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An Alternative Route to Enantioenriched α-Alkoxyalkylstannanes by Stereoselective Opening of Chiral α-Stannylacetals with Organometallic Reagents

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Abstract: α-Tributylstannylacetals derived from chiral C_2 symmetry axis diols were reacted with miscellaneous organometallic reagents to give chiral α-oxygenated organotins in high yields. The Lewis acid promoted ring opening of the these chiral α-tributylstannylacetals by organocopper reagents, allyltins or silylenol ethers has been considered to occur mainly according to an *anti* process (d.r. = 70/30 to 93/7), the absolute configuration of the newly created centre being *S* when the reaction was performed with Me_2CuLi/BF_3 on the α-stannylacetal derived from (2*S*,4*S*)-2,4-pentanediol. Of interest is the reverse stereochemical trend obtained using organo-aluminium reagents (d.r. = 30/70 to 15/85) since it becomes possible to reach selectively the new chiral centre with a preferential *R* or *S* configuration starting from the same precursor. The obtained α-alkoxyalkylstannanes can be transmetallated with *n*-butyllithium (THF, -78°C) to give configurationally stable α-alkoxyalkyllithiums. Furthermore, if desired, the enantioenriched α-alkoxyalkylstannanes derived from 2,4-pentanediol can be converted into enantioenriched α-hydroxyalkylstannanes (subsequently protected as MOM derivatives) with retention of the configuration at the asymmetric carbon using an appropriate oxidation-β-elimination sequence.

Optically active secondary alcohols are components of numerous biologically active compounds and, occasionally, of materials. They are also important as synthetic intermediates towards various functionalities such as halides, esters, ethers, etc... Access to this class of compounds can be achieved by two general ways. The first one is the enantioselective reduction of ketones by chiral hydrides such as binaphtol derived aluminium hydrides which have been employed with great success[1]. The second route is the enantioselective addition of organometallic reagents on aldehydes which achieves at the same time the formation of a new chiral centre and the elongation of the molecule skeleton[2]. One of the most powerful methods is the enantioselective addition of dialkylzinc reagents to aldehydes catalysed by optically active compounds like amino alcohols or transition metal complexes.[3] However, since Still described the configurational stability of α-alkoxyorganolithium reagents, the use of α-alkoxyalkylanions offers an alternative approach to the above mentioned structures. In this context, α-alkoxyalkyltriorganotins appear to be of high interest because of the facile transmetallation reaction of this type of compounds with *n*-butyllithium or *s*-butyllithium in ether, THF or DME.[4] Furthermore, when the triorganostannyl group is borne by an allylic carbon atom, the possible control of the chemo-, regio- and stereoselectivities of the reactions involving these α-alkoxyallyltins allows the transfer of the umpoled unit as a d^1 or as a d^3 synthon according to the experimental conditions.[5,6,7] In this series, non-racemic α-alkoxyallyltins obtained by separation of diastereoisomers were first exploited by

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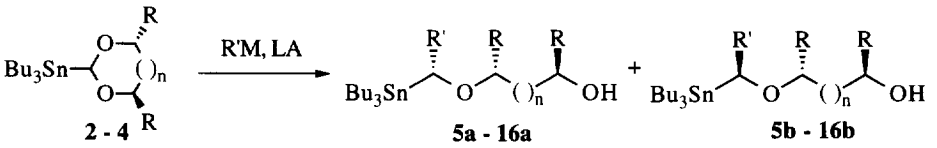
Thomas *and al.* to prepare α-methyl β-hydroxyesters with enantiomeric excess above 90%.[8a] More recently, the resolution of α-stannylalcohols via methoxymenthylethers has been also proposed by Linderman [8b].

These results demonstrate the usefulness of non racemic chiral α-alkoxyorganotins and have lead a number of chemists to propose various approaches to this class of compounds. Among these, the stannylation of chiral electrophilic substrates such as β-hydroxyaldehydes[9], α-chloroboronic ethers[10] or α-D-chloro C-glycosides[11] by tributylstannyllithium has been proved to be efficient. An enzymatic resolution of racemic α-trimethylstannylalcohols has also been recently proposed by Chong, but moderate yields appear to be a limitation in spite of interesting enantiomeric excess.[12] The major drawback, however, for these methods is their lack of generality. A different approach is the (*R*)- or (*S*)-BINAL-H enantioselective reduction of the acyltins followed by the trapping of the corresponding α-hydroxyalkyltins as α-alkoxymethylethers.[13] According to this route, the title compounds were obtained in good yields and with high enantiomeric excesses (above 95 %), the limitation being the relative instability of acyltins which are air sensitive compounds.[14] However starting from enantioenriched α-alkoxyorganotins, numerous interesting applications have been recently published especially in allylic series.[15]

Since we previously established that organoaluminium bromides can react with α-stannylacetals without transmetallation,[16] we thought that the reaction between organometallic reagents and chiral α-stannylacetals might offer a useful alternative route to chiral α-alkoxyalkyltriorganotins even if transmetallation of the Sn-C bond in dialkoxymethyltributyltins can be considered as a possible competitive reaction.[17]

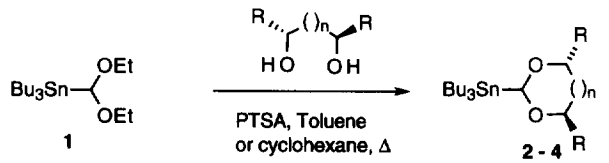
Following the results described in the organic series,[18] we have explored the possibility of extending this method to obtain enantioenriched α-alkoxyorganotins. We have therefore studied the reaction between various organometallics and α-stannylacetals **2-4** (cf Table 1). Special attention was paid to chemical yields and diastereoselectivities in order to evaluate the scope and the limitations of the reaction according to the scheme 1:[19]

Scheme 1 :



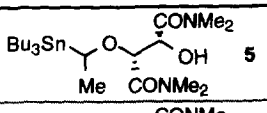
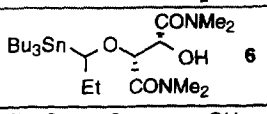
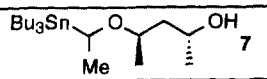
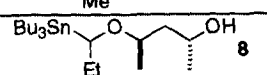
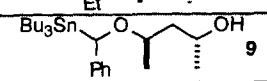
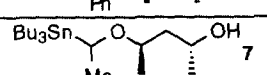
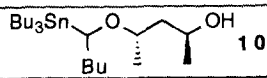
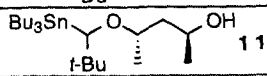
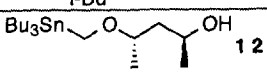
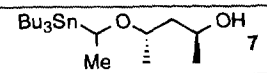
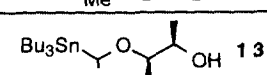
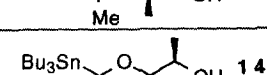
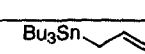
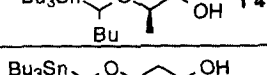
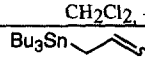
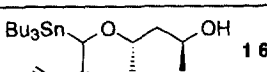
Indeed, we have recently obtained non-racemic chiral α-stannylacetals in good yields *via* transacetalisation of **1** with the corresponding diols having a C_2 symmetry axis (scheme 2) :[20]

Scheme 2 :



2(4*R*,5*R*) : R=CONMe$_2$, n=0 (59%) ; **3** (4*R*,5*R*) : R =Me, n=0 (83%) ; **4a** (4*R*,6*R*) : R =Me, n=1 (93%) ; **4b** (4*S*,6*S*) : R =Me, n=1 (93%) .

Table 1 : Selective Opening of Cyclic Acetals 2–4 with Organometallic Reagents

entry	tin acetal	RM (eq) / L.A.(eq)	Product(s)	Yield	dr*
1	**2**	Me_3Al (5 eq), CH_2Cl_2 -10° C to 20° C (16h)	 **5**	86%	20/80 **5a/5b**
2	**2**	Et_2AlCl (5 eq) CH_2Cl_2, -78° C to 0° C	 **6**	98%	14/86 **6a/6b**
3	**4a**	$MeAlCl_2$ (4 eq) CH_2Cl_2, -30° C to 0° C	 **7**	82%	30/70 **7a/7b**
4	**4a + 4b**	Et_2AlCl (2.2 eq) hexane -10° C to 20° C (12h)	 **8**	90%	35/65 **8a/8b**
5	**4a + 4b**	$Ph_2CuLi/BF_3.Et_2O$ (3 eq) Et_2O, -78° C	 **9**	62%	85/15 **9a/9b**
6	**4a**	$Me_2CuLi/BF_3.Et_2O$ (1.2 eq) Et_2O, -78° C	 **7**	15%	87/13 **7a/7b**
7	**4a**	$Me_2CuLi/BF_3.Et_2O$ (3 eq) Et_2O, -78° C	**7**	97%	85/15 **7a/7b**
8	**4a**	$Me_2CuLi/BF_3.Et_2O$ (3 eq) Et_2O, -100° C	**7**	62%	90/10 **7a/7b**
9	**4a**	$MeCu/BF_3.Et_2O$ (3 eq) Et_2O, -78° C	**7**	93%	80/20 **7a/7b**
10	**4b**	$Bu_2CuLi/BF_3.Et_2O$ (3 eq) Et_2O, -78° C (1 h) to 20° C	 **10**	67%	81/19 **10a/10b**
11	**4b**	*t*-$Bu_2CuLi/BF_3.Et_2O$ (3 eq) Et_2O, -78° C (1 h) to 20° C	 **11**	68%	78/22 **11a/11b**
12	**4b**	*i*-$PrCu/BF_3.Et_2O$ (3 eq) Et_2O, -78° C (1 h) to 20° C	 **12**	62%	**12**
13	**4b**	$Me_2CuLi/BF_3.Et_2O$ (3 eq) Et_2O, -78° C	 **7**	92%	85/15 **7a/7b**
14	**3**	$Me_2CuLi/BF_3.Et_2O$ (3 eq) Et_2O, -78° C	 **13**	77%	86/14 **13a/13b**
15	**3**	$Bu_2CuLi/BF_3.Et_2O$ (3 eq) Et_2O, -78° C	 **14**	69%	89/11 **14a/14b**
16	**4b**	 (1.5 eq) $TiCl_2(Oi\text{-}Pr)_2$ (10 eq) CH_2Cl_2, -78°C	 **15**	95%	93/7 **15a/15b**
17	**4b**	 (1.5 eq) $TiCl_2(Oi\text{-}Pr)_2$ (10 eq) CH_2Cl_2, -78°C	 **16**	84%	85/15 **16a/16b**

* Diastereoisomeric ratios were determined by GC or NMR (^1H, ^{13}C, ^{119}Sn). Compound **7a** has been shown to be *RRR* (or *SSS*) while **7b** has been shown to be *SRR* (or *RSS*). By analogy, for compounds **7-16** the notation "**a**" is believed to refer to *RRR* (or *SSS*) compounds while "**b**" is believed to refer to *SRR* (or *RSS*) compounds.

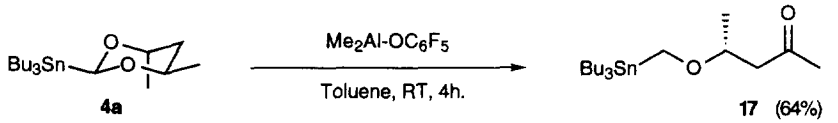
Our first attempts (entries 1, 2) were related to the reaction of organoaluminium reagents with the α-stannylacetal **2** derived from tartramide (in organic series such acetals have been proved to give good selectivities when reacted with organoaluminium reagents).[21] The reactions were achieved using a large excess of organoaluminium reagent (5 eq.) and gave good chemical yields and interesting diastereoselectivities.

In order to extend this method, we have investigated this reaction with other organometallic reagents which have already been used in organic series[22] and found that copper or cuprate reagents associated with boron trifluoride also afford α-alkoxyalkylstannanes. Three equivalents of the RCu/BF_3 couple are necessary to obtain good yields (with only 1.2 equivalent, yields are very low: *cf.* entry 6). Surprisingly, isopropyl copper (entry 12) does not lead to the isopropyl adduct but to a reduction product in moderate yield. This result might be due to the reaction of a copper hydride generated by β-elimination or to a single electron transfer mechanism involving an α-stannylated radical able to abstract hydrogen from the solvent or from the β-position of the butyl chain in the tributylstannyl group. Observed diastereomeric excesses are relatively independent of the nature of the alkyl group, and have been found to be above 60% for the reactions performed at -78°C. Lowering the reaction temperature to -100°C lead to an expected increase in diastereoselectivity (entry 8) but with a loss of yield. On the other hand, the replacement of dioxane ring by dioxolane ring leads to similar yields and diastereoselectivities (entries 14–15). When an allylation reaction was performed using allyltributyltin and $TiCl_2(O\textit{i}\text{-}Pr)_2$ as Lewis acid according to Denmark [23] the diastereomeric excess increased to 86%. When crotyltributyltin was used (entry 17), the double stereoinduction afforded only two of the four possible diastereoisomers in a 85/15 ratio. On the basis of ^1H and ^{13}C NMR spectra, it seems likely to assign the two diastereoisomers as the *syn* and *anti* products resulting from the junction between the allylic carbon and the acetal carbon atom. It is worth noticing that prenyltributyltin is unreactive in similar experimental conditions.

In order to test other organometallic reagents known to give acetal displacement, we noticed some disagreements with various systems like $EtMgBr/TiCl_4$[18] or $P(OEt)_3/TiCl_4$[24] in ether which gave complex mixtures containing large amounts of tributyltin chloride. Nevertheless, Nakai has recently described similar results with the couple $RMgBr$(5 eq.)/$TiCl_4$(2 eq.) on **4b** using THF as solvent.[25] They obtained fairly good yields but the selectivities were highly dependent on the nature of the R group (R=Et, d.e.=95%; R= Me ; d.e.=30%).

The use of pentafluorophenoxydimethylaluminium as described by Yamamoto in organic series[26] lead to a Meerwein-Verley-Ponndorf reduction combined with an Oppenauer intramolecular oxidation as shown in scheme 3. This reaction was also observed when poor nucleophiles like $Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3$ associated with $BF_3.Et_2O$ or $TiCl_2(O\textit{i}\text{-}Pr)_2$ were used. These results suggest a transition state having an oxocarbonium ion character certainly stabilised by the tributyltin group.

Scheme 3 :

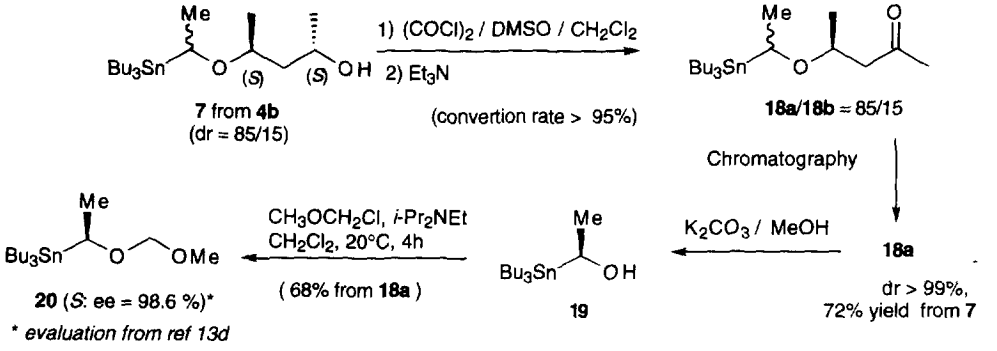


4a **17** (64%)

In order to rationalise our results, the absolute configuration of the new asymmetric centre was firmly established on compounds **7a** and **7b** (entries 3, 7 and 13) after transformation of their adducts into α-stannylalcohols *via* a conventional oxidation-elimination sequence. For example, oxidation of a mixture

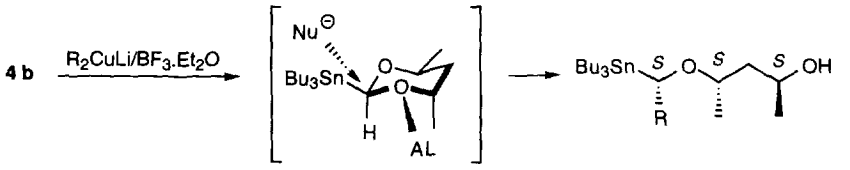
7a/7b = 85/15 (from **4b**, entry 13) using the Swern protocol[27] led to a mixture of ketones (**18a/18b** = 85/15) in which the major isomer **18a** was isolated in 72% yield with a purity above 99% (undetectable doublet at 1.10 ppm using 400 MHz ^{1}H NMR) by careful liquid chromatography on silica gel (eluent : hexane/ether = 90/10). The treatment of **18a** with potassium carbonate in methanol gave the unstable 1-tributylstannylethanol **19** which was transformed into its MOM derivative **20** as depicted in scheme 4.

Scheme 4 :



The absolute configuration of **20** was established as (*S*) by comparison of the optical rotation $[\alpha]_D^{20}$ = +34.8° (c = 1.09, $CHCl_3$) with the reported value for the (*R*) derivative in 91% enantiomeric excess ($[\alpha]_D^{20}$ = - 32.1°; c = 1.1, $CHCl_3$)[13d]. For the practitioner, it is worth noticing that the epimerisation of the newly created chiral centre was avoided when the conversion of **18a** into **19** was performed at 15°C. This result is in agreement with those reported by NAKAI[25] but mild experimental conditions are required since partial epimerisation was observed when the reaction was performed above 30°C. Therefore, taking into account the possible separation of the diastereomeric alcohols **7a** and **7b** or of the ketones **18a** and **18b** by liquid chromatography, **the above procedure has been proved to be efficient enough to obtain compounds 19 and 20 with enantiomeric excess above 98%.** Concerning the mechanism of the reaction, the stereochemical outcome (*S,S*)-**4b** -> (*S,S,S*)-**7** is in agreement with previous reports related to non-stannylated 1,3-dioxanes[22, 23], the overall result being an *anti* attack of the nucleophile after complexation of boron trifluoride on the less hindered oxygen of the acetal function (*cf* scheme 5).

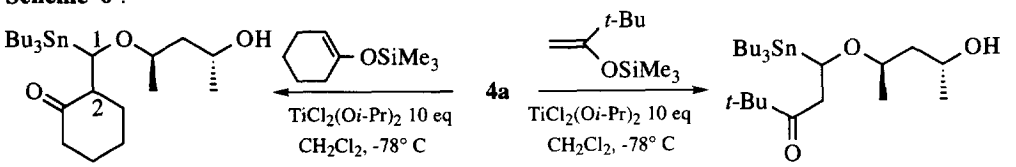
Scheme 5 :



Organoaluminium and organocuprate reagents (entries 3 and 7) give opposite diastereoselectivities indicating that two different transition states are involved. Contrary to organocuprates associated with BF_3, organoaluminium halides coordinate the less hindered oxygen atom, near the axial methyl group, but transfer the R group in a *syn* fashion. On the other hand, and referring to previous results related to organic acetals, reaction in the presence of titanium catalysts is expected to react like R_2CuLi/BF_3 (*anti* process).

Due to the immolative character of the method towards the chiral diol, we decided to extend this method to the synthesis of α-alkoxyallyltins which are known to give, after reaction, vinylether adducts[7] or after isomerisation γ-alkoxyallyltins[28] in order to recover the chiral diol after reaction of the enantioenriched organotin. Unfortunately, attempted reaction of lithium divinylcuprate / $BF_3.Et_2O$ with **4a**, at -78°C in ether, did not lead to the expected allyltin. Nevertheless, according to the results of Quayle[29] concerning the possibility to make enolates bearing both tin and alkoxy groups in β-position without β-elimination occurring, we tested the reactivity of α-stannylacetals towards silyl enol ethers in order to reach α- and γ-dialkoxyallyltin derivatives. Reaction of pinacolone or cyclohexanone silyl enol ethers[30] with **4a** under Lewis acid catalysis affords the functionalised adducts **21** and **22** with diastereoisomeric ratios near 82/18 for the acetal opening (scheme 6).

Scheme 6 :

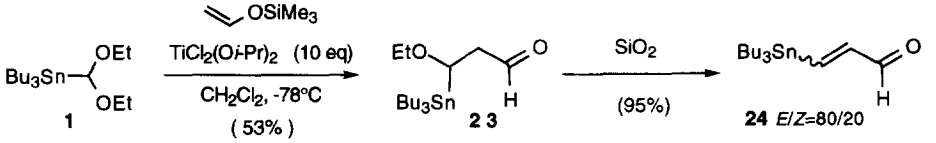


22 dr = 83/17 (C_1 related to diol) (59%)
dr = 50/50 (C_2 related to C_1)

(56%) **21** dr = 81/19

Reaction between vinyloxytrimethylsilane[31] and diethoxymethyltributyltin **1** afforded the unstable aldehyde **23** in 53% yield which gave β-tributylstannylacroleine **24** during the purification step (scheme 7), as already observed for β-tributylstannyl α,β-unsaturated ketones.[32] Similarly, when the conversion of aldehyde **23** into silyl enol ether was attempted, once more **24** was obtained as the product.

Scheme 7 :

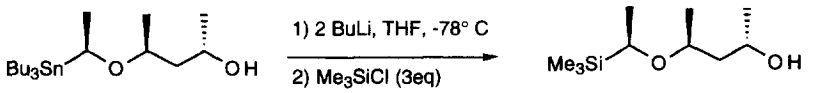


1 (53%) **2 3** **24** *E/Z*=80/20

Under the same experimental conditions, reaction of vinyloxytrimethylsilane with acetal **4b** led to the oxydo-reduction product **17** instead of the expected aldehyde.

Finally, we decided to confirm the fact that α-stannylacetals could be considered as "a C_1 synthon bearing virtual cationic and anionic charges". α-Alkoxyalkyltributyltin **7** was transmetallated with *n*-butyllithium at -78°C and subsequently trapped by chlorotrimethylsilane (scheme 8). α-Alkoxyethyltrimethylsilane **25** was found to have same diastereoisomeric ratio as **7** in agreement with the kwown configurational stability of α-alkoxyalkyllithium reagents.

Scheme 8 :



7a/7b = 88/12 **25a/25b** = 87/13 (74%)

In conclusion, the above results clearly show that selective opening of chiral α-stannylacetals by organometallic reagents associated with Lewis acids can constitute a new route to obtain enantioenriched chiral α-oxygenated organotin compounds. The reaction exhibits a general character and the diastereoselectivity can be controlled using appropriate organometallic systems since R_2CuLi/BF_3 reagents react according to an *anti* mode, while organoaluminium halides react in a *syn* fashion. In spite of its immolative character towards the chiral diol, this method should find several applications as a key step in the synthesis of chiral α-oxygenated anions and subsequently in the total synthesis of natural products.

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Experimental section

All reactions were carried out under inert atmosphere (Ar or N_2). THF and ether were freshly distilled over sodium/benzophenone and CH_2Cl_2 over calcium hydride. Flash chromatographies were performed on silica gel 230-400 mesh. GLC analyses were performed on a Carlo-Erba 4200 instrument (FID detector, fitted with a 25 m x 0.32 mm SE 52 capillary column). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 200 or a Bruker ARX 400 spectrometer. Chemical shifts are given in ppm relative to Me_4Si used as internal standard for ^1H and ^{13}C NMR spectra (solvent = $CDCl_3$), while ^{119}Sn chemical shifts are given referring to Me_4Sn used as external standard (solvent = C_6D_6). Coupling constants are given in Hertz. Mass spectra were obtained on a Hewlett Packard apparatus (engine 5989A) in direct introduction mode (70eV) or in GC/MS mode. The isotopic patterns were given for ^{120}Sn in organotin fragments ; this means that the reported abundances (values in brackets) for organotin fragments are roughly one third of the real abundance if compared with organic fragments. IR spectra were recorded on a Beckman Acculab 2 or a Perkin Elmer 1420 apparatus. Copper salts, organoaluminium reagents and diols are commercially available products from Aldrich. Organolithium reagents are available from Chemetall g.m.b.h.. Silyl enol ethers were prepared according to known procedures[31]. Diethoxymethyltributyltin was obtained at a 0.5 mol scale in over 70% yield by reaction of tributylstannylmagnesium chloride with diethylphenyl orthoformate[33]. Other α-stannylacetals were obtained by transacetalisation of diethoxymethyltributyltin with 2,3- or 2,4-diols under acidic catalysis (compounds **3** and **4** have been already described).[20]

*Elemental analyses : A problem occurs with elemental analyses which exhibit lower values than expected, especially for carbon (lack of 1 to 2 %). While organic impurities might be masked in the ^1H NMR spectra (possible overlapping of signals), decoupled ^{13}C and ^{119}Sn NMR spectra attest of a remarkable purity (no extra signals and perfect observation of ^{117}Sn and ^{119}Sn satellites in ^{13}C NMR spectra). Therefore, we consider that a pollution with microparticles of silica gel eventually associated with traces of water might be responsible for this problem. It means that an inorganic pollution might be involved in range of 1-3 % (with concomitant decrease in the yield) even if the given structures are perfectly established as attested by physicochemical data and by the obtention of **20**, an already known product, at the end of the sequence.*

(*R*,*R*)-2-tributylstannyl-4,5-bis(dimethylformamido)-1,3-dioxolane (2)

To a solution of 3.94 g (10 mmol) of diethoxymethyltributyltin **1** in 100 mL of toluene were added 2.45 g (12 mmol) of N,N,N',N'-tetramethyltartramide and 50 mg of *p*-toluene sulphonic acid. After azeotropic distillation and removal of the solvent, the mixture was heated to 200°C. The reaction was monitored by TLC. After complete disappearance of **1**, the reaction mixture was washed with a 0.1N NaOH solution, extracted with ether (3x50mL) and dried over magnesium sulphate before liquid chromatography using hexane, ethyl acetate, triethylamine 70/29/1 as eluent. **5** was obtained in 59% yield (2.98 g) as a clear colourless oil.

$[\alpha]_D^{22}$ = - 36.7° (c = 3.2, $CHCl_3$). ^1H NMR δ (ppm) : 0.6-1.8 (m, 27H) ; 2.95 (s, 6H) ; 3.15 (s, 3H) ; 3.18 (s, 3H) ; 5.08 and 5.2 (AB system, 2H, $^3J_{1H}$ = 5) ; 5.3 (s, 1H, $^2J_{Sn-H}$ = 90-94). ^{13}C NMR δ (ppm) : 9.2 (3C, $^1J_{Sn-C}$ = 314-329) ; 13.7 (3C) ; 27.25 (3C, $^3J_{Sn-C}$ = 49.5) ; 28.9 (3C, $^2J_{Sn-C}$ = 20.5) ; 35.9 (2C) ; 37.1 ; 37.2 ; 75.4 ; 77.9 ; 108.6 ; 167.7 ; 169.8. MS (70eV) organotin fragments : m/z = 506 (3) ; 449 (34) ; 393 (3) ; 291 (6) ; 235 (7) ; 177 (13) ; 121 (10). organic fragments : m/z = 215 (11) ; 98 (17) ; 72 (100).

N,N,N',N' tetramethyl-3-(1'-tributylstannylethoxy)-2-hydroxy succinamide (5)
To a solution of 0.506g (1 mmol) of **3** in 15 mL of chloroform cooled to -10°C, were added dropwise 2.5 mL (5 mmol) of trimethylaluminium (2M in hexanes). After stirring from -10° C to 20°C for 16h, the reaction was quenched by 10 mL of 10% NaOH solution. The mixture was extracted with ether (3x15 mL), washed with brine (10mL), dried over magnesium sulphate and concentrated. Flash chromatography using hexane/ethyl acetate (95/5) as eluent gave 0.448g (86% yield) of a 20/80 mixture of diastereoisomers **5a** and **5b**.
MS (70eV) organotin fragments : m/z = 465 (3) ; 406 (4) ; 392 (3) ; 291 (7) ; 235 (12) ; 179 (10) ; 121 (9) ; organic fragments : 142 (7) ; 126 (7) ; 98 (8) ; 72 (100) ; 46 (15) ; 45 (11) ; 44 (24) ; 42 (14) ; 31 (9) ; 27 (34); 15 (30). ***Major isomer* 5b :** ^{1}H NMR δ (ppm) : 0.7-1.8 (m, 30H) ; 2.2 (bd, 1H) ; 2.95 (s, 3H) ; 2.98 (s, 3H) ; 3.12 (s, 3H) ; 3.25 (s, 3H) ; 3.7 (q, 1H, $^{3}J_{3H}$ = 7.3) ; 4.26 (d, 1H, $^{3}J_{1H}$ = 3.3) ; 4.64 (m, 1H). ^{13}C NMR δ (ppm) : 8.75 (3C, $^{1}J_{Sn-C}$ = 295-311) ; 13.7 ; 20.5 ; 27.5 (3C, $^{3}J_{Sn-C}$ = 52) ; 29.2 (3C, $^{2}J_{Sn-C}$ = 22) ; 36 ; 36.6 ; 37 ; 37.5 ; 70.6 ($^{3}J_{Sn-C}$ = 72) ; 73.8 ($^{1}J_{Sn-C}$ = 372-388) ; 83 ; 171.1 (2C). ***Minor isomer* 5a** : ^{1}H NMR δ (ppm) : 0.7-1.8 (m, 30H) ; 2.15 (1H $_{hydroxyl}$) ; 2.95 (s, 3H) ; 2.98 (s, 3H) ; 3.12 (s, 3H) ; 3.24 (s, 3H) ; 3.8 (q, 1H, $^{3}J_{3H}$ = 7.3) ; 4.57 (d, 1H, $^{3}J_{1H}$ = 3.7) ; 4.64 (m, 1H). ^{13}C NMR δ (ppm) : 8.75 (3C, $^{1}J_{Sn-C}$ = 295-311) ; 13.7 (3C) ; 18.9 ; 27.5 (3C, $^{3}J_{Sn-C}$ = 52) ; 29.2 (3C, $^{2}J_{Sn-C}$ = 22) ; 36 ; 36.4 ; 37.1 ; 37.5 ; 70.2 ; 78.5 ; 83 ; 170.2

N,N,N',N'-tetramethyl-3-(1'-tributylstannylpropoxy)-2-hydroxy succinamide (6)
The detailed procedure described for **5** was employed. Reaction of **2** with diethylaluminium chloride (3 eq) gave 0.525 g of **6a** and **6b** (98% yield) in a 14/86 ratio. ***Major isomer* 6b :** ^{1}H NMR δ (ppm) : 0.7-2 (m, 32H) ; 2.95 (s, 3H) ; 3 (s, 3H) ; 3.1 (s, 3H) ; 3.25 (s, 3H) ; 3.7 (t, 1H, $^{3}J_{2H}$ = 6.3) ; 3.8 (bd, 1H $_{hydroxyl}$, $^{3}J_{1H}$ = 6.7) ; 4.27 (d, 1H, $^{3}J_{1H}$ = 3.5) ; 4.65 (dd, 1H, $^{3}J_{1H}$ = 3.5, $^{3}J_{1H}$ = 6.7). ^{13}C NMR δ (ppm) : 8.9 (3C, $^{1}J_{Sn-C}$ = 293-305) ; 11.3 ; 13.1 ; 26.9 (3C, $^{3}J_{Sn-C}$ = 54.4) ; 27.2 ; 28.7 (3C, $^{2}J_{Sn-C}$ = 22.4) ; 35.3 ; 35.7 ; 36.3 ; 36.7 ; 70.3 ; 80.4 ; 82.1 ; 170.1 ; 170.6. ***Minor isomer* 6a :** (meaningful signals) ^{1}H NMR δ (ppm): 4.3 (d, 1H, $^{3}J_{1H}$ = 4.2); 4.72 (dd, 1H, $^{3}J_{1H}$ = 4.5, $^{3}J_{1H}$ = 5.8). ^{13}C NMR δ (ppm) : 68.9; 84.2; 169.1; 169.6

4-(1'-tributylstannylethoxy)-pentan-2-ol (7) from methylaluminium dichloride
To a solution of 0.406 g (1 mmol) of **4a** in 15 mL of CH_2Cl_2 cooled to -30°C, were added dropwise 4 mL (4 mmol) of methylaluminium dichloride (1M in hexanes). After slow warming up to room temperature and further stirring for 16h, the reaction was quenched by 10 mL of a saturated aqueous solution of NH_4Cl. The mixture was then extracted with ether (3x15 mL), washed with brine (10 mL), dried over magnesium sulphate and concentrated. Flash chromatography using hexane/ether (95/5) as eluent gave 0.346g (82% yield) of a 30/70 mixture of diastereoisomers **7a** and **7b**. MS (70eV) organotin fragments : m/z = 365 (2) ; 321 (5) ; 291 (2) ; 235 (6) ; 179 (9) ; 177 (10) ; 121 (9). Organic fragments : m/z =131 (3) ; 87 (6) ; 69 (22) ; 57 (5) ; 45 (100) ; 43 (23) ; 41 (22). IR : 3436 (OH) ; 2871 ; 2854 ; 1465 ; 1376 ; 1056.
***Minor isomer* 7a** (*RRR*). ^{1}H NMR δ (ppm) : 0.6-1.7 (m, 27H) ; 1.17 (d, 3H, $^{3}J_{1H}$ = 5.8) ; 1.22 (d, 3H, $^{3}J_{1H}$ = 6.2) ; 1.5 (d, 3H, $^{3}J_{1H}$ = 7.4) ; 1.75 (m, 2H) ; 3.3 (bs, 1H $_{hydroxyl}$) ; 3.7 (m, 1H) ; 3.96 (q, 1H, $^{3}J_{3H}$ = 7.4) ; 4.1 (m, 1H). ^{13}C NMR δ (ppm) : 8.8 (3C, $^{1}J_{Sn-C}$ = 287-300) ; 13.7 (3C) ; 19.3 ; 21.7 ; 23.7 ; 27.5 (3C, $^{3}J_{Sn-C}$ = 53) ; 29.3 (3C, $^{2}J_{Sn-C}$ = 20.2) ; 44.3 ; 64.3 ; 69.7 ($^{1}J_{Sn-C}$ = 390-407) ; 74.1 ($^{3}J_{Sn-C}$ = 21). ^{119}Sn NMR δ (ppm) : -35.6. ***Major isomer* 7b** (*SRR*) ^{1}H NMR δ (ppm): 0.6-1.7 (m, 27H) ; 1.17 (d, 3H, $^{3}J_{1H}$ = 5.8) ; 1.22 (d, 3H, $^{3}J_{1H}$ = 6.2) ; 1.5 (d, 3H, $^{3}J_{1H}$ = 7.4) ; 1.75 (m, 2H) ; 3.48 (bs, 1H $_{hydroxyl}$); 3.7 (m, H) ; 3.95 (q, 1H, $^{3}J_{3H}$ = 7.1); 4.1 (m, H). ^{13}C NMR δ (ppm) : 8.7 (3C, $^{1}J_{Sn-C}$ = 291-306) ; 13.7 (3C) ; 18.8 ; 19.8 ; 23.3 ; 27.5 (3C, $^{3}J_{Sn-C}$ = 53) ; 29.3 (3C, $^{2}J_{Sn-C}$ = 21) ; 43.9 ; 64.7 ; 67.5 ($^{1}J_{Sn-C}$ = 390-408) ; 71.6 ($^{3}J_{Sn-C}$ = 32.4). ^{119}Sn NMR δ (ppm) : - 35.3.

4-(1'-tributylstannylpropoxy)-pentan-2-ol (8) from diethylaluminium chloride
To a solution of 0.406g (1 mmol) of **4** in 15 mL of CH_2Cl_2 cooled to -10°C, were added dropwise 2.2 mL (2.2 mmol) of diethylaluminium chloride (1M in hexanes). After stirring from -10°C to 20°C for 12h, the reaction was quenched by addition of 10mL of a saturated solution of NH_4Cl. The mixture was then extracted with ether (3x15 mL), washed with brine (10 mL), dried over magnesium sulphate and concentrated. Flash chromatography using hexane/ether (95/5) as eluent gave 0.392 g (90% yield) of a 35/65 mixture of diastereoisomers **8a** and **8b**. GC/MS (70eV) organotin fragments : m/z = 379 (2) ; 321 (9) ; 291 (4) ; 235 (10); 179 (17) ; 177 (16) ; 121 (12) ; organic fragments : m/z =145 (5) ; 103 (8) ; 87 (27) ; 69 (53) ; 59 (64) ; 45 (100) ; 43 (18) ; 41 (29) ; 31 (17) ; 29 (28) ; 27 (15). IR :3437 (broad) ; 2872 ; 1463 ; 1418 ; 1309 ;

1377. ***Major isomer* 8b** ^{1}H NMR δ (ppm) : 0.8-1.7 (m, 28H) ; 0.95 (t, 3H, $^3J_{2H}$ = 7.4) ; 1.17 (d, 3H, $^3J_{1H}$ = 6.1) ; 1.22 (d, 3H, $^3J_{1H}$ = 6.2) ; 1.8 (m, 3H) ; 3.5 (bs, 1H) ; 3.7 (m, 1H) ; 3.9 (t, 1H, $^3J_{2H}$ = 6.2) ; 4.15 (m, 1H). ^{13}C NMR δ (ppm) : 9.1 (3C, $^1J_{Sn-C}$ = 284-297) ; 12.4 ($^3J_{Sn-C}$ = 32.8) ; 13.5 (3C) ; 18.5 ; 23.5 ; 27.3 (3C, $^3J_{Sn-C}$ = 54.2) ; 28.5 ; 29.1 (3C, $^2J_{Sn-C}$ = 19.4) ; 44.1 ; 64.1 ; 73.9 ($^3J_{Sn-C}$ = 15.6) ; 76.7 ($^1J_{Sn-C}$ = 387.5-405.9). ^{119}Sn NMR δ (ppm) :- 37.7. ***Minor isomer* 8a** : (meaningful signals) ^{1}H NMR δ (ppm) : 3.3 (d, 1H, $^3J_{1H}$ = 3.4). ^{13}C NMR δ (ppm) : 43.9 ; 64.4 ; 72.5 ; 75.4. ^{119}Sn NMR δ (ppm) : - 35.1

4-(1'-tributylstannylalkoxy)-pentan-2-ols from orgonocopper reagents
General procedure for **7**:
In a flame dried Schlenk tube were added dropwise, at -30°C, 6 mmol of a methyllithium solution, to a suspension of 0.588 mg (3 mmol) of copper iodide in diethyl ether (30mL). After stirring for 30 min, the resulting mixture was cooled to -78°C and (3 mmol) 0.37 mL of boron trifluoride etherate were added. After stirring for 5 min, 0.406 g (1 mmol) of tinacetal **4a** was added (syringe method). After further stirring at -60°C for 2h, the reaction was quenched by addition of 10 mL of saturated solution of NH_4Cl. The mixture was then extracted with diethyl ether (3x15 mL), washed with brine (10 mL), dried over magnesium sulphate and concentrated. Flash chromatography using hexane/ether (95/5) as eluent gave 0.409g (97% yield) of a 85/15 mixture of diastereoisomers **7a** and **7b** already described (*vide supra*).
Other complementary attempts have been done using similar experimental procedure but with modifications mentioned in table I (temperature).

4-(1'-tributylstannyl benzyloxy)-pentan-2-ol (9)
The detailed procedure described for **7** was employed. Reaction of **4** (1 mmol) with lithium diphenylcuprate (3 eq) gave 0.300g (62% yield) of a 85/15 mixture of diastereoisomers **9a** and **9b**.
***Major isomer* 9a** : ^{1}H NMR δ (ppm) : 0.6-2 (m, 29H) ; 1.15 (d, 3H, $^3J_{1H}$ = 6.1) ; 1.2 (d, 3H, $^3J_{1H}$ = 6.1); 3.45 (d, 1H $_{hydroxyl}$, $^3J_{1H}$ = 2.5) ; 3.75 (m, 1H) ; 4.15 (m, 1H) ; 4.96 (s, 1H, $^2J_{Sn-H}$ = 31.5) ; 6.7-7.5 (m, 5H). ^{13}C NMR δ (ppm) : 13.6 (3C, $^1J_{Sn-C}$ = 211-238) ; 16 (3C) ; 20.9 ; 23.2 ; 27.1 (3C) ; 27.8 (3C) ; 46.4 ; 63.7 ; 65.3 ($^3J_{Sn-C}$ = 30.4) ; 69.1; 128.42 (2C) ; 129.4 ; 129.7 (2C) ; 133.2. ***Minor isomer* 9b** : ^{1}H NMR δ (ppm) : meaningful signals 3.35 (bd, 1H, $^3J_{1H}$ = 2.1) ; 4.8 (s, 1H, $^2J_{Sn-H}$ = 31.1). ^{13}C NMR δ (ppm) : 13.6 (3C, $^1J_{Sn-C}$ = 255) ; 16 (3C) ; 22.7 ; 23.4 ; 27.1 ; 27.8 ; 45.8 ; 63.7 ; 65.3 ; 68.35 ; 128.4 (2C) ; 129.4 ; 129.7 (2C) ; 133.2

4-(1'-tributylstannylpentoxy)-pentan-2-ol (10)
The detailed procedure described for **7** was employed. Reaction of **4b** (1 mmol) with lithium di-*n*-butylcuprate (3 eq) gave 0.311g (67% yield) of a 81/19 mixture of diastereoisomers **10a** and **10b**.
MS (70eV) organotin fragments : m/z = 407 (3) ; 321 (18) ; 291 (10) ; 251 (4) ; 235 (24) ; 179 (27) ; 177 (27) ; 121 (15) ; organic fragments : m/z =173 (9) ; 131 (6) ; 115 (20) ; 87 (65) ; 69 (100) ; 45 (44) ; 43 (10) ; 41 (14). ***Major isomer* 10a** : ^{1}H NMR δ (ppm) : 0.8-1.5 (m, 36H) ; 1.1 (d, 3H, $^3J_{1H}$ = 6.1) ; 1.15 (d, 3H, $^3J_{1H}$ = 6.3) ; 1.5-1.75 (m, $2H_7$) ; 3.42 (bd, 1H $_{hydroxyl}$, $^3J_{1H}$ = 2.1) ; 3.6 (m, 1H) ; 3.87 (t, 1H,$^3J_{2H}$ = 6.3) ; 4.05 (m, 1H). ^{13}C NMR δ (ppm) : 9.2 (3C, $^1J_{Sn-C}$ = 283-296) ; 13.5 (3C) ; 13.9 ; 18.4 ; 22.6 ; 23.5 ; 27.4 (3C, $^3J_{Sn-C}$ = 53) ; 29.1 (3C, $^2J_{Sn-C}$ = 20) ; 30.2 ($^3J_{Sn-C}$ = 33) ; 35.4 ; 44.3 ; 64.1 ; 73.9 ($^3J_{Sn-C}$ = 14.5) ; 75.1 ($^1J_{Sn-C}$ = 389-407). ^{119}Sn NMR δ (ppm) : - 37.2. ***Minor isomer* 10b** : (meaningful signals). ^{1}H NMR δ (ppm) : 0.8-1.8 (m, 44H) ; 3.39 (bd, 1H $_{hydroxyl}$, $^3J_{1H}$ = 3) ; 3.6 (m, 1H) ; 3.88 (t, 1H, $^3J_{2H}$ = 6.1) ; 4.05 (m, H). ^{13}C NMR δ (ppm) : 8.9 (3C) ; 18.7 ; 22.7 ; 23.2; 43.9 ; 64.3. ^{119}Sn NMR δ (ppm) : - 36.5

4-(1'-tributylstannyl-2',2'-dimethylpropoxy)-pentan-2-ol (11)
The detailed procedure described for **7** was employed. Reaction of **4b** (1 mmol) with lithium di*t*-butylcuprate (3 eq) gave 0.315g (68% yield) of a 78/22 mixture of diastereoisomers **11a** and **11b**. MS (70eV) organotin fragments : m/z = 407 (1) ; 321 (7) ; 291 (5) ; 235 (11) ; 179 (15) ; 177 (14) ; 121 (8) ; organic fragments : m/z =173 (10) ; 115 (26) ; 103 (11) ; 87 (100) ; 69 (81) ; 45 (32). ***Major isomer* 11a** : ^{1}H NMR δ (ppm) : 0.8-1.6 (m, 27H) ; 0.9 (s, 9H) ; 1.15 (d, 3H, $^3J_{1H}$ = 5.9) ; 1.2 (d, 3H, $^3J_{1H}$ = 5.9) ; 1.6 (m, 1H) ; 1.8 (m, 1H) ; 3.55 (s, 1H, $^2J_{Sn-H}$ = 11.9) ; 3.6 (m, 1H) ; 3.85 (bs, 1H $_{hydroxyl}$) ; 4 (m, 1H). ^{13}C NMR δ (ppm) : 10.8 (3C, $^1J_{Sn-C}$ = 277-287) ; 13.6 (3C) ; 17 ; 23.5 ; 27.5 (3C, $^3J_{Sn-C}$ = 47-66) ; 28.3 (3C, $^3J_{Sn-C}$ = 29) ;

29.2 (3C, $^2J_{Sn-C}$ = 19) ; 36.1 ($^2J_{Sn-C}$ = 8.4) ; 43.9 ; 63.8 ; 73.2 ; 87.2 ($^1J_{Sn-C}$ = 399-418). ^{119}Sn NMR δ (ppm) : - 37.4. ***Minor isomer*** **11b** : ^{1}H NMR δ (ppm) : 0.8-1.6 (m, 27H) ; 0.9 (s, 9H) ; 1.15 (d, 3H, $^3J_{1H}$ = 5.9); 1.2 (d, 3H, $^3J_{1H}$ = 5.9); 1.6 (m, 1H) ; 1.8 (m, 1H); 3.42 (bd, 1H $_{hydroxyl}$, $^3J_{1H}$ = 1.5) ; 3.45 (s, 1H, $^2J_{Sn-H}$ = 19.1) ; 3.6 (m, 1H) ; 4.1 (m, 1H). ^{13}C NMR δ (ppm) : 10.6 (3C, $^1J_{Sn-C}$ = 285-298); 13.5 (3C) ; 17.4 ; 23.5 ; 27.5 (3C) ; 28.1 (3C) ; 29.2 (3C) ; 37.5 ($^2J_{Sn-C}$ = 14.5) ; 44.2 ; 64.1 ; 77.1 ; 88.2 ($^1J_{Sn-C}$ = 405-424). ^{119}Sn NMR δ (ppm) : - 38.6

4-(tributylstannylmethoxy)-pentan-2-ol (12)
A procedure similar to those described for **7** was employed. Reaction of **4b** (1 mmol) with magnesium di-*i*-propylcuprate (3 eq, made from copper iodide and *i*-propylmagnesium chloride, 2eq) gave 0.300g (62% yield) of **12**. ^{1}H NMR δ (ppm) : 0.85-1.65 (m, 33H) ; 1.7 (m, 2H) ; 3.3 (bs, 1H $_{hydroxyl}$) ; 3.55 (d, 1H, $^2J_{1H}$ = 9.9, $^2J_{Sn-H}$ = 17.6) ; 3.55 (m, 1H) ; 3.81 (d, 1H, $^2J_{1H}$ = 9.9, $^2J_{Sn-H}$ = 18.2) ; 4.1 (m, 1H). ^{13}C NMR δ (ppm) : 9.2 (3C, $^1J_{Sn-C}$ = 310-324); 14 (3C); 18.4 ; 23.7 ; 27.6 (3C, $^3J_{Sn-C}$ = 51) ; 29.5 (3C, $^2J_{Sn-C}$ = 20); 43.8 ; 59.3 ($^1J_{Sn-C}$ = 347-362) ; 65.2 ; 78.7 ($^3J_{Sn-C}$ = 42). ^{119}Sn NMR δ (ppm) : - 35.3. MS (70eV) organotin fragments : m/z = 351 (24) ; 321 (19) ; 291 (13) ; 235 (44) ; 179 (64) ; 177 (66) ; 121 (37) ; organic fragments : m/z = 117 (17) ; 69 (17) ; 45 (100) ; 43 (17) ; 41 (22) ; 29 (21)

4-(1'-tributylstannylethoxy)-butan-2-ol (13)
The detailed procedure described for **7** was employed. Reaction of **3** (1 mmol) with lithium dimethylcuprate (3 eq) gave 0.314g (77% yield) of a 86/14 mixture of diastereoisomers **13a** and **13b**. MS (70eV) organotin fragments : m/z =351 (16) ; 291 (22) ; 251 (77) ; 235 (41) ; 179 (58) ; 177 (60) ; 135 (9) ; 121 (27) ; organic fragments : m/z =117 (22) ; 73 (100) ; 55 (31) ; 45 (12) ; 29 (9). ***Major isomer*** **13a** : ^{1}H NMR δ (ppm) : 0.8-1.8 (m, 27H) ; 1.1 (d, 3H, $^3J_{1H}$ = 6.3); 1.12 (d, 3H, $^3J_{1H}$ = 6.3) ; 1.5 (d, 1H, $^3J_{1H}$ = 7.4) ; 2.65 (d, 1H$_{hydroxyl}$, $^3J_{1H}$ = 2.2) ; 3 (m, 1H) ; 3.45 (m, 1H) ; 3.95 (q, 1H, $^3J_{3H}$ = 7.4). ^{13}C NMR δ (ppm) : 8.9 (3C, $^1J_{Sn-C}$ = 287-301) ; 13.7 (3C) ; 16.7 ; 18.7 ; 21.8 ; 27.5 (3C, $^3J_{Sn-C}$ = 51) ; 29.3 (3C, $^2J_{Sn-C}$ = 19); 70.8 (C_1, $^1J_{Sn-C}$ = 389-404) ; 71.4 ; 81.1 ($^3J_{Sn-C}$ = 21.3). ^{119}Sn NMR δ (ppm) :- 36.6.
Minor isomer **13** : (meaningful signals) ^{1}H NMR δ (ppm) : 2.75 (d, 1H $_{hydroxyl}$, $^3J_{1H}$ = 1.8) ; 3.95 (q, 1H, $^3J_{1H}$ = 7.2). ^{119}Sn NMR δ (ppm) :- 35.4

4-(1'-tributylstannylpentoxy)-butan-2-ol (14)
The detailed procedure described for **7** was employed. Reaction of **3** (1 mmol) with lithium dibutylcuprate (3 eq) gave 0.310g (69% yield) of a 86/14 mixture of diastereoisomers **14a** and **14b**. GC/MS (70eV) organotin fragments : m/z =393 (4) ; 335 (2) ; 291 (14) ; 251 (44) ; 235 (20) ; 179 (27) ; 177 (26) ; 135 (5) ; 121 (14) ; organic fragments : m/z = 159 (5) ; 87 (5) ; 73 (100) ; 69 (11) ; 55 (21) ; 43 (8) ; 41 (8) ; 29 (5). ***Major isomer*** **14a** : ^{1}H NMR δ (ppm) : 0.9-1.6 (m, 32H) ; 1.1 (d, 3H, $^3J_{1H}$ = 6.5) ; 1.15 (d, 3H, $^3J_{1H}$ = 6.5) ; 1.8 (m, 2H) ; 2.7 (d, 1H $_{hydroxyl}$, $^3J_{1H}$ = 2.5) ; 3.1 (m, 1H) ; 3.5 (m, 1H) ; 4 (dd, 1H, $^3J_{1H}$ = 5.8, $^3J_{1H}$ = 7.2). ^{13}C NMR δ (ppm) : 9.4 (3C, $^1J_{Sn-C}$ = 289-295); 13.7 (3C); 14.1 ; 16.1; 18.7 ; 22.8; 27.5 (3C, $^3J_{Sn-C}$ = 53.4) ; 29.3 (3C, $^2J_{Sn-C}$ = 19.4) ; 30.3 ($^3J_{Sn-C}$ = 32) ; 35.7 ; 71.4 ; 75.8 ($^1J_{Sn-C}$ = 388-407); 80.4 ($^3J_{Sn-C}$ = 15.2). ^{119}Sn NMR δ (ppm) : - 38.6. ***Minor isomer*** **14b** : ^{1}H NMR δ (ppm) : (meaningful signals) : 2.8 (d, 1H$_{hydroxyl}$, $^3J_{1H}$ = 2.3) ; 3.2 (m, 1H) ; 3.5 (m, 1H) ; 3.9 (dd, 1H, $^3J_{1H}$ = 5.3, $^3J_{1H}$ = 7.2).
^{119}Sn NMR δ (ppm) :- 36.3

4-(1'-tributylstannylbut-3',4'-enoxy)pentan-2-ol (15)
To a degassed solution of 0.406 g (1 mmol) of **4b** and 0.483 g (1.5 mmol) of allyltributyltin in 20 mL of CH_2Cl_2 cooled to -78°C, were slowly (2h.) added dropwise 10 mL (10 mmol) of diisopropoxytitanium dichloride (1M in CH_2Cl_2). After stirring for 1h, the reaction was quenched by addition of 10 mL of 1N NaOH solution. The mixture was then extracted with ether (3x15 mL), washed with brine (10 mL), dried over magnesium sulphate and concentrated. Flash chromatography using hexane/ethyl acetate (95/5) as eluent gave 0.425 g (95% yield) of a 93/7 mixture of diastereoisomers **15a** and **15b**. MS (70eV) organotin fragments : m/z =391 (8) ; 321 (41) ; 291 (18) ; 251 (12) ; 235 (50) ; 179 (63) ; 177 (61) ; 135 (8) ; 121 (35) ; organic fragments : m/z = 157 (4) ; 99 (15) ; 87 (29) ; 71 (71) ; 69 (76) ; 45 (100) ; 43 (36) ; 41 (28) ; 29 (14). ***Major isomer*** **15a** : ^{1}H NMR δ (ppm) : 0.7-1.9 (m, 35H) ; 2.55 (m, 2H) ; 3.42 (d, 1H $_{hydroxyl}$, $^3J_{1H}$ = 1.7) ; 3.7 (m, 1H) ; 4.0 (dd, 1H, $^3J_{1H}$ = 5, $^3J_{1H}$ = 5.7) ; 4.1 (m, 1H) ; 5.05 (m, 2H) ; 5.77 (m,

1H). ^{13}C NMR δ (ppm) : 9.1 (3C, $^{1}J_{Sn-C}$ = 287-295) ; 13.2 (3C) ; 17.9 ; 22.5 ; 26 (3C, $^{3}J_{Sn-C}$ = 53.4) ; 27.6 (3C, $^{2}J_{Sn-C}$ = 19.7) ; 37.9 ; 42 ; 60.1 ; 69.4 ; 69.5 ; 108.8 ; 128.2.
***Minor isomer* 15b** : ^{1}H NMR δ (ppm) : (meaningful signal) : 3.2 ($^{3}J_{1H}$ = 3.3).

4-(1'-tributylstannyl 2'-methylbut-3',4'-enoxy)pentan-2-ol (16)
The detailed procedure described for **15** was employed starting from **4b** (1 mmol) and crotyltributyltin (1.5 mmol). Flash chromatography using hexane/ethyl acetate (95/5) as eluent gave 0.388 g (84% yield) of a 85/15 mixture of diastereoisomers **16a** and **16b**. On the four theoretical diastereoisomers, only two were detectable certainly corresponding to the *syn* and *anti* products of the created C-C bond in the α,β-position to the tin atom. When $BF_3.Et_2O$ was used as Lewis acid, a 70/30 mixture of diastereoisomers **16a** and **16b** was obtained. MS (70eV) organotin fragments : m/z = 321 (32) ; 291 (22) ; 251 (17) ; 235 (56) ; 179 (61) ; 177 (61) ; 135 (7); 121 (24) ; organic fragments : m/z = 171 (5) ; 137 (7) ; 113 (13) ; 103 (12) ; 95 (3) ; 87 (32) ; 85 (65) ; 69 (100) ; 45 (66) ; 43 (79) ; 41 (20) ; 29 (9). IR 3460 (broad) ; 2848 ; 1640 ; 1450 ; 1440 ; 1405 ; 1350 ; 1110 ; 900 ; 650. ***Major isomer* 16a** : ^{1}H NMR δ (ppm) : 0.7-1.8 (m, 29H) 0.95 (d, 3H, $^{3}J_{1H}$ = 7.1) ; 1.05 (d, 3H, $^{3}J_{1H}$ = 6.2) ; 1.15 (d, 3H, $^{3}J_{1H}$ = 6.2) ; 2.55 (m, 1H) ; 3.5 (d, 1H $_{hydroxyl}$, $^{3}J_{1H}$ = 0.8) ; 3.6 (m, 1H) ; 3.8 (d, 1H, $^{3}J_{1H}$ = 4.6, $^{2}J_{Sn-H}$ = 4.7) ; 4.05 (m, 1H) ; 5.13 (m, 2H) ; 5.72 (ddd, 1H, $^{3}J_{1H}$ = 7, $^{3}J_{1H}$ = 10.3, $^{3}J_{1H}$ = 17.3). ^{13}C NMR δ (ppm) : 10 (3C, $^{1}J_{Sn-C}$ = 284-297) ; 12.9 (3C) ; 17.1 ($^{3}J_{Sn-C}$ = 16.1) ; 17.9 ; 23.5 ; 27.5 (3C, $^{3}J_{Sn-C}$ = 55.9) ; 29.2 (3C, $^{2}J_{Sn-C}$ = 19.7); 42.7 ; 44 ; 63.9 ; 74.1 ($^{3}J_{Sn-C}$ = 11) ; 80.2 ($^{1}J_{Sn-C}$ = 381-397) ; 113.7 ; 142.8 ($^{3}J_{Sn-C}$ = 32). ***Minor isomer* 16b** : (meaningful signals). ^{1}H NMR δ (ppm) : 1 (d, $3H_3$, $^{3}J_{1H}$ = 7) ; 3.47 (d, $1H_{hydroxyl}$, $^{3}J_{1H}$ = 1.6) ; 3.6 (d, 1H, $^{3}J_{1H}$ = 6.3) ; 5.7 (ddd, 1H, $^{3}J_{1H}$ = 7, $^{3}J_{1H}$ = 10.2, $^{3}J_{1H}$ = 17.2). ^{13}C NMR δ (ppm) : 80.3 ; 114.4 ; 141.6

4-(tributylstannylmethoxy)-pentan-2-one (17)
To a solution of 1.5 mL (3 mmol) of trimethylaluminium (2M in hexanes) in 15 mL of toluene cooled to -10°C, were added dropwise 1.5 mL (3 mmol) of pentafluorophenol (2M in toluene). After stirring at 20°C for 2h, 0.203 g (0.5mmol) of **4a** in toluene solution (2mL) was added dropwise. After stirring for 4h., the reaction was quenched by addition of 10 mL of 1N NaOH solution. The mixture was then extracted with ether (3x15 mL), washed with brine (10 mL), dried over magnesium sulphate and concentrated. Flash chromatography using hexane/ether (95/5) as eluent gave 0.129 g (64% yield) of **17**. GC/MS (70eV) organotin fragments : m/z = 349 (1) ; 307 (2) ; 235 (8) ; 179 (38) ; 177 (41) ; 121 (35) ; organic fragments : m/z = 115 (19) ; 85 (6) ; 73 (12) ; 69 (20) ; 43 (100) ; 29 (10). IR 1718 ($\nu_{C=O}$) ; 1334 ; 1155. ^{1}H NMR δ (ppm) : 0.7-1.7 (m, 27H) ; 1.14 (d, 3H, $^{3}J_{1H}$ = 6) ; 2.15 (s, 3H) ; 2.35 (dd, 1H, $^{2}J_{1H}$ = 14.7, $^{3}J_{1H}$ = 5) ; 2.55 (dd, 1H, $^{2}J_{1H}$ = 14.7, $^{3}J_{1H}$ = 7.1) ; 3.5 and 3.75 (AB system , 2H, $^{2}J_{1H}$ = 9.5) ; 3.6 (m, 1H). ^{13}C NMR δ (ppm) : 8.7 (3C, $^{1}J_{Sn-C}$ = 309-323) ; 13.5 (3C) ; 18.6 ; 27.1 (3C, $^{3}J_{Sn-C}$ = 51.5) ; 28.9 ($^{2}J_{Sn-C}$ = 20.7) ; 30.9 ; 50.3 ; 58.5 ($^{1}J_{Sn-C}$ = 356-372) ; 76.1 ($^{3}J_{Sn-C}$ = 46.1) ; 207.6. ^{119}Sn NMR δ (ppm) :- 35.6

4-(1'-tributylstannylethoxy) pentan-2-one (18)
A 100mL two necks flask was charged with 0.38 mL of oxalyl chloride (4.37 mmol) and 8 mL of CH_2Cl_2 under an argon stream. After cooling to -60°C, the solution was degased, and 0.62 mL of DMSO (8.73 mmol) in CH_2Cl_2 (2 mL) were slowly added. The solution was stirred for 30 min at -60°C before addition of 1.42 g (3.36 mmol) of **7**[34] (obtained from **4b**) in CH_2Cl_2 (3.5 mL). After further stirring for 1h at -60°C, 2.43 mL of triethylamine were added before hydrolysis with aqueous NH_4Cl solution (T = -60°C).The reaction mixture was allowed to warm up to 20°C and extracted with CH_2Cl_2 (3x25mL), dried over magnesium sulphate and concentrated. The expected ketones were obtained as a crude mixture (1.39 g) and separated by liquid chromatography using hexane/ether (90/10) as eluent (Rf_{18a} = 0.53, Rf_{18b} = 0.47). Under similar experimental conditions, using flash chromatography, **18a** was obtained as a pure product (1.02 g, 72% yield, $[\alpha]_D^{20}$ = + 33.4°, c = 0.90, $CHCl_3$). MS (70eV) organotin fragments : m/z = 363 (3) ; 319 (18) ; 291 (4) ; 235 (34) ; 205 (4) ; 179 (73) ; 177 (73) ; 121 (34) ; organic fragments : m/z =129 (27) ; 87 (31) ; 85 (36) ; 43 (100); 41 (7). ***Major isomer* 18a** : ^{1}H NMR δ (ppm) : 0.8-1.6 (m, 27H) ; 1.15 (d, 3H, $^{3}J_{1H}$ = 6.1) ; 1.46 (d, 3H, $^{3}J_{1H}$ = 7.4) ; 2.15 (s, 3H) ; 2.4 (dd, 1H, $^{2}J_{1H}$ = 15.6, $^{3}J_{1H}$ = 6.1) ; 2.68 (dd, 1H, $^{2}J_{1H}$ = 15.6, $^{3}J_{1H}$ = 6.5) ; 3.82 (m, 1H) ; 3.88 (q, 1H,$^{3}J_{3H}$ = 7.4). ^{13}C NMR δ (ppm) : 8.67 (3C, $^{1}J_{Sn-C}$ = 288-302) ; 13.6 (3C) ; 20.8 ; 21.2 ($^{2}J_{Sn-C}$ = 5) ; 27.4 (3C, $^{3}J_{Sn-C}$ = 51.1-53.4) ; 29.15 (3C, $^{2}J_{Sn-C}$ = 19.8) ; 31.2 ; 50.9 ; 69.3 ($^{1}J_{Sn-C}$ = 400-419) ; 71.5 ($^{3}J_{Sn-C}$ = 27.5) ; 207.3. ^{119}Sn NMR δ (ppm) :- 36.7. ***Minor isomer* 18b** : ^{1}H NMR δ (ppm) : 0.8-1.6 (m, 27H) ; 1.10 (d, 3H, $^{3}J_{1H}$ = 6.1) ; 1.39 (d, 3H, $^{3}J_{1H}$ = 7.3) ; 2.16 (s, 3H) ; 2.37 (dd, 1H, $^{2}J_{1H}$ = 14.6, $^{3}J_{1H}$ = 5.3) ; 2.64 (dd, 1H, $^{2}J_{1H}$ = 14.6, $^{3}J_{1H}$ = 7.3) ; 3.8 (m, 1H) ; 3.85 (q, 1H,

$^3J_{3H}$ = 7.3). ^{13}C NMR δ (ppm) : 8.52 (3C, $^1J_{Sn-C}$ = 292-307) ; 13.6 (3C) ; 19.65 ; 27.4 (3C, $^3J_{Sn-C}$ = 51-53) ; 29.1 (3C, $^2J_{Sn-C}$ = 20) ; 31.35; 51.0 ; 67.2 ($^1J_{Sn-C}$ = 407-426) ; 69.83 ($^3J_{Sn-C}$ = 34) ; 208.03. ^{119}Sn NMR δ (ppm) : - 36.0

1-tributylstannyl-ethanol (19)
To a solution of 0.430g (1.026 mmol) of **18a** in 8 mL of methanol (HPLC grade) was added 1.32 g of potassium carbonate. The reaction mixture was stirred at 15°C for 4h, then quenched by addition of H_2O (20 mL). The mixture was then extracted with ether (5x20 mL), washed with brine (10 mL), dried over magnesium sulphate and concentrated under vacuum (0.1mm Hg). Due to its instability, the crude product **19** was used in the next step without further purification. ^1H NMR δ (ppm) (crude) : 0.8-1.8 (m, 27H) ; 1.4 (d, 3H, $^3J_{1H}$ = 7.2) ; 4 (q, 1H, $^3J_{3H}$ = 7.2).

1-methoxymethoxy-1-tributylstannylethane (20)
To a solution of crude **19** (0.330 g obtained from **18a**) in 5 mL of dry CH_2Cl_2 were successively added dropwise 0.357 mL of *i*-Pr_2NEt (2.05 mmol) and 0.117 mL of methoxymethylchloride (1.54 mmol). After stirring at 15°C for 14h, the reaction was quenched by addition of water (5 mL). The mixture was then extracted with ether (3x20 mL), washed with brine (10 mL), dried over magnesium sulphate and concentrated. Flash chromatography using hexane/ether (90/10) as eluent gave 0.265 g of pure **20** (68% yield from **18a**). $[\alpha]_D^{20}$ = + 34.8° (c = 1.10, $CHCl_3$). MS (70eV) organotin fragments : m/z = 323 (22) ; 291 (30) ; 235 (62); 179 (90); 177 (85); 121 (49); organic fragments : m/z = 89 (12); 59 (7); 45 (100); 29 (8). ^1H NMR δ (ppm) : 0.8-1.6 (m, 27H) ; 1.42 (d, 3H, $^3J_{1H}$ = 7.5) ; 3.35 (s, 3H) ; 4.09 (q, 1H, $^3J_{3H}$ = 7.5, $^2J_{Sn-H}$ = 5.3) ; 4.55 (1H, $^2J_{1H}$ = 6.6, $^4J_{Sn-H}$ = 2.6) and 4.67 (1H, $^2J_{1H}$ = 6.6, $^4J_{Sn-H}$ = 1.7). ^{13}C NMR δ (ppm) : 8.88 (3C, $^1J_{Sn-C}$ = 294-307); 13.5 (3C); 20.6 ; 27.7 (3C, $^3J_{Sn-C}$ = 53); 29.4 (3C, $^2J_{Sn-C}$ = 20.2); 55.4 ; 68.1 ($^1J_{Sn-C}$ = 389-407) ; 95.9 ($^3J_{Sn-C}$ = 24.4). ^{119}Sn NMR δ (ppm) : - 34.2

1-[(3'-hydroxy-1'-methyl)-butoxy]-1-tributylstannyl-4,4-dimethyl-pentan-3-one (21)
To a solution of 0.203 g (0.5 mmol) of **4a** and 0.172 g (1 mmol) of 3,3-dimethyl-2-trimethylsilyloxybut-1-ene in 20 mL of CH_2Cl_2 cooled to -78°C were slowly added (2h) 10 mL of $TiCl_2(O$*i*$-Pr)_2$ (1M in CH_2Cl_2). After stirring at -78°C for 1h, the reaction was quenched by addition of 5 mL of a saturated solution of NH_4Cl. The mixture was then extracted with ether (3x20 mL), washed with brine (10 mL), dried over magnesium sulphate and concentrated. Flash chromatography using hexane/ether (95/5) as eluent gave 0.139 g (55% yield) of a mixture of diastereoisomers **21a** and **21b** (81/19). MS (70eV) organotin fragments : m/z = 449 (90) ; 345 (30); 321 (9) ; 291 (14) ; 235 (36) ; 179 (54) ; 177 (54) ; 121 (23); organic fragments : m/z = 129 (14) , 115 (15) ; 85 (33) ; 69 (28) ; 57 (100) ; 45 (53) ; 43 (15) ; 41 (30) ; 29 (21) IR 3458 (OH) ; 1706 (CO) ; 1465 ; 1376 ; 1124 ; 1069. ***Major isomer*** **21a** : ^1H NMR δ (ppm) : 0.8-1.7 (m, 29H) ; 1.1 (s, 9H) ; 1.12 (d, 3H, $^3J_{1H}$ = 5.7) ; 1.15 (d, 3H, $^3J_{1H}$ = 6.3) ; 2.8 (1H, $^3J_{1H}$ = 5.7, $^2J_{1H}$ = 17.7) ; 2.83 (1H, $^3J_{1H}$ = 6.7, $^2J_{1H}$ = 17.7) ; 3.12 (d, 1H, $^3J_{1H}$ = 2.2) ; 3.53 (m, 1H) ; 3.96 (m, 1H) ; 4.13 (dd, 1H, $^3J_{1H}$ = 5.7, $^3J_{1H}$ = 6.7). ^{13}C NMR δ (ppm) : 9.7 (3C, $^1J_{Sn-C}$ = 294-308) ; 13.7 (3C) ; 18.4 ; 23.6 ; 26.3 ; 27 (3C, $^3J_{Sn-C}$ = 53.7-56.4) ; 29.2 (3C, $^2J_{Sn-C}$ = 19.8) ; 41.8 ; 44 ($^2J_{Sn-C}$ = 9) ; 44.5 ; 64.1 ; 69.3 ($^1J_{Sn-C}$ = 384-402) ; 74 ($^3J_{Sn-C}$ = 12.6); 215 ($^3J_{Sn-C}$ = 26.3). ^{119}Sn NMR δ (ppm) : - 31.2. ***Minor isomer*** **21b** : ^1H NMR δ (ppm) : 0.8-1.7 (m, 29H) ; 1.11 (s, 9H) ; 1.12 (d, 3H, $^3J_{1H}$ = 5.7) ; 1.15 (d, 3H, $^3J_{1H}$ = 6.3) ; 2.79 (1H, $^3J_{1H}$ = 5.7, $^2J_{1H}$ = 17.7) ; 2.88 (1H, $^3J_{1H}$ = 6.9, $^2J_{1H}$ = 17.7) ; 3.25 (d, 1H $_{hydroxyl}$, $^3J_{1H}$ = 3.2) ; 3.55 (m, 1H) ; 4 (m, 1H) ; 4.15 (dd, 1H, $^3J_{1H}$ = 5.7, $^3J_{1H}$ = 6.7). ^{13}C NMR δ (ppm) : 9.5 (3C) ; 13.7 (3C) ; 19.3 ; 23.4 ; 26.5 (3C) ; 27 (3C, $^3J_{Sn-C}$ = 53.7-56.4) ; 29 (3C, $^2J_{Sn-C}$ = 19.8) ; 41 ; 44.1; 44.2 ; 64.1 ; 67.9 ($^1J_{Sn-C}$ = 401-414) ; 73.4 ; 215.8 . ^{119}Sn NMR δ (ppm) : - 30.7

2-[1-(3'-hydroxy-1'-methyl)-butoxy-1-tributylstannyl] methylcyclohexanone (22)
The detailed procedure described for **21** was employed starting from **4a** (0.5 mmol) and 1-trimethyl silyloxycyclohex-1-ene (1 mmol). Flash chromatography using hexane/ether (95/5) as eluent gave 0.148 g (59% yield) of two products in equal quantities representing for each isolated product a mixture of 2 diastereoisomers in a 83/17 ratio. **22a/22b** = 83/17 ; **22a/22a'** = **22b/22b'** = 50/50. MS (70eV) organotin fragments : m/z = 447 (100) ; 343 (37) ; 321 (15) ; 291 (33) ; 235 (61) ; 179 (60) ; 177 (57) ; 135 (20) ; 121 (27) ; organic fragments : m/z =127 (37) ; 115 (39) ; 99 (15) ; 81 (32) ; 69 (34) ; 57 (9) ; 45 (53) ; 43 (13) ; 41 (21) ; 29 (12). IR 3450 (OH) ; 1703 (CO) ; 1465 ; 1375 ; 1122 ; 1070.

***1st eluted* 22a + 22a'** (50/50) ^{1}H NMR δ (ppm) : 0.7-2.2 (m, 41H) ; 2.7 (m, 1H) ; 3.3 (bs, 1H) ; 3.58 (m, 1H) ; 4.06 (m, 1H) meaningful signals for discrimination between **22a** and **22a'** : 3.92 (d, H_1, $^3J_{1H}$ = 6.4) and for the other isomer 4.15 (d, H_1, $^3J_{1H}$ = 3.8). ^{13}C NMR δ (ppm) : 10.5 (3C, $^1J_{Sn-C}$ = 292-306) and 10.8 (3C, $^1J_{Sn-C}$ = 292-306) ; 14 (3C) ; 18.2 and 18.8; 24 ; 25.2 and 25.6; 27.9 (3C) ; 28.15 ; 29.6 (3C, $^2J_{Sn-C}$ = 19.2) ; 32.7 (J_{Sn-C} = 20) and 32.8 (1C, J_{Sn-C} = 26.5) ; 42.2 and 42.6 ; 44.7 and 44.8 ; 55.5 and 56; 64.5 ; 73.9 ($^1J_{Sn-C}$ = 389-407) ; 74.3 ($^3J_{Sn-C}$ = 7.4) ; 74.5 ($^3J_{Sn-C}$ = 14) ; 75.2 ($^1J_{Sn-C}$ = 385-403) ; 212 ; 213 ($^3J_{Sn-C}$ = 20). ***2nd eluted* 22b + 22b' :** (50/50). ^{1}H NMR signals superimposed to those of **22a + 22a'** excepted for : 3.9 (d, 1H, $^3J_{1H}$ = 4.1, $^2J_{Sn-H}$ = 15.6) and 4.28 (d, 1H, $^3J_{1H}$ = 4.3, $^2J_{Sn-H}$ = 24.9). ^{13}C NMR δ (ppm) : signals allowing discrimination between **22b** and **22b'**; 42.3 and 42.6; 44.7 and 45 ; 64.5 and 64.7 ; 213.8 and 214.7

3-tributylstannyl-3-ethoxypropanal (23)
The detailed procedure described for **21** was employed starting from **1** (1 mmol) and 1-trimethylsilyloxy ethylene (2 mmol). The crude product **23** was obtained in 53 % yield (NMR evaluation). MS (70eV) organotin fragments : m/z = 335 (51) ; 289 (15) ; 235 (56) ; 179 (100) ; 165 (15) ; 121 (44); organic fragments : m/z =101 (14) ; 73 (38) ; 45 (52) ; 29 (25). ^{1}H NMR δ (ppm) : 0.8-1.7 (m, 27H) ; 1.1 (t, 3H, $^3J_{2H}$ = 6.9) ; 2.65 (ddd, 1H, $^2J_{1H}$ = 16.4, $^3J_{1H}$ = 4.3, $^3J_{1H}$ = 1.7, $^3J_{Sn-H}$ = 17.1) ; 2.82 (ddd, 1H, $^2J_{1H}$ = 16.4, $^3J_{1H}$ = 9.5, $^3J_{1H}$ = 2.5,$^3J_{Sn-H}$ = 15.5) ; 3.35 (m, 2H) ; 4.35 (dd, 1H, $^3J_{1H}$ = 4.3, $^3J_{1H}$ = 9.5) ; 9.75 (dd, 1H, $^3J_{1H}$ = 1.7, $^3J_{1H}$ = 2.5). ^{13}C NMR δ (ppm) : 9.3 (3C, $^1J_{Sn-C}$ = 293-307) ; 13.5 (3C) ; 15.2 ; 27.3 (3C, $^3J_{Sn-C}$ = 51) ; 29 (3C, $^2J_{Sn-C}$ = 20) ; 48.6 ($^2J_{Sn-C}$ = 7.6) ; 66.7 ($^3J_{Sn-C}$ = 14.5) ; 69.8 ($^1J_{Sn-C}$ = 357-375) ; 202.9 ($^3J_{Sn-C}$ = 47). ^{119}Sn NMR δ (ppm) = - 29.

3-tributylstannylacroleine (24)
Attempting purification of **23** on silicagel using a mixture of hexane / ether and triethylamine (95/3/2) afforded β-stannylacroleine **24** as a mixture of E and Z isomers[35].
E isomer : 0.8-1.7 (m, 27H); 6.61 (dd, 1H, $^3J_{1H}$ = 7.5, $^3J_{1H}$ = 19.7, $^3J_{Sn-H}$ = 48.9); 7.82 (d, 1H, $^3J_{1H}$ = 19.7, $^2J_{Sn-H}$ = 53.7); 9.44 (d, 1H, $^3J_{1H}$ = 7.5). **Z isomer** : 0.8-1.7 (m, 27H); 7 (dd, 1H, $^3J_{1H}$ = 6.9, $^3J_{1H}$ = 13) ; 7.7 (d, 1H, $^3J_{1H}$ = 13, $^2J_{Sn-H}$ = 48) ; 9.52 (d, 1H, $^3J_{1H}$ = 6.9).

4-(1'-trimethylsilylethoxy)-pentan-2-ol (25)
To a solution of 0.210 g (0.5 mmol) of **7** (from **4b**) (**7a/7b** = 88/12) in 10 mL of THF cooled to -78°C was added 0.73 mL (1.1 mmol) of butyllithium (1.5 M in hexanes). After stirring for 15 min, 0.1 mL of trimethylsilyl chloride in THF (1 mL) was added. The reaction mixture was stirred at -78°C for 1h and quenched by 5 mL of a saturated solution of NH_4Cl. The mixture was then extracted with ether (3x20 mL), washed with brine (10 mL), dried over magnesium sulphate and concentrated. Flash chromatography using hexane/ethyl acetate (95/5) as eluent gave 0.075 g (74% yield) of a mixture of diastereoisomers **25a** and **25b**. MS (70eV) : m/z =147 (7); 117 (71); 73 (100); 69 (4); 59 (5); 45 (8). ***Major isomer* 25a** : ^{1}H NMR δ (ppm): -0.01 (s, 9H) ; 1.1 (d, 3H, $^3J_{1H}$ = 6.8) ; 1.15 (d, 3H, $^3J_{1H}$ = 7.4) ; 1.18 (d, 3H, $^3J_{1H}$ = 6.4) ; 1.43 (m, 1H, $^2J_{1H}$ = -14.3, $^3J_{1H}$ = 5.2, $^3J_{1H}$ = 2.8) ; 1.61 (m, 1H, $^2J_{1H}$ = -14.3, $^3J_{1H}$ = 9.6, $^3J_{1H}$ = 4.1) ; 3.12 (q, 1H, $^3J_{3H}$ = 7.4) ; 3.31 (d, 1H $_{hydroxyl}$, $^3J_{1H}$ = 2.5) ; 3.7 (m, 1H) ; 4.09 (m, 1H). ^{13}C NMR δ (ppm) : -3.9 (3C) ; 16.8 ; 20.1 ; 23.6 ; 44.0 (C_3) ; 64.2 (C_2) ; 68.4 ($C_{\alpha Si}$); 74.7 (C_4). ***Minor isomer* 25b** : ^{1}H NMR signals overlapped with those of **25a** excepted : -0.03 (s, 9H); 3.16 (q, 1H, $^3J_{3H}$ = 7.4); 3.26 (d, 1H $_{hydroxyl}$, $^3J_{1H}$ = 2.5) ; 3.87 (m, 1H). ^{13}C NMR δ (ppm) : -4.1 (3C) ; 14.6 ; 18.5 ; 23.1 ; 44.0 (C_3) ; 64.6 (C_2); 65.4 ($C_{\alpha Si}$); 71.0 (C_4).The assignment of **25a** and **25b** is done on the basis of ^{13}C NMR data by analogy with those of **7a** and **7b**.

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