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Evidence for Synclinal Transition State in the Reactions of Aromatic Aldehydes with α-(Alkoxy)allylstannanes

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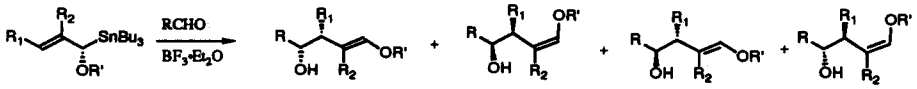
Abstract: *Unlike aliphatic aldehydes, aromatic aldehydes produce greater than 95% of syn-(Z) enol ether when treated with α-(alkoxy)allylstannanes in the presence of BF_3•Et_2O. However, in the presence of $TiCl_4$, the reaction of p-chloro-o-methoxybenzaldehyde with α-(alkoxy)crotylstannane produced predominantly the syn-(E) isomer.*

Electronic effects in electrophilic additions to chiral alkenes have become a subject of widespread interest.[1-5] However, due to the diversity in reaction mechanisms, solvent effects, and substrate variation, it is difficult to separate electronic effects from these other effects. There are several advantages in the study of the reactions of α-(alkoxyallyl)stannanes with aldehydes in the presence of a Lewis acid. The reactions of simple allylstannanes with aldehydes have been studied extensively[6] because they are useful synthetic reagents.[9] For the reactions of α-(alkoxyallyl)stannanes with aldehydes, the product stereochemistry (Z or E enol ether) clearly indicates the orientation of the allylic substituents in the transition state. For our study, all of the reactions are carried out in dichloromethane, a non-polar solvent. Hence, solvent effects are minimal. The asymmetric carbon atom in the α-(alkoxyallyl)stannanes is attached to four substituents (H, C, Sn, O) with very different electronic properties. Any electronic effects should be best displayed under these conditions.

From the results of our recent study,[7] which are summarized in **Table I**, among the three substituents of the allylstannanes, only the steric size of R_2 affects the diastereofacial selectivity significantly (entry 1-4, Table I). The change of R_1 from a methyl to a cyclohexyl (compare entry 6-10 with 11-13) and the change of R' from a benzyloxymethyl (BOM) group to a methyloxymethyl (MOM) group (compare entry 11-13 with 14-16); or to a sterically demanding group (8-phenylmenthyloxymethyl) (compare entry 6-10 with 17-20) did not have a dramatic effect on product ratio. The most striking results are from the reactions of aromatic aldehydes which react with all allylstannanes (except **1**) yielding preferentially the (Z)-enol ether products with excellent π-facial selectivity (entry 8-10, 13, 20).

Table I. Results From the Reactions Between the Chiral Stannanes and Various Aldehydes[a]



Entry	Allylstannane RCHO	Yield (%)	Distribution of diastereomeric products			
			syn-(E)	syn-(Z)	anti-(E)	anti-(Z)
	1: R'=BOM, R_1=R_2=CH_3					
1	**a** R=n-hexyl	80	>95 (**6a**)	<5	<1	<1
2	**b** =n-2-hexenyl	72	>95 (**6b**)	<5	<1	<1
3	**c** =cyclohexyl	51	>95 (**6c**)	<5	<1	<1
4	**d** =4-benzyloxy-butynyl	75	90 (**6d**)	10	<1	<1
5	**e** = C_6H_5		no reaction occurred at -78 °C			
	2: R'=BOM, R_1=CH_3, R_2=H					
6	**a** R=n-hexyl	76	55 (**10a**)	45 (**11a**)	<1	<1
7	**b** =cyclohexyl	45	80 (**10b**)	20 (**11b**)	<1	<1
8	**c** = C_6H_5	68	<1	95 (**11c**)	<1	5
9	**d** =p-ClC_6H_4	73	<1	95 (**11d**)	<1	5
10	**e** =p-$O_2NC_6H_4$	76	<1	95 (**11e**)	<1	5
	3: R'=BOM, R_1=Cyclohexyl, R_2=H					
11	**a** R=n-hexyl	66	88 (14a)	13 (**15a**)	<1	4
12	**b** =cyclohexyl	35	58 (14b)	42 (**15b**)	<1	<1
13	**c** = C_6H_5	62	3	91 (**15c**)	<1	6
	4: R'=MOM, R_1=Cyclohexyl, R_2=H					
14	**a** R= n-hexyl	71	81 (**18a**)	12 (**19a**)	<1	6
15	**b** = cyclohexyl	42	80 (**18b**)	20 (**19b**)	<1	<1
16	**c** = C_6H_5	79	11 (**18c**)	61 (**19c**)	<1	21 (21c)
	(S)-5: R'=(8-phenylmenthyl)oxymethyl, R_1=CH_3, R_2=H					
17	**a** R= n-hexyl	75	39 (22a)	61 (**23a**)	<1	<1
18	**b** = n-2-hexenyl	64	53 (22b)	47 (**23b**)	<1	<1
19	**c** = cyclohexyl	50	82 (22c)	18 (**23c**)	<1	<1
20	**d** = C_6H_5	72	<1	95 (**23d**)	<1	5

a All reactions were carried out at -78 °C in dichloromethane.

Why do the two types of aldehydes give the unprecedented reversal of π facial selectivity? We continue to be intrigued by this observation. A brief review of the S_E2' reactions of allylstannanes with the aid of Figure 1 may help clarify some key features of the mechanism. The reactions of simple allylstannanes with aldehydes have been studied extensively.[6] It is generally agreed that the stannyl group assumes a position anti to the incoming aldehyde in the transition state (see Newman projections in Fig. 1).[6,8,11,13] The relative orientation of the reactants double bond has been suggested to be antiperiplanar by Yamamoto[8a] for the reactions of simple allylstannanes with aldehydes on steric grounds. However, Denmark et al.[11] have shown that synclinal arrangement is favored in an intramolecular reaction of a simple allylstannane aldehyde.

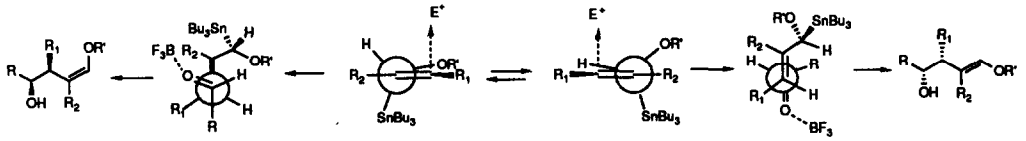


Figure 1. Attack of the electrophile on C-H eclipsed (outside alkoxy) and C-O eclipsed (inside alkoxy) conformers lead to (E)- and (Z)- enol ethers respectively.

To interpret our results, a certain structural effect other than steric has to be operating in order to produce the dramatic reversal in π facial selectivity for the two types of aldehydes. Based solely on steric interactions suggested by Yamamoto,[8a] both aliphatic and aromatic aldehydes should prefer the antiperiplanar arrangement (right hand of Fig. 1). While the steric bulkiness of a phenyl group is comparable to that of a cyclohexyl group, they gave totally different stereochemical consequences. Aromatic aldehydes fail to react with allylstannane **1** (where R_2 = Me), which is an important evidence suggesting that the aromatic aldehydes react via the synclinal arrangement. Since the size of the aldehyde substituents alone cannot explain the difference, we have attributed the reversal of π facial selection to the strength of the aldehyde-BF_3 complexes, Fig. 1.[7b] The difference in the properties between ArCHO•BF_3 and RCHO•BF_3 have been reported recently.[7c,d] In particular, the strong anti complexation of aromatic aldehydes with BF_3 renders the synclinal transition state more favorable (Fig. 1, left hand of the equilibrium). This, combined with the "inside alkoxy" effect,[1d] produces the highly selective process favoring the (Z) enol ether product.

Another possibility which can lead to the (Z)-enol ether isomer from an aromatic aldehyde was also considered. The same outcome would have been predicted if one assumes that the aromatic ring and the antibonding $\sigma^*_{C\text{-}O}$ orbital of the stannane attract each other through dipolar interactions. In terms of molecular orbital theory, the interaction between the low-lying C-O σ* of the alkoxy group and the π bond of the phenyl ring should be attractive.[14] If it was this attraction which causes the preference for the formation of (Z) enol ether, the transition state arrangement should be antiperiplanar as shown in Fig. 2. In order to differentiate which effect was responsible for the preference, one only has to differentiate whether the antiperiplanar or the synclinal transition state is operating. Now we wish to present experimental evidence that support a synclinal transition state arrangement in BF_3 mediated reactions of aromatic aldehydes.

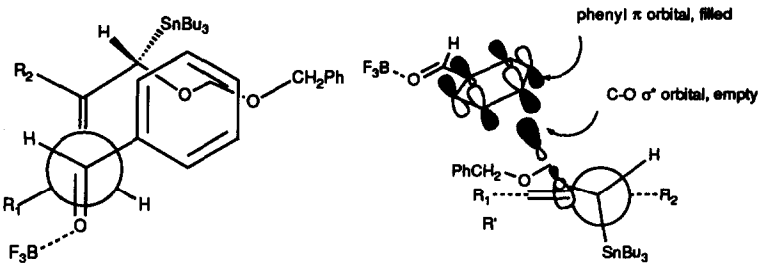


Fig. 2 Possible attraction between the low-lying C-O σ* of the alkoxy group and the phenyl π bond.

p-Chloro-*o*-methoxybenzaldehyde, **26**, was chosen as the probing substrate. At -78 °C, the aldehyde **26** was allowed to complex with $TiCl_4$ followed by the addition of allylstannane **2**. Our intention was to form a "syn" complex of ArCHO•$TiCl_4$ by using the Ti(IV) to chelate the carbonyl with the *o*-methoxy group. As shown in Fig. 3, this "syn" complex should destabilize the synclinal orientation of the transition state, **C**. Thus, if the BF_3 mediated high yield of syn-(Z) product was formed from the synclinal arrangement, the syn-(E) isomer should now be produced preferentially through **A**. This is exactly what happened. The distribution of the diastereomeric products is 72% syn-(E), 24% anti-(Z), and 4% syn-(Z). The syn-(Z) isomer was reduced to only 4%. On the other hand, if there were an attraction between the phenyl ring and the alkoxy moiety and the syn-(Z) products were formed through the antiperiplanar arrangement (**D**), we would have observed a high yield of the syn-(Z) enol ether because the transition state **D** should not have been affected by the chelated process. The anti-(Z) isomer was produced in considerable amount, which can be explained by the rotamer **B**. In fact, Keck et al.[8b] have shown that by changing the Lewis acid employed in the reactions of α, or β-alkoxyaldehyde with simple allylstannane, either syn or anti isomer can be produced selectively through either an open or chelated transition state.

To ascertain that Sn/Ti exchange did not take place, the reaction between *p*-ClC_6H_4CHO and allylstannane **2** were attempted in the presence of $TiCl_4$. Two equivalents of *p*-ClC_6H_4CHO were premixed with $TiCl_4$ and cooled to -78 °C. The allylstannane **2** was then added to the $TiCl_4$-aldehyde mixture. Decomposition of the stannane immediately occurred as evidenced by the appearance of a dark purple color. Evidently chelation by the methoxy group of aldehyde **26** is essential for the application of $TiCl_4$ as a Lewis acid in the reactions of α–(alkoxy)allylstannanes. The weak Lewis acid, $MgBr_2$, did not promote the reaction between *p*-ClC_6H_4CHO and allylstannane **2** even at 0 °C. At room temperature, the stannane **2** again decomposes. Other Lewis acids, such as $SnCl_4$ and $Ti(OPr\text{-}i)_2Cl_2$ did not give any useful yield of products. In any event, the α-(alkoxy)allylstannanes are easily decomposed by a strong Lewis acid, such as $TiCl_4$. Therefore, it is highly unlikely that a Sn/Ti exchange had occurred in the reaction of aldehyde **26** and allylstannane **2** because any free $TiCl_4$ would have decomposed the α–(alkoxy)allylstannane.

This significant change in the outcome of the diastereofacial selection is consistent with our previous suggestion. The same reaction in the presence of BF_3•Et_2O gave (40% total yield) a mixture of all four

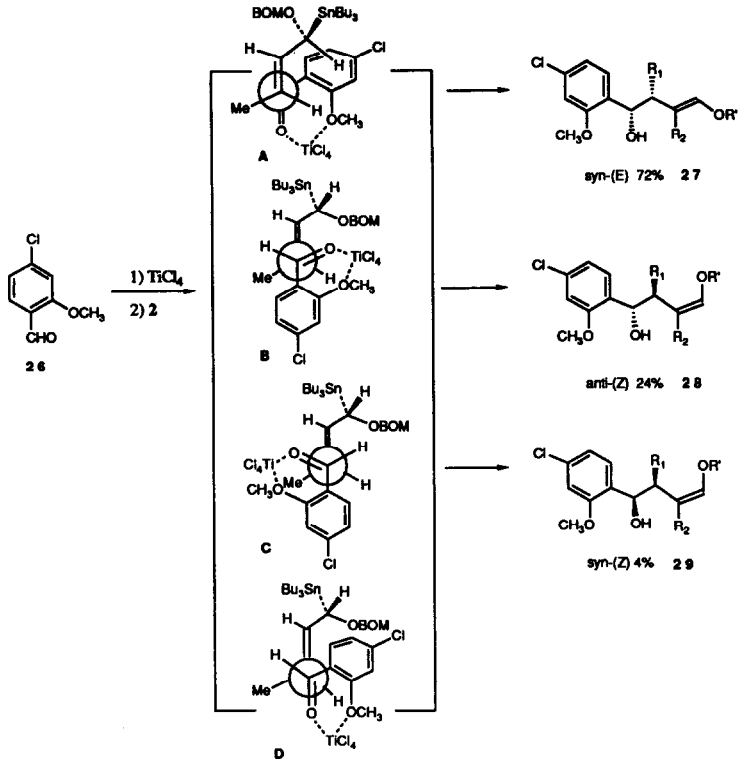


Fig. 3 Diastereofacial selection for the reaction of *p*-chloroanisaldehyde (**26**) and chiral allystannane **2** in the presence of $TiCl_4$.

possible isomers with the syn-(Z) isomer predominant. The relatively less reactive and less selective nature of **26** is apparently caused by the *o*-methoxy group. The chlorine atom is necessary to activate the *o*-anisaldehyde since no reaction occurred when o-anisaldehyde was treated with **2** in the presence of BF_3•Et_2O.

Next we would like to address the "inside alkoxy" effect in these reactions. Through our current results, Fig. 3, an attractive interaction between the alkoxy group of the stannane and the aromatic ring appears to be improbable. On the other hand the difference in the strength of complexation between RCHO•BF_3 and ArCHO•BF_3 complexes does offer a reasonable explanation.

Aliphatic aldehydes form rather loose complexes with BF_3, and aromatic aldehydes form strong anti-complexes with BF_3 based on both NMR experimental studies[13] and *ab initio* MO studies.[7c,d] The C-O-B angle of the PhCHO•BF_3 was shown to be 118° by a single crystal X-ray analysis.[12] This evidence plus the fact that the allylstannane **1** failed to react with benzaldehyde support the notion that aromatic aldehydes react with the chiral allylstannane via the synclinal arrangement and aliphatic aldehydes via the antiperiplanar orientation. The driving force for aromatic aldehydes to approach through the synclinal orientation is the steric interaction present in the antiperiplanar orientation between the R_1 group and the OBF_3 moiety.

The above arguments alone do not explain why the (Z)-enol ethers were the predominant product for aromatic aldehydes. The preference for an allylic alkoxy group to adopt the position parallel to the C=C bond in the transition state of an electrophilic addition to a chiral alkene has been discussed by Houk.[1] This steric model, now known as the "inside alkoxy" effect, has received both support and challenge.[2,3] The preference for the "inside alkoxy" arrangement displayed in [3+2]dipolar cycloadditions was modest.[1d,2a] The overwhelming preference for the "inside alkoxy" orientation in the reactions of aromatic aldehydes with α-(alkoxy)allylstannane is truly remarkable. We offer the following consideration. First, in these S_E2' reactions, the new chiral center is created while the old chiral center is being destroyed. In contrast, the chiral center of the chiral alkene in a [3+2]dipolar cycloaddition remains intact even after the new chiral center is formed. In other words, the communication between the asymmetric centers (most likely through hyperconjugation) is much more pronounced in the S_E2' reactions. Therefore the orientation of the allylic groups should have greater influence in the transition state of the S_E2' reactions. Secondly, the addition of a complex $RCHO{\cdot}BF_3$ to the allylstannane proceeds through a much more ionic transition state than a cycloaddition reaction. The strongly electrophilic nature of the S_E2' reaction demands that the electron-withdrawing group assumes the "inside" position to reduce electron-withdrawing from the transition state.

A good example to demonstrate the "inside alkoxy" effect in a S_E' reaction is Marshall's recent study of the intramolecular addition of the allylstannanealdehyde **30** to produce a 14-membered macrocycle.[11]

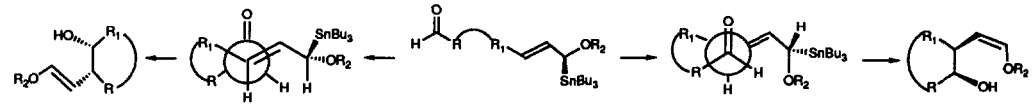


Fig. 4 "Inside alkoxy" effect in the intramolecular S_E' cyclization of α-(alkoxy)allylstannane aldehyde **30**.

For intramolecular addition, an antiperiplanar approach becomes less favorable due to the strain of the tether. Transition states **i** and **ii** would be enantiomeric if one ignores the alkoxy alignment since there is no chiral center on the tether. By inspection of molecular models of **i** and **ii**, no difference in steric effects is apparent here. The fact that the syn-(Z) product predominates suggests that the "inside alkoxy" effect, must be important in these reactions.

Having suggested that the aromatic aldehydes react via a synclinal arrangement, the fact that aliphatic aldehydes prefer the antiperiplanar transition state must due to steric effects. The $RCHO{\cdot}BF_3$ (R = alkyl) complexes are rather flexible, i.e. they do not have rigid anti configuration as their aromatic counter parts do.[7c,d,13] Consequently, the antiperiplanar arrangement experiences less steric repulsion. As depicted in Fig. 1, when the antiperiplanar transition state is operating, "outside alkoxy" arrangement of the allylstannane is preferred to avoid steric crowding. Therefore, syn-(E) products are produced preferentially. This preference is only modest because the electronic effect and steric effect are opposing each other. The minor syn-(Z) products from the reactions of aliphatic aldehydes are attributed to the synclinal transition state.

Supporting evidence came from the reactions of allylstannane **1** which gave greater than 95% syn-(E) product, Table I. The excellent diastereofacial selectivity displayed by **1** indicates that the pathway which leads to syn-(Z) products is strongly disfavored. Only when the synclinal arrangement is operating, do we expect such a strong effect from R_2, **Figure 1**. The inactivity of allylstannane **1** towards aromatic aldehydes is consistent with a synclinal transition state, where R_2 and BF_3 collide. Currently, we are expanding our investigation to other electrophilic additions involving chiral allylstannanes and allylgermanes, and will report our results in due course.

Experimental:

The apparatus and methods described by Kramer, Midland, and Levy[17] were used to maintain an argon or nitrogen atmosphere in the reaction flask. Anhydrous solvents were obtained by distillation from sodium benzophenone ketyl (diethyl ether, tetrahydrofuran), calcium hydride (dichloromethane). Infrared absorption maxima are reported in wavenumbers (cm-1). Proton magnetic resonance samples were prepared as dilute solutions in deuteriochloroform (CDCl3). Chemical shifts (d) are reported downfield from tetramethylsilane (Me_4Si), in parts per million (ppm) of the applied field. Peak multiplicities are abbreviated as follows: singlet, s; doublet, d; triplet, t; quartet, q; multiplet, m. Coupling constants(J) are reported in hertz (Hz). Analytical thin layer chromatography (TLC) was used routinely to monitor the reactions. Plates precoated with E. Merck silica gel 60 F254 of 0.25 mm thickness, supplied by Brinkman Instruments, were used. E. Merck silica gel 60 (230-400 ASTM mesh) was employed for column chromatography according to the procedure of Still.[18] The reactions of each allylstannane with aldehydes were carried out at -78 °C in CH_2Cl_2 solution with the ratio of stannane/aldehyde/BF_3 = 1.0/1.2/1.5. The product ratio was determined by ^1H NMR and GC-MS. The stereochemistry of the products was determined by ^1H NMR and NOE experiments, and confirmed by a single crystal X-ray analysis in the case of **15c**.[15]

(2E)-1-(Benzyloxymethyloxy)-2-methyl-2-butenyl(tri-n-butyl)stannane (1)

To a solution of diisopropyl amine (1.4 mL, 10 mmol) in THF (20 mL) under nitrogen atmosphere at 0°C was added n-BuLi (4 mL, 10 mmol) with stirring. After 10 min. Bu_3SnH (2.7 mL, 10 mmol) was added to the resulting LDA solution and the resulting mixture was allowed to stir for another 10 min. The Bu_3SnLi solution was then cooled to -78°C and trans-2-methyl-2-butenal (1.5 mL, 10 mmol) was added. After stirring for 10 min., the reaction was quenched with 10% HCl soln and warmed to 0°C. The mixture was then extracted with ether, washed with sat. $NaHCO_3$ and sat. NaCl, then dried over $MgSO_4$, and concentrated under reduced pressure. The residue (hydroxystannane) was immediately dissolved in methylene chloride (20mL) then cooled to 0°C under nitrogen. Diisopropylethylamine (3.5 mL, 20 mmol) and chloromethyl benzyl ether (2.08 mL, 15 mmol) were then added, in that order. The reaction mixture was allowed to stir for 3 hrs, then was quenched with 10% HCl solution. The crude product was extracted with ether, washed with sat. $NaHCO_3$ and sat. NaCl, then dried over $MgSO_4$ and concentrated under reduced pressure. The product was purified over a column of silica gel (eluted with 5% EtOAc/Hex) to give 2.9 g (60 %) of a colorless oil.
IR (neat) 2960, 1460, 1020cm^{-1}, ^1H NMR ($CDCl_3$): δ 7.34 (s, 5H), 5.30 (q, J = 6.05 Hz, 1H), 4.73 (d, J = 12.10 Hz, 1H), 4.64 (s, 2H), 4.59 (s, 1H), 4.47 (d, J = 12.10 Hz, 1H), 1.83 - 0.615 (m, 32H). *Anal.* Calcd for $C_{25}H_{44}O_2Sn$: C, 60.62; H, 8.95. Found: C, 60.43, H, 8.99.

(2E)-1-(Benzyloxymethyloxy)-2-butenyl(tri-n-butyl)stannane (2)

The above procedure described for allylstannane **1** was followed starting with 2.1 mL (25mmol) of crotonaldehyde, yielding 8.6 g (72%) of a colorless oil.
IR (neat) 2960, 1450, 1020 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.34 (s, 5H), 5.54 (m, 1 H), 5.46 (d, J = 5.50 Hz, 1 H), 4.79 (d, J = 6.6 Hz, 1 H), 4.71 (d, J = 6.6 Hz, 1 H), 4.61 (s, 2 H), 4.58 (d, J = 5.1 Hz, 1 H), 1.71 - 0.84 (m, 31H).

(2E)-1-(Benzyloxymethyloxy)-3-(cyclohexyl)-2-propenyl(tri-n-butyl)stannane (3)

The above procedure described for allylstannane **1** was followed starting with trans-3-cyclohexyl-2-propenal (1.95 g, 14.1 mmol), yielding 5.9 g (75%) of a colorless oil.
^{1}H NMR ($CDCl_3$): δ 7.34 (s, 5H), 5.45 (dd, J = 6.03 Hz, 2H), 4.72 (ABq, J_{AB} = 6.63 Hz, Δν = 12.2, 2H), 4.61 (s, 2H), 1.73 - 0.615 (m, 39H).

(2E)-1-(Methyloxymethoxy)-3-(cyclohexyl)-2-propenyl(tri-n-butyl)stannane (4)

The above procedure described for allylstannane **3** was followed replacing the chloromethyl benzyl ether with chloromethyl methyl ether. Similar yield was obtained.
^{1}H NMR ($CDCl_3$): δ 5.43 (dd, J = 6.23 Hz, J = 5.13 Hz, 2H), 4.60 (s, 1H), 4.59 (ABq, J_{AB} = 6.23 Hz, Δν = 17.6, 2H), 3.34 (s, 3H), 1.54 - 0.7 (m, 38H).

R-(+) and S-(-)-(2E)-1-[8-phenylmenthyloxy(methoxy)]-2-butenyl(tri-n-butyl)stannane [(R)-5 and (S)-5]

The above procedure described for allylstannane **2** was followed except replacing the chloromethyl benzyl ether with chloromethyl 8-phenylmenthyl ether.[16] The resulting two diastereomers can be separated through careful silica gel column chromatography with hexanes/CH_2Cl_2 mixture (9:1).
R-(+) 5: $[\alpha]_D$ = +20.4° (c 1.25, $CHCl_3$), IR (neat) 2954, 2340, 1471, 1008 cm^{-1}, ^{1}H NMR ($CDCl_3$): δ 7.26 (m, 5H), 5.45 (m, 2 H), 4.57 (m, 3 H), 3.44 (m, 2 H), 2.17-1.11 (m, 31 H), 0.89 (t, J = 6.3 Hz, 9H).
S-(-) 5: $[\alpha]_D$ = -26.7° (c 1.11, $CHCl_3$), IR (neat) 2954, 2341, 1471, 1008 cm^{-1}, ^{1}H NMR ($CDCl_3$): δ 7.26 (m, 5H), 5.50 (m, 2 H), 4.65 (d, J = 6.3 Hz, 1H), 4.57 (d, 1H), 4.47 (d, J = 6.3 Hz, 1H), 3.32 (ddd, J = 3.2, 10.1, 13.9 Hz, 1H), 2.20-0.73 (m, 32H), 0.90 (t, 7.6 Hz, 9H).

(1E)-1-(Benzyloxymethyloxy)-2,3-dimethyl-3-hydroxy-1-decene. (6a)

^{1}H NMR ($CDCl_3$): δ 7.33 (s, 5 H), 6.10 (s, 1 H), 4.92 (s, 2 H), 4.62 (s, 2 H), 3.30 (m, 1H), 2.04 (m, 1 H), 1.60 - 0.875 (m, 21 H). *Anal.* Calcd for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06. Found: C, 74.90, H, 10.12.

(1E, 5E)-1-(Benzyloxymethyloxy)-2,3-dimethyl-4-hydroxy-1,5-decadiene. (6b)

^{1}H NMR ($CDCl_3$): δ 7.33 (s, 5 H), 6.11 (s, 1 H), 5.52 (m, 1 H), 4.91 (s, 2 H), 4.62 (s, 2 H), 4.0 (dd, J = 5.8, 5.8 Hz, 1 H), 2.04 - 0.92 (m, 18 H).

(1E)-1-(Benzyloxymethyloxy)-2,3-dimethyl-4-hydroxy-4-phenyl-1-butene. (6c)

^{1}H NMR ($CDCl_3$): δ 7.33 (s, 5 H), 6.10 (s, 1 H), 4.91 (s, 2 H), 4.62 (s, 2 H), 3.27 (dd, J = 5.78, 10.05 Hz, 1 H), 2.24 (m, 1 H), 1.62 (d, J = 1.8 Hz, 3 H), 1.04 (d, J = 7.2 Hz, 3 H), 1.71 - 0.86 (m, 11 H). IR (neat): 3399.0, 2925.3, 2851.3, 1050.5 cm^{-1}. GC/MS: Retention time = 12.26 min. Calculated for $C_{20}H_{30}O_3$, 318.45; observed, 233 (M^+ - C_6H_{11}), 206 (M^+ - $C_7H_{13}O$).

(7E)-1-Benzyloxy-8-(benzyloxymethyloxy)-5-hydroxy-6,7-dimethyl-7-octen-3-yne. (6d)

IR (neat) 3450, 2925, 1100 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.33 (s, 10 H), 6.19 (s, 1 H), 4.02 (d, J = 1.62 Hz, 2 H), 4.62 (s, 2 H), 4.53 (s, 2 H), 3.57 (td, J = 2.62 Hz, 5.67 Hz, 2 H), 2.52 (m, 2 H), 1.73 - 0.85 (m, 8 H).

(1Z)-1-(Benzyloxymethyloxy)-2,3-methyl-4-hydroxy-4-phenyl-1-butene. (7c)

^{1}H NMR ($CDCl_3$): δ 7.33 (s, 5 H), 6.17 (s, 1 H), 4.91 (d, J = 3.3 Hz, 2 H), 4.62 (s, 2 H), 3.2 (m, 1 H), 2.2 (m, 1 H), 1.57 (dd, J = 1.5 Hz, 4.1 Hz, 3 H), 0.97 (d, J = 6.6 Hz, 3 H), 1.71 - 0.86 (m, 11 H).
GC/MS: Retention time = 11.93 min. Calculated for $C_{20}H_{30}O_3$, 318.45; observed, 233 (M^+ - C_6H_{11}), 206 (M^+ - $C_7H_{13}O$).

1(E)-1-(Benyloxymethyloxy)-4-cyclohexyl-4-hydroxy-3-methyl-1-butene. (10b)

^{1}H NMR ($CDCl_3$): δ 7.34 (s, 5 H), 6.10 (d, J = 12.6 Hz, 1 H), 4.92 (s, 2 H), 4.63 (s, 2 H), 4.4 (dd, J = 9.0, 12.6 Hz, 1H), 1.71 - 0.86 (m, 16 H). *Anal.* Calcd for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 74.87, H, 9.34.

(1Z)-1-(Benzyloxymethyloxy)-4-hydroxy-3-methyl-1-decene. (11a)

^{1}H NMR ($CDCl_3$): δ 7.34 (s, 5 H), 6.22 (d, J = 6.2 Hz, 1 H), 4.92 (s, 2 H), 4.63 (s, 2 H), 4.41 (dd, J = 6.2, 6.0 Hz, 1 H), 1.01 (d, J = 7.18 Hz, 3 H), 1.61 - 0.87 (m, 16 H).

(1Z)-1-(Benzyloxymethyloxy)-4-hydroxy-3-methyl-4-phenyl-1-butene. (11c)

^{1}H NMR ($CDCl_3$): δ 7.32 (s, 10 H), 6.17 (d, J = 6.3 Hz, 1 H), 4.86 (s, 2 H), 4.54 (s, 2 H), 4.34 (dd, J = 5.4, 6.3 Hz, 1 H), 3.1 (m, 1H), 1.6 (m, 1H), 1.00 (d, J = 6.8 Hz, 3 H).

(1Z)-1-(Benzyloxymethyloxy)-4-hydroxy-3-methyl-4-(p-chlorophenyl)-1-butene. (11d)

^{1}H NMR ($CDCl_3$): δ 7.32 - 7.25 (m, 9 H), 6.16 (d, J = 7.3 Hz, 1 H), 4.85 (s, 2 H), 4.54 (s, 2 H), 4.27 (dd, J = 7.3, 6.2 Hz, 1 H), 2.5 - 2.3 (m, 1 H), 0.97 (d, J = 7.0 Hz, 3 H).

(1Z)-1-(Benzyloxymethyloxy)-4-hydroxy-3-methyl-4-(p-nitrophenyl)-1-butene. (11e)

^{1}H NMR ($CDCl_3$): δ 7.81 (ABq, J_{AB} = 8.8 Hz, Δν = 59.5 Hz, 4 H), 7.32 (s, 5 H), 6.21 (d, J = 6.6 Hz, 1 H), 4.88 (s, 2 H), 4.56 (s, 2 H), 4.28 (dd, J = 6.6, 6.2 Hz, 1 H), 3.1 (m, 1 H), 2.69 (d,1 H), 0.96 (d, J = 7.0 Hz, 3 H).

(1E)-1-(benzyloxymethyloxy)-3-cyclohexyl-4-hydroxy-1-decene (14a)

^{1}H NMR ($CDCl_3$): δ 7.34 (s, 5 H), 6.26 (d, J = 12.5 Hz, 1 H), 4.94 (s, 2 H), 4.80 (dd, obscured by other protons, 1 H), 4.64 (s, 2 H), 3.65 (m, 1H) 1.26 - 0.88 (m, 25 H). *Anal.* Calcd for $C_{24}H_{38}O_3$: C, 76.96; H, 10.23. Found: C, 76.90, H, 10.55.

(1E)-1-(Benzyloxymethyloxy)-3,4-dicyclohexyl-4-hydroxy-1-butene. (14b)

^{1}H NMR ($CDCl_3$): δ 7.34 (s, 5 H), 6.22 (d, J = 12.1 Hz, 1 H), 4.94 (s, 2 H), 4.77 (dd, obscured by other protons, 1 H), 4.64 (s, 2 H), 3.40 (m, 1H), 2.44 (ddd, J = 2.5, 10.6, 2.5 Hz, 1 H), 1.67 - 0.75 (m, 23 H).

(1Z)-1-(Benzyloxymethyloxy)-3-cyclohexyl-4-hydroxy-1-decene (15a)

^{1}H NMR ($CDCl_3$): δ 7.34 (s, 5), 6.42 (d, J = 6.6 Hz, 1 H), 4.92 (s, 2 H), 4.62 (s, 2 H), 4.29 (dd, J = 6.6, 10.6 Hz, 1 H), 3.75 (m, 1 H), 1.56 - 0.65 (m, 25 H).

(1Z)-1-(Benzyloxymethyloxy)-3,4-dicyclohexyl-4-hydroxy-1-butene. (15b)

^{1}H NMR ($CDCl_3$) δ 7.34 (s, 5), 6.35 (d, J = 6.96 Hz, 1 H), 4.89 (s, 2 H), 4.61 (s, 2 H), 4.23 (dd, J = 6.9, 6.23 Hz, 1 H), 3.41 (dd, J = 5.9, 10.3 Hz, 1 H), 2.71 (ddd, J = 2.9, 10.3, 2.9 Hz, 1 H), 1.65 - 0.89 (m, 23 H).

(1Z)-1-(Benzyloxymethyloxy)-3-cyclohexyl-4-hydroxy-4-phenyl-1-butene. (15c)

^{1}H NMR ($CDCl_3$): δ 7.34 (s, 10 H), 6.20 (d, J = 6.6 Hz, 1 H), 4.78 (s, 2 H), 4.45 (s, 2 H), 4.16 (dd, J = 6.3, 11.3 Hz, 1 H), 2.97 (m, 1H), 2.23 (m, 1 H), 1.69 - 0.84 (m, 12 H). IR (Neat) 3390.2, 2922.9, 1675.1, 1448.7, 1044.2, 749.0 cm^{-1}. GC/MS: 260 (4.3), 229 (19), 139 (14.2), 107 (19), 91 (100).

(1E)-1-(Methyloxymethoxy)-3-cyclohexyl-4-hydroxy-1-decene. (18a)

^{1}H NMR ($CDCl_3$): δ 6.15 (d, J = 12.5 Hz, 1 H), 4.81 (s, 2 H), 4.77 (dd, J = 10.6, 12.1 Hz, 1 H), 3.52 (m, 1 H), 3.41 (s, 3 H), 2.18 - 0.83 (m, 26 H). *Anal.* Calcd for $C_{18}H_{34}O_3$: C, 72.44; H, 11.48. Found: C, 72.34, H, 11.58.

(1Z)-1-(Methyloxymethoxy)-3-cyclohexyl-4-hydroxy-1-decene. (19a)

^{1}H NMR ($CDCl_3$): δ 6.30 (d, J = 6.97 Hz, 1 H), 4.79 (s, 2 H), 4.27 (dd, J = 6.97, 10.6 Hz, 1 H), 3.69 (m, 1 H), 3.38 (s, 3 H), 1.92 - 0.85 (m, 26 H).

(1Z)-1-(Methyloxymethoxy)-3-cyclohexyl-4-hydroxy-4-phenyl-1-butene. (19c)

^{1}H NMR ($CDCl_3$): δ 7.29 (s, 5 H), 6.14 (d, J = 6.6 Hz, 1 H), 4.67 (s, 2 H), 4.13 (dd, J = 6.6, 11.0 Hz, 1 H), 3.48 (d, J = 7.0 Hz, 1 H), 3.25 (s, 3 H), 2.18 - 0.83 (m, 13 H).

(1E)-1-(Methyloxymethoxy)-3-cyclohexyl-4-hydroxy-4-phenyl-1-butene. (21c)

^{1}H NMR ($CDCl_3$): δ 7.33 (s, 5 H), 6.38 (d, J = 6.2 Hz, 1 H), 4.74 (s, 2 H), 4.53 (dd, J = 6.6, 10.6 Hz, 1 H), 3.30 (s, 3 H), 3.18 (d, J = 7.0 Hz, 1 H), 2.18 - 0.92 (m, 13H).

(3R,4R),(1E,5E)-1-[((S)-8-phenylmenthyloxy)methoxy]-3-methyl-1,5-decadien-4-ol (22b)

^{1}H NMR ($CDCl_3$): δ 7.22-7.09 (m, 5H), 6.11 (d, J = 12.5 Hz, 1H), 5.66-5.25 (m, 2H), 4.75 (dd, J = 8.7, 12.8 Hz, 1H), 4.76 (d, J = 7.0 Hz, 1H), 4.55 (d, J = 7.0 Hz, 1H), 3.80 (dd, J = 5.0, 5.0 Hz, 1H), 3.42 (m, 1H), 1.34 (s, 3H), 1.23 (s, 3H), 0.91 (d, J = 7.0 Hz, 3H), 2.13-0.69 (m, 22H). *Anal.* Calcd for $C_{28}H_{44}O_3$: C, 78.46; H, 10.35. Found: C, 78.45, H, 10.38.

(3R,4R),(1E)-1-[((S)-8-phenylmenthyloxy)methoxy]-4-cyclohexyl-3-methyl-1-buten-4-ol (22c)

^{1}H NMR ($CDCl_3$): δ 7.32-7.16 (m, 5H), 6.17 (d, J = 12.5 Hz, 1H), 4.89 (dd, J = 7.9, 12.5 Hz, 1H), 4.82 (d, J = 7.3 Hz, 1H), 4.63 (d, J = 7.0 Hz, 1H), 3.45 (m, 1H), 3.14 (m, 1H), 1.41 (s, 3H), 1.30 (s, 3H), 0.86 (d, J = 5.5 Hz, 3H), 2.08-0.81 (m, 24H).

(3S,4S),(1Z)-1-[((S)-8-phenylmenthyloxy)methoxy]-3-methyl-1-decen-4-ol (23a)

^{1}H NMR ($CDCl_3$): δ 7.35-7.16 (m, 5H), 6.06 (d, J = 6.2Hz, 1H), 4.83 (d, J = 7.0, 1H), 4.62 (d, J = 7.0, 1H), 4.32 (dd, J = 6.7, 9.5Hz, 1H), 3.49 (m, 2H), 2.74 (m, 1H), 1.42 (s, 3H), 1.29 (s, 3H), 0.87 (d, J = 5.9Hz, 3H), 2.10-0.72 (m, 25H).

(3S,4S),(1Z,5E)-1-[((S)-8-phenylmenthyloxy)methoxy]-3-methyl-1,5-decadien-4-ol (23b)

^{1}H NMR ($CDCl_3$): δ 7.38-7.16 (m, 5H), 6.06 (d, J = 6.6 Hz, 1H), 5.68-5.29 (m, 2H), 4.79 (d, J = 7.0 Hz, 1H), 4.62 (d, J = 7.0 Hz, 1H), 4.32 (dd, J = 6.6, 9.5 Hz, 1H), 3.88 (dd, J = 5.0, 5.0 Hz, 1H), 3.45 (m, 1H), 2.81 (m, 1H), 1.34 (s, 3H), 1.22 (s, 3H), 0.89 (d, J = 7.0 Hz, 3H), 1.98-0.76 (m, 21H).

(3S,4S),(1Z)-1-[((S)-8-phenylmenthyloxy)methoxy]-4-cyclohexyl-3-methyl-1-buten-4-ol (23c)

^{1}H NMR ($CDCl_3$): δ 7.38-7.17 (m, 5H), 6.01 (d, J = 7.3 Hz, 1H), 4.79 (d, J = 7.0 Hz, 1H), 4.62 (d, J = 7.0 Hz, 1H), 4.36 (dd, J = 6.2, 9.1 Hz, 1H), 3.44 (m, 1H), 3.12 (s, 1H), 2.77 (dd, 1H), 1.40 (s, 3H), 1.30 (s, 3H), 0.98 (d, J = 7.0 Hz, 3H), 2.02-0.71 (m, 23H).

(3S,4S),(1Z)-1-[((S)-8-phenylmenthyloxy)methoxy]-3-methyl-4-phenyl-1-buten-4-ol (23d)

$[\alpha]_D$ = -32.9° (c 2.51, $CHCl_3$), ^1H NMR ($CDCl_3$): δ 7.31-7.16 (m, 10H), 6.05 (d, J = 6.3 Hz, 1H), 4.74 (d, J = 6.9 Hz, 1H), 4.60 (d, J = 7.0 Hz, 1H), 4.26 (dd, J = 6.3, 9.5 Hz, 1H), 3.45 (m, 1H), 3.11 (m, 1H), 1.40 (s, 3H), 1.30 (s, 3H), 0.95 (d, J = 5.1 Hz, 3H), 2.25-0.70 (m, 13H).

rel-(1E,3R,4S)-1-(benzyloxy)methoxy-3-methyl-4-(p-chloro-o-methoxy)phenyl-1-buten-4-ol, 27 and 28

To a solution of *p*-chloro-*o*-anisaldehyde (0.24 g, 1.5 mmol) in CH_2Cl_2 (10mL) at -78°C under nitrogen atmosphere was added $TiCl_4$ (0.16mL, 1.5 mmol)with stirring. Chiral crotyl stannane **1** (0.48 g, 1.0 mmol) was then added and the reaction was allowed to stir for 2 hrs. The reaction was then quenched with sat. $NaHCO_3$ solution, extracted with ether, washed with sat. NaCl solution, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by a column of silica gel (eluted with 5% EtOAc/Hex followed by 10% and 20%) to yield 290 mg (80%) of a colorless oil.

27: Syn (E): ^1H NMR ($CDCl_3$): δ 7.4 - 6.74 (m, 8 H), 6.19 (d, J = 12.0 Hz, 1 H), 5.01 (dd, J = 8.3 Hz, J = 12.6 Hz, 1 H), 4.86 (s, 2 H), 4.83 (d, J = 4.2 Hz, 1 H), 4.57 (s, 2 H), 3.81 (s, 3 H), 3.20 (m, 1 H), 1.01 (d, J = 6.9 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 144.5, 143.5, 137.2, 130.9, 128.4, 128.2, 128.0, 127.9, 126.5, 111.3, 110.0, 93.6, 71.3, 69.8, 39.9, 26.8, 16.5. IR (neat): 3450, 2950, 2860, 1240 cm^{-1}.

28: Anti (Z): ^1H NMR ($CDCl_3$): δ 7.4 - 6.74 (m, 8 H), 6.32 (d, J = 6.6 Hz, 1 H), 4.88 (s, 2 H), 4.52 (s, 2 H), 4.79 (d, J = 4.2 Hz, 1 H), 4.52 (dd, J = 6.6 Hz, J = ? Hz, 1 H), 3.81 (s, 3 H), 3.20 (m, 1 H), 1.05 (d, J = 6.8 Hz, 3 H).

rel-(1Z,3S,4R)-1-(benzyloxy)methoxy-3-methyl-4-(p-chloro-o-methoxy)phenyl-1-buten-4-ol, 29

To a solution of *p*-chloro-*o*-anisaldehyde (0.24 g, 1.5 mmol) and crotyl stannane (0.48 g, 1.0 mmol) in CH_2Cl_2 (10 mL) under nitrogen atmosphere at -78°C was added BF_3·Et_2O (0.18 mL, 1.5 mmol) with stirring. After 2 hrs the reaction was quenched with sat. $NaHCO_3$, extracted with ether, washed with sat. NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified over a column of silica gel (eluted with 10% EtOAc/Hex followed by 20% and 50%) to give 145 mg (40% yield) of a colorless oil. Proton NMR indicates a mixture of diastereomers with the syn-(Z) isomer predominant.

29: Syn (Z): ^1H NMR ($CDCl_3$): δ 7.4 - 6.74 (m, 8 H), 6.11 (d, J = 6.4 H, 1 H), 4.81 (s, 2 H), 4.51 (s, 2 H), 4.38 (dd, J = 6.4 Hz, J = 9.5 Hz, 1 H), 3.79 (s, 3 H), 3.20 (m, 1 H), 1.05 (d, J = 6.8 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 143.8, 142.3, 137.1, 133.0, 128.4, 127.8, 127.6, 125.4, 111.6, 110.7, 110.6, 109.7, 94.1, 73.5, 69.7, 55.6, 27.8, 17.5. IR (neat) 3450, 2955, 2470, 1245 cm^{-1}.

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