Carbohydrate Carbocyclization by a Zinc-Mediated Tandem Reaction and Ring-Closing Enyne Metathesis

Carina Storm Poulsen and Robert Madsen*

Department of Chemistry, Building 201, Technical University of Denmark, DK-2800 Lyngby, Denmark

rm@kemi.dtu.dk

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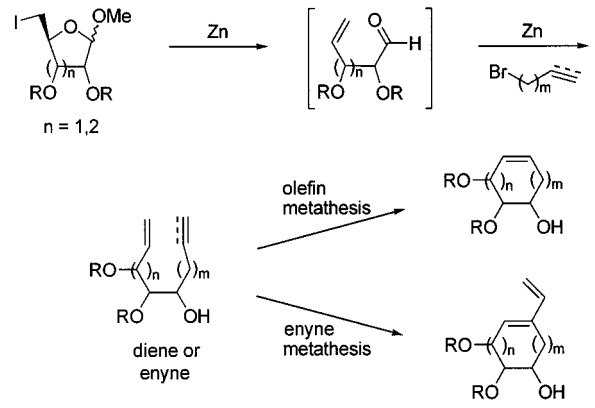
Methyl 5-deoxy-5-iodo-pentofuranosides are reductively ring-opened and propargylated in a tandem fashion in the presence of zinc. The 1,7-enynes thus obtained are subjected to ring-closing enyne metathesis with catalyst **B** to produce functionalized 1-vinyl cyclohexenes. By adding $BnNH_2$ to the tandem reaction, an amino group can be introduced in the 1,7-enyne products. Addition of 2-TMS-ethynylcerium(III) chloride after the reductive ring-opening produces the corresponding 1,6-enynes. Further annulation of the product 1,3-dienes can be achieved through a Diels−Alder reaction with good control of stereochemistry. These procedures constitute efficient methods for rapid carbocyclization and annulation of carbohydrates to produce a variety of functionalized five- and six-membered ring systems.

Introduction

A polyhydroxylated carbocyclic ring is found in many biologically important molecules and natural products,[1] such as glycosidase inhibitors,[2a] aminoglycoside antibiotics,[2b] inositol phosphates,[2c] and carbanucleosides.[2d] Synthetic approaches to these compounds from the chiral pool often commence with the carbocyclization of a suitable carbohydrate. Indeed, chemical synthesis of carbocyclic rings from carbohydrates has been the subject of numerous studies for more than two decades.[3] Significant contributions include the Ferrier II reaction and similar rearrangements, cycloadditions, radical cyclizations, ring-contractions with organometallic reagents, and carbanion cyclizations.[3] Some of these methods, however, do require a significant number of steps for preparation of the starting materials or employ toxic metal reagents for the cyclization event.

During the last five years ring-closing olefin metathesis has been developed for converting sugars into carbocycles.[4,5] This is a very versatile method which can be applied to a wide variety of sugars and ring-sizes. We have recently introduced a zinc-mediated domino reaction

Scheme 1



for preparation of the diene precursors in one step from methyl ω-iodo glycosides (Scheme 1).[6] Subsequent ring-closing olefin metathesis forms the carbocyclic ring and all ring-sizes from five- to eight-membered rings have been prepared by the combination of these two reactions.[6,7]

An alternative metathesis reaction involves ring-closure of enynes to produce 1-vinyl cycloalkenes.[8,9] A variety of different late transition metal catalysts have been shown to mediate the enyne metathesis reaction.[8] In general, ring-closing enyne metathesis is more difficult to achieve than ring-closing olefin metathesis particularly when forming ring-sizes larger than five.[10] Only a few examples exist where enyne metathesis has been applied in carbohydrate chemistry.[11] We envisioned that our zinc-mediated reactions could also be employed for the formation of enynes (Scheme 1). Zinc would serve a dual

* To whom correspondence should be addressed. Fax: (+45) 4593 3968.

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purpose in this process. First, it would mediate the fragmentation of the iodoglycoside, and second, it would activate an alkynyl bromide species for the Barbier alkylation. The enyne thus formed would be directly set up for metathesis to form a carbocyclic 1,3-diene product. This, on the other hand, can undergo further synthetic transformations, especially cycloaddition reactions to generate additional rings.

Herein, we report a full account on synthesis of carbohydrate-derived enynes by a zinc-mediated tandem reaction and subsequent metathesis of these to form carbocycles. We also demonstrate that the obtained dienes can be further annulated in a Diels−Alder reaction.

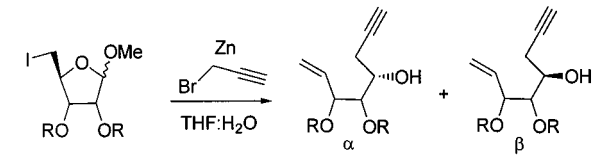
Results and Discussion

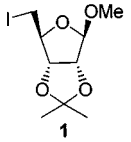
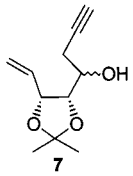
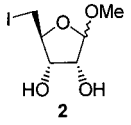
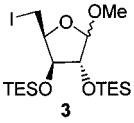
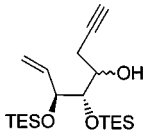
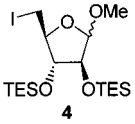
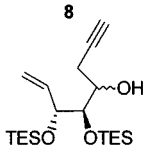
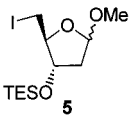
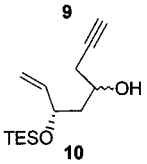
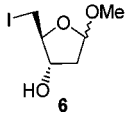
Tandem Reaction. We have previously established general reaction conditions for the zinc-mediated reductive ring-opening−allylation of methyl 5-deoxy-5-iodopentofuranosides.[6] With these procedures in hand, we then decided to probe the tandem reaction with propargyl bromide on isopropylidene 5-iodo-ribofuranoside **1**.[12] It was soon realized that the mode of addition of propargyl bromide played a major role. Carrying out the tandem reaction on **1** with 5 equiv of propargyl bromide all added from the start of the reaction gave a modest 37% yield of the desired 1,7-enyne **7** together with the intermediate unsaturated aldehyde. However, shifting to dropwise addition of the propargyl bromide over 5 h by syringe pump led to an improved 73% yield with no unsaturated aldehyde remaining (Table 1, entry 1). Enyne **7** was formed in an excellent 9:1 diastereomeric ratio. The stereochemistry at the newly generated stereogenic center was assigned after Lindlar reduction to the corresponding diene which have been prepared earlier.[6a]

Several other conditions were investigated in an attempt to further improve the yield of **7** in the tandem reaction. Anhydrous conditions with an added Lewis acid to promote the reaction has been shown to work very well with several alkylating agents.[6a] However, carrying out the ring-opening and propargylation of **1** in anhydrous THF with added $MgBr_2 \cdot OEt_2$ led mainly to decomposition. Additional studies with other substrates have shown that the generated enynes are usually unstable toward acidic conditions. As a result, several experiments were conducted with added base instead. We have previously shown that if Et_3N is added to the tandem reaction in aqueous THF the rate of the overall transformation is decreased while the diastereoselectivity in some cases is improved.[6a] In this case added Et_3N would mainly serve as an acid scavenger to improve the yield. In fact, utilizing the optimized conditions for **1** the addition of 0.5 equiv of Et_3N did cause a slight improvement in the yield of **7** (entry 2). However, increasing the amount of Et_3N to 2 equiv gave rise to a very slow transformation and only a low yield of the desired enyne **7** was obtained together with a significant amount of the intermediate aldehyde and unreacted **1**. Utilizing propargyl chloride instead of the bromide under the optimized conditions gave a 50% yield of enyne **7**. As a result, the following studies with other pentofuranosides were carried out with propargyl bromide in THF−H_2O mixture.

Unprotected 5-iodo-ribofuranoside **2** did not afford any enyne product in the tandem reaction (entry 3). The reductive ring-opening of **2** with zinc proceeded smoothly,[6a] but the propargylation of the resulting enal led only to decomposition. The same result has been observed with other substrates containing a free hydroxyl group (e.g., **6**[13] in entry 7). Consequently, the iodopentofuranosides were protected, and the triethylsilyl (TES) group has previously been shown to be a convenient hydroxyl-protecting group in these reactions.[6] Hereby, substrates **3**, **4**, and **5** were prepared[6] and subjected to zinc and propargyl bromide. In all three cases the desired enynes

Table 1. Zinc-Mediated Tandem Reaction[a]



Entry	Starting furanoside	$THF:H_2O$	Product	α : β	Yield
1	 **1**	2 : 1	 **7**	9 : 1	73%
2		2 : 1[b]		9 : 1	81%
3	 **2**	2 : 1	—	—	0%
4	 **3**	9 : 1	 **8**	7 : 3	61%
5	 **4**	9 : 1	 **9**	3 : 7	56%
6	 **5**	4 : 1	 **10**	2 : 3	64%
7	 **6**	4 : 1	—	—	0%

[a] All reactions were carried out by sonication at 40 °C. [b] 0.5 equiv. of Et_3N was also added.

(10) For recent examples, see: Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236. Timmer, M. S. M.; Ovaa, H.; Filippov, D. V.; van der Marel, G. A.; van Boom, J. H. *Tetrahedron Lett.* **2001**, *42*, 8231. Yao, Q. *Org. Lett.* **2001**, *3*, 2069. Mori, M.; Kitamura, T.; Sato, Y. *Synthesis* **2001**, 654.

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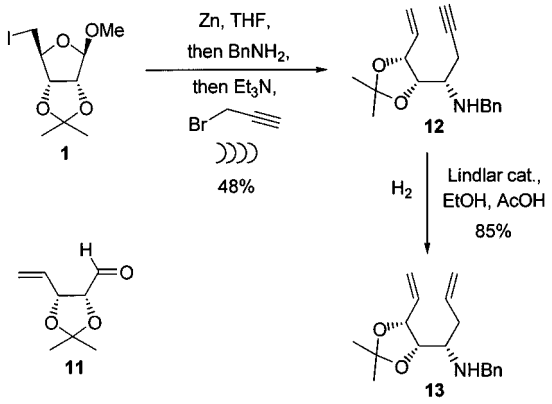
(12) Lerner, L. M. *Carbohydr. Res.* **1977**, *53*, 177.

(13) Aly, Y. L.; Abdel-Megied, A. E.-S.; Pedersen, E. B.; Nielsen, C. *Liebigs Ann. Chem.* **1992**, 127.

were formed in satisfying yields (entries 4−6). For these compounds, no improvement in yields were observed on addition of Et_3N and even small amounts of Et_3N (0.5 equiv) led to a significant decrease in the rate of the reaction. Enynes **8** and **9** are enantiomers. They were both formed in a 7:3 diastereomeric ratio favoring the erythro relationship between the newly generated stereogenic center and the center at C-2 in the starting pentose. The stereochemistry was assigned after hydrogenation of the enynes with Lindlar catalyst to produce the corresponding dienes which have been prepared previously.[6a] The stereochemical outcome of the propargylations with **1**, **3**, and **4** can all be rationalized based on the predictions in the Felkin−Anh model.[14] With 2-deoxyribose substrate **5**, however, the diastereoselectivity was low[15] (entry 6). The structure of the main product **10**β was assigned after conversion into the corresponding MEM-protected enyne,[16] which has been used earlier for synthesis of the A-ring in 1α-hydroxy vitamin D_3 by enyne carbopalladation.[17] In fact, all the hydroxylated enynes in Table 1 are useful for synthesis of vitamin D analogues by this carbopalladation technique.[18] At last, it should be noticed that the formation of allenes has never been observed in any of the experiments in Table 1. Usually, the zinc-mediated propargylation of aldehydes gives rise to various amounts of the corresponding allene.[19] However, it should also be noted that very little allene product has been observed in previous zinc-mediated propargylations of carbohydrate-derived aldehydes.[20] Maybe allenes are indeed formed in the experiments in Table 1, but are not stable under the reaction conditions, which would account for the slightly lower yields in these propargylation reactions as compared to the corresponding allylation reactions.[6a]

In the tandem reactions with allyl bromide it has previously been possible to intercept the intermediate aldehyde with $BnNH_2$ prior to the allylation.[6,7a] This is a very attractive method for the introduction of an amino group in these reactions. Generally, this protocol is carried out in anhydrous THF with slow addition of the alkylating agent in order to ensure imine formation and prevent alkylation of the intermediate aldehyde. However, dropwise addition of propargyl bromide to a mixture of **1**, zinc, and $BnNH_2$ in THF under sonication did not provide any enyne product, but instead led to Wurtz-type homocoupling of **1** as the only identifiable product. This dimerization of **1** is known to occur with other zinc sources,[21] but has not been observed before in our reactions. Attempts with added Lewis acids to facilitate the reductive ring-opening led to complex mixtures of products. Although zinc-mediated propargylation of imines is known[22] it appears that propargyl bromide requires other conditions than allyl bromide in these reactions. As a result, it was decided to analyze the individual steps more carefully (Scheme 2). First, treatment of **1** with zinc gave cleanly enal **11** which was isolated by extraction.[23] Second, treatment of this with $BnNH_2$ in anhydrous THF containing 3 Å molecular sieves gave complete conversion into the corresponding imine. To this solution zinc was added, and the mixture was sonicated for 3 h during which time propargyl bromide was added dropwise. This now gave a mixture of products from which enyne **12** could be isolated in about 20% yield. Like the enynes in Table 1, enyne **12** also appears to be unstable to acidic conditions. In an attempt to improve the yield, Et_3N was added to the reaction mixture based on the result in Table 1, entry 2. Hereby, the following one-pot procedure was developed with no isolation of the intermediate components: furanoside **1** was sonicated with zinc in THF for 30 min followed by addition of $BnNH_2$ and continued sonication for 2 h. Then Et_3N was added followed by dropwise addition of propargyl bromide over 2.5 h with continuous sonication. Workup gave the desired enyne **12** in 48% yield as a single diastereomer. The stereochemistry was verified by hydrogenation over Lindlar catalyst to produce known diene **13**.[6a]

Scheme 2



Finally, it was investigated whether a two-carbon nucleophile could be employed in the tandem reaction. Several experiments were carried out with various ethynylmetal species and ribofuranoside **1**. First, furanoside **1** was fragmented with zinc to afford unsaturated aldehyde **11**. Direct addition of HC≡CMgBr[24] after the fragmentation gave a complex mixture of products. Instead, the zinc salts were allowed to precipitate and the solution of **11** was then cannulated into a solution of HC≡CMgBr in THF. Hereby, 1,6-enyne **14** was isolated in 26% yield as a 2:1 mixture of diastereomers after standard acetylation in the workup (Scheme 3). Several byproducts were also formed, but were not identified. In an attempt to optimize this reaction magnesium was replaced by a number of other metals. However, only

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(18) Kittaka, A.; Suhara, Y.; Takayanagi, H.; Fujishima, T.; Kurihara, M.; Takayama, H. *Org. Lett.* **2000**, *2*, 2619. Furishima, T.; Konno, K.; Nakagawa, K.; Kurobe, M.; Okano, T.; Takayama, H. *Bioorg. Med. Chem.* **2000**, *8*, 123. Moriarty, R. M.; Brumer, H., III *Tetrahedron Lett.* **1995**, *36*, 9265.

(19) Yi, X.-H.; Meng, Y.; Hua, X.-G., Li, C.-J. *J. Org. Chem.* **1998**, *63*, 7472. Bieber, L. W., da Silva, M. F.; da Costa, R. C.; Silva, L. O. S. *Tetrahedron Lett.* **1998**, *39*, 3655.

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(23) Kobori, Y.; Myles, D. C.; Whitesides, G. M. *J. Org. Chem.* **1992**, *57*, 5899.

(24) Suzuki, M.; Kimura, Y.; Terashima, S. *Chem. Pharm. Bull.* **1986**, *34*, 1531.

Scheme 3

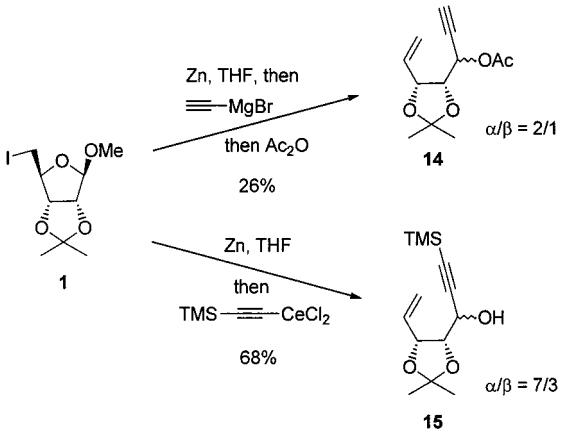
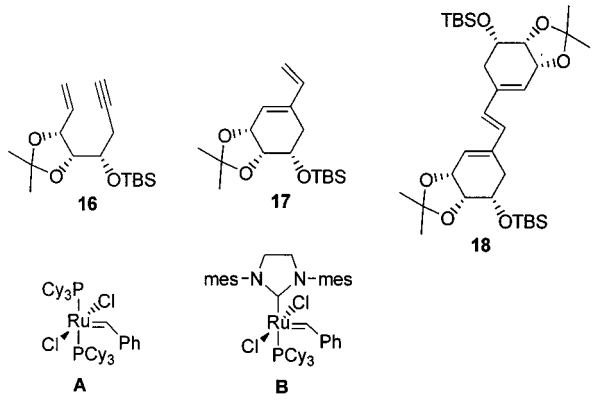


Chart 1



complex mixtures of products were obtained when the crude fragmentation product was treated with HC≡CLi,[24] $(HC≡C)_3Ce$,[24] or HC≡CZnOTf.[25] When $HC≡CCeCl_2$[24] or HC≡CZnBr[26] were employed for the addition, reduction of the intermediate aldehyde **11** to alcohol occurred as the main reaction. As a result, the corresponding TMS-protected ethynylmetal reagents were also investigated. Interestingly, TMSC≡CMgBr,[24] $TMSC≡CCeCl_2$,[24] and $(TMSC≡C)_2Zn$[27] all gave rise to various amounts of the desired enyne **15**. To prevent reduction of aldehyde **11** to the alcohol, it appeared important to remove the zinc salts from the fragmentation prior to the addition of the alkylating agent. The best result was obtained with $TMSC≡CCeCl_2$[28] giving rise to a 68% yield of **15** as a 7:3 mixture of diastereomers. The stereochemistry was verified after removal of the TMS group and Lindlar reduction to the corresponding 1,6-diene, which have been prepared previously.[6a]

Enyne Metathesis. Ring-closing metathesis of enynes to produce 1-vinyl cyclohexenes has been known for more than a decade.[8] In general, there are two catalyst systems for this reaction operating by different mechanisms. A variety of low-valent late transition metal complexes will catalyze the rearrangement by an oxidative addition−reductive elimination pathway.[8] On the other hand, several metal carbene complexes will catalyze the same rearrangement by a series of [2 + 2] cycloadditions−retrocycloadditions, as in olefin metathesis.[8] We decided to use enyne **7**α and the corresponding TBS-protected compound **16** as test substrates for these cyclization experiments (Chart 1).

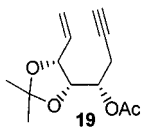
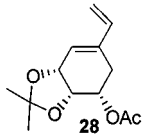
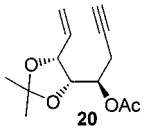
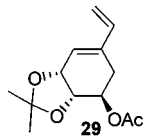
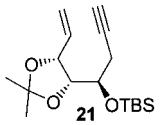
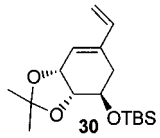
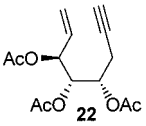
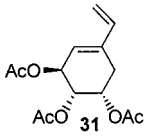
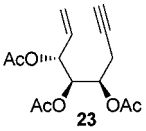
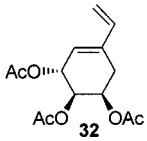
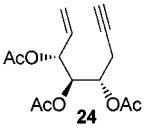
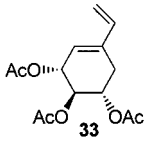
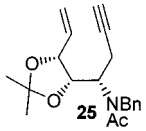
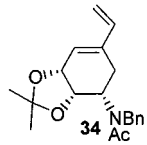
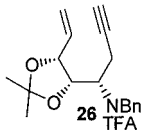
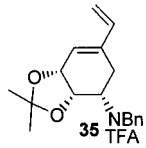
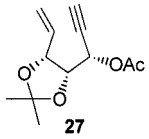
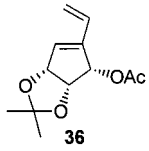
Complexes $[Ru(CO)_3Cl_2]_2$ (with CO atm), $PtCl_2$, and $PtCl_4$ have been some of the most effective catalysts for metathesis of simple enynes in toluene at 60−80 °C.[29] However, with enynes **7**α and **16** only decomposition was observed under these conditions with no sign of the cyclic 1,3-diene product. Several similar complexes were also investigated, but only with **16**, which appeared to be more stable. Zeise's dimer $[PtCl_2(C_2H_4)]_2$ caused rapid decomposition of **16** already at room temperature. Other Pt(II) complexes $PtCl_2(PhCN)_2$ and $PtCl_2(MeCN)_2$ did not react at room temperature, and at 50 °C only decomposition of **16** was observed. A variety of other complexes did not react with **16** at 50 °C, including $PtCl_2(COD)$, $PdCl_2(PhCN)_2$, $PdCl_2(PPh_3)_2$, and $[Rh(CO)_2Cl]_2$. With these somewhat disappointing results in hand, attention was then shifted toward the metal carbene complexes.

Ruthenium carbene complexes **A** and **B** commonly employed in olefin metathesis will also catalyze enyne metathesis. With terminal alkynes these reactions are best carried out under an atmosphere of ethylene gas to ensure better turnover of the active catalyst.[30] Treatment of enyne **7**α with 10% of **A** in CH_2Cl_2 at 40 °C led to decomposition while virtually no reaction occurred at room temperature. Carrying out the same reaction with TBS-protected enyne **16** and **A** gave now for the first time significant conversion into the desired diene **17** with some unreacted **16** remaining. Encouraged by this result focus now shifted toward the more reactive catalyst **B**. Treatment of unprotected **7**α with this catalyst still led to decomposition. However, when **16** was reacted with 8% of **B** at room temperature in CH_2Cl_2 under an ethylene atmosphere a gratifying 66% yield (72% based on recovered **16**) of **17** was obtained. Interestingly, if the same reaction was run under an argon atmosphere the dimer **18** was formed as a significant byproduct in 29% yield. The structure of **18** was confirmed by ^1H and ^{13}C NMR as well as mass spectroscopy. This clearly shows the importance of the ethylene atmosphere in these reactions.

With this protocol in hand, the enynes from the tandem reactions could now be transformed into cyclic 1,3-dienes with catalyst **B** (Table 2). Free hydroxyl and amino groups had to be protected in order for the enyne metathesis to take place. The acetyl group was here chosen as a convenient blocking group. In addition, we have previously experienced in the ring-closing olefin metathesis reaction that acetyl protection was superior to benzyl or silyl protection.[6a,31] Standard acetylation of enyne **7**α gave acetate **19**, which was cyclized in good yield into the corresponding 1,3-diene (entry 1). A similar result was obtained for the acetylated epimer **20** and TBS-protected **21** (entries 2 and 3). The triethylsilyl protected enynes in Table 1 would not undergo the metathesis reaction and were converted into fully acetylated substrates **22**−**24** by a one-pot reaction involving treatment with TBAF in THF followed by addition of Ac_2O, Et_3N, and DMAP. These triacetates turned out to

(25) Sasaki, H.; Boyall, D.; Carreira, E. M. *Helv. Chim. Acta* **2001**, *84*, 964.
(26) Negishi, E.; Kotora, M.; Xu, C. *J. Org. Chem.* **1997**, *62*, 8957.
(27) Niwa, S.; Soai, K. *J. Chem. Soc., Perkin Trans. 1* **1990**, 937.
(28) For a recent review on organocerium reagents, see: Liu, H.-J.; Shia, K.-S.; Shang, X.; Zhu, B.-Y. *Tetrahedron* **1999**, *55*, 3803.
(29) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901. Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049.
(30) Mori, M.; Sakakibara, N.; Kinoshita, A. *J. Org. Chem.* **1998**, *63*, 6082.
(31) Jørgensen, M.; Iversen, E. H.; Paulsen, A. L.; Madsen, R. *J. Org. Chem.* **2001**, *66*, 4630.

Table 2. Ring-Closing Enyne Metathesis with Catalyst B[a]

Entry	Enyne	Amount of B	Product	Yield[b]
1	 **19**	10%	 **28**	70% (76%)
2	 **20**	10%	 **29**	68%
3	 **21**	8%	 **30**	72%
4	 **22**	5%	 **31**	74% (79%)
5	 **23**	5%	 **32**	72%
6	 **24**	8%	 **33**	58%
7	 **25**	10%	 **34**	50%
8	 **26**	10%	 **35**	60% (63%)
9	 **27**	10%	 **36**	32%
10		10%[c]		70%

[a] All reactions were carried out in CH_2Cl_2 at room temperature under an atmosphere of ethylene. [b] Yields in parentheses are based on recovered starting material. [c] Catalyst **A** was used instead of **B**.

be good substrates for the enyne metathesis reaction (entries 4−6). Attempted metathesis of aminoenyne **12** in the presence of TsOH to protonate the amine led to decomposition. Instead, **12** was converted into acetamide **25** and trifluoroacetamide **26**, the latter being easier to deprotect. Both compounds could be transformed into the vinyl cyclohexenes (entries 7 and 8). All in all, these enyne metathesis reactions proceeded well with catalyst **B** and ethylene atmosphere. We did not observe other carbocyclic ring isomers in any of the metathesis reactions as recently reported for other substrates.[32]

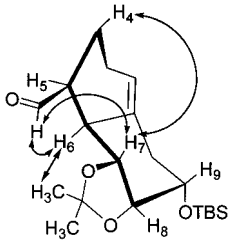
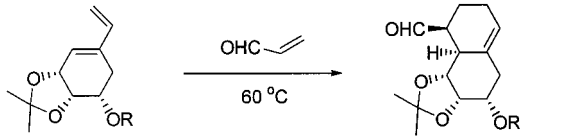


Figure 1. 2D-NOESY for **37**. Arrows show observed enhancements.

Scheme 4



17: R = TBS
28: R = Ac

37: R = TBS (69%)
38: R = Ac (56%)

Acetylated 1,6-enyne **27** was prepared directly from **15**α by the same one-pot desilylation−acetylation protocol as employed above. When **27** was subjected to 10% of catalyst **B** only a 32% yield was obtained of the desired 1,3-diene **36** together with several byproducts (entry 9). Interestingly, when less reactive catalyst **A** was used for this cyclization the yield increased to 70% (entry 10). In general, five-membered rings are formed more readily by enyne metathesis than six-membered rings,[10] which allows for the use of the weaker catalyst **A** in this case.

Diels−Alder Reaction. The cyclic 1,3-dienes thus prepared are perfect substrates for a subsequent Diels−Alder reaction. This would give rise to highly functionalized decalins which are important subunits in a number of biologically significant compounds.[33] We decided to investigate this possibility, and particularly whether the regioselectivity could be controlled with unsymmetrical dienophiles.[34] Indeed, warming **17** in an acrolein solution at 60 °C for 24 h gave mainly one Diels−Alder adduct which was isolated in 69% yield (Scheme 4). The ^{1}H NMR spectrum was fully assigned by selective decoupling experiments. The 9.4 Hz coupling constant between H_6 and H_7 is noteworthy. Subsequent 2D-NOESY studies verified the structure to be that of **37** (Figure 1). This is the product of endo addition from the face opposite the isopropylidene group. The regioselectivity is in line with earlier observations in similar systems.[34] Interestingly, this cycloaddition reaction can give eight possible products, and only trace amounts were observed of some of the other isomers.

Subjecting acetate protected diene **28** to warm acrolein also gave one main product **38** in 56% yield. Analysis of the ^{1}H NMR revealed that the coupling constants were

(32) Kitamura, T.; Sato, Y.; Mori, M. *Chem. Commun.* **2001**, 1258.
(33) For some recent syntheses of functionalized decalins, see: Gössinger, E.; Schwartz, A.; Sereining, N. *Tetrahedron* **2001**, *57*, 3045. Labadie, G. R.; Cravero, R. M.; Conzález-Sierra, M. *Tetrahedron Lett.* **2001**, *42*, 1811. Mehta, G.; Ramesh, S. S. *Chem. Commun.* **2000**, 2429. Jarosz, S.; Skóra, S. *Tetrahedron: Asymmetry* **2000**, *11*, 1433. Tsai, Y.-F.; Peddinti, K.; Liao, C.-C. *Chem. Commun.* **2000**, 475.
(34) Very good regioselectivity has recently been reported in Diels−Alder reactions with similar 1,3-diene systems, see: Ling, T.; Chowdhury, C.; Kramer, B. A.; Vong, B. G.; Palladino, M. A.; Theodorakis, E. A. *J. Org. Chem.* **2001**, *66*, 8843. Pai, C.-C.; Liu, R.-S. *Org. Lett.* **2001**, *3*, 1295. Bentz, D.; Laschat, S. *Synthesis* **2001**, 1766. Renaud, J.; Graf, C.-D.; Oberer, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3101.

virtually identical to those found in the spectrum of **37**. Accordingly, **38** was also assigned to be the product of endo addition from the face opposite the isopropylidene group.

In conclusion, carbohydrates have been converted into functionalized 1-vinyl cyclopentenes and -hexenes by the combination of a zinc-mediated tandem reaction and ring-closing enyne metathesis. Further annulation can be achieved by a Diels−Alder reaction, which provides functionalized decalins in very few steps from carbohydrates. These methods complement our previously developed carbocyclization method using ring-closing olefin metathesis.[6a]

Experimental Section

General Procedures. All sonications were performed 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 20 min, and then filtered and washed with H_2O and Et_2O. Finally, the zinc was dried under high vacuum with a heat gun. Propargyl bromide was prepared according to literature procedures[35] and occasionally redistilled (note: distillations should be carried out behind a safety shield. Neat propargyl bromide has been reported to be shock-sensitive). Thin-layer chromatography was performed on aluminum plates precoated with silica gel (Merck 1.05554). Compounds were visualized by heating after dipping in a solution of $Ce(SO_4)_2$ (2.5 g) and $(NH_4)_6Mo_7O_{24}$ (6.25 g) in 10% aqueous H_2SO_4 (250 mL) or in a solution of $KMnO_4$ (3 g) and K_2CO_3 (20 g) in 1% aqueous NaOH (300 mL). Flash chromatography was performed using silica gel 60. Microanalyses were conducted by the Department of Chemistry at the University of Copenhagen.

General Procedure for Tandem Reaction. Zinc (2.5 g) was added to a solution of the methyl 5-iodo-furanoside (1 g) in THF:H_2O (20 mL). The mixture was sonicated at 40 °C under an argon atmosphere during which time propargyl bromide (5 equiv) was added dropwise by syringe pump over 5−8 h. Zinc salts were removed by filtration through Celite. The Celite was washed with CH_2Cl_2. The filtrate was diluted with more CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried and concentrated, and the residue was purified by flash chromatography eluting with a pentane:Et_2O mixture containing 0.5% Et_3N.

(4*S*,5*S*,6*R*)-5,6-(Isopropylidenedioxy)-7-octen-1-yn-4-ol (7α) and (4*R*,5*S*,6*R*)-5,6-[(Isopropylidene)dioxy]-7-octen-1-yn-4-ol (7*β*). For **7**α. $R_f = 0.57$ (pentane/Et_2O = 4:1). $[\alpha]_D^{26}$: −14.3 (*c* 1.21, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.98 (ddd, J = 17.3, 10.4, 6.9 Hz, 1H), 5.40 (ddd, J = 17.3, 1.5, 0.8 Hz, 1H), 5.25 (ddd, J = 10.4, 1.4, 0.8 Hz, 1H), 4.66 (ddd, J = 6.9, 6.5, 0.8 Hz, 1H), 4.03 (dd, J = 8.7, 6.5 Hz, 1H), 3.73 (m, 1H), 2.61 (ddd, J = 16.9, 3.6, 2.7 Hz, 1H), 2.42 (ddd, J = 16.9, 7.2, 2.7 Hz, 1H), 2.04 (t, J = 2.7 Hz, 1H), 2.10 (s, 1H), 1.42 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.7, 118.1, 108.8, 80.2, 79.2, 78.4, 70.9, 67.9, 27.7, 25.2, 24.3. EI (positive mode) *m*/*z* calcd for $C_{10}H_{13}O_3$ ($(M - CH_3)^+$) 181.0865. Found 181.0867. A solution of **7**α (200 mg) in EtOH (15 mL) was hydrogenated over Lindlar catalyst (18 mg) under 1 atm of H_2 at room temperature for 7 h. The catalyst was removed by filtration and the filtrate concentrated. The residue was dissolved in MeOH (10 mL) and stirred with acidic ion-exchange resin (2 mL) for 2 h at 40 °C. Filtration, concentration, and purification by flash chromatography (Et_2O) gave (3*R*,4*S*,5*S*)-1,7-octadiene-3,4,5-triol with ^{1}H and ^{13}C NMR data in accordance with previous values.[6a]

For **7***β*. $R_f = 0.57$ (pentane/Et_2O = 4:1). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.6, 119.7, 108.5, 80.7, 78.9, 78.5, 70.4, 68.2, 27.1, 24.8, 24.1.

(35) Gaudemar, M. *Ann. Chim., 13. Ser.* **1956**, *1*, 161.

(4*S*,5*S*,6*S*)-5,6-Bis[(triethylsilyl)oxy]-7-octen-1-yn-4-ol (8α) and (4*R*,5*S*,6*S*)-5,6-Bis[(triethylsilyl)oxy]-7-octen-1-yn-4-ol (8*β*). For **8**α. $R_f = 0.63$ (pentane/Et_2O = 9:1). $[\alpha]_D^{25}$: −61.5 (*c* 1.64, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.06 (ddd, J = 17.2, 10.7, 4.4 Hz, 1H), 5.36 (dt, J = 17.2, 1.8 Hz, 1H), 5.26 (dt, J = 10.7, 1.8 Hz, 1H), 4.38 (m, 1H), 4.06 (s, 1H), 3.82 (m, 1H), 3.70 (dd, J = 8.6, 4.3 Hz, 1H), 2.55 (dt, J = 16.7, 2.6 Hz, 1H), 2.35 (ddd, J = 16.7, 6.4, 2.6 Hz, 1H), 2.01 (t, J = 2.6 Hz, 1H), 0.98 (t, J = 8.1 Hz, 18H), 0.71−0.55 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.2, 116.2, 81.4, 76.2, 74.0, 71.0, 69.8, 23.6, 6.8, 6.6, 5.0, 4.6. Anal. Calcd for $C_{20}H_{40}O_3Si_2$: C, 62.44; H, 10.48. Found: C, 62.23; H, 10.60. Hydrogenation over Lindlar catalyst and removal of the silyl groups with TBAF gave the corresponding octadiene triol with NMR data in accordance with literature values.[6a]

For **8***β*. $R_f = 0.63$ (pentane/Et_2O = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.01 (ddd, J = 17.3, 10.5, 5.7 Hz, 1H), 5.27 (ddd, J = 17.3, 1.8, 1.5 Hz, 1H), 5.16 (ddd, J = 10.5, 1.8, 1.5 Hz, 1H), 4.19 (ddt, J = 5.7, 4.9, 1.5 Hz, 1H), 3.91 (dddd, J = 7.4, 6.8, 6.4, 2.8 Hz, 1H), 3.81 (dd, J = 4.9, 2.8 Hz, 1H), 2.56 (d, J = 6.8 Hz, 1H), 2.43 (ddd, J = 16.7, 6.4, 2.8 Hz, 1H), 2.36 (ddd, J = 16.7, 7.4, 2.8 Hz, 1H), 1.97 (t, J = 2.8 Hz, 1H), 1.05−0.92 (m, 18H), 0.74−0.55 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.2, 115.5, 81.2, 74.9 (2C), 69.8, 68.2, 24.8, 6.8, 6.8, 5.1, 4.8.

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

(4*R*,6*S*)-6-[(Triethylsilyl)oxy]-7-octen-1-yn-4-ol (10*β*) and (4*S*,6*S*)-6-[(Triethylsilyl)oxy]-7-octen-1-yn-4-ol (10α). For **10***β*. R_f = 0.36 (pentane/Et_2O = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.89 (ddd, J = 17.1, 10.4, 5.6 Hz, 1H), 5.26 (dt, J = 17.2, 1.4 Hz, 1H), 5.14 (dq, J = 10.4, 1.4 Hz, 1H), 4.54 (m, 1H), 4.06 (m, 1H), 3.53 (s, 1H), 2.45−2.27 (m, 2H), 2.01 (t, J = 2.8 Hz, 1H), 1.81−1.75 (m, 2H), 0.96 (t, J = 8.0 Hz, 9H), 0.63 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.8, 114.6, 80.9, 72.2, 70.2, 67.0, 42.1, 27.2, 6.7, 4.7. Removal of the silyl group with TBAF and subsequent protection with MEMCl provided (4*R*,6*S*)-4,6-bis[(2-methoxyethoxymethyl)oxy]-7-octen-1-yne with NMR data in accordance with literature values.[16]

For **10**α. R_f = 0.36 (pentane/Et_2O = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.84 (ddd, J = 17.1, 10.3, 7.2 Hz, 1H), 5.26 (dt, J = 17.2, 1.4 Hz, 1H), 5.08 (dq, J = 10.3, 1.4 Hz, 1H), 4.38 (m, 1H), 3.96 (m, 1H), 3.52 (s, 1H), 2.45−2.27 (m, 2H), 2.02 (t, J = 2.8 Hz, 1H), 1.81−1.75 (m, 2H), 0.96 (t, J = 8.0 Hz, 9H), 0.63 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.8, 114.8, 80.9, 74.7, 70.2, 69.3, 43.1, 27.2, 6.7, 4.9. Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.09; H, 10.30. Found: C, 66.31; H, 10.39.

(4*S*,5*S*,6*R*)-4-[(*N*-Benzyl)amino]-5,6-(isopropylidenedioxy)-7-octen-1-yne (12). A mixture of furanoside **1** (500 mg, 1.6 mmol) and zinc (2 g) in dry THF (15 mL) was sonicated under an argon atmosphere at 40 °C for 30 min. $BnNH_2$ (0.52 mL, 4.8 mmol) was added and the mixture sonicated for an additional 2 h at 40 °C. Et_3N (0.7 mL, 4.8 mmol) was then added and the sonication continued for 2.5 h during which time propargyl bromide (1.1 mL, 14.4 mmol) was added dropwise by syringe pump. The mixture was filtered through Celite. The Celite was rinsed with Et_2O and the filtrate washed with H_2O. The organic phase was dried and concentrated, and the residue was purified by flash chromatography (CH_2Cl_2/MeOH/Et_3N = 98:1:1) to afford 217 mg (48%) of **12** as a colorless syrup. R_f = 0.71 (hexane/EtOAc = 3:1). $[\alpha]_D^{24}$: +79.6 (*c* 1.07, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35−7.20 (m, 5H), 5.98 (ddd, J = 17.0, 10.5, 6.5 Hz, 1H), 5.37 (ddd, J = 17.0, 2.0, 1.4 Hz, 1H), 5.20 (ddd, J = 10.5, 2.0, 1.2 Hz, 1H), 4.69 (m, 1H), 4.13 (dd, J = 9.3, 6.2 Hz, 1H), 3.89 (d, J = 12.5 Hz, 1H), 3.62 (d, J = 12.5 Hz, 1H), 2.82 (ddd, J = 9.3, 4.0, 3.9 Hz, 1H), 2.70 (ddd, J = 17.1, 4.0, 2.6 Hz, 1H), 2.57 (ddd, J = 17.1, 3.9, 2.6 Hz, 1H), 2.00 (t, J = 2.6 Hz, 1H), 1.47 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.0, 134.6, 128.2, 128.1, 126.9, 116.8, 108.1, 80.3, 78.7, 78.3, 70.8, 54.4, 50.7, 27.7, 25.3, 19.9. Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91. Found: C, 75.21; H, 8.22; N, 4.95. Hydrogenation over Lindlar catalyst in the presence of 2 equiv of AcOH gave **13** with NMR data in accordance with previous values.[6a]

Acetylation of **12** with Ac_2O and Et_3N in CH_2Cl_2 gave **25** as an almost equal mixture of two rotamers by NMR: R_f = 0.37 (hexane/EtOAc = 2:1). $[\alpha]_D^{23}$: +21.0 (*c* 0.73, $CHCl_3$). Mp: 69−

70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40−7.20 (m, 10H), 5.93 (ddd, J = 17.2, 10.4, 7.0 Hz, 1H), 5.75 (m, 1H), 5.39 (bd, J = 17.2 Hz, 1H), 5.34 (bd, J = 10.4 Hz, 1H), 5.50 (bs, 1H), 5.25 (bd, J = 6.3 Hz, 1H), 5.08 (m, 1H), 5.02 (d, J = 15.0 Hz, 1H), 4.70 (d, J = 17.6 Hz, 1H), 4.57 (d, J = 17.6 Hz, 1H), 4.49 (m, 1H), 4.27 (m, 1H), 4.23−4.15 (m, 2H), 4.07 (m, 1H), 3.88 (dd, J = 7.3, 6.8 Hz, 1H), 2.63−2.56 (m, 2H), 2.56−2.50 (m, 2H), 2.30 (s, 3H), 2.03 (t, J = 2.6 Hz, 1H), 2.03 (s, 3H), 1.95 (t, J = 2.6 Hz, 1H), 1.44 (bs, 6H), 1.22 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.4, 172.2, 138.8, 137.9, 133.5, 133.3, 128.5, 128.3 (2C), 128.0, 127.1, 126.1, 119.1, 118.8, 108.4 (2C), 81.1, 79.9, 78.8 (2C), 78.7, 78.3, 71.7, 70.2, 56.6, 52.2, 48.8, 44.9, 27.3, 27.0, 24.7, 24.6, 22.7, 22.4, 20.5, 18.9. Anal. Calcd for $C_{20}H_{25}NO_3$: C, 73.37; H, 7.70; N, 4.28. Found: C, 73.19; H, 7.76; N, 4.30.

Trifluoroacetylation of **12** with TFAA and Et_3N in CH_2Cl_2 gave **26** as an almost equal mixture of two rotamers by NMR: R_f = 0.60 (hexane/EtOAc = 2:1). $[\alpha]_D^{23}$: −52.1 (c 0.95, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40−7.20 (m, 10H), 5.81 (ddd, J = 17.0, 10.3, 6.9 Hz, 1H), 5.73 (ddd, J = 17.6, 10.4, 7.0 Hz, 1H), 5.44 (bd, J = 17.0 Hz, 1H), 5.41 (bd, J = 10.3 Hz, 1H), 5.28 (bd, J = 10.4 Hz, 1H), 5.25 (bd, J = 17.6 Hz, 1H), 4.80 (d, J = 15.3 Hz, 1H), 4.73 (d, J = 7.4 Hz, 1H), 4.68 (d, J = 15.3 Hz, 1H), 4.63 (d, J = 7.4 Hz, 1H), 4.58 (m, 1H), 4.36 (bd, J = 8.0 Hz, 1H), 4.33−4.17 (m, 4H), 2.62 (m, 1H), 2.59 (m, 1H), 2.45 (m, 1H), 2.32 (dt, J = 17.9, 3.0 Hz, 1H), 1.99−1.94 (m, 2H), 1.49 (s, 3H), 1.39 (s, 3H), 1.27 (s, 3H), 1.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.1 (q, J = 35.6 Hz), 157.9 (q, J = 35.3 Hz), 136.6, 135.7, 133.0, 132.0, 128.6, 128.2, 128.1, 127.9, 127.6, 127.3, 119.9, 119.5, 116.6 (q, J = 288.3 Hz), 116.5 (q, J = 288.5 Hz), 109.2, 108.5, 80.0 (2C), 79.0, 78.7, 78.5, 77.9, 71.5, 70.7, 56.8, 55.8, 49.5, 47.3, 27.0, 26.3, 24.5, 24.2, 18.6, 18.5. Anal. Calcd for $C_{20}H_{22}F_3NO_3$: C, 62.98; H, 5.81; N, 3.67. Found: C, 63.04; H, 5.85; N, 3.70.

(3*S*,4*S*,5*R*)-4,5-(Isopropylidenedioxy)-1-(trimethylsilyl)-6-hepten-1-yn-3-ol (15α) and (3*R*,4*S*,5*R*)-4,5-(Isopropylidenedioxy)-1-(trimethylsilyl)-6-hepten-1-yn-3-ol (15*β*). A suspension of anhydrous $CeCl_3$ (2.4 g, 9.6 mmol, dried at 225 °C under high vacuum overnight) in anhydrous THF (15 mL), was stirred at room temperature for 1 day and then cooled to −78 °C followed by addition of a 0.6 M solution of trimethylsilylethynylmagnesium chloride in THF (16 mL, 9.6 mmol). The mixture was stirred at −78 °C for 1 h and then allowed to warm to 0 °C and stirred for an additional 1 h at this temperature. In the meantime, a solution of furanoside **1** (750 mg, 2.4 mmol) in THF (15 mL) was sonicated with activated zinc dust (1.8 g) and TMSCl (0.15 mL, 1.2 mmol) at 40 °C for 2 h. The mixture was then filtered through Celite, and the Celite was rinsed with CH_2Cl_2. The filtrate was washed with saturated aqueous $NaHCO_3$, dried, and concentrated. The crude aldehyde **11** thus obtained was dissolved in dry THF (5 mL) and added to the freshly prepared solution of trimethylsilylethynylcerium chloride (9.6 mmol) at 0 °C. This mixture was stirred at 0 °C for 10 min and then at room temperature for 45 min. TLC (pentane/Et_2O = 2:1) indicated full conversion of the aldehyde. Excess alkylating agent was quenched by stirring with H_2O (25 mL) for 5 min. The mixure was diluted with CH_2Cl_2, and the phases were separated. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were dried and concentrated. The residue was purified by flash chromatography (CH_2Cl_2/Et_3N = 99:1, R_f = 0.20) to afford 415 mg (68%) of enynes **15**α and **15***β* as an inseparable mixture in a 7:3 ratio. R_f = 0.66 (hexane/EtOAc = 2:1).

For **15**α. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.14 (ddd, J = 17.4, 10.4, 7.2 Hz, 1H), 5.42 (bd, J = 17.4 Hz, 1H), 5.30 (bd, J = 10.4 Hz, 1H), 4.70 (m, 1H), 4.33 (d, J = 4.1 Hz, 1H), 4.23 (dd, J = 7.2, 4.1 Hz, 1H), 1.56 (bs, 3H), 1.39 (bs, 3H), 0.17 (bs, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.1, 119.0, 109.1, 103.6, 91.8, 80.4, 78.2, 62.9, 26.9, 25.1, −0.4.

For **15***β*. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.95 (ddd, J = 17.4, 10.4, 7.0 Hz, 1H), 5.39 (bd, J = 17.4 Hz, 1H), 5.28 (bd, J = 10.4 Hz, 1H), 4.67 (m, 1H), 4.25 (d, J = 6.6 Hz, 1H), 4.25 (m, 1H), 1.52 (bs, 3H), 1.40 (bs, 3H), 0.16 (bs, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.7, 119.0, 109.3, 102.8, 91.5, 80.6, 78.3, 62.0, 27.6, 25.2, −0.4. Anal. Calcd for $C_{13}H_{22}O_3Si$: C, 61.38; H, 8.72. Found: C, 61.36; H, 8.51. Removal of the silyl groups with TBAF followed by hydrogenation over Lindlar catalyst and cleavage of the isopropylidene acetal gave the corresponding heptadiene triols. These could be separated by flash chromatography and the major isomer was identified as 1,2,6,7-tetradeoxy-*ribo*-hept-1,6-dienitol by comparison with literature data.[6a]

(4*S*,5*R*,6*R*)-5,6-(Isopropylidenedioxy)-4-[(*tert*-butyldimethylsilyl)oxy]-7-octen-1-yne (16) and (4*R*,5*R*,6*R*)-5,6-(Isopropylidenedioxy)-4-[(*tert*-butyldimethylsilyl)oxy]-7-octen-1-yne (21). The crude product from the tandem fragmentation−propargylation of **1** was dried azeotropically with toluene. The residue (consisting of **7**α and **7***β*) was dissolved in CH_2Cl_2 and 2,6-lutidine (2 equiv). TBSOTf (1.2 equiv) was added dropwise over 1 h at 0 °C, and the mixture was then allowed to stir at room temperature for an additional 1 h. The solution was diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$, dried, and concentrated. The title compounds **16** and **21** were separated by flash chromatography (pentane/Et_2O = 98:2 with 0.5% Et_3N) in a combined yield of 57% starting from **1**.

For **16**. R_f = 0.54 (pentane/Et_2O = 95:5). $[\alpha]_D^{24}$: +40.1 (c 1.23, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.98 (ddd, J = 17.2, 10.3, 7.1 Hz, 1H), 5.36 (ddd, J = 17.2, 1.5, 0.6 Hz, 1H), 5.23 (ddd, J = 10.3, 1.5, 0.6 Hz, 1H), 4.62 (m, 1H), 4.26 (dd, J = 7.2, 6.8 Hz, 1H), 3.89 (ddd, J = 7.2, 4.6, 4.5 Hz, 1H), 2.56 (ddd, J = 17.2, 4.5, 2.7 Hz, 1H), 2.48 (ddd, J = 17.2, 4.6, 2.7 Hz, 1H), 1.98 (t, J = 2.7 Hz, 1H), 1.46 (s, 3H), 1.38 (s, 3H), 0.90 (s, 9H), 0.13 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.4, 117.8, 108.2, 80.6, 79.1, 78.5, 70.4, 69.0, 27.7, 25.9, 25.3, 24.5, 18.1, −3.9, −4.5. Anal. Calcd for $C_{17}H_{30}O_3Si$: C, 65.76; H, 9.74. Found: C, 65.63; H, 9.89.

For **21**. R_f = 0.50 (pentane/Et_2O = 95:5). $[\alpha]_D^{24}$: +15.5 (c 0.73, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.90 (ddd, J = 17.3, 10.0, 8.4 Hz, 1H), 5.31 (ddd, J = 17.3, 1.5, 1.0 Hz, 1H), 5.26 (ddd, J = 10.0, 1.5, 0.8 Hz, 1H), 4.48 (dddd, J = 8.4, 6.1, 1.0, 0.8 Hz, 1H), 4.19 (dd, J = 7.1, 6.1 Hz, 1H), 3.82 (ddd, J = 7.1, 6.1, 4.6 Hz, 1H), 2.43 (ddd, J = 16.9, 4.6, 2.7 Hz, 1H), 2.33 (ddd, J = 16.9, 6.1, 2.7 Hz, 1H), 1.97 (t, J = 2.7 Hz, 1H), 1.50 (s, 3H), 1.37 (s, 3H), 0.91 (bs, 9H), 0.12 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.7, 119.2, 108.8, 81.3, 80.6, 79.1, 77.4, 70.3, 28.1, 26.2, 25.7, 24.1, 18.6, −4.1, −4.2. Anal. Calcd for $C_{17}H_{30}O_3Si$: C, 65.76; H, 9.74. Found: C, 65.41; H, 9.53.

(4*S*,5*R*,6*R*)-4-(Acetyloxy)-5,6-(isopropylidenedioxy)-7-octen-1-yne (19) and (4*R*,5*R*,6*R*)-4-(Acetyloxy)-5,6-(isopropylidenedioxy)-7-octen-1-yne (20). The crude product from the fragmentation−propargylation of **1** was dried azeotropically with toluene. The residue was dissolved in CH_2Cl_2 and treated with Ac_2O (1.5 equiv), Et_3N (2 equiv) and a catalytic amount of DMAP overnight. The mixture was washed with H_2O, dried and concentrated. The title compounds **19** and **20** were separated by flash chromatography (pentane/Et_2O = 4:1 with 0.5% Et_3N) in a combined yield of 75% starting from **1**.

For **19**. R_f = 0.58 (pentane/Et_2O = 4:1). $[\alpha]_D^{26}$: +36.1 (c 1.25, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.78 (ddd, J = 17.3, 10.4, 7.0 Hz, 1H), 5.37 (ddd, J = 17.3, 1.5, 1.0 Hz, 1H), 5.22 (ddd, J = 10.4, 1.5, 1.0 Hz, 1H), 4.86 (ddd, J = 8.8, 4.8, 4.0 Hz, 1H), 4.67 (ddd, J = 7.0, 6.3, 1.0 Hz, 1H), 4.39 (dd, J = 8.8, 6.3 Hz, 1H), 2.71 (ddd, J = 17.4, 4.0, 2.7 Hz, 1H), 2.61 (ddd, J = 17.4, 4.8, 2.7 Hz, 1H), 2.03 (s, 3H), 1.99 (t, J = 2.7 Hz, 1H), 1.48 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 132.5, 118.1, 108.9, 79.1, 78.3, 76.5, 70.4, 68.9, 27.6, 25.2, 21.1, 20.9. Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.55; H, 7.60.

For **20**. R_f = 0.50 (pentane/Et_2O = 4:1). $[\alpha]_D^{25}$: −42.0 (c 0.93, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.78 (ddd, J = 17.3, 10.1, 7.3 Hz, 1H), 5.37 (dt, J = 17.3, 1.4 Hz, 1H), 5.28 (dt, J = 10.1, 1.4 Hz, 1H), 4.88 (ddd, J = 7.2, 5.6, 4.0 Hz, 1H), 4.66 (bt, J = 7.3 Hz, 1H), 4.43 (dd, J = 6.8, 4.0 Hz, 1H), 2.57 (ddd, J = 16.7, 7.2, 2.8 Hz, 1H), 2.49 (ddd, J = 16.7, 5.6, 2.8 Hz, 1H), 2.06 (s, 3H), 2.00 (t, J = 2.8 Hz, 1H), 1.50 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 133.0, 119.5, 109.5, 79.3,

78.5, 77.5, 71.1, 70.0, 27.2, 25.8, 21.4 (2C). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.30; H, 7.48.

(4*R*,5*R*,6*R*)-4,5,6-Tris(acetyloxy)-7-octen-1-yne (23) and (4*S*,5*R*,6*R*)-4,5,6-Tris(acetyloxy)-7-octen-1-yne (24). The diastereomeric mixture of triethylsilyl-protected enynes **9***β* and **9**α (437 mg, 1.14 mmol, ratio 7:3) was dissolved in anhydrous THF (10 mL). A 1.0 M solution of TBAF in THF (2.5 mL, 2.5 mmol) was added, and the mixture was stirred at room temperature for 30 min. At this point TLC indicated full desilylation of **9***β*/α. Ac_2O (0.43 mL, 4.5 mmol), Et_3N (0.71 mL, 5.1 mmol), and a catalytic amount of DMAP were then added, and the solution was stirred for an additional 2 h at room temperature. The mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried and concentrated, and the residue was purified by flash chromatography (hexane/EtOAc = 4:1) to yield 214 mg (67%) of **23** and 81 mg (25%) of **24**.

For **23**. R_f = 0.48 (hexane/EtOAc = 2:1). $[\alpha]_D^{26}$: +40.9 (*c* 1.01, $CHCl_3$). Mp: 60−61 °C. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 5.77 (ddd, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.57 (dddd, *J* = 5.6, 3.9, 1.4, 1.2 Hz, 1H), 5.38 (dd, *J* = 7.7, 3.9 Hz, 1H), 5.33 (ddd, *J* = 17.2, 1.4, 1.2 Hz, 1H), 5.29 (dt, *J* = 10.4, 1.2 Hz, 1H), 5.17 (ddd, *J* = 7.7, 6.3, 4.8 Hz, 1H), 2.61 (ddd, *J* = 17.3, 4.8, 2.7 Hz, 1H), 2.50 (ddd, *J* = 17.3, 6.3, 2.7 Hz, 1H), 2.12 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H), 2.03 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 169.6 (3C), 131.9, 118.5, 78.4, 72.2, 71.5, 70.8, 68.3, 20.8, 20.7 (2C), 20.6. Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.66; H, 6.34.

For **24**. R_f = 0.39 (hexane/EtOAc = 2:1). $[\alpha]_D^{24}$: +19.3 (*c* 1.73, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 5.75 (ddd, *J* = 16.8, 10.7, 6.4 Hz, 1H), 5.48−5.27 (m, 4H), 5.12 (dt, *J* = 6.1, 4.4 Hz, 1H), 2.50 (dd, *J* = 6.1, 2.8 Hz, 2H), 2.10 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.03 (t, *J* = 2.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 169.7 (2C), 169.5, 131.4, 119.8, 77.8, 72.7, 72.3, 71.3, 69.3, 20.9, 20.8, 20.7, 20.6. Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.69; H, 6.37.

Compound **22** is the enantiomer of **23** and was prepared from **8**α by the same procedure as described for **23**.

(3*S*,4*R*,5*R*)-3-(Acetyloxy)-4,5-(isopropylidenedioxy)-6-hepten-1-yne (27). The diastereomeric mixture of trimethylsilyl protected enynes **15**α and **15***β* was desilylated with TBAF and acetylated with Ac_2O as described above. The title enyne **27** was isolated diastereomerically pure by flash chromatography (pentane/Et_2O = 4:1). R_f = 0.67 (hexane/EtOAc = 2:1). $[\alpha]_D^{22}$: −26.6 (*c* 1.11, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 5.93 (ddd, *J* = 17.2, 10.3, 7.4 Hz, 1H), 5.42 (bd, *J* = 17.2 Hz, 1H), 5.30 (bd, *J* = 10.3 Hz, 1H), 5.30 (dd, *J* = 5.2, 2.2 Hz, 1H), 4.72 (dd, *J* = 7.4, 6.4 Hz, 1H), 4.33 (dd, *J* = 6.4, 5.2 Hz, 1H), 2.50 (dd, *J* = 2.2, 0.5 Hz, 1H), 2.08 (d, *J* = 0.4 Hz, 3H), 1.56 (bs, 3H), 1.41 (bs, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 169.0, 131.8, 119.3, 109.5, 78.7, 78.3, 78.0, 75.0, 63.0, 27.1, 25.0, 20.7. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 63.83; H, 7.36.

General Procedure for Enyne Metathesis (Table 2). The enyne (0.3 mmol, dried azeotropically with toluene) was dissolved in CH_2Cl_2 (6 mL), and ethylene gas was passed through the solution for 20 min. Ruthenium catalyst **B** (or catalyst **A**) 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 until TLC revealed full conversion or that the reaction had stopped (3−24 h). Silica gel was then added and the solvent removed in vacuo. The cyclized product was obtained after flash chromatography.

(3*R*,4*R*,5*S*)-3,4-(Isopropylidenedioxy)-5-[(*tert*-butyldimethylsilyl)oxy]-1-vinylcyclohexene (17). R_f = 0.39 (pentane/Et_2O = 95:5). $[\alpha]_D^{26}$: +17.5 (*c* 1.20, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 6.31 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.48 (m, 1H), 5.23 (d, *J* = 17.5 Hz, 1H), 5.07 (d, *J* = 10.8 Hz, 1H), 4.63 (m, 1H), 4.29 (m, 1H), 3.86 (ddd, *J* = 9.7, 6.2, 2.1 Hz, 1H), 2.38 (dt, *J* = 15.6, 2.1 Hz, 1H), 2.29 (dd, *J* = 15.6, 5.9 Hz, 1H), 1.35 (s, 3H), 1.31 (s, 3H), 0.95 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 138.5, 135.9, 126.4, 114.1, 110.0, 76.9, 74.8, 69.3, 28.1, 27.8, 27.1, 26.2, 18.7, −4.1, −4.3. Anal. Calcd for $C_{17}H_{30}O_3Si$: C, 65.76; H, 9.74. Found: C, 65.85; H, 10.00.

(3*R*,4*R*,5*S*)-5-(Acetyloxy)-3,4-(isopropylidenedioxy)-1-vinylcyclohexene (28). R_f = 0.40 (pentane/Et_2O = 4:1). $[\alpha]_D^{23}$: +25.7 (*c* 1.59, $CHCl_3$). Mp: 111−113 °C. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 6.34 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.62 (m, 1H), 5.24 (d, *J* = 17.5 Hz, 1H), 5.12 (d, *J* = 10.8 Hz, 1H), 5.10 (ddd, *J* = 10.5, 5.8, 5.3 Hz, 1H), 4.75 (m, 1H), 4.43 (bdd, *J* = 5.4, 5.3 Hz, 1H), 2.51 (dd, *J* = 15.5, 5.8 Hz, 1H), 2.40 (ddt, *J* = 15.5, 10.5, 2.2 Hz, 1H), 2.15 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 170.5, 137.6, 134.8, 125.9, 114.4, 110.2, 74.2, 73.9, 69.6, 27.6, 26.8, 23.7, 21.2. Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.47; H, 7.62.

(3*R*,4*R*,5*R*)-5-(Acetyloxy)-3,4-(isopropylidenedioxy)-1-vinylcyclohexene (29). R_f = 0.41 (pentane/Et_2O = 4:1). $[\alpha]_D^{22}$:−14.0 (*c* 0.56, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 6.38 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.80 (m, 1H), 5.23 (d, *J* = 17.5 Hz, 1H), 5.14 (d, *J* = 10.8 Hz, 1H), 5.10 (dt, *J* = 8.2, 5.0 Hz, 1H), 4.71 (m, 1H), 4.18 (dd, *J* = 8.2, 6.2 Hz, 1H), 2.68 (dd, *J* = 16.6, 5.0 Hz, 1H), 2.11 (m, 1H), 2.09 (s, 3H), 1.46 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 170.4, 137.5, 136.8, 123.8, 115.0, 109.5, 75.2, 72.7, 70.9, 27.9, 26.9, 26.0, 21.2. EI (positive mode) *m*/*z* calcd for $C_{12}H_{15}O_4$ ($(M - CH_3)^+$) 223.0970. Found 223.0976.

(3*R*,4*R*,5*R*)-3,4-(Isopropylidenedioxy)-5-[(*tert*-butyldimethylsilyl)oxy]-1-vinylcyclohexene (30). R_f = 0.38 (pentane/Et_2O = 95:5). $[\alpha]_D^{22}$: −17.7 (*c* 0.55, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 6.38 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.74 (m, 1H), 5.24 (d, *J* = 17.3 Hz, 1H), 5.10 (d, *J* = 10.7 Hz, 1H), 4.70 (m, 1H), 4.01 (t, *J* = 6.6 Hz, 1H), 3.94 (dt, *J* = 7.4, 4.5 Hz, 1H), 2.43 (dd, *J* = 16.7, 4.5 Hz, 1H), 2.09 (dd, *J* = 16.7, 7.4 Hz, 1H), 1.42 (s, 3H), 1.38 (s, 3H), 0.89 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 138.3, 136.7, 124.3, 114.1, 108.8, 78.3, 73.1, 69.6, 30.1, 28.1, 26.1, 25.8, 18.0, −4.5, −4.8.

(3*S*,4*S*,5*S*)-3,4,5-Tris(acetyloxy)-1-vinylcyclohexene (31). R_f = 0.40 (pentane/Et_2O = 2:1). $[\alpha]_D^{23}$: +181.9 (*c* 1.59, $CHCl_3$). Mp: 72−74 °C. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 6.36 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.65 (m, 1H), 5.56 (m, 1H), 5.43 (ddd, *J* = 5.3, 5.2, 2.4 Hz, 1H), 5.23 (dd, *J* = 17.5, 0.5 Hz, 1H), 5.18−5.13 (m, 2H), 2.62 (m, 1H), 2.46 (bdd, *J* = 17.7, 5.6 Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 170.3, 170.2, 170.1, 137.2, 136.3, 123.5, 115.0, 70.8, 69.5, 68.0, 27.7, 21.0 (2C), 20.8. Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.52; H, 6.37.

Compound **32** is the enantiomer of **31**.

(3*R*,4*R*,5*S*)-3,4,5-Tris(acetyloxy)-1-vinylcyclohexene (33). R_f = 0.37 (pentane/Et_2O = 4:1). $[\alpha]_D^{23}$: −62.0 (*c* 1.32, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 6.34 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.62−5.53 (m, 2H), 5.31 (dd, *J* = 10.6, 7.3 Hz, 1H), 5.22 (bd, *J* = 17.5 Hz, 1H), 5.17 (bd, *J* = 10.9 Hz, 1H), 5.15 (ddd, *J* = 10.6, 10.3, 5.8 Hz, 1H), 2.85 (dd, *J* = 16.8, 5.8 Hz, 1H), 2.29 (ddd, *J* = 16.8, 10.3, 2.4 Hz, 1H), 2.06 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 170.3, 170.0 (2C), 136.6, 135.6, 124.3, 115.4, 72.3, 72.0, 68.9, 29.0, 20.9, 20.8, 20.7. Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.10; H, 6.28.

(3*R*,4*S*,5*S*)-5-(*N*-Acetyl-*N*-benzylamino)-3,4-(isopropylidenedioxy)-1-vinylcyclohexene (34). NMR shows the product as a 9:1 mixture of rotamers. NMR data are given for the major rotamer. R_f = 0.52 (hexane/EtOAc = 1:1). $[\alpha]_D^{27}$: −11.7 (*c* 0.58, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.40−7.20 (m, 5H), 6.30 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.50 (bs, 1H), 5.19−4.97 (m, 3H), 4.83 (bs, 2H), 4.70 (m, 1H), 4.28 (bd, *J* = 4.9 Hz, 1H), 2.29−2.22 (m, 2H), 2.12 (s, 3H), 1.26 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 170.5, 138.8, 138.0, 135.9, 128.5, 126.8, 126.0, 125.5, 113.6, 109.6, 75.0, 74.8, 49.9, 48.7, 27.8, 26.4, 22.5, 22.1. Anal. Calcd for $C_{20}H_{25}NO_3$: C, 73.37; H, 7.70; N, 4.28. Found: C, 72.84; H, 7.61; N, 4.15.

(3*R*,4*S*,5*S*)-5-[*N*-Benzyl-*N*-(trifluoroacetyl)amino]-3,4-(isopropylidenedioxy)-1-vinylcyclohexene (35). NMR shows the product as an almost equal mixture of rotamers. R_f = 0.77 (hexane/EtOAc = 3:1). $[\alpha]_D^{24}$: −25.8 (*c* 1.23, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.44−7.19 (m, 10H), 6.40−6.24 (m, 2H), 5.59−5.50 (m, 2H), 5.16−4.88 (m, 8H), 4.75 (m, 2H), 4.39 (bd, *J* = 4.7 Hz, 2H), 4.35−4.24 (m, 2H), 2.66−2.53 (m, 2H), 2.30−2.18 (m, 2H), 1.36 (s, 3H), 1.30 (s, 3H), 1.26 (s, 3H),

1.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.4 (q, J = 34.1 Hz), 157.5 (q, J = 33.3 Hz), 137.6 (2C), 137.4, 137.3, 135.6, 135.4, 128.3 (2C), 127.2, 127.0, 126.8 (2C), 125.8 (2C), 116.7 (q, J = 286.6 Hz), 116.5 (q, J = 292.4 Hz), 114.4, 114.0, 110.5, 110.0, 75.5, 74.9, 74.7, 73.6, 54.7, 53.3, 48.2, 47.9, 27.7 (2C), 26.6, 26.4, 24.1, 22.3. Anal. Calcd for $C_{20}H_{22}F_3NO_3$: C, 62.98; H, 5.81; N, 3.67. Found: C, 63.30; H, 5.35; N, 3.66.

(3*R*,4*R*,5*S*)-5-(Acetyloxy)-3,4-(isopropylidenedioxy)-1-vinylcyclopentene (36). R_f = 0.67 (hexane/EtOAc = 2:1). $[\alpha]_D^{22}$: −175.7 (*c* 1.17, $CHCl_3$). Mp: 62−63 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.41 (dd, J = 17.6, 11.0 Hz, 1H), 5.99 (m, 1H), 5.54 (d, J = 17.6 Hz, 1H), 5.28 (d, J = 11.0 Hz, 1H), 5.04 (dd, J = 6.0, 2.3 Hz, 1H), 4.91 (dd, J = 6.0, 5.8 Hz, 1H), 2.11 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 142.6, 131.2, 130.3, 118.6, 112.9, 82.1, 76.9, 74.0, 27.1, 26.4, 20.7. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.33; H, 7.31.

(5*S*,6*R*,7*R*,8*R*,9*S*)-5-Formyl-7,8-(isopropylidenedioxy)-9-[(*tert*-butyldimethylsilyl)oxy]bicyclo[4.4.0]dec-1-ene (37). A solution of diene **17** (50 mg, 0.16 mmol) in acrolein (5 mL) was heated to 60 °C in a sealed pressure tube for 24 h. At this point, TLC showed almost complete consumption of **17** and the formation of one major product and a few minor products. The mixture was concentrated and the residue purified by flash chromatography (hexane/EtOAc = 9:1) to afford 41 mg (69%) of **37**. R_f = 0.50 (hexane/EtOAc = 4:1). $[\alpha]_D^{22}$: −71.1 (*c* 1.01, $CHCl_3$). Mp: 55−56 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.89 (bs, 1H), 5.59 (m, 1H, H-2), 4.18 (dd, J = 5.4, 4.4 Hz, 1H, H-8), 3.87 (dd, J = 9.4, 5.4 Hz, 1H, H-7), 3.80 (ddd, J = 10.5, 5.1, 4.0 Hz, 1H, H-9), 2.85 (m, 1H, H-6), 2.68 (m, 1H, H-5), 2.46 (dt, J = 12.2, 1.4 Hz, 1H, H-10), 2.22 (dd, J = 12.2, 5.1 Hz, 1H, H-10′), 2.10−1.94 (m, 2H), 1.85 (m, 1H), 1.52 (m, 1H), 1.55 (s, 3H), 1.30 (s, 3H), 0.90 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.4, 132.0, 124.1, 109.2, 77.4, 75.4, 70.8, 49.4, 40.9, 38.9, 28.3, 25.9 (4C), 24.1, 18.3, 17.8, −4.6, −4.7. Anal. Calcd for $C_{20}H_{34}O_4Si$: C, 65.53; H, 9.35. Found: C, 65.48; H, 9.52.

(5*S*,6*R*,7*R*,8*R*,9*S*)-9-(Acetyloxy)-5-formyl-7,8-(isopropylidenedioxy)bicyclo[4.4.0]dec-1-ene (38). Prepared from **28** using the same procedure as described above. R_f = 0.50 (hexane/EtOAc = 2:1). $[\alpha]_D^{22}$: −100.8 (*c* 0.61, $CHCl_3$). Mp: 121−123 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.88 (d, J = 1.5 Hz, 1H), 5.68 (bdd, J = 5.0, 0.5 Hz, 1H, H-2), 4.92 (ddd, J = 10.5, 5.5, 3.9 Hz, 1H, H-9), 4.32 (m, 1H, H-8), 3.97 (dd, J = 9.3, 4.9 Hz, 1H, H-7), 2.83 (m, 1H, H-6), 2.68 (dddd, J = 12.1, 5.4, 2.9, 1.5 Hz, 1H, H-5), 2.47 (m, 1H, H-10), 2.38 (dd, J = 12.3, 5.5 Hz, 1H, H-10′), 2.11 (s, 3H), 2.10−1.94 (m, 2H), 1.92 (m, 1H), 1.55 (s, 3H), 1.53 (m, 1H), 1.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.1, 170.2, 130.3, 125.7, 109.8, 75.6, 74.6, 70.7, 49.4, 40.9, 35.0, 28.2, 26.1, 24.2, 21.2, 17.6. Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.33; H, 7.53.

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