Hydrostannylation of Propargylic Alcohols Using Mixed Tin Hydrides

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The hydrostannylation of a series of alkynols and propargylic ethers with mixed tin hydrides Bu_2SnHCl and Bu_2SnHBr has been studied. These highly reactive tin hydrides undergo radical chain reactions at low to ambient temperatures (–78 °C to 25 °C). Their higher Lewis acidity (in comparison with the most commonly used hydrostannylation reagent Bu_3SnH) leads to much better regio- and stereoselectivities irrespective of the size and nature of the substituents in the propargylic position. Hydrostannylation of terminal propargylic alcohols and ethers gives almost solely (> 90 %) the products of *anti*-addition; these are stabilized by intramolecular coordination. When non-terminal propargylic alcohols are used, the isomerisation to the thermodynamically favoured *syn*-addition product, which normally takes place in free radical hydrostannylations, can be prevented by choosing appropriate reaction conditions. Hydrostannylation of allyl propargyl ether shows that these reagents are highly chemoselective towards C–C triple bonds.

Introduction

Stereospecific hydrometallation of alkynes is of great importance for synthetic chemistry because of the use which can be made of the resulting metallated alkenes for C−C bond formations (e.g. Suzuki and Stille couplings).[1] Hydrostannylation in its turn is probably the most important of the hydrometallations and has been known in its free radical form for many years;[2] a further important advance was the introduction of palladium-catalysed hydrostannylation a number of years ago.[3−5] The control of regio- and stereoselectivity still needs long optimization times. For metal-catalyzed hydrostannylations control of stereoselectivity is not a problem, but control of regioselectivity can pose huge challenges.[6] Using tributyltin hydride, arguably the most important organotin reagent, regiocontrol is never a problem, while stereocontrol is however far from perfect[3], due to isomerization of the reaction product.

Dibutyltin hydride halides Bu_2SnHX have been known for many years and can readily be prepared simply by mixing dibutyltin dihydride and the appropriate dibutyltin dihalide.[7] The equilibrium is fast, but the resulting mixture reacts as if it contains only the hydride halide.[8] Few examples of hydrostannylation of alkynes using these reagents have been reported.[9−12]

The hydride halides are prepared in situ from the dihydride and the dihalide; a little work on additions of dibutyltin dihydride itself to acetylenic alcohols has appeared.[13,14]

Following from work by Davies[12,15] we recently[16] described the hydrostannylation of terminal propargylic ethers using the hydride halides, a reaction which is rapid at room temperature and leads exclusively to the product of *anti*-addition in the β-position to the CR_2OR moiety (Scheme 1).

Scheme 1. Reaction of propargylic ethers with tin hydride halides (cf. ref.[16])

In this case the reaction is controlled by intramolecular coordination between the ether oxygen and the tin; it appeared to us that this might well be a general feature of reactions involving propargylic alcohols and ethers and possibly also of corresponding homopropargylic species. This paper descibes the results of a detailed study of such reactions.

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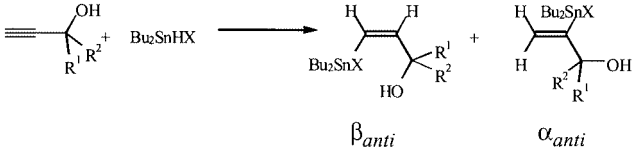
Results and Discussion

a) Hydrostannylation of Terminal Propargylic Alcohols

In order to make these reactions as efficient as possible, propyn-1-ol as a model compound was allowed to react with dibutyltin hydride halide under various conditions (temperature, initiator, catalyst). The best results were obtained using AIBN as room-temperature catalyst or 9-BBN as low temperature catalyst (−78 °C).[17] Dibutyltin hydride chloride and hydride bromide give roughly comparable results even if no initiator was used, the regioselectivity lying slightly higher with the chloride although workup is slightly easier with the bromide, which is also slightly less susceptible to oxidation to give $Bu_4Sn_2X_2O$ as by-product.

Thus in what follows we generally restricted ourselves to the use of the hydride chloride either at room temperature with AIBN or at −78 °C with 9-BBN.



Scheme 2. Reaction products in the hydrostannylation of propargylic alcohols with dibutyltin hydride halide (X = Cl, Br)

Reactions took place according to Scheme 2.

Table 1 gives the results obtained. Equimolar amounts of the reactants were used after initial experiments with a 20 % excess of the alcohol brought no improvement. Table 1 shows the isolated yields of major products (β_{anti}) unless otherwise noted.

Overall yields were excellent, lying generally close to 90 %. There appear to be no systematic differences between the use of AIBN and 9-BBN, the regioselectivity of all reactions being relatively high. The addition takes place in β-position to the CR_2OH moiety giving solely the product of *anti*-addition (β_{anti}). There is only one other route to this isomer, known as the Lewis acid catalyzed hydrostannylation,[18] which cannot readily be applied to alcohols. Only very little influence of the steric and electronic demand of the substituents in the propargylic position can be detected, in clear contrast to transition metal catalyzed hydrostannylations, which are very sensitive towards a change of the substitution pattern in the propargylic position.

Spectroscopic investigations, particularly using ^{119}Sn NMR, showed that the β_{anti}-products are stabilised by intramolecular coordination as expected. The complete data are given in the Exp. Sect., but the following features are typical:

a) Tin chemical shift between $\delta = -3$ and -10 ppm

b) $^3J(HC{=}CH) = 11.8-12$ Hz

c) $^3J(^{119}SnC{=}CH) = 209-210$ Hz

d) $^1J(^{119}Sn\text{-}^{13}C{=}CH) = 559-568$ Hz.

The signal of the product experiences an upfield shift of approximately 60 ppm in the ^{119}Sn NMR (in comparison with the uncoordinated reaction products), thus falling clearly in the region expected for pentacoordinate tin. This is also confirmed by the large coupling constants to tin [$^3J(^{119}Sn\text{-}^1H)$ and $^1J(^{119}Sn\text{-}^{13}C)$]. The size of the three-bond proton-proton coupling is in the region for *cis*-olefinic protons, thus showing the (*Z*)-substitution and therefore *anti*-addition.

For chiral starting materials the carbon atoms of the *n*-butyl residues on tin become diastereotopic (denoted C_α and C_β in the Exp. Sect.).

Table 1. Reactions between terminal propargylic alcohols and dibutyltin hydride halides

Alcohol		Reaction conditions	Yield of β_{anti} product	Compound	Yield of α product[a]
R^1	R^2				
H	H	9-BBN, −78 °C, 5 h	80 %	**1a**	n. o.[b]
		AIBN, room temp.	90 %	**1a**	6 %
H	Me	9-BBN, −78 °C, 5 h	65 %	**1b**	9 %
Me	Me	9-BBN, −78 °C, 5 h	80 %	**1c**	< 4 %
cyclohexyl		AIBN, room temp., 60 h	87 %	**1d**	n. o.[b]
		9-BBN, −78 °C, 7 h	80 %	**1d**	< 4 %
H	Ph	AIBN, room temp., 12 h	79 %	**1e**	5 %
		9-BBN, −78 °C, 6 h	74 %	**1e**	4 %
Me	Ph	9-BBN, −78 °C, 6h	70 %	**1f**	4 %
		AIBN, room temp., 12 h	85 %	**1f**	5 %
Ph	Ph	9-BBN, −78 °C, 6 h	71 %	**1g**	4 %
		AIBN, room temp., 12 h	66 %	**1g**	< 4 %

[a] As estimated from NMR spectra. [b] Not observed.

Purification involved either distillation or column chromatography and it was not always easy to remove the propargylic alcohol by distillation. $Bu_4Sn_2X_2O$ was almost always present in small amounts, and could only be removed completely by carrying out the column chromatography at −78 °C; under these conditions isomer separation was also possible in some cases.

Reagent purity and freedom from traces of oxygen or moisture are extremely important if good product yields are to be obtained.

In three cases [$R^1 = R^2 = H$ (**2a**), $R^1 = H$, $R^2 = Me$ (**2b**) and R^1R^2 = cyclohexyl (**2c**)] we carried out experiments using Bu_2SnHBr; while the overall yields were better, the regioselectivity was not as good.

b) Hydrostannylation of Non-terminal Propargylic Alcohols

If non-terminal propargylic alcohols are subjected to radical hydrostannylation conditions using tributyltin hydride, the addition usually takes place in α-position to the CR_2OH group. We had hoped that the stabilisation due to the coordination of the tin atom by the alcohol oxygen would be big enough to achieve *anti*-addition in the (for radical hydrostannylations) unusual β-position.

When the triple bond is internal the formation of an additional product can be observed originating from the isomerisation of the initial *anti*-addition product in α-position; thus reactions with Bu_2SnHCl took place as described in Scheme 3.

Three products are generally observed (Table 2), the originally expected β_{anti} isomer being accompanied by both α_{anti} and α_{syn} products. Identification of the products was readily possible on the basis of their NMR spectroscopic data.

Typical of the β_{anti} isomer are the following NMR data:

a) Tin chemical shift between −8 and −20 ppm

b) $^3J(^{119}SnC{=}CH)$ = 201−210 Hz

These values are similar to those observed for the β_{anti} addition products to terminal propargylic alcohols.

The α_{anti} isomer, in contrast, has:

a) Tin chemical shift between 44 and 79 ppm

b) $^3J(^{119}SnC{=}CH)$ = 178−191 Hz

The low-field shift of the tin resonance (in comparison with the β_{anti} isomer) shows that this species does not undergo intramolecular coordination, while the three-bond coupling constant [^3J (^{119}Sn-^{1}H)] demonstrates that the tin is *trans* to the proton.[19]

For the α-*syn* isomer we found:

a) Tin chemical shift between 29 and 66 ppm

b) $^3J(^{119}SnC{=}CH)$ = 98−101 Hz

Again there is no intramolecular coordination, the low value of the three-bond coupling [^3J (^{119}Sn-^{1}H)] being diagnostic of the *cis* relation between tin and the vinyl proton.

There is a complete change in the regiochemistry (in comparison with the terminal propargylic alcohols), the β-*anti* isomer almost always being the minor one. Under the free radical conditions used, attack is possible at either acetylenic carbon centre, and is no longer directed by the gain in radical stability due to intramolecular coordination between oxygen and tin. When TMS is used as the substituent at the triple bond the regiochemistry moves towards the β_{anti} isomer (at least for the case of the unsubstituted propargylic alcohol); this might be due to the β-stabilizing effect of the TMS group (β to the TMS group, α to the CH_2OH group).

The question of product isomerisation however also arises: although vinyl radicals are themselves configurationally stable, *cis*-to-*trans* isomerisation of vinyltins has been known for decades.[20] By carefully choosing the reaction conditions the reaction can with very few exceptions be halted at the stage of the *anti*-addition product.

Again the relative reactivity of the dibutyltin hydride bromide was tested. The results are shown in Table 3. The same reaction products are observed as in the addition of the dibutyltin hydride chloride (cf. Table 2).

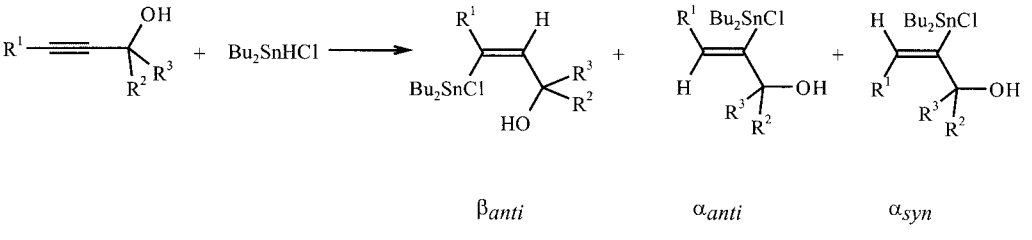
As with dibutyltin hydride chloride, three isomers are generally observed. The regioselectivity is mainly the same, but it is easier to control stereochemistry. It was possible to halt the reaction at the stage of the α_{anti} addition product when using 9-BBN as a low-temperature catalyst, the isomerised α_{syn} product not even being observed in traces in 3 out of 4 cases. The overall yields are better, due to the easier purification of the reaction products.

The NMR spectroscopic data are essentially in the same range for the three different isomers as in the products of hydrostannylation with dibutyltin hydride chloride.

c) Hydrostannylation of Propargyl Ethers

The chemoselectivity of the hydride halides was first checked by carrying out reactions with allyl propargyl ether in ratios of both 1:1 and 2:1. In neither case could hydrostannylation of the double bond be observed, so that only the results obtained from 1:1 additions will be discussed (Scheme 4).

As expected, the main product was the β_{anti} isomer, the α_{anti} isomer only being formed in low yield (Table 4). Some



β_{anti} α_{anti} α_{syn}

Scheme 3. Products of the reaction of dibutyltin chloride hydride with non-terminal propargylic alcohols

Table 2. Reactions between non-terminal propargylic alcohols and dibutyltin hydride chloride

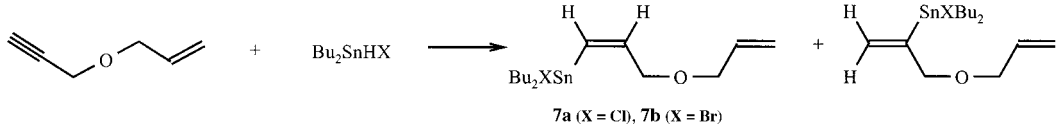
Alcohol			Reaction conditions	Yield of β_{anti} product	Compound	Yield of α_{anti} product	Compound	Yield of α_{syn} product	Compound
R^1	R^2	R^3							
Me	H	H	AIBN, room temp., 20 h	n. o.[a]		21 %	**4a**	70 %	**5a**
			9−BBN, −78 °C, 6 h	10 %[b]		60 %	**4a**	20 %	**5a**
Me	Me	H	9−BBN, −78 °C, 7 h	5 %[b]		30 %[c]	**4b**	5 %[b]	
			AIBN, room temp., 12 h	10 %[b]		49 %	**4b**	14 %[b]	
Bu	Me	H	9−BBN, −78 °C, 6 h	10 %[b]		70 %	**4c**	2 %[b]	
			AIBN, room temp., 20 h	16 %[b]		75 %	**4c**	8 %[b]	
Bu	Ph	Me	9−BBN, −78 °C, 6 h	12 %[b]		46 %	**4d**	2 %[b]	
			AIBN, room temp., 20 h	24 %[b]		47 %	**4d**	4 %[b]	
TMS	H	H	9−BBN, −78 °C, 7 h	31 %	**3e**	6 %[b]		14 %	**5e**
			AIBN, room temp., 60 h	50 %	**3e**	n.o.[a]		14 %	**5e**
TMS	Me	H	9−BBN, −78 °C, 7 h	27 %	**3f**	12 %[b]		15 %	**5f**
			AIBN, room temp., 60 h	34 %	**3f**	4 %[b]		27 %	**5f**

[a] Not observed. [b] As estimated from NMR spectra. [c] Considerable loss during column chromatography, conversion: 56 %.

Table 3. Reactions between non-terminal propargylic alcohols and dibutyltin hydride bromide

Alcohol			Reaction conditions	Yield of β_{anti} product[a]	Yield of α_{anti} product	Compound	Yield of α_{syn} product[a]
R^1	R^2	R^3					
Me	H	H	9-BBN, −78 °C, 6 h	13 %	47 %	**6a**	28 %[b]
			AIBN, room temp., 20 h	18 %	26 %	**6a**	49 %[b]
			room temp., 20 h	15 %	49 %	**6a**	24 %[b]
Me	Me	H	9-BBN, −78 °C, 7 h	<5 %	75 %[c]	**6b**	n. o.[d]
			AIBN, room temp., 20 h	12 %	64 %	**6b**	11 %
			room temp., 20h	8 %	61 %	**6b**	5 %
Bu	Me	H	9-BBN, −78 °C, 6 h	10 %	84 %	**6c**	n. o.[d]
			AIBN, room temp., 20 h	20 %	65 %	**6c**	10 %
			room temp., 20 h	22 %	71 %	**6c**	3 %
Bu	Ph	Me	9-BBN, −78 °C, 6 h	32 %	64 %	**6d**	n. o.[d]
			AIBN, room temp., 20 h	30 %	50 %	**6d**	3 %
			room temp., 20 h	24 %	50 %	**6d**	3 %

[a] As estimated from NMR spectra. [b] Considerable decomposition during column chromatography; no clean isolation possible. [c] Crude yield > 95 %. [d] Not observed.



Scheme 4. Hydrostannylation of allyl propargyl ether

Table 4. Reactions of allyl propargyl ether with dibutyltin hydride halides (X = Cl or Br)

X	Reaction conditions	Yield of β_{anti} isomer	Compound	Yield of α_{anti} isomer[a]	Other products[b]
Cl	9-BBN, −78 °C, 6 h	54 %	**7a**	12 %	10 %
Cl	AIBN, room temp., 20 h	61 %	**7a**	11 %	11 %
Cl	room temp., 20 h	57 %	**7a**	8 %	10 %
Br	9-BBN, −78 °C, 6 h	42 %	**7b**	4 %	8 %
Br	AIBN, room temp., 20 h	51 %[c]	**7b**	9 %	12 %
Br	room temp., 20 h	66 %	**7b**	8 %	12 %

[a] As estimated from NMR spectra. [b] ^{1}H and ^{13}C NMR spectra show resonances of *n*-butyl groups only. [c] Crude yield: 70 %, after column chromatography at −78 °C; the rest is isolated together with the other regioisomer.

organotin by-product formation was noted. No great difference in the reactivity or selectivity of the hydride halides was visible.

We next turned our attention to terminal trimethylsilyl propargyl ethers because of the importance of silyl protecting groups. Reactions were carried out with both the hydride chloride and the hydride bromide according to Scheme 5.

As expected, and in analogy with the situation for the propargylic alcohols, the β-*anti* product predominated (Table 5), although the regioselectivity was not as good as with the non-protected alcohols. This might be due to less effective stabilisation of the intermediate radical.

Dibutyltin hydride chloride and bromide gave essentially the same results, showing no differences in regio- or stereoselectivity. One major difference must however be stated: when using the dibutyltin hydride chloride for hydrostannylation product isolation was sometimes complicated by desilylation, so that the deprotected alcohol was isolated. This did not occur with the hydrostannylation products obtained from the dibutyltin hydride bromide.

Intramolecular coordination is present in the major β_{anti} isomer, as shown by the following NMR parameters:

a) Tin chemical shift between 30 and 60 ppm
b) ^3J(HC=CH) = 12.2−12.5 Hz
c) $^3J(^{119}$SnC=CH) = 199−207 Hz
d) $^1J(^{119}$Sn-^{13}C=CH) = 515−542 Hz.

The tin chemical shift values show that the strength of the coordinative bond is lower than in the corresponding vinylic alcohols.

Interestingly, the cyclohexyl derivative shows predominant formation of the β_{syn} rather than the β_{anti} isomer. It seems likely that with respect to the cyclohexyl ring the $OSiMe_3$ group is equatorial and the ethynyl group axial. The stannyl radical then prefers to attack in such a way that it does not undergo repulsion by the siloxy group. If no initiator is used yields are higher for this derivative. Again the NMR parameters are diagnostic of the proposed geometry:

a) Tin chemical shift 75 and 93 ppm, respectively
b) ^3J(HC=CH) 18.9 Hz
c) $^3J(^{119}$SnC=CH) 95 Hz
d) $^1J(^{119}$Sn-^{13}C=CH) 434 and 449 Hz, respectively

The large $^3J(^1$H-^{1}H) coupling constant and the small $^3J(^{119}$Sn-^{1}H) coupling constant in the case of the β_{syn} isomer are clear evidence for the proposed structure.

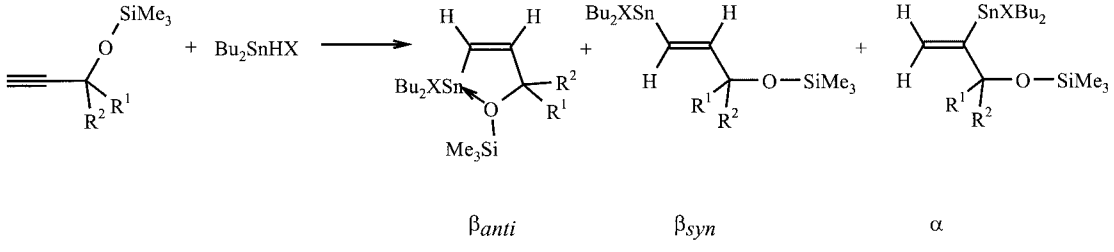
d) Related Substrates

In this section we present the outcome of reactions involving substrates other than propargylic alcohols. It occurred to us that it might be interesting to elongate the chain of the alcohol, thus going from propargylic alcohols to homopropargylic alcohols and further to 4-pentyn-1-ols. Furthermore it is of interest to see whether the coordinating oxygen atom in the alcohol moiety can be replaced by nitrogen; we therefore tested *N*,*N*-dimethylpropargylamine as a starting material.

The reaction of the homopropargyl alcohols is described in Scheme 6 and the product distribution shown in Table 6.

In some cases the overall yields are quite low; an unidentified butyltin compound was the by-product in such cases. This was formed in particular large amounts when 9-BBN was used as initiator. As can be seen by comparing the first and second entries, in some cases yields were even better if no initiator was used and the reagents were just stirred together.

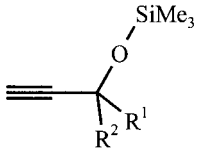
The compounds studied have a terminal acetylenic bond, so that the main products are those of γ_{anti} and γ_{syn} type; only in one case were small amounts of the β-product observed. This demonstrates once again that the stabilisation

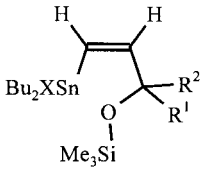


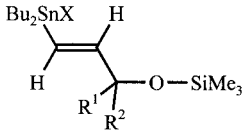
β_{anti} β_{syn} α

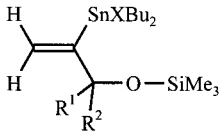
Scheme 5. Reactions of trimethylsilyl progargyl ethers with dibutyltin halide hydride

Table 5. Products of hydrostannylation of terminal trimethylsilyl propargyl ethers



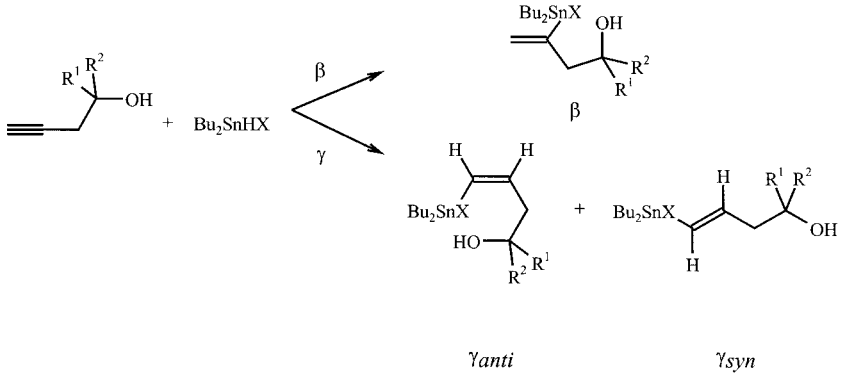






Ether			Reaction conditions	Yield of β_{anti} product	Compound	Yield of β_{syn} product	Compound	Yield of α product	Compound
R^1	R^2	X							
	H	Cl	9-BBN, −78 °C, 6 h	80 %	**8a**	–		14 %	**10a**
			AIBN, room temp., 20 h	60 %[a]	**8a**	–		15 %	**10a**
		Br	9-BBN, −78 °C, 6 h	75 %	**8b**	–		15 %[b]	
			AIBN, room temp., 20 h	68 %[c]	**8b**	–		16 %[b]	
H	Me	Cl	9-BBN, −78 °C, 6 h	59 %[b]	**8c**	–		24 %[b]	
			AIBN, room temp., 20 h	23 %[d]	**8c**	–		25 %[e]	
		Br	9-BBN, −78 °C, 6 h	53 %[b]	**8d**	–		27 %[b]	**10d**
			AIBN, room temp., 20 h	33 %[f]	**8d**	–		23 %[g]	**10d**
cyclohexyl		Cl	9-BBN, −78 °C, 6 h	5 %[b]		42 %	**9e**	6 %[b]	
			AIBN, room temp., 20 h	5 %[b]		45 %	**9e**	5 %[b]	
			room temp., 20 h	8 %[b]		43 %[h]	**9e**	6 %[b]	
		Br	9-BBN, −78 °C, 6 h	7 %[b]		74 %	**9f**	4 %[b]	
			AIBN, room temp., 20 h	7 %[b]		21 %[i]	**9f**	7 %[b]	
			room temp., 20 h	5 %[b]		90 %	**9f**	5 %[b]	
Ph	Ph	Cl	9-BBN, −78 °C, 6 h	32 %	**8g**	–		n. o.[b]	
			AIBN, room temp., 20 h	16 %	**8g**	–		n. o.[b]	
		Br	9-BBN, −78 °C, 6 h	18 %	**8h**	–		n. o.[b]	
			AIBN, room temp., 20 h	10 %	**8h**	–		n. o.[j]	

[a] Crude yield: 69 %. [b] Crude yield: 77 %. [c] Crude yield: 63 %, desilylation occurred to a large extent giving **1b**. [d] Isolated together with **1b**. [e] Crude yield 63 %, no desilylation, the rest is isolated together with the other isomer. [f] Mixture with **8d**. [g] Crude yield: 57 %, the rest is isolated as mixture with the two other isomers. [h] Crude yield: 67 %, the rest is isolated as mixture with the two other isomers. [i] Crude yield: 67 %, the rest is isolated as mixture with the two other isomers. [j] Not observed.



Scheme 6. Possible reaction products of homopropargylic alcohols with dibutyltin halide hydride

that would be gained due to intramolecular coordination in the β isomer is not sufficient to drive the reaction towards addition at the non-terminal acetylenic carbon atom. This has already been seen in the case of non-terminal propargylic alcohols. The γ-isomers are formed in similar amounts, and in contrast to the situation observed for the non-terminal propargylic alcohols reduction of the reaction temperature does not lead to a change in the isomer ratio, so that isomerisation does not appear to play an important role in its determination. This is somewhat surprising, since the γ_{anti} isomer undergoes intramolecular coordination between oxygen and tin, as shown by the following NMR spectroscopic data:

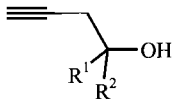
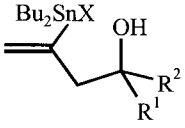
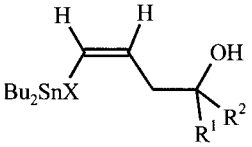
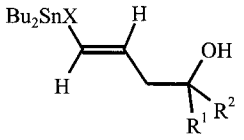
a) Tin chemical shift between −15 and −24 ppm

b) ^3J(HC=CH) = 12.2−12.8 Hz

c) $^3J(^{119}SnC=CH)$ = 205−212 Hz

d) $^1J(^{119}Sn\text{-}^{13}C=CH)$ = 479−535 Hz.

Table 6. Products of hydrostannylation of homopropargylic alcohols

Alcohol			Reaction conditions	Yield of β product	Yield of γ_{anti} product	Compound	Yield of γ_{syn} product	Compound
R^1	R^2	X						
H	H	Cl	AIBN, room temp., 20 h	n.o.[a]	36 %	**11a**	22 %[b]	
			room temp., 20 h	n.o.[a]	38 %	**11a**	22 %[b]	
Me	Ph	Cl	9-BBN, −78 °C, 6 h	14 %[c]	40 %	**11b**	28 %	**12b**
			AIBN, room temp., 20 h	n. o.[a]	38 %	**11b**	19 %[d]	**12b**
			room temp., 20 h	12 %	29 %	**11b**	30 %	**12b**
H	H	Br	AIBN, room temp., 20 h	n. o.[a]	23 %[e]	**11c**	58 %[f]	
			room temp., 20 h	n. o.[a]	40 %	**11c**	56 %	
Me	Ph	Br	9-BBN, −78 °C, 6h	n. o.[a]	33 %	**11d**	33 %	**12d**
			AIBN, room temp., 20 h	n. o.[a]	36 %[g]	**11d**	35 %[g]	**12d**
			room temp., 20 h	n. o.[a]	40 %	**11d**	55 %	**12d**

[a] Not observed. [b] Contaminated by an unknown *n*-butyltin species. [c] As estimated from NMR spectra. [d] Crude yield: 46 %, the rest is contaminated by $Bu_4Sn_2Cl_2O$. [e] Crude yield: 42 %, the rest is isolated as mixture with other isomer. [f] Isolated as mixture with other isomer. [g] Crude yield: 40 % (for *anti*) and 49 % (for *syn*), respectively.

Intramolecular coordination is of course not possible for the γ_{syn} isomer, which is again manifested in the NMR spectroscopic data:

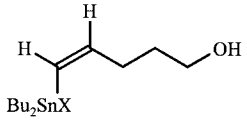
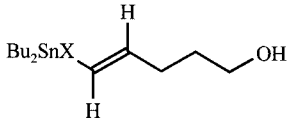
a) Tin chemical shift between 64 and 84 ppm
b) ^3J(HC=CH) = 18.8 Hz
c) $^3J(^{119}SnC=CH)$ = 87−102 Hz
d) $^1J(^{119}Sn\text{-}^{13}C=CH)$ = 430−448 Hz.

The ^{1}H NMR spectra of the γ_{syn} isomers exhibit higher order effects and can only be solved by spin simulation.

Further chain elongation affords alcohols derived from 4-pentyn-1-ol; only the "parent" compound was studied (Table 7, Scheme 7). Here, again as expected, only attack at the terminal acetylenic carbon was observed.

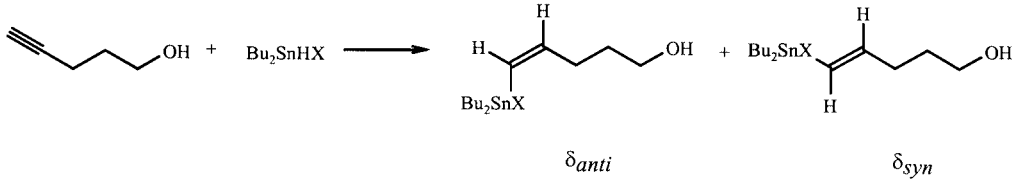
Irrespective of the reaction conditions and the hydride used, the main product was the δ_{syn} isomer; the total yield generally being 80−85 %. Intramolecular coordination is not observed for both isomers, as shown by the NMR spectroscopic data (see Exp. Sect.).

Table 7. Products of hydrostannylation of 4-pentyn-1-ol

X	Reaction conditons	Yield of δ_{anti} product	Compound	Yield of δ_{syn} product	Compound
Cl	9-BBN, −78 °C, 6h	5 %	**13a**	20 %	**14a**
	AIBN, room temp., 20 h	18 %	**13a**	61 %	**14a**
	room temp., 20 h	19 %	**13a**	61 %	**14a**
Br	9-BBN, −78 °C, 6h	15 %	**13b**	64 %	**14b**
	AIBN, room temp., 20 h	11 %[a]	**13b**	68 %	**14b**
	room temp., 20 h	20 %	**13b**	63 %	**14b**

[a] Crude yield: 17 %.



Scheme 7. Reaction products for the hydrostannylation of 4-pentyn-1-ol

Although it has been known for decades that amines catalyse the decomposition of organotin hydrides, we felt that the reactivity of the hydride halides at −78 °C in the presence of 9-BBN might permit hydrostannylation of *N*,*N*-dimethylpropargylamine; this was indeed the case. Though product yields were only about 20 %, and a large number of unidentified side-products were formed, it was possible to identify the product as the expected β_{anti} isomer, stabilised by intramolecular coordination between nitrogen and tin [tin chemical shift −46 ppm, ^3J(HC=CH) 11.3 Hz].

Conclusion

Hydrostannylations of terminal propargylic alcohols give almost exclusively the products of *anti*-addition at the terminal carbon atom, irrespective of the dibutyltin halide hydride and/or initiator used; yields are generally excellent. This reaction opens a new route for regio- and stereoselective hydrostannylations: the predominant isomer formed can only otherwise be obtained by Lewis-acid catalyzed hydrostannylations as described by Yamamoto. The high stereoselectivity is due to the formation of a five-membered ring, with intramolecular coordination of the alcohol oxygen with the Lewis acidic tin atom. Terminal propargylic ethers show similar behaviour.

If non-terminal propargylic alcohols are used the regioselectivity is reversed, giving products typical of free radical hydrostannylations. The major drawback of such hydrostannyltions, namely the isomerisation of the reaction product to give a mixture of stereoisomers, can be circumvented by carefully adjusting the reaction conditions, so that the sole product is that of *anti*-addition.

If additional carbon atoms are inserted between the two functional groups, the formation of a five-membered ring (due to intramolecular coordination) is no longer observed. As is typical of free radical hydrostannylation, isomer mixtures are formed.

The products of the hydrostannylation reaction can be used as substrates in Stille reactions using a TBAF protocol; our work in this area, as well as the mechanistic studies which we have carried out, will be the subject of further papers.[21]

Experimental Section

General Remarks: Hydrostannylations were carried out in flame dried glassware under argon. Column chromatography was usually carried out using the flash technique on MN Silica Gel 60 (70−230 mesh, Macherey and Nagel). If column chromatography was performed at low temperature a double-walled glass column was used, the outer jacket filled with dry ice. The reaction products were fully characterised by NMR spectroscopy using Bruker Avance DPX 300 and DRX 400 instruments operating at 300 MHz and 400 MHz for ^{1}H and by MS and CH-analyses. MS analyses were conducted with a Finnigan MAT 8200 with a typical accelerating voltage (electron energy) of 70 eV. Elemental analyses were carried out with a LECO CHNS 932. Chemical shifts are reported in ppm (δ scale) relative to residual non-deuterated solvent signals ($CHCl_3$) for ^{1}H, relative to $CDCl_3$ for ^{13}C, relative to an external standard (TMS, Me_4Sn) for ^{29}Si and ^{119}Sn. Only the couplings to the isotope ^{119}Sn are reported. All new compounds exhibited satisfactory elemental analyses.

Toluene and diethyl ether were predried with sodium wire, distilled from sodium and stored under an argon atmosphere. 1-Phenyl-2-propyn-1-ol, 2-phenyl-3-butyn-2-ol, 1,1-diphenyl-2-propyn-1-ol, 3-octyn-2-ol, and 2-phenyl-3-octyn-2-ol were synthesized as described by Brandsma,[22] 2-butyn-1-ol and 3-pentyn-2-ol as described by Audin,[23] 3-trimethylsilyl-2-propyn-1-ol, 4-trimethylsilyl-3-butyn-2-ol and 1,1-diphenyl-1-trimethylsilyloxy-2-propyne as described by Gawley.[24] 1-Trimethylsilyloxy-2-propyne, 2-trimethylsilyloxy-3-butyne and 2-ethynyl-1-trimethylsilyloxycyclohexane as described by Demina.[25] 2-Phenyl-4-pentyn-2-ol was synthesized using the procedure described by Schmidt.[26] Di-*n*-butyl-tin dihydride was synthesized according to van der Kerk[27] and the mixed tin hydrides bromo-di-*n*-butyltin hydride and di-*n*-butylchlorotin hydride were prepared in situ according to Sawyer. All other chemicals were commercially available and were recrystallised (solids) or distilled (liquids) prior to use.

General Procedure for Hydrostannylations: Under argon, di-*n*-butyltin dihalide (2.5 mmol) was dissolved in toluene (10 mL) and di-*n*-butyltin dihydride (2.5 mmol) was added. The mixture was stirred at room temperature for about 30 minutes before the mixture was brought to reaction temperature (−78 °C, 0 °C, 25 °C). The alkynol (5.0 mmol) was added in one portion followed by the radical initiator (9-BBN or AIBN) if necessary. The reaction mixture was left stirring at the reaction temperature for 6 h (9-BBN, −78 °C) to 20 h (AIBN, room temp.). After evaporation of the solvent the product was purified by distillation or the isomers were separated by flash column chromatography (at low temperature in most cases) to give a colourless to slightly yellow oil.

(*Z*)-3-Dibutylchlorostannyl-2-propen-1-ol (1a): After following the general procedure purification was achieved by kugelrohr distillation, b.p. 240 °C at 1×10^{-3} mbar (1.30 g; 80 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.60 (dt, J = 2.4, 11.8 Hz, $^3J_{Sn,H}$ = 209 Hz, 1 H, H2), 6.21 (dt, J = 2.5, 11.8 Hz, $^2J_{Sn,H}$ = 100 Hz, 1 H, H3), 4.33 (m, $^4J_{Sn,H}$ = 22 Hz, 2 H, H1), 4.08 (s, 1 H, OH), 1.56 (m, 4 H, H2′), 1.27 (m, 8 H, H3′ + H1′), 0.82 (m, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 142.1 ($^2J_{Sn,C}$ < 2 Hz, C2), 129.0 ($^1J_{Sn,C}$ = 572 Hz, C3), 64.3 ($^3J_{Sn,C}$ = 33 Hz, C1), 27.9 ($^2J_{Sn,C}$ = 29 Hz, C2′), 26.5 ($^3J_{Sn,C}$ = 80 Hz, C3′), 21.0 ($^1J_{Sn,C}$ = 475 Hz, C1′), 13.6 (C4′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −1.6 ppm. MS: m/z = 292 [M^+ − Cl + H^+], 267 [M^+ − Bu], 250 [M^+ − Bu − H_2O], 155 [HSnCl], 57 [Bu].

Spectroscopic evidence for the other regioisomer (**2-Dibutylchlorostannyl-2-propen-1-ol**) is given by the following data (recorded before purification). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.86 (br. s, 1 H, $H3_\beta$), 5.54 (br. s, 1 H, $H3_\alpha$) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 69.8 ppm.

(*Z*)-4-Dibutylchlorostannyl-3-buten-2-ol (1b): After following the general procedure purification was achieved by kugelrohr distillation, b.p. 180 °C at 1×10^{-3} mbar (1.15 g; 68 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.59 (dd, J = 1.2, 12.0 Hz, $^3J_{Sn,H}$ = 210 Hz, 1 H, H3), 6.22 (dd, J = 2.1, 12.0 Hz, $^2J_{Sn,H}$ = 98 Hz, 1 H, H4), 4.60 (dq, J = 6.5, 2.4 Hz, 1 H, H2), 3.42 (s, 1 H, OH), 1.63 (m, 4 H, H2′), 1.26−1.38 (m, 8 H, H3′ + H1′), 1.33 (d, J = 6.5 Hz, 3 H, H1), 0.89 (m, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 146.7 ($^2J_{Sn,C}$ < 2 Hz, C3). 130.4 ($^1J_{Sn,C}$ = 578 Hz, C4), 70.3 ($^3J_{Sn,C}$ = 31 Hz, C2), 28.0 ($^2J_{Sn,C}$ = 36 Hz, C2′), 26.6 ($^3J_{Sn,C}$ =

80 Hz, C3′), 23.7 (C1), 21.9 ($^1J_{Sn,C}$ = n. d., C1′$_\beta$), 21.4 ($^1J_{Sn,C}$ = n. d., C1′$_\alpha$), 13.6 (C4′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −2.0 ppm. MS: *m*/*z* = 341 [M^+], 281 [M^+ − Bu], 269 [Bu_2SnCl], 250 [M^+ − Bu − Me − H_2O], 57 [Bu].

Spectroscopic evidence for the other regioisomer (**3-Dibutylchlorostannyl-3-buten-2-ol**) is given by the following data (recorded before purification). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.83 (d, *J* = 1.4 Hz, $^3J_{Sn,H}$ = 196 Hz, 1 H, H4$_\beta$), 5.67 (d, *J* = 1.4 Hz, $^3J_{Sn,H}$ = 97 Hz, 1 H, H4$_\alpha$) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 61.5 ppm.

(*Z*)-4-Dibutylchlorostannyl-2-methyl-3-buten-2-ol (1c): After following the general procedure purification was achieved by kugelrohr distillation, b.p. 180 °C at 2.4 × 10^{-2} mbar (1.41 g; 80 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.55 (d, *J* = 11.6 Hz, $^3J_{Sn,H}$ = 209 Hz, 1 H, H3), 6.10 (d, *J* = 11.6 Hz, $^2J_{Sn,H}$ = 98 Hz, 1 H, H4), 3.39 (s, 1 H, OH), 1.64 (m, 4 H, H2′), 1.32−1.38 (m, 4 H, H3′), 1.36 (s, 6 H, H1), 1.25−1.29 (m, 4 H, H1′), 0.89 (m, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 150.6 ($^2J_{Sn,C}$ < 2 Hz, C3), 128.9 ($^1J_{Sn,C}$ = 587 Hz, C4), 75.7 ($^3J_{Sn,C}$ = 28 Hz, C2), 30.0 (C1), 28.0 ($^2J_{Sn,C}$ = 29 Hz, C2′), 26.6 ($^3J_{Sn,C}$ = 80 Hz, C3′), 21.2 ($^1J_{Sn,C}$ = 477 Hz, C1′), 13.6 (C4′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −5.0 ppm. MS: *m*/*z* = 319 [M^+ − Cl], 269 [Bu_2SnCl], 259 [M^+ − Bu − Cl], 57 [Bu].

Spectroscopic evidence for the other regioisomer (**3-Dibutylchlorostannyl-2-methyl-3-buten-2-ol**) is given by the following data (recorded before purification). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.78 (s, 1 H, $^3J_{Sn,H}$ = 200 Hz, H4$_\beta$), 5.67 (s, 1 H, $^3J_{Sn,H}$ = 102 Hz, H4$_\alpha$), ^{119}Sn (112 MHz, $CDCl_3$, 23 °C): δ = 45.6 ppm.

(*Z*)-1-(2′-Dibutylchlorostannyl)ethenyl-1-cyclohexanol (1d): After following the general procedure purification was achieved by kugelrohr distillation, bp. 240 °C at 2.0·10^{-2} mbar (1.58 g; 80 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.66 (d, 1 H, *J* = 11.8 Hz, $^3J_{Sn,H}$ = 211 Hz, H1′), 6.15 (d, 1 H, *J* = 11.8, $^2J_{Sn,H}$ = 97 Hz, H2′), 2.85 (s, 1 H, OH), 1.57 (m, 4 H, H2′′), 1.54−1.42 (m, 10 H, H2−H4), 1.28 (sext, *J* = 7.5 Hz, 4 H, H3′′), 1.20 (t, *J* = 8.5 Hz, 4 H, H1′′), 0.89 (t, *J* = 7.5 Hz, 6 H, H4′′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 149.9 ($^2J_{Sn,C}$ < 2 Hz, C1′), 129.9 ($^1J_{Sn,C}$ = 583 Hz, C2′), 76.8 (C1), 39.7 (C2), 28.0 ($^2J_{Sn,C}$ = 29 Hz, C2′′), 26.6 ($^3J_{Sn,C}$ = 80 Hz, C3′′), 24.7 (d, C3), 21.1 (C4), 21.1 ($^1J_{Sn,C}$ = 474 Hz, C1′′), 13.6 (C4′′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −5.4 ppm. MS: *m*/*z* = 375 [M^+ − H_2O], 358 [M^+ − HCl], 315 [M^+ − HCl − C_3H_7], 297 [M^+ − HCl − C_3H_7 − H_2O], 269 [Bu_2SnCl], 245 [M^+ − 2Bu − HCl], 177 [HS*n*Bu], 81 [Cyclohex], 57 [Bu].

Spectroscopic evidence for the other regioisomer [**1-(1′-Dibutylchlorostannyl)ethenyl-1-cyclohexanol**] is given by the following data (recorded before purification). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.81 (s, $^3J_{Sn,H}$ = 203 Hz, 1 H, H2′$_\beta$), 5.70 (s, $^3J_{Sn,H}$ = 104 Hz, 1 H, H2′$_\alpha$) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 43.6 ppm.

(*Z*)-3-Dibutylchlorostannyl-1-phenyl-2-propen-1-ol (1e): After following the general procedure (2.5 mmol instead of 5.0 mmol) purification was carried out by flash column chromatography at low temperature, R_f = 0.11 using *n*-hexane/Et_2O (3:1) as solvent (0.74 g; 74 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.28−7.41 (m, 5 H, H2′−H4′). 6.61 (dd, *J* = 11.6 Hz, 1.1 Hz, $^3J_{Sn,H}$ = 206 Hz, 1 H, H2), 6.30 (dd, *J* = 11.8 Hz, 2.1 Hz, $^2J_{Sn,H}$ = 95 Hz, 1 H, H3), 5.42 (d, *J* = 2.1 Hz, 1 H, H1), 4.00 (s, 1 H, OH), 1.65 (m, 4 H, H2′′), 1.27−1.42 (m, 6 H, H1′′ + H3′′), 0.91 (m, 6 H, H4′′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 144.6 ($^2J_{Sn,C}$ < 2 Hz, C2). 141.0 (C1′), 131.0 ($^1J_{Sn,C}$ = 565 Hz, C3), 128.9 (C2′), 128.8 (C4′), 127.0 (C3′), 76.2 ($^3J_{Sn,C}$ = 28 Hz, C1), 28.0 ($^2J_{Sn,C}$ = 30 Hz, C2′′$_\beta$), 27.9 ($^2J_{Sn,C}$ = 30 Hz, C2′′$_\alpha$), 26.6 ($^3J_{Sn,C}$ = 79 Hz, C3′′$_\beta$), 26.6 ($^3J_{Sn,C}$ = 79 Hz, C3′′$_\alpha$), 21.2 ($^1J_{Sn,C}$ = 473 Hz, C1′′$_\beta$), 20.7 ($^1J_{Sn,C}$ = 473 Hz, C1′′$_\alpha$), 13.7 (C4′′$_\beta$), 13.6 (C4′′$_\alpha$) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = −1.2 ppm. MS: *m*/*z* = 402 [M^+], 384 [M^+ − H_2O], 365 [M^+ − HCl], 345 [M^+ − Bu], 327 [M^+ − Bu − H_2O], 269 [Bu_2SnCl], 251 [M^+ − 2Bu − HCl], 155 [HSnCl], 133 [M^+ − Bu_2SnCl], 115 [M^+ − Bu_2SnCl − H_2O], 91 [C_7H_7], 77 [Ph], 57 [Bu].

Spectroscopic evidence for the other regioisomer (**2-Dibutylchlorostannyl-1-phenyl-2-propen-1-ol**) is given by the following data: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.75 (d, *J* = 2.2 Hz, $^3J_{Sn,H}$ = 186 Hz, 1 H, H3$_\alpha$). 5.69 (d, *J* = 2.2 Hz, $^3J_{Sn,H}$ = 186 Hz, 1 H, H3$_\beta$) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 63.6 ppm. R_f (*n*-hexane/Et_2O, 3:1) = 0.21.

(*Z*)-4-Dibutylchlorostannyl-2-phenyl-3-buten-2-ol (1f): After following the general procedure purification was carried out by flash column chromatography, R_f = 0.14 using *n*-hexane/Et_2O (4:1) as solvent (1.16 g; 56 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.35−7.41 (m, 4 H, H2′ + H3′), 7.28−7.32 (m, 1 H, H4′), 6.67 (d, *J* = 12.0 Hz, $^3J_{Sn,H}$ = 204 Hz, 1 H, H3), 6.28 (d, *J* = 12.0, $^2J_{Sn,H}$ = 92 Hz, 1 H, H4), 3.69 (s, 1 H, OH), 1.75 (s, 3 H, H1), 1.57−1.73 (m, 4 H, H2′′), 1.27−1.42 (m, 6 H, H1′′ + H3′′), 0.93 (t, *J* = 7.3 Hz, 3 H, H′′$_\beta$), 0.87 (t, *J* = 7.3 Hz, 3 H, H4′′$_\alpha$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 149.8 ($^2J_{Sn,C}$ < 2 Hz, C3), 144.1 ($^4J_{Sn,C}$ = 10 Hz, C1′), 128.8 (C4′), 128.6 (C2′), 127.8 ($^1J_{Sn,C}$ = n.d., C4), 125.2 (C3′), 78.1 ($^3J_{Sn,C}$ = 26 Hz, C2), 28.8 (C1), 28.1 ($^2J_{Sn,C}$ = 37 Hz, C2′′$_\beta$), 28.0 ($^2J_{Sn,C}$ = 37 Hz, C2′′$_\alpha$), 26.7 ($^3J_{Sn,C}$ = 79 Hz, C3′′), 21.1 ($^1J_{Sn,C}$ = 474 Hz, C1′′$_\beta$), 21.1 ($^1J_{Sn,C}$ = 474 Hz, C1′′$_\alpha$), 13.7 (C4′′$_\beta$), 13.6 (C4′′$_\alpha$) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = −1.8 ppm. MS: *m*/*z* = 416 [M^+], 398 [M^+ − H_2O], 363 [M^+ − HCl − H_2O], 341 [M^+ − Bu − H_2O], 323 [M^+ − Bu − HCl], 269 [Bu_2SnCl], 211 [BuSnCl], 155 [HSnCl], 77 [Ph], 57 [Bu].

Spectroscopic evidence for the other regioisomer (**3-Dibutylchlorostannyl-2-phenyl-3-buten-2-ol**) is given by the following data (recorded before purification). ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 53.7 ppm. R_f (*n*-hexane/Et_2O, 4:1) = 0.20.

(*Z*)-3-Dibutylchlorostannyl-1,1-diphenyl-2-propen-1-ol (1g): After following the general procedure purification was carried out flash column chromatography, R_f = 0.14 using *n*-hexane/Et_2O (4:1) as solvent (1.44 g; 60 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.33 (m, 5 H, H2′−H4′). 7.03 (dd, *J* = 11.8 Hz, 1.2 Hz, $^3J_{Sn,H}$ = 203 Hz, 1 H, H2), 6.40 (d, *J* = 11.8 Hz, 88 Hz, 1 H, H3), 3.94 (d, *J* = 1.2 Hz, 1 H, OH), 1.60 (m, 4 H, H2′′), 1.30 (m, 6 H, H1′′ + H3′′), 0.86 (t, *J* = 7.2 Hz, 6 H, H4′′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 148.2 ($^2J_{Sn,C}$ < 2 Hz, C2), 144.1 ($^4J_{Sn,C}$ = 10 Hz, C1′), 130.9 ($^1J_{Sn,C}$ = 561 Hz, C3), 128.5 (C2′), 128.5 (C4′), 126.8 (C3′), 82.8 ($^3J_{Sn,C}$ = 24 Hz, C1), 27.9 ($^2J_{Sn,C}$ = 30 Hz, C2′′), 26.6 ($^3J_{Sn,C}$ = 79 Hz, C3′′), 20.7 ($^1J_{Sn,C}$ = 470 Hz, C1′′), 13.6 (C4′′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 2.1 ppm. MS: *m*/*z* = 477 [M^+], 421 [M^+ − Bu], 385 [M^+ − Bu − Cl], 365 [M^+ − Bu − HCl − H_2O], 329 [M^+ − 2Bu − Cl], 191 [BuSnMe], 167 [CH_2Ph_2], 77 [Ph], 57 [Bu].

Spectroscopic evidence for the other regioisomer (**2-Dibutylchlorostannyl-1,1-diphenyl-2-propen-1-ol**) is given by the following data (recorded before purification). ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 53.1 ppm. R_f (*n*-hexane/Et_2O, 4:1) = 0.28.

(*Z*)-3-Bromodibutylstannyl-2-propen-1-ol (2a): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.23 using *n*-hexane/Et_2O (2:1) as solvent (1.78 g; 89 %). ^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.63 (dt, *J* = 12.0 Hz, 2.0 Hz, $^3J_{Sn,H}$ = 210 Hz, 1 H, H2), 6.33 (dt, *J* = 12.0 Hz, 2.0 Hz, $^2J_{Sn,H}$ = 101 Hz, 1 H, H3), 4.42 (m, $^4J_{Sn,H}$ = 22 Hz, 2 H, H1), 3.83 (s, 1 H, OH), 1.62 (m, 4 H, H2′), 1.35 (m, 8 H, H3′ + H1′) and 0.89 (m, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 141.7 (d, $^2J_{Sn,C}$ < 5 Hz, C2), 130.5 (d, $^1J_{Sn,C}$ = 559 Hz, C3), 64.3 (t, $^3J_{Sn,C}$ = 34 Hz, C1), 28.1 (t, $^2J_{Sn,C}$ = 28 Hz, C2′), 26.4 (t, $^3J_{Sn,C}$ = 78 Hz, C3′), 21.5 (t, $^1J_{Sn,C}$ = 464 Hz, C1′), 13.6 (q, C4′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −2.8 ppm. MS: *m*/*z* = 370 [M^+], 353 [$M^+ - H_2O$], 313 [M^+ − Bu], 273 [$M^+ - Br - H_2O$], 257 [BuSnBr], 199 [SnBr], 57 [Bu].

Spectroscopic evidence for the other regioisomer (8 %**, 2-Bromodibutylstannyl-2-propen-1-ol**) is given by the following data. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 64.2 ppm.

(*Z*)-4-Bromodibutylstannyl-3-buten-2-ol (2b): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.25 using *n*-hexane/Et_2O (3:1) as solvent (1.80 g; 91 %). ^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.54 (dd, *J* = 11.8 Hz, 2.0 Hz, $^3J_{Sn,H}$ = 209 Hz, 1 H, H3), 6.25 (dd, *J* = 11.8 Hz, 2.0 Hz, $^2J_{Sn,H}$ = 103 Hz, 1 H, H4), 4.62 (q, *J* = 6.4 Hz, 1 H, H2), 3.90 (s, 1 H, OH), 1.63 (m, 4 H, H2′), 1.41−1.21 (m, 8 H, H3′ + H1′), 1.33 (d, *J* = 6.4 Hz, 3 H, H1), 0.89 (m, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 146.6 (d, $^2J_{Sn,C}$ < 5 Hz, C3), 130.4 (d, $^1J_{Sn,C}$ = 568 Hz, C4), 70.4 (d, $^3J_{Sn,C}$ = 29 Hz, C2), 28.7 (t, $^2J_{Sn,C}$ = 30 Hz, C2′), 26.9 (t, $^3J_{Sn,C}$ = 76 Hz, C3′), 23.7 (q, C1), 22.4 (t, $^1J_{Sn,C}$ = 460 Hz, C1′$_\alpha$), 22.1 (t, $^1J_{Sn,C}$ = 464 Hz, C1′$_\beta$), 14.0 (q, C4′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = −6.1 ppm. MS: *m*/*z* = 370 [M^+ − Me], 327 [M^+ − Bu], 309 [$M^+ - Bu - H_2O$], 273 [$M^+ - Me - Br - H_2O$], 199 [SnBr], 57 [Bu].

Spectroscopic evidence for the other regioisomer (9 %, **3-Bromodibutylstannyl-3-buten-2-ol)** is given by the following data. ^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.83 (d, *J* = 1.7 Hz, $^3J_{Sn,H}$ = 198, $^3J_{Sn,H}$ = 189 Hz, 1 H, H4$_\beta$), 5.67 (d, *J* = 2.1 Hz, $^3J_{Sn,H}$ = 97 Hz, 1 H, H4$_\alpha$) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 57.4 ppm.

(*Z*)-1-(2′-Bromodibutylstannyl)ethenyl-1-cyclohexanol (2c): After following the general procedure purification was carried out by flash column chromatography, R_f = 0.19 using *n*-hexane/Et_2O (2:1) as solvent (2.08 g; 92 %). ^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.61 (d, *J* = 11.8 Hz, $^3J_{Sn,H}$ = 210 Hz, 1 H, H1′), 6.23 (d, *J* = 11.8 Hz, $^2J_{Sn,H}$ = 98 Hz, 1 H, H2′), 2.46 (s, 1 H, OH), 1.72−1.44 (2 m, 10 H, H2−H4), 1.63 (m, 4 H, H2′′) 1.35 (m, 8 H, H1′′, H3′′), 0.90 (t, 6 H, 7.4 Hz, H4′′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 149.7 (d, $^2J_{Sn,C}$ < 5 Hz, C1′), 130.3 (d, $^1J_{Sn,C}$ = 564 Hz, C2′), 76.9 (s, C1), 37.7 (d, C2), 29.7 (t, $^2J_{Sn,C}$ = 29 Hz, C2′′), 26.5 (t, $^3J_{Sn,C}$ = 79 Hz, C3′′), 24.7 (d, C3), 21.8 (d, C4), 21.5 (t, $^1J_{Sn,C}$ = 460 Hz, C1′′), 13.7 (q, C4′′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −9.5 ppm. MS: *m*/*z* = 438 [M^+], 381 [M^+ − Bu], 363 [$M^+ - Bu - H_2O$], 313 [Bu_2SnBr], 199 [SnBr], 57 [Bu].

Spectroscopic evidence for the other regioisomer (8 %, **1-(1′-Bromodibutylstannyl)ethenyl-1-cyclohexanol**) is given by the following data. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 42.6 ppm.

(*Z*)-2-Dibutylchlorostannyl-2-buten-1-ol (4a): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.18 using *n*-hexane/Et_2O (4:1) as solvent (0.4 g; 21 %). ^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.41 (q, *J* = 6.6 Hz, $^3J_{Sn,H}$ = 178 Hz, 1 H, H3), 4.30 (s, $^3J_{Sn,H}$ = 53 Hz, 2 H, H1), 1.84 (d, *J* = 6.6 Hz, 3 H, H4), 1.65 (m, 4 H, H2′), 1.38 (m, 8 H, H1′ + H3′), 0.90 (t, *J* = 7.3 Hz, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 144.9 (s, $^1J_{Sn,C}$ = 462 Hz, C2), 137.5 (d, $^2J_{Sn,C}$ = 33 Hz, C3), 68.8 (t, $^2J_{Sn,C}$ = 40 Hz, C1), 27.6 (t, $^2J_{Sn,C}$ = 24 Hz, C2′), 26.5 (t, $^3J_{Sn,C}$ = 73 Hz, C3′), 19.3 (t, $^1J_{Sn,C}$ = 380 Hz, C1′), 19.2 (q, $^3J_{Sn,C}$ = 48 Hz, C4), 13.5 (q, C4′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 79.0 ppm. MS: *m*/*z* = 339 [M^+], 283 [M^+ − Bu], 265 [$M^+ - Bu - H_2O$], 213 [BuSnCl], 57 [Bu]. Isomer separation was possible:

(*E*)-2-Dibutylchlorostannyl-2-buten-1-ol (5a): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.11 using *n*-hexane/Et_2O (4:1) as solvent (1.13 g; 70 %). ^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.03 (q, *J* = 6.7 Hz, $^3J_{Sn,H}$ = 98 Hz, 1 H, H3), 4.51 (s, $^3J_{Sn,H}$ = 40 Hz, 2 H, H1), 1.69 (d, *J* = 6.7 Hz, 3 H, H4), 1.64 (m, 4 H, H2′), 1.39−1.26 (8 H, 2 m, H1′ + H3′), 0.91 (t, *J* = 7.5 Hz, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 147.1 (s, $^1J_{Sn,C}$ = 553 Hz, C1), 134.0 (d, $^2J_{Sn,C}$ = 15 Hz, C3), 63.7 (t, $^2J_{Sn,C}$ = 30 Hz, C1), 27.7 (t, $^2J_{Sn,C}$ = 28 Hz, C2′), 26.5 (t, $^3J_{Sn,C}$ = 75 Hz, C3′), 19.6 (t, $^1J_{Sn,C}$ = 403 Hz, C1′), 16.1 (q, $^3J_{Sn,C}$ = 80 Hz, C4), 13.5 (q, C4′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = 66.4 ppm.

Spectroscopic evidence for the other regioisomer [10 %, **(*Z*)-3-Dibutylchorostannyl-2-buten-1-ol**] is given by the following data.^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.63 (d, *J* = 10 Hz, $^3J_{Sn,H}$ = 206 Hz, 1 H, H2) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −7.6 ppm.

(*Z*)-3-Dibutylchlorostannyl-3-penten-2-ol (4b): After following the general procedure purification was carried out by flash column chromatography, R_f = 0.16 using *n*-hexane/Et_2O (4:1) as solvent (0.69 g; 30 %). Considerable decomposition is observed during column chromatography. ^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.36 (qd, *J* = 6.8 Hz, 1.2 Hz, $^3J_{Sn,H}$ = 187 Hz, 1 H, H4), 4.53 (q, *J* = 6.3 Hz, $^3J_{Sn,H}$ = 60 Hz, 1 H, H2), 1.89 (d, *J* = 6.8 Hz, 3 H, H5), 1.66 (m, 4 H, H2′), 1.38 (q, *J* = 7.4 Hz, 8 H, H3′ + H1′), 1.32 (d, *J* = 6.3 Hz, 3 H, H1), 0.92 (t, *J* = 7.4 Hz, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 150.3 (s, $^1J_{Sn,C}$ = 477 Hz, C3), 135.6 (d, $^2J_{Sn,C}$ = 25 Hz, C4), 74.0 (d, $^2J_{Sn,C}$ = 37 Hz, C2), 27.8 (t, $^2J_{Sn,C}$ = 25 Hz, C2′), 26.7 (t, $^3J_{Sn,C}$ = 76 Hz, C3′), 24.5 (q, $^3J_{Sn,C}$ = 13 Hz, C1), 20.8 (t, $^1J_{Sn,C}$ = n.d., C1′$_\alpha$), 20.1 (t, $^1J_{Sn,C}$ = n.d., C1′), 18.6 (q, $^3J_{Sn,C}$ = 47 Hz, C5), 13.6 (q, C4′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 65.3 ppm. MS: *m*/*z* = 355 [M^+], 297 [M^+ − Bu], 279 [$M^+ - Bu - H_2O$], 269 [Bu_2SnCl], 155 [HSnCl], 85 [$M^+ - Bu_2SnCl$], 67 [$M^+ - Bu_2SnCl - H_2O$], 57 [Bu]

Spectroscopic evidence for the two other regio- and stereoisomers is given by the following data.

(*E*)-3-Dibutylchlorostannyl-3-penten-2-ol: ^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.02 (qd, *J* = 6.9 Hz, 2.4 Hz, $^3J_{Sn,H}$ = 97 Hz, 1 H, H4) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 59.2 ppm.

(*Z*)-2-Dibutylchlorostannyl-2-penten-4-ol: ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = −17.6 ppm.

(*Z*)-3-Dibutylchlorostannyl-3-octen-2-ol (4c): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.19 using *n*-hexane/Et_2O (9:1) as solvent (1.2 g; 70 %). ^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.26 (t, *J* = 7.7 Hz, $^3J_{Sn,H}$ = 188 Hz, 1 H, H4), 4.53 (m, $^3J_{Sn,H}$ = 60 Hz, 1 H, H2), 2.23 (m, 2 H, H5), 1.65 (m, 4 H, H2′), 1.34 (m, 15 H, H1, H6, H7, H1′, H3′), 0.91 (m, 9 H, H8, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 149.1 (s, $^1J_{Sn,C}$ = 479 Hz,

C3), 141.4 (d, $^2J_{Sn,C}$ = 28 Hz, C4), 73.9 (d, $^2J_{Sn,C}$ = 37 Hz, C2), 32.9 (t, $^3J_{Sn,C}$ = 45 Hz, C5), 32.0 (t, $^4J_{Sn,C}$ = 8 Hz, C6), 27.7 (t, $^2J_{Sn,C}$ = 28 Hz, C2′), 26.7 (t, $^3J_{Sn,C}$ = 76 Hz, C3′), 24.6 (q, $^3J_{Sn,C}$ = 13 Hz, C1), 22.3 (t, C7), 20.8 (t, $^1J_{Sn,C}$ = n.d., C1′$_\alpha$), 20.2 (t, $^1J_{Sn,C}$ = n.d., C1′$_\beta$), 14.0 (q, C8), 13.6 (q, C4′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 62.7 ppm. MS: *m*/*z* = 396 [M^+], 340 [M^+ − Bu], 322 [M^+ − Bu − H_2O], 109 [M^+ − Bu_2SnCl −H_2O], 57 [Bu].

Spectroscopic evidence for the two other regio- and stereoisomers is given by the following data.

(*Z*)-4-Dibutylchlorostannyl-3-octen-2-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.14 (s, $^3J_{Sn,H}$ = 201 Hz, 1 H, H3) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −19.7 ppm. R_f = 0.13.

(*E*)-3-Dibutylchlorostannyl-3-octen-2-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.88 (t, *J* = 6.7 Hz, $^3J_{Sn,H}$ = 101 Hz, 1 H, H4) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 59.2 ppm.

(*Z*)-3-Dibutylchlorostannyl-2-phenyl-3-octen-2-ol (4d): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.13 using *n*-hexane/Et_2O (9:1) as solvent (1.1 g; 46 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.38 (d, *J* = 7.6 Hz, 2 H, H2′), 7.30 (t, *J* = 7.6 Hz, 2 H, H3′), 7.22 (m, 1 H, H4′), 6.17 (t, *J* = 7.4, $^3J_{Sn,H}$ = 191 Hz, 1 H, H4), 2.36 (q, *J* = 6.8 Hz, 2 H, H5), 1.65 (s, 3 H, H1), 1.58 (m, 4 H, H2′′), 1.45−1.13 (m, 12 H, H6, H7, H1′′, H3′′), 0.89 (m, 3 H, H8), 0.87 (m, 6 H, H4′′) ppm.^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 152.5 (s, $^1J_{Sn,C}$ = 507 Hz, C3), 146.5 (s, C1′), 141.2 (d, $^2J_{Sn,C}$ = 22 Hz, C4), 80.1 (s, $^2J_{Sn,C}$ = 36 Hz, C2), 32.2 (t, $^3J_{Sn,C}$ = 40 Hz, C5), 30.8 (q, $^3J_{Sn,C}$ = 15 Hz, C1), 30.8 (t, $^4J_{Sn,C}$ = 7 Hz, C6), 27.8 (t, $^2J_{Sn,C}$ = 28 Hz, C2′′$_\alpha$), 27.5 (t, $^2J_{Sn,C}$ = 28 Hz, C2′′$_\beta$), 26.7 (br. t, $^3J_{Sn,C}$= n. b., C3′′$_\alpha$ + C3′′$_\beta$), 22.2 (t, C7), 21.2 (t, $^1J_{Sn,C}$ = n. d., C1′′$_\alpha$), 20.8 (t, $^1J_{Sn,C}$ = n. d., C1′′$_\beta$), 14.0 (q, C8), 13.5 (q, C4′′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 44.1 ppm. MS(APCI): *m*/*z* = 419 [M^+ − HCl − H_2O], 345 [M^+ − HCl − H_2O − Bu], 269 [Bu_2SnCl], 203 [M^+ − Bu_2SnCl], 185 [M^+ − Bu_2SnCl − H_2O], 129 [3-octen-2-ol], 91 [C_7H_7], 77 [C_6H_5], 57 [Bu].

Spectroscopic evidence for the two other regio- and stereoisomers is given by the following data.

(*Z*)-4-Dibutylchlorostannyl-2-phenyl-3-octen-2-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.24 (m, $^3J_{Sn,H}$ = 210 Hz, 1 H, H3) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −16.1 ppm.

(*E*)-3-Dibutylchlorostannyl-2-phenyl-3-octen-2-ol: ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 29.2 ppm.

(*Z*)-3-Dibutylchlorostannyl-3-trimethylsilyl-2-propen-1-ol (3e): After following the general procedure purification was carried out by flash column chromatography, R_f = 0.40 using *n*-hexane/Et_2O (2:1) as solvent (0.62 g; 31 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.87 (t, *J* = 2.4, $^3J_{Sn,H}$ = 250 Hz, 1 H, H2), 4.44 (s, $^3J_{Sn,H}$ = 21 Hz, 2 H, H1), 3.26 (br. s, 1 H, OH), 1.63 (m, 4 H, H2′), 1.40−1.24 (8 H, 2 m, H3′ + H1′), 0.89 (m, 6 H, H4′), 0.22 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 148.4 (d, $^2J_{Sn,C}$ = 26 Hz, C2), 143.0 (s, $^1J_{Sn,C}$ = 537 Hz, C3), 66.0 (t, $^2J_{Sn,C}$ = 50 Hz, C1), 28.1 (t, $^2J_{Sn,C}$ = 28 Hz, C2′), 26.7 (t, $^3J_{Sn,C}$ = 81 Hz, C3′), 22.6 (t, $^1J_{Sn,C}$ = 467 Hz, C1′), 13.7 (q, C4′), 0.0 (q, $^1J_{Si,C}$ = 52 Hz, TMS) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 6.3 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 0.6 ppm. MS: *m*/*z* = 380 [M^+ − H_2O], 323 [M^+ − TMS], 269 [Bu_2SnCl], 112 [M^+ − Bu_2SnCl −H_2O], 73 [TMS], 57 [Bu]. Isomer separation was possible.

(*Z*)-2-Dibutylchlorostannyl-3-trimethylsilyl-2-propen-1-ol (5e): After following the general procedure purification was carried out by flash column chromatography, R_f = 0.45 using *n*-hexane/Et_2O (2:1) as solvent (0.28 g; 14 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.46 (t, *J* = 2.5 Hz, $^3J_{Sn,H}$ = 161 Hz, 1 H, H3), 4.56 (d, *J* = 2.5 Hz, $^3J_{Sn,H}$ = 42 Hz, 2 H, H1), 2.63 (br. s, 1 H, OH), 1.64 (m, 4 H, H2′), 1.34 (m, 8 H, H1′ + H3′), 0.90 (t, *J* = 7.4 Hz, 6 H, H4′), 0.12 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 167.9 (s, $^1J_{Sn,C}$ = 511 Hz, C2), 141.6 (d, $^2J_{Sn,C}$ = 24 Hz, C3), 66.5 (t, $^2J_{Sn,C}$ = 46 Hz, C1), 27.9 (t, $^2J_{Sn,C}$ = 26 Hz, C2′), 26.5 (t, $^3J_{Sn,C}$ = 73 Hz, C3′), 19.9 (t, $^1J_{Sn,C}$ = 385 Hz, C1′), 13.6 (q, C4′), −0.5 (q, $^1J_{Si,C}$ = 52 Hz, TMS) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 54.4 ($^3J_{Sn,Si}$ = n.d.) ppm. ^{29}Sn NMR (60 MHz, $CDCl_3$, 23 °C): δ = −9.5 ($^3J_{Sn,Si}$ = 114 Hz) ppm.

Spectroscopic evidence for the other regio- and stereoisomer [**(*E*)-2-Dibutylchlorostannyl-3-trimethylsilyl-2-propen-1-ol**] is given by the following data: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.65 (t, *J* = 1.7 Hz, $^3J_{Sn,H}$ = 247 Hz, 1 H, H3) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 48.7 ppm.

(*Z*)-4-Dibutylchlorostannyl-4-trimethylsilyl-3-buten-2-ol (3f): After following the general procedure purification was carried out by flash column chromatography, R_f = 0.42 using *n*-hexane/Et_2O (4:1) as solvent (0.71 g; 34 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.75 (s, $^3J_{Sn,H}$ = 251 Hz, 1 H, H3), 4.55 (q, *J* = 6.4, $^3J_{Sn,H}$ = n. d., 1 H, H2), 1.60 (m, 4 H, H2′), 1.39−1.20 (2 m, 8 H, H3′ + H1′), 1.31 (d, 3 H, *J* = 6.4 Hz, H1), 0.87 (m, 6 H, H4′), 0.20 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 153.4 (d, $^2J_{Sn,C}$ = 24 Hz, C3), 142.0 (s, $^1J_{Sn,C}$ = n. d., C4), 71.5 (d, $^2J_{Sn,C}$ = 48 Hz, C2), 28.0 (t, $^2J_{Sn,C}$ = n.d., C2′$_\alpha$), 28.1 (t, $^2J_{Sn,C}$ = n. d., C2′$_\beta$), 26.7 (t, $^3J_{Sn,C}$ = 81 Hz, C3′), 23.4 (t, $^1J_{Sn,C}$ = n.d., C1′$_\alpha$), 23.0 (q, C1), 22.8 (t, $^1J_{Sn,C}$ = n. d., C1′$_\beta$), 13.6 (q, C4′), 0.1 (q, $^1J_{Si,C}$ = 52 Hz, TMS) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 2.0 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 0.1 ppm. MS: *m*/*z* = 411 [M^+], 394 [M^+ − H_2O], 375 [M^+ − Cl], 355 [M^+ − Bu], 269 [Bu_2SnCl], 126 [M^+ − Bu_2SnCl −H_2O], 73 [TMS], 57 [Bu]. Isomer separation was possible:

(*Z*)-3-Dibutylchlorostannyl-4-trimethylsilyl-3-buten-2-ol (5f): After following the general procedure purification was carried out by flash column chromatography, R_f = 0.70 using *n*-hexane/Et_2O (4:1) as solvent (0.57 g; 27 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.35 (d, *J* = 2.0 Hz, $^3J_{Sn,H}$ = 161 Hz, 1 H, H4), 4.91 (qt, *J* = 6.3 Hz, 2.0 Hz, $^3J_{Sn,H}$ = 75 Hz, 1 H, H2), 2.56 (s, 1 H, OH), 1.62 (m, 4 H, H2′), 1.30 (d, *J* = 6.3 Hz, 3 H, H1), 1.39−1.25 (m, 8 H, H3′ + H1′), 0.89 (m, 6 H, H4′), 0.14 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 171.8 (s, $^1J_{Sn,C}$ = 506 Hz, C3), 141.1 (d, $^2J_{Sn,C}$ = 21 Hz, C4), 71.9 (d, $^2J_{Sn,C}$ = 46 Hz, C2), 27.9 (t, $^2J_{Sn,C}$ = n. d., C2′), 26.7 (t, $^3J_{Sn,C}$ = 79 Hz, C3′), 25.2 (q, C1), 20.1 (t, $^1J_{Sn,C}$ = 379 Hz, C1′), 13.6 (q, C4′), 0.0 (q, $^1J_{Si,C}$ = n. d., TMS) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 51.5 ($^3J_{Sn,Si}$ = n.d.) ppm. ^{29}Si NMR (60 MHz, $CDCl_3$): δ = −9.7 ($^3J_{Sn,Si}$ = 112 Hz) ppm.

Spectroscopic evidence for the other regio- and stereoisomer [**(*E*)-3-Dibutylchlorostannyl-4-trimethylsilyl-3-buten-2-ol**] is given by the following data. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.50 (d, *J* = 1.8 Hz, $^3J_{Sn,H}$ = 255 Hz, 1 H, H4) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 51.0 ppm.

(*E*)-2-Bromodibutylstannyl-2-buten-1-ol (6a:) After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.45 using *n*-hexane/Et_2O (4:1) as solvent (0.89 g; 47 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.02 (qt, *J* = 6.7 Hz, 2.6 Hz, $^3J_{Sn,H}$ = 99 Hz, 1 H, H3), 4.51 (s,

$^3J_{Sn,H}$ = 40 Hz, 2 H, H1), 2.57 (s, 1 H, OH), 1.68 (d, J = 6.7 Hz, 3 H, H4), 1.62 (m, 4 H, H2′), 1.38−1.31 (m, 8 H, H1′ + H3′), 0.89 (t, J = 7.4 Hz, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 146.4 (s, $^1J_{Sn,C}$ = 537 Hz, C1), 134.6 (d, $^2J_{Sn,C}$ = 15 Hz, C3), 63.9 (t, $^2J_{Sn,C}$ = 29 Hz, C1), 28.0 (t, $^2J_{Sn,C}$ = 26 Hz, C2′), 26.4 (t, $^3J_{Sn,C}$ = 73 Hz, C3′), 19.8 (t, $^1J_{Sn,C}$ = 393 Hz, C1′), 16.0 (q, $^3J_{Sn,C}$ = 79 Hz, C4), 13.5 (q, C4′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 66.0 ppm. MS: m/z = 386 [M^+], 327 [M^+ − Bu], 309 [M^+ − Bu − H_2O], 255 [BuSnBr], 57 [Bu].

A separation of the two other isomers was not possible, considerable decomposition was observed during column chromatography. Characteristic spectroscopic data for the two other regio- and stereoisomers are:

(*Z*)-2-Bromodibutylstannyl-2-buten-1-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.43 (q, J = 6.5 Hz, $^3J_{Sn,H}$ = 177 Hz, 1 H, H3), 4.35 (s, 2 H, H1) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 64.0 ppm. R_f = 0.27 (*n*-hexane/Et_2O, 4:1).

(*Z*)-3-Bromodibutylstannyl-2-buten-1-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.28 (s, $^3J_{Sn,H}$ = 199 Hz, 1 H, H2), 4.35 (s, 2 H, H1) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = −13.7 ppm. R_f = 0.24 (*n*-hexane/Et_2O, 4:1).

(*Z*)-3-Bromodibutylstannyl-3-penten-2-ol (6b): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.28 using *n*-hexane/Et_2O (4:1) as solvent (1.5 g; 75 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.31 (q, J = 6.8 Hz, $^3J_{Sn,H}$ = 185 Hz, 1 H, H4), 4.50 (m, $^3J_{Sn,H}$ = 61 Hz, 1 H, H2), 1.88 (d, J = 6.8 Hz, 3 H, H5), 1.64 (m, 4 H, H2′), 1.43−1.33 (8 H, 2 m, H1′ + H3′), 1.30 (d, J = 6.5 Hz, 3 H, H1), 0.90 (t, J = 7.4 Hz, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 150.9 (s, $^1J_{Sn,C}$ = 456 Hz, C3), 135.6 (d, $^2J_{Sn,C}$ = 26 Hz, C4), 74.0 (d, $^2J_{Sn,C}$ = 38 Hz, C2), 28.1 (t, $^2J_{Sn,C}$ = 25 Hz, C2′), 26.5 (t, $^3J_{Sn,C}$ = 78 Hz, C3′), 24.3 (q, $^3J_{Sn,C}$ <3 Hz, C1), 19.8 (t, $^1J_{Sn,C}$ = 392 Hz, C1′), 16.1 (q, $^3J_{Sn,C}$ = 46 Hz, C5), 13.6 (q, C4′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 49.7 ppm. MS: m/z = 394 [M^+], 341 [M^+ − Bu], 323 [M^+ − Bu − H_2O], 313 [Bu_2SnBr], 85 [M^+ − Bu_2SnBr], 67 [M^+ − Bu_2SnBr − H_2O], 57 [Bu].

Spectroscopic evidence for the two other regio- and stereoisomers is given by the following data.

(*Z*)-4-Bromodibutylstannyl-3-penten-2-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.16 (s, $^3J_{Sn,H}$ = 195 Hz, 1 H, H3) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −14.2 ppm. R_f = 0.41 (*n*-hexane/Et_2O, 4:1).

(*E*)-3-Bromodibutylstannyl-3-penten-2-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.99 (qd, J = 6.6 Hz, 1.9 Hz, $^3J_{Sn,H}$ = 103 Hz, 1 H, H4) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 58.4 ppm. R_f = 0.37 (*n*-hexane/Et_2O, 4:1).

(*Z*)-3-Bromodibutylstannyl-3-octen-2-ol (6c): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.32 using *n*-hexane/Et_2O (1:1) as solvent (1.85 g; 84 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.25 (t, J = 7.3 Hz, $^3J_{Sn,H}$ = 188 Hz, 1 H, H4), 4.51 (s, $^3J_{Sn,H}$ = 60 Hz, 1 H, H2), 2.23 (q, J = 7.3 Hz, $^4J_{Sn,H}$ = 54 Hz, 2 H, H5), 1.65 (quint., J = 7.5 Hz, 4 H, H2′), 1.37−1.23 (m, 15 H, H1, H6, H7, H1′, H3′), 0.85 (m, 9 H, H8, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 148.5 (s, $^1J_{Sn,C}$ = 463 Hz, C3), 141.2 (d, $^2J_{Sn,C}$ = 28 Hz, C4), 73.9 (d, $^2J_{Sn,C}$ = 39 Hz, C2), 33.0 (t, $^3J_{Sn,C}$ = 43 Hz, C5), 31.9 (t, $^4J_{Sn,C}$ < 5 Hz, C6), 28.1 (t, $^2J_{Sn,C}$ = 25 Hz, C2′), 26.6 (t, $^3J_{Sn,C}$ = 77 Hz, C3′), 24.4 (q, $^3J_{Sn,C}$ = 13 Hz, C1), 22.3 (t, C7), 20.6 (t, C1′), 13.9 (q, C8), 13.5 (q, C4′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 48.7 ppm. MS: m/z = 439 [M^+], 421 [M^+ − H_2O], 383 [M^+ − Bu], 365 [M^+ − Bu − H_2O], 313 [Bu_2SnBr], 109 [M^+ − Bu_2SnBr −H_2O], 57 [Bu].

Spectroscopic evidence for the two other regio- and stereoisomers is given by the following data.

(*Z*)-4-Bromodibutylstannyl-3-octen-2-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.12 (s, $^3J_{Sn,H}$ = 205 Hz, 1 H, H4) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −14.4 ppm. R_f = 0.45 (*n*-hexane/Et_2O, 1:1).

(*E*)-3-Bromodibutylstannyl-3-octen-2-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.91 (t, J = 6.3 Hz, $^3J_{Sn,H}$ = 107 Hz, 1 H, H4) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 58.0 ppm.

(*Z*)-3-Bromodibutylstannyl-2-phenyl-3-octen-2-ol (6d): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.08 using *n*-hexane/Et_2O (4:1) as solvent (1.59 g; 64 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.39 (d, J = 8.0 Hz, 2 H, H2′), 7.31 (t, J = 8.0 Hz, 2 H, H3′), 7.22 (t, J = 8.0 Hz, 1 H, H4′), 6.19 (t, J = 7.3 Hz, $^3J_{Sn,H}$ = 191 Hz, 1 H, H4), 2.40 (q, J = 7.3 Hz, 2 H, H5), 1.66 (s, 3 H, H1), 1.57−1.18 (m, 16 H, H6, H7, H1′′, H2′′, H3′′), 0.89 (m, 3 H, H8), 0.85 (m, 6 H, H4′′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 151.7 (s, C1′), 146.4 (s, $^1J_{Sn,C}$ = 482 Hz, C3), 142.0 (d, $^2J_{Sn,C}$ = 24 Hz, C4), 80.0 (s, $^2J_{Sn,C}$ = 36 Hz, C2), 31.7 (t, $^3J_{Sn,C}$ = 40 Hz, C5), 31.0 (t, $^4J_{Sn,C}$ = 34 Hz, C6), 30.0 (q, $^3J_{Sn,C}$ = 16 Hz, C1), 27.1 (t, $^2J_{Sn,C}$ = 26 Hz, C2′′), 25.6 (t, $^3J_{Sn,C}$ = 82 Hz, C3′′), 21.3 (t, C7), 20.1 (t, $^1J_{Sn,C}$ = 388 Hz, C1′′), 13.1 (q, C8), 12.6 (q, C4′′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 34.0 ppm. MS: m/z = 497 [M^+ − H_2O], 440 [M^+ − Bu − H_2O], 420 [M^+ − Br − H_2O], 185 [M^+ − Bu_2SnBr − H_2O], 129 [3-Octen-2-ol], 77 [Ph], 57 [Bu].

Spectroscopic evidence for the two other regio- and stereoisomers is given by the following data.

(*Z*)-4-Bromodibutylstannyl-2-phenyl-3-octen-2-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.24 (s, $^3J_{Sn,H}$ = 201 Hz, 1 H, H4) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = −10.3 ppm. R_f = 0.04 (*n*-hexane/Et_2O, 4:1).

(*E*)-3-Bromodibutylstannyl-2-phenyl-3-octen-2-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.00 (t, J = 7.5, $^3J_{Sn,H}$ = 112 Hz, 1 H, H4) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 34.1 ppm.

(*Z*)-1-Allyloxy-3-dibutylchlorostannyl-2-propene (7a): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.14 using *n*-hexane/Et_2O (4:1) as solvent (0.98 g; 54 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.60 (dt, J = 12.5 Hz, 2.6, $^3J_{Sn,H}$ = 207 Hz, 1 H, H2), 6.24 (dt, J = 12.5 Hz, 2.6, $^2J_{Sn,H}$ = 88 Hz, 1 H, H3), 5.86 (m, 1 H, H2′), 5.35 (d, J = 11.0 Hz, 1 H, H3′$_\alpha$), 5.34 (dd, J = 16.3 Hz, 5.6 Hz, 1 H, H3′$_\beta$), 4.14 (t, J = 2.6, $^4J_{Sn,H}$ = 22 Hz, 2 H, H1), 4.12 (m, 2 H, H1′), 1.63 (quint, J = 7.5 Hz, 4 H, H2′′), 1.34 (sext, J = 7.4 Hz, 4 H, H3′′), 1.26 (m, 4 H, H1′′), 0.89 (t, J = 7.4 Hz, 6 H, H4′′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 140.9 (d, $^2J_{Sn,C}$ < 6 Hz, C2), 132.1 (d, C2′), 131.1 (d, $^1J_{Sn,C}$ = 556 Hz, C3), 120.6 (t, C3′), 72.3 (t, C1′), 71.1 (t, $^3J_{Sn,C}$ = 31 Hz, C1), 27.7 (t, $^2J_{Sn,C}$ = 30 Hz, C2′′), 26.5 (t, $^3J_{Sn,C}$ = 77 Hz, C3′′), 20.4 (t, $^1J_{Sn,C}$ = 462 Hz, C1′′), 13.6 (q, C4′′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 7.2 ppm. MS: m/z = 331 [M^+ − Cl], 309 [M^+ − Bu], 269 [Bu_2SnCl], 57 [Bu].

A separation of the other regioisomer from **7a** was not possible. Characteristic spectroscopic data for the other regioisomer are:

1-Allyloxy-2-dibutylchlorostannyl-2-propene: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.92 (m, $^3J_{Sn,H}$ = 190 Hz, 1 H, H3$_\beta$), 5.83 (m, 1 H, H2′) 5.69 (m, $^3J_{Sn,H}$ = 94 Hz, 1 H, H3$_\alpha$), 5.26 (d, *J* = 18.0 Hz, 1 H, H3′$_\beta$), 5.22 (d, *J* = 12.0 Hz, 1 H, H3′$_\alpha$), 4.27 (t, *J* = 2.2 Hz, $^3J_{Sn,H}$ = 43 Hz, 2 H, H1), 4.01 (d, *J* = 5.6 Hz, 2 H, H1′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 63.8 ppm. R_f = 0.50 (*n*-hexane/Et_2O, 4:1).

(*Z*)-1-Allyloxy-3-bromodibutylstannyl-2-propene (7b): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.14 using *n*-hexane/Et_2O (4:1) as solvent (1.06 g; 51 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.56 (dt, *J* = 12.5 Hz, 2.5 Hz, $^3J_{Sn,H}$ = 207 Hz, 1 H, H2), 6.30 (dt, *J* = 12.5 Hz, 2.3 Hz, $^2J_{Sn,H}$ = 92 Hz, 1 H, H3), 5.83 (m, 1 H, H2′), 5.34 (d, *J* = 12.0 Hz, 1 H, H3′$_\alpha$), 5.33 (d, *J* = 16.0 Hz, 1 H, H3′$_\beta$), 4.14 (m, 4 H, H1 + H1′), 1.63 (m, 4 H, H2′′), 1.34 (m, 8 H, H3′′ + H1′′), 0.89 (t, *J* = 7.3 Hz, 6 H, H4′′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 140.6 (d, $^2J_{Sn,C}$ < 8 Hz, C2), 132.1 (d, C2′), 131.2 (d, $^1J_{Sn,C}$ = 538 Hz, C3), 120.6 (t, C3′), 72.4 (t, C1′), 71.1 (t, $^3J_{Sn,C}$ = 30 Hz, C1), 28.0 (t, $^2J_{Sn,C}$ = 31 Hz, C2′′), 26.4 (t, $^3J_{Sn,C}$ = 77 Hz, C3′′), 20.8 (t, $^1J_{Sn,C}$ = 450 Hz, C1′′), 13.6 (q, C4′′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 2.0 ppm. MS: *m*/*z* = 411 [M^+], 353 [M^+ − Bu], 331 [M^+ − Br], 313 [Bu_2SnBr], 57 [Bu].

A separation of the other regioisomer from **7b** was not possible. Characteristic spectroscopic data for the other regioisomer are:

1-Allyloxy-2-bromodibutylstannyl-2-propene: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.86 (d, *J* = 1 Hz, $^3J_{Sn,H}$ = 190 Hz, 1 H, H3$_\beta$), 5.80 (m, 1 H, H2′) 5.63 (d, *J* = 1 Hz, $^3J_{Sn,H}$ = 91 Hz, 1 H, H3$_\alpha$), 5.19 (d, *J* = 18.8 Hz, 1 H, H3′$_\beta$), 5.15 (d, *J* = 12.8 Hz, 1 H, H3′$_\alpha$) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 58.8 ppm. R_f = 0.50 (*n*-hexane/Et_2O, 4:1).

(*Z*)-3-Dibutylchlorostannyl-1-trimethylsilyloxy-2-propene (8a): 6.64 (dt, *J* = 12.4 Hz, 2.4 Hz, $^3J_{Sn,H}$ = 205 Hz, 1 H, H2), 6.22 (dt, *J* = 12.4 Hz, 2.4 Hz, $^2J_{Sn,H}$ = 86 Hz, 1 H, H3), 4.27 (t, *J* = 2.4 Hz, $^4J_{Sn,H}$ = 21 Hz, 2 H, H1), 1.62 (m, 4 H, H2′), 1.37 (m, 4 H, H1′), 1.29 (m, 4 H, H3′), 0.87 (t, *J* = 7.3 Hz, 6 H, H4′), 0.23 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 142.3 (d, $^2J_{Sn,C}$ < 7 Hz, C2), 129.1 (d, $^1J_{Sn,C}$ = 542 Hz, C3), 65.2 (t, $^3J_{Sn,C}$ = 36 Hz, C1), 27.7 (t, $^2J_{Sn,C}$ = 30 Hz, C2′), 26.5 (t, $^3J_{Sn,C}$ = 80 Hz, C3′), 21.3 (t, $^1J_{Sn,C}$ = 456 Hz, C1′), 13.6 (q, C4′), −0.6 (q, $^1J_{Si,C}$ = 58 Hz, TMS) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 28.9 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 26.0 ppm. MS: *m*/*z* = 383 [M^+ − Me], 363 [M^+ − Cl], 341 [M^+ − Bu], 129 [M^+ − Bu_2SnHCl], 73 [TMS], 57 [Bu]. A separation of isomers was possible:

2-Dibutylchlorostannyl-1-trimethylsilyloxy-2-propene (10a): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.48 using *n*-hexane/Et_2O (9:1) as solvent (0.26 g; 14 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.89 (dt, *J* = 2.3 Hz, 0.7 Hz, $^3J_{Sn,H}$ = 198 Hz, 1 H, H3$_\beta$), 5.67 (dt, *J* = 2.3 Hz, 0.7 Hz, $^3J_{Sn,H}$ = 98 Hz, 1 H, H3$_\alpha$), 4.40 (t, *J* = 2.3 Hz, $^3J_{Sn,H}$ = 40 Hz, 2 H, H1), 1.65 (m, 4 H, H2′), 1.38 (m, 4 H, H1′), 1.27 (m, 4 H, H3′), 0.91 (m, 6 H, H4′), 0.15 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 157.5 (s, $^1J_{Sn,C}$ = 553 Hz, C2), 122.7 (t, $^2J_{Sn,C}$ = 11 Hz, C3), 67.2 (t, $^2J_{Sn,C}$ = 35 Hz, C1), 27.8 (t, $^2J_{Sn,C}$ = 28 Hz, C2′), 26.5 (t, $^3J_{Sn,C}$ = 72 Hz, C3′), 19.5 (t, $^1J_{Sn,C}$ = 406 Hz, C1′), 13.6 (q, C4′), −0.7 (q, TMS) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 59.0 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 21.0 ppm.

(*Z*)-3-Bromodibutylstannyl-1-trimethylsilyloxy-2-propene (8b): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.04 using *n*-hexane/Et_2O (19:1) as solvent (1.72 g; 75 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.62 (dt, *J* = 12.4 Hz, 2.5 Hz, $^3J_{Sn,H}$ = 204 Hz, 1 H, H2), 6.30 (dt, *J* = 12.4 Hz, 2.5 Hz, $^2J_{Sn,H}$ = 89 Hz, 1 H, H3), 4.30 (t, *J* = 2.5 Hz, $^4J_{Sn,H}$ = 21 Hz, 2 H, H1), 1.64 (m, 4 H, H2′), 1.36 (m, 8 H, H1′ + H3′), 0.89 (t, *J* = 7.4 Hz, 6 H, H4′), 0.24 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 142.0 (d, $^2J_{Sn,C}$ = n.d., C2), 129.3 (d, $^1J_{Sn,C}$ = 525 Hz, C3), 65.2 (t, $^3J_{Sn,C}$ = 36 Hz, C1), 28.0 (t, $^2J_{Sn,C}$ = 31 Hz, C2′), 26.4 (t, $^3J_{Sn,C}$ = 81 Hz, C3′), 21.7 (t, $^1J_{Sn,C}$ = 445 Hz, C1′), 13.6 (q, C4′), −0.5 (q, $^1J_{Si,C}$ = 59 Hz, TMS) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 26.3 ppm. ^{29}Si NMR (79 MHz, $CDCl_3$, 23 °C): δ = 26.1 ($^1J_{Si,C}$ = 59 Hz) ppm. MS: *m*/*z* = 427 [M^+ − Me], 385 [M^+ − Bu], 363 [M^+ − Br], 313 [Bu_2SnBr], 129 [M^+ − Bu_2SnHBr], 73 [TMS], 57 [Bu].

A separation of the other regioisomer from **8b** was not possible. Characteristic spectroscopic data for the other regioisomer are:

2-Bromodibutylstannyl-1-trimethylsilyloxy-2-propene: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.89 (dt, *J* = 2.0 Hz, 0.7 Hz, $^3J_{Sn,H}$ = 200 Hz, 1 H, H3$_\beta$), 5.68 (dt, *J* = 2.5 Hz, 0.7 Hz, $^3J_{Sn,H}$ = 99 Hz, 1 H, H3$_\alpha$) 4.39 (t, *J* = 2.3 Hz, 2 H, H1), 0.14 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 156.8 (s, $^1J_{Sn,C}$ = n.d., C2), 123.2 (t, $^2J_{Sn,C}$ = 14 Hz, C3), 67.1 (t, $^2J_{Sn,C}$ = 33 Hz, C1), −0.8 (q, $^1J_{Si,C}$ = n.d., TMS) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 55.4 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 21.1 ppm. R_f = 0.30 (*n*-hexane/Et_2O, 19:1).

(*Z*)-4-Dibutylchlorostannyl-2-trimethylsilyloxy-3-butene (8c): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.20 using *n*-hexane/Et_2O (4:1) as solvent (0.48 g; 23 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.64 (dd, *J* = 12.2 Hz, 3.2 Hz, $^3J_{Sn,H}$ = 207 Hz, 1 H, H3), 6.13 (dd, *J* = 12.2 Hz, 2.0 Hz, $^2J_{Sn,H}$ = 83 Hz, 1 H, H4), 4.52 (m, 1 H, H2), 1.70 (m, 4 H, H2′), 1.42−1.26 (m, 11 H, H1′ + H3′ + H1), 0.89 (m, 6 H, H4′), 0.24 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 148.7 (d, $^2J_{Sn,C}$ < 7 Hz, C3), 128.0 (d, $^1J_{Sn,C}$ = 539 Hz, C4), 71.3 (d, $^3J_{Sn,C}$ = 34 Hz, C2), 27.0 (t, $^2J_{Sn,C}$ = 31 Hz, C2′$_\alpha$), 27.0 (t, $^2J_{Sn,C}$ = 31 Hz, C2′$_\beta$), 25.9 (t, $^3J_{Sn,C}$ = 81 Hz, C3′), 23.5 (q, $^4J_{Sn,C}$ = 12 Hz, C1), 21.3 (t, $^1J_{Sn,C}$ = 469 Hz, C1′$_\alpha$), 19.9 (t, $^1J_{Sn,C}$ = 423 Hz, C1′$_\beta$), 13.6 (q, C4′), 0.8 (q, TMS) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 37.7 ppm. ^{29}Si NMR (79 MHz, $CDCl_3$, 23 °C): δ = 22.7 ($^1J_{Si,C}$ = 59 Hz) ppm. MS: *m*/*z* = 397 [M^+ − Me], 377 [M^+ − Cl], 355 [M^+ − Bu], 319 [M^+ − Bu − HCl], 301 [HCl -TMS], 143 [M^+ − Bu_2SnCl], 73 [TMS], 57 [Bu]. Considerable desilylation occurred during column chromatography, leading to **1b**. Therefore the other regioisomer could not be obtained clean. Spectroscopic evidence for the other regioisomer **3-Dibutylchlorostannyl-2-trimethylsilyloxy-3-butene** is given by the following data.

^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.83 (d, *J* = 2.3 Hz, $^3J_{Sn,H}$ = 196 Hz, 1 H, H4$_\beta$), 5.68 (d, *J* = 2.3 Hz, $^3J_{Sn,H}$ = 94 Hz, 1 H, H4$_\alpha$) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 54.3 ppm. R_f = 0.50.

(*Z*)-4-Bromodibutylstannyl-2-trimethylsilyloxy-3-butene (8d): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.25 using *n*-hexane/Et_2O (4:1) as solvent (0.70 g; 31 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.60 (dd, *J* = 12.0 Hz, 3.0 Hz, $^3J_{Sn,H}$ = 206 Hz, 1 H, H3), 6.17 (dd, *J* = 12.0 Hz, 1.7 Hz, $^2J_{Sn,H}$ = 87 Hz, 1 H, H4), 4.52 (m, 1 H, H2), 1.66 (m, 4 H, H2′), 1.35 (m, 8 H, H3′ + H1′), 1.23 (d, *J* = 6.0 Hz, 3 H, H1), 0.89 (m, 6 H, H4′), 0.23 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 148.5 (d, $^2J_{Sn,C}$ < 6 Hz, C3), 127.9 (d, $^1J_{Sn,C}$ = 522 Hz, C4), 71.3 (d, $^3J_{Sn,C}$ = 71 Hz,

C2), 28.1 (t, $^2J_{Sn,C}$ = 26 Hz, C2′), 26.5 (t, $^3J_{Sn,C}$ = 81 Hz, C3′), 24.2 (q, $^4J_{Sn,C}$ = 11 Hz, C1), 22.4 (t, $^1J_{Sn,C}$ = 458 Hz, C1′$_\alpha$), 20.9 (t, $^1J_{Sn,C}$ = 414 Hz, C1′$_\beta$), 13.5 (q, C4′), 0.8 (q, TMS) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 36.3 ppm. ^{29}Si NMR (79 MHz, $CDCl_3$, 23 °C): δ = 22.9 ($^1J_{Si,C}$ = 59 Hz) ppm. MS: *m*/*z* = 441 [M^+ − Me], 401 [M^+ − Bu], 377 [M^+ − Br], 143 [M^+ − Bu_2SnBr], 73 [TMS], 57 [Bu]. Isomer separation was possible: however, a large amount (0.9 g) was isolated as a mixture of both isomers.

(*Z*)-3-Bromodibutylstannyl-2-trimethylsilyloxy-3-butene (10d): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.66 using *n*-hexane/Et_2O (4:1) as solvent (0.70 g; 31 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.80 (dd, *J* = 1.9 Hz, 0.5 Hz, $^3J_{Sn,H}$ = 200 Hz, 1 H, H4$_\beta$), 5.68 (dd, *J* = 1.9 Hz, 0.5, $^2J_{Sn,H}$ = 101 Hz, 1 H, H4$_\alpha$), 4.65 (qt, *J* = 6.3 Hz, 1.9 Hz, 1 H, H2), 1.64 (m, 4 H, H2′), 1.38 (m, 8 H, H3′ + H1′), 1.27 (d, *J* = 6.2 Hz, 3 H, H1), 0.92 (m, 6 H, H4′), 0.15 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 162.1 (s, $^1J_{Sn,C}$ = 522 Hz, C3), 123.2 (t, $^2J_{Sn,C}$ = 15 Hz, C4), 74.2 (d, $^2J_{Sn,C}$ = 31 Hz, C2), 28.2 (t, $^2J_{Sn,C}$ = 29 Hz, C2′$_\alpha$), 28.1 (t, $^2J_{Sn,C}$ = 29 Hz, C2′$_\beta$), 26.5 (t, $^3J_{Sn,C}$ = 79 Hz, C3′$_\alpha$), 26.5 (t, $^3J_{Sn,C}$ = 79 Hz, C3′$_\beta$), 25.3 (q, C1), 20.4 (t, $^1J_{Sn,C}$ = 399 Hz, C1′$_\alpha$), 19.5 (t, $^1J_{Sn,C}$ = 393 Hz, C1′$_\beta$), 13.6 (q, C4′), 0.4 (q, $^1J_{Si,C}$ = 59 Hz, TMS) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 53.4 ppm. ^{29}Si NMR (79 MHz, $CDCl_3$, 23 °C): δ = 18.7 ppm. MS: *m*/*z* = 443 [M^+ − Me], 401 [M^+ − Bu], 143 [M^+ − Bu_2SnBr], 73 [TMS], 57 [Bu].

(*E*)-1-(2′-Dibutylchlorostannyl)ethenyl-1-trimethylsilyloxy-cyclohexane (9e): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.10 using *n*-hexane/Et_2O (9:1) as solvent (0.96 g; 42 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.35 (d, *J* = 18.9, $^3J_{Sn,H}$ = 94 Hz, 1 H, H1′), 6.14 (d, *J* = 18.9, $^2J_{Sn,H}$ = 119 Hz, 1 H, H2′), 1.66−1.36 (m, 18 H, H1′′−H3′′, H2−H4), 0.91 (t, 6 H, 7.6 Hz, H4′′), 0.09 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 158.4 (d, $^2J_{Sn,C}$ < 6 Hz, C1′), 124.4 (d, $^1J_{Sn,C}$ = 449 Hz, C2′), 75.9 (s, $^3J_{Sn,C}$ = 72 Hz, C1), 37.9 (t, C2), 27.7 (t, $^2J_{Sn,C}$ = 25 Hz, C2′′), 26.7 (t, $^3J_{Sn,C}$ = 67 Hz, C3′′), 25.7 (t, C3), 22.2 (t, C4), 17.6 (t, $^1J_{Sn,C}$ = 384 Hz, C1′′), 13.5 (q, C4′′), 2.6 (q, $^1J_{Si,C}$ = 59 Hz, TMS) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 92.6 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 10.1 ppm. MS: *m*/*z* = 466 [M^+], 409 [M^+ − Bu], 301 [M^+ − TMS − BuCl], 197 [M^+ − Bu_2SnCl], 73 [TMS], 57 [Bu].

The two other isomers were isolated as mixture. Characteristic spectroscopic data are as follows:

(*Z*)-1-(2′-Dibutylchlorostannyl)ethenyl-1-trimethylsilyloxy-cyclohexane: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.18 (d, *J* = 12.5 Hz, $^3J_{Sn,H}$ = 207 Hz, 1 H, H1′), 6.09 (d, *J* = 12.5 Hz, $^2J_{Sn,H}$ = n. d., 1 H, H2′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 149.9 (d, $^2J_{Sn,C}$ = n. d., C1′), 127.8 (d, $^1J_{Sn,C}$ = 532 Hz, C2′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 44.7 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 15.5 ppm. R_f = 0.30 (*n*-hexane/Et_2O, 9:1).

1-(1′-Dibutylchlorostannyl)ethenyl-1-trimethylsilyloxy-cyclohexane: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.09 (s, 1 H, $^3J_{Sn,H}$ = n. d., H2′$_\beta$), 5.70 (s, 1 H, $^2J_{Sn,H}$ = 115 Hz, H2′$_\alpha$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 166.1 (s, $^1J_{Sn,C}$ = n. d., C1′), 122.9 (t, $^2J_{Sn,C}$ = 14 Hz, C2′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 36.6 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 12.7 ppm. R_f = 0.30 (*n*-hexane/Et_2O, 9:1).

(*E*)-1-(2′-Bromodibutylstannyl)ethenyl-1-trimethylsilyloxy-cyclohexane (9f): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.05 using *n*-hexane/Et_2O (9:1) as solvent (1.89 g; 74 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.34 (d, *J* = 18.9 Hz, $^3J_{Sn,H}$ = 95 Hz, 1 H, H1′), 6.17 (d, *J* = 18.9 Hz, $^2J_{Sn,H}$ = 121 Hz, 1 H, H2′), 1.66 (m, 4 H, H2′′), 1.71−1.22 (m, 8 H, H2−H4), 1.42−1.36 (m, 8 H, H1′′ + H3′′), 0.92 (t, *J* = 7.0 Hz, 6 H, H4′′), 0.10 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.5 (d, $^2J_{Sn,C}$ < 4 Hz, C1′), 123.8 (d, $^1J_{Sn,C}$ = 434 Hz, C2′), 75.8 (s, $^3J_{Sn,C}$ = 72 Hz, C1), 37.9 (t, C2), 28.1 (t, $^2J_{Sn,C}$ = 24 Hz, C2′′), 26.6 (t, $^3J_{Sn,C}$ = 66 Hz, C3′′), 25.7 (t, C3), 22.2 (t, C4), 17.4 (t, $^1J_{Sn,C}$ = 373 Hz, C1′′), 13.5 (q, C4′′), 2.6 (q, $^1J_{Si,C}$ = 58 Hz, TMS) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 74.8 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 9.8 ppm. MS: *m*/*z* = 509 [M^+], 452 [M^+ − Bu], 312 [Bu_2SnBr], 197 [M^+ − Bu_2SnBr], 107 [M^+ − OTMS − Bu_2SnBr], 73 [TMS], 57 [Bu].

The two other isomers were isolated as a mixture. Characteristic spectroscopic data are as follows:

(*Z*)-1-(2′-Bromodibutylstannyl)ethenyl-1-trimethylsilyloxy-cyclohexane: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.15 (d, *J* = 12.4 Hz, $^3J_{Sn,H}$ = 207 Hz, 1 H, H1′), 6.18 (d, 1 H, 12.4, $^2J_{Sn,H}$ = 86 Hz, H2′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 149.8 (d, $^2J_{Sn,C}$ = n. d., C1′), 127.9 (d, $^1J_{Sn,C}$ = 514 Hz, C2′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 44.2 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 15.5. R_f = 0.35 (*n*-hexane/Et_2O, 4:1).

1-(1′-Bromodibutylstannyl)ethenyl-1-trimethylsilyloxy-cyclohexane: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.12 (s, $^3J_{Sn,H}$ = 216 Hz, 1 H, H2′$_\beta$), 5.76 (s, $^2J_{Sn,H}$ = 116 Hz, 1 H, H2′$_\alpha$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 165.4 (s, $^1J_{Sn,C}$ = n. d., C1′), 123.6 (t, $^2J_{Sn,C}$ = 15 Hz, C2′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 41.2 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 12.8 ppm. R_f = 0.35 (*n*-hexane/Et_2O, 9:1).

(*Z*)-3-Dibutylchlorostannyl-1,1-diphenyl-1-trimethylsilyloxy-2-propene (8g): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.20 using *n*-hexane/Et_2O (6:1) as solvent (0.86 g; 32 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.29−7.16 (m, 10 H, H2′−H4′), 6.70 (d, *J* = 12.5 Hz, $^3J_{Sn,H}$ = 199 Hz, 1 H, H2), 5.99 (d, *J* = 12.5 Hz, $^2J_{Sn,H}$ = 67 Hz, 1 H, H3), 1.62 (m, 4 H, H2′′), 1.36 (m, 4 H, H1′′), 1.28 (q, *J* = 7.3 Hz, 4 H, H3′′), 0.81 (t, *J* = 7.3 Hz, 6 H, H4′′), −0.25 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 153.5 (d, $^2J_{Sn,C}$ = n. d., C2), 141.7 (s, $^4J_{Sn,C}$ = 8 Hz, C1′), 128.8 (d, C2′), 128.1 (d, C3′), 127.9 (d, C4′), 124.7 (d, $^1J_{Sn,C}$ = 515 Hz, C3), 85.6 (s, $^3J_{Sn,C}$ = 29 Hz, C1), 29.7 (t, $^2J_{Sn,C}$ = 31 Hz, C2′′), 27.8 (t, $^3J_{Sn,C}$ = 83 Hz, C3′′), 21.4 (t, $^1J_{Sn,C}$ = 431 Hz, C1′′), 13.7 (q, C4′′), 2.9 (q, $^1J_{Si,C}$ = 60 Hz, TMS) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 60.6 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 20.8 ($^1J_{Si,C}$ = 60 Hz) ppm. MS: *m*/*z* = 549 [M^+], 457 [M^+ − H_2O − TMS], 279 [M^+ − Bu_2SnHCl], 73 [TMS].

(*Z*)-3-Bromodibutylstannyl-1,1-diphenyl-1-trimethylsilyloxy-2-propene (8h): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.20 using *n*-hexane/Et_2O (9:1) as solvent (0.27 g; 18 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.29−7.13 (m, 10 H, H2′−H4′), 6.66 (d, *J* = 12.2 Hz, $^3J_{Sn,H}$ = 199 Hz, 1 H, H2), 6.04 (d, *J* = 12.2, $^2J_{Sn,H}$ = 72 Hz, 1 H, H3), 1.61 (m, 4 H, H2′′), 1.41 (m, 4 H, H1′′), 1.28 (q, *J* = 7.3 Hz, 4 H, H3′′), 0.81 (t, *J* = 7.3 Hz, 6 H, H4′′), −0.25 (s, 9 H, TMS) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 153.5 (d, $^2J_{Sn,C}$ = 12 Hz, C2), 141.7 (s, $^4J_{Sn,C}$ < 6 Hz, C1′),

128.7 (d, C2′), 128.0 (d, C3′), 127.9 (d, C4′), 124.6 (d, $^1J_{Sn,C}$ = 498 Hz, C3), 85.6 (s, $^3J_{Sn,C}$ = 28 Hz, C1), 28.2 (t, $^2J_{Sn,C}$ = 32 Hz, C2′′), 26.7 (t, $^3J_{Sn,C}$ = 84 Hz, C3′′), 21.5 (t, $^1J_{Sn,C}$ = 418 Hz, C1′′), 13.5 (q, C4′′), 2.9 (q, $^1J_{Si,C}$ = 59 Hz, TMS) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 59.4 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$, 23 °C): δ = 20.4 ppm. MS: *m*/*z* = 592 [M^+], 519 [M^+ − TMS], 495 [M^+ − H_2O − Br], 315 (8 %, Bu_2SnHBr), 283 [M^+ − Bu_2SnBr], 256 [M^+ − Bu_2SnBr − H_2O], 57 [Bu].

(*Z*)-4-Dibutylchlorostannyl-3-buten-1-ol (11a): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.80 using Et_2O as solvent (0.66 g; 38 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.76 (dt, *J* = 2.8 Hz, 6.2 Hz, $^3J_{Sn,H}$ = 212 Hz, 1 H, H3), 6.08 (d, *J* = 12.8 Hz, $^2J_{Sn,H}$ = 94 Hz, 1 H, H4), 3.81 (m, 2 H, H1), 3.04 (br. s, 1 H, OH), 2.36 (dt, *J* = 6.2 Hz, 5.3 Hz, 2 H, H2), 1.67 (m, 4 H, H2′), 1.40−1.32 (m, 8 H, H3′ + H1′), 0.91 (m, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 145.8 (d, $^2J_{Sn,C}$ < 10 Hz, C3), 134.8 (d, $^1J_{Sn,C}$ = 535 Hz, C4), 61.9 (t, C1), 34.6 (t, C2), 27.9 (t, $^2J_{Sn,C}$ = 29 Hz, C2′), 26.7 (t, $^3J_{Sn,C}$ = 78 Hz, C3′), 20.6 (br. t, $^1J_{Sn,C}$ = 431 Hz, C1′), 13.6 (q, C4′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = −13.1 ppm. MS: *m*/*z* = 326 [M^+ − Me], 305 [M^+ − Cl], 283 [M^+ − Bu], 71 [M^+ − Bu_2SnCl], 57 [Bu].

The other isomer was isolated together with an unknown *n*-butyltin compound. Characteristic spectroscopic data are:

(*E*)-4-Dibutylchlorostannyl-3-buten-1-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.16 (dt, *J* = 18.8 Hz, 5.8 Hz, $^3J_{Sn,H}$ = 87 Hz, 1 H, H3), 6.06 (d, *J* = 18.8 Hz, $^2J_{Sn,H}$ = 119 Hz, 1 H, H4), 3.76 (t, *J* = 5.2 Hz, 1 H, H1$_\alpha$), 3.66 (t, *J* = 6.7 Hz, 1 H, H1$_\beta$), 2.42 (m, 2 H, H2), 1.60 (m, 4 H, H2′), 1.40−1.22 (m, 8 H, H3′ + H1′), 0.86 (m, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 148.1 (d, $^2J_{Sn,C}$ = 11 Hz, C3), 130.9 (d, $^1J_{Sn,C}$ = 448 Hz, C4), 61.3 (t, C1), 40.4 (t, $^3J_{Sn,C}$ = 80 Hz, C2) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 84.3 ppm. R_f = 0.4 (Et_2O).

The protons of the groups 1, 2 and 4 exhibit strong higher order effects in the ^{1}H NMR spectrum. A prefect match of simulated versus observed spectra can be achieved with the parameters (Table 8): frequency: 400 MHz, strong coupling, 4 groups of 1 proton.

Table 8. Simulation parameters for (*E*)-4-dibutylchlorostannyl-3-buten-1-ol

δ = 6.16 ppm	δ = 6.08 ppm	δ = 3.66 ppm	δ = 3.76 ppm
	18.8 Hz	6.2 Hz	5.7 Hz
		0	−0.8 Hz
			6 Hz

(*Z*)-5-Dibutylchlorostannyl-2-phenyl-4-penten-2-ol (11b): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.57 using Et_2O as solvent (0.82 g; 38 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.40−7.20 (m, 5 H, H1′−H4′), 6.47 (dt, *J* = 12.2 Hz, 7.0 Hz, $^3J_{Sn,H}$ = 209 Hz, 1 H, H4), 6.17 (d, *J* = 12.2 Hz, $^2J_{Sn,H}$ = 98 Hz, 1 H, H5), 2.50 (m, 2 H, H3), 1.67 (m, 4 H, H2′′), 1.60 (s, 3 H, H1), 1.37 (m, 8 H, H3′′ + H1′′), 0.91 (m, 6 H, H4′′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 146.7 (s, C1′), 143.7 (d, $^2J_{Sn,C}$ < 10 Hz, C4), 136.6 (d, $^1J_{Sn,C}$ = 509 Hz, C5), 128.3 (d, C3′), 127.0 (d, C4′), 124.5 (d, C2′), 75.7 (s, C2), 47.3 (t, $^3J_{Sn,C}$ = 44 Hz, C3), 29.4 (q, C1), 27.8 (t, $^2J_{Sn,C}$ = 27 Hz, C2′′), 26.6 (t, $^3J_{Sn,C}$ = 76 Hz, C3′′), 19.8 (t, $^1J_{Sn,C}$ = 422 Hz, C1′′), 13.6 (q, C4′′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 23.5 ppm. MS: *m*/*z* = 429 [M^+], 394 [M^+ − HCl], 355 [M^+ − Bu − H_2O], 337 [M^+ − Bu − HCl], 269 [Bu_2SnCl], 161 [M^+ − Bu_2SnCl], 143 [M^+ − Bu_2SnCl − H_2O], 77 [Ph], 57 [Bu].

Isomer separation was possible:

(*E*)-5-Dibutylchlorostannyl-2-phenyl-4-penten-2-ol (12b): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.30 using Et_2O as solvent (0.41 g; 19 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.40−7.20 (3m, 5 H, H1′−H4′), 6.05 (d, *J* = 18.8 Hz, $^2J_{Sn,H}$ = 115 Hz, 1 H, H5), 6.00 (dt, *J* = 18.8 Hz, 5.8 Hz, $^3J_{Sn,H}$ = 89 Hz, 1 H, H4), 2.73 (dd, *J* = 14.1 Hz, 5.5 Hz, 1 H, H3$_\alpha$), 2.59 (dd, *J* = 14.1 Hz, 6.4 Hz, 1 H, H3$_\beta$), 1.58 (m, 4 H, H2′′), 1.51 (s, 3 H, H1), 1.32−1.22 (m, 8 H, H3′′ + H1′′), 0.81 (m, 6 H, H4′′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 147.3 (d, $^2J_{Sn,C}$ = 14 Hz, C4), 147.0 (s, C1′), 132.7 (d, $^1J_{Sn,C}$ = 445 Hz, C5), 128.0 (d, C3′), 126.7 (d, C4′), 124.6 (d, C2′), 73.9 (s, C2), 52.0 (t, $^3J_{Sn,C}$ = 76 Hz, C3), 29.5 (q, C1), 27.5 (t, $^2J_{Sn,C}$ = 24 Hz, C2′′), 26.6 (t, $^3J_{Sn,C}$ = 68 Hz, C3′′), 17.6 (t, $^1J_{Sn,C}$ = 385 Hz, C1′′), 13.5 (q, C4′′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 82.4 ppm. The protons of the groups 3, 4 and 5 exhibit strong higher order effects in the ^{1}H NMR spectrum. A perfect match of simulated versus observed spectra can be achieved with the parameters (Table 9): frequency: 400 MHz, strong coupling, 4 groups of 1 proton.

Table 9. Simulation parameters for (*E*)-5-dibutylchlorostannyl-2-phenyl-4-penten-2-ol (**12b**)

δ = 6.005 ppm	δ = 6.052 ppm	δ = 2.73 ppm	δ = 2.595 ppm
	18.8 Hz	6.3 Hz	7.3 Hz
		−1.0 Hz	−1.2 Hz
			14.1 Hz

(*Z*)-4-Bromodibutylstannyl-3-buten-1-ol (11c): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.80 using Et_2O as solvent (0.44 g; 19 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.72 (dt, *J* = 12.7 Hz, 6.1 Hz, $^3J_{Sn,H}$ = 212 Hz, 1 H, H3), 6.14 (d, *J* = 12.7 Hz, $^2J_{Sn,H}$ = 98 Hz, 1 H, H4), 3.79 (t, *J* = 5.3 Hz, 2 H, H1), 3.36 (br. s, 1 H, OH), 2.36 (dt, *J* = 6.1 Hz, 5.3 Hz, 2 H, H2), 1.66 (m, 4 H, H2′), 1.42−1.32 (m, 8 H, H3′ + H1′), 0.90 (m, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 145.7 (d, $^2J_{Sn,C}$ = n. d., C3), 134.7 (d, $^1J_{Sn,C}$ = 516 Hz, C4), 61.9 (t, C1), 34.9 (t, $^3J_{Sn,C}$ = 40 Hz, C2), 28.2 (t, $^2J_{Sn,C}$ = 29 Hz, C2′), 26.5 (t, $^3J_{Sn,C}$ = 78 Hz, C3′), 20.8 (t, $^1J_{Sn,C}$ = 437 Hz, C1′), 13.6 (q, C4′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = −14.7 ppm. MS: *m*/*z* = 371 [M^+ − Me], 313 [Bu_2SnBr], 71 [M^+ − Bu_2SnCl], 57 [Bu].

The other isomer was isolated together with the rest of **11c**. Characteristic spectroscopic data are:

(*E*)-4-Bromodibutylstannyl-3-buten-1-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.17 (dt, *J* = 18.8 Hz, 5.2 Hz, $^3J_{Sn,H}$ = n. d., 1 H, H3), 6.16 (d, *J* = 18.8 Hz, $^2J_{Sn,H}$ = n. d., 1 H, H4), 3.78 (t, *J* = 5.2 Hz, 1 H, H1$_\alpha$), 3.68 (t, *J* = 6.4 Hz, 1 H, H1$_\beta$), 2.45 (m, 2 H, H2), 1.63 (m, 4 H, H2′), 1.42−1.28 (m, 8 H, H3′ + H1′), 0.90 (m, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 148.2 (d, $^2J_{Sn,C}$ = 10 Hz, C3), 130.3 (d, $^1J_{Sn,C}$ = 434 Hz, C4), 61.2 (t, C1), 40.3 (t, $^3J_{Sn,C}$ = 79 Hz, C2), 28.0 (t, $^2J_{Sn,C}$ = 23 Hz, C2′), 26.5 (t, $^3J_{Sn,C}$ = 69 Hz, C3′), 17.5 (t, $^1J_{Sn,C}$ = 377 Hz, C1′), 13.5 (q, C4′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = 68.5 ppm. R_f = 0.2 (Et_2O). The protons of the groups 1, 2 and 4 exhibit strong higher order effects in the ^{1}H NMR spectrum. A

perfect match of simulated versus observed spectra can be achieved with the parameters (Table 10): frequency: 400 MHz, strong coupling, 4 groups of 1 proton:

Table 10. Simulation parameters for (*E*)-4-bromodibutylstannyl-3-buten-1-ol

δ = 6.187 ppm	δ = 6.145 ppm	δ = 3.70 ppm	δ = 3.78 ppm
	18.8 Hz	6.1 Hz 0	5.4 Hz −0.8 Hz 6 Hz

(*Z*)-5-Bromodibutylstannyl-2-phenyl-4-penten-2-ol (11d): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.70 using Et_2O as solvent (0.84 g; 36 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.30−7.18 (m, 5 H, H2′−H4′), 6.38 (dt, J = 12.3 Hz, J = 7.1, $^3J_{Sn,H}$ = 205 Hz, 1 H, H4), 6.17 (d, J = 12.3, $^2J_{Sn,H}$ = 100 Hz, 1 H, H5), 2.55 (dd, J = 14.1 Hz, 6.5 Hz, 1 H, H3$_\alpha$), 2.45 (dd, J = 14.1 Hz, 7.5 Hz, 1 H, H3$_\beta$), 1.63 (m, 4 H, H2′′), 1.60 (s, 3 H, H1), 1.39−1.30 (m, 8 H, H3′′ + H1′′), 0.85 (m, 6 H, H4′′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 146.8 (s, C1′), 144.0 (d, $^2J_{Sn,C}$ < 10 Hz, C4), 135.8 (d, $^1J_{Sn,C}$ = 479, $^1J_{Sn,C}$ = 459 Hz, C5), 128.3 (d, C3′), 127.0 (d, C4′), 124.5 (d, C2′), 75.5 (s, C2), 47.9 (t, $^3J_{Sn,C}$ = 43 Hz, C3), 29.6 (q, C1), 28.2 (t, $^2J_{Sn,C}$ = 29 Hz, C2′′), 26.6 (t, $^3J_{Sn,C}$ = 76 Hz, C3′′), 19.6 (t, $^1J_{Sn,C}$ = 402 Hz, C1′′), 13.6 (q, C4′′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 22.3 ppm. MS: 417 [M^+ − Bu], 399 [M^+ − Bu − H_2O], 394 [M^+ − Br], 313 [Bu_2SnBr], 77 [Ph], 57 [Bu]. Isomer separation was possible:

(*E*)-5-Bromodibutylstannyl-2-phenyl-4-penten-2-ol (12d): After following the general procedure purification was carried out by flash column chromatography at −78 °C, R_f = 0.43 using Et_2O as solvent (0.80 g; 35 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.40−7.20 (3m, 5 H, H1′−H4′), 6.05 (d, J = 18.8 Hz, $^2J_{Sn,H}$ = 118 Hz, 1 H, H5), 6.00 (dt, J = 18.8 Hz, 6.3, $^3J_{Sn,H}$ = 102 Hz, 1 H, H4), 2.72 (dd, J = 13.6 Hz, 5.6 Hz, 1 H, H3$_\alpha$), 2.59 (dd, J = 13.7 Hz, 6.6 Hz, 1 H, H3$_\beta$), 1.56 (m, 4 H, H2′′), 1.53 (s, 3 H, H1), 1.32 (m, 8 H, H3′′ + H1′′), 0.87 (m, 6 H, H4′′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 147.4 (d, $^2J_{Sn,C}$ = 13 Hz, C4), 147.1 (s, C1′), 132.0 (d, $^1J_{Sn,C}$ = 430 Hz, C5), 128.0 (d, C3′), 126.7 (d, C4′), 124.6 (d, C2′), 73.8 (s, C2), 51.9 (t, $^3J_{Sn,C}$ = 76 Hz, C3), 29.4 (q, C1), 27.9 (t, $^2J_{Sn,C}$ = 25 Hz, C2′′), 26.4 (t, $^3J_{Sn,C}$ = 68 Hz, C3′′), 17.4 (t, $^1J_{Sn,C}$ = 374 Hz, C1′′), 13.4 (q, C4′′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 64.0 ppm. R_f = 0.43 (Et_2O).- The protons of the groups 3, 4 and 5 exhibit strong higher order effects in the ^{1}H NMR spectrum. A perfect match of simulated versus observed spectra can be achieved with the parameters (Table 11): frequency: 400 MHz, strong coupling, 4 groups of 1 proton.

Table 11. Simulation parameters for (*E*)-5-bromodibutylstannyl-2-phenyl-4-penten-2-ol (**12d**)

δ = 5.995 ppm	δ = 6.065 ppm	δ = 2.72 ppm	δ = 2.59 ppm
	18.8 Hz	6.2 Hz −0.2 Hz	7.6 Hz −0.4 Hz 13.7 Hz

(*Z*)-5-Dibutylchlorostannyl-4-penten-1-ol (13a): After following the general procedure purification was carried out by flash column chromatography at −78 °C, starting with *n*-hexane/Et_2O (2:1), gradually moving to neat Et_2O as solvent (0.34 g; 19 %). The R_f values are strongly dependent on the concentration, but it can be stated that R_f (**13a**) > R_f (**14a**). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.62 (dt, J = 11.7 Hz, 7.3 Hz, $^3J_{Sn,H}$ = 197 Hz, 1 H, H4), 5.99 (d, J = 11.7, $^2J_{Sn,H}$ = 105 Hz, 1 H, H5), 3.68 (t, J = 6.2 Hz, 2 H, H1), 2.25 (q, J = 7.1 Hz, 2 H, H3), 1.68 (m, 6 H, H2, H2′), 1.38 (m, 8 H, H3′ + H1′), 0.92 (m, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 149.8 (d, $^2J_{Sn,C}$ = 8 Hz, C4), 129.8 (d, $^1J_{Sn,C}$ = 460 Hz, C5), 61.3 (t, C1), 32.7 (t, $^3J_{Sn,C}$ = 54 Hz, C3), 31.3 (t, C2), 27.8 (t, $^2J_{Sn,C}$ = 25 Hz, C2′), 26.7 (t, $^3J_{Sn,C}$ = 69 Hz, C3′), 19.2 (t, $^1J_{Sn,C}$ = 391 Hz, C1′), 13.6 (q, C4′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$): δ = 69.4 ppm. MS: *m*/*z* = 353 [M^+], 319 (3 %, [M^+ − Cl], 301 [M^+ − Cl − H_2O], 297 [M^+ − Bu], 85 [M^+ − Bu_2SnCl], 67 [M^+ − Bu_2SnCl − H_2O], 57 [Bu].

Isomer separation was possible:

(*E*)-5-Dibutylchlorostannyl-4-penten-1-ol (14a): After following the general procedure purification was carried out by flash column chromatography at −78 °C, starting with *n*-hexane/Et_2O, 2:1, gradually moving to neat Et_2O as solvent (1.09 g; 61 %). The R_f values are strongly dependent on the concentration, but it can be stated that R_f (**13a**) > R_f (**14a**). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.22 (dt, J = 18.5 Hz, 6.2, $^3J_{Sn,H}$ = 87 Hz, 1 H, H4), 6.02 (d, J = 18.5, $^2J_{Sn,H}$ = 122 Hz, 1 H, H5), 3.62 (t, J = 6.4 Hz, 2 H, H1), 2.26 (q, J = 6.8 Hz, 2 H, H3), 2.10 (s, 1 H, OH), 1.70−1.58 (m, 6 H, H2, H2′), 1.33 (m, 8 H, H3′ + H1′), 0.89 (m, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 151.7 (d, $^2J_{Sn,C}$ = 9 Hz, C4), 127.7 (d, $^1J_{Sn,C}$ = 460 Hz, C5), 62.0 (t, C1), 33.3 (t, $^3J_{Sn,C}$ = 80 Hz, C3), 31.1 (t, C2), 27.6 (t, $^2J_{Sn,C}$ = 24 Hz, C2′), 26.6 (t, $^3J_{Sn,C}$ = 68 Hz, C3′), 17.6 (t, $^1J_{Sn,C}$ = 388 Hz, C1′), 13.5 (q, C4′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 83.6 ppm.

(*Z*)-5-Bromodibutylstannyl-4-penten-1-ol (13b): After following the general procedure purification was carried out by flash column chromatography at −78 °C, starting with *n*-hexane/Et_2O (2:1), gradually moving to neat Et_2O as solvent (0.22 g; 11 %). The R_f values are strongly dependent on the concentration, but it can be stated that R_f (**13b**) > R_f (**14b**). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.59 (dt, J = 11.8 Hz, 7.3 Hz, $^3J_{Sn,H}$ = 196 Hz, 1 H, H4), 6.02 (d, J = 11.7 Hz, $^2J_{Sn,H}$ = 106 Hz, 1 H, H5), 3.68 (tJ = 6.0 Hz, 2 H, , H1), 2.25 (q, J = 7.3 Hz, 2 H, H3), 1.67 (m, 6 H, H2, H2′), 1.47−1.33 (m, 8 H, H3′ + H1′), 0.93 (t, J = 7.4 Hz, 6 H, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 149.8 (d, $^2J_{Sn,C}$ = 8 Hz, C4), 129.2 (d, $^1J_{Sn,C}$ = 443 Hz, C5), 61.5 (t, C1), 32.7 (t, $^3J_{Sn,C}$ = 51 Hz, C3), 31.4 (t, C2), 28.2 (t, $^2J_{Sn,C}$ = 25 Hz, C2′), 26.6 (t, $^3J_{Sn,C}$ = 72 Hz, C3′), 19.0 (t, $^1J_{Sn,C}$ = 377 Hz, C1′), 13.6 (q, C4′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 51.6 ppm. MS: *m*/*z* = 398 [M^+], 341 [M^+ − Bu], 313 [Bu_2SnBr], 261 [M^+ − HBr − Bu], 85 [M^+ − Bu_2SnBr], 67 [M^+ − Bu_2SnBr − H_2O], 57 [Bu].

Isomer separation was possible:

(*E*)-5-Bromodibutylstannyl-4-penten-1-ol (14b): After following the general procedure purification was carried out by flash column chromatography at −78 °C, starting with *n*-hexane/Et_2O (2:1), gradually moving to neat Et_2O as solvent (1.34 g; 68 %). The R_f values are strongly dependent on the concentration, but it can be stated that R_f (**13b**) > R_f (**14b**). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 6.23 (dt, J = 18.5 Hz, 6.2 Hz, $^3J_{Sn,H}$ = 100 Hz, 1 H, H4), 6.06 (d, J = 18.5 Hz, $^2J_{Sn,H}$ = 121 Hz, 1 H, H5), 3.67 (t, J = 6.4 Hz, 2 H, H1), 2.30 (dt, J = 7.4 Hz, 6.2 Hz, 2 H, H3), 1.75−1.58 (m, 6 H, H2, H2′), 1.40−1.33 (m, 8 H, H3′ + H1′), 0.92 (t, 6 H, J = 7.4 Hz, H4′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 152.0 (d, $^2J_{Sn,C}$ = 10 Hz, C4), 127.1 (d, $^1J_{Sn,C}$ = 441 Hz, C5), 62.2

(t, C1), 33.6 (t, $^3J_{Sn,C}$ = 80 Hz, C3), 31.3 (t, C2), 28.1 (t, $^2J_{Sn,C}$ = 25 Hz, C2′), 26.6 (t, $^3J_{Sn,C}$ = 68 Hz, C3′), 17.4 (t, $^1J_{Sn,C}$ = 373 Hz, C1′), 13.6 (q, C4′) ppm. ^{119}Sn NMR (112 MHz, $CDCl_3$, 23 °C): δ = 69.6 ppm.

The reaction of *N*,*N*-dimethylpropargylamine with Bu_2SnHCl following the general procedure gave *N*,*N*-dimethyl-3-dibutylchlorostannyl-(*Z*)-2-propenyl-1-amine in approximately 20 percent yield; a large number of tin-containing by-products was formed, so that it was not possible to obtain the product in a pure state. Spectroscopic evidence for ***N*,*N*-dimethyl-3-dibutylchlorostannyl-(*Z*)-2-propenyl-1-amine** is as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.51 (dt, *J* = 11.3 Hz, 3.0 Hz, $^3J_{Sn,H}$ = 220 Hz, 1 H, H2), 6.45 (d, *J* = 11.3 Hz, $^2J_{Sn,H}$ = 114 Hz, 1 H, H3), 3.00 (m, 2 H, H1), 2.24 (s, 6 H, NMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 140.0 (d, $^2J_{Sn,C}$ = n. d., C2), 137.2 (d, $^1J_{Sn,C}$ = 516 Hz, C3), 62.3 (t, $^3J_{Sn,C}$ = 50 Hz, C1), 45.7 (q, NMe), 17.9 (t, $^1J_{Sn,C}$ = 486 Hz, C1′), 13.2 (q, C4′) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 23 °C): δ = −45.6 ppm.

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