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Enantioconvergent Hydroboration of a Racemic Allene: Enantioselective Synthesis of (*E*)-δ-Stannyl-*anti*-homoallylic Alcohols via Aldehyde Crotylboration

Ming Chen and William R. Roush*

Department of Chemistry, Scripps Florida, Jupiter, Florida 33458, United States

Supporting Information

ABSTRACT: The enantioconvergent hydroboration of racemic allenylstannane (±)-**1** with (^{d}Ipc)$_2$BH converts both enantiomers of (±)-**1** into the enantioenriched crotylborane (*S*)-*E*-**3**. Subsequent crotylboration of aldehydes with (*S*)-*E*-**3** provides (*E*)-stannyl-homoallylic alcohols **5** in good yields and with excellent enantioselectivity.

Asymmetric synthesis of chiral, nonracemic molecules is a major objective in organic chemistry. A wide variety of highly enantiomerically enriched molecules can be generated with excellent selectivity owing to the many classes of highly enantioselective chiral reagents, auxiliaries, and catalysts that have been developed over the past several decades.[1]

The prevailing approach in asymmetric synthesis focuses on introducing chirality in reactions of prochiral substrates using chiral reagents or chiral catalysts. Other strategies, however, are available for the synthesis of highly enantiomerically enriched compounds. Because it is often easier and more cost-effective to synthesize racemates, resolution remains a valuable tool to access highly enantiomerically enriched molecules (especially in the pharmaceutical industry). Kinetic resolution is a well-established approach that enables partial or complete separation of a racemate based on the different rates of reaction of each enantiomer with a chiral, nonracemic reagent or catalyst.[2] However, even in an ideal case, the overall efficiency of kinetic resolution is limited to a theoretical maximum yield of 50%. The other 50% of enantiomeric material is discarded or recycled. Additional strategies, such as dynamic kinetic resolution (DKR),[3] address this limitation when applicable. DKR involves rapid racemization of substrates or symmetrization of reaction intermediates, with product formation occurring under Curtin−Hammett control via a rate-determining enantioselective transition state. In this way, both enantiomers of the substrate are converted into a single enantiomerically enriched product with 100% theoretical yield.

We describe here a remarkable example of the enantioconvergent reaction of a racemic allene to give an enantiomerically enriched product.[4] Unlike dynamic kinetic resolution, the enantioconvergent process does not involve racemization of the substrate or the symmetrization of a reaction intermediate prior to the enantioselective step. Rather, both enantiomers of the racemate are converted into different enantiomerically enriched intermediates by chemically distinct, kinetically controlled pathways. Subsequent transformations of the nonracemic intermediates provide the same enantiomer of a reaction product with high enantiomeric excess.

As part of ongoing studies to expand the utility of the double allylboration chemistry developed in our laboratory,[5] we studied the hydroboration of racemic 3-methyl-allenylstannane (±)-**1** with *d*-diisopinocampheylborane [(^{d}Ipc)$_2$BH]. As depicted in Figure 1, this reaction could lead either to reagent **2** or **3**, which when treated with aldehydes should react to provide **4** or **5**, respectively.[6] The homoallylic alcohol products **4** and **5** are properly functionalized for use in subsequent C−C bond forming reactions.[7] Yet, because (±)-**1** is racemic, we assumed at the outset that the enantioselective hydroboration would need to be occur in the kinetic resolution manifold.[8]

Treatment of (±)-**1** with 1.0 equiv of (^{d}Ipc)$_2$BH at 0 °C in diethyl ether followed by addition of 1.0 equiv of hydrocinnamaldehyde at −78 °C provided (*E*)-δ-stannyl-*anti*-homoallylic alcohol **5a** in 71% yield. *Significantly, **5a** was obtained with 92% ee from racemic (±)-**1**.* Several other aldehydes were also examined in this sequence (Table 1). In all cases, (*E*)-δ-stannyl-*anti*-homoallylic alcohols **5** were obtained in 56−73% yields with high enantioselectivities (88−94% ee[9]); however, the yields of **5** are 81−89% when RCHO is the limiting reagent (0.7 equiv) (Table 1). Each reaction also provided 3−5% of the (*E*)-δ-stannyl-*syn*-homoallylic alcohol isomer **6** (20−30% ee).

Assuming that the crotylboration proceeds through a chairlike transition state,[6] the results in Table 1 indicate that the intermediate produced in the hydroboration of racemic allene (±)-**1** with (^{d}Ipc)$_2$BH is (*S*)-α-tributylstannyl-(*E*)-crotylborane [(*S*)-*E*-**3**] (Figure 2). The Bu$_3$Sn group is positioned α to the boron atom in (*S*)-*E*-**3** presumably due to the ability of the C−Sn bond to interact with the empty p orbital on boron.[10,11] Subsequent crotylboration of aldehydes with (*S*)-*E*-**3** via the chairlike **TS-1** (with equatorial placement of the α-Bu$_3$Sn group) provides **5**.

Based on the data in Table 1, it was immediately apparent that these reactions do not involve the kinetic resolution of (±)-**1** with (^{d}Ipc)$_2$BH, as the maximum yield of the kinetic resolution would be only 50%. Rather, the efficiency and enantioselectivity of this process led to the supposition that hydroboration of (±)-**1** with (^{d}Ipc)$_2$BH converted both allene enantiomers, (*P*)-**1** and (*M*)-**1**, into the same nonracemic intermediate (*S*)-*E*-**3**.

Direct evidence in support of this deduction was obtained by performing the hydroboration of the two enantiomerically enriched allenes, (*P*)-**1** and (*M*)-**1**, with (^{d}Ipc)$_2$BH (Figure 2).[12] Hydroboration of (*P*)-**1** (≥95% ee)[12] with 1 equiv of (^{d}Ipc)$_2$BH at

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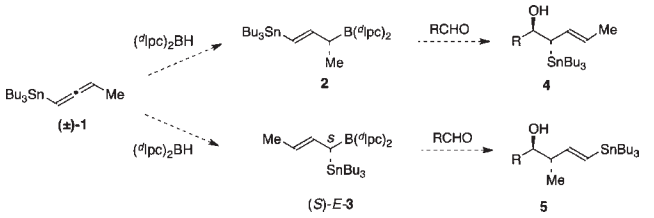
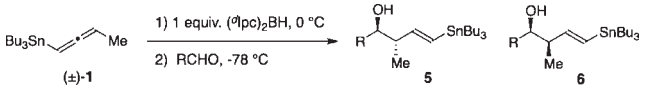


Figure 1. Proposed enantioselective hydroboration of racemic allenylstannane (±)-**1** and subsequent crotylboration reactions.

Table 1. Synthesis of Homoallylic Alcohols 5 from (±)-1[a]



entry	RCHO	product[b]	% yield (5)[b,c]	% ee (5)[d]
1	$Ph(CH_2)_2CHO$	**5a**	71	92
2	$Ph(CH_2)_2CHO$[e]	***ent*-5a**	67 (84)	88
3	$PhCH_2CHO$	**5b**	69	92
4	PhCHO	**5c**	67 (89)	89
5	$BnO(CH_2)_2CHO$	**5d**	73	94
6	$BnOCH_2CHO$	**5e**	70	90
7	PhCH=CHCHO	**5f**	71 (87)	92
8	CyCHO	**5g**	64 (81)	93
9	*t*-Bu[f]	**5h**	56	90[g]

[a] The reactions were performed by treating (±)-**1** in Et_2O (0.1 M) with (^{d}Ipc)$_2$BH (1.0 equiv) at 0 °C followed by addition of RCHO (1.0 equiv) at −78 °C. The mixture was stirred at −78 °C for 8 h. The reactions were terminated by addition of $NaHCO_3$ and H_2O_2 at 0 °C prior to product isolation. [b] Isolated yield of **5**. In addition, small amounts of *syn*-homoallylic alcohols **6** (20−30% ee) were also obtained in each experiment (3−5%). The diastereoselectivity of these reactions was typically ≥15:1 (ratio of **5**/**6**). [c] Yields in parentheses are based on RCHO (0.7 equiv) used as the limiting reagent. [d] Determined by Mosher ester analysis. [e] (^{l}Ipc)$_2$BH was used. [f] Reaction was warmed to ambient temperature after the addition of *t*-BuCHO. [g] Determined by Mosher ester analysis of the diol obtained after ozonolysis of **5h**.

0 °C, followed by addition of hydrocinnamaldehyde at −78 °C, provided alcohol (*R*,*S*)-**5a** in 81−88% yield and >95% ee. Monitoring of this hydroboration reaction by ^{1}H NMR revealed that (*S*)-*E*-**3** is the major allylborane species present (see Supporting Information (SI)). Notably, when (*M*)-**1** (≥95% ee)[12] was treated under identical conditions with 1 equiv of (^{d}Ipc)$_2$BH and then 1 equiv of hydrocinnamaldehyde, the identical alcohol (*R*,*S*)-**5a** was isolated, albeit in reduced yield (42%) and diminished enantioselectivity (82% ee). Here again, (*S*)-*E*-**3** was observed when the hydroboration of (*M*)-**1** with (^{d}Ipc)$_2$BH was monitored by ^{1}H NMR (data not shown). Based on the mechanism discussed subsequently, the hydroboration of allene (*P*)-**1** with (^{d}Ipc)$_2$BH likely is a matched double asymmetric reaction, while hydroboration of allene (*M*)-**1** with (^{d}Ipc)$_2$BH is presumed to be the mismatched pair.[13] The minor *syn* diastereomer **6a** and *ent*-**6a** from these two experiments are enantiomeric; thus, an enantioconvergent process is not dominant in the pathway(s) leading to the minor *syn* diastereomers **6a**/*ent*-**6a**. The diminished chemical efficiency of the mismatched hydroboration of (*M*)-**1** is likely due to the competitive addition of

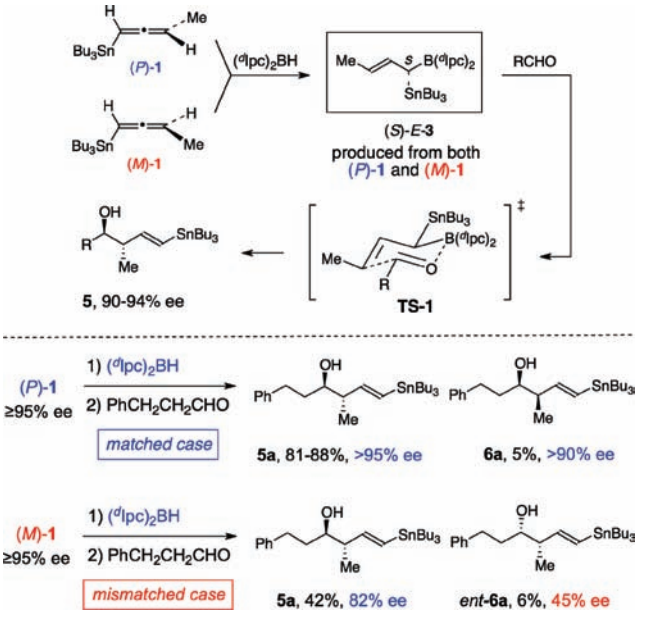


Figure 2. Proposed reaction pathway and hydroboration−allylboration of single enantiomeric allenes (*P*)-**1** and (*M*)-**1**.

boron to the central allene carbon in this series.[8b,c] The overall chemical efficiency and enantioselectivity of the reactions of the racemic allene **1** summarized in Table 1 are thus approximated by the weighted average of the efficiencies (yield and enantioselectivity) of the matched and mismatched double asymmetric hydroboration reactions of (*P*)-**1** and (*M*)-**1**, respectively.

We considered the possibility that if (*P*)-**1** and (*M*)-**1** equilibrate under the hydroboration conditions, the results in Table 1 and Figure 2 could be explained by a DKR.[4b] However, this possibility was eliminated by experiments in which single enantiomer allene (*P*)-**1** (≥95% ee) was treated with 0.5 equiv of (^{d}Ipc)$_2$BH or (^{l}Ipc)$_2$BH. In all cases the recovered allene (≥95% ee) showed no detectable sign of racemization even when the hydroboration reactions were extended to 12 h at 0 °C (see Table S1 in SI). Therefore, the enantioconvergent hydroboration of racemic **1** does not involve a DKR process.

As depicted in Figure 3, we propose that the hydroboration of allene (*P*)-**1** with (^{d}Ipc)$_2$BH occurs on the *re*-face (bottom face, as drawn) of the methyl substituted olefin unit of (*P*)-**1**, *anti* to the Bu_3Sn group to give intermediate (*R*)^d-*Z*-**7**. The face selectivity of this step is consistent with the known enantioselectivity of hydroboration of (*Z*)-olefins by (^{d}Ipc)$_2$BH,[8b,14] as well as by the preference of allene hydroboration to occur *anti* to bulky substituents at the distal position.[5,15h,15i] The hydroboration of (*P*)-**1** by (^{d}Ipc)$_2$BH is thus stereochemically matched. The resulting crotylborane (*R*)^d-*Z*-**7** can undergo a stereochemically controlled, stereospecific, suprafacial 1,3-boratropic shift,[15] to give (*S*)^d-*E*-**3**. As noted in the second equation of Figure 3, hydroboration of (*P*)-**1** on the olefin adjacent to the Bu_3Sn group inexorably leads, via σ bond rotations and the indicated stereospecific 1,3-boratropic shifts, to the diastereomeric reagent (*R*)^d-*E*-**3** (which will undergo crotylboration of aldehydes to give *ent*-**5**).[16] Thus, the regiochemistry of the enantioselective hydroboration (e.g., right- vs left-hand allenyl double bond) determines the absolute stereochemistry of the 1,1-boryl stannyl stereocenter in intermediate **3**. To explain the enantioconvergent hydroboration process, we propose that hydroboration of the

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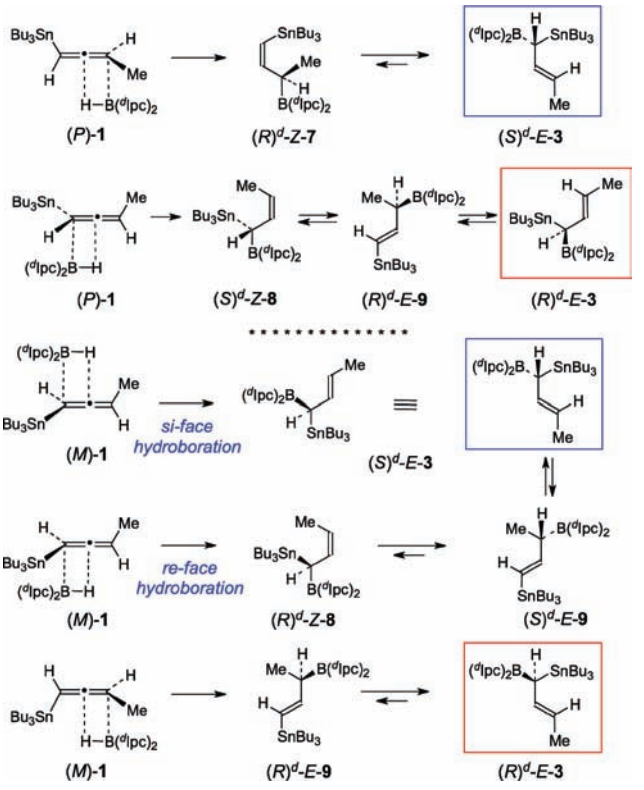

Figure 3. Proposed hydroboration pathways for the two enantiomers of allenylstannane (±)-**1**. The (*R*)- or (*S*)-descriptor defines the configuration of the allylic borane stereocenter in each intermediate; *E* and *Z* denote the double bond configuration, and the "d" superscript denotes the absolute configuration of the Ipc_2B-unit. Thus, $(S)^d$-*E*-**3** and $(R)^d$-*E*-**3** are diastereomers and not enantiomers.

enantiomeric allene (*M*)-**1** with $(^dIpc)_2BH$ occurs (preferentially) on the *si*-face (top face, as drawn in the third equation of Figure 3) of the Bu_3Sn-substituted olefin of (*M*)-**1**, *syn* to the methyl group, to provide, directly, reagent $(S)^d$-*E*-**3**, the same intermediate as obtained from (*P*)-**1** in the first equation. The sense of hydroboration in the conversion of (*M*)-**1** to (*S*)-*E*-**3** is again consistent with the enantioselectivity of hydroboration of (*Z*)-olefins by $(^dIpc)_2BH$[8b,14] but is mismatched in that the hydroboration occurs on the sterically disfavored olefin face *syn* to the distal methyl substituent. A second possible pathway that permits (*S*)-*E*-**3** to be generated from (*M*)-**1** is shown in the fourth equation of Figure 3. In this case, hydroboration of (*M*)-**1** by $(^dIpc)_2BH$ on the Bu_3Sn-substituted olefin *anti* to the distal methyl group requires that $(^dIpc)_2BH$ interact with the allene in a manner opposite to that previously documented[8b,14] for hydroborations of (*Z*)-alkenes by this reagent (hence, this pathway is stereochemically disfavored on the part of $(^dIpc)_2BH$)). The resulting product, $(R)^d$-*Z*-**8**, can isomerize to (*S*)-*E*-**3** by way of $(S)^d$-*E*-**9** via two successive σ bond rotations and suparafacial 1,3-boratropic shifts.[15] These insights indicate that the "top" vs "bottom" sense of allene hydroboration does not influence the enantiomeric purity of the 1,1-boryl stannyl stereocenter in **3**. However, as is the case with (*P*)-**1**, hydroboration of (*M*)-**1** at the opposite end of the allene, in this case on the methyl-substituted allenyl double bond as shown in the fifth equation of Figure 3, inevitably produces the diastereomeric reagent, $(R)^d$-*E*-**3**. The latter pathway presumably contributes to the reduced enantioselectivity of the crotylboration reactions of the reagent generated from (*M*)-**1** and $(^dIpc)_2BH$.[16]

This analysis also provides the basis to rationalize that the dominant pathways that give rise to the minor *syn*-homoallylic alcohols **6** (Table 1) are not enantioconvergent (Figure 2): **6a** [from (*P*)-**1**] derives from $(S)^d$-*Z*-**8**, whereas *ent*-**6a** [from (*M*)-**1**] derives at least in part from $(R)^d$-*Z*-**8**.

The 1,3-boratropic shifts presented in Figure 3 are concerted, stereospecific suparafacial sigmatropic rearrangements that involve the transfer of chirality from one center (in the precursor) to a new center in the product. As such, the stereochemistry at the new center established in the product of each boratropic shift [e.g., the α-boryl-α-stannyl center in (*S*)-*E*-**3**] is determined by the configuration and enantiomeric purity of the stereocenter in the 1,3-transposed precursor [e.g., (*R*)-*Z*-**7** in the hydroboration of (*P*)-**1**].[15f,g] Thus, the success of this method for generation of (*S*)-*E*-**3** translates directly to the enantioselectivity of the allene hydroboration step using $(^dIpc)_2BH$. This is in contrast to our recent report on the hydroboration of the parent monosubstituted allenylstannane,[15k] in which the stereochemistry and enantiomeric purity of the α-boryl-α-stannyl center is induced by the diisopinocampheylborane unit during the 1,3-boratropic shift.

Other racemic allenes are also substrates for the enantioconvergent hydroboration reaction. As illustrated in Table 2, subjection of racemic allene (±)-**10** to the standard hydroboration−crotylboration conditions using 1 equiv of $(^dIpc)_2BH$ and 1 equiv of aldehyde provides the (*E*)-δ-stannyl-*anti*-homoallylic alcohols **12a** and **12b** in 71−76% yields with excellent diastereo- and enantioselectivities (>25:1 dr, 94% ee). Similarly, homoallylic alcohols **12c** and **12d** were obtained in 59−61% yields and 95−97% ee, along with approximately 10% of (*E*)-δ-stannyl-*syn*-homoallylic alcohols **13c** and **13d** from racemic allene (±)-**11**.[17] The stoichiometries, chemical efficiencies, and enantioselectivity of these reactions, as for those in Table 1, are consistent with both enantiomers of racemic allenes (±)-**10** and (±)-**11** undergoing enantioconvergent hydroboration reactions with $(^dIpc)_2BH$.

In conclusion, we have documented a remarkable enantioconvergent and highly enantioselective allene hydroboration reaction. Hydroboration of (±)-**1** with $(^dIpc)_2BH$ converts both enantiomers, (*P*)-**1** and (*M*)-**1**, into the same intermediate, (*S*)-*E*-**3**. Subsequent crotylboration of (*S*)-*E*-**3** with a variety of aldehydes provides (*E*)-δ-stannyl-*anti*-homoallylic alcohols **5** in good yields and high enantioselectivities.

There are a few points worth noting. First, these studies constitute the first examples of the highly enantioselective hydroborations of chiral allenes.[8] The sense of asymmetric induction is dictated by the enantioselectivity of the chiral, nonracemic borane, $(^dIpc)_2BH$, which parallels the enantioselectivity of the hydroboration of (*Z*)-alkenes with this reagent.[14] Second, the hydroboration of the two enantiomers of racemic allene **1** proceed with different modes of allene addition (Figure 3), a regiochemical divergence also noted by Bergman.[4a] The crotylborane reagent (*S*)-*E*-**3** is then obtained from the initial hydroboration intermediates, (*R*)-*Z*-**7** and/or (*R*)-*Z*-**8**, via reversible but stereospecific 1,3-boratropic shifts.[15] *The ability of both allene enantiomers to converge to a single, highly enantioselective reagent (S)-E-3 via this hydroboration sequence represents a remarkable example of the enantioconvergent reaction of the two enantiomers of a racemate.* Therefore, synthesis of enantiomerically pure allenylstannanes (*P*)-**1** or (*M*)-**1** is not necessary to obtain homoallylic alcohols **5** with high enantiomeric excess, nor is it necessary to utilize a kinetic resolution in the hydroboration

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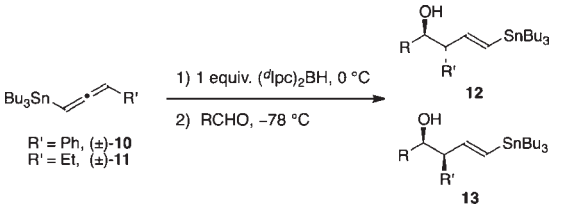
Table 2. Enantioconvergent Hydroboration and Allylboration Reactions of Racemic Allenes (±)-10 and (±)-11[a]



allene	RCHO	ratio (12/13)	% yield[b]	% ee (12)[c]
10	$Ph(CH_2)_2CHO$	>25:1	71 (**12a**)	94
10	PhCHO	>25:1	76 (**12b**)	94
11	$Ph(CH_2)_2CHO$	5:1	59 (**12c**) + 10 (**13c**)	95
11	PhCHO	6:1	61 (**12d**) + 11 (**13d**)	97

[a] The reactions were performed by treating (±)-**10** or (±)-**11** in Et_2O (0.1 M) with (^{d}Ipc)$_2$BH (1.0 equiv) at 0 °C for 5 h followed by addition of RCHO (1.0 equiv) at −78 °C. The mixture was stirred at −78 °C for 8 h. The reactions were terminated by addition of $NaHCO_3$ and H_2O_2 at 0 °C prior to product isolation. [b] Isolated yield of the indicated products (listed in parentheses). [c] Determined by Mosher ester analysis.

step. Finally, the highly diastereo- and enantioselective stannylcrotylboration reaction described here, however, provides *anti*-3-alkyl-homoallylic alcohols with an (*E*)-vinylstannane that can be used directly in a variety of C−C bond-forming reactions.[7]

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and spectroscopic data for all new compounds. Control experiments, stereochemistry assignments, and results of hydroboration of (P)-1 with dicyclohexylborane. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
roush@scripps.edu

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(12) Racemic allenylstannane **1** is prepared in two steps from commercially available (±)-3-butyn-2-ol using the route described for (*M*)-**1** and (*P*)-**1**. The enantiomeric purity of allenes (*M*)-**1** and (*P*)-**1** was determined by Mosher ester analyses of the homopropargyl alcohols derived from their BF_3•Et_2O catalyzed propargylation reactions of hydrocinnamaldehyde. (a) Marshall, J. A.; Lu, Z.-H.; Johns, B. A. *J. Org. Chem.* **1998**, *63*, 817. (b) Marshall, J. A.; Chobanian, H. *Org. Synth.* **2005**, *82*, 43.

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(16) The preference for the α-stannyl group to occupy an equatorial position in the transition state overrides the enantioselectivity of the $(Ipc)_2$B-unit, as shown in ref 15k. Thus, the reactions of $(S)^d$-*E*-**3** and $(R)^d$-*E*-**3** with aldehydes will lead to enantiomeric homoallylic alcohols **5a** and *ent*-**5a**.

(17) The decreased diastereoselectivity with **11** may be due to decreased *si*-face hydroboration of the (*M*) enantiomer of **11**.