Ti^{IV}-BINOLate-Catalyzed Highly Enantioselective Additions of β-Substituted Allylstannanes to Aldehydes**

Stefan Weigand and Reinhard Brückner*

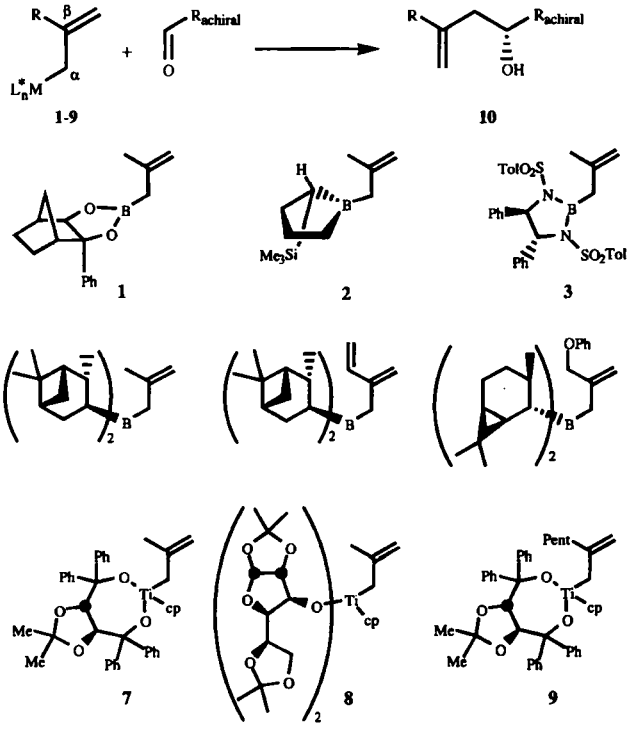
Abstract: Enantiomerically pure homoallyl alcohols were prepared from aldehydes R^1-CH=O (R^1 = Ph, pentyl, Ph-CH=CH-, *i*Pr) and β-substituted allylstannanes $H_2C=CR^2-CH_2-SnBu_3$ (R^2 = pentyl, *t*BuPh$_2$SiO-CH$_2$-, *t*BuPh$_2$SiO-CH$_2$-CH$_2$-, PhS-CH$_2$-CH$_2$-). These reactions were catalyzed by the same additives—Ti(OR)$_4$ (10 mol%) and (*R*)-BINOL (20 mol%)—that Keck et al. used in analogous reactions with methallyl- and allyltributylstannane. To attain optimum *ee* values (96.4–99.2% in the reaction with hexanal) these additives had to be premixed for 2 h at room temperature. Ti(OEt)$_4$ and Ti(O*i*Pr)$_4$ gave equally good results, while Ti(OMe)$_4$, Ti(OCHEt$_2$)$_4$, and Ti(O*t*Bu)$_4$ were inferior. Our procedure works in the absence of molecular sieves [which were previously found to give rather unreliable results in reactions catalyzed by Ti(O*i*Pr)$_4$/(*R*)-BINOL] and can be extended to enantioselective addition reactions with allyl- and methallyltributylstannane, too (+ hexanal: 97.4 and 97.0% *ee*, respectively).

Keywords
allylstannanes · asymmetric allylations · catalysis · C–C bond formation · homoallylic alcohols

Introduction

Catalytic asymmetric syntheses are reactions by which a substrate, a reagent, and less than one equivalent—ideally no more than a few mol percent—of an enantiopure catalyst furnish chiral products in an enantiocontrolled manner.[1] Two of the most powerful synthetic methods developed in the eighties were the stereocontrolled addition of enolates[2] and of allylmetals[3] to aldehyde C=O bonds. However, enantiopure addition products were only accessible if the substrate and/or the reagent were optically pure. This situation changed in the nineties with the advent of catalytic asymmetric variants of the same or related addition reactions.[4] The present study concerns catalytic asymmetric additions of β-substituted allyltributylstannanes to aldehydes. It increases the usefulness of a transformation which was discovered by Mikami, Nakai, et al.[5] (2-alkenyltributylstannane additions to glyoxylates) and extended to ordinary aldehydes by the groups of Tagliavini and Umani-Ronchi[6] (allyltributylstannane additions) and of Keck (allyl-,[7] methallyl-,[8] and allenyltributylstannane additions[9]).

In view of the large body of data on the enantioselective addition of allyl- and crotylmetals to aldehydes,[3] it is surprising how little is known about analogous addition reactions of β-substituted allylmetals in the literature. Just eight reagents **1**–**8**[10–16] and/or their antipodes have been published so far



Scheme 1. Enantioselective additions of β-substituted allylmetals to aldehydes [10–17] (see Table 1). In order to facilitate comparisons some reactions are mirror images of the actually performed experiments [10–12,14,16].

(Table 1). The diisopinocampheylborane **5** adds a β-vinylated allyl residue to aldehydes with 90–93% *ee*,[14] and the diisocaranylborane **6** a β-phenoxymethylated allyl residue with 74–84% *ee*.[15]

[*] Prof. Dr. R. Brückner, Dipl.-Chem. S. Weigand
Institut für Organische Chemie der Georg-August-Universität
Tammannstr. 2, D-37077 Göttingen (Germany)
Fax: Int. code +(551)39-2944

 0947-6539/96/0209-1076 $ 15.00+.25/0

Table 1. Enantioselective excesses (%) of alcohols **10** obtained in the additions of β-substituted allylmetals **1–9** to aldehydes (see Scheme 1).

	Ref.	Me	$R_{achiral}$ R_{prim}	R_{sec}	Ph
1	[10]	74	74	76	40
2	[11]			81	
3	[12]		88		
4	[13]	90	96		
5	[14]	90		90	93
6	[15]		74	74	84
7	[16]				73
8	[16]				38
9	[17]		76		25

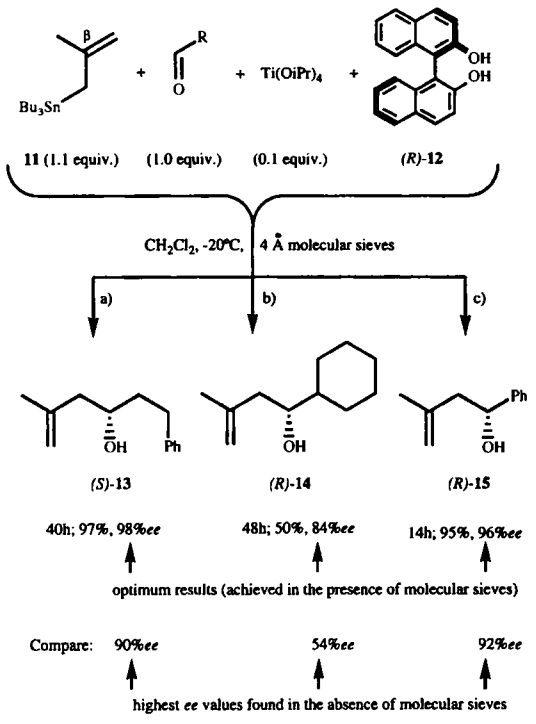
Results and Discussion

The homoallylic alcohols **10** that are accessible by the reactions of Scheme 1 do not show enough structural variety and are not optically pure enough (Table 1) to be useful starting materials for a synthetic project in which we are currently involved. We therefore decided to prepare these alcohols by a different method. We first examined the Duthaler/Hafner synthesis of a β-methylated homoallylic alcohol from the *methallyl*-containing Ti^{IV}-(*S*,*S*)-TADDOLate **7** and benzaldehyde[16] (Table 1; *ee* = 73%) as a methodological lead. Accordingly, we prepared the Ti^{IV}-(*S*,*S*)-TADDOLate **9** from (β-pentylallyl)chloride and Mg, from (β-pentylallyl)tributyltin and *n*BuLi, or from (β-pentylallyl)phenylselenide and *n*BuLi.[17] It differs from **7** only in the presence of a pentyl chain at the β position of the allyl moiety. Disappointingly, this reagent added to hexanal with no more than 76% *ee* and to benzaldehyde with only 25% *ee*[17] (Table 1). Since the β-unsubstituted analogue of TADDOLates **7** and **9** adds to benzaldehyde with 95% *ee*,[20] it can be concluded that increasingly large β-substituents (H → Me → pentyl) lower the enantiocontrol of Duthaler/Hafner additions to this aldehyde from 95 through 73 to 25% *ee*.

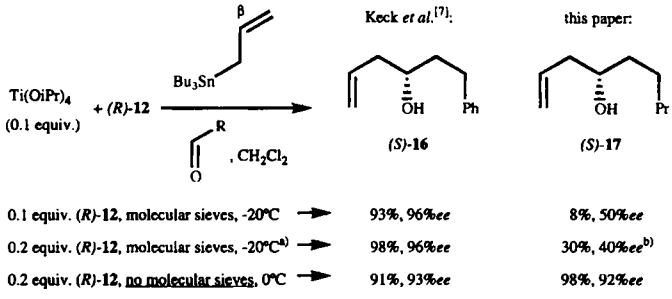
We therefore abandoned our efforts to adapt the Duthaler/Hafner method and wondered whether Keck's catalytic asymmetric (β-methyl)allylation of aldehydes[8] might give better results (Scheme 2). In this method 10 mol% of $Ti(OiPr)_4$ in dichloromethane is combined with either 10 mol% of (*R*)-BINOL ((*R*)-**12**; 1 h reflux in the presence of 4 Å molecular sieves) or 20 mol% of (*R*)-BINOL (1 h reflux in the presence of 3 mol% CF_3CO_2H and 4 Å molecular sieves). Addition of aldehydes at −20 °C gives the corresponding addition products in excellent ((*S*)-**13**: 98% *ee*; (*R*)-**15**: 96% *ee*) or moderate ((*R*)-**14**: 84% *ee*) optical and chemical yields.[8]

From the outset we were determined to deviate in one important detail from the conditions used to obtain the optimum *ee* values of Scheme 2: we decided to work in the absence of molecular sieves. Keck et al. had also done so, for example, in the methallyl additions summarized at the bottom of Scheme 2. However, this change had the effect of lowering *ee* values by 4% in the case of (*R*)-**15**, by 8% in the case of (*S*)-**13**, and by as much as 30% in the case of (*R*)-**14**.

Our reasons for not wanting to use molecular sieves become clear when one considers the optical yields depicted in Schemes 3 and 4. Scheme 3 compares the $Ti(OiPr)_4$/(*R*)-BINOL catalyzed additions of allyltributylstannane to hydrocinnamic aldehyde reported by Keck et al.[7] with those to hexanal performed in the present study. In the presence of molecular sieves, reference [7] reports 96% *ee*, while we inexplicably obtained only 40–50% *ee*. In the absence of molecular sieves, the *ee* values from the literature[7] (93%) and ours (92%) were, although not optimal, at least almost identical. Our *ee* value was subsequently increased under modified conditions to 97.6% (Scheme 4).

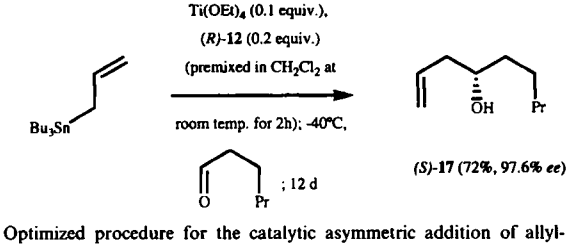


Scheme 2. Catalytic asymmetric additions of tributylmethallylstannane to representative aldehydes [8]: a) (*R*)-**12** (0.1 equiv); b) (*R*)-**12** (0.1 equiv); c) (*R*)-**12** (0.2 equiv), CF_3COOH (0.03 equiv).



Scheme 3. Comparison of the literature precedence and our results for the catalytic asymmetric additions of allyltributylstannane to model aldehydes of structure R-CH_2-CH_2-CH(=O). a) In the presence of CF_3SO_3H or CF_3CO_2H. b) Reaction performed at 0 °C.

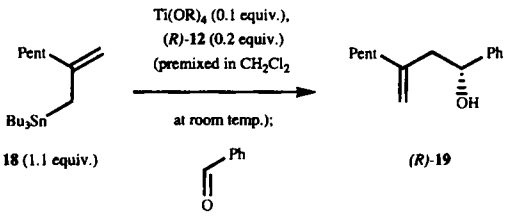
This last result[21] encouraged us to strive to achieve highly enantioselective additions of β-substituted allylstannanes to aldehydes, catalyzed by $Ti(OR)_4$/(*R*)-BINOL in the absence of molecular sieves. First we investigated the enantioselective addition of the (β-pentylallyl)stannane **18**[22] to benzaldehyde (Scheme 5). We were able to increase the *ee* value considerably



Scheme 4. Optimized procedure for the catalytic asymmetric addition of allyltributylstannane to hexanal.

0947-6539/96/0209-1078 $ 15.00+.25/0 Chem. Eur. J. 1996, 2, No. 9

by changing the titanium alkoxide (Table 2), the reaction temperature (Table 3), and the time span between combining (*R*)-**12**[23] with the titanium alkoxide and the addition of aldehyde and stannane (Table 3).



Scheme 5. Catalytic asymmetric addition of stannane **18** [22] to benzaldehyde (see Tables 2 and 3).

Table 2. Optimization of the titanium alkoxide in the catalytic asymmetric addition of stannane **18** to benzaldehyde (Scheme 5, premixing time 1 h, reaction temperature −78 °C).

Entry	$Ti(OR)_4$	Time/d	Yield/%	*ee*/%
1	$Ti(OMe)_4$	7	8	26
2	$Ti(OMe)_4$	7	8	27
3	$Ti(OEt)_4$	7	21	88
4	$Ti(OEt)_4$	7	28	90
5	$Ti(O\mathit{i}Pr)_4$	14	50	81
6	$Ti(O\mathit{i}Pr)_4$	14	50	81
7	$Ti(OCHEt_2)_4$	13	22	68
8	$Ti(O\mathit{t}Bu)_4$	7	21	56

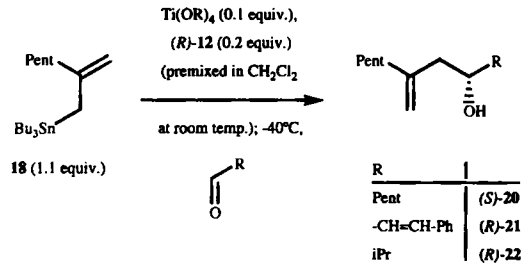
First, we varied the substituent R in the titanium alkoxide $Ti(OR)_4$ along the series Me → Et → *i*Pr → $CHEt_2$ → *t*Bu at a reaction temperature of −78 °C (Table 2). Knochel et al. have described an increase in enantioselectivity in this order for the asymmetric catalytic additions of diorganozinc compounds to aldehydes.[24] However, in our case the medium-sized alkoxides $Ti(OEt)_4$ and $Ti(O\mathit{i}Pr)_4$ gave maximum yields (28 and 50%, respectively) and enantioselectivities (90 and 81% *ee*, respectively). $Ti(OMe)_4$, which is sterically less congested, and $Ti(OCHEt_2)_4$ or $Ti(O\mathit{t}Bu)_4$, which are sterically more congested, gave *lower* chemical and optical yields.

When the temperature of addition of the (β-pentylallyl)stannane **18**[22] to benzaldehyde was examined (Table 3), higher *ee* values were obtained at −20 or −40 °C than at +4 or −78 °C. Yet, these temperatures only improved *ee* values when the titanium alkoxide had previously been allowed to react with the (*R*)-**12**[23] for a sufficiently long time: a comparison of entries 4/5 with 2/3, 10/11 with 8/9, and 16/17 with 14/15 shows that the formation of the optimum catalyst requires—at the chosen concentrations and at room temperature—a premixing time of *more than 1 h* in dichloromethane solution. This observation may appear trivial, but its implications certainly are not: the prototypical substituted homoallylic alcohol (*R*)-**19** becomes accessible from the (β-pentylallyl)stannane **18** in excellent optical and chemical yields; in the presence of $Ti(OEt)_4$ and at −20 °C, 98.9% *ee* and 98% yield were achieved (entry 4, Table 3), at −40 °C 98.7% *ee* and 95% yield (entry 10 of Table 3).

Table 3. Optimization of reaction temperature (*T*) and premixing time (t_{premix}) for the catalyst in the asymmetric addition of stannane **18** to benzaldehyde (Scheme 5).

Entry	Catalyst	t_{premix}/h	*T*/°C	$t_{reaction}$/d	Yield/%	*ee*/%
1	$Ti(O\mathit{i}Pr)_4$	1	+4	2	96	64
2	$Ti(O\mathit{i}Pr)_4$	1	−20	3	99	74
3	$Ti(O\mathit{i}Pr)_4$	1	−20	12	91	70
4	$Ti(OEt)_4$	2	−20	8	98	98.9
5	$Ti(OEt)_4$	2	−20	12	82	97.3
6	$Ti(O\mathit{i}Pr)_4$	3	−20	11	87	98.6
7	$Ti(O\mathit{i}Pr)_4$	3	−20	11	87	98.5
8	$Ti(OEt)_4$	1	−40	14	81	90
9	$Ti(OEt)_4$	1	−40	14	75	90
10	$Ti(OEt)_4$	2	−40	8	95	98.7
11	$Ti(OEt)_4$	2	−40	8	77	97.2
12	$Ti(OEt)_4$	1	−78	7	21	88
13	$Ti(OEt)_4$	1	−78	7	28	90
14	$Ti(O\mathit{i}Pr)_4$	1	−78	14	50	81
15	$Ti(O\mathit{i}Pr)_4$	1	−78	14	50	81
16	$Ti(O\mathit{i}Pr)_4$	3	−78	13	39	89
17	$Ti(O\mathit{i}Pr)_4$	3	−78	13	39	87

Similar efficiencies were recorded in asymmetric catalytic additions of stannane **18** to hexanal in the presence of $Ti(OEt)_4$ (Scheme 6) (99.1% *ee*, 95% yield; Table 4, entry 1) or $Ti(O\mathit{i}Pr)_4$ (98.9% *ee*, 96% yield; Table 4, entry 2). *trans*-Cinnamaldehyde gave slightly less spectacular results (Table 4, entries 3–10).



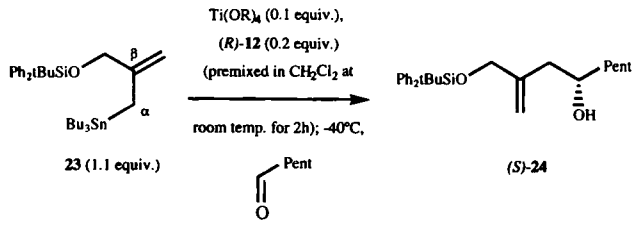
Scheme 6. Catalytic asymmetric addition of stannane **18** [22] to various aldehydes (see Table 4).

Table 4. Yields and enantioselectivities for the reactions in Scheme 6 under various conditions.

Entry	R	Catalyst	t_{premix}/h	$t_{reaction}$/d	Yield/%	*ee*/%
1	pentyl	$Ti(OEt)_4$	2	13	95	99.1
2	pentyl	$Ti(O\mathit{i}Pr)_4$	1	7	96	98.9
3	-CH=CH-Ph	$Ti(OEt)_4$	1	14	80	88
4	-CH=CH-Ph	$Ti(OEt)_4$	1	10	80	87
5	-CH=CH-Ph	$Ti(O\mathit{i}Pr)_4$	1	18	91	85
6	-CH=CH-Ph	$Ti(O\mathit{i}Pr)_4$	1	18	85	86
7	-CH=CH-Ph	$Ti(OEt)_4$	2	10	76	91.7
8	-CH=CH-Ph	$Ti(OEt)_4$	3	12	78	92.0
9	-CH=CH-Ph	$Ti(OEt)_4$	6	12	74	90
10	-CH=CH-Ph	$Ti(OEt)_4$	12	14	62	87
11	*i*Pr	$Ti(OEt)_4$	2	10	19	93

Again, the highest *ee* value (92%) was observed after 2–3 h premixing time instead of only 1 h (*ee* = 87–88%). Isobutyraldehyde reacted with **18** to give a comparable *ee* value (93%), but in only 19% yield. This low value seems to reflect the increased steric hindrance. A similar decrease in yield compared to other aldehydes was reported by Keck et al. in the catalytic asymmetric addition of allyltributylstannane to cyclohexanecarbaldehyde:[7] the alcohol (*R*)-**14** was obtained in lower yield than any other alcohol prepared in the same investigation (cf. Scheme 2).

Stirring titanium alkoxides for 2 h at room temp. with twice the amount of (*R*)-**12**[23] also provided efficient catalysts for the enantioselective addition of allylstannanes **23** (Scheme 7),[22] **25**

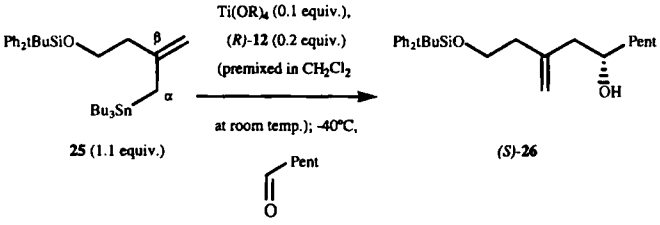


Scheme 7. Addition of **23** [22] to hexanal (see Table 5).

Table 5. Effect of catalyst on the reaction in Scheme 7.

Catalyst	$t_{reaction}$/d	Yield/%	*ee*/%
$Ti(OEt)_4$	8	70	96.9
$Ti(OEt)_4$	8	61	97.4
$Ti(OiPr)_4$	12	73	97.3
$Ti(OiPr)_4$	12	65	96.5

(Scheme 8),[22] and **27** (Scheme 9)[22] to hexanal. These stannanes have heteroatom-containing β-substituents, namely, $Ph_2tBuSiO\text{-}CH_2\text{-}$, $Ph_2tBuSiO\text{-}CH_2\text{-}CH_2\text{-}$, and $PhS\text{-}CH_2\text{-}CH_2\text{-}$ groups, respectively. That these reagents add in a highly entio-controlled manner, too, is far from self-evident. The best *ee* values and yields were 97.4% *ee*/61% yield in the case of alcohol (*S*)-**24** (Table 5), 99.2% *ee*/64% yield in the case of alcohol (*S*)-**26** (Table 6), and 96.4% *ee*/60% yield in the case of alcohol

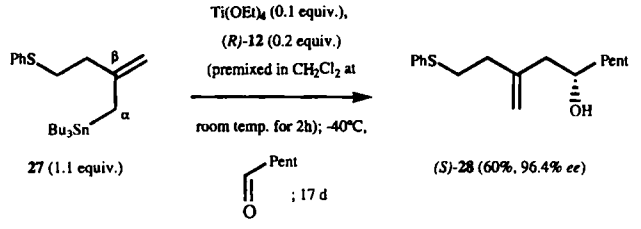


Scheme 8. Addition of **25** [22] to hexanal (see Table 6).

Table 6. Effect of catalyst on the reaction in Scheme 8.

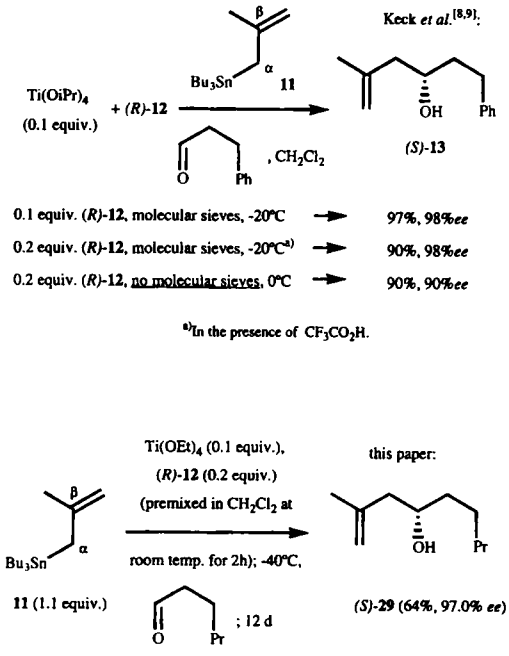
Catalyst	t_{premix}/h	$t_{reaction}$/d	Yield/%	*ee*/%
$Ti(OEt)_4$	1	9	65	95.0
$Ti(OEt)_4$	1	11	61	93.9
$Ti(OEt)_4$	2	14	82	98.3
$Ti(OEt)_4$	2	11	64	99.2
$Ti(OiPr)_4$	2	15	80	95.1
$Ti(OiPr)_4$	2	15	75	94.2

(*S*)-**28** (Scheme 9). In the synthesis of alcohol (*S*)-**26**, $Ti(OEt)_4$ was a better additive (99.2% *ee*) than $Ti(OiPr)_4$ (95.1% *ee*), provided that the alkoxide was pretreated with the bisnaphthol for 2 h rather than for only 1 h.



Scheme 9. Addition of **27** [22] to hexanal.

According to Scheme 10 our reaction conditions may prove equally suited for the enantioselective addition of tributylmethallylstannane—the simplest β-substituted allyltributylstannane—to aldehydes: Our test system (Scheme 10, bottom) gave homoallylic alcohol (*S*)-**29** with 97.0% *ee*. This is nearly as good as the 98% *ee* obtained for the related homoallylic alcohol (*S*)-**13** in the presence of molecular sieves;[8, 9] in their absence (*S*)-**13** forms with only 90% *ee* (Scheme 10, top).[8, 9]



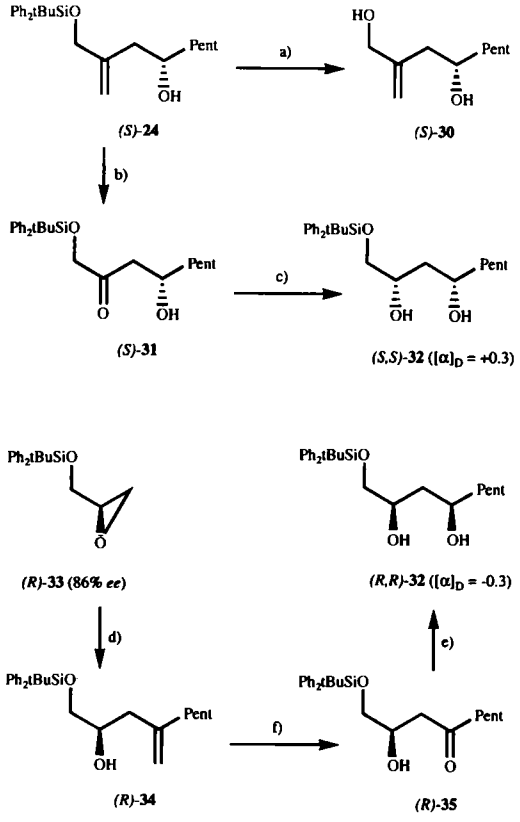
Scheme 10. Comparison of the literature precedence and our results for the catalytic asymmetric addition of tributylmethallylstannane to aldehydes.

The enantiomeric purities of the alcohols prepared in this study were determined by gas chromatography directly ((*S*)-**17**, (*R*)-**19**, (*S*)-**20**, (*R*)-**22**, (*S*)-**29**), or indirectly after desilylation ((*S*)-**24** → (*S*)-**30**, Scheme 11; (*S*)-**26** → (*S*)-**36**, Scheme 12) or oxidation ((*S*)-**28** → (*S*)-**36**, Scheme 12). In one case ((*R*)-**21**) we used HPLC. The quality of these determinations can be assessed from the chromatograms of Figure 1 (see Experimental Procedure).

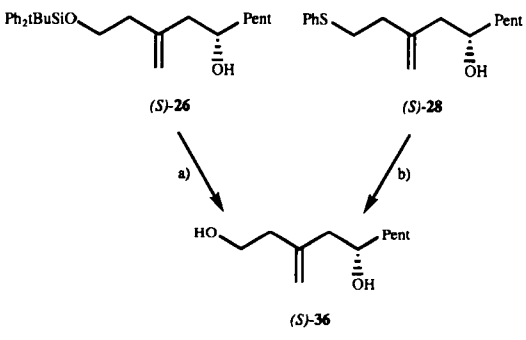
The absolute configuration of the newly prepared alcohol **24** was determined to be (*S*) by the stereochemical correlations depicted in Scheme 11. The C=C bond of (*S*)-**24** was ozonolyzed to give the hydroxyketone (*S*)-**31**, which was reduced with chelation control[25] to the *syn*-diol (*S,S*)-**32**. The enantiomer of this diol was synthesized[26] from the *tert*-butyldiphenylsilylated glycidol (*R*)-**33**[27] (86% *ee*) as follows: Ring opening of the epoxide at the sterically less hindered site through a Normant cuprate furnished the unsaturated alcohol (*R*)-**34**. Its C=C bond was ozonolyzed to provide the hydroxyketone (*R*)-**35**. The chelation-controlled reduction of the C=O bond[25] led to *syn*-diol (*R,R*)-**32**. The latter compound and the sample of (*S,S*)-**32** that stemmed from (*S*)-**24** exhibited specific rotations of low magnitude, but opposite sign (−0.3 and +0.3, respectively, in dichloromethane solutions). The dimethyl ethers prepared from these diols[26, 28] showed opposite rotations in the polarimeter, too ($[\alpha]_D^{23}$ = +8.9 (86% *ee*!) and −9.3, respectively, in dichloromethane solutions).

The absolute configuration of alcohol (*S*)-**17** was unambiguously assigned: the sense of the specific rotation of (*S*)-**17** is

0947-6539/96/0209-1080 $ 15.00+.25/0 Chem. Eur. J. 1996, 2, No. 9



Scheme 11. Configurational assignment of alcohol (*S*)-**24**: a) Bu_4NF, THF, RT, 10 h; 92%. b) O_3, CH_2Cl_2, −78 °C; PPh_3, → RT; 61%. c) Et_3B, THF, MeOH, RT, 1 h; addition to a solution of (*S*)-**31** in THF, −78 °C, 30 min; $NaBH_4$, 3 h; 67%. d) Mg, 2-bromo-1-heptene, THF, RT, 4 h; → −40 °C; CuI, THF, 15 min; addition to a solution of (*R*)-**33** in THF, 0 °C, 2.5 h; 83%. e) Et_3B, THF, MeOH, RT, 1 h; addition to a solution of (*R*)-**34** in THF, −78 °C, 1 h; $NaBH_4$, 3 h; 85%. f) O_3, CH_2Cl_2, −78 °C; PPh_3, → RT; 82%.



Scheme 12. Chemical modification and stereochemical correlation of alcohols (*S*)-**26** and (*S*)-**28**: a) Bu_4NF, THF, RT, 2 h, 98%. b) *n*BuLi, THF, −78 °C, 30 min; LiNaph, THF, −78 °C, 1 h; $FB(OMe)_2$, THF, −78 °C, 20 min, → RT; NaOH, H_2O_2, 24 h; 56%.

opposite to that published for (*R*)-**17**.[6a] The absolute configurations of the remaining alcohols (*R*)-**19**, (*S*)-**20**, (*R*)-**21**, (*R*)-**22**, (*S*)-**24**, (*S*)-**26**, and (*S*)-**28** were not proven. They are assumed to be identical with 1) the absolute configurations of the umabiguously assigned alcohols (*S*)-**17** and (*S*)-**24**, 2) the absolute configurations of various differently substituted yet uniformly configurated homoallylic alcohols prepared by the Duthaler/Hafner[20] or Keck methods,[8] and 3) the absolute configurations encountered in the majority of Ti^{IV}-(*S*,*S*)-TADDOLate and Ti^{IV}-(*R*)-BINOLate mediated addition reactions.[29]

Conclusion

We have shown that functionalized allyltributylstannanes can add their β-substituted allyl groups—with or without heteroatoms in the side chain—to aldehydes with a high degree of enantiocontrol, when the reaction is catalyzed by a species generated in situ from 10 mol% of $Ti(OEt)_4$ or $Ti(OiPr)_4$ and 20 mol% of enantiopure BINOL (*R*)-**12** (which can be recycled in >95% yield). The enantioselectivities of most additions could be increased by allowing these catalyst components to react for approximately 2 h, rather than only 1 h, before the reagent and the aldehyde were added. This effect was not described by Keck et al. for the analogous addition reactions of allyltributylstannane[7] or methallyltributylstannane[8] to aldehydes, but operates there, too, as exemplified by our reactions in Schemes 4 and 10.

Apart from their preparative value, our results contribute one more facet to the complicated chemistry of the $Ti(OR)_4$/(*R*)-BINOL mixtures, which is affected by a multitude of factors, such as, how long catalyst components are premixed, the temperature of reaction, whether a solvent is used, and whether molecular sieves are present [the molecular sieves may also interact differently with the catalyst(s) and/or its precursors as a function of water content or supplier[21]]. It seems to be clear that 1:2 mixtures of $Ti(OR)_4$ and (*R*)-BINOL without molecular sieves afford *at least* two different catalysts and that these catalysts each impose different degrees of enantiocontrol on the stannane additions described. The formation of dimers from $Ti(OiPr)_2Cl_2$ and BINOL,[30] from $Ti(OiPr)_4$ and substituted BINOLs,[31] from $TiCl_4$ and substituted dilithium BINOLATes,[31] and from $Ti(OiPr)_4$ and a related bisphenol[32] is known.[33] However, other oligomers or *n*-mers with a Ti–O_{BINOL} bond in nonchelated Ti/BINOL moieties might also form and be involved in the catalytic process. No mechanistic discussion of our result can therefore be properly undertaken.

Experimental Procedure

General methods: All reactions were performed in oven-dried (100 °C) glassware under dry N_2. THF was freshly distilled from K, CH_2Cl_2 from CaH_2. Products were purified by flash chromatography [34] on Merck silica gel 60 (particle size 0.040–0.063 mm, 230–240 mesh ASTM); for each separation, the column diameter, the eluent, and the product-containing fractions are given in parantheses (e.g., 2 cm, #1–10 petroleum ether:*t*BuOMe 10:1; then petroleum ether:*t*BuOMe 5:1; product in #5–11). Yields refer to analytically pure samples. ^1H NMR (tetramethylsilane or $CHCl_3$ internal standard in $CDCl_3$): Varian VXL-200, Bruker AC250, Bruker AMX300, or Varian VXR-500S; integrals in accord with assignments; coupling constants in Hz; AB spectra: H_A refers to high- and H_B to low-field resonance. IR (film): Perkin-Elmer FT-IR 1600. Combustion analyses: Mr. Beller, Institute of Organic Chemistry, Universität Göttingen. Mass spectra: Finnigan MAT95 spectrometer. The enantiomeric purity was determined by gas chromatography on an enantiomerically pure chiral stationary phase ("chiral gas chromatography") with heptakis(2,6-di-*O*-dimethyl-3-*O*-pentyl)-β-cyclodextrin or by HPLC on a commercially available Chiracel OD-R column from DAICEL Industries (cf. Fig. 1).

(4*S*)-Non-1-en-4-ol ((*S*)-**17**): A mixture of (*R*)-(+)-BINOL ((*R*)-**12**; 0.050 g, 0.17 mmol, 0.2 equiv) and $Ti(OEt)_4$ (0.018 mL, 0.020 g, 0.087 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) was stirred at RT for 2 h. Hexanal (0.11 mL, 0.087 g, 0.87 mmol, 1.0 equiv) was added. After the mixture had been stirred for 10 min, it was cooled to −78 °C, and allyltributylstannane (0.3180 g, 0.9605 mmol, 1.1 equiv) was added. The reaction proceeded for 12 d at −40 °C in the refrigerator. Addition of a saturated aqueous solution of $NaHCO_3$ (5 mL), 1 h of stirring, filtration through a frit filled with powdered NH_4Cl, extraction with CH_2Cl_2 (3 × 10 mL), and flash chromatography (2 cm, petroleum ether:*t*BuOMe 10:1; product in #8–16) yielded the homoallylic alcohol (*S*)-**17** (0.0898 g, 72%). Chiral gas chromatography (80 °C, 50 kPa H_2, R_T = 22.05 min for (*S*)-**17**, R_T = 22.93 min for (*R*)-**17**) revealed *ee* = 97.6%. $[\alpha]_D^{22} = -8.2$ (*c* = 2.02 in $CHCl_3$); ref. [6a]: 98.4% *ee*, $[\alpha]_D^{22} = 8.3$ for (*R*)-**17**. ^1H NMR (300 MHz): δ = 0.89 (t, $J_{9,8}$ = 6.8, 9-H_3), 1.23–1.60 (m, 5-H_2, 6-H_2, 7-H_2, 8-H_2, OH), AB signal [δ_A = 2.14, δ_B = 2.31, J_{AB} = 13.8, in addition split

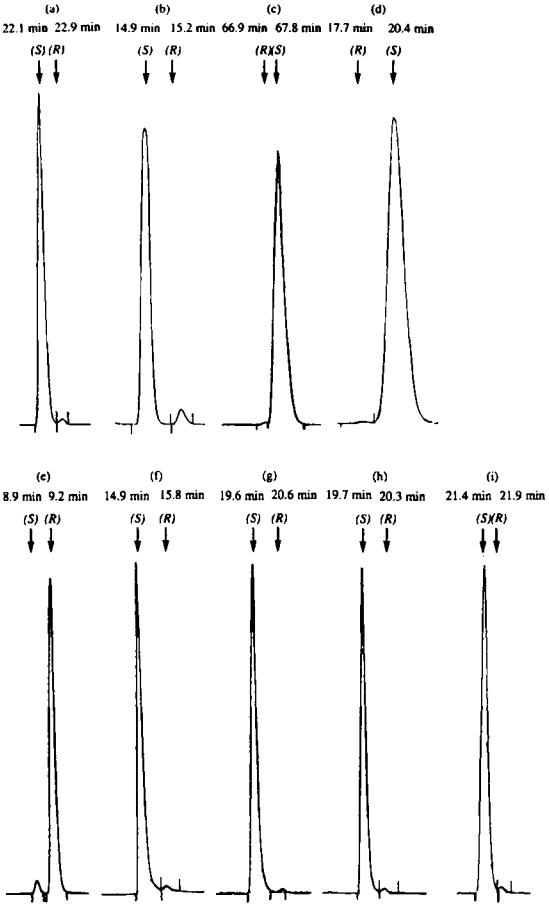


Fig. 1. Determination of *ee* values for allyl alcohols (*S*)-**17** [a] (a), (*R*)-**19** [a] (b), (*S*)-**20** [a] (c), (*R*)-**21** [b] (d), (*R*)-**22** [a] (e), (*S*)-**24** [a] (after desilylation to (*S*)-**30**, cf. Scheme 11) (f), (*S*)-**26** [a] (after desilylation to (*S*)-**36**, cf. Scheme 12 [c]) (g), (*S*)-**28** [a] (after oxidation to (*S*)-**36**, cf. Scheme 12) (h), (*S*)-**29** [a] (i). [a] By GLC. [b] By HPLC. [c] The electronic integral (ee_{app} = 99.5%) was incorrect and replaced by the value *ee* = 99.2% obtained manually.

by $J_{A,2} \approx J_{A,4} \approx 7.5$, J_{allyl} (not completely resolved) = 1.1, $J_{B,2}$ = 6.1*, $J_{B,4}$ = 4.3*, J_{allyl} = 1.2, 3-H$_2$], 3.65 (m$_c$, 4-H), 5.12 and 5.16 (2m$_c$, 1-H$_2$), 5.76–5.91 (m, 2-H); * assignments interchangeable. IR: $\tilde{\nu}$ = 3360, 3075, 2955, 2930, 2860, 1640, 1465, 1125, 1030, 995, 910, 735, 640 cm^{-1}. $C_9H_{18}O$ (142.2): calcd. C 76.00, H 12.76; found C 75.94, H 12.68.

(1*R*)-3-Methylene-1-phenyloctan-1-ol ((*R*)-**19**): A mixture of (*R*)-(+)-BINOL ((*R*)-**12**; 0.050 g, 0.17 mmol, 0.2 equiv) and Ti(OEt)$_4$ (0.018 mL, 0.020 g, 0.087 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) was stirred at RT for 2 h. Benzaldehyde (0.088 mL, 0.092 g, 0.87 mmol, 1.0 equiv) was added. After the mixture had been stirred for 10 min, it was cooled to −78 °C and 2-[(tributylstannyl)methyl]hept-1-ene (**18**; 0.3854 g, 0.9605 mmol, 1.1 equiv) was added. The reaction proceeded for 8 d at −20 °C in the refrigerator. Addition of a saturated aqueous solution of $NaHCO_3$ (5 mL), stirring for 1 h, filtration through a frit filled with powdered NH_4Cl, extraction with CH_2Cl_2 (3 × 15 mL), and flash chromatography (2 cm, #1–5 petroleum ether:*t*BuOMe 20:1; #6–14 petroleum ether:*t*BuOMe 15:1; subsequently petroleum ether:*t*BuOMe 10:1; product in #11–20) yielded the homoallylic alcohol (*R*)-**19** (0.1868 g, 98%). Chiral gas chromatography (140 °C, 150 kPa H_2, R_T = 14.9 min for (*S*)-**19**, 15.2 min for (*R*)-**19**) revealed *ee* = 98.9%. $[\alpha]_D^{23}$ = + 40.8 (*c* = 1.47 in $CHCl_3$). ^{1}H NMR (300 MHz): δ = 0.90 (t, $J_{8,7}$ = 6.8, 8-H$_3$), 1.23–1.52 (m, 5-H$_2$, 6-H$_2$, 7-H$_2$), 2.07 (t, $J_{4,5}$ = 7.7, 4-H$_2$), 2.15 (brs, OH), AB signal (δ_A = 2.39, δ_B = 2.46, J_{AB} = 14.0, in addition split by $J_{A,1}$ = 9.0, $J_{B,1}$ = 4.2, 2-H$_2$), 4.80 (dd, $J_{1,2\text{-H(A)}}$ = 9.1, $J_{1,2\text{-H(B)}}$ = 4.2, 1-H), 4.91 and 4.94 (s and d with *J* = 1.5, respectively, 3 = CH$_2$), 7.24–7.41 (m, Ph). IR: $\tilde{\nu}$ = 3385, 2955, 2925, 2855, 1645, 1455, 1050, 890, 755, 700, 540 cm^{-1}. $C_{15}H_{22}O$ (218.3): calcd. C 82.52, H 10.16; found C 82.41 H 10.02.

(6*S*)-8-Methylenetridecan-6-ol ((*S*)-**20**): A mixture of (*R*)-(+)-BINOL ((*R*)-**12**; 0.050 g, 0.17 mmol, 0.2 equiv) and Ti(OEt)$_4$ (0.018 mL, 0.020 g, 0.087 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) was stirred at RT for 2 h. Hexanal (0.11 mL, 0.087 g, 0.87 mmol, 1.0 equiv) was added. After the mixture had been stirred for 10 min, it was cooled to −78 °C and 2-[(tributylstannyl)methyl]-1-heptene (**18**; 0.3855 g, 0.9605 mmol, 1.1 equiv) was added. The reaction was allowed to proceed for 13 d at −40 °C in the refrigerator. Addition of a saturated aqueous solution of $NaHCO_3$ (5 mL), stirring for 1 h, filtration through a frit filled with powdered NH_4Cl, extraction with CH_2Cl_2 (3 × 15 mL), and flash chromatography (2 cm, #1–6 petroleum ether:*t*BuOMe 30:1; #7–12 petroleum ether:*t*BuOMe 20:1; #13–17 petroleum ether:*t*BuOMe 15:1; subsequently petroleum ether:*t*BuOMe 10:1; product in #6–17) yielded the homoallylic alcohol (*S*)-**20** (0.1760 g, 95%). Chiral gas chromatography (112 °C, 50 kPa H_2, R_T = 66.9 min for (*R*)-**20**, 67.8 min for (*S*)-**20**) revealed *ee* = 99.1%. $[\alpha]_D^{22}$ = − 4.8 (*c* = 1.26 in CH_2Cl_2). ^{1}H NMR (300 MHz): δ = 0.90 (2 superimposed t, J_{vic} = 7.6, 1-H$_3$, 13-H$_3$), 1.23–1.52 (m, 2-H$_2$, 3-H$_2$, 4-H$_2$, 5-H$_2$, 10-H$_2$, 11-H$_2$, 12-H$_2$), 1.72 (d, $J_{OH,6}$ = 2.7, OH), 2.03 (presumably t, $J_{9,10}$ = 7.7, 9-H$_2$), superimposed by A part of AB signal (δ_A = 2.04, δ_B = 2.24, J_{AB} = 13.9, in addition split by $J_{A,6} \approx$ 10.6, $J_{B,6}$ = 3.1, 7-H$_2$), 3.64–3.75 (m, 6-H), 4.83 and 4.88 (s and m$_c$, respectively, 8 = CH$_2$). IR: $\tilde{\nu}$ = 3385, 3070, 2930, 2860, 1735, 1645, 1460, 1380, 1125, 1035, 890, 725 cm^{-1}. $C_{14}H_{28}O$ (212.4): calcd. C 79.18, H 13.29; found C 79.24, H 13.32.

(3*R*)-5-Methylene-1-decen-3-ol ((*R*)-**21**): A mixture of (*R*)-(+)-BINOL ((*R*)-**12**; 0.050 g, 0.17 mmol, 0.2 equiv) and Ti(OEt)$_4$ (0.018 mL, 0.020 g, 0.087 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) was stirred at RT for 3 h. *trans*-cinnamaldehyde (0.11 mL, 0.12 g, 0.87 mmol, 1.0 equiv) was added. After the mixture had been stirred for 10 min, it was cooled to −78 °C. 2-[(Tributylstannyl)methyl]-1-heptene (**18**; 0.3855 g, 0.9605 mmol, 1.1 equiv) was added. The reaction was allowed to proceed for 12 d at −40 °C in the refrigerator. Addition of a saturated aqueous solution of $NaHCO_3$ (5 mL), stirring for 1 h, extraction with CH_2Cl_2 (3 × 20 mL), drying over Na_2SO_4, and flash chromatography (2 cm, #1–6 petroleum ether:*t*BuOMe 20:1; #7–12 petroleum ether:*t*BuOMe 15:1; #13–22 petroleum ether:*t*BuOMe 10:1; product in #14–21) yielded the alcohol (*R*)-**21** (0.1665 g, 78%). Chiral HPLC (0.5 mL min^{-1}, 250 nm, MeOH/H_2O = 9:1, R_T = 17.7 min for (*R*)-**21**, 20.4 min for (*S*)-**21**) revealed *ee* = 92.0%. $[\alpha]_D^{23}$ = 7.0 (*c* = 0.96 in CH_2Cl_2). ^{1}H NMR (300 MHz): δ = 0.90 (t, $J_{10,9}$ = 7.0, 10-H$_3$), 1.21–1.54 (m, 7-H$_2$, 8-H$_2$, 9-H$_2$), 1.91 (d, $J_{OH,3}$ = 3.0, OH), 2.08 (t, $J_{6,7}$ = 7.8, 6-H$_2$), AB signal (δ_A = 2.30, δ_B = 2.38, J_{AB} = 14.0, in addition split by $J_{A,3}$ = 8.7, $J_{B,3}$ = 4.5, 4-H$_2$), 4.42 (m$_c$, 3-H), 4.90 and 4.93 (s and hardly resolved d with *J* = 1.5, respectively, 5 = CH$_2$), 6.24 (dd, J_{trans} = 15.9, $J_{2,3}$ = 6.4, 2-H), 6.63 (d, J_{trans} = 16.2, 1-H), 7.19–7.42 (m, Ph). IR: $\tilde{\nu}$ = 3380, 3025, 2930, 2860, 1645, 1495, 1450, 1030, 965, 895, 745, 695 cm^{-1}. $C_{17}H_{24}O$ (244.4): calcd. C 83.55, H 9.90; found C 83.40, H 10.07.

(3*R*)-2-Methyl-5-methylenedecan-3-ol ((*R*)-**22**): A mixture of (*R*)-(+)-BINOL ((*R*)-**12**; 0.050 g, 0.17 mmol, 0.2 equiv) and Ti(OEt)$_4$ (0.018 mL, 0.020 g, 0.087 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) was stirred at RT for 2 h. Isobutyraldehyde (0.08 mL, 0.06 g, 0.9 mmol, 1.0 equiv) was added. After the mixture had been stirred for 10 min, it was cooled to −78 °C and 2-[(tributylstannyl)methyl]-1-heptene (**18**; 0.3854 g, 0.9605 mmol, 1.1 equiv) was added. The reaction was allowed to proceed for 10 d at −40 °C in the refrigerator. Addition of a saturated aqueous solution of $NaHCO_3$ (5 mL), stirring for 1 h, filtration through a frit filled with powdered NH_4Cl, extraction with CH_2Cl_2 (3 × 15 mL), and flash chromatography (2 cm, #1–6 petroleum ether:*t*BuOMe 30:1; #7–13 petroleum ether:*t*BuOMe 20:1; product in #7–13) yielded the title compound (0.308 g, 19%). Chiral gas chromatography (100 °C, 120 kPa H_2, R_T = 8.9 min for (*S*)-**22**, 9.2 min for (*R*)-**22**) revealed *ee* = 93.1%. $[\alpha]_D^{23}$ = 9.59 (*c* = 2.01 in $CHCl_3$). ^{1}H NMR (300 MHz): δ = 0.90 (t, $J_{10,9}$ = 7.4, 10-H$_3$), 0.94 and 0.96 (2d, $J_{1,2} = J_{2\text{-Me},2}$ = 5.3, 1-H$_3$, 2-Me), 1.20–1.53 and 1.58–1.76 (2m, 2 and 6H, 2-H, 7-H$_2$, 8-H$_2$, 9-H$_2$), superimposed by 1.69 (d, $J_{OH,3}$ = 2.6, OH), 2.03 (t, $J_{6,7}$ = 7.6, 6-H$_2$), superimposes A part of AB signal ($\delta_A \approx$ 2.01, δ_B = 2.27, J_{AB} = 13.6, in addition split by $J_{A,3}$ = 10.9, $J_{B,3}$ = 1.9, 4-H$_2$), 3.46 (m$_c$, presumably dddd, but only 9 lines visible, $J_{3,4\text{-H(A)}}$ = 10.1, $J_{3,2}$ = 5.3, $J_{3,4\text{-H(B)}} = J_{3,OH}$ = 2.6, 3-H), 4.84 und 4.89 (brs and d with *J* = 1.5, respectively, 5 = CH$_2$). IR: $\tilde{\nu}$ = 3445, 2960, 2875, 1715, 1645, 1465, 1385, 1045, 1000, 890 cm^{-1}. $C_{12}H_{24}O$ (184.3): calcd. C 78.21, H 13.12; found C 78.39, H 13.30.

(4*S*)-2-[(*tert*-Butyldiphenylsilyloxy)methyl]non-1-en-4-ol ((*S*)-**24**): A mixture of (*R*)-(+)-BINOL ((*R*)-**12**; 0.050 g, 0.17 mmol, 0.2 equiv) and Ti(OEt)$_4$ (0.018 mL, 0.020 g, 0.087 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) was stirred at RT for 2 h. Hexanal (0.11 mL, 0.087 g, 0.87 mmol, 1.0 equiv) was added. After the mixture had been stirred for 10 min, it was cooled to −78 °C and 2-[(*tert*-butyldiphenylsilyloxy)methyl]-3-(tributylstannyl)propene (**23**; 0.5759 g, 0.9605 mmol, 1.1 equiv) was added. The reaction was allowed to proceed for 8 d at −40 °C in the refrigerator. Addition of a saturated aqueous solution of $NaHCO_3$ (5 mL) and HCl (2N, 5 mL), stirring for 1 h, extraction with CH_2Cl_2 (3 × 20 mL), and flash chromatography (2 cm, #1–6 petroleum ether:*t*BuOMe 20:1; #7–14 petroleum ether:*t*BuOMe 15:1; product in #6–14) yielded the homoallylic alcohol ((*S*)-**24**; 0.2510 g, 70%). Chiral gas chromatography after desilylation to **30** (130 °C, 120 kPa H_2, R_T = 14.9 min for (*S*)-**30**, 15.8 min for (*R*)-**30**) revealed *ee* = 96.9%. $[\alpha]_D^{23}$ = 0.00 (*c* = 1.05 in CH_2Cl_2). ^{1}H NMR [300 MHz; impurities at δ = 0.92 (t, *J* = 7.2) and 1.58–1.70 (m)]: δ = 0.88 (t, $J_{9,8}$ = 6.6, 9-H$_3$), 1.07 (s, *t*Bu), 1.20–1.48 (m, 5-H$_2$, 6-H$_2$, 7-H$_2$, 8-H$_2$), 2.12 (d, $J_{OH,4}$ = 3.0, OH), AB signal (δ_A = 2.08, δ_B = 2.27, J_{AB} = 13.9, in addition split by $J_{A,4}$ = 9.1, $J_{B,4}$ = 3.5, 3-H$_2$), 3.62 (m$_c$, 4-H), 4.11 (s, 1'-H$_2$), 4.97 and 5.23 (s and d with J_{gem} = 1.8, respectively, 1-H$_2$), 7.35–7.47 and 7.65–7.73 (2m, 6 and 4H, respectively, 2 × Ph). IR: $\tilde{\nu}$ = 3445, 3070, 2955, 2930, 2855, 1650, 1470, 1430, 1390, 1360, 1110, 1010, 900, 825, 740, 700, 615, 505 cm^{-1}. $C_{26}H_{38}O_2Si$ (410.7): calcd. C 76.04, H 9.33; found C 76.21, H 9.39.

0947-6539/96/0209-1082 $ 15.00+.25/0 Chem. Eur. J. 1996, 2, No. 9

(4*S*)-2-[(*tert*-Butyldiphenylsilyloxy)ethyl]non-1-en-4-ol ((*S*)-**26**): A mixture of (*R*)-(+)-BINOL ((*R*)-**12**; 0.050 g, 0.17 mmol, 0.2 equiv) and $Ti(OEt)_4$ (0.018 mL, 0.020 g, 0.087 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) was stirred at RT for 2 h. Hexanal (0.11 mL, 0.087 g, 0.87 mmol, 1.0 equiv) was added. After the mixture had been stirred for 10 min, it was cooled to −78 °C and 4-(*tert*-butyldiphenylsilyloxy)-2-[(tributylstannyl)methyl]but-1-ene (**25**; 0.5894 g, 0.9605 mmol, 1.1 equiv) was added. The reaction was allowed to proceed for 11 d at −40 °C in the refrigerator. Addition of a saturated aqueous solution of $NaHCO_3$ (5 mL) and HCl (2N, 5 mL), stirring for 1 h, extraction with CH_2Cl_2 (3 × 20 mL), drying over Na_2SO_4, and flash chromatography (2 cm, #1–7 petroleum ether:*t*BuOMe 20:1; #8–16 petroleum ether:*t*BuOMe 15:1; #17–22 petroleum ether:*t*BuOMe 10:1; product in #9–21) yielded the homoallylic alcohol ((*S*)-**26**; 0.2368 g, 64%). Chiral gas chromatography after desilylation to **36** (130 °C, 120 kPa H_2, R_T = 19.6 min for (*S*)-**36**, 20.6 min for (*R*)-**36**) revealed *ee* = 99.2%. $[\alpha]_D^{23} = -4.59$ (*c* = 3.49 in $CHCl_3$). ^{1}H NMR (300 MHz; impurity at δ = 0.95): δ = 0.90 (t, $J_{9,8}$ = 7.5, 9-H_3), 1.04 (s, *t*Bu), 1.22–1.50 (m, 5-H_2, 6-H_2, 7-H_2, 8-H_2), 1.84 (d, $J_{OH,4}$ = 2.6, OH), AB signal (δ_A = 2.00, δ_B = 2.20, J_{AB} = 13.8, in addition split by $J_{A,4}$ = 9.6, $J_{B,4}$ = 3.2, 3-H_2), 2.28 (t, $J_{1',2'}$ = 6.6, 1'-H_2), 3.63 (m_c, 4-H), 3.77 (t, $J_{2',1'}$ = 6.8, 2'-H_2), 4.90 (brs, 1-H_2), 7.35–7.47 and 7.64–7.70 (2m, 6 and 4H, respectively, 2 × Ph). IR: $\tilde{\nu}$ = 3420 cm^{-1}, 3070, 2930, 2860, 1645, 1465, 1430, 1385, 1110, 895, 825. $C_{27}H_{40}O_2Si$ (424.7): calcd. C 76.36, H 9.49; found C 76.38, H 9.31.

(5*S*)-3-Methylene-1-(phenylthio)decan-5-ol ((*S*)-**28**): A mixture of (*R*)-(+)-BINOL ((*R*)-**12**; 0.050 g, 0.17 mmol, 0.2 equiv) and $Ti(OEt)_4$ (0.018 mL, 0.020 g, 0.087 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) was stirred at RT for 2 h. Hexanal (0.11 mL, 0.088 g, 0.87 mmol, 1.0 equiv) was added. After the mixture had been stirred for 10 min, it was cooled to −78 °C. 2-[(Tributylstannyl)methyl]-4-(phenylthio)prop-1-ene (**27**; 0.4488 g, 0.9605 mmol, 1.1 equiv) was added. The reaction was allowed to proceed for 17 d at −40 °C in the refrigerator. Addition of a saturated aqueous solution of $NaHCO_3$ (5 mL), stirring for 1 h, extraction with CH_2Cl_2 (3 × 15 mL), and flash chromatography (2 cm, #1–6 petroleum ether:*t*BuOMe 20:1; #7–12 petroleum ether:*t*BuOMe 15:1; subsequently petroleum ether:*t*BuOMe 10:1; product in #15–21) yielded alcohol (*S*)-**28** (0.1459 g, 60%). Chiral gas chromatography after oxidation to **36** (130 °C, 120 kPa H_2, R_T = 19.7 min for (*S*)-**36**, 20.3 min for (*R*)-**36**) revealed *ee* = 96.4%. $[\alpha]_D^{23} = -3.2$ (*c* = 1.51 in CH_2Cl_2). ^{1}H NMR (300 MHz): δ = 0.89 (t, $J_{10,9}$ = 6.8, 10-H_3), 1.21–1.59 (m, 6-H_2, 7-H_2, 8-H_2, 9-H_2), 1.69 (brs, OH), AB signal (δ_A = 2.09, δ_B = 2.25, J_{AB} = 14.0, in addition split by $J_{A,5}$ = 9.3, $J_{B,5}$ = 3.0, 4-H_2), 2.38 (t, $J_{2,1}$ = 7.6, 2-H_2), 3.05 (m_c, 1-H_2), 3.67 (m_c, 5-H), 4.95 (m_c, 3=CH_2), 7.15–7.22 and 7.25–7.37 (2 × m, Ph). IR: $\tilde{\nu}$ = 3420, 2930, 2865, 1640, 1585, 1470, 1440, 1075, 895, 740, 690 cm^{-1}. $C_{17}H_{26}OS$ (278.5): calcd. C 73.33, H 9.41; found C 73.45, H 9.37.

(4*S*)-2-Methylnon-1-en-4-ol ((*S*)-**29**): A mixture of (*R*)-(+)-BINOL ((*R*)-**12**; 0.050 g, 0.17 mmol, 0.2 equiv) and $Ti(OEt)_4$ (0.018 mL, 0.020 g, 0.087 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) was stirred at RT for 2 h. Hexanal (0.11 mL, 0.087 g, 0.87 mmol, 1.0 equiv) was added. After the mixture had been stirred for 10 min, it was cooled to −78 °C and methallyltributylstannane (**11**; 0.3316 g, 0.9605 mmol, 1.1 equiv) was added. The reaction was allowed to proceed for 12 d at −40 °C in the refrigerator. Addition of a saturated aqueous solution of $NaHCO_3$ (5 mL), stirring for 1 h, filtration through a frit filled with powdered NH_4Cl, extraction with CH_2Cl_2 (3 × 15 mL), and flash chromatography (2 cm, #1–10 petroleum ether:*t*BuOMe 12:1; #11–15 petroleum ether:*t*BuOMe 15:1; subsequently petroleum ether:*t*BuOMe 10:1; product in #6-14) yielded the homoallylic alcohol (*S*)-**29** (0.0876 g, 64%). Chiral gas chromatography (88 °C, 50 kPa H_2, R_T = 21.40 min for (*S*)-**29**, R_T = 21.94 min for (*R*)-**29**) revealed *ee* = 97.0%. $[\alpha]_D^{22} = -5.8$ (*c* = 1.47 in $CHCl_3$). ^{1}H NMR [300 MHz; impurities at δ = 0.95 (s), 1.59–1.70 (m)]: δ = 0.90 (t, $J_{9,8}$ = 7.7, 9-H_3), 1.24–1.52 (m, 5-H_2, 6-H_2, 7-H_2, 8-H_2), 1.76 (s, 2-Me), AB signal (δ_A = 2.09, δ_B = 2.21, J_{AB} = 13.8, in addition split by $J_{A,4}$ = 9.5, J_{allyl} = 0.8, $J_{B,4}$ = 3.2, 3-H_2), 3.72 (m_c, 4-H), 4.80 and 4.88 (2 dm_c, 1-H_2); OH signal presumably at δ = 1.67 (s). IR: $\tilde{\nu}$ = 3375, 2930, 2860, 1645, 1460, 1380, 1125, 1025, 890, 730 cm^{-1}. No correct combustion analysis was obtained.

(4*S*)-2-Methylenenonane-1,4-diol ((*S*)-**30**): Tetrabutylammonium fluoride (0.51 mL of a 1.1 M solution in THF, 0.55 mmol, 1.2 equiv) was added at RT to a stirred solution of alcohol (*S*)-**24** (0.1901 g, 0.4629 mmol, 1.0 equiv) in THF (4 mL). After 10 h the reaction was quenched with H_2O (5 mL). The mixture was extracted with *t*BuOMe (3 × 10 mL), dried over Na_2SO_4, and purified by flash chromatography (1 cm, #1–6 petroleum ether:*t*BuOMe 5:1; #7–11 petroleum ether:*t*BuOMe 3:1; subsequently petroleum ether:*t*BuOMe 1:1; product in #8–13) to yield (*S*)-**30** (0.0730 g, 92%). Chiral gas chromatography (130 °C, 120 kPa H_2, R_T = 14.9 min for (*S*)-**30**, 15.8 min for (*R*)-**30**) revealed *ee* = 96.9%. $[\alpha]_D^{23} = +6.17$ (*c* = 2.53 in $CHCl_3$). ^{1}H NMR (300 MHz): δ = 0.90 (t, $J_{9,8}$ = 6.8, 9-H_3), 1.23–1.51 (m, 5-H_2, 6-H_2, 7-H_2, 8-H_2), AB signal (δ_A = 2.16, δ_B = 2.36, J_{AB} = 14.1, in addition split by $J_{A,4}$ = 8.9, $J_{B,4}$ = 2.7, 3-H_2), 3.03 (brs, 2 × OH), 3.73 (m_c, 4-H), 4.09 (s, 1-H_2), 4.96 and 5.13 (s and d with J_{gem} = 1.1, respectively, 1'-H_2). IR: $\tilde{\nu}$ = 3330, 2930, 2860, 1650, 1460, 1125, 1035, 905 cm^{-1}. $C_{10}H_{20}O_2$ (172.3): calcd. C 69.72, H 11.70; found C 69.52, H 11.50.

(4*S*)-1-(*tert*-Butyldiphenylsilyloxy)-4-hydroxynonan-2-one ((*S*)-**31**): O_3 was bubbled at −78 °C through a solution of the unsaturated alcohol (*S*)-**24** (0.6888 g, 1.677 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) until the blue color persisted (1 h). Addition of PPh_3 (0.6601 g, 2.527 mmol, 1.5 equiv), concentrating in vacuo, and flash chromatography (3 cm, #1–7 petroleum ether:*t*BuOMe 30:1; #8–12 petroleum ether:*t*BuOMe 20:1; #13–20 petroleum ether:*t*BuOMe 15:1; #21–25 petroleum ether:*t*BuOMe 10:1; #26–40 petroleum ether:*t*BuOMe 4:1; product in #32–40) yielded the title compound (0.4197 g, 61%). $[\alpha]_D^{23} = +9.37$ (*c* = 2.68 in CH_2Cl_2). ^{1}H NMR (300 MHz): δ = 0.89 (t, $J_{9,8}$ = 6.6, 9-H_3), 1.10 (s, *t*Bu), 1.22–1.56 (m, 5-H_2, 6-H_2, 7-H_2, 8-H_2), AB signal (δ_A = 2.57, δ_B = 2.71, J_{AB} = 17.6, in addition split by $J_{A,4}$ = 9.0, $J_{B,4}$ = 2.9, 3-H_2), 2.81 (d, $J_{OH,4}$ = 3.8, OH), 4.01 (m_c, 4-H), 4.19 (s, 1-H_2), 7.31–7.48 and 7.61–7.72 (2m, 6 and 4H, respectively, 2 × Ph). IR: $\tilde{\nu}$ = 3450, 2930, 2880, 1720, 1465, 1425, 1110, 825, 740, 705 cm^{-1}. $C_{25}H_{36}O_3Si$ (412.6): calcd. C 72.77, H 8.79; found C 72.91, H 8.69.

(2*S*,4*S*)-1-(*tert*-Butyldiphenylsilyloxy)nonane-2,4-diol ((*S*,*S*)-**32**): A solution of Et_3B (1.11 mL of a 1.0 M solution in THF, 1.11 mmol, 1.1 equiv) was added at RT to a mixture of THF (7 mL) and MeOH (2 mL). After 1 h of stirring, the mixture was cooled to −78 °C. The ketone (*S*)-**31** (0.4166 g, 1.010 mmol, 1.0 equiv) in THF (2 mL) was added and stirring continued for 30 min. Then $NaBH_4$ (0.0420 g, 1.11 mmol, 1.1 equiv) was added, and the mixture was stirred for 3 h. AcOEt (4 mL) and a saturated aqueous solution of NH_4Cl (10 mL) were added. Extraction with *t*BuOMe (3 × 15 mL), concentration in vacuo, azeotropic distillation with MeOH (3 × 15 mL), and flash chromatography (2 cm, #1–6 petroleum ether:*t*BuOMe 8:1; #7–10 petroleum ether:*t*BuOMe 6:1; #11–15 petroleum ether:*t*BuOMe 4:1; #16–20 petroleum ether:*t*BuOMe 3:1; #21–23 petroleum ether:*t*BuOMe 2:1; subsequently petroleum ether:*t*BuOMe 1:1; product in #19–29) yielded (*S*,*S*)-**32** (0.2799 g, 67%). $[\alpha]_D^{22} = +0.3$ (*c* = 2.31 in CH_2Cl_2). The ^{1}H NMR and IR data were identical with those of (*R*,*R*)-**32**.

(2*R*,4*R*)-1-(*tert*-Butyldiphenylsilyloxy)-2,4-nonanediol ((*R*,*R*)-**32**): A solution of Et_3B (18 mL of a 1.0 M solution in THF, 18 mmol, 1.1 equiv) was added at RT to a mixture of THF (80 mL) and MeOH (20 mL). After 1 h of stirring, the mixture was cooled to −78 °C. The ketone (*R*)-**35** (6.9121 g, 16.75 mmol, 1.0 equiv) in THF (10 mL) was added and stirring continued for 30 min. Then $NaBH_4$ (0.6971 g, 18.40 mmol, 1.1 equiv) was added under continuous stirring (3 h). AcOEt (20 mL) and a saturated aqueous solution of NH_4Cl (30 mL) were added. Extraction with *t*BuOMe (3 × 100 mL), concentration in vacuo, azeotropic distillation with MeOH (3 × 40 mL), and flash chromatography yielded (*R*,*R*)-**32** (6.3736 g, 92%). $[\alpha]_D^{23} = -0.3$ (*c* = 2.0 in CH_2Cl_2). ^{1}H NMR (250 MHz): δ = 0.88 (t, $J_{9,8}$ = 6.5, 9-H_3), 1.07 (s, *t*Bu), 1.22–1.60 (m, 3-H_2, 5-H_2, 6-H_2, 7-H_2, 8-H_2), 3.15 (d, *J* = 2.7, 1 OH*), 3.45 (d, *J* = 1.8, 1 OH*), AB signal (δ_A = 3.53, δ_B = 3.60, J_{AB} = 10.1, in addition split by $J_{A,2}$ = 7.1, $J_{B,2}$ = 4.2, 1-H_2), 3.84 (m_c, 4-H), 3.97 (m_c, 2-H), 7.33–7.49 and 7.60–7.71 (2m, 6 and 4H, respectively, 2 × Ph); * exchangeable with D_2O. IR: $\tilde{\nu}$ = 3375, 2930, 2880, 1590, 1465, 1430, 1195, 1110, 935, 825, 740, 705 cm^{-1}. $C_{25}H_{38}O_3Si$ (414.7): calcd. C 72.41, H 9.24; found C 72.38, H 9.11.

(2*R*)-1-(*tert*-Butyldiphenylsilyloxy)-4-methylenenonan-2-ol ((*R*)-**34**): 2-Bromo-1-heptene [35] (12.79 g, 72.23 mmol, 1.5 equiv) in THF (50 mL) was added at 35–40 °C to a vigorously stirred suspension of Mg (2.391 g, 98.39 mmol, 2.0 equiv) in THF (40 mL). The resulting solution was stirred for 4 h at RT and then transferred within 10 min to a −40 °C suspension of CuI (983.7 mg, 5.2 mmol, 0.1 equiv) in THF (30 mL). After 15 min the mixture was treated with (*R*)-**33** (15.05 g, 48.18 mmol) in THF (25 mL), allowed to warm to 0 °C after 12 min, and quenched after 2.5 h with a saturated aqueous solution of NH_4Cl (90 mL). Extraction with *t*BuOMe (3 × 100 mL), drying with Na_2SO_4, and flash chromatography yielded the title compound (18.79 g, 95%). $[\alpha]_D^{21} = +3.0$. ^{1}H NMR (250 MHz): δ = 0.88 (t, $J_{9,8}$ = 6.7, 9-H_3), 1.07 (s, *t*Bu), 1.20–1.48 (m, 6-H_2, 7-H_2, 8-H_2), 1.99 (t, $J_{5,6}$ = 7.5, 5-H_2), 2.09–2.28 (m, 3-H_2), 2.42 (d, $J_{OH,2}$ = 3.1, OH), AB signal (δ_A = 3.57, δ_B = 3.65, J_{AB} = 10.1, in addition split by $J_{A,2}$ = 6.8, $J_{B,2}$ = 4.0, 1-H_2), 3.86 (m_c, 2-H), 4.76 and 4.79 (2 brs, 1'-H_2), 7.30–7.48 and 7.61–7.75 (2m, 6 and 4H, respectively, 2 × Ph). $C_{26}H_{38}O_2Si$ (216.4): calcd. C 76.04, H 9.33; found C 76.35, H 9.52.

(2*R*)-1-(*tert*-Butyldiphenylsilyloxy)-2-hydroxynonan-4-one ((*R*)-**35**): O_3 was bubbled at −78 °C through a solution of the unsaturated alcohol (*R*)-**34** (7.8264 g, 19.06 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) until the blue color persisted (3 h). Addition of PPh_3 (7.869 g, 30.00 mmol, 1.5 equiv), concentrating in vacuo, and flash chromatography yielded the title compound (7.0589 g, 90%). $[\alpha]_D^{22} = -10.1$ (*c* = 2.36 in CH_2Cl_2). ^{1}H NMR (250 MHz): δ = 0.89 (t, $J_{9,8}$ = 6.8, 9-H_3), 1.06 (s, *t*Bu), 1.21–1.37 (m, 7-H_2, 8-H_2), 1.56 (tt, $J_{6,7} = J_{6,5}$ = 7.3, 6-H_2), 2.42 (t, $J_{5,6}$ = 7.4, 5-H_2), 2.53–2.68 (m, 3-H_2), 2.96 (d, $J_{OH,2}$ = 4.1, OH), 3.56–3.68 (m, 1-H_2), 4.18 (brddddd, all values of $J \approx 5.5$, 2-H), 7.32–7.49 and 7.58–7.70 (2m, 6 and 4H, respectively, 2 × Ph). $C_{25}H_{36}O_3Si$ (412.6): calcd. C 72.77, H 8.79; found C 72.77, H 8.80.

(5*S*)-3-Methylenedecane-1,5-diol ((*S*)-**36**): **Method A**: Bu_4NF (0.33 mL of a 1.1 M solution in THF, 0.36 mmol, 2.0 equiv) was added at RT to a stirred solution of silylether (*S*)-**26** (0.0774 g, 0.182 mmol, 1.0 equiv) in THF (1 mL). After 2 h at RT the reaction was quenched with H_2O (5 mL). The mixture was extracted with *t*BuOMe (3 × 15 mL), dried over Na_2SO_4, and purified by flash chromatography (1 cm, #1–6 petroleum ether:*t*BuOMe 4:1; #7–16 petroleum ether:*t*BuOMe 1:1; product in #8–14) to yield diol (*S*)-**36** (0.0334 g, 98%). Chiral gas chromatography (130 °C, 120 kPa H_2, R_T = 19.6 min for (*S*)-**36**, 20.6 min for (*R*)-**36**) revealed *ee* = 99.2%. $[\alpha]_D^{23} = 3.04$ (*c* = 1.11 in $CHCl_3$).

Method B: BuLi (0.12 mL of a 2.27 M solution in cyclohexane, 0.27 mmol, 1.0 equiv) was added at −78 °C to hydroxysulfide (*S*)-**28** (0.0763 g, 0.274 mmol) in THF (3 mL). After 30 min lithium naphthalenide (0.96 mL of a ca. 0.35 M solution in THF, 0.69 mmol, 2.5 equiv) and after another hour $FB(OMe)_2$ (0.05 g of a ca. 80% solution in Et_2O, 0.7 mmol, 3.0 equiv) were added. After 20 min of stirring, the solution was allowed to warm to RT. NaOH (0.99 mL of a 10% aqueous solution, 2.5 mmol, 9 equiv) and H_2O_2 (0.13 mL of a 35% aqueous solution, 1.4 mmol, 5 equiv) were added. After 24 h of stirring at RT, addition of a saturated aqueous $NaHSO_3$ solution (5 mL) and of H_2O (15 mL), extraction with *t*BuOMe (3 × 20 mL), and flash chromatography (1 cm, #1–5 petroleum ether:*t*BuOMe 3:1; subsequently petroleum ether:*t*BuOMe 1:1; product in #9–15) yielded the title compound (0.0285 g, 56%). Chiral gas chromatography (130 °C, 120 kPa H_2, R_T = 19.7 min for (*S*)-**36**, 20.3 min for (*R*)-**36**) revealed *ee* = 96.4%. ^1H NMR (300 MHz): δ = 0.90 (t, $J_{10,9}$ = 6.6, 10-H_2), 1.22–1.55 (m, 6-H_2, 7-H_2, 8-H_2, 9-H_2), 1.67–1.96 (m, 2 × OH), AB signal ($\delta_A \approx 2.09$, $\delta_B \approx 2.29$, $J_{AB} \approx 14.4$, in addition split by $J_{A,5}$ = 9.5, $J_{B,5} \approx 3.0$, 4-H_2), low-field branch of B part superimposed by 2.34 (t, $J_{2,1}$ = 6.3, 2-H_2), 3.77 (t, $J_{1,2}$ = 6.3, 1-H_2), superimposes 3.77 (m_c, 5-H), 5.00 (s, 3 = CH_2). IR: $\tilde{\nu}$ = 3370, 2925, 1725, 1460, 1380, 1265, 1045, 895 cm^{-1}. $C_{11}H_{22}O_2$ (186.3): calcd. C 70.92, H 11.90; found C 70.20, H 11.50. No better CH analysis could be obtained.

Acknowledgement: This work was made possible by the Fonds der Chemischen Industrie through a Doktorandenstipendium for S. W.. We are indebted to Prof. Dr. W. König (Universität Hamburg) for measuring the *ee* value of compound (*R*)-**33** and to Dr. R. O. Duthaler (Ciba-Geigy, Basel) for advice on how to perform reactions with compound **9**.

Received: January 15, 1996 [F280]
Revised: May 3, 1996

[1] *Catalytic Asymmetric Synthesis* (Ed: I. Ojima), VCH, Weinheim, 1993.
[2] Reviews: a) C. H. Heathcock, *Modern Synthetic Methods* **1992**, pp. 3–102; b) C. H. Heathcock, *Aldrichimica Acta* **1990**, *23*, 99–111; c) cf. also the literature cited in S. E. Denmark, B. R. Henke, *J. Am. Chem. Soc.* **1991**, *113*, 2177–2194.
[3] Review: Y. Yamamoto, N. Asao, *Chem. Rev.* **1993**, *93*, 2207–2293.
[4] Review: T. Bach, *Angew. Chem.* **1994**, *106*, 433–435; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 417.
[5] S. Aoki, K. Mikami, M. Terada, T. Nakai, *Tetrahedron* **1993**, *49*, 1783–1792.
[6] a) A. L. Costa, M. G. Piazza, E. Tagliavini, C. Trombini, A. Umani-Ronchi, *J. Am. Chem. Soc.* **1993**, *115*, 7001–7002; cf. also b) P. Bedeschi, S. Casolari, A. L. Costa, E. Tagliavini, A. Umani-Ronchi, *Tetrahedron Lett.* **1995**, *36*, 7897–7900.
[7] a) Original procedure: G. E. Keck, K. H. Tarbet, L. S. Geraci, *J. Am. Chem. Soc.* **1993**, *115*, 8467–8468; b) improved procedure: G. E. Keck, L. S. Geraci, *Tetrahedron Lett.* **1993**, *34*, 7827–7828.
[8] G. E. Keck, D. Krishnamurthy, M. C. Grier, *J. Org. Chem.* **1993**, *58*, 6543–6544. In this paper the absolute configurations of the addition products are drawn with a configuration opposite to the entries in the table.
[9] G. E. Keck, D. Krishnamurty, X. Chen, *Tetrahedron Lett.* **1994**, *35*, 8323–8324.
[10] R. W. Hoffmann, T. Herold, *Chem. Ber.* **1981**, *114*, 375–383.
[11] R. P. Short, S. Masamune, *J. Am. Chem. Soc.* **1989**, *111*, 1892–1894.
[12] E. J. Corey, C.-M. Yu, S. S. Kim, *J. Am. Chem. Soc.* **1989**, *111*, 5495–5496.
[13] P. K. Jadhav, K. Bhat, P. T. Perumal, H. C. Brown, *J. Org. Chem.* **1986**, *51*, 432–439.
[14] H. C. Brown, R. S. Randad, *Tetrahedron* **1990**, *46*, 4463–4472.
[15] T. A. J. van der Heide, J. L. van der Baan, E. A. Bijpost, F. J. J. de Kanter, F. Bickelhaupt, G. W. Klumpp, *Tetrahedron Lett.* **1993**, *34*, 4655–4656.
[16] R. O. Duthaler, A. Hafner, P. L. Alsters, P. Rothe-Streit, G. Rihs, *Pure Appl. Chem.* **1992**, *64*, 1897–1910.
[17] S. Weigand, Diplomarbeit, Universität Göttingen, **1994**.
[18] The enantioselective addition of a chiral (β-bromoallyl)boronate to aldehydes was described by S. Hara, Y. Yamamoto, A. Fujita, A. Suzuki, *Synlett* **1994**, 639–640.
[19] Stereoselective additions of a β-(1-methoxyethylated) allyltributylstannane to aldehydes were described by Y. Nishigaishi, H. Kuramoto, A. Takuwa, *Tetrahedron Lett.* **1995**, *36*, 3353–3356. However, this reagent is conceptually unrelated to the reagents **1**–**9** of Scheme 1.
[20] A. Hafner, R. O. Duthaler, R. Marti, G. Rihs, P. Rothe-Streit, F. Schwarzenbach, *J. Am. Chem. Soc.* **1992**, *114*, 2321–2336; R. O. Duthaler, A. Hafner, P. L. Alsters, G. Bold, G. Rihs, P. Rothe-Streit, B. Wyss, *Inorg. Chim. Acta* **1994**, *222*, 95–113.
[21] In a recent study (G. H. Posner, H. Dai, D. S. Bull, J.-K. Lee, F. Eydoux, Y. Ishihara, W. Welsh, N. Pryov, S. Petr, Jr., *J. Org. Chem.* **1996**, *61*, 671–676) stoichiometric amounts of $TiCl_2(OiPr)_2$, (*R*)-BINOL, and 4 Å molecular sieves were used to induce enantioselectivity in inverse electron demand Diels–Alder reactions between pyrone-3-carboxylates and enol ethers. The critical dependence of the enantiomeric excesses on the nature of the molecular sieves (water content, trace elements) was investigated at length. Hence, in retrospect, our failure to reproduce Keck's best results by his method may have been caused by differences in the molecular sieves. Since molecular sieves are omitted in our protocol, the necessity of exploring which molecular sieves give best results is circumvented.
[22] Preparation of β-substitued allylstannanes: S. Weigand, R. Brückner, *Synthesis* **1996**, 475–483.
[23] (*R*)-**12** was prepared by resolving racemic **12** (synthesized from 2-naphthol and $FeCl_3$ according to L.-F. Tietze, T. Eicher, *Reaktionen und Synthesen im organisch-chemischen Praktikum*, Thieme, Stuttgart, **1981**, 394) by the procedure of D. Cai, D. L. Hughes, T. T. Verhoeven, P. J. Reider, *Tetrahedron Lett.* **1995**, *36*, 7991–7994.
[24] S. Nowotny, S. Vettel, P. Knochel, *Tetrahedron Lett.* **1994**, *35*, 4539–4540.
[25] Method: a) K. N. Narasaka, F.-C. Pai, *Chem. Lett.* **1980**, 1415–1418; b) K. N. Narasaka, F.-C. Pai, *Tetrahedron* **1984**, *40*, 2233–2238; c) M. Sletzinger, T. R. Verhoeven, R. P. Volante, J. M. McNamara, E. G. Corley, T. M. H. Liu, *Tetrahedron Lett.* **1985**, *26*, 2951–2954; d) K.-M. Chen, G. E. Hardtmann, K. Prasad, O. Repic, M. J. Shapiro, *ibid.* **1987**, *28*, 155–158; e) K.-M. Chen, K. G. Gunderson, G. E. Hardtmann, K. Prasad, O. Repic, M. J. Shapiro, *Chem. Lett.* **1987**, 1923–1926.
[26] H. Priepke, *Dissertation*, Universität Würzburg, **1993**.
[27] Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, S. Masamune, K. B. Sharpless, *J. Am. Chem. Soc.* **1987**, *109*, 5765–5780.
[28] S. Weigand, unpublished results.
[29] D. Seebach, R. Dahinden, R. E. Marti, A. K. Beck, D. A. Plattner, F. N. M. Kühnle, *J. Org. Chem.* **1995**, *60*, 1788–1799.
[30] K. Mikami, Y. Motoyama, M. Terada, *J. Am. Chem. Soc.* **1994**, *116*, 2812–2820.
[31] T. J. Boyle, D. L. Barnes, J. A. Heppert, L. Morales, F. Takusagawa, J. W. Connolly, *Organometallics* **1992**, *11*, 1112–1126. T. J. Boyle, N. W. Eilerts, J. A. Heppert, F. Takusagawa, *Organometallics* **1994**, *13*, 2218–2229.
[32] E. J. Corey, M. A. Letavic, M. C. Noe, S. Sarshar, *Tetrahedron Lett.* **1994**, *35*, 7553–7556.
[33] Very recently, J. W. Faller, D. W. I. Sams, and X. Liu (*J. Am. Chem. Soc.* **1996**, *118*, 1217–1218) observed chiral amplification in allyltributylstannane additions to benzaldehyde catalyzed by $Ti(OiPr)_4$/(*R*)-BINOL/ molecular sieves: e.g., (*R*)-Binol of 70% *ee* furnished a product with >95% *ee*. They discuss a dimer of type $Ti_2X_4((R)\text{-BINOL})_2$ as the most active catalyst in this system as opposed, inter alia, to the dimer $Ti_2X_4((R)\text{-BINOL})((S)\text{-BINOL})$.
[34] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.
[35] J. Cousseau, *Synthesis* **1980**, 805–806.