JOC Article

# An Efficient Way to 1,7-Enynes and Ethyl 8-Yn-2-enoates from Aldohexoses and to Polyhydroxylated 1-Vinylcyclohexenes

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In this paper, we report the synthesis of carbohydrate-derived 1,7-enynes and subsequent metathesis to yield polyhydroxylated 1-vinylcyclohexenes. For example, we converted D-glucose **2** to the (6,7)-dideoxy-D-*gluco*-hept-6-ene-pyranose **7**, which led to the desired 1,7-enyne **16**. The ring-closing metathesis of this 1,7-enyne **16** with the second generation Grubbs catalyst, under Mori's conditions, gave the corresponding polyhydroxylated 1-vinylcyclohexene **25** in 76% yield. The conversion of several aldohexoses into polyhydroxylated 1-vinylcyclohexenes was carried out with satisfying yields. We report also the synthesis of two carbohydrate-derived ethyl 8-yn-2-enoates from D-glucose derivatives.

## Introduction

Carbohydrates are widely recognized as versatile building blocks in synthetic organic chemistry as a result of their wealth of functional, conformational, and stereochemical information. The diversity and availability of these relatively cheap chiral compounds has led to their use as starting materials for the design and synthesis of naturally occurring compounds.[1] Our laboratory is especially interested in the transformation of aldoses into enitols[2−6] and ynitols.[5−8] These compounds are versatile intermediates for the synthesis of optically active target compounds.[9] Recently, we reported a new route toward polyhydroxylated 1-vinylcyclopentenes and 1-vinylcyclohexenes via perbenzyled 1,6- and 1,7-enynes.[10] These intermediates were synthesized in four steps from *glyco*-ynitols, which were readily available from monosaccharides.[8] These 1,6- and 1,7-enynes were cyclized by ring-closing enyne metathesis to give the title compounds. Herein, we wish to report another way to prepare these 1,7-enynes from aldoses and their cyclization by ring-closing enyne metathesis with Grubbs catalyst, under Mori's conditions,[11] to produce the peracetylated polyhydroxylated 1-vinylcyclohexenes. We also report the synthesis of two polyhydroxylated ethyl 8-yn-2-enoates, which are useful scaffolds for the construction of bridged and fused bicyclic systems.

## Results and Discussion

As shown in Scheme 1, enynes **IIIa** and **IIb** were readily obtained from aldohexoses via the same intermediate **I**. By this strategy, first we can generate the carbon−carbon double bond (pathway a) or triple bond (pathway b) from the primary hydroxy group and, second, the other unsaturated bond from the hemiacetal position. These enynes **IIIa** and **IIb** are interesting scaffolds that can be used in many transformations. Thus enynes **IIIa** were subjected to a ring-closing metathesis catalyst for the formation of carbocycles **IVa**. We have used the second generation Grubbs catalyst[12] **A** (Figure 1), which is commonly employed in olefin metathesis and also in catalyzed enyne metathesis.[13]

**Synthesis of 1,7-Enynes IIIa.** As shown in Scheme 2, compounds **Ia** were obtained in a one-step procedure from aldohexoses by pathway a.

The activated DMSO reagents, well-known for oxidizing alcohol to the corresponding carbonyl compounds under mild conditions, can also oxidize trimethyl and triethylsilyl ethers.[14] Furthermore, primary trimethyl and triethylsilyl ethers are more reactive than their secondary analogues, allowing the selective oxidation of the for-

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[1] (a) Hanessian, S. *Total Synthesis of Natural Products: The "Chiron" Approach*; Pergamon Press: Oxford, 1983. (b) Rollin, P.; Klaffke, W. *J. Carbohydr. Chem.* **1991**, *10*, 115.

[2] Lièvre, C. Dissertation, Université d'Amiens, 1996.

[3] (a) Lièvre, C.; Fréchou, C.; Demailly, G. *Tetrahedron Lett.* **1995**, *36*, 6467. (b) Le Mignot, V.; Lièvre, C.; Fréchou, C.; Demailly, G. *Tetrahedron Lett.* **1998**, *39*, 983. (c) Lièvre, C.; Fréchou, C.; Demailly, G. *Carbohydr. Res.* **1997**, *303*, 1.

[4] Dolhem, F.; Lièvre, C.; Demailly, G. *Tetrahedron Lett.* **2002**, *43*, 1847.

[5] Dolhem, F. Dissertation, Université d'Amiens, 2003.

[6] Thiéry, J.-C. Dissertation, Université d'Amiens, 2000.

[7] Thiéry, J.-C.; Fréchou, C.; Demailly, G. *Tetrahedron Lett.* **2000**, *41*, 6337.

[8] Dolhem, F.; Lièvre, C.; Demailly, G. *Tetrahedron* **2003**, *59*, 155.

[9] (a) Ferrier, R. R.; Middleton, S. *Chem. Rev.* **1993**, *93*, 2279. (b) Collins, P.; Ferrier, R. R. *Monosaccharides*; Wiley: Chichester, 1995.

[10] Dolhem, F.; Lièvre, C.; Demailly, G. *Eur. J. Org. Chem.* **2003**, 2336.

[11] Mori, M.; Sakakira, N.; Kinoshita, A. *J. Org. Chem.* **1998**, *63* (18), 6082.

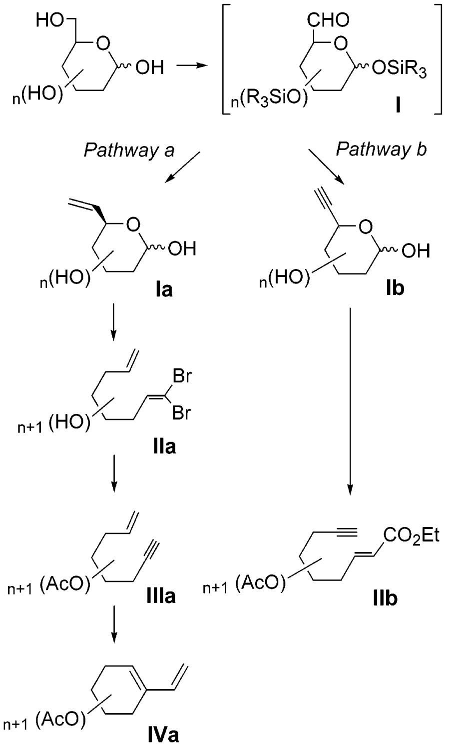
[12] Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1* (6), 953.

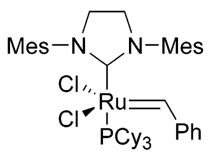
[13] (a) Kapferer, P.; Sarabia, F.; Vasella, A. *Helv. Chim. Acta* **1999**, 82, 645. (b) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012. (c) Marco-Contelles, J.; de Opazo, E. *J. Org. Chem.* **2002**, *67*, 3705. (d) Storm-Paulsen, C.; Madsen, R. *Synthesis* **2003**, *1*, 1.

[14] Muzart, J. *Synthesis* **1993**, 11.

10.1021/jo035437e CCC: $27.50

**SCHEME 1. Synthetic Approach**

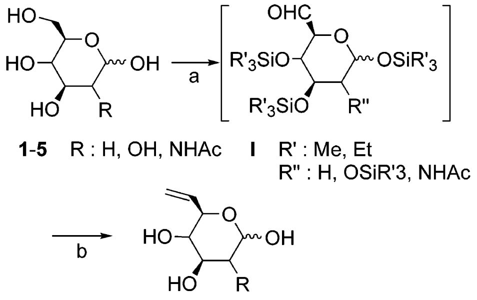




Catalyst **A**

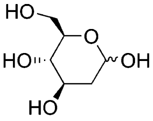
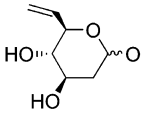
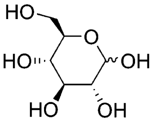
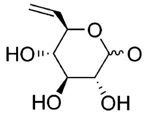
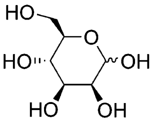
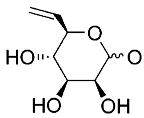
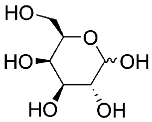
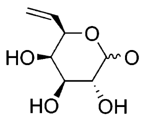
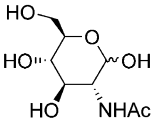
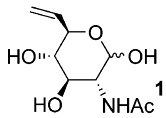
**FIGURE 1.** Grubbs catalyst.

**SCHEME 2. Synthesis of Compounds 6−10**[a]



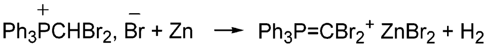
[a] Reagents and conditions: (a) (i) $R'_3SiCl$, imidazole, DMF, rt, 12 h, (ii) $(COCl)_2$, DMSO, $CH_2Cl_2$, −70 °C then $Et_3N$; (b) (i) $Ph_3PCH_3Br$, *t*-BuOK, THF, rt, 1 h, (ii) TBAF, $THF-H_2O$, rt.

**TABLE 1. Synthesis of 6,7-Dideoxy-D-*glyco*-hept-6-enoses 6−10**[a]

| Aldohexose | Product **Ia** | Yield* |
|---|---|---|
|  **1** |  | **6** : 21% |
|  **2** |  | **7** : 20% |
|  **3** |  | **8** : 42% |
|  **4** |  | **9** : 49% |
|  **5** |  | **10** : 18% |

[a] Yield represents isolated yield.

**SCHEME 3. Formation of Ylide**



$$\overset{+}{Ph_3P}CHBr_2,\ \overset{-}{Br} + Zn \longrightarrow Ph_3P{=}CBr_2{}^{+}\ ZnBr_2 + H_2$$

mer in the presence of the latter by the Swern reagent, oxalyl chloride, a good activator for DMSO.[15] So, in a one-step procedure on 2-deoxy-D-glucose **1**, we carried out a standard silylation (trimethylsilyl chloride, imidazole in DMF at room temperature) followed by a Swern oxidation. Unfortunately, the carbonyl compound decomposed during the usual workup on silica gel, making its isolation impossible. However, the starting material **1** was successfully converted into 2,6,7-trideoxy-D-*gluco*-hept-6-ene-pyranose **6** in 21% yield by a one-pot sequence involving silylation followed by Swern oxidation, an addition of preprepared methylenetriphenylphosphorane and a subsequent deprotection (Scheme 2, Table 1). We have tested the same sequence using triethylsilyl ethers, and the yield of this conversion is similar (21%). Therefore, the cheaper trimethylsilyl ethers were used for the other compounds. D-Glucose **2** treated under these conditions led to the desired compound **7** in 20% yield. From D-mannose **3** and D-galactose **4**, the corresponding 6,7-dideoxy-*glyco*-hept-6-enoses **8** and **9** were obtained with superior yields (42% and 49%, respectively). We also carried out this sequence on 2-deoxy-*N*-acetyl-D-glucosamine **5**. The yield in the desired product **10** is similar to that of D-glucose derivatives **1** and **2** (18%). By this synthetic approach, we have quickly synthesized the five 6,7-dideoxy-D-*glyco*-hept-6-enoses **6**−**10**, which are used to en route to dienes **IIa**.

Recently, we reported an efficient method for olefination of aldoses to 1,1-dibromo-1-alkenes.[4] The mildness of our conditions allowed us to form the dibromoolefins on aldoses with free hydroxyl groups. This is due to the formation of the ylide, the dibromomethylenetriphenylphosphorane, in situ from the corresponding phosphonium salt and zinc (Scheme 3). Using these conditions, the reaction proceeded smoothly, and no byproducts were detected during the course of the reaction.

We have applied our olefination conditions to 6,7-dideoxy-*glyco*-hept-6-enoses **6**−**10** (Scheme 4, Table 2). From

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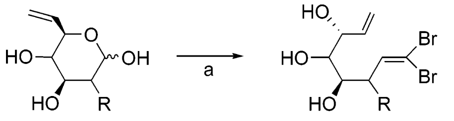
(15) Rodriguez, A.; Nomen, M.; Spur, B. W.; Godfroid, J. J. *Tetrahedron Lett.* **1999**, *40*, 5161.

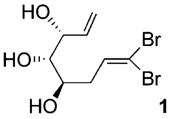
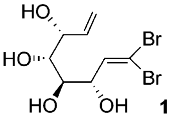
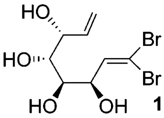
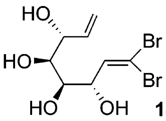
**SCHEME 4. Synthesis of Compounds 11−14**[a]



**Ia : 6-9** R : H, OH **IIa :11-14** R : H, OH

[a] Reagents: (a) $Ph_3PCHBr_3$, Zn, 1,4-dioxane, reflux.

**TABLE 2. Synthesis of 1,1-Dibromo-1,7-dienes 11−14**

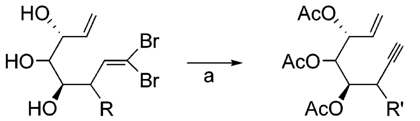
| **Ia** | Conditions | Product **IIa** | Yield[a] |
|---|---|---|---|
| **6** | Salt[b] (4.8 equiv.)<br>Zn (5.3 equiv.)<br>30 min |  | **11** : 74% |
| **7** | Salt[b] (5 equiv.)<br>Zn (5 equiv.)<br>80 min |  | **12** : 70% |
| **8** | Salt[b] (6 equiv.)<br>Zn (6.5 equiv.)<br>40 min |  | **13** : 68% |
| **9** | Salt[b] (5 equiv.)<br>Zn (5.3 equiv.)<br>30 min |  | **14** : 70% |

[a] Isolated yield. [b] $Ph_3PCHBr_3$

2-deoxy-D-glucose **6**, the reaction with dibromomethyltriphenylphosphonium bromide in the presence of zinc in refluxing 1,4-dioxane led to the corresponding olefin **11** in 74% yield. NMR and mass spectrometry were used to established the structure of **11**. This reaction needs a large excess of phosphonium salt (4 equiv) and zinc (4.4 equiv) to bring it to completion. We then extended these conditions to substrates **7**, **8**, and **9**. However, when these compounds were reacted with phosphonium salt and zinc in 1,4-dioxane, the corresponding dienes **12**, **13**, and **14** were obtained in 70%, 68%, and 70% yields, respectively. These olefination conditions were then applied to the derivative of 2-deoxy-*N*-acetyl-D-glucosamine **10**. This reaction with **10** recovered starting material, and a complex reaction occurred from which we could not reliably identify a reaction product. In modified experimental conditions, unsuccessful results have been obtained from this compound **10**. It would seem that these olefination conditions were not mild enough for this substrate, which is known for its fragility in the Wittig reaction.[16] However, we have achieved the synthesis of really interesting chiral scaffolds **11**−**14** in very few steps starting from monosaccharides and with relatively good yields. We have chosen to use polyhydroxylated dienes **IIa** as precursors of enynes **IIIa**.

In a preceding study on conversion of 1,1-dibromoalkenes into *glyco*-ynitols,[8] we were involved in a search for a reagent that would be compatible with a range of substrates. However, magnesium metal,[17] zinc dust,[18] and *t*-BuOK[19] proved to be ineffective. Nevertheless, by using *n*-BuLi we were able to effect dehalogenation to form the desired acetylene, in addition to forming the terminal alkyne as a result of further addition.

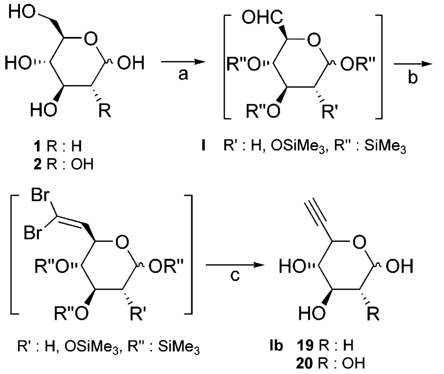
**SCHEME 5. Synthesis of Compounds 15−18**[a]



**IIa : 11-14** R : H, OH **IIIa : 15-18** R' : H, OAc

[a] Reagents and conditions: (a) (i) *n*-BuLi, THF, −70 °C, 15 min, (ii) $Ac_2O$, pyr, rt, 12 h.

**SCHEME 6. Synthesis of Compounds 19−20**[a]



[a] Reagents and conditions: (a) (i) $Me_3SiCl$, imidazole, DMF, rt, 12 h, (ii) $(COCl)_2$, DMSO, $CH_2Cl_2$, −70 °C then $Et_3N$; (b) $Ph_3PCHBr_3$, *t*-BuOK, THF, 0 °C, (c) (i) *n*-BuLi, THF, −70 °C, (ii) TBAF, THF−$H_2O$, rt.

The reaction of diene **11** with an excess of *n*-butyllithium (5 equiv) in THF at low temperature (−70 °C) produced the corresponding enyne **15** in 75% yield after acetylation (Scheme 5).

NMR, IR, and mass spectrometry have established the structure of this compound. On derivitization of D-glucose **12**, enyne **16** was obtained with lower yield (57%). When these reaction conditions were applied to dienes **13** and **14**, the expected enynes **17** and **18** were obtained in 85% and 60% yields, respectively. It appears that the relative configuration at the α-carbone of dibromoolefin has an effect: for D-*manno* **17**, the yield is better than that for D-*gluco* **16** and D-*galacto* **18** derivatives. Nevertheless, in a few steps from monosaccharides, we have achieved the synthesis of interesting polyhydroxylated chiral enynes **15**−**18** with satisfying yields.

**Synthesis of Ethyl-8-yn-2-enoates IIb.** We have tried to extend this synthetic approach to the synthesis of other types of enynes, the ethyl 8-yn-2-enoates **IIb**. From the same intermediate **I**, by pathway b, we created the carbon−carbon triple bond **Ib** from aldehyde and the double bond **IIb** from hemiacetal position (Scheme 1).

As shown in Scheme 6, acetylenic compounds were obtained from dibromo-alkenes. In this pathway b, Rassat conditions have been used (dibromomethyltriphenylphosphonium bromide and *t*-BuOK in THF).[19] The

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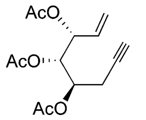
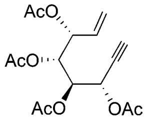
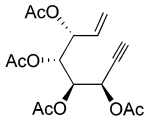
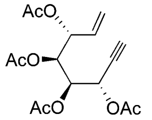
[16] Nicotra, F.; Ronchetti, F.; Russo, G.; Toma, L. *Tetrahedron Lett.* **1984**, *49*, 5697.

[17] Kolb, M.; Witz, P.; van Hijfte, L. *Tetrahedron Lett.* **1989**, *30*, 3769.

[18] Corey, E. J.; Fuchs. P. L. *Tetrahedron Lett.* **1972**, *36*, 3769.

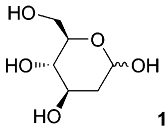
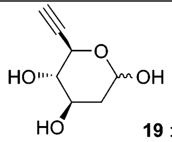
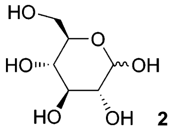
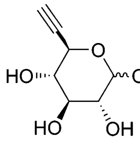
[19] Gennet, D.; Michel, P.; Rassat, A. *Tetrahedron Lett.* **1999**, *40*, 8575.

**TABLE 3. Synthesis of 1,7-Enynes 15−18**[a]

| IIa | Product IIIa | Yield* |
|---|---|---|
| 11 |  | **15** : 75% |
| 12 |  | **16** : 57% |
| 13 |  | **17** : 85% |
| 14 |  | **18** : 60% |

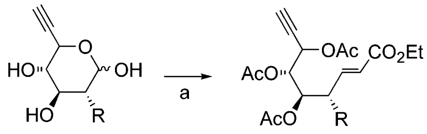
[a] Yield represents isolated yield.

**TABLE 4. Synthesis of D-*Gluco*-hept-6-yne-pyranoses 19 and 20**[a]

| Aldohexose | Product Ib | Yield* |
|---|---|---|
|  **1** |  | **19** : 23% |
|  **2** |  | **20** : 20% |

[a] Yield represents isolated yield.

**SCHEME 7**[a]



**Ib** : **19** R : H
**20** R : OH

**IIb** : **21** R : H
**22** R : OAc

[a] Reagents and conditions: (a) (i) $BrCH_2CO_2Et$ (2 equiv), *n*-$Bu_3P$ (2 equiv), Zn (2 equiv), 1,4-dioxane, reflux, (ii) $Ac_2O$, pyr, rt.

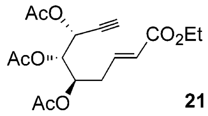
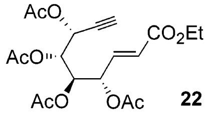
synthetic approach has been tested on two aldohexoses, 2-deoxy-D-glucose **1** and D-glucose **2** (Scheme 6, Table 4).

In these two cases, the desired compounds **19** and **20** were obtained in 23% and 20% yields, respectively.

These compounds were so transformed into ethyl 8-yn-2-enoates **IIb** by a Wittig type reaction[3] using ethylbromoacetate, tri-*n*-butylphosphine, and zinc in refluxing 1,4-dioxane (Scheme 7, Table 5) followed by acetylation of the hydroxy groups. We noticed that the presence of hydroxyl group at the α-carbon center has an effect on the yield, which is better for **19** (75%) than **20** (57%).

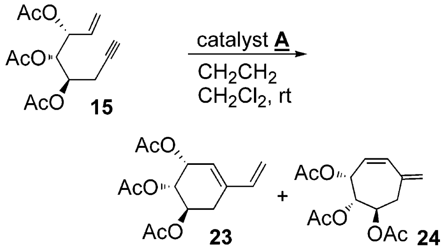
**Synthesis of 1-Vinylcyclohexenes IVa.** Recently, we have described the conversion of polyhydroxylated perbenzyled 1,6- and 1,7-enynes into 1-vinylcyclopentenes and 1-vinylcyclohexenes, respectively.[10] The cyclization was carried out by ring-closing metathesis using Grubbs catalyst (2nd generation, Figure 1) in $CH_2Cl_2$ under an ethylene atmosphere, in Mori's conditions.[11]

**TABLE 5. Synthesis of Ethyl-8-yn-2-enoates 21 and 22**[a]

| Ib | Product IIb | Yield* |
|---|---|---|
| **19** |  | **21** : 75% |
| **20** |  | **22** : 57% |

[a] Yield represents isolated yield.

**SCHEME 8**



| catalyst **A** : | yields | **23/24** |
|---|---|---|
| 15% mol. | 74% | 2/1 |
| 8% mol. | 76% | 5/1 |

We then extended these ring-closing metathesis conditions to peracetylated 1,7-enynes **15**−**18** described above, converting them into their corresponding 1-vinylcyclohexenes. Surprisingly, the reaction of 1,7-enyne **15** with ruthenium catalyst (15 mol %) under an ethylene atmosphere produced a mixture of **23** and **24** isomers in 74% yield, in a 2 to 1 ratio that we were unable to separate (Scheme 8). However, in the $^1H$ NMR spectrum of the mixture, the signals for methylene groups were clearly detected. We could observe H-2′a and H-2′b for **23** at 5.16 and 5.21 ppm, respectively, as two doublets with $J_{1'-2'a} = 10.8$ Hz and $J_{1'-2'b} = 17.6$ Hz. For **24**, we could observe H-1′a and H-1′b at 5.11 and 5.16 ppm as two singles.

Recently, Mori observed in the ring-closing metathesis reaction the formation of the six-membered ring[20] from 1,6-enynes but never from 1,7-enynes. The authors explained this formation as the possibility of two pathways in the reaction of the alkyne part of the enyne with methylidene ruthenium carbene complex. It is also very surprisingly that the ring-closing metathesis reaction of compound **15** resulted in the formation of isomer **24**, which was never detected when the protecting groups of hydroxyls were benzyl groups (Scheme 9).[10]

Apparently, this result shows that the nature of the protecting group of hydroxyls could define the product of this cyclization. In the case of the derivative of 2-deoxy-D-glucose, the benzyl protection of 1,7-enyne led only to the desired 1,3-diene in 72% yield (Scheme 9), whereas

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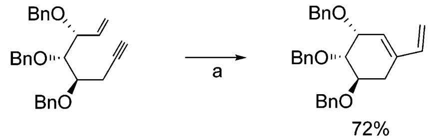
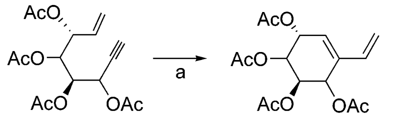
[20] (a) Kitamura, T.; Sato, Y.; Mori, M. *J. Chem. Soc., Chem. Commun.* **2001**, 1258. (b) Kitamura, T.; Sato, Y.; Mori, M. *Adv. Synth. Catal.* **2002**, *344*, 678.

**SCHEME 9**[a]



[a] Reagents and conditions: Catalyst **A** (15% mol.), $CH_2CH_2$, $CH_2Cl_2$, rt, 3 h.

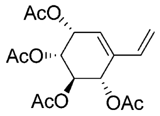
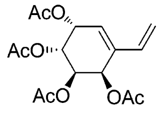
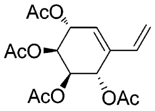
**SCHEME 10. Synthesis of Compounds 25–27**[a]



**IIIa : 16-18** **IVa : 25-27**

[a] Reagents and conditions: Catalyst **A** (10% mol), $CH_2CH_2$, $CH_2Cl_2$, rt.

**TABLE 6. Synthesis of 1-Vinylcyclohexenes 25–27**[a]

| IIIa | 1-vinylcyclohexene IVa | Yield* |
|---|---|---|
| 16 |  | 25 : 76% |
| 17 |  | 26 : 72% |
| 18 |  | 27 : 80% |

[a] Yield represents isolated yield.

acetyl protection produced an inseparable mixture of isomers **23** and **24** in a similar yield (74%) (Scheme 8). Moreover, if the reaction is run under the same conditions but with 8 mol % of Grubbs catalyst **A**, a mixture is always obtained but the ratio is different (5/1) in favor of the desired 1-vinyclyclohexene **23** in 76% yield. However, we did not avoid the formation of this isomer **24**.

We extended the ruthenium-catalyzed metathesis, under Mori's conditions, to enynes **16**–**18** (Scheme 10, Table 6). When the reaction is performed with 10 mol % of catalyst on enyne **16**, the desired 1-vinylcyclohexene **25** is isolated as the only product with satisfying yield (76%). No trace of isomer is detected. With the same conditions, 1,7-enynes **17** and **18** produced the desired 1-vinylcyclohexenes **26** and **27** in 72% and 80% yields, respectively.

So, it appears that in the case of derivatives of D-glucose **16**, D-mannose **17**, and D-galactose **18**, the acetyl protection of the hydroxyl group was superior to benzyl protection.[10] In fact, when the acetyl protection is chosen, the yields were better and the quantity of ruthenium catalyst necessary for the reaction to bring it to completion was lower. As electron-poor olefins are usually not good substrates for ring-closing metathesis when compounds **21** and **22** were reacted with catalyst **A**, we did not observed any cyclization. We are pursuing our study on these cyclization methods, and results will be reported in due course.

## Conclusion

In summary, several polyhydroxylated 1,7-enynes and two ethyl 8-yn-2-enoateswere prepared in a versatile manner in few steps from aldohexoses with satisfying yields. From these 1,7-enynes, functionalized 1-vinylcyclohexenes were obtained by ring-closing metathesis reaction mediated by ruthenium carbene complexes. Such polyhydroxylated carbocycles are interesting scaffolds for the construction of bridged and fused bicyclic systems. We are pursuing our study on further carbohydrate derivatives and uses of the polyhydroxylated 1-vinylcyclohexenes provided by our methodology.

## Experimental Section

**General Procedure 1 for the Synthesis of 6,7-Dideoxy-*aldo*-hept-6-enoses (6–10).** To the starting material (2-deoxy-D-glucose **1**, D-glucose **2**, D-mannose **3**, D-galactose **4**, and *N*-acetyl-D-glucosamine **5**) dissolved in dry DMF (15 mL) were successively added imidazole (2 equiv per OH) and dropwise trimethylchlorosilane or triethylchlorosilane (2 equiv per OH). The reaction was stirred under an argon atmosphere for 12 h at room temperature as monitored by TLC. The mixture was concentrated, and the residue was diluted in hexane and washed with water. This material was used in subsequent reactions without further treatment. To a $CH_2Cl_2$ (10 mL) solution of oxalyl chloride (4 equiv) was added dropwise dry methyl sulfoxide (8 equiv) at −70 °C under an argon atmosphere. After 5 min under stirring, a solution of the substrate in $CH_2Cl_2$ (5 mL) was added. The reaction was monitored by TLC. After 15 min, triethylamine (10 equiv) was then carefully added. After being stirred at low temperature for 30 min, the reaction mixture was warmed to room temperature, and a saturated solution of $NH_4Cl$ was added. The mixture was extracted, and the combined organic layers were washed with water, dried ($Na_2SO_4$), and concentrated. The residue was diluted in dry THF. The flask was then immersed in a water bath. Methylenetriphenylphosphorane (5 equiv), prepared from methyltriphenylphosphonium bromide and *t*-BuOK in THF (10 mL) at room temperature under an argon atmosphere for 15 min, was then added dropwise during 1 h. $H_2O$ was added (1 mL) and then TBAF (1.1 equiv per OH). The mixture was concentrated, and the residue was purified by flash chromatography.

**2,6,7-Trideoxy-D-*gluco*-hept-6-ene-pyranose (6).** The compound **6** was prepared by general procedure 1 from 2-deoxy-D-glucose **1** (1 g, 6.1 mmol). The crude residue was purified by two consecutive flash chromatographies ($CH_2Cl_2$/MeOH 95:5 then EtOAc/MeOH 99:1) and **6** was obtained as a colorless oil (200 mg, 21%): $R_f = 0.28$ (EtOAc/MeOH 98:2); IR ($CHCl_3$) $\upsilon$ 3079, 3030 and 1655 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) anomeric $\beta$: $\delta$ 7.60 (m, 1 H), 5.29 (m, 1 H, $J = 1.1$, 3.6 Hz), 5.25 (m, 2 H), 4.17 (m, 1 H), 3.87 (ddd, 1 H, $J = 5.0$, 5.1, 11.8 Hz), 3.07 (t, 1 H, $J = 5.1$ Hz), 2.08 (ddd, 1 H, $J = 12.8$ Hz), 1.63 (ddd, 1 H). $^{13}C$ NMR ($CDCl_3$) anomeric $\beta$: $\delta$ 136.3, 116.7, 94.1, 76.3, 72.7, 68.5, 38.5. $^{13}C$ NMR ($CDCl_3$) anomeric $\alpha$: $\delta$ 135.6, 116.9, 91.8, 77.0, 75.5, 71.3, 40.8. Anal. Calcd for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.70; H, 7.78. MS: $m/z$ 183.1 $[M + Na]^+$.

**6,7-Dideoxy-D-*gluco*-hept-6-ene-pyranose (7).** The compound **7** was prepared by general procedure 1 from D-glucose **2** (1 g, 5.55 mmol). The crude residue was purified by two consecutive flash chromatographies ($CH_2Cl_2$/MeOH 90:10 then EtOAc/MeOH 96:4), and **7** was obtained as a colorless oil (195 mg, 20%): $R_f = 0.30$ ($CH_2Cl_2$/MeOH 9:1); IR ($CHCl_3$) $\upsilon$ 3079, 3030 and 1655 $cm^{-1}$. $^1H$ NMR ($CD_3OD$) anomeric $\alpha$: $\delta$ 5.13 (d, 1 H, $J = 3.7$ Hz), 3.17 (dd, 1 H, $J = 9.3$ Hz); anomeric $\beta$: $\delta$ 4.53 (d, 1 H, $J = 7.7$ Hz), 3.30 (m, 1 H). $^{13}C$ NMR ($CD_3OD$)

anomerics α and *β*: *δ* 136.1, 135.4, 116.7, 116.4, 93.0, 97.1, 76.9, 75.3, 73.7, 72.9, 72.0, 74.4, 74.8. Anal. Calcd for $C_7H_{12}O_5$: C, 47.55; H, 6.87. Found: C, 47.83; H, 6.99. MS: *m*/*z* 199.1 [M + Na]$^+$.

**6,7-Dideoxy-D-*manno*-hept-6-ene-pyranose (8).** The compound **8** was prepared by general procedure 1 from D-mannose **3** (1 g, 5.55 mmol). The crude residue was purified by two consecutive flash chromatographies ($CH_2Cl_2$/MeOH 95:5 then EtOAc/MeOH 98:2), and **8** was obtained as a colorless oil (412 mg, 42%): $R_f = 0.22$ (EtOAc/MeOH 98:2); IR ($CHCl_3$) $\upsilon$ 3079, 3030 and 1655 cm$^{-1}$. $^1$H NMR ($CD_3OD$) anomeric *β*: *δ* 5.97 (ddd, 1 H, *J* = 6.1, 10.5, 17.0 Hz), 5.41 (ddd, 1 H, *J* = 1.2, 2.0 Hz), 5.23 (ddd, 1 H, *J* = 1.3 Hz), 5.09 (d, 1 H, *J* = 1.6 Hz), 4.18 (m, 1 H), 3.83 (dd, 1 H, *J* = 3.3 Hz), 3.49 (m, 2 H). $^{13}$C NMR ($CD_3OD$) anomeric *β*: *δ* 136.3, 116.7, 94.9, 73.3, 72.1, 72.0, 71.1. $^{13}$C NMR ($CD_3OD$) anomeric α: *δ* 135.6, 116.9, 94.6, 77.2, 74.1, 72.1, 70.8. Anal. Calcd for $C_7H_{12}O_5$: C, 47.55; H, 6.87. Found: C, 47.63; H, 7.02. MS: *m*/*z* 199.1 [M + Na]$^+$.

**6,7-Dideoxy-D-*galacto*-hept-6-ene-pyranose (9).** The compound **9** was prepared by general procedure 1 from D-galactose **4** (1 g, 5.55 mmol). The crude residue was purified by two consecutive flash chromatographies ($CH_2Cl_2$/MeOH 90:10 then EtOAc/MeOH 96:4), and **9** was obtained as a colorless oil (480 mg, 49%): $R_f = 0.30$ ($CH_2Cl_2$/MeOH 9:1); IR ($CHCl_3$) $\upsilon$ 3080, 3030 and 1655 cm$^{-1}$. $^1$H NMR ($CD_3OD$) anomeric α: *δ* 5.11 (d, 1 H, *J* = 3.2 Hz); anomeric *β*: *δ* 4.54 (d, 1 H, *J* = 6.7 Hz). $^{13}$C NMR ($CD_3OD$) anomerics α and *β*: *δ* 135.8, 135.3, 116.4, 116.1, 93.0, 97.6, 76.1, 74.0, 72.6, 72.0, 71.4, 70.3, 69.2. Anal. Calcd for $C_7H_{12}O_5$: C, 47.55; H, 6.87. Found: C, 47.85; H, 7.03. MS: *m*/*z* 199.1 [M + Na]$^+$.

**2-Acetamido-2,6,7-trideoxy-D-*gluco*-hept-6-ene-pyranose (10).** The compound **10** was prepared by general procedure 1 from 2-acetamido-2-deoxy-D-glucose **5** (1 g, 4.55 mmol). The crude residue was purified by two consecutive flash chromatographies ($CH_2Cl_2$/MeOH 95:5 then EtOAc/MeOH 99:1), and **10** was obtained as a colorless oil (170 mg, 18%): $R_f =$ 0.36 ($CH_2Cl_2$/MeOH 98:2); IR ($CHCl_3$) $\upsilon$ 3079, 3030, 1689 and 1655 cm$^{-1}$. $^1$H NMR ($CD_3OD$) anomeric α: *δ* 7.95 (d, 1 H, *J* = 8.5 Hz), 5.97 (ddd, 1 H, *J* = 5.9, 10.6, 16.9 Hz), 5.36 (ddd, 1 H, *J* = 1.5 Hz), 5.21 (ddd, 1 H, *J* = 1.5 Hz), 5.12 (d, 1 H, *J* = 3.4 Hz), 4.23 (bdd, 1 H, *J* = 9.2 Hz), 3.88 (ddd, 1 H, *J* = 10.7 Hz), 3.72 (dd, 1 H, *J* = 8.8 Hz), 3.16 (dd, 1 H), 2.05, 2.03 (s, 3 H). $^{13}$C NMR ($CD_3OD$) anomeric α: *δ* 172.8, 136.2, 116.3, 91.5, 75.4, 72.0, 71.5, 55.0, 21.7. $^{13}$C NMR ($CD_3OD$) anomeric *β*: *δ* 136.4, 116.6, 96.0, 76.8, 74.8, 72.0, 55.1. Anal. Calcd for $C_9H_{15}NO_5$: C, 49.76; H, 6.96. Found: C, 49.83; H, 7.10. MS: *m*/*z* 240.2 [M + Na]$^+$.

**General Procedure 2 for the Synthesis of Compounds 11−14.** An anhydrous 1,4-dioxane (20 mL) solution of starting material **6**−**9** (1 mmol), zinc (4.4 equiv), and dibromomethyltriphenylphosphonium bromide (4 equiv) was stirred under an argon atmosphere and allowed to reflux. The reaction was monitored by TLC, and after completion the mixture was cooled to room temperature and filtered on a glass frit. After concentration, the crude residue was purified by flash chromatography to give the desired compounds **11**−**14**.

**(4*R*,5*S*,6*R*)-1,1-Dibromo-octa-1,7-diene-4,5,6-triol (11).** The compound **11** was prepared by general procedure 2 from **6** (195 mg, 1.21 mmol). The crude residue was purified by flash chromatography ($CH_2Cl_2$/EtOAc 7:3), and **11** was obtained as a colorless oil (280 mg, 74%): $R_f = 0.2$ ($CH_2Cl_2$/MeOH 85:15); $[\alpha]^{28}_D = +20$ (*c* 1.0, MeOH); IR ($CHCl_3$) $\upsilon$ 3080, 3030, 2970, 1655 and 1640 cm$^{-1}$. $^1$H NMR ($CD_3OD$): *δ* 6.52 (t, 1 H, *J* = 7.2 Hz), 5.92 (ddd, 1 H, *J* = 5.6, 10.5, 17.3 Hz), 5.37 (dd, 1 H, *J* = 0.7 Hz), 5.24 (dd, 1 H), 4.32 (dd, 1 H, *J* = 4.1 Hz), 3.94 (ddd, 1 H, *J* = 2.4, 5.3, 7.8 Hz), 3.26 (dd, 1 H), 2.36 (m, 2 H). $^{13}$C NMR ($CD_3OD$): *δ* 137.2, 135.6, 117.5, 90.7, 75.2, 74.9, 69.5, 37.8. Anal. Calcd for $C_8H_{12}Br_2O_3$: C, 30.41; H, 3.83. Found: C, 30.77; H, 3.78. MS: *m*/*z* 339.0 [M + Na]$^+$.

**(3*S*,4*R*,5*R*,6*R*)-1,1-Dibromo-octa-1,7-diene-3,4,5,6-tetrol (12).** The compound **12** was prepared by general procedure 2 from **7** (147 mg, 0.83 mmol). The crude residue was purified by three consecutive flash chromatographies (EtOAc/$CH_3CN$ 90:10, $CH_2Cl_2$/MeOH 90:10 then EtOAc/MeOH 98:2), and **12** was obtained as a colorless oil (190 mg, 70%): $R_f = 0.4$ ($CH_2Cl_2$/MeOH 85:15); $[\alpha]^{26}_D = +7$ (*c* 1.5, MeOH); IR ($CHCl_3$) $\upsilon$ 3080, 3030, 2970, 1655 and 1640 cm$^{-1}$. $^1$H NMR ($CD_3OD$): *δ* 6.61 (d, 1 H, *J* = 8.7 Hz), 6.03 (ddd, 1 H, *J* = 6.1, 10.5, 17.3 Hz), 5.35 (dt,1 H, *J* = 1.7 Hz), 5.22 (dt,1 H, *J* = 1.7 Hz), 4.45 (dd, 1 H, *J* = 5.9 Hz), 4.16 (tt, 1 H, *J* = 6.1 Hz), 3.78 (dd, 1 H, *J* = 2.3 Hz), 3.45 (dd, 1 H, *J* = 6.1 Hz). $^{13}$C NMR ($CD_3OD$): *δ* 138.9, 138.7, 115.7, 91.6, 73.8, 73.0, 71.9. Anal. Calcd for $C_8H_{12}Br_2O_4$: C, 28.94; H, 3.64. Found: C, 29.21; H, 3.78. MS: *m*/*z* 354.9 [M + Na]$^+$.

**(3*R*,4*R*,5*R*,6*R*)-1,1-Dibromo-octa-1,7-diene-3,4,5,6-tetrol (13).** The compound **13** was prepared by general procedure 2 from **8** (380 mg, 2.15 mmol). The crude residue was purified by three consecutive flash chromatographies (EtOAc/$CH_3CN$ 90:10, $CH_2Cl_2$/MeOH 90:10, then EtOAc/MeOH 98:2), and **13** was obtained as a powder (480 mg, 68%): $R_f = 0.31$ ($CH_2Cl_2$/MeOH 90:10); $[\alpha]^{26}_D = +16$ (*c* 0.4, MeOH); mp 125−129 °C; IR ($CHCl_3$) $\upsilon$ 3080, 3030, 2970, 1655 and 1640 cm$^{-1}$. $^1$H NMR ($CD_3OD$): *δ* 6.61 (d, 1 H, *J* = 8.9 Hz), 6.06 (ddd, 1 H, *J* = 7.4, 10.5, 17.3 Hz), 5.35 (ddd, 1 H, *J* = 1.3, 2.0 Hz), 5.21 (ddd, 1 H, *J* = 1.3 Hz), 4.40 (dd, 1 H, *J* = 7.6 Hz), 4.15 (ddt, 1 H, *J* = 5.3 Hz), 3.79 (dd, 1 H, *J* = 1.7 Hz), 3.61 (dd, 1 H). $^{13}$C NMR ($CD_3OD$): *δ* 139.9, 139.2, 115.2, 91.8, 73.0, 72.4, 72.0. Anal. Calcd for $C_8H_{12}Br_2O_4$: C, 28.94; H, 3.64. Found: C, 29.28; H, 3.83. MS: *m*/*z* 354.9 [M + Na]$^+$.

**(3*S*,4*R*,5*S*,6*R*)-1,1-Dibromo-octa-1,7-diene-3,4,5,6-tetrol (14).** The compound **14** was prepared by general procedure 2 from **9** (460 mg, 2.61 mmol). The crude residue was purified by three consecutive flash chromatographies (EtOAc/$CH_3CN$ 90:10, $CH_2Cl_2$/MeOH 90:10, then EtOAc/MeOH 98:2), and **14** was obtained as a colorless oil (640 mg, 70%): $R_f = 0.45$ (EtOAc/MeOH 98:2); $[\alpha]^{24}_D = +33$ (*c* 0.2, MeOH); IR ($CHCl_3$) $\upsilon$ 3080, 3030, 2970, 1655 and 1640 cm$^{-1}$. $^1$H NMR ($CD_3OD$): *δ* 6.77 (d, 1 H, *J* = 8.5 Hz), 6.05 (ddd, 1 H, *J* = 5.7, 10.5, 17.3 Hz), 5.37 (dt, 1 H, *J* = 1.8 Hz), 5.24 (dt, 1 H, *J* = 1.8 Hz), 4.63 (dd, 1 H, *J* = 2.0 Hz), 4.37 (m, 1 H), 3.58 (m, 2 H). $^{13}$C NMR ($CD_3OD$): *δ* 140.1, 139.4, 114.6, 94.0, 72.7, 72.6, 71.9. Anal. Calcd for $C_8H_{12}Br_2O_4$: C, 28.94; H, 3.64. Found: C, 29.20; H, 3.85. MS: *m*/*z* 355.1 [M + Na]$^+$.

**General Procedure 3 for Synthesis of Enynes 15−18.** To a THF (10 mL) solution of starting material **11**−**14** (1 mmol) was added dropwise *n*-BuLi (2.5 M in hexanes, 5 equiv for **11** and 6 equiv for **12**−**14**) at −70 °C under an argon atmosphere. After being stirred at low temperature for 15 min, the reaction mixture was warmed to room temperature, and EtOH was added (2 mL). After that the solvents were evaporated under vacuum. Pyridine (10 mL) and acetic anhydride were added to the residue. After 12 h at room temperature, the reaction mixture was concentrated and extracted with EtOAc/$H_2O$. The organic layers were dried ($Na_2SO_4$) and concentrated. The crude residue was purified by flash chromatography.

**(4*R*,5*S*,6*R*)-4,5,6-Tri-*O*-acetyl-oct-7-en-1-yne-4,5,6-triol (15).** The compound **15** was prepared by general procedure 3 from **11** (200 mg, 0.63 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc 87:13), and **15** was obtained as a colorless oil (135 mg, 75%): $R_f = 0.25$ (hexane/EtOAc 85:15); $[\alpha]^{24}_D = +19$ (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) $\upsilon$ 3300, 3075, 3020 and 2100 cm$^{-1}$. $^1$H NMR ($CDCl_3$): *δ* 5.73 (ddd, 1 H, *J* = 7.1, 10.3, 17.8 Hz), 5.33 (m, 5 H), 2.47 (m, 2 H, *J* = 2.7 Hz), 2.11, 2.10, 2.06 (s, 3H), 2.03 (t, 1 H). $^{13}$C NMR ($CDCl_3$): *δ* 170.4, 170.2, 170.0, 132.8, 121.1, 78.6, 72.2, 71.5, 68.7, 21.4, 21.2. Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.77; H, 6.78. MS: *m*/*z* 305.2 [M + Na]$^+$.

**(3*S*,4*R*,5*R*,6*R*)-3,4,5,6-Tetra-*O*-acetyl-oct-7-en-1-yne-3,4,5,6-tetrol (16).** The compound **16** was prepared by general procedure 3 from **12** (70 mg, 0.21 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc 82:18), and **16** was obtained as a colorless oil (40 mg, 57%): $R_f = 0.3$ (hexane/EtOAc 8:2); $[\alpha]^{21}_D = +53$ (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) $\upsilon$

3300, 3075, 3020 and 2100 cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 5.75 (ddd, 1 H, $J$ = 7.8, 10.2, 17.1 Hz), 5.47 (m, 3 H, $J$ = 0.6, 7.8 Hz), 5.38 (dt, 1 H, $J$ = 1.0, 1.0 Hz), 5.31 (dt, 1 H), 5.25 (t, 1 H), 2.57 (d, 1 H), 2.09, 2.08, 2.06 (s, 3 H). $^{13}$C NMR (CDCl$_3$): $\delta$ 169.8, 132.4, 121.6, 77.0, 76.9, 72.4, 70.7, 70.5, 63.0, 21.3, 21.2, 21.0, 20.9. Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H, 5.92. Found: C, 56.59; H, 6.00. MS: *m/z* 363.3 [M + Na]$^+$.

**(3*R*,4*R*,5*R*,6*R*)-3,4,5,6-Tetra-*O*-acetyl-oct-7-en-1-yne-3,4,5,6-tetrol (17).** The compound **17** was prepared by general procedure 3 from **13** (160 mg, 0.48 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc 82:18), and **17** was obtained as a colorless oil (130 mg, 85%): $R_f$ = 0.29 (hexane/EtOAc 8:2); $[\alpha]^{27}_{D} = -4$ ($c$ 1.4, CHCl$_3$); IR (CHCl$_3$) $\upsilon$ 3300, 3075, 3020 and 2100 cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 5.70 (ddd, 1 H, $J$ = 7.5, 10.2, 17.6 Hz), 5.51 (dd,1 H, $J$ = 2.5, 8.0 Hz), 5.43 (dd, 1 H, $J$ = 2.0 Hz), 5.36 (m, 2 H, $J$ = 1.0, 8.3 Hz), 5.26 (dt, 1 H, $J$ = 1.0, 1.0 Hz), 5.23 (ddt, 1 H), 2.45 (d, 1 H), 2.09, 2.08, 2.05 (s, 3 H). $^{13}$C NMR (CDCl$_3$): $\delta$ 170.1, 170.0, 169.9, 169.6, 132.6, 121.4, 78.0, 75.4, 71.8, 69.8, 69.6, 61.2, 21.3, 21.1, 21.0. Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H, 5.92. Found: C, 56.69; H, 6.11. MS: *m/z* 363.3 [M + Na]$^+$.

**(3*S*,4*R*,5*S*,6*R*)-3,4,5,6-Tetra-*O*-acetyl-oct-7-en-1-yne-3,4,5,6-tetrol (18).** The compound **18** was prepared by general procedure 3 from **14** (190 mg, 0.57 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc 82:18), and **18** was obtained as a colorless oil (110 mg, 60%): $R_f$ = 0.27 (hexane/EtOAc 8:2); $[\alpha]^{27}_{D} = +58$ ($c$ 0.7, CHCl$_3$); IR (CHCl$_3$) $\upsilon$ 3300, 3075, 3020 and 2100 cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 5.66 (ddd, 1 H, $J$ = 5.0, 10.6, 17.2 Hz), 5.54 (dd, 1 H, $J$ = 2.2, 2.4 Hz), 5.49 (dd, 1 H, $J$ = 2.7, 9.5 Hz), 5.44 (m, 1 H), 5.32 (dd, 1 H), 5.25 (dt, 1 H, $J$ = 1.3 Hz), 5.20 (dt, 1 H, $J$ = 1.3 Hz), 2.45 (d, 1 H), 2.09, 2.08, 2.06 (s, 3 H). $^{13}$C NMR (CDCl$_3$): $\delta$ 170.3, 170.0, 169.8, 132.1, 118.5, 77.0, 75.6, 71.2, 69.7, 69.5, 61.7, 21.2, 21.0, 20.9. Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H, 5.92. Found: C, 56.69; H, 5.99. MS: *m/z* 363.3 [M + Na]$^+$.

**General Procedure 4 for Synthesis of Compounds 19−20.** To the starting material (2-deoxy-D-glucose **1**, D-glucose **2**) dissolved in dry DMF (15 mL) were successively added imidazole (2 equiv per OH) and dropwise trimethylchlorosilane (2 equiv per OH). The reaction was stirred under an argon atmosphere for 12 h at room temperature as monitored by TLC. The mixture was concentrated, and the residue was diluted in hexane and washed with water. This material was used in subsequent reactions without further treatment. To a CH$_2$Cl$_2$ (10 mL) solution of oxalyl chloride (3 equiv) was added dropwise dry methyl sulfoxide (6 equiv) at −70 °C under an argon atmosphere. After 5 min under stirring, a solution of substrate in CH$_2$Cl$_2$ (5 mL) was added. The reaction was monitored by TLC. After 15 min, triethylamine (9 equiv) was then carefully added. After being stirred at low temperature for 30 min, the reaction mixture was warmed to room temperature, and a saturated solution of NH$_4$Cl was added. The mixture was extracted, and the combined organic layers were washed with water, dried (Na$_2$SO$_4$), and concentrated. The residue was diluted in dry THF. The flask was then immersed in a water bath. Dibromomethylenetriphenylphosphorane, prepared from dibromomethyltriphenylphosphonium bromide[4] (2.5 equiv) and *t*-BuOK (2.4 equiv) in THF (5 mL) at room temperature under an argon atmosphere for 15 min, was then added per portion during 1 h. The reaction was stirred under argon and monitored by TLC. At −70 °C, *n*-BuLi (2.5 M in hexanes, 2.2 equiv) was added dropwise. After 15 min, MeOH was added. The reaction mixture was warmed to room temperature and concentrated. The residue was purified by flash chromatography.

**2,6,7-Trideoxy-D-*gluco*-hept-6-yne-pyranose (19).** The compound **19** was prepared by general procedure 4 from **1** (500 mg, 3 mmol). The crude residue was purified by two consecutives flash chromatographies (CH$_2$Cl$_2$/MeOH 95:5 then EtOAc/MeOH 99:1), and **19** was obtained as a colorless oil (111 mg, 23%): $R_f$ = 0.2 (CH$_2$Cl$_2$/MeOH 95:5); IR (CHCl$_3$) $\upsilon$ 3300 and 2100 cm$^{-1}$. $^1$H NMR (CD$_3$OD) anomeric α: $\delta$ 4.80 (dd, 1 H, $J$ = 3.8, 8.2 Hz), 2.85 (d, 1 H, $J$ = 2.1 Hz), 2.43 (m, 2 H); anomeric $\beta$: $\delta$ 4.62 (dd, 1 H, $J$ = 3.5, 8.1 Hz), 2.80 (d, 1 H, $J$ = 2.1 Hz), 2.48 (m, 2 H). $^{13}$C NMR (CD$_3$OD) anomerics α and $\beta$: $\delta$ 94.3, 92.0, 82.0, 81.6, 76.3, 74.9, 73.3, 72.5, 67.4, 63.0, 74.2, 73.6, 40.5, 38.3. Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.46; H, 6.52. MS: *m/z* 181.1 [M + Na]$^+$.

**6,7-Trideoxy-D-*gluco*-hept-6-yne-pyranose (20).** The compound **20** was prepared by general procedure 4 from **2** (1 g, 5.55 mmol). The crude residue was purified by flash chromatography (CH$_2$Cl$_2$/MeOH 90:10), and **20** was obtained as a colorless oil (220 mg, 22%): $R_f$ = 0.1 (CH$_2$Cl$_2$/MeOH 9:1); IR (CHCl$_3$) $\upsilon$ 3300 and 2100 cm$^{-1}$. $^1$H NMR (CD$_3$OD) anomeric α: $\delta$ 5.10 (d, 1 H, $J$ = 3.6 Hz), 3.17 (dd, 1 H, $J$ = 9.3 Hz), 2.82 (d, 1 H, $J$ = 2.2 Hz); anomeric $\beta$: $\delta$ 4.48 (d, 1 H, $J$ = 7.8 Hz), 3.30 (m, 1 H), 2.91 (d, 1 H, $J$ = 2.1 Hz); $^{13}$C NMR (CD$_3$OD) anomerics α and $\beta$: $\delta$ 97.1, 93.1, 81.5, 80.5, 76.3, 74.9, 73.3, 72.5, 67.4, 63.0, 74.6, 74.3, 74.2, 73.6. Anal. Calcd for $C_7H_{10}O_5$: C, 48.28; H, 5.79. Found: C, 48.68; H, 5.89. MS: *m/z* 197.2 [M + Na]$^+$.

**General Procedure 5 for Synthesis of Compounds 21 and 22.** To an anhydrous 1,4-dioxane (5 mL) solution of zinc (2 equiv) were successively added *n*-tributylphosphine (2 equiv), ethylbromoacetate (2 equiv), and starting material solubilized in anhydrous 1,4-dioxane (5 mL). The reaction was stirred under an argon atmosphere and allowed to reflux. The reaction was monitored by TLC, and after completion the mixture was cooled to room temperature and filtered on a glass frit. After concentration, the crude residue was purified by flash chromatography.

**(*E*)-Ethyl 2,3,4,8,9-Pentadeoxy-D-*gluco*-non-8-yn-2-enoate (21).** The compound **21** was prepared by general procedure 5 from **1** (100 mg, 0.63 mmol). The crude residue was purified by flash chromatography (CH$_2$Cl$_2$/MeOH 98:02), and **21** was obtained as a colorless oil (106 mg, 73%): $R_f$ = 0.6 (CH$_2$Cl$_2$/MeOH 85:15); $[\alpha]^{25}_{D} = -5$ ($c$ 0.88, MeOH); IR (CHCl$_3$) $\upsilon$ 3300, 2100, 1780 and 1640 cm$^{-1}$. $^1$H NMR (CD$_3$OD): $\delta$ 7,04 (dt, 1 H, $J$ = 7.4, 15.6 Hz), 5.95 (dt, 1 H, $J$ = 1.5 Hz), 4.39 (dd, 1 H, $J$ = 2.2, 7.3 Hz), 4.18 (q, 2 H, $J$ = 7.1 Hz), 3.41 (dd, 1 H, $J$ = 2.4 Hz), 3.40 (ddd, 1 H, $J$ = 1.6, 5.7 Hz), 2.84 (d, 1 H), 2.51 (ddd, 1 H, $J$ = 8.3 Hz), 2.45 (m, 1 H), 1.29 (t, 3 H). $^{13}$C NMR (CD$_3$OD): $\delta$ 167.2, 146.6, 123.2, 83.8, 75.3, 73.9, 69.2, 63.1, 60.5, 36.7, 13.6. Anal. Calcd for $C_{11}H_{16}O_5$: C, 55.88; H, 7.07. Found: C, 55.49; H, 7.21. MS: *m/z* 251.2 [M + Na]$^+$. Acetylated **21**: $R_f$ = 0.38 (hexane/EtOAc 7:3); $[\alpha]^{28}_{D} = -13$ ($c$ 1.5, CHCl$_3$). $^1$H NMR (CDCl$_3$): $\delta$ 6.77 (dt, 1 H, $J$ = 7.5, 15.6 Hz), 5.80 (d, 1 H), 5.44 (dd, 1 H, $J$ = 2.2, 6.7 Hz), 5.25 (m, 2 H), 4.09 (q, 2 H, $J$ = 7.1 Hz), 2.44 (m, 3 H), 2.08, 2.00 (s, 3 H), 1.22 (t, 3 H). $^{13}$C NMR (CDCl$_3$): $\delta$ 170.2, 170.1, 169.5, 166.1, 142.0, 125.1, 77.8, 75.7, 72.4, 65.0, 61.5, 60.7, 34.0, 21.0, 20.9, 14.5. Anal. Calcd for $C_{16}H_{22}O_8$: C, 57.62; H, 6.26. Found: C, 58.00; H, 6.16. MS: *m/z* 373.3 [M + Na]$^+$.

**(*E*)-Ethyl 2,3,8,9-Tetradeoxy-D-*gluco*-non-8-yn-2-enoate (22).** The compound **22** was prepared by general procedure 5 from **2** (140 mg, 0.81 mmol). The crude residue was purified by two consecutive flash chromatographies (CH$_2$Cl$_2$/MeOH 95:5 then EtOAc/MeOH 98:02), and **22** was obtained as a colorless oil (156 mg, 79%): $R_f$ = 0.2 (CH$_2$Cl$_2$/MeOH 95:5); $[\alpha]^{25}_{D} = -28$ ($c$ 1.4, MeOH); IR (CHCl$_3$) $\upsilon$ 3300, 2100, 1780 and 1640 cm$^{-1}$. $^1$H NMR (CD$_3$OD): $\delta$ 7,06 (dd, 1 H, $J$ = 5.1, 15.7 Hz), 6.14 (dd, 1 H, $J$ = 1.6 Hz), 4.44 (m, 2 H, $J$ = 2.2, 2.3, 2.4 Hz), 4.20 (q, 2 H, $J$ = 8.1 Hz), 3.85 (dd, 1 H, $J$ = 7.0 Hz), 3.80 (d, 1 H), 3.60 (dd, 1 H), 1.20 (t, 3 H). $^{13}$C NMR (CD$_3$OD): $\delta$ 167.1, 148.2, 121.5, 83.8, 74.1, 73.5, 72.6, 63.0, 60.7, 13.6. Anal. Calcd for $C_{11}H_{16}O_6$: C, 54,69; H, 6.60. Found: C, 54.49; H, 6.99. MS: *m/z* 267.2 [M + Na]$^+$. Acetylated **22**: $R_f$ = 0.3 (hexane/EtOAc 65:35); $[\alpha]^{25}_{D} = -21$ ($c$ 0.9, CHCl$_3$). $^1$H NMR (CDCl$_3$): $\delta$ 6.76 (dd, 1 H, $J$ = 4.9, 15.8 Hz), 5.90 (dd, 1 H, $J$ = 1.7 Hz), 5.52 (dt, 1 H, $J$ = 4.9 Hz), 5.42 (dd, 1 H, $J$ = 2.3, 5.1 Hz), 5.33 (dd, 1 H, $J$ = 10.0 Hz), 5.31 (dd, 1 H), 4.15 (q, 2 H, $J$ = 8.1 Hz), 3.80 (d, 1 H), 2.05, 1.90 (s, 3 H), 1.20 (t, 3 H). $^{13}$C NMR (CDCl$_3$): $\delta$ 169.9, 169.7, 169.6, 165.5, 165.6, 140.2, 124.1, 77.0, 76.4, 70.4, 70.0, 61.9, 60.7, 20.9, 14.5. Anal. Calcd for $C_{19}H_{24}O_{10}$: C, 55.34; H, 5.87. Found: C, 55.59; H, 6.02. MS: $m/z$ 435.4 $[M + Na]^+$.

**General Procedure 6 for Enyne Metathesis (23−27).** Freshly distilled $CH_2Cl_2$ was degassed for 1 h. The enyne (0.5 mmol) was dissolved in $CH_2Cl_2$ (8 mL), and ethylene gas was passed through the solution for 45 min. Ruthenium catalyst **A** in $CH_2Cl_2$ (2 mL) was then added, and the solution was degassed again with ethylene for 20 min. The mixture was stirred under an atmosphere of ethylene at room temperature. The reaction was monitored by TLC. The mixture was then concentrated, and the residue was purified by flash chromatography.

**(3*R*,4*S*,5*R*)-3,4,5-Tri-*O*-acetyl-1-vinylcyclohexene-3,4,5-triol (23) and (4*R*,5*S*,6*R*)-4,5,6-Tri-*O*-acetyl-1-methylenecyclohept-2-ene-4,5,6-triol (24).** By general procedure 6, from reaction of **15** (75 mg, 0.26 mmol), the two compounds **23** and **24** were obtained. After a flash chromatography (hexane/EtOAc 82:18), an isomer mixture was obtained (60 mg, 73%) (**23**/**24** = 5/1). $R_f$ = 0.22 (hexane/EtOAc 8:2). Data for **23**: $^1$H NMR ($CDCl_3$): $\delta$ 6.35 (dd, 1 H, $J$ = 10.8, 17.6 Hz), 5.70 (m, 1 H), 5.66 (d, 1 H, $J$ = 3.5 Hz), 5.33 (m, 1 H, $J$ = 5.9, 7.5 Hz), 5.25 (m, 1 H), 5.21 (d, 1 H), 5.16 (d, 1 H), 2.92 (dd, 1 H, $J$ = 17.3 Hz), 2.22 (dd, 1 H), 2.00 (m, 3 H). $^{13}$C NMR ($CDCl_3$): $\delta$ 170.4, 170.2, 170.0, 139.0, 137.4, 123.0, 116.1, 70.1, 67.5, 67.2, 29.7, 21.4, 21.3, 21.2. MS: $m/z$ 305.3 $[M + Na]^+$. Data for **24**: $^1$H NMR ($CDCl_3$): $\delta$ 6.40 (d, 1 H, $J$ = 10.4 Hz), 5.67 (m, 1 H, $J$ = 1.5 Hz), 5.52 (dd, 1 H, $J$ = 6.8 Hz), 5.23 (m, 1 H, $J$ = 4.3, 4.8 Hz), 5.19 (m, 1 H), 5.16 (br s, 1 H), 5.11 (br s, 1 H), 2.89 (dd, 1 H, $J$ = 14.0 Hz), 2.57 (dd, 1 H), 2.00 (m, 3 H). $^{13}$C NMR ($CDCl_3$): $\delta$ 170.4, 170.2, 170.0, 139.8, 138.1, 124.8, 121.9, 75.9, 73.4, 70.8, 37.6, 21.4, 21.3, 21.2. MS: $m/z$ 305.3 $[M + Na]^+$.

**(3*R*,4*R*,5*R*,6*S*)-3,4,5,6-Tetra-*O*-acetyl-1-vinylcyclohexene-3,4,5,6-tetrol (25).** The compound **25** was prepared by general procedure 6 from **16** (110 mg, 0.32 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc 82:18), and **25** was obtained as a colorless oil (87 mg, 76%): $R_f$ = 0.65 (hexane/EtOAc 5:5); $[\alpha]^{29}_{D}$ = −52 ($c$ 0.84, $CHCl_3$); IR ($CHCl_3$) $\upsilon$ 1650, 1600 and 930 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 6.20 (dd, 1 H, $J$ = 11.2, 17.7 Hz), 5.99 (d, 1 H, $J$ = 5.7 Hz), 5.83 (m, 2 H, $J$ = 0.7, 6.1 Hz), 5.64 (dd, 1 H, $J$ = 3.7 Hz), 5.58 (dd, 1 H, $J$ = 10.4 Hz), 5.22 (dd, 1 H), 5.16 (dd, 1 H), 2.30, 2.20, 1.90 (m, 3 H). $^{13}$C NMR ($CDCl_3$): $\delta$ 170.8, 170.5, 170.3, 139.7, 134.0, 125.5, 118.0, 70.8, 70.5, 68.4, 66.2, 21.3, 21.2, 21.1. Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H, 5.92. Found: C, 56.80; H, 6.22. MS: $m/z$ 363.3 $[M + Na]^+$.

**(3*R*,4*R*,5*R*,6*R*)-3,4,5,6-Tetra-*O*-acetyl-1-vinylcyclohexene-3,4,5,6-tetrol (26).** The compound **26** was prepared by general procedure 6 from **17** (136 mg, 0.4 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc 82:18), and **26** was obtained as a colorless oil (100 mg, 72%): $R_f$ = 0.30 (hexane/EtOAc 8:2); $[\alpha]^{25}_{D}$ = −164 ($c$ 0.9, $CHCl_3$); IR ($CHCl_3$) $\upsilon$ 1650, 1600 and 930 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 6.27 (dd, 1 H, $J$ = 11.1, 17.7 Hz), 6.12 (d, 1 H, $J$ = 3.2 Hz), 5.90 (d, 1 H, $J$ = 5.6 Hz), 5.77 (dd, 1 H, $J$ = 3.5 Hz), 5.46 (m, 2 H), 5.33 (d, 1 H), 5.22 (d, 1 H), 2.10 (m, 3 H). $^{13}$C NMR ($CDCl_3$): $\delta$ 170.9, 170.7, 170.5, 138.2, 134.7, 127.0, 117.7, 67.3, 66.6, 66.5, 64.9, 21.2, 21.1. Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.80; H, 5.92. Found: C, 56.80; H, 6.22. MS: $m/z$ 363.3 $[M + Na]^+$.

**(3*R*,4*S*,5*R*,6*S*)-3,4,5,6-Tetra-*O*-acetyl-1-vinylcyclohexene-3,4,5,6-tetrol (27).** The compound **27** was prepared by general procedure 6 from **18** (100 mg, 0.29 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc 82:18), and **27** was obtained as a colorless oil (80 mg, 80%): $R_f$ = 0.65 (hexane/EtOAc 5:5); $[\alpha]^{26}_{D}$ = −33 ($c$ 0.75, $CHCl_3$); IR ($CHCl_3$) $\upsilon$ 1650, 1600 and 930 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 6.25 (dd,1 H, $J$ = 11.1, 17.7 Hz), 5.86 (d, 1 H, $J$ = 3.0 Hz), 5.64 (t, 1 H, $J$ = 5.6 Hz), 5.40 (d, 1 H, $J$ = 3.4 Hz), 5.37 (m, 1 H, $J$ = 8.2 Hz), 5.30 (dd, 1 H), 5.22 (d, 1 H), 5.17 (d, 1 H), 2.10 (m, 3 H). $^{13}$C NMR ($CDCl_3$): $\delta$ 170.9, 170.6, 170.1, 170.0, 135.0, 134.9, 129.2, 116.8, 69.9, 69.5, 69.3, 66.2, 21.4, 21.2. Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H, 5.92. Found: C, 56.69; H, 6.15. MS: $m/z$ 363.3 $[M + Na]^+$.

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**Supporting Information Available:** General methods and $^{13}$C NMR spectra of compounds **15**−**18**, **21**, **22, 25**−**27**, and a mixture of **23** and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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