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Intramolecular 1,8-Hydrogen Atom Transfer. Stereoselectivity of the Hexopyranos-5′-yl Radical Reactions in Hex*p*-(1→4)-Hex*p* Disaccharide Systems

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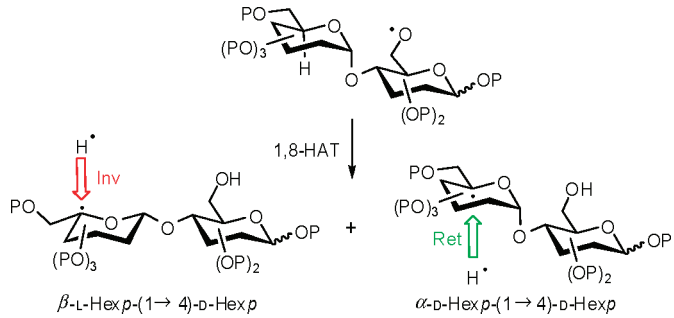

The stereoselective reduction of hexopyranos-5′-yl radicals in α-D-Hex*p*-(1→4)-D-Hex*p* disaccharide models is described. These radicals are generated from a 6-*O*-yl radical located in the other monosaccharic unit through a 1,8-hydrogen atom transfer. The reaction, which is strongly influenced by steric and stereoelectronic effects, permits in some cases the transformation of α-D-Hex*p*-(1→4)-D-Hex*p* into *β*-L-Hex*p*-(1→4)-D-Hex*p* disaccharides in a single step with high diastereoselectivity.

Introduction

The conformational aspects of hexopyranos-1-yl radicals and the stereoselectivity of their reactions have been extensively studied in recent years.[1] It was found that the conformation of these radicals depends critically on the electronegativity and stereochemistry of the 2-oxygenated substituent.[2] Thus, mannopyranos-1-yl radicals (**I**) retain the $^4C_1$ chair of their precursor **1**, while glucopyranos-1-yl radicals (**II**) exist preferentially in a $B_{2,5}$ boat conformation (Scheme 1). Both radicals, with the 2-oxygenated substituent axially disposed, show a high propensity for quenching along the α-axial direction. This stereoselectivity is caused by two main stereoelectronic effects that have been termed the *radical anomeric effect* and the *quasi-homo-anomeric effect* [*β-oxygen effect*].[3]

Less is known about the stereoselectivity of hexopyranos-5-yl radical reactions and detailed studies have not been reported so far except for a few examples.[4] These radicals with a pseudo-*C*-glycoside structure appear to be in a similar situation with regard to the pyranose ring conformation and stereoelectronic stabilization effects. Indeed, the galactopyranos-5-yl radical (**III**) with an axial oxygenated substituent at C-4 remains in the $^4C_1$ chair of its precursor **2**, while the glucopyranos-5-yl radical (**IV**) adopts a $B_{1,4}$ boat conformation as determined by ESR spectroscopy (Scheme 1).[5] In consequence, we should expect a preponderant formation of α-axial substitution products. This seems to be especially the case for the two examples known

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(3) (a) Beckwith, A. L. J.; Duggan, P. J. *Tetrahedron* **1998**, *54*, 4623–4632. (b) Beckwith, A. L. J.; Duggan, P. J. *Tetrahedron* **1998**, *54*, 6919–6928. (c) Korth, H.-G.; Sustmann, R.; Dupuis, J.; Giese, B. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1453–1459. (d) Barton, D. H. R.; Hartwig, W.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1982**, 4397–4410.

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(5) Korth, H.-G.; Praly, J.-P.; Somsák, L.; Sustmann, R. *Chem. Ber.* **1990**, *123*, 1155–1160.

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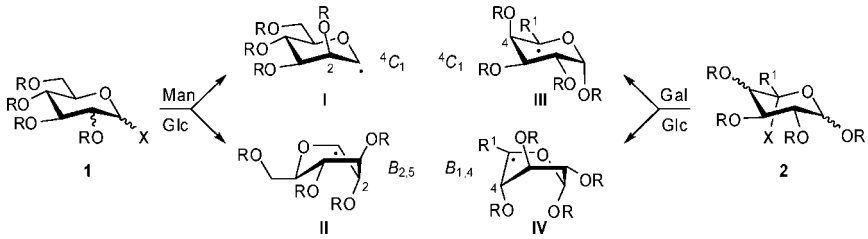
SCHEME 1. Conformation of Hexopyranos-1-yl and Hexopyranos-5-yl Radicals[a]



[a] R = protective group; R^1 = see text; X = Br.

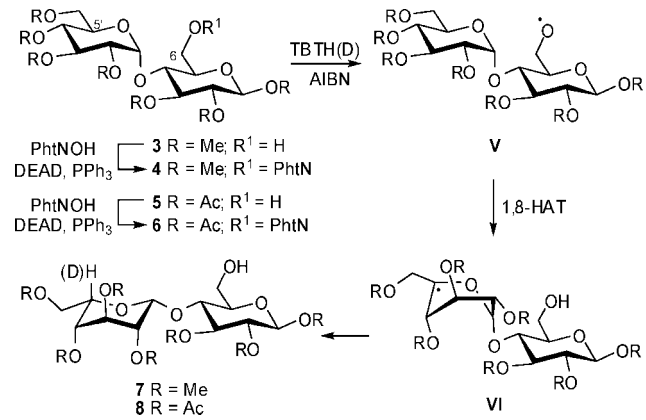
where the *n*-Bu_3SnH reduction of (5*S*)-1,2,3,4-tetra-*O*-acetyl-5-bromo-8-cyano-6,7,8-trideoxy-β-D-*xylo*-octopyranose (**2**, R = Ac; $R^1 = (CH_2)_2CN$; X = Br)[4d] and (5*S*)-1,2,3,4,6-penta-*O*-acetyl-5-bromo-α-D-*xylo*-hexopyranose (**2**, R = Ac; $R^1 = CH_2OAc$, X = Br)[4c] apparently proceed by axial quenching with total retention of configuration.

The reduction of methyl (5*R*)-1,2,3,4-tetra-*O*-acetyl-5-bromo-D-*xylo*-hexopyranuronate (**2**, R = Ac; $R^1 = CO_2Me$; X = Br) has been studied in more detail.[6] The stereochemistry of the reaction seems to be dependent on the temperature and/or concentration of the tin hydride as well as on the configuration of the substituent at C-1.[6c] Surprisingly, the products were obtained with diastereoselectivities up to 3:1 in favor of the inverted L-iduronic acid derivative. At first sight, this is probably attributable to a radical stabilization by the carboxylate group, which permits ring inversion to a $^1C_4$ chair and stannane quenching along the β-axial direction. This apparently anomalous behavior has attracted some preparative interest because L-iduronic acid is a key constituent of heparin and other related glycosaminoglycans and is essential for the construction of heparin-based oligosaccharides.[7]

Results and Discussion

In a previous paper from this laboratory we have described an example of 1,8-hydrogen atom transfer (HAT) between the two glucopyranose units of a heptamethylated α-D-Glc*p*-(1→4)-β-D-Glc*p* disaccharide (β-maltose) (**3**)[8] through a nine-membered transition state (Scheme 2).[9] The hydrogen abstraction from C-5′ is promoted, in a highly efficient and completely regioselective manner, by the 6-*O*-yl radical (**V**) generated in situ from reaction of the 6-*O*-phthalimide derivative **4** with *n*-Bu_3SnH/AIBN. In this case the *C*-radical (**VI**) reduction gave also predominant inversion of the configuration at C-5′ and consequent transformation of this D-glucose moiety in L-idose (L-Ido/D-Glc, 1.6:1) (Table 1, entry 1). After some experimentation, we have now found that this stereoselectivity can be improved up to a inversion/retention ratio of 2.5:1 by slowing down the stannane quenching reducing the amount and concentration of tin hydride (entry 2).

SCHEME 2. Reduction of Hexopyranos-5′-yl Radicals in α-D-Glc*p*-(1→4)-β-D-Glc*p* Disaccharides[a]



[a] PhtNOH = *N*-hydroxyphthalimide; TBTH = *n*-Bu_3SnH; TBTD = *n*-Bu_3SnD.

This last result, which suggests that 1,8-HAT may be a synthetically useful protocol for the inversion of configuration at C-5′ and consequent transformation of this β-maltose derivative **4** into a β-L-Ido*p*-(1→4)-β-D-Glc*p* system (**7**) in a single step, encouraged a further exploratory effort with variously structured disaccharide substrates.[10]

It has been suggested that the *quasi-homo-anomeric* effect increases with the increase in electronegativity of the β-oxygenated substituent[2b] so we decided to prepare the heptaacetylated 6-*O*-phthalimide[11] derivative **6** from the alcohol **5** and *N*-hydroxyphthalimide under Mitsunobu conditions.[12] To our delight, the HAT reaction afforded the inverted product **8** with excellent diastereoselectivity (**8/5**, 14:1) (entry 3). In these aldose systems, as in the uronate system, a mechanism of β-axial radical quenching on the inverted $^1C_4$ chair could also be operating.

In order to calculate correct diastereoselective ratios deuterium incorporation studies using *n*-Bu_3SnD/AIBN as reagent were carried out to discriminate between deuterated alcohol **5** produced by abstraction with retention and the undeuterated one generated by reduction of the alkoxyl radical prior to the abstraction reaction. As expected, complete incorporation of

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(8) (a) Aspinall, G. O.; Igarashi, O.; Krishnamurthy, T. N.; Mitura, W.; Funabashi, M. *Can. J. Chem.* **1976**, *54*, 1708–1713. (b) Aspinall, G. O.; Krishnamurthy, T. N.; Mitura, W.; Funabashi, M. *Can. J. Chem.* **1975**, *53*, 2182–2188.

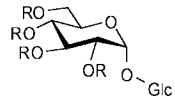
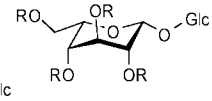
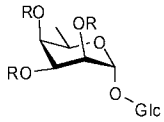
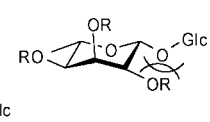
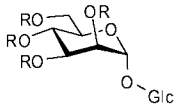
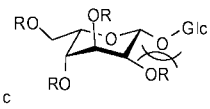
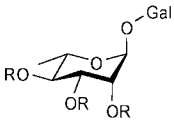
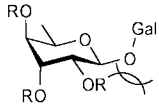
(9) Francisco, C. G.; Herrera, A. J.; Kennedy, A. R.; Melián, D.; Suárez, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 856–858.

(10) This disaccharide model is closely related to α-L-Ido*p*-(1→4)-α-D-Glc*p*, a repetitive unit in heparin glycosaminoglycan.

(11) (a) Kim, S.; Lee, T. A.; Song, Y. *Synlett* **1998**, 471–472. (b) Okada, K.; Okamoto, K.; Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8736–8738. (c) Okada, K.; Okamoto, K.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1636–1637. (d) Barton, D. H. R.; Blundell, P.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1989**, *30*, 2341–2344.

(12) (a) Mitsunobu, O. *Synthesis* **1981**, 1–28. (b) Grochowski, E.; Jurczak, J. *Synthesis* **1976**, 682–684.

TABLE 1. Stereoselective Reduction of Hexopyranos-5′-yl Radicals

entry	precursor	product	abst.,[a,b] %	inv.:ret.[b]
1[c]	 D-Glc **4** R = Me	 L-Ido **7** R = Me	60	1.6:1
2[d]	**4** R = Me	**7** R = Me	46	2.5:1
3	**6** R = Ac	**8** R = Ac	63	14:1
4	 D-Tal **10** R = Me	 L-All **13** R = Me	60	13:1
5	**12** R = Ac	**14** R = Ac	82[e]	0.5:1
6	 D-Man **18** R = Me	 L-Gul **21** R = Me	67	3.5:1
7	**20** R = Ac	**22** R = Ac	59	2:1
8	 L-Rha **24** R = Me	 D-Gul **27** R = Me	76	4.3:1
9	**26** R = Ac	**28** R = Ac	72[f]	3.7:1

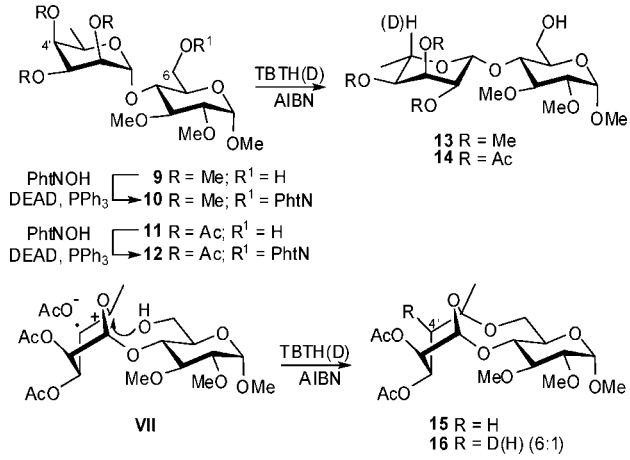
[a] Isolated 1,8-abstraction yield. [b] The yield of retention product was estimated by *n*-Bu_3SnD/AIBN experiments. [c] *n*-Bu_3SnH (9 equiv), AIBN (0.15 equiv), PhH 1.8 M, reflux, 1 h. [d] *n*-Bu_3SnH (1 equiv), AIBN (0.1 equiv), PhH 0.01 M, reflux, 1 h. [e] Included retained product **15** (22%). [f] Included abstraction product **30** (5%).

deuterium at C-5′ is detected in the inverted product **8** and there is no observable deuterium scrambling at other positions of the molecule within NMR detection limits. The results are summarized in Table 1 and in Supporting Information.

To better understand the scope and stereoselectivity of this C-5′ radical stannane quenching, we decided to prepare various disaccharides with the correct relative stereochemistry at the four chiral centers (C-4, C-5, C-1′, and C-5′) involved in the 1,8-HAT reaction:[13] α-D-Tal*p*-(1→4)-α-D-Glc*p* (**9**, **11**), α-D-Man*p*-(1→4)-α-D-Glc*p* (**17**, **19**), and α-L-Rha*p*-(1→4)-α-D-Gal*p* (**23**, **25**) (Schemes 3−5). Compounds **9** and **17** were effectively synthesized by TMSOTf-mediated glycosylation of methyl 6-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-methyl-α-D-glucopyranoside, using 2,3,4-tri-*O*-methyl-6-deoxy-α-D-talopyranosyl and 2,3,4,6-tetra-*O*-methyl-α-D-mannopyranosyl trichloroacetimidates, respectively, as glycosyl donors.[14] Analogously, compound **23** (Scheme 5) was synthesized by glycosylation of methyl 6-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-methyl-α-D-galactopyranoside with 2,3,4-tri-*O*-methyl-α-L-rhamnopyranosyl trichloroacetimidate.[15] The corresponding acetates **11**, **19**, and **25** were prepared by a completely analogous synthetic protocol as described in Supporting Information.

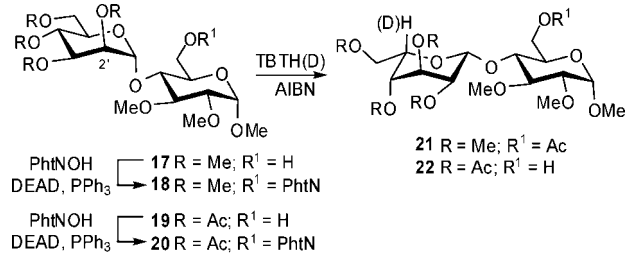
The α-D-Tal*p*-(1→4)-α-D-Glc*p* disaccharide **9** with the D-talose moiety was selected, because the presence of the three axial substituents was expected to enhance the chair inversion rate (Scheme 3). Indeed, when methylated 6-*O*-phthalimide **10** was treated with *n*-Bu_3SnH/AIBN the β-L-All*p*-(1→4)-α-D-Glc*p*

SCHEME 3. Reduction of Hexopyranos-5′-yl Radicals in α-D-Tal*p*-(1→4)-α-D-Glc*p* Disaccharides[a]



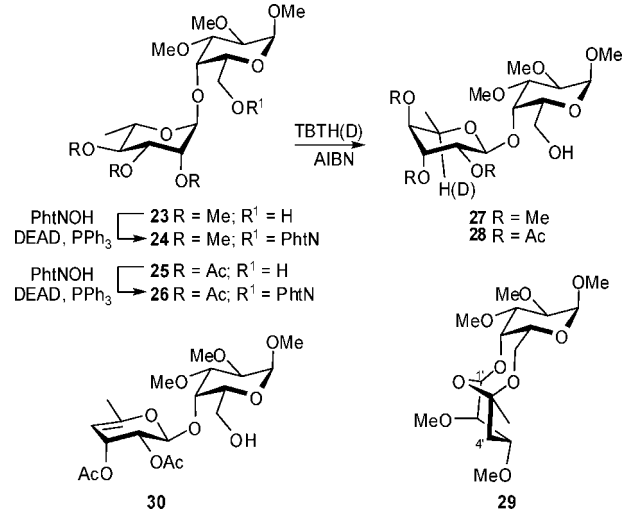
[a] PhtNOH = *N*-hydroxyphthalimide; TBTH = *n*-Bu_3SnH; TBTD = *n*-Bu_3SnD.

SCHEME 4. Reduction of Hexopyranos-5′-yl Radicals in α-D-Man*p*-(1→4)-α-D-Glc*p* Disaccharides[a]



[a] PhtNOH = *N*-hydroxyphthalimide; TBTH = *n*-Bu_3SnH; TBTD = *n*-Bu_3SnD.

SCHEME 5. Reduction of Hexopyranos-5′-yl Radicals in α-L-Rha*p*-(1→4)-α-D-Gal*p* Disaccharides[a]



[a] PhtNOH = *N*-hydroxyphthalimide; TBTH = *n*-Bu_3SnH; TBTD = *n*-Bu_3SnD.

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(14) (a) Matsuo, I.; Isomura, M.; Miyazaki, T.; Sakakibara, T.; Ajisaka, K. *Carbohydr. Res.* **1997**, *305*, 401–413. (b) Kerékgyártó, J.; Kamerling, J. P.; Bouwstra, J. B.; Vliegenthart, J. F. G.; Lipták, A. *Carbohydr. Res.* **1989**, *186*, 51–62. For a review on disaccharide synthesis with trichloroacetimidates, see: (c) Schmidt, R. R.; Jung, K.-H. In *Preparative Carbohydrate Chemistry*; Hanessian, S., Ed.; Marcel Dekker: New York, 1997; pp 283−312.

disaccharide **13** was obtained in good yield and excellent inversion-retention ratio (**13/9**, 13:1) (entry 4). In stark contrast, the 6-*O*-phthalimide **12** with the peracetylated D-talose moiety afforded preferentially retained product **11** with modest diastereoselectivity (**14/11**, 0.5:1) (entry 5). In this last case the reaction was accompanied by an unexpected side product **15** in low yield (22%). The structure and stereochemistry of **15** with a 4′-deoxygenated carbon and a 1,3,5-trioxocane cycle as principal features were determined by extensive use of ^{1}H and ^{13}C NMR including DEPT, and 2D-COSY, HMBC, and HSQC experiments. When the reaction was carried out with *n*-Bu_3SnD, compound **16** was obtained with approximately 86% deuterium incorporation at C-4′. The axial disposition of the deuterium was determined by ^{1}H NMR indicating an effective shielding of the α-pyranose ring by the 1,3,5-trioxocane moiety.[16] These results suggest that the formation of **15** takes place by two different mechanisms: (a) a 5′-radical reductive elimination to give a 4′-enol ether and subsequent alcohol addition which is responsible for the minor undeuterated compound (vide infra) and (b) an interesting tandem 1,8-HAT-intramolecular *cine* substitution mechanism with the 4′-acetate as the leaving group and the oxygen at C-6 acting with an umpolung reactivity during the reaction, first as an electrophilic alkoxyl radical and then as a nucleophile.[17] The stereochemistry of **15** suggests that the nucleophilic attack occurred by the α-axial side on the stabilized radical in a $^4C_1$ chair conformation (**VII**) with retention of configuration at C-5′ (Scheme 3).

Next, we were interested in studying the influence of the stereochemistry of substituents other than C-4′. In this context, disaccharide α-D-Man*p*-(1→4)-α-D-Glc*p* (**17**), which differs from **3** only in the configuration at C-2′, was selected (Scheme 4). The reaction of permethylated 6-*O*-phthalimide **18** with *n*-Bu_3SnH/AIBN afforded, after acetylation, disaccharide *β*-L-Gul*p*-(1→4)-α-D-Glc*p* **21** with an inversion-retention ratio of 3.5:1, which is somewhat higher than that of compound **4** (2.5:1) (compare entries 6 and 2). On the other hand, compound **22** with an inversion-retention ratio of 2:1, substantially lower than in the case of compound **6** (14:1), is obtained during the reaction of tetraacetyl 6-*O*-phthalimide **20** (compare entries 7 and 3). From the results of these two experiments, it is evident that the stereochemistry of the reduction of the C-5′ radical is strongly influenced by both the stereochemistry and nature of the C-2′ substituent.

Our next models, the α-L-Rha*p*-(1→4)-α-D-Gal*p* derivatives (**23** and **25**), may not be so useful from the synthetic point of view (Scheme 5). Indeed, the C-5′ inversion should transform the L-rhamnose moiety into a readily accessible 6-deoxy-D-gulose, but we believe them to be important to shed some light on the stereochemistry of the reaction mechanism and further extend the scope of the methodology. In both cases the reaction predominantly produced inverted D-disaccharides (**27** and **28**, respectively) with high diastereoselectivity (entries 8 and 9). Contrary to the other examples discussed above during the inversion reaction, the pyranose ring undergoes conformational changes from $^1C_4$ to $^4C_1$ chair and the radical quenching is now from the α-axial side of the molecule. The formation of two minor products **29** and **30** from these reactions deserves a brief comment (Scheme 5). The 4-deoxy-1,3,5-trioxocane **29** was formed in 5% yield during the reduction of 6-*O*-phthalimide **24**. In principle, this product is analogous to **15**, but the absence of deuterium incorporation at C-4′ when the reaction was carried out using *n*-Bu_3SnD suggests that only one mechanism operates in this case and argues in favor of a 5′-radical reductive elimination and subsequent alcohol addition to the 4′-enol ether. The isolation of a small amount of undeuterated 4′-enol ether **30** during the reaction of 6-*O*-phthalimide **26** with *n*-Bu_3SnD/AIBN supports the proposed mechanism.

From the study of the results summarized in Table 1 several general conclusions can be drawn. With the *O*-methyl-protected carbohydrates **4**, **10**, **18**, and **24** the steric effects clearly govern the stereochemical course of the reaction, whereas stereoelectronic factors appear to be less important (entries 2, 4, 6, and 8). The observed inversion/retention ratio is in reasonably good agreement with the expected instability of the $^4C_1$ chair, and the number of axial substituents in the starting monosaccharide α-D-Tal > α-L-Rha ≥ α-D-Man > α-D-Glc, 13, 4.5, 3.5, and 2.5, respectively.[18]

On the contrary, it is also clear that stereoelectronic factors are much more important than steric effects in the cases of the *O*-acetyl-protected carbohydrates **6** and **12**. The reaction of acetylated α-D-Glc **6** occurs by *β*-axial radical quenching to give the *β*-L-Ido derivative **8** where the 4′-acetyl group is axially disposed, with excellent inversion/retention ratio (entry 3). The reaction of acetylated α-D-Tal **12** is illustrative of the greater importance of stereoelectronic over steric effects in these esterified carbohydrates, an α-axial radical attack now giving principally retention of configuration at 5′ (entry 5). In striking contrast the *O*-methyl-α-D-Tal derivative **10**, in a relatively unstable $^4C_1$ conformation and with the 4′-methoxyl group in the axial position, almost exclusively gives inversion (entry 4).

In the reaction of the esterified D-Man **20** and L-Rha **26** models, the equatorial-equatorial interaction between the glycosidic bond and the 2′-acetyl substituent seems to be an important source of instability for the inverted product and a substantial decrease in the inversion preference is observed (compare entries 7 and 9 with 3). This effect is not observed in the case of *O*-methyl-D-Man **18** and L-Rha **24** models, perhaps due to the lower steric demand of the methoxyl groups (compare entries 6 and 8 with 2).[19] We are currently engaged in further studies using more electronegative and more sterically demanding substituents to expand the synthetic utility of this methodology.

Experimental Section

General Methods. Melting points were determined with a hot-stage apparatus. Optical rotations were measured at the sodium line at ambient temperature in $CHCl_3$ solutions. IR spectra were recorded in film unless otherwise stated. NMR spectra were determined at 500 MHz for ^{1}H and 125.7 MHz for ^{13}C in $CDCl_3$ unless otherwise stated, in the presence of TMS as internal standard. Mass spectra were determined at 70 eV unless otherwise stated. Merck silica gel 60 PF (0.063−0.2 mm) was used for column chromatography.

(15) (a) Wang, J.; Li, J.; Tuttle, D.; Takemoto, J. Y.; Chang, C.-W. T. *Org. Lett.* **2002**, *4*, 3997–4000. (b) van Steijn, A. M. P.; Kamerling, J. P.; Vliegenthart, J. F. G. *Carbohydr. Res.* **1991**, *211*, 261–277.

(16) By comparison of the 4-H coupling constant with those of the undeuterated compound **15**. Compound **16**: 2.03 (1H, br d, $J_{3',4'eq}$ = 5.0 Hz, 4′-H_{eq}). Compound **15**: 1.98 (1H, dd, J_{gem} = 12.6, $J_{3',4'ax}$ = 12.6 Hz, 4′-H_{ax}); 2.06 (1H, dd, J_{gem} = 12.6, $J_{3',4'eq}$ = 4.8 Hz, 4′-H_{eq}).

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(18) Rao, V. S. R.; Qasba, P. K.; Balaji, P. V.; Chandrasekaran, R. *Conformation of Carbohydrates*, Harwood Academic: Australia, 1998; pp 49−90.

(19) Beckwith, A. L. J.; Page, D. M. *J. Org. Chem.* **1998**, *63*, 5144–5153.

Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use. All reactions involving air- or moisture-sensitive materials were carried out under a nitrogen atmosphere. The spray reagents for TLC analysis were conducted with 0.5% vanillin in H_2SO_4−EtOH (4:1) and further heating until development of color.

Reductive HAT of Methyl 2,3,4,6-Tetra-*O*-methyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (4). Method A with *n*-Bu_3SnH. A solution of phthalimide **4**[9] (32 mg, 0.055 mmol) in dry benzene (4.1 mL) containing *n*-Bu_3SnH (15 μL, 0.055 mmol) and AIBN (1 mg, 0.006 mmol) was heated at reflux temperature for 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Column chromatography of the crude residue (hexanes−EtOAc, 10:90 → 0:100) afforded methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-methyl-β-D-glucopyranoside (**3**) (7 mg, 0.016 mmol, 29%) and methyl 2,3,4,6-tetra-*O*-methyl-β-L-idopyranosyl-(1→4)-2,3-di-*O*-methyl-β-D-glucopyranoside (**7**) (13 mg, 0.030 mmol, 54%), both as colorless oils.

Method B with *n*-Bu_3SnD. A solution of phthalimide **4** (25 mg, 0.042 mmol) in dry benzene (3.2 mL) containing *n*-Bu_3SnD (12 μL, 0.043 mmol) and AIBN (1 mg, 0.004 mmol) was heated at reflux temperature for 1 h. After this time another portion of *n*-Bu_3SnD (12 μL, 0.043 mmol) and AIBN (1 mg, 0.004 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Column chromatography of the crude residue (hexanes−EtOAc, 10:90 → 0:100) afforded methyl 2,3,4,6-tetra-*O*-methyl-α-D-[5-^{2}H]glucopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**3-[D]**) (7.8 mg, 0.018 mmol, 41%, $^1H/^2H$ ratio 7:3) and methyl 2,3,4,6-tetra-*O*-methyl-α-L-(5-^{2}H)idopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside [**7-(D)**] (6.3 mg, 0.014 mmol, 33%), both as colorless oils.

Methyl 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-phthalimido-β-D-glucopyranoside (6). DEAD (50 μL, 0.306 mmol) was added dropwise to a stirred solution of methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-α-D-glucopyranoside (**5**)[20] (74.5 mg, 0.122 mmol), *N*-hydroxyphthalimide (50.5 mg, 0.306 mmol) and PPh_3 (79 mg, 0.306 mmol) in dry THF (1.2 mL) and the resulting solution was stirred at 0 °C for 1.5 h. Then the solvent was removed and the crude was quenched with water and extracted with ether. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography (hexanes−EtO_2, 30:70) to give compound **6** (70 mg, 0.093 mmol, 76%) as a white foam: $[\alpha]_D$ +76.6 (*c*, 0.325); IR 1746 cm^{-1}; ^1H NMR (400 MHz) δ_H 1.983 (3H, s), 1.986 (3H, s), 2.00 (3H, s), 2.026 (3H, s), 2.035 (3H, s), 2.08 (3H, s), 3.19 (3H, s), 3.82 (1H, ddd, J = 9.8, 4.5, 1.6 Hz), 4.03−4.09 (2H, m), 4.28 (1H, dd, J = 12.7, 4.5 Hz), 4.39 (1H, dd, J = 7.9, 4.5 Hz), 4.42 (1H, d, J = 9.0 Hz), 4.46 (1H, dd, J = 13.0, 4.8 Hz), 4.58 (1H, dd, J = 13.0, 1.6 Hz), 4.80 (1H, dd, J = 9.3, 7.7 Hz), 4.87 (1H, dd, J = 10.6, 4.0 Hz), 5.03 (1H, dd, J = 9.8, 9.8 Hz), 5.24 (1H, dd, J = 9.0, 9.0 Hz), 5.35 (1H, dd, J = 10.6, 9.8 Hz), 5.45 (1H, d, J = 4.0 Hz), 7.71−7.75 (2H, m), 7.79−7.83 (2H, m); ^{13}C NMR (100.6 MHz) δ_C 20.5 (CH_3), 20.56 (2 × CH_3), 20.62 (2 × CH_3), 20.9 (CH_3), 56.3 (CH_3), 61.9 (CH_2), 68.1 (CH), 68.5 (CH), 69.5 (CH), 70.1 (CH), 71.7 (CH), 71.8 (CH), 73.8 (CH), 75.2 (CH), 75.4 (CH_2), 95.5 (CH), 101.0 (CH), 123.5 (2 × CH), 128.8 (2 × C), 134.5 (2 × CH), 163.1 (2 × C), 169.5 (C), 169.6 (C), 169.9 (C), 170.2 (C), 170.4 (C), 170.6 (C); MS *m*/*z* (rel int) 722 ($M^+ - CH_3O$, <1), 694 (1), 634 (1), 331 (66), 169 (100); HRMS *m*/*z* calcd for $C_{32}H_{36}NO_{18}$ 722.1932, found 722.1902. Anal. Calcd for $C_{33}H_{39}NO_{19}$: C, 52.59; H, 5.22; N, 1.86. Found: C, 52.70; H, 5.24; N, 1.99.

Reductive HAT of Methyl 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-phthalimido-β-D-glucopyranoside (6). Method A with *n*-Bu_3SnH. A solution of phthalimide **6** (24 mg, 0.032 mmol) in dry benzene (2.4 mL) containing *n*-Bu_3SnH (9 μL, 0.003 mmol) and AIBN (1 mg, 0.003 mmol) was heated at reflux temperature for 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Column chromatography of the crude residue (hexanes−EtOAc, 50:50 → 30:70) afforded methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-β-D-glucopyranoside (**5**) (1.5 mg, 0.002 mmol, 8%) and methyl 2,3,4,6-tetra-*O*-acetyl-β-L-idopyranosyl-(1→4)-2,3-di-*O*-acetyl-β-D-glucopyranoside (**8**) (13.5 mg, 0.022 mmol, 69%), both as colorless oils. Compound **8**: $[\alpha]_D$ −2.1 (*c*, 0.12); IR 3545, 1752 cm^{-1}; ^1H NMR (400 MHz) δ_H 2.03 (3H, s), 2.04 (3H, s), 2.08 (3H, s), 2.108 (6H, s), 2.111 (3H, s), 3.42 (1H, ddd, J = 9.5, 2.6, 2.6 Hz), 3.49 (3H, s), 3.88 (1H, dd, J = 12.4, 2.6 Hz), 3.98 (1H, dd, J = 9.5, 9.5 Hz), 4.05 (1H, dd, J = 12.7, 3.2 Hz), 4.14 (1H, dd, J = 10.3. 7.9 Hz), 4.19 (1H, ddd, J = 11.1, 7.9, 1.6 Hz), 4.25 (1H, dd, J = 10.3, 3.2 Hz), 4.41 (1H, d, J = 7.7 Hz), 4.79−4.80 (2H, m), 4.84 (1H, dd, J = 9.8, 7.9 Hz), 4.93 (1H, d, J = 1.6 Hz), 5.05 (1H, dd, J = 2.9, 2.9 Hz), 5.17 (1H, dd, J = 9.8, 9.8 Hz); ^{13}C NMR (100.6 MHz) δ_C 20.57 (2 × CH_3), 20.60 (CH_3), 20.64 (CH_3), 20.68 (CH_3), 20.71 (CH_3), 57.1 (CH_3), 61.3 (CH_2), 62.543 (CH_2), 65.176 (CH), 66.1 (CH), 67.8 (CH), 71.94 (CH), 71.98 (CH), 74.5 (CH), 74.6 (CH), 76.1 (CH), 98.9 (CH), 101.5 (CH), 167.7 (C), 169.2 (C), 169.3 (C), 169.4 (C), 169.9 (C), 170.6 (C); MS *m*/*z* (rel int) 577 ($M^+ - CH_3O$, 4), 549 (1), 517 (1), 331 (52), 169 (100); HRMS *m*/*z* calcd for $C_{24}H_{33}O_{16}$ 577.1769, found 577.1783. Anal. Calcd for $C_{25}H_{36}O_{17}$: C, 49.34; H, 5.96. Found: C, 49.58; H, 5.74.

Method B with *n*-Bu_3SnD. A solution of phthalimide **6** (28 mg, 0.037 mmol) in dry benzene (2.8 mL) containing *n*-Bu_3SnD (10 μL, 0.037 mmol) and AIBN (1 mg, 0.004 mmol) was heated at reflux temperature for 1 h. After this time another portion of *n*-Bu_3SnD (10 μL, 0.037 mmol) and AIBN (1 mg, 0.004 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Column chromatography of the crude residue (hexanes−EtOAc, 50:50 → 30:70) afforded methyl 2,3,4,6-tetra-*O*-acetyl-α-D-[5-^{2}H]glucopyranosyl-(1→4)-2,3-di-*O*-methyl-β-D-glucopyranoside (**5-[D]**) (4.7 mg, 0.008 mmol, 21%, $^1H/^2H$ ratio, 8:2 by ^1H NMR) (contaminated with ca. 10% of an inseparable, unidentified product) and methyl 2,3,4,6-tetra-*O*-acetyl-β-L-(5-^{2}H)idopyranosyl-(1→4)-2,3-di-*O*-acetyl-β-D-glucopyranoside [**8-(D)**] (13.4 mg, 0.022 mmol, 59%), as colorless oils. Compound (**5-[D]**): ^{13}C NMR δ_C 20.5 (CH_3), 20.56 (CH_3), 20.60 (CH_3), 20.63 (CH_3), 20.7 (CH_3), 20.9 (CH_3), 57.2 (CH_3), 61.2 (CH_2), 61.794 (CH_2, C-6′-D), 61.853 (CH_2), 68.139 (CH, C-4′-D), 68.198 (2 × CH), 69.4 (CH), 70.2 (CH), 70.4 (CH), 72.2 (CH), 74.3 (CH), 75.4 (CH), 95.06 (CH), 101.5 (CH), 169.5 (C), 169.6 (C), 170.0 (C), 170.3 (C), 170.5 (C), 170.7 (C); MS *m*/*z* (rel int) 578 ($M^+ - CH_3O$, <1), 577 (<1), 550 (<1), 549 (<1), 332 (12), 331 (38), 169 (100); HRMS *m*/*z* calcd for $C_{24}H_{32}{}^2HO_{16}$ 578.1831, found 578.1829; calcd for $C_{24}H_{33}O_{16}$ 577.1769, found 577.1783. Compound **8-(D)**: ^1H NMR (400 MHz) δ_H 2.03 (3H, s), 2.04 (3H, s), 2.08 (3H, s), 2.109 (6H, s), 2.111 (3H, s), 3.42 (1H, ddd, J = 9.8, 2.9, 2.9 Hz), 3.50 (3H, s), 3.88 (1H, br d, J = 12.7 Hz), 3.98 (1H, dd, J = 9.5, 9.5 Hz), 4.05 (1H, br d, J = 12.7 Hz), 4.14 (1H, d, J = 11.7 Hz), 4.25 (1H, d, J = 11.7 Hz), 4.41 (1H, d, J = 8.0

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Hz), 4.79−4.80 (2H, m), 4.85 (1H, dd, J = 9.5, 7.7 Hz), 4.93 (1H, d, J = 1.6 Hz), 5.06 (1H, dd, J = 2.9, 2.9 Hz), 5.17 (1H, dd, J = 9.5, 9.5 Hz); ^{13}C NMR (100.6 MHz) δ_C 20.57 (2 × CH_3), 20.61 (CH_3), 20.65 (CH_3), 20.69 (CH_3), 20.72 (CH_3), 57.1 (CH_3), 61.3 (CH_2), 62.487 (CH_2), 65.127 (CH), 66.1 (CH), 67.8 (CH), 71.9 (CH), 74.5 (CH), 74.6 (CH), 76.1 (CH), 98.9 (CH), 101.5 (CH), 167.8 (CH), 169.2 (CH), 169.3 (C), 169.4 (C), 169.9 (C), 170.6 (C); MS m/z (rel int) 578 ($M^+ - CH_3O$, <1), 532 (<1), 518 (1), 332 (31), 170 (100); HRMS m/z calcd for $C_{24}H_{32}{}^2HO_{16}$ 578.1831, found 578.1818.

Methyl 6-Deoxy-2,3,4-tri-*O*-methyl-α-D-talopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (10). DEAD (230 μL, 1.462 mmol) was added dropwise to a stirred solution of the alcohol **9** (240 mg, 0.585 mmol), *N*-hydroxyphthalimide (238 mg, 1.462 mmol) and PPh_3 (383 mg, 1.462 mmol) in dry THF (6.4 mL) and the resulting solution was stirred at 0 °C for 1.5 h. Then the solvent was removed and the crude was quenched with water and extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography (Et_2O−AcOEt, 90:10 → 0:100) to give compound **10** (147 mg, 0.265 mmol, 45%) as a foam: $[\alpha]_D$ +89.6 (*c*, 0.435); IR 1789, 1734 cm^{-1}; ^{1}H NMR δ_H 1.19 (3H, d, J = 6.5 Hz), 3.25 (1H, dd, J = 9.5, 3.5 Hz), 3.35 (1H, m), 3.42 (1H, dd, J = 3.5, 3.5 Hz), 3.45 (3H, s), 3.460 (1H, m), 3.463 (3H, s), 3.48 (3H, s), 3.49 (3H, s), 3.52 (3H, s), 3.53 (1H, dd, J = 9.5, 9.5 Hz), 3.57 (1H, dd, J = 9.0, 9.0 Hz), 3.60 (3H, s), 3.89 (1H, dddd, J = 6.5, 6.5, 6.5, 1.5 Hz), 3.93 (1H, ddd, J = 9.0, 7.0, 2.0 Hz), 4.36 (1H, dd, J = 11.5, 6.5 Hz), 4.42 (1H, dd, J = 11.0, 2.0 Hz), 4.80 (1H, d, J = 3.5 Hz), 5.26 (1H, d, J = 1.5 Hz), 7.72−7.76 (2H, m), 7.80−7.83 (2H, m); ^{13}C NMR δ_C 16.5 (CH_3), 55.6 (CH_3), 56.6 (CH_3), 58.7 (CH_3), 59.1 (CH_3), 60.9 (CH_3), 61.4 (CH_3), 67.7 (CH), 69.1 (CH), 76.9 (CH), 77.2 (CH), 77.3 (CH), 77.8 (CH_2), 78.0 (CH), 81.9 (CH), 82.8 (CH), 97.2 (CH), 99.7 (CH), 123.5 (2 × CH), 128.8 (2 × C), 134.5 (2 × CH), 163.2 (2 × C); MS m/z (%) 578 (M^+ + Na, 100), 556 (M^+ + H, 33); HRMS m/z calcd for $C_{26}H_{37}NNaO_{12}$ 578.2213, found 578.2230. Anal. Calcd for $C_{26}H_{37}NO_{12}$: C, 56.21; H, 6.71; N, 2.52. Found: C, 56.02; H, 6.92; N, 2.35.

Reductive HAT of Methyl 6-Deoxy-2,3,4-tri-*O*-methyl-α-D-talopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (10). Method A with *n*-Bu_3SnH. A solution of phthalimide **10** (33 mg, 0.059 mmol) in dry benzene (4.5 mL) containing *n*-Bu_3SnH (16 μL, 0.059 mmol) and AIBN (1 mg, 0.006 mmol) was heated at reflux temperature for 1 h. After this time another portion of *n*-Bu_3SnH (16 μL, 0.059 mmol) and AIBN (1 mg, 0.006 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Chromatotron chromatography ($CHCl_3$−MeOH, 100:0 → 99:1) gave methyl 6-deoxy-2,3,4-tri-*O*-methyl-β-L-allopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**13**) (16.5 mg, 0.040 mmol, 68%) and methyl 6-deoxy-2,3,4-tri-*O*-methyl-α-D-talopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**9**) (2 mg, 0.005 mmol, 8%), both as colorless oils. Compound **13**: $[\alpha]_D$ +87.1 (*c*, 0.56); IR 3498 cm^{-1}; ^{1}H NMR (400 MHz) δ_H 1.25 (3H, d, J = 6.3 Hz), 2.81 (1H, dd, J = 9.6, 2.5 Hz), 2.93 (1H, dd, J = 7.8, 2.5 Hz), 3.21 (1H, dd, J = 9.6, 3.8 Hz), 3.40 (3H, s), 3.42 (3H, s), 3.517 (3H, s), 3.521 (3H, s), 3.55 (1H, ddd, J = 10.1, 2.5, 2.5 Hz), 3.57 (1H, dd, J = 9.3, 9.3 Hz), 3.59 (3H, s), 3.64 (3H, s), 3.65 (1H, dd, J = 12.7, 2.4 Hz), 3.69 (1H, dd, J = 10.1, 9.1 Hz), 3.85 (1H, dddd, J = 9.1, 6.1, 6.1, 6.1 Hz), 3.95 (1H, dd, J = 12.6, 2.5 Hz), 3.96 (1H, dd, J = 2.5, 2.5 Hz), 4.82 (1H, d, J = 3.8 Hz), 5.09 (1H, d, J = 8.1 Hz); ^{13}C NMR (100.6 MHz) δ_C 17.467 (CH_3), 55.1 (CH_3), 57.4 (CH_3), 59.0 (CH_3), 59.3 (CH_3), 61.0 (CH_3), 61.1 (CH_3), 61.7 (CH_2), 68.9 (CH), 70.2 (CH), 75.08 (CH), 75.14 (CH), 81.8 (CH), 82.1 (CH), 83.109 (CH), 83.5 (CH), 97.9 (CH), 101.063 (CH); MS m/z (%) 379 ($M^+ - CH_3O$, <1), 346 (<1), 307 (2), 265 (29), 101 (62), 88 (100); HRMS m/z calcd for $C_{17}H_{31}O_9$ 379.1968, found 379.1975. Anal. Calcd for $C_{18}H_{34}O_{10}$: C, 52.67; H, 8.35. Found: C, 52.72; H, 8.32.

Method B with *n*-Bu_3SnD. A solution of phthalimide **10** (33 mg, 0.059 mmol) in dry benzene (4.5 mL) containing *n*-Bu_3SnD (16 μL, 0.059 mmol) and AIBN (1 mg, 0.006 mmol) was heated at reflux temperature for 1 h. After this time another portion of *n*-Bu_3SnD (16 μL, 0.059 mmol) and AIBN (1 mg, 0.006 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Chromatotron chromatography ($CHCl_3$−MeOH, 100:0 → 99:1) gave methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-L-(5-^{2}H)allopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside [**13-(D)**] (13.6 mg, 0.033 mmol, 56%) and methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-[5-^{2}H]talopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**9-[D]**) (1.5 mg, 0.004 mmol, 6%, ^{1}H/^{2}H ratio, 3:7), both as colorless oils. Compound **13-(D)**: ^{1}H NMR (400 MHz) δ_H 1.24 (3H, s), 2.81 (1H, d, J = 2.4 Hz), 2.93 (1H, dd, J = 7.9, 2.4 Hz), 3.21 (1H, dd, J = 9.5, 3.7 Hz), 3.39 (3H, s), 3.41 (3H, s), 3.51 (3H, s), 3.52 (3H, s), 3.55 (1H, ddd, J = 9.8, 2.6, 2.6 Hz), 3.57 (1H, dd, J = 9.3, 9.3 Hz), 3.59 (3H, s), 3.64 (3H, s), 3.66 (1H, m), 3.69 (1H, dd, J = 10.1, 9.0 Hz), 3.94 (1H, dd, J = 12.7, 2.6 Hz), 3.96 (1H, dd, J = 2.4, 2.4 Hz), 4.81 (1H, d, J = 3.7 Hz), 5.09 (1H, d, J = 8.0 Hz); ^{13}C NMR (100.6 MHz) δ_C 17.328 (CH_3), 55.1 (CH_3), 57.4 (CH_3), 59.0 (CH_3), 59.3 (CH_3), 60.9 (CH_3), 61.1 (CH_3), 61.7 (CH_2), 70.2 (CH), 75.06 (CH), 75.13 (CH), 81.8 (CH), 82.1 (CH), 83.002 (CH), 83.5 (CH), 97.9 (CH), 101.031 (CH); MS m/z (%) 380 ($M^+ - CH_3O$, <1), 307 (2), 265 (24), 101 (50), 88 (100); HRMS m/z calcd for $C_{17}H_{30}{}^2HO_9$ 380.2031 found 380.2045. Compound **9-[D]**: ^{1}H NMR δ_H 1.33 (3H, s), 3.24 (1H, dd, J = 9.0, 3.4 Hz), 3.36 (1H, dd, J = 2.9, 0.8 Hz), 3.42 (3H, s), 3.44−3.47 (2H, m), 3.49 (3H, s), 3.50 (3H, s), 3.51 (3H, s), 3.52 (1H, m), 3.55 (3H, s), 3.56−3.60 (2H, m), 3.62 (3H, s), 3.73−3.81 (2H, m), 4.83 (1H, d, J = 3.7 Hz), 5.29 (1H, d, J = 2.1 Hz); ^{13}C NMR (100.6 MHz) δ_C 16.370 (CH_3), 16.496 (CH_3), 55.2 (CH_3), 57.1 (CH_3), 58.8 (CH_3), 59.2 (CH_3), 61.0 (CH_3), 61.1 (CH_3), 62.1 (CH_2), 68.5 (CH), 70.3 (CH), 76.8 (CH), 77.5 (CH), 77.6 (CH), 78.011 (CH), 78.074 (CH), 82.4 (CH), 83.2 (CH), 97.4 (CH), 100.051 (CH), 100.079 (CH); MS (FAB) m/z (%) 434 (M^+ + Na, 100), 433 (28); HRMS m/z calcd for $C_{18}H_{33}{}^2HNaO_{10}$ 434.2112, found 434.2133; calcd for $C_{18}H_{34}NaO_{10}$ 433.2050, found 433.2050.

Methyl 2,3,4-Tri-*O*-acetyl-6-deoxy-α-D-talopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (12). DEAD (120 μL, 0.760 mmol) was added dropwise to a stirred solution of the alcohol **11** (150 mg, 0.304 mmol), *N*-hydroxyphthalimide (124 mg, 0.760 mmol) and PPh_3 (199 mg, 0.760 mmol) in dry THF (3.3 mL) and the resulting solution was stirred at 0 °C for 1 h. Then the solvent was removed and the crude was quenched with water and extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography (hexanes−Et_2O, 50:50 → 0:100) to give compound **12** (187 mg, 0.293 mmol, 96%) as a colorless oil: $[\alpha]_D$ +99.2 (*c*, 0.36); IR 1789, 1738 cm^{-1}; ^{1}H NMR (400 MHz) δ_H 1.16 (3H, d, J = 6.3 Hz), 1.98 (3H, s), 2.12 (3H, s), 2.14 (3H, s), 3.26 (1H, dd, J = 9.5, 3.4 Hz), 3.46 (3H, s), 3.49 (3H, s), 3.58 (1H, dd, J = 9.5, 8.7 Hz), 3.59 (3H, s), 3.76 (1H, dd, J = 10.1, 8.7 Hz), 3.92 (1H, ddd, J = 10.1, 3.4, 3.4 Hz), 4.26 (1H, dddd, J = 6.3, 6.3, 6.3, 1.6 Hz), 4.41 (2H, d, J = 3.4 Hz), 4.78 (1H, d, J = 3.4 Hz), 5.17 (1H, ddd, J = 3.4, 1.6, 1.6 Hz), 5.20 (1H, ddd, J = 3.7, 1.6, 1.6 Hz), 5.25 (1H, d, J = 1.6 Hz), 5.26 (1H, dd, J = 3.7, 3.7 Hz), 7.75 (2H, m), 7.83 (2H, m); ^{13}C NMR (100.6 MHz) δ_C 16.1 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 20.9 (CH_3), 55.7 (CH_3), 58.8 (CH_3), 61.0 (CH_3), 65.8 (CH), 65.9 (CH), 67.3 (CH), 68.9 (CH), 69.0 (CH), 76.8 (CH), 77.1 (CH_2), 81.9 (CH), 82.7 (CH), 97.4 (CH), 100.4 (CH), 123.6 (2 × CH), 128.9 (2 × C), 134.5 (2 × CH), 163.2 (2 × C), 169.6 (C), 169.8 (C), 170.6 (C); MS m/z (%) 579 (M^+ − AcOH, <1), 435 (1), 273

(96), 88 (100); HRMS *m/z* calcd for $C_{27}H_{33}NO_{13}$ 579.1952, found 579.1948. Anal. Calcd for $C_{29}H_{37}NO_{15}$: C, 54.46; H, 5.83; N, 2.19. Found: C, 54.13; H, 6.22; N, 2.30.

Reductive HAT of Methyl 2,3,4-Tri-*O*-acetyl-6-deoxy-α-D-talopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (12). Method A with *n*-Bu_3SnH. A solution of phthalimide **12** (41 mg, 0.064 mmol) in dry benzene (4.8 mL) containing *n*-Bu_3SnH (17 μL, 0.064 mmol) and AIBN (1 mg, 0.006 mmol) was heated at reflux temperature for 2 h. After this time another portion of *n*-Bu_3SnH (17 μL, 0.064 mmol) and AIBN (1 mg, 0.006 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Chromatotron chromatography (hexanes−EtOAc, 60:40 → 40:60) gave methyl (5*R*)-5,6-anhydro-2,3-di-*O*-acetyl-4,6-dideoxy-α-L-*erythro*-hexos-5-ulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**15**) (6 mg, 0.014 mmol, 22%), methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-L-allopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**14**) (5.5 mg, 0.011 mmol, 17%), and methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-talopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**11**) (12 mg, 0.024 mmol, 38%), all as colorless oils. Compound **15**: $[\alpha]_D$ +77.7 (*c*, 0.26); IR 1748 cm^{-1}; ^1H NMR δ_H 1.40 (3H, s), 1.98 (1H, dd, *J* = 12.6, 12.6 Hz), 2.01 (3H, s), 2.06 (1H, dd, *J* = 12.6, 4.8 Hz), 2.13 (3H, s), 3.14 (1H, dd, *J* = 9.2, 3.6 Hz), 3.40 (3H, s), 3.49 (1H, dd, *J* = 9.0, 9.0 Hz), 3.51 (3H, s), 3.56 (1H, dd, *J* = 9.0, 9.0 Hz), 3.58 (3H, s), 3.61−3.66 (2H, m), 3.83 (1H, dd, *J* = 12.3, 11.2 Hz), 4.75 (1H, d, *J* = 3.6 Hz), 4.96 (1H, d, *J* = 1.7 Hz), 5.21 (1H, m), 5.52 (1H, ddd, *J* = 12.0, 5.0, 3.1 Hz); ^{13}C NMR δ_C 20.88 (CH_3), 20.94 (CH_3), 25.4 (CH_3), 35.375 (CH_2), 55.1 (CH_3), 59.1 (CH_3), 61.4 (CH_3), 64.0 (CH_2), 64.355 (CH), 66.1 (CH), 67.3 (CH), 79.6 (CH), 81.1 (CH), 81.5 (CH), 97.6 (CH), 98.4 (CH), 100.626 (C), 169.8 (C), 170.0 (C); MS *m/z* (%) 434 (M^+, 2), 403 (3), 374 (5), 273 (29), 101 (50), 88 (100); HRMS *m/z* calcd for $C_{19}H_{30}O_{11}$ 434.1788, found 434.1780. Anal. Calcd for $C_{19}H_{30}O_{11}$: C, 52.53; H, 6.96. Found: C, 52.81; H, 6.62. Compound **14**: $[\alpha]_D$ +60.3 (*c*, 0.36); IR 3520, 1752 cm^{-1}; ^1H NMR (400 MHz) δ_H 1.23 (3H, d, *J* = 6.1 Hz), 2.014 (3H, s), 2.015 (3H, s), 2.13 (3H, s), 3.22 (1H, dd, *J* = 9.5, 3.7 Hz), 3.40 (3H, s), 3.52 (3H, s), 3.54 (1H, dd, *J* = 9.5, 9.5 Hz), 3.55 (1H, m), 3.62 (3H, s), 3.68 (1H, br dd, *J* = 12.4, 1.9 Hz), 3.72 (1H, dd, *J* = 10.1, 9.3 Hz), 3.94 (1H, br dd, *J* = 12.5, 2.9 Hz), 4.00 (1H, dddd, *J* = 9.8, 6.1, 6.1, 6.1 Hz), 4.70 (1H, dd, *J* = 10.1, 2.9 Hz), 4.81 (1H, dd, *J* = 8.5, 2.9 Hz), 4.84 (1H, d, *J* = 3.7 Hz), 5.22 (1H, d, *J* = 8.5 Hz), 5.60 (1H, dd, *J* = 2.9, 2.9 Hz); ^{13}C NMR (100.6 MHz) δ_C 17.157 (CH_3), 20.57 (2 × CH_3), 20.63 (CH_3), 55.2 (CH_3), 59.0 (CH_3), 61.0 (CH_3), 61.3 (CH_2), 68.5 (CH), 68.6 (CH), 69.7 (CH), 70.0 (CH), 71.062 (CH), 74.5 (CH), 82.3 (CH), 83.4 (CH), 97.6 (CH), 98.8 (CH), 169.0 (C), 169.3 (C), 169.8 (C); MS *m/z* (%) 434 (M^+ − AcOH, 1), 390 (1), 375 (1), 273 (18), 105 (100), 88 (80); HRMS *m/z* calcd for $C_{19}H_{30}O_{11}$ 434.1788, found 434.1795. Anal. Calcd for $C_{21}H_{34}O_{13}$: C, 51.01; H, 6.93. Found: C, 51.06; H, 6.94.

Method B with *n*-Bu_3SnD. A solution of phthalimide **12** (44 mg, 0.069 mmol) in dry benzene (5.2 mL) containing *n*-Bu_3SnD (19 μL, 0.069 mmol) and AIBN (1 mg, 0.007 mmol) was heated at reflux temperature for 2 h. After this time another portion of *n*-Bu_3SnD (19 μL, 0.069 mmol) and AIBN (1 mg, 0.007 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Chromatotron chromatography (hexanes−EtOAc, 60:40 → 40:60) gave methyl 5,6-anhydro-2,3-di-*O*-acetyl-4,6-dideoxy-β-L-[4-^2H]*ribo*-hexos-5-ulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**16**) (13 mg, 0.014 mmol, 43%, $^1H/^2H$ ratio, 1:6), methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-L-(5-^2H)allopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside [**14-(D)**)] (4.2 mg, 0.008 mmol, 12%), and methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-(5-^2H)talopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside [**11-(D)**)] (9.3 mg, 0.019 mmol, 27%), all as colorless oils. Compound **16**: ^1H NMR (Only the deuterated compound is described) δ_H 1.40 (3H, s), 2.01 (3H, s), 2.035 (1H, br d, *J* = 5.0 Hz), 2.13 (3H, s), 3.14 (1H, dd, *J* = 9.2, 3.6 Hz), 3.40 (3H, s), 3.49 (1H, dd, *J* = 9.0, 9.0 Hz), 3.51 (3H, s), 3.55 (1H, dd, *J* = 9.0, 9.0 Hz), 3.58 (3H, s), 3.62−3.66 (2H, m), 3.83 (1H, dd, *J* = 12.3, 11.2 Hz), 4.75 (1H, d, *J* = 3.6 Hz), 4.96 (1H, d, *J* = 1.7 Hz), 5.21 (1H, m), 5.51 (1H, dd, *J* = 4.8, 3.1 Hz); ^{13}C NMR δ_C 20.88 (CH_3), 20.94 (CH_3), 25.4 (CH_3), 35.042 (CH, t, J_{CD} = 19.6 Hz), 35.372 (CH_2), 55.1 (CH_3), 59.1 (CH_3), 61.4 (CH_3), 64.0 (CH_2), 64.306 (CH), 64.352 (CH), 66.1 (CH), 67.3 (CH), 79.6 (CH), 81.1 (CH), 81.5 (CH), 97.6 (CH), 98.4 (CH), 100.598 (C), 169.8 (C), 170.0 (C); MS *m/z* (%) 435 (M^+, 1), 404 (1), 375 (1), 274 (13), 101 (46), 88 (100); HRMS *m/z* calcd for $C_{19}H_{29}{}^2HO_{11}$ 435.1851, found 435.1842. Compound **14-(D)**: ^1H NMR δ_H 1.22 (3H, s), 2.01 (6H, s), 2.13 (3H, s), 2.71 (1H, br s), 3.22 (1H, dd, *J* = 9.5, 3.8 Hz), 3.40 (3H, s), 3.52 (3H, s), 3.54 (1H, dd, *J* = 9.5, 9.5 Hz), 3.55 (1H, m), 3.62 (3H, s), 3.68 (1H, m), 3.72 (1H, dd, *J* = 9.2, 9.2 Hz), 3.94 (1H, br d, *J* = 12.9 Hz), 4.69 (1H, d, *J* = 2.8 Hz), 4.81 (1H, dd, *J* = 8.1, 2.8 Hz), 4.84 (1H, d, *J* = 3.6 Hz), 5.22 (1H, d, *J* = 8.1 Hz), 5.60 (1H, dd, *J* = 2.8, 2.8 Hz); ^{13}C NMR δ_C 17.022 (CH_3), 20.57 (2 × CH_3), 20.63 (CH_3), 55.2 (CH_3), 59.0 (CH_3), 61.0 (CH_3), 61.3 (CH_2), 68.6 (CH), 69.7 (CH), 70.0 (CH), 70.985 (CH), 74.5 (CH), 82.3 (CH), 83.4 (CH), 97.6 (CH), 98.8 (CH), 169.0 (C), 169.3 (C), 169.8 (C); MS *m/z* (%) 435 (M^+ − AcOH, 7), 274 (98), 101 (24), 88 (100); HRMS *m/z* calcd for $C_{19}H_{29}{}^2HO_{11}$ 435.1851, found 435.1843. Compound **11-(D)**: ^1H NMR (400 MHz) δ_H 1.22 (3H, s), 2.00 (3H, s), 2.13 (3H, s), 2.15 (3H, s), 3.21 (1H, dd, *J* = 9.3, 3.4 Hz), 3.43 (3H, s), 3.50 (3H, s), 3.56 (1H, dd, *J* = 9.3, 9.3 Hz), 3.60 (3H, s), 3.61−3.64 (2H, m, 4-H), 3.75 (1H, br dd, *J* = 12.2, 2.9 Hz), 3.81 (1H, dd, *J* = 12.2, 1.1 Hz), 4.82 (1H, d, *J* = 3.4 Hz), 5.15 (1H, m), 5.19 (1H, ddd, *J* = 4.0, 1.6, 1.1 Hz), 5.25 (1H, dd, *J* = 3.7, 3.7 Hz), 5.25 (1H, m); ^{13}C NMR (100.6 MHz) δ_C 15.996 (CH_3), 20.59 (CH_3), 20.63 (CH_3), 20.8 (CH_3), 55.2 (CH_3), 58.8 (CH_3), 61.2 (CH_3), 61.8 (CH_2), 65.9 (CH), 67.3 (CH), 68.715 (CH), 70.0 (CH), 76.5 (CH), 82.4 (CH), 83.0 (CH), 97.4 (CH), 100.4 (CH), 169.7 (C), 169.8 (C), 170.5 (C); MS *m/z* (%) 435 (M^+ − AcOH, 2), 274 (61), 101 (22), 88 (100); HRMS *m/z* calcd for $C_{19}H_{29}{}^2HO_{11}$ 435.1851, found 435.1849.

Methyl 2,3,4,6-Tetra-*O*-methyl-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (18). DEAD (330 μL, 2.09 mmol) was added dropwise to a stirred solution of the alcohol **17** (368 mg, 0.836 mmol), *N*-hydroxyphthalimide (272 mg, 1.67 mmol) and PPh_3 (548 mg, 2.09 mmol) in dry THF (9.2 mL) and the resulting solution was stirred at 0 °C for 1 h. Then the solvent was removed and the crude was quenched with water and extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography (hexanes−EtOAc, 30:70) to give compound **18** (224 mg, 0.383 mmol, 46%) as a white foam: $[\alpha]_D$ +76.0 (*c*, 0.213); IR 1790, 1734 cm^{-1}; ^1H NMR (C_6D_6) δ_H 3.06 (3H, s), 3.11 (3H, s), 3.17 (1H, dd, *J* = 9.7, 3.3 Hz), 3.22 (3H, s), 3.29 (3H, s), 3.34 (3H, s), 3.44 (3H, s), 3.516 (3H, s), 3.522 (1H, dd, *J* = 10.1, 6.1 Hz), 3.59 (1H, dd, *J* = 10.6, 1.6 Hz), 3.68−3.73 (3H, m), 3.76 (1H, dd, *J* = 9.7, 8.9 Hz), 3.99 (1H, dd, *J* = 10.1, 8.9 Hz), 4.01 (1H, m), 4.10 (1H, ddd, *J* = 10.2, 5.3, 1.2 Hz), 4.60 (1H, d, *J* = 3.6 Hz), 4.74 (1H, dd, *J* = 11.4, 5.3 Hz), 4.88 (1H, dd, *J* = 11.8, 1.6 Hz), 5.52 (1H, d, *J* = 1.6 Hz), 6.78 (2H, m), 7.30 (2H, m); ^{13}C NMR (100.6 MHz, C_6D_6) δ_C 55.2 (CH_3), 57.1 (CH_3), 57.6 (CH_3), 58.5 (CH_3), 58.9 (CH_3), 60.3 (CH_3), 60.8 (CH_3), 70.4 (CH), 72.7 (CH_2), 73.5 (CH), 77.0 (CH), 78.0 (CH_2), 78.1 (CH), 78.5 (CH), 81.7 (CH), 82.3 (CH), 83.2 (CH), 97.5 (CH), 100.7 (CH), 122.9 (2 × CH), 129.5 (2 × C), 133.5 (2 × CH), 163.2 (2 × C); MS (FAB) *m/z* (rel int) 608 (M^+ + Na, 17), 219 (48), 187 (100); HRMS *m/z* calcd for $C_{27}H_{39}NNaO_{13}$ 608.2319,

found 608.2330. Anal. Calcd for $C_{27}H_{39}NO_{13}$: C, 55.38; H, 6.71; N, 2.39. Found: C, 55.45; H, 6.44; N, 2.10.

Reductive HAT of Methyl 2,3,4,6-Tetra-*O*-methyl-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (18). Method A with *n*-Bu_3SnH. A solution of phthalimide **18** (100 mg, 0.170 mmol) in dry benzene (12 mL) containing *n*-Bu_3SnH (68 μL, 0.255 mmol) and AIBN (5.5 mg, 0.034 mmol) was heated at reflux temperature for 2.5 h. After this time another portion of *n*-Bu_3SnH (23 μL, 0.086 mmol) and AIBN (5.5 mg, 0.034 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Acetylation of the crude residue in dry pyridine (3 mL) containing Ac_2O (1 mL) at room temperature for 4 h gave after chromatotron chromatography (hexanes−EtOAc, 40:60) methyl 2,3,4,6-tetra-*O*-methyl-β-L-gulopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-methyl-α-D-glucopyranoside (**21**) (38 mg, 0.078 mmol, 46%) and methyl 2,3,4,6-tetra-*O*-methyl-α-D-mannopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-methyl-α-D-glucopyranoside (**41S**) (14 mg, 0.029 mmol, 17%) both as colorless oils. Compound **21**: $[\alpha]_D$ +89.6 (*c*, 0.24); IR 1739 cm^{-1}; ^1H NMR (C_6D_6) δ_H 1.75 (3H, s), 3.11 (3H, s), 3.136 (3H, s), 3.138 (1H, dd, J = 8.9, 3.6 Hz), 3.16 (3H, s), 3.18 (3H, s), 3.28 (1H, dd, J = 3.6, 1.4 Hz), 3.29 (3H, s), 3.36 (3H, s), 3.46 (1H, dd, J = 8.1, 3.1 Hz), 3.55 (1H, dd, J = 9.2, 5.9 Hz), 3.67 (1H, dd, J = 3.6, 3.6 Hz), 3.68 (1H, dd, J = 9.2, 7.6 Hz), 3.75 (3H, s), 3.85−3.91 (2H, m), 4.00 (1H, ddd, J = 8.9, 6.7, 1.9 Hz), 4.14 (1H, ddd, J = 7.6, 6.2, 1.4 Hz), 4.64 (1H, dd, J = 12.3, 6.7 Hz), 4.65 (1H, d, J = 3.6 Hz), 4.83 (1H, dd, J = 12.0, 2.2 Hz), 5.43 (1H, d, J = 8.1 Hz); ^{13}C NMR (C_6D_6) δ_C 20.6 (CH_3), 54.8 (CH_3), 58.1 (CH_3), 58.4 (CH_3), 58.8 (CH_3), 59.3 (CH_3), 59.5 (CH_3), 61.1 (CH_3), 64.6 (CH_2), 68.9 (CH), 71.160 (CH_2), 71.9 (CH), 76.3 (CH), 77.4 (CH), 77.574 (CH), 80.0 (CH), 82.5 (CH), 84.0 (CH), 97.7 (CH), 101.6 (CH), 170.0 (C); MS *m*/*z* (rel int) 450 (M^+ − CH_3OH, <1), 419 (<1), 307 (48), 247 (100); HRMS *m*/*z* calcd for $C_{20}H_{34}O_{11}$ 450.2101, found 450.2108. Anal. Calcd for $C_{21}H_{38}O_{12}$: C, 52.27; H, 7.94. Found: C, 52.28; H, 7.91. Compound **41S**: $[\alpha]_D$ +62.3 (*c*, 0.96); IR 1742 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ_H 1.77 (3H, s), 3.06 (1H, dd, J = 9.5, 3.4 Hz), 3.08 (3H, s), 3.09 (3H, s), 3.28 (3H, s), 3.34 (3H, s), 3.36 (3H, s), 3.48 (3H, s), 3.51 (3H, s), 3.69−3.82 (7H, m), 3.89 (1H, dd, J = 9.8, 9.8 Hz), 4.01 (1H, ddd, J = 9.8, 5.0, 1.9 Hz), 4.40 (1H, dd, J = 12.2, 4.8 Hz), 4.58 (1H, d, J = 3.4 Hz), 4.67 (1H, dd, J = 11.9, 2.1 Hz), 5.55 (1H, d, J = 1.8 Hz); ^{13}C NMR (100.6 MHz, C_6D_6) δ_C 20.5 (CH_3), 54.8 (CH_3), 57.3 (CH_3), 57.6 (CH_3), 58.6 (CH_3), 59.1 (CH_3), 60.4 (CH_3), 60.8 (CH_3), 63.9 (CH_2), 68.8 (CH), 72.4 (CH_2), 73.8 (CH), 76.9 (CH), 77.3 (CH), 78.2 (CH), 81.9 (CH), 82.6 (CH), 83.8 (CH), 97.4 (CH), 100.2 (CH), 170.0 (C); MS *m*/*z* (rel int) 419 (M^+ − $C_2H_7O_2$, 1), 405 (1), 307 (100); HRMS *m*/*z* calcd for $C_{19}H_{31}O_{10}$ 419.1917, found 419.1927. Anal. Calcd for $C_{21}H_{38}O_{12}$: C, 52.27; H, 7.94. Found: C, 52.25; H, 8.03.

Method B with *n*-Bu_3SnD. A solution of phthalimide **18** (82 mg, 0.140 mmol) in dry benzene (10 mL) containing *n*-Bu_3SnD (56 μL, 0.210 mmol) and AIBN (4.6 mg, 0.028 mmol) was heated at reflux temperature for 2.5 h. After this time another portion of *n*-Bu_3SnD (37 μL, 0.138 mmol) and AIBN (4.6 mg, 0.028 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Acetylation of the crude residue in dry pyridine (3 mL) containing Ac_2O (1 mL) at room temperature for 4 h after gave chromatotron chromatography (hexanes−EtOAc, 40:60) methyl 2,3,4,6-tetra-*O*-methyl-β-L-(5-^{2}H)gulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside [**21-(D)**] (35 mg, 0.072 mmol, 52%) and methyl 2,3,4,6-tetra-*O*-methyl-α-D-[5-^{2}H]mannopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**41S-[D]**) (14 mg, 0.029 mmol, 21%, $^1H/^2H$ ratio, 3:7) both as colorless oils. Compound **21-(D)**: ^1H NMR (C_6D_6) δ_H 1.75 (3H, s), 3.11 (3H, s), 3.136 (3H, s), 3.137 (1H, dd, J = 9.2, 3.6 Hz), 3.16 (3H, s), 3.18 (3H, s), 3.28 (1H, d, J = 3.6 Hz), 3.29 (3H, s), 3.36 (3H, s), 3.45 (1H, dd, J = 8.1, 2.8 Hz), 3.55 (1H, d, J = 9.2 Hz), 3.67 (1H, dd, J = 3.6, 3.4 Hz), 3.68 (1H, d, J = 9.5 Hz), 3.75 (3H, s), 3.85−3.91 (2H, m), 4.00 (1H, ddd, J = 8.9, 6.7, 2.2 Hz), 4.64 (1H, dd, J = 12.3, 6.7 Hz), 4.65 (1H, d, J = 3.6 Hz), 4.83 (1H, dd, J = 11.8, 2.2 Hz), 5.43 (1H, d, J = 8.1 Hz); ^{13}C NMR (C_6D_6) δ_C 20.6 (CH_3), 54.8 (CH_3), 58.1 (CH_3), 58.4 (CH_3), 58.8 (CH_3), 59.3 (CH_3), 59.5 (CH_3), 61.1 (CH_3), 64.6 (CH_2), 68.9 (CH), 71.091 (CH_2), 76.3 (CH), 77.47 (CH), 77.522 (CH), 80.0 (CH), 82.5 (CH), 84.0 (CH), 97.7 (CH), 101.6 (CH), 170.0 (C); MS *m*/*z* (rel int) 452 (M^+ − CH_3O, <1), 307 (43), 247 (70), 88 (100); HRMS *m*/*z* calcd for $C_{20}H_{34}{}^2HO_{11}$ 452.2242, found 452.2242. Compund **41S-[D]**: ^1H NMR (400 MHz, C_6D_6) δ_H 1.77 (3H, s), 3.06 (1H, dd, J = 9.5, 3.4 Hz), 3.08 (3H, s), 3.09 (3H, s), 3.28 (3H, s), 3.34 (3H, s), 3.36 (3H, s), 3.48 (3H, s), 3.51 (3H, s), 3.69−3.82 (7H, m), 3.89 (1H, d, J = 9.0 Hz), 3.90 (1H, dd, J = 9.8, 9.8 Hz), 4.01 (1H, ddd, J = 9.8, 5.0, 1.9 Hz), 4.40 (1H, dd, J = 12.2, 4.8 Hz), 4.58 (1H, d, J = 3.4 Hz), 4.67 (1H, dd, J = 11.9, 2.1 Hz), 5.55 (1H, d, J = 1.8 Hz); ^{13}C NMR (125.7 MHz, C_6D_6) δ_C 20.5 (CH_3), 54.8 (CH_3), 57.3 (CH_3), 57.6 (CH_3), 58.6 (CH_3), 59.1 (CH_3), 60.4 (CH_3), 60.8 (CH_3), 63.9 (CH_2), 68.8 (CH), 72.312 (CH_2), 72.376 (CH_2), 73.8 (CH), 76.894 (CH), 76.947 (CH), 77.3 (CH), 78.3 (CH), 81.9 (CH), 82.6 (CH), 83.8 (CH), 97.4 (CH), 100.2 (CH), 170.0 (C); MS *m*/*z* (rel int) 451 (M^+ − CH_3OH, <1), 450 (<1), 307 (19), 247 (26), 88 (100); HRMS *m*/*z* calcd for $C_{20}H_{34}{}^2HO_{11}$ 451.2164, found 451.2179.

Methyl 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (20). DEAD (192 μL, 1.22 mmol) was added dropwise to a stirred solution of the alcohol **19** (270 mg, 0.489 mmol), *N*-hydroxyphthalimide (199 mg, 1.22 mmol) and PPh_3 (320 mg, 1.22 mmol) in dry THF (5.3 mL) and the resulting solution was stirred at 0 °C for 2 h. Then the solvent was removed and the crude was quenched with water and extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography (hexanes−EtOAc, 70:30 → 30:70) to give compound **20** (284 mg, 0.407 mmol, 83%) as a white foam: $[\alpha]_D$ +72.9 (*c*, 0.122); IR 1791, 1734 cm^{-1}; ^1H NMR δ_H 1.98 (3H, s), 2.04 (3H, s), 2.06 (3H, s), 2.13 (3H, s), 3.25 (1H, dd, J = 9.8, 3.5 Hz), 3.41 (3H, s), 3.48 (3H, s), 3.59 (1H, dd, J = 8.6, 8.6 Hz), 3.61 (3H, s), 3.88 (1H, ddd, J = 10.0, 2.6, 2.6 Hz), 3.95 (1H, dd, J = 10.0, 8.6 Hz), 4.07 (1H, dd, J = 11.8, 2.3 Hz), 4.11 (1H, ddd, J = 9.2, 5.5, 2.0 Hz), 4.23 (1H, dd, J = 12.1, 5.5 Hz), 4.43−4.48 (2H, m), 4.71 (1H, d, J = 3.4 Hz), 5.260 (1H, d, J = 2.0 Hz), 5.262 (1H, dd, J = 9.8, 9.8 Hz), 5.31 (1H, dd, J = 9.8, 3.2 Hz), 5.36 (1H, dd, J = 3.2, 2.0 Hz), 7.73 (2H, m), 7.81 (2H, m); ^{13}C NMR (100.6 MHz) δ_C 20.58 (CH_3), 20.63 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 55.6 (CH_3), 58.8 (CH_3), 61.1 (CH_3), 62.8 (CH_2), 66.1 (CH), 69.0 (CH), 69.36 (CH), 69.43 (CH), 69.6 (CH), 76.4 (CH_2), 77.7 (CH), 81.8 (CH), 82.6 (CH), 97.5 (CH), 99.9 (CH), 123.4 (2 × CH), 128.9 (2 × C), 134.4 (2 × CH), 163.1 (2 × C), 169.7 (C), 169.8 (C), 169.9 (C), 170.7 (C); MS *m*/*z* (rel int) 577 (M^+ − 2AcOH, <1), 492 (<1), 417 (1), 331 (70), 88 (100); HRMS *m*/*z* calcd for $C_{27}H_{31}NO_{13}$ 577.1795, found 577.1814. Anal. Calcd for $C_{31}H_{39}NO_{17}$: C, 53.37; H, 5.63; N, 2.01. Found: C, 53.61; H, 5.62; N, 1.80.

Reductive HAT of Methyl 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (20). Method A with *n*-Bu_3SnH. A solution of phthalimide **20** (80 mg, 0.114 mmol) in dry benzene (8 mL) containing *n*-Bu_3SnH (37 μL, 0.136 mmol) and AIBN (2 mg, 0.011 mmol) was heated at reflux temperature for 2 h. After this time another portion of *n*-Bu_3SnH (15 μL, 0.057 mmol) and AIBN (2 mg, 0.011 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more

polar extracts were concentrated under reduced pressure. Column chromatography of the crude residue (hexanes−EtOAc, 80:20 → 20:80) afforded methyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**19**) (26.7 mg, 0.048 mmol, 42%) and methyl 2,3,4,6-tetra-*O*-acetyl-β-L-gulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**22**) (27 mg, 0.049 mmol, 43%), as colorless oils. Compound **22**: $[\alpha]_D$ +66.2 (*c*, 0.12); IR 3544, 1750 cm^{-1}; ^1H NMR δ_H 2.01 (3H, s), 2.10 (3H, s), 2.13 (3H, s), 2.17 (3H, s), 2.70 (1H, dd, *J* = 9.0, 5.5 Hz), 3.24 (1H, dd, *J* = 9.5, 3.5 Hz), 3.41 (3H, s), 3.52 (3H, s), 3.54 (1H, m), 3.55 (1H, dd, *J* = 9.3, 9.3 Hz), 3.62 (3H, s), 3.67 (1H, ddd, *J* = 12.5, 9.1, 2.0 Hz), 3.74 (1H, dd, *J* = 9.5, 9.5 Hz), 3.97 (1H, dd, *J* = 11.0, 8.0 Hz), 4.03 (1H, ddd, *J* = 12.5, 6.0, 2.5 Hz), 4.23−4.29 (2H, m), 4.86 (1H, d, *J* = 3.5 Hz), 4.92 (1H, d, *J* = 3.5 Hz), 4.95 (1H, dd, *J* = 8.5, 3.5 Hz), 5.21 (1H, d, *J* = 8.5 Hz), 5.38 (1H, dd, *J* = 3.5, 3.5 Hz); ^{13}C NMR δ_C 20.6 (CH_3), 20.7 (3 × CH_3), 55.2 (CH_3), 58.9 (CH_3), 60.8 (CH_2), 61.1 (CH_3), 62.560 (CH_2), 67.8 (CH), 68.122 (CH), 68.4 (CH), 70.0 (CH), 70.9 (CH), 74.9 (CH), 82.3 (CH), 83.1 (CH), 97.5 (CH), 99.1 (CH), 168.8 (C), 169.36 (C), 169.44 (C), 170.6 (C); MS *m*/*z* (rel int) 492 (M^+ − AcOH, <1), 331 (35), 169 (26), 88 (100); HRMS *m*/*z* calcd for $C_{21}H_{32}O_{13}$ 492.1843, found 492.1826. Anal. Calcd for $C_{23}H_{36}O_{15}$: C, 50.00; H, 6.57. Found: C, 50.06; H, 6.72.

Method B with *n*-Bu_3SnD. A solution of phthalimide **20** (129 mg, 0.185 mmol) in dry benzene (13 mL) containing *n*-Bu_3SnH (55 μL, 0.277 mmol) and AIBN (3 mg, 0.018 mmol) was heated at reflux temperature for 2 h. After this time another portion of *n*-Bu_3SnD (55 μL, 0.277 mmol) and AIBN (3 mg, 0.018 mmol) was added and heating at reflux continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Column chromatography of the crude residue (hexanes−EtOAc, 80:20 → 20:80) afforded methyl 2,3,4,6-tetra-*O*-acetyl-α-D-[5-^2H]mannopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**19-[D]**) (30 mg, 0.054 mmol, 29%, $^1H/^2H$ ratio, 3:7) and methyl 2,3,4,6-tetra-*O*-acetyl-β-L-(5-^2H)gulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside [**22-(D)**)] (40.2 mg, 0.072 mmol, 39%), as colorless oils. Compound **19-[D]**: ^1H NMR δ_H 1.99 (3H, s), 2.04 (3H, s), 2.11 (3H, s), 2.14 (3H, s), 3.19 (1H, dd, *J* = 9.3, 3.7 Hz), 3.42 (3H, s), 3.49 (3H, s), 3.58 (1H, dd, *J* = 8.9, 8.9 Hz), 3.59 (3H, s), 3.62−3.65 (2H, m), 3.81 (2H, m), 4.05 (1H, ddd, *J* = 8.9, 6.1, 2.0 Hz), 4.134 (1H, d, *J* = 12.1 Hz), 4.137 (1H, dd, *J* = 12.1, 2.8 Hz), 4.210 (1H, d, *J* = 12.2 Hz), 4.215 (1H, d, *J* = 12.2, 4.5 Hz), 4.81 (1H, dd, *J* = 3.6 Hz), 5.236 (1H, d, *J* = 9.7 Hz), 5.238 (1H, dd, *J* = 9.7, 9.7 Hz), 5.25 (1H, d, *J* = 1.6 Hz), 5.30 (1H, dd, *J* = 9.8, 3.2 Hz), 5.31 (1H, dd, *J* = 3.2, 1.6 Hz). ^{13}C NMR δ_C 20.6 (3 × CH_3), 20.8 (CH_3), 55.3 (CH_3), 58.9 (CH_3), 61.3 (CH_3), 61.5 (CH_2), 62.942 (CH_2), 63.011 (CH_2), 62.235 (CH), 66.287 (CH), 68.8 (CH), 69.5 (CH), 69.6 (CH), 70.0 (CH), 76.6 (CH), 82.4 (CH), 83.0 (CH), 97.5 (CH), 99.5 (CH), 169.7 (C), 169.8 (C), 169.9 (C), 170.7 (C); MS *m*/*z* (rel int) 493 (M^+ − AcOH, 2), 492 (<1), 332 (44), 331 (15), 88 (100); HRMS *m*/*z* calcd for $C_{21}H_{31}{}^2HO_{13}$ 493.1906, found 493.1914. Compound **22-(D)**: ^1H NMR δ_H 2.00 (3H, s), 2.08 (3H, s), 2.12 (3H, s), 2.16 (3H, s), 2.69 (1H, dd, *J* = 8.9, 6.1 Hz, OH), 3.22 (1H, dd, *J* = 9.3, 3.6 Hz), 3.40 (3H, s), 3.506 (3H, s), 3.510 (1H, m), 3.55 (1H, dd, *J* = 9.4, 9.4 Hz), 3.61 (3H, s), 3.66 (1H, ddd, *J* = 12,6, 8.9, 2.0 Hz), 3.73 (1H, dd, *J* = 9.4, 9.4 Hz), 3.96 (1H, d, *J* = 11.8 Hz), 4.01 (1H, ddd, *J* = 13.0, 6.1, 2.4 Hz), 4.26 (1H, d, *J* = 11.8 Hz), 4.85 (1H, d, *J* = 3.6 Hz), 4.90 (1H, d, *J* = 3.7 Hz), 4.94 (1H, dd, *J* = 8.5, 3.2 Hz), 5.20 (1H, d, *J* = 8.5 Hz), 5.37 (1H, dd, *J* = 3.2, 3.2 Hz); ^{13}C NMR δ_C 20.5 (CH_3), 20.6 (3 × CH_3), 55.2 (CH_3), 58.9 (CH_3), 60.7 (CH_2), 61.0 (CH_3), 62.439 (CH_2), 67.8 (CH), 68.021 (CH), 68.4 (CH), 69.9 (CH), 74.9 (CH), 82.2 (CH), 83.1 (CH), 97.5 (CH), 99.0 (CH), 168.8 (C), 169.3 (C), 169.4 (C), 170.5 (C); MS *m*/*z* (rel int) 493 (M^+ − AcOH, 2), 332 (59), 170 (36), 88 (100); HRMS *m*/*z* calcd for $C_{21}H_{31}{}^2HO_{13}$ 493.1906, found 493.1894.

Methyl 2,3,4-Tri-*O*-methyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-galactopyranoside (24). DEAD (234 μL, 1.462 mmol) was added dropwise to a stirred solution of the alcohol **23** (300 mg, 0.732 mmol), *N*-hydroxyphthalimide (239 mg, 1.464 mmol) and PPh_3 (383 mg, 1.464 mmol) in dry THF (8 mL) and the resulting solution was stirred at 0 °C for 3 h. Then the solvent was removed and the crude was quenched with water and extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography (hexanes−AcOEt, 50:50 → 30:70) to give compound **24** (331 mg, 0.596 mmol, 82%) as a foam: $[\alpha]_D$ +17.5 (*c*, 0.12); IR 1793, 1739 cm^{-1}; ^1H NMR (400 MHz) δ_H 1.21 (3H, d, *J* = 6.1 Hz), 3.08 (1H, dd, *J* = 9.4, 9.4 Hz), 3.42 (1H, dd, *J* = 9.3, 3.2 Hz), 3.45 (3H, s), 3.47 (3H, s), 3.48 (3H, s), 3.496 (3H, s), 3.501 (6H, s), 3.54 (1H, m), 3.56 (1H, dd, *J* = 9.3, 2.9 Hz), 3.61 (1H, dd, *J* = 10.1, 2.6 Hz), 3.71 (1H, dd, *J* = 3.4, 2.1 Hz), 4.15 (1H, ddd, *J* = 5.6, 5.6, 0 Hz), 4.31 (1H, m), 4.33 (2H, d, *J* = 5.6 Hz), 4.90 (1H, d, *J* = 3.2 Hz), 5.15 (1H, d, *J* = 1.9 Hz), 7.73−7.76 (2H, m), 7.82−7.84 (2H, m); ^{13}C NMR (100.6 MHz) δ_C 17.6 (CH_3), 55.7 (CH_3), 57.6 (CH_3), 58.48 (CH_3), 58.53 (CH_3), 58.67 (CH_3), 60.7 (CH_3), 68.2 (CH), 68.8 (CH), 74.0 (CH), 77.4 (CH), 77.7 (CH), 78.3 (CH_2), 80.0 (CH), 80.6 (CH), 81.8 (CH), 98.0 (CH), 98.5 (CH), 123.6 (2 × CH), 128.9 (2 × C), 134.5 (2 × CH), 163.4 (2 × C); MS *m*/*z* (%) 554 (M^+ − H, 4), 524 (6), 492 (100); HRMS *m*/*z* calcd for $C_{26}H_{36}NO_{12}$ 554.2238, found 554.2216. Anal. Calcd for $C_{26}H_{37}NO_{12}$: C, 56.21; H, 6.71; N, 2.52. Found: C, 56.40; H, 6.98; N, 2.40.

Reductive HAT of Methyl 2,3,4-Tri-*O*-methyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (24). Method A with *n*-Bu_3SnH. A solution of phthalimide **24** (40 mg, 0.072 mmol) in dry benzene (5.5 mL) containing *n*-Bu_3SnH (19 μL, 0.072 mmol) and AIBN (1.2 mg, 0.007 mmol) was heated at reflux temperature for 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Column chromatography (hexanes−EtOAc, 50:50 → 30:70) gave methyl 6-deoxy-2,3,4-tri-*O*-methyl-β-D-gulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside (**27**) (18 mg, 0.044 mmol, 61%) and the alcohol **23** (4.5 mg, 0.011 mmol, 15%), both as colorless oils. Compound **27**: $[\alpha]_D$ +20.0 (*c*, 0.18); IR 3482 cm^{-1}; ^1H NMR (400 MHz) δ_H 1.25 (3H, d, *J* = 6.6 Hz), 3.08 (1H, dd, *J* = 3.4, 1.6 Hz), 3.27 (1H, dd, *J* = 8.0, 3.2 Hz), 3.39 (3H, s), 3.45 (3H, s), 3.47 (3H, s), 3.49 (3H, s), 3.50 (3H, s), 3.55 (1H, m), 3.57 (1H, dd, *J* = 10.1, 2.9 Hz), 3.60 (3H, s), 3.62 (1H, dd, *J* = 10.1, 3.2 Hz), 3.73 (1H, dd, *J* = 3.2, 3.2 Hz), 3.75−3.82 (2H, m), 3.96 (1H, dddd, *J* = 6.4, 6.4, 6.4, 1.6 Hz), 4.26 (1H, dd, *J* = 2.7, 0 Hz), 4.81 (1H, d, *J* = 3.2 Hz), 4.90 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100.6 MHz) δ_C 15.668 (CH_3), 55.3 (CH_3), 58.6 (CH_3), 59.1 (CH_3), 59.3 (CH_3), 59.4 (CH_3), 59.9 (CH_2), 60.0 (CH_3), 68.9 (CH), 69.3 (CH), 71.2 (CH), 77.7 (CH), 78.26 (CH), 78.31 (CH), 79.212 (CH), 79.6 (CH), 98.3 (CH), 101.4 (CH); MS (FAB) *m*/*z* (%) 433 (M^+ + Na, 88), 411 (26), 133 (100); HRMS *m*/*z* calcd for $C_{18}H_{34}NaO_{10}$ 433.2050, found 433.2051. Anal. Calcd for $C_{18}H_{34}O_{10}$: C, 52.67; H, 8.35. Found: C, 52.73; H, 8.06.

Method B with *n*-Bu_3SnD. A solution of phthalimide **24** (43 mg, 0.078 mmol) in dry benzene (5.8 mL) containing *n*-Bu_3SnD (21 μL, 0.078 mmol) and AIBN (1.3 mg, 0.008 mmol) was heated at reflux temperature for 1 h. After this time another portion of *n*-Bu_3SnD (21 μL, 0.078 mmol) and AIBN (1.3 mg, 0.008 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. Column chromatography (hexanes−EtOAc, 50:50 → 30:70) gave methyl 6-deoxy-2,3,4-tri-*O*-acetyl-β-D-(5-^2H)gulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside [**27-(D)**)] (16.6 mg, 0.040 mmol, 52%), methyl 2,3,4-tri-*O*-methyl-α-L-[5-^2H]rhamnopyranosyl-(1→4)-2,3-

di-*O*-methyl-α-D-galactopyranoside (**23-[D]**) (4.8 mg, 0.012 mmol, 15%, $^1H/^2H$ ratio 2:8) (contaminated with ca. 30% of compound **29**), and methyl (5*S*)-5,6-anhydro-2,3-di-*O*-methyl-4,6-dideoxy-α-D-*erythro*-hexos-5-ulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**29**) (3.6 mg, 0.010 mmol, 12%), all as colorless oils. Compound **27-(D)**: ^1H NMR δ_H 1.24 (3H, s), 3.07 (1H, d, J = 3.5 Hz), 3.27 (1H, dd, J = 8.0, 3.0 Hz), 3.38 (3H, s), 3.45 (3H, s), 3.47 (3H, s), 3.48 (3H, s), 3.49 (3H, s), 3.55 (1H, m), 3.57 (1H, dd, J = 10.0, 3.0 Hz), 3.60 (3H, s), 3.61 (1H, dd, J = 10.0, 3.0 Hz), 3.72 (1H, dd, J = 3.5, 3.5 Hz), 3.74−3.82 (2H, m), 4.25 (1H, dd, J = 2.5, 0 Hz), 4.80 (1H, d, J = 3.5 Hz), 4.90 (1H, d, J = 8.0 Hz); ^{13}C NMR δ_C 15.541 (CH_3), 55.3 (CH_3), 58.6 (CH_3), 59.1 (CH_3), 59.3 (CH_3), 59.4 (CH_3), 59.9 (CH_2), 60.0 (CH_3), 69.2 (CH), 71.1 (CH), 77.6 (CH), 78.20 (CH), 78.26 (CH), 79.075 (CH), 79.6 (CH), 98.3 (CH), 101.3 (CH); MS (FAB) *m/z* (%) 434 (M^+ + Na, 100), 133 (51); HRMS *m/z* calcd for $C_{18}H_{33}{}^2HNaO_{10}$ 434.2112, found 434.2109. Compound **23-[D]** (data taken from a mixture **23-[D]/29**, 7:3): ^1H NMR (400 MHz) δ_H 1.29 (3H, s), 3.13 (1H, d, J = 9.3 Hz), 3.42 (3H, s), 3.46 (1H, dd, J = 9.3, 2.7 Hz), 3.48 (3H, s), 3.51 (6H, s), 3.52 (3H, s), 3.55 (3H, s), 3.58 (1H, dd, J = 2.1, 2.1 Hz), 3.63−3.69 (2H, m), 3.75 (1H, dd, J = 3.2, 1.8 Hz), 3.78 (1H, dd, J = 11.1, 7.2 Hz), 3.86 (1H, ddd, J = 6.9, 6.9, 0 Hz), 4.16 (1H, br s), 4.89 (1H, d, J = 2.6 Hz), 5.11 (1H, d, J = 1.9 Hz); ^{13}C NMR δ_C 17.589 (CH_3), 17.648 (CH_3), 55.2 (CH_3), 57.6 (CH_3), 58.48 (CH_3), 58.51 (CH_3), 58.61 (CH_3), 60.7 (CH_3), 61.7 (CH_2), 69.8 (CH), 73.8 (CH), 77.3 (CH), 77.8 (CH), 79.8 (CH), 80.5 (CH), 81.553 (CH), 81.628 (CH), 97.7 (CH), 99.1 (CH); MS *m/z* (%) 411 (M^+ + H, 6), 393 (17), 88 (100). Compound **29**: $[\alpha]_D$ +103.3 (*c*, 0.12); IR 2930, 1104, 1053 cm^{-1}; ^1H NMR (400 MHz) δ_H 1.36 (3H, s), 1.93 (1H, dd, J = 12.5, 12.5 Hz), 2.09 (1H, dd, J = 12.7, 4.8 Hz), 3.39 (3H, s), 3.40 (3H, s), 3.46−3.54 (2H, m), 3.47 (3H, s), 3.51 (3H, s), 3.52 (3H, s), 3.61 (1H, dd, J = 10.0, 3.7 Hz), 3.74 (1H, m), 3.78 (1H, dd, J = 13.5, 2.4 Hz), 3.95 (1H, ddd, J = 11.9, 4.8, 2.9 Hz), 4.08 (1H, dd, J = 13.5, 1.3 Hz), 4.16 (1H, dd, J = 3.2, 0 Hz), 4.95 (1H, d, J = 3.7 Hz), 5.01 (1H, d, J = 1.8 Hz); ^{13}C NMR (100.6 MHz) δ_C 25.3 (CH_3), 35.6 (CH_2), 55.3 (CH_3), 56.0 (CH_3), 58.1 (CH_3), 58.7 (CH_3), 59.1 (CH_3), 63.2 (CH_2), 67.4 (CH), 72.1 (CH), 73.5 (CH), 74.4 (CH), 77.3 (CH), 78.6 (CH), 98.0 (CH), 98.7 (CH), 100.4 (C); MS *m/z* (%) 378 (M^+, 18), 347 (11), 88 (100); HRMS *m/z* calcd for $C_{17}H_{30}O_9$ 378.1890, found 378.1886. Anal. Calcd for $C_{17}H_{30}O_9$: C, 53.96; H, 7.99. Found: C, 54.07; H, 7.97.

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-galactopyranoside (26). DEAD (278 μL, 1.77 mmol) was added dropwise to a stirred solution of the alcohol **25** (350 mg, 0.708 mmol), *N*-hydroxyphthalimide (388 mg, 1.77 mmol) and PPh_3 (464 mg, 1.77 mmol) in dry THF (7.7 mL) under nitrogen at 0 °C and the resulting solution was stirred at this temperature for 1.5 h. The reaction was quenched with water and extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography (hexanes−EtOAc, 80:20) to give *N*-phthalimide **26** (380 mg, 0.595 mmol, 84%) as an amorphous solid: $[\alpha]_D$ +17.5 (*c*, 0.245); IR 1791, 1735 cm^{-1}; ^1H NMR δ_H 1.15 (3H, d, J = 6.3 Hz), 1.97 (3H, s), 2.04 (3H, s), 2.12 (3H, s), 3.44 (3H, s), 3.48 (3H, s), 3.52 (3H, s), 3.59 (1H, dd, J = 10.1, 2.7 Hz), 3.66 (1H, dd, J = 10.1, 3.5 Hz), 3.95 (1H, dddd, J = 9.9, 6.3, 6.3, 6.3 Hz), 4.13 (1H, ddd, J = 6.1, 6.1, 0 Hz), 4.33 (1H, dd, J = 11.1, 5.9 Hz), 4.36 (1H, dd, J = 11.1, 6.2 Hz), 4.40 (1H, dd, J = 1.1, 0 Hz), 4.87 (1H, d, J = 3.5 Hz), 5.05 (1H, dd, J = 9.9, 9.9 Hz), 5.07 (1H, d, J = 1.5 Hz), 5.29 (1H, dd, J = 10.1, 3.3 Hz), 5.50 (1H, dd, J = 3.0, 2.1 Hz), 7.76 (2H, m), 7.84 (2H, m); ^{13}C NMR (100.6 MHz) δ_C 17.3 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.8 (CH_3), 58.6 (CH_3), 59.3 (CH_3), 67.3 (CH), 67.6 (CH), 69.1 (CH), 69.9 (CH), 70.8 (CH), 75.0 (CH), 77.4 (CH_2), 77.6 (CH), 79.6 (CH), 98.4 (CH), 99.3 (CH), 123.6 (2 × CH), 128.8 (2 × C), 134.6 (2 × CH), 163.5 (2 × C), 169.8 (C), 169.9 (C), 170.0 (C); MS (FAB) *m/z* (%) 663 (M^+ + H + Na, 3), 662 (9), 273 (28), 55 (100); HRMS calcd for $C_{29}H_{38}NNaO_{15}$ 663.2139, found 663.2166. Anal. Calcd for $C_{29}H_{37}NO_{15}$: C, 54.46; H, 5.83; N, 2.19. Found: C, 54.10; H, 5.78; N, 2.38.

Reductive HAT of Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-galactopyranoside (26). Method A with *n*-Bu_3SnH. A solution of phthalimide **26** (95 mg, 0.149 mmol) in dry benzene (11.2 mL) containing *n*-Bu_3SnH (40 μL, 0.149 mmol) and AIBN (2.4 mg, 0.015 mmol) was heated at reflux temperature for 1.5 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. The residue was purified by column chromatography (hexanes−EtOAc, 50:50 → 30:70) to give methyl 2,3-di-*O*-acetyl-4,6-dideoxy-β-D-*erythro*-hex-4-enopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside (**30**) (3.5 mg, 0.008 mmol, 5%), the alcohol **25** (16.5 mg, 0.033 mmol, 22%), previously described, and the methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-D-gulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside (**28**) (38.2 mg, 0.077 mmol, 52%) as colorless oils. Compound **30**: $[\alpha]_D$ −33.8 (*c*, 0.29); IR 3468, 1747 cm^{-1}; ^1H NMR (400 MHz) δ_H 1.83 (3H, s), 2.05 (3H, s), 2.10 (3H, s), 2.21 (1H, dd, J = 9.8, 7.5 Hz), 3.41 (3H, s), 3.50 (3H, s), 3.51 (3H, s), 3.57−3.58 (2H, m), 3.60−3.75 (2H, m), 3.82 (1H, ddd, J = 6.6, 6.6, 1.3 Hz), 4.24 (1H, dd, J = 1.1, 1.1 Hz), 4.66 (1H, br d, J = 3.7 Hz), 4.85 (1H, d, J = 1.6 Hz), 5.25 (1H, dd, J = 5.0, 5.0 Hz), 5.30 (1H, d, J = 5.3 Hz), 5.51 (1H, ddd, J = 5.3, 3.7, 1.6 Hz); ^{13}C NMR (100.6 MHz) δ_C 19.5 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.4 (CH_3), 58.7 (CH_3), 59.1 (CH_3), 61.4 (CH_2), 64.1 (CH), 66.0 (CH), 69.6 (CH), 73.4 (CH), 78.0 (CH), 79.6 (CH), 95.1 (CH), 97.9 (CH), 98.4 (CH), 151.1 (C), 169.9 (C), 170.2 (C); MS *m/z* (%) 435 (M^+ + H, <1), 402 (<1), 374 (1), 212 (11), 88 (100); HRMS calcd for $C_{19}H_{31}O_{11}$ 435.1866, found 435.1877. Anal. Calcd for $C_{19}H_{30}O_{11}$: C, 52.53; H, 6.96. Found: C, 52.23; H, 6.90. Compound **28**: crystalline solid, mp 153.2−154.9 °C (from *n*-hexane−acetone); $[\alpha]_D$ +60.0 (*c*, 0.53); IR 3506, 1748 cm^{-1}; ^1H NMR δ_H 1.19 (3H, d, J = 6.4 Hz), 2.03 (3H, s), 2.13 (3H, s), 2.17 (3H, s), 3.23 (1H, m), 3.39 (3H, s), 3.47 (1H, dd, J = 10.1, 3.5 Hz), 3.48 (3H, s), 3.49 (3H, s), 3.57 (1H, dd, J = 10.1, 3.0 Hz), 3.63 (1H, m), 3.77−3.83 (2H, m), 4.15 (1H, dddd, J = 6.5, 6.5, 6.5, 1.3 Hz), 4.19 (1H, br d, J = 3.1 Hz), 4.81 (1H, d, J = 3.5 Hz), 4.83 (1H, dd, J = 3.7, 1.4 Hz), 4.94 (1H, d, J = 8.3 Hz), 5.04 (1H, dd, J = 8.3, 3.5 Hz), 5.34 (1H, dd, J = 3.6, 3.6 Hz); ^{13}C NMR (100.6 MHz) δ_C 15.715 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 55.4 (CH_3), 58.4 (CH_3), 59.1 (CH_3), 60.2 (CH_2), 67.9 (CH), 68.4 (CH), 68.8 (CH), 69.0 (CH), 70.100 (CH), 73.3 (CH), 78.0 (CH), 79.2 (CH), 97.9 (CH), 99.8 (CH), 168.9 (C), 169.5 (C), 169.8 (C); MS (FAB) *m/z* (%) 518 (M^+ + H + Na, 6), 517 (21), 391 (32), 273 (63), 73 (100); HRMS calcd for $C_{21}H_{35}NaO_{13}$ 518.1975, found 518.1984. Anal. Calcd for $C_{21}H_{34}O_{13}$: C, 51.01; H, 6.93. Found: C, 51.15; H, 6.89.

Method B with *n*-Bu_3SnD. A solution of phthalimide **26** (90 mg, 0.141 mmol) in dry benzene (10.6 mL) containing *n*-Bu_3SnD (38 μL, 0.141 mmol) and AIBN (2.3 mg, 0.014 mmol) was heated at reflux temperature for 1 h. After this time another portion of *n*-Bu_3SnD (38 μL, 0.141 mmol) and AIBN (2.3 mg, 0.014 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. The residue was purified by column chromatography (hexanes−EtOAc, 50:50 → 30:70) to give the olefin **30** (9 mg, 0.021 mmol, 15%), described above, methyl 2,3,4-tri-*O*-acetyl-α-L-[5-^{2}H]rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside (**25-[D]**) (12.6 mg, 0.025 mmol, 18%, $^1H/^2H$ ratio, 3:7), and methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-D-(5-^{2}H)gulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside [**28-(D)**)] (31.2 mg, 0.063 mmol, 45%) as colorless oils. Compound **25-[D]**: ^1H NMR δ_H 1.22 (3H, s), 1.23 (3H, d, J = 6.6 Hz), 1.99 (3H, s), 2.05 (3H, s), 2.14 (3H, s), 3.42 (3H, s), 3.47 (3H, s), 3.54 (3H, s), 3.56 (1H, dd, J = 10.1, 2.9 Hz), 3.64

(1H, dd, J = 10.1, 3.5 Hz), 3.66 (1H, m), 3.80−3.86 (2H, m), 3.98 (1H, dddd, J = 10.0, 6.3, 6.3, 6.3 Hz), 4.12 (1H, dd, J = 2.7, 0 Hz), 4.88 (1H, d, J = 3.5 Hz), 5.05 (1H, d, J = 2.1 Hz), 5.071 (1H, d, J = 10.0 Hz), 5.073 (1H, dd, J = 9.8, 9.8 Hz), 5.31 (1H, dd, J = 10.0, 3.3 Hz), 5.47 (1H, dd, J = 3.3, 2.1 Hz); ^{13}C NMR (100.6 MHz) δ_C 17.350 (CH_3), 17.489 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.4 (CH_3), 58.8 (CH_3), 59.3 (CH_3), 62.0 (CH_2), 67.5 (CH), 69.0 (CH), 69.8 (CH), 69.9 (CH), 70.869 (CH), 70.932 (CH), 75.1 (CH), 78.0 (CH), 79.8 (CH), 98.1 (CH), 99.7 (CH), 169.8 (C), 170.0 (C), 170.0 (C); MS (FAB) m/z (%) 519 (M^+ + Na + H, 7), 518 (26), 517 (5), 274 (46), 273 (27), 73 (100); HRMS calcd for $C_{21}H_{34}{}^2HNaO_{13}$ 519.2038, found 519.2042. Compound **28-(D)**: ^{1}H NMR δ_H 1.18 (3H, s), 2.02 (3H, s), 2.12 (3H, s), 2.16 (3H, s), 3.24 (1H, m), 3.38 (3H, s), 3.46 (1H, dd, J = 10.1, 3.5 Hz), 3.47 (3H, s), 3.48 (3H, s), 3.56 (1H, dd, J = 10.1, 3.0 Hz), 3.63 (1H, m), 3.76−3.82 (2H, m), 4.19 (1H, dd, J = 3.0, 0 Hz), 4.80 (1H, d, J = 3.5 Hz), 4.81 (1H, d, J = 3.7 Hz), 4.94 (1H, d, J = 8.3 Hz), 5.03 (1H, dd, J = 8.3, 3.5 Hz), 5.33 (1H, dd, J = 3.6, 3.6 Hz); ^{13}C NMR (100.6 MHz) δ_C 15.576 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 20.7 (CH_3), 55.4 (CH_3), 58.4 (CH_3), 59.0 (CH_3), 60.2 (CH_2), 67.9 (CH), 68.4 (CH), 69.0 (CH), 70.036 (CH), 73.3 (CH), 78.0 (CH), 79.2 (CH), 97.9 (CH), 99.8 (CH), 168.8 (C), 169.5 (C), 169.8 (C); MS (FAB) m/z (%) 519 (M^+ + H + Na, 2), 518 (7), 355 (10), 274 (27), 73 (100); HRMS calcd for $C_{21}H_{34}{}^2HNaO_{13}$ 519.2038, found 519.2014.

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Supporting Information Available: A complete description of experimental details of precursors and copies of NMR spectra (^{1}H and ^{13}C) for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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