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S_E' ADDITION OF HOMOCHIRAL α-ALKOXYALLYLSTANNANES TO ALDEHYDES

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Abstract. Addition of the homochiral (*S*)-[1-(benzyloxy)methoxy-2-(*E*)-hexenyl] (tri-*n*-butyl)stannane (**5b**) to heptanal (**1a**), (*E*)-2-heptenal (**1b**), and 2-heptynal (**1c**) under BF_3 catalysis was examined. In all cases the addition proceeded by anti S_E' attack to give mainly the syn E adducts **se8a-c** with high ee.

Additions of allylstannanes to aldehydes have attracted widespread interest in recent years.[1] Early studies by Yamamoto showed that BF_3 catalyzed additions of both (*E*) and (*Z*)-allylstannanes afford syn adducts stereoselectively suggestive of an extended acyclic transition state.[2] On the other hand, under thermal or hyperbaric conditions, (*E*)-allylstannanes yield anti products and (*Z*)-allylstannanes give syn products in accord with a chelated six-membered cyclic transition state.[2] In $TiCl_4$ promoted reactions the diastereoselectivity depends upon the order of mixing. Addition of the allylstannane to a mixture of the Lewis acid and the aldehyde gives the syn adduct whereas premixing the allylstannane with excess $TiCl_4$ followed by addition of the aldehyde leads to the anti adduct.[3] The latter conditions are thought to involve conversion of the allylstannane to a reactive (*E*)-allyltitanium species which condenses with the aldehyde through a cyclic six-membered transition state.[3]

In studies directed toward cembranolide natural products, we found that upon treatment with $BF_3 \cdot Et_2O$, the homochiral (*S*)-α-alkoxyallylstannane aldehyde II cyclizes in excellent yield to a mixture of the four isomeric hydroxy enol ethers III-VI in the ratio 80:8:8:4 (Figure 1).[4] The present investigation was undertaken to extend these findings to intermolecular additions with a view toward a better understanding of the intrinsic factors controlling the stereochemistry and as a possible route to homochiral gamma-lactones.

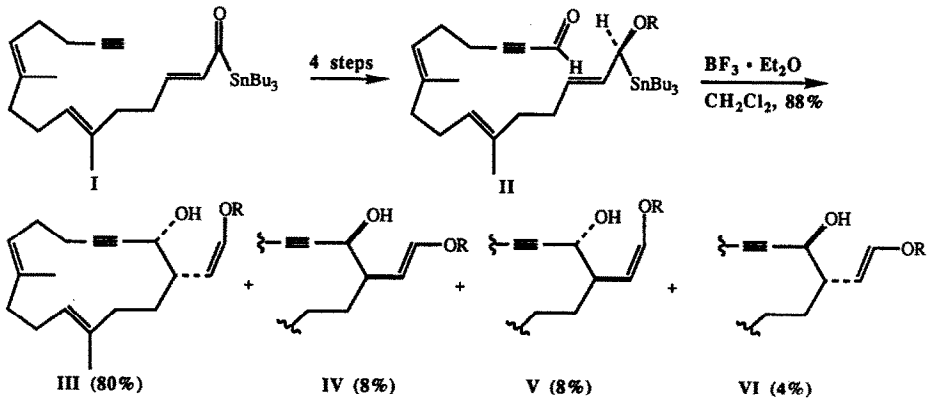
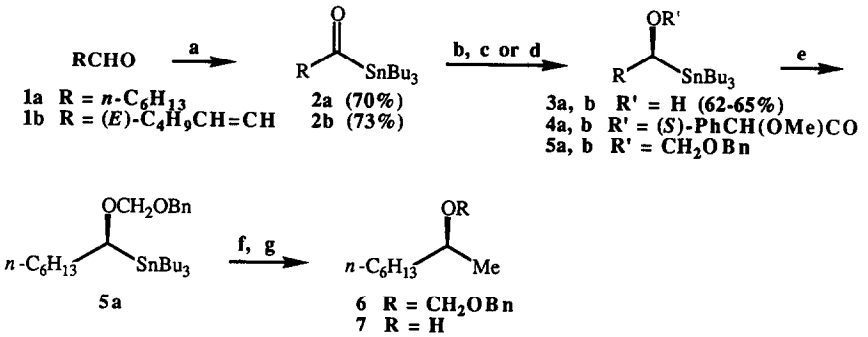


Figure 1. Cyclization of a homochiral α-alkoxyallylstannyl aldehyde to homochiral cembranolide precursors

The synthesis of homochiral α-alkoxyallylstannanes developed in connection with the aforementioned cembranolide work was easily applicable to aldehyde **1b**.[4] Thus, addition of Bu_3SnLi, according to the procedure of Still,[5] followed by *in situ* oxidation of the adducts by the Mukaiyama protocol[6] employing azodicarbonyldipiperidide (ADD) as a hydride acceptor, afforded the acylstannane **2b**. This was reduced with Noyori's (*R*)-BINAL-H reagent[7] to the optically active stannylcarbinol **3b** of greater than 95% ee.[8]

Scheme 1



(a) LDA, Bu_3SnH, THF; *t*-BuOH, ADD, -20° to 0°C; (b) (*R*)-(+)-BINAL-H, THF, -85°C; (c) (*S*)-PhCH(OMe)CO_2H, DCC, DMAP, CH_2Cl_2; (d) $BnOCH_2Cl$, *i*-Pr_2NEt, CH_2Cl_2; (e) $TsNHNH_2$, NaOAc, EtOH, Δ; (f) *n*-BuLi, THF; Me_2SO_4; (g) Na, NH_3

The enantiomeric purity of this carbinol was determined from the ^1H NMR spectrum of the (*S*)-O-methyl mandelate **4b**. Chemical shift differences between the vinylic protons of this derivative and the corresponding (*R*)-O-methyl mandelate were used to assign the absolute configuration.[9] An additional independent check on this assignment was achieved through conversion of the saturated stannyl carbinol **3a**, prepared analogously to **3b**, to the benzyloxymethyl (BOM) ether **5a**. Lithiation followed by methylation afforded the BOM ether **6**, $[\alpha]_D$ +27°.[8,10] Dissolving metal hydrogenolysis of the BOM grouping led to (*S*)-(+)-2-octanol of 80% ee.[11] Diimide reduction[8b,12] of the alkenyl ether **5b** afforded the BOM ether **5a**, $[\alpha]_D$ +32°, of somewhat greater optical rotation than that of the sample obtained from alcohol **3a**. Thus, reduction of acylstannanes **2a** and **2b** with (*R*)-BINAL-H[7] proceeds with high enantioselectivity to give carbinols **3a** and **3b** of the (*S*) configuration.

These results differ in several important respects from those reported by Noyori for reductions of aryl, vinyl and alkynyl ketones with BINAL-H.[7] (1) (*R*)-BINAL-H reduces acylstannanes to *S* alcohols whereas aryl, vinyl and alkynyl ketones are reduced to *R* alcohols. (2) Reductions of acylstannanes are generally fast (2-5 h at -78°C) but reductions of the aforementioned ketones are slow (~14-16 h at -78°C). (3) Saturated acylstannanes are reduced with high ee whereas saturated ketones are not.[13]

The foregoing differences suggest that acylstannane and ketone reductions are not subject to the same controlling factors. Noyori views repulsive electronic interactions between the pi electrons of an unsaturated substituent and the unshared electrons of an axial BINAL oxygen in a chelated chair-like arrangement as the factor that disfavors transition state **A** relative to **B** in reductions of unsaturated ketones (Figure 2). The small steric size of Bu_3Sn[14] and the possibility for chelation with a BINAL oxygen should favor the analogous Noyori transition state **D** for acylstannanes. However, this transition state predicts that reduction with (*R*)-BINAL-H[7] should yield (*R*)-stannylcarbinols, contrary to fact. Because acyl substitution should enhance the Lewis acidity of the Sn atom in acylstannanes, an alternative transition state in which the more basic alkoxy grouping of the BINAL-H reagent[7] is associated with the Sn atom becomes an attractive possibility.[15] The resulting transition state **C** is in accord with the observed steric sense of the reduction and accounts for the enhanced rates observed with acylstannanes compared to ketones.

Addition of the (*S*)-benzyloxymethyl-(*E*)-1-hexenylstannane (**5b**) to aldehydes **1a-1c** took place readily at -78°C to give a mixture of enol ether products **se8**, **sz8**, **ae8** and **az8**[16] (Table 1). The hexyl and hexynyl substituted adducts were inseparable, but the ratio of isomers could be measured by ^1H NMR analysis. The Hα signal was particularly informative showing well separated peaks with typical *Z* couplings of 6.4-6.9 Hz for **sz8** and **az8** compared with 12.4 Hz for **se8**. The fourth adduct, **ae8**, was not formed in quantities sufficient to measure in the case of **8a** and **8b** (Table 2).

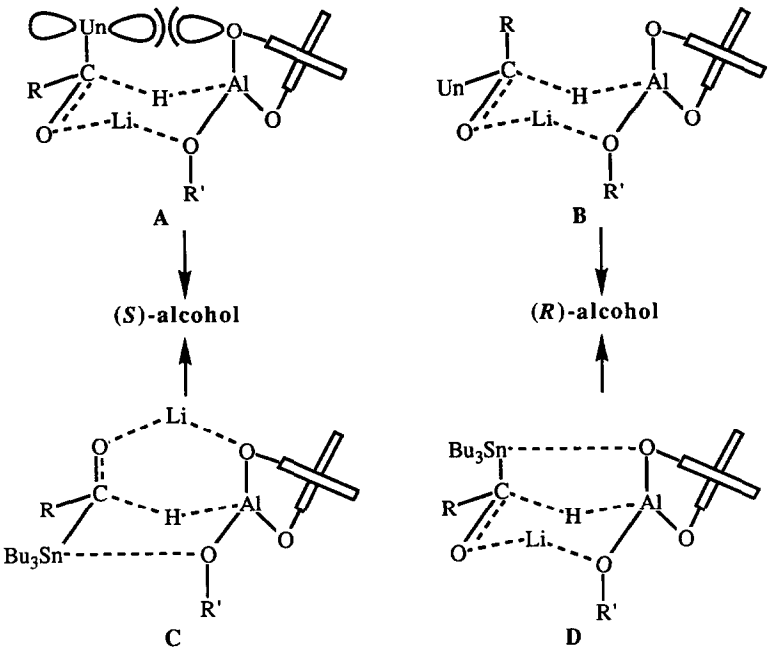
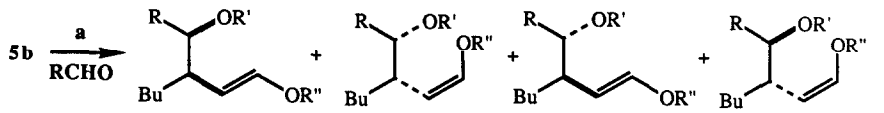


Figure 2. Transition states for (*R*)-BINAL-H reductions of ketones and acylstannanes (R' = Me or Et, Un = Ph, RC≡C, or RCH=CH)

Table 1. Addition of (*S*)-Alkoxyallylstannane **5b** to Aldehydes **1a-1c**

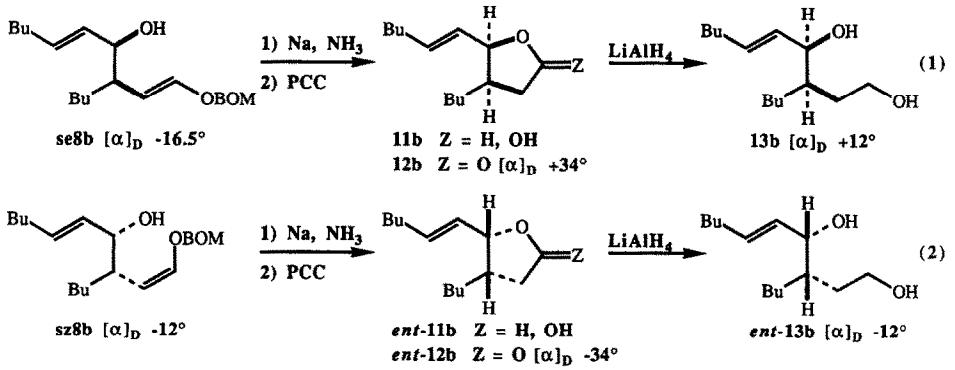


R' = H	se8	sz8	ae8	az8
R' = (*S*)-PhCH(OMe)CO	se9	sz9	ae9	az9
R' = (*R*)-PhCH(OMe)CO	se10	sz10		

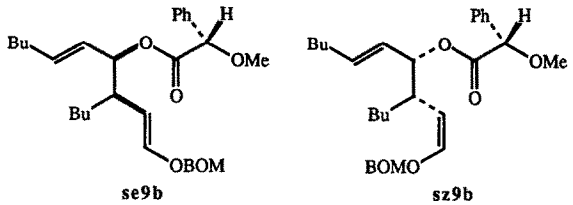
		Products (%)				Ratios	
R	yield (%)	se8[b]	sz8	ae8	az8	syn/anti	(E)/(Z)
n-C_6H_{13} (1a)	80	70	27	<1	3	97:3	70:30
	75[c]	52[c]	40[c]	<1[c]	8[c]	82:8[c]	52:48[c]
(*E*)-C_4H_9CH=CH (1b)	72	80	17	1	2	97:3	81:19
	70[c]	79[c]	19[c]	1[c]	1[c]	98:2[c]	80:20[c]
C_4H_9C≡C (1c)	88	51	25	7	17	76:24	58:42

[a] $BF_3 \cdot Et_2O$, CH_2Cl_2, -78°C; [b] 90-95% ee according to ^1H NMR analysis of the *O*-methyl mandelate; [c] R" = MOM. The MOM analog of **5b** was used.

The (*E*)-hexenyl isomers **8b** could be separated by careful chromatography. Analysis of the (*S*)-O-methyl mandelates **9b** showed each to be of high (~95% ee) enantiomeric purity equal to that of the starting alkoxyallylstannane **5b**. The relative stereochemistry of the two major isomers (**se8b** and **sz8b**) was established through removal of the BOM grouping and oxidation of the resulting lactols **11b** and *ent*-**11b** to the lactones **12b** and *ent*-**12b** of equal but opposite rotation (equations 1 and 2). The chemical shift (4.9 ppm) of the carbinyl proton in these lactones was in exact agreement with that reported for a closely related *cis*-lactone.[17] The related trans isomers show this proton at 4.4 ppm. Reduction of lactones **12b** and *ent*-**12b** yielded the enantiomeric diols **13b** and *ent*-**13b**, respectively. These diols were also obtained as by-products in the reductive cleavage of the BOM ethers **se8b** and **sz8b**.



The configuration of the carbinyl centers in **se8b** and **sz8b** was deduced from the relative chemical shifts of the vinylic protons in the O-methyl mandelates **se9b** and **sz9b**. Figure 3 shows Newman pro-



jections of these mandelates in their preferred conformation.[9] The carbonyl grouping of the ester is omitted for the sake of clarity. The (*S*)-O-methyl mandelate of the (*R*,*R*) product, **se9b**, would expectedly show shielding of the vinylic hexenyl protons H_5 and H_6 by the phenyl ring whereas the (*S*,*S*) isomer, **sz9b**, would not. By the same token, we might expect the enol ether vinylic protons of **sz9b** to experience shielding whereas those of **se9b** would not. Because **sz9b** and **se9b** differ in their enol ether geometry, a direct comparison of chemical shifts is not appropriate. However, a comparison of the differences in chemical shift between Hβ in the alcohols **se8b**/**sz8b** and the mandelates **se9b**/**sz9b** (ΔHβ) confirms that Hβ in **sz9b** experiences greater relative shielding than Hβ in **se9b** (0.30 *vs.* 0.04 ppm) (Table 2). As an added check we prepared the (*R*)-O-methyl mandelates **se10b** and **sz10b** from the respective alcohols **se8b** and **sz8b**. The chemical shifts of the vinylic protons in these esters (Figure 3 and Table 2) are in perfect accord with the assigned configurations.

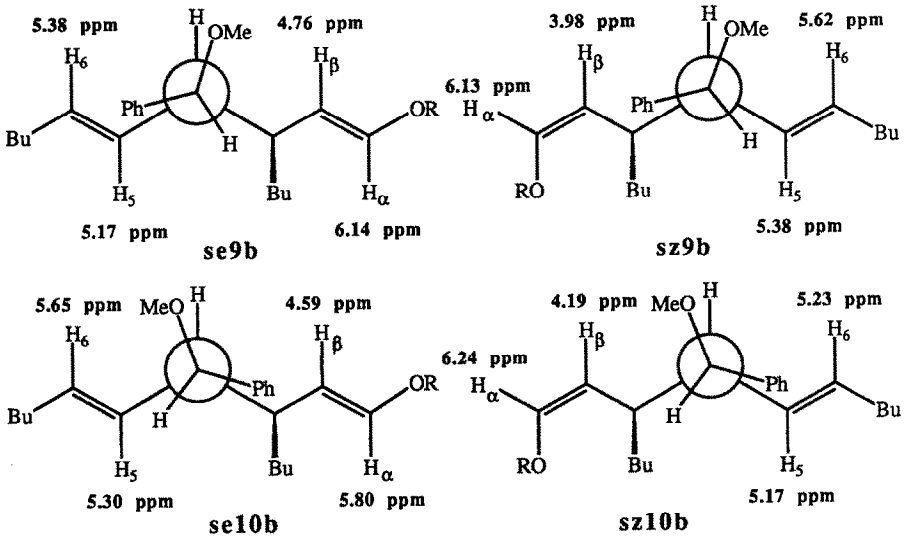
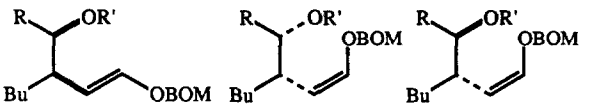


Figure 3. Modified Newman projections of (*S*)-O-methyl mandelates **9b** (R = BOM) and (*R*)-O-methyl mandelates **10b**

Based on the foregoing analysis of the purified adducts **se8b** and **sz8b** we were able to assign stereochemistry to the components of the inseparable mixtures (**8a** and **8c**) obtained by addition of stannane **5b** to heptanal (**1a**) and 2-heptynal (**1c**). In each case, a mixture of cis and trans lactones was prepared through enol ether hydrolysis and oxidation. Capillary gc and ^{1}H NMR analysis of these lactone mixtures established the syn:anti ratios. The percentage of *E* and *Z* enol ethers could be estimated from the characteristic coupling constant and chemical shift of Hα as shown in Table 2. The assignment of absolute configuration is based on the chemical shift of Hβ and ΔHβ in the ^{1}H NMR spectrum of the O-methyl mandelate derivatives **9a** and **9c** of each mixture (Table 2).

Table 2. ^{1}H NMR Characteristics of Enol Ethers **8** and Their *O*-Methyl Mandelates **9** and **10**



se8/9/10 **sz8/9/10** **az8/9**

R	Alcohol 8		Mandelate 9/10		
	H_β	H_α	H_β	H_α	$\Delta H\beta^a$
n-C_6H_{13} (**se8/9a**)	4.81 (dd; 10, 12.4)	6.22 (d, 12.4)	4.75	6.13	0.06
(*E*)-BuCH=CH (**se8/9b**)	4.80 (dd; 10, 12.4)	6.26 (d, 12.4)	4.76	6.13	0.04
(*E*)-BuCH=CH (**se10b**)			4.59	5.80	0.21
BuC≡C (**se8/9c**)	4.98 (dd; 10, 12.4)	6.30 (d, 12.4)	4.92	6.18	0.06
n-C_6H_{13} (**sz8/9a**)	4.29 (dd; 6.4; 10)	6.31 (d, 6.4)	3.94	6.15	0.35
(*E*)-BuCH=CH (**sz8/9b**)	4.28 (dd; 6.4; 10)	6.35 (d, 6.4)	3.98	6.13	0.30
(*E*)-BuCH=CH (**sz10b**)			4.19	6.24	0.09
BuC≡C (**sz8/9c**)	4.48 (dd; 6.4; 10)	6.42 (d, 6.4)	4.08	6.15	0.40
n-C_6H_{13} (**az8/9a**)	*b*	6.36 (d, 6.9)	*b*	*b*	
(*E*)-BuCH=CH (**az8/9b**)	*b*	6.39 (d, 6.4)	4.25	6.23	
BuC≡C (**az8/9c**)	4.32 (dd; 6.4, 10)	6.38 (d, 6.4)	4.29	6.25	0.30

[a] difference in chemical shift between H_β in alcohol **8** and the corresponding O-methyl mandelate **9** or **10**; [b] obscured by other peaks

Several interesting points emerge from these studies. (1) Homochiral α-alkoxystannanes can be readily prepared through reduction of both saturated and conjugated acylstannanes with Noyori's BINAL-H reagent.[4,7] (2) These reductions proceed in the opposite stereochemical sense from those of unsaturated ketones in accord with a Sn-chelated transition state. (3) The stereochemical relationships established for the alkoxy allylstannane **5b** and the addition products **8** support a highly stereoselective anti S_E' pathway for the allylation reaction as previously proposed.[4] (4) The intermolecular allylations of this study and the earlier reported intramolecular allylations both lead to syn products preferentially.[4] However, the major products of the intermolecular additions possess the opposite geometry and absolute configuration from those of the intramolecular additions (Figure 1).[4,18,19]

Possible transition state arrangements for the two syn selective additions are shown in Figure 4. Conceivably, the intermolecular reactions proceed mainly through the **AP** conformer, as suggested by Yamamoto.[20] This arrangement would be disfavored by steric strain in the intramolecular reactions. **APse** and **APsz** are enantiomeric except for the alkoxy stannane center. Hence the steric environment of R" is the major determinant of energy differences between the two. The same is true for the remaining two pairs of SC transition state conformers. As a first approximation **APse** is of lower energy than **APsz**. Accordingly, intermolecular additions would expectedly favor *E* products. The enhanced *E*/*Z* ratios observed with **1b** *vs.* **1a** suggest that electronic as well as steric factors are involved.

Examination of the SC transition states fails to account for the observed *Z* selectivity of the intramolecular addition (Figure 1) as both (-)**SCse** and (+)**SCse** would appear to be of marginally lower energy than their **SCsz** counterparts. However, conformational preferences of the forming macrocyclic

ring that are not readily evaluated by simple first order analysis could favor the SCsz manifold in this cyclization reaction. In fact, we have recently found that remote substituents in stannanes such as II can markedly influence the ratios of diastereomeric cyclic products.[18]

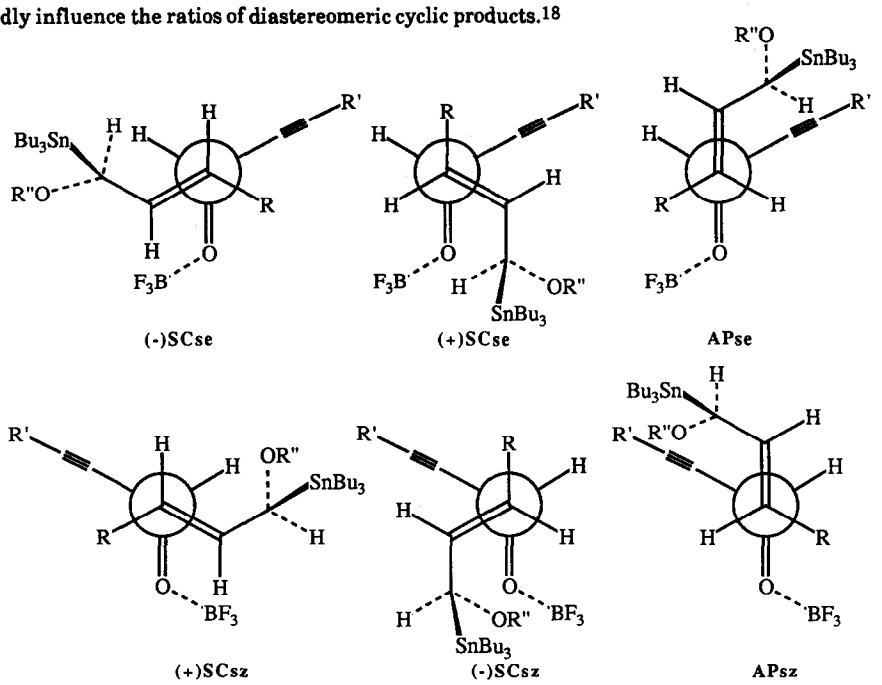


Figure 4. Newman projections of transition states for BF_3 promoted, syn selective additions of (*R*)-α-alkoxyallylstannanes to 2-alkynals (acyclic; R = R' = Bu, R" = BOM: cyclic; R,R' = ring; R" = MOM). **SC** = synclinal, **AP** = antiperiplanar; (+)/(-) refers to the relationship between the C=C and the C=O.

These studies establish the feasibility of using homochiral α-alkoxyallylstannanes to prepare δ-hydroxy enol ethers of high enantiomeric integrity. In the present examples syn/anti ratios are excellent but *E*/*Z* selectivity is modest. According to the analysis depicted in Figure 4, the R" and aldehyde substituents should most strongly influence *E* selectivity, assuming an **AP** transition state arrangement. Further investigation of these matters is in progress.

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Experimental

The apparatus and methods described by G. W. Kramer, M. M. Midland, and A. B. Levy[21] 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), or sodium (benzene). Infrared absorption maxima are reported in wavenumbers (cm^{-1}). Proton magnetic resonance samples were prepared as dilute solutions in deuteriochloroform ($CDCl_3$). Chemical shifts (δ) are reported downfield from tetramethylsilane (Me_4Si), in parts per million (ppm) of the applied field. Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; quartet, q; pentuplet, p; envelope, e; multiplet, m. Coupling constants (J) are reported in hertz (Hz). Glass capillary gas chromatography was performed on a Superox 4 25M column. Combustion microanalyses were performed by Atlantic Laboratories, Atlanta, GA. Analytical thin-layer chromatography (TLC) was routinely used to monitor reactions. Plates precoated with E. Merck silica gel 60 F254 of 0.25 mm thickness, supplied by Brinkmann Instruments, were used. E. Merck silica gel 60 (230-400 ASTM mesh) was employed for column chromatography according to the procedure of Still.[22]

1-[(Tri-*n*-butyl)stannyl]-1-heptanone (2a). The procedure of Still[5] and Mukaiyama[6] was modified. To a solution of 37.5 mL (15 mmol) of 0.4 *M* LDA in THF was added 4 mL (15 mmol) of Bu_3SnH at -20°C with stirring. After 15 min, a solution of 1.14 g (10 mmol) of heptaldehyde in 5 mL of THF was added at -78°C. The reaction solution was stirred for 20 min before 3.8 g (15 mmol) of 1,1'-azodicarbonyldipiperidine was added. The dry ice-acetone bath was replaced with an ice water bath. After 30 min at 0°C, aq NH_4Cl was added to the dark-purple colored reaction mixture. The resulting mixture was

extracted with ether, the organic layer was washed with diluted HCl, saturated $NaHCO_3$, and brine, and dried over $MgSO_4$. After removal of the solvent under reduced pressure and column chromatography, 2.4 g (60%) of unstable light yellow oil was obtained. IR (neat) 2900, 1640 cm^{-1}. MS: Calcd for $C_{19}H_{40}OSn$: 403.0. Found, 403.

2(*E*)-1-[(Tri-*n*-butyl)stannyl]-2-hepten-1-one (2b). The preparation of **2b** was carried out as described above for **2a** starting with 1.6 g (14 mmol) of 2-heptenal, 15 mL (15 mmol) of a 1 *M* solution of Bu_3SnLi in THF, and 6 g (24 mmol) of ADD, producing 4.5 g (80%) of **2b** as a yellow oil. IR (neat) 2900, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.57 (dt, J = 15.7, 6.0 Hz, 1H, vinyl H), 6.05 (d, J = 15.7 Hz, 1H, vinyl H), 2.30 (q, J = 6.0 Hz, 2H, allylic H), 0.9-1.6 (m, 34H). MS: Calcd for $C_{19}H_{38}OSn$, 401.0. Found, 401.

(*S*)-1-[(Tri-*n*-butyl)stannyl]heptyl (*S*)-O-Methyl mandelate (4a). To a solution of 64 mg (0.16 mmol) of the freshly prepared stannylcarbinol **3a** in 2 mL of CH_2Cl_2 at 0°C was added 50 mg (0.20 mmol) of (*S*)-O-methyl mandelic acid, 57 mg (0.276 mmol) of DCC and 17 mg (0.138 mmol) of DMAP with stirring at 25°C. After 3 h, analysis by TLC indicated no starting material remained. The reaction mixture was diluted with hexane and was filtered through Celite. The filtrate was washed with 1 N HCl, aq $NaHCO_3$, and brine. After drying over anhydrous $MgSO_4$, the solvent was removed under reduced pressure. The residue was dissolved in hexane and again filtered through Celite. After removal of solvent under reduced pressure, a colorless oil was obtained (81 mg, 92%), which showed two sets of signals in the ^1H NMR spectrum arising from the (*S,S*) diastereomer **4a** (90%) and the 1*R* epimer (10%). Major: ^1H NMR ($CDCl_3$) δ 7.28-7.42 (m, 5H, phenyl H), 4.80 (dd, J = 4.9, 9.6 Hz, 1H, CHSn), 4.68 (s, 1H, CHPh), 3.39 (s, 3H, CH_3O), 0.86-1.90 (m, 40H). IR (neat) 2900, 1720 cm^{-1} (C=O). MS: Calcd for $C_{28}H_{48}O_3Sn$, 551.05. Found, 551. Minor: ^1H NMR ($CDCl_3$) δ 7.28-7.42 (m, 5H, phenyl H), 4.87 (dd, J = 5.1, 9.3 Hz, 1H, CHSn), 4.68 (s, 1H, CHPh), 3.37 (s, 3H, CH_3O), 0.86-1.90 (m, 40H).

(*S*)-1-[(Tri-*n*-butyl)stannyl]-2-heptenyl (*S*)-O-Methyl Mandelate (4b). The procedure described for **4a** was followed starting with 70 mg (0.20 mmol) of carbinol **3b**, 50 mg (0.3 mmol) of (*S*)-O-methyl mandelic acid, 62 mg (0.3 mmol) of DCC and 24 mg (0.2 mmol) of DMAP, producing 93 mg (85%) of **4b** as an oil. ^1H NMR ($CDCl_3$) δ 7.25-7.43 (m, 5H, phenyl H), **5.53** (dd, J = 6.6, 15.0 Hz, 1H, vinyl H), 5.30 (d, J = 6.6 Hz, 1H, CHSn), **5.02** (dt, J = 6.9, 15.0 Hz, 1H, vinyl H), 4.73 (s, 1H, CHPh), 3.40 (s, 3H, CH_3O), 0.8-1.90 (m, 38H). IR (neat) 2900, 1720 cm^{-1} (C=O). MS: Calcd for $C_{28}H_{46}O_3Sn$, 549.03. Found, 549.

The (*R*)-O-methyl mandelate was prepared as described above with (*R*)-O-methyl mandelic acid: ^1H NMR ($CDCl_3$) δ 7.25 (m, 5H, phenyl H), **5.58** (dd, J = 7.0, 15.3 Hz, 1H, vinyl H), 5.35 (d, J = 6.8 Hz, 1H, CHSn), **5.26** (dt, J = 6.8, 15.3 Hz, 1H, vinyl H), 0.74 (s, 1H, CHPh), 3.38 (s, 3H, CH_3O), 0.8-2.0 (m, 38H).

The relative chemical shifts of the vinylic protons (5.53 and 5.02 ppm for the (*S*)-O-methyl mandelate *vs.* 5.58 and 5.26 ppm for the (*R*)-O-methyl mandelate) could be used to assign absolute configuration at C-1 of these allylstannanes.[9]

(*S*)-1-[(Tri-*n*-butyl)stannyl]-1-[1-(benzyloxy)methoxy]heptane (5a). The procedure of Noyori was employed.[7] To a well stirred solution of 6 mL (6 mmol) of 1 *M* LAH in THF was added dropwise 6 mL (6 mmol) of 1 *M* MeOH in THF at room temperature. After 15 min, a solution of 1.72 g (6.0 mmol) of (*R*)-(+)-binaphthol in THF was added dropwise over 30 min with efficient stirring. The resulting cloudy solution was cooled to -80°C in a dry ice-acetone bath. A THF solution of 0.80 g (2.0 mmol) of stannylketone **2a** was added slowly with stirring. After 3 h at -78°C, analysis by TLC indicated no starting material remained. The excess hydride was quenched at -78°C by addition of 1 mL of MeOH. After warming to room temperature, the whole was taken up in ether, and was washed with 1 N HCl, aq $NaHCO_3$, and brine, and dried over $MgSO_4$. After removal of solvent under reduced pressure, the residue was filtered through a short column of silica gel with 10% EtOAc in hexanes. The stannyl carbinol was characterized by its unique stain pattern (blue stain with peroxymolybdic acid at room temperature) on a silica gel TLC plate.

The unstable carbinol was immediately divided into two parts and used for two reactions. A 64-mg (0.16 mmol) sample was converted to the (*S*)-O-methyl mandelate **4a** which was shown to be 80% enantiomerically pure by high field ^1H NMR analysis (see above). The remaining 0.54 g (1.3 mmol) was dissolved in 2 mL of CH_2Cl_2 and cooled to 0°C. To this solution was added 2.2 mL (13 mmol) of diisopropylethylamine, and 0.54 mL (3.9 mmol) of benzyl chloromethyl ether with stirring. After 3 h at room temperature, TLC analysis indicated no stannylcarbinol remained. The reaction mixture was diluted with hexanes, and was washed with 1 N HCl, aq $NaHCO_3$, and brine. The solution was dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (5% EtOAc in hexanes) affording 0.66 g (85%) of the BOM ether **5a** as a colorless oil. $[\alpha]_D$ +27° (c 1.0, CH_2Cl_2). IR (neat) 2900, 1450, 1010 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.3 (m, 5H, Ph H), 4.74, 4.64 (ABq, J_{AB} = 6.7 Hz, Δν = 29 Hz, 2H, $-OCH_2O-$), 4.59, 4.55 (ABq, J_{AB} = 11.8 Hz, Δν = 22 Hz, 2H, $PhCH_2O-$), 4.15 (t, J = 6.6 Hz, 1H, CHSn), 1.25-1.80 (m, 26H), 0.87 (t, J = 7.2 Hz, 12H, 4 CH_3). MS: Calcd for $C_{27}H_{48}O_2Sn$, 523.06. Found, 523. *Anal.* Calcd for $C_{27}H_{48}O_2Sn$: C, 61.46; H, 9.24. Found: C, 61.62; H, 9.21.

(*S*),(*E*)-1-[(Tri-*n*-butyl)stannyl]-1-[1-(benzyloxy)methoxy]-2-heptene (5b). The procedure described for **5a** was followed starting with 4 g (10 mmol) of stannylketone **2b**, producing 3.40 g (65%) of **5b** as a colorless oil. $[\alpha]_D$ -50° (c 1.0, CH_2Cl). IR (neat) 2900, 1440, 1020 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.32 (m, 5H, Ph H), 5.53 (dd, J = 7.8, 15.2 Hz, 1H, vinyl H), 5.38 (dt, J = 6.0, 15.2 Hz, 1H, vinyl H), 4.76, 4.63 (ABq, J_{AB} = 6.5 Hz, Δν = 38 Hz, 2H, $-OCH_2O-$), 4.64 (d, J = 7.8 Hz, 1H, CHSn), 4.61, 4.50 (ABq, J_{AB} = 11.7 Hz, Δν = 40 Hz, 2H, $PhCH_2O-$), 2.0 (q, J = 7 Hz, 2H, allylic H), 0.9-1.60 (m, 34H). MS: Calcd for $C_{27}H_{46}O_2Sn$, 521.04. Found, 521. *Anal.* Calcd for $C_{27}H_{46}O_2Sn$: C, 62.20; H, 8.89. Found: C, 61.98; H, 8.90.

1-[1-(Benzyloxy)methoxy]-3-*n*-butyl-1-decen-4-ol (8a). To a solution of 0.12 mL (1.0 mmol) of $BF_3 \cdot Et_2O$ in 1 mL of CH_2Cl_2 at -78°C was added slowly a solution of 90 mg (0.8 mmol) of heptanal and 0.42 g (0.80 mmol) of stannane **2b** in 1 mL of CH_2Cl_2.[23] The mixture was stirred for 4 h at -78°C before 1 mL of saturated $NaHCO_3$ was added and the dry ice-acetone bath was replaced with an ice water bath. The

mixture was extracted with ether, and the organic layer was washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (15% EtOAc in hexanes) affording 0.22 g (80%) of a colorless oil, identified as a mixture of diastereomers. IR (neat) 3400, 2900, 1640, 1050 cm^{-1}. MS: Calcd for $C_{22}H_{36}O_3$, 348.26. Found, 348. *Anal.* Calcd for $C_{22}H_{36}O_3$, C, 76.25; H, 9.88. Found: C, 76.06; H, 9.89.

se8a (70%): ^1H NMR ($CDCl_3$) δ 6.23 (d, J = 12.4 Hz, 1H, C=CHOR), 4.92 (s, 2H, $-OCH_2O-$), 4.81 (dd, J = 12.4, 10 Hz, 1H, CH=COR), 4.61 (s, 2H, $PhCH_2O-$), 3.38 (m, 1H, CHOH), 1.90 (m, 1H, allylic H), 0.8-1.70 (m, 22H).

sz8a (27%): ^1H NMR ($CDCl_3$) δ 6.31 (d, J = 6.4 Hz, 1H, C=CH(OR)), 4.90 (s, 2H, $-OCH_2O-$), 4.60 (s, 2H, $PhCH_2O-$), 4.29 (dd, J = 6.4, 10 Hz, 1H, CH=COR), 3.47 (m, 1H, CHOH).

(5*E*)-1-[1-(Benzyloxy)methoxy]-3-*n*-butyl-1,5-decadien-4-ol (8b). The procedure described above for **8a** was followed starting with 90 mg (0.80 mmol) of 2-heptenal, 0.42 g (0.80 mmol) of allylstannane **5b**, and 0.12 mL (1.0 mmol) of $BF_3 \cdot Et_2O$, producing 0.17 g (63%) of **se8b** and 44 mg (16%) of **sz8b**, which were separated on a silica gel column.

se8b: $[\alpha]_D$ -14° (c 0.1, CH_2Cl_2). TLC R_f = 0.46 (30% EtOAc). IR (neat) 3400, 2900, 1650, 1050 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.25 (d, J = 12.4 Hz, 1H, C=CHOR), 5.63 (dt, J=7.6, 15.3 Hz, 1H, vinyl H), 5.39 (dd, J = 7.0, 15.3 Hz, 1H, vinyl H), 4.91 (s, 2H, $-OCH_2O-$), 4.80 (dd, J = 12.4, 10 Hz, 1H, CH=COR), 4.61 (s, 2H, $PhCH_2O-$), 3.92 (m, 1H, CHOH), 0.8-2.10 (m, 19H). MS: Calcd for $C_{22}H_{34}O_3$, 346.25. Found, 346. *Anal.* Calcd for $C_{22}H_{34}O_3$: C, 76.26; H, 9.89. Found: C, 76.15; H, 9.91.

sz8b: $[\alpha]_D$ +17° (c 1.0, CH_2Cl_2). TLC R_f = 0.51 (30% EtOAc). IR (neat) 3400, 2900, 1650, 1050 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.35 (d, J = 6.4 Hz, 1H, C=CHOR), 5.63 (dt, 7.6, 15.2 Hz, 1H, vinyl H), 5.45 (dd, J = 7.0, 15.2 Hz, 1H, vinyl H), 4.90 (ABq, J_{AB} = 6.7 Hz, Δv = 3.4 Hz, 2H, $-OCH_2O-$), 4.60 (ABq, J_{AB} = 11.6 Hz, Δv = 10.7 Hz, 2H, $PhCH_2O-$), 4.28 (dd, J = 6.4, 10 Hz, 1H, CH=COR), 4.0 (m, 1H, CHOH), 0.8-2.10 (m, 19H). MS: Calcd for $C_{22}H_{34}O_3$, 346.25. Found, 346. *Anal.* Calcd for $C_{22}H_{34}O_3$: C, 76.26; H, 9.89. Found: C, 76.06; H, 9.89.

1-[1-(Benzyloxy)methoxy]-3-*n*-butyl-5-decyn-4-ol (8c). The procedure described above for **8a** was followed starting with 82 mg (0.70 mmol) of 2-heptynal, 0.36 g (0.70 mmol) of allylstannane **5b**, and 0.13 mL (1.0 mmol) of $BF_3 \cdot Et_2O$, producing 0.21 g (88%) of a mixture of **se8c**, **sz8c**, **az8c**, and **ae8c** in a ratio of 51:25:17:7. IR (neat) 3400, 2900, 2200, 1650 cm^{-1}. MS: Calcd for $C_{22}H_{32}O_3$, 344.23. Found, 344. *Anal.* Calcd for $C_{22}H_{36}O_3$: C, 76.70; H, 9.36. Found: C, 76.92; H, 9.42.

se8c: ^1H NMR ($CDCl_3$) δ 6.30 (d, J = 12.5 Hz, 1H, C=CHOR), 4.96 (dd, J = 10.2, 12.5 Hz, 1H, CH=COR), 4.93 (s, 2H, $-OCH_2O-$), 4.62 (ABq, J_{AB} = 6.0 Hz, Δv = 4.1 Hz, 2H, $PhCH_2O-$), 4.22 (m, 1H, CHOH), 0.8-2.20 (m, 19H).

sz8c: ^1H NMR ($CDCl_3$) δ 6.42 (d, J = 6.4 Hz, 1H, C=CH(OR)), 4.91 (s, 2H, $-OCH_2O-$), 4.60 (s, 2H, $PhCH_2O-$), 4.48 (dd, J = 6.4, 10.0 Hz, 1H, CH=C(OR)), 4.35 (m, 1H, CHOH), 0.8-2.20 (m, 19H).

az8c: ^1H NMR ($CDCl_3$) δ 6.38 (d, J = 6.4 Hz, 1H, C=CH(OR)), 4.90 (s, 2H, $-OCH_2O-$), 4.61 (s, 2H, $PhCH_2O-$), 4.31 (dd, J = 6.4, 10.0 Hz, 1H, CH=C(OR)).

ae8c: ^1H NMR ($CDCl_3$) δ 6.31 (d, J = 12.5 Hz, 1H, C=CH(OR)).

(3*R*,4*R*),(1*E*)-1-[1-(Benzyloxy)methoxy]-3-*n*-butyl-1-decen-4-yl (*S*)-O-Methyl Mandelate (se9a). To a solution of 84 mg (0.24 mmol) of alcohol **8a** in 2 mL of CH_2Cl_2 at 0°C was added 80 mg (0.48 mmol) of (*S*)-O-methyl mandelic acid, 100 mg (0.48 mmol) of DCC and 29 mg (0.24 mmol) of DMAP with stirring. The resulting mixture was stirred for 3 h at 25°C, whereupon TLC analysis indicated no starting material remained. The reaction mixture was diluted with hexane and was filtered through Celite. The filtrate was washed with 1 N HCl, aq $NaHCO_3$, and brine. After drying over anhydrous $MgSO_4$, the solvent was removed under reduced pressure. The residue was dissolved in hexane and again filtered through Celite. Removal of solvent under reduced pressure afforded a colorless oil (112 mg, 90%). ^1H NMR analysis indicated that it is 90% enantiomerically pure. MS: Calcd for $C_{31}H_{44}O_5$, 496.32. Found, 496. IR (neat) 2900, 1750 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.3-7.5 (m, 10H, phenyl H), 6.15 (d, J = 12.4 Hz, 1H, C=CHOR), 4.89 (s, 2H, OCH_2O), 4.81 (dd, J = 10.2, 12.4 Hz, 1H, CH=COR), 4.72 (s, 1H, CH(Ph)), 4.60 (s, 2H, $PhCH_2$), 3.4 (s, 3H, CH_3O), 2.10 (m, 1H, allylic H), 0.8-1.5 (m, 22H, CH_2).

Peaks arising from the minor diastereomer **sz9a** were seen as follows: ^1H NMR ($CDCl_3$) δ 7.2-7.5 (m, 10H, phenyl H), 6.14 (d, J = 6.5 Hz, 1H, C=CHOR), 4.82 (s, 2H, OCH_2O), 4.73 (s, 1H, CHPh), 4.54 (ABq, J_{AB} = 11.6 Hz, Δv = 9 Hz, 2H, $PhCH_2$), 3.96 (dd, J = 10.2, 6.5 Hz, 1H, CH=COR), 3.4 (s, 3H, CH_3O), 2.65 (m, 1H, allylic H), 0.8-1.6 (m, 22H, CH_2).

(3*R*,4*R*),(1*E*,5*E*)-1-[1-(Benzyloxy)methoxy]-3-*n*-butyl-1,5-decadien-4-yl (*S*)-O-Methyl Mandelate (se9b). The procedure described for **9a** was followed starting with 70 mg (0.20 mmol) of alcohol **se8b**, 50 mg (0.3 mmol) of (*S*)-O-methyl mandelic acid, 62 mg (0.3 mmol) of DCC, and 24 mg (0.2 mmol) of DMAP, producing 82 mg (83%) of the corresponding O-methyl mandelate **se9b** as an oil. IR (neat) 2900, 1750 cm^{-1}. MS: Calcd for $C_{31}H_{42}O_5$, 494.31. Found, 494. ^1H NMR ($CDCl_3$) δ 7.3-7.5 (m, 10H, phenyl H), 6.15 (d, J = 12.4 Hz, 1H, C=CH(OR)), 5.34 (dt, J = 7.6, 15.3 Hz, 1H, vinyl H), 5.14 (dd, J = 7.0, 15.3 Hz, 1H, vinyl H), 4.88 (ABq, J_{AB} = 6.6 Hz, Δv = 7.7 Hz, 2H, OCH_2O), 4.75 (dd, J = 10.0, 12.4 Hz, 1H, CH=COR), 4.73 (s, 1H, CHPh), 4.60 (s, 2H, $PhCH_2$), 3.39 (s, 3H, CH_3O), 0.8-2.1 (m, 18H, CH_2).

(3*S*,4*S*),(1*Z*,5*E*)-1-[1-(Benzyloxy)methoxy]-3-*n*-butyl-1,5-decadien-4-yl (*S*)-O-Methyl Mandelate (sz9b). The procedure described for **9a** was followed starting with 17 mg (0.05 mmol) of **sz8b**, 12 mg (0.07 mmol) of (*S*)-O-methyl mandelic acid, 16 mg (0.08 mmol) of DCC, and 6 mg (0.05 mmol) of DMAP,

producing 20 mg (77%) of the corresponding O-methyl mandelate **sz9b** as an oil. IR (neat) 2900, 1750 cm^{-1}. MS: Calcd for $C_{31}H_{42}O_5$, 494.31. Found, 494. ^{1}H NMR ($CDCl_3$) δ 7.3-7.5 (m, 10H, phenyl H), 6.14 (d, J = 6.4 Hz, 1H, C=CH(OR)), 5.62 (dt, J = 7.6, 15.3 Hz, 1H, vinyl H), 5.38 (dd, J = 7.0, 15.3 Hz, 1H, vinyl H), 4.87 (ABq, J_{AB} = 6.6 Hz, Δν = 7.7 Hz, 2H, OCH_2O), 4.72 (s, 1H, CH(Ph)), 4.59 (s, 2H, $PhCH_2$), 3.96 (dd, J = 10.2, 6.4 Hz, 1H, CH=COR), 3.39 (s, 3H, CH_3O), 0.8-2.1 (m, 18H, CH_2).

(3*R*,4*R*),(1*E*,5*E*)-1-[1-(Benzyloxy)methoxy]-3-*n*-butyl-1,5-decadien-4-yl (*R*)-O-Methyl Mandelate (se10b). The procedure described for **9a** was followed starting with 38 mg (0.1 mmol) of **se8b**, 20 mg (0.12 mmol) of (*S*)-O-methyl mandelic acid, 23 mg (0.11 mmol) of DCC, and 12 mg (0.1 mmol) of DMAP, producing 41 mg (76%) of the corresponding O-methyl mandelate **se10b** as an oil. IR (neat) 2900, 1750 cm^{-1}. MS: Calcd for $C_{31}H_{42}O_5$, 494.31. Found, 494. ^{1}H NMR ($CDCl_3$) δ 7.3-7.5 (m, 10H, phenyl H), 5.80 (d, J = 12.4 Hz, 1H, C=CH(OR)), 5.65 (dt, J = 7.6, 15.3 Hz, 1H, vinyl H), 5.30 (dd, J = 7.0, 15.3 Hz, 1H, vinyl H), 5.12 (t, J = 6.1 Hz, 1H, CHOCO), 4.80 (ABq, J_{AB} = 6.6 Hz, Δν = 7.7 Hz, 2H, OCH_2O), 4.69 (s, 1H, CH(Ph)), 4.59 (dd, J = 10.2, 12.4 Hz, 1H, CH=COR), 4.56 (s, 2H, $PhCH_2$), 3.37 (s, 3H, CH_3O), 0.8-2.1 (m, 18H, CH_2).

(3*S*,4*S*),(1*Z*,5*E*)-1-[1-(Benzyloxy)methoxy]-3-*n*-butyl-1,5-decadien-4-yl (*R*)-O-Methyl Mandelate (sz10b). The procedure described for **9a** was followed starting with 35 mg (0.2 mmol) of **sz8b**, 25 mg (0.15 mmol) of (*S*)-O-methyl mandelic acid, 31 mg (0.3 mmol) of DCC, and 12 mg (0.1 mmol) of DMAP, producing 42 mg (82%) of the corresponding O-methyl mandelate **sz10b** as an oil. IR (neat) 2900 1750 cm^{-1}. MS: Calcd for $C_{31}H_{42}O_5$, 494.31. Found, 494. ^{1}H NMR ($CDCl_3$) δ 7.3-7.5 (m, 10H, phenyl H), 6.24 (d, J = 6.4 Hz, 1H, C=CH(OR)), 5.23 (dt, J = 7.6, 15.3 Hz, 1H, vinyl H), 5.17 (dd, J = 7.0, 15.3 Hz, 1H, vinyl H), 4.87 (ABq, J_{AB} = 6.6 Hz, Δν = 7.7 Hz, 2H, OCH_2O), 4.72 (s, 1H, CH(Ph)), 4.59 (s, 2H, $PhCH_2$), 4.19 (dd, J = 10.2, 6.4 Hz, 1H, CH=COR), 3.39 (s, 2H, CH_3O), 0.8-2.1 (m, 18H, CH_2).

Cis-3-*n*-Butyl-4-hydroxy-5-decanoic Acid γ-Lactone (12a). To a solution of 35 mg (0.1 mmol) of the hydroxy enol ether mixture **8a** in 1 mL of THF was added 1 mL of 10% HCl. The mixture was stirred for 10 h at room temperature. The reaction solution was extracted with ether, and the ether layer was washed with $NaHCO_3$, brine, and dried over $MgSO_4$. After removal of solvent under reduced pressure, the residue was purified by column chromatography, and oxidized with PCC in CH_2Cl_2 to produce 12 mg (80%) of the lactone as an oil. Capillary GC analysis indicates a cis/trans ratio of 97:3. IR (neat) 2900, 1750, 1150, 710 cm^{-1}. MS: Calcd for $C_{14}H_{26}O_2$, 226.18. Found, 226. ^{1}H NMR ($CDCl_3$) δ 4.46 (m, 1H, CHOCO), 2.58 (ABX, J_{AX} = 7.8, J_{AB} = 16.0 Hz, 1H, CHC=O), 2.44 (m, 1H, methine H), 2.25 (ABX, J_{BX} = 6.5, J_{AB} = 16.0 Hz, 1H, CHC=O), 0.8-1.60 (m, 22H).

(3*R*,4*R*),(5*E*)-3-*n*-Butyl-4-hydroxy-5-decenoic Acid γ-Lactone (12b). To a solution of 35 mg (0.10 mmol) of the hydroxy enol ether **se8b** in 2 mL of THF at -78°C was introduced 5 mL of liquid NH_3 followed by addition of 10 mg (0.5 mmol) of Na. The dry ice-acetone bath was removed and the solution was allowed to reflux for 30 min before 1 mL of aq NH_4Cl was added. The liquid NH_3 was allowed to evaporate, and ether was added to the mixture. The organic layer was washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (10% EtOAc in hexanes) affording 9 mg (41%) of lactol **11b** and 9 mg (41%) of the diol **13b** as colorless oils. The lactol was treated with 20 mg of PCC in 5 mL of CH_2Cl_2 in the presence of 10 mg of NaOAc at room temperature for 2 h. Filtration through a short column of Florisil and removal of solvent under reduced pressure afforded 6 mg (66%) of the γ-lactone **12b**. $[\alpha]_D$ +34° (c 0.5, $CHCl_3$). IR (neat) 2900, 1750 cm^{-1}. MS: Calcd for $C_{14}H_{24}O_2$, 224.17. Found, 224. ^{1}H NMR ($CDCl_3$) δ 5.77 (dt, J = 6.8, 15.2 Hz, 1H, vinyl H), 5.42 (dd, J = 7.7, 15.2 Hz, 1H, vinyl H), 4.90 (t, J = 7.7 Hz, 1H, CHOCO), 0.8-2.60 (m, 21H).

Diol 13b. $[\alpha]_D$ +12° (c 0.9, $CHCl_3$). IR (neat) 3400 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.66 (dt, J=6.6, 15.4 Hz, 1H, vinyl H), 5.52 (dd, J=6.9, 15.4 Hz, 1H, vinyl H), 4.12 (m, 1H, CHOH), 3.5-3.7 (m, 2H, CH_2OH), 2.7 (b, 2H, OH), 2.04 (q, J=6.6 Hz, 2H, allylic H), 1.2-1.8 (m, 13H), 0.87 (t, J=4 Hz, 6H, 2 Me). MS: Calcd for $C_{14}H_{28}O_2$, 228.22. Found, 228.

(3*S*,4*S*),(5*E*)-3-*n*-Butyl-4-hydroxy-5-decenoic Acid γ-Lactone (*ent*-12b). The procedure described above for lactone **12b** was followed starting with 35 mg (0.10 mmol) of **sz8b**, 5 mL of NH_3, and 10 mg (0.5 mmol) of Na producing 10 mg (45%) of lactol (*ent*-**11b**), and 8 mg (38%) of diol (*ent*-**13b**). The lactol was oxidized to lactone *ent*-**12b** with PCC in CH_2Cl_2 as described above. $[\alpha]_D$ -34° (c 0.6, $CHCl_3$).

3-*n*-Butyl-4-hydroxy-5-decynoic Acid γ-Lactone (12c). To a solution of 0.50 g (1.86 mmol) of alcohol **8c** (a mixture of four isomers) in 5 mL of THF was added 5 mL of 10% HCl at 0°C. The resulting mixture was stirred for 10 h at room temperature, then was extracted with ether. The combined ether layers were washed with saturated $NaHCO_3$, brine and dried over $MgSO_4$. After evaporation of solvent under reduced pressure, the residue was purified by column chromatography affording 0.36 g (82%) of lactol, which was oxidized to lactone **12c** as described above. Capillary gc analysis indicates a cis/trans ratio of 76:24.

Cis-**12c**: ^{1}H NMR ($CDCl_3$) δ 5.13 (d, J=7.0 Hz, 1H, CHOCO). 2.1-2.55 (m, 4H, CH_2CO and $CH_2C{\equiv}C$), 1.2-1.7 (m, 11H, CH_2's), 0.89 (t, J=6.0 Hz, 6H, 2 CH_3).
Trans-**12c**: ^{1}H NMR ($CDCl_3$) δ 4.65 (d, J=6.8 Hz, 1H, CHOCO), 2.70 (ABX, J_{AX}=8.1 Hz, J_{AB}=17.1 Hz, 1H, CHC=O). The rest of the peaks were obscured by those of the cis isomer.

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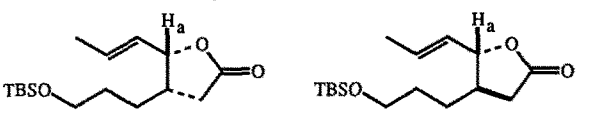
13. 2-Octanone is reduced by the (*S*)-reagent to (*R*)-2-octanol of 24% ee.[7]

14. An A-value of 1.0 to 1.2 has been determined for R_3Sn groupings. *Cf.* ref. 10.

15. A five-membered Sn-O chelated structure has recently been found for *cis*-3-(dimethylchloro)stannylcyclohexyl benzyl ether. Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Shiro, M.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4606.

16. se = syn-*E*, sz = syn-*Z*, ae = anti-*E* and az = anti-*E*.

17. Marshall, J. A.; DeHoff, B. S. *J. Org. Chem.* **1986**, *51*, 866.



δ H_a = 4.9 ppm δ H_a = 4.4 ppm

18. Marshall, J. A.; Markwalder, J. A. *Tetrahedron Lett.* **1988**, *29*, 4811.

19. The MOM protected stannylcarbinol **5b** reacts with aldehydes **1a**-**1c** to give the addition products **8** in comparable ratios to those of **5b**.

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23. Use of a larger excess (2-3 eq) of $BF_3 \cdot Et_2O$ led to by-products containing isomeric 1,2-diol mono ethers arising from isomerization of the allylstannane. *Cf.* Quintard, J.-P.; Elissondo, B.; Pereyre, M. *J. Org. Chem.* **1983**, *48*, 1559.