then added, and the mixture was heated at 60 °C for 4 h. The mixture was then evaporated to dryness and the residue purified on a Dynamax reversed-phase column (21.4 mm × 25 cm) with a gradient of 2-5% acetonitrile/0.1 M ammonium bicarbonate. Evaporation of appropriate fractions gave pure **11** (0.444 g, 1.49 mmol, 50%): mp 118 °C; UV (H_2O) λ_{max} 280 nm; UV λ_{min} 241 nm; ^1H NMR (DMSO-d_6) δ 9.8 (br, 1, NHO), 7.74 (s, 1, H_8), 6.53 (d, 2, J = 89 Hz, NH_2), 6.05 ("t", 1, J_{app} = 7.4 Hz, $H_{1'}$), 5.25 (d, 1, J = 3.0 Hz, 3'-OH), 5.01 (t, 1, J = 5.4 Hz, 5'-OH), 4.31 (m, 1, $H_{3'}$), 3.8 (m, 1, $H_{4'}$), 3.75 (s, 3, OCH_3), 3.51 (m, 1, $H_{5'}$), 2.45 and 2.20 (m and m, 1 and 1, $H_{2'}$ and $H_{2''}$); EI MS m/z 297 (M^+), 267, 208, 181, 151, 136, 109.

[2-^{15}N]-2'-Deoxyguanosine (12). To 0.424 g (1.43 mmol) of **11** dissolved in 28.6 mL of 0.1 M TEAA buffer (pH 6.8) was added adenosine deaminase (660 units). The mixture was allowed to stir at room temperature for 2 days, during which time the product crystallized. The mixture was then cooled to 4 °C and filtered to give a first crop of 0.31 g (1.07 mmol, 75%) of **12**: mp >250 °C; ^1H NMR (DMSO-d_6) δ 10.58 (s, 1, H_1), 7.92 (s, 1, H_8), 6.47 (d, 2, J = 90 Hz, NH_2), 6.12 ("t", 1, J_{app} = 6.3 Hz, $H_{1'}$), 5.26 (d, 1, J = 4.0 Hz, 3'-OH), 4.94 (t, 1, J = 5.4 Hz, 5'-OH), 4.3 (m, 1, $H_{3'}$), 3.79 (m, 1, $H_{4'}$), 3.51 (m, 2, $H_{5'}$), 2.50 and 2.21 (m and m, 1 and 1, $H_{2'}$ and $H_{2''}$); ^{13}C NMR (^1H decoupled, DMSO-d_6) δ 157.093 (s, C_6), 154.189 (d, C_2, J = 23 Hz), 151.2 (d, C_4, J = 4 Hz), 135.613 (s, C_8), 116.963 (s, C_5), 87.88 (s, $C_{4'}$), 82.87 (s, $C_{1'}$), 71.05 (s, $C_{3'}$), 62.025 (s, $C_{5'}$); ^{15}N NMR (10 mM sodium phosphate, 0.1 M NaCl, 0.1 mM EDTA, pH 6.5, H_2O/D_2O = 80/20) δ 50.786 (t, J = 90 Hz), ref $^{15}NH_4Cl$ in 10% HCl. Anal. ($C_{10}H_{13}N_4{}^{15}NO_4 \cdot {}^1/_2H_2O$) C, H, N: calcd, 25.61; found, 25.19.

Acknowledgment. This work was supported by grants from the National Institutes of Health (GM31483) and the Busch Memorial Fund and an American Cancer Society Faculty Research Award to R.A.J.

Registry No. 1, 106568-85-8; **2**, 130434-93-4; **7**, 130434-94-5; **8**, 130434-96-7; **9**, 3506-01-2; **11**, 130434-95-6; **12**, 121409-37-8; CNBr, 506-68-3; adenosine deaminase, 9026-93-1.

On the 1,3-Isomerization of Nonracemic α-(Alkoxy)allyl Stannanes

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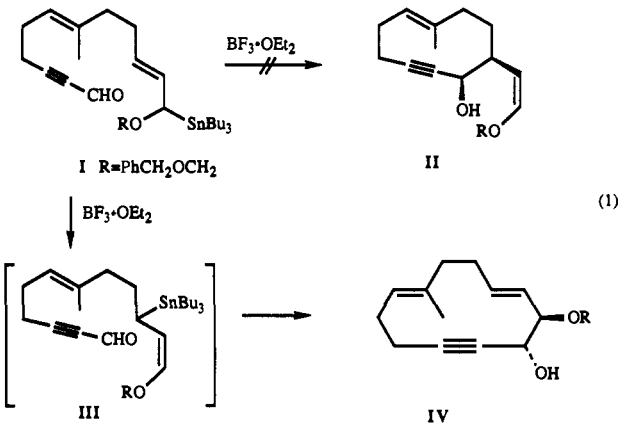
Contribution from the Department of Chemistry, The University of South Carolina, Columbia, South Carolina 29208. *Received June 27, 1990*

Abstract: A set of optically active (*E*)-α-(alkoxy)allyl stannanes **10–13** and *ent*-**10–13** was prepared by reduction of the acyl stannanes **4–6** with (*R*)-(+)-BINAL-H or $LiAlH_4$–Chirald and protection of the resulting hydroxy stannanes with MOMCl or BOMCl. On treatment with $BF_3 \cdot OEt_2$ these stannanes rearranged stereospecifically to the (*Z*)-γ-(alkoxy)allyl stannanes **21–24** by 1,3-migration of Bu_3Sn. The rearrangement was shown to take place by an intermolecular anti pathway. Addition of the γ-alkoxy stannanes **21–24** to representative aldehydes afforded optically active *syn*-1,2-diol monoethers **25–28** as the major diastereomers with high anti S_E' stereoselectivity.

α-Alkoxy stannanes[1] and allylic stannanes[2] have played a useful role as nucleophilic reagents in carbon–carbon bond forming reactions with electrophiles.[3] We recently described a highly efficient macrocyclization involving α-(alkoxy)allyl stannanes and acetylenic aldehydes.[4] Our initial application yielded 14-membered cyclic intermediates related to cembranolides. In a further extension of the methodology we examined a possible application to 10-membered carbocycles (eq 1).[5] However, the precursor stannane I afforded none of the desired enol ether II upon treatment with $BF_3 \cdot OEt_2$ under the usual cyclization conditions. The sole isolable product was the 12-membered 1,2-diol derivative IV. Evidently, alkoxy stannane I is not favorably disposed to undergo direct intramolecular S_E' addition. Consequently, isomerization to stannane III precedes cyclization, which then affords the 12-membered product IV.



(1)

Interestingly, when nonracemic alkoxy stannane I was employed, the cyclododecynol IV was formed as a single nonracemic diastereoisomer with an ee equal to that of starting I. Thus, the presumed rearrangement of I to III must occur stereospecifically. This intriguing observation prompted our further study of the 1,3-isomerization process.[6]

The nonracemic α-(hydroxy)allyl stannanes **7–9** were prepared from the appropriate enals **1–3**. Accordingly, addition of Bu_3SnLi and direct oxidation of the intermediate alkoxides, as previously described, afforded the stannyl enones **4–6**.[7] These isolable, air-sensitive, yellow ketones were readily purified by careful column chromatography. Reduction with (*R*)-(+)-BINAL-H afforded the *S* alcohols (e.g., **7**) of >95% ee.[8] The *R* alcohols

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(3) Pereyre, M.; Quintard, J-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987; pp 211–231.

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(5) Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* **1989**, *30*, 2183.

(6) For recent observations on 1,3-isomerizations of racemic α-(alkoxy)-allylic stannanes see: Quintard, J-P.; Dumartin, G.; Elissondo, B.; Rahm, A.; Pereyre, M. *Tetrahedron* **1989**, *45*, 1017. Quintard, J-P.; Elissondo, B.; Pereyre, M. *J. Org. Chem.* **1983**, *48*, 1559.

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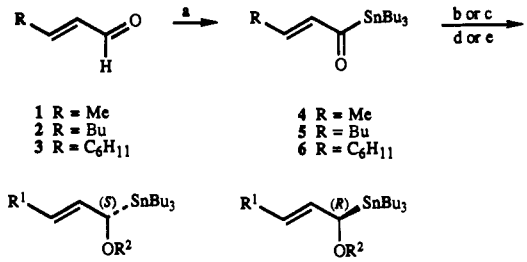
Scheme I[a]



7	R^1 = Me, R^2 = H	*ent*-**7**	R^1 = Me, R^2 = H
8	R^1 = Bu, R^2 = H	*ent*-**8**	R^1 = Bu, R^2 = H
9	R^1 = C_6H_{11}, R^2 = H	*ent*-**9**	R^1 = C_6H_{11}, R^2 = H
10	R^1 = Me, R^2 = MOM	*ent*-**10**	R^1 = Me, R^2 = MOM
11	R^1 = Bu, R^2 = MOM	*ent*-**11**	R^1 = Bu, R^2 = MOM
12	R^1 = C_6H_{11}, R^2 = MOM	*ent*-**12**	R^1 = C_6H_{11}, R^2 = MOM
13	R^1 = Bu, R^2 = BOM	*ent*-**13**	R^1 = Bu, R^2 = BOM

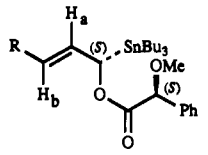
[a] (a) Bu_3SnLi, THF, −78 °C; ADD, THF, 0 °C; (b) (*R*)-(+)-BINAL-H, THF, −78 °C; (c) $LiAlH_4$–Chirald, THF, −78 °C; (d) $EtN(iPr)_2$, MOMCl, CH_2Cl_2, 0 °C; (e) $EtN(iPr)_2$, BOMCl, CH_2Cl_2, 0 °C.

(e.g., *ent*-**7**) of equally high ee could be secured through reduction of the ketones with (*S*)-(−)-BINAL-H. However, the *R* alcohols were more conveniently prepared by using $LiAlH_4$–Chirald as the reducing agent, albeit at some sacrifice in ee (ca. 65% vs 95%).[9]

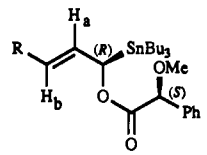
It should be noted that, in our hands, reductions of acyl stannanes and other ketones with BINAL-H prepared by the Noyori procedure gave highly variable results. While in the throes of experiments in which ee's of only 30–70% were being obtained, we learned that J. C. Saddler and his co-workers at the Upjohn Co. had experienced similar problems and had found that heating the mixture of binaphthol, $LiAlH_4$, and EtOH in THF to reflux for a brief period afforded a reagent which performed efficiently and reproducibly[10] (see Scheme I). Since adopting their procedure, we have experienced no difficulties in these reductions. It should also be noted that ~95% of the currently expensive binaphthol can be recovered from these reactions and reused with no loss of effectiveness (see the Experimental Section).

Stannylcarbinols (e.g., **7**) readily revert to their aldehyde precursors under acidic or basic conditions. However, they smoothly afford alkoxymethyl ethers (e.g., **10**) upon treatment with alkoxymethyl chlorides in the presence of a hindered amine base.[1] They can also be esterified.

Esterification of enantiomerically enriched samples of alcohols **7–9** with (*S*)-*O*-methylmandelic acid afforded the diastereomeric pairs **14**/**17**, **15**/**18**, and **16**/**19**. These pairs showed distinctive chemical shift differences for the vinylic protons, H_a and H_b, which could be used to assign absolute configuration to the major and minor diastereoisomers.[11]

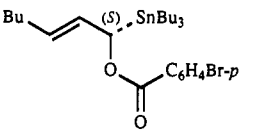


		δH_a	δH_b
14	R = Me	5.58	5.10
15	R = Bu	5.51	5.01
16	R = C_6H_{11}	5.50	4.98



		δH_a	δH_b
17	R = Me	5.62	5.36
18	R = Bu	5.58	5.26
19	R = C_6H_{11}	5.59	5.23

As an added check on these configurational assignments we employed the circular dichroic exiton chirality method of Nakanishi. Nakanishi and Sharpless have shown that the *p*-bromobenzoates of acyclic allylic alcohols exhibit Cotton effects in their CD spectra characteristic of the absolute configuration.[12] The *p*-bromobenzoate **20** of allylic alcohol **8** gave use to a λ_{ext} 241 nm with $\Delta\epsilon$ = 14.9 in agreement with the assigned *S* configuration.



20

Treatment of alcohols **7–9** with either methoxymethyl chloride or benzyloxymethyl chloride in the presence of Hunig's base as the proton scavenger afforded the MOM ethers **10–12** or the BOM ether **13**, respectively. These ethers and their enantiomers *ent*-**10–13** were used for the 1,3-isomerization studies. The *S* ethers were prepared from alcohols of >90% ee, whereas the *R* ethers were derived from alcohols of 54–86% ee. Isomerization was effected with $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at −78 °C. The γ-(alkoxy)allyl stannanes **21–24** and *ent*-**21–24** were obtained in 70–85% yield following chromatographic purification (Table I). In each case none of the starting α-(alkoxy)allyl stannane was observed. Furthermore, treatment of the γ-alkoxy isomers **21–24** with $BF_3{\cdot}OEt_2$ at −78 °C afforded small amounts of the (*E*)-γ-(alkoxy)allyl stannanes but failed to produce any of the α-alkoxy isomers. Apparently, the isomerization strongly favors the γ-alkoxy products. Unfortunately, we were unable to examine the $Z \rightarrow E$ enol ether isomerization in detail owing to the rapid decomposition of these stannanes under the reaction conditions. In the case of **21** ca. 10% of the *E* isomer could be seen after

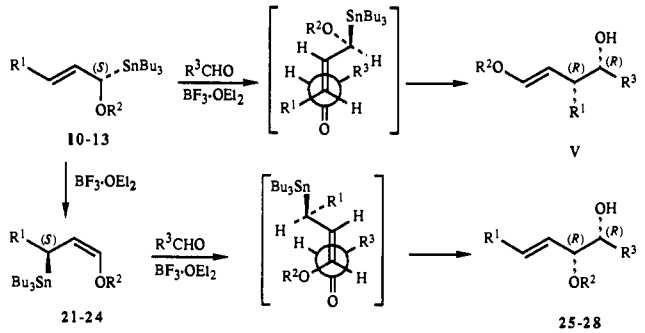
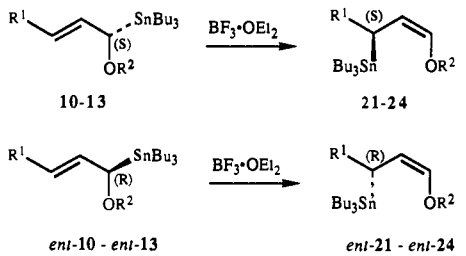


Figure 1. Predicted stereochemical course of anti S_E' addition of allyl stannanes to aldehydes.

Table I. Optical Properties of α- and γ-(Alkoxy)allyl Stannanes



R^1	R^2	α-(alkoxy) stannane	$[\alpha]_D$	ee, %	γ-(alkoxy) stannane	$[\alpha]_D$
Me	MOM	**10**	−56	95	**21**	+135
Bu	MOM	**11**	−58	95	**22**	+119
C_6H_{11}	MOM	**12**	−53	90	**23**	+105
Bu	BOM	**13**	−54	95	**24**	+116
Me	MOM	*ent*-**10**	+52	86	*ent*-**21**	−120
Bu	MOM	*ent*-**11**	+46	76	*ent*-**22**	−92
C_6H_{11}	MOM	*ent*-**12**	+33	54	*ent*-**23**	−63
Bu	BOM	*ent*-**13**	+44	77	*ent*-**24**	−91

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(11) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 2370. For relevant applications, see ref 7.

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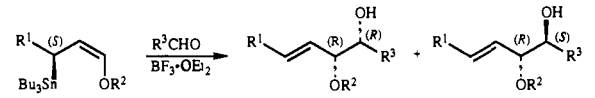
Table II. Addition of γ-(Alkoxy)allyl Stannanes to Aldehydes



21 R^1 = Me, R^2 = MOM
22 R^1 = Bu, R^2 = MOM
23 R^1 = C_6H_{11}, R^2 = MOM
24 R^1 = Bu, R^2 = BOM
25 R^1 = Me, R^2 = MOM
26 R^1 = Bu, R^2 = MOM
27 R^1 = C_6H_{13}, R^2 = MOM
28 R^1 = Bu, R^2 = BOM
29 R^1 = Me, R^2 = MOM
30 R^1 = Bu, R^2 = MOM
31 R^1 = C_6H_{13}, R^2 = MOM
32 R^1 = Bu, R^2 = BOM

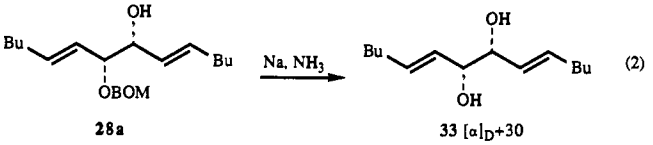
stannane	R^1	R^2	R^3	series[a]	yield,[b] %	syn:anti
21	CH_3	MOM	(*E*)-BuCH=CH	**a**	84	94:6
21	CH_3	MOM	C_6H_{11}	**b**	74	95:5
21	CH_3	MOM	*n*-C_6H_{13}	**c**	75	96:4
21	CH_3	MOM	BuC≡C	**d**	70	90:10
21	CH_3	MOM	Ph	**e**	89	95:5
22	Bu	MOM	(*E*)-BuCH=CH	**a**	73	90:10
22	Bu	MOM	C_6H_{11}	**b**	80	98:2
22	Bu	MOM	*n*-C_6H_{13}	**c**	81	85:15
22	Bu	MOM	BuC≡C	**d**	75	87:13
22	Bu	MOM	Ph	**e**	83	85:15
23	C_6H_{11}	MOM	(*E*)-BuCH=CH	**a**	67	65:35
23	C_6H_{11}	MOM	C_6H_{11}	**b**	78	98:2
24	Bu	BOM	(*E*)-BuCH=CH	**a**	61	88:12
24	Bu	BOM	C_6H_{11}	**b**	62	96:4
24	Bu	BOM	*n*-C_6H_{13}	**c**	78	88:12
24	Bu	BOM	BuC≡C	**d**	75	86:14
24	Bu	BOM	Ph	**e**	61	85:15

[a] **a** R^3 = (*E*)-BuCH=CH; **b** R^3 = C_6H_{11}; **c** R^3 = *n*-C_6H_{13}; **d** R^3 = BuC≡C; **e** R^3 = Ph. [b] Hydroxy ether. Various amounts (2–20%) of diols were also obtained (see text).

exposure to BF_3·OEt_2 at −78 °C for 1 h, but the total recovery of material was less than 40%.

Attempts to measure the ee's of the γ-(alkoxy)allyl stannanes through chemical degradation and subsequent derivatization with chiral reagents were unsuccessful.[13] Accordingly, we examined additions of these stannanes to various aldehydes (Table II). We have previously shown that α-(alkoxy)allyl stannanes **10–13** undergo highly selective anti S_E' additions to aldehydes affording homoallylic alcohols V with complete chirality transfer (Figure 1).[7] Additions involving the γ-(alkoxy)allyl stannanes would expectedly follow the same pathway.[14] Thus, the absolute configuration of the addition products should reflect the configuration of the stannane. Furthermore, a comparison of the ee's of the alcohol products **25–28** with those of the α-alkoxy stannane precursors should provide a check on the stereoselectivity of the 1,3-isomerization.

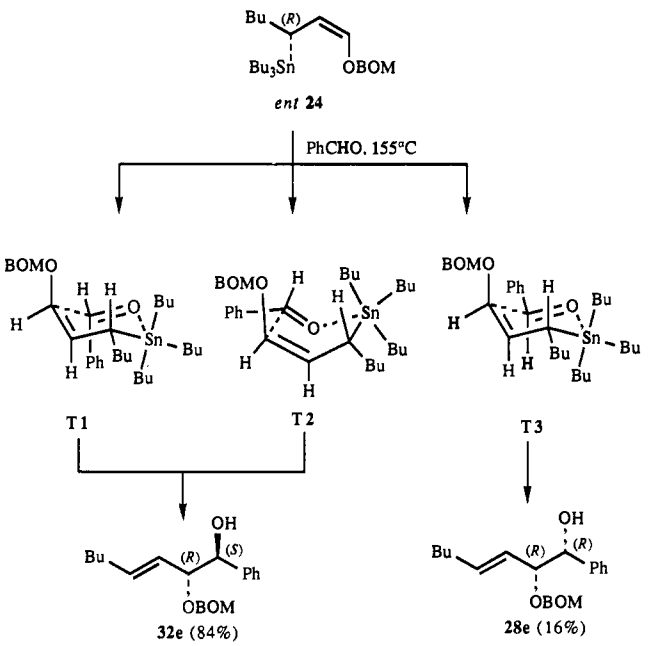
This plan was implemented with the (*S*)-γ-alkoxy stannanes **21–24** and five representative aldehydes listed in Table II. In each case a mixture of syn and anti addition products **25**/**29**, **26**/**30**, **27**/**31**, and **28**/**32** was obtained along with the related diols, approximately 20% for **24** and less than 10% for **21–23**. In the reaction of stannane **24** with (*E*)-2-heptenal the percentage of diol increased with increasing reaction time (25% after 1 h, 38% after 4 h). Consequently, this product most likely arises through cleavage of the BOM grouping in the initial addition products **28** and **32**. The relative stereochemistry of the major product **28a** in this case was established by hydrogenolysis to the optically active diol **33** (eq 2).



28a **33** $[\alpha]_D$+30 (2)

(13) Attempted hydrogenation or hydrogenolysis with a variety of catalysts caused decomposition of the stannane as did attempted epoxidation, hydroboration–oxidation, acidic hydrolysis, and ozonolysis. Direct oxidation of the C–Sn bond was also unsuccessful. Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Shiro, M.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4606.

(14) For recent work on additions involving achiral γ-(alkoxy)allylstannanes, see: Keck, G. E.; Abbott, D. E.; Wiley, M. R. *Tetrahedron Lett.* **1987**, *28*, 139. Koreeda, M.; Tanaka, Y. *Tetrahedron Lett.* **1987**, *28*, 143. An anti pathway is predicted for synchronous S_E2' displacements. Ahn, N. T. *J. Chem. Soc., Chem. Commun.* **1968**, 1089.

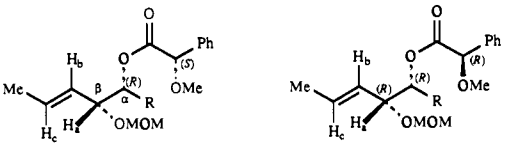


***ent* 24**

32e (84%) **28e** (16%)

Figure 2. Transition states for thermal additions of γ-(alkoxy)allyl stannanes.

Table III. Chemical Shifts of β and Vinylic Protons in the *O*-Methylmandelates of γ-(Alkoxy)allyl Stannane Adducts



34 **35**

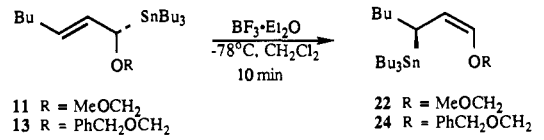
R	series	δ H_a	δ H_b	δ H_c	series	δ H_a	δ H_b	δ H_c
(*E*)-BuCH=CH	**a**	4.00	5.26	5.62	**a**	3.89	4.90	5.48
C_6H_{11}	**b**	4.11	5.18	5.68	**b**	4.01	4.63	5.47
n-C_6H_{13}	**c**	3.97	5.21	5.65	**c**	3.85	4.86	5.41
BuC≡C	**d**	4.11	5.36	5.75	**d**	3.94	5.11	5.49
Ph	**e**	4.21	5.11	5.51	**e**	4.12	4.86	5.34

The syn and anti hydroxy ethers **25**/**29**, **26**/**30**, **27**/**31**, and **28**/**32** were inseparable, but isomer ratios could be calculated from the ^{1}H NMR spectra. The absolute configuration of the hydroxy center of the major alcohols **25a–e**, derived from stannane **21** and representative aldehydes, was surmised from ^{1}H NMR analysis of the (*S*)-*O*-methylmandelate derivatives **34a–e** and the (*R*)-*O*-methylmandelate derivatives **35a–e**.[11] Comparison of these mandelates revealed a characteristic upfield shift of proton H_a and the vinylic protons H_b and H_c attributable to shielding by the phenyl group (Table III). A similar shielding effect was noted in the mandelates of partially racemic samples of these alcohols, thus indicating that the carbinyl center (α in **34**) must possess the *R* configuration.[11] The established syn relationship between the α and β centers requires the latter center to be *R* as well. Assuming an anti S_E' pathway (Figure 1), the precursor γ-(alkoxy)allyl stannane **21** must have the *S* configuration. This stannane is derived from the (*S*)-α-(alkoxy)allyl stannane **10**. Accordingly, the 1,3-isomerization **10** → **21** must proceed by an anti pathway.

The ^{1}H NMR spectra of the *O*-methylmandelate derivatives could also be used to measure the ee of adducts **25–28**. In all cases examined the calculated ee was in good accord with the ee of the α-alkoxy stannane precursor. Thus, the 1,3-isomerization is highly stereoselective, if not stereospecific.

Additional support for the configuration of the γ-alkoxy stannane **24** was secured through thermolysis of *ent*-**24** with benzaldehyde (Figure 2). The two products **32e** and **28e**, obtained as an 84:16 mixture, were assigned the indicated structures on

Table IV. Concentration Effects on the 1,3-Isomerization of α-(Alkoxy)allyl Stannanes



11 R = $MeOCH_2$
13 R = $PhCH_2OCH_2$

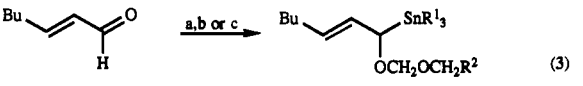
22 R = $MeOCH_2$
24 R = $PhCH_2OCH_2$

entry	stannane	concn, M: stannane	concn, M: BF_3·OEt_2	% reaction
1	**13**	0.1	0.1	100
2	**13**	0.01	0.01	25
3	**11**	0.02	0.02	99
4	**11**	0.002	0.002	34
5	**11**	0.002	0.001	13
6	**11**	0.1	0.05	99
7	**11**	0.1	0.01	99

the basis of ^1H NMR analysis of the *O*-methylmandelates and comparison with samples prepared previously by BF_3·OEt_2-catalyzed addition (Table II). The thermal reaction of allyl stannanes with aldehydes has been shown to proceed through a six-center chairlike transition state.[15] When this analysis is applied to the thermal reaction of *ent*-**24**, transition state T1 appears somewhat surprisingly favored over T3. Alternatively, reaction may proceed through the boat conformer T2. Regardless of conformation, the observed configuration of **32e** and **28e** requires *ent*-**24** to possess the *R* configuration if a cyclic process is involved. As *ent*-**24** is derived from *ent*-**13** the 1,3-isomerization must proceed by an anti pathway in accord with the previous conclusion.

Because an intramolecular anti 1,3-migration (antarafacial process) is highly disfavored on steric grounds, we felt that the isomerization must be intermolecular.[16] Support for this conclusion was obtained from the dilution experiments summarized in Table IV. These studies also showed the reaction to be catalytic in BF_3·OEt_2 (entries 6 and 7).[17]

Additional more compelling evidence came from crossover experiments involving the α-(alkoxy)allyl stannanes **36** and **37** prepared as shown in



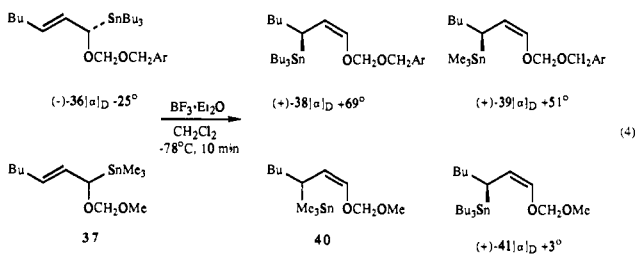
(3)

2

36 R^1 = Bu, R^2 = *p*-$MeOC_6H_4$
37 R^1 = Me, R^2 = H

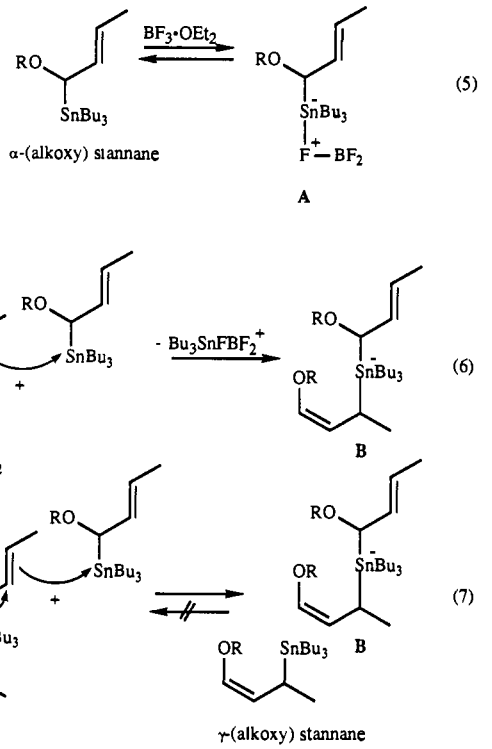
(a) $R_3{}^1SnLi$, THF; (b) *p*-$MeOC_6H_4CH_2OCH_2Cl$, (*i*-Pr)$_2$NEt; (c) $MeOCH_2Cl$, (*i*-Pr)$_2$NEt

A 1:1 mixture of the foregoing stannanes was converted within 10 min at −78 °C in the presence of BF_3·OEt_2 to a nearly equal mixture of **38**–**41** (eq 4). Ratios were determined from the vinylic



(4)

γ-proton signals which were clearly resolved in the ^1H NMR spectrum of the mixture. The individual γ-(alkoxy)allyl stannanes could also be isolated by preparative TLC on silica gel.



(5)

(6)

(7)

Figure 3. Possible pathway for BF_3-catalyzed isomerization of allyl stannanes.

In contrast to the above result, a 1:1 mixture of the γ-(alkoxy)allyl stannanes **38** and **40** was recovered unchanged upon brief treatment with BF_3·OEt_2 at −78 °C. Thus, the γ-(alkoxy)allyl stannane isomerization is not only favorable, it is irreversible as well. Interestingly, when we repeated the crossover experiment using an equimolar mixture of nonracemic (−)-**36** and racemic **37**, the product (+)-**41** derived from Bu_3Sn transfer to racemic **37** showed small but definite optical rotation. This finding implies that the Bu_3Sn stannylating agent is chiral. A possible pathway consistent with these results employs the novel pentacoordinated stannane B as a self-replicating catalytic transfer intermediate (Figure 3).[18]

Intermediate B could arise through BF_3-assisted destannylation of the α-(alkoxy)allyl stannane (eq 5). It should be noted that, because of its catalytic role, only trace amounts of B would be required. In principle, either of the two allyl–Sn bonds of B could cleave (eq 7). However, the failure of γ-(alkoxy)allyl stannanes **38** and **40** to equilibrate indicates that the depicted one is the more labile. Of the several catalysts examined to date only BF_3·OEt_2 has proven effective in the α-(alkoxy)allyl stannane isomerization. No reaction was observed upon treatment of stannane **13** with CF_3CO_2H, Bu_4NF, or Me_3SnCl at −78 °C. Anhydrous HCl gave only protonolysis, whereas $TiCl_4$ and Et_2AlCl caused decomposition.

Figure 4 depicts possible pathways for anti S_E' reactions of nonracemic allyl stannanes with electrophiles. (*E*)-Allyl stannanes VI can afford *E* products VII through a W conformer (eq 8) or *Z* products VIII through a sickle conformer (eq 9).[19] (*Z*)-Allyl stannanes IX likewise have two options. The sickle transition-state

(15) Hull, C.; Mortlock, S. V.; Thomas, E. J. *Tetrahedron* **1989**, *45*, 1007. Jephcote, V. J.; Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1984**, 800.

(16) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970; pp 114–124.

(17) For recent mechanistic studies on the 1,3-isomerization of allylic stannanes, see: Denmark, S. E.; Wilson, T.; Willson, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 984. Denmark, S. E.; Weber, E. J.; Wilson, T. M.; Willson, T. M. *Tetrahedron* **1989**, *45*, 1053.

(18) For experimental evidence in support of such a stannane complex see: Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102. The more obvious isomerization pathway involving Bu_3SnF as the electrophile appears unlikely in view of Denmark's studies on BF_3-promoted metathesis of $Me_3SnCH_2CH{=}CH_2$.[17] In the absence of an aldehyde, rapid exchange of allyl and CH_3 was observed and no Me_3SnF could be detected.

(19) For previous use of the terms "W, sickle and U" to describe geometry in allylic systems, see: Bates, R. B.; Carnighan, R. H., Staples, C. E. *J. Am. Chem. Soc.* **1963**, *85*, 3031. Nickon, A.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1967**, *89*, 3914. Marshall, J. A. *Synthesis* **1972**, 517.

conformer leads to *E* products, *ent*-VII, (eq 10), and the U arrangement would afford *Z* products, *ent*-VIII, (eq 11). The reaction of aldehydes with (*E*)-α-(alkoxy)allyl stannanes has been found to give primarily (*E*)-enol ethers VII (R^1 = alkyl, R^2 = OR) for intermolecular additions and (*Z*)-enol ethers VIII (R^1 = alkyl, R^2 = OR) for intramolecular additions leading to 14-membered rings. 1,3-Isomerizations of (*E*)-α-(alkoxy)allyl stannanes also afford (*Z*)-enol ethers VIII (R^1 = alkyl, R^2 = OMOM, E = $SnBu_3$). Aldehydes react with (*Z*)-γ-(alkoxy)allyl stannanes to yield (*E*)-allylic ethers *ent*-VII (R^1 = OR, R^2 = alkyl) in both intermolecular and intramolecular additions leading to 12-membered rings. Additions involving nonracemic (*Z*)-α-(alkoxy)allyl stannanes IX (R^1 = alkyl, R^2 = OR) and (*E*)-γ-(alkoxy)allyl stannanes VI (R^1 = OR, R^2 = alkyl) have not yet been examined.

The foregoing examples reflect conformational preferences in the S_E' transition state which are a composite of steric and electronic effects. Our studies show that nonracemic (alkoxy)allyl stannanes react with virtually complete anti S_E' selectivity. However, the data are insufficient to establish *E*/*Z* preferences that might be of predictive value. The syn diastereoselectivity of intermolecular reactions with aldehydes is good to excellent depending on aldehyde structure. For intramolecular applications conformational constraints would expectedly play a major role in determining isomer ratios. These factors are currently under study and will be reported in due course.

Experimental Section[20]

(*E*)-1-(Tri-*n*-butylstannyl)-2-buten-1-one (4). To a stirred, cooled (0 °C) solution of 35 mL (18 mmol) of 0.5 M LDA in THF was added 4.7 mL (18 mmol) of Bu_3SnH. After 15 min, the resulting solution was cooled to −78 °C and a solution of 1.1 g (16 mmol) of crotonaldehyde (**1**) in 15 mL of THF was introduced. The reaction solution was stirred for 10 min before 4.5 g (18 mmol) of 1,1′-(azodicarbonyl)dipiperidine was added, and the reaction mixture was warmed to 0 °C. After stirring for 1 h at 0 °C, the dark orange reaction mixture was quenched with saturated aqueous NH_4Cl. The resulting mixture was extracted with ether, and the organic layer was washed with 3% HCl, saturated $NaHCO_3$, and brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure and column chromatography, the acyl stannane (3.7 g, 65%) was obtained as a light yellow oil: IR (neat) 2910, 1600, 1450, 1380, 1140, 1070, 960, 880 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 6.58 (dq, 1 H, *J* = 15.6, 6.8 Hz, H3), 6.10 (d, 1 H, *J* = 15.6 Hz, H2), 2.0 (d, 3 H, *J* = 6.7 Hz, H4), 0.8–1.6 (m, 27 H, $SnBu_3$).

(*E*)-1-(Tri-*n*-butylstannyl)-2-hepten-1-one (5). The procedure described for stannyl ketone **4** was employed, whereby 1.1 g (10 mmol) of *trans*-2-heptenal (**2**) afforded 2.4 g (60%) of the acyl stannane **5** as a light yellow oil: IR (neat) 2960, 2920, 2860, 1550 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 6.57 (dt, 1 H, *J* = 15.7, 6.8 Hz, H2), 6.05 (d, 1 H, *J* = 15.7 Hz, H3), 2.30 (q, 2 H, *J* = 7.4 Hz, H4), 1.6–0.9 (m, 34 H, H5, H6, H7, and $SnBu_3$).

(*E*)-1-(Tri-*n*-butylstannyl)-3-cyclohexyl-2-propen-1-one (6). The procedure described for stannyl ketone **4** was followed, whereby 1.5 g (11 mmol) of cyclohexanecarboxaldehyde (**3**) gave 3.3 g (70%) of the acyl stannane **6** as a yellow oil: IR (neat) 2932, 2856, 1763, 1720, 1692, 1654, 1605, 1447, 1343, 967, 880, 668 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 6.46 (dd, 1 H, *J* = 6.6, 15.8 Hz, H3), 6.00 (d, 1 H, *J* = 15.8 Hz, H2), 2.24–0.79 (m, 38 H, cyclohexyl H's and $SnBu_3$).

(1*S*,2*E*)-1-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-2-butene (10). To a stirred, cooled (0 °C) solution of 2.4 mL (17 mmol) of $HN(i\text{-}Pr)_2$ in 100 mL of THF was added 8.6 mL (17 mmol) of 2.5 M *n*-BuLi in hexanes. The solution was stirred for 25 min at 0 °C, and then 4.6 mL (17 mmol) of $HSnBu_3$ was introduced. The resulting solution was stirred for 30 min at 0 °C and then cooled to −78 °C. To this solution was added 1.0 g (14 mmol) of crotonaldehyde (**1**) in 8 mL of THF. The reaction mixture was stirred for 10 min at −78 °C, and then 4.3 g (17 mmol) of 1,1′-(azodicarbonyl)dipiperidine was added. The suspension was warmed to 0 °C and stirred for 1.5 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl, the phases were separated, and the aqueous phase was extracted with ether. The combined organic layers were dried over $MgSO_4$, concentrated under reduced pressure, dissolved in hexanes, filtered, and again concentrated under reduced pressure to give 3.8 g (75%) of crude acyl stannane **4**.

A solution of 25 mL (25 mmol) of 1.0 M $LiAlH_4$ in THF was added to 50 mL of THF with stirring, and then 25 mL (25 mmol) of 1.0 M EtOH in THF was added over 30 min. The reaction mixture was stirred for 30 min. To this mixture was added a solution of 7.2 g (25 mmol) of (*R*)-1,1′-bi-2-naphthol in 50 mL of THF over 1 h. The milky white reaction mixture was heated to reflux for 50 min. It was then allowed to reach ambient temperature and cooled to −78 °C. To this suspension was added the crude acyl stannane **4** in 17 mL of THF over 1 h. The reaction mixture was stirred for 24 h at −78 °C and then quenched with MeOH, followed by saturated aqueous NH_4Cl. The phases were separated, and the aqueous phase was treated with 3% HCl and extracted with ether. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. This residue was titrated with 300 mL of hexanes and filtered, affording 6.9 g (96%) of binaphthol: $[\alpha]_D$ +34 (*c* 1.0, THF), mp 207 °C; reported $[\alpha]_D$ +34 (*c* 1.0, THF), mp 208–210 °C;[23] ^1H NMR (300 MHz) ($CDCl_3$) δ 7.98–7.87 (m, 4 H, Ph), 7.39–7.12 (m, 8 H, Ph), 5.02 (s, 2 H, OH).

The filtrate was concentrated under reduced pressure, affording the crude hydroxy stannane **7**. This material was dissolved in 10 mL of CH_2Cl_2, and 4.4 mL (25 mmol) of $(i\text{-}Pr)_2NEt$ was added, followed by 1.0 mL (12 mmol) of MOMCl. After stirring overnight, the reaction mixture was quenched with saturated aqueous NH_4Cl. The phases were separated, and the aqueous phase was extracted with ether. The combined organic phases were dried over $MgSO_4$, concentrated under reduced pressure, and chromatographed slowly (elution with hexanes) through silica gel to yield 2.6 g (45% from starting aldehyde **1**) of the

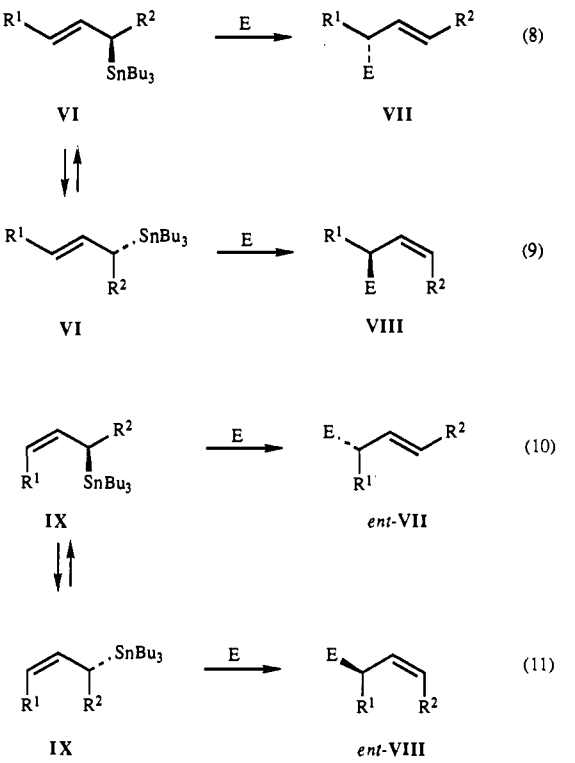


Figure 4. S_E' additions to nonracemic allyl stannanes.

(20) 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 benzophenone ketyl (diethyl ether, tetrahydrofuran), P_2O_5 (dichloromethane), calcium hydride (hexamethylphosphoramide), or sodium (benzene, toluene). Infrared absorption maxima are reported in wavenumbers (cm^{-1}) and are standardized by reference to the 1601-cm^{-1} peak of polystyrene. Proton magnetic resonance samples were prepared as dilute solutions in $CDCl_3$. Chemical shifts (δ) are reported downfield from 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 Hewlett-Packard 5890A GC equipped with a Superox 4 25M column. Combustion microanalyses were performed by Atlantic Laboratories, Norcross, GA. Analytical thin-layer chromatography (TLC) was routinely used to monitor reactions. Plates precoated with E. Merck silica gel 60 F_{254} of 0.25-mm thickness were used. E. Merck silica gel 60 (230–400 ASTM mesh) was employed for column chromatography according to the procedure of Still, Kahn, and Mitra.[22]

(21) Brown, H. C. *Organic Syntheses via Boranes*; Wiley: New York, 1975; pp 191–202.

(22) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(23) *Aldrich Catalog Handbook of Fine Chemicals 1990–1991*; Aldrich Chemical Co.: Milwaukee, WI; p 150.

α-(alkoxy) stannane **10**: $[\alpha]_D$ −56 (*c* 1.4, CH_2Cl_2); IR (neat) 2941, 2927, 1464, 1376, 1155, 1017, 965, 923 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.51 (dd, 1 H, *J* = 7.5, 15.3 Hz, H2), 5.36 (dq, 1 H, *J* = 6.3, 15.3 Hz, H3), 4.56 (ABq, 2 H, *J* = 6.3 Hz, Δν = 49.6 Hz, OCH_2O), 4.54 (d, 1 H, *J* = 7.5 Hz, H1), 3.32 (s, 3 H, OCH_3), 1.66 (q, 3 H, *J* = 1.3 Hz, H4), 1.23–1.54 (m, 18 H, CH_2's); 0.85–0.97 (m, 12 H, CH_3's). MS Calcd for $C_{18}H_{38}O_2Sn$: 405. Found: 405. ^1H NMR analysis of the *O*-methylmandelate **14** indicated an ee of >95% for this material.

(1*S*,2*E*)-1-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-2-heptene (11). The procedure described for α-(alkoxy) stannane **10** was employed, whereby 1.0 g (8.9 mmol) of *trans*-2-heptenal (**2**) afforded 1.4 g (42%) of the α-(alkoxy) stannane **11**: $[\alpha]_D$ −58 (*c* 2.2, CH_2Cl_2); IR (neat) 2954, 2921, 2856, 1458, 1376, 1153, 1017, 962, 919, 869, 663 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.53 (dd, 1 H, *J* = 7.7, 15.3 Hz, H2), 5.36 (dt, 1 H, *J* = 6.6, 15.3 Hz, H3), 4.56 (ABq, 2 H, *J* = 6.4 Hz, Δν = 33.7 Hz, OCH_2O); 4.54 (d, 1 H, *J* = 7.6 Hz, H1), 3.32 (s, 3 H, OCH_3), 1.66 (q, 2 H, *J* = 6.3 Hz, H4), 1.23–1.54 (m, 22 H, CH_2's), 0.85–0.97 (m, 12 H, CH_3's). MS Calcd for $C_{21}H_{44}O_2Sn$: 448. Found: 403 ($M^+ - CH_2OCH_3$). ^1H NMR analysis of the *O*-methylmandelate **15** indicated an ee of >95% for this material.

(1*S*,2*E*)-1-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-3-cyclohexyl-2-propene (12). The procedure described for α-alkoxystannane **10** was employed, whereby 1.5 g (11 mmol) of cyclohexanecarboxaldehyde (**3**) afforded 2.3 g (45%) of the α-(alkoxy) stannane **12**. $[\alpha]_D$ −53 (*c* 2.0, CH_2Cl_2); IR (neat) 2924, 1449, 1376, 1154, 1018, 966, 924, 874, 668 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.49 (dd, 1 H, *J* = 15.5, 7.4 Hz, H3), 5.33 (dd, 1 H, *J* = 15.5, 7.5 Hz, H2), 4.57 (ABq, 2 H, *J* = 6.3 Hz, Δν = 58.7 Hz, OCH_2O), 4.54 (d, 1 H, *J* = 7.3 Hz, H1), 3.32 (s, 3 H, OCH_3), 1.90–0.86 (m, 38 H, cyclohexyl H's and $SnBu_3$). MS Calcd for $C_{23}H_{46}O_2Sn$: 474. Found: 429 ($M^+ - CH_2OCH_3$). Anal. Calcd for $C_{23}H_{46}O_2Sn$: C, 58.37; H, 9.80. Found: C, 58.28; H, 9.83. ^1H NMR analysis of the *O*-methylmandelate **16** indicated an ee of ~90% for this material.

(1*S*,2*E*)-1-(Tri-*n*-butylstannyl)-1-[(benzyloxy)methoxy]-2-heptene (13). The procedure described for α-(alkoxy) stannane **10** was employed, whereby 1.8 g (16 mmol) of *trans*-2-heptenal (**2**) afforded 3.4 g (41% overall yield) of the BOM ether **13** as a colorless oil: $[\alpha]_D$ −54 (*c* 2.0, CH_2Cl_2); IR (neat) 2932, 2861, 1449, 1373, 1273, 1208, 1150, 1097, 1032, 967, 921 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.32 (m, 5 H, Ph), 5.53 (dd, 1 H, *J* = 7.8, 15.2 Hz, H2), 5.38 (dt, 1 H, *J* = 6.0, 15.2 Hz, H3), 4.76, 4.63 (ABq, 2 H, *J* = 6.5 Hz, OCH_2O), 4.64 (d, 1 H, *J* = 7.8 Hz, H1), 4.61, 4.50 (ABq, 2 H, *J* = 11.7 Hz, OCH_2Ph), 2.0 (q, 2 H, *J* = 7 Hz, H4), 0.9–1.60 (m, 34 H, H5, H6, H7, and $SnBu_3$). ^1H NMR analysis of the *O*-methylmandelate indicated an ee of >95% for this material.

(1*R*,2*E*)-1-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-2-butene (*ent*-10). Acyl stannane **4** was prepared as described above from 1.5 g (21 mmol) of crotonaldehyde (**1**). The crude product was reduced as follows.

To a stirred solution of 11 g (38 mmol) of Chirald in 200 mL of ether was added 17 mL (17 mmol) of 1.0 M $LiAlH_4$ in THF. The reaction mixture was stirred for 2 min and then cooled to −78 °C. A white precipitate formed upon cooling. To this suspension was added the crude stannyl ketone **4** in 300 mL of ether over 1 h. The reaction mixture was stirred for 1.5 h at −78 °C and quenched with wet ether. The suspension was warmed to room temperature and washed with 3% aqueous HCl, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, concentrated under reduced pressure, and chromatographed quickly (elution with 10% ether–hexanes) through a column of silica gel (deactivated with 5% TEA in hexanes), affording crude hydroxy stannane *ent*-**7**. This hydroxy stannane was dissolved in 15 mL of CH_2Cl_2, and 4.5 mL (26 mmol) of $(i\text{-}Pr)_2NEt$ was added, followed by 1.0 mL (13 mmol) of MOMCl. After stirring for 8 h, the reaction mixture was quenched with saturated aqueous NH_4Cl. The phases were separated, and the aqueous phase was extracted with ether. The combined organic phases were dried over $MgSO_4$, concentrated under reduced pressure, and chromatographed slowly (elution with hexanes) through silica gel to yield 3.2 g (37%) of the α-(alkoxy) stannane *ent*-**10**: $[\alpha]_D$ +52 (*c* 2.1, CH_2Cl_2); IR (neat) 2941, 2927, 1464, 1376, 1155, 1017, 965, 923 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.51 (dd, 1 H, *J* = 7.5, 15.3 Hz, H2), 5.36 (dq, 1 H, *J* = 6.3, 15.3 Hz, H3), 4.56 (ABq, 2 H, *J* = 6.3 Hz, Δν = 49.6 Hz, OCH_2O), 4.54 (d, 1 H, *J* = 7.5 Hz, H1), 3.32 (s, 3 H, OCH_3), 1.66 (q, 3 H, *J* = 6.3 Hz, H4), 1.23–1.54 (m, 18 H, CH_2's), 0.85–0.97 (m, 12 H, CH_3's). MS Calcd for $C_{18}H_{38}O_2Sn$: 405. Found: 405. ^1H NMR analysis of the *O*-methylmandelate **17** indicated an ee of ~86% for this material.

(1*R*,2*E*)-1-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-2-heptene (*ent*-11). The procedure described for α-(alkoxy) stannane *ent*-**10** was employed, whereby 0.75 g (6.7 mmol) of *trans*-2-heptenal (**2**) afforded 1.4 g (47%) of the α-(alkoxy) stannane *ent*-**11**: $[\alpha]_D$ +46 (*c* 2.0, CH_2Cl_2); IR (neat) 2954, 2921, 2856, 1458, 1376, 1153, 1017, 962, 919, 869, 663 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.53 (dd, 1 H, *J* = 7.7, 15.3 Hz, H2), 5.36 (dt, 1 H, *J* = 6.6, 15.3 Hz, H3), 4.56 (ABq, 2 H, *J* = 6.4 Hz, Δν = 33.7 Hz, OCH_2O), 4.54 (d, 1 H, *J* = 7.6 Hz, H1), 3.32 (s, 3 H, OCH_3), 1.66 (q, 2 H, *J* = 6.3 Hz, H4), 1.23–1.54 (m, 22 H, CH_2's), 0.85–0.97 (m, 12 H, CH_3's). MS Calcd for $C_{21}H_{44}O_2Sn$: 448. Found: 403 ($M^+ - CH_2OCH_3$). ^1H NMR analysis of the *O*-methylmandelate **18** indicated an ee of ~76% for this material.

(1*R*,2*E*)-1-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-3-cyclohexyl-2-propene (*ent*-12). The procedure described for α-(alkoxy) stannane **10** was employed, whereby 1.8 g (13 mmol) of cyclohexanecarboxaldehyde (**3**) yielded 2.0 g (36%) of the α-(alkoxy) stannane *ent*-**12**: $[\alpha]_D$ +33 (*c* 2.4, CH_2Cl_2); IR (neat) 2924, 1449, 1376, 1154, 1018, 966, 924, 874, 668 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.49 (dd, 1 H, *J* = 15.5, 7.4 Hz, H3), 5.33 (dd, 1 H, *J* = 15.5, 7.5 Hz, H2), 4.57 (ABq, 2 H, *J* = 6.3 Hz, Δν = 58.7 Hz, OCH_2O), 4.54 (d, 1 H, *J* = 7.3 Hz, H1), 3.32 (s, 3 H, OCH_3), 1.90–0.86 (m, 38 H, cyclohexyl H's and $SnBu_3$). MS Calcd for $C_{23}H_{46}O_2Sn$: 474. Found: 429 ($M^+ - CH_2OCH_3$). Anal. Calcd for $C_{23}H_{46}O_2Sn$: C, 58.37; H, 9.80. Found: C, 58.28; H, 9.83. ^1H NMR analysis of the *O*-methylmandelate **19** indicated an ee of ~54% for this material.

(1*R*,2*E*)-1-(Tri-*n*-butylstannyl)-1-[(benzyloxy)methoxy]-2-heptene (*ent*-13). The procedure described for α-(alkoxy) stannane **10** was employed, whereby 1.0 g (8.9 mmol) of *trans*-2-heptenal (**2**) afforded 1.8 g (39%) of the BOM ether *ent*-**13** as a colorless oil: $[\alpha]_D$ +44 (*c* 2.0, CH_2Cl_2); IR (neat) 2932, 2861, 1449, 1373, 1273, 1208, 1150, 1097, 1032, 967, 921 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.32 (m, 5 H, Ph), 5.53 (dd, 1 H, *J* = 7.8, 15.2 Hz, H2), 5.38 (dt, 1 H, *J* = 6.0, 15.2 Hz, H3), 4.76, 4.63 (ABq, 2 H, *J* = 6.5 Hz, OCH_2O), 4.64 (d, 1 H, *J* = 7.8 Hz, H1), 4.61, 4.50 (ABq, 2 H, *J* = 11.7 Hz, OCH_2Ph), 2.0 (q, 2 H, *J* = 7 Hz, H4), 0.9–1.60 (m, 34 H, H5, H6, H7, and $SnBu_3$). ^1H NMR analysis of the *O*-methylmandelate indicated an ee of ~77% for this material.

(1*S*,2*E*)-1-(Tri-*n*-butylstannyl)-2-butenyl (*S*)-*O*-methylmandelate (14). To a solution of 50 mg (0.14 mmol) of the freshly prepared hydroxy stannane **7** in 2 mL of CH_2Cl_2 was added 43 mg (0.21 mmol) of dicyclohexylcarbodiimide, 35 mg (0.21 mmol) of (*S*)-(+)-α-methoxyphenylacetic acid, and 5 mg (0.04 mmol) of DMAP, sequentially with stirring. After 1 h, TLC analysis indicated no starting material remained. The reaction mixture was diluted with hexane and filtered. The filtrate was washed with 1 N HCl, aqueous $NaHCO_3$, and brine. After drying over anhydrous $MgSO_4$, the solvent was removed under reduced pressure. Chromatography on silica gel (elution with 5% ethyl acetate–hexanes) afforded, after removal of solvent, 53 mg (75%) of a colorless oil: IR (neat) 2956, 2925, 2360, 1735, 1456, 1376, 1178, 1117, 999, 961, 734, 696, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–7.4 (m, 5 H, Ph), 5.58 (dd, 1 H, *J* = 7.1, 15.3 Hz, H2), 5.38 (d, 1 H, *J* = 7.1 Hz, H1), 5.10 (dt, 1 H, *J* = 15.3, 6.9 Hz, H3), 4.71 (s, 1 H, CHPh), 3.40 (s, 3 H, OCH_3), 0.86–1.90 (m, 30 H, H4 and $SnBu_3$). MS Calcd for $C_{25}H_{42}O_3Sn$: 510. Found: 453 (M^+ − Bu). An ee of >95% was calculated for the alcohol precursor of this product from integration of the MeO and methine signals in the ^1H NMR spectrum of **14**.

(1*S*,2*E*)-1-(Tri-*n*-butylstannyl)-2-heptenyl (*S*)-*O*-Methylmandelate (15). The procedure described for mandelate **14** was employed, whereby 50 mg (0.12 mmol) of the freshly prepared hydroxy stannane **8** afforded 54 mg (79%) of **15** as a colorless oil: IR (neat) 2956, 2944, 2921, 1705, 1178 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–7.4 (m, 5 H, Ph), 5.51 (dd, 1 H, *J* = 7.0, 15.3 Hz, H2), 5.33 (d, 1 H, *J* = 6.9 Hz, H1), 5.01 (dt, 1 H, *J* = 8.2, 15.3 Hz, H3), 4.73 (s, 1 H, CHPh), 3.40 (s, 3 H, OCH_3), 1.94 (m, 2 H, H4), 0.8–1.6 (m, 36 H, H5, H6, H7, and $SnBu_3$). MS Calcd for $C_{28}H_{48}O_3Sn$: 552. Found: 552. An ee of >95% was calculated for the alcohol precursor of this product from the ^1H NMR spectrum of **15**.

(1*S*,2*E*)-1-(Tri-*n*-butylstannyl)-3-cyclohexyl-2-propenyl (*S*)-*O*-Methylmandelate (16). The procedure described for mandelate **14** was employed, whereby 50 mg (0.12 mmoL) of the freshly prepared hydroxy stannane *ent*-**9** gave 48 mg (72%) of **16** as a colorless oil: IR (neat) 2954, 2921, 2845, 1725, 1447, 1197, 1175, 1115, 962 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.44–7.24 (m, 5 H, Ph), 5.50 (dd, 1 H, *J* = 6.5, 8.9 Hz, H2), 5.45 (d, 1 H, *J* = 8.0 Hz, H1), 5.33 (dd, 1 H, *J* = 6.9, 8.6 Hz, H3), 4.73 (s, 1 H, CHPh), 3.40 (s, 3 H, OCH_3), 1.77–0.64 (m, 36 H, cyclohexyl H's and $SnBu_3$). MS Calcd for $C_{30}H_{50}O_3Sn$: 578. Found: 521 (M^+ − Bu). An ee of ~90% was calculated for the alcohol precursor of this product from the ^1H NMR spectrum of **16**.

(1*R*,2*E*)-1-(Tri-*n*-butylstannyl)-2-butenyl (*S*)-*O*-Methylmandelate (17). The procedure described for mandelate **14** was employed, whereby 100 mg (0.28 mmol) of the freshly prepared hydroxy stannane *ent*-**7** gave 120 mg (83%) of **17** as a colorless oil: IR (neat) 2956, 2925, 2360, 1735, 1456, 1376, 1178, 1117, 999, 961, 734, 696, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–7.4 (m, 5 H, Ph), 5.58 (dd, 1 H, *J* = 7.1, 15.3 Hz, H2), 5.38 (d, 1 H, *J* = 7.1 Hz, H1), 5.36 (dt, 1 H, *J* = 15.3, 6.9 Hz, H3), 4.74 (s, 1 H, CHPh), 3.39 (s, 3 H, OCH_3), 0.86–1.90 (m, 30 H, H4 and $SnBu_3$).

MS Calcd for $C_{25}H_{42}O_3Sn$: 510. Found: 453 (M^+ - Bu). An ee of ~86% was calculated for the alcohol precursor of this product from the ^1H NMR spectrum of **17**.

(1*R*,2*E*)-1-(Tri-*n*-butylstannyl)-2-heptenyl (*S*)-*O*-Methylmandelate (18). The procedure described for mandelate **14** was employed, whereby 50 mg (0.12 mmol) of the freshly prepared hydroxy stannane ***ent*-8** afforded 54 mg (79%) of **15** as a colorless oil: IR (neat) 2956, 2944, 2921, 1705, 1178 cm^{-1}; ^1H NMR (500 MHz) ($CDCl_3$) δ 7.3–7.4 (m, 5 H, Ph), 5.58 (dd, 1 H, J = 7.0, 15.3 Hz, H2), 5.37 (d, 1 H, J = 6.9 Hz, H1), 5.26 (dt, 1 H, J = 8.2, 15.3 Hz, H3), 4.74 (s, 1 H, CHPh), 3.39 (s, 3 H, OCH_3), 1.94 (m, 2 H, H4), 0.8–1.6 (m, 36 H, H5, H6, H7, and $SnBu_3$). MS Calcd for $C_{28}H_{48}O_3Sn$: 552. Found: 552. An ee of ~76% was calculated for the alcohol precursor of this product from the ^1H NMR spectrum of **18**.

(1*R*,2*E*)-1-(Tri-*n*-butylstannyl)-3-cyclohexyl-2-propenyl (*S*)-*O*-Methylmandelate (19). The procedure described for mandelate **14** was employed, whereby 50 mg (0.12 mmol) of the freshly prepared hydroxy stannane ***ent*-9** gave 47 mg (70%) of **16** as a colorless oil: IR (neat) 2954, 2921, 2845, 1725, 1447, 1197, 1175, 1115, 962 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.24–7.44 (m, 5 H, Ph), 5.59 (dd, 1 H, J = 6.5, 8.9 Hz, H2), 5.36 (d, 1 H, J = 8.0 Hz, H1), 5.23 (dd, 1 H, J = 6.9, 8.6 Hz, H3), 4.75 (s, 1 H, CHPh), 3.39 (s, 3 H, OCH_3), 1.77–0.64 (m, 36 H, cyclohexyl H's and $SnBu_3$). MS Calcd for $C_{30}H_{50}O_3Sn$: 578. Found: 521 (M^+ - Bu). An ee of ~54% was calculated for the alcohol precursor of this product from the ^1H NMR spectrum of **19**.

(1*S*,2*E*)-1-(Tri-*n*-butylstannyl)-2-heptenyl *p*-Bromobenzoate (20). To a solution of freshly prepared hydroxy stannane **8** (0.3 g, 0.74 mmol, >95% ee by ^1H NMR analysis of the *O*-methylmandelate) in 15 mL of CH_2Cl_2 was added 0.2 g (1 mmol) of *p*-bromobenzoic acid, 0.2 g (1.0 mmol) of DCC, and 24 mg (0.2 mmol) of DMAP at 0 °C. After 2 h at room temperature, the reaction mixture was diluted with ether and washed with 5% HCl, $NaHCO_3$, and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, affording 0.4 g (93%) of a colorless oil: $[\alpha]_D$ +20 (*c* 0.8, hexanes); CD spectrum λ = 241 nm, $\delta\epsilon$ = +14.9; IR (neat) 2960, 2910, 2860, 1700, 1590, 1460, 1270, 1180, 1100, 1010, 960, 760 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.86, 7.55 (ABq, 4 H, J = 8.7 Hz, Ar), 5.78 (dd, 1 H, J = 8.3, 15.1 Hz, H2), 5.55 (d, 1 H, J = 8.3 Hz, H1), 5.42 (m, 1 H, H3), 0.8–2.3 (m, 36 H, Bu_3Sn, Bu).

(3*S*,1*Z*)-3-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-1-butene (21). To a stirred, cooled (-78 °C) solution of 2.0 g (4.9 mmol) of α-(alkoxy) stannane **10** in 10 mL of CH_2Cl_2 was added 0.7 mL (5.7 mmol) of BF_3·Et_2O. The solution was stirred for 1 h at -78 °C and then quenched with saturated aqueous $NaHCO_3$ and warmed to room temperature. The phases were separated, and the aqueous phase was extracted with ether. The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Chromatography (elution with hexanes) of the crude product gave 1.6 g (80%) of the γ-(alkoxy) stannane **21**: $[\alpha]_D$ +135 (*c* 2.0, CH_2Cl_2), IR (neat) 2952, 2927, 1651, 1464, 1379, 1245, 1162, 1119, 1043, 924 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.93 (d, 1 H, J = 6.2 Hz, H1), 4.73 (ABq, 2 H, J_{AB} = 6.3 Hz, $\Delta\nu$ = 9.5 Hz, OCH_2O), 4.47 (dd, 1 H, J = 6.1, 11.3 Hz, H2), 3.36 (s, 3 H, OCH_3), 2.47 (dt, 1 H, J = 5.4, 10.2 Hz, H3), 1.63–1.17 (m, 18 H, CH_2's), 1.00–0.71 (m, 12 H, CH_3's). MS Calcd for $C_{18}H_{38}O_2Sn$: 406. Found: 361 (M^+ - CH_2OCH_3). Anal. Calcd for $C_{18}H_{38}O_2Sn$: C, 53.36; H, 9.45. Found: C, 53.21; H, 9.50.

(3*S*,1*Z*)-3-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-1-heptene (22). The procedure described for **21** was employed, whereby 1.5 g (2.4 mmol) of α-(alkoxy) stannane **11** gave 1.3 g (87%) of the γ-(alkoxy) stannane **22**: $[\alpha]_D$ +119 (*c* 2.8, CH_2Cl_2); IR (neat) 2956, 2924, 1651, 1464, 1376, 1159, 1109, 1043, 924 cm^{-1}; ^1H NMR ($CDCl_3$) (500 MHz) δ 5.93 (d, 1 H, J = 6.2 Hz, H1), 4.73 (ABq, 2 H, J_{AB} = 6.3 Hz, $\Delta\nu$ = 9.5 Hz, OCH_2O), 4.47 (dd, 1 H, J = 6.1, 11.3 Hz, H2), 3.36 (s, 3 H, OCH_3), 2.47 (dt, 1 H, J = 5.4, 10.2 Hz, H3), 1.63–1.17 (m, 24 H, CH_2's), 1.00–0.71 (m, 12 H, CH_3's). MS Calcd for $C_{21}H_{44}O_2Sn$: 448. Found: 403 (M^+ - CH_2OCH_3).

(3*S*,1*Z*)-3-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-3-cyclohexyl-1-propene (23). The procedure described for **21** was employed, whereby 0.50 g (1.1 mmol) of α-(alkoxy) stannane **12** afforded 0.42 g (84%) of the γ-(alkoxy) stannane **23**: $[\alpha]_D$ +105 (*c* 1.0, CH_2Cl_2); IR (neat) 2953, 2922, 2851, 1158, 1112, 1042 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 5.95 (d, 1 H, J = 6.2 Hz, H1), 4.73 (ABq, 2 H, J = 6.3 Hz, $\Delta\nu$ = 10.9 Hz, OCH_2O), 4.51 (dd, 1 H, J = 6.2, 11.9 Hz, H2), 3.36 (s, 3 H, OCH_3), 2.44 (dd, 1 H, J = 8.1, 11.9 Hz, H3), 1.66–0.76 (m, 38 H, cyclohexyl H's and $SnBu_3$). MS Calcd for $C_{23}H_{46}O_2Sn$: 474. Found: 429 (M^+ - CH_2OCH_3).

(3*S*,1*Z*)-3-(Tri-*n*-butylstannyl)-1-[(benzyloxy)methoxy]-1-heptene (24). The procedure described for stannane **21** was employed, whereby 1.40 g (2.6 mmol) of the α-(alkoxy) stannane **13** gave 1.20 g (84%) of the γ-(alkoxy)allyl stannane **24** as a colorless oil: $[\alpha]_D$ +116 (*c* 1.1, CH_2Cl_2); IR (neat) 3020, 2940, 2910, 1440, 1370, 1100, 1050, 740, 690 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.3 (m, 5 H, Ph), 6.02 (d, 1 H, J = 6.1 Hz, H1), 4.86 (s, 2 H, OCH_2O), 4.60 (ABq, 2 H, J_{AB} = 11.6 Hz, $\Delta\nu$ = 15 Hz, $PhCH_2O$), 4.55 (dd, 1 H, J = 6.1, 11.2 Hz, H2), 2.5 (m, 1 H, H3), 1.20–1.45 (m, 18 H, CH_2's), 0.87 (m, 12 H, CH_3's).

(3*R*,1*Z*)-3-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-1-butene (*ent*-21). The procedure described for stannane **21** was employed, whereby 100 mg (0.25 mmol) of the α-(alkoxy)allyl stannane ***ent*-10** afforded 82 mg (82%) of the γ-(alkoxy)allyl stannane ***ent*-21** as a colorless oil: $[\alpha]_D$ -120 (*c* 1.3, CH_2Cl_2); IR (neat) 2952, 2927, 1651, 1464, 1379, 1245, 1162, 1119, 1043, 924 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.93 (d, 1 H, J = 6.2 Hz, H1), 4.73 (ABq, 2 H, J_{AB} = 6.3 Hz, $\Delta\nu$ = 9.5 Hz, OCH_2O), 4.47 (dd, 1 H, J = 6.1, 11.3 Hz, H2), 3.36 (s, 3 H, OCH_3), 2.47 (dt, 1 H, J = 5.4, 10.2 Hz, H3), 1.63–1.17 (m, 18 H, CH_2's), 1.00–0.71 (m, 12 H, CH_3's). MS Calcd for $C_{18}H_{38}O_2Sn$: 406. Found: 361 (M^+ - CH_2OCH_3). Anal. Calcd for $C_{18}H_{38}O_2Sn$: C, 53.36; H, 9.45. Found: C, 53.21; H, 9.50.

(3*R*,1*Z*)-3-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-1-heptene (*ent*-22). The procedure described for **21** was employed, whereby 100 mg (0.22 mmol) of α-(alkoxy) stannane ***ent*-11** gave 88 mg (88%) of the γ-(alkoxy) stannane ***ent*-22**: $[\alpha]_D$ -92 (*c* 2.7, CH_2Cl_2); IR (neat) 2956, 2924, 1651, 1464, 1376, 1159, 1109, 1043, 924 cm^{-1}; ^1H NMR ($CDCl_3$) (500 MHz) δ 5.93 (d, 1 H, J = 6.2 Hz, H1), 4.73 (ABq, 2 H, J_{AB} = 6.3 Hz, $\Delta\nu$ = 9.5 Hz, OCH_2O), 4.47 (dd, 1 H, J = 6.1, 11.3 Hz, H2), 3.36 (s, 3 H, OCH_3), 2.47 (dt, 1 H, J = 5.4, 10.2 Hz, H3), 1.63–1.17 (m, 24 H, CH_2's), 1.00–0.71 (m, 12 H, CH_3's). MS Calcd for $C_{21}H_{44}O_2Sn$: 448. Found: 403 (M^+ - CH_2OCH_3).

(3*R*,1*Z*)-3-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-3-cyclohexyl-1-propene (*ent*-23). The procedure described for **21** was employed, whereby 100 mg (0.21 mmol) of α-(alkoxy) stannane ***ent*-12** afforded 72 mg (72%) of the γ-(alkoxy) stannane ***ent*-23**: $[\alpha]_D$ -63 (*c* 1.8, CH_2Cl_2); IR (neat) 2953, 2922, 2851, 1158, 1112, 1042 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 5.95 (d, 1 H, J = 6.2 Hz, H1), 4.73 (ABq, 2 H, J = 6.3 Hz, $\Delta\nu$ = 10.9 Hz, OCH_2O), 4.51 (dd, 1 H, J = 6.2, 11.9 Hz, H2), 3.36 (s, 3 H, OCH_3), 2.44 (dd, 1 H, J = 8.1, 11.9 Hz), 1.66–0.76 (m, 38 H, cyclohexyl H's and $SnBu_3$). MS Calcd for $C_{23}H_{46}O_2Sn$: 474. Found: 429 (M^+ - CH_2OCH_3).

(3*R*,1*Z*)-3-(Tri-*n*-butylstannyl)-1-[(benzyloxy)methoxy]-1-heptene (*ent*-24). The procedure described for stannane **21** was employed, whereby 1.5 g (3.0 mmol) of the α-(alkoxy)allyl stannane ***ent*-13** afforded 1.20 g (80%) of the γ-(alkoxy)allyl stannane ***ent*-24** as a colorless oil: $[\alpha]_D$ -91 (*c* 2.3, CH_2Cl_2); IR (neat) 3020, 2940, 2910, 1440, 1370, 1100, 1050, 740, 690 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.3 (m, 5 H, Ph), 6.02 (d, 1 H, J = 6.1 Hz, H1), 4.86 (s, 2 H, OCH_2O), 4.60 (ABq, 2 H, J_{AB} = 11.6 Hz, $\Delta\nu$ = 15 Hz, $PhCH_2O$), 4.55 (dd, 1 H, J = 6.1, 11.2 Hz, H2), 2.5 (m, 1 H, H3), 1.20–1.45 (m, 18 H, CH_2's), 0.87 (m, 9 H, CH_3).

(4*R*,5*R*,2*E*,6*E*)-4-(Methoxymethoxy)-2,6-undecadien-5-ol (25a). To a stirred, cooled (-78 °C) solution of 200 mg (0.49 mmol) of γ-(alkoxy)allyl stannane **21** in 0.5 mL of CH_2Cl_2 was added 30 μL (0.24 mmol) of BF_3·Et_2O. The solution was stirred at -78 °C for 5 min, and then a solution of 61 mg (0.54 mmol) of *trans*-2-heptenal (**2**) in 0.5 mL of CH_2Cl_2 was added, followed by 60 μL (0.48 mmol) of BF_3·Et_2O. The reaction mixture was stirred at -78 °C for 1 h and then quenched with saturated aqueous $NaHCO_3$. The mixture was warmed to ambient temperature, and the phases were separated. The aqueous phase was extracted with ether, and the combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography on silica gel (elution with 15% ethyl acetate–hexanes) gave 95 mg (84%) of alcohol **25a** as a 94:6 mixture of the syn:anti isomers: IR (neat) 3472, 2957, 2926, 1671, 1450, 1378, 1212, 1152, 1099, 1035, 969, 921 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.67 (m, 2 H, H2 and H7), 5.38 (dd, 1 H, J = 6.7, 15.4 Hz, H3), 5.25 (dd, 1 H, J = 8.3, 15.3 Hz, H6), 4.61 (ABq, 2 H, J = 6.7 Hz, $\Delta\nu$ = 55.1 Hz, OCH_2O), 3.96 (dt, 1 H, J = 2.8, 6.8 Hz, H5), 3.80 (t, 1 H, J = 7.9 Hz, H4), 3.36 (s, 3 H, OCH_3), 2.65 (d, 1 H, J = 3.4 Hz, OH), 2.01 (q, 2 H, J = 7.0 Hz, H8), 1.69 (dd, 3 H, J = 1.6, 6.4 Hz, H1), 1.20–1.40 (m, 4 H, H9 and H10), 0.85 (t, 3 H, J = 7.0 Hz, H11). MS Calcd for $C_{13}H_{24}O_3$: 228. Found: 183 (M^+ - CH_2OCH_3). Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.27; H, 10.54.

(1*R*,2*R*,3*E*)-2-(Methoxymethoxy)-1-cyclohexyl-3-penten-1-ol (25b). The procedure described for **25a** was employed, whereby 200 mg (0.49 mmol) of γ-(alkoxy) stannane **21**, 61 mg (0.54 mmol) of cyclohexanecarboxaldehyde, and 90 μL (0.73 mmol) of BF_3·OEt_2 gave 84 mg (74%) of alcohol **25b** as a 94:6 mixture of syn:anti isomers: IR (neat) 3492, 2925, 2852, 2360, 1450, 1212, 1151, 1099, 1030, 971, 920 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 5.70 (dq, 1 H, J = 6.5, 15.4 Hz, H4), 5.34 (dd, 1 H, J = 8.6, 15.5 Hz, H3), 4.61 (ABq, 2 H, J = 6.7 Hz, $\Delta\nu$ = 66.1 Hz, OCH_2O), 3.98 (dd, 1 H, J = 6.4, 8.5 Hz, H2), 3.35 (s, 3 H, OCH_3), 3.23 (q, 1 H, J = 6.2 Hz, H1), 2.35 (d, 1 H, J = 4.3 Hz, OH), 1.70 (d, 3 H, J = 6.5 Hz, H5), 1.63–1.14 (m, 11 H, cyclohexyl H's). MS Calcd

for $C_{13}H_{24}O_3$: 228. Found: 183 ($M^+ - CH_2OCH_3$). Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.35; H, 10.65.

(4*R*,5*R*,2*E*)-4-(Methoxymethoxy)-2-undecen-5-ol (25c). The procedure described for **25a** was employed, whereby 200 mg (0.49 mmol) of γ-(alkoxy) stannane **21**, 62 mg (0.54 mmol) of heptanal, and 90 μL (0.73 mmol) of $BF_3{\cdot}OEt_2$ gave 86 mg (75%) of alcohol **25c** as a 96:4 mixture of syn:anti isomers: IR (neat) 3486, 2929, 1670, 1453, 1400, 1379, 1280, 1211, 1152, 1033, 970, 923, 870, 790, 725 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 5.69 (dq, 1 H, *J* = 6.5, 15.4 Hz, H2), 5.25 (dd, 1 H, *J* = 8.6, 15.5 Hz, H3), 4.61 (ABq, 2 H, *J* = 6.6 Hz, Δν = 63.2 Hz, OCH_2O), 3.75 (dd, 1 H, *J* = 7.2, 15.6 Hz, H4), 3.47 (m, 1 H, H5), 3.34 (s, 3 H, OCH_3), 2.57 (d, 1 H, *J* = 3.3 Hz, OH), 1.70 (d, 3 H, *J* = 6.5 Hz, H1), 1.48–1.24 (m, 10 H, CH_2's), 0.84 (t, 3 H, *J* = 6.5 Hz, H11). MS Calcd for $C_{13}H_{26}O_3$: 230. Found: 185 ($M^+ - CH_2OCH_3$).

(4*R*,5*R*,2*E*)-4-(Methoxymethoxy)-2-undecen-6-yn-5-ol (25d). The procedure described for **25a** was employed, whereby 130 mg (0.32 mmol) of γ-(alkoxy) stannane **21**, 40 mg (0.36 mmol) of 2-heptynal, and 60 μL (0.49 mmol) of $BF_3{\cdot}OEt_2$ gave 51 mg (70%) of alcohol **25d** as a 90:10 mixture of syn:anti isomers: IR (neat) 3445, 2934, 1450, 1152, 1102, 1034, 969, 920 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 5.78 (dq, 1 H, *J* = 6.5, 15.4, Hz, H2), 5.39 (dd, 1 H, *J* = 8.5, 15.3 Hz, H3), 4.61 (ABq, 2 H, *J* = 6.6 Hz, Δν = 42.8 Hz, OCH_2O), 4.27 (m, 1 H, H5), 3.98 (dd, 1 H, *J* = 7.9, 14.4 Hz, H4), 3.37 (s, 3 H, OCH_3), 2.60 (d, 1 H, *J* = 5.3 Hz, OH), 2.18 (dt, 2 H, *J* = 2.0, 6.9 Hz, H8), 1.72 (d, 3 H, *J* = 6.5 Hz, H1), 1.50–1.22 (m, 4 H, CH_2's), 0.87 (t, 3 H, *J* = 7.2 Hz, H11). MS Calcd for $C_{13}H_{22}O_3$: 226. Found: 181 ($M^+ - CH_2OCH_3$). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.01; H, 9.82.

(1*R*,2*R*,3*E*)-2-(Methoxymethoxy)-1-phenyl-3-penten-1-ol (25e). The procedure described for **25a** was employed, whereby 200 mg (0.49 mmol) of γ-(alkoxy) stannane **21**, 57 mg (0.54 mmol) of benzaldehyde, and 90 μL (0.73 mmol) of $BF_3{\cdot}OEt_2$ gave 98 mg (89%) of alcohol **25e** as a 95:5 mixture of syn:anti isomers: IR (neat) 3458, 3050, 2889, 1670, 1496, 1452, 1196, 1150, 1098, 1032, 970, 919, 760, 701 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.35–7.20 (m, 5 H, Ph), 5.54 (dq, 1 H, *J* = 6.5, 15.4 Hz, H4), 5.25 (dd, 1 H, *J* = 8.0, 15.5 Hz, H3), 4.61 (ABq, 2 H, *J* = 6.7 Hz, Δν = 60.7 Hz, OCH_2O), 4.56 (dd, 1 H, *J* = 3.2, 6.7 Hz, H1), 3.05 (dd, 1 H, *J* = 7.4, 14.8 Hz, H2), 3.24 (s, 3 H, OCH_3), 3.15 (d, 1 H, *J* = 3.2 Hz, OH), 1.59 (d, 3 H, *J* = 6.4 Hz, H5). MS Calcd for $C_{13}H_{18}O_3$: 222. Found: 177 ($M^+ - CH_2OCH_3$). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.25; H, 8.16. Found: C, 70.16; H, 8.19.

(7*R*,8*R*,5*E*,9*E*)-7-(Methoxymethoxy)-5,9-tetradecadien-8-ol (26a). The procedure described for **25a** was employed, whereby 250 mg (0.56 mmol) of γ-(alkoxy) stannane **22**, 63 mg (0.56 mmol) of *trans*-2-heptenal (**2**), and 83 μL (0.67 mmol) of $BF_3{\cdot}OEt_2$ gave 110 mg (73%) of alcohol **26a** as a 90:10 mixture of syn:anti isomers: IR (neat) 3450, 2957, 2926, 1466, 1152, 1099, 1030, 971 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.66 (m, 2 H, H5 and H10), 5.39 (dd, 1 H, *J* = 15.5, 6.7 Hz, H9), 5.24 (dd, 1 H, *J* = 15.5, 8.3 Hz, H7), 4.73, 4.54 (ABq, 2 H, *J* = 6.6 Hz, OCH_2O), 3.97 (m, 1 H, H8), 3.81 (t, 1 H, *J* = 7.9 Hz, H8), 3.37 (s, 3 H, OCH_3), 2.65 (d, 1 H, *J* = 3.1 Hz, OH), 2.03 (m, 4 H, H4 and H11), 1.30 (m, 8 H, H2, H3, H12, and H13), 0.86 (t, 6 H, *J* = 6.9 Hz, H1 and H14). MS Calcd for $C_{16}H_{30}O_3$: 270. Found: 225 ($M^+ - CH_2OCH_3$). Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.01; H, 11.18. Found: C, 71.04; H, 11.15.

(1*R*,2*R*,3*E*)-1-Cyclohexyl-2-(Methoxymethoxy)-3-octen-1-ol (26b). The procedure described for **25a** was employed, whereby 250 mg (0.56 mmol) of γ-(alkoxy) stannane **22**, 63 mg (0.56 mmol) of cyclohexanecarboxaldehyde, and 83 μL (0.67 mmol) of $BF_3{\cdot}OEt_2$ gave 120 mg (80%) of alcohol **26b** as a 98:2 mixture of syn:anti isomers: IR (neat) 3504, 2926, 2853, 1450, 1151, 1098, 1031, 974, 920 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.66 (dt, 1 H, *J* = 6.9, 15.5 Hz, H4), 5.39 (dd, 1 H, *J* = 15.5, 6.7 Hz, H3), 4.73, 4.54 (ABq, 2 H, *J* = 6.9 Hz, OCH_2O), 3.97 (dd, 1 H, *J* = 6.5, 8.6 Hz, H2), 3.34 (s, 3 H, OCH_3), 3.28 (q, 1 H, *J* = 6.5 Hz, H1), 2.38 (d, 1 H, *J* = 4.0 Hz, OH), 2.04 (q, 2 H, *J* = 6.9 Hz, H5), 1.72–1.11 (m, 15 H, H6, H7, and cyclohexyl H's), 0.86 (t, 3 H, *J* = 7.0 Hz, H8). MS Calcd for $C_{16}H_{30}O_3$: 270. Found: 225 ($M^+ - CH_2OCH_3$). Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.07; H, 11.18. Found: C, 71.05; H, 11.18.

(7*R*,8*R*,5*E*)-7-(Methoxymethoxy)-5-tetradecen-8-ol (26c). The procedure described for **25a** was employed, whereby 250 mg (0.56 mmol) of γ-(alkoxy) stannane **22**, 64 mg (0.56 mmol) of heptanal, and 83 μL (0.67 mmol) of $BF_3{\cdot}OEt_2$ gave 101 mg (73%) of alcohol **26c** as an 85:15 mixture of syn:anti isomers: IR (neat) 3477, 2932, 2856, 2665, 1463, 1398, 1376, 1147, 1098, 1039, 973, 919 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.70 (dt, 1 H, *J* = 6.9, 15.4 Hz, H5), 5.27 (dd, 1 H, *J* = 8.7, 15.4 Hz, H6), 4.73, 4.54 (ABq, 2 H, *J* = 6.6 Hz, OCH_2O), 3.97 (m, 1 H, H8), 3.81 (t, 1 H, *J* = 7.9 Hz, H9), 3.37 (s, 3 H, OCH_3), 2.65 (d, 1 H, *J* = 3.1 Hz, OH), 2.03 (m, 2 H, H4), 1.30 (m, 14 H, CH_2's), 0.86 (m, 6 H, CH_3's). MS Calcd for $C_{16}H_{32}O_3$: 272. Found: 227 ($M^+ - CH_2OCH_3$).

(7*R*,8*R*,5*E*)-7-(Methoxymethoxy)-5-tetradecen-9-yn-8-ol (26d). The procedure described for **25a** was employed, whereby 250 mg (0.56 mmol) of γ-(alkoxy) stannane **22**, 62 mg (0.56 mmol) of 2-heptynal, and 83 μL (0.67 mmol) of $BF_3{\cdot}OEt_2$ gave 112 mg (75%) of alcohol **26d** as an 87:13 mixture of syn:anti isomers: IR (neat) 3444, 2932, 2867, 1670, 1464, 1382, 1213, 1147, 1098, 1039, 973, 919, 733 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.70 (dt, 1 H, *J* = 6.9, 15.4 Hz, H5), 5.27 (dd, 1 H, *J* = 8.7, 15.4 Hz, H6), 4.73, 4.54 (ABq, 2 H, *J* = 6.6 Hz, OCH_2O), 3.97 (m, 1 H, H8), 3.97 (dd, 1 H, *J* = 8.1, 14.7 Hz, H7), 3.37 (s, 3 H, OCH_3), 2.65 (d, 1 H, *J* = 3.1 Hz, OH), 2.18 (dt, 2 H, *J* = 2.0, 7.0 Hz, H11), 2.03 (dt, 2 H, *J* = 6.3, 6.9 Hz, H3), 1.30 (m, 8 H, CH_2's), 0.86 (t, 6 H, *J* = 6.8 Hz, CH_3's). MS Calcd for $C_{16}H_{28}O_3$: 268. Found: 223 ($M^+ - CH_2OCH_3$). Anal. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.51. Found: C, 71.61; H, 10.56.

(1*R*,2*R*,3*E*)-1-Phenyl-2-(methoxymethoxy)-3-octen-1-ol (26e). The procedure described for **25a** was employed, whereby 250 mg (0.56 mmol) of γ-(alkoxy) stannane **22**, 63 mg (0.56 mmol) of benzaldehyde, and 83 μL (0.67 mmol) of $BF_3{\cdot}OEt_2$ gave 122 mg (83%) of alcohol **26e** as an 85:15 mixture of syn:anti isomers: IR (neat) 3455, 3053, 3030, 2953, 2921, 1496, 1453, 1382, 1197, 1147, 1098, 1033, 973, 913, 755, 695 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 7.3 (m, 5 H, Ph), 5.66 (dt, 1 H, *J* = 6.9, 15.5 Hz, H4), 5.39 (dd, 1 H, *J* = 15.5, 6.7 Hz, H3), 4.73, 4.54 (ABq, 2 H, *J* = 6.9 Hz, OCH_2O), 4.56 (m, 1 H, H2), 4.05 (t, 1 H, *J* = 7.6 Hz, H1), 3.26 (s, 3 H, OCH_3), 3.20 (d, 1 H, *J* = 2.7 Hz, OH), 1.91 (m, 2 H, H5), 1.30–1.06 (m, 4 H, H6 and H7), 0.80 (t, 3 H, *J* = 7.0 Hz, H8). MS Calcd for $C_{16}H_{24}O_3$: 264. Found: 219 ($M^+ - CH_2OCH_3$). Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.87; H, 9.21.

(4*R*,5*R*,1*E*,5*E*)-3-(Methoxymethoxy)-1-cyclohexyl-1,5-decadien-4-ol (27a). The procedure described for **25a** was employed, whereby 100 mg (0.21 mmol) of γ-(alkoxy) stannane **23**, 25 mg (0.22 mmol) of *trans*-2-heptenal, and 39 μL (0.30 mmol) of $BF_3{\cdot}OEt_2$ gave 42 mg (67%) of alcohol **27a** as a 65:35 mixture of syn:anti isomers: IR (neat) 3474, 2925, 2852, 1449, 1152, 1098, 1034, 971, 920 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.72–5.59 (m, 2 H, vinyl H's), 5.41–5.13 (m, 2 H, vinyl H's); 4.72, 4.54 (ABq, 2 H, *J* = 6.6 Hz, OCH_2O), 3.95 (m, 1 H, H6), 3.80 (t, 1 H, *J* = 7.7 Hz, H7), 3.37 (s, 3 H, OCH_3), 2.66 (s, 1 H, OH), 2.02–1.06 (m, 17 H, H2, H3, H4, and cyclohexyl H's); 0.86 (t, 3 H, *J* = 6.9 Hz, H1). MS Calcd for $C_{18}H_{32}O_3$: 296. Found: 251 ($M^+ - CH_2OCH_3$).

(1*R*,2*R*,3*E*)-2-(Methoxymethoxy)-1,4-dicyclohexyl-3-buten-1-ol (27b). The procedure described for **25a** was employed, whereby 100 mg (0.21 mmol) of γ-(alkoxy) stannane **23**, 25 mg (0.22 mmol) of cyclohexanecarboxaldehyde, and 39 μL (0.30 mmol) of $BF_3{\cdot}OEt_2$ gave 49 mg (78%) of alcohol **27b** as a 98:2 mixture of syn:anti isomers: IR (neat) 3490, 2924, 2851, 1449, 1151, 1099, 1031, 974, 920 cm^{-1}; ^1H NMR ($CDCl_3$) (300 MHz) δ 5.64 (dd, 1 H, *J* = 15.6, 6.7 Hz, H3), 5.22 (dd, 1 H, *J* = 15.7, 7.5 Hz, H4), 4.71, 4.49 (ABq, 2 H, *J* = 6.6 Hz, OCH_2O), 3.97 (t, 1 H, *J* = 6.6 Hz, H2), 3.35 (s, 3 H, OCH_3), 3.28 (m, 1 H, H1), 2.36 (d, 1 H, *J* = 3.8 Hz, OH), 2.06–1.05 (m, 22 H, cyclohexyl H's). MS Calcd for $C_{18}H_{32}O_3$: 296. Found: 251 ($M^+ - CH_2OCH_3$).

(7*R*,8*R*,5*E*,9*E*)-7-[(Benzyloxy)methoxy]-5,9-tetradecadien-8-ol (28a). The procedure described for **25a** was employed, whereby 150 mg (0.28 mmol) of γ-(alkoxy) stannane **24**, 32 mg (0.28 mmol) of *trans*-2-heptenal (2), and 52 μL (0.42 mmol) of $BF_3{\cdot}OEt_2$ gave 52 mg (61%) of alcohol **28a** as an 88:12 mixture of syn:anti isomers: IR (neat) 3400, 2900, 1640, 1050 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.3 (m, 5 H, Ph), 5.70 (m, 2 H, H5 and H10), 5.40 (dd, 1 H, *J* = 15.4, 6.7 Hz, H6), 5.26 (dd, 1 H, *J* = 15.5, 8.3 Hz, H7), 4.82, 4.74 (ABq, 2 H, J_{AB} = 6.8 Hz, OCH_2O), 4.69, 4.49 (ABq, 2 H, J_{AB} = 11.7 Hz, $PhCH_2O$), 4.0 (dd, 1 H, *J* = 6.8, 13.6 Hz, H8), 3.94 (dd, 1 H, *J* = 7.9, 7.4 Hz, H7), 2.02 (m, 4 H, H3 and H11), 1.3–1.5 (m, 8 H, CH_2's), 0.86 (t, 6 H, *J* = 6.9 Hz, H1 and H14).

(1*R*,2*R*,3*E*)-1-Cyclohexyl-2-[(benzyloxy)methoxy]-3-octen-1-ol (28b). The procedure described for **25a** was employed, whereby 150 mg (0.28 mmol) of γ-(alkoxy) stannane **24**, 32 mg (0.28 mmol) of cyclohexanecarboxaldehyde, and 52 μL (0.42 mmol) of $BF_3{\cdot}OEt_2$ gave 53 mg (62%) of alcohol **28b** as a 96:4 mixture of syn:anti isomers: ^1H NMR (300 MHz) ($CDCl_3$) δ 7.3 (m, 5 H, Ph), 5.70 (dt, 1 H, *J* = 15.5, 6.9 Hz, H4), 5.30 (dd, 1 H, *J* = 15.5, 8.6 Hz, H3), 4.82, 4.71 (ABq, 2 H, *J* = 6.9 Hz, OCH_2O), 4.68, 4.50 (ABq, 2 H, J_{AB} = 11.7 Hz, $PhCH_2O$), 4.09 (dd, 1 H, *J* = 6.6, 8.6 Hz, H2), 3.32 (m, 1 H, H1), 2.03 (q, 2 H, *J* = 6.7 Hz, H5), 1.13–1.75 (m, 15 H, CH_2's), 0.87 (t, 3 H, *J* = 6.9 Hz, H8).

(7*R*,8*R*,5*E*)-7-[(Benzyloxy)methoxy]-5-tetradecen-8-ol (28c). The procedure described for **25a** was employed, whereby 420 mg (0.80 mmol) of γ-(alkoxy) stannane **24**, 90 mg (0.80 mmol) of *n*-heptanal, and 0.12 mL (1.0 mmol) of $BF_3{\cdot}OEt_2$ gave 0.20 g (78%) of alcohol **28c** as an 88:12 mixture of syn:anti isomers: ^1H NMR ($CDCl_3$) δ 7.3 (m, 5 H, Ph), 5.70 (dt, *J* = 6.9, 15.4 Hz, 1 H, H5), 5.27 (dd, *J* = 15.4, 8.7 Hz, 1 H, H6), 4.81, 4.72 (ABq, J_{AB} = 6.8 Hz, 2 H, OCH_2O), 4.68, 4.52 (ABq, *J* = 11.6 Hz, 2 H, $PhCH_2O$), 3.87 (dd, *J* = 7.1, 8.5 Hz, 1 H, H7), 3.5 (m, 1 H,

H8), 2.05 (q, J = 5.6 Hz, 2 H, H3), 0.8–1.70 (m, 20 H, H1, H2, H9, H10, H11, H12, H13, H14).

(7*R*,8*R*,5*E*)-7-[(Benzyloxy)methoxy]-5-tetradecen-9-yn-8-ol (28d). The procedure described for **25a** was employed, whereby 100 mg (0.19 mmol) of γ-(alkoxy) stannane **24**, 24 mg (0.20 mmol) of 2-heptynal, and 35 μL (0.29 mmol) of BF_3·OEt_2 gave 50 mg (75%) of alcohol **28d** as an 86:14 mixture of syn:anti isomers: IR (neat) 3400, 2900, 2220, 1640, 1050 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.3 (m, 5 H, Ph), 5.80 (dt, 1 H, J = 8.5, 15.5 Hz, H5), 5.40 (dd, 1 H, J = 15.5, 8.2 Hz, H6), 4.81 4.78 (ABq, 2 H, J_{AB} = 6.8 Hz, OCH_2O), 4.72, 4.55 (ABq, 2 H, J_{AB} = 11.6 Hz, $PhCH_2O$), 4.3 (m, 1 H, H8), 4.1 (dd, 1 H, J = 6.3, 8.2 Hz, H7), 2.2 (t, 2 H, J = 5.0 Hz, H3), 2.07 (t, 2 H, J = 6.9 Hz, H11), 1.3–1.5 (m, 8 H, CH_2's), 0.87 (m, 6 H, CH_3's).

(1*S*,2*S*,3*E*)-1-Phenyl-2-[(benzyloxy)methoxy]-3-octen-1-ol (28e). The procedure described for **25a** was employed, whereby 150 mg (0.30 mmol) of γ-(alkoxy) stannane **24**, 32 mg (0.30 mmol) of benzaldehyde, and 52 μL (0.45 mmol) of BF_3·OEt_2 gave 62 mg (61%) of alcohol **28e** as an 85:15 mixture of syn:anti isomers: ^1H NMR (300 MHz) ($CDCl_3$) δ 7.3 (m, 5 H, Ph), 5.50 (dt, 1 H, J = 6.8, 15.5 Hz, H4), 5.26 (dd, 1 H, J = 15.5, 8.1 Hz, H3), 4.81, 4.73 (ABq, 2 H, J = 6.8 Hz, OCH_2O), 4.50, 4.40 (ABq, 2 H, J = 11.6 Hz, $PhCH_2O$), 4.15 (dd, 1 H, J = 7.4, 7.4 Hz, H2), 4.60 (d, 1 H, J = 7.4 Hz, H1), 2.05 (q, 2 H, J = 5.6 Hz, H5), 0.8–1.70 (m, 7 H, H6, H7, and H8).

(1*S*,2*R*,3*E*)-1-Phenyl-2-[(benzyloxy)methoxy]-3-octen-1-ol (32e). A mixture of 0.5 g (4.7 mmol) of benzaldehyde and 0.15 g (0.3 mmol) of stannane *ent*-**24** was sealed in a tube and heated for 18 h at 155 °C, affording a 5:1 mixture of **32e** and **28e** in 20% yield after chromatographic purification: IR (neat) 3400, 2900, 1640, 1050 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.3 (m, 5 H, Ph), 5.70 (dt, 1 H, J = 6.8, 15.5 Hz, H4), 5.35 (dd, 1 H, J = 15.5, 8.4 Hz, H3), 4.62, 4.74 (ABq, 2 H, J = 6.9 Hz, OCH_2O), 4.29, 4.24 (ABq, 2 H, J = 11.7 Hz, $PhCH_2O$), 4.17 (dd, 1 H, J = 5.6, 8.4 Hz, H2), 4.68 (dd, 1 H, J = 3.0, 5.6 Hz, H1), 2.05 (q, 2 H, J = 5.6 Hz, H5), 0.8–1.70 (m, 7 H, H6, H7, and H8).

(7*R*,8*R*,5*E*,9*E*)-5,9-Tetradecadiene-7,8-diol (33). A solution of 15 mg (0.04 mmol) of BOM ether **23c** in 2 mL of THF was added to 5 mL of liquid NH_3 at −78 °C. A 5-mm segment of Li wire was added, the mixture was allowed to reflux for 20 min, and then it was diluted with ether and slowly quenched with saturated aqueous NH_4Cl. After evaporation of the NH_3, the organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, affording 6 mg (66%) of diol after chromatographic purification: $[\alpha]_D$ +30 (*c* 0.5, THF); IR (neat) 3433, 2965, 2921, 2867, 1458, 973 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 5.75 (dt, 2 H, J = 7.8, 15.5 Hz, H5 and H10), 5.42 (dd, 2 H, J = 15.5, 6.2 Hz, H6 and H9), 3.90 (b, 2 H, H7 and H8), 2.02 (q, 4 H, J = 6.6 Hz, H4 and H11), 1.3–1.5 (m, 8 H, CH_2's), 0.86 (m, 6 H, H1 and H14).

(4*R*,5*R*,2*E*,6*E*)-4-(Methoxymethoxy)-2,6-undecadien-5-yl (*S*)-*O*-Methylmandelate (34a). The procedure described for mandelate **14** was employed, whereby 15 mg (0.066 mmol) of alcohol **25a** afforded 20 mg (80%) of **34a** as a colorless oil: IR (neat) 3030, 2954, 2921, 1752, 1671, 1453, 1251, 1175, 1098, 1028, 968, 924, 695 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.45–7.30 (m, 5 H, Ph), 5.62 (dq, 1 H, J = 6.5, 15.4 Hz, H2), 5.37 (dt, 1 H, J = 6.7, 15.4 Hz, H7), 5.28 (dd, 1 H, J = 6.0, 12.5 Hz, H6), 5.26 (m, 2 H, H3 and H5), 4.76 (s, 1 H, CHOMe), 4.54 (ABq, 2 H, J = 6.7 Hz, Δν = 44.2 Hz, OCH_2O), 4.00 (dd, 1 H, J = 7.7, 14.6 Hz, H4), 3.41 (s, 3 H, OCH_3), 3.30 (s, 3 H, OCH_3), 1.84 (q, 2 H, J = 6.8 Hz, H8), 1.65 (d, 3 H, J = 6.5 Hz, H1), 1.23–1.13 (m, 4 H, H9 and H10), 0.80 (t, 3 H, J = 6.9 Hz, H11). MS Calcd for $C_{22}H_{32}O_5$: 376. Found: 394 ($M^+ + NH_4^+$).

(1*R*,2*R*,3*E*)-1-Cyclohexyl-2-(methoxymethoxy)-3-penten-1-yl (*S*)-*O*-Methylmandelate (34b). The procedure described for mandelate **14** was employed, whereby 15 mg (0.066 mmol) of alcohol **25b** afforded 18 mg (72%) of **34b** as a colorless oil: IR (neat) 3019, 2921, 2856, 1752, 1447, 1175, 1110, 1028, 968, 919, 733, 695 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.49–7.30 (m, 5 H, Ph), 5.68 (dq, 1 H, J = 6.5, 15.4 Hz, H4), 5.18 (dd, 1 H, J = 6.6, 15.4 Hz, H3), 4.80 (dd, 1 H, J = 6.2, 11.6 Hz, H1), 4.76 (s, 1 H, CHOMe), 4.54 (ABq, 2 H, J = 6.9 Hz, Δν = 54.4 Hz, OCH_2O), 4.11 (dd, 1 H, J = 6.5, 14.6 Hz, H2), 3.42 (s, 3 H, OCH_3), 3.32 (s, 3 H, OCH_3), 1.66 (d, 3 H, J = 6.5 Hz, H5), 1.48–1.23 (m, 10 H, cyclohexyl H's). MS Calcd for $C_{22}H_{32}O_5$: 376. Found: 394 ($M^+ + NH_4^+$).

(4*R*,5*R*,2*E*)-4-(Methoxymethoxy)-2-undecen-5-yl (*S*)-*O*-Methylmandelate (34c). The procedure described for mandelate **14** was employed, whereby 15 mg (0.065 mmol) of alcohol **21c** afforded 23 mg (92%) of **34c** as a colorless oil: IR (neat) 3030, 2921, 2856, 1747, 1447, 1251, 1197, 1175, 1147, 1098, 1027, 968, 913, 733, 695 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.46–7.29 (m, 5 H, Ph), 5.65 (dq, 1 H, J = 6.5, 15.4 Hz, H2), 5.21 (dd, 1 H, J = 6.3, 15.3 Hz, H3), 4.96 (m, 1 H, H5), 4.75 (s, 1 H, CHOMe), 4.54 (ABq, 2 H, J = 6.7 Hz, Δν = 49.2 Hz, OCH_2O), 3.97 (dd, 1 H, J = 7.8, 14.4 Hz, H4), 3.41 (s, 3 H, OCH_3), 3.32 (s, 3 H, OCH_3), 1.67 (d, 3 H, J = 6.5 Hz, H1), 1.47–1.01 (m, 6 H, CH_2's), 0.79 (t, 3 H, J = 6.9 Hz, H11). MS Calcd for $C_{22}H_{34}O_5$: 378. Found: 396 ($M^+ + NH_4^+$).

(4*R*,5*R*,2*E*)-4-(Methoxymethoxy)-2-undecen-6-yn-5-yl (*S*)-*O*-Methylmandelate (34d). The procedure described for mandelate **14** was employed, whereby 6 mg (0.027 mmol) of alcohol **21d** gave 8 mg (80%) of **34d** as a colorless oil: IR (neat) 2932, 2812, 1752, 1447, 1246, 1197, 1169, 1147, 1104, 1022, 962, 919 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.43–7.30 (m, 5 H, Ph), 5.75 (dq, 1 H, J = 6.7, 15.4 Hz, H2), 5.44 (d, 1 H, J = 6.7, H5), 5.36 (dd, 1 H, J = 7.0, 15.6 Hz, H3), 4.78 (s, 1 H, CHOMe), 4.56 (ABq, 2 H, J = 6.7 Hz, Δν = 33.4 Hz, OCH_2O), 4.11 (dd, 1 H, J = 6.7, 15.3 Hz, H4), 3.42 (s, 3 H, OCH_3), 3.31 (s, 3 H, OCH_3), 2.09 (t, 2 H, J = 5.2 Hz, H8), 1.69 (d, 3 H, J = 6.5 Hz, H1), 1.34 (m, 4 H, CH_2's), 0.84 (t, 3 H, J = 7.2 Hz, H11). MS Calcd for $C_{22}H_{30}O_5$: 374. Found: 392 ($M^+ + NH_4^+$).

(1*R*,2*R*,3*E*)-1-Phenyl-2-(methoxymethoxy)-3-penten-1-yl (*S*)-*O*-Methylmandelate (34e). The procedure described for mandelate **14** was employed, whereby 17 mg (0.045 mmol) of alcohol **21e** afforded 14 mg (82%) of **34e** as a colorless oil: IR (neat) 3054, 3019, 2943, 2889, 2823, 1747, 1496, 1453, 1251, 1197, 1175, 1153, 1104, 1028, 918, 696 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.38–6.98 (m, 10 H, Ph's), 5.79 (d, 1 H, J = 6.2 Hz, H1), 5.51 (dq, 1 H, J = 7.4, 15.4 Hz, H4), 5.11 (dd, 1 H, J = 6.3, 15.4 Hz, H3), 4.83 (s, 1 H, CHOMe), 4.49 (ABq, 2 H, J = 6.7 Hz, Δν = 49.9 Hz, OCH_2O), 4.21 (dd, 1 H, J = 6.9, 14.2 Hz, H2), 3.40 (s, 3 H, OCH_3), 3.12 (s, 3 H, OCH_3), 1.57 (d, 3 H, J = 6.5 Hz, H4). MS Calcd for $C_{22}H_{26}O_5$: 370. Found: 388 ($M^+ + NH_4^+$).

(4*R*,5*R*,2*E*,6*E*)-4-(Methoxymethoxy)-2,6-undecadien-5-yl (*R*)-*O*-Methylmandelate (35a). The procedure described for mandelate **14** was employed, whereby 15 mg (0.066 mmol) of alcohol **21a** afforded 22 mg (88%) of **35a** as a colorless oil: IR (neat) 3030, 2954, 2921, 1752, 1671, 1453, 1251, 1175, 1098, 1028, 968, 924, 695 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.45–7.30 (m, 5 H, Ph), 5.71 (dt, 1 H, J = 6.7, 15.4 Hz, H7), 5.48 (dq, 1 H, J = 6.5, 15.4 Hz, H2), 5.41 (dd, 1 H, J = 7.6, 14.0 Hz, H6), 5.28 (dd, 1 H, J = 7.4, 13.1 Hz, H5), 4.90 (dd, 1 H, J = 8.4, 15.5 Hz, H3), 4.75 (s, 1 H, CHOMe), 4.38 (ABq, 2 H, J = 6.8 Hz, Δν = 40.2 Hz, OCH_2O), 3.89 (dd, 1 H, J = 5.7, 8.3 Hz, H4), 3.38 (s, 3 H, OCH_3), 3.15 (s, 3 H, OCH_3), 2.00 (q, 2 H, J = 6.8 Hz, H8), 1.50 (d, 3 H, J = 6.4 Hz, H1), 1.29–1.18 (m, 4 H, H9 and H10), 0.85 (t, 3 H, J = 7.0 Hz, H11). MS Calcd for $C_{22}H_{32}O_5$: 376. Found: 394 ($M^+ + NH_4^+$).

(1*R*,2*R*,3*E*)-1-Cyclohexyl-2-(methoxymethoxy)-3-penten-1-yl (*R*)-*O*-Methylmandelate (35b). The procedure described for mandelate **14** was employed, whereby 15 mg (0.066 mmol) of alcohol **21b** gave 20 mg (80%) of **35b** as a colorless oil: IR (neat) 3019, 2921, 2856, 1752, 1447, 1175, 1110, 1028, 968, 919, 733, 695 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.48–7.30 (m, 5 H, Ph), 5.47 (dq, 1 H, J = 6.5, 15.4 Hz, H2), 4.78 (s, 1 H, CHOMe), 4.77 (m, 1 H, H1), 4.63 (dd, 1 H, J = 6.0, 10.2 Hz, H3), 4.34 (ABq, 2 H, J = 6.9 Hz, Δν = 47.2 Hz, OCH_2O), 4.01 (dd, 1 H, J = 5.5, 8.4 Hz, H4), 3.39 (s, 3 H, OCH_3), 3.17 (s, 3 H, OCH_3), 1.40 (d, 3 H, J = 6.4 Hz, H5), 1.72–0.93 (m, 10 H, cyclohexyl H's). MS Calcd for $C_{22}H_{32}O_5$: 376. Found: 394 ($M^+ + NH_4^+$).

(4*R*,5*R*,2*E*)-4-(Methoxymethoxy)-2-undecen-5-yl (*R*)-*O*-Methylmandelate (35c). The procedure described for mandelate **14** was employed, whereby 15 mg (0.065 mmol) of alcohol **21c** afforded 21 mg (84%) of **35c** as a colorless oil: IR (neat) 3030, 2921, 2856, 1747, 1447, 1251, 1197, 1175, 1147, 1098, 1027, 968, 913, 733, 695 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.47–7.30 (m, 5 H, Ph), 5.41 (dq, 1 H, J = 6.5, 15.4 Hz, H2), 4.95 (m, 2 H, H3 and H5), 4.76 (s, 1 H, CHOMe), 4.37 (ABq, 2 H, J = 6.8 Hz, Δν = 43.3 Hz, OCH_2O), 3.85 (dd, 1 H, J = 3.3, 8.4 Hz, H4), 3.39 (s, 3 H, OCH_3), 3.16 (s, 3 H, OCH_3), 1.48 (d, 3 H, J = 6.5 Hz, H1), 1.30 (m, 6 H, CH_2's), 0.85 (t, 3 H, J = 6.7 Hz, H11). MS Calcd for $C_{22}H_{34}O_5$: 378. Found: 396 ($M^+ + NH_4^+$).

(4*R*,5*R*,2*E*)-4-(Methoxymethoxy)-2-undecen-6-yn-5-yl (*R*)-*O*-Methylmandelate (35d). The procedure described for mandelate **14** was employed, whereby 7 mg (0.031 mmol) of alcohol **21d** afforded 10 mg (83%) of **35d** as a colorless oil: IR (neat) 2932, 2812, 1752, 1447, 1246, 1197, 1169, 1147, 1104, 1022, 962, 919 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.42–7.32 (m, 5 H, Ph), 5.41 (m, 2 H, H2 and H3), 5.11 (dd, 1 H, J = 6.7, 15.4 Hz, H5), 4.79 (s, 1 H, CHOMe), 4.38 (ABq, 2 H, J = 6.8 Hz, Δν = 27.4 Hz, OCH_2O), 3.94 (dd, 1 H, J = 3.6, 8.4 Hz, H4), 3.40 (s, 3 H, OCH_3), 3.18 (s, 3 H, OCH_3), 2.19 (t, 2 H, J = 4.9 Hz, H8), 1.54 (d, 3 H, J = 7.6 Hz, H1), 1.40 (m, 4 H, CH_2's), 0.87 (t, 3 H, J = 7.2 Hz, H11). MS Calcd for $C_{22}H_{30}O_5$: 374. Found: 392 ($M^+ + NH_4^+$).

(1*R*,2*R*,3*E*)-1-Phenyl-2-(methoxymethoxy)-3-penten-1-yl (*R*)-*O*-Methylmandelate (35e). The procedure described for mandelate **14** was employed, whereby 12 mg (0.054 mmol) of alcohol **21e** afforded 17 mg (85%) of **35e** as a colorless oil: IR (neat) 3054, 3019, 2943, 2889, 2823, 1747, 1496, 1453, 1251, 1197, 1175, 1153, 1104, 1028, 918, 696 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.49–7.24 (m, 10 H, Ph's), 5.80 (d, 1 H, J = 5.8 Hz, H1), 5.34 (dq, 1 H, J = 6.5, 15.4 Hz, H4), 4.86 (dd, 1

H, J = 7.3, 15.3 Hz, H3), 4.81 (s, 1 H, CHOMe), 4.31 (ABq, 2 H, J = 6.8 Hz, $\Delta\nu$ = 43.8 Hz, OCH_2O), 4.12 (dd, 1 H, J = 5.9, 14.0 Hz, H2), 3.36 (s, 3 H, OCH_3), 2.93 (s, 3 H, OCH_3), 1.43 (d, 3 H, J = 6.5 Hz, H4). MS Calcd for $C_{22}H_{26}O_5$: 370. Found: 388 ($M^+ + NH_4^+$).

(1*S*,2*E*)-1-(Tri-*n*-butylstannyl)-1-[[(*p*-methoxybenzyl)oxy]methoxy]-2-heptene (36). The procedure described for ether **11** was employed with *p*-methoxybenzyl chloromethyl ether as the alkylating agent: $[\alpha]_D$ −25 (*c* 1.3, CH_2Cl_2): IR (neat) 2954, 2921, 2856, 1611, 1507, 1458, 1371, 1295, 1246, 1169, 1093, 1022, 962, 821, 690, 668 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.24, 6.86 (ABq, 4 H, J = 8.7 Hz, aryl H), 5.54 (dd, 1 H, J = 7.5, 15.2 Hz, H2), 5.40 (dt, 1 H, J = 6.8, 15.2 Hz, H3), 4.72, 4.62 (ABq, 2 H, J = 6.5 Hz, OCH_2O), 4.64 (d, 1 H, J = 7.6 Hz, H1), 4.55, 4.41 (ABq, 2 H, J = 11.4 Hz, $PhCH_2O$), 3.78 (s, 3 H, OCH_3), 2.01 (q, 2 H, J = 6.3 Hz, H4), 0.8–1.6 (m, 34 H, H5, H6, H7, and $SnBu_3$). MS Calcd for $C_{28}H_{50}O_3Sn$: 554. Found: 497 (M^+ − Bu).

For this particular experiment, the ee of the starting alcohol was determined to be 36% by integration of the MeO peak in the ^1H NMR spectrum of the (*S*)-*O*-methylmandelate.

(*E*)-1-(Trimethylstannyl)-1-(methoxymethoxy)-2-heptene (37). To a solution of 2.5 g (7.6 mmol) of $(Me_3Sn)_2$ in 15 mL of THF was added 3 mL (7.6 mmol) of 2.5 M *n*-BuLi in THF at −78 °C. After 15 min, a solution of 1.1 g (8 mmol) of *trans*-2-heptenal (**2**) in 5 mL of THF was added. The mixture was stirred at −78 °C for 30 min, and then it was quenched with saturated aqueous NH_4Cl and diluted with ether. The organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, affording 1.2 g of hydroxy stannane which was treated with 0.75 mL (10 mmol) of MOMCl and 2.6 mL (15 mmol) of $(i\text{-}Pr)_2NEt$ in 10 mL of CH_2Cl_2. The product was isolated by extraction with ether and purified by chromatography on silica gel, affording 1.4 g (58%) of **37** as a colorless oil: IR (neat) 2954, 2921, 2878, 1463, 1147, 1093, 1022, 962, 919, 766 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 5.51 (dd, J = 7.8, 15.4 Hz, 1 H, H2), 5.40 (dt, J = 6.7, 15.4 Hz, 1 H, H3), 4.63, 4.45 (ABq, J = 6.8 Hz, 2 H, OCH_2O), 3.37 (s, 3 H, OCH_3), 2.0 (m, 2 H, H4), 0.8–1.5 (m, 7 H, H5, H6, and H7), 0.12 (s, 9 H, $Sn(CH_3)_3$). MS Calcd for $C_{12}H_{26}O_2Sn$: 322. Found: 307 (M^+ − CH_3).

Crossover Experiment. To a mixture of 0.55 g (1.0 mmol) of the α-(alkoxy)allyl stannane (−)-**36** and 0.32 g (1.0 mmol) of the α-(alkoxy)allyl stannane **37** in 20 mL of CH_2Cl_2 at −78 °C was added 0.24 mL (2.0 mmol) of freshly distilled $BF_3{\cdot}Et_2O$ with stirring. After 10 min at −78 °C, the solution was quenched with saturated $NaHCO_3$ solution. The mixture was diluted with ether, washed with brine, and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude mixture (0.81 g, 90%) showed four γ-(alkoxy)allyl stannanes in a ratio of nearly 1:1:1:1 by ^1H NMR analysis of the vinylic enol ether protons. Preparative thin-layer chromatographic isolation afforded each of the four stannanes as colorless oils.

(1*Z*,3*S*)-3-(Tri-*n*-butyl)stannyl)-1-[[(*p*-methoxybenzyl)oxy]methoxy]-1-heptene (38). R_f (10% ethyl acetate–hexanes) = 0.50; $[\alpha]_D$ −68 (*c* 2.30, CH_2Cl_2); ^1H NMR (300 MHz) ($CDCl_3$) δ 7.24, 6.86 (ABq, 4 H, J = 8.7 Hz, Ar), 6.02 (d, 1 H, J = 6.2 Hz, H1), 4.83 (s, 2 H, OCH_2O), 4.54 (ABq, 2 H, J = 11.2 Hz, $\Delta\nu$ = 23 Hz, $PhCH_2O$), 4.49 (dd, 1 H, J = 5.1, 6.6 Hz, H2), 3.78 (s, 3 H, OCH_3), 2.50 (m, 1 H, H3), 1.20–1.45 (m, 24 H, CH_2's), 0.87 (m, 12 H, CH_3's).

(1*Z*,3*S*)-3-(Trimethylstannyl)-1-[[(*p*-methoxybenzyl)oxy]methoxy]-1-heptene (39). R_f (10% EtOAc–hexanes) = 0.44; $[\alpha]_D$ +51 (*c* 2.90, CH_2Cl_2); ^1H NMR (300 MHz) ($CDCl_3$) δ 7.24, 6.85 (ABq, 4 H, J = 9.3 Hz, Ar), 6.06 (d, 1 H, J = 6.2 Hz, H1), 4.84 (s, 2 H, OCH_2O), 4.52 (ABq, 2 H, J = 11.0 Hz, $\Delta\nu$ = 8.7 Hz, $PhCH_2O$), 4.46 (dd, 1 H, J = 6.2, 11.0 Hz, H2), 3.79 (s, 3 H, OCH_3), 2.44 (m, 1 H, H3), 1.20–1.55 (m, 6 H, CH_2's), 0.86 (t, 3 H, CH_3), 0.05 (s, 9 H, $Sn(CH_3)_3$).

(*Z*)-3-(Trimethylstannyl)-1-(methoxymethoxy)-1-heptene (40). R_f (10% ethyl acetate–hexanes) = 0.59; ^1H NMR (300 MHz) ($CDCl_3$) δ 5.96 (d, 1 H, J = 6.2 Hz, H1), 4.73 (ABq, 2 H, J = 6.4 Hz, $\Delta\nu$ = 6.1 Hz, OCH_2O), 4.45 (dd, 1 H, J = 6.2, 11.0 Hz, H2), 3.36 (s, 3 H, OCH_3), 2.39 (m, 1 H, H3), 1.20–1.45 (m, 6 H, CH_2's), 0.87 (m, 3 H, CH_3), 0.03 (s, 9 H, $Sn(CH_3)_3$).

(1*Z*,3*S*)-3-(Tri-*n*-butylstannyl)-1-(methoxymethoxy)-1-heptene (41). R_f (10% ethyl acetate–hexanes) = 0.66; $[\alpha]_D$ +3 (*c* 0.71, CH_2Cl_2); ^1H NMR (300 MHz) ($CDCl_3$) δ 5.93 (d, 1 H, J = 6.2 Hz, H1), 4.75 (ABq, 2 H, J = 6.3 Hz, $\Delta\nu$ = 6.5 Hz, OCH_2O), 4.45 (dd, 1 H, J = 6.1, 11.3 Hz, H2), 3.37 (s, 3 H, OCH_3), 2.44 (m, 1 H, H3), 1.20–1.45 (m, 24 H, CH_2's), 0.87 (m, 9 H, CH_3's).

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Supplementary Material Available: ^1H NMR spectra of *O*-methyl mandelates **26a**, **27a,b**, **34a–e**, and **35a–e** (13 pages). Ordering information is given on any current masthead page.