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Insights into the Reaction Behaviour of Stannylated Allylic Substrates

Christian Bukovec,[a] Alexander O. Wesquet,[a] and Uli Kazmaier*[a]

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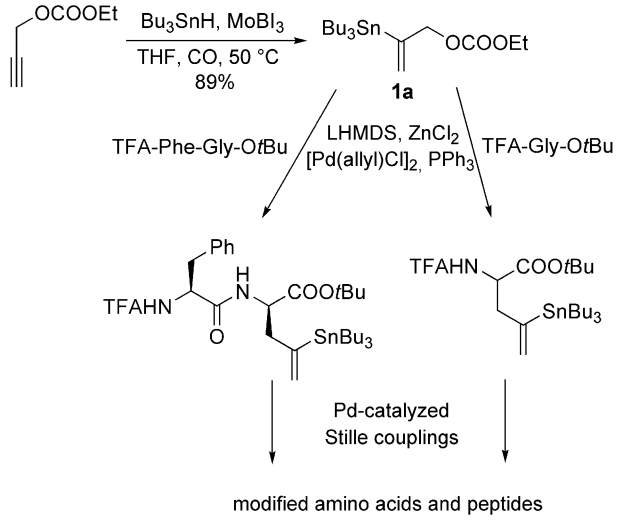
Stannylated allylic substrates are versatile building blocks for organic synthesis. Pd^0-catalysed coupling reactions of 2-stannylated allylic carbonates, acetates and phenoxides with amines, malonates, phenoxides, imides and distannanes provide the corresponding substituted allylic compounds, which are suitable for subsequent modifications including Stille coupling reactions. The reaction mechanisms are dependent on the temperature and the nucleophiles used. Tsuji–Trost allylic substitution takes place with organic nucleophiles at low temperature. When distannane is employed at higher temperature, on the other hand, Pd^0-catalysed bismetallation of allenes formed in situ by elimination of tributyltin methoxide predominates.

Introduction

In chemical biology and pharmaceutical chemistry, diverse libraries of small molecules are often investigated in order to identify lead structures for new drug candidates.[1] A key point for the success of such an approach is the choice of a suitable building block allowing a wide range of modifications and different reaction modes, generating scaffold diversity. Good candidates for this purpose are stannylated allyl carbonates such as **1a** (Scheme 1), which combine the structural features of two important cross-coupling reactions: the Stille coupling[2] and allylic alkylation.[3] Both reactions have been investigated intensively and are often used in natural product syntheses and combinatorial chemistry.

Stannylated compounds of type **1** can be obtained by hydrostannation of the corresponding propargyl alcohol derivatives either under radical or under transition-metal-catalysed conditions. Whereas the radical version in general gives mixtures of regio- (α,β) and stereoisomers (*E*/*Z*), the catalytic approach proceeds stereoselectively in a *syn* manner,[4] although the control of the regioselectivity is not a trivial issue.[5] In addition, the commonly used Pd catalysts are unsuitable for the hydrostannation of propargylic esters and carbonates, providing only decomposition products under the typical reaction conditions. This forced our group to develop new hydrostannation catalysts, based on molybdenum[6] and tungsten[7] complexes. Our favourite catalyst – $Mo(CN\mathit{t}Bu)_3(CO)_3$ ($MoBl_3$) – allows the hydrostannation of a wide range of electron-poor alkynes with high yields and good regioselectivities.[8] Propargylic ethers and esters are also good substrates, giving rise to the required α-stannylated products of type **1** in only one step. Best results are obtained under CO, under which the formation of side products can be suppressed almost completely.[9]



Scheme 1. Synthesis and conversion of stannylated allylic carbonates.

With these building blocks to hand, we have been able to show that the proposed allylic alkylation/Stille approach can be applied successfully in amino acid and peptide chemistry. With chelated glycine enolates the corresponding stannylated allyl glycines are formed.[10] Even peptides can be allylated successfully, allowing highly stereoselective peptide backbone modifications.[11] In such cases, the formation of the new stereogenic centre can be controlled through the adjacent stereocentres in the peptide chain.[12] The stannylated amino acids can be further modified by subsequent Stille couplings, allowing the generation of amino acid and peptide libraries.[13]

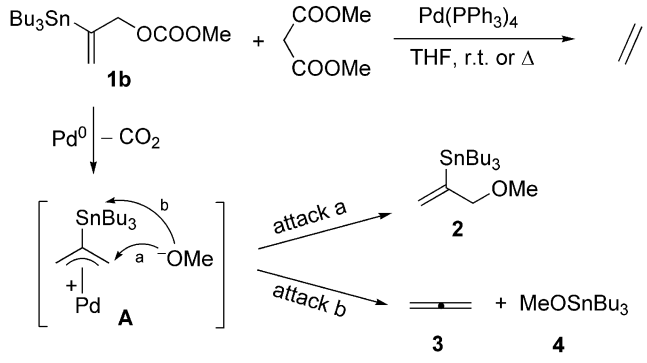
[a] Institute of Organic Chemistry, Saarland University,
P. O. Box 151150, 66041 Saarbrücken, Germany
Fax: +49-681-302-2409
E-mail: u.kazmaier@mx.uni-saarland.de

These examples clearly show that with reactive nucleophiles the allylic alkylation can proceed selectively without affecting the vinylstannane subunit, which can be coupled separately afterwards.

Results and Discussion

To increase the synthetic potential of these stannylated compounds, we were interested in finding other nucleophiles suitable for allylic alkylation and in developing completely new reactions of these substrates. This is not a trivial issue, because β-metallated alcohol derivatives can easily undergo elimination,[14] which should result here in the formation of allenes.[15] In addition, vinylstannanes can also be used as nucleophiles in allylic alkylations,[16] which might result in oligo- or polymerization of the allylic substrate.

Because of our good results obtained with the chelated enolates we used malonate in our initial experiments (Scheme 2). To keep the reaction conditions as mild as possible we worked under neutral conditions with the stannylated allyl carbonate **1b**. In general, the methoxide liberated during π-allyl complex formation deprotonates the malonate, generating the reactive nucleophile.[17] Surprisingly, the expected substitution product was obtained only in traces, although the allylic substrate **1b** was consumed completely. Whereas no reaction was observed at low temperatures (–20 to 0 °C), decomposition of the substrate obviously occurs at or above room temperature. Because **1b** is obtained by hydrostannation of the corresponding alkyne at 50 °C in THF, the allylic substrate per se should be (thermally) stable under the reaction conditions. Obviously the Pd catalyst is responsible for the undesired decomposition.



Scheme 2. Pd-catalysed decomposition of stannylated allyl carbonates.

From our previous experiments with chelated enolates[8] we knew that the allyl carbonate **1b** forms the π-allyl complex **A** at very low temperatures, even at –70 °C. We can therefore be sure that the allyl complex **A** is formed, but obviously at higher temperature it undergoes side reactions/decomposition, which is not a problem with highly reactive nucleophiles that react already at low temperature. One can think of two possibilities: a) a direct nucleophilic attack of the liberated methoxide could occur on the π-allyl complex to provide the decarboxylated product **2**, a reaction not normally observed, or b) the methoxide could attack the tin fragment to liberate the allene **3** and the tin methoxide **4** (Scheme 2). All of these compounds should provide unmistakable signals in their ^{1}H NMR spectra, so we carried out the "reaction without the nucleophile" in a NMR tube to follow the kinetics of the decomposition and to analyse the intermediates and products.

In this experiment the generally used $CDCl_3$ was replaced by [D_8]toluene to avoid possible side reactions between the solvent and the vinylstannane. All ingredients were mixed together at 0 °C and the measurements were started immediately after the sample had been placed in the NMR machine. ^{1}H NMR spectra were taken every minute at room temp. and Figure 1 shows the composition of the NMR sample as a function of time. The formation of the allene **3** as an elimination product could already be observed after 1 min. Obviously, this decomposition starts immediately after the addition of the catalyst. The amount of allene **3** grows continuously as the amount of **1b** is reduced. After 25 min, the starting material had been completely consumed.

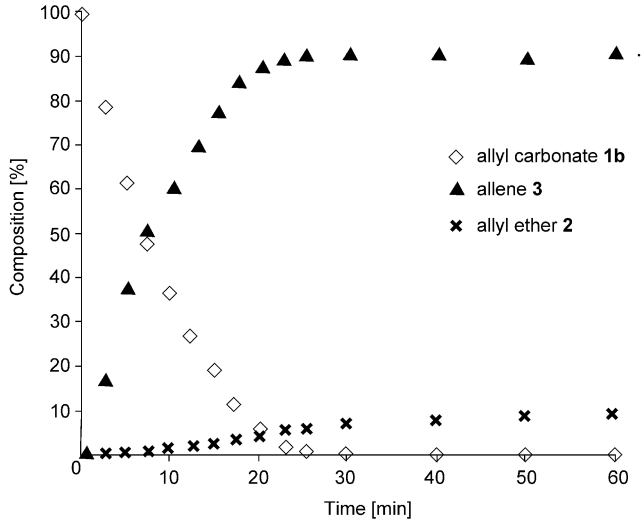


Figure 1. Pd-catalysed decomposition of stannylated allyl carbonates.

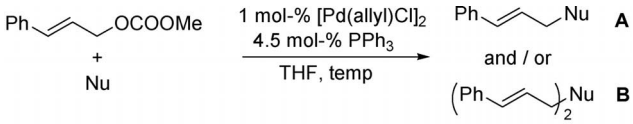
Decomposition to the allene **3** is definitely the major pathway (attack b, ca. 90%), but nucleophilic attack of the methoxide on the π-allyl complex (attack a), resulting in the formation of the allyl ether **2** (ca. 10%), obviously also plays a role.

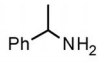
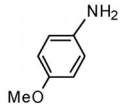
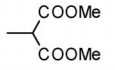
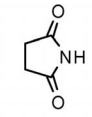
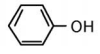
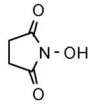
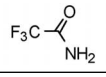
Although the decomposition limits the scope of nucleophiles that can be used for the allylic alkylations, it might also provide an easy and mild process for the generation of allenes, probably coordinated with the Pd in the initial phase of their formation. If one were able to trap these allene-Pd complexes this would open up new synthetic perspectives.

To find nucleophiles that would react by allylic alkylation at 0 °C, and would hence be suitable for the reaction with **1**, and also to minimize the side reactions, we undertook a screening of several types of nucleophiles commonly used

in these allylations. To obtain the required information as quickly as possible we decided to use a competitive approach. Amines, especially secondary ones, are known to be good nucleophiles in allylic alkylations, being applied in, for example, the cleavage of allyl protecting groups.[18] We therefore subjected a stoichiometric mixture of three different amines to our standard reaction conditions (Table 1, Entries 1–3). For these model studies cinnamyl carbonate was used as substrate (instead of **1**) to allow easy monitoring of the reaction by GC–MS. Naphthalene was used as internal standard. The reaction was started at –78 °C and the reaction mixture was warmed stepwise to room temperature. After 18 h at room temperature the mixture was heated at reflux for an additional three hours.

Table 1. Reactivities of several nucleophiles.



Entry	Nu	Reaction starts at	Additive	Product type	Reaction status
1		–20 °C	—	**A**	20 °C, 1h (100% conv.)
2		20 °C	—	**B**	20 °C, 18h (80% conv.)
3		20 °C	—	**B**	60 °C, 3h (100% conv.)
4		–20 °C	NaOMe	**A**	20 °C, 18h (100% conv.)
5		–20 °C	NaOMe	**A**	20 °C, 18h (75% conv.)
6		–20 °C	NaOMe	**A**	20 °C, 18h (90% conv.)
7		0 °C	NaOMe	**A**	20 °C, 18h (60% conv.)
8		20 °C	NaOMe	**A**	20 °C, 18h (65% conv.)

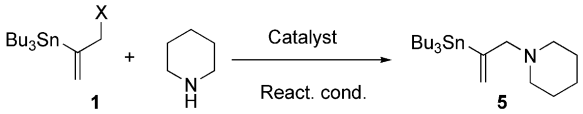
With piperidine the reaction started slowly at –20 °C, and after 1 h around 10% of the allylation product could be determined.[19] After 1 h at 0 °C the level of conversion was ca. 45% and after a further 1 h at room temperature it was complete (Entry 1). 1-Phenylethylamine (Entry 2) and anisidine (Entry 3) were significantly less reactive. Phenylethylamine reacted very slowly at room temperature (80% conversion after 18 h) and anisidine required subsequent heating. Interestingly, with these two primary amines only the formation of the diallylated product **B** was observed. No monoallylated product **A** could be determined.

On the basis of these results we set up another set of nucleophiles, containing less reactive representatives such as methyl malonate, succinimide, *N*-hydroxysuccinimide, phenol and trifluoroacetamide. In principle, all these nucleophiles contain acidic hydrogens that should be removed by the liberated alkoxide. Unfortunately, though, no reaction was observed with any of them under these "neutral" reaction conditions. Addition of an excess of NaOMe changed the situation dramatically. All nucleophiles showed good levels of conversion. Whereas the malonate (Entry 4) was the most reactive of these substrates, showing a significant degree of conversion at –20 °C,[20] succinimide[21] (Entry 5) and phenol[22] (Entry 6) started slowly at this temperature. With *N*-hydroxysuccinimide[23] (Entry 7) the reaction set in at 0 °C, and the trifluoroacetamide (Entry 8) required room temperature to show significant reactivity. With all substrates more than 60% conversion was observed after 18 h, but this is probably too long for the sensitive stannylated substrates. Piperidine was definitely the nucleophile of choice, but 1-phenylethylamine, malonate, succinimide and phenol also seemed worth investigation.

On the basis of the good results obtained with the secondary cyclic amine, piperidine was used to optimize the reaction conditions for the conversion of the stannylated allylic substrate (Table 2).[24] No allylation product was obtained if the reaction was run in THF at room temperature (Entry 1), although **1a** was completely consumed. These results are comparable to those obtained earlier with malonate. On reduction of the reaction temperature to 0 °C, the decomposition reactions were diminished and the stannylated allylamine **5** was obtained in good yield (Entry 2). Interestingly, the decomposition seems to be highly dependent on the solvent used. In other solvents such as CH_2Cl_2 or DMF the side reactions were less significant and **5** was obtained at room temperature in acceptable to good yields (Entries 3 and 4). The highly polar solvent DMF seems to be the solvent of choice, showing the fastest conversion and the best yield. Even at 0 °C the reaction was finished after 2 h (Entry 5). Further reduction of the reaction temperature does not improve the yield considerably (Entry 6). Therefore, for further optimization the reactions were carried out at 0 °C.

We next investigated the influence of the leaving group on the outcome of the reaction. Whereas the corresponding methyl carbonate **1b** gave comparable results (Entry 7), the sterically more demanding *tert*-butyl carbonate **1c** was significantly less suitable (Entry 8). The best yield was obtained with the corresponding acetate **1d** (Entry 9), but in this case some impurities that could not be removed completely from the product were formed. To our great surprise, even the THP ether **1e** (Entry 10) gave the coupling product in good yield, although this is normally a protecting and not a leaving group. Interestingly, when phenoxides were employed different reaction temperatures had to be chosen, depending on their substituents. The electron poor *p*-NO_2-phenoxide **1f** (Entry 11) reacted similarly to the carbonate **1a** at 0 °C, whereas the unsubstituted phenoxide **1g** (Entry 12) had to be warmed to 65 °C for 2 h or to 45 °C over-

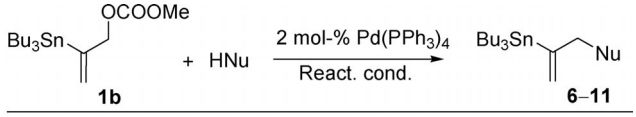
Table 2. Optimization of the reaction conditions.

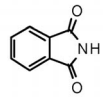


Entry	1	X	React. cond.	Cat.[a]	Yield [%]
1	**1a**	OCOOEt	THF, 20 °C, 1 h	**A**	0
2	**1a**	OCOOEt	THF, 0 °C, 5 h	**A**	74
3	**1a**	OCOOEt	CH_2Cl_2, 20 °C, 5 h	**A**	49
4	**1a**	OCOOEt	DMF, 20 °C, 1 h	**A**	70
5	**1a**	OCOOEt	DMF, 0 °C, 2 h	**A**	79
6	**1a**	OCOOEt	DMF, –20 °C, 2 h	**A**	80
7	**1b**	OCOOMe	DMF, 0 °C, 2 h	**A**	79
8	**1c**	OCOO*t*Bu	DMF, 0 °C, 2 h	**A**	56
9	**1d**	OAc	DMF, 0 °C, 2 h	**A**	88
10	**1e**	OTHP	DMF, 0 °C, 2 h	**A**	71
11	**1f**	O-*p*-NO_2-Ph	DMF, 0 °C, 2 h	**A**	88
12	**1g**	OPh	DMF, 65 °C, 2 h	**A**	62
13	**1g**	OPh	DMF, 45 °C, 16 h	**A**	76
14	**1a**	OCOOEt	DMF, 0 °C, 2 h	**B**	79
15	**1a**	OCOOEt	DMF, 0 °C, 2 h	**C**	94

[a] Catalysts: **A**) $[Pd(allyl)Cl]_2$ (1 mol-%), PPh_3 (4.5 mol-%), **B**) $[Pd(allyl)Cl]_2$ (1 mol-%), dppf (4.5 mol-%), **C**) $Pd(PPh_3)_4$ (2 mol-%).

Table 3. Allylic substitution of various nucleophiles.



Entry	HNu	Reaction conditions	Prod.	Yield [%]
1		DMF, 0 °C, 2h	**6**	87
2		DMF, 0 °C, 2h	**7**	86
3		DMF, 0 °C, 2h	**8**	90
4		DMF, 0 °C, 2h	**9**	84
5		NaOMe, DMF, 0 °C to r.t., 48h	**10**	43
6		NaH, DMF, –20 °C to r.t., 18h	**1g**	36
7		NaH, DMF, 40 °C, 48h	**11**	46

night (Entry 13) in order to afford the desired product. With this less reactive leaving group the substrate was observed to be more stable to higher temperatures in the presence of Pd^0, with no decomposition being observed in DMF even at 65 °C.

To confirm the influence of the catalyst system, we also varied the phosphane ligands used. Whereas slow and incomplete conversion was observed in the presence of electron-donating PBu_3, the ferrocenyl ligand dppf gave results comparable to those seen with PPh_3 (Entry 14). The best yield was obtained with $Pd(PPh_3)_4$, which provided **5** in a very clean reaction (Entry 15).

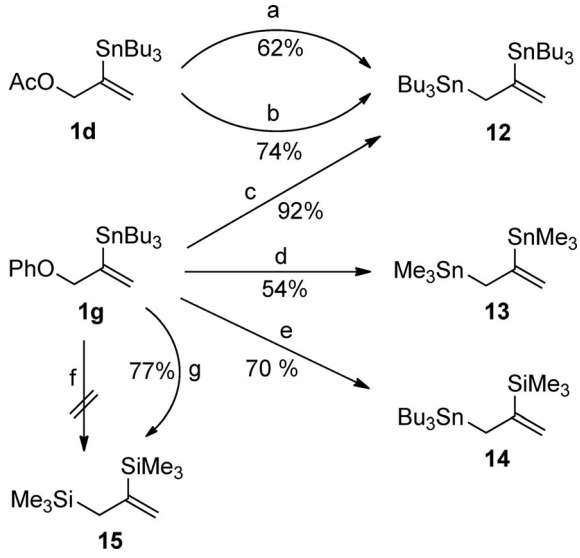
These optimized conditions were used to investigate the allylation of various types of nucleophiles (Table 3). Other nucleophilic secondary amines such as morpholine (Entry 1), pyrrolidine (Entry 2) and diethylamine (Entry 3) gave results comparable to those obtained with piperidine, with yields between 86 and 90%. Although most primary amines exclusively reacted twice, not forming monoallylation products, in our test reactions with cinnamyl carbonate, we also checked phenethylamine as nucleophile. With our sterically more demanding allylic substrate **1b** only the monoallylamine **9** was formed, in good yield (Entry 4).

We next focused on other types of nucleophiles, especially those that gave the best results in our test reaction. In the presence of additional base, malonate (Entry 5), phenol (Entry 6) and phthalimide (Entry 7) gave the desired allylation products, although in lower yields than the more nucleophilic amines. In the first experiments we used methoxide (the same as was liberated from the allylic substrate **1b**) as a base. Although malonate gave acceptable yields under these conditions, significant amounts of the stannylated allyl ether **2** (Scheme 2) were formed in the reactions with phthalimide and phenol. Therefore, in these two examples we used NaH for deprotonation. Interestingly, in the reaction with phthalimide the mixture had to be warmed to 40 °C for 2 d to afford acceptable conversion of this rather unreactive nucleophile. This example clearly shows that in DMF the decomposition of the π-allyl complex **A** (Scheme 1) to the allene is rather slow. In contrast, in THF this side reaction seems to be favoured.

According to the proposed mechanism discussed in Scheme 2, one might expect that the decomposition pathway b should provides an allene still coordinated to the Pd in the initial phase of the "decomposition". To establish whether or not this was true we tried to trap this "activated" allene directly by a Pd-catalysed addition reaction.[25] Our hope was to control the regioselectivity in the addition step through selective addition to the activated double bond formed in the elimination step. Of course, such an approach would only be successful if the addition were faster than the dissociation of the Pd. A further requirement is that the transition metal not undergo migration between the cumulated double bonds.

During our search for suitable reactions for this purpose we became familiar with some interesting work by Mitchell et al. describing distannylations and silastannylations of allenes.[26] These reactions provide highly interesting building blocks each containing both a vinylic and an allylic carbon metal bond. These bifunctional organometallics can be coupled independently at one or the other position, which allows the synthesis of a variety of highly functionalized molecules.[27] Meanwhile a range of other bismetallations such as diborylations,[28] germastannylations,[29] silaborations[30] and disilylations[31] have been described. Recently Cheng et al. reported on Pd-catalysed three-component couplings proceeding through one-pot dimetallation/Stille couplings.[32] With regard to our long-term interest in hydrome-

tallations[6–10] and our previous work on transition-metal-catalysed hydrostannation of allenes[33] and distannylations[7] the dimetallation of allenes formed in situ became a highly interesting goal.[34] We therefore treated the stannylated allyl acetate **1d** with $(Bu_3Sn)_2$ in THF at 60 °C – conditions we know to favour allene formation – and the distannane **12** was indeed obtained in acceptable yield (Scheme 3). In a detailed investigation of the reaction we observed that this dimetallation is also very sensitive towards impurities in the catalyst and the distannane, and to circumvent these problems we also investigated distannylation with Bu_3SnH. It is well known that Bu_3SnH "decomposes" in the presence of Pd^0 to give distannane,[35] generally as an undesired side product. In our case, however, this reaction could be used to produce the required distannane freshly in situ. Indeed, with Bu_3SnH the same distannylated product **12** was formed, even in better yield.



Scheme 3. Bismetallation of allenes generated in situ. Reaction conditions and reagents: $Pd(PPh_3)_4$ (2 mol-%), THF, 60 °C; a) $(Bu_3Sn)_2$ (1.05 equiv.), 2.5 h, b) Bu_3SnH (3.15 equiv.), 2.5 h, c) $(Bu_3Sn)_2$ (1.05 equiv.), 6 h, d) $(Me_3Sn)_2$ (1.05 equiv.), 18 h, e) $Me_3SiSnBu_3$ (0.7 equiv.), 18 h, f) $(Me_3Si)_2$ (1.05 equiv.), 18 h, g) $Me_3SiSnBu_3$ (2.2 equiv.), 18 h.

During the optimization of the allylic amination we observed that even stannylated allylic ethers are good substrates for this reaction. To establish whether or not this would also be true for the bismetallation, we subjected the phenyl ether **1g** to the same reaction conditions. Although the reaction was slightly slower than that of the acetate, the distannane **12**[36] was obtained in excellent yield.

To verify the hypothesis that the reaction proceeds via an allene-Pd complex and not via a π-allyl complex that is attacked by a tin nucleophile, we performed the cross-experiment. The reaction with $(Me_3Sn)_2$ provided the stannane **13**[37] exclusively, and the formation of Bu_3SnOPh was observed by NMR spectroscopy. This clearly indicates that the distannanes are formed by an elimination/addition process. The high yield of **12** obtained in the previous reaction is also very strong evidence that the allene stays coordinated to the Pd before the addition. Otherwise, the free allene would immediately evaporate under the reaction conditions used.

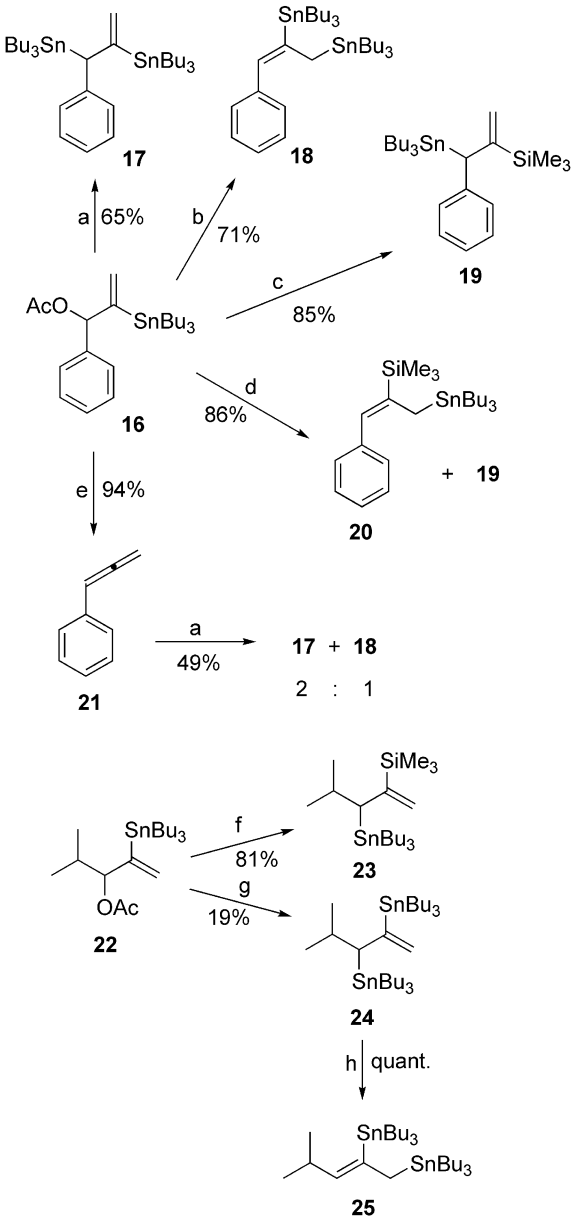
With these results to hand, we also investigated some other bismetallations. Whereas the silylated allylstannane **14** was formed in good yield with $Bu_3Sn–SiMe_3$, no reaction was observed with $(Me_3Si)_2$. The result of the reaction with disilane was not surprising: Watanabe et al. had previously reported that this reaction requires harsh conditions.[31] Under such conditions decomplexation of the allene is probably faster than the addition, which explains the complete consumption of **1g** without product formation. On the other hand, the outcome of the reaction with the mixed silylstannane was highly interesting. With a substoichiometric amount, **14** was formed as the sole product with excellent regioselectivity, which is in full agreement with the observations made by Mitchell, Cheng et al.[32]

In contrast, if the silylstannane was used in large excess (more than 2 equiv.) only the disilane **15**[31] was obtained, in high yield, so this protocol is an excellent alternative for the critical disilylation. If less than 2 equiv. $Bu_3SnSiMe_3$ is used, mixtures of **14** and **15** are obtained. NMR studies indicate that **14** is formed first in both cases, and that in the presence of additional silylstannane slow transmetallation occurs.

To establish whether or not the coordination of the allene to the Pd could also be used for regioselective bismetallations, we next investigated some substituted stannylated allyl acetates, such as **16** (Scheme 4). This substrate showed reaction behaviour similar to that of **1g**, but the substituted allene intermediate generated additional selectivity issues that had to be addressed. The reaction with $(Bu_3Sn)_2$, for example, provided the distannane **17**[38] with excellent regioselectivity. The distannane addition occurred exclusively at the double bond formed in the elimination step. Interestingly, if the reaction time was prolonged, complete conversion into the isomeric distannane **18** was observed. The thermodynamically more stable *E* isomer was formed, which is in good agreement with observations made previously by Mitchell et al.[26b] Therefore, both isomeric distannanes can be obtained selectively simply by changing the reaction time.

A similar observation was made on addition of $Me_3SiSnBu_3$. The reaction occurred regioselectively at the substituted double bond to provide **19** (Scheme 4) in high yield. Again, an isomerization was observed during the reaction time, although here the conversion was not complete, with a 2:1 mixture of **19** and the isomerized product **20** being obtained.[39] It is worth mentioning that no transmetallation to the disilylated product was observed with an excess of the silastannane.

This exchange probably does not occur for steric reasons, and the same 2:1 product mixture was obtained. As expected, no reaction occurred either with $(Me_3Si)_2$, but in this case we were able to isolate the substituted allene **21**,[40] clearly indicating that the decomplexation of the allene is much faster than the disilylation. In the absence of any bismetal species, the allene **21** was obtained in excellent yield.



Scheme 4. Regioselective bismetallation of substituted allenes generated in situ. Reaction conditions and reagents: $Pd(PPh_3)_4$ (2 mol-%), THF, 60 °C; a) $(Bu_3Sn)_2$ (1.20 equiv.), 5 h, b) $(Bu_3Sn)_2$ (1.2 equiv.), 18 h, c) $Me_3SiSnBu_3$ (0.8 equiv.), 2 h, d) $Me_3SiSnBu_3$ (0.8 equiv.), 16 h, e) 2 h, f) $Me_3SiSnBu_3$ (0.95 equiv.), 11 h, g) $(Bu_3Sn)_2$ (1.05 equiv.), 21 h, h) SiO_2, flash chromatography.

We used this reaction to prepare **21** for a control experiment. The isolated allene was subjected to reaction conditions identical to those used with the stannylated acetate **16**. Although the products obtained, **17** and **18**, were the same as from the allene generated in situ, the reaction was much slower. After 5 h an incomplete reaction had provided a 2:1 mixture of **17** and **18** in a moderate 49% yield. This also supports the idea that a Pd-coordinated allene is formed in situ and is the reacting species.

To verify the scope and limitations of this interesting process, we also subjected the isopropyl-substituted allyl acetate **22** to the same reaction conditions. Although the silastannation proceeded with high yield and regioselectivity (**23**), the corresponding distannylation was a very slow process. Even after 20 h less than a 20% yield of product **24** was obtained. Interestingly, even after such a long reaction time, no isomerization was observed under the reaction conditions, as determined by NMR spectroscopy. Surprisingly, though, the isomerized product **25** was obtained after flash chromatography. Obviously, the isomerization is catalysed by the silica gel.

Conclusions

In conclusion, we have been able to show that stannylated allylic substrates are excellent building blocks for combinatorial chemistry. Depending on the reaction conditions used, they can either be modified through allylic substitutions or they can be converted into Pd-activated allenes that undergo regioselective additions. These additions occur with high regioretention, and the substrate spectrum can be broadened by taking advantage of isomerization processes. The scope and limitations of these processes are being evaluated in ongoing studies.

Experimental Section

General Remarks: All air- or moisture-sensitive reactions were carried out in oven-dried glassware (70 °C). Dried solvents were distilled before use: THF was distilled from $LiAlH_4$ and CH_2Cl_2 was dried with CaH_2 before distillation. Hexabutyldistannane was purified before use by flash chromatography (silica, hexanes). The products were purified by flash chromatography on silica gel columns (Macherey–Nagel 60, 0.063–0.2 mm). Analytical TLC was performed on pre-coated silica gel plates (Macherey–Nagel, Polygram® SIL G/UV_{254}). Visualization was accomplished with the aid of UV light, $KMnO_4$ solution or iodine. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded with Bruker AC 400 [400 MHz (^1H), 100 MHz (^{13}C) and 149 MHz (^{119}Sn)] or Bruker DRX 500 [500 MHz (^1H), 125 MHz (^{13}C) and 186 MHz (^{119}Sn)] spectrometers in $CDCl_3$. Chemical shifts are reported in ppm (δ) with respect to TMS, and $CHCl_3$ was used as the internal standard. Selected signals for minor isomers are extracted from the spectra of the isomeric mixtures. Mass spectra were recorded with a Finnigan MAT 95 spectrometer by the CI technique. Elemental analyses were performed at the Saarland University.

General Procedure for the Allylic Aminations (GP1): $Pd(PPh_3)_4$ (6 mg, 5.0 μmol, 2 mol-%) was dissolved in dry DMF (2 mL) in a Schlenk flask and the mixture was stirred for 15 min at room temperature under nitrogen. After addition of the amine (0.275 mmol, 1.1 equiv.), the solution was cooled to 0 °C and the 2-(tributylstannyl)allyl carbonate (**1**, 0.25 mmol, 1 equiv.) was added dropwise. The reaction mixture was stirred at 0 °C for 2 h. After evaporation of the solvent in vacuo and flash chromatography (hexanes/EtOAc/NEt_3 99:0:1 to 97:2:1) the pure product was obtained.

General Procedure for Pd-Catalysed Bismetallations (GP2): It is strongly recommended that the $Pd(PPh_3)_4$ be prepared freshly before use,[41] because only the pure catalyst (pale yellow crystals) shows activity in this reaction. The same is true for the distannane used. It should be purified by flash chromatography directly before use.

The stannylated allylic substrate **1** (0.5 mmol) was dissolved in abs. THF (1 mL) under Ar in a Schlenk tube. A solution of $Pd(PPh_3)_4$ (12 mg, 10.4 μmol, 2 mol-%) in THF (0.5 mL) was added by syringe, followed either by the bimetal compound (0.55 or 1.05 mmol) or by the tin hydride (480 mg, 1.65 mmol). The reaction mixture was warmed to 60 °C and the reaction was monitored by TLC. After the reaction was complete, the solvent was removed in vacuo and the crude product was purified by flash chromatography (silica, hexanes/Et_2O + 1% NEt_3).

GC–MS Screening of Amines: Piperidine (43 mg, 0.5 mmol, 0.33 equiv.), 1-phenylethylamine (61 mg, 0.5 mmol, 0.33 equiv.), 4-methoxyaniline (62 mg, 0.5 mmol, 0.33 equiv.) and naphthalene (62 mg, 0.5 mmol, 0.33 equiv.) were dissolved in dry THF (2.5 mL) in a Schlenk flask and cooled to –78 °C. In a second Schlenk flask, $[Pd(allyl)Cl]_2$ (5.5 mg, 15 μmol, 1 mol-%) and PPh_3 (17.7 mg, 67 μmol, 4.5 mol-%) were dissolved in dry THF (5 mL) and the mixture was stirred under argon at room temp. for 15 min. The yellowish catalyst solution was then cooled to –78 °C, cinnamyl methyl carbonate (618 mg, 3.0 mmol, 2.0 equiv.) was added, and the resulting mixture was stirred for 15 min at –78 °C and then added dropwise to the amine solution. Samples for GC–MS analyses were taken after 1 h at –78 °C, 1 h at –20 °C, 1 h at 0 °C, 1 h at room temp., 18 h at room temp. and 3 h at 60 °C and directly injected in the GC–MS machine (Hewlett–Packard HP 5890 GC with HP 591A mass detector, DB5 column, 30 m length, 0.25 mm internal diameter, 0.25 μm film, helium as carrier gas, injector: 250 °C, detector: 300 °C, temperature program: 60–175 °C, 5 °C min^{-1}; 175–275, 15 °C min^{-1}, 275 °C, 5 min). Starting materials were identified by their retention times, products were identified by their MS spectra, and naphthalene was used as a internal standard to allow quantitative statements.

GC–MS Screening of Other Nucleophiles: Dimethyl methylmalonate (87 mg, 0.5 mmol, 0.20 equiv.), succinimide (50 mg, 0.5 mmol, 0.20 equiv.), phenol (47 mg, 0.5 mmol, 0.20 equiv.), *N*-hydroxysuccinimide (58 mg, 0.5 mmol, 0.20 equiv.), trifluoroacetamide (57 mg, 0.5 mmol, 0.20 equiv.) and naphthalene (62 mg, 0.5 mmol, 0.20 equiv.) were dissolved in dry THF (2.5 mL) under argon in a Schlenk flask and the mixture was cooled to 0 °C. NaOMe (135 mg, 2.5 mmol, 1 equiv.) was added and the mixture was stirred for 15 min at 0 °C and then cooled to –78 °C. In a second Schlenk flask, $[Pd(allyl)Cl]_2$ (9.2 mg, 25 μmol, 1 mol-%) and PPh_3 (29.5 mg, 0.11 mmol, 4.5 mol-%) were dissolved in dry THF (5 mL) and the mixture was stirred under argon at RT for 15 min. The yellowish catalyst solution was then cooled to –78 °C, cinnamyl methyl carbonate (618 mg, 3.0 mmol, 1.2 equiv.) was added, and the resulting mixture was stirred for 15 min at –78 °C and then added dropwise to solution 1 at –78 °C. Samples for GC–MS analyses were taken and analysed as described for the screening of amines.

In Situ NMR Studies: The substrate **1b** (41 mg, 0.1 mmol, 1 equiv.) was dissolved in [D_8]toluene (0.3 mL) in a NMR tube and the mixture was cooled to 0 °C. A solution of $[Pd(allyl)Cl]_2$ (0.37 mg, 1 μmol, 1 mol-%) and PPh_3 (1.2 mg, 4.5 μmol, 4.5 mol-%) in [D_8]-toluene (0.3 mL) was cooled to 0 °C and added, directly before insertion of the NMR tube with the mixture into the NMR machine (Bruker DRX 500, 500 MHz, ^1H). Measurements were taken over one hour, every minute for the first 10 min, then every 2 min for 10 min, then every 4 min for 20 min and every 5 min for 20 min. The residual solvent peak was used as internal reference for quantification.

1-[2-(Tributylstannyl)allyl]piperidine (5): This compound was obtained by GP1 from piperidine (24 mg, 0.275 mmol, 1.1 equiv.) and ethyl 2-(tributylstannyl)allyl carbonate (**1a**, 105 mg, 0.25 mmol, 1 equiv.) after 2 h at 0 °C. After evaporation of the solvent in vacuo and flash chromatography (hexanes/EtOAc/NEt_3 99:0:1 to 97:2:1) the desired product could be isolated in 94% yield (98 mg, 0.236 mmol) as a colourless oil. R_f (hexanes/EtOAc 8:2): 0.70. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.81–0.97 (m, 15 H, 1-H, 4-H), 1.31 (tq, $^3J_{2,3}$ = 7.3, $^3J_{2,1}$ = 7.2 Hz, 6 H, 2-H), 1.36–1.60 (m, 12 H, 3-H, 9-H, 10-H), 2.27 (br. s, 4 H, 8-H), 2.98 (m, $^3J_{7,Sn}$ = 47.1 Hz, 2 H, 7-H), 5.17 (m, $^3J_{5cis,Sn}$ = 62.8 Hz, 1 H, 5-H_{cis}), 5.76 (m, $^3J_{5trans,Sn}$ = 138.6 Hz, 1 H, 5-H_{trans}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6 (t, $^1J_{4,Sn}$ = 336 Hz, C-4), 13.7 (q, C-1), 24.5 (t, C-10), 26.1 (t, C-9), 27.5 (t, $^3J_{2,Sn}$ = 58 Hz, C-2), 29.2 (t, $^2J_{3,Sn}$ = 19 Hz, C-3), 54.7 (t, C-8), 69.8 (t, C-7), 124.9 (t, C-5), 155.8 (s, C-6) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –50.1 ppm. HRMS (CI): calcd. for $C_{20}H_{41}N^{120}Sn$ 415.2261 $[M]^+$; found 415.2273. $C_{20}H_{41}NSn$ (414.24): calcd. C 57.99, H 9.98, N 3.38; found C 57.89, H 10.04, N 3.27.

4-[2-(Tributylstannyl)allyl]morpholine (6): This compound was obtained by GP1 from morpholine (24 mg, 0.275 mmol, 1.1 equiv.) and methyl 2-(tributylstannyl)allyl carbonate (**1b**, 101 mg, 0.25 mmol, 1 equiv.) after 2 h at 0 °C. After evaporation of the solvent in vacuo and flash chromatography (hexanes/EtOAc/NEt_3 99:0:1 to 97:2:1) the desired product could be isolated in 87% yield (91 mg, 0.219 mmol) as a colourless oil. R_f (hexanes/EtOAc 8:2): 0.59. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.81–0.98 (m, 15 H, 1-H, 4-H), 1.32 (tq, $^3J_{2,3}$ = 7.4, $^3J_{2,1}$ = 7.2 Hz, 6 H, 2-H), 1.47 (m, 6 H, 3-H), 2.36 (br. s, 4 H, 8-H), 3.05 (dd, $^3J_{7,Sn}$ = 46.5, $^4J_{7,5cis}$ = 1.2, $^4J_{7,5trans}$ = 1.2 Hz, 2 H, 7-H), 3.67 (t, $^3J_{9,8}$ = 4.6 Hz, 4 H, 9-H), 5.22 (dt, $^3J_{5cis,Sn}$ = 61.5, $^2J_{5cis,5transs}$ = 2.8, $^4J_{5cis,7}$ = 1.4 Hz, 1 H, 5-H_{cis}), 5.79 (dt, $^3J_{5trans,Sn}$ = 135.6, $^2J_{5trans,5cis}$ = 2.8, $^4J_{5trans,7}$ = 1.4 Hz, 1 H, 5-H_{trans}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6 (t, $^1J_{4,Sn}$ = 330 Hz, C-4), 13.7 (q, C-1), 27.5 (t, $^3J_{2,Sn}$ = 58 Hz, C-2), 29.2 (t, $^2J_{3,Sn}$ = 19 Hz, C-3), 53.7 (t, C-8), 67.1 (t, C-9), 69.4 (t, C-7), 126.3 (t, C-5), 154.1 (s, C-6) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –48.9 ppm. HRMS (CI): calcd. for $C_{19}H_{39}NO^{120}Sn$ 417.2054 $[M]^+$; found 417.2044.

1-[2-(Tributylstannyl)allyl]pyrrolidine (7): This compound was obtained by GP1 from pyrrolidine (20 mg, 0.275 mmol, 1.1 equiv.) and methyl 2-(tributylstannyl)allyl carbonate (**1b**, 101 mg, 0.25 mmol, 1 equiv.) after 2 h at 0 °C. After evaporation of the solvent in vacuo and flash chromatography (hexanes/EtOAc/NEt_3 99:0:1 to 97:2:1) the desired product could be isolated in 86% yield (86 mg, 0.215 mmol) as a colourless oil. R_f (hexanes/EtOAc 8:2): 0.59. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.79–0.96 (m, 15 H, 1-H, 4-H), 1.31 (tq, $^3J_{2,3}$ = 7.4, $^3J_{2,1}$ = 7.2 Hz, 6 H, 2-H), 1.49 (m, 6 H, 3-H), 1.71 (m, 4 H, 9-H), 2.39 (br. s, 4 H, 8-H), 3.17 (m, $^3J_{7,Sn}$ = 44.9 Hz, 2 H, 7-H), 5.14 (dt, $^3J_{5cis,Sn}$ = 63.3, $^2J_{5cis,5trans}$ = 2.6, $^4J_{5cis,7}$ = 1.3 Hz, 1 H, 5-H_{cis}), 5.79 (dt, $^3J_{5trans,Sn}$ = 139.1, $^2J_{5trans,5cis}$ = 2.7, $^4J_{5trans,7}$ = 1.3 Hz, 1 H, 5-H_{trans}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.5 (t, C-4), 13.7 (q, C-1), 23.6 (t, C-9), 27.5 (t, C-2), 29.2 (t, C-3), 54.0 (t, C-8), 66.1 (t, C-7), 123.8 (t, C-5), 152.5 (s, C-6) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –49.0 ppm. HRMS (CI): calcd. for $C_{19}H_{39}N^{120}Sn$ 401.2104 $[M]^+$; found 401.2152.

***N*,*N*-Diethyl-1-[2-(tributylstannyl)allyl]amine (8):** This compound was obtained by GP1 from diethylamine (20 mg, 0.275 mmol, 1.1 equiv.) and methyl 2-(tributylstannyl)allyl carbonate (**1b**, 101 mg, 0.25 mmol, 1 equiv.) after 2 h at 0 °C. After evaporation of the solvent in vacuo and flash chromatography (hexanes/EtOAc/NEt_3 99:0:1 to 97:2:1) the desired product could be isolated in 90% yield (90 mg, 0.224 mmol) as a colourless oil. R_f (hexanes/EtOAc 8:2): 0.54. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.80–0.94 (m, 15 H, 1-H, 4-H), 0.96 (t, $^3J_{9,8}$ = 7.1 Hz, 6 H, 9-H), 1.31 (tq, $^3J_{2,3}$ = 7.3, $^3J_{2,1}$ = 7.2 Hz, 6 H, 2-H), 1.49 (m, 6 H, 3-H), 2.43 (q, $^3J_{8,9}$ = 7.1 Hz,

4 H, 8-H), 3.11 (dd, $^3J_{7,Sn}$ = 47.1, $^4J_{7,5cis}$ = $^4J_{7,5trans}$ = 1.4 Hz, 2 H, 7-H), 5.18 (m, $^3J_{5cis,Sn}$ = 63.0, $^2J_{5cis,5trans}$ = 2.8, $^4J_{5cis,7}$ = 1.4 Hz, 1 H, 5-H$_{cis}$), 5.79 (m, $^3J_{5trans,Sn}$ = 138.7, $^2J_{5trans,5cis}$ = 2.8, $^4J_{5trans,7}$ = 1.4 Hz, 1 H, 5-H$_{trans}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.5 (t, $^1J_{4,Sn}$ = 328 Hz, C-4), 11.0 (q, C-9), 13.7 (q, C-1), 27.5 (t, $^3J_{2,Sn}$ = 58 Hz, C-2), 29.2 (t, $^2J_{3,Sn}$ = 19 Hz, C-3), 45.9 (t, C-8), 64.1 (t, $^2J_{7,Sn}$ = 34 Hz, C-7), 124.9 (t, $^2J_{5,Sn}$ = 27 Hz, C-5), 156.2 (s, C-6) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –49.4 ppm. HRMS (CI): calcd. for $C_{19}H_{41}N^{120}Sn$ 403.2261 [M]$^+$; found 403.2265.

***N*-(1-Phenylethyl)-2-(tributylstannyl)prop-2-en-1-amine (9):** This compound was obtained by GP1 from 1-phenylethylamine (33 mg, 0.275 mmol, 1.1 equiv.) and methyl 2-(tributylstannyl)allyl carbonate (**1b**, 101 mg, 0.25 mmol, 1 equiv.) after 2 h at 0 °C. After evaporation of the solvent in vacuo and flash chromatography (hexanes/EtOAc/NEt_3 99:0:1 to 97:2:1) the desired product could be isolated in 84% yield (94 mg, 0.209 mmol) as a colourless oil. R_f (hexanes/EtOAc 8:2): 0.56. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82–0.99 (m, 15 H, 1-H, 4-H), 1.27–1.35 (m, 9 H, 2-H, 9-H), 1.49 (m, 6 H, 3-H), 3.23 (dd, $^3J_{7,Sn}$ = 40.7, $^4J_{7,5cis}$ = $^4J_{7,5trans}$ = 1.3 Hz, 2 H, 7-H), 3.75 (q, $^3J_{8,9}$ = 6.6 Hz, 1 H, 8-H), 5.18 (dt, $^3J_{5cis,Sn}$ = 62.8, $^3J_{5cis,5trans}$ = 2.6, $^4J_{5cis,7}$ = 1.3 Hz, 1 H, 5-H$_{cis}$), 5.77 (dt, $^3J_{5trans,Sn}$ = 136.5, $^2J_{5trans,5cis}$ = 2.5, $^4J_{5trans,7}$ = 1.5 Hz, 1 H, 5-H$_{trans}$), 7.23 (m, 1 H, 13-H), 7.29–7.34 (m, 4 H, 11-H, 12-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7 (t, $^1J_{4,Sn}$ = 328 Hz, C-4), 13.7 (q, C-1), 24.2 (q, C-9), 27.4 (t, $^3J_{2,Sn}$ = 57 Hz, C-2), 29.2 (t, $^2J_{3,Sn}$ = 20 Hz, C-3), 57.2 (t, C-7), 57.8 (d, C-8), 124.4 (t, $^2J_{5,Sn}$ = 25 Hz, C-5), 126.6 (d, C-11), 126.8 (d, C-13), 128.3 (d, C-12), 145.9 (s, C-10), 154.9 (s, C-6) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –46.8 ppm. HRMS (CI): calcd. for $C_{23}H_{41}N^{120}Sn$ 451.2261 [M]$^+$; found 451.2271.

Dimethyl 2-[2-(Tributylstannyl)allyl]malonate (10): $Pd(PPh_3)_4$ (6 mg, 5.0 μmol, 2 mol-%) was dissolved in dry DMF (2 mL) in a Schlenk flask and the mixture was stirred under nitrogen at room temperature for 15 min. The solution was cooled to 0 °C and methyl 2-(tributylstannyl)allyl carbonate (**1b**, 101 mg, 0.25 mmol, 1 equiv.) was added. In a second Schlenk flask, dimethyl malonate (36 mg, 0.275 mmol, 1.1 equiv.) was dissolved in dry DMF (2 mL) and NaOMe (14 mg, 0.26 mmol, 1.05 equiv.) was added. The solution was cooled to 0 °C and the catalyst solution was added dropwise. The reaction mixture was allowed to warm to room temp. over 18 h and then stirred for 48 h at room temp. After evaporation of the solvent in vacuo and flash chromatography (hexanes/EtOAc/NEt_3 98:1:1) the desired product could be isolated in 43% yield (49 mg, 0.106 mmol) as a colourless oil. R_f (hexanes/EtOAc 8:2): 0.62. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{1,2}$ = 7.3 Hz, 9 H, 1-H), 0.92 (m, 6 H, 4-H), 1.31 (tq, $^3J_{2,1}$ = 7.3, $^3J_{2,3}$ = 7.2 Hz, 6 H, 2-H), 1.48 (m, 6 H, 3-H), 2.82 (ddd, $^3J_{7,Sn}$ = 39.1, $^3J_{7,8}$ = 7.6, $^3J_{7,5cis}$ = 1.3, $^3J_{7,5trans}$ = 1.6 Hz, 2 H, 7-H), 3.53 (t, $^3J_{8,7}$ = 7.6 Hz, 1 H, 8-H), 3.72 (s, 6 H, 10-H), 5.18 (dt, $^3J_{5cis,Sn}$ = 60.9, $^2J_{5cis,5trans}$ = 2.0, $^4J_{5cis,7}$ = 1.3 Hz, 1 H, 5-H$_{cis}$), 5.70 (dt, $^3J_{5trans,Sn}$ = 130.6, $^2J_{5trans,5cis}$ = 1.9, $^4J_{5trans,7}$ = 1.5 Hz, 1 H, 5-H$_{trans}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6 (t, $^1J_{4,Sn}$ = 334 Hz, C-4), 13.7 (q, C-1), 27.4 (t, $^3J_{2,Sn}$ = 57 Hz, C-3), 29.0 (t, $^2J_{3,Sn}$ = 20 Hz, C-2), 39.3 (t, C-7), 51.3 (d, C-8), 52.4 (q, C-10), 127.1 (t, C-5), 150.5 (s, C-6), 169.4 (s, C-9) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –42.4 ppm. HRMS (CI): calcd. for $C_{20}H_{38}O_4{}^{120}Sn$ [M]$^+$: 405.1088; found 405.1121.

1-[2-(Tributylstannyl)allyl]phenoxide (1g): The stannylated phenyl ether **1g** could be obtained either through hydrostannation of phenylpropargyl ether[9] or by allylic alkylation. $Pd(PPh_3)_4$ (6 mg, 5.0 μmol, 2 mol-%) was dissolved in dry DMF (2 mL) in a Schlenk flask and the mixture was stirred under nitrogen at room temperature for 15 min. The solution was cooled to 0 °C and methyl 2-(tributylstannyl)allyl carbonate (**1b**, 101 mg, 0.25 mmol, 1 equiv.) was added. In a second Schlenk flask, phenol (26 mg, 0.275 mmol, 1.1 equiv.) was dissolved in dry DMF (2 mL), after which NaH (7 mg, 0.30 mmol, 1.2 equiv.) was added. The solution was cooled to –20 °C and the catalyst solution was added dropwise. The reaction mixture was allowed to warm to room temp. over 18 h. After evaporation of the solvent in vacuo and flash chromatography (hexanes/EtOAc/NEt_3 98:1:1) the desired product could be isolated in 36% yield (38 mg, 0.090 mmol) as a colourless oil. R_f (hexanes/EtOAc 8:2): 0.88. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, $^3J_{1,2}$ = 7.3 Hz, 9 H, 1-H), 0.96 (m, 6 H, 4-H), 1.31 (tq, $^3J_{2,1}$ = 7.4, $^3J_{2,3}$ = 7.3 Hz, 6 H, 2-H), 1.51 (m, 6 H, 3-H), 4.66 (m, $^3J_{7,Sn}$ = 30.2 Hz, 2 H, 7-H), 5.36 (m, $^3J_{5cis,Sn}$ = 60.3 Hz, 1 H, 5-H$_{cis}$), 5.98 (td, $^3J_{5trans,Sn}$ = 126.2, $^4J_{5trans,7}$ = 1.8, $^2J_{5trans,5cis}$ = 1.7 Hz, 1 H, 5-H$_{trans}$), 6.89 (d, $^3J_{9,10}$ = 8.6 Hz, 2 H, 9-H), 6.94 (dt, $^3J_{11,10}$ = 7.3, $^3J_{11,9}$ = 0.7 Hz, 1 H, 11-H), 7.28 (m, 2 H, 10-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 9.7 (t, $^1J_{4,Sn}$ = 334 Hz, C-4), 13.7 (q, C-1), 27.3 (t, $^3J_{2,Sn}$ = 57 Hz, C-3), 29.1 (t, $^2J_{3,Sn}$ = 20 Hz, C-2), 74.8 (t, C-7), 114.6 (d, C-9), 120.5 (d, C-11), 125.1 (t, C-5), 129.3 (d, C-10), 151.6 (s, C-6), 158.7 (s, C-8) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –42.4 ppm. HRMS (CI): calcd. for $C_{21}H_{36}O^{120}Sn$ 367.1084 [M – Bu]$^+$; found 367.1111. $C_{21}H_{36}OSn$ (423.20): calcd. C 59.60, H 8.57; found C 59.86, H 8.68.

1-[2-(Tributylstannyl)allyl]phthalimide (11): $Pd(PPh_3)_4$ (6 mg, 5.0 μmol, 2 mol-%) was dissolved in dry DMF (2 mL) in a Schlenk flask and the mixture was stirred under nitrogen at room temperature for 15 min. The solution was cooled to 0 °C, after which methyl 2-(tributylstannyl)allyl carbonate (**1b**, 101 mg, 0.25 mmol, 1 equiv.) was added. In a second Schlenk flask, phthalimide (41 mg, 0.275 mmol, 1.1 equiv.) was dissolved in dry DMF (2 mL) and NaH (7 mg, 0.30 mmol, 1.2 equiv.) was added. The solution was cooled to 0 °C and the catalyst solution was added dropwise. The reaction mixture was allowed to warm to room temp. and then stirred at 40 °C for 48 h. After evaporation of the solvent in vacuo and flash chromatography (hexanes/EtOAc/NEt_3 98:1:1) the desired product could be isolated in 46% yield (55 mg, 0.115 mmol) as a colourless oil. R_f (hexanes/EtOAc 8:2): 0.56. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, $^3J_{1,2}$ = 7.3 Hz, 9 H, 1-H), 0.93 (m, 6 H, 4-H), 1.27 (tq, $^3J_{2,1}$ = 7.3, $^3J_{2,3}$ = 7.3 Hz, 6 H, 2-H), 1.47 (m, 6 H, 3-H), 4.41 (dd, $^3J_{7,Sn}$ = 24.0, $^3J_{7,5cis}$ = 1.6, $^3J_{7,5trans}$ = 1.6 Hz, 2 H, 7-H), 5.26 (dt, $^3J_{5cis,Sn}$ = 58.1, $^2J_{5cis,5trans}$ = 1.6, $^4J_{5cis,7}$ = 1.6 Hz, 1 H, 5-H$_{cis}$), 5.70 (dt, $^3J_{5trans,Sn}$ = 122.5, $^2J_{5trans,5cis}$ = 1.8, $^4J_{5trans,7}$ = 1.7 Hz, 1 H, 5-H$_{trans}$), 7.71 (m, 2 H, 11-H), 7.85 (m, 2 H, 10-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.4 (t, $^1J_{4,Sn}$ = 332 Hz, C-4), 13.6 (q, C-1), 27.3 (t, $^3J_{2,Sn}$ = 58 Hz, C-3), 29.0 (t, $^2J_{3,Sn}$ = 20 Hz, C-2), 45.6 (t, $^2J_{7,Sn}$ = 55 Hz, C-7), 123.2 (d, C-10), 125.4 (t, $^2J_{5,Sn}$ = 20 Hz, C-5), 132.1 (s, C-9), 133.9 (d, C-11), 147.4 (s, C-6), 168.0 (s, C-8) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –40.0 ppm. HRMS (CI): calcd. for $C_{23}H_{35}NO_2{}^{120}Sn$ 420.0986 [M – Bu]$^+$; found 420.0935.

3-(Tributylstannyl)-2-(trimethylsilyl)prop-1-ene (14): This compound was obtained by GP2 (reaction time: 18 h) from **1g** (213 mg, 0.50 mmol) and $Bu_3SnSiMe_3$ (128 mg, 0.35 mmol) as a colourless liquid; yield: 99 mg (0.26 mmol, 70%). R_f (hexanes): 0.67. ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.05 (d, $^2J_{1,Si}$ = 6.8 Hz, 9 H, 1-H), 0.81 (dt, $^2J_{8,Sn}$ = 50.2, $^2J_{8,7}$ = 8.2 Hz, 6 H, 8-H), 0.87 (t, $^3J_{5,6}$ = 7.3 Hz, 9 H, 5-H), 1.28 (tq, $^3J_{6,7}$ = 8.2, $^3J_{6,5}$ = 7.3 Hz, 6 H, 6-H), 1.42–1.51 (m, 6 H, 7-H), 1.87 (dd, $^2J_{4,Sn}$ = 62.7, $^4J_{4,2cis}$ = 1.1 Hz, 2 H, 4-H), 5.05 (dd, $^4J_{2trans,Sn}$ = 20.8, $^2J_{2trans,2cis}$ = 3.0 Hz, 1 H, 2-H$_{trans}$), 5.32 (ddt, $^4J_{2cis,Sn}$ = 19.8, $^2J_{2cis,2trans}$ = 3.0, $^4J_{2cis,1}$ = 1.1 Hz, 1 H, 2-H$_{cis}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.59 (q, C-1), 9.73 (t, J_{Sn} = 307.4 Hz, C-8), 13.7 (q, C-5), 17.2 (t, C-4), 27.4 (t, J_{Sn} = 54.3 Hz, C-7), 29.3 (t, J_{Sn} = 29.0 Hz, C-6), 120.0 (t, C-2), 152.1 (s,

C-3) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –16.8 ppm. HRMS (CI): calcd. for $C_{14}H_{31}Si^{120}Sn$ 347.1217 $[M]^+$; found 347.1260.

(*E*)-1-Phenyl-2,3-bis(tributylstannyl)prop-1-ene [(*E*)-18]: This compound was obtained by GP2 (reaction time: 18 h) from **16** (235 mg, 0.50 mmol) and $(Bu_3Sn)_2$ (348 mg, 0.60 mmol) as a colourless liquid; yield: 250 mg (0.36 mmol, 71%). R_f (hexanes): 0.55. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77 (dt, $^2J_{4,Sn}$ = 49.5, $^3J_{4,3}$ = 8.2 Hz, 6 H, 4-H), 0.84 [t, $^3J_{1(8),2(9)}$ = 7.3 Hz, 9 H, 1(8)-H], 0.90 [t, $^3J_{8(1),9(2)}$ = 7.3 Hz, 9 H, 8(2)-H], 0.93 (dt, $^2J_{11,Sn}$ = 50.1, $^3J_{11,10}$ = 8.4 Hz, 6 H, 11-H), 1.23 [tq, $^3J_{2(9),3(11)}$ = 7.4, $^3J_{2(9),1(8)}$ = 7.3 Hz, 6 H, 2(9)-H], 1.25–1.45 [m, 6 H, 9(2)-H], 1.45–1.67 (m, 12 H, 3-H, 10-H), 2.42 (ddd, $^2J_{7,Sn}$ = 67.8, $^3J_{7,Sn'}$ = 67.8, $^4J_{7,5}$ = 1.0 Hz, 2 H, 7-H), 6.19 (ddd, $^3J_{5,Sn}$ = 73.8, $^4J_{5,Sn}$ = 22.6, $^4J_{5,7}$ = 1.0 Hz, 1 H, 5-H), 7.11 (tt, $^3J_{15,14}$ = 7.2, $^4J_{15,13}$ = 1.7 Hz, 1 H, 15-H), 7.22–7.31 (m, 4 H, 13-H, 14-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7 (t, J_{Sn} = 316.1 Hz, C-4), 10.2 (t, J_{Sn} = 303.0 Hz, C-11), 13.6 (q, C-12), 13.7 (q, C-8), 19.8 (t, C-7), 27.4 (t, C-2), 27.5 (t, C-9), 29.1 (t, J_{Sn} = 19.1 Hz, C-3), 29.2 (t, J_{Sn} = 19.1 Hz, C-10), 123.5 (d, C-15), 128.1 (d, C-13), 128.5 (d, C-14), 132.9 (d, C-5), 139.2 (s, C-12), 148.9 (s, C-6) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –37.9, –19.9 ppm. Selected signals from the stereoisomer (*Z*)-**18**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (ddd, $^2J_{7,Sn}$ = 59.5, $^3J_{7,Sn}$ = 59.5, $^4J_{7,5}$ = 1.0 Hz, 2 H, 7-H), 7.06 (ddd, $^3J_{5,Sn}$ = 132.0, $^4J_{5,Sn}$ = 21.6, $^4J_{5,7}$ = 1.0 Hz, 1 H, 5-H) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –49.6, –14.3 ppm.

3-Phenyl-3-tributylstannyl-2-(trimethylsilyl)prop-1-ene (19): This compound was obtained by GP2 (reaction time: 2 h) from **16** (282 mg, 0.61 mmol) and $Bu_3SnSiMe_3$ (182 mg, 0.50 mmol) as a colourless liquid; yield: 98 mg (0.20 mmol, 85%). R_f (hexanes): 0.50. ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.06 (d, $^2J_{1,Si}$ = 6.5 Hz, 9 H, 1-H), 0.79 (t, $^3J_{12,11}$ = 8.2 Hz, 6 H, 12-H), 0.83 (t, $^3J_{9,10}$ = 7.3 Hz, 6 H, 9-H), 1.23 (tq, $^3J_{10,11}$ = 7.3, $^3J_{10,9}$ = 7.3 Hz, 6 H, 10-H), 1.26–1.45 (m, 6 H, 11-H), 3.56 (dd, $^2J_{4,Sn}$ = 60.7, $^4J_{4,2cis}$ = 1.0 Hz, 1 H, 4-H), 5.60 (dd, $^4J_{2trans,Sn}$ = 9.5, $^2J_{2trans,2cis}$ = 2.3 Hz, 1 H, 2-H$_{trans}$), 5.63 (dd, $^4J_{2cis,Sn}$ = 8.5, $^2J_{2cis,2trans}$ = 2.3, $^4J_{2cis,4}$ = 1.0 Hz, 1 H, 2-H$_{cis}$), 6.96 (tt, $^3J_{8,7}$ = 7.3, $^4J_{8,6}$ = 1.4 Hz, 1 H, 8-H), 7.04 (dd, $^3J_{6,7}$ = 8.5, $^4J_{6,8}$ = 1.4 Hz, 2 H, 6-H), 7.15 (ddd, $^3J_{7,6}$ = 7.3, $^3J_{7,8}$ = 7.3, $^4J_{7,7'}$ = 1.8 Hz, 2 H, 7-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.4 (q, J_{Si} = 51.4 Hz, C-1), 10.4 (t, J_{Sn} = 296.4 Hz, C-12), 13.7 (q, C-9), 27.4 (t, J_{Sn} = 55.8 Hz, C-11), 29.0 (t, J_{Sn} = 19.1 Hz, C-10), 41.3 (d, J_{Sn} = 242.1 Hz, C-4), 123.5 (t, J_{Sn} = 13.2 Hz, C-2), 126.5 (d, J_{Sn} = 21.3 Hz, C-7), 127.0 (d, C-8), 128.0 (d, J_{Sn} = 11.0 Hz, C-6), 144.6 (s, J_{Sn} = 31.5 Hz, C-5), 153.7 (s, J_{Sn} = 30.8 Hz, C-3) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –10.0 ppm. HRMS (CI): calcd. for $C_{20}H_{35}Si^{120}Sn$ 423.1530 $[M]^+$; found 423.153.

4-Methyl-3-(tributylstannyl)-2-(trimethylsilyl)pent-1-ene (23): This compound was obtained by GP2 (reaction time: 11 h) from **22**[11] (255 mg, 0.59 mmol) and $Bu_3SnSiMe_3$ (207 mg, 0.57 mmol) as a colourless liquid; yield: 206 mg (0.46 mmol, 81%). R_f (hexanes): 0.67. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (d, $^2J_{1,Si}$ = 6.5 Hz, 9 H, 1-H), 0.81 (dt, $^2J_{10,Sn}$ = 48.7, $^3J_{10,9}$ = 8.3 Hz, 6 H, 10-H), 0.86 (d, $^3J_{6,5}$ = 6.5 Hz, 3 H, 6-H), 0.87 (t, $^3J_{7,8}$ = 7.3 Hz, 9 H, 7-H), 0.95 (d, $^3J_{6',5}$ = 6.5 Hz, 3 H, 6′-H), 1.29 (tq, $^3J_{8,9}$ = 7.3, $^3J_{8,7}$ = 7.3 Hz, 6 H, 8-H), 1.35–1.55 (m, 6 H, 9-H), 1.84 (dd, $^2J_{4,Sn}$ = 54.5, $^3J_{4,5}$ = 10.8 Hz, 1 H, 4-H), 2.11 (dqq, $^3J_{5,Sn}$ = 10.8, $^3J_{5,6}$ = $^3J_{5,6'}$ = 6.5 Hz, 1 H, 5-H), 5.29 (ddd, $^4J_{2trans,Sn}$ = 21.6, $^3J_{2trans,Si}$ = 9.8, $^2J_{2trans,2cis}$ = 2.3 Hz, 1 H, 2-H$_{trans}$), 5.36 (dd, $^4J_{2a,Sn}$ = 18.3, $^2J_{2cis,5trans}$ = 2.3 Hz, 1 H, 2-H$_{cis}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.6 (q, C-1), 10.6 (t, J_{Sn} = 292.7 Hz, C-10), 13.6 (q, C-7), 22.9 (q, J_{Sn} = 50.6 Hz, C-6′), 24.6 (q, J_{Sn} = 24.7 Hz, C-6), 27.6 (t, J_{Sn} = 57.2 Hz, C-9), 29.3 (t, J_{Sn} = 19.1 Hz, C-8), 31.7 (d, J_{Sn} = 16.1 Hz, C-5), 43.4 (d, C-4), 120.9 (t, C-2), 156.3 (s, J_{Sn} = 30.8 Hz, C-3) ppm. ^{119}Sn NMR (149.2 MHz, $CDCl_3$): δ = –21.5 ppm. HRMS (CI): calcd. for $C_{17}H_{37}Si^{120}Sn$ 389.1687 $[M]^+$; found 389.1719. $C_{21}H_{46}SiSn$ (445.37): calcd. C 56.63, H 10.41; found C 55.92, H 10.10.

All other dimetallated products are known compounds. The references are given in the text.

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