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Synthesis, characterization and primary evaluation of the synthetic efficiency of supported vinyltins and allyltins

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ABSTRACT

Supported vinyltins and allyltins grafted to an insoluble cross-linked polystyrene matrix were prepared using methods usually employed in solution, like hydrostannylation of alkynes, transmetallation of a tin halide with organomagnesium or organozinc reagents, and substitution of an allyl halide by a supported stannylanion or S_N2' substitution of a supported β-stannylacrolein acetal by cyanocopper reagents in the presence of boron trifluoride etherate. The insoluble grafted organotin reagents were analysed by HRMAS NMR, allowing an unambiguous assignment of their isomeric distribution or the identification of side products. When involved in Stille cross-coupling reactions (vinyltins) or in addition on aldehydes (allyltins), these supported reagents exhibit similar reactivity and similar stereoselectivity when compared to the tributyltin analogues, with the advantage to prevent problems due to the contamination by tin residues.

1. Introduction

Triorganotin compounds are welcomed as powerful reagents in organic synthesis due to their versatile reactivity and high tolerance against numerous functional groups [1]. For instance, vinyltins have been used as irreplaceable reagents in the total synthesis of complex molecules [2] and γ-substituted allyltins have been used in the stereocontrolled synthesis of homoallylic alcohols [3]. In spite of their synthetic potential, these reagents have been scarcely used for the synthesis of bioactive molecules like pharmaceuticals because of their toxicity and the difficulty to remove tin by-products from the desired reaction products. Several possibilities have been disclosed to alleviate this issue and have been recently reviewed [4]. Among these, using insoluble solid-state supported organotin reagents appears to be the most promising approach because the grafted organotin residues can be efficiently removed by simple filtration of the solid support to which they are grafted. Pioneering studies have been devoted to supported organotin hydrides in reduction reactions [5] and to supported organotin oxides used as transesterification catalysts [6,7]. More recently, we have pointed out the efficiency of supported *N*-stannylanilines to obtain regioselective para-iodination [8] and, even more interestingly, we have used supported allyltins in order to obtain cleanly homoallyllic alcohols [9] or supported vinyltins and aryltins to achieve Stille-Migita cross-coupling reactions [10,11], a topic which remains of high interest as illustrated by reports from other groups [12–14]. High Resolution Magic Angle Spinning NMR (HRMAS NMR) [6] enables one to monitor more efficiently supported organotin reagents in order to exploit further their synthetic potential in novel solid phase synthetic procedures. The present contribution reports on the synthesis, the characterization and the reactivity of vinyltins and allyltins grafted onto a solid support of polystyrene cross-linked divinylbenzene (Amberlite XE 305). The choice of the latter support has been dictated by the mechanical resistance of the polymer to abrasion, the size of the pores and the ability of this cross-linked material to swell optimally in usual organic solvents [15], which is a prerequisite to both favourable reaction and HRMAS NMR measurement conditions. As previously described [5,8] a grafted *n*-butyl group was used as a spacer for a di-*n*-butyltin unit in order to preserve a perfect analogy with the tri-*n*-butyltin analogues (Scheme 1).

The obtained supported triorganotin halides **3a–c** can be subsequently converted into supported triorganotin hydride **4** upon reaction with $LiAlH_4$ [10] or reacted with Grignard reagents or zinc reagents [9], affording a series of grafted allyltins, vinyltins and aryltins [9–11].

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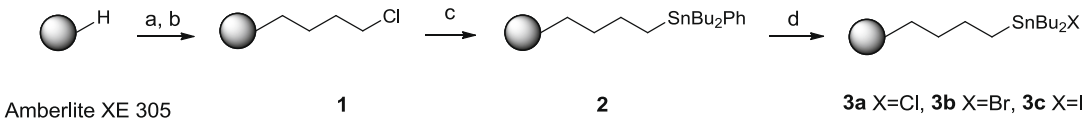


Scheme 1. Grafting of organotin reagents on Amberlite XE 305. Reagents and conditions: (a) n-BuLi/TMEDA, cyclohexane, 65 °C. (b) Br–$(CH_2)_4$–Cl, THF, 0 °C to rt. (c) $Bu_2SnPhLi$, THF, rt. (d) I_2, EtOH, 65 °C; Br_2, EtOH, 65 °C or HCl, Et_2O/THF, 20 °C.

2. Results

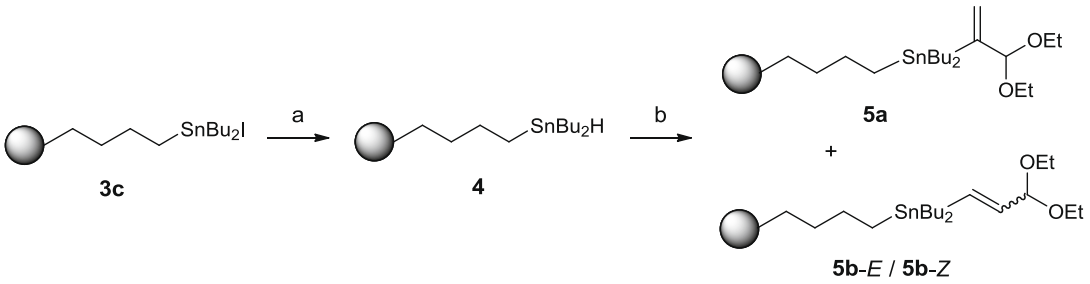
2.1. Synthesis and structural analysis of isomeric mixtures of supported vinyltins

When functional groups have to be preserved on the vinyl unit, hydrostannation of the appropriate alkyne is the straightforward route. Accordingly, we focused on the reaction of propargyl or homopropargyl acetals with the supported tin hydride **4** (Scheme 2) [16–18].

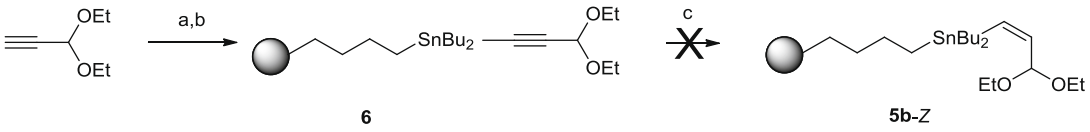
While characterization of supported organotin reagents can be achieved using solid-state ^{119}Sn MAS NMR, in the present case, the signal of **5a** is overlapping with the one of **5b**-*E* preventing complete discrimination between the three isomers. The iododestannylation, known to be quantitative [16], has been used as an indirect method to evaluate broadly the ratio of **5a**/**5b**-*E*/**5b**-*Z* to be 13/73/14, but this method is questionable on more complex examples. Accordingly, the isomeric mixture composition was investigated using HRMAS NMR, allowing the application of typical high-resolution liquid NMR techniques to solid supported grafted moieties dipped in the liquid [19–21], thanks to their isotropic conformational mobility characteristic to the liquid state. However, as in the solid-state ^{119}Sn MAS spectrum, the resonances of **5a** and **5b**-*E* also overlap in the ^{119}Sn HRMAS spectrum. By contrast, in the ^{13}C spectrum, three resonances, representative for the three isomers present, are observed for several carbon atoms. The spectrum was simulated with the PERCH programme [22,23] in order to determine the relative amplitudes of each of the three resonances of a given carbon atom type, which turned out to be 17–72–11% for the vinyl resonances, 12–76–12% for the $CH(OEt)_2$ ones, 14–71–15% for OCH_2 ones and 13–73–14% for $SnCH_2$ signals. These relative amplitudes, averaging at 14.0 ± 2.2, 73.0 ± 2.2, 13.0 ± 1.8%, respectively, are in the same range for all sets of three ^{13}C resonances within experimental error and are therefore representative for the percentage molar fractions of the three isomers. In order to address the assignment issue, the synthesis of pure isomer **5b**-*Z* was attempted, starting from **3c** according to the procedure used in tributyltin series (Scheme 3) [24].

While **6** was correctly obtained, the subsequent Sato type reaction failed when performed on the supported alkynyltin **6**, probably because adding the reagents in the same order as in homogeneous liquid phase is not possible. Indeed, the dropwise addition of the grafted alkynyltin **6** to $Ti(OiPr)_4$ prior to treatment with isopropylmagnesium chloride (2 equiv.) [24] is simply not applicable.

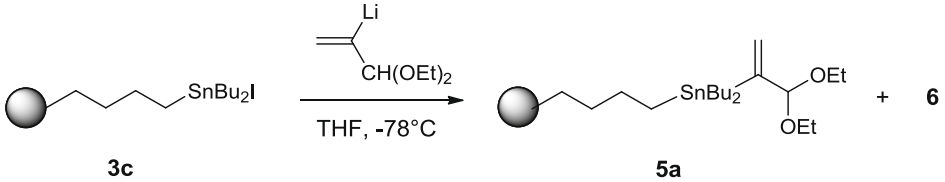
The second target was pure vinyltin **5a** and for this purpose 2-lithioacrolein acetal obtained by halogen/metal exchange with the corresponding bromoacetal was reacted with the supported triorganotin iodide **3c** (Scheme 4).



Scheme 2. Preparation of supported vinyltins via hydrostannylation of alkynes. Reagents and conditions: (a) $LiAlH_4$ THF, 60 °C, 3 h. (b) AIBN, 3,3-diethoxypropyne, toluene, 110 °C, 3 h.



Scheme 3. Attempted synthesis of supported vinyltin **5b**-*Z*. Reagents and conditions: (a) *n*-BuLi, THF, −78 °C. (b) **3c**. (c) $Ti(OiPr)_4$, i-PrMgCl (2 equiv.), Et_2O, −78 °C.



Scheme 4. Synthesis of branched supported organotin **5a**.

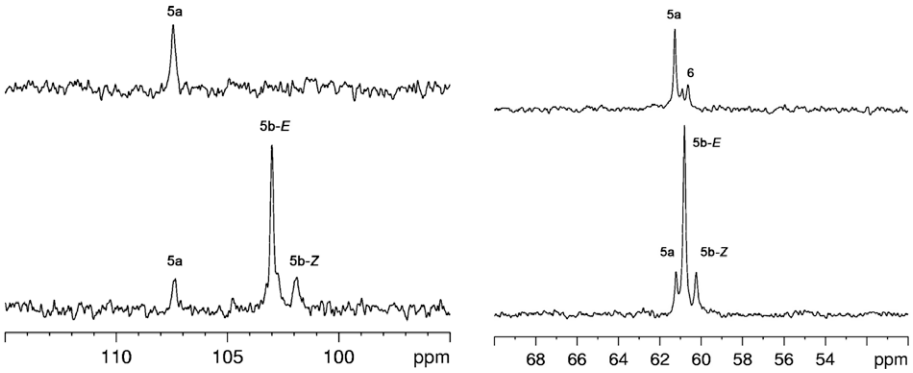


Fig. 1. Expansions of ^{13}C spectra of the mixture of the three isomers (**5a** + **5b**-*E* + **5b**-*Z*) (bottom) and **5a** (top) (**5a** is contaminated with **6**).

Unfortunately, a competitive dehydrobromination occurred during the halogen metal exchange reaction, affording diethoxypropyne which was converted into the corresponding alkynyllithium to afford **6** after quenching with the supported tin halide (see the first step of Scheme 3). In spite of the formation of side-product **6** an unambiguous discrimination of the relevant signals related to the different isomers in the ^{13}C HRMAS spectrum was now possible, as in three of the previously mentioned sets of differentiated carbon atoms the resonances of **5a** could formally be identified (Fig. 1).

The full assignment of the ^{1}H resonances could be completed thanks to $^{1}H/^{13}C$ HSQC and $^{1}H/^{119}Sn$ HMQC [21] spectra and the results are provided in the experimental part (Table 1). In order to assess the potentials of the method on another structure, where the vinylic protons have very close chemical shifts for the *E* isomer, the supported homoallyl vinyltin acetals **7** were synthesized similarly. In this series, the α-isomer was not observed after hydrostannylation in the tributyltin series; a similar trend is observed for the supported tin hydride affording a *Z*/*E* mixture of the supported vinyltin **7** (Scheme 5).

The generation of a 74/26 mixture of *E*/*Z* isomers was easily established from the solid-state ^{119}Sn MAS NMR spectrum due to the similarity of the ^{119}Sn chemical shifts with those of the soluble tributyltin derivatives, and the HRMAS NMR spectra enabled us to complete the ^{1}H and ^{13}C resonance assignment of the vinyl part.

Although the resonances are broad in the ^{1}H HRMAS spectrum and, as a consequence no reliable relation exists between the isomer concentrations and their relative resonance amplitudes, the ^{13}C NMR data confirm the presence of an excess of *E* isomer thanks

Table 1
^{1}H, ^{13}C and ^{119}Sn chemical shifts in $CDCl_3$ of the grafted parts of **5a** and **5b**-(*E*/*Z*).

Moiety	δ ^{13}C	δ 1H	δ ^{119}Sn
Vinyl 1	144.9 (**5b**-*E*)	6.08 (**5b**-*E*)	
		5.94 (**5a**)	
		6.24 (**5b**-*Z*)	
Vinyl 2	134.0	6.02 (**5b**-*Z*)	
	132.5 (**5b**-*E*)	6.41 (**5b**-*E*)	
	131.2	5.43 (**5a**)	
CH$(OEt)_2$	107.4 (**5a**)	4.78 (**5a**)	
	103.0 (**5b**-*E*)	4.84 (**5b**-*E*)	
	101.9 (**5b**-*Z*)	4.87 (**5b**-*Z*)	
O**CH$_2$**	61.2 (**5a**)	3.66, 3.53	
	60.8 (**5b**-***E***)		
	60.2 (**5b**-***Z***)		
OCH_2**CH$_3$**	15.3	1.24	
Butyl α	10.9 (**5a**)		
	10.0 (**5b**-**Z**)	0.92	
	9.5 [335](**5b**-*E*)		
Butyl *β*	29.1	1.55	
Butyl *γ*	27.2	1.35	
Butyl *δ*	13.7	0.92	
Sn			−46.6 (13% **5a** + 73% **5b**-*E*),−60.6 (14% **5b**-*Z*)

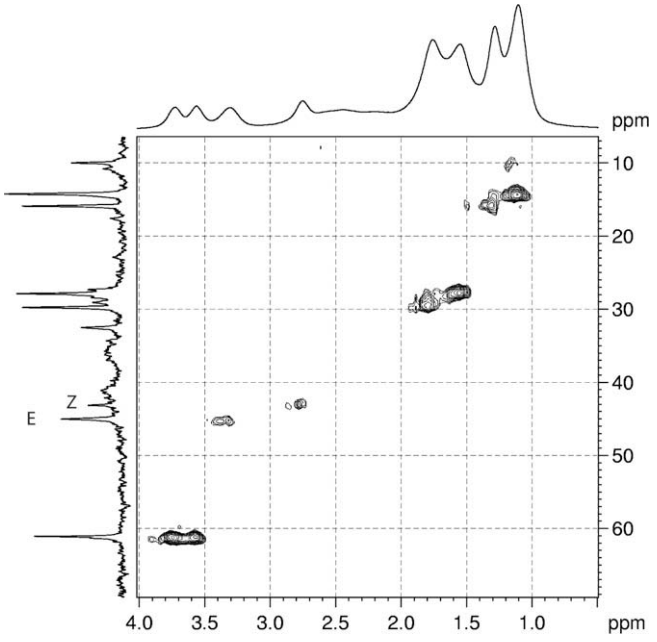
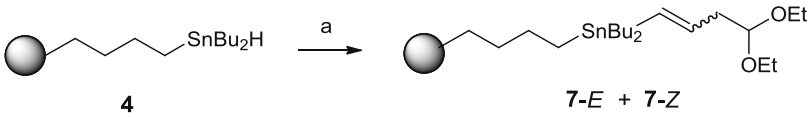


Fig. 2. Expansion of the $^{1}H/^{13}C$ HSQC HRMAS spectrum of **7**-*E*/*Z* with the ^{1}H and ^{13}C HRMAS spectra on the horizontal and vertical axes respectively. The relevant ^{13}C allylic resonances are indicated.



Scheme 5. Synthesis of supported homoallyl vinyltin acetals 7-E and 7-Z. Reagents and conditions: (a) AIBN, 4,4-diethoxybut-1-yne, toluene, 110 °C, 3 h.

Table 2
^{1}H, ^{13}C and ^{119}Sn chemical shifts in C_6D_6 of the grafted parts of **7-**(*E*/*Z*).

Atom	δ ^{13}C	δ ^{1}H	δ ^{119}Sn
Vinyl 1	145.5	6.32	
Vinyl 2	130.9	6.30	
CH$(OEt)_2$	102.9	4.73	
O**CH$_2$**	61.3	3.74, 3.57	
OCH_2**CH$_3$**	15.8	1.31	
C=C–**CH$_2$**	45.2 (*E*); 43.0 (*Z*)	3.32 (*E*); 2.78 (*Z*)	
Butyl α	10.0	1.17	
Butyl β	29.6	1.79	
Butyl γ	27.9	1.55	
Butyl δ	14.3	1.11	
Sn			−51.9 (79%); −62.3 (21%)

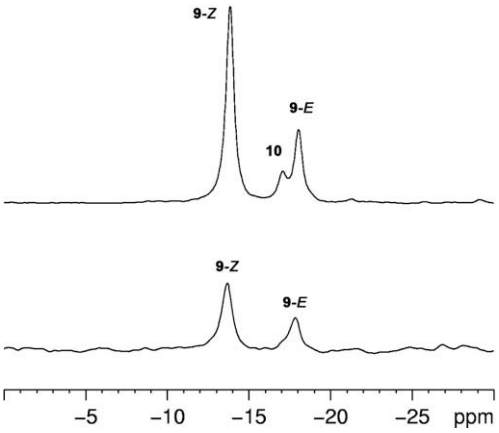


Fig. 3. ^{119}Sn HR-MAS spectra of supported crotyltins **9**. Bottom: spectrum of the Barbier reaction mixture; top: spectrum of the mixture obtained after quenching of the stannylanion.

to the possible spectral discrimination of the allylic ^{13}C (−C=C−**C**H_2) resonances from the *Z* and *E* isomers, at 43.0 and 45.2 ppm, respectively. Further analysis involving a $^{1}H/^{13}C$ HSQC experiment (Fig. 2) makes a complete assignment possible (see Table 2).

2.2. Synthesis and structural analysis of supported isomeric mixtures of allyltins

2.2.1. Supported crotyltins

Differences in reactivity of supported crotyltins toward benzaldehyde were observed when compared to crotyltributyltin, due to a matrix effect on the kinetics of 1,3-metallotropy [25]. HRMAS NMR techniques enable one to estimate semi-quantitatively the differences in isomeric composition of the supported reagents as a function of their preparation method. Two samples were obtained from crotyl chloride through two different procedures (Scheme 6). A supported stannylanion has been generated here *in situ* for the first time: the compatibility of cross-linked styrene/divinylbenzene matrix (Amberlite XE 305) with THF gives access to the supported triorganostannyllithium reagent **8** from the tin hydride **4**.

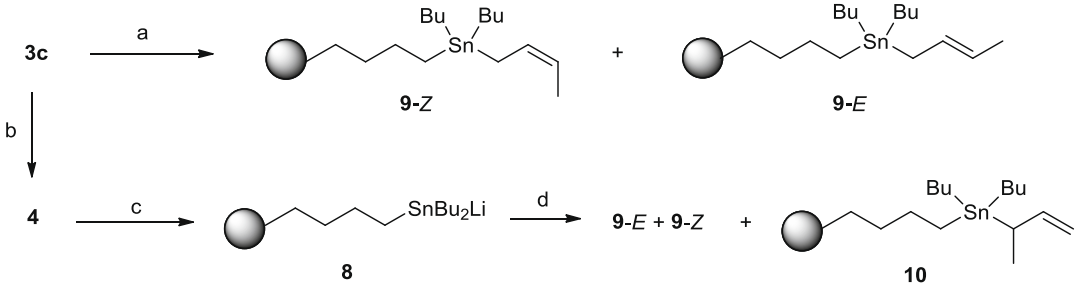
Whereas the solid-state ^{119}Sn MAS spectra of the two samples resulting from a Barbier reaction or from the quenching of the intermediate supported stannylanion **8** are quite similar, the corresponding ^{119}Sn HRMAS spectra enable one to unravel the outcome of these reactions (Fig. 3). The latter reaction mixture shows the presence of a third isomer, with a slightly different ^{119}Sn chemical shift, assigned to the branched isomer **10** from its 2D ^{1}H-^{119}Sn HSQC HRMAS NMR spectrum (Fig. 4), in which all ^{119}Sn resonances clearly display cross-peaks with the α and β proton resonances from the butyl groups, the Sn−C**H**–Me proton and with the vinylic protons. A complete assignment for the three isomers is provided in Table 3.

The NMR studies of the crotyltin series in $CDCl_3$ reveal a partial halodestannylation. In this solvent, the ^{119}Sn NMR spectrum exhibits an additional resonance at +150 ppm assigned to the supported triorganotin chloride **3a** and therefore, spectra must be preferably recorded in C_6D_6 to avoid this side-problem.

The assignment of the *E*/*Z* configuration of compound **9** was performed by comparison with the spectra of the soluble model compounds, *E*/*Z*-(2-butenyl)tributylstannane. Although these products were described several years ago [26], divergent assignments have been published because no complete NMR characterization had been performed so far. Therefore an elaborate study including 1D ^{1}H, ^{13}C, ^{119}Sn and 2D ^{1}H–^{1}H, ^{1}H–^{13}C and ^{1}H–^{119}Sn correlation NMR spectra was performed and the results are gathered in Table 4. A ^{1}H–^{1}H NOESY spectrum, revealing a correlation peak between the resonances from the $SnCH_2$ and the vinylic protons in position 3, confirmed the *E* configuration of the major compound in the mixture of the soluble model compounds, which was prepared according to the Barbier type reaction from *E*/*Z* crotyl chloride (85/15). The grafted compounds show an excess of *Z*-isomer in both preparations.

Even though, quite surprising at first glance, this result can be understood as a difference in kinetics of the 1,3-metallotropy inducing an isomerisation process and/or by a matrix effect favouring the *Z*-isomer Scheme 7.

The difference in the distribution of product **9**−(*Z*+*E*) and **10** as a function of the experimental procedure can also be interpreted by a thermodynamic mixture of isomers when preparation is achieved in Barbier mode, while a mixture not yet at equilibrium can be expected using the stannylanion **8**, because triorganostannyllithium



Scheme 6. Synthesis of supported crotyltins **9**-(*E* and *Z*) and **10**. Reagents and conditions: (a) Zn^{*}, crotylchloride (*E*/*Z* = 85/15), Barbier method, (b) $LiAlH_4$, THF, 60 °C, 3 h. (c) *i*-Pr_2NLi, THF, −10 °C. (d) Crotylchloride (*E*/*Z* = 85/15).

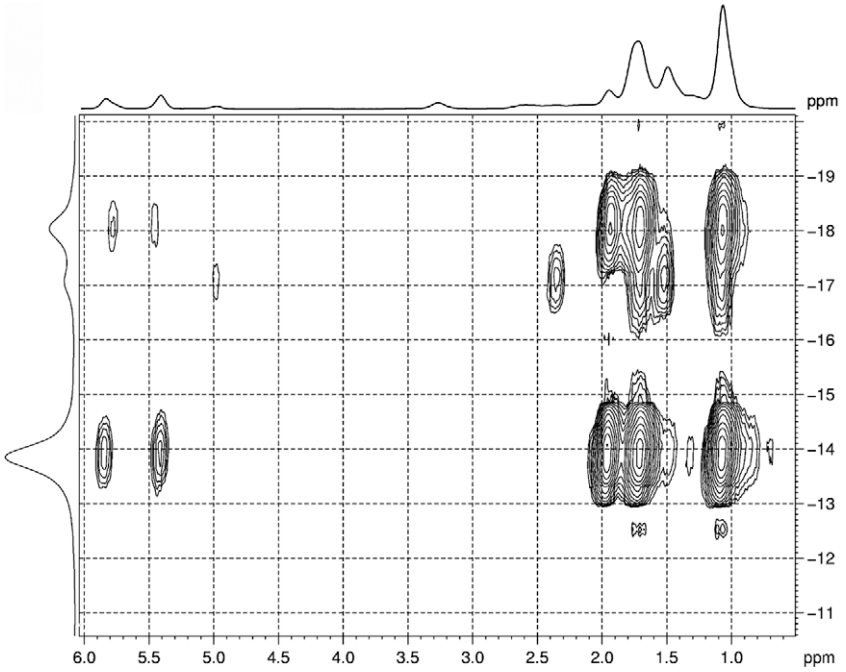
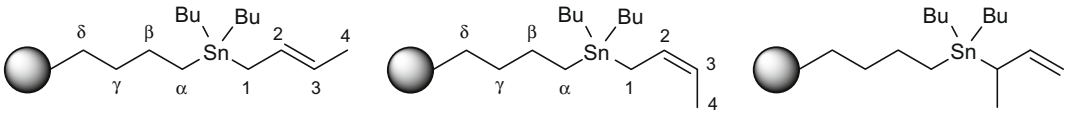


Fig. 4. Part of the $^{1}H/^{119}Sn$ HSQC HRMAS NMR spectrum of the mixture **9**-*Z*, **9**-*E* and **10** obtained after quenching of the stannylanion.

Table 3
^{1}H, ^{13}C and ^{119}Sn chemical shifts in C_6D_6 of the grafted parts of **9**-(*Z*/*E*) and **10**. The first value concerns the major isomer, with *Z*-configuration.

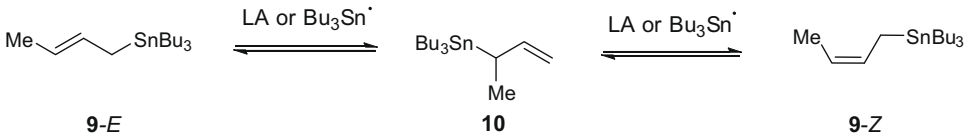


9-*E* **9-*Z*** **10**

9-(*Z*/*E*)	δ ^{13}C	δ ^{1}H	δ ^{119}Sn	10	δ ^{1}H	δ ^{119}Sn
Butyl α	9.8/9.6	1.07		Butyl α	1.00	
Butyl β	29.7/28.7	1.71/1.75		Butyl β	1.71	
Butyl γ	27.9/27.2	1.50/1.43				
Butyl δ	14.1	1.07				
Butenyl 1	10.6/14.7	1.96/1.94		Butenyl CH	2.35	
Butenyl 2	129.5/130.5	5.85/5.78		Butenyl CH=	4.98	
Butenyl 3	118.4/120.5	5.42/5.45				
Butenyl 4	12.9/18.3	1.77/1.81		Butenyl CH_3	1.51	
Sn in mixture *(Barbier)*			−14.0 (*Z* 64%)			
			−18.0 (*E* 36%)			
Sn in mixture *(stannylanion)*			−14.0 (*Z* 66%)			−17.1 (8%)
			−18.0 (*E* 26%)			

Table 4
^{1}H, ^{13}C and ^{119}Sn chemical shifts in C_6D_6 of a mixture of *E*/*Z* 2-butenyl tri-*n*-butyltin (for numbering scheme see Table 3). $^{n}J(^{13}C/^{119/117}Sn)$ coupling constants in Hz are mentioned between brackets.

	Major (*E*)			Minor (*Z*)		
Atom	δ ^{13}C	δ ^{1}H	δ ^{119}Sn	δ ^{13}C	δ ^{1}H	δ ^{119}Sn
Butyl α	9.4 [313/299]	0.91		9.6 [313/299]	0.91	
Butyl β	29.6 [19.8]	1.55		29.6 [19.8]	1.54	
Butyl γ	27.7 [51.2]	1.34		27.8 [53.3]	1.35	
Butyl δ	13.9	0.92		13.8	0.86	
Butenyl 1 (CH_2)	14.5 [267/256]	1.79		10.4 [255/245]	1.82	
Butenyl 2	130.4 [44.3]	5.65		129.5 [44.7]	5.72	
Butenyl 3	120.4 [46.8]	5.32		118.3 [45.4]	5.29	
Butenyl 4 (CH_3)	18.1 [11.6]	1.67		12.7 [13.0]	1.63	
Sn			−19.2 (57%)			−15.0 (43%)



Scheme 7. Isomerisation of crotyltins.

has been described to react primary with allyl chlorides [27] and tosylates [28] through an S_N2 pathway, the partial isomerisation occurring subsequently depending on the substrates and on the experimental conditions.

2.2.2. Supported α-substituted γ-alkoxyallyltins

In the tributyltin series, α-substituted γ-alkoxyallyltins were obtained from acrolein β-tributylstannylacetals through a S_N2' reaction [29,30]; therefore, a similar reaction for the supported analogues **5b**-*E* and **5b**-*Z* according to Scheme 8, was expected, see Table 5.

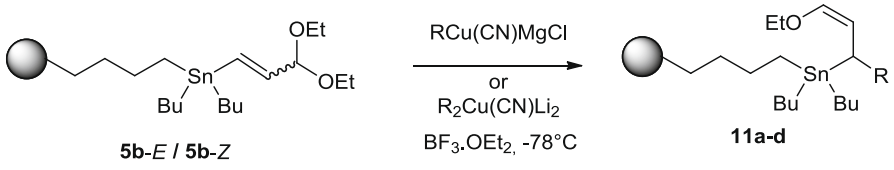
In practice, using tributyltin reagents [29,30] for the synthesis of supported allyltins appears to be much less efficient. For instance, using MeCu(CN)Li and LiBr in diethyl ether or THF, the S_N2' reaction product **11a** could not be obtained, whatever the reaction conditions. When the reaction was attempted with Et-Cu(CN)MgCl in diethyl ether, the desired product **11b** was obtained in 32% yield, and with *i*-PrCu(CN)MgCl, allyltin **11c** was obtained with 47% yield, using THF as a solvent. Surprisingly, when attempted with a *t*-butyl copper reagent, the reaction works in diethyl ether but only when a 2/1 ratio of *t*-BuMgCl/CuCN was used, **11d** being likewise obtained in 47% yield. In every case, side-products such as supported triorganotin chloride **3a** or supported tetraorganotins (transmetallation products) were observed.

Obviously this reaction is far from being optimal and some discrepancies in the reactivity might be due to differences in the aggregation state of the organocopper reagent, which is believed to be higher with MeCu(CN)Li or $Me_2Cu(CN)Li_2$, because of the incorporation of LiBr into the structure of the organometallic reagent [31] or to other problems related to the organocopper structure [32].

In spite of these poor yields, compounds **11c** and **11d** have been characterized from 2D ^{1}H HRMAS correlation spectra. Full chemical shift data for the α-*t*-butyl-substituted γ-ethoxy allyltin moiety (**11d**) are provided in Table 6, in the experimental part. In the 2D ^{1}H–^{119}Sn HRMAS correlation spectrum (in C_6D_6), only the ^{119}Sn resonance at −29.8 ppm shows correlations with protons from the allyl moiety at 5.83, 4.50 and 3.72 ppm. According to information from soluble model compounds formal indicators of the configuration around the double bond are the ^{1}H chemical shifts of the vinylic protons, which resonate at lower frequency and display a larger $\Delta\delta$ for the *Z*-configuration. The values 5.83, 4.50 and 3.72 ppm are in accordance with those found for the *Z*-configuration of $Bu_3SnCH(t\text{-Bu})CH{=}CH{-}OEt$, reported as 5.74, 4.39 and 3.65 ppm, whereas those of the *E*-configuration resonate at 6.05, 4.88 and 3.45 ppm. [30] Further confirmation of the *Z*-configuration for this compound can be gathered from a ^{1}H–^{1}H NOESY experiment (Fig. 5), in which only one of the vinylic protons, *i.e.* the one at 5.83 ppm assigned to the proton on the same carbon atom as the ethoxy group, displays a correlation peak with the OCH_2 protons of the ethoxy group. For the *E*-configuration, correlation peaks with both the vinylic protons are to be expected. These observations allow the assignment of a *Z*-configuration for the major isomer in each case, in agreement with previous observations on tributyltin derivatives [29]. The sample with the isopropyl

Table 6
^{1}H, ^{13}C and ^{119}Sn meaningful chemical shifts in $CDCl_3$ of the grafted parts of **11c** and **11d**. The values between brackets are the ^{1}H chemical shifts in C_6D_6.

Atom	δ ^{13}C		δ ^{1}H		δ ^{119}Sn	
	11c	**11d**	**11c**	**11d**	**11c**	**11d**
Vinyl 1	141.0	141.3	5.82	5.83 (5.93)		
Vinyl 2	109.4	108.4	4.46	4.50 (4.72)		
O**CH$_2$**	67.2	67.2	3.72	3.72 (3.66)		
OCH_2**CH$_3$**	15.4	15.4		1.30		
C=C–**CH**		39.9	2.48	2.63 (3.02)		
C(**CH$_3$**)$_3$	13.8?	30.7		0.98		
CH$(CH_3)_2$			1.94			
CH(**CH$_3$**)$_2$						
Butyl α	9.9	10.8	0.93	0.94		
Butyl β	29.3	29.3	1.54	1.54		
Butyl γ	27.6	27.7	1.36	1.36		
Butyl δ	13.8	13.8	0.93	0.92		
Sn					−25.6	−29.8



Scheme 8. Synthesis of supported α-substituted γ-alkoxyallyltins **11a**–**d** (R = Me, **11a**; R = Et, **11b**; R = *i*-Pr, **11c**; R = *t*-Bu, **11d**).

Table 5
Attempted preparations of supported γ-ethoxyallyltins via reaction of alkylcyanocuprates with **5b**–*E* + *Z*, in the presence of $BF_3.OEt_2$.

Entry	R–M	CuCN	$BF_3.OEt_2$	solvent	Conversion (%)
1	MeLi.LiBr (6 eq.)	3 or 6 eq.	3 or 6 eq	THF or Et_2O	0 (**11a**)
2	EtMgCl (6 eq.)	6 eq.	8 eq.	Et_2O	32 (**11b**)
3	*i*-PrMgCl (6 eq.)	6 eq	8 eq	THF	47 (**11c**)
4	*t*-BuMgCl (6 eq.)	3 eq	3 eq	Et_2O	47 (**11d**)

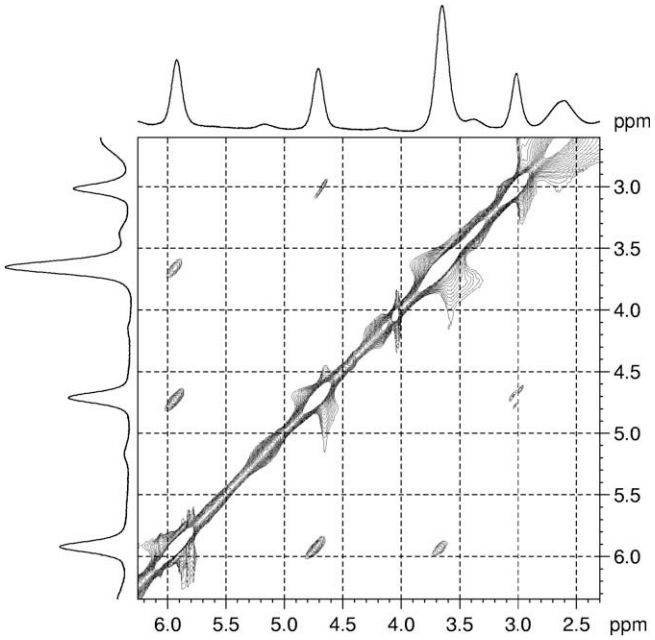


Fig. 5. Part of the ^{1}H NOESY spectrum of **11d**, recorded in C_6D_6 with a mixing time of 50 ms, displaying cross-peaks between the vinylic proton resonances mutually and between the vinylic proton resonances and their respective neighbours.

substituent (**11c**) shows very similar results (see Table 6 in experimental part). The solid-state ^{119}Sn MAS spectrum of the compound with the ethyl substituent (**11b**) exhibits three isotropic ^{119}Sn chemical shifts at 145 (broad signal), −7 and −9 ppm, assigned respectively to Sn–Cl, Sn–Et (transmetallation) and allyltin **11b**. These samples were used for assessing the stereochemical course of the reaction with benzaldehyde.

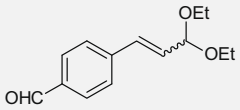
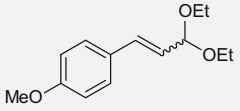
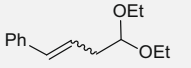
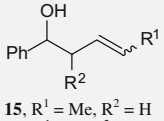
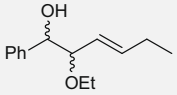
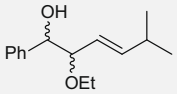
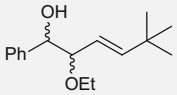
2.3. Assessment of the reactivity of the supported vinyltins and allyltins

The results reported in Table 7 focus on the use of vinyltins in Stille cross-coupling reactions and of allyltins in Lewis acid assisted reactions on aldehydes.

The reactions performed with vinyl- or allyltin reagents grafted to cross-linked polystyrene afford very similar results, both in terms of yields and selectivity, when compared to reactions involving tributyltin analogues in homogeneous solution.

The experimental conditions used in solution for the vinyltributyltin derivatives can in general be extrapolated to supported analogues, resulting in similar yields, but with the advantage of minimizing pollution of final products by tin residues [9–11]. With supported crotyltins we have already observed a slower 1,3–metallotropy when compared to crotyltributyltin [25], and in the case of α-substituted γ-ethoxyallyltins, their poor ability to give a 1,3-metallotropy due to the stabilization occurring in the *Z*-isomer, possibly because of coordination expansion of the tin atom by an oxygen one, results in a regioselective reaction affording the mono-protected α-glycols. Comparison of the reaction using the supported allyltin with its analogue in solution reveals that the diastereoselectivity remains nearly unaffected. The *anti*-isomer was obtained when the allyl unit contains a bulky α-substituent, while a *syn* preference remains the major pathway when this

Table 7
Reactivity of supported vinyltins and allyltins.

Entry	Substrate	Reagent	Conditions	Product	Yield or (conversion)[a] (%)	Yield (%)[b]
1	*p*-Br–C_6H_4–CHO	**5**	$Pd(PPh_3)_4$, toluene 110 °C, 40 h		(100)[10]	65[16]
2	*p*-Br–C_6H_4–OMe	**5**	$Pd(PPh_3)_4$, toluene 110 °C, 40 h		(78)[10]	67
3	Br–Ph	**7**	$Pd(PPh_3)_4$, toluene 110 °C, 40 h		49	85[17a]
4	Ph–CHO	**9**	$InCl_3$, CH_3CN	 **15**, R^1 = Me, R^2 = H **+ 16**, R^1 = H, R^2 = Me	**15** = (63) {*Z/E:* 72/28} **+ 16** = (9) {*syn/anti*: 99/1}	**15** = 32 {*Z/E:* 60/40} **+ 16** = 47 {*syn/anti*: 84/16}[25]
5	Ph–CHO	**11b**	$BF_3.OEt_2$, CH_2Cl_2, 2 h−78 °C		(100) {*syn/anti*: 73/27}	82[33]{*syn/anti*: 72/28}
6	Ph–CHO	**11c**	$BF_3.OEt_2$, CH_2Cl_2, 2 h−78 °C		(100) {*syn/anti*: 21/79}	97[33]{*syn/anti*: 19/81}
7	Ph–CHO	**11d**	$BF_3.OEt_2$, CH_2Cl_2, 2 h−78 °C		(100) {*syn/anti*: 2/98}	92[33]{*syn/anti*: 3/97}

[a] Reactions carried out with supported vinyltins or allyltins, values in brackets are percentage conversions based on initial amounts of the supported organotin reagent.
[b] Reactions carried out with the tributyltin analogues.

α-substituent is an ethyl group. These results have been previously rationalized by a competition between synclinal and antiperiplanar transition states [31].

3. Conclusion

The results reported in this work are highly promising because three original elements of information could be obtained:

(1) Among the synthetic methods used in solution, the hydrostannation of alkynes appears reasonably straightforward for the synthesis of supported vinyltins. The same holds for the reaction of organomagnesium or organozinc reagents with supported organotin halides. Unfortunately, the use of much more complex reagents like alkylcyanocuprates to modify functional vinyltin, still requires major improvements for an efficient preparation of the desired precursors. The possibility to prepare supported stannylanions appears to be new and should allow the synthesis of promising functionalized targets;

(2) HRMAS NMR constitutes an invaluable tool to identify functional groups linked to tin, for the determination of their structures as well as for determining semi-quantitatively the relative amounts of species or even isomers generated.

(3) Solid-state grafted vinyltins and allyltins display roughly the same reactivity and diastereoselectivity patterns as their soluble tributyltin analogues; since pollution by tin residues has been shown to minimized to about 5–20 ppm, supported organotin reagents in general should afford interesting potentials in environment friendly organic synthesis, especially when the organotin reagents are required in a late synthesis step.

4. Experimental

4.1. General remarks

Starting materials were purchased from commercial suppliers and used without further purification. Di-*n*-butyltin dichloride, tri-*n*-butyltin chloride and tri-*n*-butyltin hydride were obtained from Chemtura (Bergkamen). The polystyrene-divinylbenzene matrix (Amberlite XE-305) was purchased from Interchim. THF was distilled from sodium-benzophenone, toluene from sodium and cyclohexane from CaH_2 prior to use. TLC analyses were achieved on silica-coated plates (Merck Kieselgel $60F_{254}$).

4.2. NMR measurements

Solution NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300.13 MHz for ^1H, 75.47 MHz for ^{13}C and 111.92 MHz for ^{119}Sn or on a Bruker ARX 400 spectrometer operating at 400.13 MHz for ^1H, 100.62 MHz for ^{13}C and 149.21 MHz for ^{119}Sn nuclei. Chemical shifts are given in ppm as δ values related to tetramethylsilane (^1H, ^{13}C) or tetramethyltin (^{119}Sn) and scalar coupling constants are given in Hz.

HRMAS NMR spectra were recorded on a Bruker Avance 2 500 operating at 500.08, 125.75 and 186.48 MHz for ^1H, ^{13}C and ^{119}Sn nuclei, respectively, or on a 700 MHz Bruker Avance 2 spectrometer operating at 700.13, 176.05 and 261.08 MHz, respectively, each involving a dedicated Bruker $^1H/^{13}C/^{119}Sn$ HRMAS probe equipped with gradient coils. Sample rotors were filled with *ca.* 15 mg of resin beads, swollen in approximately 80 μl of $CDCl_3$ or C_6D_6; magic angle spinning rate is *ca* 4 kHz. ^1H and ^{13}C chemical shifts were determined from the residual solvent signal (7.26 and 77.0 ppm for $CDCl_3$ and 7.15 and 128.0 ppm for C_6D_6 respectively). ^{119}Sn NMR measurements were referenced to Ξ = 37.290665 MHz [34].

4.3. Organotin synthesis procedures and characterization

4.3.1. Dibutylphenyltin hydride

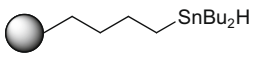
Dibutylphenyltin hydride was obtained by reduction of the corresponding iodide according to the literature [8].

4.3.2. Poly[4-(di-n-butylhalogenostannyl)butyl]styrene compounds **3a-c**

The supported reagents were obtained according to literature procedures by electrophilic cleavage of the supported phenyltin analogue **2.**

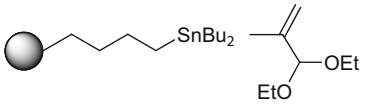
^{119}Sn MAS NMR: data: **2:** −43 ppm; **3a**: 146 ppm; **3b:** 130 ppm; **3c**: 80 ppm

4.3.3. Poly[4-(di-n-butylhydridostannyl)butyl]styrene, **4**



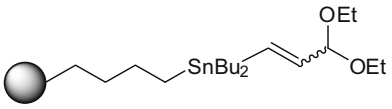
A solution of $LiAlH_4$ in THF (2.4 M, 1.69 mL, 4.06 mmol, 5 eq.) was added dropwise under argon to a suspension of poly[4-(di-*n*-butyliodostannyl)butyl]styrene **3c** (0.7 g, 0.7 mmol) in dry THF (8 mL) and the resulting mixture was stirred at 40 °C for 2.5 h in the dark. The grafted material was successively washed, under argon, with THF (5 × 10 mL), absolute ethanol (2 × 10 mL) and dried under vacuum (0.5 mbar) at 60 °C for 2 h. Compound **4** was obtained as a white resin. $\delta^{119}Sn$ MAS NMR: −90 ppm.

4.3.4. Poly{4-[di-n-butyl-(3,3-diethoxyprop-1-en-2-yl)stannyl]butyl} styrene, **5a**



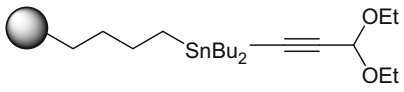
To a suspension of compound **3c** (500 mg, 0.55 mmol) in dry THF (5 mL) at −78 °C, a solution of 3,3-diethoxyprop-1-en-2-yllithium in THF (10 mL, 1.1 mmol), obtained from 2-bromo-3,3-diethoxyprop-1-ene and *t*-BuLi, was added under argon. The resulting mixture was then stirred at −78 °C for 3 h and allowed to warm up slowly to room temperature in 2 h. Compound **5a** was successively washed with a mixture of THF/water (1:1 v/v, 20 mL), THF (6 × 20 mL), absolute ethanol (4 × 20 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h.

4.3.5. Poly{4-[di-n-butyl-(3,3-diethoxyprop-1-en-1-yl)stannyl] butyl}styrene **5b**



To a suspension of grafted derivative **4** (1.65 g, 1.65 mmol) in dry THF (28 mL), 3,3-diethoxypropyne (0.356 mL, 2.48 mmol) and a catalytic amount of AIBN were added under argon. The resulting mixture was then stirred at 110 °C for 3 h. The insoluble material was successively washed with a mixture of THF/water (1:1 v/v, 20 mL), THF (6 × 20 mL), absolute ethanol (4 × 20 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h. Compound **5** was obtained as a white resin (1.9 g).

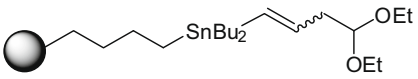
4.3.6. Poly{4-[di-n-butyl-(3,3-diethoxyprop-1-yn-1-yl)stannyl]butyl} styrene ***6***



To a suspension of grafted derivative **3c** (500 mg, 0.55 mmol) in dry THF (5 mL) at −78 °C, a solution of 3,3-diethoxyprop-1-yn-1-yllithium in THF (10 mL, 1.1 mmol), obtained from 3,3-diethoxypropyne and *n*-BuLi, was added under argon. The resulting mixture was then stirred at −78 °C for 3 h and allowed to warm up slowly to room temperature in 2 h. Compound **6** was successively washed with a mixture of THF/water (1:1 v/v, 20 mL), THF (6 × 20 mL), absolute ethanol (4 × 20 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h.

^{1}H HRMAS NMR ($CDCl_3$): 0.92 (CH_2, α Sn), 1.05 (CH_2, δ Sn), 1.22 (CH_3), 1.36 (CH_2, γ Sn), 1.61 (CH_2, β Sn), 3.60 (1H, CH_2), 3.77 (1H, CH_2), 5.25 (1H, CH) ; ^{13}C HRMAS NMR ($CDCl_3$): 11.2 (CH_2, α Sn), 13.8 (CH_2, δ Sn), 15.2 (CH_3), 26.7 (CH_2, γ Sn), 28.9 (CH_2, β Sn), 60.7 (CH_2O), 89.2 (C, α Sn), 91.4 (CH), 104.9 (C, β Sn); ^{119}Sn HRMAS NMR ($CDCl_3$): −64.5 ppm.

4.3.7. Poly{4-[di-n-butyl-(4,4-diethoxybut-1-en-1-yl)stannyl]butyl} styrene ***7***

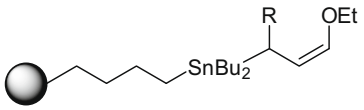


4.3.8. Poly[4-(di-n-butyl-crotyl-stannyl)butyl]styrenes ***9*** *(+* ***10****)*

4.3.8.1. Preparation using Barbier conditions. To a suspension of **3c** (500 mg, 0.55 mmol) and zinc powder (30 mesh, 2.75 mmol) in dry THF (10 mL), crotylchloride (*E/Z*: 85/15 ; 2.75 mmol) was added and the resulting mixture was stirred at 45 °C for 18 h. The insoluble material was successively washed, under argon, with THF/water (1:1 v/v, 10 mL), THF (6 × 10 mL), absolute ethanol (4 × 10 mL) and dried under vacuum (0.5 mbar) at 60 °C for 2 h.

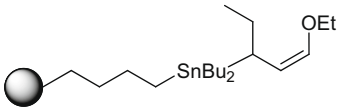
4.3.8.2. Preparation using a supported stannylanion. To a suspension of grafted organotin hydride **4** (500 mg, 0.5 mmol) in dry THF (10 mL) at 0 °C, was added, under argon, a solution of lithium diisopropylamide (1 M in THF, 0.5 mmol). The resulting mixture was then stirred at 0 °C for 30 min; subsequently, crotylchloride was added (*E/Z*: 85/15, 50 μL, 0.5 mmol). The resulting mixture was then stirred at 0 °C for 30 min, thereafter 18 h at room temperature. The insoluble material was successively washed with a mixture of THF/water (1:1 v/v, 20 mL), THF (6 × 20 mL), absolute ethanol (4 × 20 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h.

4.3.9. Synthesis of supported α-substituted γ-alkoxyallyltins ***11b–d***



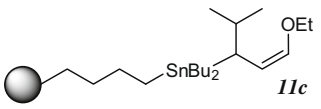
To a suspension of copper(I) cyanide (3.0 or 6.0 equiv.) in dry THF (10 mL), a solution of organometallic reagent (RM) in diethyl ether (3.0 or 6.0 equiv.) was added, at −78 °C, under argon. The reaction mixture is allowed to warm up until organocopper is formed and then cooled down again to −78 °C. The reaction mixture was stirred for 15 min and $BF_3{\cdot}OEt_2$ (4.0 or 8.0 equiv.) was added. After stirring for 20 min, the reaction mixture was transferred through a canula onto **5b**(*E+Z*) (1 equiv., 440 mg, 0.5 mmol) and the resulting mixture was stirred at −50 °C for 17 h. The reaction mixture was hydrolyzed with a saturated solution of $NaHCO_3$ and, after filtration, the insoluble material was successively washed with a mixture of THF/aqueous NH_4Cl (1:1 v/v, 10 mL), THF (6 × 10 mL), absolute ethanol (4 × 10 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h.

4.3.9.1. Poly{4-[di-n-butyl(1-ethoxy-penten-3-yl)stannyl]butyl}styrene 11b.

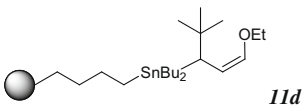


δ^{119}Sn MAS NMR: −29 ppm.

4.3.9.2. Poly{4-[di-n-butyl(1-ethoxy-4-methyl-penten-3-yl)stannyl]butyl}styrene 11c andPoly{4-[di-n-butyl(1-ethoxy-4,4-dimethyl-penten-3-yl)stannyl]butyl}styrene 11d.



11c



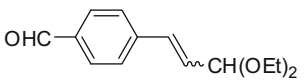
11d

4.4. Stille cross-coupling involving supported vinyltins and alkynyltins

4.4.1. General procedure for the Stille cross-coupling reaction

In an oven-dried Schlenk flask compound **5**, **6** or **7** (1.1 equiv.), the halide aryl (1.0 equiv.), catalyst (0.05 equiv.) and dry solvent, as mentioned in the Table 7, were successively added under argon. The reaction mixture was then heated up to reflux temperature. The insoluble material was washed with THF (6 × 10 mL) and the filtrate was concentrated under vacuum. The resulting crude residue was analyzed by GC, and was subsequently purified by column chromatography using silica gel. (Petroleum ether/AcOEt: 9/1). Otherwise, the resulting insoluble material was washed with absolute ethanol (4 × 10 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h.

4.4.2. 4-[3,3-diethoxyprop-1-en-1-yl]benzaldehyde, ***12****.*



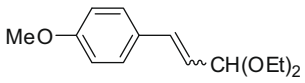
HRMS (EI) Calc. for $C_{14}H_{18}O_3$: 234.1256. Found: 234.1256.

isomer *E*: ^{1}H NMR (400 MHz; $CDCl_3$): 1.26 (t, 3H, ^3J = 7), 3.58 (dq, 2H, ^2J = 9.4, ^3J = 7), 3.72 (dq, 2H, ^2J = 9.4, ^3J = 7), 5.10 (dd, 1H, ^3J = 4.9, ^3J = 1.2), 6.36 (dd, 1H, ^3J = 16.1, ^3J = 4.9), 6.78 (dd, 1H, ^3J = 16.1, ^4J = 1.2), 7.55 (d, 2H, ^3J = 8.0), 7.84 (d, 2H, ^3J = 8.0), 9.99 (s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): 15.3 (2C), 61.3 (2C), 100.9, 129.6 ($2C_{Ar}$), 130.1 ($2C_{Ar}$), 130.5, 131.7, 135.8 (C^{IV}_{Ar}), 142.3 (C^{IV}_{Ar}), 191.6. MS (EI): *m/z* = 234 (13), 206 (3), 205 (4), 189 (100), 177 (3), 163 (26), 161 (47), 160 (13), 147 (8), 135 (14), 133 (62), 132 (30), 131 (39), 115 (42), 105 (25), 103 (40), 91 (11), 79 (9), 77 (30), 75 (7), 55 (25).

isomer *Z*: ^{1}H NMR (400 MHz; $CDCl_3$): 1.22 (t, 3H, ^3J = 7.1), 3.56 (dq, 2H, ^2J = 9.5, ^3J = 7.1), 3.67 (dq, 2H, ^2J = 9.5, ^3J = 7.1), 5.19 (dd,

1H, ^3J = 7.3, ^4J = 1.1), 5.93 (dd, 1H, ^3J = 12.0, ^3J = 7.3), 6.68 (bd, 1H, ^3J = 12.0), 7.55 (d, 2H, ^3J = 8.0), 7.86 (d, 2H, ^3J = 8.0), 10.0 (s, 1H); ^{13}C (100.62 MHz, $CDCl_3$): 15.2 (2C, CH_3), 60.6 (2C, CH_2O), 97.6, 129.6 (2C, CH_{Ar}), 129.7 (2C, CH_{Ar}), 131.5 (Ar–CH=), 132.1, 135.3 ($C^{I-V}Ar$), 142.4 ($C^{IV}Ar$), 191.7. MS (EI): *m*/*z* = 234 (11), 206 (5), 205 (10), 189 (100), 177 (4), 163 (26), 161 (52), 160 (15), 147 (8), 135 (12), 133 (68), 132 (32), 131 (47), 115 (49), 105 (27), 103 (53), 91 (12), 79 (10), 77 (36), 75 (14), 55 (31), 47 (10).

4.4.3. 1-[3,3-diethoxyprop-1-en-1-yl]-4-methoxybenzene, **13**

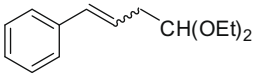


HRMS (EI) Calc. for $C_{14}H_{20}O_3$: 236.1412. Found: 236.1412.

Isomer *E*: ^{1}H NMR (400 MHz; $CDCl_3$): 1.24 (t, 6H, ^3J = 7.1, CH_3), 3.64 (dq, 2H, ^2J = 9.5, ^3J = 7.1), 3.64 (dq, 2H, ^2J = 9.5, ^3J = 7.1), 3.83 (s, 3H), 5.06 (d, 1H, ^3J = 5.3, ^4J = 1.1), 6.09 (d, 1H, ^3J = 16.1, ^3J = 5.3), 6.67 (bd, ^{1}H, ^3J = 16.1), 6.87 (d, 2H, ^3J = 8.4), 7.36 (d, 2H, ^3J = 8.4). ^{13}C NMR (100.62 MHz, $CDCl_3$): 15.3 (2C), 55.3, 61.0 (2C), 101.8, 113.9 ($2C_{Ar}$), 124.5, 128.2 ($2C_{Ar}$), 132.4, 154.1 (C^{IV}_{Ar}), 159.6 (C^{IV}_{Ar}). MS EI: *m*/*z* = 236 (16), 207 (29), 191 (100), 165 (24), 163 (36), 161 (12), 145 (17), 135 (24), 131 (12), 121 (13), 103 (9), 91 (12), 55 (15).

Isomer *Z*: ^{1}H NMR (400 MHz; $CDCl_3$): 1.22 (t, 6H, ^3J = 7.1), 3.45 (dq, 2H, ^2J = 9.6, ^3J = 7.1), 3.53 (dq, 2H, ^2J = 9.6, ^3J = 7.1), 3.83 (s, 3H), 4.83 (dd, 1H, ^3J = 5.1, ^4J = 1.2), 6.23 (dd, ^3J = 13.4, ^4J = 1.2), 6.54 (dd, 1H, ^3J = 13.4, ^3J = 5.1), 6.88 (d, 2H, ^3J = 8.4), 7.35 (d, 2H, ^3J = 8.4). ^{13}C NMR (100.62 MHz, $CDCl_3$): 15.3 (2C), 55.3, 60.9 (2C), 102.3, 113.9 ($2C_{Ar}$), 128.2 (2 C_{Ar}), 134.2, 144.7, 154.1 (C^{IV}_{Ar}), 159.6 (C^{IV}_{Ar}). MS (EI): *m*/*z* = 236 (16), 207 (33), 191 (100), 165 (28), 163 (39), 161 (14), 145 (21), 135 (27), 131 (12), 103 (10), 91 (15), 55 (20).

4.4.4. [(1E)-4,4-diethoxybut-1-en-1-yl]benzene, **14**



Isomer *E*: ^{1}H NMR (400 MHz; $CDCl_3$): 1.24 (t, 6H, ^3J = 7), 2.56 (ddd, 2H, ^4J = 1.4, ^3J = 5.7, ^3J = 7.1); 3.56 (dq, 2H, ^3J = 7.0, ^2J = 9.5), 3.70 (dq, 2H, ^3J = 7.0, ^2J = 9.5), 4.59 (t, 1H, ^3J = 5.7), 6.21 (dt, 1H, ^3J = 15.9, ^3J = 7.1), 6.50 (dt, 1H, ^3J = 15.9, ^3J = 1.4), 7.21-7.37 (m, 5H). ^{13}C NMR (100.62 MHz, $CDCl_3$): 15.3 (2C), 37.8 , 61.4 (2C), 102.6, 125.3, 126.1 ($2C_{Ar}$), 127.1 (C_{Ar}), 128.5 (2C, Ar), 132.4, 137.6 ($C^{IV}Ar$). MS CI(NH_3): *m*/*z* = 238 (2), 192 (4), 175 (57), 163 (32), 146 (100), 103 (29).

Isomer *Z*: ^{1}H NMR (400 MHz; $CDCl_3$): 1.21 (t, 6H, ^3J = 7.0), 2.69 (ddd, 2H, ^4J = 1.9, ^3J = 5.9, ^3J = 7.3), 3.52 (dq, 2H, ^3J = 7.0, ^2J = 9.5), 3.65 (dq, 2H, ^3J = 7.0, ^2J = 9.5), 4.6 (t, 1H, ^3J = 5.9), 5.73 (dt, 1H, ^3J = 12.0, ^3J = 7.3), 6.55 (dt, 1H, ^3J = 12.0, ^4J = 1.9), 7.21–7.37 (m, 5H). ^{13}C NMR (100.62 MHz, $CDCl_3$): 15.3 (2C), 33.3 ($CH–CH_2$), 61.2 (2C), 102.4, 126.7, 128.1 ($2C_{Ar}$), 128.2 ($1C_{Ar}$), 128.8 ($2C_{Ar}$), 130.9, 137.3 (C^{IV}, Ar). MS CI(NH_3): *m*/*z* = 238 (2), 192 (16), 175 (64), 163 (38), 146 (100), 103 (37).

4.5. Allylation of benzaldehyde by supported allyltins

4.5.1. Allylation of benzaldehyde by supported crotyltins

To a suspension of supported material (1.0 g, 1.1 mmol) in MeCN (10 mL), aldehyde (1.0 mmol) and $InCl_3$ (1.0 mmol) were added. The reaction mixture was stirred for 18 h at 25 °C and then quenched with HCl (0.1 M, 10 mL). The crude insoluble material was filtered and washed with diethyl ether (6 × 30 mL) and then with THF (6 × 30 mL). The filtrate was extracted with diethyl ether and washed with brine (50 mL), dried over $MgSO_4$ and concentrated in vacuum.

Compounds **15-*E***, **15-*Z***, **16-*syn*** and **16-*anti*** have been previously characterized [25,35].

4.5.2. Allylation of benzaldehyde by supported γ-ethoxyallyltins

To a suspension of grafted derivative **11** (150 mg) in dry CH_2Cl_2 (2 mL), benzaldehyde (0.014 mL, 0.14 mmol) and, dropwise at −78 °C, a solution of $BF_3{\cdot}OEt_2$ (0.076 mL, 0.6 mmol) were added under argon. The reaction mixture was stirred at −78 °C for 2 h and was then quenched with a mixture of THF/aqueous $NaHCO_3$ (1:1 v/v). The insoluble material was filtered and washed with THF (6 × 10 mL). The filtrate was extracted with diethyl ether (3 × 20 mL), washed with brine (50 mL), dried over $MgSO_4$ and concentrated under vacuum. The resulting crude residue was analyzed by GC. Otherwise, the resulting insoluble material was washed with absolute ethanol (4 × 10 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h.

The characterization of compounds **17–19** has been previously reported including the assignment of the *syn* or *anti* configuration of the homoallylic alcohols [33].

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