DOI: 10.1002/ejoc.200600440

Stereoselective Glycosylations Using (*R*)- or (*S*)-(Ethoxycarbonyl)benzyl Chiral Auxiliaries at C-2 of Glycopyranosyl Donors

Jin-Hwan Kim,[a] Hai Yang,[a] Vishal Khot,[a] Dennis Whitfield,*[b] and Geert-Jan Boons*[a]

Keywords: Carbohydrates / Glycosylation / Anomeric control / Chiral auxiliary

The stereoselective introduction of a glycosidic bond presents the greatest challenge to complex oligosaccharide synthesis. Important developments such as automated polymer-supported oligosaccharide synthesis will not realize their full potential until this problem is addressed. In this paper, a novel approach for stereoselective glycosylations is described whereby a chiral auxiliary at C-2 of a glycosyl donor controls the anomeric outcome of a glycosylation. It was found that participation of an (*S*)-ethoxycarbonylbenzyl auxiliary led to the formation of 1,2-*cis* glycosides, probably through a *trans*-fused dioxolenium ion intermediate. On the other hand, the use of an auxiliary with (*R*) configuration gave 1,2-*trans* glycosides, and this glycosylation proceeds through a *cis*-fused dioxolenium ion intermediate. The auxiliary could conveniently be removed by Birch reduction. Computational studies support the formation of the proposed ethoxy-carbonium ion intermediate with all pseudo-equatorial substituents.

Introduction

It is now well established that protein- and lipid-bound saccharides play essential roles in many molecular processes impacting eukaryotic biology and disease.[1–3] Examples of such processes include fertilization, embryogenesis, neuronal development, hormone activities, the proliferation of cells and their organization into specific tissues. Remarkable changes in cell-surface carbohydrates occur with tumor progression, an event that appears to be intimately associated with the dreaded state of metastasis. Furthermore, carbohydrates are capable of inducing a protective antibody response, which is a major contributor to the survival of an organism during infection. In plants, oligosaccharides have been found to control development and defense mechanisms.

A major obstacle to advances in glycobiology is the lack of pure and structurally well-defined carbohydrates and glycoconjugates. These compounds are often found in low concentrations and in microheterogeneous forms, greatly complicating their isolation and characterization. In many cases, well-defined oligosaccharides can only be obtained by chemical synthesis.[4]

The last two decades have witnessed dramatic improvements in the methods available for the synthesis of complex oligosaccharides. New anomeric leaving groups such as anomeric fluorides, trichloroacetimidates, and thioglycosides have been introduced which can be prepared under mild conditions, are sufficiently stable for purification, may be stored for a considerable period of time and undergo glycosylations under mild conditions. These beneficial features permit the synthesis of complex oligosaccharides by highly convergent strategies in which most synthetic efforts are directed towards the preparation of monomeric glycosyl acceptors and donors, which can be assembled into complex structures using a minimum number of synthetic steps. The synthesis of complex oligosaccharides has been further streamlined by one-pot multi-step glycosylations[5,6] and automated polymer-supported syntheses,[7–9] which reduces the need for time-consuming purification protocols.

Despite these important developments, the problem remains that there is no general method for the preparation of complex oligosaccharides of biological importance. One of the main stumbling blocks in complex oligosaccharide synthesis is the formation of mixtures of α/β-anomers during glycosylations. Separation of these anomers requires time-consuming purification protocols resulting in loss of material. The formation of anomeric mixtures also severely limits the use of one-pot multi-step glycosylations or polymer-supported syntheses.

Currently, the most reliable method for stereoselective glycosylations is based on neighboring-group participation by a 2-*O*-acyl functionality (Scheme 1, a).[10] In these reactions, a promoter activates an anomeric leaving group resulting in its departure and the formation of an oxacarben-

[a] Complex Carbohydrate Research Center, University of Georgia,
315 Riverbend Road, Athens, GA 30602, USA
E-mail: gjboons@ccrc.uga.edu
[b] National Research Council of Canada, Institute for Biological Sciences,
100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada
E-mail: dennis.whitfield@nrc-cnrc.gc.ca
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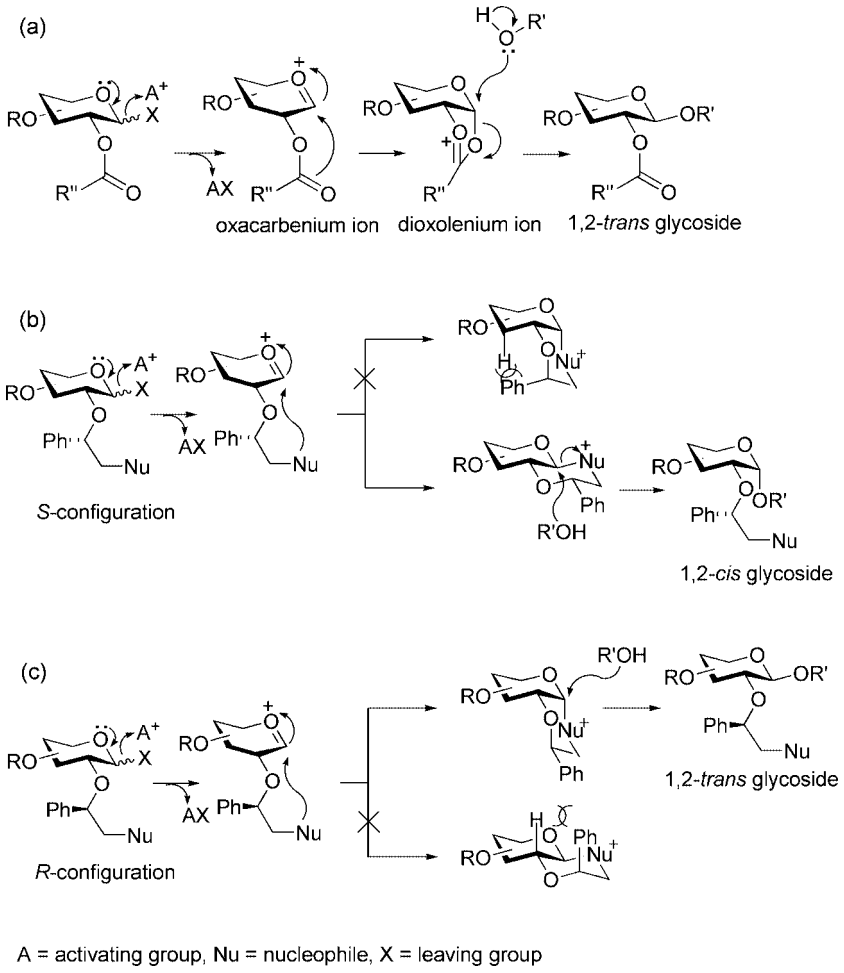


Scheme 1. Conventional and new approaches for stereoselective glycosylation. (a) Classical neighboring-group participation by C-2 ester leading to 1,2-*trans* glycosides. (b) Neighboring-group participation by an (*S*) auxiliary at C-2 leading to 1,2-*cis* glycosides. (c) Neighboring-group participation by an (*R*) auxiliary at C-2 leading to 1,2-*trans* glycosides.

ium ion. Subsequent neighboring-group participation of the 2-*O*-acyl protecting group will give a more stable dioxolenium ion. This bicyclic intermediate will only be formed as a 1,2-*cis* isomer because the alternate 1,2-*trans* configuration will experience considerable ring strain. An alcohol can attack the anomeric center of the dioxolenium ion from only one face leading to the stereospecific formation of a 1,2-*trans* glycoside. Thus, in the case of glucosyl-type donors, β-linked products will be formed while mannosyl donors will give α-glycosides.

The introduction of 1,2-*cis*-glycosidic linkages, such as α-glucosides and α-galactosides, requires glycosyl donors with a non-assisting functionality at C-2. Invariably, the use of these glycosyl donors leads to the formation of mixtures of anomers.[11,12] Thus, the stereoselective formation of 1,2-*cis* glycosides is the principal challenge of complex oligosaccharide synthesis.

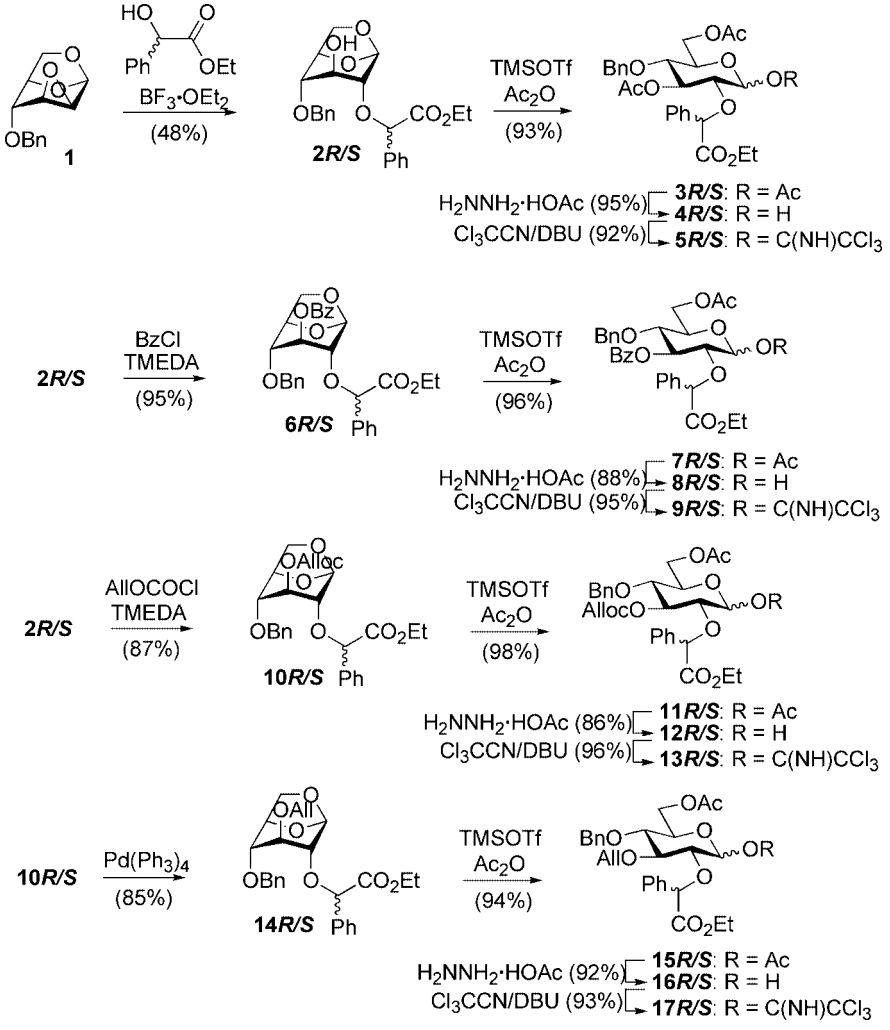
Here, we describe a novel strategy for stereoselective glycosylations using a chiral auxiliary at C-2 of a glycosyl donor (Scheme 1b, c). The auxiliary is a C-1 substituted ethyl moiety that contains a nucleophilic group (Nu). Upon formation of an oxacarbenium ion, the nucleophilic moiety of the auxiliary will participate, leading to the formation of either a *trans*- or *cis*-decalin system. It is expected that an auxiliary with (*S*) stereochemistry will lead only to the formation of *trans*-decalin because the alternate *cis*-fused system will place the phenyl substituent in an axial position inducing unfavorable steric interactions (Scheme 1, b). Subsequent displacement of the anomeric moiety of the *trans*-decalin intermediate will lead to the formation of a 1,2-*cis* glycoside. Alternatively, the use of an auxiliary with (*R*) stereochemistry will lead to the formation of a 1,2-*trans* glycoside because in this case the *trans*-decalin system will experience unfavorable steric interactions. Therefore glycosylation will only take place from the *cis*-decalin intermediate (Scheme 1, c).

Results and Discussion

Ethyl mandelate was explored as a first-generation chiral auxiliary because both enantiomers of this compound are readily available. Furthermore, esters are well-established as

appropriate participating functionalities in glycosylations and the benzylic nature of the auxiliary will make it possible to remove it under reductive conditions. Glucosyl donors **5*R*** and **5*S***, containing a (*R*)- or (*S*)-ethoxycarbonylbenzyl moiety, could be prepared from the readily available epoxide **1**.[13] Thus, reaction of **1** with ethyl (*R*)-mandelate in the presence of $BF_3{\cdot}OEt_2$ led to a *trans*-diaxial opening of the epoxide to give **2*R*** in a yield of 48%. Next, acetolysis of the 1,6-anhydro bridge of **2*R*** with acetic anhydride and TMSOTf gave compound **3*R*** in an almost quantitative yield. The anomeric acetyl group of **3*R*** was selectively removed with hydrazinium acetate to give hemiacetal **4*R***, which was converted into the trichloroacetimidate **5*R*** using trichloroacetonitrile in the presence of DBU.[14] The glycosyl donor **5*S*** was prepared by a similar protocol using ethyl (*S*)-mandelate as the starting material (Scheme 2).

It is well known that the protecting-group pattern of a glycosyl donor can influence the anomeric outcome of a glycosylation. Therefore, the glucosyl donors **9*R/S***, **13*R/S*** and **17*R/S***, were prepared which have a benzoyl ester, an allyl carbonate or an allyl ether at C-3, respectively. These glycosyl donors were expected to be convenient for complex oligosaccharide synthesis because the C-6 acetyl ester can be removed in the presence of a benzoyl group, whereas the allyl- or allyloxycarbonyl-protecting group can be cleaved without affecting the acetyl group at C-6. The glycosyl donors could easily be prepared from the key intermediates **2*R/S***. Thus benzoylation of the individual diastereoisomers **2*R/S*** followed by acetolysis of the 1,6-anhydro-bridge of the resulting **6*R/S*** gave the acetates **7*R/S***, which were converted into the trichloroacetimidates **9*R/S*** by a standard two-step procedure. The allyloxycarbonyl (Alloc) protected derivatives **13*R/S*** could be prepared by a similar approach by first reacting **2*R/S*** with allyloxycarbonyl chloride in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) to give **10*R/S***, which were converted into the anomeric trichloroacetimidates by standard chemical manipulation. The glycosyl donors **17*R/S***, which have an allyl ether at C-3, could



Bn = benzyl, Bz = benzoyl, Alloc = allyloxycarbonyl, All = allyl, TMEDA = tetramethyl ethylenediamine, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, TMSOTf = trimethylsilyl trifluoromethanesulfonate.

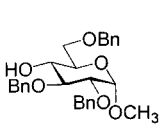
Scheme 2. Preparation of glycosyl donors **5*R/S***, **9*R/S***, **13*R/S*** and **17*R/S***.

be synthesized by decarboxylation of the allyloxycarbonyl moiety of **10*R*/*S*** using $Pd(PPh_3)_4$ to give the allyl ethers **14*R*/*S***, followed by introduction of an anomeric trichloroacetimidate using standard manipulations.

Having a number of differently protected glycosyl donors at hand, attention was focused on glycosylations with the glycosyl acceptors **23**–**27**. Thus, coupling of **5*S*** with **23** using a catalytic amount of trimethylsilyl triflate (TMSOTf) in dichloromethane (DCM) at –78 °C gave the disaccharide **28*S*** mainly as the α-glycoside in high yield (Table 1, Entry 1). At this low temperature, the reaction was completed within 15 min, indicating that the glycosyl donor **5*S*** is highly reactive. Dilution of the reaction mixture led to a small increase in anomeric selectivity, whereas higher reaction temperatures led to reductions of α-anomeric selectivity. As expected, the coupling of **5*R*** with **23** under similar reaction conditions gave **28*R*** as mainly the β-anomer albeit with somewhat lower selectivity (Table 1, Entry 2).

The fact that an inversion of configuration of the asymmetric center of the auxiliary led to a reversal of the stereochemical outcome of the glycosylation supports the proposed mode of participation outlined in Scheme 1 (b, c). In

Table 1. Stereoselective glycosylations with glucosyl donor **5*R*/*S***, **9*R*/*S***, **13*R*/*S*** and **17*R*/*S***.



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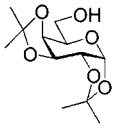

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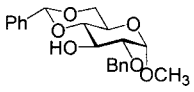

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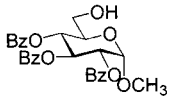

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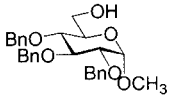

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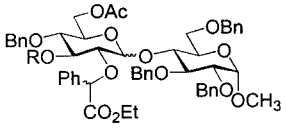
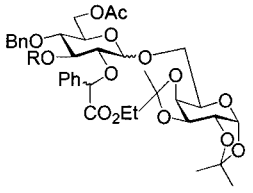
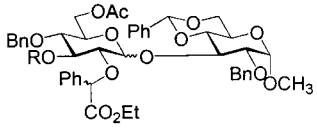


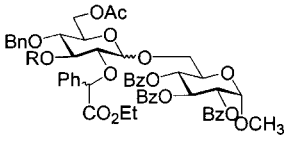
28*S*/*R* (R = Ac)
33*S*/*R* (R = Bz)
35*S*/*R* (R = Alloc)
37*S*/*R* (R = All)



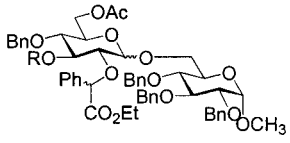
29*S*/*R* (R = Ac)
34*S*/*R* (R = Bz)
36*S*/*R* (R = Alloc)
38*S*/*R* (R = All)



30*S*/*R* (R = Ac)



31*S*/*R* (R = Ac)



32*S*/*R* (R = Ac)

Entry	Glycosyl donor	Glycosyl acceptor	Product	α/β Ratio (yield, %)[a]
1	**5*S***	**23**	**28*S***	20:1 (89%)
2	**5*R***		**28*R***	1:5 (91%)
3	**5*S***	**24**	**29*S***	12:1 (92%)
4	**5*R***		**29*R***	1:3 (88%)
5	**5*S***	**25**	**30*S***	10:1 (95%)
6	**5*R***		**30*R***	1:8 (94%)
7	**5*S***	**26**	**31*S***	18:1 (94%)
8	**5*R***		**31*R***	1:1 (89%)
9	**5*S***	**27**	**32*S***	4:1 (93%)
10	**5*R***		**32*R***	1:6 (96%)
11	**9*S***	**23**	**33*S***	7:1 (88%)
12	**9*R***		**33*R***	1:3 (94%)
13	**9*S***	**24**	**34*S***	α (93%)
14	**9*R***		**34*R***	β (84%)
15	**13*S***	**23**	**35*S***	6:1 (81%)
16	**13*R***		**35*R***	1:9 (85%)
17	**13*S***	**24**	**36*S***	10:7 (79%)
18	**13*R***		**36*R***	β (90%)
19	**17*S***	**23**	**37*S***	1:3 (87%)
20	**17*R***		**37*R***	1:4 (80%)
21	**17*S***	**24**	**38*S***	4:1 (95%)
22	**17*R***		**38*R***	1:5 (75%)

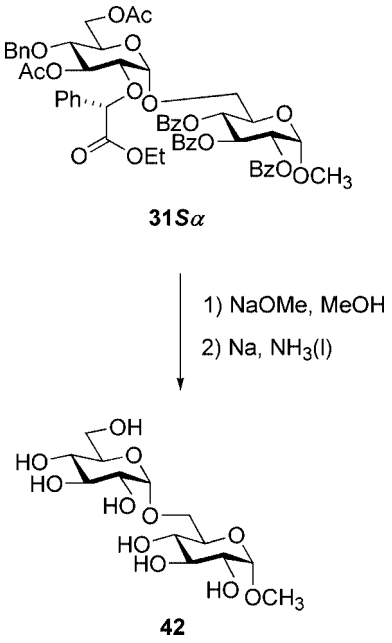
[a] Product ratios were determined by ^{1}H NMR analysis of the crude reaction products.

order to demonstrate the generality of the approach, **5*R*** and **5*S*** were glycosylated with a range of glycosyl acceptors. As can be seen in Table 1, TMSOTf-mediated coupling of **5*S*** with the glycosyl acceptors **24**, **25**, **26** and **27** gave the disaccharides **29*S***, **30*S***, **31*S*** and **32*S***, respectively, with high α-selectivity (Table 1, Entries 3, 5, 7 and 9). In each case, the use of glycosyl donor **5*R*** led to a reversal of anomeric selectivity and the disaccharides **29*R***, **30*R***, **31*R*** and **32*R*** were isolated in excellent yields with modest to good β-anomeric selectivity (Table 1, Entries 4, 6, 8 and 10).

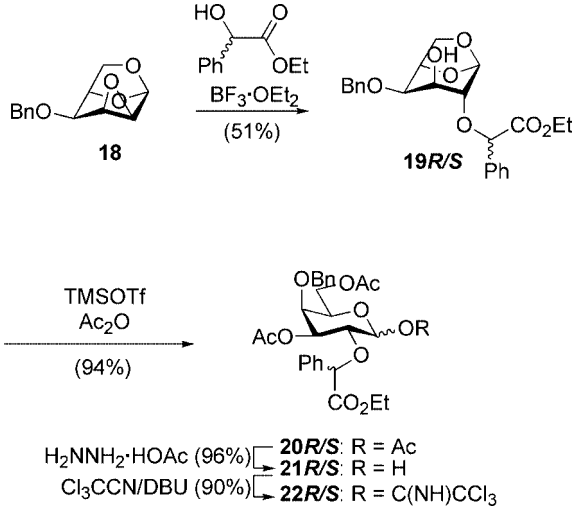
In order to determine the influence of the protecting-group pattern of the glycosyl donor on the anomeric outcome of glycosylations, the trichloroacetimidates **9*S*/*R***, **13*S*/*R*** and **17*S*/*R*** were coupled with the acceptors **23** and **24**, which have a secondary and primary alcohol, respectively. As can be seen in Table 1, the glycosylations with the glycosyl donors **9*S*** and **13*S*** gave the corresponding disaccharides **33*S***, **34*S***, **35*S*** and **36*S*** in excellent yields with good to exclusive α-anomeric selectivity (Table 1, Entries 11, 13, 15 and 17). When the corresponding **9*R*** and **13*R*** were employed as glycosyl donors an expected reversal of anomeric selectivity was observed, and the disaccharides **33*R***, **34*R***, **35*R*** and **36*R*** were isolated as mainly β-anomers (Table 1, Entries 12, 14, 16 and 18). Surprisingly, the glycosylations of **17*S*/*R***, which have an allyl ether at C-3, with the glycosyl acceptors **23** and **24** gave the corresponding disaccharides **37*S*/*R*** and **38*S*/*R*** with modest anomeric selectivity (Table 1, Entries 19–22). These results indicate that an ester protecting group at C-3 is important for efficient participation of the (*S*)-ethoxycarbonylbenzyl auxiliary.

To be useful for target synthesis, it is important that the auxiliary can be removed under mild conditions. The auxiliary was designed in such a way that it contains a substituted benzyl ether, and therefore should be removable by catalytic hydrogenation over Pd/C or by Birch reduction. Indeed, saponification of the benzoyl ester of **31*Sα*** by treatment with NaOMe in methanol followed by removal of the benzyl ethers and chiral auxiliary using sodium in liquid ammonia led to a clean formation of the deprotected compound **42** (Scheme 3). On the other hand, catalytic hydrogenation over Pd/C was sluggish probably due to steric hindrance at the benzylic carbon.

Finally, it was investigated whether the novel methodology can also be applied to galactosyl donors. For this purpose, the galactosyl trichloroacetimidates **22*R*/*S*** were prepared by starting from the readily available 1,6:2,3-di-anhydro-β-D-talopyranose (**18**). Thus, a *trans*-diaxial opening of the epoxide of **18** with ethyl (*R*)-mandelate in the presence of $BF_3{\cdot}OEt_2$ gave **19*R*** in a yield of 51%. Treatment of **19*R*** with acetic anhydride and TMSOTf resulted in the opening of the 1,6-anhydro bridge to give compound **20*R*** in an almost quantitative yield, which was converted into the trichloroacetimidate **22*R*** by selective removal of the anomeric acetyl group using hydrazinium acetate to give the hemiacetal **21*R***, followed by treatment with trichloroacetonitrile in the presence of DBU. The glycosyl donor **22*S*** (Scheme 4) was prepared by a similar protocol using ethyl (*S*)-mandelate as the starting material.



Scheme 3. Deprotection of disaccharide **31*Sα***.

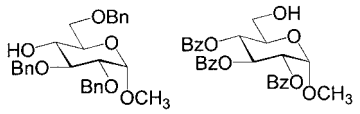


Scheme 4. Preparation of glycosyl donor **22*R*/*S***.

Gratifyingly, TMSOTf-mediated glycosylation of **22*S*** with the glycosyl acceptors **23** and **26** gave the corresponding disaccharides **39*S*** and **40*S*** with good α-anomeric selectivity, whereas the use of the glycosyl donor **22*R***, which has a (*R*)-mandelate at C-2, gave **39*R*** and **40*R*** with modest β-selectivity (Table 2).

The anomeric selectivities summarized in Table 1 and Table 2 show that glycosylations with glycosyl donors having an (*S*)-ethoxycarbonylbenzyl moiety at C-2 give predominantly α-glycosides, whereas the donors containing an auxiliary with opposite stereochemistry give mainly β-glycosides. It was, however, observed that the β-anomeric selectivities were somewhat lower. These glycosylations are proposed to proceed through a *cis*-decalin intermediate, which places the phenyl substituent of the auxiliary in an equato-

Table 2. Stereoselective glycosylations with galactosyl donor **22*R*/*S***.



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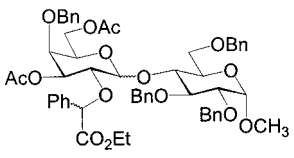
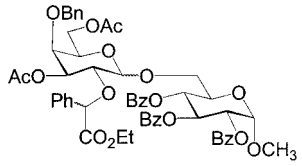


39*S*/*R*



40*S*/*R*

Entry	Glycosyl donor	Glycosyl acceptor	Product	α/β Ratio (yield, %)[a]
1	**22*S***	**23**	**39*S***	10:1 (75%)
2	**22*R***		**39*R***	1:4 (79%)
3	**22*S***	**26**	**40*S***	6:1 (78%)
4	**22*R***		**40*R***	1:2 (82%)

[a] Product ratios were determined by ^{1}H NMR analysis of the crude reaction products.

rial orientation (Scheme 1, c). It is, however, important to note that a *cis*-decalin does experience unfavorable *gauche* interactions. The (*S*)-ethoxycarbonylbenzyl auxiliary, which reacts through a *trans*-decalin intermediate, does not experience these unfavorable interactions rationalizing its more efficient anomeric control.

In general, participation by conventional C-2 ester leads to the exclusive formation of 1,2-*trans* glycosides. Although the glycosyl donors that have an ethyl (*S*)-mandelate at C-2 led to disaccharides with high α-anomeric selectivity, small amounts of the unwanted β-anomers were formed. The formation of the unwanted anomer was significant when glycosyl donor **17*S*** was used, which has an allyl ether at C-3. Participation by an ethoxycarbonylbenzyl moiety is probably slower than that of a conventional ester because of slower six-membered than five-membered ring formation. Thus, it is possible that in the case of an ethoxycarbonylbenzyl-participating group, some glycosylation takes place from the oxacarbenium ion leading to anomeric mixtures. This proposal is supported by the observation that dilution of the reaction mixture resulted in an improvement of anomeric selectivity. The oxacarbenium ion is disfavored by electron withdrawing substituent such as an ester at C-3, which may facilitate the participation. Differences in stability of the intermediate oxacarbenium ion may rationalize the more efficient participation of glycosyl donors **5*S***, **9*S*** and **13*S*** compared to **17*S***.

Computational Studies: Recent advances in computer hardware and software have made it possible to study protected monosaccharides by high-level quantum-mechanical methods.[15] Of particular interest are intermediates or transition states that are not easily amenable to study by experimental methods. In this section, we present an assessment of the intuitive models which form the basis of the new glycosylation methodology with Density Functional Theory (DFT) quantum-mechanical calculations (see Experimental Section). These intuitive models suggest that (*R*)-configured auxiliaries, like all equatorial dioxolenium ion species, should have a *cis*-decalin that is more stable than the corresponding *trans*-decalin species and the ring-opened parent oxacarbenium ion (Scheme 1, c). Similarly, the (*S*)-configured auxiliary should have an all equatorial *trans*-decalin dioxolenium ion that is more stable than its *cis* isomer and its ring-opened oxacarbenium ion (Scheme 1, b). These postulates are the basis of the model, which also assumes that glycosylation reactions proceed through fully cationic intermediates without significant perturbation by solvent or counterions.[16] Such a method assumes the limitation that the effects of solvents and counterions are equivalent for all ions calculated. Other inherent limitations of the DFT program and the model system studied are the basis set imperfections, truncated protecting groups and incomplete consideration of correlation, all of which lead to relatively large errors estimated at up to 5 kJ mol^{-1} based on experience with similar systems.

Specifically, this study focused on the following cations: 3,6-di-*O*-acetyl-4-*O*-methyl-2-*O*-(*R*)-methoxycarbonylbenzyl-D-glucopyranosyl (**43*R***) and its 2-*O*-(*S*) isomer (**43*S***). These cations are derived from **5*R*/*S*** with the ethoxy replaced by methoxy and the 4-*O*-benzyl replaced by *O*-methyl. A drawback of these truncations is that they limit the conformational degrees of freedom and thus simplify the computational studies. Previous studies of D-*gluco*-configured pyranosyl oxacarbenium ions have consistently found two stable conformers for both the 2,3,4,6-tetra-*O*-methyl[17] and the 2-*O*-acetyl-3,4,6-tri-*O*-methyl[18] analogs of **43*R*** and **43*S***. In both cases, the two conformers can be characterized as $^4H_3$ and $^5S_1$ conformations. With respect to the dioxolenium ions related to the 2-*O*-acetyl analog, two conformers characterized as $^4H_5$ and $^3S_1$ were found. Finally, the possibility of 3-*O*-acetyl participation, as found experimentally and computationally for L-fucopyranosyl donors,[19] was considered. Thus, for both **43*R*** and **43*S*** seven distinct conformers were considered: **B0** and **B1** (oxacarbenium ions), $\mathbf{C0_{ax}}$ and $\mathbf{C1_{ax}}$ (dioxolenium ions with C-1···O-7 axial), $\mathbf{C0_{eq}}$ and $\mathbf{C1_{eq}}$ (dioxolenium ions with C-1···O-7 equatorial) and **3Ac** (dioxolenium ions formed from 3-*O*-acetyl participation), where O-7 is the former carbonyl oxygen of the auxiliary (see Figure 1, a–l and Figure 2, a,b, for ball-and-stick representations).

The relative energies of these 14 species are tabulated in Table 3. For **43*R*** with the (*R*)-configured auxiliary, the trends are consistent with the model, specifically the (***R***)-$\mathbf{C0_{ax}}$ and (***R***)$\mathbf{C1_{ax}}$ (*cis*-decalin type) are more stable by >20 kJ mol^{-1} than either the (***R***)$\mathbf{C0_{eq}}$ or (***R***)$\mathbf{C1_{eq}}$ (*trans*-decalin type). In particular, the (***R***)$\mathbf{C0_{eq}}$ ion that most resembles the disfavored case in Scheme 1, c, is strongly destabilized even with respect to either the (***R***)**3Ac** or (***R***)**B0** ions. The (***R***)**B1** is more stable than intuitive arguments would suggest. It should be noted that this conformer allows O-2 to be pseudo-equatorial and O-3, O-4 and C-6 to be pseudo-axial. This preference for O-2 of pyranosyl oxacar-

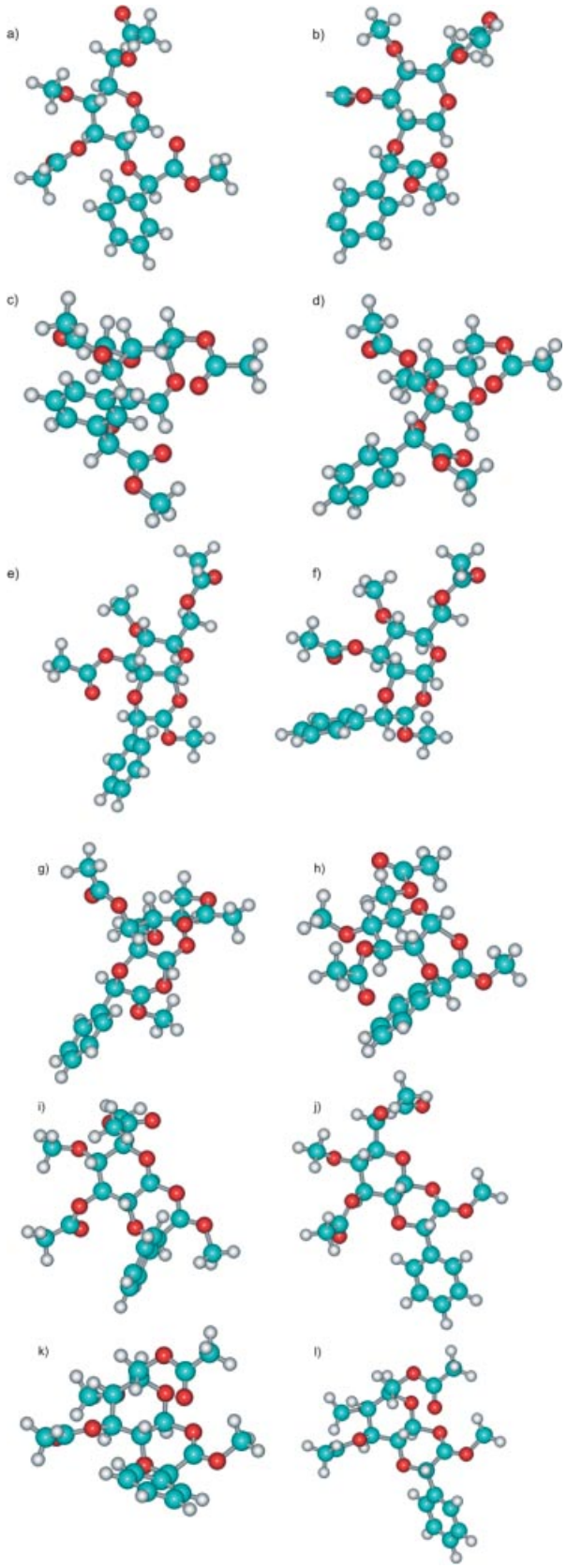


Figure 1. Ball-and-stick representations of a) (***R***)**B0** b) (***S***)**B0** c) (***R***)**B1** d) (***S***)**B1** e) (***R***)**C0**$_{ax}$ f) (***S***)**C0**$_{ax}$g) (***R***)**C1**$_{ax}$ h) (***S***)**C1**$_{ax}$ i) (***R***)-**C0**$_{eq}$ j) (***S***)**C0**$_{eq}$ k) (***R***)**C1**$_{eq}$ l) (***S***)**C1**$_{eq}$.

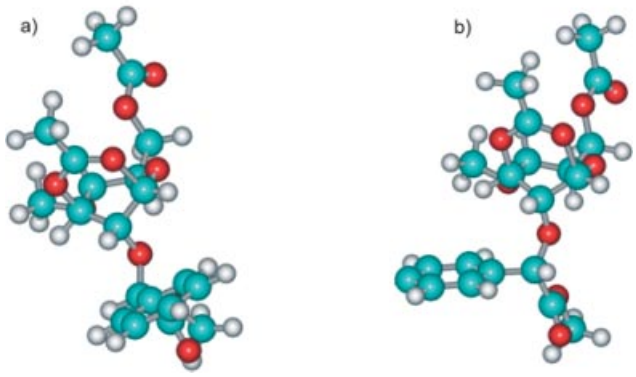


Figure 2. Ball-and-stick representations of 3-*O*-acetyl neighboring-group participation, a) (***R***)**3Ac** b) (***S***)**3Ac**.

benium ions to be pseudo-equatorial has been noted before and was estimated to provide an approximate stabilization of 15 kJ mol^{-1}.[20] For the diastereomer **43*S*** the results are in accordance to the model but with smaller distinctions. In this case, only one of the two *trans*-decalin isomers (***S***)**C1**$_{eq}$ is more stable than the (***S***)**C0**$_{ax}$ and (***S***)**C1**$_{ax}$ isomers by only about 7 kJ mol^{-1}. The (***S***)**C0**$_{ax}$ isomer shows an interaction between the phenyl of the auxiliary and the acetate at O-3, perhaps leading to its destabilization (see Figure 1, f).

Table 3. Relative energies of oxacarbenium ions **43*R*** and **43*S***.

Conformers	Δ*E* kJ mol^{-1}	Conformers	Δ*E* kJ mol^{-1}
***R*B0**	0	***S*B0**	–17.2
***R*B1**	–51.2	***S*B1**	–31.3
***R*C0**$_{ax}$	–72.8	***S*C0**$_{ax}$	–43.8
***R*C1**$_{ax}$	–62.8	***S*C1**$_{ax}$	–35.9
***R*C0**$_{eq}$	–17.4	***S*C0**$_{eq}$	–33.4
***R*C1**$_{eq}$	–41.6	***S*C1**$_{eq}$	–50.1
***R*3Ac**	–43.9	***S*3Ac**	–46.7

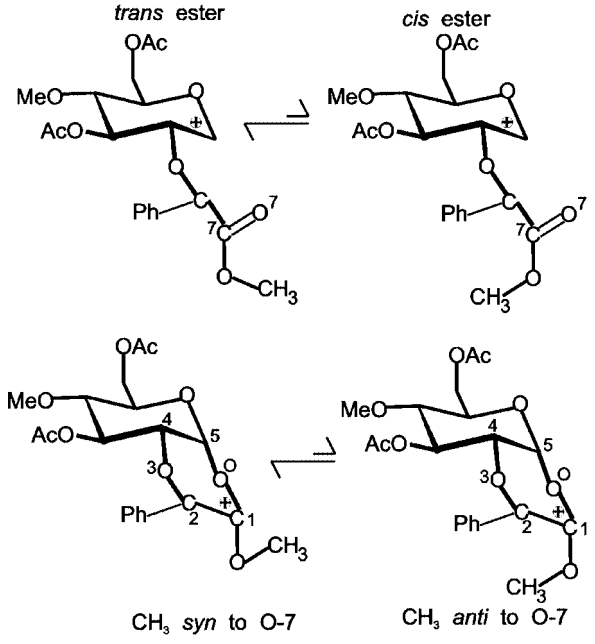
Table 4 depicts the ring dihedrals, which exhibit many of the expected trends. Notably τ_5 (C-5–O-5···C-1–C-2) is nearly planar in the **B0** and **B1** oxacarbenium ions.[21] However, once the dioxolenium ion is formed, this torsion angle changes dramatically, reflecting the hybridization change at C-1. Also shown is the ω_H (CH-5–C-5···C-6–O-6) torsion angle which was varied over the three staggered rotamers for all 14 species. Only the lowest energy rotamers are shownand these adopt the standard *gg* (ω_H about 180°) or *gt* (ω_H about –60°) conformations typical of D-glucopyranoses.[22] The unfavorable *tg* (ω_H about 60°) rotamer was consistently about 10 kJ mol^{-1} higher in energy. No evidence for pronounced O-6 participation was found in any of the calculated species. The *O*-acetyl and the *O*-methyl substituents were in each case found in conformations near their expected minimum-energy conformations.[23] In the dioxolenium ions, two possible conformers are inherently possible, one with the *O*-methyl carbon *syn* to O-7 and its *anti* isomer. These extremes correspond to the *trans* and *cis* isomers of normal *O*-esters. In all cases except for the high

Table 4. Ring dihedrals for six-membered sugar rings.

Conformers	τ_1 [°] C1C2–C3C4	τ_2 [°] C2C3–C4C5	τ_3 [°] C3C4–C5O5	τ_4 [°] C4C5–O5C1	τ_5 [°] C5O5–C1C2	τ_6 [°] O5C1–C2C3	ω_H [°] O6C6–C5H5	C1–O7 [Å]
***R*B0**	–58.5	64.7	–37.8	7.3	–4.1	30.4	179.4	2.499
***R*B1**	–12.5	–34.7	61.5	–41	–8.5	37.5	–50.5	2.724
***R*C0$_{ax}$**	–46.1	55.9	–55.8	47.8	–39.4	38.7	179.4	1.681
***R*C1$_{ax}$**	–8	–33.6	54.3	–30.8	–14.1	34.6	–63.1	1.722
***R*C0$_{eq}$**	–54.2	46.6	–46.1	55.6	–68.7	68.5	168.4	1.511
***R*C1$_{eq}$**	–35.3	–20.1	59.6	–38.6	–20.1	60.8	–58.8	1.583
***R*3Ac**	53.6	–8.9	–37.2	37.9	11.7	–58	173.8	1.694[a]
***S*B0**	–56.8	63.8	–36.5	3.6	1.7	25.7	–179.4	2.674
***S*B1**	–13.7	–26.5	53.6	–40.1	–3.4	31.9	–63.2	2.85
***S*C0$_{ax}$**	–47.9	58	–54.3	42.1	–35	38.4	175.5	1.745
***S*C1$_{ax}$**	–13.1	42.7	–64.1	59.3	–29.8	5.7	176.4	1.844
***S*C0$_{eq}$**	–56.7	48.8	–46.22	54	–66.6	68.4	168.5	1.508
***S*C1$_{eq}$**	–34.8	–20.8	59.1	–36.8	–22.2	61.7	–61.9	1.699
***S*3Ac**	53.9	–9.8	–36.4	37.9	11.3	–57.7	173.8	1.694[a]

[a] Former carbonyl oxygen of O-3 acetate to C-1 bond length.

energy isomer (***R*)C0$_{eq}$** (Figure 1, i), the *syn* isomers were >10 kJ mol^{-1} more stable than the *anti* isomers. This adds a further subtlety to the ring-closure step as presumably only the *trans* ester can cyclize (see Scheme 5).



Scheme 5. Schematic representation of the relationship between *cis* and *trans* ester conformation and the *syn* or *anti* conformation in the dioxolenium ions. Also depicted is the sugar-like numbering used for the six-membered rings of the dioxolenium ions.

Table 4 also shows the C-1···O-7 or C-1–O (3Ac, C=O) bond lengths, which might have been expected to correlate with relative energies. All bond lengths are close to 1.6 Å as observed in similar species.[16] No correlation with energies is apparent, so the main determinant of relative energies appears to be subtle interactions between protecting groups and the extra stabilization provided by dioxolenium ion formation.

Table 5 depicts the coefficients which correspond to the canonical vector representation of six-membered rings that quantitatively describe the conformations based on the 38 standard IUPAC conformations.[24] This method uses chair ($^1C_4$), boat ($^{1,4}B$) and skew-boat (^2S_O) canonical vectors as an orthogonal basis set. In cases where intermediate half chair or envelope conformations are populated, appropriate permutations of the *C*, *B* and *S* vectors lead to a new set of three vectors where the *H* or *E* conformer has the highest coefficient. The residual coefficients of the two less populated canonical vectors quantitatively show both the direction and magnitude of the distortion from the principle canonical vector. For example, conformation (***R*)B0** is close to half a chair and half a boat, therefore adopting an envelope (E_3) with some distortion towards $^4H_5$ and a very little towards $^4C_1$. It is important to note that its (*S*) isomer is an almost perfect E_3 envelope. In fact, all (*R*)/(*S*) pairs show the same ring conformation with the exception of the (***R*)-C1$_{ax}$/(*S*)C1$_{ax}$** pair. It was predicted in Scheme 1b that the **(*S*)C0$_{ax}$** and **(*S*)C1$_{ax}$** ions (*cis*-decalin type) were to be destabilized, which perhaps results in distortions. Figure 3 depicts the positions of all fourteen isomers in conformational space on a spherical representation.

The **B0** conformers are predominantly E_3 which is close in conformational space to the $^4H_3$ found for its analogs. Similarly, the **B1** conformations are $^5S_1$ as found for the analogs. Taken together, these results suggest that the collection of protecting groups has only a small influence on ring conformation. Because four of the decalin-type dioxolenium species are found to have chair conformers, they conform to the intuitive model. Of the remaining four, three have $^5S_1$ conformers with only the **(*S*)C1$_{ax}$** adopting the E_5 conformation. All of these conformations are quite distinct from the fused five-membered ring dioxolenium species discussed above.

While 5-membered ring dioxolenium ions are typically planar,[25] the situation for the six-membered rings considered here is less clear. One report found a half-chair conformation.[26] The ring dihedrals for the eight isomers consid-

Table 5. Coefficients for canonical vector representation of the conformations of the six-membered rings of the sugar.

Conformers	Chair	Boat	Skew-boat	Half chair envelope	Boat or other	Skew-boat or other
RB0	$^4C_1$ 0.563	$B_{O,3}$ 0.466	$^1S_5$ 0.067	E_3 0.932	$^4H_5$ 0.134	$^4C_1$ 0.030
RB1	$^1C_4$ 0.219	$B_{O,3}$ 0.043	$^5S_1$ 0.818	$^5S_1$ 0.818	$^1C_4$ 0.219	$B_{O,3}$ 0.043
RC0$_{ax}$	$^4C_1$ 0.788	$^{1,4}B$ 0.140	$^OS_2$ 0.011	$^4C_1$ 0.788	$^{1,4}B$ 0.140	$^OS_2$ 0.011
RC1$_{ax}$	$^1C_4$ 0.172	$^{O,3}B$ 0.037	$^5S_1$ 0.734	$^5S_1$ 0.734	$^1C_4$ 0.172	$^{O,3}B$ 0.037
RC0$_{eq}$	$^4C_1$ 0.944	$B_{1,4}$ 0.185	$^OS_2$ 0.007	$^4C_1$ 0.944	$B_{1,4}$ 0.185	$^OS_2$ 0.007
RC1$_{eq}$	$^1C_4$ 0.004	$B_{O,3}$ 0.141	$^5S_1$ 0.984	$^5S_1$ 0.984	$B_{O,3}$ 0.141	$^1C_4$ 0.004
R3Ac	$^1C_4$ 0.158	$B_{2,5}$ 0.778	$^1S_3$ 0.026	$B_{2,5}$ 0.778	$^1C_4$ 0.158	$^1S_3$ 0.026
SB0	$^4C_1$ 0.513	$B_{O,3}$ 0.495	$^1S_5$ 0.094	E_3 0.989	$^1S_5$ 0.094	$^4C_1$ 0.019
SB1	$^1C_4$ 0.198	$^{2,5}B$ 0.100	$^5S_1$ 0.707	$^5S_1$ 0.707	E_O 0.199	$^1C_4$ 0.098
SC0$_{ax}$	$^4C_1$ 0.766	$B_{2,5}$ 0.043	$^1S_3$ 0.188	$^4C_1$ 0.766	$^1S_3$ 0.188	$B_{2,5}$ 0.043
SC1$_{ax}$	$^4C_1$ 0.596	$B_{2,5}$ 0.436	$^1S_3$ 0.106	E_5 0.872	$^4H_3$ 0.212	$^4C_1$ 0.054
SC0$_{eq}$	$^4C_1$ 0.946	$B_{1,4}$ 0.167	^2S_O 0.027	$^4C_1$ 0.946	$B_{1,4}$ 0.167	^2S_O 0.027
SC1$_{eq}$	$^4C_1$ 0.005	$B_{O,3}$ 0.119	$^5S_1$ 0.989	$^5S_1$ 0.989	$B_{O,3}$ 0.119	$^4C_1$ 0.005
S3Ac	$^1C_4$ 0.157	$B_{2,5}$ 0.768	$^1S_3$ 0.035	$B_{2,5}$ 0.768	$^1C_4$ 0.157	$^1S_3$ 0.035

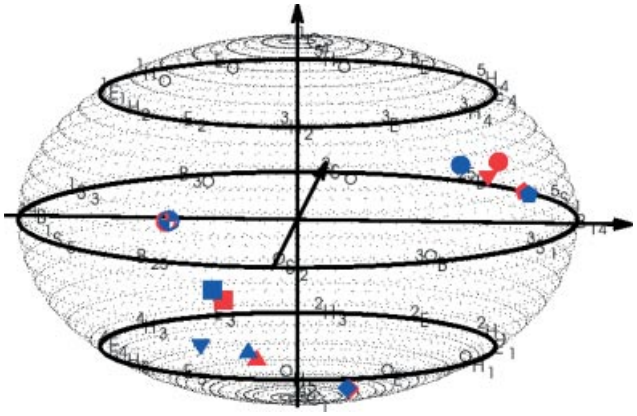


Figure 3. Spherical representation of the conformational space of six-membered rings with the 14 isomers of **43*R*** and **43*S***. Blue symbols represent (*S*)-configured auxiliaries and red symbols represent isomeric (*R*)-configuration. Squares **B0**, pentagons **B1**, triangles **C0$_{ax}$**, diamonds **C0$_{eq}$**, filled circles **C1$_{eq}$**, inverted triangles **C1$_{ax}$** and half filled circles **3-Ac**.

ered here and the corresponding canonical vector coefficients are tabulated in Table 6 and Table 7. In order to conform with the sugar numbering used for the descriptors, the former carbonyl oxygen is considered the ring oxygen and the former carbonyl carbon C-1, C-2 has the phenyl substituent etc. with clockwise numbering. All rings are half chairs with the (*R*)-auxiliary diastereomers having $^3H_4$ or the closely related E_4 and ^3E conformers, whereas the (*S*)-auxiliary diastereomers all exhibit the $^4H_3$ conformation. Using the above sugar numbering, τ_5 has a nearly planar conformation in all cases, strongly suggesting that considerable positive charge is delocalized onto the former ester atoms. In support of this concept the LUMOs for the two lowest energy species (***R***)**C0$_{ax}$** and (***S***)**C1$_{eq}$** are shown in Figure 4. These figures are consistent with considerable charge delocalization to the fused ring. Note that the parent **B**-type species have LUMOs concentrated on C-1···O-5 of the sugar ring and the five-membered dioxolenium ions have LUMOs with considerable *p* character on the former carbonyl carbon. The species considered in this work more closely resembles the five-membered dioxolenium species, but with a more delocalized charge.

The mechanism of nucleophilic attack on these new six-membered ring-fused dioxolenium ions remains to be addressed, in addition to a number of other issues including the lifetimes of these species and barriers to their formation and interconversions. All of these issues require detailed experimental and theoretical studies in order to arrive at suitable conclusions, as presently only speculations based on results with five-membered fused dioxolenium ions can be made. For example, five-membered dioxolenium ions can be isolated and studied.[27] Given that our calculations suggest these species are stable, it is likely that they would have a significant lifespan under some experimental conditions. The lifespan issue is one plausible explanation for the observed difference between 3-*O*-acetyl- vs. 3-*O*-allyl-substituted donors. Although our calculations show that such ions are predicted to be stable, the large conformational shift (see Figure 3) to obtain the requisite ring conformation (Figure 2, a,b) and the lesser stability of these ions

Table 6. Ring dihedrals for six-membered rings of the dioxolenium ions (see text for numbering).

Conformers	τ_1 [°] C1C2–C3C4	τ_2 [°] C2C3–C4C5	τ_3 [°] C3C4–C5O5	τ_4 [°] C4C5–O5C1	τ_5 [°] C5O5–C1C2	τ_6 [°] O5C1–C2C3
RC0$_{ax}$	44.9	–70.1	51.7	–21.3	0.2	–9.5
SC0$_{ax}$	33	–67.2	56.2	–26.7	–3.3	2.9
RC1$_{ax}$	44.2	–70.1	49.1	–14.5	–8.8	–3.6
SC1$_{ax}$	61.6	–58.7	25	–3	7.8	–33.4
RC0$_{eq}$	–49.8	69.3	–55.2	25.9	–8.2	19.5
SC0$_{eq}$	–40.2	68.7	–57.2	22	4.4	3.6
RC1$_{eq}$	–40.9	74.6	–60.9	22.8	7	0.6
SC1$_{eq}$	–41.2	74.5	–60.4	21	8.8	0.1

Table 7. Coefficients for canonical vector representation of the conformations of the six-membered rings of the dioxolenium ions (see text for numbering).

Conformers	Chair	Boat	Skew-boat	Half chair envelope	Boat or other	Skew-boat or other
***R*C0$_{ax}$**	$^{1}C_4$ 0.549	$^{2,5}B$ 0.077	$^{3}S_1$ 0.571	**$^{3}H_4$ 1.098**	$^{2,5}B$ 0.077	$^{3}S_1$ 0.022
***S*C0$_{ax}$**	$^{1}C_4$ 0.491	$B_{1,4}$ 0.540	$^{O}S_2$ 0.067	**E_4 0.983**	$^{O}S_2$ 0.067	$B_{1,4}$ 0.048
***R*C1$_{ax}$**	$^{1}C_4$ 0.480	$^{2,5}B$ 0.066	$^{3}S_1$ 0.647	**$^{3}H_4$ 0.959**	$^{3}S_1$ 0.167	$^{2,5}B$ 0.066
***S*C1$_{ax}$**	$^{1}C_4$ 0.526	$^{O,3}B$ 0.456	$^{1}S_5$ 0.068	**^{3}E 0.912**	$^{1}H_2$ 0.137	$^{1}C_4$ 0.002
***R*C0$_{eq}$**	$^{4}C_1$ 0.633	$B_{2,5}$ 0.049	$^{1}S_3$ 0.505	**$^{4}H_3$ 1.010**	$^{4}C_1$ 0.127	$B_{2,5}$ 0.049
***S*C0$_{eq}$**	$^{4}C_1$ 0.520	$B_{2,5}$ 0.147	$^{1}S_3$ 0.605	**$^{4}H_3$ 1.041**	$B_{2,5}$ 0.147	$^{1}S_3$ 0.085
***R*C1$_{eq}$**	$^{4}C_1$ 0.535	$B_{2,5}$ 0.176	$^{1}S_3$ 0.671	**$^{4}H_3$ 1.071**	$B_{2,5}$ 0.176	$^{1}S_3$ 0.136
***S*C1$_{eq}$**	$^{4}C_1$ 0.523	$B_{2,5}$ 0.167	$^{1}S_3$ 0.686	**$^{4}H_3$ 1.047**	$B_{2,5}$ 0.167	$^{1}S_3$ 0.163

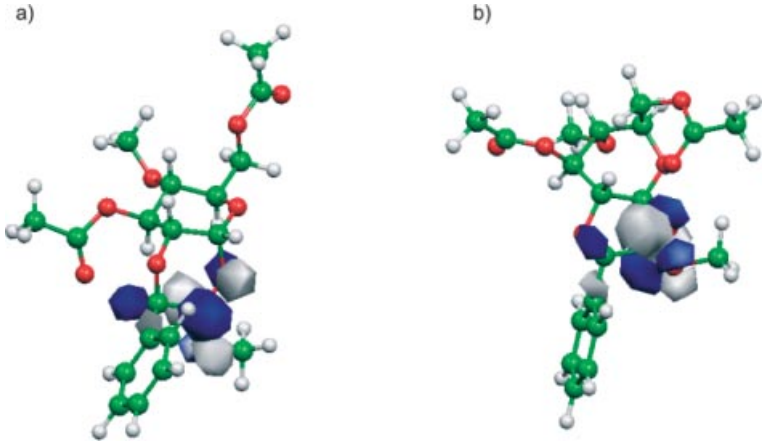


Figure 4. LUMOs of lowest energy isomers a) (***R***)**C0$_{ax}$** and b) (***S***)**C1$_{eq}$**.

when compared to the six-membered dioxolenium species (Table 3) suggests that there could be a significant kinetic barrier to their formation.[28] Because *O*-allyl is expected to be activating as compared to *O*-acetyl,[29] the corresponding **B0** and **B1** species should be more reactive and plausibly could react before either the six-membered dioxolenium species or the 3-Ac species form to any appreciable extent. Thus, it logically follows that more electron-withdrawing species at O-3 then acetyl could lead to more stereospecific glycosylations, obviously at the expense of reactivity. Clearly, a more complete set of protecting-group strategies should be studied before any firm conclusions can be made.

Conclusions

For the first time it has been shown that the anomeric selectivity of a glycosylation can be controlled by a chiral auxiliary. This new method for anomeric control is in particular suited for the introduction of α-glucosides. It is to be expected that a systematic optimization of the structure of the auxiliary will lead to a stereospecific glycosylation protocol. In particular, an improved auxiliary may be obtained by increasing its nucleophilicity or reducing the flexibility of rotatable bonds. Only such a method will make it possible for polymer supported and one-pot multi-step oligosaccharide syntheses to realize their potential for routine use for a large number of oligosaccharide targets.

Experimental *S*ection

The DFT calculations were carried out with the Amsterdam Density Functional (ADF) program system, ADF2000.[30] The atomic orbitals were described as an uncontracted double-ζ Slater function basis set with a single-ζ polarization function on all atoms which were taken from the ADF library. The 1s electrons on carbon and oxygen were assigned to the core and treated by the frozen core approximation. A set of s, p, d, f, and g Slater functions centered on all nuclei were used to fit the electron density, and to evaluate the Coulomb and exchange potentials accurately in each SCF cycle. The local part of the V_{xc} potential (LDA) was described using the VWN parametrization,[31] in combination with the gradient-corrected (CGA) Becke's functional[32] for the exchange and Perdew's function for correlation (BP86).[33] The CGA approach was applied self-consistently in geometry optimizations. Second derivatives were evaluated numerically by a two-point formula. The solvation parameters were dielectric constant $\varepsilon = 9.03$, ball radius 2.4 Å, with atomic radii of 1.7 (C), 1.4 (O) and 1.2 Å (H).

All input structures were generated using the Hyperchem 7.0 program package. Initial conformations were made using standard geometries according to ref.[23] above, and all side chains were minimized after extensive conformational searching using semi empirical methods. Side-chain conformations were further tested using DFT above. In particular all 3 rotamers about C-5···C-6 were considered and the conformation about the former carbonyl bond in the six-membered dioxolenium species were varied between the two minimum. Ball-and-stick representations were made using Hyperchem 7.0 from the ADF output. The spherical representations of the conformations were plotted using Gnu-plot. The LUMOs were plotted from the ADF output using the Molekel program.

General Procedures: All reactions were carried out under a positive pressure of argon unless otherwise noted. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. Dichloromethane was distilled from calcium hydride under nitrogen. Toluene was distilled from molten sodium under nitrogen. Dimethylformamide (DMF) was distilled from barium oxide under nitrogen. Column chromatography was performed on silica gel 60 (EM Science, 70–230 mesh). Reactions were monitored by TLC on kieselgel 60 F_{254} (EM Science), and the compounds were detected by examination under UV light and visualized by dipping the plates in a cerium sulfate/ammonium molybdate solution followed by heating. Organic solutions were concentrated by rotary evaporation below 40 °C under reduced pressure. Molecular sieves (3 Å and 4 Å) were crushed and activated in vacuo at 400 °C for 5 h. Optical rotations were measured with a "Jasco P-1020" polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian Inova 300 spectrometer and a Varian Inova 500 spectrometer equipped with Sun workstations. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, *t* = triplet, dd = double of doublet, m = multiplet and/or multiple resonances), integration, coupling constant in Hertz (Hz). High-resolution mass spectrometry was run in a JMS SX/SX102A tandem mass spectrometer, equipped with FAB source. The matrix used was DHB and the internal standards ultramark 1621 and PEG.

1,6-Anhydro-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-glucopyranose (2*S*): BF_3–OEt_2 (543 μL, 4.27 mmol) was added dropwise to a mixture of 1,6:2,3-di-anhydro-4-*O*-benzyl-β-D-mannopyranose (**1**) (5 g, 21.3 mmol), ethyl (*S*)-mandelate (11.5 g, 63.9 mmol) and activated molecular sieves (4 Å, 2 g) in toluene (20 mL) at room temperature. After stirring for 1 h, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ solution (30 mL) and then diluted with ethyl acetate (30 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford **2*S*** (4.23 g, 48%): colorless syrup, R_f = 0.34 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +40.3 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.48 (m, 10 H, aromatic), 5.54 (s, 1 H, 1-H), 5.22 (s, 1 H, >C*H*Ph), 4.63 (d, *J* = 12.3 Hz, 1 H, C*H*HPh), 4.61 (d, *J* = 12.3 Hz, 1 H, C*H*HPh), 4.54 (d, *J* = 5.4 Hz, 1 H, 5-H), 4.13–4.23 (m, 2 H, COOCH_2CH$_3$), 3.88 (t, *J* = 4.8 Hz, 1 H, 3-H), 3.73 (d, *J* = 7.5 Hz, 1 H, 6-H$_a$), 3.61 (dd, *J* = 5.4, 7.2 Hz, 1 H, 6-H$_b$), 3.33 (d, *J* = 4.8 Hz, 1 H, 2-H), 3.29 (d, *J* = 4.8 Hz, 1 H, 4-H), 2.61 (br, 1 H, OH), 1.21 (t, *J* = 7.2 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.07, 137.79, 136.01, 128.73, 128.59, 128.43, 127.78, 127.75, 127.50, 101.80, 80.49, 80.17, 80.02, 75.48, 71.80, 71.25, 66.85, 61.43, 14.01 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{23}H_{26}O_7$ [M + Na]$^+$ 437.1577, found 437.1532.

1,6-Anhydro-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranose (2*R*): Compound **2*R*** was synthesized from compound **1** and ethyl (*R*)-mandelate according to the procedure described for the synthesis of compound **2*S***: Colorless syrup, R_f = 0.35 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = –10.3 (*c* = 1.2, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.45 (m, 10 H, aromatic), 5.34 (s, 1 H, 1-H), 5.11 (s, 1 H, >C*H*Ph), 4.83 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.67 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.51 (d, *J* = 5.1 Hz, 1 H, 5-H), 4.06–4.23 (m, 2 H, COOCH_2CH$_3$), 3.99 (t, *J* = 6.3 Hz, 1 H, 3-H), 3.57–3.65 (m, 2 H, 6-H$_a$, 6-H$_b$), 3.34 (d, *J* = 6.3 Hz, 1 H, 2-H), 3.24 (d, *J* = 6.3 Hz, 1 H, 4-H), 1.17 (t, *J* = 7.2 Hz, 1 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.84, 138.04, 135.85, 128.65, 128.46, 128.27, 127.70, 127.56, 127.06, 101.78, 83.17, 81.24, 79.89, 76.18, 72.57, 71.81, 67.31, 61.67, 13.82 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{23}H_{26}O_7$ [M + Na]$^+$ 437.1577, found 437.1548.

1,3,6-Tri-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α/β-D-glucopyranose (3*S*): Trimethylsilyl trifluoromethanesulfonate (24 μL, 0.13 mmol) was added to a solution of **2*S*** (6.52 g, 6.52 mmol) in acetic anhydride (10 mL) at 0 °C. After the reaction mixture was stirred at 0 °C for 20 min, it was quenched with an aqueous saturated solution of $NaHCO_3$, and the resulting mixture was extracted with DCM (2 × 30 mL). The organic phase was washed with water (30 mL) and brine (30 mL) and dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford **3*Sα*** (2.69 g, 74%): colorless syrup, R_f = 0.57 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +164 (*c* = 2.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.35 (m,10 H, aromatic), 6.44 (d, *J* = 3.6 Hz, 1 H, 1-H), 5.57 (t, *J* = 9.6 Hz, 1 H, 3-H), 4.96 (s, 1 H, >C*H*Ph), 4.55 (d, *J* = 11.1 Hz, 1 H, C*H*HPh), 4.48 (d, *J* = 11.1 Hz, 1 H, C*H*HPh), 4.25 (d, *J* = 3.0 Hz, 2 H, 6-H$_a$, 6-H$_b$), 4.08–4.20 (m, 2 H, COOCH_2CH$_3$), 3.97–4.02 (m, 1 H, 5-H), 3.61 (dd, *J* = 3.6, 9.9 Hz, 1 H, 2-H), 3.55 (t, *J* = 9.6 Hz, 1 H, 4-H) 2.18 (s, 3 H, COCH$_3$), 2.05 (s, 3 H, COCH$_3$), 1.88 (s, 3 H, COCH$_3$), 1.20 (t, *J* = 7.2 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.46, 169.93, 169.47, 169.23, 137.02, 135.82, 128.83, 128.54, 128.13, 128.09, 127.22, 89.40, 81.44, 76.27, 75.48, 74.58, 73.21, 70.71, 62.37, 61.48, 20.97, 20.86, 20.77, 13.93 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{29}H_{34}O_{11}$ [M + Na]$^+$ 581.1999, found 581.1983. **3*Sβ*)** (0.69 g, 19%): colorless syrup, R_f = 0.62 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +120 (*c* = 1.2, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19–7.38 (m,10 H, aromatic), 5.73 (d, *J* = 8.1 Hz, 1 H, 1-H), 5.37 (t, *J* = 9.0 Hz, 1 H, 3-H), 4.99 (s, 1 H, >C*H*Ph), 4.51 (d, *J* = 11.1 Hz, 1 H, C*H*HPh), 4.46 (d, *J* = 11.1 Hz, 1 H, C*H*HPh), 4.29 (dd, *J* = 2.4, 12.3 Hz, 1 H, 6-H$_a$), 4.21 (dd, *J* = 4.5, 12.3 Hz, 1 H, 6-H$_b$), 4.05–4.17 (m, 2 H, COOCH_2CH$_3$), 3.71–3.76 (m, 1 H, 5-H), 3.49–3.56 (m, 2 H, 4-H, 2-H), 2.15 (s, 3 H, COCH$_3$), 2.04 (s, 3 H, COCH$_3$), 1.60 (s, 3 H, COCH$_3$), 1.83 (t, *J* = 7.2 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.51, 170.20, 169.43, 168.53, 137.04, 136.65, 128.71, 128.54, 128.15, 128.07, 127.18, 93.51, 83.08, 80.00, 77.20, 75.47, 74.71, 74.31, 73.50, 62.44, 61.37, 20.97, 20.82, 20.62, 13.98 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{29}H_{34}O_{11}$ [M + Na]$^+$ 581.1999, found 581.1947.

1,3,6-Tri-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α/β-D-glucopyranose (3*R*): Compound **3*R*** was synthesized according to the procedure described for the synthesis of compound **3*S***. **3*Rα*:** Colorless syrup, R_f = 0.55 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +99.9 (*c* = 2.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.37 (m, 10 H, aromatic), 6.29 (d, *J* = 3.6 Hz, 1 H, 1-H), 5.58 (t, *J* = 9.9 Hz, 1 H, 3-H), 4.98 (s, 1 H, >C*H*Ph), 4.66 (d, *J* = 10.8 Hz, 1 H, C*H*HPh), 4.55 (d, *J* = 10.8 Hz, 1 H, C*H*HPh), 4.26 (d, *J* = 2.7 Hz, 2 H, 6-H$_a$, 6-H$_b$), 4.09–4.21 (m, 2 H, COOCH_2CH$_3$), 3.96–4.01 (m, 1 H, 5-H), 3.68 (dd, *J* = 3.6, 9.9 Hz, 1 H, 2-H), 3.66 (t, *J* = 9.9 Hz, 1 H, 4-H), 2.18 (s, 3 H, COCH$_3$), 2.05 (s, 3 H, COCH$_3$), 2.01 (s, 3 H, COCH$_3$), 1.20 (t, *J* = 7.2 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.46, 170.05, 169.94, 169.04, 137.19, 135.85, 128.72, 128.54, 128.49, 128.11, 128.07, 127.01, 88.72, 79.66, 75.89, 75.06, 74.65, 72.95, 70.84, 62.36, 61.25, 21.15, 20.76, 14.00 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{29}H_{34}O_{11}$ [M + Na]$^+$ 581.1999, found 581.1989. **3*Rβ*):** colorless syrup, R_f = 0.60 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = –38 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.34 (m,10 H, aromatic), 5.59 (d, *J* = 8.1 Hz, 1 H, 1-H), 5.44 (t, *J* = 9.3 Hz, 1 H, 3-H), 5.10 (s, 1 H, >C*H*Ph), 4.63 (d, *J* = 11.1 Hz, 1 H, C*H*HPh), 4.54 (d, *J* =

11.1 Hz, 1 H, C*H*HPh), 4.20–4.30 (m, 2 H, 6-H_a, 6-H_b), 4.05–4.21 (m, 2 H, COOCH_2CH$_3$), 3.55–3.74 (m, 3 H, 5-H, 2-H, 4-H), 2.15 (s, 3 H, COCH_3), 2.03 (s, 3 H, COCH_3), 1.85 (s, 3 H, COCH_3), 1.20 (t, J = 7.2 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.51, 170.11, 169.94, 168.45, 137.18, 136.47, 128.61, 128.57, 128.51, 128.15, 128.09, 126.80, 93.57, 82.00, 79.10, 75.33, 75.00, 74.46, 73.65, 62.45, 61.29, 21.19, 20.82, 20.65, 14.06 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{29}H_{34}O_{11}$ [M + Na]$^+$ 581.1999, found 581.1983.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α/β-D-glucopyranosyl Trichloroacetimidate (5*S*): Hydrazinium acetate (254 mg, 2.76 mmol) was added to a solution of **3*S*** (1.40 g, 2.51 mmol) in DMF (10 mL) at room temperature. After stirring the reaction mixture for 18 h, it was quenched with an aqueous saturated solution of $NaHCO_3$. The mixture was extracted with ethyl acetate (30 mL), and the organic phase was washed with an aqueous saturated solution of NH_4Cl (30 mL) and dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford **4*S*** (1.23 g, 95%). Trichloroacetonitrile (2.38 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (143 μL) were added to a solution of **4*S*** (1.23 g, 2.38 mmol) in dichloromethane (10 mL) at 0 °C. After stirring the reaction mixture for 1 h, it was concentrated in vacuo. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford **5*S*α** (1.21 g, 77%): R_f = 0.65 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +107.4 (c = 2.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68 (s, 1 H, NH), 7.23–7.38 (m,10 H, aromatic), 6.68 (d, J = 3.6 Hz, 1 H, 1-H), 5.65 (t, J = 9.6 Hz, 1 H, 3-H), 5.03 (s, 1 H, >C*H*Ph), 4.56 (d, J = 11.1 Hz, 1 H, C*H*HPh), 4.51 (d, J = 11.1 Hz, 1 H, C*H*HPh), 4.32 (dd, J = 2.1, 12.0 Hz, 1 H, 6-H_a), 4.24 (dd, J = 3.9, 12.0 Hz, 1 H, 6-H_b), 4.08–4.19 (m, 3 H, COOCH_2CH$_3$, 5-H), 3.72 (dd, J = 3.6, 9.9 Hz, 1 H, 2-H), 3.61 (t, J = 9.9 Hz, 1 H, 4-H), 2.04 (s, 3 H, COCH_3), 1.87 (s, 3 H, COCH_3), 1.20 (t, J = 7.2 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.46, 170.25, 169.31, 161.20, 137.01, 135.78, 128.77, 128.57, 128.48, 128.27, 128.20, 127.05, 93.93, 81.80, 76.67, 75.35, 74.47, 73.35, 71.10, 62.35, 61.51, 20.85, 20.78, 14.01. **5*S***(β) (0.24 g, 15%): R_f = 0.69 (ethyl acetate/hexane, 1:1) ppm. $[\alpha]_D^{20}$ = +126.7 (c = 1.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.73 (s, 1 H, NH), 7.19–7.43 (m,10 H, aromatic), 6.03 (d, J = 6.9 Hz, 1 H, 1-H), 5.32 (t, J = 8.1 Hz, 1 H, 3-H), 5.32 (s, 1 H, >C*H*Ph), 4.52 (d, J = 11.4 Hz, 1 H, C*H*HPh), 4.46 (d, J = 11.4 Hz, 1 H, C*H*HPh), 4.32 (dd, J = 2.1, 12.0 Hz, 1 H, 6-H_a), 4.21 (dd, J = 3.9, 12.0 Hz, 1 H, 6-H_b), 4.02–4.15 (m, 2 H, COOCH_2CH$_3$), 3.78–3.83 (m, 1 H, 5-H), 3.65–3.71 (m, 2 H, 2-H, 4-H), 2.00 (s, 3 H, COCH_3), 1.75 (s, 3 H, COCH_3), 1.14 (t, J = 7.2 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.49, 169.82, 169.56, 160.26, 137.08, 136.46, 128.86, 128.59, 128.50, 128.10, 127.99, 97.61, 81.06, 75.10, 74.92, 74.04, 72.89, 62.36, 61.24, 20.86, 20.80, 13.95 ppm.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α/β-D-glucopyranosyl Trichloroacetimidate (5*R*): Compound **5*R*** was synthesized according to the procedure described for the synthesis of compound **5*S***. **5*R*α**: R_f = 0.67 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +61.0 (c = 1.8, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (s, 1 H, NH), 7.26–7.37 (m,10 H, aromatic), 6.49 (d, J = 3.3 Hz, 1 H, 1-H), 5.70 (t, J = 9.6 Hz, 1 H, 3-H), 5.04 (s, 1 H, >C*H*Ph), 4.68 (d, J = 11.1 Hz, 1 H, C*H*HPh), 4.57 (d, J = 11.1 Hz, 1 H, C*H*HPh), 4.11–4.34 (m, 5 H, 6-H_a, 6-H_b, 5-H, COOCH_2CH$_3$), 3.77 (dd, J = 3.6, 9.9 Hz, 1 H, 2-H), 3.71 (t, J = 9.9 Hz, 1 H, 4-H), 2.17 (s, 3 H, COCH_3), 2.03 (s, 3 H, COCH_3), 1.21 (t, J = 7.2 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.42, 169.97, 169.90, 160.77, 137.15, 135.91, 128.54, 128.47, 128.29, 128.19, 128.15, 126.81, 92.96, 79.72, 76.37, 74.89, 74.58, 72.74, 71.21, 62.28, 61.25, 21.13, 20.74, 14.03. **5*R***(β): R_f = 0.71 (ethyl acetate/hexane, 1:1) ppm. $[\alpha]_D^{20}$ = +47 (c = 1.3, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (s, 1 H, NH), 7.26–7.37 (m,10 H, aromatic), 5.83 (d, J = 7.5 Hz, 1 H, 1-H), 5.45 (s, 1 H, >C*H*Ph), 5.44 (t, J = 9.6 Hz, 1 H, 3-H), 4.68 (d, J = 11.4 Hz, 1 H, C*H*HPh), 4.58 (d, J = 11.4 Hz, 1 H, C*H*HPh), 4.33 (d, J = 12.3 Hz, 1 H, 6-H_a), 4.26 (dd, J = 2.4, 12.3 Hz, 1 H, 6-H_b), 4.08–4.22 (m, 3 H, COOCH_2CH$_3$, 5-H), 3.73–3.82 (m, 2 H, 2-H, 4-H), 2.19 (s, 3 H, COCH_3), 2.02 (s, 3 H, COCH_3), 1.20 (t, J = 7.2 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.54, 170.42, 170.36, 160.30, 137.29, 136.14, 128.76, 128.54, 128.44, 128.13, 126.83, 97.85, 79.90, 77.24, 77.20, 74.96, 74.26, 73.32, 62.41, 61.15, 21.28, 20.82, 14.08 ppm.

1,6-Anhydro-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranose (6*R*): Tetramethyl ethylenediamine (117 μL, 0.78 mmol) was added to a solution of **2*R*** (250 mg, 0.60 mmol) and benzoyl chloride (139 μL, 1.20 mmol) in dichloromethane (10 mL) at 0 °C. After stirring the reaction mixture for 1 h at 0 °C, it was warmed to room temperature and stirring was continued for 2 h. The reaction mixture was quenched with an aqueous saturated solution of $NaHCO_3$ (10 mL), and then diluted with dichloromethane (10 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate, 3:1) to afford **6*R*** (296 mg, 95%): colorless syrup, R_f = 0.65 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = –27 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.0 Hz, 2 H), 7.26–7.60 (m, 13 H), 5.51 (s, 1 H), 5.38 (s, 1 H), 5.29 (d, J = 5.5 Hz, 1 H), 4.94 (dd, J = 12.5 Hz, 1 H, CH*H*Ph), 4.77 (dd, J = 12.5 Hz, 1 H, C*H*HPh), 4.65 (d, J = 5.5 Hz, 1 H), 4.15 (m, 2 H, COOCH_2CH$_3$), 3.97 (d, J = 7.5 Hz, 1 H), 3.76 (t, J = 7.0 Hz, 1 H), 3.46 (s, 1 H), 3.40 (s, 1 H), 1.19 (t, J = 8.5 Hz, 3 H, COOCH$_2$CH_3) ppm. HR MALDI-TOF MS: m/z calcd. for $C_{30}H_{30}O_8$ [M + Na]$^+$ 541.1838, found 541.1827.

1,6-Anhydro-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-glucopyranose (6*S*): Compound **6*S*** was synthesized according to the procedure described for the synthesis of compound **6*R***. R_f = 0.51 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = –37 (c = 0.7, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21–8.03 (m, 15 H, Ar), 5.78 (s, 1 H, 1-H), 5.36 (s, 1 H, >CHPh), 5.27 (s, 1 H, 3-H), 4.71 (d, J = 12.0 Hz, 1 H, CH*H*Ph), 4.61 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.16–4.22 (m, 2 H, COOCH_2CH$_3$), 4.05 (d, J = 7.5 Hz, 1 H, 6-H_b), 3.84 (t, J = 7.0 Hz, 1 H, 6-H_a), 3.52 (s, 1 H, 2-H), 3.42 (s, 1 H, 4-H), 1.22 (t, J = 7.5 Hz, 3 H, COOCH$_2$CH_3) ppm. HR MALDI-TOF MS: m/z calcd. for $C_{30}H_{30}O_8$ [M + Na]$^+$ 541.1838, found 541.1843.

1,6-Di-*O*-acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α/β-D-glucopyranose (7*R*): Trimethylsilyl trifluoromethanesulfonate (0.2 μL, 0.01 mmol) was added to a solution of **6*R*** (215 mg, 0.41 mmol) in acetic anhydride (3 mL) at 0 °C. After stirring the reaction mixture for 30 min at 0 °C, it was quenched with an aqueous saturated solution of $NaHCO_3$ (10 mL) and then diluted with dichloromethane (10 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash silica gel column chromatography (20% ethyl acetate in hexane) to afford **7*R*** (244 mg, 96%). **7*R*α**: colorless syrup, R_f = 0.62 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +97 (c = 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.13–8.18 (m, 15 H, Ar), 6.26 (d, J = 3.5 Hz, 1 H, 1-H), 5.87 (t, J = 10.0 Hz, 1 H, 3-H), 4.98 (s, 1 H, >CHPh), 4.60 (d, J = 11.0 Hz, 1 H, CH*H*Ph), 4.49 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.27–4.28 (m, 1 H, 6-H_b), 4.03–4.05 (m, 1 H, 5-H), 3.94–3.97 (m, 2 H, COOCH_2CH$_3$), 3.89

(dd, J = 3.5 Hz, 10.0 Hz, 1 H, 2-H), 3.84–3.88 (m, 1 H, 6-H_a), 3.77 (t, J = 10.0 Hz, 1 H, 4-H), 2.07 (s, 3 H, $COCH_3$), 2.05 (s, 3 H, $COCH_3$), 0.97 (t, J = 7.5 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: m/z calcd. for $C_{34}H_{36}O_{11}$ $[M + Na]^+$ 643.2155, found 643.2138.

1,6-Di-*O*-acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α/β-D-glucopyranose (7*S*): Compound **7*S*** was synthesized according to the procedure described for the synthesis of compound **7*R***. **7*S*α:** R_f = 0.55 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = –47 (c = 0.3, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.08–7.99 (m, 15 H, Ar), 6.54 (d, J = 3.6 Hz, 1 H, 1-H), 5.82 (t, J = 9.6 Hz, 1 H, 3-H), 4.95 (s, 1 H, >CHPh), 4.52 (d, J = 10.8 Hz, 1 H, CH*H*Ph), 4.43 (d, J = 10.8 Hz, 1 H, C*H*HPh), 4.28–4.29 (m, 2 H, 6-H_a, 6-H_b), 4.07–4.15 (m, 3 H, 5-H, $COOCH_2CH_3$), 3.76 (dd, J = 3.5, 9.6 Hz, 1 H, 2-H), 3.70 (t, J = 9.6 Hz, 1 H, 4-H), 2.20 (s, 3 H, $COCH_3$), 2.07 (s, 3 H, $COCH_3$), 1.15 (t, J = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: m/z calcd. for $C_{34}H_{36}O_{11}$ $[M + Na]^+$ 643.2155, found 643.2098.

6-*O*-Acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α/β-D-glucopyranosyl Trichloroacetimidate (9*R*): Hydrazinium acetate (33 mg, 0.36 mmol) was added to a solution of compound **7*R*** (205 mg, 0.33 mmol) in DMF (5 mL) at room temperature. After stirring for 18 h, the reaction mixture was quenched with an aqueous saturated solution of $NaHCO_3$ (10 mL), and diluted with ethyl acetate (10 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate; 3:1) to afford **8*R*** (168 mg, 88%). Trichloroacetonitrile (290 μL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 17 μL) were added to a solution of **8*R*** (168 mg, 0.29 mmol) in dichloromethane (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and after which it was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate, 3:1) to afford **9*R***. (199 mg, 95%). **9*R*α:** yellowish syrup, R_f = 0.65 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +104 (c = 0.8, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.46 (s, 1 H, =NH), 7.13–8.18 (m, 15 H, Ar), 6.47 (d, J = 3.6 Hz, 1 H, 1-H), 5.97 (t, J = 9.6 Hz, 1 H, 3-H), 5.04 (s, 1 H, >CHPh), 4.61 (d, J = 10.5 Hz, 1 H, CH*H*Ph), 4.51 (d, J = 10.5 Hz, 1 H, C*H*HPh), 4.28–4.31 (m, 1 H, 5-H), 4.17–4.20 (m, 1 H, 6-H_a), 4.12 (q, J = 7.2 Hz, 2 H, $COOCH_2CH_3$), 3.99 (dd, J = 3.6, 9.9 Hz, 1 H, 2-H), 3.92–3.94 (m, 1 H, 6-H_b), 3.83 (t, J = 9.9 Hz, 1 H, 4-H), 2.04 (s, 3 H, $COCH_3$), 1.20 (t, J = 7.2 Hz, 3 H, $COOCH_2CH_3$) ppm.

6-*O*-Acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α/β-D-glucopyranosyl Trichloroacetimidate (9*S*): Compound **9*S*** was synthesized according to the procedure described for the synthesis of compound **9*R***. **9*S*α:** R_f = 0.58 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +72 (c = 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.68 (s, 1 H, =NH), 7.06–7.62 (m, 15 H, Ar), 6.75 (d, J = 3.0 Hz, 1 H, 1-H), 5.94 (t, J = 9.5 Hz, 1 H, 3-H), 4.99 (s, 1 H, >CHPh), 4.34 (dd, J = 2.0, 12.0 Hz, 1 H, 6-H_a), 4.28 (dd, J = 3.5, 12.0 Hz, 1 H, 6-H_b), 4.19–4.21 (m, 1 H, 5-H), 4.11 (q, J = 7.0 Hz, 2 H, $COOCH_2CH_3$), 3.86 (dd, J = 3.0, 9.5 Hz, 1 H, 2-H), 3.76 (t, J = 9.5 Hz, 1 H, 4-H), 2.05 (s, 3 H, $COCH_3$), 1.15 (t, J = 7.0 Hz, 3 H) ppm.

1,6-Anhydro-3-*O*-allyloxycarbonyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranose (10*R*): Tetramethyl ethylenediamine (98 μL, 0.65 mmol) was added to a solution of **2*R*** (207 mg, 0.50 mmol) and allyloxycarbonyl chloride (106 μL, 1.0 mmol) in dichloromethane (10 mL) at 0 °C. Then the reaction mixture was warmed to room temperature and stirred for 2 hours. The reaction mixture was quenched with an aqueous saturated solution of $NaHCO_3$ (10 mL) and then diluted with dichloromethane (10 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate, 3:1) to afford **10*R*** (217 mg, 87%): colorless syrup, R_f = 0.58 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +17 (c = 0.8, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.48 (m, 10 H, Ar), 5.89–5.97 (m, 1 H, C*H*=CH_2), 5.41 (s, 1 H, 1-H), 5.36 (d, J = 17.0 Hz, 1 H, CH*H*=CH), 5.29 (d, J = 10.5 Hz, 1 H, C*H*H=CH), 5.21 (s, 1 H, >CHPh), 4.96 (s, 1 H), 4.84 (d, J = 12.5 Hz, 1 H, CH*H*Ph), 4.70 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.64 (d, J = 6.0 Hz, 2 H), 4.59 (d, J = 5.5 Hz, 1 H), 4.14–4.19 (m, 2 H, $COOCH_2CH_3$), 3.85 (d, J = 12.5 Hz, 1 H), 3.67 (dd, J = 10.0, 12.0 Hz, 1 H), 3.37 (d, J = 8.5 Hz, 2 H, 2-H, 6-H_b), 1.19 (t, J = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: m/z calcd. for $C_{27}H_{30}O_9$ $[M + Na]^+$ 521.1787, found 521.1762.

3-*O*-Allyloxycarbonyl-1,6-anhydro-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-glucopyranose (10*S*): Compound **10*S*** was synthesized according to the procedure described for the synthesis of compound **10*R***. Colorless syrup, R_f = 0.53 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = –35 (c = 0.7, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.21–7.81 (m, 10 H, Ar), 5.90–5.91 (m, 1 H, C*H*=CH_2), 5.70 (s, 1 H, 1-H), 5.39–5.40 (m, 1 H, CH*H*=CH), 5.35–5.36 (m, 1 H, C*H*H=CH), 5.29 (s, 1 H, >CHPh), 4.80–4.83 (m, 1 H), 4.61–4.66 (m, 2 H, OC*H*HCH=CH_2, OCH*H*CH=CH_2), 4.62 (d, J = 12.0 Hz, 1 H, CH*H*Ph), 4.55 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.15–4.23 (m, 3 H, $COOCH_2CH_3$), 3.91 (d, J = 7.5 Hz, 1 H), 3.83 (dd, J = 6.0, 8.0 Hz, 1 H), 3.72 (dd, J = 6.0, 7.5 Hz, 1 H), 3.45–3.46 (m, 1 H), 1.23 (t, J = 7.5 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: m/z calcd. for $C_{27}H_{30}O_9$ $[M + Na]^+$ 521.1787, found: 521.1782.

1,6-Di-*O*-acetyl-3-*O*-allyloxycarbonyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α-D-glucopyranose (11*R*): Trimethylsilyl trifluoromethanesulfonate (0.2 μL, 0.01 mmol) was added to a solution of **10*R*** (175 mg, 0.35 mmol) in acetic anhydride (3 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min. After which it was quenched with an aqueous saturated solution of $NaHCO_3$ (10 mL) and then diluted with dichloromethane (10 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate, 3:1) to afford **11*R*** (206 mg, 98%): colorless syrup, R_f = 0.59 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = –67 (c = 2.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.38 (m, 10 H, Ar), 6.21 (d, J = 3.0 Hz, 1 H, 1-H), 5.93–6.03 (m, 1 H, C*H*=CH_2), 5.39 (t, J = 9.5 Hz, 1 H, 3-H), 5.29 (dd, J = 7.5, 18.0 Hz, 1 H, CH=CH*H*), 5.25 (dd, J = 10.5, 18.0 Hz, 1 H, CH=C*H*H), 5.00 (s, 1 H, >CHPh), 4.72 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.68–4.73 (m, 2 H, OC*H*HCH=CH_2, OCH*H*CH=CH_2), 4.55 (d, J = 11.0 Hz, 1 H, CH*H*Ph), 4.21–4.28 (m, 2 H, 6-H_a, 6-H_b), 4.15 (q, J = 7.0 Hz, 2 H, $COOCH_2CH_3$), 3.95–3.97 (m, 1 H, 5-H), 3.73 (dd, J = 3.0, 9.5 Hz, 1 H, 2-H), 3.66 (t, J = 9.5 Hz, 1 H, 4-H), 2.02 (s, 6 H, $COCH_3$), 1.19 (t, J = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: m/z calcd. for $C_{31}H_{36}O_{12}$ $[M + Na]^+$ 623.2104, found 623.2124.

1,6-Di-*O*-acetyl-3-*O*-allyloxycarbonyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranose (11*S*): Compound **11*S*** was synthesized according to the procedure described for the synthesis of compound **11*R***. R_f = 0.68 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +43.8 (c = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.38 (m, 10 H, Ar), 6.48 (d, J = 3.5 Hz, 1 H, 1-H), 5.82–5.87 (m, 1 H, C*H*=CH_2), 5.37 (t, J = 9.5 Hz, 1 H, 3-H), 5.30–5.35 (m, 1 H, CH*H*=CH), 5.23 (d, J = 11.0 Hz, 1 H, C*H*H=CH), 5.03 (s, 1 H, >CHPh), 4.63 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.50 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.48–4.52 (m, 2 H, OC*H*HCH=CH_2,

OCH*H*CH=CH_2), 4.25 (m, 2 H, 6-H_a, 6-H_b), 4.09–4.19 (m, 2 H, COOC$H_2$$CH_3$), 3.97–3.99 (m, 1 H, 5-H), 3.65 (dd, *J* = 3.5, 9.5 Hz, 1 H, 2-H), 3.60 (t, *J* = 9.5 Hz, 1 H, 4-H), 2.18 (s, 3 H, $COCH_3$), 2.03 (s, 3 H, $COCH_3$), 1.20 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{31}H_{36}O_{12}$ $[M + Na]^+$ 623.2104, found 623.2111.

6-*O*-Acetyl-3-*O*-allyloxycarbonyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl Trichloroacetimidate (13*R*): Hydrazinium acetate (28 mg, 0.30 mmol) was added to a solution of compound **11*R*** (165 mg, 0.27 mmol) in DMF (5 mL) at room temperature. After stirring for 18 h, the reaction mixture was then quenched with an aqueous saturated solution of $NaHCO_3$ (10 mL), and diluted with ethyl acetate (10 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate, 3:1) to afford **12*R*** (130 mg, 86%). Trichloroacetonitrile (230 μL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 14 μL) were added to a solution of **12*R*** (130 mg, 0.23 mmol) in dichloromethane (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was concentrated in vacuo and the residue was purified by flash silica gel column chromatography (hexane/ethyl acetate, 3:1) to afford **13*R***. (155 mg, 95%): R_f = 0.74 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +53 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.41 (s, 1 H, =NH), 7.26–7.47 (m, 10 H, Ar), 6.43 (d, *J* = 3.5 Hz, 1 H, 1-H), 5.92–5.99 (m, 1 H, C*H*=CH_2), 5.50 (t, *J* = 10.0 Hz, 1 H, 3-H), 5.38–5.41 (m, 1 H, CH=C*H*H), 5.24–5.26 (m, 1 H, CH=CH*H*), 5.06 (s, 1 H, >CHPh), 4.74 (d, *J* = 10.5 Hz, 1 H, C*H*HPh), 4.70–4.75 (m, 2 H, OC*H*HCH=CH_2, OCH*H*CH=CH_2), 4.57 (d, *J* = 10.5 Hz, 1 H, C*H*HPh), 4.24–4.27 (m, 2 H, 6-H_a, 6-H_b), 4.14–4.17 (m, 2 H, COOC$H_2$$CH_3$), 4.10 (d, *J* = 13.5 Hz, 1 H, 5-H), 3.82 (dd, *J* = 3.0, 9.5 Hz, 1 H, 2-H), 3.71 (t, *J* = 9.5 Hz, 1 H, 4-H), 2.02 (s, 3 H, $COCH_3$), 1.20 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm.

6-*O*-Acetyl-3-*O*-allyloxycarbonyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl Trichloroacetimidate (13*S*): Compound **13*S*** was synthesized according to the procedure described for the synthesis of compound **13*R***. R_f = 0.68 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +10 (*c* = 0.4, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.70 (s, 1 H, =NH), 7.25–7.37 (m, 10 H, Ar), 6.72 (d, *J* = 3.6 Hz, 1 H, 1-H), 5.73–5.85 (m, 1 H, C*H*=CH_2), 5.46 (t, *J* = 9.9 Hz, 1 H, 3-H), 5.29 (d, *J* = 17.1 Hz, 1 H, CH=CH*H*), 5.20 (d, *J* = 11.4 Hz, 1 H, CH=C*H*H), 5.10 (s, 1 H, >CHPh), 4.65 (d, *J* = 11.1 Hz, 1 H, CH*H*Ph), 4.53 (d, *J* = 11.1 Hz, 1 H, C*H*HPh), 4.42–4.47 (m, 2 H, OC*H*HCH=CH_2, OCH*H*CH=CH_2), 4.26–4.29 (m, 2 H, 6-H_a, 6-H_b), 4.07–4.16 (m, 3 H, 5-H, COOC$H_2$$CH_3$), 3.75 (dd, *J* = 3.6, 9.9 Hz, 1 H, 2-H), 3.66 (t, *J* = 9.9 Hz, 1 H, 4-H), 2.02 (s, 3 H, $COCH_3$), 1.19 (t, *J* = 7.2 Hz, 3 H, $COOCH_2CH_3$) ppm.

1,6-Anhydro-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranose (14*R*): Tetrakis(triphenylphosphane)palladium (27 mg, 0.02 mmol) was added to a solution of compound **10*R*** (580 mg, 1.16 mmol) in benzene (10 mL) at room temperature. The reaction mixture was stirred for 3 h at 70 °C, and then cooled to room temperature. After filtration, the mixture was concentrated under reduced pressure and the residue was purified by flash silica gel column chromatography (hexane/ethyl acetate, 4:1) to afford compound **14*R*** (448 mg, 85%); Colorless syrup, R_f = 0.56 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +40 (*c* = 0.6, $CHCl_3$). ^1H NMR (500 MHz, CDCl3): δ = 7.26–7.6 (m, 10 H, Ar), 5.85–5.90 (m, 1 H, C*H*=CH_2), 5.43 (s, 1 H, 1-H), 5.27 (dd, *J* = 1.0, 7.6 Hz, 1 H, CH*H*=CH), 5.18 (dd, *J* = 1.0, 10.5 Hz, 1 H, C*H*H=CH), 5.13 (s, 1 H, >CHPh), 4.72 (d, *J* = 12.5 Hz, 1 H, CH*H*Ph), 4.66 (d, *J* = 12.5 Hz, 1 H, C*H*HPh), 4.57 (d, *J* = 5.5 Hz, 1 H, 3-H), 4.22–4.9 (m, 1 H, OC*H*HCH=CH_2), 4.08–4.15 (m, 2 H, COOC$H_2$$CH_3$), 3.95–4.03 (m, 1 H, OC*H*H=CH_2), 3.82–3.83 (m, 1 H, 6-H_a), 3.71–3.73 (m, 1 H, 5-H), 3.62–3.65 (m, 1 H, 6-H_b), 3.40 (d, *J* = 2.0 Hz, 1 H, 2-H), 3.32–3.34 (m, 1 H, 4-H), 1.21 (t, *J* = 7.5 Hz, 3 H, CO-OC$H_2$$CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{26}H_{30}O_7$ $[M + Na]^+$ 477.1889, found 477.1865.

1,6-Di-*O*-acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α-D-glucopyranose (15*R*): Trimethylsilyl trifluoromethanesulfonate (2 μL, 0.01 mmol) was added to a solution of compound **14*R*** (390 mg, 0.86 mmol) in acetic anhydride (10 mL) at 0 °C. After stirring the reaction mixture for 30 min at 0 °C, it was quenched with an aqueous saturated solution of $NaHCO_3$ and diluted with dichloromethane. After washing with an aqueous saturated solution of $NaHCO_3$ (10 mL), the organic layer was dried ($MgSO_4$), concentrated in vacuo, and the residue was purified by flash silica gel column chromatography (hexane/ethyl acetate; 4:1) to afford compound **15*R*** (450 mg, 94%). R_f = 0.70 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +119.72 (*c* = 1.9, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.42 (m, 10 H, Ar), 6.05–6.09 (m, 1 H, C*H*=CH_2), 6.02 (d, *J* = 3.5 Hz, 1 H, 1-H), 5.11 (s, 1 H, >CHPh), 4.91 (d, *J* = 10.5 Hz, 1 H, CH*H*Ph), 4.62 (dd, *J* = 6.5, 13.0 Hz, 1 H, CH*H*=CH), 4.57 (d, *J* = 10.5 Hz, 1 H, C*H*HPh), 4.56 (dd, *J* = 5.0, 10.5 Hz, 1 H, C*H*H=CH), 4.36–4.39 (m, 2 H, OCH*H*CH=CH_2, OC*H*HCH=CH_2), 4.22–4.27 (m, 2 H, 6-H_a, 6-H_b), 4.10–4.15 (m, 2 H, COOC$H_2$$CH_3$), 3.91 (t, *J* = 9.5 Hz, 1 H, 3-H), 3.83–3.85 (m, 1 H, 5-H), 3.60 (dd, *J* = 3.5, 9.5 Hz, 1 H, 2-H), 3.49 (t, *J* = 9.5 Hz, 1 H, 4-H), 2.05 (s, 3 H,$COCH_3$), 2.00 (s, 3 H, $COCH_3$), 1.20 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{30}H_{36}O_{10}$ $[M + Na]^+$ 579.2206, found 579.2198.

1,6-Di-*O*-acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranose (15*S*): Compound **15*S*** was synthesized according to the procedure described for the synthesis of compound **15*R***. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.43 (m, 10 H, Ar), 6.46 (d, *J* = 3.0 Hz, 1 H, 1-H), 5.89–5.96 (m, 1 H, C*H*=CH_2), 5.26 (dd, *J* = 0.5, 17.0 Hz, 1 H, CH*H*=CH), 5.16–5.19 (m, C*H*H=CH), 5.19 (s, >CHPh), 4.85 (d, *J* = 11.0 Hz, 1 H, CH*H*Ph), 4.55 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.36 (dd, *J* = 5.5, 10.0 Hz, 1 H, OCH*H*CH=CH_2), 4.29 (dd, *J* = 5.5, 11.5 Hz, 1 H, OC*H*HCH=CH_2), 4.10–4.26 (m, 4 H, COOC$H_2$$CH_3$, 6-$H_a$, 6-$H_b$), 3.87–3.89 (m, 1 H, 5-H), 3.87 (t, *J* = 10.0 Hz, 1 H, 3-H), 3.57 (dd, *J* = 3.5, 9.5 Hz, 1 H, 2-H), 3.47 (t, *J* = 10.0 Hz, 1 H, 4-H), 2.15 (s, 3 H, $COCH_3$), 2.02 (s, 3 H, $COCH_3$), 1.19 (t, *J* = 7.5 Hz, 3 H, $COOCH_2CH_3$) ppm. MALDI-TOF MS: *m*/*z* calcd. for $C_{30}H_{36}O_{10}$ $[M + Na]^+$ 579.2206, found 579.2221.

6-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl Trichloroacetimidate (17*R*): Hydrazinium acetate (76 mg, 0.83 mmol) was added to a solution of compound **15*R*** (458 mg, 0.82 mmol) in DMF (5 mL) at room temperature. After the reaction mixture was stirred for 18 h, it was quenched with an aqueous saturated solution of $NaHCO_3$, and then diluted with ethyl acetate. The organic phase was dried ($MgSO_4$), and the solvent was removed in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate, 2:1) to afford **16*R*** (388 mg, 92%). Trichloroacetonitrile (0.75 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 45 μL) were added to a solution of **16*R*** (388 mg, 0.75 mmol) in dichloromethane (10 mL) at 0 °C. After stirring the reaction mixture at 0 °C for 1 h, it was concentrate in vacuo. The residue was purified by flash silica gel column chromatography (20% ethyl acetate in hexane) to afford **17*R*** (458 mg, 93%); R_f = 0.80 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = –94 (*c* = 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.45 (s, 1 H,

=NH), 7.26–7.43 (m, 10 H, Ar), 6.22 (d, J = 3.6 Hz, 1 H, 1-H), 6.02–6.15 (m, 1 H, C*H*=CH$_2$), 5.37 (d, J = 17.4 Hz, 1 H, CH=CH*H*), 5.22 (d, J = 10.2 Hz, 1 H, CH=C*H*H), 5.13 (s, 1 H, >HPh), 4.92 (d, J = 10.8 Hz, 1 H, CH*H*Ph), 4.66 (dd, J = 5.7, 12.6 Hz, 1 H, OCH*H*CH=CH$_2$), 4.59 (d, J = 10.8 Hz, 1 H, C*H*HPh), 4.40 (dd, J = 5.7, 12.6 Hz, 1 H, OC*H*HCH=CH$_2$), 3.96–4.24 (m, 6 H, COOCH_2CH$_3$, 3-H, 5-H, 6-H$_a$, 6-H$_b$), 3.69 (dd, J = 3.3, 9.6 Hz, 1 H, 2-H), 3.54 (t, J = 9.3 Hz, 1 H, 4-H), 1.99 (s, 3 H, COCH$_3$), 1.21 (t, J = 6.9 Hz, 3 H, COOCH$_2$CH_3) ppm.

6-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl Trichloroacetimidate (17*S*): Compound **17*S*** was synthesized according to the procedure described for the synthesis of compound **17*R***. R_f = 0.83 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +64 (c = 0.5, CHCl$_3$). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.68 (s, 1 H, =NH), 7.26–7.44 (m, 10 H, Ar), 6.68 (d, J = 3.5 Hz, 1 H, 1-H), 5.86–5.94 (m, 1 H, C*H*=CH$_2$), 5.26 (s, 1 H, >CHPh), 5.23 (dd, J = 1.5, 19.0 Hz, 1 H, CH=CH*H*), 5.14 (d, J = 11.0 Hz, 1 H, CH=C*H*H), 4.86 (d, J = 11.0 Hz, 1 H, CH*H*Ph), 4.57 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.26–4.30 (m, 4 H, 5-H, 6-H$_a$, OC*H*HCH=CH$_2$, OCH*H*CH=CH$_2$), 4.14 (q, J = 6.5 Hz, 1 H, COOCH_2CH$_3$), 3.99–4.01 (m, 1 H, 6-H$_b$), 3.96 (t, J = 9.0 Hz, 1 H, 3-H), 3.65 (dd, J = 3.0, 9.5 Hz, 1 H, 2-H), 3.53 (t, J = 9.5 Hz, 1 H, 4-H), 2.01 (s, 3 H, COCH$_3$), 1.19 (t, J = 6.5 Hz, 3 H, COOCH$_2$CH_3) ppm.

1,6-Anhydro-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-galactopyranose (19*S*): BF_3–OEt_2 (218 μL, 1.7 mmol) was added dropwise to a mixture of 1,6:2,3-di-anhydro-4-*O*-benzyl-β-D-talopyranose (**18**, 2.0 g, 8.58 mmol), ethyl (*S*)-mandelate (4.6 g, 43 mmol) and activated molecular sieves (4 Å, 2 g) in toluene (50 mL) at room temperature. After stirring for 1 h, the reaction mixture was quenched with an aqueous saturated solution of NaHCO$_3$ (50 mL) and then diluted with ethyl acetate (50 mL). The organic phase was dried (MgSO$_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash silica gel column chromatography (20% ethyl acetate in hexane) to afford **19*S*** (1.81 g, 51%): colorless syrup, R_f = 0.31 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +52 (c = 1.0, CHCl$_3$). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.21–7.41 (m, 10 H, Ar), 5.60 (s, 1 H, 1-H), 5.03 (s, 1 H, >CHPh), 4.61 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.56 (d, J = 11.5 Hz, 1 H, CH*H*Ph), 4.39 (t, J = 4.5 Hz, 1 H, 5-H), 4.24 (d, J = 7.5 Hz, 1 H, 6-H$_a$), 4.15 (q, J = 7.0 Hz, 2 H, COOCH_2CH$_3$), 4.05 (dd, J = 1.5, 3.5 Hz, 1 H, 3-H), 3.81 (t, J = 4 Hz, 1 H, 4-H), 3.59 (s, 1 H, 2-H), 3.58 (d, J = 9.0 Hz, 1 H, 6-H$_b$), 2.79 (d, J = 2.0 Hz, 1 H, OH), 1.18 (t, J = 7.0 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 170.48, 137.15, 135.98, 128.54, 128.47, 128.40, 128.09, 127.65, 127.05, 127.00, 100.34, 80.14, 77.91, 71.99, 71.86, 71.69, 67.22, 63.73, 61.25, 13.87 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{23}H_{26}O_7$ [M + Na]$^+$ 437.1577, found 437.1526.

1,6-Anhydro-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-galactopyranose (19*R*): Compound **19*R*** was synthesized from compound **18** and (*R*)-ethyl mandelate according to the procedure described for the synthesis of compound **19*S***: Colorless syrup, R_f = 0.49 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = –131 (c = 1.0, CHCl$_3$). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.33–7.47 (m, 10 H, Ar), 5.31 (s, 1 H, 1-H), 4.99 (s, 1 H, >CHPh), 4.72 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.65 (d, J = 12.0 Hz, 1 H, CH*H*Ph), 4.41 (t, J = 4.5 Hz, 1 H, 3-H), 4.24 (d, J = 7.0 Hz, 1 H, 6-H$_a$), 4.21–4.22 (m, 1 H, 5-H), 4.16 (q, J = 7.5 Hz, 2 H, COOCH_2CH$_3$), 3.95 (t, J = 4.5 Hz, 1 H, 4-H), 3.57–3.60 (m, 2 H, 6-H$_b$, 2-H), 2.79 (d, J = 2.0 Hz, 1 H, OH), 2.68 (br, 1 H, OH), 1.20 (t, J = 7.5 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 170.33, 137.36, 136.03, 128.95, 128.75, 128.70, 128.33, 127.86, 127.43, 100.23, 80.73, 77.80, 72.22, 72.17, 71.99, 67.72, 64.01, 61.44, 14.05 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{23}H_{26}O_7$ [M + Na]$^+$ 437.1577, found 437.1524.

1,3,6-Tri-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α/β-D-galactopyranose (20*S*): Trimethylsilyl trifluoromethanesulfonate (5 μL, 0.03 mmol) was added to a solution of compound **19*S*** (281 mg, 0.68 mmol) in acetic anhydride (10 mL) at 0 °C. After stirring the reaction mixture at 0 °C for 20 min, it was quenched with an aqueous saturated solution of NaHCO$_3$. The organic phase was washed with water (30 mL) and brine (30 mL) and dried (MgSO$_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash silica gel column chromatography (20% ethyl acetate in hexane) to afford **20*S*** (357 mg, 94%). **20*Sα*:** Colorless syrup, R_f = 0.57 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = –49 (c = 0.15, CHCl$_3$). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.21–7.39 (m, 10 H, Ar), 6.56 (d, J = 3.5 Hz, 1 H, 1-H), 5.21 (dd, J = 3.0, 10.5 Hz, 1 H, 3-H), 5.04 (s, 1 H, >CHPh), 4.59 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.48 (d, J = 11.0 Hz, 1 H, CH*H*Ph), 4.17 (q, J = 7.5 Hz, 2 H, COOCH_2CH$_3$), 4.10–4.16 (m, 3 H, 6-H$_a$, 2-H, 5-H), 4.02–4.05 (m, 2 H, 6-H$_b$, 4-H), 2.15 (s, 3 H, COCH$_3$), 2.00 (s, 3 H, COCH$_3$), 1.91 (s, 3 H, COCH$_3$), 1.20 (t, J = 7.5 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 170.39, 170.35, 170.28, 169.29, 137.32, 136.21, 128.76, 128.51, 128.47, 128.14, 128.10, 127.35, 90.44, 81.51, 75.28, 74.49, 72.66, 70.09, 62.23, 61.52, 21.02, 20.84, 20.78, 14.00 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{29}H_{34}O_{11}$ [M + Na]$^+$ 581.1999, found 581.1913.

1,3,6-Tri-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α/β-D-galactopyranose (20*R*): Compound **20*R*** was synthesized according to the procedure described for the synthesis of compound **20*S***. **20*Rα*:** R_f = 0.53 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = –70 (c = 1, CHCl$_3$). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.31–7.37 (m, 10 H, Ar), 6.23 (d, J = 4.0 Hz, 1 H, 1-H), 5.33 (dd, J = 2.5, 10.5 Hz, 1 H, 3-H), 5.03 (s, 1 H, >CHPh), 4.74 (d, J = 11.0 Hz, 1 H, CH*H*Ph), 4.55 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.13–4.18 (m, 3 H, 6-H$_a$, 2-H, 4-H), 4.10 (q, J = 7.0 Hz, 2 H, COOCH_2CH$_3$), 3.97–4.03 (m, 2 H, 6-H$_b$, 5-H), 2.16 (s, 3 H, COCH$_3$), 2.04 (s, 3 H, COCH$_3$), 1.99 (s, 3 H, COCH$_3$), 1.20 (t, J = 7.0 Hz, 3 H, COOCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 170.99, 170.91, 170.88, 169.48, 137.26, 136.20, 128.73, 128.56, 128.45, 128.14, 128.06, 126.95, 91.43, 80.11, 75.89, 74.92, 71.66, 71.12, 62.34, 60.21, 22.02, 21.84, 21.63, 14.15 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{29}H_{34}O_{11}$ [M + Na]$^+$ 581.1999, found 581.1981.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α/β-D-galactopyranosyl Trichloroacetimidate (22*S*): Hydrazinium acetate (80 mg, 0.87 mmol) was added to a solution of compound **20*S*** (440 mg, 0.79 mmol) in DMF (15 mL) at room temperature. After stirring the reaction mixture for 18 h, it was quenched with an aqueous saturated solution of NaHCO$_3$. The organic phase was washed with an aqueous saturated solution of NH_4Cl (30 mL) and dried (MgSO$_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash silica gel column chromatography (20% ethyl acetate in hexane) to afford **21*S*** (391 mg, 96%). Trichloroacetonitrile (0.39 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 45 μL) were added to a solution of **21*S*** (391 mg, 0.76 mmol) in dichloromethane (10 mL) at 0 °C. After stirring the reaction mixture at 0 °C for 1 h, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford **22*S*** (452 mg, 90%). **22*Sα*:** R_f = 0.69 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +92 (c = 1, CHCl$_3$). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.67 (s, 1 H, NH), 7.55–7.40 (m, 10 H, Ar), 6.79 (d, J = 3.0 Hz, 1 H, 1-H), 5.28 (dd, J = 2.5, 10.5 Hz, 1 H, 3-H), 5.12 (s, 1 H, >CHPh), 4.63 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.50 (d, J = 11.5 Hz, 1 H, CH*H*Ph), 4.24–4.26 (m, 1 H,

5-H), 4.22 (dd, J = 3.0, 10.0 Hz, 1 H, 2-H), 4.12–4.17 (m, 1 H, 4-H), 4.14 (q, J = 7.0 Hz, 2 H, $COOCH_2CH_3$), 4.11–4.12 (m, 1 H, 6-H_b), 4.07 (dd, J = 6.5, 11.0 Hz, 1 H, 6-H_a), 1.98 (s, 3 H, $COCH_3$), 1.91 (s, 3 H, $COCH_3$), 1.20 (t, J = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.64, 170.34, 170.30, 161.15, 137.30, 136.23, 128.63, 128.55, 128.40, 128.19, 128.16, 127.07, 94.90, 81.95, 75.24, 74.38, 73.17, 73.10, 70.42, 62.34, 61.52, 20.86, 20.75, 14.04 ppm.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α/β-D-galactopyranosyl Trichloroacetimidate (22*R*): Compound **22*R*** was synthesized according to the procedure described for the synthesis of compound **22*S***. **22*Rα*:** R_f = 0.69 (ethyl acetate/hexane, 1:1). $[\alpha]_D^{20}$ = +48 (c = 0.33, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.44 (s, 1 H, NH), 7.28–7.40 (m, 10 H, Ar), 6.41 (d, J = 3.5 Hz, 1 H, 1-H), 5.44 (dd, J = 2.5, 10 Hz, 1 H, 3-H), 5.08 (s, 1 H, >CHPh), 4.75 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.56 (d, J = 11.5 Hz, 1 H, CH*H*Ph), 4.25 (dd, J = 4.0, 8.0 Hz, 1 H, 2-H), 4.22–4.24 (m, 1 H, 6-H_a), 4.14 (q, J = 7.0 Hz, 2 H, $COOCH_2CH_3$), 4.10–4.11 (m, 1 H, 4-H), 4.09 (d, J = 2.0 Hz, 1 H, 6-H_b), 4.06 (dd, J = 6.0, 11.0 Hz, 1 H, 5-H), 2.15 (s, 3 H, $COCH_3$), 1.96 (s, 3 H, $COCH_3$), 1.19 (t, J = 7.5 Hz, 3 H, $COOCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.46, 170.31, 169.96, 160.76, 137.38, 136.32, 128.67, 128.53, 128.46, 128.24, 128.15, 127.07, 94.24, 90.98, 80.82, 75.22, 74.44, 73.00, 71.59, 70.59, 62.32, 61.19, 21.09, 20.71, 14.06 ppm.

General Procedure for the Glycosylations: A mixture of glycosyl donor **5*R*** or **5*S*** (20 mg, 0.03 mmol), glycosyl acceptor (0.036 mmol) and activated molecular sieves (4 Å) in dichloromethane (10 mL) was stirred at room temperature for 1 h under argon. After cooling the mixture to –78 °C, trimethylsilyl trifluoromethanesulfonate (2.2 μL, 0.012 mmol) was added, and the reaction mixture was stirred at –78 °C for 1 h and then warmed to 0 °C over a period of 1 h. The reaction mixture was quenched with an aqueous saturated solution of $NaHCO_3$ (10 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (dichloromethane/hexane/ethyl acetate, 2:2:1).

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (28*Sα*): $[\alpha]_D^{20}$ = +251 (c = 1.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.16–7.37 (m, 25 H, aromatic), 5.81 (d, J = 3.5 Hz, 1 H, 1′-H), 5.54 (t, J = 9.5 Hz, 1 H, 3′-H), 5.06 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.93 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.91 (s, 1 H, >C*H*Ph), 4.67 (d, J = 12.5 Hz, 1 H, C*H*HPh), 4.61 (d, J = 3.5 Hz, 1 H, 1-H), 4.56 (d, J = 12.5 Hz, 1 H, C*H*HPh), 4.51 (s, 2 H, CH_2Ph), 4.50 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.43 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.00–4.08 (m, 6 H, 3-H, 6-H_a, 6′-H_a, 6′-H_b, CO-OCH_2CH_3), 3.85–3.93 (m, 3 H, 5′-H, 4-H, 6-H_b), 3.64 (d, J = 10.0 Hz, 1 H, 5-H), 3.59 (dd, J = 3.5, 9.0 Hz, 1 H, 2-H), 3.43 (t, J = 9.5 Hz, 1 H, 4′-H), 3.39 (dd, J = 3.5, 9.5 Hz, 1 H, 2′-H), 3.38 (s, 3 H, OCH_3), 1.97 (s, 3 H, $COCH_3$), 1.92 (s, 3 H, $COCH_3$), 1.12 (t, J = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.47, 170.09, 169.52, 139.36, 137.98, 137.54, 135.82, 128.71, 128.47, 128.43, 128.24, 128.17, 128.01, 127.93, 127.89, 127.45, 127.41, 126.92, 97.67, 95.28, 81.60, 80.53, 80.23, 77.21, 76.42, 76.04, 74.15, 73.84, 73.38, 73.26, 73.20, 71.75, 69.28, 68.85, 68.79, 62.75, 61.26, 55.13, 21.04, 20.86, 13.98 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{55}H_{62}O_{15}$ $[M + Na]^+$ 985.3986, found 985.3965.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (28*Rβ*): $[\alpha]_D^{20}$ = +91 (c = 0.9, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.20–7.38 (m, 25 H, aromatic), 5.14 (s, 1 H, >C*H*Ph), 5.14 (t, J = 9.5 Hz, 1 H, 3′-H), 4.98 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.73 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.69 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.60 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.57 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.53 (d, J = 4.0 Hz, 1 H, 1-H), 4.51 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.49 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.14–4.19 (m, 4 H, 6′-H_a, 6′-H_b, 1′-H, C*H*HPh), 4.03–4.10 (m, 2 H, CO-OCH_2CH_3), 3.89 (t, J = 9.5 Hz, 1 H, 4-H), 3.77 (t, J = 9.5 Hz, 1 H, 3-H), 3.54 (t, J = 9.5 Hz, 1 H, 4′-H), 3.45 (dd, J = 4.0, 9.5 Hz, 1 H, 2-H), 3.32 (s, 3 H, OCH_3), 3.28 (dd, J = 2.0, 11.5 Hz, 1 H, 6-H_a), 3.20–3.26 (m, 2 H, 2′-H, 5′-H), 3.16 (d, J = 10.5 Hz, 1 H, 5-H), 2.91 (dd, J = 1.5, 11.0 Hz, 1 H6-H_b), 2.17 (s, 3 H, $COCH_3$), 1.88 (s, 3 H, $COCH_3$), 1.18 (t, J = 7.5 Hz, 3 H, $COOCH_2CH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.65, 170.60, 170.30, 139.44, 138.30, 137.59, 137.35, 136.88, 128.64, 128.49, 128.33, 128.30, 128.25, 128.22, 128.13, 128.05, 128.00, 127.95, 127.88, 127.81, 127.73, 127.20, 127.09, 101.93, 98.21, 81.02, 80.19, 80.01, 78.47, 75.85, 75.07, 74.85, 74.21, 73.47, 73.31, 72.53, 69.33, 66.98, 62.97, 60.99, 55.16, 21.36, 20.70, 14.07 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{55}H_{62}O_{15}$ $[M + Na]^+$ 985.3986, found 985.3898.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (29*Sα*): $[\alpha]_D^{20}$ = +169 (c = 1.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.23–7.40 (m, 10 H, aromatic), 5.61 (t, J = 9.5 Hz, 1 H, 3′-H), 5.51 (d, J = 5.0 Hz, 1 H, 1-H), 5.09 (d, J = 3.5 Hz, 1 H, 1′-H), 5.08 (s, 1 H, >C*H*Ph), 4.61 (dd, J = 2.5, 8.0 Hz, 1 H, 3-H), 4.54 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.50 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.35 (dd, J = 2.0, 8.0 Hz, 1 H, 4-H), 4.30 (dd, J = 2.5, 5.0 Hz, 1 H, 2-H), 4.26–4.28 (m, 2 H), 4.03–4.18 (m, 4 H), 3.76–3.81 (m, 2 H), 3.50 (t, J = 9.5 Hz, 1 H, 4′-H), 3.47 (dd, J = 3.5, 9.5 Hz, 1 H, 2′-H), 2.05 (s, 3 H, $COCH_3$), 1.94 (s, 3 H, $COCH_3$), 1.55 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.20 (t, J = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.72, 170.42, 169.61, 137.49, 135.96, 128.79, 128.59, 128.48, 128.10, 127.96, 127.32, 109.25, 108.78, 97.41, 96.29, 80.45, 76.67, 75.96, 73.51, 73.24, 70.85, 70.69, 70.66, 68.17, 67.49, 66.44, 62.95, 61.31, 26.16, 26.13, 24.97, 24.65, 20.10, 20.90, 14.05 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{39}H_{50}O_{15}$ $[M + Na]^+$ 781.3047, found 781.3033.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (29*Sβ*): $[\alpha]_D^{20}$ = –98 (c = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.19–7.43 (m, 10 H, aromatic), 5.55 (s, 1 H, >C*H*Ph), 5.54 (d, J = 5.0 Hz, 1 H, 1-H), 5.34 (t, J = 9.5 Hz, 1 H, 3′-H), 4.61 (dd, J = 2.5, 7.5 Hz, 1 H, 3-H), 4.60 (d, J = 7.5 Hz, 1 H, 1′-H), 4.50 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.42 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.33 (dd, J = 2.5, 5.0 Hz, 1 H, 2-H), 4.04–4.29 (m, 7 H), 3.73 (dd, J = 9.0, 11.5 Hz, 1 H), 3.54–3.57 (m, 1 H, 5-H), 3.42 (t, J = 9.5 Hz, 1 H, 4′-H), 3.23 (dd, J = 7.5, 9.5 Hz, 1 H, 2′-H), 2.03 (s, 3 H, $COCH_3$), 1.86 (s, 3 H, $COCH_3$), 1.60 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.34 (s, 6 H, 2 × CH_3), 1.18 (t, J = 7.0 Hz, 3 H, CO-OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.67, 170.57, 169.62, 137.26, 136.73, 128.58, 128.52, 128.50, 128.33, 128.05, 127.99, 109.50, 108.53, 104.06, 96.41, 80.19, 76.60, 76.01, 74.85, 74.37, 72.63, 71.30, 70.86, 70.35, 70.16, 67.00, 62.96, 60.98, 26.03, 26.00, 24.95, 24.52, 20.96, 20.88, 14.02 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{39}H_{50}O_{15}$ $[M + Na]^+$ 781.3047, found 781.3028.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (29*Rα*): $[\alpha]_D^{20}$ = +54 (c = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.28–7.53 (m, 10 H), 5.66 (t, J = 9.5 Hz, 1 H), 5.48 (d, J =

4.5 Hz, 1 H), 5.07 (s, 1 H), 4.91 (d, *J* = 4.0 Hz, 1 H), 4.64 (d, *J* = 11.5 Hz, 1 H), 4.57 (d, *J* = 11.5 Hz, 1 H), 4.51 (d, *J* = 10.0 Hz, 1 H), 3.96–4.34 (m, 8 H), 3.57–3.73 (m, 4 H), 2.12 (s, 3 H), 2.07 (s, 3 H), 1.56 (s, 3 H), 1.44 (s, 3 H), 1.33 (s, 3 H), 1.27 (s, 3 H), 1.23 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.71, 170.16, 170.06, 137.55, 136.51, 128.71, 128.67, 128.30, 127.10, 109.25, 108.80, 96.79, 96.26, 79.45, 77.22, 76.92, 75.76, 73.78, 72.87, 70.79, 70.62, 68.25, 66.93, 66.17, 62.89, 61.25, 26.15, 26.12, 24.93, 24.73, 21.18, 20.89, 14.10 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{39}H_{50}O_{15}$ [M + Na]$^+$ 781.3047, found 781.3108.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (29*R*β): $[\alpha]_D^{20}$ = +126 (*c* = 1.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49–7.51 (m, 2 H), 7.26–7.35 (m, 8 H), 5.66 (s, 1 H), 5.53 (d, *J* = 4.5 Hz, 1 H), 5.36 (t, *J* = 9.5 Hz, 1 H), 4.68 (d, *J* = 11.5 Hz, 1 H), 4.57 (dd, *J* = 3.5, 8.0 Hz, 1 H), 4.55 (d, *J* = 11.5 Hz, 1 H), 4.50 (d, *J* = 8.0 Hz, 1 H), 4.29–4.32 (m, 2 H), 4.24 (dd, *J* = 5.0, 12.0 Hz, 1 H), 4.12–4.19 (m, 2 H), 4.02–4.09 (m, 3 H), 3.62–3.70 (m, 2 H), 3.56–3.59 (m, 1 H), 3.47 (dd, *J* = 8.0, 9.5 Hz, 1 H), 2.26 (s, 3 H), 2.07 (s, 3 H), 1.54 (s, 3 H), 1.43 (s, 3 H), 1.37 (s, 3 H), 1.34 (s, 3 H), 1.19 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.28, 170.68, 170.50, 137.49, 136.96, 128.54, 128.30, 128.03, 127.36, 109.50, 108.65, 103.91, 96.25, 79.54, 77.94, 75.72, 75.11, 74.55, 72.87, 71.44, 70.76, 70.48, 69.98, 67.19, 62.91, 60.73, 26.13, 25.97, 25.12, 24.49, 21.35, 20.90, 14.14 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{39}H_{50}O_{15}$ [M + Na]$^+$ 781.3047, found 781.3053.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl]-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (30*S*α): $[\alpha]_D^{20}$ = +101 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.64–7.57 (m, 20 H), 5.59 (t, *J* = 9.5 Hz, 1 H), 5.59 (s, 1 H), 5.41 (d, *J* = 3.0 Hz, 1 H), 4.87 (s, 1 H), 4.71 (d, *J* = 3.5 Hz, 1 H), 4.59 (s, 2 H), 4.45 (d, *J* = 11.0 Hz, 1 H), 4.38 (d, *J* = 11.0 Hz, 1 H), 4.22–4.32 (m, 3 H), 4.08–4.12 (m, 2 H), 4.06 (d, *J* = 11.5 Hz, 1 H), 3.82–3.86 (m, 2 H), 3.66–3.74 (m, 3 H), 3.40 (s, 3 H), 3.35 (t, *J* = 9.5 Hz, 1 H), 3.16 (dd, *J* = 4.0, 10.0 Hz, 1 H), 2.06 (s, 3 H), 1.98 (s, 3 H), 1.22 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.60, 169.73, 169.64, 137.85, 137.39, 137.34, 134.93, 129.52, 128.72, 128.64, 128.54, 128.48, 128.40, 128.32, 128.04, 127.95, 127.84, 127.75, 127.14, 102.41, 98.34, 94.94, 82.60, 77.74, 77.53, 75.42, 73.72, 73.48, 73.01, 72.95, 72.78, 69.17, 67.78, 62.51, 61.81, 61.14, 55.33, 21.08, 20.81, 14.09 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{48}H_{54}O_{15}$ [M + Na]$^+$ 893.3360, found: 893.3347.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (30*S*β): $[\alpha]_D^{20}$ = –73 (*c* = 0.7, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.14–7.52 (m, 20 H), 5.54 (s, 1 H), 5.35 (s, 1 H), 5.24 (t, *J* = 9.5 Hz, 1 H), 5.09 (d, *J* = 8.0 Hz, 1 H), 4.88 (d, *J* = 12.0 Hz, 1 H), 4.59 (d, *J* = 12.0 Hz, 1 H), 4.55 (d, *J* = 4.0 Hz, 1 H), 4.40 (d, *J* = 11.0 Hz, 1 H), 4.37 (d, *J* = 11.0 Hz, 1 H), 4.34 (t, *J* = 9.0 Hz, 1 H), 4.23 (dd, *J* = 4.5, 10.0 Hz, 1 H), 4.15–4.18 (m, 2 H), 4.01–4.09 (m, 2 H), 3.81 (dd, *J* = 4.5, 9.5 Hz, 1 H), 3.71–3.75 (m, 2 H), 3.57 (t, *J* = 9.5 Hz, 1 H), 3.42 (t, *J* = 9.0 Hz, 1 H), 3.34–3.37 (m, 2 H), 3.32 (s, 3 H), 1.93 (s, 3 H), 1.66 (s, 3 H), 1.18 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.65, 170.36, 169.56, 138.03, 137.39, 137.31, 137.02, 129.10, 128.67, 128.60, 128.57, 128.48, 128.45, 128.25, 128.15, 128.01, 127.93, 126.24, 101.94, 101.45, 98.40, 82.18, 80.64, 79.97, 79.17, 76.28, 75.44, 74.95, 74.16, 73.24, 72.17, 69.06, 62.96, 62.06, 61.08, 55.26, 20.88, 20.82, 14.07 ppm. HR MALDI-TOF MS: *m*/*z*: calcd. for $C_{48}H_{54}O_{15}$ [M + Na]$^+$ 893.3360, found 893.3328.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl]-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (30*R*α): $[\alpha]_D^{20}$ = +114 (*c* = 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.03–7.39 (m, 20 H), 5.68 (t, *J* = 9.5 Hz, 1 H), 5.59 (d, *J* = 3.5 Hz, 1 H), 5.01 (s, 1 H), 4.85 (s, 1 H), 4.66 (d, *J* = 4.0 Hz, 1 H), 4.63 (d, *J* = 11.5 Hz, 1 H), 4.59 (d, *J* = 11.5 Hz, 1 H), 4.58 (d, *J* = 11.0 Hz, 1 H), 4.48 (d, *J* = 11.0 Hz, 1 H), 4.38 (d, *J* = 10.5 Hz, 1 H), 4.26 (t, *J* = 9.5 Hz, 1 H), 4.08–4.14 (m, 2 H), 4.00–4.05 (m, 2 H), 3.96 (dd, *J* = 3.0, 12.5 Hz, 1 H), 3.72–3.77 (m, 1 H), 3.52–3.63 (m, 3 H), 3.50 (dd, *J* = 3.5, 10.0 Hz, 1 H), 3.45 (t, *J* = 10.0 Hz, 1 H), 3.37 (s, 3 H), 2.13 (s, 3 H), 2.04 (s, 3 H), 1.10 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.65, 170.37, 170.32, 137.97, 137.31, 137.11, 136.07, 129.18, 128.64, 128.53, 128.40, 128.35, 128.29, 128.21, 128.07, 127.96, 127.76, 126.29, 126.15, 126.11, 101.30, 98.29, 95.13, 82.46, 77.70, 77.57, 76.28, 75.31, 73.97, 73.11, 73.06, 72.97, 68.99, 68.05, 62.58, 61.64, 60.93, 55.29, 21.29, 20.88, 14.07 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{48}H_{54}O_{15}$ [M + Na]$^+$ 893.3360, found 893.3384.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (30*R*β): $[\alpha]_D^{20}$ = +168 (*c* = 1.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.16–7.49 (m, 20 H), 5.67 (s, 1 H), 5.55 (s, 1 H), 5.33 (t, *J* = 9.5 Hz, 1 H), 4.95 (d, *J* = 8.5 Hz, 1 H), 4.61 (d, *J* = 11.0 Hz, 1 H), 4.51 (d, *J* = 11.0 Hz, 1 H), 4.42 (d, *J* = 4.0 Hz, 1 H), 4.06–4.25 (m, 7 H), 3.98 (d, *J* = 11.0 Hz, 1 H), 3.71–3.78 (m, 2 H), 3.62 (d, *J* = 9.5 Hz, 1 H), 3.58 (d, *J* = 9.5 Hz, 1 H), 3.47 (dd, *J* = 8.0, 9.5 Hz, 1 H), 3.37–3.43 (m, 2 H), 3.27 (s, 3 H), 2.22 (s, 3 H), 1.93 (s, 3 H), 1.17 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.03, 170.70, 170.54, 137.78, 137.51, 137.30, 137.01, 129.07, 128.49, 128.41, 128.38, 128.35, 128.22, 128.01, 127.99, 127.28, 126.13, 102.63, 101.25, 98.26, 80.85, 80.14, 79.62, 78.68, 77.20, 75.84, 74.95, 74.38, 73.20, 72.39, 68.93, 63.04, 61.99, 60.89, 55.21, 21.39, 20.81, 14.12 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{48}H_{54}O_{15}$ [M + Na]$^+$ 893.3360, found 893.3356.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (31*S*α): $[\alpha]_D^{20}$ = –65 (*c* = 3.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87–8.01 (m, 6 H, aromatic), 7.25–7.54 (m, 19 H, aromatic), 6.19 (t, *J* = 10.0 Hz, 1 H, 3-H), 5.67 (t, *J* = 10.0 Hz, 1 H, 3′-H), 5.43 (t, *J* = 10.0 Hz, 1 H, 4-H), 5.29 (dd, *J* = 3.5, 10.0 Hz, 1 H, 2-H), 5.23 (d, *J* = 3.5 Hz, 1 H, 1-H), 5.08 (d, *J* = 3.0 Hz, 1 H, 1′-H), 5.05 (s, 1 H, >C*H*Ph), 4.58 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.53 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.42 (t, *J* = 10.0 Hz, 1 H, 5-H), 4.32 (d, *J* = 11.0 Hz, 1 H, 6′-H_a), 4.20–4.26 (m, 2 H, 6′-H_b, 5′-H), 4.07–4.12 (m, 2 H, COOCH_2CH$_3$), 3.92 (dd, *J* = 8.0, 10.0 Hz, 1 H, 6-H_a), 3.66 (d, *J* = 8.0 Hz, 1 H, 6-H_b), 3.57 (dd, *J* = 3.0, 10.0 Hz, 1 H, 2′-H), 3.52 (t, *J* = 10.0 Hz, 1 H, 4′-H), 3.50 (s, 3 H, OCH_3), 2.10 (s, 3 H, $COCH_3$), 1.86 (s, 3 H, $COCH_3$), 1.15 (t, *J* = 7.0 Hz, 3 H, COOCH$_2$C*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.82, 170.67, 169.59, 165.81, 165.48, 137.50, 136.17, 133.42, 133.29, 133.04, 129.96, 129.68, 129.29, 129.16, 128.92, 128.54, 128.48, 128.42, 128.39, 128.25, 128.01, 127.96, 126.86, 97.31, 96.61, 81.59, 78.32, 76.13, 73.82, 73.20, 72.21, 70.58, 69.84, 68.74, 68.59, 67.33, 62.91, 61.39, 55.64, 20.89, 14.01 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{55}H_{56}O_{18}$ [M + Na]$^+$ 1027.3364, found 1027.3344.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (31*S*β): $[\alpha]_D^{20}$ = +16 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.98 (m, 6 H, aromatic), 7.17–7.54 (m, 19 H, aromatic), 6.17 (t, *J* = 10.0 Hz, 1 H, 3-H), 5.41 (t, *J* = 10.0 Hz, 1

H, 3′-H), 5.23–5.32 (m, 4 H, 4-H, 2-H, 1-H, >C*H*Ph), 4.60 (d, *J* = 7.5 Hz, 1 H, 1′-H), 4.48 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.38–4.43 (m, 2 H, 5-H, C*H*HPh), 4.22 (dd, *J* = 2.5, 12.0 Hz, 1 H, 6′-H_a), 4.11–4.19 (m, 3 H, 6′-H_b, 5′-H, $COOCH_2CH_3$), 3.98 (dd, *J* = 2.5, 11.0 Hz, 1 H, 6-H_a), 3.82 (dd, *J* = 8, 11.0 Hz, 1 H, 6-H_b), 3.55–3.58 (m, 1 H), 3.54 (s, 3 H, OCH_3), 3.39 (t, *J* = 9.5 Hz, 1 H, 4′-H), 3.26 (dd, *J* = 7.5, 9.5 Hz, 1 H, 2′-H), 1.95 (s, 3 H, $COCH_3$), 1.70 (s, 3 H, $COCH_3$), 1.18 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.62, 170.26, 169.48, 165.84, 165.79, 165.44, 137.18, 137.02, 133.53, 133.37, 133.10, 129.93, 129.88, 129.66, 129.24, 129.09, 128.91, 128.59, 128.52, 128.50, 128.43, 128.27, 128.07, 128.01, 127.83, 103.64, 96.93, 81.40, 78.61, 76.16, 74.68, 74.32, 72.60, 72.09, 70.30, 70.08, 69.77, 68.90, 62.99, 61.17, 55.89, 20.85, 20.67, 14.12 ppm. HR MALDI-TOF MS: *m*/*z*: calcd. for $C_{55}H_{56}O_{18}$ [M + Na]$^+$: 1027.3364; found: 1027.3378.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (31*Rα*): $[\alpha]_D^{20}$ = +144 (*c* = 0.7, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.98 (m, 6 H, aromatic), 7.09–7.54 (m, 19 H, aromatic), 6.14 (t, *J* = 9.5 Hz, 1 H, 3-H), 5.68 (t, *J* = 9.5 Hz, 1 H, 3′-H), 5.34 (t, *J* = 9.5 Hz, 1 H, 4-H), 5.19 (s, 1 H, 1-H), 5.18 (dd, *J* = 3.5, 9.5 Hz, 1 H, 2-H), 4.96 (s, 1 H, >C*H*Ph), 4.68 (d, *J* = 3.5 Hz, 1 H, 1′-H), 4.61 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.54 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.24–4.28 (m, 2 H, 5-H, 5′-H), 4.20 (dd, *J* = 4.5, 12.5 Hz, 1 H, 6′-H_a), 4.08–4.13 (m, 3 H, 6′-H_b, CO-OCH_2CH_3), 3.75 (dd, *J* = 8.5, 10.5 Hz, 1 H, 6-H_a), 3.61 (dd, *J* = 3.5, 9.5 Hz, 1 H, 2′-H), 3.55 (t, *J* = 9.5 Hz, 1 H, 4′-H), 3.49 (s, 3 H, OCH_3), 3.33 (d, *J* = 10.5 Hz, 1 H, 6-H_b), 2.06 (s, 3 H, $COCH_3$), 2.01 (s, 3 H, $COCH_3$), 1.17 (t, *J* = 7.5 Hz, 3 H, $COOCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.63, 170.11, 169.89, 165.76, 165.36, 137.56, 136.77, 133.51, 133.31, 133.06, 129.94, 129.90, 129.66, 129.23, 129.12, 128.85, 128.58, 128.48, 128.41, 128.25, 128.01, 127.95, 127.03, 96.60, 96.48, 80.01, 77.90, 75.91, 73.88, 72.19, 72.14, 70.46, 69.72, 68.56, 68.52, 66.56, 62.82, 61.26, 55.62, 21.03, 20.86, 14.02 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{55}H_{56}O_{18}$ [M + Na]$^+$ 1027.3364, found 1027.3405.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (31*Rβ*): $[\alpha]_D^{20}$ = +164 (*c* = 1.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.99 (m, 6 H, aromatic), 7.25–7.53 (m, 19 H, aromatic), 6.17 (t, *J* = 9.5 Hz, 1 H, 3-H), 5.70 (s, 1 H, >C*H*Ph), 5.36 (t, *J* = 9.5 Hz, 2 H, 3′-H, 4-H), 5.28 (s, 1 H, 1-H), 5.27 (dd, *J* = 4.0, 9.5 Hz, 1 H, 2-H), 4.66 (d, *J* = 10.5 Hz, 1 H, C*H*HPh), 4.53 (d, *J* = 10.5 Hz, 1 H, C*H*HPh), 4.52 (d, *J* = 9.5 Hz, 1 H, 1′-H), 4.38 (t, *J* = 9.5 Hz, 1 H, 5-H), 4.13–4.21 (m, 3 H, 6′-H_a, CO-OCH_2CH_3), 4.06 (dd, *J* = 7.5, 10.5 Hz, 1 H, 6′-H_b), 4.00 (d, *J* = 10.0 Hz, 1 H, 6-H_b), 3.74 (dd, *J* = 9.0, 10.0 Hz, 1 H, 6-H_a), 3.55–3.61 (m, 2 H, 4′-H, 5′-H), 3.45 (s, 3 H, OCH_3), 3.42 (t, *J* = 9.5 Hz, 1 H, 2′-H), 2.24 (s, 3 H, $COCH_3$), 1.85 (s, 3 H, $COCH_3$), 1.14 (t, *J* = 7.5 Hz, 3 H, $COOCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.97, 170.56, 170.44, 165.86, 165.74, 165.51, 137.37, 136.66, 133.58, 133.41, 133.13, 129.93, 129.84, 129.63, 129.16, 129.03, 128.72, 128.59, 128.53, 128.49, 128.44, 128.28, 128.06, 128.00, 127.14, 103.45, 96.85, 79.65, 78.21, 75.86, 74.94, 74.52, 72.78, 72.07, 70.27, 69.93, 68.88, 63.01, 60.88, 55.69, 21.31, 20.57, 14.08 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{55}H_{56}O_{18}$ [M + Na]$^+$ 1027.3364, found 1027.3352.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (32*Sα*): $[\alpha]_D^{20}$ = –112 (*c* = 2.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18–7.37 (m, 25 H), 5.63 (t, *J* = 10.0 Hz, 1 H), 5.32 (d, *J* = 3.0 Hz, 1 H), 5.04 (s, 1 H), 4.97 (d, *J* = 12.5 Hz, 1 H), 4.87 (d, *J* = 11.0 Hz, 1 H), 4.82 (d, *J* = 11.0 Hz, 1 H), 4.76 (d, *J* = 12.5 Hz, 1 H), 4.65 (d, *J* = 13.0 Hz, 1 H), 4.63 (d, *J* = 13.0 Hz, 1 H), 4.61 (d, *J* = 3.5 Hz, 1 H), 4.54 (d, *J* = 9.5 Hz, 1 H), 4.48 (d, *J* = 9.5 Hz, 1 H), 4.26 (d, *J* = 12.0 Hz, 1 H), 4.20 (dd, *J* = 4.5, 12.0 Hz, 1 H), 3.96–4.07 (m, 4 H), 3.72–3.83 (m, 4 H), 3.65 (dd, *J* = 4.0, 9.5 Hz, 1 H), 3.49 (t, *J* = 10.5 Hz, 1 H), 3.47 (dd, *J* = 3.0, 10.0 Hz, 1 H), 3.37 (s, 3 H), 2.02 (s, 3 H), 1.90 (s, 3 H), 1.13 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.78, 170.62, 169.46,138.98, 138.52, 138.42, 137.42, 135.93, 128.61, 128.54, 128.49, 128.35, 128.34, 128.28, 128.10, 128.07, 128.00, 127.88, 127.71, 127.54, 127.46, 127.06, 98.01, 97.00, 82.16, 81.55, 80.18, 77.76, 76.17, 75.72, 75.04, 74.08, 73.07, 73.36, 70.82, 68.44, 65.59, 62.88, 61.30, 55.15, 20.96, 20.86, 14.03 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{55}H_{62}O_{15}$ [M + Na]$^+$ 985.3986, found 985.3998.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (32*Sβ*): $[\alpha]_D^{20}$ = –198 (*c* = 1.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17–7.37 (m, 25 H), 5.27 (s, 1 H), 5.26 (t, *J* = 9.5 Hz, 1 H), 4.99 (d, *J* = 10.5 Hz, 1 H), 4.89 (d, *J* = 11.0 Hz, 1 H), 4.79–4.82 (m, 2 H), 4.66 (d, *J* = 11.5 Hz, 1 H), 4.59 (d, *J* = 3.3 Hz, 1 H), 4.57 (d, *J* = 11.0 Hz, 1 H), 4.47 (d, *J* = 11.5 Hz, 1 H), 4.40–4.44 (m, 2 H), 4.28 (d, *J* = 12.0 Hz, 1 H), 4.13 (dd, *J* = 4.5, 12.0 Hz, 1 H), 3.95–4.07 (m, 4 H), 3.84–3.88 (m, 1 H), 3.58 (dd, *J* = 6.0, 11.0 Hz, 1 H), 3.48–3.53 (m, 2 H), 3.41 (s, 3 H), 3.35–3.42 (m, 2 H), 3.28 (t, *J* = 8.5 Hz, 1 H), 1.97 (s, 3 H), 1.71 (s, 3 H), 1.02 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.58, 170.05, 169.48, 138.73, 138.17, 138.16, 137.24, 136.83, 128.67, 128.50, 128.47, 128.35, 128.16, 128.04, 127.96, 127.94, 127.89, 127.83, 127.61, 103.47, 98.03, 81.88, 81.23, 79.90, 78.31, 77.90, 76.12, 75.75, 75.01, 74.70, 74.34, 73.40, 72.59, 69.81, 69.28, 62.79, 61.07, 55.37, 20.91, 20.79, 13.96 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{55}H_{62}O_{15}$ [M + Na]$^+$ 985.3986, found 985.3876.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (32*Rβ*): $[\alpha]_D^{20}$ = +94 (*c* = 1.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09–7.39 (m, 25 H), 5.53 (s, 1 H), 5.32 (t, *J* = 9.5 Hz, 1 H), 4.96 (d, *J* = 11.0 Hz, 1 H), 4.82 (d, *J* = 12.0 Hz, 1 H), 4.76 (d, *J* = 11.0 Hz, 1 H), 4.70 (d, *J* = 12.0 Hz, 1 H), 4.68 (d, *J* = 11.0 Hz, 1 H), 4.61 (d, *J* = 3.0 Hz, 1 H), 4.55 (t, *J* = 11.0 Hz, 2 H), 4.22–4.33 (m, 3 H), 4.17 (dd, *J* = 4.5, 11.0 Hz, 1 H), 4.12 (dd, *J* = 7.5, 11.0 Hz, 1 H), 4.02–4.07 (m, 2 H), 3.96 (t, *J* = 9.0 Hz, 1 H), 3.76–3.80 (m, 1 H), 3.63 (t, *J* = 9.5 Hz, 1 H), 3.51 (dd, *J* = 3.5, 10.0 Hz, 1 H), 3.39–3.48 (m, 3 H), 3.31 (s, 3 H), 3.29 (t, *J* = 9.5 Hz, 1 H), 2.22 (s, 3 H), 1.99 (s, 3 H), 1.15 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.86, 170.63, 170.56, 138.78, 138.14, 138.12, 137.51, 136.59, 128.53, 128.49, 128.41, 128.34, 128.15, 128.05, 127.97, 127.70, 127.60, 127.0, 103.48, 97.99, 81.85, 79.89, 79.76, 78.17, 77.99, 75.73, 74.89, 74.76, 74.57, 73.33, 72.88, 69.70, 68.58, 62.75, 60.87, 55.29, 21.35, 20.81, 14.10 ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{55}H_{62}O_{15}$ [M + Na]$^+$ 985.3986, found 985.3993.

Methyl [6-*O*-Acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (33*Sα*): $[\alpha]_D^{20}$ = +38 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.80–7.52 (m, 30 H, Ar), 5.83 (d, *J* = 3.5 Hz, 1 H, 1-H), 5.75 (t, *J* = 9.5 Hz, 1 H, 3′-H), 5.04 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.92 (d, *J* = 12.0 Hz, 1 H, CH*H*Ph), 4.90 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.88 (s, 1 H, >CHPh), 4.69 (d, *J* = 12.0 Hz, 1 H, CH*H*Ph), 4.61 (d, *J* = 12.0 Hz, 1 H, C*H*HPh), 4.56 (d, *J* = 12.0 Hz, 1 H, CH*H*Ph), 4.55 (d, *J* = 3.5 Hz, 1 H, 1′-H), 4.43 (d, *J* = 12.0 Hz, 1 H, CH*H*Ph), 4.32 (d, *J* = 12.0 Hz, 1 H,

C*H*HPh), 4.04–4.06 (m, 2 H, 6-H_a, 6-H_b), 3.83–3.97 (m, 4 H), 3.71 (t, *J* = 9.5 Hz, 1 H, 4-H), 3.60–3.63 (m, 3 H), 3.51 (t, *J* = 9.5 Hz, 1 H, 4′-H), 3.46 (dd, *J* = 3.5, 9.5 Hz, 1 H, 2′-H), 3.43 (dd, *J* = 3.5, 9.5 Hz, 1 H, 2-H), 3.32 (s, 3 H, OCH_3), 1.91 (s, 3 H, $COCH_3$), 0.98 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{60}H_{64}O_{15}$ [M + Na]$^+$ 1047.4142, found 1047.4138.

Methyl [6-*O*-Acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (33*Rα*): Selected ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.84 (d, *J* = 3.6 Hz, 1 H, 1′-H), 3.39 (s, 3 H, CH_3), 2.03 (s, 3 H, $COCH_3$), 1.22 (t, *J* = 7.2 Hz, 3 H, $COOCH_2CH_3$) ppm.

Methyl [6-*O*-Acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (33*Rβ*): Selected ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.62 (d, *J* = 7.5 Hz, 1 H, 1′-H), 3.37 (s, 3 H, CH_3), 1.96 (s, 3 H, $COCH_3$), 1.18 (t, *J* = 7.2 Hz, 3 H, $COOCH_2CH_3$) ppm.

6-*O*-Acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (34*Sα*): $[\alpha]_D^{20}$ = +44 (*c* = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12–8.02 (m, 15 H, Ar), 5.88 (t, *J* = 9.5 Hz, 1 H, 3′-H), 5.52 (d, *J* = 5.0 Hz, 1 H, 1-H), 5.17 (d, *J* = 3.5 Hz, 1 H, 1′-H), 5.03 (s, 1 H, >CHPh), 4.61 (dd, *J* = 2.5, 7.5 Hz, 1 H, 3-H), 4.53 (d, *J* = 11.0 Hz, 1 H, CH*H*Ph), 4.40 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.38 (dd, *J* = 2.5, 8.5 Hz, 1 H, 4-H), 4.29–4.32 (m, 3 H, 2-H, 6-H_a, 6-H_b), 4.13–4.15 (m, 1 H, 5′-H), 4.11–4.13 (m, 1 H, 5-H), 4.08 (q, 2 H, $COOCH_2CH_3$), 3.81–3.83 (m, 2 H, 6′-H_a, 6′-H_b), 3.64 (t, *J* = 9.5 Hz, 1 H, 4′-H), 3.60 (dd, *J* = 3.5, 9.5 Hz, 1 H, 2′-H), 2.06 (s, 3 H, $COCH_3$), 1.56 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.12 (t, *J* = 7.5 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{44}H_{52}O_{15}$ [M + Na]$^+$ 843.3204, found 843.3192.

6-*O*-Acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (34*Rβ*): $[\alpha]_D^{20}$ = –32 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.13–8.22 (m, 15 H, Ar), 5.63 (s, 1 H, >CHPh), 5.63 (t, *J* = 9.5 Hz, 1 H, 3′-H), 5.53 (d, *J* = 5.0 Hz, 1 H, 1-H), 4.60 (d, *J* = 10.5 Hz, 1 H, C*H*HPh), 4.58 (d, *J* = 7.5 Hz, 1 H, 1′-H), 4.55–4.57 (m, 1 H, 5′-H), 4.48 (d, *J* = 10.5 Hz, 1 H, CH*H*Ph), 4.34 (dd, *J* = 2.5, 12.5 Hz, 1 H, 3-H), 4.31 (dd, *J* = 2.5, 5.0 Hz, 1 H, 2-H), 4.26 (dd, *J* = 4.0, 12.5 Hz, 1 H, 4-H), 4.14–4.15 (m, 1 H, 6′-H_a), 4.05 (dd, *J* = 4.0, 11.0 Hz, 1 H, 6-H_a), 4.01–4.03 (m, 1 H, 6-H_b), 3.94 (q, *J* = 7.0 Hz, 2 H, $COOCH_2CH_3$), 3.79 (dd, *J* = 2.0, 9.5 Hz, 1 H, 2′-H), 3.73 (t, *J* = 9.5 Hz, 1 H, 4′-H), 3.61–3.65 (m, 2 H, 5-H, 6′-H_b), 2.07 (s, 3 H, $COCH_3$), 1.52 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 0.97 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{44}H_{52}O_{15}$ [M + Na]$^+$ 843.3204, found 843.3197.

Methyl [6-*O*-Acetyl-3-*O*-allyloxycarbonyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (35*Sα*): $[\alpha]_D^{20}$ = +52 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20–7.38 (m, 25 H, Ar), 5.88 (d, *J* = 3.5 Hz, 1 H), 5.28–5.91 (m, 1 H), 5.30–5.38 (m, 3 H), 5.23 (d, *J* = 11.0 Hz, 1 H), 5.06 (d, *J* = 11.5 Hz, 1 H), 5.03 (d, *J* = 11.5 Hz, 1 H), 4.99 (s, 1 H), 4.68 (d, *J* = 11.0 Hz, 1 H), 4.60 (d, *J* = 4.0 Hz, 1 H), 4.51–4.58 (m, 6 H), 4.45 (d, *J* = 11.0 Hz, 1 H), 4.10 (t, *J* = 7.5 Hz, 2 H), 3.96–4.04 (m, 3 H), 3.84–3.93 (m, 3 H), 3.59–3.63 (m, 2 H), 3.44 (dd, *J* = 8.5, 10.0 Hz, 1 H), 3.37 (s, 3 H, CH_3), 1.95 (s, 3 H, $COCH_3$), 1.10 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{57}H_{64}O_{16}$ [M + Na]$^+$ 1027.4092, found 1027.4103.

Methyl [6-*O*-Acetyl-3-*O*-allyloxycarbonyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (35*Sβ*): $[\alpha]_D^{20}$ = +33 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19–7.38 (m, 25 H, Ar), 5.76–5.82 (m, 1 H), 5.21 (d, *J* = 10.0 Hz, 1 H), 5.04 (s, 1 H), 4.96 (d, *J* = 11.0 Hz, 1 H), 4.87 (t, *J* = 9.5 Hz, 1 H), 4.70–4.75 (m, 3 H), 4.59–4.62 (m, 2 H), 4.43–4.52 (m, 4 H), 4.37–4.39 (m, 2 H), 4.03–4.13 (m, 7 H), 3.81 (t, *J* = 9.5 Hz, 1 H), 3.67–3.70 (m, 2 H), 3.51 (dd, *J* = 3.5, 9.5 Hz, 1 H), 3.42 (t, *J* = 9.5 Hz, 1 H), 3.38 (s, 3 H, $COCH_3$), 3.22 (dd, *J* = 8.5, 9.5 Hz, 1 H), 3.13–3.15 (m, 1 H), 2.04 (s, 3 H, $COCH_3$), 1.18 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{57}H_{64}O_{16}$ [M + Na]$^+$ 1027.4092, found 1027.4088.

Methyl [6-*O*-Acetyl-3-*O*-allyloxycarbonyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (35*Rβ*): $[\alpha]_D^{20}$ = +10 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20–7.37 (m, 25 H, Ar), 5.92–6.05 (m, 1 H, C*H*=CH_2), 5.39 (dd, *J* = 1.5, 17.1 Hz, 1 H, CH*H*=CH), 5.24 (dd, *J* = 1.5, 10.5 Hz, 1 H, C*H*H=CH), 5.09 (s, 1 H, >CHPh), 4.91 (t, *J* = 9.3 Hz, 1 H, 3′-H), 4.70–4.74 (m, 3 H), 4.70 (d, *J* = 11.0 Hz, 1 H, CH*H*Ph), 4.66 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.57 (d, *J* = 11.0 Hz, 1 H, CH*H*Ph), 4.50 (d, *J* = 9.3 Hz, 1 H, 1′-H), 4.48 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.05–4.19 (m, 5 H, 5-H, 6′-H_a, 6′-H_b, OC*H*HCH=CH_2, OCH*H*CH=CH_2), 3.86 (t, *J* = 9.3 Hz, 1 H, 3-H), 3.73 (t, *J* = 9.3 Hz, 1 H, 2′-H), 3.54 (t, *J* = 9.3 Hz, 1 H, 4′-H), 3.43 (dd, *J* = 3.6, 9.3 Hz, 1 H), 3.31 (s, 3 H, OCH_3), 3.26–3.32 (m, 1 H, 4-H), 3.13–3.16 (m, 1 H, 5′-H), 3.08 (d, *J* = 9.6 Hz, 1 H, 6-H_a), 2.92 (d, *J* = 10.5 Hz, 1 H, 6-H_b), 1.86 (s, 3 H, $COCH_3$), 1.17 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{57}H_{64}O_{16}$ [M + Na]$^+$ 1027.4092, found: 1027.4116.

6-*O*-Acetyl-3-*O*-allyloxycarbonyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (36*Sα*): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25–7.40 (m, 10 H, Ar), 5.81–5.88 (m, 1 H, C*H*=CH_2), 5.51 (d, *J* = 5.0 Hz, 1 H, 1-H), 5.40 (t, *J* = 10.0 Hz, 1 H, 3′-H), 5.31 (d, *J* = 17.0 Hz, 1 H, CH=CH*H*), 5.21 (d, *J* = 11.0 Hz, 1 H, CH=C*H*H), 5.16 (d, *J* = 3.0 Hz, 1 H, 1′-H), 5.12 (s, 1 H, >CHPh), 4.61–4.63 (m, 2 H, 3-H, 5-H), 4.49–4.52 (m, 2 H, OCH*H*CH=CH_2, OC*H*HCH=CH_2), 4.38 (d, *J* = 8.5 Hz, 1 H, 4-H), 4.30 (d, *J* = 5.0 Hz, 1 H), 4.24–4.31 (m, 3 H, 2-H, 6-H_a, 6-H_b), 4.14 (q, 2 H, $COOCH_2CH_3$), 4.03–4.07 (m, 1 H, 5′-H), 3.77–3.88 (m, 2 H, 6′-H_a, 6′-H_b), 3.54 (t, *J* = 10.0 Hz, 1 H, 4′-H), 3.51 (dd, *J* = 3.0, 10.0 Hz, 1 H, 2′-H), 2.03 (s, 3 H, $COCH_3$), 1.53 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.19 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{41}H_{52}O_{16}$ [M + Na]$^+$ 823.3153, found 823.3175.

6-*O*-Acetyl-3-*O*-allyloxycarbonyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (36*Sβ*): $[\alpha]_D^{20}$ = –60 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22–7.33 (m, 10 H, Ar), 5.91–5.96 (m, 1 H, CH_2=C*H*), 5.61 (s, 1 H, >CHPh), 5.55 (d, *J* = 5.0 Hz, 1 H, 1-H), 5.37 (d, *J* = 17.5 Hz, 1 H, CH*H*=CH), 5.26 (d, *J* = 11.0 Hz, 1 H, C*H*H=CH), 5.14 (t, *J* = 10.0 Hz, 1 H, 3′-H), 4.59–4.64 (m, 5 H, 3-H, 1′-H, OCH*H*CH=CH_2, OC*H*HCH=CH_2, CH*H*Ph), 4.20 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.33 (dd, *J* = 2.0, 5.0 Hz, 1 H, 2-H), 4.16–4.19 (m, 2 H, 6′-H_b, 6-H_a), 4.05–4.07 (m, 2 H, 6′$_a$-H, 6-H_b), 3.46 (t, *J* = 9.5 Hz, 1 H, 4′-H), 3.28 (t, *J* = 9.5 Hz, 1 H, 2′-H), 2.00 (s, 3 H, $COCH_3$), 1.60 (s, 3 H, CH_3), 1.55 (s, 6 H, CH_3), 1.45 (s, 3 H, CH_3), 1.17 (t, *J* = 7.5 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{41}H_{52}O_{16}$ [M + Na]$^+$ 823.3153, found: 823.3136.

6-*O*-Acetyl-3-*O*-allyloxycarbonyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (36*R*β): $[\alpha]_D^{20}$ = –25 (*c* = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.54 (m, 10 H, Ar), 5.95–6.01 (m, 1 H, C*H*=CH_2), 5.63 (s, 1 H, >CHPh), 5.52 (d, *J* = 5.0 Hz, 1 H, 1-H), 5.41 (dd, *J* = 1.0, 17.0 Hz, 1 H, CH=CH*H*), 5.24 (d, *J* = 10.0 Hz, 1 H, CH=C*H*H), 5.14 (t, *J* = 9.5 Hz, 1 H, 3′-H), 4.73–4.75 (m, 2 H, OC*H*HCH=CH_2, OCH*H*CH=CH_2), 4.74 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.54 (d, *J* = 11.0 Hz, 1 H, CH*H*Ph), 4.50 (d, *J* = 7.5 Hz, 1 H, 4-H), 4.28–4.31 (m, 2 H, 2-H, 6-H_a), 4.21–4.25 (m, 1 H, 6-H_b), 4.13–4.17 (m, 3 H, 5-H, $COOCH_2CH_3$), 4.01 (d, *J* = 7.0 Hz, 1 H, 1′-H), 3.67 (t, *J* = 9.5 Hz, 1 H, 4′-H), 3.61 (dd, *J* = 7.0, 9.5 Hz, 1 H, 2′-H), 3.53–3.56 (m, 2 H, 3-H, 5′-H), 2.03 (s, 3 H, $COCH_3$), 1.51 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.17 (t, *J* = 7.5 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{41}H_{52}O_{16}$ [M + Na]$^+$ 823.3153, found 823.3146.

Methyl [6-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (37*S*α): $[\alpha]_D^{20}$ = +128 (*c* = 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.22–7.38 (m, 25 H, Ar), 5.92–5.98 (m, 1 H), 5.85 (d, *J* = 3.3 Hz, 1 H), 5.28–5.29 (m, 1 H), 5.23 (s, 1 H), 5.09–5.17 (m, 2 H), 5.03 (d, *J* = 12.0 Hz, 1 H), 4.81 (d, *J* = 12.0 Hz, 1 H), 4.67 (d, *J* = 12.0 Hz, 1 H), 4.59 (d, *J* = 3.6 Hz, 1 H), 4.53 (d, *J* = 12.0 Hz, 1 H), 4.51–4.53 (m, 2 H), 4.50 (d, *J* = 12.0 Hz, 1 H), 4.24–4.29 (m, 2 H), 3.98–4.12 (m, 6 H), 3.75–3.84 (m, 4 H), 3.57–3.64 (m, 3 H), 3.40–4.31 (m, 1 H), 3.36 (s, 3 H, OCH_3), 1.96 (s, 3 H, $COCH_3$), 1.17 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{41}H_{52}O_{16}$ [M + Na]$^+$ 823.3153, found 823.3141.

Methyl [6-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (37*S*β): $[\alpha]_D^{20}$ = +61 (*c* = 0.2, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.25–7.41 (m, 25 H), 5.25 (s, 1 H), 5.70–5.79 (m, 1 H), 5.11 (dd, *J* = 1.5, 15.6 Hz, 1 H), 5.04–5.05 (m, 1 H), 4.98 (d, *J* = 12.0 Hz, 1 H), 4.78 (d, *J* = 5.0 Hz, 1 H), 4.76 (d, *J* = 12.0 Hz, 1 H), 4.75 (d, *J* = 12.0 Hz, 1 H), 4.70 (d, *J* = 12.0 Hz, 1 H), 4.69 (d, *J* = 12.0 Hz, 1 H), 4.61 (d, *J* = 3.6 Hz, 1 H), 4.60 (d, *J* = 12.0 Hz, 1 H), 4.49 (d, *J* = 12.0 Hz, 1 H), 4.44 (d, *J* = 12.0 Hz, 1 H), 4.37 (d, *J* = 7.5 Hz, 1 H, 1′-H), 4.04–4.21 (m, 1 H), 4.02–4.14 (m, 7 H), 3.82 (t, *J* = 9.5 Hz, 1 H), 3.60–3.73 (m, 1 H), 3.67–3.70 (m, 1 H), 3.51 (dd, *J* = 3.5, 9.5 Hz, 1 H), 3.39 (s, 3 H, OCH_3), 3.29–3.31 (m, 1 H), 3.18–3.26 (m, 2 H), 1.84 (s, 3 H, $COCH_3$), 1.18 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{56}H_{64}O_{14}$ [M + Na]$^+$ 983.4194, found: 983.4174.

Methyl [6-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (37*R*α): Selected ^1H NMR (300 MHz, $CDCl_3$): δ = 5.57 (d, *J* = 3.6 Hz, 1 H, 1′-H), 3.34 (s, 3 H, CH_3), 1.78 (s, 3 H, $COCH_3$), 1.16 (t, *J* = 7.2 Hz, 3 H, $COOCH_2CH_3$) ppm.

Methyl [6-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (37*R*β): Selected ^1H NMR (300 MHz, $CDCl_3$): δ = 4.46 (d, *J* = 7.5 Hz, 1 H, 1′-H), 3.43 (s, 3 H, CH_3), 1.98 (s, 3 H, $COCH_3$), 1.19 (t, *J* = 7.2 Hz, 3 H, $COOCH_2CH_3$) ppm.

6-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (38*S*α): $[\alpha]_D^{20}$ = +30 (*c* = 0 ppm.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.46 (m, 10 H, Ar), 5.90–6.00 (m, 1 H, C*H*=CH_2), 5.52 (d, *J* = 5.1 Hz, 1 H, 1-H), 5.30 (s, 1 H, >CHPh), 5.28–5.30 (m, 1 H, CH*H*=CH), 5.20 (dd, *J* = 1.8, 19.8 Hz, 1 H, C*H*H=CH), 5.14 (d, *J* = 3.3 Hz, 1 H, 1′-H), 4.83 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.62 (dd, *J* = 2.1, 7.5 Hz, 1 H), 4.54 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.39 (dd, *J* = 2.0, 7.5 Hz, 1 H, OCH*H*CH=CH_2), 4.31 (dd, *J* = 2.4, 4.8 Hz, 1 H, OC*H*HCH=CH_2), 4.27–4.29 (m, 1 H), 4.18–4.22 (m, 2 H), 4.11–4.15 (m, 2 H, $COOCH_2CH_3$), 4.02–4.04 (m, 1 H), 3.89 (t, *J* = 9.0 Hz, 2 H, 3′-H, 5′-H), 3.79–3.81 (m, 2 H), 3.43 (t, *J* = 9.0 Hz, 1 H, 4′-H), 3.38 (dd, *J* = 3.3, 9.0 Hz, 1 H, 2′-H), 2.02 (s, 3 H, $COCH_3$), 1.53 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.19 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{40}H_{52}O_{14}$ [M + Na]$^+$ 779.3255, found: 779.3243.

6-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (38*S*β): $[\alpha]_D^{20}$ = +56 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.56 (m, 10 H, Ar), 5.90–6.03 (m, 1 H, C*H*=CH_2), 5.77 (s, 1 H, >CHPh), 5.58 (d, *J* = 4.8 Hz, 1 H, 1-H), 5.29 (dd, *J* = 1.8, 17.4 Hz, 1 H, C*H*H=CH), 5.18 (dd, *J* = 1.8, 10.5 Hz, 1 H, CH=C*H*H), 4.83 (d, *J* = 10.5 Hz, 1 H, C*H*HPh), 4.60–4.63 (m, 2 H), 4.47 (d, *J* = 10.5 Hz, 1 H, C*H*HPh), 4.46 (d, *J* = 7.5 Hz, 1 H, 1′-H), 4.34 (dd, *J* = 2.1, 4.8 Hz, 1 H, 2-H), 4.16–4.25 (m, 4 H, $COOCH_2CH_3$, 4-H, 6-H_a), 4.03–4.09 (m, 1 H, 6-H_b, 6′-H_b), 3.68 (dd, *J* = 9.0, 11.1 Hz, 1 H, 5′-H), 3.59 (t, *J* = 9.0 Hz, 1 H, 3′-H), 3.41–3.43 (m, 1 H, 6′-H_a), 3.33 (d, *J* = 9.0 Hz, 1 H, 4′-H), 3.23 (dd, *J* = 7.5, 9.0 Hz, 1 H, 2′-H), 1.99 (s, 3 H, $COCH_3$), 1.61 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.18 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{40}H_{52}O_{14}$ [M + Na]$^+$ 779.3255, found 779.3263.

6-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (38*R*α): Selected ^1H NMR (300 MHz, $CDCl_3$): δ = 5.42 (s, 1 H, 1′-H), 1.93 (s, 3 H, $COCH_3$), 1.20 (t, *J* = 7.2 Hz, 3 H, $COOCH_2CH_3$) ppm.

6-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (38*R*β): $[\alpha]_D^{20}$ = –24 (*c* = 0.2, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.58 (m, 10 H, Ar), 6.13 (m, 1 H, C*H*=CH), 5.71 (s, 1 H, >CHPh), 5.54 (d, *J* = 4.5 Hz, 1 H, 1-H), 5.36 (d, *J* = 17.0 Hz, 1 H, CH*H*=CH), 5.20 (d, *J* = 10.5 Hz, 1 H, C*H*H=CH), 4.94 (d, *J* = 10.5 Hz, 1 H, 1′-H), 4.81 (dd, *J* = 5.5 Hz, 1 H, OCH*H*CH=CH_2), 4.57 (t, *J* = 9.5 Hz, 1 H, 2′-H), 4.55 (d, *J* = 3.5 Hz, 1 H, 3-H), 4.39 (d, *J* = 7.5 Hz, 1 H, OC*H*HCH=CH_2), 4.31 (d, *J* = 11.0 Hz, 1 H, C*H*HPh), 4.26 (d, *J* = 11.0 Hz, 1 H, CH*H*Ph), 4.24 (d, *J* = 4.5 Hz, 1 H, 2-H), 4.20 (q, *J* = 7.0 Hz, 2 H, $COOCH_2CH_3$), 4.12 (t, *J* = 9.5 Hz, 1 H, 3′-H), 4.01–4.02 (m, 2 H, 6-H_b, 5′-H), 3.57–3.62 (m, 2 H, 6-H_a, 6′-H_a), 3.49–3.53 (m, 2 H, 5-H, 6′-H_b), 3.43–3.45 (m, 1 H, 4-H, 4′-H), 2.02 (s, 3 H, $COCH_3$), 1.53 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.18 (t, *J* = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: *m*/*z* calcd. for $C_{40}H_{52}O_{14}$ [M + Na]$^+$ 779.3255, found 779.3271.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-galactopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (39*S*α): $[\alpha]_D^{20}$ = +191 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.17–7.34 (m, 25 H, Ar), 5.93 (d, *J* = 3.5 Hz, 1 H, 3′-H), 5.19–5.22 (m, 1 H, 4′-H), 5.04 (s, 1 H, >CHPh), 5.03 (d, *J* = 11.5 Hz, 1 H, CH*H*Ph), 4.98 (d, *J* = 11.5 Hz, 1 H, C*H*HPh), 4.68 (d, *J* = 11.5 Hz, 1 H, C*H*HPh), 4.60 (t, *J* = 9.5 Hz, 1 H, 3-H), 4.57 (d, *J* = 11.5 Hz, 1 H, CH*H*Ph), 4.54 (s, 1 H, 1′-H), 4.53 (d, *J* = 11.5 Hz, 1 H, CH*H*Ph), 4.42 (d, *J* = 11.5 Hz, 1 H, C*H*HPh), 4.10 (t, *J* = 9.5 Hz, 1 H, 4-H), 3.92–4.06 (m, 7 H, 2′-H, 1-H, 6-H_b, 6′-H_a, 6′-H_b, $COOCH_2CH_3$), 3.87–3.89 (m, 1 H, 5′-H), 3.78 (dd, *J* =

4.5, 11.0 Hz, 1 H, 6-H_a), 3.65 (d, J = 9.5 Hz, 1 H, 5-H), 3.59 (dd, J = 3.0, 9.5 Hz, 1 H, 2-H), 3.37 (s, 3 H, CH_3), 1.91 (s, 3 H, $COCH_3$), 1.85 (s, 3 H, $COCH_3$), 1.09 (t, J = 7.0 Hz, 3 H, CO-OCH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.41, 170.17, 170.05, 139.26, 138.21, 138.01, 137.53, 136.21, 128.62, 128.42, 128.29, 128.19, 127.98, 127.90, 127.54, 127.46, 127.29, 127.07, 127.00, 97.61, 96.33, 81.56, 81.13, 80.36, 77.22, 75.03, 74.84, 73.95, 73.32, 73.27, 73.09, 72.54, 69.35, 68.22, 62.49, 61.24, 55.13, 20.93, 20.68, 14.02 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{55}H_{62}O_{15}$ $[M + Na]^+$ 985.3986, found 985.3975.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-galactopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (39*S*β): $[\alpha]_D^{20}$ = +253 (c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.15–7.37 (m, 25 H, Ar), 5.06 (s, 1 H, >CHPh), 4.95 (d, J = 10.5 Hz, 1 H, C*H*HPh), 4.83 (d, J = 11.5 Hz, 1 H, C*H*HPh), 4.73 (d, J = 10.5 Hz, 1 H, CH*H*Ph), 4.71 (d, J = 12.5 Hz, 1 H, C*H*HPh), 4.66 (dd, J = 4.5, 10.0 Hz, 1 H, 3′-H), 4.65 (d, J = 11.5 Hz, 1 H, CH*H*Ph), 4.60 (d, J = 4.0 Hz, 1 H, 1-H), 4.51 (d, J = 12.0 Hz, 1 H, CH*H*Ph), 4.48 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.39 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.36 (d, J = 8.0 Hz, 1 H, 1′-H), 3.97–4.15 (m, 7 H, 4-H, 6-H_a, 6-H_b, 6′-H_a, 6′-H_b, $COOCH_2CH_3$), 3.81 (t, J = 9.0 Hz, 1 H, 3-H), 3.76–3.76 (m, 1 H, 4′-H), 3.66–3.69 (m, 2 H, 2′-H, 5′-H), 3.52 (dd, J = 4.0, 9.5 Hz, 1 H, 2-H), 3.38 (s, 3 H, CH_3), 3.30 (t, J = 7.0 Hz, 1 H, 5-H), 1.97 (s, 3 H, $COCH_3$), 1.64 (s, 3 H, $COCH_3$), 1.19 (t, J = 6.5 Hz, 3 H, $COOCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.42, 170.26, 170.17, 139.06, 138.49, 138.04, 137.83, 136.99, 128.52, 128.48, 128.34, 128.19, 128.09, 127.99, 127.89, 127.82, 127.77, 127.48, 127.23, 101.46, 98.52, 82.80, 80.08, 78.89, 77.95, 75.49, 75.13, 74.58, 74.10, 73.66, 73.26, 71.53, 69.76, 68.17, 61.82, 60.97, 55.26, 20.79, 20.57, 14.15 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{55}H_{62}O_{15}$ $[M + Na]^+$ 985.3986, found 985.3877.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-galactopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (39*R*β): $[\alpha]_D^{20}$ = –53 (c = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18–7.38 (m, 25 H, aromatic), 5.05 (s, 1 H, >CHPh), 4.93 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.81 (dd, J = 3.3, 9.9 Hz, 1 H, 3′-H), 4.80 (d, J = 11.0 Hz, 1 H, CH*H*Ph), 4.74 (d, J = 12.0 Hz, 1 H, CH*H*Ph), 4.69 (d, J = 12.0 Hz, 1 H, CH*H*Ph), 4.61 (d, J = 12.0 Hz, 1 H, CH*H*Ph), 4.54 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.53 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.52 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.50 (d, J = 3.0 Hz, 1 H, 1-H), 4.11 (d, J = 9.0 Hz, 1 H, 1′-H), 4.02–4.20 (m, 6 H, 6′-H_a, 6′-H_b, 5′-H, C*H*HPh, $COOCH_2CH_3$), 3.88 (t, J = 9.0 Hz, 1 H, 4-H), 3.78 (d, J = 3.0 Hz, 1 H, 4′-H), 3.66–3.72 (m, 2 H, 2′-H, 3-H), 3.43 (dd, J = 3.0, 9.5 Hz, 1 H, 2-H), 3.31 (s, 3 H, CH_3), 3.27–3.29 (m, 1 H, 6-H_a), 2.94–3.02 (m, 2 H, 5-H, 6-H_b), 2.16 (s, 3 H, $COCH_3$), 1.97 (s, 3 H, $COCH_3$), 1.18 (t, J = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. HR MALDI-TOF MS: m/z calcd. for $C_{55}H_{62}O_{15}$ $[M + Na]^+$ 985.3986, found 985.3971.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-α-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (40*S*α): $[\alpha]_D^{20}$ = +249 (c = 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25–7.98 (m, 25 H, Ar), 6.16 (t, J = 9.5 Hz, 1 H, 3-H), 5.48 (t, J = 9.5 Hz, 1 H, 4-H), 5.30 (dd, J = 3.0, 11.0 Hz, 1 H, 3′-H), 5.26 (dd, J = 3.5, 9.5 Hz, 1 H, 2-H), 5.23 (d, J = 3.5 Hz, 1 H, 1-H), 5.21 (d, J = 4.0 Hz, 1 H, 1′-H), 5.12 (s, 1 H, >CHPh), 4.64 (d, J = 11.0 Hz, 1 H, CH*H*Ph), 4.48 (d, J = 11.0 Hz, 1 H, C*H*HPh), 4.37 (t, J = 8.5 Hz, 1 H, 5-H), 4.20 (t, J = 6.5 Hz, 1 H, 5′-H), 4.12–4.13 (m, 1 H, 2′-H), 4.09 (q, J = 7.0 Hz, 2 H, CO-OCH_2CH_3), 4.05–4.08 (m, 1 H, 4′-H), 4.03–4.04 (m, 2 H, 6′-H_a, 6′-H_b), 3.93 (dd, J = 7.5, 11.0 Hz, 1 H, 6-H_a), 3.75 (d, J = 10.0 Hz, 1 H, 6-H_b), 3.44 (s, 3 H, CH_3), 2.00 (s, 3 H, $COCH_3$), 1.88 (s, 3 H, $COCH_3$), 1.16 (t, J = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.63, 170.25, 170.13, 165.38, 164.64, 164.38, 129.94, 129.90, 129.67, 129.27, 129.15, 128.96, 128.50, 128.44, 128.40, 128.24, 128.20, 128.06, 126.96, 97.95, 96.63, 82.05, 75.35, 75.14, 74.85, 73.02, 72.20, 70.62, 69.69, 68.71, 68.14, 66.96, 63.02, 61.39, 55.47, 20.87, 20.79, 14.03 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{55}H_{56}O_{18}$ $[M + Na]^+$ 1027.3364, found 1027.3354.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*S*)-ethoxycarbonylbenzyl]-β-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (40*S*β): $[\alpha]_D^{20}$ = +155 (c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09–7.98 (m, 25 H, Ar), 6.16 (t, J = 9.5 Hz, 1 H, 3-H), 5.37 (t, J = 9.5 Hz, 1 H, 4-H), 5.36 (s, 1 H, >CHPh), 5.23 (dd, J = 3.5, 9.5 Hz, 1 H, 2-H), 5.22 (s, 1 H, 1-H), 4.92 (dd, J = 3.0, 10.0 Hz, 1 H, 3′-H), 4.57 (d, J = 7.5 Hz, 1 H, 1′-H), 4.48 (d, J = 12.0 Hz, 1 H, CH*H*Ph), 4.40–4.43 (m, 1 H, 5-H), 4.39 (d, J = 12.0 Hz, 1 H, C*H*HPh), 4.19 (q, J = 7.0 Hz, 2 H, $COOCH_2CH_3$), 4.12 (dd, J = 7.0, 11.0 Hz, 1 H, 6′-H_a), 4.01 (dd, J = 2.0, 11.0 Hz, 1 H, 6-H_b), 3.95 (dd, J = 6.5, 11.0 Hz, 1 H, 6′-H_b), 3.82 (d, J = 2.0 Hz, 1 H, 4′-H), 3.78 (dd, 1 H, 6-H_a), 3.72 (dd, J = 7.5, 9.5 Hz, 1 H, 2′-H), 3.63 (t, J = 6.5 Hz, 1 H, 5′-H), 3.54 (s, 3 H, CH_3), 1.89 (s, 3 H, $COCH_3$), 1.75 (s, 3 H, $COCH_3$), 1.20 (t, J = 7.0 Hz, 3 H, $COOCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.51, 170.36, 170.23, 165.84, 165.75, 165.54, 137.45, 137.05, 133.50, 133.35, 133.07, 129.93, 129.86, 129.65, 129.25, 129.09, 128.82, 128.52, 128.47, 128.42, 128.31, 128.26, 128.09, 127.99, 127.86, 103.88, 96.77, 81.51, 74.06, 73.62, 72.18, 71.74, 70.33, 70.07, 69.53, 68.85, 62.15, 61.21, 55.82, 20.70, 20.60, 14.14 ppm. HR MALDI-TOF MS: m/z calcd. for $C_{55}H_{56}O_{18}$ $[M + Na]^+$ 1027.3364, found 1027.3382.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-α-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (40*R*α): Selected ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.73 (s, 1 H, 1′-H), 3.61 (s, 3 H, CH_3), 2.04 (s, 3 H, $COCH_3$), 1.99 (s, 3 H, $COCH_3$), 1.19 (t, J = 7.2 Hz, 3 H, $COOCH_2CH_3$) ppm.

Methyl [3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(*R*)-ethoxycarbonylbenzyl]-β-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (40*R*β): Selected ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.49 (d, J = 7.5 Hz, 1 H, 1′-H), 3.46 (s, 3 H, CH_3), 2.26 (s, 3 H, $COCH_3$), 1.82 (s, 3 H, $COCH_3$), 1.17 (t, J = 7.2 Hz, 3 H, $COOCH_2CH_3$) ppm.

Methyl α-D-Glucopyranosyl-(1→6)-α-D-glucopyranoside (42): Sodium methoxide (3.0 mg, 0.055 mmol) was added to a solution of **31*S*α** (55 mg, 0.055 mmol) in methanol (5 mL). The reaction mixture was stirred for 1 d, then quenched with Amberlite IRC-50 ion exchange resin (weakly acidic). After filtration, the filtrate was concentrated in vacuo. The residue was purified by column chromatography on Iatrobeads (dichloromethane/methanol, 2:1) to afford **41** (30 mg, 93%). A solution of **41** (30 mg, 0.052 mmol) in THF (3 mL) was added to liquid ammonia (5 mL) at –78 °C. Sodium (≈ 20 mg) was then added until a persistent blue color was obtained. Solid NH_4Cl (0.1 g) was then added and the solvents were evaporated. The crude reaction mixture was purified by column chromatography on Iatrobeads (dichloromethane/methanol/H_2O, 15:5:1) to afford **42** (18 mg, 97%): R_f = 0.34 (dichloromethane/methanol/H_2O, 15:5:1). $[\alpha]_D^{20}$ = +26.9 (c = 1.0, CH_3OH). ^{1}H NMR (500 MHz, D_2O): δ = 4.87 (d, J = 4.0 Hz, 1 H), 4.73 (d, J = 3.5 Hz, 1 H), 3.90 (dd, J = 4.5, 9.0 Hz, 1 H), 3.76 (dd, J = 2.0, 12.5 Hz, 1 H), 3.33–3.73 (m, 10 H), 3.34 (s, 3 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 99.56, 98.04, 73.56, 73.25, 72.02, 71.66, 71.34, 70.25, 69.70, 69.59, 65.67, 60.65, 55.38 ppm.

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of all compounds.

Acknowledgments

This research was supported by the NIH Research Resource Center for Biomedical Complex Carbohydrates (P41-RR-5351). The authors gratefully acknowledge the use of the RSCC computer situated in the RIKEN Computer Center, Wako-shi, Saitama, Japan and A. Ionescu for making the spherical plot and the LUMO plots.

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Received: May 19, 2006
Published Online: August 15, 2006

