Carbohydrate Carbocyclization by a Novel Zinc-Mediated Domino Reaction and Ring-Closing Olefin Metathesis

Lene Hyldtoft and Robert Madsen*

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

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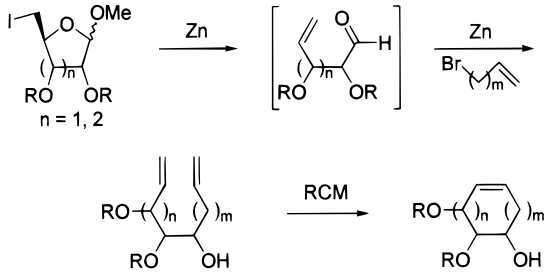
Abstract: A general method for carbocyclization of carbohydrates is described using two consecutive organometallic transformations: a novel zinc-mediated domino reaction to give functionalized dienes followed by ring-closing olefin metathesis. In the first reaction, methyl ω-deoxy-ω-iodo glycosides undergo reductive elimination with zinc to produce a terminal double bond. This also liberates the aldehyde which is immediately alkylated in situ by various organozinc reagents. The alkylation occurs under Barbier conditions with methylene iodide and several allyl bromides. Zinc plays a dual role by both promoting the reductive elimination and activating the alkyl halide. Vinylation is carried out by adding divinylzinc. When a new stereogenic center is generated, moderate to excellent stereocontrol is generally observed. An amino group can be introduced by trapping the intermediate aldehyde as an imine prior to the alkylation. The reductive elimination−allylation sequence can also be promoted by indium metal. All the alkylations produce a second double bond, and the obtained dienes are subsequently subjected to ring-closing olefin metathesis to produce the corresponding carbocycles. Newly developed catalyst **30** with an N-heterocyclic carbene ligand is more reactive toward these carbohydrate-derived dienes than commercially available catalyst **18**. Acetylation of the free hydroxy groups improves the metathesis reaction significantly. Both five- and six-membered carbocycles are available by this route, including a number of conduritols and quercitols.

Introduction

Modern synthetic design demands high efficiency in terms of minimization of synthetic steps together with maximization of molecular complexity.[1] Domino reactions are becoming a very attractive tool in this regard.[2] In these processes several bond forming transformations take place under the same reaction conditions, without adding additional reagent, and in which the subsequent reactions are due to the functionality formed in the previous step.[2c] The need for synthetic efficiency is particularly acute in the area of carbohydrate chemistry. Carbohydrates are densely functionalized molecules, and as a result their synthetic application often requires many reaction steps, usually for manipulation of different protecting groups. In particular the conversion of carbohydrates into carbocycles is a major task and has been the subject of many studies.[3] This is due to the fact that many biologically important molecules and natural products contain a polyhydroxylated five- or six-membered carbocycle.[4] To improve the use of carbohydrates as synthetic starting materials, we have embarked on a program to develop more efficient transformations on carbohydrates by the use of organometallic chemistry.[5]

Scheme 1



In this regard we were interested in the zinc-mediated reductive elimination of ω-iodo glycosides which generates an aldehyde and a terminal double bond[6] (Scheme 1). Originally discovered by Bernet and Vasella in 1979, this transformation has found many applications in carbohydrate chemistry.[7] However, a general drawback is the instability of the liberated aldehyde and related reproducibility problems caused by different zinc sources. In some applications the aldehyde has been

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(7) For some recent examples, see: (a) Dransfield, P. J.; Moutel, S.; Shipman, M.; Sik, V. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3349. (b) Ovaa, H.; Codée, J. D. C.; Lastdrager, B.; Overkleeft, H. S.; van der Marel, G. A.; van Boom, J. H. *Tetrahedron Lett.* **1999**, *40*, 5063. (c) Désiré, J.; Prandi, J. *Tetrahedron Lett.* **1997**, *38*, 6189. (d) Hümmer, W.; Dubois, E.; Gracza, T.; Jäger, V. *Synthesis* **1997**, 634. (e) Grové, J. J. C.; Holzapfel, C. W. *Carbohydr. Lett.* **1997**, *2*, 329.

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trapped in situ by a nitrogen nucleophile.[8] We reasoned that carbon nucleophiles could also be used for trapping the aldehyde, e.g., in a Barbier-type alkylation.[9] Zinc would then serve a dual function by promoting both the reductive elimination and activation of an alkyl halide for the alkylation. In addition, if the alkyl halide contains a double bond, this transformation would convert the ω-iodo glycosides directly into functionalized dienes. These then can be converted into carbocycles by ring-closing olefin metathesis (RCM). Since the key catalyst development by Schrock and Grubbs, the area of olefin metathesis has emerged as a powerful new tool for C−C bond formation.[10−12]

Herein, we report a full account on a novel zinc-mediated domino reaction that allows stereocontrolled synthesis of carbohydrate-derived dienes from ω-iodo glycosides. These dienes are then converted into five- and six-membered carbocycles by ring-closing olefin metathesis. This sequence thus constitutes an easy and efficient method for carbohydrate carbocyclization by the use of two consecutive organometallic transformations.

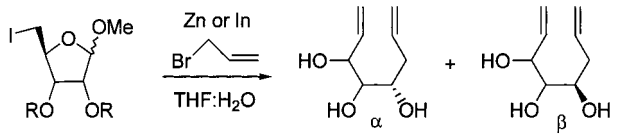
Results and Discussion

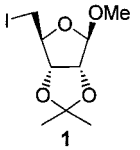
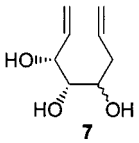
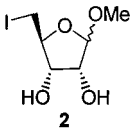
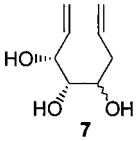
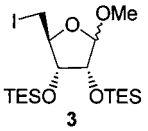
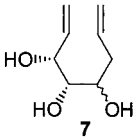
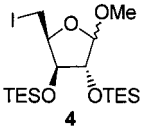
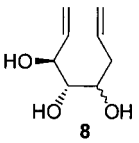
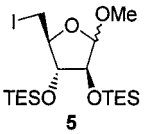
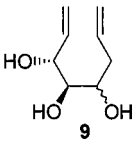
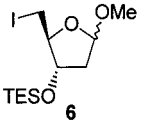
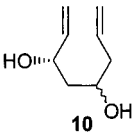
Elimination−Allylation. We first examined the domino reaction with 5-iodo-ribofuranosides **1** and **2** in the presence of zinc and allyl bromide (Table 1). A variety of zinc sources and reaction conditions were investigated. In general, activated zinc dust in tetrahydrofuran (THF) under sonication conditions proved to be a very reliable procedure that consistently gave full conversion and very high yield of the desired diene **7** (entries 1−3 and 5−7). No Wurtz coupling of the starting iodofuranosides was observed,[13] and the conditions were sufficiently mild to prevent the intermediate aldehyde from undergoing side reactions before the allylation. Simple reflux instead of sonication proved less reliable and sometimes caused the reaction to stall, presumably due to precipitation of zinc(II) salts. More reactive Rieke zinc,[14] zinc graphite and zinc−silver graphite[15] were found to be less convenient for general use as compared to zinc dust. In addition, these highly reactive forms of zinc, which are prepared from $ZnCl_2$ and potassium, in our hands sometimes caused base-catalyzed epimerization and decomposition of the intermediate aldehyde.

The solvent was also an important parameter in the domino reaction. The reductive elimination of the ω-iodo glycosides proceeded slowly in THF alone when zinc dust was used. Enhanced reactivity could be obtained by adding a Lewis acid or by using a protic solvent/cosolvent. If alcohols were used as solvent,[6a] the corresponding acetal of the intermediate aldehyde could sometimes be isolated due to the Lewis acidity of the zinc(II) salts. However, H_2O was found to be an efficient cosolvent together with THF.[9] The THF:H_2O ratio influenced the rate in the sense that more H_2O generally enhanced the rate of the overall transformation. Faster conversion could also be achieved by adding a Lewis acid (entries 3 and 7).

The reaction with isopropylidene ribofuranoside **1** gave the desired diene **7** in a 4:1 diastereomeric ratio (entries 1−3).[16] Pure **7α** could be obtained by recrystallization. This diastereoselectivity can be rationalized on the basis of the Felkin−Anh model.[17] It also corresponds with what has previously been observed in zinc-mediated allylations of α-alkoxy aldehydes

Table 1. Zinc- and Indium-Mediated Elimination−Allylation[a]



Entry	Starting furanoside	Metal/THF:H_2O	Product[d]	α : β	Yield
1		Zn/4 : 1		4 : 1	quant.
2		Zn/2 : 1		4 : 1	quant.
3		Zn/1 : 0[b]		4 : 1	quant.
4	**1**	In/4 : 1	**7**	4 : 1	72%
5		Zn/4 : 1		2 : 3	89%
6		Zn/1 : 4		3 : 7	quant.
7		Zn/1 : 0[b]		5 : 6	quant.
8	**2**	In/1 : 4	**7**	1 : 5	62%
9		Zn/9 : 1		5 : 1	85%
	3		**7**		
10		Zn/9 : 1		3 : 1	89%
11	**4**	In/9 : 1	**8**	2 : 7	85%
12		Zn/9 : 1		3 : 7	82%
	5		**9**		
13		Zn/4 : 1		5 : 6	94%
14	**6**	Zn/4 : 1[c]	**10**	1 : 2	89%

[a] All reactions were carried out by sonication at 40 °C. [b] 2 eq of $MgBr_2 \cdot OEt_2$ was added instead of H_2O. [c] 5 eq of Et_3N was also added. [d] Hydroxyl protecting groups were removed with ion-exchange resin in the workup.

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(12) For a recent review on olefin metathesis in carbohydrate chemistry, see: Jørgensen, M.; Hadwiger, P.; Madsen, R.; Stütz, A. E.; Wrodnigg, T. M. *Curr. Org. Chem.* **2000**, *4*, 565.

(13) Blanchard, P.; Da Silva, A. D.; El Kortbi, M. S. Fourrey, J.-L.; Robert-Géro, M. *J. Org. Chem.* **1993**, *58*, 6517.

(14) Rieke, R. D.; Hanson, M. V. in *Organozinc Reagents-A Practical Approach*; Knochel, P., Jones, P., Eds.; Oxford University Press: Oxford, U.K., 1999; p 23.

(15) Fürstner, A. in *Active Metals-Preparation, Characterization, Applications*; Fürstner, A., Ed.; VCH: Weinheim, Germany, 1996; p 381.

(16) The stereochemistry of the products were assigned after ring-closing olefin metathesis.

(17) Chérest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199. Anh, N. T. *Top. Curr. Chem.* **1980**, *88*, 145.

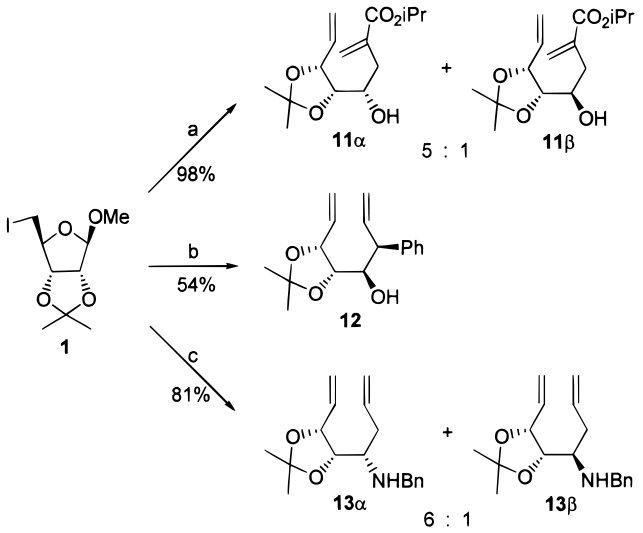
under aqueous conditions.[18] However, it should be noted that both the reductive elimination and the allylation reaction are believed to be initiated by single electron transfer on the zinc surface.[19] As a result, the diastereoselectivity might also be influenced by factors on this surface. Notably, when the isopropylidene group is removed as in **2**, the opposite diastereomer **7*β*** is obtained as the major product (entries 5−7). That this reaction proceeds at all is an interesting result since we and others[20] have been unable to allylate unprotected aldoses with zinc and allyl bromide under aqueous conditions.

Since the hydroxyl protecting group seems to have an impact on the stereochemical outcome, we were interested in other suitable protecting groups. Use of the isopropylidene group is limited to glycosides with two cis oriented hydroxy groups. Acetyl groups gave rise to complex mixtures in the elimination−allylation reaction, presumably due to rapid decomposition of the intermediate aldehyde. Instead, triethylsilyl (TES) groups were found to be a convenient alternative. These are easily introduced and then removed in the final workup. Furthermore, the elimination−allylation with triethylsilylated ribofuranoside **3** proceeded well to give **7** in a slightly better diastereomeric ratio than that observed in the reaction with **1** (entry 9).

Following these studies on ribofuranosides **1**−**3** other 5-iodopentofuranosides were then investigated. Unfortunately, unprotected methyl 5-deoxy-5-iodo-D-xylo- and -D-arabinofuranosides turned out to be less stable and produced dienes **8** and **9** in only about 50% yield. Furthermore, the observed α:*β* ratio was 1:1 in both cases. Therefore, the more stable triethylsilylated substrates **4** and **5** were prepared and subjected to zinc and allyl bromide (entries 10 and 12). This now gave **8** and **9** in good yields and about 3:1 diastereoselectivity, in both cases favoring the *erythro* relationship between the newly formed stereocenter and the original stereocenter at C-2 in the starting pentose. The 2-deoxyribose substrate **6** gave diene **10** in high yield, although the selectivity was poor (entry 13). This could, however, be slightly improved by adding Et_3N which serves as an inhibitor slowing down the rate of the reaction (entry 14). The formation of **10*β*** as the major product is in accordance with the predictions from the Evans model for 1,3-induction.[21] For the other substrates **1**−**5** the addition of Et_3N did not produce better results. In these cases the allylation became too slow with added Et_3N for the overall transformation to proceed at a resonable rate.

Besides zinc, the reductive elimination of *ω*-iodo glycosides has also been accomplished with SmI_2.[22] Indium metal, however, has never been used for this fragmentation. Stimulated by previous studies on indium-mediated allylation of aldoses,[23] we decided to probe the elimination−allylation in the presence of indium. Gratifyingly, the reaction proceeded to give the desired dienes (Table 1, entries 4, 8, and 11). The reaction was significantly slower with indium than with zinc, but the stereochemical outcome is remarkable. Isopropylidene ribofuranoside **1** gave the same 4:1 diastereomeric ratio with indium as with zinc (entries 1 and 4). Unprotected ribofuranoside **2**, on the other hand, gave a significantly improved 1:5 diastereomeric ratio with indium (entries 6 and 8). These diastereoselectivities are in line with what has previously been observed in indium-mediated allylation of aldoses in aqueous media.[20,24,25] Isopropylidene protected aldoses give products where the stereochemistry in the major diastereomer is *erythro* between the newly generated stereocenter and the one originally present at C-2 in the starting aldose.[24] This is also observed with zinc[18a] and corresponds with the Felkin−Anh model.[17] Unprotected aldoses, on the contrary, all undergo indium-mediated allylation to give products where the stereochemistry in the major diastereomer is *threo* between these stereocenters.[20,25] This has been explained on the basis of indium chelation to the α-hydroxy group.[26] Surprisingly, in the case of xylofuranoside **4** the diastereomeric ratio was reversed when indium was used as compared to zinc (entries 10 and 11). The reason for this change is not immediately clear.[27] However, these results do show that besides varying the substituents in the substrates the metal can also be used as a tool in optimizing these transformations.

Scheme 2[a]



[a] (a) $CH_2{=}C(CH_2Br)CO_2{}^iPr$, Zn, THF:$H_2O$ (2:1), ultrasound, 40 °C. (b) $PhCH{=}CHCH_2Br$, Zn, THF:H_2O (2:1), ultrasound, 40 °C. (c) $CH_2{=}CHCH_2Br$, $BnNH_2$, Zn, THF, ultrasound, 40 °C.

Other allylating agents have also been investigated using zinc as the metal. Reaction of **1** with isopropyl α-(bromomethyl)-acrylate gave dienes **11α** and **11*β*** in very high yield and a 5:1 ratio (Scheme 2). Both the yield and the selectivity are similar to the results obtained with allyl bromide in Table 1, entries 1−3. However, when **1** was reacted with cinnamyl bromide the *π*-facial selectivity changed, giving **12** as the major product isolated in 54% yield. Only minor amounts of the remaining three diastereomers were formed. Further studies are necessary to elucidate why the presence of a phenyl group in cinnamyl bromide causes this crossover in *π*-facial discrimination as compared to allyl bromide.[28] The *erythro* relationship between

(18) (a) Chattopadhyay, A. *J. Org. Chem.* **1996**, *61*, 6104. (b) Chan, T. H.; Li, C. J. *Can. J. Chem.* **1992**, *70*, 2726.

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(26) Paquette, L. A.; Mitzel, T. M. *J. Am. Chem. Soc.* **1996**, *118*, 1931.

(27) Normally, the stereochemical outcome in the aqueous Barbier-type allylation does not depend on the metal. However, one previous exception has been reported: Rübsam, F.; Seck, S.; Giannis, A. *Tetrahedron* **1997**, *53*, 2823.

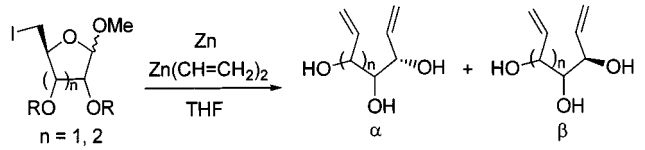
the two newly generated stereocenters in **12** is that expected from a chair transition state.[28]

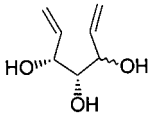
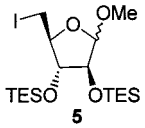
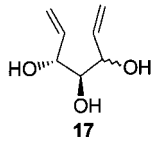
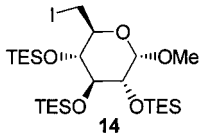
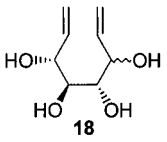
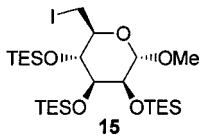
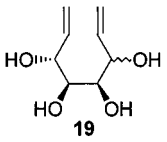
Finally, it was investigated whether the intermediate aldehyde could be intercepted with an amine prior to the allylation. This allylation would then take place on the formed imine and result in the introduction of an amino group. In fact, treatment of **1** with zinc, benzylamine, and allyl bromide succeeded in giving the amino diene **13** in both good yield and diastereoselectivity. This is an excellent example of a domino sequence: reductive elimination followed by imine formation followed by allylation, all in the same pot without changing conditions during the transformation. Strictly anhydrous conditions were necessary in order to form the intermediate imine. Only 2 equiv of benzylamine were added. When more equivalents of benzylamine were used, the amine substituted the iodide in the starting iodofuranoside.

Elimination−Vinylation. Following the success of the elimination−allylation sequence we then decided to investigate the corresponding elimination−vinylation reaction. Instead of adding a three carbon allyl group in the alkylation step, a two carbon vinyl group would now be employed. The vinylation, however, cannot be carried out directly under Barbier conditions because vinyl bromide will not insert zinc under the conditions for the reductive elimination. As a consequence[29] we decided to preform divinyl zinc prior to the reaction by magnesium−zinc transmetalation from vinylmagnesium bromide and $ZnCl_2$. Divinyl zinc has previously been shown to give higher diastereoselectivity in addition to sugars than vinylmagnesium bromide.[30]

Indeed, treatment of isopropylidene ribofuranoside **1** with zinc dust and divinyl zinc in THF gave diene **16** in excellent diastereoselectivity (Table 2, entry 1). Triethylsilylated ribofuranoside **3** gave the same result while the reaction with arabinofuranoside **5** was less stereoselective (entries 2 and 3). The transformation also proceeded well for hexopyranosides, as seen for the conversion of glucose and mannose substrates **14** and **15** (entries 4 and 5). For the latter only one diastereomer of **19** could be observed. Unprotected ribofuranoside **2**, however, did not undergo the vinylation reaction, indicating the need for the isopropylidene or silyl blocking groups for this transformation. The product ratios in Table 2 deserve some further comments. For the ribose and mannose substrates **1**, **3**, and **15**, very high selectivity is obtained for the Felkin−Anh products **16**α and **19**β. This is, however, not the case for arabino and glucose substrates **5** and **14**. The vinyl addition is less selective in these two cases, and the major products **17**α and **18**β are not consistent with the predictions made by the Felkin−Anh model. This is part of a general pattern for the addition to these triethylsilylated substrates **3**, **4**, **5**, **14**, and **15** in Tables 1 and 2. For the substrates with 2,3-*erythro* configuration (**3** and **15**) the addition always occurs with high selectivity for the Felkin-Anh product. For the substrates with 2,3-*threo* configuration (**4**, **5**, and **14**) the diastereoselectivity is lower and in some cases even reverses. Chelation control is not believed to be involved in these addition reactions. The reason for this difference must then lie in a different steric and/or electronic influence of the C-3 silyloxy group in the *erythro* and the *threo* cases. To the best of our knowledge there has not yet been any systematic study on additions to *erythro* and *threo* 2,3-dialkoxy aldehydes under nonchelating conditions.[31]

Table 2. Zinc-Mediated Elimination−Vinylation[a]



Entry	Starting glycoside	Product[b]	α : β	Yield
1	**1**	 **16**	10 : 1	70%
2	**3**		10 : 1	85%
3	 **5**	 **17**	5 : 2	77%
4	 **14**	 **18**	1 : 4	77%
5	 **15**	 **19**	0 : 1	73%

[a] All reactions were carried out by sonication at 40 °C. [b] Hydroxyl protecting groups were removed with ion-exchange resin in the workup.

Elimination−Olefination. Another possibility for introducing a double bond in the alkylation step would be to add just one carbon to form an olefin with the intermediate aldehyde. This could potentially be done by talking advantage of the zinc-mediated olefination with CH_2I_2,[32] which furthermore requires a Lewis acid that will also benefit the reductive elimination. In fact, when glucose and mannose substrates **14** and **15** were treated with zinc, CH_2I_2 and (TMS)Cl dienes **17**α and **17**β were obtained, respectively (Table 3). It turned out to be important to add a catalytic amount of $PbCl_2$ in order to get the olefination to proceed,[33] otherwise the reaction would stop at the aldehyde step. Since there are no stereocenters generated in this transformation, it is a better method for preparing **17**α and **17**β than the elimination−vinylation reaction in Table 2, entry 3.

Ring-Closing Olefin Metathesis. With the advent of efficient catalysts, the ring-closing metathesis (RCM) reaction has emerged as a powerful process for cyclization of dienes.[11] Also the area of carbohydrate chemistry has taken advantage of the RCM reaction although synthesis of the diene precursors can sometimes be cumbersome.[12] The zinc-mediated domino reaction provides an easy protocol for preparation of dienes, and in the following the RCM reaction of these will be studied.

(28) For reaction of an α-siloxy aldehyde with cinnamyl bromide and indium under aqueous conditions, see: Isaac, M. B.; Paquette, L. A. *J. Org. Chem.* **1997**, *62*, 5333.

(29) Magnesium metal inserts vinyl bromide easily but will not perform the reductive elimination of ω-iodo glycosides due to competing dimerization by Wurtz coupling: Fürstner, A.; Weidmann, H. *J. Org. Chem.* **1989**, *54*, 2307. Stout, E. I.; Doane, W. M.; Trinkus, V. C. *Carbohydr. Res.* **1976**, *50*, 282.

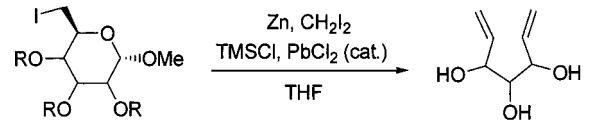
(30) Boschetti, A.; Nicotra, F.; Panza, L.; Russo, G. *J. Org. Chem.* **1988**, *53*, 4181.

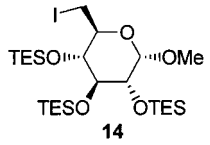
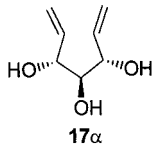
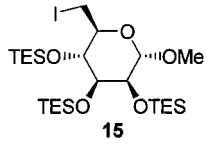
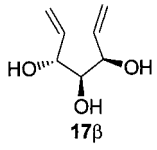
(31) For a recent review on 1,2- and 1,3-induction in carbonyl addition reactions, see: Mengel, A.; Reiser, O. *Chem. Rev.* **1999**, *99*, 1191.

(32) (a) Takai, K.; Hotta, Y.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1698. (b) Lombardo, L. *Org. Synth.* **1987**, *65*, 81.

(33) Takai, K.; Kakiuchi, T.; Kataoka, Y.; Utimoto, K. *J. Org. Chem.* **1994**, *59*, 2668.

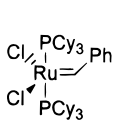
Table 3. Zinc-Mediated Elimination−Methylenation[a]

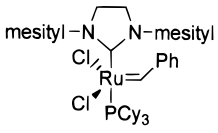


Entry	Starting pyranoside	Product[b]	Yield
1	 **14**	 **17α**	80%
2	 **15**	 **17β**	61%

[a] All reactions were carried out by sonication at 40 °C. [b] Silyl groups were removed with ion-exchange resin in the workup.

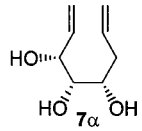
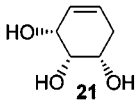
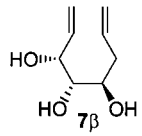
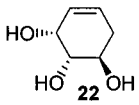
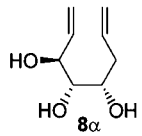
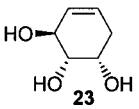
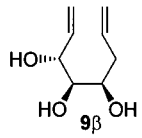
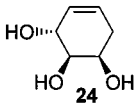
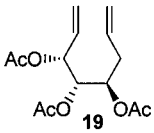
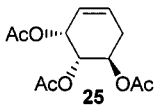
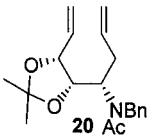
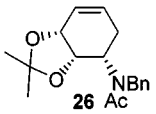
Previous work on RCM in carbohydrate chemistry has concentrated on the use of commercially available Grubbs catalyst **18**.[12,34]


18


30

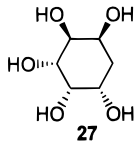
When the major diene isomers from Table 1 were treated with this catalyst in CH_2Cl_2, very high yields were obtained of the desired cyclohexenes **21**−**24** (Table 4, entries 1−4). It is noteworthy that these unprotected triols are metathesized so well. However, there are some differences. Cyclohexenes **21**, **23**, and **24** all crystallized out from the reaction mixture during the course of the reaction. Cyclohexene **22** did not crystallize, and in this case a higher catalyst loading was necessary to force the reaction to go to completion. Although catalyst **18** is known to tolerate alcohols in the substrates,[11] the active ruthenium−methylene catalyst, generated after the first catalytic cycle, has been shown to decompose rapidly in methanol.[35] We speculated that the hydroxy groups after all may inhibit the reaction in entry 2. In fact, when **7*β*** was acetylated to give **19**, the ring closure could be carried out with only half the amount of catalyst (entry 5). The amino diene **13α**, on the other hand, turned out to be more difficult. Even after converting **13α** into its corresponding ammonium salt with TsOH,[36] the RCM reaction only gave about 50% conversion with 10% of **18**. Full conversion could first be achieved after conversion of the amine into amide **20** (entry 6). The structure of the obtained cyclohexene **26** was elucidated by ^{1}H NMR after saturation of the double bond. For the remaining cyclohexenes **21**−**24** the structure was determined after dihydroxylation of the double bond to give the corresponding quercitols. These cyclohexanepentols have previously been the target of many syntheses due

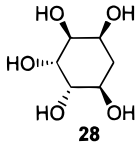
Table 4. RCM with Catalyst **18**[a]

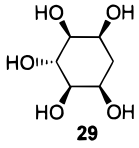
Entry	Diene	Amount of **18**	Product	Yield
1	 **7α**	6%	 **21**	96%
2	 **7β**	10%	 **22**	95%
3	 **8α**	6%	 **23**	95%
4	 **9β**	6%	 **24**	97%
5	 **19**	5%	 **25**	98%
6	 **20**	10%	 **26**	94%

[a] All reactions were carried out in CH_2Cl_2 at room temperature.

to their close resemblance to the inositols.[37,38] The dihydroxylation with OsO_4 occurs predominately anti to the allylic hydroxy group to afford (+)-*talo*-quercitol **27** (from **21**), (−)-*gala*-quercitol **28** (from **22**), and *muco*-quercitol **29** (from **23** and **24**). This constitutes one of the shortest syntheses of these quercitols in nonracemic form.


27

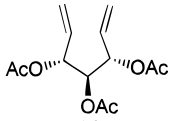
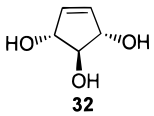
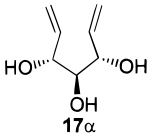
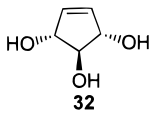
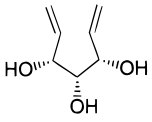
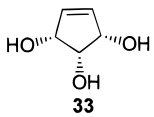
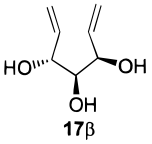
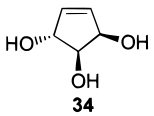

28


29

When we subsequently carried out the RCM of dienes **31** and **17α** ,full conversion could not be achieved (Table 5, entries 1 and 2). If **17α** was protected with benzyl groups, even lower conversion was obtained. This prompted us to look for a more reactive catalyst. Carbohydrate dienes are often electron deficient and, as our results show, can sometimes be intrinsicly difficult to metathesize. In previous RCM of carbohydrate-derived dienes double digit percentages for the catalyst loading with **18** are commonly employed.[12] Very recently an entire new family of more reactive metathesis catalysts has been developed, all of which are derived from **18** by substituting one of the phosphine

(34) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.
(35) Kirkland, T. A.; Lynn, D. M.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 9904.
(36) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856.
(37) Hudlicky, T.; Cebulak, M. *Cyclitols and Their Derivatives*; VCH: New York, 1993.
(38) For recent examples, see: (a) Maezaki, N.; Nagahashi, N.; Yoshigami, R.; Iwata, C.; Tanaka, T. *Tetrahedron Lett.* **1999**, *40*, 3781. (b) Kim, K. S.; Park, J. I.; Moon, H. K.; Yi, H. *Chem. Commun.* **1998**, 1945. (c) Biamonte, M. A.; Vasella, A. *Helv. Chim. Acta* **1998**, *81*, 688. (d) Maraş, A.; Seçen, H.; Sütbeyaz, Y.; Balci, M. *J. Org. Chem.* **1998**, *63*, 2039.

Table 5. RCM with Catalysts **18** and **30**[a]

Entry	Diene	Catalyst	Product	Yield
1	 **31**	10% **18**	 **32**	44%[b]
2	 **17α**	10% **18**	 **32**	35%[c]
3		7% **30**		95%
4	 **16α**	7% **30**	 **33**	90%
5	 **17β**	7% **30**	 **34**	89%

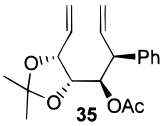
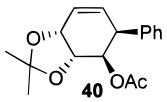
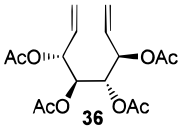
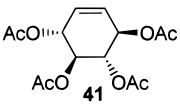
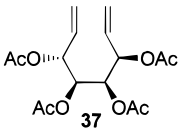
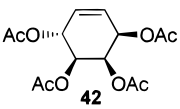
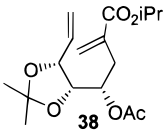
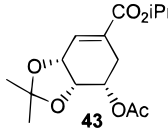
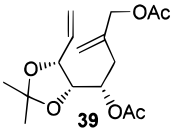
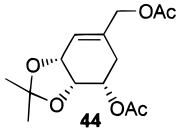
[a] All reactions were carried out in CH_2Cl_2 at room temperature except in entry 2 where 40 °C was used. [b] Acetyl groups were removed in the workup. 51% of **17α** was also obtained. [c] 29% of **17α** was recovered.

ligands with an N-heterocyclic carbene.[39] We found catalyst **30** easy to prepare without any special precautions.[39a] In fact, when **17α** was treated with 7% of **30**, full conversion could now be achieved and cyclopentene **32** was isolated in high yield (entry 3). Similar results were obtained with dienes **16α** and **17*β*** (entries 4 and 5). This clearly demonstrates the increased reactivity of **30** as compared to **18**. Cyclopentene **32** has previously been isolated from a plant of the Achariaceae family.[40]

For synthesis of the corresponding cyclohexenes it turned out to be necessary to use peracetylated dienes **35**−**37** (Table 6, entries 1−3).[41] The correponding unprotected dienes **12**, **18*β***, and **19*β*** did not undergo the ring closure very efficiently. Instead, treatment of **35**−**37** with catalyst **30** all gave high yield of cyclohexenes **40**−**42**. The latter two are the peracetates of (−)-conduritol B and C which hereby are available in very few steps from glucose and mannose, respectively. This clearly shows the strength of the developed synthetic strategy. Numerous stereocontrolled syntheses of the conduritols have been reported,[37,42] but this strategy using a zinc-mediated domino reaction and subsequent RCM is one of the shortest.

The RCM reaction is sensitive to substituents on the double bond.[43] As a consequence, ester diene **11α** was expected to be a very difficult substrate. No RCM could be achieved directly with **11α**. Acetylation was then performed to give **38** while

Table 6. RCM with Catalyst **30**[a]

Entry	Diene	Amount of **30**	Product	Yield
1	 **35**	5%	 **40**	95%
2	 **36**	7.5%	 **41**	83%
3	 **37**	7.5%	 **42**	93%
4	 **38**	10%	 **43**	56%[b]
5	 **39**	10%	 **44**	64%[c]

[a] All reactions were carried out in CH_2Cl_2 at 40 °C. [b] 32% of **38** was recovered. [c] 25% of **39** was recovered.

reduction and acetylation gave **39** (entries 4 and 5). Treatment of **38** and **39** with catalyst **18** gave only little conversion, while catalyst **30** gave moderate yields of **43** and **44** in both cases together with some recovered starting material. Deprotection of **43** yielded the 5-epimer of shikimic acid. Although these substituted dienes remain a problem in the RCM reaction, two main conclusions can be drawn from these studies on carbohydrate-derived dienes. First, acetylated dienes generally give better RCM than unprotected or benzylated dienes. Second, catalyst **30** with an N-heterocyclic carbene ligand is more powerful for these substrates than commercially available **18**.

In conclusion, we have developed an efficient method for carbocyclization of carbohydrates by combining a novel zinc-mediated domino reaction with the ring-closing olefin metathesis reaction. The procedure can be used on both pentoses and hexoses and gives rise to both five- and six-membered carbocycles. As a result, this technique constitutes one of the most versatile and general methods developed so far for carbocyclization of sugars. Application of these reactions to short total syntheses of biologically significant natural products is currently in progress.

Experimental Section

General procedures are in the Supporting Information. All sonications were carried out in a Branson 1210 sonic bath. Zinc dust (Aldrich 20.998-8) was activated and dried immediately before use: Zinc (5 g) in 1 M aqueous HCl (50 mL) was stirred at room temperature for 15 min, then filtered, and washed with H_2O (2 × 50 mL) and Et_2O (50 mL). Finally, the material was dried under high vacuum with a heatgun.

General Procedure for Elimination−Allylation (Table 1). Zinc (8.3 g, 127 mmol) and allyl bromide (3.3 mL, 39 mmol) were added to a deoxygenated mixture of the methyl 5-iodofuranoside (12.7 mmol) in a THF:H_2O solution (40 mL) under argon. The mixture was sonicated at 40 °C until thin layer chromatography (TLC) revealed full conversion of the starting material and then filtered through Celite. The Celite

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(40) Jensen, S. R.; Nielsen, B. J. *Phytochemistry* **1986**, *25*, 2349.

(41) The perbenzylated dienes were recently shown to require 30% of **18** for the RCM reaction: Gallos, J. K.; Koftis, T. V.; Sarli, V. C.; Litinas, K. E. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3075.

(42) (a) Balci, M. *Pure Appl. Chem.* **1997**, *69*, 97. (b) Carless, H. A. J. *Tetrahedron: Asymmetry* **1992**, *3*, 795. (c) Balci, M.; Sütbeyaz, Y.; Seçen, H. *Tetrahedron* **1990**, *46*, 3715.

(43) Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62*, 7310.

was washed with Et_2O (20 mL). The filtrate was stirred with Amberlite IR-120 (H^+) (25 mL) for 1 h to remove hydroxyl protecting groups. The mixture was transferred onto a column of mixed bed ion-exchange resin consisting of Amberlite IR-120 (H^+) (75 mL) and IRA-400 (OH^-) (75 mL). The column was eluted with H_2O (500 mL). The eluate was concentrated, and the residue purified by flash chromatography.

1,2,3,7,8-Pentadeoxy-D-*ribo*-oct-1,7-dienitol (7α). $R_f = 0.62$ (Et_2O). mp 84−85 °C (MeOH). $[\alpha]_D$ −32.4 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.01 (ddd, *J* = 6.6, 10.5, 17.2 Hz, 1H), 5.88 (m, 1H), 5.42 (dt, *J* = 1.4, 17.3 Hz, 1H), 5.33 (dt, *J* = 1.4, 10.5 Hz, 1H), 5.19−5.23 (m, 2H), 4.33 (ddt, *J* = 1.2, 6.1, 6.6 Hz, 1H), 3.72 (ddd, *J* = 3.3, 7.2, 8.4, 1H), 3.54 (dd, *J* = 5.5, 7.1 Hz, 1H), 2.60 (ddddd, *J* = 1.4, 1.5, 3.3, 4.7, 14.2 Hz, 1H), 2.34 (s, OH, 3H), 2.28 (ddddd, *J* = 1.2, 1.3, 8.3, 8.4, 14.1 Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 136.6, 134.3, 118.7, 117.8, 75.1, 74.7, 71.9, 37.9. Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.72; H, 8.97.

1,2,3,7,8-Pentadeoxy-D-*arabino*-oct-1,7-dienitol (7β). R_f = 0.60 (Et_2O). $[\alpha]_D$ +50 (c 0.4, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95 (ddd, *J* = 5.6, 10.7, 17.5 Hz, 1H), 5.85 (m, 1H), 5.41 (dt, *J* = 1.3, 17.5 Hz, 1H), 5.29 (dt, *J* = 1.3, 10.7 Hz, 1H), 5.17 (dq, *J* = 1.7, 11.3 Hz, 1H), 5.14 (dq, *J* = 0.9, 11.3 Hz, 1H), 4.36 (dd, *J* = 1.2, 5.5 Hz, 1H), 3.92 (m, 1H), 3.50 (m, 1H), 2.61 (bd, *J* = 7.7 Hz, 1H), 2.54 (bd, *J* = 6.0 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 136.1, 133.8, 118.3, 117.4, 75.0, 73.6, 70.1, 37.8.

Acetylation gave **19**: $R_f = 0.87$ (pentane:Et_2O = 1:1). $[\alpha]_D$ +31 (c 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.65−5.79 (m, 2H), 5.37 (dt, *J* = 1.3, 17.1 Hz, 1H), 5.28−5.33 (m, 2H), 5.19−5.24 (m, 2H), 5.11 (ddd, *J* = 1.3, 1.7, 7.0 Hz, 1H), 5.09 (dt, *J* = 1.3, 4.7 Hz, 1H), 2.30 (m, 2H), 2.11 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.1, 170.0, 169.5, 132.4, 132.3, 120.4, 118.6, 72.5, 72.0, 69.7, 35.5, 20.9. 20.7, 20.7. Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 59.60; H, 7.38.

1,2,3,7,8-Pentadeoxy-L-*lyxo*-oct-1,7-dienitol (8α). $R_f = 0.59$ (Et_2O). $[\alpha]_D$ −22 (c 0.6, MeOH). ^{1}H NMR (300 MHz, CD_3OD): δ 5.79−5.98 (m, 2H), 5.25 (dt, *J* = 1.3, 15.1 Hz, 1H), 5.11 (dt, *J* = 1.3, 10.0 Hz, 1H), 4.98−5.03 (m, 2H), 4.26 (ddt, *J* = 1.7, 3.1, 4.5 Hz, 1H), 3.62 (dt, *J* = 3.6, 9.0 Hz, 1H), 3.25 (dd, *J* = 2.9, 8.6 Hz, 1H), 2.45 (m, 1H), 2.14 (m, 1H). ^{13}C NMR (75 MHz, CD_3OD): δ 139.9, 136.8, 117.2, 115.9, 77.0, 73.2, 72.2, 38.8. Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.66; H, 9.41.

1,2,3,7,8-Pentadeoxy-L-*xylo*-oct-1,7-dienitol (8β). $R_f = 0.57$ (Et_2O). ^{1}H NMR (500 MHz, CD_3OD): δ 5.81−5.94 (m, 2H), 5.32 (ddd, *J* = 1.4, 1.6, 17.1 Hz, 1H), 5.18 (ddd, *J* = 1.3, 2.1, 10.7 Hz, 1H), 5.10 (dddd, *J* = 1.3, 1.7, 2.1, 17.1 Hz, 1H), 5.04 (dddd, *J* = 1.0, 1.3, 2.1, 10.2 Hz, 1H), 4.17 (m, 1H), 3.68 (ddd, *J* = 3.0, 6.0, 7.3 Hz, 1H), 3.29 (dd, *J* = 3.0, 6.0 Hz, 1H), 2.28−2.38 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ 139.1, 136.2, 117.2, 117.0, 76.5, 75.2, 72.3, 39.5.

Compounds 9α/β are the enantiomers of **8β**/α.

(3*S*,5*R*)-Octa-1,7-dien-3,5-diol (10β). $R_f = 0.27$ (pentane:Et_2O = 1:1). $[\alpha]_D$ +7.0 (c 1, $CHCl_3$). ^{1}H NMR(300 MHz, $CDCl_3$): δ 5.93 (ddd, *J* = 5.3, 10.6, 17.2 Hz, 1H), 5.82 (m, 1H), 5.30 (dt, *J* = 1.5, 17.2 Hz, 1H), 5.11−5.18 (m, 3H), 4.48 (m, 1H), 4.40 (m, 1H), 2.24−2.31 (m, 2H), 1.69−1.79 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 140.5, 134.3, 118.2, 114.3, 70.4, 67.9, 42.0, 41.6. The stereochemistry was determined after chemical correlation with the corresponding enyne; see Table 1 in ref 5a.

(3*S*,5*S*)-Octa-1,7-dien-3,5-diol (10α). $R_f = 0.29$ (pentane:Et_2O = 1:1). $[\alpha]_D$ +5.2 (c 1, $CHCl_3$). ^{1}H NMR(300 MHz, $CDCl_3$): δ 5.79−5.88 (m, 2H), 5.27 (dt, *J* = 1.4, 17.2 Hz, 1H), 5.10−5.19 (m, 3H), 4.39 (m, 1H), 3.95 (m, 1H), 2.24−2.31 (m, 2H), 1.58−1.76 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 140.5, 134.1, 118.3, 114.5, 73.5, 71.2, 42.4, 42.4.

1,2,3,7,8-Pentadeoxy-5,6-*O*-isopropylidene-2-*C*-(isopropyloxycarbonyl)-D-*ribo*-oct-1,7-dienitol (11α). Zinc (1.00 g, 15.3 mmol) was added to a solution of furanoside **1** (0.50 g, 1.59 mmol) in 2:1 THF:H_2O (12 mL). The mixture was sonicated at 40 °C under argon for 4 h during which time isopropyl α-(bromomethyl)acrylate (1.00 g, 4.83 mmol) was added dropwise by syringe pump. The sonication was continued for an additional 2 h, and the mixture was then allowed to shake at room temperature overnight and was then filtered through Celite. The Celite was washed with Et_2O (30 mL). The filtrate was washed with H_2O (20 mL) and the aqueous phase extracted with CH_2Cl_2 (2 × 40 mL). The combined organic phases were dried and concentrated to a syrup. ^{13}C NMR revealed the formation of **11α** and **11β** in a ratio of 5:1. Flash chromatography (pentane:Et_2O = 2:1) gave 0.44 g (98%) of **11α** and **11β** as an inseparable mixture; $R_f = 0.35$.

For **11**α: ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.25 (m, 1H), 6.04 (ddd, *J* = 6.8, 10.7, 17.1 Hz, 1H), 5.70 (m, 1H), 5.41 (ddd, *J* = 1.7, 1.8, 17.1 Hz, 1H), 5.27 (dddd, *J* = 1.3, 1.5, 1.6, 10.7 Hz, 1H), 5.08 (septet, *J* = 6.0 Hz, 1H), 4.68 (dt, *J* = 0.9, 6.3 Hz, 1H), 3.96 (dd, *J* = 6.4, 8.5 Hz, 1H), 3.77 (dt, *J* = 2.6, 8.5 Hz, 1H), 2.84 (ddd, *J* = 0.9, 2.6, 14.2 Hz, 1H), 2.43 (dd, *J* = 9.0, 14.2 Hz, 1H), 1.50 (s, 3H), 1.37 (s, 3H), 1.30 (d, *J* = 6.0 Hz, 3H), 1.29 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.9, 137.3, 134.2, 127.9, 117.6, 108.5, 80.1, 78.7, 69.3, 68.3, 36.7, 27.7, 25.3, 21.7.

For **11**β: ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.9, 137.3, 134.1, 127.3, 119.5, 108.5, 80.1, 79.1, 69.3, 68.3, 36.9, 27.1, 24.8, 21.7. Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.30; H, 8.53.

Compounds **11**α and **11β** were separated after acetylation. For **38**: $R_f = 0.81$ (pentane:Et_2O = 2:1). $[\alpha]_D$ −11.6 (c 3.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.18 (m, 1H), 5.85 (dddd, *J* = 2.5, 7.8, 10.3, 17.6 Hz, 1H), 5.56 (bs, 1H), 5.36 (ddd, *J* = 0.8, 2.3, 17.2 Hz, 1H), 5.24 (ddd, *J* = 0.8, 1.2, 10.2 Hz, 1H), 5.06−5.11 (m, 2H), 4.64 (bt, *J* = 7.0 Hz, 1H), 4.17 (t, *J* = 6.7 Hz, 1H), 2.97 (dd, *J* = 2.1, 14.4 Hz, 1H), 2.40 (dd, *J* = 8.6, 14.4 Hz, 1H), 1.92 (s, 3H), 1.54 (s, 3H), 1.39 (s, 3H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.29 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.5, 165.9, 136.7, 132.6, 127.2, 118.6, 108.9, 78.7, 78.3, 70.0, 68.0, 34.1, 27.4, 25.2, 21.6, 21.6, 20.9. Anal. Calcd for $C_{17}H_{26}O_6$: C, 62.56; H, 8.03. Found: C, 62.42; H, 7.97.

Reduction of **11**α with DIBAL-H followed by acetylation gave **39**: $R_f = 0.65$ (pentane:Et_2O = 2:1). $[\alpha]_D$ −6.4 (c 3.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.83 (ddd, *J* = 7.3, 10.3, 17.2 Hz, 1H), 5.37 (dt, *J* = 1.3, 17.2 Hz, 1H), 5.25 (dt, *J* = 1.3, 10.3 Hz, 1H), 5.12 (m, 1H), 4.99−5.03 (m, 2H), 4.65 (t, *J* = 7.1 Hz, 1H), 4.61 (d, *J* = 13.3 Hz, 1H), 4.54 (d, *J* = 13.3 Hz, 1H), 4.21 (t, *J* = 6.9 Hz, 1H), 2.56 (bdd, *J* = 2.2, 14.6 Hz, 1H), 2.36 (dd, *J* = 8.6, 14.6 Hz, 1H), 2.09 (s, 3H), 1.98 (s, 3H), 1.51 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.5, 169.7, 139.4, 132.7, 118.5, 116.1, 108.9, 78.5, 78.0, 70.0, 66.5, 34.9, 27.3, 25.0, 20.9, 20.8. Anal. Calcd for $C_{16}H_{24}O_6$: C, 61.52; H, 7.74. Found: C, 61.47; H, 7.72.

1,2,3,7,8-Pentadeoxy-5,6-*O*-isopropylidene-3-*C*-phenyl-D-*manno*-oct-1,7-dienitol (12). Furanoside **1** (0.5 g, 1.59 mmol) was treated with zinc (1.0 g, 15.3 mmol) and a solution of cinnamyl bromide (0.9 g, 4.6 mmol) in THF (10 mL) as described above for **11α** to give after flash chromatography 241 mg (55%) of **12**, $R_f = 0.56$ (pentane:Et_2O = 4:1). $[\alpha]_D$ +38.0 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31−7.34 (m, 2H), 7.21−7.25 (m, 3H), 6.24 (ddd, *J* = 8.7, 10.2, 16.9 Hz, 1H), 6.09 (ddd, *J* = 7.9, 10.2, 16.9 Hz, 1H), 5.34 (ddd, *J* = 0.8, 1.6, 16.9 Hz, 1H), 5.33 (ddd, *J* = 0.8, 1.6, 10.2 Hz, 1H), 5.19 (ddd, *J* = 0.8, 2.0, 10.2 Hz, 1H), 5.10 (ddd, *J* = 1.2, 2.0, 16.9 Hz, 1H), 4.50 (dd, *J* = 7.1, 7.9 Hz, 1H), 3.96 (dd, *J* = 3.5, 7.1 Hz, 1H), 3.47 (dd, *J* = 7.3, 8.1 Hz, 1H), 2.23 (bd, *J* = 6.7 Hz, 1H), 1.55 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 141.3, 138.0, 134.2, 128.5, 128.0, 126.5, 119.5, 117.0, 108.4, 78.9, 77.4, 72.2, 53.3, 27.0, 24.7. Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.48; H, 8.08.

Acetylation gave **35**: $R_f = 0.37$ (pentane:Et_2O = 9:1). $[\alpha]_D$ +47.7 (c 1.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.34 (m, 5H), 6.02 (dt, *J* = 10.0, 16.8 Hz, 1H), 5.77 (ddd, *J* = 7.2, 10.1, 17.0 Hz, 1H), 5.24−5.30 (m, 2H), 5.17 (dd, *J* = 2.7, 9.4 Hz, 1H), 5.10 (dd, *J* = 1.7, 17.0 Hz, 1H), 5.06 (dd, *J* = 1.8, 10.0 Hz, 1H), 4.47 (t, *J* = 7.1 Hz, 1H), 3.93 (dd, *J* = 2.7, 6.9 Hz, 1H), 3.69 (t, *J* = 9.6 Hz, 1H), 2.02 (s, 3H), 1.57 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.2, 140.4, 137.7, 133.0, 128.8, 128.0, 126.9, 118.8, 117.1, 108.7, 78.3, 76.4, 73.2, 52.7, 26.9, 25.5, 21.4. Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.65. Found: C, 71.95; H, 7.57.

4-Benzylamino-1,2,3,4,7,8-hexadeoxy-5,6-*O*-isopropylidene-D-*ribo*-oct-1,7-dienitol (13α). To a solution of furanoside **1** (1.0 g, 3.18 mmol) and benzylamine (0.7 mL, 6.41 mmol) in THF (20 mL) under argon was added zinc (2.0 g, 30.6 mmol). The mixture was sonicated at 40 °C for 3 h during which time allyl bromide (0.6 mL, 7.1 mmol) was added dropwise. The sonication was continued for an additional 2 h until TLC indicated full conversion of **1**, and the mixture was then

filtered through Celite. The organic phase was concentrated and purified by flash chromatography (pentane:Et_2O:Et_3N = 66:33:1) through a short column to give 745 mg (81%) of a syrup. ^{13}C NMR revealed the formation of **13α** and **13*β*** in a ratio of 6:1. The title product **13α** was obtained pure in a yield of 644 mg (70%) after further purification by flash chromatography (pentane:Et_2O:Et_3N = 85:15:1), R_f = 0.5. $[\alpha]_D$ +53.6 (c 1.0, $CHCl_3$).

^1H NMR (500 MHz, $CDCl_3$): δ 7.21−7.31 (m, 5H), 5.96 (ddd, *J* = 6.8, 10.2, 17.1 Hz, 1H), 5.87 (m, 1H), 5.34 (ddd, *J* = 1.4, 1.6, 17.1 Hz, 1H), 5.21 (ddd, *J* = 1.4, 1.6, 10.3 Hz, 1H), 5.11−5.16 (m, 2H), 4.63 (bt, *J* = 6.6 Hz, 1H), 4.02 (dd, *J* = 6.4, 9.0 Hz, 1H), 3.83 (d, *J* = 12.6 Hz, 1H), 3.63 (d, *J* = 12.6 Hz, 1H), 2.81 (ddd, *J* = 3.8, 5.5, 8.9 Hz, 1H), 2.49 (m, 1H), 2.38 (m, 1H), 1.49 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 140.4, 134.9, 134.3, 128.3, 128.2, 126.9, 118.1, 117.3, 108.1, 79.1, 78.9, 55.6, 51.0, 34.1, 27.8, 25.3. Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.20; H, 8.75; N, 4.80.

For **13*β***: ^{13}C NMR (50 MHz, $CDCl_3$): δ 140.6, 134.7, 133.9, 128.3, 128.2, 126.7, 118.7, 117.3, 108.3, 80.1, 79.3, 55.6, 51.2, 34.4, 28.0, 25.5.

Acetylation of **13α** gave **20** as a 1:1 mixture of two rotamers by NMR: R_f = 0.35 (pentane:Et_2O = 1:1). $[\alpha]_D$ +19.2 (c 2.8, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 7.22−7.36 (m, 10H), 5.94 (ddd, *J* = 6.8, 10.2, 17.1 Hz, 1H), 5.64−5.78 (m, 3H), 5.38 (ddd, *J* = 1.3, 1.4, 13.0 Hz, 1H), 5.31 (ddd, *J* = 1.3, 1.7, 10.3 Hz, 1H), 5.26 (bs, 1H), 5.23 (bd, *J* = 7.7 Hz, 1H), 4.99−5.07 (m, 4H), 4.57 (d, *J* = 5.6 Hz, 2H), 4.48−4.51 (m, 2H), 4.19−4.23 (m, 4H), 3.88 (m, 1H), 3.84 (t, *J* = 7.3 Hz, 1H), 2.29−2.48 (m, 4H), 2.14 (s, 3H), 1.99 (s, 3H), 1.46 (s, 3H), 1.45 (s, 3H), 1.24 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.1, 172.0, 138.9, 137.9, 135.1, 133.8, 133.6, 133.3, 128.3, 128.2, 127.1, 127.0, 126.0, 119.0, 118.6, 118.5, 116.5, 108.2, 79.4, 79.3, 78.8, 78.4, 58.0, 52.7, 48.2, 44.8, 34.2, 32.8, 27.2, 26.9, 24.7, 24.4, 22.4, 21.3. Anal. Calcd for $C_{20}H_{27}NO_3$: C, 72.92; H, 8.26; N, 4.25. Found: C, 73.12; H, 8.26; N, 4.36.

General Procedure for Elimination−Vinylation (Table 2). To a solution of the ω-iodo glycoside (1.0 mmol) in THF (10 mL) under argon was added zinc (660 mg, 10 mmol) (for 6-iodo glycosides **14** and **15**, 15 mg of $ZnCl_2$ was also added and the mixture sonicated for 1 h at 40 °C prior to the divinyl zinc addition). Then the mixture was sonicated at 40 °C for 2 h while a 0.5 M divinyl zinc solution[30] in THF (6.0 mL, 3.0 mmol) was added dropwise by syringe pump. The sonication was continued for an additional 4 h at 40 °C. The mixture was filtered through Celite and rinsed with Et_2O. To the filtrate were added MeOH (10 mL) and Amberlite IR-120 (H^+) (10 mL). After stirring at 40 °C for 1 h, the resin was filtered off and washed with MeOH (20 mL). The filtrate was concentrated and purified by flash chromatography.

1,2,6,7-Tetradeoxy-*ribo*-hept-1,6-dienitol (16α). R_f = 0.48 (EtOAc). ^1H NMR (500 MHz, $CDCl_3$): δ 6.03 (ddd, *J* = 6.1, 10.1, 17.0 Hz, 2H), 5.40 (dt, *J* = 1.6, 17.0 Hz, 2H), 5.31 (dt, *J* = 1.2, 10.5 Hz, 2H), 4.26 (tt, *J* = 1.4, 6.1 Hz, 2H), 3.61 (t, *J* = 6.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.0 (2C), 117.5 (2C), 75.3, 74.4 (2C). Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 57.96; H, 8.35.

1,2,6,7-Tetradeoxy-D-*arabino*-hept-1,6-dienitol (16*β* = 17*β*). R_f = 0.53 (EtOAc). $[\alpha]_D$ +66.5 (c 0.4, MeOH). ^1H NMR (500 MHz, $CDCl_3$): δ 5.99 (ddd, *J* = 5.9, 10.6, 17.1 Hz, 1H), 5.93 (ddd, *J* = 5.9, 10.6, 17.1 Hz, 1H), 5.32 (dt, *J* = 1.5, 17.1 Hz, 2H), 5.21−5.30 (m, 2H), 4.25 (m, 1H), 4.12 (m, 1H), 3.47 (dd, *J* = 3.6, 6.6 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.0, 136.4, 117.3, 117.0, 74.8, 74.6, 72.1. Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.19; H, 8.59.

1,2,6,7-Tetradeoxy-*xylo*-hept-1,6-dienitol (17α). R_f = 0.60 (EtOAc). ^1H NMR (500 MHz, $CDCl_3$): δ 5.98 (ddd, *J* = 6.0, 10.2, 16.0 Hz, 2H), 5.41 (ddd, *J* = 1.3, 2.1, 17.5 Hz, 2H), 5.29 (ddd, *J* = 1.3, 2.1, 10.5 Hz, 2H), 4.27 (d, *J* = 4.7 Hz, 1H), 4.29 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.3 (2C), 117.2 (2C), 75.5, 73.4 (2C). Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.17; H, 8.37.

Acetylation gave **31**: R_f = 0.41 (hexane:EtOAc = 4:1). ^1H NMR (500 MHz, $CDCl_3$): δ 5.73 (ddd, *J* = 6.4, 10.7, 17.1 Hz, 2H), 5.44 (m, 2H), 5.28−5.32 (m, 4H), 5.22 (t, *J* = 5.5 Hz, 1H), 2.09 (s, 6H), 2.08 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.5 (2C), 131.7 (2C), 119.4 (2C), 73.3, 72.6 (2C), 20.8 (2C), 20.5. Anal. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.16; H, 6.22.

1,2,7,8-Tetradeoxy-D-*ido*-oct-1,7-dienitol (18*β*). R_f = 0.71 (acetone). $[\alpha]_D$ 0 (c 3.0, $CHCl_3$). ^1H NMR (300 MHz, CD_3OD): δ 5.90 (ddd, *J* = 6.4, 10.6, 17.4 Hz, 2H), 5.34 (ddd, *J* = 1.4, 1.8, 17.4 Hz, 2H), 5.18 (ddd, *J* = 1.1, 1.8, 10.6 Hz, 2H), 4.21 (tt, *J* = 1.1, 6.4 Hz, 2H), 3.49 (bd, *J* = 6.4 Hz, 2H). ^{13}C NMR (50 MHz, CD_3OD): δ 139.1 (2C), 117.0 (2C), 75.1 (4C).

Acetylation gave **36**: R_f = 0.73 (pentane:EtOAc = 2:1). $[\alpha]_D$ 0 (c 3.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 5.76 (dddd, *J* = 1.0, 6.2, 10.0, 17.1 Hz, 2H), 5.40 (m, 2H), 5.30 (ddd, *J* = 0.9, 1.2, 17.6 Hz, 2H), 5.28 (ddd, *J* = 0.8, 1.0, 10.4 Hz, 2H), 5.25 (m, 2H), 2.10 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.5 (2C), 167.9 (2C), 131.3 (2C), 119.9 (2C), 72.5 (2C), 70.8 (2C), 20.8 (2C), 20.6 (2C). Anal. Calcd for $C_{16}H_{22}O_8$: C, 56.14; H, 6.48. Found: C, 56.34; H, 6.48.

1,2,7,8-Tetradeoxy-D-*talo*-oct-1,7-dienitol (19*β*). R_f = 0.65 (acetone). mp 140−141 °C. $[\alpha]_D$ +28.6 (c 2.1, MeOH). ^1H NMR (300 MHz, CD_3OD): δ 5.94−6.06 (m, 2H), 5.31 (ddd, *J* = 1.3, 1.9, 17.3 Hz, 2H), 5.15−5.21 (m, 2H), 4.36 (m, 1H), 4.26 (m, 1H), 3.71 (dd, *J* = 4.6, 8.4 Hz, 1H), 3.44 (dd, *J* = 2.1, 8.5 Hz, 1H). ^{13}C NMR (50 MHz, CD_3OD): δ 140.2, 138.3, 117.2, 115.7, 75.5, 75.4, 74.8, 73.0.

Acetylation gave **37**: R_f = 0.74 (pentane:EtOAc = 2:1). $[\alpha]_D$ +13.0 (c 0.8, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 5.83 (ddd, *J* = 7.0, 10.8, 17.4 Hz, 1H), 5.70 (ddd, *J* = 5.5, 10.4, 16.9 Hz, 1H), 5.53 (m, 1H), 5.41 (m, 1H), 5.23−5.34 (m, 6H), 2.10 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.8 (2C), 169.5 (2C), 131.8, 130.6, 119.6, 118.0, 73.0, 71.2, 70.2, 69.9, 20.8 (2C), 20.6 (2C). Anal. Calcd for $C_{16}H_{22}O_8$: C, 56.14; H, 6.48. Found: C, 56.27; H, 6.48.

General Procedure for Elimination−Methylenation (Table 3). To a solution of the 6-iodopyranoside (500 mg, 0.77 mmol) in THF (10 mL) under argon were added (TMS)Cl (0.28 mL, 2.2 mmol), zinc (500 mg, 7.6 mmol), and $PbCl_2$ (20 mg, 0.07 mmol). The mixture was sonicated at 40 °C for 1 h while CH_2I_2 (0.18 mL, 2.2 mmol) was added dropwise by syringe pump. More (TMS)Cl (0.28 mL) was added, and the sonication was continued for an additional 4 h. The mixture was filtered through Celite and rinsed with pentane (40 mL). The filtrate was washed with 10% aqueous citric acid (2 × 20 mL), dried, and concentrated. The residue was suspended in MeOH (10 mL), and Amberlite IR-120 (H^+) (7.5 mL) was added. After stirring for 2 h at 40 °C Amberlite IRA-400 (OH^-) (10 mL) was added until neutral pH. The resin was filtered off and washed with MeOH (50 mL). The filtrate was concentrated and the residue purified by flash chromatography.

General Procedure for Ring-Closing Olefin Metathesis (Tables 4−6). To a deoxygenated solution of the diene (100 mg) in CH_2Cl_2 (10 mL) under argon was added a deoxygenated solution of **18** or **30** in CH_2Cl_2 (1 mL) by syringe. The solution was stirred at either room temperature or 40 °C as indicated in the tables until TLC revealed full conversion or that the reaction had stopped. The mixture was concentrated (in the case of a precipitated product this was first filtered off) and the residue purified by flash chromatography.

(1*S*,2*S*,3*R*)-Cyclohex-4-en-1,2,3-triol (21). R_f = 0.59 (acetone). mp 95−96 °C (MeOH:Et_2O). $[\alpha]_D$ −69.2 (c 1.0, MeOH). ^1H NMR (250 MHz, CD_3OD): δ 5.67 (dddd, *J* = 2.1, 3.0, 4.8, 10.2 Hz, 1H), 5.53 (m, 1H), 4.18 (m, 1H), 3.99 (m, 1H), 3.81 (dt, *J* = 2.1, 6.0 Hz, 1H), 2.31(m, 1H), 2.22 (m, 1H). ^{13}C NMR (50 MHz, CD_3OD): δ 129.1, 126.9, 72.8, 69.8, 69.6, 30.9. Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.58; H, 7.53.

(1*R*,2*S*,3*R*)-Cyclohex-4-en-1,2,3-triol (22). R_f = 0.41 (acetone). mp 127−128 °C (MeOH:acetone) (Lit.:[44] mp 130 °C). $[\alpha]_D$ −167.1 (c 0.6, MeOH). ^1H NMR (500 MHz, CD_3OD): δ 5.70−5.73 (m, 2H), 4.19 (m, 1H), 3.87 (ddd, *J* = 5.6, 8.3, 9.2 Hz, 1H), 3.50 (dd, *J* = 4.3, 9.4 Hz, 1H), 2.48 (ddd, *J* = 2.1, 5.6, 17.5 Hz, 1H), 1.98 (ddd, *J* = 1.0, 8.5, 17.5 Hz, 1H). ^{13}C NMR (50 MHz, CD_3OD): δ 129.0, 128.3, 74.9, 68.2, 67.9, 34.4. Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.09; H, 7.85.

(44) Hudlicky, T.; Luna, H.; Olivo, H. F.; Andersen, C.; Nugent, T.; Price, J. D. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2907.

(1*S*,2*S*,3*S*)-Cyclohex-4-en-1,2,3-triol (23). $R_f = 0.63$ (acetone). mp 128−129 °C (MeOH:acetone). $[\alpha]_D$ +509 (c 0.4, MeOH). ^{1}H NMR (500 MHz, CD_3OD): δ 5.67 (ddt, $J = 1.3, 3.4, 9.8$ Hz, 1H), 5.62 (ddt, $J = 1.8, 3.4, 9.8$ Hz, 1H), 4.15 (m, 1H), 4.00 (ddd, $J = 2.1, 4.7, 5.5$ Hz, 1H), 3.63 (dd, $J = 2.7, 6.0$ Hz, 1H), 2.31 (m, 1H), 2.22 (m, 1H). ^{13}C NMR (126 MHz, CD_3OD): δ 128.5, 127.4, 75.6, 70.8, 68.8, 32.3. Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.19; H, 7.78.

Compound **24** is the enantiomer of **23**.

(1*R*,2*S*,3*R*)-1,2,3-Tris(acetyloxy)cyclohex-4-ene (25). $R_f = 0.71$ (pentane:Et_2O = 1:1). $[\alpha]_D$ −34 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.88 (ddd, $J = 3.1, 4.9, 10.2$ Hz, 1H), 5.71 (m, 1H), 5.60 (bt, $J = 4.4$ Hz, 1H), 5.30 (ddd, $J = 5.8, 8.0, 10.2$ Hz, 1H), 5.19 (dd, $J = 4.4, 10.2$ Hz, 1H), 2.77 (m, 1H), 2.19 (m, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.2, 170.0, 169.9, 129.8, 123.1, 69.9, 66.8, 66.6, 30.8, 20.9, 20.8, 20.6. Anal. Calcd for $C_{12}H_{16}O_6$: C, 56.25; H, 6.29. Found: C, 56.23; H, 6.42.

(1*S*,2*S*,3*R*)-1-(*N*-Benzyl)acetamido-2,3-*O*-isopropylidenecyclohex-4-en-2,3-diol (26). $R_f = 0.67$ (Et_2O). $[\alpha]_D$ −83.7 (c 2.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21−7.35 (m, 5H), 5.69 (ddd, $J = 1.7, 6.0, 10.2$ Hz, 1H), 5.53 (m, 1H), 5.13 (dddd, $J = 1.7, 5.5, 11.9$ Hz, 1H), 4.85 (d, $J = 17.9$ Hz, 1H), 4.78 (d, $J = 17.9$ Hz, 1H), 4.63 (m, 1H), 4.29 (bd, $J = 5.1$ Hz, 1H), 2.29 (m, 1H), 2.08 (s, 3H), 1.98 (dddd, $J = 1.3, 4.7, 6.4, 16.2$ Hz, 1H), 1.34 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.9, 138.6, 128.3, 127.7, 126.8, 126.6, 126.0, 125.2, 109.3, 75.3, 74.4, 49.7, 48.5, 29.4, 27.6, 23.4, 21.9. Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.61; H, 7.91; N, 4.63.

(1α,2*β*,3α)-Cyclopent-4-en-1,2,3-triol (32). $R_f = 0.53$ (acetone). mp 106−107 °C (Et_2O:acetone) (Lit.:[45] mp 111 °C). ^{1}H NMR (250 MHz, CD_3OD): δ 5.76 (s, 2H), 4.34 (d, $J = 5.0$ Hz, 2H), 3.81 (t, $J = 5.1$ Hz, 1H). ^{13}C NMR (63 MHz, CD_3OD): δ 134.6 (2C), 90.1 (2C), 81.0. NMR data were in accordance with literature data.[40]

(1α,2α,3α)-Cyclopent-4-en-1,2,3-triol (33). $R_f = 0.56$ (acetone). mp 61−62 °C (Lit.:[46] mp 64−65 °C). ^{1}H NMR (500 MHz, CD_3OD): δ 5.93 (s, 2H), 4.40 (d, $J = 5.4$ Hz, 2H), 4.01 (t, $J = 5.4$ Hz, 1H). ^{13}C NMR (63 MHz, CD_3OD): δ 135.8 (2C), 75.1 (2C), 72.9. Anal. Calcd for $C_5H_8O_3$: C, 51.72; H, 6.94. Found: C, 51.56; H, 6.99.

(1*β*,2*β*,3α)-Cyclopent-4-en-1,2,3-triol (34). $R_f = 0.52$ (acetone). $[\alpha]_D$ −3.7 (c 0.9, MeOH). 1H NMR (500 MHz, CD_3OD): δ 5.90−5.92 (m, 2H), 4.61 (bd, $J = 4.3$ Hz, 1H), 4.59 (bd, $J = 5.4$ Hz, 1H), 3.88 (dd, $J = 4.3, 5.6$ Hz, 1H). ^{13}C NMR (63 MHz, CD_3OD): δ 137.4, 134.0, 81.0, 79.2, 74.2. Anal. Calcd for $C_5H_8O_3$: C, 51.72; H, 6.94. Found: C, 51.68; H, 6.57.

(1*R*,2*R*,3*R*,4*S*)-3-Acetyloxy-1,2-*O*-isopropylidene-4-phenylcyclohex-5-en-1,2-diol (40). $R_f = 0.35$ (pentane:EtOAc = 5:1). mp 84−85 °C. $[\alpha]_D$ −283.5 (c 0.8, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23−7.34 (m, 3H), 7.07−7.10 (m, 2H), 6.08 (ddd, $J = 1.6, 3.5, 10.1$ Hz, 1H), 5.96 (dd, $J = 4.3, 10.1$ Hz, 1H), 5.25 (dd, $J = 5.1, 7.4$ Hz, 1H), 4.77 (dd, $J = 3.5, 5.8$ Hz, 1H), 4.23 (dd, $J = 5.9, 7.7$ Hz, 1H), 3.95 (bt, $J = 4.8$ Hz, 1H), 1.95 (s, 3H), 1.50 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.8, 137.0, 129.9, 128.6, 127.7, 126.6, 125.4, 108.8 72.5, 72.5, 71.6, 42.2, 27.4, 25.5, 20.4. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.70; H, 7.00.

(−)-Conduritol B Tetraacetate (41). $R_f = 0.48$ (pentane:EtOAc = 2:1). mp 117−118 °C (Lit.:[47] mp 120−121 °C). $[\alpha]_D$ −182 (c 0.7, $CHCl_3$) (Lit.:[47] $[\alpha]_D^{25}$ −172.4 (c 1.1, $CHCl_3$)). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.70 (bs, 2H), 5.59 (m, 2H), 5.53 (m, 2H), 2.06 (s, 6H), 2.04 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.8 (4C), 127.4 (2C), 71.4 (2C), 71.2 (2C), 20.8 (4C).

(−)-Conduritol C Tetraacetate (42). $R_f = 0.53$ (pentane:EtOAc = 2:1). mp 88−89 °C (Lit.:[48] mp 95−97 °C). $[\alpha]_D$ −194 (c 3.0, $CHCl_3$) (Lit.:[48] $[\alpha]_D^{25}$ −186 (c 2, $CHCl_3$)). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.76 (ddd, $J = 1.3, 3.3, 10.7$ Hz, 1H), 5.64−5.69 (m, 4H), 5.20 (dd, $J = 1.9, 7.8$ Hz, 1H), 2.12 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.4, 170.2, 169.8, 169.6, 127.4, 127.0, 70.5, 70.0, 69.4, 67.5, 20.8, 20.7 (3C).

(1*S*,2*S*,3*R*)-1-Acetyloxy-2,3-*O*-isopropylidene-5-isopropyloxycarbonylcyclohex-4-en-2,3-diol (43). $R_f = 0.41$ (pentane:Et_2O = 2:1). $[\alpha]_D$ +30.0 (c 2.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.71 (dt, $J = 0.9, 2.7$ Hz, 1H), 5.10 (m, 1H), 5.08 (septet, $J = 6.4$ Hz, 1H), 4.78 (m, 1H), 4.45 (ddd, $J = 0.9, 1.3, 5.2$ Hz, 1H), 2.70 (ddd, $J = 0.9, 5.6, 16.2$ Hz, 1H), 2.52 (ddt, $J = 3.0, 10.7, 16.2$ Hz, 1H), 2.15 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.29 (d, $J = 6.4$ Hz, 3H), 1.28 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.4, 165.3, 134.4, 129.2, 110.6, 73.5, 73.5, 69.0, 68.5, 27.6, 26.5, 24.0, 21.7, 21.1. Anal. Calcd for $C_{15}H_{22}O_6$: C, 60.39; H, 7.43. Found: C, 60.23; H, 7.35. The structure was confirmed by deesterification (aqueous NaOH) and acetal removal (aqueous TFA) to give 5-*epi*-shikimic acid with ^{1}H and ^{13}C NMR data in accordance with literature values.[49]

(1*S*,2*S*,3*R*)-1-Acetyloxy-5-acetyloxymethyl-2,3-*O*-isopropylidenecyclohex-4-en-2,3-diol (44). $R_f = 0.64$ (pentane:Et_2O = 1:1). $[\alpha]_D$ +4.0 (c 1.0, EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.64 (m, 1H), 5.10 (ddd, $J = 2.4, 5.6, 7.5$ Hz, 1H), 4.70 (m, 1H), 4.50 (bs, 2H), 4.45 (ddd, $J = 0.9, 2.0, 5.2$ Hz, 1H), 2.43 (m, 1H), 2.23 (dd, $J = 5.2, 16.0$ Hz, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.4, 170.4, 132.5, 123.2, 110.2, 73.8, 73.7, 69.1, 66.3, 27.6, 26.8, 25.7, 21.1, 20.7. Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 59.20; H, 7.20.

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Supporting Information Available: Experimental procedure and characterization data for quercitols **27**−**29** as well as proof of structure for cyclohexenes **26** and **40** (7 pages, print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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