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Diastereoselective Synthesis of All Eight L-Hexoses from L-Ascorbic Acid

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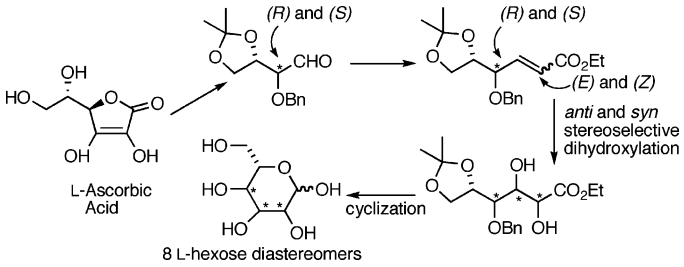

A novel versatile method for the synthesis of all eight diastereomerically pure L-hexoses was developed. L-Ascorbic acid was converted to two diastereomers **A**. These α-hydroxy esters were transformed into four γ-alkoxy-α,β-unsaturated esters **C** via the intermediates **B** and subsequent Wittig olefination reactions. Each one of compounds **C** was subjected to dihydroxylation to provide a set of two diols **D**. *Anti/syn*-differentiation in diol formation was manipulated by using $(DHQD)_2PHAL$ and $(DHQ)_2PHAL$ as chiral ligands. Further two-step reaction sequence affords all eight diastereopure L-hexoses.

Introduction

The rare L-hexoses are key components of numerous biologically important oligosaccharides, glycopeptides, steroid glycosides, antibiotics, and other biologically active natural products. L-Altrose, for instance, is a constituent of extracellular polysaccharide from *Buturivibrio fibrisolvents* strain CF3.[1] L-Gulose constitutes the disaccharide subunit of bleomycin A_3, the major component of a family of glycopeptide antibiotics.[2] L-Idose is a constituent of heparin and heparane sulfates that are found on the cell surfaces and the extracellular matrix of all eukaryotes where they play pivotal role in a large number of biological events.[3−6] L-Mannose has been found in the sugars units of steroid glycosides.[7] Recently, isolation of the first α-L-galactosyl saponin from a marine octocoral has been reported.[8] L-Hexoses have also demonstrated potential as noncaloric sweeteners,[9] laxatives,[10] and selectively toxic insecticides.[11]

Although replacing an L-amino acid with its D-isomer in a bioactive peptide is quite relevant in order to alter its physiological consequences, this sort of enantiomer-exchange has hardly been practiced in the domain of glycoconjugates.

Given the importance of L-hexoses in the field of glycobiology and limited natural sources, the need to develop efficient methodologies for their synthesis continues to exist. Among the methods known in the literature ranging from classical modification of readily available D-sugars to the recent organocatalytic aldol synthesis and iterative dihydroxylation of dienes,[12] there are only two versatile strategies that can provide all eight hexoses. These are the Masamune−Sharpless synthesis employing asymmetric epoxidation as a key step[13] and the Ogasawara procedure starting from furfural via levoglucosenone by oxidative ring expansion.[14]

(1) Stack, R. J. *FEMS Microbiol. Lett.* **1987**, *48*, 83−87.
(2) Dondoni, A.; Marra, A.; Massi, A. *J. Org. Chem.* **1997**, *62*, 6261−6267.
(3) van Boeckel, C. A. A.; Beetz, T.; Vos, A. J. M.; de Jong, A. J. M.; van Aelst, S. F.; van den Bosch, R. H.; Mertens, J. M. R.; van der Vlugt, F. A. *J. Carbohydr. Chem.* **1985**, *4*, 293−321.
(4) Prabhu, A.; Venot, A.; Boons, G.-J. *Org. Lett.* **2003**, *26*, 4975−4978.
(5) Lee, J.-C.; Chang, S.-W.; Liao, C.-C.; Chi, F.-C.; Chen, C.-S.; Wen, Y.-S.; Wang, C.-C.; Kulkarni, S. S.; Puranik, R.; Liu, Y.-H.; Hung, S.-C. *Chem. Eur. J.* **2004**, *10*, 399−415.
(6) Kovensky, J.; Duchaussoy, P.; Bono, F.; Salmivirta, M.; Sizun, P.; Herbert, J.-M.; Petitou, M.; Sinay, P. *Biorg. Med. Chem.* **1999**, *7*, 1567−1580.
(7) Kubelka, W. *Phytochemistry* **1974**, *13*, 1805−1808.
(8) Guttiérrez, M.; Capson, T.; Guzmán, H. M.; Quiñoá, E.; Riguera, R. *Tetrahedron Lett.* **2004**, *45*, 7833−7836.
(9) (a) Shallenberger, R. S.; Acree, T. E.; Lee, C. Y. *Nature* **1961**, *221*, 555−556. (b) Levin, G. V. U.S. Patent 4262032, 1981.
(10) Tarka Jr., S. M.; Shively, C. A.; Apgar, J. L.; Koch, K. L. U.S. Patent 5219573, 1989.
(11) Levin, G. V.; Zehner, L. R. U.S. Patent 5166193, 1992.

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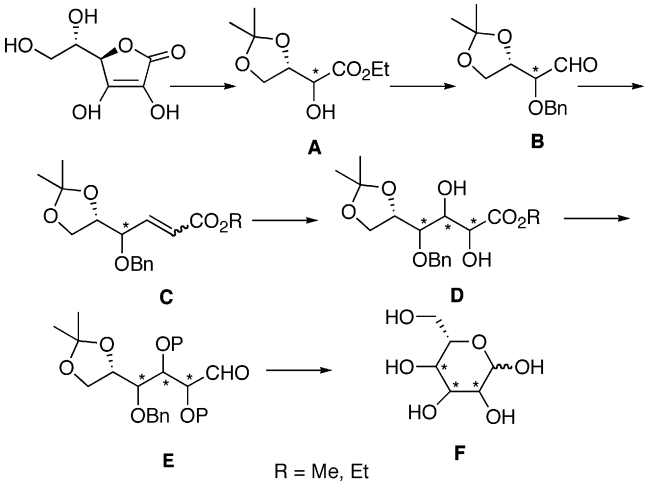
SCHEME 1. General Strategy for the Synthesis of L-Hexoses



Results and Discussion

In our preliminary communication, we have reported a novel stereodivergent approach to L-hexoses using L-ascorbic acid as a single starting material by exploiting the inherent chirality at the C-5 stereocenter of final products.[15] As illulstrated in Scheme 1, our strategy to synthesize all eight diastereopure L-hexoses comprises the following major steps: (i) preparation of two chiral aldehydes **B**, one of which involving Mitsunobu inversion, from α-hydroxy ester **A** that is in turn readily available from L-ascorbic acid; (ii) transformation of aldehydes **B** into four α,*β*-unsaturated esters **C** with the specified (*E*) or (*Z*) configuration via the Wittig olefination reactions; (iii) stereoselective dihydroxylation of each one of α,*β*-unsaturated esters **C** followed by partial reduction of resulting eight polyol esters **D**; (iv) cyclization of thus obtained aldehydes **E** to provide L-hexopyranoses **F**.

As a result of our efforts in developing this methodology into a truly practical method, we describe herein the synthesis of all eight diastereoisomers of L-hexoses by employing Sharpless asymmetric dihydroxylation as a key step.

The key compound of the series, ethyl (2*R*,3*S*)-3,4-*O*-isopropylidene-2,3,4-trihydroxybutanoate **1**, was prepared from L-ascorbic acid in two steps by the known procedure.[16] Inversion of configuration at C-2 in **1** by the convenient chloroacetate modification of the Mitsunobu reaction[17] provided ethyl (2*S*,3*S*)-3,4-*O*-isopropylidene-2,3,4-trihydroxybutanoate **2** in 65% yield after the selective chloroacetate alcoholysis in mild basic conditions (Scheme 2). For pursuing the synthesis, the free hydroxyl group in **1** and **2** must be protected. To this end, we chose benzyl group that facilitated easy removal under neutral conditions. Benzylation of a substrate possessing both base-sensitive ester and acid-labile acetal functionalities is rather challenging task. Benzylation of a hydroxy group by treatment of **1** and **2** with benzyl trichloroacetimidate in the presence of catalytic amount of triflic acid[18] was attempted only to recover starting material after 24 h under standard conditions. Under more acidic conditions, the isopropylidene group was partially removed. Eventually, benzylation of **1** with benzyl bromide in the presence of silver oxide[19] in dichloromethane was proved to be efficient for affording the *O*-benzyl ether **3** in 85% yield after 3 h. As for the hydroxyester **2**, the same *O*-benzylation conditions gave **4** only in 70% yield after 72 h. Better result was obtained when the reaction was performed in boiling acetonitrile in the presence of catalytic amount of Bu_4NI.[20] The *O*-benzyl ester **4** was isolated in 80% yield after 12 h. Since a direct reduction of these esters to the corresponding aldehydes gave mixtures, the two-step procedure was applied**.** The reduction of **3** and **4** with $LiBH_4$ in ether[21] furnished the alcohols **5** and **6** in 95% yield. Subsequent Swern oxidation of these alcohols afforded the pure aldehydes **7** and **8** that can be directly used in the following olefination step.

Olefination of α-alkoxy-substituted aldehydes and ketones has been shown to be sensitive to the reagent, solvent, occasional additives, and reaction temperature. The reaction of semistabilized phosphoranes $Ph_3P{=}CHCOOR$ (R = Me or Et) with α-alkoxy aldehydes have been reported to give the α,*β*-unsaturated esters in *E*/*Z* ratios varied from 10:1 (CH_2Cl_2, rt)[22] to 1:10 (MeOH, 0 °C).[23] In accordance with these results, the reaction of aldehyde **7** with $Ph_3P{=}CO_2Et$ in CH_2Cl_2 provided the α,*β*-unsaturated ester **9** with an *E*/*Z* ratio of 10:1 in 80% yield (Scheme 2). However, under the same conditions, aldehyde **8** gave the corresponding enoate **10** in *E*/*Z* ratio of 2:1. In benzene, the reaction became nonselective (*E*/*Z* = 1:1). To resolve this problem, we turned our attention to the stabilized phosphonates that, in general, exhibit a strong (*E*)-selectivity with α-alkoxy aldehydes.[24] Indeed, the coupling of triethyl phosphonoacetate with aldehydes **7** and **8** in benzene at room temperature resulted in the unsaturated esters **9** and **10** in high

(12) (a) Humoller, F. L.; Frush, H. L.; Isbell, H. S.; Sowden, J. C.; Whistler, R. L.; BeMiller, J. N.; Shafizaden, F. In *Methods in Carbohydrate Chemistry*; Academic Press: New York, 1962; Vol. 1, pp 105−145. (b) Evans, M. E.; Parrish, F. W.; Blanc-Muesser, M.; DeFaye, J.; Horton, D.; Tsai, J.-H. In *Methods in Carbohydrate Chemistry*; Academic Press: New York, 1980; Vol. VIII, pp 173−185. (c) Hudlicky, T.; Entwistle, D. A.; Pitzer, K. K.; Thorpe, A. J. *Chem. Rev.* **1996**, *96*, 1195−1220 and references therein. (d) Hung, S.-C.; Wang, C.-C.; Chang, S.-W.; Chen, C.-S. *Tetrahedron Lett.* **2001**, *42*, 1321−1324. (e) Hung, S.-C.; Wang, C.-C.; Thopate, S. R. *Tetrahedron Lett.* **2000**, *41*, 3119−3122. (f) Harris, J. M.; Keränen, M. D.; Nguyen, H.; Yong, V. G.; O'Doherty, G. A. *Carbohydr. Res.* **2000**, *328*, 17−36. (g) Adinolfi, M.; Barone, G.; De Lorenzo, F.; Iadonisi, A. *Synlett* **1999**, *3*, 336−338. (h) Hajkó, J.; Lipták, A.; Pozsgay, V. *Carbohydr. Res.* **1999**, *321*, 116−120. (i) Tietze, L. F.; Montenbruck, A.; Schneider, C. *Synlett* **1994**, 509−510. (j) Bazin, H. G.; Wolff, M. W.; Linhardt, R. J. *J. Org. Chem*, **1999**, *64*, 144−152. (k) Harris, J. M.; Keränen, M. D.; O'Doherty, G. A. *J. Org. Chem*, **1999**, *64*, 2982−2983. (l) Takahashi, H.; Hitomi, Y.; Iwai, Y.; Ikegami, S. *J. Am. Chem. Soc.* **2000**, *122*, 2995−2998. (m) Northrup, A. B.; MacMillan, D. W. C. *Science* **2004**, 1752−1755. (n) Ahmed, Md. M.; Berry, B. P.; Hunter, T. J.; Tomcik, D. J.; O'Doherty, G. A. *Org. Lett.* **2005**, *7*, 745−748.

(13) Ko, S. Y.; Lee, A. W. M.; Masamune, S.; Reed, L. A., III; Sharpless, K. B.; Walker, F. J. *Tetrahedron* **1990**, *46*, 245−264.

(14) (a) Takeuchi, M.; Taniguchi, T.; Ogasawara, K. *Synthesis* **1999**, *2*, 341−354. (b) Takeuchi, M.; Taniguchi, T.; Ogasawara, K. *Chirality* **2000**, 338−341.

(15) Ermolenko, L.; Sasaki, N. A.; Potier P. *Helv. Chim. Acta* **2003**, *86*, 3578−3582.

(16) Abushanab, E.; Vemishetti, P.; Leiby, R. W.; Singh, H. K.; Mikkilineni, A. B.; Wu, D. C.-J.; Saibaba, R.; Panzica, R. P. *J. Org. Chem.* **1988**, *53*, 2598−2602.

(17) Saïah, M.; Bessodes, M.; Antonakis, K. *Tetrahedron Lett.* **1992**, *33*, 4317−4320.

(18) Nakajima, N.; Horita, K.; Abe, R.; Yonemitsu, O. *Tetrahedron Lett.* **1988**, *29*, 4139−4142.

(19) Bouzide, A.; Sauvé, G. *Tetrahedron Lett.* **1997**, *38*, 5945−5948.

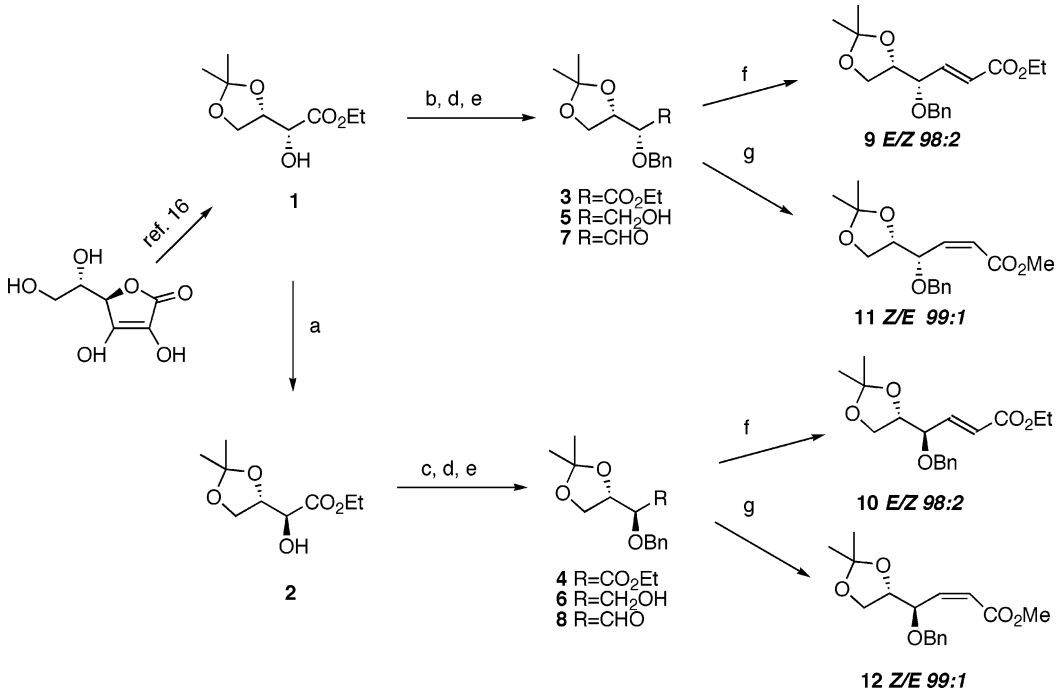
(20) André, C.; Bolte, J.; Demuynck C. *Tetrahedron: Asymmetry* **1998**, *9*, 1359−1367.

(21) Soai, K.; Ookawa, A. *J. Org. Chem.* **1986**, *51*, 4000−4005.

(22) (a) Mulzer, J.; Kappert, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 63−64. (b) Mulzer, J.; Kappert, M. *Angew. Chem. Suppl.* **1982**, *22*, 23−33. (c) Hu, T.-S.; Yu, Q.; Wu, Y.-L.; Wu, Y. *J. Org. Chem.* **2001**, *66*, 853−861.

(23) (a) Sánchez-Sancho, F.; Valverde, S.; Herradón, B. *Tetrahedron: Asymmetry* **1996**, *7*, 3209−3246. (b) Valverde, S.; Martin-Lomas, M.; Herradón, B.; Garcia-Ochoa, S. *Tetrahedron* **1987**, *43*, 1895−1901.

SCHEME 2. Synthesis of α,β-Unsaturated Esters 9−12[a]



[a] Key: (a) $ClCH_2COOH$, Ph_3P, DIAD, THF, 12 h, then Et_3N−EtOH, 65% in two steps; (b) BnBr, Ag_2O, CH_2Cl_2, rt, 3 h, 85%; (c) BnBr, Ag_2O, CH_3CN, reflux, 12 h, 80%; (d) $LiBH_4$, Et_2O, 0 °C, 2 h, 95%; (e) $(COCl)_2$, DMSO, CH_2Cl_2, −70 °C, 20 min, Et_3N, −78 °C, 1 h, 95%; (f) $(C_2H_5O)_2POCH_2CO_2Et$, NaH, benzene, rt, 2h; (g) $(CF_3CH_2O)_2POCH_2CO_2Me$, 18-crown-6, $KN(TMS)_2$, THF, −78 °C.

yield and selectivity (E/Z = 98:2). For the preparation of (*Z*) unsaturated esters, the Still modification[25] of the Horner−Emmons procedure was applied to the aldehydes **7** and **8** resulting in esters **11** and **12**, respectively, with excellent (*Z*) selectivity (>99:1). It should be noted that all the (*E*)- and (*Z*)-isomers obtained in this series are easily separable by column chromatography on silica gel. With all four α,β-unsaturated esters (**9**−**12**) in hand, the dihydroxylation of these substrates was addressed to set the remaining two stereogenic centers on the hexose precursors.

The stereochemical outcome of the osmium-catalyzed dihydroxylation of γ-alkoxy-α,β-unsaturated esters follows the Kishi−Stork empirical rule that predicts 1,2-*anti* relationship between the resident and newly formed stereogenic centers in case of (*E*)-γ-alkoxy enoates, and 1,2-*syn* product for the (*Z*)-γ-alkoxy conjugate esters.[26] The (*E*)-γ-alkoxy-α,β-unsaturated esters typically show strong facial preference, though (*Z*)-enoates often exhibit irregular magnitude of diastereofacial selectivity that can vary from very low (1:1) to very high (25:1).[27] With regard to dihydroxylation of our α,β-unsaturated esters, a low selectivity for some diol products and inaccessibility of others could be the issue.[28]

Ever since the introduction of asymmetric dihydroxylation, the double-asymmetric induction principle has been applied to dihydroxylation of γ-alkoxy-α,β-unsaturated esters. However, improvements in selectivity have remained moderate, even under stoichiometric conditions.[27f,29] It is assumed that the use of a more efficient second-generation chiral ligands can override the inherent facial selectivity of (*E*)-γ-alkoxy-α,β-unsaturated ester by its own induction efficacy. This makes the otherwise minor diastereomer available in acceptable yield. The catalytic asymmetric dihydroxylation using the latest techniques has been successfully applied to a number of (*E*)-γ-alkoxy-α,β-unsaturated esters and α,β-unsaturated lactones. However, to the best of our knowledge, no data is available for the corresponding (*Z*)-enoates, and no systematic application of asymmetric dihydroxylation to the synthesis of sugars, particularly to hexoses, has been reported. We expected the Sharpless asymmetric dihydroxylation would provide a powerful tool to overcome the inherent facial selectivity of our substrates and to gain access, from the same α,β-unsaturated ester, to both stereoisomers of diol in acceptable yields regardless the configuration of double bond and γ-stereogenic center. Previously reported results on the double diastereoselection in asymmetric dihydroxylation of the α,β-unsaturated esters[30] prompted

(24) (a) Katsuki, T.; Lee, A. W. M.; Ma, P.; Martin, V., S.; Masamune, S.; Sharpless, K., B.; Tuddenham, D.; Walker, F. J. *J. Org. Chem.* **1982**, *47*, 1373−1378. (b) Minami, N.; Ko, S., S.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1109−1111. (c) Trost, B. M.; Lynch, J.; Renaut, P.; Steinman, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 284−291. (d) Larsen, R. O.; Aksnes, G. *Phosphorus Sulfur* **1983**, *16*, 339−344.

(25) Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405−4408.

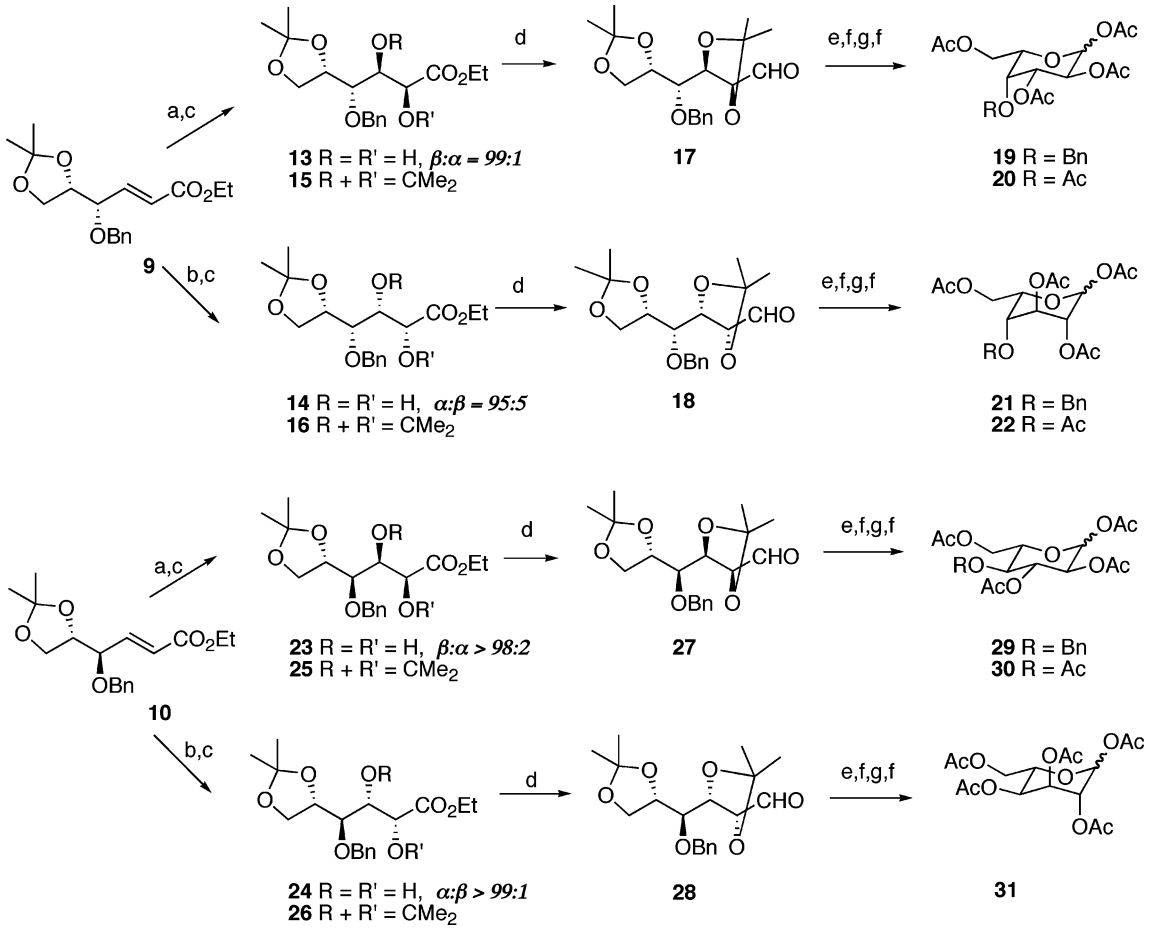
(26) (a) Christ, W. C.; Cha, J. K.; Kishi, Y. *Tetrahedron Lett.* **1983**, *24*, 3947−3950. (b) Stork, G.; Kahn, M. *Tetrahedron Lett.* **1983**, *24*, 3951−3954. (c) Cha, J. K.; Christ, W. C.; Kishi, Y. *Tetrahedron* **1984**, *40*, 2247−2255.

(27) (a) Saito, S.; Morikawa, Y.; Moriwake, T. *J. Org. Chem.* **1990**, *55*, 5424−5426. (b) Brimacombe, J. S.; Hanna, R.; Kabir, A. K. M. S.; Bennet, F.; Taylor, I. D. *J. Chem. Soc., Perkin Trans. 1* **1986**, 815−821. (c) Izquierdo, I.; Plaza, M. T.; Robles, R.; Rodriguez, C. *Tetrahedron: Asymmetry* **1996**, *7*, 3593−3604. (d) DeNinno, M. P.; Danishefsky, S. J.; Schulte, G. *J. Am. Chem. Soc.* **1988**, *110*, 3925−3929. (e) Evans, D. A.; Kaldor, S. W. *J. Org. Chem.* **1990**, *55*, 1698−1670. (f) Annunziata, R.; Cinquini, M.; Cozzi, F.; Raimondi, L. *Tetrahedron* **1988**, *44*, 6897−6902. (e) Jorgensen, M.; Iversen, E. H.; Madsen, R. *J. Org. Chem.* **2001**, *68*, 4625−4629.

(28) In our preliminary studies on OsO_4/NMO dihydroxylation of TBDPS-protected analogues of **9**, **10**, **11**, and **12**, the diols were produced in ratios 90:10, 85:15, 30:70, and 40:60, respectively.

(29) Brimacombe, J. S.; McDonald, G.; Abdur Rahman, M. *Carbohydr. Res.* **1990**, *205*, 422−427.

SCHEME 3. Synthesis of l-Galactose19, L-Idose 21, L-Glucose 29, and L-Altrose 31[a]



[a] Key: (a) OsO_4, $(DHQD)_2PHAL$, $K_3Fe(CN)_6$, $MeSO_2NH_2$, *t*-BuOH/H_2O, 90%; (b) OsO_4, $(DHQ)_2PHAL$, $K_3Fe(CN)_6$, $MeSO_2NH_2$, *t*-BuOH/H_2O, 90%; (c) DMP, acetone; (d) DIBAL, toluene; (e) 80% acetic acid; (f) Ac_2O, Et_3N, DMAP, CH_2Cl_2; (g) H_2, Pd/C, EtOAc.

us to opt for the phthalazine ligands, $(DHQD)_2PHAL$ and $(DHQ)_2PHAL$, as the ligands of choice. In view of wide variety of steric and electronic factors involved in the reaction, each major diol product obtained during our studies was converted into corresponding sugar pentaacetate to confirm unequivocally its stereochemistry by comparing its ^{13}C NMR spectrum with the known data of the D-series.[31] Selectivities of dihydroxylation were determined by HPLC using pure diols as references.

L-Galactose, L-Idose, L-Glucose, and L-Altrose. Syntheses of these four hexoses were achieved by asymmetric dihydroxylation of (*E*)-unsaturated esters **9** and **10** using the "reinforced AD-mix" reagent formulations (6% OsO_4, 10% of the corresponding ligand, 3 equiv of $K_3Fe(CN)_6$, 3 equiv of K_2CO_3, 1 equiv of $MeSO_2NH_2$). When (*E*)-unsaturated ester **9** was dihydroxylated in the presence of the β-directing $(DHQD)_2PHAL$ ligand, the easily separable diols **13** (β-face attack product) and **14** (α-face attack product) were obtained in 99:1 ratio and in 90% yield (Scheme 3). As in the case of esters **1** and **2**, an appropriate protection of the free hydroxyls of **13** was needed for the next reduction step. From our earlier experience in the synthesis of 2-amino sugars[32] and L-sugars,[15] the selective monoprotection of one of the two newly formed hydroxy groups of diol esters was expected to be difficult in some cases.

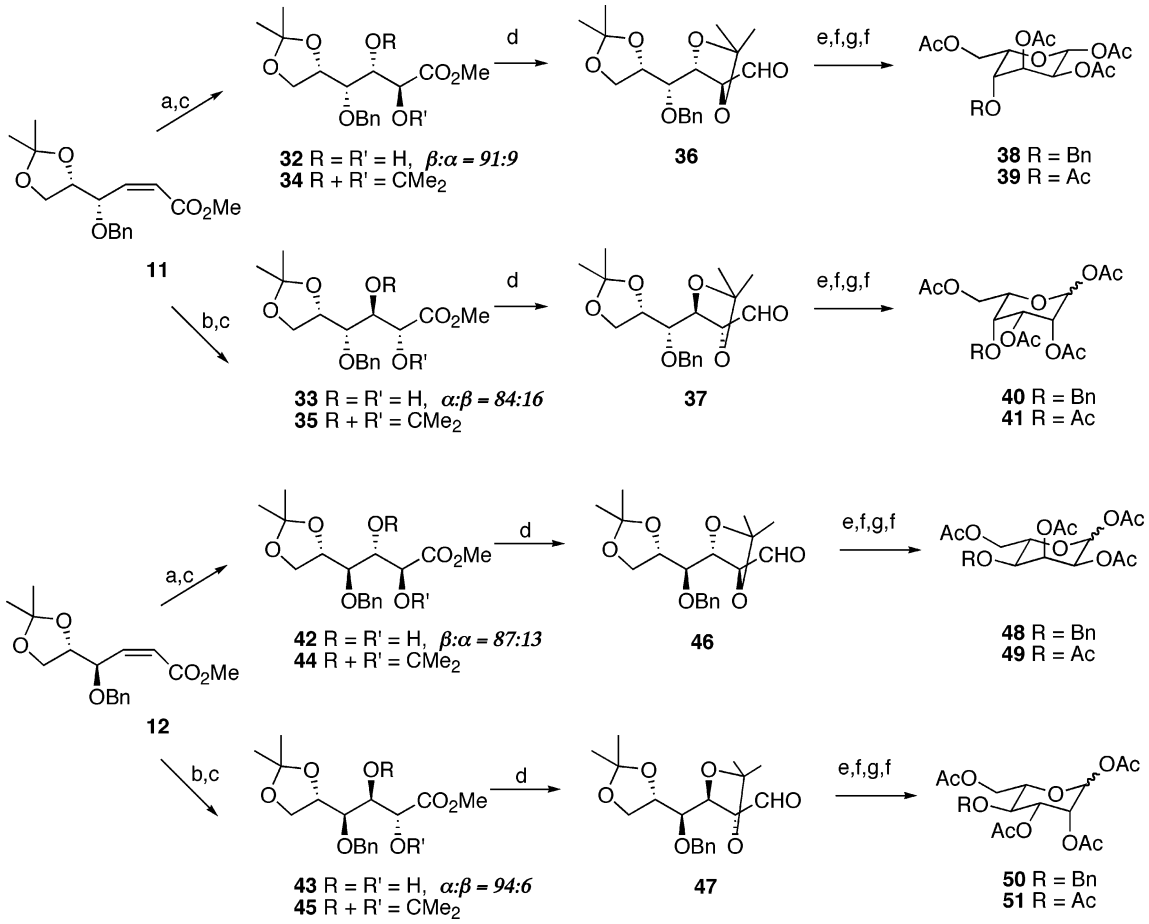
To keep results consistent along with all the series, we chose the isopropylidene protecting group which is stable to DIBAL reduction conditions. Accordingly, the diol **13** was converted into its acetonide **15** (2,2-dimethoxypropane, 3% of *p*-TsOH) in 95% yield after 6 h. The totally protected hydroxy ester **15** was reduced with DIBAL in toluene at −78 °C to give the aldehyde **17** in excellent yield (95%).[20] Although no over-reduction to the alcohol was observed, quenching of the reaction with methanol resulted in 30% of the corresponding dimethylacetal. Since both of these compounds were useful for our synthetic purpose, thus obtained crude product was subjected to cyclization without further purification. Hydrolysis of the product with Amberlite IR 120 in 1/1 dioxane−water followed by acetylation afforded the fully protected L-galactose **19** in 60% yield (three steps) as a mixture of α- and β-anomers in 22:78 ratio. Hydrogenolysis of the benzyl group in **19** followed by acetylation gave pentaacetate of L-galactose **20** in 95% yield (two steps). The ^{13}C NMR spectrum of **20** was proved identical

(30) (a) Wang, L.; Sharpless, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 7568−7570. (b) Xu, D.; Crispino, G. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 7570−7571. (c) Morikawa, K.; Sharpless K., B. *Tetrahedron Lett.* **1993**, *34*, 5575−5578. (d) Ziegler, F. E.; Wang, Y. *J. Org. Chem.* **1998**, *63*, 7920−7930. (e) Kim, N.-S.; Choi, J.-R.; Cha, J. K. *J. Org. Chem.* **1993**, *58*, 7096−7099. (f) Abdur Rahman, M.; Adams, J. P.; Boyes, A. L.; Kelly M. J.; Mansfield, D. J.; Procopiou, P. A.; Roberts, S. M.; Slee, D. H.; Sidebottom, P. J.; Sik, V.; Watson, N. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1841−1843.

(31) Bock, K.; Thogersen, H. *Annu. Rep. NMR Spectrosc.* **1982**, *13*, 1−57.

(32) Ermolenko, L.; Sasaki, N. A.; Potier, P. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2465−2473.

SCHEME 4. Synthesis of l-Gulose 38, L-Talose 40, L-Allose 48, and L-Mannose 50[a]



[a] Key: (a) OsO_4, $(DHQD)_2PHAL$, $K_3Fe(CN)_6$, $MeSO_2NH_2$, *t*-BuOH/H_2O, 90%; (b) OsO_4, $(DHQ)_2PHAL$, $K_3Fe(CN)_6$, $MeSO_2NH_2$, *t*-BuOH/H_2O, 90%; (c) DMP, acetone; (d) DIBAL, toluene; (e) 80% acetic acid; (f) Ac_2O, Et_3N, DMAP, CH_2Cl_2; (g) H_2, Pd/C, EtOAc.

to those published for the corresponding pentaacetates of D-galactose.[31]

The example of the *galacto*-isomer **13** was rather trivial since both the diastereofacial selectivity of the substrate **9** and the directing effect of the chiral ligand were matching. On the contrary, the *ido*-isomer **14** was not expected to be available in reasonable yield by ligand-free dihydroxylation of **9** (*see the note above*). However, to our delight, under the influence of the α-directing $(DHQ)_2PHAL$ ligand the direction of dihydroxylation was changed drastically to give diols **14** (α-face attack) and **13** (*β*-face attack) in 95:5 ratio and in 90% yield (Scheme 3). Conversion of the diol ester **14** into its acetonide **16** proceeded sluggishly (48 h, compared to 6 h required for **13**), but in 96% yield. The aldehyde **18** was obtained in 95% yield by reducing with DIBAL. Deprotection of both of the acetonide groups of aldehyde **18** in 1/1 dioxane−water in the presence of Amberlite IR 120 followed by acetylation led to the 1,2,3,6-*O*-teraacetyl-4-*O*-benzyl-L-idose **21** in 60% yield as a mixture of α- and *β*-anomers in ca. 4:6 ratio. Pentaacetate of L-idose **22** was obtained by hydrogenolysis of the benzyl ester **21** followed by acetylation in 95% yield (2 steps). The ^{13}C NMR spectrum of **22** was identical to that published for the pentaacetates of D-idose.[31]

L-Glucose and L-altrose are the epimers at C-4 of L-galactose and L-idose, respectively. The preparation of these hexoses was attained with high diastereoselectivity from the (*E*)-unsaturated ester **10** in the same synthetic sequence as described above. Thus, dihydroxylation of (*E*)-ester **10** in the presence of $(DHQD)_2PHAL$ ligand afforded diols in 55:1 ratio in favor of the *β*-diol **23** with gluco-configuration in 72% yield. Rewardingly, the use of α-directing $(DHQ)_2PHAL$ ligand gave predominantly the α-diol **24** with altro-configuration that was obtained virtually as a single isomer in 88% yield. Thus, the catalytic asymmetric dihydroxylation of our (*E*)-α,*β*-unsaturated esters **9** and **10** proceeded under the control of a chiral ligand and provided all four corresponding L-hexoses in high selectivity and in good overall yield.

It was noted that 2,3-*O*-isopropylidene protection of the diol **23** proceeded rapidly and in 90% yield as in case of the diol **13**. On the other hand, the diol **24** reacted sluggishly (exactly the same as for the diol **14**). The reduction of the fully protected hydroxy ester **25** and **26** was carried out at −78 °C with DIBAL in toluene to give the aldehydes **27** and **28**, respectively, in 95% yield in both cases. Acetonide deprotection of the aldehyde **27** in the presence of Amberlite IR 120 followed by acetylation afforded fully protected L-glucose **29** in 70% yield (two steps) as a mixture of α- and *β*-anomers in approximately 42:58 ratio. Pentaacetate of L-glucose **30** was obtained by hydrogenolysis of the benzyl group of **29** followed by acetylation in 95% yield (two steps). The same reaction sequence was applied to the aldehyde **28** to furnish pentaacetate of L-altrose **31** as a mixture (71:29) of α- and *β*-anomers. The ^{13}C NMR spectra of thus obtained pentaacetates match to the corresponding data known in the literature on the fingerprint level.[31]

L-Gulose, L-Talose, L-Allose, and L-Mannose. The structure of these four hexoses can be easily related to *cis*-dihydroxylation of the (*Z*)-enoates **11** and **12** (see Scheme 4). Unfortunately, little is known with certitude about the diastereofacial selectivity of this transformation, and its magnitude could not be predicted *a priori* as was mentioned above. Among a limited number of reports on osmylation of (*Z*)-conjugated carbonyl substrates, the 1,2-*syn* stereochemistry of dihydroxylation was found in accordance with the Kishi−Stork rule in most cases. Nevertheless, several authors have reported the 1,2-anti addition that presumably involves other factors. Taking into account that the Sharpless AD of (*Z*) olefins is less selective than that of (*E*) olefins, the catalytic asymmetric dihydroxylation of our (*Z*)-enoates **11** and **12** has been expected to be the most intriguing of the series. In the event, the dihydroxylation of unsaturated (*Z*)-ester **11** in the presence of $(DHQD)_2PHAL$ ligand afforded the mixture of the diol esters **32** and **33** in 91:9 ratio, while the dihydroxylation with α-directing ligand $(DHQ)_2PHAL$ proceeded less selective to give the diol **33** with a 84:16 diastereoselectivity.

Dihydroxylation of (*Z*)-unsaturated ester **12** followed the same direction regardless of the C-4 stereocenter. Thus, in the presence of $(DHQD)_2PHAL$ ligand, the dihydroxylation of **12** furnished in a 87:13 ratio the diols **42** and **43**. Similarly, the use of $(DHQ)_2PHAL$ provided the mixture of products in ratio 94:6 in favor of the diol **43**. These results clearly demonstrated that the asymmetric dihydroxylation of our α,*β*-unsaturated esters **9**−**12** proceeded under the total control of the chiral ligand used, regardless of the chirality of C-4 stereogenic center and double-bond configuration. As in the previous cases, the stereochemistry of these products was unequivocally proved by ^{13}C NMR spectroscopy of the corresponding pentaacetates of pyranoses that were obtained by the same reaction sequence described above. The acetonide protection of the diols **32**, **33**, **42**, and **43** proceeded in good yields but in different rates as for the diols **13**, **14**, **23**, and **24**. The reduction of these fully protected esters provided corresponding aldehydes without overreduction in high yield. Cyclization of *gulo*-aldehyde **36** with 80% acetic acid (24 h, rt) followed by acetylation afforded 1,2,3,6-*O*-tetraacetyl-4-*O*-benzyl-*β*-L-gulose **38** in 95% yield. Under the same conditions, the cyclization of *talo*-aldehyde **37** provided 1,2,3,6-*O*-tetraacetyl-4-*O*-benzyl-L-talose **40** in 75% yield as a mixture of α- and *β*-anomers in 5:1 ratio.

Deprotection of acetonide groups for *allo*-aldehyde **46** was accomplished in the presence of Amberlite IR 120. After subsequent acetylation, 1,2,3,6-*O*-tetraacetyl-4-*O*-benzyl-L-allose **48** was obtained as a mixture of α- and *β*-anomers in 1:2 ratio. The anomeric sugar derivatives **48a** and **48b** were easily separated by column chromatography and each of them was subjected to hydrogenolysis followed by acetylation to provide the pentaacetates of L-allose **49a** and **49b**, respectively, in good yield. Under the same conditions, 1,2,3,6-*O*-tetraacetyl-4-*O*-benzyl-L-mannose **50** was obtained as a mixture of α- and *β*-anomers in 3:1 ratio. The fully protected sugars **50a** and **50b** were easily separated by column chromatography and converted into the corresponding pentaacetates of L-mannose **51a** and **51b**.

Conclusion

We have developed a novel methodology for the highly selective synthesis of the diastereometrically pure L-hexoses. According to our strategy, any one of eight L-hexoses can be prepared in good overall yield from L-ascorbic acid. Appropriate selection of reagents in the Horner−Wittig−Emmons olefination and chiral ligand in subsequent dihydroxylation step is the key feature for the versatility of our new method.

Experimental Section

General Procedure for Preparation of Diols 13, 14, 23, 24, 32, 33, 42, and 43. To a well-stirred mixture of $(DHQD)_2PHAL$ or $(DHQ)_2PHAL$ (156 mg, 0.2 mmol), $K_3Fe(CN)_6$ (1.974 g, 6 mmol), K_2CO_3 (828 mg, 6 mmol), and $CH_3SO_2NH_2$ (190 mg, 2 mmol) in 1:1 *t*-BuOH−H_2O (24 mL) at 0 °C was added OsO_4 (1.2 mL of 0.1 M *t*-BuOH solution, 0.12 mmol). After 15 min, α,*β*-unsaturated ester (640 mg, 2 mmol) in *t*-BuOH (1 mL) was added over 15 min, and the mixture was stirred for another 36 h at 4 °C. Solid sodium sulfite (6 g) was added, and the mixture was stirred for 30 min at 4 °C and allowed to warm to room temperature. EtOAc was added, and the layers were separated. The aqueous layer was further extracted with EtOAc. The combined organic phases were washed successively with 2 M NaOH, H_2O, and brine and then dried, concentrated, and chromatographed with heptane-EtOAc (2:1) to afford a diol.

Ethyl (2*S*,3*S*,4*S*,5*S*)-4-*O*-benzyl-5,6-*O*-isopropylidene-2,3,4,5,6-pentahydroxyhexanoate (L-galacto-diol) 13 was prepared from **9** in the presence of $(DHQD)_2PHAL$ in 90% yield by the general procedure. **13** (colorless oil): $[\alpha]_D$ −15.9 (*c* 1.0); IR ($CHCl_3$) cm^{-1} 3446, 2983, 2935, 1731, 1497, 1454, 1369, 1269, 1240, 1212, 1113, 1058, 1028, 857; ^1H NMR 7.35 (m, 5H), 4.78, 4.68 (2d, J = 11.0 Hz, 2H), 4.48 (dd, J = 6.0, 1.5 Hz, 1H), 4.42 (m, 1H), 4.26 (m, 2H), 4.04 (m, 2H), 3.89 (dd, J = 8.5, 7.6 Hz, 1H), 3.67 (dd, J = 8.9, 5.1 Hz, 1H), 3.29 (d, J = 6.0 Hz, 1H), 2.87 (d, J = 7.3 Hz, 1H), 1.45 (s, 3H), 1.38 (s, 3H); 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR 173.6, 138.0, 127.9, 128.5, 128.1, 109.2, 77.8, 76.8, 74.6, 72.2, 70.5, 65.9, 62.1, 26.3, 25.3, 14.2; MS (ESI) *m*/*z* 377 $[M + Na]^+$; HRMS calcd for $C_{18}H_{26}O_7Na$ $[M + Na]^+$ 377.1576, found 377.1572.

Ethyl (2*R*,3*R*,4*S*,5*S*)-4-*O*-benzyl-5,6-*O*-isopropylidene-2,3,4,5,6-pentahydroxyhexanoate (L-ido-diol) 14 was prepared from **9** in the presence of $(DHQ)_2PHAL$ in 90% yield by the general procedure. **14** (colorless oil): $[\alpha]_D$ −18.4 (*c* 1.3); IR ($CHCl_3$) cm^{-1} 3547, 3024, 2988, 2938, 2907, 1735, 1686, 1654, 1560, 1456, 1383, 1373, 1227, 1205, 1156, 1118, 1071, 1028, 883, 854; ^1H NMR 7.36 (m, 5H), 4.85, 4.62 (2d, J = 11.0 Hz, 2H), 4.42 (dd, J = 12.8, 6.4 Hz, 1H), 4.30 (dd, J = 5.0, 3.0 Hz, 1H), 4.22−4.02 (m, 3H), 3.85 (dd, J = 7.9, 7.6 Hz, 1H), 3.70 (dd, J = 5.6, 4.4 Hz, 1H), 3.50 (d, J = 5.1 Hz, 1H), 2.95 (d, J = 8.4 Hz, 1H), 1.46 (s, 3H), 1.39 (s, 3H), 1.23 (t, J = 7.4 Hz, 3H); ^{13}C NMR 172.9, 137.9, 128.5, 128.3, 128.0, 109.6, 78.5, 76.3, 74.2, 71.6, 71.2, 65.9, 62.0, 26.5, 25.5, 14.1; MS (ESI) *m*/*z* 377 $[M + Na]^+$; HRMS calcd for $C_{18}H_{26}O_7Na$ $[M + Na]^+$ 377.1576, found 377.1569.

Ethyl (2*S*,3*S*,4*R*,5*S*)-4-*O*-benzyl-5,6-*O*-isopropylidene-2,3,4,5,6-pentahydroxyhexanoate (L-gluco-diol) 23 was prepared from **10** in the presence of $(DHQD)_2PHAL$ in 70% yield by the general procedure. **23** (colorless oil): $[\alpha]_D$ −15.0 (*c* 2.30); IR ($CHCl_3$) cm^{-1} 3531, 3027, 3015, 2990, 2938, 2892, 1733, 1603, 1497, 1455, 1383, 1373, 1248, 1228, 1205, 1158, 1122, 1074, 1028, 915, 854; ^1H NMR 7.34 (m, 5H), 4.80, 4.68 (2d, J = 11.0 Hz, 2H), 4.35 (m, 2H), 4.22−3.92 (m, 5H), 3.82 (dd, J = 5.6, 4.3 Hz, 1H), 3.40 (d, J = 5.9 Hz, 1H), 3.20 (d, J = 8.8 Hz, 1H), 1.44 (s, 3H), 1.37 (s, 3H), 1.24 (t, J = 7.0 Hz, 3H); ^{13}C NMR 173.2, 137.8, 128.5, 128.1, 128.0, 109.0, 78.3, 76.9, 74.3, 72.3, 71.0, 66.3, 62.0, 26.6, 25.2, 14.1; MS (ESI) *m*/*z* 377 $[M + Na]^+$; HRMS calcd for $C_{18}H_{26}O_7Na$ $[M + Na]^+$ 377.1576, found 377.1568.

Ethyl (2*R*,3*R*,4*R*,5*S*)-4-*O*-benzyl-5,6-*O*-isopropylidene-2,3,4,5,6-pentahydroxyhexanoate (L-altro-diol) 24 was prepared from **10** in the presence of $(DHQ)_2PHAL$ in 88% yield by the general procedure. **24** (colorless oil): $[\alpha]_D$ −7.5 (*c* 1.20); IR ($CHCl_3$) cm^{-1} 3458, 2990, 2986, 2936, 1736, 1498, 1455, 1382, 1372, 1238, 1217, 1140, 1118, 1066, 962, 859, 754, 699; ^1H NMR 7.40 (m, 5H), 4.79, 4.72 (2d, J = 11.1 Hz, 2H), 4.42 (d, J = 6.3 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 4.11 (dd, J = 8.2, 6.5 Hz, 1H), 3.95 (m, 2H), 3.75 (dd, J = 8.6, 6.3 Hz, 1H), 3.52 (d, J = 6.6 Hz, 1H), 3.35 (d, J =

6.4 Hz, 1H), 1.45 (s, 3H), 1.37 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR 173.5, 138.0, 128.6, 128.1, 128.0, 109.4, 77.8, 77.6, 74.7, 74.0, 70.5, 66.3, 62.1, 26.5, 25.3, 14.2; MS (ESI) *m*/*z* 377 [M + Na]$^+$; HRMS calcd for $C_{18}H_{26}O_7Na$ [M + Na]$^+$ 377.1576, found 377.1608.

Methyl (2*S*,3*R*,4*S*,5*S*)-4-*O*-benzyl-5,6-*O*-isopropylidene-2,3,4,5,6-pentahydroxyhexanoate (L-gulo-diol) 32 was prepared from **11** in the presence of $(DHQD)_2PHAL$ in 70% yield by the general procedure. **32** (colorless oil): $[\alpha]_D$ −9.0 (*c* 1.3); IR ($CHCl_3$) cm^{-1} 3547, 3023, 2990, 2955, 2937, 1734, 1497, 1455, 1440, 1382, 1372, 1230, 1156, 1109, 1076, 1028, 986, 849; ^{1}H NMR 7.37 (m, 5H), 4.85, 4.62 (2d, J = 11.2 Hz, 2H), 4.42 (dd, J = 13.1, 6.4 Hz, 1H), 4.22 (dd, J = 8.5, 6.5 Hz, 1H), 4.05 (dd, J = 8.3, 6.5 Hz, 1H), 3.65 (dd, J = 6.3, 2.4 Hz, 1H), 3.73 (s, 3H), 3.38 (d, J = 8.5 Hz, 1H), 3.05 (d, J = 9.0 Hz, 1H), 1.44 (s, 3H), 1.38 (s, 3H); ^{13}C NMR 173.4, 137.9, 128.6, 128.4, 128.1, 109.8, 78.7, 76.8, 74.2, 72.4, 72.1, 66.0, 52.6, 26.6, 25.7; MS (ESI) *m*/*z* 363 [M + Na]$^+$; HRMS calcd for $C_{17}H_{24}O_7Na$ [M + Na]$^+$ 363.1420, found 363.1408.

Methyl (2*R*,3*S*,4*S*,5*S*)-4-*O*-benzyl-5,6-*O*-isopropylidene-2,3,4,5,6-pentahydroxyhexanoate (L-talo-diol) 33 was prepared from **11** in the presence of $(DHQ)_2PHAL$ in 76% yield by the general procedure. **33** (colorless oil): $[\alpha]_D$ −26.9 (*c* 1.1); IR ($CHCl_3$) cm^{-1} 3522, 3031, 3015, 2991, 2955, 2935, 1734, 1496, 1455, 1442, 1382, 1372, 1228, 1203, 1157, 1071, 983, 917, 898, 853; ^{1}H NMR 7.32 (m, 5H), 4.75, 4.55 (2d, J = 10.7 Hz, 2H), 4.42−4.30 (m, 2H), 4.11−4.05 (m, 2H), 3.85 (dd, J = 8.6, 7.6 Hz, 1H), 3.75 (dd, J = 8.6, 5.9 Hz, 1H), 3.58 (d, J = 4.8 Hz, 1H), 3.55 (s, 3H), 3.35 (d, J = 6.1 Hz, 1H), 1.45 (s, 3H), 1.37 (s, 3H); ^{13}C NMR 172.7, 138.0, 128.5, 128.4, 127.9, 109.1, 77.6, 77.5, 74.0, 73.4, 72.1, 66.3, 52.4, 26.4, 25.3; MS (ESI) *m*/*z* 363 [M + Na]$^+$; HRMS calcd for $C_{17}H_{24}O_7Na$ [M + Na]$^+$ 363.1420, found 363.1413.

Methyl (2*S*,3*R*,4*R*,5*S*)-4-*O*-benzyl-5,6-*O*-isopropylidene-2,3,4,5,6-pentahydroxyhexanoate (L-allo-diol) 42 was prepared from **12** in the presence of $(DHQD)_2PHAL$ in 90% yield by the general procedure. **42** (colorless oil): $[\alpha]_D$ −6.1 (*c* 1.2); IR ($CHCl_3$) cm^{-1}: 3523, 3025, 3015, 2989, 2937, 1729, 1454, 1440, 1383, 1374, 1349, 1226, 1200, 1137, 1098, 1067, 1028, 909, 856, 799; ^{1}H NMR 7.32 (m, 5H), 4.75, 4.55 (2d, J = 11.0 Hz, 2H), 4.45 (m, 2H), 4.10 (m, 1H), 3.95 (m, 2H), 3.80 (m, 1H), 3.55 (s, 3H), 3.40 (d, J = 5.5 Hz, 1H), 3.05 (d, J = 6.4 Hz, 1H), 1.43 (s, 3H), 1.37 (s, 3H); ^{13}C NMR 172.7, 137.9, 128.4, 128.2, 127.9, 109.5, 77.3, 76.5, 74.0, 73.7, 71.9, 65.9, 52.5, 26.5, 25.1; MS (ESI) *m*/*z* 363 [M + Na]$^+$; HRMS calcd for $C_{17}H_{24}O_7Na$ [M + Na]$^+$ 363.1420, found 363.1432.

Methyl (2*R*,3*S*,4*R*,5*S*)-4-*O*-benzyl-5,6-*O*-isopropylidene-2,3,4,5,6-pentahydroxyhexanoate (L-manno-diol) 43 was prepared from **12** in the presence of $(DHQ)_2PHAL$ in 65% yield by the general procedure. **43** (colorless oil): $[\alpha]_D$ −15.3 (*c* 1.6); IR ($CHCl_3$) cm^{-1} 3546, 3024, 3015, 2991, 2957, 2934, 2892, 1737, 1497, 1455, 1440, 1383, 1373, 1224, 1158, 1074, 1028, 977, 909, 878, 850; ^{1}H NMR 7.34 (m, 5H), 4.80, 4.65 (2d, J = 11.0 Hz, 2H), 4.27 (m, 2H), 4.10 (dd, J = 8.4, 6.4 Hz, 1H), 3.98−3.82 (m, 3H), 3.74 (s, 3H), 3.02 (d, J = 7.6 Hz, 1H), 2.82 (d, J 8.9 Hz, 1H), 1.42 (s, 3H), 1.25 (s, 3H); ^{13}C NMR 173.6, 137.7, 128.5, 128.2, 128.1, 108.7, 78.0, 76.9, 74.7, 72.4, 72.2, 66.0, 52.5, 26.6, 25.1; MS (ESI) *m*/*z* 379 [M + K]$^+$, 363 [M + Na]$^+$; HRMS calcd for $C_{17}H_{24}O_7Na$ [M + Na]$^+$ 363.1420, found 363.1424.

General Procedure for the Preparation of Acetonides 15, 16, 25, 26, 34, 35, 44, and 45. To a solution of the diol in acetone (1 mmol/mL) were added 2,2-dimethoxypropane (2 mmol) and *p*-TSA (6 mg, 3% mol). The reaction mixture was stirred at room temperature for the time indicated in each case. Upon completion of the reaction, triethylamine was added to neutralize the reaction mixture, acetone was evaporated, and the residue was purified by flash chromatography in heptane−EtOAc (4:1) to afford the corresponding acetonide.

Ethyl (2*S*,3*R*,4*R*,5*S*)-2,3;5,6-di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanoate (L-galacto-acetonide) 15 was prepared from **13** by the general procedure. The reaction came to completion in 6 h to afford the acetonide in 95% yield. **15** (colorless oil): $[\alpha]_D$ +15.0 (*c* 2.5); IR ($CHCl_3$) cm^{-1} 2986, 2936, 1744, 1454, 1383, 1370, 1350, 1254, 1211, 1161, 1083, 1054, 904, 862; ^{1}H NMR 7.33 (m, 5H), 4.83 (s, 2H), 4.62 (d, J = 6.8 Hz, 1H), 4.37 (dd, J = 6.8, 4.0 Hz, 1H), 4.25−4.10 (m, 3H), 4.02 (dd, J = 8.5, 6.4 Hz, 1H), 3.78 (dd, J = 8.3, 7.4 Hz, 1H), 3.68 (dd, J = 6.4, 4.0 Hz, 1H), 1.46 (s, 3H), 1.41 (s, 3H), 1.34 (s, 3H), 1.26 (t, J = 7.4 Hz, 3H); ^{13}C NMR 171.0, 138.3, 128.3, 127.9, 127.6, 111.0, 109.3, 79.9, 79.0, 77.3, 75.9, 74.7, 66.0, 61.4, 26.8, 26.3, 25.7, 25.6, 14.1; *m*/*z* 417 [M + Na]$^+$; HRMS calcd for $C_{21}H_{30}O_7Na$ [M + Na]$^+$ 417.1889, found 417.1873.

Ethyl (2*R*,3*S*,4*R*,5*S*)-2,3;5,6-di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanoate (L-ido-acetonide) 16 was obtained from **14** for 48 h in 96% yield. **16** (colorless oil): $[\alpha]_D$ −48.3 (*c* 1.10); IR ($CHCl_3$) cm^{-1} 3020, 3011, 2991, 2939, 1750, 1602, 1497, 1455, 1383, 1373, 1350, 1301, 1249, 1213, 1205, 1159, 1103, 1028, 980, 901, 857; ^{1}H NMR 7.37 (m, 5H), 4.95, 4.75 (2d, J = 11.8 Hz, 2H), 4.54 (d, J = 7.4 Hz, 1H), 4.42 (dd, J = 14.0, 7.0 Hz, 1H), 4.20 (m, 3H), 4.08 (dd, J = 8.1, 6.6 Hz, 1H), 3.78 (t, J = 8.1 Hz, 1H), 3.65 (dd, J = 7.4, 3.0 Hz, 1H), 1.48 (s, 3H), 1.46 (s, 3H), 1.42 (s, 3H), 1.39 (s, 3H), 1.26 (t, J = 7.4 Hz, 3H); ^{13}C NMR 170.7, 138.3, 128.4, 128.2, 127.8, 111.6, 109.5, 78.8, 77.6, 76.9, 75.3, 74.0, 66.3, 61.5, 26.7 (two carbons), 26.0, 25.7, 14.2; MS (ESI) *m*/*z* 417 [M + Na]$^+$; HRMS calcd for $C_{21}H_{30}O_7Na$ [M + Na]$^+$ 417.1889, found 417.1906.

Ethyl (2*S*,3*R*,4*S*,5*S*)-2,3;5,6-di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanoate (L-gluco-acetonide) 25 was obtained from **23** for 6 h in 95% yield. **25** (colorless oil): $[\alpha]_D$ +9.2 (*c* 1.44); IR ($CHCl_3$) cm^{-1} 3032, 2991, 2939, 2905, 1752, 1586, 1497, 1455,1383, 1373, 1352, 1244, 1226, 1203, 1159, 1075, 1053, 1028, 988, 908, 857, 824; ^{1}H NMR 7.35 (m, 5H), 4.88, 4.72 (2d, J = 11.8 Hz, 2H), 4.50 (d, J = 7.4 Hz, 1H), 4.30 (m, 2H), 4.21 (q, J = 7.4 Hz, 2H), 4.02 (m, 2H), 3.80 (dd, J = 4.4, 3.7 Hz, 1H), 1.45 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H), 1.28 (t, J = 7.0 Hz, 3H); ^{13}C NMR 170.5, 138.1, 128.4, 127.9, 127.8, 111.2, 108.7, 79.8, 77.5, 77.0, 75.2, 75.0, 66.0, 61.4, 26.6 (two carbons), 26.1, 25.3, 14.2; MS (ESI) *m*/*z* 417 [M + Na]$^+$; HRMS calcd for $C_{21}H_{30}O_7Na$ 417.1889, found 417.1859.

Ethyl (2*R*,3*S*,4*S*,5*S*)-2,3;5,6-di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanoate (L-altro-acetonide) 26 was obtained from **24** for 24 h in 78% yield. **26** (colorless oil): $[\alpha]_D$ −41.9 (*c* 1.70); IR ($CHCl_3$) cm^{-1} 2988, 2937, 1756, 1497, 1455, 1381, 1259, 1211, 1164, 1140, 1078, 925, 856, 809, 738, 699; ^{1}H NMR 7.34 (m, 5H), 4.85, 4.70 (2d, J = 11.7 Hz, 2H), 4.64 (d, J = 6.8 Hz, 1H), 4.48 (dd, J = 7.4, 2.9 Hz, 1H), 4.20 (m, 3H), 4.05 (dd, J = 8.8, 5.9 Hz, 1H), 3.85 (m, 2H), 1.50 (s, 3H), 1.44 (s, 3H), 1.41(s, 3H), 1.32 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR 171.2, 137.9, 128.3, 127.8, 127.7, 111.1, 109.1 79.8, 78.5, 74.9, 74.7, 74.5, 66.7, 61.3, 26.7, 26.5, 25.2, 25.1, 14.0; MS (ESI) *m*/*z* 417 [M + Na]$^+$; HRMS calcd for $C_{21}H_{30}O_7Na$ [M + Na]$^+$ 417.1889, found 417.1862.

Methyl (2*S*,3*S*,4*R*,5*S*)-2,3;5,6-di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanoate (L-gulo-acetonide) 34 was obtained from **32** for 48 h in 94% yield. **34** (colorless oil): $[\alpha]_D$ −30.4 (*c* 1.20); IR ($CHCl_3$) cm^{-1} 3030, 3018, 2990, 2937, 1727, 1497, 1454, 1439, 1382, 1373, 1245, 1229, 1083, 1072, 983, 887, 851; ^{1}H NMR 7.34 (m, 5H), 4.95 (d, J = 12.1 Hz, 1H), 4.70 (d, J = 7.4 Hz, 1H), 4.52−4.34 (m, 3H), 4.05 (dd, J = 8.1, 6.4 Hz, 1H), 3.82 (t, J = 8.1 Hz, 1H), 3.73 (dd, J = 6.4, 3.7 Hz, 1H), 3.46 (s, 3H), 1.63 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H); ^{13}C NMR 170.4, 138.7, 128.1, 127.1, 126.8, 110.9, 109.5, 78.1, 77.1 (two carbons), 75.3, 72.6, 66.1, 51.9, 26.6, 26.5, 25.7, 25.5; MS (ESI) *m*/*z* 403 [M + Na]$^+$; HRMS calcd for $C_{20}H_{28}O_7Na$ [M + Na]$^+$ 403.1733, found 403.1719.

Methyl (2*R*,3*R*,4*R*,5*S*)-2,3;5,6-di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanoate (L-talo-acetonide) 35 was obtained from **33** for 14 h in 90% yield. **35** (colorless oil): $[\alpha]_D$ −29.4 (*c* 1.60); IR ($CHCl_3$) cm^{-1} 3027, 3017, 2990, 2953, 2938, 2858, 1750, 1497, 1455, 1438, 1382, 1372, 1228, 1203, 1183, 1159,

1131, 1092, 1072, 1030, 966, 911, 869; ^{1}H NMR 7.35 (m, 5H), 5.00 (d, J = 11.0 Hz, 1H), 4.69 (d, J = 5.9 Hz, 1H), 4.44 (d, J = 11.0 Hz, 1H), 4.28 (m, 2H), 4.05 (dd, J = 8.8, 5.9 Hz, 1H), 3.82 (dd, J = 8.8, 7.8 Hz, 1H), 3.65 (dd, J = 7.8, 6.8 Hz, 1H), 3.49 (s, 3H), 1.59 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H); ^{13}C NMR 170.1, 138.5, 128.3, 127.6, 127.5, 111.0, 108.9, 79.0, 78.1, 76.1, 73.6, 66.8, 51.9, 27.0, 26.6, 25.8, 25.6; MS (ESI) *m*/*z* 403 [M + Na]$^+$; HRMS calcd for $C_{20}H_{28}O_7Na$ [M + Na]$^+$ 403.1733, found 403.1718.

Methyl (2*S*,3*S*,4*S*,5*S*)-2,3;5,6-di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanoate (L-allo-acetonide) 44 was obtained from **42** for 6 h in 95% yield. **44** (colorless oil): $[\alpha]_D$ −13.6 (*c* 2.0); IR ($CHCl_3$) cm^{-1} 3067, 3029, 3012, 2989, 2939, 2891, 1750, 1497, 1455, 1382, 1374, 1348, 1226, 1205, 1160, 1138, 1089, 1030, 969, 918, 856; ^{1}H NMR 7.33 (m, 5H), 4.75, 4.65 (2d, J = 11.1 Hz, 2H), 4.68 (d, J = 6.8 Hz, 1H), 4.47 (dd, J = 6.6, 4.7 Hz, 1H), 4.35 (dd, J = 12.6, 6.2 Hz, 1H), 4.04 (dd, J = 8.3, 6.4 Hz, 1H), 3.92 (m, 2H), 3.45 (s, 3H), 1.69 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H); ^{13}C NMR 170.8, 138.1, 128.3, 128.1, 127.7, 110.6, 109.5, 79.2, 77.1, 75.6, 75.0, 74.9, 66.4, 52.0, 27.0, 26.8, 25.6, 25.3; MS (ESI) *m*/*z* 403 [M + Na]$^+$; HRMS calcd for $C_{20}H_{28}O_7Na$ [M + Na]$^+$ 403.1733, found 403.1724.

Methyl (2*R*,3*R*,4*S*,5*S*)-2,3;5,6-di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanoate (L-manno-acetonide) 45 was obtained from **43** for 24 h in 77% yield. **45** (colorless oil): $[\alpha]_D$ +8.5 (*c* 1.3); IR ($CHCl_3$) cm^{-1} 3030, 2991, 2938, 2905, 1731, 1455, 1440,1383, 1373, 1223, 1208, 1159, 1069, 851; ^{1}H NMR 7.32 (m, 5H), 4.90, 4.45 (2d, J = 11.7 Hz, 2H), 4.72 (d, J = 7.4 Hz, 1H), 4.52 (dd, J = 7.4, 3.3 Hz, 1H), 4.27 (m, 1H), 4.10−3.96 (m, 3H), 3.47 (s, 3H), 1.57 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H); ^{13}C NMR 170.1, 138.5, 128.2, 127.2, 126.8, 110.6, 108.4, 79.1, 77.4, 76.4, 75.3, 73.2, 66.1, 51.9, 26.4 (two carbons), 25.5, 25.1; MS (ESI) *m*/*z* 403 [M + Na]$^+$; HRMS calcd for $C_{20}H_{28}O_7Na$ [M + Na]$^+$ 403.1733, found 403.1723.

General Procedure for the Reduction of Esters in Aldehydes. To a solution of ester in toluene (1 mmol/ 7 mL) at −78 °C was added DIBAL (1.5 mmol, 1 mL of 1.5 M solution in toluene). The reaction mixture was stirred for 1 h at −78 °C and quenched with 1 mL of methanol, and the solution was slowly warmed to room temperature. A sodium potassium tartrate saturated solution (0.2 mL), 0.4 mL of brine, and EtOAc (20 mL) were added with $MgSO_4$ (1 g), and the mixture was stirred for 1 h. The solids were removed by filtration, filtrate and washings were concentrated, and the residue was purified by flash chromatography (heptane−EtOAc 2:1) to afford the corresponding aldehyde.

(2*S*,3*R*,4*R*,5*S*)-2,3;5,6-Di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanal (L-galacto-aldehyde) 17 was prepared from **15** by the general procedure in 95% yield and subjected to cyclization without further purification. The analytical simple was obtained by flash chromatography (heptane−EtOAc 2:1). **17** (colorless oil): $[\alpha]_D$ −14.1 (*c* 2.0); IR ($CHCl_3$) cm^{-1} 2986, 2935, 1735, 1497, 1454, 1383, 1370, 1252, 1210, 1157, 1064, 905, 860; ^{1}H NMR 9.70 (d, J = 1.2 Hz, 1H), 7.36 (m, 5H), 4.86, 4.81 (2d, J = 11.4 Hz, 2H), 4.55 (dd, J = 6.8, 1.2 Hz, 1H), 4.20−4.15 (m, 2H), 4.05 (dd, J = 8.3, 6.4 Hz, 1H), 3.78 (dd, J = 6.0, 4.5, Hz, 1H), 1.47 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H); ^{13}C NMR 200.1, 138.0, 128.4, 128.15, 127.8, 111.0, 109.4, 81.6, 79.0, 77.9, 77.6, 74.7, 66.1, 26.6, 26.4, 25.8, 25.7; MS (ESI) *m*/*z* 373 [M + Na]$^+$; HRMS calcd for $C_{19}H_{26}O_6Na$ [M + Na]$^+$ 373.1627, found 373.1611.

(2*R*,3*S*,4*R*,5*S*)-2,3;5,6-Di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanal (L-ido-aldehyde) 18 was prepared from **16** by general procedure in 95% yield and subjected to cyclization without further purification. **18** (colorless oil): $[\alpha]_D$ −18.7 (*c* 2.0); IR ($CHCl_3$) cm^{-1} 3410, 2986, 2935, 1731, 1454, 1371, 1247, 1216, 1128, 1067, 1027, 855; ^{1}H NMR 9.70 (d, J = 1.5 Hz, 1H), 7.36 (m, 5H), 4.89, 4.72 (2d, J = 11.7 Hz, 2H), 4.42−4.32 (m, 2H), 4.15 (dd, J = 7.4, 3.7 Hz, 2H), 4.04 (dd, J = 8.2, 6.4 Hz, 1H), 3.78 (t, J = 8.0, Hz, 1H), 3.58 (dd, J = 6.4, 3.7 Hz, 1H), 1.48 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H); ^{13}C NMR 200.6, 138.0, 128.4, 128.1, 127.8, 111.6, 109.4, 81.1, 77.5, 76.8, 76.4, 74.0, 66.2, 26.6, 26.5, 26.2, 25.6; MS (ESI) *m*/*z* 373 [M + Na]$^+$; HRMS calcd for $C_{19}H_{26}O_6Na$ [M + Na]$^+$ 373.1627, found 373.1599.

(2*S*,3*R*,4*S*,5*S*)-2,3;5,6-Di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanal (L-gluco-aldehyde) 27 was prepared from **25** by the general procedure and purified by flash chromatography (heptane−EtOAc 1:1), yield 90%. **27** (colorless oil): $[\alpha]_D$ −4.7 (*c* 1.1); IR ($CHCl_3$) cm^{-1} 3028, 3012, 2989, 2937, 2899, 1732, 1455, 1383, 1373, 1243, 1229, 1159, 1072, 908, 857; ^{1}H NMR 9.76 (d, J = 1.4 Hz, 1H), 7.39 (m, 5H), 4.84, 4.72 (2d, J = 11.7 Hz, 2H), 4.32 (dd, J = 7.4, 1.4 Hz, 1H), 4.20−4.15 (m, 2H), 4.08 (dd, J = 8.5, 6.3 Hz, 1H), 3.95 (dd, J = 8.5, 6.8 Hz, 1H), 3.65 (dd, J = 5.3, 4.2 Hz, 1H), 1.46 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H); ^{13}C NMR 200.7, 137.5, 128.1, 128.0, 127.5, 110.9, 108.6, 80.4, 77.8, 76.3, 74.6, 65.8, 26.2, 26.1, 26.0, 24.9; MS (ESI) *m*/*z* 373 [M + Na]$^+$; HRMS calcd for $C_{19}H_{26}O_6Na$ [M + Na]$^+$ 373.1627, found 373.1604.

(2*R*,3*S*,4*S*,5*S*)-2,3;5,6-Di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanal (L-altro-aldehyde) 28 was prepared from **26** in 78% yield by the general procedure and purified by flash chromatography (heptane−EtOAc 2:1). **28** (colorless oil): $[\alpha]_D$ −22.9 (*c* 0.9); IR ($CHCl_3$) cm^{-1} 2990, 2938, 1735, 1497, 1455, 1383, 1374, 1247, 1220, 1210, 1161, 1076, 912, 860; ^{1}H NMR 9.73 (d, J = 2.0 Hz, 1H), 7.34 (m, 5H); 4.85, 4.72 (2d, J = 11.0 Hz, 2H), 4.47 (dd, J = 7.3, 2.0 Hz, 1H), 4.33 (dd, J = 7.3, 3.5 Hz, 1H), 4.15 (dd, J = 12.7, 6.3 Hz, 1H), 4.05 (dd, J = 8.1, 6.3 Hz, 1H), 3.85 (m, 2H), 1.52 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H); ^{13}C NMR 200.6, 137.8, 128.5, 128.1, 128.0, 111.3, 109.5, 81.0, 78.3, 77.7, 75.0, 74.8, 66.7, 26.8, 26.7, 25.8, 25.2; MS (ESI) *m*/*z* 373 [M + Na]$^+$; HRMS calcd for $C_{19}H_{26}O_6Na$ [M + Na]$^+$ 373.1627, found 373.1616.

(2*S*,3*S*,4*R*,5*S*)-2,3;5,6-Di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanal (L-gulo-aldehyde) 36 was prepared from **34** by general procedure in 94% yield and purified by flash chromatography (heptane−EtOAc 1:1). **36** (colorless oil): $[\alpha]_D$ −60.3 (*c* 1.3); IR ($CHCl_3$) cm^{-1} 3029, 2990, 2937, 2875, 1724, 1498, 1455, 1383, 1373, 1247, 1221, 1205, 1160, 1132, 1087, 988, 896, 845; ^{1}H NMR 9.52 (d, J = 2 Hz, 1H), 7.34 (m, 5H), 4.95 (d, J = 11.5 Hz, 1H), 4.45 (m, 2H), 4.34 (dd, J = 8.0, 2.0 Hz, 1H), 4.25 (d, J = 11.5 Hz, 1H), 4.09 (dd, J = 8.1, 6.2 Hz, 1H), 3.77(t, J = 8.1 Hz, 1H), 3.44 (dd, J = 7.2, 2.3 Hz, 1H), 1.59 (s, 3H), 1.43 (s, 3H), 1.36 (s, 6H); ^{13}C NMR 201.7, 138.3, 128.2, 127.3, 127.2, 111.4, 109.6, 80.7, 80.3, 77.3, 76.9, 72.2, 66.2, 26.7, 26.6, 25.8, 25.1; MS (ESI) *m*/*z* 373 [M + Na]$^+$; HRMS calcd for $C_{19}H_{26}O_6Na$ [M + Na]$^+$ 373.1627, found 373.1604.

(2*R*,3*R*,4*R*,5*S*)-2,3;5,6-Di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanal (L-talo-aldehyde) 37 was prepared from **35** by the general procedure in 90% yield and purified by flash chromatography (heptane−EtOAc 2:1). **37** (colorless oil): $[\alpha]_D$ −54.0 (*c* 1.50); IR ($CHCl_3$) cm^{-1} 3026, 2990, 2938, 2891, 1730, 1455, 1382, 1374, 1243, 1228, 1158, 1088, 1070, 1028, 911, 866; ^{1}H NMR 9.68 (s, 1H), 7.33 (m, 5H), 4.70−4.60 (m, 3H), 4.52 (dd, J = 7.0, 4.3 Hz, 1H), 4.20 (ddd, J = 12.0, 7.8, 4.3 Hz, 1H), 4.00 (dd, J = 7.8, 6.6 Hz, 1H), 3.85−3.75 (m, 2H), 1.64 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H); ^{13}C NMR 197.5, 137.5, 128.5, 128.0, 110.0, 109.7, 81.6, 81.2, 77.4, 76.2, 74.0, 66.0, 27.2, 26.3, 25.8, 25.4; MS (ESI) *m*/*z* 373 [M + Na]$^+$; HRMS calcd for $C_{19}H_{26}O_6Na$ [M + Na]$^+$ 373.1627, found 373.1624.

(2*S*,3*S*,4*S*,5*S*)-2,3;5,6-Di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanal (L-allo-aldehyde) 46 was prepared from **44** by general procedure in 70% yield and purified by flash chromatography (heptane−EtOAc 2:1). **46** (colorless oil): $[\alpha]_D$ −4.8 (*c* 1.3); IR ($CHCl_3$) cm^{-1} 3025, 3020, 2990, 2937, 2890, 1728, 1602, 1497, 1454, 1383, 1374, 1348, 1264, 1245, 1161, 1137, 1074, 1027, 985, 909, 856; ^{1}H NMR 9.61 (d, J = 2.3 Hz, 1H), 7.31 (m, 5H), 4.73 (s, 2H), 4.60 (dd, J = 7.2, 3.7 Hz, 1H), 4.52 (dd, J = 7.2, 2.3 Hz, 1H), 4.20 (dd, J = 12.5, 6.6 Hz, 1H), 4.00 (dd, J = 8.1, 6.6 Hz, 1H), 3.85 (dd, J = 6.9, 3.7 Hz, 1H), 3.78 (dd, J = 8.1, 5.9 Hz,

1H), 1.65 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H); ^{13}C NMR 198.5, 137.5, 128.5, 128.1, 128.0, 110.3, 109.7, 80.9 (two carbons), 77.7, 75.2, 74.7, 66.7, 27.3, 26.7, 25.1, 24.9; MS (ESI) *m/z* 373 $[M + Na]^+$; HRMS calcd for $C_{19}H_{26}O_6Na$ $[M + Na]^+$ 373.1627, found 373.1616.

(2*R*,3*R*,4*S*,5*S*)-2,3;5,6-Di(*O*-isopropylidene)-4-*O*-benzyl-2,3,4,5,6-pentahydroxyhexanal (L-manno-aldehyde) 47 was prepared from **45** by general procedure in 70% yield and purified by flash chromatography (heptane−EtOAc 2:1). **47** (colorless oil): $[\alpha]_D$ +23.5 (*c* 1.2); IR ($CHCl_3$) cm^{-1}: 3019, 2990, 2937, 1724, 1497, 1455, 1383, 1374, 1224, 1208, 1158, 1146, 1079, 1059, 905, 847; ^{1}H NMR 9.52 (d, *J* = 1.9 Hz, 1H), 7.31 (m, 5H), 4.93 (d, *J* = 11.3 Hz, 1H), 4.57 (dd, *J* = 8.1, 5.8 Hz, 1H), 4.38 (dd, *J* = 8.1, 6.2 Hz, 1H), 4.31 (ddd, *J* = 10.0, 7.2, 3.0 Hz, 1H), 4.25 (d, *J* = 11.3 Hz, 1H), 3.83 (dd, *J* = 2.8 Hz, 1H), 1.54 (s, 3H), 1.40 (s, 3H), 1.35 (s, 6H); ^{13}C NMR 201.8, 138.1, 128.4, 128.3, 127.5, 127.2, 111.1, 108.2, 81.9, 80.2, 77.4, 75.2, 72.8, 65.7, 26.5, 26.4, 25.2, 24.9; MS (ESI) *m/z* 373 $[M + Na]^+$; HRMS calcd for $C_{19}H_{26}O_6Na$ $[M + Na]^+$ 373.1627, found 373. 1603.

General Procedure for the Cyclization of Aldehydes to Fully Protected Sugars. (A) Aldehyde **(**1 mmol) was dissolved in 80% acetic acid (15 mL). The reaction mixture was stirred at the temperature and for the time indicated in each case. Upon completion of the reaction, the mixture was evaporated with toluene. To a solution of the residue in CH_2Cl_2 (5 mL) were successively added triethylamine (10 mmol), Ac_2O (8 mmol), and DMAP (100 mg), and the reaction mixture was stirred until the reaction was complete. The solvent was evaporated, and the residue was dissolved in EtOAc, washed successively with water, 1 M HCl, saturated aq $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography (heptane−EtOAc 1:1) to afford the corresponding fully protected sugar.

(B) A solution of aldehyde (1 mmol) in the mixture of dioxane−water 1:1 (25 mL) was stirred in the presence of Amberlite IR 120 (H^+) for 12 h. After removal of the resin, the solvents were evaporated with toluene and the residue was acetylated as above giving the fully protected sugar.

General Procedure for the Hydrogenolysis of Fully Protected 4-*O*-Benzyl-L-hexoses. A stirred solution of 4-*O*-benzyl-L-hexose (1 mmol) in EtOAc (25 mL) was hydrogenated in the presence of 10% Pd/C at atmospheric pressure for 12 h. After removal of the catalyst by filtration through Celite, the solvent was evaporated. The residue was acetylated as above and purified by column chromatography to give the pentaacetate of the corresponding sugar.

1,2,3,6-*O*-Tetraacetyl-4-*O*-benzyl-L-galactopyranose 19 was prepared from **17** by general procedure A in 60% yield (α-/β-anomers 22:78). **19** (colorless oil): IR ($CHCl_3$) cm^{-1} 2938, 1744, 1431, 1368, 1214, 1123, 1062, 1043, 903; ^{1}H NMR 7.34 [m, 5H (α-anomer) and 5H (β-anomer)], 6.36 (d, *J* = 3.8 Hz, 1H, α-anomer), 5.67 (d, *J* = 8.1 Hz, 1H, β-anomer), 5.52 (dd, *J* = 7.2, 3.8 Hz, 1H, α-anomer), 5.49 (dd, *J* = 10.3, 8.3 Hz, 1H, β-anomer), 5.29 (dd, *J* = 10.9, 2.9 Hz, 1H, α-anomer), 5.01 (dd, *J* = 10.3, 3.0 Hz, 1H, β-anomer), 4.76, 4.56 (2d, *J* = 11.5 Hz, 2H, β-anomer), 4.73, 4.53 (2d, *J* = 11.2 Hz, 2H, α-anomer), 4.26−4.15 [m, 2H (α-anomer) and 1H (β-anomer)], 4.14−4.04 [m, 2H (α-anomer) and 1H (β-anomer)], 3.97 (m, 1H, β-anomer), 3.86 (m, 1H, β-anomer), 2.13, 2.09, 2.06, 2.04, 2.04, 2.01, 2.00 [7s, 15H (α-anomer) and 15H (β-anomer)]; ^{13}C NMR 170.5, 170.4, 170.3, 170.3, 169.7, 169.4, 169.2, 169.0, 92.2, 90.1, 75.3, 75.1, 74.3, 73.7, 73.2, 73.1, 70.4, 70.3, 68.6, 67.0, 62.2, 62.1, 20.9, 20.9, 20.9, 20.8, 20.8, 20.7, 20.6; MS (ESI) *m/z* 461 $[M + Na]^+$; HRMS calcd for $C_{21}H_{26}O_{10}Na$ $[M + Na]^+$ 461.1424, found 461.1445.

L-Galactopyranose pentaacetate 20 was obtained from **19** by hydrogenolysis followed by acetylation in 95% yield (α-/β-anomers 22:78). **20** (colorless oil): IR ($CHCl_3$) cm^{-1} 2982, 1742, 1433, 1368, 1207, 1170, 1125, 1062, 1042, 953, 929, 899, 754; ^{1}H NMR 6.38 (d, *J* = 1.9 Hz, 1H, α-anomer), 5.72 (d, *J* = 8.3 Hz, 1H, β-anomer), 5.51 (m, 1H, α-anomer), 5.43 (d, *J* = 3.4 Hz, 1H, β-anomer), 5.37−5.28 [m, 2H (α-anomer) and 1H (β-anomer)], 5.10 (dd, *J* = 10.0, 3.4 Hz, 1H (β-anomer), 4.35 (m, 1H (α-anomer), 4.22−4.10 [m, 2H (α-anomer) and 3H (β-anomer)], 2.17, 2.13, 2.05, 2.05, 2.03, 2.01, 2.00 [7s, 15H (α-anomer) and 15H (β-anomer)]; ^{13}C NMR (β-anomer) 92.1, 71.7, 70.8, 67.9, 66.9, 61.1 (lit.[30] 91.8, 71.5, 70.6, 67.8, 66.8, 61.0); (α-anomer) 89.7, 68.8, 67.4, 67.4, 66.4, 61.3 (lit.[30] 89.5, 68.5, 67.2, 67.2, 66.2, 61.0); MS (ESI) *m/z* 413 $[M + Na]^+$; HRMS calcd for $C_{16}H_{22}O_{11}Na$ $[M + Na]^+$ 413.1060, found 413.1063.

1,2,3,6-*O*-Tetraacetyl-4-*O*-benzyl-L-idopyranose 21 was prepared from **18** by general procedure B in 60% yield (α-/β-anomers 40:60). **21** (colorless oil): IR ($CHCl_3$) cm^{-1} 2937, 1737, 1497, 1454, 1433, 1369, 1212, 1169, 1134, 1044, 1013, 960, 908; ^{1}H NMR 7.35 (m, 5H), 6.05 (d, *J* = 2.1 Hz, 1H), 5.37 (dd, *J* = 9.4, 3.4 Hz, 1H), 5.25 (dd, *J* = 3.4, 2.1 Hz, 1H), 4.70, 4.60 (2d, *J* = 11.1 Hz, 2H), 4.32 (d, *J* = 3.8 Hz, 2H), 3.97(ddd, *J* = 10.0, 3.6, 3.2 Hz, 1H), 3.88 (t, *J* = 9.6 Hz, 1H), 2.17, 2.14, 2.08, 2.01 (4s, 12H); ^{13}C NMR 170.6, 169.8, 169.7, 168.3, 137.3, 128.6, 128.1, 127.8, 90.7, 75.1, 72.5, 71.7, 71.5, 68.8, 62.8, 20.9, 20.8, 20.8, 20.8; MS (ESI) *m/z* 461 $[M + Na]^+$; HRMS calcd for $C_{21}H_{26}O_{10}Na$ $[M + Na]^+$ 461.1424, found 461.1418.

L-Idopyranose pentaacetate 22 was obtained from **21** by hydrogenolysis followed by acetylation in 95% yield (α-/β-anomers 40:60). **22** (colorless oil): IR ($CHCl_3$) cm^{-1} 2977, 1738, 1433, 1369, 1208, 1166, 1124, 1093, 1044, 961, 898, 755; ^{1}H NMR 6.09 (d, *J* = 2.3 Hz, 1H, α-anomer), 6.06 (d, *J* = 1.7 Hz, 1H, β-anomer), 5.25 (t, *J* = 4.9 Hz, 1H, α-anomer), 5.07 (dd, *J* = 3.7, 3.0 Hz, 1H, β-anomer), 5.02 (dd, *J* = 4.9, 2.6 Hz, 1H, α-anomer), 4.93 [m, 1H (α-anomer and 1H (β-anomer)], 4.88 (m, 1H, β-anomer), 4.48 (ddd, *J* = 8.7, 6.4, 2.3 Hz, 1H, β-anomer), 4.39 (m, 1H, α-anomer), 4.26 (dd, *J* = 6.9, 6.1 Hz, 2H, α-anomer), 4.20 (dd, *J* = 6.4, 1.0 Hz, 2H, β-anomer), 2.14, 2.13, 2.12, 2.12, 2.11, 2.07, 2.07 [7 s, 15H (α-anomer and 15H (β-anomer)]; ^{13}C NMR (α-anomer) 90.7, 66.2, 66.2, 66.3, 66.3, 61.8 (lit.[30] 90.4, 65.9, 65.9, 66.2, 66.2, 61.8); (β-anomer) 89.9, 72.0, 67.2, 66.7, 66.2, 62.2; MS (ESI) *m/z* 413 $[M + Na]^+$; HRMS calcd for $C_{16}H_{22}O_{11}Na$ $[M + Na]^+$ 413.1060, found 413.1075.

1,2,3,6-*O*-Tetraacetyl-4-*O*-benzyl-L-glucopyranose 29 was prepared from **27** by general procedure B in 70% yield (α-/β-anomers 42:58). **29** (colorless oil): IR ($CHCl_3$) cm^{-1} 3029, 3013, 1753, 1431, 1371, 1227, 1207, 1156, 1064, 1015, 974; ^{1}H NMR 7.33, 7.28 (2m, 5H, α- and β-anomers), 6.25 (d, *J* = 3.6 Hz, 1H, α-anomer), 5.70 (d, *J* = 8.3 Hz, 1H, β-anomer), 5.56 (dd, *J* = 10.4, 9.2 Hz, 1H, α-anomer), 5.30 (m, 1H, β-anomer), 5.05 (m, 2H, α- and β-anomers), 4.58 (m, 4H, α- and β-anomers), 4.38−4.20 (m, 4H, α- and β-anomers), 4.02 (m, 1H, β-anomer), 3.74 (m, 3H, α- and β-anomers), 2.15, 2.10, 2.07, 2.06, 2.03, 2.01, 2.01, 1.98 (8s, 24 H); ^{13}C NMR 170.5, 170.0, 169.9, 169.7, 169.0, 168.9, 137.0, 128.6, 128.6, 128.2, 128.2, 128.1, 128.0, 91.6, 89.2, 75.3, 75.1, 75.0, 74.9, 74.8, 73.8, 71.9, 71.0, 70.8, 69.6, 62.3, 62.2, 20.9, 20.9, 20.8, 20.8, 20.8, 20.8, 20.6, 20.5; MS (ESI) *m/z* 461 $[M + Na]^+$; HRMS calcd for $C_{21}H_{26}O_{10}Na$ $[M + Na]^+$ 461.1424, found 461.1431.

L-Glucopyranose pentaacetate 30 was prepared from **29** by hydrogenolysis followed by acetylation in 95% yield (α-/β-anomers 49:51). **30** (colorless oil): IR ($CHCl_3$) cm^{-1} 3032, 2962, 1756, 1430, 1368, 1241, 1207, 1153, 1079, 1040, 1012, 939, 909; NMR ^{1}H 6.32 (d, *J* = 3.6 Hz, 1H, α-anomer), 5.71 (d, *J* = 8.3 Hz, 1H, β-anomer), 5.48 (t, *J* = 10.0 Hz, 1H), 5.25 (t, *J* = 9.4 Hz, 1H), 5.18−5.05 (m, 4H), 4.35−4.25 (m, 2H), 4.15−4.05 (m, 3H), 3.85 (ddd, *J* = 10.0, 4.5, 2.3 Hz, 1H), 2.19, 2.12, 2.10, 2.09, 2.05, 2.04, 2.03, 2.02, 2.02 (9s, 30H); ^{13}C NMR (β-anomer) 91.7, 72.8, 72.7, 70.2, 67.9, 61.4 (lit.[30] 91.8, 72.8, 72.8, 70.5, 68.1, 61.7); (α-anomer) 89.1, 69.8, 69.8, 69.2, 67.7, 61.4 (lit[30] 89.2, 70.0, 70.0, 69.4, 68.1, 61.1); MS (ESI) *m/z* 413 $[M + Na]^+$; HRMS calcd for $C_{16}H_{22}O_{11}Na$ $[M + Na]^+$ 413.1060, found 413.1044.

L-Altropyranose pentaacetate 31 was obtained from **28** by general procedure B and subsequent hydrogenolysis followed by acetylation in 60% yield (4 steps), (α-/β-anomers 71:29). **31** (colorless oil): IR ($CHCl_3$) cm^{-1} 3029, 3013, 1753, 1431, 1371, 1227, 1207, 1156, 1064, 1015, 974; ^{1}H NMR 6.16 (d, *J* = 2.0 Hz,

1H, α-anomer), 6.0 (br s, 1H, β-anomer), 5.44 (dd, J = 5.6, 3.2 Hz, 1H, α-anomer), 5.32 (t, J = 3.4 Hz, 1H, β-anomer), 5.24−5.18 [m, 2H (α-anomer) and 1H (β-anomer)], 4.98 (dd, J = 3.7, 1.4 Hz, 1H (β-anomer), 4.42−4.25 [m, 1H (α-anomer) and 2H (β-anomer)], 4.22−4.10 [m, 2H (α-anomer) and 1H (β-anomer)], 2.17, 2.15, 2.14, 2.14, 2.11, 2.10, 2.05, 2.03 [8s, 15H (α-anomer) and 15H (β-anomer)]; ^{13}C NMR (α-anomer) 90.5, 68.4, 66.6, 66.6, 64.6, 62.3 (lit.[30] 90.2, 68.2, 66.4, 66.4, 64.6, 62.1); (β-anomer) 90.1, 72.2, 67.3, 65.5, 62.7; MS (ESI) m/z 413 [M + Na]$^+$; HRMS calcd for $C_{16}H_{22}O_{11}Na$ [M + Na]$^+$ 413.1060, found 413.1044.

1,2,3,6-*O*-Tetraacetyl-4-*O*-benzyl-β-L-gulopyranose 38 was obtained from **36** by general procedure A (for 24 h at room temperature) in 85% yield. **38** (colorless oil): $[\alpha]_D$ + 58.5 (c 2.2); IR ($CHCl_3$) cm^{-1} 3029, 3012, 2976, 1744, 1455, 1430, 1369, 1213, 1151, 1065, 1052, 922, 745, 701; ^{1}H NMR 7.28 (m, 5H), 6.00 (d, J = 7.0 Hz, 1H), 5.65 (dd, J = 3.7, 3.0 Hz, 1H), 5.25 (dd, J = 6.8, 3.0 Hz, 1H), 4.82, 4.55 (2d, J = 11.7 Hz, 2H), 4.25−4.10 (m, 3H), 3.52 (d, J = 3.7 Hz, 1H), 2.14, 2.12, 2.05, 1.99 (4s, 12H); ^{13}C NMR 170.5, 169.6, 169.5, 169.3, 136.7, 128.6, 128.5, 128.4, 89.9, 72.8, 72.3, 72.3, 67.6, 67.0, 62.6, 21.0, 20.9, 20.8, 20.7; MS (ESI) m/z 461 [M + Na]$^+$; HRMS calcd for $C_{20}H_{26}O_8Na$ [M + Na]$^+$ 461.1424, found 461.1443.

β-L-Gulopyranose pentaacetate 39 was prepared from **38** by hydrogenolysis followed by acetylation in 95% yield. **39** (colorless oil): $[\alpha]_D$ + 2.9 (c 1.9); IR ($CHCl_3$) cm^{-1}: 3030, 3010, 2970, 1755, 1430, 1371, 1229, 1205, 1151, 1131, 1072, 941, 918, 893; ^{1}H NMR 6.00 (d, J = 8.6 Hz, 1H), 5.42 (dd, J = 3.7, 3.5 Hz, 1H), 5.12 (dd, J = 8.6, 3.5 Hz, 1H), 5.01 (dd, J = 4.0, 1.5 Hz, 1H), 4.20−4.10 (m, 2H), 2.16, 2.15, 2.13, 2.10, 2.00 (5s, 15H); ^{13}C NMR 89.9, 71.4, 67.6, 67.4, 67.3, 61.5 (lit.[30] 89.7, 71.1, 67.3, 67.1, 67.1, 61.3); MS (ESI) m/z 413 [M + Na]$^+$; HRMS calcd for $C_{16}H_{22}O_{11}Na$ [M + Na]$^+$ 413.1060, found 413.1075.

1,2,3,6-*O*-Tetraacetyl-4-*O*-benzyl-L-talopyranose 40 was obtained from **37** by general procedure A (for 4 h at room temperature) in 75% yield (α-/β-anomers 5:1). **40** (colorless oil): IR ($CHCl_3$) cm^{-1} 3031, 3020, 3010, 2928, 1747, 1497, 1455, 1371, 1228, 1206, 1147, 1105, 1051, 1027, 975; 953; 914; 867; ^{1}H NMR 7.34 (m, 5H, α- and β-anomers), [6.15 (d, J = 2.0 Hz, α-anomer), 5.85 (d, J = 2.2 Hz, β-anomer), 1H], [5.35 (m, α-anomer), 5.30 (m, β-anomer), 1H], [5.18 (m, α- anomer), 5.13 (m, β-anomer), 1H], [4.75 (d, J = 11.4 Hz, α-anomer), 4.72 (d, J = 11.4 Hz, β-anomer), 1H], [4.60 (d, J = 11.4 Hz, α-anomer), 4.57 (d, J = 11.4 Hz, β-anomer), 1H], 4.50−4.15 (m, α- and β-anomers, 3H), 3.95−3.80 (m, α- and β-anomers, 1H), 2.13, 2.12, 2.10, 2.08, 2.07, 2.06, 2.03, 2.0 (8s, 12H); ^{13}C NMR 170.6, 170.2, 169.8, 168.7, 168.3, 137.8, 128.6, 128.1, 91.6, 90.3, 74.5, 74.1, 73.8, 72.4, 71.8, 71.2, 69.7, 68.3, 66.9, 62.8, 62.4, 20.9; MS (ESI) m/z 461 [M + Na]$^+$; HRMS calcd for $C_{21}H_{26}O_{10}Na$ [M + Na]$^+$ 461.1424, found 461.1429.

α-L-Talopyranose pentaacetate 41 was prepared from **40** by hydrogenolysis followed by acetylation in 85% yield. **41** (colorless oil): $[\alpha]_D$ −40.0 (c 1.0); IR ($CHCl_3$) cm^{-1} 3030, 2994, 2928, 2855, 1755, 1648, 1454, 1430, 1372, 1234, 1203, 1145, 1099, 1049, 1019, 1001, 962, 909, 869; NMR ^{1}H 6.17 (d, J = 1.7 Hz, 1H), 5.40−5.25 (m, 2H), 5.05 (m, 1H), 4.25 (m, 1H), 4.15 (m, 2H), 2.16 (s, 6H), 2.15, 2.05, 2.01 (3 s, 9H); ^{13}C NMR 91.5, 68.9, 66.4, 65.4, 65.2, 61.5 (lit.[30] 91.4, 68.8, 66.3, 65.3, 65.2, 61.5); MS (ESI) m/z 413 [M + Na]$^+$; HRMS calcd for $C_{16}H_{22}O_{11}Na$ [M + Na]$^+$ 413.1060, found 413.1048.

1,2,3,6-*O*-Tetraacetyl-4-*O*-benzyl-L-allopyranose 48 was obtained from **46** by general procedure B in 85% yield as a mixture of α- and β-anomers in 1:2 ratio, which were separated by flash chromatography (heptane−EtOAc 3:1).

48a (α-anomer): $[\alpha]_D$ −95.2 (c 1.1); IR ($CHCl_3$) cm^{-1} 3030, 3008, 2957, 1744, 1454, 1372, 1226, 1207, 1132, 1061, 1016, 966, 910; NMR ^{1}H 7.33 (m, 5H), 6.20 (d, J = 4.1 Hz, 1H), 5.87 (t, J = 3.0 Hz, 1H), 5.03 (dd, J = 4.0, 3.6 Hz, 1H), 4.63, 4.37 (2d, J = 11.3 Hz, 2H), 4.22 (m, 3H), 3.65 (dd, J = 9.8, 3.0 Hz, 1H), 2.17, 2.14, 2.03, 1.97 (4s, 12H); ^{13}C NMR 170.7, 170.5, 169.7, 169.3, 136.7, 128.7, 128.5, 128.4, 88.6, 71.0, 70.7, 67.1, 66.6, 65.4, 62.6, 21.1, 21.0, 20.9, 20.6; MS (ESI) m/z 461 [M + Na]$^+$; HRMS calcd for $C_{21}H_{26}O_{10}Na$ [M + Na]$^+$ 461.1424, found 461.1442.

48b (β-anomer): $[\alpha]_D$ −40.5 (c 1.0); IR ($CHCl_3$) cm^{-1} 3031, 2925, 1746, 1454, 1372, 1226, 1207, 1074, 1019, 951, 907; NMR ^{1}H 7.32 (m, 5H), 6.01 (d, J = 8.7 Hz, 1H), 5.91 (t, J = 2.8 Hz, 1H), 4.87 (dd, J = 8.7, 2.8 Hz, 1H), 4.61, 4.34 (2d, J = 11.3 Hz, 2H), 4.32−4.20 (m, 2H), 4.10 (m, 1H), 3.62 (dd, J = 9.8, 2.8 Hz, 1H), 2.16, 2.10, 2.04, 1.96 (4s, 12H); ^{13}C NMR 171.4, 170.9, 170.3, 170.0, 137.4, 129.4, 129.2, 129.1, 90.8, 72.9, 72.2, 72.0, 69.6, 67.3, 63.5, 21.8, 21.6, 21.6, 21.4; MS (ESI) m/z 461 [M + Na]$^+$; HRMS calcd for $C_{21}H_{26}O_{10}Na$ [M + Na]$^+$ 461.1424, found 461.1434.

α-L-Allopyranose pentaacetate 49a was obtained from **48a** by hydrogenolysis followed by acetylation in 90% yield. **49a** (colorless oil): $[\alpha]_D$ −69.7 (c 1.1); IR ($CHCl_3$) cm^{-1} 3020, 3014, 1748, 1431, 1371, 1218, 1206, 1127, 1047, 1014, 969, 950, 908; ^{1}H NMR 6.23 (d, J = 4.2 Hz, 1H), 5.66 (t, J = 3.0 Hz, 1H), 5.12 (dd, J = 4.1, 3.6 Hz, 1H), 5.04 (dd, J = 10.2, 3.0 Hz, 1H), 4.35 (m, 1H), 4.30 (dd, J = 12.2, 4.1 Hz, 1H), 4.14 (dd, J = 12.2, 1.9 Hz, 1H), 2.17, 2.16, 2.09, 2.02 (4s, 15H); ^{13}C NMR 170.7, 170.1, 169.3, 169.1, 169.0, 88.5, 67.0, 65.9, 65.9, 65.2, 61.7, 20.9, 20.8, 20.7, 20.5, 20.4; MS (ESI) m/z 413 [M + Na]$^+$; HRMS calcd for $C_{16}H_{22}O_{11}Na$ [M + Na]$^+$ 413.1060, found 413.1073.

β-L-Allopyranose pentaacetate 49b was prepared from **48b** by the same procedure and in the same yield. **49b** (colorless oil): $[\alpha]_D$ +12.1 (c 1.2); IR ($CHCl_3$) cm^{-1}: 3029, 2960, 1753, 1431, 1370, 1218, 1205, 1170, 1046, 1020, 951, 914; ^{1}H NMR 6.02 (d, J = 8.7 Hz, 1H), 5.70 (t, J = 3.0 Hz, 1H), 5.00 (m, 2H), 4.30−4.10 (m, 3H), 2.17, 2.13, 2.08, 2.02, 2.01 (5s, 15H); ^{13}C NMR 90.1, 71.1, 68.2, 68.1, 65.7, 61.9 (lit.[30] 90.1, 71.2, 68.2, 68.2, 65.8, 61.9); MS (ESI) m/z 413 [M + Na]$^+$; HRMS calcd for $C_{16}H_{22}O_{11}Na$ [M + Na]$^+$ 413.1060, found 413.1053

1,2,3,6-*O*-Tetraacetyl-4-*O*-benzyl-L-mannopyranose 50 was obtained from **47** by procedure B as a mixture of α- and β-anomers (3:1) easily separated by flash chromatography (heptane−EtOAc 3:1). α-anomer **50a** (colorless oil): $[\alpha]_D$ −57.5 (c 1.5); IR ($CHCl_3$) cm^{-1}: 3030, 3013, 1751, 1455, 1371, 1226, 1205, 1153, 1083, 1026, 973, 908; ^{1}H NMR 7.35 (m, 5H), 6.05 (d, J = 2.1 Hz, 1H), 5.37 (dd, J = 9.4, 3.4 Hz, 1H), 5.25 (dd, J = 3.4, 2.1 Hz, 1H), 4.70, 4.60 (2d, J = 11.1 Hz, 2H), 4.32 (d, J = 3.8 Hz, 2H), 3.97 (ddd, J = 10.0, 3.6, 3.2 Hz, 1H), 3.88 (t, J = 9.6 Hz, 1H), 2.17, 2.14, 2.08, 2.01 (4s, 12H); ^{13}C NMR 170.6, 169.8, 169.7, 168.3, 137.3, 128.6, 128.1, 127.8, 90.7, 75.1, 72.5, 71.7, 71.5, 68.8, 62.8, 20.9, 20.8, 20.8, 20.8; MS (ESI) m/z 461 [M + Na]$^+$; HRMS calcd for $C_{21}H_{26}O_{10}Na$ [M + Na]$^+$ 461.1424, found 461.1438.

β-Anomer 50b (colorless oil): $[\alpha]_D$ +25.8 (c 0.5); IR ($CHCl_3$) cm^{-1} 3031, 1751, 1368, 1228, 1205, 1087, 1036, 911; NMR ^{1}H 7.33 (m, 5H), 5.85 (d, J = 1.1 Hz, 1H), 5.48 (dd, J = 3.2, 1.1 Hz, 1H), 5.13 (dd, J = 9.4, 3.2 Hz, 1H), 4.67, 4.57 (2d, J = 11.1 Hz, 2H), 4.37 (dd, J = 12.0, 2.3 Hz, 1H), 4.30 (dd, J = 12.3, 4.9 Hz, 1H), 3.83 (t, J = 9.4 Hz, 1H), 3.74 (ddd, J = 9.4, 4.9, 2.3 Hz, 1H), 2.21, 2.09, 2.08, 1.99 (4s, 12H); ^{13}C NMR 170.7, 170.2, 169.7, 168.4, 137.4, 128.6, 128.2, 127.8, 90.4, 75.1, 74.3, 73.4, 72.5, 68.7, 62.9, 20.9, 20.8, 20.8, 20.7; MS (ESI) m/z 461 [M + Na]$^+$; HRMS calcd for $C_{21}H_{26}O_{10}Na$ [M + Na]$^+$ 461.1424, found 461.1431.

α-L-Mannopyranose pentaacetate 51a was prepared from **50a** by hydrogenolysis followed by acetylation in 95% yield. **51a** (colorless oil): $[\alpha]_D$ −54.9 (c 1.1); IR ($CHCl_3$) cm^{-1} 3031, 2959, 1753, 1431, 1371, 1226, 1207, 1152, 1088, 1054, 1025, 975, 909; ^{1}H NMR 6.09 (d, J = 1.9 Hz, 1H), 5.35 (m, 2H), 5.25 (dd, J = 2.5, 1.9 Hz, 1H), 4.35 (dd, J = 12.4, 4.9 Hz, 1H), 4.05 (m, 2H), 2.18, 2.18, 2.10, 2.06, 2.01 (5s, 15H); ^{13}C NMR 170.6, 169.9, 169.7, 169.5, 168.0, 90.5, 70.6, 68.7, 68.3, 65.5, 62.1, 20.8, 20.7, 20.7, 20.6, 20.6 (lit.[30] 90.4, 70.5, 68.6, 68.2, 65.4, 62.0); MS (ESI) m/z 413 [M + Na]$^+$; HRMS calcd for $C_{16}H_{22}O_{11}Na$ [M + Na]$^+$ 413.1060, found 413.1049.

β-L-Mannopyranose pentaacetate 51b was obtained from **50b** by the same procedure and in the same yield. **51b** (colorless oil): $[\alpha]_D$ +23.3 (c 1.1); IR ($CHCl_3$) cm^{-1}: 3031, 1754, 1602, 1460, 1430, 1369, 1226, 1207, 1169, 1090, 1057, 970, 909, 859; ^{1}H NMR

5.85 (d, $J = 1.0$ Hz, 1H), 5.49 (dd, $J = 3.2$, 1.0 Hz, 1H), 5.29 (t, $J = 10.0$ Hz, 1H), 5.16 (dd, $J = 10.0$, 3.2 Hz, 1H), 4.32 (dd, $J = 12.3$, 5.1 Hz, 1H), 4.14 (dd, $J = 12.3$, 2.5 Hz, 1H), 3.83 (ddd, $J = 10.0$, 5.2, 2.5 Hz, 1H), 2.22, 2.11, 2.10, 2.06, 2.01 (5s, 15H); ^{13}C NMR 170.6, 170.2, 169.8, 169.6, 168.4, 90.4, 73.2, 70.6, 68.2, 65.4, 62.1, 20.8, 20.8, 20.8, 20.7, 20.5; MS (ESI) *m*/*z* 413 $[M + Na]^+$; HRMS calcd for $C_{16}H_{22}O_{11}Na$ $[M + Na]^+$ 413.1060, found 413.1057.

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Supporting Information Available: General conditions, experimental procedures, and spectroscopic data for compounds **2**−**12** and copies of ^{1}H and ^{13}C spectra for compounds **9**−**51**. This material is available free of charge via the Internet at http://pubs.acs.org.

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