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Intramolecular 1,8-Hydrogen Atom Transfer Reactions in Disaccharide Systems Containing Furanose Units

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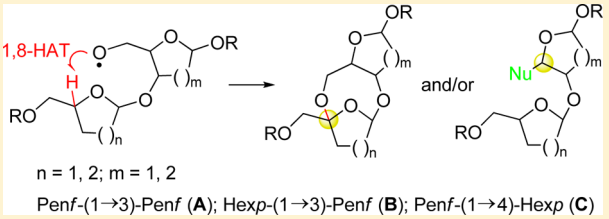
Supporting Information

ABSTRACT: A previously developed 1,8-hydrogen atom transfer (HAT) reaction promoted by 6-*O*-yl alkoxyl radicals between the two pyranose units in Hex*p*-(1→4)-Hex*p* disaccharides has been extended to other systems containing at least a furanose ring in their structures. In Pen*f*-(1→3)-Pen*f* (**A**) and Hex*p*-(1→3)-Pen*f* (**B**) disaccharides, the 1,8-HAT reaction and concomitant cyclization to a 1,3,5-trioxocane ring are in competition with radical *β*-scission of the C4−C5 bond and formation of dehomologated products. The influence of the stereoelectronic *β*-oxygen effect on the *β*-scission and consequently on the 1,8-HAT reaction has been studied using the four possible isomeric D-furanoses. D-*xylo*- and D-*lyxo*-derivatives afforded preferentially 1,8-HAT products, whereas D-*arabino*- and D-*ribo*-derivatives gave exclusively direct *β*-scission of the alkoxyl radical. When the 6-*O*-yl radical is on a pyranose ring, as occurs in Pen*f*-(1→4)-Hex*p* (**C**), it has been shown to provide the cyclized products exclusively.



INTRODUCTION

Much attention has been devoted to free radical reactions in carbohydrate chemistry in recent years.[1] Although the vast majority of the work reported in this area has been focused on anomeric radicals of hexopyranose systems, the conformation, lifetime, and reactivity of the C4 radical in pentofuranoses have also been investigated in some detail.[2] The importance of these radicals in the DNA damage through the metabolism of oxygen and in the mode of action of certain DNA cleavage agents (e.g., iron bleomycin, $(1,10\text{-phen})_2Cu$ complex, and enediyne natural products) has motivated these studies.[3]

These C4 radicals, in either aldofuranose or oligonucleotide systems, have been usually generated by reductive fragmentation of 4-phenylseleno derivatives[4] or Norrish type 1 photochemical cleavage of ketones.[5] The homolytic rupture of the inactive C4−H bond by intramolecular 1,5- and 1,6-hydrogen atom transfer (HAT) reactions from aryl *C*-radicals,[6] alkoxyl radicals,[7] *N*-radicals,[8] or Norrish−Yang photocyclization of 1,2-diketones[9] have also been occasionally used, and a few examples of these reactions can be found in the literature.

Over the past few years, we have been particularly interested in intramolecular HAT reactions promoted by properly positioned alkoxyl radicals as a method for the regioselective functionalization of remote inactive carbons in the carbohydrate skeleton.[7,10] In most cases, the reaction proceeded via thermodynamically stable six- or seven-membered transition states (TSs) to give tetrahydrofuran or tetrahydropyran rings, respectively. Recently, we have described the stereochemical and conformational factors that control a novel 1,8-HAT reaction between the two pyranose units in Hex*p*-(1→4)-Hex*p* disaccharide systems when promoted by a primary 6-*O*-yl radical (Scheme 1).[11] The results show that the process requires a well-defined conformation of the glycosidic (Φ) and aglyconic (Ψ) bonds, which, as expected, are highly dependent on the stereochemistry of the four chiral centers involved in the cyclization step (C5, C4, C1′, and C5′). In conclusion, we have established that if, under oxidative conditions, a conformationally stable boat−chair 1,3,5-trioxocane ring can be formed, the abstraction would occur preferentially at C5′ (1,8-HAT), whereas if this process is energetically disfavored, namely, a 1,3,5-trioxocane ring in boat−boat or crown ether conformation, the abstraction should take place mainly at C1′ (1,6-HAT) to give an interglycosidic spiro *ortho* ester motif.[12] In both cases the cyclization mechanism implicates an oxonium ion intermediate formed by oxidation of the *C*-radical with an excess of (diacetoxyiodo)benzene (DIB).[11a] We also found that under reductive conditions a predominant inversion of the configuration at C5′ may take place and hence the transformation of D-Hex*p*-(1→4)-D-Hex*p* disaccharides into more valuable L-Hex*p*-(1→4)-D-Hex*p* systems can be accomplished in good yields.

RESULTS AND DISCUSSION

Since in the results we have published, until now, the hydrogen donor and acceptor have always been located in hexopyranose moieties, a logical extension of these studies would be to include furanose residues in the disaccharide. Three principal structural arrangements, Pen*f*-(1→3)-Pen*f* (**A**), Hex*p*-(1→3)-Pen*f* (**B**), and Pen*f*-(1→4)-Hex*p* (**C**), are outlined in Scheme 2. Additionally, examples of related Pen*p*-(1→4)-Hex*p* (e.g., **41**)

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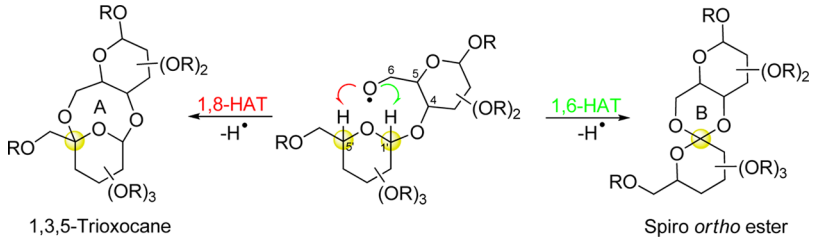
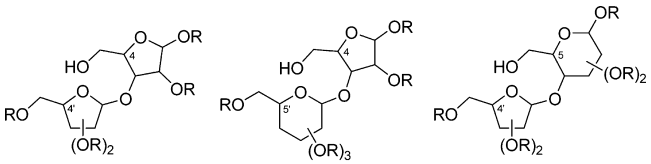
Scheme 1. 1,8-HAT versus 1,6-HAT in Hex*p*-(1→4)-Hex*p* Disaccharide Systems



and Hex*f*-(1→4)-Hex*p* (e.g., **58**) systems have also been included in this study.

Scheme 2. Furanose Disaccharide Arrangements



At first sight, the differences between the 1,8-HAT reaction in the hexopyranose disaccharides and these three systems may seem trivial. Upon close examination, however, four important differences arise: (a) There is an increased conformational flexibility of the aldofuranosyl ring in solution as compared to the well-defined chair conformation of the aldopyranosyl ring. (b) A greater flexibility of the glycosidic (Φ) bond is expected in these tetrahydrofuran systems, where the electronic effects tend to be less pronounced.[13] (c) Easy dehomologation of 5-*O*-yl radicals by *β*-scission with loss of formaldehyde has been described in furanose rings, and under oxidative[14] and reductive[15] conditions, the homologous reaction in pyranose systems has not been observed. (d) An additional concern comes from the stability of the final 1,3,5-trioxocane ring, which in the case of furanoses (2,6,10-trioxabicyclo[5.2.1]decane system) could be more prone to hydrolyze.[16] The first two differences may play a critical role in the nine-membered TS, and in general, these drawbacks may transform the process into a much more difficult task.

To illustrate the effect that the furanose ring conformation could have on the 1,8-HAT reaction, we prepared two theoretical models of methyl 2,3,5-tri-*O*-methyl-*α*-D-Ara*f*-(1→3)-2-*O*-methyl-*α*-D-Ara*f* (arrangement **A**) using molecular mechanics (Figure 1).[17] In the first one both arabinofuranose rings adopt a constrained east °*E* conformation (P = 90°), which leaves the H*α*−C4′ (pseudoaxial), the H*β*−C1′ (pseudoequatorial), and the 5-*O*-yl radical on a pseudoequatorial side chain in a global disposition very similar to that found in our earlier *α*-D-Hex*p*-(1→4)-D-Hex*p* models. In the second one the arabino rings adopt an opposite west E_o conformation (P = 270°) with the H*α*−C4′ (pseudoequatorial), the H*β*−C1′ (pseudoaxial), and the 5-*O*-yl radical on a pseudoaxial side chain. The energies of the staggered conformations *exo-syn*, non-*exo*, and *exo-anti* around the glycosidic torsion angle were calculated by performing a coordinated scan of Φ and Ψ dihedrals.[18] Since it is generally accepted that a narrow range of distances of approximately 2.5−3.0 Å are required for the abstraction to take place,[19] the distances between the oxygen at C5 and the extractable hydrogens were also calculated as indicative of HAT reaction feasibility.

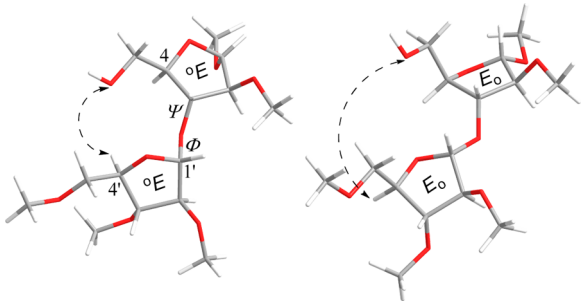


Figure 1. Minimized *exo-syn* conformers of *α*-D-Ara*p*°*E*-(1→3)-*α*-D-Ara*p*°*E* and *α*-D-Ara*p*E_o-(1→3)-*α*-D-Ara*p*E_o disaccharides. The distances between 5O and H4′ are shown by arrows.

The results of this study highlight the clear influence of the furanose ring conformation on the 1,6- and 1,8-HAT TSs. In the Ara*f*E_o-(1→3)-Ara*f*E_o model, the distances between the 5-*O*-yl radical and the extractable hydrogens (H1′ and H4′) are excessively long (4.9−7.0 Å) and HAT reactions are clearly unfavorable. Notwithstanding, in the Ara*f*°*E*-(1→3)-Ara*f*°*E* model, the global minimum was found to be an *exo-syn* conformer with an ideal distance O5−H4′ of 2.9 Å (see Table 1S of the Supporting Information for details).

The intuitive extrapolation of these results suggests that 1,8-HAT should be favored with restricted or stabilized furanose ring conformers at the east side of the pseudorotational itinerary with phase angle values of about 90° and disfavored with conformers at the opposite west side (P = 270°).

The easy dehomologation of 5-*O*-yl radicals by *β*-scission poses a difficult problem, but an example previously described from this laboratory encourages us to think that intramolecular HAT could effectively compete with the dehomologation reaction. The reaction of diol **1**[20] with the DIB/I_2 system afforded exclusively 2,6-anhydro-*β*-D-*ribo*-hex-2-ulose (2,6-anhydro-*β*-D-psicose) derivative **3** in high yield via an evident 1,5-HAT reaction, while no products coming from *β*-scission could be detected in the reaction mixture (Scheme 3).[7] Notwithstanding, under the same conditions the selectively monosilyl-protected **2**[21] gave only the mixture of dehomologated anomeric acetates **4**.[22]

To arrive at a reasonable explanation of the factors governing these differences, the conformation of the furanose ring was determined by pseudorotational analysis of NMR ring coupling constants ($^3J_{H,H}$).[23] Due probably to the restrictions imposed by the [3.3.0]bicycle, the furanose ring conformations in **1** and **2** are very similar, with the most populated conformers at phase angles of P = 292° (^1T_o) and P = 276° (E_o), respectively (see Table 2S of the Supporting Information for details).[24] In these northern conformations, the furanose side chain at C4 and the

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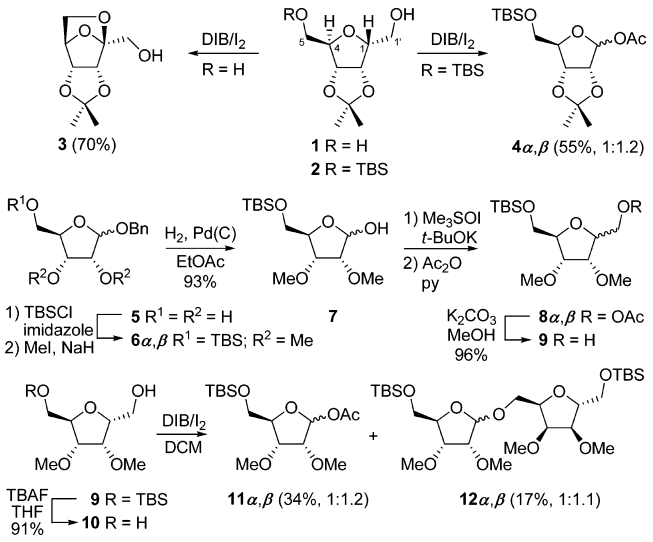
Scheme 3. HAT versus Dehomologation in Ribose Derivatives



hydrogen at C1 lie in a *syn*-1,3-pseudodiaxial relationship favoring the 1,5-abstraction whereas the tether at C1 and the hydrogen at C4 are in a disfavored *syn*-1,3-pseudodiequatorial orientation. The distances C1′−O−H4 and C5−O−H1 on the minimum energy conformers were then calculated by performing a coordinated scan of H1−C1−C1′−O and H4−C4−C5−O dihedrals.[17] As shown in Table 2S, the 1,5-HAT reaction can only be performed from the 5-*O*-yl radical (d = 2.5 Å), being impossible from the 1′-*O*-yl radical (d = 4.5−4.7 Å), thereby confirming the experimental results.

In comparative terms, the reaction was also studied with more flexible 2,3-di-*O*-methylribose derivatives **9** and **10**. The preparation of these compounds was carried out as outlined in Scheme 3. Protection of the 5-OH group in benzyl D-ribofuranoside (**5**) as a *tert*-butyldimethylsilyl ether and subsequent dimethylation gave saccharide **6** as an anomeric mixture of isomers. The *C*-glycosidation of the deprotected anomeric alcohol **7** with trimethylsulfoxonium ylide following the Fréchou et al.[25] protocol afforded after acetylation a chromatographically separable mixture of isomers **8**. The major α-isomer was deprotected consecutively with K_2CO_3 and TBAF to give the diol **10**[26] and the intermediate alcohol **9**. When the radical reaction was applied to diol **10**, a complex mixture of inseparable acetates was obtained upon β-fragmentation and we were unable to detect the formation of any HAT product in the reaction mixture. Monosilylated **9** also afforded only β-fragmented products, including a 1-*O*-acetyl-D-ribofuranose mixture of anomers **11** and a small amount of unexpected disaccharide structures **12** promoted by intermolecular glycosidation via a ribofuranosylium cation intermediate. The preferred conformations of **9** and **10** calculated analogously indicate that distances are too large for the 1,5-HAT reaction to take place (Table 2S, Supporting Information).

Considerable attention has been focused on conformational analysis of aldofuranosides because of their biological importance, and the most important structural features of these compounds have been published.[27] A quick survey of the literature reveals that methyl α-D-arabinofuranoside exists preferentially in a conformation of the eastern region of the pseudorotational itinerary (E_4) as determined by computational methods and X-ray crystallographic analysis and therefore could be a good candidate to test our 1,8-HAT reaction.

Keeping the above considerations in mind, a series of disaccharides belonging to each one of the above-mentioned arrangements were synthesized and are outlined in Table 1.

Table 1. Synthesis of Disaccharides[a]

Donor	Acceptor	Disaccharide (yield)[b]
24	**14**	**25** R = Ac (95%) → **26** R = Me (98%)
24	**16**	**27** R = Ac (96%) → **28** R = Me (76%)
29	**23**	**30** R = Ac (99%) → **31** R = Me (95%)
32	**18**	**33** (93%)
24	**34**	**35** R = Ac (99%) → **36** R = Me (70%)
37[d]	**34**	**38** R = Ac (60%) → **39** R = Me (65%)
40	**34**	**41** (73%)

[a]Glycosylations by the trichloroacetimidate method were performed with peracetylated donors (2.3 equiv), acceptors (1 equiv), (TMS)-OTf (0.025 equiv), and 3 Å molecular sieves (50 wt %) in anhydrous CH_2Cl_2 at 0 °C. [b]Isolated yield after chromatographic purification. [c]Reagents and conditions: (a) acetate (1 equiv), K_2CO_3 (3 equiv) in MeOH at rt, then Amberlyst 15 H^+; (b) alcohol (1 equiv), NaH (6 equiv), MeI (7.5 equiv) in DMF at 0 °C. [d]Reagents and conditions: *n*-pentenyl glycoside (1 equiv), acceptor (1 equiv), *N*-iodosuccinimide (NIS) (1.3 equiv), (TMS)OTf (0.3 equiv) in dry CH_2Cl_2 at 0 °C → rt. TCA = trichloroacetimidyl.

The glycosyl donors α-D-Ara*f* **24**,[28] α-L-Ara*f* **29**,[29] α-L-Rha*p* **32**,[30] α-D-Man*f* **37**,[31] and α-D-Lyx*p* **40**[32] were prepared according to the literature procedures. The incorporation of acetyl protecting groups in all trichloroacetimidate derivatives serves to ensure the control of the glycosylation stereochemistry by neighboring C2 group participation.[33]

The preparation of monosaccharide alcohols α-D-Ara*f* **14**, β-D-Rib*f* **16**, β-D-Xyl*f* **18**, and α-D-Lyx*f* **23** used as glycosyl acceptors was carried out according to well-established experimental procedures as described in Scheme 4. Protection of the 5-OH group as a *tert*-butyldiphenylsilyl ether in **13**[34] and **15**[35] afforded methyl α-D-arabinofuranoside (**14**) and methyl β-D-ribofuranoside (**16**), respectively, in excellent yield. Methyl β-D-xylofuranoside derivative (**18**) was obtained in two steps from β-D-ribofuranoside **16** involving initial Dess−Martin

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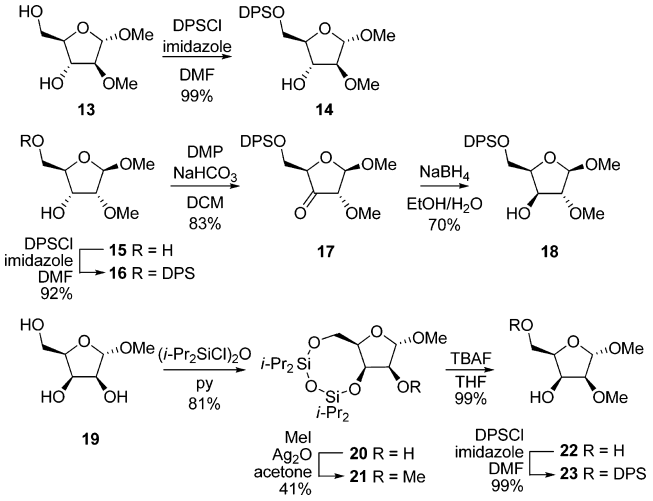
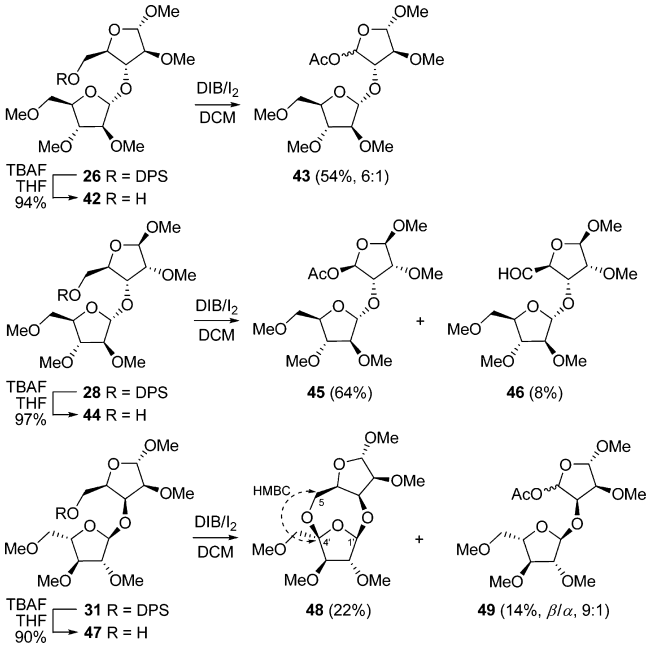
Scheme 4. Preparation of Glycosyl Donors



Scheme 5. HAT Reactions of Arrangement A Disaccharide Models under Oxidative Conditions



periodinane oxidation to ketone **17** and subsequent reduction with sodium borohydride to afford the 3-β-isomeric alcohol **18** preferentially. The synthesis of α-D-lyxofuranoside derivative **23** began with the known methyl α-D-lyxofuranoside (**19**),[36] which was partially protected by 3,5-di-*O*-silylation using $(i\text{-}Pr_2SiCl)_2O$ in pyridine to give compound **20** in 81% yield. The latter was in turn methylated with the MeI/Ag_2O system to afford **21**; probably due to the highly congested β-face of the ring, the reaction was very slow and the yield was only 41% (84% brsm) after 5 days. The 1,1,3,3-tetraisopropyldisiloxane-1,3-diyl group of **21** was removed by TBAF to give the diol **22** in 99% yield. The usual *tert*-butyldiphenylsilylation of **22** gave the desired 5-masked product **23** in 99% yield.

The known methyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3-di-*O*-methyl-α-D-glucopyranoside (**34**) also used as a glycosyl acceptor was prepared by a previously described method.[11a]

The required disaccharides **25**, **27**, **30**, **33**, **35**, and **41** were prepared by the trichloroacetimidate method using a catalytic amount of (TMS)OTf as a Lewis acid;[33a] as expected an exclusive 1,2-*trans* relative disposition of the glycosidic bond and the 2-acetyl group was always observed (Table 1). The *n*-pentenyl glycoside **37**[31] was activated with *N*-iodosuccinimide (NIS)/(TMS)OTf and used as a glycosyl acceptor for the synthesis of α-D-Man*f*-(1→4)-α-D-Glc*p* disaccharide **38**.[33b] In most of the prepared disaccharides, **25**, **27**, **30**, **35**, and **38**, and to favor the HAT reaction by the electrophilic alkoxyl radical, the electron-withdrawing acetyl protecting groups (EWGs) were substituted by methyl ethers.[10b] The models **26**, **28**, **31**, **36**, and **39** thus obtained were desilylated with TBAF, and the free primary alcohols were then ready for the generation of the alkoxyl radicals under oxidative conditions.

Pseudorotational analysis of ring $^3J_{H,H}$ coupling constants of α-D-Ara*f*-(1→3)-α-D-Ara*f* derivative **42**, our first disaccharide model (Scheme 5), indicated that both furanose rings adopt a preferential population of E_4 conformations.[37] Analogously to the Ara*f*^{o}E-(1→3)-Ara*f*^{o}E theoretical model previously studied, the global minimum was found to be an *exo-syn* conformer with an ideal distance C5−O−H4′ of 2.7 Å for the 1,8-HAT to take place. Unfortunately, **42** failed to undergo the desired 1,8-HAT reaction upon treatment with the DIB/I_2 system under a variety of differently modified conditions. The β-fragmentation reaction is faster, and only an inseparable mixture of isomeric dehomologated acetates **43** in moderate yield could be detected (Scheme 5).

Recently, it was claimed that, under reductive conditions in ribo- and xylofuranose derivatives where the neighboring hydroxyl group at C3 is protected, the β-fragmentation is prevented and the 5-*O*-yl radical is simply quenched by the stannane.[15d] Although this is in apparent contradiction with a previous finding by Robins et al.[15a] in protected ribonucleosides where, under similar conditions, the β-scission occurs exclusively, we decided to prepare α-D-Ara*f*-(1→3)-β-D-Rib*f* derivative **44** to check this possibility. Again, only β-fragmented products, the acetate **45** together with a small amount of aldehyde **46**, were obtained (Scheme 5). There is no evidence for the formation of any 1,8-HAT product within the limits of ^{1}H NMR detection. A pseudorotational study showed α-D-Ara*f*E_4-(1→3)-β-D-Rib*f*E_2 conformations for **44** and seems to confirm the results. The β-D-ribofuranose moiety adopts preferentially a west E_2 conformation, and the calculated C5−O−H4′ distance (3.5 Å) in the global *exo-syn* minimum is unfavorable for the 1,8-HAT.

After these unsuccessful efforts, we decided to try a different approach to avoid the dehomologation reaction by destabilization of the C4 radical intermediate. The fragmentation of the C4−C5 bond should be favored by a trans disposition of the oxygen substituent at C3 (as in preceding models) due to a stereoelectronic β-oxygen effect. Consequently, a cis disposition of this substituent on the β-face of the ring may prevent the β-fragmentation.[14a]

The stereochemistry of such a disaccharide should follow the pattern established in our previous research on Hex*p*-(1→4)-Hex*p* models to accommodate the final 1,3,5-trioxocane ring in a stable boat−chair conformation.[11] The synthesis of a Pen*f*-(1→3)-Pen*f* disaccharide model with a 3β-aglyconic bond would require an α-L-sugar as a glycosyl donor to have a stable transition state for the 1,8-HAT reaction. Therefore, α-L-Ara*f*-(1→3)-α-D-Lyx*f* disaccharide **47** was prepared and irradiated under the DIB/I_2 conditions. To our delight, the desired 1,3,5-

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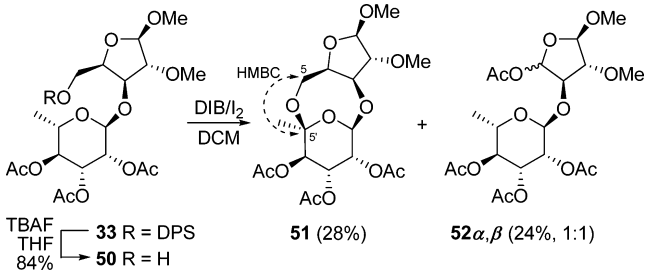
trioxocane derivative **48** was obtained, along with a small amount of dehomologated acetates **49** as an inseparable 9:1 mixture of diastereomers. Products arising from 1,6-HAT of the anomeric H1′ were not isolated. We are aware of only one previous example in the literature of the 2,6,10-trioxabicyclo[5.2.1]decane system present in the structure of compound **48** and are unaware of any examples in the carbohydrate field.[16] As expected, **48** was very sensitive to acid decomposition, but it could be purified by rapid column chromatography on neutral alumina, albeit in low recovery yield (22%). The regioselectivity of the process was assured by NMR spectroscopy; namely, the hydrogens at C5′ appear now as doublets (δ_H 3.40 and 3.45 ppm) with a strong correlation observed between the C4′ signal (δ_C 108.1 ppm) and protons at C5 (δ_H 3.85 and 4.36 ppm, dd) in the 2D HMBC experiment.

Next the reaction of α-L-Rha*p*-(1→3)-β-D-Xyl*f* derivative **50**, an arrangement **B** model, was examined (Scheme 6).

Scheme 6. HAT Reaction of the Arrangement B Disaccharide Model under Oxidative Conditions



Compound **50** was designed with D-xylofuranose to minimize the stabilizing β-oxygen effect, assessing its influence as a general strategy to avoid the dehomologation reaction. D-Xylose and D-lyxose are the only two pentofuranoses which have a cis relationship between the hydroxyl substituent at C3 and the adjacent side chain.

Likewise, when **50** was subjected to similar reaction conditions, the same trend was also followed and led to the formation of 1,3,5-trioxocane derivative **51** and a mixture of dehomologated acetates **52**. The yield of **51** can be slightly improved by running the reaction at low temperature (0 °C). The NMR characteristics of **51** clearly indicate that oxidation has taken place at C5′. Accordingly, the methyl at C5′ appears now as a singlet at δ_H 1.40 ppm, and the HMBC correlations of C5 proton signals at δ_H 4.02 and 4.09 ppm with the C5′ carbon atom (δ_C 101.4 ppm) confirm the new connectivity of both sugar rings.

This methodology was also applied to α-D-Ara*f*-(1→4)-α-D-Glc*p* **53**, a disaccharide belonging to the arrangement **C** type (Scheme 7). As expected, no dehomologated products were produced by β-scission of this 6-*O*-pyranosyl radical, and as a consequence, the cyclized product **54** was formed in significantly better yield (55%) than those in the other models previously obtained.

For comparative purposes the reaction was also applied to disaccharide analogue **55**, where the hydroxyl groups at the furanose ring are acetylated. Two products, **56** and **57**, coming from the 1,8-HAT reaction are now formed in lower yield due to the EWG influence of the neighboring acetyl groups. Interestingly, we were able to isolate the acetal **57**, clearly an intermediate in the hydrolysis of the 1,3,5-trioxocane ring, which gives us some idea on the hydrolysis mechanism. Reasonable evidence for the assignment of the C1′ *R* stereochemistry to the acetal **57** was obtained from the NOESY experiment, which showed significant cross-peaks correlating the axial H1′ with H4 and the axial H6. As described in the Experimental Section, a small amount of methyl 2,3-di-*O*-methyl-α-D-glucopyranoside, one of the final hydrolyzed monosaccharides, was also obtained.

In this section we have included the related disaccharide α-D-Man*f*-(1→4)-α-D-Glc*p* **58** (Scheme 7). The reaction proceeded analogously to that of **53** to give the trioxocane **59** in similar yield. The only side product detected was the methylenedioxy **60** generated by 1,7-HAT of one hydrogen of the methoxyl group at C3 through a conformational equilibrium between glucopyranose $^4C_1$ and $^1C_4$ ring chairs. The structure and conformation of **60** were confirmed by analysis of the vicinal $^3J_{H,H}$ coupling constants in the ^{1}H NMR spectrum together with DEPT and 2D HSQC and HMBC experiments. Of particular relevance is the HMBC connectivity of C6 (δ_C 64.1 ppm) with the protons at the methylenedioxy bridge (δ_H 4.66 and 4.81 ppm, d).

Finally, we carried out the reaction with α-D-Lyx*p*-(1→4)-α-D-Glc*p* derivative **41**, where the hydrogen donor is a pentose in pyranose form (Scheme 8). Surprisingly, the major product was the orthoacetate **61** as a sole isomer, resulting from initial 1,8-HAT and subsequent neighboring participation of the acetate group after oxidation of the *C*-radical intermediate. The minor product was the spiro *ortho* ester **62**, obtained as a mixture of isomers and evidently formed by a competitive 1,6-HAT. Although compound **61** could be purified by silica gel column chromatography, it is unstable and in the presence of a catalytic amount of acid undergoes a partial hydrolysis to give in quantitative yield the dialdose derivative **63**. As a global result of the intramolecular HAT reaction, a regio- and stereoselective oxidative functionalization at C5′ has been produced with a concomitant ester shift.[38]

For comparative purposes, a number of models belonging to arrangements **B** and **C** were also studied under reductive conditions. With this aim, the phthalimide derivatives **64**, **70**, **74**, and **78** were prepared from the corresponding alcohols **50**, **53**, **55**, and **58** by reaction with *N*-hydroxyphthalimide via Mitsunobu condensation (Schemes 9 and 10).[39]

The reaction of α-L-Rha*p*-(1→3)-β-D-Xyl*f* phthalimide **64** with *n*-Bu_3SnH/AIBN afforded three compounds (Scheme 9). Two minor products resulted from 1,8-HAT reactions, the β-D-Gul*p*-(1→3)-β-D-Xyl*f* **65** (26%) formed by hydrogen abstraction at C5′ and subsequent radical quenching with inversion of configuration and alcohol **50** (19%), which could arise either by abstraction and retention of the configuration at C5′ or simply by reduction of the 6-*O*-yl radical prior to the abstraction or very probably by a combination of both mechanisms. Unfortunately, as happened under oxidizing conditions, the third and most abundant product was the dehomologated α-L-Rha*p*-(1→3)-α-L-Threo*f* disaccharide **66** (49%). Repetition of this reaction with *n*-Bu_3SnD showed, after exhaustive analysis of the isotopic distribution, the complete monodeuteration for the β-scission product **69** and also for the inverted alcohol **67**. Moreover, 50% deuterium labeling was found in compound **68**, the reduction of the *O*-radical being responsible for the unlabeled molecules. We can therefore conclude that in this model the global process occurs in low yield but predominantly with inversion of configuration (inversion:retention ratio 3.8:1).

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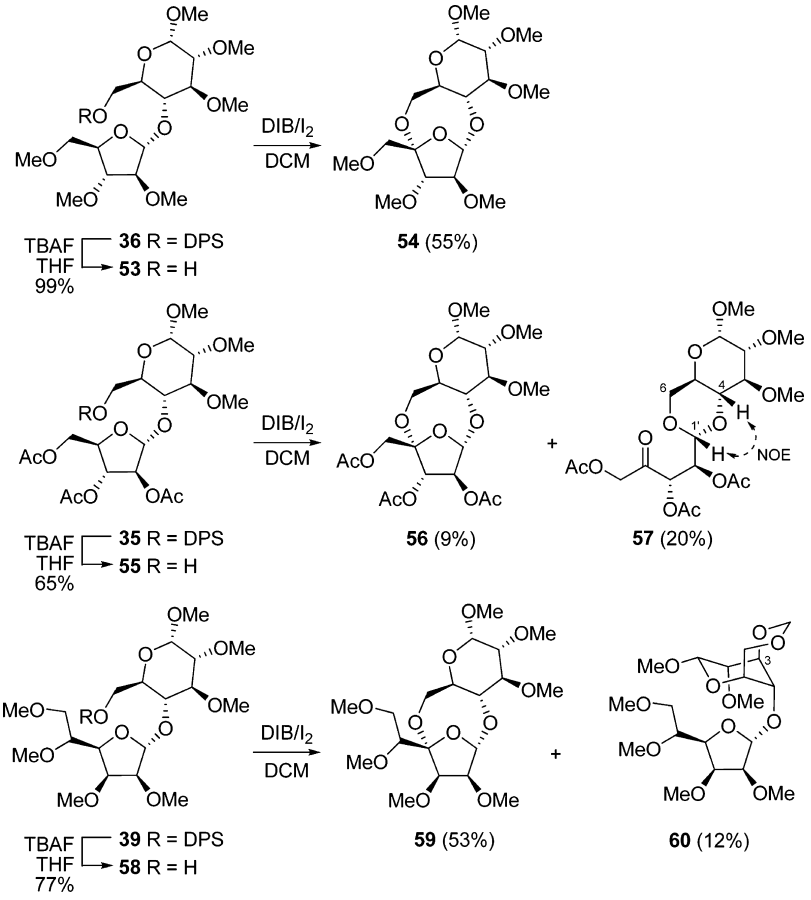
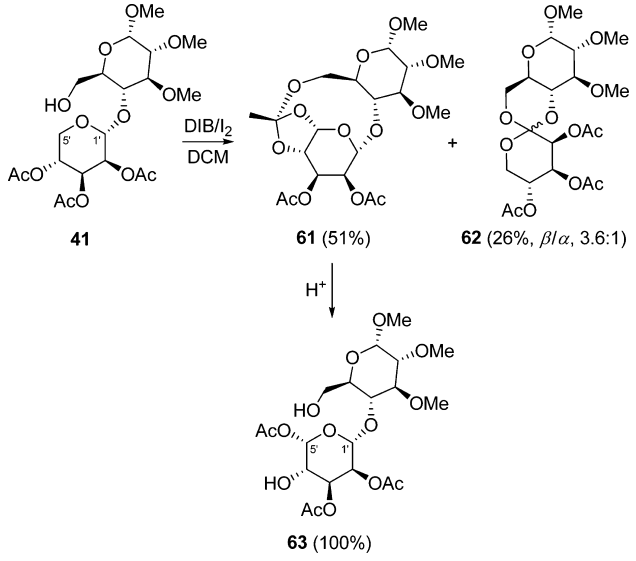
Scheme 7. HAT Reactions of Arrangement C Disaccharide Models under Oxidative Conditions



Scheme 8. HAT Reaction of the α-D-Lyxp-(1→4)-α-D-Glcp Model under Oxidative Conditions



The reduction of β-D-Araf-(1→4)-β-D-Glcp phthalimide **70** by treatment with *n*-Bu_3SnH/AIBN afforded exclusively compounds by hydrogen abstraction at C4′: the β-L-Xylf-(1→4)-β-D-Glcp derivative **71** (46%) formed by inversion to generate a β-L-xylofuranose moiety and the alcohol **53** (41%) with retention of configuration at this carbon (Scheme 10). The experiment using *n*-Bu_3SnD confirmed a complete deuteration at C4′ in compound **72**, while 75% deuterium labeling was found in the alcohol **73**. These results permit us to establish that the abstraction at C4′ occurs in a 63% yield with an inversion:retention ratio of approximately 1.4:1.

For the related 6-*O*-phthalimide **74** with the peracetylated D-arabino moiety, the reaction gave preferentially the inverted product **75**, and the use of *n*-Bu_3SnD as a reagent showed a lower abstraction yield at C4′ in comparison with that of substrate **70** but an improved inversion:retention ratio, 2.6:1. This higher inversion:retention ratio of acetylated α-D-Ara **74** versus methylated α-D-Ara **70** could be explained with the increase in electronegativity of the β-oxygenated substituent as observed in the pyranose series between peracetylated and permethylated β-maltose.[11b]

Finally, when the reductive HAT was performed with the phthalimide **78**, the inverted product **79** was generated in lower yield and the alcohol precursor derivative **80** was then the major isomer with a 48% yield. Repetition of the experiment with *n*-Bu_3SnD/AIBN originated a mixture of compounds **81** (29%), with complete deuteration at C4′, and **82** (49%), with a 70% labeling at C4′. Thus, the deuterium was only incorporated at position 4′, with no deuterium detected at other sites within NMR limits, unlike the experiment under oxidative conditions where abstraction at the methoxyl group at C3 was also observed (Scheme 7). 1,8-HAT occurs in this model with a 63% yield with an inversion:retention ratio of approximately 1:1.2, slightly favoring the retained product.

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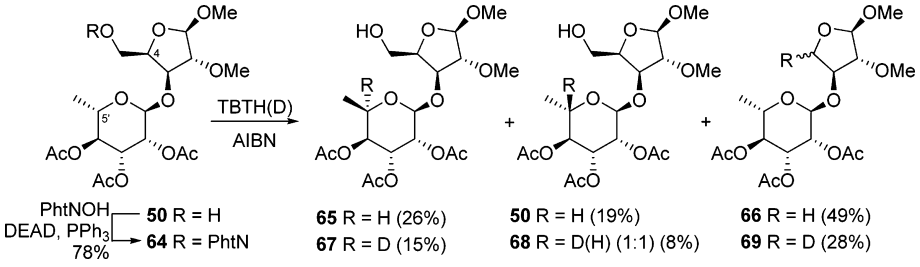
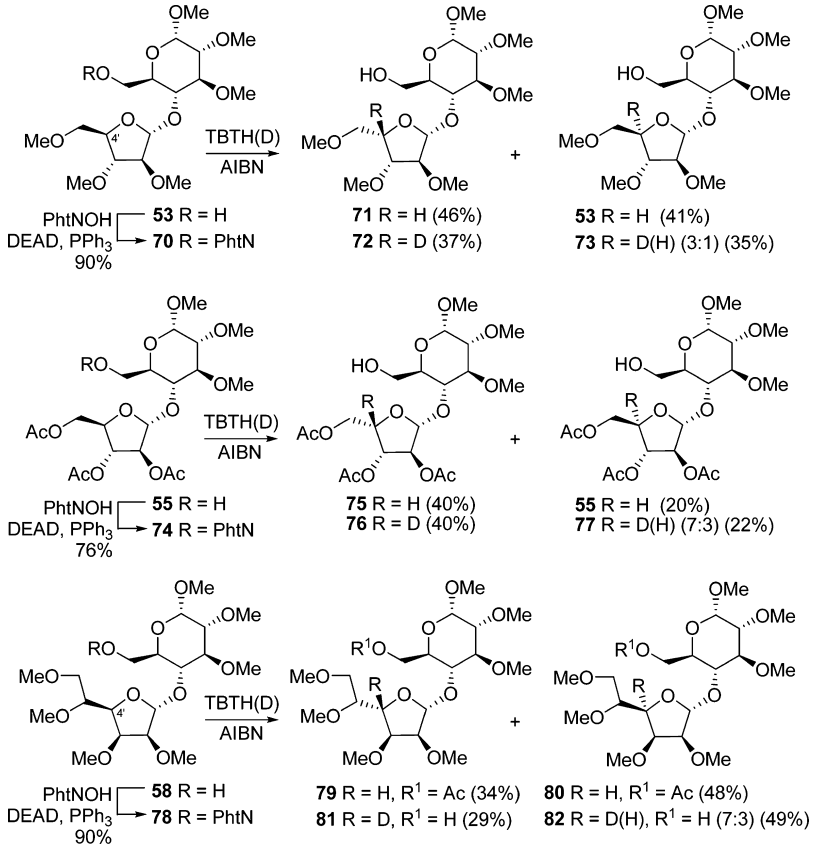
Scheme 9. HAT Reaction of the Arrangement B Disaccharide Model under Reductive Conditions



Scheme 10. HAT Reactions of Arrangement C Disaccharide Models under Reductive Conditions



CONCLUSIONS

On the basis of the experimental evidence presented, the previously developed 1,8-HAT reaction between the two pyranose units in Hex*p*-(1→4)-Hex*p* systems can be extended to other disaccharides containing at least a furanose ring in their structures. Some limitations have been observed: when the 5-*O*-yl radical is generated on D-arabinofuranose or D-ribofuranose rings such as in **42** and **44**, no HAT products can be detected. Instead, the 5-*O*-yl radicals underwent faster *β*-scission to give exclusively dehomologated products. This may be explained by the stabilizing *β*-oxygen effect on the C4−O bond breaking, providing an impetus for the *β*-fragmentation to occur. Notwithstanding, if the alkoxyl radical is part of 3*β*-isomeric D-lyxofuranose **47** or D-xylofuranose **50** moieties, 1,8-HAT reaction occurs preferentially in moderate to low yield in competition with the *β*-scission. No dehomologation products were observed with 6-*O*-yl radicals in pyranose systems, and the yields of the 1,8-HAT products increased significantly. See, for example, arrangement **C** models **53** and **58** in Scheme 7.

The HAT reactions in these models proceeded with excellent regioselectivity, and only 1,8-abstraction was generally observed. The possible competitive 1,6-abstraction of the H1′ was only detected in alcohol **41** and may be attributable to reactivity differences between the secondary H5′ and the tertiary H1′. Furthermore, a 1,7-HAT is involved in the functionalization of the methoxyl group at C3, which results in the formation of a small amount of **60** during the reaction of alcohol **58**.

We found that the sensitive 2,6,10-trioxabicyclo[5.2.1]decane ring system present in **48**, **54**, **56**, and **59** may be susceptible to partial hydrolysis either under the reaction conditions or during the purification process by chromatography, and at least in one case we have managed to isolate intermediate **57**.

Under reductive conditions the HAT reaction proceeded analogously; the same competitive *β*-fragmentation was observed by *n*-Bu_3SnH/AIBN treatment of D-xylofuranose phthalimide **64**. The observed inversion:retention ratio at C4′ in D-arabinofuranose **70** is modest (1.4:1) and increased significantly in triacetylated phthalimide **74**; an analogous result

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was already observed for peracetylated hexopyranose systems.[11b]

These results allow us to conclude that the principal drawback of these reactions is the β-fragmentation; the adverse entropic effects caused by the furanose ring flexibility and by the decrease in the anomeric effects may have a negative influence on the competition with the dehomologation but do not seem to be critical.

EXPERIMENTAL SECTION

General Experimental Methods. Melting points were measured on a hot-stage apparatus. Optical rotations were recorded on a polarimeter at a wavelength of 589 nm at ambient temperature in $CHCl_3$ solutions. IR spectra were recorded on an FT-IR spectrophotometer in a film. ^1H and ^{13}C NMR spectra were obtained from 400 or 500 MHz spectrometers. The chemical shifts are given in parts per million (ppm) relative to TMS at δ 0.00 ppm or to residual $CDCl_3$ at δ 7.26 ppm for proton spectra and relative to $CDCl_3$ at δ 77.00 ppm for carbon spectra, unless otherwise noted. ^{13}C DEPT and 2D COSY, HSQC, and HMBC experiments were performed routinely for all new compounds. Low- and high-resolution mass spectra were recorded with TOF analyzer mass spectrometers by using electrospray ioniazation (ESI+) or electron impact (EI) at 70 eV, as specified in each case. Reaction progress was monitored by thin-layer chromatography (TLC) carried out on 0.25 mm coated commercial silica gel plates impregnated with a fluorescent indicator (254 nm) visualized by UV light and/or submersion in standard vanillin TLC stains followed by heating on a hot plate until development of color. Flash column chromatography was performed on Merck silica gel 60 PF (0.063−0.2 mm), unless otherwise indicated. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. All reactions were performed in single-neck round-bottom flasks fitted with rubber septa under a positive pressure of nitrogen with magnetic stirring, unless otherwise noted. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use.

2,5-Anhydro-3,4-*O*-isopropylidene-D-altritol (1). We have detected some coupling constant errors in the data described previously for this compound.[7] The corrected data are as follows: ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.32 (3H, s), 1.49 (3H, s), 3.61 (1H, dd, J = 11.7, 6.6 Hz), 3.65 (1H, dd, J = 11.7, 4.1 Hz), 3.85 (1H, dd, J = 12.0, 5.1 Hz), 3.89 (1H, dd, J = 11.7, 6.0 Hz), 4.12 (1H, ddd, J = 6.0, 4.7, 4.7 Hz), 4.18 (1H, ddd, J = 6.3, 4.1, 1.6 Hz), 4.67 (1H, dd, J = 6.0, 1.6 Hz), 4.79 (1H, dd, J = 6.3, 4.4 Hz).

2,5-Anhydro-6-*O*-(*tert*-butyldimethylsilyl)-3,4-*O*-isopropylidene-D-altritol (2). A solution of trimethylsulfoxonium iodide (3.256 g, 14.8 mmol) and potassium *tert*-butoxide (1.329 g, 11.8 mmol) in dry DMSO (13.8 mL) was stirred at 0 °C under nitrogen for 30 min. 5-*O*-(*tert*-Butyldimethylsilyl)-2,3-*O*-isopropylidene-D-ribofuranose[40] (3 g, 9.87 mmol) in dry DMSO (6.7 mL) was then added and the mixture stirred at room temperature for 2 h. An aqueous saturated solution of NH_4Cl was added and the mixture extracted with Et_2O. The organic layer was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes−EtOAc, 90:20 → 70:30) to give **2** (1355 mg, 4.6 mmol, 47%) as a colorless oil: $[\alpha]_D$ −16.0 (c 0.412, $CHCl_3$); IR 3468, 2933, 1463, 1258, 1083 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.057 (3H, s), 0.060 (3H, s), 0.89 (9H, s), 1.34 (3H, s), 1.51 (3H, s), 3.70 (1H, dd, J = 11.0, 3.5 Hz), 3.74 (1H, dd, J = 11.0, 3.5 Hz), 3.83 (1H, dd, J = 11.7, 5.4 Hz), 3.87 (1H, dd, J = 12.0, 5.7 Hz), 4.15 (1H, ddd, J = 3.5, 3.5, 0.0 Hz), 4.21 (1H, ddd, J = 5.4, 5.4, 4.4 Hz), 4.79 (1H, dd, J = 6.0, 4.1 Hz), 4.83 (1H, dd, J = 6.3, 0.9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C −5.6 (CH_3), −5.5 (CH_3), 18.1 (C), 24.6 (CH_3), 25.8 (3 × CH_3), 26.1 (CH_3), 62.1 (CH_2), 64.9 (CH_2), 82.0 (CH), 82.2 (CH), 83.3 (CH), 84.2 (CH), 112.5 (C); MS (ESI^+) m/z (rel intens) 341 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{15}H_{30}NaO_5Si$ 341.1760, found 341.1760. Anal. Calcd for $C_{15}H_{30}O_5Si$: C, 56.57; H, 9.49. Found: C, 56.28; H, 9.49.

Oxidative HAT of 2. A solution of alcohol **2** (51 mg, 0.16 mmol) in dry CH_2Cl_2 (6.3 mL) containing DIB (56.7 mg, 0.176 mmol), I_2 (20.3 mg, 0.08 mmol), and powdered molecular sieves 3 Å (52 mg) was stirred under nitrogen at 32 °C for 3 h while being irradiated with two 80 W tungsten-filament lamps. An excess of solid $Na_2S_2O_3$ was then added and stirring continued until complete disappearance of the iodine color. The reaction mixture was then filtered and concentrated under reduced pressure. Silica gel column chromatography of the reaction residue (hexanes−EtOAc, 90:10 → 70:30) afforded the known[22] 1-*O*-acetyl-5-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-isopropylidene-β-D-ribofuranose (**4β**) (12.6 mg, 0.036 mmol, 23%), 1-*O*-acetyl-5-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-isopropylidene-α-D-ribofuranose (**4α**) (10.4 mg, 0.03 mmol, 18.7%), and unreacted starting material **2** (12.7 mg, 0.04 mmol, 25%). Attempts to increase the yield of **4** by varying the reaction times and the number of equivalents of DIB were unsuccessful.

Benzyl 5-*O*-(*tert*-Butyldimethylsilyl)-2,3-di-*O*-methyl-β-D-ribofuranoside (6β) and Benzyl 5-*O*-(*tert*-Butyldimethylsilyl)-2,3-di-*O*-methyl-α-D-ribofuranoside (6α). To a solution of benzyl D-ribofuranoside (**5**) (0.92 g, 3.8 mmol) in dry DMF (30.7 mL) were added imidazole (388 mg, 5.7 mmol) and *tert*-butyldimethylsilyl chloride [(TBDMS)Cl] (689 mg, 4.563 mmol) under nitrogen at 0 °C, and the mixture was stirred at that temperature for 1 h. EtOH was then added, and the reaction mixture was concentrated under reduced pressure. The residue was then coevaporated with toluene and purified by column chromatography (hexanes−EtOAc, 9:1 → 7:3) to give the diol intermediate (1.09 g, 3.076 mmol, 80%) as a colorless oil. This material was used in the next reaction without separation of isomers. To a solution of benzyl 5-*O*-(*tert*-butyldimethylsilyl)-D-ribofuranoside (1089 mg, 3.076 mmol) in dry DMF (36.6 mL) cooled to 0 °C was added NaH, 60% dispersion in mineral oil (492 mg, 12.3 mmol), and the mixture was stirred at this temperature under nitrogen until all hydrogen evolution had ceased. Then an excess of methyl iodide (957 μL, 15.3 mmol) was added and stirring continued at room temperature for 2 h. Excess reagent was destroyed by addition of MeOH, and the mixture was concentrated under high vacuum. Column chromatography (hexanes−EtOAc, 90:10 → 80:20) of the residue afforded **6β** (841 mg, 2.2 mmol, 72%) and **6α** (312 mg, 0.82 mmol, 26%). Data for compound **6β**: colorless oil; $[\alpha]_D$ −49.8 (c 0.41, $CHCl_3$); IR 2929, 1464, 1254, 1133, 1099 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.07 (3H, s), 0.08 (3H, s), 0.90 (9H, s), 3.42 (3H, s), 3.47 (3H, s), 3.72 (1H, dd, J = 11.0, 5.0 Hz), 3.78 (1H, dd, J = 11.0, 4.7 Hz), 3.80 (1H, dd, J = 4.7, 1.6 Hz), 3.93 (1H, dd, J = 6.6, 4.7 Hz), 4.09 (1H, ddd, J = 6.3, 4.7, 4.7 Hz), 4.50 (1H, d, J = 11.7 Hz), 4.78 (1H, d, J = 12.0 Hz), 5.10 (1H, d, J = 1.6 Hz), 7.33 (5H, m); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C −5.43 (CH_3), −5.35 (CH_3), 18.3 (C), 25.9 (3 × CH_3), 58.2 (CH_3), 58.3 (CH_3), 64.2 (CH_2), 69.3 (CH_2), 80.2 (CH), 81.9 (CH), 82.4 (CH), 103.6 (CH), 127.7 (CH), 127.9 (2 × CH), 128.3 (2 × CH), 137.6 (C); MS (ESI^+) m/z (rel intens) 405 (M^+ + Na); HRMS (ESI^+) m/z calcd for $C_{20}H_{34}NaO_5Si$ 405.2073, found 405.2075. Anal. Calcd for $C_{20}H_{34}O_5Si$: C, 62.79; H, 8.96. Found: C, 63.03; H, 8.67. Data for compound **6α**: colorless oil; $[\alpha]_D$ +97.1 (c 0.52, $CHCl_3$); IR 2928, 1464, 1254, 1111, 1046 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.05 (3H, s), 0.07 (3H, s), 0.89 (9H, s), 3.43 (3H, s), 3.44 (3H, s), 3.61 (1H, dd, J = 11.0, 5.0 Hz), 3.67 (1H, dd, J = 6.6, 4.4 Hz), 3.71 (1H, dd, J = 10.7, 3.5 Hz), 3.78 (1H, dd, J = 6.6, 2.2 Hz), 4.16 (1H, ddd, J = 4.7, 3.5, 2.5 Hz), 4.68 (1H, d, J = 12.6 Hz), 4.83 (1H, d, J = 12.6 Hz), 5.06 (1H, d, J = 4.4 Hz), 7.31 (5H, m); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C −5.5 (CH_3), −5.4 (CH_3), 18.2 (C), 25.8 (3 × CH_3), 58.5 (CH_3), 58.6 (CH_3), 63.8 (CH_2), 68.6 (CH_2), 78.4 (CH), 80.8 (CH), 83.1 (CH), 98.8 (CH), 127.4 (CH), 128.1 (2 × CH), 128.2 (2 × CH), 138.0 (C); MS (ESI^+) m/z (rel intens) 405 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{20}H_{34}NaO_5Si$ 405.2073, found 405.2076. Anal. Calcd for $C_{20}H_{34}O_5Si$: C, 62.79; H, 8.96. Found: C, 62.79; H, 8.84.

5-*O*-(*tert*-Butyldimethylsilyl)-2,3-di-*O*-methyl-D-ribofuranose (7). A solution of **6β,α** (2.19 gr, 5.73 mmol) in EtOAc (64 mL) containing Pd/C (10%) hydrogenation catalyst (219 mg) was deoxygenated and stirred under hydrogen at room temperature and atmospheric pressure for 6 h. The mixture was then filtered through

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Celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes−EtOAc, 75:25 → 70:30) to give **7** (1.56 gr, 5.34 mmol, 93%) as an anomeric mixture: colorless oil (ratio α:β = 63:37); IR 3443, 2931, 1471, 1256, 1130, 1046 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H complex spectrum; ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C complex spectrum; MS (ESI$^+$) m/z (rel intens) 315 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{13}H_{28}NaO_5Si$ 315.1604, found 315.1604. Anal. Calcd for $C_{13}H_{28}O_5Si$: C, 53.39; H, 9.65. Found: C, 53.41; H, 9.58.

1-*O*-Acetyl-2,5-anhydro-6-*O*-(*tert*-butyldimethylsilyl)-3,4-di-*O*-methyl-D-altritol (8α) and 1-*O*-Acetyl-2,5-anhydro-6-*O*-(*tert*-butyldimethylsilyl)-3,4-di-*O*-methyl-D-allitol (8β). A solution of trimethylsulfoxonium iodide (1763 mg, 8.01 mmol) and potassium *tert*-butoxide (719 mg, 6.41 mmol) in dry DMSO (7.5 mL) was stirred at 0 °C under nitrogen for 30 min. Then **7** (1560 mg, 5.34 mmol) dissolved in dry DMSO (3.7 mL) was added and the mixture stirred at room temperature for 4 h. An aqueous saturated solution of NH_4Cl was added and the mixture extracted with Et_2O. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexanes−EtOAc, 90:10 → 65:35). The alcohols (773 mg, 2.53 mmol, 47%) were acetylated with Ac_2O (4 mL) in pyridine (12 mL) for 16 h at room temperature to give a mixture of acetates which was purified by silica gel column chromatography (hexanes−EtOAc, 95:5 → 85:15) to afford **8α** (667 mg, 1.92 mmol, 76%) and **8β** (143 mg, 0.41 mmol, 16%) as colorless oils. Data for compound **8α**: $[\alpha]_D$ +33.2 (*c* 0.91, $CHCl_3$); IR 2929, 1731, 1463, 1371, 1258, 1131 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.06 (3H, s), 0.07 (3H, s), 0.90 (9H, s), 2.07 (3H, s), 3.43 (3H, s), 3.49 (3H, s), 3.67 (1H, dd, *J* = 11.0, 3.5 Hz), 3.69 (1H, dd, *J* = 11.0, 3.8 Hz), 3.87 (1H, dd, *J* = 4.7, 4.7 Hz), 3.95 (1H, dd, *J* = 5.0, 5.0 Hz), 4.05 (1H, ddd, *J* = 4.1, 4.1, 4.1 Hz), 4.22 (1H, dd, *J* = 10.7, 8.5 Hz), 4.26 (1H, ddd, *J* = 8.5, 5.4, 2.8 Hz), 4.35 (1H, dd, *J* = 10.7, 2.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C −5.5 (CH_3), −5.4 (CH_3), 18.2 (C), 20.9 (CH_3), 25.8 (3 × CH_3), 58.2 (CH_3), 59.5 (CH_3), 63.4 (CH_2), 64.1 (CH_2), 77.7 (CH), 80.4 (CH), 80.8 (CH), 81.6 (CH), 170.9 (C); MS (ESI$^+$) m/z (rel intens) 371 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{16}H_{32}NaO_6Si$ 371.1866, found 371.1865. Anal. Calcd for $C_{16}H_{32}O_6Si$: C, 55.14; H, 9.25. Found: C, 55.15; H, 9.07. Data for compound **8β**: $[\alpha]_D$ −35.6 (*c* 0.50, $CHCl_3$); IR 2929, 1747, 1471, 1373, 1241, 1135 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.065 (3H, s), 0.07 (3H, s), 0.90 (9H, s), 2.08 (3H, s), 3.425 (3H, s), 3.431 (3H, s), 3.59 (1H, dd, *J* = 7.3, 5.4 Hz), 3.62 (1H, dd, *J* = 11.0, 5.1 Hz), 3.68 (1H, dd, *J* = 11.0, 3.8 Hz), 3.80 (1H, dd, *J* = 5.4, 3.5 Hz), 4.03 (1H, dd, *J* = 11.4, 6.3 Hz), 4.04 (1H, ddd, *J* = 4.1, 2.8, 2.8 Hz), 4.11 (1H, ddd, *J* = 6.6, 6.6, 3.5 Hz), 4.30 (1H, dd, *J* = 11.4, 3.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C −5.6 (CH_3), −5.4 (CH_3), 18.2 (C), 20.8 (CH_3), 25.8 (3 × CH_3), 57.7 (CH_3), 58.0 (CH_3), 63.3 (CH_2), 65.0 (CH_2), 78.1 (CH), 79.3 (CH), 80.7 (CH), 82.6 (CH), 170.7 (C); MS (ESI$^+$) m/z (rel intens) 371 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{16}H_{32}NaO_6Si$ 371.1866, found 371.1868. Anal. Calcd for $C_{16}H_{32}O_6Si$: C, 55.14; H, 9.25. Found: C, 55.29; H, 9.04.

2,5-Anhydro-6-*O*-(*tert*-butyldimethylsilyl)-3,4-di-*O*-methyl-D-altritol (9). To a solution of **8α** (706 mg, 2.03 mmol) in MeOH (32 mL) was added K_2CO_3 (280 mg, 2.03 mmol). The mixture was stirred at room temperature under nitrogen for 2 h, neutralized with Amberlist 15H$^+$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes−EtOAc, 70:30 → 60:40) to give **9** (597 mg, 1.95 mmol, 96%) as a colorless oil: $[\alpha]_D$ +2.1 (*c* 1.16, $CHCl_3$); IR 3442, 2929, 1465, 1253, 1133 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.06 (3H, s), 0.07 (3H, s), 0.90 (9H, s), 3.44 (3H, s), 3.49 (3H, s), 3.64 (1H, dd, *J* = 11.0, 4.4 Hz), 3.66 (1H, dd, *J* = 11.0, 3.8 Hz), 3.74 (1H, dd, *J* = 11.7, 4.7 Hz), 3.79 (1H, dd, *J* = 11.7, 4.7 Hz), 3.87 (1H, dd, *J* = 5.4, 3.5 Hz), 4.06 (1H, dd, *J* = 5.4, 6.6 Hz), 4.11 (1H, ddd, *J* = 3.5, 3.5, 3.5 Hz), 4.19 (1H, ddd, *J* = 6.6, 4.7, 4.7 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C −5.6 (CH_3), −5.4 (CH_3), 18.2 (C), 25.8 (3 × CH_3), 58.1 (CH_3), 59.2 (CH_3), 62.0 (CH_2), 63.7 (CH_2), 79.3 (CH), 80.4 (CH), 80.8 (CH), 82.0 (CH), MS (ESI$^+$) m/z (rel intens) 329 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{14}H_{30}NaO_5Si$ 329.1760, found 329.1762. Anal. Calcd for $C_{14}H_{30}O_5Si$: C, 54.87; H, 9.87. Found: C, 54.74; H, 9.87.

Oxidative HAT of 9. A solution of alcohol **9** (63 mg, 0.206 mmol) in dry CH_2Cl_2 (8.1 mL) containing DIB (73 mg, 0.227 mmol), I_2 (26 mg, 0.103 mmol), and powdered molecular sieves 3 Å (63 mg) was stirred under nitrogen at 27 °C for 1 h while being irradiated with two 80 W tungsten-filament lamps. An excess of solid $Na_2S_2O_3$ was then added and stirring continued until complete disappearance of the iodine color. The reaction mixture was then filtered and concentrated under reduced pressure. Silica gel column chromatography of the reaction residue (hexanes−EtOAc, 90:10 → 50:50) afforded 1-*O*-acetyl-5-*O*-(*tert*-butyldimethylsilyl)-2,3-di-*O*-methyl-β-D-ribofuranose (**11β**) (12.8 mg, 0.038 mmol, 19%), 5-*O*-(*tert*-butyldimethylsilyl)-2,3-di-*O*-methyl-β-D-ribofuranosyl-(1→1)-2,5-anhydro-6-*O*-(*tert*-butyldimethylsilyl)-3,4-di-*O*-methyl-D-altritol (**12β**) (5.2 mg, 0.009 mmol, 9%), 1-*O*-acetyl-5-*O*-(*tert*-butyldimethylsilyl)-2,3-di-*O*-methyl-α-D-ribofuranose (**11α**) (9.9 mg, 0.03 mmol, 15%), and 5-*O*-(*tert*-butyldimethylsilyl)-2,3-di-*O*-methyl-α-D-ribofuranosyl-(1→1)-2,5-anhydro-6-*O*-(*tert*-butyldimethylsilyl)-3,4-di-*O*-methyl-D-altritol (**12α**) (4.5 mg, 0.008 mmol, 8%). Data for compound **11β**: colorless oil; $[\alpha]_D$ +3.0 (*c* 0.96, $CHCl_3$); IR 2933, 1747, 1465, 1373, 1232, 1133, 1098 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 0.06 (3H, s), 0.07 (3H, s), 0.91 (9H, s), 2.05 (3H, s), 3.44 (3H, s), 3.52 (3H, s), 3.70 (1H, dd, *J* = 11.6, 3.8 Hz), 3.80 (1H, dd, *J* = 11.4, 3.5 Hz), 3.80 (1H, dd, *J* = 4.8, 1.0 Hz), 3.96 (1H, dd, *J* = 7.2, 4.7 Hz), 4.09 (1H, ddd, *J* = 7.0, 3.5, 3.5 Hz), 6.14 (1H, d, *J* = 1.1 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C −5.5 (CH_3), −5.4 (CH_3), 18.3 (C), 21.2 (CH_3), 25.9 (3 × CH_3), 58.2 (CH_3), 58.3 (CH_3), 62.7 (CH_2), 78.4 (CH), 81.9 (CH), 82.6 (CH), 98.3 (CH), 169.7 (C); MS (ESI$^+$) m/z (rel intens) 357 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{15}H_{30}NaO_6Si$ 357.1709, found 357.1714. Anal. Calcd for $C_{15}H_{30}O_6Si$: C, 53.86; H, 9.04. Found: C, 53.83; H, 8.95. Data for compound **11α**: colorless oil; $[\alpha]_D$ +44.7 (*c* 0.43, $CHCl_3$); IR 2929, 1747, 1465, 1378, 1241, 1111, 1011 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.06 (3H, s), 0.07 (3H, s), 0.90 (9H, s), 2.14 (3H, s), 3.44 (3H, s), 3.47 (3H, s), 3.63 (1H, dd, *J* = 11.0, 4.7 Hz), 3.70 (1H, dd, *J* = 11.0, 3.2 Hz), 3.86 (1H, dd, *J* = 6.3, 1.9 Hz), 3.88 (1H, dd, *J* = 6.3, 4.1 Hz), 4.28 (1H, ddd, *J* = 4.4, 2.8, 1.6 Hz), 6.34 (1H, d, *J* = 4.4 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C −5.6 (CH_3), −5.4 (CH_3), 18.2 (C), 21.4 (CH_3), 25.8 (3 × CH_3), 58.5 (CH_3), 59.1 (CH_3), 63.6 (CH_2), 78.2 (CH), 80.6 (CH), 84.7 (CH), 94.3 (CH), 170.8 (C); MS (ESI$^+$) m/z (rel intens) 357 (M^++ Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{15}H_{30}NaO_6Si$ 357.1709, found 357.1710. Anal. Calcd for $C_{15}H_{30}O_6Si$: C, 53.86; H, 9.04. Found: C, 54.11; H, 9.23. Data for compound **12β**: colorless oil; $[\alpha]_D$ −2.7 (*c* 0.3, $CHCl_3$); IR 2929, 1464, 1255, 1136, 1107 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.060 (6H, s), 0.063 (3H, s), 0.067 (3H, s), 0.897 (9H, s), 0.899 (9H, s), 3.40 (3H, s), 3.42 (3H, s) 3.47 (3H, s), 3.48 (3H, s), 3.64 (1H, dd, *J* = 11.0, 8.5 Hz), 3.66−3.69 (3H, m), 3.73 (1H, dd, *J* = 10.7, 4.4 Hz), 3.80 (1H, dd, *J* = 4.7, 1.3 Hz), 3.84−3.91 (4H, m), 4.00−4.05 (2H, m), 4.19 (1H, ddd, *J* = 8.5, 5.4, 3.2 Hz), 5.06 (1H, d, *J* = 0.9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C −5.09 (CH_3), −5.02 (CH_3), −4.98 (CH_3), −4.95 (CH_3), 18.66 (C), 18.72 (C), 26.3 (6 × CH_3), 58.5 (CH_3), 58.69 (CH_3), 58.65 (CH_3), 59.9 (CH_3), 63.9 (CH_2), 64.8 (CH_2), 67.7 (CH_2), 79.8 (CH), 80.7 (CH), 81.4 (CH), 81.7 (2 × CH), 82.0 (CH), 82.5 (CH), 105.3 (CH); MS (ESI$^+$) m/z (rel intens) 603 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{27}H_{56}NaO_9Si_2$ 603.3361, found 603.3369. Anal. Calcd for $C_{27}H_{56}O_9Si_2$: C, 55.83; H, 9.72. Found: C, 55.53; H, 9.87. Data for compound **12α**: colorless oil; $[\alpha]_D$ +33.5 (*c* 0.48, $CHCl_3$); IR 2929, 1471, 1257, 1136, 1078 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 0.05 (3H, s), 0.054 (3H, s), 0.06 (3H, s), 0.07 (3H, s), 0.89 (9H, s), 0.90 (9H, s), 3.40 (3H, s), 3.42 (3H, s), 3.47 (3H, s), 3.54 (3H, s), 3.62 (1H, dd, *J* = 10.7, 5.1 Hz), 3.65 (1H, dd, *J* = 11.4, 3.2 Hz), 3.68 (1H, dd, *J* = 6.6, 4.4 Hz), 3.71 (1H, dd, *J* = 10.7, 3.5 Hz), 3.73 (1H, dd, *J* = 10.7, 3.2 Hz), 3.76 (1H, dd, *J* = 6.9, 2.8 Hz), 3.79 (1H, dd, *J* = 10.4, 7.9 Hz), 3.84 (1H, dd, *J* = 10.4, 5.7 Hz), 3.87 (1H, dd, *J* = 6.6, 4.1 Hz), 3.91 (1H, ddd, *J* = 6.6, 3.5, 3.5 Hz), 3.94 (1H, dd, *J* = 4.4, 4.4 Hz), 4.14 (1H, ddd, *J* = 5.1, 3.5, 2.6 Hz), 4.25 (1H, ddd, *J* = 7.6, 5.7, 4.1 Hz), 5.07 (1H, d, *J* = 4.4 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C −5.48 (CH_3), −5.47 (CH_3), −5.35 (CH_3), −5.30 (CH_3), 18.26 (C), 18.32 (C), 25.85 (3 × CH_3), 25.92

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(3 × CH_3), 58.3 (CH_3), 58.4 (CH_3), 58.6 (CH_3), 59.8 (CH_3), 63.1 (CH_2), 63.8 (CH_2), 66.0 (CH_2), 78.1 (CH), 78.6 (CH), 79.2 (CH), 80.4 (CH), 80.9 (CH), 81.4 (CH), 82.9 (CH), 101.2 (CH); MS (ESI^+) m/z (rel intens) 603 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{27}H_{56}NaO_9Si_2$ 603.3361, found 603.3373. Anal. Calcd for $C_{27}H_{56}O_9Si_2$: C, 55.83; H, 9.72. Found: C, 55.98; H, 9.58.

2,5-Anhydro-3,4-di-*O*-methyl-D-altritol (10). To a solution of **9** (200 mg, 0.653 mmol) in dry THF (16.8 mL) was added TBAF/THF 1 M (1.63 mL, 1.63 mmol), and the mixture was stirred at room temperature for 2 h. The reaction was concentrated under reduced pressure and the residue purified by silica gel column chromatography ($CHCl_3$ → $CHCl_3$–MeOH, 95:5) to give **10** (114 mg, 0.59 mmol, 91%) as a colorless oil: $[\alpha]_D$ +2.1 (c 1.16, $CHCl_3$); IR 3412, 2936, 1456, 1144, 1067 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 3.46 (3H, s), 3.52 (3H, s), 3.60 (1H, dd, J = 12.3, 3.8 Hz), 3.77 (1H, dd, J = 12.0, 4.7 Hz), 3.82 (1H, dd, J = 12.0, 3.2 Hz), 3.83 (1H, dd, J = 5.7, 5.7 Hz), 3.84 (1H, dd, J = 11.7, 5.7 Hz), 3.99 (1H, dd, J = 5.1, 5.1 Hz), 4.09 (1H, ddd, J = 6.0, 3.5, 3.5 Hz), 4.18 (1H, ddd, J = 5.4, 5.4, 4.6 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 58.5 (CH_3), 59.7 (CH_3), 61.8 (CH_2), 62.6 (CH_2), 80.2 (CH), 80.4 (CH), 80.9 (CH), 81.1 (CH); MS (ESI^+) m/z (rel intens) 215 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_8H_{16}NaO_5$ 215.0895, found 215.0893. Anal. Calcd for $C_8H_{16}O_5$: C, 49.99; H, 8.39. Found: C, 49.73; H, 8.56.

Oxidative HAT of 10. A solution of alcohol **10** (55 mg, 0.286 mmol) in dry CH_2Cl_2 (11.3 mL) containing DIB (101.3 mg, 0.315 mmol), I_2 (36.3 mg, 0.143 mmol), and powdered molecular sieves 3 Å (55 mg) was stirred under nitrogen at 26 °C for 1 h while being irradiated with two 80 W tungsten-filament lamps. An excess of solid $Na_2S_2O_3$ was then added and stirring continued until complete disappearance of the iodine color. The reaction mixture was then filtered and concentrated under reduced pressure. TLC and ^1H NMR analyses clearly showed that this substrate afforded a complex mixture of fragmentation products that was not studied.

Methyl 5-*O*-(*tert*-Butyldiphenylsilyl)-2-*O*-methyl-α-D-arabinofuranoside (14). To a solution of methyl 2-*O*-methyl-α-D-arabinofuranoside (**13**)[34] (357 mg, 2.0 mmol) in dry DMF (8.2 mL) were added imidazole (341 mg, 5.0 mmol) and *tert*-butyldiphenylsilyl chloride [(TBDPS)Cl] (576 μL, 2.2 mmol) under nitrogen at 0 °C, and the mixture was stirred at that temperature for 1 h. MeOH was then added and the reaction mixture concentrated under reduced pressure. The residue was coevaporated with toluene and purified by column chromatography (hexanes–EtOAc, 9:1 → 85:15) to give the alcohol **14** (826 mg, 1.99 mmol, 99%) as an oil: $[\alpha]_D$ +43.1 (c 0.420, $CHCl_3$); IR 3446, 2936, 1430, 1195, 1046 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.07 (9H, s), 3.35 (3H, s), 3.37 (3H, s), 3.68 (1H, dd, J = 2.5, 1.3 Hz), 3.72 (1H, dd, J = 10.4, 6.3 Hz), 3.85 (1H, dd, J = 10.4, 5.0 Hz), 4.07 (2H, m), 4.86 (1H, d, J = 1.3 Hz), 7.36–7.44 (6H, m), 7.67–7.69 (4H, m); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 19.2 (C), 26.8 (3 × CH_3), 54.9 (CH_3), 57.5 (CH_3), 64.3 (CH_2), 76.4 (CH), 84.5 (CH), 90.2 (CH), 106.8 (CH), 127.68 (2 × CH), 127.70 (2 × CH), 129.7 (2 × CH), 133.3 (2 × C), 135.58 (2 × CH); 135.60 (2 × CH); MS (ESI^+) m/z (rel intens) 439 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{23}H_{32}NaO_5Si$ 439.1917, found 439.1914. Anal. Calcd for $C_{23}H_{32}O_5Si$: C, 66.31; H, 7.74. Found: C, 66.24; H, 7.53.

Methyl 5-*O*-(*tert*-Butyldiphenylsilyl)-2-*O*-methyl-β-D-ribofuranoside (16). To a solution of methyl 2-*O*-methyl-β-D-ribofuranoside (**15**)[35] (449 mg, 2.52 mmol) in dry DMF (10 mL) were added imidazole (428 mg, 6.3 mmol) and (TBDPS)Cl (724 μL, 2.77 mmol) under nitrogen at 0 °C, and the mixture was stirred at that temperature for 0.5 h. Then MeOH was added, and the reaction mixture was concentrated under reduced pressure. The residue was then coevaporated with toluene and purified by column chromatography (hexanes–EtOAc, 85:15) to give the alcohol **16** (970 mg, 2.33 mmol, 92%) as an oil: $[\alpha]_D$ −2.5 (c 0.440, $CHCl_3$); IR 3468, 2933, 1465, 1426, 1111, 1046 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.07 (9H, s), 2.48 (1H, br s), 3.35 (3H, s), 3.51 (3H, s), 3.65 (1H, dd, J = 5.4, 0.9 Hz), 3.74 (1H, dd, J = 11.0, 4.7 Hz), 3.83 (1H, dd, J = 11.0, 4.1 Hz), 3.99 (1H, ddd, J = 4.7, 4.7, 4.7 Hz), 4.31 (1H, dd, J = 5.4, 5.4 Hz), 4.91 (1H, s), 7.36–7.44 (6H, m), 7.69–7.71 (4H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 19.2 (C), 26.8 (3 × CH_3), 55.2 (CH_3), 58.4 (CH_3), 64.6 (CH_2), 70.9 (CH), 84.1 (CH), 84.6 (CH), 105.2 (CH), 127.6 (2 × CH), 127.7 (2 × CH), 129.6 (CH), 129.7 (CH), 133.38 (C), 133.42 (C), 135.61 (2 × CH), 135.62 (2 × CH); MS (ESI^+) m/z (rel intens) 439 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{23}H_{32}NaO_5Si$ 439.1917, found 439.1920. Anal. Calcd for $C_{23}H_{32}O_5Si$: C, 66.31; H, 7.74. Found: C, 66.00; H, 7.78.

Methyl 5-*O*-(*tert*-Butyldiphenylsilyl)-2-*O*-methyl-β-D-*erythro*-pentofuranosid-3-ulose (17). To a solution of alcohol **16** (720 mg, 1.73 mmol) in dry CH_2Cl_2 (40 mL) containing solid $NaHCO_3$ (1.67 g, 19.91 mmol) was added Dess–Martin periodinane (1.10 g, 2.60 mmol) under nitrogen at 0 °C, and the mixture was stirred at room temperature for 1 h. Then the reaction mixture was poured into a saturated solution of $NaHCO_3$ and $Na_2S_2O_3$ and extracted with CH_2Cl_2. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 95:5) to give the ketone **17** (598 mg, 1.44 mmol, 83%) as a colorless oil: $[\alpha]_D$ +16.3 (c 0.560, $CHCl_3$); IR 2933, 2858, 1773, 1465, 1428, 1113 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.04 (9H, s), 3.57 (3H, s), 3.59 (3H, s), 3.80 (1H, dd, J = 5.0, 1.1 Hz), 3.86 (1H, s), 3.87 (1H, s), 4.16 (1H, ddd, J = 3.2, 3.2, 1.1 Hz), 5.04 (1H, d, J = 5.0 Hz), 7.36–7.45 (6H, m), 7.65–7.74 (4H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 19.2 (C), 26.7 (3 × CH_3), 55.9 (CH_3), 58.9 (CH_3), 63.8 (CH_2), 81.2 (CH), 83.6 (CH), 105.0 (CH), 127.68 (2 × CH), 127.74 (2 × CH), 129.7 (CH), 129.8 (CH), 133.86 (C), 133.89 (C), 135.6 (2 × CH), 135.7 (2 × CH), 210.0 (C); MS (ESI^+) m/z (rel intens) 437 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{23}H_{30}NaO_5Si$ 437.1760, found 437.1763. Anal. Calcd for $C_{23}H_{30}O_5Si$: C, 66.63; H, 7.29. Found: C, 66.53; H, 7.19.

Methyl 5-*O*-(*tert*-Butyldiphenylsilyl)-2-*O*-methyl-β-D-xylofuranoside (18). To a solution of ketone **17** (634 mg, 1.531 mmol) in EtOH/H_2O (5.7 mL, 9:1) was added $NaBH_4$ (104 mg, 2.756 mmol), and the mixture was stirred at room temperature for 1 h. After this time the mixture was cooled to 0 °C, solid NH_4Cl was added, and the stirring was continued for 1 h. The mixture was then filtered over Celite and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 90:10) to give in order of elution the alcohol **18** (446 mg, 1.072 mmol, 70%) and the alcohol **16** (89 mg, 0.214 mmol, 14%) described previously. Data for compound **18**: $[\alpha]_D$ −35.1 (c 0.730, $CHCl_3$); IR 3509, 2933, 2858, 1465, 1428, 1111, 1050 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.06 (9H, s), 3.34 (3H, s), 3.44 (3H, s), 3.75 (1H, s), 3.88 (1H, dd, J = 10.7, 5.4 Hz), 4.04 (1H, dd, J = 10.7, 5.7 Hz), 4.24 (1H, d, J = 4.4 Hz), 4.31 (1H, ddd, J = 5.4, 5.4, 5.4 Hz), 4.90 (1H, s), 7.37–7.45 (6H, m), 7.70–7.73 (4H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 19.1 (C), 26.8 (3 × CH_3), 55.3 (CH_3), 57.6 (CH_3), 63.3 (CH_2), 74.2 (CH), 82.5 (CH), 89.2 (CH), 106.8 (CH), 127.7 (4 × CH), 129.7 (CH), 129.8 (CH), 133.09 (C), 133.14 (C), 135.6 (4 × CH); MS (ESI^+) m/z (rel intens) 439 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{23}H_{32}NaO_5Si$ 439.1917, found 439.1916. Anal. Calcd for (%) for $C_{23}H_{32}O_5Si$: C, 66.31; H, 7.74. Found: C, 66.03; H, 7.72.

Methyl 3,5-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-α-D-lyxofuranoside (20). To a solution of methyl α-D-lyxofuranoside (**19**)[36] (960 mg, 5.85 mmol) in dry pyridine (17.4 mL) was added 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (1.94 mL, 6.1 mmol), and the mixture was stirred at room temperature for 1.5 h. After this time water was added and the mixture concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 100:0 → 98:2) to give compound **20** (1928 mg, 4.75 mmol, 81%) as a colorless oil: $[\alpha]_D$ +41.2 (c 0.427, $CHCl_3$); IR 3520, 2947, 2869, 1460, 1096, 1039 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.05 (28H, m), 2.90 (1H, d, J = 9.5 Hz, OH), 3.37 (3H, s), 3.89 (1H, dd, J = 10.1, 4.7 Hz), 3.92 (1H, dd, J = 10.4, 9.8 Hz), 4.10 (1H, ddd, J = 9.5, 5.4, 2.8 Hz), 4.13 (1H, ddd, J = 9.8, 4.7, 3.2 Hz), 4.43 (1H, dd, J = 5.4, 3.2 Hz), 4.79 (1H, d, J = 2.8 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 12.4 (CH), 12.7 (CH), 12.8 (CH), 13.3 (CH), 16.95 (CH_3), 17.00 (CH_3), 17.16 (CH_3), 17.24 (CH_3), 17.27 (CH_3), 17.37 (2 × CH_3), 17.39 (CH_3), 55.6 (CH_3), 59.0 (CH_2), 71.2 (CH), 77.3 (CH), 79.5 (CH), 109.8 (CH); MS (ESI^+) m/z (rel intens) 429 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for

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$C_{18}H_{38}NaO_6Si_2$ 429.2105, found 429.2102. Anal. Calcd for $C_{18}H_{38}O_6Si_2$: C, 53.16; H, 9.42. Found: C, 53.22; H, 9.11.

Methyl 2-*O*-Methyl-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-D-lyxofuranoside (21). To a solution of **20** (1.89 g, 4.65 mmol) in dry acetone (24.2 mL) were added Ag_2O (4.31 g, 18.6 mmol) and methyl iodide (3.67 mL, 58.95 mmol) with stirring at room temperature. After 5 days the mixture was filtered over Celite and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes−EtOAc, 100:0 → 95:5) to give **21** as a colorless oil (800 mg, 1.9 mmol, 41%, 84% brsm) and starting material **20** (972 mg, 2.39 mmol, 51%). Data for compound **21**: $[\alpha]_D$ +54.8 (*c* 0.425, $CHCl_3$); IR 2944, 2869, 1467, 1094, 1054, 1037 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.05 (28H, m), 3.441 (3H, s), 3.443 (3H, s), 3.64 (1H, dd, *J* = 5.4, 4.1 Hz), 3.82 (1H, dd, *J* = 10.1, 4.7 Hz), 3.89 (1H, dd, *J* = 10.1, 10.1 Hz), 4.15 (1H, ddd, *J* = 10.1, 4.7, 2.2 Hz), 4.40 (1H, dd, *J* = 3.8, 2.2 Hz), 4.96 (1H, d, *J* = 5.4 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 12.5 (CH), 12.6 (CH), 13.1 (CH), 13.4 (CH), 17.00 (CH_3), 17.01 (CH_3), 17.1 (CH_3), 17.2 (CH_3), 17.28 (CH_3), 17.33 (CH_3), 17.4 (CH_3), 17.5 (CH_3), 56.5 (CH_3), 58.7 (CH_3), 59.0 (CH_2), 70.1 (CH), 79.6 (CH), 86.6 (CH), 107.6 (CH); MS (ESI^+) *m*/*z* (rel intens) 443 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{19}H_{40}NaO_6Si_2$ 443.2261, found 443.2263. Anal. Calcd for $C_{19}H_{40}O_6Si_2$: C, 54.25; H, 9.58. Found: C, 54.25; H, 9.31.

Methyl 2-*O*-Methyl-α-D-lyxofuranoside (22). To a solution of compound **21** (1038 mg, 2.47 mmol) in dry THF (16.9 mL) was added a 1 M solution of TBAF/THF (6.2 mL, 6.2 mmol), and the mixture was stirred at room temperature for 1.5 h. The reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (hexanes−EtOAc, 50:50 → 0:100) to give diol **22** (434 mg, 2.44 mmol, 99%) as a colorless oil: $[\alpha]_D$ +96.1 (*c* 0.31, $CHCl_3$); IR 3420, 2944, 2836, 1456, 1119, 1042 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 3.36 (3H, s), 3.48 (3H, s), 3.67 (1H, dd, *J* = 5.4, 1.6 Hz), 3.83 (1H, dd, *J* = 12.2, 3.8 Hz), 3.87 (1H, dd, *J* = 12.3, 4.4 Hz), 4.10 (1H, ddd, *J* = 5.7, 4.4, 4.4 Hz), 4.47 (1H, dd, *J* = 5.4, 5.4 Hz), 4.90 (1H, d, *J* = 1.6 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 55.2 (CH_3), 58.8 (CH_3), 61.4 (CH_2), 71.5 (CH), 79.1 (CH), 84.5 (CH), 105.3 (CH); MS (ESI^+) *m*/*z* (rel intens) 201 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_7H_{14}NaO_5$ 201.0739, found 201.0734. Anal. Calcd for $C_7H_{14}O_5$: C, 47.18; H, 7.92. Found: C, 47.42; H, 7.76.

Methyl 5-*O*-(*tert*-Butyldiphenylsilyl)-2-*O*-methyl-α-D-lyxofuranoside (23). To a solution of diol **22** (402 mg, 2.26 mmol) in dry DMF (9.2 mL) were added imidazole (384 mg, 5.6 mmol) and (TBDPS)Cl (649 μL, 2.49 mmol) under nitrogen at 0 °C, and the mixture was stirred at that temperature for 1 h. MeOH was then added, and the reaction mixture was concentrated under reduced pressure. The residue was then coevaporated with toluene and purified by column chromatography (hexanes−EtOAc, 90:10 → 85:15) to give the alcohol **23** (928 mg, 2.23 mmol, 99%) as an oil: $[\alpha]_D$ +52 (*c* 0.54, $CHCl_3$); IR 3498, 2933, 2858, 1471, 1428, 1115, 1052 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.06 (9H, s), 3.39 (3H, s), 3.48 (3H, s), 3.73 (1H, dd, *J* = 5.1, 2.8 Hz), 3.90 (1H, dd, *J* = 10.7, 5.4 Hz), 4.03 (1H, dd, *J* = 10.7, 5.4 Hz), 4.14 (1H, ddd, *J* = 5.4, 5.4, 4.0 Hz), 4.37 (1H, dd, *J* = 5.0, 4.0 Hz), 4.93 (1H, d, *J* = 2.8 Hz), 7.36−7.44 (6H, m), 7.39−7.73 (4H, m); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 19.2 (C), 26.7 (3 × CH_3), 55.5 (CH_3), 58.6 (CH_3), 62.4 (CH_2), 70.6 (CH), 80.6 (CH), 86.2 (CH), 106.6 (CH), 127.62 (2 × CH), 127.64 (2 × CH), 129.6 (2 × CH), 133.3 (C), 133.4 (C), 135.6 (2 × CH), 135.7 (2 × CH); MS (ESI^+) *m*/*z* (rel intens) 439 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{23}H_{32}NaO_5Si$ 439.1917, found 439.1919. Anal. Calcd for $C_{23}H_{32}O_5Si$: C, 66.31; H, 7.74. Found: C, 66.30; H, 7.63.

General Procedure for the Glycosylations. To a stirred 0.12 M solution of trichloroacetimidate (2.3 equiv) and alcohol acceptor (1 equiv) in dry CH_2Cl_2 containing freshly activated powdered 3 Å molecular sieves (50 wt % with respect to the acceptor) was added dropwise at 0 °C a 0.2 M solution of (TMS)OTf/CH_2Cl_2 (0.025 equiv), and the mixture was stirred at that temperature for ca. 2 h. The reaction mixture was then poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes−EtOAc mixtures).

Methyl 2,3,5-Tri-*O*-acetyl-α-D-arabinofuranosyl-(1→3)-5-*O*-(*tert*-butyldiphenylsilyl)-2-*O*-methyl-α-D-arabinofuranoside (25). Compound **25** was prepared from **24**[28,29a] (761 mg, 1.808 mmol) and **14** (327 mg, 0.786 mmol) following the general procedure. The residue was purified by column chromatography (hexanes−EtOAc, 85:15 → 75:25) to give the disaccharide **25** (503 mg, 0.747 mmol, 95%) as a colorless oil: $[\alpha]_D$ +87.4 (*c* 0.310, $CHCl_3$); IR 2933, 1757, 1745, 1428, 1369, 1228, 1113 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.06 (9H, s), 1.98 (3H, s), 2.04 (3H, s), 2.10 (3H, s), 3.38 (3H, s), 3.41 (3H, s), 3.80 (1H, dd, *J* = 3.5, 1.6 Hz), 3.84 (2H, br d, *J* = 3.8 Hz), 4.06−4.10 (2H, m), 4.13 (1H, dd, *J* = 11.7, 5.4 Hz), 4.25 (1H, dd, *J* = 6.6, 3.5 Hz), 4.26 (1H, dd, *J* = 11.7, 3.5 Hz), 4.89 (1H, d, *J* = 1.6 Hz), 4.97 (1H, ddd, *J* = 5.1, 1.6, 0.6 Hz), 5.09 (1H, d, *J* = 1.6 Hz), 5.18 (1H, s), 7.35−7.44 (6H, m), 7.69−7.71 (4H, m); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 19.3 (C), 20.63 (CH_3), 20.64 (CH_3), 20.71 (CH_3), 26.7 (3 × CH_3), 54.9 (CH_3), 57.6 (CH_3), 63.1 (CH_2), 63.2 (CH_2), 76.9 (CH), 79.7 (CH), 80.4 (CH), 81.4 (CH), 81.8 (CH), 90.1 (CH), 104.7 (CH), 106.9 (CH), 127.57 (2 × CH), 127.64 (2 × CH), 129.59 (CH), 129.66 (CH), 133.42 (C), 133.49 (C), 135.58 (2 × CH), 135.66 (2 × CH), 169.6 (C), 170.0 (C), 170.5 (C); MS (ESI^+) *m*/*z* (rel intens) 697 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{34}H_{46}NaO_{12}Si$ 697.2656, found 697.2650. Anal. Calcd for $C_{34}H_{46}O_{12}Si$: C, 60.52; H, 6.87. Found C, 60.23; H, 6.57.

Methyl 2,3,5-Tri-*O*-methyl-α-D-arabinofuranosyl-(1→3)-5-*O*-(*tert*-butyldiphenylsilyl)-2-*O*-methyl-α-D-arabinofuranoside (26). To a solution of compound **25** (452 mg, 0.671 mmol) in MeOH (32 mL) was added K_2CO_3 (278 mg, 2 mmol), and the mixture was stirred at room temperature for 2 h, then neutralized with Amberlyst 15 H^+ ion-exchange resin for 1 h, filtered, and concentrated. To the crude residue (550 mg) in dry DMF (8 mL) was added NaH, 60% dispersion in mineral oil (161 mg, 4 mmol), and the mixture was stirred at 0 °C under nitrogen until all hydrogen evolution had ceased. Then an excess of methyl iodide (313 μL, 5 mmol) was added and stirring continued at room temperature for 3 h. Excess reagent was destroyed by addition of MeOH, and the mixture was concentrated under high vacuum. Column chromatography (hexanes−EtOAc, 85:15) of the residue afforded **26** (386.5 mg, 0.655 mmol, 98%) as a colorless oil: $[\alpha]_D$ +100.0 (*c* 0.470, $CHCl_3$); IR 2929, 1428, 1188, 1112 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (hydrogens at C5′a and C5′b have very similar chemical shifts, and as a consequence, the coupled hydrogen at C4′ appears as a complex signal by virtual coupling; the data for hydrogens at C4′ and C5′ shown here have been calculated by iterative simulation using DAISY) δ_H 1.06 (9H, s), 3.32 (3H, s), 3.37 (3H, s), 3.38 (3H, s), 3.39 (3H, s), 3.40 (3H, s), 3.44 (2H, br d, *J* = 4.2 Hz), 3.63 (1H, dd, *J* = 6.9, 3.2 Hz), 3.75 (1H, dd, *J* = 3.2, 1.3 Hz), 3.76 (1H, dd, *J* = 3.5, 1.6 Hz), 3.85 (1H, dd, *J* = 11.3, 5.4 Hz, H-5′a), 3.86 (1H, dd, *J* = 11.3, 2.8 Hz, H-5′b), 3.91 (1H, ddd, *J* = 6.6, 4.1, 4.1 Hz), 4.09 (1H, ddd, *J* = 6.6, 4.4, 3.5 Hz, H-4′), 4.21 (1H, dd, *J* = 6.6, 3.2 Hz), 4.88 (1H, d, *J* = 1.6 Hz), 5.12 (1H, br s), 7.34−7.41 (6H, m), 7.70−7.72 (4H, m); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 19.3 (C), 26.7 (3 × CH_3), 54.8 (CH_3), 57.5 (2 × CH_3), 58.0 (CH_3), 59.3 (CH_3), 63.5 (CH_2), 71.8 (CH_2), 79.5 (CH), 80.6 (CH), 82.3 (CH), 85.3 (CH), 90.0 (CH), 90.4 (CH), 104.8 (CH), 106.9 (CH), 127.5 (2 × CH), 127.6 (2 × CH), 129.48 (CH), 129.51 (CH), 133.66 (C), 133.69 (C), 135.66 (2 × CH), 135.70 (2 × CH); MS (ESI^+) *m*/*z* (rel intens) 613 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{31}H_{46}NaO_9Si$ 613.2809, found 613.2819. Anal. Calcd for $C_{31}H_{46}O_9Si$: C, 63.02; H, 7.85. Found C, 63.20; H, 7.65.

Methyl 2,3,5-Tri-*O*-methyl-α-D-arabinofuranosyl-(1→3)-2-*O*-methyl-α-D-arabinofuranoside (42). To a solution of disaccharide **26** (338.5 mg, 0.574 mmol) in dry THF (14.7 mL) was added dropwise a 1 M solution of Bu_4NF/THF (1.43 mL, 1.43 mmol), and the mixture was stirred at room temperature for 4.5 h. The solvent was then removed in vacuo and the residue purified by column chromatography (hexanes−EtOAc, 1:1 → 0:1) to give the alcohol **42** (190 mg, 0.540 mmol, 94%) as a colorless oil: $[\alpha]_D$ +157.0 (*c* 1.120, $CHCl_3$); IR 3494, 2933, 2828, 1456, 1109, 1052 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 3.357 (3H, s), 3.360 (3H, s), 3.37 (6H,

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s), 3.38 (3H, s), 3.50 (1H, dd, J = 10.4, 5.4 Hz), 3.55 (1H, dd, J = 10.7, 3.8 Hz), 3.56 (1H, dd, J = 6.6, 3.2 Hz), 3.73 (1H, dd, J = 12.3, 3.8 Hz), 3.74 (1H, dd, J = 3.2, 1.6 Hz), 3.74 (1H, dd, J = 3.5, 1.9 Hz), 3.82 (1H, dd, J = 12.0, 3.2 Hz), 4.02 (2H, m), 4.06 (1H, dd, J = 6.6, 3.2 Hz), 4.84 (1H, d, J = 1.3 Hz), 5.10 (1H, br s); ^{1}H NMR (500 MHz, C_6D_6 + D_2O) δ_H 3.05 (3H, s), 3.07 (3H, s), 3.072 (3H, s), 3.13 (3H, s), 3.15 (3H, s), 3.40 (2H, m), 3.68 (1H, dd, J = 6.9, 3.2 Hz), 3.86 (1H, dd, J = 3.2, 1.3 Hz), 3.90 (2H, m), 3.96 (1H, dd, J = 3.2, 1.3 Hz), 4.28 (2H, m), 4.43 (1H, dd, J = 6.6, 3.2 Hz), 4.88 (1H, br s), 5.30 (1H, br s);^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 54.8 (CH_3), 57.51 (CH_3), 57.54 (CH_3), 58.0 (CH_3), 59.3 (CH_3), 62.0 (CH_2), 72.3 (CH_2), 80.2 (CH), 80.7 (CH), 82.0 (CH), 85.4 (CH), 89.7 (CH), 90.4 (CH), 105.4 (CH), 106.7 (CH); MS (ESI$^+$) m/z (rel intens) 375 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{15}H_{28}NaO_9$ 375.1631, found 375.1628. Anal. Calcd for $C_{15}H_{28}O_9$: C, 51.13; H, 8.01. Found C, 51.48; H, 7.95.

Methyl 2,3,5-Tri-*O*-acetyl-α-D-arabinofuranosyl-(1→3)-5-*O*-(*tert*-butyldiphenylsilyl)-2-*O*-methyl-β-D-ribofuranoside (27). Compound **27** was prepared from **24**[28,29a] (327 mg, 0.768 mmol) and **16** (139 mg, 0.334 mmol) following the general procedure. The residue was purified by column chromatography (hexanes−EtOAc, 80:20) to give the disaccharide **27** (216 mg, 0.320 mmol, 96%) as a colorless oil: $[\alpha]_D$ +49.0 (c 0.390, $CHCl_3$); IR 2933, 1747, 1430, 1371, 1228, 1044 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.07 (9H, s), 1.98 (3H, s), 2.04 (3H, s), 2.10 (3H, s), 3.36 (3H, s), 3.48 (3H, s), 3.68 (1H, dd, J = 11.4, 4.5 Hz), 3.72 (1H, dd, J = 4.8, 1.6 Hz), 3.84 (1H, dd, J = 11.4, 3.4 Hz), 4.09−4.19 (3H, m), 4.29 (1H, dd, J = 11.4, 2.9 Hz), 4.48 (1H, dd, J = 6.6, 4.5 Hz), 4.93 (1H, d, J = 1.6 Hz), 4.96 (1H, d, J = 4.8, 1.6 Hz), 5.13 (1H, d, J = 1.3 Hz), 5.15 (1H, s), 7.35−7.44 (6H, m), 7.68−7.71 (4H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 19.2 (C), 20.6 (CH_3), 20.68 (CH_3), 20.70 (CH_3), 26.8 (3 × CH_3), 55.8 (CH_3), 58.4 (CH_3), 63.1 (CH_2), 63.9 (CH_2), 73.9 (CH), 76.9 (CH), 80.9 (CH), 81.1 (CH), 81.9 (CH), 82.2 (CH), 104.8 (CH), 106.0 (CH), 127.6 (2 × CH), 127.7 (2 × CH), 129.6 (CH), 129.7 (CH), 133.3 (C), 133.4 (C), 135.6 (4 × CH), 169.4 (C), 170.0 (C), 170.5 (C); MS (ESI$^+$) m/z (rel intens) 697 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{34}H_{46}NaO_{12}Si$ 697.2656, found 697.2657. Anal. Calcd for $C_{34}H_{46}O_{12}Si$: C, 60.52; H, 6.87. Found C, 60.30; H, 6.92.

Methyl 2,3,5-Tri-*O*-methyl-α-D-arabinofuranosyl-(1→3)-5-*O*-(*tert*-butyldiphenylsilyl)-2-*O*-methyl-β-D-ribofuranoside (28). To a solution of compound **27** (405 mg, 0.601 mmol) in MeOH (28.5 mL) was added K_2CO_3 (249 mg, 1.803 mmol), and the mixture was stirred at room temperature for 2 h, then neutralized with Amberlyst 15 H^+ ion-exchange resin for 1 h, filtered, and concentrated. To the crude residue in dry DMF (7.2 mL) was added NaH, 60% dispersion in mineral oil (144 mg, 3.606 mmol), and the mixture was stirred at 0 °C under nitrogen until all hydrogen evolution had ceased. Then an excess of methyl iodide (281 μL, 4.507 mmol) was added and stirring continued at room temperature for 3 h. Excess reagent was destroyed by addition of MeOH, and the mixture was concentrated under high vacuum. Column chromatography (hexanes−EtOAc, 80:20) of the residue afforded **28** (269 mg, 0.456 mmol, 76%) as a colorless oil: $[\alpha]_D$ +54.0 (c 0.715, $CHCl_3$); IR 2933, 2828, 1463, 1111, 1054 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.06 (9H, s), 3.33 (3H, s), 3.35 (3H, s), 3.38 (3H, s), 3.42 (3H, s), 3.46 (3H, s), 3.47 (1H, dd, J = 10.7, 4.7 Hz), 3.50 (1H, dd, J = 10.7, 3.5 Hz), 3.64 (1H, dd, J = 7.2, 3.5 Hz), 3.71 (1H, dd, J = 11.4, 4.7 Hz), 3.75 (1H, dd, J = 4.7, 1.6 Hz), 3.80 (1H, dd, J = 3.5, 0.9 Hz), 3.82 (1H, dd, J = 11.4, 3.5 Hz), 3.99 (1H, ddd, J = 7.6, 4.4, 4.4 Hz), 4.16 (1H, ddd, J = 6.3, 4.4, 3.5 Hz), 4.46 (1H, dd, J = 6.3, 4.7 Hz), 4.94 (1H, d, J = 1.6 Hz), 5.08 (1H, s), 7.35−7.43 (6H, m), 7.70−7.72 (4H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 19.3 (C), 26.8 (3 × CH_3), 55.3 (CH_3), 57.5 (CH_3), 57.9 (CH_3), 58.1 (CH_3), 59.3 (CH_3), 64.4 (CH_2), 71.8 (CH_2), 73.5 (CH), 80.5 (CH), 82.4 (CH), 82.6 (CH), 85.3 (CH), 90.1 (CH), 104.8 (CH), 105.8 (CH), 127.60 (2 × CH), 127.64 (2 × CH), 129.5 (CH), 129.6 (CH), 133.6 (2 × C), 135.65 (2 × CH), 135.67 (2 × CH); MS (ESI$^+$) m/z (rel intens) 613 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{31}H_{46}NaO_9Si$ 613.2809, found 613.2803. Anal. Calcd for $C_{31}H_{46}O_9Si$: C, 63.02; H, 7.85. Found C, 63.39; H, 7.86.

Methyl 2,3,5-Tri-*O*-methyl-α-D-arabinofuranosyl-(1→3)-2-*O*-methyl-β-D-ribofuranoside (44). To a solution of disaccharide **28** (269 mg, 0.456 mmol) in dry THF (11.7 mL) was added dropwise a 1 M solution of Bu_4NF/THF (1.14 mL, 1.14 mmol), and the mixture was stirred at room temperature for 2 h. The solvent was then removed in vacuo and the residue purified by column chromatography (hexanes−EtOAc, 10:90) to give the alcohol **44** (156 mg, 0.443 mmol, 97%) as a colorless oil: $[\alpha]_D$ +78.3 (c 0.650, $CHCl_3$); IR 3490, 2929, 2828, 1456, 1107, 1052 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 3.39 (3H, s), 3.397 (3H, s), 3.403 (3H, s), 3.41 (3H, s), 3.48 (3H, s), 3.53 (1H, dd, J = 10.7, 5.7 Hz), 3.57−3.61 (2H, m), 3.65 (1H, dd, J = 11.7, 4.1 Hz), 3.73 (1H, d, J = 5.1 Hz), 3.77 (1H, dd, J = 12.0, 3.5 Hz), 3.81 (1H, d, J = 2.8 Hz), 4.07 (1H, ddd, J = 6.0, 6.0, 3.5 Hz), 4.16 (1H, ddd, J = 6.9, 3.8, 3.8 Hz), 4.38 (1H, dd, J = 6.9, 5.0 Hz), 4.90 (1H, s), 5.07 (1H, s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 55.5 (CH_3), 57.5 (CH_3), 57.9 (CH_3), 58.3 (CH_3), 59.3 (CH_3), 63.2 (CH_2), 72.3 (CH_2), 74.3 (CH), 80.9 (CH), 82.4 (CH), 82.6 (CH), 85.5 (CH), 89.6 (CH), 105.0 (CH), 106.1 (CH); MS (ESI$^+$) m/z (rel intens) 375 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{15}H_{28}NaO_9$ 375.1631, found 375.1629. Anal. Calcd for $C_{15}H_{28}O_9$: C, 51.13; H, 8.01. Found C, 51.08; H, 8.05.

Methyl 2,3,5-Tri-*O*-acetyl-α-L-arabinofuranosyl-(1→3)-5-*O*-(*tert*-butyldiphenylsilyl)-2-*O*-methyl-α-D-lyxofuranoside (30). Compound **30** was prepared from **29**[29] (850 mg, 2.02 mmol) and **23** (365 mg, 0.878 mmol) following the general procedure. The residue was purified by column chromatography (hexanes−EtOAc, 85:15 → 75:25) to give the disaccharide **30** (587 mg, 0.871 mmol, 99%) as a colorless oil: $[\alpha]_D$ −38.7 (c 0.23, $CHCl_3$); IR 2936, 2858, 1758, 1747, 1734, 1430, 1373, 1228, 1046 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.05 (9H, s), 1.78 (3H, s), 2.05 (3H, s), 2.07 (3H, s), 3.40 (3H, s), 3.41 (3H, s), 3.70 (1H, dd, J = 3.8, 3.8 Hz), 3.86 (1H, dd, J = 11.0, 6.6 Hz), 3.93 (1H, dd, J = 10.7, 5.4 Hz), 4.05 (1H, ddd, J = 5.4, 3.8, 3.8 Hz), 4.08 (1H, dd, J = 11.7, 5.4 Hz), 4.20 (1H, ddd, J = 6.6, 5.7, 3.8 Hz), 4.27 (1H, dd, J = 11.7, 3.5 Hz), 4.42 (1H, dd, J = 4.1, 4.1 Hz), 4.87 (1H, ddd, J = 4.1, 0.9, 0.9 Hz), 4.95 (1H, d, J = 3.8 Hz), 5.08 (1H, d, J = 1.2 Hz), 5.30 (1H, br s), 7.34−7.42 (6H, m), 7.65−7.69 (4H, m); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 19.2 (C), 20.3 (CH_3), 20.7 (2 × CH_3), 26.8 (3 × CH_3), 55.8 (CH_3), 58.7 (CH_3), 62.7 (CH_2), 63.2 (CH_2), 73.4 (CH), 77.1 (CH), 79.9 (CH), 80.7 (CH), 81.2 (CH), 86.8 (CH), 105.1 (CH), 106.8 (CH), 127.67 (2 × CH), 127.68 (2 × CH), 129.69 (CH), 129.72 (CH), 133.5 (C), 133.8 (C), 135.5 (2 × CH), 135.6 (2 × CH), 169.1 (C), 170.0 (C), 170.4 (C); MS (ESI$^+$) m/z (rel intens) 697 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{34}H_{46}NaO_{12}Si$ 697.2656, found 697.2657. Anal. Calcd for $C_{34}H_{46}O_{12}Si$: C, 60.52; H, 6.87. Found C, 60.41; H, 6.60.

Methyl 2,3,5-Tri-*O*-methyl-α-L-arabinofuranosyl-(1→3)-5-*O*-(*tert*-butyldiphenylsilyl)-2-*O*-methyl-α-D-lyxofuranoside (31). To a solution of compound **30** (550 mg, 0.816 mmol) in MeOH (39 mL) was added K_2CO_3 (338 mg, 2.45 mmol), and the mixture was stirred at room temperature for 2 h, then neutralized with Amberlyst 15 H^+ ion-exchange resin for 1 h, filtered, and concentrated. To the crude residue (627 mg) in dry DMF (9.7 mL) was added NaH, 60% dispersion in mineral oil (196 mg, 4.9 mmol), and the mixture was stirred at 0 °C under nitrogen until all hydrogen evolution had ceased. Then an excess of methyl iodide (381 μL, 6.12 mmol) was added and stirring continued at room temperature for 3 h. Excess reagent was destroyed by addition of MeOH, and the mixture was concentrated under high vacuum. Column chromatography (hexanes−EtOAc, 85:15) of the residue afforded **31** (459 mg, 0.778 mmol, 95%) as a colorless oil: $[\alpha]_D$ −27.5 (c 0.335, $CHCl_3$); IR 2933, 1471, 1191, 1115, 1046 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.05 (9H, s), 3.27 (3H, s), 3.32 (3H, s), 3.36 (3H, s), 3.39 (1H, dd, J = 10.7, 5.1 Hz), 3.402 (3H, s), 3.404 (3H, s), 3.41 (1H, dd, J = 10.4, 3.8 Hz), 3.53 (1H, dd, J = 6.3, 2.5 Hz), 3.68 (1H, dd, J = 4.1, 4.1 Hz), 3.70 (1H, dd, J = 2.8, 0.9 Hz), 3.86 (1H, dd, J = 11.0, 6.6 Hz), 3.91 (1H, ddd, J = 6.6, 5.1, 3.8 Hz), 3.97 (1H, dd, J = 11.0, 4.4 Hz), 4.21 (1H, ddd, J = 6.9, 4.7, 4.7 Hz), 4.40 (1H, dd, J = 4.1, 4.1 Hz), 4.93 (1H, d, J = 3.8 Hz), 5.18 (1H, br s), 7.34−7.42 (6H, m), 7.67−7.71 (4H, m); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 19.3 (C), 26.9 (3 × CH_3), 55.7 (CH_3), 57.4 (CH_3), 57.7 (CH_3), 58.6 (CH_3), 59.2 (CH_3), 63.3 (CH_2), 72.2 (CH_2), 73.1 (CH), 80.4 (CH), 80.7 (CH), 85.3 (CH), 87.0 (CH), 89.6 (CH), 105.0 (CH), 106.7 (CH), 127.5 (2 × CH), 127.6 (2 × CH), 129.5 (2 ×

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CH), 133.9 (C), 134.1 (C), 135.6 (2 × CH), 135.7 (2 × CH); MS (ESI$^+$) m/z (rel intens) 613 (M$^+$ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{31}H_{46}NaO_9Si$ 613.2809, found 613.2808. Anal. Calcd for $C_{31}H_{46}O_9Si$: C, 63.02; H, 7.85. Found C, 62.96; H, 7.72.

Methyl 2,3,5-Tri-*O*-methyl-α-L-arabinofuranosyl-(1→3)-2-*O*-methyl-α-D-lyxofuranoside (47). To a solution of disaccharide **31** (389 mg, 0.659 mmol) in dry THF (16.9 mL) was added dropwise a 1 M solution of Bu_4NF/THF (1.65 mL, 1.65 mmol), and the mixture was stirred at room temperature for 3 h. The solvent was then removed in vacuo and the residue purified by column chromatography (hexanes−EtOAc, 1:1 → 0:1) to give the alcohol **47** (209 mg, 0.594 mmol, 90%) as a colorless oil: $[\alpha]_D$ −67 (c 0.215, $CHCl_3$); IR 3498, 2936, 2832, 1456, 1113, 1042 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.10 (1H, br dd, J = 6.6, 6.6 Hz, OH), 3.38 (3H, s), 3.395 (3H, s), 3.399 (3H, s), 3.41 (3H, s), 3.45 (3H, s), 3.51 (2H, d, J = 5.7 Hz), 3.57 (1H, dd, J = 4.7, 1.8 Hz), 3.71 (1H, dd, J = 5.1, 2.5 Hz), 3.73 (1H, m), 3.80 (1H, m), 3.82 (1H, dd, J = 1.9, 0.6 Hz), 4.15 (1H, ddd, J = 5.4, 5.4, 5.4 Hz), 4.18 (1H, ddd, J = 7.3, 5.7, 4.1 Hz), 4.60 (1H, dd, J = 5.4, 5.4 Hz), 4.96 (1H, d, J = 2.5 Hz), 5.20 (1H, s); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 55.4 (CH_3), 57.5 (CH_3), 57.8 (CH_3), 58.6 (CH_3), 59.3 (CH_3), 61.0 (CH_2), 72.9 (CH_2), 74.0 (CH), 78.2 (CH), 82.2 (CH), 84.6 (CH), 85.2 (CH), 88.1 (CH), 104.9 (CH), 106.1 (CH); MS (ESI$^+$) m/z (rel intens) 375 (M$^+$ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{15}H_{28}NaO_9$ 375.1631, found 375.1628. Anal. Calcd for $C_{15}H_{28}O_9$: C, 51.13; H, 8.01. Found C, 51.29; H, 7.86.

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-5-*O*-(*tert*-butyldiphenylsilyl)-2-*O*-methyl-β-D-xylofuranoside (33). Compound **33** was prepared from **32**[30] (959 mg, 2.215 mmol) and **18** (384 mg, 0.923 mmol) following the general procedure. The residue was purified by column chromatography (hexanes−EtOAc, 85:15) to give the disaccharide **33** (590 mg, 0.857 mmol, 93%) as a colorless oil: $[\alpha]_D$ −67.2 (c 0.360, $CHCl_3$); IR 2936, 2858, 1751, 1432, 1371, 1224, 1052 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.07 (9H, s), 1.13 (3H, d, J = 6.1 Hz), 1.91 (3H, s), 2.00 (3H, s), 2.15 (3H, s), 3.33 (3H, s), 3.41 (3H, s), 3.75 (1H, dd, J = 1.6, 1.6 Hz), 3.82 (1H, dd, J = 10.6, 5.0 Hz), 3.97 (1H, dddd, J = 9.5, 6.1, 6.1, 6.1 Hz), 4.10 (1H, dd, J = 10.6, 6.6 Hz), 4.23−4.28 (2H, m), 4.82 (1H, d, J = 1.6 Hz), 4.92 (1H, d, J = 1.6 Hz), 5.04 (1H, dd, J = 9.8, 9.8 Hz), 5.24 (1H, dd, J = 3.5, 1.6 Hz), 5.30 (1H, dd, J = 10.1, 3.4 Hz), 7.36−7.42 (6H, m), 7.69−7.72 (4H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 17.6 (CH_3), 19.2 (C), 20.7 (2 × CH_3), 20.9 (CH_3), 27.0 (3 × CH_3), 55.5 (CH_3), 57.8 (CH_3), 62.1 (CH_2), 66.9 (CH), 68.9 (CH), 69.9 (CH), 71.1 (CH), 76.5 (CH), 80.9 (CH), 87.2 (CH), 95.3 (CH), 107.3 (CH), 127.7 (4 × CH), 129.6 (CH), 129.7 (CH), 133.4 (C), 133.6 (C), 135.5 (4 × CH), 169.54 (C), 169.96 (C), 170.05 (C); MS (ESI$^+$) m/z (rel intens) 711 (M$^+$ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{35}H_{48}NaO_{12}Si$ 711.2813, found 711.2819. Anal. Calcd for $C_{35}H_{48}O_{12}Si$: C, 61.03; H, 7.02. Found C, 61.12; H, 7.03.

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-methyl-β-D-xylofuranoside (50). To a solution of disaccharide **33** (590 mg, 0.858 mmol) in dry THF (21.9 mL) was added dropwise a 1 M solution of Bu_4NF/THF (3.0 mL, 3.0 mmol), and the mixture was stirred at room temperature for 5 h. The solvent was then removed in vacuo and the residue purified by column chromatography (hexanes−EtOAc, 40:60) to give the alcohol **50** (326 mg, 0.724 mmol, 84%) as a colorless oil: $[\alpha]_D$ −75.3 (c 0.933, $CHCl_3$); IR 3494, 2936, 2832, 1749, 1373, 1226, 1048 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.23 (3H, d, J = 6.3 Hz), 1.99 (3H, s), 2.05 (3H, s), 2.15 (3H, s), 3.40 (3H, s), 3.44 (3H, s), 3.78−3.83 (2H, m), 3.858 (1H, dddd, J = 10.1, 6.4, 6.4, 6.4 Hz), 3.860 (1H, dd, J = 3.5, 2.2 Hz), 4.31 (1H, ddd, J = 6.9, 6.9, 4.7 Hz), 4.33 (1H, dd, J = 6.9, 3.5 Hz), 4.85 (1H, d, J = 2.2 Hz), 4.94 (1H, d, J = 1.9 Hz), 5.07 (1H, dd, J = 9.8, 9.8 Hz), 5.23 (1H, dd, J = 9.8, 3.5 Hz), 5.25 (1H, dd, J = 3.5, 1.9 Hz); ^{1}H NMR (500 MHz, C_6D_6) δ_H 5.70 (1H, dd, J = 10.1, 3.5 Hz), 5.62 (1H, dd, J = 3.2, 1.9 Hz), 5.53 (1H, dd, J = 10.1, 10.1 Hz), 5.18 (1H, d, J = 1.9 Hz), 4.80 (1H, d, J = 1.9 Hz), 4.36 (1H, dd, J = 6.6, 3.8 Hz), 4.23 (1H, ddd, J = 6.3, 5.1, 5.1 Hz), 4.12 (1H, dddd, J = 9.8, 6.3, 6.3, 6.3 Hz), 3.96 (1H, dd, J = 3.8, 1.9 Hz), 3.85 (1H, dd, J = 11.7, 5.4 Hz), 3.80 (1H, dd, J = 11.7, 5.4), 3.12 (3H, s), 3.06(3H, s), 1.69 (3H, s), 1.66 (3H, s), 1.61, (3H, s), 1.24 (3H, d, J = 6.0 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 17.5 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 20.9 (CH_3), 55.7 (CH_3), 57.9 (CH_3), 62.0 (CH_2), 67.3 (CH), 68.8 (CH), 69.8 (CH), 70.9 (CH), 79.1 (CH), 80.5 (CH), 88.6 (CH), 96.4 (CH), 107.6 (CH), 169.8 (C), 169.9 (C), 170.1 (C); MS (ESI$^+$) m/z (rel intens) 473 (M$^+$ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{19}H_{30}NaO_{12}$ 473.1635, found 473.1639. Anal. Calcd for $C_{19}H_{30}O_{12}$: C, 50.66; H, 6.71. Found C, 50.58; H, 6.58.

Methyl 2,3,5-Tri-*O*-acetyl-α-D-arabinofuranosyl-(1→4)-6-*O*-(*tert*-butyldiphenylsilyl)-2,3-di-*O*-methyl-α-D-glucopyranoside (35). Compound **35** was prepared from **24**[28,29a] (425 mg, 0.98 mmol) and **34**[11a] (101 mg, 0.22 mmol) following the general procedure. The residue was purified by column chromatography (hexanes−EtOAc, 7:3) to give the disaccharide **35** (160 mg, 0.22 mmol, 99%) as a colorless oil: $[\alpha]_D$ +83.6 (c 0.420, $CHCl_3$); IR 2933, 2855, 1745, 1369, 1223, 1043 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.05 (9H, s), 1.96 (3H, s), 1.97 (3H, s), 2.07 (3H, s), 3.19 (1H, dd, J = 9.5, 3.7 Hz), 3.43 (3H, s), 3.52 (3H, s), 3.54−3.59 (2H, m), 3.55 (3H, s), 3.68 (1H, m), 3.79 (1H, dd, J = 11.1, 6.1 Hz), 3.83 (1H, m), 3.86 (1H, dd, J = 11.1, 2.1 Hz), 3.96 (1H, dd, J = 11.9, 5.0 Hz), 4.07 (1H, dd, J = 4.0, 11.9 Hz), 4.84 (1H, d, J = 3.7 Hz), 4.92 (1H, ddd, J = 4.8, 1.6, 0.5 Hz), 5.07 (1H, dd, J = 1.6, 0.5 Hz), 5.45 (1H, s), 7.33−7.42 (6H, m), 7.68−7.70 (4H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 19.2 (C), 20.59 (CH_3), 20.62 (CH_3), 20.7 (CH_3), 26.7 (3 × CH_3), 54.8 (CH_3), 58.9 (CH_3), 60.9 (CH_3), 63.0 (CH_2), 63.2 (CH_2), 70.8 (CH), 73.8 (CH), 76.9 (CH), 80.7 (CH), 81.0 (CH), 82.3 (CH), 83.6 (CH), 97.0 (CH), 106.3 (CH), 127.5 (2 × CH), 127.6 (2 × CH), 129.6 (2 × CH), 133.56 (C), 133.64 (C), 135.6 (2 × CH), 135.7 (2 × CH), 169.3 (C), 169.9 (C), 170.4 (C); MS (ESI$^+$) m/z (rel intens) 741 (M$^+$ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{36}H_{50}NaO_{13}Si$ 741.2918, found 741.2938. Anal. Calcd for $C_{36}H_{50}O_{13}Si$: C, 60.15; H, 7.01. Found C, 59.98; H, 6.83.

Methyl 2,3,5-Tri-*O*-methyl-α-D-arabinofuranosyl-(1→4)-6-*O*-(*tert*-butyldiphenylsilyl)-2,3-di-*O*-methyl-α-D-glucopyranoside (36). To a solution of compound **35** (450 mg, 0.627 mmol) in MeOH (30 mL) was added K_2CO_3 (258 mg, 1.88 mmol), and the mixture was stirred at room temperature for 2 h, then neutralized with Dowex (50 × 8) H$^+$ ion-exchange resin for 1 h, filtered, and concentrated. To the crude residue in dry DMF (7.5 mL) was added NaH, 55% dispersion in mineral oil (164 mg, 3.76 mmol), and the mixture was stirred at 0 °C under nitrogen until all hydrogen evolution had ceased. Then an excess of methyl iodide (293 μL, 4.70 mmol) was added and stirring continued at this temperature for 3 h. Excess reagent was destroyed by addition of MeOH, and the mixture was concentrated under high vacuum. Column chromatography (hexanes−EtOAc, 70:30) of the residue afforded **36** (278 mg, 0.438 mmol, 70%) as a colorless oil: $[\alpha]_D$ +98.2 (c 0.510, $CHCl_3$); IR 2931, 2827, 1363, 1112, 1045 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.05 (9H, s), 3.18 (1H, dd, J = 10.6, 4.2 Hz), 3.20 (1H, dd, J = 9.5, 3.7 Hz), 3.23 (3H, s), 3.25 (1H, dd, J = 10.6, 4.5 Hz), 3.30 (3H, s), 3.40 (3H, s), 3.44 (3H, s), 3.45 (1H, dd, J = 9.3, 9.3 Hz), 3.51 (3H, s), 3.54 (1H, dd, J = 6.1, 2.6 Hz), 3.568 (1H, dd, J = 9.2, 9.2 Hz), 3.574 (3H, s), 3.67 (1H, dd, J = 2.6, 0.8 Hz), 3.68−3.74 (2H, m), 3.78 (1H, dd, J = 10.9, 7.2 Hz), 3.96 (1H, dd, J = 10.9, 1.6 Hz), 4.84 (1H, d, J = 3.7 Hz), 5.33 (1H, s), 7.33−7.42 (6H, m), 7.68−7.73 (4H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 19.3 (C), 26.8 (3 × CH_3), 54.7 (CH_3), 57.5 (CH_3), 57.8 (CH_3), 58.6 (CH_3), 59.1 (CH_3), 60.8 (CH_3), 63.7 (CH_2), 71.2 (CH), 71.9 (CH_2), 74.7 (CH), 80.9 (CH), 82.5 (CH), 83.5 (CH), 85.5 (CH), 90.0 (CH), 96.7 (CH), 106.5 (CH), 127.5 (4 × CH), 129.4 (CH), 129.5 (CH), 133.8 (C), 133.9 (C), 135.68 (2 × CH), 135.71 (2 × CH); MS (ESI$^+$) m/z (rel intens) 657 (M$^+$ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{33}H_{50}NaO_{10}Si$ 657.3071, found 657.3062. Anal. Calcd for $C_{33}H_{50}O_{10}Si$: C, 62.43; H, 7.94. Found C, 62.34; H, 7.96.

Methyl 2,3,5-Tri-*O*-acetyl-α-D-arabinofuranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (55). To a solution of disaccharide **35** (224 mg, 0.31 mmol) in dry THF (9 mL) was added dropwise a 1 M solution of Bu_4NF/THF (0.77 mL, 0.77 mmol), and the mixture was stirred at room temperature for 24 h. The solvent was then removed in vacuo and the residue purified by column chromatography (hexanes−EtOAc, 30:70) to give the alcohol **55** (97.2 mg, 0.202 mmol, 65%) as a colorless oil: $[\alpha]_D$ +102.8 (c 0.140,

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$CHCl_3$); IR 3450, 2966, 1750, 1228, 1039 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.10 (3H, s), 2.107 (3H, s), 2.108 (3H, s), 2.30 (1H, br s), 3.21 (1H, dd, J = 9.1, 3.5 Hz), 3.42 (3H, s), 3.51 (3H, s), 3.57 (3H, s), 3.57−3.67 (3H, m), 3.74−3.81 (2H, m), 4.19 (1H, dd, J = 11.4, 6.3 Hz), 4.31 (1H, ddd, J = 6.1, 4.5, 4.5 Hz), 4.37 (1H, dd, J = 11.4, 3.8 Hz), 4.82 (1H, d, J = 3.5 Hz), 5.01 (1H, dd, J = 4.6, 1.8 Hz), 5.17 (1H, dd, J = 2.0, 0.8 Hz), 5.49 (1H, s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 20.62 (CH_3), 20.64 (CH_3), 20.7 (CH_3), 55.2 (CH_3), 59.0 (CH_3), 61.0 (CH_3), 61.7 (CH_2), 63.4 (CH_2), 70.0 (CH), 74.2 (CH), 77.0 (CH), 80.7 (CH), 81.1 (CH), 82.2 (CH), 83.2 (CH), 97.6 (CH), 107.0 (CH), 169.3 (C), 169.9 (C), 170.6 (C); MS (ESI^+) m/z (rel intens) 503 (M^+ + Na, 100); HRMS (ESI^+) calcd for $C_{20}H_{32}NaO_{13}$ 503.1741, found 503.1743. Anal. Calcd for $C_{20}H_{32}O_{13}$: C, 50.00; H, 6.71. Found C, 50.22; H, 6.78.

Methyl 2,3,5-Tri-*O*-methyl-α-D-arabinofuranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (53). To a solution of compound **36** (280 mg, 0.442 mmol) in dry THF (11.4 mL) was added a 1 M solution of TBAF/THF (1.11 mL, 1.11 mmol), and the mixture was stirred at room temperature for 6 h. The reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (EtOAc) to give the alcohol **53** (174 mg, 0.439 mmol, 99%) as a colorless oil: $[\alpha]_D$ +160.8 (c 0.375, $CHCl_3$); IR 3468, 2926, 2830, 1459, 1096, 1051 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.23 (1H, dd, J = 9.3, 3.7 Hz), 3.387 (3H, s), 3.391 (3H, s), 3.395 (3H, s), 3.43 (3H, s), 3.488 (3H, s), 3.489 (1H, dd, J = 10.6, 5.8 Hz), 3.53 (1H, dd, J = 10.6, 4.8 Hz), 3.54−3.59 (2H, m), 3.57 (1H, dd, J = 9.3, 9.3 Hz), 3.58 (3H, s), 3.65 (1H, dd, J = 9.8, 9.1 Hz), 3.72 (1H, br d, J = 12.7 Hz), 3.75 (1H, dd, J = 2.9, 1.3 Hz), 3.84 (1H, br d, J = 12.2 Hz), 4.12 (1H, ddd, J = 6.1, 6.1, 4.5 Hz), 4.82 (1H, d, J = 3.7 Hz), 5.41 (1H, s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 55.1 (CH_3), 57.6 (CH_3), 58.0 (CH_3), 58.7 (CH_3), 59.3 (CH_3), 60.9 (CH_3), 61.7 (CH_2), 70.4 (CH), 72.6 (CH_2), 74.8 (CH), 81.3 (CH), 82.4 (CH), 83.1 (CH), 85.7 (CH), 89.6 (CH), 97.4 (CH), 107.2 (CH); MS (ESI^+) m/z (rel intens) 419 (M^+ + Na, 100). HRMS (ESI^+) m/z calcd for $C_{17}H_{32}NaO_{10}$ 419.1893, found 419.1886. Anal. Calcd for $C_{17}H_{32}O_{10}$: C, 51.51; H, 8.14. Found C, 51.44; H, 8.29.

Methyl 2,3,5,6-Tetra-*O*-acetyl-α-D-mannofuranosyl-(1→4)-6-*O*-(*tert*-butyldiphenylsilyl)-2,3-di-*O*-methyl-α-D-glucopyranoside (38). To a solution of **37**[31] (1.77 g, 4.25 mmol) and **34**[11a] (1.90 g, 4.25 mmol) in dry CH_2Cl_2 (6 mL) were added *N*-iodosuccinimide (1.24 g, 5.51 mmol) and, at 0 °C, (TMS)OTf (230 μL, 1.27 mmol), and the mixture was stirred at room temperature for 1 h. Then the reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified column chromatography (hexanes−EtOAc, 8:2) to give the disaccharide **38** (2.02 g, 2.55 mmol, 60%) as an amorphous solid: $[\alpha]_D$ +89.6 (c 0.240, $CHCl_3$); IR 2933, 1755, 1229 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.03 (9H, s), 1.83 (3H, s), 1.90 (3H, s), 2.00 (3H), 2.02 (3H, s), 3.15 (1H, dd, J = 9.7, 3.6 Hz), 3.33 (1H, dd, J = 10.1, 8.7 Hz), 3.46 (3H, s), 3.48−3.55 (2H, m), 3.49 (3H, s), 3.51 (3H, s), 3.60 (1H, dd, J = 8.6, 4.4 Hz), 3.67 (1H, m), 3.75 (1H, dd, J = 10.9, 6.9 Hz), 3.84 (1H, dd, J = 11.1, 1.6 Hz), 4.30 (1H, dd, J = 12.0, 2.5 Hz), 4.83 (1H, d, J = 3.4 Hz), 5.0 (1H, dd, J = 4.9, 3.3 Hz), 5.09 (1H, dd, J = 6.5, 2.0 Hz), 5.29 (1H, dd, J = 4.6, 4.6 Hz), 5.40 (1H, d, J = 3.4 Hz), 7.35−7.44 (6H, m), 7.67−7.71 (4H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 19.1 (C), 20.2 (2 × CH_3), 20.5 (CH_3), 20.6 (CH_3), 26.6 (3 × CH_3), 54.9 (CH_3), 58.8 (CH_3), 60.9 (CH_3), 62.7 (CH_2), 63.7 (CH_2), 68.1 (CH), 70.6 (CH), 71.4 (CH), 75.7 (CH), 75.9 (2 × CH), 82.1 (CH), 83.2 (CH), 96.9 (CH), 105.6 (CH), 127.7 (4 × CH), 129.6 (2 × CH), 133.4 (2 × C), 135.5 (2 × CH), 135.7 (2 × CH), 169.2 (C), 169.4 (2 × C), 170.3 (C); MS (ESI^+) m/z (rel intens) 813 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{39}H_{54}NaO_{15}Si$, 813.3130, found 813.3109. Anal. Calcd for $C_{39}H_{54}O_{15}Si$: C, 59.22; H, 6.88. Found: C, 59.36; H, 6.86.

Methyl 2,3,5,6-Tetra-*O*-methyl-α-D-mannofuranosyl-(1→4)-6-*O*-(*tert*-butyldiphenylsilyl)-2,3-di-*O*-methyl-α-D-glucopyranoside (39). To a solution of compound **38** (654 mg, 0.828 mmol) in MeOH (27 mL) was added K_2CO_3 (457 mg, 3.31 mmol), and the mixture was stirred at room temperature for 3 h, then neutralized with Dowex (50 × 8) H^+ ion-exchange resin for 1 h, filtered, and concentrated. To the crude residue in dry acetone (8.3 mL) were added Ag_2O (1.53 g, 6.62 mmol) and methyl iodide (412 μL, 6.62 mmol), and the mixture was stirred at room temperature under nitrogen for 24 h. Then the reaction mixture was filtered through Celite and concentrated under reduced pressure. Column chromatography (hexanes−EtOAc, 70:30) of the residue afforded the title compound **39** (368 mg, 0.543 mmol, 65%) as a colorless oil: $[\alpha]_D$ +78.7 (c 0.240, $CHCl_3$); IR 2931, 1107, 1064 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.03 (9H, s), 2.99 (1H, dd, J = 10.6, 6.1 Hz), 3.02 (3H, s), 3.17 (1H, dd, J = 9.6, 3.7 Hz), 3.27−3.39 (3H, m), 3.33 (3H, s), 3.42−3.58 (3H, m), 3.44 (3H, s), 3.46 (3H, s), 3.47 (3H, s), 3.50 (3H, s), 3.55 (3H, s), 3.66−3.73 (3H, m), 3.89 (1H, dd, J = 9.5, 0 Hz), 4.84 (1H, d, J = 3.7 Hz), 5.30 (1H, d, J = 4.0 Hz), 7.35−7.43 (6H, m), 7.69−7.72 (4H, m);^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 19.2 (C), 26.7 (3 × CH_3), 54.9 (CH_3), 57.9 (CH_3), 58.5 (CH_3), 58.7 (CH_3), 58.8 (CH_3), 59.9 (CH_3), 60.8 (CH_3), 64.0 (CH_2), 71.8 (CH), 72.8 (CH_2), 74.8 (CH), 77.2 (CH), 77.9 (CH), 79.8 (CH), 82.3 (CH), 83.4 (CH), 87.0 (CH), 96.9 (CH), 105.9 (CH), 127.6 (4 × CH), 129.5 (2 × CH), 133.6 (2 × C), 135.6 (2 × CH), 135.7 (2 × CH); MS (ESI^+) m/z (rel intens) 701 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{35}H_{54}NaO_{11}Si$, 701.3333, found 701.3334. Anal. Calcd for $C_{35}H_{54}O_{11}Si$: C, 61.92; H, 8.02. Found: C, 61.80; H, 7.92.

Methyl 2,3,5,6-Tetra-*O*-methyl-α-D-mannofuranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (58). To a solution of compound **39** (217 mg, 0.320 mmol) in dry THF (30 mL) was added a 1 M solution of TBAF/THF (0.96 mL, 0.960 mmol), and the mixture was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (EtOAc) to give the alcohol **58** (108 mg, 0.245 mmol, 77%) as a colorless oil: $[\alpha]_D$ +103.6 (c 0.110, $CHCl_3$); IR 3684, 3512, 2932, 1102 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.99 (1H, br s), 3.19 (1H, dd, J = 9.5, 3.7 Hz), 3.35 (3H, s), 3.37 (3H, s), 3.38 (3H, s), 3.44 (3H, s), 3.46 (3H, s), 3.48−3.58 (4H, m), 3.50 (3H, s), 3.55 (3H, s), 3.62−3.65 (3H, m), 3.70 (1H, dd, J = 3.7 Hz), 3.81 (1H, dd, J = 12.4, 2.9 Hz), 3.88 (1H, dd, J = 3.4, 3.4 Hz), 4.10 (1H, dd, J = 9.0, 3.2 Hz), 4.77 (1H, d, J = 3.4 Hz), 5.41 (1H, d, J = 4.0 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 54.9 (CH_3), 57.0 (CH_3), 58.6 (2 × CH_3), 59.2 (CH_3), 60.1 (CH_3), 60.7 (CH_2), 60.7 (CH_3), 69.7 (CH_2), 70.4 (CH), 74.5 (CH), 76.9 (CH), 77.8 (CH), 79.7 (CH), 82.1 (CH), 83.1 (CH), 87.2 (CH), 97.4 (CH), 107.0 (CH); MS (ESI^+) m/z (rel intens) 463 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{19}H_{36}NaO_{11}$, 463.2155, found 463.2153. Anal. Calcd for $C_{19}H_{36}O_{11}$: C, 51.81; H, 8.24. Found: C, 52.02; H, 8.07.

Methyl 2,3,4-Tri-*O*-acetyl-α-D-lyxopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (41). Compound **41** was prepared from **40**[32] (664 mg, 1.584 mmol) and **34**[11a] (331 mg, 0.720 mmol) following the general procedure. The residue was purified by column chromatography (hexanes−EtOAc, 1:1) to give the alcohol **41** (554 mg, 1.154 mmol, 73%) as a colorless oil: $[\alpha]_D$ +160.0 (c 0.03, $CHCl_3$); IR 3530, 2933, 1753, 1123 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.01 (3H, s), 2.03 (6H, s), 2.37 (1H, br s), 3.15 (1H, dd, J = 9.1, 3.3 Hz), 3.37 (3H, s), 3.45 (3H, s), 3.49−3.57 (4H, m), 3.55 (3H, s), 3.69−3.83 (2H, m), 3.88 (1H, dd, J = 11.8, 4.1 Hz), 4.77 (1H, d, J = 3.4 Hz), 5.00 (1H, m), 5.11 (2H, br s), 5.27 (1H, d, J = 5.3 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 20.5 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 55.1 (CH_3), 58.8 (CH_3), 61.0 (CH_3), 61.7 (2 × CH_2), 67.3 (CH), 68.2 (CH), 69.2 (CH), 69.9 (CH), 75.6 (CH), 82.2 (CH), 83.0 (CH), 97.3 (CH), 99.0 (CH), 169.5 (C), 169.6 (C), 169.8 (C); MS (ESI^+) m/z (rel intens) 503 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{20}H_{32}NaO_{13}$, 503.1741, found 503.1741. Anal. Calcd for $C_{20}H_{32}O_{13}$: C, 50.00; H, 6.71. Found: C, 50.13; H, 7.01.

General Procedure for the Oxidative HAT Reactions. A 0.025 M solution of the alcohol (1 equiv) in dry CH_2Cl_2 containing DIB (1.1−2.5 equiv) and I_2 (0.5−1.2 equiv) under nitrogen was irradiated with two 80 W tungsten-filament lamps at room temperature for the specified time. The reaction mixture was then poured into 10% aqueous $Na_2S_2O_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexanes−EtOAc mixtures).

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Oxidative HAT of 42. Method A at Room Temperature. The reaction proceeded from **42** (46 mg, 0.131 mmol) containing DIB (72 mg, 0.223 mmol) and I_2 (33 mg, 0.130 mmol) following the general procedure by irradiation for 2 h. Chromatotron chromatography of the reaction residue (hexanes−EtOAc, 6:4) gave **43** as an inseparable mixture of isomers (27 mg, 0.071 mmol, dr 6:1, 54%): colorless oil; IR 2936, 2828, 1757, 1749, 1456, 1117, 1055 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (major isomer) δ_H 2.09 (3H, s), 3.38 (3H, s), 3.39 (6H, s), 3.42 (3H, s), 3.45 (3H, s), 3.51 (1H, dd, J = 10.7, 4.7 Hz), 3.56 (1H, dd, J = 10.7, 3.5 Hz), 3.64 (1H, dd, J = 6.9, 3.2 Hz), 3.70 (1H, dd, J = 2.8, 2.8 Hz), 3.78 (1H, d, J = 3.2 Hz), 4.06 (1H, ddd, J = 6.9, 4.7, 5.5 Hz), 4.13 (1H, dd, J = 2.8, 2.8 Hz), 5.04 (1H, d, J = 2.8 Hz), 5.09 (1H, s), 6.20 (1H, d, J = 2.2 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) (major isomer) δ_C 21.1 (CH_3), 56.4 (CH_3), 57.6 (CH_3), 58.0 (CH_3), 58.1 (CH_3), 59.3 (CH_3), 71.8 (CH_2), 80.9 (CH), 83.2 (CH), 85.1 (CH), 87.6 (CH), 89.9 (CH), 100.0 (CH), 105.6 (CH), 108.5 (CH), 169.6 (C); MS (ESI^+) m/z (rel intens) 403 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{16}H_{28}NaO_{10}$ 403.1580, found 403.1584. Anal. Calcd for $C_{16}H_{28}O_{10}$: C, 50.52; H, 7.42. Found C, 50.46; H, 7.34.

Oxidative HAT of 44. *Method A at Room Temperature.* The reaction proceeded from alcohol **44** (44 mg, 0.125 mmol) containing DIB (68 mg, 0.212 mmol) and I_2 (32 mg, 0.125 mmol) following the general procedure by irradiation for 1.5 h. After this time another portion of DIB (20 mg, 0.062 mmol) was added, and irradiation was continued for an additional 0.5 h. Chromatotron chromatography of the residue (hexanes−EtOAc, 50:50) gave in order of elution methyl 2,3,5-tri-*O*-methyl-α-D-arabinofuranosyl-(1→3)-2-*O*-methyl-β-D-*ribo*-pentodialdo-1,4-furanose (**46**) (3.5 mg, 0.01 mmol, 8%) and methyl (4*R*)-2,3,5-tri-*O*-methyl-α-D-arabinofuranosyl-(1→3)-4-*O*-acetyl-2-*O*-methyl-β-D-*erythro*-tetrodialdo-1,4-furanose (**45**) (30.3 mg, 0.08 mmol, 64%), both as colorless oils. Data for compound **46**: $[\alpha]_D$ +79.1 (*c* 0.230, $CHCl_3$); IR 2933, 2828, 1736, 1454, 1107, 1050 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 3.39 (6H, s), 3.40 (3H, s), 3.41 (3H, s), 3.48 (3H, s), 3.52 (1H, dd, J = 10.9, 5.0 Hz), 3.58 (1H, dd, J = 10.9, 3.4 Hz), 3.63 (1H, dd, J = 7.2, 3.2 Hz), 3.71 (1H, d, J = 4.8 Hz), 3.81 (1H, d, J = 3.2 Hz), 4.07 (1H, ddd, J = 8.2, 5.0, 3.4 Hz), 4.38 (1H, dd, J = 6.6, 1.9 Hz), 4.58 (1H, dd, J = 6.6, 4.8 Hz), 4.99 (1H, s), 5.05 (1H, s), 9.62 (1H, d, J = 1.9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 55.5 (CH_3), 57.5 (CH_3), 58.0 (CH_3), 58.6 (CH_3), 59.3 (CH_3), 71.9 (CH_2), 74.9 (CH), 80.6 (CH), 82.0 (CH), 85.1 (CH), 85.3 (CH), 89.9 (CH), 105.1 (CH), 106.5 (CH), 199.4 (CH); MS (ESI^+) m/z (rel intens) 373 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{15}H_{26}NaO_9$ 373.1475, found 373.1478. Anal. Calcd for $C_{15}H_{26}O_9$: C, 51.42; H, 7.48. Found C, 51.44; H, 7.43. Data for compound **45**: $[\alpha]_D$ +81.5 (*c* 0.390, $CHCl_3$); IR 2933, 2832, 1747, 1456, 1232, 1113, 1055 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 2.08 (3H, s), 3.398 (3H, s), 3.403 (3H, s), 3.41 (6H, s), 3.46 (3H, s), 3.53 (1H, dd, J = 10.7, 5.4 Hz), 3.59 (1H, dd, J = 11.0, 3.2 Hz), 3.62 (1H, dd, J = 7.3, 3.2 Hz), 4.09 (1H, ddd, J = 7.3, 5.4, 3.2 Hz), 4.37 (1H, dd, J = 4.7, 2.2 Hz), 5.04 (1H, d, J = 3.2 Hz), 5.12 (1H, s), 6.16 (1H, d, J = 2.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 21.1 (CH_3), 56.1 (CH_3), 57.5 (CH_3), 58.0 (CH_3), 58.5 (CH_3), 59.3 (CH_3), 72.1 (CH_2), 77.7 (CH), 80.6 (CH), 82.9 (CH), 85.4 (CH), 90.0 (CH), 99.9 (CH), 105.8 (CH), 107.8 (CH), 169.7 (C); MS (ESI^+) m/z (rel intens) 403 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{16}H_{28}NaO_{10}$ 403.1580, found 403.1576. Anal. Calcd for $C_{16}H_{28}O_{10}$: C, 50.52; H, 7.42. Found C, 50.35; H, 7.38.

Method B at 0 °C. The reaction proceeded from alcohol **44** (44 mg, 0.125 mmol) containing DIB (68 mg, 0.212 mmol) and I_2 (32 mg, 0.125 mmol) following the general procedure by irradiation for 2 h. After this time another three portions of DIB (40 mg, 0.125 mmol) were added every 2 h, and irradiation was continued for 7.5 h in total. Chromatotron chromatography of the residue (hexanes−EtOAc, 50:50) gave in order of elution aldehyde **46** (1 mg, 0.003 mmol, 2%) and acetate **45** (24.2 mg, 0.06 mmol, 51%).

Oxidative HAT of 47. The reaction proceeded from **47** (40 mg, 0.114 mmol) containing DIB (40.4 mg, 0.125 mmol), I_2 (14.5 mg, 0.057 mmol), and powdered 3 Å molecular sieves following the general procedure by irradiation for 7 h at 40 °C. After this time another portion of DIB (7.5 mg, 0.023 mmol) was added, and irradiation was continue for a further 8 h. The residue (56 mg) was subjected to purification by rapid alumina (Merck 90 active neutral) column chromatography (hexanes−EtOAc, 6:3 → 0:1) to give **48** (8.7 mg, 0.025 mmol, 22%) and **49** as an inseparable mixture of isomers (6.3 mg, 0.016 mmol, β/α 9:1, 14%). Data for compound **48**: colorless oil, $[\alpha]_D$ +61 (*c* 0.39, $CHCl_3$); IR 2929, 2828, 1456, 1146, 1111, 1046 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.36 (3H, s), 3.40 (1H, d, J = 10.1 Hz), 3.42 (3H, s), 3.43 (3H, s), 3.44 (3H, s), 3.45 (1H, d, J = 10.2 Hz), 3.48 (3H, s), 3.71 (1H, dd, J = 5.0, 1.9 Hz), 3.80 (1H, d, J = 1.2 Hz), 3.85 (1H, dd, J = 12.9, 1.9 Hz), 3.92 (1H, d, J = 1.6 Hz), 4.19 (1H, ddd, J = 7.3, 5.4, 1.9 Hz), 4.34 (1H, dd, J = 5.4, 5.4 Hz), 4.36 (1H, dd, J = 13.2, 7.3 Hz), 4.86 (1H, d, J = 2.2 Hz), 5.15 (1H, s); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 55.2 (CH_3), 57.4 (CH_3), 58.78 (CH_3), 58.84 (CH_3), 59.7 (CH_3), 64.2 (CH_2), 74.1 (CH), 75.8 (CH_2), 79.9 (CH), 84.0 (CH), 86.8 (CH), 89.7 (CH), 103.3 (CH), 104.7 (CH), 108.1 (C), MS (ESI^+) m/z (rel intens) 373 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{15}H_{26}NaO_9$ 373.1475, found 373.1474. Anal. Calcd for $C_{15}H_{26}O_9$: C, 51.42; H, 7.48. Found C, 51.30; H, 7.38. Data for compound **49** (contaminated with 10% α-epimer): colorless oil, IR 2936, 2832, 1747, 1234, 1115, 1057, 1013 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (β-isomer) δ_H 2.07 (3H, s), 3.38 (3H, s), 3.39 (3H, s), 3.40 (3H, s), 3.41 (6H, s), 3.45 (3H, s), 3.53 (1H, dd, J = 10.7, 5.0 Hz), 3.59 (1H, dd, J = 10.7, 3.2 Hz), 3.62 (1H, dd, J = 7.3, 3.2 Hz), 3.81 (1H, dd, J = 3.2, 1.0 Hz), 3.85 (1H, dd, J = 4.7, 2.8 Hz), 4.09 (1H, ddd, J = 6.9, 5.0, 3.2 Hz), 4.37 (1H, dd, J = 4.7, 2.2 Hz), 5.03 (1H, d, J = 3.2 Hz), 5.11 (1H, br s), 6.15 (1H, d, J = 2.2 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) (β-isomer) δ_C 21.1 (CH_3), 56.1 (CH_3), 57.5 (CH_3), 58.0 (CH_3), 58.5 (CH_3), 59.3 (CH_3), 72.0 (CH_2), 77.7 (CH), 80.6 (CH), 82.9 (CH), 85.3 (CH), 90.0 (CH), 99.9 (CH), 105.8 (CH), 107.8 (CH), 169.7 (C); MS (ESI^+) m/z (rel intens) 403 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{16}H_{28}NaO_{10}$ 403.1580, found 403.1575. Anal. Calcd for $C_{16}H_{28}O_{10}$: C, 50.52; H, 7.42. Found C, 50.86; H, 7.34.

Oxidative HAT of 50. *Method A at Room Temperature.* The reaction proceeded from **5** (42 mg, 0.093 mmol) containing DIB (51 mg, 0.159 mmol) and I_2 (24 mg, 0.093 mmol) following the general procedure by irradiation for 0.75 h. Column chromatography of the residue (hexanes−EtOAc, 70:30) gave in order of elution methyl (4*R*)-2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-methyl-β-D-*erythro*-tetrodialdo-1,4-furanose (**52β**) (7.5 mg, 0.016 mmol, 17%), methyl (4*S*)-2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-methyl-β-D-*erythro*-tetrodialdo-1,4-furanose (**52α**) (9 mg, 0.019 mmol, 20%), and methyl 5′,5-anhydro-(2′,3′,4′-tri-*O*-acetyl-6′-deoxy-α-L-*lyxo*-hexos-5′-ulopyranosyl)-(1→3)-2-*O*-methyl-β-D-xylofuranoside (**51**) (9 mg, 0.020 mmol, 22%) as colorless oils. Data for compound **52β**: $[\alpha]_D$ −42.0 (*c* 0.560, $CHCl_3$); IR 2936, 2851, 1747, 1373, 1226, 1054 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.18 (3H, d, J = 6.4 Hz), 1.98 (3H, s), 2.05 (3H, s), 2.15 (3H, s), 2.16 (3H, s), 3.43 (3H, s), 3.44 (3H, s), 3.84 (1H, dddd, J = 9.8, 6.4, 6.4, 6.4 Hz), 3.93 (1H, dd, J = 7.2, 3.4 Hz), 4.15 (1H, dd, J = 7.2, 4.5 Hz), 4.87 (1H, d, J = 3.4 Hz), 4.94 (1H, d, J = 1.6 Hz), 5.06 (1H, dd, J = 10.1, 10.1 Hz), 5.21 (1H, dd, J = 10.3, 3.4 Hz), 5.29 (1H, dd, J = 3.4, 1.9 Hz), 6.24 (1H, d, J = 4.8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 17.3 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 21.2 (CH_3), 56.0 (CH_3), 58.5 (CH_3), 67.3 (CH), 68.8 (CH), 69.7 (CH), 70.7 (CH), 80.1 (CH), 86.7 (CH), 94.6 (CH), 97.8 (CH), 108.0 (CH), 170.0 (2 × C), 170.1 (C), 170.2 (C); MS (ESI^+) m/z (rel intens) 501 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{20}H_{30}NaO_{13}$ 501.1584, found 501.1587. Anal. Calcd for $C_{20}H_{30}O_{13}$: C, 50.21; H, 6.32. Found C, 50.23; H, 6.36. Data for compound **52α**: $[\alpha]_D$ −93.6 (*c* 0.405, $CHCl_3$); IR 2936, 2847, 1749, 1371, 1226, 1052 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.20 (3H, d, J = 6.3 Hz), 1.98 (3H, s), 2.05 (3H, s), 2.10 (3H, s), 2.15 (3H, s), 3.42 (3H, s), 3.47 (3H, s), 3.70 (1H, dd, J = 2.8, 2.8 Hz), 3.93 (1H, dddd, J = 9.8, 6.3, 6.3, 6.3 Hz), 4.12 (1H, dd, J = 2.8, 2.8 Hz), 4.87 (1H, d, J = 1.6 Hz), 5.071 (1H, dd, J = 9.8, 9.8 Hz), 5.074 (1H, d, J = 2.8 Hz), 5.24 (1H, dd, J = 3.5, 1.9 Hz), 5.27 (1H, dd, J = 9.8, 3.5 Hz), 6.21 (1H, d, J = 2.2 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 17.2 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 21.1 (CH_3), 56.3 (CH_3), 58.2 (CH_3), 67.2 (CH), 68.8 (CH), 69.8 (CH), 70.9 (CH), 84.1 (CH), 87.4 (CH), 97.2 (CH), 99.7 (CH), 108.8 (CH), 169.6 (C), 169.8 (C), 170.0 (C), 170.1 (C); MS (ESI^+) m/z (rel intens) 501 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for

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$C_{20}H_{30}NaO_{13}$ 501.1584, found 501.1585. Anal. Calcd for $C_{20}H_{30}O_{13}$: C, 50.21; H, 6.32. Found C, 50.44; H, 6.21. Data for compound **51**: $[\alpha]_D$ −18.6 (*c* 0.333, $CHCl_3$); IR 2929, 2847, 1751, 1373, 1226, 1057 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.40 (3H, s), 1.97 (3H, s), 2.10 (3H, s), 2.15 (3H, s), 3.41 (3H, s), 3.42 (3H, s), 3.91 (1H, dd, *J* = 4.4, 2.2 Hz), 4.02 (1H, dd, *J* = 13.2, 4.7 Hz), 4.09 (1H, dd, *J* = 13.3, 7.6 Hz), 4.10 (1H, dd, *J* = 5.0, 4.4 Hz), 4.45 (1H, ddd, *J* = 7.6, 5.0, 5.0 Hz), 4.83 (1H, d, *J* = 2.2 Hz), 4.90 (1H, d, *J* = 1.3 Hz), 5.34 (1H, d, *J* = 10.7 Hz), 5.43 (1H, dd, *J* = 3.2, 1.3 Hz), 5.71 (1H, dd, *J* = 10.7, 3.5 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 20.6 (CH_3), 20.79 (CH_3), 20.82 (CH_3), 21.1 (CH_3), 55.0 (CH_3), 58.1 (CH_3), 62.6 (CH_2), 66.0 (CH), 70.1 (CH), 71.2 (CH), 77.3 (CH), 81.6 (CH), 89.3 (CH), 97.9 (CH), 101.4 (C), 107.0 (CH), 169.5 (C), 169.9 (C), 170.4 (C); MS (ESI^+) *m*/*z* (rel intens) 471 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{19}H_{28}NaO_{12}$ 471.1478, found 471.1483. Anal. Calcd for $C_{19}H_{28}O_{12}$: C, 50.89; H, 6.29. Found C, 50.66; H, 6.22.

Method B at 0 °C. The reaction proceeded from **5** (40 mg, 0.089 mmol) containing DIB (49 mg, 0.151 mmol) and I_2 (23 mg, 0.089 mmol) following the general procedure by irradiation at 0 °C for 3 h. After this time another portion of DIB (49 mg, 0.151 mmol) was added, and irradiation was continued for an additional 1 h. Chromatotron chromatography of the residue (hexanes−EtOAc, 75:25) gave in order of elution **52*β*** (4.6 mg, 0.010 mmol, 11%), **52*α*** (5.6 mg, 0.012 mmol, 13%), and **51** (11.3 mg, 0.025 mmol, 28%), all identical as previously described.

Oxidative HAT of 53. The reaction proceeded from **53** (30 mg, 0.076 mmol) containing DIB (49 mg, 0.193 mmol) and I_2 (19.3 mg, 0.076 mmol) following the general procedure by irradiation for 5 h. Chromatotron chromatography of the residue (hexanes−EtOAc, 30:70) gave methyl 4′,6-anhydro-(2′,3′,5′-tri-*O*-acetyl-*α*-D-*threo*-pentos-4′-ulofuranosyl)-(1→4)-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**54**) (16.6 mg, 0.042 mmol, 55%) as a colorless oil: $[\alpha]_D$ +71.2 (*c* 0.170, $CHCl_3$); IR 2936, 2828, 1452, 1106, 1052 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.14 (1H, dd, *J* = 9.5, 3.7 Hz), 3.34 (3H, s), 3.41 (3H, s), 3.42 (3H, s), 3.45 (1H, d, *J* = 10.9 Hz), 3.49 (3H, s), 3.500 (3H, s), 3.503 (1H, m), 3.51 (1H, d, *J* = 10.9 Hz), 3.59 (3H, s), 3.64 (1H, m), 3.67 (1H, dd, *J* = 9.5, 9.5 Hz), 3.75 (1H, dd, *J* = 11.7, 8.2 Hz), 3.79 (1H, dd, *J* = 5.8, 2.9 Hz), 3.85 (1H, d, *J* = 2.9 Hz), 3.93 (1H, dd, *J* = 11.7, 9.8 Hz), 4.73 (1H, d, *J* = 3.7 Hz), 5.22 (1H, s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 54.9 (CH_3), 57.6 (CH_3), 59.0 (CH_3), 59.1 (CH_3), 59.6 (CH_3), 61.2 (CH_3), 65.1 (CH_2), 66.5 (CH), 71.9 (CH), 77.3 (CH), 81.0 (CH), 81.4 (CH), 87.7 (CH), 90.5 (CH), 97.5 (CH), 104.2 (CH), 106.0 (C); MS (70 eV, EI) *m*/*z* (rel intens) 394 (M^+, <1), 363 (10), 277 (7), 145 (15), 101 (100); HRMS (EI) *m*/*z* calcd for $C_{17}H_{30}O_{10}$ 394.1839, found 394.1836. Anal. Calcd for $C_{17}H_{30}O_{10}$: C, 51.77; H, 7.67. Found C, 51.62; H, 7.58.

Oxidative HAT of 55. The reaction proceeded from **55** (54 mg, 0.112 mmol) containing DIB (62 mg, 0.191 mmol) and I_2 (29 mg, 0.112 mmol) following the general procedure by irradiation for 2 h. After this time another portion of DIB (18 mg, 0.056 mmol) was added, and irradiation was continued for an additional 1.5 h. Column chromatography of the reaction residue (hexanes−EtOAc, 50:50) gave methyl 4′,6-anhydro-(2′,3′,5′-tri-*O*-acetyl-*α*-D-*threo*-pentos-4′-ulofuranosyl)-(1→4)-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**56**) (5.1 mg, 0.011 mmol, 9%), methyl (1′*R*)-4,6-*O*-(2′,3′,5′-tri-*O*-acetyl-*α*-D-*threo*-pentos-4′-ulosylidene)-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**57**) (10.7 mg, 0.022 mmol, 20%), and methyl 2,3-di-*O*-methyl-*α*-D-glucopyranoside[41] (3 mg, 0.014 mmol, 12%). Data for compound **56**: unstable oil; ^1H NMR (500 MHz, $CDCl_3$) δ_H 2.10 (3H, s), 2.12 (3H, s), 2.16 (3H, s), 3.14 (1H, dd, *J* = 9.5, 3.5 Hz), 3.40 (3H, s), 3.51 (3H, s), 3.52 (1H, dd, *J* = 9.1, 9.1 Hz), 3.57−3.62 (2H, m), 3.61 (3H, s), 3.76 (1H, dd, *J* = 12.3, 3.8 Hz), 3.95 (1H, dd, *J* = 12.3, 9.8 Hz), 4.12 (1H, d, *J* = 11.7 Hz), 4.36 (1H, d, *J* = 11.7 Hz), 4.75 (1H, d, *J* = 3.8 Hz), 5.11 (1H, d, *J* = 1.9 Hz), 5.20 (1H, d, *J* = 1.9 Hz), 5.22 (1H, s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 20.68 (CH_3), 20.70 (CH_3), 20.74 (CH_3), 55.3 (CH_3), 59.2 (CH_3), 61.4 (CH_3), 63.2 (CH_2), 65.4 (CH_2), 66.4 (CH), 78.3 (CH), 78.8 (CH), 80.8 (CH), 81.5 (CH), 81.7 (CH), 97.7 (CH), 98.7 (C), 104.9 (CH), 169.7 (C), 170.0 (C), 170.6 (C); MS (ESI^+) *m*/*z* (rel intens) 501 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{20}H_{30}NaO_{13}$ 501.1584, found 501.1590. Data for compound **57**: crystalline solid; mp 159.4−160.9 °C (from *n*-hexane−EtOAc); $[\alpha]_D$ +80.0 (*c* 0.100, $CHCl_3$); IR 2933, 2832, 1751, 1338, 1219, 1054 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 2.09 (3H, s), 2.16 (3H, s), 2.17 (3H, s), 3.20 (1H, dd, *J* = 9.5, 3.8 Hz), 3.28 (1H, dd, *J* = 9.5, 9.5 Hz), 3.42 (3H, s), 3.47 (1H, dd, *J* = 10.4, 10.4 Hz), 3.52 (3H, s), 3.54 (3H, s), 3.58 (1H, dd, *J* = 9.5, 9.5 Hz), 3.66 (1H, ddd, *J* = 10.1, 10.1, 5.0 Hz), 4.15 (1H, dd, *J* = 10.4, 5.1 Hz), 4.71 (1H, d, *J* = 5.7 Hz), 4.80 (1H, d, *J* = 3.8 Hz), 4.84 (1H, d, *J* = 17.3 Hz), 4.88 (1H, d, *J* = 17.3 Hz), 5.47 (1H, dd, *J* = 5.7, 3.8 Hz), 5.50 (1H, dd, *J* = 3.8 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 20.36 (CH_3), 20.39 (CH_3), 20.5 (CH_3), 55.4 (CH_3), 59.4 (CH_3), 60.7 (CH_3), 61.8 (CH), 66.7 (CH_2), 68.8 (CH_2), 70.2 (CH), 73.9 (CH), 79.5 (CH), 81.2 (CH), 81.8 (CH), 98.1 (CH), 98.5 (CH), 169.5 (C), 169.78 (C), 169.80 (C), 197.5 (C); MS (ESI^+) *m*/*z* (rel intens) 501 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{20}H_{30}NaO_{13}$ 501.1584, found 501.1583. Anal. Calcd for $C_{20}H_{30}O_{13}$: C, 50.21; H, 6.32. Found C, 50.02; H, 6.21.

Oxidative HAT of 58. The reaction proceeded from **58** (108 mg, 0.245 mmol) containing DIB (118 mg, 0.366 mmol) and I_2 (74 mg, 0.291 mmol) following the general procedure by irradiation for 3 h. Column chromatography of the reaction residue (hexanes−EtOAc, 30:70) gave methyl 4′,6-anhydro-(2′,3′,5′,6′-tetra-*O*-methyl-*α*-D-*lyxo*-pentos-4′-ulofuranosyl)-(1→4)-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**59**) (57.3 mg, 0.131 mmol, 53%) and methyl 2,3,5,6-tetra-*O*-methyl-*α*-D-mannofuranosyl-(1→4)-2-*O*-methyl-3,6-*O*-methylidene-*α*-D-glucopyranoside (**60**) (13 mg, 0.030 mmol, 12%), both as colorless oils. Data for compound **59**: $[\alpha]_D$ +91.4 (*c* 0.140, $CHCl_3$); IR 2933, 1106 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.10 (1H, dd, *J* = 9.4, 3.6 Hz), 3.15−3.56 (5H, m), 3.33 (3H, s), 3.35 (3H, s), 3.42 (6H, s), 3.47 (3H, s), 3.54 (3H, s), 3.55 (3H, s), 3.69 (1H, dd, *J* = 12.2, 3.4 Hz), 3.72 (1H, dd, *J* = 12.0, 1.8 Hz), 3.82 (1H, d, *J* = 5.3 Hz), 4.04 (1H, d, *J* = 5.3 Hz), 4.12 (1H, dd, *J* = 12.4, 10.1 Hz), 4.71 (1H, d, *J* = 3.7 Hz), 5.19 (1H, s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 55.0 (CH_3), 58.6 (CH_3), 58.9 (2 × CH_3), 59.6 (CH_3), 60.7 (CH_3), 61.1 (CH_3), 65.5 (CH_2), 67.4 (CH), 73.6 (CH_2), 78.9 (CH), 81.0 (CH), 81.5 (CH), 82.4 (CH), 82.8 (CH), 90.5 (CH), 97.5 (CH), 103.7 (CH), 107.7 (C); MS (ESI^+) *m*/*z* (rel intens) 461 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{19}H_{34}NaO_{11}$, 461.1999, found 461.1998. Anal. Calcd for $C_{19}H_{34}O_{11}$: C, 52.05; H, 7.82. Found: C, 52.29; H, 7.73. Data for compound **60**: $[\alpha]_D$ +61.4 (*c* 0.070, $CHCl_3$); IR 2932, 1044 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.29 (1H, dd, *J* = 9.7, 3.6 Hz), 3.36 (1H, dd, *J* = 10.3, 2.6 Hz), 3.40−3.63 (3H, m), 3.40 (3H, s), 3.44 (3H, s), 3.49 (6H, s), 3.54 (3H, s), 3.58 (3H, s), 3.79 (1H, dd, *J* = 4.8, 2.9 Hz), 3.88 (1H, dd, *J* = 10.7, 1.2 Hz), 3.93 (1H, dd, *J* = 4.8, 2.1 Hz), 3.96 (1H, dd, *J* = 10.1, 10.1 Hz), 4.05 (1H, dd, *J* = 10.7, 1.7 Hz), 4.10−4.15 (2H, m), 4.66 (1H, d, *J* = 7.4 Hz), 4.81 (1H, d, *J* = 7.4 Hz), 4.87 (1H, d, *J* = 3.4 Hz), 5.46 (1H, d, *J* = 2.9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 55.3 (CH_3), 56.6 (CH_3), 58.5 (CH_3), 58.7 (CH_3), 60.3 (CH_3), 60.9 (CH_3), 64.1 (CH_2), 65.0 (CH_2), 69.3 (CH), 71.7 (CH), 76.6 (2 × CH), 80.3 (CH), 82.1 (CH), 83.5 (CH), 89.5 (CH), 94.8 (CH_2), 97.7 (CH), 105.6 (CH); MS (ESI^+) *m*/*z* (rel intens) 461 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{19}H_{34}NaO_{11}$, 461.1999, found 461.1999. Anal. Calcd for $C_{19}H_{34}O_{11}$: C, 52.05; H, 7.82. Found: C, 52.01; H, 7.84.

Oxidative HAT of 41. The reaction proceeded from **41** (50.6 mg, 0.105 mmol) in dry CH_2Cl_2 (2.1 mL) containing DIB (68 mg, 0.211 mmol) and I_2 (32 mg, 0.126 mmol) following the general procedure by irradiation for 3 h. Column chromatography of the residue (hexanes−EtOAc, 6:4) gave the orthoacetate **61** (26 mg, 0.054 mmol, 51%) and methyl 4,6-*O*-(2,3,4-tri-*O*-acetyl-*α*-D-lyxopyranosylidene)-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**62**) (13 mg, 0.027 mmol, *β*/*α* 3.6:1, 26%), both as colorless oils. Data for compound **61**: unstable for complete characterization; ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.54 (3H, s), 2.07 (3H, s), 2.11 (3H, s), 3.16 (1H, dd, *J* = 9.8, 3.4 Hz), 3.40 (3H, s), 3.50 (3H, s), 3.56 (3H, s), 3.60 (1H, dd, *J* = 9.5, 9.5 Hz), 3.67 (1H, dd, *J* = 8.7, 2.9 Hz), 3.76 (1H, dd, *J* = 9.7, 2.8 Hz), 3.82 (1H, dd, *J* = 8.6, 4.6 Hz), 3.83 (1H, ddd, *J* = 9.3, 9.3, 4.0 Hz), 4.46 (1H, dd, *J* = 7.0, 6.0 Hz), 4.75 (1H, d, *J* = 3.4 Hz), 5.30 (1H, dd, *J* = 3.0, 3.0 Hz), 5.38 (1H, d, *J* = 2.9 Hz), 5.80 (1H, d, *J* = 7.1 Hz), 5.82 (1H, dd, *J* = 5.8, 3.2 Hz);^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 20.2 (CH_3), 20.7 (CH_3), 20.9 (CH_3), 55.2 (CH_3), 58.9 (CH_3), 60.9 (CH_3), 66.1 (CH_2) 66.2 (CH),

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68.3 (CH), 70.0 (CH), 76.0 (CH), 76.8 (CH), 81.9 (CH), 83.0 (CH), 95.4 (CH), 97.3 (CH), 97.4 (CH), 122.3 (C), 169.6 (C), 169.7 (C). Data for compound **62** (mixture of isomers): IR 2932, 1757, 1222 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.01, (3H, s), 2.02 (3H, s), 2.04 (3H, s), 2.09 (3H, s), 2.12 (3H, s), 2.15 (3H, s), 3.15 (1H, dd, J = 9.4, 3.6 Hz), 3.22 (1H, dd, J = 9.6, 4.5 Hz), 3.41 (3H, s), 3.42 (3H, s), 3.45−4.13 (14H, m), 3.51 (6H, s), 3.52 (3H, s), 3.53 (3H, s), 4.76 (1H, d, J = 3.5 Hz), 4.80 (1H, d, J = 3.6 Hz), 5.04 (1H, ddd, J = 10.2, 10.2, 6.0 Hz), 5.14 (2H, d, J = 9.7 Hz), 5.23 (1H, m), 5.33−5.36 (2H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 20.63 (4 × CH_3), 20.7 (CH_3), 20.8 (CH_3), 55.37 (CH_3), 55.45 (CH_3), 59.4 (CH_3), 59.5 (CH_3), 61.0 (CH_3), 61.2 (2 × CH_2), 61.5 (2 × CH_2), 61.6 (CH_3), 66.6 (2 × CH), 69.0 (CH), 69.1 (CH), 69.4 (2 × CH), 70.5 (CH), 70.7 (CH), 74.4 (CH), 74.5 (CH), 79.4 (CH), 79.6 (CH), 81.1 (CH), 81.2 (CH), 98.7 (2 × CH), 108.5 (C), 109.2 (C), 169.3 (2 × C), 169.8 (2 × C), 169.9 (2 × C); MS (ESI^+) m/z (rel intens) 501 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{20}H_{30}NaO_{13}$, 501.1584, found 501.1590. Anal. Calcd for $C_{20}H_{30}O_{13}$: C, 50.21; H, 6.32. Found: C, 50.18; H, 6.37.

Methyl (5′*S*)-2′,3′,5′-Tri-*O*-acetyl-α-D-*lyxo*-pentos-5′-ulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (63). A solution of compound **61** (10 mg, 0.021 mmol) in $CHCl_3$ (10 mL) was treated with a catalytic amount of HCl and stirred at room temperature for 24 h. The reaction mixture was poured into aqueous saturated $NaHCO_3$ and extracted with $CHCl_3$. The organic layer was evaporated to give compound **63** (10.3 mg, 0.021 mmol, quant) as a colorless oil: $[\alpha]_D$ +94.9 (c 0.920, $CHCl_3$); IR 3477, 2931, 1751, 1223 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.02 (3H, s), 2.09 (3H, s), 2.13 (3H, s), 2.63 (2H, br s), 3.20 (1H, dd, J = 9.5, 3.4 Hz), 3.42 (3H, s), 3.50 (1H, m), 3.51 (3H, s), 3.55−3.63 (2H, m), 3.58 (3H, s), 3.71 (1H, dd, J = 9.8, 9.8 Hz), 3.83 (1H, d, J = 2.4 Hz), 4.81 (1H, d, J = 3.4 Hz), 5.06 (1H, d, J = 7.7 Hz), 5.14 (1H, dd, J = 9.5, 7.7 Hz), 5.27−5.32 (3H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 20.6 (CH_3), 20.76 (CH_3), 20.79 (CH_3), 55.3 (CH_3), 58.9 (CH_3), 61.2 (CH_3), 61.6 (CH_2), 67.8 (CH), 69.3 (CH), 69.9 (CH), 71.0 (CH), 75.7 (CH), 82.4 (CH), 83.1 (CH), 91.9 (CH), 97.5 (CH), 98.6 (CH), 169.7 (2 × C), 170.5 (C); MS (ESI^+) m/z (rel intens) 519 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{20}H_{32}NaO_{14}$, 519.1690, found 519.1689. Anal. Calcd for $C_{20}H_{32}O_{14}$: C, 48.39; H, 6.50. Found: C, 48.54; H, 6.83.

General Procedure for the Synthesis of *N*-Hydroxyphthalimides. DEAD (2.5 equiv) was added dropwise to a stirred 0.09 M solution of the alcohol (1 equiv) in dry THF containing *N*-hydroxyphthalimide (2.5 equiv) and PPh_3 (2.5 equiv) under nitrogen at 0 °C, and the stirring continued at this temperature for the time specified. Then the solvent was removed, and the reaction was quenched with water and extracted with EtOAc. The combined extracts were dried over Na_2SO_4 and evaporated. The residue obtained was purified by column chromatography.

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-methyl-5-*O*-phthalimido-β-D-xylofuranoside (64). The reaction prceeded from alcohol **50** (260 mg, 0.578 mmol) following the general procedure by stirring at 0 °C for 1.5 h. The residue obtained was purified by column chromatography (hexanes−EtOAc, 70:30) to give compound **64** (269 mg, 0.452 mmol, 78%) as a white foam: $[\alpha]_D$ −100.0 (c 0.415, $CHCl_3$); IR 2940, 2832, 1790, 1744, 1731, 1371, 1226, 1046 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.24 (3H, d, J = 6.4 Hz), 1.97 (3H, s), 2.04 (3H, s), 2.15 (3H, s), 3.35 (3H, s), 3.39 (3H, s), 3.74 (1H, dd, J = 1.6, 1.6 Hz), 3.96 (1H, dddd, J = 9.8, 6.4, 6.4, 6.4 Hz), 4.42 (1H, dd, J = 11.1, 7.2 Hz), 4.45 (1H, d, J = 6.4, 2.1 Hz), 4.54 (1H, dd, J = 11.1, 5.0 Hz), 4.68 (1H, ddd, J = 6.6, 6.6, 5.0 Hz), 4.84 (1H, d, J = 1.3 Hz), 4.92 (1H, d, J = 1.6 Hz), 5.07 (1H, dd, J = 9.8, 9.8 Hz), 5.21 (1H, dd, J = 9.8, 3.4 Hz), 5.24 (1H, dd, J = 3.4, 1.9 Hz), 7.76 (2H, m), 7.85 (2H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 17.4 (CH_3), 20.6 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.4 (CH_3), 57.7 (CH_3), 67.3 (CH), 68.9 (CH), 69.8 (CH), 70.8 (CH), 76.7 (CH_2), 77.75 (CH), 77.80 (CH), 87.8 (CH), 95.8 (CH), 107.5 (CH), 123.5 (2 × CH), 129.0 (2 × C), 134.5 (2 × CH), 163.4 (2 × C), 169.7 (C), 170.0 (C), 170.1 (C); MS (ESI^+) m/z (rel intens) 618 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{27}H_{33}NNaO_{14}$ 618.1799, found 618.1793. Anal. Calcd for $C_{27}H_{33}NO_{14}$: C, 54.45; H, 5.59; N, 2.35. Found: C, 54.25; H, 5.65; N, 2.17.

Methyl 2,3,5-Tri-*O*-methyl-α-D-arabinofuranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (70). The reaction proceeded from alcohol **53** (160 mg, 0.404 mmol) following the general procedure by stirring at 0 °C for 3 h. The residue obtained was purified by column chromatography (hexanes−Et_2O, 30:70) to give *N*-phthalimide **70** (196 mg, 0.362 mmol, 90%) as a colorless oil: $[\alpha]_D$ +108.4 (c 0.694, $CHCl_3$); IR 2933, 2829, 1791, 1733, 1374, 1107, 1039 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.239 (1H, dd, J = 9.5, 3.4 Hz), 3.244 (3H, s), 3.31 (3H, s), 3.408 (3H, s), 3.411 (1H, dd, J = 10.9, 5.6 Hz), 3.45 (1H, dd, J = 10.6, 4.5 Hz), 3.49 (3H, s), 3.50 (3H, s), 3.51 (1H, dd, J = 5.8, 2.1 Hz), 3.58 (3H, s), 3.59 (1H, dd, J = 9.5, 9.5 Hz), 3.61 (1H, dd, J = 10.3, 8.8 Hz), 3.72 (1H, dd, J = 2.4, 0.8 Hz), 3.98 (1H, m), 4.08 (1H, ddd, J = 5.8, 5.8, 4.5 Hz), 4.38 (1H, dd, J = 11.4, 6.9 Hz), 4.53 (1H, dd, J = 11.4, 1.6 Hz), 4.82 (1H, d, J = 3.2 Hz), 5.36 (1H, s), 7.72 (2H, m), 7.82 (2H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_H 55.6 (CH_3), 57.5 (CH_3), 57.8 (CH_3), 58.7 (CH_3), 59.1 (CH_3), 60.8 (CH_3), 69.2 (CH), 72.6 (CH_2), 74.9 (CH), 77.9 (CH_2), 81.1 (CH), 82.0 (CH), 82.9 (CH), 85.8 (CH), 89.7 (CH), 97.3 (CH), 106.9 (CH), 123.4 (2 × CH), 129.1 (2 × C), 134.2 (2 × CH), 163.2 (2 × C); MS (ESI^+) m/z (rel intens) 564 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{25}H_{35}NNaO_{12}$ 564.2057, found 564.2053. Anal. Calcd for $C_{25}H_{35}NO_{12}$: C, 55.45; H, 6.51; N, 2.59. Found C, 55.20; H, 6.48; N, 2.87.

Methyl 2,3,5-Tri-*O*-acetyl-α-D-arabinofuranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (74). The reaction proceeded from alcohol **55** (61.6 mg, 0.128 mmol) following the general procedure by stirring at 0 °C for 1 h. The residue obtained was purified by column chromatography (hexanes−EtOAc, 50:50) to give *N*-phthalimide **74** (60.7 mg, 0.097 mmol, 76%) as a white amorphous solid: $[\alpha]_D$ +64.0 (c 0.100, $CHCl_3$); IR 2929, 2847, 1792, 1732, 1369, 1224, 1042 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.05 (3H, s), 2.08 (3H, s), 2.10 (3H, s), 3.25 (1H, dd, J = 9.5, 3.4 Hz), 3.47 (3H, s), 3.51 (3H, s), 3.57 (3H, s), 3.62 (1H, dd, J = 9.5, 8.7 Hz), 3.78 (1H, dd, J = 10.1, 8.7 Hz), 3.93 (1H, ddd, J = 10.1, 5.6, 1.6 Hz), 4.17 (1H, m), 4.31−4.36 (2H, m), 4.40 (1H, dd, J = 11.1, 5.6 Hz), 4.46 (1H, dd, J = 11.1, 1.9 Hz), 4.80 (1H, d, J = 3.4 Hz), 5.00 (1H, ddd, J = 4.8, 1.9, 0.8 Hz), 5.17 (1H, dd, J = 1.9, 0.8 Hz), 5.52 (1H, s), 7.75 (2H, m), 7.83 (2H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 20.6 (3 × CH_3), 55.6 (CH_3), 58.9 (CH_3), 60.8 (CH_3), 63.3 (CH_2), 68.9 (CH), 73.9 (CH), 77.0 (CH), 77.1 (CH_2), 80.96, (CH), 80.99 (CH), 81.7 (CH), 83.0 (CH), 97.4 (CH), 106.6 (CH), 123.4 (2 × CH), 128.9 (2 × C), 134.4 (2 × CH), 163.1 (2 × C), 169.3 (C), 170.1 (C), 170.5 (C); MS (ESI^+) m/z (rel intens) 648 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{28}H_{35}NaNO_{15}$ 648.1904, found 648.1896. Anal. Calcd for $C_{28}H_{35}NO_{15}$: C, 53.76; H, 5.64; N, 2.24. Found C, 53.59; H, 5.47; N, 2.58.

Methyl 2,3,5,6-Tetra-*O*-methyl-α-D-mannofuranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (78). The reaction proceeded from alcohol **58** (227 mg, 0.516 mmol) following the general procedure by stirring at 0 °C for 1 h. The residue obtained was purified by column chromatography (Et_2O) to give *N*-phthalimide **78** (254 mg, 0.434 mmol, 84%) as a white crystalline solid: mp 117.2−117.9 °C (from *n*-hexane−EtOAc); $[\alpha]_D$ +127.1 (c 0.070, $CHCl_3$); IR 1932, 1790, 1738, 1102 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.16 (1H, dd, J = 9.3, 3.4 Hz), 3.21 (3H, s), 3.33 (3H, s), 3.35 (1H, m), 3.38 (3H, s), 3.41 (3H, s), 3.42 (3H, s), 3.45 (3H, s), 3.47−3.58 (4H, m), 3.51 (3H, s), 3.66 (1H, dd, J = 4.1, 4.1 Hz), 3.83 (1H, dd, J = 3.2, 3.2 Hz), 3.88 (1H, ddd, J = 8.2, 8.2, 0 Hz), 3.97 (1H, dd, J = 8.7, 3.2 Hz), 4.30 (1H, dd, J = 11.7, 6.9 Hz), 4.39 (1H, d, J = 3.4 Hz), 4.69 (1H, d, J = 3.4 Hz), 5.33 (1H, d, J = 4.0 Hz), 7.67 (2H, m), 7.75 (2H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 55.4 (CH_3), 57.2 (CH_3), 58.5 (CH_3), 58.6 (CH_3), 59.0 (CH_3), 59.9 (CH_3), 60.6 (CH_3), 69.2 (CH), 70.7 (CH_2), 74.9 (CH), 76.9 (CH), 77.1 (CH_2), 77.6 (CH), 79.7 (CH), 81.5 (CH), 82.8 (CH), 87.4 (CH), 97.2 (CH), 106.6 (CH), 123.2 (2 × CH), 128.9 (2 × C), 134.2 (2 × CH), 163.1 (2 × C); MS (ESI^+) m/z (rel intens) 608 (M^+ + Na, 100); HRMS (ESI^+) m/z calcd for $C_{27}H_{39}NNaO_{13}$, 608.2319, found 608.2322. Anal.

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Calcd for $C_{27}H_{39}NO_{13}$: C, 55.38; H, 6.71; N, 2.39. Found: C, 55.56; H, 6.43; N, 2.44.

General Procedure for the Reductive HAT Reactions with *n*-Bu_3SnH or *n*-Bu_3SnD. A 0.013 M solution of phthalimide (1 equiv) in dry benzene containing *n*-Bu_3SnH or *n*-Bu_3SnD (1 equiv) and AIBN (0.1 equiv) was heated at reflux temperature for 1.5 h. After this time another portion of *n*-Bu_3SnH or *n*-Bu_3SnD (1 equiv) and AIBN (0.1 equiv) were added, and heating at reflux was continued for an additional 1 h. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN and washed with *n*-hexane, and the combined more polar extracts were concentrated under reduced pressure. The residue was purified by chromatography.

Reductive HAT of 64. *Method A with n-Bu_3SnH.* The reaction proceeded from phthalimide **64** (70 mg, 0.118 mmol) following the general procedure. The residue was purified by column chromatography (hexanes−EtOAc, 75:25 → 40:60) to give in order of elution methyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-methyl-α-L-threofuranoside (**66**) (18.4 mg, 0.044 mmol, 49%), the alcohol **50** (10.1 mg, 0.022 mmol, 19%), previously described, and methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-D-gulopyranosyl-(1→3)-2-*O*-methyl-β-D-xylofuranoside (**65**) (14 mg, 0.031 mmol, 26%) as colorless oils. Data for compound **66**: $[\alpha]_D$ −88.8 (*c* 0.125, $CHCl_3$); IR 2929, 2828, 1747, 1373, 1230, 1055 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.21 (3H, d, *J* = 6.3 Hz), 1.98 (3H, s), 2.04 (3H, s), 2.15 (3H, s), 3.37 (3H, s), 3.39 (3H, s), 3.74 (1H, dd, *J* = 2.9, 1.3 Hz), 3.78−3.85 (2H, m), 4.11−4.17 (2H, m), 4.82 (1H, d, *J* = 1.3 Hz), 4.85 (1H, d, *J* = 1.3 Hz), 5.06 (1H, dd, *J* = 9.8, 9.8 Hz), 5.25 (1H, dd, *J* = 3.4, 1.9 Hz), 5.26 (1H, dd, *J* = 9.3, 3.4 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 17.3 (CH_3), 20.67 (CH_3), 20.74 (CH_3), 20.9 (CH_3), 54.8 (CH_3), 57.8 (CH_3), 67.0 (CH), 68.8 (CH), 69.382 (CH_2), 69.9 (CH), 71.0 (CH), 81.353 (CH), 89.6 (CH), 97.4 (CH), 106.9 (CH), 169.88 (C), 169.91 (C), 170.0 (C); MS (ESI^+) *m*/*z* (rel intens) 443 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{18}H_{28}NaO_{11}$ 443.1529, found 443.1526. Anal. Calcd for $C_{18}H_{28}O_{11}$: C, 51.42; H, 6.71. Found C, 51.28; H, 6.63. Data for compound **65**: $[\alpha]_D$ −51.0 (*c* 0.100, $CHCl_3$); IR 3498, 2936, 2832, 1745, 1228, 1048 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.17 (3H, d, *J* = 6.6 Hz), 2.01 (3H, s), 2.14 (3H, s), 2.17 (3H, s), 3.37 (3H, s), 3.43 (3H, s), 3.70 (1H, dd, *J* = 12.2, 4.5 Hz), 3.78 (1H, dd, *J* = 3.4, 1.9 Hz), 3.80 (1H, dd, *J* = 11.7, 5.8 Hz), 4.12 (1H, dddd, *J* = 6.6, 6.6, 6.6, 1.6 Hz), 4.28 (1H, dd, *J* = 6.6, 3.4 Hz), 4.31 (1H, ddd, *J* = 6.4, 6.4, 4.2 Hz), 4.82 (1H, d, *J* = 1.9 Hz), 4.83 (1H, dd, *J* = 3.7, 1.9 Hz), 4.84 (1H, d, *J* = 8.5 Hz), 5.01 (1H, dd, *J* = 8.5, 3.4 Hz), 5.33 (1H, dd, *J* = 3.7, 3.7 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 15.733 (CH_3), 20.5 (CH_3), 20.69 (CH_3), 20.72 (CH_3), 55.4 (CH_3), 57.8 (CH_3), 61.6 (CH_2), 67.9 (CH), 68.4 (CH), 69.0 (CH), 70.182 (CH), 80.8 (CH), 82.5 (CH), 89.3 (CH), 98.4 (CH), 106.9 (CH), 168.9 (C), 169.4 (C), 169.8 (C); MS (ESI^+) *m*/*z* (rel intens) 473 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{19}H_{30}NaO_{12}$ 473.1635, found 473.1643. Anal. Calcd for $C_{19}H_{30}O_{12}$: C, 50.66; H, 6.71. Found C, 50.79; H, 6.63.

Method B with n-Bu_3SnD. The reaction proceeded from phthalimide **64** (80 mg, 0.134 mmol) following the general procedure. The residue was purified by column chromatography (hexanes−EtOAc, 75:25 → 40:60) to give in order of elution methyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-methyl-α-L-(4-^2H)-threofuranoside (**69**) (15.7 mg, 0.037 mmol, 28%, ^2H-4a:^2H-4b ratio 70:30), methyl 2′,3′,4′-tri-*O*-acetyl-α-L-[5′-^2H]rhamnopyranosyl-(1→3)-2-*O*-methyl-β-D-xylofuranoside (**68**) (9.5 mg, 0.021 mmol, 8%, ^1H:^2H ratio 1:1), and methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-D-(5-^2H)-gulopyranosyl-(1→3)-2-*O*-methyl-β-D-xylofuranoside (**67**) (9 mg, 0.02 mmol, 15%) as colorless oils. Data for compound **69**: ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.21 (3H, d, *J* = 6.4 Hz), 1.98 (3H, s), 2.04 (3H, s), 2.15 (3H, s), 3.37 (3H, s), 3.39 (3H, s), 3.74 (1H, dd, *J* = 3.2, 1.3 Hz), 3.77−3.79 (1H, m), 3.81 (1H, dddd, *J* = 9.8, 6.4, 6.4, 6.4 Hz), 4.11−4.14 (1H, m), 4.82 (1H, d, *J* = 1.3 Hz), 4.85 (1H, d, *J* = 1.1 Hz), 5.05 (1H, dd, *J* = 9.8, 9.8 Hz), 5.25 (1H, dd, *J* = 3.4, 1.9 Hz), 5.27 (1H, dd, *J* = 9.3, 3.7 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 17.3 (CH_3), 20.66 (CH_3), 20.73 (CH_3), 20.9 (CH_3), 54.8 (CH_3), 57.8 (CH_3), 67.0 (CH), 68.8 (CH), 69.073 (CH, t, J_{CD} = 23.3 Hz), 69.9 (CH), 71.0 (CH), 81.283 (CH), 89.6 (CH), 97.4 (CH), 106.9 (CH), 169.88 (C), 169.90 (C), 170.0 (C); MS (ESI^+) *m*/*z* (rel intens) 444 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{18}H_{27}{}^2HNaO_{11}$ 444.1592, found 444.1599. Data for compound **68**: ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.22 (3H, s), 1.23 (3H, d, *J* = 6.1 Hz), 1.99 (3H, s), 2.05 (3H, s), 2.15 (3H, s), 3.40 (3H, s), 3.44 (3H, s), 3.78−3.89 (3.25H, m), 4.31 (1H, ddd, *J* = 6.9, 6.9, 4.5 Hz), 4.33 (1H, dd, *J* = 6.9, 3.7 Hz), 4.85 (1H, d, *J* = 1.9 Hz), 4.94 (1H, d, *J* = 1.9 Hz), 5.063 (1H, d, *J* = 9.5 Hz), 5.065 (1H, dd, *J* = 9.8, 9.8 Hz), 5.22 (1H, dd, *J* = 9.8, 3.4 Hz), 5.25 (1H, dd, *J* = 3.4, 1.9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 17.369 (CH_3), 17.502 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.7 (CH_3), 57.9 (CH_3), 61.666 (CH, t, J_{CD} = 21.9 Hz), 61.996 (CH_2), 67.3 (CH), 68.8 (CH), 69.8 (CH), 70.814 (CH), 70.870 (CH), 79.1 (CH), 80.447 (CH), 80.511 (CH), 88.6 (CH), 96.4 (CH), 107.6 (CH), 169.8 (C), 169.9 (C), 170.1 (C); MS (ESI^+) *m*/*z* (rel intens) 474 (M^+ + Na, 100), 473 (28); HRMS (ESI^+) *m*/*z* calcd for $C_{19}H_{29}{}^2HNaO_{12}$ 474.1698, found 474.1705; calcd for $C_{19}H_{30}NaO_{12}$ 473.1635, found 473.1644. Data for compound **67**: ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.16 (3H, s), 2.01 (3H, s), 2.14 (3H, s), 2.17 (3H, s), 3.38 (3H, s), 3.43 (3H, s), 3.70 (1H, dd, *J* = 11.9, 4.0 Hz), 3.78 (1H, dd, *J* = 3.4, 2.1 Hz), 3.81 (1H, dd, *J* = 11.7, 5.8 Hz), 4.28 (1H, dd, *J* = 6.6, 3.4 Hz), 4.31 (1H, ddd, *J* = 6.6, 6.6, 4.5 Hz), 4.82 (1H, d, *J* = 1.9 Hz), 4.83 (1H, d, *J* = 4.0 Hz), 4.84 (1H, d, *J* = 8.5 Hz), 5.01 (1H, dd, *J* = 8.5, 3.4 Hz), 5.33 (1H, dd, *J* = 3.7, 3.7 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 15.634 (CH_3), 20.5 (CH_3), 20.70 (CH_3), 20.73 (CH_3), 55.4 (CH_3), 57.8 (CH_3), 61.6 (CH_2), 67.9 (CH), 68.4 (CH), 70.133 (CH), 80.8 (CH), 82.5 (CH), 89.3 (CH), 98.4 (CH), 106.9 (CH), 168.9 (C), 169.4 (C), 169.8 (C); MS (ESI^+) *m*/*z* (rel intens) 474 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{19}H_{29}{}^2HNaO_{12}$ 474.1698, found 474.1705.

Reductive HAT of 70. *Method A with n-Bu_3SnH.* The reaction proceeded from phthalimide **70** (50 mg, 0.092 mmol) following the general procedure. The residue was purified by Chromatotron chromatography ($CHCl_3$−MeOH, 99:1) to give methyl 2,3,5-tri-*O*-methyl-β-L-xylofuranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**71**) (16.9 mg, 0.043 mmol, 46%) as a colorless oil and the precursor alcohol **53** (14.8 mg, 0.037 mmol, 41%). Data for compound **71**: $[\alpha]_D$ +145.4 (*c* 0.240, $CHCl_3$); IR 3505, 2933, 2832, 1456, 1100, 1050 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 3.22 (1H, dd, *J* = 9.7, 3.8 Hz), 3.40 (6H, s), 3.45 (3H, s), 3.49 (3H, s), 3.55 (1H, ddd, *J* = 10.1, 3.2, 3.2 Hz), 3.56 (1H, dd, *J* = 9.5, 9.5 Hz), 3.60 (3H, s), 3.61 (1H, dd, *J* = 10.1, 6.9 Hz), 3.65 (1H, dd, *J* = 9.5, 9.5 Hz), 3.66 (1H, dd, *J* = 10.1, 4.7 Hz), 3.70 (1H, dd, *J* = 4.7, 2.2 Hz), 3.72 (1H, dd, *J* = 12.3, 3.8 Hz), 3.77 (1H, dd, *J* = 1.9, 1.9 Hz), 3.88 (1H, dd, *J* = 12.3, 2.8 Hz), 4.29 (1H, ddd, *J* = 6.9, 4.7, 4.7 Hz), 4.81 (1H, d, *J* = 3.8 Hz), 5.41 (1H, d, *J* = 1.3 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 55.1 (CH_3), 57.6 (CH_3), 58.1 (CH_3), 58.8 (CH_3), 59.1 (CH_3), 60.9 (CH_3), 62.3 (CH_2), 70.3 (CH), 70.738 (CH_2), 76.0 (CH), 80.1 (CH), 82.4 (CH), 83.023 (CH), 83.2 (CH), 87.2 (CH), 97.5 (CH), 107.2 (CH); MS (ESI^+) *m*/*z* (rel intens) 419 (M^+ + Na, 100); HRMS (ESI^+) *m*/*z* calcd for $C_{17}H_{32}NaO_{10}$ 419.1893, found 419.1892. Anal. Calcd for $C_{17}H_{32}O_{10}$: C, 51.51; H, 8.14. Found C, 51.69; H, 8.23.

Method B with n-Bu_3SnD. The reaction proceeded from phthalimide **70** (50 mg, 0.092 mmol) following the general procedure. The residue was purified by Chromatotron chromatography ($CHCl_3$−MeOH, 99:1) to give methyl 2,3,5-tri-*O*-methyl-β-L-(4-^2H)-xylofuranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**72**) (13.6 mg, 0.034 mmol, 37%) and methyl 2,3,5-tri-*O*-methyl-α-D-[4-^2H]-arabinofuranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**73**) (12.7 mg, 0.032 mmol, 35%, ^1H:^2H ratio 25:75). Data for compound **72**: ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.22 (1H, dd, *J* = 9.3, 3.7 Hz), 3.40 (6H, s), 3.45 (3H, s), 3.50 (3H, s), 3.55 (1H, ddd, *J* = 9.8, 3.2, 3.2 Hz), 3.56 (1H, dd, *J* = 9.3, 9.3 Hz), 3.596 (1H, d, *J* = 10.3 Hz), 3.602 (3H, s), 3.65 (1H, dd, *J* = 9.3, 9.3 Hz), 3.66 (1H, d, *J* = 10.3 Hz), 3.70 (1H, d, *J* = 2.2 Hz), 3.72 (1H, dd, *J* = 12.2, 3.4 Hz), 3.77 (1H, dd, *J* = 2.4, 1.6 Hz), 3.89 (1H, dd, *J* = 12.4, 2.7 Hz), 4.81 (1H, d, *J* = 3.7 Hz), 5.42 (1H, d, *J* = 1.3 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 55.1 (CH_3), 57.6 (CH_3), 58.1 (CH_3), 58.8 (CH_3), 59.1 (CH_3), 60.9 (CH_3), 62.3 (CH_2), 70.3 (CH), 70.667 (CH_2), 76.0 (CH), 82.4 (CH), 82.940 (CH), 83.2 (CH), 87.2 (CH), 97.5 (CH), 107.2 (CH); MS (ESI^+) *m*/*z* (rel intens) 420 (M^+ + Na, 100). HRMS (ESI^+) calcd for

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$C_{17}H_{31}{}^2HNaO_{10}$ 420.1956, found 420.1956. Data for compound **73**: ^{1}H NMR (only the deuterated compound is described) (400 MHz, $CDCl_3$) δ_H 3.23 (1H, dd, J = 9.3, 3.4 Hz), 3.39 (3H, s), 3.396 (3H, s), 3.400 (3H, s), 3.44 (3H, s), 3.491 (1H, d, J = 10.3 Hz), 3.494 (3H, s), 3.53 (1H, d, J = 10.3 Hz), 3.55−3.59 (2H, m), 3.58 (1H, dd, J = 9.3, 9.3 Hz), 3.59 (3H, s), 3.66 (1H, dd, J = 9.3, 9.3 Hz), 3.72 (1H, dd, J = 12.7, 2.4 Hz), 3.76 (1H, dd, J = 2.9, 1.1 Hz), 3.84 (1H, dd, J = 12.7, 3.2 Hz), 4.83 (1H, d, J = 3.4 Hz), 5.41 (1H, s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 55.1 (CH_3), 57.7 (CH_3), 58.0 (CH_3), 58.7 (CH_3), 59.3 (CH_3), 60.9 (CH_3), 61.7 (CH_2), 70.4 (CH), 72.556 (CH_2), 72.626 (CH_2), 74.8 (CH), 81.3 (CH), 82.4 (CH), 83.1 (CH), 85.650 (CH), 85.699 (CH), 89.6 (CH), 97.4 (CH), 107.2 (CH); MS (ESI$^+$) m/z (rel intens) 420 (M^+ + Na, 100), 419 (17); HRMS (ESI$^+$) m/z calcd for $C_{17}H_{31}{}^2HNaO_{10}$ 420.1956, found 420.1961; calcd for $C_{17}H_{32}NaO_{10}$ 419.1893, found 419.1897.

Reductive HAT of 74. *Method A with n-Bu$_3$SnH.* The reaction proceeded from phthalimide **74** (31.5 mg, 0.050 mmol) following the general procedure. The residue was purified by Chromatotron chromatography ($CHCl_3$−MeOH, 100:0.2) to give methyl 2,3,5-tri-*O*-acetyl-*β*-L-xylofuranosyl-(1→4)-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**75**) (9.7 mg, 0.020 mmol, 40%) as a colorless oil and the precursor alcohol **55** (4.8 mg, 0.010 mmol, 20%). Data for compound **75**: $[\alpha]_D$ +95.0 (c 0.360, $CHCl_3$); IR 3524, 2929, 2840, 1745, 1228, 1048 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 2.09 (3H, s), 2.10 (3H, s), 2.11 (3H, s), 3.20 (1H, dd, J = 9.5, 3.5 Hz), 3.41 (3H, s), 3.50 (3H, s), 3.54−3.57 (2H, m), 3.56 (3H, s), 3.63 (1H, dd, J = 9.5, 9.5 Hz), 3.76 (1H, dd, J = 12.3, 2.8 Hz), 3.90 (1H, dd, J = 12.3, 3.5 Hz), 4.25 (1H, dd, J = 11.7, 7.3 Hz), 4.31 (1H, dd, J = 11.7, 4.7 Hz), 4.51 (1H, ddd, J = 7.3, 4.7, 4.7 Hz), 4.81 (1H, d, J = 3.5 Hz), 5.16 (1H, dd, J = 1.6, 1.6 Hz), 5.26 (1H, dd, J = 4.7, 1.9 Hz), 5.44 (1H, d, J = 0.9 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 20.61 (CH_3), 20.62 (CH_3), 20.7 (CH_3), 55.2 (CH_3), 59.0 (CH_3), 61.1 (CH_3), 61.6 (CH_2), 61.992 (CH_2), 70.2 (CH), 74.328 (CH), 75.7 (CH), 78.3 (CH), 79.6 (CH), 82.3 (CH), 83.1 (CH), 97.6 (CH), 107.4 (CH), 168.9 (C), 169.5 (C), 170.6 (C); MS (ESI$^+$) m/z (rel intens) 503 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{20}H_{32}NaO_{13}$ 503.1741, found 503.1745. Anal. Calcd for $C_{20}H_{32}O_{13}$: C, 55.00; H, 6.71. Found C, 49.91; H, 6.57.

Method B with n-Bu$_3$SnD. The reaction proceeded from phthalimide **74** (27 mg, 0.043 mmol) following the general procedure. The residue was purified by Chromatotron chromatography ($CHCl_3$−MeOH, 100:0.2) to give methyl 2,3,5-tri-*O*-acetyl-*β*-L-(4-^{2}H)-xylofuranosyl-(1→4)-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**76**) (8.2 mg, 0.017 mmol, 40%) and methyl 2,3,5-tri-*O*-acetyl-*α*-D-[5-^{2}H]-arabinofuranosyl-(1→4)-6-*O*-phthalimido-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**77**) (4.6 mg, 0.010 mmol, 22%, ^{1}H:^{2}H ratio 30:70). Data for compound **76**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 2.09 (3H, s), 2.10 (3H, s), 2.11 (3H, s), 3.20 (1H, dd, J = 9.5, 3.5 Hz), 3.41 (3H, s), 3.50 (3H, s), 3.54−3.57 (2H, m), 3.56 (3H, s), 3.63 (1H, dd, J = 9.5, 9.5 Hz), 3.77 (1H, dd, J = 12.3, 2.8 Hz), 3.90 (1H, dd, J = 12.3, 3.2 Hz), 4.25 (1H, d, J = 11.7 Hz), 4.31 (1H, d, J = 11.7 Hz), 4.81 (1H, d, J = 3.5 Hz), 5.17 (1H, dd, J = 1.6, 1.6 Hz), 5.26 (1H, d, J = 2.2 Hz), 5.44 (1H, d, J = 1.3 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 20.61 (CH_3), 20.63 (CH_3), 20.7 (CH_3), 55.2 (CH_3), 59.0 (CH_3), 61.1 (CH_3), 61.6 (CH_2), 61.934 (CH_2), 70.2 (CH), 74.263 (CH), 75.7 (CH), 79.6 (CH), 82.3 (CH), 83.1 (CH), 97.6 (CH), 107.4 (CH), 168.9 (C), 169.5 (C), 170.6 (C); MS (ESI$^+$) m/z (rel intens) 504 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{20}H_{31}{}^2HNaO_{13}$ 504.1803, found 504.1803. Data for compound **77**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 2.10 (3H, s), 2.105 (3H, s), 2.107 (3H, s), 3.20 (1H, dd, J = 9.1, 3.8 Hz), 3.42 (3H, s), 3.51 (3H, s), 3.57 (3H, s), 3.58−3.67 (3H, m), 3.76 (1H, dd, J = 12.3, 2.2 Hz), 3.79 (1H, dd, J = 12.3, 3.5 Hz), 4.189 (1H, d, J = 11.7 Hz), 4.192 (1H, dd, J = 11.4, 6.3 Hz), 4.31 (1H, ddd, J = 6.3, 4.7, 4.7 Hz), 4.364 (1H, d, J = 11.7 Hz), 4.368 (1H, dd, J = 11.4, 4.4 Hz), 4.82 (1H, d, J = 3.8 Hz), 5.006 (1H, dd, J = 1.9 Hz), 5.010 (1H, dd, J = 4.4, 1.8 Hz), 5.18 (1H, dd, J = 1.9, 0.9 Hz), 5.49 (1H, s); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_C 20.61 (CH_3), 20.64 (2 × CH_3), 55.2 (CH_3), 59.0 (CH_3), 61.0 (CH_3), 61.7 (CH_2), 63.346 (CH_2), 63.411 (CH_2), 70.0 (CH), 74.2 (CH), 76.974 (CH), 77.0 (CH), 80.7 (CH), 81.1 (CH), 82.2 (CH), 83.2 (CH), 97.6 (CH), 107.0 (CH), 169.3 (C), 169.9 (C), 170.5 (C); MS (ESI$^+$) m/z (rel intens) 504 (M^+ + Na, 100), 503 (27); HRMS (ESI$^+$) m/z calcd for $C_{20}H_{31}{}^2HNaO_{13}$ 504.1803, found 504.1798; calcd for $C_{20}H_{32}O_{13}Na$ 503.1741, found 503.1742.

Reductive HAT of 78. *Method A with n-Bu$_3$SnH.* The reaction proceeded from phthalimide **78** (82 mg, 0.140 mmol) following the general procedure, except that the addition of the second portion of reagents was omitted, and the reaction was heated at reflux temperature for 4 h. The residue was purified by column chromatography on silica gel 60 PF (0.063−0.2 mm) with 10% KF (hexanes−EtOAc, 10:90 → 0:100) to give an inseparable mixture of alcohols (50.3 mg, 0.114 mmol, 82%, 1.4:1). Acetylation of the mixture of alcohols (50.3 mg, 0.114 mmol) in dry pyridine (3.3 mL) containing Ac_2O (1.1 mL) at room temperature for 2 h gave after Chromatotron chromatography (hexanes−EtOAc, 1:1) methyl 2,3,5,6-tetra-*O*-methyl-*α*-D-mannofuranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**80**) (30.3 mg, 0.063 mmol, 55%) and methyl 2,3,5,6-tetra-*O*-methyl-*α*-D-talofuranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**79**) (24.8 mg, 0.051 mmol, 45%), both as colorless oils. Data for compound **80**: $[\alpha]_D$ +148.2 (c 0.110, $CHCl_3$); IR 2931, 1743, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 2.06 (3H, s), 3.20 (1H, dd, J = 9.3, 3.4 Hz), 3.36−3.61 (4H, m), 3.36 (3H, s), 3.39 (3H, s), 3.44 (3H, s), 3.48 (3H, s), 3.49 (3H, s), 3.53 (3H, s), 3.58 (3H, s), 3.67−3.74 (3H, m), 3.91 (1H, dd, J = 4.5, 3.4 Hz), 4.04 (1H, dd, J = 8.7, 3.4 Hz), 4.17 (1H, dd, J = 11.9, 6.6 Hz), 4.37 (1H, dd, J = 12.0, 2.2 Hz), 4.80 (1H, d, J = 3.4 Hz), 5.36 (1H, d, J = 3.7 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 20.8 (CH_3), 55.0 (CH_3), 57.5 (CH_3), 58.7 (CH_3), 58.8 (CH_3), 59.1 (CH_3), 60.2 (CH_3), 61.0 (CH_3), 63.5 (CH_2), 68.0 (CH), 71.2 (CH_2), 75.7 (CH), 77.1 (CH), 78.0 (CH), 79.8 (CH), 82.0 (CH), 83.1 (CH), 87.5 (CH), 97.2 (CH), 106.9 (CH), 170.6 (C); MS (ESI$^+$) m/z (rel intens) 505 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{21}H_{38}NaO_{12}$, 505.2261, found 505.2256. Anal. Calcd for $C_{21}H_{38}O_{12}$: C, 52.27; H, 7.94. Found: C, 52.32; H, 8.02. Data for compound **79**: $[\alpha]_D$ +21.3 (c 0.530, $CHCl_3$); IR 2930, 1743, 1056 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 2.07 (3H, s), 3.21 (1H, dd, J = 9.4, 3.6 Hz), 3.37−3.59 (5H, m), 3.35 (3H, s), 3.40 (3H, s), 3.42 (3H, s), 3.46 (3H, s), 3.49 (3H, s), 3.50 (3H, s), 3.61 (3H, s), 3.37−3.74 (2H, m), 3.91 (1H, dd, J = 7.7, 4.5 Hz), 4.02 (1H, dd, J = 7.7, 3.4 Hz), 4.24 (1H, dd, J = 12.0, 6.2 Hz), 4.58 (1H, dd, J = 11.9, 1.85 Hz), 4.81 (1H, d, J = 3.7 Hz), 5.34 (1H, br s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 20.9 (CH_3), 55.0 (CH_3), 57.9 (CH_3), 58.0 (CH_3), 58.8 (2 × CH_3), 59.0 (CH_3), 61.1 (CH_3), 63.8 (CH_2), 68.4 (CH), 72.2 (CH_2), 76.5 (CH), 78.5 (CH), 79.0 (CH), 80.6 (CH), 82.1 (2 × CH), 83.2 (CH), 97.1 (CH), 105.7 (CH), 170.7 (C); MS (ESI$^+$) m/z (rel intens) 505 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{21}H_{38}NaO_{12}$, 505.2261, found 505.2263. Anal. Calcd for $C_{21}H_{38}O_{12}$: C, 52.27; H, 7.94. Found: C, 52.44; H, 8.14.

Method B with n-Bu$_3$SnD. The reaction proceeded from phthalimide **78** (30.7 mg, 0.052 mmol) following the general procedure, except that the addition of the second portion of reagents was omitted, and the reaction was heated at reflux temperature for 4 h. The residue was purified by column chromatography on silica gel 60 PF (0.063−0.2 mm) with 10% KF (hexanes−EtOAc, 10:90 → 0:100) to give an inseparable mixture of methyl 2,3,5,6-tetra-*O*-methyl-*α*-D-[4-^{2}H]mannofuranosyl-(1→4)-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**82**) (11.2 mg, 0.025 mmol, 49%, ^{1}H:^{2}H ratio 30:70) and methyl 2,3,5,6-tetra-*O*-methyl-*α*-D-(4-^{2}H)talofuranosyl-(1→4)-2,3-di-*O*-methyl-*α*-D-glucopyranoside (**81**) (6.8 mg, 0.015 mmol, 29%). ^{1}H NMR (only deuterated compounds are described) (400 MHz, $CDCl_3$) δ_H 3.23 (1H, dd, J = 7.6, 3.7 Hz), 3.25 (1H, dd, J = 7.7, 3.7 Hz), 3.35 (3H, s), 3.38 (3H, s), 3.39 (3H, s), 3.40 (3H, s), 3.41 (3H, s), 3.42−3.56 (8H, m), 3.43 (3H, s), 3.48 (6H, s), 3.49 (6H, s), 3.50 (3H, s), 3.53 (3H, s), 3.57 (3H, s), 3.60 (3H, s), 3.61−3.68 (6H, m), 3.72 (1H, dd, J = 7.7, 4.5 Hz), 3.74 (1H, dd, J = 7.2, 2.6 Hz), 3.84 (1H, dd, J = 12.4, 2.9 Hz), 3.87 (1H, d, J = 4.5 Hz, 3′-H inv), 3.91 (1H, d, J = 4.8 Hz, 3′-H ret), 3.98 (1H, dd, J = 12.6, 2.5 Hz), 4.82 (2H, d, J = 3.7 Hz), 5.43 (1H, d, J = 4.0 Hz), 5.50 (1H, br s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C 55.0 (CH_3), 55.1 (CH_3), 57.1 (CH_3), 57.7 (CH_3), 58.1 (CH_3), 58.7 (3 × CH_3), 59.0 (CH_3), 59.2 (CH_3), 59.4 (CH_3), 60.2 (CH_3), 60.7 (2 × CH_2), 60.8 (CH_3), 60.9 (CH_3), 69.7 (CH_2), 70.6 (CH), 70.7 (CH), 72.7 (CH_2), 74.5 (CH), 74.6 (CH), 76.9 (CH), 78.1 (CH), 78.2

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(CH), 79.7 (CH), 79.8 (CH), 81.7 (CH), 82.2 (CH), 82.3 (CH), 83.2 (CH), 83.6 (CH), 87.2 (2 × CH), 97.5 (2 × CH), 105.2 (CH), 107.1 (CH); MS (ESI$^+$) m/z (rel intens) 464 (M^+ + Na, 100); HRMS (ESI$^+$) m/z calcd for $C_{19}H_{35}{}^2HNaO_{11}$, 464.2218, found 464.2211.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for all new compounds and molecular modeling calculations (Figures S1−S3 and Tables S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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