Stereochemistry in the Synthesis and Reaction of *exo*-Glycals

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Two general methods are explored for the stereoselective synthesis of *exo*-glycals. One method utilizes a nucleophilic addition of fully protected sugar lactones of *gluco*-, *galacto*-, and *manno*-types, followed by the subsequent dehydration, to give the desired *exo*-glycals with (*Z*)-configuration. The other method proceeds with selenylation of *C*-glycosides in a stereoselective manner. The subsequent selenoxide elimination also provides (*Z*)-*exo*-glycals. The prepared *exo*-glycal conjugated esters of either *gluco*- or *manno*-type react with allyl alcohol to give exclusively α-anomers.

Introduction

endo-Glycals, 1,2-unsaturated sugars, have been shown to be indispensable chiral synthons in the preparation of various biomolecules. For instance, the reaction of *endo*-glucals with the silyl enol ether of acetophenone is catalyzed by Lewis acid to give *C*-glycosides in an excellent yield.[1] Allylation of *endo*-glycals with allyltrimethylsilane[2] provides the substrate applicable to the construction of the ABC rings of brevetoxin B.[3] Epoxidation of *endo*-glycals leads to a myriad of complex oligosaccharides and glycosylated natural products with high stereoselectivity.[4−9] Michael additions of 2-nitrogalactal have been explored for the synthesis of T_N and sialyl T_N antigens, as well as the *O*-glycans of core 1 and core 7 structures.[10−12]

The chemistry with regard to *exo*-glycals is less addressed in the literature. 1-*exo*-Methylene sugars have been obtained by methylenation of sugar lactones with Tebbe reagent,[13] or by elimination reaction of the appropriate pyranoketosyl bromides.[14] The reported preparations of substituted or functionalized *exo*-glycals usually require more laborious efforts. These preparations include Ramburg−Bäcklund rearrangement of *S*-glycosides,[15,16] Wittig olefination of sugar lactones (for conjugated *exo*-glycal esters),[17] Keck reaction of glycosyl dihalides (sugar dienes),[18] and [2,3]-Wittig sigmatropic rearrangement (for the *exo*-glycal analogue of glycosyl serine).[19] Nevertheless, most of these procedures are limited to some special types of *exo*-glycals. We recently reported a two-step synthesis of various conjugated *exo*-glycals from sugar lactones.[20,21] This method is general and stereoselective to give exclusively the (*Z*)-isomers of *exo*-glycals.[21] We present herein a detailed study of such stereoselective reactions and provide some insight for the interpretation underlying the exclusive stereochemistry.

Results and Discussion

The fully protected benzylated gluconolactone (**1**) was obtained in 95% yield from the commercially available 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose by oxidation with DMSO and acetic anhydride. The *galacto*- and *manno*-type lactones **2** and **3** were prepared from D-galactose and

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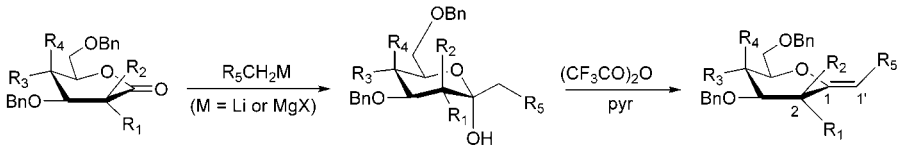
Scheme 1. Stereoselective Synthesis of Various (*Z*)-*exo*-Glycals by a Nucleophilic Addition and a Subsequent Dehydration



$R_1 = R_3 = OBn$, $R_2 = R_4 = H$,	gluconolactone (**1**)	**4** (90%) $R_5 = H$ **5** (92%) $R_5 = C_2H_5$ **6** (95%) $R_5 = CO_2Et$ **7** (82%) $R_5 = CH{=}CH_2$ **8** (92%) $R_5 = PO(OMe)_2$ **9** (81%) $R_5 = SO_3Et$ **10** (95%) $R_5 = C_6H_5$	**18** (45%) $R_5 = H$ **19** (72%) $R_5 = C_2H_5$ **20** (90%) $R_5 = CO_2Et$ **21** (85%) $R_5 = CH_2{=}CH_2$ **22** (81%) $R_5 = PO(OMe)_2$ **23** (83%) $R_5 = SO_3Et$ **24** (87%) $R_5 = C_6H_5$
$R_1 = R_4 = OBn$, $R_2 = R_3 = H$,	galactonolactone (**2**)	**11** (91%) $R_5 = H$ **12** (90%) $R_5 = C_2H_5$ **13** (95%) $R_5 = CO_2Et$	**25** (53%) $R_5 = H$ **26** (70%) $R_5 = C_2H_5$ **27** (81%) $R_5 = CO_2Et$
$R_2 = R_3 = OBn$, $R_1 = R_4 = H$,	mannolactone (**3**)	**14** (86%) $R_5 = H$ **15** (80%) $R_5 = C_2H_5$ **16** (95%) $R_5 = CO_2Et$ **17** (85%) $R_5 = CH{=}CH_2$	**28** (51%) $R_5 = H$ **29** (85%) $R_5 = C_2H_5$ **30** (89%) $R_5 = CO_2Et$ **31** (76%) $R_5 = CH{=}CH_2$

D-mannose according to known procedures: (i) conversion of the aldose to methyl glycoside (~50% yield),[22] (ii) benzylation of all the hydroxyl groups by using benzyl bromide and sodium hydride (~80% yield),[23] (iii) hydrolysis of methyl glycoside (~80% yield),[24] and (iv) oxidation with DMSO/Ac_2O (~92% yield).[25] The three sugar lactones **1**−**3**[26] reacted with a variety of organolithium and Grignard reagents to give the pyranoketoses **4**−**17** in good to excellent yields (Scheme 1).[20,21] These products existed dominantly as α-anomers (>90%) as shown by the NMR analyses including the NOESY experiments.[27] Such stereoselectivity was in accordance with the well-known anomeric effect.

The subsequent dehydration of pyranoketoses **4**−**17** was realized by treatment with trifluoroacetic anhydride (TFAA) and pyridine to give *exo*-glycals **18**−**31** as exclusive (*Z*)-isomers,[28] including all the *gluco*-, *galacto*-, and *manno*-type precursors. Most of the dehydration reactions were carried out in yields from 70% to 89% except for the preparation of 1-*exo*-methylene sugars **18**, **25**, and **28.** These molecules further reacted with TFAA under dehydration conditions and were found labile in silica gel chromatography. The configuration of the reaction products was rigorously determined by comparison with the reported NMR spectral data[14−19,29] along with NOE studies. For instance, a 10.7% enhancement of H1′ (at δ 5.41) in compound **31** was observed upon irradiation of H2 (at δ 4.01). A 7.4% enhancement of H2 was found by irradiation of H1′. The NOESY spectrum of sugar diene **31** also showed the correlation between H1′ and H2.

Direct dehydration of molecules **4**−**17** is less feasible as the C1′ protons are not acidic especially when the compounds (**4**, **5**, **11**, **12**, **14**, and **15**) lack an electron-withdrawing group. Thus, formation of (*Z*)-*exo*-glycals is considered to proceed with an intermediary oxonium ion. For example, the anomeric hydroxyl group of compound **5** would be activated by treatment with TFAA, and facilitated to form oxonium intermediate **A**, which conceivably has C1′ protons with a substantially lower pK_a value (Scheme 2). Once the anomeric carbon became sp^2 hybridized, the conformer **B** would be disfavored due to the 1,3-allylic strain between the C2 benzyloxy and C1′ ethyl groups. Thus, the preorganized intermediate **A** having a C−H bond antiperiplanar to the p-orbitals of oxocarbonium would readily undergo a deprotonation to give the observed (*Z*)-*exo*-glycal **19**.

Other evidence to support the existence of oxocarbonium intermediate is shown by the preparation of furanosyl *exo*-glycals (Scheme 3). The 1:1 anomeric mixture of **33**, obtained by the addition of allylmagnesium chloride to lactone **32**, was treated with TFAA and pyridine to give sugar diene **34** with (*Z*)-configuration. Likewise, ozonolysis of **33** (1:1 anomeric mixture) followed by dehydration also produces a single product, **35**, with (*Z*)-configuration. The stereochemistry is in agreement with a common intermediate of oxonium ion similar to that delineated in Scheme 2.

It was noted that Xie and co-workers have reported a synthesis of compound **30** by Wittig reaction of *manno*-type lactone **3** with phosphorane $Ph_3P{=}CHCO_2Et$.[17] However, their reported ^1H NMR data are similar to those of the *gluco*-type *exo*-glucal, but different from our data for the *manno*-type *exo*-glycal **30**. We repeated their experiment and found the actual product was the *gluco*-type *exo*-glucal **20** (20% yield, similar to the reported yield). It is evident that Xie and co-workers have ne-

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(27) For instance, the NOESY spectrum of ester **13** indicated the cross-peaks between H1′ (δ 2.35 and 2.81) and H2 (δ 3.79), and thus supported their close correlation in space.

(28) We reported previously that ester **20** was synthesized in 75% yield in company with the other isomer in 15% yield (see ref 20). The yield of **20** can be improved to 90%.

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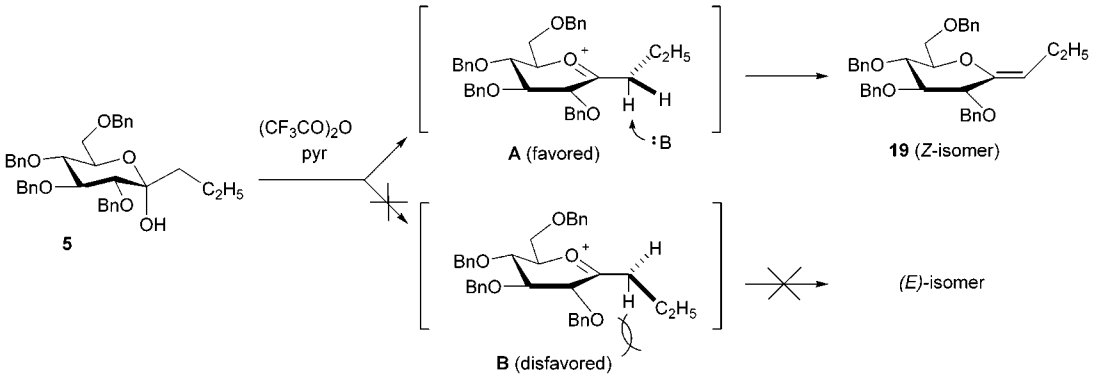
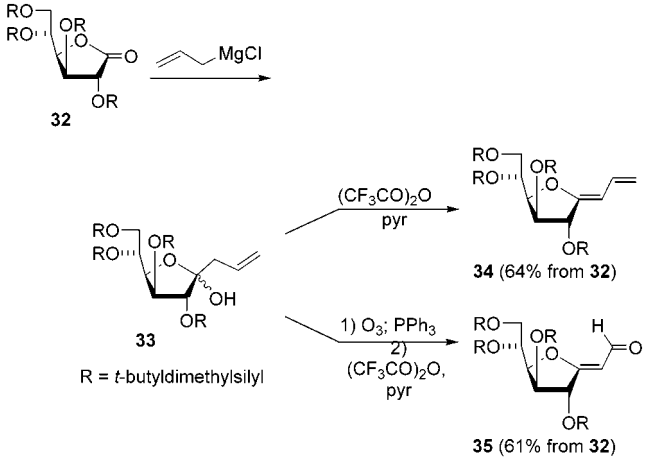
Scheme 2. Proposed Formation of an Oxocarbonium Ion To Explain the Resulting Stereoselectivity in the *exo*-Glycal Synthesis



Scheme 3. Preparation of Furanosyl *exo*-Glycals 34 and 35 as Exclusive (*Z*)-Isomers from a Mixture of α- and *β*-Anomeric Precursors



glected the possible epimerization at the C-2 position during the Wittig reaction.

We also explored an alternative route to the synthesis of *exo*-glycals (Scheme 4). *C*-Mannoside **36**, prepared by the known procedure,[30] was subjected to ozonolysis. The resulting ozonide was treated with NaOEt to give ester **37** in 83% yield. Lithiation of **37**, followed by treatment with phenylselenyl chloride, afforded the desired product **38** as a single isomer (27% yield) accompanied by the ring-opening product **39** (56% yield) with (*E*)-configuration ($J_{2,3}$ = 15.6 Hz). Oxidation of **38** with $NaIO_4$, followed by an in situ selenoxide elimination, provided a 75% yield of the conjugated ester **30** with (*Z*)-configuration, which is identical to that prepared by the previous two-step synthesis from lactone **3** (Scheme 1). We propose the transition state **D** to account for the *syn* elimination of selenoxides, giving the observed (*Z*)-double bond. Thus, selenide **38** was deduced to have the (1*S*,1′*S*) chirality. The stereochemistry might result from an attack of PhSeCl from the *exo* face of the chelated transition state **C**. On the other hand, treatment of **39** with PhSeCl led to two ring-closure products (Scheme 5), α-isomer **38** (16%) and *β*-isomer **40** (65%). Two isomers were separated by silica gel chromatography with elution of EtOAc/hexanes (1:10). Reductions of **38** and **40** with $NiCl_2 \cdot 6H_2O$ were individually carried out to give quantitative yields of *C*-mannosides **37**[31] and **41**[31], respectively. Upon oxidation of **40** with $NaIO_4$, the resulting selenide underwent elimination consecutively to give *exo*-glycal **30**. When a mixture of **38** and **40** (1:4) was treated with $NaIO_4$, a single product, **30**, was also obtained in a high yield. By mechanistic considerations, selenide **40** likely exhibited the (1*R*,1′*R*) configuration to account for the formation of (*Z*)-*exo*-glycal via transition state **E**.

exo-Glycals are potentially versatile building blocks in organic synthesis. The Michael addition reactions to conjugated esters **20** and **30** have been investigated. Treatment of the *gluco*-type *exo*-glycal **20** with allyl alcohol in the presence of $BF_3 \cdot OEt_2$ gave a single product that was determined to have a *C*-substituent on the *β*-position and an *O*-allyl group on the α-position. By a similar procedure, Michael reaction of the *manno*-type *exo*-glycal **30** with allyl alcohol also afforded a single isomer with the α-*O*-allyl group by analogy to the aforementioned stereochemical outcome that often occurred in the reactions of *manno*-type sugars. The detailed results will be published in due course. The products of Michael addition with two tethers on anomeric centers can be elaborated for other applications. For example, Schmidt et al. recently reported the synthesis of α(1,3)-galactosyltransferase inhibitors based on a new type of disubstrate analogue,[32] which relied on the buildup of quaternary carbon in the anomeric center.[33]

In conclusion, we have established two different methods to prepare *exo*-glycals. The two-step synthesis via addition and elimination procedures (Scheme 1) is general for preparation of the *exo*-glycals with five- and six-membered rings. The exclusive formation of (*Z*)-isomers suggests an oxocarbonium ion intermediate, which adapts a preferable conformation during the process of dehydration. The alternative synthesis (Schemes 4 and 5) incorporates selenylation of *C*-glycosides and the subsequent selenoxide elimination to give *exo*-glycals. This method also affords exclusively the (*Z*)-isomers of *exo*-glycals. Our preliminary study on the reactions of *exo*-glycals indicated that Michael additions occurred in a highly stereoselective manner. Further application of *exo*-glycals to

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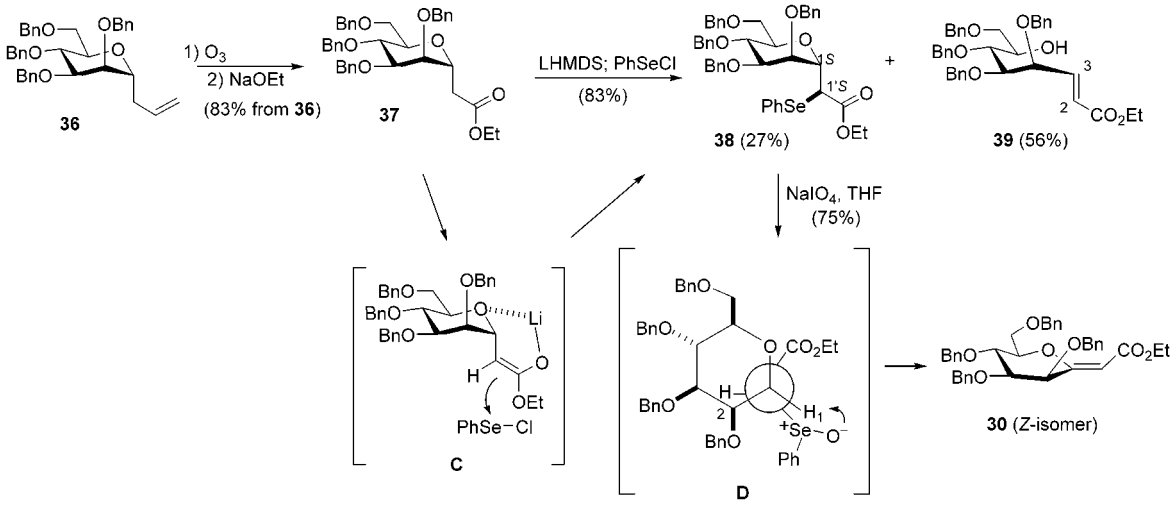
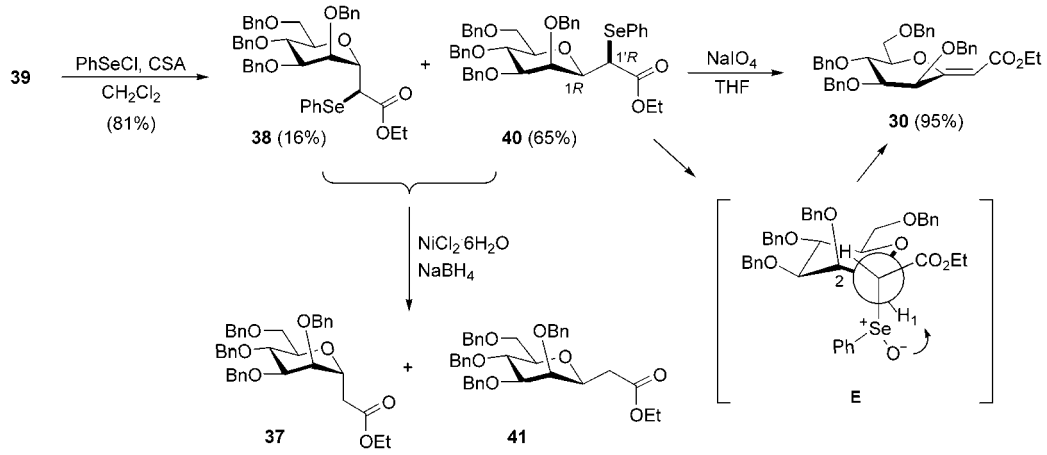
Scheme 4. Synthesis of Ester 30 as a (*Z*)-Isomer by the Selenylation of *C*-Glycoside 37 and a Subsequent Selenoxide Elimination



Scheme 5. Synthesis of Ester 30 as a (*Z*)-Isomer by the Treatment of Ring-Opening Ester 39 with PhSeCl and a Subsequent Selenoxide Elimination



the synthesis of uncommon carbohydrates is currently under investigation.

Experimental Section

General Methods. All reactions were conducted under an argon atmosphere. THF and diethyl ether were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Methanol was distilled from magnesium. Solutions of compounds in organic solvents were dried over sodium sulfate prior to rotary evaporation. DMF was 99.5% pure and anhydrous. Benzyl bromide was filtered through alumina prior to use. TLC plates (layer thickness, 250 μm) were Kieselgel 60 F_{254}. Carbohydrate compounds were visualized with TLC by the stain solution *p*-anisaldehyde/H_2SO_4/EtOH (6:1:100), phosphomolybdic acid (PMA)/EtOH (1:20), and H_2SO_4/EtOH/H_2O (1:10:10). Column chromatography was carried out with silica gel 60 (70−230 mesh); gradients of EtOAc/hexanes and gradients of MeOH/$CHCl_3$ were used as eluents. Optical rotations were measured on a digital polarimeter with a cuvette of 10 cm length. ^{1}H NMR spectra were recorded at 400 or 500 MHz with $CHCl_3$ (δ_H 7.24) or CD_3OD [δ_H 3.30 (central line of a quintet)] as the internal standard; ^{13}C NMR spectra were recorded at 100 or 125 MHz with $CDCl_3$ [δ_c 77.0 (central line of a triplet)] or CD_3OD [δ_c 49.0 (central line of a septet)] as the internal standard. Mass spectra were recorded at an ESI or FAB ionization.

General Procedure for Preparing *exo-Glycals*. Sugar lactones in fully protective forms of benzyl or TBDMS groups were prepared from direct protection of free lactones (commercially available)[26] or according to the reported procedures.[22−25] In a typical reaction, a fully protected lactone (1.0 mmol) in anhydrous THF (10 mL) was stirred at −78 °C under N_2 and subjected to the dropwise addition of Grignard reagent or organolithoum (1.2 mmol). After another 3 h of stirring until the disappearance of starting material, the reaction was stopped by the addition of water and then extracted with EtOAc (100 mL × 3). The combined organic layer was dried over Na_2SO_4, and the filtrate was evaporated to give a dry residue which was purified by silica gel column chromatography with an appropriate eluent. The resulting product was dissolved in THF (anhydrous, 10 mL) and treated with a mixture of pyridine (10 mmol) and trifluoroacetic anhydride (5.0 mmol) at 0 °C. After 4 h, the reaction mixture was subjected to saturated $NaHCO_3$ solution and extracted with EtOAc (100 mL × 3). The combined organic layer was dried over Na_2SO_4 and evaporated to provide the crude residue, which was further purified by silica gel chromatography.

2,3,4,6-Tetra-*O*-benzyl-1-methyl-α-D-glucopyranose (4).[34] The purification was carried out by silica gel chromatography with hexanes/EtOAc (2:1) to give compound **4** in 90% yield (of the nucleophilic addition): the ^{1}H NMR data were consistent with those reported previously;[34] ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.56, 68.84, 71.54, 73.41, 74.84, 75.57, 75.68, 78.45, 83.21, 83.62, 97.38, 127.58 (2×), 127.64, 127.74, 127.81,

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127.85, 127.90, 128.29, 128.33, 128.35, 128.40 (2×), 137.87, 138.19, 138.26, 138.65; ESI-MS *m/z* (rel intens) 537.2 (M − H_2O + H^+, 2), 429 (100); FAB-MS *m/z* (rel intens) 537.3 (M − H_2O + H^+, 4), 307.1 (31), 154 (100); HRMS (FAB) *m/z* calcd for $C_{35}H_{37}O_5$ (M − H_2O + H^+) 537.2641, found 537.2657.

2,3,4,6-Tetra-*O*-benzyl-1-propyl-α-D-glucopyranose (5). To a stirred solution of gluconolactone **1** (247 mg, 0.5 mmol) in anhydrous THF (10 mL) at −78 °C was added C_3H_7MgBr (1.0 M in THF, 0.6 mL, 0.6 mmol). The resulting mixture was warmed from −78 to −20 °C in a 3 h period, quenched by addition of NH_4Cl_{aq}, and extracted with EtOAc (50 mL × 3). The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with hexanes/EtOAc (3:1) to give 268 mg of product **5** as a colorless syrup in 92% yield: R_f 0.4 (EtOAc/hexanes, 1:3; PMA); $[\alpha]^{25}_D$ +10° (*c* 5.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, 3H, J = 7.3 Hz, $H_{3'}$) 1.25−1.47 (m, 2H, $H_{2'}$), 1.62 (t, 2H, J = 8.8 Hz, $H_{1'}$), 3.41 (d, 1H, J = 9.2 Hz, H_2), 3.63 (t, 1H, J = 9.3 Hz, H_3), 3.65 (dd, 1H, J = 10.8, 1.7 Hz, H_{6a}), 3.75 (dd, 1H, J = 10.8, 3.9 Hz, H_{6b}), 3.96 (ddd, 1H, J = 9.3, 3.9, 1.7 Hz, H_5), 3.98 (t, 1H, J = 9.3 Hz, H_4), 4.52 (d, 1H, J = 12.3 Hz, Ph*CH*$_2$), 4.60 (d, 1H, J = 10.7 Hz, Ph*CH*$_2$), 4.61 (d, 1H, J = 12.3 Hz, Ph*CH*$_2$), 4.67 (d, 1H, J = 11.1 Hz, Ph*CH*$_2$), 4.81 (d, 1H, J = 10.7 Hz, Ph*CH*$_2$), 4.85 (d, 1H, J = 11.0 Hz, Ph*CH*$_2$), 4.88 (d, 1H, J = 11.0 Hz, Ph*CH*$_2$), 4.91 (d, 1H, J = 11.1 Hz, Ph*CH*$_2$), 7.6∼7.1 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.23, 15.86, 40.86, 68.85, 71.59, 73.32, 74.87, 75.41, 75.60, 78.46, 81.48, 83.87, 98.84, 127.47, 127.59, 127.61, 127.65, 127.74, 127.81, 127.84, 127.88, 128.21, 128.27, 128.29, 128.37, 137.96, 138.30, 138.31, 138.64; ESI-MS *m/z* (rel intens) 583 (M + H^+, 22), 555 (39), 457 (100); FAB-MS *m/z* (rel intens) 565.3 (M − H_2O + H^+, 31), 457.2 (66), 391.2 (9); HRMS (FAB) *m/z* calcd for $C_{37}H_{41}O_5$ (M − H_2O + H^+) 565.2954, found 565.2961.

2,3,4,6-Tetra-*O*-benzyl-1-(ethoxycarbonyl)methyl-α-D-glucopyranose (6).[35] The purification was carried out by silica gel chromatography with hexanes/EtOAc (5:1) to give compound **6** as a colorless syrup in 95% yield (of the nucleophilic addition): R_f 0.5 (EtOAc/hexanes, 1/3; PMA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 2.33 (d, 1H, J = 15.4 Hz, $H_{1'a}$), 2.76 (d, 1H, J = 15.4 Hz, $H_{1'b}$), 3.32 (d, 1H, J = 9.4 Hz, H_2), 3.61 (dd, 1H, J = 11.1, 1.5 Hz, H_{6a}), 3.69 (t, 1H, J = 9.9 Hz, H_4), 3.73 (dd, 1H, J = 11.1, 3.8 Hz, H_{6b}), 4.01 (ddd, 1H, J = 9.9, 3.8, 1.5 Hz, H_5), 4.12 (dd, 1H, J = 9.9, 9.4 Hz, H_3), 4.14 (q, 2H, J = 7.1 Hz, OCH_2CH_3), 4.49 (d, 1H, J = 12.2 Hz, Ph*CH*$_2$), 4.57 (d, 1H, J = 12.2 Hz, Ph*CH*$_2$), 4.59 (d, 1H, J = 10.9 Hz, Ph*CH*$_2$), 4.65 (d, 1H, J = 11.5 Hz, Ph*CH*$_2$), 4.84 (d, 1H, J = 10.9 Hz, Ph*CH*$_2$), 4.90 (s, 2H, Ph*CH*$_2$), 4.96 (d, 1H, J = 11.5 Hz, Ph*CH*$_2$), 5.32 (s, 1H, OH), 7.18−7.21 (m, 2H, Ph), 7.24−7.32 (m, 18H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.01, 40.45, 61.01, 68.53, 71.42, 73.26, 74.84, 75.19, 75.61, 78.45, 81.88, 83.15, 97.09, 127.51, 127.59, 127.62, 127.70, 127.73, 127.79, 127.91, 128.27, 128.33, 128.40, 128.42 (2×), 137.81, 138.22, 138.26, 138.52, 172.39; ESI-MS *m/z* (rel intens) 650 (M + Na + H^+, 100), 609 (M − H_2O + H^+, 30), 563 (6); HRMS (FAB) *m/z* calcd for $C_{38}H_{41}O_7$ (M − H_2O + H^+) 609.2852, found 609.2857.

1-Allyl-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (7). To a stirred solution of gluconolactone **1** (280 mg, 0.52 mmol) in anhydrous THF (12 mL) at −78 °C was added allylmagnesium chloride (2.0 M in THF, 0.3 mL, 0.6 mmol). The resulting mixture was warmed from −78 to −20 °C in a 1 h period, quenched by addition of NH_4Cl_{aq}, and extracted with EtOAc (50 mL × 3). The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with hexanes/EtOAc (3:1) to give 247 mg of product **7** as a colorless syrup in 82% yield: R_f 0.19 ($CHCl_3$, PMA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (dd, 1H, J = 13.8, 7.5 Hz, $H_{1'a}$), 2.47 (dd, 1H, J = 13.8, 7.5 Hz, $H_{1'b}$), 3.44 (d, 1H, J = 9.1 Hz, H_4), 3.65 (dd, 1H, J = 11.0, 2.0 Hz, H_{6a}), 3.68 (d, 1H, J = 9.1 Hz, H_2), 3.76 (dd, 1H, J = 11.0, 3.9 Hz, H_{6b}), 3.97 (ddd, 1H, J = 9.3, 3.9, 2.0 Hz, H_5), 4.02 (t, 1H, J = 9.3 Hz, H_3), 4.53 (d, 1H, J = 12.3 Hz, Ph*CH*$_2$), 4.60 (d, 1H, J = 10.8 Hz, Ph*CH*$_2$), 4.61 (d, 1H, J = 12.3 Hz, Ph*CH*$_2$), 4.69 (d, 1H, J = 11.1 Hz, Ph*CH*$_2$), 4.83 (d, 1H, J = 10.8 Hz, Ph*CH*$_2$), 4.87 (d, 1H, J = 11.0 Hz, Ph*CH*$_2$), 4.91 (d, 1H, J = 11.0 Hz, Ph*CH*$_2$), 4.93 (d, 1H, J = 11.1 Hz, Ph*CH*$_2$), 5.13 (dd, 1H, J = 17.3, 2.0 Hz, $H_{3'a}$), 5.19 (dd, 1H, J = 10.2, 2.0 Hz, $H_{3'b}$), 5.88 (ddd, 1H, J = 17.3, 10.2, 7.5 Hz, $H_{2'}$), 7.19−7.21 (m, 2H, Ph), 7.24−7.33 (m, 18H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.82, 68.75, 71.58, 73.31, 74.84, 75.30, 75.55, 78.45, 81.48, 83.74, 97.59, 120.04, 127.47, 127.54, 127.59, 127.61, 127.69, 127.80, 127.81, 127.85, 128.14, 128.28, 128.32, 128.37, 132.20, 137.97, 138.27, 138.39, 138.60. FAB-MS *m/z* (rel intens) 563 (M − H_2O + H^+, 5), 455 (40), 253 (30), 181 (100); HRMS (FAB) *m/z* calcd for $C_{37}H_{39}O_5$ (M − H_2O + H^+) 563.2797, found 563.2772.

2,3,4,6-Tetra-*O*-benzyl-1-(dimethoxyphosphoryl)methyl-α-D-glucopyranose (8).[29a] The purification was carried out by silica gel chromatography with hexanes/EtOAc (1:1) to give compound **8** as a white solid in 92% yield (of the nucleophilic addition): R_f 0.44 (EtOAc/hexanes, 1/1; PMA); $[\alpha]^{25}_D$ −13.3° (*c* 6.2, $CHCl_3$); ^{1}H NMR (400 MHz,$CDCl_3$) δ 1.68 (dd, 1H, J = 18.5,15.2 Hz, $H_{1'a}$), 2.30 (dd, 1H, J = 17.6, 15.2 Hz, $H_{1'b}$), 3.27 (dd, 1H, J = 9.4,1.1 Hz, H_2), 3.60 (dd, 1H, J = 10.7, 2.0 Hz, H_{6a}), 3.61 (d, 3H, J = 11.1 Hz, OCH_3), 3.66 (d, 3H, J = 11.1 Hz, OCH_3), 3.70 (dd, 1H, J = 10.0, 9.4 Hz, H_4), 3.73 (dd, 1H, J = 10.7, 3.6 Hz, H_{6b}), 4.08 (ddd, 1H, J = 10.0, 3.6, 2.0 Hz, H_5), 4.12 (t, 1H, J = 9.4 Hz, H_3), 4.47 (s, 2H, Ph*CH*$_2$), 4.58 (d, 1H, J = 11.0 Hz, Ph*CH*$_2$), 4.64 (d, 1H, J = 11.7 Hz, Ph*CH*$_2$), 4.85 (d, 1H, J = 11.0 Hz, Ph*CH*$_2$), 4.91 (s, 2H, Ph*CH*$_2$), 4.96 (d, 1H, J = 11.7 Hz, Ph*CH*$_2$), 5.73 (s, 1H, OH), 7.18∼7.21 (m, 2H, Ph), 7.22−7.34 (m, 18H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.54 (d, $J_{P,C1}$ = 536.8 Hz), 51.73 (d, $J_{P,OMe}$ = 25.2 Hz), 53.25 (d, $J_{P,OMe}$ = 24.8 Hz), 68.46, 71.00, 73.26, 74.78, 75.08, 75.55, 78.31, 82.55 (d, J_{P-C} = 53.2 Hz), 83.10 (d, J_{P-C} = 12.8 Hz), 96.61 (d, J_{P-C3} = 32.0 Hz), 127.53, 127.57, 127.65, 127.68, 127.76, 127.90, 127.93, 128.27 (2×), 128.33, 128.38, 128.59, 137.75, 137.84, 138.20, 138.50; ESI-MS *m/z* (rel intens) 663 (M + H^+, 26), 645 (M − H_2O + H^+, 62), 537 (100), 429 (55); FAB-MS *m/z* (rel intens) 663 (M + H^+, 7), 645 (M − H_2O + H^+, 3), 537 (30), 154 (100); HRMS (FAB) *m/z* calcd for $C_{37}H_{45}O_9P$ (M + H^+) 663.2722, found 663.2711; calcd for $C_{37}H_{43}O_8P$ (M −H_2O + H^+) 645.2617, found 645.2603. Anal. Calcd for $C_{37}H_{43}O_9P$: C, 67.06; H, 6.54. Found C, 67.11; H, 6.70.

2,3,4,6-Tetra-*O*-benzyl-1-(ethoxysulfonyl)methyl-α-D-glucopyranose (9).[29b] The purification was carried out by silica gel chromatography with hexanes/EtOAc (5:1, 3:1) to give compound **9** as a colorless syrup in 81% yield (of the nucleophilic addition): R_f 0.75 (EtOAc/hexanes, 1:1; PMA); $[\alpha]^{25}_D$ −9.2° (*c* 4.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, 3H, J = 7.0 Hz, OCH_2CH_3), 2.98 (d, 1H, J = 14.5 Hz, $H_{1'a}$), 3.39 (d, 1H, J = 14.5 Hz, $H_{1'b}$), 3.39 (d, 1H, J = 9.4 Hz, H_2), 3.64 (dd, 1H, J = 11.0, 1.0 Hz, H_{6a}), 3.73 (t, 1H, J = 9.4 Hz, H_4), 3.74 (d, 1H, J = 11.0 Hz, H_{6b}), 4.03 (dm, 1H, J = 9.4 Hz, H_5), 4.10 (t, 1H, J = 9.4 Hz, H_3), 4.20 (q, 2H, J = 7.0 Hz, OCH_2CH_3), 4.48 (d, 1H, J = 12.0 Hz, Ph*CH*$_2$), 4.53 (d, 1H, J = 12.0 Hz, Ph*CH*$_2$), 4.59 (d, 1H, J = 11.5 Hz, Ph*CH*$_2$), 4.61 (s, 1H, OH), 4.64 (d, 1H, J = 11.5 Hz, Ph*CH*$_2$), 4.84 (d, 1H, J = 10.9 Hz, Ph*CH*$_2$), 4.89 (d, 1H, J = 10.9 Hz, Ph*CH*$_2$), 4.93 (d, 1H, J = 11.7 Hz, Ph*CH*$_2$), 4.96 (d, 1H, J = 11.7 Hz, Ph*CH*$_2$), 7.18−7.22 (m, 2H, Ph), 7.25−7.37 (m, 18H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.89, 55.30, 67.83, 68.39, 71.90, 73.39, 74.92, 75.11, 75.64, 77.97, 80.92, 82.86, 95.75, 127.64, 127.67, 127.71, 127.72, 127.74, 127.76, 128.28, 128.33, 128.36, 128.42, 128.63, 128.72, 137.36, 137.90, 138.01, 138.27; ESI-MS *m/z* (rel intens) 685 (M + Na^+, 100), 627 (2), 357 (2), 339 (4). Anal. Calcd for $C_{37}H_{42}O_9S$: C, 67.05; H, 6.39. Found C, 67.14; H, 6.32.

2,3,4,6-Tetra-*O*-benzyl-1-(phenyl)methyl-α-D-glucopyranose (10). To a stirred solution of gluconolactone **1** (540 mg, 1.0 mmol) in anhydrous THF (20 mL) at −78 °C was added $PhCH_2MgBr$ (1.0 M in diethyl ether, 3.0 mL, 3.0 mmol). The resulting mixture was warmed from −78 to −40 °C in a 2 h period, quenched by addition of NH_4Cl_{aq}, and extracted with EtOAc (100 mL × 3). The organic phase was washed with

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brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography with hexanes/EtOAc (5:1, 3:1) to give 599 mg of product **10** as a colorless syrup in 95% yield: R_f 0.5 (EtOAc/hexanes, 1:3; PMA); $[\alpha]^{25}_D$ +13° (*c* 3.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 1H, OH), 2.86 (d, 1H, J = 13.6 Hz, $H_{1'a}$), 3.04 (d, 1H, J = 13.6 Hz, $H_{1'b}$), 3.43 (d, 1H, J = 9.3 Hz, H_2), 3.62 (dd, 1H, J = 10.8, 1.8 Hz, H_{6a}), 3.67 (t, 1H, J = 9.6 Hz, H_4), 3.74 (dd, 1H, J = 10.8, 3.8 Hz, H_{6b}), 3.89 (ddd, 1H, J = 10.0, 3.8, 1.8 Hz, H_5), 4.06 (t, 1H, J = 9.3 Hz, H_3), 4.53 (d, 1H, J = 12.3 Hz, PhCH_2), 4.58 (d, 1H, J = 12.3 Hz, PhCH_2), 4.61 (d, 1H, J = 10.9 Hz, PhCH_2), 4.64 (s, 1H, OH), 4.70 (d, 1H, J = 11.3 Hz, PhCH_2), 4.83 (d, 1H, J = 10.9 Hz, PhCH_2), 4.87 (d, 1H, J = 11.0 Hz, PhCH_2), 4.92 (d, 1H, J = 11.0 Hz, PhCH_2), 4.98 (d, 1H, J = 11.3 Hz, PhCH_2), 7.21−7.37 (m, 25H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.81, 65.24, 68.87, 71.35, 73.32, 74.89, 75.31, 75.59, 78.49, 81.43, 83.89, 97.87, 126.91, 126.96, 127.49, 127.56, 127.58, 127.65, 127.74, 127.83, 127.86, 128.20, 128.23, 128.30, 128.35, 128.40, 128.43, 131.11, 134.68, 138.07, 138.28, 138.42, 138.56; ESI-MS *m*/*z* (rel intens) 653 (M + Na^+, 100), 545 (85), 505 (15); HRMS (FAB) *m*/*z* calcd for $C_{41}H_{41}O_5$ (M − H_2O + H^+) 613.2955, found 613.2962.

2,3,4,6-Tetra-*O*-benzyl-1-methyl-α-D-galactopyranose (11). To a stirred solution of galactonolactone **2** (600 mg, 1.1 mmol) in anhydrous THF (20 mL) at −78 °C was added CH_3MgCl (3.0 M in THF, 0.4 mL, 1.2 mmol). The resulting mixture was warmed from −78 to −20 °C in a 2 h period, quenched by addition of 1 N AcOH, and extracted with EtOAc (50 mL × 3). The collected organic layers were washed with saturated $NaHCO_3$, dried over Na_2SO_4, and evaporated in vacuo. The resulting residue was purified by silica gel chromatography with hexanes/EtOAc (3:1) to give 554 mg of product **11** in 91% yield: R_f 0.4 (EtOAc/hexanes, 1:3, PMA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 3H, CH_3), 2.52 (s, 1H, OH), 3.53 (dd, 1H, J = 9.0, 5.8 Hz, H_{6a}), 3.57 (dd, 1H, J = 9.0, 7.6 Hz, H_{6b}), 3.82 (d, 1H, J = 9.7 Hz, H_2), 3.89 (dd, 1H, J = 9.7, 2.7 Hz, H_3), 4.01 (dd, 1H, J = 2.7, 1.0 Hz, H_4), 4.11 (ddd, 1H, J = 7.6, 5.8, 1.0 Hz, H_5), 4.43 (d, 1H, J = 11.9 Hz, PhCH_2), 4.48 (d, 1H, J = 11.9 Hz, PhCH_2), 4.62 (d, 1H, J = 11.6 Hz, PhCH_2), 4.68 (d, 1H, J = 11.6 Hz, PhCH_2), 4.70 (d, 1H, J = 11.1 Hz, PhCH_2), 4.74 (d, 1H, J = 11.6 Hz, PhCH_2), 4.73 (d, 1H, J = 11.6 Hz, PhCH_2), 4.98 (d, 1H, J = 11.0 Hz, PhCH_2), 7.25−7.38 (m, 20H, Ph); ^{13}C NMR (100 MHZ, $CDCl_3$) δ 26.60, 68.84, 70.18, 72.39, 73.40, 74.33, 74.45, 75.74, 79.77, 80.92, 97.78, 127.47, 127.49, 127.55, 127.68, 127.74, 127.88, 128.02, 128.16, 128.29, 128.34 (2×), 128.38, 138.02, 138.16, 138.45, 138.83; ESI-MS *m*/*z* (rel intens) 555 (M + H^+, 15), 537 (12), 429 (100); FAB-MS *m*/*z* (rel intens) 555.3 (M + H^+, 2), 537.3 (10), 459.3 (2), 391.3 (5); HRMS (FAB) *m*/*z* calcd for $C_{35}H_{37}O_5$ (M − H_2O + H^+) 537.2641, found 537.2648.

2,3,4,6-Tetra-*O*-benzyl-1-propyl-α-D-galactopyranose (12). To a stirred solution of galactonolactone **2** (90 mg, 1.17 mmol) in anhydrous THF (5 mL) at −78 °C was added C_3H_7-MgCl (1.0 M in THF, 0.2 mL, 0.2 mmol). The resulting mixture was warmed from −78 to −20 °C in a 2 h period, quenched by addition of NH_4Cl_{aq}, and extracted with EtOAc (50 mL × 3). The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography with toluene/EtOAc (8:1) to give 89 mg of product **12** as a colorless syrup in 90% yield: R_f 0.4 (EtOAc/toluene, 1:8; anisaldehyde); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, 3H, J = 7.3 Hz, CH_3), 1.31−1.45 (m, 2H, $H_{2'}$), 1.57−1.69 (m, 2H, $H_{1'}$), 2.36 (s, 1H, OH), 3.52 (dd, 1H, J = 9.0, 5.5 Hz, H_{6a}), 3.59 (dd, 1H, J = 9.0, 7.8 Hz, H_{6b}), 3.85 (d, 1H, J = 9.5 Hz, H_2), 3.92 (dd, 1H, J = 9.5, 2.5 Hz, H_3), 4.02 (dd, 1H, J = 2.5, 0.9 Hz, H_4), 4.09 (ddd, 1H, J = 7.8, 5.5, 0.9 Hz, H_5), 4.43 (d, 1H, J = 11.8 Hz, PhCH_2), 4.47 (d, 1H, J = 11.8 Hz, PhCH_2), 4.62 (d, 1H, J = 11.7 Hz, PhCH_2), 4.67 (d, 1H, J = 11.6 Hz, PhCH_2), 4.69 (d, 1H, J = 11.4 Hz, PhCH_2), 4.75 (d, 1H, J = 11.6 Hz, PhCH_2), 4.94 (d, 1H, J = 11.7 Hz, PhCH_2), 5.00 (d, 1H, J = 11.4 Hz, PhCH_2), 7.15−7.41 (m, 20H, Ph); ^{13}C NMR (100 MHZ, $CDCl_3$) δ 14.10, 15.51, 40.85, 68.68, 70.00, 72.19, 73.31, 73.98, 74.22, 75.50, 78.29, 81.14, 98.69, 127.30, 127.43, 127.47, 127.59, 127.67, 127.72, 127.76, 128.08, 128.21, 128.24, 128.28, 128.32, 138.15, 138.26, 138.50, 138.91; HRMS (FAB) *m*/*z* calcd for $C_{37}H_{41}O_5$ (M − H_2O + H^+) 565.2955, found 565.2961.

2,3,4,6-Tetra-*O*-benzyl-1-(ethoxycarbonyl)methyl-α-D-galactopyranose (13). To a stirred solution of galactonolactone **2** (250 mg, 0.46 mmol) in anhydrous THF (10 mL) at −78 °C were added a THF (3 mL) solution containing EtOAc (230 μL, 2.3 mmol) and LHMDS (1.0 M in THF, 2.07 mL, 2.7 mmol). The reaction was warmed from −78 to −50 °C in a 2 h period, quenched by addition of saturated NH_4Cl_{aq}, and extracted with EtOAc (100 mL × 3). The organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with hexanes/EtOAc (5:1) to give 274 mg of product **13** in 95% yield: R_f 0.34 (EtOAc/hexanes, 1:3, anisaldehyde); $[\alpha]^{25}_D$ −3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, 3H, J = 7.0 Hz, OCH_2CH_3), 2.35 (d, 1H, J = 15.6 Hz, $H_{1'a}$), 2.81 (d, 1H, J = 15.6 Hz, $H_{1'b}$), 3.47 (dd, 1H, J = 9.3, 5.5 Hz, H_{6a}), 3.59 (dd, 1H, J = 9.3, 7.7 Hz, H_{6b}), 3.79 (dd, 1H, J = 9.8, 1.3 Hz, H_2), 4.02 (dd, 1H, J = 2.7, 1.4 Hz, H_4), 4.04−4.14 (m, 3H, OCH_2CH_3, H_3), 4.16 (ddd, 1H, J = 7.7, 5.5 Hz, H_5), 4.41 (d, 1H, J = 11.8 Hz, PhCH_2), 4.47 (d, 1H, J = 11.8 Hz, PhCH_2), 4.60 (d, 1H, J = 11.4 Hz, PhCH_2), 4.67 (d, 1H, J = 11.4 Hz, PhCH_2), 4.73 (d, 1H, J = 11.6 Hz, PhCH_2), 4.76 (d, 1H, J = 11.6 Hz, PhCH_2), 4.93 (d, 1H, J = 11.4 Hz, PhCH_2), 4.99 (d, 1H, J = 11.4 Hz, PhCH_2), 5.34 (d, 1H, J = 1.3 Hz, OH), 7.25−7.38 (m, 20H, Ph); ^{13}C NMR (125 MHZ, $CDCl_3$) δ 13.99, 40.59, 60.59, 68.65, 70.15, 72.59, 73.36, 74.67, 74.81, 75.23, 78.40, 80.42, 97.64, 127.54 (2×), 127.58, 127.66, 127.77, 127.80, 128.11, 128.20, 128.35, 128.36, 128.41, 128.56, 138.11 (2×), 138.45, 138.83, 172.55; HRMS (FAB) *m*/*z* calcd for $C_{38}H_{41}O_7$ (M − H_2O + H^+) 609.2852, found 609.2859.

2,3,4,6-Tetra-*O*-benzyl-1-methyl-α-D-mannopyranose (14). To a stirred solution of mannolactone **3** (270 mg, 0.5 mmol) in anhydrous THF (10 mL) at −78 °C was added CH_3MgCl (3.0 M in THF, 0.2 mL, 0.6 mmol). The resulting mixture was warmed to 0 °C in a 2 h period, quenched by addition of 1 N AcOH, and extracted with EtOAc (50 mL × 3). The collected organic layers were washed with saturated $NaHCO_3$, dried over Na_2SO_4, and evaporated in vacuo. The resulting residue was purified by silica gel chromatography with hexanes/EtOAc (3:1) to give 238 mg of product **14** in 86% yield: R_f 0.3 (EtOAc/hexanes, 1:3, PMA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 3H, CH_3), 2.25 (s, 1H, OH), 3.63−3.72 (m, 2H, H_{6a}, H_{6b}), 3.72 (d, 1H, J = 2.7 Hz, H_2), 3.85 (t, 1H, J = 9.7 Hz, H_4), 3.94−3.99 (m, 1H, H_5), 4.12 (dd, 1H, J = 9.4, 2.7 Hz, H_3), 4.51 (d, 1H, J = 10.8 Hz, PhCH_2), 4.55 (d, 1H, J = 12.6 Hz, PhCH_2), 4.60 (d, 1H, J = 12.6 Hz, PhCH_2), 4.68 (d, 1H, J = 11.6 Hz, PhCH_2), 4.75 (s, 2H, PhCH_2), 4.86 (d, 1H, J = 10.8 Hz, PhCH_2), 4.97 (d, 1H, J = 11.6 Hz, PhCH_2), 7.14−7.38 (m, 20H, Ph); ^{13}C NMR (100 MHZ, $CDCl_3$) δ 26.58, 69.81, 72.64, 72.80, 73.35, 74.74, 74.98, 75.11, 78.01, 81.45, 98.18, 127.47, 127.55 (3×), 127.75, 127.88, 128.04, 128.10, 128.20, 128.30 (2×), 128.40, 138.44, 138.50, 138.57, 138.58; ESI-MS *m*/*z* (rel intens) 555 (M + H^+, 15), 537 (12), 429 (100); FAB-MS *m*/*z* (rel intens) 555.3 (M + H^+, 2), 537.3 (10), 459.3 (2), 391.3 (5); HRMS (FAB) *m*/*z* calcd for $C_{35}H_{37}O_5$ (M − H_2O + H^+) 537.2641, found 537.2648.

2,3,4,6-Tetra-*O*-benzyl-1-propyl-D-mannopyranose (15). To a stirred solution of mannolactone **3** (225 mg, 0.42 mmol) in anhydrous THF (10 mL) at −78 °C was added C_3H_7MgBr (1.0 M in THF, 0.84 mL, 0.84 mmol). The resulting mixture was warmed from −78 to −20 °C in a 3 h period, quenched by addition of NH_4Cl_{aq}, and extracted with EtOAc (100 mL × 3). The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with toluene/EtOAc (12:1) to give 189 mg of product **15** as a colorless syrup in 80% yield: R_f 0.2 (EtOAc/hexanes, 1:5, PMA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 7.2 Hz, CH_3), 1.11−1.22 (m, 1H, $H_{2'a}$), 1.37−1.49 (m, 1H, $H_{2'b}$), 1.59−1.69 (m, 1H, $H_{1'a}$), 1.76−1.85 (m, 1H, $H_{1'b}$), 3.67 (dd, 1H, J = 10.8, 5.5 Hz, H_{6a}), 3.71 (dd, 1H, J = 10.8, 2.0 Hz, H_{6b}), 3.78 (d, 1H, J = 2.6 Hz, H_2), 3.89 (t, 1H, J = 9.7, Hz, H_4), 3.96 (ddd, 1H, J = 9.5, 5.5, 2.0 Hz, H_5), 4.41 (dd, 1H, J = 9.3, 2.6 Hz, H_3), 4.53 (d, 1H, J = 10.9 Hz, PhCH_2), 4.54 (d, 1H, J = 12.3 Hz, PhCH_2), 4.60 (d,

1H, J = 12.3 Hz, PhCH_2), 4.64 (d, 1H, J = 11.5 Hz, PhCH_2), 4.75 (d, 1H, J = 11.8 Hz, PhCH_2), 4.78 (d, 1H, J = 11.8 Hz, PhCH_2), 4.86 (d, 1H, J = 10.9 Hz, PhCH_2), 5.02 (d, 1H, J = 11.5 Hz, PhCH_2), 7.17−7.38 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.21, 16.04, 40.09, 69.84, 72.68, 72.78, 73.35, 74.61, 74.99, 75.38, 76.55, 81.97, 99.38, 127.43 (2×), 127.48, 127.50, 127.52, 127.83, 127.94, 128.02, 128.17, 128.25, 128.27, 128.37, 138.47, 138.53, 138.68, 138.75; HRMS (FAB) m/z calcd for $C_{37}H_{41}O_5$ 565.2954 (M − H_2O + H^+), found 565.2956.

2,3,4,6-Tetra-*O*-benzyl-1-(ethoxycarbonyl)methyl-D-mannopyranose (16). To a stirred solution of mannolactone **3** (338 mg, 0.63 mmol) in anhydrous THF (20 mL) at −78 °C were added a THF (3 mL) solution containing EtOAc (0.37 mL, 3.77 mmol) and LHMDS (1.0 M in THF, 5.65 mL, 5.65 mmol). The reaction was warmed from −78 to −20 °C in a 1 h period, quenched by addition of saturated NH_4Cl_{aq}, and then extracted with EtOAc (100 mL × 3). The organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with hexanes/EtOAc (3:1) to give 373 mg of product **16** as a colorless syrup in 95% yield: R_f 0.35 (EtOAc/hexanes, 1:3; anisaldehyde); $[\alpha]^{31}_D$ +7.6° (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, 3H, J = 7.2 Hz, OCH_2CH_3), 2.33 (d, 1H, J = 15.7 Hz, $H_{1'a}$), 3.00 (d, 1H, J = 15.7 Hz, $H_{1'b}$), 3.67 (dd, 1H, J = 11.2, 2.0 Hz, H_{6a}), 3.75 (d, 1H, J = 11.2, 4.0 Hz, H_{6b}), 3.78 (d, 1H, J = 2.5 Hz, H_2), 3.90−4.02 (m, 2H, H_4, H_5), 4.09−4.20 (m, 3H, OCH_2CH$_3$, H_3), 4.50 (d, 1H, J = 12.0 Hz, PhCH_2), 4.57 (d, 1H, J = 10.9 Hz, PhCH_2), 4.64 (d, 1H, J = 12.1 Hz, PhCH_2), 4.65 (d, 1H, J = 11.5 Hz, PhCH_2), 4.77 (m, 2H, PhCH_2), 4.86 (d, 1H, J = 10.9 Hz, PhCH_2), 5.01 (d, 1H, J = 11.5 Hz, PhCH_2), 7.21−7.38 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.05, 40.45, 60.98, 69.27, 72.90, 73.05, 73.26, 74.44, 74.92, 75.00, 77.62, 81.37, 97.41, 127.31, 127.51, 127.55, 127.56, 127.60, 127.79, 127.92, 128.11, 128.23, 128.29, 128.32, 128.38, 138.40, 138.57, 138.63, 138.74, 172.61; ESI-MS m/z (rel intens) 609.0 (M − H_2O + H^+, 100); HRMS (FAB) m/z calcd for $C_{38}H_{41}O_7$ (M − H_2O + H^+) 609.2852, found 609.2854.

1-Allyl-2,3,4,6-tetra-*O*-benzyl-D-mannopyranose (17). To a stirred solution of mannolactone **3** (108 mg, 0.2 mmol) in anhydrous THF (5 mL) at −78 °C was added allylmagnesium chloride (2.0 M in THF, 0.12 mL, 2.4 mmol). The resulting mixture was warmed from −78 to −20 °C in a 4-h period, quenched by addition of NH_4Cl_{aq}, and extracted with EtOAc (50 mL × 3). The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with hexanes/EtOAc (3:1) to give 99 mg of product **17** as a colorless syrup in 85% yield: R_f 0.6 (EtOAc/hexanes, 1:2; PMA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (dd, 1H, J = 13.7, 9.5 Hz, $H_{1'a}$), 2.50 (s, 1H, OH), 2.78 (dd, 1H, J = 13.7, 5.3 $H_{1'b}$), 3.68∼3.74 (m, 2H, H_{6a}, H_{6b}), 3.75 (d, 1H, J = 2.7 Hz, H_2), 3.91−3.95 (m, 1H, H_5), 3.95 (t, 1H, J = 9.1 Hz, H_4), 4.14 (dd, 1H, J = 9.1, 2.7 Hz, H_3), 4.54 (d, 1H, J = 12.2 Hz, PhCH_2), 4.55 (d, 1H, J = 10.8 Hz, PhCH_2), 4.64 (d, 1H, J = 12.2 Hz, PhCH_2), 4.66 (d, 1H, J = 11.5 Hz, PhCH_2), 4.75 (d, 1H, J = 11.8 Hz, PhCH_2), 4.78 (d, 1H, J = 11.8 Hz, PhCH_2), 4.87 (d, 1H, J = 10.8 Hz, PhCH_2), 5.03 (d, 1H, J = 11.5 Hz, PhCH_2), 5.14 (d, 1H, J = 17.1 Hz, $H_{3'a}$), 5.23 (dd, 1H, J = 10.2, 1.8 Hz, $H_{3'b}$), 5.77−5.89 (m, 1H, H_2), 7.17−7.39 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.60, 69.64, 72.66, 72.96, 73.34, 74.58, 75.02, 75.22, 77.55, 81.82, 97.85, 120.92, 127.38, 127.47, 127.50, 127.53, 127.76, 127.95, 128.01, 128.21, 128.25 (2×), 128.28, 128.39, 132.26, 138.49, 138.63 (3×); HRMS (FAB) m/z calcd for $C_{37}H_{39}O_5$ (M − H_2O + H^+) 563.2797, found 663.2787.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-methylidene-D-glucopyranose (18).[34] The purification was carried out by silica gel chromatography with hexanes/EtOAc (10:1) to give compound **18** as a colorless syrup in 45% yield (of the dehydration): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69−3.78 (m, 5H, H_3, H_4, H_5, H_{6a}, H_{6b}), 3.96 (d, 1H, J = 7.2 Hz, H_2), 4.51 (d, 1H, J = 11.1 Hz, PhCH_2), 4.53 (d, 1H, J = 12.1 Hz, PhCH_2), 4.62 (s, 1H, $H_{1'a}$), 4.63 (d, 1H, J = 12.1 Hz, PhCH_2), 4.64 (d, 1H, J = 11.6 Hz, PhCH_2), 4.71 (d, 1H, J = 11.2 Hz, PhCH_2), 4.76 (s, 1H, $H_{1'b}$), 4.77 (d, 1H, J = 11.6 Hz, PhCH_2) 4.77 (d, 1H, J = 11.2 Hz, PhCH_2), 4.86 (d, 1H, J = 11.1 Hz, PhCH_2), 7.12−7.15 (m, 2H, Ph), 7.24−7.37 (m, 18H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.77, 72.78, 73.54, 74.41, 74.47, 77.53, 78.54, 78.95, 84.72, 94.70, 127.63, 127.67, 127.69, 127.77, 127.85, 127.87 (2×), 127.90, 128.34, 128.36, 128.38, 128.43, 137.87, 138.04, 138.10, 138.34, 156.33; ESI-MS m/z (rel intens) 554.8 (M + H_2O + H^+, 8), 429 (M − $PhCH_2O$ + H^+, 100), 391.0 (35); HRMS m/z calcd for $C_{35}H_{37}O_5$ (M + H^+) 537.2641, found 537.2638.

(1(1′)*Z*)-2,3,4,6-*Tetra*-O-benzyl-1-deoxy-1-propylidene-D-glucopyranose (19). To a solution of **5** (212 mg, 0.36 mmol) in anhydrous THF (10 mL) at 0 °C were added pyridine (0.72 mL, 9.0 mmol) and trifluoroacetic anhydride (0.21 mL, 1.5 mmol). The resulting reaction was stirred at 0 °C for 2 h, stopped by adding saturated $NaHCO_3$, and extracted with EtOAc (100 mL). The resulting organic layer was dried over Na_2SO_4 and concentrated at reduced pressure. The purification by silica gel chromatography with hexanes/EtOAc (10:1) afforded 148 mg of product **19** in 72% yield as a white solid: R_f 0.5 (EtOAc/hexanes, 1:3; PMA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, 3H, J = 7.6 Hz, CH_3), 2.09−2.23 (m, 2H, $H_{2'}$), 3.65 (ddd, 1H, J = 9.9, 3.8, 1.9 Hz, H_5), 3.65 (t, 1H, J = 7.5 Hz, H_3), 3.73 (dd, 1H, J = 10.8, 3.8 Hz, H_{6a}), 3.76 (dd, 1H, J = 9.9, 7.5, Hz, H_4), 3.78 (dd, 1H, J = 10.8, 1.9 Hz, H_{6b}), 3.90 (dd, 1H, J = 7.4, 1.1 Hz, H_2), 4.50 (d, 1H, J = 11.0 Hz, PhCH_2), 4.54 (d, 1H, J = 12.2 Hz, PhCH_2), 4.59 (d, 1H, J = 11.6 Hz, PhCH_2), 4.65 (d, 1H, J = 12.2 Hz, PhCH_2), 4.69 (d, 1H, J = 11.6 Hz, PhCH_2), 4.72 (d, 1H, J = 12.2 Hz, PhCH_2), 4.77 (d, 1H, J = 11.0 Hz, PhCH_2), 4.85 (d, 1H, J = 11.2 Hz, PhCH_2), 4.99 (td, 1H, J = 7.3, 1.1 Hz, $H_{1'}$), 7.14−7.17 (m, 2H, Ph), 7.23−7.37 (m, 18H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.78, 29.87, 68.93, 72.60, 73.53, 74.44, 74.56, 77.84, 78.47, 79.37, 85.41, 112.64, 127.63, 127.69, 127.74, 127.76, 127.80, 127.83, 127.85, 127.97, 128.37, 128.39, 128.43, 128.47, 138.26, 138.30 (2×), 138.52, 147.56; ESI-MS m/z (rel intens) 587.3 (M + Na^+, 100), 565.4 (M + H^+, 11), 457.3 (18); FAB-MS m/z (rel intens) 565.3 (M + H^+, 20), 457.2 (67), 391.2 (40), 307.2 (100); HRMS (FAB) m/z calcd for $C_{37}H_{41}O_5$ (M + H^+) 565.2954, found 565.2955.

(1(1′)*Z*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-(ethoxycarbonyl)methylidene-D-glucopyranose (20).[17a] The purification was carried out by silica gel chromatography with hexanes/EtOAc (5:1) to give compound **20** as a colorless syrup in 90% yield (of the dehydration). The other isomer was sometimes obtained as the minor product. Data for compound **20**: R_f 0.5 (EtOAc/hexanes, 1:3); $[\alpha]^{25}_D$ +50.1° (*c* 2.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 3.82 (dd, 1H, J = 11.8, 3.5 Hz, H_{6a}), 3.83−3.89 (m, 3H, H_2, H_3, H_4), 3.89 (dd, 1H, J = 11.8, 2.0 Hz, H_{6b}), 4.16 (q, 2H, J = 7.1 Hz, OCH_2CH$_3$), 4.32 (ddd, 1H, J = 9.6, 3.5, 2.0 Hz, H_5), 4.51 (d, 1H, J = 11.8 Hz, PhCH_2), 4.53 (d, 1H, J = 11.2 Hz, PhCH_2), 4.54 (d, 1H, J = 12.1 Hz, PhCH_2), 4.61 (d, 1H, J = 11.8 Hz, PhCH_2), 4.63 (d, 1H, J = 12.3 Hz, PhCH_2), 4.66 (d, 1H, J = 11.2 Hz, PhCH_2), 4.72 (d, 1H, J = 12.1 Hz, PhCH_2), 4.75 (d, 1H, J = 12.3 Hz, PhCH_2), 5.20 (s, 1H, $H_{1'}$), 7.16−7.8 (m, 2H, Ph), 7.23−7.38 (m, 18H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.32, 59.64, 68.28, 71.43, 72.82, 73.50, 73.64, 77.25, 77.34, 77.75, 82.76, 99.88, 127.48, 127.72, 127.77, 127.85, 127.88 (3×), 127.96, 128.28, 128.30, 128.41, 128.48, 137.08, 137.56, 137.81, 138.26, 161.82, 164.73; ESI-MS m/z (rel intens) 609 (M + H^+, 100), 563 (25), 531 (7), 415 (5); FAB-MS m/z (rel intens) 609 (M + H^+, 10), 391 (4), 307 (33), 289 (18), 154 (100); HRMS (FAB) m/z calcd for $C_{38}H_{41}O_7$ (M + H^+) 609.2852, found 609.2851. Data for the other isomer: $[\alpha]^{25}_D$ +24.4° (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 3.68 (dd, 1H, J = 11.2, 4.7 Hz, H_{6a}), 3.70 (dd, 1H, J = 10.2, 4.0 Hz, H_4), 3.77 (dd, 1H, J = 11.2, 1.9 Hz, H_{6b}), 3.94 (dd, 1H, J = 4.0, 1.8 Hz, H_3), 4.14 (q, 2H, J = 7.1 Hz, OCH_2CH$_3$), 4.40 (d, 1H, J = 11.5 Hz, PhCH_2), 4.42 (d, 1H, J = 11.4 Hz, PhCH_2), 4.53 (d, 1H, J = 11.4 Hz, PhCH_2), 4.54 (d, 1H, J = 12.2 Hz, PhCH_2), 4.60 (d, 1H, J = 12.2 Hz, PhCH_2), 4.61 (d, 1H, J = 11.7 Hz, PhCH_2), 4.62 (ddd, 1H, J = 10.2, 4.7, 1.9 Hz, H_5), 4.67 (d, 1H, J = 11.5 Hz, PhCH_2), 4.69 (d, 1H, J = 11.7 Hz, PhCH_2), 5.67 (s, 1H, $H_{1'}$), 5.95 (d, 1H, J = 1.8 Hz, H_2), 7.14−7.16 (m, 2H, Ph), 7.25−7.36 (m, 18H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.32, 59.71, 68.75, 69.42, 70.79, 71.05, 72.34, 73.34, 74.88, 76.68, 80.55, 100.91, 127.56, 127.66, 127.68, 127.81, 127.87, 127.91, 128.27, 128.29

(2×), 128.31 (2×), 128.40, 137.33, 137.76, 137.98, 138.08, 165.56, 167.54; ESI-MS *m/z* (rel intens) 639 (72), 609 (M + H^+, 100), 531 (15), 415 (20); FAB-MS *m/z* (rel intens) 639 (7), 609 (M + H^+, 10), 471 (15), 289 (20), 147 (100); HRMS (FAB) *m/z* calcd for $C_{38}H_{41}O_7$ (M + H^+) 609.2852, found 609.2846.

(1(1′)*Z*)-1-Allylidene-2,3,4,6-tetra-*O*-benzyl-1-deoxy-α-D-glucopyranose (21). To compound **7** (145 mg, 0.25 mmol) in anhydrous THF (10 mL) were added pyridine (0.4 mL, 5.0 mmol) and trifluoroacetic anhydride (0.3 mL, 2.0 mmol) at 0 °C, and the mixture was stirred for 1 h. The reaction mixture was quenched with saturated $NaHCO_3$ and extracted with EtOAc (100 mL × 3). The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with hexanes/EtOAc (10:1) to give 119 mg of product **21** as a colorless syrup in 85% yield: R_f 0.47 (EtOAc/hexanes, 1:3; PMA); $[\alpha]^{21}_D$ +61° (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (dd, 1H, *J* = 9.7, 6.3 Hz, H_4), 3.75 (t, 1H, *J* = 6.3 Hz, H_3), 3.78 (dd, 1H, *J* = 11.3, 3.6 Hz, H_{6a}), 3.81 (dd, 1H, *J* = 11.3, 1.9 Hz, H_{6b}), 3.86 (ddd, 1H, *J* = 9.7, 3.6, 1.9 Hz, H_5), 3.96 (d, 1H, *J* = 6.3 Hz, H_2), 4.53 (d, 1H, *J* = 11.2 Hz, PhCH_2), 4.56 (d, 1H, *J* = 12.2 Hz, PhCH_2), 4.59 (d, 1H, *J* = 11.8 Hz, PhCH_2), 4.65 (d, 1H, *J* = 12.2 Hz, PhCH_2), 4.67 (d, 1H, *J* = 11.3 Hz, PhCH_2), 4.74 (d, 1H, *J* = 11.8 Hz, PhCH_2), 4.76 (d, 1H, *J* = 11.2 Hz, PhCH_2), 4.80 (d, 1H, *J* = 11.3 Hz, PhCH_2), 4.99 (dd, 1H, *J* = 10.6, 1.8 Hz, $H_{3'a}$), 5.16 (dd, 1H, *J* = 17.3, 1.8 Hz, $H_{3'b}$), 5.60 (d, 1H, *J* = 10.6 Hz, $H_{1'}$), 6.76 (dt, 1H, *J* = 17.3, 10.6 Hz, $H_{2'}$), 7.15−7.37 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.69, 72.35, 73.47, 74.01, 74.27, 77.54, 77.95, 78.77, 84.61, 111.15, 115.18, 127.60, 127.67, 127.69, 127.74 (2×), 127.76, 127.83, 127.87, 128.31, 128.35, 128.37, 128.43, 129.90, 137.79, 138.05, 138.07, 138.17, 149.59; ESI-MS *m/z* (rel intens) 563 (M + H^+, 60), 555 (100), 455 (51), 359 (10); HRMS (FAB) *m/z* calcd for $C_{37}H_{39}O_5$ (M + H^+) 563.2797, found 563.2772.

(1(1′)*Z*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-(dimethoxyphosphoryl)methylidene-D-glucopyranose (22).[29a] The purification was carried out by silica gel chromatography with hexanes/EtOAc (1:1) to give compound **22** as a colorless syrup in 81% yield (of the dehydration): R_f 0.17 (EtOAc/hexanes, 1:1; PMA); $[\alpha]^{25}_D$ +52.5° (*c* 8.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (d, 3H, J_{P-OCH3} = 5.0 Hz, OCH_3), 3.70 (d, 3H, J_{P-OCH3} = 5.0 Hz, OCH_3), 3.75−3.89 (m, 4H, H_3, H_4, H_{6a}, H_{6b}), 3.95 (d, 1H, *J* = 5.8 Hz, H_2), 4.11 (ddd, 1H, *J* = 9.8, 3.1, 2.0 Hz, H_5), 4.52−4.74 (m, 8H, PhCH_2), 5.06 (d, 1H, J_{P-H1} = 12.0 Hz, $H_{1\_}$), 7.17−7.19 (m, 2H, Ph), 7.24−7.34 (m, 18H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.18 (d, J_{P-OMe} = 21.7 Hz), 52.52 (d, J_{P-OMe} = 21.7 Hz), 68.19, 72.55, 73.47, 73.73, 74.02, 76.96, 78.22, 78.40 (d, J_{P-C} = 54.0 Hz), 83.26, 94.02 (d, J_{P-C} = 630 Hz), 127.67, 127.76, 127.80, 127.83, 127.90, 127.92, 127.94, 128.06, 128.37 (2×), 128.46, 128.56, 137.06, 137.72, 137.84, 137.96, 165.37 (d, J_{P-C} = 30 Hz); ESI-MS *m/z* (rel intens) 1289 (2M + H^+, 18), 645 (M + H^+, 100), 537 (3), 429 (3); FAB-MS *m/z* (rel intens) 645 (M + H^+, 55), 537 (5), 307 (25), 154 (100); HRMS (FAB) *m/z* calcd for $C_{37}H_{42}O_8P$ (M + H^+) 645.2618, found 645.2609.

(1(1′)*Z*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-(ethoxysulfonoyl)methylidene-D-glucopyranose (23).[29b] The purification was carried out by silica gel chromatography with hexanes/EtOAc (1:1) to give compound **23** as a colorless syrup in 83% yield (of the dehydration): R_f 0.78 (EtOAc/hexanes, 1:1; PMA); $[\alpha]^{25}_D$ +76.8° (*c* 1.64, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, 3H, *J* = 7.0 Hz, OCH_2CH_3), 3.78 (dd, 1H, *J* = 11.5, 3.2 Hz, H_{6a}), 3.83 (dd, 1H, *J* = 5.9, 5.0 Hz, H_3), 3.87 (dd, 1H, *J* = 11.5, 2.1 Hz, H_{6b}), 3.90 (dd, 1H, *J* = 9.5, 5.9 Hz, H_4), 3.91 (d, 1H, *J* = 5.0 Hz, H_2), 4.14 (q, 2H, *J* = 7.0 Hz, OCH_2CH_3), 4.29 (ddd, 1H, *J* = 9.5, 3.2, 2.1 Hz, H_5), 4.55 (d, 1H, *J* = 11.0 Hz, PhCH_2), 4.56 (d, 1H, *J* = 11.2 Hz, PhCH_2), 4.57 (d, 1H, *J* = 11.8 Hz, PhCH_2), 4.58 (d, 1H, *J* = 12.0 Hz, PhCH_2), 4.60 (d, 1H, *J* = 11.0 Hz, PhCH_2), 4.63 (d, 1H, *J* = 12.0 Hz, PhCH_2), 4.69 (d, 1H, *J* = 11.2 Hz, PhCH_2), 4.70 (d, 1H, *J* = 11.8 Hz, PhCH_2), 5.65 (s, 1H, $H_{1'}$), 7.20−7.36 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.82, 66.71, 67.86, 72.38, 73.33, 73.51, 73.73, 76.68, 76.87, 78.50, 82.31, 104.22, 127.64, 127.72, 127.88 (2×), 127.90, 127.99, 128.03, 128.28, 128.36, 128.40, 128.49, 128.65, 136.54, 137.38, 137.58, 137.93, 161.97; ESI-MS *m/z* (rel intens) 645 (M + H^+, 57), 549 (30), 415 (27), 341 (18); FAB-MS *m/z* (rel intens) 645 (M + H^+, 5), 627 (1), 537 (3), 307 (20), 154 (100); HRMS (FAB) *m/z* calcd for $C_{37}H_{41}O_8S$ (M + H^+) 645.2522, found 645.2523.

(1(1′)*Z*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-(phenyl)methylidene-D-glucopyranose (24).[15a] The purification was carried out by silica gel chromatography with hexanes/EtOAc (3:1) to give compound **24** as a colorless syrup in 87% yield (of the dehydration): R_f 0.6 (EtOAc/hexane, 1:3); $[\alpha]^{25}_D$ +59.1° (*c* 1.86, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (dd, 1H, *J* = 10.8, 4.3 Hz, H_{6a}), 3.82−3.86 (m, 2H, H_3, H_4), 3.88 (dd, 1H, *J* = 10.8, 1.9 Hz, H_{6b}), 4.03 (d, 1H, *J* = 4.7 Hz, H_2), 4.11 (ddd, 1H, *J* = 9.5, 4.3, 1.9 Hz, H_5), 4.56 (d, 1H, *J* = 11.3 Hz, PhCH_2), 4.59 (d, 1H, *J* = 12.3 Hz, PhCH_2), 4.62 (d, 1H, *J* = 11.8 Hz, PhCH_2), 4.66 (d, 1H, *J* = 12.3 Hz, PhCH_2), 4.67 (d, 1H, *J* = 11.0 Hz, PhCH_2), 4.76 (d, 1H, *J* = 11.0 Hz, PhCH_2), 4.78 (d, 1H, *J* = 11.8 Hz, PhCH_2), 4.79 (d, 1H, *J* = 11.3 Hz, PhCH_2), 5.73 (s, 1H, $H_{1'}$), 7.20−7.39 (m, 23H, Ph), 7.68 (dd, 2H, *J* = 7.3, 1.3 Hz, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.09, 71.68, 73.41, 73.45, 73.99, 76.83, 77.80, 79.17, 84.48, 109.45, 126.33, 127.58, 127.68 (2×), 127.71, 127.79, 127.84, 127.87, 127.97, 128.14, 128.32, 128.35, 128.39, 128.47, 128.69, 135.09, 137.82, 138.08, 138.12, 138.14, 148.97; HRMS (FAB) *m/z* calcd for $C_{41}H_{40}O_5$ (M^+) 612.2876, found 612.2889.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-methylidene-D-galactopyranose (25). To a solution of **11** (200 mg, 0.36 mmol) in anhydrous THF (10 mL) at 0 °C were added pyridine (0.87 mL, 10.8 mmol) and trifluoroacetic anhydride (0.26 mL, 1.8 mmol). The reaction was stirred for 2 h at 0 °C, stopped by addition of $NaHCO_3$, and extracted with EtOAc (100 mL). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The purification by silica gel chromatography with hexanes/EtOAc (10:1) afforded 103 mg of product **25** as a colorless syrup in 53% yield: R_f 0.63 (EtOAc/hexanes, 1:3; PMA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (dd, 1H, *J* = 9.6, 6.5 Hz, H_{6a}), 3.66 (d, 1H, *J* = 9.0, 2.7 Hz, H_3), 3.70 (dd, 1H, *J* = 9.6, 6.0 Hz, H_{6b}), 3.82 (ddd, 1H, *J* = 6.5, 6.0, 2.0 Hz, H_5), 4.05 (t, 1H, *J* = 2.5 Hz, H_4), 4.36 (d, 1H, *J* = 9.0 Hz, H_2), 4.45 (d, 1H, *J* = 11.9 Hz, PhCH_2), 4.52 (d, 1H, *J* = 11.9 Hz, PhCH_2), 4.60 (d, 1H, *J* = 11.5 Hz, PhCH_2), 4.70 (d, 1H, *J* = 1.4 Hz, $H_{1'a}$), 4.71 (d, 1H, *J* = 11.8 Hz, PhCH_2), 4.72 (d, 1H, *J* = 11.8 Hz, PhCH_2), 4.73 (d, 1H, *J* = 11.9 Hz, PhCH_2), 4.74 (d, 1H, *J* = 1.4 Hz, $H_{1'b}$), 4.77 (d, 1H, *J* = 11.9 Hz, PhCH_2) 4.92 (d, 1H, *J* = 11.5 Hz, PhCH_2), 7.25−7.37 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.62, 72.79, 73.53, 73.73, 74.38, 74.56, 77.35, 78.38, 82.07, 95.11, 127.47, 127.58, 127.60, 127.66, 127.77, 127.91, 127.93, 128.01, 128.21, 128.28, 128.37, 128.43, 138.00, 138.21, 138.52, 138.88, 157.39; ESI-MS *m/z* (rel intens) 554.8 (M + H_2O + H^+, 18), 429 (M − $PhCH_2O$ + H^+, 100), 391.0 (35); HRMS (FAB) *m/z* calcd for $C_{35}H_{37}O_5$ (M + H^+) 537.2639, found 537.2635.

(1(1′)*Z*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-propylidene-D-galactopyranose (26). To compound **12** (69 mg, 0.12 mmol) in anhydrous THF (5 mL) were added pyridine (0.29 mL, 3.6 mmol) and trifluoroacetic anhydride (0.85 mL, 0.6 mmol) at 0 °C. The reaction was stirred for 3 h at 0 °C, stopped by addition of saturated $NaHCO_3$, and extracted with EtOAc (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The purification by silica gel chromatography with hexanes/EtOAc (10:1) afforded product **26** (47 mg) in 70% yield: R_f 0.84 (EtOAc/hexanes, 1:2; PMA); $[\alpha]^{25}_D$ +27.6° (*c* 4.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, 3H, *J* = 7.5 Hz, CH_3), 2.07−2.21 (m, 2H, $H_{2'}$), 3.66 (dd, 1H, *J* = 8.1, 2.7 Hz, H_3), 3.67 (dd, 1H, *J* = 9.8, 6.0 Hz, H_{6a}), 3.75 (dd, 1H, *J* = 9.8, 6.4 Hz, H_{6b}), 3.86 (ddd, 1H, *J* = 6.4, 6.0, 2.5 Hz, H_5), 4.07 (t, 1H, *J* = 2.7 Hz, H_4), 4.24 (dd, 1H, *J* = 8.1, 1.0 Hz, H_2), 4.45 (d, 1H, *J* = 11.8 Hz, PhCH_2), 4.52 (d, 1H, *J* = 11.8 Hz, PhCH_2), 4.60 (d, 1H, *J* = 11.6 Hz, PhCH_2), 4.64 (d, 1H, *J* = 11.5 Hz, PhCH_2), 4.70 (d, 1H, *J* = 11.9 Hz, PhCH_2), 4.71 (d, 1H, *J* = 11.5 Hz, PhCH_2), 4.75 (d, 1H, *J* = 11.9 Hz, PhCH_2), 4.88 (d, 1H, *J* = 11.6 Hz, PhCH_2), 5.07 (dt, 1H, *J* = 7.4, 1.0 Hz, $H_{1\_}$), 7.24−7.36 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.46, 17.85, 68.80, 72.94, 73.47, 73.91, 74.52, 74.57, 77.10, 78.12, 81.59, 114.38, 127.43, 127.47, 127.49, 127.56, 127.58, 127.82, 127.89,

127.95, 127.97, 128.25, 128.32, 128.37, 138.34, 138.54, 138.66, 138.66, 147.40; ESI-MS *m/z* (rel intens) 564.7 ($M + H^+$, 20), 457.0 (100), 349.0 (21); HRMS (FAB) *m/z* calcd for $C_{37}H_{41}O_5$ ($M + H^+$) 565.2954, found 565.2963. Anal. Calcd for $C_{37}H_{40}O_5$: C, 78.69; H, 7.14. Found C, 78.36; H, 7.35.

(1(1′)*Z*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-(ethoxycarbonyl)methylidene-D-galactopyranose (27). The preparation used **13** as the starting material as was described for the synthesis of **20.** Compound **13** (274 mg, 0.44 mmol) in anhydrous THF (10 mL) was treated with pyridine (0.35 mL, 0.44 mmol) and trifluoroacetic anhydride (0.31 mL, 2.2 mmol) at 0 °C. The reaction was stirred for 2 h and stopped by addition of saturated $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated to give a residue which was puried by silica gel chromatography with hexanes/EtOAc (9:1) to give **27** (216 mg) in 81% yield: R_f 0.67 (EtOAc/hexanes, 1:5; PMA); $[\alpha]^{25}_D$ −20° (*c* 3.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, 3H, J = 7.2 Hz, OCH_2CH_3), 3.73 (dd, 1H, J = 9.3, 2.8 Hz, H_3), 3.78 (dd, 1H, J = 9.3, 6.0 Hz, H_{6a}), 3.79 (dd, 1H, J = 9.3, 7.2 Hz, H_{6b}), 3.99 (ddd, 1H, J = 7.2, 6.0, 1.0 Hz, H_5), 4.12 (q, 2H, J = 7.2 Hz, OCH_2CH_3), 4.13 (dd, 1H, J = 2.8, 1.0 Hz, H_4), 4.44 (dd, 1H, J = 9.3, 1.4 Hz, H_2), 4.45 (d, 1H, J = 11.6 Hz, PhCH_2), 4.54 (d, 1H, J = 11.6 Hz, PhCH_2), 4.61 (d, 1H, J = 11.4 Hz, PhCH_2), 4.71 (s, 2H, PhCH_2), 4.73 (d, 1H, J = 11.2 Hz, PhCH_2), 4.78 (d, 1H, J = 11.2 Hz, PhCH_2), 4.94 (d, 1H, J = 11.4 Hz, PhCH_2), 5.78 (d, 1H, J = 1.4 Hz, $H_{1'}$), 7.25−7.34 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.30, 59.59, 67.93, 72.60, 73.59, 73.59, 74.39, 74.66, 76.46, 78.48, 81.77, 100.02, 127.53, 127.59, 127.74, 127.79, 127.82 (2×), 127.96, 127.98, 128.25, 128.42 (2×), 128.44, 137.63, 137.80, 137.99, 138.39, 164.91, 165.12; FAB-MS *m/z* (rel intens) 609.1 ($M + H^+$, 100), 563 (10), 517 (8); HRMS (FAB) *m/z* calcd for $C_{38}H_{41}O_7$ ($M + H^+$) 609.2852, found 609.2852.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-methylidene-D-mannopyranose (28). To a solution of **11** (83 mg, 0.15 mmol) in anhydrous THF (10 mL) at 0 °C were added pyridine (0.36 mL, 4.5 mmol) and trifluoroacetic anhydride (0.11 mL, 0.75 mmol). The reaction was stirred at 0 °C for 1 h and warmed to room temperature, THF was removed, and the reaction was diluted with EtOAc (100 mL) and extracted with saturated $NaHCO_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The purification by silica gel chromatography with hexanes/EtOAc (10:1) afforded 41 mg of product **28** as a colorless syrup in 51% yield: R_f 0.60 (EtOAc/hexanes, 1:3; PMA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (ddd, 1H, J = 9.2, 4.4, 2.5 Hz, H_5), 3.66 (dd, 1H, J = 9.2, 3.2 Hz, H_3), 3.77 (dd, 1H, J = 10.7, 2.5 Hz, H_{6a}), 3.80 (dd, 1H, J = 10.7, 4.4 Hz, H_{6b}), 4.07 (d, 1H, J = 3.2 Hz, H_2), 4.16 (t, 1H, J = 9.2 Hz, H_4), 4.37 (s, 1H, $H_{1'a}$), 4.42 (d, 1H, J = 12.5 Hz, PhCH_2), 4.53 (d, 1H, J = 10.8 Hz, PhCH_2), 4.54 (d, 1H, J = 11.9 Hz, PhCH_2), 4.57 (d, 1H, J = 12.2 Hz, PhCH_2), 4.62 (d, 1H, J = 11.9 Hz, PhCH_2), 4.66 (d, 1H, J = 12.2 Hz, PhCH_2), 4.76 (d, 1H, J = 12.5 Hz, PhCH_2), 4.83 (s, 1H, $H_{1'b}$), 4.92 (d, 1H, J = 10.8 Hz, PhCH_2), 7.16−7.40 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.35, 69.41, 71.40, 73.44, 73.63, 74.12, 75.07, 80.22, 81.50, 99.55, 127.53, 127.59, 127.64, 127.73 (2×), 127.80, 127.98, 128.15 (2×), 128.31, 128.33, 128.35, 138.03, 138.19, 138.28, 138.39, 154.87; ESI-MS *m/z* (rel intens) 554.8 ($M + H_2O + H^+$, 18), 429 ($M - PhCH_2O + H^+$, 100), 391.0 (35); HRMS (FAB) *m/z* calcd for $C_{35}H_{37}O_5$ ($M + H^+$) 537.2639, found 537.2635.

(1(1′)*Z*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-propylidene-D-mannopyranose (29). To a solution of **15** (60 mg, 0.1 mmol) in anhydrous THF (5 mL) were added pyridine (0.25 mL, 3.1 mmol) and trifluoroacetic anhydride (0.73 mL, 0.5 mmol) at 0 °C. The reaction was stirred for 2 h at 0 °C. The reaction was quenched by addition of saturated $NaHCO_3$ solution and extracted with EtOAc (50 mL × 3). The organic layer was dried over Na_2SO_4 and concentrated. The purification by silica gel chromatography with hexanes/EtOAc (10:1) gave 50 mg of product **29** in 85% yield: R_f 0.38 (EtOAc/hexanes, 1:6.5; anisaldehyde); $[\alpha]^{25}_D$ +5.7° (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, 3H, J = 7.5, Hz, $H_{3'}$), 2.10−2.25 (m, 2H, $H_{2'}$), 3.53 (ddd, 1H, J = 9.4, 3.8, 3.0 H_5), 3.62 (dd, 1H, J = 9.2, 3.3 Hz, H_3), 3.78−3.87 (m, 2H, H_6), 3.97 (d, 1H, J = 3.3 Hz, H_2), 4.18 (t, 1H, J = 9.4 Hz, H_4), 4.40 (d, 1H, J = 12.6 Hz, PhCH_2), 4.52 (d, 1H, J = 12.0 Hz, PhCH_2), 4.56 (d, 1H, J = 10.9 Hz, PhCH_2), 4.58 (d, 1H, J = 12.4 Hz, PhCH_2), 4.61 (d, 1H, J = 12.0 Hz, PhCH_2), 4.70 (d, 1H, J = 12.4 Hz, PhCH_2), 4.73 (d, 1H, J = 12.6 Hz, PhCH_2), 4.77 (t, 1H, J = 7.3 Hz, $H_{1'}$), 4.95 (d, 1H, J = 10.9 Hz, PhCH_2), 7.18−7.40 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.41, 18.11, 68.91, 69.50, 71.15, 73.40, 74.09, 74.45, 75.16, 80.26, 82.25, 118.93, 127.42, 127.50, 127.56, 127.72, 127.74, 127.84, 127.94, 127.96, 128.20, 128.27, 128.30, 128.32, 138.31 (2×), 138.46, 138.58, 147.41; HRMS (FAB) *m/z* calcd for $C_{37}H_{41}O_5$ ($M + H^+$) 565.2954, found 565.2960.

(1(1′)*Z*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-(ethoxycarbonyl)methylidene-D-mannopyranose (30). The preparation used **16** as the starting material as was described for the synthesis of **20.** Compound **16** (266 mg, 0.43 mmol) in anhydrous THF (20 mL) was treated with pyridine (1.5 mL, 18.5 mmol) and trifluoroacetic anhydride (0.6 mL, 4.3 mmol) at 0 °C. The reaction was stirred for 2 h and stopped by addition of saturated $NaHCO_3$. After extraction with EtOAc (100 mL), the organic layer was dried over Na_2SO_4 and concentrated to give a dry residue. The purification by silica gel chromatography with hexanes/EtOAc (5:1) generated **30** (232 mg) as a colorless syrup in 89% yield: R_f 0.3 (EtOAc/hexanes, 1:3; anisaldehyde); $[\alpha]^{24}_D$ +1.65° (*c* 3.61, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, 3H, J = 7.2 Hz, OCH_2CH_3), 3.77 (dd, 1H, J = 6.0, 2.5 Hz, H_3), 3.78−3.84 (m, 2H, H_{6a}, H_{6b}), 3.98 (m, 1H, H_5), 4.08∼4.13 (m, 2H, H_2, H_4), 4.14 (q, 2H, J = 7.2 Hz, OCH_2CH_3), 4.44 (d, 1H, J = 12.2 Hz, PhCH_2), 4.45 (d, 1H, J = 11.1 Hz, PhCH_2), 4.58 (d, 1H, J = 12.2 Hz, PhCH_2), 4.59 (d, 1H, J = 11.9 Hz, PhCH_2), 4.63 (d, 1H, J = 11.1 Hz, PhCH_2), 4.64 (d, 1H, J = 11.8 Hz, PhCH_2), 4.67 (d, 1H, J = 11.8 Hz, PhCH_2), 4.70 (d, 1H, J = 11.9 Hz, PhCH_2), 5.27 (s, 1H, $H_{1\_}$), 7.14−7.36 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$ δ 14.32, 59.66, 69.05, 71.13, 72.13, 73.49, 73.53, 74.77, 77.22, 78.03, 79.47, 99.86, 127.49, 127.75, 127.78, 127.84 (2×), 127.88 (2×), 128.28, 128.36 (2×), 128.45 (2×), 137.25, 137.79, 137.90, 138.24, 162.64, 164.80; FAB-MS *m/z* (rel intens) 609.3 ($M + H^+$, 80), 563.3 (15), 519.3 (10), 501.3 (15), 391.3 (10); HRMS (FAB) *m/z* calcd for $C_{38}H_{41}O_7$ ($M + H^+$) 609.2852, found 609.2858.

(1(1′)*Z*)-1-Allylidene-2,3,4,6-tetra-*O*-benzyl-1-deoxy-d-mannopyranose (31). To a solution of **17** (70 mg, 0.12 mmol) in anhydrous THF (5 mL) at 0 °C were added pyridine (0.24 mL, 3.0 mmol) and trifluoroacetic anhydride (0.1 mL, 0.5 mmol). The reaction was stirred for 1.5 h and quenched by addition of saturated $NaHCO_3$. After extraction with EtOAc (50 mL × 3), the organic layer was dried over Na_2SO_4 and concentrated to give a dry residue. The purification by silica gel chromatography with hexanes/EtOAc (5:1) generated **31** (52 mg) in 76% yield as a colorless syrup: R_f 0.75 (EtOAc/hexanes, 1:2; PMA); $[\alpha]^{25}_D$ +15° (*c* 2.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (dt, 1H, J = 9.2, 3.4 Hz, H_5), 3.65 (dd, 1H, J = 9.2, 3.3 Hz, H_3), 3.82 (dd, 1H, J = 10.0, 3.4 Hz, H_{6a}), 3.86 (dd, 1H, J = 10.0, 3.4 Hz, H_{6b}), 4.01 (d, 1H, J = 3.3 Hz, H_2), 4.22 (t, 1H, J = 9.2 Hz, H_4), 4.39 (d, 1H, J = 12.5 Hz, PhCH_2), 4.54 (d, 1H, J = 11.7 Hz, PhCH_2), 4.56 (d, 1H, J = 10.9 Hz, PhCH_2), 4.57 (d, 1H, J = 11.7 Hz, PhCH_2), 4.62 (d, 1H, J = 12.0 Hz, PhCH_2), 4.70 (d, 1H, J = 12.0 Hz, PhCH_2), 4.74 (d, 1H, J = 12.5 Hz, PhCH_2), 4.93 (d, 1H, J = 10.9 Hz, PhCH_2), 5.05 (dd, 1H, J = 10.4, 1.8 Hz, $H_{3'a}$), 5.19 (dd, 1H, J = 17.3, 1.8 Hz, $H_{3'b}$), 5.41 (d, 1H, J = 10.7 Hz, $H_{1'}$), 6.75 (dt, 1H, J = 17.3, 10.5 Hz, $H_{2'}$), 7.19−7.41 (m, 20H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.32, 71.41, 73.42, 74.11, 74.23, 74.39, 75.04, 80.31, 81.53, 116.20, 116.38, 127.50, 127.57, 127.59, 127.62, 127.73 (2×), 127.85, 127.91, 128.10, 128.30 (2×), 128.33, 129.93, 138.04, 138.14, 138.32, 138.42, 148.54; ESI-MS *m/z* (rel intens) 563.2 ($M + H^+$, 72), 555.2 (100), 415.2 (20), 359.2 (10); FAB-MS *m/z* (rel intens) 563.2 ($M + H^+$, 23), 455.2 (17), 391.2 (16); HRMS (FAB) *m/z* calcd for $C_{37}H_{39}O_5$ ($M + H^+$) 563.2720, found 563.2733.

(1(1′)*Z*)-1-Allylidene-2,3,5,6-tetra-*O*-tert-butyldimethylsily-1-deoxy-D-gluconofuranose (34). Compound **34** was prepared as described in two steps (64% overall yield)[20] starting from **32**:[26b] colorless syrup; $[\alpha]^{23}_D$ −3.85° (*c* 2.1, $CHCl_3$);

R_f 0.6 (EtOAc/hexanes, 1:50); UV λ_{max} = 255 nm; IR (KBr, cm^{-1}) 2931, 2858, 1699, 1472, 1255, 1097, 835, 777; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 6H, $SiCH_3$), 0.76 (s, 3H, $SiCH_3$), 0.92 (s, 9H, $SiCH_3$), 0.11 (s, 3H, $SiCH_3$), 0.13 (s, 3H, $SiCH_3$), 0.86 (s, 18H, $C(CH_3)_3$), 0.88 (s, 9H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$), 3.78 (dd, 1H, J = 11.0, 5.4 Hz, H_{6a}), 3.89 (dd, 1H, J = 11.0, 2.4 Hz, H_{6b}), 4.03 (dd, 1H, J = 2.8, 1.7 Hz, H_3), 4.08 (ddd, 1H, J = 7.2, 5.4, 2.4 Hz, H_5), 4.22 (d, 1H, J = 1.7 Hz, H_2), 4.37 (dd, 1H, J = 7.2, 2.8 Hz, H_4), 4.85 (dd, 1H, J = 10.5, 2.0 Hz, $H_{3'a}$), 5.01 (dd. 1H, J = 17.2, 2.0 Hz, $H_{3'b}$), 5.09 (d, 1H, J = 10.5 Hz, $H_{1'}$), 6.59 (dt, 1H, J = 17.2, 10.5 Hz, $H_{2'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.38, −5.33, −4.56, −4.48, −4.26, −4.22, −4.03, −3.55, 17.90, 18.04, 18.30, 18.44, 25.62, 25.83, 25.96, 25.99, 65.06, 71.62, 76.47, 77.62, 84.20, 102.15, 112.09, 131.20, 157.28; ESI-MS m/z (rel intens) 659.6 (M + H^+, 65), 529.5 (25), 397.4 (27), 661.5 (100); HRMS (FAB) m/z calcd for $C_{33}H_{71}O_5Si_4$ (M + H^+) 659.4378, found 659.4359.

(1(1′)*Z*)-2,3,5,6-Tetra-*O*-tert-butyldimethylsily-1-deoxy-1-(carbonyl)methylidene-D-gluconofuranose (35). Compound **35** was prepared as described in three steps (61% overall yield)[20] starting from **32**:[26b] colorless syrup; R_f 0.2 (EtOAc/hexanes, 1:50); $[\alpha]^{25}_D$ +14.0° (*c* 1.0, $CHCl_3$); UV λ_{max} = 260 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 6H, $SiCH_3$), 0.09 (s, 3H, $SiCH_3$), 0.10 (s, 3H, $SiCH_3$), 0.11 (s, 3H, $SiCH_3$), 0.13 (s, 3H, $SiCH_3$), 0.14 (s, 3H, $SiCH_3$), 0.15 (s, 3H, $SiCH_3$), 0.86 (s, 9H, $C(CH_3)_3$), 0.87 (s, 9H, $C(CH_3)_3$), 0.88 (s, 9H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$), 3.80 (dd, 1H, J = 11.1, 4.6 Hz, H_{6a}), 3.91 (dd, 1H, J = 11.1, 3.0 Hz, H_{6b}), 4.13 (dd, 1H, J = 3.1, 2.1 Hz, H_3), 4.13 (ddd, 1H, J = 7.0, 4.6, 3.0 Hz, H_5), 4.42 (d, 1H, J = 2.1 Hz, H_2), 4.65 (dd, 1H, J = 7.0, 3.1 Hz, H_4), 5.18 (d, 1H, J = 8.4 Hz, $H_{1'}$), 9.96 (d, 1H, J = 8.4 Hz, CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.49, −5.32, −4.59, −4.55, −4.41, −4.19, −4.10, −3.66, 17.81, 17.94, 18.22, 18.34, 25.36, 25.48, 25.86, 26.00, 64.39, 77.14, 75.33, 78.53, 86.69, 103.43, 175.62, 189.67; FAB-MS m/z (rel intens) 661.3 (M + H^+, 100), 529.3 (12), 387.3 (8); HRMS (FAB) m/z calcd for $C_{32}H_{69}O_6Si_4$ (M + H^+) 661.4267, found 661.4269.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-(ethoxycarbonyl)-methylidene-1′(*S*)-(phenyl)selenyl-α-D-mannopyranose (38) and (*Z*)-4,5,6,8-Tetra-*O*-benzyl-7-hydroxy-D-manno-oct-2-enoic Acid Ethyl Ester (39). To a THF solution (anhydrous 20 mL) of compound **37** (497 mg, 0.79 mmol) were added at −78 °C LHMDS (1.0 M in THF, 1.57 mL, 1.57 mmol) dropwise in a 10 min period and PhSeCl (526 mg, 2.75 mmol) in THF. The color of the solution changed from orange to yellow. The reaction was then warmed to −60 °C. H_2O workup and diluting with EtOAc(100 mL) gave **38** (150 mg, 27%) and **39** (518 mg, 56%). Data for compound **38**: colorless syrup; R_f 0.3 (EtOAc/hexanes, 1:4; anisaldehyde); $[\alpha]^{25}_D$ +7.60° (*c* 3.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J = 6.9 Hz, 3H, OCH_2CH_3), 3.31 (dd, J = 9.1, 3.0 Hz, 1H, H_3), 3.64 (dd, J = 10.3, 1.8 Hz, 1H, H_{6a}), 3.70−3.78 (m, 2H, H_5, H_{6b}), 3.84−3.91 (m, 3H, $H_{1'}$, $PhCH_2$), 3.95 (t, 1H, J = 9.1 Hz, H_4), 4.13 (q, J = 7.0 Hz, 2H, OCH_2CH_3), 4.19 (t, 1H, J = 2.5 Hz, H_2), 4.46 (d, 1H, J = 10.6 Hz, $PhCH_2$), 4.47 (d, 1H, J = 12.1 Hz, $PhCH_2$), 4.57 (dd, 1H, J = 11.8, 1.8 Hz, H_1), 4.61 (d, 1H, J = 11.6 Hz, $PhCH_2$), 4.63 (d, 1H, J = 12.3 Hz, $PhCH_2$), 4.76 (d, 1H, J = 12.6 Hz, $PhCH_2$), 4.78 (d, 1H, J = 10.6 Hz, $PhCH_2$), 7.10∼7.37 (m, 25H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.94, 44.61, 61.51, 69.28, 71.01, 71.14, 71.39, 73.27, 73.86, 74.37, 75.02, 76.51, 79.61, 127.25, 127.36, 127.40, 127.62, 127.77, 127.97, 128.15, 128.21 (2×), 128.30 (3×), 128.54, 129.46, 134.83, 138.13 (3×), 138.17, 138.34, 170.32; EI-MS m/z (rel intens) 767.2 (M + H^+, 100), 765.4 (57), 609.4 (M − $SePh^+$, 55); HRMS (FAB) m/z calcd for $C_{44}H_{47}O_780Se$ 767.2487 (M + H^+) found 767.2484; calcd for $C_{44}H_{47}O_778Se$ (M + H^+) 765.2495, found 765.2504. Data for compound **39**: colorless syrup; R_f 0.3 (EtOAc/hexanes, 1:2; anisaldehyde); $[\alpha]^{25}_D$ +28.9° (*c* 9.0, $CHCl_3$); IR (cm^{-1}) 1656.5, 1716.9, 3490.3 (−OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 2.56 (d, J = 5.4 Hz, 1H, OH), 3.57 (dd, J = 9.6, 5.3 Hz, 1H, H_{8a}), 3.62 (dd, J = 9.6, 3.4 Hz, 1H, H_{8b}), 3.81 (dd, J = 7.7, 2.8 Hz, 1H, H_6), 3.88 (dd, J = 6.9, 2.9 Hz, 1H, H_5), 3.98 (m, 1H, H_7), 4.16−4.22 (m, 3H, OCH_2CH_3, $PhCH_2$), 4.26 (t, J = 6.8 Hz, 1H, H_4), 4.46−4.59 (m, 7H, $PhCH_2$), 6.13 (d, J = 15.6 Hz, 1H, H_2), 7.05 (dd, J = 15.6, 6.6 Hz, 1H, H_3), 7.15−7.32 (m, 20H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.24, 60.47, 70.01, 71.08, 71.14, 73.37, 73.84, 74.57, 78.41, 78.53, 80.99, 124.03, 127.60, 127.70, 127.74, 127.82, 127.84, 127.87 (2×), 128.29 (2×), 128.41 (2×), 128.46, 137.73, 137.84, 137.89, 138.24, 146.04, 165.98; FAB-MS m/z (rel intens) 611.1 (M + H^+, 100); HRMS (FAB) m/z calcd for $C_{38}H_{43}O_7$ 611.3008 (M + H^+), found 611.3005.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-(ethoxycarbonyl)-methylidene-1′(*R*)-(phenyl)selenyl-β-D-mannopyranose (40). Compound **39** (128.4 mg, 0.21 mmol) in anhydrous CH_2Cl_2 (10 mL) was treated with PhSeCl (48.4 mg, 0.25 mmol) at room temperature. After 12 h, the reaction was mixed with CSA (48.9 mg, 0.21 mmol) and stirred for 6 days. The reaction mixture was quenched with saturated $NaHCO_3$, extracted with EtOAc (100 mL × 3), washed with brine, and dried over Na_2SO_4. The filtrate was concentrated and purified by silica gel chromatography with hexanes/EtOAc (6:1, 4:1) to give 108 mg of product **40** (71%) as a colorless syrup: R_f 0.30 (EtOAc/hexanes, 1:4; anisaldehyde); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 3.42 (ddd, 1H, J = 9.7, 2.8, 2.8 Hz, H_5), 3.62 (dd, 1H J = 9.5, 2.7 Hz, H_3), 3.64−3.68 (m, 4H, $H_{1'}$, H_2, H_{6a}, H_{6b}), 3.97 (t, 1H, J = 9.3 Hz, H_4), 4.00∼4.08 (m, 2H, OCH_2CH_3), 4.38 (d, 1H, J = 10.9 Hz, $PhCH_2$), 4.16 (d, 1H J = 2.4 Hz, H_1), 4.45 (d, 1H, J = 11.9 Hz, $PhCH_2$), 4.58 (d, 2H, J = 11.8 Hz, $PhCH_2$), 4.77 (d, 1H, J = 11.8 Hz, $PhCH_2$), 4.81 (d, 1H, J = 11.8 Hz, $PhCH_2$), 4.85 (d, 1H, J = 10.8 Hz, $PhCH_2$), 5.07 (d, 1H, J = 11.0 Hz, $PhCH_2$), 7.20−7.37 (m, 23H, Ph), 7.49−7.52 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.94, 43.60, 60.95, 69.21, 72.68, 73.29, 73.89, 74.44, 75.06, 75.13, 78.08, 80.42, 85.25, 127.28, 127.58, 127.66, 127.70, 127.73, 127.79, 127.99, 128.13, 128.16, 128.28, 128.30, 128.47, 128.54, 129.17, 134.89, 135.00, 138.28, 138.39, 138.62, 138.83, 171.47; FAB-MS m/z (rel intens) 767.2 (M + H^+, 100), 765.2(60), 675.1(5), 673.1(3), 569.1(3), 567.1(2); HRMS (FAB) m/z calcd for $C_{44}H_{47}O_780Se$ 767.2487 (M + H^+), found 767.2502; calcd for $C_{44}H_{47}O_778Se$ 765.2494 (M + H^+), found 765. 2491.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **18**−**31**, **34**, **35**, and **37**−**41** and NOESY spectra of compounds **26**, **30**, and **31** to indicate the correlation of H1′ and H2 in space. This material is available free of charge via the Internet at http://pubs.acs.org.

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