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Journal of Organometallic Chemistry 691 (2006) 1488–1497
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Diastereoselective synthesis of chiral α-aminoorganotributyltins via ring-opening of 2-tributylstannyloxazolidines

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Received 25 November 2005; accepted 28 November 2005
Available online 31 January 2006

Abstract

Reactions of 2-tributylstannyloxazolidines **2a**–**d** (*cis* or *trans*), derived from (*R*)-phenylglycinol protected as *N*-carbamate, with lithium diorganocuprates in presence of boron trifluoride in diethyl ether provide the corresponding functionalized tributylstannyl-α-aminoalcohols **3**–**10** with diastereoselectivities close to 85:15 in favour of the (*S*,*R*)-isomer. The stereochemical trend is preserved using allyltributyltin as nucleophile and $TiCl_2(O\textit{i}\text{-}Pr)_2$ as Lewis acid in dichloromethane. The assignments of the (*S*,*R*) or (*R*,*R*) configurations in **3**–**10** were achieved on the basis of physicochemical data combined with a radiocrystallographic structure. Stereochemical preferences were rationalized by consideration of the interactions occurring in the iminium intermediates.

Keywords: α-Aminoalkyltributyltins; 2-Stannyloxazolidines; Iminium intermediates; Organocopper reagents; Diastereoselective reaction

1. Introduction

Due to the importance of functional α-amino-derivatives with fixed configuration like bioactive molecules (α-amino-acids, β-amino-alcohols, etc.), the synthesis of building blocks able to be convenient precursors of chiral α-amino-carbanions with fixed *R* or *S* configuration appears of high interest [1]. For this purpose, metalation reactions using an organolithium reagent in the presence of a chiral diamine can constitute a possible route and numerous results have been reported using commercially available (−)-sparteine [2–4]. However, when the reversed configuration is desired, (+)-sparteine [5] or (+)-sparteine surrogates derived from (−)-cytisine [6] are much less available.

Since previous reports have already shown that chiral α-aminoorganotributyltins can be suitable candidates as precursors of α-aminocarbanions, both in achiral or in chiral series [7–18], we decided to explore a new route to reach this type of reagents. Our choice was oriented towards the ring-opening of 2-tributylstannyloxazolidines in order to avoid the use of hardly storable α-iodoalkyltins, acyltins or α-stannylalcohols which have been previously used for the stereoselective synthesis of chiral α-aminoorganotributyltins [12–17,19,20].

In our previous research programs, we have studied the preparation of 2-tributylstannyloxazolidines [21] from the easy available and storable diethoxymethyltributyltin [22,23] and pointed out that, upon treatment with *n*-butyllithium, *N*-Boc-2-tributylstannyloxazolidines derived from chiral β-amino-alcohols undergo clean transmetalation to afford 2-lithio-oxazolidines which are configurationally stable at −78 °C [24–28]. Furthermore, preliminary experiments have shown that organocopper reagents in the presence of Lewis acids are able to open the 2-triorganostannyloxazolidines heterocycle to afford chiral α-aminoorganotins in a diastereoselective fashion [27]. Here we wish to report further results on this reaction in order to

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doi:10.1016/j.jorganchem.2005.11.070

evaluate its scope for obtaining enantioenriched α-aminoorganotins since stereochemistry of the reaction and subsequently the configuration of the α-stannylated carbon is subject to be controlled by the use of a removable (*R*)-or (*S*)-phenylglycinol unit.

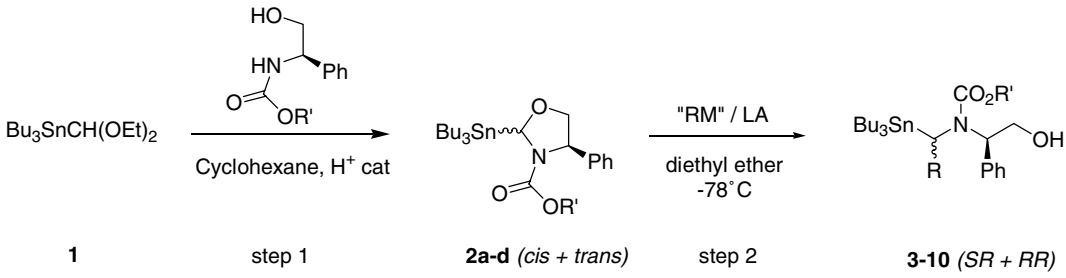
2. Results

Considering the reaction sequence presented in Scheme 1, the present work will be devoted to a careful examination of step 2 in order to assign the configuration of the diastereomers and to attempt a rationalization of the obtained results in function of the involved reagents.

The first step of the reaction sequence reported in Scheme 1 was shown to occur diastereoselectively with a preference for the *trans* isomer in the *N*-CO_2R series, a major isomer which is kinetically and thermodynamically favoured [21]. For the second step, further information is required in order to unambiguously determine if a concerted mechanism can be involved, as observed in the case of 2-stannylated 1,3-dioxanes or dioxolanes [29,30] or if the occurrence of an iminium intermediate is the general trend as already suggested in a preliminary report [27].

For this purpose, the reaction of 2-tributylstannyloxazolidines **2a–d** derived from (*N*-alkoxycarbonyl)-(*R*)-phenylglycinol with soft nucleophiles in the presence of Lewis acids was examined in function of the substrate (nature of the alcohol moiety in the carbamate group) and in function of the nature of the nucleophilic reagent and the Lewis acid.

The obtained results are summarized in Table 1. The 2-tributylstannyloxazolidines **2a–d** were opened in a diastereoselective fashion to afford a mixture of diastereomers identified on the basis of their NMR spectra after unambiguous assignment of the *SR* configuration in the trimethylstannylated isomer (Scheme 2) [27].

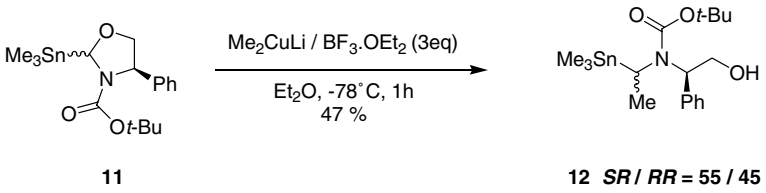


Scheme 1.

Table 1
Ring-opening of 2-tributylstannyloxazolidines derived from (*R*)-phenylglycinol by organometallic nucleophiles in the presence of Lewis acids

Entry	2-Tributylstannyloxazolidines			Nucleophile[a]	*N*-(α-stannylorgano)-aminoalcohols			
	No.	OR′	*cis*/*trans*		No.	*R*	Yield (%)[c]	*SR*/*RR*[f]
1	**2a**	*O*-*t*-Bu	40/60	Me_2CuLi	**3a**	Me	69	84/16
2			25/75	$(iBu)_2CuCN(MgCl)_2$	**4a**	*i*-Bu	84	38/62
3			25/75	$(iPr)_2CuCN(MgCl)_2$	**5a**	*i*-Pr	52	48/52
					6a	H	8	–
4			40/60	$(Vinyl)_2CuLi$	**7a**	Vinyl	40[d]	84/16
5	**2b**	*O*-Me	20/80	Me_2CuLi	**3b**	Me	78	91/9
6			20/80	$i\text{-}Pr_2CuLi$	**5b**	*i*-Pr	65	93/7
					6b	H	12	–
7			20/80	Bn_2CuLi	**8b**	Bn	87	84/16
8	**2c**	*O*-Bn	30/70	Me_2CuLi	**3c**	Me	66	84/16
9			0/100	Me_2CuLi	**3c**	Me	66	82/18
10			100/0	Me_2CuLi	**3c**	Me	63	76/24
11			30/70	Bu_2CuLi	**9c**	*n*-Bu	61	87/13
12			30/70	$AllylSnBu_3$[b]	**10c**	Allyl	71	88/12
13	**2d**	*O*-All	40/60	Me_2CuLi	**3d**	Me	20[e]	91/9

[a] Unless mentioned otherwise, oxazolidine/nucleophile and Lewis acid ($BF_3 \cdot OEt_2$) were used in a ratio 1/3/4, in diethyl ether at −78 °C.
[b] $AllylSnBu_3$ = 1.5 equiv.; Lewis acid = $TiCl_2(OiPr)_2$, 10 equiv., CH_2Cl_2, −78 °C.
[c] Yields in isolated products (liquid chromatography).
[d] Product highly sensitive to protonolysis.
[e] Unoptimized yield.
[f] The *SR* and *RR* assignments were achieved on the basis of the physicochemical data after determination of a radiocrystallographic structure for an *SR* derivative in the trimethylstannylated series.



11 **12** ***SR*** **/** ***RR*** **= 55 / 45**

Scheme 2.

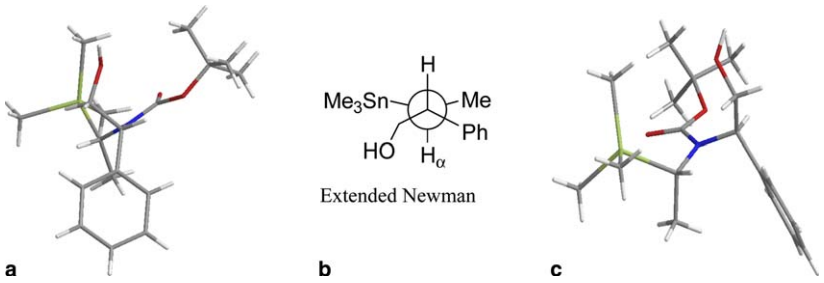


Fig. 1. A computer-generated drawing of *N*-[(1*S*)-[(trimethylstannyl)ethyl]-*N*-[2-hydroxy-(1*R*)-phenyl)ethyl]-*t*-butylcarbamate **12** from X-ray coordinates.

In this case, the major diastereomer (m.p. = 64 °C) was shown to be the *SR* isomer on the basis of its radiocrystallographic structure, considering the value of the Flack parameter [31]. The structure points out a strong chelation between tin and carbonyl oxygen of the carbamate group (bond length Sn–O = 299 pm instead of 351 pm for a Van der Waals contact between Sn and O) associated with a position of the hydroxyl group able to allow further hydrogen bonding between OH and *O*-*t*-Bu. This structure, which has been recently reported [27], is presented in Fig. 1 on two views to allow an easy appreciation of the spatial position of the hydrogen and the methyl group borne by the newly created asymmetric center (Fig. 1). On the basis of the information contained in the X-ray structure a representation is also given in an extended Newman mode, according to Trost [32].

From these views, the methyl group appears to be broadly orthogonal to the plane of the aromatic ring in the *SR* isomer, a position which should induce a meaningful shielding effect in the ^{1}H NMR spectra. In opposition, the hydrogen borne by this newly created asymmetric center (H_α) appears to be outside of this shielding area. If we assume that the tin-carbonyl chelation is the driving structural force, one could reasonably expect reverse effects for methyl and hydrogen H_α in the *RR* isomer.

Indeed, an higher shielding of the methyl group and a lower shielding of the hydrogen (H_α) were observed in the **12** *SR* isomer compared to the **12** *RR* isomer (entry 1, Table 2) [27]. These observations are explained on the basis of the above mentioned structural data and accordingly these criteria were subsequently applied to distinguish between *SR* and *RR* isomers in the *N*-CO_2*t*Bu series (entry 2–5, Table 2). These double criteria appear to be nearly homogeneous along the series of the obtained α-stannylated chiral aminoalcohols **3**–**10**, even when extended to substituents other than methyl, by considering the chemical shift of the meaningful part of the introduced group (CH_2 for *i*-Bu, allyl and benzyl or CH for *i*-Pr). In the *N*-CO_2Me and *N*-CO_2Bn derivatives, one of the two criteria remains in agreement with the expected sequence (entries 6–11, Table 2). When two signals have nearly the same chemical shift, whatever the *SR* or *RR* configuration of the product, as observed for the methyl in **3b** and **3c** (entries 6 and 9, Table 2), the assignment was confirmed by conversion of **3b** and **3c** into the corresponding known tributylstannylated oxazolidinone [15].

Table 2
Meaningful parameters allowing the discrimination between *SR* and *RR* diastereomers in the obtained *N*-(α-trialkylstannylorgano) aminoalcohols **3**–**10**

Entry	Compound	^{1}H NMR[a]		$[\alpha]_D^{19}$[c]	
		$\Delta\delta$ (H_α)	$\Delta\delta$[b] (R)	*SR*	*RR*
1	**12**	+0.20	−0.33 (Me)	−72.2	+7.5
2	**3a**	+0.15	−0.43 (Me)	−42.8	+2.0
3	**4a**	+0.13	−0.40 (CH_2-*i*-Pr)	−31.6	+13.7
4	**5a**	+0.12	−0.17 ($CHMe_2$)	−13.3	+18.4
5	**7a**	+0.1	−0.37 (CH=CH_2)	−57.1	−29.2
6	**3b**	+0.07	−0.01 (Me)[d]	−30.5	−1.0
7	**5b**	+0.02	nd[e]	−10.7	nd
8	**8b**	+0.07	−0.37* (CH_2Ph)	−28.9	+6.7
9	**3c**	+0.22	0 (Me)[d]	nd	nd
10	**9c**	+0.14	−0.44* (CH_2-*n*-Pr)	−54.7	nd
11	**10c**	+0.12	−0.42* (CH_2-vinyl)	−26.5	+0.25

[a] $\Delta\delta = \delta(SR) - \delta(RR)$.
[b] The values noted * are the average of the chemical shifts for the two unequivalent H.
[c] $[\alpha]_D^{19}$ values were not determined (nd) when compounds were not obtained pure enough to have reliable values.
[d] The *SR* configuration was confirmed by conversion in the corresponding known oxazolidinone [15].
[e] Signals of **5b**-*RR* overlapped with those of **6b**.

Furthermore, when the obtained diastereomeric stannylated derivatives **3**–**10** can be isolated pure enough to allow meaningful measurement of $[\alpha]_D^{19}$ values, negative optical rotations were obtained for the *SR* isomers while positive values or weaker negative values were obtained for the *RR* isomers. The weak $[\alpha]_D^{19}$ value measured in the reduced compound **6a** ($[\alpha]_D^{19} = -2.4$) makes this statement much more reliable because it suggests that the origin of the optical rotation is mainly due to the difference of the polarizability of the bonds around the newly created asymmetric center in the α-position related to tin.

3. Discussion

On the basis of the results reported in Table 1, the opening of the oxazolidine ring by soft nucleophiles in the presence of a Lewis acid appears to be a stereoselective reaction nearly independent of the geometry of the starting 2-tributylstannyloxazolidine (entries 8–10, Table 1). This result is consistent with a major mechanism involving the addition of the nucleophile on an iminium intermediate formed in the presence of the Lewis acid (Scheme 3).

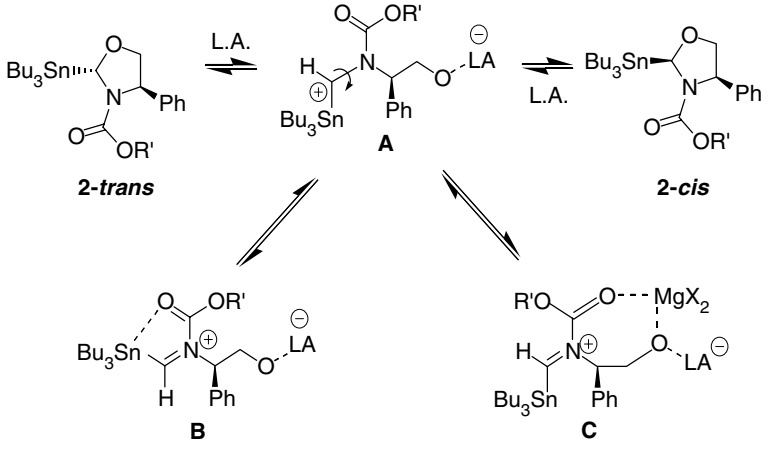
The formation of the iminium intermediates has been often reported in reactions involving oxazolidines and Lewis acids [33] and has also been used to explain the *cis*/*trans* isomerisation of 2-tributylstannyloxazolidines through this type of intermediates as shown in the upper part of Scheme 3 [21].

The nature of the alkoxy group in the *N*-CO_2R' protective groups appears to be nearly ineffective on the observed diastereoselection while the size of the entering nucleophile induces only minor modification on the diastereomeric ratio (*SR*/*RR* = 91/9–79/21). However, when the nucleophilic species were obtained from higher order magnesium cyanocuprates (entries 2 and 3, Table 1), the possible occurrence of a bidentate MgX_2 complex able to strongly modify the structure of the iminium intermediate might be involved, as shown in Scheme 3 (intermediate **C**).

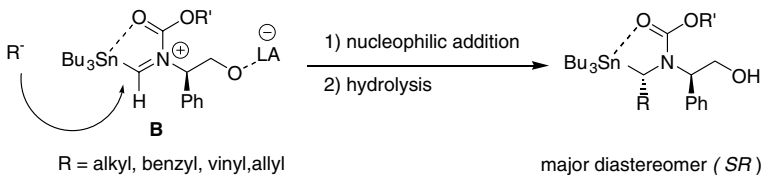
Considering the main stereochemical trend observed for ring-opening of 2-tributylstannyloxazolidines (high preference for the *SR* diastereomer), this result can be explained by an entry of the nucleophile on the less hindered side of the iminium intermediate which is expected to offer the higher stability due to a chelation between the tin nucleus and the carbonyl group of the carbamate function (Scheme 4).

When 2-trimethylstannyloxazolidines are involved, due to lower steric hindrance of the trimethylstannyl group, one can reasonably expect an easier approach on an iminium intermediate of type **B** (Schemes 3 and 4) and a more "reactant like" transition state with a lower interaction between the phenyl group of the phenylglycinol moiety and the entering nucleophile, inducing a lower (*SR*) preference.

On the basis of the structure of the possible iminium intermediates shown in Scheme 3, the presence of MgX_2 is also likely to compete with tin for a chelation with the carbonyl group of the carbamate function. Accordingly, intermediate **C** might get the more favourable structure, explaining the preference for the (*RR*) diastereomer (nucleophilic attack on the face unhindered by the phenyl group).



Scheme 3.



Scheme 4.

Reversed diastereoselectivities observed for 1,4-addition of lithium and magnesium higher order cyanocuprates on α, β-enals have been already justified by considering the ability of magnesium to give bidentate intermediates [34].

4. Conclusion

We have shown that 2-tributylstannyloxazolidines derived from (*R*)-phenylglycinol react at −78 °C with organocopper reagents or allyltributyltin in the presence of Lewis acids like $BF_3 \cdot Et_2O$ or $TiCl_2$ (*O-i*-Pr)$_2$ to afford the corresponding α-stannylated aminoalcohols in good yields.

The diastereoselectivity of the reaction close to 85/15 in favour of the (*SR*) diastereomer can be inflected in favour of the (*RR*) diastereomer when higher order magnesium cyanocuprates were used. These results might be explained by a nucleophilic addition of the nucleophile on the less hindered side of the iminium intermediate in its more stabilized conformation.

For synthetic applications, the availability of (*R*) or (*S*)-phenylglycinol offers the possibility to obtain (*S*) or (*R*) enantioenriched chiral α-aminoorganotributyltins which could constitute good precursors of chiral α-aminocarbanions through transmetalation of the obtained *O*-protected α-stannylated aminoalcohols. Furthermore, the conversion of these α-stannylated aminoalcohols into the corresponding stannylated oxazolidinones could also provide an access to another type of stabilized α-aminocarbanions. Work is currently in progress in order to evaluate the actual potential of these types of applications.

5. Experimental

5.1. General remarks

^1H, ^{13}C and ^{119}Sn spectra were recorded on Bruker AC 200, Bruker Advance 300 or Bruker ARX 400 spectrometers. Chemical shifts are given in ppm as δ values related to tetramethylsilane (^1H, ^{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 (Engine 5989 A) in direct introduction mode. Organostannyl fragments are given for ^{120}Sn what means that the given abundance are broadly one third of the overall abundance of the organostannyl fragment when compared to organic ones. IR spectra were recorded with a Bruker IFS Vector 22 apparatus. Optical rotations were measured using a Perkin–Elmer 341 apparatus. Elemental analyses were performed by CNRS microanalysis centre (Vernaison). Diethylether and THF were distilled from sodium-benzophenone prior to use. Liquid chromatography separations were achieved on silicagel Merck Geduran Si 60 (40–63 mesh), TLC analyses on silica-coated plates (Merck Kieselgel $60F_{254}$). Filtration were achieved on Celite. Diethoxymethyltributylstannane **1** was obtained in 90% yield according to previous reports [22,23]. The tributyltin hydride allowing the synthesis of the tributylstannylmagnesium chloride reagent was a Crompton GmbH product while *n*-butyllithium was a Chemetall GmbH product. The *N*-Boc-(*R*)-phenylglycinol-derived 2-trialkylstannyloxazolidines **2** were prepared according to previously described procedures [21,27].

5.2. Typical procedure for the preparation of compounds *3–10*

Diethyl ether (25 mL) was added to CuX (3 mmol) placed in a Schlenk tube and the mixture was cooled to −78 °C. The organometallic reagent (RLi or RMgX) (6 mmol) was added dropwise, and the mixture was stirred for 30 min at −78 °C and then warmed to −50 °C. The Schlenk tube was then cooled to −78 °C and $BF_3 \cdot OEt_2$ (4 mmol) was added dropwise. After 15 min stirring, a solution of **2** (1 mmol) in diethyl ether (5 mL) was added and the mixture was stirred for 2 h. The reaction was monitored by TLC (eluant = hexanes/diethyl ether: 85/15). When finished, the reaction was quenched with NH_4Cl and the crude was filtrated through a pad of Celite. The product was extracted with diethyl ether and purified by flash chromatography on silica gel (eluant = hexanes/diethyl ether/ Et_3N: 80/18/2 or 85/15/0).

5.3. Characterization of the obtained compounds

5.3.1. *N-[1-(Tributylstannyl)ethyl]-N-[(2-hydroxy-(1 R)-phenyl)ethyl]-t-butylcarbamate (yield = 69%, SR/RR = 84/16) (**3a**) [27]*

IR: 3436, 1675, 1453, 1420, 1312, 1069, 699. MS: organostannyl fragments: *m*/*z* (%) = 498 (12), 442 (37), 422 (5), 322 (2), 291 (3), 282 (4), 276 (3), 235 (10), 179 (14), 177 (15), 121 (18); organic fragments: *m*/*z* (%) = 264 (1), 164 (100), 121 (18), 105 (5), 103 (8), 57 (29), 44 (25), 41 (10), 29 (9). Elemental Anal. Calc. for $C_{27}H_{49}NO_3Sn$ (554.39 g mol^{-1}): C, 58.49; H, 8.91; N, 2.53. Found: C, 58.21; H, 8.72; N, 2.72%.

5.3.1.1. Diastereomer SR. ^1H NMR (C_6D_6, 340 K): 0.9–1.85 (m, 28H, H_{Bu} + OH), 1.2 (d, 3H, $^3J = 7.1$, CHCH_3), 1.45 (s, 9H, (CH_3)$_3$C), 3.08 (q, $^3J = 7.1$, $^2J_{Sn-H} = 49.1$, C*H*Sn,), 3.87–4.13 (m, 2H, CH_2OH), 5.1 (dd, 1H, $^3J = 7$, $^3J = 6.8$, C*H*C$_6$H$_5$,), 7.1–7.4 (m, 5H, C$_6H_5$). ^{13}C NMR (C_6D_6, 340 K): 11.3 (3 C, $^1J_{Sn-C} = 307$–321), 13.8 (3C), 18.9 (1C, CH*C*H$_3$), 27.9 (3C, $^3J_{Sn-C} = 53.8$–56.1), 28.6 (1C, (*C*H$_3$)$_3$C), 29.7 (3C, $^2J_{Sn-C} = 19.1$), 42.0 (1C, $^1J_{Sn-C} = 375$–393, *C*HSn), 63.3 (1C, *C*H$_2$OH), 63.7 (1C, $^3J_{Sn-C} = 15.3$, *C*HC$_6$H$_5$,), 80.0 (1C, (CH$_3$)$_3$*C*), 127.5 (2C, *C*$_6$H$_5$), 127.7 (1C, *C*$_6$H$_5$), 128 (2C, *C*$_6$H$_5$), 139.7 (1C, *C*$_6$H$_5$), 156.1(1C, *C*=O). ^{119}Sn NMR ($CDCl_3$, 300 K): −24.0 (83%), −16.7 (17%). $[\alpha]_D^{19} = -42.8$ ($c = 1.3$, $CHCl_3$).

5.3.1.2. Diastereomer RR. ^1H NMR (C_6D_6, 340 K): 0.8–1.5 (m, 21H, H_{Bu}), 1.52 (s, 9H, (CH_3)$_3$C), 1.63 (d, 3H,

$^3J = 7.2$, $CHCH_3$), 1.55–1.72 (m, 7H, H_{Bu}, +OH), 2.93 (q, 1H, $^3J = 7.2$, $^2J_{Sn-H} = 50.1$, $CHSn$), 3.95–4.15 (m, 2H, CH_2OH), 5.4 (t, 1H, $^3J = 6.5$, CHC_6H_5), 7.15–7.25 (m, 5H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): 11.1 (3C, $^1J_{Sn-C} = 307–320$), 13.9 (3C), 20.0 (1C, $CHCH_3$), 28.0 (3C, $^3J_{Sn-C} = 56.2$), 28.7 (3C, $(CH_3)_3C$), 29.7 (3C, $^2J_{Sn-C} = 17.7$), 40.2 (1C, $^1J_{Sn-C} = 373–389$, $CHSn$), 62.6 (1C, CHC_6H_5), 62.7 (1C, CH_2OH), 80.0 (1C, $(CH_3)_3C$), 127.8–128.3 (5C, C_6H_5), 139.3 (1C, C_6H_5), 156.3 (1C, C=O). ^{119}Sn NMR ($CDCl_3$, 300 K): −20.0 (76%), −15.0 (24%). $[\alpha]_D^{19} = +2$ ($c = 0.6$, $CHCl_3$).

*5.3.2. N-[1-(Tributylstannyl)-3-methylbutyl]-N-[(2-hydroxy-(1 R)-phenyl)ethyl]-t-butylcarbamate (yield = 84%, SR/RR = 38/62) (**4a**)*

IR: 3431, 3032, 2955, 1674, 1455, 1164, 1100, 80, 700. MS: organostannyl fragments: *m/z* (%) = 540 (13), 484 (40), 466 (3), 291 (7), 235 (12), 179 (13), 177 (15); organic fragment: *m/z* (%) = 206 (100), 121 (10), 103 (7), 86 (20), 57 (8). Elemental Anal. Calc. for $C_{30}H_{55}NO_3Sn$ (596.47 g mol^{-1}): C, 60.41; H, 9.29; N, 2.35. Found: C, 60.76; H, 9.35; N, 2.12%.

5.3.2.1. Diastereomer SR. ^1H NMR ($CDCl_3$, 300 K): $\delta = 0.43$ (br s, 3H, $(CH_3)_2CHCH_2$), 0.69 (br s, 3H, $(CH_3)_2CHCH_2$), 0.82 (m, 6H, H_{Bu}), 0.87–0.9 (m, 9H, H_{Bu}), 1.25–1.3 (m, 6H, H_{Bu}), 1.3–1.5 (m, 7H, $H_{Bu} + (CH_3)_2CHCH_2$), 1.50 (s, 9H, $(CH_3)_3C$), 1.85 (m, 2H, $(CH_3)_2CHCH_2$), 2.85 (m, 1H, $CHSn$), 4.03 (m, 2H, CH_2OH), 5.16 (m, 1H, $CHPh$), 7.25–7.33 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$, 300 K): $\delta = 10.6$ (3C, $^1J_{Sn-C} = 310.3$), 11.5 (rotamer), 13.8 (3C), 14.2 (rotamer), 21.4 (1C, $(CH_3)_2CHCH_2$), 22.8 (rotamer), 23.9 (1C, $(CH_3)_2CHCH_2$), 26.1 (1C, $(CH_3)_2CHCH_2$), 27.7 (3C, $^3J_{Sn-C} = 60.3$), 28.8 (3C, $(CH_3)_3C$), 29.4 (3C), 29.8 (rotamer), 41.6 (1C, $(CH_3)_2CHCH_2$), 44.9 (1C, $CHSn$), 46.3 (rotamer), 62.9 (3C, $CH_2OH + CHC_6H_5$), 80 (1C, $(CH_3)_3C$), 127.9–128.8 (5C, C_6H_5), 138.1 (1C, C_6H_5), 155.4 (1C, C=O). ^{119}Sn NMR ($CDCl_3$, 300 K): −12.5 (25%), −19.3 (75%). $[\alpha]_D^{19} = -31.6$ ($c = 1.24$, $CHCl_3$).

5.3.2.2. Diastereomer RR. ^1H NMR ($CDCl_3$, 300 K): $\delta = 0.5–0.6$ (m, 6H, H_{Bu}), 0.85–0.90 (m, 15H, $(CH_3)_2CHCH_2 + H_{Bu}$), 1.20–1.26 (m, 6H, H_{Bu}), 1.3–1.5 (m, 7H, $H_{Bu} + (CH_3)_2CHCH_2$), 1.50 (s, 10H, $(CH_3)_3C + (CH_3)_2CHCH_2$), 2.25 (m, 2H, $(CH_3)_2CHCH_2$), 2.71–2.74 (m, 1H, $CHSn$), 3.9–4.1 (m, 2H, CH_2OH), 5.35 (m, 1H, $CHPh$), 7.25–7.35 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$, 300 K): $\delta = 10.3$ (3C, $^1J_{Sn-C} = 290.9$), 13.6 (3C), 14.1 (rotamer), 21.8 (1C, $(CH_3)_2CHCH_2$), 22.7 (rotamer), 24 (1C, $(CH_3)_2CHCH_2$), 26.5 (1C, $(CH_3)_2CHCH_2$), 27.8 (3C, $^3J_{Sn-C} = 56$), 28.6 (3C, $(CH_3)_3C$), 28.9 (3C), 29.3 (rotamer), 30.3 (1C, $(CH_3)_2CHCH_2$), 43.1 (1C, $CHSn$), 46.3 (rotamer), 61.8 (2C, $CH_2OH + CHC_6H_5$), 79.8 (1C, $(CH_3)_3C$), 127.9–128.2 (5C, C_6H_5), 137.7 (1C, C_6H_5), 155.6 (1C, C=O). ^{119}Sn NMR ($CDCl_3$, 300 K): −10.8 (29%), −16.2 (71%). $[\alpha]_D^{19} = +13.7$ ($c = 1.12$, $CHCl_3$).

*5.3.3. N-[1-(Tributylstannyl)-2-methylpropyl]-N-[(2-hydroxy-(1 R)-phenyl)ethyl]-t-butylcarbamate (yield = 52%, SR/RR = 48/52) (**5a**)*

IR: 3437, 3031, 2956, 1745, 1668, 1164, 765, 699. MS: organostannyl fragments: *m/z* (%) = 526 (13), 470 (37), 429 (13), 235 (11), 179 (12), 177 (14); organic fragments: *m/z* (%) = 192 (100), 150 (19), 121 (20), 103 (13), 72 (37), 57 (65), 41 (28), 29 (18). Elemental Anal. Calc. for $C_{29}H_{53}NO_3Sn$ (582.45 g mol^{-1}): C, 59.80; H, 9.17; N, 2.40. Found: C, 60.10; H, 8.76; N, 2.46%.

5.3.3.1. Diastereomer SR. ^1H NMR (C_6D_6, 340 K): $\delta = 0.73$ (d, 3H, $^3J = 6.5$, $(CH_3)_2CH$), 0.91 (d, 3H, $^3J = 7$ $(CH_3)_2CH$), 0.95–1.03 (m, 15H, H_{Bu}), 1.30 (s, 9H, $(CH_3)_3C$), 1.37–1.57 (m, 6H, H_{Bu}), 1.60–1.65 (m, 6H, H_{Bu}), 2.27 (m, 1H, $(CH_3)_2CH$), 2.77 (m, 1H, $CHSn$), 4.0 (m, 1H, CH_2OH), 4.13 (m, 1H, CH_2OH), 4.79 (m, 1H, $CHPh$,), 7.0–7.35 (m, 5H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): $\delta = 12.6$ (3C, $^1J_{Sn-C} = 302$), 13.8 (3C), 21.2 (1C, $(CH_3)_2CH$), 22 (1C, $(CH_3)_2CH$), 28 (3C), 28.7 (3C, $(CH_3)_3C$), 29.8 (3C), 32.2 (1C, $(CH_3)_2CH$), 58.1 (1C, $CHSn$), 64.4 (1C, CH_2OH), 67.1 (1C, CHC_6H_5), 80.2 (1C, $(CH_3)_3C$), 127.8–129.1 (5C, C_6H_5), 140 (1C, C_6H_5), 156.5 (1C, C=O). ^{119}Sn NMR (C_6D_6, 340 K): −30.7. $[\alpha]_D^{19} = -13.3$ ($c = 1.07$, $CHCl_3$).

5.3.3.2. Diastereomer RR. ^1H NMR (C_6D_6, 340 K): $\delta = 0.82$ (m, 6H, H_{Bu}), 0.98 (m, 15H, $(CH_3)_2CH + H_{Bu}$), 1.40 (s, 9H, $(CH_3)_3C$), 1.35–1.54 (m, 12H, H_{Bu}), 2.44 (m, 1H, $(CH_3)_2CH$), 2.65 (m, 1H, $CHSn$), 3.95 (m, 1H, $^2J = 10$, $^3J = 7$, CH_2OH), 4.04 (m, 1H, $^2J \sim {}^3J \sim 10$, CH_2OH), 5.19 (m, 1H, $CHPh$,), 6.84–7.02 (m, 5H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): $\delta = 12.4$ (3C, $^1J_{Sn-C} = 238$), 13.8 (3C), 21.8 (1C, $(CH_3)_2CH$), 22.2 (1C, $(CH_3)_2CH$), 28 (3C, $^3J_{Sn-C} = 60.4$), 28.7 (3C, $(CH_3)_3C$), 29.7 (3C), 32.5 (1C, $(CH_3)_2CH$), 55.7 (1C, $^1J_{Sn-C} = 287$, $CHSn$), 63.6 (1C, CH_2OH), 64.1 (1C, CHC_6H_5), 80.1 (1C, $(CH_3)_3C$), 127.8–129.2 (5C, C_6H_5), 139 (1C, C_6H_5), 156.9 (1C, C=O). ^{119}Sn (C_6D_6, 340 K): −27.5. $[\alpha]_D^{19} = +18.4$ ($c = 1.4$, $CHCl_3$).

*5.3.4. N-[1-(Tributylstannyl)methyl]-N-[(2-hydroxy-(1 R)-phenyl)ethyl]-t-butylcarbamate (yield = 8%) (**6a**)*

MS: organostannyl fragments: *m/z* (%) = 484 (22), 428 (83), 410 (11), 310 (4), 291 (8), 235 (17), 179 (23); organic fragment: *m/z* (%) = 150 (100), 132 (10), 121 (34), 103 (19), 57 (33), 30 (29). Elemental Anal. Calc. (%) for $C_{26}H_{47}NO_3Sn$ (540.37 g mol^{-1}): C, 57.79; H, 8.77; N, 2.59. Found: C, 57.45; H, 8.85; N, 2.47%.

^1H NMR (C_6D_6, 340 K): $\delta = 0.86–1.00$ (m, 15H, H_{Bu}), 1.36–1.44 (m, 6H, H_{Bu}), 1.44 (s, 9H, $(CH_3)_3C$), 1.51–1.65 (m, 6H, H_{Bu}), 2.61 and 2.79 (AB syst, 2H, $^2J = 13$, CH_2Sn), 3.90 and 4.01 (ABX syst, 2H, $^3J = 6$, $^3J = 9$, $^2J = 11$, CH_2OH), 5.29 (dd, 1H, $^3J = 6$, $^3J = 9$, $CHPh$), 7.02–7.25 (m, 5H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): $\delta = 12.2$ (3C), 14.4 (3C), 28.4 (3C, $^3J_{Sn-C} = 55$), 29.2 (4C, $(CH_3)_3C + CH_2Sn$), 30.2 (3C), 63.0 (1C, CH_2OH), 63.2

(1C, CHC$_6$H$_5$), 80.5 (1C, (CH$_3$)$_3C$), 128.4–129.7 (5C, C_6H$_5$), 139.9 (1C, C_6H$_5$), 155.7 (1C, C=O). ^{119}Sn NMR (C$_6$D$_6$, 340 K): −33.7. $[\alpha]_D^{19} = -2.4$ ($c = 0.95$, CHCl$_3$).

*5.3.5. N-[1-Vinyl-1-(tributylstannyl)methyl]-N-[(2-hydroxy-(1 R)-phenyl)ethyl]-t-butylcarbamate (yield = 40%, SR/RR = 84/16) (**7a**)*

IR: 3447, 2955, 2923, 1669, 1454, 1367, 1170, 699. MS: (CI, NH$_3$): 568 [M + H$^+$].

5.3.5.1. Diastereomer SR. ^{1}H NMR (CDCl$_3$, 300 K): $\delta = 0.7$–1.9 (m, 27H, H_{Bu}), 1.42 (s, 9H, (CH_3)$_3$C), 3.5 (d, 1H, $^3J = 7.4$, $^2J_{Sn-H} = 64$, CHSn), 3.90–4.20 (m, 2H, CH_2OH), 4.50 (bd, 1H, $^3J = 17.1$, CH=CH_2), 4.58 (bd, 1H, $^3J = 10.5$, CH=CH_2), 4.85 (br t, 1H, $^3J = 7.3$, CHPh), 5.75 (ddd, 1H, $^3J = 7.4$, $^3J = 10.5$, $^3J = 17.1$, CH=CH$_2$), 7.20–7.38 (m, 5H, C$_6H_5$). ^{13}C NMR (CDCl$_3$, 300 K): $\delta = 11.1$ (3C, $^1J_{Sn-C} = 320$–332), 13.7 (3C), 27.5 (3C, $^3J_{Sn-C} = 58.2$), 28.4 (3C, (CH$_3$)$_3$C), 30.2 (3C, $^2J_{Sn-C} = 17.6$), 52.2 (1C, $^1J_{Sn-C} = 301$–316, CHSn), 63.4 (1C, CH$_2$OH), 64.6 (1C, CHC$_6$H$_5$), 80.4 (1C, (CH$_3$)$_3C$), 106.8 (1C, CH=CH$_2$), 127.5–128.4 (5C, C_6H$_5$), 138.7 (1C, C_6H$_5$), 139.1 (1C, $^2J_{Sn-C} = 19.2$, CH=CH$_2$), 155.9 (1C, C=O). ^{119}Sn NMR (CDCl$_3$, 300 K): −34.1. $[\alpha]_D^{19} = -57.1$ ($c = 1.0$, CHCl$_3$).

5.3.5.2. Diastereomer RR. ^{1}H NMR (CDCl$_3$, 300 K): $\delta = 0.6$–1.5 (m, 27H, H_{Bu}), 1.50 (s, 9H, (CH_3)$_3$C), 3.40 (d, 1H, $^3J = 6.8$, $^2J_{Sn-H} = 68$, CHSn), 3.85–4.15 (m, 2H, CH_2OH), 4.78 (bd, 1H, $^3J = 17$, CH=CH_2), 4.81 (bd, 1H, $^3J = 10.6$, CH=CH_2), 5.45 (dd, 1H, $^3J = 4.5$, $^3J = 9.4$, CHPh), 6.12 (ddd, 1H, $^3J = 6.8$, $^3J = 10.6$, $^3J = 17$, CH=CH$_2$), 7.20–7.37 (m, 5H, C$_6H_5$). ^{13}C NMR (CDCl$_3$, 300 K): $\delta = 11.4$ (3C, $^1J_{Sn-C} = 318$–332), 13.7 (3C), 28.4 (3C, $^3J_{Sn-C} = 58$), 28.5 (3C, (CH$_3$)$_3$C), 28.9 (3C, $^2J_{Sn-C} = 18.4$), 46.9 (1C, CHSn), 61.4 (1C, CHC$_6$H$_5$), 61.8 (1C, CH$_2$OH), 80.2 (1C, (CH$_3$)$_3C$), 106.5 (1C, CH=CH$_2$), 127.6–128.5 (5C, C_6H$_5$), 138.3 (1C, C_6H$_5$), 140.9 (1C, CH=CH$_2$), 156 (1C, C=O). ^{119}Sn NMR (CDCl$_3$, 300 K): −27.2. $[\alpha]_D^{19} = -29.2$ ($c = 0.5$, CHCl$_3$).

*5.3.6. N-[1-(Tributylstannyl)ethyl]-N-[(2-hydroxy-(1 R)-phenyl)ethyl]-methylcarbamate (yield = 78%, SR/RR = 91/9) (**3b**)*

IR (cm^{-1}): 3440, 1685, 1456, 1295, 1072, 700. MS: organostannyl fragments: m/z (%) = 456 (51), 424(100), 336 (18), 282 (12), 235 (24), 179 (55), 177 (58), 121 (38); organic fragments: m/z (%) = 222 (17), 190 (48), 146 (53), 102 (72), 91 (10), 77 (10), 58 (13), 41 (15), 29 (49). Elemental Anal. Calc. for C$_{24}$H$_{43}$NO$_3$Sn (512.31 g mol^{-1}): C, 56.27; H, 8.46; N, 2.73. Found: C, 56.34; H, 8.87; N, 2.57%.

5.3.6.1. Diastereomer SR. ^{1}H NMR (C$_6$D$_6$, 340 K): $\delta =$ 0.9–1 (m, 15H, H_{Bu}), 1.11 (d, 3H, $^3J = 7.3$, CHCH_3), 1.25–1.55 (m, 12H, H_{Bu}), 3.07 (q, 1H, $^3J = 7.3$, $^2J_{Sn-H} =$ 48–51, CHSn), 3.53 (s, 3H, CH_3O), 3.90 (m, 1H, CH_2OH), 4.05 (m, 1H, CH_2OH), 5.18 (∼t, 1H, $^3J \sim 7.2$, CHPh), 7–7.3 (m, 5H, C$_6H_5$). ^{13}C NMR (C$_6$D$_6$, 340 K): $\delta = 10.4$ (3C, $^1J_{Sn-C} = 307$), 13.5 (3C), 18.8 (1C, CHCH$_3$), 27.6 (3C, $^3J_{Sn-C} = 54$), 29.4 (3C, $^2J_{Sn-C} = 19$), 41.3 (1C, $^1J_{Sn-C} =$ 374, CHSn), 52.1 (1C, CH$_3$O), 62.6 (1C, CH$_2$OH), 63.3 (1C, CHC$_6$H$_5$), 127.5–129.3 (5C, C_6H$_5$), 138.8 (1C, C_6H$_5$), 157.1 (1C, C=O).^{119}Sn NMR (C$_6$D$_6$, 300 K): $\delta = -24$ (51), −15 (49). $[\alpha]_D^{19} = -30.5$ ($c = 1.0$, CHCl$_3$).

5.3.6.2. Diastereomer RR. ^{1}H NMR (C$_6$D$_6$, 340 K): $\delta = 0.8$–1.8 (m, 27H, H_{Bu}), 1.12 (d, 3H, $^3J = 7.2$, CHCH_3), 3.00 (q, 1H, $^3J = 7.2$, $^2J_{Sn-H} = 51$, CHSn), 3.51 (s, 3H, CH_3O), 3.81 (m, 1H, CH_2OH), 3.99 (m, 1H, CH_2OH), 5.16 (m, 1H, CHPh), 7–7.3 (m, 5H, C$_6H_5$). ^{13}C NMR (C$_6$D$_6$, 340 K): $\delta = 10.5$ (3C), 12.4 (3C), 17.4 (1C, CHCH$_3$), 26.4 (3C), 28.2 (3C, $^2J_{Sn-C} = 19$), 40.4 (1C, CHSn), 51 (1C, CH$_3$O), 58.4 (1C, CH$_2$OH), 61.6 (1C, CHC$_6$H$_5$), 126.5–127.4 (5C, C_6H$_5$), 137 (1C, C_6H$_5$), 156 (1C, C=O). ^{119}Sn NMR (C$_6$D$_6$, 300 K): $\delta = -13.1$ (50), −4.7 (50). $[\alpha]_D^{19} = -1.0$ ($c = 1.0$, CHCl$_3$).

*5.3.7. N-[1-(Tributylstannyl)-2-methylpropyl]-N-[(2-hydroxy-(1 R)-phenyl)ethyl]-methylcarbamate (yield = 65%, SR/RR = 93/7) (**5b**)*

IR: 3213, 1684, 1456, 1339, 1193, 1070, 699. MS: organostannyl fragments: m/z (%) = 452 (8), 291 (5), 235 (40), 179 (70), 177 (69); organic fragments: m/z (%) = 218 (60), 104 (76), 91 (80), 78 (13), 55 (100), 41 (61), 29 (30). Elemental Anal. Calc. (%) for C$_{26}$H$_{47}$NO$_3$Sn (540.37 g mol^{-1}): C, 57.79; H, 8.77; N, 2.59. Found: C, 57.87; H, 9.12; N, 2.45%.

5.3.7.1. Diastereomer SR. ^{1}H NMR (C$_6$D$_6$, 340 K): $\delta = 0.7$–1 (m, 15H, H_{Bu}), 0.91 (d, 6H, $^3J = 6.9$, (CH_3)$_2$CH), 1.3–1.5 (m, 12H, H_{Bu}), 2.41 (m, 1H, (CH$_3$)$_2$CH), 2.67 (d, 1H, $^3J = 8.4$, $^2J_{Sn-H} = 51$, CHSn), 3.51 (s, 3H, CH_3O), 3.89 (m, 1H, CH_2OH), 4.03 (m, 1H, CH_2OH), 5.3 (∼t, 1H, CHPh), 7–7.3 (m, 5H, C$_6H_5$). ^{13}C NMR (C$_6$D$_6$, 340 K): $\delta = 11.7$ (3C), 13.5 (3C), 21.5 (1C, $^3J_{Sn-C} = 28$, (CH$_3$)$_2$CH), 21.8 (1C, (CH$_3$)$_2$CH), 27.7 (3C, $^3J_{Sn-C} = 59$), 29.2 (3C, $^2J_{Sn-C} = 19$), 32.1 (1C, (CH$_3$)$_2C$H), 52.2 (3C, CH$_3$O), 55.5 (1C, $^1J_{Sn-C} = 359$–375, CHSn), 63.2 (1C, CH$_2$OH), 63.9 (1C, CHC$_6$H$_5$), 127.5–129.2 (5C, C_6H$_5$), 138 (1C, C_6H$_5$), 157.9 (1C, C=O). ^{119}Sn NMR (C$_6$D$_6$, 300 K): −11 (40), −23 (60). $[\alpha]_D^{19} = -10.7$ ($c = 1.0$, CHCl$_3$).

5.3.7.2. Diastereomer RR. This compound has been obtained as an inseparable mixture of **5b** and **6b** (70/30). ^{1}H NMR (C$_6$D$_6$, 340 K): meaningful data: $\delta = 2.65$ (d, 1H, $^3J = 8.2$, CHSn), 3.56 (s, 3H, CH_3O), 4.35–4.45 (m, 2H, CH_2OH), 5.65 (m, 1H, CHPh). ^{119}Sn NMR (C$_6$D$_6$, 300 K): −21.5 (27), −30.4 (73).

*5.3.8. N-[1-(Tributylstannyl)methyl]-N-[(2-hydroxy-(1 R)-phenyl)ethyl]-methylcarbamate (yield = 12%) (**6b**)*

MS: organostannyl fragments: m/z (%) = 410 (100), 354 (5), 296 (25), 235 (8), 179 (20), 148 (13); organic fragments:

m/*z* (%) = 132 (93), 105 (21), 91 (22), 78 (6), 65 (3), 56 (5), 41 (6), 29 (6).

^{1}H NMR (C_6D_6, 340 K): $\delta = 0.8$–1.8 (m, 27H, H_{Bu}), 2.69 (d, 1H, $^2J = 10.2$, CH_2Sn), 2.88 (d, 1H, $^2J = 10.2$, CH_2Sn), 3.63 (s, 3H, CH_3O), 3.92 (m, 1H, CH_2OH), 4.05 (m, 1H, CH_2OH), 5.4 (∼t, 1H, C*H*Ph), 7.1–7.3 (m, 5H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): $\delta = 13.6$ (3C), 18.2 (3C), 27.8 (3C), 28.7 (1C, *C*H$_2$Sn), 29.6 (3C), 52.4 (1C, *C*H$_3$O), 61.5 (1C, *C*HC$_6$H$_5$), 62.1 (3C, *C*H$_2$OH), 127.6–128.8 (5C, C_6H_5), 138.3 (1C, C_6H_5), 157 (1C, *C*=O). ^{119}Sn NMR (C_6D_6, 300 K): −21.1 (50), −31.8 (50).

*5.3.9. N-[1-(Tributylstannyl)-1-phenylethyl]-N-[(2-hydroxy-(1 R)-phenyl)ethyl]-methylcarbamate (yield = 87%, SR/RR = 84/16) (**8b**)*

IR: 3213, 1684, 1456, 1339, 1193, 1070, 699; MS: organostannyl fragments: *m*/*z* (%) = 532 (60), 500 (10), 412 (15), 291 (6), 235 (9); organic fragments: *m*/*z* (%) = 178 (100), 146 (50), 121 (15), 103 (8). Elemental Anal. Calc. for $C_{30}H_{47}NO_3Sn$ (588.41 g mol^{-1}): C, 61.24; H, 8.05; N, 2.38. Found: C, 61.48; H, 7.85; N, 2.11%.

5.3.9.1. Diastereomer SR. ^{1}H NMR (C_6D_6, 340 K): $\delta = 0.8$–1.5 (m, 27H, H_{Bu}), 2.68 (m, 1H, CH_2Ph), 3.10 (m, 1H CH_2Ph,), 3.28 (dd, 1H, $^3J = 5.6$, $^3J = 10.5$, C*H*Sn), 3.59 (s, 3H, CH_3O), 3.91 (m, 1H, CH_2OH), 4.00 (m, 1H, CH_2OH), 5.06 (t, 1H, $^3J = 6.5$, C*H*Ph), 6.8–7.5 (m, 10H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): $\delta = 10.8$ (3C, $^1J_{Sn-C} = 320$), 13.5 (3C), 27.6 (3C, $^3J_{Sn-C} = 57$), 29.2 (3C, $^2J_{Sn-C} = 18$), 39.7 (1C, *C*H$_2$Ph), 49.7 (1C,*C*HSn), 52.3 (1C, *C*H$_3$O), 63.1 (2C, *C*H$_2$OH and *C*HC$_6$H$_5$), 126.3–129 (10C, C_6H_5), 138.5 (1C, C_6H_5), 139.9 (1C, C_6H_5), 159.2 (1C, *C*=O). ^{119}Sn (C_6D_6, 300 K): $\delta = -17.5$ (50), −10.7 (50). $[\alpha]_D^{19} = -28.9$ ($c = 1.0$, $CHCl_3$).

5.3.9.2. Diastereomer RR. ^{1}H NMR (C_6D_6, 340 K): $\delta = 0.7$–1.6 (m, 27H, H_{Bu}), 3.18–3.24 (m, 2H, C*H*Sn + CH_2Ph), 3.25–3.37 (m, 1H, CH_2Ph), 3.60 (s, 3H, CH_3O), 3.69 (m, 1H, CH_2OH), 3.82 (m, 1H, CH_2OH), 5.41 (m, 1H, C*H*Ph), 7.0–7.2 (m, 10H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): $\delta = 11.6$ (3C), 14.3 (3C), 28.4 (3C, $^3J_{Sn-C} = 58$), 29.9 (3C), 40.9 (1C, *C*H$_2$Ph), 48.5 (1C, *C*HSn), 53.2 (1C, *C*H$_3$O), 63.1 (1C, *C*H$_2$OH), 63.3 (1C,*C*HC$_6$H$_5$), 127.4–130 (10C, C_6H_5), 139.0 (1C, C_6H_5), 142.6 (1C, C_6H_5), 158.3 (1C, *C*=O). ^{119}Sn (C_6D_6, 300 K): $\delta = -14.7$. $[\alpha]_D^{19} = +6.7$ ($c = 1.0$, $CHCl_3$).

*5.3.10. N-[1-(Tributylstannyl)ethyl]-N-[(2-hydroxy-(1R)-phenyl)ethyl]-benzylcarbamate (yield = 66%, SR/RR = 82/18) (**3c**)*

MS: organostannyl fragments: *m*/*z* (%) = 532 (37), 424 (100), 291 (8), 277 (10), 235 (25), 179 (29), 177 (27), 121 (18); organic fragment: *m*/*z* (%) = 254 (46), 230 (29), 190 (28), 146 (32), 134 (14), 108 (16), 105 (15), 91 (60).

5.3.10.1. Diastereomer SR. ^{1}H NMR (C_6D_6, 340 K): 0.9–1.9 (m, 27H, H_{Bu}), 1.3 (d, 3H, $^3J = 7.2$, CHCH_3), 3.25 (q, 1H, $^3J = 7.2$, $^2J_{Sn-H} = 47.6$–49.7, C*H*Sn), 4.02 (m, 1H, CH_2OH), 4.15 (m, 1H, CH_2OH), 5.18 and 5.37 (AB syst, 2H, CH_2Ph), 5.35 (dd, 1H, $^3J = 6.1$, $^3J = 7.5$, C*H*Ph), 7.15–7.45 (m, 10H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): 10.7 (3C, $^1J_{Sn-C} = 300$–319), 13.5 (3C), 18.8 (1C, CH*C*H$_3$), 27.6 (3C, $^3J_{Sn-C} = 54.9$), 29.4 (3C, $^2J_{Sn-C} = 18.5$), 41.7 (1C, $^1J_{Sn-C} = 361$–383), 62.7 (1C, *C*H$_2$OH), 63.4 (1C, *C*HC$_6$H$_5$), 67.5 (1C, *C*H$_2$Ph), 127.3–128.4 (10C, C_6H_5), 137.2 (1C, C_6H_5), 138.8 (1C, C_6H_5), 156.6 (1C, *C*=O). ^{119}Sn NMR (C_6D_6, 300 K): −22.4 (85), −13.6 (15).

5.3.10.2. Diastereomer RR. ^{1}H NMR (C_6D_6, 340 K): meaningful data: 1.30 (d, 3H, $^3J = 7.5$, CHCH_3), 3.03 (q, 1H, $^3J = 7.5$, C*H*Sn). ^{13}C NMR (C_6D_6, 340 K): meaningful data: 19.8 (1C, CH*C*H$_3$), 40.0 (1C, *C*HSn), 62.1 (1C, *C*H$_2$OH), 62.5 (1C, *C*HC$_6$H$_5$); ^{119}Sn NMR (C_6D_6, 300 K): −19.4 (84), −12.3 (16).

*5.3.11. N-[1-(Tributylstannyl)pentyl]-N-[(2-hydroxy-(1 R)-phenyl)ethyl]-benzylcarbamate (yield = 61%, SR/RR = 87/13) (**9c**)*

IR: 3446, 3089, 3065, 2956, 2850, 1684, 1456, 1281, 1123, 698. MS: organostannyl fragments: *m*/*z* (%) = 574 (8), 466 (6), 324 (2), 291 (3), 235 (7), 179 (12), 177 (14), 121 (13); organic fragment: *m*/*z* (%) = 340 (2), 296 (18), 239 (3), 204 (2), 176 (15), 91 (100), 86 (7), 79 (5), 77 (4), 69 (3), 65 (4), 57 (2), 51 (2), 43 (3), 41 (7).

5.3.11.1. Diastereomer SR. ^{1}H NMR (C_6D_6, 340 K): 0.81 (t, 3H, $^3J = 7.1$), 0.9–1.35 (m, 19H), 1.38 (m, 1H, CH_2-*n*-Pr), 1.40–1.80 (m, 12H), 2.05 (m, 1H, CH_2-*n*-Pr), 3.11 (dd, 1H, $^3J = 4.6$, $^3J = 10.4$, C*H*Sn), 3.95–4.25 (m, 2H, CH_2OH), 5.10 and 5.31 (AB syst, 2H, CH_2Ph), 5.12 (∼t, 1H, $^3J \sim 7$, C*H*Ph), 7.1–7.5 (m, 10H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): 11.0 (3C, $^1J_{Sn-C} = 300$–320), 13.5 (3C), 13.7 (1C), 22.6 (1C), 27.6 (3C, $^3J_{Sn-C} = 52.3$), 29.4 (3C, $^2J_{Sn-C} = 18.4$), 30.1 (1C), 33.3 (1C, *C*H$_2$-*n*-Pr), 48.0 (1C, $^1J_{Sn-C} = 361$–377, Sn*C*H), 62.7 (1C, *C*H$_2$OH), 63.9 (*C*HC$_6$H$_5$), 67.5 (1C, *C*H$_2$Ph), 127.3–128.8 (10C, C_6H_5), 137.2 (1C, C_6H_5), 138.8 (1C, C_6H_5), 156.7 (1C, *C* = O). ^{119}Sn NMR (C_6D_6, 300 K): −22.2 (74), −14.3 (26). $[\alpha]_D^{19} = -54.7$ ($c = 0.84$, $CHCl_3$).

5.3.11.2. Diastereomer RR. ^{1}H NMR (C_6D_6, 340 K): 0.91 (t, 3H, $^3J = 7.3$), 0.8–1.8 (m, 32H), 1.91 (m, 1H, CH_2-*n*-Pr), 2.42 (m, 1H, CH_2-*n*-Pr), 2.97 (dd, 1H, $^3J = 4.3$, $^3J = 11$, C*H*Sn), 3.98 (m, 1H, CH_2OH), 4.11 (m, 1H, CH_2OH), 5.15 and 5.37 (AB syst, 2H, $^2J = 12.3$, CH_2Ph), 5.55 (t, 1H, $^3J = 7.3$, C*H*Ph), 7.1–7.45 (m, 10H, C_6H_5).

*5.3.12. N-[1-(Tributylstannyl)but-3-enyl]-N-[(2-hydroxy-(1 R)-phenyl)ethyl]-benzylcarbamate (yield = 71%, SR/RR = 88/12) (**10c**)*

IR: 3443, 3066, 3033, 2956, 2850, 1679, 1455, 1295, 1072, 993, 915, 700. MS: organostannyl fragments: *m*/*z* (%) = 558 (20), 450 (63), 291 (8), 275 (10), 235 (16), 179 (24), 177 (33), 121(22); organic fragment: *m*/*z* (%) = 280

(26), 216 (21), 160 (11), 108 (17), 107 (11), 91 (100), 79 (26), 77 (14), 65 (4). Elemental Anal. Calc. (%) for $C_{32}H_{49}NO_3Sn$ (614.45 g mol^{-1}): C, 62.55; H, 8.04; N, 2.28. Found: C, 62.14; H, 8.21; N, 2.12%.

5.3.12.1. Diastereomer SR. ^{1}H NMR (C_6D_6, 340 K): 0.8–1.8 (m, 27H, H_{Bu}), 2.15 (m, 1H, $^3J_{Sn-H} = 78$, CH_2CH=CH$_2$), 2.67 (m, 1H, CH_2CH=CH$_2$), 3.09 (dd, 1H, $^3J = 5.4$, $^3J = 9.9$, $^2J_{Sn-H} = 46$, C*H*Sn), 3.97 (m, 1H, CH_2OH), 4.12 (m, 1H, CH_2OH), 4.88 (d, 1H, $^3J = 17.9$, CH$_2$CH=CH_2), 4.92 (d, 1H, $^3J = 10.5$, CH$_2$CH=CH_2), 5.11 and 5.22 (AB syst, 2H, $^2J = 11.6$, CH_2Ph), 5.23 (t, 1H, $^3J = 7.5$, C*H*Ph), 5.58 (m, CH$_2$C*H*=CH$_2$), 7.1–7.35 (m, 10H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): 11.6 (3C, $^1J_{Sn-C} = 303$–321), 13.8 (3C), 27.3 (3C, $^3J_{Sn-C} = 58$), 29.6 (3C, $^2J_{Sn-C} = 18.3$), 38.3 (1C, *C*H$_2$CH=CH$_2$), 47.7 (1C, $^1J_{Sn-C} = 351$–368, *C*HSn), 63.1 (1C, *C*H$_2$OH), 64.3 (1C, *C*HPh), 67.8 (1C, *C*H$_2$Ph), 116.6 (1C, CH=*C*H$_2$), 127.8–129.0 (10C, C_6H_5), 136.7 (1C, $^3J_{Sn-C} = 11.5$, *C*H=CH$_2$), 137.4 (1C, C_6H_5), 138.8 (1C, C_6H_5), 156.9 (1C, *C*=O). ^{119}Sn NMR (C_6D_6, 300 K): −19.7 (65%), −12.0 (35%). $[\alpha]_D^{19} = -26.5$ ($c = 1.34$, $CHCl_3$).

5.3.12.2. Diastereomer RR. ^{1}H NMR (C_6D_6, 340 K): 0.7–1.8 (m, 27H, H_{Bu}), 2.77 (m, 1H, CH_2CH=CH$_2$), 2.92 (m, 1H, CH_2CH=CH$_2$), 2.97 (dd, 1H, $^3J = 5.1$, $^3J = 9.5$, $^2J_{Sn-H} = 45$, C*H*Sn), 3.95 (m, 1H, CH_2OH), 4.10 (m, 1H, CH_2OH), 5.09 (d, 1H, $^3J = 10.7$, CH$_2$CH=CH_2), 5.15 (d, 1H, $^3J = 17.0$, CH$_2$CH=CH_2), 5.11 (m, 1H, CH_2Ph), 5.35 (m, 1H, CH_2Ph), 5.55 (m, 1H, C*H*Ph), 5.87 (m, 1H, CH$_2$C*H*=CH$_2$), 7.1–7.4 (m, 10H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): 11.2 (3C, $^1J_{Sn-C} = 305$–319), 13.6 (3C), 27.6 (3C, $^3J_{Sn-C} = 58$), 29.3 (3C, $^2J_{Sn-C} = 18.0$), 38.7 (1C, *C*H$_2$CH=CH$_2$), 45.5 (1C, $^1J_{Sn-C} = 349$–365, *C*HSn), 62.0 (1C, *C*H$_2$OH), 62.7 (1C, *C*HPh), 67.7 (1C, *C*H$_2$Ph), 116.6 (1C, CH=*C*H$_2$), 127.4–128.7 (10C, C_6H_5), 137.1 (1C, $^3J_{Sn-C} = 16.8$, *C*H=CH$_2$), 137.3 (1C, C_6H_5), 138.3 (1C, C_6H_5), 157.0 (1C, *C*=O). ^{119}Sn NMR (C_6D_6, 300 K): −16.2 (86), −9.9 (14); $[\alpha]_D^{19} = +0.25$ ($c = 2$, $CHCl_3$).

*5.3.13. N-[1-(Tributylstannyl)ethyl]-N-[(2-hydroxy-(1R)-phenyl)ethyl]-allylcarbamate (yield = 20%, SR/RR = 91/9) (**3d**)*

IR: 3436, 1675, 1453, 1420, 1312, 1069, 699. MS: organostannyl fragments: *m*/*z* (%) = 498 (12), 442 (37), 422 (5), 322 (2), 291 (3), 282 (4), 276 (3), 235 (10); organic fragment: *m*/*z* (%) = 264 (1), 164 (100), 121 (18), 105 (5), 57 (29), 44 (25).

5.3.13.1. Diastereomer SR. ^{1}H NMR (C_6D_6, 340 K): 0.9–1.8 (m, 27H, H_{Bu}), 1.17 (d, 3H, $^3J = 7.2$, $^3J_{Sn-H} = 27$, CHCH_3), 3.12 (q, 1H, $^3J = 7.2$, C*H*Sn), 3.8 (m, 1H, CH_2OH), 4.04 (m, 1H, CH_2OH), 4.45–4.75 (m, 2H, CO$_2$CH_2), 4.9–5.25 (m, 2H, CH=CH_2), 5.22 (m, 1H, CHC$_6$H$_5$), 5.83 (m, 1H, C*H*=CH$_2$), 7.0–7.4 (m, 5H, C_6H_5). ^{13}C NMR (C_6D_6, 340 K): 10.8 (3C, $^1J_{Sn-C} =$ 313.5–329.8), 13.8 (3C), 27.8 (3C, $^3J_{Sn-C} = 55.7$), 29.5 (3C, $^2J_{Sn-C} = 29.5$), 41.6 (1C, $^1J_{Sn-C} = 400.3$–414.5, *C*HSn), 62.8 (1C, *C*H$_2$OH), 66.2 (1C, *C*HPh), 89.5 (1C, CO$_2$CH_2), 117.1 (1C, CH=*C*H$_2$), 127.2–128.5 (5C, C_6H_5), 133.6 (1C, *C*H=CH$_2$), 142.7 (1C, C_6H_5), 152.8 (1C, *C*=O). ^{119}Sn NMR (C_6D_6, 300 K): −24.1 (87), −15.8 (13).

Acknowledgements

The authors are grateful to ORIL-industrie (Bolbec), to CNRS, and to MESR for financial support. They also acknowledge Crompton GmbH and Rhodia Silicones for gifts of organometallic starting materials.

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