): δ = 5.00 (d, $^3J_{1,2}$ = 7.6 Hz, 1H; H1′), 4.71 (d, $^3J_{1,2}$ = 8.1 Hz, 1H; H1), 4.47 (dd, $^3J_{4,5a}$ = 5.3, $^2J_{5a,5b}$ = 11.9 Hz, 1H; H5a), 4.42 (d, $^3J_{3,4}$ = 3.4 Hz, 1H; H4′), 4.27 (dd, $^3J_{5,6a}$ = 7.5, $^2J_{6a,6b}$ = 12.0 Hz, 1H; H6a′), 4.24 (dd, $^3J_{5,6b}$ = 4.6 Hz, 1H; H6b′), 4.18 (dd, 1H; H5′), 4.15 (dd, $^3J_{2,3}$ = 9.8 Hz, 1H; H3′), 4.07 (dd, 1H; H2′), 4.02 (s, 3H; OCH_3), 3.88 (dd, $^3J_{2,3}$ = 9.6, $^3J_{3,4}$ = 9.5 Hz, 1H; H3), 3.75 (dd, $J_{4,5b}$ = 10.8 Hz, 1H; H5b), 3.40 (ddd, 1H; H4), 3.23 (dd, 1H; H2) ppm; ^{13}C NMR (67.8 MHz, D_2O, 25 °C, acetone): δ = 104.8, 104.2 (C1, C1′), 86.9, 75.4, 72.8, 71.3, 68.6, 66.1, 61.0, 57.4, 56.4, 50.5 (C2, C3, C4, C5, C6, C2′, C3′, C4′, C5′, OCH_3) ppm; HRMS (ESI): calcd for $C_{12}H_{25}N_2O_8$ $[M+H]^+$: 325.1611; found 325.1624.

Compound **10** (14 mM) + 0.5 equiv $Hg(OAc)_2$: ^{1}H NMR (400 MHz, 50 mM [D_3]AcONa buffer, 80 °C, DOH): δ = 5.15 (d, $^3J_{1,2}$ = 6.7 Hz, 1H; H1′), 5.07 (d, $^3J_{1,2}$ = 5.2 Hz, 1H; H1), 4.78 (m, 1H; H5a), 4.52 (m, 1H; H4′), 4.39–4.36(m, 3H; H3, H6a′, H6b′), 4.30 (m, 1H; H5′), 4.24 (dd, $^3J_{2,3}$ = 9.9, $^3J_{3,4}$ = 3.4 Hz, 1H; H3′), 4.17 (dd, 1H; H2′), 4.11 (dd, $^3J_{4,5b}$ = 6.9, $^2J_{5a,5b}$ = 12.4 Hz, 1H; H5b), 4.10 (s, 3H; OCH_3), 3.99 (ddd, $^3J_{3,4}$ = 6.7, $^3J_{4,5a}$ = 4.0 Hz, 1H; H4), 3.76 (t, 1H; H2), 2.45 ppm (s, 3H; HgO-$COCH_3$).

Compound **10** (24 mM) + 1.25 equiv $Zn(OAc)_2$: ^{1}H NMR (400 MHz, 50 mM [D_3]AcONa buffer, 80 °C, DOH): δ = 5.11 (d, $^3J_{1,2}$ = 7.6 Hz, 1H; H1′), 5.06 (d, $^3J_{1,2}$ = 5.6 Hz, 1H; H1), 4.78 (m, 1H; H5a), 4.52 (dd, $^3J_{3,4}$ = 2.0, $^3J_{4,5}$ = 1.1 Hz, 1H; H4′), 4.38 (t, ^3J = 6.5 Hz, 1H; H3), 4.37–4.35 (m, 2H; H6a′, H6b′), 4.24 (dd, $^3J_{2,3}$ = 10.1 Hz, 1H; H3′), 4.17 (dd, $^3J_{2,3}$ = 9.9 Hz, 1H; H2′), 4.11 (dd, $^3J_{4,5b}$ = 7.3, $^3J_{5a,5b}$ = 12.4 Hz, 1H; H5b), 4.09 (s, 3H; OCH_3), 3.91 (dt, $^3J_{4,5a}$ = 4.0 Hz, 1H; H4), 3.67 (brt, 1H; H2), 2.50 ppm (s, 7.5H; $ZnOCOCH_3$).

Methyl (2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-α-D-mannopyranoside (13): H_2S gas was bubbled at 0 °C for 10 min into a solution of methyl (2,4-diazido-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-α-D-mannopyranoside (**12**; 464 mg, 710 μmol) in pyridine/H_2O (1:1, 20 mL). The mixture was kept at room temperature for 12 h, evaporated, and chromatographed on silica gel ($CHCl_3$/MeOH/H_2O 3:1:0, then 65:35:6) to give a product with an R_f value of 0.35 ($CHCl_3$/MeOH/H_2O 65:35:6). The product was dissolved in liquid ammonia (ca. 20 mL) and sodium was added to the solution in small portions at −78 °C until a blue color of the solution was maintained for more than 10 min. After addition of ethanol, the solution was carefully evaporated and chromatographed on spherical silica gel (*i*PrOH/H_2O/28% NH_3 8:1:1, then 7:3:1) to give **13** (127 mg, 55%) as a white solid: R_f = 0.37 (*i*PrOH/H_2O/28% NH_3 7:3:1); m.p. 116–118 °C; $[\alpha]_D^{25} = +10.5$ (c = 1.52 in H_2O); ^{1}H NMR (400 MHz, D_2O, 80 °C, DOH): δ = 5.31 (d, $^3J_{1,2}$ = 1.4 Hz, 1H; H1), 4.90 (d, $^3J_{1,2}$ = 8.1 Hz, 1H; H1′), 4.69 (dd, $^3J_{5,6a}$ = 1.8, $^2J_{6a,6b}$ = 11.4 Hz, 1H; H6a), 4.52 (dd, $^3J_{4,5a}$ = 11.8 Hz, 1H; H5a′), 4.50 (dd, $^3J_{2,3}$ = 3.1 Hz, 1H; H2), 4.42 (dd, $^3J_{5,6b}$ = 5.3 Hz, 1H; H6b), 4.35–4.24 (m, 3H; H4, H5), 3.98 (s, 3H; OCH_3), 3.82 (dd, $^3J_{4,5b}$ = 10.8 Hz, 1H; H5b′), 3.76 (dd, $^3J_{2,3}$ = 9.8, $^3J_{3,4}$ = 9.6 Hz, 1H; H3′), 3.37 (ddd, 1H; H4′), 3.19 (dd, 1H; H2′) ppm; ^{13}C NMR (67.8 MHz, D_2O, 25 °C, acetone): δ = 103.8, 100.2 (C1, C1′), 75.3, 70.6, 69.7, 69.0, 68.2, 65.7, 65.4, 56.0, 54.1, 51.1 (C2, C3, C4, C5, C6, C2′, C3′, C4′, C5′, OCH_3) ppm; HRMS (ESI): calcd for $C_{12}H_{25}N_2O_8$ $[M+H]^+$: 325.1611; found 325.1598.

Compound **13** (34 mM) + 0.5 equiv $Hg(OAc)_2$: ^{1}H NMR (400 MHz, 50 mM [D_3]AcONa buffer, 70 °C, DOH): δ = 5.24 (brs, 1H; H1), 5.14 (d, $^3J_{1,2}$ = 5.5 Hz, 1H; H1′), 4.71 (dd, $^3J_{4,5a}$ = 4.0 Hz, $^2J_{5a,5b}$ = 12.1 Hz, 1H; H5a′), 4.60 (d, $^2J_{6a,6b}$ = 11.3 Hz, 1H; H6a), 4.43 (dd, $^3J_{1,2}$ = 1.7, $^3J_{2,3}$ = 3.2 Hz, 1H; H2), 4.35 (dd, $^3J_{5,6b}$ = 5.9 Hz, 1H; H6b), 4.27–4.13 (m, 4H; H3, H4, H5, H3′), 4.02 (dd, $^3J_{4,5b}$ = 7.3 Hz, 1H; H5b′), 3.90 (s, 3H; OCH_3), 3.73 (m, 1H; H4′), 3.61 (brt, ^3J = 6 Hz, 1H; H2′), 2.39 ppm (s, 3H; $HgOCOCH_3$).

Compound **13** (32 mM) + 2.1 equiv $Zn(OAc)_2$: ^{1}H NMR (400 MHz, 50 mM [D_3]AcONa buffer, 80 °C, DOH): δ = 5.30 (brs, 1H; H1), 5.18 (d, $^3J_{1,2}$ = 5.6 Hz, 1H; H1′), 4.75 (m, 1H; H5a′), 4.66 (d, $^3J_{5,6a}$ = 11.4 Hz, 1H; H6a), 4.50 (dd, $^3J_{1,2}$ = 1.9, $^3J_{2,3}$ = 3.2 Hz, 1H; H2), 4.41 (dd, $^3J_{5,6b}$ = 5.5 Hz, 1H; H6b), 4.33–4.22 (m, 4H; H3, H4, H5, H3′), 4.06 (dd, $^3J_{4,5b}$ = 7.8, $^2J_{5a,5b}$ = 12.2 Hz, 1H; H5b′), 3.97 (s, 3H; OCH_3), 3.61 (br, 1H; H4′), 3.48 (br, 1H; H2′), 2.50 ppm (s, 12.6H; $ZnOCOCH_3$).

Methyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2,4-diazido-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (14): A mixture of **12** (280 mg, 433 μmol) and crushed MS (4 Å, 600 mg) in CH_2Cl_2 (8 mL) was stirred under Ar for 1 h and cooled at −40 °C. TMSOTf (14.5 μL, 80 μmol) in CH_2Cl_2 (145 μL), and then a solution of 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl trichloroacetimidate (**11**; 392 mg, 615 μmol) in CH_2Cl_2 (3 mL) were slowly added to the mixture. The temperature was allowed to increase slowly to room temperature over 2 h and the mixture was stirred for a further 30 min at room temperature. The reaction was quenched by addition of triethylamine (22 μL, 158 μmol). The insoluble material was removed by celite filtration and the filtrate was evaporated and chromatographed on a column of silica gel (toluene/ethyl acetate 20:1 to 8:1) to give trisaccharide **14** (446 mg, 92%) as a syrup: R_f = 0.30 (toluene/ethyl acetate 8:1); $[\alpha]_D^{24} = +30.9$ (c = 1.01 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.37–7.15 (m, 30H; Ph×6), 5.42 (brs, 1H; H2″), 5.27 (d, $^3J_{1,2}$ = 1.7 Hz, 1H; H1″), 4.98–4.46 (m, 13H; CH_2Ph×6, H1), 4.23 (d, $^3J_{1,2}$ = 7.5 Hz, 1H; H1′), 4.11–3.75 (m, 11H; H2, H3, H4, H5, H6a, H6b, H5a′, H3″, H4″, H5″, H6a″), 3.71 (dd, $^3J_{5,6b}$ = 1.5, $^2J_{6a,6b}$ = 10.7 Hz, 1H; H6b″), 3.49 (ddd, $^3J_{3,4}$ = 9.2, $^3J_{4,5a}$ = 5.3, $^3J_{4,5b}$ = 10.7 Hz, 1H; H4′), 3.33 (t, $^3J_{2,3}$ = 9.6 Hz, 1H; H3′), 3.31 (s, 3H; OCH_3), 3.26 (dd, 1H; H2′), 3.08 (t, $^2J_{5a,5b}$ = 11.6 Hz, 1H; H5b′), 2.15 (s, 3H; $COCH_3$) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 170.4 (C=O), 138.5, 138.4, 138.3, 138.0, 128.35, 128.3, 128.25, 128.2, 128.0, 127.85, 127.8, 127.7, 127.65, 127.6, 127.55, 127.5, (Ph×6), 103.1 (C1′), 99.1 (C1), 98.9 (C1″), 80.3, 77.9, 75.0, 74.4, 74.0, 72.4, 71.4 (C2, C3, C4, C5, C3″, C4″, C5″), 79.5 (C3′), 75.1, 74.9, 73.4, 72.7, 72.0, 71.9 (CH_2Ph×6), 69.3 (C6), 69.0 (C2″), 68.5 (C6″), 65.3 (C2′), 63.5 (C5′), 61.3 (C4′), 54.7 (OCH_3), 21.1 (CH_3CO) ppm; HRMS (ESI): calcd for $C_{62}H_{68}N_6O_{14}Na$ $[M+Na]^+$: 1143.4691; found 1143.4686; elemental analysis calcd (%) for $C_{62}H_{68}N_6O_{14}\cdot 3/2\,H_2O$ (1148.3): C 64.85, H 6.23, N 7.32; found: C 64.77, H 5.89, N 7.64.

Methyl (3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2,4-diazido-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (15): A solution of NaOMe in MeOH (50 mM, 6 mL) was added to a stirred solution of **14** (446 mg, 398 μmol) in CH_2Cl_2 (2 mL). After 9 h, the reaction mixture was evaporated and chromatographed on a column of silica gel (hexane/ethyl acetate 2:1) to give **15** (253 mg, 59%) as a syrup: R_f = 0.22 (hexane/ethyl acetate 2:1), $[\alpha]_D^{25} = +34.1$ (c = 0.94 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.37–7.16 (m, 30H; Ph×6), 5.28 (d, $^3J_{1,2}$ = 1.5 Hz, 1H; H1″), 4.98–4.48 (m, 13H; CH_2Ph×6, H1), 4.25 (d, $^3J_{1,2}$ = 7.8 Hz, 1H; H1′), 4.12–3.68 (m, 13H; H2, H3, H4, H5, H6a, H6b, H5a′, H2″, H3″, H4″, H5″, H6a″, H6b″), 3.47 (ddd, $^3J_{3,4}$ = 9.3, $^3J_{4,5a}$ = 5.3, $^3J_{4,5b}$ = 10.8 Hz, 1H; H4′), 3.35 (t, $^3J_{2,3}$ = 9.6 Hz, 1H; H3′), 3.31 (s, 3H; OCH_3), 3.26 (dd, 1H; H2′), 3.08 (t, $^2J_{5a,5b}$ = 11.6 Hz, 1H; H5b′), 2.54 (brs, 1H; OH) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.45, 138.4, 138.35, 138.3, 138.25, 137.9, 128.4, 128.35, 128.3, 128.25, 128.2, 127.9, 127.85, 127.8, 127.75, 127.7, 127.6, 127.5, 127.4 (Ph×6), 103.1 (C1′), 100.5 (C1″), 99.0 (C1), 79.2 (C3′), 80.3, 79.8, 75.0, 74.4, 73.9, 72.0, 71.4 (C2, C3, C4, C5, C3″, C4″, C5″), 75.0, 74.9, 73.4, 72.7, 72.0 (CH_2Ph×6), 69.3 (C6), 68.6 (C2″), 68.5 (C6″), 65.3 (C2′), 63.4 (C5′), 61.5 (C4′), 54.7 (OCH_3) ppm; HRMS (ESI): calcd for $C_{60}H_{66}N_6O_{13}$ Na $[M+Na]^+$: 1101.4586; found 1101.4585; elemental analysis calcd (%) for $C_{60}H_{66}N_6O_{13}\cdot H_2O$ (1097.2): C 65.68, H 6.25, N 7.66; found: C 65.39, H 6.02, N 7.31.

Methyl (3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (16): Ar gas was bubbled at 0 °C for 20 min into a solution of **15**

(369 mg, 342 μmol) in pyridine/H_2O (10:1, 15.4 mL), followed by H_2S gas for 10 min. The mixture was kept at room temperature for 12 h. After the mixture had been evaporated, the residue was taken up with methanol, and the insoluble material was removed by celite filtration. The filtrate was evaporated and chromatographed on silica gel ($CHCl_3$/MeOH 20:1) to give **16** (291 mg, 83%) as an amorphous solid; R_f = 0.27 ($CHCl_3$/MeOH 10:1); $[\alpha]_D^{25}$ = +41.5 (c = 1.01 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.47–7.17 (m, 30H; Ph×6), 5.10 (d, $^3J_{1,2}$ = 2.9 Hz, 1H; H1″), 4.92–4.43 (m, 12H; CH_2Ph×6), 4.74 (d, $^3J_{1,2}$ = 1.8 Hz, 1H; H1), 4.13–4.08 (m, 2H; H6a, H1′), 4.04 (q, 1H; H5″), 3.99 (t, $^3J_{2,3}$ = 3.1 Hz, 1H; H2″), 3.90–3.72 (m, 8H; H2, H3, H4, H5, H6a, H5a′, H3″, H4″), 3.69–3.60 (m, 2H; H6a″, H6b″), 3.27 (s, 3H; OCH_3), 3.12 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.3 Hz, 1H; H3′), 3.01 (t, $^3J_{4,5b}$ = 11.0, $^2J_{5a,5b}$ = 11.1 Hz, 1H; H5b′), 2.85 (ddd, $^3J_{4,5a}$ = 5.0 Hz, 1H; H4′), 2.75 (dd, $^3J_{1,2}$ = 7.9 Hz, 1H; H2′) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 138.4, 138.3, 138.1, 138.05, 138.0, 137.9, 128.4, 128.25, 128.2, 128.15, 127.85, 127.8, 127.75, 127.7, 127.65, 127.6, 127.55, 127.5, 127.45, 127.4 (Ph×6), 105.5 (C1′), 101.0 (C1″), 98.6 (C1), 87.8 (C3′), 80.0, 78.9, 75.0, 74.6, 74.4, 72.1, 71.3 (C2, C3, C4, C5, C3″, C4″, C5″), 74.8, 74.2, 73.2, 72.4, 72.2, 71.9 (CH_2Ph×6), 69.3 (C2″), 69.2 (C6″), 69.0 (C6), 67.3 (C5′), 56.2 (C2′), 54.6 (OCH_3), 52.1 (C4′) ppm; HRMS (ESI): calcd for $C_{60}H_{71}N_2O_{13}$ $[M+H]^+$: 1027.4956; found 1027.4951; elemental analysis calcd (%) for $C_{60}H_{70}N_2O_{13}\cdot H_2O$ (1045.2): C 68.95, H 6.94, N 2.68; found: C 69.17, H 6.86, N 2.79.

Methyl (α-D-mannopyranosyl)-(1→3)-(2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-α-D-mannopyranoside (17): Sodium metal (87 mg) was added in small portions at −78°C under Ar to a solution of **16** (333 mg, 324 μmol) in THF (1 mL) and liquid ammonia (ca.5 mL). The mixture was heated at reflux at room temperature for 10 min, while the blue color of the solution persisted. The reaction was quenched by careful addition of ethanol. The mixture was carefully evaporated and chromatographed on spherical silica gel (*i*PrOH/H_2O/28% NH_3 7:3:1) to give **17** (66 mg, 42%) as an amorphous solid: R_f = 0.23 (*i*PrOH/H_2O/28% NH_3 7:3:1); m.p. 135–137°C; $[\alpha]_D^{23}$ = +40.1 (*c* = 0.96 in H_2O); ^{1}H NMR (400 MHz, D_2O, 40°C, DOH): δ = 5.27 (d, $^3J_{1,2}$ = 1.8 Hz, 1H; H1″), 4.97 (d, $^3J_{1,2}$ = 1.2 Hz, 1H; H1), 4.60 (d, $^3J_{1,2}$ = 7.8 Hz, 1H; H1′), 4.36 (dd, $^3J_{5,6a}$ = 1.5, $^2J_{6a,6b}$ = 11.4 Hz, 1H; H6a), 4.31 (t, $^3J_{2,3}$ = 2.9 Hz, 1H; H2″), 4.20 (dd, $^3J_{4,5a}$ = 5.2, $^2J_{5a,5b}$ = 11.7 Hz, 1H; H5a′), 4.15 (dd, $^3J_{2,3}$ = 3.1 Hz, 1H; H2), 4.13–3.87 (m, 9H; H3, H4, H5, H6b, H3″, H4″, H5″, H6a″, H6b″), 3.65–3.60 (m, 4H; H3′, OCH_3), 3.54 (t, $^3J_{4,5}$ = 11.0 Hz, 1H; H5b′), 3.22 (ddd, $^3J_{3,4}$ = 9.3 Hz, 1H; H4′), 3.03 (dd, $^3J_{2,3}$ = 9.2 Hz, 1H; H2) ppm; ^{13}C NMR (100.6 MHz, D_2O, 40°C, acetone): δ = 105.0 (C1′), 102.3 (C1″), 101.6 (C1), 87.4 (C3′), 74.5, 72.0, 71.15, 71.1, 71.0, 67.6, 67.2 (C3, C4, C5, C2″, C3″, C4″, C5″), 70.5 (C2), 69.8 (C6), 66.2 (C5′), 61.6 (C6″), 56.1 (C2′), 55.5 (OCH_3), 51.6 (C4′) ppm; HRMS (ESI): calcd for $C_{18}H_{35}N_2O_{13}$ $[M+H]^+$: 487.2139; found 487.2136; elemental analysis calcd (%) for $C_{18}H_{34}N_2O_{13}\cdot H_2O$ (504.5): C 42.85, H 7.19, N 5.55; found: C 43.03, H 6.93, N 5.73.

Methyl (2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl)-(1→2)-α-D-mannopyranoside (19): H_2S gas was bubbled for 10 min at 0°C into a solution of methyl (2,4-diazido-2,4-dideoxy-β-D-xylopyranosyl)-(1→2)-α-D-mannopyranoside (**18**; 68 mg, 104 μmol) in pyridine/H_2O (1:1, 4 mL). The mixture was kept at room temperature for 12 h, evaporated, and chromatographed on silica gel ($CHCl_3$/MeOH/H_2O 3:1:0, then 65:35:6) to give a product with an R_f value of 0.29 ($CHCl_3$/MeOH/H_2O 65:35:6). The product was dissolved in liquid ammonia (ca. 5 mL), and sodium was added to the solution in small portions at −78°C until the blue color of the solution was maintained for more than 10 min. After addition of ethanol, the solution was carefully evaporated and chromatographed on spherical silica gel (*i*PrOH/H_2O/28% NH_3 8:1:1 then 7:3:1) to give **19** (13 mg, 40%) as a white solid: R_f = 0.19 (*i*PrOH/H_2O/28% NH_3 8:1:1); $[\alpha]_D^{24}$ = −13.2 (*c* = 0.57 in H_2O); ^{1}H NMR (400 MHz, D_2O, 70°C, DOH): δ = 5.33 (d, $^3J_{1,2}$ = 1.8 Hz, 1H; H1), 5.14 (d, $^3J_{1,2}$ = 8.2 Hz, 1H; H1′), 4.68 (dd, $^3J_{4,5a}$ = 5.2 Hz, $^2J_{5a,5b}$ = 11.9 Hz, 1H; H5a′), 4.59 (dd, $^3J_{2,3}$ = 3.5 Hz, 1H; H2), 4.34 (dd, $^3J_{5,6a}$ = 2.6, $^2J_{6a,6b}$ = 12.5 Hz, 1H; H6a), 4.30 (dd, $^3J_{3,4}$ = 9.5 Hz, 1H; H3), 4.27 (dd, $^3J_{5,6b}$ = 4.8 Hz, 1H; H6b), 4.20 (dd, $^3J_{2,3}$ = 10.1, $^3J_{3,4}$ = 9.9 Hz, 1H; H3′), 4.15 (dd, $^3J_{4,5}$ = 9.9 Hz, 1H; H4), 4.08 (ddd, 1H; H5), 4.00 (dd, $^3J_{4,5b}$ = 10.7 Hz, 1H; H5b′), 3.89 (s, 3H; OCH_3), 3.77 (ddd, 1H; H4′), 3.54 (dd, 1H; H2′) ppm; ^{13}C NMR (67.8 MHz, D_2O, 25°C, acetone): δ = 100.2, 98.6 (C1, C1′), 76.5, 72.5, 71.6, 69.4, 66.8, 63.5, 60.4, 56.1, 54.9, 51.7 (C2, C3, C4, C5, C6, C2′, C3′, C4′, C5′, OCH_3) ppm; HRMS (ESI): calcd for $C_{12}H_{25}N_2O_8$ $[M+H]^+$: 325.1611; found 325.1607.

Compound **19** (29 mM) + 0.5 equiv $Hg(OAc)_2$: ^{1}H NMR (400 MHz, 50 mM [D_3]AcONa buffer, 70°C, DOH): δ = 5.16 (s, 1H; H1), 5.01 (d, $^3J_{1,2}$ = 7.8 Hz, 1H; H1′), 4.54 (dd, $^3J_{4,5a}$ = 5.0, $^2J_{5a,5b}$ = 11.9 Hz, 1H; H5a′), 4.40 (m, 1H; H2), 4.17–4.07 (3H; H3; H6a, H6b), 4.07 (t, ^3J = 9.4 Hz, 1H; H3′), 3.97 (t, ^3J = 9.6 Hz, 1H; H4), 3.90 (m, 1H; H5), 3.85 (dd, $^3J_{4,5b}$ = 10.4 Hz, 1H; H5b′), 3.70 (s, 3H; OCH_3), 3.64 (ddd, 1H; H4′), 3.44 (dd, 1H; H2′), 2.24 ppm (s, 3H; $HgOCOCH_3$).

Compound **19** (29 mM) + 2.0 equiv $Zn(OAc)_2$: ^{1}H NMR (400 MHz, 50 mM [D_3]AcONa buffer, 70°C, DOH): δ = 5.34 (brs, 1H; H1), 5.14 (d, $^3J_{1,2}$ = 7.8 Hz, 1H; H1′), 4.70 (dd, $^3J_{4,5a}$ = 5.0, $^2J_{5a,5b}$ = 11.9 Hz, 1H; H5a′), 4.58 (dd, $^3J_{1,2}$ = 1.8, $^3J_{2,3}$ = 3.5 Hz, 1H; H2), 4.37–4.25 (m, 3H; H3, H6a, H6b), 4.18 (t, ^3J = 9.6 Hz, 1H; H3′), 4.15 (t, ^3J = 9.9 Hz, 1H; H4), 4.08 (ddd, $^3J_{5,6a}$ = 2.4, $^3J_{5,6b}$ = 4.9 Hz, 1H; H5), 4.00 (t, $^3J_{5,6b}$ = 10.4 Hz, H5b′), 3.90 (s, 3H; OCH_3), 3.75 (dt, 1H; H4′), 3.54 (t, 1H; H2′), 2.42 ppm (s, 12H; $ZnOCOCH_3$).

Methyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2,4-diazido-2,4-dideoxy-β-D-xylopyranosyl)-(1→2)-2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (20): A mixture of **18** (79 mg, 122 μmol) and crushed MS (4 Å; 130 mg) in CH_2Cl_2 (4.5 mL) was stirred under Ar for 1 h and cooled at −40°C. TMSOTf (3.3 μL, 18.2 μmmol) in CH_2Cl_2 (33 μL), and then a solution of **11** (87 mg, 137 μmol) in CH_2Cl_2 (870 μL) were slowly added to the mixture. The temperature was allowed to increase slowly to room temperature over 2 h, and the mixture was stirred for a further 30 min at room temperature. The reaction was quenched by addition of triethylamine (5 μL, 36 μmol). The insoluble material was removed by celite filtration and the filtrate was evaporated and chromatographed on a column of silica gel (hexane/ethyl acetate 3:1 to 2:1) to give trisaccharide **20** (116 mg, 85%) as a syrup: $[\alpha]_D^{24}$ = +13.8 (c = 1.04 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.37–7.14 (m, 30H; Ph×6), 5.43 (t, $^3J_{2,3}$ = 2.3 Hz, 1H; H2″), 5.28 (d, $^3J_{1,2}$ = 1.7 Hz, 1H; H1″), 4.87–4.42 (m, 12H; CH_2Ph×6), 4.83 (d, $^3J_{1,2}$ = 1.7 Hz, 1H; H1), 4.27 (d, $^3J_{1,2}$ = 7.6 Hz, 1H; H1′), 4.13 (dd, $^3J_{2,3}$ = 3.4 Hz, 1H; H2), 4.07–3.99 (m, 4H; H4, H5′a, H3″, H4″), 3.93–3.65 (m, 7H; H3, H5, H6a, H6b, H5″, H6a″, H6b″), 3.56 (ddd, $^3J_{3,4}$ = 9.6, $^3J_{4,5a}$ = 5.5, $^3J_{4,5b}$ = 10.8 Hz, 1H; H4′), 3.42 (dd, $^3J_{2,3}$ = 9.6 Hz, 1H; H2′), 3.38 (s, 3H; OCH_3), 3.35 (t, 1H; H3′), 3.14 (t, $^2J_{5a,5b}$ = 11.6 Hz, 1H; H5b′), 2.16 (s, 3H; $COCH_3$) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 170.5 (C=O), 138.45, 138.4, 138.35, 138.3, 138.0, 137.9, 128.35, 128.3, 128.25, 128.2, 128.0, 127.9, 127.7, 127.65, 127.6, 127.55, 127.5, 127.4 (Ph×6), 101.8 (C1′), 98.9 (C1″), 98.0 (C1), 79.4 (C3′), 78.2 (C3), 77.9, 74.9, 74.0, 72.4, 71.7 (C4, C5, C3″, C4″, C5″), 75.1, 75.0, 73.5, 73.1, 71.9, 71.5 (CH_2Ph×6), 74.3 (C2), 69.6, 68.4 (C6, C6″), 69.0 (C2″), 64.9 (C2′), 63.8 (C5′), 61.2 (C4′), 54.8 (OCH_3), 21.1 (CH_3CO) ppm; HRMS (ESI): calcd for $C_{62}H_{68}N_6O_{14}Na$ $[M+Na]^+$: 1143.4691; found 1143.4690.

Methyl (3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2,4-diazido-2,4-dideoxy-β-D-xylopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (21): A solution of NaOMe in MeOH (50 mM, 2 mL) was added to a stirred solution of **20** (116 mg, 103 μmol) in CH_2Cl_2 (0.4 mL). After 15 h, the reaction mixture was evaporated and chromatographed on a column of silica gel (hexane/ethyl acetate 2:1) to give **21** (86 mg, 78%) as a syrup: R_f = 0.18 (hexane/ethyl acetate 2:1); $[\alpha]_D^{22}$ = +73.6 (c = 1.83 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.38–7.14 (m, 30H; Ph×6), 5.29 (d, $^3J_{1,2}$ = 1.4 Hz, 1H; H1″), 4.83 (d, $^3J_{1,2}$ = 1.8 Hz, 1H; H1), 4.87–4.42 (m, 12H; CH_2Ph×6), 4.27 (d, $^3J_{1,2}$ = 7.6 Hz, 1H; H1′), 4.13–4.12 (bm, 2H; H2, H2′), 4.06–4.01 (m, 2H; H5a′, H5″), 3.98 (t, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.6 Hz, 1H; H4″), 3.91 (m, 2H; H3, H3″), 3.84 (dd, $^3J_{5,6a}$ = 3.5, $^2J_{6a,6b}$ 10.8 Hz, 1H; H6a″), 3.78 (dt, 1H; H5), 3.73–3.65 (m, 4H; H4, H6a, H6b, H6b″), 3.54 (ddd, $^3J_{4,5a}$ = 5.5, $^3J_{4,5b}$ = 10.7 Hz, 1H; H4′), 3.44–3.35 (m, 5H; H2′, H3′, OCH_3), 3.13 (t, $^2J_{5a,5b}$ = 11.6 Hz, 1H; H5b′), 2.53 (brs, 1H; OH) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 138.4, 138.3, 138.0, 137.9, 128.5, 128.3, 128.25, 128.2, 127.9, 127.85, 127.7, 127.6, 127.55, 127.45, 127.4 (Ph×6), 101.9 (C1′), 100.6 (C1″), 98.0 (C1), 79.9 (C3″), 79.1 (C3′), 78.3 (C3), 75.1, 75.0, 73.5, 73.1, 72.1, 71.5 (CH_2Ph×6), 74.9 (C4), 74.3 (C2), 73.9 (C4″), 72.0 (C5″), 71.7 (C5), 69.6 (C6), 68.7

(C2″), 68.5 (C6″), 64.9 (C2′), 63.8 (C5′), 61.4 (C4′), 54.8 (OCH_3) ppm; HRMS (ESI): calcd for $C_{60}H_{66}N_6O_{13}Na$ $[M+Na]^+$: 1101.4586; found 1101.4587; elemental analysis calcd (%) for $C_{60}H_{66}N_6O_{13}$ (1079.2): C 66.78, H 6.16, N 7.79; found: C 66.60, H 6.15, N 7.58.

Methyl (3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl)-(1→2)-2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (22): Ar gas was bubbled at 0°C for 20 min into a solution of **21** (629 mg, 583 μmol) in pyridine/H_2O (10:1, 28 mL), followed by H_2S gas for 10 min. The mixture was kept at room temperature for 15 h. After the mixture had been evaporated, the residue was taken up with methanol, and the insoluble material was removed by celite filtration. The filtrate was evaporated and chromatographed on spherical silica gel ($CHCl_3$/MeOH 15:1) to give **22** (485 mg, 81%) as an amorphous solid: R_f = 0.20 ($CHCl_3$/MeOH 15:1); $[\alpha]_D^{24}$ = +23.5 (c = 1.14 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.39–7.17 (m, 30H; Ph×6), 5.11 (d, $^3J_{1,2}$ = 2.7 Hz, 1H; H1″), 4.91–4.42 (m, 12H; CH_2Ph×6), 4.84 (d, $^3J_{1,2}$ = 1.5 Hz, 1H; H1), 4.20 (d, $^3J_{1,2}$ = 7.8 Hz, 1H; H1′), 4.07 (br s, 1H; H2), 3.99–3.96 (m, 2H; H2″, H5″), 3.78 (t, $^3J_{3,4}$ = $^3J_{4,5}$ = 8.7 Hz, 1H; H4″), 3.74–3.66 (m, 3H; H4, H6a, H6b), 3.64 (dd, $^3J_{5,6a}$ = 5.3, $^2J_{6a,6b}$ = 10.4 Hz, 1H; H6a″), 3.58 (dd, $^3J_{5,6b}$ = 2.3 Hz, 1H; 6b″), 3.34 (s, 3H; OCH_3), 3.18 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.3 Hz, 1H; H3′), 3.08 (dd, $^3J_{4,5b}$ = 10.0, $^2J_{5a,5b}$ = 11.1 Hz, 1H; H5b′), 2.93 (dt, $^3J_{4,5a}$ = 5.0 Hz, 1H; H4′), 2.85 (dd, 1H; H2′), 2.08 (br s, 5H; NH_2, OH) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 138.6, 138.3, 138.17, 138.1, 138.0, 137.95, 128.4, 128.3, 128.25, 128.2, 127.9, 127.85, 127.8, 127.75, 127.6, 127.5, 127.45, 127.4, 127.35 (Ph×6), 104.1 (C1′), 101.1 (C1″), 98.7 (C1), 87.8 (C3′), 79.0 (C3″), 78.2 (C3), 75.0, 74.3, 73.3, 73.1, 72.3, 71.3 (CH_2Ph×6), 74.4, 72.2, 71.4, 69.3 (C4, C5, C4′, C2″, C5″), 74.0 (C2), 69.1 (C6), 69.1 (C6″), 67.6 (C5′), 55.3 (C2′), 54.8 (OCH_3), 51.9 (C4′) ppm; HRMS (ESI): calcd for $C_{60}H_{71}N_2O_{13}$ $[M+H]^+$: 1027.4956; found 1027.4955; elemental analysis calcd (%) for $C_{60}H_{70}N_2O_{13}\cdot{}^1/_2H_2O$ (1036.2): C 69.55, H 6.91, N 2.70; found: C 69.61, H 6.95, N 2.81.

Methyl (α-D-mannopyranosyl)-(1→3)-(2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl)-(1→2)-α-D-mannopyranoside (23): Sodium metal (68 mg) was added in small portions at −78°C under Ar to a solution of **22** (92 mg, 90 μmol) in THF (0.5 mL) and liquid ammonia (4 mL). The mixture was heated at reflux at room temperature for 40 min, while the blue color of the solution persisted. The reaction was quenched by careful addition of ethanol. The mixture was carefully evaporated and chromatographed on spherical silica gel (*i*PrOH/H_2O/28% NH_3 7:3:1) to give **23** (34 mg, 77%) as an amorphous solid: R_f = 0.30 (*i*PrOH/H_2O/28% NH_3 7:3:1); m.p. 165–167°C; $[\alpha]_D^{23}$ = +10.9 (c = 1.16 in H_2O); ^{1}H NMR (400 MHz, D_2O, 25°C, DOH): δ = 5.10 (d, $^3J_{1,2}$ = 2.1 Hz, 1H; H1″), 4.93 (d, $^3J_{1,2}$ = 1.7 Hz, 1H; H1), 4.44 (d, $^3J_{1,2}$ = 7.9 Hz, 1H; H1′), 4.15 (dd, $^3J_{2,3}$ = 3.4 Hz, 1H; H2″), 4.12 (dd, $^3J_{2,3}$ = 3.5 Hz, 1H; H2), 4.05 (dd, $^3J_{4,5a}$ = 5.3, $^2J_{5a,5b}$ = 11.9 Hz, 1H; H5a′), 3.97–3.66 (m, 10H; H3, H4, H5, H6a, H6b, H3″, H4″, H5″, H6a″, H6b″), 3.48 (s, 3H; OCH_3), 3.44 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.3 Hz, 1H; H3′), 3.34 (t, $^3J_{4,5}$ = 11.1 Hz, 1H; H5b′), 3.08 (ddd, 1H; H4′), 2.90 (dd, 1H; H2′) ppm; ^{13}C NMR (100.6 MHz, D_2O, 25°C, acetone): δ = 102.4 (C1′), 102.0 (C1″), 98.7 (C1), 87.1 (C3′), 76.7 (C2), 74.0, 72.7, 70.4, 69.6, 67.2, 67.0 (C3, C4, C5, C3″, C4″, C5″), 70.6 (C2″), 65.7 (C5′), 61.1, 60.9 (C6, C6″), 55.2 (C2′), 55.0 (OCH_3), 50.9 (C4′) ppm; HRMS (ESI): calcd for $C_{18}H_{35}N_2O_{13}$ $[M+H]^+$: 487.2139; found 487.2137; elemental analysis calcd (%) for $C_{18}H_{34}N_2O_{13}\cdot{}^3/_2H_2O$ (513.5): C 42.10, H 7.26, N 5.46; found: C 42.00, H 6.94, N 5.58.

Compound **23** (16 mM) + 0.5 equiv $Hg(OAc)_2$: ^{1}H NMR (400 MHz, 50 mM [D$_3$]AcONa buffer, 70°C, DOH): δ = 5.53 (d, $^3J_{1,2}$ = 1.8 Hz, 1H; H1″), 5.38 (d, $^3J_{1,2}$ = 1.7 Hz, 1H; H1), 5.23 (d, $^3J_{1,2}$ = 3.4 Hz, 1H; H-1′), 4.92 (br d, $^2J_{5a,5b}$ = 12.7 Hz, 1H; H-5a′), 4.54 (dd, $^3J_{2,3}$ = 3.4 Hz, 1H; H2), 4.51 (dd, $^3J_{2,3}$ = 3.1 Hz, 1H; H2″), 4.45–4.35 (m, 4H; H3, H6a, H3″, H6a″), 4.32–4.24 (m, 3H; H6b, H5″, H6b″), 4.22–4.10 (m, 3H; H4, H3′, H4″), 4.15–4.10 (m, 1H; H5), 4.02 (dd, $^3J_{4,5b}$ = 5.3 Hz, 1H; H5b′), 3.95 (s, 3H; OCH_3), 3.89 (br dt, 1H; H4′), 3.82 (br t, 1H; H2′), 2.42 ppm (s, 3H; $HgOCOCH_3$).

Compound **23** (16 mM) + 1.5 equiv $Zn(OAc)_2$: ^{1}H NMR (400 MHz, 50 mM [D$_3$]AcONa buffer, 80°C, DOH): δ = 5.62 (s, $^3J_{1,2}$ = 2.3 Hz, 1H; H1″), 5.46 (s, 1H; H1), 5.37 (d, $^3J_{1,2}$ = 2.8 Hz, 1H; H1′), 5.04 (d, $^3J_{4,5a}$ = 2.8, $^2J_{5a,5b}$ = 12.1 Hz, 1H; H5a′), 4.63 (d, $^3J_{2,3}$ = 3.8 Hz, 1H; H2), 4.60 (dd, $^3J_{2,3}$ = 3.2 Hz, 1H; H2″), 4.52–4.44 (m, 5H; H3, H6a, H3′, H3″, H6b″), 4.41–4.35 (m, 3H; H6b, H5″, H6b″), 4.30, 4.27 (t×2, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.5, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.9 Hz, 2H; H4, H4″), 4.24–4.20 (m, 1H; H5), 4.13 (dd, $^3J_{4,5b}$ = 4.8 Hz, 1H; H5b′), 3.90 (dt, $^3J_{3,4}$ = 4.8 Hz, 1H; H4′), 3.86 (dd, $^3J_{2,3}$ = 3.8 Hz, 1H; H2′), 2.53 ppm (s, 9H; $ZnOCOCH_3$).

Methyl (2,4-diazido-2,4-dideoxy-α,β-D-xylopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (27): A mixture of methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (**25**; 1.621 g, 3.49 mmol) and crushed MS (4 Å; 3 g) in CH_3CN (20 mL) was stirred under Ar for 1 h and cooled at −40°C. TMSOTf (85 μL, 470 μmol), and then a solution of 2,4-diazido-2,4-dideoxy-α,β-D-xylopyranosyl trichloroacetimidate (**24**;[7] 900 mg, 2.33 mmol, α:β 1:1) in CH_3CN (10 mL), were slowly added to the mixture. The temperature was allowed to increase slowly to room temperature over 3 h. The reaction was quenched by addition of triethylamine (130 μL, 930 μmol). The insoluble material was removed by celite filtration, and the filtrate was evaporated and chromatographed on a column of silica gel (hexane/ethyl acetate 10:1 to 1:1) to give disaccharide **26** (1.380 g) as a syrup; R_f = 0.27 (hexane/EtOAc 9:2). A solution of NaOMe in MeOH (1M, 0.4 mL) was added to a stirred solution of **26** (1.380 g) in methanol (20 mL). After 18 h, the reaction mixture was evaporated and chromatographed on a column of silica gel (hexane/ethyl acetate 4:1 to 3:1) to give **27** (834 mg, 55%, α/β 1:2) as a syrup: R_f = 0.20 (hexane/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.41–7.25 (m, 15H; Ph-αβ×3), 5.00–4.58 (m, 15H; *H*-1αβ, CH_2Ph-αβ×3), 4.64 (d, $^3J_{1,2}$ = 3.5 Hz, 0.33H; H1′α), 4.22 (d, $^3J_{1,2}$ = 7.8 Hz, 0.67H; H1′β), 4.06–4.01 (m, 1H; H2αβ), 3.96–3.85, 3.78–3.63, 3.59–3.42, 3.36–3.28 (each m, 8.33H; H3α, H4α, H5α, H6aα, H6bα, H3′α, H4′α, H5a′α, H5b′α, H3β, H4β, H5β, H6aβ, H6bβ, H3′β, H4′β, H5a′β), 3.39 (s, 2.01H; OCH_3β), 3.37 (s, 0.99H; OCH_3α), 3.21 (dd, $^3J_{2,3}$ = 9.6 Hz, 0.67H; H2′β), 3.13 (dd, $^3J_{2,3}$ = 10.1 Hz, 0.33H; H2′α), 3.06 (dd, $^3J_{4,5b}$ = 10.8, $^2J_{5a,5b}$ = 11.1 Hz, 0.67H; H5b′β), 2.74 (d, $^3J_{3,OH}$ = 3.2 Hz, 0.67H; OHβ), 2.65 (d, $^3J_{3,OH}$ = 3.7 Hz, 0.33H; OHα) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 138.75, 138.7, 138.5, 138.4, 138.35, 128.4, 128.35, 128.32, 128.30, 128.2, 128.1, 127.7, 127.65, 127.6, 127.55, 127.5, 127.45 (Phαβ×3), 102.6 (C1′β), 98.8 (C1β), 98.7 (C1α), 97.4 (C1′α), 79.0, 78.9, 76.3, 75.4, 75.1, 70.8, 69.7, 62.0, 60.8 (C2α, C3α, C4α, C5α, C3′α, C4′α, C2β, C3β, C4β, C5β, C4′β), 74.6, 74.5, 73.55, 73.5, 73.5, 73.4 (CH_2Phαβ×3), 74.0 (C3′β), 69.0 (C6β), 67.4, 59.6 (C6α, 5′α), 66.4 (C2′β), 63.8 (C5′β), 63.2 (C2′α), 55.4 (OCH_3β), 55.3 (OCH_3α) ppm; HRMS (ESI): calcd for $C_{33}H_{38}N_6O_8Na$ $[M+Na]^+$: 669.2649; found 669.2679; elemental analysis calcd (%) for $C_{33}H_{38}N_6O_8\cdot{}^1/_5H_2O$ (650.3): C 60.95, H 5.95, N 12.92; found: C 60.93, H 5.89, N 12.74.

Methyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2,4-diazido-2,4-dideoxy-α,β-D-xylopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (28): A mixture of **27** (396 mg, 612 μmol) and crushed MS (4 Å, ca. 1 g) in CH_2Cl_2 (8 mL) was stirred under Ar for 1 h and cooled at −40°C. TMSOTf (22 μL, 122 μmol) in CH_2Cl_2 (220 μL), and then a solution of **11** (586 mg, 921 μmol) in CH_2Cl_2 (8 mL), were slowly added to the mixture. The temperature was allowed to increase slowly to room temperature over 3 h. The reaction was quenched by addition of triethylamine (34 μL, 244 μmol). The insoluble material was removed by celite filtration, and the filtrate was evaporated and chromatographed on a column of silica gel (toluene/ethyl acetate 15:1 to 8:1) to give trisaccharide **28** (402 mg, 59%) as a foam (the corresponding α isomer was obtained as a mixture with trichloroacetamide and was not isolable): R_f = 0.20 (toluene/ethyl acetate 10:1); $[\alpha]_D^{23}$ = +26.1 (*c* = 0.99 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.40–7.14 (m, 30H; Ph×6), 5.42 (t, $^3J_{2,3}$ = 2.7 Hz, 1H; H2″), 5.25 (d, $^3J_{1,2}$ = 1.7 Hz, 1H; H1″), 4.97–4.48 (m, 13H; H1′, CH_2Ph×6), 4.21 (d, $^3J_{1,2}$ = 7.9 Hz, 1H; H1), 4.04–3.83 (m, 9H; H2, H3, H4, H5, H5a′, H3″, H4″, H5″, H6a″), 3.77–3.67 (m, 3H; H6a, H6b, H6b″), 3.48 (ddd, $^3J_{4,5a}$ = 5.0, $^3J_{4,5b}$ = 11.0 Hz, 1H; H4′), 3.37 (s, 3H; OCH_3), 3.31 (t, $^3J_{2,3}$ = 9.6 Hz, 1H; H3′), 3.16 (dd, 1H; H2′), 3.08 (t, $^2J_{5a,5b}$ = 11.8 Hz, 1H; H5b′), 2.15 (s, 3H; $COCH_3$) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 170.4 (C=O), 138.7, 138.4, 138.3, 138.2, 137.9, 128.35, 128.33, 128.3, 128.25, 128.2, 128.0, 127.95, 127.9, 127.7, 127.65, 127.6, 127.55, 127.5, 127.45 (Ph×6), 102.9 (C1′), 98.85, 98.8 (C1, C1″), 79.3 (C3′), 78.9, 77.8, 76.2, 75.3, 74.0, 72.4, 69.6 (C2, C3, C4, C5, C3″, C4″, C5″), 75.1, 74.6, 73.5, 73.4, 73.3, 71.8 (CH_2Ph×6), 69.1 (C6), 68.9 (C2″), 68.5 (C6″), 65.2 (C2′), 63.5 (C5′), 61.4 (C4′), 55.4

(OCH_3), 21.1 (CH_3CO) ppm; HRMS (ESI): calcd for $C_{62}H_{68}N_6O_{14}Na$ $[M+Na]^+$: 1143.4691; found 1143.4701; elemental analysis calcd (%) for $C_{62}H_{68}N_6O_{14}\cdot{}^1/_2\,H_2O$ (1130.3): C 65.89, H 6.15, N 7.44; found: C 65.83, H 6.04, N 7.39.

Methyl (3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2,4-diazido-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (29): A solution of NaOMe in MeOH (0.1 M, 0.1 mL) was added to a stirred solution of **28** (77 mg, 69 μmol) in CH_2Cl_2 (1 mL) and methanol (1 mL). After 18 h, the reaction mixture was evaporated and chromatographed on a column of silica gel (toluene/ethyl acetate 8:1 to 4:1) to give **29** (64 mg, 87%) as a foam: R_f = 0.20 (toluene/ethyl acetate 4:1); $[\alpha]_D^{23}$ = +30.7 (c = 0.94 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.40–7.16 (m, 30H; Ph×6), 5.27 (d, $^3J_{1,2}$ = 1.5 Hz, 1H; H1″), 4.97–4.49 (m, 13H; H1′, CH_2Ph×6), 4.22 (d, $^3J_{1,2}$ = 7.9 Hz, 1H; H1′), 4.12 (dd, $^3J_{2,3}$ = 3.1 Hz, 1H; H2″), 4.04–4.01 (m, 2H; H2, H5″), 3.97–3.86 (m, 6H; H3, H4, H5, H5a′, H3″, H4″), 3.81 (dd, $^3J_{5,6a}$ = 3.7, $^2J_{6a,6b}$ = 10.8 Hz, 1H; H6a″), 3.77–3.68 (m, 3H; H6a, H6b, H6b″), 3.47 (ddd, $^3J_{3,4}$ = 9.5, $^3J_{4,5a}$ = 5.3, $^3J_{4,5b}$ = 10.8 Hz, 1H; H4′), 3.37 (s, 3H; OCH_3), 3.34 (t, $^3J_{2,3}$ = 9.8 Hz, 1H; H3′), 3.16 (dd, 1H; H2′), 3.08 (t, $^2J_{5a,5b}$ = 11.6 Hz, 1H; H5b′) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 138.7, 138.4, 138.3, 138.2, 137.9, 128.5, 128.4, 128.35, 128.3, 128.25, 128.2, 128.0, 127.9, 127.85, 127.8, 127.75, 127.7, 127.6, 127.55, 127.5, 127.45 (Ph×6), 103.0 (C1′), 100.6 (C1″), 98.8 (C1), 79.8, 78.9, 75.3, 73.9, 69.6 (C3, C4, C5, C3″, C4″), 79.0 (C3′), 76.2 (C2), 75.1, 74.6, 73.5, 73.4, 73.3, 72.0 (CH_2Ph×6), 72.0 (C5″), 69.1 (C6), 68.6 (C2″, C6″), 65.1 (C2′), 63.5 (C5′), 61.6 (C4′), 55.4 (OCH_3) ppm; HRMS (ESI): calcd for $C_{60}H_{66}N_6O_{13}Na$ $[M+Na]^+$: 1101.4586; found 1101.4583; elemental analysis calcd (%) for $C_{60}H_{66}N_6O_{13}$ (1079.2): C 66.78, H 6.16, N 7.79; found: C 66.81, H 6.29, N 7.73.

Methyl (3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (30): Ar gas was bubbled at 0°C for 20 min into a solution of **29** (364 mg, 338 μmol) in pyridine/H_2O (10:1, 14 mL), followed by H_2S gas for 20 min. The mixture was kept at room temperature for 12 h. After the mixture had been evaporated, the residue was taken up with methanol, and the insoluble material was removed by celite filtration. The filtrate was evaporated and chromatographed on silica gel ($CHCl_3$/MeOH 15:1) to give **30** (298 mg, 86%) as a foam: R_f = 0.20 ($CHCl_3$/MeOH 15:1); $[\alpha]_D^{25}$ = +46.5 (c = 1.03 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.39–7.17 (m, 30H; Ph×6), 5.08 (d, $^3J_{1,2}$ = 2.9 Hz, 1H; H1″), 4.95–4.45 (m, 12H; CH_2Ph×6), 4.66 (d, $^3J_{1,2}$ = 3.5 Hz, 1H; H1), 4.07 (d, $^3J_{1,2}$ = 7.5 Hz, 1H; H1′), 4.02 (dd, $^3J_{2,3}$ = 10.1 Hz, 1H; H2), 4.06–4.00 (m, 1H; H5″), 3.97 (dd, $^3J_{2,3}$ = 3.2 Hz, 1H; H2″), 3.92 (dd, $^3J_{3,4}$ = 2.7 Hz, 1H; H3), 3.89–3.85 (m, 3H; H4, H5, H3″), 3.83–3.78 (m, 2H; H6a, H5a′), 3.82 (dd, $^3J_{3,4}$ = 9.1, $^3J_{4,5}$ = 7.5 Hz, 1H; H4″), 3.69–3.51 (m, 3H; H6b, H6a″, H6b″), 3.34 (s, 3H; OCH_3), 3.11 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.3 Hz, 1H; H3′), 3.02 (dd, $^3J_{4,5b}$ = 11.1, $^2J_{5a,5b}$ = 11.3 Hz, 1H; H5b′), 2.85 (ddd, $^3J_{4,5a}$ = 5.0 Hz, 1H; H4′), 2.64 (dd, $^3J_{1,2}$ = 7.7 Hz, 1H; H2′) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$, 25°C): δ = 138.8, 138.6, 138.5, 138.0, 137.95, 137.9, 128.5, 128.4, 128.3, 128.25, 128.2, 128.15, 128.0, 127.95, 127.9, 127.85, 127.75, 127.7, 127.6, 127.55, 127.5, 127.4 (Ph×6), 105.3 (C1′), 101.1 (C1″), 98.7 (C1), 88.2 (C3′), 79.0 (C3, C3″), 76.4 (C2), 75.3 (C4), 74.6 (CH_2Ph), 74.6 (C4″), 74.3, 73.5, 73.3, 73.3, 72.4 (CH_2Ph×5), 72.2 (C5″), 69.5 (C5), 69.5 (C2″), 69.3 (C6″), 68.9 (C6), 67.5 (C5′), 56.4 (C2′), 55.3 (OCH_3), 52.2 (C4′) ppm; HRMS (ESI): calcd for $C_{60}H_{71}N_2O_{13}$ $[M+H]^+$: 1027.4956; found 1027.4958; elemental analysis calcd (%) for $C_{60}H_{70}N_2O_{13}\cdot H_2O$ (1045.2): C 68.95, H 6.94, N 2.68; found: C 69.21, H 6.93, N 2.72.

Methyl (α-D-mannopyranosyl)-(1→3)-(2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-α-D-galactopyranoside (31): Sodium metal (95.8 mg) was added in small portions at −78°C under Ar to a solution of **30** (436 mg, 425 μmol) in THF (1 mL) and liquid ammonia (4 mL). The mixture was heated at reflux at room temperature for 1 h, while the blue color of the solution persisted. The reaction was quenched by careful addition of ethanol. The mixture was carefully evaporated and chromatographed on spherical silica gel (iPrOH/H_2O/28% NH_3 7:3:1) to give **31** (101 mg, 49%) as an amorphous solid: R_f = 0.22 (iPrOH/H_2O/28% NH_3 7:3:1); m.p. 158–159°C; $[\alpha]_D^{23}$ = +72.3 (c = 0.22 in H_2O); ^{1}H NMR (400 MHz, D_2O, 40°C, DHO): δ = 5.15 (d, $^3J_{1,2}$ = 2.0 Hz, 1H; H1″), 4.95 (d, $^3J_{1,2}$ = 2.9 Hz, 1H; H1), 4.45 (d, $^3J_{1,2}$ = 8.0 Hz, 1H; H1′), 4.20 (dd, $^3J_{2,3}$ = 3.3 Hz, 1H; H2″), 4.17 (m, 1H; H5), 4.12 (dd, $^3J_{5,6a}$ = 3.8, $^2J_{6a,6b}$ = 11.0 Hz, 1H; H6a), 4.08 (m, 1H; H4), 4.07 (dd, $^3J_{4,5a}$ = 5.2, $^2J_{5a,5b}$ = 11.6 Hz, 1H; H5a″), 4.00 (dd, $^3J_{5,6a}$ = 2.1, $^2J_{6a,6b}$ = 12.1 Hz, 1H; H6a″), 3.96 (dd, $^3J_{3,4}$ = 9.5 Hz, 1H; H3″), 3.94 (dd, $^3J_{5,6b}$ = 8.2 Hz, 1H; H6b), 3.93–3.89 (m, 3H; H2, H3, H5″), 3.84 (dd, $^3J_{5,6b}$ = 6.5 Hz, 1H; H6b″), 3.77 (dd, $^3J_{4,5}$ = 9.5 Hz, 1H; H4″), 3.53 (s, 3H; OCH_3), 3.46 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 9.3 Hz, 1H; H3′), 3.40 (dd, $^3J_{4,5b}$ = 10.8 Hz, 1H; H5b′), 3.06 (ddd, 1H; H4′), 2.85 (dd, 1H; H2′) ppm; ^{13}C NMR (67.8 MHz, D_2O, 40°C, acetone): δ = 107.2 (C1′), 104.4 (C1″), 102.1 (C1), 90.1 (C3′), 76.40 (C5″), 73.1 (C2″), 72.9 (C3″), 72.4 (C6), 72.1 (C5), 71.9 (C4), 71.85, 70.7 (C2, C3), 69.5 (C4″), 68.4 (C5′), 63.6 (C6″), 58.2 (C2′), 57.9 (OCH_3), 53.6 (C4′) ppm; HRMS (ESI): calcd for $C_{18}H_{35}N_2O_{13}$ $[M+H]^+$: 487.2139; found 487.2138.

Methyl (2,4-diamino-2,4-*N*-carbonyl-2,4-dideoxy-β-D-xylopyranosyl)-(1→2)-α-D-mannopyranoside (34): A solution of 1,1′-carbonylbis-1*H*-imidazole (12 mg, 86 μmol) in DMF (1.5 mL) was added at room temperature to a stirred solution of **19** (23 mg, 71 μmol) in DMF (3 mL). After 14 h at room temperature the reaction was incomplete, so the bath temperature was raised to 120°C and the reaction was continued for further 24 h. The mixture was evaporated and the residue was taken up with H_2O and passed through a column of Dowex 50W X-8 (H^+ form). The effluents were chromatographed on a column of spherical silica gel ($CHCl_3$/MeOH 5:1 to $CHCl_3$/MeOH/H_2O 65:35:6) to give **34** (12 mg, 48%) as an amorphous solid: R_f = 0.20 ($CHCl_3$/MeOH/H_2O 65:35:6); $[\alpha]_D^{26}$ = −67.3 (c = 0.43 in H_2O); ^{1}H NMR (400 MHz, D_2O, 25°C, DHO): δ = 4.98 (s, 1H; H1), 4.88 (d, $^3J_{1,2}$ = 1.5 Hz, 1H; H1′), 4.36 (d, $^2J_{5a,5b}$ = 11.9 Hz, 1H; H5′), 4.23 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 3.8 Hz, 1H; H3′), 4.05 (dd, $^3J_{2,3}$ = 3.8 Hz, 1H; H2), 3.91–3.85 (m, $^3J_{3,4}$ = 6.1, $^2J_{6a,6b}$ = 12.2 Hz, 2H; H3, H6a), 3.76 (ddd, $^3J_{5,6b}$ = 4.3 Hz, 1H; H6b), 3.64–3.62 (m, $^3J_{5,6a}$ = 1.7 Hz, 2H; H4, H5), 3.57–3.52 (m, $^3J_{3,4}$ = 1.7 Hz, 2H; H2′, H5b′), 3.43 (m, 1H; H4′), 3.40 (s, 3H; OCH_3) ppm; ^{13}C NMR (100.6 MHz, D_2O, 30°C, acetone): δ = 159.6 (C=O), 98.6 (C1′), 97.9 (C1), 74.4 (C2), 73.1 (C5), 70.1 (C3), 67.6 (C4), 63.4 (C3′), 61.3 (C6), 60.8 (C5′), 55.5 (OCH_3), 49.1 (C2′), 48.8 (C4′) ppm; HRMS (ESI): calcd for $C_{13}H_{23}N_2O_9$ $[M+H]^+$: 351.1404; found 351.1408.

Methyl (β-D-galactopyranosyl)-(1→3)-(2,4-diamino-2,4-*N*-carbonyl-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-α-D-mannopyranoside (35): 1,1′-Carbonylbis-1*H*-imidazole (6 mg, 38 μmol) was added at room temperature to a stirred solution of **6** (15 mg, 30.4 μmol) in DMF (2 mL). After 5 h, the reaction mixture was evaporated and the residue was taken up with H_2O and passed through a column of Dowex 50W X-8 (H^+ form). The effluents were chromatographed on a column of spherical silica gel (ethyl acetate/MeOH/H_2O 5:3:1) to give **35** (14 mg, 87%) as an amorphous solid: R_f = 0.27 (ethyl acetate/MeOH/H_2O 5:3:1); m.p. 196–198°C; $[\alpha]_D^{26}$ = −38.7 (c = 0.87 in H_2O); ^{1}H NMR (400 MHz, D_2O, 30°C, DHO): δ = 4.99 (br s, 1H; H1′), 4.90 (d, $^3J_{1,2}$ = 1.7 Hz, 1H; H1), 4.70 (d, $^3J_{1,2}$ = 7.6 Hz, 1H; H1″), 4.50 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 3.7 Hz, 1H; H3′), 4.42 (d, $^2J_{5a,5b}$ = 11.8 Hz, 1H; H5a′), 4.18 (d, $^2J_{6a,6b}$ = 9.6 Hz, 1H; H6a), 4.05–4.03 (m, 2H; H2, H4″), 3.95–3.86 (m, 5H; H3, H4, H6b, H6a″, H6b″), 3.82–3.78 (m, 3H; H2′, H4′, H3″), 3.75–3.70 (m, 3H; H5, H2″, H5″), 3.66 (br d, 1H; H5b′), 3.57 (s, 3H; OCH_3) ppm; ^{13}C NMR (100.6 MHz, D_2O, 30°C, acetone): δ = 159.6 (C=O), 102.9 (C1″), 102.1 (C1′), 101.5 (C1), 75.9, 72.8, 72.3, 71.4, 70.9, 70.4, 69.0, 67.6 (C2, C3, C4, C5, C2″, C3″, C4″, C5″), 70.2 (C3′), 69.3 (C6), 61.4 (C6″), 60.5 (C5′), 55.8 (OCH_3), 47.9 (C4′), 47.5 (C2′) ppm; HRMS (ESI): calcd for $C_{19}H_{33}N_2O_{14}$ $[M+H]^+$: 513.1932; found 513.1932; elemental analysis calcd (%) for $C_{19}H_{32}N_2O_{14}\cdot 2H_2O$ (548.5): C 41.61, H 6.62, N 5.11; found: C 41.87, H 6.36, N 5.11.

Methyl (α-D-mannopyranosyl)-(1→3)-(2,4-diamino-2,4-*N*-carbonyl-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-α-D-mannopyranoside (36): A solution of 1,1′-carbonylbis-1*H*-imidazole (6 mg, 36 μmol) in DMF (1 mL) was added at room temperature to a stirred solution of **17** (17 mg, 35 μmol) in DMF (2 mL). After 5 h, the reaction mixture was evaporated and the residue was taken up with H_2O and passed through a column of Dowex 50W X-8 (H^+ form). The effluents were chromatographed on a column of spherical silica gel (EtOAc/MeOH/H_2O 5:3:1) to give **36** (15 mg,

86%) as an amorphous solid: R_f = 0.25 (ethyl acetate/MeOH/H_2O 5:3:1); m.p. 178–180°C; $[\alpha]_D^{25}$ = −1.5 (*c* = 0.66 in H_2O); ^{1}H NMR (400 MHz, D_2O, 30°C, DOH): δ = 5.09 (d, $^3J_{1,2}$ = 1.5 Hz, 1H; H1″), 4.93 (brs, 1H; H1′), 4.88 (d, $^3J_{1,2}$ = 1.7 Hz, 1H; H1), 4.39 (d, $^2J_{5a,5b}$ = 11.9 Hz, 1H; H5a′), 4.36 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 3.5 Hz, 1H; H3′), 4.13 (dd, $^3J_{2,3}$ = 3.2 Hz, 1H; H2″), 4.12 (d, $^2J_{6a,6b}$ = 10.1 Hz, 1H; H6a), 4.07–4.04 (m, 2H; H2, H3″), 4.01–3.76 (m, 8H; H3, H4, H5, H6b, H4″, H5″, H6a″, H6b″), 3.70 (brs, 2H; H2′, H4′), 3.62 (brd, 1H; H5b′), 3.55 (s, 3H; OCH_3) ppm; ^{13}C NMR (100.6 MHz, D_2O, 30°C, acetone): δ = 159.4 (C=O), 101.5 (C1′), 101.2 (C1), 99.3 (C1″), 73.6, 72.1, 70.8, 70.6, 70.0, 67.3, 67.2, 67.0 (C2, C3, C4, C5, C3′, C3″, C4″, C5″), 70.4 (C2″), 68.7 (C6), 61.2 (C6″), 60.0 (C5′), 55.2 (OCH_3), 48.8 (C2′), 45.8 (C4′) ppm; HRMS (ESI): calcd for $C_{19}H_{33}N_2O_{14}$ $[M+H]^+$: 513.1932; found 513.1931.

Methyl (α-D-mannopyranosyl)-(1→3)-(2,4-diamino-2,4-*N*-carbonyl-2,4-dideoxy-β-D-xylopyranosyl)-(1→2)-α-D-mannopyranoside (37): A solution of 1,1′-carbonylbis-1*H*-imidazole (9 mg, 57 μmol) in DMF(1.5 mL) was added at room temperature to a stirred solution of **23** (23 mg, 47 μmol) in DMF (3 mL). After 5 h, the reaction mixture was evaporated and the residue was taken up with H_2O and passed through a column of Dowex 50W X-8 (H^+ form). The effluents were chromatographed on a column of spherical silica gel (ethyl acetate/MeOH/H_2O 5:3:1) to give **37** (18 mg, 75%) as an amorphous solid: R_f = 0.20 (EtOAc/MeOH/H_2O 5:3:1); $[\alpha]_D^{26}$ = −20.3 (*c* = 0.875 in H_2O); ^{1}H NMR (400 MHz, D_2O, 25°C, DHO): δ = 5.05 (d, $^3J_{1,2}$ = 1.7 Hz, 1H; H1″), 4.94 (brs, 1H; H1′), 4.93 (d, $^3J_{1,2}$ = 1.5 Hz, 1H; H1), 4.43 (d, $^2J_{5a,5b}$ = 11.8 Hz, 1H; H5a′), 4.33 (t, $^3J_{2,3}$ = $^3J_{3,4}$ = 3.7 Hz, 1H; H3′), 4.08–4.06 (m, 2H; H2, H2″), 4.01–3.66 (m, 9H; H3, H5, H6a, H6b, H4′, H3″, H5″, H6a″, H6b″), 3.74 (t, 2H; H4, H4″), 3.64–3.63 (m, 1H; H2′), 3.56 (brd, 1H; H5b′), 3.47 (s, 3H; OCH_3) ppm; ^{13}C NMR (67.8 MHz, D_2O, 30°C, acetone): δ = 159.7 (C=O), 99.6 (C1″), 99.2 (C1′), 98.6 (C1), 75.7 (C2), 73.9, 73.4 (C5, C5″), 71.1 (C3″), 70.6 (C2″), 70.3 (C3′), 68.0, 67.4 (C4, C4″), 67.4 (C3′), 61.6, 61.5 (C6, C6″), 60.6 (C5′), 55.4 (OCH_3), 49.2 (C2′), 45.9 (C4′) ppm; HRMS (ESI): calcd for $C_{19}H_{33}N_2O_{14}$ $[M+H]^+$: 513.1932; found 513.1928.

Methyl (α-D-mannopyranosyl)-(1→3)-(2,4-diamino-2,4-*N*-carbonyl-2,4-dideoxy-β-D-xylopyranosyl)-(1→6)-α-D-galactopyranoside (38): 1,1′-Carbonylbis-1*H*-imidazole (6 mg, 38 μmol) in DMF (1 mL) was added at room temperature to a stirred solution of **31** (15 mg, 31 μmol) in DMF (2 mL). After 5 h, the reaction mixture was evaporated and the residue was taken up with H_2O and passed through a column of Dowex 50W X-8 (H^+ form). The effluents were chromatographed on a column of spherical silica gel (ethyl acetate/MeOH/H_2O 5:3:1) to give **38** (11 mg, 68%) as an amorphous solid; R_f = 0.15 (ethyl acetate/MeOH/H_2O 5:3:1), $[\alpha]_D^{25}$ = +37.1 (*c* = 0.46 in H_2O); ^{1}H NMR (400 MHz, D_2O, 30°C, DHO): δ = 5.04 (d, $^3J_{1,2}$ = 1.7 Hz, 1H; H1″), 4.90 (d, $^3J_{1,2}$ = 3.1 Hz, 1H; H1), 4.87 (brs, 1H; H1′), 4.30–4.28 (m, 2H; H3′, H5a′), 4.13 (m, 1H; H5), 3.99 (dd, $^3J_{3,4}$ = 2.4, $^3J_{4,5}$ = 1.2 Hz, 1H; H4), 4.04 (dd, $^3J_{2,3}$ = 3.4 Hz, 1H; H2″), 3.99 (dd, $^3J_{5,6a}$ = 5.5, $^2J_{6a,6b}$ = 10.7 Hz, 1H; H6a), 3.95–3.86 (m, 5H; H2, H3, H3″, H5″, H6a″), 3.80 (dd, $^3J_{5,6b}$ = 6.3, $^2J_{6a,6b}$ = 11.9 Hz, 1H; H6b″), 3.75 (dd, $^3J_{5,6b}$ = 6.8 Hz, 1H; H6b), 3.73 (t, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.8 Hz, 1H; H4″), 3.63 (m, 1H; H4′), 3.62 (dd, $^3J_{1,2}$ = 1.6, $^3J_{2,3}$ = 3.6 Hz, 1H; H2′), 3.57 (brd, $^2J_{5a,5b}$ = 11.8 Hz, 1H; H5b′) ppm; ^{13}C NMR (67.8 MHz, D_2O, 30°C, acetone): δ = 161.6 (C=O), 103.2 (C1′), 102.1 (C1), 101.9 (C1″), 75.8, 73.1, 72.0, 70.6 (C2, C3, C3″, C5″), 72.7 (C2″), 71.9 (C4), 71.6 (C5), 70.0 (C3′), 69.8 (C6), 69.3 (C4″), 63.5 (C6″), 62.4 (C5′), 57.9 (OCH_3), 51.1 (C2′), 48.3 (C4′) ppm; HRMS (ESI): calcd for $C_{19}H_{33}N_2O_{14}$ $[M+H]^+$: 513.1932; found 513.1938.

General method of determining the first order rate constants for Pt complex formations: The first order rate constants, *k* (s^{-1}), were calculated by fitting the processed data from the optical rotation measurement to Equation (1):

$$\ln [\text{sugar}]/[\text{sugar}]_0 = -kt/3600 \quad (1)$$

where [sugar] is the concentration (mM) of a sugar at *t* h and $[\text{sugar}]_0$ is the concentration (mM) of the sugar at 0 h. [sugar] is calculated from Equation (2):

$$[\text{sugar}]\ (\text{mM}) = 26 \times (\alpha_{obs}-\alpha_{12\,h})/\alpha_{0\,h}-\alpha_{12\,h}) \quad (2)$$

where α_{obs}, $\alpha_{12\,h}$, and $\alpha_{0\,h}$ denote the optical rotations at the given time, 12 h, and 0 h, respectively.

Dichloro[methyl 2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl-(1→2)-α-D-mannopyranoside-*N,N′*]platinum (40): A solution of $K_2[PtCl_4]$ (29 mg, 63 μmol) in $[D_3]$AcONa/D_2O buffer (50 mM, pH 7.0, 262 μL) was added at 30°C to a stirred solution of compound **19** (20 mg, 63 μmol) in the same buffer (2157 μL). The reaction was monitored by optical rotation (2.0 mL aliquot) at intervals of 0.5 h. After 12 h, the solution was passed through the column of Sephadex G-15 (∅ = 2.5×100 cm) to give **40** (18 mg, 43%) as a pale yellow solid: m.p. 178–179°C; $[\alpha]_D^{25}$ = −44.3 (*c* = 1.00 in H_2O); ^{1}H NMR (400 MHz, D_2O, 30°C, DHO): δ = 5.07 (s, 1H; H1′), 4.91 (d, $^3J_{1,2}$ = 1.3 Hz, 1H; H1), 4.50 (d, $^2J_{5a,5b}$ = 13.1 Hz, 1H; H5a′), 4.06 (dd, $^3J_{2,3}$ = 3.5 Hz, 1H; H2), 3.89–3.86 (m, 2H; H3, H6a), 3.76 (dd, $^3J_{5,6b}$ = 5.5, $^2J_{6a,6b}$ = 12.4 Hz, 1H; H6b), 3.71–3.60 (m, 4H; H4, H5, H3′, H5b′), 3.44 (s, 3H; OCH_3), 2.78 (s, 1H; H2′), 2.68 (s, 1H; H4′) ppm; ^{13}C NMR (100.6 MHz, D_2O, 30°C, acetone): δ = 98.2 (C1), 95.6 (C1′), 75.1 (C2), 73.3 (C5), 70.3 (C3), 67.3 (C4), 66.7 (C3′), 61.3 (C6), 56.8 (C5′), 55.6 (OCH_3), 49.9 (C2′), 48.4 (C4′) ppm; HRMS (ESI): calcd for $C_{12}H_{24}{}^{35}Cl_2N_2O_8K^{195}Pt$ $[M+K]^+$: 628.0196; found 628.0195.

Dichloro[methyl β-D-galactopyranosyl-(1→3)-2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl-(1→6)-α-D-mannopyranoside-*N,N′*]platinum (41): A solution of $K_2[PtCl_4]$ (28 mg, 68 μmol) in $[D_3]$AcONa/D_2O buffer (50 mM, pH 7.0, 283 μL) was added at 30°C to a stirred solution of compound **6** (33 mg, 68 μmol) in the same buffer (2334 μL). The reaction was monitored by optical rotation at intervals of 0.5 h. After 12 h, the solution was passed through the column of Sephadex G-15 (∅ = 2.5×100 cm) to give **41** (24 mg, 46%) as a pale yellow solid: m.p. 253°C (decomp); $[\alpha]_D^{30}$ = −29.6 (*c* = 0.96 in H_2O); ^{1}H NMR (400 MHz, D_2O, 30°C, DHO): δ = 5.09 (s, 1H; H1′), 4.89 (d, $^3J_{1,2}$ = 1.5 Hz, 1H; H1), 4.62 (d, $^3J_{1,2}$ = 7.8 Hz, 1H; H1″), 4.48 (dd, $^3J_{4,5a}$ = 1.9, $^2J_{5a,5b}$ = 13.2 Hz, 1H; H5a′), 4.21 (d, $^2J_{6a,6b}$ = 9.9 Hz, 1H; H6a″), 4.05 (dd, $^3J_{2,3}$ = 3.2 Hz, 1H; H2), 4.02 (d, $^3J_{3,4}$ = 3.5 Hz, 1H; H4″), 3.94–3.75 (m, 10H; H3, H4, H5, H6a, H6b, H3′, H5b′, H3″, H5″, H6b″), 3.64 (dd, $^3J_{2,3}$ = 9.9 Hz, 1H; H2″), 3.54 (s, 3H; OCH_3), 3.04 (brs, 1H; H4′), 3.02 (brs, 1H; H2′) ppm; ^{13}C NMR (100.6 MHz, D_2O, 30°C, acetone): δ = 103.5 (C1″), 101.6 (C1), 98.4 (C1′), 76.1, 74.1 (C3′), 72.9, 72.0, 71.3 (C2″), 71.0, 70.5 (C2), 69.1 (C4″), 68.6, 67.6, 61.7, 56.9 (C5′), 55.7 (OCH_3), 47.9 (C2′), 47.5 (C4′) ppm; HRMS (ESI): calcd for $C_{18}H_{34}{}^{35}Cl_2N_2O_{13}K^{195}Pt$ $[M+K]^+$: 790.0723; found 790.0688; elemental analysis calcd (%) for $C_{18}H_{34}Cl_2N_2O_{13}Pt\cdot 2H_2O$ (788.5): C 27.42, H 4.86, N 3.55; found: C 27.28, H 4.88, N 3.56.

Dichloro [methyl α-D-mannopyranosyl-(1→3)-2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl-(1→6)-α-D-mannopyranoside-*N,N′*] platinum (42): A solution of $K_2[PtCl_4]$ (28 mg, 68 μmol) in $[D_3]$AcONa/D_2O buffer (50 mM, pH 7.0, 283 μL) was added at 30°C to a stirred solution of compound **17** (33 mg, 68 μmol) in the same buffer (2334 μL). The reaction was monitored by optical rotation at intervals of 0.5 h. After 12 h, the solution was passed through a column of Sephadex G-15 (∅ 2.5×100 cm) to give **42** (11 mg, 21%) as a pale yellow solid: m.p. 270°C (decomp); $[\alpha]_D^{30}$ = +10.8 (*c* = 0.54 in H_2O); ^{1}H NMR (400 MHz, D_2O, 30°C, DHO): δ = 5.06 (d, $^3J_{1,2}$ = 1.7 Hz, 1H; H1″), 5.02 (s, 1H; H1′), 4.88 (d, $^3J_{1,2}$ = 1.8 Hz, 1H; H1) 4.49 (dd, $^3J_{4,5a}$ = 1.9, $^2J_{5a,5b}$ = 13.2 Hz, 1H; H5a′), 4.16 (d, $^2J_{6a,6b}$ = 10.7 Hz, 1H; H6a), 4.07–4.06 (m, 2H; H2, H2″), 4.02 (dd, $^3J_{5,6a}$ = 1.4, $^2J_{6a,6b}$ = 11.4 Hz, 1H; H6a″), 3.95 (dd, $^3J_{2,3}$ = 3.4, $^3J_{3,4}$ = 9.3 Hz, 1H; H3″), 3.92–3.77 (m, 8H; H2, H3, H5, H6a, H2′, H3′, H5″, H6b″), 3.74 (t, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.4 Hz, 1H; H4″), 3.54 (s, 3H; OCH_3), 2.91 (m, 2H; H2′, H4′) ppm; ^{13}C NMR (100.6 MHz, D_2O, 30°C, acetone): δ = 101.5 (C1), 99.5 (C1″), 98.0 (C1′), 74.3 (C5″), 72.1 (C4), 71.1 (C3), 71.1 (C3′), 70.9 (C3″), 70.6 (C2), 70.4 (C2″), 68.5 (C6), 67.5 (C5), 67.4 (C4″), 61.7 (C6″), 56.7 (C5′), 55.5 (OCH_3), 49.3 (C2′), 45.5 (C4′) ppm; HRMS (ESI): calcd for $C_{18}H_{34}{}^{35}Cl_2N_2O_{13}K^{195}Pt$ $[M+K]^+$: 790.0723; found 790.0724.

Dichloro [methyl α-D-mannopyranosyl-(1→3)-2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl-(1→2)-α-D-mannopyranoside-*N,N′*] platinum (43): A solution of $K_2[PtCl_4]$ (29 mg, 69 μmol) in $[D_3]$AcONa/D_2O buffer (50 mM, pH 7.0, 285 μL) was added at 30°C to a stirred solution of compound **23** (33 mg, 69 μmol) in the same buffer (2348 μL). The reaction was monitored by optical rotation (2.0 mL aliquots) at intervals of 0.5 h. After 12 h, the solution was passed through a column of Sephadex G-15 (∅

2.5×100 cm) to give **43** (25 mg, 49%) as a pale yellow solid: R_f 0.39 (*i*PrOH/H_2O/NH_4OH 7:3:1); m.p. 255°C (decomp); $[\alpha]_D^{30} = -17.2$ (c = 1.09 in H_2O); ^{1}H NMR (400 MHz, D_2O, 30°C, DHO): δ = 5.12 (s, 1H; H1′), 5.08 (d, $^3J_{1,2}$ = 1.6 Hz, 1H; H1″), 4.97 (br s, 1H; H1), 4.67 (dd, $^3J_{4,5a}$ = 1.8, $^2J_{5a,5b}$ = 13.2 Hz, 1H; H5a′), 4.17 (dd, $^3J_{1,2}$ = 1.6, $^3J_{2,3}$ = 3.6 Hz, 1H; H2), 4.07 (dd, $^3J_{2,3}$ = 3.4 Hz, 1H; H2″), 4.04–3.99 (m, 3H; H3, H6a, H6a″), 3.96 (dd, $^3J_{3,4}$ = 9.5 Hz, 1H; H3″), 3.91–3.73 (m, 8H; H4, H5, H6b, H3′, H5b′, H4″, H5″, H6b″), 3.54 (s, 3H; OCH_3), 2.92 (m, 2H; H2′, H4′) ppm; ^{13}C NMR (100.6 MHz, D_2O, 30°C, acetone): δ = 100.0 (C1), 98.5 (C1″), 95.6 (C1′), 75.1 (C2), 74.2, 73.6, 71.5, 70.2, 61.7, 61.5 (C3, C4, C5, C6, C3′, C4″, C5″, C6″), 71.1 (C3″), 70.7 (C2″), 56.9 (C5′), 55.5 (OCH_3), 49.4 (C2′), 45.9 (C4′) ppm; HRMS (ESI): calcd for $C_{18}H_{34}{}^{35}Cl_2N_2O_{13}K^{195}Pt$ $[M+K]^+$: 790.0723; found 790.0674; elemental analysis calcd (%) for $C_{18}H_{34}Cl_2N_2O_{13}Pt\cdot 2H_2O$ (788.5): C 27.42, H 4.86, N 3.55; found: C 27.09, H 4.87, N 3.56.

Dichloro [methyl α-D-mannopyranosyl-(1→3)-2,4-diamino-2,4-dideoxy-β-D-xylopyranosyl-(1→6)-α-D-galactopyranoside-*N,N′*] platinum (44): A solution of $K_2[PtCl_4]$ (29 mg, 69 μmol) in [D_3]AcONa/D_2O buffer (50 mM, pH 7.0, 286 μL) was added at 30°C to a stirred solution of compound **31** (34 mg, 69 μmol) in the same buffer (2339 μL). The reaction was monitored by optical rotation at an interval of 0.5 h. After 12 h, the solution was passed through a column of Sephadex G-15 (∅ = 2.5×100 cm) to give **44** (31 mg, 60%) as a pale yellow solid: m.p. 270°C (decomp); $[\alpha]_D^{30}$ = +16.4 (c = 1.57 in H_2O); ^{1}H NMR (400 MHz, D_2O, 30°C, DHO): δ = 5.08 (d, $^3J_{1,2}$ = 1.6 Hz, 1H; H1″), 5.04 (s, 1H; H1′), 4.97 (d, $^3J_{1,2}$ = 2.9 Hz, 1H; H1), 4.45 (dd, $^3J_{4,5a}$ = 1.9, $^2J_{5a,5b}$ = 11.6 Hz, 1H; H5a′), 4.19 (t, ^3J = 6.6 Hz, 1H; H5), 4.13 (s, 1H; H4), 4.09 (dd, $^3J_{5,6a}$ = 5.1, $^2J_{6a,6b}$ = 10.5 Hz, 1H; H6a), 4.05 (dd, $^3J_{2,3}$ = 3.2 Hz, 1H; H2″), 4.02 (dd, $^3J_{5,6a}$ = 1.5, $^2J_{6a,6b}$ = 11.7 Hz, 1H; H6a″), 3.99–3.96 (m, 2H; H2, H3), 3.90–3.57 (m, 7H; H6b, H3′, H5b′, H3″, H4″, H5″, H6b″), 3.55 (s, 3H; OCH_3), 2.93 (s, 1H; H4′), 2.91 (s, 1H; H2′) ppm; ^{13}C NMR (100.6 MHz, D_2O, 30°C, acetone): δ = 100.2 (C1), 99.7 (C1″), 97.8 (C1′), 74.2 (C5″), 71.4 (C3′), 71.0 (C3″), 70.6 (C2″), 70.1, 70.0 (C2, C4), 69.6 (C5), 68.7 (C3), 67.8 (C6), 67.4 (C4″), 61.7 (C6″), 56.7 (C5′), 55.9 (OCH_3), 49.2 (C2′), 45.6 (C4′) ppm; HRMS (ESI): calcd for $C_{18}H_{34}{}^{35}Cl_2N_2O_{13}K^{195}Pt$ $[M+K]^+$: 790.0723; found 790.0649.

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