Vinyl Glycosides in Oligosaccharide Synthesis. 2. The Use of Allyl and Vinyl Glycosides in Oligosaccharide Synthesis

Geert-Jan Boons* and Stephen Isles

School of Chemistry, The University of Birmingham, Edgbaston, Birmingham, B15 2TT, U.K.

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A novel latent−active glycosylation strategy has been described that relies on the isomerization of substituted allyl glycosides to give the corresponding vinyl glycosides, which can subsequently be used in Lewis acid-mediated glycosylations. The isomerization reaction was performed by a rhodium catalyst obtained by treating tris(triphenylphosphine)rhodium(I) chloride with *n*-butyllithium. This catalyst has many advantageous properties over the use of conventional Wilkinson's catalyst. The glycosylation reactions gave high yields for both primary and secondary sugar alcohols, and the anomeric selectivity could be controlled by the constitution of the glycosyl donor and reaction conditions. The new isomerization and glycosylation approach enables complex oligosaccharides of biological importance to be prepared in a highly convergent manner.

Introduction

It is now well established that, in the living cell, carbohydrates play key roles in many different processes.[1] Examples include fertilization, embryogenesis, neuronal development, hormone activities, and cell proliferation and their organization into specific tissues. To establish the biological roles of oligosaccharides, sufficient amounts of pure and well-defined saccharides of different sizes are often required. Organic synthesis provides an important means of obtaining these fragments. The preparation of complex oligosaccharide fragments requires a highly convergent synthetic strategy.[2] In such a glycosylation strategy, most of the synthetic effort is directed toward the preparation of the monomeric glycosyl donors and acceptors. The assembly of these units to an oligomer should involve a minimum number of synthetic steps, and each reaction should proceed with high stereoselectivity and yield. Furthermore, an efficient synthetic strategy should make optimal use of common intermediates and saccharide building blocks. The anomeric substituent of a saccharide building block should be sufficiently stable to withstand protecting group manipulations (*i.e.*, acts as a protecting group) but also have an adequate reactivity to permit its use as a glycosyl donor (*i.e.*, acts as a leaving group). Thioglycosides[3] and *n*-pentenyl glycosides[4] have been shown to possess these features. These substrates have also been used in chemoselective glycosylations (the "armed−disarmed" approach). In this approach, a C-2 ether-protected donor (armed) is coupled with a C-2 ester protected acceptor (disarmed), in the presence of the mild activator iodonium dicollidine perchlorate (IDCP), to give a dimer. Next, the disarmed dimer can be further glycosylated using the more powerful activating system *N*-iodosuccinimide/catalytic triflic acid (NIS/TfOH) to yield a trisaccharide. Thus, the difference in reactivity between the two anomeric centers of the glycosyl donor and acceptor is achieved through differential protection of the 2-OH (ether/ester, armed/disarmed). Therefore, the preparation of oligosaccharide donors by this approach is limited as only very few types of protecting groups are available.[5] A glycosylation strategy in which the reactivity of the carbohydrate units is controlled only by the anomeric group[6] would not require differential protection and, hence, would allow the synthesis of oligosaccharide building blocks of any size.

Isopropenyl glycosides, which can be prepared by reacting anomeric acetates with Tebbe reagent, undergo glycosylation reactions with primary and secondary carbohydrate alcohols in the presence of trimethylsilyl triflate or boron trifluoride etherate.[7] Since many functional and protecting groups are sensitive toward Tebbe reagent, this glycosylation method is not widely applicable.

We report here in full[8] a novel latent−active glycosylation strategy based on the isomerization of 3-buten-2-yl glycosides to give 2-buten-2-yl glycosides that, in turn, can undergo Lewis acid-catalyzed glycosylations. In this glycosylation strategy, the anomeric 3-buten-2-yl group acts as an effective anomeric protecting group (latent) but can be converted efficiently into a leaving group by isomerization to a 2-buten-2-yl glycoside (active). The latter glycosyl donor can be coupled to a suitably protected 3-buten-2-yl glycosyl acceptor (latent), and the resulting dimer can be converted into a glycosyl donor by isomerization of the 3-buten-2-yl moiety or into a glycosyl acceptor by selective removal of a protecting group. Thus, the reactivity of the carbohydrate units is

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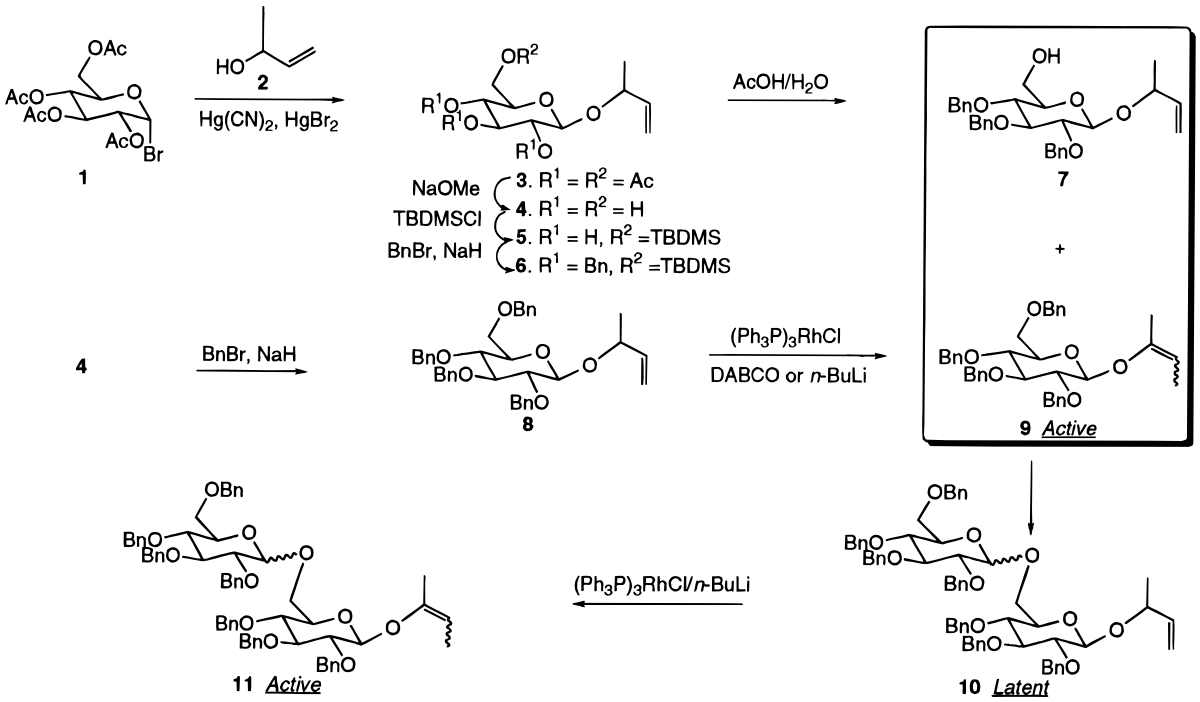
Scheme 1



controlled only by the anomeric group and does not require differential protection. The isomerization reactions have been performed by a new isomerization procedure[9] involving the treatment of tris(triphenylphosphine)rhodium(I) chloride with *n*-butyllithium. This rhodium catalyst is able to isomerize a wide range of substituted and unsubstituted allylic ethers and glycosides and has many advantageous properties over the use of conventional Wilkinson's catalyst.[10] The new isomerization procedure also allows the isomerization and glycosylation to be performed as a one-pot procedure.

Results and Discussion

The substituted allyl glycoside **3** was readily prepared by coupling acetoxy bromide **1** with 3-buten-2-ol (**2**) under modified Koenigs–Knorr conditions.[11] Compound **3** can undergo many different functional and protecting group manipulations. For example, glycosyl acceptor **7** was readily available from compound **3** *via* a four-step procedure. Thus, deacetylation of compound **3** with sodium methoxide in methanol gave compound **4**, and regioselective silylation of this product with TBDMSCl in pyridine yielded compound **5** which was benzylated with benzyl bromide and sodium hydride in DMF to afford the fully protected compound **6**. The TBDMS protecting group of compound **6** was removed by treatment with a mixture of acetic acid/water to yield glycosyl acceptor **7**. Benzylation of compound **4** with benzyl bromide and sodium hydride in DMF gave the fully benzylated glycoside **8**.

In order to prepare glycosyl donor **9**, the allyl group of the latent compound **8** has to be isomerized to an active vinyl moiety. Many metal catalysts have been applied successfully for the conversion of unsubstituted allyl ethers into propenyl ethers. However, isomerization of the substituted allyl moiety of **8** proved to be more difficult, and the application of commonly used catalysts such as dihydrotetrakis(triphenylphosphine)ruthenium(II),[12] 10% palladium on active charcoal,[13] and *trans*-dichlorodiaminepalladium(II)[14] failed to perform the required isomerization. However, treatment of **8** with Wilkinson's catalyst[10] in the presence of diazabicyclo[2.2.2]octane (DABCO) in a refluxing mixture of methanol/water gave the substituted vinyl glycoside **9** as a mixture of cis and trans isomers in a 71% yield. Minor amounts of hydrolyzed and reduced products were observed.

Having vinyl glycosyl donor **9** in hand, we turned our attention to Lewis acid-promoted glycosylations (Scheme 1). Thus, coupling of acceptor **7** with active donor **9** in the presence of a catalytic amount of TMSOTf (0.25 equiv) at −25 °C in acetonitrile gave, after a reaction time of 1.5 h, mainly the β-linked dimer **10** in an excellent yield (78%, α/β 1/20). When the same glycosylation was performed in dichloromethane, a mixture of anomers (72%, α/β 4/3) was obtained. The α-selectivity could be improved (74%, α/β 4/1) by using NIS/TfOH as the activator in a mixture of ether/dichloroethane at 0 °C, and under these conditions the glycosylation was almost instantaneous. Dimer **10** could be converted into glycosyl donor **11** by isomerization of its allyl group to a vinyl moiety (latent → active).

Previously Sinaÿ *et al.* reported the use of isopropenyl glycosides as glycosyl donors, and it is of interest to note that the activation of these compounds requires stoichiometric amounts of Lewis acid.[7] The higher reactivity of the substituted vinyl glycoside **9** can be explained as

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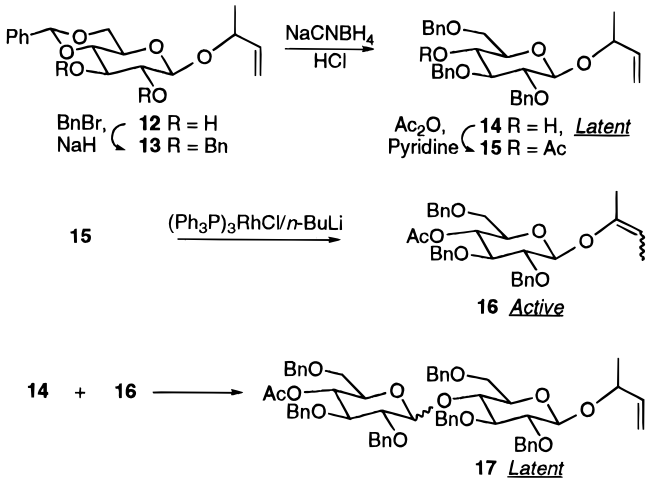
follows: protonation of the double bond is the rate-determining step in the activation of a vinyl glycoside,[15] and the additional methyl substituent of the vinyl moiety of **9** makes the double bond more electron rich and hence more susceptible to protonation and glycosylation. Furthermore, these results indicate that vinyl glycosyl donor **9** is less prone to form trehaloses than the corresponding isopropenyl glycoside.[7]

Racemic 3-buten-2-ol was used for the preparation of **3**, resulting in the formation of a mixture of diastereoisomers. While the diastereoisomeric nature of the glycoside does not affect the chemistry, it complicates the interpretation of the NMR spectra. Multigram quantities of optically pure 3-buten-2-ol can, however, easily be obtained by resolving the corresponding acid phthalate as the (*S*)- or (*R*)-α-phenylethylamine salt.[16]

The isomerization reaction that the novel latent−active strategy relies upon initially could only be achieved by the use of Wilkinson's catalyst. A drawback of this catalyst is that it partly reduces an allyl ether into a propyl ether.[17] Furthermore, the mild base, DABCO, has to be included to avoid hydrolysis of the enol ether since the ketone produced will poison the catalyst. Prior to glycosylation, the DABCO has to be removed by basic alumina column chromatography. These factors account for the relatively low yield of the isomerization. The drawbacks associated with the use of this catalyst led us to search for an alternative isomerization procedure. Motherwell *et al.* have shown[18] that in the presence of Wilkinson's catalyst a wide range of allylic alkoxides in THF can be isomerized to enolates which may undergo *in situ* aldol condensations with ketones. Wilkinson's catalyst in THF, however, is unable to isomerize allylic alcohols.[19] Therefore, we expected that under the applied reaction conditions the rhodium catalyst was being converted into another more reactive catalytic species. Indeed, treatment of Wilkinson's catalyst (5−10 mol %) in freshly distilled THF with *n*-BuLi, for 10 min, gave a deep red solution which isomerizes compound **8** smoothly to give, after flash silica gel column chromatography, pure **9** as a mixture of cis−trans isomers in an excellent yield of 92%. The unpurified enol ether could also be cleaved by treatment with $HgCl_2$/HgO in acetone to give the corresponding lactol in high yield (93%). It is important to note that *n*-BuLi alone failed to promote a reaction, proving that the isomerization is not catalyzed by the base. In order to find out whether reduction of the allyl ether to a propyl ether could occur, the allyl glycoside **8** was subjected to the reaction conditions ($(Ph_3P)_3RhCl$/BuLi in refluxing THF) for a prolonged period of time (16 h). ^1H NMR spectroscopy and FAB-mass spectroscopy of the product thus obtained did not reveal the presence of any reduced material, and the isomerized compound was isolated in high yield.

We believe that under the applied reaction conditions the chloride of the Wilkinson's catalyst is substituted by a butyl group which undergoes a β-hydride shift to give

Scheme 2



hydrido tris[triphenylphosphine]rhodium(I).[20] This rhodium species has been described,[21] and we have prepared $(Ph_3P)_3RhH$ by a published procedure. The catalyst thus obtained was also able to isomerize allyl ethers and glycosides at similar reaction rates as for the procedure described above, and the products were isolated in similar yields.

Recently, one-pot multistep reactions have received considerable attention.[22] This type of synthetic procedure minimizes tedious workup and purification steps and often gives better overall yields. We envisaged that the new isomerization conditions could allow the isomerization and glycosylation to be performed as a one-pot procedure. Thus, after isomerization of the allyl moiety of compound **8**, glycosyl acceptor **7** in acetonitrile was added to the mixture, the reaction mixture was cooled to −25 °C, and a promotor was added. Unfortunately, TMSOTf or $BF_3{\cdot}OEt_2$ was unable to promote the glycosylation. It appeared that the rhodium catalyst had, in some way, reacted with the Lewis acid, resulting in the slow hydrolysis of the donor. However, when, prior to glycosylation, the Rh-catalyst was exposed to O_2, $BF_3{\cdot}OEt_2$-promoted glycosylation gave clean formation of disaccharide **10** in high overall yield (71%, α/β 1/20).

Encouraged by the promising results obtained, we explored glycosylations with the less reactive glycosyl acceptor **14** (Scheme 2). Compound **14** could easily be obtained from compound **4** *via* a three-step procedure. Thus, treatment of **4** with benzaldehyde dimethyl acetal and a catalytic amount of camphorsulfonic acid gave regioselectively the partially protected saccharide **12**. Benzylation of compound **12** under standard conditions afforded the fully protected species **13** and reductive cleavage of the benzylidene acetal with sodium cyanoborohydride, and hydrogen chloride yielded the required glycosyl acceptor **14**. Also, a minor amount of the other regioisomer (6-OH) was isolated. Acceptor **14** was also the starting material for compound **16**, Thus, the latent substrate **15** was obtained by acetylation with acetic anhydride and pyridine, and glycosyl donor **16**

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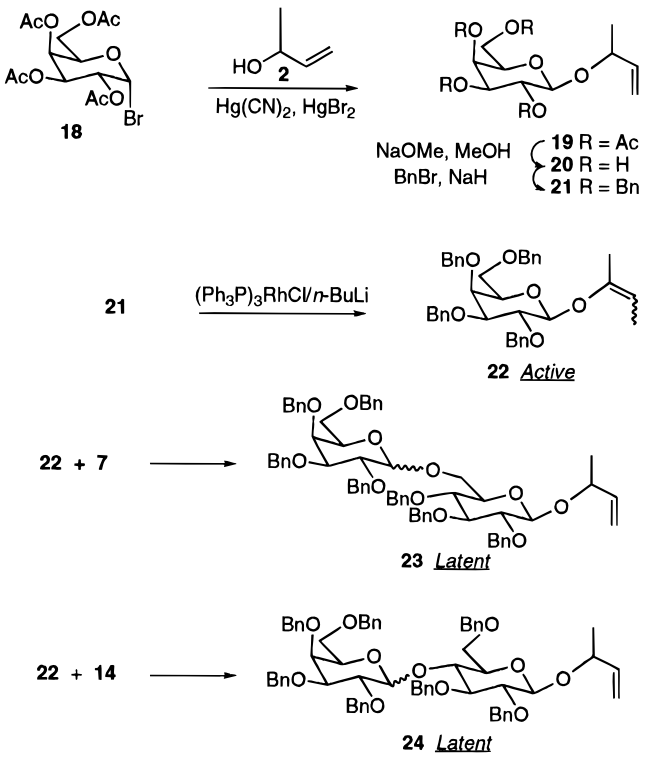
Scheme 3

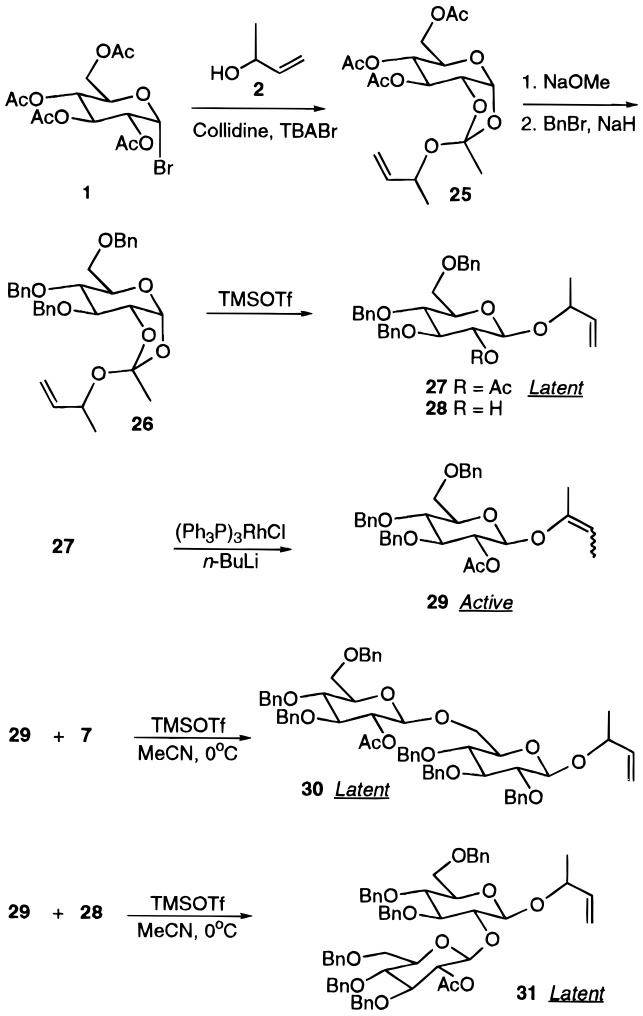


could be prepared by isomerization of the allyl moiety with $(Ph_3P)_3RhCl/n$-BuLi. This example illustrates that base labile functionalities are compatible with the new isomerization conditions. TMSOTf-promoted condensation of **16** with **14** in acetonitrile for 1.5 h gave disaccharide **17** in a 78% yield as mainly the β-anomer (α/β = 1/8). When the same glycosylation reaction was performed in dichloromethane, dimer **17** was isolated in excellent yield (75%), but the α/β ratio was rather disappointing (α/β = 1.5/1). The use of ether as solvent or $BF_3{\cdot}Et_2O$ as activator had no observable effect on the product ratio. However, an improved α-selectivity was obtained (73%, α/β = 3/1) when the coupling was performed in ether/dichloroethane at 0 °C with NIS/TfOH as activator.

In order to study galactosylation reactions, the vinyl galactoside **22** was prepared (Scheme 3). Thus, condensation of acetoxy bromide **18** with alcohol **2** under Koenigs−Knorr conditions gave glycoside **19**. Treatment of glycoside **19** with KO^{t}Bu in methanol gave compound **20**, and benzylation of this compound afforded the fully protected latent substrate **21**. Isomerization of the allyl moiety of compound **21** with Wilkinson's catalyst treated with *n*-BuLi gave the glycosyl donor **22** in a good overall yield. Treatment of a mixture of acceptor **7** and donor **22** with a catalytic amount of TMSOTf in acetonitrile at −25 °C afforded the dimer **23** in high yield with modest β-selectivity (79%, α/β = 1/3). A reasonable α-selectivity (75%, α/β = 4/1) was obtained when the same coupling was performed in dichloromethane. In this case, the use of NIS/TfOH as activator did not improve the α/β ratio. TfOH-mediated coupling of the less reactive alcohol **14** with galactoside **22** in acetonitrile or dichloromethane gave in both cases dimer **24** in high yield but with modest β (68%, α/β = 1/1.5) and reasonable α-selectivity (66%, α/β = 4/1), respectively.

Examination of glycosylations of vinyl gluco- and galactosyl donors reveals that the glucosides give more

Scheme 4



favorable β-selectivities when the glycosylation is performed in acetonitrile. This behavior has been reported by others[23] and may be due to a steric or electronic influence of the axial oriented benzyl group at C-4 of the galactoside. Furthermore, coupling with primary sugar alcohols gives under these reaction conditions better β-selectivities.

The diastereochemical outcome of the previously discussed glycosylations has been controlled by the choice of solvent and, to some extent, the choice of activator. Another approach to control the α/β ratio of a glycosylation reaction which leads to the formation of 1,2-*trans* glycosides is based on neighboring group participation by a 2-hydroxyl protecting group. It is to be expected that a vinyl glycoside having a neighboring participating protecting group at the 2-hydroxyl position can easily be obtained by isomerization of the corresponding substituted allyl glycoside. We have prepared the vinyl glucoside **29** which could be coupled to the glycosyl acceptors **7** and **28** (Scheme 4). Thus, treatment of the acetoxy bromide **1** with alcohol **2** in the presence of collidine and *tert*-butyl ammonium bromide gave orthoester **25** in an excellent yield. Orthoester **25** was converted into the benzylated compound **26** by deacetylation followed by benzylation. Rearrangement of compound **26** with a catalytic amount of TMSOTf in dichloromethane at −20 °C resulted in the almost quantitative formation of

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compound **27**. Base-mediated removal of the acetate protecting group of compound **27** gave glycosyl acceptor **28**. The latent glycoside **27** could be converted cleanly into active glycosyl donor **29** by isomerization with the new catalytic system. Treatment of a mixture of donor **29** and acceptor **7** with a catalytic amount of TMSOTf in acetonitrile at 0 °C gave, as expected, pure β-linked dimer **30** in a good yield (71%). Compound **28** is a suitable glycosyl acceptor and was also condensed under standard coupling conditions with donor **29** to give dimer **31** in a yield of 72%. The dimers **30** and **31** can be converted into glycosyl donors by isomerization of the allyl moiety.

In conclusion, we have described a new latent−active glycosylation strategy that allows glycosyl donors and acceptors to be prepared from common building blocks. The anomeric allyl moiety of such a building block can act as an effective anomeric protecting group but can easily be converted into a leaving group. These features allow oligosaccharides to be prepared by an convergent strategy. Furthermore, we have shown that treatment of Wilkinson's catalyst with *n*-BuLi results in a more efficient isomerization catalyst.

Experimental Section

General Methods and Materials. All solvents were distilled prior to use from an appropriate drying agent. Toluene, CH_2Cl_2, and $CHCl_3$ were distilled from P_2O_5. DMF and CH_3CN were distilled from CaH_2. THF and diethyl ether were distilled from $LiAlH_4$. Column chromatography was carried out on silica gel (Merck 7734). Flash silica ES70X was obtained from Crosfield Catalysts, Warrington. TLC analysis was conducted on silica gel plates (Merck 1.05554 Kieselgel 60 F254). Compounds were visualized by UV light (254 nm) or by dipping with concentrated H_2SO_4/methanol 1/10, v/v) and subsequent charring. (±)-3-Buten-2-ol was purchased from Fluka. (Trimethylsilyl)trifluoromethanesulfonate (TMSOTf) was purchased from Lancaster, and all other reagents were purchased from Aldrich and used without further purification. Aqueous NaCl (saturated) and $NaHCO_3$ (10% w/v) were prepared in advance. Sephadex LH-20 (Pharmacia) was used for gel filtration chromatography.

(*R/S*)-3-Buten-2-yl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (3). A solution of bromide **1** (30.5 g, 74 mmol) and (±)-3-buten-2-ol (**2**) (30 mL, 340 mmol) in acetonitrile (35 mL) was added to a stirred suspension of mercury(II) cyanide (23.1 g, 91 mmol), mercury(II) bromide (34.1 g, 94 mmol), and powdered 4 Å molecular sieves (30 g) in acetonitrile (60 mL). After the reaction mixture was stirred for 12 h, TLC analysis (acetone/CH_2Cl_2, 2/98, v/v) showed complete conversion of starting material (R_f 0.53) into a product (R_f 0.64). The reaction mixture was filtered, and the filtrate was concentrated under reduced pressure to yield an oil which was dissolved in CH_2Cl_2 (100 mL) and washed with $NaHCO_3$ (3 × 60 mL) and aqueous NaCl (3 × 60 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to give an orange crystalline residue. This crude product was applied to a column of silica gel (300 g, eluant: acetone/CH_2Cl_2, 3/97, v/v), and concentration of the appropriate fractions afforded **3** (20.8 g, 70%). δ^1H (300 MHz; $CDCl_3$) 5.85−5.60 (1H, m, C*H*=CH_2), 5.20−4.93 (5H, m, CH=C*H*$_2$, H-2, H-3, H-4), 4.54 (1H, d, $^3J_{1,2}$ = 8 Hz, H-1), 4.30−4.04 (3H, m, CH_3C*H*, H-6(a,b)), 3.64 (1H, m, H-5), 2.10−1.93 (12H, m, Ac CH_3), 1.23 (3H, q, ^3J = 7 Hz, CHC*H*$_3$); δ^{13}C (75 MHz; $CDCl_3$) 170.6−169.2 (Ac C=O), 139.6, 138.6 (*C*H=CH_2), 117.0, 115.3 (*C*H$_2$=CH), 99.3, 97.9 (C-1), 77.6, 75.7, 72.9, 68.5 (C-2, C-3, C-4, C-5), 71.9, 71.5 (*C*HCH$_3$), 62.1 (C-6), 20.7 (CH*C*H$_3$), 20.5 (Ac CH_3); *m*/*z* 425 (100, [M + Na]$^+$), 331 (43, [M − *O*-3-buten-2-yl]$^+$).

(*R/S*)-3-Buten-2-yl β-D-Glucopyranoside (4). Potassium *tert*-butoxide (3.0 g) was added to a stirred solution of **3** (8.34 g, 20 mmol) in methanol (100 mL). After a reaction time of 5 h, TLC analysis (acetone/CH_2Cl_2, 1/49, v/v) showed complete conversion of the starting material (R_f 0.64) into a product (R_f 0.09). The reaction mixture was neutralized with Dowex 50 WX4 (H^+) (60 mL), filtered, and concentrated in *vacuo*. After coevaporation from toluene (3 × 5 mL), compound **4** was obtained as hygroscopic white crystals (4.36 g, 90%): δ^1H (300 MHz; D_2O) 5.95−5.60 (1H, m, C*H*=CH_2), 5.30−5.12 (2H, m, CH=C*H*$_2$), 4.50 (1H, 2 × d, $^3J_{1,2}$ = 8 Hz, H-1), 4.30 (1H, m, CH_3C*H*), 3.82 (1H, m, H-3), 3.63 (1H, m, H-4), 3.45−3.25 (3H, m, H-2, H-6(a,b)), 3.21 (1H, m, H-5), 1.23 (3H, d, ^3J = 2.9 Hz, CH_3); δ^{13}C (75 MHz; D_2O) 142.3, 141.2 (*C*H=CH_2), 120.7, 118.9 (CH=*C*H$_2$), 103.2, 102.0 (C-1), 80.2, 78.7, 76.1, 76.0, 72.6 (C-2, C-3, C-4, C-5, *C*HCH$_3$), 63.7 (C-6), 23.5, 22.1 (CH*C*H$_3$); *m*/*z* 234 (17, [M]$^+$), 257 (13, [M + Na]$^+$), $C_{10}H_{18}O_6Na$ requires 257.1001, found 257.1006.

(*R/S*)-3-Buten-2-yl 6-*O*-(*tert*-Butyldimethylsilyl)-β-D-glucopyranoside (5). *tert*-Butyldimethylsilyl chloride (2.63 g, 17 mmol) was added to a solution of **4** (3.37 g, 14 mmol) in pyridine (75 mL), and the mixture was stirred at room temperature for 18 h. TLC analysis (methanol/CH_2Cl_2, 1/4, v/v) showed conversion of **4** (R_f 0.09) into a product (R_f 0.43). Water (50 mL) was added, and the mixture was stirred for 1 h. Then, the solution was diluted with CH_2Cl_2 (125 mL), and the organic phase was extracted with an aqueous $NaHCO_3$ solution (3 × 60 mL) and brine (3 × 60 mL). The combined organic phases were dried ($MgSO_4$) and filtered, and the filtrate was concentrated under reduced pressure to afford **5** (3.34 g, 66%) as an oil: δ^1H (300 MHz; $CDCl_3$) 5.95−5.60 (1H, m, C*H*=CH_2), 5.30−5.01 (2H, m, CH=C*H*$_2$), 4.29 (2H, m, H-1, C*H*-CH_3), 3.88−3.71 (2H, m, H-6(a,b)), 3.42 (1H, m, H-3), 3.31 (2H, m, H-2, H-4), 3.23 (1H, m, H-5), 1.22 (3H, 2 × d, ^3J = 2.9 Hz, CHC*H*$_3$), 0.91 (9H, s, C(C*H*$_3$)$_3$), 0.08 (6H, m, (Si(CH_3)$_2$); δ^{13}C (75 MHz; $CDCl_3$) 140.1, 139.0 (*C*H=CH_2), 117.1, 114.9 (CH=*C*H$_2$), 100.6, 99.2 (C-1), 76.6, 76.5 (*C*HCH$_3$), 75.3, 75.2 (C-2), 74.8, 73.3, 71.8 (C-3, C-4, C-5), 62.4 (C-6), 25.8 (C(*C*H$_3$)$_3$), 21.6, 20.0 (CH*C*H$_3$), 18.3 (*C*(CH$_3$)$_3$), −5.2, −5.3 (Si(*C*H$_3$)$_2$).

(*R/S*)-3-Buten-2-yl 2,3,4-Tri-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranoside (6). Tetra-*n*-butylammonium iodide (0.83 g, 2.2 mmol) and sodium hydride (80% dispersion in oil, 2.5 g, 83 mmol) were added to a cooled (0 °C) and vented solution of **5** (2.51 g, 72 mmol) in *N*,*N*-dimethylformamide (60 mL). Benzyl bromide (7.17 g, 5 mL, 41 mmol) was added dropwise (30 min) to the suspension. The reaction mixture was stirred for 3 h, and then TLC analysis (acetone/CH_2Cl_2, 2/96, v/v) showed complete conversion of **5** (R_f 0.2) into a product (R_f 0.9). After the reaction was quenched with methanol (30 mL), the mixture was poured into brine (100 mL) and extracted with ether (4 × 75 mL). The combined organic extracts were washed with water (3 × 40 mL), and the aqueous layers were washed with ether (2 × 10 mL). The combined ether extracts were dried ($MgSO_4$) and filtered, and the filtrate was concentrated under reduced pressure to give a yellow oil that was purified on a column of silica gel (150 g, eluant: acetone/CH_2Cl_2, 3/97, v/v). Concentration of the appropriate fractions afforded **6** (3.49 g, 78%): δ^1H (300 MHz; $CDCl_3$) 7.46−7.22 (15H, m, Ar CH), 6.00−5.68 (1H, m, C*H*=CH_2), 5.29−5.04 (2H, m, CH=C*H*$_2$), 5.01−4.62 (6H, m, 3 × Ar CH_2), 4.46 (1H, d, $^3J_{1,2}$ = 8 Hz, H-1), 4.33 (1H, m, CH_3C*H*), 3.82 (2H, m, H-6(a,b)), 3.61 (2H, m, H-3, H-4), 3.43 (1H, t, $^3J_{1,2}$ = 8 Hz, $^3J_{2,3}$ = 8 Hz, H-2), 3.24 (1H, m, H-5), 1.32 (3H, 2 × d, ^3J = 4 Hz, CHC*H*$_3$), 0.91 (9H, 2 × s, C(C*H*$_3$)$_3$), 0.08 (6H, m, (Si(CH_3)$_2$); δ^{13}C (75 MHz; $CDCl_3$) 140.5, 139.3 (*C*H=CH_2), 138.6−138.1 (Ar C quaternary), 128.6−127.6 (Ar CH), 116.7, 114.5 (CH=*C*H$_2$), 101.8, 100.3 (C-1), 84.9, 82.6, 75.0 (C-3, C-4, C-5), 77.8, 77.7 (C-2), 76.3, 75.8 (*C*HCH$_3$), 75.7, 74.9, 72.2 (Ar CH_2), 62.4 (C-6), 25.9 (C(*C*H$_3$)$_3$), 21.6, 20.0 (CH*C*H$_3$), 18.3 (Si*C*(CH$_3$)$_2$), −5.2, −5.3 (Si(CH$_3$)$_2$); *m*/*z* 641 (40, [M + Na]$^+$), 617 (8, [M − H]$^+$), 439 (100, [M − *O*Bn − 3-buten-2-yl]$^+$), $C_{37}H_{50}O_6NaSi$ requires 641.3274, found 641.3284.

(*R/S*)-3-Buten-2-yl 2,3,4-Tri-*O*-benzyl-β-D-glucopyranoside (7). Compound **6** (1.42 g, 2.3 mmol) was dissolved in a mixture of acetic acid/water (4/1, v/v, 50 mL), and the solution was stirred at 50 °C for 8 h. TLC analysis (acetone/CH_2Cl_2, 1/24, v/v) showed complete conversion of the starting material (R_f 0.70) into a product (R_f 0.36). The reaction mixture was concentrated under reduced pressure, and the resulting oil was coevaporated from toluene (5 × 10 mL). The crude product was purified on a short column of silica gel (30 g, eluant:

acetone/CH_2Cl_2, 1/24, v/v) to afford **7** (1.04 g, 91%): δ^1H (300 MHz; $CDCl_3$) 7.38−7.22 (15H, m, Ar CH), 5.95−5.60 (1H, m, C*H*=CH_2), 5.29−5.07 (2H, m, CH=CH_2), 4.83−4.52 (6H, m, 3 × Ar CH_2), 4.53 (1H, 2 × d, $^3J_{1,2}$ = 8 Hz, H-1), 4.32 (1H, m, CH_3C*H*), 3.81 (1H, m, H-4), 3.65−3.40 (3H, m, H-3, H-6(a,b)), 3.22 (1H, m, H-5), 1.96 (1H, bs, O*H*), 1.34 (3H, 2 × d, ^3J = 3.5 Hz, CHCH_3); δ^{13}C (75 MHz; $CDCl_3$) 140.8, 139.6 (*C*H=CH_2), 138.6−138.1 (Ar C quaternary), 128.6−127.6 (Ar CH), 117.1, 114.9 (CH=*C*H_2), 104.2, 102.3 (C-1), 82.4, 82.3 (C-2), 84.7, 82.3, 77.7 (C-3, C-4, C-5), 75.5, 75.1 (*C*HCH$_3$), 75.7, 75.0, 74.9 (3 × Ar CH_2), 62.3 (C-6), 21.9, 20.8 (CH*C*H$_3$); *m*/*z* 527 (32, [M + Na]$^+$), 433 (5, [M − *O*-3-buten-2-yl]$^+$), 181 (100, [M − 3-*O*Bn]$^+$), $C_{31}H_{36}O_6Na$ requires 527.2409, found 527.2393.

(*R*/*S*)-3-Buten-2-yl 2,3,4,6-Tetra-*O*-benzyl-*β*-D-glucopyranoside (8). Sodium hydride (80% dispersion in oil, 2.5 g, 83 mmol) was added to a cooled (0 °C) and vented solution of **4** (3.12 g, 13 mmol) in *N*,*N*-dimethylformamide (60 mL). Benzyl bromide (10 mL, 84 mmol) was added dropwise (30 min) to the suspension. The reaction mixture was stirred for 12 h, and then TLC analysis (acetone/CH_2Cl_2, 1/99, v/v) showed complete conversion of **4** (R_f 0.05) into a product (R_f 0.47). The reaction was quenched by the addition of methanol (30 mL), and the resulting mixture was concentrated under reduced pressure to yield a solid. The solid was dissolved in ether (100 mL) and washed with water (3 × 40 mL), and the combined water layers were washed with ether (2 × 10 mL). The combined ether extracts were dried ($MgSO_4$) and filtered, and the filtrate was concentrated under reduced pressure to give a crude product that was purified on a column of silica gel (150 g, eluant: acetone/CH_2Cl_2, 1/99, v/v) to afford **8** (6.51 g, 82 %): δ^1H (400 MHz; $CDCl_3$), 7.40−7.22 (20H, m, Ar CH), 5.99−5.72 (1H, m, C*H*=CH_2), 5.25−5.07 (2H, m, CH=CH_2), 4.98−4.51 (6H, m, Ar CH_2), 4.49 (1H, 2 × d, $^3J_{1,2}$ = 8 Hz, H-1), 4.30 (1H, m, C*H*CH$_3$), 3.70−3.41 (6H, m, H-6(a,b), H-2, H-3, H-4, H-5), 1.30 (3H, 2 × d, ^3J = 4 Hz, CHCH_3); δ^{13}C (75 MHz; $CDCl_3$) 140.5, 139.2 (*C*H=CH_2), 138.6−138.2 (Ar C quaternary), 128.3−127.5 (Ar CH), 117.0, 114.8 (CH=*C*H_2), 101.9, 100.5 (C-1), 85.0, 78.0, 74.8 (C-3, C-4, C-5), 82.5, 82.4 (C-2), 76.9, 75.3 (*C*HCH$_3$), 75.7, 74.9, 73.4 (Ar CH_2), 69.1 (C-6), 21.9, 20.4 (CH*C*H$_3$); *m*/*z* 593 (11, [M − H]$^+$), 523 (4, [M − *O*-3-buten-2-yl]$^+$), 415 (17, [M − H-*O*Bn-*O*-3-buten-2-yl]$^+$), 271 (70, [M − H − 3-*O*Bn]$^+$), 253 (100, [M − H − 2-*O*Bn − *O*-3-buten-2-yl]$^+$), $C_{38}H_{42}O_6Na$ requires 617.2879, found 617.2881.

2-Buten-2-yl 2,3,4,6-Tetra-*O*-benzyl-*β*-D-glucopyranoside (9). Method A. Compound **8** (1.01 g, 1.7 mmol), 1,4-diazabicyclo[2.2.2]octane (0.4 g, 3.5 mmol), and Wilkinson's catalyst ([$(C_6H_5)_3$P]$_3$RhCl) (50 mg, 0.05 mmol) in a methanol/water (9/1, v/v, 7 mL) mixture was refluxed for 2 h. TLC analysis (acetone/CH_2Cl_2, 1/49, v/v) showed mainly the formation of **9** (R_f 0.74). The mixture was diluted with CH_2Cl_2 (15 mL), and the aqueous phase was extracted with CH_2Cl_2 (2 × 1 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to yield an orange crystalline residue. This residue was purified on a basic alumina column (50 g, eluant: CH_2Cl_2), and concentration of the appropriate fractions afforded **9** (720 mg, 71%).

Method B. *n*-Butyllithium (1.6 M in hexane, 28 μL, 45 μmol) was added to a stirred, orange solution of Wilkinson's catalyst (30 mg, 33 μmol) in THF (1.5 mL) that was thoroughly degassed and placed under an argon admosphere. The resulting red solution was stirred at 20 °C for 5 min and then transferred *via* cannula into a refluxing solution of **8** (200 mg, 0.33 mmol) in THF (1 mL) under an argon atmosphere. TLC analysis (acetone/CH_2Cl_2, 1/49, v/v) after 5 min showed complete conversion of starting material (R_f 0.65) into product (R_f 0.74). The reaction mixture was diluted with CH_2Cl_2 (10 mL) and concentrated to an orange/red residue. The residue was purified by flash silica column chromatography (40 g, eluant: CH_2Cl_2) to afford the required product **9** (182 mg, 91%): δ^1H (400 MHz; $CDCl_3$) 7.40−7.23 (20H, Ar CH), 4.90 (1H, m, C=CH), 4.86 (8H, m, Ar CH_2), 4.75 (1H, d, $^3J_{1,2}$ = 8 Hz, H-1), 3.76−3.58 (5H, m, H-2, H-3, H-4, H-6(a,b)), 3.43 (1H, m, H-5), 1.92 (1.5H, m, CH_3 (trans)), 1.86 (1.5H, m, CH_3 (cis)), 1.62 (1.5H, 2 × q, ^3J = 6.9 Hz, ^5J = 1.45 Hz, CH_3 (trans)), 1.59 (1.5H, 2 × q, ^3J = 6.9 Hz, ^5J = 1.1 Hz, CH_3 (cis)); δ^{13}C (75 MHz; $CDCl_3$) 149.4 (OC(CH$_3$)=C), 138.7−138.2 (Ar C quaternary), 128.2−127.1 (Ar CH), 105.1, 100.5 (*C*HCH$_3$), 100.5, 100.2 (C-1), 84.9, 82.0, 80.9, 77.9 (C-2, C-3, C-4, C-5), 75.0, 74.9, 73.5 (Ar CH_2), 69.6 (C-6), 18.7, 15.7 (*C*H$_3$), 12.0, 10.5 (CH*C*H$_3$); *m*/*z* 617 (100, [M + Na]$^+$), 593 (7, [M − H]$^+$), 523 (12, [M − *O*-2-buten-2-yl]$^+$), 415 (19, [M − H − *O*-Bn − *O*-2-buten-2-yl]$^+$), 271 (70, [M − H − 3-*O*-Bn]$^+$), 253 (17, [M − H − 2-*O*-Bn − *O*-2-buten-2-yl]$^+$), $C_{38}H_{42}O_6Na$ requires 617.2879, found 617.2895.

(*R*/*S*)-3-Buten-2-yl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/*β*-D-glucopyranosyl)-*β*-D-glucopyranoside (10). Method A. A suspension of **9** (285 mg, 0.48 mmol), **7** (200 mg, 0.40 mmol), and powdered 4 Å molecular sieves (450 mg) in acetonitrile (5 mL) was stirred for 30 min. The mixture was cooled (−25 °C), and TMSOTf (20 μL, 0.10 mmol) was added. After 90 min, TLC analysis (acetone/CH_2Cl_2, 3/97, v/v) showed conversion of the starting materials into a product (R_f 0.41). The reaction mixture was neutralized with triethylamine (50 μL) diluted with CH_2Cl_2 (25 mL), and filtered through Celite. The filtrate was concentrated under reduced pressure to afford a solid residue. This residue was purified on a column of Sephadex LH-20 (100 g, eluant: methanol/CH_2Cl_2, 1/1 v/v) affording **10** (320 mg, 78%) as a 1:20 ratio of **10**α and **10***β*.

Method B. When the reaction was performed in CH_2Cl_2 a 4:3 ratio of **10**α and **10***β* (72%) was recovered.

Method C. A suspension of **9** (285 mg, 0.48 mmol), **7** (200 mg, 0.40 mmol), and powdered 4 Å molecular sieves (450 mg) in dichloroethane/ether (1/1 v/v, 4 mL) was stirred for 30 min under N_2. The mixture was cooled (0 °C), and a solution of NIS (40 mg, 0.18 mmol) and TfOH (3.3 μL, 11 μmol) in DCM/diethyl ether (1/1, v/v, 1.8 mL) was added. After 1 min, TLC analysis (acetone/CH_2Cl_2, 3/97, v/v) showed conversion of the starting materials into a product (R_f 0.41). The reaction mixture was neutralized with triethylamine (15 μL), diluted with CH_2Cl_2 (25 mL), and filtered through Celite. The filtrate was concentrated under reduced pressure to afford a solid residue. This residue was purified on a column of Sephadex LH-20 (100 g, eluant: methanol/CH_2Cl_2, 1/1 v/v), affording **10** (300 mg, 74%) as a 4:1 ratio of **10**α and **10***β*.

Method D. *n*-Butyllithium (1.6 M in hexane, 28 μL, 45 μmol) was added to a stirred, degassed solution of Wilkinson's catalyst (30 mg, 33 μmol) in THF (1.5 mL). The resulting red solution was stirred at 20 °C for 5 min and then transferred *via* cannula into a refluxing solution of **8** (200 mg, 0.33 mmol) in THF (1 mL). After the reaction mixture was heated under reflux for 5 min, the mixture was cooled to room temperature and placed under an atmosphere of O_2, and stirring was continued for 30 min. The resulting mixture was added by cannula to a suspension of **7** (150 mg, 0.30 mmol) and powdered 4 Å molecular sieves (350 mg) in acetonitrile (5 mL) After being stirred for 30 min, the mixture was cooled (−25 °C), and BF_3·OEt_2 (0.15 mmol) was added dropwise. After 90 min, TLC analysis (acetone/CH_2Cl_2, 3/97, v/v) showed conversion of the starting materials into a product (R_f 0.41). The reaction mixture was neutralized with triethylamine (50 μL), diluted with CH_2Cl_2 (25 mL), and filtered through Celite. The filtrate was concentrated under reduced pressure to afford a solid residue. This residue was purified on a column of Sephadex LH-20 (100 g, eluant: methanol/CH_2Cl_2, 1/1 v/v), affording **10** (218 mg, 71%) as a 1:20 ratio of **10**α and **10***β*.

10α: δ^1H (400 MHz; $CDCl_3$) 7.36−7.20 (35H, m, Ar CH), 5.99−5.72 (1H, m, C*H*=CH_2), 5.21−5.00 (2H, m, CH=CH_2), 4.98−4.53 (14H, m, Ar CH_2), 4.49 (1H, d, $^3J_{1,2}$ = 8 Hz, H-1), 4.30 (1H, m, C*H*CH$_3$), 4.26 (1H, t, $^3J_{1',2'}$ = 4 Hz, H-1′), 3.73−3.32 (12H, m, H-2, H-2′, H-3, H-3′, H-4, H-4′, H-5, H-5′, H-6(a,b), H-6′(a,b)), 1.30 (3H, t, ^3J = 4 Hz, CHCH_3); δ^{13}C (100 MHz; $CDCl_3$) 140.1, 139.0 (*C*H=CH_2), 138.5−139.0 (Ar C quaternary), 128.3−127.5 (Ar CH), 116.9, 114.7 (CH=*C*H_2), 103.8 (C-1′), 101.4, 100.3 (C-1), 84.8, 84.7, 82.2, 82.1, 78.2, 77.8, 75.9, 75.3 (C-2, C-2′, C-3, C-3′, C-4, C-4′, C-5, C-5′), 75.6, 75.1, 75.0, 74.9, 74.8, 74.7, 73.5 (Ar CH_2), 68.9 (C-6′), 68.4 (C-6), 21.9, 19.9 (CH*C*H$_3$).

10*β*: δ^1H (400 MHz; $CDCl_3$) 7.36−7.20 (35H, m, Ar CH), 5.99−5.72 (1H, m, C*H*=CH_2), 5.21−5.00 (2H, m, CH=CH_2), 4.98−4.54 (14H, m, Ar CH_2), 4.49 (1H, d, $^3J_{1,2}$ = 8 Hz, H-1), 4.30 (1H, m, C*H*CH$_3$), 4.26 (1H, t, $^3J_{1',2'}$ = 8 Hz, H-1′), 3.73−

3.32 (12H, m, H-2, H-2′, H-3, H-3′, H-4, H-4′, H-5, H-5′, H-6(a,b), H-6′(a,b)), 1.30 (3H, t, ^3J = 4 Hz, CHCH_3); δ^{13}C (100 MHz; $CDCl_3$) 140.1, 139.0 (*C*H=CH_2), 138.5−139.0 (Ar C quaternary), 128.3−127.5 (Ar CH), 116.9, 114.7 (CH=*C*H_2), 103.8 (C-1′), 101.4, 100.3 (C-1), 84.8, 84.7, 82.2, 82.1, 78.2, 77.8, 75.9, 75.3 (C-2, C-2′, C-3, C-3′, C-4, C-4′, C-5, C-5′), 75.6, 75.1, 75.0, 74.9, 74.8, 74.7, 73.5 (Ar CH_2), 68.9 (C-6′), 68.4 (C-6), 21.9, 19.9 (CH*C*H_3); *m*/*z* 1065 (28, [M + K]$^+$), 1049 (100, [M + Na]$^+$), 1025 (38, [M − H]$^+$), 523 (6, [M − *O*-(3-buten-2-yl)-tri-*O*-benzyl-*β*-D-glucopyranosyl]$^+$), 415 (30, [M − *O*-(3-buten-2-yl)tetra-*O*-benzyl-*β*-D-glucopyranosyl]$^+$), $C_{65}H_{70}O_{11}Na$ requires 1049.4815, found 1049.4794.

2-Buten-2-yl-2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl)-*β*-D-glucopyranoside (11). Treatment of compound **10***β* (100 mg, 0.97 mmol) with $[(C_6H_5)_3P]_3$RhCl/BuLi as described for the preparation of **9** (method B) gave, after workup and silica gel comumn chromatography, compound **11** (92 mg, 92%). **11***β*: δ^1H (400 MHz; $CDCl_3$) 7.36−7.20 (35H, m, Ar CH), 4.93 (1H, m, C=CH), 4.98−4.53 (14H, m, Ar CH_2), 4.71 (1H, d, $^3J_{1,2}$ = 8 Hz, H-1), 4.26 (1H, 2 × d, $^3J_{1',2'}$ = 8 Hz, H-1′), 3.73−3.32 (12H, m, H-2, H-2′, H-3, H-3′, H-4, H-4′, H-5, H-5′, H-6(a,b), H-6′(a,b)), 1.91 (1.5H, m, CH_3 (trans)), 1.80 (1.5H, m, CH_3 (cis)), 1.60 (1.5H, 2 × q, ^3J = 6.8 Hz, ^5J = 1.4 Hz, CH_3 (trans)), 1.57 (1.5H, 2 × q, ^3J = 6.8 Hz, ^5J = 1.2 Hz, CH_3 (cis)); δ ^{13}C (75 MHz; $CDCl_3$) 148.3 (O*C*(CH_3)=C), 138.5−139.0 (Ar C quaternary), 128.3−127.5 (Ar CH), 104.2, 103.6 (*C*HCH_3), 101.6 (C-1′), 100.3, 99.7 (C-1), 84.9, 84.6, 82.2, 82.0, 78.3, 76.5, 75.7, 75.2 (C-2, C-2′, C-3, C-3′, C-4, C-4′, C-5, C-5′), 75.5, 75.3, 75.2, 74.8, 74.5, 74.1, 72.9 (Ar CH_2), 68.6 (C-6′), 68.3 (C-6), 18.5, 15.9 (*C*H_3), 11.6, 10.9 (CH*C*H_3); *m*/*z* 1049 (100, [M + Na]$^+$), 523 (20, [M − *O*-(2-buten-2-yl)-tri-*O*-benzyl-*β*-D-glucopyranosyl]$^+$).

(*R*/*S*)-3-Buten-2-yl 4,6-*O*-Benzylidene-*β*-D-glucopyranoside (12). Camphorsulfonic acid (1 g) was added to a solution of **4** (4.0 g, 17 mmol) and benzylidenedimethyl acetal (3.58 mL, 24 mmol) in $CHCl_3$ (10 mL). After the reaction mixture was heated for 12 h under reflux, TLC analysis (methanol/CH_2Cl_2, 1/9, v/v) showed conversion of starting material **4** (R_f 0.1) into a product (R_f 0.55). The solution was neutralized with K_2CO_3 and filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified on a column of silica gel (80 g, eluant: methanol/CH_2Cl_2, 2/98, v/v) to afford pure **12** (3.52 g, 64%): δ^1H (300 MHz; $CDCl_3$) 7.53−7.37 (5H, Ar CH), 5.95−5.60 (1H, m, C*H*=CH_2), 5.56 (1H, s, PhC*H*), 5.30−5.12 (2H, m, CH=CH_2), 4.50 (1H, d, $^3J_{1,2}$ = 8 Hz, H-1), 4.34 (2H, m, C*H*CH_3, H-4), 3.76 (2H, m, H-6(a,b)), 3.61−3.40 (3H, m, H-2, H-3, H-5,), 3.31 (1H, bs, O*H*), 3.07 (1H, bs, O*H*), 1.31 (3H, 2 × d, ^3J = 2.8 Hz, CHCH_3); δ^{13}C (75 MHz; $CDCl_3$) 139.7, 138.7 (*C*H=CH_2), 137.0 (Ar C quaternary), 129.2, 128.3, 126.3 (Ar CH), 117.6, 115.4 (CH=*C*H_2), 101.9 (Ph*C*H), 101.4, 100.0 (C-1), 80.6 (C-2), 76.9, 75.5 (*C*H-CH_3), 74.5, 73.2 (C-3, C-5), 68.7 (C-6), 66.4 (C-4), 21.6, 20.6 (CH*C*H_3); *m*/*z* 323 (100, [M + H]$^+$), 305 (11, [M − OH]$^+$), 288 (5, [M − 2(OH)]$^+$), 267 (23, [M − 3-buten-2-yl]$^+$), 251 (90, [M − *O*-3-buten-2-yl]$^+$), $C_{17}H_{22}O_6Na$ requires 345.1314, found 345.1334.

(*R*/*S*)-3-Buten-2-yl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranoside (13). Benzyl bromide (2.25 mL, 18.9 mmol) was added dropwise to a cooled (0 °C) suspension of **12** (2.91 g, 9 mmol) and sodium hydride (80% dispersion in oil, 3.5 g, 112 mmol) in DMF (40 mL). After the reaction mixture was stirred for 12 h, TLC analysis (acetone/CH_2Cl_2, 1/99, v/v) showed conversion of **12** (R_f 0.05) into a product (R_f 0.73). Excess NaH was quenched with methanol (25 mL), and the reaction mixture was poured into water (70 mL) and extracted with ether (4 × 30 mL). The combined ether extracts were washed with brine (2 × 30 mL), dried ($MgSO_4$), and concentrated under reduced pressure to an orange crystalline solid. This crude product was purified on a column of silica gel (150 g, eluant: light petroleum ether/CH_2Cl_2, 1/3, v/v) to afford **13** (3.27 g, 72%) as a white solid: δ^1H (300 MHz; $CDCl_3$) 7.43−7.24 (15H, Ar CH), 5.97−5.68 (1H, m, C*H*=CH_2), 5.55 (1H, s, PhC*H*), 5.30−5.11 (2H, m, CH=CH_2), 4.83−4.71 (4H, m, Ar CH_2), 4.57 (1H, 2 × d, $^3J_{1,2}$ = 8 Hz, H-1), 4.32 (2H, m, C*H*CH_3, H-4), 3.73 (3H, m, H-3, H-6(a,b)), 3.47 (1H, m, $^3J_{1,2}$ = 8 Hz, $^3J_{2,3}$ = 3 Hz, H-2), 3.38 (1H, m, H-5), 1.34 (3H, dd, ^3J = 3 Hz, CHCH_3); δ^{13}C (75 MHz; $CDCl_3$) 140.1, 139.1 (*C*H=CH_2), 138.6, 137.5 (Ar C quaternary), 128.9−126.6 (Ar CH), 117.3, 115.3 (CH=*C*H_2), 102.2 (Ph*C*H), 101.2, 100.9 (C-1), 82.3, 81.6, 81.1 (C-2, C-3, C-5), 77.3, 75.7 (*C*HCH$_3$), 75.5, 75.1 (Ar CH_2), 68.9 (C-6), 66.1 (C-4), 21.9, 20.4 (CH*C*H_3); *m*/*z* 525 (100, [M + Na]$^+$), 501 (22, [M − H]$^+$), 431 (9, [M − *O*-3-buten-2-yl]$^+$).

(*R*/*S*)-3-Buten-2-yl 2,3,6-Tri-*O*-benzyl-*β*-D-glucopyranoside (14). A solution of HCl in ether (1 M, 30 mL) was added dropwise over a period of 30 min to a mixture of **13** (2.05 g, 4.1 mmol), sodium cyanoborohydride (3.12 g, 49 mmol), and powdered 3 Å molecular sieves (2.4 g) in THF (35 mL). TLC analysis (acetone/CH_2Cl_2, 1/99, v/v) was performed 5 min after the evolution of gas had ceased and showed complete conversion of **13** (R_f 0.73) into a product (R_f 0.48). The mixture was diluted with CH_2Cl_2 (100 mL) and filtered through Celite. The filtrate was washed with water (3 × 40 mL) and aqueous $NaHCO_3$ (3 × 40 mL). The organic phase was dried ($MgSO_4$) and filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified on a column of silica gel (60 g, eluant: petroleum ether 40−60 °C/ethyl acetate, 2/1, v/v), affording **14** (1.76 g, 86 %) as a waxy white solid: δ^1H (300 MHz; $CDCl_3$) 7.40−7.25 (15H, Ar CH), 6.05−5.70 (1H, m, C*H*=CH_2), 5.30−5.08 (2H, m, CH=CH_2), 4.96−4.61 (6H, m, Ar CH_2), 4.52 (1H, dd, $^3J_{1,2}$ = 8 Hz, H-1), 4.36 (1H, m, C*H*CH_3), 3.74 (2H, m, H-6(a,b)), 3.59 (1H, m, H-4), 3.45 (3H, m, H-2, H-3, H-5), 2.58 (1H, dd, ^3J = 2 Hz, O*H*), 1.36 (3H, 2 × d, ^3J = 3 Hz, CHCH_3); δ^{13}C (75 MHz; $CDCl_3$) 140.2, 139.1 (*C*H=CH_2), 138.6, 138.4, 137.9 (Ar C quaternary), 128.4−127.6 (Ar CH), 117.0, 114.8 (CH=*C*H_2), 101.8, 100.4 (C-1), 84.2, 81.7 (C-3, C-5), 76.9, 75.3 (*C*HCH$_3$), 75.2, 74.8, 73.5 (Ar CH_2), 73.9, 71.7 (C-2, C-4), 70.4 (C-6), 21.8, 20.3 (CH*C*H_3); *m*/*z* 527 (28, [M + Na]$^+$), 503 (5, [M − H]$^+$), 433 (10, [M − *O*-3-buten-2-yl]$^+$), 325 (7, [M − H − *O*Bn-*O*-3-buten-2-yl]$^+$), 181 (100, [M − 3-*O*-Bn]$^+$), $C_{31}H_{36}O_6Na$ requires 527.2409, found 527.2402.

(*R*/*S*)-3-Buten-2-yl 2,3,6-Tri-*O*-benzyl-4-*O*-acetyl-*β*-D-glucopyranoside (15). Acetic anhydride (5 mL) was added to a stirred solution of **14** (520 mg, 1.03 mmol) in pyridine (7 mL). The resulting mixture was stirred at room temperature for 5 h, after which time TLC analysis (acetone/CH_2Cl_2, 2/98, v/v) showed complete conversion of starting material (R_f 0.23) to product (R_f 0.47). The mixture was concentrated in *vacuo*, and the resulting oil was coevaporated from toluene (3 × 2 mL) to afford **15** (500 mg, 0.91 mmol, 88%) as a colorless oil: δ^1H (300 MHz; $CDCl_3$) 7.38−7.25 (15H, Ar CH), 6.05−5.70 (1H, m, C*H*=CH_2), 5.30−5.08 (2H, m, CH=CH_2), 4.96−4.56 (6H, m, Ar CH_2), 4.50 (2H, m, H-1, H-4), 4.35 (1H, m, C*H*CH_3), 3.52 (5H, m, H-2, H-3, H-5, H-6(a,b)), 1.84, 1.83 (3H, 2 × s, Ac CH_3), 1.36 (3H, 2 × d, ^3J = 4 Hz, CHCH_3); δ^{13}C (75 MHz; $CDCl_3$) 170.2 (Ac C=O), 140.2, 139.0 (*C*H=CH_2), 138.5−137.7 (Ar C quaternary), 128.4−127.6 (Ar CH), 117.0, 115.0 (CH=*C*H_2), 101.7, 100.3 (C-1), 82.1, 82.0 (C-3, C-5), 75.4 (*C*HCH$_3$), 75.1, 75.0, 74.9 (Ar CH_2), 73.3, 73.2 (C-2, C-4), 69.9 (C-6), 21.9 (Ac CH_3), 20.8, 20.4 (CH*C*H_3); *m*/*z* 569 (100, [M + Na]$^+$), 546 (8, [M − H]$^+$), 475 (12, [M − *O*-3-buten-2-yl]$^+$), 439 (17, [M − OBn]$^+$).

2-Buten-2-yl 3,4,6-Tri-*O*-benzyl-4-*O*-acetyl-*β*-D-glucopyranoside (16). Treatment of **15** (200 mg, 0.36 mmol) with $[(C_6H_5)_3P]_3$RhCl/BuLi as for described for the preparation of **9** gave, after flash silica gel column chromatography (eluent: CH_2Cl_2), **16** (176 mg, 88%): δ^1H (300 MHz; $CDCl_3$) 7.38−7.25 (15H, Ar CH), 4.96−4.56 (6H, m, Ar CH_2), 4.50 (2H, m, H-1, H4), 3.58 (5H, m, H-2, H-3, H-5, H-6(a,b)), 1.93 (1.5H, m, CH_3 (trans)), 1.86 (1.5H, m, CH_3 (cis)), 1.85, 1.84 (3H, 2 × s, Ac CH_3), 1.61 (1.5H, 2 × q, ^3J = 6.9 Hz, ^5J = 1.6 Hz, CH_3 (trans)), 1.60 (1.5H, m, CH_3 (cis)); δ^{13}C (75 MHz; $CDCl_3$) 169.8 (Ac C=O), 151.5, 149.0 (O*C*(CH_3)=C), 138.4−138.0 (Ar C quaternary), 128.4−127.5 (Ar CH), 105.3, 100.0 (*C*H(CH_3)), 100.3, 98.3 (C-1), 81.9, 73.5, 71.0, 70.9 (C-2, C-3, C-4, C-5), 75.1−74.9 (Ar CH_2), 69.6 (C-6), 20.8 (Ac CH_3), 18.6, 15.6, (CH_3), 11.9, 10.4 (CH*C*H_3); *m*/*z* 617 (100, [M + Na]$^+$), 593 (11, [M − H]$^+$), 523 (18, [M − *O*-2-buten-2-yl]$^+$), 415 (23, [M − H − *O*-Bn − *O*-2-buten-2-yl]$^+$), 271 (65, [M − H − 3-*O*-Bn]$^+$).

(*R*/*S*)-3-Buten-2-yl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-acetyl-α/*β*-D-glucopyranosyl)-*β*-D-glucopyranoside (17). Glycosylation of **16** (170 mg, 0.31 mmol) with **14** (131 mg, 0.26 mmol) was performed as described for the synthesis of **10** (method A, TMSOTf, CH_3CN, −25 °C, 90 min)

to afford **17** as a mixture of anomers (189 mg, 78%, α/β 1/8). The anomers were separated on a column of silica gel (100 g, eluant acetone/CH_2Cl_2, 1/99, v/v), affording the pure anomers **17**α (23 mg) and **17**β (91 mg) and unseparated anomers (71 mg).

The same reaction was performed according to method B to give, after purification, **17** (75%, α/β 1.5/1). The same reaction was performed according to method C to give, after purification, **17** (73%, α/β 3/1). **17**α**:** δ^1H (300 MHz; $CDCl_3$) 7.36−7.19 (30H, m, Ar CH), 6.04−5.64 (1H, m, C*H*=CH_2), 5.21−5.00 (2H, m, CH=CH_2), 4.98−4.20 (16H, m, Ar CH_2, C*H*CH_3, H-1, H-1′, H-4′), 4.00 (1H, m, H-4), 3.59−3.28 (10H, m, H-2, H-2′, H-3, H-3′, H-5, H-5′, H-6(a,b), H-6′(a,b)), 1.83, 1.82 (3H, 2 × s, Ac CH_3), 1.31 (3H, 2 × d, ^3J = 5.5 Hz, CHCH_3); δ^{13}C (100 MHz; $CDCl_3$) 169.8 (Ac C=O), 140.5, 139.2 (*C*H=CH_2), 139.1−138.2 (Ar C quaternary), 128.3−126.5 (Ar CH), 116.8, 114.6 (CH=*C*H_2), 102.2 (C-1′), 101.9, 100.4 (C-1), 82.8, 82.4, 82.0, 81.6, 77.4, 77.9, 76.5, 75.6, 75.2, 71.5 (*C*H-CH_3, C-2, C-2′, C-3, C-3′, C-4, C-4′, C-5, C-5′) 75.3−73.2 (Ar CH_2), 70.0 (C-6′), 68.0 (C-6), 20.9 (Ac CH_3), 21.9, 20.5 (CH*C*H_3).

17β**:** δ^1H (300 MHz; $CDCl_3$) 7.36−7.19 (30H, m, Ar CH), 6.04−5.64 (1H, m, C*H*=CH_2), 5.21−5.00 (2H, m, CH=CH_2), 4.98−4.20 (16H, m, Ar CH_2, C*H*CH_3, H-1, H-1′, H-4′), 4.00 (1H, m, H-4), 3.59−3.28 (10H, m, H-2, H-2′, H-3, H-3′, H-5, H-5′, H-6(a,b), H-6′(a,b)), 1.83, 1.82 (3H, 2 × s, Ac CH_3), 1.31 (3H, 2 × d, ^3J = 5.5 Hz, CHCH_3); δ^{13}C (100 MHz; $CDCl_3$) 169.8 (Ac C=O), 140.5, 139.2 (*C*H=CH_2), 139.1−138.2 (Ar C quaternary), 128.3−126.5 (Ar CH), 116.8, 114.6 (CH=*C*H_2), 102.2 (C-1′), 101.9, 100.4 (C-1), 82.8, 82.4, 82.0, 81.6, 77.4, 77.9, 76.5, 75.6, 75.2, 71.5 (*C*H-CH_3, C-2, C-2′, C-3, C-3′, C-4, C-4′, C-5, C-5′) 75.3−73.2 (Ar CH_2), 70.0 (C-6′), 68.0 (C-6), 20.9 (Ac CH_3), 21.9, 20.5 (CH*C*H_3); *m*/*z* 1001 (100, $[M + Na]^+$), $C_{58}H_{64}O_{11}Na$ requires 1001.4451, found 1001.4446.

(*R*/*S*)-3-Buten-2-yl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranoside (19). A solution of bromide **18** (14.45 g, 35 mmol) and (±)-3-buten-2-ol (**2**) (10 mL, 115 mmol) in acetonitrile (35 mL) was added to a stirred suspension of mercury(II) cyanide (7.67 g, 30 mmol), mercury(II) bromide (10.03 g, 30 mmol), and powdered 4 Å molecular sieves (11 g) in acetonitrile (50 mL). After the reaction mixture was stirred for 12 h, TLC analysis (acetone/CH_2Cl_2, 2/98, v/v) showed complete conversion of starting material (R_f 0.53) into a product (R_f 0.60). The reaction mixture was filtered, and the filtrate was concentrated under reduced pressure to yield an oil. The oil was dissolved in CH_2Cl_2 (100 mL) and washed with $NaHCO_3$ (3 × 40 mL) and aqueous NaCl (3 × 40 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to give an orange crystalline residue. This crude product was applied to a column of silica gel (100 g, eluant: acetone/CH_2Cl_2, 3/97, v/v), and concentration of the appropriate fractions afforded **19** (8.54 g, 60%): δ^1H (300 MHz; $CDCl_3$) 5.89−5.50 (1H, m, C*H*=CH_2), 5.30−4.91 (5H, m, CH=CH_2, H-2, H-3, H-4), 4.48 (1H, d, $^3J_{1,2}$ = 8 Hz, H-1), 4.30 (1H, m, C*H*CH_3), 4.09 (2H, m, H-6(a,b)), 3.82 (1H, m, H-5), 2.10−1.92 (12H, m, Ac CH_3), 1.20 (3H, 2 × d, ^3J = 6 Hz, CHCH_3); δ^{13}C (75 MHz; $CDCl_3$), 170.3−169.1 (Ac C=O), 139.6, 138.3 (*C*H=CH_2), 116.8, 115.1 (*C*H_2=CH), 99.8, 98.5 (C-1), 77.7, 75.8 (*C*HCH_3), 71.0, 69.1, 67.1, 67.0 (C-2, C-3, C-4, C-5), 61.3 (C-6), 21.5−19.7 (Ac CH_3, CH*C*H_3); *m*/*z* 425 (100, $[M + Na]^+$), 331 (52, $[M - O$-3-buten-2-yl$]^+$).

(*R*/*S*)-3-Buten-2-yl β-D-galactopyranoside (20). Potassium *tert*-butoxide (3.0 g) was added to a stirred solution of **19** (8.04 g, 20 mmol) in methanol (100 mL). After a reaction time of 5 h, TLC analysis (acetone/CH_2Cl_2, 2/98, v/v) showed complete conversion of the starting material (R_f 0.60) into a product (R_f 0.06). The reaction mixture was neutralized with Dowex 50 WX4 (H^+) (60 mL), filtered, and concentrated in *vacuo*. After coevaporation from toluene (3 × 5 mL), compound **20** was obtained as a white oil (3.53 g, 75%): δ^1H (300 MHz; D_2O) 5.95−5.60 (1H, m, C*H*=CH_2), 5.30−5.12 (2H, m, CH=CH_2), 4.50 (1H, 2 × d, $^3J_{1,2}$ = 8 Hz, H-1), 4.30 (1H, m, C*H*=CH_3), 3.82−3.64 (2H, m, H-3, H-4), 3.45−3.25 (4H, m, H-2, H-5, H-6(a,b)), 3.21 (1H, m, CH_3C*H*), 1.23 (3H, 2 × d, ^3J = 2.9 Hz, CHCH_3); δ^{13}C (75 MHz; D_2O) 142.3, 141.2 (*C*H=CH_2), 120.6, 117.8 (CH=*C*H_2), 103.7, 102.5 (C-1), 80.1, 78.8, 77.8, 76.2, 72.3 (C*H*CH_3, C-2, C-3, C-4, C-5), 63.6 (C-6), 23.2, 22.0 (CH*C*H_3); *m*/*z* 234 (12, $[M]^+$), 257 (48, $[M + Na]^+$), $C_{10}H_{18}O_6$-Na requires 257.1001, found 257.1010.

(*R*/*S*)-3-Buten-2-yl 2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranoside (21). Sodium hydride (80% dispersion in oil, 3 g, 100 mmol) was added to a cooled (0 °C) and vented solution of **20** (3.21 g, 14 mmol) in *N*,*N*-dimethylformamide (50 mL). Benzyl bromide (10 mL, 84 mmol) was added dropwise (30 min) to the suspension. The resulting mixture was stirred for 12 h at room temperature, and after this time TLC analysis (acetone/CH_2Cl_2, 1/99, v/v) showed complete conversion of **20** (R_f 0.06) into a product (R_f 0.57). The reaction was quenched by the addition of methanol (30 mL), and the resulting mixture was concentrated to a solid under reduced pressure. The solid was dissolved in ether (100 mL) and washed with water (3 × 40 mL), and the combined water layers were washed with ether (2 × 10 mL). The combined ether extracts were dried ($MgSO_4$) and filtered, and the filtrate was concentrated under reduced pressure to give a crude product that was purified on a column of silica gel (100 g, eluant: acetone/CH_2Cl_2, 1/99, v/v) to afford **21** (6.23 g, 76%) as a colorless oil: δ^1H (400 MHz; $CDCl_3$), 7.40−7.23 (20H, m, Ar CH), 6.00−5.68 (1H, m, C*H*=CH_2), 5.23−5.07 (2H, m, CH=CH_2), 4.98−4.41 (8H, m, Ar CH_2), 4.41−4.28 (2H, m, H-1, C*H*CH_3), 3.70 (2H, m, H-3, H-4), 3.58−3.42 (4H, m, H-2, H-5, H-6(a,b)), 1.30 (3H, dd, ^3J = 3 Hz, CHCH_3); δ^{13}C (75 MHz; $CDCl_3$) 140.5, 139.2 (*C*H=CH_2), 138.6−138.2 (Ar C quaternary), 129.3−127.7 (Ar CH), 117.3, 114.5 (CH=*C*H_2), 102.2, 100.7 (C-1), 82.5, 79.7, 77.2, 76.5 (C-2, C-3, C-4, C-5), 75.3 (*C*HCH_3), 75.4−73.2 (Ar CH_2), 69.0 (C-6), 21.9, 20.5 (CH*C*H_3); *m*/*z* 593 (8, $[M - H]^+$), 523 (10, $[M - O$-3-buten-2-yl$]^+$), 415 (23, $[M - H - O$-Bn $- O$-3-buten-2-yl$]^+$), 271 (65, $[M - H - 3\ O$-Bn$]^+$), 253 (100, $[M - H - 2\ O$-Bn $- O$-3-buten-2-yl$]^+$), $C_{38}H_{42}O_6Na$ requires 617.2879, found 617.2883.

2-Buten-2-yl 2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranoside (22). Treatment of **21** (100 mg, 0.16 mmol) with $[(C_6H_5)_3P]_3RhCl$/BuLi as described for the preparation of **9** gave, after flash silica gel column chromatography (eluent: CH_2Cl_2), **22** (90 mg, 90%): δ^1H (300 MHz; $CDCl_3$) 7.40−7.23 (20H, m, Ar CH), 4.9−4.83 (5H, m, Ar CH_2, C*H*CH_3), 4.79 (1H, d, $^3J_{1,2}$ = 8 Hz, H-1), 4.71−4.43 (4H, Ar CH_2), 3.77−3.46 (5H, m, H-3, H-4, H-5, H-6(a,b)), 1.91 (1.5H, m, CH_3 (trans)), 1.84 (1.5H, m, CH_3 (cis)), 1.60 (1.5H, 2 × q, ^3J = 6.8 Hz, ^5J = 1.4 Hz, CH_3 (trans)), 1.57 (1.5H, 2 × q, ^3J = 6.8 Hz, ^5J = 1.2 Hz, CH_3 (cis)); δ^{13}C (75 MHz; $CDCl_3$) 151.1, 149.5 (O*C*(CH_3)=C), 138.7−138.0 (Ar C quaternary), 128.4−127.6 (Ar CH), 104.4, 100.7 (*C*HCH_3), 102.2, 100.6 (C-1), 82.5, 82.1, 81.1, 79.4 (C-2, C-3, C-4, C-5), 75.0−73.5 (Ar CH_2), 68.9 (C-6), 18.8,15.7 (CH_3), 12.0, 10.5 (CH*C*H_3); *m*/*z* 617 (100, $[M + Na]^+$), 593 (7, $[M - H]^+$), 523 (12, $[M - O$-2-buten-2-yl$]^+$), 415 (15, $[M - H - O$-Bn $- O$-2-buten-2-yl$]^+$), 271 (79, $[M - H - 3\ O$-Bn$]^+$), $C_{38}H_{42}O_6$-Na requires 617.2879, found 617.2885.

(*R*/*S*)-3-Buten-2-yl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-β-D-glucopyranoside (23). Glycosylation of **22** (106 mg, 0.18 mmol) with **7** (61 mg, 0.12 mmol) was performed as described for the synthesis of **10** (method A, TMSOTf, CH_3CN, −25 °C, 90 min), affording **23** (97 mg, 78%) as a mixture of anomers (α/β = 1/3). The same glycosylation was also performed according to method B (TMSOTf, CH_2Cl_2, −25 °C, 90 min) to give **23** (75%) as a separable mixture of anomers (α/β = 4/1). **23**β: δ^1H (300 MHz; $CDCl_3$) 7.41−7.19 (35H, m, Ar CH), 5.89−5.58 (1H, m, C*H*=CH_2), 5.23−5.03 (2H, m, CH=CH_2), 5.00−4.73 (14H, m, Ar CH_2), 4.45 (1H, d, $^3J_{1,2}$ = 8 Hz, H-1′), 4.43 (1H, 2 × d, $^3J_{1',2'}$ = 8 Hz, H-1), 4.35 (1H, m, C*H*CH_3), 3.79 (1H, m, H2′), 3.69−3.25 (11H, m, H-2, H-3, H-3′, H-4, H-4′, H-5, H-5′, H-6(a,b), H-6′(a,b)), 1.28 (3H, 2 × d, ^3J = 4.5 Hz, CHCH_3); δ^{13}C (75 MHz; $CDCl_3$) 140.1, 139.9 (*C*H=CH_2), 139.2−138.1 (Ar C quaternary), 128.4−126.2 (Ar CH), 117.0, 115.6 (CH=*C*H_2,), 102.8 (J_{H1-C1} = 160 Hz, C-1′(β)), 101.5, 100.3 (C-1), 84.9, 82.3, 82.2, 79.6, 79.5, 78.5, 78.0, 75.4 (C-2, C-2′, C-3, C-3′, C-4, C-4′, C-5, C-5′), 75.7−71.9 (Ar CH_2), 69.1 (C-6′), 68.6 (C-6), 21.9, 20.5 (CH*C*H_3); *m*/*z* 1049 (100, $[M + Na]^+$), 1025 (21, $[M - H]^+$), 523 (17, $[M - O$-(3-buten-2-yl)tri-*O*-benzyl-β-D-glucopyranosyl$]^+$), 415 (28, $[M - O$-(3-buten-2-yl)tetra-*O*-benzyl-β-D-glucopyranosyl$]^+$). Note: 97.9 (J_{H1-C1} = 169 Hz, C-1′(α)).

(*R/S*)-3-Buten-2-yl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α/*β*-D-galactopyranosyl)-*β*-D-glucopyranoside (24). Glycosylation of **22** (95 mg, 0.16 mmol) with **14** (61 mg, 0.12 mmol) carried out as described for the synthesis of **10** (method A, TMSOTf, CH_3CN, −25 °C, 90 min) afforded **24** (90 mg, 73%, α/*β* = 1/1.5) as a mixture of anomers. **24***β*: δ^1H (300 MHz; $CDCl_3$) 7.39−7.18 (35H, m, Ar CH), 6.01−5.63 (1H, m, C*H*=CH_2), 5.21−5.00 (2H, m, CH=C*H*$_2$), 4.97−4.32 (16H, m, Ar CH_2, H-1, H-1′), 4.30 (1H, m, C*H*CH_3), 4.00−3.71 (6H, m, H-4, H-4′, H-6(a,b), H-6′(a,b)), 3.59−3.31 (6H, m, H-2, H-2′, H-3, H-3′, H-5, H-5′), 1.37 (3H, m, CHC*H*$_3$); δ^{13}C (75 MHz; $CDCl_3$) 140.6, 139.4 (*C*H=CH_2), 139.2−138.1 (Ar C quaternary), 128.3−126.6 (Ar CH), 117.1, 114.7 (CH=*C*H$_2$), 102.8 (J_{H1-C1} = 161 Hz, C-1′(*β*)), 101.9, 100.2 (C-1),) 85.0, 83.2, 82.6, 82.3, 80.0, 79.2, 76.9, 74.3, 73.7, 73.0 (CH-CH_3, C-2, C-2′, C-3, C-3′, C-4, C-4′, C-5, C-5′), 75.4−72.6 (Ar CH_2), 68.8 (C-6′), 68.1 (C-6), 21.9, 20.5 (CH*C*H$_3$); *m*/*z* 1049 (100, [M + Na]$^+$), 1025 (18, [M − H]$^+$), 523 (10, [M − *O*-(3-buten-2-yl)tri-*O*-benzyl-*β*-D-glucopyranosyl]$^+$), 415 (37, [M − *O*-(3-buten-2-yl)tetra-*O*-benzyl-*β*-D-glucopyranosyl]$^+$). Note: 97.2 (J_{H1-C1} = 173 Hz, C-1′(α)).

α-D-Glucopyranosyl 3,4,6-Tri-*O*-acetyl-1,2-(3-buten-2-yl)orthomethanoate (25). 2,4,6-Collidine (5.45 g, 45 mmol), 3-buten-2-ol (5.2 mL, 60 mmol), and tetra-*n*-ethylammonium bromide (9.03g, 43 mmol) were added to a stirred solution of **1** (12.3 g, 30 mmol) in CH_2Cl_2 (100 mL) containing powdered 4 Å molecular sieves (8 g). The resulting mixture was stirred at room temperature for 18 h. TLC analysis (acetone/CH_2Cl_2, 4/96, v/v) at this time showed conversion of **1** (R_f 0.58) into a product (R_f 0.52). The mixture was filtered through Celite and concentrated to a white solid. The solid was redissolved in CH_2Cl_2 (75 mL) and extracted with water (3 × 25 mL), $NaHCO_3$ (3 × 25 mL), brine (3 × 25 mL), and water (3 × 25 mL). Each extract was itself reextracted with CH_2Cl_2 (2 × 5 mL). The combined CH_2Cl_2 extracts were dried ($MgSO_4$), filtered, and concentrated to a white solid. This compound was further purified on a silica gel column (200 g, eluant: acetone/CH_2Cl_2, 1/99, v/v) to give pure **25** (7.21 g, 60%) as a white solid: δ^1H (300 MHz; $CDCl_3$) 5.78 (1H, m, C*H*=CH_2), 5.63 (1H, d, $^3J_{1,2}$ = 3.5 Hz, H-1), 5.18−4.82 (4H, m, CH=C*H*$_2$, H-2, H-3), 4.29 (1H, m, C*H*CH_3), 4.21 (1H, m, H-4), 4.15 (2H, m, H-6(a,b)), 3.92 (1H, m, H-5), 2.04 (9H, m, Ac CH_3), 1.68 (3H, s, CH_3C), 1.19 (3H, 2 × s, CHC*H*$_3$); δ^{13}C (75 MHz; $CDCl_3$) 170.6, 169.6, 169.0 (Ac C=O), 140.7, 140.5 (*C*H=CH_2), 121.4 (C quaternary), 114.3, 114.1 (CH=*C*H$_2$), 96.9, 96.8 (C-1), 73.2, 72.9 (C*H*CH_3), 70.9, 70.15, 68.2, (C-3, C-4, C-5), 66.9 (C-2), 63.1 (C-6), 22.3, 22.1, 21.9 (Ac CH_3), 21.7 (*C*H$_3$C), 20.7 (*C*H$_3$CH).

α-D-Glucopyranosyl 3,4,6-Tri-*O*-benzyl-1,2-(3-buten-2-yl)orthomethanoate (26). Potassium *tert*-butoxide (2.6 g) was added to a stirred solution of **25** (8.34 g, 20 mmol) in methanol (100 mL). After a reaction time of 5 h, TLC analysis (acetone/CH_2Cl_2, 2/98, v/v) showed complete conversion of the starting material (R_f 0.64) into a product (R_f 0.09). The reaction mixture was concentrated in *vacuo*. After coevaporation from toluene (3 × 15 mL) the crude product was dissolved in DMF (100 mL). NaH (80% suspension in oil, 2.5 g) was added, and the resulting mixture was cooled (0 °C). BnBr (7.1 mL, 58.2 mmol) was added dropwise, and the reaction was allowed to warm to 20 °C and stirred at this temperature for 5 h, after which time TLC analysis (acetone/CH_2Cl_2, 2/98, v/v) showed conversion into **26** (R_f 0.62). Excess NaH was neutralized by the addition of methanol (25 mL), and the mixture was concentrated to a brown residue. The residue was taken up in ether (60 mL) and extracted with water (3 × 25 mL). The organic phase was dried ($MgSO_4$) and concentrated to an orange oil. Purification on a silica gel column (200 g, eluant: acetone/CH_2Cl_2, 1/99, v/v) gave **26** (9.2 g, 73%) as an off white oil: δ^1H (300 MHz; $CDCl_3$) 7.39−7.19 (15H, m, Ar CH), 5.84 (1 H, m, C*H*=CH_2), 5.63 (1H, 2 × d, $^3J_{1,2}$ = 3.5 Hz, H-1), 5.18−5.00 (2H, m, CH=C*H*$_2$), 4.70−4.40 (6H, m, Ar CH_2), 4.38 (1H, m, H-2), 4.23 (1H, m, C*H*-CH_3), 3.88 (1H, m, H-3), 3.78 (4H, m, H-4, H-5, H-6(a,b)), 1.68 (3H, 2 × s, C*H*$_3$C), 1.19 (3H, 2 × d, CHC*H*$_3$); δ^{13}C (75 MHz; $CDCl_3$) 141.1 (*C*H=CH_2), 138.2, 138.0, 137.8 (Ar C quaternary), 128.5−127.6 (Ar CH), 121.2, 121.1 (C quaternary), 113.9, 113.8 (CH=*C*H$_2$), 97.9, 97.8 (C-1), 73.4, 72.7, 71.8 (Ar CH_2), 73.2, 70.1, 69.2, 68.2, 66.9 (C*H*CH_3, C-2, C-3, C-4, C-5), 69.2 (C-6), 30.9 (*C*H$_3$C), 22.6, 22.4 (*C*H$_3$CH$_3$); *m*/*z* 569 (75, [M + Na]$^+$), 475 (100, [M − *O*-3-buten-2-yl]$^+$), $C_{33}H_{38}O_7Na$ requires 569.2515, found 569.2505.

(*R/S*)-3-Buten-2-yl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (27). TMSOTf (300 *μ*L, 1.5 mmol) was added to a cooled (−20 °C) stirred solution of **26** (4.5 g, 8.25 mmol) in CH_2Cl_2 (60 mL) containing powdered 4 Å molecular sieves (4 g). TLC analysis (acetone/CH_2Cl_2, 2/98, v/v) after 4 h showed conversion of **26** (R_f 0.50) into a product (R_f 0.46). The reaction was neutralized with Et_3N (50 *μ*L), diluted with CH_2Cl_2, and filtered through Celite. The filtrate was washed with $NaHCO_3$ (2 × 30 mL). The organic phase was dried ($MgSO_4$) and concentrated to a yellow oil. Purification on a silica gel column (110 g, eluant: acetone/CH_2Cl_2, 1/99, v/v) afforded pure **27** (4.05 g, 90%): δ^1H (300 MHz; $CDCl_3$) 7.38−7.19 (15H, Ar CH), 6.00−5.55 (1H, m, C*H*=CH_2), 5.30−5.08 (3H, m, CH=C*H*$_2$, H-2), 4.95−4.59 (6H, m, Ar CH_2), 4.50 (2H, 2 × d, $^3J_{1,2}$ = 8 Hz, H-1), 4.24 (1H, m, C*H*CH_3), 3.71−3.62 (4H, m, H-3, H-4, H-6(a,b), 3.48 (1H, m, H-5), 1.96 (3H, 2 × s, Ac CH_3), 1.36 (3H, 2 × d, ^3J = 4 Hz, CHC*H*$_3$); δ^{13}C (75 MHz; $CDCl_3$) 169.4 (Ac C=O), 140.2, 139.0 (*C*H=CH_2), 138.5−137.7 (Ar C quaternary), 128.4−127.6 (Ar CH), 117.0, 115.0 (CH=*C*H$_2$), 101.7, 100.3 (C-1), 83.1, 83.0 (C-2), 82.0, 78.5, 75.4, 74.3, 71.2 (*C*HCH_3, C-3, C-4, C-5), 75.1−74.9 (Ar CH_2), 70.0 (C-6), 21.9 (Ac CH_3), 20.8, 20.4 (CH*C*H$_3$); *m*/*z* 569 (100, [M + Na]$^+$), 546 (8, [M − H]$^+$), 475 (51, [M − *O*-3-buten-2-yl]$^+$).

(*R/S*)-3-Buten-2-yl 3,4,6-Tri-*O*-benzyl-*β*-D-glucopyranoside (28). Potassium *tert*-butoxide (100 mg) was added to a stirred suspension of **27** (460 mg, 0.84 mmol) in methanol (15 mL). After 8 h, TLC analysis (acetone/CH_2Cl_2, 3/97, v/v) showed complete conversion of **27** (R_f 0.68) into a product (R_f 0.37). The mixture was neutralized with Dowex 50 WX4 (H$^+$) (10 mL), filtered, and concentrated to a white oil. Further purification on a silica gel column (50 g, eluant: acetone/CH_2Cl_2, 1/49, v/v) furnished pure **28** (360 mg, 85%) as a colorless oil: δ^1H (300 MHz; $CDCl_3$) 7.41−7.18 (15H, Ar CH), 6.08−5.68 (1H, m, C*H*=CH_2), 5.30−5.08 (2H, m, CH=C*H*$_2$), 4.86−4.53 (6H, m, Ar CH_2), 4.53 (2H, m, H-1, C*H*CH_3), 3.74 (2H, m, H-6(a,b)), 3.59 (3H, m, H-2, H-3, H-4), 3.48 (1H, m, H-5), 2.35 (1H, bs, O*H*), 1.37 (3H, dd, ^3J = 4 Hz, CHC*H*$_3$); δ^{13}C (75 MHz; $CDCl_3$) 140.1, 138.9 (*C*H=CH_2), 138.7, 138.2, 137.8 (Ar C quaternary), 128.6−127.7 (Ar CH), 117.3, 115.0 (CH=*C*H$_2$), 101.0, 99.6 (C-1), 84.7, 84.6 (C-2), 77.6, 76.4, 75.2, 74.7 (*C*HCH_3, C-3, C-4, C-5), 75.1, 74.9, 73.4 (Ar CH_2), 69.0 (C-6), 21.7, 20.1 (CH*C*H$_3$); *m*/*z* 527 (90, [M + Na]$^+$), 433 (15, [M − *O*-3-buten-2-yl]$^+$), $C_{31}H_{36}O_6Na$ requires 527.2409, found 527.2421.

2-Buten-2-yl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (29). Treatment of **27** (100 mg, 0.18 mmol) with [$(C_6H_5)_3P$]$_3$RhCl) as described for the preparation of **9** gave, after flash silica gel column chromatography (eluent: CH_2Cl_2), **29** (85 mg, 85%): δ^1H (300 MHz; $CDCl_3$) 7.39−7.20 (15H, Ar CH), 5.14 (1H, m, C*H*CH_3), 4.81−4.53 (7H, m, Ar CH_2, H-1,), 3.78−3.61 (5H, m, H-2, H-3, H-4, H-6(a,b), 3.51 (1H, m, H-5), 1.98 (3H, 2 × s, Ac CH_3), 1.86 (1.5H, m, CH_3 (trans)), 1.72 (1.5H, m, CH_3 (cis)), 1.60 (1.5H, m, CH_3 (trans)), 1.59 (1.5H, m, CH_3 (cis)); δ^{13}C (75 MHz; $CDCl_3$) 169.5 (Ac C=O), 151.8, 149.5 (OC(CH_3)=C), 138.2−137.9 (Ar C quaternary), 128.5−127.6 (Ar CH), 106.3 (*C*HCH_3), 98.6, 98.5 (C-1), 83.0, 78.0, 75.1, (C-3, C-4, C-5), 73.2, 73.0 (C-2), 75.1, 75.0, 73.5 (Ar CH_2), 68.8 (C-6), 21.0 (Ac CH_3), 19.1, 15.5 (CH_3), 11.9, 10.2 (CH*C*H$_3$); *m*/*z* 617 (100, [M + Na]$^+$), 593 (9, [M − H]$^+$), 523 (24, [M − *O*-2-buten-2-yl]$^+$), 415 (18, [M − H − *O*-Bn − *O*-2-buten-2-yl]$^+$), 271 (43, [M − H − 3-*O*-Bn]$^+$).

(*R/S*)-3-Buten-2-yl 2,3,4-Tri-*O*-benzyl-6-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-*β*-D-glucopyranoside (30). Glycosylation of **29** (190 mg, 0.32 mol) with **7** (122 mg, 0.24 mol) as described for the synthesis of **10** (method A, TMSOTf, CH_3CN, 0 °C, 90 min) afforded **30** (156 mg, 69%): δ^1H (300 MHz; $CDCl_3$) 7.43−7.21 (30H, m, Ar CH), 6.01−5.76 (1H, m, C*H*=CH_2), 5.21−5.00 (2H, m, CH=C*H*$_2$), 4.99−4.38 (14H, m, Ar CH_2, H1, H1′), 4.32 (1H, m, C*H*CH_3), 3.87−3.61 (10H, m, H-2, H-2′, H-3, H-3′, H-4, H-4′, H6(a,b), H-6′(a,b)), 3.44 (2H, m, H-5, H-5′), 1.72, 1.71 (3H, 2 × s, Ac CH_3), 1.38 (3H, 2 × d, ^3J = 2 Hz, CHC*H*$_3$); δ^{13}C (75 MHz; $CDCl_3$) 169.4

(Ac C=O), 140.5, 139.3 (*C*H=CH_2), 138.5−137.9 (Ar C quaternary), 128.4−127.5 (Ar CH), 116.2, 114.6 (CH=*C*H_2), 100.4 (C-1′), 99.4, 99.1 (C-1), 84.6, 84.2, 83.2, 82.6, 81.8, 80.8, 75.7, 72.3 (*C*HCH_3, C-2, C-2′, C-3, C-3′, C-4, C-4′, C-5, C-5′), 75.9−72.6 (Ar CH_2), 69.1 (C-6′), 68.9 (C-6), 21.6 (Ac *C*H_3) 20.9, 20.2 (CH*C*H_3).

(*R/S*)-3-Buten-2-yl 2-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (31). Glycosylation of **29** (208 mg, 0.38 mol) with **28** (160 mg, 0.317 mol) was performed as described for the synthesis of **10** (method A, TMSOTf, CH_3CN, 0 °C, 90 min) afforded **31** as an oil (214 mg, 72%): δ^1H (400 MHz; $CDCl_3$) 7.40−7.18 (30H, m, Ar CH), 5.99−5.75 (1H, m, C*H*=CH_2), 5.21−5.00 (3H, m, H1′, CH=C*H*$_2$), 4.99−4.4.51 (12H, m, Ar CH_2), 4.48 (1H, 2 × d, $^3J_{1,2}$ = 8 Hz, H1), 4.32 (1H, m, C*H*CH_3), 3.83−3.60 (10H, m, H-2, H-2′, H-3, H-3′, H-4, H-4′, H-6(a,b), H-6′(a,b)), 3.43 (2H, m, H-5, H-5′), 1.81, 1.80 (3H, 2 × s, Ac CH_3), (3H, 2 × d, ^3J = 1.5 Hz, CHC*H*$_3$); δ^{13}C (75 MHz; $CDCl_3$) 169.5 (*C*=O), 140.5, 139.3 (*C*H=CH_2), 138.5−137.9 (Ar C quaternary), 128.4−127.5 (Ar CH), 116.6, 114.8 (CH=*C*H_2), 100.3 (C-1′), 99.2, 99.0 (C-1), 84.8, 84.7, 82.2, 82.1, 81.5, 80.3, 75.5, 75.3 (*C*HCH_3, C-2, C-2′, C-3, C-3′, C-4, C-4′, C-5, C-5′), 75.7−73.2 (Ar CH_2), 68.9 (C-6′), 68.7 (C-6), 21.8 (Ac *C*H_3) 21.0, 20.5 (CH*C*H_3); *m*/*z* 1001 (100, $[M + Na]^+$), 475 (23, $[M - 2$-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl$]^+$), $C_{60}H_{66}O_{12}Na$ requires 1001.4451, found 1001.4441.

Supporting Information Available: Copies of NMR spectra (52 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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