# Synthesis of α- and *β*-*C*-Aryl Δ²-Glycopyranosides from *p*-*tert*-Butylphenyl Δ²-Glycopyranosides via Grignard Reagents

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Treatment of *p*-*tert*-butylphenyl 4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**1a**α) or the 4,6-di-*O*-(*tert*-butyldimethylsilyl) analogue (**1b**α) with various functionalized arylmagnesium bromides in the presence of a catalytic amount of $PdCl_2$(dppf) at 25 °C in THF afforded the corresponding unsaturated *C*-arylglycosides **2**−**14** having the α-configuration in quite good yields. Benzyl-, allyl-, and vinylmagnesium bromides gave also the corresponding unsaturated α-*C*-glycosides **15**−**18**, although in lower yields. When the same reaction was performed in the presence of $NiCl_2$(dppe) as the catalyst at −40 °C, only the formation of the corresponding unsaturated *C*-arylglycosides having the *β*-configuration was observed. As expected, reaction of phenylmagnesium bromide with *p*-*tert*-butylphenyl 4,6-di-*O*-benzyl-2,3-dideoxy-*β*-D-*erythro*-hex-2-enopyranoside (**1a***β*) in the presence of $NiCl_2$(dppe) gave only the unsaturated *β*-*C*-phenylglycoside **2a***β*, while palladium-catalyzed reaction led to the preponderant formation of *C*-phenylglycoside **2a**α. Reaction of PhMgBr with *p*-*tert*-butylphenyl 4-*O*-benzyl-2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranoside (**20**) afforded stereospecifically the unsaturated α- and *β*-*C*-phenylglycoside **25** in the presence of $PdCl_2$(dppf) and $NiCl_2$(dppe), respectively.

*C*-Arylglycosides have attracted considerable synthetic work during the past decade,[1] because of the antibiotic and/or antiviral activities of many products containing this structural unit. Such derivatives also constitute attractive intermediates for the construction of more complex and exciting targets. In particular, *C*-arylglycopyranosides with a double bond in the 2,3-position are versatile synthons, since this unsaturation can further be functionalized by epoxidation, hydroxylation, or hydroboration for the synthesis of natural products. The usual synthetic approaches to such unsaturated compounds involved palladium(II)-mediated arylation of glycals,[2] palladium(0)-catalyzed addition of arylzinc derivatives to hex-2-enopyranosides,[3] Lewis acid promoted reaction of phenols with glycals,[4] or addition of halogenomagnesium phenates to these glycals.[5] Although the chemical yields of these different methodologies are generally high, they actually suffer either from lack of selectivity or from the formation of one anomer only, the α derivative being generally preponderant.

As part of our interest in the field of organometallic-catalyzed functionalization at the anomeric center of carbohydrates,[6] we recently described the stereospecific palladium- and nickel-catalyzed access to unsaturated α- and *β*-*C*-arylglycopyranosides.[7] In this paper, we give a full account of the formation of these *C*-arylglycopyranosides.

## Results and Discussion

Transition-metal catalyzed substitution of allylic substrates with organometallic reagents is an important and well-documented carbon−carbon bond-forming reaction in organic synthesis.[8] These organometallic reagents mainly based on aluminum,[9] boron,[10] magnesium,[11] tin,[12]

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zinc,[13] and zirconium[14] are known to couple under very mild conditions in the presence of palladium and/or nickel catalysts with net inversion of configuration. We expected that reaction of an appropriate organometallic reagent with *p*-*tert*-butylphenyl 4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**1a**)[15] in the presence of a palladium or nickel catalyst would give regio- and stereoselectively the unsaturated *C*-arylglycopyranoside.

**Initial Studies.** Thus, we initiated a study to determine which organometallic reagent/catalyst system will allow the stereospecific introduction of a phenyl moiety at the anomeric center of unsaturated carbohydrate **1aα**. From the literature data we selected $NaBPh_4$, $PhSnBu_3$, PhZnCl, and PhMgBr as the organometallic reagent and various palladium and nickel complexes as the catalysts. The reactions were explored with unsaturated sugar **1a**. Preliminary experiments show that $NaBPh_4$ in the presence of $Pd(dba)_2 + 4\ PPh_3$ or $PhSnBu_3$ in the presence of various catalysts such as $Pd_2(dba)_3$, $Pd_2(dba)_3$ + LiCl, $Pd_2(dba)_3$ + 2 dppb [dppb = 1,4-bis(diphenylphosphino)-butane], $PdCl_2(PPh_3)_2$, or $PdCl_2$(dppf) [dppf = 1,1′-bis-(diphenylphosphino)ferrocene] gave no reaction. The use of PhZnCl in the presence of $Pd_2(dba)_3 + 4\ PPh_3$, $PdCl_2(PPh_3)_2$, or $PdCl_2$(dppf) as the catalyst gave also no reaction or only degradation products. However, when PhMgBr (5 equiv) was used as the organometallic reagent in the presence of 10 mol % of a palladium complex, in THF at 25 °C, the yield of unsaturated *C*-aryl carbohydrate appears to be ligand dependent (Table 1). Formation of *C*-phenylglycoside **2aα** occurred in 95% yield using $PdCl_2$(dppf) as the catalyst (Table 1, entry 5). $PdCl_2$(dppp) [dppp = 1,3-bis(diphenylphosphino)propane] as catalyst gave compound **2aα** in 40% yield (Table 1, entry 7), all other combinations of palladium with bidentate ligands such as dppe [dppe = 1,2-bis(diphenylphosphino)-ethane)], dppb, or dpppe [dpppe = 1,5-bis(diphenylphosphino)pentane] gave very low yields of coupling product or no reaction at all (Table 1, entries 6, 8, and 9). The palladium complex $PdCl_2L_2$, where L is a monodentate phosphine, gave no reaction (Table 1, entries 2−4), although the combination of $Pd_2(dba)_3$ and $4PPh_3$ gave degradation products (Table 1, entry 1). It is to be noticed that the preformed catalyst $PdCl_2L_2$ or the system obtained by mixing $PdCl_2(CH_3CN)_2$ and 2 equiv of a monophosphine or 1 equiv of a diphosphine in situ gave the same results.

**Table 1. Catalyst Effect in Palladium and Nickel Catalyzed Coupling of $C_6H_5MgBr$ and 1Aα[a]**

| entry | organo-metallic | catalyst | temp (°C) | time (h) | product (yield %)[b] |
|---|---|---|---|---|---|
| 1 | PhMgBr | $Pd_2(dba)_3 + 4PPh_3$ | 25 | 24 | degradation |
| 2 | PhMgBr | $PdCl_2(PPh_3)_2$ | 25 | 20 | no reaction |
| 3 | PhMgBr | $PdCl_2[P(o\text{-tolyl})_3]_2$ | 25 | 20 | no reaction |
| 4 | PhMgBr | $PdCl_2[P(2\text{-furyl})_3]_2$ | 25 | 20 | no reaction |
| 5 | PhMgBr | $PdCl_2$(dppf) | 25 | 2 | **2aα** (95) |
| 6 | PhMgBr | $PdCl_2$(dppe) | 25 | 20 | **2aα** (10) |
| 7 | PhMgBr | $PdCl_2$(dppp) | 25 | 20 | **2aα** (40) |
| 8 | PhMgBr | $PdCl_2$(dppb) | 25 | 20 | **2aα** (14) |
| 9 | PhMgBr | $PdCl_2$(dpppe) | 25 | 20 | no reaction |
| 10 | PhMgBr | $NiCl_2$(dppe) | −40 | 2 | **2aβ** (70) |
| 11 | PhMgBr | $NiCl_2$(dppp) | −20 | 48 | **2aβ** (64) |
| 12 | PhMgBr | $NiCl_2$(dppb) | −20 | 24 | no reaction |
| 13 | PhMgBr | $NiCl_2$(dppb) | 0 | 24 | degradation |
| 14 | PhMgBr | $NiCl_2$(dpppe) | −20 | 24 | no reaction |
| 15 | PhMgBr | $NiCl_2$(dpppe) | 0 | 24 | degradation |
| 16 | PhMgBr | $NiCl_2(PPh_3)_2$ | −20 | 24 | no reaction |
| 17 | PhMgBr | $NiCl_2(PPh_3)_2$ | 0 | 24 | degradation |

[a] Reactions were carried out with 5 equiv of organometallic reagent in the presence of 10 mol % of the catalyst in THF. [b] Isolated yield of analytical pure material.

The coupling reaction of PhMgBr with unsaturated carbohydrate **1aα** in THF catalyzed by 10 mol % nickel complexes is also ligand dependent. When $NiCl_2$(dppe) or $NiCl_2$(dppp) were used as the catalyst (Table 1, entries 10 and 11), the *C*-arylglycoside **2aβ** was obtained in 70% and 64% yield, respectively. The other catalysts $NiCl_2$(dppb), $NiCl_2$(dppe), and $NiCl_2(PPh_3)_2$ gave degradation products at 0 °C or no reaction at −20 °C (Table 1, entries 12−17).

The α- and β-configurations of compounds **2a** were determined on the basis of $^1H$ and $^{13}C$ nuclear magnetic resonance,[6a,16] some pertinent data concerning pairs of anomers being summarized in Table 2. As shown before, the β-anomer is conformationally stable in the $^0H_5$ conformation, whereas the α-anomer exists as an equilibrating mixture of the $^0H_5$ and $^5H_0$ conformations. Thus,

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**Table 2. Spectral Data Pertinent to Stereochemical Assignments of the Pairs of α- and *β*-*C*-Arylglycosides[a]**

| compd | $[\alpha]^{20}_D$[b] | δ H-1′ [c] | $J_{4',5'}$ | δ C-1′ | δ C-5′ |
|---|---|---|---|---|---|
| **2aα** | +18.5 | 5.30 | 7.3 | 74.1 | 70.1 |
| **2a*β*** | +60.8 | 5.18 | 8.6 | 77.8 | 77.4 |
| **2bα** | +3.9 | 5.28 | 8.1 | 74.6 | 73.7 |
| **2b*β*** | +189.1 | 5.16 | 8.5 | 77.3 | 80.7 |
| **3aα** | −2.6 | 5.30 | 7.0 | 74.0 | 70.5 |
| **3a*β*** | +171.0 | 5.15 | 8.4 | 78.0 | 77.4 |
| **3b*β*** | −3.1 | 5.23 | 8.0 | 74.4 | 73.6 |
| **3b*β*** | +145.5 | 5.13 | 8.5 | 77.2 | 80.8 |
| **5aα** | −3.8 | 5.26 | 7.5 | 73.9 | 70.3 |
| **5a*β*** | +175.8 | 5.14 | 8.7 | 77.3 | 78.1 |
| **6aα** | +9.1 | 5.28 | 7.9 | 74.2 | 71.1 |
| **6a*β*** | +169.0 | 5.17 | 8.7 | 77.9 | 77.4 |
| **7aα** | +15.5 | 5.69 | 7.4 | 71.5 | 70.3 |
| **7a*β*** | +151.0 | 5.61 | 8.5 | 71.6 | 78.0 |
| **8aα** | +11.7 | 5.20 | 7.1 | 73.9 | 70.4 |
| **8a*β*** | +162.5 | 5.12 | 8.3 | 77.9 | 77.3 |
| **10aα** | −9.2 | 5.27 | 7.2 | 73.9 | 70.4 |
| **10a*β*** | +123.8 | 5.12 | 8.2 | 78.1 | 77.3 |
| **25α**[d] | −20.6 | 5.21 | | 75.8 | 67.9 |
| **25*β***[d] | −219.2 | 5.14 | 8.4 | 77.8 | 76.7 |

[a] δ in ppm; *J* in hertz. [b] In $CH_2Cl_2$. [c] brs. [d] L series.

the higher coupling constant would be attributed to the *β*-anomer; we effectively observed $J_{4',5'} = 8.6$ Hz for **2*β*** and $J_{4',5'} = 7.3$ Hz for **2α**.

This assignment was confirmed by $^{13}C$ NMR. Due to the *γ*-gauche effect described by Stothers[17] and also recently observed for unsaturated *C*-glycopyranosyl compounds,[16] derivative **2α** shows a C-5′ signal at a higher field (δ 70.1 ppm) than compound **2*β*** (δ 77.4 ppm). An upfield shift of the C-1′ in **2α** (δ 74.1 ppm) was also observed compared to the downfield shift for **2*β*** (δ 77.8 ppm).

NOE experiments were also used to confirm the configuration at the anomeric center. Irradiation of the C-1′ methine proton (δ 5.18 ppm) in compound **2*β*** obtained via nickel catalysis shows an enhancement of 10% of the C-5′ methine proton signal at δ 3.75 ppm, in agreement with a syn disposition of these two atoms. A similar experiment on compound **2aα** obtained via palladium catalysis shows no enhancement.

**Coupling Reaction Catalyzed by Palladium Complexes.** To survey the coupling reaction catalyzed by $PdCl_2$(dppf), various Grignard reagents and unsaturated carbohydrates **1a**−**bα** were subjected to this reaction in THF. The results are shown in Table 3.

Reactions of (4- and 2-methylphenyl)magnesium bromides as well as (4-, 3-, and 2-methoxyphenyl)magnesium bromides with **1aα** gave high yields of the corresponding α-*C*-arylglycosides **3a**−**7aα** (Table 3, entries 3 and 5−8). Using *p*-*tert*-butylphenyl 4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**1b**) instead of **1a** also gave quite good yields of the α-anomer with phenyl- or (4-methylphenyl)magnesium bromide (Table 3, entries 2 and 4).

Grignard reagents derived from 1-bromo-3,4-dioxomethylbenzene and 1-bromo-4-chlorobenzene, as well as from 1-bromo-4-[(*tert*-butyldimethylsilyl)oxy]benzene and 4-bromobenzaldehyde dimethyl acetal, reacted under these conditions to give respectively the corresponding α-*C*-glycosides **8a**, **9a**, **10a**, and **11a** in quite good yields (Table 3, entries 9−12).

**Table 3. Palladium-Catalyzed Coupling Reaction of 1α and Various Grignard Reagents[a]**

| entry | **1α** | RMgBr | temp (°C) | time (h) | product (yield, %)[b] |
|---|---|---|---|---|---|
| 1 | **a** | $C_6H_5MgBr$ | 25 | 2 | **2aα** (95) |
| 2 | **b** | $C_6H_5MgBr$ | 25 | 2 | **2bα** (80) |
| 3 | **a** | 4-$MeC_6H_4MgBr$ | 25 | 2 | **3aα** (70) |
| 4 | **b** | 4-$MeC_6H_4MgBr$ | 25 | 2 | **3bα** (70) |
| 5 | **a** | 2-$MeC_6H_4MgBr$ | 25 | 2 | **4aα** (80) |
| 6 | **a** | 4-$MeOC_6H_4MgBr$ | 25 | 2 | **5aα** (73) |
| 7 | **a** | 3-$MeOC_6H_4MgBr$ | 25 | 2 | **6aα** (60) |
| 8 | **a** | 2-$MeOC_6H_4MgBr$ | 25 | 2 | **7aα** (87) |
| 9 | **a** | 3,4-$(CH_2O_2)C_6H_3MgBr$ | 25 | 2 | **8aα** (95) |
| 10 | **a** | 4-$ClC_6H_4MgBr$ | 25 | 2 | **9aα** (76) |
| 11 | **a** | 4-$Bu^tMe_2SiOC_6H_4MgBr$ | 25 | 2 | **10aα** (65) |
| 12 | **a** | 4-$[(MeO)_2CH]C_6H_4MgBr$ | 25 | 2 | **11aα** (65) |
| 13 | **a** | 4-$C_2H_3C_6H_4MgBr$ | 25 | 2 | **13aα** (72) |
| 14 | **a** | 2-MgBr-thiophene | 25 | 2 | **14aα** (81) |
| 15 | **a** | 2-MgBr-naphthalene | 25 | 2 | degradation |
| 16 | **a** | 2-MgBr-naphthalene | 0 | 1 | **15aα** (78) |
| 17 | **a** | $PhCH_2MgBr$ | 25 | 2 | **16aα** (70) |
| 18 | **a** | $CH_2{=}CHCH_2MgBr$ | 25 | 2 | degradation |
| 19 | **a** | $CH_2{=}CHCH_2MgBr$ | −10 | 4 | **17aα** (72) |
| 20 | **a** | $CH_2{=}CHMgBr$ | 25 | 2 | degradation |
| 21 | **a** | $CH_2{=}CHMgBr$ | 0 | 2 | **18aα** (14) |

[a] Reactions were carried out with 5 equiv of the Grignard reagent in the presence of 10 mol % of $PdCl_2$(dppf) in THF. [b] Isolated yields of analytically pure material. [c] Catalyst $PdCl_2$(dppp).

(4-Vinylphenyl)- and thiopheneylmagnesium bromides also coupled with carbohydrate **1aα** to give the interesting α-*C*-styryl and *C*-thiopheneyl carbohydrates **13** and **14**, respectively (Table 3, entries 13 and 14). The Grignard reagent of 2-bromonaphthalene led to the expected coupling product **15αa** in 78% yield, but only at 0 °C; performing the reaction at 25 °C gave degradation products (Table 3, entries 15 and 16).

We extended the reaction to nonaromatic Grignard reagents. Thus, benzyl- and allylmagnesium bromides reacted with **1aα** to give the α-*C*-benzyl and allyl compounds **16** and **17** in 70 and 72% yield, respectively, although the reaction has to be performed at −10 °C in the last case (Table 3, entries 17−19). The α-configuration at C-1′ was confirmed for compound **17** by NOE experiments. Irradiation of the benzylic protons at δ 2.82 and 3.08 ppm effectively shows an enhancement of 7% of the signal of H-5′ at δ 3.91 ppm. Vinylmagnesium bromide formed **18α** in 14% yield at 0 °C (Table 3, entries 20−21), whereas (phenylacetylenyl)magnesium bromide gave no reaction.

Methylmagnesium bromide did not give the expected coupling product, the *C*-glycoside **19α** being obtained in 52% yield (Scheme 2). Such a O → C transformation was used before by Casiraghi et al.[5] for the preparation of *C*-arylglycosides.

**Coupling Reaction Catalyzed by Nickel Complexes.** Various Grignard reagents were also reacted with unsaturated substrates **1a**−**bα** in THF in the presence of 10% $NiCl_2$(dppe) as the catalyst. The results are summarized in Table 4.

Reaction of phenyl- and (4-methylphenyl)magnesium bromides with **1aα** or **1bα** at −40 °C gave the expected unsaturated phenylglycosides **2*β*** and **3*β*** in quite good yields (Table 4, entries 1−3 and 6). It is to be noticed that the use of $NiCl_2$(dppf) as the catalyst gave no reaction at −40 °C and only 12% yield at 0 °C (Table 4, entries 4−5).

While (4- and 3-methoxyphenyl)magnesium bromides reacted at −40 °C to give **5a*β*** and **6a*β*** in 75 and 60%

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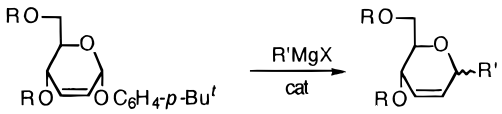
**Scheme 1**

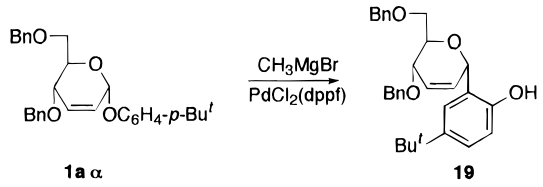



**1α** **2-18**

**a** R = Bn
**b** R = SiBu$^t$Me$_2$

**2** R' = $C_6H_5$
**3** R' = 4-Me$C_6H_4$
**4** R' = 2-Me$C_6H_4$
**5** R' = 4-Me$OC_6H_4$
**6** R' = 3-Me$OC_6H_4$
**7** R' = 2-Me$OC_6H_4$
**8** R' = 3,4-$(CH_2O_2)C_6H_3$
**9** R' = 4-Cl$C_6H_4$
**10** R' = 4-$^t$BuMe$_2$Si$OC_6H_4$
**11** R' = 4-$(MeO)_2CHC_6H_4$
**12** R' = 4-$CH_3OCH_2OC_6H_4$
**13** R' = 4-$C_2H_3C_6H_4$
**14** R' = 2-thienyl
**15** R' = α-naphtyl
**16** R' = $CH_2C_6H_5$
**17** R' = $CH_2$-CH=$CH_2$
**18** R' = -CH=$CH_2$

**Scheme 2**




**1a α** **19**

**Table 4. Nickel-Catalyzed Coupling Reaction of 1α and Various Grignard Reagents**[a]

| entry | 1α | RMgBr | temp (°C) | time (h) | product (yield, %)[b] |
|---|---|---|---|---|---|
| 1 | **a** | $C_6H_5$MgBr | −40 | 2 | **2aβ** (70) |
| 2 | **b** | $C_6H_5$MgBr | −40 | 2 | **2bβ** (83) |
| 3 | **a** | 4-Me$C_6H_4$MgBr | −40 | 2 | **3aβ** (85) |
| 4 | **a** | 4-Me$C_6H_4$MgBr[c] | −40 | 2 | no reaction |
| 5 | **a** | 4-Me$C_6H_4$MgBr[c] | 0 | 15 | **3aβ** (12) |
| 6 | **b** | 4-Me$C_6H_4$MgBr | −40 | 2 | **3bβ** (83) |
| 7 | **a** | 4-Me$OC_6H_4$MgBr | −40 | 2 | **5aβ** (75) |
| 8 | **a** | 3-Me$OC_6H_4$MgBr | −40 | 2 | **6aβ** (60) |
| 9 | **a** | 2-Me$OC_6H_4$MgBr | −40 | 24 | no reaction |
| 10 | **a** | 2-Me$OC_6H_4$MgBr | −20 | 2 | **7aβ** (64) |
| 11 | **a** | 3,4-$(CH_2O_2)C_6H_3$MgBr | −40 | 2 | **8aβ** (70) |
| 12 | **b** | 4-Cl$C_6H_4$MgBr | +10 | 2 | **9bβ** (60) |
| 13 | **a** | 4-Bu$^t$Me$_2$Si$OC_6H_4$MgBr | −40 | 2 | **10aβ** (90) |
| 14 | **b** | 4-Bu$^t$Me$_2$Si$OC_6H_4$MgBr | −40 | 20 | **10bβ** (81) |
| 15 | **b** | 4-MOM$OC_6H_4$MgBr | −40 | 2 | **12bβ** (80) |
| 16 | **a** | 2-MgBr-thiophene | −20 | 2 | no reaction |
| 17 | **a** | 2-MgBr-thiophene | 0 | 2 | degradation |

[a] Reactions were carried out with 5 equiv of the Grignard reagent in the presence of 10 mol % of $NiCl_2$(dppe) in THF. [b] Isolated yields of analytically pure material. [c] Catalyst $NiCl_2$(dppf).

yield, respectively (Table 4, entries 7 and 8), (2-methoxyphenyl)magnesium bromide reacted at −20 °C to produce the expected **7aβ** in 64% yield (Table 4, entries 9 and 10).

Grignard reagents derived from 1-bromo-3,4-dioxomethylbenzene, 1-bromo-4-[(*tert*-butyldimethylsilyl)oxy]-benzene, and 1-bromo-4-(methoxymethoxy)benzene readily reacted at −40 °C to give the unsaturated carbohydrates **8aβ**, **10β** and **12bβ** in quite good yields (Table 4, entries 11 and 13−15). (4-Chlorophenyl)magnesium bromide reacted only at 10 °C, giving **9bβ** in 60% yield (Table 4, entry 12), although thiopheneylmagnesium bromide gave no alkylated compound whatever the conditions (Table 4, entries 16 and 17).

So, in all examined cases leading to the formation of unsaturated *C*-aryl carbohydrates, the reaction was totally stereoselective, with only the α-anomer being observed in the case of palladium-catalyzed reaction and the β-anomer in the case of nickel-catalyzed reaction. However, in the case of nickel catalysts, the temperature seems very important for the success of the coupling.

**Coupling Reaction of Phenylmagnesium Bromide with Other Carbohydrates.** In the above sections, we described the palladium and the nickel coupling of various arylmagnesium bromides and *p-tert*-butylphenyl 4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**1a**). To gain a deeper insight into the potentialities of this transformation in carbohydrate chemistry, we applied these experimental conditions to other carbohydrates.

*p-tert*-Butylphenyl 4-*O*-benzyl-2,3,6-trideoxy-α-L-*erythro*-hex-2-eno pyranoside (**20**) was prepared according to the literature.[15] The synthesis of *p-tert*-butylphenyl 4,6-di-*O*-benzyl-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside (**1aβ**) is described in Scheme 3. The mother liquor obtained after recrystallization during the preparation of **1aα**[16] was subjected to deacetylation. The mixture was then treated with 1 equiv of TBDMSCl in $CH_2Cl_2$ in the presence of imidazole to give the monosilylated compounds **21α** and **21β**. Separation of both anomers by column chromatography gave pure **21β** in 30% yield. Subsequent desilylation of **21β** using $Bu_4NF{\cdot}3H_2O$ in THF followed by benzylation with benzyl bromide in the presence of $Bu_4NBr$ and sodium hydroxide led to **1aβ** in 91% yield.

The 2,3-unsaturated threo derivatives **23** and **24c** were prepared according to Scheme 4. Inversion of configuration at C-4 of **21α** via a Mitsunobu reaction[18] gave the threo derivative **22**. Desilylation of **22** followed by alkylation of the resulting diol with benzyl bromide led to the 4,6-di-*O*-benzyl-2,3-unsaturated threo derivative **23**. Treatment of alcohol **22** with NaH and methyl iodide in THF led to the *O*-methyl carbohydrate **24a**. Subsequent desilylation of **24a** followed by benzylation under the conditions already described formed the unsaturated compound **24c**.

Reaction of phenylmagnesium bromide with the unsaturated carbohydrate **20** in the presence of a catalytic amount of $PdCl_2$(dppf) (Scheme 5) gave glycoside **25α** in 51% yield, whereas the nickel-catalyzed reaction gave **25β** in 68% yield. Thus, we found the same stereoselectivities as with the unsaturated carbohydrates **1a**−**b**.

Arylation of **1aβ** under the same conditions gave phenylglycoside **2a** in 87% yield as a mixture of anomers α/β = 95/5, in the case of the palladium-catalyzed reaction, and only the β-anomer in 50% yield for the nickel-catalyzed reaction (Scheme 6). These results excluded the possibility of an ionic intermediate in the arylation reaction.

Finally, this arylation process was extended to the threo derivatives **23** and **24c**. In the case of the di-*O*-benzyl derivative **23**, no reaction was observed using $PdCl_2$(dppf) at 0−50 °C or $NiCl_2$(dppe) at −20 °C as the catalysts, although performing the reaction at 0 °C in the latter case gave degradation products. However, in the arylation of the methoxy derivative **24c**, while the nickel catalysis gave no reaction or degradation products, the palladium-catalyzed reaction led to the formation of *C*-phenylglycoside **26α** in 44% yield. The difference of reactivity between **23** and **24c** could be attributed to the

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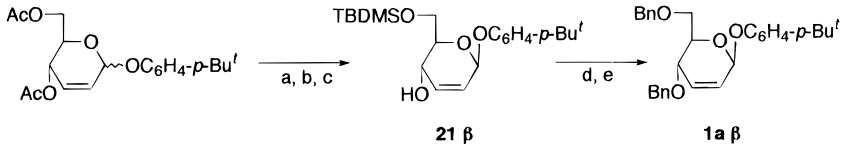
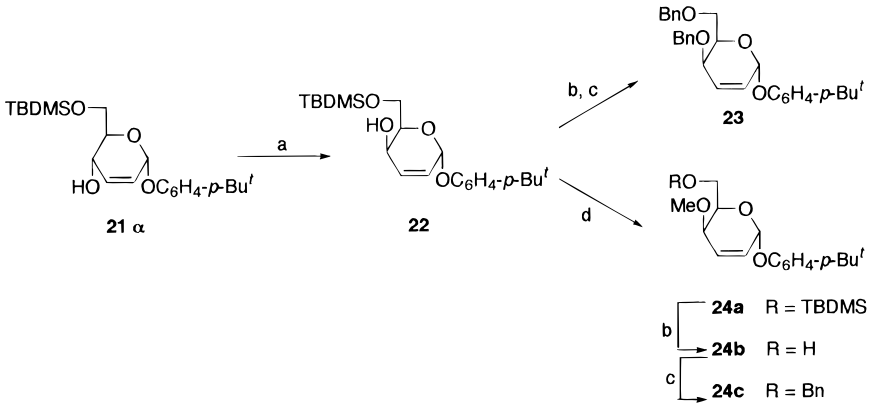
**Scheme 3**[a]




21 β 1a β

[a] (a) $CH_3OH$, $CH_3ONa$; (b) TBDMSCl, $NEt_3$, imidazole, $CH_2Cl_2$, 25 °C; (c) separation; (d) $Bu_4NF{\cdot}3H_2O$, THF, 25 °C; (e) BnCl, $Bu_4NBr$, NaOH 50%.

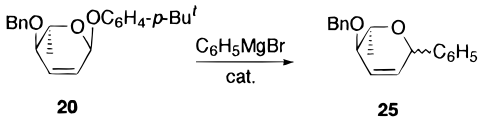
**Scheme 4**[a]




21 α 22 23

[a] (a) $ClCH_2COOH$, $PPh_3$, DEAD, toluol, the $CH_3ONa$, $CH_3OH$; (b) $Bu_4NF{\cdot}3H_2O$, THF, 25 °C; (c) BnCl, $Bu_4NBr$, NaOH 50%; (d) NaH, $CH_3I$, THF, 25 °C.

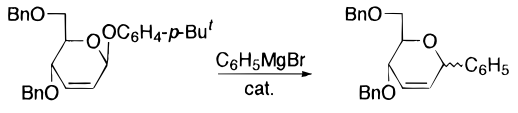
**Scheme 5**




20 25

cat. $PdCl_2$(dppf), 25 °C, 24 h α 51% yield
cat. $NiCl_2$(dppe), -40 °C, 24 h β 68% yield

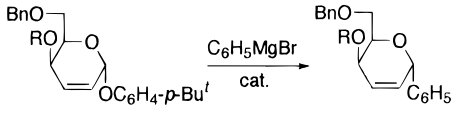
**Scheme 6**




1a β 2

cat. $PdCl_2$(dppf), 0 °C, 0.5 h α/β = 95/5, 87% yield
cat. $NiCl_2$(dppe), -40 °C, 24 h α/β = 0/100, 50% yield

**Scheme 7**




**23**: R = Bn
**24c**: R = $CH_3$

**26**: R = $CH_3$

presence of a benzyloxy group at C-4, which overcrowded the upper face of the double bond, so inhibiting the formation of the $\pi$-allyl intermediate.

**Structural Assignments.** The structures of the *C*-arylglycosides, and particularly the α- or *β*-configuration, were determined on the basis of spectrometric data.[16] Pertinent $^1H$ and $^{13}C$ nuclear magnetic resonance data for some pairs of *C*-arylglycosides are summarized in Table 2.

As previously shown,[16] comparison of $J_{4',5'}$ for α- and *β*-anomers show a larger coupling constant for the *β*-derivative, although these values cannot be used as the sole criterion for assignment of the anomeric configuration.

Comparison of the $^{13}C$ chemical shifts for C-1′ and C-5′ of both anomers show that these atoms for α-*C*-arylglycoside anomers are shielded with respect to the corresponding carbons of *β*-anomers, the effect being more pronounced for C-5′ than for C-1′. This is in agreement with the predictions of the *γ*-gauche effect.[17]

We also observed that the anomeric proton resonates at higher frequency for the *β*-anomer in agreement with previous results.[16]

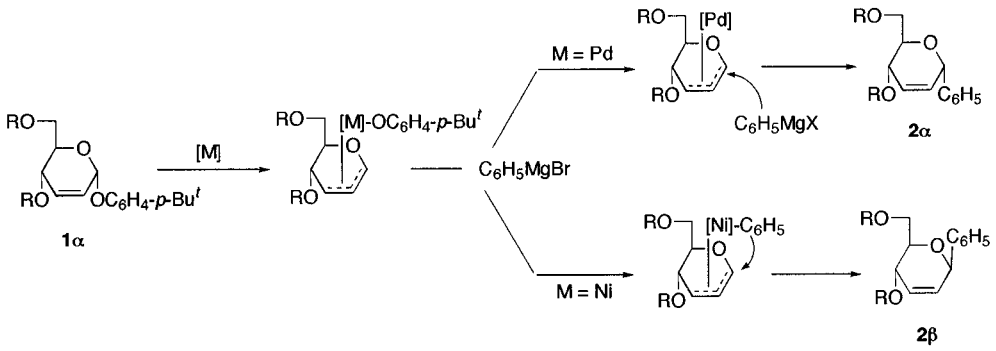
It is to be noticed that for a given pair of unsaturated α- and *β*-*C*-glycosylarenes in the D series, the *β*-anomer is the more dextrorotatory, disobeying Hudson's rule[18] of isorotation, but in agreement with previous results published by other groups.[2c,5] This rule also applies for the anomeric L-rhamnosylbenzene **25**α and **25*β***, the *β*-anomer now being the less dextrorotatory.

However, as previously described,[16] these assignments have to be confirmed by NOE experiments.

**Mechanism.** The stereochemical aspect of the reaction of various organometallic reagents, such as magnesium, boron, aluminum, tin, zinc, or zirconium reagents, on $\pi$-allyl complexes derived from palladium[9c,11n−q,12a,g,h,13d−f,14c] and nickel[11j,q−t] has been studied by different groups. In all cases, the reaction proceeded with overall inversion of configuration, whatever the metal used.

If the present nickel-catalyzed reaction proceeds with overall inversion, in agreement with the literature data, the palladium-catalyzed process shows an overall retention. It is conceivable that the reaction proceeds as depicted in Scheme 8. After formation of a Pd(0) or Ni(0) complex, oxidative addition to the unsaturated carbohydrate **1**α occurs with inversion of configuration to give a $\pi$-allyl complex. In the case of the allyl−Ni intermediate, transmetalation with the Grignard reagent leads to a ($\pi$-

**Scheme 8**



allyl)(aryl)−Ni complex which undergoes a syn reductive elimination to form the unsaturated *C*-glycosylarene, so with overall inversion of configuration.

In the case of the allyl−Pd intermediate and in light of the preceding results, the formation of the unsaturated *C*-arylglycoside with an overall retention of configuration is only consistent with an exo attack of the Grignard reagent on this π-allyl intermediate. However more experiments are needed to explain in this last case the mechanistic pathway and to clarify the possible role of the different oxygen atoms of the molecule.

## Conclusion

We have presented new reagent/catalyst systems for the regio- and totally stereoselective synthesis of 2,3-unsaturated *C*-arylglycosides. The reaction proceeds under very mild conditions, and catalyst-controlled stereoselection is observed in all cases. Palladium-catalyzed coupling of *p-tert*-butylphenyl α-*O*-Δ²-glycopyranoside with various substituted arylmagnesium bromides provides the corresponding α-*C*-aryl-Δ²-glycopyranosides, while nickel-mediated reaction allows the β-*C*-aryl anomers to be prepared. To the best of our knowledge, overall retention of configuration with a "hard" organometallic is realized for the first time. Application of this coupling reaction to natural product synthesis and particularly to *C*-arylglycosides is now in progress in the laboratory and will be presented in due course.

## Experimental Section

**General Methods and Materials.** All reactions were monitored by thin-layer chromatography carried out on 0.2 mm silica gel plates (60 F-254, Merck). Column chromatography was performed on silica gel 60 (40−63 mesh ASTM, Macherey-Nagel). NMR spectra were obtained in $CDCl_3$, and chemical shifts are given in ppm on the δ scale from internal tetramethylsilane. THF was distilled from sodium/benzophenone, purged, and kept under a nitrogen atmosphere. Reactions involving palladium or nickel complexes were carried out in a Schlenk tube under a nitrogen atmosphere. Tri-*O*-acetyl-D-glucal, di-*O*-acetyl-L-rhamnal, bromoaryl compounds, phosphines, $Pd_2(dba)_3$, and TBDMSCl were purchased from Aldrich Chemical Co.

The following compounds were prepared by literature methods: *p-tert*-butylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside,[15] *p-tert*-butyl phenyl 4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**1a**),[15] *p-tert*-butylphenyl 4-*O*-benzyl-2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranoside (**20**),[15] $PdCl_2(CH_3CN)_2$,[20] $PdCl_2$(dppf),[21] $NiCl_2$(dppe),[22] $NiCl_2$(dppp),[23] $NiCl_2$(dppb),[22] $NiCl_2$(dpppe),[22] $NiCl_2$(dppf),[24] $NiCl_2(PPh_3)_2$,[22] 1-bromo-4-[(*tert*-butyldimethylsilyl)oxy]benzene,[25] 4-bromobenzaldehyde dimethyl acetal,[26] and 1-bromo-4-(methoxymethoxy)benzene.[27]

***p-tert*-Butylphenyl 4,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (1b).** A solution of 4.0 g (11 mmol) of *p-tert*-butylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside[15] in methanol (100 mL) containing 18 mg (0.33 mmol) of $CH_3ONa$ was stirred at 25 °C for 1 h. The methanol was evaporated under vacuum, the crude diol obtained was dissolved in DMF (30 mL), and then imidazole (3.53 mg, 58.7 mmol) and TBDMSCl (7.83 g, 51.7 mmol) were added under nitrogen. The reaction mixture was stirred at room temperature for 48 h and then partitioned between water (20 mL) and $CH_2Cl_2$ (100 mL). After separation, the organic layer was dried over sodium sulfate and evaporated. The crude product was purified by column chromatography, eluting with petroleum ether/ethyl acetate (30:1) to give 5.1 g (90%) of **1b** as an oil: $R_f$ 0.42; $[\alpha]^{20}_D$ +107.0 (*c* 1.1, $CH_2Cl_2$); $^1$H NMR (200 MHz) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.11 (s, 3H), 0.13 (s, 3H), 0.87 (s, 9H), 0.91 (s, 9H), 1.31 (s, 9H), 3.70−3.80 (m, 3H), 4.32 (brd, 1H, *J* = 8.5 Hz), 5.61 (brs, 1H), 5.82 (brd, 1H, *J* = 10.1 Hz), 6.00 (brd, 1H, *J* = 10.1 Hz), 7.05 (d, 2H, *J* = 8.8 Hz), 7.29 (d, 2H, *J* = 8.8 Hz); $^{13}$C NMR (50 MHz) δ −5.2, −4.9, −4.7, −4.1, 18.1, 18.6, 25.4, 26.1, 31.7, 34.3, 62.3, 63.6, 73.4, 93.4, 116.6, 124.9, 135.7, 144.7, 155.5. Anal. Calcd for $C_{28}H_{50}O_4Si_2$: C, 66.35; H, 9.94. Found: C, 66.01; H, 9.89.

***p-tert*-Butylphenyl 6-*O*-(*tert*-Butyldimethylsilyl)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside (21β).** The solution resulting from the recrystallization in the preparation of *p-tert*-butylphenyl 4,6-di-*O*-acetyl-α-D-*erythro*-hex-2-enopyranoside was evaporated and the mixture of α- and β-anomers was deacetylated in methanol in the presence of a catalytic amount of $CH_3ONa$ to give after evaporation of the solvent *p-tert*-butylphenyl D-*erythro*-hex-2-enopyranoside as a mixture of the two anomers. The crude mixture (7.5 g, 26.4 mmol) was dissolved in $CH_2Cl_2$ (60 mL), and imidazole (90 mg, 1.3 mmol), triethylamine (5.3 mL, 37.0 mmol), and TBDMSCl (5.44 g, 36.2 mmol) in $CH_2Cl_2$ (50 mL) were added at room temperature under argon. The reaction mixture was stirred for 24 h and then partitioned between water (100 mL) and $CH_2Cl_2$ (50 mL). After separation, the organic layer was evaporated and the residue was chromatographed eluting with petroleum ether/diethyl ether (2:1) to give 3.11 g (30%) of **21β** as an oil: $R_f$ 0.30; $[\alpha]^{20}_D$ −14.7 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) δ 0.01 (s, 3H), 0.10 (s, 3H), 0.91 (s, 9H), 1.31 (s, 9H), 2.86 (d, 1H, *J* =

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4.1 Hz), 3.77−3.95 (m, 3H), 4.33 (m, 1H), 5.75 (d, 1H, $J$ = 1.5 Hz), 5.92 (ddd, 1H, $J$ = 10.2, 1.5, 1.5 Hz), 6.11 (ddd, 1H, $J$ = 10.2, 2.4, 1.6 Hz), 7.01 (d, 2H, $J$ = 8.8 Hz), 7.31 (d, 2H, $J$ = 8.8 Hz); $^{13}$C NMR (50 MHz) $\delta$ −5.6, −5.5, 18.2, 25.9, 31.6, 34.2, 65.0, 65.7, 77.2, 94.8, 116.3, 126.2, 127.3, 132.0, 148.8, 154.8. Anal. Calcd for $C_{22}H_{36}O_4Si$: C, 67.30; H, 9.24. Found: C, 67.31; H, 9.28.

***p*-*tert*-Butylphenyl 4,6-Di-*O*-benzyl-2,3-dideoxy-*β*-D-*erythro*-hex-2-enopyranoside (1a*β*).** The unsaturated carbohydrate **21*β*** (3.11 g, 7.8 mmol) was dissolved in THF (50 mL), and $Bu_4NF{\cdot}3H_2O$ (2.5 g, 7.9 mmol) was added. The reaction mixture was stirred for 2 h, and the solvent was evaporated. The residue was partitioned between $CH_2Cl_2$ (100 mL) and water (30 mL). After separation, the organic larger was dried and the solvent evaporated under reduced pressure to give quantitatively *p*-*tert*-butylphenyl *β*-D-*erythro*-hex-2-enopyranoside as an oil. The crude diol (2.17 g, 7.8 mmol) was dissolved in toluol (10 mL), and NaOH 50% (6.2 mL) and *n*-$Bu_4NF{\cdot}3H_2O$ (465 mg, 1.57 mmol) were added. A solution of benzyl chloride (1.98 mL, 17.17 mmol) in toluol (5 mL) was added slowly at 60 °C. The reaction mixture was stirred for 24 h, the toluol was evaporated, and the residue was partitioned between diethyl ether (100 mL) and water (20 mL). After evaporation of the solvent, the crude product was purified by column chromatography, eluting with petroleum ether/ethyl acetate (4:1) to give 3.25 g (91%) of compound **1a*β*** as an oil: $R_f$ 0.55; $[\alpha]^{20}_D$ +9.6 (*c* 1.3, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 1.30 (s, 9H), 3.67 (dd, 1H, $J$ = 10.2, 6.0 Hz), 3.63 (dd, 1H, $J$ = 10.2, 5.7 Hz), 4.02 (dm, 1H, $J$ = 4.5 Hz), 4.21 (ddd, 1H, $J$ = 6.0, 5.7, 4.5 Hz), 4.49 (s, 2H), 4.60 (s, 2H), 5.76 (brs, 1H), 6.00 (ddd, 1H, $J$ = 10.2, 2.0, 1.1 Hz), 6.15 (ddd, 1H, $J$ = 10.2, 3.6, 1.3 Hz), 7.03 (d, 2H, $J$ = 8.8 Hz), 7.20−7.50 (m, 12H); $^{13}$C NMR (50 MHz) $\delta$ 31.5, 34.1, 68.8, 70.0, 70.9, 73.3, 75.1, 93.3, 116.0, 126.2, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 137.9, 138.2, 144.8, 154.8. Anal. Calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47. Found: C, 78.49; H, 7.57.

***p*-*tert*-Butylphenyl 6-*O*-(*tert*-Butyldimethylsilyl)-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (22).** To *p*-*tert*-butylphenyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**21**) (0.39 g, 1.0 mmol) in toluol (10 mL) was added $PPh_3$ (0.52 g, 2.0 mmol) and $ClCH_2CO_2H$ (0.19 g, 2.0 mmol). The solution was stirred for 15 min at 0 °C, and DEAD (0.35 g, 2.0 mmol) was slowly added. After the solution was stirred for 30 min at 0 °C, and 24 h at room temperature, $OPPh_3$ was separated and the solution was concentrated under vacuum. The resulting oil was directly treated with a catalytic amount of sodium methoxide in methanol (50 mL). After being stirred for 1 h, the solution was concentrated under vacuum, and the resulting oil was purified by column chromatography, eluting with petroleum ether/diethyl ether (2:1) to give 0.32 g (81%) of **22** as an oil: $R_f$ 0.40; $[\alpha]^{20}_D$ +10.4 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 0.06 (s, 3H), 0.08 (s, 3H), 0.88 (s, 9H), 1.32 (s, 9H), 2.36 (d, 1H, $J$ = 7.3 Hz), 3.86 (dd, 1H, $J$ = 12.1, 6.1 Hz), 3.93 (dd, 1H, $J$ = 12.1, 6.1 Hz), 4.05 (ddd, 1H, $J$ = 7.3, 5.5, 2.2 Hz), 4.19 (ddd, 1H, $J$ = 6.1, 6.1, 2.2 Hz), 5.72 (d, 1H, $J$ = 3.1 Hz), 6.06 (dd, 1H, $J$ = 9.9, 3.1 Hz), 6.32 (ddd, 1H, $J$ = 9.9, 5.5, 0.6 Hz), 7.06 (d, 2H, $J$ = 8.9 Hz), 7.32 (d, 2H, $J$ = 8.9 Hz); $^{13}$C NMR (50 MHz) $\delta$ −5.4, −5.3, 18.3, 25.9, 31.6, 34.3, 61.9, 62.8, 71.1, 93.4, 116.6, 126.4, 127.8, 130.4, 145.0, 155.2. Anal. Calcd for $C_{22}H_{36}O_4Si$: C, 67.30; H, 9.24. Found: C, 67.12; H, 9.16.

***p*-*tert*-Butylphenyl 4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (23).** To compound **22** (3.0 g, 7.9 mmol) in THF (50 mL) was added $Bu_4NF{\cdot}3H_2O$ (2.5 g, 7.9 mmol). After being stirred for 2 h at room temperature, the solution was treated with water (20 mL) and $CH_2Cl_2$ (100 mL). Evaporation of the solvent gave quantitatively the corresponding alcohol. This alcohol was benzylated according to the procedure used for compound **1a*β*** to give 1.88 g (yield 52%) of **23** as an oil: $R_f$ 0.40 (petroleum ether/ethyl acetate, 8:1); $[\alpha]^{20}_D$ −42.3 (*c* 1.1, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 3.70−3.90 (m, 3H), 4.42 (dm, 1H, $J$ = 6.3 Hz), 4.67, 4.59, 4.54 and 4.48 (4d, 4 × 1H, $J$ = 11.9 Hz), 5.73 (brd, 1H, $J$ = 2.9 Hz), 6.11 (brdd, 1H, $J$ = 10.0, 2.9 Hz), 6.25 (brdd, 1H, $J$ = 10.0, 5.2 Hz), 7.07 (d, 2H, $J$ = 8.7 Hz), 7.20−7.40 (m, 12H); $^{13}$C NMR (50 MHz) $\delta$ 31.6, 34.2, 67.1, 69.3, 70.4, 71.4, 73.4, 93.2, 116.7, 126.3, 127.6, 127.7, 127.8, 127.9, 128.4, 128.8, 138.3, 138.4, 145.0, 155.2. Anal. Calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47. Found: C, 78.51; H, 7.54.

***p*-*tert*-Butylphenyl 6-*O*-(*tert*-Butyldimethylsilyl)-4-*O*-methyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (24a).** To compound **22** (1.7 g, 4.4 mmol) in THF (50 mL) was added NaH (0.18 g, 6.6 mmol). After the solution was stirred for 15 min at 40 °C, $CH_3I$ (0.55 mL, 8.8 mmol) was added. After 24 h, the solution was hydrolyzed with water (10 mL) and extracted with diethyl ether. Concentration of the solution under vacuum and purification of the resulting oil by column chromatography, eluting with petroleum ether/diethyl ether (2/1), gave 1.61 g (yield 90%) of **24a** as an oil: $R_f$ 0.67; $[\alpha]^{20}_D$ −17.0 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz) $\delta$ 0.02 (s, 3H), 0.05 (s, 3H), 0.85 (s, 9H), 1.30 (s, 9H), 3.45 (s, 3H), 3.63 (dd, 1H, $J$ = 5.2, 2.4 Hz), 3.73 (dd, 1H, $J$ = 9.9, 6.3 Hz), 3.89 (dd, 1H, $J$ = 9.9, 7.3 Hz), 4.21 (ddd, 1H, $J$ = 7.3, 6.3, 2.4 Hz), 5.73 (brd, 1H, $J$ = 2.9 Hz), 6.13 (dd, 1H, $J$ = 10.0, 2.9 Hz), 6.40 (brdd, 1H, $J$ = 10.0, 5.2 Hz), 7.05 (d, 2H, $J$ = 8.8 Hz), 7.30 (d, 2H, $J$ = 8.8 Hz); $^{13}$C NMR (50 MHz) $\delta$ −5.5, −5.4, 18.2, 25.9, 31.6, 34.2, 57.0, 61.7, 68.3, 71.8, 93.0, 116.5, 126.2, 127.7, 129.0, 149.1, 155.2. Anal. Calcd for $C_{23}H_{38}O_4Si$: C, 67.94; H, 9.42. Found: C, 68.17; H, 9.34.

***p*-*tert*-Butylphenyl 4-*O*-Methyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (24b).** Compound **24b** was obtained by desilylation of compound **24a** according to the same procedure used for the desilylation of compound **23** (yield 100%): oil; $R_f$ 0.35 (petroleum ether/ethyl acetate, 2:1); $[\alpha]^{20}_D$ −29.0 (*c* 1.1, $CH_2Cl_2$); $^1$H NMR (300 MHz) $\delta$ 1.30 (s, 9H), 3.44 (s, 3H), 3.69 (dd, 1H, $J$ = 5.1, 2.7 Hz), 3.74−3.79 (m, 1H), 3.81 (dd, 1H, $J$ = 11.8, 4.5 Hz), 3.95 (dd, 1H, $J$ = 11.8, 6.3 Hz), 4.23 (m, 1H), 5.79 (brd, 1H, $J$ = 2.9 Hz), 6.18 (dd, 1H, $J$ = 10.1, 2.9 Hz), 6.37 (ddd, 1H, $J$ = 10.1, 5.1, 0.8 Hz), 7.04 (d, 2H, $J$ = 8.8 Hz), 7.31 (d, 2H, $J$ = 8.8 Hz); $^{13}$C NMR (50 MHz) $\delta$ 31.5, 34.2, 56.6, 62.5, 69.7, 71.3, 93.0, 116.4, 126.4, 126.9, 129.4, 145.1, 154.9. Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.41; H, 8.15.

***p*-*tert*-Butylphenyl 6-*O*-Benzyl-4-*O*-methyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (24c).** Compound **24c** was prepared from *p*-*tert*-butylphenyl 4-*O*-methyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside **24b** according to the procedure used for compound **1a*β*** (yield 56%): oil; $R_f$ 0.80 (petroleum ether/ethyl acetate, 2:1); $[\alpha]^{20}_D$ −13.3 (*c* 1.1, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 1.29 (s, 9H), 3.43 (s, 3H), 3.63 (dd, 1H, $J$ = 5.1, 2.6 Hz), 3.70 (dd, 1H, $J$ = 10.2, 6.6 Hz), 3.84 (dd, 1H, $J$ = 10.2, 6.1 Hz), 4.41 (ddd, 1H, $J$ = 6.6, 6.1, 2.6 Hz), 4.55 and 4.56 (2d, 2 × 1H, $J$ = 11.9 Hz), 5.71 (brd, 1H, $J$ = 3.0 Hz), 6.14 (dd, 1H, $J$ = 10.1, 3.0 Hz), 6.36 (brdd, 1H, $J$ = 10.1, 5.1 Hz), 7.07 (d, 2H, $J$ = 8.8 Hz), 7.28 (d, 2H, $J$ = 8.8 Hz); $^{13}$C NMR (50 MHz) $\delta$ 31.5, 34.1, 56.9, 67.0, 68.8, 69.2, 70.3, 93.2, 116.8, 126.2, 127.4, 127.4, 127.6, 127.8, 129.0, 138.3, 144.9, 155.1. Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.32; H, 7.87.

**General Procedure for Palladium- and Nickel-Catalyzed Reaction.** To a solution of the unsaturated carbohydrate (0.44 mmol) and $PdCl_2$(dppf) (31.9 mg, 0.044 mmol) or $NiCl_2$(dppe) (23 mg, 0.044 mmol) in 2 mL of THF was added at the desired temperature a solution of the Grignard reagent prepared from magnesium (64 mg, 2.6 mmol) and the appropriate bromide (2.18 mmol) in 5 mL of THF. The reaction was followed by TLC. After the time indicated in the tables, diethyl ether (50 mL) was added, and the ethereal solution was washed with water (2 × 10 mL) and dried. Concentration and column chromatography using the indicated solvents furnished the *C*-glycosides.

**(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)benzene (2a). α-Anomer:** oil; $R_f$ 0.41 (hexane/ethyl acetate, 4:1); $[\alpha]^{20}_D$ +18.5 (*c* 0.9, $CH_2Cl_2$); $^1$H NMR (300 MHz) $\delta$ 3.50−3.70 (m, 3H), 4.19 (brd, 1H, $J$ = 7.3 Hz), 4.46 and 4.61 (2d, 2 × 1H, $J$ = 11.5 Hz), 4.43 and 4.58 (2d, 2 × 1H, $J$ = 12.1 Hz), 5.30 (brs, 1H), 6.06 (brd, 1H, $J$ = 10.9 Hz), 6.13 (brd, 1H, $J$ = 10.9 Hz), 7.20−7.50 (m, 15H); $^{13}$C NMR (50 MHz) $\delta$ 69.1, 70.1, 70.7, 71.1, 73.2, 74.1, 127.1, 127.5, 127.7, 127.8, 127.9,

128.0, 128.1, 128.3, 128.3, 128.3, 129.5, 138.2, 138.2, 139.5. Anal. Calcd for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78. Found: C, 80.37; H, 6.69.

***β*-Anomer:** oil; $R_f$ 0.46 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +60.8 (*c* 0.7, $CH_2Cl_2$); $^1$H NMR (300 MHz) $\delta$ 3.60−3.90 (m, 3H), 4.16 (dm, 1H, $J$ = 8.6 Hz), 4.51 and 4.66 (2d, 2 × 1H, $J$ = 11.5 Hz), 4.56 and 4.64 (2d, 2 × 1H, $J$ = 12.1 Hz), 5.18 (brs, 1H), 5.86 (ddd, 1H, $J$ = 10.3, 1.6, 1.6 Hz), 6.01 (ddd, 1H, $J$ = 10.3, 2.0, 2.0 Hz), 7.20−7.40 (m, 15H); $^{13}$C NMR (50 MHz) $\delta$ 69.9, 70.5, 71.2, 73.4, 77.4, 77.8, 125.8, 126.0, 127.1, 127.5, 127.9, 128.2, 128.3, 128.4, 128.5, 131.7, 138.1, 138.4, 140.8. Anal. Calcd for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78. Found: C, 80.38; H, 6.82.

**[4,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl]benzene (2b). α-Anomer:** oil; $R_f$ 0.30 (petroleum ether/ethyl acetate, 30:1); $[\alpha]^{20}_D$ +3.9 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 0.02 (s, 3H), 0.04 (s, 3H), 0.07 (s, 3H), 0.08 (s, 3H), 0.87 (s, 9H), 0.89 (s, 9H), 3.41 (ddd, 1H, $J$ = 8.1, 6.2, 2.3 Hz), 3.70 (dd, 1H, $J$ = 11.1, 6.2 Hz), 3.85 (dd, 1H, $J$ = 11.1, 2.3 Hz), 4.20 (dq, 1H, $J$ = 8.1, 1.9 Hz), 5.28 (m, 1H), 5.88 (ddd, 1H, $J$ = 10.3, 1.9, 1.9 Hz), 6.07 (ddd, 1H, $J$ = 10.3, 3.1, 1.7 Hz), 7.25−7.49 (m, 5H); $^{13}$C NMR (50 MHz) $\delta$ −5.2, −5.0, −4.6, −4.0, 18.1, 18.5, 25.9, 26.1, 63.4, 64.3, 73.7, 74.6, 127.5, 127.6, 128.4, 128.5, 130.9, 140.4. Anal. Calcd for $C_{24}H_{42}O_3Si_2$: C, 66.30; H, 9.74. Found: C, 66.51; H, 9.84.

***β*-Anomer:** oil; $R_f$ 0.52 (petroleum ether/ethyl acetate, 30:1); $[\alpha]^{20}_D$ +189.1 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 0.04 (s, 6H), 0.13 (s, 3H), 0.14 (s, 3H), 0.90 (s, 9H), 0.93 (s, 9H), 3.51 (ddd, 1H, $J$ = 8.5, 4.5, 2.1 Hz), 3.84 (dd, 1H, $J$ = 11.4, 4.5 Hz), 3.93 (dd, 1H, $J$ = 11.4, 2.1 Hz), 4.38 (dd, 1H, $J$ = 8.5, 2.9 Hz), 5.16 (d, 1H, $J$ = 2.9 Hz), 5.77 (s, 2H), 7.27−7.36 (m, 5H); $^{13}$C NMR (50 MHz) $\delta$ −5.0, −4.9, −4.6, −4.1, 18.2, 18.6, 26.0, 26.1, 63.1, 63.6, 77.3, 80.7, 127.1, 127.8, 128.4, 129.9, 130.7, 141.5. Anal. Calcd for $C_{24}H_{42}O_3Si_2$: C, 66.30; H, 9.74. Found: C, 66.00; H, 9.71.

**1-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)-4-methylbenzene (3a). α-Anomer:** oil; $R_f$ 0.62 (hexane/ethyl acetate, 5:1); $[\alpha]^{20}_D$ −2.6 (*c* 1.1, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 2.2 (s, 3H), 3.50−3.70 (m, 3H), 4.21 (brd, 1H, $J$ = 7.0 Hz), 4.44 and 4.59 (2d, 2 × 1H, $J$ = 12.1 Hz), 4.48 and 4.62 (2d, 2 × 1H, $J$ = 11.5 Hz), 5.30 (brs, 1H), 6.06 (dm, 1H, $J$ = 10.4 Hz), 6.14 (dm, 1H, $J$ = 10.4 Hz), 7.10−7.40 (m, 14H); $^{13}$C NMR (50 MHz) $\delta$ 21.1, 69.2, 70.2, 70.5, 71.1, 73.2, 74.0, 127.0, 127.5, 127.7, 127.85, 127.9, 128.1, 128.3, 128.4, 129.0, 129.7, 136.4, 137.6, 138.2. Anal. Calcd for $C_{27}H_{28}O_3$: C, 80.97; H, 7.05. Found: C, 80.48; H, 7.35.

***β*-Anomer:** oil; $R_f$ 0.54 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +171.0 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 2.33 (s, 3H), 3.70−3.90 (m, 3H), 4.15 (dm, 1H, $J$ = 8.4 Hz), 4.51 and 4.66 (2d, 2 × 1H, $J$ = 11.5 Hz), 4.55 and 4.63 (2d, 2 × 1H, $J$ = 12.3 Hz), 5.15 (brs, 1H), 5.84 (dt, 1H, $J$ = 10.3, 1.4 Hz), 6.00 (ddd, 1H, $J$ = 10.3, 2.0, 1.8 Hz), 7.10−7.40 (m, 14H); $^{13}$C NMR (50 MHz) $\delta$ 21.3, 70.1, 70.7, 71.3, 73.5, 77.4, 78.0, 126.0, 127.2, 127.6, 127.9, 128.0, 128.4, 129.2, 131.9, 137.7, 137.9, 138.2, 138.6. Anal. Calcd for $C_{27}H_{28}O_3$: C, 80.97; H, 7.05. Found: C, 80.54; H, 7.20.

**1-[4,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl]-4-methylbenzene (3b). α-Anomer:** oil; $R_f$ 0.38 (petroleum ether/ethyl acetate, 30:1); $[\alpha]^{20}_D$ −3.1 (*c* 1.3, $CH_2Cl_2$); $^1$H NMR (300 MHz) $\delta$ 0.02 (s, 3H), 0.03 (s, 3H), 0.07 (s, 3H), 0.10 (s, 3H), 0.86 (s, 9H), 0.88 (s, 9H), 2.33 (s, 3H), 3.40 (ddd, 1H, $J$ = 8.0, 6.2, 2.3 Hz), 3.68 (dd, 1H, $J$ = 11.1, 2.3 Hz), 3.82 (dd, 1H, $J$ = 11.1, 6.2 Hz), 4.16 (dm, 1H, $J$ = 8.0 Hz), 5.23 (brs, 1H), 5.86 (ddd, 1H, $J$ = 10.4, 3.1, 1.8 Hz), 6.03 (dt, 1H, $J$ = 10.4, 1.8 Hz), 7.14 (d, 2H, $J$ = 7.5 Hz), 7.33 (d, 2H, $J$ = 7.5 Hz); $^{13}$C NMR (50 MHz) $\delta$ −5.2, −5.0, −4.6, −4.0, 18.1, 18.5, 21.2, 25.9, 26.1, 63.4, 64.3, 73.6, 74.3, 127.6, 128.6, 129.0, 130.8, 137.1, 137.4. Anal. Calcd for $C_{25}H_{44}O_3Si_2$: C, 66.91; H, 9.88. Found: C, 66.50; H, 9.81.

***β*-Anomer:** oil; $R_f$ 0.40 (petroleum ether/ethyl acetate, 30:1); $[\alpha]^{20}_D$ +145.5 (*c* 1.1, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 0.04 (s, 6H), 0.14 (s, 3H), 0.15 (s, 3H), 0.90 (s, 9H), 0.94 (s, 9H), 2.35 (s, 3H), 3.51 (ddd, 1H, $J$ = 8.5, 4.6, 1.9 Hz), 3.84 (brdd, 1H, $J$ = 11.4, 4.6 Hz), 3.93 (brdd, 1H, $J$ = 11.4, 1.9 Hz), 4.38 (brdd, 1H, $J$ = 8.5, 2.8 Hz), 5.13 (brd, 1H, $J$ = 2.8 Hz), 5.76 (brs, 2H), 7.14 (d, 2H, $J$ = 8.7 Hz), 7.25 (d, 2H, $J$ = 8.7 Hz); $^{13}$C NMR (50 MHz) $\delta$ −5.1, −5.0, −4.7, −4.2, 18.1, 18.5, 21.2, 25.9, 26.0, 62.7, 63.1, 77.2, 80.8, 127.0, 128.0, 129.99, 129.7, 130.8, 137.3, 138.4. Anal. Calcd for $C_{25}H_{44}O_3Si_2$: C, 66.91; H, 9.88. Found: C, 66.63; H, 9.78.

**1-(4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-2-methylbenzene (4a):** oil; $R_f$ 0.50 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +38.1 (*c* 1.1, $CH_2Cl_2$); $^1$H NMR (300 MHz) $\delta$ 2.16 (s, 3H), 3.50−3.70 (m, 3H), 4.22 (dt, 1H, $J$ = 7.8, 2.0 Hz), 4.52 and 4.65 (2d, 2 × 1H, $J$ = 11.5 Hz), 4.43 and 4.55 (2d, 2 × 1H, $J$ = 12.2 Hz), 5.48 (m, 1H), 6.02 (ddd, 1H, $J$ = 10.4, 3.0, 1.6 Hz), 6.20 (dt, 1H, $J$ = 10.4, 2.0 Hz), 7.10−7.40 (m, 15H); $^{13}$C NMR (50 MHz) $\delta$ 19.2, 69.0, 70.4, 71.2, 71.6, 73.1, 125.2, 127.5, 127.7, 127.8, 127.9, 128.2, 128.4, 128.7, 129.8, 130.7, 136.7, 138.2, 138.3. Anal. Calcd for $C_{27}H_{28}O_3$: C, 80.97; H, 7.05. Found: C, 80.61; H, 7.14.

**1-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)-4-methoxybenzene (5a). α-Anomer:** oil; $R_f$ 0.46 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ −3.8 (*c* 0.7, $CH_2Cl_2$); $^1$H NMR (300 MHz) $\delta$ 3.50−3.70 (m, 3H), 3.79 (s, 3H), 4.19 (dm, 1H, $J$ = 7.5 Hz), 4.48 and 4.62 (2d, 2 × 1H, $J$ = 11.4 Hz), 4.44 and 4.58 (2d, 2 × 1H, $J$ = 12.1 Hz), 5.26 (brs, 1H), 6.04 (ddd, 1H, $J$ = 10.4, 2.9, 1.5 Hz), 6.13 (dt, 1H, $J$ = 10.4, 1.8 Hz), 6.90 (brd, 2H, $J$ = 8.6 Hz), 7.20−7.40 (m, 14H); $^{13}$C NMR (50 MHz) $\delta$ 55.3, 69.2, 70.3, 71.2, 73.3, 73.9, 113.7, 127.1, 127.6, 127.8, 127.9, 128.0, 128.3, 128.4, 129.6, 129.8, 131.6, 138.3, 159.4. Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78. Found: C, 77.73; H, 6.67.

***β*-Anomer:** oil; $R_f$ 0.40 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +175.8 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 3.80 (s, 3H), 3.60−3.90 (m, 3H), 4.15 (dm, 1H, $J$ = 8.7 Hz), 4.51 and 4.66 (2d, 2 × 1H, $J$ = 11.5 Hz), 4.55 and 4.63 (2d, 2 × 1H, $J$ = 12.2 Hz), 5.14 (brs, 1H), 5.84 (brd, 1H, $J$ = 10.3 Hz), 6.01 (brd, 1H, $J$ = 10.3 Hz), 6.89 (brd, 2H, $J$ = 8.6 Hz), 7.20−7.40 (m, 12H); $^{13}$C NMR (50 MHz) $\delta$ 55.5, 70.2, 70.8, 71.5, 73.6, 77.3, 78.1, 114.1, 126.2, 127.7, 128.0, 128.2, 128.4, 128.5, 128.6, 128.8, 132.1, 133.2, 138.3, 138.7, 159.6. Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78. Found: C, 77.32; H, 6.49.

**1-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)-3-methoxybenzene (6a). α-Anomer:** oil; $R_f$ 0.40 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +9.1 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz) $\delta$ 3.63−3.75 (m, 3H), 3.75 (s, 3H), 4.17 (brd, 1H, $J$ = 7.9 Hz), 4.47 and 4.59 (2d, 2 × 1H, $J$ = 12.0 Hz), 4.49 and 4.62 (2d, 2 × 1H, $J$ = 12.0 Hz), 5.28 (brs, 1H), 6.11 (s, 2H), 6.83 (dd, 1H, $J$ = 8.4, 2.0 Hz), 6.99 (brd, 1H, $J$ = 7.9 Hz), 7.02 (d, 1H, J = 2.0 Hz), 7.21−7.32 (m, 11H); $^{13}$C NMR (50 MHz) $\delta$ 55.2, 69.5, 70.5, 71.1, 71.3, 73.6, 74.2, 113.3, 113.5, 120.2, 127.1, 127.6, 127.7, 127.9, 128.3, 128.4, 129.3, 129.6, 138.2, 141.2, 159.7. Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78. Found: C, 77.69; H, 6.69.

***β*-Anomer:** oil; $R_f$ 0.46 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +169.0 (*c* 0.9, $CH_2Cl_2$); $^1$H NMR (300 MHz) $\delta$ 3.71−3.86 (m, 3H), 3.79 (s, 3H), 4.16 (dm, 1H, $J$ = 8.7 Hz), 4.52 and 4.66 (2d, 2 × 1H, $J$ = 11.5 Hz), 4.57 and 4.63 (2d, 2 × 1H, $J$ = 12.3 Hz), 5.17 (m, 1H), 5.86 (ddd, 1H, $J$ = 10.4, 1.7, 1.5 Hz), 6.00 (ddd, 1H, $J$ = 10.4, 2.2, 1.9 Hz), 6.82 (dd, 1H, $J$ = 8.3, 2.7 Hz), 6.91 (brs, 1H), 6.93 (brd, 1H), 7.22−7.37 (m, 11H); $^{13}$C NMR (50 MHz) $\delta$ 55.3, 70.0, 70.6, 71.3, 73.5, 77.4, 77.9, 112.7, 113.6, 119.5, 126.1, 127.6, 127.9, 128.0, 128.4, 128.5, 129.6, 131.7, 138.1, 138.5, 142.4, 159.8. Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78. Found: C, 77.57; H, 6.68.

**1-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)-2-methoxybenzene (7a). α-Anomer:** oil; $R_f$ 0.44 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +15.5 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz) $\delta$ 3.66 (dd, 1H, $J$ = 10.5, 3.4 Hz), 3.70 (dd, 1H, $J$ = 10.5, 4.6 Hz), 3.83 (s, 3H), 3.87 (ddd, 1H, $J$ = 7.4, 4.6, 3.4 Hz), 4.09 (brd, 1H, $J$ = 7.4 Hz), 4.48 and 4.57 (2d, 2 × 1H, $J$ = 12.0 Hz), 4.52 and 4.65 (2d, 2 × 1H, $J$ = 11.4 Hz), 5.69 (brs, 1H), 6.02 (ddd, 1H, $J$ = 10.4, 2.6, 1.3 Hz), 6.10 (ddd, 1H, $J$ = 10.4, 1.8, 1.8 Hz), 6.89 (d, 1H, $J$ = 8.2 Hz), 6.91 (dd, 1H, $J$ = 7.5, 7.5 Hz), 7.20−7.30 (m, 11H), 7.44 (dd, 1H, $J$ = 7.5, 1.6 Hz); $^{13}$C NMR (50 MHz) $\delta$ 55.6, 68.8, 69.4, 70.3, 70.9, 71.5, 73.2, 110.8, 120.1, 126.3, 127.4, 127.5, 127.7, 127.8, 127.9,

128.3, 128.4, 128.6, 129.2, 130.3, 138.4, 138.4, 157.4. Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78. Found: C, 77.44; H, 6.69.

***β*-Anomer:** oil; $R_f$ 0.50 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +151.0 (*c* 1.3, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 3.83 (s, 3H), 3.70−3.90 (m, 3H), 4.17 (dm, 1H, $J$ = 8.5 Hz), 4.52 and 4.66 (2d, 2 × 1H, $J$ = 11.5 Hz), 4.59 and 4.67 (2d, 2 × 1H, $J$ = 12.3 Hz), 5.61 (brs, 1H), 5.89 (brd, 1H, $J$ = 10.8 Hz), 5.94 (brd, 1H, $J$ = 10.8 Hz), 6.80−7.10 (m, 3H), 7.20−7.50 (m, 11H); $^{13}$C NMR (50 MHz) $\delta$ 55.5, 70.1, 70.7, 71.2, 71.6, 73.4, 78.0, 110.3, 120.9, 125.3, 127.3, 127.5, 127.8, 128.0, 128.4, 128.5, 128.6, 131.8, 138.3, 138.7, 156.1. Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78. Found: C, 77.63; H, 6.50.

**1-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)-3,4-(methylenedioxy)benzene (8a). α-Anomer:** oil; $R_f$ 0.37 (hexane/ethyl acetate, 4:1); $[\alpha]^{20}_D$ +11.7 (*c* 0.8, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 3.50−3.70 (m, 3H), 4.19 (dm, 1H, $J$ = 7.1 Hz), 4.47 and 4.61 (2d, 2 × 1H, $J$ = 11.5 Hz), 4.44 and 4.58 (2d, 2 × 1H, $J$ = 12.1 Hz), 5.20 (brs, 1H), 5.91 (s, 2H), 6.01 (ddd, 1H, $J$ = 10.4, 2.5, 1.2 Hz), 6.12 (ddd, 1H, $J$ = 10.4, 1.7, 1.7 Hz), 6.75 (d, 1H, $J$ = 8.0 Hz), 6.90 (dd, 1H, $J$ = 8.0, 1.4 Hz), 6.95 (d, 1H, $J$ = 1.4 Hz), 7.20−7.40 (m, 10H); $^{13}$C NMR (50 MHz) $\delta$ 69.1, 70.1, 70.4, 71.1, 73.3, 73.9, 101.0, 107.9, 108.8, 121.8, 125.2, 127.2, 127.5, 127.7, 127.8, 127.9, 128.0, 128.1, 128.1, 128.3, 128.4, 129.5. Anal. Calcd for $C_{27}H_{26}O_5$: C, 75.33; H, 6.09. Found: C, 75.29; H, 6.01.

***β*-Anomer:** oil; $R_f$ 0.38 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +162.5 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 3.70−3.90 (m, 3H), 4.16 (dm, 1H, $J$ = 8.3 Hz), 4.52 and 4.68 (2d, 2 × 1H, $J$ = 11.5 Hz), 4.57 and 4.64 (2d, 2 × 1H, $J$ = 12.2 Hz), 5.12 (brs, 1H), 5.84 (ddd, 1H, $J$ = 10.3, 2.2, 1.8 Hz), 5.95 (s, 2H), 6.01 (dt, 1H, $J$ = 10.3, 1.6 Hz), 6.78 (dd, 1H, $J$ = 7.5, 1.0 Hz), 6.82 (d, 1H, $J$ = 1.0 Hz), 6.84 (d, 1H, $J$ = 7.5 Hz), 7.20−7.40 (m, 10H); $^{13}$C NMR (50 MHz) $\delta$ 70.0, 70.6, 71.4, 73.5, 77.3, 77.9, 101.1, 108.0, 108.2, 120.9, 126.3, 127.6, 127.9, 127.9, 128.0, 128.4, 128.5, 131.7, 134.8, 138.1, 138.5, 147.4, 147.8. Anal. Calcd for $C_{27}H_{26}O_5$: C, 75.33; H, 6.09. Found: C, 75.20; H, 6.02.

**1-(4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-4-chlorobenzene (9a). α-Anomer:** oil; $R_f$ 0.42 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +1.9 (*c* 0.9, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 3.50−3.70 (m, 3H), 4.17 (dm, 1H, $J$ = 7.4 Hz), 4.46 and 4.59 (2d, 2 × 1H, $J$ = 12.1 Hz), 4.48 and 4.62 (2d, 2 × 1H, $J$ = 11.5 Hz), 5.28 (brs, 1H), 6.05 (ddd, 1H, $J$ = 10.4, 2.7, 1.3 Hz), 6.15 (dt, 1H, $J$ = 10.4, 1.8 Hz), 7.20−7.40 (m, 14H); $^{13}$C NMR (50 MHz) $\delta$ 69.1, 70.0, 70.8, 71.3, 73.3, 73.4, 127.6, 128.9, 128.0, 128.3, 128.4, 128.5, 129.1, 129.4, 133.8, 138.1. Anal. Calcd for $C_{26}H_{25}O_3Cl$: C, 74.19; H, 5.99. Found: C, 73.92; H, 5.82.

**1-[4,6-Di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-*β*-D-*erythro*-hex-2-enopyranosyl]-4-chlorobenzene (9b). *β*-Anomer:** oil; $R_f$ 0.49 (petroleum ether/dichloromethane, 10:3); $[\alpha]^{20}_D$ +190.1 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 0.03 (s, 6H), 0.13 (s, 3H), 0.14 (s, 3H), 0.90 (s, 9H), 0.93 (s, 9H), 3.49 (ddd, 1H, $J$ = 8.4, 4.4, 2.2 Hz), 3.83 (dd, 1H, $J$ = 11.4, 4.4 Hz), 3.92 (dd, 1H, $J$ = 11.4, 2.2 Hz), 4.37 (ddt, 1H, $J$ = 8.4, 3.0, 1.5 Hz), 5.13 (brs, 1H), 5.71 (dt, 1H, $J$ = 10.2, 1.5 Hz), 5.80 (ddd, 1H, $J$ = 10.2, 1.5, 1.5 Hz), 7.24−7.34 (m, 4H); $^{13}$C NMR (50 MHz) $\delta$ −5.0, −4.9, −4.7, −4.2, 18.1, 18.6, 25.9, 26.1, 62.9, 63.4, 76.6, 80.7, 128.5, 128.6, 130.1, 130.4, 133.5, 140.0. Anal. Calcd for $C_{24}H_{41}O_3Si_2Cl$: C, 61.44; H, 8.81. Found: C, 61.55; H, 8.92.

**4-[(*tert*-Butyldimethylsilyl)oxy]-1-(4,6-di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)benzene (10a). α-Anomer:** oil; $R_f$ 0.53 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ −9.2 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 0.19 (s, 6H), 0.99 (s, 9H), 3.58−3.71 (m, 3H), 3.95 (brd, 1H, $J$ = 7.2 Hz), 4.45 and 4.60 (2d, 2 × 1H, $J$ = 12.1 Hz), 4.56 and 4.64 (2d, 2 × 1H, $J$ = 11.9 Hz), 5.27 (brs, 1H), 6.05 (dm, 1H, $J$ = 10.5 Hz), 6.16 (dm, 1H, $J$ = 10.5 Hz), 6.80 (brd, 2H, $J$ = 8.5 Hz), 7.27−7.32 (m, 12H); $^{13}$C NMR (50 MHz) $\delta$ −4.3, 18.3, 25.8, 69.3, 70.3, 70.4, 71.2, 73.3, 73.9, 119.9, 127.1, 127.6, 127.8, 127.9, 128.0, 128.4, 128.5, 129.6, 129.9, 132.3, 138.3, 138.3, 155.5. Anal. Calcd for $C_{32}H_{40}O_4Si$: C, 74.38; H, 7.80. Found: C, 74.01; H, 7.75.

***β*-Anomer:** oil; $R_f$ 0.60 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +123.8 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 0.16 (s, 6H), 0.96 (s, 9H), 3.60−3.84 (m, 3H), 4.13 (dm, 1H, $J$ = 8.2 Hz), 4.49 and 4.54 (2d, 2 × 1H, $J$ = 11.5 Hz), 4.62 and 4.64 (2d, 2 × 1H, $J$ = 12.1 Hz), 5.12 (brs, 1H), 5.83 (ddd, 1H, $J$ = 10.3, 1.5, 1.3 Hz), 5.98 (dt, 1H, $J$ = 10.3, 1.9 Hz), 6.78 (d, 2H, $J$ = 8.5 Hz), 7.19 (d, 2H, $J$ = 8.5 Hz), 7.20−7.34 (m, 10H); $^{13}$C NMR (50 MHz) $\delta$ −4.2, 18.3, 25.9, 70.1, 70.7, 71.4, 73.6, 77.3, 78.1, 120.2, 126.1, 127.7, 127.9, 128.0, 128.1, 128.5, 128.6, 128.7, 132.1, 133.8, 138.3, 138.6, 155.6. Anal. Calcd for $C_{32}H_{40}O_4Si$: C, 74.38; H, 7.80. Found: C, 73.79; H, 7.90.

**4-[(*tert*-Butyldimethylsilyl)oxy]-1-[4,6-di-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-*β*-D-*erythro*-hex-2-enopyranosyl]benzene (10b):** oil; $R_f$ 0.31 (petroleum ether/dichloromethane, 5:1); $[\alpha]^{20}_D$ +101.2 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ −0.07 (s, 3H), −0.06 (s, 3H), 0.04 (s, 3H), 0.06 (s, 3H), 0.10 (s, 6H), 0.80 (s, 9H), 0.84 (s, 9H), 0.90 (s, 9H), 3.40 (ddd, 1H, $J$ = 8.4, 4.6, 2.0 Hz), 3.73 (dd, 1H, $J$ = 11.4, 4.6 Hz), 3.83 (dd, 1H, $J$ = 11.4, 2.0 Hz), 4.27 (dd, 1H, $J$ = 8.4, 2.9 Hz), 5.00 (brd, 1H, $J$ = 2.9 Hz), 5.68 (s, 2H), 6.71 (brd, 2H, $J$ = 8.5 Hz), 7.11 (brd, 2H, $J$ = 8.5 Hz); $^{13}$C NMR (50 MHz) $\delta$ −5.1, −5.0, −4.7, −4.4, −4.2, 18.1, 18.3, 18.5, 25.8, 25.9, 26.0, 63.0, 63.6, 76.8, 80.7, 119.9, 128.3, 129.8, 130.7, 134.1, 155.2. Anal. Calcd for $C_{30}H_{56}O_4Si_3$: C, 63.77; H, 9.99. Found: C, 64.06; H, 10.11.

**1-(4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-4-(dimethoxymethyl)benzene (11a):** oil; $R_f$ 0.31 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +4.1 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 3.33 (s, 6H), 3.57−3.74 (m, 3H), 4.20 (brd, 1H, $J$ = 8.1 Hz), 4.47 and 4.61 (2d, 2 × 1H, $J$ = 12.1 Hz), 4.50 and 4.64 (2d, 2 × 1H, $J$ = 11.5 Hz), 5.31 (s, 1H), 5.39 (s, 1H), 6.09 (d, 1H, $J$ = 10.5 Hz), 6.16 (d, 1H, $J$ = 10.5 Hz), 7.27−7.44 (m, 14H); $^{13}$C NMR (50 MHz) $\delta$ 52.6, 69.2, 70.1, 70.8, 71.1, 73.2, 73.8, 102.9, 126.7, 126.8, 127.2, 127.5, 127.7, 127.8, 127.8, 127.9, 128.3, 128.4, 129.5, 137.7, 138.2, 138.2, 139.8. Anal. Calcd for $C_{29}H_{32}O_5$: C, 75.63; H, 7.00. Found: C, 75.45; H, 7.14.

**1-[4,6-Bis-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-*β*-D-*erythro*-hex-2-enopyranosyl]-4-(methoxymethoxy)benzene (12a). *β*-Anomer:** oil; $R_f$ 0.37 (petroleum ether/diethyl ether, 30:1); $[\alpha]^{20}_D$ +160.4 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 0.04 (s, 6H), 0.14 (s, 3H), 0.15 (s, 3H), 0.90 (s, 9H), 0.94 (s, 9H), 3.49 (s, 3H), 3.50 (m, 1H), 3.83 (dd, 1H, $J$ = 11.4, 4.4 Hz), 3.92 (dd, 1H, $J$ = 11.4, 1.9 Hz), 4.36 (brdd, 1H, $J$ = 8.6, 2.9 Hz), 5.12 (brd, 1H, $J$ = 2.4 Hz), 5.19 (s, 2H), 5.76 (brs, 2H), 7.01 (d, 2H, $J$ = 8.5 Hz), 7.28 (d, 2H, $J$ = 8.5 Hz); $^{13}$C NMR (50 MHz) $\delta$ −5.1, −5.0, −4.7, −4.2, 18.1, 18.5, 25.9, 26.0, 55.9, 62.9, 63.5, 76.8, 80.7, 94.5, 116.1, 128.3, 129.8, 130.7, 134.8, 156.9. Anal. Calcd for $C_{26}H_{46}O_5Si_2$: C, 63.11; H, 9.37. Found: C, 63.53; H, 9.56.

**1-(4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-4-vinylbenzene (13a):** oil; $R_f$ 0.50 (petroleum ether/ethyl acetate 5:1); $[\alpha]^{20}_D$ −26.5 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz) $\delta$ 3.57−3.71 (m, 3H), 4.20 (dm, 1H, $J$ = 7.5 Hz), 4.46 and 4.59 (2d, 2 × 1H, $J$ = 12.1 Hz), 4.48 and 4.62 (2d, 2 × 1H, $J$ = 11.5 Hz), 5.25 (dd, 1H, $J$ = 10.9, 0.9 Hz), 5.30 (m, 1H), 5.75 (dd, 1H, $J$ = 17.6, 0.9 Hz), 6.08 (ddd, 1H, $J$ = 10.4, 2.7, 1.4 Hz), 6.14 (dt, 1H, $J$ = 10.4, 1.7 Hz), 6.71 (dd, 1H, $J$ = 17.6, 10.9 Hz), 7.23−7.43 (m, 10H); $^{13}$C NMR (50 MHz) $\delta$ 69.4, 70.4, 71.0, 71.4, 73.5, 74.2, 114.3, 126.4, 127.5, 127.8, 128.0, 128.1, 128.2, 128.6, 128.6, 128.6, 129.7, 136.7. Anal. Calcd for $C_{28}H_{28}O_3$: C, 81.52; H, 6.84. Found: C, 81.31; H, 6.81.

**2-(4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)thiophene (14a):** oil; $R_f$ 0.24 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +22.4 (*c* 1.2, $CH_2Cl_2$); $^1$H NMR (200 MHz) $\delta$ 3.50−3.80 (m, 3H), 4.24 (brd, 1H, $J$ = 8.3 Hz), 4.45 and 4.60 (2d, 2 × 1H, $J$ = 12.1 Hz), 4.47 and 4.61 (2d, 2 × 1H, $J$ = 11.4 Hz), 5.50 (brs, 1H), 6.08 (d, 1H, $J$ = 11.0 Hz), 6.14 (d, 1H, $J$ = 11.0 Hz), 6.90−7.00 (m, 2H), 7.20−7.30 (m, 11H); $^{13}$C NMR (50 MHz) $\delta$ 69.0, 70.1, 70.2, 70.5, 71.2, 73.3, 126.0, 126.6, 126.8, 127.5, 127.6, 127.7, 127.7, 127.8, 127.9, 127.3, 128.1, 128.3, 128.4, 128.6, 138.1, 138.2, 142.9. Anal. Calcd for $C_{24}H_{24}O_3S$: C, 73.44; H, 6.16. Found: C, 73.18; H, 5.98.

**1-(4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)naphthalene (15a):** oil; $R_f$ 0.38 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ −73.8 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300

MHz) δ 3.59−3.76 (m, 3H), 4.25 (brdd, 1H, *J* = 7.8, 2.0 Hz), 4.46 and 4.60 (2d, 2 × 1H, *J* = 12.1 Hz), 4.51 and 4.65 (2d, 2 × 1H, *J* = 11.5 Hz), 5.47 (brs, 1H), 6.21 (s, 2H), 7.25−7.34 (m, 10H), 7.45−7.49 (m, 2H), 7.59 (dd, 1H, *J* = 8.4, 1.5 Hz), 7.78−7.85 (m, 4H); $^{13}$C NMR (50 MHz) δ 69.5, 70.6, 71.0, 71.5, 73.6, 74.5, 126.2, 126.4, 127.0, 127.6, 127.6, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5, 129.5, 133.1, 133.1, 137.0, 138.2, 138.3. Anal. Calcd for $C_{30}H_{28}O_3$: C, 82.54; H, 6.47. Found: C, 82.11; H, 6.45.

**α-(4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)toluene (16a):** oil; $R_f$ 0.48 (hexane/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +78.4 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz) δ 2.82 (dd, 1H, *J* = 13.5, 7.6 Hz), 3.08 (dd, 1H, *J* = 13.5, 6.8 Hz), 3.71 (d, 2H, *J* = 3.8 Hz), 3.91 (dt, 1H, *J* = 7.4, 3.8 Hz), 4.01 (dm, 1H, *J* = 7.4 Hz), 4.42 (m, 1H), 4.52 and 4.62 (2d, 2 × 1H, *J* = 12.0 Hz), 4.48 and 4.60 (2d, 2 × 1H, *J* = 11.2 Hz), 5.80 (ddd, 1H, *J* = 10.5, 2.7, 1.6 Hz), 5.95 (dt, 1H, *J* = 10.5, 2.1 Hz), 7.10−7.40 (m, 15H); $^{13}$C NMR (50 MHz) δ 39.7, 69.4, 70.1, 71.3, 72.0, 73.3, 73.7, 125.7, 126.3, 127.5, 127.7, 127.8, 127.9, 128.3, 128.3, 128.4, 129.4, 130.9, 138.1, 138.2. Anal. Calcd for $C_{27}H_{28}O_3$: C, 80.97; H, 7.05. Found: C, 80.43; H, 7.10.

**3-(4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)propene (17a):** oil; $R_f$ 0.52 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +47.3 (*c* 1.1, $CH_2Cl_2$); $^1$H NMR (300 MHz) δ 2.31 (ddd, 1H, *J* = 14.1, 7.6, 6.3 Hz), 2.49 (ddd, 1H, *J* = 14.1, 8.5, 5.9 Hz), 3.65 (dd, 1H, *J* = 10.4, 3.4 Hz), 3.69 (dd, 1H, *J* = 10.4, 4.3 Hz), 3.82 (ddd, 1H, *J* = 7.9, 4.3, 3.4 Hz), 3.99 (dm, 1H, *J* = 7.3 Hz), 4.25 (brdd, 1H, *J* = 6.3, 5.9 Hz), 4.45 and 4.60 (2d, 2 × 1H, *J* = 11.6 Hz), 4.52 and 4.62 (2d, 2 × 1H, *J* = 12.2 Hz), 5.08 (dm, 1H, *J* = 10.0 Hz), 5.10 (dm, 1H, *J* = 17.0 Hz), 5.84 (dm, 1H, *J* = 10.4 Hz), 5.93 (dm, 1H, *J* = 10.4 hz), 5.79−5.95 (m, 1H), 7.20−7.50 (m, 10H); $^{13}$C NMR (50 MHz) δ 38.1, 69.3, 70.0, 71.1, 71.4, 72.2, 73.4, 117.4, 125.7, 127.6, 127.8, 127.9, 128.0, 128.4, 128.5, 131.2, 134.7, 138.3, 138.4. Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48. Found: C, 78.75; H, 7.39.

**(4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)ethylene (18a):** oil; $R_f$ 0.40 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ +34.6 (*c* 0.9, $CH_2Cl_2$); $^1$H NMR (300 MHz) δ 3.48−3.76 (m, 3H), 4.09 (dm, 1H, *J* = 8.1 Hz), 4.45 and 4.60 (2d, 2 × 1H, *J* = 11.5 Hz), 4.52 and 4.63 (2d, 2 × 1H, *J* = 12.2 Hz), 4.73 (m, 1H), 5.24 (dm, 1H, *J* = 10.3 Hz), 5.29 (dm, 1H, *J* = 17.3 Hz), 5.83 (ddd, 1H, *J* = 10.4, 3.2, 1.7 Hz), 5.78−6.03 (m, 1H), 5.99 (ddd, 1H, *J* = 10.4, 2.1, 2.1 Hz), 7.22−7.35 (m, 10H); $^{13}$C NMR (50 MHz) δ 69.3, 70.2, 70.9, 71.1, 73.3, 73.4, 117.4, 127.0, 127.7, 127.9, 128.0, 128.1, 128.5, 128.5, 129.3, 135.6, 138.3, 138.4. Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.09; H, 7.11.

**(4-*O*-Benzyl-2,3,6-trideoxy-L-*erythro*-hex-2-enopyranosyl)benzene (25). α-Anomer:** oil; $R_f$ 0.66 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ −20.6 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) δ 1.25 (d, 3H, *J* = 6.0 Hz), 3.69−3.77 (m, 2H), 4.60 and 4.70 (2d, 2 × 1H, *J* = 11.6 Hz), 5.21 (s, 1H), 6.07 (brd, 1H, *J* = 11.3 Hz), 6.14 (brd, 1H, *J* = 11.3 Hz), 7.25−7.45 (m, 10H); $^{13}$C NMR (50 MHz) δ 18.4, 67.9, 71.1, 73.7, 75.8, 126.7, 127.9, 128.0, 128.1, 128.1, 128.5, 128.7, 130.3, 138.5, 140.1. Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.23; H, 7.15.

***β*-Anomer:** oil; $R_f$ 0.70 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{20}_D$ −219.2 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (200 MHz) δ 1.38 (d, 3H, *J* = 5.9 Hz), 3.73 (dq, 1H, *J* = 8.4, 5.9 Hz), 3.85 (dm, 1H, *J* = 8.4 Hz), 4.60 and 4.73 (2d, 2 × 1H, *J* = 11.6 Hz), 5.14 (brs, 1H), 5.85 (brd, 1H, *J* = 10.3 Hz), 6.02 (brd, 1H, *J* = 10.3 Hz), 7.24−7.39 (m, 10H); $^{13}$C NMR (50 MHz) δ 19.2, 71.6, 74.5, 76.7, 77.8, 126.6, 127.6, 128.1, 128.3, 128.3, 128.8, 128.9, 131.9, 138.6, 141.2. Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.17; H, 7.10.

**(6-*O*-Benzyl-4-*O*-methyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranosyl)benzene (26):** oil; $R_f$ 0.59 (petroleum ether/ethyl acetate, 2:1); $[\alpha]^{20}_D$ −173.6 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz) δ 3.45 (s, 3H), 3.68 (dd, 1H, *J* = 10.2, 7.0 Hz), 3.75 (dd, 1H, *J* = 10.2, 5.4 Hz), 3.64−3.71 (m, 1H), 3.96 (ddd, 1H, *J* = 7.0, 5.4, 2.8 Hz), 4.49 and 4.56 (2d, 2 × 1H, *J* = 11.9 Hz), 5.35 (brs, 1H), 6.23 (ddd, 1H, *J* = 10.3, 2.8, 1.5 Hz), 6.32 (dd, 1H, *J* = 10.3, 2.8 Hz), 7.22−7.44 (m, 10H); $^{13}$C NMR (50 MHz) δ 56.8, 69.2, 70.2, 71.2, 73.3, 73.8, 114.9, 124.6, 126.4, 127.6, 127.7, 127.8, 128.5, 138.5, 139.3, 132.5. Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 78.07; H, 7.16.

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**Supporting Information Available:** $^1$H and $^{13}$C NMR spectra for new compounds having microanalyses which do not come within 0.45% for C calculated values (six compounds) (24 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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