Preparation of Chiral 2-Stannyloxazolidines and First Considerations on the Transacetalisation Reaction Mechanism

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Keywords: Chirality / Isomerisation / Oxazolidine / Tin / Transacetalisation

N-Protected 2-tributylstannyl-1,3-oxazolidines derived from *N*-monoprotected chiral β-amino alcohols were obtained through transacetalisation of (diethoxymethyl)tributylstannane under acidic conditions. In the case of 4-substituted 2-tributylstannyl-1,3-oxazolidines, the kinetic product of the reaction was shown to be the *trans* isomer whatever the nature of the protective group, while the thermodynamic product was the *cis* isomer in the *N*-Ts series and the *trans* isomer in *N*-CO_2R compounds. Aspects of the transacetalisation reaction are discussed along with those concerning the isomerisation of the products, allowing an interpretation of the obtained results.

Introduction

α-Stannyl acetals have been widely studied and have been involved in transmetallation reactions to provide dialkoxymethyllithiums[1−4] or in substitution reactions on the acetal function to obtain functionalized α-alkoxyorganostannanes[5−11] or alkoxycyclopropanes.[5,12,13] In spite of early reports in the field of dithioacetals,[14,15] 1,3-oxathianes[16] or dihalomethyl analogues,[17−19] extension to 2-triorganostannyl-1,3-oxazolidines has only rarely been attempted.[20−23] However, the preparation of enantiopure α-aminoalkyltriorganotins as potential precursors of enantiopure α-amino anions upon transmetallation with *n*-butyllithium appears to offer great potential[24,25] and initiated our investigations into the synthesis of *N*-protected 2-triorganostannyl-1,3-oxazolidines. The advantage of this approach in comparison with enantioselective deprotonation by *n*-butyllithium or *sec*-butyllithium in the presence of (−)-sparteine[26−30], (+)-sparteine[31] or a (+)-sparteine surrogate derived from cytisine[32] should be the obtaining of chiral α-aminoorganolithium reagent uncomplexed with a diamine ligand. Accordingly, an efficient route to provide 2-triorganostannyl-1,3-oxazolidines selectively would seem to be of great interest in order subsequently to provide chiral α-aminoorganostannanes through ring opening of the oxazolidine component. Among non-stannylated compounds, organolithium and organoaluminium reagents,[33−39] and also Grignard reagents[40,41] and radical anions[42] are known to afford ring-opening products efficiently when treated with 2-aryl- or 2-alkyl-substituted 1,3-oxazolidines. In the case of 2-triorganostannyl-1,3-oxazolidines, *anti*-S_N2 substitution is expected to occur instead of a transmetallation reaction when a soft nucleophile is used in the presence of a Lewis acid, as previously observed with α-stannyl acetals.[9−11] Indeed, we have shown in a preliminary work that the opening of the oxazolidine ring proceeds stereoselectively when carried out on (*R*)-phenylglycinol-derived 2-triorganostannyl-1,3-oxazolidines.[43]

This article is devoted to a detailed study of the preparation of *N*-protected 2-triorganostannyl-1,3-oxazolidines and related compounds through transacetalisation, focussing on reaction mechanisms. Detailed NMR characterisation of compounds, allowing *cis* and *trans* configuration assignment, and X-ray analyses of one pair of diastereomers are reported separately in the accompanying contribution.[44]

Results and Discussion

Because of the high instability of formylstannanes,[3,5] the preparation of 2-tributylstannyl-1,3-oxazolidines only appears feasible through transacetalisation of the readily available (diethoxymethyl)tributylstannane (**1**).[2,45] This reaction has previously been used for the synthesis of 2-tributylstannyl-1,3-dioxanes or 2-tributylstannyl-1,3-dioxolanes, with yields over 90% as shown for **2**, for instance, in Scheme 1.[2,46]

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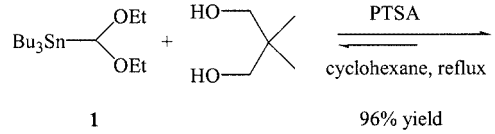
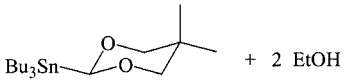


1 96% yield



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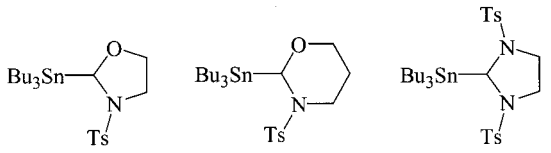
Scheme 1. Transacetalisation reaction of **1** with 2,2-dimethylpropanediol

When extended to β-amino alcohols, this strategy requires *N*-protected β-amino alcohols bearing a protective group capable of decreasing the basicity of the nitrogen atom and of increasing the acidity of the remaining N−H function. Under such conditions, transacetalisation can be achieved in the presence of *para*-toluenesulfonic acid (PTSA) or camphorsulfonic acid (CSA) as demonstrated both by Colombo's reports[20−22] involving norephedrine- and camphor-derived β-amino alcohols and by our own results.[23,43] Mixed acetals [Scheme 2, Equation (1)] were usually obtained from unprotected amino alcohols, while production of cyclic α-stannylamino acetals [Scheme 2, Equation (2)] required the use of amino alcohols bearing a strongly withdrawing group on nitrogen (PG = Ts, Ms, trifluoroacetyl or alkoxycarbonyl).

Preparation of 3-Sulfonylated 2-Tributylstannyl-1,3-oxazolidines and Related Species

β-Amino alcohols were protected as *N*-Ts or *N*-Ms derivatives according to the literature.[47,48] These *N*-protected amino alcohols were initially heated at reflux in cyclohexane or toluene with an equimolar amount of **1** and a catalytic amount of PTSA over a period of 18 h. The distillation of the ethanol/solvent azeotrope allows the equilibrium to be shifted in the desired direction. The reaction was first tested on *N*-Ts-aminoethanol and *N*-Ts-aminopropanol and afforded the expected achiral 2-tributylstannyl-1,3-oxazolidine **3** and the 2-tributylstannyl-1,3-perhydroxazine **4** in 89% and 82% yields, respectively. The extension to the aminal-type homologue **5** was also shown to be possible when starting from bis(*N*-Ts)-ethylenediamine (57% yield) (Scheme 3).



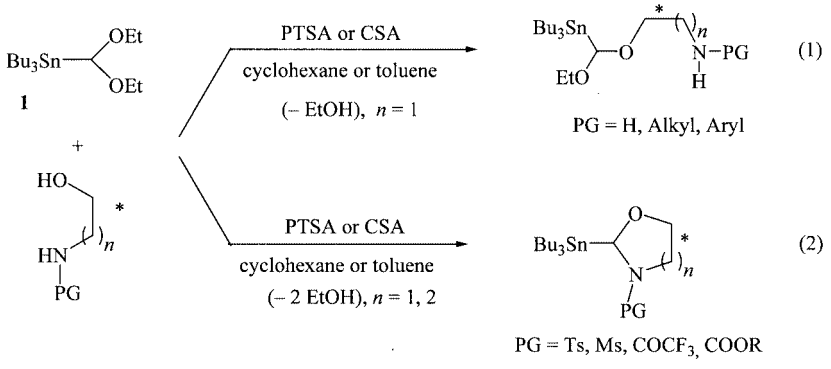
3 (89% yield) **4** (82% yield) **5** (57% yield)

Scheme 3. 3-Tosyl-2-tributylstannyl-1,3-oxazolidine and analogues

When stereochemical aspects were encountered in compounds based on chiral β-amino alcohols, diastereomeric mixture of 2-tributylstannyl-1,3-oxazolidines were obtained as reported in Table 1. (For 2,4,5-trisubstituted-1,3-oxazolidines, the *trans* and *cis* nomenclature refers to the relative positions of the tributylstannyl group and the substituent on the 4-position (α to nitrogen), to distinguish the diastereomers.) The unambiguous assignment of the *cis* or *trans* configurations was established from the multinuclear NMR spectra and X-ray analyses described in the accompanying paper.[44] In all cases, 3-mesyl- or 3-tosyl-2-tributylstannyl-1,3-oxazolidines were obtained in high yields, with strong preferences for the *cis* isomers, as shown for (*R*)-phenylglycinol-derived oxazolidines in Scheme 4.

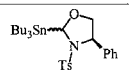
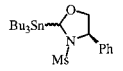
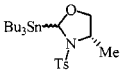
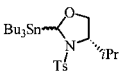
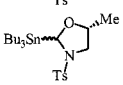
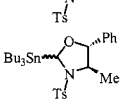
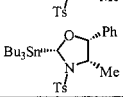
While the nature of the protecting group (Ms or Ts) has only a minor effect on the diastereoselection, the presence of a substituent on the 4-position seems much more favourable to the *cis* isomer than substitution on the 5-position (Entry 5). Obviously, when a convergent effect occurs, as in the norephedrine-derived 1,3-oxazolidine, only the *cis* isomer is obtained (Entry 7).

At this stage it was of importance to check if this *cis* preference was due to higher stability of the *cis* isomer or to kinetic control. For this purpose, (diethoxymethyl)tributylstannane (**1**) was treated with (*R*)-*N*-Ts-phenylglycinol under the usual conditions (PTSA, toluene reflux), and the evolution of the diastereomeric ratio was monitored by HPLC. By this method, an interesting evolution of the **6-*trans*/6-*cis*** diastereomeric ratio was observed during the course of the reaction. The **6-*trans*/6-*cis*** ratio, which after

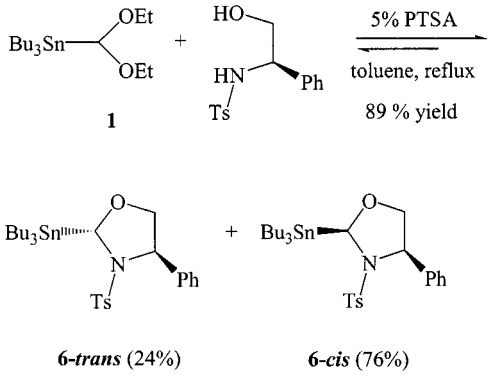


Scheme 2. Transacetalisation reaction of **1** with amino alcohols

Table 1. Transacetalisation of **1** with chiral *N*-sulfonylated β-amino alcohols

Entry	*N*-Protected β-amino alcohols	2-(Tributylstannyl)-1,3-oxazolidines	N°	Yield (%)[a]	*dr* (*trans*/*cis*)[b]
1			**6**	89	24/76
2			**7**	77	25/75
3			**8**	80	17/83
4			**9**	93	18/82
5			**10**	78	35/65[c]
6			**11**	70	20/80[d]
7			**12**	72	0/100[d]

[a] Isolated yield (flash chromatography) after 18 h at reflux. [b] The identification of the *trans* and *cis* isomers was carried out through the detailed structural analysis reported in the accompanying paper.[44] The *trans* isomers were eluted before the *cis* isomers on silica gel (eluent: hexanes/ethyl acetate, 95:5). [c] After 24 h heating. [d] The *trans*/*cis* nomenclature relates to the positions of the methyl group and the tributylstannyl group.



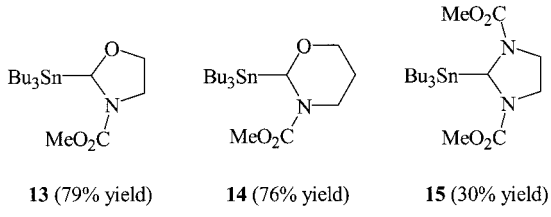
Scheme 4. Transacetalisation reaction of **1** with (*R*)-*N*-Ts-phenylglycinol

15 minutes was 75:25 (low conversion rate) had become 70:30 after 1 h and 30:70 after 18 h, this result suggesting that the *trans* isomer is the kinetic product of the reaction while the *cis* isomer is the thermodynamic product. This was corroborated by isomerisation experiments starting from pure *trans* or *cis* isomers obtained after separation by liquid chromatography and placed in the presence of PTSA that had previously been dried by azeotropic distillation (5 h reflux) before addition of the oxazolidines **6-*trans*** and **6-*cis*** (Scheme 5).

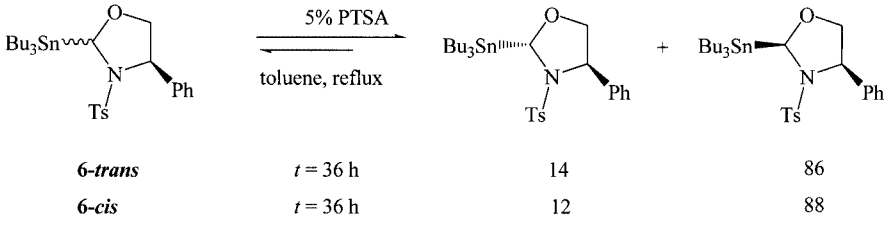
While isomerisation led roughly to the thermodynamic mixture of isomers after 36 h whether starting either from **6-*trans*** or from **6-*cis***, the isomerisation of **6-*cis*** was slower. The use of imperfectly dried PTSA (azeotropic distillation for 30 min before addition of oxazolidines) allowed an easier isomerisation, with a *cis*/*trans* mixture near 80:20 obtained in 2 h when starting from either isomer. These results strongly support the above hypothesis and allow an approximate evaluation of the diastereomeric mixture under thermodynamic conditions (**6-*trans*/6-*cis***, 14:86 to 20:80), the composition of thermodynamic mixture being slightly dependent on the availability of the protons in the reaction mixture.

Preparation of 3-Alkoxycarbonyl-2-tributylstannyl-1,3-oxazolidines and Related Species

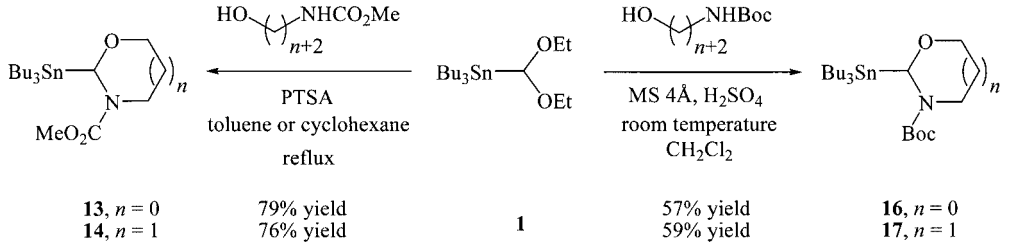
The method previously used for *N*-Ts derivatives was first extended to the transacetalisation of **1** by *N*-alkoxycarbonyl amino alcohols in order to prepare 3-alkoxycarbonyl-2-tributylstannyl-1,3-oxazolidines. This method using azeotropic distillation of ethanol in the presence of paratoluenesulfonic acid (Method A) was efficient when starting from *N*-(methoxycarbonyl)aminoethanol and -aminopropanol or from bis(*N*,*N*′-methoxycarbonyl)ethylenediamine, allowing preparation of compounds **13**, **14** and **15** (Scheme 6).



Scheme 6. 3-Methoxycarbonyl-2-tributylstannyl-1,3-oxazolidine and analogues



Scheme 5. Isomerisation of (4*R*)-4-phenyl-3-tosyl-2-tributylstannyl-1,3-oxazolidines



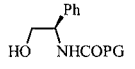
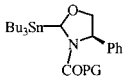
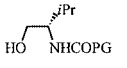
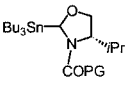
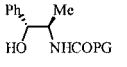
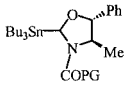
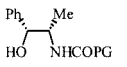
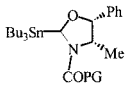
Scheme 7. Transacetalisation of **1** with *N*-(alkoxycarbonyl)amino alcohols

When this procedure was attempted on *N*-Boc-amino alcohols, however, Boc removal occurred and the expected amino acetal was not obtained. To circumvent this problem, transacetalisation was performed at room temperature in CH_2Cl_2 in the presence of 4 Å molecular sieves containing 5 equiv./mol of adsorbed sulfuric acid (Method B), as shown in Scheme 7. By this procedure, compounds **16** and **17** (*N*-Boc analogues of **13** and **14**) were obtained in 57% and 59% yields, respectively (Scheme 7).

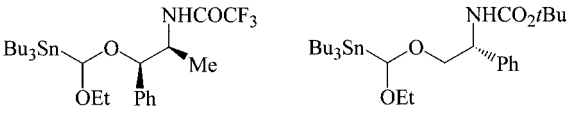
Furthermore, according to Colombo,[20] this reaction was also shown to be possible with CSA (5 equiv., cyclohexane, reflux: Method C). This procedure was also extended to *N*-protected chiral α-amino alcohols for comparison in order to determine the more appropriate experimental conditions. The obtained results are reported in Table 2.

By method A, 2-tributylstannyl-1,3-oxazolidines were obtained in good yields (77−85%) while lower yields were obtained with methods B or C (43−69%). The use of CSA (method C) gave slightly better results than method B. However, when a catalytic amount of CSA (10−50% mol on activated molecular sieves) in CH_2Cl_2 was used, the transacetalisation reaction occurred at the alcohol function to afford the mixed acetal **31** (Scheme 8) accompanied by the oxazolidine **20** in poor yield (46%, *trans*/*cis* = 75:25). Similarly, the reaction stopped at the stage of the mixed acetal **30** with *N*-(trifluoroacetyl)norephedrine (Entry 15) (Scheme 8). In terms of the diastereoselectivity, while a strong preference for or exclusive formation of the *cis* isomer was observed with *N*-alkoxycarbonylated norephedrine (Entries 12−14, compounds **27**−**29**), poor selectivities were

Table 2. 3-Alkoxycarbonyl-2-tributylstannyl-1,3-oxazolidines and analogues

Entry	*N*-Protected β-amino alcohols	PG	Experimental conditions[a]	2-(Tributylstannyl)-1,3-oxazolidines	N°	Yield (%)[b]	*dr* (*trans*/*cis*)[c]
1		OMe	A		**18**	82	60/40
2		OBn	B		**19**	53	72/28
3		O*t*Bu	B		**20**	52	61/39
4		O*t*Bu	C		**20**	69	60/40
5		OAllyl	C		**21**	60	60/40
6		OMe	A		**22**	85	60/40
7		O*t*Bu	B		**23**	55	68/32
8		O*t*Bu	C		**23**	65	65/35
9		OMe	A		**24**	77	90/10
10		O*t*Bu	B		**25**	43	94/6
11		CF_3	B		**26**	49	100/0
12		OMe	A		**27**	79	13/87
13		OBn	B		**28**	52	0/100[d]
14		O*t*Bu	B		**29**	48	0/100[d]
15		CF_3	B		**30**	[e]	[e]

[a] Method A: protected β-amino alcohols and **1** were placed in toluene or in cyclohexane in the presence of PTSA (5% mol) and heated at reflux over 18 h. Method B: reaction carried out in the presence of H_2SO_4 adsorbed on activated molecular sieves in CH_2Cl_2 as solvent over 2 h at room temperature. Method C: reaction carried out in the presence of CSA (5 equiv.) in cyclohexane for 15 min at reflux. [b] Isolated yield (liquid chromatography) in %. [c] The identification of the *trans* and *cis* isomers was achieved by a detailed structural analysis.[44] The *trans* isomers are eluted on silica gel (eluent: hexanes/ethyl acetate, 95:5) before their *cis* isomer counterparts. The *trans*/*cis* nomenclature refers to the relative positions of the group on C^4 and the tributylstannyl group.[d] Despite complete *cis* selectivity, DFT calculations indicate a stabilisation of only 0.85 kcal·mol^{-1} between *cis* and *trans* isomers in these series (calculations done on Me_3Sn derivatives).[e] The mixed acetal **30** was obtained as a mixture of diastereomers, but the oxazolidine ring was not formed.



30 **31**

Scheme 8. Mixed acetals **30** and **31**

obtained with *N*-alkoxycarbonylated (*R*)-phenylglycinol and (*S*)-valinol (Entries 1−8, compounds **18−23**), with a preference for the *trans* isomers (*dr* = 72:28 to 60:40). A *trans* selectivity was also obtained for norpseudoephedrine derivatives (Entries 9−11, compounds **24−26**).

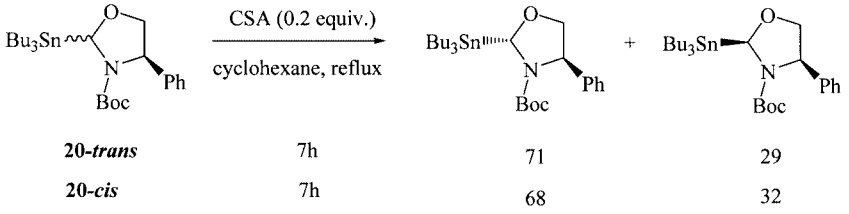
In order to determine the kinetic or thermodynamic natures of the products, the reaction corresponding to Entry 4 (Table 2) was monitored by HPLC; the evolution of the *trans*/*cis* ratio appeared to be stable over time and around 70:30 when a catalytic amount of CSA (0.5 equiv.) in cyclohexane was used. In another experiment, after separation by liquid chromatography, pure **20-*trans*** and pure **20-*cis*** were each heated at reflux in cyclohexane in the presence of CSA (0.2 equiv.) for 7 h, similar mixtures of isomers being obtained in both cases (Scheme 9).

On the basis of these results, even if slightly modulated by the concentration of the reagents, the solvent, or by the availability of the acid catalyst, the *trans*/*cis* ratios of the 4-substituted 2-tributylstannyl-1,3-oxazolidines obtained appear to be close to the thermodynamic mixtures, with a preference for the *trans* isomers (*trans*/*cis* ≈ 70:30), as opposed to the *N*-Ts series, in which the *cis* isomers were thermodynamically favoured. Furthermore, the isomerisation reaction appeared to proceed much more easily in the *N*-Boc series than in the *N*-Ts series. Concerning acid catalysis, it is worth noting that the reaction occurs much more rapidly when a trace amount of water remains in the solvent, which can be explained in terms of greater dissociation of the acid in this case (in comparison with a perfectly dried medium, which prevents efficient dissociation of the acid catalyst).

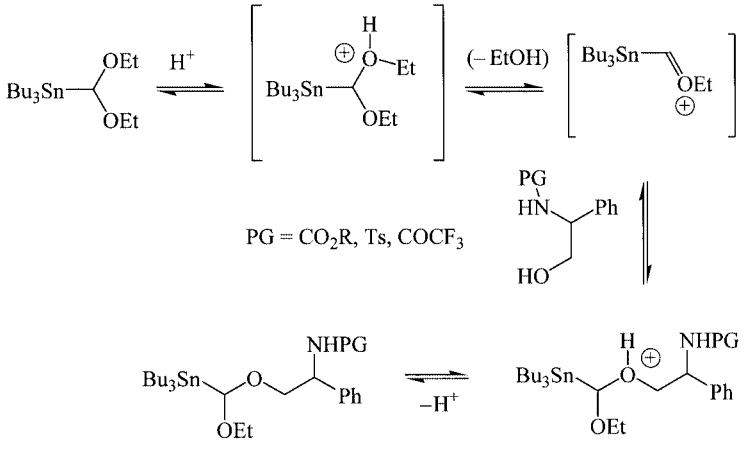
Discussion

The isolation of the trifluoroacetamide derivative **30** or the monoexchanged (*R*)-*N*-Boc-phenylglycinol derivative **31** is consistent with a true transacetalisation reaction (exchange of an ethoxy group of (diethoxymethyltributyl)stannane with the alcohol function of the amino alcohol unit) in the first step of the reaction. The obtaining of this intermediate compound in transacetalisation reactions was previously mentioned by Scolastico.[49] Accordingly, the first step of the reaction mechanism can be seen as an S_N1 substitution occurring on the α-stannyloxonium cation (Scheme 10) even if an S_N2 mechanism on the protonated acetal might also warrant consideration.

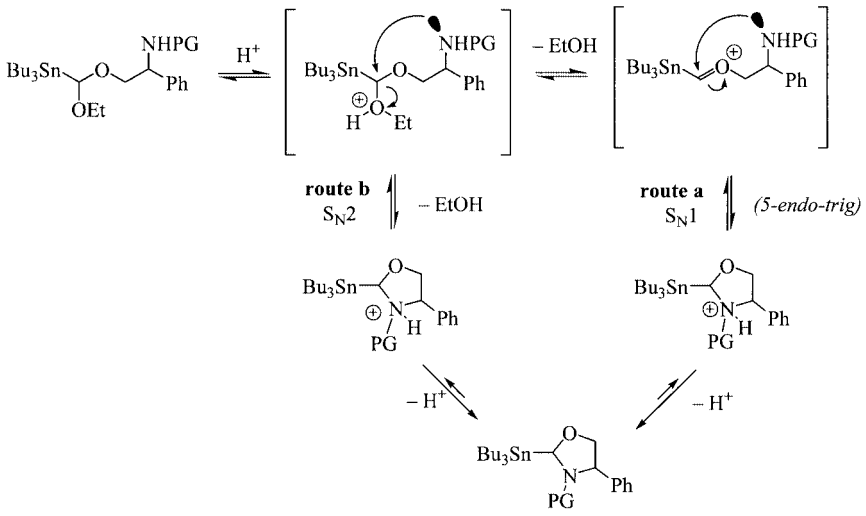
We have never observed such an intermediate in the *N*-Ts series, probably due to the higher acidity of the remaining N−H function (in relation to NH−CO_2R compounds), which, in association with the favourable entropy factor, allows for easier closure of the oxazolidine ring (easier expul-



Scheme 9. Isomerisation of (4*R*)-3-(*tert*-butoxycarbonyl)-4-phenyl-2-tributylstannyl-1,3-oxazolidines



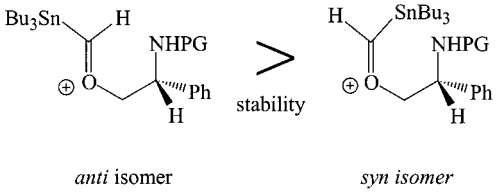
Scheme 10. First step of the mechanism of the transacetalisation reaction



Scheme 11. Second step of the mechanism of the transacetalisation reaction

sion of the remaining hydrogen). Although theoretically unfavourable,[50] this cyclisation through a 5-*endo*-*trig* closure in oxazolidine syntheses has been widely described in the literature[51] and may be involved (route a), as well as the S_N2 reaction, with the protonated acetal (route b), as shown in Scheme 11.

As far as kinetic stereochemical preference observed in the phenylglycinol series are concerned, the fact that *trans* isomers are usually obtained first with *N*-Ts derivatives and probably with *N*-alkoxycarbonyl derivatives can be explained by consideration of the more stable geometry of the oxonium intermediate (much less steric hindrance in the *anti* isomer than in the *syn* isomer) (Scheme 12). From DFT calculations performed on trimethylstannyl *N*-Boc-valinol derivatives, the *anti* oxonium ion was shown to be stabilised by 2.79 kcal·mol^{-1} relative to its *syn* isomer.

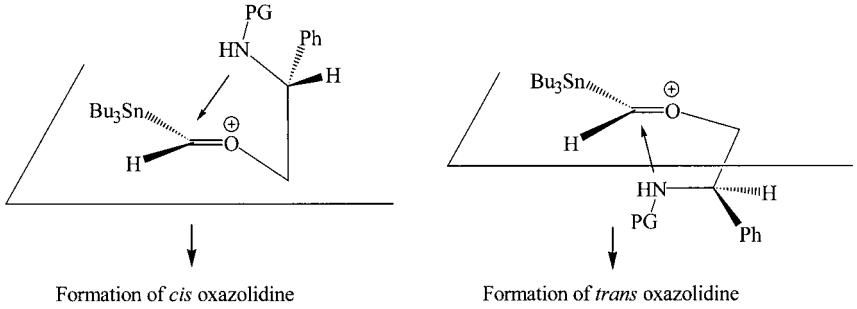


Scheme 12. Conformations of the oxonium intermediates

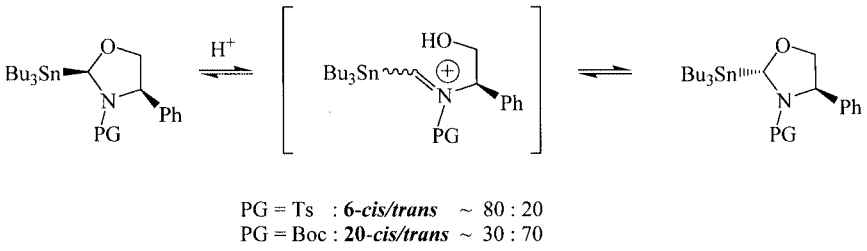
Subsequently, the nucleophilic attack on the carbon of the oxonium species of the *anti* isomer should occur in a conformation suitable for minimising the compression effect between tributylstannyl and phenyl groups (Scheme 13).

As shown in Scheme 13, the tributylstannyl and phenyl groups appear to be remote from one another in the transition state giving the *trans* oxazolidine, while an increased compression effect would be expected in the cyclisation giving the *cis* oxazolidine. The obtained results under kinetic control can be explained accordingly. By such an explanation, we would consider kinetic selectivity driven by the ring closure of an iminium intermediate highly improbable because the obtaining of the mixed acetal **31** (observed with the use of a catalytic amount of CSA under experimental conditions allowing elimination of ethanol by azeotropic distillation) can be reasonably justified only from the oxonium intermediate.

With regard to the *cis*-*trans* isomerisation of 2-tributylstannyl-1,3-oxazolidines under acidic conditions, further considerations must be taken into account. In *N*-Boc compounds, the reaction mixture remains close to the kinetic product of the reaction, since the *trans*-2-tributylstannyl-1,3-oxazolidine appears to be more stable than the *cis* isomer, probably due in part to stronger chelation in the *trans*



Scheme 13. Formation of *cis*- and *trans*-2-tributylstannyl-1,3-oxazolidines from the *anti* oxonium species



Scheme 14. Isomerisation of (4*R*)-*cis* and (4*R*)-*trans* 3-protected 4-phenyl-2-tributylstannyl-1,3-oxazolidines

diastereomer. Such an assumption was corroborated both by the radiocrystallographic structures obtained for triphenylstannyl *N*-Boc valinol derivatives (2.76 Å bond length between tin and carbonyl oxygen in the *trans* isomer against 3.34 Å in the *cis* isomer) and by DFT calculations performed for trimethylstannyl *N*-Boc valinol derivatives (O→Sn = 2.90 Å in the *trans* isomer and 3.32 Å in the *cis* isomer).[44]

In the *N*-Ts compounds, the *cis* isomer appears to be the more stable isomer (major isomer after isomerisation) probably due to a conformation that simultaneously minimises the steric interactions between the tosyl group and both the tributylstannyl group and the substituent on the 4-position (cf. structural analysis given in the accompanying paper[44]).

The isomerisation of *cis*- and *trans*-2-tributylstannyl-1,3-oxazolidines can be interpreted in terms of reversible formation of an iminium cation under protonolysis, as illustrated by the isomerisation of (*R*)-phenylglycinol-derived oxazolidines (Scheme 14).

DFT calculations performed for protonation of the *cis*-3-(*tert*-butoxycarbonyl)-2-(trimethylstannyl)-1,3-oxazolidine derived from (*S*)-valinol demonstrate significant stabilisation of the iminium intermediates: 18.2 kcal·mol^{-1} when the trimethylstannyl group is *syn* relative to the carbamate and 16.3 kcal·mol^{-1} in the case of an *anti* relationship. The chelation occurring between oxygen and tin results in a bond length of 2.88 Å between these two elements in the iminium species, which appear to be about 10 kcal·mol^{-1} more stable than the oxonium species formed in the first step of the transacetalisation reaction.

Accordingly, the overall qualitative energetic profile for these transacetalisation and isomerisation reactions can be presented as shown in Figure 1 and Figure 2.

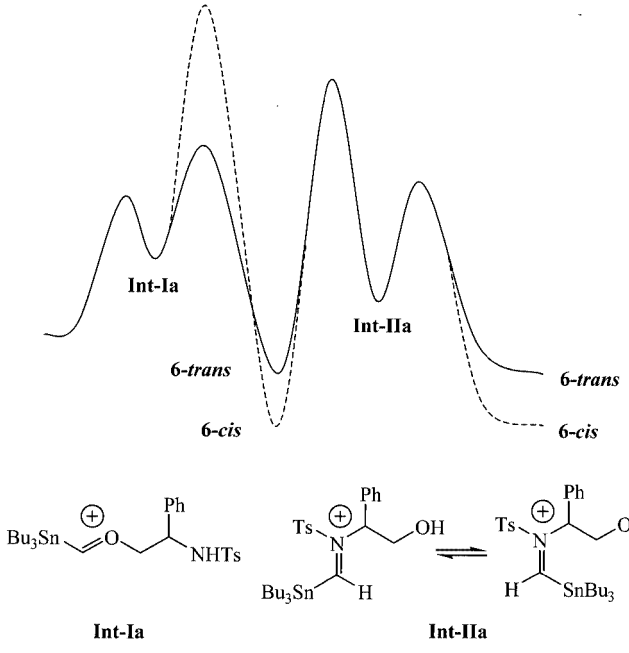


Figure 1. Simplified qualitative energetic profile for the formation and isomerisation of *cis* and *trans* isomers of 4-phenyl-3-tosyl-2-tributylstannyl-1,3-oxazolidine (**6**)

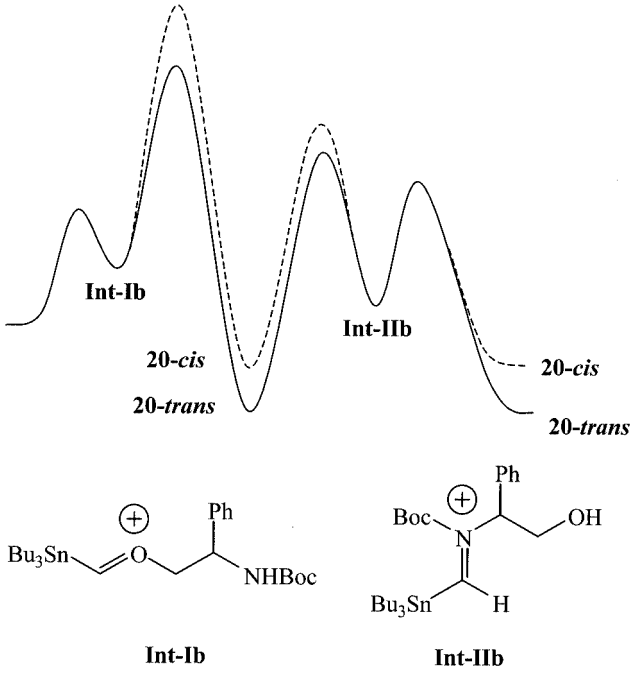


Figure 2. Simplified qualitative energetic profile for the formation and isomerisation of the *cis* and *trans* isomers of (4*R*)-3-(*tert*-butoxycarbonyl)-4-phenyl-2-tributylstannyl-1,3-oxazolidine (**20**)

In the *N*-Ts series (Figure 1), the transition state leading to the *cis* isomer from **Int-Ia** is higher in energy than that affording the *trans* isomer, and subsequent isomerisation of the adduct through **Int-IIa** appears to be less easy than the formation of the *trans* oxazolidine. On the other hand, while the formation of **20-*trans*** from **Int-Ib** (Figure 2) appears to be easier than the formation of **20-*cis*,** subsequent isomerisation of **20-*cis*** into **20-*trans*** through **Int-IIb** requires much less energy than needed to obtain the 3-(*tert*-

butoxycarbonyl)-2-tributylstannyl-1,3-oxazolidine from **Int Ib**.

In order to simplify Figure 2, the iminium intermediate **IIb** was shown in its more stable geometry (Bu_3Sn and Boc with a *syn* relationship). Subsequent recyclisation affording **20-*cis*** and **20-*trans*** is the result of a suprafacial or an antarafacial approach, respectively, of the hydroxy group.

For preparative purposes it is worth noting that a diastereoselective synthesis of stannylated β-amino alcohols from these *N*-protected 2-tributylstannyl-1,3-oxazolidines by use of organocopper reagents in the presence of boron trifluoride has been shown to be possible.[43] Using appropriate protection, these types of reagents should constitute interesting chiral α-amino stannylated species, a class of compounds that has recently received special attention[52,53] as possible precursors of chiral α-aminoorganolithium reagents through transmetallation reactions.[43,44] The expected advantage over the deprotonation reaction in the presence of the available (−)-sparteine[26,30,54−56] or the less readily available (+)-sparteine[31] and its surrogate cytisine derivative[32] should be a stereospecific transmetallation instead of a stereoselective deprotonation, allowing access to enantioenriched chiral α-amino anions not associated as diamine complexes.

Conclusion

A comprehensive study of the synthesis of *N*-protected 2-tributylstannyl-1,3-oxazolidines from (diethoxymethyl)tributylstannane, focussing mainly on chiral β-amino alcohol-derived oxazolidines, is described. These compounds were obtained in good yields as mixtures of *cis* and *trans* isomers through transacetalisation reactions. The stereoselectivity of the transacetalisation is discussed after consideration of the relative stabilities of the *cis* and *trans* isomers in the *N*-Ts and *N*-CO_2R series. In the first case (*N*-Ts derivatives), for 4-substituted-2-tributylstannyl-1,3-oxazolidines the *trans* diastereomer appears to be the kinetic compound and the *cis* diastereomer the thermodynamic one, while in the *N*-CO_2R derivatives the *trans* isomer appears to be both kinetically and thermodynamically favoured. Consideration of the interactions involved in the possible intermediates leading to transacetalisation and to isomerisation of the oxazolidines has allowed a preliminary explanation of the obtained results.

Experimental Section

General Remarks: ^{1}H, ^{13}C and ^{119}Sn spectra were recorded with Bruker AC 200, Bruker Avance 300 or Bruker ARX 400 spectrometers. Chemical shifts are given in ppm as δ values relative to tetramethylsilane (^{1}H, ^{13}C) or tetramethylstannane (^{119}Sn), and coupling constants are given in Hz. Mass spectra were obtained in EI mode (70 eV) with a HP apparatus (5989A) in direct introduction mode. Organostannyl fragments are given for ^{120}Sn, which means that the given abundances are broadly one third of the overall abundances of the organostannyl fragments relative to organic ones. HRMS were recorded at the CRUS in Rouen (Centre Régional Universitaire de Spectroscopie de l'Université de Rouen). IR spectra were recorded with a Bruker IFS Vector 22 apparatus. Optical rotations were measured with a Perkin−Elmer 341 apparatus. Elemental analyses were performed by the CNRS microanalysis centre (Vernaison). Diethyl ether and THF were distilled from sodium-benzophenone prior to use. Liquid chromatography separations were carried out on Merck silica gel (Geduran Si 60, 40−63 mesh), TLC analyses on silica-coated plates (Merck Kieselgel $60F_{254}$) and HPLC analyses with a Chrompack column (Chromsep Inertsil 5 Si, 250 × 3 mm) with a HPLC chromatograph (HP series 1100), with UV detection at 254 nm. Of the starting materials, the amino alcohols or diamines [(*R*)- and (*S*)-phenylglycinol, norephedrine, norpseudoephedrine, (*R*)- and (*S*)-valinol, 3-aminopropanol, 2-aminoethanol, 1,2-diaminoethane] used in this work were purchased from commercial sources. They were modified into *N*-protected species by use of mesyl chloride, tosyl chloride, methyl, allyl and benzyl chloroformates or diethyl pyrocarbonate by previously described procedures.[47−49] For organometallic starting materials, (diethoxymethyl)tributylstannane (**1**) was obtained by treatment of (tributylstannyl)magnesium chloride with diethylphenylorthoformate as previously.[3,5] The tributyltin hydride allowing the synthesis of the stannylmagnesium reagent was a Crompton GmbH product.

Preparation of 3-Tosyl- and 3-Mesyl-2-(tributylstannyl)oxazolidines and Related Compounds 3−12: *N*-Sulfonylated amino alcohol (or diamine) (2.2 mmol) and PTSA (20 mg) in toluene or cyclohexane (150 mL) were placed successively in a 250 mL round-bottomed flask fitted with a Dean-Stark apparatus. The reaction mixture was warmed until reflux over 5 h in order to remove traces of water. After the mixture had been cooled to room temperature, (diethoxymethyl)tributylstannane (**1**, 0.8 g, 2 mmol) was added, and the reaction mixture was heated at reflux for about 18 h in order to effect azeotropic distillation of ethanol and complete conversion of **1** (the evolution of the reaction was monitored by TLC, eluent: hexanes/ethyl acetate, 95:5). At the end of the reaction, the solution was filtered at room temperature through neutral alumina with diethyl ether as eluent. The organostannane compounds were concentrated by evaporation of the solvents. The obtained residue was chromatographed on silica gel (eluent: hexanes/ethyl acetate, 95:5), and the 2-stannylated heterocycles were isolated as pure compounds. Under such experimental conditions, when two diastereomers were possible, the *trans* isomer was eluted before the *cis* isomer. The obtained *N*-sulfonylated 2-tributylstannyl heterocycles were subsequently completely characterized by their physicochemical data, mainly on the basis of their NMR spectra as discussed in the accompanying paper.[44]

It is worth noting that residual traces of water strongly increase the isomerisation rate of the *trans* isomer into the *cis* isomer when 4-substituted 2-tributylstannyl-1,3-oxazolidines are involved.

Physicochemical Data for Compounds 3−12

3-Tosyl-2-tributylstannyl-1,3-oxazolidine (3): (89% Yield, 920 mg). ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.8−1.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 2.42 (s, 3 H, CH_3), 3.12−3.37 (m, 2 H, NCH_2), 3.4−3.57 (m, 1 H, OCH_2), 3.61−3.74 (m, 1 H, OCH_2), 5.36 [s, ^2J(Sn,H) = 48.5 Hz, 1 H, SnCH], 7.3 [d, ^3J(H,H) = 7.7 Hz, 2 H, C_6H_4], 7.72 [d, ^3J(H,H) = 7.7 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 9.9 [^1J(Sn,C) = 307−321 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.7 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 21.5 (1 C, CH_3), 27.4 [^3J(Sn,C) = 54.5−56.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.9 [^2J(Sn,C) = 20.2 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 46.9 [^3J(Sn,C) = 6.8 Hz, 1 C, NCH_2], 66.2

[^3J(Sn,C) = 14.5 Hz, 1 C, OCH_2], 89.7 [1 C, ^1J(Sn,C) = 390−408 Hz, SnCH], 127.8 (2 C, C_6H_4), 129.7 (2 C, C_6H_4), 134.1 (1 C, C_6H_4), 143.9 (1 C, C_6H_4) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −33.2 ppm. IR: ṽ = 1605, 1470, 1355, 1170, 1100, 825, 680 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 460 (8), 389 (7), 325 (10), 291 (6), 269 (6), 235 (8), 211 (8), 179 (17), 121 (17); organic fragments: *m*/*z* (%) = 226 (100), 155 (43), 91 (47), 65 (10), 41 (8), 29 (6). $C_{22}H_{39}NO_3SSn$ (516.3): calcd. C 51.18, H 7.61, N 2.71, S 6.21; found C 51.39, H 7.66, N 2.87, S 6.05.

3-Tosyl-2-tributylstannyl-1,3-perhydroxazine (4): (82% Yield, 870 mg). ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.85−1.8 [m, 29 H, $(CH_3CH_2CH_2CH_2)_3Sn$, CH_2], 2.42 (s, 3 H, CH_3), 3.42 (m, 1 H, NCH_2), 3.57 (m, 1 H, NCH_2), 3.73 (m, 2 H, OCH_2), 5.66 [s, ^2J(Sn,H) = 20.5 Hz, 1 H, SnCH], 7.28 [d, ^3J(H,H) = 8 Hz, 2 H, C_6H_4], 7.82 [d, ^3J(H,H) = 8 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 11.2 [^1J(Sn,C) = 308−322 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.6 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 21.4 (C, CH_3), 22.5 (C, CH_2), 27.3 [^3J(Sn,C) = 58.6 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.8 [^2J(Sn,C) = 20.5 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 44.9 [^3J(Sn,C) = 7 Hz, 1 C, NCH_2], 68 [^3J(Sn,C) = 23 Hz, 1 C, OCH_2], 86.9 [^1J(Sn,C) = 372−391 Hz, 1 C, SnCH], 127.8 (2 C, C_6H_4), 129.5 (2 C, C_6H_4), 138.4 (1 C, C_6H_4), 143.1 (1 C, C_6H_4) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −37.1 ppm. IR: ṽ = 1605, 1470, 1380, 1350, 1340, 1250, 1165, 1010, 960, 880, 820, 760, 690, 675 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 474 (4), 389 (19), 376 (1), 325 (3), 291 (1), 265 (1), 235 (2), 213 (5), 177 (7), 121 (6); organic fragments: *m*/*z* (%) = 240 (100), 155 (19), 91 (24), 65 (3), 57 (2), 41 (4), 29 (6). $C_{23}H_{41}NO_3SSn$ (530.4): calcd. C 52.09, H 7.79, N 2.64; found C 52.48, H 7.88, N 2.85.

1,3-Bis(tosyl)-2-(tributylstannyl)imidazolidine (5): (57% Yield, 760 mg). ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.77−1.7 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 2.33 (s, 2 × 3 H, CH_3), 2.97 and 3.2 (m, 4 H, CH_2CH_2), 5.08 [s, ^2J(Sn,H) = 26.5 Hz, 1 H, SnCH], 7.05 [d, ^3J(H,H) = 8.5 Hz, 2 H, C_6H_4], 7.35 [d, ^3J(H,H) = 8.5 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 10.6 [^1J(Sn,C) = 309−323 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.8 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 21.6 (2 C, CH_3), 27.4 [^3J(Sn,C) = 56.8−59.1 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.9 [^2J(Sn,C) = 19.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 46.7 (2 C, CH_2CH_2), 67.8 [^1J(Sn,C) = 371−388 Hz, 1 C, SnCH], 127.5 (4 C, C_6H_4), 129.6 (4 C, C_6H_4), 133.8 (2 C, C_6H_4), 143.6 (2 C, C_6H_4) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −7.9 ppm. IR: ṽ = 1598, 1465, 1351, 1160, 1089, 1036, 838, 815, 724 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 613 (3), 515 (15), 389 (10), 325 (18), 291 (8), 269 (4), 235 (19), 211 (14), 179 (24), 121 (9); organic fragments: *m*/*z* (%) = 379 (88), 224 (10), 183 (4), 155 (39), 139 (5), 91 (100), 69 (14), 65 (18), 42 (12), 39 (10). $C_{29}H_{46}N_2O_4S_2Sn$ (669.5): calcd. C 52.02, H 6.93, N 4.18; found C 52.09, H 7.18, N 3.91.

(4*R*)-4-Phenyl-3-tosyl-2-tributylstannyl-1,3-oxazolidine (6): (89% Yield, 1.055 g, *trans*/*cis* = 24:76). IR: ṽ = 1596, 1492, 1461, 1452, 1375, 1342, 1302, 1287, 1157, 1090, 960, 927, 865, 812, 756, 700, 670 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 536 (4), 389 (8), 325 (15), 269 (12), 235 (7), 211 (18), 177 (18), 119 (15); organic fragments: *m*/*z* (%) = 302 (100), 274 (15), 155 (45), 91 (67), 69 (11), 57 (17), 55 (14), 43 (20), 41 (17), 29 (13). $C_{28}H_{43}NO_3SSn$ (592.4): calcd. C 56.77, H 7.32, N 2.36; found C 56.46, H 7.36, N 2.22.

Isomer 6-*trans*: ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.7−1.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 2.35 (s, 3 H, CH_3), 3.69 [dd, ^3J(H,H) = 6, ^2J(H,H) = 8.3 Hz, 1 H, OCH_2], 4.37 [dd, ^2J(H,H) = 8.3, ^3J(H,H) = 7.3 Hz, 1 H, OCH_2], 4.83 [s, ^2J(Sn,H) = 27.6 Hz, 1 H, SnCH], 4.85 [dd, ^3J(H,H) = 6, ^3J(H,H) = 7.3 Hz, 1 H, NCH], 6.95−7.25 (m, 7 H, C_6H_4, C_6H_5), 7.5 [d, ^3J(H,H) = 8.5 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 11.6 [^1J(Sn,C) = 330−346 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.9 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 21.5 (1 C, CH_3), 27.6 [^3J(Sn,C) = 59 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.1 [^2J(Sn,C) = 16.9 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 62.1 [^3J(Sn,C) = 10.5 Hz, 1 C, NCH], 75.8 [^3J(Sn,C) = 33.8 Hz, 1 C, OCH_2], 89.5 [^1J(Sn,C) = 308−323 Hz, 1 C, SnCH], 126.8 (2 C, Ar), 127.6 (1 C, Ar), 127.8 (2 C, Ar), 128.5 (2 C, Ar), 129.3 (2 C, Ar), 136.9 (1 C, Ar), 139.5 (1 C, Ar), 143.3 (1 C, Ar) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −36.8 ppm. $[\alpha]_D^{19}$ = −96.6 (*c* = 0.8 in $CHCl_3$).

Isomer 6-*cis*: ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.7−1.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 2.45 (s, 3 H, CH_3), 3.50 [dd, ^2J(H,H) = 8.6, ^3J(H,H) = 6.6 Hz, 1 H, OCH_2], 3.9 [dd, ^3J(H,H) = 3.2, ^2J(H,H) = 8.6 Hz, 1 H, OCH_2], 4.62 [dd, ^3J(H,H) = 3.2, ^3J(H,H) = 6.6 Hz, 1 H, NCH], 5.26 [s, ^2J(Sn,H) = 57.2 Hz, 1 H, SnCH], 7.2−7.5 (m, 7 H, C_6H_5, C_6H_4), 7.75 [d, ^3J(H,H) = 8.4 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 10.6 [^1J(Sn,C) = 311−325 Hz, 3 C, $CH_3CH_2CH_2CH_2)_3Sn$], 13.8 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 21.7 (1 C, CH_3), 27.5 [^3J(Sn,C) = 57.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.1 [^2J(Sn,C) = 19.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 61.5 [^3J(Sn,C) = 7.2 Hz, 1 C, NCH], 74.9 [^3J(Sn,C) = 21.9 Hz, 1 C, OCH_2], 91.5 [^1J(Sn,C) = 380−402 Hz, 1 C, SnCH], 126.9 (2 C, Ar), 127.8 (1 C, Ar), 128.3 (2 C, Ar), 128.6 (2 C, Ar), 129.9 (2 C, Ar), 133.7 (1 C, Ar), 140.3 (1 C, Ar), 144.1 (1 C, Ar) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −34.8 ppm. $[\alpha]_D^{19}$ = +30.7 (*c* = 0.91 in $CHCl_3$).

(4*R*)-3-Mesyl-4-phenyl-2-tributylstannyl-1,3-oxazolidine (7): (77% Yield, 795 mg, *trans*/*cis* = 25:75). IR: ṽ = 1499, 1468, 1457, 1339, 1153, 1077, 758, 699 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 460 (15), 438 (3), 313 (17), 291 (8), 235 (15), 177 (23), 121 (15); organic fragments: *m*/*z* (%) = 226 (100), 119 (36), 103 (13), 91 (10), 79 (6), 57 (3), 41 (6), 29 (8). HRMS (CI, isobutane): calcd. for $C_{22}H_{40}NO_3SSn$ [M + H^+] (518.1750), found (518.1755).

Isomer 7-*trans*: ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.85−1.75 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 2.75 (s, 3 H, CH_3), 3.69 [dd, ^3J(H,H) = 6.5, ^2J(H,H) = 8.4 Hz, 1 H, OCH_2], 4.59 [s, ^2J(Sn,H) = 14.6 Hz, 1 H, SnCH], 4.58 [dd, ^3J(H,H) = 7.6, ^2J(H,H) = 8.4 Hz, 1 H, OCH_2], 5.03 [dd, ^3J(H,H) = 6.6, ^3J(H,H) = 7.6 Hz, 1 H, NCH], 7.35 (m, 5 H, C_6H_5) ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 11.2 [^1J(Sn,C) = 333−349 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.6 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 27.3 [^3J(Sn,C) = 59.5 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.8 [^2J(Sn,C) = 19.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 38.7 (1 C, CH_3), 61.85 [^3J(Sn,C) = 12.6 Hz, 1 C, NCH], 75.5 [^3J(Sn,C) = 34.3 Hz, 1 C, OCH_2], 89.0 [^1J(Sn,C) = 284−298 Hz, 1 C, SnCH], 126.2 (2 C, C_6H_5), 127.8 (1 C, C_6H_5), 128.9 (2 C, C_6H_5), 139.6 (1 C, C_6H_5) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −37.1 ppm. $[\alpha]_D^{19}$ = −53.1 (*c* = 0.64 in $CHCl_3$).

Isomer 7-*cis*: ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.75−1.5 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 2.75 (s, 3 H, CH_3), 3.93 [dd, ^3J(H,H) = 4.1, ^2J(H,H) = 8.7 Hz, 1 H, OCH_2], 4.18 [dd, ^2J(H,H) = 8.7, ^3J(H,H) = 7.3 Hz, 1 H, OCH_2], 4.72 [dd, ^3J(H,H) = 7.3, ^3J(H,H) = 4.1 Hz, 1 H, NCH], 5.38 [s, ^2J(Sn,H) = 50.6 Hz, 1 H, SnCH], 7.3 (m, 5 H, C_6H_5) ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 10.1 [^1J(Sn,C) = 311−325 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.8 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 27.5 [^2J(Sn,C) = 59.7 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.9 [^3J(Sn,C) = 20.2 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 36.5 (1 C, CH_3), 61.4 [^3J(Sn,C) = 7.6 Hz, 1 C, NCH], 75.8 [^3J(Sn,C) = 21.3 Hz, 1 C, OCH_2], 91.4

[^1J(Sn,C) = 375−392 Hz, 1 C, SnCH], 126.7 (2 C, C_6H_4), 127.6 (1 C, C_6H_4), 128.8 (2 C, C_6H_4), 140.1 (1 C, C_6H_4) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −32.1 ppm. $[\alpha]_D^{19}$ = +5.4 (*c* = 0.73 in $CHCl_3$).

(4*S*)-4-Methyl-3-tosyl-2-tributylstannyl-1,3-oxazolidine (8): (80% Yield, 850 mg, *trans*/*cis* = 17:83). The NMR spectroscopic data were recorded for the mixture of the two diastereomers because of the difficulty involved in their separation by liquid chromatography.

Isomer 8-*cis*: ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.8−1.6 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.2 [d, ^3J(H,H) = 6.4 Hz, 3 H, CHCH_3], 2.35 (s, 3 H, CH_3), 3.17 [dd, ^3J(H,H) = 6.3, ^2J(H,H) = 8.4 Hz, 1 H, OCH_2], 3.38 [dd, ^2J(H,H) = 8.4, ^3J(H,H) = 3.4 Hz, 1 H, OCH_2], 3.57 (m, 1 H, NCH), 5.0 [s, ^2J(Sn,H) = 62.5 Hz, 1 H, SnCH], 7.2 [d, ^3J(H,H) = 8 Hz, 2 H, C_6H_4], 7.6 [d, ^3J(H,H) = 8 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 9.8 [^1J(Sn,C) = 311−325 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.6 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 20.5 (1 C, CHCH_3), 21.4 (1 C, CH_3), 27.3 [^3J(Sn,C) = 56 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.9 [^2J(Sn,C) = 20.2 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 54.4 (1 C, NCH), 74.1 [^3J(Sn,C) = 21.3 Hz, 1 C, OCH_2], 90.5 [^1J(Sn,C) = 397−416 Hz, 1 C, SnCH], 127.8 (2 C, C_6H_4), 129.6 (2 C, C_6H_4), 133.4 (1 C, C_6H_4), 143.6 (1 C, C_6H_4) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −33.2 ppm.

Observable Data for the Minor Isomer 8-*trans*: ^{1}H NMR ($CDCl_3$, 300 K): δ = 2.33 (s, 3 H, CH_3), 3.12 [dd, ^3J(H,H) = 5.6, ^2J(H,H) = 7.8 Hz, 1 H, OCH_2], 3.56 (m, 1 H, NCH), 4.52 [s, ^2J(Sn,H) = 18.3 Hz, 1 H, SnCH], 7.18 [d, ^3J(H,H) = 8 Hz, 2 H, C_6H_4], 7.65 [d, ^3J(H,H) = 8 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 11.3 [^1J(Sn,C) = 332−349 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.5 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 19.0 (1 C), 21.3 (1 C), 27.7 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 54.4 (1 C, NCH), 74.4 [^3J(Sn,C) = 34 Hz, 1 C, OCH_2], 86 (1 C, SnCH), 127.7 (2 C, C_6H_4), 129.4 (2 C, C_6H_4), 137 (1 C, C_6H_4), 143.4 (1 C, C_6H_4) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −38.3 ppm.

(4*S*)-4-Isopropyl-3-tosyl-2-tributylstannyl-1,3-oxazolidine (9): (93% Yield, 1.040 g, *trans*/*cis* = 18:82). IR: ṽ = 1599, 1465, 1349, 1161, 668, 583, 547 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 502 (8), 404 (1), 389 (7), 325 (12), 291 (2), 235 (5), 177 (18), 121 (9), 269 (23), 211 (16); organic fragments: *m*/*z* (%) = 268 (100), 211 (16), 155 (29), 91 (33), 69 (9), 41 (9), 29 (9). $C_{25}H_{45}NO_3SSn$ (558.4): calcd. C 53.77, H 8.12, N 2.51; found C 53.85, H 8.24, N 2.78.

Isomer 9-*trans*: ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.78 [d, ^3J(H,H) = 6.7 Hz, 6 H, CH(CH_3)$_2$], 0.85−1.75 [m, 28 H, $(CH_3CH_2CH_2CH_2)_3Sn$, CH(CH$_3$)$_2$], 2.42 (s, 3 H, CH_3), 3.4 (m, 2 H, OCH_2), 3.75 (m, 1 H, NCH), 4.38 [s, ^2J(Sn,H) = 9.6 Hz, 1 H, SnCH], 7.3 [d, ^3J(H,H) = 7.8 Hz, 2 H, C_6H_4], 7.75 [d, ^3J(H,H) = 7.8 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 12.0 [^1J(Sn,C) = 335−350 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.0 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 18.2 [1 C, CH(CH_3)$_2$], 20.0 [1 C, CH(CH_3)$_2$], 21.8 (1 C, CH_3), 27.7 [^3J(Sn,C) = 59.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.3 [^2J(Sn,C) = 19.1 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 31.5 [1 C, CH(CH$_3$)$_2$], 64.6 (1 C, NCH), 69.4 [^3J(Sn,C) = 35 Hz, 1 C, OCH_2], 87.4 [^1J(Sn,C) = 310−323 Hz, 1 C, SnCH], 128.6 (2 C, C_6H_4), 129.7 (2 C, C_6H_4), 136.8 (1 C, C_6H_4), 143.9 (1 C, C_6H_4) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −40.0 ppm.

Isomer 9-*cis*: ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.7−1.6 [m, 33 H, $(CH_3CH_2CH_2CH_2)_3Sn$, CH(CH_3)$_2$], 1.75 [m, CH(CH$_3$)$_2$], 2.35 (s, 3 H, CH_3), 2.8 [dd, ^3J(H,H) = 6.4, ^2J(H,H) = 8.6 Hz, 1 H, OCH_2], 3.25 (m, 1 H, NCH), 3.65 [dd, ^2J(H,H) = 8.6, ^3J(H,H) = 1.5 Hz, 1 H, OCH_2], 4.9 [s, ^2J(Sn,H) = 59.8 Hz, 1 H, SnCH], 7.2 [d, ^3J(H,H) = 8.3 Hz, 2 H, C_6H_4], 7.6 [d, ^3J(H,H) = 8.3 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 9.6 [^1J(Sn,C) = 312−326 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.5 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 18.1 [1 C, CH(CH_3)$_2$], 19.8 [1 C, CH(CH_3)$_2$], 21.3 (1 C, CH_3), 27.2 [^3J(Sn,C) = 57.2 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.8 [^2J(Sn,C) = 19.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 31.1 [1 C, CH(CH$_3$)$_2$], 64.3 [^3J(Sn,C) = 8.4 Hz, 1 C, NCH], 69.5 [^3J(Sn,C) = 23.6 Hz, 1 C, SnCH], 90.5 [^1J(Sn,C) = 400−418 Hz, 1 C, SnCH], 127.9 (2 C, C_6H_4), 129.5 (2 C, C_6H_4), 133.3 (1 C, C_6H_4), 143.5 (1 C, C_6H_4) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −32.2 ppm. $[\alpha]_D^{19}$ = −109.1 (*c* = 0.88 in $CHCl_3$).

(5*R*)-5-Methyl-3-tosyl-2-tributylstannyl-1,3-oxazolidine (10): (78% yield, 825 mg, *trans*/*cis* = 35:65). The data were recorded for the mixture of the two diastereomers because of the difficulty involved in their separation by liquid chromatography. IR: ṽ = 1595, 1490, 1344, 1160, 815, 670 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 474 (2), 389 (5), 325 (9), 291 (3), 269 (8), 211 (11), 179 (13), 177 (14), 121 (12); organic fragments: *m*/*z* (%) = 240 (100), 155 (35), 91 (47), 65 (10), 57 (4), 42 (30), 29 (18).

Isomer 10-*trans*: ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.85−1.7 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.14 [d, ^3J(H,H) = 5.9 Hz, 3 H, CHCH_3], 2.33 (s, 3 H, CH_3), 2.73 [dd, ^3J(H,H) = 7.4, ^2J(H,H) = 10.5 Hz, 1 H, NCH_2], 3.37 [dd, ^3J(H,H) = 6.5, ^2J(H,H) = 10.5 Hz, 1 H, NCH_2], 3.86 (m, 1 H, OCH), 5.61 [s, ^2J(Sn,H) = 44.6 Hz, 1 H, SnCH], 7.22 [d, ^3J(H,H) = 7.9 Hz, 2 H, C_6H_4], 7.65 [d, ^3J(H,H) = 7.9 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 10.4 [^1J(Sn,C) = 300−314 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.0 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 18.6 (1 C, CHCH_3), 21.8 (1 C, CH_3), 27.7 [^3J(Sn,C) = 55 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.3 [^2J(Sn,C) = 19.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 52.9 (1 C, NCH_2), 74.3 [^3J(Sn,C) = 10.3 Hz, 1 C, OCH], 89.9 [^2J(Sn,C) = 394−413 Hz, 1 C, SnCH], 128.3 (2 C, C_6H_4), 129.9 (2 C, C_6H_4), 134.3 (1 C, C_6H_4), 144.1 (1 C, C_6H_4) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −33.4 ppm.

Isomer 10-*cis*: ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.85−1.7 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.05 [d, ^3J(H,H) = 7.6 Hz, 3 H, CHCH_3], 2.33 (s, 3 H, CH_3), 2.7 [dd, ^3J(H,H) = 9.4, ^2J(H,H) = 11 Hz, 1 H, NCH_2], 3.06 (m, 1 H, OCH), 3.44 [dd, ^3J(H,H) = 5.7, ^2J(H,H) = 11 Hz, 1 H, NCH_2], 5.12 (s, ^2J(Sn,H) = 62−64 Hz, 1 H, SnCH], 7.22 [d, ^3J(H,H) = 7.9 Hz, 2 H, C_6H_4], 7.6 [d, ^3J(H,H) = 7.9 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 10.2 [^1J(Sn,C) = 313−327 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.1 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 17.9 (1 C, CHCH_3), 21.8 (1 C, CH_3), 27.7 [^3J(Sn,C) = 55 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.3 [^2J(Sn,C) = 19.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 53.4 [^3J(Sn,C) = 9 Hz, 1 C, NCH_2], 74.7 (^3J(Sn,C) = 20.2 Hz, 1 C, OCH], 90.1 (^2J(Sn,C) = 397−415 Hz, 1 C, SnCH], 128.1 (2 C, C_6H_4), 130.1 (2 C, C_6H_4), 134.3 (1 C, C_6H_4), 144.1 (1 C, C_6H_4) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −33.4 ppm.

(4*R*,5*R*)-4-Methyl-5-phenyl-3-tosyl-2-tributylstannyl-1,3-oxazolidine (11): (70% yield, 850 mg, *trans*/*cis* = 20:80). IR: ṽ = 1598, 1494, 1455, 1349, 1163, 1090, 814, 755, 699, 678 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 550 (4), 452 (1), 389 (9), 325 (12), 291 (6), 269 (6), 235 (4), 211 (8), 179 (8), 121 (4); organic fragments: *m*/*z* (%) = 316 (100), 288 (30), 161 (6), 155 (10), 133 (5), 91 (15), 55 (9), 41 (2), 29 (2). $C_{29}H_{45}NO_3SSn$ (606.4): calcd. C 57.43, H 7.48, N 2.31; found C 57.20, H 7.48, N 2.34.

Isomer 11-*trans*: ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.8−1.75 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.05 [d, ^3J(H,H) = 6.2 Hz, 3 H, CH_3CH], 2.42 (s, 3 H, CH_3), 3.66 [qd, ^3J(H,H) = 6.7, ^3J(H,H) =

6.2 Hz, 1 H, NCH], 4.24 [d, ^3J(H,H) = 6.7 Hz, 1 H, OCH], 4.82 [s, ^2J(Sn,H) = 17.2 Hz, 1 H, SnCH], 7.25 (m, 7 H, C_6H_5, C_6H_4), 7.7 [d, ^3J(H,H) = 8.3 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 12.1 [^1J(Sn,C) = 333−349 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.2 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 18.2 (1 C, CH_3CH), 21.9 (1 C, CH_3), 28.7 [^3J(Sn,C) = 59 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.5 [^2J(Sn,C) = 19.7 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 62.8 [^3J(Sn,C) = 11.4 Hz, 1 C, NCH], 87.3 [^1J(Sn,C) = 298−312 Hz, 1 C, SnCH], 91.1 [^3J(Sn,C) = 37.9 Hz, 1 C, OCH], 126.8 (2 C, Ar), 127.9 (2 C, Ar), 128.1 (1 C, Ar), 128.4 (2 C, Ar), 129.2 (2 C, Ar), 137.4 (1 C, Ar), 138.8 (1 C, Ar), 143.7 (1 C, Ar) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −36.7 ppm.

Isomer 11-*cis*: ^{1}H NMR($CDCl_3$, 300 K): δ = 0.85−2.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.45 [d, ^3J(H,H) = 6.3 Hz, 3 H, CH_3CH], 2.4 (s, 3 H, CH_3), 3.3 [qd, ^3J(H,H) = 6.3, ^3J(H,H) = 7.2 Hz, 1 H, NCH], 4.2 [d, ^3J(H,H) = 7.2 Hz, 1 H, OCH], 5.9 [s, ^2J(Sn,H) = 42.6 Hz, 1 H, SnCH], 6.7 (m, 2 H, Ar), 7.2 (m, 5 H, Ar), 7.7 (m, 2 H, Ar) ppm. ^{13}C NMR($CDCl_3$, 30 K): δ = 10.1 [^1J(Sn,C) = 297−312 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.7 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 18.4 (1 C, CH_3CH), 21.5 (1 C, CH_3), 27.4 [^3J(Sn,C) = 55.3 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.9 [^2J(Sn,C) = 20.2 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 62.0 (1 C, NCH), 87.7 (1 C, OCH), 90.7 [^1J(Sn,C) = 404−423 Hz, 1 C, SnCH], 126.2 (2 C, Ar), 128.1 (2 C, Ar), 128.3 (1 C, Ar), 128.5 (2 C, Ar), 129.7 (2 C, Ar), 133.5 (1 C, Ar), 137.4 (1 C, Ar), 143.8 (1 C, Ar) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −35.8 ppm.

(4*S*,5*R*)-4-Methyl-5-phenyl-3-tosyl-2-tributylstannyl-1,3-oxazolidine (12-*cis*):(72% Yield, 875 mg). IR: $\tilde{\nu}$ = 1598, 1497, 1465, 1349, 1162, 1114, 705 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 550 (2), 452 (3), 389 (9), 325 (9), 269 (4), 235 (5), 213 (3), 177 (12), 121 (9); organic fragments: *m*/*z* (%) = 316 (100), 288 (46), 161 (8), 155 (20), 133 (9), 91 (35), 65 (4), 55 (8), 41 (3), 29 (5). $C_{29}H_{45}NO_3SSn$ (606.4): calcd. C 57.43, H 7.48, N 2.31, S 5.29, Sn 19.57; found C 56.88, H 7.34, N 2.34, S 4.96, Sn 19.59. $[\alpha]_D^{19}$ = −73.5 (*c* = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.8 [d, ^3J(H,H) = 6.6 Hz, 3 H, CH_3CH), 0.8−1.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 2.4 (s, 3 H, CH_3), 3.82 [qd, ^3J(H,H) = 5.6, ^3J(H,H) = 6.6 Hz, 1 H, NCH], 3.93 [d, ^3J(H,H) = 5.6 Hz, 1 H, OCH], 5.03 [s, ^2J(Sn,H) = 66.7−69.4 Hz, 1 H, SnCH], 7−7.2 (m, 5 H, C_6H_5), 7.3 [d, ^3J(H,H) = 8.1 Hz, 2 H, C_6H_4], 7.8 [d, ^3J(H,H) = 8.1 Hz, 2 H, C_6H_4] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 9.9 [^1J(Sn,C) = 324−335 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.8 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 17.3 (1 C, $CHCH_3$), 21.5 (1 C, CH_3), 27.5 [^3J(Sn,C) = 51 Hz, [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.1 [^2J(Sn,C) = 20.5 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 57.8 [^3J(Sn,C) = 10.2 Hz, 1 C, NCH], 83.8 [^3J(Sn,C) = 25.6, 1 C, OCH], 89.4 [^1J(Sn,C) = 389−410 Hz, 1 C, SnCH], 126.1 (2 C, Ar), 127.7 (1 C, Ar), 127.9 (2 C, Ar), 128.3 (2 C, Ar), 129.9 (2 C, Ar), 133.6 (1 C, Ar), 136 (1 C, Ar), 143.9 (1 C, Ar) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −29.5 ppm.

Isomerisation of 6-*cis*/*trans*: The pure **6-*trans*** or **6-*cis*** isomers were isomerised under experimental conditions similar to those used for their preparation (cat. PTSA, toluene, reflux). The isomerisation reaction was monitored by HPLC. HPLC conditions: flow rate = 0.8 mL/min, eluent: hexanes/ethyl acetate, 95:5, sample concentration = 0.2 g/L. Retention time: 5.08 min (**6-*trans***), 7.54 min (**6-*cis***).

Preparation of 3-Alkoxycarbonyl-2-tributylstannyl-oxazolidines 13−29

The preparation of these compounds was achieved under three sets of experimental conditions, as shown in Table 2 (Method A, B or C).

Method A: The same experimental conditions as used for the preparation of 3-tosyl- and 3-mesyl-2-tributylstannyl-oxazolidines.

Method B: In a 100 mL flask, molecular sieves (4 Å, 10 g) were activated by warming under vacuum (0.1 Torr). After this system had been cooled to room temp. under argon, (diethoxymethyl)tributylstannane (**1**, 0.8 g, 2 mmol) and *N*-Boc-amino alcohol (2.5 mmol) in CH_2Cl_2 (70 mL) were added. The reaction mixture was degassed before addition of sulfuric acid (0.5 mL) and subsequently stirred at room temperature for 2 h prior to neutralisation with K_2CO_3. The mixture was filtered at room temperature through neutral alumina with diethyl ether as eluent, concentrated by evaporation and chromatographed on silica gel (eluent: hexanes/diethyl ether/Et_3N, 95:3:2).

Method C: Camphorsulfonic acid (2.3 g, 10 mmol) in cyclohexane (50 mL) was heated at reflux for 2 h in a 100 mL flask equipped with a Dean−Stark apparatus. After the solution had been cooled to room temperature, (diethoxymethyl)tributylstannane (**1**, 0.8 g, 2 mmol) and 3-(alkoxycarbonyl)amino alcohol (2 mmol) were added. After stirring for 15 min at reflux, the mixture was neutralised with K_2CO_3. The workup was the same as that used for method B.

Physicochemical Data for Compounds 13−29

3-Methoxycarbonyl-2-tributylstannyl-1,3-oxazolidine (13): (79% Yield, 665 mg). MS: organostannyl fragments: *m*/*z* (%) = 364 (17), 291 (1), 265 (1), 235 (3), 179 (6), 177 (5), 151 (1), 121 (3); organic fragments: *m*/*z* (%) = 130 (100), 58 (4), 30 (2). $C_{17}H_{35}NO_3Sn$ (420.1): calcd. C 48.59, H 8.40, N 3.33; found C 48.61, H 8.46, N 3.51. ^{1}H NMR (C_6D_6, 340 K): δ = 0.7−1.7 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 3.05 (m, 2 H, NCH_2), 3.20 (m, 1 H, OCH_2), 3.35 (s, 3 H, OCH_3), 3.6 (m, 1 H, OCH_2), 4.8 [s, ^2J(Sn,H) = 71.4 Hz, 1 H, SnCH] ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 10.8 [^1J(Sn,C) = 315−329 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.7 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 27.6 [^3J(Sn,C) = 53.4 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.4 [^2J(Sn,C) = 20.6 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 43.2 (1 C, NCH_2), 51.9 (1 C, OCH_3), 68.7 [^3J(Sn,C) = 32.4 Hz, 1 C, OCH_2], 87.7 [^1J(Sn,C) = 397−415 Hz, 1 C, SnCH], 153.4 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 340 K): δ = −38.4 (56%) and −32.8 (44%) ppm.

3-Methoxycarbonyl-2-tributylstannyl-1,3-perhydroxazine (14): (76% Yield, 660 mg). ^{1}H NMR (C_6D_6, 340 K): δ = 0.8−1.9 [m, 29 H, $(CH_3CH_2CH_2CH_2)_3Sn$, CH_2], 2.86 (m, 1 H, NCH_2), 3.27 (m, 1 H, NCH_2), 3.4 (s, 3 H, OCH_3), 3.75 (m, 1 H, OCH_2), 3.91 (m, 1 H, OCH_2), 4.58 (s, 1 H, SnCH) ppm. ^{13}C NMR (CD_3OD, 300 K): δ = 12.5 [^1J(Sn,C) = 350 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.3 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 27.9 (1 C, CH_2), 28.5 [^3J(Sn,C) = 56.5 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 30.2 [^2J(Sn,C)= 20.1 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 46.7 [^3J(Sn,C) = 14.5 Hz, 1 C, NCH_2], 53.5 (1 C, OCH_3), 71.2 [^3J(Sn,C) = 34.3 Hz, 1 C, OCH_2], 88.3 [^1J(Sn,C) = 435 Hz, 1 C, SnCH], 158.2 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −56.4 (76%) and −44.6 (24%) ppm. IR: $\tilde{\nu}$ = 1698, 1472, 1445, 1407, 1269, 1221, 1131, 1001, 883 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 378 (8), 291 (< 1), 265 (< 1), 235 (1), 179 (2), 177 (2), 121 (1); organic fragments: *m*/*z* (%) = 144 (100), 88 (9), 44 (4). $C_{18}H_{37}NO_3Sn$ (434.2): calcd. C 49.79, H 8.59, N 3.23; found C 49.79, H 8.46, N 3.13.

1,3-Bis(methoxycarbonyl)-2-tributylstannyl-1,3-imidazolidine (15): (30% Yield, 285 mg). ^{1}H NMR (C_6D_6, 340 K): δ = 0.7−1.6 [m, 27

H, $(CH_3CH_2CH_2CH_2)_3Sn$], 3.39 (m, 2 H, NCH_2), 3.6 (m, 2 H, NCH_2), 3.7 (s, 6 H, OCH_3), 5.2 [s, ^2J(Sn,H) = 54.1 Hz, 1 H, SnCH] ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 11.0 [^1J(Sn,C) = 294−307 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.7 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 27.8 [^3J(Sn,C) = 53.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.3 [^2J(Sn,C) = 19.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 34.6 (2 C, NCH_2), 52.2 (2 C, OCH_3), 66.6 [^1J(Sn,C) = 393−407 Hz, 1 C, SnCH], 153.0 (2 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −11.2 (16%), −14.5 (57%), −17.1 (27%) ppm. IR: ν̃ = 1713, 1698, 1450, 1386, 1110, 765 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 421 (29), 391 (1), 307 (3), 235 (2), 179 (3), 177 (4), 121 (2); organic fragments: *m*/*z* (%) = 187 (100), 171 (5), 129 (2), 125 (3), 55 (6), 43 (8), 41 (5). HRMS (CI, isobutane): calcd. for $C_{19}H_{39}N_2O_4Sn$ [M + H$^+$] 479.1932, found 479.1950.

3-*tert*-Butoxycarbonyl-2-tributylstannyl-1,3-oxazolidine (16): (57% Yield, 530 mg). ^{1}H NMR ($CDCl_3$, 300 K): δ = 1−1.9 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.55 [s, 9 H, $(CH_3)_3$], 3.2 (m, 2 H, NCH_2), 3.45 (m, 1 H, OCH_2), 3.8 (m,1 H, OCH_2), 5.09 [s, ^2J(Sn,H) = 70.9 Hz,1 H, SnCH] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 11.9 [^1J(Sn,C) = 314−329 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.6 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.6 [^3J(Sn,C) = 53.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.5 [3 C, $(CH_3)_3$], 30.3 [^2J(Sn,C) = 20.2 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 45.7 [^3J(Sn,C) = 8.4 Hz, 1 C, NCH_2], 69.6 [^3J(Sn,C) = 31.3 Hz, 1 C, OCH_2], 80.2 [1 C, $(CH_3)_3C$], 88.5 [^1J(Sn,C) = 398/416 Hz, 1 C, SnCH], 153.6 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 300 K): δ = −43.5 ppm. IR: ν̃ = 1806, 1687, 1420, 1367, 1166 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 406 (7), 350 (34), 291 (8), 235 (22), 179 (27), 177 (23), 121 (10); organic fragments: *m*/*z* (%) = 172 (9), 116 (100), 72 (48), 57 (59), 41 (9). $C_{20}H_{41}NO_3Sn$ (462.2): calcd. C 51.97, H 8.84, N 3.03; found C 51.92, H 8.56, N 3.33.

3-*tert*-Butoxycarbonyl-2-tributylstannyl-1,3-perhydroxazine (17): (59% Yield, 560 mg). ^{1}H NMR ($CDCl_3$): δ = 0.8−1.8 [m, 28 H, $(CH_3CH_2CH_2CH_2)_3Sn$, CH_2], 1.47 [s, 9 H, $(CH_3)_3$], 1.92 (m, 1 H, CH_2), 3.2 (m, 1 H, NCH_2), 3.6 (m, 1 H, NCH_2), 3.7−4.0 (m, 2 H, OCH_2), 4.53 (s, 1 H, SnCH) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.0 [^1J(Sn,C) = 350 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.1 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 27.1 (1 C, CH_2), 27.8 [^3J(Sn,C) = 58 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.6 [3 C, $(CH_3)_3$], 29.4 [^2J(Sn,C) = 20 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 46.1 (1 C, NCH_2), 70.4 [^3J(Sn,C) = 29.8 Hz, 1 C, OCH_2], 80.1 [1 C, $(CH_3)_3C$], 87.0 [^1J(Sn,C) = 433 Hz, 1 C, SnCH], 155.6 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −61.8 (91%) and −37.8 (9%) ppm. IR: ν̃ = 1699, 1471, 1270, 1002, 883 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 420 (11), 364 (45), 291 (4), 235 (9), 177 (15), 121 (10); organic fragments: *m*/*z* (%) = 186 (6), 130 (100), 102 (26), 88 (10), 86 (24), 58 (12), 57 (28), 41 (15), 19 (12). $C_{21}H_{43}NO_3Sn$ (476.3): calcd. C 52.96, H 9.10, N 2.94; found C 52.71, H 8.86, N 2.91.

(4*R*)-3-*tert*-Butoxycarbonyl-4-phenyl-2-tributylstannyl-1,3-oxazolidine (18): (82% Yield, 815 mg, *trans*/*cis* = 60:40). IR: ν̃ = 1694, 1455, 1393, 1068, 699 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 440 (20), 336 (1), 265 (3), 235 (4), 179 (10), 177 (7), 121 (6); organic fragments: *m*/*z* (%) = 206 (100), 178 (33), 146 (29), 128 (3), 103 (5), 91 (3), 59 (4), 42 (6), 29 (2). $C_{23}H_{39}NO_3Sn$ (496.3): calcd. C 55.66, H 7.92, N 2.82, Sn 23.92; found C 55.57, H 7.90, N 2.86, Sn 23.68.

Isomer 18-*trans*: ^{1}H NMR (C_6D_6, 340 K): δ = 1−1.9 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 3.3 (s, 3 H, OCH_3), 3.55 [dd, ^3J(H,H) = 6.4, ^2J(H,H) = 8.5 Hz, 1 H, OCH_2], 4.18 [dd, ^2J(H,H) = 8.5, ^3J(H,H) = 7 Hz, 1 H, OCH_2], 4.75 [dd, ^3J(H,H) = 7, ^3J(H,H) = 6.4 Hz, 1 H, NCH], 5.37 [s, ^2J(Sn,H) = 60.4−63.1 Hz, 1 H, SnCH], 7−7.2 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 11.6 [^1J(Sn,C) = 319−334 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.8 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 27.8 [^3J(Sn,C) = 54.5 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.5 [^2J(Sn,C) = 20.2 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 52.2 (1 C, OCH_3), 60.8 [^3J(Sn,C) = 8 Hz, 1 C, NCH], 77.0 [^3J(Sn,C) = 27.5 Hz, 1 C, OCH_2], 89.9 [^1J(Sn,C) = 376−394 Hz, 1 C, SnCH], 126.5−129.2 (5 C, C_6H_5), 141.7 (1 C, C_6H_5), 154.6 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −42.6 (94%) and −31.8 (6%) ppm. $[\alpha]_D^{19}$ = −58.56 (*c* = 1.46 in $CHCl_3$).

Isomer 18-*cis*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.95−1.7 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 3.37 (s, 3 H, OCH_3), 3.62 [dd, ^3J(H,H) = 6.4, ^2J(H,H) = 8.5 Hz, 1 H, OCH_2], 3.92 [dd, ^2J(H,H) = 8.5, ^3J(H,H) = 1.5 Hz, 1 H, OCH_2], 4.6 [dd, ^3J(H,H) = 6.4, ^3J(H,H) = 1.5 Hz, 1 H, NCH], 5.21 [s, ^2J(Sn,H) = 69.4−72.3 Hz, 1 H, SnCH], 7−7.74 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 10.6 [^1J(Sn,C) = 313−327 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.8 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 27.8 [^3J(Sn,C) = 55.3 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.5 [^2J(Sn,C) = 19.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 51.9 (1 C, OCH_3), 59.8 [^3J(Sn,C) = 10.3 Hz, 1 C, NCH], 76.9 [^3J(Sn,C) = 35.5 Hz, 1 C, OCH_2], 89.5 [^1J(Sn,C) = 404−422 Hz, 1 C, SnCH], 127.2−128.5 (5 C, C_6H_5), 142.7 (1 C, C_6H_5), 153.4 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −39 (76%) and −34.5 (24%) ppm. $[\alpha]_D^{19}$ = +47.05 (*c* = 1.36 in $CHCl_3$).

(4*R*)-3-Benzyloxycarbonyl-4-phenyl-2-tributylstannyl-1,3-oxazolidine (19): (53% Yield, 610 mg, *trans*/*cis* = 72:28). IR: ν̃ = 1747, 1692, 1491, 1456, 1390, 1258, 697 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 572 (1), 516 (3), 438 (1), 291 (2), 235 (4), 179 (7), 177 (7), 121 (6); organic fragments: *m*/*z* (%) = 282 (7), 238 (23), 132 (5), 104 (8), 91 (100), 77 (6), 65 (6), 51 (3), 41 (3), 39 (3), 29 (3). $C_{29}H_{43}NO_3Sn$ (572.4): calcd. C 60.85, H 7.57, N 2.45; found C 61.55, H 7.38, N 2.58.

Isomer 19-*trans*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.8−1.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 3.56 [t, ^3J(H,H) = 7, ^2J(H,H) = 8.5 Hz, 1 H, OCH_2], 4.17 [t, ^2J(H,H) = 8.5, ^3J(H,H) = 7 Hz, 1 H, OCH_2], 4.75 [t, ^3J(H,H) = 7 Hz, 1 H, NCH], 4.90 [d, ^2J(H,H) = 12.5 Hz, 1 H, CH_2Ph], 4.97 [d, ^2J(H,H) = 12.5 Hz, 1 H, CH_2Ph], 5.38 [s, ^2J(Sn,H) = 61.4 Hz, 1 H, SnCH], 6.8−7.2 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 11.4 [^1J(Sn,C) = 319−334 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.6 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 27.5 [^3J(Sn,C) = 54.5 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.3 [^2J(Sn,C) = 20.6 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 60.7 [^3J(Sn,C) = 8 Hz, 1 C, NCH], 67.0 (1 C, CH_2Ph), 77.1 [^3J(Sn,C) = 29 Hz, 1 C, OCH_2], 89.8 [^1J(Sn,C) = 373−391 Hz, 1 C, SnCH], 126.4−141.4 (10 C, C_6H_5), 136.9 (1 C, C_6H_5), 141.1 (1 C, C_6H_5), 153.7 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −41.5 ppm. $[\alpha]_D^{19}$ = −136.9 (*c* = 1 in $CHCl_3$).

Isomer 19-*cis*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.8−1.7 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 3.6 [dd, ^3J(H,H) = 6.6, ^2J(H,H) = 8.4 Hz, 1 H, OCH_2], 3.9 [dd, ^2J(H,H) = 8.4, ^3J(H,H) = 1.2 Hz, 1 H, OCH_2], 4.6 (m, 1 H, NCH), 4.9 [d, ^2J(H,H) = 12.5 Hz, 1 H, CH_2Ph], 5.08 [d, ^2J(H,H) = 12.5 Hz, 1 H, CH_2Ph], 5.22 [s, ^2J(Sn,H) = 68−71 Hz, 1 H, SnCH], 6.9−7.3 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 300 K): δ = 10.7 [^1J(Sn,C) = 314−328 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.8 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 27.7 [^3J(Sn,C) = 57.2 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.5 [^2J(Sn,C) = 19.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 59.9 [^3J(Sn,C) = 10 Hz, 1 C, OCH_2], 67.0 (1 C, CH_2Ph), 77 [^3J(Sn,C) = 32 Hz, 1 C, NCH], 89.4 [^1J(Sn,C) = 398−416 Hz, 1 C, SnCH], 127.3−129.2 (10 C, C_6H_5), 137.3 (1 C, C_6H_5), 142.7 (1 C, C_6H_5), 152.8 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −39.1 ppm. $[\alpha]_D^{19}$ = +53.77 (*c* = 1 in $CHCl_3$).

(4*R*)-3-(*tert*-Butyloxycarbonyl)-4-phenyl-2-tributylstannyl-1,3-oxazolidine (20): (69% Yield, 745 mg, *trans*/*cis* = 60:40). IR: $\tilde{\nu}$ = 1726, 1685, 1417, 1162, 699 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 482 (6), 426 (20), 291 (4), 233 (9), 179 (15); organic fragments: *m*/*z* (%) = 248 (18), 192 (100), 148 (94), 120 (19), 69 (12). $C_{26}H_{45}NO_3Sn$ (538.4): calcd. C 58.01, H 8.43, N 2.6; found C 57.65, H 8.37, N 2.53.

Isomer 20-*trans*: ^{1}H NMR (C_6D_6, 300 K): δ = 0.8−1.9 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.2 [s, 9 H, $(CH_3)_3$], 3.5 [t, ^2J(H,H) = ^3J(H,H) = 8.4 Hz, 1 H, OCH_2], 4.2 [dd, ^2J(H,H) = 8.4, ^3J(H,H) = 7.3 Hz, 1 H, OCH_2], 4.6 [dd, ^3J(H,H) = 7.3, ^2J(H,H) = 8.4 Hz, 1 H, NCH], 5.37 [s, ^2J(Sn,H) = 61.6 Hz, 1 H, SnCH], 7.1 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 300 K): δ = 10.9 [^1J(Sn,C) = 324−338 Hz, 3 C, $(CH_3CH_2CH_2\mathit{C}H_2)_3Sn$], 13.5 [3 C, $(\mathit{C}H_3CH_2CH_2CH_2)_3Sn$], 27.4 [$^3J$(Sn,C) = 55.1 Hz, 3 C, $(CH_3\mathit{C}H_2CH_2CH_2)_3Sn$], 27.6 [3 C, $(CH_3)_3$], 29.0 [^2J(Sn,C) = 17.1 Hz, 3 C, $(CH_3CH_2\mathit{C}H_2CH_2)_3Sn$], 60.5 [$^3J$(Sn,C) = 9.1 Hz, 1 C, NCH], 77.4 [^3J(Sn,C) = 34.3 Hz, 1 C, OCH_2], 78.9 [1 C, $(CH_3)_3\mathit{C}$], 88.8 [^1J(Sn,C) = 382−400 Hz, 1 C, SnCH], 126.1−128 (5 C, C_6H_5), 141.4 (1 C, C_6H_5), 152.8 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −40.1 ppm. $[\alpha]_D^{19}$ = −144.1 (*c* = 1.1 in $CHCl_3$).

Isomer 20-*cis*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.7−1.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.25 [s, 9 H, $(CH_3)_3$], 3.59 [dd, ^2J(H,H) = 8.5, ^3J(H,H) = 6.5 Hz, 1 H, OCH_2], 3.87 [dd, ^2J(H,H) = 8.5, ^3J(H,H) = 2 Hz, 1 H, OCH_2], 4.27 [dd, ^3J(H,H) = 6.5, ^3J(H,H) = 2 Hz, 1 H, NCH], 5.27 [s, ^2J(Sn,H) = 66.9 Hz, 1 H, SnCH], 6.8−7.2 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 11.6 [^1J(Sn,C) = 313−320 Hz, 3 C, $(CH_3CH_2CH_2\mathit{C}H_2)_3Sn$], 13.7 [3 C, $(\mathit{C}H_3CH_2CH_2CH_2)_3Sn$], 27.8 [$^3J$(Sn,C) = 54.6 Hz, 3 C, $(CH_3\mathit{C}H_2CH_2CH_2)_3Sn$], 28.3 [3 C, $(CH_3)_3$], 29.5 [^2J(Sn,C) = 19.8 Hz, 3 C, $(CH_3CH_2\mathit{C}H_2CH_2)_3Sn$], 59.9 [$^3J$(Sn,C) = 10.2 Hz, 1 C, NCH], 77.3 [^3J(Sn,C) = 37.3 Hz, 1 C, OCH_2], 79.4 [1 C, $(CH_3)_3\mathit{C}$], 89.6 [^1J(Sn,C) = 409−428 Hz, 1 C, SnCH], 127−129 (5 C, C_6H_5), 143.4 (1 C, C_6H_5), 152.3 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −43.3 ppm. $[\alpha]_D^{19}$ = +58.3 (*c* = 0.9 in $CHCl_3$).

(4*R*)-3-Allyloxycarbonyl-4-phenyl-2-tributylstannyl-1,3-oxazolidine (21): (60% Yield, 630 mg, *trans*/*cis* = 60:40). IR: $\tilde{\nu}$ = 1702, 1650, 1463, 1455, 700 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 522(1), 466 (6), 291 (4), 235 (6), 179 (10), 121 (7); organic fragments: *m*/*z* (%) = 232 (100), 160 (34), 70 (11), 41 (27). $C_{25}H_{41}NO_3Sn$ (522.3): calcd. C 57.49, H 7.91, N 2.68; found C 57.47, H 7.88, N 2.67.

Isomer 21-*trans*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.7−1.9 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 3.5 [dd, ^2J(H,H) = 8.5, ^3J(H,H) = 6.6 Hz, 1 H, OCH_2], 4.2 [dd, ^2J(H,H) = 8.5, ^3J(H,H) = 7.0 Hz, 1 H, OCH_2], 4.35 (m, 2 H, $C\mathit{H}_2CH{=}CH_2$), 4.7 [dd, ^3J(H,H) = 6.6, ^3J(H,H) = 7.0 Hz, 1 H, NCH], 4.8−4.95 (m, 2 H, $CH_2CH{=}C\mathit{H}_2$), 5.37 [s, ^2J(Sn,H) = 60.7−62.8 Hz, SnCH], 5.6 (m, $CH_2\mathit{C}H{=}CH_2$), 7.1 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 11.7 [^1J(Sn,C) = 326−337 Hz, 3 C, $(CH_3CH_2CH_2\mathit{C}H_2)_3Sn$], 13.8 [3 C, $(\mathit{C}H_3CH_2CH_2CH_2)_3Sn$], 27.9 [$^3J$(Sn,C) = 54.9−57.6 Hz, 3 C, $(CH_3\mathit{C}H_2CH_2CH_2)_3Sn$], 29.6 [$^2J$(Sn,C) = 20.6 Hz, 3 C, $(CH_3CH_2\mathit{C}H_2CH_2)_3Sn$], 60.9 [$^3J$(Sn,C) = 9.1 Hz, 1 C, NCH], 66.0 (1 C, $\mathit{C}H_2CH{=}CH_2$), 77.3 [^3J(Sn,C) = 32.8 Hz, 1 C, OCH_2], 90.0 [^1J(Sn,C) = 369−386 Hz, 1 C, SnCH], 117.0 (1 C, $CH_2CH{=}\mathit{C}H_2$), 126.6−128.8 (5 C, C_6H_5), 133.3 (1 C, $CH_2\mathit{C}H{=}CH_2$), 141.7 (1 C, C_6H_5), 153.9 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −43.8 ppm. $[\alpha]_D^{19}$ = −166 (*c* = 1.5 in $CHCl_3$).

Isomer 21-*cis*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.9−1.9 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 3.6 [dd, ^2J(H,H) = 8.5, ^3J(H,H) = 6.6 Hz, 1 H, OCH_2], 3.9 [dd, ^2J(H,H) = 8.5, ^3J(H,H) = 1.4 Hz, 1 H, OCH_2], 4.3−4.57 (m, 2 H, $C\mathit{H}_2CH{=}CH_2$), 4.6 [dd, ^3J(H,H) = 6.6, ^3J(H,H) = 1.4 Hz, 1 H, NCH], 4.85−5.10 (m, 2 H, $CH_2CH{=}C\mathit{H}_2$), 5.25 [s, ^2J(Sn,H) = 68.5−71.7 Hz, 1 H, SnCH], 5.7 (m, 1 H, $CH_2\mathit{C}H{=}CH_2$), 7.0−7.4 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 10.8 [^1J(Sn,C) = 313−330 Hz, 3 C, $(CH_3CH_2CH_2\mathit{C}H_2)_3Sn$], 13.8 [3 C, $(\mathit{C}H_3CH_2CH_2CH_2)_3Sn$], 27.8 [$^3J$(Sn,C) = 55.7 Hz, 3 C, $(CH_3\mathit{C}H_2CH_2CH_2)_3Sn$], 29.5 [$^2J$(Sn,C) = 19.8 Hz, 3 C, $(CH_3CH_2\mathit{C}H_2CH_2)_3Sn$], 59.9 [$^3J$(Sn,C) = 9.8 Hz, 1 C, NCH], 65.7 (1 C, $\mathit{C}H_2CH{=}CH_2$), 77.0 (1 C, OCH_2), 89.5 [^1J(Sn,C) = 400−414 Hz, 1 C, SnCH], 117.1 (1 C, $CH_2CH{=}\mathit{C}H_2$), 127.2−128.5 (5 C, C_6H_5), 133.6 (1 C, $CH_2\mathit{C}H{=}CH_2$), 142.7 (1 C, C_6H_5), 152.8 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 340 K): δ = −40.5 ppm. $[\alpha]_D^{19}$ = +45.6 (*c* = 1.8 in $CHCl_3$).

(4*S*)-4-Isopropyl-3-methoxycarbonyl-2-tributylstannyl-1,3-oxazolidine (22): (85% Yield, 785 mg, *trans*/*cis* = 60:40). IR: $\tilde{\nu}$ = 1695, 1456, 1395, 1125, 982, 768 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 406 (4), 235 (2), 179 (5), 177 (5), 121 (4); organic fragments: *m*/*z* (%) = 172 (100), 112 (2), 88 (3), 69 (7), 59 (3), 42 (3), 41 (7). HRMS (CI, isobutane): calcd. for $C_{20}H_{42}NO_3Sn$ [M + H^+] 464.2190, found 464.2193.

Isomer 22-*trans*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.76 [d, ^3J(H,H) = 6.9 Hz, 3 H, $CH(C\mathit{H}_3)_2$], 0.8 [d, ^3J(H,H) = 6.9 Hz, 3 H, $CH(C\mathit{H}_3)_2$], 0.9−1.85 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 2.01 [m, ^3J(H,H) = 6.9 Hz, 1 H, $C\mathit{H}(CH_3)_2$], 3.50 (s, 3 H, OCH_3), 3.51 [dd, ^3J(H,H) = 4.9, ^2J(H,H) = 7.6 Hz, 1 H, OCH_2], 3.69 (m, 1 H, NCH), 3.77 (m, 1 H, OCH_2), 4.96 [s, ^2J(Sn,H) = 61.5 Hz, 1 H, SnCH] ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 11.4 [^1J(Sn,C) = 319−333 Hz, 3 C, $(CH_3CH_2CH_2\mathit{C}H_2)_3Sn$], 13.6 [3 C, $(\mathit{C}H_3CH_2CH_2CH_2)_3Sn$], 17.0 [1 C, $CH(\mathit{C}H_3)_2$], 19.0 [1 C, $CH(\mathit{C}H_3)_2$], 27.6 [^3J(Sn,C) = 53.8 Hz, 3 C, $(CH_3\mathit{C}H_2CH_2CH_2)_3Sn$], 29.3 [$^2J$(Sn,C) = 20.2 Hz, 3 C, $(CH_3CH_2\mathit{C}H_2CH_2)_3Sn$], 52.0 (1 C, OCH_3), 61.7 [^3J(Sn,C) = 7 Hz, 1 C, NCH], 69.8 [^3J(Sn,C) = 28.6 Hz, 1 C, OCH_2], 88.5 [^1J(Sn,C) = 389−407 Hz, 1 C, SnCH], 155.0 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −42.3 (67%) and − 31.8 (33%) ppm. $[\alpha]_D^{19}$ = −118.75 (*c* = 0.96 in $CHCl_3$).

Isomer 22-*cis*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.84 [d, ^3J(H,H) = 7.1 Hz, 3 H, $CH(C\mathit{H}_3)_2$], 0.89 [d, ^3J(H,H) = 7.1 Hz, 3 H, $CH(C\mathit{H}_3)_2$], 0.9−1.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.98 [m, 1 H, $C\mathit{H}(CH_3)_2$], 3.32 [dd, ^3J(H,H) = 6.1, ^2J(H,H) = 8.6 Hz, 1 H, OCH_2], 3.52 (s, 3 H, OCH_3), 3.54 (m, 1 H, NCH), 3.84 [d, ^2J(H,H) = 8.6 Hz, 1 H, OCH_2], 5.08 [s, ^2J(Sn,H) = 72.6−75.6 Hz, 1 H, SnCH] ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 10.1 [^1J(Sn,C) = 311−325 Hz, 3 C, $(CH_3CH_2CH_2\mathit{C}H_2)_3Sn$], 13.5 [3 C, $(\mathit{C}H_3CH_2CH_2CH_2)_3Sn$], 17.9 [1 C, $CH(\mathit{C}H_3)_2$], 19.47 [1 C, $CH(\mathit{C}H_3)_2$], 27.5 [^3J(Sn,C) = 54.5 Hz, 3 C, $(CH_3\mathit{C}H_2CH_2CH_2)_3Sn$], 29.2 [$^2J$(Sn,C) = 20.2 Hz, 3 C, $(CH_3CH_2\mathit{C}H_2CH_2)_3Sn$], 31.0 [1 C, $\mathit{C}H(CH_3)_2$], 51.6 (1 C, OCH_3), 61.9 [^3J(Sn,C) = 10.6 Hz, 1 C, NCH], 70.8 [^3J(Sn,C) = 35.1 Hz, 1 C, OCH_2], 89.17 [^1J(Sn,C) = 428−448 Hz, 1 C, SnCH], 153.8 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −38.7 (21%) and −35.3 (79%) ppm. $[\alpha]_D^{19}$ = +71.25 (*c* = 1 in $CHCl_3$).

(4*S*)-3-(*tert*-Butoxycarbonyl)-4-isopropyl-2-tributylstannyl-1,3-oxazolidine (23): (65% Yield, 655 mg, *trans*/*cis* = 65:35). IR: $\tilde{\nu}$ = 1680, 1414, 1171, 1086 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 448 (0.5), 392 (6), 291 (2), 235 (8), 179 (14), 121 (7); organic fragments: *m*/*z* (%) = 214 (3), 158 (100), 114 (53), 69 (7), 57 (87), 41 (14), 29 (6). $C_{23}H_{47}NO_3Sn$ (504.3): calcd. C 51.37, H 8.82, N 2.61; found C 51.63, H 8.97, N 2.38.

Isomer 23-*trans*: ^{1}H NMR (C_6D_6, 300 K): δ = 0.8 [d, ^3J(H,H) = 6.5 Hz, 3 H, $CH(C\mathit{H}_3)_2$], 0.9 [d, ^3J(H,H) = 6.5 Hz, 3 H,

$CH(CH_3)_2$], 0.8−1.9 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.5 [s, 9 H, $(CH_3)_3$], 1.95 [m, $CH(CH_3)_2$], 3.5 [dd, ^2J(H,H) = 8.4, ^3J(H,H) = 5.2 Hz, 1 H, OCH_2], 3.7 [dd, ^3J(H,H) = 5.2, ^3J(H,H) = 6.3 Hz, 1 H, NCH], 3.93 [dd, ^2J(H,H) = 8.4, ^3J(H,H) = 6.3 Hz, 1 H, OCH_2], 4.90 [s, ^2J(Sn,H) = 64 Hz, 1 H, SnCH] ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 11.7 [^1J(Sn,C) = 333−339 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.3 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 17.1 [1 C, $CH(CH_3)_2$], 18.9 [1 C, $CH(CH_3)_2$], 27.4 [^3J(Sn,C) = 54 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.3 [3 C, $(CH_3)_3$], 29.2 [^2J(Sn,C) = 20.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 30.7 [1 C, $CH(CH_3)_2$], 61.7 (1 C, NCH), 70.1 [^3J(Sn,C) = 30.3 Hz, 1 C, OCH_2], 79.5 [1 C, $(CH_3)_3C$], 88.1 [^1J(Sn,C) = 397−416 Hz, 1 C, SnCH], 154.5 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 340 K): δ = −47.4 (88%) and −37.0 (12%) ppm.

Isomer 23-*cis*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.9 [d, ^3J(H,H) = 7.4 Hz, 6 H, $CH(CH_3)_2$], 0.8−1.9 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.55 [s, 9 H, $(CH_3)_3$], 1.87 [m, $CH(CH_3)_2$], 3.35 [dd, ^3J(H,H) = 6.3, ^2J(H,H) = 8.5 Hz, 1 H, OCH_2], 3.50 (m, 1 H, NCH), 3.91 [dd, ^3J(H,H) = 1, ^2J(H,H) = 8.5 Hz, 1 H, OCH_2], 5.09 [s, ^2J(Sn,H) = 74.3−77 Hz, 1 H, SnCH] ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 10.1 [^1J(Sn,C) = 310−324 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.3 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 17.8 [1 C, $CH(CH_3)_2$], 19.5 [1 C, $CH(CH_3)_2$], 24.4 [^3J(Sn,C) = 54 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.4 [3 C, $(CH_3)_3$], 29.1 [^2J(Sn,C) = 20.1 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 31.1 [1 C, $CH(CH_3)_2$], 61.7 (1 C, NCH), 70.9 [^3J(Sn,C) = 34 Hz, 1 C, OCH_2], 79.1 [1 C, $(CH_3)_3C$], 89.5 [^1J(Sn,C) = 418−436 Hz, 1 C, SnCH], 152.5 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 340 K): δ = −40.0 (72%) and −37.0 (28%) ppm.

(4*R*,5*R*)-3-Methoxycarbonyl-4-methyl-5-phenyl-2-tributylstannyl-1,3-oxazolidine (24): (77% Yield, 790 mg, *trans*/*cis* = 90:10). IR: ṽ = 1697, 1458, 1393, 1280, 1194, 1126, 992, 766, 756 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 454 (4), 336 (6), 291 (3), 265 (5), 235 (5), 179 (10), 177 (9), 121 (8); organic fragments: *m*/*z* (%) = 220 (100), 192 (53), 160 (16), 149 (11), 142 (3), 117 (15), 91 (7), 65 (1), 56 (2). $C_{24}H_{41}NO_3Sn$ (510.3): calcd. C 56.49, H 8.10, N 2.74, Sn 23.26; found C 56.16, H 7.90, N 2.68, Sn 23.46.

Isomer 24-*trans*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.9−1.8 [m, 30 H, $(CH_3CH_2CH_2CH_2)_3Sn$, $CHCH_3$], 3.49 (s, 3 H, OCH_3), 3.7 [qd, ^3J(H,H) = 6.1, ^3J(H,H) = 7.6 Hz, 1 H, NCH], 4.3 [d, ^3J(H,H) = 7.6 Hz, 1 H, OCH], 5.17 [s, ^2J(Sn,H) = 54.6−57.2 Hz, 1 H, SnCH], 7.0−7.4 (m, 5 H) ppm. ^{13}C NMR (C_6D_6, 340): δ = 11.4 [^1J(Sn,C) = 328−342 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.5 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 16.8 (1 C, $CHCH_3$), 27.5 [^3J(Sn,C) = 53.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.2 [^2J(Sn,C) = 20.6 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 51.8 (1 C, OCH_3), 60.1 [^3J(Sn,C) = 10.7 Hz, 1 C, NCH], 87.3 [^1J(Sn,C) = 371−389 Hz, 1 C, SnCH], 90.4 [^3J(Sn,C) = 38.5 Hz, 1 C, OCH], 126.4−128.4 (5 C, C_6H_5), 139.2 (1 C, C_6H_5), 154.3 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 340 K): δ = −43.8 ppm. $[\alpha]_D^{19}$ = −143.3 (*c* = 2.1 in $CHCl_3$).

Isomer 24-*cis*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.6−1.7 [m, 30 H, $(CH_3CH_2CH_2CH_2)_3Sn$, $CHCH_3$], 3.45 (s, 3 H, OCH_3), 4.02 [qd, ^3J(H,H) = 6.3, ^3J(H,H) = 3.8 Hz, 1 H, NCH], 4.62 [d, ^3J(H,H) = 3.8 Hz, 1 H, OCH], 5.74 [s, ^2J(Sn,H) = 75−78 Hz, 1 H, SnCH], 7.0−7.3 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 10.5 [^1J(Sn,C) = 301−315 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.8 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 19 (1 C, $CHCH_3$), 27.6 [^3J(Sn,C) = 51.9−53.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.5 [^2J(Sn,C) = 20.2 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 51.9 (1 C, OCH_3), 57.9 (1 C, NCH), 87.6 [^3J(Sn,C) = 19.1 Hz, 1 C, OCH], 88.0 [^1J(Sn,C) = 423−442 Hz, 1 C, SnCH], 126.8−129.2 (5 C, C_6H_5), 139.4 (1 C, C_6H_5), 152.8 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 300 K): δ = −35.8 (14%), −40.8 (86%) ppm. ^{119}Sn NMR (C_6D_6, 340 K): δ = −40.5 ppm. $[\alpha]_D^{19}$ = +70 (*c* = 0.7 in $CHCl_3$).

(4*R*,5*R*)-3-(*tert*-Butoxycarbonyl)-4-methyl-5-phenyl-2-tributylstannyl-1,3-oxazolidine (25): (43% Yield, 475 mg, *trans*/*cis* = 94:6). The NMR spectroscopic data were recorded for the mixture of the two diastereomers because of the difficulty involved in their separation by liquid chromatography. IR: ṽ = 1694, 1456, 1393, 1001, 698 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 496 (8), 440 (19), 291 (6), 235 (12), 179 (16), 177 (18), 121 (11); organic fragments: *m*/*z* (%) = 262 (10), 206 (100), 162 (41), 134 (24), 57 (84), 41 (20), 29 (14).

Isomer 25-*trans*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.8−1.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.45 [d, ^3J(H,H) = 6.2 Hz, 3 H, $CHCH_3$], 1.5 [s, 9 H, $(CH_3)_3$], 3.76 [qd, ^3J(H,H) = 7.7, ^3J(H,H) = 6.2 Hz, 1 H, NCH], 4.40 [d, ^3J(H,H) = 7.7 Hz, 1 H, OCH], 5.26 [s, ^2J(Sn,H) = 54.4−56.7 Hz, 1 H, SnCH], 7.15−7.5 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 11.9 [^1J(Sn,C) = 329−344 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.7 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 17.3 (1 C, $CHCH_3$), 27.7 [^3J(Sn,C) = 55.7 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.4 [3 C, $(CH_3)_3$], 29.5 [^2J(Sn,C) = 20.6 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 60.5 [^3J(Sn,C) = 10.7 Hz, 1 C, NCH], 79.6 [1 C, $(CH_3)_3C$], 87.1 [^1J(Sn,C) = 380−397 Hz, 1 C, SnCH], 90.5 [^3J(Sn,C) = 40.4 Hz, 1 C, OCH], 126.6 (2 C, C_6H_5), 128.6 (2 C, C_6H_5), 139.7 (1 C, C_6H_5), 153.9 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 300 K): δ = −47.5 ppm.

Observable Data for the Minor Isomer 25-*cis*: ^{1}H NMR (C_6D_6, 340 K): δ = 4.10 (m, 1 H, NCH), 4.78 [d, ^3J(H,H) = 4.3 Hz, 1 H, OCH], 5.94 [s, ^2J(Sn,H) = 72−75 Hz, 1 H, SnCH] ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 10.4 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 18.8 (1 C, $CHCH_3$), 57.9 (1 C, NCH), 79.4 [1 C, $(CH_3)_3C$], 87.8 (1 C, OCH or SnCH), 88.3 (1 C, OCH or SnCH) ppm. ^{119}Sn NMR (C_6D_6, 300 K): δ = −40.8 ppm.

(4*R*,5*R*)-4-Methyl-5-phenyl-2-tributylstannyl-3-(trifluoroacetyl)-1,3-oxazolidine (26-*trans*): (49% Yield, 540 mg). IR: ṽ = 1730, 1668, 1465, 1151 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 492 (< 1), 464 (< 1), 346 (1), 291 (6), 235 (9), 177 (13), 121 (7); organic fragments: *m*/*z* (%) = 230 (100), 212 (4), 117 (28), 91 (5), 69 (3), 29 (5). $C_{24}H_{38}F_3NO_2Sn$ (548.2): calcd. C 52.58, H 6.99, N 2.55; found C 52.71, H 7.02, N 2.96. ^{1}H NMR (C_6D_6, 340 K): δ = 0.8−1.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.0 [d, ^3J(H,H) = 6.3 Hz, 3 H, CH_3], 3.85 [quint, ^3J(H,H) = 6.3 Hz, 1 H, NCH], 4.2 [d, ^3J(H,H) = 6.3 Hz, 1 H, OCH], 5.06 [s, ^2J(Sn,H) = 43 Hz, 1 H, SnCH], 7−7.2 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 11.7 [^1J(Sn,C) = 330−346 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.5 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 18.2 (1 C, CH_3), 27.5 [^3J(Sn,C) = 55.3−57.6 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.2 [^2J(Sn,C) = 20.6 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 60.2 [q, ^4J(C,F) = 2.3 Hz, 1 C, NCH], 88.1 [^1J(Sn,C) = 329−344 Hz, 1 C, SnCH], 90.7 [^3J(Sn,C) = 32.4 Hz, 1 C, OCH], 115.1 [q, ^1J(C,F) = 287 Hz, 1 C, CF_3], 126.5−128.7 (5 C, C_6H_5), 138.5 (1 C, C_6H_5), 153.9 [q, ^2J(C,F) = 37 Hz, 1 C, CO] ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −35 (88%) and −32.7 (12%) ppm.

(4*S*,5*R*)-3-Methoxycarbonyl-4-methyl-5-phenyl-2-tributylstannyl-1,3-oxazolidine (27): (79% Yield, 805 mg, *trans*/*cis* = 13:87). IR: ṽ = 1695, 1456, 1384, 1058, 959, 768 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 454 (13), 424 (2), 336 (2), 291 (4), 265 (4), 235 (8), 179 (14), 177 (13), 121 (9); organic fragments: *m*/*z* (%) = 220 (85), 192 (100), 160 (22), 149 (6), 142 (4), 117 (18), 91 (6), 65 (0.4), 59 (3), 56 (2), 31 (2). $C_{24}H_{41}NO_3Sn$ (510.3): calcd. C 56.49, H 8.10, N 2.74; found C 55.63, H 7.53, N 2.61.

Isomer 27-*trans*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.86 [d, ^3J(H,H) = 6.6 Hz, 3 H, CHCH_3], 1.0−1.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 3.6 (s, 3 H, OCH_3), 4.25 [qd, ^3J(H,H) = 5.7, ^3J(H,H) = 6.6 Hz, 1 H, NCH], 5.07 [d, ^3J(H,H) = 5.7 Hz, 1 H, OCH], 5.83 [s, ^2J(Sn,H) = 79−82.8 Hz, 1 H, SnCH], 7−7.35 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 11.8 [^1J(Sn,C) = 297−310 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.5 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 15.2 (1 C, CHCH_3), 28.5 [^3J(Sn,C) = 52.6 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 30.3 [^2J(Sn,C) = 20.2 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 52.7 (1 C, OCH_3), 56.5 (1 C, NCH), 83.5 (1 C, OCH), 89.2 [^1J(Sn,C) = 411−430 Hz, 1 C, SnCH], 127.3−129.2 (5 C, C_6H_5), 138.3 (1 C, C_6H_5), 153.3 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 340 K): δ = −37.6 ppm. $[\alpha]_D^{19}$ = +50.0 (*c* = 1.08 in $CHCl_3$).

Isomer 27-*cis*: ^{1}H NMR (C_6D_6, 340 K): δ = 0.9 [d, ^3J(H,H) = 6.4 Hz, 3 H, CHCH_3], 0.8−1.8 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 3.6 (s, 3 H, OCH_3), 4.06 (m, 1 H, NCH), 4.68 [d, ^3J(H,H) = 5.6 Hz, 1 H, OCH], 5.34 [s, ^2J(Sn,C) = 76.3 Hz, 1 H, SnCH], 7.1−7.4 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 9.7 [^1J(Sn,C) = 313−327 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.2 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.7 (1 C, CHCH_3), 27.6 [^3J(Sn,C) = 55.1 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.2 [^2J(Sn,C) = 18.7 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 52.0 (1 C, OCH_3), 55.4 (1 C, NCH), 85.2 [^3J(Sn,C) = 28.2 Hz, 1 C, OCH], 87.9 [^1J(Sn,C) = 397−417 Hz, 1 C, SnCH], 126.2 (2 C, C_6H_5), 127.7 (1 C, C_6H_5), 128.3 (2 C, C_6H_5), 136.9 (1 C, C_6H_5), 153.1 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 340 K): δ = −36.6 (70%) and −32.8 (30%) ppm. $[\alpha]_D^{19}$ = −129.7 (*c* = 1.38 in $CHCl_3$).

(4*S*,5*R*)-3-Benzyloxycarbonyl-4-methyl-5-phenyl-2-tributylstannyl-1,3-oxazolidine (28-*cis*): (52% Yield, 610 mg). MS: organostannyl fragments: *m*/*z* (%) = 586 (2), 530 (5), 412 (0.4), 341 (1), 291 (3), 235 (5), 179 (8), 177 (7), 121 (5); organic fragments: *m*/*z* (%) = 296 (16), 252 (11), 224 (5), 91 (100), 79 (2), 77 (2), 65 (4), 57 (1), 55 (3), 41 (2), 29 (3). ^{1}H NMR (C_6D_6, 340 K): δ = 0.85 [d, ^3J(H,H) = 6.9 Hz, 3 H, CHCH_3], 0.9−1.95 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 4.05 (m, 1 H, NCH), 4.63 [d, ^3J(H,H) = 5.8 Hz, 1 H, OCH], 5.09 [d, ^2J(H,H) = 12 Hz, 1 H, CH_2Ph], 5.21 [d, ^2J(H,H) = 12 Hz, 1 H, CH_2Ph], 5.47 [s, ^2J(Sn,H) = 71.3−74.6 Hz, 1 H, SnCH], 7−7.4 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 300 K): δ = 10.4 [^1J(Sn,C) = 312−326 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.6 [3 C, $CH_3CH_2CH_2CH_2)_3Sn$], 15.5 (1 C, CHCH_3), 27.7 [^3J(Sn,C) = 54.4 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.4 [^2J(Sn,C) = 20.2 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 55.6 (1 C, NCH), 66.9 (1 C, CH_2Ph), 85.3 [^3J(Sn,C) = 28.6 Hz, 1 C, OCH], 87.9 [^1J(Sn,C) = 399−420 Hz, 1 C, SnCH], 126.4−128.5 (10 C, C_6H_5), 137.3 (1 C, C_6H_5), 137.5 (1 C, C_6H_5), 152.1 (CO) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −36.2 (77%) and −32.1 (23%) ppm. $[\alpha]_D^{19}$ = −117.1 (*c* = 0.76 in $CHCl_3$).

(4*S*,5*R*)-3-*tert*-Butoxycarbonyl-4-methyl-5-phenyl-2-tributylstannyl-1,3-oxazolidine (29-*cis*): (48% Yield, 530 mg). IR: ṽ = 1693, 1457, 1389, 1019, 703 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 496 (8), 452 (3), 440 (19), 396 (1), 291 (6), 251 (2), 235 (11), 179 (12), 177 (12), 121 (6); organic fragments: *m*/*z* (%) = 262 (10), 206 (100), 162 (35), 134 (18), 57 (54). $C_{27}H_{47}NO_3Sn$ (552.4): calcd. C 58.71, H 8.58, N 2.54; found C 58.74, H 8.62, N 2.56. ^{1}H NMR ($CDCl_3$, 300 K): δ = 0.83 [d, ^3J(H,H) = 6.4 Hz, 3 H, CHCH_3], 0.8−1.75 [m, 27 H, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.45 [s, 9 H, $(CH_3)_3$], 4.02 [qd, ^3J(H,H) = 6.4, ^3J(H,H) = 5.7 Hz, 1 H, NCH], 4.71 [d, ^3J(H,H) = 5.7 Hz, 1 H, OCH], 5.35 [s, ^2J(Sn,H) = 74.9−78.7 Hz, 1 H, SnCH], 7.0−7.3 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 10.2 [^1J(Sn,C) = 310−325 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.3 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 15.2 (1 C, CHCH_3), 27.4 [^3J(Sn,C) = 54.1 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 28.3 [3 C, $(CH_3)_3$], 29.1 [^2J(Sn,C) = 20.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 5.0 (1 C, NCH), 78.9 [1 C, $(CH_3)_3C$], 85.0 [^3J(Sn,C) = 28 Hz, 1 C, OCH], 87.6 [^1J(Sn,C) = 424−438 Hz, 1 C, SnCH], 126.1−128.0 (5 C, C_6H_5), 137.3 (1 C, C_6H_5), 151.5 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −36.3 (79%) and −31.5 (21%) ppm. $[\alpha]_D^{19}$ = +144.1 (*c* = 0.76 in $CHCl_3$).

(1*R*,2*S*)-*N*-{2-[(1′-Ethoxy-1′-tributylstannyl)methoxy]-1-methyl-2-phenylethyl}trifluoroacetamide (30): (52% Yield, 620 mg, *dr* = 79:21). IR: ṽ = 3432, 3319, 1723, 1555, 1460, 1209, 1163 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 487 (4), 405 (7), 291 (16), 235 (19), 179 (23), 177 (24); organic fragments: *m*/*z* (%) = 276 (4), 256 (53), 255 (39), 230 (100), 117 (47). $C_{26}H_{44}F_3NO_3Sn$ (594.3): calcd. C 52.54, H 7.46, N 2.36; found C 52.93, H 7.56, N 2.55.

Major Isomer: ^{1}H NMR (C_6D_6, 340 K): δ = 0.8−1.8 [m, 30 H, $(CH_3CH_2CH_2CH_2)_3Sn$, CH_2CH_3], 1.05 [d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3CH], 3.41 [qd, ^3J(H,H) = 7, ^2J(H,H) = 9 Hz, 1 H, CH_2CH$_3$], 3.55 [qd, ^3J(H,H) = 7, ^2J(H,H) = 9 Hz, 1 H, CH_2CH$_3$], 4.33 (m, 1 H, NCH), 4.78 [d, ^3J(H,H) = 3.3 Hz, 1 H, OCH], 5.05 [s, ^2J(Sn,H) = 42.7 Hz, 1 H, SnCH], 7.1−7.4 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 10.2 [^1J(Sn,C) = 299−313 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.6 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.1 (1 C, CHCH_3), 15.3 (1 C, CH_2CH_3), 27.7 [^3J(Sn,C) = 51.9−53.8 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.5 [^2J(Sn,C) = 21 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 51.4 (1 C, NCH), 65.6 [^3J(Sn,C) = 19.8 Hz, 1 C, CH_2CH_3], 82.9 [^3J(Sn,C) = 41.2 Hz, 1 C, OCH], 108.2 [^1J(Sn,C) = 472−494 Hz, 1 C, SnCH], 117.0 [q, ^1J(C,F) = 289 Hz, 1 C, CF_3], 126.9−128.7 (5 C, C_6H_5), 138.8 (1 C, C_6H_5), 156.4 [q, ^2J(C,F) = 36.6 Hz, 1 C, CO] ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −48.4 ppm.

Minor Isomer: ^{1}H NMR (C_6D_6, 340 K): Significant signals: δ = 4.66 [d, ^3J(H,H) = 2.7 Hz, 1 H, OCH], 5.45 [s, ^2J(Sn,H) = 26.7 Hz, 1 H, SnCH] ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 10.4 [^1J(Sn,C) = 300−307 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 13.6 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.1 (1 C, CHCH_3), 15.0 (1 C, CH_2CH_3), 27.6 [^3J(Sn,C) = 52.6−54.9 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 29.5 [^2J(Sn,C) = 21 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 51.3 (1 C, NCH), 66.9 [^3J(Sn,C) = 32.8 Hz, 1 C, CH_2CH_3], 85.3 [^3J(Sn,C) = 35.1 Hz, 1 C, OCH], 111.1 [^1J(Sn,C) = 447−468 Hz, 1 C, SnCH], 119.8 [q, ^1J(C,F) = 273 Hz, 1 C, CF_3], 126.9−128.7 (5 C, C_6H_5), 140.1 (1 C, C_6H_5), 156.5 [q, ^2J(C,F) = 36.6 Hz, 1 C, CO] ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −52.6 ppm.

***tert*-Butyl (2*R*)-*N*-{2-[(1′-Ethoxy-1′-tributylstannyl)methoxy]-1-phenylethyl}carbamate (31):** (*dr* = 50:50). The NMR spectroscopic data were recorded for the crude mixture of the two diastereomers because of the difficulty involved in their separation by liquid chromatography. IR: ṽ = 1720, 1706, 1495, 1366, 1172, 1087, 699 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 454 (29), 410 (30), 350 (5), 296 (5), 291 (9), 235 (24), 179 (23), 177 (24), 121 (13), 120 (10); organic fragments: *m*/*z* (%) = 220 (28), 192 (7), 146 (100), 128 (21), 75 (18). ^{1}H NMR (C_6D_6, 340 K): δ = 0.9−1.5 [m, 30 H, $(CH_3CH_2CH_2CH_2)_3Sn$, CH_2CH_3], 1.4 [s, 9 H, $(CH_3)_3$], 3.31−3.44 (m, 2 H, OCH_2CH$_3$), 3.64−3.84 (m, 2 H, OCH_2CH), 5.0 (m, 1 H, NCH), 5.13 [s, ^2J(Sn,H) = 34 Hz, 1 H, SnCH] for one isomer and 5.18 [s, ^2J(Sn,H) = 32 Hz, 1 H, SnCH] for the second, 5.20 [d, ^3J(H,H) = 7 Hz, 1 H, NH] for one isomer and 5.27 [d, ^3J(H,H) = 7 Hz, 1 H, NH] for the second, 7.02−7.3 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 10.8 [^1J(Sn,C) = 296−309 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 14.3 [3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 16.0 (1 C, CH_2CH_3), 28.2 [^3J(Sn,C) = 51.3 Hz, 3 C,

$(CH_3CH_2CH_2CH_2)_3Sn$], 29.1 [3 C, $(CH_3)_3$], 30.1 [^2J(Sn,C) = 21 Hz, 3 C, $(CH_3CH_2CH_2CH_2)_3Sn$], 56.0 (1 C, NCH), 66.1 (1 C, OCH_2CH_3) for one isomer and 66.2 (1 C, OCH_2CH_3) for the second, 73.6 (1 C, OCH_2CH) for one isomer and 73.8 (1 C, OCH_2CH) for the second, 79.6 [1 C, $(CH_3)_3C$], 109.9 [^1J(Sn,C) = 481−505 Hz, 1 C, SnCH] for one isomer and 110.0 [^1J(Sn,C) = 481−505 Hz, 1 C, SnCH] for the second, 127.7−129.0 (5 C, C_6H_5), 142.3 (1 C, C_6H_5) for one isomer and 142.4 (1 C, C_6H_5) for the second, 155.9 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −53.9 for one isomer and −54.2 ppm for the second.

Isomerisation of 20-*cis*/*trans*: The pure **20-*trans*** or **20-*cis*** isomers were isomerised under experimental conditions similar to those used for their preparation (cat. CSA, cyclohexane, reflux). HPLC conditions: flow rate = 0.5 mL/min, eluent: Hexane/diethyl ether, 85:15, sample concentration = 0.2 g/L. Retention time: 3.73 min (**20-*trans***), 4.12 min (**20-*cis***).

DFT Calculations: All calculations were performed by use of the Gaussian98 program.[57] The calculations of energetics and geometry optimisations were carried out at the B3LYP level of theory, which consists of a hybrid Becke + Hartree−Fock exchange and a Lee−Yang−Parr correlation functional with non-local corrections.[58,59] The basis set used for the optimization is the lanl2dz level for all atoms, H, C, O, N and Sn. Energies include zero-point energy (ZPE) correction. Harmonic frequencies were calculated at the same level to characterise the stationary points and to determine the zero-point energies.

Acknowledgments

The authors are grateful to ORIL-industrie (Bolbec), to CNRS and to MESR for financial support and to M.-J. Bertrand for her help in HPLC analyses. They wish also to acknowledge Crompton GmbH and Rhodia Silicones for gifts of organometallic starting materials.

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Received March 25, 2004

