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Stereochemistry of Pd^{II}-Catalyzed THF Ring Formation of ε-Hydroxy Allylic Alcohols and Synthesis of 2,3,5-Trisubstituted and 2,3,4,5-Tetrasubstituted Tetrahydrofurans

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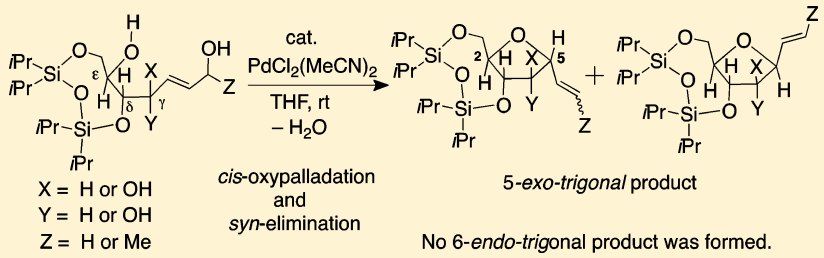
Supporting Information



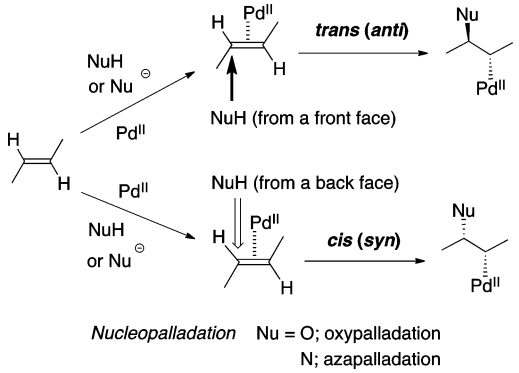
ABSTRACT: Pd^{II}-catalyzed ring formation of 2,3,5-trisubstituted and 2,3,4,5-tetrasubstituted tetrahydrofurans is described. Oxypalladation of a chiral ε-hydroxy allylic alcohol provides a 5-alkenyltetrahydrofuran ring in excellent yields via a 5-*exo*-*trigonal* process. Nine substrates including six secondary allylic alcohols and three primary allylic alcohols with or without an additional secondary hydroxy substituent at the γ-position have been examined. Their structures are restricted by a 2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocane ring. The stereochemistry of the resulting tetrahydrofuran products was determined by chemical transformation. The reaction mechanism is discussed on the basis of the stereochemical results. The steps in the chiral allylic alcohol directed or the nucleophilic alcohol directed facial selection for the formation of the alkene–Pd^{II}–π-complex, the *cis*-oxypalladation, and a *syn*-elimination mechanism account for the observed stereochemistry of the reaction.

INTRODUCTION

Oxypalladation is an addition reaction of an oxygen functional group to an alkene promoted by a Pd^{II}-catalyst. The process has been utilized as a fundamental step in a variety of synthetically useful O–C bond formations. Numerous Pd^{II}-catalyzed oxygenetive transformation reactions have been used in organic synthesis.[1] In particular, the intramolecular oxypalladation reaction is important for the formation of oxygen rings.[2] With respect to the synthesis of chiral oxygen heterocycles, the stereochemistry of oxypalladation becomes more important in enantioselective and diastereoselective oxygen ring formation.[3] Many arguments related to the mechanism for the oxypalladation and aminopalladation have been proposed in the long history of the nucleopalladation reaction. Both *cis*- and *tran*-additions have been proposed for inter- and intramolecular nucleopalladation reactions (Scheme 1).[4]

The process of the reaction involves three steps: (i) coordination of an alkene to the Pd^{II} catalyst to form an alkene–Pd^{II}–π complex; (ii) oxypalladation to form the alkyl–Pd^{II}–σ complex with a new O–C bond formation; and (iii) reductive elimination to produce an alkene product with the formation of a Pd^{0} species which is oxidized to regenerate the Pd^{II} catalyst. The reaction mechanism has been discussed in terms of the results conducted under various reaction conditions with different Pd^{II} catalysts, solvents, temperatures, and oxidants. When an allylic alcohol is used as a substrate, this reaction becomes simpler. The dehydration reaction can proceed in the presence of a $PdCl_2(MeCN)_2$ catalyst at room temperature in THF without an oxidant because the catalytic cycle works without the formation of Pd^{0} species under these mild conditions. We have studied the reaction of various allylic alcohol substrates and their stereochemistry.[5] For example, as shown in Scheme 2, the Pd^{II}-catalyzed reaction of ε-hydroxy allylic alcohol (**1**) gave a chiral 2,5-substituted THF product

Scheme 1. Nucleopalladation to Alkene



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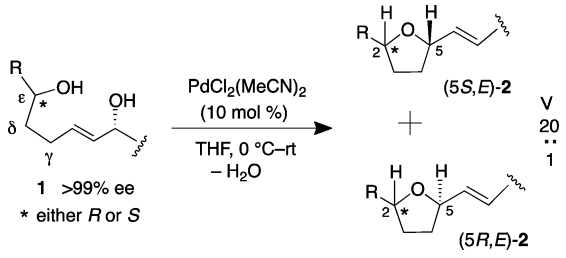
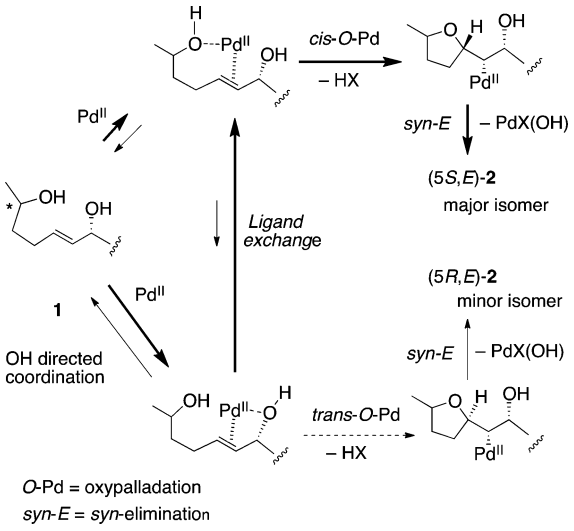
Scheme 2. Intramolecular Oxypalladation to Allylic Alcohol



bearing an alkenyl group at the 5-position in excellent yield with high diastereoselectivity (>20:1).[6]

We have proposed a reaction mechanism (Scheme 3) that involves the chiral allylic alcohol-directed formation[7] of the

Scheme 3. Proposed Mechanism of the Intramolecular Oxypalladation to Allylic Alcohol

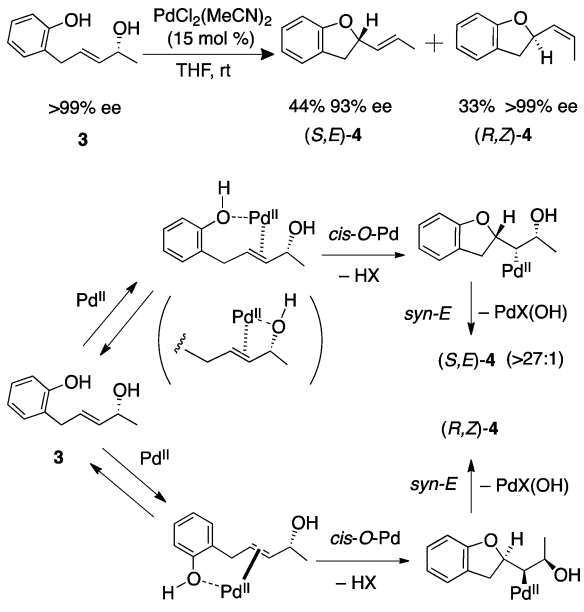


alkene–Pd^{II}–π complex followed by ligand exchange to form another alkene–Pd^{II}–π complex, which then undergoes *cis*-oxypalladation leading to the alkyl–Pd^{II}–σ complex. Dissociation of the Pd^{II} species furnished the major stereoisomer predominantly. The original chiral allylic hydroxy center was transmitted to the newly generated chiral center at the C-5 carbon. On the other hand, the minor stereoisomer may be produced from the initial alkene–Pd^{II}–π complex via a *trans*-oxypalladation pathway.

In contrast, the reaction of the phenol substrate **3** displayed quite different stereochemical results (Scheme 4).[8] The reaction afforded (*S*,*E*)-**4** as a major isomer in 44% yield with 93% ee through the same pathway as described in Scheme 3, while another isomer (*R*,*Z*)-**4** was produced in 33% yield with 99% ee. The latter product had an opposite stereocenter with a (*Z*)-alkene. The phenol-directed opposite face recognition of the alkene–π face, *cis*-oxypalladation, and *syn*-elimination occurred.

Quite different stereochemical results were observed in 5-*exo*-*trigonal* cyclization for the two types of substrates, termed types A and B (Figure 1). Type A had saturated carbons from the γ- to ε-positions, and type B had two sp^2-hybridized atoms at the δ- and ε-positions. We were interested in substrates like type C (Figure 1). Configurational restriction in type C substrates by a ring might influence the stereochemical course of the

Scheme 4. Synthesis of Dihydrobenzofuran by Intramolecular Oxypalladation



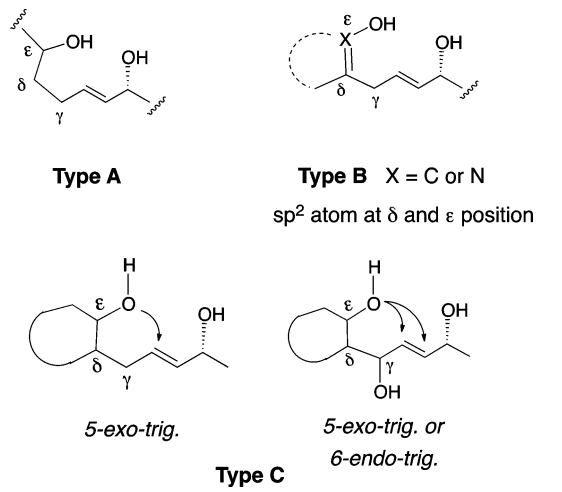


Figure 1. Types of substrates in oxypalladation of ε-hydroxy allylic alcohol.

cyclization reaction. Furthermore, if an additional hydroxy group is placed at the γ-position, either 5-*exo*-*trigonal* cyclization leading to 2,3,4,5-tetrasubstituted tetrahydrofuran or 6-*endo*-*trigonal* cyclization leading to 2,3,6-trisubstituted 3,6-dihydro-2*H*-pyran would be expected.[9] Both the tetrahydrofuran and 3,6-dihydro-2*H*-pyran are important moieties in biologically active natural products[10,11] and *C*-nucleosides.[12] Based on this idea, we report here an intramolecular oxypalladation reaction of nine substrates **5** to **13** (Figure 2) and describe the stereochemistry of the products.

RESULTS AND DISCUSSION

Preparation of Precursors 5 to 13 for Cyclization. We started the synthesis of these ε-hydroxy allylic alcohols from commercial D-pentose. Two hydroxy groups of D-2-deoxyribose, D-arabinose, and D-ribose were protected with cyclic bis-silyl ethers to give **14**, **15**, and **16** by the reported procedure.[13] Wittig reaction of **14**, **15**, and **16** with methyl (triphenylphosphoranylidene)acetate gave α,β-unsaturated esters **17**, **18**,

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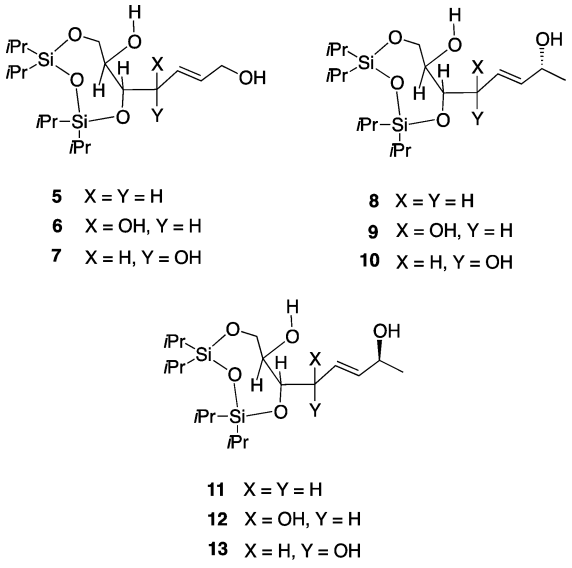
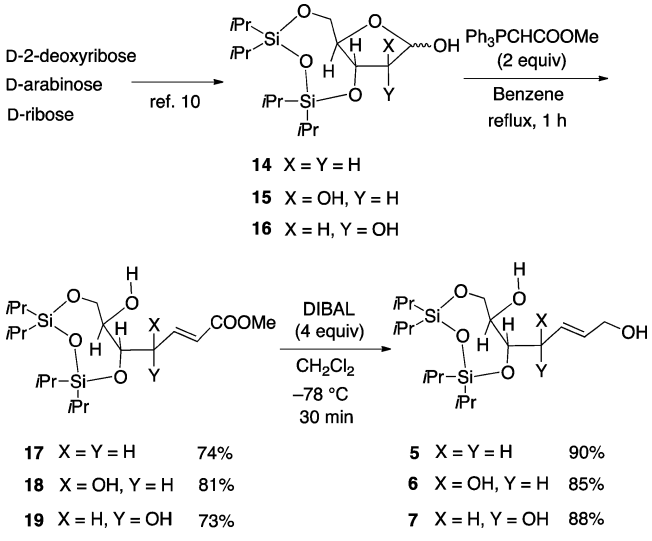


Figure 2. Substrates for oxypalladation.

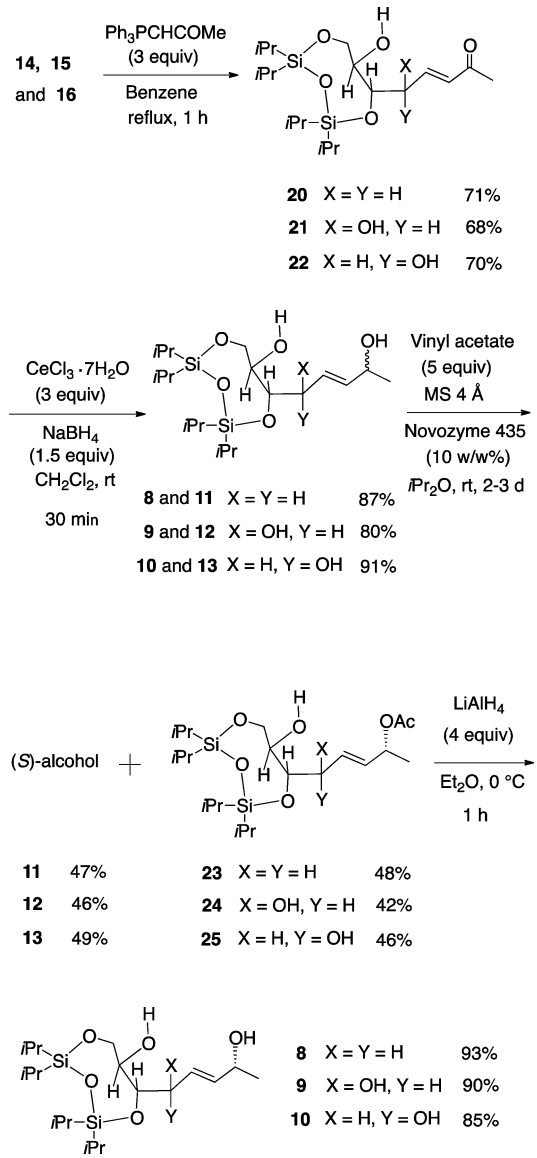
and **19** in 74%, 81%, and 73% yields, respectively. These esters were reduced with DIBAL-H in CH_2Cl_2 to give allylic alcohols **5**, **6**, and **7** in 90%, 85%, and 88% yields, respectively (Scheme 5).

Scheme 5. Preparation of Precursors 5−7 for Cyclization



For the synthesis of compounds **8**−**13**, a diastereomeric pair of three allylic alcohols was prepared (Scheme 6). The first step was a Wittig reaction of **14**, **15**, and **16** with (triphenylphosphoranylidene)acetone which gave α,β-unsaturated ketones **20**, **21**, and **22** in 71%, 68%, and 70% yields, respectively. The resulting methyl ketones were reduced by $NaBH_4$ in the presence of $CeCl_3{\cdot}7H_2O$ to give a diastereomeric mixture of the secondary alcohols **8** and **11**, **9** and **12**, and **10** and **13**, in 87%, 80%, and 91% yields, respectively. These diastereomeric alcohols were differentiated by kinetic acetylation catalyzed with *Cal*-B (*Candida antartica* lipase B; Novozyme 435). A mixture of alcohols **8** and **11** was treated with vinyl acetate in the presence of *Cal*-B for 3 days to provide the (*R*)-acetate **23** in 48% yield along with recovery of the (*S*)-alcohol **11** in 47% yield. Diastereomeric purities of both compounds were over

Scheme 6. Preparation of Precursors 8−13 for Cyclization



>98%. (*R*)-Alcohol **8** was obtained in 91% yield by the reduction of **23** with $LiAlH_4$. The same two steps afforded the diastereomeric alcohols **9** and **12** and **10** and **13** effectively with satisfactory yields and purities in the same manner described for the case of **8** and **11**.

Pd^{II}-Catalyzed Cyclization. First, we examined the cyclization of primary allylic alcohol **5**. The reaction of **5** with 10 mol % of $PdCl_2(CH_3CN)_2$ in THF at rt gave a mixture of the 5-vinyl-substituted THF products 2,5-*trans*-**26** and 2,5-*cis*-**26** in 89% yield (Scheme 7 and Table 1, entry 1). Although the products were not separable, the ratio was determined to be approximately 3:1 by the proton NMR spectrum. We examined other reaction conditions using other Pd^{II} catalysts, solvents, and additives, which are summarized in Table 1. The reaction was completed after 2 h at 0 °C and in less than 1 min at 60 °C (entries 2 and 3). However, the chemical yields decreased a little, and while the selectivity did not change much at 0 °C it decreased at 60 °C. When 1 mol % of Pd^{II} catalyst was employed, the reaction took 3 h (entry 4). No influence was observed when acetic acid was added to the reaction (entry 5). On the other hand, when triethylamine or its hydrochloride was

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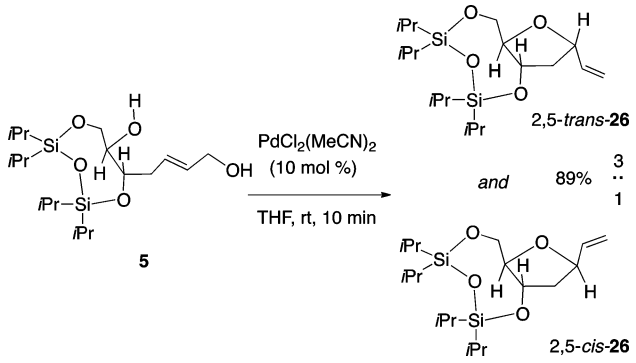
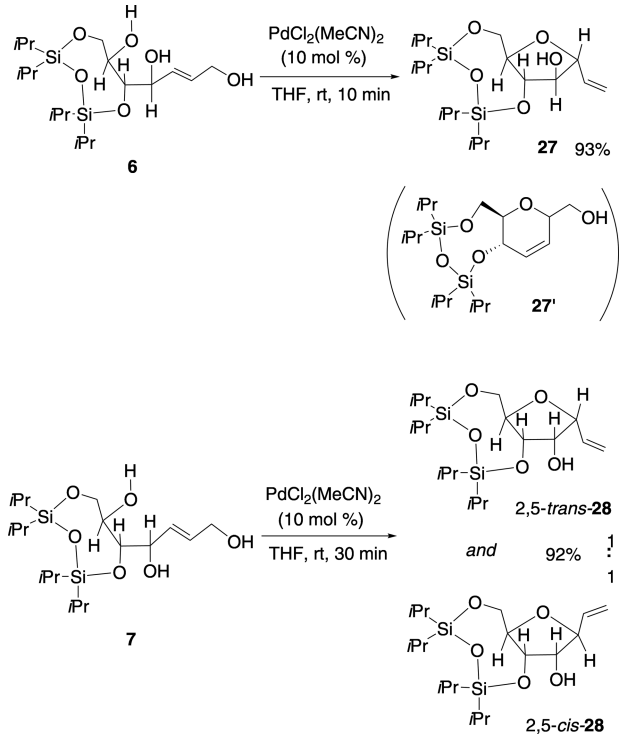
Scheme 7. Pd^{II}-Catalyzed Cyclization of 5



Scheme 8. Pd^{II}-Catalyzed Cyclization of 6 and 7



used as an additive, no reaction occurred (entries 6 and 7). $PdCl_2$ also catalyzed the reaction (entry 8). Other Pd^{II} catalysts such as $Pd(OAc)_2$ or $PdCl_2(PPh_3)_2$ were not effective at all (entries 9 and 10). The use of $Pd(OCOCF_3)_2$ provided the cyclized product in 31% yield with a 2:1 ratio of isomers (entry 11). Methylene chloride and toluene could be used as a solvent (entries 12 and 13); however, their chemical yields and selectivities were lower than those in THF. Polar solvents such as methanol or acetonitrile gave the product with poor yield and selectivity (entries 14 and 15). In summary, $PdCl_2(CH_3CN)_2$ was found to be an appropriate catalyst for the reaction, and THF was the best solvent for this reaction.

The reaction of γ-(*R*)-hydroxy allylic alcohol **6** under the optimum reaction conditions for **5** afforded a single stereoisomer **27** in 93% yield (Scheme 8). Neither the 2,5-*cis* stereoisomer nor the 3,6-dihydro-2*H*-pyran **27′** was produced in this reaction. The cyclization of **7** gave a mixture of 2,5-*trans*-**28** and 2,5-*cis*-**28** in 92% yield with a ratio of 1:1. In the cases of **6** and **7**, the cyclization proceeded in a 5-*exo*-*trigonal* fashion but not in a 6-*endo*-*trigonal* fashion.

Next, we examined secondary allylic alcohols. The reaction of (*R*)-allylic alcohols **8**, **9**, and **10** gave the single 2,5-*trans* stereoisomers **29**, **30**, and **31** in 97, 95, and 95% yields, respectively (Scheme 9). With or without the γ-hydroxyl group, the 2,5-*trans* products bearing the (*E*)-1-propenyl substituent group were obtained. Each chemical yield was excellent: over 95% with an exclusive diastereoselectivity.

In contrast to the results for (*R*)-allylic alcohols, cyclization of (*S*)-allylic alcohols was not simple (Scheme 10). The reaction of **11** gave a mixture of 2,5-*trans*-**32** with the (*Z*)-propenyl substituent and 2,5-*cis*-**33** with the (*E*)-propenyl substituent in 91% combined yield with a ratio of 1:5. The formation of the (*Z*)-alkene was also found in the reaction of **12**. An approximately 1:1 mixture of 2,5-*trans*-**34** with the (*Z*)-propenyl substituent and 2,5-*cis*-**35** with the (*E*)-propenyl substitutent was formed in a combined 93% yield from **12**. However, the reaction of diastereoisomer **13** afforded a single stereoisomer **36** in 95% yield.

In all cases, no dihydropyran via 6-*endo*-*trigonal* cyclization was detected. The stereochemistries of these cyclized products were determined by their transformation to appropriate derivatives.

Table 1. Pd^{II}-Catalyzed Cyclization of 5

entry	Pd catalyst (mol %)		additive	solvent	temp (°C)	time	yield[a] (%)	2,5-*trans*:2,5-*cis*[b]
1	$PdCl_2(MeCN)_2$	10		THF	rt	10 min	89	77:23
2	$PdCl_2(MeCN)_2$	10		THF	0	2 h	84	79:21
3	$PdCl_2(MeCN)_2$	10		THF	60	<1 min	84	69:31
4	$PdCl_2(MeCN)_2$	1		THF	rt	3 h	87	79:21
5	$PdCl_2(MeCN)_2$	10	AcOH[c]	THF	rt	2.5 h	85	78:22
6	$PdCl_2(MeCN)_2$	10	Et_3N[d]	THF	rt	3 d	0	
7	$PdCl_2(MeCN)_2$	10	Et_3NHCl[d]	THF	rt	3 d	0	
8	$PdCl_2$	10		THF	rt	15 min	87	72:29
9	$Pd(OAc)_2$	10		THF	rt	1 d	0	
10	$PdCl_2(PPh_3)_2$	10		THF	rt	1 d	0	
11	$Pd(OCOCF_3)_2$	10		THF	rt	2 h	31	67:33
12	$PdCl_2(MeCN)_2$	10		CH_2Cl_2	rt	10 min	76	67:33
13	$PdCl_2(MeCN)_2$	10		toluene	rt	20 min	78	71:29
14	$PdCl_2(MeCN)_2$	10		MeOH	rt	15 h	54	43:57
15	$PdCl_2(MeCN)_2$	10		CH_3CN	rt	2 h	41	60:40

[a]Isolated yield. [b]Ratio was calculated by the integration value of the ^1H NMR spectrum; see the Experimental Section. [c]3 equiv. [d]1 equiv.

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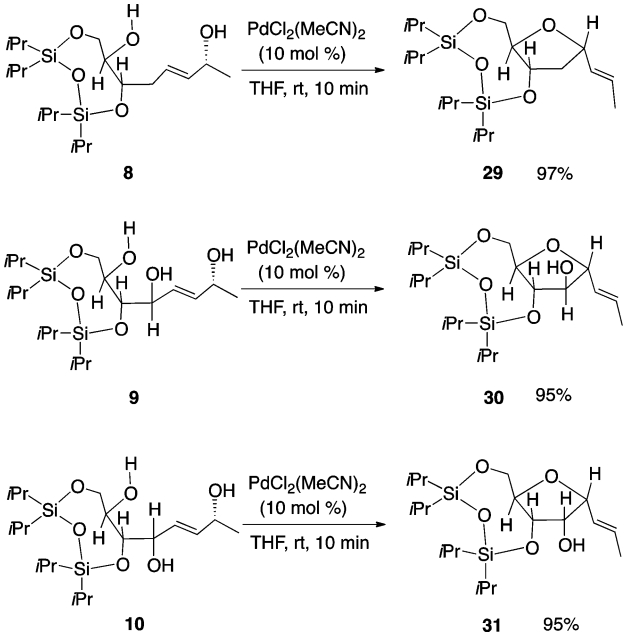
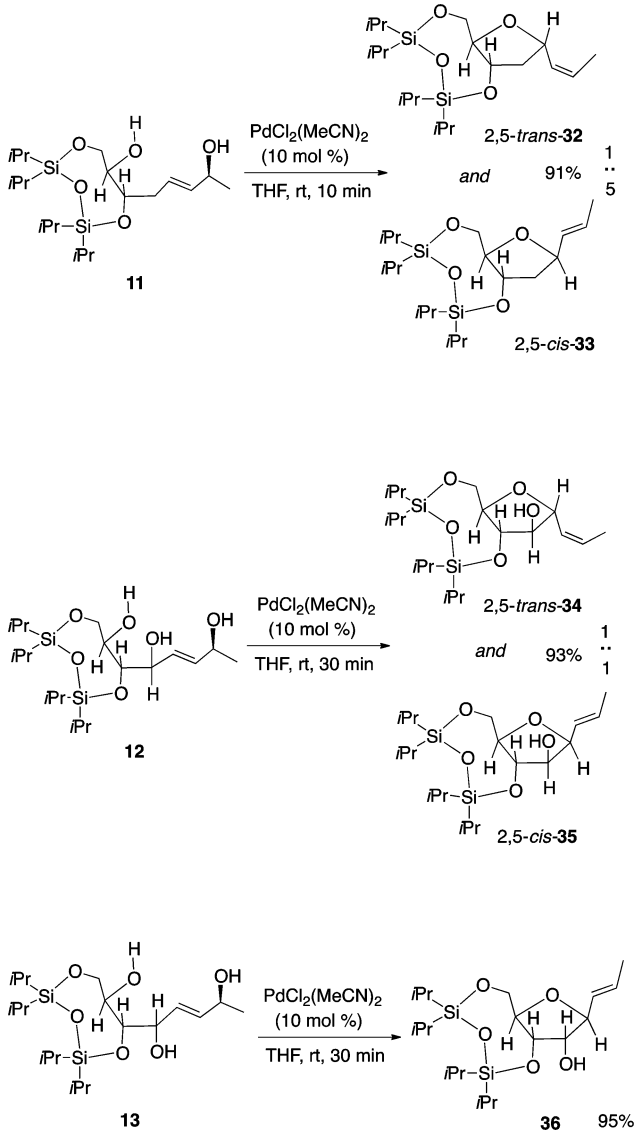
Scheme 9. Pd^{II}-Catalyzed Cyclization of Secondary (*R*)-Allylic Alcohols 8−10



Scheme 10. Pd^{II}-Catalyzed Cyclization of Secondary (*S*)-Allylic Alcohols 11−13



Determination of the Stereochemistry. The stereochemistries of 2,5-*trans*-**26** and 2,5-*cis*-**26** were determined by leading to the known compounds 2,5-*trans*-**39** and 2,5-*cis*-**39** (Scheme 11).[14] The cyclic bis-silyl ether of **26** was replaced with a *p*-toluoyl ester by desilylation with TBAF and acylation of the resulting diol **37** with toluoyl chloride. A mixture of 2,5-*trans*-**38** and 2,5-*cis*-**38** was obtained in 79% yield in two steps. Ozonolytic cleavage of the isomers followed by $NaBH_4$ reduction gave 2,5-*trans*-**39** and 2,5-*cis*-**39** in 90% yield. They were separable by HPLC with a ratio of 74:26. The minor isomer was identified as 2,5-*cis*-**39** and the major isomer as 2,5-*trans*-**39**. In the same manner, product **29** led to 2,5-*trans*-**39** in 71% overall yields in four steps via compounds **40** and **41**. This transformation showed that compound **29** was a 2,5-*trans* isomer. Similarly, the stereochemistries of 2,5-*trans*-**32** and 2,5-*cis*-**33** were confirmed by the same four steps. The major isomer and minor isomer were identified to be 2,5-*cis*-**33** and 2,5-*trans*-**32** by the transformation to 2,5-*cis*-**39** via the intermediates 2,5-*cis*-**43** and 2,5-*cis*-**45** and 2,5-*trans*-**39** via the intermediates 2,5-*trans*-**42** and 2,5-*trans*-**44**, respectively.

The stereochemistry of **27** was determined in two steps (Scheme 12). Ozonolysis of **27** and successive $NaBH_4$ reduction gave diol **46** in 89% yield. The resulting diol was transformed to the cyclic bis-silyl ether with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane to give **47** in 80% yield, for which ^1H and ^{13}C NMR spectra showed a simple pattern of the spectrum due to the molecular symmetry. On the basis of this result, the structure of **27** with *trans* 2,5-substituents was determined. Similarly, compound **30** was transformed to 2,5-*trans*-**46** in 91% yield, and it was assigned to be the 2,5-*trans*-substituted structure. Ozonolysis of a mixture of 2,5-*trans*-**34** and 2,5-*cis*-**35** followed by successive reduction with $NaBH_4$ afforded 2,5-*trans*-**46** in 38% yield and another isomer in 36% yield, which was identified to be 2,5-*cis*-**46**.

Because a diastereomeric mixture of **28** was not separable, their secondary hydroxy groups were acylated as a benzoate (Scheme 13). The resulting benzoates were separable by HPLC to give less polar isomer 2,5-*cis*-**48** in 44% yield and polar isomer 2,5-*trans*-**48** in 40% yield. The less polar isomer was subjected to ozonolysis followed by the reduction with $LiBH_4$ to give alcohol 2,5-*cis*-**49** in 80% yield. Removal of the silyl group and the resulting tetraol was acetylated with acetic anhydride to give tetraacetate 2,5-*cis*-**50**[15] in 86% yield, whose symmetrical structure in the ^1H NMR spectrum confirmed a *cis* relation of the 2,5-substituents. On the other hand, the polar isomer led to the corresponding tetraacetate 2,5-*trans*-**50**[16] in the same steps via 2,5-*trans*-**49**, in which the ^1H NMR spectrum showed four acetoxy groups due to the unsymmetrical structure. These results suggest that the stereochemistry of the less polar product must be the 2,5-*cis* isomer and polar product the 2,5-*trans* isomer. The stereochemistries of compounds **31** and **36** were determined to be 2,5-*trans* and 2,5-*cis* in two steps. Ozonolysis of **31** and **36** followed by the reduction with $NaBH_4$ afforded 2,5-*trans*-**49** and 2,5-*cis*-**49** in 80% and 70% yields, respectively.

Structures of all of the cyclized products were assigned. Depending on the stereochemistry of the chiral allylic alcohol, 2,5-*trans*- or 2,5-*cis*-5-alkenyltetrahydrofurans were synthesized. In particular, 2,5-*trans* THF derivatives could be formed from

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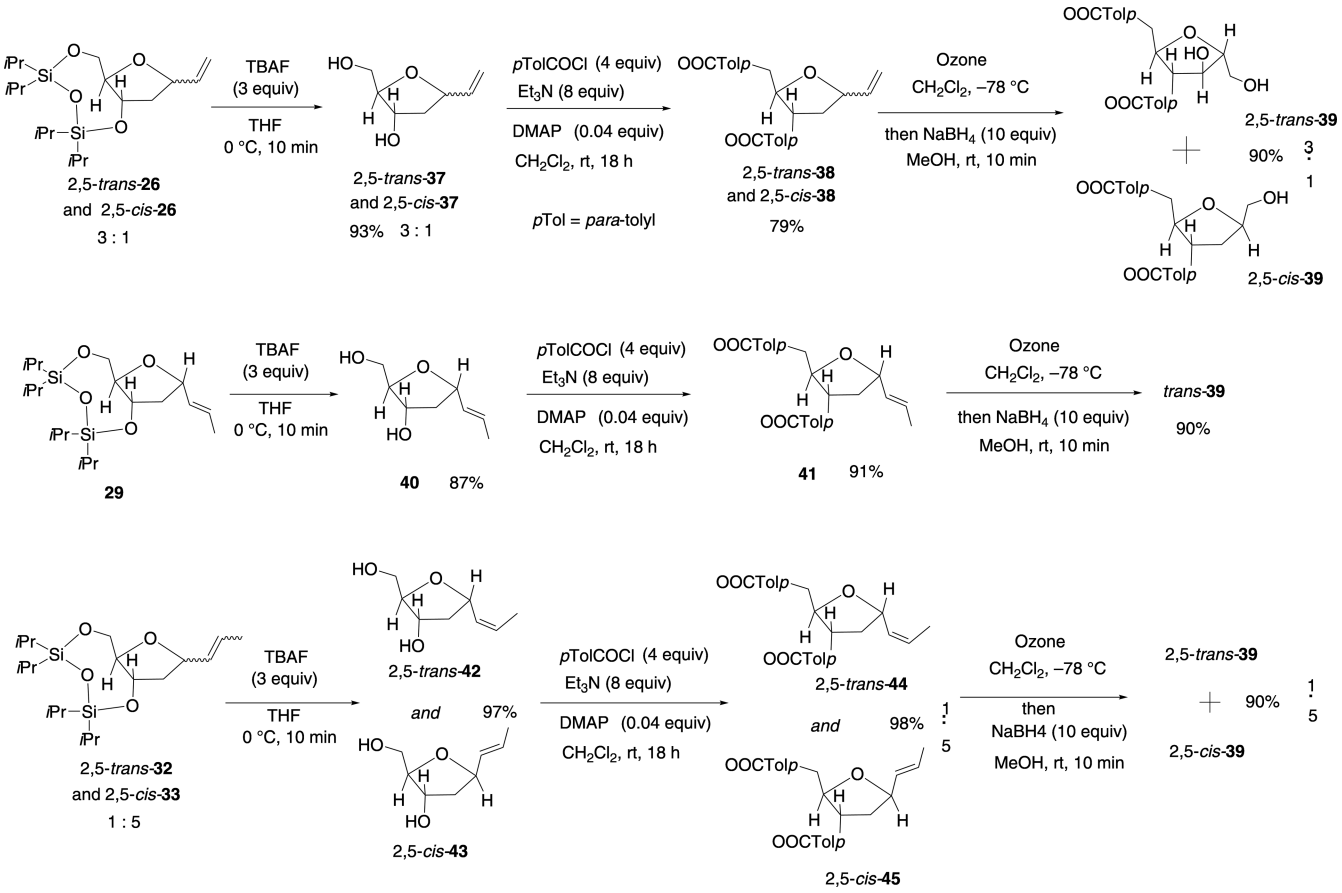
Scheme 11. Assignment of Stereochemistry for Cyclized Products 26, 29, 32, and 33



(*R*)-allylic alcohols **8**, **9**, and **10**, specifically. The 2,5-*cis* THF derivatives **27** and **36** were obtained from **6** and **13** exclusively.

Reaction Mechanism of Pd^{II}-Catalyzed Dehydrative Cyclization. A new stereogenic carbon center arises by the O–C bond formation (Scheme 14). Facial selection from the *si*-face on the alkene must afford the 2,5-*trans* isomer through the conformer **I**, while that from the *re*-face afforded the 2,5-*cis* isomer through the conformer **II**.

In the simple case of the reactions, precursors **8**, **9**, and **10** possess an (*R*)-allylic alcohol that provided the single stereoisomer, **29**, **30**, or **31**, respectively (Scheme 15). When either an additional (*R*)- or (*S*)-secondary hydroxy group existed at the γ-position, the 2,5-trans isomer with an (*E*)-propenyl substituent was formed specifically. The product would be produced via the conformer **I**, with either the allyl hydroxyl group or the nucleophilic hydroxyl group directing formation of this conformer **I**. Then the conformer would undergo *cis*-oxypalladation to give the σ-Pd intermediate. A *syn*-relationship between the Pd and the hydroxide would lead to the *syn*-elimination of PdCl(OH) that dissociated to give the (*E*)-alkene stereospecifically. It is notable that neither *cis*-oxypalladation nor *trans*-oxypalladation reactions through the conformer **II** took place because no 2,5-*cis* isomer was detected in the reaction product. On the other hand, the results obtained with (*S*)-allylic alcohol **11**, **12**, and **13** were more complicated. Not only the (*E*)-alkene but also the (*Z*)-alkene were formed. The initial chiral allylic alcohol directed the facial recognition of Pd^{II} catalyst that could lead to the conformer **II** that is able to stabilize with the nucleophilic hydroxy group. Successive *cis*-oxypalladation and *syn*-elimination reactions gave the 2,5-*cis* isomers 2,5-*cis*-**33**, 2,5-*cis*-**35**, and **36** with an (*E*)-propenyl substituent. When the nucleophilic hydroxy group directed formation of the Pd–π complex in the conformer **I** occurred *cis*-oxypalladation followed by *syn*-elimination provided the 2,5-*trans* isomers, 2,5-*trans*-**32** or 2.5-*trans*-**34** bearing a (*Z*)-propenyl substituent. In the case of the primary alcohols **5**, **6**, and **7**, conformer **I** derived by nucleophilic hydroxy group-directed or the primary allylic alcohol-directed facial selection in coordination of alkene to $PdCl_2$, afforded the 2,5-*trans* isomer predominantly. However, the other isomer through the conformer **II** was also produced with **5** and **7**. In the case of compound **7**, the secondary hydroxy group at the γ carbon might influence the intermediate conformer **II** to give the 2,5-*cis* isomer, although the effect of the γ-hydroxy group remains unclear.

In our proposed reaction mechanism, none of the intermediates in the above models suffer from allylic strain. Interestingly, no products assembled via 6-*endo*-*trigonal* cyclization were observed in any of the cases. All of the products were consistent with a *cis*-oxypalladation and *syn*-elimination pathway via a 5-*exo*-*trigonal* cyclization. Our hypothesis provides a rationale for explaining the stereochemical course of the reactions. Although Aponick et al. proposed an *anti*-oxypalladation and *anti*-elimination pathway based on the DFT calculation studies in the case of a 6-*exo*-*trigonal* cyclization for the formation of the simple tetrahydropyran,[17] we were unable to account for the current results according to their *anti*-oxypalladation and *anti*-elimination mechanism. Stabilization of the five-membered chelation intermediate by mean of the internal hydrogen bonding

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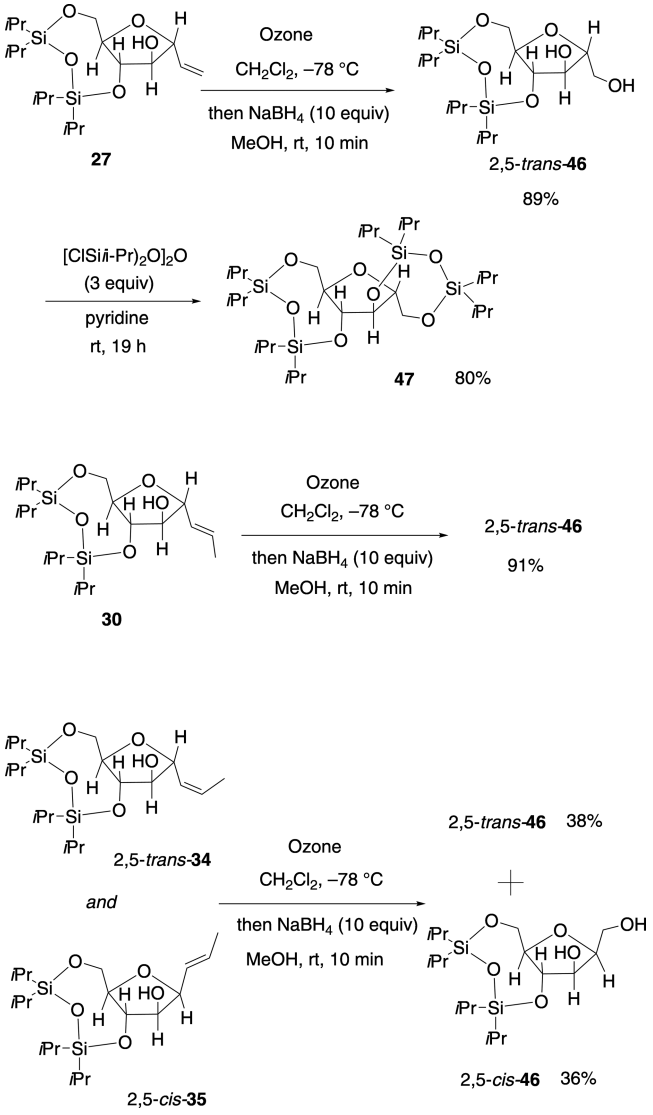
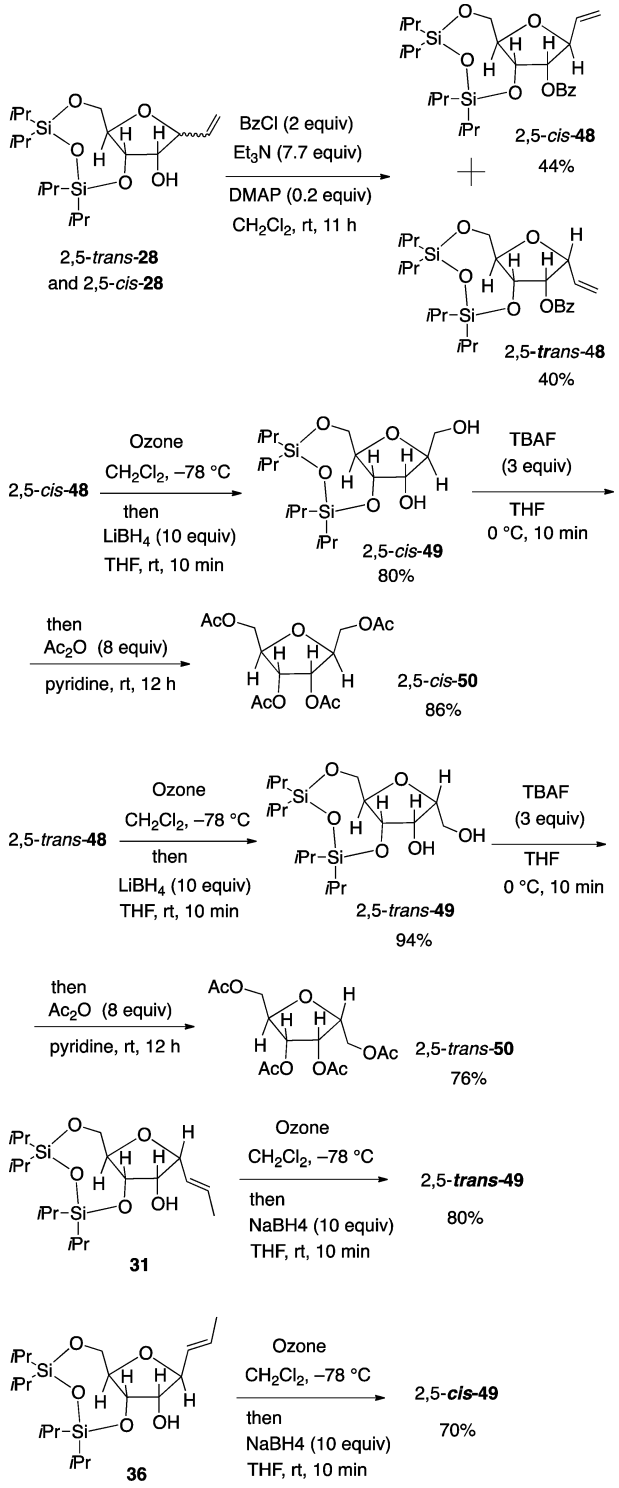
Scheme 12. Assignment of Stereochemistry for Cyclized Product 27, 30, 34, and 35



Scheme 13. Assignment of Stereochemistry for Cyclized Product 28, 31, and 36



between the nucleophilic hydroxy group and the allylic hydroxy group would not be operable in the presence of multiple hydroxy groups with different stereochemistries.

CONCLUSION

In summary, we have disclosed the stereochemistry of oxypalladation for the chiral ϵ-hydroxy allylic alcohols. This reaction proceeded via a 5-*exo*-*trigonal* fashion and effectively provided 5-alkenyl-substituted tetrahydrofuran. In the case of the structurally restricted ϵ-hydroxy allylic alcohol with an external ring, categorized as type C (Figure 1), the stereochemical course was influenced by the neighboring hydroxy groups of the alkene: (i) the chiral center of (*R*)-allylic alcohol was transmitted to the C-5 position to give the 2,5-*trans*-substituted THF ring product; (ii) in contrast, the chiral center of the (*S*)-allylic alcohol was transmitted to give 2,5-*cis*-substituted THF ring product, but partially to give the 2,5-*trans*-substituted THF ring product with a (*Z*)-alkenyl unit; and (iii) primary allylic alcohols gave 2,5-*trans*- and/or 2,5-*cis*-substituted THF ring products with or without the hydroxy group located at the γ-position. These results make it possible to explain the hydroxy group directed facial recognition of alkene to the Pd catalyst, *cis*-oxypalladation, and *syn*-elimination mechanism.

EXPERIMENTAL SECTION

General Information. The ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz spectrometer. Proton chemical shifts were internally referenced to the residual proton signals in $CDCl_3$ (δ 7.26), and ^{13}C NMR chemical shifts were internally referenced to the

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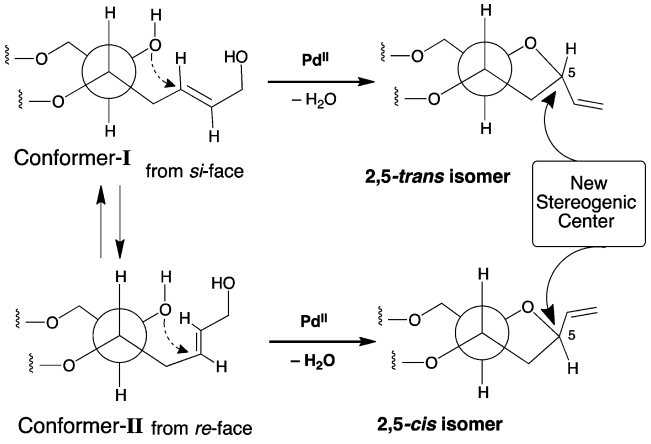
Scheme 14. Facial Selection and Stereochemistry of the Products



deuterated solvent signals in $CDCl_3$ (δ 77.00). THF was dried over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_4O_{10}. These solvents were freshly distilled before use. Low- and high-resolution mass spectra were obtained on a double-focusing high-resolution magnetic sector mass analyzer operating in a fast atom bombardment (FAB) mode or electron (EI) mode.

Preparation of the Precursors for Pd(II)-Catalyzed Cyclization. *General Procedure for the Preparation of Compounds **17**, **18** and **19**.* A mixture of lactol **14**,[13a] **15**,[13b] or **16**[13c] (20 mmol) and methyl (triphenylphosphoranylidene)acetate (14 g, 42 mmol) in benzene (100 mL) was stirred for 15 h at room temperature. Hexane was added to the mixture, and resulting solid was removed by filtration. The filtrate was condensed and purified by chromatography on silica gel eluted with 25% EtOAc in hexane to give unsaturated esters **17**, **18**, or **19**, respectively.

*Methyl (E)-4-((6S,7R)-7-Hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)-but-2-enoate (**17**).* Compound **17** (6.40 g) was obtained in 74% yield from **14** (7.53 g): colorless oil; R_f = 0.30 (15% EtOAc in hexane); $[\alpha]_D^{20}$ +6.45 (*c* 1.29, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (ddd, *J* = 15.7, 8.6, 6.3 Hz, 1H), 5.93 (dt, *J* = 15.7, 1.2 Hz, 1H), 4.15 (dd, *J* = 11.6, 1.0 Hz, 1H), 3.82 (dt, *J* = 9.2, 4.6 Hz, 1H), 3.77 (dd, *J* = 11.6, 2.2 Hz, 1H), 3.72 (s, 3H), 3.34 (brt, *J* = 7.4 Hz, 1H), 2.68 (dddd, *J* = 14.4, 6.3, 4.6, 1.2 Hz, 1H), 2.57 (dddd, *J* = 14.4, 8.6, 4.6, 1.0 Hz, 1H), 1.11–0.98 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 145.7, 123.7, 73.9, 69.9, 62.4, 51.6, 36.9, 17.6, 17.5, 17.48 (2C), 17.44 (2C), 17.43, 17.42, 13.5, 13.4, 12.8, 12.7; IR (film) 3445, 2945, 1728, 1464, 1029, 885 cm^{-1}; MS (FAB) *m*/*z* = 455 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{40}O_6Si_2Na$ 455.2261, found 455.2267.

*Methyl (R,E)-4-Hydroxy-4-((6S,7R)-7-hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)but-2-enoate (**18**).* Compound **18** (7.26 g) was obtained in 81% yield from **15** (7.85 g): white solid; mp 81–83 °C; R_f = 0.30 (40% EtOAc in hexane); $[\alpha]_D^{20}$ +23.0 (*c* 1.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 15.7, 3.4 Hz, 1H), 6.25 (dd, *J* = 15.7, 2.2 Hz, 1H), 4.59 (brs, 1H), 4.10 (dd, *J* = 12.0, 1.2 Hz, 1H), 3.89 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.80 (dd, *J* = 12.0, 2.2 Hz, 1H), 3.75 (s, 3H), 3.66 (d, *J* = 9.2 Hz, 1H), 3.01 (brs, 1H), 2.37 (brs, 1H), 1.10–0.96 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 148.8, 121.6, 72.5, 72.4, 71.3, 62.5, 51.7, 17.6, 17.4 (2C), 17.39, 17.38, 17.36, 17.35, 17.31, 13.45, 13.40, 12.77, 12.76; IR (film) 3583, 2945, 2867, 1727, 1464, 1033, 885 cm^{-1}; MS (FAB) *m*/*z* = 449 $[M + H]^+$; HRMS (FAB) *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{41}O_7Si_2$ 449.2391, found 449.2397. Anal. Calcd for $C_{20}H_{40}O_7Si_2$: C, 53.54; H, 8.99. Found: C, 53.76 H, 9.08.

*Methyl (S,E)-4-Hydroxy-4-((6S,7R)-7-hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)but-2-enoate (**19**).* Compound **19** (6.54 g) was obtained in 73% yield from **16** (7.85 g): white solid; mp 77–79 °C; R_f = 0.30 (30% EtOAc in hexane); $[\alpha]_D^{20}$ +16.0 (*c* 0.93, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 15.6, 3.2 Hz, 1H), 6.25 (dd, *J* = 15.6, 2.1 Hz, 1H), 4.58 (dd, *J* = 5.4, 2.9 Hz, 1H), 4.09 (dd, *J* = 11.9, 1.1 Hz, 1H), 3.88 (dd, *J* = 9.3, 2.7 Hz, 1H), 3.79 (dd, *J* = 11.9, 2.1 Hz, 1H), 3.75 (s, 3H), 3.65 (ddd, *J* = 9.3, 2.1, 1.1 Hz, 1H), 1.10–0.97 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 148.9, 121.6, 72.48, 72.45, 71.4, 62.4, 51.8, 17.6, 17.45 (2C), 17.43, 17.42, 17.40, 17.37, 17.33, 13.49, 13.44, 12.8, 12.7; IR (film) 3435, 2945, 1727, 1464, 1033, 885 cm^{-1}; MS (FAB) *m*/*z* = 471 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{40}O_7Si_2Na$ 471.2210, found 471.2205. Anal. Calcd for $C_{20}H_{40}O_7Si_2$: C, 53.54; H, 8.99. Found: C, 53.43 H, 9.09.

*General Procedure for the Preparation of Compounds **5**, **6**, and **7** by DIBALH Reduction.* To a solution of α,β-unsaturated ester **17**, **18**, or **19** (1.5 mmol) in CH_2Cl_2 (10 mL) was added DIBALH (4.5 mL, 1 M in hexane solution) at −78 °C. The reaction mixture was stirred for 30 min at the same temperature. Saturated potassium and sodium tartrate was added and the mixture stirred vigorously. Then the mixture was extracted with ether. The extract was washed with water and brine and dried over $MgSO_4$. The crude product was chromatographed on silica gel eluted with 20–40% EtOAc in hexane to give allylic alcohol **5**, **6**, or **7**, respectively.

*(7S)-6-((E)-4-Hydroxybut-2-en-1-yl)-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-7-ol (**5**).* The reaction of **17** (649 mg) gave **5** (546 mg) in 90% yield: colorless oil; R_f = 0.30 (25% EtOAc in hexane); $[\alpha]_D^{20}$ +14.7 (*c* 1.26, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86–5.72 (m, 2H), 4.14 (dd, *J* = 11.7, 1.0 Hz, 1H), 4.11 (d, *J* = 5.3 Hz, 2H), 3.77 (dd, *J* = 11.7, 1.9 Hz, 1H), 3.76 (dd, *J* = 9.2, 4.2 Hz, 1H), 3.54 (ddd, *J* = 9.2, 1.9, 1.0 Hz, 1H), 2.54 (dt, *J* = 14.2, 4.2 Hz, 1H), 2.43 (ddd, *J* = 14.2, 7.1, 4.2 Hz, 1H), 1.10–0.97 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2, 128.7, 73.7, 70.2, 63.9, 62.7, 36.8, 17.6, 17.59, 17.52, 17.49 (2C), 17.48, 17.45, 17.44, 13.55, 13.52, 12.87, 12.80; IR (film) 3359, 2944, 2867, 1464, 1028, 885 cm^{-1}; MS (FAB) *m*/*z* = 427 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{40}O_5Si_2Na$ 427.2312, found 427.2317.

*(R,E)-1-((6S,7R)-7-Hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)but-2-ene-1,4-diol (**6**).* The reaction of **18** (673 mg) gave **6** (536 mg) in 85% yield: colorless oil; R_f = 0.30 (60% EtOAc in hexane); $[\alpha]_D^{20}$ +22.4 (*c* 1.27, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (dtd, *J* = 15.7, 5.3, 1.5 Hz, 1H), 5.89 (ddt, *J* = 15.7, 4.3, 1.5 Hz, 1H), 4.45 (brs, 1H), 4.21 (dt, *J* = 5.2, 1.5 Hz, 2H), 4.16 (dd, *J* = 11.9, 1.1 Hz, 1H), 3.81 (dd, *J* = 8.7, 2.3 Hz, 1H), 3.80 (dd, *J* = 11.9, 1.1 Hz, 1H), 3.71 (brd, *J* = 8.6 Hz, 1H), 3.07 (brs, 1H), 2.70 (brs, 1H), 1.10–0.97 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5, 130.4, 72.7, 72.2, 71.6, 63.3, 62,8, 17.6, 17.47, 17.46, 17.44, 17.43 (2C), 17.39, 17.37, 13.5, 13.4, 12.8, 12.7; IR (film) 3361, 2943, 2867, 1464, 885 cm^{-1}; MS (FAB) *m*/*z* = 443 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{40}O_6Si_2Na$ 443.2261, found 443.2266.

*(S,E)-1-[(6S,7R)-7-Hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl]but-2-ene-1,4-diol (**7**).* The reaction of **19** (673 mg) gave **7** (555 mg) in 88% yield.: colorless oil; R_f = 0.30 (60% EtOAc in hexane); $[\alpha]_D^{20}$ +15.7 (*c* 1.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (dtd, *J* = 15.7, 5.2, 1.6 Hz, 1H), 5.89 (ddt, *J* = 15.7, 2.9, 1.3 Hz, 1H), 4.54 (m, 1H), 4.20 (dt, *J* = 5.1, 1.3 Hz, 2H), 4.10 (dd, *J* = 11.9, 0.9 Hz, 1H), 3.81 (dd, *J* = 11.9, 2.3 Hz, 1H), 3.80 (t, *J* = 3.3 Hz, 1H), 3.71 (m, 1H) 1.01–0.99 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.6, 130.4, 72.5, 72.1, 71.9, 63.4, 62,6, 17.6, 17.48 (5C), 17.42, 17.40, 13.55, 13.52, 12.89, 12.82; IR (film) 3353, 2943, 2867, 1464, 885 cm^{-1}; MS (FAB) *m*/*z* = 443 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{40}O_6Si_2Na$ 443.2261, found 443.2266.

*General Procedure for the Preparation of Compounds **20**, **21**, and **22** by Wittig Reaction.* A mixture of lactol **14**, **15**, or **16** (5 mmol) and (triphenylphosphoranylidene)acetone (2.4 g, 7.5 mmol) in benzene (25 mL) was stirred for 2 h at refluxing temperature. Hexane was added, and the resulting solid was removed by filtration. The filtrate was condensed and purified by chromatography on silica gel eluted with 20–40% EtOAc in hexane to give unsaturated ketone **20**, **21**, or **22**, respectively.

*(E)-5-((7S)-7-Hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)pent-3-en-2-one (**20**).* Compound **20** (1.48 g) was obtained in 71% yield from **14** (1.88 g): colorless oil; R_f = 0.30 (25% EtOAc in hexane); $[\alpha]_D^{20}$ +4.56 (*c* 1.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (ddd, *J* = 15.8, 8.5, 6.4 Hz, 1H), 6.18 (dt, *J* = 15.8, 1.1 Hz, 1H),

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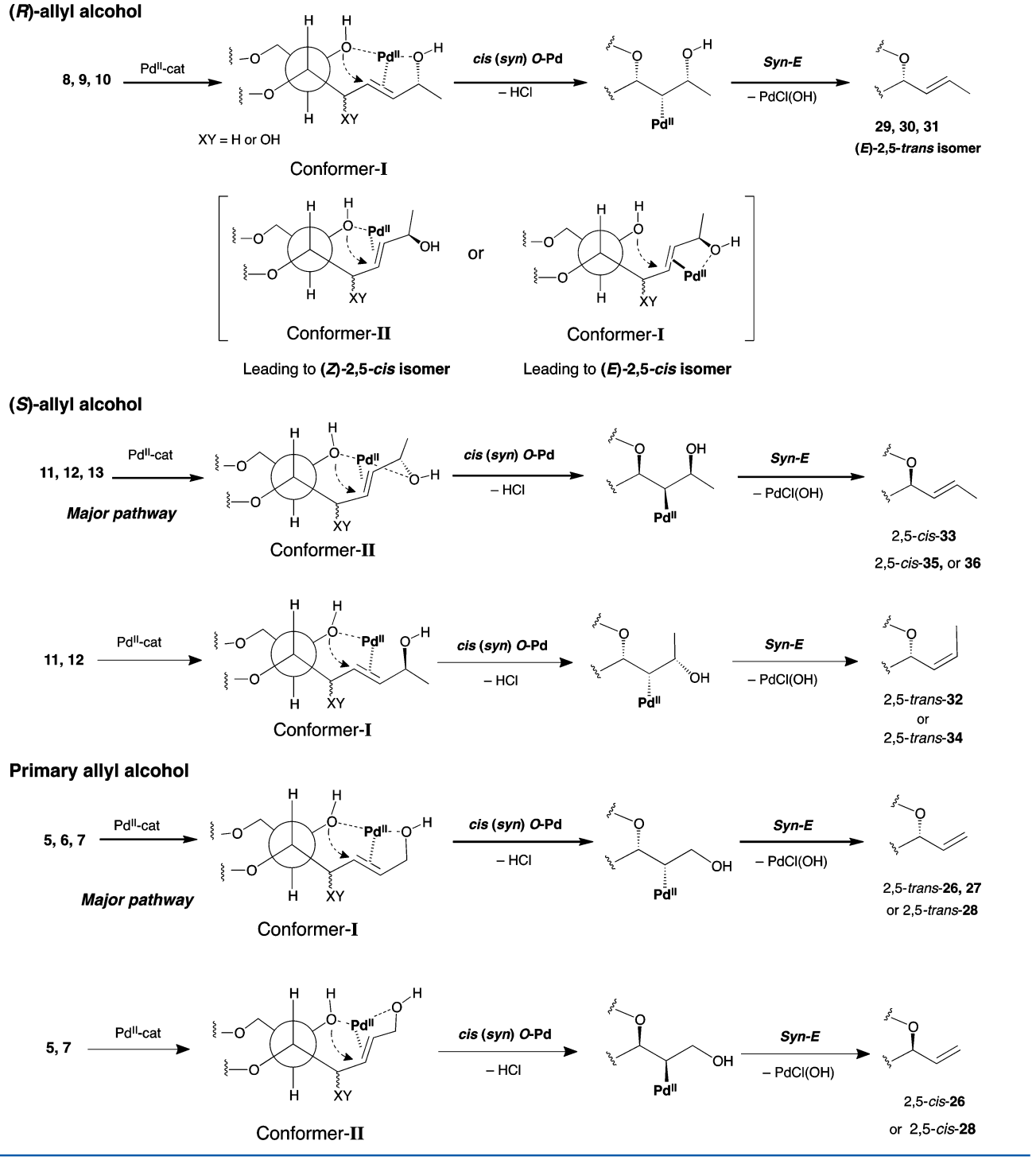
Scheme 15. Mechanism of 5-*Exo-Trigonal* Cyclization by Pd^{II} Catalyst



4.15 (dd, J = 11.7, 1.1 Hz, 1H), 3.84 (dt, J = 9.3, 4.6 Hz, 1H), 3.78 (dd, J = 11.7, 2.2 Hz, 1H), 3.34 (brt, J = 9.3 Hz, 1H), 2.71 (dddd, J = 14.4, 6.4, 4.6, 1.1 Hz, 1H), 2.60 (dddd, J = 14.4, 8.5, 4.6, 1.1 Hz, 1H), 2.25 (s, 3H), 1.10–0.96 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 144.5, 133.9, 73.9, 70.0, 62.4, 37.3, 27.1, 17.6, 17.5, 17.48, 17.47, 17.43 (2C), 17.41 (2C), 13.55, 13.51, 12.84, 12.79; IR (film) 3446, 2944, 2867, 1675, 1464, 1031, 885 cm^{-1}; MS (FAB) m/z = 439 $[M + Na]^+$; HRMS (FAB) m/z $[M + Na]^+$ calcd for $C_{20}H_{40}O_5Si_2Na$ 439.2312, found 439.2309.

*(5R,E)-5-Hydroxy-5-[(7R)-7-hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl]pent-3-en-2-one (**21**).* Compound **21** (1.47 g) was obtained in 68% yield from **15** (1.96 g): white solid; mp 64–66 °C; R_f = 0.30 (30% EtOAc in hexane); $[\alpha]_D^{20}$ +12.6 (c 1.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (dd, J = 15.9, 3.5 Hz, 1H), 6.50 (dd, J = 15.9, 2.0 Hz, 1H), 4.61 (d, J = 1.9 Hz, 1H), 4.10 (dd, J = 11.9, 1.2 Hz, 1H), 3.86 (dd, J = 9.3, 2.8 Hz, 1H), 3.80 (dd, J = 11.9, 2.2 Hz, 1H), 3.65 (d, J = 9.2 Hz, 1H), 3.16 (brs, 1H), 2.28 (s, 3H), 1.10–0.96 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 147.1, 130.5, 72.5 (2C), 71.5, 62.5, 28.1, 17.5, 17.44 (2C), 17.42 (2C), 17.39 (2C), 17.36, 13.5, 13.4, 12.8, 12.7; IR (film) 3399, 2944, 2867, 1676, 1464, 1032, 885 cm^{-1}; MS (FAB) m/z = 455 $[M + Na]^+$; HRMS (FAB) m/z $[M + Na]^+$ calcd for $C_{20}H_{40}O_6Si_2Na$ 455.2261, found 455.2267. Anal. Calcd for $C_{20}H_{40}O_6Si_2$: C, 55.52; H, 9.32. Found: C, 55.23 H, 9.29.

*(5S,E)-5-Hydroxy-5-((7R)-7-hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)pent-3-en-2-one (**22**).* Compound **22**

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(1.52 g) was obtained in 70% yield from **16** (1.96 g): white solid; mp 126−129 °C; R_f = 0.30 (30% EtOAc in hexane); $[\alpha]_D^{20}$ +16.2 (*c* 1.18, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (dd, *J* = 16.0, 5.4 Hz, 1H), 6.35 (dd, *J* = 16.0, 1.7 Hz, 1H), 4.57 (brs, 1H), 4.13 (d, *J* = 11.6 Hz, 1H), 3.81 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.80 (dd, *J* = 11.6, 2.4 Hz, 1H), 3.61 (t, *J* = 10.1 Hz, 1H), 2.98 (brs, 1H), 2.28 (s, 3H), 1.10−0.97 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 145.2, 130.1, 74.1, 73.6, 72.5, 62.6, 27.5, 17.6, 17.48, 17.42, 17.38, 17.37, 17.36, 17.34, 17.32, 13.49, 13.43, 12.8, 12.7; IR (film) 3400, 2944, 2867, 1676, 1464, 1032, 885 cm^{-1}; MS (FAB) *m*/*z* = 455 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{40}O_6Si_2Na$ 455.2261, found 455.2258. Anal. Calcd for $C_{20}H_{40}O_6Si_2$: C, 55.52; H, 9.32. Found: C, 55.33 H, 9.06.

*General Procedure for the Preparation of Compounds **11**, **12**, and **13** by $NaBH_4$ Reduction of Ketones **20**, **21**, and **22** and Lipase-Catalyzed Kinetic Acetylation of the Alcohols.* To a solution of ketone (1 mmol) in CH_2Cl_2 (5 mL) was added cerium chloride (3 mmol) at −78 °C. The mixture was stirred for 30 min at the same temperature, and $NaBH_4$ (57 mg, 1.5 mmol) was added in several portions. The reaction was warmed to room temperature. Water and CH_2Cl_2 were added to the mixture, and the organic layer was washed with water and brine. The solvent was evaporated, and the residue was purified by column chromatography on silica gel to give diastereomeric mixture of alcohol. Reduction of **20** (417 mg), **21** (432 mg), and **22** (432 mg) gave a mixture of **8** and **11** (364 mg) in 87% yield, **9** and **12** (348 mg) in 80% yield, and **10** and **13** (396 mg) in 91% yield, respectively. They were able to separate by the following lipase-catalyzed kinetic acetylation and reductive deacetylation. To a mixture of allylic alcohols (0.5 mmol) in *i*-Pr_2O (3 mL) were added molecular sieves 4 Å (215 mg), vinyl acetate (154 μL, 215 mg, 2.5 mmol), and Novozyme 435 (22 mg, 10 w/v%). The mixture was stirred for 1 day at room temperature. The solid was filtered through a Celite pad, and the filtrate was condensed. The residue was purified by chromatography on silica gel eluted with 20% EtOAc in hexane to give (*R*)-acetate and with 60% EtOAc in hexane recovery of (*S*)-alcohol.

Reaction of a mixture of **8** and **11** (209 mg) gave acetate **23** (110 mg) in 48% yield with recovery of **11** (98 mg) in 47% yield.

*(R,E)-2-Acetoxy-5-((6S,7R)-7-hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)pent-3-ene (**23**):* colorless oil; R_f = 0.80 (30% EtOAc in hexane); $[\alpha]_D^{20}$ +18.2 (*c* 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (dddd, *J* = 15.4, 8.1, 4.5, 1.0 Hz, 1H), 5.58 (ddt, *J* = 15.4, 6.4 1.2 Hz, 1H), 5.33 (qd, *J* = 6.4. 6.3, 1H), 4.14 (dd, *J* = 11.6, 1.2 Hz, 1H), 3.77 (dd, *J* = 11.6, 2.1 Hz, 1H), 3.75 (q, *J* = 4.5 Hz, 1H), 3.34 (brt, *J* = 7.5 Hz, 1H), 2.52 (dt, *J* = 14.2, 4.5 Hz, 1H), 2.39 (ddd, *J* = 14.2, 8.1, 4.5 Hz, 1H), 2.02 (s, 3H), 1.29 (d, *J* = 6.4 Hz, 3H), 1.10−1.00 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 132.6, 128.6, 73.6, 71.2, 70.3, 62.7, 36.7, 21.6, 20.5, 17.69, 17.66, 17.5, 17.49, 17.48, 17.47, 17.46, 17.44, 13.55, 13.50, 12.9, 12.8; IR (film) 3471, 2944, 2867, 1740, 1464, 1028, 885 cm^{-1}; MS (FAB) *m*/*z* = 483 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{44}O_6Si_2Na$ 483.2574, found 483.2565.

*(S,E)-5-((6S,7R)-7-Hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)pent-3-en-2-ol (**11**):* white solid; mp 99−101 °C; R_f = 0.30 (30% EtOAc in hexane); $[\alpha]_D^{20}$ +3.36 (*c* 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (ddd, *J* = 15.2, 7.7, 0.7 Hz, 1H), 5.64 (ddd, *J* = 15.4, 6.4, 1.0 Hz, 1H), 4.28 (dq, *J* = 6.4, 6.3 Hz, 1H), 4.14 (dd, *J* = 11.6, 1.2 Hz, 1H), 3.76 (dd, *J* = 11.6, 2.1 Hz, 1H), 3.75 (dt, *J* = 8.6, 4.5 Hz, 1H), 3.38 (brd, *J* = 8.7 Hz, 1H), 2.50 (dt, *J* = 14.2, 4.5 Hz, 1H), 2.43 (ddd, *J* = 14.2, 7.7, 4.5 Hz, 1H), 1.26 (d, *J* = 6.4 Hz, 3H), 1.10−0.96 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 126.5, 73.7, 70.4, 69.2, 62.7, 36.6, 23.5, 17.7, 17.6, 17.54, 17.51 (2C), 17.49, 17.47, 17.45, 13.56, 13.53, 12.9, 12.8; IR (film) 3326, 2944, 2867, 1512, 1464, 1062, 884 cm^{-1}; MS (FAB) *m*/*z* = 441 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{42}O_5Si_2Na$ 441.2469, found 441.2474. Anal. Calcd for $C_{20}H_{42}O_5Si_2$: C, 57.37; H, 10.11. Found: C, 57.63 H, 10.07.

Reaction of a mixture of **9** and **12** (217 mg) gave **24** (100 mg) in 42% yield with recovery of **12** (100 mg) in 46% yield.

*(1R,4R,E)-4-Acetoxy-2-hydroxy-1-((6S,7R)-7-hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)pent-2-ene (**24**):* colorless oil; R_f = 0.80 (60% EtOAc in hexane); $[\alpha]_D^{20}$ +36.6 (*c* 1.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90−5.81 (m, 2H), 5.41 (m, 1H), 4.43 (d, *J* = 7.1 Hz, 1H), 4.08 (dd, *J* = 11.8, 1.0 Hz, 1H), 3.83 (dd, *J* = 9.3, 2.5 Hz, 1H), 3.80 (dd, *J* = 11.8, 1.8 Hz, 1H), 3.66 (t, *J* = 5.0 Hz, 1H), 2.95 (brd, *J* = 9.1 Hz, 1H), 2.42 (brd, *J* = 8.3 Hz, 1H), 2.03 (s, 3H), 1.32 (d, *J* = 6.5 Hz, 3H), 1.10−0.97 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 131.9, 130.7, 72.5, 72.1, 71.7, 70.5, 62.7, 21.5, 20.4, 17.59, 17.54, 17.44, 17.43 (2C), 17.41, 17.38, 17.35, 13.49, 13.47, 12.8, 12.7; IR (film) 3421, 2944, 2867, 1739, 1465, 1035, 885 cm^{-1}; MS (FAB) *m*/*z* = 499 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{44}O_7Si_2Na$ 499.2523, found 499.2520.

*(1R,4S,E)-5-((6S,7R)-7-Hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)pent-2-ene-1,4-diol (**12**):* white solid; mp 131−132 °C; R_f = 0.30 (60% EtOAc in hexane); $[\alpha]_D^{20}$ +20.8 (*c* 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (ddd, *J* = 15.6, 6.0, 1.3 Hz, 1H), 5.82 (ddd, *J* = 15.6, 4.3, 0.7 Hz, 1H), 4.39 (brs, 1H), 4.35 (qd, *J* = 6.3, 6.0 Hz, 1H), 4.09 (dd, *J* = 11.6, 1.1 Hz, 1H), 3.83 (dd, *J* = 9.3. 2.7 Hz, 1H), 3.80 (dd, *J* = 11.6, 2.2 Hz, 1H), 3.70 (t, *J* = 8.3 Hz, 1H), 3.02 (brd, *J* = 9.2 Hz, 1H), 2.60 (brs, 1H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.10−0.97 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 129.7, 73.1, 72.2, 71.1, 68.6, 63.1, 23.3, 17.55, 17.52, 17.4, 17.3 (4C), 17.2, 13.4, 13.3, 12.74, 12.71; IR (film) 2944, 2867, 1733, 1456, 1042 cm^{-1}; MS (FAB) *m*/*z* = 457 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{42}O_6Si_2Na$ 457.2418, found 457.2411. Anal. Calcd for $C_{20}H_{42}O_6Si_2$: C, 55.26; H, 9.74. Found: C, 55.03 H, 9.86.

Reaction of a mixture of **10** and **13** (240 mg) gave **25** (121.4 mg) in 46% yield with recovery of **13** (116.8 mg) in 49% yield.

*(1S,4R,E)-4-Acetoxy-1-hydroxy-1-((6S,7R)-7-hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)pent-2-ene (**25**):* colorless oil; R_f = 0.80 (60% EtOAc in hexane); $[\alpha]_D^{20}$ +14.6 (*c* 0.92, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88−5.74 (m, 2H), 5.33 (qd, *J* = 6.5, 6.4 Hz, 1H), 4.36 (dd, *J* = 5.9, 3.6 Hz, 1H), 4.08 (dd, *J* = 11.7, 1.1 Hz, 1H), 3.80 (dd, *J* = 9.9, 3.6 Hz, 1H), 3.79 (dd, *J* = 11.7, 2.3 Hz, 1H), 3.47 (brt, *J* = 8.2 Hz, 1H), 2.65 (brs, 1H), 2.55 (brd, *J* = 8.2 Hz, 1H), 2.04 (s, 3H), 1.32 (d, *J* = 6.5 Hz, 3H), 1.10−0.97 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 132.0, 129.9, 74.4, 73.8, 72.4, 70.7, 62.8, 21.5, 20.4, 17.7, 17.58, 17.50, 17.49, 17.48, 17.45, 17.44, 17.41, 13.54, 13.51, 13.0, 12.8; IR (film) 3445, 2944, 2867, 1738, 1464, 1030, 885 cm^{-1}; MS (FAB) *m*/*z* = 499 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{44}O_7Si_2Na$ 499.2523, found 499.2518.

*(1S,4S,E)-5-((6S,7R)-7-Hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)pent-2-ene-1,4-diol (**13**):* white solid; mp 92−95 °C; R_f = 0.30 (60% EtOAc in hexane); $[\alpha]_D^{20}$ −10.3 (*c* 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94−5.78 (m, 2H), 4.40 (brs, 1H), 4.35 (qd, *J* = 6.4, 5.9 Hz, 1H), 4.12 (d, *J* = 10.9 Hz, 1H), 3.79 (dd, *J* = 8.2, 3.2 Hz, 1H), 3.78 (dd, *J* = 10.9, 3.2 Hz, 1H), 3.55 (brt, *J* = 8.2 Hz, 1H), 2.91 (brs, 1H), 2.47 (brs, 1H), 2.35 (brd, *J* = 9.2 Hz, 1H), 1.29 (d, *J* = 6.4 Hz, 3H), 1.10−0.98 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 128.2, 74.7, 73.7, 72.6, 68.4, 62.7, 23.4, 17.7, 17.58, 17.50 (2C), 17.49, 17.46, 17.42, 17.41, 13.55, 13.52, 13.0, 12.8; IR (film) 3352, 2944, 2867, 1652, 1464, 1058, 885 cm^{-1}; MS (FAB) *m*/*z* = 457 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{42}O_6Si_2Na$ 457.2418, found 457.2422. Anal. Calcd for $C_{20}H_{42}O_6Si_2$: C, 55.26; H, 9.74. Found: C, 55.37 H, 9.55.

*General Procedure for the Preparation of Compounds **8**, **9**, and **10** from **23**, **24**, and **25**.* To a solution of acetate **23**, **24**, or **25** (1 mmol) in anhydrous ether (30 mL) was added $LiAlH_4$ (4 mmol) at 0 °C. The mixture was stirred for 1 h at the same temperature and quenched with acetone. Aqueous potassium sodium tartrate was added to the mixture and stirred vigorously. The mixture was extracted with ether, and the extract was dried over $MgSO_4$. Solvent was removed, and the residue was purified by chromatography on silica gel eluted with 30% EtOAc in hexane.

*(R,E)-5-((6S,7R)-7-Hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)pent-3-en-2-ol (**8**).* $LiAlH_4$ reduction of **23** (99 mg) gave **8** (83.5 mg) in 93% yield: colorless oil; R_f = 0.30 (30% EtOAc in hexane); $[\alpha]_D^{20}$ +11.3 (*c* 1.70, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (dddd, *J* = 15.2, 7.9, 5.3, 0.8 Hz, 1H), 5.64 (ddt, *J* = 15.5, 6.2, 1.2 Hz, 1H), 4.29 (qd, *J* = 6.3, 6.2 Hz, 1H), 4.14 (dd, *J* = 11.6, 1.2 Hz, 1H), 3.76 (dd, *J* = 11.6, 2.2 Hz, 1H), 3.75 (dt, *J* = 9.1, 5.3 Hz, 1H), 3.36 (t, *J* = 9.1 Hz, 1H), 2.51 (dt, *J* = 14.3, 5.3 Hz, 1H), 2.41 (ddd, *J* = 14.3, 7.9, 5.3 Hz, 1H), 2.05 (brd, *J* = 10.4 Hz, 1H), 1.26 (d, *J* = 6.3 Hz,

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3H), 1.10−0.98 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 126.5, 73.7, 70.3, 69.1, 62.7, 36.7, 23.5, 17.7, 17.6, 17.55, 17.51 (2C), 17.49, 17.46, 17.45, 13.55, 13.53, 12.9, 12.8; IR (film) 3367, 2944, 2867, 1464, 1058, 885 cm^{-1}; MS (FAB) m/z = 441 $[M + Na]^+$; HRMS (FAB) m/z $[M + Na]^+$ calcd for $C_{20}H_{42}O_5Si_2Na$ 441.2469, found 441.2471.

(1R,4R,E)-5-((6S,7R)-7-Hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)pent-2-ene-1,4-diol (**9**). $LiAlH_4$ reduction of **24** (114 mg) gave **9** (93.7 mg) in 90% yield: white solid; mp 127−130 °C; R_f = 0.30 (60% EtOAc in hexane); $[\alpha]_D^{20}$ +18.8 (c 1.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (ddd, J = 15.6, 5.3, 1.3 Hz, 1H), 5.84 (ddd, J = 15.6, 4.3, 3.3 Hz, 1H), 4.57 (brs, 1H), 4.36 (qd, J = 6.3, 5.3 Hz, 1H), 4.09 (dd, J = 11.8, 1.1 Hz, 1H), 3.82 (dd, J = 9.0. 2.7 Hz, 1H), 3.80 (dd, J = 11.8, 2.1 Hz, 1H), 3.68 (t, J = 7.7 Hz, 1H), 2.90 (brd, J = 9.0 Hz, 1H), 2.44 (brd, J = 7.6 Hz, 1H), 1.29 (d, J = 6.3 Hz, 3H), 1.10−0.97 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 129.7, 72.7, 72.2, 71.9, 68.4, 62.7, 23.5, 17.6, 17.5, 17.47, 17.46, 17.45 (2C), 17.399, 17.395, 13.5, 13.4, 12.89, 12.81; IR (film) 2944, 2867, 1733, 1456, 1040 cm^{-1}; MS (FAB) m/z = 457 $[M + Na]^+$; HRMS (FAB) m/z $[M + Na]^+$ calcd for $C_{20}H_{42}O_6Si_2Na$ 457.2418, found 457.2411. Anal. Calcd for $C_{20}H_{42}O_6Si_2$: C, 55.26; H, 9.74. Found: C, 55.07 H, 9.62.

(1S,4R,E)-5-((6S,7R)-7-Hydroxy-2,2,4,4-tetraisopropyl-1,3,5,2,4-trioxadisilocan-6-yl)pent-2-ene-1,4-diol (**10**). $LiAlH_4$ reduction of **25** (60.7 mg) gave **10** (46.9 mg) in 85% yield: white solid; mp 115−117 °C; R_f = 0.30 (60% EtOAc in hexane); $[\alpha]_D^{20}$ −12.1 (c 1.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88−5.78 (m, 2H), 4.38 (t, J = 4.1 Hz, 1H), 4.32 (qd, J = 6.4, 5.9 Hz, 1H), 4.11 (d, J = 11.0 Hz, 1H), 3.79 (dd, J = 10.5, 2.3 Hz, 2H), 3.53 (brd, J = 8.7 Hz, 1H), 2.61 (brs, 1H), 1.29 (d, J = 6.4 Hz, 3H), 1.10−0.96 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 128.3, 74.6, 73.7, 72.4, 68.5, 62.7, 23.4, 17.7, 17.58, 17.51 (2C), 17.49, 17.46, 17.423, 17.420, 13.56, 13.53, 13.0, 12.8; IR (film) 3358, 2944, 2867, 1464, 1058, 886 cm^{-1}; MS (FAB) m/z = 457 $[M + Na]^+$; HRMS (FAB) m/z $[M + Na]^+$ calcd for $C_{20}H_{42}O_6Si_2Na$ 457.2418, found 457.2412. Anal. Calcd for $C_{20}H_{42}O_6Si_2$: C, 55.26; H, 9.74. Found: C, 55.09 H, 9.50.

$PdCl_2(MeCN)_2$-Catalyzed Cyclization. *General Method.* To a solution of allylic alcohol (0.1 mmol) in THF (0.5 mL) was added $PdCl_2(MeCN)_2$ (2.6 mg, 10 mol %), and the mixture was stirred for 5−20 min at room temperature. The mixture was diluted with ether (10 mL) and washed with water and brine. The extract was condensed, and the residue was purified by column chromatography on silica gel eluted with 5−10% EtOAc in hexane. The chemical yields, product ratio, and physical and spectroscopic data are as follows.

*Mixture of 2,5-trans-**26** and 2,5-cis-**26** (3:1).* Diol **5** (26.8 mg) gave a mixture of 2,5-*trans*-**26** and 2,5-*cis*-**26** (22.8 mg) in 89% yield: colorless oil; R_f = 0.30 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (ddd, J = 17.1, 10.2, 6.8 Hz, 3/4H), 5.81 (ddd, J = 17.0, 10.3, 6.5 Hz, 1/4H), 5.28 (dt, J = 17.1, 1.3 Hz, 1/4H), 5.23 (dt, J = 17.1, 1.1 Hz, 3/4H), 5.12 (dt, J = 10.3, 1.3 Hz, 1/4H), 5.11 (dt, J = 10.2, 1.1 Hz, 3/4H), 4.52−4.38 (m, 2H), 4.05 (dd, J = 10.1, 2.1 Hz, 1/4H), 3.99 (dd, J = 11.4, 3.0 Hz, 3/4H), 3.83−3.74 (m, 2H), 2.38 (ddd, J = 12.1, 6.3, 5.9 Hz, 3/4H), 2.12 (ddd, J = 12.7, 6.6, 4.4 Hz, 1/4H), 1.95−1.84 (m, 1H), 1.13−0.98 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8 (3/4C), 138.3 (1/4C), 116.4 (1/4C), 115.9 (3/4C), 86.2 (1/4C), 83.3 (3/4C), 78.6 (1/4C), 78.2 (3/4C), 73.8 (1/4C), 73.6 (3/4C), 64.1 (1/4C), 63.4 (3/4C), 41.0 (1/4C), 40.8 (3/4C), 17.74 (1/4C), 17.71 (3/4C), 17.59 (3/4C), 17.58 (3/4C), 17.57 (2/4C), 17.56 (3/4C), 17.50 (1/4C), 17.48 (3/4C), 17.45 (1/4C), 17.34 (1/4C), 17.33 (3/4C), 17.30 (1/4C), 17.22 (1/4C), 17.20 (3/4C), 17.15 (3/4C), 17.14 (1/4C), 13.66 (1/4C), 13.62 (3/4C), 13.5 (1/4C), 13.4 (3/4C), 13.1 (1/4C), 13.0 (3/4C), 12.75 (3/4C), 12.72 (1/4C); IR (film) 2944, 2867, 1732, 1464, 1034, 885 cm^{-1}; MS (FAB) m/z = 409 $[M + Na]^+$; HRMS (FAB) m/z $[M + Na]^+$ calcd for $C_{19}H_{38}O_4Si_2Na$ 409.2206, found 409.2203.

(6aR,8R,9R,9aS)-2,2,4,4-Tetraisopropyl-8-vinyltetrahydro-6H-furo[3,2-f][1,3,5,2,4]trioxadisilocin-9-ol (**27**). Triol **6** (82.3 mg) gave **27** (73.3 mg) in 93% yield: colorless oil; R_f = 0.30 (10% EtOAc in hexane); $[\alpha]_D^{20}$ −17.9 (c 1.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (ddd, J = 17.1, 10.2, 6.7 Hz, 1H), 5.34 (ddd, J = 17.1, 1.4, 1.0 Hz, 1H), 5.22 (ddd, J = 10.2, 1.4, 1.0 Hz, 1H), 4.28 (t, J = 7.0 Hz, 1H), 4.15 (tt, J = 6.7, 1.0 Hz, 1H), 4.04 (dd, J = 7.4, 6.9 Hz, 1H), 3.97 (dd, J = 11.7, 3.2 Hz, 1H), 3.89 (dd, J = 11.7, 7.0 Hz, 1H), 3.83 (dd, J = 7.0, 3.2 Hz, 1H), 1.96 (brs, 1H), 1.12−0.99 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 117.7, 82.5, 81.5, 81.4, 78.7, 63.4, 17.6, 17.55, 17.54, 17.53, 17.3, 17.28, 17.22, 17.1, 13.6, 13.4, 13.0, 12.7; IR (film) 3443, 2944, 2867, 1716, 1464, 1037, 885 cm^{-1}; MS (FAB) m/z = 425 $[M + Na]^+$; HRMS (FAB) m/z $[M + Na]^+$ calcd for $C_{19}H_{38}O_5Si_2Na$ 425.2156, found 425.2148.

*Mixture of 2,5-trans-**28** and 2,5-cis-**28** (1:1).* Triol **7** (32.0 mg) gave a mixture of 2,5-*trans*-**28** and 2,5-*cis*-**28** (28.2 mg) in 92% yield: colorless oil; R_f = 0.30 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (ddd, J = 17.1, 10.3, 6.8 Hz, 1/2H), 5.86 (ddd, J = 17.1, 10.1, 5.9 Hz, 1/2H), 5.42 (dt, J = 17.1, 1.6 Hz, 1/2H), 5.36 (ddd, J = 17.1, 1.8, 1.1 Hz, 1/2H), 5.30 (ddd, J = 10.5, 1.6, 1.1 Hz, 1/2H), 5.21 (dt, J = 10.5, 1.6 Hz, 1/2H), 4.45 (ddt, J = 6.8, 3.8, 1.1 Hz, 1/2H), 4.40 (dd, J = 7.3, 4.8 Hz, 1/2H), 4.27−4.22 (m, 1H), 4.17 (t, J = 4.3 Hz, 1/2H), 4.05−3.83 (m, 7/2H), 1.13−0.98 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ135.9 (1/2C), 133.7 (1/2C), 118.2 (1/2C), 117.1 (1/2C), 84.4 (1/2C), 82.5 (1/2C), 81.9 (1/2C), 81.0 (1/2C), 75.3 (1/2C), 74,8 (1/2C), 73.7 (1/2C), 72.4 (1/2C), 63.3 (1/2C), 63.0 (1/2C), 17.64 (1/2C), 17.63 (1/2C), 17.54 (1/2C), 17.51 (2C), 17.4 (1/2C), 17.38 (1/2C), 17.33 (1/2C), 17.23 (1/2C), 17.21 (1/2C), 17.20 (1/2C), 17.18 (1/2C), 17.13 (1/2C), 17.12 (1/2C), 13.56 (1/2C), 13.55 (1/2C), 13.39 (1/2C), 13.38 (1/2C), 13.0 (1/2C), 12.9 (1/2C), 12.8 (1/2C), 12.7 (1/2C); IR (film) 3526, 2944, 2868, 1717, 1464, 1037, 885 cm^{-1}; MS (FAB) m/z = 425 $[M + Na]^+$; HRMS (FAB) m/z $[M + Na]^+$ calcd for $C_{19}H_{38}O_5Si_2Na$ 425.2156, found 425.2161.

(6aR,8S,9aS)-2,2,4,4-Tetraisopropyl-8-((E)-prop-1-en-1-yl)-tetrahydro-6H-furo[3,2-f][1,3,5,2,4]trioxadisilocine (**29**). Diol **8** (21.5 mg) gave **29** (19.9 mg) in 97% yield: colorless oil; R_f = 0.30 (5% EtOAc in hexane); $[\alpha]_D^{20}$ −20.0 (c 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (dq, J = 15.1, 6.2 Hz, 1H), 5.57 (ddq, J = 15.1, 7.6, 1.3 Hz, 1H), 4.43 (dt, J = 9.1, 6.6 Hz, 1H), 4.35 (ddd, J = 9.1, 7.6, 5.7 Hz, 1H), 3.97 (dd, J = 11.2, 2.8 Hz, 1H), 3.79 (dd, J = 11.2, 6.6 Hz, 1H), 3.75 (td, J = 6.6, 2.8 Hz, 1H), 2.33 (ddd, J = 12.1, 6.8, 5.7 Hz, 1H), 1.87 (dt, J = 12.1, 9.1 Hz, 1H), 1.69 (dd, J = 6.2, 1.3 Hz, 3H), 1.10−0.88 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.6, 83.1, 78.1, 73.8, 63.6, 41.1, 17.8, 17.7, 17.59, 17.58, 17.56, 17.4, 17.3, 17.2, 17.1, 13.6, 13.4, 13.0, 12.7; IR (film) 2943, 2867, 1464, 1034, 885 cm^{-1}; MS (FAB) m/z = 423 $[M + Na]^+$; HRMS (FAB) m/z $[M + Na]^+$ calcd for $C_{20}H_{40}O_4Si_2Na$ 423.2363, found 423.2371.

(6aR,8R,9R,9aS)-2,2,4,4-Tetraisopropyl-8-((E)-prop-1-en-1-yl)-tetrahydro-6H-furo[3,2-f][1,3,5,2,4]trioxadisilocin-9-ol (**30**). Triol **9** (93.7 mg) gave **30** (85.5 mg) in 95% yield: colorless oil; R_f = 0.30 (10% EtOAc in hexane); $[\alpha]_D^{20}$ −19.4 (c 0.79, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (dqd, J = 15.1, 6.5, 0.5 Hz, 1H), 5.54 (ddq, J = 15.1, 7.8, 1.5 Hz, 1H), 4.26 (t, J = 6.9 Hz, 1H), 4.09 (t, J = 7.7 Hz, 1H), 4.01 (dd, J = 7.7, 6.9 Hz, 1H), 3.97 (dd, J = 11.3, 3.0 Hz, 1H), 3.86 (dd, J = 11.3, 6.9 Hz, 1H), 3.82 (td, J = 6.9, 3.0 Hz, 1H), 1.79 (brs, 1H), 1.73 (dd, J = 6.5, 1.5 Hz, 3H), 1.11−0.78 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.0, 129.4, 82.3, 81.5, 81.2, 78.8, 63.7, 18.0, 17.6, 17.57, 17.56, 17.55, 17.3, 17.29, 17.23, 17.1, 13.6, 13.4, 13.0, 12.7; IR (film) 3440, 2944, 2867, 1671, 1464, 1037, 885 cm^{-1}; MS (FAB) m/z = 439 $[M + Na]^+$; HRMS (FAB) m/z $[M + Na]^+$ calcd for $C_{20}H_{40}O_5Si_2Na$ 439.2312, found 439.2306.

(6aR,8R,9S,9aS)-2,2,4,4-Tetraisopropyl-8-((E)-prop-1-en-1-yl)-tetrahydro-6H-furo[3,2-f][1,3,5,2,4]trioxadisilocin-9-ol (**31**). Triol **10** (26.5 mg) gave **31** (23.0 mg) in 95% yield: colorless oil; R_f = 0.30 (10% EtOAc in hexane); $[\alpha]_D^{20}$ −28.2 (c 1.29, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84−5.71 (m, 2H), 4.40−4.36 (m, 2H), 4.09 (dd, J = 4.7, 3.7 Hz, 1H), 4.00 (dd, J = 11.3, 3.5 Hz, 1H), 3.98 (td, J = 7.1, 3.5 Hz, 1H), 3.83 (dd, J = 11.5, 6.3 Hz, 1H), 1.75 (d, J = 4.8 Hz, 3H), 1.11−0.82 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.1, 126.3, 81.8, 80.9, 75.1, 73.9, 63.6, 18.1, 17.6, 17.55, 17.53, 17.52, 17.3, 17.2 (2C), 17.1, 13.5, 13.3, 13.0, 12.7; IR (film) 3545, 2944, 2867, 1733, 1464, 1036, 885 cm^{-1}; MS (FAB) m/z = 439 $[M + Na]^+$; HRMS (FAB) m/z $[M + Na]^+$ calcd for $C_{20}H_{40}O_5Si_2Na$ 439.2312, found 439.2309.

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*Mixture of 2,5-trans-**32** and 2,5-cis-**33** (1:5).* Triol **11** (99.5 mg) gave a mixture of 2,5-*trans*-**32** and 2,5-*cis*-**33** (87.0 mg) in 91% yield: colorless oil; R_f = 0.30 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (dqd, J = 15.1, 6.4, 0.8 Hz, 5/6H), 5.66−5.51 (m, 2/6H), 5.42 (ddq, J = 15.1, 7.5, 1.3 Hz, 5/6H), 4.79 (ddd, J = 9.4, 7.7, 5.9 Hz, 1/6H), 4.44 (q, J = 7.8 Hz, 5/6H), 4.39 (dt, J = 7.8, 3.3 Hz, 5/6H), 4.04 (dd, J = 10.2, 2.4 Hz, 5/6H), 3.99 (dd, J = 11.7, 2.7 Hz, 1/6H), 3.82−3.69 (m, 13/6), 2.36 (ddd, J = 12.2, 6.9, 5.9 Hz, 1/6H), 2.07 (ddd, J = 12.8, 6.4, 4.0 Hz, 5/6H), 1.88 (dt, J = 12.8, 7.8 Hz, 5/6H), 1.84 (dt, J = 12.5, 3.2 Hz, 1/6H), 1.69 (dd, J = 6.4, 1.3 Hz, 15/6H), 1.66 (dd, J = 6.4, 1.1 Hz, 3/6H), 1.10−0.96 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.4 (1/6C), 131.2 (5/6C), 129.1 (5/6C), 127.1 (1/6C), 86.1 (5/6C), 83.1 (1/6C), 78.7 (5/6C), 74.2 (5/6C), 73.8 (1/6C), 72.3 (1/6C), 64.3 (5/6C), 63.5 (1/6C), 41.34 (1/6C), 41.33 (5/6C), 17.9 (5/6C), 17.74 (5/6C), 17.71 (1/6C), 17.62 (2/6C), 17.61 (10/6C), 17.60 (1/6C), 17.57 (5/6C), 17.50 (1/6C), 17.4 (5/6C), 17.35 (1/6C), 17.31 (5/6C), 17.23 (5/6C), 17.22 (1/6C), 17.16 (1/6C), 17.15 (5/6C), 17.14 (1/6C), 13.68 (5/6C), 13.67 (1/6C), 13.64 (1/6C), 13.5 (5/6C), 13.4 (1/6C), 13.1 (5/6C), 12.75 (1/6C), 12.72 (5/6C); IR (film) 2943, 1730, 1464, 1036, 885 cm^{-1}; MS (FAB) m/z = 423 [M + Na]$^+$; HRMS (FAB) m/z [M + Na]$^+$ calcd for $C_{20}H_{40}O_4Si_2Na$ 423.2363, found 423.2357.

*Mixture of 2,5-trans-**34** and 2,5-cis-**35** (1:1).* Triol **12** (29.3 mg) gave a mixture of 2,5-*trans*-**34** and 2,5-*cis*-**35** (26.2 mg) in 93% yield: yield 93%; colorless oil; R_f = 0.30 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dqd, J = 15.3, 6.4, 1.0 Hz, 1/2H), 5.76 (dqd, J = 10.9, 7.0, 1.0 Hz, 1/2H), 5.54 (ddq, J = 15.3, 6.5, 1.5 Hz, 1/2H), 5.50 (ddq, J = 10.9, 9.0, 1.7 Hz, 1/2H), 4.57 (ddd, J = 8.7, 7.6, 1.0 Hz, 1/2H), 4.43 (ddt, J = 6.5, 4.4, 1.0 Hz, 1/2H), 4.29 (t, J = 6.9 Hz, 1/2H), 4.23 (dd, J = 4.6, 2.7 Hz, 1/2H), 4.12−3.73 (m, 4H), 1.76 (ddd, J = 6.5, 1.5, 0.9 Hz, 3/2H), 1.72 (dd, J = 7.0, 1.7 Hz, 3/2H), 1.11−0.99 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.0 (1/2C), 128.9 (1/2C), 128.8 (1/2C), 127.8 (1/2C), 84.6 (1/2C), 82.3 (1/2C), 81.3 (1/2C), 81.0 (1/2C), 80.5 (1/2C), 79.3 (1/2C), 78.8 (1/2C), 76.5 (1/2C), 64.3 (1/2C), 63.8 (1/2C), 17.7 (1/2C), 17.6 (1/2C), 17.59 (1/2C), 17.58 (1/2C), 17.57 (1/2C), 17.56 (1/2C), 17.55 (1/2C), 17.53 (1/2C), 17.49 (1/2C), 17.46 (1/2C), 17.44 (1/2C), 17.43 (1/2C), 17.36 (1/2C), 17.35 (1/2C), 17.29 (1/2C), 17.23 (1/2C), 17.19 (1/2C), 17.15 (1/2C), 13.7 (1/2C), 13.68 (1/2C), 13.64 (1/2C), 13.5 (1/2C), 13.4 (1/2C), 13.0 (1/2C), 12.7 (1/2C), 12.6 (1/2C); IR (film) 3444, 2943, 2867, 1716, 1464, 1037, 885 cm^{-1}; MS (FAB) m/z = 439 [M + Na]$^+$; HRMS (FAB) m/z [M + Na]$^+$ calcd for $C_{20}H_{40}O_5Si_2Na$ 439.2312, found 439.2309.

*(6aR,8S,9S,9aS)-2,2,4,4-Tetraisopropyl-8-((E)-prop-1-en-1-yl)-tetrahydro-6H-furo[3,2-f][1,3,5,2,4]trioxadisilocin-9-ol (**36**).* Triol **13** (31.5 mg) gave **36** (28.8 mg) in 95% yield: colorless oil; R_f = 0.30 (10% EtOAc in hexane); $[\alpha]_D^{20}$ −36.9 (c 1.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (dqd, J = 15.1, 6.4, 1.0 Hz, 1H), 5.45 (ddq, J = 15.1, 7.1, 1.5 Hz, 1H), 4.25 (t, J = 6.0 Hz, 1H), 4.14 (dd, J = 7.1, 4.5 Hz, 1H), 4.02 (m, 1H), 3.90−3.83 (m, 2H), 3.80 (brt, J = 4.5 Hz, 1H), 2.85 (brs, 1H), 1.71 (ddd, J = 6.4, 1.5, 0.6 Hz, 3H), 1.09−0.86 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.0, 128.8, 84.5, 82.6, 75.3, 72.6, 63.3, 18.0, 17.6, 17.5 (2C), 17.4, 17.3, 17.2, 17.19, 17.14, 13.5, 13.4, 13.0, 12.8; IR (film) 3526, 2944, 2867, 1464, 1037, 885 cm^{-1}; MS (FAB) m/z = 439 [M + Na]$^+$; HRMS (FAB) m/z [M + Na]$^+$ calcd for $C_{20}H_{40}O_5Si_2Na$ 439.2312, found 439.2317.

Stereochemical Assignment of the Cyclized Products. *General Procedure of the Deprotection of the Cyclic Bis-siloxy Group for Compounds **26**, **29**, **32**, and **33**.* To a solution of cyclic 1,3-disiloxanediyl-protected compounds (0.5 mmol) in THF (2.5 mL) was added a THF solution of tetrabutylammonium fluoride (1.5 mL, 1.0 M solution in THF) at 0 °C. The mixture was stirred for 10 min at the same temperature and condensed. The crude product was purified by column chromatography on silica gel eluted with EtOAc to give diol.

*Mixture of 2,5-trans-**37** and 2,5-cis-**37**.* A mixture of 2,5-*trans*-**37** and 2,5-*cis*-**37** (28 mg) was obtained in 93% yield from a mixture of 2,5-*trans*-**26** and 2,5-*cis*-**26** (83 mg): colorless oil; R_f = 0.30 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (ddd, J = 16.9, 10.0, 5.9 Hz, 3/4H), 5.83 (ddd, J = 16.9, 10.5, 5.3 Hz, 1/4H), 5.31 (td, J = 16.9, 1.3 Hz, 1/4H), 5.30 (td, J = 16.9, 1.3 Hz, 3/4H), 5.17−5.13 (m, 1H), 4.62−4.50 (m, 1H), 4.33−4.03 (m, 1H), 3.92 (q, J = 4.6 Hz, 3/4H), 3.89 (q, J = 4.8 Hz, 1/4H), 3.77−3.71 (m, 1H), 3.67−3.62 (m, 1H), 2.41 (dt, J = 13.2, 6.6 Hz, 1H), 2.17 (brs, 1H), 1.88−1.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2 (3/4C), 138.0 (1/4C), 116.0 (1/4C). 115.9 (3/4C), 87.1 (1/4C), 85.2 (3/4C), 79.7 (1/4C), 79.2 (3/4C), 73.6 (1/4C), 73.0 (3/4C), 63.3 (1/4C), 62.6 (3/4C), 41.6 (1/4C), 41.0 (3/4C); MS (EI) m/z = 144 [M]$^+$; HRMS (EI) m/z [M]$^+$ calcd for $C_7H_{12}O_3$ 144.0787, found 144.0780.

*(2R,3S,5R)-2-(Hydroxymethyl)-5-((E)-prop-1-en-1-yl)-tetrahydrofuran-3-ol (**40**).* Compound **40** (24.9 mg) was obtained in 87% yield from **29** (72.5 mg): colorless oil; R_f = 0.30 (EtOAc); $[\alpha]_D^{20}$ +12.9 (c 1.14, $CHCl_3$); H NMR (400 MHz, $CDCl_3$) δ 5.72 (1H, ddd, J = 15.2, 6.3, 0.7 Hz), 5.60 (1H, ddd, J = 15.2, 7.0, 1.4 Hz), 4.46 (1H, ddd, J = 7.6, 7.0, 6.6 Hz), 4.32 (1H, ddd, J = 6.7, 6.6, 5.1 Hz), 3.89 (1H, ddd, J = 5.1, 4.9, 4.0 Hz), 3.72 (1H, dd, J = 11.6, 4.0 Hz), 3.64 (dd, J = 11.6, 4.9 Hz), 2.38 (1H, ddd, J = 12.7, 6.6, 6.6 Hz), 1.81 (1H, ddd, J = 12.7, 7.6, 6.7 Hz), 1.71 (3H, ddd, J = 6.9, 6.3, 1.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1, 128.5, 84.8, 79.2, 73.2, 62.8, 41.5, 17.8; IR (film) cm^{-1} 3362, 2921, 1740, 1450, 1038, 927; EI-MS m/z 158 [M]$^+$; EI-HRMS m/z 158.0937 (calcd for $C_8H_{14}O_3$ 158.0943).

*Mixture of 2,5-trans-**42** and 2,5-cis-**43**.* A mixture of 2,5-*trans*-**42** and 2,5-*cis*-**43** (35.4 mg) was obtained in 97% yield from a mixture of 2,5-*trans*-**32** and 2,5-*cis*-**33** (92.1 mg): colorless oil; R_f = 0.30 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (dqd, J = 15.1, 6.5, 0.7 Hz, 5/6H), 5.64−5.55 (m, 2/6H), 5.44 (ddq, J = 15.1, 7.6, 1.5 Hz, 5/6H), 4.86 (ddd, J = 8.1, 7.6, 6.2 Hz, 1/6H), 4.55 (ddd, J = 9.8, 7.6, 5.5 Hz, 5/6H), 4.33 (ddd, J = 7.0, 6.6, 5.0 Hz, 1/6H), 4.29 (ddd, J = 6.4, 3.1, 2.3 Hz, 5/6H), 3.88 (ddd, J = 4.9, 4.4, 3.7 Hz, 1/6H), 3.84 (ddd, J = 4.8, 4.4, 3.1 Hz, 5/6H), 3.69 (dd, J = 11.6, 4.4 Hz, 5/6H), 3.76−3.64 (m, 2/6H), 3.62 (dd, J = 11.6, 4.8 Hz, 5/6H), 2.89 (brs, 2/6H), 2.59 (brs, 10/6H), 2.41 (ddd, J = 12.6, 6.6, 6.2 Hz, 1/6H), 1.98 (ddd, J = 13.2, 5.5, 2.1 Hz, 5/6H), 1.85 (ddd, J = 13.2, 9.8, 6.3 Hz, 5/6H), 1.72 (m, 1/6H), 1.71 (dd, J = 6.5, 1.5 Hz, 15/6H), 1.68 (dd, J = 6.2, 1.1 Hz, 3/6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5 (1/6C), 130.9 (5/6C), 129.7 (5/6C), 127.2 (1/6C), 86.9 (5/6C), 84.7 (1/6C), 79.7 (5/6C), 73.8 (5/6C), 73.5 (1/6C), 73.0 (1/6C), 63.4 (5/6C), 62.7 (1/6C), 42.0 (5/6C), 41.6 (1/6C), 17.9 (5/6C), 13.3 (1/6C); IR (film) 3353, 2920, 1716, 1455, 1037, 851 cm^{-1}; MS (EI) m/z = 158 [M]$^+$; HRMS (EI) m/z [M]$^+$ calcd for $C_8H_{14}O_3$ 158.0943, found 158.0941.

*General Procedure of Acylation of Compounds **37**, **40**, **42**, and **43** with Toluoyl Chloride and **28** with Benzoyl Chloride.* To a mixture of alcohol (0.2 mmol), triethylamine (223 μL, 1.6 mmol), and DMAP (2 mg, 0.016 mol) in CH_2Cl_2 (1 mL) was added acyl chloride (toluoyl chloride or benzoyl chloride; 0.6 to 0.8 mmol) at room temperature. The mixture was stirred for 10 h. Ice−water (5 mL) was added to the reaction mixture, and the mixture was extracted with CH_2Cl_2. The extract was washed with brine and dried over $MgSO_4$. Solvent was removed, and the residue was purified by column chromatography eluted with 5−10% EtOAc in hexane to give the corresponding acylated product.

Compounds 2,5-*trans*-**38** and 2,5-*cis*-**38** (58.7 mg) were obtained of from a mixture of 2,5-*trans*-**37** and 2,5-***cis***-**37** (28.2 mg) in 79% yield by toluoylation. They were separated in part to give pure 2,5-*trans*-**38** and 2,5-*cis*-**38** by HPLC.

*(2R,3S,5S)-3-(4-Methylbenzoyloxy)-2-(4-methylbenzoyloxymethyl)-5-vinyltetrahydrofuran (2,5-trans-**38**):* colorless oil; R_f = 0.30 (5% EtOAc in hexane); $[\alpha]_D^{20}$ +32.2 (c 0.29, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.92 (m, 4H), 7.26−7.22 (m, 4H), 5.88 (ddd, J = 17.0, 10.2, 5.8 Hz, 1H), 5.51 (dt, J = 6.1, 1.3 Hz, 1H), 5.36 (dt, J = 17.0, 1.2 Hz, 1H), 5.18 (dt, J = 10.2, 1.2 Hz, 1H), 4.67 (ddd, J = 10.6, 6.6, 5.2 Hz, 1H), 4.51 (dd, J = 4.9, 0.8 Hz, 2H), 4.12 (td, J = 3.6, 1.3 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.31 (ddd, J = 13.7, 5.2, 1.4 Hz, 1H), 2.08 (ddd, J = 13.7, 10.6, 6.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.3, 144.3, 143.9, 137.5, 129.89 (2C), 129.88 (2C), 129.35 (2C), 129.32 (2C), 127.3, 127.2, 117.4, 82.8, 80.4, 77.3, 64.9, 39.3, 21.89, 21.87; IR (film) 1718, 1448, 1020, 839 cm^{-1}; MS (CI) m/z = 381 [M + 1]$^+$; HRMS (CI) m/z [M + 1]$^+$ calcd for $C_{23}H_{25}O_5$: 381.1702, found 381.1708.

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*(2R,3S,5R)-3-(4-Methylbenzoyloxy)-2-(4-methylbenzoyloxymethyl)-5-vinyltetrahydrofuran (2,5-cis-**38**):* colorless oil; R_f = 0.32 (5% EtOAc in hexane); $[\alpha]_D^{20}$ +40.7 (*c* 0.49, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.89 (m, 4H), 7.25−7.21 (m, 4H), 6.01 (ddd, *J* = 17.0, 10.3, 6.5 Hz, 1H), 5.51 (ddd, *J* = 6.4, 3.5, 3.2 Hz, 1H), 5.31 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.17 (dt, *J* = 10.3, 1.2 Hz, 1H), 4.74 (dddd, *J* = 7.2, 6.5, 5.4 1.3 Hz, 1H), 4.53 (ddd, *J* = 4.4, 4.3, 3.2 Hz, 1H), 4.49 (d, *J* = 4.3 Hz, 2H), 2.71 (ddd, *J* = 13.7, 7.2, 6.4 Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.07 (ddd, *J* = 13.7, 5.4, 3.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.3, 144.3, 143.9, 137.5, 129.89 (2C), 129.88 (2C), 129.35 (2C), 129.32 (2C), 127.3, 127.2, 117.4, 82.8, 80.2, 77.3, 64.9, 39.2, 21.89, 21.87; IR (film) 1717, 1456, 1020, 927 cm^{-1}; MS (CI) *m*/*z* = 381 $[M + 1]^+$; HRMS (CI) *m*/*z* $[M + 1]^+$ calcd for $C_{23}H_{25}O_5$ 381.1702, found 381.1706.

*(2R,3S,5S)-3-(4-Methylbenzoyloxy)-2-(4-methylbenzoyloxymethyl)-5-((E)-prop-1-en-1-yl)tetrahydrofuran-3-ol (**41**).* Compound **41** (29.0 mg) was obtained from **40** (12.8 mg) in 91% yield by toluoylation of **40**: colorless oil; R_f = 0.30 (5% EtOAc in hexane); $[\alpha]_D^{20}$ +25.6 (*c* 1.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.91 (m, 4H,), 7.26−7.20 (m, 4H), 5.75 (dq, *J* = 15.1, 6.3, Hz, 1H), 5.64 (ddq, *J* = 15.1, 7.4, 1.3 Hz, 1H), 5.49 (ddd, *J* = 7.0, 4.2, 3.0 Hz, 1H), 4.68 (dt, *J* = 7.4, 6.7 Hz, 1H), 4.53−4.44 (m, 3H), 2.67 (ddd, *J* = 13.6, 7.0, 6.7 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.03 (ddd, *J* = 13.6, 6.6, 3.0 Hz, 1H), 1.72 (dd, *J* = 6.3, 1.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.3, 144.2, 143.9, 131.5, 129.9 (2C), 129.8 (2C), 129.3 (2C), 129.2 (2C), 128.8, 127.3, 127.1, 81.4, 80.1, 76.7, 64.9, 38.5, 21.88, 21.86, 17.9; IR (film) 1719, 1449, 1020, 932 cm^{-1}; MS (EI) *m*/*z* = 394 $[M]^+$; HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{24}H_{26}O_5$ 394.1780, found 394.1783.

Compounds 2,5-*trans*-**44** and 2,5-*cis*-**45** (71.6 mg) were obtained in 98% yield from a mixture of 2,5-*trans*-**42** and 2,5-*cis*-**43** (1:5) (29.3 mg) by toluoylation. They were separated in part to give pure 2,5-*trans*-**44** and 2,5-*cis*-**45** by HPLC.

*(2R,3S,5S)-3-(4-Methylbenzoyloxy)-2-(4-methylbenzoyloxymethyl)-5-((Z)-prop-1-en-1-yl)tetrahydrofuran (2,5-trans-**44**):* colorless oil; R_f = 0.30 (5% EtOAc in hexane); $[\alpha]_D^{20}$ +27.7 (*c* 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.91 (m, 4H), 7.26−7.21 (m, 4H), 5.68−5.59 (m, 2H), 5.51 (ddd, *J* = 7.1, 4.3, 2.9 Hz, 1H), 5.09 (dddd, *J* = 6.6, 6.4, 3.5, 3.3 Hz, 1H), 4.55−4.45 (m, 3H), 2.70 (ddd, *J* = 13.4, 7.1, 6.6 Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 1.98 (ddd, *J* = 13.4, 6.4, 4.3 Hz, 1H), 1.69 (dd, *J* = 5.3, 2.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.4, 144.2, 143.9, 131.0, 129.9 (2C), 129.8 (2C), 129.3 (2C), 129.2 (2C), 127.7, 127.3, 127.1, 81.4, 76.8, 74.4, 64.9, 38.9, 21.89, 21.86, 13.3; IR (film) 1717, 1455, 1020 cm^{-1}; MS (EI) *m*/*z* = 394 $[M]^+$; HRMS (CI) *m*/*z* $[M]^+$ calcd for $C_{24}H_{26}O_5$ 394.1780, found 394.1777.

*(2R,3S,5R)-3-(4-Methylbenzoyloxy)-2-(4-methylbenzoyloxymethyl)-5-((E)-prop-1-en-1-yl)tetrahydrofuran (2,5-cis-**45**):* colorless oil; R_f = 0.30 (5% EtOAc in hexane); $[\alpha]_D^{20}$ +14.0 (*c* 1.56, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.93 (m, 4H), 7.24−7.22 (m, 4H), 5.82 (qd, *J* = 15.0, 6.5 Hz, 1H), 5.50 (ddq, *J* = 15.0, 7.5, 1.5 Hz, 1H), 5.49 (m, 1H), 4.62 (ddd, *J* = 10.7, 7.5, 5.0 Hz, 1H), 4.49 (d, *J* = 4.3 Hz, 2H), 4.38 (td, *J* = 4.3, 2.1 Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.23 (ddd, *J* = 13.8, 5.0, 1.0 Hz, 1H), 2.05 (ddd, *J* = 13.8, 10.6, 6.1 Hz, 1H), 1.72 (dd, *J* = 6.5, 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.1, 143.9, 143.7, 130.2, 129.7, 129.69 (2C), 129.66 (2C), 129.1 (2C), 129.0 (2C), 127.1, 127.0, 82.2, 80.1, 76.7, 64.8, 39.1, 21.67, 21.64, 17.7; IR (film) 1719, 1450, 1020, 934 cm^{-1}; MS (EI) *m*/*z* = 394 $[M]^+$; HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{24}H_{26}O_5$ 394.1780, found 394.1776.

Benzoylation of a mixture of 2,5-*trans*-**28** and 2,5-*cis*-**28** (78.3 mg) and separation by HPLC gave 2,5-*trans*-**48** (39.3 mg) in 40% yield and 2,5-***cis*-48** (43.1 mg) in 44% yield.

*(6aR,8S,9S,9aR)-9-Benzoyloxy-2,2,4,4-tetraisopropyl-8-vinyltetrahydro-6H-furo[3,2-f][1,3,5,2,4]trioxadisilocine (2,5-cis-**48**):* colorless oil; R_f = 0.30 (5% EtOAc in hexane); $[\alpha]_D^{20}$ −7.78 (*c* 0.54, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.06 (m, 2H), 7.59−7.55 (m, 1H), 7.47−7.43 (m, 2H), 5.95 (ddd, *J* = 16.9, 10.5, 5.4 Hz, 1H), 5.51 (dt, *J* = 16.9, 1.3 Hz, 1H), 5.30 (dd, *J* = 5.0, 1.9 Hz, 1H), 5.24 (dt, *J* = 10.5, 1.2 Hz, 1H), 4.56 (ddd, *J* = 5.4, 1.9, 1.2 Hz, 1H), 4.42 (dd, *J* = 8.3, 5.0 Hz, 1H), 4.11−4.00 (m, 3H), 1.09−0.99 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 135.6, 133.2, 130.4, 129.9 (2C), 128.5 (2C), 117.2, 82.3, 81.7, 77.5, 70.4, 61.6, 17.6, 17.52, 17.51, 17.4, 17.2, 17.1, 17.07, 17.04, 13.6, 13.3, 12.9, 12.8; IR (film) 2944, 2867, 1727, 1464, 1036, 885 cm^{-1}; MS (FAB) *m*/*z* = 529 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{26}H_{42}O_6Si_2Na$ 529.2418, found 529.2414.

*(6aR,8R,9S,9aR)-9-Benzoyloxy-2,2,4,4-tetraisopropyl-8-vinyltetrahydro-6H-furo[3,2-f][1,3,5,2,4]trioxadisilocine (2,5-trans-**48**):* colorless oil; R_f = 0.30 (5% EtOAc in hexane); $[\alpha]_D^{20}$ −4.73 (*c* 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−8.05 (m, 2H), 7.58−7.54 (m, 1H), 7.46−7.42 (m, 2H), 5.93 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.73 (t, *J* = 4.2 Hz 1H), 5.37 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.22 (dt, *J* = 10.3, 1.3 Hz, 1H), 4.72 (ddt, *J* = 6.7, 4.1, 1.3 Hz, 1H), 4.54 (dd, *J* = 8.2, 4.2 Hz, 1H), 4.08 (dd, *J* = 8.4, 3.5 Hz, 1H), 4.01 (d, *J* = 3.5 Hz, 2H), 1.12−0.96 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 133.1, 133.0, 130.4, 129.9 (2C), 128.5 (2C), 118.8, 81.0, 80.2, 75.5, 73.1, 62.3, 17.6, 17.5 (2C), 17.4, 17.28, 17.23, 16.99, 16.96, 13.6, 13.3, 12.9, 12.8; IR (film) 2944, 2867, 1727, 1464, 1035, 885 cm^{-1}; MS (FAB) *m*/*z* = 529 $[M + Na]^+$; HRMS (FAB) *m*/*z* $[M + Na]^+$ calcd for $C_{26}H_{42}O_6Si_2Na$ 529.2418, found 529.2424.

*General Procedure for the Oxidative Cleavage of Alkenyl Bond and Successive Reduction for Compounds **38**, **41**, **44**, **45**, **27**, **30**, **31**, **34**, **35**, **36**, and **48**.* Ozone was bubbled into a solution of alkene (0.1 mmol) in CH_2Cl_2 (1.5 mL) at −78 °C. The reaction was monitored by TLC analysis. After the starting material was consumed on TLC, an excess of ozone was removed by nitrogen stream. Methanol (1 mL) and $NaBH_4$ (40 mg) were added. The cooling bath was removed, and the mixture was diluted with CH_2Cl_2. The solution was washed with water and brine and dried over $MgSO_4$. The crude product was purified by flash column chromatography on silica gel eluted with 30−40% EtOAc in hexane to give primary alcohol. Compounds 2,5-*trans*-**39** and 2,5-*cis*-**39** (35.4 mg) were obtained in 90% yield from a mixture of 2,5-*trans*-**38** and 2,5-*cis*-**38** (38.9 mg) by ozonolysis and reduction with $NaBH_4$. They were separated by HPLC. Ozonolysis of **41** (25.1 mg) and successive reduction gave 2,5-*trans*-**39** (21.7 mg) in 90% yield. Ozonolysis of a mixture of 2,5-*trans*-**44** and 2,5-*cis*-**45** (1:5) (70.6 mg) and successive reduction gave a mixture of 2,5-*trans*-**39** and 2,5-*cis*-**39** (61.8 mg) in 90% yield. HPLC purification of the mixture gave 2,5-*trans*-**39** and 2,5-*cis*-**39** in a ratio of 1:5.

*(2R,3S,5S)-5-Hydroxymethyl-3-(4-methylbenzoyloxy)-2-(4-methylbenzoyloxymethyl)tetrahydrofuran (2,5-trans-**39**):* colorless oil; R_f = 0.30 (40% EtOAc in hexane); $[\alpha]_D^{20}$ +55.8 (*c* 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.89 (m, 4H), 7.25−7.22 (m, 4H), 5.51 (ddd, *J* = 6.4, 3.4, 3.0 Hz, 1H), 4.53−4.45 (m, 3H), 4.42 (ddt, *J* = 7.6, 6.6, 3.8 Hz, 1H), 3.77−3.69 (m, 2H), 2.60 (ddd, *J* = 13.9, 7.0, 6.4 Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.09 (ddd, *J* = 13.9, 6.6, 3.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.3, 144.3, 144.1, 129.87 (2C), 129.84 (2C), 129.38 (2C), 129.34 (2C), 127.1, 126.9, 82.0, 79.9, 76.5, 64.9, 64.7, 33.8, 21.87, 21.86; IR (film) 3841, 2922, 1718, 1455, 1020, 840 cm^{-1}; MS (CI) *m*/*z* = 385 $[M + 1]^+$; HRMS (CI) *m*/*z* $[M + 1]^+$ calcd for $C_{22}H_{25}O_6$ 385.1651, found 385.1645.

*(2R,3S,5R)-5-Hydroxymethyl-3-(4-methylbenzoyloxy)-2-(4-methylbenzoyloxymethyl)tetrahydrofuran (2,5-cis-**39**):*.[14] colorless oil; R_f = 0.30 (40% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.91 (m, 4H), 7.26−7.23 (m, 4H), 5.48 (d, *J* = 6.1 Hz, 1H), 4.62 (dd, *J* = 11.4, 5.3 Hz, 1H), 4.49−4.39 (m, 3H), 3.92 (dd, *J* = 12.2, 2.7 Hz, 1H), 3.57 (dd, *J* = 12.2, 3.5 Hz, 1H), 2.42 (s, 3H), 2.41 (s, 3H), 2.39 (ddd, *J* = 13.8, 12.1, 6.1 Hz, 1H), 2.13 (ddd, *J* = 13.8, 5.5, 1.2 Hz, 1H).

Compound 2,5-*trans*-**46** (19.4 mg) was obtained in 89% yield from **27** (21.7 mg) by ozonolysis and reduction. Compound 2,5-*trans*-**46** (40.3 mg) was also obtained in 90% from **30** (45.5 mg). Ozonolysis of a mixture of 2,5-*trans*-**34** and 2,5-*cis*-**34** (47.0 mg) and successive reduction provided 2,5-*cis*-**46** (16.6 mg) in 36% yield and 2,5-*trans*-**46** (17.5 mg) in 38% yield. They were separated by flash column chromatography on silica gel eluted with 30% EtOAc in hexane. Compound 2,5-*cis*-**49** (15.3 mg) was obtained from 2,5-*cis*-**48** (23.8 mg) in 80% yield by ozonolysis and successive reduction. Compound

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2,5-*trans*-**49** (15.0 mg) was obtained in 94% yield from 2,5-*trans*-**48** (19.7 mg) by ozonolysis and successive reduction.

*(6aR,8R,9R,9aS)-8-(Hydroxymethyl)-2,2,4,4-tetraisopropyltetrahydro-6H-furo[3,2-f][1,3,5,2,4]trioxadisilocin-9-ol (2,5-trans-**46**):* colorless oil; R_f = 0.30 (10% EtOAc in hexane); $[\alpha]_D^{20}$ −33.4 (*c* 0.78, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 (dd, *J* = 7.3, 6.3 Hz, 1H), 4.19 (dd, *J* = 7.1, 6.3 Hz, 1H), 4.09 (dt, *J* = 7.1, 3.2 Hz, 1H), 4.00 (ddd, *J* = 12.5, 3.2 Hz, 1H), 3.94 (dd, *J* = 12.5, 4.1 Hz, 1H), 3.89−3.83 (m, 2H), 3.63 (ddd, *J* = 7.3, 4.1, 3.2 Hz, 1H), 2.91 (br d, 1H), 2.49 (br s, 1H), 1.13−0.98 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.5, 79.1, 78.6, 78.1, 62.2, 61.9, 17.6, 17.5, 17.49, 17.48, 17.27 (2C), 17.22, 17.1, 13.8, 13.4, 12.9, 12.7; IR (film) 3409, 2944, 2867, 1464, 1036, 885 cm^{-1}; MS (FAB) *m*/*z* = 429 [M + Na]$^+$; HRMS (FAB) *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{38}O_6Si_2Na$ 429.2105, found 429.2099.

*(6aR,8S,9R,9aS)-8-(Hydroxymethyl)-2,2,4,4-tetraisopropyltetrahydro-6H-furo[3,2-f][1,3,5,2,4]trioxadisilocin-9-ol (2,5-cis-**46**):* colorless oil; R_f = 0.30 (10% EtOAc in hexane); $[\alpha]_D^{20}$ −5.6 (*c* 0.64, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (t, *J* = 7.5 Hz, 1H), 4.22 (dd, *J* = 7.5, 7.0 Hz, 1H), 3.95 (dd, *J* = 12.3, 3.4 Hz, 1H), 3.89 (dd, *J* = 12.3, 4.9 Hz, 1H), 3.86 (ddd, *J* = 7.5, 4.9, 3.4 Hz, 1H), 3.81−3.69 (m, 3H), 2.21 (br-s, 1H), 2.01 (br-s, 1H), 1.12−0.99 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.4, 81.1, 78.0, 76.9, 62.6, 62.5, 17.4, 17.33, 17.32, 17.31, 17.17, 17.10, 17.0, 16.9, 13.5, 13.2, 12.8, 12.5; IR (film) 3402, 2944, 2867, 1464, 1036, 885 cm^{-1}; MS (FAB) *m*/*z* = 429 [M + Na]$^+$; HRMS (FAB) *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{38}O_6Si_2Na$ 429.2105, found 429.2111.

*(6aR,8S,9S,9aS)-8-(Hydroxymethyl)-2,2,4,4-tetraisopropyltetrahydro-6H-furo[3,2-f][1,3,5,2,4] trioxadisilocin-9-ol (2,5-cis-**49**):* colorless oil; R_f = 0.30 (30% EtOAc in hexane); $[\alpha]_D^{20}$ −22.2 (*c* 1.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 (dd, *J* = 7.8, 5.7 Hz, 1H), 4.07 (dd, *J* = 5.8, 2.6 Hz, 1H), 3.99 (d, *J* = 3.5 Hz, 2H), 3.97 (dt, *J* = 5.7, 3.1 Hz, 1H), 3.87 (dt, *J* = 7.8, 3.3 Hz, 1H), 3.81 (dd, *J* = 11.9, 3.3 Hz, 1H), 3.65 (dd, *J* = 11.9, 3.3 Hz, 1H), 1.12−0.97 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 84.9, 81.7, 72.5, 71.9, 63.3, 61.8, 17.6, 17.48 (2C), 17.43, 17.3, 17.2, 17.18, 17.12, 13.6, 13.3, 12.9, 12.8; IR (film) 3437, 2944, 2867, 1464, 1037, 885 cm^{-1}; MS (FAB) *m*/*z* = 429 [M + Na]$^+$; HRMS (FAB) *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{38}O_6Si_2Na$ 429.2105, found 429.2110.

*(6aR,8R,9S,9aS)-8-(Hydroxymethyl)-2,2,4,4-tetraisopropyltetrahydro-6H-furo-[3,2-f][1,3,5,2,4]trioxadisilocin-9-ol (2,5-trans-**49**):* colorless oil; R_f = 0.30 (30% EtOAc in hexane); $[\alpha]_D^{20}$ −14.2 (*c* 1.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36−4.31 (m, 2H), 4.13 (dd, *J* = 9.3, 5.3 Hz, 1H), 4.02−3.84 (m, 5H), 1.11−0.96 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.6, 79.9, 73.9, 73.1, 62.5, 62.2, 17.6, 17.49, 17.48, 17.47, 17.3, 17.2 (2C), 17.1, 13.5, 13.3, 12.9, 12.8; IR (film) 3430, 2944, 2867, 1464, 1036, 885 cm^{-1}; MS (FAB) *m*/*z* = 429 [M + Na]$^+$; HRMS (FAB) *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{38}O_6Si_2Na$ 429.2105, found 429.2100.

*Silylation of Compound **47**; (6aR,7aR,13aR,13bR)-2,2,4,4,10,10,12,12-Octaisopropylhexahydrofuro[3,2-f:4,5-f′]bis([1,3,5,2,4]trioxadisilocine) (**47**).* A mixture of 2,5-*trans*-**46** (19.4 mg, 0.048 mmol) and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (46 μL, 0.144 mmol) was stirred for 19 h at rt. The mixture was diluted with EtOAc and washed with water and brine. The organic extract was dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography on silica gel eluted with 5% EtOAc in hexane to give **47** (25 mg) in 80% yield: colorless oil; R_f = 0.50 (5% EtOAc in hexane); $[\alpha]_D^{20}$ −26.5 (*c* 0.81, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 (ddd, *J* = 8.0, 6.2, 3.9 Hz, 2H), 3.93 (dd, *J* = 12.1, 3.4 Hz, 2H), 3.85 (dd, *J* = 12.1, 6.1 Hz, 2H), 3.76−3.71 (m, 2H), 1.12−0.84 (m, 56H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.7 (2C), 78.6 (2C), 63.3 (2C), 17.7 (2C), 17.6 (2C), 17.55 (2C), 17.51 (2C), 17.3 (2C), 17.2 (2C), 17.13 (2C), 17.12 (2C), 13.6 (2C), 13.4 (2C), 13.1 (2C), 12.9 (2C); IR (film) 2943, 1095, 1034, 885 cm^{-1}; MS (FAB) *m*/*z* = 671 [M + Na]$^+$; HRMS (FAB) *m*/*z* [M + Na]$^+$ calcd for $C_{30}H_{64}O_7Si_4Na$ 671.3627, found 671.3624.

*Desilylation of **49** and Acetylation: (2R,3R,4S,5S)-2,5-Bis(acetoxymethyl)-3,4-bis(acetoxy)tetrahydrofuran (2,5-cis-**50**).*[15] Desilylation of 2,5-*cis*-**49** (11.8 mg, 0.029 mmol) was conducted in THF under the silylation conditions. After the reaction, solvent was removed, and pyridine (100 μL) and acetic anhydride (22 μL) were added at room temperature. The mixture was stirred overnight at room temperature. Water was added, and the mixture was extracted with CH_2Cl_2. The organic extract was washed with water and brine and dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel eluted with 40% EtOAc in hexane to give tetraacetate 2,5-*cis*-**50** (8.3 mg) in 86% yield: colorless oil; R_f = 0.46 (50% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17−5.16 (m, 2H), 4.32 (dd, *J* = 11.9, 3.2 Hz, 2H), 4.23−4.20 (m, 2H), 4.12 (dd, *J* = 11.9, 4.8 Hz, 2H), 2.11 (s, 6H), 2.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ171.3 (2C), 170.5 (2C), 80.0 (2C), 72.2 (2C), 64.2 (2C), 21.5 (2C), 21.3 (2C).

*(2R,3R,4S,5R)-2,5-Bis(acetoxymethyl)-3,4-bis(acetoxy)-tetrahydrofuran (2,5-trans-**50**).*[16] 2,5-*trans*-**50** (6.9 mg) was obtained in 76% yield from 2,5-*trans*-**49** (11.3 mg) under the same conditions described for the synthesis of 2,5-*cis*-**50**: colorless oil; R_f = 0.43 (50% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (t, *J* = 4.7 Hz, 1H), 5.27 (dd, *J* = 7.1, 4.9 Hz, 1H), 4.46 (dt, *J* = 7.1, 5.0 Hz, 1H), 4.31 (dd, *J* = 11.8, 3.0 Hz, 1H), 4.29−4.19 (m, 3H), 4.13 (dd, *J* = 11.8, 4.2 Hz, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.8, 169.9, 169.8, 77.8, 77.0, 72.0, 71.5, 63.6, 62.5, 21.0 (2C), 20.69, 20.67.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01154.

HPLC charts of compounds **38**, **39**, **44**, **45**, and **48** and ^{1}H and ^{13}C NMR spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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