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Use of Allyl, 2-Tetrahydrofuryl, and 2-Tetrahydropyranyl Ethers as Useful C_3-, C_4-, and C_5-Carbon Sources: Palladium-Catalyzed Allylation of Aldehydes

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Abstract: Palladium–diethylzinc or palladium–triethylborane catalytically promotes self-allylation of 2-(allyloxy)tetrahydrofurans, 2-(allyloxy)tetrahydropyrans, and their hydroxy derivatives on the rings (ribose, glucose, mannose, deoxyribose, deoxyglucose). All the reactions proceed at room temperature and provide polyhydroxyl products, sharing a structural motif of a homoallyl alcohol, in good to excellent yields with high levels of stereoselectivity. Useful C_3-unit elongation, which makes the best use of an allyl ether as a protecting group and a nucleophilic allylation agent, is demonstrated. Mechanisms for the *umpolung* reaction (of an allyl ether into an allylic anion) and stereoselectivity associated with allylation of aldehydes are discussed.

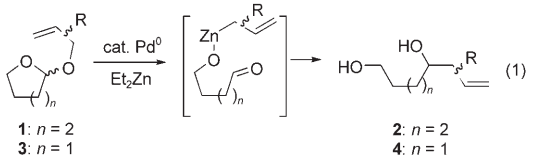
Keywords: allyl compounds · allylation · asymmetric catalysis · palladium

Introduction

2-Tetrahydrofuryl (2-THF) and 2-tetrahydropyranyl (2-THP) ethers[1] as well as allyl ethers[1,2] have been utilized most widely as the useful protecting groups of a hydroxy functionality. They are usually removed after the expected transformations having been completed. Needless to say, from practical, economical, and environmental view points, it is beneficial if they could be utilized not only as protecting groups, but also as carbon sources of target molecules.

Recently, we and others have developed efficient methods that enable the direct use of allyl alcohols as allyl anion equivalents under the catalysis of palladium.[3] The method which uses a Pd/Et_2Zn reaction system relies on the ability of a palladium(0) species to undergo oxidative addition to the C–O bond of an allyl alcohol and also the capability of a π-allylpalladium species, thus formed, to undergo transmetallation with Et_2Zn giving rise to an allylzinc species. Diethylzinc serves not only as a Lewis acid in the former process to render a hydroxy group a better leaving group, but also as a reducing agent in the latter process, converting a cationic π-allylpalladium species into an anionic allylzinc species and Pd^0 (Umpolung).[4]

The same method has been successfully applied to the activation of allyl ethers as allyl anion equivalents [Eq. (1)].[5] Thus, the combination of a catalytic amount of $Pd(OAc)_2$ and a stoichiometric amount of Et_2Zn has nicely promoted the conversion of 2-(allyloxy)tetrahydropyrans (**1**) and 2-(allyloxy)tetrahydrofurans (**3**) into 7-octen-1,5-diols (**2**) and 6-hepten-1,4-diols (**4**), respectively. Thus, the catalytic system has enabled allyl, 2-tetrahydrofuryl and 2-tetrahydropyranyl ethers to serve as C_3-, C_4-, and C_5-carbon sources, respectively. During this process, allyl ethers **1** or **3** might split into two fragments: allylzincs and ω-hydroxyaldehydes, which combine to give **2** or **4**, respectively.



This paper is a full account of our preliminary communication[5] and discloses a full scope of the reactivity, regioselectivity, and stereoselectivity associated with the unique self-allylation of **1** and **3** catalyzed by Pd/Et_2Zn. The method has been extended to 2-(allyloxy)-THF (**6**, **12** and **14**) and 2-

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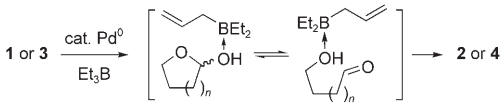
(allyloxy)-THP derivatives (**8** and **10**) bearing hydroxy substituents on their five- and six-membered skeletons. A new useful synthetic method that utilizes allyl alcohols both as protecting groups and as allylating agents is demonstrated. Some characteristic features of the catalytic self-allylation promoted by Pd/Et_3B, instead of Pd/Et_2Zn, are also discussed.

Results and Discussion

Self-allylation of 2-(allyloxy)tetrahydropyrans (1) and 2-(allyloxy)tetrahydrofurans (3) promoted by Pd^0/Et_2Zn or Pd^0/Et_3B: In the past few years, Et_2Zn and Et_3B, which are themselves feeble nucleophiles toward addition reaction to carbonyl compounds, have been recognized to play unique roles in the transition-metal catalyzed C–C bond formation reactions between carbonyl compounds and non-activated alkenes and alkynes. For example, under nickel catalysis,[6] Et_2Zn and Et_3B serve as a formal hydride donor or an alkyl donor and activate dienes and alkynes as nucleophiles to add to carbonyl compounds[7] and epoxides.[8]

Under palladium catalysis, Et_2Zn promotes allyl alcohols to undergo nucleophilic allylation of a wide range of carbonyl compounds, encompassing *aromatic* and *aliphatic* aldehydes as well as the less reactive ketones. On the other hand, Et_3B is only capable of promoting the allylation of *aromatic* aldehydes;[9] with this promoter, enolizable aliphatic aldehydes undergo both nucleophilic allylation at the carbonyl carbon (C1 allylation) and electrophilic allylation at the α-position of carbonyl groups (C_α allylation).[10] For example, as illustrated in Table 1, the reaction of cyclohexanecarboxaldehyde and cinnamyl alcohol provides a mixture of 1-cyclohexyl-2-phenyl-3-buten-1-ol (C1 allylation) and 1-(*trans*-cinnamyl)cyclohexanecarboxaldehyde (Cα allylation) in comparable amounts. The product distributions change dramatically depending on additives and the kinds of phosphane ligands (Table 1). Selective α-allylation of aliphatic aldehydes has been achieved in the presence of additives, LiCl/Et_3N.[10]

Interestingly, in sharp contrast to these, under the catalysis of Pd^0/Et_3B, 5-hydroxypentanal and 4-hydroxybutanal, aliphatic aldehydes derived from **1** and **3**, respectively [Eq. (2)], behave differently from ordinary enolizable aliphatic aldehydes and selectively undergo C1 allylation.



(2)

Table 2 outlines the scope of self-allylation of **1** and **3** under Pd/Et_3B catalysis, the conditions being identical to those applied in run 2, Table 1. Notably, all the reactions were clean and provided diols **2** and **4** in good yields. Neither aldol condensation products nor Cα-allylation products were detected at all.

The success of the self-allylation of **1** and **3** may be primarily attributed to a unique mechanism that the reaction follows. Under ordinary C1-allylation conditions, for example, Table 1, an aldehyde is exposed to reagents all the time and is susceptible to not only C1 allylation, but also Cα allylation (and aldol and other reactions as well via enolization). On the other hand, according to the mechanism shown in Equation (2), the generation of ω-hydroxyaldehyde synchronizes with the generation of allylborane. This electrophile–nucleophile pair might be generated in a small quantity (never larger than the amount of the catalyst), and each component would be present in close proximity to each other so as to react as soon as formed.

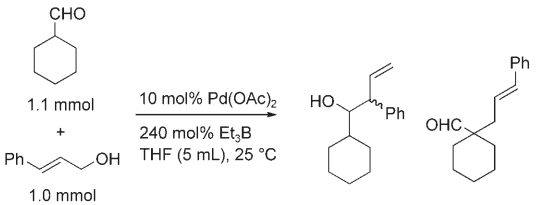
In Scheme 1 is illustrated a plausible catalytic cycle for the generation of allylborane and ω-hydroxyaldehyde. A palladium(0) species undergoes oxidative addition upon the allyl–oxygen ether bond activated by coordination with Et_3B. A π-allyl–palladium species, thus formed, might undergo allyl–ethyl exchange with BEt_3 to give an ethyl–palladium species, which undergoes β-H elimination regenerating a palladium(0) species. During the final step are also formed ethylene and an allyl(diethyl)borane–ω-hydroxyaldehyde complex, an active species for the self-allylation [Eq. (2)].

For the present self-allylation, both Ph_3P and nBu_3P work with similar efficiency. For example, by the use of Ph_3P instead of nBu_3P, **2a** was obtained in 80% yield (25°C, 30 h, c.f., run 1, Table 2). For clarity, Table 2 lists only the results obtained by the use of nBu_3P.

Table 2 also compiles the results obtained using Et_2Zn as a promoter. As was mentioned in our original paper,[5] the reaction medium optimized is rather unique, which consists of non-polar solvents: toluene (0.5–5.0 mL) and *n*-hexane (3.6 mL, the solvent of Et_2Zn) for 1 mmol scale experiments. In general, there seemed to be a general trend that the lower the polarity of the solvents, the better the yields of **2** or **4** (see below). Accordingly, the amount of toluene was minimized so as to make the reaction mixture homogeneous at the start at 0°C. The progress of the reaction is indicated visually by the increasing amount of white copious precipitate due to zinc alkoxides (see Experimental Section).

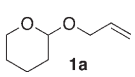
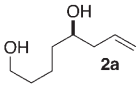
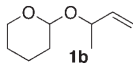
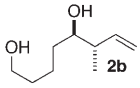
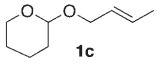
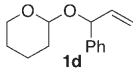
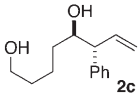
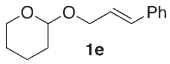
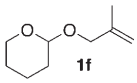
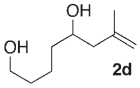
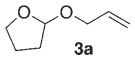
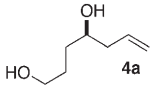
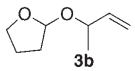
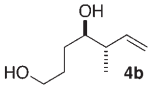
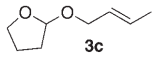
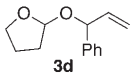
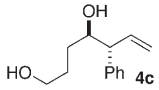
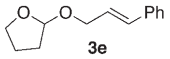
Generally, Et_2Zn promotes the allylation much faster and provides **2** or **4** in better yields within shorter periods of re-

Table 1. Allylation of cyclohexanecarboxaldehyde with cinnamyl alcohol promoted by Pd/Et_3B catalytic system.

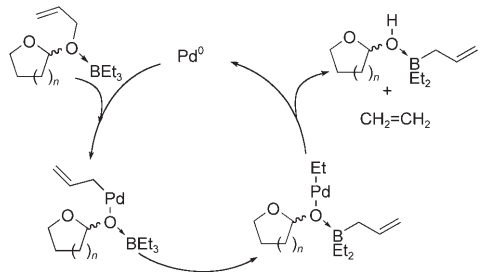


	Phosphane	*t* [h]	C1 allylation (%)	Cα allylation (%)
1	Ph_3P (20 mol%)	4	39	30
2	nBu_3P (20 mol%)	23	21	51

Table 2. Pd-catalyzed self-allylation of 2-(allyloxy)tetrahydropyrans **1** and 2-(allyloxy)tetrahydrofurans **3** promoted by Et_3B or Et_2Zn.

Run	**1** or **3**	Product	Et_3B[a]		Et_2Zn[b]	
			t [h]	Yield [*anti*,*syn*] (%)	*t* [h]	Yield [*anti*,*syn*] (%)
1	 **1a**	 **2a**	22	86	2	86
2	 **1b**	 **2b**	48	82 [4:1]	1	94 [2:1]
3	 **1c**	**2b**	23	67 [4:1]	1	94 [2:1]
4	 **1d**	 **2c**	60[c]	74 [6:1]	3	90 [3:1]
5	 **1e**	**2c**	48	66 [6:1]	2	85 [3:1]
6	 **1f**	 **2d**	31	73	3	72
7	 **3a**	 **4a**	16	56	2	87
8	 **3b**	 **4b**	43	83 [5:1]	1	78 [1:1]
9	 **3c**	**4b**	34	71 [5:1]	1	68 [1:1]
10	 **3d**	 **4c**	32[c]	70 [17:1]	2	70 [4:1]
11	 **3e**	**4c**	27	67 [5:1]	2	87 [3:1]

[a] **1** or **3** (1 mmol), $Pd(OAc)_2$ (10 mol%), nBu_3P (20 mol%), and Et_3B (2.4 mmol, 1 M in hexane) in dry THF (5 mL) at 25 °C under N_2. [b] **1** or **3** (1 mmol), $Pd(OAc)_2$ (10 mol%), nBu_3P (40 mol%), and Et_2Zn (3.6 mmol, 1 M in hexane) in dry toluene (5 mL) at 25 °C under N_2. [c] At 50 °C.



Scheme 1. Plausible catalytic cycle for the generation of allylborane species.

action time than Et_3B does. On the other hand, the reactions promoted by Et_3B have an advantage; they generally provide anti-diastereomers, that is *anti*-**2** and *anti*-**4**, in much higher selectivities.

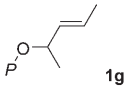
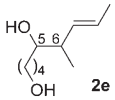
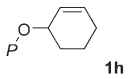
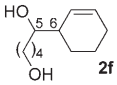
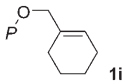
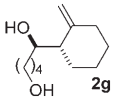
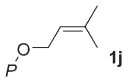
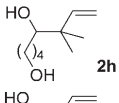
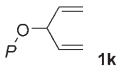
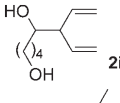
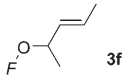
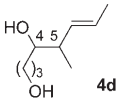
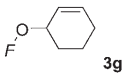
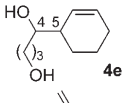
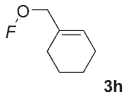
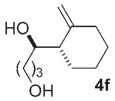
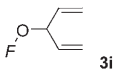
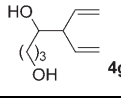
In Table 3 the reactions are summarized using Et_2Zn as a promoter. Under the catalysis of Pd/Et_3B, all the substrates listed in this table did not react in an expected way and either remained intact or provided, under forcing conditions, intractable mixtures only including **2** or **4** as minor components (TLC monitoring). Except for **1k** (and **3i**), these substrates share a common structural feature bearing two substituents on the allyl ether skeleton. Judging from the reaction times (Tables 2 and 3), these substituents significantly slow down the reaction.

The self-allylation of **1g** (run 1, Table 3) offers typical examples of the solvent polarity effects on the yields and reaction times: THF (5 mL), hexane (3.6 mL), 34%, 64 h; toluene (5 mL), hexane (3.6 mL), 63%, 60 h; toluene (2 mL), hexane (3.6 mL), 80%, 48 h; toluene (0.2 mL), hexane (3.6 mL), 89%, 34 h.

It is apparent, through Tables 2 and 3, that the allylation takes place regioselectively providing the most branched isomers exclusively, irrespective of the substitution patterns of the starting materials. For example, α-methylallyl ether **1b** (run 2, Table 2) and γ-methylallyl ether **1c** (run 3) provide the same branched product **2b**. Similar regioselectivities are also observed in many examples listed in Table 3.

In almost all cases, the stereoselectivity is also independent to the substitution pattern of the starting materials. Only one exception was observed for a pair of reactions of runs

Table 3. Pd-catalyzed self-allylation of **1** and **3** bearing allyl ether groups of some structural complexity.[a]

Run	**1** or **3**[b]	Product	*t* [h]	Yield (%)[c]
1	 **1g**	 **2e**	34	89 [2:1:2][d,e]
2	 **1h**	 **2f**	17	78 [2:1][d]
3	 **1i**	 **2g**	4	90 [12:1]
4	 **1j**	 **2h**	9	73
5	 **1k**	 **2i**	1	92
7	 **3f**	 **4d**	27	80 [2:1:1][d,f]
8	 **3g**	 **4e**	17	90 [2:1][d]
9	 **3h**	 **4f**	5	98 [5:1]
10	 **3i**	 **4g**	1	82

[a] **1** or **3** (1 mmol), $Pd(OAc)_2$ (10 mol%), nBu_3P (40 mol%), and Et_2Zn (3.6 mmol, 1 M in hexane) in dry toluene (0.5 mL) at 25 °C under N_2. [b] *P* and *F* stand for 2-tetrahydropyranyl and 2-tetrahydrofuryl groups, respectively. [c] Isolated yields of spectroscopically homogeneous materials. Ratios of diastereomers in brackets were determined on the basis of ^1H NMR spectra (400 MHz). [d] The stereochemistry around C5–C6 (for **2**) or C4–C5 (for **4**) are unknown. [e] (*E*)-**2e**/(*E*)-**2e′**/(*Z*)-**2e**. [f] (*E*)-**4d**/(*E*)-**4d′**/(*Z*)-**4d**.

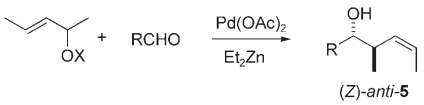
10 and 11, Table 2. Under the Pd/Et_3B catalysis, the substrate **3d** was so unreactive at 25 °C that it required heating at 50 °C for the reaction to proceed at a reasonable rate. Even under such conditions, **3d** showed much higher selectivity than **3e** did at 25 °C. The reason for the unusual behavior on reactivity and stereoselectivity associated with **3d** is not clear at the moment.[11] It should be noted that corresponding THP analogue **1d** exhibited similarly low reactivity, but provided the allylation product **2c** in the same selectivity as **1e** did under the Pd/Et_3B catalysis.

In a previous paper, we have demonstrated that under Pd/Et_2Zn umpolung conditions, *trans*-3-buten-2-yl benzoate[4b] reacts with benzaldehydes and provides one of the four possible diastereomers, (*Z*),*anti*-**5a**, in excellent selectivity (Table 4). Furthermore, the benzoate even reacts with an aliphatic aldehyde, providing (*Z*),*anti*-**5b** with high stereoselectivity. In the light of these precedents, the poor stereoselectivity observed for the self-allylation of **1g** is quite unexpected (run 1, Table 3).

In order to address the unusual stereoselectivity, we examined the reaction of **1g** with three equivalents of benzaldehyde and found that **1g** also furnished (*Z*),*anti*-**5a** exclusively (Table 4). Similar results, with somewhat lower stereoselectivity, are obtained for the reaction with an aliphatic aldehyde.

The results observed in Table 4 clearly indicate that 1) **1g** shows better performance than benzoate regarding the yields of products,[14] 2) allylzinc species generated from different sources (benzoate and **1g**) might be regarded structurally similar to each other, and 3) they *intermolecularly* react with aldehydes most likely via a transition state **I** shown in Scheme 2. The special structural feature associated with this six-membered chair-like transition state **I**, leading to thermodynamically less

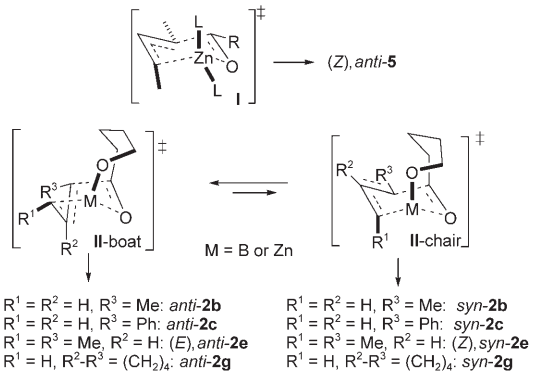
Table 4. Comparison of reactivity of **1g** and its benzoic acid derivative.[a]



(*Z*)-*anti*-**5**

	Aldehyde (R)	**1g**: X = 2-THP[a,c,d]	X = Bz[b,c]
1	Ph-	**5a**: 89 [100:0]	**5a**: 63 [100:0]
2	$PhCH_2CH_2$-	**5b**: 68 [83:17]	**5b**: 36 [94:6]

[a] a) Aldehyde (3 mmol), **1g** (1 mmol), $Pd(OAc)_2$ (10 mol%), nBu_3P (40 mol%), Et_2Zn (3.6 mmol, 1 M in hexane), dry toluene (0.5 mL) at 25 °C under N_2. b) Aldehyde (1.0 mmol), benzoate (1.2 mmol), $Pd(OAc)_2$ (10 mmol), nBu_3P (40 mol%), Et_2Zn (2.4 mmol, 1 M in hexane), THF (5 mL). c) Ratios of (*Z*),*anti*-**5** to a mixture of other isomers [(*Z*),*syn*-, (*E*),*syn*-, and (*E*),*anti*-**5**]. d) No **2e** was obtained.



Scheme 2. Plausible transition states for the self-allylation of **1**.

stable (*Z*)-isomers, is that the methyl group α to Zn occupies a quasi-axial position so as to minimize the steric repulsion against the two ligands on Zn and hence, renders a quasi-equatorial conformation of the methyl group γ to Zn most suitable.

The poor stereoselectivity associated with the *intramolecular* self-allylation of **1g**, on the other hand, might be attributed to the formation of a cyclic zinc ω-formylalkanolate species involving coordination of the aldehyde oxygen to Zn, which forces an aldehyde to approach to an allyl anion with its substituent in a quasi-axial position in such way as depicted in transition states **II**-boat and **II**-chair (Scheme 2). In these transition states, being characterized by a bicyclic [5.3.1] skeleton, both the aldehyde substituent and the Zn–alkoxide bond are forced to locate in quasi-diaxial positions. Under such circumstances, **II**-chair might not be necessarily preferred over **II**-boat. In fact, a transition state **II**-boat leading to (*E*)-**2e** seems be slightly lower in energy than a transitions state **II**-chair leading to (*Z*)-**2e**, as judged from the product distribution, [(*E*)-**2e** + (*E*)-**2e′**]/(*Z*)-**2e** 3:2 (run 1, Table 3 and footnote [e]). The product mixture of **2e** was inseparable; however, the *E*/*Z* (3:2) ratio could be deduced on the basis of the ^{1}H NMR spectra of the mixture. Unfortunately the relative stereochemistry around C5–C6 could not be determined.

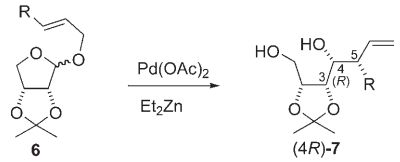
The *anti* stereoselectivity generally observed for a series of reactions of **1**, all through Tables 2 and 3, might be rationalized similarly, supposing **II**-boat as the most favored transition state. The remarkably high *anti*-selectivity observed for **1i** (run 3, Table 3) might further lend support for a transition state **II**-boat. In this particular case, **II**-boat might predominate over **II**-chair, since **II**-chair suffers from substantial steric repulsion between R^2–R^3 = $(CH_2)_4$ and the bicyclic C_5 bridge.

Self-allylation of carbohydrate derivatives 6, 8, 10, 12, and 14: The present self-allylation turned out to be successfully applicable to the allylation of carbohydrate derivatives (Tables 5–8 and Scheme 3). In all cases, the yields are satisfactory and range from 75 to 98% with one exception of **12b**. Unsymmetrically substituted ethers reacted as usual, providing the most branched isomers exclusively.

It might seem to be very challenging to examine the stereoselection for these carbohydrate derivatives, since in addition to the metal–alkoxide control discussed in the foregoing section (e.g., transition state **II**-chair or **II**-boat), the other ether coordination controls (the so called "Cram control" due to α-ether and remote ether controls due to β- or γ-ethers) might become a subject to be taken into consideration. However, the stereochemical outcomes turned out to be much simpler than expected; among many transition models, the Cram control was by far the most important and the metal–alkoxide control was less important. The remote ether groups seemed not to participate in controlling the stereoselection to any appreciable extent.

In order to assess the abilities of the Cram control, two sets of substrates, α-oxy-carbohydrates **6** (Table 5), **8** (Table 6), and **10** (Scheme 3) and α-deoxy-carbohydrates **12** and **14**, were subjected to the self-allylation (Tables 7 and 8). As is evident from the results shown in Tables 7 and 8, a series of α-deoxy ether derivatives did not show any preferences of all possible stereoisomers.[15] In sharp contrast to this, α-oxy ether derivatives showed an interesting stereoselectivity at a synthetically useful level (Tables 5 and 6 and Scheme 3).[16] The parent **6a** did not show any diastereoselectivity and provided a mixture of **7a** in a 1:1 ratio; however, surprisingly, as the steric size of allyl moieties increased, the diastereofacial selectivity (around C4 stereocenter) as well as the diastereoselectivity (around C5 stereocenter) increased gradually, and finally (4*R*,5*R*)-**7d** was obtained predominantly over the other stereoisomers (run 4). In sharp contrast to this, in the case of the glucose derivatives, even the parent **8a** exhibited a high level of diastereofacial selectivity and provided (6*R*)-**9a** in excellent yield. Similarly high diastereoselectivity was observed for the mannose derivative **10**, where a mixture of (6*S*)-**11**/(6*R*)-**11** was obtained in a 30:1 ratio in 90% yield.

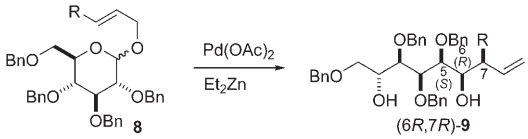
Table 5. Self-allylation of 2-oxycarbohydrate derivative **6**.[a]



	R	*t* [h]	Yield (%)
1	**6a**: R = H	2	**7a**: 91 [1:1]
2	**6b**: R = Me	2	**7b**: 88 [2:2:1:1]
3	**6c**: R = *t*Bu	5	**7c**: 85 [10:2:2:1]
4	**6d**: R = Ph	2	**7d**: 76 [15:2:1:1]

[a] Conditions: **6** (1 mmol), $Pd(OAc)_2$ (10 mol%), nBu_3P (40 mol%), and Et_2Zn (3.6 mmol, 1 M in hexane), dry toluene (2 mL) at 25 °C under N_2.

Table 6. Self-allylation of 2-oxycarbohydrate derivative **8**.[a]

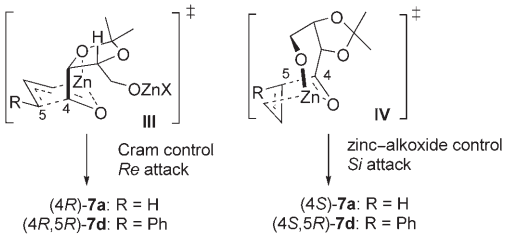


	R	*t* [h]	Yield (%)
1	**8a**: R = H	1.5	**9a**: 97 [12:1]
2	**8b**: R = Ph	5	**9b**: 72 [single]

[a] For reaction conditions, see Table 5; 1 mmol **8**.

Scheme 3. Self-allylation of 2-oxycarbohydrate derivative **10** (for reaction conditions, see Table 5; 1 mmol **10**).

The contrasting stereoselectivity that **6a** and a pair of **8a** and **10** display may be accounted for by supposing two types of transitions states, a Cram-control transition state **III** and a zinc–alkoxide control transition state **IV** (Scheme 4), the

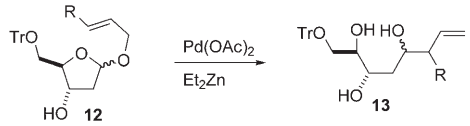


Scheme 4. Plausible transition states for the self-allylation of **6**.

latter having been invoked as a transition state for the self-allylation of **1** and **3** in the previous section. A Cram transition state **III** would give rise to (4*R*)-**7**, while a transition state **IV** would lead to the other enantiomer, (4*S*)-**7**. In the case of **6a**, these two transition states might equally operate, resulting in the formation of a 1:1 mixture of (4*R*)-**7a** and (4*S*)-**7a**. Although the precise mechanism is not clear at the moment, as the steric size of allyl ether moiety increases, a Cram transition state **III** would become favorable over a zinc–alkoxide transition state **IV**. One reason for this may be due to steric repulsion between the C_4 and C_3 bridges in a transition state **IV** of a bicyclo[4.3.1] structure, which might rapidly increase as the steric bulk of the C_3 bridge increases.

A Cram transition state **III** creating a (4*R*) stereocenter is correlated to the creation of a (5*R*) stereocenter (R ≠ H), as evidenced by the selective formation of (4*R*,5*R*)-**7d**.

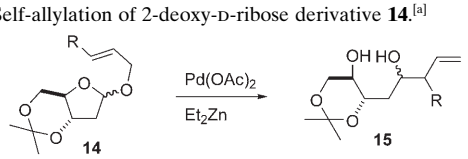
Table 7. Self-allylation of 2-deoxy-D-ribose derivative **12**.[a]



	R	*T* [°C]/*t* [h]	Yield (%)
1	**12a**: R = H	25/1	**13a**: 76 [1:1]
2	**12b**: R = Ph	25/5	**13b**: 49 [3:2:1:1]

[a] For conditions, see footnote of Table 5; 1 mmol **12**; the same amount of Et_2Zn was used, despite the presence of a hydroxy group.

Table 8. Self-allylation of 2-deoxy-D-ribose derivative **14**.[a]



	R	*T* [°C]/*t* [h]	Yield (%)
1	**14a**: R = H	25/3	**15a**: 98 [1:1]
1	**14b**: R = Ph	25/5	**15b**: 98 [2:2:1:1]

[a] For conditions, see footnote of Table 5; 1 mmol **14**.

In the cases of the self-allylation of **8** and **10**, as compared with **6**, a zinc–alkoxide transition state such as **IV** would become less favorable, since in these cases a tether connecting zinc and aldehyde becomes longer by one carbon unit (C_5 bridge vs C_4 bridge) and the repulsion between C_5 and C_3 bridges becomes more serious; hence even the parent **8a** and **10** would selectively react through a Cram transition state such as **III** to furnish **9a** and **11**, respectively.

Structure determination of products: Fortunately, **7d** formed a nice crystalline solid and the structure of (4*R*,5*R*)-**7d** was determined unequivocally by means of X-ray crystallographic analysis.[17] Chem 3D perspective view of the crystal structure is shown in Figure 1.

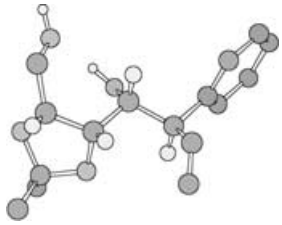
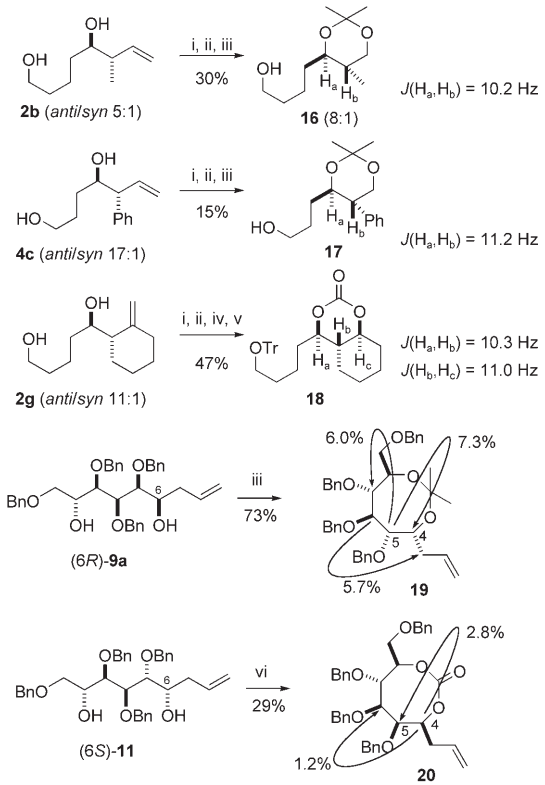


Figure 1. Chem 3D presentation of X-ray structure of (4*R*,5*R*)-**7d**. For clarity, only relevant hydrogen atoms are shown.

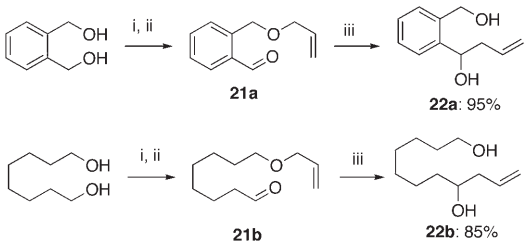
The structures of **2b**, **2g**, **4c**, **9a** and **11** were deduced on the basis of either coupling constants ^3J(H,H) or increments of area intensities by NOE experiments observed for the ^{1}H NMR spectra of their cyclic derivatives, which were prepared according to the standard procedures as outlined in Scheme 5.

The transformation of **2g** to **18** may deserve some comments; reduction with $NaBH_4$ of the cyclohexanone moiety of the ozonolysis product of **2g** took place selectively from the axial side[18] and bicyclic carbonate **18** was obtained as a single diastereomer. Two methyne protons H_a and H_c of **18** appeared separately and showed well-resolved absorptions with splitting patterns, being characteristic of axial orientation of *trans*-fused bicyclo[4.4.0]decane with a chair-conformation: H_a, 4.12 ppm (ddd, ^3J(H,H) = 2.7, 7.1, 10.2 Hz); H_c, 3.98 ppm (dt, ^3J(H,H) = 4.4, 11.0 Hz). The H_a and H_c protons of the acetonide derivative of **18** give almost the same chemical shifts and were give complex spectra in $CDCl_3$ or in C_6D_6.

An eight-membered cyclic acetonide such as **19** was prepared also from **9b**, however, no useful information to determine the C7 configuration was obtained by extensive examinations of the ^{1}H NMR spectra. Accordingly, the 7*R* configuration of (6*R*,7*R*)-**9b** was tentatively assigned by analogy with the stereoselectivity observed for (4*R*,5*R*)-**7d**. Acetonization of (6*S*)-**11** did not proceed at all under the conditions applied to the conversion of (6*R*)-**9a** to **19**, probably owing to steric repulsion of C4-allyl and C5-OBn groups against one of the acetonide methyl group. A cyclic carbonate **20** was prepared under rather forcing conditions (see Experimental Section).



Scheme 5. Structure determination of products. i) O_3/CH_2Cl_2 at −78 °C, ii) $NaBH_4$/MeOH-H_2O, iii) excess $Me_2C(OMe)_2$, cat. *p*-toluenesulfonic acid, iv) Ph_3CCl, Et_3N/CH_2Cl_2, v) $(Imd)_2CO$/THF, vi) $(Imd)_2CO$/NaH/dioxane. Tr = triphenylmethyl, Imd = imidazolyl.



Scheme 6. C_3 elongation of diols without protection–deprotection technique. i) NaH (210 mol%), allyl chloride (110 mol%), DMF, ii) pyridinium chlorochromate (200 mol%), AcONa (80 mol%), CH_2Cl_2; **21a** (40% overall), **21b** (35% overall). iii) $Pd(OAc)_2$ (10 mol%), nBu_3P (40 mol%), Et_2Zn (240 mol%, 1 M hexane), toluene (0.5 mL) at room temperature under N_2.

C_3 Unit elongation of diols in shorter steps: A general strategy for the C_3-unit elongation of diols may consists of 1) semi-protection of diols to form mono-alcohols, 2) oxidation of the mono-alcohols to aldehydes, 3) allylation of the aldehydes with an appropriate allylating agent, and 4) deprotection. In this sequence, an allylating agent must be prepared separately to perform the step 3. Accordingly, totally five steps are necessary to achieve this transformation.

According to the sequence of reactions illustrated in Scheme 6, the allylation of alcohol (step i) may be regarded as a semi-protection step of a diol and as a step of preparation of allylating agent as well. Furthermore, with a single step iii, can be achieved both nucleophilic allylation and deprotection, the steps 3 and 4 mentioned above. Thus, as compared with the existing general strategy, the process shown in Scheme 6 is shorter in steps by 2 and might be more efficient and economical. Both aromatic **21a** and aliphatic aldehydes **21b** undergo self-allylation smoothly at room temperature and provide diols **22a** and **22b** in quantitative yields, respectively.[19]

Self-allylation of 1a with reduced amounts of catalysts: All the experiments examined so far have used 10 mol% of $Pd(OAc)_2$. In Table 9 are summarized the results examined using reduced amounts of $Pd(OAc)_2$ together with the results examined under standard conditions for references (runs 1 and 4).

In practice, the experimental runs 2, 3, 5, and 6 were undertaken with fixed amounts of the catalyst/ligand (i.e., 0.1 mmol/0.2 mmol for Et_3B and 0.1 mmol/0.4 mmol for Et_2Zn), scaling up the amounts of **1a**, Et_3B or Et_2Zn, and the solvents. The reactions in runs 2 and 3 were not complete after 22 h at 25 °C and the reactions were continued at 55 °C.

As the loading amounts of the catalyst decrease, the isolated yields of **2a** gradually decrease and reaction times get longer. Yet, even with 1 mol% of the catalyst, the yields of **2a** still amount to about 60%.

Table 9. Self-allylation of **1a** under reduced loading of the catalysts.[a]

	$Pd(OAc)_2$(mol%)/nBu_3P(mol%)	Scale [mmol]	Et_nM	*T* [°C]/*t* [h]	Yield **2a** (%)
1	10/20	1	Et_3B	25/2	86
2	3/6	3.4	Et_3B	25/22→55/10	77
3	1/2	10	Et_3B	25/22→55/24	61
4	10/40	1	Et_2Zn	25/1	91
5	3/12	3.4	Et_2Zn	25/3	84
6	1/4	10	Et_2Zn	25/8	63

[a] See footnote [a] and [b] (toluene, 0.5 mL instead of 5.0 mL) in Table 2 for reaction conditions. For larger scale experiments, the amounts of Et_nM and the solvent were increased proportionally.

Conclusion

A full scope of allylation of aldehydes using allyl ethers as allyl nucleophiles is described. The reaction proceeds nicely under very mild conditions, in almost all cases at ambient temperature, under the catalysis of Pd/Et_3B or Pd/Et_2Zn. The Pd/Et_2Zn system is applicable to a wide structural variety of allyl ethers **1**, **3**, **6**, **8**, **10**, **12**, **14**, and **21**. The success of the reaction under the Pd/Et_3B conditions is limited only to allyl ethers **1** and **3** of structural simplicity, but this catalytic system shows higher diastereoselectivity than Pd/Et_2Zn does. Under the Pd/Et_2Zn conditions, a 2-oxy-THP group

serves as a better leaving group than a benzoate group and provides homoallyl alcohols in much better yields (Table 4). The allyl group and 2-THF and 2-THP groups of **3** and **1** have been, so far, recognized as protecting groups; however, through the present methodology, they have been proved to be the useful C_3-, C_4-, and C_5-building blocks, respectively. The allylation methodology of carbohydrates disclosed here may find wide application in chiral natural product synthesis. The chiral homoallyl alcohols obtained here may also be utilized for the chiral allyl group transfer via the 2-oxonium-Cope rearrangement, the methodology developed recently.[20]

Synthetic advantage using an allyl ether not only as a protecting group but also as an allyl nucleophile is demonstrated by short and high-yield C_3-unit elongation reactions of diols (Scheme 6).

Experimental Section

Solvents and reagents: Tetrahydrofuran was dried and distilled from benzophenone and sodium immediately prior to use under nitrogen atmosphere. Toluene was distilled over calcium hydride. $Pd(OAc)_2$ (purity 97.0%, Nakarai tesque), Ph_3P (purity 97+%, Wako), nBu_3P (purity 90.0+%, Tokyo Kasei), Et_3B (1.0 M hexane, KANTO), Et_2Zn (1.0 M hexane, KANTO), allyl alcohol (KANTO), 2,3-*O*-isopropylidene-D-erythronolactone (Aldrich), 2-deoxy-D-ribose (Tokyo Kasei), D-glucose (Wako), D-mannose (Wako), triphenylmethyl chloride (Tokyo Kasei), *o*-bis(hydroxymethyl)benzene (Tokyo Kasei), 2,2-dimethoxypropane (Tokyo Kasei), NaH (purity 60.0+%, Kishida Chemicals), *p*-toluenesulfonic acid (*p*-TsOH, Nakarai tesque), DIBAL (1.0 M hexane, KANTO), and dry DMF (purity 99.5%, water <0.005%, KANTO) were purchased and used as received.

Preparation of starting materials

2-(Allyloxy)tetrahydrofurans (1a–k) and 2-(allyloxy)tetrahydropyrans (3a–i): Tetrahydrofuran **1a** as a typical example: 3,4-Dihydro-2*H*-pyran (10 mL, 30 mmol) was added via syringe at 0°C under N_2 to a solution of allyl alcohol (1.55 mL, 20 mmol) and *p*-TsOH (0.34 mg, 2.0 mmol) in dry THF (10 mL). The mixture was stirred at ambient temperature overnight and then diluted with AcOEt and washed with sat. $NaHCO_3$ and brine, and the organic phase was dried ($MgSO_4$) and concentrated in vacuo to give an oil, which was purified by Kugelrohr distillation (100°C at 30 mm Hg) to give **1a** (2.73 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta=1.50$–1.90 (m, 6H), 3.52 (m, 1H), 3.89 (m, 1H), 3.99 (dd, ^3J(H,H) = 12.9, 6.1 Hz, 1H), 4.26 (dd, ^3J(H,H) = 12.9, 4.9 Hz, 1H), 4.66 (t, ^3J(H,H) = 3.4 Hz, 1H), 5.18 (d, ^3J(H,H) = 10.4 Hz, 1H), 5.30 (d, ^3J(H,H) = 16.9 Hz, 1H), 5.95 (dddd, ^3J(H,H) = 16.9, 10.4, 6.1, 4.9 Hz, 1H); IR (neat): $\tilde{\nu}=3078$, 2939, 2870, 1736, 1643, 1443, 1373, 1319, 1265, 1126, 1072, 1026, 995, 926, 871, 810, 748 cm^{-1}.

4-(Allyloxy)-tetrahydro-2,2-dimethylfuro[3,4-*d*][1,3]dioxole (6a): i) A solution of DIBAL (40.7 mmol, 1.0 M hexane) was added dropwise over 0.5 h into a well-stirred solution of 2,3-*O*-isopropylidene-D-erythronolactone (3.0 g, 19 mmol) in CH_2Cl_2 (60 mL) kept at −78°C. After stirring for 4 h at −78°C, successively methanol (15 mL) and water (15 mL) were added dropwise. After being allowed to warm to room temperature, Et_2O (150 mL) and $MgSO_4$ were added. The mixture was filtrated and the filter cake was washed with ether (60 mL). The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel (AcOEt/hexane 1:16) to give 2,3-*O*-isopropylidene-D-erythronolactol (2.47 g, 81%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta=$ 1.33 (s, 3H), 1.47 (s, 3H), 3.53 (brs, 1H), 4.02 (d, ^3J(H,H) = 10.2 Hz, 1H), 4.07 (dd, ^3J(H,H) = 10.2, 3.3 Hz, 1H), 4.57 (d, ^3J(H,H) = 5.8 Hz, 1H), 4.84 (dd, ^3J(H,H) = 5.8, 3.3 Hz, 1H), 5.42 (s, 1H); IR (neat): $\tilde{\nu}=3425$, 2986, 2947, 2885, 1458, 1380, 1335, 1211, 1165, 1072, 987, 910, 856 cm^{-1}.

ii) To a mixture of 2,3-*O*-isopropylidene-D-erythronolactol (1.0 g, 6.2 mmol) and NaH (0.3 g, 7.5 mmol) in dry DMF (10 mL) was added dropwise a solution of allyl bromide (0.83 g, 6.9 mmol) in dry DMF (10 mL) at 0°C under N_2. After stirring for 5 h at ambient temperature, the mixture was quenched with MeOH/H_2O (53 mL, 1:17) and extracted with Et_2O (2×200 mL). The combined extracts were dried ($MgSO_4$) and concentrated in vacuo to give an oil, which was purified by column chromatography on silica gel (AcOEt/hexane 1:10) to give **6a** (770 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta=1.32$ (s, 3H), 1.47 (s, 3H), 3.89 (dd, ^3J(H,H) = 10.4, 3.6 Hz, 1H), 3.95–4.01 (m, 2H), 4.13 (ddq, ^3J(H,H) = 12.9, 5.2, 1.4 Hz, 1H), 4.58 (d, ^3J(H,H) = 5.8 Hz, 1H), 4.80 (dd, ^3J(H,H) = 5.8, 3.6 Hz, 1H), 5.08 (s, 1H), 5.19 (dd, ^3J(H,H) = 10.2, 1.4 Hz, 1H), 5.27 (dd, ^3J(H,H) = 17.3, 1.4 Hz, 1H), 5.95 (dddd, ^3J(H,H) = 17.3, 10.2, 5.2, 3.6 Hz, 1H); IR (neat): $\tilde{\nu}=3082$, 2939, 2876, 1649, 1458, 1373, 1354, 1271, 1163, 1045, 1026, 995, 929, 858, 815, 764, 675 cm^{-1}. **6b–d** were prepared similarly.

2-(Allyloxy)-3,4,5-tris(benzyloxy)-6-(benzyloxymethyl)-tetrahydro-2*H*-pyran (8a): i) Conc. H_2SO_4 (0.023 g, 0.28 mmol) at ambient temperature was added to a solution of D-glucose (0.93 g, 5.2 mmol) in allyl alcohol (8.46 g, 0.145 mol). The mixture was stirred at 85°C for 3 h. The mixture was neutralized with 28% aq. NH_3 and volatile materials were removed in vacuo at room temperature to give an oil.

ii) To a mixture of the oil and NaH (1.10 g, 27.5 mmol) in dry DMF (40 mL) was added dropwise a solution of benzyl bromide (4.27 g, 25.0 mmol) in dry DMF (15 mL) at 0°C under N_2. After stirring for 24 h at ambient temperature, the mixture was quenched with MeOH/H_2O (112 mL, 1:8) and extracted with Et_2O (2×400 mL). The combined extracts were dried ($MgSO_4$) and concentrated in vacuo to give an oil, which was purified by column chromatography on silica gel (AcOEt/hexane 1:8) to give **8a** (1.68 g, 57%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta=3.40$–3.82 (m, 6H), 4.03 (m, 2H), 4.15 (dd, ^3J(H,H) = 13.4, 5.2 Hz, 1H), 4.42–5.06 (m, 8H), 5.20 (d, ^3J(H,H) = 11.3 Hz, 1H), 5.30 (d, ^3J(H,H) = 17.0 Hz, 1H), 5.95 (dddd, ^3J(H,H) = 17.0, 11.3, 6.1, 5.4 Hz, 1H); IR (neat): $\tilde{\nu}=3063$, 3030, 2866, 1647, 1585, 1496, 1454, 1359, 1329, 1261, 1209, 1072, 1028, 928, 819, 737 cm^{-1}. Compound **8b** was prepared similarly.

2-Allyloxy-3,4,5-tris(benzyloxy)-6-(benzyloxymethyl)-tetrahydro-2*H*-pyran (10): Conc. H_2SO_4 (50 μL, 1 mmol) at room temperature was added to a solution of D-mannose (1.8 g, 10 mmol) in allyl alcohol (10 mL, 147 mmol) and the mixture was stirred at 80°C for 2 h. The mixture was neutralized with 28% aq. ammonia (150 μL) and the excess amount of allyl alcohol was removed under reduced pressure (70°C/0.1 mm Hg). To the mixture of the residual oil and NaH (50% dispersion in mineral oil; 2.4 g, 50 mmol) in dry DMF (80 mL) was added a solution of benzyl bromide (6.0 mL, 50 mmol) dissolved in dry DMF (20 mL) through a dropping funnel at 0°C under nitrogen atmosphere. After stirring for 6 h at room temperature, the reaction mixture was quenched with aqueous methanol (100 mL; MeOH/water 1:8) and extracted with Et_2O (3×80 mL). The combined organic phase was dried ($MgSO_4$) and concentrated in vacuo to give a viscous oil, which was purified by column chromatography on silica gel (AcOEt/hexane 1:8) to give **10** (3.29 g, 58%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta=3.71$–3.81 (m, 3H), 3.92–4.00 (m, 2H), 4.15 (m, 1H), 4.50 (brd, ^3J(H,H) = 10.8 Hz, 1H), 4.56 (brs, 1H), 4.62–4.77 (m, 4H), 4.87 (brd, ^3J(H,H) = 10.8 Hz, 1H), 4.92 (brs, 1H), 5.14 (brd, ^3J(H,H) = 10.5 Hz, 1H), 5.20 (brd, ^3J(H,H) = 16.0 Hz, 1H), 5.84 (brddm, ^3J(H,H) = 10.5, 16.0 Hz, 1H), 7.16–7.45 (m, 20H); IR (neat): $\tilde{\nu}=3032$ (s), 2862 (s), 1103 (s), 741 cm^{-1} (s).

5-(Allyloxy)tetrahydro-2-(triphenylmethoxymethyl)furan-3-ol (12a): i) Conc. H_2SO_4 (0.07 g, 0.8 mmol) was added to a solution of 2-deoxy-D-ribose (2.5 g, 18.6 mmol) in allyl alcohol (101.8 g, 1.7 mol) and the mixture was stirred at 25°C for 1.5 h. The mixture was neutralized with 28% aq. NH_3 and volatile materials were removed in vacuo to give an oil. ii) To a mixture of the oil and Et_3N (2.67 g, 26.4 mmol) in dry CH_2Cl_2 (50 mL) was added dropwise a solution of triphenylmethyl chloride (6.58 g, 23.6 mmol) in dry CH_2Cl_2 (20 mL) at 0°C under N_2. After stirring at ambient temperature for 21 h, the mixture was washed with 0.1 M HCl, sat. $NaHCO_3$, and brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to give an oil, which was purified by column chroma-

tography on silica gel (AcOEt/hexane 1:7) to give **12a** (4.57 g, 59%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 1.87 (d, ^3J(H,H) = 4.4 Hz, 1H), 2.05 (dd, ^3J(H,H) = 13.5, 5.2 Hz, 1H), 2.21 (ddd, ^3J(H,H) = 13.5, 6.6, 1.6 Hz, 1H), 3.17 (dd, ^3J(H,H) = 9.6, 6.6 Hz, 1H), 3.31 (dd, ^3J(H,H) = 9.6, 5.2 Hz, 1H), 3.87 (dd, ^3J(H,H) = 12.6, 6.6 Hz, 1H), 3.98 (q, ^3J(H,H) = 5.5 Hz, 1H), 4.10 (m, 1H), 4.42 (m, 1H), 5.10 (d, ^3J(H,H) = 10.4 Hz, 1H), 5.15 (d, ^3J(H,H) = 17.3 Hz, 1H), 5.19 (m, 1H), 5.95 (dddd, ^3J(H,H) = 17.3, 10.4, 6.6, 5.5 Hz, 1H), 7.18–7.52 (m, 15H); IR (neat): $\tilde{\nu}$ = 3460, 2924, 2870, 1491, 1448, 1223, 1080, 1001, 926, 900, 839, 763, 746, 705, 636 cm^{-1}. Compound **12b** was prepared similarly.

6-(Allyloxy)tetrahydro-2,2-dimethyl-4*H*-furo[3,2-*d*][1,3]dioxine (14a): i) Conc. H_2SO_4 (0.04 g, 0.4 mmol) was added to a solution of 2-deoxy-D-ribose (1.34 g, 10 mmol) in allyl alcohol (26.7 g, 0.46 mol) and the mixture was stirred at 25°C for 1.5 h. The mixture was neutralized with 28% aq. NH_3 and volatile materials were removed in vacuo to give an oil. ii) A solution of the oil and *p*-TsOH (0.20 g, 1.1 mmol) in dry acetone (12 mL) was stirred for 12 h at ambient temperature under N_2. The mixture was diluted with AcOEt and the mixture was washed with sat. $NaHCO_3$ and brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to give an oil, which was purified by column chromatography on silica gel (AcOEt/hexane 1:3) to give **14a** (1.35 g, 63%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 1.35 (s, 3H), 1.52 (s, 3H), 1.84 (ddd, ^3J(H,H) = 14.5, 6.1, 4.6 Hz, 1H), 2.17 (dt, ^3J(H,H) = 14.5, 4.6 Hz, 1H), 3.74 (dd, ^3J(H,H) = 12.9, 2.5 Hz, 1H), 3.74 (dd, ^3J(H,H) = 12.9, 3.0 Hz, 1H), 4.01 (m, 1H), 4.15 (dt, ^3J(H,H) = 7.0, 2.5 Hz, 1H), 4.24 (m, 1H), 4.46 (q, ^3J(H,H) = 7.0 Hz, 1H), 4.92 (dd, ^3J(H,H) = 6.1, 4.6 Hz, 1H), 5.19 (d, ^3J(H,H) = 10.2 Hz, 1H), 5.28 (d, ^3J(H,H) = 17.0 Hz, 1H), 5.91 (dddd, ^3J(H,H) = 17.0, 10.2, 6.1, 4.6 Hz, 1H); IR (neat): $\tilde{\nu}$ = 2986, 2939, 2878, 2361, 1458, 1373, 1272, 1211, 1165, 1088, 995, 926, 864, 756 cm^{-1}. Compound **14b** was prepared similarly.

***o*-(Allyloxymethyl)benzaldehyde (21a)**: i) A solution of allyl chloride (0.85 g, 11.1 mmol) in dry DMF (12 mL) was added dropwise at 0°C under N_2 to a mixture of *o*-bis(hydroxymethyl)benzene (1.39 g, 10.0 mmol) and NaH (0.85 g, 21.1 mmol) in dry DMF (20 mL). After stirring for 24 h at ambient temperature, the mixture was quenched with MeOH/H_2O (48 mL, 1:3). The mixture was extracted with Et_2O (2× 150 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo to give an oil.

ii) To a solution of the oil in CH_2Cl_2 (30 mL) were added pyridinium chlorochromate (4.33 g, 20 mmol) and sodium acetate (0.66 g, 8 mmol) at room temperature. After stirring for 1 h at room temperature, the mixture was diluted with ether. The organic extract was concentrated in vacuo. The residue was purified by column chromatography on silica gel (AcOEt/hexane 1:8) to give **21a** (704 mg, 40% overall yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 4.14 (dt, ^3J(H,H) = 5.5, 1.6 Hz, 2H), 4.94 (s, 2H), 5.23 (dd, ^3J(H,H) = 10.4, 1.6 Hz, 1H), 5.32 (dd, ^3J(H,H) = 15.9, 1.6 Hz, 1H), 5.98 (ddt, ^3J(H,H) = 15.9, 10.4, 5.5 Hz, 1H), 7.26–7.88 (m. 5H), 10.22 (s, 1H); IR (neat): $\tilde{\nu}$ = 2855, 2783, 2360, 1697, 1597, 1350, 1195, 1080, 995, 925, 856, 756 cm^{-1}. Compound **21b** was prepared similarly.

General procedure for the self-allylation of 1 or 3 (with Et_2Zn, run 1, Table 2): Compound **1a** (142.2 mg, 1.0 mmol) and diethylzinc (3.6 mL, 1.0 M in hexane) via syringe at 0°C were added successively to a solution of $Pd(OAc)_2$ (22.6 mg, 0.1 mmol) and nBu$_3$P (80.9 mg, 0.4 mmol) in dry toluene (5 mL). The mixture was stirred at room temperature for 2 h under N_2 and then diluted with AcOEt, washed with 2 M HCl, sat. $NaHCO_3$, and brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to give an oil, which was purified by column chromatography on silica gel (AcOEt/hexane gradient 1:4 → 4:1) to give 7-octene-1,5-diol (**2a**) in (123 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 1.40–1.64 (m, 6H), 2.13–2.21 (m, 2H), 2.55 (brs, 2H), 3.62 (m, 1H), 3.63 (t, ^3J(H,H) = 6.2 Hz, 2H), 5.11 (d, ^3J(H,H) = 11.7 Hz, 1H), 5.12 (dm, ^3J(H,H) = 15.8 Hz, 1H), 5.83 (ddt, ^3J(H,H) = 15.8, 11.7, 7.7, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 21.8, 32.4, 36.3, 42.0, 62.3, 70.7, 117.6, 135.0; IR (neat): $\tilde{\nu}$ = 3331, 3076, 2936, 2864, 1641, 1435, 1340, 914 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_8H_{16}O_2$: 144.1150, found: 144.1098 (1) [M^+], 126 (4), 116 (2), 71 (100).

6-Methyloct-7-ene-1,5-diol (2b): ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 1.03 (d, ^3J(H,H) = 7.0 Hz, 3H), 1.37–1.65 (m, 6H), 2.42–3.12 (m, 2H), 2.20 (sext, ^3J(H,H) = 7.0 Hz, 1H, *anti*-isomer), 2.25 (sext, ^3J(H,H) = 7.0 Hz, 1H, *syn*-isomer), 3.41 (m, 1H, *anti*-isomer), 3.46 (m, 1H, *syn*-isomer), 3.65 (t, ^3J(H,H) = 6.0 Hz, 2H), 5.11 (d, ^3J(H,H) = 16.7 Hz, 1H), 5.12 (d, ^3J(H,H) = 10.8 Hz, 1H), 5.75 (ddd, ^3J(H,H) = 16.7, 10.8, 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *anti*-isomer: δ = 16.2, 69.9, 32.6, 33.7, 44.2, 62.5, 74.7, 116.1, 140.4; *syn*-isomer: δ = 14.4, 22.0, 32.6, 33.7, 43.7, 62.5, 74.7, 115.1, 141.1; IR (neat): $\tilde{\nu}$ = 3332, 3076, 2868, 1828, 1639, 1456, 1417, 1373, 1336, 912 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_9H_{18}O_2-H_2O$: 140.1201, found: 140.1201 (2) [M^+-H_2O], 103 (23), 85 (100), 67 (23).

6-Phenyl-7-octene-1,5-diol (2c): ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *anti*-isomer: δ = 1.32–1.66 (m, 6H), 2.29–2.42 (m, 2H), 3.22 (brt, ^3J(H,H) = 8.4 Hz, 1H), 3.54 (brt, ^3J(H,H) = 3.5 Hz, 2H), 3.75–3.80 (m, 1H), 5.16 (dd, ^3J(H,H) = 17.2, 0.7 Hz, 1H), 5.20 (dd, ^3J(H,H) = 9.9, 1.5 Hz, 1H), 6.11 (ddd, ^3J(H,H) = 17.2, 9.9, 9.3 Hz, 1H), 7.18–7.28 (m, 5H); *syn*-isomer: δ = 1.32–1.66 (m, 6H), 2.29–2.42 (m, 2H), 3.28 (brt, ^3J(H,H) = 8.4 Hz, 1H), 3.54 (brt, ^3J(H,H) = 3.5 Hz, 2H), 3.75–3.80 (m, 1H), 5.16 (dd, ^3J(H,H) = 17.2, 0.7 Hz, 2H), 5.20 (dd, ^3J(H,H) = 9.9, 1.5 Hz, 1H), 6.11 (ddd, ^3J(H,H) = 17.2, 9.9, 9.2 Hz, 1H), 7.18–7.28 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): *anti*-isomer: δ = 21.9, 32.4, 35.2, 57.5, 62.7, 73.8, 117.9, 126.6, 127.9, 128.1, 128.7, 129.2, 138.2, 141.4; *syn*-isomer: δ = 22.0, 32.6, 35.4, 57.4, 62.3, 74.1, 116.8, 126.8, 128.0, 128.1, 128.8, 129.0, 138.4, 144.2; IR (neat): $\tilde{\nu}$ = 3352, 3028, 2937, 2866, 1726, 1600, 1493, 1452, 1335, 1244, 916 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_{14}H_{20}O_2$: 220.1463, found: 220.1442 (3) [M^+], 147 (8), 118 (100), 103 (8), 85 (16).

7-Methyl-7-octene-1,5-diol (2d): ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 1.39–1.64 (m, 6H), 1.76 (s, 3H), 2.08–2.11 (m, 2H), 2.11 (dd, ^3J(H,H) = 13.5, 9.2 Hz, 1H), 2.21 (ddm, ^3J(H,H) = 13.5, 3.8 Hz, 1H), 3.65 (tm, ^3J(H,H) = 6.6 Hz, 2H), 3.73 (m, 1H), 4.80 (s, 1H), 4.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 21.9, 22.5, 32.6, 36.7, 46.2, 62.5, 68.9, 113.3, 142.9; IR (neat): $\tilde{\nu}$ = 3333, 3074, 2935, 2864, 1651, 1452, 1375, 889 cm^{-1}; HRMS (EI): *m*/*z* (%):calcd for $C_9H_{18}O_2$ 158.1307, found: 158.1340 (1) [M^+], 128 (1), 104 (3), 85 (100).

6-Methyl-7-nonene-1,5-diol (2e): ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 0.99 (d, ^3J(H,H) = 6.5 Hz, 3H), 1.32–1.62 (m, 6H), 1.63 (dd, ^3J(H,H) = 5.1, 1.8 Hz, 3H), 2.01 (brs, 2H), 2.53 (dm, ^3J(H,H) = 7.0 Hz, 1H), 3.35 (m, 1H), 3.65 (tm, ^3J(H,H) = 5.7 Hz, 2H), 5.26 (ddq, ^3J(H,H) = 10.3, 8.8, 1.8 Hz, 1H), 5.62 (dq, ^3J(H,H) = 10.6, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 15.0, 16.8, 21.9, 33.7, 37.6, 43.2, 62.7, 74.9, 127.2, 133.0; IR(neat): $\tilde{\nu}$ = 3344, 2935, 2869, 1726, 1454, 1375, 1259, 1055, 970, 921 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_{10}H_{20}O_2$ 172.1463, found: 172.1465 (10) [M^+], 171(7), 155 (7), 142 (14), 137 (100), 136 (14).

1-(2-Cyclohexenyl)pentane-1,5-diol (2f): a mixture in a ratio of 2:1; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 1.34–1.47 (m, 2H), 1.68–1.87 (m, 4H), 1.96–2.02 (m, 2H), 2.18–2.24 (m, 1H), 3.46 (ddm, ^3J(H,H) = 8.4, 5.1 Hz, 1H), 3.56 (ddd, ^3J(H,H) = 5.8, 5.5, 4.8 Hz, 1H, minor), 3.66 (t, ^3J(H,H) = 6.2, 1H), 5.69 (dm, ^3J(H,H) = 10.3 Hz, 1H), 5.55 (dm, ^3J(H,H) = 10.3 Hz, 1H, minor), 5.85 (ddm, ^3J(H,H) = 10.3, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): major δ = 21.8, 22.3, 25.3, 25.9, 32.7, 33.4, 41.5, 62.8, 75.4, 126.9, 130.2; minor isomer: δ = 21.5, 22.4, 22.9, 25.3, 32.7, 34.3, 41.5, 62.9, 74.5, 128.7, 130.5; IR (neat): $\tilde{\nu}$ = 3344, 3024, 2931, 2862, 1649, 1448, 1435, 1105, 1028 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_{11}H_{20}O_2$ 184.1463, found: 184.1460 (0.2) [M^+], 167.1428 (0.4), 104 (100).

1-(2-Methylenecyclohexyl)pentane-1,5-diol (2g): a mixture in a ratio of 12:1; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 1.38 (m, 1H), 1.43–1.53 (m, 3H), 1.56–1.67 (m, 6H), 1.67–1.74 (m, 2H), 1.83 (s, 2H), 2.13 (dt, ^3J(H,H) = 9.9, 4.8 Hz, 1H), 2.17 (t, ^3J(H,H) = 6.2 Hz, 2H), 3.67 (t, ^3J(H,H) = 6.2 Hz, 2H), 3.78 (ddd, ^3J(H,H) = 9.2, 8.8, 2.2 Hz, 1H), 4.75 (d, ^3J(H,H) = 2.2 Hz, 1H), 4.66 (s, 1H, minor), 4.86 (m, 1H), 4.73 (s, 1H, minor); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): major isomer: δ = 21.6, 22.4, 28.1, 29.0, 32.8, 33.0, 33.5, 50.1, 69.1, 70.2, 110.3, 149.8; minor isomer: δ = 22.1, 23.1, 27.8, 28.5, 32.6, 34.6, 34.9, 49.5, 60.4, 70.2, 107.9, 150.5; IR (neat): $\tilde{\nu}$ = 3342, 2932, 2858, 1645, 1447, 1058, 889 cm^{-1}; HRMS

(EI): *m/z* (%): calcd for $C_{12}H_{22}O_2-H_2O$: 180.1514, found: 180.1208 (10) [M^+-H_2O], 179 (100).

6,6-Dimethyl-7-octene-1,5-diol (2h): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.00 (s, 6H), 1.25 (m, 1H), 1.36 (m, 1H), 1.45–1.56 (m, 2H), 1.58–1.70 (m, 2H), 3.25 (dd, ^3J(H,H) = 10.3, 1.7 Hz, 2H), 3.62 (t, ^3J(H,H) = 3.1 Hz, 2H), 5.03 (dd, ^3J(H,H) = 17.2, 1.5 Hz, 1H), 5.06 (dd, ^3J(H,H) = 11.0, 1.5 Hz, 1H), 5.82 (dd, ^3J(H,H) = 17.6, 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 22.4, 22.9, 23.2, 31.0, 32.5, 62.5, 78.2, 113.1, 145.6; IR (neat): $\tilde{\nu}$ = 3354, 3082, 2941, 2869, 1637, 1460, 1413, 1379, 1361, 912 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{10}H_{20}O_2-H_2O$: 155.1436, found: 155.1402 (47) [M^+-H_2O], 139 (100), 137 (99), 124 (31).

6-Vinyl-7-octene-1,5-diol (2i): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.35–1.86 (m, 8H), 2.80 (brq, ^3J(H,H) = 7.4 Hz, 1H), 3.56 (m, 1H), 3.64–3.68 (m, 2H), 5.12 (dm, ^3J(H,H) = 10.1 Hz, 1H), 5.16 (dm, ^3J(H,H) = 15.5 Hz, 1H), 5.17 (dm, ^3J(H,H) = 15.1 Hz, 1H), 5.79 (ddd, ^3J(H,H) = 15.1, 10.7, 4.7 Hz, 1H), 5.85 (ddd, ^3J(H,H) = 15.5, 10.1, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 22.0, 32.6, 33.8, 55.0, 62.8, 73.2, 116.9, 117.6, 137.0, 137.6; IR (neat): $\tilde{\nu}$ = 3344, 3078, 2937, 2866, 2360, 2343, 1636, 1458, 1418, 1338, 1056, 1028, 1000, 912 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{10}H_{18}O_2$ 170.1307, found: 170.1242 (1) [M^+], 169.1293 (0.2), 153.1381 (0.3), 104 (100).

6-Heptene-1,4-diol (4a): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.39–1.73 (m, 4H), 2.17–2.31(m, 2H), 3.37 (brs, 2H), 3.60–3.72 (m, 2H), 5.11 (d, ^3J(H,H) = 11.0 Hz, 1H), 5.12 (d, ^3J(H,H) = 16.1 Hz, 1H), 5.82 (ddt, ^3J(H,H) = 16.5, 11.0, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 29.2, 33.8, 42.1, 62.9, 70.6, 118.0, 134.8; IR (neat): $\tilde{\nu}$ = 3333, 3076, 2935, 2634, 1641, 1435, 1344, 1057, 1011, 914 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_7H_{14}O_2$ 131.1099, found: 131.1080 (3) [M^+], 115 (2), 112 (4), 89 (100).

5-Methyl-6-heptene-1,4-diol (4b): *anti*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.03 (d, ^3J(H,H) = 7.0 Hz, 2H), 1.44 (m, 1H), 1.59–1.73 (m, 3H), 2.23 (dq, ^3J(H,H) = 8.1, 7.0 Hz, 1H), 3.29 (brs, 1H), 3.45 (m, 1H), 3.58–3.70 (m, 2H), 5.09 (d, ^3J(H,H) = 18.3 Hz, 1H), 5.10 (d, ^3J(H,H) = 11.5 Hz, 1H), 5.76 (ddd, ^3J(H,H) = 8.1, 18.3, 11.5 Hz, 1H); *syn*-isomer: δ = 1.04 (d, ^3J(H,H) = 7.0 Hz, 2H), 1.37–1.50 (m, 1H), 1.60–1.73 (m, 3H), 2.23 (dq, ^3J(H,H) = 8.1, 7.0 Hz, 1H), 3.29 (brs, 1H), 3.45 (m, 1H), 3.58–3.70 (m, 2H), 5.05 (d, ^3J(H,H) = 10.4 Hz, 1H), 5.06 (d, ^3J(H,H) = 17.4 Hz, 1H), 5.78 (ddd, ^3J(H,H) = 17.4, 10.4, 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): *anti*-isomer: δ = 16.2, 29.3, 31.1, 44.3, 62.8, 74.8, 116.1, 140.4; *syn*-isomer: δ = 14.7, 29.5, 31.3, 43.9, 62.8, 74.9, 115.1, 141.1; IR (neat): $\tilde{\nu}$ = 3333, 3078, 2937, 2868, 1639, 1456, 1417, 1373, 1338, 912 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_8H_{16}O_2$: 144.1150, found: 144.1176 (6) [M^+], 126 (100).

5-Phenyl-6-heptene-1,4-diol (4c): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *anti*-isomer: δ = 1.36 (m, 1H), 1.52 (m, 1H), 1.60–1.66 (m, 2H), 2.87 (brs, 1H), 3.24 (brt, ^3J(H,H) = 8.2 Hz, 2H), 3.50–3.66 (m, 2H), 3.81(tm, ^3J(H,H) = 8.2 Hz, 1H), 5.18 (dm, ^3J(H,H) = 16.9 Hz, 1H), 5.20 (dm, ^3J(H,H) = 9.5 Hz, 1H), 6.12 (ddd, ^3J(H,H) = 16.9, 10.3, 9.5 Hz, 1H), 7.18–7.35 (m, 5H); *syn*-isomer: δ = 1.43 (m, 1H), 1.66–1.75 (m, 2H), 1.83 (m, 1H), 2.87 (brs, 1H), 3.30 (brt, ^3J(H,H) = 8.4 Hz, 2H), 3.50–3.66 (m, 2H), 3.88 (tm, ^3J(H,H) = 8.4 Hz, 1H), 5.11 (d, ^3J(H,H) = 11.4 Hz, 1H), 5.12 (d, ^3J(H,H) = 16.1 Hz, 1H), 6.02 (ddd, ^3J(H,H) = 16.1, 11.0, 9.5 Hz, 1H), 7.18–7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): *anti*-isomer: δ = 29.3, 31.5, 57.6, 63.0, 74.0, 118.0, 126.8, 128.0, 128.8, 138.4, 141.5; syn-isomer: δ = 29.3, 31.5, 57.6, 63.0, 74.3, 117.0, 127.0, 128.0, 128.5, 138.4, 140.9; IR (neat): $\tilde{\nu}$ = 3344, 3028, 2873, 1637, 1601, 1492, 1452, 1001, 916 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{13}H_{18}O_2-OH$: 189.1279, found: 189.1295 (1) [M^+-OH], 118 (100), 89 (10).

5-Methyl-6-octene-1,4-diol (4d): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.00 (d, *J* = 6.6 Hz, 1H), 1.43 (m, 1H), 1.62–1.76 (m, 7H), 2.25 (dddd, ^3J(H,H) = 0.7, 6.6, 8.8, 17.5 Hz, 1H), 2.79 (brs, 1H), 3.37 (m, 1H), 3.59–3.72 (m, 2H), 5.25 (ddq, ^3J(H,H) = 16.2, 11.0, 1.8 Hz, 1H), 5.61 (dddd, ^3J(H,H) = 0.7, 7.0, 11.0, 11.7 Hz, 1H); ^{13} C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 15.3, 16.7, 29.3, 31.1, 42.9, 62.9, 75.0, 126.1, 132.9; IR (neat): $\tilde{\nu}$ = 3340, 2933, 2873, 1448, 1375, 1056, 977 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_9H_{18}O_2-H_2O$: 141.1279, found: 141.1183 (1) [M^+-H_2O], 140 (1), 71 (100).

1-(2-Cyclohexenyl)butane-1,4-diol (4e): a mixture of diastereomers in a ratio of 2:1; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.39 (m, 1H), 1.48–1.58 (m, 2H), 1.60–1.81 (m, 6H), 1.96–2.02 (brs, 2H), 2.20–2.24 (m, 2H), 3.49 (m, 1H), 3.58 (m, 1H), 3.70 (tm, ^3J(H,H) = 5.6 Hz, 2H), 3.66 (tm, ^3J(H,H) = 5.85 Hz, 2H), 5.69 (dm, ^3J(H,H) = 10.3 Hz, 1H), 5.55 (dm, ^3J(H,H) = 10.3 Hz, 1H), 5.84 (dm, ^3J(H,H) = 10.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) major isomer: δ = 21.7, 23.0, 25.3, 29.6, 31.7, 41.6, 63.0, 75.4, 126.8, 129.9; minor isomer: δ = 21.4, 23.8, 25.7, 29.7, 30.9, 41.7, 63.0, 74.6, 128.3, 130.4; IR(neat): $\tilde{\nu}$ = 3330, 3024, 2930, 2864, 2845, 1435, 1055, 1011, 970 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{10}H_{18}O_2$: 170.1307, found: 170.1279 (3) [M^+], 152 (24), 137 (100).

1-(2-Methylenecyclohexyl)butane-1,4-diol (4f): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): a mixture in a ratio of 5:1; δ = 1.38–1.56 (m, 4H), 1.60–1.68 (m, 2H), 1.69–1.82 (m, 3H), 1.88 (m, 1H), 2.13–2.20 (m, 2H), 2.17 (s, 1H), 2.78 (m, 1H), 3.66–3.73 (m, 2H), 3.82 (tm, ^3J(H,H) = 8.2 Hz, 1H), 4.67 (s, 1H, minor), 4.74 (s, 1H, minor), 4.78 (m, 1H), 4.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): major isomer: δ = 22.3, 28.0, 29.0, 30.8, 32.9, 49.9, 63.0, 69.1, 110.4, 149.4; minor isomer: δ = 22.9, 28.4, 30.8, 32.4, 34.4, 49.6, 63.0, 70.2, 108.0, 150.3; IR(neat): $\tilde{\nu}$ = 3344, 2932, 2856, 1447, 1055, 1007, 889 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{11}H_{20}O_2$: 184.1463, found: 184.1421 (3) [M^+], 166 (58), 151(100).

5-Vinyl-6-heptene-1,4-diol (4g): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.47 (m, 1H), 1.62–1.75 (m, 3H), 2.81 (brdt, ^3J(H,H) = 5.9, 7.7 Hz, 1H), 3.15 (brs, 2H), 3.54–3.70 (m, 3H), 5.12 (dm, ^3J(H,H) = 17.2 Hz, 1H), 5.13 (dm, ^3J(H,H) = 10.6 Hz, 1H), 5.14 (dm, ^3J(H,H) = 17.2 Hz, 1H), 5.18 (dm, ^3J(H,H) = 10.3 Hz, 1H), 5.81 (ddd, ^3J(H,H) = 17.2, 10.6, 7.7 Hz, 1H), 5.84 (ddd, ^3J(H,H) = 17.2, 10.3, 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 29.3, 31.3, 54.9, 62.7, 73.3, 116.8, 117.3, 137.1, 137.6; IR (neat): $\tilde{\nu}$ = 3332, 3078, 2941, 2873, 1633, 1417, 1055, 999, 916 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_9H_{16}O_2$: 156.1150, found: 156.1135 (11) [M^+], 138 (100).

Intermolecular allylation of aldehydes with 1g: Allyl ether **1g** (170.2 mg, 1.0 mmol), aldehyde (3.0 mmol), and diethylzinc (3.6 mL, 1.0 M hexane) were added successively via syringe at 0 °C under N_2 to a solution of Pd(OAc)$_2$ (22.6 mg, 0.1 mmol) and *n*Bu$_3$P (80.9 mg, 0.4 mmol) in dry toluene (0.5 mL). The mixture was allowed to warm to 25 °C and stirred at the same temperature. The mixture was diluted with AcOEt and washed with 0.2 M HCl, sat. $NaHCO_3$, and brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to give an oil, which was purified by column chromatography on silica gel (AcOEt/hexane 1:7).Compound **5a** was identified by comparison of the spectral data with those in literature.[4b]

(*Z*),*anti*-4-Methyl-1-phenyl-5-hepten-3-ol (5b): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.95 (d, ^3J(H,H) = 6.6 Hz, 3H), 1.65 (dd, ^3J(H,H) = 7.0, 1.8 Hz, 3H), 1.67–1.74 (m, 2H), 1.85 (ddq, ^3J(H,H) = 10.3, 9.9, 3.3 Hz, 1H), 2.56 (dquint, ^3J(H,H) = 10.3, 6.6 Hz, 1H), 2.67 (ddd, ^3J(H,H) = 13.6, 9.9, 6.6 Hz, 1H), 2.86 (dq, ^3J(H,H) = 13.6, 5.1 Hz, 1H), 3.36 (dt, ^3J(H,H) = 2.9, 8.1 Hz, 1H), 5.25 (ddq, ^3J(H,H) = 11.0, 10.1, 1.8 Hz, 1H), 5.62 (dq, ^3J(H,H) = 11.0, 6.6 Hz, 1H), 7.16–7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.3, 16.9, 32.2, 36.0, 37.7, 74.7, 125.7, 126.2, 128.3, 128.4, 132.8, 154.5; IR (neat): $\tilde{\nu}$ = 3418, 3026, 2930, 2870, 1497, 1454, 1036, 968, 700 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{12}H_{16}O$: 204.1514, found: 204.1532(3) [M^+], 135 (9), 69 (100).

1-(5-Hydroxymethyl-2,2-dimethyl-[1,3]dioxolan-4-yl)-3-buten-1-ol (7a): a mixture in a ratio of 1:1, isomer 1: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.38 (s, 3H), 1.52 (s, 3H), 2.29–2.45 (m, 2H), 2.82–2.92 (m, 2H), 3.78–3.99 (m, 3H), 4.11 (dd, ^3J(H,H) = 6.9, 3.0 Hz, 1H), 4.23 (dt, ^3J(H,H) = 6.9, 5.0 Hz, 1H), 5.13 (dd, ^3J(H,H) = 10.2, 1.4 Hz, 1H), 5.16 (dd, ^3J(H,H) = 17.3, 1.4 Hz, 1H), 5.86 (ddt, ^3J(H,H) = 17.3, 10.2, 7.1 Hz 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.02, 27.24, 39.58, 61.26, 68.58, 77.30, 78.39, 108.36, 118.05, 134.28; isomer 2: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.36 (s, 3H), 1.41 (s, 3H), 2.21 (dt, ^3J(H,H) = 14.3, 8.4 Hz, 1H), 2.60–2.66 (m, 2H), 2.80 (brs, 1H), 3.76 (ddd, ^3J(H,H) = 11.7, 7.0, 5.1, 1H), 3.81–3.90 (m, 2H), 3.99 (dd, ^3J(H,H) = 9.2, 5.1 Hz, 1H), 4.32 (dt, ^3J(H,H) = 8.1, 5.1 Hz, 1H), 5.20 (dd, ^3J(H,H) = 14.7, 1.5 Hz, 1H), 5.21 (dd, ^3J(H,H) = 11.7, 1.5 Hz, 1H), 5.86 (dddd, ^3J(H,H) = 14.7, 11.7, 8.4, 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.34, 27.95, 38.84, 61.03, 68.54, 77.41, 79.36, 108.39, 119.21, 133.93;

IR (neat): $\tilde{\nu}$ = 3396, 3078, 2986, 2937, 2359, 2341, 1643, 1456, 1380, 1246, 1217, 1167, 1042, 918, 874, 797 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_{10}H_{19}O_4$: 203.1302, found: 203.1283 (3) [M^+], 188 (10), 187 (100), 171 (23), 169 (1).

1-(5-Hydroxymethyl-2,2-dimethyl-[1,3]dioxolan-4-yl)-2-methyl-3-buten-1-ol (7b): a mixture in a ratio of 2:2:1:1; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): an isomer corresponding to $^2/_6$: δ = 1.16 (d, ^3J(H,H) = 7.0 Hz, 3H), 1.34 (s, 3H), 1.41 (s, 3H), 2.57 (d, ^3J(H,H) = 5.5 Hz, 1H), 2.66 (m, 1H), 2.73 (t, ^3J(H,H) = 5.5 Hz, 1H), 3.68–3.89 (m, 3H), 4.07 (dd, ^3J(H,H) = 9.9, 5.5 Hz, 1H), 4.28 (ddd, ^3J(H,H) = 7.7, 5.5, 4.8 Hz, 1H), 5.16 (dd, ^3J(H,H) = 17.2, 1.8 Hz, 1H), 5.19 (dd, ^3J(H,H) = 10.6, 1.8 Hz, 1H), 5.89 (ddd, ^3J(H,H) = 17.2, 10.6, 7.7 Hz 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 16.66, 25.38, 28.02, 39.66, 61.14, 72.63, 77.41, 77.84, 108.32, 117.19, 138.05; an isomer corresponding to $^2/_6$: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.07 (d, ^3J(H,H) = 7.0 Hz, 3H), 1.36 (s, 3H), 1.42 (s, 3H), 2.38 (d, ^3J(H,H) = 2.9 Hz, 1H), 2.66 (m, 1H), 2.88 (dd, ^3J(H,H) = 7.3, 4.8 Hz, 1H), 3.68–3.89 (m, 3H), 4.12 (dd, ^3J(H,H) = 9.2, 5.5 Hz, 1H), 4.33 (dt, ^3J(H,H) = 7.3, 5.1 Hz, 1H), 5.16 (dd, ^3J(H,H) = 17.2, 1.8 Hz, 1H), 5.18 (dd, ^3J(H,H) = 10.6, 1.8 Hz, 1H), 5.92 (ddd, ^3J(H,H) = 17.2, 10.6, 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 10.90, 25.38, 28.02, 38.77, 61.03, 71.15, 76.83, 77.41, 108.32, 115.83, 140.97; an isomer corresponding to $^1/_6$: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.10 (d, ^3J(H,H) = 7.0 Hz, 3H), 1.38 (s, 3H), 1.51 (s, 3H), 2.41 (m, 1H), 2.48–2.80 (m, 2H), 3.57 (brs, 1H), 3.75–3.80 (m, 2H), 4.17–4.24 (m, 2H), 5.11 (d, ^3J(H,H) = 16.1 Hz, 1H), 5.12 (d, ^3J(H,H) = 9.9 Hz, 1H), 5.87 (ddd, ^3J(H,H) = 16.1, 9.9, 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 16.62, 25.22, 27.36, 42.22, 61.50, 71.93, 76.52, 77.61, 108.36, 116.02, 139.99; an isomer corresponding to $^1/_6$: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.12 (d, ^3J(H,H) = 7.0 Hz, 3H), 1.36 (s, 3H), 1.51 (s, 3H), 2.41 (m, 1H), 2.48–2.80 (m, 2H), 3.48 (brs, 1H), 3.75–3.80 (m, 2H), 4.20 (m, 1H), 4.28 (dd, ^3J(H,H) = 7.0, 1.8 Hz, 1H), 5.06 (dd, ^3J(H,H) = 10.3, 1.8 Hz, 1H), 5.12 (d, ^3J(H,H) = 16.9 Hz, 1H), 5.70 (ddd, ^3J(H,H) = 16.9, 10.3, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 16.54, 24.91, 27.17, 43.24, 61.50, 71.93, 76.21, 77.22, 108.12, 115.83, 140.70; IR (neat): $\tilde{\nu}$ = 3385, 3076, 2985, 2359, 2341, 1638, 1458, 1371, 1220, 1168, 1008, 918, 885, 796 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_{11}H_{21}O_4$: 217.1471, found: 217.1440 (13) [M^+], 216 (2), 199 (2), 186 (16), 185 (100), 183 (5).

2-*tert*-Butyl-1-(5-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-buten-1-ol (7c): a mixture of isomers in a ratio of 10:2:2:1; major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.99 (s, 9H), 1.34 (s, 3H), 1.50 (s, 3H), 2.09 (dd, ^3J(H,H) = 10.3, 8.4 Hz, 1H), 2.47 (brs, 1H), 2.98 (brs, 1H), 3.71–3.78 (brs, 2H), 3.82 (dt, ^3J(H,H) = 1.5, 8.4 Hz, 1H), 4.16 (dt, ^3J(H,H) = 7.0, 5.1 Hz, 1H), 4.34 (dt, ^3J(H,H) = 7.0, 1.5 Hz, 1H), 5.07 (dd, ^3J(H,H) = 17.0, 2.2 Hz, 1H), 5.14 (dd, ^3J(H,H) = 10.3, 2.2 Hz, 1H), 5.61 (dt, ^3J(H,H) = 17.0, 10.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 24.91, 27.24, 29.15, 32.62, 59.16, 61.65, 68.89, 76.71, 77.80, 107.89, 118.44, 137.04; IR (KBr): $\tilde{\nu}$ = 3406, 3074, 2954, 2908, 2872, 1639, 1467, 1419, 1381, 1369, 1244, 1217, 1163, 1105, 1072, 1040, 980, 916, 874, 862, 800 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{26}O_4$ (258.4): C 65.09, H, 10.14; found: C 65.30, H 10.29.

(2*R*,3*S*,4*R*,5*R*)-1-(5-Hydroxymethyl-2,2-dimethyl-[1,3]dioxolan-4-yl)-2-phenyl-3-buten-1-ol (7d): m.p. 91.0–92.0 (Et_2O/hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 1.38 (s, 3H), 1.52 (s, 3H), 2.48 (brs, 1H), 2.83 (brs, 1H), 3.62 (dd, ^3J(H,H) = 9.2, 8.8 Hz, 1H), 3.78–3.84 (m, 2H), 4.02 (m, 1H), 4.20 (dt, ^3J(H,H) = 6.8, 5.1 Hz, 1H), 4.33 (dd, ^3J(H,H) = 6.8, 1.8 Hz, 1H), 5.18 (dd, ^3J(H,H) = 9.5, 1.5 Hz, 1H), 5.21 (dd, ^3J(H,H) = 16.9, 1.5 Hz, 1H), 6.03 (ddd, ^3J(H,H) = 16.9, 9.5, 9.2 Hz, 1H), 7.21–7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.34, 27.95, 55.27, 61.50, 71.03, 75.70, 77.57, 108.23, 117.62, 128.28, 128.83, 137.97, 140.70; IR (KBr): $\tilde{\nu}$ = 3330, 2989, 2893, 2345, 1633, 1602, 1454, 1379, 1261, 1211, 1164, 1123, 1043, 1022, 1005, 931, 899, 844, 700, 628 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_{16}H_{23}O_4$: 278.1520, found: 278.1518 (3) [M^+], 263.13 (100), 262.15 (3), 260.14 (8), 247.13 (2), 220.132 (3).

(2*R*,3*R*,4*R*,5*S*,6*R*)-1,3,4,5-Tetrabenzyloxy-8-nonene-2,6-diol (9a): a mixture in a ratio of 12:1, major isomer: ^{1}H NMR (400 MHz, C_6D_6, 25 °C, TMS): δ = 2.11 (dtd, ^3J(H,H) = 14.3, 7.3, 1.1 Hz, 1H), 2.21–2.29 (m, 2H), 2.92 (d, ^3J(H,H) = 5.5 Hz, 1H), 3.59–3.65 (m, 3H), 3.70 (dd, ^3J(H,H) = 7.7, 1.8 Hz, 1H), 3.72 (dd, ^3J(H,H) = 7.0, 2.9 Hz, 1H), 4.05 (brs, 1H), 4.05 (dd, ^3J(H,H) = 7.7, 2.9 Hz, 1H), 4.51 (dd, ^3J(H,H) = 11.4, 2.9 Hz, 1H), 4.52–4.53 (m, 3H), 4.59 (dd, ^3J(H,H) = 11.4, 1.8 Hz, 1H), 4.63 (d, ^3J(H,H) = 11.4 Hz, 1H), 4.75 (d, ^3J(H,H) = 11.4 Hz, 1H), 4.86 (d, ^3J(H,H) = 11.4 Hz, 1H), 5.00 (dd, ^3J(H,H) = 17.2, 1.8 Hz, 1H), 5.01 (dd, ^3J(H,H) = 10.3, 1.1 Hz, 1H), 5.65 (ddt, ^3J(H,H) = 17.2, 10.3, 7.0 Hz, 1H), 7.23–7.36 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 38.84, 70.64, 71.34, 73.05, 73.52, 74.81, 75.00, 77.49, 79.44, 80.45, 117.46, 127.78, 127.96, 128.11, 128.31, 128.40, 134.94, 137.94, 138.15, 138.32; minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.22 (dt, ^3J(H,H) = 14.3, 8.1 Hz, 1H), 2.37 (m, 1H), 2.90 (d, ^3J(H,H) = 4.4 Hz, 1H), 3.62 (d, ^3J(H,H) = 4.4 Hz, 2H), 3.62–3.65 (m, 1H), 3.85 (dd, ^3J(H,H) = 6.6, 3.7 Hz, 1H), 3.90 (m, 1H), 3.94 (t, ^3J(H,H) = 4.2 Hz, 1H), 4.03 (m, 1H), 4.50 (d, ^3J(H,H) = 11.7 Hz, 1H), 4.53 (d, ^3J(H,H) = 7.9 Hz, 2H), 4.58 (d, ^3J(H,H) = 7.9 Hz, 2H), 4.63 (d, ^3J(H,H) = 11.0 Hz, 1H), 4.67 (d, ^3J(H,H) = 11.0 Hz, 1H), 5.05–5.08 (brs, 2H), 5.82 (dddd, ^3J(H,H) = 17.2, 9.9, 7.7, 6.6 Hz, 1H), 7.22–7.37 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 37.98, 71.11, 71.26, 71.26, 73.50, 73.99, 77.45, 78.78, 79.48, 117.35, 127.79, 128.05, 128.20, 128.48, 135.13, 137.62, 137.94, 138.09; IR (KBr): $\tilde{\nu}$ = 3445, 3062, 3030, 3007, 2864, 1952, 1871, 1811, 1641, 1607, 1585, 1497, 1454, 1209, 1001, 916, 819, 698 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_{37}H_{42}O_6$: 582.2981, found: 582.2966 (13) [M^+], 492.2517 (40), 491.2459 (100).

(2*R*,3*R*,4*R*,5*S*,6*R*,7*R*)-1,3,4,5-Tetrabenzyloxy-7-phenyl-8-nonene-2,6-diol (9b): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.09 (d, ^3J(H,H) = 8.0 Hz, 1H), 2.93 (d, ^3J(H,H) = 5.2 Hz, 1H), 3.53 (dt, ^3J(H,H) = 10.2, 8.0 Hz, 1H), 3.63 (d, ^3J(H,H) = 4.7 Hz, 2H), 3.72 (dd, ^3J(H,H) = 6.6, 3.0 Hz, 1H), 3.93 (t, ^3J(H,H) = 8.0 Hz, 1H), 4.02–4.12 (m, 2H), 4.14 (dd, ^3J(H,H) = 8.0, 3.0 Hz, 1H), 4.49 (d, ^3J(H,H) = 11.4 Hz, 1H), 4.51 (d, ^3J(H,H) = 11.4 Hz, 1H), 4.54 (d, ^3J(H,H) = 12.5 Hz, 1H), 4.55 (d, ^3J(H,H) = 12.5 Hz, 1H), 4.60 (d, ^3J(H,H) = 11.3 Hz, 1H), 4.64 (d, ^3J(H,H) = 11.3 Hz, 1H), 4.78 (d, ^3J(H,H) = 11.2 Hz, 1H), 4.91 (d, ^3J(H,H) = 11.2 Hz, 1H), 4.90 (d, ^3J(H,H) = 16.8 Hz, 1H), 4.98 (d, ^3J(H,H) = 10.2 Hz, 1H), 5.76 (dt, ^3J(H,H) = 16.8, 10.2 Hz, 1H), 7.12–7.38 (m, 25H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 54.3, 70.5, 71.3, 72.8, 73.3, 73.4, 74.5, 74.7, 77.8, 78.0, 79.3, 116.9, 126.5, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 137.8, 137.9, 138.0, 138.4, 138.5, 141.2; IR (KBr): $\tilde{\nu}$ = 3447, 3062, 3030, 2866, 2361, 2341, 1716, 1600, 1585, 1497, 1454, 1361, 1261, 1211, 1070, 1028, 918, 734, 698, 667 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_{43}H_{46}O_6$: 658.3294, found: 658.3357 (7) [M^+], 568 (33), 538 (44), 537 (100), 524 (41).

(2*R*,3*R*,4*R*,5*R*,6*S*)-1,3,4,5-Tetrakis(benzyloxy)-8-nonene-2,6-diol [(6*S*)-11]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.30 (dt, ^3J(H,H) = 13.9, 7.0 Hz, 1H), 2.37 (dt, ^3J(H,H) = 13.9, 7.0 Hz, 1H), 2.69 (d, ^3J(H,H) = 5.6 Hz, 1H), 2.97 (d, ^3J(H,H) = 6.0 Hz, 1H), 3.62 (dd, ^3J(H,H) = 5.6, 9.6 Hz, 1H), 3.67 (m, 1H), 3.68 (dd, ^3J(H,H) = 4.0, 9.6 Hz, 1H), 3.78 (dd, ^3J(H,H) = 4.0, 7.0 Hz, 1H), 3.95–4.06 (m, 3H), 4.49–4.59 (m, 4H), 4.61 (brs, 2H), 4.75 (brs, 2H), 5.03 (brd, ^3J(H,H) = 14.1 Hz, 1H), 5.05 (brd, ^3J(H,H) = 10.5 Hz, 1H), 5.78 (brddt, ^3J(H,H) = 10.5, 14.1, 7.0 Hz, 1H), 7.23–7.35 (m, 20H); ^{13}C NMR (400 MHz, $CDCl_3$ 25 °C, TMS): δ = 38.9, 70.4, 70.6, 71.1, 73.1, 73.3, 73.4, 74.6, 78.6, 79.4, 79.7, 117.2, 127.5, 127.6, 127.7, 127.9, 128.1, 128.2, 128.3, 135.0, 137.7, 137.8, 137.9, 138.1; IR (neat): $\tilde{\nu}$ = 3464 (s), 2870 (s), 1096 (s), 741 cm^{-1} (s); HRMS (EI): *m*/*z* (%): calcd for $C_{37}H_{42}O_6$: 582.2981, found: 582.2987 (2) [M^+], 491 (100), 433 (71).

(2*R*,3*S*)-1-Triphenylmethoxy-7-octene-2,3,5-triol (13a): a mixture in a ratio of 1:1, isomer 1: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.52 (ddd, ^3J(H,H) = 14.3, 8.2, 4.9 Hz, 1H), 1.63 (ddd, ^3J(H,H) = 14.3, 6.6, 4.9 Hz, 1H), 2.13–2.32 (m, 3H), 2.69 (d, ^3J(H,H) = 4.7 Hz, 1H), 2.88 (d, ^3J(H,H) = 5.5 Hz, 1H), 3.29 (dd, ^3J(H,H) = 9.6, 3.6 Hz, 1H), 3.42 (dd, ^3J(H,H) = 9.6, 3.8 Hz, 1H), 3.70 (dquint, ^3J(H,H) = 5.5, 4.7 Hz, 1H), 3.88–4.00 (m, 2H), 5.12 (dd, ^3J(H,H) = 15.9, 0.9 Hz, 1H), 5.13 (dd, ^3J(H,H) = 11.3, 0.9 Hz, 1H), 5.79 (dddd, ^3J(H,H) = 15.9, 11.8, 9.9, 6.9 Hz, 1H), 7.22–7.45 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 38.02, 42.02, 64.65, 68.05, 70.39, 72.85, 87.05, 118.16, 126.99, 127.73, 128.36, 134.21, 143.35; isomer 2: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.40 (dt, ^3J(H,H) = 14.3, 9.9 Hz, 1H), 1.62 (dt, ^3J(H,H) = 14.3, 2.5 Hz, 1H), 2.16

(dt, ^3J(H,H) = 14.3, 7.2 Hz, 1H), 2.22 (dt, ^3J(H,H) = 14.3, 5.2 Hz, 1H), 2.76 (brs, 1H), 2.91 (brs, 1H), 3.32 (d, ^3J(H,H) = 5.2 Hz, 2H), 3.45 (brs, 1H), 3.67 (quint, ^3J(H,H) = 5.2 Hz, 1H), 3.82–3.96 (m, 2H), 5.10 (d, ^3J(H,H) = 16.8 Hz, 1H), 5.11 (d, ^3J(H,H) = 10.4 Hz, 1H), 5.76 (dddd, ^3J(H,H) = 16.8, 10.4, 7.2, 5.2 Hz, 1H), 7.22–7.45 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 37.67, 42.39, 64.31, 71.06, 72.84, 73.47, 87.01, 118.12, 126.97, 127.71, 128.36, 133.94, 143.36; IR (neat): $\tilde{\nu}$ = 3363, 3060, 2881, 2341, 1965, 1645, 1596, 1488, 1446, 1418, 1219, 1184, 1001, 900, 748, 705, 633 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_{27}H_{30}O_4$ 418.2144, found: 418.2149 (56) [M^+], 400 (19), 380 (25), 359 (19), 358 (69), 341 (100).

(2*R*,3*S*)-6-Phenyl-1-triphenylmethoxy-7-octene-2,3,5-triol (13b): a mixture in a ratio of 3:2:1:1, an isomer corresponding to $^3/_7$: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.45 (m, 1H), 2.18 (m, 1H), 2.35 (brs, 1H), 2.66 (d, ^3J(H,H) = 4.7 Hz, 1H), 2.68 (d, ^3J(H,H) = 7.7 Hz, 1H), 3.13 (m, 1H), 3.11 (d, ^3J(H,H) = 4.7 Hz, 1H), 3.12 (d, ^3J(H,H) = 4.7 Hz, 1H), 3.63 (quint, ^3J(H,H) = 4.7 Hz, 1H), 3.92 (m, 1H), 4.15 (m, 1H), 5.19 (d, ^3J(H,H) = 17.9 Hz, 1H), 5.20 (d, ^3J(H,H) = 10.2 Hz, 1H), 6.06 (ddd, ^3J(H,H) = 17.9, 10.2, 9.1 Hz, 1H), 7.12–7.45 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 35.91, 57.62, 64.39, 72.63, 73.27, 74.34, 86.93, 117.86, 126.90, 127.66, 128.34, 137.52, 140.71, 143.42; an isomer corresponding to $^2/_7$: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.53 (m, 1H), 1.82 (dm, ^3J(H,H) = 10.7 Hz, 1H), 2.70 (brs, 1H), 2.94 (d, ^3J(H,H) = 6.1 Hz, 1H), 3.16–3.32 (m, 3H), 3.40 (dd, ^3J(H,H) = 9.6, 3.9 Hz, 1H), 3.11 (d, ^3J(H,H) = 4.7 Hz, 1H), 3.12 (d, ^3J(H,H) = 4.7 Hz, 1H), 3.68 (m, 1H), 3.94 (m, 1H), 4.18 (m, 1H), 5.08 (d, ^3J(H,H) = 11.5 Hz, 1H), 5.09 (d, ^3J(H,H) = 16.6 Hz, 1H), 5.94 (ddd, ^3J(H,H) = 17.2, 11.5, 9.1 Hz, 1H), 7.12–7.44 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 36.32, 57.34, 64.85, 72.88, 73.23, 74.29, 87.01, 116.91, 126.59, 127.74, 128.54, 137.84, 140.33, 143.39; an isomer corresponding to $^1/_7$: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.38 (dt, ^3J(H,H) = 14.8, 9.4 Hz, 1H), 1.53 (d, ^3J(H,H) = 14.8 Hz, 1H), 2.66 (d, ^3J(H,H) = 4.1 Hz, 1H), 2.86 (brs, 1H), 3.21 (t, ^3J(H,H) = 9.4 Hz, 1H), 3.22 (d, ^3J(H,H) = 5.5 Hz, 2H), 3.50 (d, ^3J(H,H) = 3.0 Hz, 1H), 3.60 (dq, ^3J(H,H) = 4.1, 5.5 Hz, 1H), 3.86 (m, 1H), 4.04 (t, ^3J(H,H) = 9.4 Hz, 1H), 5.17 (dd, ^3J(H,H) = 16.8, 1.7 Hz, 1H), 5.21 (dd, ^3J(H,H) = 10.2, 1.7 Hz, 1H), 6.11 (ddd, ^3J(H,H) = 16.8, 10.2, 9.4 Hz, 1H), 7.12–7.44 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 35.91, 57.75, 64.37, 72.65, 73.27, 74.32, 86.93, 117.11, 126.91, 127.67, 128.34, 137.52, 140.71, 143.42; an isomer corresponding to $^1/_7$: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.39 (dt, ^3J(H,H) = 15.3, 8.8 Hz, 1H), 1.93 (d, ^3J(H,H) = 15.3 Hz, 1H), 2.46 (brs, 1H), 2.70 (d, ^3J(H,H) = 4.4 Hz, 1H), 3.23 (t, ^3J(H,H) = 8.8 Hz, 1H), 3.30 (d, ^3J(H,H) = 5.2 Hz, 2H), 3.55 (d, ^3J(H,H) = 2.5 Hz, 1H), 3.66 (dq, ^3J(H,H) = 4.4, 5.5 Hz, 1H), 3.92 (m, 1H), 4.04 (t, ^3J(H,H) = 9.4 Hz, 1H), 5.10 (d, ^3J(H,H) = 16.8 Hz, 1H), 5.11 (d, ^3J(H,H) = 11.7 Hz, 1H), 5.96 (ddd, ^3J(H,H) = 16.8, 11.7, 8.8 Hz, 1H), 7.12–7.44 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 35.91, 57.60, 64.44, 72.80, 73.37, 74.65, 86.95, 117.86, 126.93, 127.69, 128.37, 137.71, 140.05, 143.44; IR (neat): $\tilde{\nu}$ = 3412, 3059, 3032, 2928, 2876, 2247, 1734, 1597, 1491, 1448, 1421, 1223, 1184, 1076, 991, 949, 910, 849, 764, 733, 706, 648, 633 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_{27}H_{29}O_4$: 417.2070, found: 417.2039 (7) [M^+−Ph], 376 (5), 359 (4), 299 (14), 260 (39), 259 (100), 258 (50).

4-(2-Hydroxy-4-pentenyl)-2,2-dimethyl-1,3-dioxan-5-ol (15a): a mixture in a ratio of 1:1, isomer 1: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.38 (s, 3H), 1.46 (s, 3H), 1.65 (ddd, ^3J(H,H) = 14.3, 9.6, 5.0 Hz, 1H), 1.81 (ddd, ^3J(H,H) = 14.3, 8.5, 2.8 Hz, 1H), 2.16–2.39 (m, 3H), 3.57–3.72 (m, 2H), 3.88 (brs, 1H), 4.23 (dt, ^3J(H,H) = 6.3, 5.2 Hz, 1H), 4.45 (ddd, ^3J(H,H) = 8.5, 6.3, 5.0 Hz, 1H), 5.15 (d, ^3J(H,H) = 15.7 Hz, 1H), 5.16 (d, ^3J(H,H) = 10.7 Hz, 1H), 5.81 (dddd, ^3J(H,H) = 15.7, 10.7, 8.0, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.42, 28.09, 35.46, 42.51, 61.58, 68.12, 74.29, 77.79, 107.72, 118.41, 134.13; isomer 2: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.38 (s, 3H), 1.49 (s, 3H), 1.66–1.71 (m, 2H), 1.95 (brs, 1H), 2.25–2.32 (m, 2H), 3.14 (brs, 1H), 3.64 (dd, ^3J(H,H) = 5.6, 5.2 Hz, 2H), 3.89 (quint, ^3J(H,H) = 6.0 Hz, 1H), 4.21 (dt, ^3J(H,H) = 6.3, 5.6 Hz, 1H), 4.38 (dt, ^3J(H,H) = 6.9, 6.3 Hz, 1H), 5.11 (d, ^3J(H,H) = 10.4 Hz, 1H), 5.12 (d, ^3J(H,H) = 17.3 Hz, 1H), 5.83 (ddt, ^3J(H,H) = 17.3, 10.4, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.4, 28.0, 35.1, 41.7, 61.5, 70.6, 76.6, 77.9, 108.6, 117.6, 134.4; IR (neat): $\tilde{\nu}$ = 3408, 2986, 2936, 1641, 1456, 1371, 1218, 1167, 1043, 999, 918, 827 cm^{-1}; HRMS: *m*/*z* (%): calcd for $C_{10}H_{17}O_4$: 201.1127, found: 201.1130 (100) [M^+−Me], 185 (60), 157 (90).

4-(2-Hydroxy-3-phenyl-4-pentenyl)-2,2-dimethyl-1,3-dioxan-5-ol (15b): a mixture in a ratio of 2:2:2:1, an isomer corresponding to $^2/_7$: ^{1}H NMR (400 MHz, C_6D_6, 25 °C, TMS) δ = 1.42 (s, 3H), 1.50 (s, 3H), 1.66 (ddd, ^3J(H,H) = 14.4, 10.5, 5.6 Hz, 1H), 1.77 (brs, 1H), 1.94 (brs, 1H), 2.13 (ddd, ^3J(H,H) = 14.4, 7.6, 2.2 Hz, 1H), 3.21 (t, ^3J(H,H) = 8.1 Hz, 1H), 3.54–3.70 (brs, 2H), 4.05 (brs, 1H), 4.17 (q, ^3J(H,H) = 5.8 Hz, 1H), 4.50 (dt, ^3J(H,H) = 7.6, 5.8 Hz, 1H), 5.05 (dd, ^3J(H,H) = 10.2, 1.7 Hz, 1H), 5.08 (dd, ^3J(H,H) = 17.1, 1.7 Hz, 1H), 5.95 (ddd, ^3J(H,H) = 17.1, 10.2, 1.7 Hz, 1H), 7.07–7.47 (m, 5H); ^{13}C NMR (100 MHz, C_6D_6, 25 °C, TMS): δ = 25.73, 28.46, 34.43, 58.28, 61.84, 71.92, 75.25, 78.41, 107.43, 116.65, 126.98, 128.86, 128.95, 138.94, 141.19; an isomer corresponding to $^2/_7$: ^{1}H NMR (400 MHz, C_6D_6, 25 °C, TMS): δ = 1.39 (s, 3H), 1.43 (s, 3H), 1.71 (ddd, ^3J(H,H) = 14.2, 10.2, 5.9 Hz, 1H), 1.83 (ddd, ^3J(H,H) = 14.4, 7.6, 2.4 Hz, 1H), 1.94 (brs, 1H), 2.04 (brs, 1H), 3.19 (dd, ^3J(H,H) = 8.6, 7.3 Hz, 1H), 3.52–3.67 (brs, 2H), 3.98 (brs, 1H), 4.19 (q, ^3J(H,H) = 5.9 Hz, 1H), 4.48 (dt, ^3J(H,H) = 7.6, 5.9 Hz, 1H), 5.09 (dd, ^3J(H,H) = 17.0, 1.7 Hz, 1H), 5.13 (dd, ^3J(H,H) = 10.2, 1.7 Hz, 1H), 6.10 (ddd, ^3J(H,H) = 17.0, 10.2, 8.6 Hz, 1H), 7.08–7.47 (m, 5H); ^{13}C NMR (100 MHz, C_6D_6, 25 °C, TMS): δ = 25.79, 28.44, 34.44, 58.01, 61.76, 71.92, 75.29, 78.44, 107.43, 117.56, 126.85, 128.43, 128.84, 138.40, 141.82; an isomer corresponding to $^2/_7$: ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = 1.15 (s, 3H), 1.24 (s, 3H), 1.36 (brs, 1H), 1.42 (ddd, ^3J(H,H) = 13.7, 4.1, 2.5 Hz, 1H), 1.68 (m, 1H), 2.85 (s, 1H), 3.20–3.36 (m, 2H), 3.32 (t, ^3J(H,H) = 5.8 Hz, 1H), 3.87 (q, ^3J(H,H) = 6.0 Hz, 1H), 3.97 (m, 1H), 4.12 (dt, ^3J(H,H) = 8.0, 6.0 Hz, 1H), 5.04 (dd, ^3J(H,H) = 10.2, 1.1 Hz, 1H), 5.09 (dd, ^3J(H,H) = 17.0, 1.1 Hz, 1H), 6.11 (ddd, ^3J(H,H) = 17.0, 10.2, 8.5 Hz, 1H), 7.05–7.28 (m, 5H); ^{13}C NMR (100 MHz, C_6D_6, 25 °C, TMS): δ = 25.41, 27.98, 33.72, 57.19, 61.47, 73.83, 76.64, 78.20, 108.15, 116.23, 126.68, 128.33, 129.15, 139.37, 141.33; an isomer corresponding to $^1/_7$: ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = 1.14 (s, 3H), 1.25 (s, 3H), 1.58–1.78 (m, 3H), 3.03 (s, 1H), 3.25 (dd, ^3J(H,H) = 6.6, 5.5 Hz, 1H), 3.79 (q, ^3J(H,H) = 6.0 Hz, 1H), 4.03 (m, 1H), 5.10 (dd, ^3J(H,H) = 17.0, 1.1 Hz, 1H), 5.12 (dd, ^3J(H,H) = 10.4, 1.1 Hz, 1H), 6.33 (ddd, ^3J(H,H) = 17.0, 10.4, 8.2 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6, 25 °C, TMS): δ = 34.17, 57.14, 61.41, 73.92, 76.72, 78.20, 116.70, 128.59, 128.74, 138.81, 142.21; IR (neat): $\tilde{\nu}$ = 3418, 2984, 2934, 2876, 1637, 1601, 1495, 1454, 1371, 1246, 1219, 1165, 1059, 1003, 920, 845, 762, 704 cm^{-1}; HRMS: *m*/*z* (%): calcd for $C_{16}H_{21}O_4$: 277.1440, found: 277.1433 (18) [M^+−Me], 292 (1), 278 (3), 203 (8), 185 (9), 175 (8), 157 (100).

General Procedure for the self-allylation of ω-formyl allyl ether 21: Compound **21** (1.0 mmol) and diethylzinc (2.4 mmol, 1.0 M hexane) were added successively via syringe at 0 °C under N_2 to a solution of $Pd(OAc)_2$ (22.6 mg, 0.1 mmol) and nBu$_3$P (80.9 mg, 0.4 mmol) in dry toluene (0.5 mL). The mixture was allowed to warm to ambient temperature and stirred for 3 h. The mixture was diluted with AcOEt and then washed with 0.2 M HCl, sat. $NaHCO_3$, and brine, and the organic phase was dried ($MgSO_4$) and concentrated in vacuo to give an oil, which was purified by column chromatography on silica gel (AcOEt/hexane 1:10) to give **22a** in 95% yield or **22b** in 85% yield.

1-(*o*-Hydroxyphenyl)-3-buten-1-ol (22a): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.61 (t, ^3J(H,H) = 6.9 Hz, 2H), 2.99 (brs, 2H), 4.65 (d, ^3J(H,H) = 12.1 Hz, 1 H), 4.73 (d, ^3J(H,H) = 12.1 Hz, 1 H), 4.97 (t, ^3J(H,H) = 6.9 Hz, 1 H), 5.16 (d, ^3J(H,H) = 10.2 Hz, 1H), 5.18 (d, ^3J(H,H) = 17.0 Hz, 1H), 5.87 (ddt, ^3J(H,H) = 17.0, 10.2, 6.9 Hz, 1H), 7.24–7.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 41.9, 63.5, 70.4, 118.2, 126.5, 127.8, 128.3, 129.6, 134.6, 137.9, 141.6; IR (neat): $\tilde{\nu}$ = 3333, 3071, 2916, 1643, 1450, 1319, 1211, 1003, 918, 871, 764 cm^{-1}; HRMS (EI): *m*/*z* (%): calcd for $C_{11}H_{14}O_2$: 178.0994, found: 178.0936 (3) [M^+], 177 (11), 160 (100).

Tridec-12-ene-1,10-diol (22b): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.23–1.68 (m, 16H), 1.69–1.98 (brs, 2H), 2.15 (ddd, ^3J(H,H) = 13.7, 7.4, 6.8 Hz, 1H), 2.30 (dt, ^3J(H,H) = 13.7, 5.9 Hz, 1H), 3.55 (m, 1H), 3.64 (t, ^3J(H,H) = 6.6 Hz, 2H), 5.12 (dd, ^3J(H,H) = 15.8, 1.4 Hz, 1H), 5.13 (dqm, ^3J(H,H) = 11.4, 1.4 Hz, 1H), 5.83 (dddd, ^3J(H,H) = 15.8, 11.4, 6.8, 5,9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.6, 25.7, 29.2, 29.4, 29.5, 29.6, 32.8, 36.8, 41.9, 62.9, 70.6, 117.9, 134.8; IR(neat): $\tilde{\nu}$ =

3333, 3078, 2924, 2855, 2361, 1712, 1643, 1458, 1365, 1265, 1057, 910, 725 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{13}H_{26}O_2$: 214.1933, found: 214.1858 (20) [M^+], 213 (100), 196 (9), 184 (6).

Structure determination

Conversion of 2b to a cyclic acetal, *trans*-2,2-dimethyl(4-(4-hydroxybutyl))-5-methyl-1,3-dioxacyclohexane (16): i) A solution of **2b** (59 mg, 0.37 mmol, *anti*/*syn* 5:1) in dichloromethane (13 mL) was cooled to −78 °C, and ozone was bubbled through until a blue color appeared (ca. 5 min). The excess of ozone was removed by a flow of O_2. The mixture was allowed to warm to 0 °C. To this solution was added a solution of $NaBH_4$ (238.2 mg, 6.3 mmol) in MeOH/H_2O (4 mL, 1:1) and then the mixture was stirred at ambient temperature for 12 h. The mixture was diluted with AcOEt and washed with 2 M HCl and sat. $NaHCO_3$. The organic phase was dried ($MgSO_4$) and the solvent was removed in vacuo to give an oil.

ii) A solution of the oil and *p*-TsOH (8 mg, 0.04 mmol) in 2,2-dimethoxypropane (5 mL) was stirred at ambient room temperature for 3 h. The mixture was diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ and brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to give an oil, which was purified by column chromatography on silica gel (AcOEt/hexane 1:7) to give **16** (*trans*/*cis* 8:1; 22 mg, in 30% overall yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.74 (d, ^3J(H,H) = 6.8 Hz, 1H), 1.05 (d, ^3J(H,H) = 7.1 Hz, 1H, *cis*), 1.38 (s, 3H), 1.39 (s, 3H, *cis*), 1.42 (s, 3H), 1.43 (s, 3H, *cis*), 1.34–1.71 (m, 7H), 3.44 (ddd, ^3J(H,H) = 10.2, 7.9, 2.4 Hz, 1H), 3.48 (t, ^3J(H,H) = 11.7 Hz, 1H), 3.57 (dd, ^3J(H,H) = 11.7, 1.7 Hz, 1H, *cis*), 3.65 (t, ^3J(H,H) = 6.4 Hz, 2H), 3.66 (dd, ^3J(H,H) = 11.7, 5.2 Hz, 1H), 3.92 (ddd, ^3J(H,H) = 7.9, 4.9, 2.7 Hz, 1H, *cis*), 4.08 (dd, ^3J(H,H) = 11.7, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS, *trans*-**16**): δ = 12.7, 19.2, 21.2, 29.7, 32.6, 32.7, 34.0, 62.8, 66.1, 74.9, 98.1; *cis*-**16**: δ = 10.6, 19.1, 21.7, 30.9, 31.8, 32.7, 33.9, 62.7, 66.9, 71.4, 98.1; IR (neat): $\tilde{\nu}$ = 3410, 2939, 2862, 1651, 1458, 1380, 1265, 1203, 1111, 1065, 910, 864, 802, 756 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{11}H_{22}O_3$: 202.1569: found: 202.1563 (0.1) [M^+], 188 (12), 187 (100), 173 (1).

***trans*-2,2-Dimethyl-4-(3-hydroxypropyl)-5-phenyl-1,3-dioxacyclohexane (17)**: This compound was obtained in 15% overall yield by using the procedure to obtain **16**; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.23–1.65 (m, 4H), 1.48 (s, 3H), 1.61 (s, 3H), 2.29 (br s, 1H), 2.80 (dt, ^3J(H,H) = 5.3, 11.5 Hz, 1H), 3.57 (tm, ^3J(H,H) = 5.5 Hz, 1H), 3.84 (dd, ^3J(H,H) = 5.3, 11.5 Hz, 1H), 3.97 (t, ^3J(H,H) = 11.5 Hz, 1H), 4.08 (ddd, ^3J(H,H) = 11.5, 8.6, 2.4 Hz, 1H), 7.16–7.35 (m, 5H); IR (neat): $\tilde{\nu}$ = 3437, 3030, 2995, 2941, 2873, 1949, 1454, 1383, 1267, 1201, 1055, 922, 723 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{15}H_{22}O_3$: 250.1569, found: 250.1605 (4) [M^+], 235 (43), 191 (10), 175 (100).

(4*S*′,4a*R*′,8a*R*′)-Hexahydro-4-(4-triphenylmethoxybutyl)-4*H*-benzo[*d*]-[1,3]dioxin-2-one (18): i) A solution of **2g** (35 mg, 0.18 mmol) in dichloromethane (12 mL) was cooled to −78 °C, and ozone was bubbled through until a blue color appeared (ca. 5 min.). The excess of ozone was removed by a flow of O_2. The mixture was allowed warm to 0 °C. To this solution was added a solution of $NaBH_4$ (114 mg, 3.0 mmol) in MeOH/H_2O (2 mL, 1:1) at 0 °C and the resultant mixture was stirred at ambient temperature for 12 h. The mixture was diluted with AcOEt and washed 2 M HCl and sat. $NaHCO_3$. The organic phase was dried ($MgSO_4$) and the solvent was removed in vacuo to give an oil.

ii) To a solution of the oil in dichloromethane (2 mL) were added triethylamine (59 mg, 0.59 mmol) and triphenylmethyl chloride (53 mg, 0.19 mmol), and the mixture was stirred at ambient room temperature for 3 h. After dilution with AcOEt (50 mL), the mixture was washed with sat. $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated in vacuo to give an oil. iii) A solution of the oil and 1,1′-carbonyl-diimidazole (221 mg, 1.36 mmol) in dry THF (2 mL) was stirred at ambient temperature for 48 h. The solvent was removed in vacuo and the residue was directly subjected to column chromatography on silica gel (AcOEt/hexane gradient 1:4→1:1) to give **18** (40 mg, 47% overall yield). ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): δ = 0.94 (dq, ^3J(H,H) = 3.7, 11.9 Hz, 1H), 1.21–1.89 (m, 13H), 2.14 (br dd, ^3J(H,H) = 10.8, 4.4 Hz, 1H), 3.08 (t, ^3J(H,H) = 10.8, 4.2 Hz, 2H), 3.98 (dt, ^3J(H,H) = 4.4, 11.0 Hz, 1H), 4.12 (ddd, ^3J(H,H) = 2.7, 7.1, 10.2 Hz, 1H), 7.10–7.45 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.9, 23.6, 24.4, 26.1, 29.6, 31.0, 32.3, 41.3, 63.0, 80.4, 84.0, 86.3, 126.7, 127.6, 128.2, 128.5, 144.2, 149.0; IR (neat): $\tilde{\nu}$ = 3031, 2939, 2869, 1751, 1489, 1450, 1373, 1204, 1087, 903, 849, 764, 702 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{31}H_{34}O_4$: 470.2457: found: 470.2455 (9) [M^+], 409 (19), 408 (57), 394 (27), 393 (100).

(4*R*,5*S*,6*R*,7*R*,8*R*)-4-Allyl-5,6,7-tris(benzyloxy)-8-(benzyloxymethyl)-2,2-dimethyl-1,3-dioxaoctane (19): *p*-TsOH (6.5 mg, 0.034 mmol) at ambient temperature under N_2 was added to a solution of **9a** (80.9 mg, 0.34 mmol) in 2,2-dimethoxypropane (5 mL). The mixture was stirred at reflux for 3 h, diluted with AcOEt, washed with sat. $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated in vacuo to give an oil, which was purified by column chromatography on silica gel (AcOEt/hexane 1:10) to give **19** (155 mg, 73%). ^{1}H NMR (400 MHz, C_6D_6, 27 °C, TMS): δ = 1.25 (s, 3H), 1.26 (s, 3H), 2.45 (ddd, ^3J(H,H) = 15.1, 7.3, 3.9 Hz, 1H), 2.79 (ddd, ^3J(H,H) = 15.1, 10.0, 7.3 Hz, 1H), 3.51 (dd, ^3J(H,H) = 10.0, 1.1 Hz, 1H), 3.83 (dd, ^3J(H,H) = 10.0, 3.9 Hz, 1H), 3.91 (dd, ^3J(H,H) = 10.0, 7.8 Hz, 1H), 4.02 (t, ^3J(H,H) = 7.8 Hz, 1H), 4.10 (dt, ^3J(H,H) = 10.0, 3.9 Hz, 1H), 4.21 (dd, ^3J(H,H) = 7.8, 1.1 Hz, 1H), 4.26 (dd, ^3J(H,H) = 7.8, 3.9 Hz, 1H), 4.28–4.41 (m, 3H), 4.56 (d, ^3J(H,H) = 11.0 Hz, 1H), 4.68 (d, ^3J(H,H) = 11.4 Hz, 1H), 4.80 (d, ^3J(H,H) = 11.0 Hz, 1H), 4.92 (d, ^3J(H,H) = 12.0 Hz, 1H), 5.09 (d, ^3J(H,H) = 11.4 Hz, 1H), 5.12 (d, ^3J(H,H) = 10.0 Hz, 1H), 5.19 (d, ^3J(H,H) = 17.3 Hz, 1H), 6.02 (ddt, ^3J(H,H) = 17.1, 10.0, 7.3 Hz, 1H), 7.04–7.35 (m, 20H); ^{13}C NMR (100 MHz, C_6D_6, 25 °C, TMS): δ = 24.5, 26.3, 35.1, 71.2, 71.9, 72.0, 73.3, 74.2, 74.5, 74.7, 74.8, 77.5, 80.9, 81.4, 100.4, 116.0, 127.1, 127.2, 127.3, 127.4, 127.5, 127.7, 127.8, 127.9, 128.1, 128.2, 128.3, 136.6, 138.9, 139.1, 139.2, 139.4, 139.5; IR (neat): $\tilde{\nu}$ = 3063, 3030, 2990, 2864, 2360, 1641, 1497, 1454, 1381, 1327, 1207, 1074, 1028, 999, 912, 827, 734, 698 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{40}H_{46}O_6$: 622.3294, found: 622.3290 (8) [M^+], 581 (10), 564 (10), 552 (5), 532 (39), 531 (100).

5,6,7-Tris(benzyloxy)-4-benzyloxymethyl-2,2-dimethyl-8-(1-phenylallyl)-1,3-dioxaoctane: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.68 (s, 3H), 1.08 (s, 3H), 3.44 (dd, ^3J(H,H) = 10.4, 2.0 Hz, 1H), 3.58 (t, ^3J(H,H) = 9.9 Hz, 1H), 3.72 (dd, ^3J(H,H) = 10.4, 2.9 Hz, 1H), 3.83 (dd, ^3J(H,H) = 8.8, 1.2 Hz, 1H), 3.90 (d, ^3J(H,H) = 7.1 Hz, 1H), 3.99 (dd, ^3J(H,H) = 7.1, 1.2 Hz, 1H), 4.27 (d, ^3J(H,H) = 9.9 Hz, 1H), 4.28 (d, ^3J(H,H) = 11.2 Hz, 1H), 4.35 (d, ^3J(H,H) = 12.2, 1H), 4.40–4.49 (m, 3H), 4.43 (d, ^3J(H,H) = 8.8 Hz, 1H), 4.55 (d, ^3J(H,H) = 12.2 Hz, 1H), 4.58 (d, ^3J(H,H) = 12.2 Hz, 1H), 4.70 (d, ^3J(H,H) = 11.2 Hz, 1H), 4.84 (dd, ^3J(H,H) = 17.1, 1.7 Hz, 1H), 4.93 (dd, ^3J(H,H) = 9.9, 1.7 Hz, 1H), 5.93 (dt, ^3J(H,H) = 17.1, 9.9 Hz, 1H), 7.11–7.34 (m, 25H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 23.7, 26.4, 53.3, 71.1, 71.2, 72.0, 72.3, 73.3, 76.0, 77.3, 78.3, 100.4, 116.7, 126.0, 127.3, 127.4, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.7, 129.0, 138.3, 138.4, 138.5, 138.6, 138.8, 143.0; IR (neat): $\tilde{\nu}$ = 3032, 2862, 2360, 1497, 1458, 1380, 1211, 1072, 918, 864, 810, 740, 702 cm^{-1}; HRMS (EI): *m/z* (%): calcd for $C_{46}H_{50}O_6$: 698.3607, found: 698.3558 (15) [M^+], 699 (100).

(4*S*,5*R*,6*R*,7*R*,8*R*)-4-Allyl-5,6,7-tris(benzyloxy)-8-(benzyloxymethyl)-1,3-dioxaoctan-2-one (20): THF (5 mL) via a syringe was added to a N_2 purged two-necked round bottom flask containing (6*S*)-**11** (140 mg, 0.24 mmol) and 1,1′-carbonyldiimidazole (60 mg, 0.36 mmol). The mixture was stirred at room temperature for 12 h and then refluxed for 24 h. The reaction mixture was diluted with ethyl acetate (30 mL), washed with sat. NaCl (20 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo, and the residue was subjected to column chromatography on silica gel (hexane/ethyl acetate 4:1) to give a semicarbamate (81 mg, 50%) at the C2-OH (R_f = 0.15, hexane/AcOEt 2:1). Into a N_2 purged two-necked round bottom flask containing the carbamate (0.12 mmol) and NaH (50% dispersion in mineral oil; 10 mg, 0.2 mmol), dry dioxane (3 mL) was introduced via a syringe and the reaction mixture was stirred at 80 °C for 6 h. The reaction mixture was diluted Et_2O (20 mL) and washed with sat. NH_4Cl (10 mL), and sat. NaCl (10 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo, and the residue was purified by column chromatography on silica gel (AcOEt/hexane 1:8) to give a cyclic carbonate **20** (85 mg, 58%; R_f = 0.60, hexane/AcOEt 2:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 2.45 (br dt, ^3J(H,H) = 14.2, 7.0 Hz, 1H), 2.61 (br dt, ^3J(H,H) = 14.2, 7.0 Hz, 1H), 3.76 (dd, ^3J(H,H) = 4.3, 11.3 Hz, 1H), 3.83 (br d, ^3J(H,H) = 11.3 Hz,

1H), 3.90 (d, ^3J(H,H) = 9.5 Hz, 1H), 4.05 (d, ^3J(H,H) = 9.5 Hz, 1H), 4.33 (d, ^3J(H,H) = 10.0 Hz, 1H), 4.40–4.54 (m, 4H), 4.57 (t, ^3J(H,H) = 12.0 Hz, 2H), 4.69 (br d, ^3J(H,H) = 12.0 Hz, 2H), 5.00 (d, ^3J(H,H) = 10.0 Hz, 1H), 5.07 (d, ^3J(H,H) = 16.0 Hz, 1H), 5.13 (t, ^3J(H,H) = 7.0 Hz, 1H), 5.28 (br dd, ^3J(H,H) = 4.3, 10.0 Hz, 1H), 5.70 (ddt, ^3J(H,H) = 10.0, 16.0, 7.0 Hz, 1H), 7.14–7.34 (m, 20H); ^{13}C NMR (400 MHz, $CDCl_3$ 25 °C, TMS): δ = 36.1, 69.0, 72.3, 73.0, 73.1, 73.2, 74.8, 75.0, 75.7, 118.1, 126.8, 127.1, 127.2, 127.3, 127.4, 127.5, 127.9, 128.1, 128.2, 128.3, 133.1, 137.8, 138.0, 138.6, 154.3; IR (neat): $\tilde{\nu}$ = 1744 (s), 1258 (s), 1096 (s), 733 cm^{-1} (s); HRMS (EI): *m*/*z* (%): calcd for $C_{38}H_{40}O_7$: 608.2774, found: 608.2768 (100) [M^+].

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