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Lewis Acid Catalyzed Allylstannylation of Unactivated Alkynes[†]

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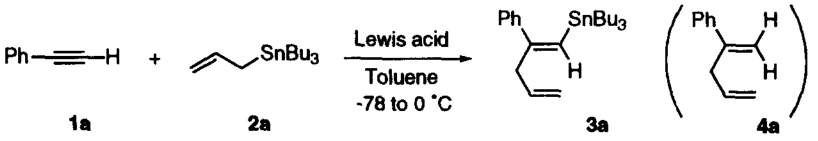
Abstract: The addition of allyltributylstannane **2** to unactivated aromatic alkynes **1** in the presence of catalytic amounts of $ZrCl_4$ or $EtAlCl_2$ produced the stannylated 1,4-dienes **3** with very high regio- and stereoselectivities in good to high yields. The exclusive *trans* manner of addition was confirmed by ^{1}H NMR analysis of crude reaction mixtures. On the other hand, the stereochemistries of addition products produced from the reactions using aliphatic acetylenes depended on the reaction conditions and the Lewis acid type. The mechanisms for the $ZrCl_4$ and $EtAlCl_2$ catalyzed allylstannylation of alkynes are proposed.

Introduction

Since the first carbometallation discovered by Ziegler and Bähr,[1] an ever-increasing number of additions of organometallics to carbon-carbon multiple bonds have been reported.[2] The allylmetalation of activated alkynes, such as alkynyl ketones (Michael acceptors) and alkynols (functionally substituted alkynes), in both intramolecular and intermolecular versions proceeds smoothly with various allylmetals.[2,3] However, the allylmetalation of simple unactivated alkynes is not easy, and only a limited number of allylmetals can serve for this purpose.[2,4] In general, these reactions proceed predominantly in *cis*-selective manner, however, usually with poor regio- and stereoselectivity. Recently we reported the first example of Lewis acid catalyzed *trans*-allylsilylation[5] and allylstannylation[6] of unactivated alkynes. Now we report the detailed study of the allylstannylation reactions catalyzed by Lewis acids including $ZrCl_4$ and $EtAlCl_2$.

Results and Discussion

Allylstannylation of Phenylacetylene Catalyzed by Lewis Acids. The addition of allyltributylstannane **2a** to phenylacetylene **1a** was examined in the presence of catalytic amounts of Lewis acids (eq 1) and the results are summarized in Table 1.



(eq 1)

[†]Dedicated to the memory of Professor Sir Derek Barton

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The $TiCl_4$ catalyzed reaction of phenylacetylene **1a** with allyltributylstannane **2a** afforded a complex mixture of products (entry 1). However, the allylstannylation in the presence of 0.2 equiv. of $ZrCl_4$ proceeded smoothly in toluene at -78 to 0 °C. The reaction was quenched with excess Et_3N at 0 °C and the product was purified by silica gel column chromatography. The protonolysis product **4a** was obtained in 52% yield (entry 2). Since it was anticipated that protonolysis of the carbon-stannane bond would take place during work-up and/or purification, we changed the method for isolation of the stannylated product **3a**. Allylstannylation in the presence of $ZrCl_4$ (0.2 equiv.) followed by quenching the reaction mixture with saturated aq. $NaHCO_3$ at 0 °C, and subsequent purification by basic alumina column chromatography at 0 °C using a jacket column filled with ice water gave the *trans*-allylstannylation product **3a** regio- and stereoselectively in 83% yield (entry 3). The chemical yield was slightly enhanced to 87% by using 0.5 equiv. of $ZrCl_4$ (entry 4). However, the use of stoichiometric amount of $ZrCl_4$ did not give a better yield than entries 3-4 (entry 5). Previously we reported the $ZrCl_4$ catalyzed *trans*-hydrostannylation reaction of unactivated alkynes and in those reactions $HfCl_4$ was also found to be effective as a catalyst.[7] In the present reaction, however, **3a** was obtained in very low yield in the presence of catalytic amounts of $HfCl_4$ (entry 6). The use of $AlCl_3$ as a Lewis acid afforded only the destannylated product **4a** in low yield (entry 7), perhaps owing to its higher Lewis acidity which may induce the transmetalation of allylstannane to the corresponding allyl aluminium derivative. However, $EtAlCl_2$ was found to be very effective as a catalyst for the present allylstannylation reaction as well as $ZrCl_4$ (entry 8). It should be noted that $ZrCl_4$ was not soluble in toluene at 0 °C and therefore the reaction was carried out in a heterogeneous system. On the other hand, $EtAlCl_2$ can be dissolved easily in non-polar solvents such as toluene and hexane at 0 °C and the reaction was carried out in a homogeneous system. The Et_2AlCl catalyzed reaction did not proceed at all, maybe due to its lower Lewis acidity (entry 9).[8] The *trans*-allylstannylation was unambiguously confirmed by the stereochemistry of **3a**. Thus, irradiation of methylene protons of the allylic position of **3a** enhanced a vinyl proton (9.0% NOE) as shown in Fig. 1.

Table 1. Lewis Acid Catalyzed Allylstannylation of Phenylacetylene **1a**[a]

entry	Lewis Acid (equiv.)	isolated yield (%) **3a**	isolated yield (%) **4a**
1[b]	$TiCl_4$ (0.2)	0	0
2[b]	$ZrCl_4$ (0.2)	0	52
3[c]	$ZrCl_4$ (0.2)	83	0
4[c]	$ZrCl_4$ (0.5)	87	0
5[c]	$ZrCl_4$ (1.0)	53	0
6[c]	$HfCl_4$ (0.2)	8	0
7[c]	$AlCl_3$ (0.5)	0	23
8[c]	$EtAlCl_2$ (0.2)	83	0
9[c]	Et_2AlCl (0.2)	0	0

[a] All reactions were carried out with 2 equiv. of allylstannane. [b] The reaction was quenched with Et_3N, and the crude product was purified by silica gel column chromatography. [c] The reaction was quenched with aq. $NaHCO_3$, and the crude product was purified by basic alumina column chromatography at 0 °C.

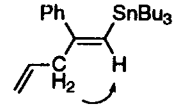
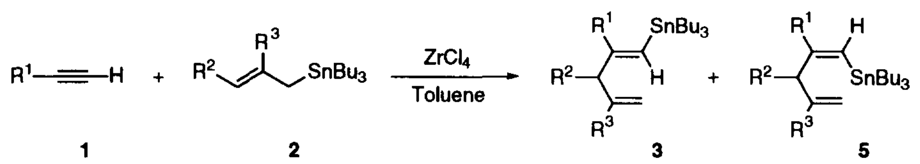


Figure 1

Allylstannylation of Unactivated Alkynes Catalyzed by $ZrCl_4$. The selected $ZrCl_4$ catalyzed allylstannylation of various unactivated alkynes listed in Table 2 provides the following conclusions: 1) Reactions of the aromatic acetylenes **1b**, **1c**, and **1d**, proceed smoothly to give the corresponding *trans*-allylstannylated products (**3b**, **3c**, and **3d**, respectively), with very high regio- and stereoselectivity in high yields (entries 1-3). 2) The conjugated enyne **1e** also produced the *trans*-allylstannylation product **3e** (entry 4). 3) Stoichiometric amount of $ZrCl_4$ was needed for obtaining good yields in the reaction of the aliphatic acetylene **1f** (entries 5-6). Interestingly, the *cis*-addition products were afforded predominantly in the reaction of the aliphatic acetylenes **1f**, **1g**, **1h**, and **1i** in toluene at 0 °C, in contrast to the reactions of aromatic acetylenes (entries 6,8,10-11). Particularly, the reaction of cyclopentylacetylene **1i** gave the *cis*-adduct **5i** as a sole product. Without solvents, however, allyltributylstannane added to the acetylenic bonds of **1f** and **1g** with *trans*-fashion (entries 7,9). Consequently, stereodivergent synthesis of (*E*)- and (*Z*)-alkenylstannanes can be carried out in the



(eq 2)

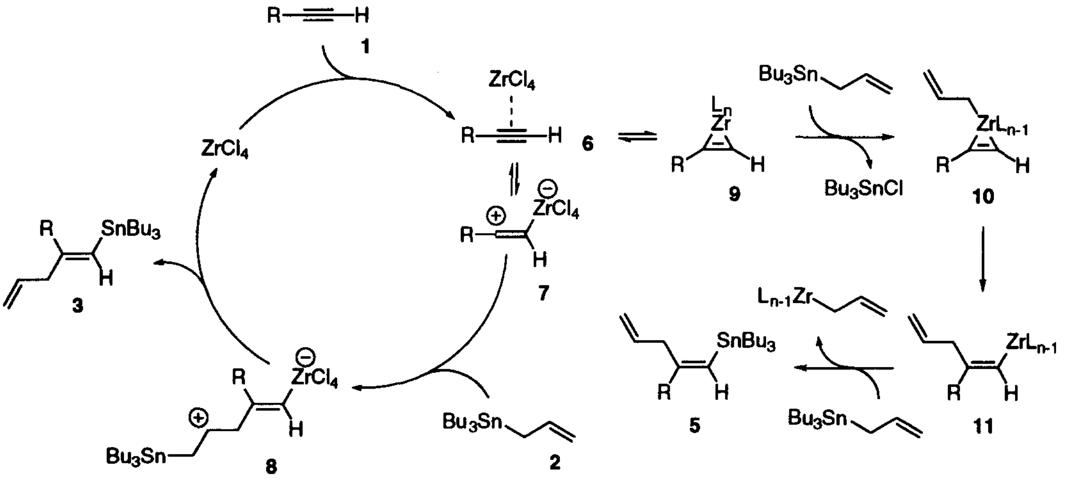
Table 2. $ZrCl_4$ Catalyzed Allylstannylation of Unactivated Alkynes[a]

entry	$ZrCl_4$ (equiv.)	temp (°C)	alkyne	R^1	R^2	R^3	product 3	5	yield[b] (%)	ratio[c] 3 : 5
1	0.2	-78 to 0	**1b**	p-$CH_3C_6H_4$	H	H	**3b**		84	100 : 0
2	0.2	-78 to 0	**1c**	p-ClC_6H_4	H	H	**3c**		65	100 : 0
3	0.2	-78 to 0	**1d**	p-$CH_3OC_6H_4$	H	H	**3d**		79	100 : 0
4	0.2	-78 to 0	**1e**	1-cyclohexenyl	H	H	**3e**		99	100 : 0
5	0.3	-78 to 0	**1f**	C_6H_{13}	H	H	**3f**		0	-
6	1.0	0	**1f**	C_6H_{13}	H	H	**3f** +	**5f**	68	17 : 83
7[d]	1.0	0	**1f**	C_6H_{13}	H	H	**3f**		51	100 : 0
8	1.0	0	**1g**	$C_{10}H_{21}$	H	H	**3g** +	**5g**	70	27 : 73
9[d,e]	1.0	0	**1g**	$C_{10}H_{21}$	H	H	**3g**		32	100 : 0
10	1.0	0	**1h**	$PhCH_2$	H	H	**3h** +	**5h**	47	14 : 86
11	1.0	0	**1i**	cyclopentyl	H	H		**5i**	30	0 : 100
12	1.0	0	**1j**	^{t}Bu	H	H	**3j**		0	-
13[f,g]	1.0	0	**1k**	H	H	H		**5k**	32	0 : 100
14[f,g,h]	1.0	0	**1k**	H	H	H		**5k**	55	0 : 100
15	0.2	-78 to 0	**1a**	Ph	Me	H	**3l**		56	100 : 0
16	0.2	-78 to 0	**1a**	Ph	H	Me	**3m**		55	100 : 0

[a] All reactions were carried out with 2 equiv. of allylstannane. [b] Isolated yield. [c] Ratio was determined by ^1H NMR. [d] Reaction was carried out without solvent. [e] Destannylated product was obtained in 10% yield in addition to 32% yield of alkenylstannane **3g**. [f] Excess amounts of acetylene **1k** was used. [g] Isolated yield based on allylstannane. [h] 1,5-Cyclooctadiene (1 equiv.) was added.

reactions of aliphatic acetylenes by changing the solvent system. 4) The reaction of 3,3-dimethyl-1-butyne **1j** did not proceed at all, perhaps owing to the steric factor of *t*-Bu group (entry 12). 5) Stereoselective *cis*-allylstannylation was observed in the reaction of acetylene **1k** (entry 13). The chemical yield was enhanced to 55% by the addition of 1 equiv. of 1,5-cyclooctadiene (entry 14). 6) Crotyl- and methallylstannane (**2b** and **2c**) also underwent the *trans* addition to phenylacetylene **1a** to give the corresponding alkenylstannanes (**3l** and **3m**, respectively) in reasonable yields (entries 15-16). In the case of crotylstannane, only the γ-adduct was isolated. The stereochemistries of the adducts (**3** and **5**) were determined unambiguously by NOE experiments by using a similar procedure as mentioned in the case of **3a**.

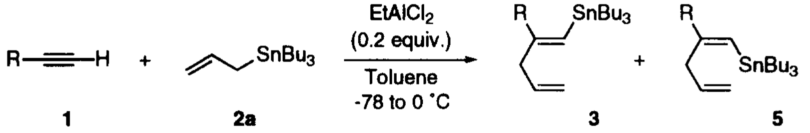
The addition order of reagents and substrates is essential for obtaining the allylstannylated products in the present reaction. Treatment of alkynes with a suspension of $ZrCl_4$ in toluene, followed by addition of allyltributylstannane to the reaction mixture, gave allylstannylation products. However, the reverse mode of the addition of the reagents and substrates gave no products; the addition of allylstannane to $ZrCl_4$ in toluene and subsequent addition of alkynes did not afford the adducts. Probably the treatment of allyltributylstannane with $ZrCl_4$ induced transmetalation to produce an allylzirconium species, which would not undergo the addition to alkynes under the reaction conditions. The interaction between Lewis acidic $ZrCl_4$ and a triple bond is a key for this addition reaction; actually the color of the reaction mixture changed to orange when alkynes were added to a suspension of $ZrCl_4$ in toluene. Consequently, a plausible mechanism for the $ZrCl_4$-catalyzed *trans*-allylstannylation is shown in Scheme 1, as we previously proposed for the Lewis acid catalyzed hydro-[7] and allylstannylation,[6] and hydro-[9] and allylsilylation[5] of alkynes. The coordination of $ZrCl_4$ to alkynes would produce the π-complex **6**, which would be stabilized by the π-system of R group in the case of aromatic acetylenes to form the zwitterionic intermediate **7**. Allyltributylstannane would attack the electron-deficient carbon from the side opposite to the Lewis acid to produce the adduct **8** stereoselectively, which would undergo elimination of Bu_3Sn^+ and form the corresponding zirconium ate complex in the similar manner as mentioned in the case of the $HfCl_4$ catalyzed allylsilylation of acetylenes.[5] Transmetalation of zirconium halide by the



Scheme 1

tributylstannyl group would afford the *trans*-allylstannylated product **3** and regenerate the catalyst. On the other hand, aliphatic alkynes might produce the η^2-complex **9** because the resonance stabilization of vinyl cation by a π-system, as observed in the case of aromatic acetylenes, is not expected. Allyltributylstannane would react with zirconium (ZrL_n) of **9**, instead of reacting with the unsaturated bond, to form allyl zirconium **10**, which would undergo the regioselective intramolecular allylation to give the vinylzirconium derivative **11**. Transmetalation of zirconium halide by the tributylstannyl group would afford the *cis*-allylstannylated product **5**.

Allylstannylation of Unactivated Alkynes Catalyzed by $EtAlCl_2$. We next examined the $EtAlCl_2$ catalyzed allylstannylation to various alkynes (eq 3) and the results are summarized in Table 3. Addition of allyltributylstannane to arylsubstituted alkynes (**1b** and **1d**) and the conjugated enyne **1e** in the presence of 0.2 equiv. of $EtAlCl_2$ proceeded smoothly, giving regio- and stereoselectively the corresponding allylstannylated products (**3b**, **3d**, and **3e**, respectively) in good to excellent yields (entries 1-3). In contrast to the $ZrCl_4$ catalyzed reaction, allylstannane reacted with aliphatic acetylenes even in the presence of catalytic amounts of $EtAlCl_2$ in reasonable yields and the *trans*-allylstannylated products were obtained predominantly (entries 4-5). On the other hand, no product was obtained in the reaction using acetylene **1k** (entry 6).



(eq 3)

Table 3. $EtAlCl_2$ Catalyzed Allylstannylation of Unactivated Alkynes[a]

entry	alkyne 1	R^1	product 3 5	yield[b] (%)	ratio[c] 3 : 5
1	**1b**	$p\text{-}CH_3C_6H_4$	**3b**	98	100 : 0
2	**1d**	$p\text{-}CH_3OC_6H_4$	**3d**	62	100 : 0
3	**1e**	1-cyclohexenyl	**3e**	54	100 : 0
4	**1f**	C_6H_{13}	**3f** + **5f**	50	86 : 14
5	**1g**	$C_{10}H_{21}$	**3g** + **5g**	51	82 : 18
6[d]	**1k**	H	**3k**	0	-

[a] All reactions were carried out with 2 equiv. of allylstannane. [b] Isolated yield. [c] Ratio was determined by ^1H NMR. [d] Excess amounts of acetylene **1k** was used.

The outline of the proposed reaction mechanism for the $EtAlCl_2$ catalyzed *trans*-allylstannylation of alkynes is the same as that for the $ZrCl_4$ catalyzed *trans*-allylstannylation of aromatic alkynes (Scheme 1). $EtAlCl_2$ would coordinate to the acetylenic bond of alkynes **1** to form the vinyl cation intermediate, which would attack allyltributylstannane in the stereoselective manner, and the subsequent transmetalation of aluminum halide with stannane would produce the *trans*-allylstannylated product **3** and regenerate the catalyst.

Conclusion

We are now in a position to effectively prepare (regio- and stereoselectively in good to excellent yields) various types of stannylated 1,4-dienes *via* the Lewis acid catalyzed allylstannylation of unactivated alkynes. The resulting stannylated 1,4-dienes are not easily available *via* the previously known methodologies and would be useful as building blocks in organic chemistry because of the widely existence of 1,4-dienes in naturally occurring compounds. For example, our methodology was used for the synthesis of H ring unit of Gambierol, which has a polycyclic ether skeleton including a triene side chain.[10] Formation of carbocation intermediates such as **7** (and aluminum analogue) followed by allyl transfer from the side opposite to Zr (or Al) can explain the regio- and stereoselectivity of the Lewis acid catalyzed allylstannylation reaction.

Experimental Section

General. All reactions are performed under Ar atmosphere in oven-dried glassware. Column chromatography was carried out employing Merck aluminum oxide 90 (activity II-III, basic) at 0 °C in a jacket column filled with ice water. Analytical thin layer chromatography (TLC) was performed on Merck 0.2 mm precoated silica gel plates (Kieselgel 60 F254). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-270 spectrometer at 270 and 60 MHz, respectively, in $CDCl_3$ using TMS as an internal standard. Infrared (IR) spectra were obtained as neat films between NaCl plates and were recorded on a SHIMAZU FTIR-8200A spectrometer. High resolution mass spectra were recorded on a JEOL HX110 spectrometer. As a rule, MS spectra of alkenyltributylstannane are characterized by the presence of an important peak (often the base peak) at M^+-57, which corresponds to the loss of a *n*-butyl fragment. The M^+ peak is, in almost every case, not detected. Toluene and the other solvents were used as stored in Schlenk flasks over molecular sieves 4A under an Ar atmosphere.

Procedure for the $ZrCl_4$ Catalyzed *trans*-Allylstannylation of Aromatic Alkynes. The preparation of **3a** is representative. $ZrCl_4$ (46 mg, 0.2 mmol) was added into the two necked flask (3 ml) under an Ar atmosphere, and cooled to -78°C, and toluene (1.0 ml) was added. The white suspension was stirred for 10 minutes, followed by the addition of phenylacetylene (**1a**: 0.11 ml, 1.0 mmol). After stirring for 5 minutes, the mixture became a red-violet tarry solution. Then, allyltributylstannane (0.620 ml, 2.0 mmol) was added, and the reaction mixture was allowed to warm to 0°C over 3 hours. The reaction mixture became a dark red tarry solution and red-brown precipitate was formed at about -10°C. The reaction mixture was stirred for another 10 minutes at 0°C. Excess amounts of satd. $NaHCO_3$ aq. solution (2 ml) were poured into the reaction mixture at 0°C. Pentane (100 ml) was added to the reaction mixture, and the mixture was washed 5 times with $NaHCO_3$ aq. (30 ml) and satd. brine (30 ml). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by basic alumina column chromatography at 0°C using a jacket column filled with ice water. Hexane was used as an effluent. (Z)-2-Phenyl-1-tributylstannyl-1,4-pentadiene (**3a**) was isolated as a colorless oil. Obtained: 360 mg, Yield: 83%.

On the other hand, when the reaction was quenched with Et_3N at 0°C and the product was purified by silica gel column chromatography, the corresponding protonolysis product, 2-phenyl-1,4-pentadiene (**4a**) was obtained in 52% yield.

Procedure for the $ZrCl_4$ Promoted *cis*-Allylstannylation of Aliphatic Alkynes. The preparation of **3g** and **5g** is representative. $ZrCl_4$ (233 mg, 1.0 mmol) was added into the two necked flask (3 ml) under an Ar atmosphere, and toluene (1.0 ml) was added. The white suspension was stirred for 1 hour at r.t., and then for 30 minutes at 0°C, followed by the addition of 1-octyne (**1g**: 0.148 ml, 1.0 mmol). To the resulting orange tarry solution was added allyltributylstannane (0.620 ml, 2.0 mmol). After stirring for 30 minutes at 0°C, the reaction mixture became a light brown tarry solution and orange precipitate was formed. Excess amounts of satd. $NaHCO_3$ aq. solution (2 ml) were poured into the reaction mixture at 0°C. Pentane (100 ml) was added, and the reaction mixture was washed 5 times with satd. $NaHCO_3$ aq. (30 ml) and satd. brine (30 ml). The organic phase was dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude product was purified by basic alumina column chromatography at 0°C using a jacket column filled with ice water. Hexane was used as an effluent. Stereoisomeric mixture of 2-Hexyl-1-tributylstannyl-1,4-pentadiene **3g** and **5g** was isolated as a colorless oil. Obtained: 300 mg, Yield: 68 %. The ratio was determined by NMR; **3g/5g=17/83**. The two stereoisomers could be completely separated by an additional purification by basic alumina column chromatography at 0°C.

Procedure for the $ZrCl_4$ Promoted *cis*-Allylstannylation of Acetylene. The preparation of **5l** is representative. The acetylene gas obtained in the cylinder was purified by passing it through a trap at -78°C. $ZrCl_4$ (233 mg, 1.0 mmol) was added into the two necked flask(3 ml) under acetylene gas atmosphere (**1l**). Toluene (1.0 ml) was added, and the yellow tarry solution was stirred for 1 hour at rt. and then for 30 minutes at 0°C. 1,5-Cyclooctadiene (0.125 ml, 1.0 mmol) was added, and an orange tarry solution was stirred for another 5 minutes. Allyltributylstannane (0.620 ml, 2.0 mmol) was added, and the reaction mixture was stirred at 0°C for 15 minutes to become a light brown tarry solution. Yellow precipitate was formed. Excess amounts of satd. $NaHCO_3$ aq. (2 ml) were poured into the reaction mixture at 0°C. Pentane (100 ml) was added, and the reaction mixture was washed 5 times with satd. $NaHCO_3$ aq. (30 ml) and satd. brine (30 ml). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by alumina column chromatography at 0°C using a jacket column filled with ice water. Hexane was used as an effluent. (Z)-1-Tributylstannyl-1,4-pentadiene (**5l**) was isolated as a colorless oil. Obtained: 360 mg, Yield: 55% based on allyltributylstannane.

Procedure for the $ZrCl_4$ Promoted *trans*-Allylstannylation of Aliphatic Alkynes under the Neat (No Solvent) Condition. The preparation of **3g** is representative. The mixture of $ZrCl_4$ (233 mg, 1.0 mmol) and 1-octyne (**1g**: 0.148 ml, 1.0 mmol) was stirred for 5 minutes at 0°C under Ar. To the resulting orange tarry mixture was added allyltributylstannane (0.620 ml, 2.0 mmol), and the reaction mixture was stirred at 0°C for 30 minutes. The reaction was quenched with excess amounts of satd. $NaHCO_3$ aq. solution (2 ml). Pentane

(100 ml) was added, and the reaction mixture was washed 5 times with satd. $NaHCO_3$ aq. (30 ml) and satd. brine (30 ml). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by basic alumina column chromatography at 0°C using a jacket column filled with ice water. Hexane was used as an effluent. 2-Hexyl-1-tributylstannyl-1,4-pentadiene **3g** was isolated as a colorless oil. Obtained: 226 mg, Yield: 51%.

Procedure for the $EtAlCl_2$ Catalyzed *trans*-Allylstannylation of Alkynes. The preparation of **3a** is representative. Toluene (2.0 ml) was added into the two necked flask (3 ml) under an Ar atmosphere, and cooled to -78°C, followed by the addition of $EtAlCl_2$ (0.11 ml of 1.8N in toluene, 0.2 mmol). Phenylacetylene (**1a**: 0.11 ml, 1.0 mmol) was added, and the reaction mixture became a orange solution. Allyltributylstannane (0.620 ml, 2.0 mmol) was added, and the reaction mixture was allowed to warm to 0°C over 3 hours. The reaction mixture became a yellow solution and orange precipitate was formed at about -10°C. The reaction mixture was stirred for another 10 minutes at 0°C. Excess amounts of satd. $NaHCO_3$ aq. solution (2 ml) were poured into the reaction mixture at 0°C. Pentane (100 ml) was added, and the reaction mixture was washed 5 times with $NaHCO_3$ aq. (30 ml) and satd. brine (30 ml). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by basic alumina column chromatography at 0°C using a jacket column filled with ice water. Hexane was used as an effluent. (Z)-2-Phenyl-1-tributylstannyl-1,4-pentadiene (**3a**) was isolated as a colorless oil. Obtained: 360 mg, Yield: 83%.

(Z)-2-Phenyl-1-tributylstannyl-1,4-pentadiene (3a). ^1H NMR δ 7.32-7.15 (m, 5H), 5.90 (s, $^2J_{119SnH}$ = 65.6 Hz, $^2J_{117SnH}$ = 62.3 Hz, 1H), 5.85 (ddt, J = 16.8, 10.4 and 6.9 Hz, 1H), 5.03 (d, J = 16.8 Hz, 1H), 5.02 (d, J = 10.4 Hz, 1H), 3.26 (d, J = 6.9 Hz, 2H), 1.32 (tt, J = 8.2 and 7.8 Hz, 6H), 1.19 (tq, J = 7.8 and 7.3 Hz, 6H), 0.83 (t, J = 7.3 Hz, 9H), 0.58 (t, J = 8.2 Hz, $^2J_{119SnH}$ = 61.9 Hz, $^2J_{117SnH}$ = 54.0 Hz, 6H). ^{13}C NMR δ 157.73, 145.53, 136.33, 128.09, 127.89, 127.49, 126.89, 115.89, 46.11, 29.09, 27.29, 13.66, 10.50. IR (neat) 3073, 2941, 2853, 1633, 1589, 1487, 1462, 911 cm^{-1}. MS(EI) m/z (relative intensity) 337 (100, M^+ - C_4H_9). HRMS(EI) m/z calcd for $C_{19}H_{29}Sn$ (M^+ - C_4H_9) 377.1291, found 377.1291. Anal. Calcd for $C_{23}H_{38}Sn$: C 63.75; H, 8.86. Found: C, 62.726; H, 8.434.

(Z)-2-*p*-Tolyl-1-tributylstannyl-1,4-pentadiene (3b). ^1H NMR δ 7.08 (s, 4H), 5.86 (s, $^2J_{119SnH}$ = 66.5 Hz, $^2J_{117SnH}$ = 63.3 Hz, 1H), 5.85 (ddt, J = 16.9, 10.4 and 6.8 Hz, 1H), 5.03 (d, J = 16.9 Hz, 1H), 5.01 (d, J = 10.4 Hz, 1H), 3.24 (d, J = 6.8 Hz, 2H), 2.33 (s, 3H), 1.32 (tt, J = 8.3 and 8.3 Hz, 6H), 1.19 (tq, J = 6.2 and 7.3 Hz, 6H), 0.83 (t, J = 7.3 Hz, 9H), 0.58 (t, J = 8.3 Hz, $^2J_{119SnH}$ = 54.0 Hz, $^2J_{117SnH}$ = 49.8 Hz, 6H). ^{13}C NMR δ 157.54, 142.56, 136.51, 128.52, 127.57, 127.28, 115.82, 46.02, 29.05, 27.30, 21.11, 13.66, 10.48. IR(neat) 3075, 2925, 2850, 1889, 1815, 1630, 1585, 1500, 1459, 825 cm^{-1}. MS(EI) m/z (relative intensity) 391 (100, M^+ - C_4H_9). HRMS(EI) m/z calcd for $C_{20}H_{31}Sn$ (M^+ - C_4H_9) 391.1448, found 391.1451. Anal. Calcd for $C_{23}H_{38}Sn$: C, 64.44; H, 9.03. Found: C, 64.952; H, 8.959.

(*Z*)-2-*p*-Chlorophenyl-1-tributylstannyl-1,4-pentadiene (3c). ^{1}H NMR δ 7.26 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.83 (s, $^2J_{119SnH}$ = 62.3 Hz, $^2J_{117SnH}$ = 60.2 Hz, 1H), 5.81 (ddt, *J* = 17.7, 6.3 and 6.9 Hz, 1H), 5.17 (d, *J* = 17.7 Hz, 1H), 5.17 (d, *J* = 9.3 Hz, 1H), 3.22 (d, *J* = 6.9 Hz, 2H), 1.32 (tt, *J* = 8.3 and 6.8 Hz, 6H), 1.20 (tq, *J* = 6.8 and 7.3 Hz, 6H), 0.84 (t, *J* = 7.3 Hz, 9H), 0.61 (t, *J* = 8.3 Hz, $^2J_{119SnH}$ = 53.0 Hz, $^2J_{117SnH}$ = 51.4 Hz, 6H). ^{13}C NMR δ 156.33, 143.85, 136.02, 132.76, 129.16, 128.87, 128.03, 116.21, 46.05, 29.05, 27.27, 13.64, 10.53. IR(neat) 3064, 2921, 2853, 1901, 1836, 1637, 1588, 1489, 1467, 843 cm^{-1}. MS(EI) m/z (relative intensity) 411 (100, M$^+$ - C_4H_9). HRMS(EI) m/z calcd for $C_{19}H_{28}SnCl$ (M$^+$ - C_4H_9) 411.0902, found 411.0899. Anal. Calcd for $C_{23}H_{37}SnCl$: C, 59.05; H, 7.99. Found: C, 59.234; H, 7.565.

(*Z*)-2-*p*-Methoxyphenyl-1-tributylstannyl-1,4-pentadiene (3d). ^{1}H NMR δ 7.13 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 5.85 (s, $^2J_{119SnH}$ = 66.5 Hz, $^2J_{117SnH}$ = 63.3 Hz, 1H), 5.84 (ddt, *J* = 16.8, 10.4 and 6.9 Hz, 1H), 5.03 (d, *J* = 16.8 Hz, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 3.81 (s, 3H), 3.24 (d, *J* = 7.0 Hz, 2H). 1.33 (tt, *J* = 7.3 and 7.3 Hz, 6H), 1.20 (tq, *J* = 7.3 and 8.3 Hz, 6H), 0.81 (t, *J* = 7.3 Hz, 9H), 0.60 (t, *J* = 8.3 Hz, $^2J_{119SnH}$ = 52.5 Hz, $^2J_{117SnH}$ = 49.8 Hz, 6H). ^{13}C NMR δ 158.68, 157.15, 138.02, 136.56, 128.51, 127.40, 115.18, 113.27, 55.21, 46.15, 29.07, 27.03, 13.66, 10.53. IR(neat) 3067, 2924, 2859, 1633, 1607, 1508, 1246, 834 cm^{-1}. MS(EI) m/z (relative intensity) 407 (100, M$^+$ - C_4H_9). HRMS(EI) m/z calcd for $C_{20}H_{31}SnO$ (M$^+$ - C_4H_9) 407.1397, found 407.1420. Anal. Calcd for $C_{24}H_{40}SnO$: C, 62.22; H, 8.72. Found: C, 60.158; H, 8.680.

(*Z*)-2-*p*-Cyclohexenyl-1-tributylstannyl-1,4-pentadiene (3e). ^{1}H NMR δ 5.79 (ddt, *J* = 17.1, 10.4 and 7.1 Hz, 1H), 5.53-5.47 (m, 1H), 5.45 (s, $^2J_{119SnH}$ = 74.3 Hz, $^2J_{117SnH}$ = 71.7 Hz, 1H), 5.01 (d, *J* = 17.1 Hz, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 2.96 (d, *J* = 7.1 Hz, 2H), 2.10-1.95 (m, 1H), 1.70-1.50 (m, 4H), 1.47 (tt, *J* = 8.3 and 7.3 Hz, 6H), 1.30 (tq, *J* = 7.3 and 7.3 Hz, 6H), 0.88 (t, *J* = 7.3 Hz, 9H), 0.82 (t, *J* = 8.3 Hz, 6H). ^{13}C NMR δ 160.51, 1142.80, 136.90, 123.65, 123.55, 115.16, 42.89, 29.36, 27.46, 25.28, 22.70, 22.09, 13.73, 10.77, 8.78. MS(EI) m/z (relative intensity) 407 (64, M$^+$ - C_4H_9), 291(100). HRMS(EI) m/z calcd for $C_{19}H_{33}Sn$ (M$^+$ - C_4H_9) 381.1604, found 381.1612. Anal. Calcd for $C_{23}H_{42}Sn$: C, 63.16; H, 9.70. Found: C, 61.005; H, 9.575.

(*E*)-2-Hexyl-1-tributylstannyl-1,4-pentadiene (3f). ^{1}H NMR δ 5.83 (ddt, *J* = 17.5, 9.5 and 7.0 Hz, 1H), 5.46 (s, $^2J_{119SnH}$ = 72.5 Hz, $^2J_{117SnH}$ = 69.8 Hz, 1H), 5.03 (d, *J* = 17.5 Hz, 1H), 5.03 (d, *J* = 9.5 Hz, 1H), 2.88 (d, *J* = 7.0 Hz, 2H), 2.02 (t, *J* = 7.9 Hz, 2H), 1.60-1.20 (m, 20H) 1.00-0.74 (m, 18H). ^{13}C NMR δ 157.37, 137.15, 122.97, 115.53, 43.24, 39.69, 31.93, 29.67, 29.33, 29.25, 27.42, 22.69, 14.12, 13.73, 10.23. MS(EI) m/z (relative intensity) 385 (100, M$^+$ - C_4H_9). HRMS(EI) m/z calcd for $C_{19}H_{37}Sn$ (M$^+$ - C_4H_9) 358.1917, found 385.1934. Anal. Calcd for $C_{23}H_{46}Sn$: C, 62.59; H, 10.53. Found: C, 62.196; H, 9.920.

(*E*)-2-Decyl-1-tributylstannyl-1,4-pentadiene (3g). ^{1}H NMR δ 5.82 (ddt, *J* = 15.0, 12.0 and 7.0 Hz, 1H), 5.46 (s, ${}^2J_{119SnH}$ = 174 Hz, ${}^2J_{117SnH}$ = 116 Hz, 1H), 5.02 (d, J = 15.0 Hz, 1H), 5.02 (d, J = 12.0 Hz, 1H), 2.88 (d, J = 7.0 Hz, 2H), 2.02 (t, J = 8.0 Hz, 2H), 1.62-0.74 (m, 46H). MS(EI) m/z (relative intensity) 441 (100, M^+ - C_4H_9). HRMS(EI) m/z calcd for $C_{23}H_{45}Sn$ (M^+ - C_4H_9) 441.2543, found 441.2592. Anal. Calcd for $C_{27}H_{54}Sn$: C, 65.19; H, 10.94. Found: C, 65.707; H, 10.286.

(Z)-2-Benzyl-1-tributylstannyl-1,4-pentadiene (3h). ${}^1H$ NMR δ 7.32-7.13 (m, 5H), 5.78 (ddt, J = 17.0, 10.2 and 7.0 Hz, 1H), 5.71 (s, ${}^2J_{119SnH}$ = 70.0 Hz, ${}^2J_{117SnH}$ = 67.0 Hz, 1H), 5.00 (d, J = 10.2 Hz, 1H), 4.94 (d, J = 17.0 Hz, 1H), 3.41 (s, 2H), 2.72 (d, J = 7.0 Hz, 2H), 1.60-1.20 (m, 12H), 1.02-0.78 (m, 15H),. ${}^{13}C$ NMR δ 155.01, 139.80, 136.84, 128.67, 128.30, 126.14, 126.08, 115.91, 45.00, 42.89, 29.21, 27.33, 13.68, 10.20.

(Z)-3-Methyl -2-phenyl -1-tributylstannyl-1,4-pentadiene (3l). ${}^1H$ NMR δ 7.26 (m, 3H), 7.12 (m, 3H), 5.91 (d, J = 1.0 Hz, 1H), 5.87 (m, 1H), 4.99 (m, 1H), 4.95 (m, 1H), 3.27 (m, 1H), 1.38-1.18 (m, 12H), 1.15 (d, J = 6.8 Hz, 3H), 0.83 (t, J = 6.6 Hz, 9H), 0.54 (m, 6H). MS(EI) m/z (relative intensity) 391 (100, M^+ - C_4H_9). HRMS(EI) m/z calcd for $C_{20}H_{31}Sn$ (M^+ - C_4H_9) 391.1422, found 391.1448. Anal. Calcd for $C_{24}H_{40}Sn$: C 64.45; H, 9.01. Found: C, 63.64; H, 8.67.

(Z)-4-Methyl -2-phenyl -1-tributylstannyl-1,4-pentadiene (3m). ${}^1H$ NMR δ 7.26 (m, 5H), 5.93 (s, ${}^2J_{119SnH}$ = 65.5 Hz, ${}^2J_{117SnH}$ = 62.5 Hz, 1H), 4.74 (s, 1H), 4.66 (s, 1H), 3.22 (s, 2H), 1.70 (s, 3H), 1.32 (tt, J = 8.0 and 7.0 Hz, 6H), 1.20 (tq, J = 7.0 and 7.0 Hz, 6H), 0.85 (t, J = 7.0 Hz, 9H), 0.60 (t, J = 8.0 Hz, ${}^2J_{119SnH}$ = 52.0 Hz, ${}^2J_{117SnH}$ = 50.0 Hz, 6H). ${}^{13}C$ NMR δ 157.14, 145.71, 143.57, 129.64, 128.00, 127.71, 127.14, 112.79, 50.79, 29.29, 27.29, 22.14, 13.57, 10.57. MS(EI) m/z (relative intensity) 391 (100, M^+ - C_4H_9). HRMS(EI) m/z calcd for $C_{20}H_{31}Sn$ (M^+ - C_4H_9) 391.1448, found 391.1458. Anal. Calcd for $C_{24}H_{40}Sn$: C, 64.44; H, 9.03. Found: C, 64.284; H, 8.994.

(Z)-2-Hexyl-1-tributylstannyl-1,4-pentadiene (5f). ${}^1H$ NMR δ 5.75 (ddt, J = 17.0, 10.0 and 6.5 Hz, 1H), 5.52 (s, ${}^2J_{119SnH}$ = 73.5 Hz, ${}^2J_{117SnH}$ = 65.8 Hz, 1H), 5.05 (d, J = 17.0 Hz, 1H), 5.01 (d, J = 10.0 Hz, 1H). 2.78 (d, J = 6.5 Hz, 2H), 2.11 (t, J = 7.5 Hz, 2H), 1.60-1.20 (m, 20H) 1.00-0.74 (m, 18H). ${}^{13}C$ NMR δ 157.14, 137.14, 122.71, 115.43, 43.57, 38.57, 31.93, 29.12, 28.93, 28.21, 27.29, 22.71, 14.29, 13.71, 10.14. MS(EI) m/z (relative intensity) 385 (100, M^+ - C_4H_9). HRMS(EI) m/z calcd for $C_{19}H_{37}Sn$ (M^+ - C_4H_9) 358.1917, found 385.1934. Anal. Calcd for $C_{23}H_{46}Sn$: C, 62.59; H, 10.53. Found: C, 62.196; H, 9.920.

(Z)-2-Decyl-1-tributylstannyl-1,4-pentadiene (5g). ${}^1H$ NMR δ 5.78 (m, 1H), 5.52 (s, 1H), 5.00 (m, 1H), 4.98 (m, 1H), 2.78 (d, J = 6.2 Hz, 2H), 2.11 (t, J = 7.1 Hz, 2H), 1.62-0.74 (m, 46H). IR(neat) 2957, 1599, 1464, 910 cm^{-1}. MS(EI) m/z (relative intensity) 441 (100, M^+ - C_4H_9). HRMS(EI) m/z calcd for $C_{23}H_{45}Sn$ (M^+ - C_4H_9) 441.2543, found 441.2557. Anal. Calcd for $C_{27}H_{54}Sn$: C, 65.19; H, 10.94. Found: C, 61.627; H, 10.394.

(*E*)-2-Benzyl-1-tributylstannyl-1,4-pentadiene (5h). ^{1}H NMR δ 7.32-7.12 (m, 5H), 5.76 (ddt, J = 16.6, 11.3 and 6.5 Hz, 1H), 5.60 (s, $^2J_{119SnH}$ = 71.0 Hz, $^2J_{117SnH}$ = 67.0 Hz, 1H), 5.05 (d, J = 11.3 Hz, 1H), 5.04 (d, J = 16.6 Hz, 1H), 3.46 (s, 2H), 2.71 (d, J = 6.5 Hz, 2H), 1.60-1.36 (m, 6H), 1.35-1.23 (m, 6H) 0.98-0.80 (m, 15H),. ^{13}C NMR δ 155.36, 140.00, 136.79, 129.14, 128.36, 126.71, 125.86, 116.07, 45.71, 42.86, 29.29, 27.50, 13.79, 10.43.

(*E*)-2-Cyclopentyl-1-tributylstannyl-1,4-pentadiene (5i). ^{1}H NMR δ 5.76 (ddt, J = 17.0, 10.0 and 6.5 Hz, 1H), 5.59 (s, $^2J_{119SnH}$ = 68.4 Hz, $^2J_{117SnH}$ = 66.0 Hz, 1H), 5.06 (d, J = 17.0 Hz, 1H), 5.00 (d, J = 10.0 Hz, 1H), 2.84 (d, J = 6.5 Hz, 2H), 2.49 (m, 1H), 1.85-1.20 (m, 20H), 0.88 (m, 15H),. ^{13}C NMR δ 160.36, 137.86, 120.00, 115.71, 47.50, 44.36, 32.43, 29.36, 27.43, 25.21, 13.93, 10.43. IR(neat) 3064, 2924, 2853, 1630, 1579, 1459, 902 cm^{-1}. MS(EI) m/z (relative intensity) 369 (100, M$^+$ - C_4H_9). HRMS(EI) m/z calcd for $C_{18}H_{33}Sn$ (M$^+$ - C_4H_9) 369.1604, found 369.1605. Anal. Calcd for $C_{22}H_{42}Sn$: C, 62.13; H, 9.97. Found: C, 59.741; H, 9.271.

(*Z*)-1-Tributylstannyl-1,4-pentadiene (5k). ^{1}H NMR δ 6.49 (dt, J = 12.5 and 7.3 Hz, $^3J_{119SnH}$ = 140.8 Hz, $^3J_{117SnH}$ = 137.6 Hz, 1H), 5.89 (d, J = 112.5 Hz, $^2J_{119SnH}$ = 70.6 Hz, $^2J_{117SnH}$ = 68.5 Hz, 1H), 5.82 (ddt, J = 17.1, 10.4 and 6.2 Hz, 1H), 5.05 (d, J = 17.1 Hz, 1H), 5.00 (d, J = 10.4 Hz, 1H), 2.80 (dd, J = 7.3 and 6.2 Hz, 2H), 1.50 (tt, J = 8.1 and 7.1 Hz, 6H), 1.19 (tq, J = 7.1 and 7.3 Hz, 6H), 0.91 (t, J = 8.1 Hz, 9H), 0.58 (t, J = 7.3 Hz, $^2J_{119SnH}$ = 51.9 Hz, $^2J_{117SnH}$ = 48.8 Hz, 6H). ^{13}C NMR δ 145.99, 136.85, 129.63, 115.13, 41.14, 29.30, 27.40, 13.74, 10.38. IR(neat) 3067, 2918, 2859, 1630, 1585, 1459, 911 cm^{-1}. MS(EI) m/z (relative intensity) 301 (100, M$^+$ - C_4H_9). HRMS(EI) m/z calcd for $C_{13}H_{25}Sn$ (M$^+$ - C_4H_9) 301.0978, found 301.0993. Anal. Calcd for $C_{17}H_{34}Sn$: C, 57.16; H, 9.61. Found: C, 57.81; H, 9.55.

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