

Platinum-Catalyzed Ring Opening of 1,2-Cyclopropanated Sugars with O-Nucleophiles. Convenient Synthesis of 2-C-Branched Carbohydrates

Jürgen Beyer, Philip R. Skaanderup, and Robert Madsen*

Contribution from the Department of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

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Abstract: A new reaction is described catalyzed by Zeise's dimer that allows for ring opening of 1,2-cyclopropanated sugars with O-nucleophiles to give 2-C-branched carbohydrates. A number of O-nucleophiles can participate in the ring opening including alcohols, phenols, and water. A wide range of alcohols has been employed giving 2-C-branched glycosides ranging from simple methyl glycosides to more complex disaccharides. A very high diastereoselectivity is obtained at the newly formed C-1 stereocenter. The α -glycoside, favored by the anomeric effect, is always the major product in the ring opening with alcohols regardless of the stereochemistry of the starting cyclopropane. When electron-rich phenols are employed as O-nucleophiles, rearrangement to the glycosyl arene has been observed. In general, the ring opening occurs readily with unsubstituted sugar cyclopropanes to give 2-C-methyl carbohydrates. However, cyclopropanes with ester or alkyl substituents are significantly less reactive and some even completely inert to ring opening. When the ring opening is carried out with $\text{PdCl}_2(\text{PhCN})_2$ catalyst, a Ferrier-type rearrangement occurs, giving 2,3-unsaturated glycosides containing a 2-C-alkyl substituent.

Introduction

C-Branched sugars occur widely in nature and have been the focus of intense studies in carbohydrate chemistry. Many antibiotics contain C-branched sugars as the glycosidic components,¹ and they have also been identified as structural subunits in many other natural products.^{2,3} As a result, C-branched sugars have often been used for total synthesis of natural products^{2,4} and carbohydrate mimetics.⁵ However, C-branched sugars constitute some of the most difficult carbohydrates to prepare in a stereocontrolled fashion.^{1,6} In addition, many procedures use toxic reagents such as mercury and tin or strongly basic organolithium and Grignard reagents.

Cyclopropanes are versatile functional groups in organic synthesis and can be prepared by a variety of procedures

including effective enantioselective methods.⁷ Relief of the ring strain in cyclopropanes provides a driving force for many different ring-opening reactions.⁸ Cyclopropanations have recently been extended to carbohydrates where several methods have been developed for stereocontrolled cyclopropanation of glycals.⁹ In general, zinc-mediated cyclopropanation under modified Simmons–Smith conditions takes place from the same face of the glycal double bond as the C-3 substituent¹⁰ while cyclopropanation with metal carbenes or dihalocarbenes occurs from the opposite face.¹¹ These 1,2-cyclopropanated sugars have been shown to undergo ring opening to give 2-C-branched sugars when subjected to solvolysis in the presence of a stoichiometric amount of mercury,^{10c} strong acid,^{11a,b} or halonium ions.^{10a,12} In addition, ring opening under Mitsunobu conditions has also been reported in a special case.^{11d} We reasoned that a catalytic ring-opening procedure could be developed by employing an appropriate transition metal. The reaction between a transition metal and a cyclopropane is due to an interaction between a vacant orbital on the metal and the

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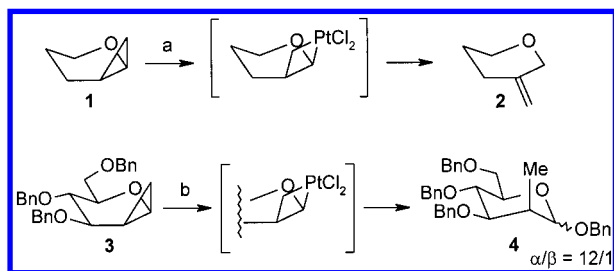
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Scheme 1^a

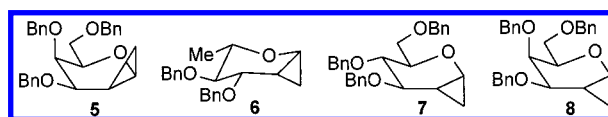
^a (a) 5% $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$, CH_2Cl_2 , rt, 74%. (b) 3.7% $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$, CH_2Cl_2 , rt, 23% or 3.7% $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$, BnOH , CH_2Cl_2 , rt, 95%.

σ -orbital of the C–C bond, the latter possessing high π -orbital character. In particular, platinum has been shown to react effectively with cyclopropanes to form platinacyclobutanes which are usually fairly stable and can be isolated.¹³ However, if the cyclopropane contains an oxy substituent, platinum has been shown to *catalyze* ring opening and subsequent rearrangement reactions.¹⁴ Especially the Pt(II)-catalyzed rearrangement of alkoxy and siloxy cyclopropanes into allylic ethers is noteworthy.^{14b,c} We anticipated that a 1,2-cyclopropanated sugar would undergo a similar rearrangement. In fact, when we treated racemic cyclopropane 1 with Zeise's dimer $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$, we obtained olefin 2 as the only product (Scheme 1). However, when we carried out the same reaction on D-glucal-derived cyclopropane 3, we did not observe any of the corresponding exocyclic olefin, but instead benzyl glycoside 4 was isolated as the major product. This is presumably formed by reaction of the intermediate platinacyclobutane with benzyl alcohol which might have been released during the reaction due to some decomposition. Indeed, when the reaction was repeated with benzyl alcohol added from the beginning, 2-C-branched glycoside 4 was obtained in 95% yield. This constitutes a new method for stereocontrolled preparation of 2-C-branched glycosides and to the best of our knowledge the first example of a Pt-catalyzed ring opening of a cyclopropane with an O-nucleophile. Herein, we report a detailed study on the scope and limitations of this new transformation.¹⁵ We demonstrate that the ring opening can take place with a variety of sugar cyclopropanes and a range of O-nucleophiles including alcohols, phenols, and water.

Results and Discussion

Cyclopropane Ring Opening with Simple Alcohols. Additional experiments revealed that the reaction between cyclopropane 3 and benzyl alcohol was best carried out in a weakly coordinating solvent such as CH_2Cl_2 or toluene while THF gave slower conversion and MeCN or DMF almost no reaction at all. Coordination also played an important role for the choice of catalyst. Platinum catalysts containing more tightly bound ligands than in Zeise's dimer gave either slower conversion (e.g., $\text{PtCl}_2(\text{PhCN})_2$) or no reaction at all (e.g., $\text{PtCl}_2(\text{MeCN})_2$, $\text{PtCl}_2(\text{COD})$, and $\text{PtCl}_2(\text{PPh}_3)_2$). A variety of other metal catalysts including $\text{PdCl}_2(\text{PPh}_3)_2$, $\text{Pd}(\text{PPh}_3)_4$, $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$, and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ also failed to open the cyclopropane. However, when Zeise's dimer was replaced by the electrophilic palladium catalyst $\text{PdCl}_2(\text{PhCN})_2$ a Ferrier-type rearrangement occurred (vide infra). A variety of other nucleophiles including thiophenol, benzoic acid, benzylamine, aniline, and diethyl malonate

Chart 1

Table 1. Ring Opening with Simple Alcohols^a

Entry	Cyclopropane	Alcohol (ROH)	Product	#	Yield (α/β ratio)
1	3	MeOH	BnO Me	9	82% (21/1)
2	3	Allyl-OH	BnO BnO	10	92% (only α)
3	3	<i>t</i> -BuOH	BnO OR	11	53% (9/1)
4	5	MeOH	BnO OBn Me	12	67% (only α)
5	5	Allyl-OH	BnO Me	13	84% (24/1)
6	5	BnOH	BnO OR	14	74% (only α)
7	6	MeOH	Me OR	15	90% (8/1)
8	6	Allyl-OH	BnO Me	16	96% (12/1)
9	6	BnOH	BnO Me	17	92% (10/1)
10	7	MeOH	BnO OBn	18	80% (7/1)
11	7	BnOH	BnO OR	19	97% (5/1)
12	8	Allyl-OH	BnO OBn	20	80% (7/1)
13	8	BnOH	BnO OR	21	87% (7/1)

^a All reactions were carried out in CH_2Cl_2 at ambient temperature with 3.7% $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ and 2 equiv of the alcohol.

failed to open the cyclopropane in the presence of Zeise's dimer, and only benzyl glycoside 4 or unreacted cyclopropane 3 was isolated from these experiments. As a result, the following studies were carried out with different cyclopropanated sugars and alcohol nucleophiles at ambient temperature in CH_2Cl_2 . The amount of Zeise's dimer could be lowered to 1 mol % in gram-scale experiments. However, to be able to weigh out accurate amounts of catalyst on a smaller scale, the 3.7 mol % used in Scheme 1 was maintained throughout these studies.

To probe the stereochemical outcome of the ring opening, we first sought to investigate the reaction with some simple alcohols. Hence, cyclopropanes 3 and 5–8 (Chart 1) were ring-opened in the presence of methyl, allyl, benzyl, or *tert*-butyl alcohol to give 2-C-methyl glycosides 9–21 (Table 1). The structures of the α - and β -anomers were verified by their $J_{\text{C}-1,\text{H}-1}$ coupling constants: with $J_{\text{C}-1,\text{H}-1}(\alpha\text{-anomer})$ always being about 10 Hz larger than $J_{\text{C}-1,\text{H}-1}(\beta\text{-anomer})$.¹⁶ In the cases where the α - and β -anomers could not be separated, the α/β ratio was determined from ^1H NMR by measuring the doublets from the 2-C-methyl groups. The results in Table 1 show that the ring opening proceeds well with the simple alcohols. High yields were generally obtained with methyl, allyl, and benzyl alcohol while *tert*-butyl alcohol gave a more moderate yield (entry 3). The diastereoselectivity at the newly formed C-1 stereocenter was very high in all cases, strongly favoring the α -glycoside, regardless of the stereochemistry of the starting cyclopropane. The selectivity is particularly high for cyclopropanes 3, 5, and 6 which give products where the anomeric substituent in the α -glycosides is *trans* to the 2-C-methyl group (entries 1–9). This is in accordance with the halonium ion mediated solvolysis reaction where cyclopropane 3 has been

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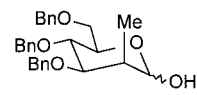
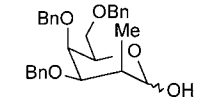
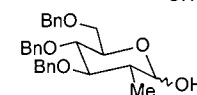
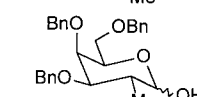
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Table 2. Ring Opening with Water^a

Entry	Cyclopropane	Product	#	Yield
1	3		22	65%
2	5		23	47%
3	7		24	60%
4	8		25	41%

^a All reactions were carried out in THF at 60 °C with 3.7% [Pt(C₂H₄)Cl₂]₂ and 2 equiv of water.

shown to give α -glycosides exclusively.^{10a,12a} For cyclopropanes 7 and 8 the platinum-catalyzed ring opening still gives α -glycosides in good selectivity (entries 10–13). This is on the other hand in contrast to the halonium ion mediated solvolysis where 7 gives mostly β -glycoside products.^{10a,12a} As a result, the stereochemical outcome of the platinum-catalyzed ring opening seems to be largely dictated by the anomeric effect.¹⁷ The results in Table 1 are in keeping with what is often observed in normal *O*-glycosylation reactions in a weakly coordinating solvent when a nonparticipating group is present at C-2. Here mannosyl and rhamnosyl donors generally give higher α -selectivity in glycosylations than the corresponding galactosyl donors which again give slightly higher α -selectivity than the glucosyl donors.¹⁸ However, in conventional *O*-glycoside synthesis, competitive reaction with water is a serious problem if rigorously anhydrous conditions are not maintained. Surprisingly, no side product arising from ring opening with water has been observed in the examples in Table 1. In fact, when the reaction was carried out in CH₂Cl₂ or toluene with 2 equiv of water no ring opening occurred but instead the catalyst “blackened out”. Zeise’s dimer and its precursor Zeise’s salt are both known to react with water upon heating to produce metallic platinum, acetaldehyde, and hydrogen chloride.¹⁹

Cyclopropane Ring Opening with Water. A number of experiments were carried out to find conditions that would allow the catalyst to react with the cyclopropane before it reacted with water. It was soon realized that an important factor was to keep a low water concentration. This was achieved by adding water in portions during the course of the reaction. In addition, THF proved to be the best solvent for these experiments with water and 60 °C seemed to be the optimum reaction temperature. Therefore, cyclopropanes 3, 5, 7, and 8 could be ring-opened to give hemiacetals 22–25 (Table 2). The yields were generally lower than the yields when the simple alcohols in Table 1 were used as nucleophiles. The major byproducts observed were dimers of 22–25 and benzyl glycosides 4, 14, 19, and 21. Hemiacetals of 2-deoxy sugars are fairly acid labile and known to dimerize easily.²⁰ The benzyl glycosides are probably formed

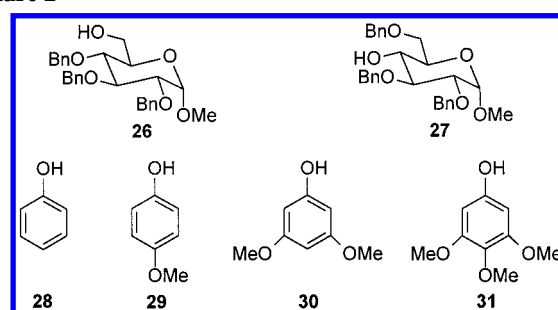
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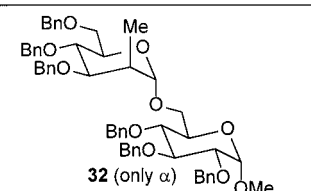
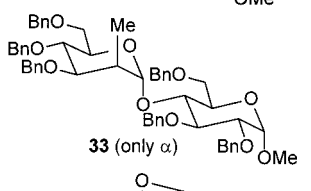
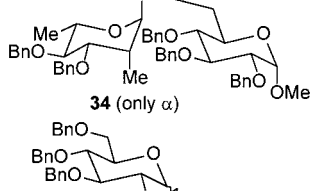
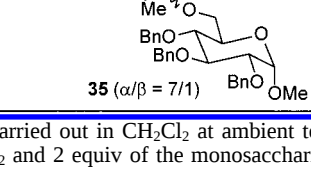
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Chart 2

Table 3. Ring Opening with Monosaccharides^a

Entry	Cyclopropane	Mono-saccharide	Product	Yield
1	3	26		65%
2	3	27		50%
3	6	26		65%
4	7	26		77%

^a All reactions were carried out in CH₂Cl₂ at ambient temperature with 3.7% [Pt(C₂H₄)Cl₂]₂ and 2 equiv of the monosaccharide.

in the same way as in Scheme 1 from some slight decomposition and release of benzyl alcohol.

Cyclopropane Ring Opening with Monosaccharides and Phenols. The ring-opening reaction makes it possible to view the 1,2-cyclopropanated sugars as special glycosyl donors. Therefore, it was decided also to investigate the reaction with some more complex nucleophiles (Chart 2). Reacting cyclopropanes 3, 6, and 7 with monosaccharides 26 and 27 gave rise to 2-*C*-branched disaccharides 32–35 in acceptable yields (Table 3). The yields were slightly lower than the yields with the simple primary alcohols in Table 1. In fact, in one experiment (entry 2) benzyl glycoside 4 was isolated in 12% yield as a significant byproduct. However, the diastereoselectivity follows the same trend as observed before, giving the α -glycoside as the major or the only product. Disaccharides 32–35 can be viewed as special carbohydrate mimetics where the 2-hydroxy group has been replaced by a hydrophobic methyl group.

Extending the reaction to phenols as nucleophiles gave rise to *O*-glycosides and glycosyl arenes (phenyl *C*-glycosides) depending on the substituents on the aromatic ring (Table 4). Reacting cyclopropane 3 with phenol (28) or *p*-methoxyphenol (29) gave phenyl *O*-glycosides 36 and 37, respectively, in acceptable yields and excellent α -selectivity. However, when

Table 4. Ring Opening of **3** with Phenols^a

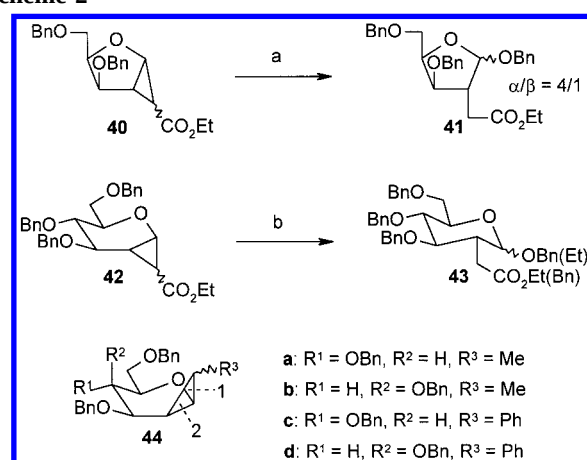
Entry	Phenol	Product	#	Yield (α/β ratio)
1	28		36	64% (21/1)
2	29		37	53% (only α)
3	30		38	29% (only β)
4	31		39	51% (1/1)

^a All reactions were carried out in CH_2Cl_2 at ambient temperature with 3.7% $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ and 2 equiv of the phenol.

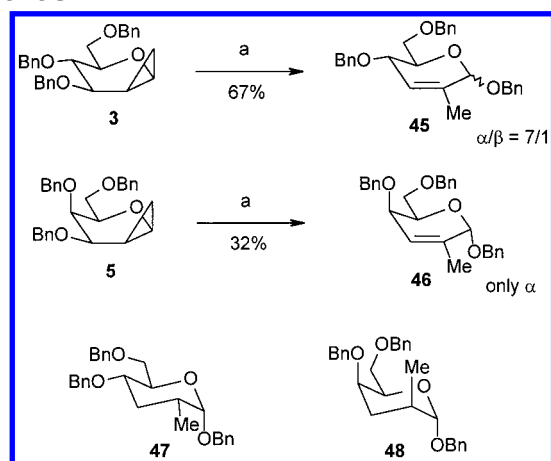
the phenol was further substituted with electron-donating groups as in **30** and **31**, glycosyl arenes **38** and **39** were obtained. These are presumably formed by a Fries-type rearrangement of the intermediate *O*-aryl glycoside.²¹ In the reactions with methoxyphenols **29**–**31** (entries 2–4), about 10–15% of benzyl glycoside **4** was also obtained as a byproduct. This follows the general trend observed so far. When a poor *O*-nucleophile is used, some decomposition of the cyclopropanated sugar will occur with release of benzyl alcohol which is then a better nucleophile in the ring-opening reaction.

Ring Opening of Substituted Cyclopropanes. Carboalkoxy-substituted cyclopropanes can be prepared by reaction of the glycol with ethyl diazoacetate by $\text{Rh}(\text{OAc})_2$ catalysis.¹¹ These were less reactive toward ring opening than the unsubstituted cyclopropanes, and it was necessary to use toluene at elevated temperature to get the reaction to proceed. Hereby, furanose cyclopropane **40** was reacted with benzyl alcohol to produce 2-*C*-branched benzyl furanoside **41** as a 4/1 α/β mixture. Although the α -anomer is still the dominating product, the α/β ratio is lower than that observed for the unsubstituted pyranose cyclopropanes in Tables 1 and 3. The ring opening of **40** could also be performed with methanol, but unfortunately in this case some transesterification with the ethyl ester did occur. This transesterification turned out to be a major problem when the ring opening was carried out on pyranose ester substituted cyclopropane **42**. This is even less reactive than furanose cyclopropane **40**, and the higher reaction temperature caused significant transesterification, giving **43** as a mixture of benzyl and ethyl glycoside as well as ethyl and benzyl ester.

Cyclopropanated sugars containing substituents other than ester groups are not known. However, we have discovered that zinc-mediated cyclopropanation directed by the 3-benzyloxy group can be extended to prepare new substituted cyclopropanes. In fact, cyclopropanating tri-*O*-benzyl-*D*-glucal and *D*-galactal with ethylidene iodide and diethyl zinc²² gave methyl-substituted cyclopropanes **44a** and **44b**, respectively, while cyclopropanating with phenyldiazomethane and zinc(II)chloride²³ gave rise to the corresponding phenyl-substituted cyclopropanes **44c** and

Scheme 2^a

^a (a) 3.7% $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$, BnOH , toluene, 70 °C, 1.5 h, 75%. (b) 3.7% $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$, BnOH , toluene, 85 °C, 14 h.

Scheme 3^a

^a (a) 10% $\text{PdCl}_2(\text{PhCN})_2$, BnOH , CH_2Cl_2 , rt.

44d. The exo/endo selectivity varied from 2/1 to 5/1. However, ring opening of these cyclopropanes with benzyl alcohol in refluxing toluene turned out to be very difficult and gave either no conversion or only very little benzyl glycoside product. In addition, when ring-opened benzyl glycosides could be isolated, they turned out to be a mixture of six- and seven-membered sugars. This shows that for the substituted cyclopropanes **44** the platinum-catalyzed ring opening is not regioselective for cyclopropane bond 1 but is also capable of breaking bond 2 (Scheme 2). In view of these results, no further experiments have been carried out on substituted cyclopropanes.

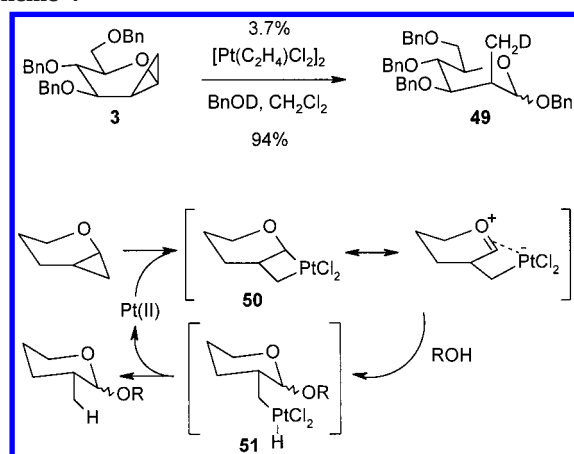
Ferrier-Type Rearrangement. During the initial studies with different catalysts, we discovered that when cyclopropane **3** was treated with a very electrophilic palladium(II) catalyst, $\text{PdCl}_2(\text{PhCN})_2$, a novel rearrangement occurred to give 2,3-unsaturated benzyl glycoside **45** (Scheme 3). The same rearrangement could be achieved with *D*-galactal-derived cyclopropane **5** although in a lower yield due to some decomposition. None of the corresponding benzyl glycosides **4** and **14** were observed in these cases. However, in the rearrangement of **3** benzyl glycoside **19** could be isolated as a byproduct in 3% yield. This is mechanistically very interesting because the configuration at C-2 in **19** has been inverted as compared to the starting cyclopropane **3**. This has never been observed in any of the ring openings with Zeise's dimer where the configuration at C-2 is always retained. The stereochemistry at the anomeric center in **45** and **46** was determined after hydrogenation of the

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Scheme 4

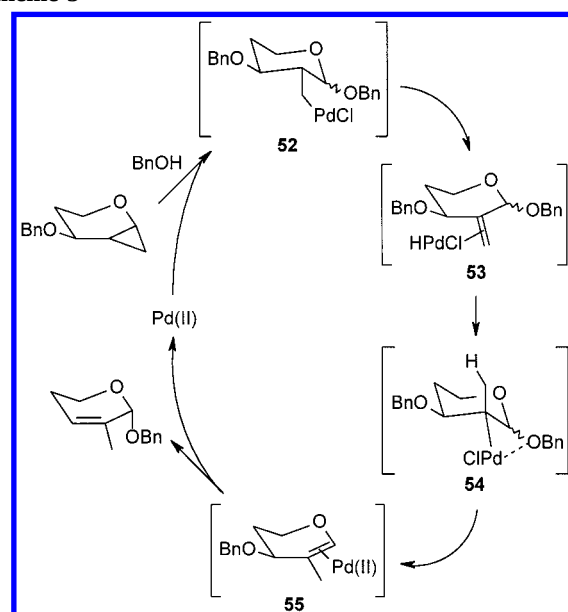


double bond to give **47** and **48**, respectively. The chemistry of cyclopropane C—C single bonds often resembles that of carbon—carbon double bonds.⁸ In fact, this palladium-catalyzed rearrangement is analogous to the acid-induced Ferrier rearrangement of normal glycals.²⁴ However, this is the first example of a similar rearrangement on 1,2-cyclopropanated glycals. It is very interesting that these seemingly similar platinum(II) and palladium(II) catalysts ring-open the cyclopropanes to give vastly different products.

Mechanism for Cyclopropane Ring Opening. To gain some more insight into the mechanism of the platinum-catalyzed ring opening with *O*-nucleophiles, we carried out a deuterium labeling experiment with monodeuterated benzyl alcohol (Scheme 4). The product **49** was found to be completely monodeuterated at the 2-C-methyl group. This allows us to propose a mechanism where an intermediate platinumacyclobutane is formed by oxidative addition of the cyclopropane to platinum(II). Platinum(IV)-cyclobutanes have previously been proposed as intermediates in rearrangements of electron-rich cyclopropanes with Zeise's dimer.^{14a,b} However, it should also be noted that platinum(IV)-cyclobutanes formed from electron-rich cyclopropanes have never actually been isolated or detected spectroscopically. The best evidence for their formation is a crystal structure on a platinum complex formed after ring opening of an electron-rich cyclopropane.²⁵ The structure shows that the cyclopropane inserts into platinum at an edge because the configuration at the cyclopropyl carbon is retained.²⁵ Literature data on platinum(IV)-cyclobutanes suggest that the platinum(IV)—carbon σ -bonds are polarized to give platinum(minus) and carbon(plus).²⁶ In platinumacyclobutane **50** the electron donation from the sugar ring oxygen will further enhance this polarization. As a result, **50** is believed to have substantial oxocarbenium ion character as previously observed for certain palladium species.²⁷ Nucleophilic attack of the *O*-nucleophile then gives the glycoside/hemiacetal with the α -anomer dominating according to the anomeric effect. Reductive elimination from **51** completes the catalytic cycle to give the C-branched sugar and regenerating platinum(II).

For the palladium-catalyzed Ferrier-type rearrangement, a different mechanistic pathway is believed to be operating (Scheme 5). Contrary to platinum(II), previous theoretical studies suggest that palladium(II) ring-opens cyclopropanes by

Scheme 5



corner attack.²⁸ This gives rise to initial formation of σ -bonded palladium glycoside **52**.²⁹ The same σ -bonded metal species is observed in mercury(II)-mediated ring openings.^{10c,30} Further reaction by β -hydride elimination affords olefin **53** which on rehydropalladation gives **54**.³¹ Previous studies have shown that these glycopyranosides with palladium at C-2 undergo a facile and unusual β -alkoxy elimination to the corresponding glycals.³² The reaction is probably mediated by coordination between palladium and the exocyclic oxygen at C-1 which also prevents a competing β -hydride elimination. Therefore, **55** is formed which then by allylic Ferrier rearrangement gives the product. In this reaction palladium(II) serves as the Lewis acid.^{33,34} Although intermediate glycal **55** cannot be observed in these rearrangements, the fact that **19** can be isolated from the rearrangement of **3** supports its existence. It should also be noted that the Ferrier rearrangement generally gives good yields for derivatives of D-glucal while the rearrangement works poorly for derivatives of D-galactal.³⁵ The exact same result is observed for the rearrangement of cyclopropanated glycals **3** and **5**.

In conclusion, we have developed a convenient procedure for platinum-catalyzed ring opening of 1,2-cyclopropanated

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sugars with *O*-nucleophiles. The 2-*C*-branched glycosides thus obtained are formed with very high α -selectivity regardless of the stereochemistry of the starting cyclopropane. In addition, we have discovered a palladium-catalyzed Ferrier-type rearrangement of 1,2-cyclopropanated sugars to give 2,3-unsaturated sugars containing a 2-*C*-alkyl substituent. All these 2-*C*-branched sugars are valuable chiral building blocks in synthetic strategies toward natural products and carbohydrate mimetics.

Experimental Section

General Procedures. All NMR spectra were recorded in CDCl₃ using TMS ($\delta = 0$) as internal reference for ¹H NMR spectra and CDCl₃ ($\delta = 77.0$) for ¹³C NMR spectra. All *R*_f values were measured in 5/1 hexane/EtOAc.

General Procedure for Platinum-Catalyzed Cyclopropane Ring Opening with Alcohols and Phenols. Zeise's dimer³⁶ (21.5 mg, 0.0366 mmol) was dissolved in CH₂Cl₂ (5 mL) under an atmosphere of nitrogen. The solution was then transferred by syringe to a flask containing the cyclopropane (1.0 mmol) and the alcohol (2.0 mmol). The mixture was stirred under nitrogen at room temperature for 15 h. After removal of the solvent in vacuo, the crude mixture was purified by flash chromatography. If α - and β -glycosides could not be separated, complete NMR data are reported for the α -anomer (major) while for the β -anomer (minor) the chemical shift and coupling constant for the anomeric carbon are reported.

General Procedure for Platinum-Catalyzed Cyclopropane Ring Opening with Water. The cyclopropane (500 mg, 1.16 mmol) was dissolved in THF (4 mL) followed by addition of Zeise's dimer (25 mg, 0.0425 mmol) and H₂O (14 μ L, 0.78 mmol). The solution was heated under an atmosphere of nitrogen at 60 °C for 24 h during which time more H₂O (14 μ L) was added after 1 and 2 h, respectively. The reaction mixture was concentrated and the residue purified by flash chromatography.

Tetrahydro-3-methylene-2H-pyran (2). Zeise's dimer (100 mg, 0.170 mmol) was dissolved during 5 min in CH₂Cl₂ (10 mL). 2-Oxabicyclo[4.1.0]heptane **1**³⁷ (330 mg, 3.36 mmol) was then added by syringe. The solution was stirred at room temperature for 20 h. The solvent was removed in vacuo and the residue purified by flash chromatography (pentane/Et₂O 5/1) to afford 243 mg (74%) of **2** as a liquid. ¹H NMR (250 MHz) δ : 4.77 (m, 2H), 4.03 (s, 2H), 3.73 (m, 2H), 2.32 (tt, *J* = 6.3, 1.1 Hz, 2H), 1.72 (m, 2H). ¹³C NMR (62.5 MHz) δ : 144.1, 109.1, 72.6, 67.8, 31.6, 28.1. ¹H NMR data are in accordance with literature values.³⁸

Benzyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methyl- α -D-mannopyranoside (4). *R*_f = 0.51. α -Anomer. ¹H NMR (250 MHz) δ : 7.38–7.09 (m, 20H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.75 (d, *J* = 1.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 11.5 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.39 (d, *J* = 10.8 Hz, 1H), 4.01 (dd, *J* = 8.8, 5.2 Hz, 1H), 3.75 (m, 1H), 3.70 (m, 2H), 3.61 (dd, *J* = 10.6, 1.9 Hz, 1H), 2.39 (m, 1H), 1.02 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (62.5 MHz) δ : 138.7, 138.5, 138.3, 137.7, 128.3, 128.0, 127.9, 127.7, 127.6, 127.6, 127.5, 101.4 (*J* = 166.9 Hz), 79.8, 75.0, 74.2, 73.4, 71.5, 71.1, 69.1, 68.9, 36.8, 11.3. β -Anomer. ¹³C NMR (62.5 MHz) δ : 100.4 (*J* = 156.7 Hz). Anal. Calcd for C₃₅H₃₈O₅: C, 78.04; H, 7.11. Found: C, 77.99; H, 7.41.

Methyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methyl- α -D-mannopyranoside (9). *R*_f = 0.56. α -Anomer. ¹H NMR (250 MHz) δ : 7.37–7.14 (m, 15H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.65 (d, *J* = 11.5 Hz, 1H), 4.61 (s, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 4.51 (d, *J* = 12.2 Hz, 1H), 4.44 (d, *J* = 10.8 Hz, 1H), 3.98 (m, 1H), 3.80–3.65 (m, 4H), 3.33 (s, 3H), 2.39 (tt, *J* = 7.3, 1.6 Hz, 1H), 1.08 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (62.5 MHz) δ : 138.7, 138.6, 138.4, 128.3, 127.9, 127.7, 127.6, 127.5, 103.2 (*J* = 171.2 Hz), 79.8, 74.9, 74.2, 73.4, 71.2, 71.0, 69.2, 54.6, 36.7, 11.2. β -Anomer. ¹³C NMR (62.5 MHz) δ : 102.8

(*J* = 157.1 Hz). Anal. Calcd for C₂₉H₃₄O₅: C, 75.30; H, 7.41. Found: C, 75.40; H, 7.40.

Allyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methyl- α -D-mannopyranoside (10). *R*_f = 0.48. [α]_D²⁵ +51.5 (c 1.0, CHCl₃). ¹H NMR (250 MHz) δ : 7.39–7.29 (m, 15H), 5.89 (m, 1H), 5.25 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.16 (dq, *J* = 10.4, 1.7 Hz, 1H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.76 (d, *J* = 1.3 Hz, 1H), 4.67 (d, *J* = 12.2 Hz, 1H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.59 (d, *J* = 11.4 Hz, 1H), 4.49 (d, *J* = 12.2 Hz, 1H), 4.44 (d, *J* = 10.8 Hz, 1H), 4.15 (ddt, *J* = 13.0, 5.1, 1.5 Hz, 1H), 4.06 (m, 1H), 3.93 (ddt, *J* = 13.0, 6.1, 1.2 Hz, 1H), 3.79–3.65 (m, 4H), 2.43 (m, 1H), 1.09 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (62.5 MHz) δ : 138.7, 138.5, 138.3, 134.1, 128.3, 128.3, 128.2, 127.9, 127.6, 127.5, 127.5, 127.4, 127.4, 116.9, 101.3 (*J* = 167.2 Hz), 79.7, 74.9, 74.2, 73.3, 71.3, 71.0, 69.1, 67.7, 36.7, 11.2. Anal. Calcd for C₃₁H₃₆O₅: C, 76.20; H, 7.43. Found: C, 75.95; H, 7.72.

tert-Butyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methyl- α -D-mannopyranoside (11). *R*_f = 0.59. α -Anomer. ¹H NMR (500 MHz) δ : 7.38–7.15 (m, 15H), 5.00 (d, *J* = 1.2 Hz, 1H), 4.83 (d, *J* = 10.7 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 4.43 (d, *J* = 10.7 Hz, 1H), 4.06 (dd, *J* = 9.0, 5.1 Hz, 1H), 3.96 (ddd, *J* = 9.0, 5.9, 2.0 Hz, 1H), 3.80–3.76 (m, 2H), 3.63 (dd, *J* = 10.5, 2.0 Hz, 1H), 2.22 (m, 1H), 1.23 (s, 9H), 1.08 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (125 MHz) δ : 138.8, 138.5, 138.3, 128.1, 128.1, 127.9, 127.6, 127.5, 127.4, 127.3, 96.4 (*J* = 164.0 Hz), 79.7, 74.8, 74.5, 74.4, 73.2, 70.8, 70.7, 69.1, 38.2, 28.4, 11.4. β -Anomer. ¹³C NMR (125 MHz) δ : 95.9 (*J* = 150.8 Hz). Anal. Calcd for C₃₂H₄₀O₅: C, 76.16; H, 7.99. Found: C, 76.52; H, 7.87.

Methyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methyl- α -D-talopyranoside (12). *R*_f = 0.47. [α]_D²⁵ +26.2 (c 1.7, CHCl₃). ¹H NMR (250 MHz) δ : 7.37–7.19 (m, 15H), 4.97 (d, *J* = 11.7 Hz, 1H), 4.64 (bs, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 11.8 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.44 (d, *J* = 11.8 Hz, 1H), 3.96 (t, *J* = 6.3 Hz, 1H), 3.85 (m, 2H), 3.66 (d, *J* = 6.3 Hz, 2H), 3.33 (s, 3H), 2.27 (m, 1H), 1.26 (d, *J* = 7.4 Hz, 3H). ¹³C NMR (62.5 MHz) δ : 139.1, 138.6, 138.1, 128.2, 128.0, 127.5, 127.5, 127.4, 127.2, 127.0, 126.9, 103.7 (*J* = 171.1 Hz), 76.2, 74.5, 74.0, 73.3, 70.0, 69.6, 69.6, 54.7, 36.2, 12.4. Anal. Calcd for C₂₉H₃₄O₅: C, 75.30; H, 7.41. Found: C, 75.25; H, 7.41.

Allyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methyl- α -D-talopyranoside (13). *R*_f = 0.54. α -Anomer. ¹H NMR (500 MHz) δ : 7.37–7.21 (m, 15H), 5.91 (m, 1H), 5.24 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.16 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.96 (d, *J* = 11.8 Hz, 1H), 4.81 (s, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.55 (d, *J* = 11.8 Hz, 1H), 4.53 (d, *J* = 11.3 Hz, 2H), 4.45 (d, *J* = 11.8 Hz, 1H), 4.16 (ddt, *J* = 13.0, 5.2, 1.5 Hz, 1H), 4.01 (dt, *J* = 6.1, 1.5 Hz, 1H), 3.97 (dd, *J* = 13.0, 6.1 Hz, 1H), 3.89 (dd, *J* = 5.2, 3.0 Hz, 1H), 3.86 (m, 1H), 3.69–3.63 (m, 2H), 2.31 (m, 1H), 1.26 (d, *J* = 7.4 Hz, 3H). ¹³C NMR (125 MHz) δ : 139.2, 138.7, 138.2, 134.2, 128.2, 128.0, 127.7, 127.5, 127.5, 127.3, 127.1, 127.0, 117.0, 101.9 (*J* = 166.9 Hz), 76.3, 74.7, 74.0, 73.3, 70.1, 69.8, 69.6, 67.8, 36.3, 12.5. β -Anomer. ¹³C NMR (125 MHz) δ : 101.6 (*J* = 156.4 Hz). Anal. Calcd for C₃₁H₃₆O₅: C, 76.20; H, 7.43. Found: C, 76.45; H, 7.40.

Benzyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methyl- α -D-talopyranoside (14). *R*_f = 0.62. [α]_D²⁵ +34.5 (c 2.9, CHCl₃). ¹H NMR (500 MHz) δ : 7.36–7.17 (m, 20H), 4.97 (d, *J* = 11.8 Hz, 1H), 4.85 (s, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.56 (bd, *J* = 12.0 Hz, 3H), 4.49 (d, *J* = 11.8 Hz, 1H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.07 (dt, *J* = 6.3, 1.6 Hz, 1H), 3.93 (dd, *J* = 5.3, 3.0 Hz, 1H), 3.90 (bs, 1H), 3.68 (m, 2H), 2.35 (m, 1H), 1.27 (d, *J* = 7.4 Hz, 3H). ¹³C NMR (62.5 MHz) δ : 139.3, 138.8, 138.2, 137.9, 128.3, 128.1, 127.9, 127.7, 127.6, 127.3, 127.2, 127.1, 102.0 (*J* = 163.8 Hz), 76.4, 74.7, 74.1, 73.4, 70.2, 70.1, 69.7, 68.9, 36.3, 12.6. Anal. Calcd for C₃₅H₃₈O₅: C, 78.04; H, 7.11. Found: C, 78.19; H, 7.38.

Methyl 3,4-Di-*O*-benzyl-2-deoxy-2-*C*-methyl- α -D-rhamnopyranoside (15). *R*_f = 0.58. α -Anomer. ¹H NMR (250 MHz) δ : 7.38–7.21 (m, 10H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.58 (d, *J* = 10.9 Hz, 1H), 4.52 (d, *J* = 11.5 Hz, 1H), 4.49 (bs, 1H), 3.95 (dd, *J* = 9.3, 5.1 Hz, 1H), 3.68 (m, 1H), 3.28 (t, *J* = 9.3 Hz, 1H), 3.30 (s, 3H), 2.38 (m, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.06 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (62.5 MHz) δ : 138.6, 138.6, 128.2, 128.2, 127.9, 127.8, 127.5, 127.4, 127.4, 127.3, 102.9 (*J* = 165.8 Hz), 80.0, 79.9, 74.9,

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70.8, 67.2, 54.4, 36.7, 18.1, 11.2. β -Anomer. ^{13}C NMR (62.5 MHz) δ : 102.6 ($J = 154.5$ Hz). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{O}_4$: C, 74.13; H, 7.92. Found: C, 73.91; H, 8.11.

Allyl 3,4-Di-O-benzyl-2-deoxy-2-C-methyl-L-rhamnopyranoside (16). $R_f = 0.58$. α -Anomer. ^1H NMR (500 MHz) δ : 7.37–7.25 (m, 10H), 5.91 (m, 1H), 5.27 (dq, $J = 17.4$, 1.4 Hz, 1H), 5.16 (dq, $J = 10.3$, 1.4 Hz, 1H), 4.91 (d, $J = 10.9$ Hz, 1H), 4.65 (s, 1H), 4.64 (d, $J = 11.5$ Hz, 1H), 4.59 (d, $J = 10.9$ Hz, 1H), 4.55 (d, $J = 11.5$ Hz, 1H), 4.11 (ddt, $J = 12.9$, 5.1, 1.3 Hz, 1H), 4.01 (dd, $J = 9.0$, 5.4 Hz, 1H), 3.92 (ddt, $J = 12.9$, 6.1, 1.3 Hz, 1H), 3.73 (m, 1H), 3.29 (t, $J = 9.3$ Hz, 1H), 2.42 (m, 1H), 1.29 (d, $J = 6.2$ Hz, 3H), 1.07 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (62.5 MHz) δ : 138.7, 138.5, 134.1, 128.2, 127.9, 127.5, 127.3, 116.8, 101.0 ($J = 166.1$ Hz), 80.1, 79.4, 75.0, 70.9, 67.5, 67.5, 36.7, 18.1, 11.2. β -Anomer. ^{13}C NMR (62.5 MHz) δ : 100.5 ($J = 154.7$ Hz). Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{O}_4$: C, 75.36; H, 7.91. Found: C, 75.49; H, 8.16.

Benzyl 3,4-Di-O-benzyl-2-deoxy-2-C-methyl-L-rhamnopyranoside (17). $R_f = 0.67$. α -Anomer. ^1H NMR (250 MHz) δ : 7.37–7.26 (m, 15H), 4.90 (d, $J = 10.8$ Hz, 1H), 4.67 (d, $J = 11.8$ Hz, 1H), 4.66 (d, $J = 11.8$ Hz, 1H), 4.60 (s, 1H), 4.59 (d, $J = 10.8$ Hz, 1H), 4.54 (d, $J = 11.8$ Hz, 1H), 4.42 (d, $J = 11.8$ Hz, 1H), 4.03 (dd, $J = 9.2$, 5.2 Hz, 1H), 3.78 (m, 1H), 3.31 (t, $J = 9.2$ Hz, 1H), 2.44 (m, 1H), 1.30 (d, $J = 6.2$ Hz, 3H), 1.06 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (62.5 MHz) δ : 138.6, 138.5, 137.7, 128.2, 127.9, 127.7, 127.6, 127.5, 127.3, 101.2 ($J = 165.6$ Hz), 80.1, 79.4, 75.0, 70.9, 68.6, 67.6, 36.8, 18.2, 11.2. β -Anomer. ^{13}C NMR (62.5 MHz) δ : 100.2 ($J = 155.9$ Hz). Anal. Calcd for $\text{C}_{28}\text{H}_{32}\text{O}_4$: C, 77.75; H, 7.46. Found: C, 77.67; H, 7.36.

Methyl 3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl-D-glucopyranoside (18). $R_f = 0.41$. α -Anomer. ^1H NMR (250 MHz) δ : 7.35–7.13 (m, 15H), 4.83 (d, $J = 11.2$ Hz, 1H), 4.79 (d, $J = 12.5$ Hz, 1H), 4.63 (d, $J = 12.5$ Hz, 1H), 4.62 (d, $J = 11.0$ Hz, 1H), 4.55 (d, $J = 3.4$ Hz, 1H), 4.51 (d, $J = 11.3$ Hz, 2H), 3.78–3.58 (m, 5H), 3.32 (s, 3H), 1.92 (m, 1H), 1.03 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (62.5 MHz) δ : 139.7, 138.4, 138.2, 128.3, 127.8, 127.7, 127.6, 102.0 ($J = 165.7$ Hz), 82.6, 79.5, 75.3, 74.7, 73.5, 70.9, 69.0, 54.9, 41.3, 12.6. β -Anomer. ^{13}C NMR (125 MHz) δ : 100.2 ($J = 160.7$ Hz). Anal. Calcd for $\text{C}_{29}\text{H}_{34}\text{O}_5$: C, 75.30; H, 7.41. Found: C, 75.45; H, 7.28.

Benzyl 3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl-D-glucopyranoside (19). $R_f = 0.53$. α -Anomer. ^1H NMR (500 MHz) δ : 7.37–7.20 (m, 20H), 4.86 (d, $J = 10.9$ Hz, 1H), 4.81 (d, $J = 10.9$ Hz, 1H), 4.78 (d, $J = 3.4$ Hz, 1H), 4.70 (d, $J = 12.1$ Hz, 1H), 4.66 (d, $J = 12.1$ Hz, 1H), 4.65 (d, $J = 10.9$ Hz, 1H), 4.53 (d, $J = 12.1$ Hz, 1H), 4.52 (d, $J = 10.9$ Hz, 1H), 4.46 (d, $J = 12.1$ Hz, 1H), 3.87 (m, 1H), 3.76 (dd, $J = 10.6$, 4.0 Hz, 1H), 3.67 (m, 3H), 1.97 (m, 1H), 1.08 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (125 MHz) δ : 138.7, 138.4, 138.1, 137.9, 128.4, 128.3, 128.3, 127.8, 127.8, 127.7, 127.6, 127.5, 100.2 ($J = 166.0$ Hz), 82.7, 79.5, 75.4, 74.8, 73.5, 71.3, 68.9, 68.9, 41.3, 12.7. β -Anomer. ^{13}C NMR (125 MHz) δ : 103.3 ($J = 158.0$ Hz). Anal. Calcd for $\text{C}_{35}\text{H}_{38}\text{O}_5$: C, 78.04; H, 7.11. Found: C, 77.80; H, 6.90.

Allyl 3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl-D-galactopyranoside (20). $R_f = 0.48$. α -Anomer. ^1H NMR (500 MHz) δ : 7.37–7.21 (m, 15H), 5.87 (m, 1H), 5.25 (dq, $J = 10.5$, 1.6 Hz, 1H), 5.14 (dq, $J = 17.2$, 1.6 Hz, 1H), 4.89 (d, $J = 11.6$ Hz, 1H), 4.75 (d, $J = 3.5$ Hz, 1H), 4.70 (d, $J = 11.6$ Hz, 1H), 4.57 (d, $J = 11.6$ Hz, 1H), 4.51 (d, $J = 11.8$ Hz, 1H), 4.50 (d, $J = 11.6$ Hz, 1H), 4.43 (d, $J = 11.8$ Hz, 1H), 4.13 (ddt, $J = 13.3$, 5.0, 1.5 Hz, 1H), 3.93 (m, 2H), 3.63–3.55 (m, 4H), 2.44 (m, 1H), 1.05 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (125 MHz) δ : 138.8, 138.3, 138.0, 134.4, 128.3, 128.1, 128.0, 127.7, 127.6, 127.5, 127.3, 116.5, 100.4 ($J = 167.2$ Hz), 79.9, 74.3, 73.4, 72.2, 71.7, 69.7, 69.5, 67.9, 35.3, 12.5. β -Anomer. ^{13}C NMR (125 MHz) δ : 103.9 ($J = 156.6$ Hz). Anal. Calcd for $\text{C}_{31}\text{H}_{36}\text{O}_5$: C, 76.20; H, 7.43. Found: C, 76.30; H, 7.20.

Benzyl 3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl-D-galactopyranoside (21). $R_f = 0.48$. α -Anomer. $[\alpha]_D^{25} + 99.0$ (c 1.9, CHCl_3). ^1H NMR (250 MHz) δ : 7.37–7.22 (m, 20H), 4.89 (d, $J = 11.6$ Hz, 1H), 4.80 (d, $J = 3.5$ Hz, 1H), 4.70 (d, $J = 11.6$ Hz, 1H), 4.68 (d, $J = 12.2$ Hz, 1H), 4.57 (d, $J = 11.6$ Hz, 1H), 4.51 (d, $J = 11.8$ Hz, 1H), 4.49 (d, $J = 11.6$ Hz, 1H), 4.45 (d, $J = 12.2$ Hz, 1H), 4.43 (d, $J = 11.8$ Hz, 1H), 3.99 (d, $J = 6.2$ Hz, 1H), 3.94 (d, $J = 6.2$ Hz, 1H), 3.66–3.53 (m, 3H), 2.45 (m, 1H), 1.06 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (62.5 MHz) δ : 138.7, 138.2, 137.9, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7,

127.6, 127.5, 127.5, 127.4, 127.3, 127.3, 100.3 ($J = 166.9$ Hz), 79.8, 74.2, 73.3, 72.1, 71.6, 69.8, 69.4, 68.8, 35.3, 12.5. β -Anomer. ^{13}C NMR (62.5 MHz) δ : 103.7 ($J = 158.2$ Hz). Anal. Calcd for $\text{C}_{35}\text{H}_{38}\text{O}_5$: C, 78.04; H, 7.11. Found: C, 78.02; H, 7.06.

3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl-D-mannopyranose (22). $R_f = 0.05$. α -Anomer. ^1H NMR (200 MHz) δ : 7.40–7.12 (m, 15H), 5.15 (d, $J = 2$ Hz, 1H), 4.85 (d, $J = 12$ Hz, 2H), 4.67–4.40 (m, 5H), 4.14–3.98 (m, 2H), 3.71–3.59 (m, 3H), 2.41 (m, 1H), 1.06 (d, $J = 8$ Hz, 3H). ^{13}C NMR (50 MHz) δ : 138.6, 138.4, 137.9, 128.7, 128.2, 127.8, 127.5, 96.4 ($J = 167$ Hz), 79.1, 74.6, 74.4, 73.1, 70.9, 70.9, 69.4, 36.7, 11.2. Data are in accordance with literature values.^{10c}

3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl-D-talopyranose (23). $R_f = 0.05$. $[\alpha]_D^{25} + 1.4$ (c 0.6, CHCl_3). α -Anomer. ^1H NMR (200 MHz) δ : 7.41–7.20 (m, 15H), 5.17 (bs, 1H), 4.93 (d, $J = 12$ Hz, 1H), 4.78–4.39 (m, 5H), 4.24 (m, 1H), 3.89 (dd, $J = 5$, 3 Hz, 1H), 3.83–3.53 (m, 3H), 2.67 (d, $J = 3$ Hz, 1H), 2.26 (m, 1H), 1.24 (d, $J = 7$ Hz, 3H). ^{13}C NMR (50 MHz) δ : 139.0, 138.7, 137.8, 128.2, 128.0, 127.9, 127.6, 127.3, 127.1, 127.0, 96.9 ($J = 167$ Hz), 76.0, 74.9, 73.7, 73.2, 70.3, 70.0, 69.9, 36.5, 12.4. β -Anomer. ^{13}C NMR (50 MHz) δ : 96.3 ($J = 159.2$ Hz). Anal. Calcd for $\text{C}_{28}\text{H}_{32}\text{O}_5$: C, 74.98; H, 7.19. Found: C, 74.66; H, 7.57.

3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl-D-glucopyranose (24). $R_f = 0.06$. $[\alpha]_D^{25} + 72.4$ (c 0.9, CHCl_3). Mp 89–90 °C (hexane/EtOAc). α -Anomer. ^1H NMR (200 MHz) δ : 7.50–7.11 (m, 15H), 5.13 (bs, 1H), 4.87 (d, $J = 11$ Hz, 1H), 4.82 (d, $J = 11$ Hz, 1H), 4.71–4.45 (m, 4H), 4.08 (m, 1H), 3.76–3.47 (m, 4H), 2.72 (bs, 1H), 1.91 (m, 1H), 1.08 (d, $J = 6$ Hz, 3H). ^{13}C NMR (50 MHz) δ : 138.1, 128.3, 127.8, 127.6, 95.2 ($J = 163.8$ Hz), 82.0, 79.7, 75.3, 74.7, 73.3, 70.8, 69.1, 41.3, 12.8. Anal. Calcd for $\text{C}_{28}\text{H}_{32}\text{O}_5$: C, 74.98; H, 7.19. Found: C, 74.69; H, 7.22.

3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl-D-galactopyranose (25). $R_f = 0.05$. $[\alpha]_D^{25} + 57.7$ (c 0.5, CHCl_3). Mp 112–113 °C (hexane/EtOAc). α -Anomer. ^1H NMR (200 MHz) δ : 7.39–7.21 (m, 15H), 5.17 (t, $J = 4$ Hz, 1H), 4.88 (d, $J = 11$ Hz, 2H), 4.70 (d, $J = 11$ Hz, 2H), 4.62–4.28 (m, 2H), 4.15 (t, $J = 6$ Hz, 1H), 3.85 (bs, 1H), 3.66–3.41 (m, 2H), 3.08 (m, 1H), 2.74 (bs, 1H), 2.42 (m, 1H), 1.05 (d, $J = 7$ Hz, 3H). ^{13}C NMR (50 MHz) δ : 138.6, 138.3, 137.8, 128.3, 128.1, 128.0, 127.7, 127.5, 95.6 ($J = 171.4$ Hz), 79.4, 74.2, 73.4, 72.3, 71.8, 70.0, 69.7, 35.3, 12.7. β -Anomer. ^{13}C NMR (50 MHz) δ : 99.4 ($J = 164.1$ Hz). Anal. Calcd for $\text{C}_{28}\text{H}_{32}\text{O}_5$: C, 74.98; H, 7.19. Found: C, 74.43; H, 7.37.

Methyl 2,3,4-Tri-O-benzyl-6-O-(3,4,6-tri-O-benzyl-2-deoxy-2-C-methyl- α -D-mannopyranosyl)- α -D-glucopyranoside (32). $R_f = 0.13$. $[\alpha]_D^{25} + 48.4$ (c 0.3, CHCl_3). ^1H NMR (500 MHz) δ : 7.45–7.10 (m, 30H), 4.99 (d, $J = 10.8$ Hz, 1H), 4.91 (d, $J = 11.1$ Hz, 1H), 4.84 (d, $J = 11.1$ Hz, 1H), 4.81 (d, $J = 10.8$ Hz, 1H), 4.79 (d, $J = 12.1$ Hz, 1H), 4.77 (s, 1H), 4.69 (d, $J = 12.1$ Hz, 1H), 4.63 (d, $J = 11.7$ Hz, 1H), 4.62 (s, 1H), 4.58 (d, $J = 12.2$ Hz, 1H), 4.55 (d, $J = 11.1$ Hz, 1H), 4.53 (d, $J = 11.7$ Hz, 1H), 4.41 (d, $J = 11.1$ Hz, 1H), 4.38 (d, $J = 12.2$ Hz, 1H), 3.99 (m, 2H), 3.85 (dd, $J = 11.4$, 4.2 Hz, 1H), 3.73 (m, 2H), 3.64 (m, 1H), 3.59 (m, 2H), 3.52 (m, 3H), 3.35 (s, 3H), 2.43 (m, 1H), 1.06 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (62.5 MHz) δ : 138.8, 138.7, 138.5, 138.3, 138.3, 138.1, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 102.4 ($J = 169.2$ Hz), 97.9 ($J = 171.0$ Hz), 82.2, 80.0, 79.2, 77.6, 77.2, 75.8, 74.9, 74.7, 74.0, 73.2, 71.4, 70.9, 69.7, 69.0, 65.7, 55.1, 36.5, 11.1. Anal. Calcd for $\text{C}_{56}\text{H}_{62}\text{O}_{10}$: C, 75.14; H, 6.98. Found: C, 74.92; H, 6.75.

Methyl 2,3,6-Tri-O-benzyl-4-O-(3,4,6-tri-O-benzyl-2-deoxy-2-C-methyl- α -D-mannopyranosyl)- α -D-glucopyranoside (33). $R_f = 0.26$. $[\alpha]_D^{25} + 33.1$ (c 2.1, CHCl_3). ^1H NMR (500 MHz) δ : 7.33–7.16 (m, 30H), 5.10 (d, $J = 1.6$ Hz, 1H), 5.06 (d, $J = 11.3$ Hz, 1H), 4.79 (d, $J = 10.9$ Hz, 1H), 4.71 (d, $J = 12.1$ Hz, 1H), 4.61 (d, $J = 3.6$ Hz, 1H), 4.60 (d, $J = 12.2$ Hz, 1H), 4.60 (d, $J = 11.3$ Hz, 1H), 4.55 (d, $J = 12.1$ Hz, 1H), 4.53 (d, $J = 12.1$ Hz, 1H), 4.46 (s, 2H), 4.44 (d, $J = 12.1$ Hz, 1H), 4.41 (d, $J = 10.9$ Hz, 1H), 4.36 (d, $J = 12.2$ Hz, 1H), 3.89–3.84 (m, 2H), 3.72–3.64 (m, 6H), 3.58 (dd, $J = 10.5$, 3.0 Hz, 1H), 3.52 (dd, $J = 9.7$, 3.5 Hz, 1H), 3.44 (d, $J = 10.1$ Hz, 1H), 3.39 (s, 3H), 2.22 (m, 1H), 0.81 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (125 MHz) δ : 138.7, 138.6, 138.3, 137.9, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 127.4, 127.3, 127.1, 104.2 ($J = 169.9$ Hz), 97.6

($J = 167.7$ Hz), 82.1, 80.1, 79.4, 76.7, 75.3, 74.6, 74.0, 73.3, 73.2, 73.1, 72.3, 71.0, 69.8, 69.5, 69.1, 55.2, 37.4, 11.2. Anal. Calcd for $C_{56}H_{62}O_{10}$: C, 75.14; H, 6.98. Found: C, 75.40; H, 7.07.

Methyl 2,3,4-Tri-O-benzyl-6-O-(3,4-di-O-benzyl-2-deoxy-2-C-methyl- α -L-rhamnopyranosyl)- α -D-glucopyranoside (34). $R_f = 0.29$. [α] $^{25}_D -1.79$ (c 1.8, $CHCl_3$). 1H NMR (500 MHz) δ : 7.24–7.39 (m, 25H), 5.00 (d, $J = 10.9$ Hz, 1H), 4.90 (d, $J = 10.5$ Hz, 1H), 4.87 (d, $J = 10.5$ Hz, 1H), 4.82 (d, $J = 10.5$ Hz, 1H), 4.79 (d, $J = 11.6$ Hz, 1H), 4.68 (d, $J = 12.1$ Hz, 1H), 4.60 (d, $J = 12.1$ Hz, 1H), 4.59 (s, 1H), 4.59 (d, $J = 10.5$ Hz, 1H), 4.54 (d, $J = 11.6$ Hz, 1H), 4.53 (d, $J = 10.9$ Hz, 1H), 4.49 (bs, 1H), 3.99 (t, $J = 9.2$ Hz, 1H), 3.93 (dd, $J = 9.2$, 5.3 Hz, 1H), 3.81 (dd, $J = 10.7$, 1.6 Hz, 1H), 3.71–3.75 (m, 2H), 3.51 (dd, $J = 9.6$, 3.6 Hz, 1H), 3.44 (t, $J = 9.6$ Hz, 1H), 3.43 (dd, $J = 10.7$, 5.5 Hz, 1H), 3.34 (s, 3H), 3.26 (t, $J = 9.2$ Hz, 1H), 2.28 (m, 1H), 1.25 (d, $J = 6.2$ Hz, 3H), 1.02 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (125 MHz) δ : 138.6, 138.6, 138.2, 138.1, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.6, 127.5, 127.4, 102.1 ($J = 166$ Hz), 97.7 ($J = 168$ Hz), 82.0, 80.2, 80.0, 79.0, 77.9, 75.7, 75.1, 74.9, 73.2, 71.0, 69.8, 67.5, 65.9, 54.9, 36.9, 18.1, 11.2. Anal. Calcd for $C_{49}H_{56}O_9$: C, 74.60; H, 7.15. Found: C, 74.30; H, 7.09.

Methyl 2,3,4-Tri-O-benzyl-6-O-(3,4,6-tri-O-benzyl-2-deoxy-2-C-methyl-D-glucopyranosyl)- α -D-glucopyranoside (35). $R_f = 0.19$. α -Anomer. [α] $^{25}_D +79.6$ (c 1.3, $CHCl_3$). Mp 88–89 °C (hexane/EtOAc). 1H NMR (500 MHz) δ : 7.37–7.14 (m, 30H), 4.97 (d, $J = 10.8$ Hz, 1H), 4.91 (d, $J = 11.0$ Hz, 1H), 4.75–4.85 (m, 5H), 4.68–4.57 (m, 5H), 4.50 (d, $J = 11.0$ Hz, 1H), 4.45 (d, $J = 12.1$ Hz, 1H), 3.99 (t, $J = 9.3$ Hz, 1H), 3.79–3.56 (m, 8H), 3.49 (dd, $J = 9.6$, 2.8 Hz, 1H), 3.47 (dd, $J = 9.6$, 2.8 Hz, 1H), 3.35 (s, 3H), 1.90 (m, 1H), 1.01 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (125 MHz) δ : 138.7, 138.6, 138.5, 138.2, 138.1, 138.1, 128.4, 128.4, 128.3, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 101.3 ($J = 169.0$ Hz), 97.8 ($J = 168.0$ Hz), 82.4, 82.1, 80.2, 79.4, 78.0, 75.8, 75.2, 75.0, 74.7, 73.4, 73.3, 71.1, 70.2, 68.8, 65.8, 55.0, 41.2, 12.9. Anal. Calcd for $C_{56}H_{62}O_{10}$: C, 75.14; H, 6.98. Found: C, 74.92; H, 6.93. β -Anomer. [α] $^{25}_D +13.2$ (c 1.3, $CHCl_3$). Mp 172–174 °C (hexane/EtOAc). 1H NMR (500 MHz) δ : 7.36–7.18 (m, 30H), 4.97 (d, $J = 10.8$ Hz, 1H), 4.90 (d, $J = 11.1$ Hz, 1H), 4.85 (d, $J = 11.0$ Hz, 1H), 4.79 (d, $J = 10.8$ Hz, 1H), 4.78 (d, $J = 11.5$ Hz, 2H), 4.65 (d, $J = 12.2$ Hz, 1H), 4.63–4.53 (m, 7H), 4.14 (dd, $J = 10.8$, 1.8 Hz, 1H), 4.05 (d, $J = 8.6$ Hz, 1H), 3.99 (t, $J = 9.3$ Hz, 1H), 3.77 (m, 1H), 3.74 (dd, $J = 10.8$, 2.8 Hz, 1H), 3.68 (dd, $J = 5.0$, 10.8 Hz, 1H), 3.64 (dd, $J = 10.8$, 4.2 Hz, 1H), 3.57–3.51 (m, 2H), 3.44 (m, 1H), 3.37 (s, 3H), 3.20 (dd, $J = 10.7$, 8.9 Hz, 1H); 1.85 (m, 1H), 1.04 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (125 MHz) δ : 138.7, 138.4, 138.2, 128.4, 128.3, 128.1, 128.1, 127.9, 127.9, 127.7, 127.7, 127.6, 127.6, 127.5, 104.8 ($J = 156.0$ Hz), 98.1 ($J = 165.0$ Hz), 85.1, 82.2, 79.8, 79.3, 77.8, 75.8, 75.4, 75.1, 74.9, 74.7, 73.4, 73.4, 69.8, 69.3, 67.8, 55.1, 42.5, 12.7. Anal. Calcd for $C_{56}H_{62}O_{10}$: C, 75.14; H, 6.98. Found: C, 75.34; H, 7.05.

Phenyl 3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl-D-mannopyranoside (36). $R_f = 0.51$. α -Anomer. 1H NMR (500 MHz) δ : 7.42–7.00 (m, 20H), 5.47 (d, $J = 1.3$ Hz, 1H), 4.87 (d, $J = 10.8$ Hz, 1H), 4.72 (d, $J = 11.6$ Hz, 1H), 4.65 (d, $J = 11.6$ Hz, 1H), 4.63 (d, $J = 12.0$ Hz, 1H), 4.48 (d, $J = 10.8$ Hz, 1H), 4.42 (d, $J = 12.0$ Hz, 1H), 4.23 (dd, $J = 8.5$, 5.2 Hz, 1H), 3.92–3.82 (m, 2H), 3.76 (dd, $J = 10.8$, 3.6 Hz, 1H), 3.62 (dd, $J = 10.8$, 1.8 Hz, 1H), 2.61 (m, 1H), 1.19 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (125 MHz) δ : 156.5, 138.6, 138.4, 138.1, 129.3, 128.3, 128.2, 128.2, 127.9, 127.8, 127.6, 127.6, 127.5, 127.5, 127.4, 121.8, 116.3, 100.1 ($J = 168.0$ Hz), 79.4, 74.8, 73.9, 73.2, 71.8, 71.2, 68.8, 36.8, 11.1. β -Anomer. ^{13}C NMR (125 MHz) δ : 99.6 ($J = 158.0$ Hz). Anal. Calcd for $C_{34}H_{36}O_5$: C, 77.84; H, 6.92. Found: C, 78.08; H, 7.21.

p-Methoxyphenyl 3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl- α -D-mannopyranoside (37). $R_f = 0.41$. [α] $^{25}_D +95.1$ (c 1.7, $CHCl_3$). 1H NMR (500 MHz) δ : 7.41–7.17 (m, 15H), 7.01 (d, $J = 9.1$ Hz, 2H), 6.79 (d, $J = 9.1$ Hz, 2H), 5.35 (d, $J = 1.1$ Hz, 1H), 4.87 (d, $J = 10.8$ Hz, 1H), 4.71 (d, $J = 11.5$ Hz, 1H), 4.63 (d, $J = 11.5$ Hz, 1H), 4.62 (d, $J = 12.0$ Hz, 1H), 4.48 (d, $J = 10.8$ Hz, 1H), 4.43 (d, $J = 12.0$ Hz, 1H), 4.21 (dd, $J = 8.4$, 5.2 Hz, 1H), 3.87 (m, 2H), 3.77 (dd, $J = 10.8$, 3.7 Hz, 1H), 3.76 (s, 3H), 3.64 (dd, $J = 10.8$, 1.7 Hz, 1H), 2.60 (m, 1H), 1.18 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (62 MHz) δ : 154.7, 150.6, 138.7, 138.6, 138.3, 128.4, 128.3, 128.3, 127.9, 127.7, 127.6, 127.5,

117.7, 114.5, 101.1 ($J = 167$ Hz), 79.5, 74.9, 74.1, 73.3, 71.8, 71.3, 69.1, 55.6, 37.0, 11.2. Anal. Calcd for $C_{35}H_{38}O_6$: C, 75.79; H, 6.90. Found: C, 75.55; H, 6.81.

2-(3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl- β -D-mannopyranosyl)-3,5-dimethoxyphenol (38). $R_f = 0.32$. [α] $^{25}_D +18.8$ (c 2.1, $CHCl_3$). 1H NMR (250 MHz) δ : 8.90 (s, 1H), 7.40–7.21 (m, 15H), 6.09 (d, $J = 2.3$ Hz, 1H), 6.00 (d, $J = 2.3$ Hz, 1H), 5.06 (d, $J = 2.2$ Hz, 1H), 4.92 (d, $J = 10.9$ Hz, 1H), 4.70 (d, $J = 11.6$ Hz, 1H), 4.61 (d, $J = 12.0$ Hz, 1H), 4.59 (d, $J = 11.6$ Hz, 1H), 4.50 (d, $J = 10.9$ Hz, 1H), 4.47 (d, $J = 12.0$ Hz, 1H), 3.93 (t, $J = 9.5$ Hz, 1H), 3.82 (dd, $J = 9.5$, 4.8 Hz, 1H), 3.77 (s, 3H), 3.75 (m, 1H), 3.74 (s, 3H), 3.69 (dd, $J = 10.3$, 2.4 Hz, 1H), 3.51 (dd, $J = 9.5$, 2.4 Hz, 1H), 2.50 (m, 1H), 1.01 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (62.5 MHz) δ : 160.4, 158.1, 156.6, 138.4, 137.9, 128.3, 128.2, 127.9, 127.7, 127.5, 127.4, 103.8, 94.1, 90.4, 83.2, 79.1, 78.2, 75.0, 73.2, 73.1, 70.6, 68.2, 55.3, 55.1, 36.7, 6.9. Stereochemistry at C-1 was assigned by NOE experiment. NOE's were observed between H-1 and H-3 as well as H-1 and H-5. Anal. Calcd for $C_{36}H_{40}O_7$: C, 73.95; H, 6.90. Found: C, 74.10; H, 7.05.

2-(3,4,6-Tri-O-benzyl-2-deoxy-2-C-methyl-D-mannopyranosyl)-3,4,5-trimethoxyphenol (39). α -Anomer. $R_f = 0.23$. [α] $^{25}_D -13.8$ (c 1.4, $CHCl_3$). 1H NMR (500 MHz) δ : 8.01 (s, 1H, exchanges with D_2O), 7.39–7.23 (m, 15H), 6.27 (s, 1H), 5.11 (d, $J = 11.1$ Hz, 1H), 4.65 (d, $J = 12.1$ Hz, 1H), 4.53 (d, $J = 11.7$ Hz, 1H), 4.53 (d, $J = 11.1$ Hz, 1H), 4.52 (s, 1H), 4.48 (d, $J = 12.1$ Hz, 1H), 4.43 (d, $J = 11.7$ Hz, 1H), 4.39 (t, $J = 6.8$ Hz, 1H), 4.03 (dd, $J = 10.1$, 7.6 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.78 (m, 1H), 3.77 (s, 3H), 3.66 (dd, $J = 3.2$, 0.7 Hz, 1H), 3.61 (t, $J = 2.6$ Hz, 1H), 2.58 (m, 1H), 0.78 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz) δ : 153.4, 152.6, 151.2, 138.1, 137.9, 137.9, 134.7, 128.4, 128.2, 127.6, 127.5, 127.5, 127.4, 110.5, 97.0, 76.7, 75.1, 73.2, 72.7, 71.4, 71.2, 68.7, 67.1, 60.9, 60.8, 55.7, 33.0, 13.5. Anal. Calcd for $C_{37}H_{42}O_8$: C, 72.29; H, 6.89. Found: C, 72.07; H, 6.76. β -Anomer. $R_f = 0.27$. [α] $^{25}_D +18.9$ (c 5.2, $CHCl_3$). 1H NMR (500 MHz) δ : 8.55 (s, 1H, exchanges with D_2O), 7.30–7.12 (m, 15H), 6.14 (s, 1H), 4.90 (d, $J = 2.2$ Hz, 1H), 4.83 (d, $J = 10.9$ Hz, 1H), 4.62 (d, $J = 11.6$ Hz, 1H), 4.50 (d, $J = 12.1$ Hz, 1H), 4.50 (d, $J = 11.6$ Hz, 1H), 4.41 (d, $J = 10.9$ Hz, 1H), 4.37 (d, $J = 12.1$ Hz, 1H), 3.82 (t, $J = 9.4$ Hz, 1H), 3.77 (s, 3H), 3.74 (dd, $J = 9.4$, 4.9 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.63 (dd, $J = 10.3$, 3.0 Hz, 1H), 3.59 (dd, $J = 10.3$, 2.2 Hz, 1H), 3.43 (dt, $J = 9.4$, 2.6 Hz, 1H), 2.39 (m, 1H), 0.92 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (125 MHz) δ : 153.2, 152.7, 149.6, 138.3, 138.3, 137.9, 134.6, 128.3, 128.2, 128.2, 127.8, 127.5, 127.5, 127.4, 107.9, 96.6, 83.2, 79.1, 78.6, 75.0, 73.2, 73.0, 70.6, 68.2, 60.7, 60.7, 55.6, 37.9, 6.7. Stereochemistry at C-1 for this β -anomer has been assigned by NOE experiment. NOE's were observed between H-1 and H-3 as well as between H-1 and H-5. Anal. Calcd for $C_{37}H_{42}O_8$: C, 72.29; H, 6.89. Found: C, 72.44; H, 7.06.

Benzyl 3,5-Di-O-benzyl-2-deoxy-2-C-(ethoxycarbonylmethyl)-D-xylofuranoside (41). The reaction was carried out in toluene at 70 °C for 1.5 h. α -Anomer. $R_f = 0.46$. [α] $^{25}_D +89.9$ (c 1.0, $CHCl_3$). 1H NMR (500 MHz) δ : 7.33–7.23 (m, 15H), 5.29 (d, $J = 5.1$ Hz, 1H), 4.75 (d, $J = 12.0$ Hz, 1H), 4.63 (d, $J = 12.0$ Hz, 1H), 4.53 (d, $J = 12.0$ Hz, 1H), 4.51 (bs, 2H), 4.45 (d, $J = 12.0$ Hz, 1H), 4.37 (dd, $J = 11.1$, 6.4 Hz, 1H), 4.05 (q, $J = 7.1$ Hz, 2H), 4.01 (t, $J = 6.4$ Hz, 1H), 3.75 (dd, $J = 10.4$, 4.7 Hz, 1H), 3.64 (dd, $J = 10.4$, 6.5 Hz, 1H), 2.75 (m, 1H), 2.65 (dd, $J = 16.4$, 10.0 Hz, 1H), 2.47 (dd, $J = 16.4$, 5.5 Hz, 1H), 1.18 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (62.5 MHz) δ : 172.2, 138.1, 138.0, 137.8, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 127.5, 127.4, 127.3, 101.7, 82.2, 77.2, 73.4, 72.7, 69.3, 69.2, 60.3, 45.8, 32.2, 14.0. Anal. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.24; H, 6.78. β -Anomer. $R_f = 0.29$. [α] $^{25}_D -55.2$ (c 1.1, $CHCl_3$). 1H NMR (500 MHz) δ : 7.33–7.21 (m, 15H), 4.94 (d, $J = 1.8$ Hz, 1H), 4.80 (d, $J = 12.0$ Hz, 1H), 4.65 (d, $J = 12.0$ Hz, 1H), 4.58 (d, $J = 12.0$ Hz, 1H), 4.52 (d, $J = 12.0$ Hz, 1H), 4.49 (d, $J = 12.0$ Hz, 1H), 4.48 (d, $J = 12.0$ Hz, 1H), 4.39 (bq, $J = 5.8$ Hz, 1H), 4.09 (q, $J = 7.1$ Hz, 2H), 3.90 (dd, $J = 5.8$, 3.0 Hz, 1H), 3.82 (dd, $J = 10.3$, 4.6 Hz, 1H), 3.76 (dd, $J = 10.3$, 7.2 Hz, 1H), 2.84 (m, 1H), 2.39 (dd, $J = 15.8$, 6.8 Hz, 1H), 2.29 (dd, $J = 15.8$, 8.7 Hz, 1H), 1.20 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 171.3, 138.2, 138.1, 138.0, 128.3, 128.2, 128.1, 127.7, 127.6, 127.5, 127.4, 127.3, 106.4, 81.8, 80.2, 73.4, 71.4, 70.1, 69.1, 60.6, 46.9, 34.7, 14.0. Stereochemistry at C-1 for this β -anomer has been assigned by NOE experiment. NOE's were observed between H-1

and H-3 as well as between H-1 and H-4. Anal. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.31; H, 6.88.

General Procedure for Ferrier-Type Rearrangement. The cyclopropane (500 mg, 1.16 mmol) and benzyl alcohol (240 μ L, 2.32 mmol) were dissolved in CH_2Cl_2 (5 mL) followed by addition of $PdCl_2 \cdot (PhCN)_2$ (44 mg, 0.118 mmol). The mixture was stirred at room temperature under an atmosphere of nitrogen for 48 h. After removal of the solvent in vacuo, the crude mixture was purified by flash chromatography.

Benzyl 4,6-Di-O-benzyl-2,3-dideoxy-2-C-methyl-D-erythro-hex-2-enopyranoside (45). $R_f = 0.49$. α -Anomer. 1H NMR (250 MHz) δ : 7.40–7.20 (m, 15H), 5.74 (bs, 1H), 4.89 (s, 1H), 4.82 (d, $J = 12.0$ Hz, 1H), 4.66–4.58 (m, 3H), 4.52 (d, $J = 12.2$ Hz, 1H), 4.43 (d, $J = 11.5$ Hz, 1H), 4.14 (d, $J = 9.4$ Hz, 1H), 3.99 (ddd, $J = 9.4, 4.2, 2.2$ Hz, 1H), 3.71 (dd, $J = 10.8, 4.2$ Hz, 1H), 3.66 (dd, $J = 10.8, 2.2$ Hz, 1H), 1.75 (s, 3H). ^{13}C NMR (62.5 MHz) δ : 138.2, 134.5, 128.2, 127.8, 127.7, 127.5, 127.4, 124.5, 96.8, 73.3, 70.8, 70.7, 69.9, 69.3, 68.9, 18.5. Anal. Calcd for $C_{28}H_{30}O_4$: C, 78.11; H, 7.02. Found: C, 77.99; H, 7.02.

Hydrogenation at room temperature and 1 atm over Pd/C in EtOAc containing 1 equiv of Et_3N gave **47** as the major product: $R_f = 0.49$. 1H NMR (500 MHz) δ : 7.39–7.22 (m, 15H), 4.75 (d, $J = 12.2$ Hz, 1H), 4.70 (d, $J = 3.2$ Hz, 1H), 4.67 (d, $J = 12.2$ Hz, 1H), 4.60 (d, $J = 11.4$ Hz, 1H), 4.55 (d, $J = 12.2$ Hz, 1H), 4.50 (d, $J = 12.2$ Hz, 1H), 4.40 (d, $J = 11.4$ Hz, 1H), 3.83–3.68 (m, 3H), 3.58 (ddd, $J = 11.0, 10.4, 4.7$ Hz, 1H), 2.00 (ddd, $J = 11.9, 4.7, 4.2$ Hz, 1H), 1.90 (m, 1H), 1.64 (dt, $J = 11.9, 11.0$ Hz, 1H), 0.97 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR

(62.5 MHz) δ : 138.4, 138.3, 138.1, 128.1, 128.1, 128.0, 127.6, 127.5, 127.4, 127.3, 127.3, 127.2, 98.8, 73.3, 72.9, 70.8, 70.5, 69.1, 68.4, 33.9, 32.0, 16.3.

Benzyl 4,6-Di-O-benzyl-2,3-dideoxy-2-C-methyl- α -D-threo-hex-2-enopyranoside (46). $R_f = 0.48$. $[\alpha]^{25}_D -45.7$ (c 0.6, $CHCl_3$). 1H NMR (250 MHz) δ : 7.40–7.23 (m, 15H), 5.81 (d, $J = 5.2$ Hz, 1H), 4.95 (s, 1H), 4.83 (d, $J = 11.8$ Hz, 1H), 4.66–4.58 (m, 4H), 4.53 (d, $J = 12.0$ Hz, 1H), 4.26 (ddd, $J = 6.8, 5.7, 2.6$ Hz, 1H), 3.82 (dd, $J = 10.0, 5.7$ Hz, 1H), 3.77–3.69 (m, 2H), 1.79 (s, 3H). ^{13}C NMR (62.5 MHz) δ : 138.6, 138.4, 138.0, 132.1, 128.3, 128.1, 127.7, 127.6, 127.5, 127.3, 121.7, 96.4, 73.4, 70.7, 69.7, 69.7, 69.4, 68.2, 19.2. Anal. Calcd for $C_{28}H_{30}O_4$: C, 78.11; H, 7.02. Found: C, 77.85; H, 7.18.

Hydrogenation as described above gave **48** as the major product: $R_f = 0.58$. 1H NMR (500 MHz) δ : 7.41–7.25 (m, 15H), 4.80 (d, $J = 11.8$ Hz, 1H), 4.68 (d, $J = 11.8$ Hz, 1H), 4.67 (d, $J = 2.5$ Hz, 1H), 4.62 (d, $J = 11.8$ Hz, 1H), 4.54 (d, $J = 11.8$ Hz, 1H), 4.53 (d, $J = 11.8$ Hz, 1H), 4.40 (d, $J = 11.8$ Hz, 1H), 4.18 (dt, $J = 6.0, 2.5$ Hz, 1H), 3.73 (dd, $J = 10.1, 5.8$ Hz, 1H), 3.71 (dd, $J = 10.1, 6.5$ Hz, 1H), 3.61 (bq, $J = 4.0$ Hz, 1H), 2.00 (dt, $J = 13.9, 4.7$ Hz, 1H), 1.85 (m, 1H), 1.78 (dt, $J = 13.9, 4.4$ Hz, 1H), 1.20 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (62.5 MHz) δ : 138.5, 138.4, 137.5, 128.0, 127.7, 127.5, 127.3, 127.2, 127.1, 101.1 ($J = 164.9$ Hz), 73.1, 72.0, 70.4, 69.6, 69.4, 68.6, 31.2, 27.7, 18.2.

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