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Preparation of α-substituted γ-alkoxyallylstannanes from β-tributylstannyl acrolein acetals: scope of the method and primary rationalization of the obtained results

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Abstract

α-Substituted γ-alkoxyallylstannanes were obtained from β-tributylstannyl acrolein acetals when reacted with lower order magnesium cyanocuprates in the presence of boron trifluoride at low temperature. In the case of *n*-alkylcyanocuprates an *anti* S_N2' substitution on a *cisoid* conformation appears to be the main reaction pathway. However, subtle competitions with other mechanisms may occur depending on the experimental conditions, on the reagents or on the substrates. These drawbacks constitute limitations for the use of the method especially when enantioenriched α-substituted γ-alkoxyallylstannanes are desired.

Keywords: Vinyltins; Allyltins; β-Tributylstannyl acrolein acetals; α-Substituted γ-Alkoxyallylstannanes; Copper cyanocuprates; S_N2' substitution

1. Introduction

Due to their efficiency in the stereoselective synthesis of polyhydroxylated targets upon reaction with α- or β-oxygenated aldehydes [1,2] or iminium salts [3–5], (γ-alkoxy)- and (γ-silyloxy)allylstannanes have become useful reagents for organic chemists. This interest has been amplified by the fact that an α-substituent or a change in the geometry of the double bond could sometimes modify in a major way the stereochemical course of the allylstannation reaction [6,7]. Furthermore stereoconvergent effects have been observed in allylstannation reactions of aldehydes involving enantiopure chiral γ-oxygenated allylstannanes or chiral aldehydes [8,9].

In order to obtain achiral γ-alkoxyallylstannanes several methods have been employed. Hydrostannation of alkoxyallenes under free radical conditions or under palladium catalysis usually affords a mixture of isomers [10–12] while metallation of allyl acetals [13] or allyl ethers [14,15] followed by quenching with a triorganotin halide works nicely with a strong preference for the *Z*-isomer in the last case due to the chelation of the metal with oxygen.

When γ-oxygenated allylstannanes with the *E* configuration were desired, the best stereochemical control was obtained through stannylcupration of α,β-enals with higher order stannyl cyanocuprates and further quenching with alkoxymethyl chloride or triorganosilylchloride [16,17]. In this last case, the obtaining of (*Z*)-γ-siloxyallylstannanes was achieved through reaction of trialkylstannyllithium on α,β-enals followed by

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quenching with triorganosilyl triflates [16]. Furthermore, the use of readily available β-tributylstannylacrolein (treatment of the acetal on wet silica gel) [18–20] has also been proved to provide a selective access to α-substituted γ-siloxyallyltributylstannanes [5,17].

The synthesis of enantioenriched γ-alkoxyallylstannanes can be achieved from allyl ethers derived from enantioenriched chiral alcohols using a metallation/tributyltin halide trapping sequence [21,22] or via transalkoxylation of a γ-methoxyallylstannane with a chiral alcohol [23]. However, these methods have been strongly challenged by the stereospecific boron trifluoride promoted rearrangement of enantioenriched (*E*)-α-alkoxyallylstannanes into enantioenriched (*Z*)-γ-alkoxyallylstannanes [24]. Accordingly, the synthesis of α-alkoxyallylstannanes previously described in achiral series [25–27] became of crucial interest when enantioenriched chiral α-oxygenated species were involved. The pioneering preparation based on separation of diastereomeric mixtures of α-(menthyloxymethyl)crotyltributylstannanes [28,29] has been rapidly replaced by enantioselective preparations.

The first one was the enantioselective reduction (BINAL-H) of α,β-ethylenic acylstannanes which afforded enantioenriched α-stannylalcohols subsequently trapped as methoxymethyl ethers [30,31]. The second one was the selective deprotonation of carbamates derived from allylic alcohols followed by trapping with a triorganotin halide. This last method developed mainly by Hoppe was first applied to carbamates of enantiopure allylic alcohols using *sec*-butyllithium-TMEDA for deprotonation and subsequently extended to the asymmetric deprotonation of racemic crotylcarbamates and related species using *n*-butyllithium/(−)-sparteine [32–34]. Using appropriate experimental conditions (direct trapping of the lithiocrotyl carbamate by triorganotin halide or trapping after transmetallation with titanium tetraisopropoxide), the (*Z*)-γ-oxygenated α-substituted allylstannanes can be obtained selectively with the *R* or with the *S* configuration at the α-carbon centre related to tin [34].

In this context, in spite of the efficiency of these methods, we decided to investigate thoroughly our initial reports about synthesis of α-substituted γ-alkoxyallylstannanes [35] or α-substituted γ-aminoallylstannanes [36] by reacting (*E*)-β-tributylstannylacrolein acetals or amino acetals with organocopper reagents in the presence of boron trifluoride. The easy access to pure (*E*)- or (*Z*)-β-tributylstannylacrolein acetals using appropriate experimental conditions [37,38] might open interesting possibilities and help in a comprehensive study allowing an evaluation of the effective potential of this strategy.

2. Results

In order to obtain efficiently γ-alkoxyallylstannanes from β-tributylstannyl acrolein acetals, the reaction must be driven to a clean S_N2' reaction as observed with non stannylated allylic acetals when reacted with aryl or vinyl copper reagents in the presence of boron trifluoride [39–41].

In the present case the difficulties might arise from the easy transmetallation of Sn–C bond by organolithium reagents [42] and by higher order cyanocuprates [43,44] or from a competitive S_N2 pathway [41].

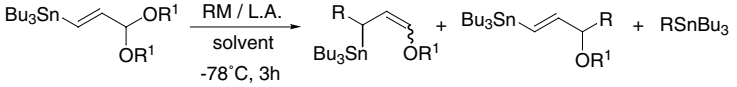
Accordingly, preliminary experiments have been achieved using different types of methyl copper reagents in the presence of boron trifluoride (Scheme 1).

The obtained results, discussed in our early report [35], have allowed the following observations:

- with Me_2CuLi, the S_N2' pathway was shown to be the major one but substitution products were obtained as a mixture of **2*E*** and **2*Z*** isomers and an important contamination by **3** and **4** was observed;
- with MeCu · LiBr in the presence of Me_2S the transmetallation reaction only was observed;
- with MeCu · LiX or MeCuCNLi the S_N2' reaction was the major or exclusive pathway with a high preference for the *Z*-isomer.

On the basis of these results, it was deduced that the use of organocopper reagents or lower order cyanocuprate reagents in ether seems preferable to obtain the higher yields in **2** (S_N2' product). Furthermore, since Grignard reagents have a lower propensity to transmetallate the vinylic tin–carbon bond, we chose to use mainly lower order magnesium cyanocuprates to achieve this transformation with different R groups.

The obtained results reported in Table 1 demonstrate an efficient preparation of α-substituted γ-ethoxyallylstannanes with isolated yields in the range 60–95% and a high preference for the *Z*-isomer (80–100%). Further-

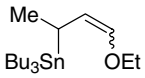
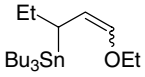
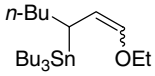
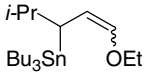
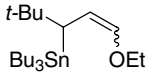
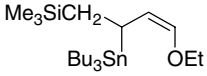
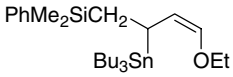
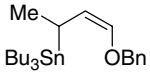
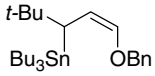
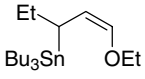
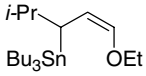
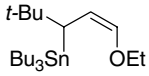
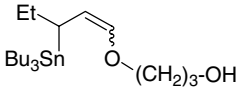
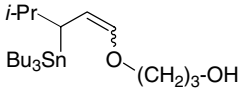
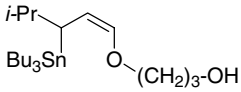
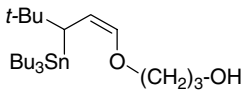


1a*E* (R^1 = Et)
1b*E* (R^1 = Bn)
1c*E* [$(OR^1)_2$ = O-$(CH_2)_3$-O]

2 (S_N2') **3** (S_N2) **4** (transmetallation)

Scheme 1.

Table 1
Synthesis of γ-alkoxyallylstannanes from vinyltin acetals **1a–c**

Entry	Substrate	Organocopper reagent[a]	γ-Alkoxystannane	No.	Yield (*Z*/*E*)[b]
1	**1a*E***	MeCu(CN)Li		**2a**	81 (80/20)
2	**1a*E***	EtCu(CN)MgBr		**2b**	75 (94/6)
3	**1a*E***	*n*-BuCu(CN)MgBr		**2c**	68 (96/4)
4	**1a*E***	*i*-PrCu(CN)MgCl		**2d**	85 (98/2)
5	**1a*E***	*t*-BuCu(CN)MgCl		**2e**	70 (98/2)
6	**1a*E***	$Me_3SiCH_2Cu(CN)MgCl$		**2f**	95 (100/0)
7	**1a*E***	$PhMe_2SiCH_2Cu(CN)MgCl$		**2g**	58 (100/0)
8	**1b*E***	MeCu(CN)MgCl		**2h**	51 (100/0)
9	**1b*E***	*t*-BuCu(CN)MgCl		**2i**	87 (100/0)
10	**1a*Z***	EtCu(CN)MgBr		**2b**	80 (100/0)[c,d]
11	**1a*Z***	*i*-PrCu(CN)MgCl		**2d**	85 (100/0)[c,d]
12	**1a*Z***	*t*-BuCu(CN)MgCl		**2e**	97 (100/0)[c]
13	**1c*E***	EtCu(CN)MgBr		**2j**	53 (50/50)
14	**1c*E***	*i*-PrCu(CN)MgCl		**2k**	68 (55/45)
15	**1c*Z***	*i*-PrCu(CN)MgCl		**2k**	68 (100/0)[c,d]
16	**1c*Z***	*t*-BuCu(CN)MgCl		**2l**	52 (100/0)[c,d]

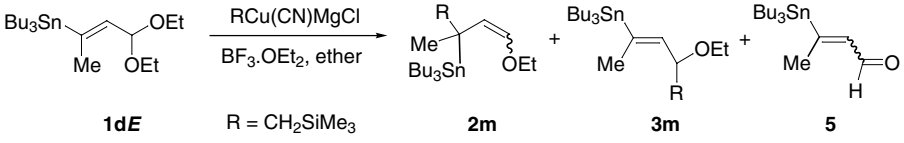
[a] Reactions were performed in ether at −78 to −30 °C using 3 equiv. of organocopper reagent and 3 equiv. of boron trifluoride etherate.
[b] Isolated yields in S_N2' substitution products after liquid chromatography on deactivated alumina.
[c] Conversion rate (NMR evaluation).
[d] The S_N2 compound was also observed (5% for entries 10–11, 10% for entry 15 and 15% for entry 16).

more, as expected, this reaction can easily be extended to the preparation of α-substituted γ-benzyloxyallylstannanes, **2h** and **2i** (Table 1, entries 8,9), which have a higher potential interest for organic synthesis due to the possible hydrogenolysis of the benzylic ether function [9].

At this stage, a comprehensive study of the reaction requires the evaluation of structural effects such as geometry of the double bond in **1**, influence of a cyclic acetal having a higher propensity for chelation with boron trifluoride or influence of a substituent on the vinylic carbon bearing the stannyl group. The results on the first two points are reported in Table 1 (comparison of entries 2–5 with entries 10–16). Starting from **1a*Z***, the S_N2' products **2b**, **2d** and **2e** were obtained as pure *Z*-isomers (in the limit of the NMR detection) with a small contamination (5%) by S_N2 products **3b** and **3d**. When the cyclic acetal **1c*E*** was used as starting material (entries 13,14), once more the S_N2' substitution products **2j** and **2k** were obtained but as a mixture of *E*- and *Z*-isomers. The weakness of the diastereoselectivity can be solved starting from **1c*Z*** (**2k** and **2l** were obtained as pure *Z*-isomers) but another contamination due to the S_N2 products **3k** and **3l** (respectively, 10% and 15%) was observed (entries 15,16).

The last parameter (α-vinylic substituent related to tin on the substrate) was examined through consideration of β-tributylstannyl crotonaldehyde diethyl acetal **1d*E*** which was reacted with (trimethylsilyl)methyl magnesium cyanocuprate according to Scheme 2. Subsequent modulations of the experimental conditions are reported in Table 2.

When compared to reactions involving β-tributylstannylacrolein acetals, the presence of the methyl group in **1d*E*** strongly modifies the distribution between S_N2 and S_N2' products. When reagents were used in a ratio close to stoechiometry or when solution S_2 was added on S_1 at −80 °C, the S_N2 product **3m** appeared to be the major component. However when we increased the amount of boron trifluoride (compared to the amount of RCu(CN)MgCl as obtained for addition of S_1 into S_2), the S_N2' product became the major component. Furthermore, use of a higher reaction temperature (−40 °C) appeared to be more favourable to S_N2' reaction. Finally, while (*Z*)-allylstannane (**2m*Z***) was obtained as the major component when the reactions were



Scheme 2.

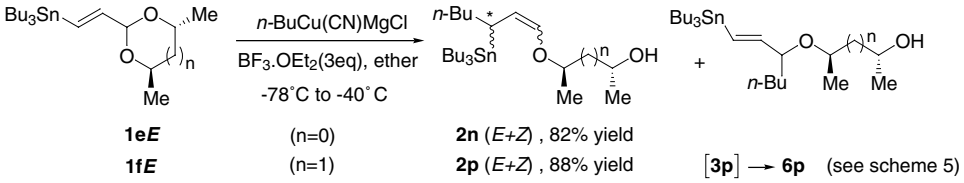
Table 2
Reaction of $Me_3SiCH_2Cu(CN)MgCl$ with (*E*)-Bu_3Sn–C(Me)=CH–$CH(OEt)_2$

Entry	Experimental conditions[a]	Products distribution[b]			
		S_N2' products		S_N2 product	Aldehyde[c]
		2m*Z*	**2m*E***	**3m**	**5**
1	(1) CuCN (1.2eq) + RMgCl (1.2eq), −40 °C, 15 min then −80 °C (2) Addition of $BF_3 \cdot OEt_2$ (1.2eq) then **1d*E*** (1eq), −80 °C, 1 h	3	23	**74**	0
2	(1) CuCN (1.5eq) + RMgCl (1.5eq), −50 °C, 2 min then −80 °C (2) Addition of **1d*E*** (1eq) + $BF_3 \cdot OEt_2$ (1.5eq), −80 °C, 2 h	11	37	**52**	0
3	S_1 = CuCN (2eq) + RMgCl (2eq), −45 °C, 30 min S_2 = **1d*E*** (1eq) + $BF_3 \cdot OEt_2$ (3eq), −80 °C, 10 min (S_2 cannulated on S_1 at −80 °C, 1 h)	3	32	**59**	6
4	S_1 = CuCN (1.5eq) + RMgCl (1.5eq), −40 °C, 10 min S_2 = **1d*E*** (1eq) + $BF_3 \cdot OEt_2$ (3eq), −40 °C, 10 min (S_1 at −80 °C cannulated on S_2 at −80 °C, 1 h)	**59**	29	12	0
5	S_1 = CuCN (2eq) + RMgCl (2eq), −45 °C, 40 min S_2 = **1d*E*** (1eq) + $BF_3 \cdot OEt_2$ (3eq), −45 °C, 40 min (S_2 at −40 °C cannulated in S_1 at −40 °C, 1 h)	**36**	31	12	21

[a] In this set of experiments R is Me_3SiCH_2 and reactions were performed in ether. Stoechiometry and reaction temperature are mentioned in the table. For entries 3–6 the cyanocuprate solution (S_1) and the **1d*E***/ $BF_3 \cdot OEt_2$ solution (S_2) were prepared separately and one of these two solutions was cannulated on the other at low temperature before being allowed to react at this temperature during the indicated time.

[b] NMR evaluation on the crude mixture.

[c] Upon treatment of **1d*E*** with $BF_3 \cdot OEt_2$ and subsequent hydrolysis (without reaction with RCu(CN)MgCl), aldehyde **5** was obtained in a ratio *E*/*Z* = 84/16 accompanied with a small amount of isomerized vinylstannane **1d*Z*** which seems to be less easily hydrolysed than its E-isomer.



Scheme 3.

performed with a large excess of boron trifluoride etherate, the preference turned to the *E*-isomer when the S_N2 is the main one for reactions performed with lower rates of Lewis acid at −80 °C.

Obviously these last results demonstrate a subtle competition between S_N2' and S_N2 pathways when **1d*E*** was involved, possibly slightly complicated by competitive addition on aldehyde **5** (cf. Table 2, footnote c).

Due to these problems, we decided to focus our efforts on the rationalization of the S_N2' substitution of β-tributylstannylacrolein acetals derived from (2*R*,3*R*)-butanediol (**1e*E***) or from (2*R*,4*R*)-pentanediol (**1f*E*** and **1f*Z***) by using the stereochemical information to improve the understanding of the reaction. In the case of *n*-BuCu-CNMgCl, the reaction occurs as depicted in Scheme 3 and the results are summarized in Table 3 (entries 1,4).

From these data, it appears clearly that (2*R*,4*R*)-pentanediol acetal **1f*E*** allows improved *Z* selectivity in obtaining S_N2' products when compared to (2*R*,3*R*)-butanediol acetal **1e*E*** and that configuration of the starting vinyltin acetal is of crucial importance since **1f*Z*** appears to be unreactive (Table 3, entry 10).

While use of higher order lithium methyl cyanocuprates (Table 3, entries 2,3) led to poor selectivities (both S_N2 and S_N2' products were obtained and S_N2' products were obtained as mixtures of *E* and *Z* isomers), lower order magnesium cyanocuprates afforded S_N2' adducts with a high *Z* selectivity (*Z*/*E* = 79/21–94/6) but with a stereocontrol on the new created centre which was strongly modified by the size of the entering group (Table 3, entries 4,6–9), as illustrated by the observed diastereomeric excesses which decrease according to the following sequence *n*-Bu (88%) > Me_3SiCH_2 (76%) > *i*-Pr (68%) > *t*-Bu (40%) in the RCu(CN)MgCl series. This type of selectivity seems to be higher for the obtained *E*-isomers but unexploitable for preparative purpose due to the low yield in this isomer.

The absolute configuration of the newly created centre has been assigned as (*S*) for **2p*Z*** (S_N2' substitution by *n*-butyl group) on the basis of its $[\alpha]_D$ value of +117.5 taking into account the $[\alpha]_D$ value of −3.2 obtained for compound **2q** and the $[\alpha]_D$ values around +120 reported by Marshall [24] for the (*S*)-enantiomer of (γ-alkoxyallyl)stannanes having very similar structures (Scheme 4). This assignment has been discussed in a previous report [35].

The lower *Z*/*E* selectivity observed with **1e*E*** might be due to a higher flexibility of the five-membered ring acetals or to different chelation pathways when compared to their six-membered analogues.

Finally, it is worth noticing that secondary α,γ- or α,α′-disubstituted products have been isolated. Their formation is the result of a subsequent S_N2 or S_N2' attack onto an initially formed S_N2 substitution product (Scheme 5).

According to this scheme, a mixture of **6o** and **7o** was obtained in 20% yield for R = Me (entry 3) while a 3% yield of **6p** was obtained for R = *n*-Bu (entry 4).

3. Discussion

The above results demonstrate the possible access to α-substituted γ-alkoxyallylstannanes from β-tributylstannyl acrolein acetals upon reaction with cyanocuprates in the presence of boron trifluoride.

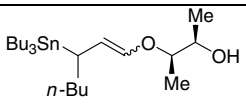
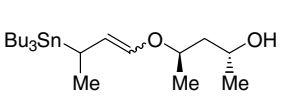
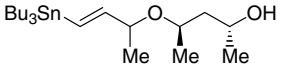
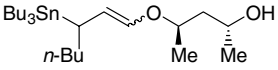
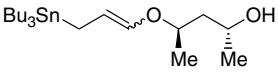
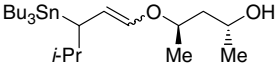
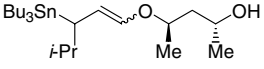
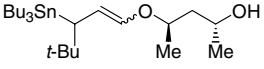
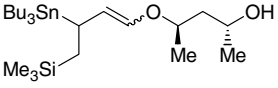
The higher *Z* selectivities in γ-alkoxyallylstannanes (S_N2' substitution products) were obtained using lower order magnesium cyanocuprates with diethyl or dibenzyl β-tributylstannyl acrolein acetals and an increased *Z* selectivity was observed for (*Z*)-β-tributylstannyl acrolein acetals with a concomitant lower reactivity (*Z*-acetals derived from (2*R*,4*R*)-pentanediol appear to be unreactive).

In the reactions leading to the higher *Z* selectivity (use of *n*-BuCu(CN)MgCl) the creation of the new asymmetric centre with an *S* configuration can be explained by an *anti* S_N2' reaction on a *cisoid* conformation according to Scheme 6.

Such an explanation has already been used to rationalize this type of substitution on purely organic allylic acetals [41] but the obtained results require some comments.

(1) This S_N2' reaction seems to be highly sensitive to steric effects, both for the approach of the Lewis acid and the nucleophiles. While approach of the Lewis acid on the less hindered oxygen seems able to drive efficiently the stereoselectivity when primary alkyl cyanocuprates are involved, the steric interaction between the equatorial methyl group on the acetal and the entering nucleophile can

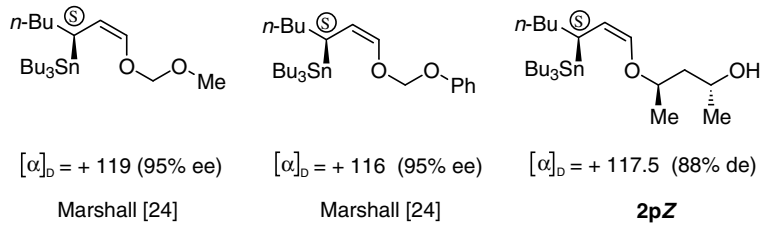
Table 3
Reaction of cyanocuprates with chiral β-tributylstannyl acrolein acetals

Entry	Substrate	Organocopper reagent[a]	Obtained product	No.	Distribution products[b]			Yields[d]
					2(S_N2')		**3**(S_N2)	
					Z (de)	*E* (de)		
1	**1e*E***	*n*-BuCu(CN)MgCl		**2n**	57 (nd)	43 (nd)	–	82
2	**1f*E***	$Me_2Cu(CN)Li_2$		**2o**	19 (nd)	61[c]	20	37
3	**1f*E***	$Me_2Cu(CN)Li_2$,LiBr		**3o**	18 (64)	47[c]	35	48
4	**1f*E***	*n*-BuCu(CN)MgCl	 $[\alpha]_D = +117.5$	**2p**	93 (88)	7 (nd)	–	82
5	**1f*E***	$Bu_2Cu(CN)Li_2$	 $[\alpha]_D = -3.2$	**2q**	100[e]	–	–	17[e]
6	**1f*E***	*i*-PrCu(CN)MgCl		**2r**	94 (68)	6[c]	–	65
7	**1f*E***	*i*-$Pr_2Cu(CN)(MgCl)_2$		**2r**	93 (46)	7 (nd)	–	64
8	**1f*E***	*t*-BuCu(CN)MgCl		**2s**	79 (40)	21[c]	–	80
9	**1f*E***	$Me_3SiCH_2Cu(CN)MgCl$		**2t**	91 (76)	9[c]	–	78
10	**1f*Z***	RCu(CN)MgCl; R = Et, *n*-Bu, *i*-Pr, *t*-Bu	No reaction	–	–	–		0

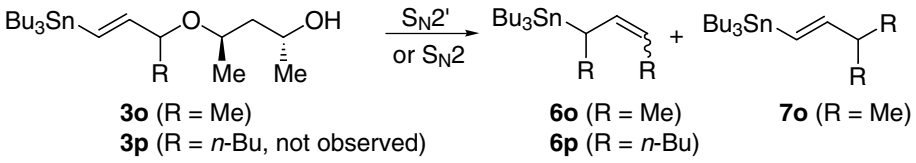
[a] Reactions were performed in the presence of $BF_3 \cdot OEt_2$ (3 equiv.) in ether from −78 to −40 °C.
[b] nd: not determined.
[c] For these *E*-allylstannanes, a single diastereomer was obtained in the limits of NMR detection.
[d] Overall yields of substitution products ($S_N2 + S_N2'$).
[e] S_N2' reduction product (hydrogen transfer).

challenge the accessibility of the Lewis acid to the less hindered oxygen, giving a lower *anti* S_N2'/*syn* S_N2' ratio.

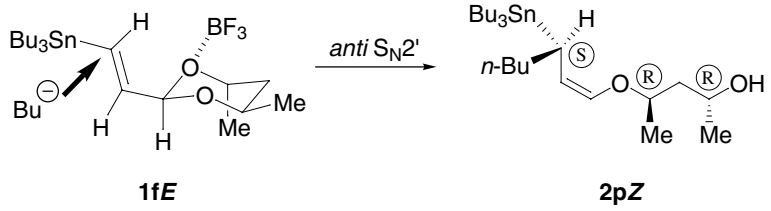
Such an explanation might account for the decrease of diastereomeric excess in the obtained α-substituted γ-alkoxyallylstannanes when moving from *n*-Bu



Scheme 4.



Scheme 5.



Scheme 6.

Cu(CN)MgCl to $Me_3SiCH_2Cu(CN)MgCl$, *i*-PrCu(CN)MgCl and *t*-BuCu(CN)MgCl. A similar trend has been already observed in substitution of allylic mesylates [45].

(2) The fact that higher *Z* selectivities were obtained using magnesium cyanocuprates instead of lithium cyanocuprates might be due to the bidentate character of magnesium (which might interact both with the organocopper moiety and with the *syn* oxygen of the acetal).

(3) In any case, the *anti* S_N2' pathway on the *cisoid* conformation cannot fully explain the obtained results. Other mechanisms are obviously involved, as for instance a *syn* S_N2' substitution on a *cisoid* conformation, an *anti* S_N2' substitution on a *transoid* conformation (stereoselective obtaining of **2*E*** derivatives), or an S_N1 mechanism when a higher stabilisation of an intermediate cation can be considered, as for instance in the case of β-tributylstannyl crotonaldehyde acetals. The interference of oxonium intermediates has already been proposed in the case of substitution of deuterium-labelled saturated acetals [46].

(4) Due to the use of a large excess of boron trifluoride and cyanocuprate (3 equiv.) and to the influence of temperature on the effective structure of the reagents, too many parameters remain unknown to allow further reasonable discussion.

4. Conclusion

The preparation of (*Z*)-α-substituted γ-alkoxyallylstannanes has been shown to be possible by reacting magnesium cyanocuprates with β-tributylstannylacrolein acetals in the presence of boron trifluoride etherate at −78 to −40 °C in ether. With less hindered systems, an *anti* S_N2' substitution on a *cisoid* conformation seems to be the main reaction pathway, but subtle competitions are likely to occur, depending on the nature of the counterion on the cyanocuprate, on the size of the entering nucleophile or on the temperature.

5. Experimental

5.1. General

^1H, ^{13}C and ^{119}Sn spectra were recorded on Bruker AC 200 or Bruker ARX 400 spectrometers. Chemical shifts are given in ppm as δ values related to tetramethylsilane (^1H, ^{13}C) or tetramethylstannane (^{119}Sn) and coupling constants are given in Hz ($CDCl_3$ was used as solvent at 300 K when nothing else is mentioned). Mass spectra were obtained in direct introduction mode or in GC/MS mode using a Hewlett–Packard Engine 5989A apparatus in EI (70 eV) or CI (using NH_3 as reacting gas) mode. Organostannyl fragments are given for ^{120}Sn

which means that the given abundance are broadly one third of the overall abundance of the organostannyl fragment when compared to organic ones. When high resolution spectra were done, they were recorded on a Jeol SX102 apparatus in FAB^+ mode (10 kV), using glycerol matrix. IR spectra (film in NaCl windows) were recorded with a Perkin–Elmer 1420 or a Bruker IFS Vector 22 apparatus. Optical rotations were measured using an "Optical Activity AA10" apparatus or a Perkin–Elmer 341 apparatus. Elemental analyses were performed by CNRS microanalysis centre (Vernaison). Liquid chromatography separations were achieved on silicagel Si 60 (40–63 or 63–200 μm) or on activated alumina (50–200 μm) and TLC analyses on silica-coated plates (Merck Kieselgel $60F_{254}$). The solvents used in the reactions are freshly distilled ones, dried on sodium–benzophenone (diethylether and THF) or on calcium hydride. When reactions were performed in Schlenk tubes, the reactor (eventually containing solid salts like CuCN) was first dried by flame heating under vacuum and placed under inert atmosphere (argon). The other reagents were added by syringue method in their solvent.

5.2. Organic starting materials

3,3-Diethoxyprop-1-yne was prepared according to the literature [47] and transacetalised into 3,3-dibenzyloxyprop-1-yne, 2-ethynyl-1,3-dioxane or (4*R*,6*R*)-2-ethynyl-4,6-dimethyl-1,3-dioxane as described below.

5.2.1. Transacetalisation of 3,3-diethoxyprop-1-yne: typical procedure

In a Dean–Stark apparatus were placed 3.9 mmol of paratoluenesulfonic acid and 0.39 mol of benzyl alcohol in cyclohexane (400 mL). The solution was stirred and refluxed for 2 h before addition of diethoxypropyne (78 mmol). The Dean Stark trap was regularly purged in order to shift the equilibrium, the reaction being monitored by TLC or GC. At completion, after cooling at room temperature, 6 mL of triethylamine were added and the remaining solution filtered on alumina. After elimination of cyclohexane, the propargylic acetals were purified by distillation, crystallisation or liquid chromatography.

5.2.1.1. 3,3-Dibenzyloxyprop-1-yne (bp_{15} = 97 °C, 15 g, 76% yield). ^{1}H NMR: δ = 2.62 (d, 1H, $^4J_{1H}$ = 1.8), 4.65 and 4.80 (A_2B_2 syst., 4H, $^2J_{1H}$ = 11.6), 5.48 (d, 1H, $^4J_{1H}$ = 1.8), 7,38 (m, $10H_{arom}$).; ^{13}C NMR: δ = 67.5 (2C), 74.4, 78.7, 90.5, 127.9 (2C), 128.1 (4C), 128.4 (4C), 137.3 (2C); IR: ν = 3285, 3065, 2876, 2125, 1498, 1454, 1200–950, 739, 697 cm^{-1}; MS: *m/z* (%) = 161 ($M^{\cdot+}$ –91, 2), 144 (2), 107 (20), 92 (71), 91 (100), 77 (9), 65 (13), 51 (3), 39 (2); elemental analysis Calc. (%) for $C_{17}H_{16}O_2$ (252.12): C, 80.93; H, 6.39. Found: C, 81.06; H, 6.39%.

5.2.1.2. 2-Ethynyl-1,3-dioxane (5.2 g, 60% yield). ^{1}H NMR: δ = 1.50–1.90 (m, 2H), 2.58 (d, 1H, $^4J_{1H}$ = 1.8), 3.76 (m, 2H), 4.12 (m, 2H), 5.31 (d, 1H, $^4J_{1H}$ = 1.8); ^{13}C NMR ($CDCl_3$, 300K): δ = 25.5, 64.5 (2C), 73.8, 78.2, 89.6; IR: ν = 3293, 2961, 2907, 2858, 2133, 1414, 1105, 1022, 872, 795 cm^{-1}; MS: *m/z* (%) = 112 ($M^{\cdot+}$, 10), 111 (75), 81 (40), 55 (100), 53 (100).

5.2.1.3. (4R,6R)-2-Ethynyl-4 6-dimethyl-1 3-dioxane (mp = 89 °C, white crystals, 8.9 g, 82% yield). ^{1}H NMR: δ = 1.26 (d, 3H, $^3J_{1H}$ = 6.4), 1.30–1.45 (m, 1H), 1.39 (d, 3H, $^3J_{1H}$ = 8.5), 1.91 (ddd, 1H, $^2J_{1H}$ = 13.2, $^3J_{1H}$ = 11.0, $^3J_{1H}$ = 6.0), 2.52 (d, 1H, $^4J_{1H}$ = 1.6), 4.03 (qdd, 1H, $^3J_{1H}$ = 11.0, $^3J_{3H}$ = 6.4, $^3J_{1H}$ = 2.7), 4.37 (qdd, 1H, $^3J_{1H}$ = 6.0, $^3J_{3H}$ = 8.5, $^3J_{1H}$ = 2.2), 5.57 (d, 1H, $^4J_{1H}$ = 1.6); ^{13}C NMR: δ = 17.0, 21.6, 36.5, 68.3, 68.5, 72.4, 79.6, 84.5; IR: ν = 3249, 2975, 2937, 2890, 2130, 1384, 1149, 1101, 991, 708 cm^{-1}; MS: *m/z* (%) = 139 ($M^{\cdot+}$–H, 29), 125 (9), 99 (19), 81 (21), 71 (38), 55 (72), 45 (49), 42 (100); $[\alpha]_D$ = +16.8 (c = 1.016 in $CHCl_3$).

5.2.2. Preparation of 1,1-diethoxybut-2-yne

In a Schlenk reactor, a *n*-butyllithium solution (7.7 mmol in hexane) was added to a 3,3-diethoxypropyne solution (7 mmol) in THF (5 mL) at room temperature. After 10 min stirring the reaction mixture was quenched with dimethylsulfate (7.7 mmol) before hydrolysis with a saturated NaCl aqueous solution. Further ether extraction and usual treatments allowed access to 1,1-diethoxybut-1-yne in 65% yield (0.65 g).

^{1}H NMR: δ = 1.23 (t, 6H, $^3J_{2H}$ = 6.8), 1.86 (d, 3H, $^5J_{1H}$ = 1), 3.54 and 3,73 (A_2B_2 syst., 4H, $^3J_{3H}$ = 6.8, $^2J_{1H}$ = 9.2), 5.22 (q, 1H, $^5J_{3H}$ = 1).

5.3. Organometallic starting materials

Organolithium reagents were Chemetall reagents while Grignard reagents were prepared using conventional methods in ether solution: EtMgBr (2M), *i*-PrMgCl (2M), *t*-BuMgCl (1M), Me_3SiCH_2MgCl (1M).

(*E*)-1-Tributylstannyl-3,3-diethoxyprop-1-ene (**1a*E***) was obtained by stannylcupration of 3,3-diethoxypropyne and (*Z*)-1-tributylstannyl-3,3-diethoxyprop-1-ene (**1a*Z***) by titanation of the corresponding alkynylstannane according to our previous described procedures [37,38] which were also used to obtain the other vinyltin acetals respectively in the *E* series (**1b*E***, **1d*E***) and in the *Z* series (**1b*Z***, **1c*Z*** and **1f*Z***). The (*E*)-vinyltin acetals **1c*E***, **1e*E*** and **1f*E*** were obtained by transacetalisation of **1a*E*** with the appropriate diols [35].

The complete physicochemical characterization of **1a*E*** [48], **1a*Z*** [48] and **1b*E*** [9] has been already reported

and the characterization of the other vinyltin acetals is given below.

*5.3.1. (E)-2-(2-Tributylstannylethylidene)-1,3-dioxane (**1cE**, 87% yield)*

^{1}H NMR: δ = 0.70–1.10 (m, 15H), 1.15–1.70 (m, 13H), 2.23 (m, 1H), 3.83 (m, 2H), 4.15 (m, 2H), 4.91 (dd, 1H, $^3J_{1H}$ = 4.1, $^4J_{1H}$ = 0.7, $^4J_{Sn–H}$ = 9.7), 5.98 (dd, 1H, $^3J_{1H}$ = 19.3, $^3J_{1H}$ = 4.1, $^3J_{Sn–H}$ = 42), 6.48 (dd, 1H, $^3J_{1H}$ = 19.3, $^4J_{1H}$ = 0.7, $^2J_{Sn–H}$ = 43); ^{13}C NMR: δ = 9.5 (3C, $^1J_{Sn–C}$ = 332/347), 13.7 (3C), 25.9, 27.3 (3C, $^3J_{Sn–C}$ = 56), 29.1 (3C, $^2J_{Sn–C}$ = 21), 66.8, 67.0, 102.2 ($^3J_{Sn–C}$ = 70), 133.6 ($^1J_{Sn–C}$ = 341/357), 144.1; MS: organostannyl fragments: *m/z* (%) = 347 ($M^{\cdot+}$ − 57, 42), 291 (32), 233 (12), 177 (17); organic fragments: *m/z* (%) = 113 (100), 87 (11), 55 (10).

*5.3.2. (Z)-2-(2-Tributylstannylethylidene)-1,3-dioxane (**1cZ**, 87% yield)*

^{1}H NMR: δ = 0.70–1.10 (m, 15H), 1.15–1.70 (m, 13H), 2.10 (m, 1H), 3.78 (td, 2H, $^2J_{1H}$ = 12.2, $^3J_{1H}$ = 12.2, $^3J_{1H}$ = 2.5), 4.15 (ddd, 2H, $^2J_{1H}$ = 12.2, $^3J_{1H}$ = 5.0, $^3J_{1H}$ = 1.3), 4.89 (dd, 1H, $^3J_{1H}$ = 3.3, $^4J_{1H}$ = 1.3), 6.21 (dd, 1H, $^3J_{1H}$ = 13.4, $^4J_{1H}$ = 1.3), 6.47 (dd, 1H, $^3J_{1H}$ = 13.4, $^3J_{1H}$ = 3.3); ^{13}C NMR: δ = 11.0 (3C, $^1J_{Sn–C}$ = 336/352), 13.6 (3C), 25.7, 27.4 (3C, $^3J_{Sn–C}$ = 55), 29.3 (3C), 66.6 (2C), 101.1 ($^3J_{Sn–C}$ = 46), 134.3 ($^1J_{Sn–C}$ = 255), 143.2; IR: ν = 2956, 2922, 2872, 2852, 1464, 1377, 1101, 1008, 960, 672 cm^{-1}; MS: organostannyl fragments: *m/z* (%) = 403 ($M^{\cdot+}$ − H, 1), 347 (100), 291 (35), 233 (46), 177 (75), 121 (25); organic fragments: *m/z* (%) = 113 (29), 57 (28), 41 (53).

*5.3.3. (E)-3-Tributylstannyl-1,1-diethoxybut-2-ene (**1dE**, 90% yield)*

^{1}H NMR: δ = 0.70–1.70 (m, 33H), 1.94 (d, 3H, $^4J_{1H}$ = 1.8, $^3J_{Sn–H}$ = 44/46), 3.50 and 3.63 (A_2B_2 syst., 4H, $^2J_{1H}$ = 9.5, $^3J_{3H}$ = 7.0), 5.26 (d, 1H, $^3J_{1H}$ = 6.0, $^4J_{Sn–H}$ = 8), 5.58 (dq, 1H, $^3J_{1H}$ = 6.0, $^4J_{3H}$ = 1.8, $^3J_{Sn–H}$ = 61/65); ^{13}C NMR: δ = 9.2 (3C, $^1J_{Sn–C}$ = 322/337), 13.6 (3C), 15.3 (2C), 20.1, 27.3 (3C, $^3J_{Sn–C}$ = 54/57), 29.1 (3C), 60.3 (2C), 96.9 ($^3J_{Sn–C}$ = 66/69), 137.6, 145.4; MS: organostannyl fragments: *m/z* (%) = 378 ($M^{\cdot+}$ − 56, 22), 331 (18), 275 (4), 235 (4), 177 (13), 165 (13); organic fragments: *m/z* (%) = 143 (100), 99 (30), 41 (6), 29 (13).

*5.3.4. (E)-(4R,5R)-2-(2-Tributylstannylethylidene)-4,5-dimethyl-1,3-dioxolane (**1eE**, 92% yield)*

^{1}H NMR: δ = 0.70–1.05 (m, 15H), 1.15–1.70 (m, 18H), 3.50–3.70 (m, 2H), 5.24 (dd, 1H, $^3J_{1H}$ = 5.9, $^4J_{1H}$ = 0.6, $^4J_{Sn–H}$ = 4.0), 5.97 (dd, 1H, $^3J_{1H}$ = 19.0, $^3J_{1H}$ = 5.9, $^3J_{Sn–H}$ = 58/60), 6.47 (dd, 1H, $^3J_{1H}$ = 19.0, $^4J_{1H}$ = 0.6, $^2J_{Sn–H}$ = 64/67); ^{13}C NMR: δ = 9.3 (3C, $^1J_{Sn–C}$ = 332/347), 13.5 (3C), 16.8, 17.0, 26.6 (3C, $^3J_{Sn–C}$ = 54/57), 28.9 (3C, $^2J_{Sn–C}$ = 21), 78.1, 79.7, 104.5 ($^3J_{Sn–C}$ = 72/76), 138.8, 144.2; ^{119}Sn NMR: δ = −48.6; IR: ν = 1465, 1457, 1376, 1146, 1115, 1079, 980 cm^{-1}; MS: organostannyl fragments: *m/z* (%) = 361 ($M^{\cdot+}$ − 57, 55), 305 (41), 249 (11), 233 (10), 177 (26), 121 (14); organic fragments: *m/z* (%) = 127 (100), 101 (10), 73 (14), 55 (47), 29 (9); elemental analysis Calc. (%) for $C_{19}H_{38}O_2Sn$ (416.19): C, 54.70; H, 9.18. Found: C, 54.79; H, 9.08%.

*5.3.5. (E)-(4R,6R)-2-(2-Tributylstannylethylidene)-4,6-dimethyl-1,3-dioxane (**1fE**, 82% yield)*

^{1}H NMR δ = 0.70–1.10 (m, 15H), 1.15–1.70 (m, 19H), 1.87 (ddd, 1H, $^3J_{1H}$ = 6.2, $^2J_{1H}$ = 11.7, $^3J_{1H}$ = 13.3), 4.01 (m, 1H), 4.15 (m, 1H), 5.19 (dd, 1H, $^3J_{1H}$ = 4.4, $^4J_{1H}$ = 1.1, $^4J_{Sn–H}$ = 6), 5.96 (dd, 1H, $^3J_{1H}$ = 19.2, $^3J_{1H}$ = 4.4, $^3J_{Sn–H}$ = 61/64), 6.40 (dd, 1H, $^3J_{1H}$ = 19.2, $^4J_{1H}$ = 1.1, $^2J_{Sn–H}$ = 67/70); ^{13}C NMR: δ = 9.4 (3C, $^1J_{Sn–C}$ = 331/347), 13.6 (3C), 17.2, 21.8, 27.3 (3C, $^3J_{Sn–C}$ = 57), 29.0 (3C, $^2J_{Sn–C}$ = 21), 36.9, 67.6, 68.2, 94.8 ($^3J_{Sn–C}$ = 73), 133.2 ($^1J_{Sn–C}$ = 345/361), 144.5 ($^2J_{Sn–C}$ = 21); MS: organostannyl fragments: *m/z* (%) = 375 ($M^{\cdot+}$ − 57, 60), 319 (21), 289 (21), 233 (39), 177 (45), 121 (15); organic fragments: *m/z* (%) = 141 (100), 99 (4), 97 (4), 69 (4), 32 (5), 28 (33).

*5.3.6. (Z)-(4R,6R)-2-(2-Tributylstannylethylidene)-4,6-dimethyl-1,3-dioxane (**1fZ**, 80% yield)*

^{1}H NMR: δ = 0.70–1.10 (m, 15H), 1.15–1.70 (m, 19H), 1.87 (ddd, 1H, $^3J_{1H}$ = 8, $^3J_{1H}$ = 12.3, $^2J_{1H}$ = 13.3), 4.0 (m, 1H, $^3J_{1H}$ = 2.7, $^3J_{3H}$ = 6.2, $^3J_{1H}$ = 12.3), 4.35 (m, 1H, $^3J_{3H}$ = 6.7, $^3J_{1H}$ = 8), 5.15 (dd, 1H, $^3J_{1H}$ = 4.6, $^4J_{1H}$ = 1.1), 6.19 (dd, 1H, $^3J_{1H}$ = 13.2, $^4J_{1H}$ = 1.1), 6.50 (dd, 1H, $^3J_{1H}$ = 13.2, $^3J_{1H}$ = 4.6); ^{13}C NMR: δ = 11.5 (3C), 14.1 (3C), 17,5, 22.3, 27.8 (3C, $^3J_{Sn–C}$ = 55), 29.5 (3C), 37.2, 68.0, 68.5, 94.7, 134.6, 144.4; IR: ν = 2956, 2922, 2872, 2854, 1458, 1375, 1150, 1018, 965, 697 cm^{-1}; MS: organostannyl fragments: *m/z* (%) = 431 ($M^{\cdot+}$ − H, 1), 375 (100), 289 (71), 233 (55), 175 (81), 121 (14); organic fragments: *m/z* (%) = 141 (16), 69 (58).

5.4. Reaction of vinyltin acetals with organocopper reagents in the presence of boron trifluoride: typical experimental procedure

In a flame dried Schlenk reactor, a solution of organolithium or organomagnesium reagent (2.2 mmol) was added dropwise at −30 °C to a stirred copper cyanide suspension (1.19 g, 2.2 mmol) in anhydrous ether (previously degassed at −50 °C) until an homogeneous solution was obtained (about 30 min). The latter was cooled at −78 °C before addition of boron trifluoride etherate (0.26 mL, 2.2 mmol), further stirring for 30 min and subsequent addition of vinyltin acetal (0.7 mmol in 2 mL ether). The reaction mixture was stirred

over 3 h and allowed to warm up to −50 °C for hydrolysis (aqueous $NaHCO_3$ solution). After ether extraction (3 × 20 mL) and usual treatments, the crude products were chromatographed on silica gel using hexane–triethylamine (98/2) as eluent.

When reactions were performed in order to examine the influence of the order of addition of the reagents, two separate solutions were prepared in two Schlenk tubes and one was cannulated in the other at low temperature as mentioned in the Table 2.

5.5. Characterization of α-substituted γ-alkoxyallylstannanes

5.5.1. 3-Tributylstannyl-1-ethoxybut-1-ene **2a**

MS: organostannyl fragments: *m/z* (%) = 390 ($M^{\cdot+}$, 1), 361 (2), 333 (13), 291 (29), 235 (69), 179 (100), 121 (30); organic fragments: *m/z* (%) = 99 (56), 71 (64), 43 (14), 41 (12), 29 (10).

Isomer **2a*Z***: ^{1}H NMR: δ = 0.70–1.60 (m, 33H), 2.42 (ddq, 1H, $^3J_{1H}$ = 10.7, $^3J_{3H}$ = 7.6, $^4J_{1H}$ = 1.1), 3.71 (q, 2H, $^3J_{3H}$ = 7.0), 4.38 (dd, 1H, $^3J_{1H}$ = 10.7, $^3J_{1H}$ = 6.1, $^3J_{Sn–H}$ = 20.2), 5.72 (dd, 1H, $^3J_{1H}$ = 6.1, $^4J_{1H}$ = 1.1, $^4J_{Sn–H}$ = 21.5); ^{13}C NMR: δ = 8.5 (3C, $^1J_{Sn–C}$ = 254/297), 13.4 (3C), 15.0, 16.3, 18.4 ($^2J_{Sn–C}$ = 19.5), 27.3 (3C, $^3J_{Sn–C}$ = 53), 29.1 (3C, $^2J_{Sn–C}$ = 21), 67.0, 113.3 ($^2J_{Sn–C}$ = 41), 139.4 ($^3J_{Sn–C}$ = 43/45); ^{119}Sn NMR: δ = −16.5.

Isomer **2a*E***: ^{1}H NMR: δ = 0.70–1.60 (m, 33H), 1.97 (ddq, 1H, $^3J_{3H}$ = $^3J_{1H}$ = 8.8, $^4J_{1H}$ = 1.3), 3.71 (q, 2H, $^3J_{3H}$ = 7.2), 5.06 (dd, 1H, $^3J_{1H}$ = 12.5, $^3J_{1H}$ = 8.8, $^3J_{Sn–H}$ = 22.2), 6.02 (dd, 1H, $^3J_{1H}$ = 12.5, $^4J_{1H}$ = 1.3, $^4J_{Sn–H}$ = 19); ^{13}C NMR: δ = 8.2 (3C, $^1J_{Sn–C}$ = 268/299), 13.4 (3C), 14.6, 16.2, 18.6, 27.2 (3C, $^3J_{Sn–C}$ = 51), 28.9 (3C, $^2J_{Sn–C}$ = 20), 64.6, 111.6 ($^2J_{Sn–C}$ = 36), 141.3 ($^3J_{Sn–C}$ = 49); ^{119}Sn NMR: = −18.5.

5.5.2. 3-Tributylstannyl-1-ethoxypent-1-ene **2b**

MS: organostannyl fragments: *m/z* (%) = 375 ($M^{\cdot+}$ − 29, 1), 347 (5), 291 (12), 235 (40), 179 (62), 121 (15); organic fragments: *m/z* (%) = 113 (100), 85 (56), 67 (30), 57 (42), 43 (34); IR: *v* = 2956, 2924, 2872, 1649, 1465, 1378, 1111, 668; HRMS: $M^{\cdot+}$ = 404.2071 / 402.2076 / 400.2073 for ^{120}Sn, ^{118}Sn and ^{116}Sn; elemental analysis Calc. (%) for $C_{19}H_{40}OSn$ (403.23): C, 56.59; H, 10.00. Found: C, 56.41; H, 9.74%.

Isomer **2b*Z***: ^{1}H NMR: δ = 0.60–1.70 (m, 35H), 2.32 (m, 1H, $^3J_{1H}$ = 11.0, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 8.8, $^4J_{1H}$ = 1.0), 3.65 (q, 2H, $^3J_{3H}$ = 7.1), 4.30 (dd, 1H, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 11.0, $^3J_{Sn–H}$ = 20.5), 5.71 (dd, 1H, $^3J_{1H}$ = 6.1, $^4J_{1H}$ = 1.0, $^4J_{Sn–H}$ = 21); ^{13}C NMR: δ = 8.7 (3C, $^1J_{Sn–C}$ = 283/296), 13.4 (3C), 14.9 ($^3J_{Sn–C}$ = 46), 15.0, 25.4 ($^1J_{Sn–C}$ = 295/311), 26.2 ($^2J_{Sn–C}$ = 16), 27.1 (3C, $^3J_{Sn–C}$ = 47), 29.2 (3C, $^2J_{Sn–C}$ = 20), 67.0, 111.2 ($^2J_{Sn–C}$ = 41), 140.3 ($^3J_{Sn–C}$ = 45).

Isomer **2b*E***: meaningful signals: ^{1}H NMR: δ = 4.88 (m, 1H, $^3J_{1H} \sim {}^3J_{1H} \sim 12.5$), 6.05 (d, 1H, $^3J_{1H}$ = 12.5); ^{13}C NMR: δ = 64.9, 109.7, 142.5.

5.5.3. 3-Tributylstannyl-1-ethoxyhept-1-ene **2c**

MS: organostannyl fragments: *m/z* (%) = 432 ($M^{\cdot+}$, 1), 403 (7), 375 (21), 291 (44), 235 (100), 179 (99), 121 (36); organic fragments: *m/z* (%) = 141 (51), 95 (20), 85 (44), 57 (91), 41 (19), 29 (30); IR: *v* = 2957, 2930, 2870, 2860, 1645, 1378, 1113; elemental analysis Calc. (%) for $C_{21}H_{44}OSn$ (431.28): C, 58.48; H, 10.28. Found: C, 58.22; H, 10.29%.

Isomer **2c*Z***: ^{1}H NMR: δ = 0.70–1.05 (m, 18H), 1.10–1.80 (m, 21H), 2.44 (m, 1H), 3.72 (q, 2H, $^3J_{3H}$ = 6.9), 4.35 (dd, 1H, $^3J_{1H}$ = 6.2, $^3J_{1H}$ = 10.8, $^3J_{Sn–H}$ = 20.2), 5.77 (dd, 1H, $^3J_{1H}$ = 6.2, $^4J_{1H}$ = 1.0, $^4J_{Sn–H}$ = 20.1); ^{13}C NMR: δ = 8.9 (3C, $^1J_{Sn–C}$ = 283/296), 13.8 (3C), 14.1, 15.3, 22.6, 23.4 ($^1J_{Sn–C}$ = 296/310), 27.6 (3C, $^3J_{Sn–C}$ = 52/53), 29.3 (3C, $^2J_{Sn–C}$ = 19), 32.8, 33.2, 67.2, 111.8 ($^2J_{Sn–C}$ = 42), 140.4 ($^3J_{Sn–C}$ = 45).

Isomer **2c*E***: ^{1}H NMR: δ = 0.70–1.05 (m, 18H), 1.10–1.80 (m, 21H), 1.93 (m, 1H), 3.65 (q, 2H, $^3J_{3H}$ = 7.0), 4.88 (dd, 1H, $^3J_{1H}$ = 12.3, $^3J_{1H}$ = 10.6, $^3J_{Sn–H}$ = 22.0), 6.04 (d, 1H, $^3J_{1H}$ = 12.3, $^4J_{Sn–H}$ = 19.5); ^{13}C NMR: δ = 8.8 (3C, $^1J_{Sn–C}$ = 285/298), 13.7 (3C), 14.0, 15.9, 22.5, 25.7, 27.4 (3C, $^3J_{Sn–C}$ = 26), 29.2 (3C, $^2J_{Sn–C}$ = 16), 32.2 ($^3J_{Sn–C}$ = 40), 33.3 ($^2J_{Sn–C}$ = 13), 64.9, 110.0 ($^2J_{Sn–C}$ = 37), 142.2 ($^3J_{Sn–C}$ = 52).

5.5.4. 3-Tributylstannyl-1-ethoxy-4-methylpent-1-ene **2d**

MS: organostannyl fragments: *m/z* (%) = 418 ($M^{\cdot+}$, 1), 389 (7), 361 (49), 291 (46), 235 (77), 179 (74); organic fragments: *m/z* (%) = 127 (100), 81 (49), 43 (80); IR: *v* = 2956, 2925, 2872, 2360, 1648, 1464, 1380, 1110, 668; HRMS: $M^{\cdot+}$ = 418.2248 /416.2249 /414.2259 for ^{120}Sn, ^{118}Sn and ^{116}Sn; elemental analysis Calc. (%) for $C_{20}H_{42}OSn$ (417.26): C, 57.57; H, 10.15. Found: C, 57.52; H, 10.13%.

Isomer **2d*Z***: ^{1}H NMR: δ = 0.60–1.70 (m, 36H), 1.80 (m, 1H), 2.35 (ddd, 1H, $^3J_{1H}$ = 11.4, $^3J_{1H}$ = 7.5, $^4J_{1H}$ = 1.0), 3.65 (q, 2H, $^3J_{3H}$ = 7.3), 4.33 (dd, 1H, $^3J_{1H}$ = 6.5, $^3J_{1H}$ = 11.4, $^3J_{Sn–H}$ = 20.5), 5.72 (dd, 1H, $^3J_{1H}$ = 6.5, $^4J_{1H}$ = 1.0, $^4J_{Sn–H}$ = 21.1); ^{13}C NMR: δ = 9.8 (3C, $^1J_{Sn–C}$ = 283/296), 13.7 (3C), 15.3, 23.0 ($^3J_{Sn–C}$ = 34), 24.0 ($^3J_{Sn–C}$ = 31), 27.6 (3C, $^3J_{Sn–C}$ = 56), 29.3 (3C, $^2J_{Sn–C}$ = 20), 31.2, 33.4 ($^1J_{Sn–C}$ = 300/315), 67.2, 109.5 ($^2J_{Sn–C}$ = 40), 140.8 ($^3J_{Sn–C}$ = 47).

Isomer **2d*E***: meaningful signals: ^{1}H NMR: δ = 4.88 (m, 1H, $^3J_{1H} \sim {}^3J_{1H} \sim 12.0$), 6.05 (d, 1H, $^3J_{1H}$ = 12.0).

5.5.5. 3-Tributylstannyl-1-ethoxy-4,4-dimethylpent-1-ene **2e**

MS: organostannyl fragments: *m/z* (%) = 432 ($M^{\cdot+}$, 3), 403 (15), 375 (72), 291 (47), 235 (58), 177 (56); organic fragments: *m/z* (%) = 141 (100), 95 (76), 43 (61); IR: *v* = 2960, 2953, 2935, 2924, 1646, 1379, 1111, 663;

HRMS: $M^{\cdot+}$ = 432.2473 /430.2393 /428.2460 for ^{120}Sn, ^{118}Sn and ^{116}Sn; elemental analysis Calc. (%) for $C_{21}H_{44}OSn$ (431.28): C, 58.48; H, 10.28. Found: C, 58.65; H, 10.15%.

Isomer **2e*Z***: ^{1}H NMR: δ = 0.60–1.60 (m, 39H), 2.49 (dd, 1H, $^3J_{1H}$ = 12.0, $^4J_{1H}$ = 1.0), 3.65 (q, 2H, $^3J_{3H}$ = 7.0), 4.39 (dd, 1H, $^3J_{1H}$ = 6.0, $^3J_{1H}$ = 12.0, $^3J_{Sn-H}$ = 21), 5.74 (dd, 1H, $^3J_{1H}$ = 6.0, $^4J_{1H}$ = 1.0, $^4J_{Sn-H}$ = 21.1); ^{13}C NMR: δ = 10.6 (3C, $^1J_{Sn-C}$ = 281/290), 13.6 (3C), 15.3, 27.6 (3C, $^3J_{Sn-C}$ = 58), 29.6 (3C, $^2J_{Sn-C}$ = 20), 30.7 (3C, $^3J_{Sn-C}$ = 26), 33.7, 39.8 ($^1J_{Sn-C}$ = 291/310), 67.1, 108.4 ($^2J_{Sn-C}$ = 39), 141.1 ($^3J_{Sn-C}$ = 48).

Isomer **2e*E***: meaningful signals: ^{1}H NMR: δ = 3.45 (q, 2H, $^3J_{3H}$ = 7.0), 4.88 (dd, 1H, $^3J_{1H}$ = 10.6, $^3J_{1H}$ = 12.3, $^3J_{Sn-H}$ = 22), 6.05 (d, 1H, $^3J_{1H}$ = 12.3, $^4J_{Sn-H}$ = 19).

5.5.6. (*Z*)-3-Tributylstannyl-1-ethoxy-4-trimethylsilylbut-1-ene **2f*Z***

^{1}H NMR (C_6D_6, 300 K): δ = 0.13 (s, 9H), 0.80–1.80 (m, 32H), 2.86 (tdd, 1H, $^3J_{2H}$ = 7.2, $^3J_{1H}$ = 11.1, $^4J_{1H}$ = 1.0), 3.45 (q, 2H, $^3J_{3H}$ = 7.1), 4.43 (dd, 1H, $^3J_{1H}$ = 6.0, $^3J_{1H}$ = 11.1, $^3J_{Sn-H}$ = 20.2), 5.53 (dd, 1H, $^3J_{1H}$ = 6.0, $^4J_{1H}$ = 1.0, $^4J_{Sn-H}$ = 22.4); ^{13}C NMR (C_6D_6, 300 K): δ = −0.7 (3C), 9.3 (3C, $^1J_{Sn-C}$ = 276/289), 13.9 (3C), 15.5, 17.7 ($^1J_{Sn-C}$ = 302/317), 21.1 ($^2J_{Sn-C}$ = 28), 28.0 (3C, $^3J_{Sn-C}$ = 51), 29.8 (3C, $^2J_{Sn-C}$ = 19), 67.3, 114.0 ($^2J_{Sn-C}$ = 42), 140.0 ($^3J_{Sn-C}$ = 48); MS: organostannyl fragments: *m/z* (%) = 433 ($M^{\cdot+}$ − 29, 11), 291 (26), 235 (63), 179 (66), 177 (18), 121 (23); organic fragments: *m/z* (%) = 171 (95), 143 (100), 73 (81), 45 (6); IR: *v* = 1640, 1460, 1450, 1375, 1240, 1105, 855, 835; HRMS: $M^{\cdot+}$ (very weak) = 462.2350 for ^{120}Sn; meaningful ions: 171.1207 $(C_9H_{19}OSi)^+$ and 291.1163 $(C_{12}H_{27}Sn)^+$ for ^{120}Sn.

5.5.7. (*Z*)-3-Tributylstannyl-1-ethoxy-4-(dimethylphenylsilyl)but-1-ene **2g*Z***

^{1}H NMR: δ = 0.23 (s, 6H), 0.77 (d, 2H, $^3J_{1H}$ = 7.9), 0.70–1.00 (m, 12H), 1.10–1.70 (m, 18H), 2.59 (m, 1H), 3.70 (q, 2H, $^3J_{3H}$ = 7.0), 4.30 (dd, 1H, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 11.0, $^3J_{Sn-H}$ = 20), 5.63 (dd, 1H, $^3J_{1H}$ = 6.1, $^4J_{1H}$ = 0.75, $^4J_{Sn-H}$ = 22.4), 7.28–7.38 and 7.40–7.55 (2m, 5H) ; ^{13}C NMR: δ = −1.2 (2C), 8.8 (3C, $^1J_{Sn-C}$ = 277/290), 13.6 (3C), 15.4, 16.9, 19.6 ($^2J_{Sn-C}$ = 27), 27.5 (3C, $^3J_{Sn-C}$ = 50/53), 29.2 (3C, $^2J_{Sn-C}$ = 19.5), 67.0, 113.5 ($^2J_{Sn-C}$ = 43.5), 127.4 (2C), 128.7 (2C), 133.2, 139.4 ($^3J_{Sn-C}$ = 46/48), 140.5; ^{119}Sn NMR: δ = −15.8.

5.5.8. (*Z*)-1-Benzyloxy-3-tributylstannylbut-1-ene **2h*Z***

^{1}H NMR: δ = 0.7–0.9 (m, 6H), 0.85 (t, 9H, $^3J_{2H}$ = 7.3), 1.1–1.7 (m, 12H), 1.29 (d, 3H, $^3J_{1H}$ = 7.6), 2.52 (ddq, 1H, $^3J_{3H}$ = 7.6, $^3J_{1H}$ = 10.8, $^4J_{1H}$ = 0.9, $^2J_{Sn-H}$ = 60), 4.45 (dd, 1H, $^3J_{1H}$ = 10.8, $^3J_{1H}$ = 6.0, $^3J_{Sn-H}$ = 20), 4.7 and 4.77 (AB syst., 2H, $^2J_{1H}$ = 12.7), 5.85 (dd, 1H, $^3J_{1H}$ = 6.0, $^4J_{1H}$ = 0.9, $^4J_{Sn-H}$ = 20), 7.2-7.4 (m, 5H); ^{13}C NMR: δ = 8.7 (3C, $^1J_{Sn-C}$ = 298/285), 13.7 (3C), 16.6, 18.7, 27.5 (3C, $^3J_{Sn-C}$ = 54), 29.3 (3C, $^2J_{Sn-C}$ = 20), 73.5, 114.6 ($^2J_{Sn-H}$ = 41), 127.4-128.3 (5C), 138.0, 139.4 ($^3J_{Sn-C}$ = 44); ^{119}Sn NMR: δ = −15,7; IR: *v* = 3029, 2924, 2956, 2870, 1648, 1457, 1420, 1050-1125, 694-730; MS: organostannyl fragments: *m/z* (%) = 395 (3, $M^{\cdot+}$ − 57), 361 (4, $M^{\cdot+}$ − 91), 291 (19), 235 (32), 179 (37), 121 (10); organic fragments: *m/z* (%) = 91 (100), 65 (8).

5.5.9. (*Z*)-1-Benzyloxy-3-tributylstannyl-4,4-dimethylpent-1-ene **2i*Z***

^{1}H NMR: δ = 0.7–0.95 (m, 15H), 0.95 (9H), 1.2–1.7 (m, 12H), 2.65 (dd, 1H, $^3J_{1H}$ = 12.4, $^4J_{1H}$ = 0.6, $^2J_{Sn-H}$ = 64), 4.52 (dd, 1H, $^3J_{1H}$ = 12.4, $^3J_{1H}$ = 6.2, $^3J_{Sn-H}$ = 22/27), 4.71 and 4.79 (AB syst., 2H, $^2J_{1H}$ = 12.5), 5.92 (dd, 1H, $^3J_{1H}$ = 6.2, $^4J_{1H}$ = 0.6, $^4J_{Sn-H}$ = 19), 7.20–7.40 (m, 5H); ^{13}C NMR: δ = 10.7 (3C, $^1J_{Sn-C}$ = 283/295), 13.7 (3C), 27.6 (3C, $^3J_{Sn-C}$ = 57), 29.3 (3C, $^2J_{Sn-C}$ = 13), 30.6 (3C, $^3J_{Sn-C}$ = 26), 33.8 ($^2J_{Sn-C}$ = 13), 39.9 ($^1J_{Sn-C}$ = 297/312), 73.4, 109.5 ($^2J_{Sn-C}$ = 38), 127.3–128.3 (5C), 138.1, 141.1 ($^3J_{Sn-C}$ = 48); ^{119}Sn NMR: δ = −29,0; IR: *v* = 3029, 2956, 2927, 2871, 1646, 1455, 1390, 1119, 1096, 732, 695; MS: organostannyl fragments: *m/z* (%) = 437 (3, M − 57), 403 (7, M − 91), 291(28), 235 (41), 179 (34), 121 (7); organic fragments: *m/z* (%) = 91(100); elemental analysis Calc. (%) for $C_{26}H_{46}OSn$ (493.35): C, 63.30; H, 9.40. Found: C, 63.23; H, 9.58%.

5.5.10. 3-(3-Tributylstannylpent-1-en-1-yloxy)propan-1-ol **2j**

MS: organostannyl fragments: *m/z* (%) = 377 ($M^{\cdot+}$ − 57, 6), 291 (32), 235 (83), 179 (100), 121 (38); organic fragments: *m/z* (%) = 143 (35), 85 (73), 69 (16), 67 (20), 59 (10), 57 (36), 55 (11), 43 (36), 41 (43), 31 (42), 29 (32); IR: *v* = 3350, 1650, 1638, 1468, 1418, 1075, 965, 740.

Isomer **2j*Z***: ^{1}H NMR: δ = 0.70–1.05 (m, 12H), 1.10–1.80 (m, 20H), 1.70–2.0 (m, 2H), 2.18–2.48 (m, 1H), 3.70–3.90 (m, 4H), 4.39 (dd, 1H, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 11.1, $^3J_{Sn-H}$ = 19.9), 5.8 (dd, 1H, $^3J_{1H}$ = 6.1, $^4J_{1H}$ = 0.7, $^4J_{Sn-H}$ = 20.8); ^{13}C NMR: δ = 9.0 (3C, $^1J_{Sn-C}$ = 284/297), 13.7 (3C), 25.9, 26.5, 27.6 (3C, $^3J_{Sn-C}$ = 53), 29.3 (3C, $^2J_{Sn-C}$ = 20), 32.1, 60.8, 69.9, 112.2 ($^2J_{Sn-C}$ = 40), 140.7 ($^3J_{Sn-C}$ = 51).

Isomer **2j*E***: ^{1}H NMR: meaningful signals: δ = 4.92 (dd, 1H, $^3J_{1H}$ = 12.6, $^3J_{1H}$ = 10.1, $^3J_{Sn-H}$ = 23.1), 6.08 (d, 1H, $^3J_{1H}$ = 12.6, $^4J_{Sn-H}$ = 19.3); ^{13}C NMR: δ = 8.9 (3C, $^1J_{Sn-C}$ = 286/300), 13.7 (3C), 25.9, 28.1, 27.6 (3C,

$^3J_{Sn-C}$ = 53), 29.3 (3C, $^2J_{Sn-C}$ = 20), 32.5, 60.9, 67.7, 110.3 ($^2J_{Sn-C}$ = 40), 142.4 ($^3J_{Sn-C}$ = 51).

5.5.11. 3-(3-Tributylstannyl-4-methylpent-1-en-1-yloxy)propan-1-ol ***2k***

MS: organostannyl fragments: *m/z* (%) = 348 ($M^{\cdot+}$, 2), 389 (14), 335 (1), 291 (36), 235 (79), 179 (100), 121 (47); organic fragments: *m/z* (%) = 157 (25), 99 (37), 83 (17), 81 (97), 59 (10), 57 (25), 55 (20), 43 (98), 41 (37), 31 (49), 29 (29), 27 (12); IR: *v* = 3340, 1648, 1632, 1462, 1418, 1373, 1362, 1105, 1070, 960, 925, 875, 865.

Isomer **2k*Z***: ^{1}H NMR: δ = 0.60–1.00 (m, 15H), 1.10–1.60 (m, 19H), 1.70-2.00 (m, 2H), 2.29 (ddd, 1H, $^3J_{1H}$ = 12.3, $^3J_{1H}$ = 6.5, $^4J_{1H}$ = 1.0), 3.60–3.85 (m, 4H), 4.35 (dd, 1H, $^3J_{1H}$ = 6.5, $^3J_{1H}$ = 12.3, $^3J_{Sn-H}$ = 20.2), 5.74 (dd, 1H, $^3J_{1H}$ = 6.5, $^4J_{1H}$ = 1.0, $^4J_{Sn-H}$ = 20.5); ^{13}C NMR: δ = 9.8 (3C, $^1J_{Sn-C}$ = 285/300), 13.7 (3C), 23.0, 24.0, 27.6 (3C, $^3J_{Sn-C}$ = 58), 29.4 (3C, $^2J_{Sn-C}$ = 20), 31.7, 32.5, 33.6 ($^1J_{Sn-C}$ = 295/309), 60.7, 69.9, 110.1 ($^2J_{Sn-C}$ = 43), 140.7 ($^3J_{Sn-C}$ = 51).

Isomer **2k*E***: ^{1}H NMR: meaningful signals: δ = 4.92 (dd, 1H, $^3J_{1H}$ = 12.3, $^3J_{1H}$ = 10.7, $^3J_{Sn-H}$ = 24.0), 6.08 (d, 1H, $^3J_{1H}$ = 12.3, $^4J_{Sn-H}$ = 17.3); ^{13}C NMR: δ = 9.7 (3C, $^1J_{Sn-C}$ = 285/299), 13.7 (3C), 22.7, 23.8, 27.6 (3C, $^3J_{Sn-C}$ = 54), 29.4 (3C, $^2J_{Sn-C}$ = 20), 31.3, 32.6, 36.0 ($^1J_{Sn-C}$ = 308/323), 60.7, 67.6, 108.1 ($^2J_{Sn-C}$ = 34), 143.0 ($^3J_{Sn-C}$ = 55).

5.5.12. (Z)-3-(3-Tributylstannyl-4,4-dimethylpent-1-en-1-yloxy)propan-1-ol ***2lZ***

^{1}H NMR: δ = 0.60-1.00 (m, 15H), 0.89 (s, 9H), 1.10–1.60 (m, 12H), 1.79 (qt, 2H, $^3J_{4H}$ = 5.6), 2.42 (dd, 1H, $^3J_{1H}$ = 12.3, $^4J_{1H}$ = 1.0), 3.60–3.85 (m, 4H), 4.42 (dd, 1H, $^3J_{1H}$ = 6.4, $^3J_{1H}$ = 12.3, $^3J_{Sn-H}$ = 22.8), 5.74 (dd, 1H, $^3J_{1H}$ = 6.4, $^4J_{1H}$ = 1.0, $^4J_{Sn-H}$ = 19.2); ^{13}C NMR: δ = 10.2 (3C, $^1J_{Sn-C}$ = 288/301), 13.3 (3C), 27.2 (3C, $^3J_{Sn-C}$ = 61), 28.9 (3C, $^2J_{Sn-C}$ = 20), 30.2 (3C, $^3J_{Sn-C}$ = 29), 32.0, 33.4, 39.5, 60.5, 70.0, 108.8 ($^2J_{Sn-C}$ = 40), 140,8; IR: *v* = 3333, 2956, 2930, 2872, 1646, 1465, 1375, 1125, 1097, 798, 668; MS: organostannyl fragments: *m/z* (%) = 461 ($M^{\cdot+}$, 4), 403 (40), 345 (10), 291 (72), 235 (98), 177 (89), 121 (20); organic fragments: *m/z* (%) = 171 (100), 113 (48), 95(93).

5.5.13. 3-Tributylstannyl-1-ethoxy-3-(trimethylsilylmethyl)but-1-ene ***2m***

(chromatographed on C-18 silica gel phase [49] using MeCN/CH_2Cl_2 80/20 as eluent).

Isomer **2m*Z***: ^{1}H NMR: δ = −0.05–0.10 (m, 11H), 0.70–1.70 (m, 33H), 3.65 (q, 2H, $^3J_{3H}$ = 7.2), 4.31 (d, 1H, $^3J_{1H}$ = 6.8, $^3J_{Sn-H}$ = 31), 5.58 (d, 1H, $^3J_{1H}$ = 6.8, $^4J_{Sn-H}$ = 24).

Isomer **2m*E***: ^{1}H NMR: δ = −0.05–0.15 (m, 11H), 0.75–1.75 (m, 33H), 3.68 (q, 2H, $^3J_{3H}$ = 7.0), 5.16 (d, 1H, $^3J_{1H}$ = 12.5, $^3J_{Sn-H}$ = 20/23), 5.82 (d, 1H, $^3J_{1H}$ = 12.5, $^4J_{Sn-H}$ = 21).

5.5.14. (2R,3R)-3-(3-Tributylstannylhept-1-en-1-yloxy)butan-2-ol ***2n***

MS: organostannyl fragments: *m/z* (%) = 419 ($M^{\cdot+}$ − 57, 5), 403 ($M^{\cdot+}$ − 73, 8), 291 (33), 269 (22), 251 (57), 235 (87), 213 (13), 179 (100), 121 (34); organic fragments: *m/z* (%) = 185 (12), 113 (52), 95 (41), 83 (16), 73 (37), 69 (12), 57 (81), 55 (59), 45 (20), 43 (16), 41 (35), 29 (23), 27 (16); IR: *v* = 3456, 1651, 1465, 1377, 1289, 1265, 1106, 961, 927 876.

Isomer **2n*Z***: Major diastereomer: ^{1}H NMR: δ = 0.75–0.95 and 1.15–1.65 (2m, 42H), 1.80–2.10 (m, 1H), 2.41 (bd, 1H, $^3J_{1H}$ = 3.1), 3.35–3.50 (m, 1H), 3.55–3.75 (m, 1H), 4.36 (dd, 1H, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 11.2, $^3J_{Sn-H}$ = 20), 5.84 (d, 1H, $^3J_{1H}$ = 6.1, $^4J_{Sn-H}$ = 20); ^{13}C NMR: δ = 8.7 (3C, $^1J_{Sn-C}$ = 284/297), 13.3, 13.4 (3C), 18.1, 22.2, 27.3 (3C, $^3J_{Sn-C}$ = 52), 29.0 (3C, $^2J_{Sn-C}$ = 20), 32.0, 32.6, 70.6, 82.1, 111.9 ($^2J_{Sn-C}$ = 40), 139.4 ($^3J_{Sn-C}$ = 46); ^{119}Sn NMR: δ = −19.3.

Isomer **2n*E***: Major diastereomer: ^{1}H NMR: meaningful signals: δ = 5.04 (dd, 1H, $^3J_{1H}$ = 10.8, $^3J_{1H}$ = 12.0), 5.91 (d, 1H, $^3J_{1H}$ = 12.0); ^{13}C NMR: δ = 8.5 (3C, $^1J_{Sn-C}$ = 285/298), 13.3, 13.4 (3C), 18.0, 22.1, 27.3 (3C, $^3J_{Sn-C}$ = 52), 28.9 (3C, $^2J_{Sn-C}$ = 20), 32.0, 32.7, 70.9, 80.9, 113.1 ($^2J_{Sn-C}$ = 37), 140.7 ($^3J_{Sn-C}$ = 54); ^{119}Sn NMR: δ = −20.9.

5.5.15. (2R,4R)-4-(3-Tributylstannylbut-1-en-1-yloxy)pentan-2-ol ***2o***

Isomer **2o*E***: ^{1}H NMR: δ = 0.70–1.70 (m, 38H), 1.88–2.27 (m, 1H), 2.20 (bd, 1H, $^3J_{1H}$ = 4.6), 3.85–4.20 (m, 2H), 5.19 (dd, 1H, $^3J_{1H}$ = 8.4, $^3J_{1H}$ = 12.2), 5.8 (dd, 1H, $^3J_{1H}$ = 12.2, $^4J_{1H}$ = 1.4); ^{13}C NMR: δ = 8.6 (3C, $^1J_{Sn-C}$ = 286/300), 13.7 (3C), 17.9 ($^2J_{Sn-C}$ = 16), 18.8 ($^1J_{Sn-C}$ = 297/311), 20.0, 23.7, 27.5 (3C, $^3J_{Sn-C}$ = 53), 29.3 (3C, $^2J_{Sn-C}$ = 20), 44.9, 64.7, 74.1, 114.7 ($^2J_{Sn-C}$ = 37), 140.2 ($^3J_{Sn-C}$ = 50).

Isomer **2o*Z***: Major diastereomer: ^{1}H NMR: meaningful signals: δ = 4.40 (dd, 1H, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 11.0), 5.73 (dd, 1H, $^3J_{1H}$ = 6.1, $^4J_{1H}$ = 1.1); ^{13}C NMR: = 8.7 (3C), 13.7 (3C), 16.7, 18.8, 20.5, 23.9, 27.5 (3C, $^3J_{Sn-C}$ = 53), 29.3 (3C, $^2J_{Sn-C}$ = 20), 45.4, 64.6, 74.8, 114.4, 198.5.

Minor diastereomer: meaningful signals: ^{1}H NMR: δ = 4.51 (dd, 1H, $^3J_{1H}$ = 6.2, $^3J_{1H}$ = 9.2), 5.78 (dd, 1H, $^3J_{1H}$ = 6.2, $^4J_{1H}$ = 1.1).

5.5.16. (2R,4R)-4-(3-Tributylstannylhept-1-en-1-yloxy)pentan-2-ol ***2p***

MS: organostannyl fragments: *m/z* (%) = 490 ($M^{\cdot+}$, <1), 433 (8), 403 (23), 321 (51), 291 (55), 235 (99), 179 (99), 121 (41); organic fragments: *m/z* (%) = 113 (84), 95 (40), 69 (59), 57 (100), 55 (17), 45 (80), 43 (27), 41

(33), 29 (20); IR: ν = 3380, 1646, 1465, 1460, 1376, 1155, 1115, 1080, 960; elemental analysis Calc. (%) for $C_{24}H_{50}O_2Sn$ (489.36): C, 58.90; H, 10.30. Found: C, 58.88; H, 10.55%. $[\alpha]_D$ = +117.5 (c = 1.02 in $CHCl_3$).

Isomer **2p*Z***: Major diastereomer: ^{1}H NMR: δ = 0.65–1.00 (m, 18H), 1.10–1.75 (m, 26H), 2.14 (bd, 1H, $^3J_{1H}$ = 4.3), 2.41 (m, 1H, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 9.2, $^3J_{1H}$ = 11.4, $^4J_{1H}$ = 0.7), 3.85-4.15 (m, 2H), 4.40 (dd, 1H, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 11.4, $^3J_{Sn-H}$ = 19.7), 5.8 (dd, 1H, $^3J_{1H}$ = 6.1, $^4J_{1H}$ = 0.7, $^4J_{Sn-H}$ = 18.6); ^{13}C NMR: δ = 8.9 (3C, $^1J_{Sn-C}$ = 284/297), 13.8 (3C), 14.1, 20.4, 22.4, 23.3 ($^1J_{Sn-C}$ = 296/309), 23.8, 27.6 (3C, $^3J_{Sn-C}$ = 53), 29.1 (3C, $^2J_{Sn-C}$ = 20), 32.7, 33.0 ($^2J_{Sn-C}$ = 15.6), 45.2, 64.6, 74.8, 112.9 ($^2J_{Sn-C}$ = 41), 139.3 ($^3J_{Sn-C}$ = 46); ^{119}Sn NMR: δ = −20.7.

Minor diastereomer: meaningful signals: ^{1}H NMR: δ = 4.38 (dd, 1H, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 11.1), 5.85 (d, 1H, $^3J_{1H}$ = 6.1).

Isomer **2p*E***: meaningful signals: ^{1}H NMR: δ = 5.05 (dd, 1H, $^3J_{1H}$ = 12.1, $^3J_{1H}$ = 10.7), 5.93 (d, 1H, $^3J_{1H}$ = 12.1).

5.5.17. (2R,4R)-4-(3-Tributylstannylprop-1-en-1-yloxy)pentan-2-ol ***2qZ***

^{1}H NMR: δ = 0.65–1.05 and 1.10–1.75 (2m, 35H), 1.65 (m, 2H), 2.20 (bd, 1H, $^3J_{1H}$ = 4.2), 3.85–4.20 (m, 2H), 4.52 (td, 1H, $^3J_{1H}$ = 6.1, $^3J_{2H}$ = 9.1), 5.82 (td, 1H, $^3J_{1H}$ = 6.1, $^4J_{2H}$ = 1.0, $^4J_{Sn-H}$ = 20); ^{13}C NMR: δ = 6.0, 9.3 (3C, $^1J_{Sn-C}$ = 298/312), 13.7 (3C), 20.6, 23.8, 27.4 (3C, $^3J_{Sn-C}$ = 54), 29.0 (3C, $^2J_{Sn-C}$ = 20), 45.0, 64.6, 75.0, 106.1 ($^2J_{Sn-C}$ = 46), 140.1 ($^3J_{Sn-C}$ = 45); MS: organostannyl fragments: m/z (%) = 377 ($M^{\cdot+}$ − Bu$^{\cdot}$ − 57, 20), 321 (56), 291 (45), 235 (79), 179 (100), 121 (35); organic fragments: m/z (%) = 69 (20), 57 (36), 45 (62), 41 (19), 29 (14); $[\alpha]_D$ = −3.2 (c = 1.017 in $CHCl_3$).

5.5.18. (2R,4R)-4-(3-Tributylstannyl-4-methylpent-1-en-1-yloxy)pentan-2-ol ***2r***

MS: organostannyl fragments: m/z (%) = 476 ($M^{\cdot+}$–Bu$^{\cdot}$, <1), 419 (8), 389 (24), 321 (47), 291 (52), 235 (92), 179 (96), 121 (39); organic fragments: m/z (%) = 99 (91), 81 (34), 69 (50), 57 (17), 55 (16), 45 (74), 43 (100), 41 (32), 29 (17); IR: ν = 3360, 1646, 1465, 1376, 1155, 1084; elemental analysis Calc. (%) for $C_{23}H_{48}O_2Sn$ (475.34): C, 58.12; H, 10.18. Found: C, 57.66; H, 10.35%.

Isomer **2r*Z***: Major diastereomer: ^{1}H NMR: δ = 0.55–1.00 and 1.1–1.65 (2m, 41H), 1.79 (qd, 1H, $^3J_{1H}$ = 7.5, $^3J_{3H}$ = 7.2), 2.09 (bs, 1H), 2.23 (ddd, 1H, $^3J_{1H}$ = 7.5, $^3J_{1H}$ = 11.9, $^4J_{1H}$ = 0.8, $^2J_{Sn-H}$ = 35), 3.83-4.1 (m, 2H), 4.39 (dd, 1H, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 11.9, $^3J_{Sn-H}$ = 20.4), 5.76 (dd, 1H, $^3J_{1H}$ = 6.1, $^4J_{1H}$ = 0.8, $^4J_{Sn-H}$ = 18.6); ^{13}C NMR: δ = 9.7 (3C, $^1J_{Sn-C}$ = 284/297), 13.7 (3C), 20.5, 22.8 ($^3J_{Sn-C}$ = 36), 23.8, 24.1 ($^3J_{Sn-C}$ = 32), 27.6 (3C, $^3J_{Sn-C}$ = 53/56), 29.3 (3C, $^2J_{Sn-C}$ = 19), 31.4 ($^2J_{Sn-C}$ = 14), 33.4 ($^1J_{Sn-C}$ = 298/312), 45.3, 64.7, 74.8, 110.7 ($^2J_{Sn-C}$ = 40), 139.8 ($^3J_{Sn-C}$ = 46); ^{119}Sn NMR: δ = −25.0.

Minor diastereomer: meaningful signals: ^{1}H NMR: δ = 4.35 (dd, 1H, $^3J_{1H}$ = 10, $^3J_{1H}$ = 6.2), 5.81 (dd, 1H, $^3J_{1H}$ = 6.2, $^4J_{1H}$ = 0.7); ^{13}C NMR: δ = 9.6 (3C), 13.24 (3C), 44.8, 64.6, 75.3, 109.3 ($^2J_{Sn-C}$ = 39), 140.0 ($^3J_{Sn-C}$ = 47).

Isomer **2r*E***: meaningful signals: ^{1}H NMR: δ = 4.96 (dd, 1H, $^3J_{1H}$ = 12.2, $^3J_{1H}$ = 11.8), 5.87 (dd, 1H, $^3J_{1H}$ = 12.2, $^4J_{1H}$ = 0.7); ^{13}C NMR: = 9.6 (3C), 13.6 (3C), 64.7, 74.0, 110.6, 141.6.

5.5.19. (2R,4R)-4-(3-Tributylstannyl-4 4-dimethylpent-1-en-1-yloxy)pentan-2-ol ***2s***

MS: organostannyl fragments: m/z (%) = 490 ($M^{\cdot+}$–Bu$^{\cdot}$, <1), 433 (7), 403 (23), 321 (41), 291 (47), 235 (75), 179 (81), 121 (33); organic fragments: m/z (%) = 199 (7), 113 (77), 95 (34), 85 (10), 69 (42), 57 (15), 55 (14), 45 (58), 43 (100), 41 (29), 29 (15); IR: ν = 3387, 1646, 1464, 1376, 1342, 1155, 1114, 1090, 960, 737; HRMS: $M^{\cdot+}$–Bu$^{\cdot}$ $(C_4H_9)^{\cdot}$ = 433.2138 / 431.2087 / 429.2093 for ^{120}Sn, ^{118}Sn and ^{116}Sn; elemental analysis Calc. (%) for $C_{24}H_{50}O_2Sn$ (489.36): C, 58.90; H, 10.30. Found: C, 58.65; H, 10.22%.

Isomer **2s*Z***: Major diastereomer: ^{1}H NMR: δ = 0.55–1.0 (m, 18H), 0.92 (s, 9H), 1.15–1.75 (m, 17H), 2.11 (bd, 1H, $^3J_{1H}$ = 4.4), 2.52 (dd, 1H, $^3J_{1H}$ = 12.4, $^4J_{1H}$ = 0.6, $^3J_{Sn-H}$ = 62), 3.9-4.2 (m, 2H), 4.53 (dd, 1H, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 12.4, $^3J_{Sn-H}$ = 22), 5.85 (dd, 1H, $^3J_{1H}$ = 6.1, $^4J_{1H}$ = 0.6, $^4J_{Sn-H}$ = 17); ^{13}C NMR: δ = 10.6 (3C, $^1J_{Sn-C}$ = 288/300), 13.7 (3C), 20.6, 24.0, 27.7 (3C, $^3J_{Sn-C}$ = 57), 29.3 (3C, $^2J_{Sn-C}$ = 19), 30.6 (3C, $^3J_{Sn-C}$ = 26), 34 ($^2J_{Sn-C}$ = 13), 39.8 ($^1J_{Sn-C}$ = 298/310), 45.3, 64.5, 74.8, 109.7 ($^2J_{Sn-C}$ = 38), 140.2 ($^3J_{Sn-C}$ = 48); ^{119}Sn NMR: δ = −29.2.

Minor diastereomer:^{1}H NMR: meaningful signals: δ = 2.17 (bd, 1H, $^3J_{1H}$ = 4.6), 2.48 (dd, 1H, $^3J_{1H}$ = 11.9, $^4J_{1H}$ = 0.6), 3.9-4.2 (m, 2H), 4.47 (dd, 1H, $^3J_{1H}$ = 6.2, $^3J_{1H}$ = 11.9, $^3J_{Sn-H}$ = 21), 5.91 (dd, 1H, $^3J_{1H}$ = 6.2, $^4J_{1H}$ = 0.6); ^{13}C NMR: δ = 10.7 (3C), 13.7 (3C), 20.7, 23.7, 27.7 (3C, $^3J_{Sn-C}$ = 57), 29.3 (3C, $^2J_{Sn-C}$ = 19), 30.7 (3C), 33.9, 40.0 ($^1J_{Sn-C}$ = 297/310), 44.9, 64.6, 75.4, 109.7, 140.4 ($^3J_{Sn-C}$ = 48); ^{119}Sn NMR: δ = −28.1.

Isomer **2s*E***: ^{1}H NMR: meaningful signals: δ = 1.89 (d, 1H, $^3J_{1H}$ = 12.5), 2.31 (bd, 1H, $^3J_{1H}$ = 4.4), 3.9–4.2 (m, 2H), 5.1 (dd, 1H, $^3J_{1H}$ = 12.5, $^3J_{1H}$ = 12.3, $^3J_{Sn-H}$ = 21), 5.92 (d, 1H, $^3J_{1H}$ = 12.3, $^4J_{Sn-H}$ = 18) ; ^{13}C NMR: δ = 10.5 (3C), 13.7 (3C), 20.1, 23.6, 27.7 (3C, $^3J_{Sn-C}$ = 57), 29.3 (3C, $^2J_{Sn-C}$ = 20), 30.7 (3C, $^3J_{Sn-C}$ = 25), 33.9, 42.8, 44.8, 64.7, 74.1, 108.3 ($^2J_{Sn-C}$ = 39), 141.9 ($^3J_{Sn-C}$ = 57); ^{119}Sn NMR: δ = −27.9.

5.5.20. (2R,4R)-4-(3-Tributylstannyl-4-trimethylsilylbut-1-en-1-yloxy)pentan-2-ol ***2t***

IR: ν = 3368, 1645, 1465, 1376, 1245, 1115, 1085, 859, 840. Isomer **2t*Z***: Major diastereomer: ^{1}H NMR: δ = −0.05 (s, 9H), 0.70–1.00 and 1.10–1.70 (2m, 37H),

2.01 (bd, 1H, $^3J_{1H}$ = 4.3), 2.51 (tdd, 1H, $^3J_{2H}$ = 11.5, $^3J_{1H}$ = 11.5, $^4J_{1H}$ = 0.9), 3.85-4.15 (m, 2H), 4.53 (dd, 1H, $^3J_{1H}$ = 6.1, $^3J_{1H}$ = 11.5, $^3J_{Sn-H}$ = 19), 5.67 (dd, 1H, $^3J_{1H}$ = 6.1, $^4J_{1H}$ = 0.9, $^4J_{Sn-H}$ = 22); ^{13}C NMR: δ = −1.20 (3C), 8.5 (3C, $^1J_{Sn-C}$ = 276/289), 13.4 (3C), 17.0, 20.3, 20.6, 23.6, 27.3 (3C, $^3J_{Sn-C}$ = 52), 29.0 (3C, $^2J_{Sn-C}$ = 9.5), 45.3, 64.1, 74.5, 114.3 ($^2J_{Sn-C}$ = 22), 137.9 ($^3J_{Sn-C}$ = 48); ^{119}Sn NMR: δ = −16.9.

Minor diastereomer: meaningful signals: ^{1}H NMR: δ = 4.30 (dd, 1H, $^3J_{1H}$ = 6.2, $^3J_{1H}$ = 11.5), 5.91 (dd, 1H, $^3J_{1H}$ = 6.2, $^4J_{1H}$ = 1.0).

Isomer **2t*E***: meaningful signals:^{1}H NMR: δ = 5.0 (dd, 1H, $^3J_{1H}$ = 10.9, $^3J_{1H}$ = 12.2), 5.88 (dd, 1H, $^3J_{1H}$ = 12.2, $^4J_{1H}$ = 0.5); ^{13}C NMR: δ = 44.6, 64.3, 73.6, 113.5, 139.7. ^{119}Sn NMR: Isomer **2t*E*** and minor diastereomer **2t*Z***: δ = −15.6 and -18.1.

5.6. Meaningful signals for S_N2 substitution products and side products

5.6.1. S_N2 products

*5.6.1.1. (E)-1-Tributylstannyl-3-ethoxybut-1-ene **3a***. Meaningful signals in the ^{1}H NMR spectrum: δ = 5.49 (dd, 1H, $^3J_{1H}$ = 19.0, $^3J_{1H}$ = 5.6), 5.80 (d, 1H, $^3J_{1H}$ = 19.0).

*5.6.1.2. (Z)-1-Tributylstannyl-3-ethoxypent-1-ene **3b***. Meaningful signals in the ^{1}H NMR spectrum: δ = 5.95 (d, 1H, $^3J_{1H}$ = 13), 6.3 (dd, 1H, $^3J_{1H}$ = 8, $^3J_{1H}$ = 13).

*5.6.1.3. (Z)-1-Tributylstannyl-3-ethoxy-4-methylpent-1-ene **3d***. Meaningful signals in the ^{1}H NMR spectrum: δ = 6.0 (d, 1H, $^3J_{1H}$ = 12), 6.28 (dd, 1H, $^3J_{1H}$ = 8, $^3J_{1H}$ = 12).

*5.6.1.4. (Z)-3-(1-Tributylstannyl-4-methylpent-1-en-3-yloxy)propanol **3k***. Meaningful signals in the ^{1}H NMR spectrum: δ = 3.18 (dd, 1H, $^3J_{1H}$ = 5, $^3J_{1H}$ = 9), 6.13 (d, 1H, $^3J_{1H}$ = 13), 6.37 (dd, 1H, $^3J_{1H}$ = 9, $^3J_{1H}$ = 13).

*5.6.1.5. (Z)-3-(1-Tributylstannyl-4,4-dimethylpent-1-en-3-yloxy)propanol **3l***. Meaningful signals in the ^{1}H NMR spectrum: δ = 2.95 (d, 1H, $^3J_{1H}$ = 9), 6.10 (d, 1H, $^3J_{1H}$ = 12.7), 6.30 (dd, 1H, $^3J_{1H}$ = 9, $^3J_{1H}$ = 12.7).

*5.6.1.6. (E)-2-Tributylstannyl-4-ethoxy-5-trimethylsilylpent-2-ene **3m***. ^{1}H NMR: δ = −0.05-0.15 (m, 11H), 0.75-1.75 (m, 30H), 1.91 (d, 3H, $^4J_{1H}$ = 2, $^3J_{Sn-H}$ = 45/47), 3.26 and 3.50 (AB syst., 2H, $^2J_{1H}$ = 9.1, $^3J_{3H}$ = 7.0), 4.29 (dt, 1H, $^3J_{1H}$ = 8.8, $^3J_{2H}$ = 7.3), 5.41 (dq, 1H, $^3J_{1H}$ = 8.8, $^4J_{3H}$ = 2, $^3J_{Sn-H}$ = 70/72).

*5.6.1.7. (E)-(2R,4R)-4-(1-Tributylstannylbut-1-en-3-yloxy)pentan-2-ol **3o***. ^{1}H NMR: δ = 0.80–1.65 (m, 38H), 3.26 (bd, 1H, $^3J_{1H}$ = 2.7), 3.75–3.95 (m, 2H), 4.00–4.18 (m, 1H), 5.80 (dd, 1H, $^3J_{1H}$ = 19.1, $^3J_{1H}$ = 7.2, $^3J_{Sn-H}$ = 60/62), 5.8 (dd, 1H, $^3J_{1H}$ = 19.1, $^2J_{Sn-H}$ = 70/73).

5.6.2. Other side products

*5.6.2.1. 3-Tributylstannylcrotonaldehyde **5***. Isomer **5*E***: ^{1}H NMR: δ = 0.75–1.70 (m, 27H), 2.45 (d, 3H, $^4J_{1H}$ = 1.8, $^3J_{Sn-H}$ = 42/44), 6.19 (dq, 1H, $^3J_{1H}$ = 7.9, $^4J_{3H}$ = 1.8, $^3J_{Sn-H}$ = 62), 10.04 (d, 1H, $^3J_{1H}$ = 7.9).

Isomer **5*Z***: ^{1}H NMR: δ = 0.75–1.70 (m, 27H), 2.22 (d, 3H, $^4J_{1H}$ = 1), 6.69 (dq, 1H, $^3J_{1H}$ = 6.9, $^4J_{3H}$ = 1, $^3J_{Sn-H}$ = 100), 9.48 (d, 1H, $^3J_{1H}$ = 6.9).

*5.6.2.2. 4-Tributylstannylpent-2-ene **6o***. Isomer **6o*Z***: ^{1}H NMR: δ = 0.70–2.20 (m, 34H), 5.08 (m, 1H, $^3J_{1H}$ = 11.3, $^3J_{3H}$ = 6.6, $^4J_{1H}$ = 1.0), 5.41 (m, 1H, $^3J_{1H}$ = 11.3, $^3J_{1H}$ = 10.3, $^4J_{3H}$ = 1.6).

Isomer **6o*E***: ^{1}H NMR: meaningful signals: δ = 5.63 (m, 1H, $^3J_{1H}$ = 7.6, $^3J_{1H}$ = 15.1, $^4J_{3H}$ = 1.5).

*5.6.2.3. (Z)-7-Tributylstannylundec-5-ene **6p***. ^{1}H NMR: δ = 0.70–1.70 (m, 43H), 1.80–2.10 (m, 2H), 2.20-2.50 (m, 1H), 5.04 (dt, 1H, $^3J_{1H}$ = 10.8, $^3J_{2H}$ = 7.0), 5.32 (ddt, 1H, $^3J_{1H}$ = 10.8, $^3J_{1H}$ = 11.7, $^4J_{2H}$ = 1.5).

*5.6.2.4. (E)-1-Tributylstannyl-3-methylbut-1-ene **7o***. ^{1}H NMR: δ = 0.70-1.70 (2m, 34H), 5.77 (dd, 1H, $^3J_{1H}$ = 5.0, $^3J_{1H}$ = 18.9), 5.92 (d, 1H, $^3J_{1H}$ = 18.9).

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