Highly Regiocontrolled and Efficient Synthesis of Vinyl- and Allylstannanes *via* Lewis Acids and Pd-Catalyzed Hydrostannation of Allenes: Scope and Limitations

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The hydrostannation of allenes **1** with tributylstannyl hydride in the presence of $B(C_6F_5)_3$ catalyst produced vinylstannanes **2** regioselectively, whereas the hydrostannation of **1** with tributylstannyl and triphenylstannyl hydride in the presence of $Pd(PPh_3)_4$ catalyst gave allylstannanes **5**,**6** regio- and stereo (in certain cases)-selectively. The mechanisms for these catalytic reactions were proposed.

Vinyl- and allylstannanes, which have great versatility as building blocks, are of increasing importance in modern synthetic organic chemistry.[1] Hydrostannation of allenes, in the case of controlled regiochemistry of this process, may serve as the most straightforward and universal way to both classes of title compounds.

Since Kuivila[2] first reported the free radical addition of Me_3SnH to allenes, only little attention has been paid to this subject. Thus, Oshima[3] showed that free radical addition of Ph_3SnH to allenes produces a complex mixture of vinyl- and allylstannanes. The only two examples of Pd-catalyzed hydrostannation of substituted allenes present in the paper[3] exhibit contradictory regiochemistry: in one case an allylstannane, and in another vinylstannane was formed exclusively (*vide post*). Shortly after Mitchell[4] reported a study on a comparison between radical and Pd-catalyzed addition of Me_3SnH to allenes. As in the previous cases[2,3] the free radical hydrostannation was characterized by unsatisfactory low degree of regio- and stereocontrol, producing a variety of products in which the tin group attached either to the central or to terminal carbon atom of allenic moiety. The Pd-catalyzed reaction was more selective, furnishing allylstannanes as a major product; however, the last were always accompanied with trace to significant amounts of isomeric vinylstannanes.[4] Taken together, it seems that due to low degree of regio- and stereocontrol neither free radical nor Pd-catalyzed addition of Me_3SnH or Ph_3SnH to allenes could serve as a synthetically useful approach to vinyl- and allylstannanes.[5]

Recently we developed highly regio- and stereocontrolled Lewis acid-catalyzed transhydrostannation of alkynes, which allowed us to obtain various vinylstannanes in good yields.[6] All mentioned above prompted us to examine whether Lewis acids could also catalyze the hydrostannation of allenes with Bu_3SnH regioselectively.

Results and Discussion

Lewis Acid-Catalyzed Hydrostannation of Allenes. We found that 20 mol % of $B(C_6F_5)_3$ at low to room temperatures catalyzed the addition of Bu_3SnH to certain monosubstituted allenes **1**, leading to vinylstannanes **2** exclusively (eq 1, Table 1). The addition of Bu_3SnH to aliphatic allenes **1a**,**b** gave vinylstannanes **2a**,**b** in moderate yields (Table 1, entries 1, 2). In contrast, hydrostannation of benzyl- (**1c**), phenyl- (**1d**), and para-substituted phenylallenes (**1e**,**g**) proceeded smoothly, leading to the corresponding vinylstannanes **2c**−**e**,**g** with 59−77% isolated yields (entries 3−5 and 7). It should be pointed out that $ZrCl_4$ also catalyzed reactions mentioned above; however, the yields of **2** in most cases were slightly lower than those *via* $B(C_6F_5)_3$ catalyst. The low yield of **2h** is presumably due to the strong affinity of the Lewis acid to the enol oxygen atom[7] of alkoxyallene **1h** that causes deactivation of the catalyst at low temperatures and decomposition of the starting allene when the reaction is carried out at the temperatures higher than −78 °C (entry 8). Siloxyallene **1i** reacted with Bu_3SnH in different manner, producing allylstannanes **5i**, **6i** (eq 1) with total isolated yield of 52% (**5**:**6** = 85:15). It is clear that replacement of the methoxy group (**1h**) by a bulky TIPSO group (**1i**) not only prevents a coordination between Lewis acid and the enol oxygen atom of **1i**, but also prevents an internal addition of the tin group to the central carbon of the allene moiety, thus leading to the terminal addition products **5i**, **6i**. Very low reactivity of **1f** (entry 6), bearing a strong electron-withdrawing substituent at the para-position of phenyl ring may be explained by destabilization of a cationic intermediate **3** as mentioned later (Scheme 1).

A plausible mechanism for the Lewis acid-catalyzed hydrostannation of allenes is shown in Scheme 1. As we proposed previously in the Lewis acid-catalyzed hydro-[6] and allylstannation,[8] and hydro-[9] and allylsilylation[10] of

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

(1) (a) Pereyre, M.; Quintard J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987. (b) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1967**, *9*, 295. (c) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1967**, *9*, 285. (d) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (e) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(2) Kuivila, H. G.; Rahman, W.; Fish, R. H. *J. Am. Chem. Soc.* **1965**, *87*, 2835.

(3) Ichinose, Y.; Oshima, K.; Utimoto, K. *Bull. Soc. Chem. Jpn.* **1988**, *61*, 2693.

(4) Mitchell, T. N.; Schneider, U. *J. Organomet. Chem.* **1991**, *405*, 195.

(5) There is an exemplary report describing the free radical hydrostannation of methoxyallene **1h** by Bu_3SnH, leading to the mixture of corresponding *Z*-(**5h**) and *E*-(**6h**) allylstannanes. Koreeda, M.; Tanaka, Y. *Tetrahedron Lett.* **1987**, *28*, 143.

(6) (a) Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4568. (b) Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Chem. Soc. Chem. Commun.* **1995**, 2405.

(7) The strong coordination of various Lewis acids to an enol oxygen atom was reported. (a) Gevorgyan, V.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 58. (b) Gevorgyan, V.; Yamamoto, Y. *Tetrahedron. Lett.* **1995**, *36*, 7765.

(8) Asao, N.; Matsukawa, Y.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1996**, 1513.

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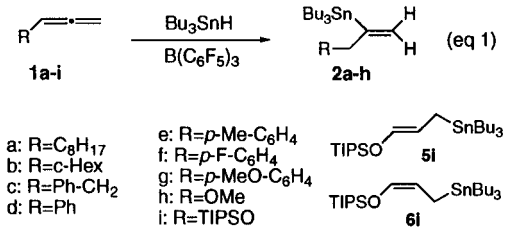
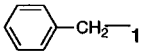
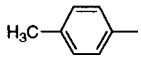
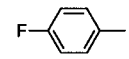
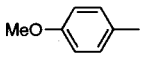
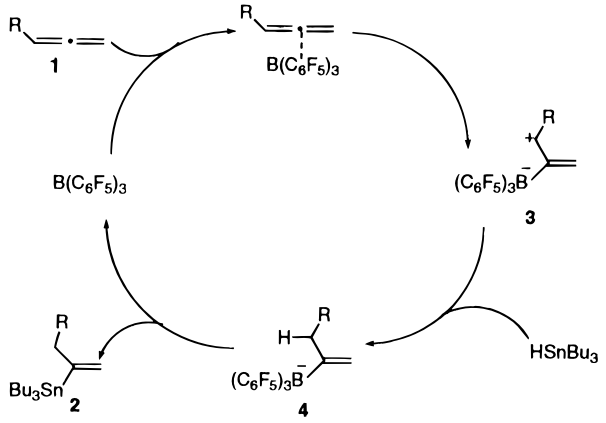
Table 1. Lewis Acid-Catalyzed Hydrostannation of Allenes with Bu_3SnH[a]



entry	R		Condition	Yield of **2** (%)[b]
1[c]	C_8H_{17}	**1a**	rt for 24h	37[d,e]
2		**1b**	-78°C for 20min 0°C for 40 min rt for 22h	41
3		**1c**	0°C→ rt 3h	57
4		**1d**	0°C→ rt 3h	60
5		**1e**	0°C→ rt 3h	77
6		**1f**	0°C→ rt 3h	traces
7		**1g**	-70°C→ -50°C 2h	59
8	MeO	**1h**	-78°C for 3h	12

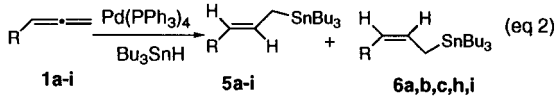
[a]All reactions were conducted in toluene in the presence of 20mol% of $B(C_6F_5)_3$. [b]Isolated yield. [c]Hexane was used as a solvent. [d]Determind by ^1H NMR using *p*-xylene as an internal standard. [e]Not separable with non-polar tin by-products, thus only characteristic ^1H NMR and IR data for **2a** were presented in the Experimental part.

Scheme 1. Proposed Mechanism for the Lewis Acids Catalyzed Hydrostannation of Allenes

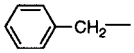
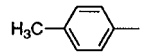
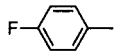
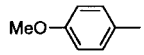


alkynes, the coordination of $B(C_6F_5)_3$ to the internal double bond of **1** would produce the zwitterionic intermediate **3** which would be transformed into the ate complex **4** *via* hydride tranfer from Bu_3SnH to the cationic center of **3**. The transmetalation from boron to tin would produce the vinylstannane **2** and regenerate $B(C_6F_5)_3$ catalyst. If a strong electron-withdrawing group is present in R, the intermediate **3** would be destabilized. Very low reactivity of **1f** can be explained by this mechanism. Perhaps, $ZrCl_4$-catalyzed hydrostannation of allenes would proceed through similar mechanism. In conclusion, the Lewis acid-catalyzed hydrostannation of allenes (which has no precedent in literature) is effective for the synthesis of various vinylstannanes **2**, irrespective of the precise mechanism.

Table 2. Pd-Catalyzed Hydrostannation of Allenes with Bu_3SnH[a]



a: R=C_8H_{17}
b: R=c-Hex
c: R=Ph-CH_2
d: R=Ph
e: R=*p*-Me-C_6H_4
f: R=*p*-F-C_6H_4
g: R=*p*-MeO-C_6H_4
h: R=OMe
i: R=TIPSO

entry	R		Yield (%)[b]	E:Z Ratio **5** : **6**[c,d]
1	C_8H_{17}	**1a**	78[e]	33 : 67
2		**1b**	52[e]	18 : 82
3		**1c**	66[e]	38 : 62
4		**1d**	60	>95 : 5
5		**1e**	62	>95 : 5
6		**1f**	77	>95 : 5
7		**1g**	75	>95 : 5
8	MeO	**1h**	69[f]	19 : 81
9	TIPSO	**1i**	73[f]	29 : 71

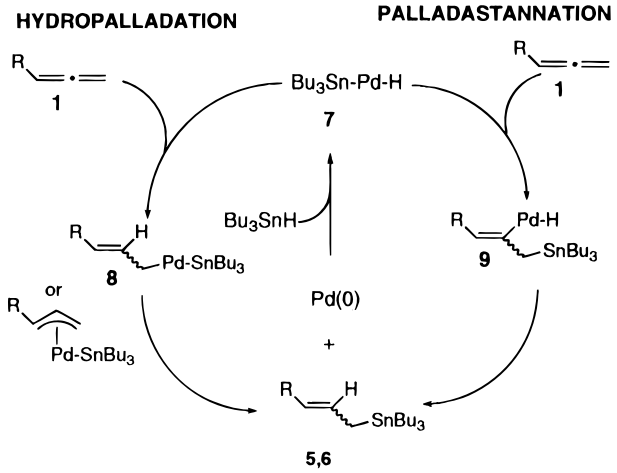
[a]All reactions were carried out in THF under Ar, either at reflux for 3h or at 25°C for 5h, in the presence of 5mol% $Pd(PPh_3)_4$. [b]Isolated yield. [c]Determined by 270 MHz ^1H NMR. [d]The ratios of **5**:**6** were not dependent upon reaction temperatures. [e]Isolated as a mixture of E-and Z-isomers. [f]**5** and **6** were readily separated by column chromatography (silica gel).

Palladium-Catalyzed Hydrostannation of Allenes with Bu_3SnH. As we have mentioned in the introduction part, the Pd-catalyzed addition of Me_3SnH to certain allenes suffers from low regio- and stereoselectivity,[4] whereas the regio- and stereochemistry of Pd-catalyzed addition of Ph_3SnH is not clear, as well.[3] We chose Bu_3SnH for the Pd-catalyzed hydrostannation of allenes for several reasons: first, this is the cheapest and the most popular among all tin hydrides available;[1a] second, tributyltin-containing products are less toxic and more hydrolytically stable than trimethyltin counterparts and thus are much more easily handled; and finally, the hydrostannation by use of more bulky Bu_3SnH was expected to be more regioselective that that with use of compact Me_3SnH.[4] The results on Pd-catalyzed addition of Bu_3SnH to certain monosubstituted allenes are summarized in the Table 2.

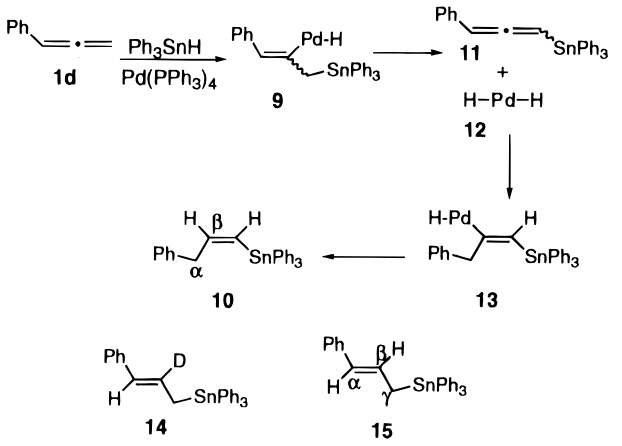
Indeed, the Pd-catalyzed hydrostannation of **1a**−**i** with Bu_3SnH proceeded smoothly, producing the correspond-

(9) Asao, N.; Sudo, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 7654.
(10) Asao, N.; Yoshikawa, E.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4784.

Scheme 2. Proposed Mechanism for the Pd-Catalyzed Hydrostannation of Allenes



Scheme 3. Oshima's Mechanism for the Formation of (*Z*)-Vinylstannane 10 via Palladium-Catalyzed Hydrostannation of 1d with Ph_3SnH



ing allylstannanes **5**, **6** in good yields (Table 2, eq 2). Although the hydrostannation of aliphatic **1a**,**b** (entries 1, 2), benzylic **1c** (entry 3), and alkoxyallenes **1h**,**i** (entries 8, 9) resulted in formation of both *E* (**5**) and *Z* (**6**) isomeric allylstannanes, any other regioisomers were not detected by 270 MHz ^{1}H NMR analyses of the crude reaction mixtures. It deserves a special note that hydrostannation of aromatic allenes **1d**−**g** (entries 4−7) proceeds not only regioselectively but also stereoselectively, producing (*E*)-allylstannanes **5** exclusively. It is apparent that this reaction is kinetically controlled since the ratios of **5**:**6** in all cases did not depend upon reaction temperatures (Table 2, note footnote *d*). A probable mechanism for the regiospecific Pd-catalyzed hydrostannation of allenes with Bu_3SnH is shown in the Scheme 2.

Palladium(0) would insert oxidatively into the Sn−H bond of hydrostannane forming the reactive species **7**.[11] The palladium intermediate **7**, either *via* the hydropalladation pathway,[12] would add across the terminal double bond of allene **1** producing the allylpalladium intermediate **8**, or *via* the palladastannation pathway[13] would give the vinylpalladium species **9**. Either **8** or **9** would undergo reductive elimination of Pd to give the products **5**, **6** along with the Pd-catalyst.

Although further investigation is needed to establish the mechanism of stereo- and regioselective Pd-catalyzed hydrostannation of allenes with Bu_3SnH, this method is useful for the synthesis of various allylstannanes **5**, **6** in good to excellent yields.

Palladium-Catalyzed Hydrostannation of Allenes with Ph_3SnH. As a final remark of this investigation we would like to disclose our several experiments on Pd-catalyzed hydrostannation of aromatic allenes with Ph_3SnH. We were intrigued by Oshima's observation on unprecedented exclusive formation of (*Z*)-vinylstannane **10** in the Pd-catalyzed hydrostannation of phenylallene **1d** with Ph_3SnH[3] (Scheme 3). They assigned the structure **10** based on ^{1}H NMR spectra. It was proposed that the β-elimination of PdH_2 species **12** from the palladastannylation product **9** and consecutive addition of **12** to a double bond of the newly formed stannylallene **11** would produce the palladavinylstannane **13**, which would give the **(***Z*)-vinylstannane **10** through reductive coupling (Scheme 3[3]).

In the case this mechanism is correct, the hydrostannation of **1d** with Ph_3SnD would cause unavoidable scrambling of deuterium atom at the α- and β-positions to the phenyl group of the product **10**. In order to clarify this point we prepared isotopically homogeneous Ph_3SnD[14] and utilized it in the reaction with phenylallene **1d**. Unexpectedly, we found (1) that no detectable scrambling occurred during that reaction, and (2) that not (*Z*)-vinylstannane **10**, but (*E*)-allylstannane **14**, was formed as a single product. Control experiments with Ph_3SnH gave the proton analogue **15**, accordingly. The geometry of the double bond in **14** and **15**[15] was unambiguously assigned by NOE experiments.[17] The location of the double bond[18] was confirmed by carbon NMR spectra[19] as well as by destannylating the Ph_3Sn group of **15** with Bu_4NF:(*E*)-1-phenyl-1-propene was produced exclusively. Furthermore, authentic **15** was prepared by the reaction of (*E*)-cinnamylmagnesium chloride with Ph_3SnCl,[20] and ^{1}H NMR data of the authentic sample was in perfect agreement with those of the product obtained by the Pd-catalyzed hydrostannation of **1d**. It is clear that Oshima and co-workers were confused by combina-

(11) The germanium analogue of **7** was reported to be synthesized and fully characterized. Bochkarev, M. N.; Maiorova, L. P.; Skobeleva, S. E.; Razuvaev, G. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1979**, 1854. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Eng. Transl.)* **1979**, 1717.

(12) For the syntheses and properties of palladium hydrides, see a recent excellent review: Grushin, V. *Chem. Rev.* **1996**, *96*, 2011 and references therein.

(13) An addition of Sn−Pd species to allenes is well known. Mitchell, T. N.; Kwetkat, K.; Rutschow, D.; Schneider, U. *Tetrahedron* **1989**, *45*, 969.

(14) The reduction of metal halides of the group 14 elements by $LiAlD_4$ in the phase-transfer conditions allows us to prepare the corresponding deuterides with high isotopic purity, similar to that in LiAlD4 used. (a) Gevorgyan, V. N.; Ignatovich, L. M.; Lukevics, E. *J. Organomet. Chem.* **1985**, *284*, C31. (b) Liepins, E.; Gevorgyan, V.; Lukevics, E. *J. Magn. Res.* **1989**, *85*, 170.

(15) The value of vicinal constant of olefinic protons (15.7 Hz)[3] is somewhat close to the borderline values of (*Z*)- and (*E*)-(triphenylstannyl)alkenes[16] and, thus, not reliable.

(16) Ichinose, Y.; Oda, H.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3468.

(17) The irradiation at either one of the olefinic protons of **15** did not display any NOE at another olefinic portion. In contrast, the irradiation of methylene protons at the γ-position of **15** exhibited significant NOE at both olefinic protons.

(18) Although the value of the chemical shift (~2.6 ppm) is somewhat low for the methylene group in **10**, it is still too high for that in allylstannanes,[16] and thus is not reliable to distinguish the structures **10** and **15** by this means.

(19) The observed high field resonance (17.5 ppm) in the carbon NMR spectra of **15** (see Experimental Section) correlates to that of an sp^3 carbon in allylstannanes. This is in a contrast to the low field chemical shift of allylbenzenes (*ca.* 40 ppm).

(20) Tanaka, H.; Abdul Hai, A. K. M.; Ogawa, H.; Torii, S. *Synlett* **1993**, 835.

tion of very specific features[15,18] of the compound **15**, and they could not make correct assignment of its structure, on the basis of ^{1}H NMR data only.

Thus, we can generalize and conclude that Pd-catalyzed hydrostannation of allenes with both Bu_3SnH and Ph_3SnH proceeds regioselectively, providing allylstannanes in good to excellent yields. In the case of aromatic allenes, the reaction is also stereoselective, furnishing (*E*)-allylstannanes exclusively.

Conclusion

We are now in a position to prepare various kinds of vinylstannanes **2** *via* the $B(C_6F_5)_3$-catalyzed hydrostannation of allenes **1**, and allylstannanes **5**, **6** *via* palladium-catalyzed hydrostannation of **1**. These vinyl- and allylstannanes may be useful as a building blocks for organic synthesis.

Experimental Section

General Information. All solvents used were specially purified and dried according to the standard procedures. Starting allenes **1a**−**i** were prepared according with known procedures.[21]

General Experimental Procedures. A. Lewis Acid-Catalyzed Hydrostannation. Preparation of **2e** from **1e** is representative. **1e** (0.07 mL, 0.5 mmol) and Bu_3SnH (0.16 mL, 0.6 mmol) were added at 0 °C to a solution of $B(C_6F_5)_3$ (51.2 mg, 0.1 mmol) in toluene (0.25 mL) under an Ar atmosphere. After the reaction was completed (reaction conditions mentioned in the Table 2), Et_3N (0.07 mL, 0.5 mmol) was added. After 5 min hexane was added, and the resulting mixture was filtered through Celite and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, 60 mesh, *n*-hexane as an eluent) gave 162.5 mg (77%) of **2e**.

B. Pd-Catalyzed Hydrostannation. Preparation of **5e** from **1e** is representative. **1e** (0.07 mL, 0.5 mmol) and Bu_3SnH (0.16 mL, 0.6 mmol) were consecutively added to a solution of $Pd(PPh_3)_4$ (14 mg, 0.02 mmol) in THF (1 mL). The mixture was stirred for 3 h at 65 °C, and then the mixture was allowed to cool down to room temperature. Hexane was added, and the resulting mixture was filtered through Celite and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, 60 mesh, *n*-hexane as an eluent) gave 131 mg (62%) of **5e**.

2-(Tributylstannyl)-1-undecene (2a): ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.65 (dt, J = 3.0 and 1.5 Hz, 1H), 5.08 (distorted dt, J = 3.0 and 1.0 Hz, 1H), 2.27 (t, J = 7.5 Hz, 2H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1640.

2-(Tributylstannyl)-3-cyclohexyl-1-propene (2b): ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.60 (dt, J = 3.0 and 1.5 Hz, 1H), 5.11 (distorted dt, J = 3.0 and 1.0 Hz, 1H), 2.12 (distorted d, J = 6.8 Hz, 2H) 1.75−0.80 (several m, 38H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1640. MS (EI) *m*/*z* (relative intensity,%) 357 ($M^+ - C_4H_9$, 100). HRMS (EI) *m*/*z* calcd for $C_{17}H_{33}Sn$ ($M^+ - C_4H_9$) 357.1604, found 357.1622.

2-(Tributylstannyl)-4-phenyl-1-butene (2c): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.32−7.14 (m, 5H), 5.73 (dt, J = 2.6 and 1.3 Hz, 1H), 5.16 (distorted dt, J = 2.6 and 1.3 Hz, 1H), 2.73−2.49 (m, 4H), 1.58−0.80 (several m, 27H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1610. MS (EI) *m*/*z* (relative intensity,%) 365 ($M^+ - C_4H_9$, 100). HRMS (EI) *m*/*z* calcd for $C_{18}H_{29}Sn$ ($M^+ - C_4H_9$) 365.1291, found 365.1329.

2-(Tributylstannyl)-3-phenyl-1-propene (2d): ^{1}H NMR δ 7.30−7.11 (m, 5H), 5.72 (dt, J = 2.8 and 1.4 Hz, 1H), 5.22 (distorted dt, J = 2.8 and 1.4 Hz, 1H), 3.56 (s, 2H), 1.41−1.15 (m, 12H), 0.84 (t, J = 7.0 Hz, 9H), 0.70 (t, J = 8.0 Hz, 6H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1610. Anal. Calcd for $C_{21}H_{36}Sn$: C, 61.9389; H, 8.9101. Found: C, 61.738; H, 9.002.

2-(Tributylstannyl)-3-(*p*-tolyl)-1-propene (2e): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.07 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 5.70 (dt, J = 3.0 and 1.2 Hz, 1H), 5.19 (dt, J = 3.0 and 1.2 Hz, 1H), 3.51 (s, 2H), 2.31 (s, 3H), 1.40−0.80 (several m, 21H), 0.70 (t, J = 8.0 Hz, 6H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1640. MS (EI) *m*/*z* (relative intensity,%) 365 ($M^+ - C_4H_9$, 100). HRMS (EI) *m*/*z* calcd for $C_{18}H_{29}Sn$ ($M^+ - C_4H_9$) 365.1291, found 365.1296.

2-(Tributylstannyl)-3-(4-methoxyphenyl)-1-propene (2g): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.05 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 5.70 (dt, J = 2.8 and 1.4 Hz, 1H), 5.19 (distorted dt, J = 2.8 and 1.4 Hz, 1H), 3.78 (s, 3H), 3.50 (s, 2H), 1.42−1.16 (m, 12H), 0.86 (t, J = 6.8 Hz, 9H), 0.71 (t, J = 8.0 Hz, 6H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1610. MS (EI) *m*/*z* (relative intensity,%) 381 ($M^+ - C_4H_9$, 100). HRMS (EI) *m*/*z* calcd for $C_{18}H_{29}OSn$ ($M^+ - C_4H_9$) 381.1240, found 381.1273.

2-(Tributylstannyl)-3-methoxy-1-propene (2h): ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.85 (m, 1H), 5.26 (distorted dt, J = 2.2 and 1.1 Hz 1H), 4.02 (q, J = 0.9 Hz, 2H), 3.29 (t, J = 0.9 Hz, 3H), 1.58−0.84 (several m, 27H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1610. Anal. Calcd for $C_{16}H_{34}OSn$: C, 53.2114; H, 9.4890. Found: C, 53.249; H, 9.592.

1-(Tributylstannyl)-2-undecene (5a, 6a) (unseparable mixture of *Z*- and *E*-isomers): ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.60−5.39 (m, 1H), 5.27−5.01 (m, 1H), 2.10−1.90 (m, 2H), 1.71 (distorted d, J = 9.0 Hz, 2H), 1.58−0.78 (several m, 32H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1640. MS (EI) *m*/*z* (relative intensity,%) 387 ($M^+ - C_4H_9$, 16), 291(100). HRMS (EI) *m*/*z* calcd for $C_{23}H_{48}Sn$ (M^+) 444.2778, found 444.2769.

1-Cyclohexyl-3-(tributylstannyl)-1-propene (5a, 6b) (unseparable mixture of *Z*- and *E*-isomers): ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.52−5.36 (m, 1H), 4.97−4.87 (m, 1H), 2.28−2.10 (m, 1H), 1.71 (dd, J = 8.7 and 1 Hz 2H), 1.69−0.84 (several m, 37H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1640. MS (EI) *m*/*z* (relative intensity,%) 357 ($M^+ - C_4H_9$, 30), 291(100). HRMS (EI) *m*/*z* calcd for $C_{21}H_{42}Sn$ (M^+) 414.2308, found 414.2299.

1-(Tributylstannyl)-4-phenyl-2-butene (5c, 6c) (unseparable mixture of *Z*- and *E*-isomers): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.30−7.13 (m, 5H), 5.76−5.54 (m, 1H), 5.42−5.22 (m, 1H), 3.37 (distorted d, J = 7.0 Hz), 3.30 (distorted d, J = 7.0 Hz, 2H), 1.82 (dd, J = 9.0 and 1.0 Hz), 1.723 (dd, J = 8.2 and 1.1 Hz, 2H), 1.56−0.81 (several m, 27H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1640. Anal. Calcd for $C_{22}H_{38}Sn$: C, 62.7277; H, 9.0920. Found: C, 62.390; H, 9.471.

(*E*)-1-Phenyl-3-(tributylstannyl)-1-propene (5d): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.26 (d, J = 4.2 Hz, 4H), 7.17−7.06 (m, 1H), 6.42 (dt, J = 15.0 and 8.7 Hz, 1H), 6.20 (d, J = 15 Hz, 1H), 1.97 (d, J = 8.7 Hz, 2H), 1.60−0.86 (several m, 27H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1634. Anal. Calcd for $C_{21}H_{36}Sn$: C, 61.9389; H, 8.9109. Found: C, 61.910; H, 9.192.

(*E*)-1-(*p*-Tolyl)-3-(tributylstannyl)-1-propene (5e): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.15 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.34 (dt, J = 15.3 and 8.5 Hz, 1H), 6.16 (d, J = 15.3 Hz, 1H), 2.30 (s, 3H), 1.93 (dd, J = 8.5 and 1.1 Hz, 2H), 1.57−0.84 (several m, 27H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1638. Anal. Calcd for $C_{22}H_{38}Sn$: C, 62.7277; H, 9.0920. Found: C, 62.907; H, 9.429.

(*E*)-1-(4-Fluorophenyl)-3-(tributylstannyl)-1-propene (5f): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.23−7.15 (m, 2H), 6.98−6.89 (m, 2H), 6.30 (dt, J = 15.2 and 8.3 Hz, 1H), 6.14 (d, J = 15.2 Hz, 1H), 1.93 (d, J = 8.3 Hz, 2H), 1.55−0.84 (m, 27H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1636. Anal. Calcd for $C_{21}H_{35}FSn$: C, 59.3184; H, 8.2961. Found: C, 59.389; H, 8.474.

(*E*)-1-(4-Methoxyphenyl)-3-(tributylstannyl)-1-propene (5g): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.18 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 6.25 (dt, J = 15 and 7.8 Hz, 1H), 6.14 (d, J = 15.0 Hz, 1H), 3.78 (s, 3H), 1.92 (d, J = 7.8 Hz, 2H), 1.57−0.84 (several m, 27H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1640. Anal. Calcd for $C_{22}H_{38}OSn$: C, 60.4325; H, 8.7593. Found: C, 60.536; H, 8.949.

(*E*)-1-Methoxy-3-(tributylstannyl)-1-propene (5h): ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.17 (dt, J = 12.0 and 1.1 Hz, 1H), 4.92 (dt, J = 12.0 and 8.4 Hz, 1H), 3.47 (s, 3H), 1.57−0.85 (several m, 29H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1643. Anal. Calcd for $C_{16}H_{34}OSn$: C, 53.2114; H, 9.4890. Found: C, 53.316; H, 9.416.

(21) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981.

(*Z*)-1-Methoxy-3-(tributylstannyl)-1-propene (6h): ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.71 (dt, J = 5.8 and 1.1 Hz, 1H), 4.52 (dt, J = 8.8 and 5.8 Hz, 1H), 3.55 (s, 3H), 1.64 (dd, J = 8.8 and 1.1 Hz, 2H), 1.56−0.84 (several m, 27H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1652.9. Anal. Calcd for $C_{16}H_{34}OSn$: C, 53.2114; H, 9.4890. Found: C, 53.598; H, 9.564.

(*E*)-1-[(Triisopropylsilyl)oxy]-3-(tributylstannyl)-1-propene (5i): ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.34 (dt, J = 11.5 and 1.3 Hz, 1H), 5.24 (dt, J = 11.5 and 8.5 Hz, 1H), 1.68−0.91 (several m, 50H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1649. Anal. Calcd for $C_{24}H_{52}OSiSn$: C, 57.2555; H, 10.4099. Found: C, 57.015; H, 10.433.

(*Z*)-1-[(Triisopropylsilyl)oxy]-3-(tributylstannyl)-1-propene (6i): ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.11 (dt, J = 5.7 and 1.2 Hz, 1H), 4.53 (dt, J = 8.8 and 5.7 Hz, 1H), 1.72 (dd, J = 8.8 and 1.2 Hz, 2H), 1.54−0.81 (m, 48H). IR (neat) $\upsilon_{C=C}$ (cm^{-1}) 1643. Anal. Calcd for $C_{24}H_{52}OSiSn$: C, 57.2555; H, 10.4099. Found: C, 57.386; H, 10.694.

(*E*)-1-Phenyl-3-(triphenylstannyl)-1-propene (15): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.80−7.09 (mm, 20H), 6.48 (dt, J = 15.7 and 7.9 Hz, 1H), 6.33 (d, J = 15.7 Hz, 1H), 2.61 (d, J = 7.9 Hz, 2H; $^2J_{Sn-H}$ = 72 Hz). ^{13}C NMR (300 MHz, $CDCl_3$) δ 138.3, 138.2, 137.1, 129.1, 128.6, 128.4, 128.2, 127.7, 126.2, 125.5, 17.5.

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