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Synthesis of Highly Enantioenriched Chiral α-Aminoorganotins via Diastereoselective Ring Opening of Chiral *N*-(Arenesulfonyl) 2-Tributylstannyloxazolidines

Vincent Coeffard,[†] Erwan Le Grognec,[†] Isabelle Beaudet,[†] Michel Evain,[‡] and Jean-Paul Quintard*,[†]

[†]*Université de Nantes, CNRS, Chimie et Interdisciplinarité: Synthèse, Analyse, Modélisation (CEISAM), UMR CNRS 6230, UFR des Sciences et des Techniques, 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France, and* [‡]*Université de Nantes, CNRS, Institut des Matériaux Jean Rouxel, UMR CNRS 6502, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France*

jean-paul.quintard@univ-nantes.fr

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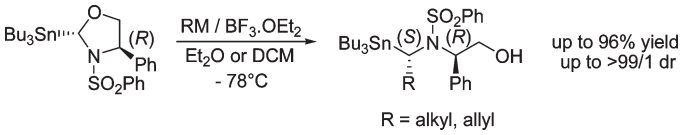

trans-*N*-(Arenesulfonyl)-2-tributylstannyloxazolidines derived from (*R*)-phenylglycinol were diastereoselectively ring-opened by soft organometallic reagents in the presence of $BF_3 \cdot OEt_2$. Both higher order organocuprates and allyltributyltin afforded the desired products in good-to-excellent yields and high diastereoselectivities (dr up to 99/1). The stereochemical assignments of tributylstannyl-*β*-aminoalcohols were firmly established from NMR data and after determination of several radiocrystallographic structures. Mechanisms were proposed in order to rationalize the observed selectivities.

Introduction

The importance of enantioenriched chiral α-heterosubstituted organolithium species as synthetic tools able to afford selectively bioactive pharmaceuticals or their epimers is fully recognized and still induces considerable attention in organic synthetic chemistry even considering only oxygen and nitrogen as heteroatoms.[1,2]

α-Aminoorganolithiums are generally obtained by sulfur−lithium exchange,[3] diastereoselective deprotonation of chiral substrates by organolithiums,[4] or by enantioselective deprotection of prochiral substrates by an organolithium reagent complexed with an enantiopure diamine.[5] In this last case, the complex *sec*-butyllithium:(−)-sparteine has been widely used due to the commercial availability of this chiral diamine,[6] but when the anionic species of the reversed

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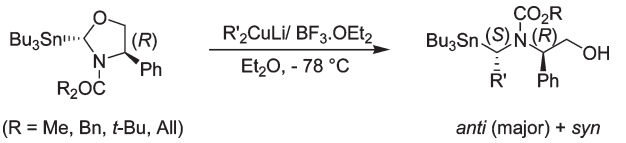
configuration is required, (+)-sparteine[7] or (+)-sparteine surrogates[8] have to be prepared. Apart from this practical aspect, the anionic species were obtained as organolithium: chiral ligand complexes, a situation which can modify their properties by strongly favoring one diastereomer of the obtained reagent as pointed out recently in the case of α-lithiated benzyl carbamates.[2b]

An alternative approach allowing access to chiral α-aminoanions uncomplexed with a diamine is the transmetalation of appropriate α-aminoorganotins with *n*-alkyllithiums.[1,9] While the preparation of dialkylaminomethyllithiums through this route was developed 40 years ago[10,11] the preparation of enantioenriched α-aminoanions has been limited by the availability of the appropriate precursors.

The pioneering syntheses of chiral α-aminoorganostannanes were based on the *N*-alkylation of oxazolidin-2-ones or imidazolidin-2-ones with α-haloalkyltins[12,13] or with α-mesylalkyltins,[14] substitution of chiral sulfones by stannyl-anions,[15] deprotonation/stannylation sequences on chiral substrates,[16] or deprotonation of achiral ones using a *sec*-butyllithium/chiral diamine system.[6a,17] Other routes involving a Mitsunobu reaction on enantioenriched α-stannyl alcohols obtained by reduction of acyltins have been used by Chong et al. to obtain α-aminoorganotins with enantiomeric excesses of up to 94%.[18] However, problems were encountered in the scale-up of this reaction; therefore, other methods involving separation of the chiral α-aminoorganotins as diastereomeric amides derived from *O*-methylmandelic acid[19] or stannylation

SCHEME 1



(R = Me, Bn, *t*-Bu, All) *anti* (major) + *syn*

of chiral *tert*-butanesulfinimines[20] have been developed by the same group.

In this context, we have recently developed a new access to chiral α-amino-organostannanes based on the stereoselective ring opening of chiral *N*-(alkoxycarbonyl)-2-tributylstannyloxazolidines derived from (*R*)-phenylglycinol (Scheme 1).[9e,21,22]

This method offers some advantages owing to the commercial availability of both enantiomers of this *β*-aminoalcohol and to the good stability of diethoxymethyltributyltin[23] used as precursor in the preparation of the 2-tributylstannyloxazolidine.[24] Thus, this methodology has been applied to the preparation of highly enriched α-aminoanions both from transmetalation with *n*-butyllithium of the derived stannylated oxazolidine-2-ones[25] or from transmetalation of the corresponding *O*-silylated derivatives allowing the synthesis of alafosfalin.[22]

In these reactions, the main drawback is the required purification on silica gel of the *anti* diastereomer from the *syn* in order to obtain the desired precursor as a pure compound. Fortunately, we were delighted to observe that some test reactions carried out with *N*-(arenesulfonyl)-2-tributylstannyloxazolidines gave rise to the corresponding tributylstannyl-*β*-aminoalcohols with excellent diastereoselectivities (dr > 99%). These exciting results prompted further interest, when we pointed out a possible electrochemical removal of the *N*-arenesulfonyl moiety (which is incompatible with a transmetalation reaction by *n*-butyllithium) without *β*-elimination of the tributylstannyl group.[26]

Therefore, a careful exploration of the stereoselective ring opening of *N*-(arenesulfonyl)-2-tributylstannyloxazolidines is of high importance since it should afford well-defined and highly enantioenriched chiral α-aminoorganotins without any tedious purification. These chiral organotin compounds should be of interest both for the synthesis of enantioenriched α-aminoanions and for cross-coupling reactions.[27]

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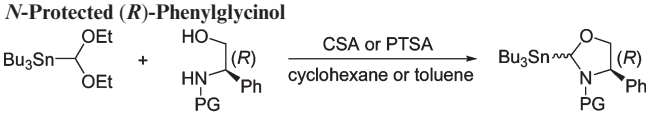
TABLE 1. Transacetalization of Diethoxymethyltributyltin 1a with *N*-Protected (*R*)-Phenylglycinol



1a **2-7**

entry	PG	product	yield (%)[a]	dr (*trans*/*cis*)[b,c]
1	COPh	**2**	42	90/10
2	Tf	**3**	43	>99/1
3	*p*-Ns	**4**	66	92/8
4	Ts	**5**	73	70/30
5	SO_2Ph	**6**	60	92/8
6	SO_2Me	**7**	75	70/30

[a]Yields in isolated products (unoptimized for **2** and **3**). [b]The identification of the *trans* and *cis* isomers was achieved on the basis of a detailed NMR analysis (vide infra) and by consideration of the $[\alpha]_D$ values. Furthermore, a radiocrystallographic structure was obtained for **4**-*trans*. [c]Determined by HPLC or ^1H NMR on the crude.

Herein, we report our results in terms of their scope and limitations by evaluating the influence of the nitrogen protecting group both on the reactivity of the 2-tributylstannyloxazolidines and on the diastereoselectivity of the ring-opening reaction. Furthermore, transition state models are proposed to rationalize the observed results.

Results

Because of the influence of the nitrogen protecting group in the ring-opening reaction of *N*-(alkoxycarbonyl)-2-tributylstannyloxazolidines,[21,22] we first decided to explore the reactivity of analogues protected as arylamides or as sulfonamides. For this purpose, *N*-protected 2-tributylstannyloxazolidines **2**−**7** were prepared through transacetalization of the readily available diethoxymethyltributyltin **1a** and appropriate *N*-protected (*R*)-phenylglycinol in the presence of camphorsulfonic acid (CSA) or paratoluenesufonic acid (PTSA). As previously reported, this reaction requires phenylglycinol bearing an electron-withdrawing group on nitrogen, so we turned our attention to benzamide and sulfonamides nitrogen protecting groups since both of them are strong electron-withdrawing groups allowing an easier cyclization (Table 1).[24]

In every case, the transacetalization reaction was stopped immediately after the consumption of diethoxymethyltributyltin **1a** (TLC monitoring, see Experimental Section). The *N*-protected 2-tributylstannyloxazolidines were obtained in moderate-to-good yields with a strong preference for the *trans* isomer, which appears to be the kinetic product of the reaction in line with previous studies.[24] Accordingly, an attempt to increase the yield by warming the reaction mixture for 30 min after consumption of **1a** induced a higher isomerization rate (entry 4). The *trans* or *cis* configuration was firmly established on the basis of the ^1H and ^{13}C NMR spectra using $^nJ_{Sn-C}$, $^nJ_{Sn-H}$, and $^3J_{H-H}$ coupling constants combined with NOE experiments.[28] Moreover, we were pleased to obtain a radiocrystallographic structure for **4**-*trans* that corroborates previous NMR assignments and exhibits the occurrence of a π-stacking between the two aromatic rings accompanied by chelation of the tin center by an oxygen of the sulfonyl group ($d_{Sn-O} < 3$ Å in **4**-*trans*, see Figure 1).

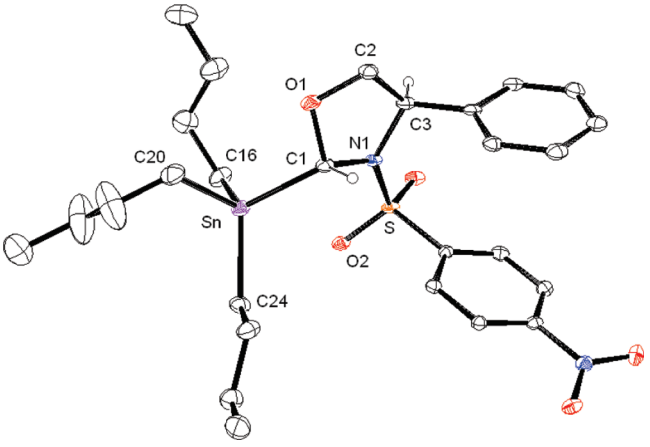


FIGURE 1. ORTEP view of compound **4**-*trans* with thermal ellipsoids drawn at the 30% probability level (except for chiral centers, hydrogens are omitted for clarity). Selected bond lengths (Å) and angles (deg) (average of the two molecules contained in the unit cell): Sn−C1 = 2.19, C1−O = 1.42, C1−N1 = 1.48, N1−C3 = 1.49, C2−C3 = 1.54, Sn−O2 = 2.96, S−O2 = 1.44, CNT(Ph)−CNT(Ph-NO2) = 4.13; Sn−C1−O1 = 107.04, Sn−C1−N1 = 120.57; C1−N1−C3 = 109.98, C1−N1−S = 127.11, C3−N1−S = 116.63, C3−C2−O1 = 106.29, C1−Sn−C16 = 109.49, C1−Sn−C2O = 100.53, C1−Sn−C24 = 112.34, C24−Sn−C20 = 106.46, C20−Sn−C16 = 111.20, C24−Sn−C16 = 115.57, Sn−C1−O1−C2 = −168.15, Sn−C1−N1−C2 = 146.44. For further details, see Supporting Information.

The reactivity of these new chiral *N*-protected 2-tributylstannyloxazolidines **2**−**7** was then examined upon treatment with organocopper reagents in the presence of a Lewis acid. Ring opening by the $Me_2CuLi\cdot LiI/BF_3\cdot OEt_2$ system was chosen as a model reaction and was carried out at −78 °C in diethyl ether using 3 equiv of $Me_2CuLi\cdot LiI$ and 4 equiv of $BF_3\cdot OEt_2$ (Table 2).

In these experimental conditions, both oxazolidines **2**-*trans* and **3**-*trans* did not lead to ring-opening products, whereas **4**-*trans* furnished the desired product with a very high diastereoselectivity along with a low yield (entries 1−3). In contrast, we were pleased to find that ring opening of **5**-*trans* and **6**-*trans* afforded the corresponding tributylstannyl-β-aminoalcohols **5a**-*anti* and **6a**-*anti* in good yields and excellent diastereoselectivities (entries 4 and 5). It should be noted that under these experimental conditions, the oxazolidines **5**-*cis* and **6**-*cis* appeared to be unreactive and were recovered. In order to examine the influence of an *N*-alkylsulfonyl group instead of an *N*-arylsulfonyl group, compound **7**-*trans* was reacted similarly ($Me_2CuLi\cdot LiI$ in the presence of $BF_3\cdot OEt_2$ in ether at −78 °C) to afford **7a** with a lower selectivity (**7a**-*anti*/**7a**-*syn* = 90/10). Finally, starting from the trimethylstannyl analogue of **5** (compound **8** obtained from diethoxymethyltrimethyltin **1b**), we have shown that **8**-*trans* reacts immediately with $Me_2CuLi\cdot LiI$ in the presence of $BF_3\cdot OEt_2$ at −78 °C to afford the ring-opening product as a single diastereomer (**8a**-*anti* by comparison of its NMR data and $[\alpha]_D$ value with those of **5a**-*anti*; Scheme 2). In this series, **8**-*cis* appeared to be much less reactive than **8**-*trans* but reacted to afford **8a**-*anti*, probably after a primary isomerization into **8**-*trans*.[29]

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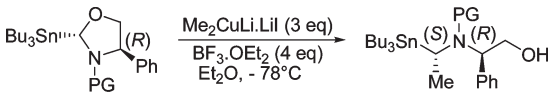
TABLE 2. Diastereoselective Ring Opening of *trans N*-Protected 2-Tributylstannyloxazolidines 2−7 with the $Me_2CuLi \cdot LiI/BF_3 \cdot OEt_2$ System

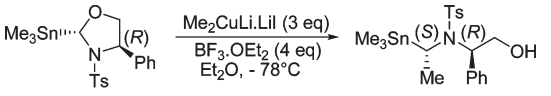


2-7 **4a-7a**

entry	oxazolidine[a]	PG	product	yield (%)	dr (*anti*/*syn*)[c,d]
1	**2**	COPh		[b]	no reaction
2	**3**	Tf		[b]	no reaction
3	**4**	*p*-Ns	**4a**	6	>99/1
4	**5**	Ts	**5a**	76	98/2
5	**6**	SO_2Ph	**6a**	96	98.5/1.5
6	**7**	SO_2Me	**7a**	40	90/10

[a]Reactions were carried out with oxazolidines of *trans* configuration. [b]The starting oxazolidine was recovered. [c]Determined by HPLC on the crude. [d]The configuration of the major diastereomer was assigned as *anti* by comparison of the sign and of the magnitude of the specific rotation with those of **6b**, which was shown to have an *anti* configuration on the basis of its X-ray analysis (vide infra). Furthermore, several *syn* isomers were obtained from magnesium cyanocuprates, allowing a convergent set of information by consideration of the specific rotation, NMR data, R_f values, and X-ray structures on the whole series of obtained compounds (see Table 3, Figure 2, and Experimental Section).

SCHEME 2



8-*trans* Yield = 54% **8a-*anti***

It is also worth noticing that the lack of reactivity of the heterocycles **2**−**4**-*trans* can be explained by electronic factors. Indeed, high electron-withdrawing groups such as Bz, Tf, or *p*-Ns strongly decrease the electronic density on nitrogen (which appears to be planar in the radiocrystallographic structure of **4**-*trans*, Figure 1) preventing the n(N) → σ^*(C−O) electron delocalization (endo anomeric effect) and decreasing the reactivity of the oxazolidine ring.[30]

Among all nitrogen protecting groups investigated, the benzenesulfonyl and paratoluenesulfonyl ones were found to give the most impressive results whereby ring-opening reaction of **5** and **6** furnished **5a** and **6a** in both high yields and diastereoselectivities (entries 4 and 5). With these two protecting groups, we can expect similar trends, but the lower reduction potential required to remove the benzenesulfonyl protection offers an additional advantage for this group.[31]

Ring Opening of *N*-(Benzenesulfonyl)-2-tributylstannyloxazolidines Derived from (*R*)-Phenylglycinol. Having established the most suitable nitrogen protective groups, we next investigated the ring-opening reaction with various organometallic reagents in order to gain more insight into the generality of this methodology. In a first step, the heterocycle **6**-*trans* was allowed to react with soft organometallic reagents (3 equiv) in the presence of $BF_3 \cdot OEt_2$ (4 equiv) at −78 °C in diethyl ether or dichloromethane. The obtained results are reported in Table 3.

As would be expected from previous results with $Me_2CuLi \cdot LiI$ (Table 2, entry 5), the treatment of **6**-*trans* with $Bu_2Cu(CN)Li_2$ and *i*-$Bu_2Cu(CN)Li_2$ in the presence of $BF_3 \cdot OEt_2$ gave the tributylstannyl-β-aminoalcohols **6b** and **6c** in good yields and with a very high *anti* preference (Table 3, entries 1−3). Only a minor amount of the diastereomer **6c**-*syn* was detected by HPLC, and we were unable to observe **6b**-*syn* from the crude reaction mixture. The absolute configuration of the new stereogenic center was unambiguously confirmed for **6b**-*anti* on the basis of its X-ray crystallographic analysis, which pointed out a strong interaction of an oxygen of the sulfonyl group with the tin center: $d_{Sn-O} \approx 3$ Å (Figure 2).

Reaction of **6**-*trans* with the bulky organocopper reagent *s*-$Bu_2Cu(CN)Li_2$ led to the expected compound **6d**-*anti* in low yield and high *anti* diastereoselectivity (29%, dr >99/1, entry 4) along with the reduction product **6e** (R = H, 60%). The steric hindrance seems of high importance, since *t*-$Bu_2Cu(CN)Li_2$ afforded only **6e** in 66% yield (entry 5) without the expected ring-opening product (R = *t*-Bu).

When allylic reagents were used, the *anti* preference remains the general trend, as exemplified by the reaction involving allyltributyltin or methallyltributyltin of dichloromethane, which afforded, respectively, **6h** and **6i** in good yields and high diastereoselectivities in favor of the *anti* isomer (entries 10 and 11). Like **6b**-*anti*, the configuration of **6h**-*anti* was firmly established on the basis of its radiocrystallographic analysis (Figure 2), which exhibits a strong interaction between the tin center and a sulfonyl oxygen: $d_{Sn-O} \approx 3$ Å.

Entries 6−9 underline the dramatic influence on the diastereoselectivity of the counterion of the cuprate reagent. While reaction of **6**-*trans* with $Me_2CuLi \cdot LiI$ led exclusively to the alcohol **6a**-*anti* (entry 1), exposure of the same substrate with the magnesio equivalent $Me_2CuCN(MgBr)_2$ gave rise to a mixture of alcohols **6a**-*anti*/**6a**-*syn* (dr = 69/31, entry 6). In a similar manner, exposure of **6**-*trans* to various magnesio organocopper reagents always produced a diastereomeric mixture of the tributylstannyl-β-aminoalcohols in comparable amounts (entries 7−9). As shown previously with lithium organocopper reagents, increasing the bulk of the alkyl group in the magnesio organocopper reagent increases the yield in reduction product **6e** (entry 8).

The comparison between allyltributyltin and lithium diallylcyanocuprate as nucleophiles was investigated. We considered the reaction with lithium diallylcyanocuprate using $BF_3 \cdot OEt_2$ as Lewis acid in diethyl ether, but compound **6h** was not obtained. When the reaction was performed in THF, a transmetalation reaction occurred on the Sn−C bond in **6**-*trans*. Another attempt was done with diphenylcyanocuprate, but we were unable to observe the expected functional benzyltin **6** (with R = Ph).

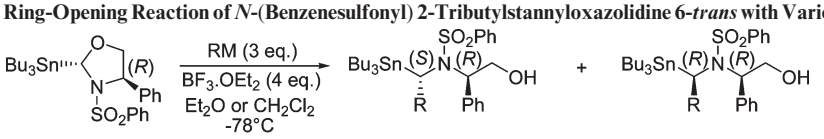
Ring Opening of *N*-(Paratoluenesulfonyl)-2-tributylstannyloxazolidines Derived from (*S*)-Valinol, (*S*)-Alaninol, and (*R*)-Phenylglycinol. To get a better understanding of the mechanism, the influence of the substituent borne by the chiral β-aminoalcohol on diastereoselectivity was examined. Accordingly, phenylglycinol was successively changed into valinol and alaninol. Ring-opening reactions were performed with *trans*-*N*-(paratoluenesulfonyl)-2-tributylstannyloxazolidines, which behave like the *N*-(benzenesulfonyl) ones in terms of reactivity and diastereoselectivity (Table 4).

Replacing the phenylglycinol auxiliary with that derived from alanine (R^1 = Me) and valine (R^1 = *i*-Pr) gave varying ratios of ring-opening compounds. Indeed, the bulk of the

(30) Sélambarom, J.; Monge, S.; Carré, F.; Roque, J. P.; Pavia, A. A. *Tetrahedron* **2002**, *58*, 9559–9568.

(31) Coeffard, V.; Thobie-Gautier, C.; Beaudet, I.; Le Grognec, E.; Quintard, J.-P. *Eur. J. Org. Chem.* **2008**, 383–391.

TABLE 3. Diastereoselective Ring-Opening Reaction of *N*-(Benzenesulfonyl) 2-Tributylstannyloxazolidine 6-*trans* with Various Organometallic Reagents



6-*trans* **6a-6i *anti*** **6a-6i *syn***

entry	reagent, solvent	R	product	yield (%)	dr (*anti*/*syn*)[b]
1	$Me_2CuLi\cdot LiI$, Et_2O	Me	**6a**	96	98.5/1.5
2	$Bu_2Cu(CN)Li_2$, Et_2O	Bu	**6b**	80	>99/1
3	*i*-$Bu_2Cu(CN)Li_2$, Et_2O	*i*-Bu	**6c**	88	96/4
4	*s*-$Bu_2Cu(CN)Li_2$, Et_2O	*s*-Bu (or H)	**6d** + (**6e**)[a]	29 + (60)[a]	>99/1
5	*t*-$Bu_2Cu(CN)Li_2$, Et_2O	*t*-Bu → H	(**6e**)[a]	(66)[a]	
6	$Me_2CuCN(MgBr)_2$, Et_2O	Me	**6a**	85	69/31
7	*i*-$Bu_2CuCN(MgCl)_2$, Et_2O	*i*-Bu	**6c**	71	56/44
8	*i*-$Pr_2CuCN(MgCl)_2$, Et_2O	*i*-Pr (or H)	**6f** + (**6e**)[a]	50 + (38)[a]	51/49
9	$Bn_2CuMgCl.MgICl$, Et_2O	Bn	**6g**	73	38/62
10	allylSnBu_3, CH_2Cl_2	allyl	**6h**	76	92/8
11	methallylSnBu_3, CH_2Cl_2	methallyl	**6i**	73	96/4

[a]When R = *s*-Bu, *t*-Bu, or *i*-Pr, hydrogen transfer affording **6e** is observed. [b]Determined by HPLC on the crude: for the assignment of the structures, see Experimental Section. The yields were the combined isolated yields of the two isomers, and therefore their ratio based on the isolated weights can slightly differ from those given in this table. [c]Obtained as two *anti* diastereomers.

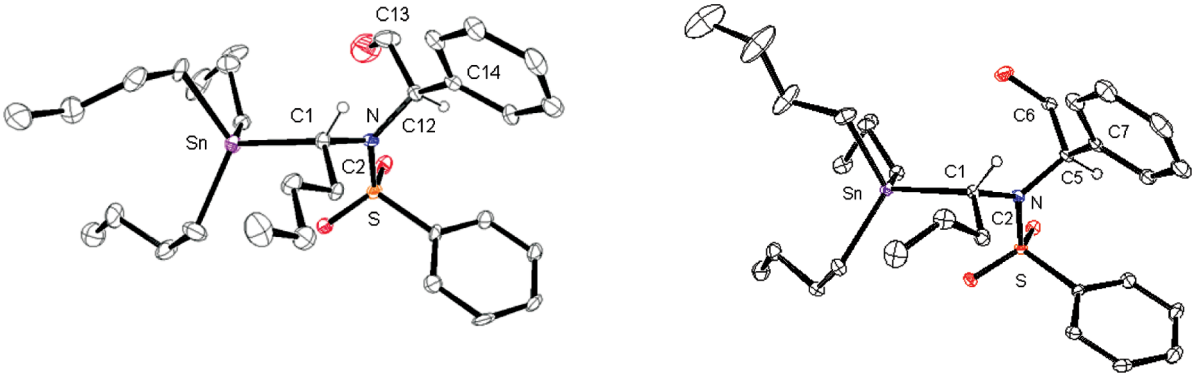


FIGURE 2. ORTEP view of compounds **6b**-*anti* (left) and **6h**-*anti* (right) with thermal ellipsoids drawn at the 30% probability level. **6b**-*anti*: selected bond lengths (Å) and angles (deg) (average of the two molecules contained in the unit cell): Sn−C1 = 2.19, C1−N = 1.48, C12−N = 1.48, C1−C2 = 1.56, Sn−O1 = 3.02; C1−N−S = 121.54, C1−N−C12 = 118.82, C12−N−S = 119.40, Sn−C1−N = 113.70, Sn−C1−C2 = 113.20, N−C1−C2 = 112.33, N−C12−C13 = 108.93, N−C12−C14 = 113.05. **6h**-*anti*: selected bond lengths (Å) and angles (deg): Sn−C1 = 2.19, C1−N = 1.49, C5−N = 1.50, C1−C2 = 1.54, Sn−O1 = 3.04; C1−N−S = 121.9, C1−N−C5 = 120.3, C5−N−S = 117.3, Sn−C1−N = 113.7, Sn−C1−C2 = 114.3, N−C1−C2 = 112.9, N−C5−C7 = 111.6, N−C5−C6 = 110.2. For further details, see Supporting Information.

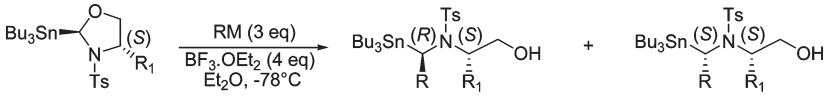
side chain into the chiral inductor influences the level of diastereoselectivity. Like the ring opening of **5** or **6** (Table 2, entries 4 and 5), reaction of oxazolidine **9** (R^1 = *i*-Pr) with $Me_2CuLi\cdot LiI$ or $Bu_2CuLi\cdot LiI$ in the presence of $BF_3\cdot OEt_2$ yielded predominantly the alcohols **9a**-*anti* or **9b**-*anti* in good yields (Table 4, entries 1 and 2), while mixtures of both diastereomers **10a**-*anti*/**10a**-*syn* and **10b**-*anti*/**10b**-*syn* were obtained in good yields from **10** (R^1 = Me, entries 4 and 5). Similarly, as observed with **5** (Table 4, entry 8) or **6** (Table 3, entry 10), exposure of oxazolidine **9** to allyltributyltin in the presence of $BF_3\cdot OEt_2$ gave rise predominantly to **10h**-*anti* in 82% yield (Table 4, entry 6). Surprisingly, allylation of **9** occurred in high yield but with an inversed diastereoselectivity in favor of **9h**-*syn* (Table 4, entry 3). The stereochemistry of **9h**-*syn* was firmly established by its X-ray structure, which exhibits an *SS* configuration with strong interaction between the tin center and an oxygen of the sulfonyl group: $d_{Sn-O} \approx 3$ Å (Figure 3). Among other stereochemical results, this shift from an *anti* preference to a *syn* one needs to be rationalized.

Discussion

The above results suggest different mechanisms to rationalize the stereochemical trends observed in the ring-opening reaction of *N*-(arenesulfonyl)- 2-tributylstannyloxazolidines. First, the ring opening of oxazolidines derived from phenylglycinol will be examined. Then the influence of the nature of the organometallic reagent and of the chiral inductor will be considered.

Ring Opening of *N*-(Arenesulfonyl)-2-stannyloxazolidines Derived from (*R*)-Phenylglycinol by Lithium Organocuprates in the Presence of Boron Trifluoride Etherate. The ring-opening reaction by lithium organocuprates in the presence of boron trifluoride etherate led to tributylstannyl-β-aminoalcohols with a high preference for the *anti* product. While a 90/10 *anti*/*syn* ratio was obtained from the *N*-mesyloxazolidine **7**-*trans*, *anti*/*syn* ratios near 99/1 were obtained with *N*-arenesulfonyloxazolidines **4**−**6**-*trans*. This feature can be rationalized by a concerted mechanism favored by every strong withdrawing *N*-protecting group, which can be depicted as

TABLE 4. Ring Opening of *trans*-*N*-(Paratoluenesulfonyl)-2-tributylstannyloxazolidines 5, 9, and 10 with Various Organometallic Reagents



5, 9, 10 *anti* *syn*

5-a,h ; 9-a,b,h ; 10-a,b,h

entry	oxazolidine[a]	R^1	reagent	R	product	yield (%)	dr (*anti*/*syn*)[b,c]
1	**9**	*i*-Pr	$Me_2CuLi \cdot LiI$	Me	**9a**	78	>95/5
2	**9**	*i*-Pr	$Bu_2CuLi \cdot LiI$	Bu	**9b**	70	>95/5
3	**9**	*i*-Pr	$allylSnBu_3$	All	**9h**	88	<5/95
4	**10**	Me	$Me_2CuLi \cdot LiI$	Me	**10a**	77	66/34
5	**10**	Me	$Bu_2CuLi \cdot LiI$	Bu	**10b**	78	73/27
6	**10**	Me	$allylSnBu_3$	All	**10h**	82	87/13
7	**5**	Ph (*R*)	$Me_2CuLi \cdot LiI$	Me	**5a**	76	98/2
8	**5**	Ph (*R*)	$allylSnBu_3$[d]	All	**5h**	79	>95/5

[a]Reactions were carried out with *trans* oxazolidines (see Experimental Section). [b]Determined by ^1H NMR on the crude or by HPLC. [c]The structures of the diastereomers were assigned to be *anti* or *syn* by comparison of the sign and the magnitude of the specific rotation with **9h**-*syn* whose geometry was determined by X-ray analysis (see Experimental Section). [d]$TiCl_2(Oi\text{-}Pr)_2$ was used as Lewis acid.

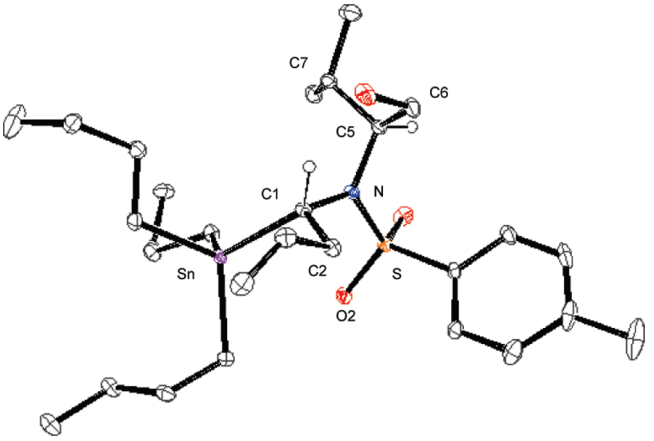


FIGURE 3. ORTEP view of compound **9h**-*syn* with thermal ellipsoids drawn at the 30% probability level. Selected values bond lengths (Å) and angles (deg) (average of the two molecules contained in the unit cell): Sn−C1 = 2.20, C1−N = 1.50, C5−N = 1.50, C1−C2 = 1.55, Sn−O2 = 3.00; C1−N−S = 121.0, C1−N−C5 = 119.0, C5−N−S = 118.3, Sn−C1−N = 114.5, Sn−C1−C2 = 111.9, N−C1−C2 = 113.6, N−C5−C7 = 111.1, N−C5−C6 = 112.0. For further details, see Supporting Information.

an *anti* attack on the C_2−O bond assisted by boron trifluoride (S_N2-like transition state). In the case of *N*-arenesulfonyl derivatives (Scheme 3, TS-1), the very high selectivity can be explained by two convergent features increasing the rigidity of the substrate: the π-stacking of the two aromatic rings and the chelation between tin and one oxygen of the sulfonyl group as suggested by the radiocrystallographic structure of **4**-*trans* (Figure 1). Such a concerted mechanism is in agreement with the exclusive reactivity of the *trans*-2-stannyloxazolidines, which can allow the entry of the nucleophile owing to the shift of the chelated sulfonyl oxygen under the plane of the five-membered ring (Scheme 3, TS-1). It also justifies the poor reactivity of *N*-*p*Ns derivative **4**-*trans* due to the difficulty in stabilizing the slight positive charge developed on the carbon center (even in an S_N2 like transition state) in a compound having no available electronic pair on the neighbor nitrogen. Concerning the *cis* oxazolidine, the consideration of dihedral angles in agreement with our previous structural study,[28] and the occurrence of π-stacking along with the Sn−O chelation should place the chelated sulfonyl oxygen near the axis of the C_2−O bond, preventing similar concerted reaction (Scheme 3, TS-2). Therefore, the reaction of the *cis* oxazolidine requires the previous formation of an iminium intermediate, which can be the first step of the isomerization of the *cis* oxazolidine into its *trans* form. This feature explains the low reactivity of **8**-*cis* that affords slowly **8a**-*anti*, probably after isomerization of **8**-*cis* into **8**-*trans*.[32] Furthermore, this concerted mechanism is expected to be quite sensitive to steric hindrance, and therefore good yields and good diastereoselectivities are expected only when the nucleophile contains a primary alkyl group. Thus, the reduction reaction affording **6e** is a competitive route with a secondary alkyl group (Table 3, entry 4), and it is the exclusive route with a tertiary alkyl one containing β-hydrogen atoms (Table 3, entry 5). Compared to previous rationalizations proposed in the literature, the S_N2-like transition state appears to be consistent with reported studies dealing with ring opening of organic acetals[33] or α-stannylacetals.[34] In the case of 1,3-oxazolidines, concerted reaction with Grignard reagents or nucleophilic addition to iminium intermediates have been suggested in order to explain the obtained results,[35] but in these studies, the nitrogen atom is not protected by a strong withdrawing sulfonyl group.

(32) Whereas isomerization of **5**-*cis* into **5**-*trans* appears to be much slower than reaction with Me_2CuLi (4% isomerization after 2.5 h at −78 °C in the presence of boron trifluoride (5 equiv), the isomerization of **8**-*cis* into **8**-*trans* appears to be much easier, allowing further reaction of the organocuprate.

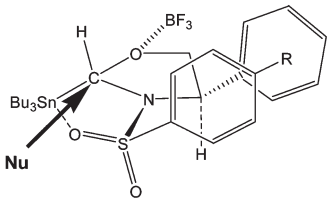
(33) (a) Alexakis, A.; Mangeney, P. *Tetrahedron: Asymmetry* **1990**, *1*, 477–511. (b) Ishihara, K.; Mori, A.; Yamamoto, H. *Tetrahedron* **1990**, *46*, 4595–4612. (c) Mori, I.; Ishihara, K.; Flippin, L. A.; Nozaki, K.; Yamamoto, H.; Bartlett, P. A.; Heathcock, C. H. *J. Org. Chem.* **1990**, *55*, 6107–6115.

(34) Cintrat, J.-C.; Blart, E.; Parrain, J.-L.; Quintard, J.-P. *Tetrahedron* **1997**, *53*, 7615–7628.

(35) (a) Poerwono, H.; Higashiyama, K.; Takahashi, H. *J. Org. Chem.* **1998**, *63*, 2711–2714. (b) Agami, C.; Comesse, S.; Kadouri-Puchot, C. *Tetrahedron Lett.* **2000**, *41*, 6059–6062. (c) Alladoum, J.; Roland, S.; Vrancken, E.; Kadouri-Puchot, C.; Mangeney, P. *Synlett* **2006**, 1855–1858. (d) Amat, M.; Escolano, C.; Gómez-Esqué, A.; Lozano, O.; Llor, N.; Griera, R.; Molins, E.; Bosch, J. *Tetrahedron: Asymmetry* **2006**, *17*, 1581–1586. (e) Huguenot, F.; Brigaud, T. *J. Org. Chem.* **2006**, *71*, 2159–2162. (f) Alladoum, J.; Roland, S.; Vrancken, E.; Mangeney, P.; Kadouri-Puchot, C. *J. Org. Chem.* **2008**, *73*, 9771–9774.

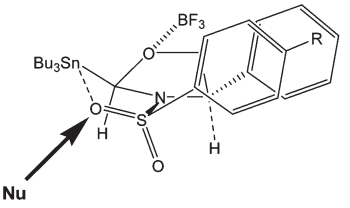
SCHEME 3. Lewis Acid Assisted Nucleophilic Ring Opening of *N*-(Arenesulfonyl)- 2-tributylstannyloxazolidines

Ring-Opening of *N*-(arenesulfonyl)-2-tributylstannyloxazolidines derived from (*R*)-phenylglycinol through an S_N2 transition state.



TS-1 with π-stacking ⟶ Anti

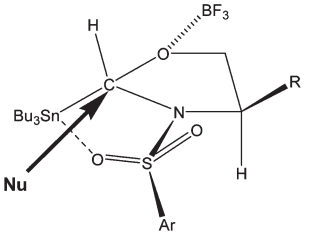
Ring-opening of **4**-**6**-*trans* through an S_N2 like transition state



TS-2 with π-stacking ⟶ no reaction

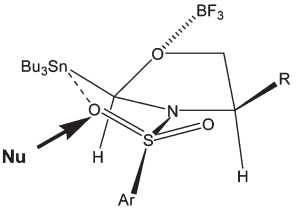
Prevented ring-opening of **5**- and **6**-*cis* through an S_N2 like transition state

Ring-Opening of *N*-(arenesulfonyl-2-tributylstannyloxazolidines derived from (*S*)-valinol and (*S*)-alaninol through an S_N2 transition state.



TS-3 without π-stacking ⟶ Anti

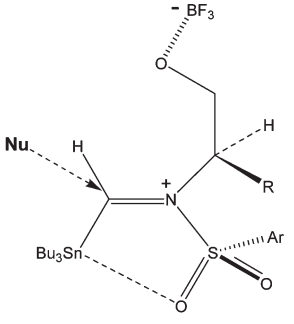
Ring-opening of **9**-*trans* and **10**-*trans* through an S_N2 like transition state



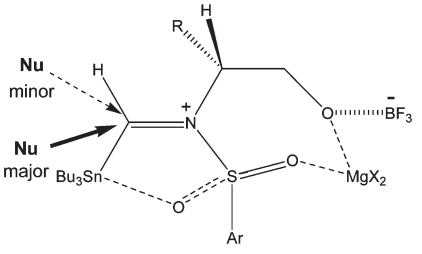
TS-4 : without π-stacking ⟶ no reaction

Prevented ring-opening of **9**-*cis* and **10**-*cis* through an S_N2 like transition state

Ring-Opening of *N*-(arenesulfonyl)-2-tributylstannyloxazolidines through iminium intermediates.



TS-5 ⟶ Syn



TS-6 ⟶ Anti or Syn

** In every case, the schemes are presented for derivatives of (R)-aminoalcohols. When the (S)-enantiomer has been used, these schemes have to be considered as a picture in a mirror.*

Ring Opening of *N*-(Arenesulfonyl)-2-tributylstannyloxazolidines Derived from (*R*)-Phenylglycinol by Allyltins or Magnesium Organocuprates in the Presence of Boron Trifluoride Etherate. When allyltributyltin or methallyltributyltin were used as nucleophiles, the general trend is quite similar since π-stacking and assistance by a monodentate Lewis acid should be preserved. However, the lower nucleophilicity of allyltins compared to lithium organocuprates should result in a lower reactivity and in a later transition state if one refers to Hammond's postulate. Thus, the addition of the allyl group should occur when the electrophilic center has acquired an electron deficiency allowing the reaction (the Lewis acid, which was the last reagent added in the reaction mixture, being the inducer). The result can be a concerted transition state as previously described (Scheme 3, TS-1), but with a possible competitive mechanism involving an iminium intermediate (Scheme 3, TS-5) slightly decreasing the diastereoselectivity.

In the case of magnesium organocuprates (less reactive than lithium organocuprates), the presence of magnesium dihalide as additional Lewis acid constitutes a new parameter that can interact in the reaction mechanism due to its bidentate character. Therefore, the reaction is likely to allow competition between transition states TS-1, TS-5, and TS-6

(Scheme 3), giving mixtures of *anti* and *syn* ring-opening products as previously suggested for 2-tributylstannyloxazolidines protected as *N*-alkoxycarbonyl compounds.[21]

Ring Opening of *N*-(Paratoluenesulfonyl)-2-tributylstannyloxazolidines Derived from (*S*)-Valinol and (*S*)-Alaninol. When 2-tributylstannyloxazolidines derived from (*S*)-valinol or (*S*)-alaninol are involved, the π-stacking between the arenesulfonyl group and the phenyl group of (*R*)-phenylglycinol should be replaced by the consideration of possible steric interactions due to the substituent of the aminoalcohol, while chelation between the tin center and the sulfonyl oxygen should be preserved. Therefore, in conditions where a concerted transition state is likely to occur (strong withdrawing *N*-protecting group), the *trans*-2-tributylstannyloxazolidine should react through transition state TS-3 (Scheme 3), whereas the approach of nucleophiles to *cis*-2-tributylstannyloxazolidine should be ruled out through this mechanistical pathway due to the presence of the chelated sulfonyl oxygen aligned with the C−O endocyclic bond (Scheme 3, TS-4). The reaction of **9**-*trans* with lithium organocuprates in the presence of boron trifluoride afforded the desired products with high *anti* selectivities (Table 4, entries 1 and 2), while a lower *anti* preference was obtained for **10**-*trans* (Table 4, entries 4 and 5).

This result might be explained by the higher conformational flexibility of the oxazolidine ring when the R group is a methyl group. For allylation reaction involving **9**-*trans* (Table 4, entry 3), the reversed diastereocontrol might be explained by the lower reactivity of the allyltin, which should react through an iminium intermediate on its less hindered face (Scheme 3, TS-5). It should be noted that in the case of allylation reaction, the steric hindrance can be brought by the R group (R = *i*-Pr or Me) but also by the aromatic group from the nitrogen protecting group on the other face (Scheme 3, TS-5). This feature explains the possible *syn* selectivity with *i*-Pr (prevalence of *i*-Pr over *p*-MePh; Table 4, entry 3) and the *anti* selectivity with Me (prevalence of *p*-MePh over Me; Table 4, entry 6).

For ring-opening reactions by allyltributyltin, another fashion to rationalize our results might be to consider preferences in the conformation of an iminium intermediate in function of the size of the substituent on the α-position related to nitrogen as previously proposed by Meyers et al. (Scheme 4).[36]

If one considers the initially formed iminium ion TS-7, TS-8, and TS-9 in which R^1 is the alkyl or aryl group derived from the various β-aminoalcohol auxiliaries, TS-7 and TS-8 minimize interactions between the arenesulfonyl moiety and the R^1 or alkoxytrifluoroborate group by directing the small hydrogen atom toward the arenesulfonyl group. By analogy with the Felkin−Ahn model, when R^1 is a small group (i.e., methyl), the alkoxytrifluoroborate might assume the role of the large group and might occupy the antiperiplanar position (TS-7), thus directing the entry of allyltributyltin from the Re-face to provide after hydrolysis alcohols *anti* (Table 4, entry 6). Alternatively, when R^1 is a large group (i.e., *i*-Pr), it should assume the role of the large group (TS-8), and then the delivery of allyltributyltin should occur from the face opposite to this group (*si*-entry) to generate after hydrolysis the product *syn* (Table 4, entry 3). However, it has to be noted that Meyers' model was proposed with titanium tetrachloride used as a Lewis acid, a situation that is quite different from those encountered with boron trifluoride etherate. Nevertheless, while our results with (*S*)-valinol and (*S*)-alaninol derivatives can be rationalized on the basis of the relative size of the α-nitrogen groups (TS-7 and TS-8), the occurrence of a π-stacking with phenylglycinol should afford a *syn* selectivity instead of an *anti* one (TS-9).

In summary, this paper intends to rationalize the stereochemical trends observed in the ring opening of *N*-(arenesulfonyl)-2-tributylstannyloxazolidines. Several arguments developed herein (Sn−O chelation, withdrawing strength of the *N*-protecting groups, etc.) can also be considered to rationalize the reactivity of *N*-(alkoxycarbonyl)-2-tributylstannyloxazolidines. Taking into account previous reports from our group dealing with ring opening of *trans* *N*-(alkoxycarbonyl)-2-tributylstannyloxazolidines derived from (*R*)-phenylglycinol, we have summarized the sequence in Scheme 5.[21,22]

From this sequence, it is clear that *trans*-2-tributylstannyloxazolidines fail to react only when the protecting group (PG) is a very strong withdrawing group (e.g., PG = *p*-Ns). Concerning the *anti* preference, the evolution along the sequence PG = CO_2t-Bu,[37] CO_2Bn, CO_2Me, Ts, $PhSO_2$, and *p*-Ns (despite the very poor yield in this case) can be explained by a competition between a mechanism involving an iminium intermediate and a concerted mechanism. The mechanism involving an iminium should be the main one with PG = CO_2t-Bu, while an overlapping of the two mechanisms is likely to occur with other carbamates. In the case of the *N*-sulfonyl series, the prevailing pathway (which can be nearly exclusive in the *N*-arenesulfonyl series) is likely to be a concerted S_N2-like mechanism. Preliminary calculations have been attempted in order to improve the understanding of the differences observed in terms of mechanisms for different protecting groups and different reagents, but due to the complexity of the systems, too heavy calculations are required in order to obtain reliable results taking into account the nature of the *N*-protecting group and the nature of the nucleophilic reagent.

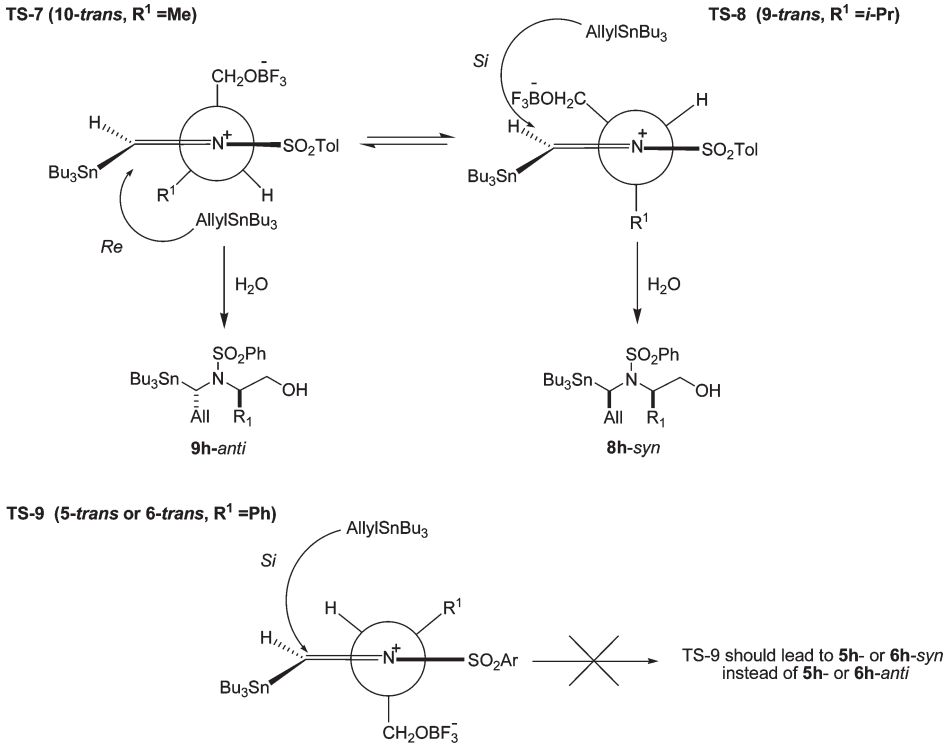
Whatever the reasons of the complexity of the competition between these two mechanisms, we wish to focus on the interest in organic synthesis. Indeed, it appears clearly that *N*-(arenesulfonyl)-tributylstannyl-
β-aminoalcohols can be obtained with high diastereomeric purities when compared to their *N*-alkoxycarbonyl analogues. Therefore, the electrochemical method developed in order to remove the phenylsulfonyl group without elimination of the tributylstannyl group should be of interest in order to obtain enantioenriched chiral organotins.[26] Such precursors should open promising routes to transfer chiral α-aminoanion equivalents both as organolithium reagents (with a possible achievement of physicochemical studies in order to evaluate their configurational stability in the absence of a complexation by a diamine)[38] or after Stille

(36) Burgess, L. E.; Meyers, A. I. *J. Am. Chem. Soc.* **1991**, *113*, 9858–9859.

(37) In the *N*-Boc series, important discrepancies (*anti*/*syn* from 52/48 to 87/13) were observed with minor change in the experimental conditions; see refs 21 and 22.

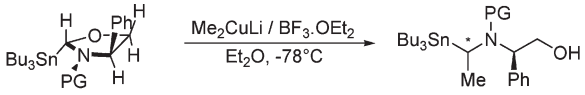
(38) (a) Gawley, R. E.; Eddings, D. B.; Santiago, M.; Vicic, D. A. *Org. Biomol. Chem.* **2006**, *4*, 4285–4291. (b) Klein, R.; Gawley, R. E. *J. Am. Chem. Soc.* **2007**, *129*, 4126–4127.

SCHEME 4. Ring Opening of the *N*-(Benzenesulfonyl)-2-tributylstannyl-oxazolidines 9-*trans* and 10-*trans* by Analogy with Meyers' Reports



** In every case, the schemes are presented for derivatives of (S)-aminoalcohols. When the (R)-enantiomer has been used, these schemes have to be considered as a picture in a mirror.*

SCHEME 5. Ring Opening of *trans*-*N*-Protected-2-tributylstannyloxazolidines by Lithium Dimethylcuprate in the Presence of Boron Trifluoride Etherate



PG	CO_2t-Bu	CO_2Bn	CO_2Me	Ts	SO_2Ph	*p*-Ns
anti/*syn*	52/48	83/17	92/8	98/2	98.5/1.5	>99/1
yield (%)	77	78	85	76	96	6

cross-coupling reactions on the basis of the pioneering work of Chong et al.[27b]

Conclusion

trans-*N*-(Arenesulfonyl)-2-tributylstannyloxazolidines have been proven to react with soft nucleophiles such as organocuprates or allyltins in the presence of boron trifluoride etherate to afford the corresponding tributylstannyl-β-aminoalcohols. This reaction affords the *anti*-tributylstannyl-β-aminoalcohols with very high diastereoselectivities when oxazolidines are derived from phenylglycinol. The configurations of the products have been firmly established on the basis of physicochemical data after determination of several radiocrystallographic structures. The results have been rationalized by a concerted S_N2-like transition state that can compete with a mechanism involving iminium intermediates. The high selectivities (dr up to 99/1) obtained from *trans*-*N*-(arenesulfonyl) 2-tributylstannyloxazolidines derived from phenylglycinol offer the advantage to open a selective route to α-aminoorganotins having an (*R*) or an (*S*) configuration depending on the chirality of the β-aminoalcohol. It is worth noting that in this case pure *anti* isomer can be very easily purified due to the high difference in polarity compared with that of possible undesired products (unreacted *cis* oxazolidine and traces of *syn* isomer). Therefore, work is in progress to evaluate the reactivity and configurational stability of these new species and to examine their potential in the synthesis of molecules of biological interest.

Experimental Section

Diethoxymethyltrimethyltin, 1b. Diethoxymethyltributylstannane **1a** (10 mmol, 3.93 g) was placed into a Schlenk tube and was dissolved in THF (60 mL). The solution was then cooled to −85 °C under an atmosphere of argon and *n*-butyllithium in hexanes (15 mmol) was added dropwise to the solution. Once this addition was complete, the solution was stirred for 10 min at the same temperature. Then, a solution of trimethyltin chloride (15 mmol, 2.98 g) in THF (10 mL) was added to the reaction mixture. After stirring for 15 min at −85 °C,

the reaction mixture was allowed to warm to 0 °C and a saturated solution of NH_4Cl (aq) was added. The aqueous phase was extracted with diethyl ether, the combined organic extract was dried ($MgSO_4$) and filtered, and the solvents were evaporated in vacuo. Distillation of the crude (bp = 50 °C/1 mbar) afforded the desired organotin compound **1b** in 40% yield (1.07 g) as a colorless oil. MS: organotin fragments m/z (%) = 223 (1), 165 (14), 135 (6); organic fragments m/z (%) = 103 (100), 75 (51), 73 (19), 47 (54), 45 (10), 29 (10); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.14 (s, 9H, $^2J_{Sn-H}$ = 52−54), 1.19 (t, 6H, ^3J = 7, CH_3CH_2O), 3.52 (dq, 2H, ^3J = 7, ^2J = 9, CH_3CH_2O), 3.57 (dq, 2H, ^3J = 7, ^2J = 9, CH_3CH_2O), 5.12 (s, 1H, $^2J_{Sn-H}$ = 35−37, C*H*Sn); ^{13}C NMR ($CDCl_3$, 300 K) δ −10.0 (3C, $^1J_{Sn-C}$ = 302−317), 15.2 (2C, CH_3CH_2O), 64.0 (2C, $^3J_{Sn-C}$ = 39, CH_3CH_2O), 107 (1C, *C*HSn); ^{119}Sn NMR($CDCl_3$, 300 K) δ −40.6.

Experimental Procedure for the Synthesis of *N*-Protected 2-Alkylstannyloxazolidines. (4*R*)-3-Benzoyl-4-phenyl-2-(tributylstannyl)-1,3-oxazolidine, 2. *N*-COPh (*R*)-phenyl glycinol (2.54 mmol, 613 mg), CSA (2.54 mmol, 590 mg) and 80 mL of cyclohexane were placed successively in a 250 mL round-bottomed flask fitted with a Dean−Stark apparatus. The reaction mixture was warmed until reflux and diethoxymethyltributylstannane **1a** (2.54 mmol, 1 g) was added. After about 15 min of reaction and complete disappearance of the starting material monitored by TLC, K_2CO_3 (s) was added to the solution. Then, the reaction mixture was filtered at room temperature through neutral alumina with diethyl ether as eluent. The reaction mixture was concentrated under reduced pressure and the crude residue was purified by flash chromatography on silica gel (eluent = hexanes/diethyl ether: 90/10) to afford pure **2**-*trans* and pure **2**-*cis* (576 mg, 42%, **2**-*trans* = 526 mg, **2**-*cis* = 50 mg). IR (neat): 3064, 3030, 2954, 2922, 2868, 2852, 1616, 1575, 1447, 1418, 1067, 697; MS (ESI): m/z = 566.1 $(M + Na)^+$; HRMS (ESI) calcd for $C_{28}H_{41}NO_2Na^{116}Sn$ $[M + Na]^+$: 562.2057. Found: 562.2056.

Diastereomer 2-*trans*. Colorless oil; R_f = 0.36 (eluent = hexanes/diethyl ether: 90/10); $[\alpha]_D^{19}$ = −224.8 (c 1.08, $CHCl_3$); ^{1}H NMR (C_6D_6, 340 K) δ 0.85 (t, 9H, ^3J = 7.2, H_{Bu}), 1.20−1.61 (m, 12H, H_{Bu}), 1.73−2.00 (m, 6H, H_{Bu}), 3.63 (dd, 1H, ^2J = 8.5, ^3J = 5.1, CH_2O), 4.05 (dd, 1H, ^3J = 8.5, ^2J = 6.8, CH_2O), 4.58 (dd, 1H, ^3J = 6.8, ^3J = 5.1, C*H*Ph), 5.72 (s, 1H, $^2J_{Sn-H}$ = 57, C*H*Sn), 6.73−7.00 (m, 8H, C_6H_5), 7.27 (bd, 2H, ^3J = 7.0, C_6H_5); ^{13}C NMR (C_6D_6, 340 K) δ 11.7 (3C, $^1J_{Sn-C}$ = 316−331), 13.9 (3C), 27.9 (3C, $^3J_{Sn-C}$ = 55), 29.7 (3C, $^2J_{Sn-C}$ = 20), 62.5 (1C, $^3J_{Sn-C}$ = 6, *C*HPh), 77.2 (1C, $^3J_{Sn-C}$ = 21, *C*H$_2$O), 90.9 (1C, $^1J_{Sn-C}$ = 391−409, *C*HSn), 126.6−129.8 (10C, C_6H_5), 137.2 (1C, C_6H_5), 141.9 (1C, C_6H_5), 168.0 (1C, *C* = O); ^{119}Sn NMR (C_6D_6, 300 K) δ −40.2.

Diastereomer 2-*cis*. Colorless oil; R_f = 0.12 (eluent = hexanes/diethyl ether: 90/10); $[\alpha]_D^{19}$ = +29.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6, 340 K) δ 0.98 (t, 9H, ^3J = 7.3, H_{Bu}), 1.22−1.55 (m, 12H, H_{Bu}), 1.73−1.95 (m, 6H, H_{Bu}), 3.64 (dd, 1H, ^2J = 8.4, ^3J = 6.1, CH_2O), 3.81 (d, 1H, ^2J = 8.4, CH_2O), 4.40 (d, 1H, ^3J = 6.1, C*H*Ph), 5.56 (s, 1H, $^2J_{Sn-H}$ = 53, C*H*Sn), 6.80−7.11 (m, 8H, C_6H_5), 7.22 (bd, 2H, ^3J = 7.8, C_6H_5); ^{13}C NMR (C_6D_6, 340 K) δ 11.4 (3C, $^1J_{Sn-C}$ = 319−333), 13.9 (3C), 27.9 (3C, $^3J_{Sn-C}$ = 57), 29.7 (3C, $^2J_{Sn-C}$ = 20), 61.7 (1C, *C*HPh), 77.9 (1C, $^3J_{Sn-C}$ = 35, *C*H$_2$O), 90.7 (1C, $^1J_{Sn-C}$ = 392−411, *C*HSn), 127.0−129.7 (10C, C_6H_5), 137.5 (1C, C_6H_5), 143.3 (1C, C_6H_5), 167.9 (1C, *C* = O); ^{119}Sn NMR (C_6D_6, 300 K) δ −43.2.

(2*S*,4*R*)-4-Phenyl-2-(tributylstannyl)-3-[(trifluoromethyl)sulfonyl]-1,3-oxazolidine, 3-*trans*. The general procedure described for the preparation of **2** was conducted with *N*-SO_2CF_3 (*R*)-phenylglycinol (695 mg, 2.58 mmol), CSA (3 g, 12.9 mmol), 100 mL of cyclohexane, and diethoxymethyltributylstannane **1a** (1 g, 2.54 mmol). Purification by flash chromatography on silica gel (eluent = hexanes/diethyl ether: 95/5) yielded the compound **3**-*trans* as a colorless oil (631 mg, a single isomer isolated, 43%). R_f = 0.73 (eluent = hexanes/diethyl ether: 95/5); MS (CI): m/z = 572 $(M + H)^+$; HRMS (CI) calcd for $C_{22}H_{37}F_3NO_3S^{116}Sn$ $[M + H]^+$: 568.1468. Found: 568.1465; ^{1}H NMR ($CDCl_3$, 300 K) δ 0.91 (t, 9H, ^3J = 7.3, H_{Bu}), 0.97−1.20 (m, 6H, H_{Bu}), 1.20−1.41 (m, 6H, H_{Bu}), 1.44−1.70 (m, 6H, H_{Bu}), 3.85 (dd, 1H, ^2J = 8.7, ^3J = 7.4, CH_2O), 4.57 (dd, 1H, ^2J = 8.7, ^3J = 7.4, CH_2O), 5.05 (s, 1H, $^2J_{Sn-H}$ = 36, C*H*Sn), 5.09 (t, 1H, ^3J = 7.4, C*H*Ph), 7.20−7.42 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$, 300 K) δ 11.4 (3C, $^1J_{Sn-C}$ = 330−346), 13.7 (3C), 27.5 (3C, $^3J_{Sn-C}$ = 59), 28.9 (3C, $^2J_{Sn-C}$ = 20), 63.4 (1C, *C*HPh), 77.5 (1C, $^3J_{Sn-C}$ = 28, *C*H$_2$O), 92.2 (1C, *C*HSn), 119.3 (q, 1C, $^1J_{C-F}$ = 323, *C*F$_3$), 127.4 (2C, C_6H_5), 128.7 (1C, C_6H_5), 128.9 (2C, C_6H_5), 138.1 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −26.3.

(4*R*)-3-[(4-Nitrophenyl)sulfonyl]-4-phenyl-2-(tributylstannyl)-1,3-oxazolidine, 4. *N*-$SO_2Ph(p\text{-}NO_2)$ (*R*)-phenylglycinol (1.55 mmol, 500 mg), PTSA (0.074 mmol, 14 mg) and 100 mL of toluene were placed successively in a 250 mL round-bottomed flask fitted with a Dean−Stark apparatus. The reaction mixture was warmed until reflux over 2 h in order to remove traces of water. After the mixture had been cooled to room temperature, diethoxymethyltributylstannane **1a** (1.41 mmol, 555 mg) was added and the reaction mixture was allowed to reflux. After about 15 min of reaction and complete disappearance of the starting material monitored by TLC, K_2CO_3 (s) was added to the solution. Then, the reaction mixture was filtered at room temperature through neutral alumina with diethyl ether as eluent. The reaction mixture was concentrated under reduced pressure and the crude residue was purified by chromatography on silica gel (eluent = hexanes/diethyl ether: 90/10) to give pure **4**-*trans* and pure **4**-*cis* (580 mg, 66%, **4**-*trans* = 540 mg, **4**-*cis* = 40 mg). IR (KBr): 2955, 2922, 2870, 2852, 1536, 1352, 1342, 1150, 738, 634; MS (EI): organostannyl fragments m/z (%) = 567 (2), 438 (7), 420 (20), 291 (22), 235 (37), 179 (35), 177 (35); organic fragments m/z (%) = 333 (100), 303 (97), 156 (83), 117 (56), 91 (21), 57 (10), 41 (18), 29 (19); HRMS (ESI) calcd for $C_{27}H_{40}N_2O_5NaS^{116}Sn$ $[M + Na]^+$: 643.1577. Found: 643.1579.

Diastereomer 4-*trans*. Yellow solid, R_f = 0.25 (eluent = hexanes/diethyl ether: 90/10); $[\alpha]_D^{19}$ = −97.2 (c = 1.0, $CHCl_3$); mp 40−42 °C; ^{1}H NMR ($CDCl_3$, 300 K) δ 0.93 (t, 9H, ^3J = 7.2, H_{Bu}), 1.07−1.20 (m, 6H, H_{Bu}), 1.27−1.46 (m, 6H, H_{Bu}), 1.52−1.75 (m, 6H, H_{Bu}), 3.79 (dd, 1H, ^2J = 8.9, ^3J = 6.0, CH_2O), 4.45 (dd, 1H, ^2J = 8.9, ^3J = 7.2, CH_2O), 4.86 (dd, 1H, ^3J = 7.2, ^3J = 6.0, C*H*Ph), 5.12 (s, 1H, $^2J_{Sn-H}$ = 42, C*H*Sn), 7.00−7.20 (m, 5H, C_6H_5), 7.56 (bd, 2H, ^3J = 8.9, C_6H_4), 8.02 (bd, 2H, ^3J = 8.9, C_6H_4). ^{13}C NMR ($CDCl_3$, 300 K) δ 11.4 (3C, $^1J_{Sn-C}$ = 340−380), 13.8 (3C), 27.5 (3C, $^3J_{Sn-C}$ = 58), 29.1 (3C, $^2J_{Sn-C}$ = 19), 62.3 (1C, *C*HPh), 77.0 (1C, *C*H$_2$O), 90.9 (1C, *C*HSn), 123.7−128.7 (9C, C_{Ar}), 138.2 (1C, C_{Ar}), 145.9 (1C, C_{Ar}), 149.6 (1C, C_{Ar}); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −29.2.

Diastereomer 4-*cis*. Yellow liquid, R_f = 0.11 (eluent = hexanes/diethyl ether: 90/10); $[\alpha]_D^{19}$ = +29.8 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.89 (t, 9H, ^3J = 7.3, H_{Bu}), 0.95−1.10 (m, 6H, H_{Bu}), 1.17−1.65 (m, 12H, H_{Bu}), 3.66 (dd, 1H, ^2J = 8.8, ^3J = 6.9, CH_2O), 3.94 (dd, 1H, ^2J = 8.8, ^3J = 3.6, CH_2O), 4.63 (dd, 1H, ^3J = 6.9, ^3J = 3.6, C*H*Ph), 5.31 (s, 1H, $^2J_{Sn-H}$ = 53, C*H*Sn), 7.27−7.38 (m, 5H, C_6H_5), 8.00 (bd, 2H, ^3J = 8.8, C_6H_4), 8.37 (bd, 2H, ^3J = 8.8, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.2 (3C, $^1J_{Sn-C}$ = 312−327), 13.8 (3C), 27.5 (3C, $^3J_{Sn-C}$ = 58), 29.0 (3C, $^2J_{Sn-C}$ = 20), 61.6 (1C, $^3J_{Sn-C}$ = 7, *C*HPh), 75.3 (1C, $^3J_{Sn-C}$ = 22, *C*H$_2$O), 91.6 (1C, $^1J_{Sn-C}$ = 357−374, *C*HSn), 124.4−129.3 (9C, C_{Ar}), 139.4 (1C, C_{Ar}), 142.5 (1C, C_{Ar}), 150.4 (1C, C_{Ar}); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −27.7.

(4*R*)-4-Phenyl-3-tosyl-2-(tributylstannyl)-1,3-oxazolidine, 5. *N*-Ts (*R*)-phenylglycinol (2.8 mmol, 810 mg), PTSA (0.13 mmol, 25 mg) and 125 mL of toluene were placed successively in a round-bottomed flask fitted with a Dean−Stark apparatus. The reaction mixture was warmed until reflux over 2 h in order to remove traces of water. After the mixture had been cooled to

room temperature, diethoxymethyltributylstannane **1a** (2.54 mmol, 1 g) was added and the reaction mixture was allowed to reflux. After about 1 h of reaction and complete disappearance of the starting material monitored by TLC, K_2CO_3 (s) was added to the solution. Then, the reaction mixture was filtered at room temperature through neutral alumina with diethyl ether as eluent. The reaction mixture was concentrated under reduced pressure and the crude residue was purified by chromatography on silica gel (eluent = hexanes/diethyl ether/triethylamine: 95/3/2) to give pure **5**-*trans* (R_f = 0.25 (eluent = hexanes/diethyl ether: 95/5)) and pure **5**-*cis* (R_f = 0.11 (eluent = hexanes/diethyl ether: 95/5)) as colorless oil (1.10 g, 73%, **5**-*trans* = 782 mg, **5**-*cis* = 318 mg). All physical and spectroscopic data for **5**-*trans* and **5**-*cis* were in complete agreement with the reported ones.[24]

(4*R*)-4-Phenyl-3-(benzenesulfonyl)-2-(tributylstannyl)-1,3-oxazolidine, 6. *N*-SO_2Ph (*R*)-phenylglycinol (14.9 mmol, 4.14 g), PTSA (0.26 mmol, 50 mg) and 500 mL of toluene were placed successively in a round-bottomed flask fitted with a Dean−Stark apparatus. The reaction mixture was warmed until reflux over 2 h in order to remove traces of water. After the mixture had been cooled to room temperature, diethoxymethyltributylstannane **1a** (13.5 mmol, 5.32 g) was added and the reaction mixture was allowed to reflux. After 30 min of reaction, CSA (0.86 mmol, 200 mg) was added and the reaction mixture was heated until complete disappearance of the starting material monitored by TLC. At the end of the reaction, K_2CO_3 (s) was added to the solution. Then, the reaction mixture was filtered at room temperature through neutral alumina with diethyl ether as eluent. The reaction mixture was concentrated under reduced pressure and the crude residue was purified by chromatography on silica gel (eluent = hexanes/diethyl ether: 95/5) to afford pure **6**-*trans* and pure **6**-*cis* (4.70 g, 60%, **6**-*trans* = 4.32 g, **6**-*cis* = 0.38 g). IR (neat): 2955, 2923, 2870, 2853, 1447, 1343, 1156, 1090, 723, 687; MS (EI): organostannyl fragments *m*/*z* (%) = 522 (2), 438 (2), 375 (8), 311 (7), 235 (7), 179 (9); organic fragments *m*/*z* (%) = 288 (100), 260 (12), 141 (10), 91 (7), 77 (30), 41 (18), 29 (19); HRMS (ESI) calcd for $C_{27}H_{41}NO_3NaS^{116}Sn$ $[M + Na]^+$: 598.1726. Found: 598.1725.

Diastereomer 6-*trans*. Colorless oil; R_f = 0.61 (eluent = hexanes/diethyl ether: 80/20); $[\alpha]_D^{19} = -89.8$ (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.93 (t, 9H, ^3J = 7.3, H_{Bu}), 1.04−1.22 (m, 6H, H_{Bu}), 1.28−1.45 (m, 6H, H_{Bu}), 1.49−1.75 (m, 6H, H_{Bu}), 3.70 (dd, 1H, ^2J = 8.5, ^3J = 6.0, CH_2O), 4.39 (dd, 1H, ^2J = 8.5, ^3J = 7.6, CH_2O), 4.87 (dd, 1H, ^3J = 7.6, ^3J = 6.0, C*H*Ph), 4.91 (s, 1H, $^2J_{Sn-H}$ = 31, C*H*Sn), 7.00−7.16 (m, 5H, C_6H_5), 7.25 (bt, 2H, ^3J = 8.0, C_6H_5), 7.34−7.42 (m, 1H, C_6H_5), 7.58 (bd, 2H, ^3J = 8.0, C_6H_5); ^{13}C NMR ($CDCl_3$, 300 K) δ 11.6 (3C, $^1J_{Sn-C}$ = 328−344), 13.8 (3C), 27.5 (3C, $^3J_{Sn-C}$ = 59), 29.1 (3C, $^2J_{Sn-C}$ = 20), 62.2 (1C, *C*HPh), 76.3 (1C, $^3J_{Sn-C}$ = 31, *C*H_2O), 89.7 (1C, $^1J_{Sn-C}$ = 310−325, *C*HSn), 126.9−128.6 (9C, C_6H_5), 132.4 (1C, C_6H_5), 139.1 (1C, C_6H_5), 139.9 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −34.2.

Diastereomer 6-*cis*. Colorless oil; R_f = 0.43 (eluent = hexanes/diethyl ether: 80/20); $[\alpha]_D^{19} = +31.7$ (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.89 (t, 9H, ^3J = 7.3, H_{Bu}), 0.95−1.08 (m, 6H, H_{Bu}), 1.18−1.70 (m, 12H, H_{Bu}), 3.49 (dd, 1H, ^2J = 8.7, ^3J = 6.8, CH_2O), 3.92 (dd, 1H, ^2J = 8.7, ^3J = 3.2, CH_2O), 4.64 (dd, 1H, ^3J = 6.8, ^3J = 3.2, C*H*Ph), 5.26 (s, 1H, $^2J_{Sn-H}$ = 57, C*H*Sn), 7.22−7.40 (m, 5H, C_6H_5), 7.49−7.65 (m, 3H, C_6H_5), 7.81−7.88 (m, 2H, C_6H_5); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.0 (3C, $^1J_{Sn-C}$ = 312−327), 13.8 (3C), 27.5 (3C, $^3J_{Sn-C}$ = 58), 29.0 (3C, $^2J_{Sn-C}$ = 20), 61.4 (1C, $^3J_{Sn-C}$ = 8.0, *C*HPh), 74.9 (1C, $^3J_{Sn-C}$ = 22.0, *C*H_2O), 91.4 (1C, $^1J_{Sn-C}$ = 380−397, *C*HSn), 126.8−129.2 (9C, C_6H_5), 133.2 (1C, C_6H_5), 136.4 (1C, C_6H_5), 140.1 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −30.2.

(4*R*)-4-Phenyl-3-methanesulfonyl-2-(tributylstannyl)-1,3-oxazolidine, 7. The general procedure described for the preparation of **5** was conducted with 1.20 g (5.58 mmol) of *N*-mesyl (*R*)-phenylglycinol, 50 mg of PTSA (0.25 mmol), 200 mL of toluene and 2.00 g of diethoxymethyltributylstannane **1a** (5.08 mmol). Purification by flash chromatography on silica gel (eluent = hexanes/diethylether: 90/10) yielded **7**-*trans* and **7**-*cis* (1.96 g, 75%, **7**-*trans* = 1.37 g, **7**-*cis* = 588 mg). All spectroscopic data for **7**-*trans* and **7**-*cis* were in complete agreement with the reported ones.[24] Diastereomer **7**-*trans* (colorless oil): R_f = 0.35 (eluent = hexanes/diethyl ether: 8:2), $[\alpha]_D^{19} = -49.9$ (*c* = 0.98, $CHCl_3$). Diastereomer **7**-*cis* (colorless oil): R_f = 0.19 (eluent = hexanes/diethyl ether: 7:3), $[\alpha]_D^{19} = +30.6$ (*c* = 1.0, $CHCl_3$).

(4*R*)-4-Phenyl-3-tosyl-2-(trimethylstannyl)-1,3-oxazolidine, 8. The general procedure described for the preparation of **5** was conducted with 810 mg (2.8 mmol) of *N*-tosyl (*R*)-phenylglycinol, 25 mg of PTSA (0.13 mmol), 125 mL of toluene and 681 mg of diethoxymethyltrimethylstannane **1b** (2.54 mmol). The reaction was stopped at an early stage in order to prevent the subsequent isomerization of **7**-*trans* to **7**-*cis*. Purification by flash chromatography on silica gel (eluent = hexanes/diethyl ether/triethylamine: 95/3/2) yielded **8**-*trans* and **8**-*cis* (332 mg, 28%, **8**-*trans* = 210 mg, **8**-*cis* = 122 mg). IR (neat): 3031, 2975−2886, 1599, 1331, 1163, 1092, 700; MS (EI): organostannyl fragments *m*/*z* (%) = 452 (1), 312 (4), 241(6), 165 (17); organic fragments *m*/*z* (%) = 302 (100), 274 (26), 165 (12), 155 (59), 91 (53), 65 (12), 39 (4).

Diastereomer 8-*trans*. Colorless oil; R_f = 0.49 (eluent = hexanes/diethyl ether triethylamine: 89/10/1); $[\alpha]_D^{19} = -100.5$ (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.34 (s, 9H, $^2J_{Sn-H}$ = 54.3−55.8, H_{Me}), 2.31 (s, 3H, CH_3Ph), 3.73 (dd, 1H, ^2J = 8.4, ^3J = 6.1, CH_2O), 4.37 (app t, 1H, $J \approx 8$, CH_2O); 4.85 (s, 1H, $^2J_{Sn-H}$ = 33.7, C*H*Sn), 4.87 (app t, 1H, $^3J \approx 7$, C*H*Ph), 7.05−7.20 (m, 7H, H_{Ar}), 7.47 (d, 2H, ^3J = 8.3, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ −7.6 (3C, $^1J_{Sn-C}$ = 324−338), 21.5 (1C, *C*H_3Ph), 62.2 (*C*HPh), 76.0 (1C, *C*H_2O, $^3J_{Sn-C}$ = 40); 89.5 (1C, *C*HSn, $^1J_{Sn-C}$ = 402), 126.8 (2C, C_{Ar}), 127.6 (1C, C_{Ar}), 127.8 (2C, C_{Ar}), 128.5 (2C, C_{Ar}), 129.3 (2C, C_{Ar}), 136.6 (1C, C_{Ar}), 140.2 (1C, C_{Ar}), 143.3 (1C, C_{Ar}); ^{119}Sn NMR (300 MHz, $CDCl_3$) δ −17.1.

Diastereomer 8-*cis*. Colorless oil; R_f = 0.36 (eluent = hexanes/diethyl ether triethylamine: 89/10/1); $[\alpha]_D^{19} = +0.5$ (*c* = 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.26 (s, 9H, $^2J_{Sn-H}$ = 53.0−55.5), 2.43 (s, 3H, CH_3Ph), 3.54 (dd, 1H, ^2J = 8.7, ^3J = 6.8, C*H*Ph); 3.94 (dd, 1H, ^2J = 8.7, ^3J = 2.9, C*H*Ph); 4.64 (dd, 1H, ^3J = 2.9, ^3J = 6.8, CH_2O), 5.17 (s, 1H, $^2J_{Sn-H}$ = 63.4−66.2, C*H*Sn), 7.25−7.40 (m, 7H, H_{Ar}); 7.7 (d, 2H, ^3J = 6.5, H_{Ar}); ^{13}C NMR ($CDCl_3$, 300 K) δ −9.4 (3C); 21.4 (1C, *C*H_3Ph); 61.2 (1C, *C*H_2O); 75.2 (1C, *C*HPh); 90.9(1C, *C*HSn); 126.5 (2C, C_{Ar}); 127.5 (1C, C_{Ar}); 127.9 (2C, C_{Ar}); 128.4 (2C, C_{Ar}); 129.7 (2C, C_{Ar}); 133.2 (1C, C_{Ar}); 140.3 (1C, C_{Ar}); 143.9 (1C, C_{Ar}); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −8.8.

(2*R*,4*S*)-4-Isopropyl-3-tosyl-2-(tributylstannyl)-1,3-oxazolidine, 9. The general procedure described for the preparation of **6** was conducted with 4.0 g (15.5 mmol) of *N*-Ts (*S*)-valinol, 50 mg of PTSA (0.26 mmol), 500 mL of toluene, 5.55 g of diethoxymethyltributylstannane **1a** (14.1 mmol) and 180 mg of CSA (0.77 mmol). Purification by chromatography on silica gel (eluent = hexanes/diethyl ether: 95/5) yielded **9**-*trans* as a colorless oil (4.40 g, 56%). R_f = 0.41 (eluent = hexanes/diethyl ether: 90/10). All physical and spectroscopic data were in complete agreement with the reported ones.[24]

(4*S*)-4-Methyl-3-tosyl-2-(tributylstannyl)-1,3-oxazolidine, 10. The general procedure described for the preparation of **6** was conducted with 2.0 g (8.7 mmol) of *N*-Ts (*S*)-alaninol, 28 mg of PTSA (0.147 mmol), 280 mL of toluene, 3.12 g of diethoxymethyltributylstannane **1a** (7.9 mmol) and 120 mg of CSA (0.52 mmol). Purification by chromatography on silica gel (eluent = hexanes/diethyl ether: 90/10) yielded pure **10**-*trans* and pure **10**-*cis* as colorless oils (2.52 g, 60%). All physical and

spectroscopic data for **10**-*trans* and **10**-*cis* were in complete agreement with the reported ones.[24]

Experimental Procedure for the Ring-Opening Reaction of *N*-Protected 2-Trialkylstannyloxazolidines. General Procedure for the Ring-Opening Reaction by Higher Organocuprates. Diethyl ether (25 mL) was added to CuX (3 mmol) placed in a Schlenk tube and the mixture was cooled to −78 °C. The organometallic reagent (RLi or RMgX) (6 mmol) was added dropwise, and the mixture was stirred for 30 min at −78 °C and then warmed to −50 °C. The Schlenk tube was then cooled to −78 °C and $BF_3 \cdot OEt_2$ (4 mmol) was added dropwise. After 15 min of stirring, a solution of *N*-protected 2-trialkylstannyloxazolidine (1 mmol) in diethyl ether (5 mL) was added and the mixture was stirred for 2 h at −78 °C. The reaction was monitored by TLC. When finished, the reaction was quenched with saturated aqueous NH_4Cl and the crude was filtrated through a pad of Celite. The crude product was extracted with diethyl ether and purified by flash chromatography on silica gel (eluent = hexanes/diethyl ether: 80/20 or eluent = hexanes/diethyl ether: 85/15) to give the desired products.

General Procedure for the Ring-Opening Reaction by Allyltin Derivatives. To a stirred, cooled (−78 °C) solution of *N*-protected 2-tributylstannyloxazolidine (1 mmol) in 20 mL of dichloromethane was added allyltributyltin (3 mmol) followed by a slow addition of $BF_3 \cdot OEt_2$ or $TiCl_2(O\text{-}i\text{-}Pr)_2$ (4 mmol). The reaction mixture was stirred at −78 °C for 2 h, quenched with saturated aqueous NH_4Cl and filtrated through a pad of Celite. The phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent = hexanes/diethyl ether: 80/20 or eluent = hexanes/diethyl ether: 85/15) to give the desired products.

Physicochemical Data and Assignment of the *anti* or *syn* Configuration. All new compounds have been fully characterized even for minor isomers. However, in some cases, we have not been able to achieve reliable $[\alpha]_D$ measurements for very minor diastereomers due to the poor amount of product. While consideration of the sign and the value of a specific optical rotation has to be used very carefully in the determination of a configuration, herein the high differences in the polarizabilities of the bonds around tin result in large absolute values for $[\alpha]_D$. In the (*R*)-phenylglycinol series, the *anti* isomers exhibit values in the range −60 to −105, while positive values were obtained for the *syn* isomers when isolated as a pure products (values between +8 and +76 were observed). Furthermore, the reduction product **6e** constitutes a reference with an $[\alpha]_D$ value of −22.8 for the parent molecule having no asymmetric center in the α-position related to tin. The combination of R_f values and ^1H, ^{13}C, and ^{119}Sn NMR spectra with two radiocrystallographic analyses allows an unambiguous assignment of the configurations due the homogeneity of the series. The same arguments can be used for derivatives of (*S*)-valinol and (*S*)-alaninol with positive $[\alpha]_D$ values for the anti isomers and negative ones for the syn isomers.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-4-nitro-*N*-[(1*S*)-1-tributylstannyl)ethyl]benzenesulfonamide, 4a-*anti* (38.4 mg, 6%).** Yellow oil; R_f = 0.36 (eluent = hexanes/diethyl ether: 80/20); $[\alpha]_D^{19}$ = −95.5 (*c* = 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 K) δ 0.87 (d, 3H, ^3J = 7.5, CHC*H*$_3$), 0.93 (t, 9H, ^3J = 7.2, H_{Bu}), 0.97−1.08 (m, 6H, H_{Bu}), 1.20−1.60 (m, 12H, H_{Bu}), 2.27 (t, 1H, ^3J = 5.8, O*H*), 3.37 (q, 1H, ^3J = 7.5, $^2J_{Sn-H}$ = 53, C*H*Sn), 4.00−4.25 (m, 2H, C*H*$_2$OH), 4.77 (bt, 1H, ^3J = 6.9, C*H*Ph), 6.89 (bd, 2H, ^3J = 7.3, C_6H_5), 7.13−7.35 (m, 3H, C_6H_5), 8.04 (bd, 2H, ^3J = 8.7, C_6H_4), 8.35 (bd, 2H, ^3J = 8.7, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 9.4 (3C), 12.7 (3C), 18.9 (1C, CH*C*H$_3$), 26.5 (3C), 28.1 (3C), 39.7 (1C, *C*HSn), 61.1 (1C, *C*H$_2$OH), 62.5 (1C, *C*HPh), 123.2−127.8 (9C, C_{Ar}), 134.5 (1C, C_{Ar}), 146.4 (1C, C_{Ar}), 148.9 (1C, C_{Ar}); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −10.1.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[(1*S*)-1-(tributylstannyl)ethyl]toluenesulfonamide, 5a (462 mg, 76%, 5a-*anti* = 457 mg, 5a-*syn* = 5 mg).** MS (EI): organostannyl fragments *m*/*z* (%) = 552 (23), 454 (8), 432 (15), 389 (19), 325 (34), 291 (11), 269 (20), 235 (18), 179 (40), 177 (38), 121 (37); organic fragments *m*/*z* (%) = 318 (7), 198 (100), 155 (65), 132 (35), 105 (19), 103 (21), 91 (77), 77 (12), 65 (11), 41 (5), 39 (5), 29 (13); HRMS (CI) calcd for $C_{29}H_{48}NO_3S^{116}Sn$ [M + H]$^+$: 606.2376. Found: 606.2374.

Diastereomer 5a-*anti*. Colorless oil; R_f = 0.56 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19}$ = −82.7 (*c* = 0.6, $CHCl_3$);. ^1H NMR ($CDCl_3$, 300 K) δ 0.81 (d, 3H, ^3J = 7.3, CHC*H*$_3$), 0.90 (bt, 9H, ^3J = 7.3, H_{Bu}), 0.95−1.70 (m, 18H, H_{Bu}), 2.50 (s, 3H, C*H*$_3$C$_6$H$_4$), 2.75 (t, 1H, ^3J = 5.9, O*H*), 3.25 (q, 1H, ^3J = 7.3, $^2J_{Sn-H}$ = 55, C*H*Sn), 3.95 (ddd, 1H, ^2J = 11.7, ^3J = 5.9, ^3J = 5.2, C*H*$_2$OH), 4.19 (ddd, 1H, ^2J = 11.7, ^3J = 8.3, ^3J = 5.9, C*H*$_2$OH), 4.75 (dd, 1H, ^3J = 8.3, ^3J = 5.2, C*H*Ph), 6.75 (bd, 2H, ^3J = 8.0, C_6H_5), 7.10−7.30 (m, 3H, C_6H_5), 7.40 (bd, 2H, ^3J = 8.0, C_6H_4), 7.40 (bd, 2H, ^3J = 8.0, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.4 (3C, $^1J_{Sn-C}$ = 308−322), 13.8 (3C), 20.0 (1C, CH*C*H$_3$), 21.6 (1C, *C*H$_3$C$_6$H$_4$), 27.6 (3C, $^3J_{Sn-C}$ = 57), 29.2 (3C, $^2J_{Sn-C}$ = 19), 39.7 (1C, $^1J_{Sn-C}$ = 333−348, *C*HSn), 61.9 (1C, *C*H$_2$OH), 62.9 (1C, *C*HPh), 127.9−129.7 (9C, C_{Ar}), 136.3 (1C, C_{Ar}), 138.6 (1C, C_{Ar}), 143.4 (1C, C_{Ar}); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −12.8.

Diastereomer 5a-*syn*. Colorless oil, ^1H NMR ($CDCl_3$, 300 K) δ 0.50−0.80 (m, 6H, H_{Bu}), 0.85 (t, 9H, ^3J = 6.8, H_{Bu}), 1.10−1.30 (m, 12H, H_{Bu}), 1.41 (d, 3H, ^3J = 7.5, $^3J_{Sn-H}$ = 49, CHC*H*$_3$), 2.43 (s, 3H, C*H*$_3$C$_6$H$_4$), 3.00 (q, 1H, ^3J = 7.5, $^2J_{Sn-H}$ = 57, C*H*Sn), 3.91 (m, 1H, C*H*$_2$OH), 3.98 (m, 1H, C*H*$_2$OH), 5.05 (dd, 1H, ^3J = 5.2, ^3J = 7.5, C*H*Ph), 7.1−7.4 (m, 7H, H_{Ar}), 7.84 (d, 2H, ^3J = 8, H_{Ar}); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.2 (3C, $^1J_{Sn-C}$ = 322), 13.7 (3C), 21.1 (1C), 21.5 (1C), 27.5 (3C, $^3J_{Sn-C}$ = 60), 28.9 (3C), 39.5 (1C, *C*HSn), 61.4 (1C, *C*H$_2$OH), 62.9 (1C, *C*HPh), 127.4 (2C, C_{Ar}), 128.3 (1C, C_{Ar}), 128.4 (2C, C_{Ar}), 128.7 (2C, C_{Ar}), 129.7 (2C, C_{Ar}), 136.4 (1C, C_{Ar}), 139.7 (1C, C_{Ar}), 143.1 (1C, C_{Ar}); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −13.7.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[1-(tributylstannyl)but-3-en-1-yl]toluenesulfonamide, 5h-*anti* (500 mg, 79%).** Colorless oil; MS (EI): organostannyl fragments *m*/*z* (%) = 578 (35), 480 (14), 458 (23), 422 (18), 389 (34), 325 (52), 291 (15), 269 (36), 235 (23), 211 (35), 177 (38), 121 (29); organic fragments *m*/*z* (%) = 224 (79), 158 (49), 155 (48), 148 (17), 131 (30), 103 (31), 91 (100), 77 (18), 69 (16), 65 (13), 57 (20), 55 (16), 44 (27), 41 (36), 29 (21); $[\alpha]_D^{19}$ = −77.3 (*c* = 0.43; $CHCl_3$); ^1H NMR ($CDCl_3$, 300 K) δ 0.80−1.75 (m, 28H, H_{Bu} + C*H*$_2$CH=CH$_2$), 2.48 (s, 3H, C*H*$_3$C$_6$H$_4$), 2.50 (m, 1H, C*H*$_2$CH=CH$_2$), 2.80 (dd, 1H, ^3J = 3.8, ^3J = 7.3, O*H*), 3.05 (dd, 1H, ^3J = 3.3, ^3J = 11.9, $^2J_{Sn-H}$ = 50.2, C*H*Sn), 3.96 (ddd, 1H, ^3J = 5.1, ^3J = 7.3, ^2J = 11.2, C*H*$_2$OH), 4.15 (ddd, 1H, ^3J = 3.8, ^3J = 8.3, ^2J = 11.2, C*H*$_2$OH), 4.61 (bd, 1H, ^3J = 16.8, =C*H*$_2$), 4.74 (dd, 1H, ^3J = 5.1, ^3J = 8.3, C*H*Ph), 4.80 (bd, 1H, ^3J = 10, =C*H*$_2$), 5.12 (tdd, 1H, ^3J = 16.8, ^3J = 10, ^3J = 6.5, =CH), 6.69 (d, 1H, ^3J = 8, H_{Ar}), 6.70 (d, 1H, ^3J = 8, H_{Ar}), 7.1−7.3 (m, 3H, H_{Ar}), 7.35 (d, 2H, ^3J = 8, H_{Ar}), 7.85 (d, 2H, ^3J = 8, H_{Ar}); ^{13}C NMR($CDCl_3$, 300 K) δ 11.2 (3C, $^1J_{Sn-C}$ = 311−325), 13.7 (3C), 21.6 (1C), 27.5 (3C, $^3J_{Sn-C}$ = 58.3−60.6), 29.1 (3C, $^2J_{Sn-C}$ = 18), 39.0 (1C, $^2J_{Sn-C}$ = 13, *C*H$_2$CH=CH$_2$), 44.3 (1C, $^1J_{Sn-C}$ = 321−336, *C*HSn), 61.8 (1C, *C*H$_2$OH), 62.9 (1C, $^3J_{Sn-C}$ = 10.3, *C*HPh), 117.5 (1C, =*C*H$_2$), 128.0 (2C, C_{Ar}), 128.3−128.4 (5C, C_{Ar}), 129.7 (2C, C_{Ar}), 134.6 (1C, =*C*H); 135.9 (1C, C_{Ar}), 138.2 (1C, C_{Ar}), 143.6 (1C, C_{Ar}). ^{119} Sn NMR δ −8.2.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[(1-(tributylstannyl)ethyl]-benzenesulfonamide, 6a (571 mg, 96%, 6a-*anti* = 564 mg, 6a-*syn* = 7 mg).** IR (neat): 3500, 2954, 2922, 2870, 2854, 1447, 1323, 1150, 734, 690; MS (EI): organostannyl fragments *m*/*z* (%) = 538 (11), 454 (5), 418 (11), 375 (19), 311 (23), 291 (10), 255 (17), 235 (16), 179 (30), 177 (30), 121 (29); organic fragments *m*/*z* (%) = 184 (100), 141 (54), 132 (39), 105 (28), 91 (23), 77 (70), 41 (19);

HRMS (ESI) calcd for $C_{28}H_{45}NO_3NaS^{116}Sn$ $[M+Na]^+$: 614.2035. Found: 614.2033.

Diastereomer 6a-*anti*. Colorless oil; R_f = 0.52 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19} = -72.0$ (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.85 (d, 3H, ^3J = 7.4, $^3J_{Sn-H}$ = 53, $CHCH_3$), 0.82−1.10 (m, 15H, H_{Bu}), 1.15−1.56 (m, 12H, H_{Bu}), 2.76 (dd, 1H, ^3J = 6.4, ^3J = 4.1, O*H*), 3.27 (q, 1H, ^3J = 7.4, $^2J_{Sn-H}$ = 57, C*H*Sn), 3.90−4.10 (m, 1H, CH_2OH), 4.19 (ddd, 1H, ^2J = 11.8, ^3J = 8.1, ^3J = 4.1, CH_2OH), 4.75 (dd, 1H, ^3J = 8.1, ^3J = 5.5, C*H*Ph), 6.76 (bd, 2H, ^3J = 7.2, C_6H_5), 7.00−7.20 (m, 3H, C_6H_5), 7.40−7.60 (m, 3H, C_6H_5), 7.96 (bd, 2H, ^3J = 7.2, C_6H_5); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.4 (3C, $^1J_{Sn-C}$ = 323), 13.8 (3C), 20.0 (1C, $CHCH_3$), 27.6 (3C, $^3J_{Sn-C}$ = 57), 29.2 (3C), 39.6 (1C, *C*HSn), 61.9 (1C, CH_2OH), 62.9 (1C, *C*HPh), 128.0−129.2 (9C, C_6H_5), 132.8 (1C, C_6H_5), 136.2 (1C, C_6H_5), 141.3 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −11.7.

Diastereomer 6a-*syn*. Colorless oil; R_f = 0.29 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19} = +8.9$ (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.56−0.90 (m, 15H, H_{Bu}), 1.12−1.38 (m, 12H, H_{Bu}), 1.42 (d, 3H, ^3J = 7.5, $^3J_{Sn-H}$ = 46, $CHCH_3$), 3.02 (q, 1H, ^3J = 7.5, $^2J_{Sn-H}$ = 57, C*H*Sn), 3.83−4.08 (m, 2H, CH_2OH), 5.08 (bt, 1H, ^3J = 7.5, C*H*Ph), 7.29−7.45 (m, 5H, C_6H_5), 7.47−7.62 (m, 3H, C_6H_5), 7.94−8.02 (m, 2H, C_6H_5); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.4 (3C, $^1J_{Sn-C}$ = 310−324), 13.8 (3C), 21.3 (1C, $CHCH_3$), 27.6 (3C, $^3J_{Sn-C}$ = 58), 29.1 (3C, $^2J_{Sn-C}$ = 18), 39.7 (1C, *C*HSn), 61.5 (1C, CH_2OH), 63.1 (1C, *C*HPh), 127.5−129.2 (9C, C_6H_5), 132.5 (1C, C_6H_5), 136.4 (1C, C_6H_5), 142.8 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −12.4.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[(1*S*)-(tributylstannyl)-pentyl]benzenesulfonamide, 6b-*anti* (509 mg, 80%).** White solid; IR (KBr): 3558, 2954, 2922, 2870, 2855, 1464, 1450, 1309, 1144, 1085, 697, 574; MS (ESI): m/z = 660.2 (M + Na)$^+$; HRMS (ESI) calcd for $C_{31}H_{51}NO_3NaS^{116}Sn$ [M + Na]$^+$: 656.2509. Found: 656.2510; mp = 50−53 °C; R_f = 0.41 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19} = -86.5$ (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.50 (m, 1H, $EtCH_2CH_2$), 0.58 (t, 3H, ^3J = 7, $CH_3(CH_2)_3$), 0.70−0.90 (m, 4H, $CH_3(CH_2)_3$), 0.80−1.10 (m, 15H, H_{Bu}), 1.30−1.60 (m, 12H, H_{Bu}), 1.80 (m, 1H, $PrCH_2$), 2.68 (dd, 1H, ^3J = 7.2, ^3J = 4.1, O*H*), 3.06 (dd, 1H, ^3J = 11.7, ^3J = 3.6, $^2J_{Sn-H}$ = 50.1, C*H*Sn), 3.96 (ddd, 1H, ^2J = 11.5, ^3J = 7.2, ^3J = 5.3, CH_2OH), 4.16 (ddd, 1H, ^2J = 11.5, ^3J = 8.5, ^3J = 4.1, CH_2OH), 4.72 (dd, 1H, ^3J = 8.5, ^3J = 5.3, C*H*Ph), 6.67 (bd, 2H, ^3J = 7.2, C_6H_5), 7.07−7.24 (m, 3H, C_6H_5), 7.51−7.68 (m, 3H, C_6H_5), 7.92−7.99 (m, 2H, C_6H_5). ^{13}C NMR ($CDCl_3$, 300 K) δ 10.9 (3C, $^1J_{Sn-C}$ = 308−320), 13.8 (3C + $CH_3(CH_2)_3$), 22.2 (1C, $CH_3CH_2(CH_2)_2$), 27.6 (3C, $^3J_{Sn-C}$ = 59), 29.3 (3C, $^2J_{Sn-C}$ = 17), 29.8 (1C, $EtCH_2CH_2$), 34.1 (1C, $PrCH_2$), 45.7 (1C, $^1J_{Sn-C}$ = 332−348, *C*HSn), 61.9 (1C, CH_2OH), 63.1 (1C, *C*HPh), 128.1−129.1 (9C, C_6H_5), 132.7 (1C, C_6H_5), 136.0 (1C, C_6H_5), 141.5 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −11.4.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[3-methyl-1-(tributylstannyl)butyl]benzenesulfonamide, 6c (561 mg, 88%, 6c-*anti* = 539 mg, 6c-*syn* = 22 mg).** IR (neat): 3499, 2955, 2925, 2870, 2853, 1465, 1446, 1323, 1149, 742, 690; MS (ESI): m/z = 660.2 (M + Na)$^+$; HRMS (ESI) calcd for $C_{31}H_{51}NO_3NaS^{116}Sn$ [M + Na]$^+$: 656.2509. Found: 656.2508.

Diastereomer 6c-*anti*. Colorless oil; R_f = 0.53 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19} = -79.6$ (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.18 (d, 3H, ^3J = 6.6, $CH(CH_3)_2$), 0.52−0.65 (m, 1H, CH_2iPr), 0.63 (d, 3H, ^3J = 6.6, $CH(CH_3)_2$), 0.89−1.10 (m, 16H, H_{Bu} + $CH(CH_3)_2$), 1.30−1.46 (m, 6H, H_{Bu}), 1.47−1.70 (m, 6H, H_{Bu}), 1.97 (dt, 1H, ^2J = ^3J = 12.6, ^3J = 2.1, CH_2iPr), 2.77 (dd, 1H, ^3J = 6.4, ^3J = 4.1, O*H*), 3.16 (dd, 1H, ^3J = 12.6, ^3J = 3.8, $^2J_{Sn-H}$ = 46.0, C*H*Sn), 4.05 (ddd, 1H, ^2J = 11.5, ^3J = 6.4, ^3J = 5.3, CH_2OH), 4.19 (ddd, 1H, ^2J = 11.5, ^3J = 7.5, ^3J = 4.1, CH_2OH), 4.73 (dd, 1H, ^3J = 7.5, ^3J = 5.3, C*H*Ph), 6.68 (bd, 2H, ^3J = 7.4, C_6H_5), 7.09−7.24 (m, 3H, C_6H_5), 7.52−7.69 (m, 3H, C_6H_5), 7.94−8.01 (m, 2H, C_6H_5); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.8 (3C, $^1J_{Sn-C}$ = 307−322), 13.9 (3C), 20.8 (1C, $CH(CH_3)_2$), 24.0 (1C, $CH(CH_3)_2$), 25.5 (1C, $CH(CH_3)_2$), 27.7 (3C, $^3J_{Sn-C}$ = 60), 29.4 (3C, $^2J_{Sn-C}$ = 16.5), 43.5 (1C, CH_2iPr), 44.9 (1C, *C*HSn), 62.2 (1C, CH_2OH), 63.1 (1C, *C*HPh), 128.1−129.2 (9C, C_6H_5), 132.8 (1C, C_6H_5), 136.0 (1C, C_6H_5), 141.6 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −10.2.

Diastereomer 6c-*syn*. Colorless oil; R_f = 0.29 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19} = +36.1$ (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.56−0.80 (m, 6H, H_{Bu}), 0.80−0.90 (m, 12H, H_{Bu} + $CH(CH_3)_2$), 0.93 (d, 3H, ^3J = 6.0, $CH(CH_3)_2$), 1.10−1.40 (m, 15H, H_{Bu} + $CH(CH_3)_2$ + CH_2iPr + O*H*), 2.18−2.30 (m, 1H, CH_2iPr), 3.05 (dd, 1H, ^3J = 12.2, ^3J = 2.8, $^2J_{Sn-H}$ = 51.1, C*H*Sn), 3.73−3.86 (m, 1H, CH_2OH), 3.88−4.20 (m, 1H, CH_2OH), 5.06 (t, 1H, ^3J = 7.5, C*H*Ph), 7.27−7.60 (m, 8H, C_6H_5), 7.97 (bd, 2H, ^3J = 7.2, C_6H_5); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.8 (3C, $^1J_{Sn-C}$ = 309−322), 13.9 (3C), 21.7 (1C, $CH(CH_3)_2$), 24.0 (1C, $CH(CH_3)_2$), 26.1 (1C, $CH(CH_3)_2$), 27.6 (3C, $^3J_{Sn-C}$ = 60), 29.8 (3C, $^2J_{Sn-C}$ = 16.5), 44.4 (1C, $^1J_{Sn-C}$ = 310−340, *C*HSn), 44.7 (1C, CH_2iPr), 60.9 (1C, CH_2OH), 63.1 (1C, *C*HPh), 127.5−129.1 (9C, C_6H_5), 132.5 (1C, C_6H_5), 136.3 (1C, C_6H_5), 142.8 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −11.1.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[2-methyl-(1*S*)-(tributylstannyl)butyl]benzenesulfonamide, 6d-*anti* (two *anti* diastereomers A/B ≈ 50/50, 184 mg, 29%).** White solid; IR (KBr): 3541, 2957, 2921, 2871, 2852, 1451, 1312, 1143, 1048, 746, 698, 572; MS (ESI): m/z = 660.2 (M + Na)$^+$; HRMS (ESI) calcd for $C_{31}H_{51}NO_3NaS^{116}Sn$ [M + Na]$^+$: 656.2509. Found: 656.2510; mp = 66−69 °C; R_f = 0.53 (eluent = hexanes/diethyl ether: 60/40); ^{1}H NMR ($CDCl_3$, 300 K) δ −0.39 (m, 3H, CH_3CHCHN **A**), 0.26 (t, 3H, **B**), 0.58−0.75 (m, 7H, **A** + CH_3CHCHN **B**), 0.85−1.16 (m, 30H, H_{Bu}), 1.28−1.64 (m, 28H, H_{Bu} + CH_2CHCH), 1.68−1.85 (m, 2H, C*H*CHSn), 2.40−2.47 (m, 2H, O*H*), 3.04 (d, 1H, ^3J = 10.7, $^2J_{Sn-H}$ = 51, C*H*Sn), 3.98−4.30 (m, 4H, CH_2OH), 4.68−4.96 (m, 2H, C*H*Ph), 6.90−7.10 (m, 4H, C_6H_5), 7.15−7.26 (m, 6H, C_6H_5), 7.46−7.64 (m, 6H, C_6H_5), 7.85−7.95 (m, 4H, C_6H_5); ^{13}C NMR ($CDCl_3$, 300 K) δ 11.7 (6C, $^1J_{Sn-C}$ = 304−317), 11.7 (2C, CH_3CH_2), 13.8 (6C), 16.6 (1C, CH_3CHCHN), 17.9 (1C, CH_3CHCHN), 27.7 (6C, $^3J_{Sn-C}$ = 66), 28.2 (2C, CH_2CHCHN), 29.4 (6C), 37.9 (1C, *C*HCHN), 38.5 (1C, *C*HCHN), 52.7 (1C, *C*HSn), 53.9 (1C, *C*HSn), 62.5 (1C, CH_2OH), 62.7 (1C, CH_2OH), 64.8 (2C, *C*HPh), 127.3−129.6 (18C, C_6H_5) 132.6 (2C, C_6H_5), 136.7 (2C, C_6H_5), 141.6 (1C, C_6H_5), 141.8 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −13.3, −14.2.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[(tributylstannyl)methyl]-benzenesulfonamide, 6e (348 mg, 60% after separation from 6d).** Colorless oil; MS (ESI): m/z = 604.1 (M + Na)$^+$; HRMS (ESI) calcd for $C_{27}H_{43}NO_3NaS^{116}Sn$ [M + Na]$^+$: 600.1883. Found: 600.1881; R_f = 0.36 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19} = -22.8$ (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.75−0.95 (m, 15H, H_{Bu}), 1.17−1.58 (m, 12H, H_{Bu}), 1.95 (t, 1H, ^3J = 6.0, O*H*), 2.51 (d, 1H, ^2J = 13.6, $^2J_{Sn-H}$ = 52, CH_2N), 2.66 (d, 1H, ^2J = 13.6, $^2J_{Sn-H}$ = 49.4, CH_2N), 3.88−4.02 (m, 2H, CH_2OH), 5.06 (bt, 1H, ^3J = 6.9, C*H*Ph), 6.97−7.07 (m, 2H, C_6H_5), 7.17−7.30 (m, 3H, C_6H_5), 7.42−7.60 (m, 3H, C_6H_5), 7.78−7.84 (m, 2H, C_6H_5); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.8 (3C, $^1J_{Sn-C}$ = 320−336), 13.8 (3C), 27.5 (3C, $^3J_{Sn-C}$ = 58), 28.3 (1C, $^1J_{Sn-C}$ = 310, CH_2N), 29.1 (3C, $^2J_{Sn-C}$ = 19.6), 61.5 (1C, CH_2OH), 63.2 (1C, *C*HPh), 127.4−129.1 (9C, C_6H_5), 132.6 (1C, C_6H_5), 136.1 (1C, C_6H_5), 139.9 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −21.0.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[2-methyl-1-(tributylstannyl)propyl]benzenesulfonamide, 6f (309 mg, 50%, 6f-*anti* = 159 mg, 6f-*syn* = 150 mg).** IR (KBr): 3549, 2955, 2922, 2870, 2852, 1464, 1311, 1143, 1053, 746, 716, 572; MS (ESI): m/z = 646.2 (M + Na)$^+$, 662.2 (M + K)$^+$; HRMS (ESI) calcd for $C_{30}H_{49}NO_3NaS^{116}Sn$ [M + Na]$^+$: 642.2352. Found: 642.2354.

Diastereomer 6f-*anti*. White solid, mp = 88−90 °C; R_f = 0.53 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19}$ = −59.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ −0.58−0.02 (m, 3H, CH(C*H*$_3$)$_2$), 0.67 (d, 3H, ^3J = 6.4, CH(C*H*$_3$)$_2$), 0.85−1.12 (m, 15H, H_{Bu}), 1.28−1.46 (m, 6H, H_{Bu}), 1.46−1.68 (m, 6H, H_{Bu}), 2.01 (m, 1H, C*H*(CH$_3$)$_2$), 2.38 (m, 1H, O*H*), 2.94 (d, 1H, ^3J=9.8, $^2J_{Sn-H}$=53, C*H*Sn), 4.15−4.30 (m, 2H, C*H*$_2$OH), 4.76−4.96 (m, 1H, C*H*Ph), 6.90−7.05 (m, 2H, C$_6$*H*$_5$), 7.15−7.27 (m, 3H, C$_6$*H*$_5$), 7.47−7.65 (m, 3H, C$_6$*H*$_5$), 7.92 (bd, 2H, ^3J = 7.5, C$_6$*H*$_5$); ^{13}C NMR ($CDCl_3$, 300 K) δ 11.6 (3C, $^1J_{Sn-C}$ = 304−318), 13.9 (3C), 20.7 (1C, $^3J_{Sn-C}$ = 35, CH(*C*H$_3$)$_2$), 21.7 (1C, $^3J_{Sn-C}$ = 35, CH(*C*H$_3$)$_2$), 27.7 (3C, $^3J_{Sn-C}$ = 61), 29.4 (3C, $^2J_{Sn-C}$ = 16), 31.5 (1C, *C*H(CH$_3$)$_2$), 53.2 (1C, *C*HSn), 62.5 (1C, *C*H$_2$OH), 64.6 (1C, *C*HPh), 127.3−129.6 (9C, C$_6$H$_5$), 132.6 (1C, C$_6$H$_5$), 136.8 (1C, C$_6$H$_5$), 141.6 (1C, C$_6$H$_5$); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −12.9.

Diastereomer 6f-*syn*. Colorless oil; R_f = 0.36 (eluent = hexanes/diethyl ether: 60/40); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.54 (d, 3H, ^3J = 6.4, CH(C*H*$_3$)$_2$), 0.81−0.92 (m, 18H, H_{Bu} + CH(C*H*$_3$)$_2$), 1.17−1.48 (m, 12H, H_{Bu}), 2.17−2.35 (m, 1H, C*H*(CH$_3$)$_2$), 2.68 (d, 1H, ^3J = 11.1, $^2J_{Sn-H}$ = 46.3, C*H*Sn), 3.80−4.06 (m, 2H, C*H*$_2$OH), 5.25 (bt, 1H, ^3J = 6.7, C*H*Ph), 6.97−7.04 (m, 2H, C$_6$*H*$_5$), 7.32−7.42 (m, 3H, C$_6$*H*$_5$), 7.50−7.62 (m, 3H, C$_6$*H*$_5$), 7.83−7.91 (m, 2H, C$_6$*H*$_5$); ^{13}C NMR ($CDCl_3$, 300 K) δ 11.7 (3C), 13.7 (3C), 22.4 (2C, CH(*C*H$_3$)$_2$), 27.7 (3C), 29.3 (3C, $^2J_{Sn-C}$ = 16), 31.1 (1C, *C*H(CH$_3$)$_2$), 56.5 (1C, *C*HSn), 62.5 (1C, *C*H$_2$OH), 63.9 (1C, *C*HPh), 127.0−129.7 (9C, C$_6$H$_5$), 132.2 (1C, C$_6$H$_5$), 136.0 (1C, C$_6$H$_5$), 142.9 (1C, C$_6$H$_5$); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −14.7.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[2-phenyl-1-(tributylstannyl)ethyl]benzenesulfonamide, 6g (489 mg, 73%, 6g-*anti* = 178 mg, 6g-*syn* = 311 mg).** IR (neat): 3452, 2953, 2922, 2869, 2851, 1454, 1437, 1306, 1146, 977, 738, 698, 588; MS (ESI): *m*/*z* = 694.2 (M + Na)$^+$, 710.2 (M + K)$^+$; HRMS (ESI) calcd for $C_{34}H_{49}NO_3NaS^{116}Sn$ [M + Na]$^+$: 690.2353. Found: 690.2354.

Diastereomer 6g-*anti*. Colorless oil; R_f = 0.46 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19}$ = −98.0 (*c* = 0.97, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.60−0.95 (m, 15H, H_{Bu}), 1.17−1.41 (m, 12H, H_{Bu}), 2.17 (dd, 1H, ^2J = 11.5, ^3J = 3.0, C*H*$_2$Ph), 2.98−3.12 (m, 2H, C*H*$_2$Ph + O*H*), 3.27 (dd, 1H, ^3J = 12.9, ^3J = 3, $^2J_{Sn-H}$ = 52, C*H*Sn), 4.00−4.12 (m, 1H, C*H*$_2$OH), 4.21 (ddd, 1H, ^2J = 11.5, ^3J = 7.5, ^3J = 4.0, C*H*$_2$OH), 4.84 (bt, 1H, $^3J \approx$ 7.5, C*H*Ph), 6.50−6.58 (m, 2H, C$_6$*H*$_5$), 6.82 (bd, 2H, ^3J = 6.8, C$_6$*H*$_5$), 7.05−7.15 (m, 3H, C$_6$*H*$_5$), 7.20−7.40 (m, 3H, C$_6$*H*$_5$), 7.55−7.72 (m, 3H, C$_6$*H*$_5$), 8.07 (bd, 2H, ^3J = 7.4, C$_6$*H*$_5$). ^{13}C NMR ($CDCl_3$, 300 K) δ 10.7 (3C, $^1J_{Sn-C}$ = 311−324), 13.8 (3C), 27.5 (3C, $^3J_{Sn-C}$ = 62), 29.0 (3C, $^2J_{Sn-C}$ = 18), 40.7 (1C, *C*H$_2$Ph), 47.4 (1C, *C*HSn), 62.1 (1C, *C*H$_2$OH), 62.9 (1C, *C*HPh), 127.4−129.1 (14C, C$_6$H$_5$), 132.6 (1C, C$_6$H$_5$), 136.1 (1C, C$_6$H$_5$), 138.1 (1C, C$_6$H$_5$), 141.3 (1C, C$_6$H$_5$); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −7.0.

Diastereomer 6g-*syn*. Colorless oil; R_f = 0.28 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19}$ = + 76.5° (*c* = 0.91, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.38−0.64 (m, 6H, H_{Bu}), 0.79−0.90 (m, 9H, H_{Bu}), 1.07−1.25 (m, 12H, H_{Bu}), 3.04 (dd, 1H, ^2J = 13.5, ^3J = 7.9, C*H*$_2$Ph), 3.06 (dd, 1H, ^2J = 13.5, ^3J = 7.9, C*H*$_2$Ph), 3.29 (t, 1H, ^3J = 7.9, $^2J_{Sn-H}$ = 50, C*H*Sn), 3.58−3.80 (m, 2H, C*H*$_2$OH), 5.16 (dd, 1H, ^3J = 8.3, ^3J = 6.2, C*H*Ph), 6.82−6.90 (m, 2H, C$_6$*H*$_5$), 7.17−7.24 (m, 3H, C$_6$*H*$_5$), 7.28−7.48 (m, 8H, C$_6$*H*$_5$), 8.05 (bd, 2H, ^3J = 7.5, C$_6$*H*$_5$); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.8 (3C, $^1J_{Sn-C}$ = 311−323), 13.8 (3C), 27.6 (3C, $^3J_{Sn-C}$ = 62.0), 29.0 (3C, $^2J_{Sn-C}$ = 19.2), 40.8 (1C, *C*H$_2$Ph), 47.8 (1C, $^1J_{Sn-C}$ = 334, *C*HSn), 61.7 (1C, *C*H$_2$OH), 63.7 (1C, *C*HPh), 127.1−129.1 (14C, C$_6$H$_5$), 132.5 (1C, C$_6$H$_5$), 136.3 (1C, C$_6$H$_5$), 140.2 (1C, C$_6$H$_5$), 143.3 (1C, C$_6$H$_5$); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −10.7.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[1-(tributylstannyl)but-3-en-1-yl]benzenesulfonamide, 6h (reaction performed on 0.5 mmol of 6, 236 mg, 76%, 6h-*anti* = 221 mg, 6h-*syn* = 15 mg).** MS (ESI): *m*/*z* = 644.2 (M + Na)$^+$; HRMS (ESI) calcd for $C_{30}H_{47}NO_3NaS^{116}Sn$ [M + Na]$^+$: 640.2197. Found: 640.2194.

Diastereomer 6h-*anti*. White crystals, mp = 60−62 °C; R_f = 0.44 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19}$ = −66.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.85−1.10 (m, 15H, H_{Bu}), 1.30−1.60 (m, 13H, H_{Bu} + C*H*$_2$CH=CH$_2$), 2.50 (m, 1H, C*H*$_2$CH=CH$_2$), 2.67 (dd, 1H, ^3J = 7.4, ^3J = 4.1, O*H*), 3.07 (dd, 1H, ^3J = 12.1, ^3J = 3.6, $^2J_{Sn-H}$ = 51, C*H*Sn), 3.96 (ddd, 1H, ^2J = 11.3, ^3J = 7.4, ^3J = 5.1, C*H*$_2$OH), 4.17 (ddd, 1H, ^2J = 11.3, ^3J = 8.3, ^3J = 4.1, C*H*$_2$OH), 4.60 (bd, 1H, ^3J = 17.3, =C*H*$_2$), 4.73 (dd, 1H, ^3J = 8.3, ^3J = 5.1, C*H*Ph), 4.79 (bd, 1H, ^3J = 9.8, =C*H*$_2$), 5.02−5.20 (m, 1H, =C*H*), 6.67 (bd, 2H, ^3J = 7.5, C$_6$*H*$_5$), 7.10−7.24 (m, 3H, C$_6$*H*$_5$), 7.52−7.70 (m, 3H, C$_6$*H*$_5$), 7.97 (bd, 2H, ^3J = 7.5, C$_6$*H*$_5$); ^{13}C NMR ($CDCl_3$, 300 K) δ 11.3 (3C, $^1J_{Sn-C}$ = 311−325), 13.8 (3C), 27.6 (3C, $^3J_{Sn-C}$ = 59), 29.2 (3C, $^2J_{Sn-C}$ = 18), 39.0 (1C, *C*H$_2$CH=CH$_2$), 44.6 (1C, $^1J_{Sn-C}$ = 320−335, *C*HSn), 61.9 (1C, *C*H$_2$OH), 63.0 (1C, *C*HPh), 117.7 (1C, =*C*H$_2$), 128.1−129.2 (9C, C$_6$H$_5$), 132.8 (1C, C$_6$H$_5$), 134.6 (1C, =*C*H), 135.9 (1C, C$_6$H$_5$), 141.2 (1C, C$_6$H$_5$); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −7.6.

Diastereomer 6h-*syn*. Colorless oil; R_f = 0.23 (eluent = hexanes/diethyl ether: 60/40); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.80−1.75 (m, 27H, H_{Bu}), 2.53 (m, 2H, C*H*$_2$CH=CH$_2$), 2.99 (t, 1H, ^3J = 7.7, $^2J_{Sn-H}$ = 62, C*H*Sn), 3.75−4.00 (m, 2H, C*H*$_2$OH), 4.72 (bd, 1H, ^3J = 17.1, =C*H*$_2$), 4.95 (bd, 1H, ^3J = 10.4, =C*H*$_2$), 5.16 (dd, 1H, ^3J = 8.5, ^3J = 6.4, C*H*Ph), 5.55−5.73 (m, 1H, =C*H*), 7.24−7.62 (m, 8H, C$_6$*H*$_5$), 7.99 (bd, 2H, ^3J = 7.2, C$_6$*H*$_5$); ^{13}C NMR ($CDCl_3$, 300 K) δ 11.0 (3C), 13.8 (3C), 28.0 (3C), 29.1 (3C), 39.3 (1C, *C*H$_2$CH=CH$_2$), 45.3 (1C, *C*HSn), 61.2 (1C, *C*H$_2$OH), 63.6 (1C, *C*HPh), 117.8 (1C, =*C*H$_2$), 127.6−129.1 (9C, C$_6$H$_5$), 132.5 (2C, C$_6$H$_5$ + =*C*H), 136.3 (1C, C$_6$H$_5$), 136.9 (1C, C$_6$H$_5$); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −10.2.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[(1*S*)-(tributylstannyl)-3-methyl-but-3-en-1-yl]-benzenesulfonamide, 6i (reaction performed on 0.5 mmol of 6, 231 mg, 73%, 6i-*anti* = 224 mg, 6i-*syn* = 7 mg). Diastereomer 6i-*anti*.** White solid, IR (neat): 3506, 2958, 2923, 2871, 2853, 1446, 1375, 1325, 1152, 1085, 743, 574; MS (ESI): *m*/*z* = 636.2 (M + H)$^+$, 658.2 (M + Na)$^+$, 674.1 (M + K)$^+$; HRMS (ESI) calcd for $C_{31}H_{49}NO_3NaS^{116}Sn$ [M + Na]$^+$: 654.2352. Found: 654.2350; mp = 62−64 °C; R_f = 0.50 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19}$ = −104.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.8−1.05 (m, 15H, H_{Bu}), 1.05 (s, 3H, C*H*$_3$C=CH$_2$), 1.30−1.60 (m, 13H, H_{Bu} + C*H*$_2$C=CH$_2$), 2.65−2.80 (m, 1H, C*H*$_2$C=CH$_2$), 2.67 (dd, 1H, ^3J = 7.2, ^3J = 4.0, O*H*), 3.28 (dd, 1H, ^3J = 13.0, ^3J = 2.8, $^2J_{Sn-H}$ = 48, C*H*Sn), 4.04 (ddd, 1H, ^2J = 11.5, ^3J = 7.2, ^3J = 5.3, C*H*$_2$OH), 4.20 (ddd, 1H, ^2J = 11.5, ^3J = 7.7, ^3J = 4.0, C*H*$_2$OH), 4.59 (bs, 1H, =C*H*$_2$), 4.63 (bs, 1H, =C*H*$_2$), 4.75 (dd, 1H, ^3J = 7.7, ^3J = 5.3, C*H*Ph), 6.67 (bd, 2H, ^3J = 7.5, C$_6$*H*$_5$), 7.09−7.25 (m, 3H, C$_6$*H*$_5$), 7.54−7.70 (m, 3H, C$_6$*H*$_5$), 8.00 (bd, 2H, ^3J = 7.7, C$_6$*H*$_5$); ^{13}C NMR ($CDCl_3$, 300 K) δ 11.2 (3C, $^1J_{Sn-C}$ = 312−325), 13.8 (3C), 21.5 (1C, *C*H$_3$C=CH$_2$), 27.7 (3C, $^3J_{Sn-C}$ = 60), 29.2 (3C, $^2J_{Sn-C}$ = 15), 43.0 (1C, *C*H$_2$C=CH$_2$), 44.4 (1C, $^1J_{Sn-C}$ = 330−344, *C*HSn), 62.1 (1C, *C*H$_2$OH), 62.9 (1C, *C*HPh), 114.2 (1C, =*C*H$_2$), 128.0−129.3 (9C, C$_6$H$_5$), 132.8 (1C, C$_6$H$_5$), 135.8 (1C), 141.3 (1C), 141.7 (1C). ^{119}Sn NMR ($CDCl_3$, 300 K) δ −6.2.

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[1-tributylstannyl)ethyl]-methanesulfonamide, 7a (reaction performed on 1.43 mmol of 7, 305 mg, 40%, 7a-*anti* = 275 mg, 7a-*syn* = 30 mg).** IR (neat): 3500, 2954, 2921, 2870, 1456, 1317, 1138, 963, 701.

Diastereomer 7a-*anti*. Colorless oil; R_f = 0.22 (eluent = hexanes/diethyl ether: 70/30); $[\alpha]_D^{19}$ = −53.2 (*c* = 0.8; $CHCl_3$) ^{1}H NMR ($CDCl_3$, 300 K) δ 0.90 (t, 9H, H_{Bu}), 0.85−0.96 (m, 6H, H_{Bu}), 0.94 (d, 3H, ^3J = 7.5, $^3J_{Sn-H}$ = 51), 1.30−1.56 (m, 12H, H_{Bu}), 2.12 (dd, 1H, ^3J = 6.2, ^3J = 5.3, O*H*), 3.0 (s, 3H, SO$_2$C*H*$_3$), 3.30 (q, 1H, ^3J = 7.5, $^2J_{Sn-H}$ = 54, C*H*Sn), 3.95 (m, 1H, ^2J = 11.3, ^3J = 6.2, ^3J = 5.5, C*H*$_2$OH), 4.11 (ddd, 1H, ^2J = 11.3, ^3J = 8.4, ^3J = 5.3, C*H*$_2$OH), 4.86 (dd, 1H, ^3J = 8.4, ^3J = 5.5, C*H*Ph), 7.4 (m, 5H,

C_6H_5); ^{13}C NMR ($CDCl_3$, 300 K) δ 8.5 (3C, $^1J_{Sn-C}$ = 311−325), 11.8 (3C), 17.3 (1C, $^2J_{Sn-C}$ = 12, CH*C*H$_3$), 25.6 (3C, $^3J_{Sn-C}$ = 57), 27.3 (3C, $^2J_{Sn-C}$ = 19), 38.5 (1C, $^1J_{Sn-C}$ = 335−351, *C*HSn), 41.5 (1C, SO_2CH_3), 60.5 (1C, *C*H$_2$OH), 62.1 (1C, *C*HPh), 126.7 (2C, C_6H_5), 126.8 (1C, C_6H_5), 127.1 (2C, C_6H_5), 134.8 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −15.6; MS (EI): organostannyl fragments *m*/*z* (%) = 476 (100), 454 (15), 396 (20), 356 (30), 313 (57), 291 (26), 235 (33), 199 (28), 179 (50), 177 (20), 121 (20); organic fragments *m*/*z* (%) = 242 (9), 162 (6), 132 (26), 122 (67), 121 (21), 103 (41), 91 (17), 44 (23); MS(CI, NH_3): organostannyl fragments *m*/*z* (%) = 551 (M + NH_4^+ ; 9), 534 (M + H^+ ; 6), 476 (35), 431 (8), 356 (12), 308 (12); organic fragments *m*/*z* (%) = 164 (100).

Diastereomer 7a-*syn*. Colorless oil; R_f = 0.11 (eluent = hexanes/diethyl ether: 70/30); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.87−0.95 (m, 15H, H_{Bu}), 1.23−1.51 (m, 12H, H_{Bu}), 1.55 (d, 3H, ^3J = 7.6, $^3J_{Sn-H}$ = 46, CHC*H*$_3$), 3.01 (q, 1H, ^3J = 7.6, $^2J_{Sn-H}$ = 56, C*H*Sn), 3.09 (s, 3H, SO_2CH_3), 4.13 (dd, 1H, ^2J = 10.8, ^3J = 4.8, CH_2OH), 4.26 (t, 1H, $^2J \approx {}^3J \approx$ 10.4, CH_2OH), 5.09 (dd, 1H, ^3J = 10, ^3J = 4.8, C*H*Ph), 7.29−7.42 (m, 5H, C_6H_5) ; ^{13}C NMR ($CDCl_3$, 300 K) δ 10.1 (3C, $^1J_{Sn-C}$ = 310−325), 13.7 (3C), 20.3 (1C, $^2J_{Sn-C}$ = 13, CH*C*H$_3$), 27.4 (3C, $^3J_{Sn-C}$ = 59), 28.9 (3C, $^2J_{Sn-C}$ = 19), 39.2 (1C, *C*HSn), 44.2 (1C, SO_2CH_3), 61.5 (1C, *C*H$_2$OH), 62.9 (1C, *C*HPh), 128.2 (1C, C_6H_5), 128.3 (2C, C_6H_5), 128.6 (2C, C_6H_5), 136.9 (1C, C_6H_5); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −15.85; MS (EI): organostannyl fragments *m*/*z* (%) = 476 (100), 454 (13), 396 (15), 356 (22), 313 (57), 291 (25), 235 (33), 199 (21), 179 (42), 177 (18), 121 (17); organic fragments *m*/*z* (%) = 242 (8), 162 (4), 132 (24), 122 (64), 121 (21), 103 (38), 91 (18), 79 (8), 44 (16); MS(CI, NH_3): organostannyl fragments *m*/*z* (%) = 551 (M + NH_4^+ ; 14), 534 (M + H^+ ; 11), 476 (31), 454 (10), 431 (7), 356 (8), 308 (9); organic fragments *m*/*z* (%) = 164 (100).

***N*-[(1*R*)-2-Hydroxy-1-phenylethyl]-*N*-[1-(trimethylstannyl)ethyl]-toluenesulfonamide, 8a-*anti* (260 mg, 54%).** Colorless oil; IR (neat): 3513, 3032, 2980, 1598, 1322, 1148, 768, 666; MS (EI): organostannyl fragments *m*/*z* (%) = 468 (3), 424 (16), 320 (70), 241 (22), 165 (25), organic fragments *m*/*z* (%) = 318 (54), 274 (1), 198 (21), 181 (23), 155 (44), 104 (19), 91 (100), 65 (15). $[\alpha]_D^{19}$ = −124.1 (*c* = 0.95; $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.21 (s, 9H, $^2J_{SnH}$ = 51.0−53.3, H_{Me}), 0.84 (d, 3H, ^3J = 7.4, $^3J_{SnH}$ = 53.2−56.1, CH_3CH), 2.48 (s, 3H, CH_3C$_6$H$_4$), 2.69 (bdd, $^3J \approx$ 5, $^3J \approx$ 4, O*H*), 3.10 (q, 1H, ^3J = 7.4, $^2J_{Sn-H}$ = 57.5−61.3, CH$_3$C*H*Sn), 3.98 (m, 1H, $^3J \approx$ 5, ^2J = 11.2, CH_2OH), 4.16 (m, 1H, ^2J = 11.2, ^3J = 4.1, ^3J = 8.7, CH_2OH), 4.72 (dd, 1H, ^3J = 5.3, ^3J = 8.7, C*H*Ph), 6.79 (bd, 2H, ^3J = 8.3, H_{Ar}), 7.15−7.25 (m, 3H, H_{Ar}), 7.36 (d, 2H, ^3J = 8, H_{Ar}), 7.81 (d, 2H, ^3J = 8.3, H_{Ar}); ^{13}C NMR ($CDCl_3$, 300 K) δ −8.27 (9C, $^1J_{Sn-C}$ = 310), 19.3 (1C, *C*H$_3$CH), 21.7 (1C, *C*H$_3$C$_6$H$_4$), 40.6 (1C, *C*HSn), 61.8 (1C, *C*H$_2$OH); 62.6 (1C, *C*HPh), 128.0 (2C, C_{Ar}), 128.3 (2C, C_{Ar}), 128.4 (1C, C_{Ar}), 128.6 (2C, C_{Ar}), 129.9 (2C, C_{Ar}), 136.3 (1C, C_{Ar}), 138.5 (1C, C_{Ar}), 143.6 (1C, C_{Ar}); ^{119}Sn NMR ($CDCl_3$, 300 K) δ 6.4.

***N*-[(1*S*)-1-(Hydroxymethyl)-2-methylpropyl]-*N*-[(1*R*)-1-(tributylstannyl)ethyl]toluenesulfonamide, 9a (448 mg of 9a-*anti*, 78%). Diastereomer 9a-*anti*.** Colorless oil; IR (neat): 3525, 1465, 1320, 1145, 1088, 667; MS (EI): organostannyl fragments *m*/*z* (%) = 518 (35), 420 (10), 389 (36), 362 (14), 325 (63), 269 (38), 235 (22), 211 (44), 177 (58), 121 (32); organic fragments *m*/*z* (%) = 284 (82), 268 (46), 198 (100), 155 (85), 91 (29), 69 (25), 55 (26), 41 (42), 29 (31); Elemental analysis calcd (%) for $C_{26}H_{49}NO_3SSn$: C 54.52; H 8.10; N 2.45; S 5.59; Sn 20.95. Found: C 54.33; H 8.29; N 2.47; S 5.36; Sn 20.10; R_f = 0.70 (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19}$ = +35.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.37 (d, 3H, ^3J = 6.6, CH(CH_3)$_2$), 0.77 (d, 3H, ^3J = 6.6, CH(CH_3)$_2$), 0.85 (bt, 9H, ^3J = 7.3, H_{Bu}), 0.95−1.22 (m, 6H, H_{Bu}), 1.26−1.35 (m, 6H, H_{Bu}), 1.41 (d, 3H, ^3J = 7.5, CH_3CHSn), 1.42−1.60 (m, 6H, H_{Bu}), 1.65−1.80 (m, 1H, C*H*(CH$_3$)$_2$), 2.35 (s, 3H, C$_6$H$_4$CH_3), 2.50 (t, 1H, ^3J = 5.0, O*H*), 3.15 (q, 1H, ^3J = 7.5, $^2J_{Sn-H}$ = 56, C*H*Sn), 3.07−3.20 (m, 1H, C*H*CH$_2$OH), 3.57 (ddd, 1H, ^2J = 11.5, ^3J = 8.3, ^3J = 5.0, CH_2OH), 3.75 (ddd, 1H, ^2J = 11.5, ^3J = 5.0, ^3J = 4.0, CH_2OH), 7.20 (bd, 2H, ^3J = 8.2, C_6H_4), 7.60 (bd, 2H, ^3J = 8.2, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.9 (3C, $^1J_{Sn-C}$ = 307−320), 13.7 (3C), 19.5 (1C, CH(*C*H$_3$)$_2$), 20.8 (1C, *C*H$_3$CHSn), 21.3 (1C, CH(*C*H$_3$)$_2$), 21.4 (1C, C$_6$H$_4$*C*H$_3$), 27.4 (3C, $^3J_{Sn-C}$ = 59), 28.6 (1C, *C*H(CH$_3$)$_2$), 29.0 (3C, $^2J_{Sn-C}$ = 19), 39.7 (1C, $^1J_{Sn-C}$ = 336−350, *C*HSn), 61.3 (1C, *C*H$_2$OH), 66.8 (1C, *C*HCH$_2$OH), 127.8 (2C, C_{Ar}), 129.5 (2C, C_{Ar}), 138.4 (1C, C_{Ar}), 143.2 (1C, C_{Ar}). ^{119}Sn NMR ($CDCl_3$, 300 K) δ −15.8.

***N*-[(1*S*)-1-(Hydroxymethyl)-2-methylpropyl]-*N*-[(1*R*)-1-(tributylstannyl)pentyl]toluenesulfonamide, 9b (431 mg of 9b-*anti*, 70%). 9b-*anti*.** Colorless oil; IR (neat): 3522, 2956, 2924, 2870, 2856, 1464, 1322, 1288, 1145, 1086, 667, 546; MS (EI): organostannyl fragments *m*/*z* (%) = 560 (45), 462 (14), 404 (16), 389 (33), 325 (60), 291 (18), 269 (24), 235 (25), 179 (38), 177 (40), 121 (24); organic fragments *m*/*z* (%) = 326 (98), 240 (100), 155 (66), 91 (65), 85 (23), 71 (37), 69 (37), 57 (59), 43 (53), 41 (53), 29 (29); HRMS (CI) calcd for $C_{29}H_{56}NO_3S^{116}Sn$ [M + H]$^+$: 614.3003. Found: 614.3002; R_f = 0.69 (eluent = hexanes/diethyl ether: 60/40), $[\alpha]_D^{19}$ = +63.8 (*c* = 1.0, $CHCl_3$), ^{1}H NMR ($CDCl_3$, 300 K) δ 0.35 (d, 3H, ^3J = 5.8, CH(CH_3)$_2$), 0.75 (d, 3H, ^3J = 5.8, CH-(CH_3)$_2$), 0.85 (bt, 9H, ^3J = 7.2, H_{Bu}), 0.90−1.15 (m, 6H, H_{Bu}), 1.10−1.80 (m, 20H, H_{Bu} + *Bu*), 1.65−1.85 (m, 1H, C*H*(CH$_3$)$_2$), 2.12−2.30 (m, 1H, CH_2CHSn), 2.35 (s, 3H, C$_6$H$_4$CH_3), 2.40 (t, 1H, ^3J = 5.0, O*H*), 3.02 (dd, 1H, ^3J = 12.1, ^3J = 3.4, $^2J_{Sn-H}$ = 51, C*H*Sn), 3.17 (td, 1H, ^3J = 8.0, ^3J = 3.6, C*H*CH$_2$OH), 3.60 (ddd, 1H, ^2J = 11.4, ^3J = 8.0, ^3J = 5.0, CH_2OH), 3.75 (ddd, 1H, ^2J = 11.4, ^3J = 3.6, ^3J = 5.0, CH_2OH), 7.20 (bd, 2H, ^3J = 8.0, C_6H_4), 7.65 (bd, 2H, ^3J = 8.0, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 11.1 (3C, $^1J_{Sn-C}$ = 305−319), 13.5 (3C), 13.8 (1C, *C*H$_3$(CH$_2$)$_3$), 19.4 (1C, CH(*C*H$_3$)$_2$), 21.2 (1C, CH(*C*H$_3$)$_2$), 21.5 (1C, C$_6$H$_4$*C*H$_3$), 22.5 (1C, CH$_3$(*C*H$_2$)$_3$), 27.3 (3C, $^3J_{Sn-C}$ = 60), 29.1 (1C, *C*H-(CH$_3$)$_2$), 29.8 (3C, $^2J_{Sn-C}$ = 19), 30.4 (1C, CH$_3$(*C*H$_2$)$_3$), 34.7 (1C, *C*H$_2$CHSn), 46.1 (1C, $^1J_{Sn-C}$ = 340−356, *C*HSn), 61.3 (1C, *C*H$_2$OH), 66.7 (1C, *C*HCH$_2$OH), 127.5 (2C, C_6H_4), 129.1 (2C, C_6H_4), 138.3 (1C, C_6H_4), 142.7 (1C, C_6H_4); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −15.1.

***N*-[(1*S*)-1-(Hydroxymethyl)-2-methylpropyl]-4-methyl-*N*-[(1*S*)-1-(tributylstannyl)but-3-en-1-yl]toluenesulfonamide, 9h (528 mg of 9h-*syn*, 88%).** White crystals; IR (KBr): 3539, 2954, 2927, 1465, 1319, 1144, 1080, 984, 913, 678; MS (EI): organostannyl fragments *m*/*z* (%) = 544 (63), 446 (12), 325 (69), 289 (40), 269 (40), 235 (26), 211 (44), 179 (47), 177 (49), 121 (32); organic fragments *m*/*z* (%) = 310 (58), 268 (43), 224 (100), 155 (84), 91 (86), 69 (31), 55 (39), 41 (44), 29 (28); R_f = 0.44 (eluent = hexanes/diethyl ether: 60/40), Mp = 72−74 °C; $[\alpha]_D^{19}$ = −86.0 (*c* = 1.0, $CHCl_3$); Elemental analysis calcd (%) for $C_{28}H_{51}NO_3SSn$: C 55.88; H 8.55; N 2.32. Found: C 56.69; H 8.73; N 2.82. ^{1}H NMR ($CDCl_3$, 300 K) δ 0.35 (d, 3H, ^3J = 6.3, CH(CH_3)$_2$), 0.77 (d, 3H, ^3J = 6.3, CH(CH_3)$_2$), 0.82 (bt, 9H, ^3J = 6.9, H_{Bu}), 0.82−1.55 (m, 18H, H_{Bu}), 1.75−2.00 (m, 1H, C*H*(CH$_3$)$_2$), 2.35 (s, 3H, C$_6$H$_4$CH_3), 2.50−2.65 (m, 1H, CH_2CHSn), 2.78 (ddd, 1H, ^2J = 13.0, ^3J = 10.8, ^3J = 8.0, CH_2CHSn), 3.10 (dd, 1H, ^3J = 10.8, ^3J = 4.3, $^2J_{Sn-H}$ = 56, C*H*Sn), 3.35−3.50 (m, 1H, C*H*CH$_2$OH), 3.52−3.72 (m, 2H, CH_2OH), 4.98 (bd, 1H, ^3J = 9.5, =CH_2), 5.02 (bd, 1H, ^3J = 17.2, =CH_2), 5.52−5.73 (m, 1H, =C*H*), 7.27 (bd, 2H, ^3J = 8.1, C_6H_4), 7.75 (bd, 2H, ^3J = 8.1, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 12.2 (3C, $^1J_{Sn-C}$ = 309−322), 14.1 (3C), 20.4 (1C, CH(*C*H$_3$)$_2$), 21.8 (1C, CH(*C*H$_3$)$_2$), 21.9 (1C, C$_6$H$_4$*C*H$_3$), 27.9 (3C, $^3J_{Sn-C}$ = 61), 29.0 (1C, *C*H(CH$_3$)$_2$), 29.6 (3C, $^2J_{Sn-C}$ = 13), 39.7 (1C, *C*H$_2$CHSn), 45.7 (1C, $^1J_{Sn-C}$ = 339−356, *C*HSn), 61.4 (1C, *C*H$_2$OH), 67.5 (1C, *C*HCH$_2$OH), 118.0 (1C, =*C*H$_2$), 128.2 (2C, C_6H_4), 129.8 (2C, C_6H_4), 136.3 (1C, =*C*H), 139.3 (1C, C_6H_4), 143.5 (1C, C_6H_4); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −12.2.

***N*-[(1*S*)-2-Hydroxy-1-methylethyl]-*N*-[1-(tributylstannyl)ethyl]-toluenesulfonamide, 10a (421 mg, 77%, 10a-*anti* = 280 mg,**

10a-*syn* = 141 mg). IR (neat): 3522, 2954, 2922, 2870, 2854, 1324, 1146, 660, 599; MS (ESI): $m/z = 570.1$ $(M + Na)^+$; HRMS (ESI) calcd for $C_{24}H_{45}NO_3NaS^{116}Sn$ $[M + Na]^+$: 566.2039. Found: 566.2037.

Diastereomer 10a-*anti*. Colorless oil; $R_f = 0.45$ (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19} = +58.5$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.89 (bt, 9H, $^3J = 7.2$, H_{Bu}), 0.94−1.05 (m, 6H, H_{Bu}), 1.02 (d, 3H, $^3J = 4.3$, CH_3CHCH_2OH), 1.20−1.65 (m, 12H, H_{Bu}), 1.37 (d, 3H, $^3J = 7.2$, CH_3CHSn), 2.40 (s, 3H, $C_6H_4CH_3$), 2.46 (t, 1H, $^3J = 5.2$, O*H*), 3.17 (q, 1H, $^3J = 7.2$, $^2J_{Sn-H} = 55$, C*H*Sn), 3.43−3.65 (m, 2H, CH_2OH), 3.72−3.87 (m, 1H, $CHCH_2OH$), 7.26 (bd, 2H, $^3J = 8.1$, C_6H_4), 7.73 (bd, 2H, $^3J = 8.1$, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.3 (3C, $^1J_{Sn-C} = 308-323$), 13.8 (3C), 15.0 (1C, CH_3CHCH_2OH), 20.9 (1C, CH_3CHSn), 21.6 (1C, $C_6H_4CH_3$), 27.6 (3C, $^3J_{Sn-C} = 59$), 29.2 (3C, $^2J_{Sn-C} = 19$), 38.9 (1C, $^1J_{Sn-C} = 334-349$, *C*HSn), 56.8 (1C, *C*HCH$_2$OH), 64.6 (1C, *C*H$_2$OH), 127.2 (2C, C_6H_4), 129.7 (2C, C_6H_4), 139.1 (1C, C_6H_4), 143.0 (1C, C_6H_4); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −13.2.

Diastereomer 10a-*syn*. Colorless oil; $R_f = 0.27$ (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19} = -20.1$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.85−0.99 (m, 15H, H_{Bu}), 1.18 (d, 3H, $^3J = 6.6$, CH_3CHCH_2OH), 1.21−1.38 (m, 6H, H_{Bu}), 1.40−1.57 (m, 6H, H_{Bu}), 1.44 (d, 3H, $^3J = 7.5$, CH_3CHSn), 2.40 (s, 3H, $C_6H_4CH_3$), 3.17 (q, 1H, $^3J = 7.5$, $^2J_{Sn-H} = 55.4$, C*H*Sn), 3.42−3.54 (m, 1H, CH_2OH), 3.56−3.67 (m, 1H, CH_2OH), 3.68−3.80 (m, 1H, $CHCH_2OH$), 7.27 (bd, 2H, $^3J = 8.1$, C_6H_4), 7.76 (bd, 2H, $^3J = 8.1$, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.4 (3C, $^1J_{Sn-C} = 304-319$), 13.8 (3C), 15.7 (1C, CH_3CHCH_2OH), 21.2 (1C, CH_3CHSn), 21.6 (1C, $C_6H_4CH_3$), 27.7 (3C, $^3J_{Sn-C} = 58$), 29.3 (3C, $^2J_{Sn-C} = 19$), 39.4 (1C, $^1J_{Sn-C} = 324$, *C*HSn), 57.6 (1C, *C*HCH$_2$OH), 64.9 (1C, *C*H$_2$OH), 127.4 (2C, C_6H_4), 129.7 (2C, C_6H_4), 139.1 (1C, C_6H_4), 143.1 (1C, C_6H_4); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −15.6.

***N*-[(1*S*)-2-Hydroxy-1-methylethyl]-*N*-[1-(tributylstannyl)pentyl]-toluenesulfonamide, 10b (reaction carried out on 0.3 mmol, 138 mg, 78%, only 10b-*anti* was isolated as a clean isomer).** IR (neat): 3475, 2956, 2923, 2871, 2855, 1465, 1327, 1145, 735, 658; MS (CI): $m/z = 590$ $(M + H)^+$; HRMS (CI) calcd for $C_{27}H_{52}NO_3S^{116}Sn$ $[M + H]^+$: 586.2689. Found: 586.2685.

Diastereomer 10b-*anti*. Colorless oil; $R_f = 0.50$ (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19} = +90.9$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.80−1.64 (m, 38H, H_{Bu} + CH_3CHCH_2OH + *Bu*CHSn), 1.97−2.17 (m, 1H, CH_2CHSn), 2.33 (dd, 1H, $^3J = 6.8$, $^3J = 4.8$, O*H*), 2.41 (s, 3H, $C_6H_4CH_3$), 2.99 (dd, 1H, $^3J = 11.7$, $^3J = 4.0$, $^2J_{Sn-H} = 51.6$, C*H*Sn), 3.42−3.64 (m, 2H, CH_2OH), 3.75−3.92 (m, 1H, $CHCH_2OH$), 7.27 (bd, 2H, $^3J = 8.1$, C_6H_4), 7.73 (bd, 2H, $^3J = 8.1$, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.9 (3C, $^1J_{Sn-C} = 314$), 13.8 (3C), 14.1 (1C, $CH_3(CH_2)_3$), 14.7 (1C, CH_3CHCH_2OH), 21.6 (1C, $C_6H_4CH_3$), 22.7 (1C, $CH_3(CH_2)_3$), 27.7 (3C, $^3J_{Sn-C} = 59.8$), 29.3 (3C), 29.9 (1C, $CH_3(CH_2)_3$), 34.9 (1C, CH_2CHSn), 44.9 (1C, *C*HSn), 56.9 (1C, *C*HCH$_2$OH), 64.7 (1C, *C*H$_2$OH), 127.3 (2C, C_6H_4), 129.6 (2C, C_6H_4), 139.2 (1C, C_6H_4), 143.0 (1C, C_6H_4); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −12.3.

Diastereomer 10b-*syn*. Colorless oil; $R_f = 0.37$ (eluent = hexanes/diethyl ether: 60/40); ^{1}H NMR ($CDCl_3$, 300 K): 0.74−1.50 (m, 38H, H_{Bu} + CH_3CHCH_2OH + *Bu*CHSn), 1.87−2.06 (m, 1H, CH_2CHSn), 2.33 (s, 3H, $C_6H_4CH_3$), 2.97 (dd, 1H, $^3J = 10.7$, $^3J = 5.5$, $^2J_{Sn-H} = 51.1$, C*H*Sn), 3.28−3.55 (m, 2H, CH_2OH), 3.65−3.80 (m, 1H, $CHCH_2OH$), 7.20 (bd, 2H, $^3J = 8.3$, C_6H_4), 7.68 (bd, 2H, $^3J = 8.3$, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 10.9 (3C, $^1J_{Sn-C} = 318-340$), 13.8 (3C), 14.1 (1C, $CH_3(CH_2)_3$), 15.5 (1C, CH_3CH_2CHOH), 21.6 (1C, $C_6H_4CH_3$), 22.8 (1C, $CH_3(CH_2)_3$), 27.7 (3C), 29.3 (3C), 30.2 (1C, $CH_3(CH_2)_3$), 35.3 (1C, CH_2CHSn), 45.7 (1C, *C*HSn), 57.6 (1C, *C*HCH$_2$OH), 64.9 (1C, *C*H$_2$OH), 127.3 (2C, C_6H_4), 129.7 (2C, C_6H_4), 139.4 (1C, C_6H_4), 143.1 (1C, C_6H_4); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −21.3.

***N*-[(1*S*)-2-Hydroxy-1-methylethyl]-*N*-[(1*R*)-1-(tributylstannyl)-but-3-en-1-yl]toluenesulfonamide, 10h (469 mg, 82%, 10h-*anti* = 416 mg, 10h-*syn* = 53 mg).** IR (neat): 3529, 2957, 2923, 2871, 2853, 1464, 1318, 1140, 993, 674, 662, 548; MS (ESI): $m/z = 596.1$ $(M + Na)^+$; HRMS (ESI) calcd for $C_{26}H_{47}NO_3NaS^{116}Sn$ $[M + Na]^+$: 592.2196. Found: 592.2199.

Diastereomer 10h-*anti*. Colorless oil; $R_f = 0.44$ (eluent = hexanes/diethyl ether: 60/40), $[\alpha]_D^{19} = +93.0$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.82−1.06 (m, 18H, H_{Bu} + CH_3CHCH_2OH), 1.23−1.70 (m, 12H, H_{Bu}), 2.28−2.42 (m, 1H, CH_2CHSn), 2.39 (s, 3H, $C_6H_4CH_3$), 2.46 (dd, 1H, $^3J = 6.4$, $^3J = 4.5$, O*H*), 2.67−2.83 (m, 1H, CH_2CHSn), 3.01 (dd, 1H, $^3J = 11.5$, $^3J = 4.1$, $^2J_{Sn-H} = 51$, C*H*Sn), 3.42−3.65 (m, 2H, CH_2OH), 3.76−3.90 (m, 1H, $CHCH_2OH$), 4.96−5.09 (m, 2H, $=CH_2$), 5.48−5.65 (m, 1H, $=CH$), 7.26 (bd, 2H, $^3J = 8.3$, C_6H_4), 7.72 (bd, 2H, $^3J = 8.3$, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 11.2 (3C, $^1J_{Sn-C} = 310-324$), 13.8 (3C), 14.7 (1C, CH_3CHCH_2OH), 21.5 (1C, $C_6H_4CH_3$), 27.6 (3C, $^3J_{Sn-C} = 60$), 29.1 (3C, $^2J_{Sn-C} = 17$), 39.7 (1C, CH_2CHSn), 43.9 (1C, $^1J_{Sn-C} = 338$, *C*HSn), 56.8 (1C, *C*HCH$_2$OH), 64.7 (1C, *C*H$_2$OH), 117.7 (1C, $=CH_2$), 127.2 (2C, C_6H_4), 129.7 (2C, C_6H_4), 135.2 (1C, $=CH$), 139.0 (1C, C_6H_4), 143.1 (1C, C_6H_4); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −9.1.

Diastereomer 10h-*syn*. Colorless oil; $R_f = 0.32$ (eluent = hexanes/diethyl ether: 60/40); $[\alpha]_D^{19} = -39.6$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 K) δ 0.83−1.03 (m, 15H, H_{Bu}), 1.16 (d, 3H, $^3J = 6.8$, CH_3CHCH_2OH), 1.22−1.70 (m, 12H, H_{Bu}), 2.40 (s, 3H, $C_6H_4CH_3$), 2.58 (dd, 2H, $^3J = 7.7$, $^3J = 7.2$, CH_2CHSn), 3.02 (t, 1H, $^3J = 7.7$, $^2J_{Sn-H} = 49$, C*H*Sn), 3.32−3.60 (m, 2H, CH_2OH), 3.80−3.98 (m, 1H, $CHCH_2OH$), 4.87 (dd, 1H, $^3J = 16.9$, $^4J = 1.3$, $=CH_2$), 4.98 (dd, 1H, $^3J = 10.2$, $^2J = 1.3$, $=CH_2$), 5.64 (dt, 1H, $^3J = 16.9$, $^3J = 10.2$, $^3J = 7.2$, $=CH$), 7.27 (bd, 2H, $^3J = 8.3$, C_6H_4), 7.76 (bd, 2H, $^3J = 8.3$, C_6H_4); ^{13}C NMR ($CDCl_3$, 300 K) δ 11.2 (3C, $^1J_{Sn-C} = 304-320$), 13.8 (3C), 15.4 (1C, CH_3CHCH_2OH), 21.6 (1C, $C_6H_4CH_3$), 27.7 (3C, $^3J_{Sn-C} = 59$), 29.3 (3C, $^2J_{Sn-C} = 16$), 39.6 (1C, CH_2CHSn), 44.2 (1C, *C*HSn), 57.8 (1C, *C*HCH$_2$OH), 64.3 (1C, *C*H$_2$OH), 117.9 (1C, $=CH_2$), 127.4 (2C, C_6H_4), 129.6 (2C, C_6H_4), 136.9 (1C, $=CH$), 139.3 (1C, C_6H_4), 143.2 (1C, C_6H_4); ^{119}Sn NMR ($CDCl_3$, 300 K) δ −12.9.

Single Crystal X-ray Structure Determination. (4-*trans*) $C_{27}H_40N_2O_5SSn$. The data set was collected on an Nonius-Brüker Kappa CCD diffractometer, using the Mo-$KL_{2,3}$ radiation. $C_{27}H_40N_2O_5SSn$, ($M = 623.4$): orthorhombic, space group $P2_12_12_1$, $D_c = 1.4339$ g cm^{-3}, $a = 7.5154(12)$, $b = 15.5547(17)$, $c = 49.389(5)$ Å, $V = 5773.6(13)$, $Z = 8$, $\lambda = 0.71069$ Å, $\mu = 0.995$ mm^{-1}, $T = 120$ K, $R(F^2) = 0.0435$ for 11674 observed reflections [$I > 2\sigma(I)$] and 649 parameters and $R_w(F^2) = 0.1140$ for all 12723 reflections. The data have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 718238.

(6b-*anti*) $C_{31}H_{50}NO_3SSn$. The data set was collected on an Nonius-Brüker Kappa CCD diffractometer, using the Mo-$KL_{2,3}$ radiation. $C_{31}H_{50}NO_3SSn$, ($M = 635.5$): orthorhombic, space group $P2_12_12_1$, $D_c = 1.3195$ g cm^{-3}, $a = 8.2236(7)$, $b = 20.444(3)$, $c = 38.045(5)$ Å, $V = 6396.3(14)$, $Z = 8$, $\lambda = 0.71069$ Å, $\mu = 0.894$ mm^{-1}, $T = 120$ K, $R(F^2) = 0.0982$ for 12972 observed reflections [$I > 2\sigma(I)$] and 662 parameters and $R_w(F^2) = 0.1802$ for all 18153 reflections. The data have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 718237.

(6h-*anti*) $C_{30}H_{47}NO_3SSn$. The data set was collected on an Nonius-Brüker Kappa CCD diffractometer, using the Mo-$KL_{2,3}$ radiation. $C_{30}H_{47}NO_3SSn$, ($M = 620.5$): orthorhombic, space group $P2_12_12_1$, $D_c = 1.3334$ g cm^{-3}, $a = 7.8641(7)$, $b = 20.288(2)$, $c = 38.732(3)$ Å, $V = 6179.6(10)$, $Z = 8$, $\lambda = 0.71069$ Å, $\mu = 0.923$ mm^{-1}, $T = 120$ K, $R(F^2) = 0.0361$ for 15537 observed reflections [$I > 2\sigma(I)$] and 655 parameters and $R_w(F^2) = 0.0900$ for all 17153 reflections. The data have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 718236.

(**9h-*syn***) **$C_{28}H_{51}NO_3SSn$.** The data set was collected on an Nonius-Brüker Kappa CCD diffractometer, using the Mo-$KL_{2,3}$ radiation. $C_{28}H_{51}NO_3SSn$, (M = 600.5): monoclinic, space group $P2_1$, D_c=1.3186 g cm^{-3}, a=15.4125(18), b=8.1024(6), c=24.215(2) Å, β = 90.175(11), V = 3023.9(5), Z = 4, λ = 0.71069 Å, μ = 0.941 mm^{-1}, T = 100 K, $R(F^2)$ = 0.0449 for 17792 observed reflections [$I > 2\sigma(I)$] and 624 parameters and $R_w(F^2)$ = 0.1015 for all 20184 reflections. A split model was used for the description of a local disorder on a butyl group. The data have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 718235.

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Supporting Information Available: General experimental methods, spectral data, ^{1}H NMR spectra, ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.