Palladium-Mediated Cyclization on Carbohydrate Templates. 2. Synthesis of Enantiopure Tricyclic Compounds

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The bromo substituted unsaturated carbohydrates **3a**−**f** were prepared from 3,4,6-tri-*O*-acetyl-D-glucal by Ferrier reaction with the appropriate allylic or homoallylic alcohol, deacetylation followed by monosilylation with TBDMSCl, and then alkylation with $BrCH_2CBr{=}CH_2$. The *N*- and *C*-analogues **4a**,**b** were synthesized by palladium alkylation of the intermediate carbonate with $TsNHCH_2CBr{=}CH_2$ and $(MeO_2C)_2CHCH_2CBr{=}CH_2$, respectively. Treatment of the unsaturated carbohydrates **3a**, **4a**, and **4b** with a catalytic amount of $Pd(OAc)_2/PPh_3$ in CH_3CN/H_2O, in the presence of Bu_4NHSO_4 and NEt_3, afforded the tricyclic compounds **5**, **6**, and **7**, respectively. Under the same conditions, the analogue tricyclic compounds **8**, **9**, and **10** were formed starting from **3b**−**d**. In the case of compounds **3e** and **3f**, the formation of the bicyclic glucal **11** *via* an already described *β*-alkoxyelimination was only observed. Moreover, trapping of the *σ*-alkylpalladium intermediate obtained from **3e** with an external nucleophile yielded the 2-deoxy carbohydrate **12** and the 2,3-unsaturated sugar **13**, using respectively sodium formate and sodium tetraphenylborate.

Carbohydrates are readily available, enantiopure materials possessing a variety of attractive functional and stereochemical features. They are very useful intermediates for further synthetic transformations and particularly for the synthesis of polycyclic enantiopure compounds, such as furo- and pyrano[2,3-*b*]pyran, closely related to the structural framework of many natural products.[1] In this field, the free-radical route is an extremely efficient methodology for the cyclization of carbohydrate derivatives. The different strategies involve radicals located either on the carbohydrate and leading to bicyclo[2,2,2] or -[2,2,1] systems[2] or to fused rings[3] or on radicals located on a chain and cyclizing on a double bond external[4] or internal[5] to the sugar ring and allowing formation of bi- or tricyclic systems.

In recent years, increasing attention has been devoted to the organometallic-catalyzed cyclization of carbohydrates. Palladium-mediated cycloisomerization[6] and the Pauson−Khand reaction[7] of appropriate glycals have been studied as tools in the synthesis of complex carbo- and heterocyclic frameworks. These cyclizations generally occur with a high degree of stereoselectivity.

We recently described the use of an intramolecular palladium-catalyzed Heck reaction in carbohydrate chemistry, leading to bicyclic glucals *via* an unusual dealkoxypalladation pathway.[8] We also communicated preliminary results of a study concerning an easy access to heterotricyclic systems *via* this cyclization reaction.[9]

In the present paper, we describe a full account of our results concerning the applications and the limitations of this methodology for the synthesis of functionalized enantiopure heterotricyclic systems. It is to be noted that, after our initial report on the use of the Heck-type cyclization in carbohydrate chemistry, other authors have described interesting results leading to enantiopure fused furo- and pyrano[2,3-*b*]pyrans, using this strategy.[10]

Results and Discussion

Preparation of the Unsaturated Starting Carbohydrates. The requisite alkenyl 4,6-di-*O*-acetyl-2,3-

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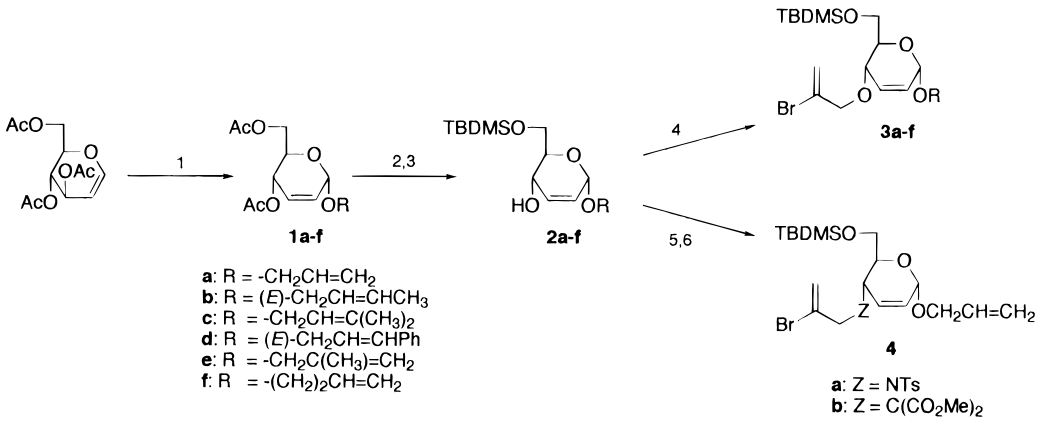
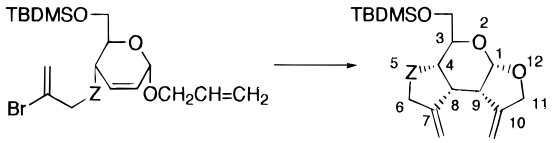
Scheme 1[a]

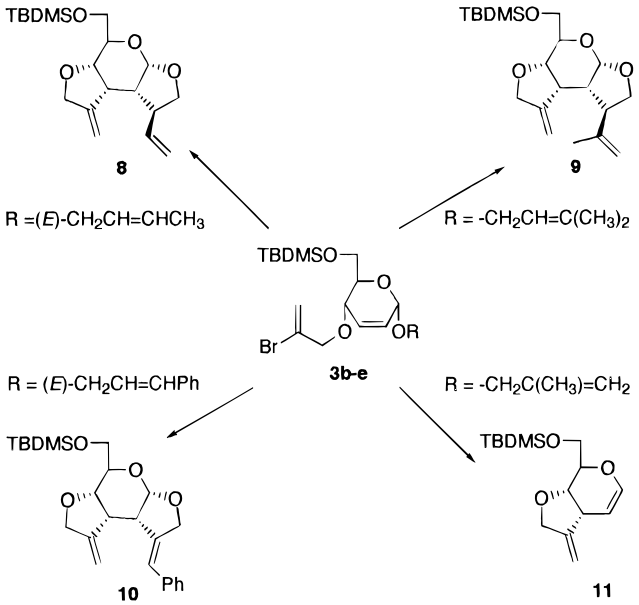


[a] Reagents and conditions: (1) ROH, $BF_3{\cdot}OEt_2$, rt; (2) cat. MeONa, MeOH, quant; (3) TBDMSCl, NEt_3, imidazole, CH_2Cl_2, rt, 24 h; (4) NaH, $BrCH_2CBr{=}CH_2$, THF, 60 °C, 24 h; (5) $ClCO_2Me$, DMAP, py, CH_2Cl_2, 0 °C to rt, 24 h; (6) for compound **4a** (**4b**): $TsNHCH_2CBr{=}CH_2$ [$(MeO_2C)_2CHCH_2CBr{=}CH_2$], Pd_2dba_3, dppb, THF, 60 °C, 24 h.

Scheme 2



Scheme 3



dideoxy-α-D-*erythro*-hex-2-enopyranosides (**1a**−**f**) were obtained in 40−75% yield from 3,4,6-tri-*O*-acetyl-D-glucal and the appropriate unsaturated alcohol using Ferrier's procedure (Scheme 1).[11] Deacetylation of **1a**−**f** using a catalytic amount of sodium methoxide in methanol afforded the diols, which were treated with TBDMSCl, NEt_3, and imidazole, in dichloromethane to give the monosilylated carbohydrates **2a**−**f** in 60−76% yield. Treatment of **2a**−**f** with NaH and 2,3-dibromopropene in THF at 60 °C gave the 4-*O*-alkylated carbohydrates **3a**−**f** in 63−84% yield.

Reaction of the unsaturated carbohydrate **2a** with methyl chloroformate gave the corresponding carbonate which was directly treated with $TsNHCH_2CBr{=}CH_2$ or $(MeO_2C)_2CHCH_2CBr{=}CH_2$ in THF at 60 °C in the presence of tris(dibenzylidene acetone)dipalladium(0) and 1,4-bis(diphenylphosphino)butane (dppb) and led respectively to the 4-*N*-alkylated carbohydrate **4a** (90% yield) and to the 4-*C*-alkylated carbohydrate **4b** (65% yield).

Palladium-Mediated Cyclization. The cyclization of compounds **3a**−**f** and **4a**,**b** was performed under the previously described conditions[8b] in the presence of $Pd(OAc)_2$, PPh_3, Bu_4NHSO_4, and NEt_3, at 80 °C in CH_3CN/H_2O (1/1) as the solvent.

Using these conditions, the unsaturated carbohydrate **3a** was transformed into the tricyclic compound **5**, after 24 h, in 75% yield (Scheme 2). This compound **5** shows characteristic chemical shifts, particularly at δ 5.59, 4.06, 3.60, 3.66, and 3.20 ppm, respectively, for the hydrogen atoms H-1, H-4, H-8, H-3, and H-9, with coupling constants $J_{1,9} = 6.6$, $J_{9,8} = 7.4$, $J_{8,4} = 7.4$, and $J_{4,3} = 7.4$ Hz, characteristic of a *cis*−*syn*−*cis* arrangement.[7d] Moreover, this relative stereochemistry was confirmed by NOE experiments. Irradiation of the H-9 signal at δ 3.20 ppm gave an enhancement of the signals corresponding to H-1 and H-8 of 16 and 12%, respectively, while irradiation of the H-8 signal showed an enhancement of the signals of H-9 and H-4 of 3% and 11%, respectively.

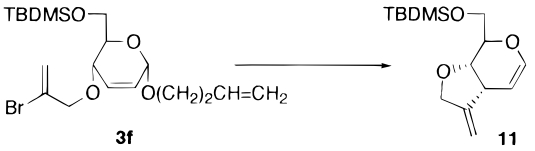
The *N*-tosyl derivative **4a** and the *C*-substituted carbohydrate **4b** gave under these conditions the tricyclic aza compound **6** and carba compound **7**, in 80 and 78% yield, respectively (Scheme 2). The ^1H and ^{13}C NMR spectra (see Experimental Section) are again characteristic of a *cis*−*syn*−*cis* junction of the cycles.

We then studied the influence of the aglycon's structure, particularly the degree and the position of the substitution on the double bond in our cyclization reaction.

The unsaturated sugars **3b** and **3c** gave respectively the tricyclic compounds **8** and **9** in 77% and 78% yield (Scheme 3). For compound **8**, the main ^1H NMR characteristics are the signals of the hydrogen atoms H-1, H-9, H-8, and H-4 at δ 5.52, 2.38, 2.90, and 3.34 ppm, respectively, with the coupling constants $J_{1,9} = 6.8$, $J_{9,8} = 6.0$, $J_{8,4} = 8.8$, and $J_{4,3} = 10.0$ Hz. For compound **9**, the chemical shifts for H-1, H-9, H-8, and H-4 are at δ 5.54, 2.58, 2.90, and 3.21 ppm, respectively, with $J_{1,9} =$

(11) Ferrier, R. J.; Prasad, M. J. *J. Chem. Soc. (C)* **1969**, 570.

Scheme 4



6.8, $J_{9,8} = 6.4$, and $J_{8,4} = 9.7$ Hz. These values are again in agreement with a *cis*−*syn*−*cis* relationship of the three cycles.[7d] The *exo* configuration of the vinyl group and so the *cis* relationship between H-9 and the vinyl group was expected from the high coupling constants (10.5 and 11.0 Hz) between H-9 and the allylic proton H-10. This stereochemistry was confirmed by NOE experiments. For product **8**, irradiation of the H-9 signal at δ 2.38 ppm shows an enhancement of the signals of H-1 (13.7%), H-8 (8.9%), and H-4 (2.5%) and more important, of the signals corresponding to the vinylic protons C*H*═ at δ 5.58 ppm (8.7%) and ═CH_2 at δ 5.06 ppm (2%) and no enhancement of the signal of the allylic proton H-10 at δ 3.06 ppm. For compound **9**, irradiation of the H-9 signal at δ 2.58 ppm shows again an enhancement of the signals of H-1 (13.9%), H-8 (8.7%), H-4 (1.9%), of the vinylic proton at δ 4.85 ppm (2.0%), and also of the methyl group at δ 1.66 ppm (7.7%); no enhancement of the allylic hydrogen H-10 was observed.

Cyclization of the unsaturated carbohydrate **3d** gave the tricyclic compound **10** in 79% yield (Scheme 3). The *cis*−*syn*−*cis* relationship of the three cycles is confirmed by the ^{1}H NMR spectrum, particularly by the coupling constants $J_{1,9} = 6.5$, $J_{9,8} = 6.8$, and $J_{8,4} = 6.9$ Hz. The *Z* configuration of the cinnamyl moiety was determined by NOE experiments. Effectively, enhancement of the H-9 signal (3.8%) was observed by irradiation of the ethylenic proton of the cinnamyl moiety at δ 6.8 ppm.

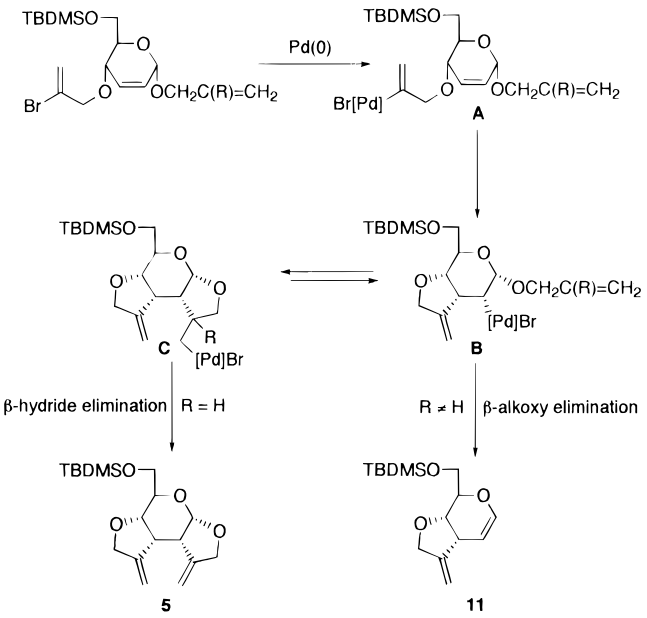
When the reaction was extended to the unsaturated carbohydrates **3c** and **3f** (Schemes 3 and 4), only the bicyclic compound **11** was obtained in 72% and 78% yield, respectively.

Discussion

The mechanism of this cyclization starts with the formation of a σ-vinylpalladium intermediate **A** by oxidative addition of compound **3** or **4** to the palladium(0) complex (Scheme 5). An association−insertion process, involving the unsaturation of the pyranose moiety, gives a new σ-alkylpalladium species **B**. Another association−insertion sequence involving the double bond of the aglycon moiety leads to the formation of the σ-alkylpalladium complex **C** *via* a 5-*exo*−*trig* process. In the case of **3a**−**d** and **4**, a β-hydride elimination occurs leading to the tricyclic compounds **5**−**10**. For **3e**, there is no hydrogen atom available for the β-hydride elimination and so the σ-alkylpalladium intermediate **B** leads to the bicyclic compound **11** *via* a β-dealkoxypalladation reaction, as shown in the preceeding paper.[8b] Concerning the cyclization of substrate **2f**, the formation of the bicyclic compound **11** instead of a tricyclic one indicates that 6-*exo*−*trig* cyclization is disfavored versus β-dealkoxypalladation.

The *exo* stereochemistry of compounds **8** and **9** or the *Z* stereochemistry for compound **10** can be explained by the mechanism proposed for the cyclization (Scheme 7). Starting from carbohydrates **3b**−**d**, the approach of the palladium complex is to the double bond of the aglycon, and so the cyclization leads to the *exo* σ-alkylpalladium

Scheme 5



complex, the formation of the *endo* σ-alkylpalladium being disfavored due to some steric effects. Compounds **8** and **9** are formed by the usual β-hydride elimination pathway. For compound **10**, the cyclization leads to the *exo* σ-alkylpalladium complex; however, the β-hydride elimination which is a *syn*-elimination process only leads to the *Z* isomer **10**.

Since the compound **3e** gave the bicyclic compound **11** under the standard conditions, we tried to trap the σ-alkylpalladium intermediate **C** by an external nucleophile, using Grigg's methodology,[12] expecting the formation of a tricyclic structure. The use of sodium formate as the trapping reagent in the case of compound **3e** gave a mixture of bicyclic compounds **11** and **12**, in 10% and 56% yield, respectively. The main ^{1}H NMR characteristics of the deoxycarbohydrate **12** are the signals of H-1 (δ 4.85 ppm), H-2 (δ 1.68 and 2.68 ppm), H-3 (δ 2.73 and 2.80 ppm), and H-4 (δ 3.95 ppm) and, more important, the coupling constants $J_{1,2} = 6.0$ Hz and 5.2 Hz, $J_{2,2} = 14.3$ Hz, $J_{2,3} = 9.3$ and 6.2 Hz, and $J_{3,4} = 7.3$ Hz. The formation of the bicyclic **12** indicates that, in this particular case, the σ-alkylpalladium intermediate **C** is less favored than **B**, probably due to some steric effects (Scheme 5).

When the cyclization of **3e** was carried out in the presence of sodium tetraphenylborate as the trapping reagent, a mixture of compounds **11** and **13** was obtained in 60% and 20% yield, respectively. Compound **13** was formed by trapping of the vinylpalladium intermediate **A** *via* a Suzuki-type reaction, and we never observed any compound resulting from the trapping of intermediate **B**. This result indicates the difficulty of trapping this intermediate **B** by a large nucleophile (Scheme 6). There is a competition with the β-dealkoxypalladation reaction, which is favored in this case.

Conclusion

The results reported here give a new insight into palladium-mediated cyclization in sugar chemistry. Thus, cyclization of unsaturated carbohydrates stereospecifi-

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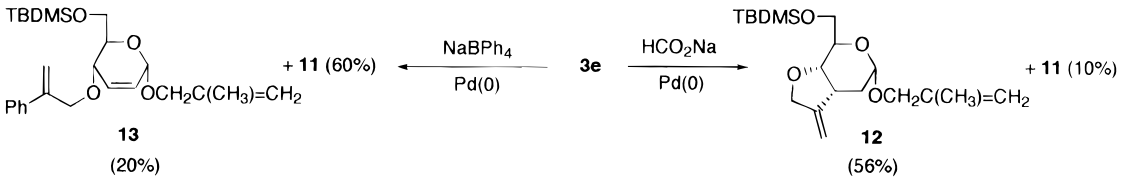
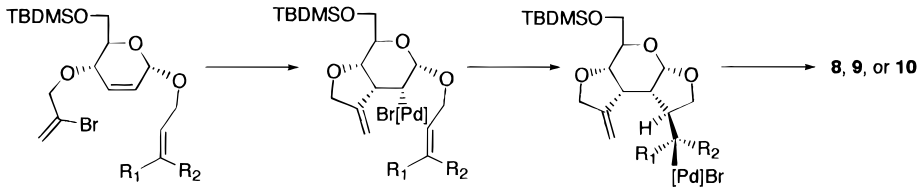
Scheme 6



Scheme 7



3b: $R_1 = CH_3$, $R_2 = H$
3c: $R_1 = R_2 = CH_3$
3d: $R_1 = Ph$, $R_2 = H$

cally gave the corresponding tricyclic systems. The reaction conditions are very mild and the yields good. The versatility of the pyranoside templates opens many synthetic possibilities, as well as the use of functionalized unsaturated chains. These endeavors as well as the use of these enantiopure synthons for the conversion to natural products will be reported 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). Compounds were visualized under UV light (254 nm) or by spraying with a H_2SO_4 solution and heating. 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 complexes were carried out in a Schlenck tube under a nitrogen atmosphere. 3,4,6-Tri-*O*-acetyl-D-glucal, 2,3-dibromopropene, Bu_4NHSO_4, TBDMSCl, DMAP, propenol, (*E*)-but-2-enol, 3-methylbut-2-enol, (*E*)-3-phenylprop-2-enol, 2-methylprop-2-enol, but-3-en-1-ol, $Pd(OAc)_2$, $Pd_2(dba)_3$, dppb, $NaBPh_4$, and HCO_2Na were purchased from Aldrich Chemical. Tosyl(2-bromoprop-2-enyl)amine,[13] and 1,1-bis(methoxycarbonyl)-3-bromobut-3-ene[14] were prepared by known procedures.

Standard Preparation of Alkenyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides (1a-f). To 3,4,6-tri-*O*-acetyl-D-glucal (5 g, 18.5 mmol) in 25 mL of benzene were added 2 equiv (37.0 mmol) of the allylic or homoallylic alcohol and 0.5 equiv (9.25 mmol, 1.15 mL) of $BF_3{\cdot}OEt_2$. The resulting mixture was stirred at room temperature until TLC showed no more starting glucal. After addition of Na_2CO_3 (5 g) and filtration of the solid, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent, to give compounds **1a**−**f**.

Standard Preparation of Alkenyl 6-*O*-(*tert*-Butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides (2a−f). The corresponding diacetate (8.66 mmol) was treated with a catalytic amount of sodium methoxide in methanol (100 mL) at room temperature. After evaporation of the solvent, the free hydroxyl unsaturated glycoside was obtained in quantitative yield and used without further purification. This diol was treated with 1.25 equiv of TBDMSCl (1.62 g, 10.77 mmol), 1.3 equiv of NEt_3 (1.6 mL, 11.2 mmol), and 0.05 equiv of imidazole (30 mg, 0.43 mmol) in CH_2Cl_2 (30 mL) at room temperature for *ca*. 24 h (until TLC analysis showed no more starting material). After addition of 25 mL of water and extraction with 3 × 30 mL of CH_2Cl_2, the organic layer was dried. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography using petroleum ether/ethyl acetate as the eluent to give compounds **2a**−**f**.

Preparation of Alkenyl 4-*O*-(2′-Bromoprop-2′-enyl)-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides (3a−f). To the 4-hydroxyl compound **2** (1.22 mmol) in 12 mL of dry THF was added 54 mg (1.34 mmol) of NaH (60%). The solution was stirred for 1 h at 60 °C and 488 mg (2.44 mmol) of 2,3-dibromopropene was added. After being stirred at 60 °C for 14 h, the solution was cooled, and the reaction was quenched with 10 mL of H_2O and extracted with 3 × 15 mL of Et_2O. After being dried, the solvent was removed under reduced pressure and the crude product was purified by column chromatography with petroleum ether/ethyl acetate as the eluent to afford the *O*-alkylated compound **3**.

Allyl 4-*O*-(2′-Bromoprop-2′-enyl)-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3a): yield 82%; oil; R_f 0.47 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +86.3 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (200 MHz) δ 6.06 (brd, 1H, J = 10.2 Hz), 5.94 (dddd, 1H, J = 5.1, 6.3, 10.3, 17.2 Hz), 5.82 (dd, 1H, J = 1.5, 3.0 Hz), 5.79 (ddd, 1H, J = 2.1, 2.6, 10.2 Hz), 5.61 (dd, 1H, J = 0.9, 1.5 Hz), 5.30 (ddd, 1H, J = 1.6, 3.0, 17.2 Hz), 5.20 (ddd, 1H, J = 1.4, 3.0, 10.3 Hz), 5.02 (brdd, 1H, J = 1.4, 2.6 Hz), 4.29 (ddt, 1H, J = 1.6, 5.1, 12.7 Hz), 4.23 (d, 1H, J = 13.9 Hz), 4.14 (d, 1H, J = 13.9 Hz), 4.08 (ddt, 1H, J = 1.2, 6.3, 12.7 Hz), 4.03−4.00 (m, 1H), 3.80−3.79 (m, 3H), 0.92 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (50 MHz) δ 134.2, 130.5, 129.3, 127.2, 118.0, 117.3, 93.5, 73.0, 70.7, 70.6, 69.0, 62.9, 26.1, 18.5, −5.0, −5.1. Anal. Calcd for $C_{18}H_{31}O_4SiBr$: C, 51.54; H, 7.45. Found: C, 51.50; H, 7.28.

***(E)*-But-2-enyl 4-*O*-(2′-Bromoprop-2′-enyl)-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3b)**: yield 67%; oil; R_f 0.72 (petroleum ether/ethyl acetate 5/1); $[\alpha]^{20}_D$ +78.2 (*c* 1.1, CH_2Cl_2); ^{1}H NMR (200 MHz) δ 6.05 (brd, 1H, J = 10.2 Hz), 5.94 (brs, 1H), 5.80 (ddd, 1H, J = 2.3, 2.4, 10.2 Hz), 5.70−5.65 (m, 2H), 5.60 (brs, 1H), 5.01 (brs, 1H), 4.26−3.78 (m, 8H), 1.72 (dd, 3H, J = 1.0, 6.1 Hz), 0.92 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (50 MHz) δ 129.4, 130.3, 129.9, 127.2, 127.3, 117.8, 93.2, 72.9, 70.7, 70.4, 68.6, 62.9, 26.0, 18.5, 17.9, −5.1, −5.2. Anal. Calcd for $C_{19}H_{33}O_4SiBr$: C, 52.64; H, 7.67. Found: C, 53.06; H, 7.58.

3-Methylbut-2-enyl 4-*O*-(2′-Bromoprop-2′-enyl)-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3c): yield 66%; oil; R_f 0.76 (petroleum ether/ethyl acetate 5/1); $[\alpha]^{20}_D$ +73.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (200 MHz) δ 6.04 (brd, 1H, J = 10.2 Hz), 5.94 (dd, 1H, J = 0.9, 2.5 Hz), 5.78 (ddd, 1H, J = 2.1, 2.5, 10.2 Hz), 5.60 (dd, 1H, J =

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0.9, 1.6 Hz), 5.41−5.32 (m, 1H), 5.01 (brd, 1H, J = 1.2, 2.5 Hz), 4.30−3.82 (m, 8H), 1.75 (s, 3H), 1.70 (s, 3H), 0.93 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (50 MHz) δ 137.9, 130.4, 129.5, 127.5, 120.7, 117.9, 93.3, 73.0, 70.8, 70.5, 64.4, 63.0, 26.0, 25.9, 18.6, 18.1, −5.0, −5.2. Anal. Calcd for $C_{20}H_{35}O_4SiBr$: C, 53.68; H, 7.88. Found: C, 53.76; H, 7.99.

***(E)*-3-Phenylprop-2-enyl 4-*O*-(2′-Bromoprop-2′-enyl)-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3d)**: yield 63%; oil; R_f 0.61 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +49.6 (c 0.95, CH_2Cl_2); ^{1}H NMR (200 MHz) δ 7.40−7.21 (m, 5H), 6.62 (brd, 1H, J = 15.9 Hz), 6.30 (ddd, 1H, J = 5.6, 6.6, 15.9 Hz), 6.07 (brd, 1H, J = 10.2 Hz), 5.93 (ddd, 1H, J = 1.4, 1.5, 1.5 Hz), 5.81 (ddd, 1H, J = 2.1, 2.5, 10.2 Hz), 5.60 (dd, 1H, J = 0.8, 1.4 Hz), 5.08 (dd, 1H, J = 1.2, 2.4 Hz), 4.43 (ddd, 1H, J = 1.3, 5.6, 12.6 Hz), 4.24 (ddd, 1H, J = 1.2, 6.6, 12.6 Hz), 4.20−4.13 (m, 2H), 4.07 (brd, 1H, J = 12.2 Hz), 3.97−3.80 (m, 3H), 0.92 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (50 MHz) δ 132.9, 130.7, 128.7, 127.8, 127.3, 126.6, 125.8, 118.1, 93.5, 73.1, 70.8, 70.7, 68.6, 62.9, 26.2, 18.6, −5.0, −5.1. Anal. Calcd for $C_{24}H_{35}O_4SiBr$: C, 58.17; H, 7.12. Found: C, 58.63; H, 6.99.

2-Methylprop-2-enyl 4-*O*-(2′-Bromoprop-2′-enyl)-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3e): yield 68%; oil; R_f 0.73 (petroleum ether/ethyl acetate 5/1); $[\alpha]^{20}_D$ +65.2 (c 1.1, CH_2Cl_2); ^{1}H NMR (200 MHz) δ 6.07 (ddd, 1H, J = 1.1, 1.2, 10.2 Hz), 5.94 (dd, 1H, J = 1.5, 3.0 Hz), 5.82 (ddd, 1H, J = 2.1, 2.5, 10.2 Hz), 5.61 (dd, 1H, J = 0.9, 2.1 Hz), 5.00 (s, 2H), 4.90 (s, 1H), 4.27−3.81 (m, 8H), 1.56 (s, 3H), 0.92 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (50 MHz) δ 141.8, 129.4, 130.4, 127.2, 117.9, 112.3, 93.3, 73.0, 71.7, 70.7, 70.6, 62.8, 26.0, 19.7, 18.4, −5.1, −5.3. Anal. Calcd for $C_{19}H_{33}O_4SiBr$: C, 52.64; H, 7.67. Found: C, 53.02; H, 7.58.

But-3-enyl 4-*O*-(2′-Bromoprop-2′-enyl)-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3f): yield 84%; oil; R_f 0.47 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +18.6 (c 1.0, CH_2Cl_2); ^{1}H NMR (200 MHz) δ 6.04 (brd, 1H, J = 10.2 Hz), 5.94 (dd, 1H, J = 1.6, 3.1 Hz), 5.91−5.78 (m, 1H), 5.79 (ddd, 1H, J = 2.2, 2.8, 10.2 Hz), 5.61 (dd, 1H, J = 1.0, 1.6 Hz), 5.12 (ddd, 1H, J = 1.7, 3.4, 17.3 Hz), 5.05 (brdd, 1H, J = 3.4, 10.2 Hz), 4.99 (brs, 1H), 4.23 (brd, 1H, J = 13.8 Hz), 4.15 (brd, 1H, J = 13.8 Hz), 4.07−3.78 (m, 5H), 3.54 (dt, 1H, J = 6.8, 9.6 Hz), 2.41−2.30 (m, 2H), 0.91 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (50 MHz) δ 135.3, 129.5, 130.4, 127.4, 118.1, 116.6, 94.4, 73.1, 70.8, 70.6, 67.9, 63.0, 34.4, 26.2, 18.6, −5.0, −5.1. Anal. Calcd for $C_{19}H_{33}O_4SiBr$: C, 52.65; H, 7.67. Found: C, 52.99; H, 7.76.

Preparation of Allyl 6-*O*-(*tert*-Butyldimethylsilyl)-4-[*N*-tosyl-*N*-(2′-bromoprop-2′-enyl)amino]-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranoside (4a) and Allyl 6-*O*-(*tert*-Butyldimethylsilyl)-4-[1′,1′-bis(methoxycarbonyl)-3′-bromobut-3′-enyl]-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranoside (4b). To a solution of **2a** (6.94 mmol) in 60 mL of CH_2Cl_2 at room temperature were added 170 mg (1.4 mmol) of DMAP, 2.8 mL (34.7 mmol) of pyridine, and 2.7 mL (34.7 mmol) of methylchloroformate. The mixture was stirred for 24 h at room temperature. After addition of 60 mL of a water solution of $CuSO_4{\cdot}5H_2O$, the product was extracted with 4 × 50 mL of Et_2O. The organic layer was dried, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography with petroleum ether/ethyl acetate 3/1 as the eluent to give the carbonate (75%). To a solution of this carbonate (1.44 mmol) in 10 mL of dry THF was added 838 mg (2.89 mmol) of $TsNHCH_2CBr{=}CH_2$ or 726 mg (2.89 mmol) of $(MeO_2C)_2CHCH_2CBr{=}CH_2$, and the catalytic system obtained by reacting $Pd_2(dba)_3$ (33 mg, 0.036 mmol) and dppb (31 mg, 0.072 mmol) in 10 mL of THF was added. The mixture was stirred at 60 °C for 24 h and quenched with 10 mL of H_2O. After extraction with 3 × 15 mL of Et_2O, the organic layer was dried. The solvent was removed under reduced pressure to give an oil which was purified by column chromatography using petroleum ether/ethyl acetate as the eluent to give **4a** or **4b**.

Allyl 6-*O*-(*tert*-Butyldimethylsilyl)-4-*O*-(methoxycarbonyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside: yield 75%; oil; R_f 0.70 (petroleum ether/ethyl acetate 5/1); $[\alpha]^{20}_D$ +34.3 (c 1.05, CH_2Cl_2); ^{1}H NMR (200 MHz) δ 6.01 (brd, 1H, J = 10.4 Hz), 5.96 (dddd, 1H, J = 5.5, 6.3, 10.6, 17.1 Hz), 5.79 (brdd, 1H, J = 2.4, 10.4 Hz), 5.36 (ddd, 1H, J = 1.6, 2.9, 17.1 Hz), 5.09 (ddd, 1H, J = 1.4, 2.9, 10.6 Hz), 5.01 (dd, 1H, J = 1.5, 9.5 Hz), 4.89 (dd, 1H, J = 1.0, 2.3 Hz), 4.36 (ddt, 1H, J = 1.6, 5.5, 12.8 Hz), 4.18 (ddt, 1H, J = 1.4, 6.3, 12.8 Hz), 3.98−3.76 (m, 3H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (50 MHz) δ 135.0, 132.0, 128.0, 117.4, 93.7, 70.6, 69.3, 69.2, 62.6, 52.9, 25.9, 18.2, −5.4, −5.3. Anal. Calcd for $C_{17}H_{30}O_6Si$: C, 56.95; H, 8.43. Found: C, 56.61; H, 8.40.

Allyl 4-[*N*-Tosyl-*N*-(2′-bromoprop-2′-enyl)amino]-6-*O*-(*tert*-butyldimethylsilyl)-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranoside (4a): yield 90%; oil; R_f 0.45 (petroleum ether/ethyl acetate 5/1); $[\alpha]^{20}_D$ +120.4 (c 1.3, CH_2Cl_2); ^{1}H NMR (300 MHz) δ 7.45 (d, 2H, J = 8.3 Hz), 7.32 (d, 2H, J = 8.3 Hz), 6.00 (brd, 1H, J = 10.3 Hz), 6.00−5.86 (m, 1H), 5.85 (ddd, 1H, J = 2.6, 2.8, 10.3 Hz), 5.63 (brd, 1H, J = 1.7 Hz), 5.26 (ddd, 1H, J = 1.6, 1.6, 17.2 Hz), 5.19 (brs, 1H), 5.17 (ddd, 1H, J = 1.6, 1.6, 10.3 Hz), 4.95 (d, 1H, J = 3.0 Hz), 4.37 (brd, 1H, J = 9.7 Hz), 4.24 (ddd, 1H, J = 1.6, 5.2, 12.6 Hz), 4.21 (d, 1H, J = 17.1 Hz), 3.99 (brdd, 1H, J = 6.6, 12.6 Hz), 3.95 (ddd, 1H, J = 1.8, 6.5, 9.7 Hz), 3.87 (dd, 1H, J = 1.8, 11.3 Hz), 3.76 (d, 1H, J = 17.1 Hz), 3.60 (dd, 1H, J = 6.5, 11.3 Hz), 2.36 (s, 3H), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (50 MHz) δ 144.5, 137.1, 135.4, 131.3, 130.3, 127.9, 127.6, 127.4, 118.7, 118.2, 93.4, 86.5, 69.1, 68.7, 63.2, 53.5, 25.9, 21.7, 18.4, −5.1, −5.2. Anal. Calcd for $C_{25}H_{38}O_5SSiNBr$: C, 52.43; H, 6.68; N, 2.44. Found: C, 52.34; H, 6.64; N, 2.48.

Allyl 6-*O*-(*tert*-Butyldimethylsilyl)-4-[1′,1′-bis(methoxycarbonyl)-3′-bromobut-3′-enyl]-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranoside (4b): yield 65%; oil; R_f 0.45 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +94.6 (c 1.2, CH_2Cl_2); ^{1}H NMR (200 MHz) δ 6.07 (dd, 1H, J = 4.4, 10.6 Hz), 5.94 (dd, 1H, J = 10.4, 17.3 Hz), 5.85 (ddd, 1H, J = 1.6, 2.7, 10.6 Hz), 5.75 (d, 1H, J = 1.8 Hz), 5.68 (d, 1H, J = 1.8 Hz), 5.28 (brd, 1H, J = 17.3 Hz), 5.15 (brdd, 1H, J = 1.3, 10.4 Hz), 5.13 (brd, 1H, J = 1.3 Hz), 4.30−4.17 (m, 2H), 3.99 (brdd, 1H, J = 6.0, 12.9 Hz), 3.77 (s, 3H), 3.75 (s, 3H), 3.84−3.75 (m, 2H), 3.24 (brd, 1H, J = 15.9 Hz), 3.15 (brd, 1H, J = 15.9 Hz), 2.88 (dd, 1H, J = 2.1, 4.3 Hz), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (50 MHz) δ 170.6, 170.1, 135.4, 130.3, 127.9, 127.6, 122.8, 117.5, 93.0, 73.4, 69.2, 64.9, 60.8, 53.5, 53.2, 44.2, 37.9, 26.7, 19.0, −4.6, −4.7. Anal. Calcd for $C_{23}H_{37}O_7SiBr$: C, 51.77; H, 6.98. Found: C, 52.01; H, 6.90.

Standard Palladium(0)-Mediated Cyclization Process. The 2,3-unsaturated glycoside (0.96 mmol) in 7.5 mL of acetonitrile and 1.5 mL of water was stirred in the presence of $Pd(OAc)_2$ (21 mg, 0.095 mmol), PPh_3 (50 mg, 0.19 mmol), NEt_3 (340 mL, 2.39 mmol), and Bu_4NHSO_4 (324 mg, 0.95 mmol) at 80 °C until TLC analysis showed that all the starting material was consumed (15−24 h). After addition of 10 mL of water, the mixture was extracted with 4 × 20 mL of ethyl ether. Evaporation of the solvent under reduced pressure gave an oil which was purified by column chromatography.

(1*S*,3*S*,4*S*,8*R*,9*S*)-3-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-7,10-bis(methylene)-2,5,12-trioxatricyclo[7,3,0,$0^{4,8}$]dodecane (5): yield 75%; oil; R_f 0.41 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +52.6 (c 1.1, CH_2Cl_2); ^{1}H NMR (400 MHz) δ 5.59 (d, 1H, J = 6.6 Hz), 5.29 (ddd, 1H, J = 2.5, 2.5, 2.5 Hz), 5.25 (ddd, 1H, J = 2.5, 2.5, 2.5 Hz), 5.19 (ddd, 1H, J = 2.1, 2.1, 2.1 Hz), 4.98 (ddd, 1H, J = 2.1, 2.2, 2.2 Hz), 4.68 (dddd, 1H, J = 2.3, 2.3, 2.4, 13.0 Hz), 4.45 (ddd, 1H, J = 1.9, 2.7, 13.6 Hz), 4.43 (ddd, 1H, J = 2.1, 3.8, 13.0 Hz), 4.31 (dddd, 1H, J = 1.1, 2.6, 3.5, 13.6 Hz), 4.06 (dd, 1H, J = 7.4, 7.4 Hz), 3.86 (dd, 1H, J = 2.8, 11.4 Hz), 3.75 (dd, 1H, J = 4.8, 11.4 Hz), 3.66 (ddd, 1H, J = 2.8, 4.8, 7.8 Hz), 3.22−3.17 (m, 1H), 3.00 (dddd, 1H, J = 1.1, 3.0, 7.4, 7.4 Hz), 0.80 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (75 MHz) δ 149.4, 147.1, 107.7, 107.1, 102.9, 77.1, 73.6, 73.5, 72.8, 64.7, 42.8, 41.1, 26.0, 18.5, −5.3, −5.2. Anal. Calcd for $C_{18}H_{30}O_4Si$: C, 63.86; H, 8.93. Found: C, 63.88; H, 8.91.

(1*S*,3*S*,4*S*,8*R*,9*S*)-3-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-7,10-bis(methylene)-5-*N*-tosyl-2,12-dioxa-5-azatricyclo[7,3,0,$0^{4,8}$]dodecane (6): yield 80%; oil; R_f 0.30 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +33.6 (c 1.33, CH_2Cl_2); ^{1}H NMR (400 MHz) δ 7.68 (d, 2H, J = 8.2 Hz), 7.32

(d, 2H, J = 8.2 Hz), 5.62 (d, 1H, J = 6.8 Hz), 5.16 (ddd, 1H, J = 2.1, 2.1, 2.3 Hz), 5.04 (m, 2H), 4.96 (brd, 1H, J = 2.1 Hz), 4.81 (ddd, 1H, J = 2.3, 4.6, 12.7 Hz), 4.36 (brd, 1H, J = 12.7 Hz), 4.29 (dd, 1H, J = 4.3, 11.9 Hz), 4.06−4.01 (m, 3H), 3.81 (dd, 1H, J = 7.1, 7.1 Hz), 3.68 (ddd, 1H, J = 2.0, 2.0, 15.1 Hz), 2.97 (dd, 1H, J = 7.0, 7.2 Hz), 2.81 (brdd, 1H, J = 7.4, 7.4 Hz), 2.51 (s, 3H), 0.91 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (75 MHz) δ 146.0, 143.9, 143.5, 132.7, 129.7, 128.2, 108.8, 108.6, 101.4, 72.8, 71.9, 64.6, 57.1, 55.3, 43.7, 41.8, 25.9, 21.5, 18.4, −4.9, −5.0. Anal. Calcd for $C_{25}H_{37}O_5SSiN$: C, 61.05; H, 7.58; N, 2.86. Found: C, 60.84; H, 7.64; N, 2.70.

(1*S*,3*S*,4*R*,8*R*,9*S*)-3-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-5,5-bis(methoxycarbonyl)-7,10-bis(methylene)-2,12-dioxatricyclo[7,3,0,0^{4,8}]dodecane (7): yield 78%; oil; R_f 0.26 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +74.5 (*c* 1.15, CH_2Cl_2); ^{1}H NMR (400 MHz) δ 5.54 (d, 1H, J = 5.8 Hz), 5.27 (ddd, 1H, J = 2.2, 2.2, 2.4 Hz), 5.17 (ddd, 1H, J = 1.7, 1.9, 2.2 Hz), 5.08 (ddd, 1H, J = 1.6, 1.8, 2.1 Hz), 4.96 (ddd, 1H, J = 1.9, 2.1, 2.3 Hz), 4.59 (ddd, 1H, J = 2.4, 4.3, 13.1 Hz), 4.38 (brd, 1H, J = 13.1 Hz), 3.87 (ddd, 1H, J = 2.2, 4.4, 5.8 Hz), 3.80 (dd, 1H, J = 2.2, 11.5 Hz), 3.72 (s, 3H), 3.66 (s, 3H), 3.59 (dd, 1H, J = 5.8, 11.5 Hz), 3.43 (ddd, 1H, J = 1.5, 1.8, 15.9 Hz), 3.21−3.19 (m, 3H), 2.77 (ddd, 1H, J = 2.3, 2.4, 15.9 Hz), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (75 MHz) δ 172.2, 169.8, 147.6, 146.5, 108.7, 108.4, 102.0, 72.6, 72.3, 65.3, 61.4, 53.0, 52.3, 44.5, 43.6, 41.4, 40.6, 25.9, 18.3, −5.2, −5.4. Anal. Calcd for $C_{23}H_{36}O_7Si$: C, 61.03; H, 8.01. Found: C, 61.40; H, 8.20.

(1*S*,3*S*,4*S*,8*R*,9*S*,10*S*)-3-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-7-methylene-10-vinyl-2,5,12-trioxatricyclo[7,3,0,0^{4,8}]dodecane (8): yield 77%; oil; R_f 0.30 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +81.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz) δ 5.58 (ddd, 1H, J = 8.2, 10.1, 17.1 Hz), 5.52 (d, 1H, J = 6.8 Hz), 5.08 (ddd, 1H, J = 2.0, 2.0, 2.6, Hz), 5.06 (dd, 1H, J = 1.6, 17.1 Hz), 4.96 (ddd, 1H, J = 1.9, 1.9, 2.0 Hz), 4.89 (dd, 1H, J = 1.6, 10.1 Hz), 4.44 (dddd, 1H, J = 1.8, 1.9, 2.1, 13.5 Hz), 4.30 (ddd, 1H, J = 2.0, 2.1, 13.5 Hz), 4.14−4.07 (m, 2H), 3.87 (dd, 1H, J = 4.9, 11.7 Hz), 3.82−3.72 (m, 2H), 3.34 (dd, 1H, J = 8.8, 10.0 Hz), 3.06 (dddd, 1H, J = 8.2, 8.4, 10.1, 10.5 Hz), 2.90 (brdd, 1H, J = 6.0, 8.8 Hz), 2.38 (ddd, 1H, J = 6.0, 6.8, 10.5 Hz), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (50 MHz) δ 147.4, 139.3, 115.5, 107.2, 101.9, 77.3, 72.3, 72.1, 71.8, 64.8, 45.3, 44.7, 41.3, 26.1, 18.6, −5.1. Anal. Calcd for $C_{19}H_{32}O_4Si$: C, 64.73; H, 9.15. Found: C, 65.17; H, 9.39.

(1*S*,3*S*,4*S*,8*R*,9*S*,10*S*)-3-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-7-methylene-10-(prop-1′-en-2′-yl)-2,5,12-trioxatricyclo[7,3,0,0^{4,8}]dodecane (9): yield 78%; oil; R_f 0.32 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +103.4 (*c* 1.3, CH_2Cl_2); ^{1}H NMR (300 MHz) δ 5.54 (d, 1H, J = 6.8 Hz), 5.06 (ddd, 1H, J = 2.0, 2.1, 2.6 Hz), 4.96 (ddd, 1H, J = 1.8, 1.9, 2.0 Hz), 4.85 (brs, 1H), 4.70 (dd, 1H, J = 1.5, 1.6 Hz), 4.49 (brd, 1H, J = 13.5 Hz), 4.27 (ddd, 1H, J = 1.9, 2.1, 13.5 Hz), 4.11−4.05 (m, 2H), 3.88 (dd, 1H, J = 2.1, 9.6 Hz), 3.84 (ddd, 1H, J = 2.1, 4.0, 8.7 Hz), 3.81 (dd, 1H, J = 4.0, 9.6 Hz), 3.42 (dd, 1H, J = 8.6, 9.7 Hz), 3.21 (ddd, 1H, J = 9.0, 9.2, 11.0 Hz), 2.90 (brdd, 1H, J = 6.4, 9.7 Hz), 2.58 (ddd, 1H, J = 6.4, 6.8, 11.0 Hz), 1.66 (s, 3H), 0.90 (s, 9H), 0.085 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (50 MHz) δ 147.8, 143.5, 113.5, 106.7, 101.9, 79.1, 77.2, 72.1, 72.0, 64.9, 48.3, 41.4, 40.7, 26.1, 18.6, 18.3, −5.1, −5.0. Anal. Calcd for $C_{20}H_{34}O_4Si$: C, 65.53; H, 9.34. Found: C, 65.07; H, 9.97.

(1*S*,3*S*,4*S*,8*R*,9*S*)-3-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-7-methylene-10(*E*)-benzylidene-2,5,12-trioxatricyclo[7,3,0,0^{4,8}]dodecane (10): yield 79%; oil; R_f 0.57 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +111.4 (*c* 0.95, CH_2Cl_2); ^{1}H NMR (300 MHz) δ 7.32 (d, 2H, J = 7.6 Hz), 7.21 (dd, 1H, J = 7.3, 7.6 Hz), 7.07 (d, 2H, J = 7.3 Hz), 6.68 (ddd, 1H, J = 2.3, 2.4, 2.5 Hz), 5.65 (d, 1H, J = 6.5 Hz), 5.31 (ddd, 1H, J = 1.7, 2.5, 2.5 Hz), 5.20 (ddd, 1H, J = 1.8, 2.0, 2.0 Hz), 5.01 (ddd, 1H, J = 2.6, 2.8, 13.6 Hz), 4.64 (ddd, 1H, J = 1.4, 1.7, 13.6 Hz), 4.42 (ddd, 1H, J = 2.3, 4.0, 13.5 Hz), 4.29 (ddd, 1H, J = 2.2, 2.4, 13.5 Hz), 4.08 (dd, 1H, J = 6.1, 6.9 Hz), 3.83 (dd, 1H, J = 2.7, 11.5 Hz), 3.79 (dd, 1H, J = 4.7, 11.5 Hz), 3.71 (ddd, 1H, J = 2.7, 4.7, 6.1 Hz), 3.32 (brdd, 1H, J = 6.5, 6.8 Hz), 3.05 (brdd, 1H, J = 6.8, 6.9 Hz), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (50 MHz) δ 148.8, 139.5, 137.3, 128.5, 128.2, 126.9, 124.2, 101.1, 76.9, 73.1, 72.3, 71.7, 64.7, 43.8, 42.1, 26.0, 18.5, −5.1, −5.2. Anal. Calcd for $C_{24}H_{34}O_4Si$: C, 69.52; H, 8.26. Found: C, 70.01; H, 8.32.

Standard Tandem Palladium(0)-Mediated Cyclization/Ion-Capture Procedure. Compound **3e** (1.01 mmol) was allowed to react under the previously described conditions for palladium(0)-catalyzed cyclization in the presence of added $NaBPh_4$ (691 mg, 1.21 mmol) or HCO_2Na (75 mg, 1.11 mmol), respectively for 15 h at 60 °C or 24 h at 80 °C. The usual workup gave the pure product after column chromatography.

(2-Methylprop-2-enyl) 2,3,4-Trideoxy-2′,3′,4′,5′-tetrahydro-6-*O*-(*tert*-butyldimethylsilyl)-4′-methylene-α-D-*ribo*-hexopyranosido[4,3-*b*]furan (12): yield 56%; oil; R_f 0.40 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +107.5 (*c* 0.9, CH_2Cl_2); ^{1}H NMR (500 MHz) δ 5.02 (ddd, 2H, J = 2.1, 2.1, 2.2 Hz), 4.95 (brs, 1H), 4.85 (dd, 1H, J = 5.2, 6.0 Hz), 4.84 (brs, 1H), 4.45 (ddd, 1H, J = 1.9, 3.7, 13.2 Hz), 4.31 (brd, 1H, J = 13.2 Hz), 4.14 (brd, 1H, J = 12.9 Hz), 3.95 (dd, 1H, J = 7.3, 8.4 Hz), 3.87 (dd, 1H, J = 1.8, 11.0 Hz), 3.83 (brd, 1H, J = 12.9 Hz), 3.69 (dd, 1H, J = 6.4, 11.0 Hz), 3.64 (ddd, 1H, J = 1.8, 6.4, 8.4 Hz), 2.74 (brdd, 1H, J = 6.2, 9.3 Hz), 2.03 (ddd, 1H, J = 5.2, 6.2, 14.3 Hz), 1.87 (ddd, 1H, J = 6.0, 9.3, 14.3 Hz), 1.68 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (50 MHz) δ 149.9, 142.2, 111.1, 104.9, 96.2, 76.6, 72.4, 70.5, 70.4, 64.3, 39.0, 30.9, 26.1, 19.6, 18.6, −5.2. Anal. Calcd for $C_{19}H_{32}O_4Si$: C, 64.73; H, 9.15. Found: C, 64.97; H, 9.04.

2-Methylprop-2-enyl 6-*O*-(*tert*-Butyldimethylsilyl)-4-*O*-(2′-phenylprop-2′-enyl)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (13): yield 20%; oil; R_f 0.44 (petroleum ether/ethyl acetate 10/1); $[\alpha]^{20}_D$ +95.8 (*c* 0.8, CH_2Cl_2); ^{1}H NMR (200 MHz) δ 7.31−7.49 (m, 5H), 6.05 (brd, 1H, J = 10.2 Hz), 5.79 (ddd, 1H, J = 2.1, 2.2, 10.2 Hz), 5.53 (d, 1H, J = 0.9 Hz), 5.34 (d, 1H, J = 0.9 Hz), 4.99 (brs, 2H), 4.89 (brs, 1H), 4.55 (d, 1H, J = 12.8 Hz), 4.40 (d, 1H, J = 12.8 Hz), 4.17 (d, 1H, J = 12.6 Hz), 4.02−4.08 (m, 1H), 3.95 (d, 1H, J = 12.6 Hz), 3.66−3.83 (m, 3H), 1.56 (s, 3H), 0.89 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H). Anal. Calcd for $C_{25}H_{38}O_4Si$: C, 69.72; H, 8.89. Found: C, 69.25; H, 8.98.

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Supporting Information Available: Experimental procedures and characterization data for compounds **1a**−**f** and **2a**−**f**, as well as copies of ^{1}H and ^{13}C NMR spectra with complete peak assignments for new compounds having microanalyses which did not come within 0.4% for C and/or H calculated values are also avalaible (16 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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