Regioselective Hydrostannations with $Mo(CO)_3(CNtBu)_3$ ($MoBI_3$) as a New, Efficient Catalyst

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$Mo(CO)_3(NCtBu)_3$ ($MoBI_3$) was found to be a suitable catalyst for the regioselective hydrostannation of several types of alkynes, preferentially giving rise to the α-stannylated products. These products are not available under radical reaction conditions, or by using other metal catalysts. This protocol tolerates a wide range of functional groups, and can also be applied to sensitive substrates, which cannot be hydrometallated with the commonly used palladium catalysts.

Introduction

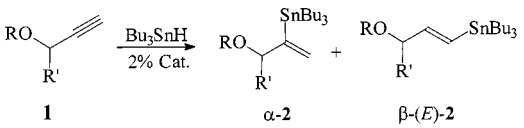
From a synthetic point of view, transition metal catalyzed reactions are extremely interesting and important, not least because many of these reactions proceed under very mild conditions.[1] In general, they also tolerate a wide variety of functional groups, and are therefore especially suited to the synthesis of complex molecules. Of the various transition metals used, palladium holds a certain supremacy and is commonly used for cyclizations, allylic alkylations, cross couplings, and many other important reactions.[2] However, other metal complexes can also be utilized for these purposes. For instance, tungsten[3] and molybdenum[4] complexes can also be applied in allylic alkylations, and in particular isocyanide complexes such as $Mo(CO)_2(CNR)_4$ ($MoBI_4$) have been shown to give good results.[5]

A further important type of reactions catalyzed by transition metal complexes are hydrometallations, and herein hydrostannations are of particular interest.[6] These reactions can be carried out under different reaction conditions. Besides a radical pathway, a palladium catalyzed version of the hydrostannation has also been developed during the last few years.[1] The hydrostannation of alkynes is frequently used for the synthesis of vinylstannanes, which can be subjected to further modifications *via* Stille coupling.[7] The major drawback of both methods results from difficulties in controlling the regioselectivity of the tin hydride addition in the case of unsymmetrical alkynes. Comparing these two protocols, the transition metal catalyzed version has the advantage of a clean *cis* addition, based on the mechanism of the reaction.[2] Therefore, only two products are formed during this process, while radical tin hydride additions generate *E*/*Z* mixtures of the corresponding stannylated alkenes. Most examples described so far employ Pd complexes as catalysts. However, other transitions metals, such as rhodium complexes can also be used,[8] and Guibé et al. described an application of a molybdenum catalyst.[9]

$MoBr(allyl)(CO)_2(CH_3CN)_2$ was found to be suitable for the hydrostannation of propargylic alcohol derivatives, but without significant regioselectivity. However, for application of these reactions to the synthesis of complex molecules by subsequent cross coupling reactions, the control of the regioselectivity is an important issue. Therefore, the search for new, especially more selective, catalysts is an interesting task.

Results and Discussion

In connection with our investigations on chelate enolate Claisen rearrangements,[10] we were interested in the synthesis of α-stannylated allylic alcohols. For this reason, we examined the hydrostannation of propargylic alcohols and derivatives thereof as well (Scheme 1). In the presence of transition metal catalysts the *cis* hydrostannation products [α,β-(*E*)] are formed exclusively as a regioisomeric mixture.[9] This is true for the generally applied palladium catalysts and the already mentioned molybdenum complex as well.[11] The molybdenum complex showed a comparable, or even slightly higher, selectivity in favor of the desired α-product.[12] This effect becomes even more significant if sterically more hindered alkynes are used.[9]



1 **α-2** **β-(*E*)-2**

Scheme 1

The catalytically active species are probably Pd^0 and Mo^0 complexes, formed in situ *via* reduction with tin hydride. This encouraged us to investigate the application of Mo^0 complexes such as $Mo(CO)_6$ as catalysts for hydrostannations. Although the reaction was slow and the yields and the selectivities obtained with our test substrate **1a** were

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Table 1. Catalytic hydrostannation of propargylic alcohols and derivatives **1**

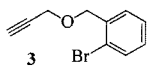
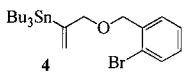
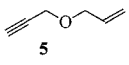
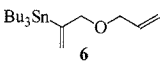
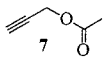
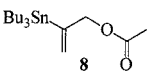
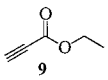
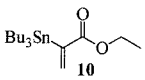
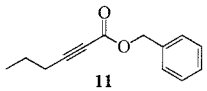
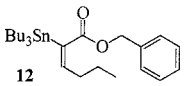
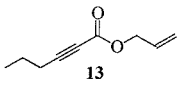
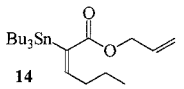
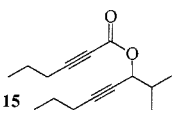
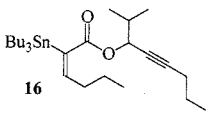
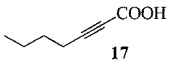
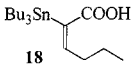
Entry	Substrate	R	R′	Catalyst	Yield [%]	Ratio α:β
1	**1a**	THP	H	$Mo(CO)_6$	64	68:32
2	**1a**	THP	H	$Mo(CO)_3(CNtBu)_3$	98	>95:<5
3	**1b**	H	H	$Mo(CO)_3(CNtBu)_3$	94	89:11
4	**1c**	TBDPS	CH_3	$Mo(CO)_3(CNtBu)_3$	88	90:10

only modest (Table 1, entry 1), these example showed that, in principle, carbon monoxide complexes of molybdenum are suitable for this reaction (Scheme 1).

How can the reactivity and selectivity towards the desired α-product be increased? To find solutions to this question we replaced several CO ligands on the molybdenum atom. Isocyanides, which are isoelectronic with carbon monoxide, appeared to be promising ligand candidates, for several reasons: i. These ligands are retained in solution if dissociated from the metal, a fact which should have a positive influence on the lifetime of the catalyst. ii. Isocyanides should be less strongly bond to the molybdenum in comparison to carbon monoxide,[5] which should facilitate their dissociation, resulting in increased reactivity. iii. The steric demand of the catalyst can be tuned by variation of the number and the size of the isocyanide ligands, which should have an effect on the regioselectivity of the hydrostannation.

Keeping this in mind, and assuming that two to three free coordination sites on the molybdenum are required for the reaction, we chose $Mo(CO)_3(CNtBu)_3$ ($MoBI_3$) as a catalyst. This complex can easily be obtained by ligand exchange from $Mo(CO)_6$,[13] and is therefore rather inexpensive. $MoBI_3$ is also stable towards air and can easily be purified by flash column chromatography. These features, coupled with its catalytic properties, make $MoBI_3$ a catalyst of choice for regioselective hydrostannations: the results obtained with our test substrates exceeded all our expectations (Table 1, entries 2−4).[14] For the reasons discussed, this complex is much more reactive in comparison to $Mo(CO)_6$, giving higher turnovers and yields. Because of its stability, the catalyst can be recovered (by flash column chromatography) and reused without any loss of reactivity. This is especially interesting for large scale preparations, although the amount of catalyst required is not very high (0.1−2%). Probably because of the sterically demanding *t*Bu groups, $MoBI_3$ shows excellent regioselectivities. For example, with

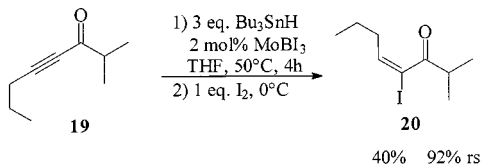
Table 2. $MoBI_3$ catalyzed hydrostannation of substituted alkynes

Entry	Substrate	Major product	Yield [%]	Ratio[a] α : β
1	 **3**	 **4**	44	>95 : <5
2	 **5**	 **6**	43	>95 : <5
3	 **7**	 **8**	91	96 : 4
4	 **9**	 **10**	98	92 : 8[b]
5	 **11**	 **12**	68	90 : 10
6	 **13**	 **14**	80	91 : 9
7	 **15**	 **16**	87	85 : 15
8	 **17**	 **18**	88[c]	63 : 37

[a] Determined by NMR. − [b] Determined by HPLC. − [c] Isolated yield after esterification with CH_2N_2 and flash column chromatography.

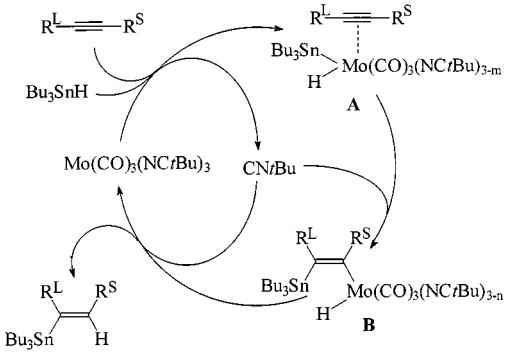
1a a nearly quantitative yield and selectivity was obtained. Although the hydrostannation of these terminal alkynes proceeds readily at room temperature, sterically more hindered alkynes might require higher reaction temperatures. In these cases, or at low catalyst concentrations, the temperature can be increased, without any problems, to 50−70 °C for good turnovers. However, under these conditions hydroquinone should be added to avoid competitive radical hydrostannations. Further applications are shown in Table 2.

In general, high α-selectivities are obtained with terminal alkynes (entries 1−4), and several functional groups are tolerated in the substrates. Halogenated benzyl ethers, such as **3,** were hydrostannated without reduction of the aromatic halide,[15] giving rise to substrates **4**. In this case, no second regioisomer could be detected by NMR. This is also true for the allyl ether **5** (entry 2). This example shows that double bonds are not attacked under the reactions conditions used.[16] Hydrostannation of propargylic acetate **7** furnished the stannylated allylic acetate **8**, with excellent regioselectivity and yield. Comparable high yields and selectivities were obtained with acetylenic esters (entries 4−7),[17] while propiolic esters such as **9** gave the best results. Moreover, the substituted esters **11** and **13** yielded the stannylated products with a similar regioselectivity. Compound **13** is an especially interesting example, because this ester could not be hydrostannated in the presence of palladium catalysts, probably because of decomposition *via* π-allyl-palladium intermediates. Alkynes bearing electron-withdrawing groups are obviously more reactive in comparison to unfunctionalized alkynes. For example, ester **15** gave the monostannylated product **16** exclusively. To our surprise, alkynoic acid **17** could also be hydrometallated in excellent yields and without protodestannylation. This side reaction is not a trivial issue, and causes problems with many substrates. In general, the hydrostannation products obtained from (protected) propargylic alcohols and acetylenic esters are rather stable, and can be purified by flash column chromatography. This is in sharp contrast to the products obtained from the corresponding ketones. For example, **19** shows a clean reaction under the conditions used, but the hydrostannylated product decomposed (protodestannylation) completely during the workup.[18] Therefore, the regioselectivity (rs) of this reaction was determined on the corresponding vinyl iodide **20**, obtained by metal−halogen exchange (Scheme 2).



Scheme 2

The selectivities observed in the $MoBI_3$ catalyzed hydrostannations, especially with terminal alkynes, can be explained by the following mechanistic rationale (Scheme 3): Probably, the reaction starts with a dissociation of several isocyanide ligands, opening coordination sites for the oxidative addition of the tin hydride and the coordination of the alkyne in a facial orientation (**A**). At this stage it is unclear if all isocyanides dissociate from the molybdenum or if some remain (enlargement of the coordination sphere on the molybdenum). With respect to the selectivities obtained, the isocyanide ligands are somehow involved in the next step, the formation of **B** via insertion of the alkyne into the molybdenum tin bond. In this product determining step, the sterically more demanding molybdenum fragment is added to the less hindered side of the alkyne. Reductive elimination is the last step of the sequence, giving rise to '*cis* addition products' and the recycled catalyst.



Scheme 3

In summary, we have shown that $MoBI_3$ is a highly efficient catalyst for the regioselective hydrostannation of various types of alkynes. This catalyst also tolerates a wide range of functional groups, and allows the reaction of substrates which cannot be hydrostannated under other reaction conditions. Further investigations concerning the reaction mechanism and applications of this catalyst are currently under investigation.

Experimental Section

General Procedure: All reactions were carried out in oven-dried glassware (80 °C) under argon. All solvents were dried before use. THF and toluene were distilled from sodium benzophenone. The starting materials and the products were purified by flash column chromatography on silica gel (32−63 μm). Mixtures of ethyl acetate and petroleum ether (40−60 °C) were generally used as eluents. 1% Triethylamine was added to the solvent if stannylated compounds were subjected to flash column chromatography. Analytical thin layer chromatography was performed by using commercially precoated Polygram© SIL-G/UV 254 plates (Macherey−Nagel). Visualization was accomplished with UV light, iodine, and potassium permanganate solution. − ^1H (300 MHz), ^{13}C (75 MHz) and ^{119}Sn (112 MHz) NMR spectra were recorded in $CDCl_3$ on a Bruker AC-300 spectrometer. Isomeric ratios were determined by NMR and/or analytical HPLC by using a Knauer Eurosphere column (250 × 4 mm, Si80, 5 μm, flow: 2 mL/min) and a Knauer UV detector. Bu_3SnH was purchased from Fluka.

General Procedure for $MoBI_3$-Catalyzed Hydrostannations: The corresponding alkyne (1 mmol), hydroquinone (10 mg), and $Mo(CO)_3(CNtBu)_3$ ($MoBI_3$) (8.6 mg, 20 μmol) were dissolved in a Schlenk tube under argon in THF (1 mL). Bu_3SnH (0.8 mL,

3.0 mmol) was added slowly and the mixture was warmed to 55 °C until all starting material was consumed (determined by TLC). After cooling to room temperature, the reaction mixture was subjected to flash column chromatography. Excess Bu_3SnH was removed by using hexane as eluent. The stannylated products were obtained by using hexanes/ethyl acetate containing 1% triethylamine as eluent.

1-Tetrahydropyranyloxy-2-tributylstannyl-2-propen (2a): Ether **2a** was obtained as the major product from ether **1a** (170 mg, 1.21 mmol) following the general procedure. Yield: 501 mg (1.16 mmol, 96%) of a colorless clear liquid. − R_F: 0.34 (hexanes/ethyl acetate, 98:2). − ^{1}H NMR: δ = 5.85 (d, J = 2.2 Hz, J_{SnH} = 131 Hz, 1 H, 1-H$_t$), 5.22 (d, J = 2.3 Hz, J_{SnH} = 61 Hz, 1 H, 1-H$_c$), 4.62 (dd, J = 3.4, 3.2 Hz, 1 H, 4-H), 4.38 (d, J = 12.8 Hz, 1 H, 3-H), 4.03 (d, J = 12.8 Hz, 1 H, 3-H), 3.84 (ddd, J = 11.4, 3.2, 3.0 Hz, 1 H, 8-H), 3.49 (ddd, J = 11.4, 7.0, 4.4 Hz, 1 H, 8-H), 1.56−1.41 (m, 8 H, 5-H, 9-H), 1.35−1.23 (m, 8 H, 7-H, 11-H), 0.98−0.78 (m, 17 H, 6-H, 10-H, 12-H). Minor regioisomer (selected signal): δ = 6.20 (d, J = 19.1 Hz, 1 H, 1-H). − ^{13}C NMR: δ = 152.5 (C-2), 124.2 (J_{SnC} = 19.5 Hz, C-1), 97.9 (C-4), 74.2 (J_{SnC} = 35 Hz, C-3), 61.7 (C-8), 30.7 (C-5), 29.1 (J_{SnC} = 20 Hz, C-11), 27.3 (J_{SnC} = 57 Hz, C-10), 25.5 (C-7), 19.3 (C-6), 13.7 (C-12), 9.60 (J_{SnC} = 333 Hz, C-9). − ^{119}Sn NMR: δ = −45.7. − $C_{20}H_{40}O_2Sn$ (431.2): calcd. C 55.70, H 9.35; found C 55.69, H 9.57.

2-Tributylstannyl-2-propen-1-ol (2b): Alcohol **2b** was obtained as the major product from alcohol **1b** (78 mg, 1.4 mmol) following the general procedure. Yield: 454 mg (1.31 mmol, 94%) of a colorless liquid. − R_F: 0.47 (hexanes/ethyl acetate, 9:1). − ^{1}H NMR δ = 5.86 (d, J = 2.1 Hz, J_{SnH} = 129 Hz, 1 H, 3-H$_t$), 5.23 (d, J = 2.1 Hz, J_{SnH} = 61 Hz, 1 H, 3-H$_c$), 4.26 (s, J_{SnH} = 28 Hz, 2 H, 1-H), 1.59−1.40 (m, 6 H, 4-H), 1.35−1.23 (m, 6 H, 6-H), 1.08−0.80 (m, 15 H, 5-H, 7-H). Minor regioisomer (selected signal): δ = 4.13 (d, J = 3.2 Hz, 2 H, 1-H). − ^{13}C NMR: δ = 154.6 (C-2), 122.7 (J_{SnC} = 19 Hz, C-3), 69.4 (J_{SnC} = 45 Hz, C-1), 28.8 (J_{SnC} = 20 Hz, C-6), 27.2 (J_{SnC} = 58 Hz, C-5), 13.5 (C-7), 9.3 (J_{SnC} = 324 Hz, C-4). − ^{119}Sn NMR: δ = −47.1. − $C_{15}H_{32}OSn$ (347.1): calcd. C 51.90, H 9.29; found C 51.78, H 9.28.

2-(*tert*-Butyldiphenyl)silyloxy-3-tributylstannyl-3-butene (2c): Ether **2c** was obtained as the major product from ether **1c**[19] (309 mg, 1.00 mmol) following the general procedure. Yield: 530 mg (0.88 mmol, 88%) of a colorless liquid. − R_F: 0.65 (hexanes/ethyl acetate, 85:15). − ^{1}H NMR: δ = 7.70 (dd, J = 7.7, 1.5 Hz, 2 H, 8-H), 7.64 (dd, J = 7.7, 1.5 Hz, 2 H, 8′-H), 7.35 (m, 6 H, 9-H, 9′-H, 10-H, 10′-H), 5.73 (d, J = 1.4 Hz, J_{SnH} = 135 Hz, 1 H, 1-H$_t$), 5.09 (d, J = 2.4 Hz, J_{SnH} = 61 Hz, 1 H, 1-H$_c$), 4.39 (q, J = 6.3 Hz, 1 H, 3-H), 1.53−1.38 (m, 6 H, 11-H), 1.35−1.24 (m, 6 H, 13-H), 1.06 (s, 9 H, 6-H), 1.02 (d, J = 6.3 Hz, 3 H, 4-H), 0.99−0.85 (m, 15 H, 12-H, 14-H). Minor regioisomer (selected signal): δ = 1.14 (d, 3 H, 4-H). − ^{13}C NMR: δ = 159.2 (C-2), 135.8 (C-9), 135.7 (C-9′), 134.5 (C-7), 134.0 (C-7′), 129.3 (C-10), 129.2 (C-10′), 127.2 (C-8), 127.1 (C-8′), 122.6 (C-1), 76.7 (C-3), 28.9 (J_{SnC} = 19 Hz, C-13)), 27.1 (J_{SnC} = 55 Hz, C-12), 26.8 (C-6), 25.2 (C-5), 19.0 (C-4), 13.5 (C-14), 9.9 (J_{SnC} = 329 Hz, C-11). − $C_{32}H_{52}OSiSn$ (599.6): calcd. C 64.11, H 8.74; found C 64.09, H 8.99.

1-(*o*-Bromobenzyloxy)-2-tributylstannyl-2-propen (4): Ether **4** was obtained as the major product from ether **3**[20] (240 mg, 1.07 mmol) following the general procedure. Yield: 245 mg (0.47 mmol, 44%) of a colorless liquid. − R_F: 0.47 (hexanes/ethyl acetate, 9:1). − ^{1}H NMR: δ = 7.53−7.48 (m, 2 H, 7-H, 10-H), 7.29 (m, 1 H, 9-H), 7.11 (m, 1 H, 8-H), 5.91 (m, J_{SnH} = 129 Hz, 1 H, 1-H$_t$), 5.30 (m, J_{SnH} = 61 Hz, 1 H, 1-H$_c$), 4.53 (s, 2 H, 4-H), 4.24−4.22 (m, J_{SnH} = 34 Hz, 2 H, 3-H), 1.59−1.41 (m, 6 H, 11-H), 1.34−1.21 (m, 6 H, 13-H), 1.07−0.80 (m, 15 H, 12-H, 14-H). − ^{13}C NMR: δ = 152.4 (C-2), 137.8 (C-5), 132.1, 128.6, 128.4, 127.0 (C-7 − C-10), 124.7 (C-1), 122.2 (C-6), 77.7 (C-3), 71.1 (C-4), 28.9 (C-12), 27.1 (C-13), 13.4 (C-14), 9.4 (C-11). − ^{119}Sn NMR: δ = −46.3. − HRMS (FAB) $C_{18}H_{28}O^{81}Br^{120}Sn$ (M − nBu$^+$): calcd. 461.0325; found 461.0346; $C_{18}H_{28}O^{81}Br^{118}Sn$ (M − nBu$^+$): calcd. 459.0319; found 459.0348.

1-Propenyloxy-2-tributylstannyl-2-propene (6): Ether **6** was obtained as the major product from ether **5**[21] (137 mg, 1.43 mmol) following the general procedure. Yield: 239 mg (0.62 mmol, 43%) of a colorless liquid. − R_F: 0.34 (hexanes/ethyl acetate, 99:1). − ^{1}H NMR: δ = 5.96−5.82 (m, J_{SnH} = 133 Hz, 2 H, 1-H$_t$, 5-H), 5.24 (m, 1 H, 6-H$_c$), 5.24 (m, J_{SnH} = 61 Hz, 1 H, 1-H$_c$), 5.14 (m, 1 H, 6-H$_t$), 4.08 (s, J_{SnH} = 35 Hz, 2 H, 3-H), 3.93 (dt, J = 5.5, 1.4 Hz, 2 H, 4-H), 1.56−1.40 (m, 6 H, 7-H), 1.36−1.23 (m, 6 H, 9-H), 1.07−0.78 (m, 15 H, 8-H, 10-H). − ^{13}C NMR: δ = 152.7 (C-2), 134.7 (C-5), 124.4 (C-1), 116.2 (C-6), 77.1 (C-3), 70.8 (C-4), 28.9 (C-8), 27.1 (C-9), 13.4 (C-10), 9.4 (C-7). − ^{119}Sn NMR: δ = −47.9. − HRMS (FAB) $C_{14}H_{27}O^{118}Sn$ (M − nBu$^+$): calcd. 329.1078; found 329.1090; $C_{14}H_{27}O^{116}Sn$ (M − nBu$^+$): calcd. 327.1080; found 327.1085.

2-Tributylstannyl-2-propenyl Acetate (8): Ester **8** was obtained as the major product from ester **7**[22] (617 mg, 6.30 mmol) following the general procedure. Yield: 2.22 g (5.72 mmol, 91%) of a colorless liquid. − R_F: 0.46 (hexanes/ethyl acetate, 95:5). − ^{1}H NMR: δ = 5.85 (m, J_{SnH} = 121 Hz, 1 H, 1-H$_t$), 5.28 (m, J_{SnH} = 60 Hz, 1 H, 1-H$_c$), 4.69 (m, J_{SnH} = 31 Hz, 2 H, 3-H), 2.05 (s, 3 H, 5-H), 1.63−1.40 (m, 6 H, 6-H), 1.35−1.23 (m, 6 H, 8-H), 1.10−0.84 (m, 15 H, 7-H, 9-H). Minor regioisomer (selected signals): δ = 6.24 (d, J = 19.1 Hz, 1 H, 1-H), 4.56 (d, J = 6.6 Hz, 2 H, 3-H). − ^{13}C NMR: δ = 170.3 (C-4), 148.9 (C-2), 125.5 (C-1), 71.0 (C-3), 28.9 (C-7), 27.1 (C-8), 20.7 (C-5), 13.4 (C-9), 9.3 (C-6). − ^{119}Sn NMR: δ = −43.2. − $C_{17}H_{34}O_2Sn$ (389.1): calcd. C 52.48, H 8.74; found C 52.23, H 8.78.

Ethyl 2-Tributylstannyl-2-propenoate (10): Ester **10** was obtained as the major product from ester **9** (98 mg, 1.0 mmol) following the general procedure. Yield: 391 mg (0.98 mmol, 98%) of a colorless oil. − R_F: 0.63 (hexanes/ethyl acetate, 85:15). − ^{1}H NMR: δ = 6.88 (d, J = 2.8 Hz, J_{SnH} = 110 Hz, 1 H, 1-H$_t$), 5.90 (d, J = 2.7 Hz, J_{SnH} = 53 Hz, 1 H, 1-H$_c$), 4.17 (q, J = 7.1 Hz, 2 H, 4-H), 1.56−1.40 (m, 6 H, 6-H), 1.35−1.23 (m, 6 H, 8-H), 0.96 (t, J = 7.9 Hz, 3 H, 5-H), 0.92−0.79 (m, 15 H, 7-H, 9-H). Minor regioisomer (selected signals): δ = 7.72 (d, J = 19.4 Hz, 1 H, 1-H), 6.28 (d, J = 19.4 Hz, 1 H, 2-H). − ^{13}C NMR: δ = 170.3 (C-3), 146.0 (C-2), 139.3 (C-1), 60.3 (C-4), 28.7 (J_{SnC} = 20 Hz, C-8), 27.1 (J_{SnC} = 59 Hz, C-7), 14.0 (C-5), 13.4 (C-9), 9.9 (J_{SnC} = 335 Hz, C-6). − $C_{17}H_{34}O_2Sn$ (389.2): calcd. C 52.47, H 8.81; found C 52.51, H 8.92.

Benzyl 2-Tributylstannyl-2-hexenoate (12): Ester **12** was obtained as the major product from ester **11**[23] (202 mg, 1.00 mmol) following the general procedure. Yield: 333 mg (0.68 mmol, 68%) of a colorless oil. − R_F: 0.65 (hexanes/ethyl acetate 85:15). − ^{1}H NMR: δ = 7.36 (m, 5 H, H$_{Ar}$), 6.06 (t, J = 7.1 Hz, J_{SnH} = 61 Hz, 1 H, 4-H), 5.13 (s, 2 H, 7-H), 2.41 (q, J = 7.2 Hz, 2 H, 3-H), 1.50−1.32 (m, 6 H, 12-H), 1.32−1.15 (m, 8 H, 2-H, 14-H), 1.10−0.81 (m, 18 H, 1-H, 13-H, 15-H). Minor regioisomer (selected signal): δ = 5.98 (s, 1 H, 5-H). − ^{13}C NMR: δ = 171.1 (C-6), 153.6 (C-5), 136.4 (C-8), 128.5, 128.4, 128.3 (C$_{Ar}$), 128.1 (C-4), 66.0 (C-7), 34.1 (C-3), 28.8 (J_{SnC} = 20 Hz, C-14), 27.2 (J_{SnC} = 59 Hz, C-13), 22.4 (C-2), 13.63 (C-1), 13.61 (C-15), 10.3 (J_{SnC} = 335 Hz, C-12). − $C_{25}H_{42}SnO_2$ (493.3): calcd. C 60.87, H 8.58; found C 61.14, H 8.65.

Allyl 2-Tributylstannyl-2-hexenoate (14): Ester **14** was obtained as the major product from ester **13**[24] (112 mg, 0.74 mmol) following the general procedure. Yield: 263 mg (0.59 mmol, 80%) of a colorless oil. − R_F: 0.24 (hexanes/ethyl acetate, 98:2). − ^{1}H NMR: δ = 6.03 (t, J = 7.1 Hz, 1 H, 4-H), 6.00−5.86 (m, 1 H, 8-H), 5.29 (m, 1 H, 9-H$_c$), 5.21 (dd, J = 10.4, 1.3 Hz, 1 H, 9-H$_t$), 4.56−4.59 (m, 2 H, 7-H), 2.38 (dt, J = 7.1 Hz, J = 7.4 Hz, 2 H, 3-H), 1.54−1.03 (m, 14 H, 2-H, 10-H, 12-H), 1.09−0.84 (m, 18 H, 1-H, 11-H, 13-H). Minor regioisomer (selected signals): δ = 6.37 (t, J = 1.3 Hz, J_{SnH} = 110 Hz, 1H, 5-H), 4.59−4.62 (m, 2 H, 7-H), 2.33 (td, J = 7.7, 1.2. Hz, 2 H, 3-H). − ^{13}C NMR: δ = 170.9 (C-6), 153.5 (C-4), 135.5 (C-5), 132.6 (C-8), 118.1 (C-9), 64.9 (C-7), 34.1 (C-3), 28.9 (C-11), 27.2 (C-12), 22.4 (C-2), 13.9 (C-1), 13.6 (C-13), 10.3 (C-10). − $C_{21}H_{40}O_2Sn$ (443.2): calcd. C 56.91 H 9.09; found C 56.68 H 9.12.

1-Isopropyl-2-hexyn-1-yl 2-Hexynoate (15): To a solution of 1-pentyne (850 mg, 12.5 mmol) in THF (5 mL) a 1.6 M *n*BuLi-solution (7.20 mL, 11.5 mmol) was added under argon at −78 °C. After stirring for 15 min isobutyraldehyde (780 mg, 10.8 mmol) was added slowly *via* a syringe. The reaction mixture was allowed to warm to room temp. before it was hydrolyzed with ice. After separation of the layers, the aqueous phase was extracted twice with ether (20 mL each). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated in vacuo. The crude product was purified by flash column chromatography, giving rise to the unsaturated alcohol as a colorless liquid (1.32 g, 9.41 mmol, 87%). A solution of this alcohol (563 mg, 4.01 mmol) in dichloromethane (DCM) (2 mL) was added to a solution of 2-hexynoic acid (550 mg, 4.90 mmol) and DMAP (73 mg, 0.6 mmol) in DCM (5 mL). The solution was cooled to −20 °C before DCC (1.2 g, 5.6 mmol) was added, and the solution was warmed to room temp. overnight. After filtration and evaporation of the solvent, the crude product was purified by flash column chromatography (hexanes/ethyl acetate, 98:2). Yield 550 mg (2.35 mmol, 59%) of a colorless liquid. − R_F: 0.52 (hexanes/ethyl acetate, 90:10). − ^{1}H NMR: δ = 5.20 (d, J = 5.7 Hz, 1 H, 12-H), 2.24 (t, J = 7.0 Hz, 2 H, 3-H), 2.13 (t, J = 6.9 Hz, 2 H, 9-H), 1.94 (sept, J = 6.5 Hz, 1 H, 13-H), 1.64−1.38 (m, 4 H, 2-H, 8-H), 1.00−0.86 (m, 12 H, 1-H, 7-H, 14-H). − ^{13}C NMR: δ = 153.5 (C-6), 90.3 (C-4), 87.8 (C-11), 75.9 (C-10), 73.5 (C-5), 71.4 (C-12), 32.9 (C-13), 22.3, 21.4, 21.1, (C-2, C-3, C-8, C-9), 18.6, 17.9, 13.8 (C-1, C-7, C-14). − HRMS (FAB) $C_{15}H_{22}O_2$ (M^+): calcd. 234.1620; found 234.1628.

1-Isopropyl-2-hexyn-1-yl 2-Tributylstannyl-2-hexenoate (16): Ester **16** was obtained as the major product from ester **15** (158 mg, 0.67 mmol) following the general procedure. Yield: 307 mg (0.58 mmol, 87%) of a colorless oil. − R_F: 0.35 (hexanes/ethyl acetate, 98:2). − ^{1}H NMR: δ = 6.00 (t, J = 7.1 Hz, 1 H, 4-H), 5.22 (dt, J = 5.4, 2.0 Hz, 1 H, 12-H), 2.41−2.33 (m, 2 H, 3-H), 2.15 (td, J = 7.0, 2.0 Hz, 2 H, 9-H), 2.02−1.91 (m, 1 H, 13-H), 1.59−1.22 (m, 16 H, 2-H, 8-H, 15-H, 17-H), 1.14−0.86 (m, 27 H, 1-H, 7-H, 14-H, 16-H, 18-H). Minor regioisomer (selected signal): δ = 5.93 (t, J = 1.3 Hz, 1 H, 5-H). − ^{13}C NMR: δ = 170.6 (C-6), 152.6 (C-4), 135.6 (C-5), 86.1 (C-11), 69.2 (C-12), 68.7 (C-10), 34.1 (C-3), 32.6 (C-13), 28.9 (C-16), 27.3 (C-17), 22.5, 22.1, 20.7 (C-2, C-8, C-9), 18.4, 17.7, 13.7 (C-1, C-7, C-13), 13.4 (C-18), 10.2 (C-15). − ^{119}Sn NMR: δ = −28.46. − $C_{20}H_{50}O_2Sn$ (525.4): calcd. C 61.73, H 9.59; found C 61.61, H 9.52.

Methyl 2-Tributylstannyl-2-hexenoate (18-OMe): Hydrostannation of acid **17**[25] (105 mg, 0.94 mmol) following the general procedure gave a mixture of the α-stannylated product **18α** and the β-substituted regioisomer **18β** (ratio **18α/18β**, 63:37). The crude mixture was dissolved in 5 mL of ether and reacted with diazomethane at 0 °C for 3 h. The methyl esters **18-OMe** obtained were purified by flash column chromatography (hexanes/ethyl acetate/NEt_3, 95:4:1). Yield: 345 mg (0.83 mmol, 88%) of a colorless oil. − **18α-OMe:** ^{1}H NMR: δ = 6.02 (t, J = 7.1 Hz, J_{SnH} = 68 Hz, 1 H, 4-H), 3.67 (s, 3 H, 7-H), 2.37 (td, J = 7.3, 7.2 Hz, 2 H, 3-H), 1.55−1.39 (m, 6 H, 8-H), 1.35−1.22 (m, 6 H, 10-H), 1.08−0.84 (m, 20 H, 2-H, 9-H, 11-H). − ^{13}C NMR: δ = 171.6 (C-6), 153.1 (C-5), 127.0 (C-4), 50.8 (C-7), 33.9 (C-3), 28.6 (J_{SnC} = 17 Hz, C-10), 27.0 (J_{SnC} = 57 Hz, C-9), 22.2 (C-2), 10.0 (C-1), 13.4 (C-11), 9.8 (J_{SnC} = 340 Hz, C-8). − **18β-OMe:** ^{1}H NMR: δ = 5.93 (s, 1H, 5-H), 3.67 (s, 3H, 7-H), 2.83 (t, J = 7.4 Hz, 2H, 3-H),1.55−1.39 (m, 6H, 8-H), 1.35−1.22 (m, 6H, 10-H), 1.08−0.84 (m, 20H, 1-H, 2-H, 9-H, 11-H). − ^{13}C NMR: δ = 174.4 (C-6), 164.4 (C-4), 135.3 (C-5), 50.5 (C-7), 37.1 (C-3), 28.6 (J_{SnC} = 17 Hz, C-10), 27.1 (J_{SnC} = 57 Hz, C-9), 22.7, 14.0 (C-1), 13.4 (C-11), 9.5 (C-8). − $C_{19}H_{38}O_2Sn$ (417.2):calcd. C 54.70, H 9.18; found C 54.52, H 9.10.

4-Iodo-2-methyl-4-octene-3-one (20): A solution of ketone **19** (163 mg, 1.18 mmol) was subjected to hydrostannation according to the general procedure. After 8 h the reaction mixture was cooled to 0 °C before a solution of iodine (1.17 g, 4.62 mmol) in THF (5 mL) was added. During stirring for 4 h the solution was warmed to room temp. Excess iodine was removed by addition of a sat. $Na_2S_2O_3$-solution (5 mL). After separation of the layers, the aqueous phase was extracted twice with ether (20 mL each). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated in vacuo. The crude product was purified by flash column chromatography (hexanes/ethyl acetate, 98:2), giving rise to a clear yellow liquid (124 mg, 0.47 mmol, 40%). − R_F: 0.17 (hexanes/ethyl acetate, 98:2). − ^{1}H NMR: δ = 6.96 (t, J = 6.8 Hz, 1 H, 4-H), 3.42 (sept, J = 6.8 Hz, 1 H, 7-H), 2.38 (td, J = 7.1, 6.8 Hz, 2 H, 3-H), 1.57 (qt, J = 7.4, 7.1 Hz, 2 H, 2-H), 1.13 (d, J = 6.8 Hz, 6 H, 8-H), 0.99 (t, J = 7.4 Hz, 3 H, 1-H). − ^{13}C NMR: δ = 198.9 (C-6), 150.9 (C-4), 111.5 (C-5), 39.7 (C-7), 34.9 (C-3), 20.9 (C-2), 19.4 (C-8), 13.6 (C-1). − HRMS (FAB) $C_9H_{15}I$ (M^+): calcd. 266.0168; found 266.0149.

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