The Regiochemical Influence of Oxo-Substitution in Palladium-Mediated Hydrostannations of 1-Alkynes

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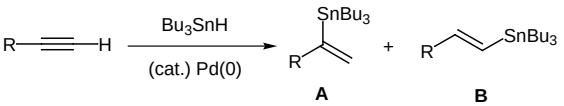
Abstract: A systematic study of hydroxyalkynes and their derivatives showed that the presence and position of the oxygen functionality can influence the regioselectivity of their Pd(0)-catalyzed and free radical hydrostannations. Regioselectivity is influenced by functional group proximity, sterics, and the nature of the substituent (hydroxyl, ether, or ester). Information provided herein may be useful when deciding which methodology and/or protective group strategy to employ when forming vinylstannanes.

Keywords: alkynes, hydrostannations, neighboring-group effects, palladium, regioselectivity

Vinylstannanes are proven synthons and building blocks for organic synthesis.[1] Due to their synthetic utility, a variety of methods have been developed for their preparation including those involving carbonyl addition chemistry;[2] transmetallation of vinylmetallic species;[3] metallometallation of alkynes;[4] and the hydrostannation of alkynes, either under free radical conditions[1a,b,4b,5] or via Lewis acid[6] or transition metal catalysis[7–9] (i.e., Pd,[3d,4b,4l,5a,b,8] Rh,[8l,9a] Mo[4l,9b]). With regards to the palladium-mediated variant, and in conjunction with our work on the development of one-pot hydrostannation/Stille cross-couplings,[10] we sought to better appreciate how various and differently positioned functional groups on 1-alkynes impact the regiochemical course of their hydrostannation.

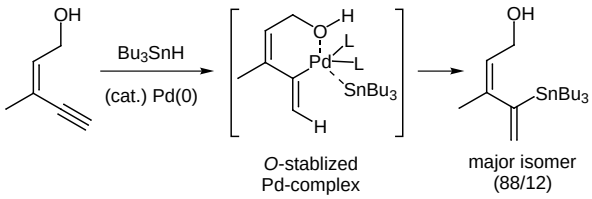
Prior studies,[7,8] especially those by Guibé,[4l] have established that Pd(0)-catalyzed hydrostannations of 1-alkynes bearing polarizing functional groups regioselectively produce the proximal isomer (**A**) (Scheme 1, entry 1), whereas sterically demanding substituents at the propargylic position promote formation of the distal tin isomer (**B**) (Scheme 1, entry 2). The regiochemical outcomes of hydrostannylating propargylic and vinylogous propargyl alcohols along with some of their derivatives have also been examined (Scheme 1, entry 3).[4b,4l,8b,8e,8f,8k,8n–p] These results were considered in Pancrazi's seminal work[4b] on free radical, stannylcuprate, and palladium-catalyzed stannations of propargylic alcohols, where it was concluded that "*In Pd(0)-catalyzed hydrostannylation reaction of propargyl alcohol derivatives, formation of the major proximal tin derivative was observed when the α-position bearing the acetylenic function was not substituted or when an additional stabilizing effect could occur between Pd and the oxygen substituent.*" In brief, though it would appear that the oxygen offers at least some inductive polarization of the triple bond,[11] the proximal regioselectivity of such hydrostannations is also enhanced by the ability of the substrate to stabilize the intermediate palladium complex as shown in Scheme 2. However, Alami[8e] has shown that relative to the *E*-enynes, Pd-mediated hydrostannations of *Z*-enynes is highly regioselective for the α-stannanes even when the alkene substituent is non-chelating. Thus, the extent to which a remote oxygen directs such hydrostannations is not completely clear.



(a) R = CO_2Me (94% yield) **A/B** (100/0)
(b) R = $CH(n\text{-}C_5H_{11})_2$ (90% yield) **A/B** (0/100)
(c) R = CH_2OPh (85% yield) **A/B** (91/9)

Scheme 1 Guibé's[4l] regiochemical observations

Heteroatom-palladium complexation has previously been shown to direct the regiochemistry of palladium-mediated allylations.[12] Systematic studies on such reactions have shown that the oxygen (or other heteroatom) does not need to be propargylic (or vinylogously propargylic) to affect the regiochemical course of the reaction.[12a,13] Unlike allylation reactions, palladium-mediated hydrostannations have not been the subject of systematic investigations documenting how the nature and position of oxygen functionality impacts the regiochemical course of these reactions. Furthermore, the few scattered reports[8b,8j,8n] of longer range directing effects by oxygen are somewhat difficult to calibrate as the different studies employ a variety of organotin hydrides, palladium sources, and general reaction conditions. Thus, we decided to carry out a series of Pd(0)-catalyzed hydrostannations on an orderly



Scheme 2 Pancrazi's[4b] proposed Pd–O complex

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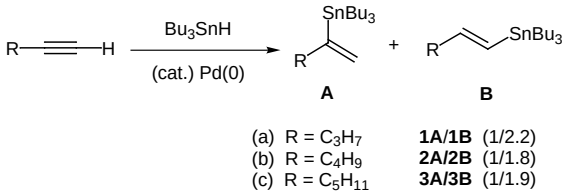
Table 1 Hydrostannation of Propargyl Alcohols and Corresponding Derivatives

Entry	R	Conditions	**A/B/C**[15]		Isolated yields (**A**+**B**+**C**) (%)
1	-CH_2OH (**4**)	I	1.3:1:0	(**5**)	60
2		II	1:9:2	(**5**)	52
3	-CH_2CH_2OH (**6**)	I	1:1.6:0	(**7**)	69
4		II	1:80:19	(**7**)	90
5	-$(CH_2)_2CH_2OH$ (**8**)	I	1:2.5:0	(**9**)	56
6		II	0:9:1	(**9**)	70
7	-$(CH_2)_3CH_2OH$ (**10**)	I	1:3:0	(**11**)	95
8		II	0:5.4:1	(**11**)	64
9	-CH_2CH_2OAc (**12**)	I	1.3:1:0	(**13**)	94
10		II	0:9.7:1	(**13**)	69
11	-$(CH_2)_2CH_2OAc$ (**14**)	I	1:1.4:0	(**15**)	60
12		II	1:18.6:1.5	(**15**)	75
13	-$(CH2)_3CH_2OAc$ (**16**)	I	1:1.3:0	(**17**)	90
14		II	0:4:1	(**17**)	61
15	-CH_2OMe (**18**)	I	16.7:5.7:1	(**19**)	49
16		II	1:7.8:1.8	(**19**)	82
17	-CH_2CH_2OMe (**20**)	I	6.6:6.5:1	(**21**)	77
18		II	0:19:1	(**21**)	50
19	-$(CH_2)_2CH_2OMe$ (**22**)	I	1:1.4:0	(**23**)	81
20		II	2:20:1	(**23**)	46
21	-$(CH_2)_3CH_2OMe$ (**24**)	I	1.3:3.5:0	(**25**)	73
22		II	1:16:1	(**25**)	48
23	-CH_2OTBS (**26**)	I	2.4:1:0	(**27**)	69
24		II	3.5:24.3:1	(**27**)	74
25	-CH_2CH_2OTBS (**28**)	I	1:1.4:0	(**29**)	63
26		II	0:11:1	(**29**)	76
27	-$(CH_2)_2CH_2OTBS$	I	1:1.6:0	(**31**)	51
28	(**30**)	II	0:4.8:1	(**31**)	57
29	-$(CH_2)_3CH_2OTBS$	I	1:1.5:0	(**33**)	60
30	(**32**)	II	0:4.8:1	(**33**)	78
31	-CH_2OTMS (**34**)	I	1.9:1:0	(**35**)	49
32	-CH_2OTIPS (**36**)	I	3:1:0	(**37**)	79
33	-CH_2ODPMS (**38**)	I	4.5:1:0	(**39**)	29[a]

[a] Significant decomposition occurred during column chromatography.

progression of different hydroxyalkynes and their derivatives. The results of these experiments are reported herein.

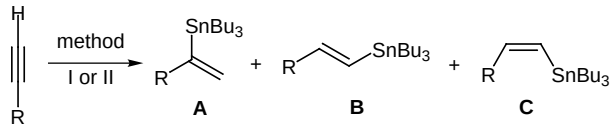
While the goal was to evaluate the influence of oxygen containing functionality on regiocontrol, we initially sought to establish the inherent regioselectivity of 1-alkynes, which lack sterically demanding, polarizing, or coordinating functional groups. As literature examples of palladium-mediated hydrostannations of simple aliphatic 1-alkynes are both few in number and varied in experimental conditions,[4l,5a,8n] hydrostannations of 1-pentyne, 1-hexyne, and 1-heptyne[14] were carried out under what would become the standard conditions of this study. As the data in Scheme 3 show,[15] a 2:1 ratio of distal to proximal vinylstannane isomers would appear to be the intrinsic regioselective bias for these reactions.



Scheme 3

With a "baseline" regioselectivity established, a variety of alkynols and their derivatives were studied.[15,16] Propargyl alcohol and each subsequent homologue through 5-hexyn-1-ol (Scheme 4; Table 1, entries 1–8) were hydrostannylated under palladium-catalyzed (conditions I) and, so as to provide an additional point of reference, free radical (conditions II) conditions. In accord with previously disclosed examples,[4b,4l,8k] palladium-catalyzed hydrostannation of propargyl alcohol (**4**) affords the proximal α-vinylstannane **5A** in slight excess (1.3:1) over the distal β-vinylstannane **5B**. This regiochemical preference is reversed upon the palladium-catalyzed hydrostannation of higher homologues. 3-Butyn-1-ol (**6**) affords[17] a 1.6:1 ratio of the distal **7B** to proximal **7A** isomers despite the ability of **6** to form a stable[18] five-membered palladacycle intermediate during the formation of the α-vinylstannane (Figure). It would appear that any directing effect offered by a hydroxyl group's ability to participate in the formation of such complexes is minimal. Indeed, while 4-pentyn-1-ol (**8**) and 5-hexyn-1-ol (**10**) are capable of forming 6- and 7-membered palladacycles respectively, they provide their α-vinylstannanes with *less* of a bias than that observed for 1-pentyne or 1-hexyne (Scheme 3). Not surprisingly, the free radical hydrostannations of **4**, **6**, **8**, and **10** were selective for the *E-trans*-vinylstannanes.

To determine how these trends are influenced by the nature of the oxygen functionality, the corresponding acetates were hydrostannylated (Scheme 4; Table 1, entries



Scheme 4 Conditions I: 1.5 equiv Bu_3SnH, 0.8 mol% $(Ph_3P)_2PdCl_2$, THF, 0 °C; Conditions II: 1.5 equiv Bu_3SnH, 8–9 mol% AlBN, PhH, 80 °C

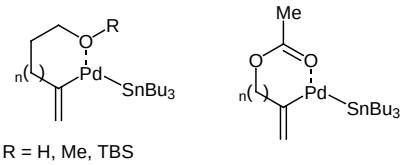
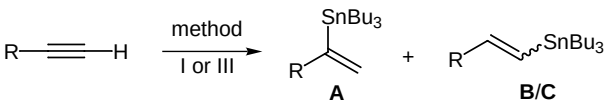


Figure Possible palladacycle intermediates

9–14). Since propargyl acetate is unstable under the reaction conditions,[19] this aspect of the investigation began with 1-acetoxy-3-butyne (**12**), which proved regioselective for α-vinylstannane formation (1.3:1; **13A**/**13B**). While the selectivity is low, it can be viewed as enhanced over that of the parent alcohol. Even when there were three methylene units (entry 13) between the triple bond and acetate-bearing carbon, the ratio of α- to β-stannane was 1:1.3 representing a threefold increase in the relative amount of α-stannane than what was observed with the free alcohol (entry 7). It is possible that the difference between the acetates and the alcohols lies in the carbonyl-containing acetate being better than the hydroxyl at stabilizing any putative palladacycle (Figure),[20] thereby providing a directing effect unseen with the alkynols. Alternatively, the acetate may be capable of long-range polarization of the alkyne. However, if polarization of the triple bond exists, it does not manifest itself in the ^{13}C NMR spectra of the corresponding alkynes.[11] In either event, ester functionality impacts the regiochemistry of palladium-mediated hydrostannations differently than does the presence of hydroxyl groups.

Methyl and silyl alkynol ethers were also examined. As indicated by Scheme 4 (Table 1, entries 15–22), the methyl ethers seem to lie in between the alcohols and the acetates in their directing ability. Consistent with the observations made during the palladium-catalyzed hydrostannations of other propargyl ethers,[4l,8k,8o,8p] methyl propargyl ether (**18**) shows a greater propensity for formation of the proximal isomer (entry 15) relative to that observed for propargyl alcohol (entry 1). Examination of the methyl ethers capable of forming palladacycle intermediates revealed that for **20** and **22**, a small but measurable increase in the relative amount of α-stannane production was observed. This may be a reflection of the fact that in contrast to free alcohols, ether oxygens can coordinate to Pd without the hindrance of hydrogen-bonded solvent (THF). This hypothesis is supported by the observation that Pd-mediated hydrostannations in benzene increase the α-stannane selectivity for propargyl alcohol (**4**), but not for methyl propargyl ether (**18**) (Scheme 5, Table 2). Hydrostannation of 1-methoxy-5-hexyne (**24**) (Table 1, entry 21) closely follows the regioselectivity of 5-hexyn-1-ol (Table 1, entry 7), perhaps indicating that when proceeding beyond the possibility of the more stable 5- and 6-membered palladium intermediate complexes (Figure), the ethers lose any directing effect offered by such complexation.



Scheme 5 Conditions I: 1.5 equiv Bu_3SnH, 0.8 mol% $(Ph_3P)_2PdCl_2$, THF, 0 °C; Conditions III: 1.5 equiv Bu_3SnH, 0.8 mol% $(Ph_3P)_2PdCl_2$, PhH, 0 °C

Table 2 Hydrostannation of Propargyl Alcohols and Their Corresponding Acetates

Entry	R	Conditions	**A:B/C**[14]		Isolated yields (%) (**A+B+C**)
1	-CH_2OH (**4**)	I	1.3:1	(**5**)	60
2	-CH_2OH (**4**)	III	2.1:1	(**5**)	61
3	-CH_2OMe (**18**)	I	2.5:1	(**19**)	49
4	-CH_2OMe (**18**)	III	2:1	(**19**)	61

To further probe the possible involvement of these hydrostannations being directed by virtue of stabilizing oxygen-palladium complexes, *tert*-butyldimethylsilyl (TBS) ethers **26**, **28**, **30**, and **32** were prepared and reacted. Although silyl ethers are typically thought of as non-chelating,[21] hydrostannation of 1-(dimethyl-*tert*-butylsilyloxy)-2-propyne (**26**) favored the α-stannane (**27A**) by a ratio of 2.4:1. Higher homologues **28**, **30**, and **32** all exhibited the same low level increased production of the α-stannane when compared to the all carbon series (Scheme 3). These results suggest that TBS ethers are capable of stabilizing palladacycle intermediates (Figure).[22] Finally, given the utility of silylethers as protective groups, the trimethylsilyl (TMS), triisopropylsilyl (TIPS), and diphenylmethylsilyl (DPMS) propargyl ethers (Scheme 4; Table 1, entries 31–33) were hydrostannylated under Pd catalysis. The alkyl-substituted TMS and TIPS ethers behave similar to the TBS ether, showing ~2.5:1 preference for the α-stannanes, whereas the relative electron-withdrawing nature of the DPMS group increased the selectivity to 4.5:1.

In summary, the presence of oxygen functionality can influence the regioselectivity of hydrostannation reactions, with a bias in the direction of the internal isomer. The degree of this influence decreases as the functional group is moved away from the alkyne and/or where there is a high degree of steric hindrance[4b,4l,5a,10] at the α-position. The nature of the oxygen-containing functional group (hydroxyl, ether, or ester) also alters the regiochemical bias of these reactions. The exact origin(s) of these directing effects remains unclear with polarization of the triple bond, stabilization of palladacycle intermediates, or conformation effects all playing possible roles in these reactions. Nonetheless, the information provided herein may be useful in predicting the regiochemical course of Pd(0)-mediated versus free radical hydrostannations thereby assisting in the decision as to which methodology and/or protective group strategy to employ when forming vinylstannanes.

Palladium-Mediated Hydrostannations (Scheme 4, Conditions I); Typical Procedure[15,16,23]

2-(Tributylstannyl)-1-penten-5-ol (9A) and 1-(Tributylstannyl)-1(*E*)-penten-5-ol (9B)

Bu_3SnH (0.4 mL, 1.5 mmol) was added dropwise to a 0°C solution of 4-pentyn-1-ol (**8**, 0.1 mL, 1.0 mmol) and $(PPh_3)_2PdCl_2$ (5.9 mg, 0.008 mmol) in THF (5 mL). The reaction mixture was stirred for 45 min, at which time TLC showed complete consumption of the alkyne. Following evaporation of the solvent, crude ^1H NMR (300 MHz, $CDCl_3$) established a 1:2.5 ratio of **9A**/**9B**. The crude material was purified by flash silica gel chromatography (petroleum ether–EtOAc, 95:5) to afford 210 mg (56%) of a clear oily mixture of 2-(tributylstannyl)-1-penten-5-ol (**9A**) and 1-(tributylstannyl)-1(*E*)-penten-5-ol (**9B**).

IR (neat): $\nu = 3330\ cm^{-1}$.

HRMS (EI): *m/z* calcd for $C_{13}H_{27}OSn$ ($M^+ - Bu$): 319.1086. Found: 319.1082.

Compound **9A**

^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.86$ (m, 15H), 1.29 (m, 6H), 1.43 (m, 6H), 1.66 (m, 2H), 2.30 (t, 2H, $J = 7.4$ Hz), 3.63 (m, 2H), 5.11 (m, 1H, $J_{Sn} = 30.5$ Hz), 5.69 (m, 1H, $J_{Sn} = 68.4$ Hz).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 154.7, 125.2, 62.4, 37.4, 32.3, 29.1, 27.3, 13.6, 9.5$.

Compound **9B**[24]

^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.86$ (m, 15H), 1.29 (m, 6H), 1.43 (m, 6H), 1.66 (m, 2H), 2.21 (m, 2H), 3.63 (m, 2H), 5.92 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 148.6, 128.1, 62.4, 34.1, 31.7, 29.1, 27.2, 13.7, 9.3$.

Free Radical-Mediated Hydrostannations (Scheme 4, Conditions II); Typical Procedure

1-(Tributylstannyl)-1(*E*)-penten-5-ol (9B) and 1-(Tributylstannyl)-1(*Z*)-penten-5-ol (9C).

Bu_3SnH (0.4 mL, 1.5 mmol) was added dropwise to a 0°C solution of 4-pentyn-1-ol (**8**, 0.1 mL, 1.0 mmol) and AIBN (9.9 mg, 0.08 mmol) in benzene (5 mL). The reaction flask was fitted with a reflux condenser, purged with N_2, placed into a pre-heated (80°C) oil bath and stirred for 3.25 h, at which time TLC showed complete consumption of the alkyne. Following evaporation of the solvent, crude ^1H NMR (300 MHz, $CDCl_3$) established a 9:1 ratio of **9B**/**9C**. The crude material was purified by flash silica gel chromatography (petroleum ether–EtOAc, 95:5) to afford 91 mg (24%) of pure 1-(tributylstannyl)-1(*E*)-penten-5-ol (**9B**) and 171 mg (46%) of a mixture of **9B** and 1-(tributylstannyl)-1(*Z*)-penten-5-ol (**9C**) both as clear oils. For spectroscopic data on **9B**, see above.

Compound **9C**

Spectroscopic data for **9C**[24] were consistent with those previously reported in the literature.

2-(Tributylstannyl)-2-propen-1-ol (5A), 1-(Tributylstannyl)-1(*E*)-propen-3-ol (5B), and 1-(Tributylstannyl)-1(*Z*)-propen-3-ol (5C)

Applying conditions I to propargyl alcohol (**4**, 1.04 mL, 0.018 mol) gave a 1.3:1 crude mixture of **5A** and **5B** which when purified by flash silica gel chromatography (petroleum ether–Et_2O, 8:2) afforded 3.74 g (60%) of a clear oily mixture of 2-(tributylstannyl)-2-propen-1-ol (**5A**) and 1-(tributylstannyl)-1(*E*)-propen-3-ol (**5B**).

Compounds **5A** and **5B**

Spectroscopic data for **5A** and **5B** were consistent with those previously reported in the literature.[4b,4l]

Applying conditions II to propargyl alcohol (**4**, 1.04 mL, 0.018 mol) gave a 1:9:2 crude mixture of **5A**, **5B**, and **5C** which when purified by flash silica gel chromatography (petroleum ether–Et_2O, 8:2) afforded 3.24 g (52%) of a clear oily mixture of 2-(tributylstannyl)-2-propen-1-ol (**5A**), 1-(tributylstannyl)-1(*E*)-propen-3-ol (**5B**), and 1-(tributylstannyl)-1(*Z*)-propen-3-ol (**5C**).

Compound **5C**

Spectroscopic data for **5C** were consistent with those previously reported in the literature.[5e]

2-(Tributylstannyl)-1-buten-4-ol (7A), 1-(Tributylstannyl)-1(*E*)-buten-4-ol (7B), and 1-(Tributylstannyl)-1(*Z*)-buten-4-ol (7C)

Applying conditions I to 1-butyn-4-ol (**6**, 0.1 mL, 1.4 mmol) gave a 1:1.6 crude mixture of **7A** and **7B** which when purified by flash silica gel chromatography (petroleum ether–Et_2O, 8:2) afforded 348 mg (69%) of a clear oily mixture of 2-(tributylstannyl)-1-buten-4-ol (**7A**) and 1-(tributylstannyl)-1(*E*)-buten-4-ol (**7B**).

Compound **7A**

IR (neat): $\nu = 3400\ cm^{-1}$.

^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.70–0.95$ (m, 15H), 1.18–1.34 (m, 6H), 1.35–1.57 (m, 6H), 2.54 (tt, 2H, $J = 6.2, 23.8$ Hz), 3.65 (t, 2H, $J = 6.2$ Hz), 5.31 (d, 1H, $J = 2.8$ Hz), 5.82 (d, 1H, $J = 1.5$ Hz).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 151.5, 128.5, 61.3, 44.2, 29.1, 27.4, 13.7. 9.6$.

HRMS (EI): *m/z* calcd for $C_{12}H_{25}OSn$ ($M^+ - Bu$): 305.0927. Found: 305.0930.

Compound **7B**

Spectroscopic data for **7B**[25] were consistent with those previously reported in the literature.

Applying conditions II to 1-butyn-4-ol (**6**, 0.1 mL, 1.4 mmol) gave a 1:80:19 crude mixture of **7A**, **7B**, and **7C** which when purified by flash silica gel chromatography (petroleum ether–Et_2O, 8:2) afforded 454 mg (90%) of a clear oily mixture of 2-(tributylstannyl)-1-buten-4-ol (**7A**), 1-(tributylstannyl)-1(*E*)-buten-4-ol (**7B**), and 1-(tributylstannyl)-1(*Z*)-buten-4-ol (**7C**).

Compound **7C**

Spectroscopic data for **7C** were consistent with those previously reported in the literature.[25]

2-(Tributylstannyl)-1-hexen-6-ol (11A), 1-(Tributylstannyl)-1(*E*)-hexen-6-ol (11B), and 1-(Tributylstannyl)-1(*Z*)-hexen-6-ol (11C)

Applying conditions I to 1-hexyn-6-ol (**10**), gave a 1:3 crude mixture of **11A** and **11B** which when purified by flash silica gel chromatography (petroleum ether–Et_2O, 8:2) afforded 356 mg (95%) of a clear oily mixture of 2-(tributylstannyl)-1-hexen-6-ol (**11A**) and 1-(tributylstannyl)-1(*E*)-hexen-6-ol (**11B**).

Compounds **11A** and **11B**

Spectroscopic data for **11A**[26] and **11B**[27] were consistent with those previously reported in the literature.

Applying conditions I to 1-hexyn-6-ol (**10**), gave a 5.4:1 crude mixture of **11B** and **11C** which when purified by flash silica gel chromatography (petroleum ether–Et_2O, 8:2) afforded 240 mg (64%) of a clear oily mixture of 1-(tributylstannyl)-1(*E*)-hexen-6-ol (**11B**) and 1-(tributylstannyl)-1(*Z*)-hexen-6-ol (**11C**).

Compound **11C**

Spectroscopic data for **11C** were consistent with those previously reported in the literature.[5a]

4-Acetoxy-2-(tributylstannyl)-1-butene (13A), 4-Acetoxy-1-(tributylstannyl)-1(*E*)-butene (13B), and 4-Acetoxy-1-(tributylstannyl)-1(*Z*)-butene (13C)

Applying conditions I to 4-acetoxy-1-butyne[28] (**12**) gave a 1.3:1 crude mixture of **13A** and **13B** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99.5:0.5) afforded 379 mg (94%) of a clear oily mixture of 4-acetoxy-2-(tributylstannyl)-1-butene (**13A**) and 4-acetoxy-1-(tributylstannyl)-1(*E*)-butene (**13B**).

IR (neat): ν = 1730 cm^{-1}.

HRMS (EI): *m/z* calcd for $C_{14}H_{27}O_2Sn$ (M^+ – Bu): 347.1036. Found: 347.1032.

Compound **13A**

^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.28 (m, 6H), 1.44 (m, 6H), 2.01 (s, 3H), 2.52 (t, 2H, *J* = 6.8 Hz), 4.09 (t, 2H, *J* = 6.9 Hz), 5.19 (m, 1H, $^3J_{Sn}$ = 60.4 Hz), 5.73 (m, 1H, $^3J_{Sn}$ = 133.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 150.3, 127.7, 64.0, 39.7, 29.0, 27.3, 21.0, 13.7, 9.5.

Compound **13B**

^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.28 (m, 6H), 1.44 (m, 6H), 2.01 (s, 3H), 2.43 (ddt, 2H, *J* = 0.8, 5.8, 6.9 Hz), 4.06 (t, 2H, *J* = 6.8 Hz), 5.91 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 143.8, 131.3, 63.5, 36.8, 29.0, 27.3, 21.0,13.7, 9.3.

Applying conditions II to 4-acetoxy-1-butyne[28] (**12**) gave a 9.7:1 crude mixture of **13B** and **13C** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99.5:0.5) afforded 280 mg (69%) of a clear oily mixture of 4-acetoxy-1-(tributylstannyl)-1(*E*)-butene (**13B**) and 4-acetoxy-1-(tributylstannyl)-1(*Z*)-butene (**13C**).

Compound **13C**

IR (neat): ν = 1740 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (m, 15H), 1.28 (m, 6H), 1.44 (m, 6H), 2.01 (s, 3H), 2.33 (ddt, 2H, *J* = 1.1, 6.8, 6.9 Hz), 4.07 (t, 2H, *J* = 6.8 Hz), 5.92 (dt, 1H, *J* =12.7, 1.1 Hz), 6.44 (dt, 1H, *J* = 12.7, 6.9 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 143.7, 131.8, 63.8, 36.0, 29.0, 27.2, 20.9, 13.7, 9.3.

HRMS (EI): *m/z* calcd for $C_{14}H_{27}O_2Sn$ (M^+–Bu): 347.1036. Found: 347.1036.

5-Acetoxy-2-(tributylstannyl)-1-pentene (15A), 5-Acetoxy-1-(tributylstannyl)-1(*E*)-pentene (15B), and 5-Acetoxy-1-(tributylstannyl)-1(*Z*)-pentene (15C)

Applying conditions I to 5-acetoxy-1-pentyne[29] (**14**) gave a 1:1.4 crude mixture of **15A** and **15B** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99.5:0.5) afforded 250 mg (60%) of a clear oily mixture of 5-acetoxy-2-(tributylstannyl)-1-pentene (**15A**) and 5-acetoxy-1-(tributylstannyl)-1(*E*)-pentene (**15B**).

IR (neat): ν = 1730 cm^{-1}.

HRMS (EI): *m/z* calcd for $C_{15}H_{29}O_2Sn$ (M^+ – Bu): 361.1192. Found: 361.1192.

Compound **15A**

^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.29 (m, 6H), 1.45 (m, 6H), 1.70 (m, 2H), 2.03 (s, 3H), 2.27 (t, 2H, *J* = 7.7 Hz), 4.02 (t, 2H, *J* = 6.6 Hz), 5.12 (m, 1H, $^3J_{Sn}$ = 61.6 Hz), 5.66 (m, 1H, $^3J_{Sn}$ = 137.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.2, 153.9, 125.5, 64.1, 37.2, 29.3, 29.1, 27.4, 20.9, 13.7, 9.5.

Compound **15B**

^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.29 (m, 6H), 1.45 (m, 6H), 1.70 (m, 2H), 2.03 (s, 3H), 2.17 (m, 2H), 4.04 (t, 2H, *J* = 6.6 Hz), 5.90 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.2, 147.7, 128.5, 64.0, 33.9, 29.2, 29.1, 27.2, 21.0, 13.7, 9.3.

Applying conditions II to 5-acetoxy-1-pentyne[30] (**14**) gave a 1:18.6:1.5 crude mixture of **15A**, **15B**, and **15C** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99.5:0.5) afforded 313 mg (75%) of a clear oily mixture of 5-acetoxy-2-(tributylstannyl)-1-pentene (**15A**), 5-acetoxy-1-(tributylstannyl)-1(*E*)-pentene (**15B**), and 5-acetoxy-1-(tributylstannyl)-1(*Z*)-pentene (**15C**).

Compound **15C**

IR (neat): ν = 1720 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (m, 15H), 1.25 (m, 6H), 1.44 (m, 6H), 1.70 (m, 2H), 2.01 (s, 3H), 2.17 (m, 2H), 4.03 (t, 2H, *J* = 6.6 Hz), 5.83 (dt, 1H, *J* = 12.4, 1.1 Hz), (dt, 1H, *J* = 12.3, 6.9 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.1, 147.4, 129.2, 64.0, 33.3, 29.2, 29.1, 27.2, 20.9, 13.7, 9.3.

HRMS (EI): *m/z* calcd for $C_{15}H_{29}O_2Sn$ (M^+ – Bu): 361.1192. Found: 361.1194.

6-Acetoxy-2-(tributylstannyl)-1-hexene (17A), 6-Acetoxy-1-(tributylstannyl)-1(*E*)-hexene (17B), 6-Acetoxy-1-(tributylstannyl)-1(*Z*)-hexene (17C)

Applying conditions I to 6-acetoxy-1-hexyne[26] (**16**) gave a 1:1.3 crude mixture of **17A** and **17B** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99.5:0.5) afforded 388 mg (90%) of a clear oily mixture of 6-acetoxy-2-(tributylstannyl)-1-hexene (**17A**) and 6-acetoxy-1-(tributylstannyl)-1(*E*)-hexene (**17B**).

Compounds **17A** and **17B**

Spectroscopic data for **17A**[26] and **17B**[5a] were consistent with those previously reported in the literature.

Applying conditions II to 6-acetoxy-1-hexyne[26] (**16**) gave a 4:1 crude mixture of **17B** and **17C** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99.5:0.5) afforded 298 mg (61%) of a clear oily mixture of 6-acetoxy-1-(tributylstannyl)-1(*E*)-hexene (**17B**) and 6-acetoxy-1-(tributylstannyl)-1(*Z*)-hexene (**17C**).

Compound **17C**

IR (neat): ν = 1770 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.29 (m, 6H), 1.46 (m, 6H), 1.59 (m, 4H), 2.01 (s, 3H), 2.13 (dt, 2H, *J* = 4.4, 7.4 Hz), 4.03 (t, 2H, *J* = 6.6 Hz), 5.88 (dt, 1H, *J* = 12.4, 1.1 Hz), 6.46 (dt, 1H, *J* = 6.8, 12.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.1, 148.3, 128.2, 64.4, 37.3, 29.2, 28.0, 27.4, 26.0, 21.1, 13.8, 9.4.

HRMS (EI): *m/z* calcd for $C_{16}H_{31}O_2Sn$ (M^+ – Bu): 375.1349. Found: 375.1347.

3-Methoxy-2-(tributylstannyl)-1-propene (19A), 3-Methoxy-1-(tributylstannyl)-1(*E*)-propene (19B), and 3-Methoxy-1-(tributylstannyl)-1(*Z*)-propene (19C)

Applying conditions I to 3-methoxy-1-propyne (**18**) gave a 16.7:5.7:1 crude mixture of **19A**, **19B**, and **19C** which when purified by flash silica gel chromatography (petroleum ether–EtOAc,

99.5:0.5) afforded 72 mg (20%) of 3-methoxy-1-(tributylstannyl)-1(*E*)-propene (**19B**), and 104 mg (29%) of a mixture of 3-methoxy-1-(tributylstannyl)-1(*Z*)-propene (**19C**) and 3-methoxy-2-(tributylstannyl)-1-propene (**19A**) both as clear oils.[30]

HRMS (EI): *m/z* calcd for $C_{12}H_{25}OSn$ (M^+–Bu): 305.0929. Found: 305.0933.

Compound **19A**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (m, 15H), 1.27 (m, 6H), 1.44 (m, 6H), 3.32 (s, 3H), 4.00 (t, 2H, *J* = 1.6 Hz), 5.24 (m, 1H, $^3J_{Sn}$ = 64.9 Hz), 5.83 (m, 1H, $^3J_{Sn}$ = 116.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0, 124.6, 79.7, 57.7, 29.1, 27.4, 13.7, 9.5.

Compound **19B**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (m, 15H), 1.27 (m, 6H), 1.44 (m, 6H), 3.32 (s, 3H), 3.93 (dd, 2H, *J* = 1.4, 4.9 Hz), 6.02 (dt, 1H, *J* = 19.2, 5.0 Hz), 6.20 (dt, 1H, *J* = 18.9, 1.1 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.4, 131.3, 76.3, 57.8, 29.1, 27.3, 13.7, 9.4.

Compound **19C**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.29 (m, 6H), 1.45 (m, 6H), 3.31 (s, 3H), 3.87 (dd, 2H, *J* = 1.3, 5.2 Hz), 6.06 (dt, 1H, *J* = 13.2, 1.4 Hz), 6.59 (dt, 1H, *J* = 13.2, 5.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.9, 131.8, 75.1, 57.7, 29.1, 27.4, 13.7, 9.5.

Applying conditions II to 3-methoxy-1-propyne (**18**) gave a 1:7.8:1.8 crude mixture of **19A**, **19B**, and **19C** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99.5:0.5) afforded 48 mg (13%) of 3-methoxy-1-(tributylstannyl)-1(*E*)-propene (**19B**), and 249 mg (69%) of a mixture of 3-methoxy-2-(tributylstannyl)-1-propene (**19A**), 3-methoxy-1-(tributylstannyl)-1(*E*)-propene (**19B**), and 3-methoxy-1-(tributylstannyl)-1(*Z*)-propene (**19C**) both as clear oils.

4-Methoxy-2-(tributylstannyl)-1-butene (21A), 4-Methoxy-1-(tributylstannyl)-1(*E*)-butene (21B), and 4-Methoxy-1-(tributylstannyl)-1(*Z*)-butene (21C)
4-Methoxy-1-butyne[31,32] (**20**) was prepared by adding NaH (2.40 g, 55 mmol, 55% dispersion in oil) to a solution of MeI (8.90 g, 63 mmol) in THF (50 mL). The reaction vessel was then placed in a preheated oil bath (65°C) and 3-butyn-1-ol (2.80 g, 40 mmol) was added dropwise. Upon complete addition, the reaction was stirred for 1 h, at which time H_2O (few millilitres) was added to destroy any remaining NaH. The mixture was extracted thrice with Et_2O, dried ($MgSO_4$), filtered, and then distilled until the distillate was no longer pure Et_2O (~30 mL). The remaining mixture was then subjected to preparatory gas chromatography (10 ft. 20% SE-30 on Chromosorb W-AW-DMCS column at 80°C). The desired product (**20**), a yellowish liquid, was collected at 6 min. Alkyne **20** was then subjected to hydrostannation conditions I, affording a 6.6:6.5:1 crude mixture of **21A**, **21B**, and **21C** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99.5:0.5) afforded 288 mg (77%) of a clear oily mixture of 4-methoxy-2-(tributylstannyl)-1-butene (**21A**), 4-methoxy-1-(tributylstannyl)-1(*E*)-butene (**21B**), and 4-methoxy-1-(tributylstannyl)-1(*Z*)-butene (**21C**).

HRMS (EI): *m/z* calcd for $C_{13}H_{27}OSn$ (M^+–Bu): 319.1086. Found: 319.1088.

Compound **21A**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.28 (m, 6H), 1.45 (m, 6H), 2.49 (t, 2H, *J* = 6.6 Hz), 3.30 (s, 3H), 3.37 (t, 2H, *J* = 6.9 Hz), 5.16 (m, 1H, $^3J_{Sn}$ = 60 Hz), 5.72 (m, 1H, $^3J_{Sn}$ = 136 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.6, 126.6, 72.2, 58.5, 35.9, 29.3, 27.3, 13.7, 9.5.

Compound **21B**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.28 (m, 6H), 1.45 (m, 6H), 2.40 (m, 2H), 3.30 (s, 3H), 3.41 (t, 2H, *J* =6.9 Hz), 5.93 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.1, 129.8, 72.6, 58.5, 38.2, 29.1, 27.4, 13.7, 9.7.

Applying conditions II to 4-methoxy-1-butyne[31,32] (**20**) gave a 19:1 crude mixture of **21B** and **21C** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99.5:0.5) afforded 187 mg (50%) of a clear oily mixture of 4-methoxy-1-(tributylstannyl)-1(*E*)-butene (**21B**) and 4-methoxy-1-(tributylstannyl)-1(*Z*)-butene (**21C**).

Compound **21C**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (m, 15H), 1.28 (m, 6H), 1.46 (m, 6H), 2.28 (m, 2H), 3.30 (s, 3H), 3.40 (m, 2H), 6.45 (dt, 2H, *J* =12.64, 7.01 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.6, 130.7, 72.4, 65.8, 37.2, 29.1, 27.3, 13.5, 10.1.

5-Methoxy-2-(tributylstannyl)-1-pentene (23A), 5-Methoxy-1-(tributylstannyl)-1(*E*)-pentene (23B), and 5-Methoxy-1-(tributylstannyl)-1(*Z*)-pentene (23C)
Applying conditions I to 120 mg (1.2 mmol) of 5-methoxy-1-pentyne[32,33] (**22**) gave a 1:1.4 crude mixture of **23A** and **23B** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99.5:0.5) afforded 379 mg (81%) of a clear oily mixture of 5-methoxy-2-(tributylstannyl)-1-pentene (**23A**), 5-methoxy-1-(tributylstannyl)-1(*E*)-pentene (**23B**), and 5-methoxy-1-(tributylstannyl)-1(*Z*)-pentene (**23C**).

HRMS (EI): *m/z* calcd for $C_{14}H_{29}OSn$ (M^+–Bu): 333.1243. Found: 333.1246.

Compound **23A**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.28 (m, 6H), 1.44 (m, 6H) 1.65 (m, 2H), 2.26 (t, 2H, *J* =7.5 Hz), 3.30 (s, 3H), 3.35 (t, 2H, *J* = 6.6 Hz), 5.09 (m, 1H, $^3J_{Sn}$ = 62.0 Hz), 5.66 (m, 1H, $^3J_{Sn}$ = 138.6 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.6, 125.0, 72.3, 58.5, 37.4, 29.3, 29.1, 27.3, 13.7, 9.5.

Compound **23B**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.28 (m, 6H), 1.44 (m, 6H) 1.65 (m, 2H), 2.16 (dt, 2H, *J* = 4.6, 7.7 Hz), 3.30 (s, 3H), 3.35 (t, 2H, *J* = 6.6 Hz), 5.89 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.6, 127.8, 72.2, 58.5, 34.1, 29.1, 28.9, 27.2, 13.7, 9.3.

Applying conditions II to 5-methoxy-1-pentyne[32,33] (**22**) gave a 2:20:1 crude mixture of **23A**, **23B**, and **23C** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99.5:0.5) afforded 179 mg (46%) of a clear oily mixture of 5-methoxy-2-(tributylstannyl)-1-pentene (**23A**), 5-methoxy-1-(tributylstannyl)-1(*E*)-pentene (**23B**), and 5-methoxy-1-(tributylstannyl)-1(*Z*)-pentene (**23C**).

Compound **23C**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.29 (m, 6H), 1.45 (m, 6H) 1.66 (m, 2H), 2.27 (m, 2H), 3.30 (s, 3H), 3.35 (t, 2H, *J* = 6.6 Hz), 5.78 (dt, 1H, *J* = 12.4, 1.1 Hz), 6.48 (dt, 1H, *J* = 12.4, 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.3, 128.3, 72.2, 58.5, 34.2, 29.3, 29.1, 27.3, 13.7, 9.4.

HRMS (EI): *m/z* calcd for $C_{14}H_{29}OSn$ (M^+ – Bu): 333.1243. Found: 333.1249.

6-Methoxy-2-(tributylstannyl)-1-hexene (25A), 6-Methoxy-1-(tributylstannyl)-1(*E*)-hexene (25B), and 6-Methoxy-1-(tributylstannyl)-1(*Z*)-hexene (25C)

Applying conditions I to 6-methoxy-1-hexyne[32,34] (**24**) gave a 1.3:3.5 crude mixture of **25A**, and **25B** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99:1) afforded 295 mg (73%) of a clear oily mixture of 6-methoxy-2-(tributylstannyl)-1-hexene (**25A**), 6-methoxy-1-(tributylstannyl)-1(*E*)-hexene (**25B**).

HRMS (EI): *m/z* calcd for $C_{15}H_{31}OSn$ (M^+ – Bu): 347.1400. Found: 347.1397.

Compound **25A**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.28 (m, 6H), 1.43 (m, 6H), 1.56 (m, 4H), 2.33 (t, 2H, *J* = 7.4 Hz), 3.30 (s, 3H), 3.34 (t, 2H, *J* = 6.6 Hz), 5.08 (m, 1H, $^3J_{Sn}$ = 62 Hz), 5.64 (m, 1H, $^3J_{Sn}$ = 140.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.2, 124.9, 72.7, 58.5, 37.6, 29.1, 27.4, 25.9, 13.7, 9.5.

Compound **25B**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.28 (m, 6H), 1.43 (m, 6H), 1.56 (m, 4H), 2.12 (dt, 2H, *J* = 4.9, 7.1 Hz), 3.30 (s, 3H), 3.35 (t, 2H, *J* = 6.5 Hz), 5.87 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.2, 127.5, 72.8, 58.5, 41.0, 29.1, 27.3, 25.4, 13.7, 9.4.

Applying conditions II to 6-methoxy-1-hexyne[32,34] (**24**) gave a 1:16:1 crude mixture of **25A**, **25B**, and **25C** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99:1) afforded 194 mg (48%) of a clear oily mixture of 6-methoxy-2-(tributylstannyl)-1-hexene (**25A**), 6-methoxy-1-(tributylstannyl)-1(*E*)-hexene (**25B**), and 6-methoxy-1-(tributylstannyl)-1(*Z*)-hexene (**25C**).

Compound **25C**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 15H), 1.28 (m, 6H), 1.43 (m, 6H), 1.56 (m, 4H), 2.03 (dt, 2H, *J* = 7.3, 7.2 Hz), 3.31 (s, 3H), 3.35 (t, 2H, *J* = 6.6 Hz), 5.87 (d, 1H, *J* = 12.4 Hz), 6.47 (dt, 1H, *J* = 12.4, 7.2 Hz).

3-(*tert*-Butyldimethylsilyloxy)-2-(tributylstannyl)-1-propene (27A), 3-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-propene (27B), 3-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*Z*)-propene (27C)

Applying conditions I to 3-(dimethyl-*tert*-butylsilyloxy)-propyne[35] (**26**) gave a 2.4:1 crude mixture of **27A** and **27B** which when purified by flash silica gel chromatography (hexanes–Et_3N, 99:1) afforded 317 mg (69%) of a clear oily mixture 3-(*tert*-butyldimethylsilyloxy)-2-(tributylstannyl)-1-propene (**27A**) and 3-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-propene (**27B**).

Compound **27A**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.04 (s, 6H), 0.86 (m, 24H), 1.28 (m, 6H), 1.49 (m, 6H), 4.26 (t, 2H, *J* = 1.9 Hz), 5.15 (dt, 1H, *J* = 2.7, 4.7 Hz), 5.84 (dt, 1H, *J* = 2.7, 4.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.8, 121.8, 69.7, 29.1, 27.4, 26.0, 18.5, 13.7, 9.5, –5.3.

HRMS (EI): *m/z* calcd for $C_{17}H_{37}OSiSn$ (M^+ – Bu): 401.1631. Found: 401.1621.

Compound **27B**

Spectroscopic data for **27B** were consistent with those previously reported in the literature.[36]

Applying conditions II to 3-(dimethyl-*tert*-butylsilyloxy)-propyne[35] (**26**) gave a 3.5:24.3:1 crude mixture of **27A**, **27B**, **27C** which when purified by flash silica gel chromatography (hexanes–Et_3N, 99:1) afforded 341 mg (74%) of a clear oily mixture 3-(*tert*-butyldimethylsilyloxy)-2-(tributylstannyl)-1-propene (**27A**), 3-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-propene (**27B**), and 3-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*Z*)-propene (**27C**).

Compound **27C**

Spectroscopic data for **27C** were consistent with those previously reported in the literature.[36a,37]

4-(*tert*-Butyldimethylsilyloxy)-2-(tributylstannyl)-1-butene (29A), 4-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-butene (29B), 4-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*Z*)-butene (29C)

Applying conditions I to 4-(dimethyl-*tert*-butylsilyloxy)-butyne[38] (**28**) gave a 1:1.4 crude mixture of **29A** and **29B** which when purified by flash silica gel chromatography (hexanes–Et_3N, 99:1) afforded 300 mg (63%) of a clear oily mixture of 4-(*tert*-butyldimethylsilyloxy)-2-(tributylstannyl)-1-butene (**29A**) and 4-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-butene (**29B**).

HRMS (EI): *m/z* calcd for $C_{18}H_{39}OSiSn$ (M^+–Bu): 415.1788. Found: 415.1786.

Compound **29A**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.04 (s, 6H), 0.85 (m, 24H), 1.28 (m, 6H), 1.47 (m, 6H), 2.46 (t, 2H, *J* = 7.7 Hz), 3.59 (t, 2H, *J* = 7.5 Hz), 5.09 (m, 1H), 5.66 (dt, 1H, *J* = 2.7, 1.6 Hz).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 151.0, 127.2, 63.4, 44.6, 29.2, 29.0, 27.4, 27.0, 26.0, 9.6, –5.2.

Compound **29B**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 6H), 0.85 (m, 24H), 1.28 (m, 6H), 1.48 (m, 6H), 2.33 (m, 2H), 3.64 (t, 2H, *J* = 6.9 Hz), 5.89 (m, 2H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 145.8, 129.9, 62.9, 41.5, 29.1, 27.3, 26.0, 18.4, 13.7, 9.3, –5.2.

Applying conditions II to 4-(dimethyl-*tert*-butylsilyloxy)-butyne[38] (**28**) gave a 11:1 crude mixture of **29B** and **29C** which when purified by flash silica gel chromatography (hexanes–Et_3N, 99:1) afforded 360 mg (76%) of a clear oily mixture of 4-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-butene (**29B**) and 4-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*Z*)-butene (**29C**).

Compound **29C**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 6H), 0.85 (m, 24H), 1.28 (m, 6H), 1.52 (series of m, 6H), 2.04 (m, 2H), 3.60 (t, 2H, *J* = 6.6 Hz), 5.77 (m, 1H), 6.49 (m, 1H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 145.1, 130.3, 63.1, 31.6, 29.2, 29.0, 27.7, 22.7, 14.1, 10.2, –5.2.

5-(*tert*-Butyldimethylsilyloxy)-2-(tributylstannyl)-1-pentene (31A), 5-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-pentene (31B), and 5-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*Z*)-pentene (31C)

Applying conditions I to 5-(*tert*-butyldimethylsilyloxy)-1-pentyne (**30**)[39] gave a 1:1.6 crude mixture of **31A** and **31B** which when purified by flash silica gel chromatography (hexanes–Et_3N, 99:1) afforded 250 mg (51%) of a clear oily mixture of 5-(*tert*-butyldimethylsilyloxy)-2-(tributylstannyl)-1-pentene (**31A**) and 5-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-pentene (**31B**).

Compounds **31A** and **31B**
Spectroscopic data for **31A** and **31B** were consistent with those previously reported in the literature.[27]

Applying conditions II to 5-(*tert*-butyldimethylsilyloxy)-1-pentyne (**30**)[39] gave a 4.8:1 crude mixture of **31B** and **31C** which when purified by flash silica gel chromatography (hexanes–Et_3N, 99:1) afforded 278 mg (57%) of a clear oily mixture of 5-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-pentene (**31B**) and 5-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*Z*)-pentene (**31C**).

Compound **31C**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 6H), 0.85 (m, 24H), 1.28 (m, 6H), 1.52 (series of m, 8H), 2.04 (m, 2H), 3.60 (t, 2H, *J* = 6.6 Hz), 5.77 (m, 1H), 6.49 (m, 1H).

6-(*tert*-Butyldimethylsilyloxy)-2-(tributylstannyl)-1-hexene (33A), 6-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-hexene (33B), and 6-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*Z*)-hexene (33C)
Applying conditions I to 6-(*tert*-butyldimethylsilyloxy)-1-hexyne (**32**)[27] gave a 1:1.5 crude mixture of **33A** and **33B** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99:1) afforded 302 mg (60%) of a clear oily mixture of 6-(*tert*-butyldimethylsilyloxy)-2-(tributylstannyl)-1-hexene (**33A**) and 6-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-hexene (**33B**).

Compounds **33A** and **33B**
Spectroscopic data for **33A** and **33B** were consistent with those previously reported in the literature.[5a]

Applying conditions II to 6-(*tert*-butyldimethylsilyloxy)-1-hexyne (**32**)[27] gave a 4.8:1 crude mixture of **33B** and **33C** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99:1) afforded 393 mg (78%) of a clear oily mixture of 6-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-hexene (**33B**) and 6-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*Z*)-hexene (**33C**).

Compounds **33B** and **33C**
Spectroscopic data for **33B** and **33C** were consistent with those previously reported in the literature.[5a]

3-(Trimethylsilyloxy)-2-(tributylstannyl)-1-propene (35A) and 3-(Trimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-propene (35B)
Applying conditions I to 3-(trimethylsilyloxy)-propyne (**34**) (674 mg, 0.5 mmol)[40] gave a 1.9:1 crude mixture of **35A** and **35B** which when purified by flash silica gel chromatography (hexane–EtOAc, 98:2, with 1% Et_3N) afforded 102 mg (49%) of a clear oily mixture of 3-(trimethylsilyloxy)-2-(tributylstannyl)-1-propene (**35A**) and 3-(trimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-propene[41] (**35B**).

Compound **35A**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.12 (s, 9H), 0.90 (m, 15H), 1.28 (m, 6H), 1.46 (m, 6H), 4.23 (t, 2H, *J* = 1.6 Hz), 5.17 (dt, 1H, *J* = 2.4, 1.9 Hz, $^3J_{Sn}$ = 30 Hz), 5.82 (dt, 1H, *J* = 2.4, 1.9 Hz, $^3J_{Sn}$ = 70 Hz).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 155.3, 122.1, 69.0, 29.1, 27.1, 13.7, 9.6, –0.5.

HRMS (EI): *m/z* calcd for $C_{14}H_{31}OSiSn$ (M^+ – Bu): 363.1166. Found: 363.1168.

Compound **35B**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.11 (s, 9H), 0.86 (m, 15H), 1.27 (m, 6H), 1.45 (m, 6H), 4.14 (dd, 2H, *J* = 2.98, 1.10 Hz), 6.07 (dm, 1H, *J* = 18.95 Hz), 6.12 (dm, 1H, *J* = 18.95 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.0, 127.8, 66.4, 29.1, 27.3, 13.7, 9.4, –0.3.

3-(Triisopropylsilyloxy)-2-(tributylstannyl)-1-propene (37A) and 3-(Triisopropylsilyloxy)-1-(tributylstannyl)-1(*E*)-propene (37B)
Applying conditions I to 3-(triisopropylsilyloxy)-propyne (**36**) (103.4 mg, 0.49 mmol)[42] gave a 3:1 crude mixture of **37A** and **37B** which when purified by flash silica gel chromatography (hexanes with 1% Et_3N) afforded 193 mg (79%) of a clear oily mixture of 3-(triisopropylsilyloxy)-2-(tributylstannyl)-1-propene (**37A**) and 3-(triisopropylsilyloxy)-1-(tributylstannyl)-1(*E*)-propene (**37B**).

HRMS (EI): *m/z* calcd for $C_{20}H_{43}OSiSn$ (M^+ – Bu): 447.2105. Found: 447.2122.

Compound **37A**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 18H), 1.04 (m, 12H), 1.28 (m, 12H), 1.44 (m, 6H), 4.34 (t, 2H, *J* = 1.9 Hz, $^3J_{Sn}$ = 12 Hz), 5.16 (dt, 1H, *J* = 3.0, 1.9 Hz, $^3J_{Sn}$ = 30 Hz), 5.91 (dt, 1H, *J* = 2.7, 2.2 Hz, $^3J_{Sn}$ = 68 Hz).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 154.2, 121.8, 69.7, 30.6, 27.4, 18.1, 13.7, 12.1 9.9, 9.4.

Compound **37B**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 18H), 1.04 (m, 12H), 1.23 (m, 12H), 1.44 (m, 6H), 4.25 (dd, 2H, *J* = 3.8, 1.6 Hz, $^3J_{Sn}$ = 12 Hz), 6.04 (dt, 1H, *J* = 19.0, 3.8 Hz), 6.20 (dt, 1H, *J* = 19.0, 1.5 Hz).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 154.2, 119.0, 69.7, 29.1, 27.4, 18.0, 13.7, 12.1, 9.4.

3-(Methyldiphenylsilyloxy)-2-(tributylstannyl)-1-propene (39A) and 3-(Methyl-diphenylsilyloxy)-1-(tributylstannyl)-1(*E*)-propene (39B)
Applying conditions I to 3-(methyldiphenylsilyloxy)-propyne (**38**) (126.7 mg, 0.5 mmol)[43] gave a 4.5:1 crude mixture of **39A** and **39B** which when purified by flash silica gel chromatography (petroleum ether–EtOAc, 99:1, with 1% Et_3N) afforded 79 mg (29%) of 3-(methyldiphenylsilyloxy)-2-(tributylstannyl)-1-propene (**39A**) as a clear oil.

Compound **39A**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.65 (s, 3H), 0.87 (m, 15H), 1.24 (m, 6H), 1.44 (m, 6H), 4.37 (t, 2H, *J* = 1.9 Hz, $^3J_{Sn}$ = 13 Hz), 5.21 (dt, 1H, *J* = 2.5, 1.9 Hz, $^3J_{Sn}$ = 30 Hz), 5.90 (dt, 1H, *J* = 2.5, 2.0 Hz, $^3J_{Sn}$ = 67 Hz), 7.39 (m, 5H), 7.59 (m, 5H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 154.3, 136.0, 134.4, 129.8, 127.8, 122.4, 69.8, 29.1, 27.4, 13.7, 9.5, –3.0.

HRMS (EI): *m/z* calcd for $C_{24}H_{35}OSiSn$ (M^+ – Bu): 487.1479. Found: 487.1470.

Compound **39B** (from the crude mixture)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72 (s, 3H), 0.95 (m, 15H), 1.34 (m, 6H), 1.54 (m, 6H), 4.34 (dd, 2H, *J* = 2.75, 1.37 Hz), 6.17 (dm, 1H, *J* = 18.95 Hz), 6.25 (dm, 1H, *J* = 18.95 Hz), 7.45 (m, 5H), 7.57 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.5, 137.6, 134.0, 129.8, 127.8, 127.7, 67.0, 29.1, 27.3, 13.7, 9.5, –2.8.

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(15) (a) Product ratios were determined by ^{1}H NMR of the crude reaction mixture usually through the integration of the vinylic protons. (b) Appropiate ion identification by high resolution mass spectrometry used the ^{120}Sn isotope for all compounds except **27A**, **29A** and **29B** which were measured with the ^{116}Sn isotope.

(16) Unless otherwise indicated, all starting materials are articles of commerce.

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