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A Catalyst-Economic One-Pot Protocol for the Synthesis and Conversion of Functionalized Vinylstannanes

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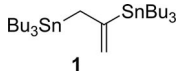
Dedicated to Professor G. Huttner on the occasion of his 75th birthday

Keywords: Allylation / Distannylations / Hydrostannylations / Tin / Palladium / Radicals

A wide range of functionalized compounds can easily be obtained by a Pd-catalyzed one-pot hydrostannylation/elimination/distannylation/radical allylation sequence. The Pd catalyst used can be involved in up to five different reaction steps.

Introduction

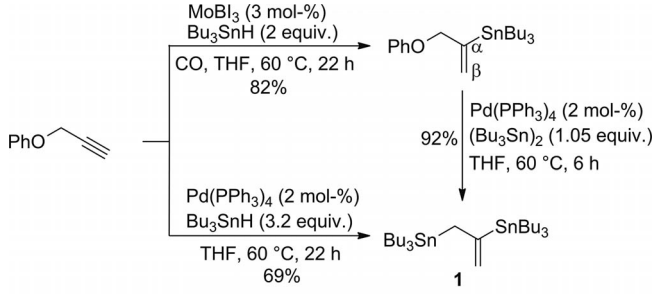
Organotin compounds are reasonably stable organometallic reagents (the C–Sn bond-dissociation energy is approximately 50 kJ/mol) that have found widespread application in organic synthesis.[1] Vinyl- and arylstannanes are popular substrates for Pd-catalyzed cross-coupling reactions (Stille couplings),[2] and allylstannanes can be used in allylation reactions. These can be carried out under Lewis acid catalysis,[3] under thermal[4] or radical conditions.[5] Therefore, distannylated alkenes such as **1**,[6] containing both a vinyl- and an allylstannane unit, should be ideal substrates for combinatorial synthesis, combining either carbonyl additions[7] or radical allylations[8] with subsequent Stille couplings (Figure 1).



1

Figure 1. Distannylated alkene **1**.

Our group is also involved in the synthesis of functionalized vinylstannanes, investigating their synthetic potential.[9] Besides stannylated allyl sulfones[10] and phosphates,[11] allyl acetates and carbonates have been found to be especially valuable synthetic building blocks.[12] The allyl acetate or carbonate moiety allows allylic substitutions, and subsequently, Stille couplings can be carried out on the vinylstannane subunit.[13] The required stannylated allylic substrates can easily be obtained by regioselective hydrostannylations of the corresponding propargyl esters catalyzed by $Mo(CO)_3(CNtBu)_3$ ($MoBl_3$).[14] This protocol allows the regioselective metallation of a wide range of propargyl alcohol derivatives, including phenyl ethers (Scheme 1).[15] If these stannylated allyl phenyl ethers are treated with hexabutyldistannane in the presence of a Pd catalyst, distannylated alkenes **1** are obtained by an elimination/addition mechanism.[16]



$MoBl_3 = Mo(CO)_3(CNtBu)_3$

Scheme 1. Syntheses of distannane **1**.

Although stannylated allyl phenyl ethers are stable in the absence of Pd^0, in its presence, elimination of Bu_3SnOPh is observed, resulting in an alkene–Pd complex (which can eliminate allene), which undergoes Pd-catalyzed distannane addition. Bearing in mind that hexabutyldistannane is formed by a Pd-catalyzed decomposition of Bu_3SnH, and that Pd^0 also catalyzes the hydrostannylation of alkynes, **1** can also be obtained directly from phenyl propargyl ether. Although the yield is lower than in the Mo-catalyzed process (because of the lower regioselectivity in the hydrostannylation step),[17] this protocol is the more convenient one. The only disadvantage results from the difficulties in the separation of **1** from the $(Bu_3Sn)_2$ formed.

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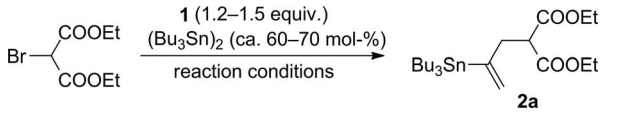
On the other hand, $(Bu_3Sn)_2$ is an excellent initiator for radical reactions, since the Sn–Sn bond can easily be cleaved thermally or under irradiation.[18] Therefore, we were interested to see whether the preparation of **1** could be combined with a subsequent radical substitution.

Results and Discussion

As a model experiment, we investigated the reaction of bromomalonate with crude **1**, containing around 50% $(Bu_3Sn)_2$. Bromomalonate generates a well-stabilized electrophilic radical that should react nicely with the electron-rich distannane. In initial experiments, we investigated several sets of reaction conditions to find the best conditions for the allylation (Table 1). With a slight excess of the distannane, high yields could be obtained under all conditions. The very mild protocol using BEt_3/O_2[19] as well as the photochemical reaction provided the expected product in around 80% yield (Table 1, Entries 1 and 2). Under thermal conditions, more than 90% yield could be obtained (Table 1, Entry 3), even after 5 min.[20] In this case, the $(Bu_3Sn)_2$ acts as a radical initiator, and so the addition of AIBN had no further positive effect (Table 1, Entry 4).

Table 1. Allylation of diethyl bromomalonate with distannane **1**.



Entry	Reaction conditions	Yield [%]
1	BEt_3 (0.5 equiv.)/O_2, THF, 0 °C, 5 min	76[a]
2	PhH, hν, 15 min	83[a]
3	PhH, 80 °C, 5 min	93[b]
4	PhH, AIBN (20 mol-%), 80 °C, 5 min	88[b]

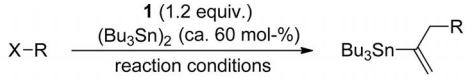
[a] 1.5 equiv. **1**. [b] 1.2 equiv. **1**.

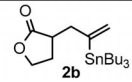
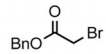
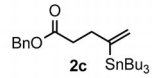
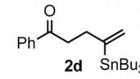
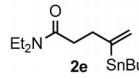
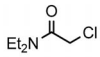
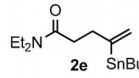
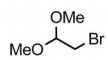
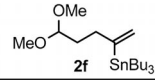
To prove the generality of this protocol and to evaluate the range of radical precursors that could be used, we subjected a series of other halogenated compounds to these reaction conditions. In general, the reactions were stopped after the halogenated compound was consumed (as determined by TLC). The results are summarized in Table 2, and the conditions that gave the best results are shown in each case. Besides bromomalonate, α-brominated esters, lactones, and ketones (Table 2, Entries 1–3) also gave good results. In principle, other halides can also be used, but the yields obtained with chlorides are significantly worse than those with bromides or iodides (Table 2, Entries 4 and 5).

Stabilization of the in situ formed radical by an electron-withdrawing carbonyl group has a positive effect on the reaction, while simple alkyl bromides or α-brominated acetals gave lower yields (Table 2, Entry 6). With such a substrate, the best result was obtained by the BEt_3-method; under irradiation conditions only 20% yield was obtained.

Encouraged by the good results obtained with the electrophilic radicals, next we tried to combine the generation of the distannanes with the radical substitution to a one-pot

Table 2. Allylation of several halogenated compounds with distannane **1**.

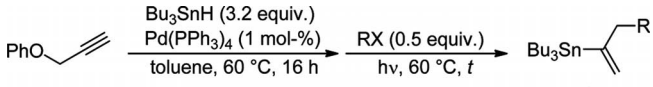


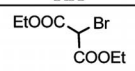
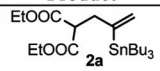
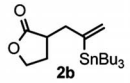
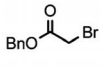
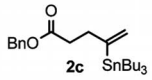
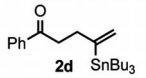
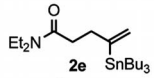
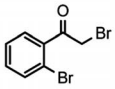
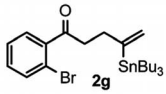
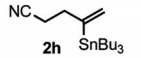
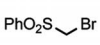
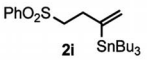
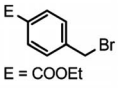
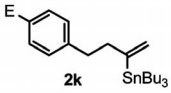
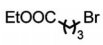
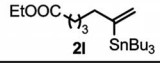
Entry	RX	Reaction conditions	Product	Yield [%]
1		hν, 30 min	 **2b**	78
2		hν, 30 min	 **2c**	81
3		hν, 10 min	 **2d**	77
4		hν, 5 min, 60–80 °C	 **2e**	71
5		hν, 1 h	 **2e**	31
6		BEt_3/O_2, THF, 0 °C to r.t., 30 min	 **2f**	31

protocol. The hydrostannylation/elimination/distannylation sequence proceeds under completely neutral conditions, as does the radical allylation. Therefore, a one-pot process should be possible. Bearing in mind that the Pd-catalyzed hydrostannylation proceeds with lower regioselectivity than the Mo version, 2 equiv. of alkyne (relative to the halide) were used. If Bu_3SnH was used as the single tin source, at least 3 equiv. (relative to the alkyne) were necessary. Because the "wrong isomer" of the hydrostannylation cannot undergo elimination to form the allene, the unconsumed $(Bu_3Sn)_2$ can act as radical initiator. The results obtained in this one-pot process are summarized in Table 3 and are comparable to those obtained in the single-step process (Table 3, Entries 1–5). Interestingly, the *o*-brominated phenacyl bromide gave a significantly lower yield than did the non-ring-brominated ketone (Table 3, Entries 4 and 6). Probably this is the result of competing aryl radical reactions caused by an unselective Br abstraction by the tin radical. Another reason might be that the product formed (i.e. **2g**) undergoes further reactions.[21] In addition, we observed that under the one-pot conditions, less electrophilic radicals react more slowly and give lower product yields, but in principle they can be used as well (Table 3, Entries 9 and 10).

Not only the functionalities arising from the halogenated compound are suitable candidates for further modifications, but also those from the vinyltin unit. For example, the one-pot reaction can be combined with a tin/iodine exchange resulting in an umpolung of the allyl chain and the formation of an electrophilic vinyl iodide (**3**) (Scheme 2). Because the allylation reaction proceeds quickly and under mild conditions, the Pd catalyst is unaffected during the radical reaction and retains its reactivity. Therefore, it should be possible to add a final Stille coupling to the one-pot sequence.

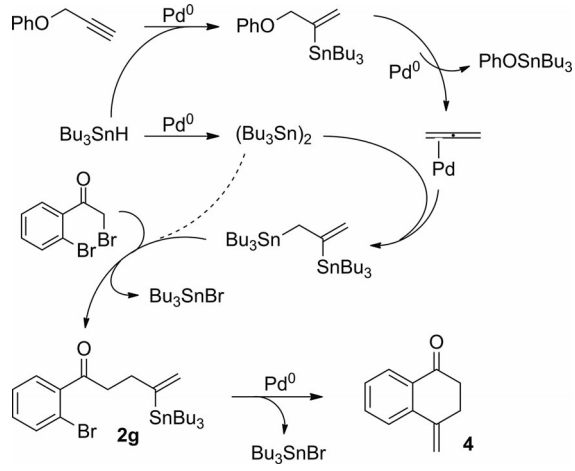
Table 3. Syntheses of vinylstannanes by a one-pot hydrostannylation/elimination/distannylation/radical allylation sequence.



Entry	RX	*t* [min]	Product	Yield [%]
1		30	 **2a**	82
2		60	 **2b**	75
3		60	 **2c**	73
4		30	 **2d**	81
5		30	 **2e**	61
6		30	 **2g**	43
7		30	 **2h**	89
8		30	 **2i**	56
9		120	 **2k**	37
10		120	 **2l**	29

When the allylation reaction mixture with *o*-bromophenacyl bromide was subsequently heated to 90 °C overnight, cyclized ketone **4** was formed. The yield obtained was almost the same as for stannylated ketone **2g** (Table 3, Entry 6), indicating that the intramolecular Stille reaction must proceed in almost quantitative yield. Interestingly, no isomerization of the exocyclic double bond was observed, even though the product of such an isomerization would be a naphthol derivative.

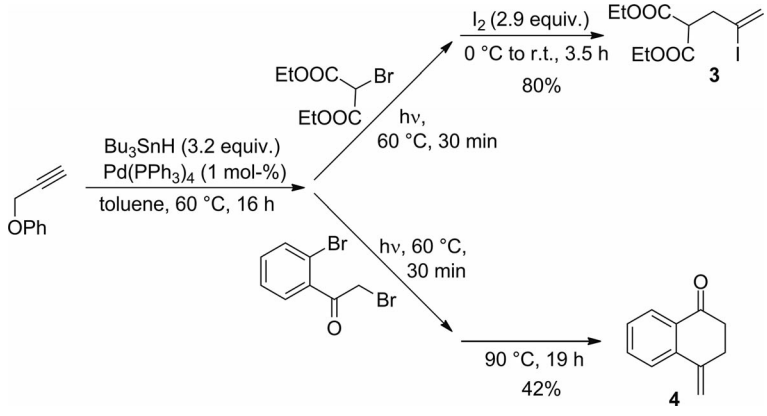
A yield of 42% is not overwhelming at first sight, but one should keep in mind how many steps are involved, and how many functions were taken on by the Pd catalyst, which was used only in small amounts (1 mol-%). The whole scenario described for the last example is summarized in Scheme 3. The first step is a Pd-catalyzed hydrostannylation of phenyl propargyl ether giving rise to the internally stannylated allyl ether with moderate regioselectivity (ca. 65%).[16] Under the influence of the Pd catalyst, this stannylated ether undergoes elimination of $PhOSnBu_3$ to give the allene.[12c] After the elimination, the allene, at least for some time, remains coordinated to Pd, otherwise it would evaporate under the reaction conditions (60 °C). In parallel, the Pd complex catalyzes the decomposition of Bu_3SnH to $(Bu_3Sn)_2$, which is added to the allene, also under the influence of Pd^0. In addition, the $(Bu_3Sn)_2$ also initiates the addition of the phenacyl bromide to the distannane, which is followed by the Pd-catalyzed Stille coupling.



Scheme 3. Proposed mechanism of the one-pot reaction leading to **4**.

Conclusions

We were able to develop a straightforward one-pot process for the conversion of phenyl propargyl ether into a



Scheme 2. Expanded one-pot reactions.

wide range of functionalized vinylstannanes, which can be modified even further. This process is characterized by a high catalyst economy, because the Pd catalyst used can catalyze up to five different processes. The Bu_3SnH used is also involved in several steps of the sequence. Applications of this new protocol to the synthesis of more complex structures such as natural products are currently under investigation.

Experimental Section

General Remarks: All air- and moisture-sensitive reactions were carried out in dried glassware under argon. All radical reactions were carried out in degassed solvents (argon). In photochemical reactions, a 300 W lamp with a Pyrex filter served as light source. The products were purified by flash chromatography on silica gel columns (0.063–0.2 mm). Mixtures of hexanes and ethyl acetate were generally used as eluents. ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded in $CDCl_3$ (^1H: 400 MHz; ^{13}C: 100 MHz; ^{119}Sn: 149 MHz). Chemical shifts are reported in ppm (δ) relative to Me_4Si by using $CHCl_3$ as internal standard. Calibration of ^{119}Sn experiments was done numerically with respect to a standard reference value. Mass spectra were recorded with a quadrupole spectrometer by using the CI technique.

General Procedure for the Photochemical Allylation with Distannane (GP1): A solution of halide (1.0 equiv.) and allyl stannane (1.2 or 1.5 equiv., ca. 50:50 mixture with hexabutyldistannane) in dry, degassed benzene or toluene (0.5 M) was irradiated until no more consumption of the starting material was observed (TLC). During irradiation, the internal temperature rose to 60 °C. After cooling to room temperature, the solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography.

General Procedure for the One-Pot Hydrostannylation/Elimination/Distannylation/Radical Allylation Sequence (GP2): Tributyltin hydride (3.2 equiv.) was slowly added to a solution of phenyl propargyl ether (1.0 equiv.) and tetrakis(triphenylphosphane)palladium(0) (1 mol-%) in dry, degassed toluene (0.75 M) at 0 °C. The color of the yellow solution changed to brown, and an effervescence of hydrogen gas was observed. After the tin hydride addition, the reaction mixture was stirred at 60 °C for 16 h. After completion of the distannylation (TLC), the corresponding halide was added, and the mixture was irradiated and stirred at 60 °C until no more consumption of the radical precursor was observed (TLC). After cooling to room temperature, the solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography.

Diethyl 2-[2-(Tributylstannyl)allyl]malonate (2a):[12c] Diethyl 2-bromomalonate (131 mg, 90%, 0.49 mmol) and **1**[16] (956 mg, 55%, 0.78 mmol, containing 45% hexabutyldistannane) were dissolved in dry, degassed benzene (1 mL), and the reaction mixture was stirred at 80 °C for 5 min. After completion of the allylation, the solvent was evaporated under reduced pressure at room temperature, and the brown, liquid residue was purified by flash chromatography (silica, hexanes/ethyl acetate, 98:2 + 2% NEt_3). Compound **2a** (225 mg, 0.46 mmol, 93%) was isolated as a colorless oil. ^1H NMR: δ = 0.89 (t, J = 7.3 Hz, 9 H), 0.93 (m, $J_{C,Sn}$ = 50.6 Hz, 6 H), 1.26 (t, J = 7.1 Hz, 6 H), 1.31 (m, 6 H), 1.54 (m, 6 H), 2.82 (dt, J = 7.6, 1.2, $J_{C,Sn}$ = 39.1 Hz, 2 H), 3.48 (t, J = 7.6 Hz, 1 H), 4.18 (q, J = 7.1 Hz, 4 H), 5.18 (dt, J = 2.1, 1.1, $J_{C,Sn}$ = 61.2 Hz, 1 H), 5.71 (m, $J_{C,Sn}$ = 132 Hz, 1 H) ppm. ^{13}C NMR: δ = 9.6 ($J_{C,Sn}$ = 334 Hz), 13.7, 14.1, 27.4, 29.0, 39.3, 51.6, 61.3, 127.0, 150.6, 169.1 ppm. ^{119}Sn NMR: δ = –42.9 ppm. HRMS (CI): calcd. for $C_{18}H_{33}O_4Sn$ $[M - C_4H_9]^+$ 433.1401; found 433.1432.

3-[2-(Tributylstannyl)allyl]dihydrofuran-2(3*H*)-one (2b): According to GP1 by starting from α-bromo-γ-butyrolactone (84.2 mg, 0.50 mmol) and **1** (675 mg, 55%, 0.60 mmol, containing 45% hexabutyldistannane) in toluene, after workup and purification (silica, hexanes/ethyl acetate, 97:3 + 2% NEt_3) of the brown, liquid crude material, compound **2b** (160 mg, 0.39 mmol, 78%) was obtained as a colorless oil. ^1H NMR: δ = 0.90 (t, J = 7.3 Hz, 9 H), 0.92 (m, $J_{C,Sn}$ = 50.3 Hz, 6 H), 1.32 (m, 6 H), 1.54 (m, 6 H), 1.90 (m, 1 H), 2.25 (dd, J = 14.6, 11.2 Hz, 1 H), 2.31 (m, 1 H), 2.61 (m, 1 H), 2.94 (dddd, J = 14.6, 3.4, 1.6, 1.6, $J_{C,Sn}$ = 37.6 Hz, 1 H), 4.21 (m, 1 H), 4.33 (m, 1 H), 5.23 (m, $J_{C,Sn}$ = 60.5 Hz, 1 H), 5.72 (m, $J_{C,Sn}$ = 131 Hz, 1 H) ppm. ^{13}C NMR: δ = 9.6, 13.7, 27.3 ($J_{C,Sn}$ = 56.4 Hz), 28.5, 29.1, 38.8, 41.8, 66.5, 126.9, 151.8, 179.1 ppm. ^{119}Sn NMR: δ = –43.1 ppm. HRMS (CI): calcd. for $C_{19}H_{37}O_2Sn$ $[M + H]^+$ 417.1813; found 417.1811.

Benzyl 4-(Tributylstannyl)pent-4-enoate (2c): According to GP1, benzyl bromoacetate (122 mg, 0.51 mmol) and **1** (661 mg, 55%, 0.59 mmol, 55:45 mixture with hexabutyldistannane) reacted in toluene. After workup and purification (silica, hexanes/ethyl acetate, 99:1 + 2% NEt_3) of the brown, liquid crude material, compound **2c** (198 mg, 0.41 mmol, 81%) was isolated as a colorless oil. ^1H NMR: δ = 0.88 (t, J = 7.3 Hz, 9 H), 0.90 (m, $J_{C,Sn}$ = 50.5 Hz, 6 H), 1.31 (m, 6 H), 1.54 (m, 6 H), 2.46 (m, 2 H), 2.58 (m, $J_{C,Sn}$ = 39.1 Hz, 2 H), 5.12 (s, 2 H), 5.15 (dt, J = 2.3, 1.2, $J_{C,Sn}$ = 62.5 Hz, 1 H), 5.69 (m, $J_{C,Sn}$ = 135 Hz, 1 H), 7.29–7.40 (m, 5 H) ppm. ^{13}C NMR: δ = 9.5 ($J_{C,Sn}$ = 333 Hz), 13.7, 27.4 ($J_{C,Sn}$ = 57.0 Hz), 29.1 ($J_{C,Sn}$ = 20.1 Hz), 34.0, 35.6, 66.2, 125.4, 128.2 (2 C), 128.5, 136.0, 153.0, 173.0 ppm. ^{119}Sn NMR: δ = –43.9 ppm. HRMS (CI): calcd. for $C_{20}H_{32}O_2Sn$ $[M - C_4H_9 + H]^+$ 424.1424; found 424.1422.

1-Phenyl-4-(tributylstannyl)pent-4-en-1-one (2d): According to GP2, phenyl propargyl ether (139 mg, 1.03 mmol) was distannylated by using tetrakis(triphenylphosphane)palladium (11.5 mg, 9.95 μmol) and tributyltin hydride (939 mg, 3.23 mmol) and treated in the second step with 2-bromoacetophenone (102 mg, 0.50 mmol). Workup and purification (silica, hexanes/ethyl acetate, 99:1 + 2% NEt_3) of the yellow, liquid crude product delivered compound **2d** (181 mg, 0.40 mmol, 81%) as a colorless oil. ^1H NMR: δ = 0.88 (t, J = 7.3 Hz, 9 H), 0.92 (m, $J_{C,Sn}$ = 50.2 Hz, 6 H), 1.32 (m, 6 H), 1.54 (m, 6 H), 2.67 (m, $J_{C,Sn}$ = 40.0 Hz, 2 H), 3.07 (m, 2 H), 5.18 (dt, J = 2.4, 1.2, $J_{C,Sn}$ = 62.7 Hz, 1 H), 5.75 (m, $J_{C,Sn}$ = 136 Hz, 1 H), 7.47 (m, 2 H), 7.56 (m, 1 H), 7.97 (m, 2 H) ppm. ^{13}C NMR: δ = 9.6, 13.7, 27.4 ($J_{C,Sn}$ = 54.0 Hz), 29.1 ($J_{C,Sn}$ = 19.8 Hz), 35.0, 38.2, 125.2, 128.0, 128.6, 133.0, 137.0, 153.7, 199.7 ppm. ^{119}Sn NMR: δ = –43.6 ppm. $C_{23}H_{38}OSn$ (449.26): calcd. C 61.49, H 8.53; found C 61.64, H 8.31. HRMS (CI): calcd. for $C_{19}H_{29}OSn$ $[M - C_4H_9]^+$ 393.1241; found 393.1238.

***N*,*N*-Diethyl-4-(tributylstannyl)pent-4-enamide (2e):** According to GP1 1,2-iodo-*N*,*N*-diethylacetamide (115 mg, 0.46 mmol) and **1** (639 mg, 58%, 0.60 mmol, 58:42 mixture with hexabutyldistannane) reacted in toluene. After workup and purification (silica, hexane/ethyl acetate, 95:5 + 2% NEt_3) of the brown, semisolid crude material, compound **2e** (144 mg, 0.32 mmol, 71%) was isolated as a pale yellow oil. ^1H NMR: δ = 0.88 (t, J = 7.3 Hz, 9 H), 0.91 (m, $J_{C,Sn}$ = 50.2 Hz, 6 H), 1.11 (t, J = 7.1 Hz, 3 H), 1.17 (t, J = 7.1 Hz, 3 H), 1.31 (m, 6 H), 1.53 (m, 6 H), 2.37 (m, 2 H), 2.57 (m, $J_{C,Sn}$ = 40.7 Hz, 2 H), 3.30 (q, J = 7.2 Hz, 2 H), 3.38 (q, J = 7.1 Hz, 2 H), 5.15 (dt, J = 2.3, 1.1, $J_{C,Sn}$ = 63.2 Hz, 1 H), 5.72 (dt, J = 2.5, 1.6, $J_{C,Sn}$ = 137 Hz, 1 H) ppm. ^{13}C NMR: δ = 9.5, 13.1, 13.7, 14.4, 27.4, 29.1 ($^3J_{6,Sn}$ = 19.8 Hz), 33.0, 36.2, 40.1, 41.9, 124.9, 154.2,

171.6 ppm. ^{119}Sn NMR: δ = –44.0 ppm. HRMS (CI): calcd. for $C_{17}H_{34}NOSn$ [M – C_4H_9]$^+$ 388.1663; found 388.1668.

Tributyl-(5,5-dimethoxypent-1-en-2-yl)stannane (2f): Triethylborane (0.25 mL, 1 M in THF, 0.25 mmol) was added to a solution 2-bromo-1,1-dimethoxyethane (88.4 mg, 0.51 mmol) and **1** (643 mg, 58%, 0.60 mmol, 58:42 mixture with hexabutyldistannane) in dry, degassed THF (0.5 M), at 0 °C. Air (5 mL) was discharged into the solution by cannula. The reaction mixture was stirred at 0 °C for 5 min and warmed to room temperature to complete the reaction (TLC). The solvent was evaporated under reduced pressure at room temperature, and the residue was purified by flash chromatography (silica, hexanes/ethyl acetate, 98:2 + 2% NEt_3), giving rise to **2f** (66 mg, 0.16 mmol, 31%) as colorless oil. ^{1}H NMR: δ = 0.89 (t, J = 7.3 Hz, 9 H), 0.91 (m, $J_{C,Sn}$ = 50.0 Hz, 6 H), 1.32 (m, 6 H), 1.49 (m, 6 H), 1.69 (m, 2 H), 2.29 (m, $J_{C,Sn}$ = 43.9 Hz, 2 H), 3.32 (s, 6 H), 4.36 (t, J = 5.7 Hz, 1 H), 5.13 (dt, J = 2.4, 1.0, $J_{C,Sn}$ = 63.1 Hz, 1 H), 5.70 (m, $J_{C,Sn}$ = 138 Hz, 1 H) ppm. ^{13}C NMR: δ = 9.6 ($J_{C,Sn}$ = 331 Hz), 13.7, 27.4 ($J_{C,Sn}$ = 56.9 Hz), 29.1 ($J_{C,Sn}$ = 19.7 Hz), 32.2, 35.9, 52.7, 104.1, 125.1, 154.4 ppm. ^{119}Sn NMR: δ = –45.0 ppm. $C_{19}H_{40}O_2Sn$ (419.24): calcd. C 54.43, H 9.62; found C 54.39, H 9.60. LRMS (CI): calcd. for $C_{15}H_{31}Sn$ [M – $C_4H_9O_2$]$^+$ 331.1; found 331.1.

1-(2-Bromophenyl)-4-(tributylstannyl)pent-4-en-1-one (2g): According to GP2, phenyl propargyl ether (132 mg, 0.99 mmol) was dimetallated by using tetrakis(triphenylphosphane)palladium(0) (11.4 mg, 9.86 μmol) and tributyltin hydride (921 mg, 3.16 mmol) and treated in the second step with 2,2′-dibromoacetophenone (161 mg, 85%, 0.49 mmol). Workup and purification (silica, hexanes/ethyl acetate, 99:1 + 2% NEt_3) of the yellow-brown, liquid crude product delivered stannane **2g** (111 mg, 0.21 mmol, 43%) as a pale yellow oil. ^{1}H NMR: δ = 0.88 (t, J = 7.3 Hz, 9 H), 0.90 (m, 6 H), 1.30 (m, 6 H), 1.54 (m, 6 H), 2.64 (m, $J_{C,Sn}$ = 38.5 Hz, 2 H), 3.02 (m, 2 H), 5.17 (dt, J = 2.3, 1.2, $J_{C,Sn}$ = 62.5 Hz, 1 H), 5.72 (m, J = 135 Hz, 1 H), 7.29 (m, 1 H), 7.34–7.38 (m, 2 H), 7.60 (m, 1 H) ppm. ^{13}C NMR: δ = 9.5, 13.7, 27.4 ($J_{C,Sn}$ = 57.1 Hz), 29.1 ($J_{C,Sn}$ = 24.9 Hz), 34.9, 42.4, 118.6, 125.4, 127.4, 128.5, 131.4, 133.6, 142.0, 153.2, 203.9 ppm. ^{119}Sn NMR: δ = –43.8 ppm. HRMS (CI): calcd. for $C_{19}H_{28}BrOSn$ [M – C_4H_9]$^+$ 471.0346; found 471.0339.

4-(Tributylstannyl)pent-4-enenitrile (2h): According to GP2, phenyl propargyl ether (141 mg, 1.05 mmol) was treated with tetrakis(triphenylphosphane)palladium(0) (11.6 mg, 10.0 μmol) and tributyltin hydride (936 mg, 3.22 mmol) and in the second step with bromoacetonitrile (61.0 mg, 0.49 mmol). Workup and purification (silica, petroleum ether/ethyl acetate, 98:2 + 2% NEt_3) of the yellow, liquid crude material provided compound **2h** (163 mg, 0.44 mmol, 89%) as a colorless oil. ^{1}H NMR: δ = 0.90 (t, J = 7.3 Hz, 9 H), 0.93 (m, 6 H), 1.32 (m, 6 H), 1.49 (m, 6 H), 2.42 (m, 2 H), 2.57 (m, $J_{C,Sn}$ = 35.6 Hz, 2 H), 5.29 (dt, J = 1.7, 1.2, $J_{C,Sn}$ = 60.0 Hz, 1 H), 5.77 (dt, J = 1.7, 1.6, $J_{C,Sn}$ = 128 Hz, 1 H) ppm. ^{13}C NMR: δ = 9.6 ($J_{C,Sn}$ = 336 Hz), 13.6, 16.9, 27.3 ($J_{C,Sn}$ = 56.5 Hz), 29.0 ($J_{C,Sn}$ = 20.4 Hz), 35.8, 119.4, 127.0, 150.7 ppm. ^{119}Sn NMR: δ = –42.3 ppm. HRMS (CI): calcd. for $C_{13}H_{22}NSn$ [M – C_4H_9 – 2H]$^+$ 312.0774; found 312.0801.

Tributyl[4-(phenylsulfonyl)but-1-en-2-yl]stannane (2i): According to GP2, phenyl propargyl ether (128 mg, 0.95 mmol) was distannylated by using tetrakis(triphenylphosphane)palladium (12.5 mg, 10.8 μmol) and tributyltin hydride (940 mg, 3.23 mmol) and treated in the second step with bromomethyl phenyl sulfone (121 mg, 0.50 mmol). Workup and purification (silica, hexanes/ethyl acetate, 97:3 + 2% NEt_3) of the yellow crude liquid yielded sulfone **2i** (138 mg, 0.28 mmol, 56%) as a colorless oil. ^{1}H NMR: δ = 0.85 (m, 6 H), 0.86 (t, J = 7.3 Hz, 9 H), 1.27 (m, 6 H), 1.42 (m, 6 H), 2.59 (m, $J_{C,Sn}$ = 35.6 Hz, 2 H), 3.14 (m, 2 H), 5.16 (dt, J = 1.8, 1.2, $J_{C,Sn}$ = 59.5 Hz, 1 H), 5.64 (dt, J = 1.8, 1.6, $J_{C,Sn}$ = 128 Hz, 1 H), 7.58 (m, 2 H), 7.67 (t, J = 7.4 Hz, 1 H), 7.92 (m, 2 H) ppm. ^{13}C NMR: δ = 9.5 ($J_{C,Sn}$ = 328 Hz), 13.6, 27.3 ($J_{C,Sn}$ = 56.5 Hz), 29.0 ($J_{C,Sn}$ = 20.0 Hz), 33.1, 55.7, 126.6, 128.1, 129.3, 133.7, 139.0, 150.2 ppm. ^{119}Sn NMR: δ = –41.3 ppm. $C_{22}H_{38}O_2SSn$ (485.32): calcd. C 54.45, H 7.89; found C 54.48, H 7.51. HRMS (CI): calcd. for $C_{22}H_{39}O_2SSn$ [M + H]$^+$ 487.1690; found 487.1689.

Ethyl 4-[3-(Tributylstannyl)but-3-enyl]benzoate (2k): According to GP2, phenyl propargyl ether (134 mg, 1.00 mmol) was treated with tetrakis(triphenylphosphane)palladium (11.6 mg, 10.0 μmol) and tributyltin hydride (940 mg, 3.23 mmol) and treated in the second step with ethyl 4-(bromomethyl)benzoate (128 mg, 0.51 mmol). Workup and purification (silica, petroleum ether/ethyl acetate, 99:1 + 2% NEt_3) of the yellow, liquid crude material delivered benzoate **2k** (92 mg, 0.19 mmol, 37%) as a colorless oil. ^{1}H NMR: δ = 0.90 (t, J = 7.3 Hz, 9 H), 0.91 (m, 6 H), 1.33 (m, 6 H), 1.39 (t, J = 7.1 Hz, 3 H), 1.55 (m, 6 H), 2.54 (m, $J_{C,Sn}$ = 42.0 Hz, 2 H), 2.75 (m, 2 H), 4.37 (q, J = 7.1 Hz, 2 H), 5.17 (dt, J = 2.1, 0.9, $J_{C,Sn}$ = 63.0 Hz, 1 H), 5.71 (dt, J = 2.6, 1.5, $J_{C,Sn}$ = 137 Hz, 1 H), 7.24 (d, J = 8.4 Hz, 2 H), 7.96 (d, J = 8.4 Hz) ppm. ^{13}C NMR: δ = 9.6, 13.7, 14.4, 27.4, 29.1 ($J_{C,Sn}$ = 19.7 Hz), 36.1, 42.6, 60.8, 125.5, 126.6, 128.4, 129.6, 147.6, 154.2, 166.7 ppm. ^{119}Sn NMR: δ = –44.8 ppm. $C_{25}H_{42}O_2Sn$ (493.32): calcd. C 60.87, H 8.58; found C 61.20, H 8.45. HRMS (CI): calcd. for $C_{21}H_{33}O_2Sn$ [M – C_4H_9]$^+$ 437.1503; found 437.1493.

Ethyl 6-(Tributylstannyl)hept-6-enoate (2l): According to GP2, phenyl propargyl ether (140 mg, 1.05 mmol) was dimetallated by using tetrakis(triphenylphosphane)palladium (11.5 mg, 9.95 μmol) and tributyltin hydride (942 mg, 3.24 mmol) and treated in the second step with ethyl 4-bromobutyrate (101 mg, 0.51 mmol). Workup and purification (silica, petroleum ether/ethyl acetate, 99:1 + 2% NEt_3) of the yellow, liquid crude product provided compound **2l** (68.0 mg, 0.15 mmol, 29%) as a colorless oil. ^{1}H NMR: δ = 0.89 (t, J = 7.3 Hz, 9 H), 0.89 (m, $J_{C,Sn}$ = 49.7 Hz, 6 H), 1.26 (t, J = 7.2 Hz, 3 H), 1.30 (m, 6 H), 1.36–1.60 (m, 8 H, 4-H), 1.62 (m, 2 H), 2.25 (m, 2 H), 2.30 (m, 2 H), 4.13 (q, J = 7.2 Hz, 2 H), 5.11 (dt, J = 2.5, 0.9, $J_{C,Sn}$ = 63.7 Hz, 1 H), 5.67 (dt, J = 2.8, 1.5, $J_{C,Sn}$ = 140 Hz, 1 H) ppm. ^{13}C NMR: δ = 9.6, 13.7, 14.3, 24.6, 29.0, 27.4, 29.1, 34.2, 40.8, 60.2, 125.0, 155.0, 173.7 ppm. ^{119}Sn NMR: δ = –45.7 ppm. $C_{21}H_{42}O_2Sn$ (445.28): calcd. C 56.65, H 9.51; found C 56.48, H 9.82. HRMS (CI): calcd. for $C_{17}H_{33}O_2Sn$ [M – C_4H_9]$^+$ 389.1503; found 389.1511.

Diethyl 2-(2-Iodoallyl)malonate (3): According to GP2, phenyl propargyl ether (140 mg, 1.05 mmol) was treated with tetrakis(triphenylphosphane)palladium(0) (12.1 mg, 10.5 μmol) and tributyltin hydride (937 mg, 3.22 mmol) and in the second step with diethyl 2-bromomalonate (133 mg, 90%, 0.50 mmol). As a third step, iodine (773 mg, 3.05 mmol) was added at 0 °C, and the reaction mixture was warmed to ambient temperature within 3.5 h.[14b] After iododestannylation was complete, the excess iodine was reduced by using concd. $Na_2S_2O_3$ solution. The aqueous phase was extracted twice with Et_2O, and the combined organic extracts were dried with Na_2SO_4. The solvent was removed in vacuo, and the yellow residue was purified by flash chromatography (silica, hexanes/ethyl acetate, 100:0 to 95:5). Vinyl iodide **3** (130 mg, 0.40 mmol, 80%) was obtained as a yellowish brown oil. ^{1}H NMR: δ = 1.27 (t, J = 7.1 Hz, 6 H), 2.98 (d, J = 7.5 Hz, 2 H), 3.73 (t, J = 7.5 Hz, 1 H), 4.21 (q, J = 7.3 Hz, 4 H), 5.77 (d, J = 1.6 Hz, 1 H), 6.13 (d, J = 1.5 Hz, 1 H) ppm. ^{13}C NMR: δ = 14.1, 44.2, 51.6, 61.7, 105.7, 128.7, 168.0 ppm. HRMS (CI): calcd. for $C_{10}H_{16}IO_4$ [M + H]$^+$ 327.0093; found 327.0068.

4-Methylene-3,4-dihydronaphthalen-1(2*H*)-one (4): According to GP2, phenyl propargyl ether (137 mg, 1.03 mmol) was distannylated by using tetrakis(triphenylphosphane)palladium (12.0 mg, 10.4 μmol) and tributyltin hydride (938 mg, 3.22 mmol), and was treated in the second step with 2,2′-dibromoacetophenone (153 mg, 90%, 0.50 mmol). Subsequently, the reaction mixture was heated to 90 °C for 19 h. The resulting green solution was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica, hexanes/ethyl acetate, 100:0 to 95:5) to yield **4** (34.0 mg, 0.21 mmol, 42%) as a pale yellow oil. ^{1}H NMR: δ = 2.77 (m, 2 H), 2.86 (m, 2 H), 5.27 (br. d, J = 0.7 Hz, 1 H), 5.59 (br. s, 1 H), 7.40 (dd, J = 7.5, 7.5 Hz, 1 H), 7.54 (ddd, J = 7.6, 7.6, 1.4 Hz, 1 H), 7.65 (d, J = 7.9 Hz, 1 H), 8.04 (dd, J = 7.9, 1.3 Hz, 1 H) ppm. ^{13}C NMR: δ = 32.4, 39.3, 111.6, 124.7, 127.1, 128.4, 131.2, 133.7, 140.9, 141.7, 197.8 ppm. HRMS (CI): calcd. for $C_{11}H_{10}O$ $[M]^+$ 158.0732; found 158.0725.

Supporting Information (see footnote on the first page of this article): Copies of NMR spectra of all new compounds.

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[20] In principle, such stannylated allyl malonates can also be obtained from stannylated allyl acetates by Pd-catalyzed allylic alkylations, albeit in significant lower yields (see ref.[12c]). An alternative approach is based on the Pd-catalyzed hydrostannations of propargyl malonates: a) A. M. Castano, M. Ruano, A. M. Echavarren, *Tetrahedron Lett.* **1996**, *37*, 6591–6594; b) A. M. Castano, M. Mendez, M. Ruano, A. M. Echavarren, *J. Org. Chem.* **2001**, *66*, 589–593.

[21] To test this possibility, we irradiated **2g** in the presence of Pd^0 and $(Bu_3Sn)_2$. After up to 6 h, mainly starting material was recovered (55%), but no definite by-product was formed.

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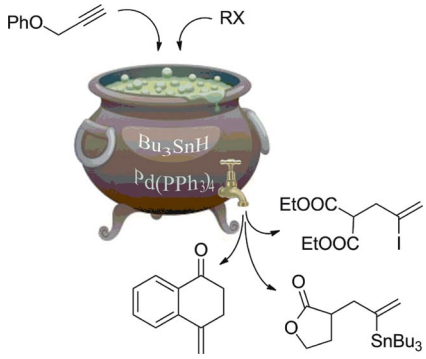
One-Pot Reaction

A wide range of functionalized compounds can easily be obtained by a Pd-catalyzed one-pot hydrostannylation/elimination/distannylation/radical allylation sequence. In this highly catalyst-economic protocol, the Pd catalyst can be involved in up to 5 different reactions.



Keywords: Allylation / Distannylations / Hydrostannylations / Tin / Palladium / Radicals

