Chemistry of *N*-Boc-*N*-*tert*-butylthiomethyl-Protected α-Aminoorganostannanes: Diastereoselective Synthesis of Primary *β*-Amino Alcohols from α-Aminoorganostannanes

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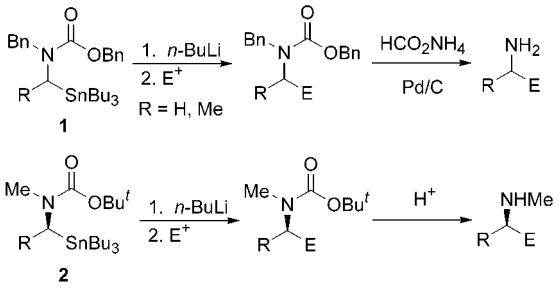
Reaction of *N*-Boc-*N*-*tert*-butylthiomethyl-protected α-aminoorganostannanes with *n*-BuLi generates the corresponding α-aminoorganolithiums. Reactions of these organolithiums with aromatic aldehydes provides N-protected *β*-amino alcohols with diastereoselectivities up to >99:1 anti/syn; with aliphatic aldehydes, diastereoselectivities were typically 1:1. Diastereoselectivities varied depending on the amount of aldehyde used. The N-protected *β*-amino alcohols could be deprotected to primary amines by treatment with NaH to generate oxazolidinones followed by basic hydrolysis. Alternatively, treatment of the protected amino alcohols with acid furnished cyclic acetals that could be deprotected to primary amines with $BF_3{\cdot}OEt_2$ and $HS(CH_2)_3SH$. Transmetalation of enantiomerically enriched organostannanes with *n*-BuLi at −95 °C provided organolithiums that, although less configurationally stable than *N*-Boc-*N*-methyl-protected α-aminoorganolithiums, could be trapped with aldehydes with near-complete retention of configuration.

Introduction

It has been known since 1970 that α-aminoorganostannanes can serve as useful precursors of α-aminoorganolithiums;[1] these organolithiums add to aldehydes to provide *β*-amino alcohols. Over the past decade, there has been considerable interest in α-aminoorganolithiums both in terms of their configurational stability and their use as building blocks for the synthesis of enantiomerically enriched amines.[2−8]For synthetic applications, more attention has been given to cyclic systems,[3−6] particularly pyrrolidines and piperidines, than to acyclic systems, and many useful advancements have been made. With acyclic systems, progress has been much slower. For example, Pearson has shown that *N*-benzyl-*N*-Cbz-protected aminostannanes **1** undergo clean transmetalation with *n*-BuLi to provide organolithiums that may be trapped with aldehydes; furthermore, it was shown that the adducts could be converted to primary *β*-amino alcohols by hydrogenolysis (Scheme 1).[8] Unfortunately, this method seems to be limited to stannanes **1** where R = H or Me since competing metalation of the Cbz group is observed when R = Et.[9] To circumvent this problem, we replaced the Cbz group with a Boc group (which has no acidic benzylic protons) and showed that *N*-Boc-*N*-methyl-protected aminostannanes **2** are excellent precursors of the corresponding organolithiums that may be trapped with electrophiles at −95 °C with complete retention of configuration.[9] This chemistry is useful for the preparation of *N*-methyl-α-amino acids and *N*-methyl-*β*-amino alcohols but is not easily applicable to primary amines since *N*-methyl groups are not readily removable.

Scheme 1



Since many biologically important amines are primary amines,[10] it would be highly desirable to be able to carry out the general sequence shown in Scheme 2 for a wide variety of R groups and electrophiles. For a protecting group to be used successfully in this sequence, it needs to (a) be readily introduced, (b) be compatible with the Sn−Li transmetalation conditions (typically *n*-BuLi, THF, −95 C), (c) provide a chemically and configurationally stable organolithium intermediate, and (d) be readily removed from the adduct. A survey of potential protecting groups revealed that the standard N-protecting groups[11] did not fulfill all of these requirements.[12] For example, a benzyl group could be easily introduced but inhibited the

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(11) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed; Wiley: New York, 1999; pp 632−647.
(12) Park, S. B. Ph.D. Dissertation, University of Waterloo, 1993.

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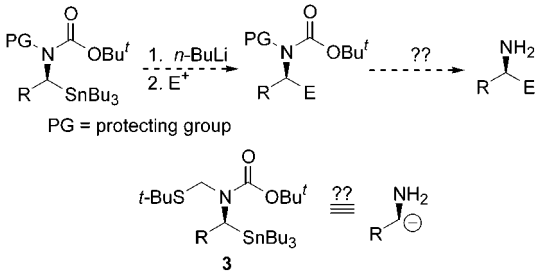
Scheme 2



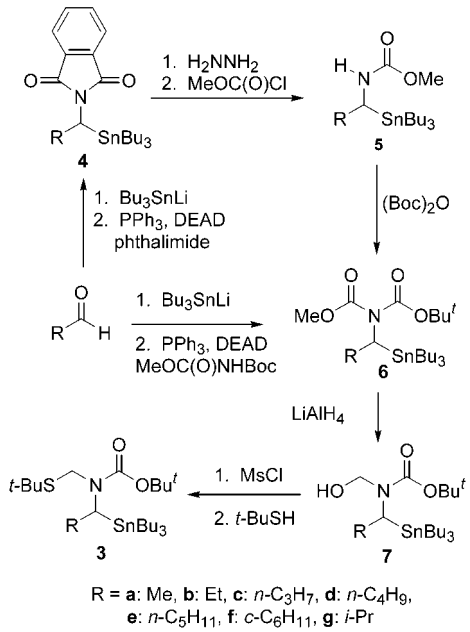
transmetalation of stannanes with more sterically demanding R groups (e.g., *i*-Pr, *c*-C_6H_{11}), while a TBS group migrated (a reverse aza-Brook rearrangement) upon transmetalation and a MOM group gave an organolithium that racemized more readily than its *N*-methyl cousin.[13] We now report our results on the development of *N*-Boc-*N*-*tert*-butylthiomethyl-protected aminoorganostannanes (**3**) as precursors to primary amines, particularly *β*-amino alcohols, and hence that they can be synthetic equivalents of α-aminocarbanions.

Results and Discussion

N-*t*-Butylthiomethyl-*N*-Boc-protected aminoorganostannanes were chosen for study since it was anticipated that deprotection to primary amines could be readily achieved under acidic conditions: removal of the Boc group would give thioaminals that should be easily hydrolyzed. In addition, the *tert*-butylthiomethyl group was speculated to have less of an effect on racemization of the organolithium intermediate than a MOM group since the *tert*-butylthiomethyl group should not coordinate as strongly to lithium. Although the mechanism for racemization of α-aminoorganolithiums has not been fully elucidated, it was clear from our prelimary results that the MOM group had a detrimental effect on configurational stability. Thus, we sought to decrease the coordinating ability of the extra heteroatom that we were introducing to facilitate deprotection with the working hypothesis that groups that compete with the Boc group for coordination to Li would decrease the configurational stability of the organolithium intermediate. In essence, it was hoped that the *tert*-butylthiomethyl group would act as an easily removed methyl group.

Synthesis of Racemic Stannanes. Aminostannanes **3** could be prepared from aldehydes using Mitsunobu chemistry via either of the methods shown in Scheme 3. Thus, addition of Bu_3SnLi to aldehydes gave hydroxystannanes[14] that could be immediately converted directly to iminodicarbonates **6** using *tert*-butyl methyl iminodicarbonate as the nucleophile; however, this method gave low yields when the hydroxystannane had a branched R group. Alternatively, the hydroxystannanes could be transformed to phthalimides **4**, which were then further manipulated into iminodicarbonates **6**. This latter route, although longer, gave more consistent overall yields of **6** reflecting the relatively lower sensitivity to steric effects of phthalimide as a Mitsunobu nucleophile compared to

Scheme 3



the effectively larger *tert*-butylmethyl iminodicarbonate. With **6** in hand, it was relatively straightforward to selectively reduce the methyl carbamate to hydroxymethyl carbamate **7**[15] and introduce the *tert*-butylthio group via sequential treatment with $MsCl/Et_3N$ followed by *t*-BuSH. The product stannanes proved to be easily handled substances that were readily purified by flash chromatography. Overall yields of stannanes **3** from aldehydes were typically 29−40%.

Transmetalation/Trapping of Stannanes 3. When stannane **3a** was treated with *n*-BuLi (1.5 equiv) followed by PhCHO (1.3 equiv), >90% transmetalation occurred (based on Bu_4Sn isolated), but only a mediocre (55%) yield of the expected alcohol was observed. The only other product isolated was 1-phenyl-1-pentanol, the product of excess *n*-BuLi addition to PhCHO. The low isolated yield was somewhat disturbing, but the formation of alcohol **8a** as what appeared to be a single diastereomer was most intriguing. Analysis of the diastereomeric purity of the adduct isolated by ^{1}H NMR spectroscopy was complicated by the presence of rotamers, but fortunately, treatment of alcohol **8a** with NaH resulted in clean cyclization to oxazolidinone *cis*-**9a** (Scheme 4). This confirmed the presence of a single diastereomer and allowed assignment of the relative configuration of alcohol **8a**: Since J_{ab} was around 8 Hz, oxazolidinone *cis*-**9a** likely has a cis configuration,[16] and thus, alcohol **8a** has an anti configuration. When other stannanes and aldehydes were treated similarly, the results shown in Table 1 were obtained.

When a limiting amount of an aromatic aldehyde was used, each of the stannanes gave only a single diastereomer that was assigned as the anti isomer (Table 1, entries 1, 2, and 5−8); in each case, the absence of the syn isomer was ascertained by ^{1}H NMR analysis of the derived oxazolidinones. The absence of signals for the

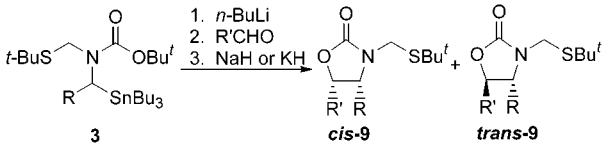
(13) When the methyl group in **2** (R = Et) was replaced with a MOM group, stannane with 97:3 er provided product with 91:9 er when treated under conditions (*n*-BuLi, THF, −95 °C, 10 min then CO_2, H^+) that gave complete retention of configuration using **2**.

(14) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481−1487.

(15) This transformation has not been previously described in the literature, but selective hydrolysis of *tert*-butyl methyl iminodicarbonates is known: Clarke, C. T.; Elliott, J. D.; Jones, J. H. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1088−1090.

(16) Futagawa, S.; Invi, T.; Shiba, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3308−3310.

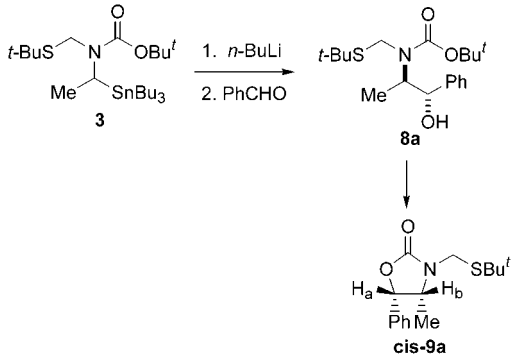
Table 1. Transmetalation of Stannanes 3 and Reactions with Aldehydes[a]



					limiting R′CHO		excess R′CHO	
entry	stannane	R	R′	oxazolidinones *cis*-**9**/*trans*-**9**	yield[b] (%)	dr[c]	yield[b] (%)	dr[c]
1	**3a**	Me	Ph	**9a**	55	>99:1	90	71:29
2	**3b**	Et	Ph	**9b**	54	>99:1	77	66:34
3	**3c**	*n*-C_3H_7	Ph	**9c**	nd		86	67:33
4	**3d**	*n*-C_4H_9	Ph	**9d**	nd		78	70:30
5	**3e**	*n*-C_5H_{11}	Ph	**9e**	55	>99:1	75	68:32
6	**3f**	*c*-C_6H_{11}	Ph	**9f**	40	>99:1	nd	
7	**3g**	*i*-Pr	Ph	**9g**	35	>99:1	68[d]	74:26
8	**3b**	Et	4-$MeOC_6H_4$	**9h**	50	>99:1	80	71:29
9	**3b**	Et	*c*-C_6H_{11}	**9i**	65	50:50	70	43:57
10	**3b**	Et	*i*-Pr	**9j**	60	50:50	69	43:57

[a] Reactions were carried out using 1.5 equiv of *n*-BuLi. For "limiting R′CHO" reactions, 1.3 equiv of aldehyde was added; for "excess R′CHO" reactions, 2.0 equiv was used. [b] Isolated yield of **9** after flash chromatography based on **3**. nd = experiment not done. [c] Determined by ^{1}H NMR spectroscopy on crude cyclization products. ">99:1" means that signals for the other diastereomer were not observed. [d] Five equivalents each of *n*-BuLi and PhCHO were used.

Scheme 4



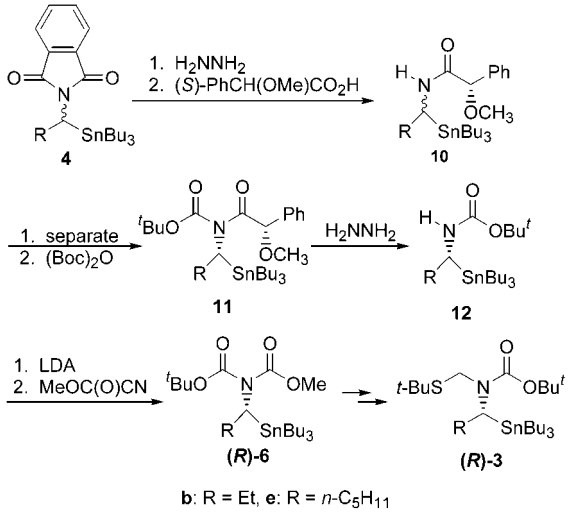
trans-oxazolidinone (derived from the syn adduct) was straightforward to establish since experiments in which excess aldehyde were employed gave mixtures of anti/syn adducts with ratios of ~2−3:1 (along with higher yields). These results suggest that there is a kinetic preference for formation of the anti adduct since it is formed as the only isolable product (albeit in low yields) when a limiting amount of aldehyde is used. It seems that the syn adduct is formed more slowly or later on during the reaction and so that it is only detected when excess aldehyde is used. A possible explanation is that the syn adduct arises from reaction of an *anti*-alkoxide−organolithium aggregate that is initially formed. Another possibility is that the initial addition might be reversible so that a mixture of diastereomers results when excess aldehyde is used. This possibility was discounted by control experiments in which **8a** was deprotonated (*n*-BuLi, THF, −78 °C) and stirred with, and without, excess PhCHO; no syn adduct was detected in either case, suggesting that there is no isomerization or reversibility under the reaction conditions.

Other α-aminoorganolithiums typically react with aldehydes with low diastereoselectivities;[7,9] for example, reactions of *N*-Boc-*N*-methyl-α-aminoorganolithiums with aldehydes usually give adducts with ratios of ~1:1.[9] It is not obvious why these *N*-*t*-butylthiomethyl systems show this very unusual behavior. Nonetheless, this serendipidous observation may be very useful synthetically. It should also be noted that stannanes with branched alkyl groups (e.g., **3f** and **3g**) gave slightly lower yields; in these cases, incomplete transmetalation was observed, likely for steric reasons.

In contrast to reactions with aromatic aldehydes, reactions with aliphatic aldehydes proceeded with no diastereoselectivity when a limiting amount of aldehyde was used. With an excess of aldehyde, slightly higher yields were observed along with a small preference for the syn adduct (anti/syn = ~1:1.5). Thus, the trend observed with aliphatic aldehydes (i.e., comparatively more syn adduct formed) when more aldehyde is used is the same as that observed with aromatic aldehydes. However, the reason(s) for the dramatic difference in selectivities observed between aromatic and aliphatic aldehydes is (are) not at all clear. For practical purposes, the diastereomeric alcohols or derived oxazolidinones from both aromatic and aliphatic aldehydes were readily separated by flash chromatography, so it was relatively easy to obtain diastereomerically pure materials regardless of the intrinsic selectivity of the reaction.

Preparation of Enantiomerically Enriched Stannanes and Studies of Configurational Stability. Having established that racemic *N*-Boc-*N*-*tert*-butylthiomethyl-protected aminostannanes could undergo transmetalation cleanly and that the intermediate organolithiums could be trapped with aldehydes, we turned our attention to studying the configurational stability of the organolithiums. For such studies, we needed to prepare enantiomerically enriched aminostannanes. There are relatively few methods to prepare acyclic enantiomerically enriched α-aminostannanes, and we chose a resolution method for convenience. While we have previously used asymmetric reduction methods to prepare these materials,[9] we found that BINAL-H reductions did not give reproducibly high selectivities on preparative scales. Thus, racemic phthalimide **4** was cleaved to the primary amine, which was then converted to diastereomeric amides with (*S*)-*O*-methylmandelic acid (Scheme 5). These diastereomers were readily separable by flash chromatography, and the less polar diastereomer was used in subsequent studies.

Scheme 5

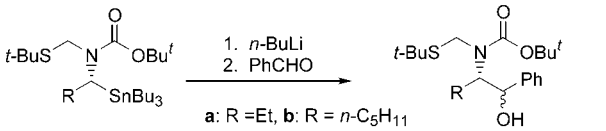


Direct cleavage of the *O*-methylmandelamides to primary amines proved to be quite difficult with various procedures (e.g., acid or basic hydrolysis, MeLi, Et_3OBF_4/aq $NaHCO_3$) providing only starting material or mixtures of unidentified products. Eventually, the route shown in Scheme 5 was developed to transform the resolved mandelamides to the required *N*-Boc-*N*-*tert*-butylthiomethyl-protected aminostannanes. In this route, a Boc group was introduced first using Ragnarsson's[17] method before cleavage of the mandelamide with hydrazine. The resulting carbamate **12** was then converted to iminodicarbonate **6** using Mander's reagent;[18] for this transformation, MeOCOCN was critical as the use of MeOCOCl in conjunction with a variety of bases proved to be completely ineffective. Enantiomerically enriched **6** was then converted to the desired *N*-Boc-*N*-*tert*-butylthiomethyl-protected amine **3** using the route previously developed for racemic **3**.

Assignment of absolute configuration was done by comparison of optical rotations of the intermediate **12** with that of the same compound prepared via a different route and of known absolute configuration.[9,12] We were thus able to show that the less polar *O*-methylmandelamide diastereomer (which is the one used) has the (1′*R*,2*S*) configuration, as depicted in Scheme **5**; it follows that stannanes **3** and **6** in Scheme 5 also have the *R* configuration. The enantiomeric purity of carbamate **12**, assayed by hydrolysis (TFA) followed by ^{19}F NMR analysis of Mosher amides, was determined to be 98:2 er. Since subsequent conversions to stannane **3** should not affect the stereogenic center, it too should also have 98:2 er.

Studies of configurational stability were carried out by treatment of **(***R***)-3b** or (*R*)-**3e** with *n*-BuLi followed by trapping of the intermediate organolithium with PhCHO and assaying the enantiomeric purity of the adducts. Results are summarized in Table 2. As we had previously noted with *N*-Boc-*N*-methylaminoorganolithiums, significant racemization occurred at −78 °C while racemization could be almost completely suppressed by cooling the reaction to −95 °C. With the *N*-*tert*-butylthiomethyl systems, a slight loss of enantiomeric purity was observed

Table 2. Configurational Stability of α-Aminoorganolithiums



(*R*)-**3b** or **3e**
er = 98:2

(2*S*)-**8b** or **8e**
anti:syn =2:1

entry	R	*T* (°C)	time (min)	yield of **8**[a] (%)	er (*anti*-**8**)[b]	er (*syn*-**8**)[b]
1	Et	−95	15	79 (**8b**)	97:3	96:4
2	Et	−78	30	70 (**8b**)	92:8	91:9
3[c]	Et	−78	30	63 (**8b**)	91:9	nd
4[d]	Et	−78	30	58 (**8b**)	76:24	74:26
5	*n*-C_5H_{11}	−95	15	60 (**8e**)	97:3	nd
6	*n*-C_5H_{11}	−78	30	68 (**8e**)	93:7	nd

[a] Isolated yields of **8** (as mixture of diastereomers). [b] Determined by HPLC on a Chiralcel OD column (nd = not determined). [c] Et_2O/THF, 1:1 was used as solvent. [d] LiBr (5 equiv) was added to the stannane solution before *n*-BuLi addition.

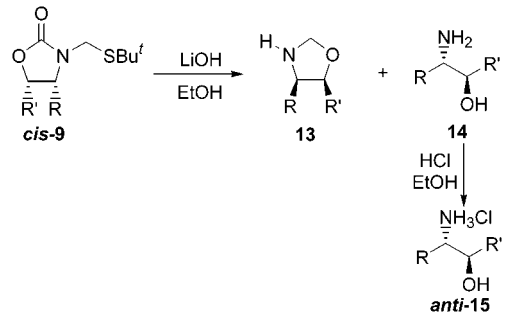
even at −95 °C. As well, comparable levels of racemization were observed for the *N*-*tert*-butylthiomethylaminolithiums after 30 min at −78 °C as had been observed for the *N*-methyl compounds after 180 min at the same temperature. Thus it seems that *N*-Boc-*N*-*tert*-butylthiomethylaminolithiums racemize slightly more rapidly than do *N*-Boc-*N*-methylaminoorganolithiums.

Since we had previously shown that more coordinating solvents increased the rate of racemization of *N*-Boc-*N*-methylaminoorganolithiums,[9] transmetalation/trapping of (*R*)-**3b** was attempted in a less polar solvent, ether. Unfortunately, <5% transmetalation was observed in Et_2O (−78 °C, 15 min). With a 1:1 mixture of Et_2O and THF, results were essentially identical to that observed with neat THF. To further probe the configurational stability of the intermediate organolithium, LiBr was added to the stannane prior to addition of *n*-BuLi (Table 2, entry 4). Considerably greater racemization was observed. The effect of LiBr, solvents, and the relative configurational stabilities of different *N*-Boc-protected aminolithiums is consistent with an inversion mechanism involving coordination to Li cations. There is evidence with cyclic α-aminoorganolithiums that such coordination plays an important role in racemization processes.[6]

It is interesting to note that when both diastereomeric amino alcohols were isolated from a single reaction and their enantiomeric purities were analyzed, the syn isomer was consistently of lower (albeit only slightly so) enantiomeric purity (Table 2, entries 1, 2, and 4) than the anti isomers. Superficially, this may be explained by suggesting that the anti isomers are formed more quickly than the syn isomers, and since racemization of the intermediate organolithium starts immediately from the time the organolithium is generated, it should be expected that the isomer formed first should have higher enantiomeric purity. The more facile formation of the anti isomer is also consistent with the observation that it is the sole product formed with limiting amounts of aromatic aldehydes and the postulate that the syn isomer is only formed after an anti adduct/organolithium aggregate is formed. However, this story fails to explain why the anti adduct should be formed faster to begin with. In any case, these results show that organolithiums derived from transmetalation of stannanes **3** can be trapped with

(17) Grehn, L.; Ragnarsson, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 510−511.
(18) Mander, L. N.; Sethi, S. P. *Tetrahedron Lett.* **1983**, *24*, 5425−5428.

Table 3. Preparation of Amino Alcohols from Oxazolidinones

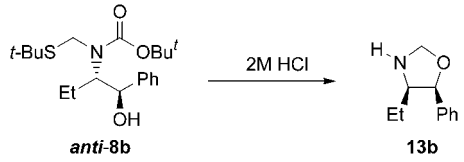


entry	oxazolidinone	R	R′	13/14[a]	yield of 15[b] (%)
1	*cis*-**9a**	Me	Ph	1:>99	84 (*anti*-**15a**)
2	*cis*-**9b**	Et	Ph	<10:>90	75 (*anti*-**15b**)
3	*cis*-**9c**	*n*-C_3H_7	Ph	1:1	nd
4	*cis*-**9d**	*n*-C_4H_9	Ph	1:1	nd
5	*cis*-**9e**	*n*-C_5H_{11}	Ph	>99:1	0[c]
6	*cis*-**9g**	*i*-Pr	Ph	<10:>90	76 (*anti*-**15g**)
7	*cis*-**9h**	Et	*p*-$MeOC_6H_4$	<10:>90	66 (*anti*-**15h**)
8	*trans*-**9h**	Et	*p*-$MeOC_6H_4$	<10:>90	76 (*syn*-**15h**)

[a] Ratio determined by ^{1}H NMR analysis of crude reaction mixtures. [b] Isolated yields of crystalline salts (nd = not determined). [c] Aminoacetal **13e** was isolated in 84% yield.

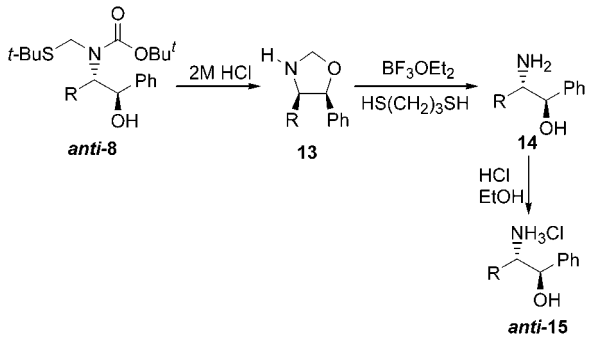
aldehydes at low temperatures with essentially no loss of enantiomeric purity.

Preparation of Primary β-Amino Alcohols. We had originally hoped that primary β-amino alcohols would be easily prepared from *N*-Boc-*N*-*tert*-butylthiomethyl-protected amino alcohols by simple acid hydrolysis. However, when adduct *anti*-**8b** was treated with 2 M HCl, none of the desired amino alcohol was formed; instead, aminoacetal **13b** was obtained in 95% yield. It is likely that **13b** is formed via intramolecular cyclization of an iminium ion intermediate.



Since we had already established that oxazolidinones *cis*-**9** could be easily prepared from adducts *anti*-**8**, we examined the hydrolysis of these oxazolidinones. When oxazolidinone ***cis*-9b** was treated with ethanolic KOH, the desired amino alcohol was the major product but aminoacetal **13b** was still formed as a major side product. Much less aminoacetal **13b** was formed when LiOH was used, and primary β-amino alcohol **14b** could be isolated in good yield (as its HCl salt **15b**, Table 3, entry 1). When other oxazolidinones were treated with LiOH in EtOH, a surprising trend emerged in which the amount of aminoacetal formed was dependent on the size of R. Thus, when R = Me, Et, or *i*-Pr, very little aminoacetal was formed but with R = *n*-C_3H_7 and *n*-C_4H_9 (Table 3, entries 3 and 4), it was formed in significant quantities and with a slightly longer *n*-C_5H_{11} chain (Table 3, entry 5), aminoacetal **13e** was the only product isolated. Our best explanation for these unexpected results is that the size (hydrophobicity?) of R somehow affects the conformation of an imine/iminium intermediate such that larger R groups favor cyclization. From a synthetic viewpoint, these results meant that oxazolidinones **9** would be useful intermediates for the preparation of primary β-amino alcohols only with small R groups (Me, Et, or *i*-Pr) and an alternative route would need to be developed for larger R groups. With a *trans*-oxazolidinone, *trans*-**9h**, reaction with LiOH in refluxing EtOH−H_2O was sluggish but proceeded smoothly in *n*-PrOH−H_2O to provide the expected syn amino alcohol in good yield (Table 3, entry 8).

Table 4. Preparation of Amino Alcohols from Aminoacetals



entry	aminoacetal	R	13/14[a]	yield of 15[b] (%)
1	**13a**	Me	1:3	nd
2	**13b**	Et	1:2.5	nd
3	**13c**	*n*-C_3H_7	1:10	70 **(15c)**
4	**13d**	*n*-C_4H_9	1:20	75 **(15d)**
5	**13e**	*n*-C_5H_{11}	1:>99	86 **(15e)**

[a] Ratio determined by ^{1}H NMR analysis of crude reaction mixtures. [b] Isolated yield of **15** based on **8**.

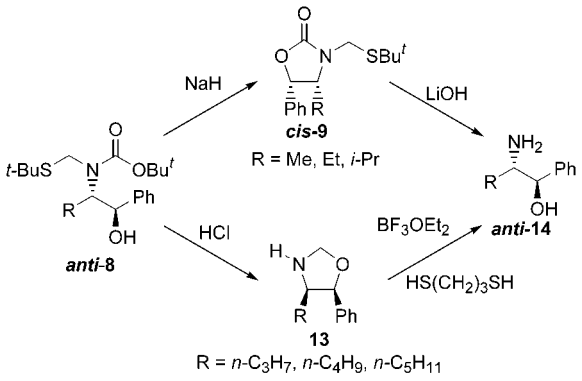
The alternative route that we developed exploited our previous observation that aminoacetals **13** were the major products formed when adducts **8** were treated with acid. These aminoacetals were treated with $BF_3{\cdot}OEt_2$ and $HS(CH_2)_3SH$ to effect a transacetalization[19] to provide amino alcohols (which were isolated as their HCl salts, Table 4). These transacetalizations are known to be equilibria that can be pushed to the desired amino alcohol by using excess dithiol. In our cases, the position of the equilibrium varied according to the size of R with more amino alcohol favored as the size of R increased. Fortunately, this gave good yields of amino alcohols where R = *n*-C_3H_7 or larger, precisely those compounds that were not easily accessible using the oxazolidinone route.

Thus, while neither of the routes that we have developed is universally applicable, they are complementary and allow for the preparation of primary β-amino alcohols from anti-*N*-Boc-*N*-*tert*-butylthiomethylamino alcohols in good overall yields (Scheme 6). Unfortunately, *trans*-aminoacetals **13** derived from syn-*N*-Boc-*N*-*tert*-butylthiomethylamino alcohols did not give synthetically useful yields of syn primary β-amino alcohols when treated with $HS(CH_2)_3SH$ (probably because the *trans*-aminoacetals are more stable than the corresponding *cis*-aminoacetals).

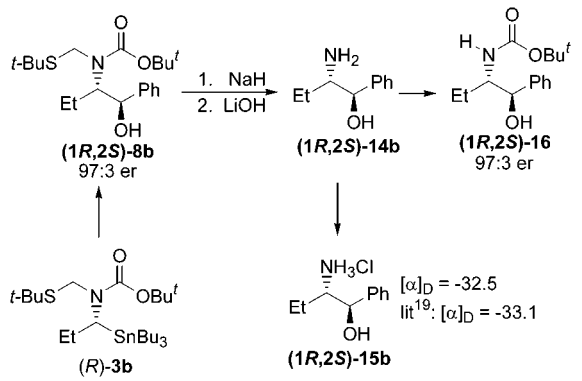
With adduct **8b** (97:3 er) derived from (*R*)-**3b**, deprotection was readily achieved to provide amino alcohol **14b** with essentially no loss of enantiomeric purity (Scheme 7). Analysis of ee was performed by HPLC analysis of Boc derivative **16**; recrystallization of this derivative raised its enantiomeric purity to >99:<1 er. Furthermore,

(19) Corey, E. J.; Reichard, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 10677−10678.

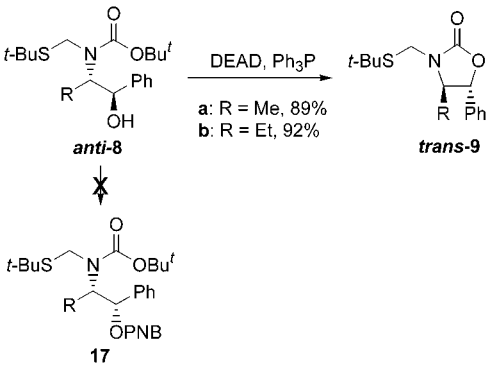
Scheme 6



Scheme 7



Scheme 8



conversion of **14b** to its HCl salt **15b** and comparison with literature data[20] established the absolute configuration as (1*R*,2*S*), thereby confirming that transmetalation/trapping of (*R*)-**3b** occurred with retention of configuration.

Inversion of Configuration of Amino Alcohols. Since *anti*-amino alcohols *anti*-**8** were usually the major products from the transmetalation/trapping sequence, we briefly examined the conversion of the anti adducts to syn adducts in order to increase the synthetic utility of this chemistry. When *anti*-**8a** was treated under typical Mitsunobu conditions[21] with *p*-nitrobenzoic acid, none of the expected benzoate **17** was isolated. Instead *trans*-oxazolidinone *trans*-**9a** was isolated in high yield (Scheme 8). When *p*-nitrobenzoic acid was left out of the reaction mixture, *trans*-**9a** was still formed in high yield. Similarly, treatment of *anti*-**8b** under with Ph_3/DEAD cleanly converted it to *trans*-**9b**. These results suggest that the Boc group is participating as an intramolecular nucleophile on the expected activated alcohol intermediate. This type of intramolecular cyclization has been reported previously for *N*-acyl *β*-amino alcohols;[22] indeed, such cyclizations are a known route to 2-oxazolines.[23] In contrast, carbamate-protected *β*-amino alcohols have been shown to undergo Mitsunobu inversion with carboxylic acids quite cleanly.[24,25] Thus, *N*-Boc-[24] as well as *N*-Cbz- and *N*-Cbz-*N*-methyl-*β*-amino alcohols[25] have been shown to undergo Mitsunobu chemistry without apparent involvement of the carbamate group. For reasons that are not readily apparent, *N*-Boc-*N*-*tert*-butylthiomethyl-*β*-amino alcohols clearly behave quite differently under Mitsunobu conditions. While cyclization to trans oxazolidinones was initially unexpected, this result may actually be very useful since these compounds could be directly hydrolyzed to syn primary *β*-amino alcohols (see Table 3).

Conclusions

In our search for α-aminoorganostannanes that might be useful for the preparation of primary amines as depicted in Scheme 2, we have found that *N*-Boc-*N*-*tert*-butylthiomethyl derivatives **3** are potential candidates. They undergo transmetalation smoothly with *n*-BuLi to afford α-aminoorganolithiums that react well with aldehydes to give the expected N-protected *β*-amino alcohols. The diastereoselectivities of these reactions, particularly with aromatic aldehydes, show an unexpected dependence on the amount of aldehyde used; with limiting amounts of aldehyde, anti adducts predominate. In many cases, these adducts can be readily converted in good yields to primary amines via the intermediacy of oxazolidinones or cyclic aminoacetals. With enantiomerically enriched stannanes, the derived α-aminoorganolithiums are less configurationally stable than their *N*-Boc-*N*-methyl congeners but can still be trapped with aldehydes with overall retention of configuration.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on 200 or 250 MHz spectrometers in $CDCl_3$ unless otherwise noted. Coupling constants reported in ^{13}C NMR spectra refer to the $^{117/119}$Sn satellites observed; an asterisk denotes the major signal observed when rotamers are present. Coupling constants are reported in Hz. Mass spectra were recorded using EI, FAB, or ES ionization; MS data reported for stannanes are for ^{120}Sn. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. All reactions were performed in dry glassware under an atmosphere of argon. Solvents were dried and distilled using standard procedures: ether and THF from Na/benzophenone; CH_2Cl_2, CH_3CN, and hexanes from CaH_2. Alkyllithiums were titrated using *N*-benzylbenzamide as acid and indicator.[26] *tert*-Butyl methyl iminodicarbonate was prepared according to Jones et al.[15] Phthalimides **4** were prepared from α-hydroxystannanes using

(20) Brussee, J.; Dofferhoff, F.; Kruse, C. G.; Van Der Gen, A. *Tetrahedron* **1990**, *46*, 1653−1658.
(21) Hughes, D. L. *Org. React.* **1992**, *42*, 335−656.
(22) Bunnage, M. E.; Burke, A. J.; Davies, S. G.; Goodwin, C. J. *Tetrahedron*: *Asymmetry* **1994**, *5*, 203−206.
(23) Roush, D. M.; Patel, M. M. *Synth. Commun.* **1985**, *15*, 675−679.
(24) Pastó, M.; Moyana, A.; Pericàs, M. A.; Riera, A. *Tetrahedron*: *Asymmetry* **1996**, *7*, 243−262.
(25) Lipshutz, B. H.; Miller, T. A. *Tetrahedron Lett.* **1990**, *31*, 5253−5256.
(26) Burchat, A. F.; Chong, J. M.; Nielsen, N. *J. Organomet. Chem.* **1997**, *542*, 281−283.

Mitsunobu chemistry as previously described.[9] A Chiracel OD column (4.6 × 250 mm) was used as the chiral HPLC column, and detection was done at 254 nm.

General Procedure A: Preparation of Carbamates 5. To a 1.0 M solution of the appropriate phthalimide in ethanol was added hydrazine hydrate (50 equiv), and the resulting mixture was stirred at reflux for the specified time. The mixture was concentrated in vacuo, and Et_2O was added to the residue. The solution was washed with water, dried ($MgSO_4$), filtered through Celite, and concentrated in vacuo to yield the crude primary amines that were used without further purification. To a cooled (0 °C) 0.2 M solution of amine in CH_2Cl_2 were added Et_3N (1.3 equiv) and then methyl chloroformate (1.5 equiv). The resulting mixture was stirred at room temperature for 30 min and diluted with Et_2O. The mixture was washed with water, dried ($MgSO_4$), filtered through Celite, and concentrated in vacuo. The resulting oils were purified by flash chromatography (35 g of silica/g of substrate; 10:1 hexane/Et_2O) to give the carbamates as colorless oils.

Methyl *N*-(1-Tributylstannylethyl)carbamate (5a). This compound was prepared from **4a** according to general procedure A with an initial reaction time of 3 h in 82% yield: IR (neat) 3339, 1702 cm^{-1}; ^1H NMR δ 4.73 (br, 1 H), 3.64 (s, 3 H,), 3.27 (m, 1 H), 1.64−1.20 (m, 15 H), 0.99−0.75 (m, 15 H); ^{13}C NMR δ 157, 51.9, 35.5 (^1J = 339), 29 (^2J = 19), 27.5 (^3J = 45), 20.7, 13.7, 9.4 (^1J = 320, 305); FABMS *m/z* (rel int) 334 (100). Anal. Calcd for $C_{16}H_{35}NO_2Sn$: C, 49.00; H, 9.00; N, 3.57. Found: C, 49.16; H, 8.88; N, 3.58.

Methyl *N*-(1-Tributylstannylbutyl)carbamate (5c). This compound was prepared from **4c** according to general procedure A with an initial reaction time of 5 h in 78% yield: IR (neat) 3326, 1704 cm^{-1}; ^1H NMR δ 4.79 (d, 1 H, J = 7.6), 3.67 (s, 0.5 H), 3.61 (s, 2.5 H), 3.26 (dt, 1 H, J = 6.5, 7.6), 1.72−1.24 (m, 16 H), 0.98−0.72 (m, 18 H); ^{13}C NMR δ 157.1, 51.7, 40.9, 37.0, 29.0 (^2J = 20), 27.3, (^3J = 55), 21.0, 13.6, 13.5, 9.6 (^1J = 311), *9.0; FABMS *m/z* (rel int) 364 ($M^+ - C_4H_9$, 100). Anal. Calcd for $C_{18}H_{39}NO_2Sn$: C, 51.45; H, 9.36; N, 3.33. Found: C, 51.58; H, 9.18; N, 3.38.

Methyl *N*-(1-Tributylstannylpentyl)carbamate (5d). This compound was prepared from **4d** according to general procedure A with an initial reaction time of 3 h in 91% yield: IR (neat) 3326, 1704; ^1H NMR δ 4.82 (d, 1 H, J = 7.6), 3.70 (s, 0.5 H), 3.64 (s, 2.5 H), 3.22 (dt, 1 H, J = 7.1, 7.6), 1.66−1.18 (m, 18 H), 1.0−0.74 (m, 18 H); ^{13}C NMR (63 MHz) δ 157.1, 51.9, 41.3, 34.5, 30.2, 29.1 (^2J = 19), 27.4 (^3J = 55), 22.4, 13.9, 13.6, 9.7 (^1J = 303, 317); FABMS *m/z* (rel int) 378 ($M^+ - C_4H_9$, 100). Anal. Calcd for $C_{19}H_{41}NO_2Sn$: C, 52.55; H, 9.52; N. 3.22. Found: C, 52.40; H, 9.38; N, 3.28.

Methyl *N*-(1-Tributylstannylhexyl)carbamate (5e). This compound was prepared from **4e** according to general procedure A with an initial reaction time of 10 h in 88% yield: IR (neat) 3326, 1703 cm^{-1}; ^1H NMR δ 4.82 (d, 1 H, J = 6.8), 3.63 (s, 3 H), 3.23 (dt, 1H, J = 7.6, 6.8), 1.60 (m, 2 H), 1.48−1.23 (m, 18 H), 1.0−0.64 (m, 18 H); ^{13}C NMR δ 157.2, 52.2, 41.3, *35.1, 34.8, 31.6, 29.2 (^2J = 19), 27.7, 27.5 (^3J = 55), 22.6, 14.0, 13.6, 9.7 (^1J = 318, 303); FABMS *m/z* (rel int) 392 (M^+-C_4H_9, 100). Anal. Calcd for $C_{20}H_{43}NO_2Sn$: C, 53.59; H, 9.67; N, 3.12. Found: C, 53.37; H, 9.42; N, 3.05.

Methyl *N*-(2-Methyl-1-tributylstannylpropyl)carbamate (5g). This compound was prepared from **4g** according to general procedure A with an initial reaction time of 24 h in 70% yield: IR (neat) 3326, 1705 cm^{-1}; ^1H NMR δ 4.87 (d, 1 H, J = 8.4), 3.69 (s, 0.3 H), 3.64 (s, 2.7 H), 3.12 (dd, 1 H, J = 8.4, 7.4), 1.98 (m, 1 H,), 1.59−1.24 (m, 12 H), 0.97−0.89 (m, 21 H); ^{13}C NMR δ 157.2, 51.8, 49.5, 32.4, 29 (^2J = 19), 27.4 (^3J = 56), 21.3, 20.6, 13.5, 10.2 (^1J = 314, 304); FABMS *m/z* (rel int) 364 ($M^+ - C_4H_9$, 100). Anal. Calcd for $C_{18}H_{44}NO_2Sn$: C, 51.45; H, 9.36; N, 3.33. Found: C, 51.71; H, 9.12; N, 3.36.

General Procedure B: Preparation of *t*-Butyl Methyl *N*-Tributylstannyliminodicarbonates. To a 0.1 M solution of the carbamate **5** in acetonitrile was added DMAP (0.1 equiv) and di-*tert*-butyl dicarbonate (2 equiv), and the solution was stirred at room temperature or sonicated for the specified time. The solvent was removed in vacuo to give a brownish residue that was diluted with Et_2O and washed several times with 1 M $KHSO_4$ followed by saturated $NaHCO_3$. The organic solution was dried ($MgSO_4$), filtered through Celite, and concentrated in vacuo. The resulting oils were purified by flash chromatography (38 g of silica/g of substrate; 10:1 hexane/Et_2O) to give the products as colorless oils.

***tert*-Butyl Methyl *N*-(1-Tributylstannylethyl)iminodicarbonate (6a).** This compound was prepared from **5a** according to general procedure B with a reaction time of 40 h in 98% yield: IR (neat) 1744, 1688 cm^{-1}; ^1H NMR δ 3.87 (q, 1 H, J = 7.4), 3.78 (s, 3 H), 1.57−1.20 (m, 15 H), 1.5 (s, 9 H), 0.98−0.74 (m, 15 H); ^{13}C NMR δ 155.5, 153.3, 82.1, 53.2, 42.3 (^1J = 344, 359), 28.9 (^2J = 19), 27.8, 27.3 (^3J = 51), 18.6, 13.5, 10.0 (^1J = 330, 314); FABMS *m/z* (rel int) 436 ($M^+ - C_4H_9$, 55), 380 (100). Anal. Calcd for $C_{21}H_{43}NO_4Sn$: C, 51.24; H, 8.81; N, 2.84. Found: C, 51.07; H, 8.87; N, 2.83.

***tert*-Butyl Methyl *N*-(1-Tributylstannylpropyl)iminodicarbonate (6b).** This compound was prepared according to the method of Park[12] in 50% yield and had the same spectral characteristics as reported.

***tert*-Butyl Methyl *N*-(1-Tributylstannylbutyl)iminodicarbonate (6c).** This compound was prepared from **5c** according to general procedure B with a reaction time of 44 h in 94% yield: IR (neat) 1743, 1692 cm^{-1}; ^1H NMR δ 3.93 (t, 1 H, J = 8.0), 3.78 (s, 3 H), 1.85−1.53 (m, 2 H), 1.50 (s, 9 H), 1.47−1.22 (m, 14 H), 0.93−0.71 (m, 18 H); ^{13}C NMR δ 155.5, 153.3, 81.9, 53.1, 47.3 (^1J = 357, 342), 35.2, 28.9 (^2J = 19), 27.8, 27.3 (^3J = 50), 20.7, 13.7, 13.5, 10.0 (^1J = 326, 311); FABMS *m/z* (rel int) 464 (M^+-C_4H_9, 45), 276 (100). Anal. Calcd for $C_{23}H_{47}NO_4Sn$: C, 53.09; H, 9.11; N, 2.69. Found: C, 52.88; H, 9.04; N, 2.69.

***tert*-Butyl Methyl *N*-(1-Tributylstannylpentyl)iminodicarbonate (6d).** This compound was prepared from **5d** according to general procedure B with a reaction time of 44 h in 92% yield: IR (neat) 1743, 1692 cm^{-1}; ^1H NMR δ 3.90 (t, 1 H, J = 8.0), 3.78 (s, 3 H). 2.11−1.57 (m, 2 H), 1.50 (s, 9 H), 1.57−1.18 (m, 16 H), 0.92−0.71 (m, 18 H); ^{13}C NMR δ 155.7, 153.4, 82.2, 53.4, 47.7, 32.7, 29.9 (^2J = 19), 27.9, 17.4 (^3J = 55), 22.4, 13.9, 13.7, 10.2 (^1J = 318); FABMS *m/z* (rel int) 478 ($M^+ - C_4H_9$, 36), 276 (100). Anal. Calcd for $C_{24}H_{49}NO_4Sn$: C, 53.94; H, 9.24; N, 2.62. Found: C, 53.88; H, 9.12 N, 2.67.

***tert*-Butyl Methyl *N*-(1-Tributylstannylhexyl)iminodicarbonate (6e).** This compound was prepared from **5e** according to general procedure B with a reaction time of 60 h in 78% yield: IR (neat) 1741, 1693 cm^{-1}; ^1H NMR δ 3.86 (t, 1 H, J = 8.0), 3.78 (s, 3 H), 1.55 (m, 2 H), 1.49 (s, 9 H), 1.47−1.17 (m, 18 H), 0.91−0.77 (m, 18 H); ^{13}C NMR (63 MHz) δ 155.7, 153.4, 82.3, 53.4, 47.8, 33.0, 31.6, 29.1 (^2J = 19), 28.0, 27.5, *27.4, 22.6, 14.0, 13.6, 10.2 (^1J = 326); FABMS *m/z* (rel int) 492 (M^+-C_4H_9, 66), 276 (100). Anal. Calcd for $C_{25}H_{51}NO_4Sn$: C, 54.76; H, 9.30; N, 2.55. Found: C, 54.88; H, 9.12; N, 2.52.

***tert*-Butyl Methyl *N*-(1-Cyclohexyl-1-tributylstannylmethyl)iminodicarbonate (6f).** This compound was prepared according to the method of Park[12] with a reaction time of 42 h in 21% yield: IR (neat) 1742, 1691 cm^{-1}; ^1H NMR δ 3.78 (s, 3 H), 3.70 (d, 0.75 H, J = 11), 1.85 (d, 0.25 H, J = 11), 1.50 (s, 9 H), 1.88−1.10 (m, 23 H), 0.98−0.73 (m, 15 H); ^{13}C NMR δ 155.7, 153.5, 82.1, *54.2, 53.3, 39.5, 32.2, 31.1, 29.0 (^2J = 19), 27.9, 27.4, 26.9, 26.5, 25.8, 13.1, 10.5 (^1J = 324, 309); FABMS *m/z* (rel int) 504 ($M^+ - C_4H_9$, 84), 446 (100). Anal. Calcd for $C_{26}H_{51}NO_4Sn$: C, 55.73; H, 9.17; N, 2.50. Found: C, 55.58; H, 8.96; N, 2.44.

***tert*-Butyl Methyl *N*-(2-Methyl-1-tributylstannylpropyl)iminodicarbonate (6g).** This compound was prepared from **5g** according to general procedure B with a reaction time of 120 h in 86% yield: IR (neat) 1743, 1692 cm^{-1}; ^1H NMR δ 3.77 (s, 3 H), 3.69 (d, 0.2 H, J = 11), 3.60 (d, 0.8 H, J = 11), 2.0 (m, 1 H), 1.56−1.10 (m, 12 H), 1.48 (s, 9 H), 0.97−0.63 (m, 21 H), ^{13}C NMR δ 155.5, 153.3, 81.8, 55.2, 51.3, 30.0, 28.9, (^2J = 19), 27.7, *27.6, 27.3, 21.3, 20.2, 13.4, 10.4 (^1J = 324, 310); FABMS *m/z* (rel int) 462 ($M^+ - C_4H_9$, 70), 364 (100). Anal. Calcd for $C_{23}H_{46}NO_4Sn$: C, 53.31; H, 9.11; N, 2.69. Found: C, 53.53; H, 8.97; N, 2.65.

General Procedure C: Preparation of *tert*-Butyl *N*-hydroxymethyl-*N*-tributylstannylcarbamates 7. To a cooled

(0 °C) 0.075 M solution of the iminodicarbonate **6** in Et_2O was added $LiAlH_4$ (0.75 equiv). The solution was stirred for 10 min, quenched with $Na_2SO_4 \cdot 10H_2O$, and stirred at room temperature for 10 min. The mixture was filtered to remove aluminum salts and concentrated in vacuo. The resulting oils were purified by flash chromatography (30 g silica/g of substrate; 5:1 hexane/Et_2O) to give the *N*-hydroxymethyl carbamates as colorless oils. ^{1}H NMR spectra were recorded using DMSO-d_6 as solvent and DMSO-d_5 (δ 2.49) was used as the internal standard.

***tert*-Butyl *N*-Hydroxymethyl-*N*-(1-tributylstannylethyl)carbamate (7a).** This compound was prepared from **6a** according to general procedure C in 83% yield: IR (neat) 3413, 1676 cm^{-1}; ^{1}H NMR δ 5.60 (t, 1 H, J = 6.9), 4.63 (m, 2 H), 3.0 (q, 1 H, J = 7.3), 1.38 (s, 9 H), 1.70−1.0 (m, 15 H), 0.87−0.62 (m, 15 H); ^{13}C NMR δ 156.1 *154.7, 79.9, 73.3, *71.7, 42.8, *41.3, 29.1 (^2J = 20), 28.3, 27.4 (^3J = 56), *19.5, 18.9, 13.6, 10.0 (^1J = 324 Hz), *9.3; FABMS m/z (rel int) 448 (M^+ − OH, 10), 408 (M^+ − C_4H_9, 46), 290 (100). Anal. Calcd for $C_{20}H_{43}NO_3Sn$: C, 51,74; H, 9.34; N, 3.02. Found: C, 52.00; H, 9.12; N, 3.13.

***tert*-Butyl *N*-Hydroxymethyl-*N*-(1-tributylstannylpropyl)carbamate (7b).** This compound was prepared from **6b** according to general procedure C in 77% yield: IR (neat) 3345, 1693 cm^{-1}; ^{1}H NMR δ 5.62 (t, 1 H, J = 6.8), 4.72 (m, 1H), 4.58 (m, 1 H), 2.92 (t, 1 H, J = 7.6), 1.76 (m, 2 H), 1.4 (s, 9 H), 1.54−1.12 (m, 12 H), 0.93−0.65 (m, 18 H); ^{13}C NMR δ 154.8, 80.2, *79.9, *74.2, 72.4, 51.2, 39.3, 29.1 (^2J = 20), 28.9, 27.4 (^3J = 56), 26.7, *26.4, 13.6, *12.8, *10.3, 9.7; FABMS m/z (rel int) 462 (M^+ − OH, 3), 422 (M^+ − C_4H_9, 19). Anal. Calcd for $C_{21}H_{45}NO_3Sn$: C, 52.74; H, 9.48; N, 2.93. Found: C, 52.55; H, 9.23; N, 2.93.

***tert*-Butyl *N*-Hydroxymethyl *N*-(1-tributylstannylbutyl)carbamate (7c).** This compound was prepared from **6c** according to general procedure C in 79% yield: IR (neat) 3418, 1674 cm^{-1}; ^{1}H NMR δ 5.80 (m, 0.15 H), 5.63 (t, 0.85 H, J = 6.9), 4.70 (m, 1 H), 4.50 (m, 1 H), 3.09 (t, 1 H, J = 7.7), 1.70−1.17 (m, 16 H), 1.37 (s, 9 H), 0.90−0.65 (m, 18 H); ^{13}C NMR (50 MHz) δ 156.4, *154.8, *80.1, 79.9, 74.1, *72.2, 48.9, *46.3, 35.7, 29.1 (^2J = 19), 28.4, 27.5 (^3J = 50), *27.4, 21.3, *20.8, *13.5, 13.6, 10.2 (^1J = 319), *9.4; FABMS m/z (rel int) 476 (M^+ − OH, 9), 436 (M^+ − C_4H_9, 30), 318 (100). Anal. Calcd for $C_{22}H_{47}NO_3Sn$: C, 53.67; H, 9.62; N, 2.84. Found: C, 53.70; H, 9.49; N, 2.85.

***tert*-Butyl *N*-Hydroxymethyl-*N*-(1-tributylstannylpentyl)carbamate (7d).** This compound was prepared from **6d** according to general procedure C in 79% yield: IR (neat) 3418, 1674 cm^{-1}; ^{1}H NMR δ 5.68 (m, 0.15 H), 5.60 (t, 0.85 H, J = 6.9), 4.60 (m, 1 H), 4.51 (m, 1 H), 2.97 (t, 1 H, J = 7.7), 1.68 (m, 2 H), 1.37 (s, 9 H), 1.56−1.12 (m, 16 H), 0.86−0.65 (m, 18 H); ^{13}C NMR δ *156.4, 154.8, *79.8, 79.6, 74.0, 49.1, *46.6, 33.0, *32.8, 30.4, *29.2, 29.1, 38.4, 27.5 (^3J = 57), 22.6, *22.5, *13.9, 13.6, 10.3 (^1J = 312), *9.43; FABMS m/z (rel int) 490 (M^+ − OH, 8), 450 (M^+ − C_4H_9, 15), 332 (100). Anal. Calcd for $C_{23}H_{49}NO_3Sn$: C, 54.56; H, 9.76; N, 2.77. Found: C, 54.70; H, 9.77; N, 2.84.

***tert*-Butyl *N*-Hydroxymethyl-*N*-(1-tributylstannylhexyl)carbamate (7e).** This compound was prepared from **6e** according to general procedure C in 79% yield: IR (neat) 3402, 1679 cm^{-1}; ^{1}H NMR δ 5.58 (m, 1 H), 4.68 (m, 1 H), 4.51 (m, 1 H), 2.97 (t, 1 H, J = 7.8), 1.60 (m, 2 H), 1.37 (s, 9 H), 1.50−1.10 (m, 18 H), 0.86−0.57 (m, 18 H); ^{13}C NMR δ 156.3, *154.8, *80.0, 79.7, 71.9, 49.2, 33.3, 31.6, *31.3, 29.1 (^2J = 19), 28.4, 27.5 (^3J = 56), *27.4, 22.6, 13.9, 13.6, 10.2 (^1J = 311), 9.4; FABMS m/z (rel int) 464 (M^+ − C_4H_9, 42), 364 (100). Anal. Calcd for $C_{24}H_{51}NO_3Sn$: C, 55.39; H, 9.88; N, 2.69. Found: C, 55.47; H, 9.77; N, 2.74.

***tert*-Butyl *N*-Hydroxymethyl-*N*-(1-cyclohexyl-1-tributylstannylmethyl)carbamate (7f).** This compound was prepared from **6f** according to general procedure C in 80% yield: IR (neat) 3425, 1665 cm^{-1}; ^{1}H NMR δ 5.67 (t, 0.24 H, J = 7.0), 5.58 (t, 0.76 H, J = 7.0), 4.78 (dd, 1 H, J = 7.0, 10.0), 4.37 (dd, 1 H, J = 7.0, 10.0), 2.76 (d, 0.8 H, J = 10.0), 1.81 (d, 0.2 H, J = 10.0), 1.66−1.10 (m, 23 H), 1.37 (s, 9 H), 0.87−0.65 (m, 15 H); ^{13}C NMR δ *159.0, 155.5, 80.0, 75.5, 57.2, 40.3, 32.4, 32.3, 29.1 (^2J = 17), 28.5, 27.5 (^3J = 58), *27.4, 26.7, *26.2, 26.1, 13.7, *13.6, 10.8, 10.1 (^1J = 310, 290); FABMS m/z (rel int) 516 (M^+ − OH, 4), 476 (M^+ − C_4H_9, 28). Anal. Calcd for $C_{25}H_{51}NO_3Sn$: C, 56.40; H, 9.66; N. 2.63. Found: C, 56.23; H, 9.41; N, 2.66.

***t*-Butyl *N*-Hydroxymethyl-*N*-(2-methyl-1-tributylstannylpropyl)carbamate (7g).** This compound was prepared from **6g** according to general procedure C in 77% yield: IR (neat) 3427, 1671 cm^{-1}; ^{1}H NMR δ 5.65 (t, 0.25 H, J = 7.0), 5.55 (t, 0.75 H, J = 7.0), 4.82 (dd, 1 H, J = 7.0, 10.3), 4.43 (dd, 1 H, J = 7.0, 10.3), 2.67 (d, 1 H, J = 9.8, J_{SnH} = 49), 2.15 (m, 1 H), 1.37 (s, 9 H), 1.55−1.27 (m, 12 H), 0.98−0.59 (m, 21 H); ^{13}C NMR δ 155.1, 88.0, 75.5, 58.3 (^1J = 347), 31.1, 28.6, 28.1, 27.6 (^3J = 56), 21.72, 21.66, 13.7, *10.9 (^1J = 319, 304), 10.23 (^1J = 308, 294); FABMS m/z (rel int) 476 (M^+ − OH, 10), 436 (M^+ − C_4H_9, 52), 318 (100). Anal. Calcd for $C_{22}H_{47}NO_3Sn$: C, 53.67; H, 9.62; N, 2.84. Found: C, 53.53; H, 9.46; 2.84.

General Procedure D: Preparation of *tert*-Butyl *N*-*tert*-Butylthiomethyl-*N*-tributylstannylcarbamates 3. To a 0.07 M solution of the *N*-hydroxymethylcarbamate **7** in hexanes was added Et_3N (0.95 equiv). The solution was cooled (−20 °C), and MsCl (25 equiv) was slowly added. The resulting mixture was stirred for 15 min, and a 1.3 M solution of *tert*-butylthiol (25 equiv) in hexane was added. The mixture was stirred at room temperature for 2 h, diluted with hexane, and washed several times with saturated $NaHCO_3$. The organic solution was dried ($MgSO_4$), filtered through Celite, and concentrated in vacuo. The resulting oils were purified by flash chromatography (40 g silica/g of substrate; 40:1 hexane/Et_2O) to give the products as colorless oils.

***tert*-Butyl *N*-*tert*-butylthiomethyl-*N*-(1-tributylstannylethyl)carbamate (3a).** This compound was prepared from **7a** according to the general procedure D in 77% yield: IR (neat) 1679 cm^{-1}; ^{1}H NMR (250 MHz) δ 4.50 (ABq, 2 H, $\Delta\delta$ = 0.14, J = 13.7), 2.97 (q, 1 H, J = 7.3), 1.46 (s, 9 H), 1.36 (s, 9 H), 1.55−1.10 (m, 15 H), 0.68−0.92 (m, 15 H); ^{13}C NMR δ 154.4, 79.7, 48.2, 42.8, 42.1, 32.3, *31.5, 29.2 (^2J = 19), *28.6, 28.4, 27.6 (^3J = 57), 17.6, 13.7, 10.4 (^1J = 318); FABMS m/z (rel int) 480 (M^+ − C_4H_9, 34), 290 (100). Anal. Calcd for $C_{24}H_{51}NO_2SSn$: C, 53.74; H, 9.58; N, 2.61. Found: C, 53.97; H, 9.58; N, 2.69.

***tert*-Butyl *N*-*tert*-Butylthiomethyl-*N*-(1-tributylstannylpropyl)carbamate (3b).** This compound was prepared from **7b** according to the general procedure D in 89% yield: IR (neat) 1680 cm^{-1}; ^{1}H NMR δ 4.49 (ABq, 2 H, $\Delta\delta$ = 0.26, J = 13.6), 3.16 (m, 0.25 H), 2.82 (dd, 0.75 H, J = 7.5, 7.0), 1.84 (m, 2 H), 1.50−1.20 (m, 12 H), 1.46 (s, 9 H), 1.36 (s, 9 H), 0.9−0.7 (m, 18 H); ^{13}C NMR δ 154.6, 79.7, 50.8, 49.2, 42.7, 31.3, 29.2 (^2J = 19), 28.5, 27.6 (^3J = 57), 25.2, 13.7, 12.7, 10.74 (^1J = 310, 322), *10.0; FABMS m/z (rel int) 494 (M^+ − C_4H_9, 81). Anal. Calcd for $C_{25}H_{53}NO_2SSn$: C, 54.55; H, 9.70; N, 2.54. Found: C, 54.44; H, 9.57; N, 2.55.

***tert*-Butyl *N*-*tert*-Butylthiomethyl-*N*-(1-tributylstannylbutyl)carbamate (3c).** This compound was prepared from **7c** according to the general procedure D in 87% yield: IR (neat) 1680 cm^{-1}; ^{1}H NMR δ 4.51 (ABq, 0.6 H, $\Delta\delta$ = 0.14, J = 13.5), 4.50 (ABq, 1.4 H, $\Delta\delta$ = 0.24, J = 13.5), 2.91 (dd, 1 H, J = 7.9, 7.6), 1.84−1.65 (m, 2 H), 1.61−1.10 (m, 14 H), 1.46 (s, 9 H), 1.36 (s, 9 H), 0.95−0.70 (m, 18 H); ^{13}C NMR δ 154.6, 79.6, 49.1, 48.7, 42.6, 34.7, 31.3, 29.2 (^2J = 18), 28.4, 27.5 (^3J = 57), 21.3, 14.1, 13.7, 10.7 (^1J = 322, 309); FABMS m/z (rel int) 508 (M^+ − C_4H_9, 17), 318 (100). Anal. Calcd for $C_{26}H_{55}NO_2SSn$: C, 55.33; H, 9.82; N, 2.48. Found: C, 55.24; H, 9.78; N, 2.40.

***tert*-Butyl *N*-*tert*-Butylthiomethyl-*N*-(1-tributylstannylpentyl)carbamate (3d).** This compound was prepared from **7d** according to the general procedure D in 88% yield: IR (neat) 1680 cm^{-1}; ^{1}H NMR δ 4.51 (ABq, 0.5 H, $\Delta\delta$ = 0.16, J = 13.5), 4.50 (ABq, 1.5 H, $\Delta\delta$ = 0.27, J = 13.5), 2.89 (t, 1 H, J = 7.8), 1.8 (q, 2 H, J = 7.7), 1.58−1.0 (m, 16 H), 1.46 (s, 9 H), 1.35 (s, 9 H), 0.99−0.73 (m, 18 H); ^{13}C NMR δ 154.5, 79.6, 49.1, 48.9, 42.7, 32.0, 31.3, *30.3, 29.2 (^2J = 19), 28.4, 27.5 (^3J = 57), 22.7, 14.1, 13.7, 10.0 (^1J = 322); FABMS m/z (rel int) 522 (M^+ − C_4H_9, 20), 332 (100). Anal. Calcd for $C_{27}H_{57}NO_2SSn$: C, 56.06; H, 9.93; N, 2.41. Found: C, 55.90; H, 9.78; N, 2.40.

***tert*-Butyl *N*-*tert*-Butylthiomethyl-*N*-(1-tributylstannylhexyl)carbamate (3e).** This compound was prepared from **7e** according to the general procedure D in 81% yield: IR (neat) 1677 cm^{-1}; ^1H NMR δ 4.48 (ABq, 2 H, $\Delta\delta = 0.48$, $J = 13.5$), 2.89 (t, 1 H, $J = 8.0$), 1.8 (m, 2 H), 1.46 (s, 9 H), 1.35 (s, 9 H), 1.5−1.2 (m, 18 H), 0.92−0.71 (m, 18 H); ^{13}C NMR δ 154.5, 79.7, 49.2, 49.0, 42.7, 32.3, 32.8, 31.3, 29.2 ($^2J = 19$), 28.4, 27.6 ($^3J = 57$), 22.6, 14.0, 13.7, 10.7 ($^1J = 322$, 307), 10.0; FABMS *m*/*z* (rel int) 536 ($M^+ - C_4H_9$, 48), 346 (100). Anal. Calcd for $C_{28}H_{59}NO_2SSn$: C, 56.76; H, 10.04; N, 2.36. Found: C, 56.80; H, 9.82; N, 2.46.

***tert*-Butyl *N*-*tert*-Butylthiomethyl-*N*-(1-cyclohexyl-1-tributylstannylmethyl)carbamate (3f).** This compound was prepared from **7f** according to the general procedure D in 83% yield: IR (neat) 1681 cm^{-1}; ^1H NMR (200 MHz, C_6D_6) δ 5.04 (d, 1 H, $J = 12.9$), 4.10 (d, 1 H, $J = 12.9$), 2.85 (d, 1 H, $J = 9.6$, $J_{SnH} = 49$), 2.3 (m, 1 H), 1.84 (m, 16 H), 1.43 (s, 9 H), 1.26 (s, 9 H), 1.21−0.94 (m, 21 H); ^1H NMR (63 MHz) δ 154.8, 79.6, 56.4, 50.4, 42.4, *40.1, 32.4, *32.3, 31.3, 29.2, *29.1, 28.4, 27.6 ($^2J = 59$), 26.8, 26.4, 26.2, 13.7, 11.2 ($^1J = 320$, 306); FABMS *m*/*z* (rel int) 548 ($M^+ - C_4H_9$, 12). Anal. Calcd for $C_{29}H_{59}NO_2SSn$: C, 57.62; H, 9.84; N, 2.32. Found: C, 57.95; H, 9.87, 2.38.

***tert*-Butyl *N*-*tert*-Butylthiomethyl-*N*-(2-methyl-1-tributylstannylpropyl)carbamate (3g).** This compound was prepared from **7g** according to the general procedure D in 87% yield: IR (neat) 1681 cm^{-1}; ^1H NMR (C_6D_6) δ 5.02 (d, 1 H, $J = 12.9$), 4.1 (d, 1 H, $J = 12.9$), 2.76 (d, 1 H, $J = 9.2$), 2.5 (m, 1 H), 1.8 (m, 12 H), 1.42 (s, 9 H), 1.24, (s, 9 H), 1.49−0.49 (m, 21 H); ^{13}C NMR δ 154.8, 79.6, 57.4, 50.3, 42.5, 31.3, 31.2, 29.3 ($^2J = 19$), 28.4, 27.6 ($^3J = 59$), *21.9, *21.7, 21.6, 21.4, *21.1, 13.7, 11.3 ($^1J = 321$); FABMS *m*/*z* (rel int) 508 ($M^+ - C_4H_9$, 52), 318 (100). Anal. Calcd for $C_{26}H_{55}NO_2SSn$: C, 55.33; H, 9.82; N, 2.48. Found: C, 55.19; H, 9.77; N, 2.39.

General Procedure E: Preparation of Oxazolidinones 9. To a cooled (−78 °C) 0.15 M solution of the α-aminoorganostannane **3** in THF was added *n*-BuLi (1.5 equiv) slowly, and the solution was stirred for 15 min. The appropriate aldehyde (2.0 equiv) was added, and the mixture was stirred for 15 min and quenched at −78 °C with saturated NH_4Cl. The mixture was diluted with Et_2O, washed with water, dried ($MgSO_4$), filtered through Celite, and concentrated in vacuo to give β-amino alcohols, which were used without purification in most cases. To a 0.1 M solution of β-amino alcohol in THF was added NaH (2 equiv), and the mixture was stirred for 30−60 min, quenched with water, diluted with Et_2O, and washed with water. The organic layer was dried ($MgSO_4$), filtered through Celite, and concentrated in vacuo. The ratios of diastereomers in the crude products are recorded in Table 1. The resulting oils were purified by flash chromatography (100 g silica/g substrate; 5:1 hexane/Et_2O) to give oxazolidinones as colorless oils or white solids. Combined yields are reported in Table 1; specific isolated yields are noted below.

For the systems where R = *n*-butyl or *n*-pentyl, it was easier to separate the two diastereomers as the protected β-amino alcohols (i.e., before cyclization). However the syn diastereomer was still contaminated with 1-phenyl-1-pentanol, which was then removed after cyclization.

***cis*/*trans*-3-*tert*-Butylthiomethyl-4-methyl-5-phenyl-2-oxazolidinone (*cis*/*trans*-9a).** *cis*-**9a** (65% yield): mp 98−99 °C; IR (KBr) 1734 cm^{-1}; ^1H NMR δ 7.43−7.26 (m, 5 H), 5.58 (d, 1 H, $J = 8.4$), 5.07 (d, 1 H, $J = 14.7$), 4.40 (quintet, 1 H, $J = 6.6$), 4.01 (d, 1 H, $J = 14.7$), 1.42 (s, 9 H), 0.78 (d, 3 H, $J = 6.6$); ^{13}C NMR δ 156.4, 134.5,128.4, 126, 78.6, 53.0, 43.4, 42.1, 31.2, 13.9; EIMS *m*/*z* (rel int) 279 (M^+, 1), 146 (94), 105 (100). Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.67; H, 7.72; N, 5.02. *trans*-**9a** (25% yield): mp 60−62 °C; IR (KBr) 1750 cm^{-1}; ^1H NMR δ 7.40−7.30 (m, 5 H), 5.06 (d, 1 H, $J = 14.9$), 4.94 (d, 1 H, $J = 8.1$), 4.1 (d, 1 H, $J = 14.9$, CH_2S), 3.98 (quintet, 1 H, $J = 6.2$), 1.37 (m, 12 H); ^{13}C NMR δ 156.3, 137.4, 128.9, 128.8, 125.9, 82.6, 57.3, 43.3, 41.9, 31.1, 16.8; EIMS *m*/*z* (rel int) 279 (M^+, 0.8), 146 (100). Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.47; H, 7.67; N, 4.88.

cis/*trans*-3-*tert*-Butylthiomethyl-4-ethyl-5-phenyl-2-oxazolidinone (*cis*/*trans*-9b). *cis*-**9b** (51% yield): mp 43−45 °C; IR (KBr) 1744 cm^{-1}; ^1H NMR δ 7.40−7.30 (m, 5 H), 5.56 (d, 1 H, $J = 8.2$), 5.12 (d, 1 H, $J = 14.8$), 4.26 (dt, 1 H, $J = 3.8$, 8.2), 4.06 (d, 1 H, $J = 14.8$), 1.42 (s, 9 H), 1.47−1.24 (m, 2 H), 0.55 (t, 3 H, $J = 7.5$); ^{13}C NMR δ 156.9, 134.7, 128.6, 128.4, 126.5, 78.9, 58.3, 43.5, 42.6, 31.2, 20.6, 9.0; EIMS *m*/*z* (rel int) 293 (M^+, 0.7), 105 (100). Anal. Calcd for $C_{16}H_{23}NO_2S$: C, 65.51; H, 7.90; N, 4.77. Found: C, 65.54; H, 7.78; N, 4.88. *trans*-**9b** (26% yield): mp 45−49 °C; IR (KBr) 1742 cm^{-1}; ^1H NMR δ 7.40−7.30 (m, 5 H), 5.12 (d, 1 H, $J = 6.4$), 5.10 (d, 1 H, $J = 14.9$), 4.04 (d, 1 H, $J = 14.9$), 3.90 (dt, 1 H, $J = 3.1$, 6.4), 1.82−1.66 (m, 2 H), 1.35 (s, 9 H), 0.98 (t, 3 H, $J = 7.5$); ^{13}C NMR δ 156.3, 138.6, 128.7, 125.9, 79.2, 61.4, 43.4, 41.9, 31.1, 23.2, 7.8; EIMS *m*/*z* (rel int) 293 (M^+, 0.8), 160 (100). Anal. Calcd for $C_{16}H_{23}NO_2S$: C, 65.51; H, 7.90; N, 4.77. Found: C, 65.69; H, 7.82; N, 4.88.

***cis*/*trans*-3-*tert*-Butylthiomethyl-5-phenyl-4-propyl-2-oxazolidinone (*cis*/*trans*-9c).** *cis*-**9c** (57% yield): mp 45−47 °C; IR (KBr) 1733 cm^{-1}; ^1H NMR δ 7.40−7.30 (m, 5 H), 5.45 (d, 1 H, $J = 8.2$), 5.10 (d, 1 H, $J = 14.8$), 4.30 (dt, 1 H, $J = 8.2$, 3.7), 4.10 (d, 1 H, $J = 14.8$), 1.42 (s, 9 H), 1.37−1.00 (m, 2 H), 1.2−0.8 (m, 2 H, $CH_3CH_2CH_2$), 0.64 (t, 3 H, $J = 7.0$, $CH_3CH_2CH_2$); ^{13}C NMR (63 MHz) δ 156.7, 134.7, 128.5, 128.2, 126.4, 78.9, 56.9, 43.3, 42.5, 31.1, 29.7, 18.0, 13.8; EIMS *m*/*z* (rel int) 307 (M^+, 0.4), 91 (100). Anal. Calcd for $C_{17}H_{25}NO_2S$: C, 66.42; H, 8.20; N, 4.55. Found: C, 66.67; H, 8.23; N, 4.67. *trans*-**9c** (29% yield): mp 63−66 °C; IR (KBr) 1741 cm^{-1}; ^1H NMR δ 7.40−7.30 (m, 5 H), 5.10 (d, 1 H, $J = 6.1$), 5.10 (d, 1 H, $J = 14.8$), 4.10 (d, 1 H, $J = 14.8$), 4.0 (m, 1 H), 1.84−1.71 (m, 2 H), 1.68−1.40 (m, 2 H), 1.34 (s, 9 H), 0.96 (t, 3 H, $J = 7.2$); ^{13}C NMR (63 MHz) δ 156.2, 138.5, 128.7, 126.0, 79.9, 60.4, 43.3, 41.9, 33.0, 31.1, 17.2, 14.0; EIMS *m*/*z* (rel int) 307 (M^+, 0.4), 132 (100). Anal. Calcd for $C_{17}H_{25}NO_2S$: C, 66.42; H, 8.20; N, 4.55. Found: C, 66.54; H, 8.25; N, 4.56.

***cis*/*trans*-4-Butyl-3-*tert*-butylthiomethyl-5-phenyl-2-oxazolidinone (*cis*/*trans*-9d).** *cis*-**9d** (55% yield): mp 48−50 °C; IR (KBr) 1730 cm^{-1}; ^1H NMR δ 7.41−7.29 (m, 5 H), 5.56 (d, 1 H, $J = 8.2$), 5.10 (d, 1 H, $J = 14.9$), 4.30 (dt, 1 H, $J = 3.7$, 8.2), 4.06 (d, 1 H, $J = 14.9$), 1.42 (s, 9 H), 1.44−0.85 (m, 6 H), 0.64 (t, 3 H, $J = 7.3$); ^{13}C NMR δ 156.8, 134.8, 128.6, 128.3, 126.6, 79.0, 57.2, 43.5, 42.6, 31.2, 27.2, 26.9, 22.4, 13.4; EIMS *m*/*z* (rel int) 321 (M^+, 0.2), 132 (100). Anal. Calcd for $C_{18}H_{27}NO_2S$: C, 67.26; H, 8.47; N, 4.43. Found: C, 67.33; H, 8.45; N, 4.39. *trans*-**9d** (24% yield): IR (neat) 1753 cm^{-1}; ^1H NMR δ 7.43−7.27 (m, 5 H), 5.11(d, 1 H, $J = 5.8$), 5.07 (d, 1H, $J = 14.9$), 4.05 (d, 1 H, $J = 14.9$), 4.04−3.97 (m, 1 H), 1.83−1.74 (m, 1 H), 1.69−1.57 (m, 1 H), 1.34 (s, 9 H), 1.46−1.20 (m, 4 H), 0.91 (t, 3 H, $J = 6.8$); ^{13}C NMR δ 156.3, 138.6, 128.7, 125.9, 79.9, 60.6, 43.4, 42.0, 31.1, 30.5, 25.9, 22.5, 13.8; EIMS *m*/*z* (rel int) 321 (M^+, 0.4), 132 (100). Anal. Calcd for $C_{18}H_{27}NO_2S$: C, 67.26; H, 8.47; N, 4.43. Found: C, 67.06; H, 8.30; N, 4.52.

***cis*/*trans*-3-*tert*-Butylthiomethyl-4-pentyl-5-phenyl-2-oxazolidinone (*cis*/*trans*-9e).** *cis*-**9e** (51% yield): IR (neat) 1754 cm^{-1}; ^1H NMR δ 7.36−7.40 (m, 5 H), 5.56 (d, 1 H, $J = 8.2$), 5.10 (d, 1 H, $J = 14.9$), 4.30 (dt, 1 H, $J = 8.2$, 3.6), 4.06 (d, 1 H, $J = 14.9$), 1.42 (s, 9 H), 1.20−0.84 (m, 8 H), 0.71 (t, 3 H, $J = 6.7$); ^{13}C NMR δ 156.9, 134.7, 128.6, 128.4, 126.6, 79.1, 57.5, 43.5, 42.6, 31.5, 31.3, 27.6, 24.3; EIMS *m*/*z* (rel int) 335 (M^+, 0.1), 132 (100). Anal. Calcd for $C_{19}H_{29}NO_2S$: C, 68.03; H, 8.71; N, 4.17. Found: C, 67.89; H, 8.67; N, 4.18. *trans*-**9e** (24% yield): IR (neat) 1748 cm^{-1}; ^1H NMR δ 7.40−7.30 (m, 5 H), 5.10 (d, 1 H, $J = 5.8$), 5.07 (d, 1 H, $J = 14.4$), 4.06 (d, 1 H, $J = 14.4$), 3.90 (m, 1 H), 1.70−1.40 (m, 2 H), 1.35 (s, 9 H), 1.30−0.94 (m, 6 H), 0.88 (t, 3 H, $J = 6.4$); ^{13}C NMR δ 156.3, 138.6, 126.6, 126.0, 79.0, 60.7, 43.4, 42.1, 31.6, 31.2, 27.6, 23.4, 2.6, 13.6; EIMS *m*/*z* (rel int) 335 (M^+, 0.3), 132 (100). Anal. Calcd for $C_{19}H_{29}NO_2S$: C, 68.03; H, 8.71; N, 4.17. Found: C, 68.14; H, 8.61; N, 3.96.

***cis*-3-*tert*-Butylthiomethyl-4-cyclohexyl-5-phenyl-2-oxazolidinone (*cis*-9f).** This compound was prepared from **3f** according to the general procedure E except that 1.3 equiv of benzaldehyde was used (40% yield): mp 109−110 °C; IR (KBr) 1738 cm^{-1}; ^1H NMR δ 7.40−7.27 (m, 5 H), 5.60 (d, 1 H, $J = 8.0$), 5.21 (d, 1 H, $J = 14.9$), 4.2 (m, 1 H), 4.15 (d, 1 H, $J = 14.9$), 1.60−1.45 (m, 5 H), 1.42 (s, 9 H), 1.26−0.78 (m, 6 H,); ^{13}C NMR δ 157.1, 134.7, 128.3, 125.9, 80.1, 61.5, 44.5, 43.6,

38.8, 31.4, 31.3, 27.2, 26.8, 26.0, 25.7; EIMS *m/z* (rel int) 290 ($M^+ - C_4H_9$, 6), 132 (100). Anal. Calcd for $C_{20}H_{29}NO_2S$: C, 69.14; H. 8.41; N, 4.03. Found: C, 69.35; H, 8.43; N, 4.03.

***cis*/*trans*-3-*tert*-Butylthiomethyl-4-isopropyl-5-phenyl-2-oxazolidinone (*cis*/*trans*-9g).** This mixture of diastereomers was prepared from **3g** according to the general procedure E except that 5 equiv of *n*-BuLi and 5 equiv of benzaldehyde were used and KH was the base used for cyclization. *cis*-**9g** (50% yield): mp 95−98 °C; IR (KBr) 1727 cm^{-1}; ^1H NMR δ 7.43−7.21 (m, 5 H), 5.58 (d, 1 H, J = 8.2), 5.22 (d, 1 H, J = 15.0), 4.29 (dd, 1 H, J = 2.2, 8.2), 4.1 (d, 1 H, J = 15.0), 1.74−1.62 (m, 1 H), 1.41 (s, 9 H), 0.87 (d, 3 H, J = 7.1), 0.68 (d, 3 H, J = 7.1); ^{13}C NMR δ 157, 134.5, 128.3, 128.1 125.9, 79.7, 61.6, 44.3, 43.5, 31.3, 28.2, 21.2, 16.3; EIMS *m/z* (rel int) 307 (M^+, 0.1), 91 (100). Anal. Calcd for $C_{17}H_{25}NO_2S$: C, 66.42; H, 8.20; N, 4.55. Found: C, 66.60; H, 8.17; N, 4.62. *trans*-**9g** (18% yield): mp 60−69 °C; IR (KBr) 1733 cm^{-1}; ^1H NMR δ 7.43−7.21 (m, 5 H), 5.18 (d, 1 H, J = 4.9), 5.10 (d, 1 H, J = 14.9), 4 03 (d, 1 H, J = 14.9), 4.00−3.95 (m, 1 H), 2.14 (m, 1 H), 1.30 (s, 9 H), 0.99 (t, 6 H, J = 6.7); ^{13}C NMR δ 156.5, 139.7, 128.7 128.5, 125.3, 75.4, 65.1, 49.4, 31.1, 27.2, 17.7, 15.0; EIMS *m/z* (rel int) 307 (M^+, 1), 174 (100). Anal. Calcd for $C_{17}H_{25}NO_2S$: C, 66.42; H, 8.20; N, 4.55. Found: C, 66.62; H, 8.14; N, 4.60.

cis/*trans*-3-*tert*-Butylthiomethyl-4-ethyl-5-(4-methoxyphenyl)-2-oxazolidinone (*cis*/*trans*-9h). *cis*-**9h** (57% yield): mp 58−62 °C; IR (KBr) 1739 cm^{-1}; ^1H NMR δ 7.25 (d, 2 H, J = 8.6), 6.90 (d, 2 H, J = 8.6), 5.52 (d, 1 H, J = 8.2), 5.10 (d, 1 H, 14.8), 4.21 (dt, 1 H, J = 3.6, 8.2), 4.06 (d, 1 H, J = 14.8), 3.82 (s, 3 H), 1.42 (s, 9 H), 1.50−1.19 (m, 2 H), 0.59 (t, 3 H, J = 7.4); ^{13}C NMR δ 159.7, 156.9, 128.9, 126.7, 114.7, 78.7, 58.4, 55.2, 43.3, 42.5, 31.2, 20.6, 9.2; EIMS *m/z* (rel int) 323 (M^+, 2), 190 (100). Anal. Calcd for $C_{17}H_{25}NO_3S$: C, 63.14; H, 7.79; N, 4.33. Found: C, 63.40; H, 7.53; N, 4.39. *trans*-**9h** (23% yield): IR (neat) 1750 cm^{-1}; ^1H NMR δ 7.26 (d, 2 H, J = 8.8), 6.9 (d, 2 H, J = 8.8), 5.08 (d, 1 H, J = 14.8), 5.05 (d, 1 H, J = 6.8), 4.05 (d, 1 H, J = 14.8), 3.98 (dt, 1 H, J = 3.2, 6.8), 3.81 (s, 3 H), 1.82−1.63 (m, 2 H), 1.37 (s, 9 H), 0.94 (t, 3 H, J = 7.4); ^{13}C NMR δ 159.9, 156.3, 130.3, 127.5, 114, 79.4, 61.2, 55.1, 43.3, 41.9, 31.1, 23.2, 7.9; EIMS *m/z* (rel int) 323 (M^+, 1), 190 (100). Anal. Calcd for $C_{17}H_{25}NO_3S$: C, 63.14; H, 7.79; N, 4.33. Found: C, 63.06; H, 7.79; N, 4.29.

***cis*/*trans*-3-*tert*-Butylthiomethyl-4-ethyl-5-cyclohexyl-2-oxazolidinone (*cis*/*trans*-9i).** *cis*-**9i** (40% yield): IR (neat) 1748 cm^{-1}; ^1H NMR δ 5.0 (d, 1 H, J = 14.8), 3.98 (d, 1 H, J = 14.8), 3.91 (dd, 1 H, J = 5.4, 6.0), 3.82 (q, 1 H, J = 5.0), 1.90−1.56 (m, 7 H), 1.37 (s, 9 H), 1.48−1.0 (m, 6 H), 0.89 (t, 3 H, J = 7.4); ^{13}C NMR δ 156.5, 81.7, 55.9, 43.3, 42.0, 41.6, 31.1, 28.1, 27.3, 26.0, 25.7, 25.4, 23.6, 7.4; EIMS *m/z* (rel int) 299 (M^+, 1), 70 (100). Anal. Calcd for $C_{16}H_{29}NO_2S$: C, 64.18; H, 9.76; N, 4.68. Found: C, 63.98; H, 9.98; N, 4.75. *trans*-**9i** (30% yield): mp 66−69 °C; IR (KBr) 1713 cm^{-1}; ^1H NMR δ 5.05 (d, 1 H, J = 14.9). 4.07 (m, 2 H), 3.94 (d, 1 H, J = 14.9), 2.05 (m, 1 H), 1.78−1.60 (m, 8 H), 1.37 (s, 9 H), 1.35−1.31 (m, 2 H), 1.21 (t, 3 H, J = 7.0); ^{13}C NMR (63 MHz) δ 157.8, 82.5, 55.7, 43.4, 42.4, 36.8, 29.4, 29, 26.1, 25.3, 25.2, 19.4, 9,4; EIMS *m/z* (rel int) 242 ($M^+ - C_4H_9$, 1), 210 (16), 166 (8), 70 (100). Anal. Calcd for $C_{16}H_{29}NO_2S$: C, 64.18; H, 9.76; N, 4.68. Found: C, 64.45; H, 9.57; N, 4.96.

***cis*/*trans*-3-*tert*-Butylthiomethyl-4-ethyl-5-isopropyl-2-oxazolidinone (*cis*/*trans*-9j).** *cis*-**9j** (30% yield): IR (neat) 1750 cm^{-1}; ^1H NMR δ 5.06 (d, 1 H, J = 14.9), 4.07−3.94 (m, 2 H), 3.90 (d, 1 H, J = 14.9), 2.10 (m, 1H), 1.70 (m, 2 H), 1.37 (s, 9 H), 1.10 (d, 3 H, J = 6.5), 0.95 (m, 6 H); ^{13}C NMR δ 157.2, 83.7, 55.7, 43.5, 42.4, 31.2, 27.3, 19.3, 19.2. 19.1, 9.2; EIMS *m/z* (rel int) 259 (M^+, 1), 70 (100). Anal. Calcd for $C_{13}H_{25}NO_2S$: C, 60.20; H, 9.72; N, 5.40. Found: C, 60.01; H, 9.59; N, 5.31. *trans*-**9j** (39% yield): mp 60−62 °C; IR (KBr) 1749 cm^{-1}; ^1H NMR δ 5.01 (d, 1 H, J = 14.9), 3.98 (d, 1 H, J = 14.9), 3.84 (dd, 1 H, J = 5.3, 6.2), 3.80 (q, 1 H, J = 4.9), 1.86−1.73 (m, 1 H), 1.68−1.57 (m, 2 H), 1.37 (s, 9 H), 1.00 (d, 3 H, J = 6.5), 0.98 (d, 3 H, J = 6.5), 0.89 (t, 3 H, J = 7.5); ^{13}C NMR δ 156.4, 82.4, 56.1, 43.4, 41.5, 32.4, 31.1, 23.7, 17.7, 17.0, 7.4; EIMS *m/z* (rel int) 259 (M^+, 1), 70 (100). Anal. Calcd for $C_{13}H_{25}NO_2S$: C, 60.20; H, 9.72; N, 5.40. Found: C, 60.40; H, 9.55; N, 5.40.

General Procedure F: Preparation of *O*-Methylmandelates 10. To a 0.2 M solution of HOBT (1.1 equiv) in CH_2Cl_2 were added (*S*)-*O*-methylmandelic acid (1.1 equiv) and DCC (1.1 equiv), and the mixture was cooled (0 °C). The crude primary stannylamine (prepared from phthalimides **4** as described in general procedure A) was then added as a 0.4 M solution in CH_2Cl_2, and the reaction mixture was stirred at room temperature for 15 h. The mixture was concentrated in vacuo, and the resulting residue was extracted with 3:1 hexane/Et_2O, filtered through a plug of silica, and concentrated in vacuo. The two diastereomers were separated by flash chromatography (60 g silica/g of substrate; 10:1 hexane/Et_2O).

***N*-(1-Tributylstannylpropyl)-2-methoxy-2-phenylacetamide (10b).** This compound was prepared from **4b** according to general procedure F as a mixture of diastereomers in 87% overall yield. The less polar diastereomer (1′*R*,2*S*)-**10b** exhibited: $[\alpha]^{20}_D = -34.5$ (*c* 1.0, $CHCl_3$); IR (neat) 3310, 1661 cm^{-1}; ^1H NMR δ 7.4−7.3 (m, 5 H), 6.93 (d, 1 H, J = 7.2), 4.58 (s, 1 H), 3.36 (s, 3 H), 3.30 (m, 1 H), 1.84−1.66 (m, 2 H), 1.52−1.18 (m, 12 H), 0.95−0.67 (m, 18 H); ^{13}C δ 169.4, 137.2, 128.3, 128.0, 126.8, 83.9, 57.0, 41.1, 29.0 (^2J = 19), 27.4 (^3J = 56), 27.2, 13.6, 12.8, 9.7 (^1J = 318, 305); FABMS *m/z* (rel int) 440 ($M^+ - C_4H_9$, 100). Anal. Calcd for $C_{27}H_{49}NO_2Sn$: C, 58.08; H, 8.73; N, 2.82. Found: C, 57.89; H, 8.64; N, 2.92.

***N*-(1-Tributylstannylhexyl)-2-methoxy-2-phenylacetamide (10e).** This compound was prepared from phthalimide **4e** according to general procedure F as a mixture of diastereomers in 77% overall yield. The less polar diastereomer (1′*R*,2*S*)-**10e** exhibited: $[\alpha]^{20}_D = -33.2$ (*c* 1.0, $CHCl_3$); IR (neat) 3305, 1660 cm^{-1}; ^1H NMR δ 7.3 (m, 5 H), 6.90 (d, 1 H, J = 7.6), 4.58 (s, 1 H), 3.35 (s, 3 H), 3.35 (m, 1 H), 1.72−1.10 (m, 20 H), 0.90−0.71 (m, 18 H); ^{13}C NMR δ 169.3, 137.3, 128.3, 128.2, 126.9, 83.9, 57.1, 39.2, 34.2, 31.4, 29.1 (^2J = 19), 27.9, 27.4 (^3J = 56), 22.5, 13.9, 13.6, 9.8 (^1J = 304, 318); FABMS *m/z* (rel int), 482 ($M^+ - C_4H_9$, 100). Anal. Calcd for $C_{27}H_{49}NO_2Sn$: C, 60.23; H, 9.17; N, 2.60. Found: C, 60.30; H, 9.37; N, 2.77.

(1′*R*,2*S*)-*N*-*tert*-Butoxycarbonyl-*N*-(1-tributylstannylpropyl)-2-methoxy-2-phenylacetamide (11b). This compound was prepared from **(1′*R*,2*S*)-10b** according to the general procedure B, with a reaction time of 48 h, in 74% yield: IR (neat) 1725, 1683 cm^{-1}; ^1H NMR δ 7.37−7.28 (m, 5 H), 5.98 (s, 1 H), 3.62 (t, 1 H, J = 8.0), 3.41 (s, 3 H), 1.53 (s, 9 H), 1.63−1.21 (m, 20 H), 0.88 (t, 9 H, J = 7.2), 0.53 (t, 3 H, J = 7.3); ^{13}C NMR δ 173.9, 153.8, 146.5, 136.7, 128.2, 128.0, 83.0, 82.6, 57.1, 48.5, 28.8 (^2J = 19), 27.5, 27.2 (^3J = 57), 24.3, 14.9, 13.4, 12.1, 10.2 (^1J = 312, 328); FABMS *m/z* (rel int) 540 ($M^+ - C_4H_9$, 14), 121 (100). Anal. Calcd for $C_{29}H_{51}NO_4Sn$: C, 58.40; H, 8.62; N, 2.35. Found: C, 58.28; H, 8.79; N, 2.38.

(1′*R*,2*S*)-*N*-*tert*-Butoxycarbonyl-*N*-(1-tributylstannylhexyl)-2-methoxy-2-phenylacetamide (11e). This compound was prepared from (1′*R*,2*S*)-**10e** according to the General Procedure B, with a reaction time of 36 h, in 77% yield: IR (neat) 1724, 1684 cm^{-1}; ^1H NMR δ 7.35−7.27 (m, 5 H), 5.98 (s, 1 H), 3.72 (dd, 1 H, J = 8.4, 7.4), 3.41 (s, 3 H), 1.43 (s, 9 H), 1.52−1.22 (m, 14 H), 1.06−0.71 (m, 24 H); ^{13}C NMR δ 171.1, 154.0, 136.9, 128.3, 128.2, 83.2, 82.8, 57.4, 46.8, 31.4, 29.1 (^2J = 19), 27.8, 27.4 (^3J = 58), 22.5, 13.9, 13.6, 10.4 (^1J = 313, 328); FABMS *m/z* (rel int) 582 (M^+-C_4H_9, 12), 121 (100). Anal. Calcd for $C_{31}H_{57}NO_4Sn$: C, 60.19; H, 9.00; N, 2.19. Found: C, 60.19; H, 9.03; N, 2.26.

Preparation of (*R*)-*tert*-Butyl Carbamates 12b and 12e. Hydrazine hydrate (10 equiv) was added to a 1 M solution of stannane **11** in MeOH. The reaction mixture was stirred at reflux for 12−15 h. The solvent was removed in vacuo, and the resulting residue was diluted with Et_2O and washed with water (three times). The organic layer was dried ($MgSO_4$), filtered though Celite, and concentrated in vacuo to give the carbamates as colorless oils in quantitative yield. The two carbamates **12b** (R = Et) and **12e** (R = *n*-C_5H_{11}) exhibited the same spectral characteristics as the ones reported in the literature.[9]

Preparation of Iminodicarbonates (*R*)-6b and (*R*)-6e. To a cooled (−78 °C) solution of LDA (0.3 M, 1.5 equiv) in THF was slowly added a solution of stannane **12** (0.5 M in THF).

After 45 min, a solution of methyl cyanoformate (2 equiv, 1 M in THF) was added, and the solution was stirred for 2 h. The reaction was quenched with saturated NH_4Cl and allowed to warm to room temperature. The resulting mixture was diluted with Et_2O and washed with water, and the organic layer was dried ($MgSO_4$), filtered through Celite, and concentrated in vacuo. The crude product was purified by flash chromatography (40 g silica/g of substrate; 10:1 hexane/Et_2O) to give the products as colorless oils. ***tert*-Butyl Methyl (*R*)-*N*-(1-Tributylstannylpropyl)iminodicarbonate [(*R*)-6b]** was prepared from **12b** in 75% yield: $[\alpha]^{20}_{578} = +61.2$ (*c* 1.0, $CHCl_3$); all the other spectral characteristic are as described above for racemic **6b**. ***tert*-Butyl methyl (*R*)-*N*-(1-tributylstannylhexyl)iminodicarbonate [(*R*)-6e]** was prepared from **12e** in 91% yield: $[\alpha]^{20}_{578} = +65.2$ (*c* 1.0, $CHCl_3$); all the other spectral characteristics are as described above for racemic **6e**.

***tert*-Butyl (*R*)-*N*-*tert*-Butylthiomethyl-*N*-(1-tributylstannylpropyl)carbamate [(*R*)-3b].** This compound was prepared from (*R*)-**6b** according to the general procedures C and D (77 and 89% yields, respectively): $[\alpha]^{20}_{578} = +51.9$ (*c* 1.0, $CHCl_3$); all the other spectral characteristics are as described for racemic **3b**.

***tert*-Butyl (*R*)-*N*-*tert*-Butylthiomethyl-*N*-(1-tributylstannylhexyl)carbamate [(*R*)-3e].** This compound was prepared from (*R*)-**6e** according to the general procedures C and D (79 and 87% yields, respectively): $[\alpha]^{20}_{578} = +46.6$ (*c* 1.0, $CHCl_3$); all the other spectral characteristics are as described for racemic **3e**.

(4*S*,5*R*)-3-*tert*-Butylthiomethyl-4-ethyl-5-phenyl-2-oxazolidinone [(4*S*,5*R*)-9b]. This compound was prepared as described in general procedure E: $[\alpha]^{20}_{578} = +58.0$ (*c* 1.0, $CHCl_3$); all the other spectral characteristics are as described for *cis*-**9b**.

(4*S*,5*S*)-3-*tert*-Butylthiomethyl-4-ethyl-5-phenyl-2-oxazolidinone [(4*S*,5*S*)-9b]. This compound was prepared as described in general procedure E: $[\alpha]^{20}_{578} = +61.1$ (*c* 1.0, $CHCl_3$); all the other spectral characteristics are as described for *trans*-**9b**.

General Procedure G: Preparation of Primary β-Amino Alcohols from Oxazolidinones 9. To a 0.1 M solution of oxazolidinone **9** (0.1−0.2 mmol) in EtOH was added 2 M LiOH (5 equiv), and the reaction mixture was stirred at reflux for the specified time. The solvent was removed in vacuo, and the remaining residue was diluted with Et_2O and extracted with 1 M HCl (four times). The combined acid extracts were basified (2 M NaOH), extracted with EtOAc, dried ($MgSO_4$), filtered through Celite, and concentrated *in vacuo* to give β-amino alcohol **14**. The crude amino alcohol was dissolved in EtOH (2 mL), and concentrated HCl (three drops) was added. The reaction mixture was concentrated in vacuo to give a white solid which was recrystallized from 2-propanol to give the amine hydrochloride salt as a white solid.

General Procedure H: Preparation of Primary β-Amino Alcohols from Aminoacetals 13. A 1.0 M solution of the β-amino alcohol **8** in 1:1 2 M HCl/THF was stirred at reflux overnight. The reaction mixture was diluted with Et_2O and extracted with 1 M HCl (several times). The combined acid extracts were basified with 2 M NaOH, extracted with EtOAc, dried ($MgSO_4$), filtered through Celite, and concentrated in vacuo to give aminoacetal **13** as a yellow oil. The aminoacetals seemed to decompose when exposed to silica gel; hence, they were used without purification. To a 1 M solution of the aminoacetal in CH_2Cl_2 was added 1,3-propanedithiol (10 equiv) followed by $BF_3{\cdot}Et_2O$ (3 equiv). The reaction mixture was stirred at room temperature for 24 h. The solution was diluted with CH_2Cl_2 and extracted with 1 M HCl. The combined acid extracts were basified (2 M NaOH), extracted with EtOAc, dried ($MgSO_4$), filtered through Celite, and concentrated in vacuo to give the crude β-amino alcohols as a white solid. The β-amino alcohols were converted to their HCl salts as described in general procedure G.

(1*R,2*S**)-2-Amino-1-phenyl-1-propanol (Norephedrine) HCl Salt [(1*R**,2*S**)-15a].** This compound was prepared from oxazolidinone *cis*-**9a** according to general procedure G, with a reaction time of 15 h, in 84% yield: mp 189−191 °C (lit.[27] mp 194−196 °C); IR (KBr) 3318, 1031 cm^{-1}; ^1H NMR δ 8.37 (broad singlet, 3 H), 7.40−7.20 (m, 5 H), 5.38 (br s, 1H), 5.27 (d, 1 H, *J* = 2.0), 3.49 (m, 1 H), 1.11 (d, 3 H, *J* = 6.7); ^{13}C NMR δ 139.7, 127.0, 126.3, 124.8, 70.5, 51.9, 10.2; ESMS *m*/*z* (rel int) 152 ($M^+ - Cl$, 100). Anal. Calcd for $C_9H_{24}ClNO$: C, 57.60; H, 7.52; N, 7.46. Found: C, 57.70; H, 7.25; N, 7.28.

(1*R,2*S**)-2-Amino-1-phenyl-1-butanol HCl Salt [(1*R**,2*S**)-15b].** This compound was prepared from oxazolidinone *cis*-**9b** according to general procedure G, with a reaction time of 12 h, in 75% yield: mp 243−245 °C; IR (KBr) 3312, 1040 cm^{-1}; ^1H NMR δ 8.16 (br s, 3 H), 7.42−7.27 (m, 5 H), 5.78 (d, 1 H, *J* = 3.7), 5.16 (s, 1 H), 3.17 (m, 1 H), 1.51−1.31 (m, 2 H), 0.89 (t, 3 H, *J* = 7.5); ^{13}C NMR δ 139.5, 127.1, 126.4, 125.1, 70.7, 57.6, 18.5, 9.5; ESMS *m*/*z* (rel int) 166 ($M^+ - Cl$, 100). Anal. Calcd for $C_{10}H_{16}ClNO$: C, 59.55; H, 8.00; N, 6.94. Found: C, 59.55; H, 7.84; N, 6.90.

(1*R*,2*S*)-2-Amino-1-phenyl-1-butanol HCl Salt [(1*R*,2*S*)-15b]. This compound was prepared from *cis*-oxazolidinone (4*S*,5*R*)-**9b** as described above: $[\alpha]^{20}_D = -32.5$ (*c* 1, MeOH) (lit.[20] $[\alpha]^{20}_D = -33.1$ (*c* 1, H_2O)); all other spectral characteristics are as described for (1*R**,2*S**)-**15b**.

(1*R,2*S**)-2-Amino-1-phenyl-1-pentanol HCl Salt [(1*R**,2*S**)-15c].** This compound was prepared from aminoacetal **13c** according to general procedure H in 70% yield: mp 212−214 °C; IR (KBr) 3308, 1043 cm^{-1}; ^1H NMR (250 MHz) δ 8.13 (broad singlet, 3 H), 7.78−7.27 (m, 5 H), 5.15 (d, 1 H, *J* = 2.5), 3.25 (m, 2 H), 1.54−1.35 (m, 3 H), 1.19−1.11 (m, 1 H), 0.79 (t, 3 H, *J* = 6.8); ^{13}C NMR δ 139.1, 126.5, 125.7, 124.5, 70.1, 54.8, 26.8, 17.1, 12.1; ESMS *m*/*z* (rel int) 180 ($M^+ - Cl$, 100). Anal. Calcd for $C_{11}H_{18}ClNO$: C, 61.24; H, 8.41; N, 6.40. Found: C, 60.97; H, 8.40; N, 6.44.

(1*R,2*S**)-2-Amino-1-phenyl-1-hexanol HCl Salt [(1*R**,2*S**)-15d].** This compound was prepared from aminoacetal **13d** according to general procedure H in 75% yield: mp 208−210 °C; IR (KBr) 3335, 1044 cm^{-1}; ^1H NMR δ 8.36 (br s, 3 H), 7.45−7.22 (m, 5 H), 5.37 (d, 1 H, *J* = 2.0), 5.30−5.00 (broad, 1 H), 3.39 (m, 1 H), 1.63−1.11 (m, 6 H), 0.76 (t, 3 H, *J* = 6.5); ^{13}C NMR δ 139.1, 126.3, 125.6, 124.3, 69.9, 54.9, 25.7, 24.1, 20.3, 11.9; ESMS *m*/*z* (rel int) 194 ($M^+ - Cl$, 100). Anal. Calcd for $C_{12}H_{20}ClNO$: C, 62.73; H, 8.77, N, 6.09. Found: C, 63.00; H, 8.79; N, 6.29.

(1*R,2*S**)-2-Amino-1-phenyl-1-heptanol HCl Salt [(1*R**,2*S**)-15e].** This compound was prepared from aminoacetal **13e** according to the general procedure H in 86% yield: mp 165−168 °C; IR (KBr) 3326 cm^{-1}; ^1H NMR δ 8.22 (br s, 3 H), 7.43−7.26 (m, 5 H), 5.23 (d, 1 H, *J* = 2.5), 3.30−3.12 (m, 2 H), 1.40−1.22 (m, 2 H), 1.19−0.88 (m, 6 H), 0.81 (t, 3 H, *J* = 6.2); ^{13}C NMR δ 139.6, 127.4, 126.6, 125.2. 71.0, 56.6, 30.4, 25.4, 24.4, 21.2, 13.0; ESMS *m*/*z* (rel int) 208 ($M^+ - Cl$, 100). Anal. Calcd for $C_{13}H_{22}ClNO$: C, 64.05; H, 9.10; N, 5.74. Found: C, 63.84; H, 8.91; N, 5.66.

(1*R,2*S**)-2-Amino-3-methyl-1-phenyl-1-butanol HCl Salt [(1*R**,2*S**)-15g].** This compound was prepared from oxazolidinone *cis*-**9g** according to general procedure G, with a reaction time of 20 h, in 76% yield: mp 233−235 °C; IR (KBr) 3294, cm^{-1}; ^1H NMR δ 8.08 (br s, 3 H), 7.72−7.25 (m, 5 H), 5.20 (d, 1 H, *J* = 3.7), 5.10 (br s, 1 H), 3.18 (m, 1 H), 1.89−1.79 (m, 1 H), 1.03 (d, 3 H, *J* = 6.8), 0.96 (d, 3 H, *J* = 6.9); ^{13}C NMR δ 139.4, 127.3, 126.5, 125.5, 70.6, 60.9, 25.1, 20.0, 17.2; ESMS *m*/*z* (rel int) 180 ($M^+ - Cl$, 100). Anal. Calcd for $C_{11}H_{18}ClNO$: C, 61.53; H, 7.98; N, 6.52. Found: C, 61.14; H, 8.26; N, 6.23.

(1*R,2*S**)-2-Amino-1-(4-methoxyphenyl)-1-butanol HCl Salt [(1*R**,2*S**)-15h].** This compound was prepared from oxazolidinone *cis*-**9h** according to general procedure G, with a reaction time of 20 h, in 66% yield: mp 200−202 °C; IR (KBr) 3346, cm^{-1}; ^1H NMR δ 8.15 (broad singlet, 3 H), 7.32 (d, 2 H, *J* = 8.6), 6.9 (d, 2 H, *J* = 8.6), 5.74 (br s, 1 H), 5.10 (m, 1 H), 3.79 (s, 3 H), 3.18 (m, 1 H), 1.50 (m, 2 H), 0.89 (t, 3 H, *J* = 7.4); ^{13}C NMR δ 157.6, 131.4, 126.2, 112.5, 70.3, 57.8, 54.0, 18.5, 9.5; ESMS *m*/*z* (rel int) 196 ($M^+ - Cl$, 100). Anal. Calcd

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for $C_{11}H_{18}ClNO_2$: C, 57.01; H, 7.83; N, 6.04. Found: C, 56.86; H, 7.77; N, 6.11.

(1*R,2*R**)-2-Amino-1-(4-methoxyphenyl)-1-butanol HCl Salt [(1*R**,2*R**)-15h].** This compound was prepared from oxazolidinone *trans*-**9h** according general procedure G but using *n*-propanol as solvent. The reaction was stirred for 48 h, and the product was obtained in 76% yield: mp 191−195 °C; IR (KBr) 3345 cm^{-1}; ^1H NMR δ 8.05 (broad singlet, 3 H), 7.30 (d, 2 H, $J = 8.6$), 6.90 (d, 2 H, $J = 8.6$), 6.01 (d, 1 H, $J = 3.6$), 4.56 (dd, 1 H, $J = 6.0, 3.6$), 3.80 (s, 3 H), 3.06 (m, 1 H), 1.52−1.45 (m, 2 H), 0.90 (t, 3 H, $J = 7.4$); ^{13}C NMR δ 157.6, 131.4, 126.2, 112.5, 70.3, 57.8, 54.0, 18.5, 9.5; ESMS *m*/*z* (rel int) 196 ($M^+ - Cl$, 95). Anal. Calcd for $C_{11}H_{18}ClNO_2$: C, 57.01; H, 7.83; N, 6.04. Found: C, 56.94; H, 7.59; N, 5.88.

(1*R*,2*S*)-*N*-*tert*-Butoxycarbonyl-2-amino-1-phenylbutanol [(1*R*,2*S*)-16]. To a 0.25 M solution of amino alcohol (1*R*,2*S*)-**14b** in THF were added Et_3N (1.2 equiv) and Boc_2O (1.2 equiv). The reaction mixture was stirred at room temperature for 1 h. The resulting mixture was diluted with Et_2O and washed with 1 M $KHSO_4$ (three times) and water. The organic solution was dried ($MgSO_4$), filtered through Celite, and concentrated in vacuo. The crude product was purified by flash chromatography (60 g silica/g of substrate; 2:1 hexane/Et_2O) to give (1*R*,2*S*)-**16** as a white solid (98% yield): mp 99−102 °C; $[\alpha]^{20}_D = -105.7$ (*c* 1.0, $CHCl_3$); IR (KBr) 3375, 1689 cm^{-1}; ^1H NMR δ 7.33 (m, 5 H), 4.86 (m, 1 H), 4.48 (broad d, 1 H, $J = 8.0$), 1.46 (s, 9 H), 1.24 (m, 2 H), 0.91 (t, 3 H, $J = 7.3$); ^{13}C NMR δ 147.1, 140.8, 128.1, 127.4, 126.5, 79.8, 76.8, 58.2, 28.3, 22.6, 10.7; ESMS *m*/*z* (relative intensity) 267 ($M^+ + 2$, 18), 266 ($M^+ + 1$, 100). Anal. Calcd for $C_{15}H_{23}NO_3$: C, 67.98; H, 8.74; N, 5.28. Found: C, 68.04; H, 8.61; N, 5.22.

General Procedure I: Mitsunobu Reaction of β-Amino Alcohols 8. To a 0.1 M solution of amino alcohol **8** in THF was added PPh_3 (1.2 equiv). The solution was cooled to 0 °C, DEAD (1.2 equiv) was slowly added, and the reaction mixture was stirred at room temperature for 1.5 h. The solvent was removed in vacuo, and the crude product was purified by flash chromatography (100 g silica/g of substrate; 5:1 hexane/Et_2O). ***trans*-3-*tert*-Butylthiomethyl-4-methyl-5-phenyl-2-oxazolidinone** (*trans*-**9a**) was prepared from *anti*-**8a** as a white solid in 89% yield while ***trans*-3-*tert*-butylthiomethyl-4-ethyl-5-phenyl-2-oxazolidinone** (*trans*-**9b**) was prepared from *anti*-**8b** in 92% yield. Both compounds exhibited spectral data identical to that obtained for the same compounds prepared by NaH cyclization of the corresponding syn amino alcohols.

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