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Synthesis of 2-Tributylstannyl-1-Alkenes from 2-Tributylstannyl-2-Propen-1-yl Acetate

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Abstract: 2-Tributylstannyl-2-propen-1-yl acetate (**2**), which can be easily prepared from ethyl propynoate (**5**), represents a useful precursor to a variety of 2-tributylstannyl-1-alkenes of general formula **1**. Thus, treatment of **2** with complex organocopper species of general formula RCu·MgBrX·LiBr (**4**) (R = alkyl, aryl, benzyl, allyl) affords compounds **1** in fair to excellent yields. However, this procedure is unsuccessful for the preparation of 2-tributylstannyl-1,4-pentadiene (**1e**) and 2,3-bis(tributylstannyl)-1-propene (**1g**). Nevertheless, compound **1g** contaminated by hexabutylditin (**13**) can be synthetized by palladium-catalyzed reaction between **2** and (tributylstannyl)diethylaluminum (**15**). The reactions of (*E*)-2-tributylstannyl-2-octen-1-yl acetate (**22**) with compounds **4h** (R = *i*-Bu; X = Br) and **4b** (R = Ph; X = Br) have been also investigated. These reactions, when carried out in THF solution, provide mixtures of two regioisomers of general formula **23** and **1**, respectively, in which the prevailing components are those derived from a γ-substitution reaction. Compound **23b**, free of the corresponding regioisomer **1k**, has been synthetized in low yield by palladium-catalyzed cross-coupling reaction between **22** and phenyltrimethylstannane (**25**). Moreover, two N-substituted derivatives of 3-amino-2-tributylstannyl-1-propene, *i.e.* compounds **1l** and **1m** have been prepared by palladium-catalyzed amination of **2**.

2-Trialkylstannyl-1-alkenes are versatile synthetic intermediates and have a large number of synthetic applications in organic chemistry[1-4]. Therefore, much attention has been paid to methods for their synthesis, which include stannylcupration of 1-alkynes[5-7] or 1-lithium-1-alkynes[8], palladium-catalyzed stannylsilylation of 1-alkynes followed by protodesilylation[9], copper(I)-catalyzed stannylalumination of 1-alkynes[10,11], the reaction between enol triflates and $Me_3SnMgCH_3$ in the presence of CuCN[11], the reaction of 2,3-bis(trimethystannyl)-1-propene with methyllithium followed by treatment with an electrophile[12], and Wittig reactions with acyltributylstannanes[13]. However, one of these methods requires the use of a molar excess of the stannylating reagent[5] and others suffer from the poor chemo- [8,12] or regio-selectivity[7,10,11] exhibited by the reagents used.

In connection with our current study of the use in organic synthesis of stereodefined 1-alkenylstannanes bearing a functional substituent in the 1-position[14], we decided to investigate a selective synthesis of 2-

In partial fulfilment of his PhD thesis.

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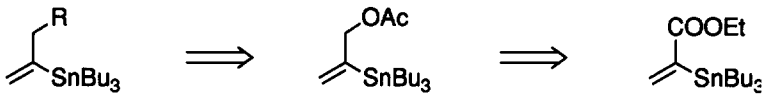
tributylstannyl-1-alkenes (**1**), involving the use of ethyl 2-tributylstannyl-2-propenoate (**3**) as precursor, which was based on the retrosynthetic analysis illustrated in Scheme 1. In principle, this strategy could allow the preparation of a variety of compounds **1** including also functionalized 2-tributylstannyl-1-alkenes, since the synthetic intermediate **2**, which is characterized by an allylic acetate moiety, could be a potent allylic source either in palladium-mediated reactions with nitrogen, oxygen or carbon nucleophiles[15], or in reactions with organocopper species which are able to tolerate the presence of a variety of functional groups in both partners of the coupling reactions[16,17].

Scheme 1



1 **2** **3**

In this paper we will describe two new methods for the selective synthesis of several types of compounds **1** from 2-tributylstannyl-2-propen-1-yl acetate (**2**). The former method, which involves a reaction between complex organocopper species of general formula RCu·MgBrX·LiBr (**4**)[18] and **2**, allows to prepare in fair to excellent yields compounds **1** where R is an alkyl, aryl, benzyl, allyl or an alkyl group containing a protected hydroxyl group. The latter method, which involves the palladium(0)-catalyzed amination of **2**, provides selectively but in modest to low yields compounds **1** in which R is a N-substituted amino group.

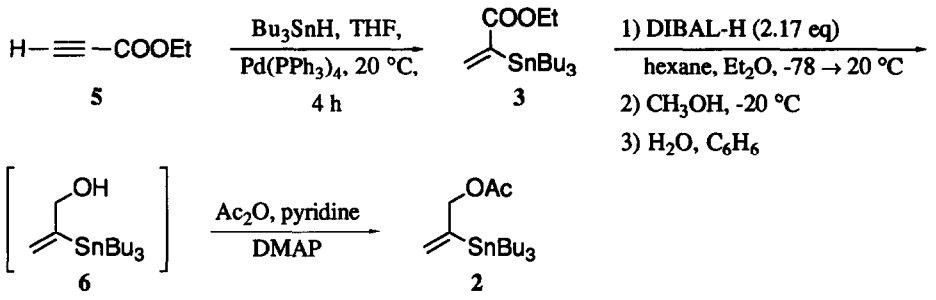
Furthermore, the results of an investigation carried out with the intent of examining more deeply the scope and defining the limitations of the reactions between organocopper species and 2-tributylstannyl-2-alken-1-yl acetates will be reported. In particular, the reactions between **2** and the organocopper species *n*-$Bu_3SnCu{\cdot}MgBr_2{\cdot}LiBr$ or $(PhMe_2Si)_2CuLi{\cdot}LiCN$ and between a 3-substituted 2-tributylstannyl-2-propen-1-yl acetate and two compounds of general formula **4** will be examined.

RESULTS AND DISCUSSION

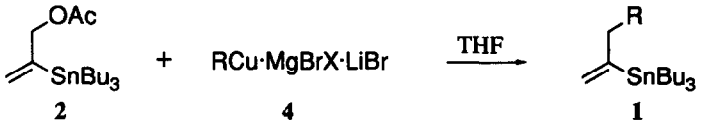
Ethyl 2-tributylstannyl-2-propenoate (**3**), which was used as starting material for the synthesis of 2-tributylstannyl-2-propen-1-yl acetate (**2**), was prepared using a procedure very similar to that reported in the literature for the synthesis of methyl 2-methylstannyl-2-propenoate[19]. In particular, a THF solution of ethyl propynoate (**5**) was reacted for 4 h at room temperature with 0.97 equiv of Bu_3SnH in the presence of 2 mol % of $Pd(PPh_3)_4$ and the resulting reaction mixture was fractionally distilled to give compound **3** in 80 % yield. This regioisomerically pure ester was then converted to **2** in 55 % overall yield by improving a procedure reported in the literature[20]. Thus, an Et_2O solution of compound **3** was added to 2.17 equiv of a 1 M hexane solution of diisobutylaluminium hydride (DIBAL-H) cooled to -78 °C under argon and the reaction mixture was stirred for 0.5 h at -78 °C and then allowed to warm to room temperature within 4 h. Crude 2-tributylstannyl-2-propen-1-ol (**6**) obtained after hydrolysis of this mixture at -20 °C was acetylated with acetic anhydride in pyridine, in the presence of a catalytic amount of DMAP, to afford crude **2**, which was purified

by MPLC on silica gel (Scheme 2).

Scheme 2

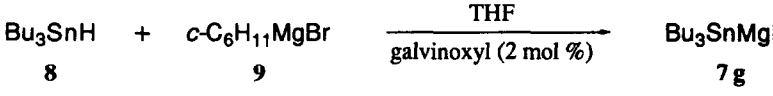


As shown in eq. (1), this compound was then reacted with 1.19 equiv of a THF solution of a complex organocopper species of general formula **4**[21], which was prepared *in situ* by addition of a THF solution of a Grignard reagent **7** to a stirred THF solution of $LiCuBr_2$[22] maintained at -65 °C.



(1)

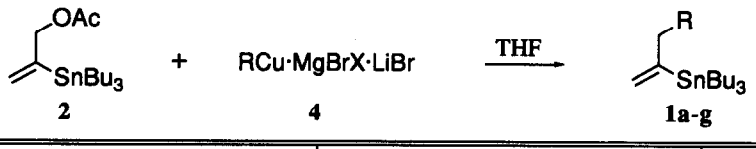
The following Grignard reagents, which were used to prepare compounds **4a-f**, were conventionally prepared or were commercially available: propylmagnesium bromide (**7a**), phenylmagnesium bromide (**7b**), benzylmagnesium chloride (**7c**), allylmagnesium chloride (**7d**), vinylmagnesium bromide (**7e**) and 6-(2-tetrahydropyranyloxy)hexylmagnesium chloride (**7f**). On the other hand, a THF solution of tributylstannylmagnesium bromide (**7g**), which was used to prepare **4g**, was prepared by a modification of a procedure reported in the literature[23]. In particular, Bu_3SnH (**8**) was added dropwise to a THF solution of 1 equiv of cycloheylmagnesium bromide (**9**) containing galvinoxyl (2 mol %), which was maintained at 0 °C and the resulting mixture was stirred for 1 h at room temperature[24] [eq. (2)].



(2)

As shown in Table 1, where the results of the reactions between **2** and compounds **4a-g** are reported, compound **2** reacted smoothly with the organocopper species **4a**, **4b**, **4c**, **4d** and **4f** to give the corresponding 2-tributylstannyl-1-alkenes, **1a**, **1b**, **1c**, **1d** and **1f**, respectively, in fair to excellent yields (entries 1-4 and 6). It is worth noticing that the reaction between **2** and **4b** (Table 1, entry 2) afforded also phenyltributylstannane (**10**) in addition to the expected 2-tributylstannyl-1-alkene, **1b**.

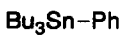
Table 1. Synthesis of 2-tributylstannyl-1-alkenes (**1**) by reaction between **2** and complex organocopper species of general formula **4**



2 **4** **1a-g**

Entry	Organocopper species			Temperature / Reaction Time	Product	Isolated yield
	4	R	X	(°C/h)	**1**	(%)
1	**4a**	n-C_3H_7	Br	-78 to -35/15 then 0/2	**1a**	99
2	**4b**	C_6H_5	Br	-78 to -30/16 then 0/20, then 20/1	**1b**	69
3	**4c**	$C_6H_5CH_2$	Cl	-78 to -15/23	**1c**	86
4	**4d**	CH_2=CH-CH_2	Cl	-78 to -30/16, then 0/48	**1d**	51
5	**4e**	CH_2=CH	Br	-78 to -35/16 then 0/25, then 20/72	**1e**	—
6	**4f**	ThpO$(CH_2)_6$	Cl	-78 to -30/15 then 0/48	**1f**	59
7	**4g**	Bu_3Sn	Br	-78 to -25/17 then 0/23	**1g**	—

On the other hand, no significant amount of 2-tributylstannyl-1,4-pentadiene (**1e**) was obtained in the reaction between **2** and (CH_2=CH)Cu·$MgBr_2$·LiBr (**4e**) carried out in experimental conditions similar to those employed to prepare **1a-d** and **1f** (Table 1, entry 5). This result was quite surprising, since it has been reported that a regioisomer of **2**, *i.e.* (*Z*)-3-tributylstannyl-2-propen-1-yl acetate (**11**), is able to react with (*Z*)-1-alkenylmagnesium bromides, in the presence of Li_2CuCl_4, to afford the desired (1*Z*,4*Z*)-1-tributylstannyl-1,4-dienes (**12**)[25].



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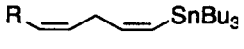

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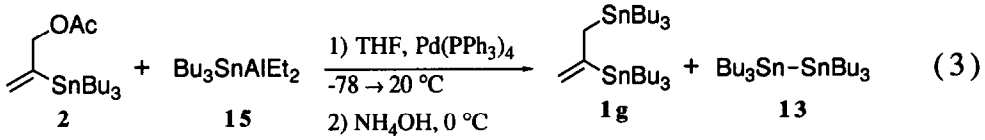
Moreover, the reaction between **2** and **4g** (Table 1, entry 7) did not afford the expected reaction product, **1g**, and the main stannylated compound obtained was hexabutylditin (**13**). Thus, other synthetic routes were selected to prepare compound **1g** starting from **2**. Nevertheless, an unsatisfactory result was obtained in the reaction between **2** and an equimolar amount of the tributylstannyl copper reagent $Bu_3SnCu·Me_2S·LiBr$ (**14**)[26] in THF at -78 °C. In fact, the reaction mixture, which was stirred for 4 h at this temperature and then allowed to warm to -10 °C within 40 h, after usual work up afforded a crude reaction product, which was essentially constituted by **13** contaminated by a very small amount of 2,3-bis(tributylstannyl)-1-propene (**1g**).

$Bu_3Sn-SnBu_3$ $Bu_3SnCu\cdot Me_2S\cdot LiBr$

13 **14**

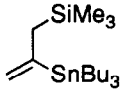
However, using experimental conditions similar to those employed to prepare allyltributylstannanes from allylic acetates[15e], when compound **2** was reacted with 1.48 equiv of (tributylstannyl)diethylaluminum (**15**) a mixture of **1g** and **13** in a 66 : 34 molar ratio, respectively, was obtained in 89 % yield based on **2** [eq. (3)].



2 **15** **1g** **13** (3)

Unfortunately, it was not possible to isolate pure **1g** from this mixture either by fractional distillation under reduced pressure or by reversed phase MPLC. Therefore, in the hopes of mimimizing the percentage of hexabutylditin (**13**) formed in this reaction, equimolar amounts of **2** and **15** were reacted in the presence of 5 mol % of $Pd(PPh_3)_4$. However, this reaction afforded too in 80 % yield based on **2** a mixture of **1g** and **13** in a 71 : 29 molar ratio, respectively.

We also attempted to prepare 2-tributylstannyl-3-trimethylsilyl-1-propene (**1h**) via a procedure recently developed to synthetize in high yields allylic silanes from the corresponding allylic acetates[27]. However, this procedure, which involved treatment of **2** with 2 equiv of hexamethyldisilane (**16**) in DMF solution at 100 °C for 40 h, in the presence of 4 mol % of $Pd(dba)_2$ and 0.5 equiv of LiCl, afforded in almost quantitative yield chlorotributyltin (**17**), and did not produce the desired compound **1h**.

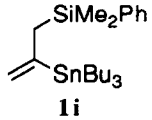


1h

$Me_3Si-SiMe_3$ Bu_3SnCl

16 **17**

It must also be mentioned that an attempt to synthetize 3-dimethyl(phenyl)silyl-2-tributylstannyl-1-propene (**1i**) by treatment of **2** with a THF solution of 2.67 equiv of the silylcuprate $(Me_2PhSi)_2CuLi\cdot LiCN$ (**18**)[28] was unsuccessful too. In fact, the reaction mixture, which was maintained at 0 °C for 1 h and at room temperature for 24 h, after usual work up afforded in high GLC yield a mixture of **13** and the disilane **19**, but did not give the desired compound **1i**.



1i

$(Me_2PhSi)_2CuLi\cdot LiCN$ $PhMe_2Si-SiMe_2Ph$

18 **19**

Finally, in order to obtain some information on the regiochemistry of the reaction between compounds **4** and a 3-substituted 2-tributylstannyl-2-propen-1-yl acetate as well as to define the synthetic potential of this

reaction, we examined the reactions between (*E*)-2-tributylstannyl-2-octen-1-yl acetate (**22**) and the organocopper species *i*-$C_4H_9Cu{\cdot}MgBr_2{\cdot}LiBr$ (**4h**) and **4b**, respectively. Compound **22** was synthetized in 83 % overall yield starting from methyl (*E*)-2-tributylstannyl-2-octenoate (**20**)[14a,b] according to a reaction sequence very similar to that employed to prepare compound **2** (Scheme 3).

Scheme 3

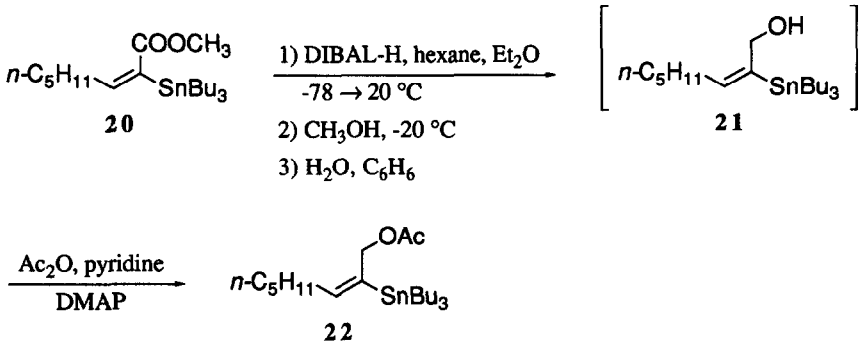
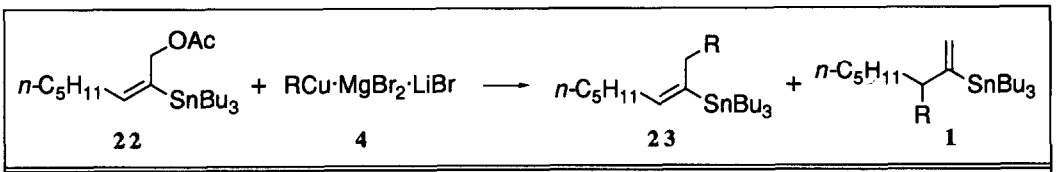


Table 2 summarizes the results obtained in the reactions between **2** and the organometallic compounds **4h** and **4b**, respectively. Two of such reactions were carried out in experimental conditions similar to those employed to prepare compounds **1a-d** and **1f** from **2** (entries 1 and 2) and the third one (entry 3) was performed in Et_2O solution.

Table 2. Reactions between compound **20** and complex organocopper species of general formula **4**

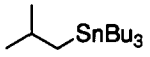


Entry	Organocopper species			Temperature / Reaction Time	Products	23/1 molar	Isolated yield
	4	R	Solvent	(°C / h)	**23** + **1**	ratio	(%)
1	**4h**	*i*-C_4H_9	THF	-78 to -30/16 then 0/5.5	**23a** + **1j**	1/10	80
2	**4b**	C_6H_5	THF	-78 to -30/16 then 0/49, then 20/23	**23b** + **1k**	1/4	46
3	**4h** [a]	*i*-C_4H_9	Et_2O	-78 to -30/20 then 0/2	[b]	—	25 [c]

[a] The organocopper species **4h** was prepared *in situ* by addition of an Et_2O solution of the corresponding Grignard reagent to a stirred Et_2O solution of $LiCuBr_2$. [b] The reaction product was isobutyltributylstannane (**24**). [c] GLC yield.

As shown in Table 2, the reactions carried out in THF solution (entries 1 and 2) produced mixtures of compounds **23** and **1** in which the prevailing products were those derived from a γ-substitution reaction. On

the other hand, the reaction between **22** and **4h** carried out in Et_2O solution (Table 2, entry 3) did not afford the expected substitution product(s), but gave isobutyltributylstannane (**24**) in 25 % GLC yield together with other unidentified tributylstannyl substituted compounds having higher GLC retention times than **24**. The formation of this last compound could be explained supposing that the reaction conditions promoted a transmetallation reaction.



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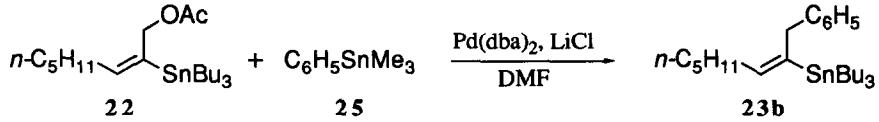
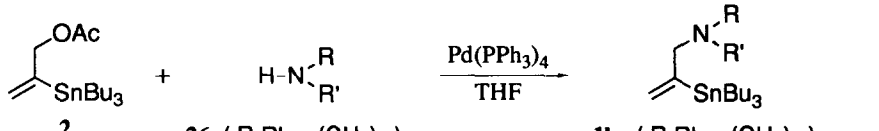
Interestingly, (*E*)-1-phenyl-2-tributylstannyl-2-octene (**23b**), free of the corresponding regioisomer **1k**, could be stereospecifically obtained, although in low GLC yield (*ca.* 11 %), by reaction between **22** and phenyltrimethylstannane (**25**) in DMF solution at room temperature, in the presence of 5 mol % of $Pd(dba)_2$ and 3 equiv of LiCl [eq. (4)], that is according to a general procedure for the palladium-catalyzed coupling of allylic acetates with aryl and vinylstannanes[29]. The other products identified in the complex reaction mixture obtained from this coupling were phenyltributylstannane (**10**), dimethyldibutylstannane and unreacted **25**.



22 **25** **23b** (4)

The fact that the GLC retention time and the MS spectrum of **23b** obtained in this stereospecific reaction were identical to those of the minor component of the mixture of products derived from the reaction of **22** with **4b** (Table 2, entry 2), allowed us to confirm an *E* stereochemistry for the α–substitution products, **23b** and **23a**, obtained in the reactions of **22** with **4b** and **4h**, respectively.

Finally, we investigated the reactivity of compound **2** in palladium-catalyzed amination reactions. In fact, these reactions could allow to prepare N-substituted 3-amino-2-tributylstannyl-1-propenes, which potentially are quite useful reagents. We found that, apart the experimental conditions used, the palladium-catalyzed amination of **2** occurred in modest to low yields. Thus, the reaction between a THF solution of **2** and 2 equiv of piperidine (**26**), in the presence of 5 mol % of $Pd(PPh_3)_4$, was complete after heating to 50 °C for 5 h and gave N-(2-tributylstannyl-2-propen-1-yl)piperidine (**1l**) in 35 % isolated yield [eq. (5)].



2

26 (R,R' = $(CH_2)_5$)
27 (R = H; R' = C_6H_5)

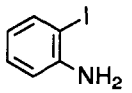
1l (R,R' = $(CH_2)_5$)
1m (R = H; R' = C_6H_5)

(5)

On the other hand, treatment of a THF solution of **2** with 1 equiv of aniline (**27**) at 50 °C for 18 h, in the presence of 5 mol % of $Pd(PPh_3)_4$, afforded N-(2-tributylstannyl-2-propen-1-yl)aniline (**1m**) in 16 % isolated

yield. Interestingly, this same reaction carried out in the presence of a molar excess of Et_3N provided compound **1m** in 11 % yield.

It must be noticed that we also attempted to use compound **2** as a conjunctive reagent in a synthesis of 3-methylindole (**29**) or its tautomer **30**. However, neither **29** nor **30** were obtained when compound **2** was reacted with a THF solution of 1 equiv of 2-iodoaniline (**28**) at 50 °C for 23 h, in the presence of 5 mol % of $Pd(PPh_3)_4$. In fact, GLC/MS analysis of the reaction mixture showed that it was essentially constituted of the unreacted reagents and that compounds derived either from the palladium(0)-catalyzed amination of **2** or a palladium(0)-catalyzed cross-coupling between **2** and **28**, *i.e.* compounds **31** and **32**, were absent. Moreover, neither **29** nor **30** were also obtained when **2** was treated with a solution of 2.0 equiv of **28** in N-methylpyrrolidinone, in the presence of 5 mol % of $Pd(dba)_2$, 10 mol % of copper(I) iodide and 10 mol % of triphenylarsine.



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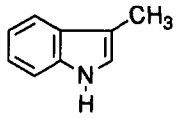

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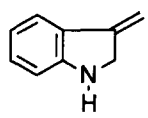

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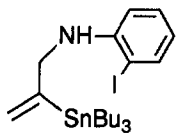

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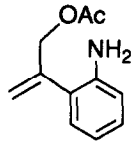


32

In conclusion, we have developed a simple and mild method for the synthesis of 2-tributylstannyl-1-alkenes of general formula **1**, where R is an alkyl, aryl, benzyl, allyl or an alkyl group containing a remote protected hydroxyl group, which is based on the reaction between 2-tributylstannyl-2-propen-1-yl acetate (**2**) and organocopper species of general formula **4**. However, a limitation of this method, which provides a useful complement to established procedures, is due to the fact that it cannot be used for the selective synthesis of 2-tributylstannyl-1-alkenes characterized by a secondary group linked to the ethenyltributylstannane moiety. In fact, the reaction between compounds **4** and a 3-substituted 2-tributylstannyl-2-propen-1-yl acetate affords mixtures of regioisomers in which the prevailing compounds are those derived from a γ-substitution reaction. Moreover, this method is not suitable for the synthesis of compounds **1** where R is a tributylstannyl or a triorganosilyl group, *i.e.* compounds **1g**, **1h** and **1i**. Nevertheless, compound **1g** contaminated by hexabutylditin can be synthetized in quite high yield by reaction of **2** with (tributylstannyl)diethylaluminum, in the presence of a palladium catalyst.

Finally, it must be noted that the palladium(0)-catalyzed amination of **2** allows the preparation, although in modest to low yields, of compounds of general formula **1** where R is a N-substituted amino group.

EXPERIMENTAL

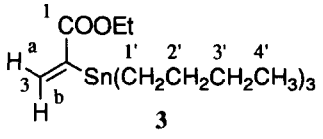
Precoated silica gel plates Merck F-254 and RP-18 $F_{254}S$ were used for TLC analyses. GLC analyses were performed on a Dani 6500 gas-chromatograph with a PTV injector and equipped with a Dani data station 86.01. Two types of capillary columns were used: a SE-30 bonded FSOT column (30 m x 0.25 mm i.d.) and a AT-35 bonded FSOT column (30 m x 0.25 mm i.d.). Purifications by MPLC were performed on a Büchi instrument, using a Bischoff 8100 differential refractometer as detector. GLC/MS analyses were performed using a Q-mass 910 spectrometer interfaced with a Perkin-Elmer 8500 gas-chromatograph. ^1H NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer using TMS as an internal standard. The $^3J_{Sn-H}$ values were reported as the average of ^{117}Sn and ^{119}Sn coupling constants.

All reactions of air and water sensitive materials were performed in flame dried glassware under an atmosphere of argon or nitrogen. Air and water sensitive solutions were transferred with hypodermic syringes or double ended needles. Solvents were dried and distilled before use.

The following compounds were prepared according to the literature: $Pd(PPh_3)_4$[30], methyl (*E*)-2-tributylstannyl-2-octenoate (**18**)[14b], 1-chloro-6-(2-tetrahydropyranyloxy)hexane[31], and bis(dibenzylideneacetone)palladium(0) $[Pd(dba)_2]$[32].

Ethyl 2-tributylstannyl-2-propenoate (3)

A degassed solution of Bu_3SnH (25.41 g, 87.3 mmol) in dry THF (125 ml) was added during 1 h to a solution of ethyl propynoate (**5**) (8.82 g, 90.0 mmol) and $Pd(PPh_3)_4$ (2.08 g, 1.8 mmol) in THF (125 ml). The resulting mixture was stirred for 4 h at room temperature under argon. THF was then removed under reduced pressure and the residue was diluted with hexane (1.5 l). After 12 h the mixture was filtered on Celite and the filtrate was concentrated under reduced pressure. The residue was diluted with hexane (400 ml), filtered on Celite and concentrated. GLC/MS analysis of the residue showed the presence of a new compound. This residue was purified by fractional distillation to give chemically pure **3** as a colorless oil (27.09 g, 80 % yield): b.p. 108-110 °C/0.15 Torr. ^1H NMR($CDCl_3$), δ: 6.91 (1 H, d, J = 2.7 Hz, $^3J_{Sn-H}$ = 110 Hz, H-3a), 5.91 (1 H, d, J = 2.7 Hz, $^3J_{Sn-H}$ = 50 Hz, H-3b), 4.19 (2H, q, J = 7.1 Hz, -O-CH_2), 1.73 - 1.08 (15 H, br m, H-2', H-3' and O-C-CH_3), 1.13 - 0.68 ppm (15 H, br m, H-1' and H-4'). MS, *m/z*(%): 333 (100), 332 (34), 331 (78), 330 (29), 329 (46), 289 (18), 235 (21), 233 (27), 231 (19), 179 (42), 177 (44), 175 (31), 165 (27), 163 (21), 57 (31), 41 (83). Anal. Calcd. for $C_{17}H_{34}O_2Sn$: C, 52.74; H, 8.33. Found: C, 52.85; H, 8.50.



3

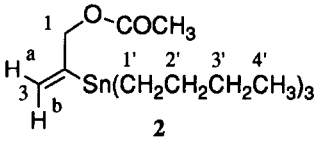
2-Tributylstannyl-2-propen-1-ol (6)

A solution of compound **3** (24.20 g, 62.19 mmol) in Et_2O (75 ml) was added during 1 h to a stirred 1 M hexane solution of DIBAL-H (135 ml, 135 mmol) cooled to -78 °C. After completion of the addition the reaction mixture was stirred for 0.5 h at -78 °C, then allowed to warm to room temperature within 4 h. GLC

analysis of a small sample of the reaction mixture hydrolyzed with methanol and water at 0 °C showed the absence of compound **3** and the presence of a new compound. Thus, the reaction mixture was cooled to -20 °C and methanol (14 ml) was slowly added, followed by water (7 ml) and benzene (70 ml). The precipitated aluminum salt was removed by filtration on Celite and washed with methanol and benzene. The combined filtrate and washing were concentrated *in vacuo* to give crude **6** (18.79 g, 87 % yield) which was used in the next step without any further purification.

2-Tributylstannyl-2-propen-1-yl acetate (2)

Crude compound **6** (18.79 g, 54.13 mmol) and 4-dimethylaminopyridine (DMAP) (0.66 g, 5.41 mmol) were dissolved in dry pyridine (12.5 ml). The solution was cooled to 0 °C and stirred while acetic anhydride (8.27 g, 77.94 mmol) was added over 0.5 h. The reaction mixture was further stirred for 5 h at room temperature and then concentrated *in vacuo*. The residue (26.3 g) was diluted with a mixture (20 ml) of cyclohexane and ethyl acetate (23 : 1 *v/v*) and an oil separated. The remaining solution was concentrated *in vacuo* and the residue was purified by MPLC on silica gel, using a mixture of hexane and benzene (7 : 3 *v/v*) as eluant, to give pure **2** as a colorless oil (13.3 g, 63 % yield). ^{1}H NMR ($CDCl_3$), δ: 5.88 (1 H, *pseudo*-q, J = 1.8 Hz, $^3J_{Sn\text{-}H}$ = 124 Hz, H-3a), 5.30 (1 H, *pseudo*-q, J = 1.8 Hz, $^3J_{Sn\text{-}H}$ = 60 Hz, H-3b), 4.71 (2 H, *pseudo*-t, J = 1.8 Hz, H-1), 2.08 (3 H, s, CH_3-CO), 1.74-1.15 (12 H, m, H-2' and H-3'), 0.93 (6 H, t, J = 9.4 Hz, H-1'), 0.89 ppm (9 H, t, J = 7.2 Hz, H-4'). MS, *m/z* (%) : 333 (19), 293 (55), 292 (20), 291 (43), 289 (25), 181 (21), 179 (96), 178 (27), 177 (99), 176 (30), 175 (55), 121 (22), 57 (31), 43 (94), 41 (100). The spectral properties of this compound were in quite good agreement with those previously reported[20].



2

General procedure for the preparation of complex organocopper species of general formula RCu·MgBrX·LiBr (4)

THF solutions of the complex organocopper species **4a** (R = *n*-C_3H_7; X = Br), **4b** (R = Ph; X = Br), **4c** (R = $PhCH_2$; X = Cl), **4d** (R = CH_2=CH-CH_2; X = Cl), **4e** (R = CH_2=CH; X = Br), **4f** (R = $ThpO(CH_2)_6$; X = Cl) and **4h** (R = *i*-C_4H_9; X = Br) were prepared by addition of 0.8 - 1.5 M THF solutions of the corresponding Grignard reagents **7a**, **7b**, **7c**, **7d**, **7e**, **7f** and **7h**, respectively (11.9 mmol), to a stirred THF solution of $LiCuBr_2$ (11.9 mmol) maintained at -65 °C, which was prepared by addition of THF (17.6 ml) to a mixture of CuBr (1.70 g, 11.9 mmol) and LiBr (1.03 g, 11.9 mmol)[19]. Stirring was continued at -65 °C for 15 min, then the mixtures were cooled to -78 °C and immediately used for the reaction with compound **2**.

The bimetallic species **4g** (R = Bu_3Sn; X = Br) was prepared in a similar way using a 0.76 M THF solution of tributylstannylmagnesium bromide (**7g**) (11.9 mmol), which was prepared by dropwise addition of tributyltin hydride (**8**) (3.46 g, 11.9 mmol) to a stirred 1.05 M THF solution of cyclohexylmagnesium bromide (**9**) (11.9 mmol) maintained at 0 °C, which contained 2 mol % of galvinoxyl (0.10 g)[23] and stirring

the resulting mixture for 4 h at room temperature.

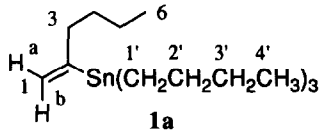
An Et_2O solution of the organocopper species **4h** was prepared by addition of a 0.79 M Et_2O solution of the corresponding Grignard reagent **7h** to an equimolar stirred Et_2O solution of $LiCuBr_2$ maintained at -65 °C.

General procedure for the reactions between the complex organocopper species 4 and compound 2

In a typical experiment a degassed solution of compound **2** (3.89 g, 10.0 mmol) in THF (6 ml) was rapidly added to a solution of a complex organocopper species **4** (11.9 mmol) maintained at -78 °C under stirring. The resulting mixture was stirred at the temperature and for the period of time reported in Table 1. The mixture was then quenched at 0 °C with a saturated aqueous NH_4Cl solution and the resulting mixture was stirred for 1 h at room temperature in the air. It was then extracted with Et_2O and the organic extract was washed with additional NH_4Cl aqueous solution and water, dried and concentrated *in vacuo*. The residue, which was analyzed by GLC, TLC and GLC/MS, was purified by MPLC. Compounds **1a**, **1b**, **1c**, **1d** and **1f** were prepared according to this general procedure. However, no significant amount of 2-tributylstannyl-1,4-pentadiene (**1e**) was obtained in the reaction between **4e** (R = CH_2=CH; X= Br) and **2** (Table 1, entry 5). Moreover, the reaction between **2** and **4g** (R = Bu_3Sn; X = Br) did not produce too 2,3-bis(tributylstannyl)-1-propene (**1g**) (Table 1, entry 7).

2-Tributylstannyl-1-hexene (1a)

The crude reaction product, which was obtained from the reaction between **2** and **4a** (Table 1, entry 1), was purified by MPLC on silica gel, using hexane as eluant, to give pure **1a** as a colorless oil in 99 % yield. ^1H NMR ($CDCl_3$), δ: 5.66 (1 H, dt, J = 2.9 and 1.5 Hz, $^3J_{Sn-H}$ = 141 Hz, H-1a), 5.09 (1 H, br d, J = 2.9 Hz, $^3J_{Sn-H}$ = 65 Hz, H-1b), 2.24 (2 H, br t, J = 7.2 Hz, H-3), 1.65 -1.15 (16 H, br m, H-4, H-5, H-2' and H-3'), 1.02 -0.72 ppm (18 H, m, H-6, H-1' and H-4'). The spectral properties of this compound were in good agreement with those previously reported[9].

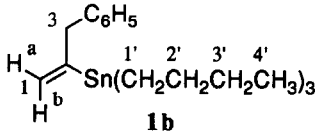


1a

3-Phenyl-2-tributylstannyl-1-propene (1b)

GLC/MS analysis of the crude reaction product which was obtained from the reaction between **2** and **4b** (Table 1, entry 2) showed the presence of two compounds in a *ca.* 85 : 15 molar ratio. This crude product was purified by MPLC on LiChroprep RP-18 (15 -25 μm) using acetonitrile as eluant. Concentration of the first eluted fractions allowed to isolate phenyltributylstannane (**10**) (10 % yield), which was identified by comparing its spectral properties with those of an authentic sample of this substance. Concentration of the last eluted chromatographic fractions allowed to obtain compound **1b** as a colorless oil (69 % yield). GLC analysis showed that this compound had chemical purity higher than 98 %. ^1H NMR ($CDCl_3$), δ: 7.44 -7.01 (5 H, m, C_6H_5), 5.72 (1 H, dt, J = 2.8 and 1.4 Hz, $^3J_{Sn-H}$ = 135 Hz, H-1a), 5.22 (1 H, dt, J = 2.8 and 1.2 Hz, $^3J_{Sn-H}$ = 62 Hz, H-1b), 3.56 (2 H, s, H-3), 1.60 -1.06 (12 H, m, H-2' and H-3'), 1.05 -0.46 ppm (15 H,

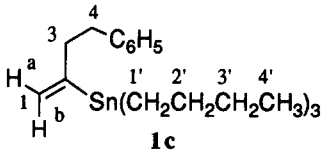
m, H-1' and H-4'). MS, *m/z* (%): 351 (40), 349 (30), 295 (23), 239 (26), 237 (41), 235 (37), 233 (18), 121 (30), 119 (26), 117 (30), 41 (100). Anal. Calcd. for $C_{21}H_{36}Sn$: C, 61.94; H, 8.91. Found: C, 62.32; H, 9.28.



1b

4-Phenyl-2-tributylstannyl-1-butene (1c)

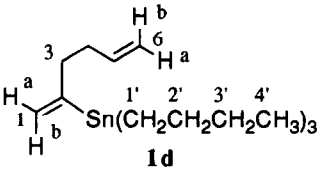
The crude reaction product which was obtained from the reaction between **2** and **4c** (Table 1, entry 3) was purified by MPLC on silica gel using hexane as eluant to give pure **1c** (86 % yield) as a colorless oil. ^{1}H NMR ($CDCl_3$), δ: 7.43 - 7.05 (5 H, m, C_6H_5), 5.73 (1 H, dt, J = 2.6 and 1.5 Hz, $^3J_{Sn-H}$ = 140 Hz, H-1a), 5.16 (1 H, dt, J = 2.6 and 1.1 Hz, $^3J_{Sn-H}$ = 65 Hz, H-1b), 2.76 - 2.63 (2 H, m, H-3 or H-4), 2.61 - 2.46 (2 H, m, H-4 or H-3), 1.65 - 1.20 (12 H, br m, H-2' and H-3'), 1.04 - 0.77 ppm (15 H, m, H-1' and H-4'). MS, *m/z* (%): 365 (67), 364 (28), 363 (50), 362 (21), 361 (28), 309 (20), 251 (30), 249 (22), 177 (24), 121 (38), 119 (30), 117 (21), 91 (47), 41 (100). Anal. Calcd. for $C_{22}H_{38}Sn$: C, 62.73; H, 9.09. Found: C, 63.00; H, 9.26.



1c

2-Tributylstannyl-1,5-hexadiene (1d)

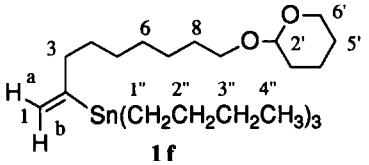
The crude reaction product, which was obtained from the reaction between **2** and **4d** (Table 1, entry 4), was purified by MPLC on silica gel, using hexane as eluant, to give compound **1d** (51 % yield) as a colorless oil. ^{1}H NMR ($CDCl_3$), δ: 5.82 (1 H, ddt, J = 17.0, 10.2 and 6.5 Hz, H-5), 5.69 (1 H, dt, J = 2.7 and 1.4 Hz, $^3J_{Sn-H}$ = 140 Hz, H-1a), 5.13 (1 H, dt, J = 2.7 and 1.0 Hz, $^3J_{Sn-H}$ = 80 Hz, H-1b), 5.02 (1 H, ddt, J = 17.0, 2.0 and 1.5 Hz, H-6a), 4.95 (1 H, ddt, J = 10.2, 2.0 and 1.5 Hz, H-6b), 2.39 - 2.23 (2 H, m, H-3 or H-4), 2.21 - 2.03 (2 H, m, H-4 or H-3), 1.61 - 1.39 (6 H, m, H-2' or H-3'), 1.39 - 1.21 (6 H, m, H-2' or H-3'), 0.98 - 0.82 ppm (15 H, m, H-1' and H-4'). MS (*m/z*): 315 (46), 313 (37), 311 (23), 203 (36), 201 (37), 199 (35), 179 (22), 177 (40), 175 (34), 121 (47), 120 (22), 119 (39), 117 (23), 41 (100). The spectral properties of this compound were in quite good agreement with those previously reported[33].



1d

9-(2-Tetrahydropyranyloxy)-2-tributylstannyl-1-nonene (1f)

The crude reaction product, which was obtained from the reaction between **2** and **4f** (Table 1, entry 6), was purified by MPLC on LiChroprep RP-18, using a mixture of acetonitrile and CH_2Cl_2 (80 : 20 *v/v*) as eluant, to give compound **1f** as a colorless oil (3.05 g, 59 %). ^1H NMR ($CDCl_3$), δ: 5.65 (1 H, dt, J = 2.9 and 1.4 Hz, $^3J_{Sn-H}$ = 140 Hz, H-1a), 5.08 (1 H, dt, J = 2.9 and 1.0 Hz, $^3J_{Sn-H}$ = 65 Hz, H-1b), 4.58 (1 H, t, J = 3.4 Hz, H-2'), 3.98 - 3.27 (4 H, br m, H-9 and H-6'), 2.23 (2 H, br t, J = 7.1 Hz, H-3), 1.74 - 1.15 (28 H, m, H-4, H-5, H-6, H-7, H-8, H-3', H-4', H-5', H-2" and H-3"), 1.06 - 0.70 ppm (15 H, m, H-1" and H-4"). Anal. Calcd. for $C_{26}H_{52}O_2Sn$: C, 60.59; H, 10.17. Found: C, 60.75 ; H, 10.35 .



1f

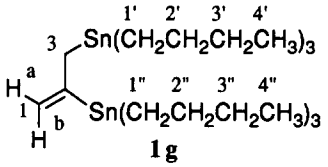
Palladium-catalyzed reaction between 2 and (tributylstannyl)diethylaluminum (15)

A 1.85 M hexane solution of butyllithium (14.6 ml, 27.0 mmol) was added during 20 min to a stirred solution of diisopropylamine (2.73 g; 27.0 mmol) in THF (27 ml) cooled to -10 °C. The mixture was stirred for 5 min at this temperature and then cooled to -35 °C. Tributyltin hydride (**8**) (7.86 g, 27.0 mmol) was dropwise added and the solution was allowed to stir for 0.5 h. A 1.8 M solution of diethylaluminum chloride (15.8 ml, 27.0 mmol) was added during 10 min and the resulting mixture, which contained (tributylstannyl)diethylaluminum (**15**), was stirred at -30 °C for 0.5 h and then cooled to -78 °C. A solution of $Pd(PPh_3)_4$ (1.04 g, 0.90 mmol) in THF (25 ml) was added, followed by addition of a solution of compound **2** (7.0 g, 18.0 mmol) in THF (10 ml). The resulting reaction mixture was stirred for 2 h at -78 °C and then allowed to warm to room temperature within 3 h. After this period a GLC analysis of a small sample of the reaction mixture hydrolyzed with diluted NH_4OH solution showed that compound **2** had disappeared. Thus, the reaction mixture was hydrolyzed at 0 °C by addition of 10 % aqueous NH_4OH solution. The resulting mixture was diluted with Et_2O and extracted repeatedly with hexane. The organic extract was washed with water, dried and concentrated *in vacuo*. The residue was diluted with hexane and filtered on Celite. The filtrate was concentrated *in vacuo* and the residue (13.69 g) was analyzed by GLC/MS. This analysis showed the presence of two compounds identified as 2,3-bis-(tributylstannyl)-1-propene (**1g**) and hexabutylditin (**13**) in a *ca.* 66 : 34 molar ratio, respectively. Compound **1g** had: MS (*m/z*): 563 (1), 353 (2), 291 (43), 289 (33), 235 (55), 233 (44), 231 (27), 179 (98), 178 (31), 177 (100), 176 (36), 175 (60), 121 (45), 119 (39), 41 (54).

On the other hand, the GLC retention time and the MS spectrum of **13** corresponded to those of an authentic sample of commercially available hexabutylditin. Attempts to obtain pure **1g** by purification of the crude reaction product either by fractional distillation or by reversed-phase MPLC were unsuccessful and gave a 66 : 34 mixture of **1g** and **13** (89 % overall yield based on **2**). However, by comparison of the ^1H NMR spectrum of this mixture with that of pure **13** it was possible to obtain the ^1H NMR parameters of compound **1g**. ^1H NMR ($CDCl_3$), δ: 5.46 (1 H, dt, J = 2.6 and 1.2 Hz, $^3J_{Sn-H}$ = 146 Hz, H-1a), 4.84 (1 H, d, J = 2.6 Hz, $^3J_{Sn-H}$ = 68 Hz, H-1b), 2.04 (2 H, s, H-3), 1.67 - 1.17 (24 H, br m, H-2', H-3', H-2" and H-3"),

1.08 - 0.64 ppm (30 H, m, H-1', H-4', H-1" and H-4").

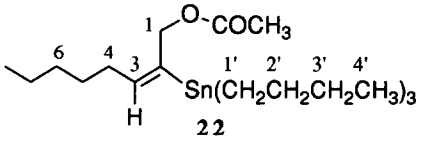
It must also be noticed that an analogous reaction between **2** and an equimolar amount of **15** prepared according to the procedure described above gave too in 80 % yield based on **2** a mixture of **1g** and **13** in a 71 : 29 molar ratio, respectively.



1g

*2-Tributylstannyl-2-octen-1-yl acetate (**22**)*

A solution of methyl (*E*)-2-tributylstannyl-2-octenoate (**20**) (16.94 g, 38.05 mmol) in Et_2O (45 ml) was added during 1 h to a stirred 1 M solution of DIBAL-H (82.5 ml, 82.5 mmol) cooled to -78 °C. After completion of the addition the reaction mixture was stirred for 0.5 h at -78 °C and then allowed to warm to room temperature within 5 h. The reaction mixture was cooled to -20 °C and methanol (8.5 ml) was added, followed by water (4.5 ml) and benzene (41 ml). The precipitated aluminum salt was removed by filtration and washed three times with methanol and benzene. The combined filtrate and washing were concentrated *in vacuo* to give crude (*E*)-2-tributylstannyl-2-octen-1-ol (**21**) (16.23 g). MS, *m/z* (%): 361 (9), 343 (5), 251 (48), 250 (16), 249 (37), 248 (14), 247 (24), 177 (14), 175 (10), 137 (22), 135 (17), 133 (11), 121 (9), 57 (15), 55 (12), 54 (15), 43 (18), 42 (10), 41 (100). The crude product and DMAP (0.47 g, 3.89 mmol) were dissolved in dry pyridine (9 ml). The solution was cooled to 0 °C and stirred while acetic anhydride (5.94 g, 56.0 mmol) was added over 5 min. The reaction mixture was further stirred for 6.5 h at room temperature and then concentrated *in vacuo*. The residue was diluted with hexane (60 ml) and filtered. The filtrate was concentrated *in vacuo* to afford a residue (17.44 g) which was purified by MPLC on silica gel, using a mixture of hexane and benzene (75 : 25 *v/v*) as eluant, to give compound **22** as an oil (14.50 g, 83 % yield). ^1H NMR ($CDCl_3$), δ: 5.63 (1 H, tt, J = 7.0 and 2.0 Hz, H-3), 4.84 - 4.74 (2 H, m, H-1), 2.08 (2 H, t, J = 7.0 Hz, H-4), 2.06 (3 H, s, CH_3CO), 1.68 - 1.09 (18 H, br m, H-5, H-6, H-7, H-2' and H-3'), 1.08 - 0.68 ppm (18 H, m, H-8, H-1' and H-4'). MS, *m/z* (%): 403 (5), 293 (66), 292 (22), 291 (50), 289 (33), 179 (46), 177 (49), 175 (29), 57 (23), 54 (49), 43 (40), 41 (100). Anal. Calcd. for $C_{22}H_{44}O_2Sn$: C, 57.53; H, 9.66. Found: C, 57.43; H, 9.30.

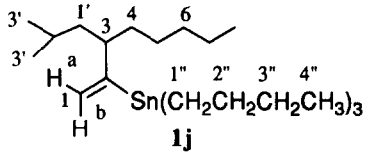


22

*Reaction between **22** and the complex organocopper species i-$C_4H_9Cu\cdot MgBr_2\cdot LiBr$ (**4h**)*

A degassed solution of compound **22** (3.0 g, 6.53 mmol) in THF (3.8 ml) was rapidly added to a THF solution of the complex organocopper species **4h** (7.84 mmol) maintained at -78 °C under stirring. The resulting mixture was stirred for 16 h at -78 °C and for 5.5 h at 0 °C and then quenched at 0 °C with a saturated aqueous NH_4Cl solution. The resulting mixture was stirred for 1 h at room temperature in the air and extracted

with Et_2O. The organic extract was washed with additional NH_4Cl aqueous solution and water, dried and concentrated *in vacuo*. GLC/MS analysis of the residue (4.43 g) showed the presence of two compounds in a *ca.* 10 : 1 molar ratio, which were subsequently identified as 3-(2-methylpropyl)-2-tributylstannyl-1-octene (**1j**) and (*E*)-2-methyl-5-tributylstannyl-5-decene (**23a**), respectively (Table 2, entry 1). This residue was purified by MPLC on silica gel, using hexane as eluant. The collected chromatographic fractions were concentrated *in vacuo* and the residue was purified by MPLC on LiChroprep RP-18 (15 - 25 μm), using a mixture of CH_3CN and CH_2Cl_2 (7 : 3 *v/v*) as eluant. The first eluted chromatographic fractions were collected and concentrated to give a mixture of **1j** and **23a** (1.68 g) in a 93 : 7 molar ratio, respectively. Concentration of the last eluted fractions allowed also to obtain a mixture of **1j** and **23a** (0.77 g) in a 90 : 10 molar ratio, respectively. Thus, these compounds were obtained in 80 % yield based on **22**. Compound **1j** had ^1H NMR ($CDCl_3$), δ: 5.61 (1 H, d, J = 2.8 Hz, $^3J_{Sn\text{-}H}$ = 140 Hz, H-1a), 5.08 (1 H, d, J = 2.8 Hz, $^3J_{Sn\text{-}H}$ = 60 Hz, H-1b), 1.59 - 1.05 (24 H, br m, H-3, H-4, H-5, H-6, H-7, H-1', H-2', H-2" and H-3"), 1.04 -0.68 ppm (24 H, m, H-8, H-3', H-1" and H-4'). MS, *m/z*(%): 401 (31), 399 (24), 179 (19), 177 (24), 175 (17), 121 (20), 119 (16), 55 (35), 43 (60), 41 (100). Anal. Calcd. for $C_{24}H_{50}Sn$: C, 63.03; H, 11.02. Found: C, 63.48; H, 11.48.



1j

Compound **23a** had MS, *m/z* (%): 401 (24), 399 (19), 179 (16), 177 (18), 175 (13), 121 (21), 119 (16), 56 (14), 55 (40), 43 (50), 41 (100).

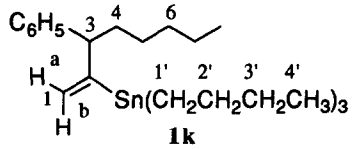
By comparison of the ^1H NMR spectrum of the first eluted chromatografic fractions with that of the last eluted fractions it was possible to obtain the ^1H NMR parameters of the olefinic proton present in compound **23a**. ^1H NMR ($CDCl_3$), δ: 5.46 ppm (1 H, t, J = 6.0 Hz).

As reported in Table 2 (entry 3) the reaction between **22** and **4h** was also carried out in Et_2O solution. In particular, a degassed solution of **22** (3.0 g, 6.53 mmol) was rapidly added to an Et_2O solution of the complex organocopper species **4h** (7.84 mmol) maintained under stirring at -78 °C. The resulting reaction mixture was stirred for 20 h while the temperature increased from -78°C to -30 °C and then maintained for 5.5 h at 0 °C. After this period a GLC analysis of a small sample of the reaction mixture hydrolyzed with aqueous NH_4Cl solution showed that compound **22** had disappeared and the presence of new four components. Thus, the reaction mixture was quenched at 0 °C with a saturated aqueous NH_4Cl solution and worked up as described above to give isobutyltributylstannane (**24**) in 25 % GLC yield. Compound **24** had: b.p. 88-89 °C/0.05 Torr (lit[34] b.p. 120°C/0.4 kPa). MS, *m/z* (%): 291 (1), 235 (2), 179 (2), 177 (2), 57 (3), 43 (2), 41 (31), 39 (10), 29 (100). This compound was identified by comparison with an authentic sample of isobutyltributylstannane prepared by reaction of a THF solution of isobutylmagnesium bromide with Bu_3SnCl.

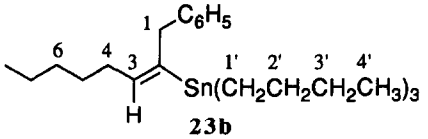
Reaction between **22** *and the complex organocopper species* $C_6H_5Cu{\cdot}MgBr_2{\cdot}LiBr$ *(**4b**)*

A degassed solution of compound **22** (2.70 g, 5.88 mmol) in THF (3.4 ml) was rapidly added to a THF

solution of **4b** (6.82 mmol) maintained at -78 °C under stirring. The reaction mixture was stirred for 16 h at this temperature, for 49 h at 0 °C and then for 23 h at room temperature. It was then quenched with a saturated NH_4Cl aqueous solution and worked up as described for the reaction between **22** and **4h**. GLC/MS analysis of the crude reaction product (4.3 g) showed the presence of phenyltributylstannane (**10**) and two other compounds, in a *ca.* 4 : 1 molar ratio, which were subsequently identified as 3-phenyl-2-tributylstannyl-1-octene (**1k**) and (*E*)-1-phenyl-2-tributylstannyl-2-octene (**23b**), respectively. This crude product was purified by MPLC on LiChroprep RP-18 (15 - 25 μm), using a mixture of CH_3CN and CH_2Cl_2 (8 : 2 *v/v*) as eluant. Concentration of the intermediate chromatographic fractions allowed to isolate a mixture of **23b** and **1k** (1.28 g, 46 % yield based on **22**), in a *ca.* 1 : 4 molar ratio, respectively. Anal. Calcd. for $C_{26}H_{46}Sn$: C, 65.42; H, 9.71. Found: C, 65.70; H, 10.10. Compound **1k** had ^1H NMR ($CDCl_3$), δ: 7.46 - 6.97 (5 H, m, C_6H_5), 5.76 (1 H, dd, J = 2.2 and 1.0 Hz, $^3J_{Sn-H}$ = 139 Hz, H-1b), 5.20 (1 H, dd, J = 2.2 and 1.2 Hz, $^3J_{Sn-H}$ = 60 Hz, H-1a), 3.42 (1 H, t, J = 7.1 Hz, H-3), 1.75 (2 H, *pseudo*-q, J = 7.1 Hz, H-4), 1.47 - 1.08 (18 H, m, H-5, H-6, H-7, H-2' and H-3'), 0.97 - 0.74 (12 H, m, H-8 and H-4'), 0.72 - 0.55 ppm (6 H, m, H-1'). MS, *m/z* (%): 421 (20), 419 (16), 197 (8), 179 (10), 177 (12), 121 (9), 119 (10), 117 (15), 91 (9), 57 (11), 43 (52), 41 (100).



1k



23b

Compound **23b** had MS, *m/z* (%): 421 (9), 419 (8), 179 (8), 177 (11), 121 (10), 117 (11), 91 (8), 57 (17), 55 (9), 44 (12), 43 (18), 41 (100).

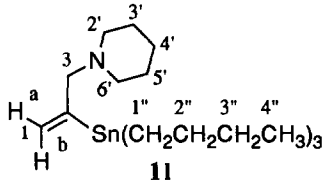
By comparison of the ^1H NMR spectrum of the mixture of compounds obtained by concentration of the intermediate chromatographic fractions with that of the mixture of the same compounds present in very small amount in the last chromatographic fractions, which contained a higher percentage of the minor component, it was possible to obtain some ^1H NMR parameters of compounds **23b**. ^1H NMR ($CDCl_3$), δ: 5.69 (1 H, tt, J = 7.0 and 1.5 Hz, H-3), 3.62 (2 H, s, H-1), 2.24 ppm (2 H, *pseudo*-q, J = 7.0 Hz, H-4).

Palladium-catalyzed reaction between 22 and phenyltrimethylstannane (25)

According to a general procedure for the palladium-catalyzed coupling of allylic acetates with aryl and vinylstannanes[29], to a mixture of compound **22** (2.76 g, 6.0 mmol), phenyltrimethylstannane (**25**) (1.50 g, 6.24 mmol) and lithium chloride (0.76 g, 18.0 mmol) in DMF (9.5 ml) was added $Pd(dba)_2$ (0.17 g, 0.30 mmol) and the dark mixture so obtained was stirred for 17 h at room temperature. After this period GLC and TLC analyses showed that compound **22** had disappeared. Thus, the reaction mixture was poured into an excess of water and extracted with Et_2O. The organic extract was filtered, washed with brine, dried and analyzed by GLC/MS. This analysis showed the presence of several components among which compounds **24** and **10**, dimethyldibutylstannane and (*E*)-1-phenyl-2-tributylstannyl-2-octene (**23b**). This last compound, which was not contaminated by the corresponding regioisomer **1k**, was obtained in 11 % GLC yield. No attempt was performed to isolate **23b** from this complex reaction mixture.

*N-(2-Tributylstannyl-2-propen-1-yl)piperidine (**11**)*

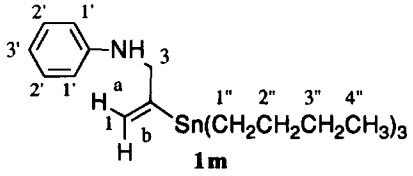
Piperidine (**26**) (1.53 g, 17.99 mmol) was added to a solution of compound **2** (3.50 g, 8.99 mmol) and $Pd(PPh_3)_4$ (0.52 g, 0.45 mmol) in THF (20 ml) stirred at room temperature and the resulting mixture was stirred at 50 °C for 5 h. GLC and TLC analyses of a small sample of this mixture treated with diluted aqueous Na_2CO_3 solution and extracted with Et_2O, showed that compound **2** had disappeared as well as the presence of a new compound. Thus, the reaction mixture was diluted with hexane and poured into an excess of 10 % aqueous Na_2CO_3 solution. The mixture was extracted with hexane and then the organic extract was filtered, washed with brine and concentrated *in vacuo*. The residue was purified by MPLC on silica gel, using a mixture of hexane and THF (98 : 2 *v/v*) as eluant, to give 98 % chemically pure **11** as an oil (1.29 g, 35 % yield). ^1H NMR ($CDCl_3$), δ: 5.75 (1 H, dt, J =2.9 and 1.5 Hz, $^3J_{Sn\text{-}H}$ = 140 Hz, H-1a), 5.17 (1 H, dt, J = 2.9 and 1.4 Hz, $^3J_{Sn\text{-}H}$ = 63 Hz, H-1b), 2.98 (2 H, dd, J = 1.5 and 1.4 Hz, H-3), 2.27 (4 H, br s, H-2' and H-6'), 1.75 - 1.15 (18 H, br m, H-3', H-4', H-5', H-2" and H-3"), 1.05 - 0.65 ppm (15 H, br m, H-1" and H-4"). MS, *m/z* (%): 358 (24), 356 (18), 179 (27), 177 (29), 175 (18), 124 (37), 121 (25), 119 (19), 98 (56), 84 (65), 57 (18), 55 (24), 42 (38), 41 (100). Anal. Calcd. for $C_{20}H_{41}NSn$: C, 57.99; H, 9.98; N 3.38. Found: C, 57.89; H, 10.05; N, 3.33.



11

*N-(2-Tributylstannyl-2-propen-1-yl)aniline (**1m**)*

(*Procedure A*) Aniline (**27**) (0.84 g, 8.99 mmol) was added to a mixture of compound **2** (3.50 g, 8.99 mmol) and $Pd(PPh_3)_4$ (0.52 g, 0.45 mmol) in THF (20 ml) and the mixture was stirred at 50 °C for 18 h. It was then cooled to room temperature and worked up using the same procedure employed in the preparation of compound **11**. The crude reaction product (3.74 g) was purified by MPLC on silica gel, using a mixture of hexane and benzene (95 : 5 *v/v*) as eluant, to give compound **1m** as an oil (0.60 g, 16 % yield). ^1H NMR ($CDCl_3$), δ: 7.26 - 7.06 (2 H, m, H-1"), 6.78 - 6.61 (3 H, m, H-2" and H-3"), 5.94 (1 H, dt, J = 2.3 and 1.7 Hz, $^3J_{Sn\text{-}H}$ = 130 Hz, H-1a), 5.29 (1 H, dt, J = 2.3 and 1.4 Hz, $^3J_{Sn\text{-}H}$ = 60 Hz, H-1b), 3.89 (2 H, dd, J = 1.7 and 1.4 Hz, H-3), 3.90 - 3.65 (1 H, br s, NH), 1.70 -1.15 (12 H, m, H-2" and H-3"), 1.05 - 0.62 ppm (15 H, m, H-1" and H-4"). MS, *m/z* (%): 366 (43), 365 (20), 364 (45), 362 (28), 212 (48), 210 (37), 208 (21), 179 (18), 177 (25), 132 (24), 121 (19), 57 (49), 41 (100). Anal. Calcd. for $C_{21}H_{37}NSn$: C, 59.74; H, 8.83; N, 3.32. Found: C, 59.60; H, 8.93; N, 3.17.



1m

(*Procedure B*) Aniline (**27**) (0.84 g, 8.99 mmol) was added to a mixture of compound **2** (3.50 g, 8.99

mmol), $Pd(PPh_3)_4$ (0.52 g, 0.45 mmol) and Et_3N (9.1 g, 89.94 mmol) in THF (20 ml) and the mixture was stirred at 50 °C for 18 h. Usual work up followed by purification of the crude reaction product by MPLC on silica gel gave compound **1m** (0.43 g, 11 % yield).

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20. Zhang, H. X.; Guibé, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857. Compound **2** was obtained using this procedure in 43 % overall yield based on methyl tributylstannyl-2-propenoate.

21. Complexation of organocopper reagents affords anionic *ate*-type complexes [MacDonald, T. L.; Still, W. C. *J. Am. Chem. Soc.* **1975**, *97*, 5280; Gilman, H. *J. Org. Chem.* **1952**, *17*, 1630; Tochterman, W. *Angew. Chem. Int. Ed. Engl.* **1966**, *6*, 351]. On this basis the complex organocopper species $RCu{\cdot}MgX_2{\cdot}LiBr$ (**4**) could be represented as $RCuX^-Li^+{\cdot}MgXBr$ or $RCuX^-MgX^+{\cdot}LiBr$. Thus, these organocuprates should be much powerful nucleophiles than the corresponding organocopper species. Moreover, coordination of the cation Li^+ or MgX^+ to the acetoxy group of compound **2** should facilitate the nucleophilic attack of the cuprate.

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24. In the procedure described in Ref. *23* Bu_3SnH was reacted with an Et_2O solution of 1.1 equiv of cyclohexylmagnesium bromide containing galvinoxyl (1-2 mol %). However, for the preparation of compounf **4g** we preferred the use of a THF solution of this Grignard reagent to reproduce the experimental conditions used to synthetize compounds **4a-d** and **4f**. Moreover, in order to avoid the presence of an excess of this Grignard reagent, which could give rise to the formation of an undesired amount of the complex organocopper species $c\text{-}C_6H_{11}Cu{\cdot}MgBr_2{\cdot}LiBr$, we used cyclohexylmagnesium bromide and Bu_3SnH in a 1 : 1 molar ratio.

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