Bull Soc Chim Fr (1997) 134, 959-967

Synthesis of monoorganotins and use as versatile reagents for organic synthesis

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(Received 4 November 1997; accepted 18 December 1997)

Summary — The direct and quantitative preparation of monoorganotins **2**, **3**, **4** and **11** starting from Lappert's stannylene **1** represents a general access to a new class of organotin reagents. Their reactivity and versatility in the field of organic synthesis is highlighted. The influence of the substituents bound to the tin atom is shown for various reactions such as nucleophilic addition onto carbonyl compounds, radical transfer of functionalized allylic moieties and coupling reactions catalysed by transition metals.

stannylene / monoorganotin / radical allylic transfer / coupling reaction / palladium

Résumé — Synthèse de monoorganoétains, nouveaux réactifs pour la synthèse organique. La préparation quantitative des monoorganoétains **2**, **3**, **4** et **11** à partir du stannylène de Lappert **1** représente une voie d'accès directe et générale à une nouvelle famille de réactifs organostanniques. Ceux-ci ont montré une réactivité variée pour la synthèse organique. L'importance de la nature des substituants liés à l'étain est démontrée pour des réactions telles que l'addition nucléophile sur des composés carbonylés, le transfert allylique par voie radicalaire et les réactions de couplage catalysées par le palladium.

stannylène / monoorganoétain / transfert allylique radicalaire / réaction de couplage / palladium

Introduction

There is a need in searching new methodologies for organic synthesis avoiding polluting or toxic side products. Organotin chemistry is particularly concerned by these environmental considerations due to the well-known toxicity of triorganotin residues [1]. In addition to catalytic organotin methods or polymer-supported organotin reagents [2], monoorganotins represent an attracting alternative to the usual tetraorganotin chemistry in the sense that after work-up tin residues would be inorganic ones.

Interestingly, the chemistry of monoorganotins has not really been exploited so far, mainly due to their high reactivity and to the difficulties in finding general preparation methods. Nevertheless has been reported the in situ preparation of transient monoorganotins, especially allyltrihalogenotins, in order to take advantage of their unique reactivity. Our initial approach has been the direct synthesis of such organotins by the direct reaction of a stannous halide with allylic bromides [3]. Nevertheless the lack of reactivity of stannous halides made us decide to use more active low-valent tin species, such as stannylenes.

Synthesis of monoorganotins

The first stannylene has been prepared more than 40 years ago [4], and they are known to be particularly reactive towards oxidative addition. But the choice of stannylenes is restricted by several factors, due to the envisaged uses of the monoorganotins in organic synthesis:

(i) The stannylene must be readily available and stable enough to avoid premature polymerization, which is a common drawback encountered with reactive low-valent tins.

(ii) Its reactivity must be as general as possible, giving the corresponding monoorganotins in quantitative yields. Moreover, the conditions must prevent unwanted redistribution reactions which could make the reaction unselective.

(iii) The Sn–heteroatom bonds must be reactive enough to be easily hydrolysed during the work-up, in order to produce removable inorganic tin side products.

We were then interested in the use of bis-[(*N*,*N*-bis trimethylsilyl)amino]stannylene **1** firstly described by Lappert and Zuckerman [5]. The preparation of this stable monomeric stannylene can scale up to 100 g, and

* Correspondence and reprints

the bulky trimethylsilylamino ligands seemed to offer a good balance between the stability towards polymerization and the reactivity with halogenated substrates. Stannylene **1** has been successfully used for preparing various functionalized monoallyltins **2** (fig 1, table I) in quantitative yields. Contrarily to stannous halides, **1** achieved this reaction even with allylic chlorides **2a** and **2c** in particularly mild conditions. Moreover this reaction is no more limited to the functionalized substrates capable of stabilizing the monoallyltin by an intramolecular five-membered coordination of the tin atom (**2e**, **2g**). Finally, the dramatic changes observed in the reaction times, to carry on the reaction to completion, upon the nature of the halogen (**2a** vs **2b**, **2c** vs **2d**) are indicative of a good chemoselectivity of the stannylene **1** when used with plurifunctional substrates.

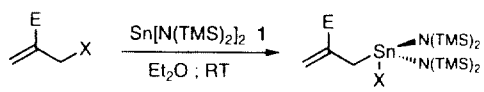


Fig 1.

Table I. Reaction of **1** with allylic halides.

E	*X*	*Time (h)*	*Allyltin*
H	Cl	48	**2a**
H	Br	0.5	**2b**
Cl	Cl	24	**2c**
Cl	I	<0.1	**2d**
CO_2Et	Br	0.25	**2e**
CN	Br	0.5	**2f**
COMe	Br	0.25	**2g**
Ph	Br	0.5	**2h**

The reaction with allylic substrates substituted at the 3-position led to monoorganotins **3** without any change in the reactivity order (fig 2, table II). It proceeds in all cases with a total retention of the (*Z*) double-bond configuration.

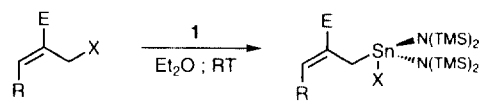


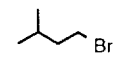
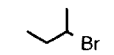
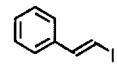
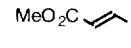
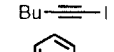
Fig 2.

Table II. Reaction of **1** with allylic halides.

R	*E*	*X*	*Time (h)*	*Allyltin*
Me	H	Cl	48	**3a**
Me	CO_2Et	I	<0.1	**3b**
Ph	CO_2Et	Br	0.5	**3c**
CO_2Me	CO_2Me	Br	0.25	**3d**
*i*Pr	CN	Br	0.5	**3e**

Finally, it is worth noting that the preparation of monoorganotins starting from stannylene **1** is not restricted to allylic ones, but may be virtually applied to all types of organic groups including alkyl (**4a–c**), alkenyl (**4d**, **4e**), alkynyl (**4f**) and aromatics (**4g**) (table III).

Table III. Reaction of **1** with organic halides.

R	*Solvent*	*Time (h)*	
$nC_{10}H_{21}I$	THF	<0.1	**4a**
	THF	1	**4b**
	Et_2O	12	**4c**
	Benzene	24	**4d**
	Benzene	3	**4e**
	Benzene	0.25	**4f**
	Benzene	24	**4g**

Mechanism of the reaction

Lappert put forward a radical chain mechanism to explain stannylene insertion [6], in which a free carbon centered radical was generated. This was in fact extrapolated to stannylene **1**, from ESR studies of the insertion of the alkyl analog $Sn[CH(SiMe_3)_2]_2$ **5**. However, theoretical calculations have shown that the radical pathway is not necessarily the most favoured, depending on the nature of the substituents of the tin atom [7]. Furthermore, considering the total retention of the (*Z*) stereochemistry of the double bond of **3a** while the (*E*) isomer would have been thermodynamically preferred, we decided to reinvestigate the insertion reaction mechanism.

As the formation of a carbon centered radical cannot be ruled out simply from the absence of isomerized (*E*) crotyltin, due to the low isomerization rate constant ($\approx 10^2$ s^{-1}), we decided to use the well-known (2-phenylcyclopropyl)methyl clock radical (fig 3). The rearrangement rate constant is largely faster than the diffusion control [8], then going through the cyclopropylmethyl radical **A** would lead to the monoorganotin **7**. In fact, reaction of the alkyl bromide **6** with

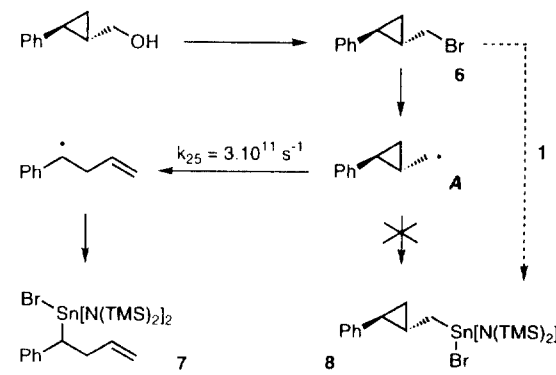


Fig 3.

stannylene **1** led to the exclusive formation of the cyclopropylmethyl tin **8**, which clearly indicates that the insertion does not proceed via the radical chain proposed above.

There is a duality in the character of stannylene **1** which is considered as a good Lewis acid [9] and may act as well as a base, however, its nucleophilcity is less pronounced than that of **5** [10]. Thus, one may imagine either a one-step synchronous mechanism already proposed for stannous bromide [7] or a nucleophilic attack of **1** onto the halogenated substrate. Following this, the controlled synthesis of allenyl tin **9** starting from propargyl bromide would account for the nucleophilic substitution, occurring with or without transposition depending on the experimental conditions (fig 4).

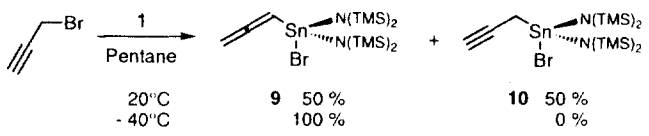


Fig 4.

Other factors may intervene in the control of the stereochemistry. One of the major is related to the Lewis acid character of the tin atom in the obtained monoorganotins, and the ability to extend its coordination sphere. A striking example is given by (*Z*) or (*E*) 3-iodopropenoic acid methyl ester which gave uniformly the (*Z*) vinyl tin **4e** due to the stabilization brought about by the intramolecular coordination of the tin atom (fig 5).

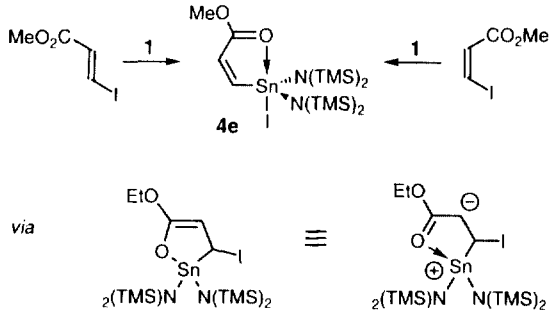


Fig 5.

Extension to other substrates

Considering that the reaction occurred via a nucleophilic mechanism, we then decided to check whether other leaving groups than halogens would be suitable for the insertion of stannylene **1**. The reaction occurred indeed, in quantitative yields with allylic sulfone, xanthate or acetate (fig 6). The ability of **1** to achieve insertion in a C–S or C–O bond considerably broadens the scope of this reaction, as acetates are far more easily accessible from the corresponding alcohols than halogenated derivatives can be.

Interestingly, when the reaction is performed with α-substituted acetates, this led exclusively to the

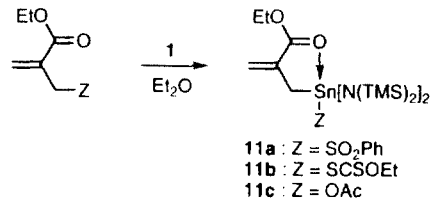


Fig 6

transposed allyltins **11d–f** with the same (*Z*) stereochemistry of the double bond as has been obtained previously with halogenated substrates (fig 7).

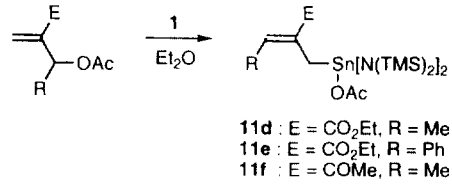


Fig 7.

Stannylene **1** then offers a direct and general route to a new class of monoorganotin reagents which may be useful for synthetic purposes for the following reasons:

(i) The reaction is quantitative and selective, as insertion of stannylene **1** led exclusively to the formation of the monoalkylation products without a redistribution side reactions. This avoids isolation and purification of monoorganotins.

(ii) The monoorganotin itself is stable enough to be handled in air and stored simply protected from moisture. This is due to the peculiar nature of silyl amino ligands bound to tin, which possess a stronger Sn–N bond than usual amino ligands. As a consequence, we did not observe exchange of ligands as has been shown with monoorganotrihalogenotins [11].

(iii) The monoorganotin nevertheless remains sensitive enough ot hydrolysis, which should greatly facilitate work-up procedures and elimination of tin side products.

The three reactions given below highlight how monoorganotins **2–4** and **11** can be useful in organic synthesis. Special attention is given to the nature of the ligands and the tin coordination state, which are the main factors controlling the reaction outcome.

Nucleophilic addition onto C=X π bonds

The easiness in the synthesis of the various monoallyltins **2**, **3** with stannylene **1** prompted us to check whether they could be of interest for nucleophilic alkylation of carbonyl compounds. Such reaction is particularly well documented indeed, but in contrast with other allylmetal reagents [12], allyltrialkyltins suffer from a lack of reactivity which demands strenuous conditions or activation with Lewis acids [13]. An elegant solution to this problem consists in forming an activated organotin in situ by a redistribution reaction between the tetraorganotin reagent and $SnCl_4$ [14]. For our part we have already demonstrated the advantage in using

stable monoallyltrihalogenotins **12** for this reaction, as the Lewis acidity of the organotin reagent is enough to activate the carbonyl compound and allows the reaction to proceed under particularly mild conditions [15].

Allyltins **2e** reacted readily with aldehydes leading to the expected α-methylene-γ-lactones **13** in similar yields to the reactions performed with allyltrihalogenotins **12** (fig 8). Moreover these reagents led as well to hydrolysable inorganic tins thus facilitating the purification procedure. Nevertheless, a lenghtening of the reaction times has been observed, presumably due to an increase of the steric hindrance of the tin atom accompanied by a lowering of the acidic character of **2e** compared to **12**.

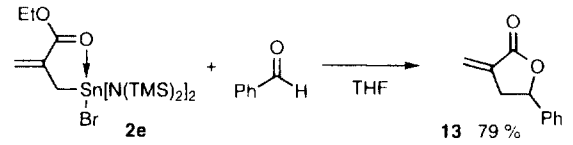


Fig 8.

We also investigated allylation of imines, however in this case monoallyltins were not found to be reactive enough to give allylation products. Nevertheless, the use of reactive silylimine **14** with allyltin **12** led in fair yield to the corresponding α-methylene-γ-lactam **15** (fig 9).

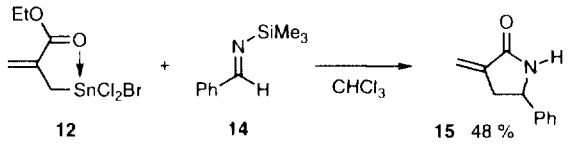


Fig 9.

Radical transfer of the allylic moiety

In contrast with trihalogenomonoallyltins, allyltins **2** derived from Lappert's stannylene exhibited a good propensity for undergoing allylic transfer under radical conditions [16]. In this reaction, the nature of the ligands bonded to the tin atom appeared to be decisive for the control of the radical chain mechanism (fig 10). While trihalogenotin radicals generated from **13** led almost exclusively to the dimerization product (path A), $Br[N(TMS)_2]_2Sn\cdot$ radicals evolved predominantly via the expected radical chain (path B) giving the allylic transfer product **16** in good yield.

A reason accounted for explaining the reversal of the reactivity is the enhancement of the electrophilicity of the $X_3Sn\cdot$ radicals compared to the $R_3Sn\cdot$ ones which render them much more prone to abstract a halogen bonded to the allyltin reagent rather than the halogen of the substrate. On the contrary, theoretical calculations of SOMO energy levels performed with semi-empirical methods (MNDO, AM1, PM3) revealed that the nucleophilicity of the $Br[N(TMS)_2]_2Sn\cdot$ radical remained close to the $R_3Sn\cdot$ one [17]. Another point lies in the reactivity of the halogen–tin bond itself which is believed to be far more reactive in trihalogenoallyltin **13** compared to the bis-amino equivalent **2e**. Indeed kinetic measurements performed with 2D NMR experiments, for halogen exchange reactions, showed that the Sn–X bond was exchanged 200 times more rapidly when using trihalogenotins instead of monoallyltins prepared from Lappert's stannylene [18].

The competition between the two possible routes is highlighted by using allyltins **11a** and **11b** (fig 11). While the xanthyl moiety is capable of being abstracted by a tin-centered radical leading to some dimerization product as well, the acetate ligand does not offer this possibility thus suppressing the side reaction (path A). These results demonstrate how slight changes in the nature of the ligands around the tin atom dramatically

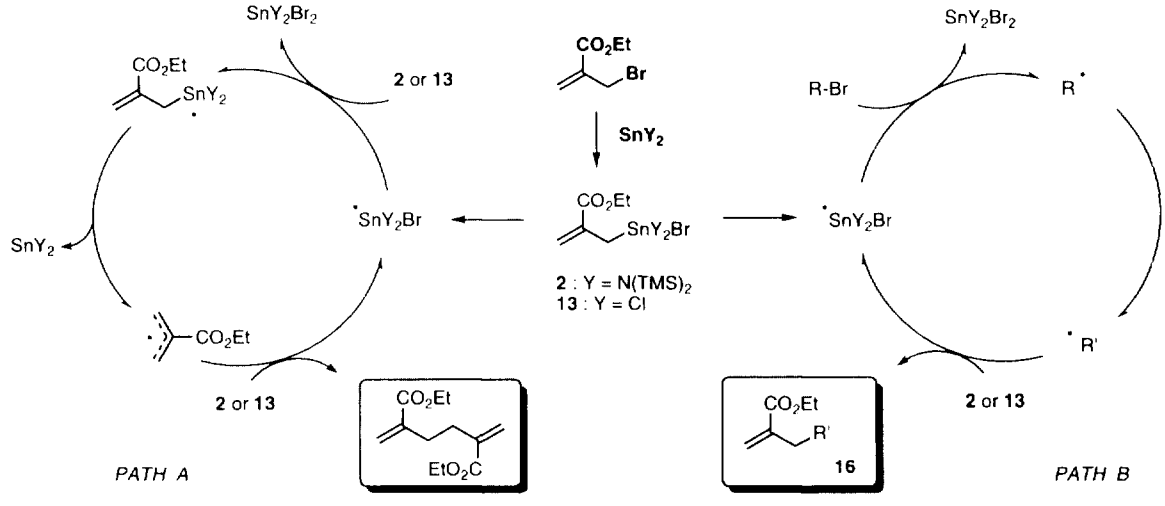


Fig 10.

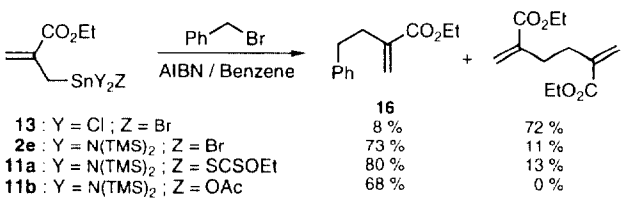


Fig 11.

influence the reactivity of the organotin itself in the radical allylic transfer.

Coupling reactions catalysed by transition metals

The latest application involving monoorganotins concerns an extension of the well-known Stille coupling reaction. During the last decade, this reaction has been essentially investigated with tetraorganotin reagents mainly due to the depleting effect caused by strong electron-withdrawing ligands [19]. Nevertheless, it has been recently reported that an extra coordination of the tin atom could act as a nucleophilic assistance [20]. This led us to investigate whether intramolecularly coordinated allyltins would be activated enough to counterbalance the slowing down of the transmetallation step brought about by halogen bounded to the tin (fig 12). Monoallyltins **2e** and **11a** prepared from stannylene **1** appeared to be the most efficient. Once again replacing

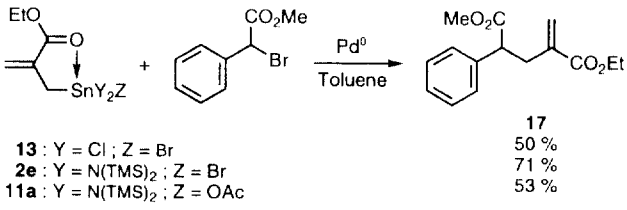


Fig 12.

the halide moiety by an acetate did not change noticeably the outcome of the reaction. It is worth noting that even trihalogenotin **13** was found to be active under palladium-catalysed conditions [21].

We then turned our attention to a general way of producing hypervalent activated organotin reagents by adding TBAF to the corresponding monoorganotins [22]. In contrast with its extensive use in organosilicon chemistry [23], such activation has received little attention in the field of organotin chemistry [24]. The reaction in which the active species are the stannates **A** (fig 13) was found to be effective with all types of monoorganotins, as a consequence of a 'nucleophilic activation' which accelerates efficiently the transmetallation step. It can be pointed out that contrarily to the usual tetraorganotins the coupling reaction of various primary alkyl groups is now achieved in good yields with these monoorganotins.

Conclusion

An evaluation of the residual level of pollution revealed that the allyl transfer products **16** or the coupling products **17** contain around 100 to 200 ppm of tin [25]. This represents at least a lowering with a factor 50 compared with the pollution levels frequently observed when using tetraorganotin reagents. Moreover speciation experiments showed that the nature of the pollution is essentially due to an inorganic tin contamination, which contrarily to other heavy metals is considered to be innocuous.

In conclusion, the direct and quantitative preparation of monoorganotins **2**–**4** and **11** from Lappert's stannylene **1** represents a general route to versatile reagents which avoid syntheses and purification of intermediate tetraorganotins. The adaptability of this method to numerous solvents (except for the halogenated ones) allows 'one-pot' procedures in which the organotin intermediate does not need to be isolated prior to use. Finally, their ability to replace tetraorganotins for various reactions, such as nucleophilic addition, allyl radical transfer, coupling reaction added to their original reactivity, clearly demonstrated their usefulness for synthetic chemists.

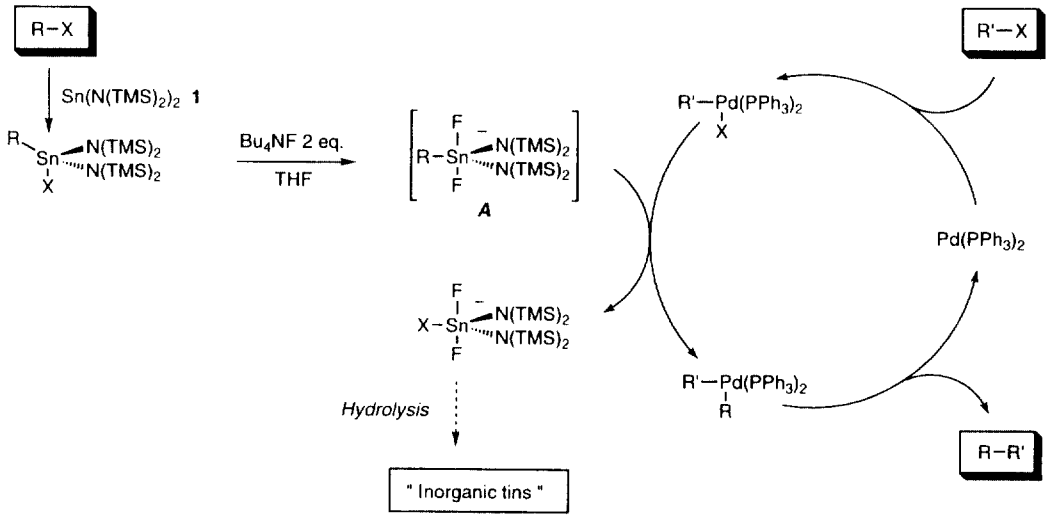


Fig 13.

Experimental section

*General procedure for the preparation of monoorganotin compounds **2–4** and **11***

Bis[*N*,*N*-bis(trimethylsilyl)amino]stannylene **1** (1.00 g, 2.27 mmol) and organic halide (1 equiv) are mixed in anhydrous solvent (10 mL) under an inert atmosphere at *T* °C, until the reaction mixture turns pale yellow. Removal of the solvent afforded the monoorganotins **2–4** and **11** in quantitative yield which are used without further purification.

- *Compound **2a***

Solvent: ethyl ether; temperature: 20 °C; reaction time: 48 h.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.95 (m, 1H), 5.15–5.04 (m, 2H), 2.50 (bd, 2H, *J* 8.3 Hz, $^2J_{Sn-H}$ 103.7 Hz), 0.22 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 132.5, 116.9, 35.8 ($^1J_{Sn-C}$ 603 Hz), 5.6 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −51.2.

- *Compound **2b***

Solvent: ether; temperature: 20 °C; reaction time: 30 min.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.03–5.85 (m, 1H), 5.17–5.07 (m, 2H), 2.58 (bd, 2H, *J* 8.3 Hz), 0.29 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 132.4 ($^2J_{Sn-C}$ 84 Hz), 116.9 ($^3J_{Sn-C}$ 107 Hz), 36.7 ($^1J_{Sn-C}$ 584 Hz), 5.6 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −84.1.

- *Compound **2c***

Solvent: ether; temperature: 20 °C; reaction time: 24 h.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.21 (bs, 1H, $^4J_{Sn-H}$ 35.7 Hz), 5.09 (bs, 1H, $^4J_{Sn-H}$ 27.2 Hz), 2.83 (bs, 2H, $^2J_{Sn-H}$ 91.6 Hz, 0.22 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 139.6, 114.1 ($^3J_{Sn-C}$ 81 Hz), 41.5 ($^1J_{Sn-C}$ 605 Hz), 5.8 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −66.6.

- *Compound **2d***

Solvent: ethyl ether; temperature: 20 °C; reaction time: immediate.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.19 (bs, 1H, $^4J_{Sn-H}$ 40.9 Hz), 5.17 (d, 1H, *J* 1.5 Hz, $^4J_{Sn-H}$ 39.6 Hz), 2.86 (bs, 2H, $^2J_{Sn-H}$ 103.0 Hz), 0.23 (36H, s).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 137.3, 113.9 ($^3J_{Sn-C}$ 81 Hz), 42.4 ($^1J_{Sn-C}$ 532 Hz), 6.3 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −194.0.

IR (KBr) 3 033, 2 955, 1 615, 1 403, 1 252, 899, 858 cm^{-1}.

- *Compound **2e***

Solvent: ethyl ether; temperature: 20 °C; reaction time: 15 min.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.18 (bs, 1H, $^4J_{Sn-H}$ 20.9 Hz), 5.69 (bs, 1H, $^4J_{Sn-H}$ 34.6 Hz), 4.25 (q, 2H, *J* 7.2 Hz), 2.64 (bs, 2H, $^2J_{Sn-H}$ 98.5 Hz), 1.31 (t, 3H, *J* 7.2 Hz), 0.22 (36H, s).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 169.3 ($^3J_{Sn-C}$ 29 Hz), 135.3 ($^2J_{Sn-C}$ 76 Hz), 125.3 ($^3J_{Sn-C}$ 76 Hz), 62.3, 34.4 ($^1J_{Sn-C}$ 650 Hz), 14.2, 5.8 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −129.1.

IR (KBr): 1 661, 1 613, 1 336, 1 249, 1 202, 898, 867, 840, 678 cm^{-1}.

SMHR: calc for $C_{18}H_{45}N_2O_2BrSi_4Sn$: 617.0529; found: 617.0589.

- *Compound **2f***

Solvent: ethyl ether; temperature: 20 °C; reaction time: 30 min.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.03 (s, 1H, $^4J_{Sn-H}$ 35.3 Hz), 5.97 (s, 1H, $^4J_{Sn-H}$ 29.4 Hz), 2.53 (bs, 2H, $^2J_{Sn-H}$ 81.4 Hz), 0.23 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 156.2 ($^3J_{Sn-C}$ 77 Hz), 117.7 ($^2J_{Sn-C}$ 26 Hz), 106.6 ($^3J_{Sn-C}$ 78 Hz), 34.3 ($^1J_{Sn-C}$ 579 Hz), 6.4 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −81.8.

IR (KBr) 3 035, 2 964, 2 218, 1 645, 1 465, 1 403, 1 252, 1 093, 843 cm^{-1}.

- *Compound **2g***

Solvent: ethyl ether; temperature: 20 °C; reaction time: 15 min.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.42 (s, 1H), 6.35 (s, 1H), 2.64 (bs, 2H), 2.45 (s, 3H), 0.22 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 200.1, 130.3, 122.4, 34.4 ($^1J_{Sn-C}$ 662 Hz), 15.0, 5.7 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −127.3.

- *Compound **2h***

Solvent: ethyl ether; temperature: 20 °C; reaction time: 30 min.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.55–7.30 (m, 5H), 5.45 (d, 1H, *J* 0.9 Hz, $^4J_{Sn-H}$ 47.3 Hz), 5.33 (bs, 1H), 3.07 (d, 2H, *J* 0.9 Hz, $^2J_{Sn-H}$ 94.6 Hz), 0.29 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 142.2, 128.7 (2C), 128.3, 126.6 (2C), 115.3 ($^3J_{Sn-C}$ 88.7 Hz), 36.3 ($^1J_{Sn-C}$ 574 Hz), 6.0 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −81.8.

IR (KBr) 3 035, 2 964, 2 218, 1 645, 1 465, 1 403, 1 252, 1 093, 843 cm^{-1}.

- *Compound **3a***

Solvent: ethyl ether; temperature: 20 °C; reaction time: 48 h.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.85–5.80 (m, 2H), 2.61 (bd, 2H, *J* 7.7 Hz, $^2J_{Sn-H}$ 102.0 Hz), 1.58 (d, 3H, *J* 5.1 Hz), 0.23 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 127.6, 124.4, 34.7, 29.7, 5.6 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −53.6.

IR (KBr) 2 954, 2 900, 1 252, 964, 906, 885, 861, 841, 795, 759 cm^{-1}.

- *Compound **3b***

Solvent: ethyl ether; temperature: 20 °C; reaction time: immediate.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.98 (qt, 1H, *J* 7.1, 1.7 Hz), 4.21 (q, 2H, *J* 7.1 Hz), 2.86 (dq, 2H, *J* 1.7, 1.5 Hz, $^2J_{Sn-H}$ 119.0 Hz), 1.85 (dt, 3H, *J* 7.1, 1.5 Hz, $^5J_{Sn-H}$ 17.4 Hz), 1.25 (t, 3H, *J* 7.1 Hz), 0.25 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 170.5, 139.4 ($^3J_{Sn-C}$ 108 Hz), 128.3 ($^2J_{Sn-C}$ 57 Hz), 62.3, 32.4 ($^1J_{Sn-C}$ 657 Hz), 16.0, 13.9, 6.4 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −236.1.

- *Compound **3c***

Solvent: ethyl ether; temperature: 20 °C; reaction time: 30 min.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.75 (bs, 1H), 7.53–7.48 (m, 2H), 7.38–7.29 (m, 3H), 4.39 (q, 2H, *J* 7.1 Hz), 2.67 (bs, 2H, $^2J_{Sn-H}$ 105.0 Hz), 1.38 (t, 3H, *J* 7.1 Hz), 0.20 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 174.7 ($^3J_{Sn-C}$ 158 Hz), 141.4 ($^3J_{Sn-C}$ 99 Hz), 134.8 ($^4J_{Sn-C}$ 15.3 Hz), 130.6 (2C, $^5J_{Sn-C}$ 10.8 Hz), 129.6, 128.7 (2C), 126.2 ($^2J_{Sn-C}$ 66 Hz), 61.4, 32.6 ($^1J_{Sn-C}$ 736 Hz), 14.3, 5.9 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −187.1.

SMHR: calc for $C_{23}H_{46}N_2O_2BrSi_4Sn$: 693.0842; found: 693.0851.

- *Compound* ***3d***

Solvent: ethyl ether; temperature: 20 °C; reaction time: 15 min.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.72 (bs, 1H), 3.80 (bs, 3H), 3.72 (s, 3H), 3.52 (bs, 2H, $^2J_{Sn-H}$ 105.0 Hz), 0.23 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 167.5, 166.4, 143.9, 124.7 ($^2J_{Sn-C}$ 72 Hz), 53.2, 51.9, 30.6 ($^1J_{Sn-C}$ 664 Hz), 6.0 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −195.2.

- *Compound* ***3e***

Solvent: ethyl ether; temperature: 20 °C; reaction time: 15 min.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.03 (d, 1H, J 10.1 Hz, $^4J_{Sn-H}$ 39.3 Hz), 2.84 (m, 1H), 2.53 (bs, 2H, $^2J_{Sn-H}$ 81.4 Hz), 1.04 (d, 6H, J 6.7 Hz), 0.25 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 156.2 ($^3J_{Sn-C}$ 77 Hz), 117.7 ($^2J_{Sn-C}$ 26.3 Hz), 106.6 ($^3J_{Sn-C}$ 78.5 Hz), 34.3 ($^1J_{Sn-C}$ 579 Hz), 31.8 ($^4J_{Sn-C}$ 18.7 Hz), 22.3 (2C, $^5J_{Sn-C}$ 29.4 Hz), 6.4 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −92.

IR (KBr) 3 035, 2 964, 2 218, 1 645, 1 465, 1 403, 1 252, 1 093, 843 cm^{-1}.

- *Compound* ***4a***

Solvent: benzene; temperature: 20 °C; reaction time: immediate.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.65 (t, 2H, J 7.0 Hz, $^2J_{Sn-H}$ 83.6 Hz), 1.51–1.40 (m, 16H), 0.98 (t, 3H, J 5.1 Hz), 0.23 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 33.6 ($^3J_{Sn-C}$ 87 Hz), 32.1, 31.7 ($^1J_{Sn-C}$ 583 Hz), 29.7, 29.6, 29.5, 28.7, 26.7 ($^2J_{Sn-C}$ 36 Hz), 22.8, 14.3, 6.1 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −141.1.

- *Compound* ***4b***

Solvent: THF; temperature: 20 °C; reaction time: 1 h.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.63–1.57 (m, 5H), 0.93 (d, 6H, J 6.1 Hz), 0.27 (s, 36H).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 34.5 ($^2J_{Sn-C}$ 22 Hz), 31.2 ($^3J_{Sn-C}$ 139 Hz), 28.7 ($^1J_{Sn-C}$ 611 Hz), 22.0 (2C), 5.8 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −54.5.

- *Compound* ***4c***

Solvent: ethyl ether; temperature: 20 °C; reaction time: 12 h.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.11-1.98 (m, 2H), 1.65–1.48 (m, 1H), 1.43 (d, 3H, J 7.3 Hz), 1.06 (t, 3H, J 7.2 Hz), 0.29 (s, 36H).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 38.3 ($^1J_{Sn-C}$ 640 Hz), 27.3 ($^2J_{Sn-C}$ 24 Hz), 16.4 ($^2J_{Sn-C}$ 28 Hz), 13.8 ($^3J_{Sn-C}$ 133 Hz), 5.9 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −49.3.

- *Compound* ***4d***

Solvent: benzene; temperature: 80 °C; reaction time: 24 h.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.53–7.33 (m, 5H), 7.18 (d, 1H, J = 18.3 Hz), 6.81 (d, 1H, J 18.3 Hz, $^2J_{Sn-H}$ 127.0 Hz), 0.37 (s, 36H).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 148.3 ($^2J_{Sn-C}$ 26 Hz), 137.7 ($^3J_{Sn-C}$ 133 Hz), 132.8 ($^1J_{Sn-C}$ 793 Hz), 130.0 (2C), 129.7 (2C), 127.9, 5.1 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −212.2.

- *Compound* ***4e***

Solvent: benzene; temperature: 80 °C; reaction time: 3 h.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.62 (d, 1H, J = 9.8 Hz, $^2J_{Sn-H}$ 167 Hz), 6.66 (d, 1H, J = 9.8 Hz, $^3J_{Sn-H}$ 60 Hz), 4.00 (s, 3H), 0.27 (s, 36H).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 173.1 ($^1J_{Sn-C}$ 818 Hz), 171.2, 129.7 ($^2J_{Sn-C}$ 26 Hz), 54.2, 6.3 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −319.9.

- *Compound* ***4f***

Solvent: benzene; temperature: 20 °C; reaction time: 0.25 h.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.23 (t, 2H, J 6.9 Hz), 1.47–1.40 (m, 4H), 0.85 (t, 3H, J 6.9 Hz), 0.27 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 111.3 ($^1J_{Sn-C}$ 198 Hz), 86.9, 30.2, 21.9, 19.5, 13.5, 5.9 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −371.

- *Compound* ***4g***

Solvent: benzene (or THF); temperature: 20 °C; reaction time: 24 h (or 3 h). Characterized in Lappert's original paper [26].

- *Compound* ***8***

Solvent: benzene; temperature: 20 °C; reaction time: immediate.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.25-7.01 (m, 5H), 2.10 (d, 2H, J 6.9 Hz, $^2J_{Sn-H}$ 104 Hz), 1.71 (m, 2H), 0.93 (m, 2H), 0.21 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 138.2, 128.8 (2C), 128.2, 126.2 (2C), 62.8, 45.3 ($^1J_{Sn-C}$ 642 Hz), 20.9, 20.6, 5.3 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −74.2.

- *Compound* ***9***

Solvent: pentane; temperature: −50 °C; reaction time: 0.5 h.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.44 (t, 1H, J 6.9 Hz, $^2J_{Sn-H}$ 54.6 Hz), 4.7 (d, 2H, J 6.9 Hz, $^4J_{Sn-H}$ 79.4 Hz), 0.23 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 211.3, 87.0 ($^1J_{Sn-C}$ 818 Hz), 71.2 ($^3J_{Sn-C}$ 94 Hz), 5.5 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −133.4.

- *Compound* ***10***

Solvent: pentane; temperature: 20 °C; reaction time: immediate. Prepared as a 1:1 mixture with **9**.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.32 (d, 1H, J 3.0 Hz, $^4J_{Sn-H}$ 93.7 Hz), 2.0 (t, 2H, J 3.0 Hz, $^2J_{Sn-H}$ 49.9 Hz), 0.24 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 80.3, 71.2, 18.5, 5.5 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −105.2.

- *Compound* ***11a***

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.75–7.70 (m, 2H), 7.45–7.41 (m, 3H), 6.21 (bs, 1H), 5.78 (bs, 1H), 4.35 (q, 2H, J 7.2 Hz), 2.58 (bt, 2H, J 1.6 Hz, $^2J_{Sn-H}$ 112.8 Hz), 1.38 (t, 3H, J 7.2 Hz), 0.20 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 173.2, 152.0, 135.2, 130.5, 128.5 (2C), 126.9, 124.6 (2C), 64.0, 32.9 ($^1J_{Sn-C}$ 758.9 Hz), 14.2, 5.7 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −182.7.

IR (KBr): 2 985, 2 978, 2 972, 2 965, 2 951, 1 716, 1 693, 1 661, 1 255 cm^{-1}.

• *Compound* **11b**

^1H NMR ($CDCl_3$, 250 MHz) δ 6.18 (bs, 1H, $^4J_{Sn-H}$ 18.5 Hz), 5.70 (bs, 1H, $^4J_{Sn-H}$ 35.1 Hz), 4.58 (q, 2H, J 7.1 Hz), 4.31 (q, 2H, J 7.1 Hz), 2.82 (s, 2H, $^2J_{Sn-H}$ 107.8 Hz), 1.41 (t, 3H, J 7.1 Hz), 1.36 (t, 3H, J 7.1 Hz), 0.22 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 217.0, 170.3 ($^3J_{Sn-C}$ 29.6 Hz), 136.5 ($^2J_{Sn-C}$ 79 Hz), 125.5 ($^3J_{Sn-C}$ 102 Hz), 70.2, 62.6, 35.4 ($^1J_{Sn-C}$ 675 Hz), 14.2, 14.1, 6.0 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −134.4.

• *Compound* **11c**

^1H NMR ($CDCl_3$, 250 MHz) δ 6.11 (bs, 1H), 5.66 (bs, 1H, $^4J_{Sn-H}$ 34.6 Hz), 4.28 (q, 2H, J 7.1 Hz), 2.47 (bs, 2H, $^2J_{Sn-H}$ 118.7 Hz), 1.96 (s, 3H), 1.32 (t, 3H, J 7.1 Hz), 0.22 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 175.9, 172.5 ($^3J_{Sn-C}$ 36 Hz), 136.2 ($^2J_{Sn-C}$ 74 Hz), 125.2 ($^3J_{Sn-C}$ 114 Hz), 63.4, 33.1 ($^1J_{Sn-C}$ 777 Hz), 23.1, 14.1, 5.4 (12C).

IR (KBr): 2 980, 2 958, 2 933, 1 710, 1 685, 1 633, 1 566, 1 381, 1 280, 1 175, 1 051, 844 cm^{-1}.

• *Compound* **11d**

^1H NMR ($CDCl_3$, 250 MHz) δ 7.03 (qt, 1H, J 7.3, 2.0 Hz), 4.33 (q, 2H, J 7.0 Hz), 2.31 (bs, 2H, $^2J_{Sn-H}$ 119.0 Hz), 2.00 (s, 3H), 1.91 (d, 3H, J 7.3 Hz, $^5J_{Sn-H}$ 17.4 Hz), 1.36 (t, 3H, J 7.0 Hz), 0.18 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 175.7 ($^3J_{Sn-C}$ 19.2 Hz, 173.6, 140.5 ($^3J_{Sn-C}$ 113 Hz), 128.2 ($^2J_{Sn-C}$ 57.4 Hz), 63.6, 26.5 ($^1J_{Sn-C}$ 813.5 Hz), 23.5, 15.9, 14.2, 5.9 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −199.4.

IR (KBr): 1 649 (C=O), 1 624, 1 401, 1 367, 1 301, 1 246, 910, 859, 837, 840, 676 cm^{-1}.

• *Compound* **11e**

^1H NMR ($CDCl_3$, 250 MHz) δ 7.66 (bd, 1H), 7.52–7.43 (m, 2H), 7.32–7.28 (m, 3H), 4.38 (q, 2H, J 7.0 Hz), 2.61 (bs, 2H, $^2J_{Sn-H}$ 118.7 Hz), 1.91 (s, 3H), 1.37 (t, 3H, J 7.0 Hz), 0.20 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 169.3, 164.9, 140.0, 137.9, 135.1, 130.3, 128.4 (2C), 127.8 (2C), 60.9, 29.3, 21.1, 14.1, 5.3 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −208.2.

• *Compound* **11f**

^1H NMR ($CDCl_3$, 250 MHz) δ 7.14 (m, 1H), 2.45 (s, 3H), 2.01 (d, 3H, J 7.2 Hz), 2.01 (bs, 2H, $^2J_{Sn-H}$ 114.8 Hz), 1.98 (s, 3H), 0.14 (s, 36H).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 204.0 ($^3J_{Sn-C}$ 19.2 Hz), 175.6 ($^2J_{Sn-C}$ 12.1 Hz), 145.8 ($^3J_{Sn-C}$ 119.3 Hz), 139.2 ($^2J_{Sn-C}$ 40.6 Hz), 24.4, 23.6, 22.2 ($^1J_{Sn-C}$ 816.9 Hz), 16.8, 5.9 (12C).

^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ −193.5.

3-Methylidene-5-phenyl-4,5-dihydrofuran-2(3H)-one **13**

Bis[*N*,*N*-bis(trimethylsilyl)amino]stannylene **1** (1.00 g, 2.27 mmol) and ethyl 2-(bromomethyl)propenoate (1 equiv) were mixed in anhydrous THF (10 mL) under nitrogen at 25 °C until the reaction mixture turned pale yellow, benzaldehyde (241 mg, 2.27 mmol) was added and the solution heated to reflux for 3 h. The reaction mixture was then cooled, concentrated and the residual oil purified by flash chromatography on silica gel (light petroleum/diethylether, 9:1), providing **13** (cf [15b] for spectroscopic data) as a white solid (312 mg, 79%).

3-Methylidene-5-phenylpyrrolidin-2-one **15**

Bis[*N*,*N*-bis(trimethylsilyl)amino]stannylene **1** (1.00 g, 2.27 mmol) and ethyl 2-(bromomethyl)propenoate (1 equiv) were mixed in anhydrous THF (10 mL) under nitrogen at 25 °C until the reaction mixture turned pale yellow. After removal of the solvent silylimine **14** (1 equiv) was added in chloroform (8 mL), and the solution heated to reflux for 3 h. The reaction mixture was then cooled, concentrated and the residual oil purified by flash chromatography on silica gel, providing **15** as a white solid (189 mg, 48%).

^1H NMR ($CDCl_3$, 250 MHz) δ 7.32–7.19 (m, 5H), 7.04 (bs, 1H), 5.96 (t, 1H, J 2.7 Hz), 5.30 (bs, 1H), 4.68 (dd, 1H, J 8.2, 4.5 Hz), 3.17 (ddt, 1H, J 17.1, 8.2, 2.5 Hz), 2.59 (ddt, 1H, J 17.1, 4.5, 2.7 Hz).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 171.0, 142.8, 138.9, 129.0 (2C), 128.1, 125.8 (2C), 116.6, 54.9, 36.9.

Anal calc for $C_{11}H_{11}NO$: C, 76.28; H, 6.40. Found: C, 76.09; H, 6.46.

Allyl radical transfer

• *Reaction with allyltrihalogenotin* **13**

Allyltrihalogenotin **13** (1.30 g, 3.4 mmol) and benzyl bromide (323 mg, 1.89 mmol) are mixed in anhydrous benzene (10 mL) under inert atmosphere. A catalytic amount of AIBN was added and the solution heated to reflux until disappearance of the substrate. The reaction mixture was then cooled, concentrated and the residual oil purified by flash chromatography on silica gel (light petroleum–diethyl ether, 9:1), providing **16** as a colourless oil.

• *Reaction with monoallyltins* **2a**, **11a**, **11b**

Bis[*N*,*N*-bis(trimethylsilyl)amino]stannylene **1** (1.00 g, 2.27 mmol) and allyl substrate (1 equiv) were mixed in anhydrous benzene (10 mL) under argon at 25 °C until the reaction mixture turned pale yellow, benzyl bromide (323 mg, 1.89 mmol) and a catalytic amount of AIBN was added and the solution heated to reflux until disappearance of the substrate. The reaction mixture was then cooled, concentrated and the residual oil purified by flash chromatography on silica gel (light petroleum/diethyl ether, 9:1), providing **16** as a colourless oil.

^1H NMR ($CDCl_3$, 250 MHz) δ 7.33–7.18 (m, 5H), 6.18 (d, 1H, J 0.7 Hz), 5.51 (d, 1H, J 0.7 Hz), 4.24 (q, 2H, J 7.1 Hz), 2.82 (m, 2H), 2.64 (m, 2H), 1.33 (t, 3H, J 7.1 Hz).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 167.2, 141.5, 139.2, 128.6 (2C), 128.4 (2C), 126.0, 125.2, 60.7, 35.0, 34.0, 14.3.

IR (film): 3 010, 2 940, 1 700, 1 610, 1 160, 1 110, 1 010, 680 cm^{-1}.

Coupling procedure without TBAF

Bis[*N*,*N*-bis(trimethylsilyl)amino]stannylene **1** (800 mg, 1.82 mmol) and allyl halide (1.82 mmol) are mixed in anhydrous toluene (5 mL) under nitrogen. After stirring for 15 min at 25 °C, the resulting yellow solution was added to a solution of Pd_2dba_3 (32 mg, 0.035 mmol) and triphenylphosphine (36 mg, 0.14 mmol) in toluene (3 mL) and the

reaction mixture is heated to 90 or 110 °C. Benzylic bromide (1.13 mmol) is added and the reaction allowed to stir until catalyst has precipitated. The mixture was then cooled, concentrated and the residual oil purified by flash chromatography on silica gel (light petroleum/diethyl ether, 9:1), providing **17** as a colourless oil.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.19–7.04 (m, 5H), 6.00 (d, 1H, J 1.3 Hz), 5.36 (ddd, 1H, J 1.3, 1.1, 0.9 Hz), 4.07 (q, 2H, J 7.1 Hz), 3.80 (dd, 1H, J 8.6, 6.7 Hz), 3.50 (s, 3H), 2.95 (ddd, 1H, J 14.2, 8.6, 0.9 Hz), 2.59 (ddd, 1H, J 14.2, 6.7, 1.1 Hz), 1.16 (t, 3H, J 7.1 Hz).

^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 173.7, 166.7, 138.5, 137.5, 128.7 (2C), 128.0 (2C), 127.5, 127.4, 60.8, 52.0, 50.4, 36.2, 14.2.

MS m/z: 262, 230 (82), 202 (20), 189 (11), 173 (53), 157 (23), 149 (11), 129 (100), 128 (25), 121 (34).

HRMS: calc for $C_{15}H_{18}O_4$: 262.1205; found: 262.1206.

Coupling procedure with TBAF

Monoorganotin reagents (1.85 mmol) are prepared following the above procedure. TBAF (5.9 mL, 1 M) is then added in situ and after concentration anhydrous solvent (8 mL, typically THF or dioxane), halogenated substrate (1.23 mmol) and tetrakis(triphenylphosphine)palladium (0.015 mmol) are added and the reaction mixture is heated at reflux until disappearance of the substrate. After cooling and removal of the solvent, purification on silica gel afforded the coupling product.

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