A Regiocontrolled Synthesis of Allylstannanes†

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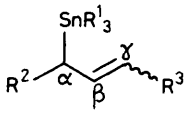
β-Stannyl ester enolates react with aldehydes with fairly high stereoselectivity, the isomeric enolates (**4**) and (**2**) respectively giving as major products the allyl hydroxy-stannylbutanoates (**6**) and (**7**) with opposite aldol relative stereochemistry. These aldols can be converted stereospecifically (steric and reactivity effects allowing) into the allylstannanes (**13**) and (**14**). The *cis* allylstannane (**14aa**) is stable to isomerisation in non-polar solvents.

Allylstannanes are useful nucleophiles for organic synthesis: they react with a range of electrophiles,[1] normally[2] at the γ position of the allylic system. Allylstannanes are more reactive than allylsilanes,[3] reacting, for example, with aldehydes without Lewis acid catalysis.[4] If the allylstannane has a substituent at the γ position, then (*Z*) allylstannanes give largely *syn* (in the Masamune sense[5]) products in the absence of Lewis acid catalysis, and (*E*) allylstannanes give *anti* products.[6] In the presence of Lewis acids, the reaction is stereoconvergent: both (*E*) and (*Z*) allylstannanes give *syn* products.[7]

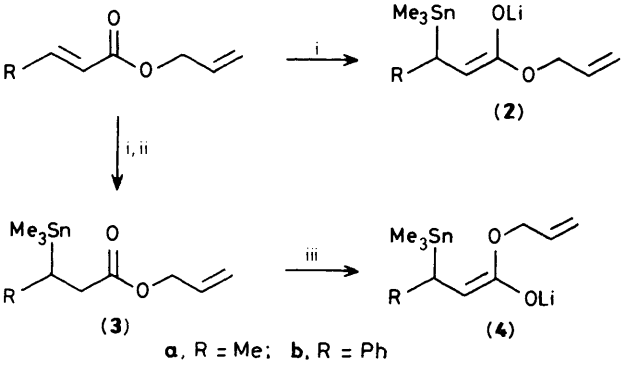
The most commonly used syntheses of allylstannanes involve either the addition of a trialkyltin anion equivalent to an allyl halide,[8] or addition of an allyl anion to a trialkyltin halide.[9] Other syntheses include Seyferth's Wittig approach,[10] and the free radical reaction of tributyltin hydride with allyl sulphides or sulphones.[11] However, all these syntheses are either not regiospecific, or, if they are, give the compound with the tin at the less substituted end of the allylic system. Thomas[12] has recently published a synthesis of allylstannanes with the tin at the more substituted end of the allylic system, but had problems making compounds with substitution at both the α and γ positions (**1**) by his method. To our knowledge, there are no



(**1**)

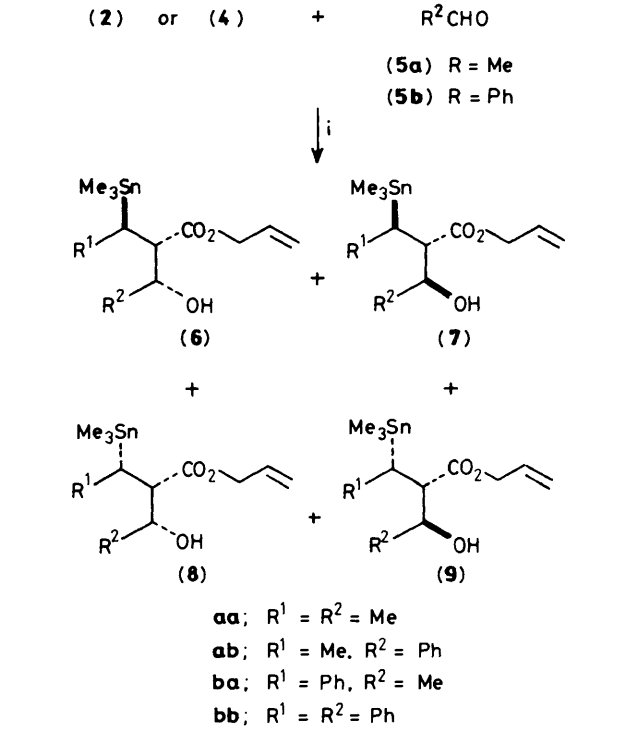
methods for regiospecific, let alone stereospecific, synthesis of allylstannanes (**1**) substituted at both ends of the allylic system. We recently presented a preliminary communication,[13] and now present full details, of such a synthesis, analogous to our regiocontrolled synthesis of allylsilanes,[14] which was based on the highly diastereoselective reaction of β-silylenolates with aldehydes.[15]

Thus, the enolates (**2**) were prepared by the conjugate addition[16] of trimethylstannyl-lithium to allyl crotonate and allyl cinnamate (Scheme 1). Alternatively, the isomeric enolates (**4**) could be made by quenching enolates (**2**) with a proton source to give esters (**3**) and regeneration of the enolates with lithium di-isopropylamide. The stereochemistry of these enolates has not been proved but is inferred by analogy to the silicon series, and by the stereochemical outcome of the aldol reactions performed with them. The enolates (**2**) and (**4**) were treated with acetaldehyde (**5a**) or benzaldehyde (**5b**) to give the aldols (**6**)—(**9**) (Scheme 2) in the proportions shown in Table 1. The major products were *anti* aldols (**7**) from enolates (**2**), and *syn* aldols (**6**) from enolates (**4**). The proportion of the product



a, R = Me; b, R = Ph

Scheme 1. *Reagents:* i, Me_3SnLi; ii, methanol; iii, lithium di-isopropylamide



aa; $R^1 = R^2 = Me$
ab; $R^1 = Me$, $R^2 = Ph$
ba; $R^1 = Ph$, $R^2 = Me$
bb; $R^1 = R^2 = Ph$

Scheme 2. *Reagent:* i, tetrahydrofuran, −78 °C

diastereoisomers was determined by isolation, except where they were not separable by chromatography: in the cases where they were not separable the proportion was determined by ^1H n.m.r. spectroscopy. The major product was separable from other diastereoisomers in all cases except for aldols (**6ba**) and (**7ba**), which were carried through as mixtures.

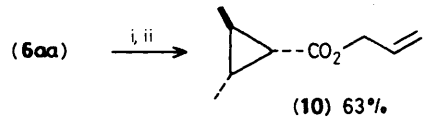
† No reprints available.

Table 1. Reaction of β-stannyl enolates with aldehydes

Enolate	Aldehyde	Proportion of diastereoisomers[a] (6)	(7)	(8)	(9)	Yield (%)
(2a)	(5a)	23[b]	54		23	98
(4a)	(5a)	80	15[b]	5[b]		84
(2a)	(5b)	21	57		22	84
(4a)	(5b)	61	39			98
(2b)	(5a)	29[b]	58[b]		13	82
(4b)	(5a)	77[b]	23[b]			70
(2b)	(5b)	14	69		17	75
(4b)	(5b)	81	19			61

[a] Estimated by isolation, except where otherwise stated. [b] Inseparable by chromatography: proportion estimated by ^{1}H n.m.r.

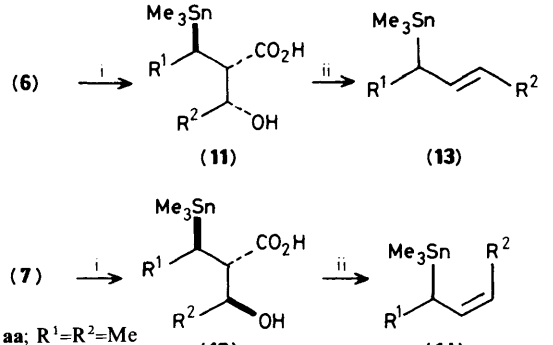
The relative stereochemistry of the major products (**6**) and (**7**) is assigned as follows. The stereochemical relationship between C-2 and C-3 can be assigned by the fact that *syn* aldols are taken through to *trans* allylstannanes, and *anti* aldols to *cis* allylstannanes, *via* an *anti* decarboxylative elimination of the β-hydroxy acids derived from them. The stereochemical relationship between C-1 and C-3 in the ester (**6aa**) was assigned by cyclisation to the cyclopropane (**10**) (Scheme 3), a reaction that



Scheme 3. *Reagents:* i, $MeSO_2Cl$, Et_3N, Et_2O, 0 °C; ii, 110 °C, dimethylsulphoxide

proceeds with inversion of configuration at both reacting centres.[17] Finally the stereochemical assignment is in agreement with that seen in the silicon series, although the selectivity is somewhat lower. This might be a reflection of the degree of geometrical purity of the enolates, which was not determined. The relative stereochemistry of the minor products (**8**) and (**9**) is assigned, tentatively, by assuming that, although they have the 1,2 relative stereochemistry arising from attack *syn* to the stannyl group of the β-stannyl enolate,[15] they have the normal pattern of 2,3 stereochemistry [enolate (**2**) giving *anti* aldol, enolate (**4**) giving *syn* aldol].

The esters (**6**) and (**7**) [the ester (**6ba**) was a mixture (77:23) with (**7ba**), and the ester (**7ba**) a mixture (67:33) with (**6ba**)] were converted (Scheme 4) in high yield into the β-hydroxy acids (**11**) and (**12**) by treatment with methyl cuprate[18] (Table 2). These acids were immediately treated with dimethyl-



aa; R^1=R^2=Me
ab; R^1=Me, R^2=Ph
ba; R^1=Ph, R^2=Me
bb; R^1=R^2=Ph

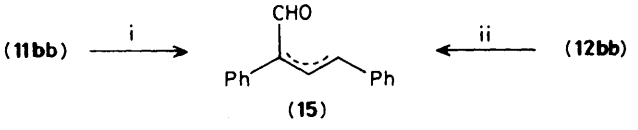
Scheme 4. *Reagents:* i, Me_2CuLi, Et_2O; ii, $Me_2NCH(OMe)_2$, CH_2Cl_2, room temp., 2 h

Table 2. Conversion of β-hydroxy esters into allylstannanes

Ester	Acid	Yield (%)	Allylstannane	Yield (%)
(6aa)	(11aa)	96	(13aa)	73
(6ab)	(11ab)	86	(13ab)	64
(6ba)	(11ba)[a]	96	(13ba)[b]	87
(6bb)	(11bb)	96		
(7aa)	(12aa)	92	(14aa)	78
(7ab)	(12ab)	67	(13ab)	41
(7ba)	(12ba)[c]	93	(14ba)[d]	68
(7bb)	(12bb)	94		

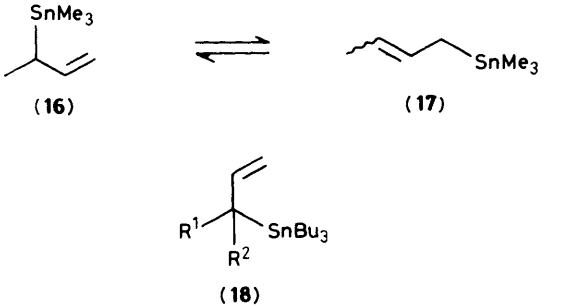
[a] This is a mixture (77:23) with (**12ba**). [b] This is a mixture (76:24) with (**14ba**). [c] This is a mixture (67:23) with (**11ba**). [d] This is a mixture (68:32) with (**13ba**).

formamide dimethyl acetal at room temperature for 2 h to give the allylstannanes (**13**) and (**14**) (Table 2). The acids (**11aa**), (**12aa**), (**11ab**), (**11ba**), and (**12ba**) reacted stereospecifically to give the allylstannanes (**13aa**), (**14aa**), (**13ab**), (**13ba**), and (**14ba**), the last two being mixtures in approximately the same proportion as the starting materials. The acid (**12ab**) did not react at room temperature. Refluxing for 24 h in dichloromethane gave *trans* allylstannane (**13ab**) instead of the expected *cis* product (**14ab**). Presumably the steric crowding of the *cis* product is too great, and either the *trans* product is formed directly, or isomerisation *via* 1,3 allylic shifts is faster than product formation. For the diphenyl acids (**11bb**) and (**12bb**), allylstannanes were not isolated. Instead, the products were the unsaturated aldehydes (**15**), arising from the reaction of the allylstannanes (**13bb**) and (**14bb**) with dimethylformamide dimethyl acetal. Again, the acid (**12bb**) required refluxing for 24 h in order to react (Scheme 5).



Scheme 5. *Reagents:* i, $Me_2NCH(OMe)_2$, CH_2Cl_2, room temp. 2 h; ii, $Me_2NCH(OMe)_2$, CH_2Cl_2, reflux, 24 h

Little work has been published on the regiostability of allylstannanes, possibly owing to the lack of regioselective syntheses. Kuivilla[19] reported that the secondary allylstannane (**16**) isomerises rapidly to the crotylstannanes (**17**) in the presence of either methanol or trimethyltin chloride. Trost[1a] also comments on the ease of isomerisation of allylstannanes. However, Thomas[12] found that the allylstannanes (**18**; R^1 = Me, R^2 = Me) and (**18**; R^1 = Me, R^2 = H) were stable in non-polar solvents, but that the former was less stable in methanol. The compound with aromatic substitution (**18**; R^1 = Ph, R^2 = H) was less stable than the aliphatic allylstannanes.



Our results with α,γ-disubstituted allylstannanes are similar to Thomas's. The *cis* allylstannane (**14aa**) was largely unchanged (^{1}H n.m.r.) after 5 days refluxing in deuteriochloroform (we expect double-bond isomerisation to accompany 1,3 shift). In refluxing perdeuteriobenzene it decomposes without isomerisation with a half-life of *ca.* 4 days, and only in methanol do we see *cis-trans* isomerisation, with a half life of *ca.* 18 h at reflux. The presence of a phenyl group lowers the barrier to 1,3 shift: (**14ba**) isomerises to (**13ab**) with a half-life of *ca.* 24 h in deuteriochloroform at room temperature.

In summary, we have a general synthesis of *cis* or *trans* allylstannanes and the allylstannanes are stable enough to allow further study of their reactions as nucleophiles.

Experimental

For tin-containing species only those peaks in the mass spectrum corresponding to ^{120}Sn are reported. Coupling to ^{119}Sn and ^{117}Sn is not reported for n.m.r. spectra. Chromatography was performed using Merck 40–63 silica gel. Tetrahydrofuran (THF) was freshly distilled from lithium aluminium hydride, dichloromethane from phosphorus pentaoxide and diethyl ether was distilled from phosphorus pentaoxide and stored over sodium wire. Other solvents were distilled before use. Light petroleum refers to the fraction with b.p. 60—80 °C unless otherwise stated. All reactions were performed under an atmosphere of dry nitrogen. Ether refers to diethyl ether, and THF to tetrahydrofuran.

Allyl 3-*Trimethylstannylbutanoate* (**3a**).—Allyl crotonate (1.97 g, 15.7 mmol) in THF (15 ml) was added dropwise during 20 min to a stirred solution of trimethylstannyl-lithium [16] (16.5 mmol) in THF (30 ml) at −78 °C. After a further 15 min, methanol (10 ml) was added, the solution brought to room temperature, water (50 ml) added, and the mixture separated. The aqueous layer was extracted with ether (2 × 20 ml), the combined organic layers washed with water and brine, dried (Na_2SO_4) and purified by flash chromatography, eluting with light petroleum–ethyl acetate (25:1 v/v), to give the ester (**3a**) (3.88 g, 85%) as an oil, R_F (light petroleum–ethyl acetate, 5:1 v/v) 0.66; $\nu_{max.}$(film) 1 735 (C=O) and 1 645 cm^{-1} (C=C); δ CDCl$_3$) 5.95 (1 H, ddt, *J* 11, 18, and 5.9 Hz, C*H*=CH$_2$), 5.5—5.1 (2 H, m, C=CH$_2$), 4.56 (2 H, dt, *J* 5.9 and 1.3 Hz, OCH$_2$), 2.51 (2 H, d, *J* 7.1 Hz, CH$_2$CO), 1.7—1.3 (1 H, m, SnCH), 1.18 (3 H, d, *J* 6.8 Hz, CH$_3$), and 0.04 (9 H, s, Me$_3$Sn); *m/z* 277 (100%, *M* − Me), and 165 (88, Me$_3$Sn).

Allyl 3-*Phenyl*-3-*trimethylstannylpropanoate* (**3b**).—This was made in the same way as the ester (**3a**), using allyl cinnamate (1.64 g, 8.7 mmol) and trimethylstannyl-lithium (8.8 mmol) to give the ester (**3b**) (2.87 g, 94%) as an oil, R_F (light petroleum–ethyl acetate, 5:1 v/v) 0.51; $\nu_{max.}$(film) 1 730 (C=O), 1 645 (C=C), and 1 600 and 1 495 cm^{-1} (Ph); δ(CDCl$_3$) 7.3—6.9 (5 H, m, Ph), 5.88 (1 H, ddt, *J* 17.3, 9.9, and 5.4 Hz, C*H*=CH$_2$), 5.4—5.1 (2 H, m, C=CH$_2$), 4.56 (2 H, dt, *J* 5.4 and 1.2 Hz, OCH$_2$), 3.0 (3 H, br s, CHCH$_2$), and 0.01 (9 H, s, Me$_3$Sn); *m/z* 354 (13%, M^+), 339 (81, *M* − Me), and 165 (100, Me$_3$Sn).

Reaction of Enolates (**2**) *with Aldehydes*.—Typically, the allyl ester (3.7 mmol) in THF (5 ml) was added dropwise during 10 min to a stirred solution of trimethylstannyl-lithium (3.9 mmol) in THF (10 ml) at −78 °C. After a further 15 min, the aldehyde (3.9 mmol) in THF (2 ml) was added dropwise during 5 min. After 10 min methanol (2 ml) and ammonium chloride solution (5 ml) were added and the mixture brought to room temperature. Water (25 ml) was added, the mixture extracted with ether (3 × 25 ml), the combined organic layers washed with water and brine, dried (Na_2SO_4), evaporated under reduced pressure, and purified by flash chromatography, eluting with light petroleum–ethyl acetate (8:1 v/v)

(2SR,3RS)-*Allyl* 2-[(SR)-1-*Hydroxyethyl*]-3-*trimethylstannylbutanoate* (**7aa**).—Allyl crotonate (462 mg, 3.67 mmol), trimethylstannyl-lithium (3.86 mmol), and acetaldehyde (**5a**) (170 mg, 3.86 mmol) gave the (2*SR*,3*RS*,1′*SR*)-ester (**7aa**) (683 mg, 52%) as an oil, R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.30; $\nu_{max.}$(film) 3 400 (OH), 1 725 (C=O), and 1 640 cm^{-1} (C=C); δ(CDCl$_3$) 5.91 (1 H, ddt, *J* 10.3, 17.2, and 5.9 Hz, C*H*=CH$_2$), 5.33 (1 H, dq, *J* 17.2 and 1.5 Hz, C=C*H*$_A$H$_B$, H$_A$ *cis* to CH$_2$), 5.24 (1 H, dq, *J* 10.3 and 1.5 Hz, C=CH$_A$*H*$_B$, H$_B$ *trans* to CH$_2$), 4.59 (2 H, dt, *J* 5.9 and 1.5 Hz, OCH$_2$), 3.94 (1 H, d quintet, *J* 7.2 and 6.4 Hz, C*H*O), 2.51 (1 H, t, *J* 6.4 Hz, CHCO$_2$), 2.42 (1 H, d, *J* 7.2 Hz, OH), 1.47 (1 H, dq, *J* 6.4 and 7.6 Hz, SnCH), 1.21 (3 H, d, *J* 6.4 Hz, C*H*$_3$CHOH), 1.20 (3 H, d, *J* 7.6 Hz, C*H*$_3$CHSn), and 0.05 (9 H, s, Me$_3$Sn); *m/z* 321 (73%, *M* − Me), 291 (26, *M* − C$_2$H$_5$O), and 165 (100, Me$_3$Sn); and a 50:50 mixture (n.m.r.) of the (2*SR*,3*RS*,1′*RS*)-ester (**6aa**) and the (2*SR*,3*SR*,1′*SR*)-ester (**9aa**) (554 mg, 46%); δ(CDCl$_3$) (**9aa**) 2.80 (1 H, d, *J* 8.2 Hz, OH), 2.47 (1 H, dd, *J* 5.0 and 7.6 Hz, CHCO$_2$), 1.22 (3 H, d, *J* 7.6 Hz, C*H*$_3$CHOH), 1.12 (3 H, d, *J* 7.6 Hz, SnCHC*H*$_3$), and 0.07 (9 H, s, Me$_3$Sn).

(2SR,3RS)-*Allyl* 2-[(RS)-1-*Hydroxybenzyl*]-3-*trimethylstannylbutanoate* (**7ab**).—Allyl crotonate (630 mg, 5.00 mmol), trimethyltin-lithium (5.19 mmol), and benzaldehyde (**5b**) (550 mg, 5.19 mmol) gave the (2*SR*,3*RS*,1′*RS*)-ester (**7ab**) (950 mg, 47%) as an oil, R_F (light petroleum–ethyl acetate, 5:1 v/v) 0.15; $\nu_{max.}$(film) 3 400 (OH), 1 720 (C=O), 1 645 (C=C), and 1 600 and 1 495 cm^{-1} (Ph); δ(CDCl$_3$) 7.3—7.2 (5 H, m, Ph), 5.82 (1 H, ddt, *J* 10.4, 17.2, and 5.9 Hz, C*H*=CH$_2$), 5.25 (1 H, d, *J* 17.2 Hz, C=C*H*$_A$H$_B$, H$_A$ *cis* to CH$_2$), 5.19 (1 H, d, *J* 10.4 Hz, C=CH$_A$*H*$_B$, H$_B$ *trans* to CH$_2$), 4.83 (1 H, dd, *J* 5.7 and 7.9 Hz, C*H*OH), 4.57 (2 H, d, *J* 5.9 Hz, OCH$_2$), 2.91 (1 H, d with other fine coupling, *J* 7.9 Hz, CHCO), 2.72 (1 H, d, *J* 5.7 Hz, OH), 1.15 (4 H, br s, CHCH$_3$), and 0.08 (9 H, s, Me$_3$Sn); *m/z* 398 (1%, M^+), 383 (26, *M* − Me), 291 (57, *M* − PhCHOH), and 165 (100, Me$_3$Sn); the (2*SR*,3*SR*,1′*RS*)-ester (**9ab**) (360 mg, 18%) as an oil; R_F (light petroleum–ethyl acetate, 5:1 v/v) 0.20; $\nu_{max.}$(film) 3 450 (OH), 1 720 (C=O), 1 645 (C=C), and 1 600 and 1 495 cm^{-1} (Ph); δ(CDCl$_3$) 7.3—7.2 (5 H, m, Ph), 5.75 (1 H, ddt, *J* 10.8, 17.8, and 5.7 Hz, C*H*=CH$_2$), 5.15 (1 H, dq, *J* 17.8 Hz and 1 Hz, C=C*H*$_A$H$_B$, H$_A$ *cis* to CH$_2$), 5.14 (1 H, dq, *J* 10.8 and 1 Hz, C=CH$_A$*H*$_B$, H$_B$ *trans* to CH$_2$), 4.91 (1 H, t, *J* 7.3 Hz, C*H*OH), 4.58 (1 H, ddt, *J* 5.7, 13.8, and 1 Hz, OC*H*$_A$H$_B$), 4.40 (1 H, ddt, *J* 5.7, 13.8, and 1 Hz, OCH$_A$*H*$_B$), 3.43 (1 H, d, *J* 7.3 Hz, OH), 2.91 (1 H, dd, *J* 7.3 and 7.5 Hz, CHCO), 1.51 (1 H, quintet, *J* 7.5 Hz, SnCH), 1.16 (3 H, d, *J* 7.5 Hz, CH$_3$), and 0.09 (9 H, s, Me$_3$Sn); *m/z* 398 (1%, M^+), 383 (28, *M* − Me), 291 (72, *M* − PhCHOH), and 165 (100, Me$_3$Sn); and the 2*SR*,3*RS*,1′*SR*)-ester (**6ab**) (350 mg, 18%).

(2SR,3SR)-*Allyl* 3-*Hydroxy*-2-[(SR)-1-*phenyl*-1-*trimethylstannylmethyl*]*butanoate* (**7ba**).—Allyl cinnamate (0.48 g, 2.55 mmol), trimethylstannyl-lithium (3.06 mmol), and acetaldehyde (**5a**) (135 mg, 3.06 mmol) gave a 67:33 mixture (n.m.r.) of the (2*SR*,3*SR*,1′*SR*)-ester (**7ba**) and the (2*SR*,3*RS*,1′*SR*)-ester (**6ba**) (720 mg, 71%) as an oil, R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.35; $\nu_{max.}$(film) 3 400, 1 720 (C=O), 1 645 (C=C), and 1 600 and 1 495 cm^{-1} (Ph); δ(CDCl$_3$) (**7ba**) 7.3—7.0 (5 H, m, Ph), 5.93 (1 H, ddt, *J* 10.4, 17.2, and 5.9 Hz, C*H*=CH$_2$), 5.38 (1 H, dq, *J* 17.2 and 1 Hz, C=C*H*$_A$H$_B$, H$_A$ *cis* to CH$_2$), 5.29 (1 H, dq, *J* 10.4 and 1 Hz, C=CH$_A$*H*$_B$, H$_B$ *trans* to CH$_2$), 4.73 (1 H, ddt, *J* 5.9, 12, and 1 Hz, OC*H*$_A$H$_B$), 4.59 (1 H, ddt, *J* 5.9, 12, and 1 Hz, OCH$_A$*H*$_B$), 3.74 (1 H, ddq, *J* 3.0, 9.1, and 6.5 Hz, C*H*OH), 3.11 (1 H, dd, *J* 3.0 and 11.7 Hz, CHCO), 2.99 (1 H, d, *J* 11.7 Hz, SnCH), 2.50 (1 H, d, *J* 9.1 Hz, OH), 1.14 (3 H, d, *J* 6.5 Hz, CH$_3$), and

−0.04 (9 H, s, Me_3Sn); *m/z* 398 (5%, M^+), 383 (37, *M* − Me), 353 (47, *M* − C_2H_5O), and 165 (100, Me_3Sn); and the (2*SR*,3*SR*,1′*RS*)-ester (**9ba**) (108 mg, 11%) as an oil; R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.40; $\nu_{max.}$(film), 3 400 (OH), 1 710 (C=O), 1 645 (C=C), and 1 595 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) 7.3—7.0 (5 H, m, Ph), 5.52 (1 H, ddt, *J* 11, 16, and 6 Hz, C*H*=CH_2), 5.06 (1 H, d, *J* 11 Hz, C=CH_AH_B, H_A *trans* to CH_2), 5.03 (1 H, d, *J* 16 Hz, C=CH_AH_B, H_B *cis* to CH_2), 4.4—4.3 (2 H, m, OCH_2), 3.90 (1 H, ddq, *J* 2.4, 9.8, and 6.5 Hz, C*H*OH), 3.15—3.05 (2 H, m, SnCHCH), 2.89 (1 H, d, *J* 9.8 Hz, OH), 1.27 (3 H, d, *J* 6.5 Hz, CH_3), and 0.02 (9 H, s, Me_3Sn); *m/z* 398 (5%, M^+), 393 (33, *M* − Me), 353 (38, *M* − C_2H_5O), and 165 (100, Me_3Sn).

(2SR,3SR)-*Allyl* 2-[(RS)-1-*Hydroxybenzyl*]-3-*phenyl*-3-*trimethylstannylpropanoate* (**7bb**).—Allyl cinnamate (1.15 g, 6.12 mmol), trimethylstannyl-lithium (6.41 mmol), and benzaldehyde (**5b**) (0.65 g, 6.12 mmol) gave the (2SR,3RS,1′RS)-*ester* (**7bb**) (1.46 g, 51%) as needles, m.p. 67—68 °C (from light petroleum) (Found: C, 57.5; H, 6.05. $C_{22}H_{28}O_3Sn$ requires C, 57.5; H, 6.15%), R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.43; $\nu_{max.}$($CHCl_3$), 3 450 (OH), 1 720 (C=O), 1 645 (C=C), and 1 600 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) 7.3—7.0 (10 H, m, Ph), 5.62 (1 H, ddt, *J* 11.8, 16.5, and 5.8 Hz, C*H*=CH_2), 5.11 (1 H, dq, *J* 11.8 and 1 Hz, C=CH_AH_B, H_A *trans* to CH_2), 5.08 (1 H, dq, *J* 16.5 and 1 Hz, C=CH_AH_B, H_B *cis* to CH_2), 4.69 (1 H, dd, *J* 3.7 and 8.8 Hz, C*H*OH), 4.51 (1 H, ddt, *J* 5.8, 13.1, and 1 Hz, OCH_AH_B), 4.38 (1 H, ddt, *J* 5.8, 13.1, and 1 Hz, OCH_AH_B), 3.44 (1 H, dd, *J* 3.7 and 11.3 Hz, CHCO), 3.37 (1 H, d, *J* 8.8 Hz, OH), 3.05 (1 H, d, *J* 11.3 Hz, SnCH), and −0.02 (9 H, s, Me_3Sn); *m/z* 460 (1%, M^+), 445 (15, *M* − Me), 353 (100, *M* − PhCHOH), and 165 (85, Me_3Sn); the (2SR,3RS,1′SR)-*ester* (**9bb**) (0.36 g, 13%) as needles, m.p. 95—96 °C (from aqueos methanol) (Found: C, 57.4; H, 6.1. $C_{22}H_{28}O_3Sn$ requires C, 57.5; H, 6.15%); R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.45; $\nu_{max.}$($CHCl_3$) 3 450 (OH), 1 710 (C=O), 1 645 (C=C), and 1 600 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) 7.3—7.0 (10 H, m, Ph), 5.28 (1 H, ddt, *J* 9.7, 17.3, and 5.7 Hz, C*H*=CH_2), 4.9—4.8 (2 H, m, C=CH_AH_B, H_A *trans*, to CH_2 and C*H*OH), 4.75 (1 H, dq, *J* 17.3 and 1 Hz, C=CH_AH_B, H_B *cis* to CH_2), 4.1—4.0 (2 H, m, OCH_2), 3.94 (1 H, d, *J* 9.6 Hz, OH), 3.48 (1 H, dd, *J* 3.4 and 11.9 Hz, CHCO), 3.17 (1 H, d, *J* 11.9 Hz, SnCH), and 0.11 (9 H, s, Me_3Sn); *m/z* 460 (1%, M^+), 445 (8, *M* − Me), 353 (80, *M* − PhCHOH), and 165 (100, Me_3Sn); and the (2SR,3SR,1′RS)-*ester* (**6bb**) (0.30 g, 10%).

Reaction of Enolates (**4**) *with Aldehydes.*—Typically, the β-stannyl ester (**3**) (3.5 mmol) in THF (2 ml) was added dropwise during 5 min to a stirred solution of LDA (3.9 mmol) in THF (20 ml) at −78 °C. After 45 min the aldehyde (**5**) (3.9 mmol) in THF (2 ml) was added dropwise during 5 min, the mixture kept at −78 °C for 10 min, methanol (2 ml) and aqueous ammonium chloride (5 ml) added and the mixture brought to room temperature, and worked up as above.

(2SR,3RS)-*Allyl* 2-[(RS)-1-*Hydroxyethyl*]-3-*trimethylstannylbutanoate* (**6aa**).—The ester (**3a**) (2.00 g, 6.88 mmol), LDA (7 mmol), and acetaldehyde (**5a**) (320 mg, 7.3 mmol) gave the (2*SR*,3*RS*,1′*RS*)-ester (**6aa**) (1.53 g, 67%) as an oil, R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.37; $\nu_{max.}$(film) 3 400 (OH), 1 710 (C=O), and 1 640 cm^{-1} (C=C); δ($CDCl_3$) 5.90 (1 H, ddt, *J* 10.3, 17.2, and 5.9 Hz, C*H*=CH_2), 5.30 (1 H, dq, *J* 17.2 and 1.4 Hz, C=CH_AH_B, H_A *cis* to CH_2) 5.23 (1 H, dq, *J* 10.3 and 1.4 Hz, C=CH_AH_B, H_B *trans* to CH_2), 4.6—4.5 (2 H, m, OCH_2), 3.98 (1 H, ddq, *J* 5.3, 8.0, and 6.1 Hz, C*H*OH), 2.58 (1 H, dd, *J* 4.8 and 8.0 Hz, CHCO), 1.89 (1 H, d, *J* 5.3 Hz, OH), 1.60 (1 H, dq, *J* 4.8 and 7.7 Hz, SnCH), 1.17 (3 H, d, *J* 6.1 Hz, CH_3CHOH), 1.15 (3 H, d, *J* 7.7 Hz, CH_3CHSn), and 0.03 (9 H, s, Me_3Sn); *m/z* 321 (61%, *M* − Me), 291 (19, *M* − C_2H_5O), and 165 (100, Me_3Sn); and a 75:25 mixture (n.m.r.) of the (2*SR*,3*RS*,1′*SR*)-ester (**7aa**) and the (2*SR*,3*SR*,1′*RS*)-ester (**8aa**) (0.40 g, 17%); δ($CDCl_3$) (**8aa**) 2.57 (1 H, dd, *J* 4.9 and 7.8 Hz, CHCO), 1.82 (1 H, d, *J* 7.1 Hz, OH), 1.16 (3 H, d, *J* 7 Hz, CH_3), and 0.03 (9 H, s, Me_3Sn).

(2SR,3RS)-*Allyl* 2-[(SR)-1-*Hydroxybenzyl*]-3-*trimethylstannylbutanoate* (**6ab**).—The ester (**3a**) (0.50 g, 1.72 mmol), LDA (2 mmol), and benzaldehyde (**5b**) (212 mg, 2 mmol), gave the (2*SR*,3*RS*,1′*SR*)-ester (**6ab**) (0.41 g, 59%) as an oil, R_F (light petroleum–ethyl acetate, 5:1 v/v) 0.28; $\nu_{max.}$(film) 3 450 (OH), 1 720 (C=O), 1 645 (C=C), and 1 600 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) 7.3—7.1 (5 H, m, Ph), 5.61 (1 H, ddt, *J* 10.7, 16.9, and 5.1 Hz, C*H*=CH_2), 5.07 (1 H, dq, *J* 10.7 and 1.3 Hz, C=CH_AH_B, H_A *trans* to CH_2), 5.04 (1 H, dq, *J* 16.9 and 1.3 Hz, C=CH_AH_B, H_B *cis* to CH_2), 4.85 (1 H, d, *J* 9.1 Hz, C*H*OH), 4.4—4.2 (2 H, m, OCH_2), 2.98 (1 H, dd, *J* 3.3 and 9.1 Hz, CHCO), 2.2 (1 H, br s, OH), 1.74 (1 H, dq, *J* 3.3 and 7.7 Hz, SnCH), 1.22 (3 H, d, *J* 7.7 Hz, CH_3), and 0.11 (9 H, s, Me_3Sn); *m/z* 398 (1%, M^+), 383 (32, *M* − Me), 291 (57, *M* − PhCHOH), and 165 (100, Me_3Sn); and the (2*SR*, 3*RS*,1′*RS*)-ester (**7ab**) (0.26 g, 39%).

(2SR,3RS)-*Allyl* 3-*Hydroxy*-2-[(SR)-1-*phenyl*-1-*trimethylstannylmethyl*]*butanoate* (**6ba**).—The ester (**3b**) 1.30 g, 3.69 mmol), LDA (4.4 mmol), and acetaldehyde (**5a**) (200 mg, 4.5 mmol) gave a 77:23 mixture of the (2*SR*,3*RS*,1′*SR*)-ester (**6ba**) and the (2*SR*,3*SR*,1′*SR*)-ester (**7ba**) (1.02 g, 70%) as an oil, R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.35; $\nu_{max.}$(film) 3 400 (OH), 1 720 (C=O), 1 645 (C=C), and 1 600 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) (**6ba**) 7.3—7.0 (5 H, m, Ph), 5.95 (1 H, ddt, *J* 10.4, 16.5, and 5.9 Hz, C*H*=CH_2), 5.38 (1 H, dq, *J* 16.5 and 1.5 Hz, C=CH_AH_B, H_A *cis* to CH_2), 5.28 (1 H, dq, *J* 10.4 and 1.5 Hz, C=CH_AH_B, H_B *trans* to CH_2), 4.66 (2 H, dt, *J* 5.9 and 1.5 Hz, OCH_2), 4.0—3.9 (1 H, m, C*H*OH), 3.37 (1 H, dd, *J* 10.9 and 4.8 Hz, CHCO), 2.77 (1 H, d, *J* 10.9 Hz, SnCH), 2.3 (1 H, br s, OH), 1.10 (3 H, d, *J* 6.5 Hz, CH_3), and −0.06 (9 H, s, Me_3Sn); *m/z* 398 (8%, M^+), 383 (73, *M* − Me), 353 (57, *M* − C_2H_5O), and 165 (100, Me_3Sn).

(2SR,3SR)-*Allyl* 2-[(SR)-1-*Hydroxybenzyl*]-3-*phenyl*-3-*trimethylstannylpropanoate* (**6bb**).—The ester (**3b**) (1.00 g, 2.84 mmol), LDA (4.26 mmol), and benzaldehyde (**5b**) (2.85 mmol) gave the (2*SR*,3*SR*,1′*SR*)-ester (**6bb**) (0.65 g, 49%), R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.46; $\nu_{max.}$(film) 3 400 (OH), 1 720 (C=O), 1 645 (C=C), and 1 600 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) 7.3—7.0 (10 H, m, Ph's), 5.67 (1 H, ddt, *J* 10.2, 17.5, and 6.1 Hz, C*H*=CH_2), 5.17 (1 H, dq, *J* 17.5 and 1 Hz, C=CH_AH_B, H_A *cis* to CH_2), 5.14 (1 H, dq, *J* 10.2 and 1 Hz, C=CH_AH_B, H_B *trans* to CH_2), 4.89 (1 H, dd, *J* 5.0 and 6.3 Hz, C*H*OH), 4.46 (1 H, ddt, *J* 6.1, 13.0, and 1 Hz, OCH_HH_B), 4.46 (1 H, ddt, *J* 6.1, 13.0, and 1 Hz, OCH_AH_B), 3.56 (1 H, dd, *J* 6.3 and 8.3 Hz, CHCO), 2.89 (1 H, d, *J* 8.3 Hz, SnCH), 2.61 (1 H, d, *J* 5.0 Hz, OH), and −0.04 (9 H, s, Me_3Sn); *m/z* 460 (2%, M^+), 445 (15, *M* − Me), 353 (97, *M* − PhCHOH), and 165 (100 Me_3Sn); and the (2*SR*,3*SR*,1′*RS*)-ester (**7bb**) (0.15 g, 12%).

(1α,2α,3β)-*Allyl* 2,3-*Dimethylcyclopropane*-1-*carboxylate* (**10**).—Methanesulphonyl chloride (80 mg, 0.7 mmol) in ether (1 ml) was added to a mixture of the hydroxy ester (**6aa**) (200 mg, 0.60 mmol) and triethylamine (71 mg, 0.7 mmol) in ether (3 ml) at 0 °C. After 1 h dilute hydrochloric acid (5 ml) and ether (10 ml) were added, the mixture separated and the aqueous layer extracted with ether (5 ml). The combined organic layers were washed with sodium hydrogen carbonate solution, water, and brine, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was dissolved in dimethyl sulphoxide (4 ml) and heated at 110 °C for 24 h. Water (10 ml) was added to the cooled solution and the mixture extracted with ether (3 × 10 ml). The

combined organic layers were washed with water and brine, dried (Na_2SO_4), evaporated under reduced pressure and purified by distillation (Kugelrohr, 160 °C) to give the *ester* (**10**) (58 mg, 63%) as an oil; $\nu_{max.}$(film) 1 735 (C=O) and 1 645 cm^{-1} (C=C); δ($CDCl_3$) 5.93 (1 H, ddt, *J* 10.3, 17.2, and 5.7 Hz, C*H*=CH_2), 5.31 (1 H, dq, *J* 17.2 and 1.5 Hz, C=CH_AH_B, H_A *cis* to CH_2), 5.21 (1 H, dq, *J* 10.3 and 1.5 Hz, C=CH_AH_B, H_B *trans* to (CH_2), 4.56 (2 H, dt, *J* 5.7 and 1.5 Hz, OCH_2), 1.40 (1 H, dd, *J* 4.8 and 8.4 Hz, CHCO), 1.3—1.2 (1 H, m, CH), 1.17 (3 H, d, *J* 5.8 Hz, CH_3), 1.1—1.0 (1 H, m, CH), and 1.08 (3 H, d, *J* 5.8 Hz, CH_3) (Found: M^+, 154.100 6. $C_9H_{14}O_2$ requires *M*, 154.099 3); *m/z* 154 (6%, M^+), 139 (29, *M* − Me), 97 (100, *M* − C_3H_5O), and 69 (91, C_5H_9).

Conversion of Allyl Esters into Acids.—This reaction was performed by a method similar to that of Ho.[18] Typically, methyl-lithium (5.4 mmol of a solution in ether) was added dropwise during 5 min to a stirred suspension of copper(I) iodide (556 mg, 2.7 mmol) in dry ether (10 ml) at 0 °C until a trace of yellow suspension remained. After a further 10 min the ester (0.9 mmol) in ether (2 ml) was added dropwise during 2 min, and the yellow mixture stirred for 20 min. Dilute hydrochloric acid (20 ml) was added, the mixture separated and the aqueous layer extracted with ether (2 × 15 ml). The combined organic layers were filtered, extracted with dilute aqueous sodium hydroxide (3 × 15 ml), the combined aqueous layers washed with ether (10 ml), and then acidified with dilute hdyrochloric acid. The mixture was extracted with ether (3 × 15 ml), the combined organic layers washed with water and brine, dried (Na_2SO_4) and evaporated under reduced pressure. This work-up was followed except for acids (**11bb**) and (**12bb**). In these cases dilute hydrochloric acid (20 ml) was added to the reaction mixture, the mixture separated, and the aqeuous layer extracted with ether (2 × 10 ml). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and evaporated under reduced pressure. The β-hydroxy acids formed were unstable and were used within 2 h.

(2SR,3RS)-2-[(RS)-1-*Hydroxyethyl*]-3-*trimethylstannyl-butanoic Acid* (**11aa**).—The ester (**6aa**) (300 mg, 0.90 mmol) gave the acid (**11aa**) (255 mg, 96%) as an oil, R_F (ether) 0.53; $\nu_{max.}$(film) 3 600—2 400 (OH) and 1 700 cm^{-1} (C=O); δ($CDCl_3$) 4.7 (2 H, br s, OH's), 4.06 (1 H, dq, *J* 7.2 and 6.2 Hz, C*H*OH), 2.61 (1 H, dd, *J* 5.3 and 7.2 Hz, CHCO), 1.57 (1 H, dq, *J* 5.3 and 7.2 Hz, SnCH), 1.24 (3 H, d, *J* 6.2 Hz, CH_3CHOH), 1.20 (3 H, d, *J* 7.2 Hz, CH_3CHSn), and 0.04 (9 H, s, Me_3Sn); *m/z* 165 (9%, Me_3Sn) and 86 (100, $C_4H_6O_2$).

(2SR,3RS)-2-[(SR)-1-*Hydroxyethyl*]-3-*trimethylstannyl-butanoic Acid* (**12aa**).—The ester (**7aa**) (300 mg, 0.90 mmol) gave the acid (**12aa**) (243 mg, 92%) as an oil, R_F (ether) 0.37 (streak); $\nu_{max.}$(film) 3 600—2 400 (OH) and 1 700 cm^{-1} (C=O); δ($CDCl_3$) 5.0 (2 H, br s, OH's), 4.00 (1 H, quintet, *J* 6 Hz, C*H*OH), 2.51 (1 H, t, *J* 6 Hz, CHCO), 1.41 (1 H, quintet, *J* 6 Hz, SnCH), 1.27 (3 H, d, *J* 6 Hz, CH_3CHOH), 1.24 (3 H, d, *J* 6 Hz, CH_3CHSn), and 0.08 (9 H, s, Me_3Sn); *m/z* 296 (1%, M^+), 281 (*M* − Me), 263 [12, *M* − (Me + H_2O)], 251 (15, *M* − C_2H_5O), and 165 (100, Me_3Sn).

(2SR,3RS)-2-[(SR)-1-*Hydroxybenzyl*]-3-*trimethylstannyl-butanoic Acid* (**11ab**).—The ester (**6ab**) (310 mg, 0.78 mmol) gave the acid (**11ab**) (240 mg, 86%) as an oil, R_F (ether) 0.50 (streak); $\nu_{max.}$($CHCl_3$) 3 600—2 400 (OH), 1 700 (C=O), and 1 495 cm^{-1} (Ph); δ($CDCl_3$) 7.34 (5 H, m, Ph), 6.0 (2 H, br s, OH's), 4.87 (1 H, d, *J* 8.8 Hz, PhCH), 2.96 (1 H, dd, *J* 3.3 and 8.8 Hz, CHCO), 1.64 (1 H, dq, *J* 3.3 and 7.3 Hz, SnCH), 1.23 (3 H, d *J* 7.3 Hz, CH_3), and 0.08 (9 H, s, Me_3Sn); *m/z* 343 (28%, *M* − Me), 325 [19, *M* − (Me + H_2O)], 251 (82, *M* − PhCHOH), and 165 (100, Me_3Sn).

(2SR,3RS)-2-[(RS)-1-*Hydroxybenzyl*]-3-*trimethylstannyl-butanoic Acid* (**12ab**).—The ester (**7ab**) (300 mg, 0.76 mmol) gave the acid (**12ab**) (181 mg, 67%) as an amorphous solid unstable to attempted recrystallisation, m.p. 109 °C (decomp.), R_F(ether) 0.50 (streak); $\nu_{max.}$($CHCl_3$) 3 600—2 400 (OH), 1 700 (C=O), and 1 495 cm^{-1} (Ph); δ($CDCl_3$) 7.34 (5 H, m, Ph), 6.0 (2 H, br s, OH's), 4.83 (1 H, d, *J* 8.4 Hz, PhCH), 2.93 (1 H, dd, *J* 3.5 and 8.4 Hz, CHCO), 1.16 (4 H, br s, CH_3CH), and 0.09 (9 H, s, Me_3Sn); *m/z* 343 (10%, *M* − Me), 251 (33, *M* − PhCHOH), and 165 (100, Me_3Sn).

(2SR,3RS)-3-*Hydroxy*-2-[(RS)-1-*phenyl*-1-*trimethylstannyl-methyl*]*butanoic Acid* (**11ba**).—A 77:23 mixture of the esters (**6ba**) and (**7ba**) (250 mg, 0.63 mmol) gave a 77:23 mixture of the acids (**11ba**) and (**12ba**) (215 mg, 96%) as an oil, R_F(ether) 0.42 (streak); $\nu_{max.}$(film) 3 600—2 400 (OH), 1 700 (C=O), and 1 600 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) (**11ba**) 7.4—7.0 (5 H, m, Ph), 6.4 (2 H, br s, OH's), 4.1—3.9 (1 H, m, C*H*OH), 3.50 (1 H, dd, *J* 5 and 12 Hz, CHCO), 2.73 (1 H, d, *J* 12 Hz, SnCH), 1.21 (3 H, d, *J* 6 Hz, CH_3), and 0.04 (9 H, s, Me_3Sn); *m/z* 297 (1%, *M* − C_3H_9O), 165 (14, Me_3Sn), and 77 (100, Ph).

(2SR,3SR)-3-*Hydroxy*-2-[(SR)-1-*phenyl*-1-*trimethylstannyl-methy*]*butanoic Acid* (**12ba**).—A 67:33 mixture of the esters (**7ba**) and (**6ba**) (400 mg, 1.0 mmol) gave a 67:33 mixture of the acids (**12ba**) and (**11ba**) (334 mg, 93%) as an oil, R_F(ether) 0.42 (streak); $\nu_{max.}$(film) 3 600—2 400 (OH), 1 700 (C=O), and 1 600 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) (**12ba**) 7.4—7.0 (5 H, m, Ph), 6.5 (2 H, br s, OH—s), 4.1—4.0 (1 H, m, C*H*OH), 3.47 (1 H, dd, *J* 5 and 11 Hz, CHCO), 2.71 (1 H, d, *J* 11 Hz, SnCH), 1.20 (3 H, d, *J* 7 Hz, CH_3), and 0.02 (9 H, s, Me_3Sn); *m/z* 271 (1%, $C_{10}H_{15}OSn$), 165 (100, Me_3Sn), and 77 (98, Ph).

(2SR,3SR)-2-[(SR)-1-*Hydroxybenzyl*]-3-*phenyl*-3-*trimethyl-stannylpropanoic Acid* (**11bb**).—The ester (**6bb**) (300 mg, 0.65 mmol) gave the acid (**11bb**) (263 mg, 96%) as a viscous oil, R_F(ether) 0.53; $\nu_{max.}$($CHCl_3$) 3 600—2 400 (OH), 1 700 (C=O), 1 600 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) 7.4—7.0 (12 H, m, Ph's and OH's), 5.03 (1 H, d, *J* 6 Hz, C*H*OH), 3.68 (1 H, dd, *J* 10 and 6 Hz, CHCO), 2.72 (1 H, d, *J* 10 Hz, SnCH), and −0.08 (9 H, s, Me_3Sn); *m/z* 313 (1%, *M* − PhCHOH), 165 (6, Me_3Sn), and 105 (100, PhCO).

(2SR,3SR)-2-[(RS)-1-*Hydroxybenzyl*]-3-*phenyl*-3-*trimethyl-stannylpropanoic Acid* (**12bb**).—The ester (**7bb**) (300 mg, 0.65 mmol) gave the acid (**12bb**) (258 mg, 94%) as a viscous oil, R_F(ether) 0.47 (streak; $\nu_{max.}$($CHCl_3$) 3 600—2 400 (OH), 1 700 (C=O), and 1 600 and 1 495 cm^{-1} (Ph); δ(CD_2Cl_2) 7.4—7.0 (12 H, m, Ph's and OH's), 4.75 (1 H, d, *J* 3.8 Hz, C*H*OH), 3.48 (1 H, dd, *J* 3.8 and 10.9 Hz, CHCO), 2.98 (1 H, d, *J* 10.9 Hz, SnCH), and 0.04 (9 H, s, Me_3Sn); *m/z* 387 [1%, *M* − H_2O)], 313 (2, *M* − PhCHOH), and 165 (100, Me_3Sn).

Conversion of β-*Hydroxy Acids into Allylstannanes.*—This was performed by an adaptation of the method of Mulzer.[20] Typically, dimethylformamide dimethyl acetal (5.1 mmol) was added to a stirred solution of the β-hydroxy acid (0.85 mmol) in dry dichloromethane (70 ml). After 2 h at room temperature the solution was filtered through flash silica (100 g), evaporated under reduced pressure, taken up in light petroleum (b.p. 30—40 °C), filtered through flash silica (5 g), and evaporated under reduced pressure to give the allylstannane.

(E)-*Trimethyl*(*pent*-3-*en*-2-*yl*)*stannane* (**13aa**).—The acid (**11aa**) (250 mg, 0.85 mmol) gave the allylstannane (**13aa**) (144

mg, 73%) as an oil, R_F (light petroleum) 0.55; $\nu_{max.}$(film) 1 645 cm^{-1} (C=C); δ($CDCl_3$) 5.61 (1 H, ddq, *J* 7.6, 13.6, and 1.5 Hz, SnCHC*H*), 5.14 (1 H, ddq, *J* 13.6, 1.5, and 6.7 Hz, C=C*H*CH_3), 2.05—1.95 (1 H, m, SnCH), 1.66 (3 H, dt, *J* 6.7 and 1.5 Hz, C=CHC*H*$_3$), 1.23 (3 H, d, *J* 7.3 Hz, SnCHC*H*$_3$), and 0.02 (9 H, s, Me_3Sn); *m/z* 233 (18%, *M* − H), 219 (6, *M* − Me), 165 (100, Me_3Sn), and 84 (71, *M* − Me_2Sn).

(Z)-*Trimethyl*(*pent*-3-*en*-2-*yl*)*stannane* (**14aa**).—The acid (**12aa**) (260 mg, 0.87 mmol) gave the allylstannane (**14aa**) (161 mg, 78%) as an oil, R_F (light petroleum) 0.65; $\nu_{max.}$(film) 1 640 cm^{-1} (C=C); δ($CDCl_3$) 5.39 (1 H, tq, *J* 9 and 1 Hz, SnCHC*H*), 5.16 (1 H, dq, *J* 9 and 6.6 Hz, C=C*H*CH_3), 2.36 (1 H, dq, *J* 9 and 7.2 Hz, SnCH), 1.55 (3 H, d, *J* 6.6 and 1 Hz, CH_3CH=C), 1.25 (3 H, d, *J* 7.2 Hz, SnCHC*H*$_3$), and 0.04 (9 H, s, Me_3Sn); *m/z* 234 (1%, M^+), 219 (1, *M* − Me), 165 (14, Me_3Sn), and 84 (100, *M* − Me_2Sn).

(E)-*Trimethyl*(1-*phenylbut*-2-*enyl*)*stannane* (**13ba**).—A 77:23 mixture of the acids (**11ba**) and (**12ba**) (210 mg, 0.59 mmol) gave a 76:24 mixture (n.m.r.) of the (E) and (Z) allylstannanes (**13ba**) and (**14b**) (110 mg, 64%) as an oil, R_F (light petroleum) 0.31; $\nu_{max.}$(film) 1 600 and 1 495 (Ph) and 980 cm^{-1} (CH=CH); δ($CDCl_3$) (**13ba**) 7.3—7.0 (5 H, m, Ph), 5.95 (1 H, ddq, *J* 10.0, 14.9, and 1.2 Hz, SnCHC*H*), 5.38 (1 H, ddq, *J* 1.0, 14.9, and 6.5 Hz, C*H*CH_3), 3.40 (1 H, d with other fine coupling, *J* 10 Hz, SnCH), 1.72 (3 H, ddd, *J* 6.5, 1.0, and 1.2 Hz, CH_3), and 0.02 (9 H, s, Me_3Sn); *m/z* 296 (4%, M^+), 165 (41, Me_3Sn), 146 (97, *M* − Me_2Sn), and 131 (100, *M* − Me_3Sn).

(Z)-*Trimethyl*(1-*phenylbut*-2-*enyl*)*stannane* (**14ba**).—A 67:23 mixture of the acids (**12ba**) and (**11ba**) (180 mg, 0.50 mmol) gave a 68:32 mixture (n.m.r.) of (*Z*) and (*E*) allylstannanes (**14ba**) and (**13ba**) (101 mg, 68%) as an oil, R_F (light petroleum) 0.31; $\nu_{max.}$(film) 1 630 (C=C), 1 600 and 1 495 (Ph), and 720 cm^{-1} (CH=CH); δ($CDCl_3$) (**14ba**) 7.3—7.0 (5 H, m, Ph), 6.02 (1 H, ddq, *J* 10.7, 11.6, and 1.7 Hz, SnCHC*H*), 5.31 (1 H, dq, *J* 10.7 and 6.9 Hz, C*H*CH_3), 3.75 (1 H, d, *J* 11.6 Hz, SnCH), 1.65 (3 H, dd, *J* 6.9 and 1.7 Hz, CH_3), and 0.01 (9 H, s, Me_3Sn); *m/z* 296 (3%, M^+), 165 (13, Me_3Sn), and 131 (100, *M* − Me).

(E)-*Trimethyl*(4-*phenylbut*-3-*en*-2-*yl*)*stannane* (**13ab**).—The acid (**11ab**) (210 mg, 0.59 mmol) gave the allylstannane (**13ab**) (151 mg, 87%) as an oil, R_F (light petroleum) 0.34; $\nu_{max.}$(film) 1 625 (C=C) and 1 600 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) 7.3—7.1 (5 H, m, Ph), 6.53 (1 H, dd, *J* 7.7 and 15.7 Hz, PhCHC*H*), 6.14 (1 H, dd, *J* 1 and 15.7 Hz, PhCH), 2.33 (1 H, ddq, *J* 7.7, 1, and 7.1 Hz, SnCH), 1.41 (3 H, d, *J* 7.1 Hz, CH_3), and 0.12 (9 H, s, Me_3Sn); *m/z* 296 (2%, M^+), 165 (47, Me_3Sn), and 131 (100, *M* − Me_3Sn).

Reaction of Acid (**12ab**) *with Dimethylformamide Dimethyl Acetal.*—When treated with dimethylformamide dimethyl acetal as above, the acid (**12ab**) (160 mg, 0.45 mmol) did not react at room temperature, but refluxing for 24 h, cooling, and working up as previously, gave the (*E*)-allylstannane (**13ab**) (54 mg, 41%).

Reaction of Acid (**11bb**) *with Dimethylformamide Dimethyl Acetal.*—When treated with dimethylformamide dimethyl acetal as above, the acid (**11bb**) (240 mg, 0.57 mmol) gave an 84:11:5 mixture (n.m.r.) of 2,4-diphenylbut-3-enal, (*Z*)-2,4,-diphenylbut-2-enal, and (*E*)-2,4-diphenylbut-2-enal (90 mg, 72%) as an oil. Major product: $\nu_{max.}$(film) 1 725 (C=O), 1 625 (C=C), and 1 600 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) 9.75 (1 H, d, *J* 1.9 Hz, CHO), 7.4—7.0 (10 H, m, Ph), 6.6—6.5 (2 H, m, CH=CH), and 4.43 (1 H, dd, *J* 5.3 and 1.9 Hz, C*H*CHO). Minor product: δ($CDCl_3$) 4.06 (d, *J* 8 Hz, CH_2). Preparative thin layer chromatography, eluting with light petroleum–ethyl acetate (3:1 v/v), gave an almost pure sample of (*Z*)-2,4-*diphenylbut*-2-*enal*, and no other isomer, R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.36; $\nu_{max.}$(film) 1 685 (C=O), 1 625 (C=C), and 1 600 and 1 495 cm^{-1} (Ph); δ($CDCl_3$) 9.65 (1 H, s, CHO), 7.5—7.0 (10 H, m, Ph), 6.86 (1 H, t, *J* 7.6 Hz, C=CH), and 3.68 (2 H, d, *J* 7.6 Hz, CH_2) (Found: M^+, 222.105 6. $C_{16}H_{14}O$ requires *M*, 222.104 4), *m/z* 222 (68%, M^+), 131 (37, *M* − $PhCH_2$), 77 (100, Ph).

Reaction of Acid (**12bb**) *with Dimethylformamide Dimethyl Acetal.*—When treated with dimethylformamide dimethyl acetal as above, the acid (**12bb**) (200 mg, 0.48 mmol) did not react at room temperature, but, after 48 h at reflux, it gave a similar mixture (27 mg, 25%) to that from the acid (**11bb**).

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