Radical Hydrostannylation, Pd(0)-Catalyzed Hydrostannylation, Stannylcupration of Propargyl Alcohols and Enynols: Regio- and Stereoselectivities

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Received June 9, 1997[⊗]

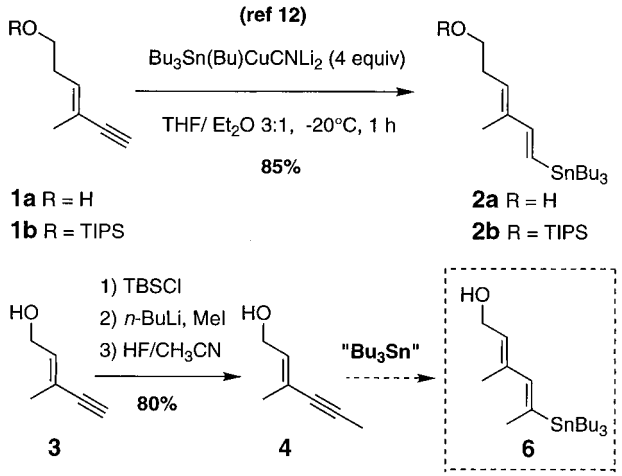
Different enynols and propargyl derivatives were sumitted to radical hydrostannylation (Bu_3SnH/AIBN), Pd(0)-catalyzed hydrostannylation [Bu_3SnH/Pd(0)], and stannylcupration [$Bu_3Sn(R)CuCNLi_2$] conditions. Except for the radical stannylation reaction, high regio- and stereoselective formation of vinyl- and dienylstannanes are obtained. Results are tentatively explained in terms of steric Interactions between the alkyne or enyne substituents and the palladium or cuprate moieties in the different reaction intermediates.

Introduction

In our project toward the total synthesis of natural products, we were interested in the construction of dienic or trienic systems *via* a stereospecific preparation of corresponding vinyl- or dienylstannanes. Stannyl derivatives can be engaged either in transmetalation, Sn−halogen exchange, or cross-coupling reactions,[1] and their importance in total synthesis is continually increasing. However the main problems encountered for the stannylation of alkynes or enynes are the regio- and stereocontrols of the addition of the stannyl residue to the triple bond function, depending on the type of reaction used.

The results we obtained during stannylation reactions of alkynes or enynes as well as the recent publications in this area [2] led us to report here some new observations. Different enynes and alkynes were submitted to radical hydrostannylation (Bu_3SnH/AIBN),[3] transition-metal catalyzed hydrostannylation [Bu_3SnH/Pd(0)][4,5] stannylcupration [$Bu_3Sn(R)CuCNLi_2$],[6−12] and the results are compared.

Scheme 1



Results

Hydroxylated Enynes. In the course of a synthetic approach to the western part of the antibiotic Tylosine,[12] both (*E*,*E*)-dienylstannanes **2a** and **2b** were obtained in 85% yield by stannylcupration of the corresponding enynes **1a** and **1b** (Scheme 1).

In a synthetic approach of another natural product, the methyl-substituted enyne **4** was prepared in 80% yield from commercially available enyne **3**, and stannylation of **4** was envisaged in order to obtain the corresponding dimethyldienylstannane **6** required for our synthesis; during this study reactivity of enyne **3** was also examined, and results are summarized in Table 1.

Radical hydrostannylation conditions were first employed. Treatment of **3** by Bu_3SnH (1.2 equiv)/AIBN (0.1 equiv) in toluene at 80 °C for 4 h led to a 80:20 mixture of dienylstannanes **5** and **5b**[8] in 75% yield (Table 1, entry

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

(1) Pereyre, M.; Quintard, J.-P.; Rahn, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.

(2) Ferri, F.; Alami, M. *Tetrahedron Lett.* **1996**, *37*, 7971. Alami, M.; Ferri, F. *Synlett* **1996**, 755.

(3) Corey, E. J.; Wollenberg, R. H. *J. Org. Chem.* **1975**, *40*, 2265. Jung, M. E.; Light, L. A. *Tetrahedron Lett.* **1982**, *23*, 3851.

(4) Ichinose, Y.; Oda, H.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3468. Kikukawa, K.; Umekawa, H.; Wada, F.; Matsuda, T. *Chem. Lett.* **1988**, 881. Zhang, H. X.; Cochran, J. C.; Bronk, B. S.; Terrence, K. M.; Phillips, H. K. *Tetrahedron Lett.* **1990**, *31*, 6621. Rossi, R.; Carpita, A.; Cossi, P. *Synth. Commun.* **1993**, *23*, 143. For *trans* hydrostannylation of alkynes, see also: Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 2405.

(5) (a) Zhang, H. X.; Guibé, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857. (b) Trost, B. M.; Li, C.-J. *Synthesis* **1994**, 1267. (c) For silastannylation see: Hada, M.; Tanaka, Y.; Ito, M.; Murakami, M.; Amii, H.; Ito, Y.; Nakatsuji, H. *J. Am. Chem. Soc.* **1994**, *116*, 8754.

(6) For stannylmetallation of alkynes, see: Barbero, A.; Cuadrado, P.; Fleming, I.; Gonzalez, A. M; Pulido, F. J. *J. Chem. Soc., Chem. Commun.* **1992**, 351. Cabezas, J. A.; Oehlschlager, A. C. *Synthesis* **1994**, 432. Hibino, J.-I.; Matsubara, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 2151. Barbero, A.; Cuadrado, P.; Fleming, I.; Gonzales, A. M.; Pulido, F. J.; Rubio, R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1657. Beaudet, I.; Launay, V.; Parrain, J.-L.; Quintard, J.-P. *Tetrahedron Lett.* **1995**, *36*, 389. See also: Lautens, M.; Huboux, A. H. *Tetrahedron Lett.* **1990**, *31*, 3105.

(7) For stannylcupration of enynes, see: Aksela, R.; Oehlschlager, A. C. *Tetrahedron* **1991**, *47*, 1163. For carbometallation of enynes, see: Uenishi, J.-I.; Kawahama, R.; Tanio, A.; Wakabayashi, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1438.

(8) Yokokawa, F.; Hamada, Y.; Shioiri, T. *Tetrahedron Lett.* **1993**, *34*, 6559.

(9) Piers, E.; Chong, J. M. *Can. J. Chem.* **1988**, *66*, 1425. Piers, E.; Morton, H. E.; Chong, J. M. *Can. J. Chem.* **1987**, *65*, 78. Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron Lett.* **1981**, *22*, 4905. Piers, E.; Morton, H. E. *J. Org. Chem.* **1980**, *45*, 4263. See also: Barrett, A. G. M.; Edmunds, J. J.; Hendrix, J. A.; Horita, K.; Parkinson, C. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1238.

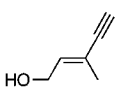
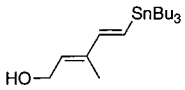
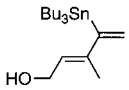
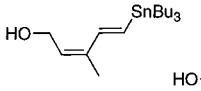
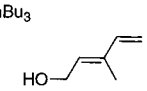
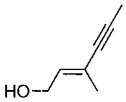
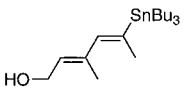
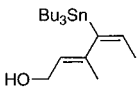
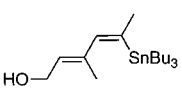
(10) Cummins, C. H.; Gordon, E. J. *Tetrahedron Lett.* **1994**, *35*, 8133.

(11) Singer R. D.; Hutzinger, M. W.; Oehlschlager, A. C. *J. Org. Chem.* **1991**, *56*, 4933.

(12) Fargeas, V.; Le Ménez, P.; Berque, I.; Ardisson, J.; Pancrazi, A. *Tetrahedron* **1996**, *52*, 6613. Le Ménez, P.; Fargeas, V.; Berque, I.; Poisson, J.; Ardisson, J.; Lallemand, J.-Y.; Pancrazi, A. *J. Org. Chem.* **1995**, *60*, 3592.

S0022-3263(97)01033-5 CCC: $14.00

Table 1. Stannylation Reactions of (*E*)-Enynols 3 and 4

Entry	Method Conditions [a]	Enynol	Yield (%) [b]	Dienylstannanes, ratio			
							
		3		5	5a	5b	5c
1	A		75	80	/	20	/
2	B		>99	60	/	/	40
3	C C_1) -30 °C, 1.5 h		92	100	/	/	/
4	C_3) -78 °C, 1.5 h		92	89	11	/	/
5	C_4) -78 °C, 1.5 h		78	67	33	/	/
							
		4		6	6a	6b	
6	A		20	70	/	30	
7	B		92	/	100	/	
8	C C_1) -10 °C, 12 h		44 [c]	95	/	5	
9	C_2) -10 °C, 12 h		62 [c]	95	/	5	
10	C_4) -10 °C, 12 h		72	100	/	/	

[a] Method **A**: 1.2 equiv Bu_3SnH/0.1 equiv AIBN, toluene, 80 °C. Method **B**: 1.2 equiv Bu_3SnH/0.02 equiv $PdCl_2(PPh_3)_2$, THF, 20°C. Method **C**: Conditions C_1) 2 equiv $Bu_3Sn(Bu)CuCNLi_2$, THF. Conditions C_2) 4 equiv $Bu_3Sn(Me)CuCNLi_2$, THF. Conditions C_3) 2 equiv $(Bu_3Sn)_2CuCNLi_2$, THF. Conditions C_4) 2 equiv $(Bu_3Sn)_2CuCNLi_2$, THF, MeOH (110 equiv).
[b] Yields are given after purification on basic silica gel.
[c] This reaction was not reproducible.

1). Under these conditions, partial isomerization of the double bond of **5** into **5b** is observed.

Pd(0)-catalyzed hydrostannylation of **3** using Bu_3SnH (1.2 equiv)/$PdCl_2(PPh_3)_2$ (0.02 equiv) in THF at 20 °C for 10 min gave the distal dienylstannane **5** and the diene derivative **5c**[13] in quantitative yield and a 60:40 ratio (Table 1, entry 2).

Stannylcupration of **3** using 2 equiv of the mixed cyanocuprate $Bu_3Sn(Bu)CuCNLi_2$[7,14] in THF/Et_2O at −30 °C for 1 h afforded the (*E*,*E*)-dienylstannane **5** as a single isomer in excellent yield (Table 1, entry 3, 92%). When stannylcupration of **3** was performed in THF at −78 °C, reaction of the same homocuprate took place in 92% yield to furnish the two regioisomeric dienylstannanes **5** and **5a** in a 89:11 ratio (Table 1, entry 4). Addition of methanol to the cuprate solution, under the previous conditions (−78 °C), resulted in a 67:33 mixture of the distal and proximal stannanes **5** and **5a** (Table 1, entry 5, 78% yield).[15] These experiments led us to postulate that the proximal isomer **5a** was the kinetic product in this stannylcupration reaction.

When the homologous enyne **4** was treated with Bu_3SnH/AIBN (80 °C, 12 h), reaction delivered a 70:30 mixture of the two expected stereomeric (*E*) and (*Z*) dienylstannanes **6** and **6b** in a modest 20% yield. Hydrostannylation of **4** under Pd(0)-catalyzed conditions produced the proximal stannyl derivative **6a** as a pure regio- and stereomer in 92% yield (Table 1, entry 7).[16]

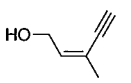
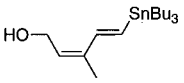
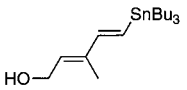
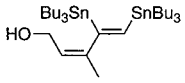
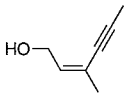
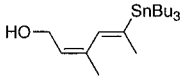
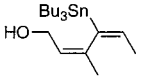
Stannylcupration of the methyl substituted enyne **4** was first attempted using $Bu_3Sn(Bu)CuCNLi_2$[17,18] in THF at a temperature ranging from −40 °C to −20 °C but no reaction occurred after 2 or 4 h. However, when the reaction with the previous cuprate or with $Bu_3Sn(Me)$-$CuCNLi_2$ was run at −10 °C for 12 h, dienylstannanes **6** and **6b** were obtained in 44% and 62% yield, respectively (Table 1, entries 8, 9, **6/6b** = 95:5).[18] Unfortunately these reactions were not reproducible, even after a careful check of all the reagents. Gratifyingly, when a large excess of methanol, used as a proton source,[9−11] was added to the homocuprate solution [$(Bu_3Sn)_2CuCNLi_2$, THF/MeOH 2:1, −10 °C, 12 h],[15] stannylcupration gave the pure (*E*,*E*)-dienylstannane **6** (distal isomer) that was required for the synthesis in 72% yield (Table 1, entry 10). This reaction was reproducible and proceeded in 77% yield on a 20 mmol scale.

The use of (*Z*)-enynes **7** and **8**, instead of (*E*)-enynes **3** and **4**, interestingly gave comparable results (Table 2). Radical hydrostannylation of **7** occurred in poor yield (19%) to give the dienylstannanes **5** and **5c** in a 32:68 ratio. Once again isomerization of the double bond was observed, and the (*E*)-isomer **5** was isolated in consequent amount (Table 2, entry 1). Palladium-catalyzed hydrostannylation of **7** provided a 12:88 mixture of the distal and proximal stannanes **5c** and **9a** in 54% yield (Table 2, entry 2). When stannylcupration of **7** was performed with the homocuprate using methanol as a cosolvent, the distal tin derivative **5c** was obtained in 76% yield as a single isomer (Table 2, entry 4).

Surprisingly the same stannylcupration, tested without methanol, gave a better yield (84%), and the bis-stannyl

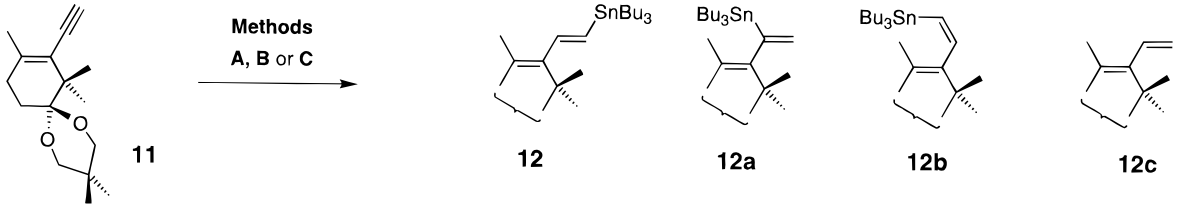
(13) Margot, C.; Rizzolio, M.; Schlosser, M. *Tetrahedron* **1990**, *46*, 2411.
(14) For preparation of Bu_3SnLi see: Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836.
(15) Betzer, J.-F.; Ardisson, J.; Lallemand, J.-Y.; Pancrazi, A. *Tetrahedron Lett.* **1997**, *38*, 2279.
(16) In all cases stereochemistry of vinyl- and dienylstannanes were deduced from ^1H NMR and ^{13}C NMR spectra analysis based on chemical shifts, $^1H-^1H$, $^1H-^{117,119}Sn$, and $^{13}C-^{117,119}Sn$ coupling constants. See: Ardisson, J.; Férézou, J.−P.; Li, Y.; Liu, L. W.; Pancrazi, A. *Bull. Soc. Chim. Fr.* **1992**, *129*, 401.
(17) Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 2065. Behling, J. R.; Babiak, K. A.; Ng, J. S.; Campbell, A. L.; Moretti, R.; Koerner, M.; Lipshutz, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 2641.
(18) Lipshutz, B. H.; Kozlowski, J. A.; Wilhelm, R. S. *J. Org. Chem.* **1984**, *49*, 3943.

Table 2. Stannylation Reactions of (*Z*)-Enynols 7 and 8

Entry	Method Conditions [a]	Enynol	Yield (%) [b]	Dienylstannanes, ratio				
								
		7		5b	9a	5	9b	
1	A		**19**	68	/	32	/	
2	B		**54**	12	88	/	/	
3	C C_3) -30 °C, 1.5 h		**84**	96	/	/	4	
4	C_4) -30 °C, 1.5 h		**76**	100	/	/	/	
								
		8			10	10a		
5	B		**62**		/	100		
6	C C_3) -10 °C, 12 h		**<5**		95	5		
7	C_4) -10 °C, 12 h		**64**		100	/		

[a] See Table I. [b] Yields are given after purification on basic silica gel.

Scheme 2



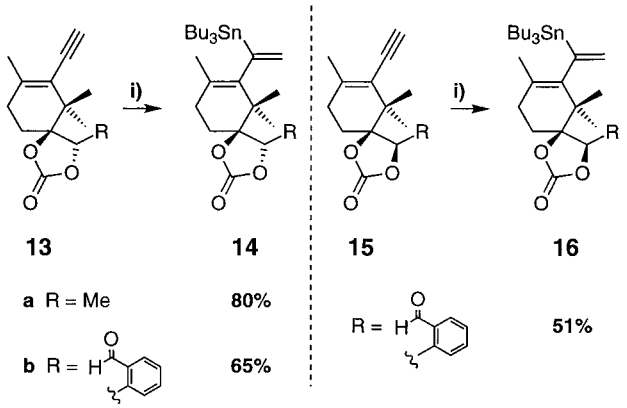
method A. (80°C, 4 h)	**50%**	100	/	/	/
method B.	**75%**	/	30	/	70
method C. (conditions C_1, 25°C, 0.5 h)	**76%**	/	70	/	30

derivative **9b** was detected together with the major **5c** isomer (Table 2, entry 3, **5c/9b** = 96:4). It should be noted that for (*E*)-enyne **3** no corresponding bis-stannane was observed.

Radical hydrostannylation of homologous (*Z*)-enyne **8** gave only traces of tin adducts. In counterpart, Pd(0)-catalyzed reaction led in this case to the exclusive formation of the proximal dienylstannane **10a** in 62% yield (Table 2, entry 5). As with (*E*)-enyne **4**, stannylcupration of (*Z*)-enyne **8** with the homocuprate in the presence of methanol led to the exclusive distal regioisomer **10** in 64% yield, whereas this reaction did not proceed without addition of methanol (Table 2, entries 6 and 7).

Hindered Enynes. For a synthetic approach of Taxol,[19,20] we were interested in the preparation of dienylstannanes **12** and **12a** (Scheme 2). Starting from **11**, vinylstannane **12** was prepared as a single stereomer[21] *via* the radical pathway in 50% yield. When hydrostannylation was performed in presence of Pd(0), the proximal tin derivative **12a** was obtained together with diene **12c** in 75% yield and a 30:70 ratio. As another surprising result, stannylcupration of **11** [$Bu_3Sn(Bu)CuCNLi_2$, THF, −25 °C, 30 min] did not lead to the expected dienylstannanes **12** and **12b** but to a 70:30 mixture of **12a** and **12c** in 76% yield.

Scheme 3



i) Method B: Bu_3SnH /$PdCl_2(PPh_3)_2$

From the analogous enynes **13a,b** and **15** (Scheme 3), Pd(0)-catalyzed hydrostannylation also gave proximal stannyldienes **14a,b** and **16** as the only products respectively.[22] It should be emphasized that in the case of **13a** (R = Me) dienylstannane **14a** was obtained in 80% yield.

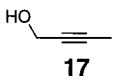
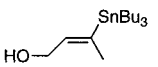
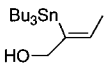
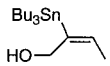
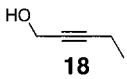
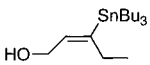
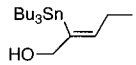
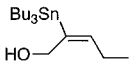
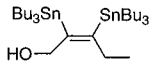
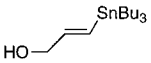
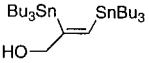
(19) Delaloge, F.; Prunet, J.; Pancrazi, A.; Lallemand, J.-Y. *Tetrahedron Lett.* **1997**, *38*, 237.

(20) Unpublished results. Delaloge, F. Thèse, Ecole Polytechnique, Palaiseau, France, 1995.

(21) If old tin hydride is used, ratios of **12**/**12a** ranging from 55:45 to 100:0 are obtained.

(22) Unpublished results. Muller, B. Thèse, Ecole Polytechnique, Palaiseau, France, 1996.

Table 3. Stannylation Reactions of Propargylic Derivatives 17−19

Entry	Method Conditions [a]	Propargyl	Yield (%) [b]	Vinylstannanes, ratio		
		 **17**		 **20**	 **20a**	 **20b**
1	**A**		**64**	/	70	30
2	**B**		**58**	25	/	75
3	**C** C_1) -10 °C, 12 h		**42**	/	100	/
4	C_1) (THF/MeOH) -10 °C, 12 h		**71**	100	/	/
5	C_2) -10 °C, 12 h		**54**	65	35	/
6	C_2) (THF/MeOH) -10 °C, 12 h		**65**	100	/	/
7	C_3) -10 °C, 12 h		**82**	30	70	/
8	C_4) (THF/MeOH) -10 °C, 12 h		**70**	100	/	/
		 **18**		 **21**	 **21a**	 **21b**	 **21c**
9	C_3) -10 °C, 12 h		**50**	26	40	22	12
10	C_4) (THF/MeOH) -10 °C, 12 h		**71**	100	/	/	/
		 **19**		 **22**	 **22a**	 **22c**
11	C_3) -25 °C, 0.5 h		**62**	66	10	24
12	C_4) (THF/MeOH)-40 to -30 °C, 0.5h		**80**	65	35	/

[a] See Table I. [b] Yields are given after purification on basic silica gel.

Propargyl Derivatives. In order to examine the selectivity of these stannylation reactions, we considered the propargyl derivatives **17**−**19**. Under radical conditions, starting from **17**, reaction took place in 64% yield leading to a 70:30 mixture of the isomeric vinylstannanes **20a (*Z*)** and **20b (*E*)** (Table 3, entry 1).[23]

Concerning the hydrostannylation reaction in the presence of Pd(0), two regioisomers **20** and **20b (*E*)** were obtained in fair yield (58%) and a 25:75 ratio (Table 3, entry 2).

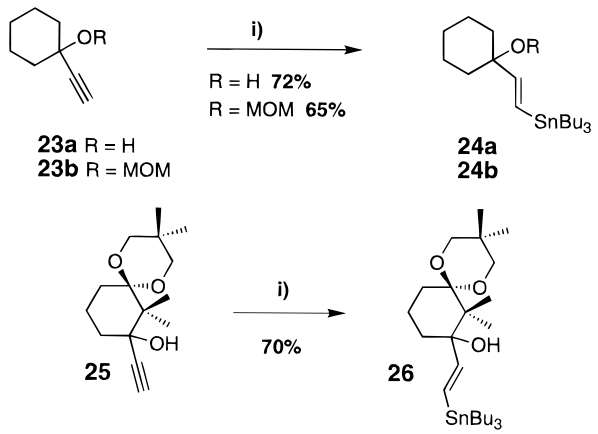
Stannylcupration of **17** gave some surprising results. Using the mixed cuprate $Bu_3Sn(Bu)CuCNLi_2$ under "classic thermodynamic conditions" (4 equiv of cuprate, THF, −10 °C, 12 h) the pure (*Z*) proximal vinylstannane **20a** was obtained in 42% yield. However, treatment of **17** with $Bu_3Sn(Me)CuCNLi_2$ under the same conditions led to a 65:35 mixture of the two regioisomers **20** and **20a** (54%). This reaction also proceeded in the presence of homocuprate $(Bu_3Sn)_2CuCNLi_2$ (4 equiv of cuprate, THF, −10 °C, 12 h) to deliver the two vinylstannanes **20** and **20a** in 82% yield and a 30:70 ratio (Table 3, entries 3, 5, 7). When this stannylcupration was performed using a proton source such as methanol (110 equiv), the only regio- and stereospecific isomer vinylstannane **20** was obtained in good yield,[18] regardless of the nature of the cuprate (Table 3, entries 4, 6, 8).

Stannylcupration reactions of the ethyl-substituted propargylic alcohol **18** (Table 3) gave comparable results with those obtained with the methyl analog **17** except that in the case of reaction was performed without methanol [2 equiv of $(Bu_3Sn)_2CuCNLi_2$, THF, −10 °C, 12 h]: the regio- and stereomers **21**, **21a** and **21b**,[24] were obtained together with bis-tributylstannane **21c** in a 26:40:22:12 ratio (Table 3, entry 9, 50% yield). In presence of methanol this stannylcupration gave the pure distal (*E*)-dienylstannane **21** in 71% yield (Table 3, entry 10).

Stannylcupration of the propargyl alcohol **19** has been described by Lipshutz with the mixed cyanocuprate $Bu_3Sn(Bu)CuCNLi_2$[25] to give the two regioisomeric vinylstannanes **22** and **22a**[3] in a 80:20 mixture. Under stannylcupration conditions using 2 equiv of the homocuprate in THF/MeOH, we isolated the two regioisomers **22** and **22a** in 80% yield as a 65:35 mixture (Table 3, entry 12). Here again, when this reaction was performed with the homocuprate without methanol, the bis-stannane derivative **22c** was obtained together with **22** and **22a** (Table 3, entry 11, 62%, **22/22a/22c** = 66:10:24).

As Scheme 4 illustrates, in the last two examples, Pd(0)-catalyzed hydrostannylation reactions of propargylic alcohol **23**[26] (R = H or MOM) and **25** gave in all

Scheme 4



i) **Method B:** $Bu_3SnH/PdCl_2(PPh_3)_2$

(23) Miyake, H.; Yamamura, K. *Chem. Lett.* **1989**, 981.
(24) Piers, E.; Chong, J. M.; Gustafson, K.; Andersen, R. J. *Can. J. Chem.* **1984**, *62*, 1.
(25) Lipshutz, B. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 4617.

cases the pure distal (*E*)-stannyl compounds **24** and **26** in good yields (65 to 72%).[19]

Discussion

Radical Hydrostannylation. The radical hydrostannylation reaction ($Bu_3SnH/AIBN/\Delta$) proceeds in the first step *via* a *trans* addition giving the kinetic product. The thermodynamic derivative is further obtained after addition−elimination processes.[3] Starting from terminal alkynes and enynes, this hydrostannylation runs in good yield; however, regio- and stereoselectivities are fair, but never excellent. Moreover partial (**5b** from **3** and **5** from **7**, Tables 1 and 2), or complete [27] isomerization of the double bond of the enyne could be observed. When substituted triple bonds are submitted to these conditions, yields drop in most cases.

Depending on the structure of the starting alkynes or enynes, regio- and stereoselectivities could not be anticipated under radical conditions. This reaction is now less employed as a synthetic tool for the stannylation of alkyne or enyne functions but remains an efficient solution for radical cyclizations.

Pd(0)-Catalyzed Hydrostannylation. In the case of the Pd(0)-catalyzed hydrostannylation reactions,[5b] the first step was assumed to be a *cis* addition.[5] These reactions seem to be under kinetic control, the ratio of isolated isomeric vinyl- or dienylstannanes reflecting the kinetic formation of the two regioisomeric intermediate palladium complexes.

(a) Considering the results obtained by Guibé *et al* in the Pd(0)-catalyzed hydrostannylation of propargyl,[5a] some explanation can be proposed (Scheme 5). When the alkyne function is not substituted on the α position, the proximal stannylated derivative is obtained as the major isomer whereas formation of the distal regioisomer increases when the α position is substituted, even when the alkyne function bears a substituent at C2.[28]

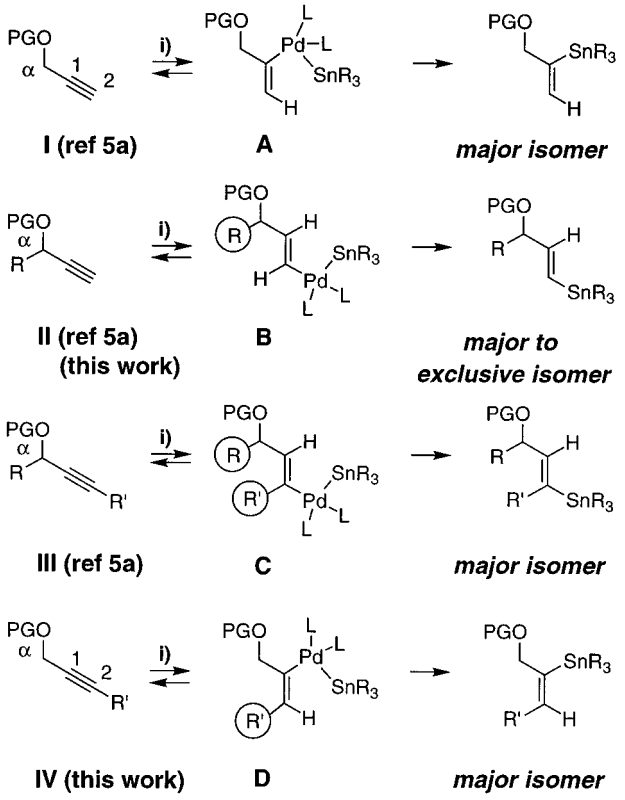
In cases **II** and **III** steric effects interfere: in intermediates **B** and **C** the palladium residue adopts the distal position to minimize the interaction between palladium and the R substituent; the distal stannane was thus obtained as the major isomer even when an additional R′ substituent was attached to the C2 position. The same results were observed in our examples (**23a,b** → **24a,b**, **25** → **26**), where the α carbon is a quaternary center.

In the case of a methyl-substituted alkyne **IV** with a R′ group attached at the C2 position and no R substituent at the α position, reaction leads to the intermediate complex **D**, and the proximal stannylated derivative is obtained as the major isomer (**17** → **major 20b**).

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.

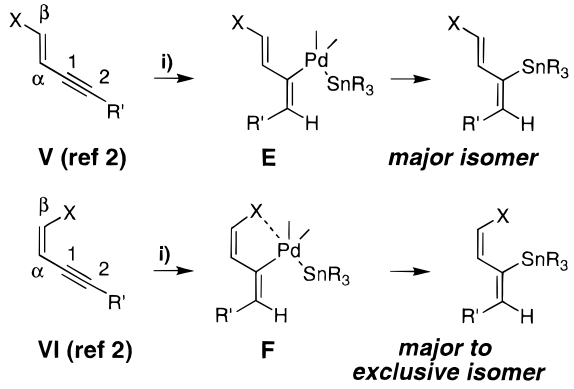
Addition of a R substituent to the α position leads to an inverse situation and the distal isomer is obtained as the major or even sole product.

Scheme 5



i) Method B: $Bu_3SnH/Pd(0)$

Scheme 6



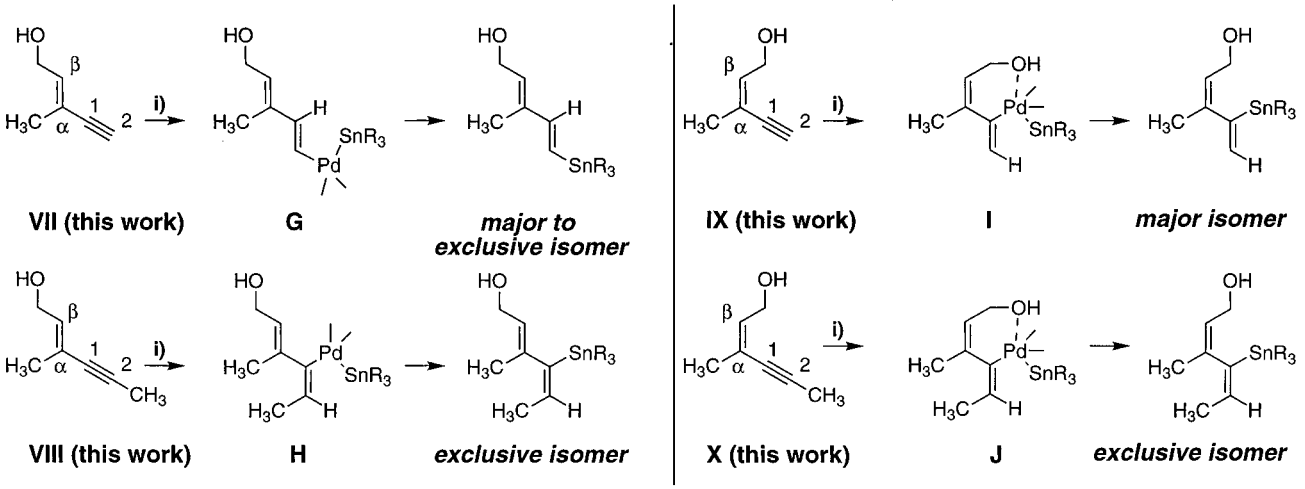
i) Method B: $Bu_3SnH/Pd(0)$

(b) For enyne derivatives, as observed by Alami[2] and Oehlschlager,[7] when the (*E*)-enyne **V** is engaged in a Pd(0)-catalyzed stannylation reaction, the proximal stannane is obtained as the major product, *via* the preferential **E** intermediate, together with some amount of the distal isomer (Scheme 6). In the case of the (*Z*)-enyne **VI** (enediyne or chloroenyne) an additional stabilizing effect could occur to gave the exclusive formation of the proximal tin derivative *via* complex **F**.

In our study on the α-substituted (*E*)-enyne **VII** (Scheme 7), the presence of the R substituent on the double bond induces the formation of the distal stannane *via* the less crowded Pd(0) complex **G** where no stabilizing effect can occur (**3** → **major 5**). On the contrary the proximal dienylstannane is exclusively delivered *via* **H** for methyl-substituted (*E*)-enyne **VIII** (**4** → **6b**). In this

(26) Carlson, R. G.; Cox, W. W. *J. Org. Chem.* **1977**, *42*, 2382.
(27) Smith, A. B., III.; Maleczka, R. E., Jr.; Leazer, J. L., Jr.; Leahy, J. W.; McCauley, J. A.; Condon, S. M. *Tetrahedron Lett.* **1994**, *35*, 4911.
(28) A secondary effect was observed in this reaction: for example reaction of propargyl alcohol **I** (PG = H) led to a 55:45 ratio of proximal/distal tin derivative and a 91:9 ratio when the hydroxyl function was protected (PG = Ph). A stabilizing complex **A** between palladium and the alcohol substituent could be involved to explain this observed regioselectivity.

Scheme 7



case, the relative importance of the methyl group *versus* the R substituent is not clear, and the stannyl residue adds to the internal position.

When (*Z*)-enynes bear an hydroxyl function, a stabilization of the intermediate palladium complex can take place and account for the formation of the major proximal dienylstannane *via* **I** or **J** complexes in regard to the result obtained with the (*E*)-enyne(**7** → **9a**, **8** → **10a**).

Nevertheless, (*Z*)-enyne **IX** protected as a TBS ether also delivers the proximal tin derivative as the exclusive isomer.[29] This result implies that the Pd atom could be stabilized either by an hydroxyl function or a OTBS group.

In the specific case of enynes **11**, **13a,b**, and **15**, formation of the corresponding proximal dienylstannanes could be explained by a stabilizing complexation of the palladium with one of the oxygen atoms present in the ketal function.

As a last remark, in the Pd(0)-catalyzed stannylation of some enynes, secondary reduction leading to the formation of diene is observed (**3** → **5d** and **11** → **12c**). To our knowledge, this side reaction has never been reported and at this time no explanation could be given.

Stannylcupration. As stannylcupration reactions are concerned, many more factors have to be considered: *cis* addition of the cyanocuprate gives in a first step the two regioisomeric intermediates $\mathbf{A_1}$ and $\mathbf{A_2}$ leading after hydrolysis of the cuprate residue to the proximal and distal tin derivatives **K** and **T** (Scheme 8). In some cases, products $\mathbf{E_{pr}}$ and $\mathbf{E_d}$ resulting from the intermediate formation of "equilibrated" *proximal* and/or *distal* $\mathbf{B_1}$ and $\mathbf{B_2}$ could be observed.

As postulated by Oehlschlager,[11] hydrolysis of the cuprate intermediates $\mathbf{A_1}$ and $\mathbf{A_2}$ starts with a protonation of the double bond function. Elimination of the cuprate moiety involves rotation around the C−C bond in order to position the C−"Cu" bond in the plan of the empty Π orbital. This situation was obtained with a specific rotation, indicated in Scheme 8, which avoids interaction between the "Cu" and the "Sn" residues, and the reaction led to the formation of the "kinetic" **K** and "thermodynamic " **T** tin derivatives. This kind of intermediate was obtained when the stannylcupration reaction was performed in the presence of methanol (conditions $\mathbf{C_4}$).

When the stannylcupration reaction was run under "thermodynamic" conditions, without addition of methanol, it is reasonable to postulate that the stannylcuprate adds to the intermediate cuprates $\mathbf{A_1}$ and $\mathbf{A_2}$ *via* an equilibrated *cis*-addition process leading to bimetallic species. A *cis* elimination of the stannylcuprate then gave the "equilibrated" intermediates $\mathbf{B_1}$ and $\mathbf{B_2}$, and to the stannyl compounds $\mathbf{E_{pr}}$ and $\mathbf{E_d}$ after hydrolysis.

This proposed mechanism could account to the different results obtained during stannylcupration reactions of propargyl and enynols derivatives in presence or absence of methanol.[30]

For simple terminal alkynes, stannylcupration proceeded at −40 °C to −50 °C and the kinetic intermediate, according to Oehlschlager,[11] was proved to be the internal product, which is designed in this work as *proximal stannyl intermediate* $\mathbf{A_1}$. At higher temperature, equilibration led to increased formation of the *distal stannyl intermediate* $\mathbf{A_2}$. After hydrolysis, these two intermediates gave the corresponding *kinetic proximal* **K** and *distal thermodynamic* **T** tin derivatives.

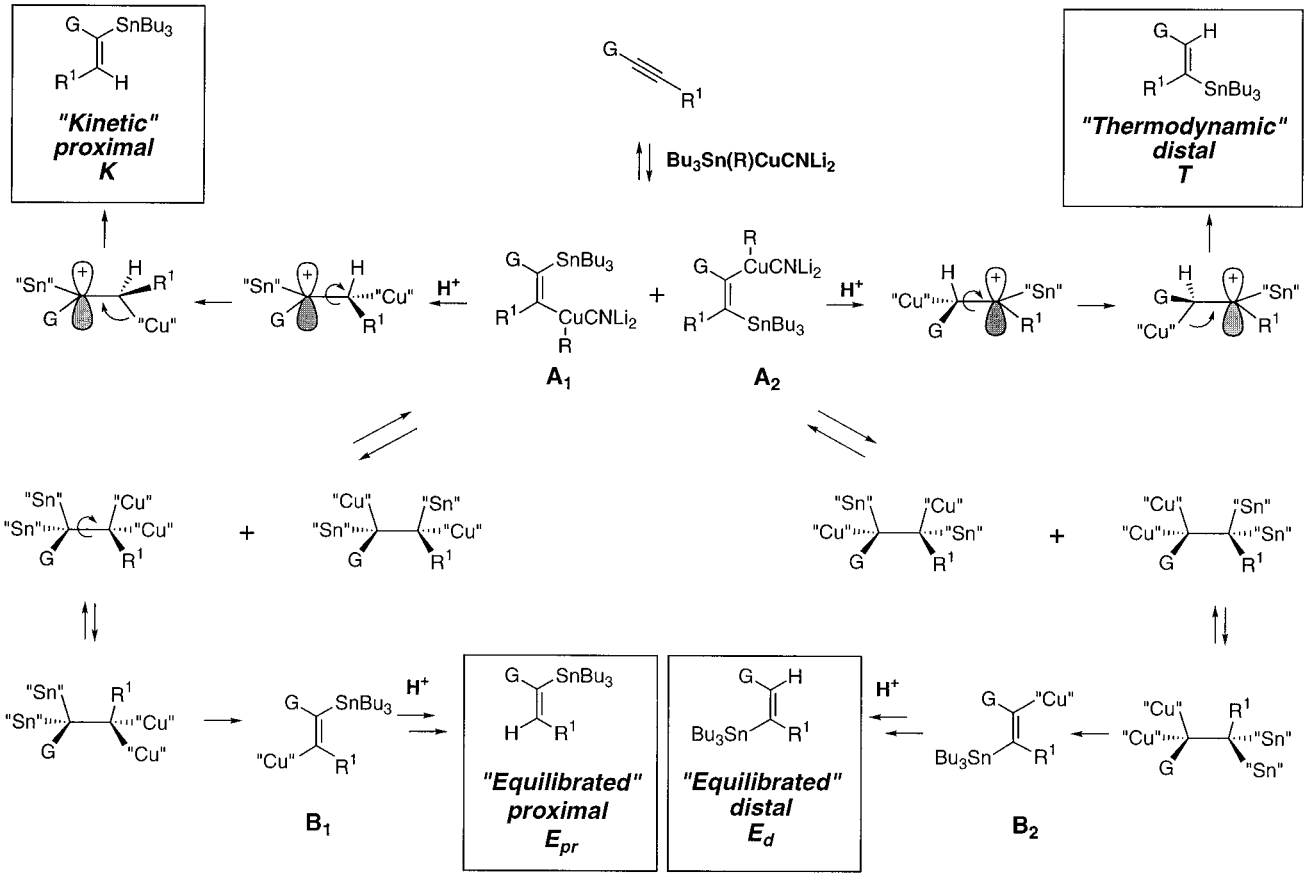
For terminal enynes, stannylcupration took place at −78 °C leading also to the formation of a *kinetic proximal* tin derivative **K** (see, Table 1, formation of **5b** at −78 °C), in most cases, and between −40 °C and −10 °C, the *distal thermodynamic* tin isomer **T** was obtained as the major or exclusive product.

For substituted enynes, stannylcupration reactions must be performed at a temperature ranging from −10 °C to 0 °C. Under these conditions a small amount of the *"equilibrated" distal* derivative $\mathbf{E_d}$ was obtained (formation of **6a** < 5%, Table 1), but degradation could also occur. Nevertheless this reaction proceeded in good

(29) When (*Z*)-enynol **IX** was protected as a TBS ether, Pd(0)-catalyzed hydrostannylation gave also the pure proximal corresponding dienylstannane in 54% yield (45% starting material recovered). Surprisingly enynol (*E*)-**VII** also protected as a TBS derivative gave the proximal isomer in only 14% yield and the (*E*)-3-methyl-[(*tert*-butyldimethylsilyl)oxy]-2,4-pentadiene in 56% yield as well.

(30) Stannylcuprations of the propargyl alcohol **19** were performed under the same conditions as described in Table 3 using in each case an addition of Bu_3SnCl to the cuprate solution. When the reaction was run in presence of methanol, less than 1% of the distannyl deivative **22c** was obtained whereas without methanol, **22c** was isolated in 61% yield.

Scheme 8



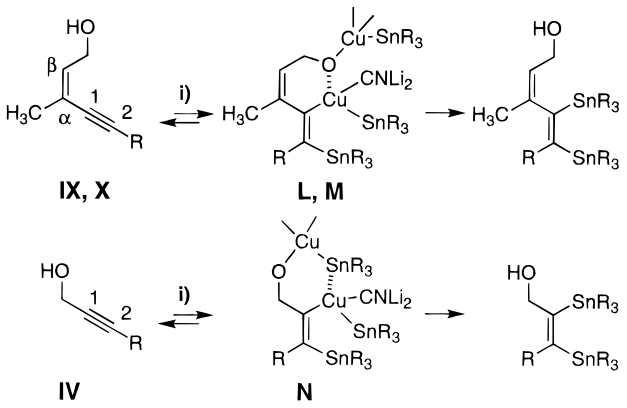
yield when methanol was added to the cuprate solution.[9−11,18] Then all the reactions with enynes or alkynes delivered the *exclusive thermodynamic distal* tin derivatives **T** in good yields.

It clearly appears that methanol is efficient to trap the intermediate cuprate adduct A_1 *and* A_2 *leading to the kinetic proximal and thermodynamic (E)-stannyl derivatives* ***K*** *and* ***T****. We also think that methanol did not allow formation of the "equilibrated" proximal or distal isomers* E_{pr} *and* E_d *from* B_1 *and* B_2.

Table 3 gives a characteristic example where the "equilibrated" proximal tin isomer ***20a*** *was obtained after stannyl cupration of* ***17*** *without addition of methanol, whereas the thermodynamic distal isomer* ***20*** *was obtained in all cases as the only derivative in presence of methanol in the cuprate solution.*

A secondary effect was observed in this work: formation of bis-stannyl derivatives when reaction was carried out without methanol.[31] We postulate in this particular case that the intermediate cuprate is partially ligated by the allylic hydroxyl function (Scheme 9). This complex could undergo a reductive elimination[32] to deliver a *cis*-bis-stannyl product, if the cuprate is acting as a transition metal derivative.[33] In the presence of methanol the cuprate could not be ligated by the hydroxyl function, and this reductive elimination did not occur.

Scheme 9



i) Method C (conditions C_3): $(Bu_3Sn)_2CuCNLi_2$, THF

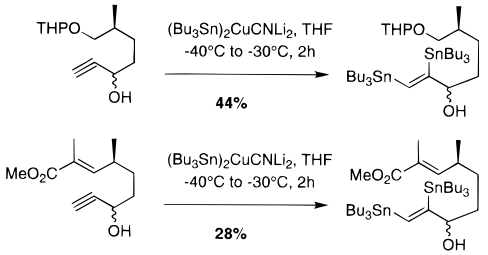
Conclusion

The analysis of the various results from the literature and our laboratory allows us to draw some conclusions

(31) *cis*-Bis-vinylstannanes were also obtained *via* other methods by Oehlschlager, A. C (ref 11) and Piers, E.; Tillyer R. D. *Can. J. Chem.* **1996**, *74*, 2048. These latter authors in the same paper, as well as Lambert, M.-P.; Ratier, M.; Duboudin, J.-G., Pétraud, N. *J. Organomet. Chem.* **1994**, *467*, 181, also described the preparation of *trans-bis*-vinylstannanes.

(32) Kochi, J. K. *Organometallic Mechanisms and Catalysis*, Academic Press, New York, 1978.

(33) In both cases described below, stannylcupration led to the corresponding *bis*-stannanes as the major products in 44% and 28% yield. The monovinylstannane was isolated in each case in 8−10% yield.



which are helpful to choose an efficient hydrostannylation method depending on the structure of the starting material and the stereo- and regiochemistry of the desired product.

In most cases radical hydrostannylation reactions proceed in fair to poor yields when applied to propargyl derivatives or enynols (especially in the case of substituted alkyne functions), and regio- and stereoselectivities are generally mediocre.

Pd(0)-catalyzed stannylation reactions on propargyl derivatives or enynols give good yields and high selectivities. Regio- and stereoselectivities are strongly dependent *on the substitution of the* α position for alkynes, and dependent *on the substitution of the double bond in the case of enynes*.

In general, stannylcupration of propargyl derivatives or enynols delivers an exclusive vinyl- or dienylstannane isomer, depending on reaction temperature, addition of methanol to the cuprate solution, and the structure of the starting material. In particular addition of methanol to the cuprate solution appears to be the best solution for the preparation of pure distal stannyl derivatives from substituted or terminal propargyl or enyne.

The choice between the stannylcupration and Pd(0)-hydrostannylation methods appears to be crucial for the preparation of a specific vinyl- or dienylstannane.

Experimental Section

All air and/or water sensitive reactions were carried out under argon atmosphere with dry, freshly distilled solvents using standard syringe−cannula/septa techniques. All corresponding glassware was oven dried (110 °C) and/or carefully dried in line with a flameless heat gun. Unless otherwise stated. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium−benzophenone, and methanol from magnesium methoxide. Flash chromatography was performed on E. Merck silica gel Si 60 (40−63 mm, ref 9385). ^{1}H NMR spectra were recorded in $CDCl_3$ on 200 MHz and 400 MHz instruments. For Sn−^{1}H or Sn−^{13}C coupling constants, the central signal is normally associated with two close pairs of satellites corresponding to both ^{117}Sn (7.5%) and ^{119}Sn (8.6%) isotopes. When detected for large coupling constants (250−300 Hz), the two different coupling constants are reported whereas in other cases (generally for small ones, <100 Hz) average values are reported.

(*E*)-3-Methylhex-2-en-4-yn-1-ol (4). To a solution of commercial (*E*)-3-methylpent-2-en-4-yn-1-ol (15.0 g, 156 mmol) in DMF (60 mL) were added imidazole (26.6 g, 390 mmol) and TBSCl (28.2 g, 187 mmol). After stirring overnight at 20 °C, the mixture was diluted with CH_2Cl_2 and washed with water, saturated aqueous NH_4Cl, water, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (diethyl ether/petroleum ether 0:100 to 10:90) gave the protected alcohol (*E*)-3-methyl-1-[(*tert*-butyldimethylsilyl)oxy]-pent-2-en-4-yne as a colorless oil (32.5 g, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (t, 1 H, J = 6.2 Hz), 4.25 (d, 2 H, J = 6.2 Hz), 2.81 (s, 1 H), 1.81 (s, 3 H), 0.91 (s, 9 H), 0.09 (s, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.7, 118.0, 86.4, 74.6, 60.0, 26.1, 18.4, 17.4, −5.1. IR (thin film) ν 3313, 2955, 2929, 2886, 2857, 1472, 1374, 1256, 1187, 1108, 1065, 835, 813, 776 cm^{-1}. MS (DI, CI, NH_3) m/z 228 (MH^+ + 17, 40), 211 (MH^+, 100), 170 (40), 153 (50), 132 (35), 96 (90), 89 (70), 79 (35), 74 (25). Anal. Calcd for $C_{12}H_{22}OSi$, 210.39: C, 68.51; H, 10.54. Found: C, 68.51; H, 10.51.

To a solution of the preceding silyl ether (21.4 g, 102 mmol) in THF (180 mL) at −78 °C was added *n*-BuLi (1.6 M solution in hexane, 66.0 mL, 106 mmol). The cold bath was removed, and the mixture was stirred at 0 °C for 1 h and cooled to −78 °C before addition of iodomethane (25.3 mL, 407 mmol). The solution was stirred at 20 °C for one night and quenched at 0 °C with saturated aqueous NH_4Cl. The mixture was allowed to warm to 20 °C and then extracted with diethyl ether (× 2). The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (diethyl ether/petroleum ether 0:100 to 10:90) gave (*E*)-3-methyl-1-[(*tert*-butyldimethylsilyl)oxy]hex-2-en-4-yne (19.66 g, 86%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (t, 1 H, J = 6.3 Hz), 4.21 (d, 2 H, J = 6.3 Hz), 1.91 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 0.90 (s, 9 H), 0.05 (s, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.3, 119.4, 83.0, 82.3, 59.9, 25.9, 18.3, 17.7, 4.0, −5.2. IR (thin film) ν 2954, 2926, 2856, 1636, 1471, 1463, 1371, 1255, 1112, 1076, 1041, 836, 776 cm^{-1}. MS (DI, CI, NH_3) m/z 242 (MH^+ + 17, 1), 225 (MH^+, 2), 184 (8), 167 (15), 110 (85), 93 (100), 91 (15), 74 (5). Anal. Calcd for $C_{13}H_{24}OSi$, 224.42: C, 69.58; H, 10.78. Found: C, 69.78; H, 10.83.

A solution of the preceding silyl derivative (2.40 g, 10.7 mmol) in CH_3CN/HF (95:5, 30 mL) was stirred overnight at 20 °C. A saturated aqueous $NaHCO_3$ solution was added at 0 °C. The mixture was extracted with diethyl ether (× 3). The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (diethyl ether/petroleum ether 50:50) gave title product **4** (1.10 g, 93%) as a pale yellow oil.

4: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (t, 1 H, J = 6.8 Hz), 4.19 (d, 2 H, J = 6.8 Hz), 1.93 (s, 3 H), 1.80 (s, 3 H), 1.76 (bs, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.0, 121.5, 84.1, 82.1, 59.1, 17.8 , 4.1. IR (thin film) ν 3331, 2917, 2855, 1634, 1440, 1463, 1378, 1260, 1100, 1003 cm^{-1}. MS (DI, CI, NH_3) m/z 128 (MH^+ + 17, 2), 111 (MH^+, 10), 110 (MH^+ + 17 - 18, 100), 93 (35). Anal. Calcd for $C_7H_{10}O$, 110.16: C, 76.33; H, 9.15. Found: C, 76.34; H, 9.26.

(*Z*)-3-Methylhex-2-en-4-yn-1-ol (8). To a solution of commercial (*Z*)-3-methylpent-2-en-4-yn-1-ol (1.0 g, 10 mmol) in diethyl ether (10 mL) and dihydropyran (1.1 mL) was added *p*-toluenesulfonic acid (22 mg, 0.01 mmol). After one night at 20 °C, the mixture was diluted with diethyl ether and washed with water, saturated aqueous NH_4Cl, water, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuum*. Purification by flash chromatography on silica gel (diethyl ether/petroleum ether 0:100 to 10:90) gave the protected alcohol (*Z*)-3-methyl-1-(tetrahydropyran-2-yloxy)pent-2-en-4-yne (1.62 g, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) *two diastereomers* δ 5.94 (t, 1 H, J = 7.4 Hz), 4.67 (t, 1 H, J = 3.9 Hz), 4.43 (d, 1 H, J = 7.4 Hz), 4.26 (d, 1 H, J = 7.4 Hz), 3.93−3.88 (m, 1 H), 3.57−3.52 (m, 1 H), 3.17 (s, 1 H), 1.92 (s, 3 H), 1.87−1.84 (m, 1 H), 1.77−1.71 (m, 1 H), 1.64−1.53 (m, 4 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.2, 120.3, 98.4, 82.1, 81.9, 65.7, 62.2, 30.6 , 25.5, 23.0, 19.5. IR (thin film) ν 3291, 3027, 2943, 2871, 2096, 1637, 1453, 1441, 1352, 1262, 1201, 1135, 1119, 1076, 1054, 1024, 906, 869, 814, 638 cm^{-1}. MS (DI, CI, NH_3) m/z 198 (MH^+ + 17, 10), 181 (MH^+, 20), 163 (10), 145 (5), 135 (5), 120 (3), 102 (100), 97 (5), 85 (40). Anal. Calcd for $C_{11}H_{16}O_2$, 180.25: C, 73.30; H, 8.95. Found: C, 73.06; H, 8.89.

To a solution of the preceding compound (1.62 g, 9.00 mmol) in THF (30 mL) at −78 °C was added *n*-BuLi (1.6 M solution in hexane, 6.7 mL, 11 mmol). The cold bath was removed, and the mixture was stirred at 0 °C for 1 h and cooled to −78 °C before addition of iodomethane (3.4 mL, 54 mmol). The solution was stirred overnight at 20 °C and quenched at 0 °C with saturated aqueous NH_4Cl. The mixture was allowed to warm to 20 °C and then extracted with diethyl ether (× 2). The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (diethyl ether/petroleum ether 0:100 to 10:90) gave (*Z*)-3-methyl-1-(tetrahydropyran-2-yloxy)hex-2-en-4-yne (1.08 g, 62%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *two diastereomers* δ 5.72 (t, 1 H, J = 6.4 Hz), 4.61−4.59 (m, 1 H), 4.38 (d, 0.5 H, J = 6.3 Hz), 4.31 (d, 0.5 H, J = 6.3 Hz), 4.19 (d, 0.5 H, J = 6.3 Hz), 4.12 (d, 0.5 H, J = 6.3 Hz), 3.93−3.81 (m, 1 H), 3.54−3.44 (m, 1 H), 1.94 (s, 3 H), 1.82 (s, 3 H), 1.89−1.49 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 132.1, 121.8, 98.4, 90.7, 78.2, 65.9, 62.2, 30.8, 25.6, 23.5, 19.6, 4.3. IR (thin film) ν 2942, 2870, 2221, 1636, 1440, 1353, 1261, 1200, 1136, 1119, 1077, 1058, 1023,

905, 869, 815 cm^{-1}. MS0 (DI, CI, NH_3) *m/z* 212 (MH^+ + 17, 15), 202 (10), 185 (25), 175 (10), 145 (5), 110 (10), 102 (100), 85 (20).

A solution of the preceding compound (0.98 g, 5.10 mmol) in methanol (15 mL) was treated with *p*-toluenesulfonic acid (290 mg, 1.5 mmol) and stirred at 20 °C for 20 min. Then triethylamine was added (430 μL), and the solution was concentrated *in vacuo*. The mixture was taken in dichloromethane and washed with water. The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (diethyl ether/petroleum ether 30:70 to 50:50) gave title product **9** (517 mg, 93%) as a colorless oil.

8: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (t, 1 H, J = 6.6 Hz), 4.22 (d, 2 H, J = 6.6 Hz), 2.57 (bs, 1 H), 1.93 (s, 3 H), 1.80 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.9, 121.0, 90.8, 78.0, 61.1, 23.4, 4.1. IR (thin film) ν 3332, 3027, 2949, 2918, 2854, 2216, 1635, 1435, 1376, 1327, 1247, 1099, 1045, 1022, 998, 824 cm^{-1}. MS (DI, CI, NH_3) *m/z* 128 (MH^+ + 17, 5), 111 (MH^+, 10), 110 (MH^+ + 17−18, 100), 93 (50). Anal. Calcd for $C_7H_{10}O$, 110.16: C, 76.33; H, 9.15. Found: C, 75.69; H, 9.23.

General Procedures for Stannylations. Method A: Radical Hydrostannylation. To a solution of enynol or propargyl derivative (1.0 mmol) in toluene (10^{-1} to 10^{-3} M sol) were added AIBN (0.1 equiv) and Bu_3SnH (1.2 equiv). After the solution was heated for 4 h at 80 °C (or 12 h at 80 °C), the solvent was removed under reduced pressure and the crude residue was purified by flash chromatography on basic silica gel (diethyl ether/petroleum ether 0:100 to 50:50).

Method B: Palladium(0)-Catalyzed Hydrostannylation. To a solution of enynol or propargyl derivative (1.0 mmol) in THF (3 mL) at 20 °C was added $PdCl_2(PPh_3)_2$ (0.02 mmol, 0.02 equiv) followed by tributyltin hydride (1.2 mmol) over a period of *ca.* 1−2 min. Toward the end of the addition, the originally light yellow solution abruptly turned orange-brown, and H_2 evolution was observed, signaling the formation of $(Bu_3Sn)_2$. After being stirred at 20 °C for 10 min, the dark brown reaction mixture was concentrated *in vacuo*. Purification was performed by flash chromatography on basic silica gel (diethyl ether/petroleum ether 0:100 to 50:50).

Method C: Stannylcupration. Conditions C_1 [$Bu_3Sn(Bu)CuCNLi_2$]. To a suspension of CuCN (2.0 mmol) in THF (8 mL) was added *n*-BuLi (2.7 mL, 4.2 mmol) at −78 °C. The solution was stirred for 10 min at −40 °C (pale yellow color) and cooled to −78 °C. Then tributyltin hydride (4.2 mmol) was added. The solution was stirred for 10 min at −40 °C (yellow gold color) and cooled to −78 °C. A solution of the enynol or propargyl derivative (1.0 mmol) in THF (1 mL) was added. The mixture was allowed to warm to −30 °C for 1 h and poured into a saturated aqueous NH_4Cl/concentrated ammonia (5:1) solution at −10 °C. After 30 min the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification was performed by flash chromatography on basic silica gel (diethyl ether/petroleum ether 0:100 to 50:50).

Conditions C_2 [$Bu_3Sn(Me)CuCNLi_2$]. To a suspension of CuCN (170 mg, 1.9 mmol) in THF (4 mL) and diethyl ether (2 mL) was added MeLi (1.6 M solution in diethyl ether, 2.4 mL, 3.8 mmol) at −78 °C. The solution was stirred for 10 min at −40 °C (pale yellow color) and cooled to −78 °C. Then tributyltin hydride (1.0 mL, 3.8 mmol) was added. The solution was stirred for 10 min at −40 °C (yellow gold color) and cooled to −78 °C. A solution of the enynol or propargyl derivative (50 mg, 0.454 mmol) in THF (1 mL) was added. The mixture was allowed to warm to −10 °C overnight and quenched with a saturated aqueous NH_4Cl/concentrated ammonia (5:1) solution at −20 °C. After 30 min the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification was performed by flash chromatography on basic silica gel (diethyl ether/petroleum ether 0:100 to 50:50).

Conditions C_3 [$Bu_3Sn(Bu)CuCNLi_2$]. To a solution of hexabutylditin (2.2 g, 3.8 mmol) in THF (3 mL) was added *n*-BuLi (1.6 M solution in hexane, 2.4 mL, 3.8 mmol) at −78 °C. The solution was stirred for 30 min at −40 °C. Then the mixture was added *via cannula* to a suspension of CuCN (170 mg, 1.9 mmol) in THF (3 mL) at −78 °C. The solution was stirred at −40 °C until obtention of a yellow solution. A solution of the enynol or propargyl derivative (0.5 mmol) in THF (1 mL) was added at −78 °C, and the temperature was allowed to warm to −10 °C overnight. Then MeOH (1 mL) was added at −20 °C. After 15 min, water (1 mL) was added at −20 °C, and 15 min later the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification was performed by flash chromatography on basic silica gel (diethyl ether/petroleum ether 0:100 to 50:50).

Conditions C_4 [$Bu_3Sn(Bu)CuCNLi_2$]. To a solution of hexabutylditin (2.2 g, 3.8 mmol) in THF (3 mL) was added *n*-BuLi (1.6 M solution in hexane, 2.4 mL, 3.8 mmol) at −78 °C. The solution was stirred for 30 min at −40 °C. Then the mixture was added *via cannula* to a suspension of CuCN (170 mg, 1.9 mmol) in THF (3 mL) at −78 °C. The solution was stirred at −40 °C until obtention of a yellow solution. MeOH (1 mL) was added at −78 °C. Then the yellow solution turned to a red gel. The temperature was allowed to warm to −10 °C for 30 min, until obtention of a red solution. A solution of the enyne (0.5 mmol) in THF (1 mL) was added at −78 °C, and the temperature was allowed to warm to −10 °C overnight. Then MeOH (1 mL) was added at −20 °C. After 15 min, water (1 mL) was added at −20 °C, and 15 min later the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification was performed by flash chromatography on basic silica gel (diethyl ether/petroleum ether 0:100 to 50:50).

Stannylations of Enynol Derivative 3. Radical Hydrostannylation. Using method **A** (80 °C, 4 h), stannylation of commercial enynol **3** (100 mg, 1.0 mmol in 5 mL toluene) led to diennylstannanes **5** (244 mg, 61%) and **5b** (55 mg, 14%).

Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of **3** (100 mg, 1.0 mmol) gave **5** (241 mg, 60%) and **5c** (40 mg, 40%) as colorless oils.

Stannylcupration. Using conditions C_1 (−30 °C, 1 h), stannylation of **3** (100 mg, 1.0 mmol) led to **5** (371 mg, 92%).

Stannylcupration. Using conditions C_3 (−78 °C, 1 h 30 min), stannylation of **3** (100 mg, 1.0 mmol) led to **5** (331 mg, 82%) and **5a** (39 mg, 10%), **5**/**5a** = 89:11.

Stannylcupration, Using conditions C_4 (−78 °C, 1 h 30 min), stannylation of **3** (100 mg, 1.0 mmol) gave **5** (210 mg, 52%) and **5a** (105 mg, 26%, **5**/**5a** = 67:33).

(2*E*,4*E*)-3-Methyl-5-(tributylstannyl)penta-2,4-dien-1-ol (5).[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (d, 1 H, J = 19.3 Hz, J ^{1}H−^{117}Sn = 62.5 Hz, J ^{1}H−^{119}Sn = 63.5 Hz), 6.27 (d, 1 H, J = 19.3 Hz, J ^{1}H−^{117}Sn = 68.1 Hz, J ^{1}H−^{119}Sn = 68.2 Hz), 5.66 (t, 1 H, J = 6.3 Hz), 4.32 (t, 2 H, J = 6.3 Hz), 1.81 (s, 3 H), 1.56−1.48 (m, 7 H), 1.37−1.28 (m, 6 H), 0.94−0.87 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.2, 138.0 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 64.0 Hz), 129.8, 128.6 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 380.0 Hz), 59.7, 29.2 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 20.4 Hz), 27.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 54.0 Hz), 13.8, 12.0, 9.7 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 335.0 Hz). IR (thin film) ν 3313, 2955, 2923, 2870, 2852, 1635, 1566, 1463, 1418, 1376, 1181, 1150, 1072, 986, 873, 760, 688 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 389 (MH^+, 15), 371 (MH^+ − 18, 10), 308 (Bu_3Sn^+ + 17, 100), 291 (Bu_3Sn^+, 30), 98 (5), 81 (3). Anal. Calcd for $C_{18}H_{36}OSn$, 387.19: C, 55.84; H, 9.37. Found: C, 55.77; H, 9.55.

(2*E*)-3-Methyl-4-(tributylstannyl)pent-2,4-dien-1-ol (5a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (d, 1 H, J = 2.0 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 132.6 Hz), 5.50 (t, 1 H, J = 5.7 Hz), 5.27 (d, 1 H, J = 2.0 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 63.4 Hz), 4.28 (t, 2 H, J = 5.7 Hz), 1.84 (s, 3 H), 1.54−1.47 (m, 7 H), 1.37−1.28 (m, 6 H), 1.00−0.88 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.7, 143.0, 128.1 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 25.0 Hz), 124.7 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 16.0 Hz), 60.0, 29.2 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 17.1 Hz), 27.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 56.3 Hz), 14.7, 13.8, 10.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 328.3 Hz). IR (thin film) ν 3314, 2955, 2925, 2870,

2853, 1463, 1376, 1292, 1072, 1001, 907, 863 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 389 (MH^+, 3), 371 ($MH^+ - 18$, 1), 331 (10), 308 (100), 291 (35), 250 (2), 98 (5). Anal. Calcd for $C_{18}H_{36}OSn$, 387.19: C, 55.84; H, 9.37. Found: C, 56.01; H, 9.58.

(2*Z*,4*E*)-3-Methyl-5-(tributylstannyl)penta-2,4-dien-1-ol (5b). ^1H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, 1 H, J = 19.4 Hz, J $^1H-^{117}Sn$ = J $^1H-^{119}Sn$ = 63.7 Hz), 6.37 (d, 1 H, J = 19.4 Hz, J $^1H-^{117}Sn$ = J $^1H-^{119}Sn$ = 69.5 Hz), 5.58 (t, 1 H, J = 6.5 Hz), 4.36 (t, 2 H, J = 6.2 Hz), 1.87 (s, 3 H), 1.57−1.48 (m, 7 H), 1.36−1.29 (m, 6 H), 0.96−0.88 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.3 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 10.6 Hz), 136.3 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 63.4 Hz), 131.6 (J $^{13}C-^{117}Sn$ = 364.1 Hz, J $^{13}C-^{119}Sn$ = 377.6 Hz), 127.6, 58.1, 29.1 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 17.7 Hz), 27.3 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 53.1 Hz), 19.9, 13.7, 9.7 (J $^{13}C-^{117}Sn$ = 326.8 Hz, J $^{13}C-^{119}Sn$ = 341.8 Hz). IR (thin film) ν 3312, 2921, 1566, 1463, 1418, 1376, 1248, 1181, 1072, 985, 864, 761, 686 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 389 (MH^+, 1), 371 ($MH^+ - 18$, 15), 308 (100), 291 (35), 98 (5), 81 (2). Anal. Calcd for $C_{18}H_{36}OSn$, 387.19: C, 55.84; H, 9.37. Found: C, 55.85; H, 9.48.

(*E*)-3-Methyl-penta-2,4-dien-1-ol (5c).[13] ^1H NMR (400 MHz, $CDCl_3$) δ 6.40 (dd, 1 H, J = 17.5, 10.7 Hz), 5.68 (t, 1 H, J = 6.4 Hz), 5.22 (d, 1 H, J = 17.5 Hz), 5.07 (d, 1 H, J = 10.7 Hz), 4.30 (t, 2 H, J = 6.4 Hz), 1.80 (s, 3 H), 1.53 (bs, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 140.9, 136.5, 130.6, 113.2, 59.5, 11.9. IR (thin film) ν 3329, 2956, 2924, 2853, 1565, 1463, 1376, 1073, 985, 864, 802, 760, 665 cm^{-1}. MS (GC/MS, IE) *m/z* 98 (M^+, 20), 83 (60), 79 10), 69 (60), 55 (90), 41 (100).

Stannylations of Enynol Derivative 4. Radical Hydrostannylation. Using method **A** (80 °C, 12 h), stannylation of enynol **4** (50 mg, 0.05 mmol in 15 mL toluene) gave a 70:30 mixture of **6** (29 mg, 14%) and **6b** (13 mg, 6%).

Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of **4** (60 mg, 0.545 mmol) led to **6a** (201 mg, 92%) as a colorless oil.

Stannylcupration. Using conditions $\mathbf{C_1}$, stannylation of **4** (50 mg, 0.45 mmol) gave a 95:5 mixture of **6** (87 mg, 42%) and **6b** (4 mg, 2%).

Stannylcupration. Using conditions $\mathbf{C_2}$, stannylation of **4** (50 mg, 0.45 mmol) gave **6** (112 mg, 62%).

Stannylcupration. Using conditions $\mathbf{C_4}$, stannylation of **4** (50 mg, 0.45 mmol) gave **6** (131 mg, 72%). On a 22 mmol scale diennylstannane **6** was obtained in 77% yield.

(2*E*,4*E*)-3-Methyl-5-(tributylstannyl)hexa-2,4-dien-1-ol (6). ^1H NMR (400 MHz, $CDCl_3$) δ 5.97 (s, 1 H, J $^1H-^{117}Sn$ = J $^1H-^{119}Sn$ = 73.0 Hz), 5.51 (t, 1 H, J = 6.7 Hz), 4.26 (t, 2 H, J = 6.7 Hz), 2.03 (s, 3 H, J $^1H-^{117}Sn$ = J $^1H-^{119}Sn$ = 47.0 Hz), 1.80 (s, 3 H), 1.57−1.47 (m, 7 H), 1.36−1.28 (m, 6 H), 0.95−0.82 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.2 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 29.6 Hz), 141.8 (J $^{13}C-^{117}Sn$ = 386.6 Hz, J $^{13}C-^{119}Sn$ = 401.8 Hz), 135.5 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 67.1 Hz), 128.0, 59.6, 29.3 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 18.3 Hz), 27.4 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 53.2 Hz), 21.2 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 38.8 Hz), 17.2, 13.6, 9.2 (J $^{13}C-^{117}Sn$ = 311.0 Hz, J $^{13}C-^{119}Sn$ = 326.0 Hz). IR (thin film) ν 3321, 2956, 2925, 2870, 2853, 1463, 1418, 1376, 1072, 1000, 1072, 874 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 403 (MH^+, 2), 385 ($MH^+ - 18$, 5), 308 (100), 291 (35), 128 (10), 111 (20), 95 (25). Anal. Calcd for $C_{19}H_{38}OSn$, 401.22: C, 56.88; H, 9.55. Found: C, 57.05; H, 9.61.

(2*E*,4*E*)-3-Methyl-4-(tributylstannyl)hexa-2,4-dien-1-ol (6a). ^1H NMR (400 MHz, $CDCl_3$) δ 5.57 (q, 1 H, J = 6.4 Hz, J $^1H-^{117}Sn$ = J $^1H-^{119}Sn$ = 60.5 Hz), 5.17 (t, 1 H, J = 6.5 Hz), 4.20 (t, 2 H, J = 6.5 Hz), 1.71 (s, 3 H), 1.68 (d, 3 H, J = 6.4 Hz), 1.52−1.45 (m, 7 H), 1.36−1.27 (m, 6 H), 0.94−0.83 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.8 (J $^{13}C-^{117}Sn$ = 360.9 Hz, J $^{13}C-^{119}Sn$ = 379.1 Hz), 142.2, 133.5 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 24.9 Hz), 122.1 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 26.7 Hz), 59.1, 29.1 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 18.8 Hz), 27.4 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 55.4 Hz), 17.3, 17.2, 15.6 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 52.9 Hz), 13.7, 9.9 (J $^{13}C-^{117}Sn$ = 312.0, J $^{13}C-^{119}Sn$ = 326.2 Hz). IR (thin film) ν 3319, 2955, 2925, 2870, 2852, 1646,1600, 1464, 1375, 1291, 1072, 1000, 874 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 403 (MH^+, 5), 385 ($MH^+ - 18$, 5), 329 (5), 308 (100), 291 (30), 111 (10), 95 (5). Anal. Calcd for $C_{19}H_{38}OSn$, 401.22: C, 56.88; H, 9.55. Found: C, 56.69; H, 9.52.

(2*E*,4*Z*)-3-Methyl-5-(tributylstannyl)hexa-2,4-dien-1-ol (6b). ^1H NMR (400 MHz, $CDCl_3$) δ 6.64 (s, 1 H, J $^1H-^{117}Sn$ = J $^1H-^{119}Sn$ = 132.4 Hz), 5.44 (t, 1 H, J = 6.5 Hz), 4.20 (t, 2 H, J = 6.5 Hz), 2.00 (s, 3 H, J $^1H-^{117}Sn$ = J $^1H-^{119}Sn$ = 40.3 Hz), 1.80 (s, 3 H), 1.51−1.43 (m, 7 H), 1.34−1.29 (m, 6 H), 0.94−0.88 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.5 (J $^{13}C-^{117}Sn$ = 355.0 Hz, J $^{13}C-^{119}Sn$ = 369.0 Hz), 139.7 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 25.0 Hz), 139.0 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 25.0 Hz), 126.3, 60.4, 29.5 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 23.0 Hz), 28.0 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 41.6 Hz), 27.5 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 58.4 Hz), 24.6, 13.8 , 10.2 (J $^{13}C-^{117}Sn$ = 315.6 Hz, J $^{13}C-^{119}Sn$ = 329.7 Hz). IR (thin film) ν 3328, 2957, 2871, 1654, 1464, 1376, 1290, 1180, 1072, 1005, 960, 863, 668 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 403 (MH^+, 1), 385 ($MH^+ - 18$, 2), 308 (100), 291 (25), 250 (5), 128 (8), 111 (15), 95 (10). Anal. Calcd for $C_{19}H_{38}OSn$, 401.22: C, 56.88; H, 9.55. Found: C, 57.01; H, 9.66.

Stannylations of Enynol Derivative 7. Radical Hydrostannylation. Using method **A** (80 °C, 4 h), stannylation of enynol **7** (200 mg, 2 mmol in 20 mL toluene) gave a mixture of **5b** (104 mg, 13%) and **5** (47 mg, 6%).

Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of **7** (150 mg, 1.6 mmol) led to **5b** (33 mg, 6%) and **9a** (262 mg, 48%) as colorless oils.

Stannylcupration. Stannylation of **7** (110 mg, 1.1 mmol) using conditions $\mathbf{C_3}$ (−30 °C, 1 h 30 min) gave **5b** (358 mg, 81%) and **9b** (22 mg, 3%).

Stannylcupration. Stannylation of **7** (110 mg, 1.1 mmol) using conditions $\mathbf{C_4}$ (−30 °C, 1 h 30 min) gave **5b** (335 mg, 76%) as a colorless oil.

(2*Z*)-3-Methyl-4-(tributylstannyl)penta-2,4-dien-1-ol (9a). ^1H NMR (400 MHz, $CDCl_3$) δ 5.58 (d, 1 H, J = 3.3 Hz, J $^1H-^{117}Sn$ = 125.9, J $^1H-^{119}Sn$ = 132.1 Hz), 5.30 (t, 1 H, J = 6.5 Hz), 5.28 (d, 1 H, J = 3.3 Hz, J $^1H-^{117}Sn$ = 56.3, J $^1H-^{119}Sn$ = 62.9 Hz), 4.06 (t, 2 H, J = 6.5 Hz), 1.76 (s, 3 H), 1.54−1.47 (m, 6 H), 1.37−1.28 (m, 6 H), 1.17 (t, 1 H, J = 6.5 Hz), 0.96−0.88 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.4, 146.7 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 22.7 Hz), 125.8 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 19.0 Hz), 121.8 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 24.7 Hz), 60.3, 29.1 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 19.6 Hz), 27.4 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 55.9 Hz), 24.7, 13.7, 10.3 (J $^{13}C-^{117}Sn$ = 315.2 Hz, J $^{13}C-^{119}Sn$ = 328.8 Hz). IR (thin film) ν 3329, 3034, 2920, 2729, 1641, 1583, 1557, 1463, 1376, 1340, 1179, 1081, 1000, 922, 874, 690, 665 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 389 (MH^+, 5), 371 ($MH^+ - 18$, 1), 308 (100), 291 (35), 250 (2), 98 (5). Anal. Calcd for $C_{18}H_{36}OSn$, 387.19: C, 56.88; H, 9.55. Found: C, 57.01; H, 9.71.

(2*Z*,4*Z*)-3-Methyl-4,5-bis(tributylstannyl)penta-2,4-dien-1-ol (9b). ^1H NMR (400 MHz, $CDCl_3$) δ 6.50 (s, 1 H, J $^1H-^{117}Sn^a$ = 171.0 Hz, J $^1H-^{119}Sn^a$ = 179.1 Hz, J $^1H-^{117}Sn^b$ = 75.1 Hz, J $^1H-^{119}Sn^b$ = 78.3 Hz), 5.18 (t, 1 H, J = 6.9 Hz), 4.02 (t, 2 H, J = 6.9 Hz), 1.72 (s, 3 H), 1.56−1.44 (m, 12 H), 1.42−1.23 (m, 12 H), 1.04 (t, 1 H, J = 6.9 Hz), 0.97−0.81 (m, 30 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.4 (J $^{13}C-^{117}Sn^b$ = J $^{13}C-^{119}Sn^b$ = 31.8 Hz), 151.4 (J $^{13}C-^{117}Sn^a$ = J $^{13}C-^{119}Sn^a$ = 39.4 Hz), 144.1 (J $^{13}C-^{117}Sn^a$ = J $^{13}C-^{119}Sn^a$ = 58.1 Hz), 119.7, 60.7, 29.4 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 19.4 Hz), 27.7 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 60.3 Hz), 27.5 (J $^{13}C-^{117}Sn$ = J $^{13}C-^{119}Sn$ = 55.7 Hz), 24.8, 13.8, 11.3 (J $^{13}C-^{117}Sn$ = 304.7, J $^{13}C-^{119}Sn$ = 319.8 Hz), 10.9 (J $^{13}C-^{117}Sn$ = 317.4, J $^{13}C-^{119}Sn$ = 332.6 Hz). IR (thin film) ν 3333, 2955, 2922, 2870, 2853, 1639, 1530, 1463, 1376, 1072, 1001, 874, 668, 665 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 677 (MH^+, 3), 619 (5), 597 (2), 428 (10), 412 (5), 329 (5), 308 (100), 291 (30), 250 (5), 97 (5), 78 (5). Anal. Calcd for $C_{30}H_{62}OSn_2$, 676.20: C, 53.29; H, 9.24. Found: C, 53.55; H, 9.28.

Stannylations of Enynol Derivative 8. Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of enynol **8** (100 mg, 0.9 mmol) led to **10a** (224 mg, 62%) and to starting material **8** (38 mg, 38%).

Stannylcupration. Stannylation of **8** (100 mg, 0.9 mmol) using conditions $\mathbf{C_3}$ proceeded in less than 5% yield.

Stannylcupration. Stannylation of **8** (100 mg, 0.9 mmol) using conditions $\mathbf{C_4}$ gave pure **10** (232 mg, 64%) and starting material **8** (28 mg, 28%).

(2*Z*,4*E*)-3-Methyl-5-(tributylstannyl)hexa-2,4-dien-1-ol (10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (s, 1 H, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 68.0 Hz), 5.47 (tq, 1 H, J = 6.6, 1.2 Hz), 4.02 (t, 2 H, J = 6.7 Hz), 1.79 (d, 3 H, J = 1.2 Hz), 1.78 (s, 3 H, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 44.9 Hz), 1.54−1.48 (m, 6 H), 1.36−1.23 (m, 7 H), 0.94−0.89 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.7, 138.6 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 29.6 Hz), 136.6 (J ^{13}C−^{117}Sn = 43.9, J ^{13}C−^{119}Sn = 60.7 Hz), 125.3, 61.2, 29.3 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 19.7 Hz), 27.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 52.1 Hz), 23.7, 21.0 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 40.4 Hz), 13.7, 9.4 (J ^{13}C−^{117}Sn = 312.7 Hz, J ^{13}C−^{119}Sn = 327.5 Hz). IR (thin film) ν 3319, 2955, 2923, 2870, 2851, 1652, 1597, 1463, 1376, 1078, 1005, 874, 688, 666, 595 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 403 (MH^+, 1), 385 (MH^+ − 18, 5), 345 (2), 308 (100), 279 (35), 235 (2), 151 (2), 128 (5), 111 (10), 95 (20). Anal. Calcd for $C_{19}H_{38}OSn$, 401.22: C, 56.88; H, 9.55. Found: C, 57.13; H, 9.58.

(2*Z*,4*E*)-3-Methyl-4-(tributylstannyl)hexa-2,4-dien-1-ol (10a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (q, 1 H, J = 6.4 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 65.4 Hz), 5.30 (tq, 1 H, J = 6.6, 0.8 Hz), 3.98 (d, 2 H, J = 5.7 Hz), 1.72 (d, 3 H, J = 0.8 Hz), 1.62 (d, 3 H, J = 6.4 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 10.1 Hz), 1.53−1.45 (m, 6 H), 1.36−1.27 (m, 6 H), 1.14 (t, 1 H, J = 6.1 Hz), 0.94−0.89 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.3, 142.1, 133.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 14.0 Hz), 120.9 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 25.0 Hz), 60.9, 29.1 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 19.8 Hz), 27.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 56.2 Hz), 23.9, 16.2 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 51.8 Hz), 13.8, 9.9 (J ^{13}C−^{117}Sn = 312.7 Hz, J ^{13}C−^{119}Sn = 326.9 Hz), 125.3, 61.2. IR (thin film) ν 3327, 2956, 2926, 2870, 2852, 1646, 1601, 1463, 1439, 1375, 1080, 1002, 874, 665 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 403 (MH^+, 1), 385 (MH^+ − 18, 3), 345 (3), 308 (100), 291 (30), 267 (2), 128 (3), 111 (10), 95 (20). Anal. Calcd for $C_{19}H_{38}OSn$, 401.22: C, 56.88; H, 9.55. Found: C, 57.05; H, 9.61.

Stannylations of Enyne Derivative 11. Radical Hydrostannylation. Using method **A** (80 °C, 4 h), stannylation of enyne **11** (480 mg, 1.9 mmol in 15 mL toluene) led to **12** (520 mg, 50%).

Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of **11** (100 mg, 0.4 mmol) gave a mixture of **12a** (50 mg, 22%) and **12c** (40, 53%) as colorless oils.

Stannylcupration. Using conditions $\mathbf{C_1}$, stannylation of **11** (100 mg, 0.4 mmol) (−25 °C, 30 min) gave **12a** (113 mg, 52%) and **12c** (24 mg, 24%).

(1*E*)-3,3,7,7,9-Pentamethyl-8-[2-(tributylstannyl)ethenyl]-1,5-dioxa-spiro[5.5]undec-8-ene (12). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (d, 1 H, J = 19.6 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 66.2 Hz), 5.92 (d, 1 H, J = 19.6 Hz, J ^{1}H−^{117}Sn = 81.4 Hz, J ^{1}H−^{119}Sn = 85.6 Hz), 3.73 (d, 2 H, J = 11.2 Hz), 3.40 (d, 2 H, J = 11.2 Hz), 2.08 (m, 4 H), 1.70 (s, 3 H), 1.5 (m, 6 H), 1.30 (m, 6 H), 1.21 (s, 3 H), 1.12 (s, 6 H), 0.86 (m, 15 H), 0.75 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.9, 140.3, 133.5, 125.6, 100.4, 70.4, 43.4, 30.0, 29.9, 29.2 (J ^{13}C−^{117,119}Sn = 19.0 Hz), 26.9 (J ^{13}C−^{117,119}Sn = 52.0 Hz), 23.4, 22.8, 22.4, 21.2, 18.6, 13.8, 9.8 (J ^{13}C−^{117}Sn = 324.0 Hz, J ^{13}C−^{119}Sn = 338.0 Hz). IR (thin film) ν 2953, 2924, 2869, 1464, 1377, 1120, 1098, 1068, 1037, 993, 907, 872 cm^{-1}. MS (CI, NH_3): *m/z calculated from major ^{120}Sn isotope* 541 (MH^+, 10), 498 (3), 483 (5), 308 (100), 291 (15), 251 (25), 196 (5), 128 (10), 121 (5). Anal. Calcd for $C_{28}H_{52}O_2Sn$, 539.41: C, 62.35; H, 9.72. Found: C, 62.68; H, 9.48.

3,3,7,7,9-Pentamethyl-8-[1-tributylstannyl)ethenyl]-1,5-dioxaspiro[5.5]undec-8-ene (12a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (d, 1 H, J = 3.5 Hz, J ^{1}H−^{117}Sn = 138.0 Hz, J ^{1}H−^{119}Sn = 147.0 Hz), 5.33 (d, 1 H, J = 3.5 Hz, J ^{1}H−^{117}Sn = 63.9 Hz, J ^{1}H−^{119}Sn = 66.3 Hz), 3.75 (d, 1 H, J = 11.2 Hz), 3.67 (d, 1 H, J = 11.2 Hz), 3.37 (d, 1 H, J = 11.2 Hz), 3.31 (d, 1 H, J = 11.2 Hz), 1.97 (m, 1 H), 1.8−2.0 (m, 3 H), 1.5 (m, 6 H), 1.44 (s, 3 H), 1.3 (m, 6 H), 1.28 (s, 3 H), 1.19 (s, 6 H), 0.9 (m, 15 H), 0.73 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.2, 142.9, 127.7, 120.3, 100.3, 70.5, 43.9, 31.9, 30.0, 29.2 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 20.0 Hz), 27.6 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 57.0 Hz), 23.6, 22.5, 21.6, 18.8, 13.7, 11.0 (J ^{13}C−^{117}Sn = 305.0 Hz, J ^{13}C−^{119}Sn = 321.0 Hz). IR (thin film) ν 2954, 2926, 2870, 1464, 1376, 1117 cm^{-1}. MS (CI, NH_3): *m/z calculated from major ^{120}Sn isotope* 541 (MH^+, 5), 483 (2), 453 (2), 395 (10), 308 (100), 291 (30), 251 (35). Anal. Calcd for $C_{28}H_{52}O_2Sn$, 539.41: C, 62.35; H, 9.72. Found: C, 62.47; H, 9.67.

(1*Z*)-3,3,7,7,9-Pentamethyl-8-[2-(tributylstannyl)ethenyl]-1,5-dioxaspiro[5.5]undec-8-ene (12b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, 1 H, J = 13.7 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 150.4 Hz), 6.16 (d, 1 H, J = 13.7 Hz, J ^{1}H−^{117}Sn = 67.8 Hz, J ^{1}H−^{119}Sn = 70.4 Hz), 3.71 (d, 2 H, J = 11.4 Hz), 3.37 (d, 2 H, J = 11.4 Hz), 2.1 (bs, 2 H), 1.99 (bs, 2 H), 1.63 (s, 3 H), 1.45 (m, 6 H), 1.3 (m, 6 H), 1.21 (s, 3 H), 1.09 (s, 6 H), 0.8 (m, 15 H), 0.75 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.8, 138.9, 133.2, 125.7, 100.2, 70.3, 43.7, 30.0, 29.7, 29.2 (J ^{13}C−^{117,119}Sn = 19.0 Hz), 26.9 (J ^{13}C−^{117,119}Sn = 56.9 Hz), 23.4, 22.4, 21.3, 18.6, 13.8, 10.0 (J ^{13}C−^{117}Sn = 320.7 Hz, J ^{13}C−^{119}Sn = 337.5 Hz). IR (thin film) ν 2954, 2922, 2869, 1581, 1464, 1377, 1122, 1088, 1069, 1033, 992 cm^{-1}. MS (CI, NH_3): *m/z calculated from major ^{120}Sn isotope* 541 (MH^+, 5), 483 (2), 395 (2), 379 (5), 308 (100), 291 (35), 251 (80), 235 (10), 178 (5), 149 (30). Anal. Calcd for $C_{28}H_{52}O_2Sn$, 539.41: C, 62.35; H, 9.72. Found: C, 62.49; H, 9.59.

3,3,7,7,9-Pentamethyl-8-vinyl-1,5-dioxaspiro[5.5]undec-8-ene (12c). ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.18 (dd, 1 H, J = 17.6, 11.2 Hz), 5.28 (dd, 1 H, J = 11.2, 2.7 Hz), 4.99 (dd, 1 H, J = 17.6, 2.7 Hz), 3.72 (d, 2 H, J = 11.2 Hz), 3.39 (d, 2 H, J = 11.2 Hz), 2.05 (m, 4 H), 1.71 (s, 3 H), 1.24 (s, 3 H), 1.11 (s, 6 H), 0.74 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.2, 135.4, 126.5, 118.9, 100.3, 70.3, 43.3, 30.4, 29.9, 23.3, 22.6, 22.4, 21.0, 18.5. IR (thin film) ν 2954, 2865, 1472, 1394, 1212, 1121, 1104, 1068, 994, 908 cm^{-1}. MS (CI, NH_3) *m/z* 268 (MH^+ + 17, 20), 251 (MH^+, 100), 165 (30), 147 (20), 128 (35). Anal. Calcd for $C_{16}H_{26}O_2$, 250.38: C, 76.75; H, 10.47. Found: C, 76.83; H, 10.28.

Stannylations of Enynes Derivatives 13a,b and 15. Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of enyne **13a** (114 mg, 0.448 mmol) led to **14a** (204 mg, 80%, 80:20 mixture of two rotamers) as a colorless oil.

Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of enyne **13b** (110 mg, 0.340 mmol) led to **14b** (135 mg, 65%, 80:20 mixture of two rotamers) as a colorless oil.

Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of enyne **15** (26 mg, 0.08 mmol) led to **16** (25 mg, 51%, 80:20 mixture of two rotamers) as a colorless oil.

(4*R,5*R**)-5,6,6,8-Tetramethyl-7-[1-(tributylstannyl)ethenyl]-1,3-dioxaspiro[4.5]dec-7-en-2-one (14a).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (d, 0.2 H, J = 2.8 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 135.0 Hz), 5.48 (d, 0.8 H, J = 3.3 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn= 137.0 Hz), 5.46 (d, 0.2 H, J = 2.8 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 64.0 Hz), 5.38 (d, 0.8 H, J = 3.3 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 64.0 Hz), 4.76 (q, 1 H, J = 6.3 Hz), 2.42−2.30 (m, 1 H), 2.10−1.80 (m, 3 H), 1.53−1.47 (m, 6 H), 1.50 (s, 3 H), 1.41 (d, 3 H, J = 6.3 Hz), 1.33 (hex, 6 H, J = 7.4 Hz), 1.04 (s, 3 H), 0.98 (s, 3 H), 0.91 (t, 9 H, J = 7.4 Hz), 0.91 (t, 6 H, J = 8.1 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 156,8, 154.3, 140.7, 128.2, 122.3, 88.2, 76.3, 40.7, 29.0 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 19.0 Hz), 27.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 53.0 Hz), 27.7, 23.7, 23.6, 20.9, 20.7, 15.9, 13.6, 11.0 (J ^{13}C−^{117}Sn = 326.0 Hz, J ^{13}C−^{119}Sn = 341.0 Hz). IR (thin film) ν 2954, 2865, 1472, 1394, 1212, 1121, 1104, 1068, 994, 908 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 544 (MH^+ + 17, 80), 527 (M^+, 5), 469 (35), 308 (20), 291 (5), 254 (20), 165 (100), 74 (20). Anal. Calcd for $C_{26}H_{46}O_3Sn$, 525.34: C, 59.44; H, 8.83. Found: C, 59.58; H, 8.75.

(4*R,5*R**)-2-{2-Oxo-6,6,8-trimethyl-7-[1-(trimethylstannyl)ethenyl]-1,3-dioxaspiro[4.5]dec-7-en-5-yl}benzaldehyde (14b).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 0.8 H), 10.07 (s, 0.2 H), 7.85 (d, 1 H, J = 7.1 Hz), 7.70 (t, 1 H, J = 7.1 Hz), 7.60 (t, 1 H, J = 7.1 Hz), 7.50 (d, 1 H, J = 7.1 Hz), 6.75

(s, 0.8 H), 6.78 (s, 0.2 H), 5.63 (d, 0.8 H, J = 3.1 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 135.0 Hz), 5.56 (d, 0.2 H, J = 3.1 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 135.0 Hz), 5.45 (d, 0.2 H, J = 3.1 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 64.0 Hz), 5.42 (d, 0.8 H, J = 3.1 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 64.0 Hz), 2.05−1.98 (m, 2 H), 1.55−1.27 (m, 14 H), 1.41 (s, 3 H), 1.22 (s, 3 H), 0.98−0.83 (m, 18 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.5, 156.2, 155.1, 141.8, 137.9, 134.5, 134.0, 134.0, 129.7, 129.2, 128.9, 122.3, 91.1, 77.1, 43.1, 29.2 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 20.0 Hz), 28.4, 24.2, 27.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 50.0 Hz), 24.2, 23.0, 20.8, 13.6, 11.3 (J ^{13}C−^{117}Sn = 310.0 Hz, J ^{13}C−^{119}Sn = 320.0 Hz). IR (thin film) ν 2956, 2926, 1803, 1706, 1654, 1632, 1600, 1578, 1464, 1174, 1049, 1018, 874 cm^{-1}. Anal. Calcd for $C_{32}H_{48}O_4Sn$, 615.42: C, 62.45; H, 7.86. Found: C, 62.64; H, 7.78.

(4*R,5*S**)-2-{2-Oxo-6,6,8-trimethyl-7-[1-(tributylstannyl)ethenyl]-1,3-dioxaspiro[4.5]dec-7-en-5-yl}benzaldehyde (16).** Mp 93−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 0.2 H), 10.00 (s, 0.8 H), 7.82−7.58 (m, 4 H), 6.60 (s, 0.2 H), 6.57 (s, 0.8 H), 5.47 (d, 0.2 H, J = 1.0 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 150.0 Hz), 5.38 (d, 0.2 H, J = 1,0 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 64.0 Hz), 5.21 (bs, 1.6 H, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 137.0 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 64.0 Hz), 2.60−2.10 (m, 4 H), 1.44 (s, 3 H), 1.40 −1.20 (m, 12 H), 0.84 (s, 3 H), 0.45 (s, 3 H), 0.97 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.5, 154.4, 142.5, 137.6, 135.2, 134.7, 133.7, 130.1, 129.7, 128.6, 122.1, 92.4, 82.7, 41.7, 32.4, 29.1 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 20.0 Hz), 28.0, 27.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 50.0 Hz), 24.0, 22.1, 21.1, 13.6, 11.4 (J ^{13}C−^{117}Sn = 320.0 Hz, J ^{13}C−^{119}Sn = 340.0 Hz). IR (thin film) ν 2955, 2926, 1804, 1700, 1577, 1458, 1247, 1179, 1047 cm^{-1}. Anal. Calcd for $C_{32}H_{48}O_4Sn$, 615.42: C, 62.45; H, 7.86. Found: C, 62.58; H, 7.81.

Stannylations of Propargyl Derivative 17. Radical Hydrostannylation. Using method **A** (80 °C, 4 h), stannylation of propargyl derivative **17** (50 mg, 0.07 mmol in 8 mL toluene) led to diennylstannanes **20a** (127 mg, 45%) and **20b** (55 mg, 19%).

Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of **17** (50 mg, 0.07 mmol) led to **20** (36 mg, 14%) and **20b** (112 mg, 44%) as colorless oils.

Stannylcupration. Using conditions $\mathbf{C_1}$, stannylation of **17** (31 mg, 0.04 mmol) gave pure **20a** (71 mg, 42%).

Stannylcupration. Using a modification of conditions $\mathbf{C_1}$, stannylation of **17** (31 mg, 0.04 mmol) (THF/MeOH 2:1) led to pure **20** (120 mg, 71%).

Stannylcupration. Using conditions $\mathbf{C_2}$, stannylation of **17** (34 mg, 0.05 mmol) gave a mixture of **20** (61 mg, 35%) and **20a** (33 mg, 19%), **20**/**20a** = 65:35.

Stannylcupration. Using a modification of conditions $\mathbf{C_2}$, stannylation of **17** (31 mg, 0.04 mmol) (THF/MeOH 2:1) led to pure **20** (127 mg, 65%).

Stannylcupration. Using conditions $\mathbf{C_3}$, stannylation of **17** (33 mg, 0.05 mmol) gave a mixture of **20** (68 mg, 25%) and **20a** (155 mg, 57%), **20**/**20a** = 30:70.

Stannylcupration. Using conditions $\mathbf{C_4}$, stannylation of **17** (55 mg, 0.08 mmol) led to pure **20** (197 mg, 70%).

(2*E*)-3-(Tributylstannyl)but-2-en-1-ol (20).[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (td, 1 H, J = 5.8, 1.7 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 64.0 Hz), 4.26 (t, 2 H, J = 5.8 Hz), 1.89 (s, 3 H, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 44.7 Hz), 1.54−1.46 (m, 7 H), 1.36−1.28 (m, 6 H), 0.97−0.82 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.6, 139.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 24.9 Hz), 59.0 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 59.0 Hz), 29.3 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 19.4 Hz), 27.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 54.8 Hz), 19.5, 13.8, 9.2 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 321.0 Hz). IR (thin film) ν 3314, 2955, 2925, 2924, 2870, 2852, 1463, 1376, 1291, 1060, 1004, 874 cm^{-1}. MS (DI, CI, NH_3) *m*/*z calculated from major ^{120}Sn isotope* 363 (MH^+, 5), 308 (100), 291 (35), 153 (10), 98 (5).

(2*Z*)-2-(Tributylstannyl)but-2-en-1-ol (20a).[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (q, 1 H, J = 6.4 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 124.7 Hz), 4.18 (d, 2 H, J = 5.5 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 38.9 Hz), 1.75 (d, 3 H, J = 6.4 Hz), 1.57−1.46 (m, 7 H) 1.36−1.28 (m, 6 H), 0.98−0.83 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.5, 136.1 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 22.0 Hz), 70.6 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 41.0 Hz), 29.3 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 18.7 Hz), 27.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 58.2 Hz), 19.6 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 33.5 Hz), 13.8, 10.2 (J ^{13}C−^{117}Sn = 318.4 Hz, J ^{13}C−^{119}Sn = 326.0 Hz). IR (thin film) ν 3329, 2956, 2925, 2871, 2852, 1626, 1463, 1376, 1066, 991, 874, 830, 668 cm^{-1}. MS (DI, CI, NH_3) *m*/*z calculated from major ^{120}Sn isotope* 363 (MH^+, 5), 308 (100), 291 (35), 235 (10), 153 (5), 102 (10).

(2*E*)-2-(Tributylstannyl)but-2-en-1-ol (20b).[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (qt, 1 H, J = 6.6, 1.9 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 68.6 Hz), 4.39 (dd, 2 H, J = 5.2, 1.9 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 40.1 Hz), 1.71 (d, 3 H, J = 6.6 Hz), 1.54−1.46 (m, 7 H), 1.37−1.28 (m, 6 H), 0.97−0.82 (m, 15H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.8, 134.1 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 22.8 Hz), 63.6 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 22.8 Hz), 29.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 18.8 Hz), 27.6 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 57.0 Hz), 15.3 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 55.6 Hz), 13.8, 10.1 (J ^{13}C−^{117}Sn = 321.3, J ^{13}C−^{119}Sn = 336.0 Hz). IR (thin film) ν 3407, 2955, 2925, 2922, 2870, 2853, 1616, 1463, 1376, 1291, 1071, 1033, 961, 874 cm^{-1}. MS (DI, CI, NH_3) *m*/*z calculated from major ^{120}Sn isotope* 363 (MH^+, 5), 308 (100), 291 (35), 235 (5), 153 (10), 98 (10).

Stannylcuprations of Propargyl Derivative 18. Stannylcupration. Using conditions $\mathbf{C_3}$, stannylation of propargyl derivative **18** (100 mg, 1.19 mmol) gave a mixture of stannanes **21** (57 mg, 13%), **21a** (90mg, 20%), **21b** (49 mg, 11%), and **21c** (50 mg, 6%), **21**/**21a**/**21b**/**21c** = 26:40:22:12.

Stannylcupration. Using conditions $\mathbf{C_4}$, stannylation of **18** (100 mg, 1.19 mmol) led to pure **21** (315 mg, 71%).

(2*E*)-3-(Tributylstannyl)pent-2-en-1-ol (21).[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (t, 1 H, J = 5.9 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 68.3 Hz), 4.26 (t, 2 H, J = 5.9 Hz), 2.29 (q, 2 H, J = 7.3 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 56.7 Hz), 1.60−1.46 (m, 6 H), 1.44−1.23 (m, 10 H), 0.97−0.87 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.1, 138.8 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 24.2 Hz), 59.0 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 60.6 Hz), 29.3 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 18.7 Hz), 27.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 55.1 Hz), 26.7 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 36.9 Hz), 15.2, 13.7, 9.9 (J ^{13}C−^{117}Sn = 313.1 Hz, J ^{13}C−^{119}Sn = 327.0 Hz). IR (thin film) ν 3300, 2956, 2926, 2870, 2853, 1463, 1376, 1072, 1019, 874, 666 cm^{-1}. MS (DI, CI, NH_3) *m*/*z calculated from major ^{120}Sn isotope* 394 (MH^+ + 17, 10), 377 (MH^+, 5), 336 (5), 308 (100), 291 (30), 196 (5), 158 (10), 141 (5), 119 (10), 102 (5), 91 (10), 69 (5). Anal. Calcd for $C_{17}H_{36}OSn$, 375.16: C, 54.43; H, 9.67. Found: C, 54.61; H, 9.58.

(2*E*)-2-(Tributylstannyl)pent-2-en-1-ol (21a).[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23 (t, 1 H, J = 7.3 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 122.7 Hz), 4.19 (d, 2 H, J = 5.4 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 38.9 Hz), 2.06 (quint, 2 H, J = 7.3 Hz), 1.53−1.47 (m, 6 H), 1.38−1.28 (m, 6 H), 1.24 (t, 1 H, J = 5.4 Hz), 1.02−0.89 (m, 18 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 22.8 Hz), 142.7 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 358.8 Hz), 70.6 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 42.2 Hz), 29.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 18.6 Hz), 27.8 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 21.9 Hz), 27.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 57.6 Hz), 14.5, 13.7, 10.4 (J ^{13}C−^{117}Sn = 318.4 Hz, J ^{13}C−^{119}Sn = 332.8 Hz). IR (thin film) ν 3313, 2957, 2926, 2871, 2852, 1622, 1376, 1081, 1001, 862, 666 cm^{-1}. MS (DI, CI, NH_3) *m*/*z calculated from major ^{120}Sn isotope* 377 (MH^+, 1), 334 (3), 308 (100), 291 (35).

(2*E*)-2-(Tributylstannyl)pent-2-en-1-ol (21b).[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (tt, 1 H, J = 7.2, 2.0 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 69.1 Hz), 4.38 (dt, 2 H, J = 5.3, 2.0 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 40.4 Hz), 2.10 (quint, 2 H, J = 7.2 Hz), 1.60−1.47 (m, 6 H), 1.38−1.30 (m, 7 H), 0.99 (t, 3 H, J = 7.5 Hz), 0.98−0.89 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.0, 142.5, 63.7 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 22.8 Hz), 29.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 18.2 Hz), 27.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 55.0 Hz), 22.9 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 53.1 Hz), 14.3, 13.7, 10.4 (J ^{13}C−^{117}Sn = 319.2 Hz, J ^{13}C−^{119}Sn = 334.8 Hz). IR (thin film) ν 3608, 3405, 2956, 2924, 2870, 2853, 1611, 1462, 1375, 1070, 1038, 1003, 960, 874, 666 cm^{-1}. MS (DI, CI, NH_3) *m*/*z calculated from major ^{120}Sn isotope* 377 (MH^+, 1), 334 (5), 308 (100), 291 (35), 235 (2).

(2*Z*)-2,3-Bis(tributylstannyl)pent-2-en-1-ol (21c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 (d, 2 H, J = 5.6 Hz, J ^{1}H−^{117}Sn^a = J ^{1}H−^{119}Sn^a = 44.8 Hz, J ^{1}H−^{117}Sn^b = J ^{1}H−^{119}Sn^b =

10.5 Hz), 2.38 (q, 2 H, J = 7.5 Hz, J ^{1}H−^{117}Sn^b = J ^{1}H−^{119}Sn^b = 55.5 Hz, J ^{1}H−^{117}Sn^a = J ^{1}H−^{119}Sn^a = 3.7 Hz), 1.53−1.45 (m, 12 H), 1.35−1.28 (m, 12 H), 1.21 (t, 1 H, J = 5.6 Hz), 0.97−0.89 (m, 33 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.6 (J ^{13}C−^{117}Sn^b = J ^{13}C−^{119}Sn^b = 53.4), 157.9 (J ^{13}C−^{117}Sn^a = J ^{13}C−^{119}Sn^a = 62.5 Hz), 63.2 (J ^{13}C−^{117}Sn^b = J ^{13}C−^{119}Sn^b = 84.7 Hz, J ^{13}C−^{117}Sn^a = J ^{13}C−^{119}Sn^a = 41.5 Hz), 29.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 19.3 Hz), 29.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 18.4 Hz), 27.6 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 60.9 Hz), 15.4, 13.7, 13.6, 11.8 (J ^{13}C−^{117}Sn = 308.7, J ^{13}C−^{119}Sn = 322.9 Hz), 11.3 (J ^{13}C−^{117}Sn = 301.6, J ^{13}C−^{119}Sn = 315.5 Hz). IR (thin film) ν 3608, 3443, 2956, 2870, 1671, 1718, 1463, 1375, 1069, 1001, 873, 665 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 665 (MH^+, 3), 411 (5), 394 (60), 378 (20), 308 (100), 291 (20), 158 (10), 102 (10). Anal. Calcd for $C_{29}H_{62}OSn_2$, 664.19: C, 52.44; H, 9.41. Found: C, 52.54; H, 9.36.

Stannylcuprations of Propargylic Alcohol 19. Stannylcupration. Using conditions **C$_3$** (−25 °C, 30 min), stannylation of propargyl alcohol **19** (50 mg, 0.09 mmol) gave a 66:10:24 mixture of **22** (127 mg, 41%), **22a** (18 mg, 6%), and **22c** (86 mg, 15%).

Stannylcupration. Using conditions **C$_4$** (−40 °C to −30 °C, 30 min), stannylation of **19** (50 mg, 0.09 mmol) led to a 65:35 mixture of **22** (162 mg, 52%) and **22a** (87 mg, 28%).

(2*E*)-3-(Tributylstannyl)prop-2-en-1-ol (22).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23 (d, 1 H, J = 19.7 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 68.7 Hz), 6.17 (dt, 1 H, J = 19.7, 4.5 Hz), 4.17 (t, 2 H, J = 4.5 Hz), 1.73 (t, 1 H, J = 4.5 Hz), 1.55−1.47 (m, 6 H), 1.35−1.28 (m, 6 H), 0.97−0.89 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 147.2, 128.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 363.9 Hz), 66.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 21.0 Hz), 29.2, 27.4, 13.8, 9.5. IR (thin film) ν 3301, 2956, 2924, 2871, 2852, 1604, 1464, 1376, 1292, 1180, 1071, 990, 874, 763, 690, 664 cm^{-1}. MS (DI, CI, NH_3) *m/z* 366 (MH^+ + 17, 10), 349 (MH^+, 15), 308 (100), 291 (40), 250 (5), 72 (5).

2-(Tributylstannyl)prop-2-en-1-ol (22a).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (d, 1 H, J = 1.8 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 128.9 Hz), 5.25 (d, 1 H, J = 1.8 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 61.5 Hz), 4.29 (t, 2 H, J = 5.9 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 30.0 Hz), 1.55−1.47 (m, 7 H), 1.35−1.28 (m, 6 H), 0.97−0.89 (m, 15 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.9, 123.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 18.2 Hz), 69.8 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 45.0 Hz), 29.3, 27.5 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 56.4 Hz), 13.8, 9.6 (J ^{13}C−^{117}Sn = 322.9, J ^{13}C−^{119}Sn = 336.6 Hz). IR (thin film) ν 3312, 2955, 2925, 2871, 2851, 1640, 1463, 1418, 1375, 1150, 1071, 1023, 919, 874 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 349 (MH^+, 5), 308 (100), 291 (40), 267 (5), 250 (5), 72 (5).

(2*Z*)-2,3-Bis(tributylstannyl)prop-2-en-1-ol (22c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (t, 1 H, J = 1.6 Hz, J ^{1}H−^{117}Sn^a = J ^{1}H−^{119}Sn^a = 174.2 Hz, J ^{1}H−^{117}Sn^b = J ^{1}H−^{119}Sn^b = 70.4 Hz), 4.25 (dd, 2 H, J = 6.1, 1.6 Hz), 1.55−1.47 (m, 13 H), 1.35−1.28 (m, 12 H), 0.97−0.89 (m, 30 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.8 (J ^{13}C−^{117}Sn^a = 383.6 Hz, J ^{13}C−^{119}Sn^a = 401.4 Hz, J ^{13}C−^{117}Sn^b = J ^{13}C−^{119}Sn^b = 34.3 Hz), 140.5 (J ^{13}C−^{117}Sn^b = 404.7 Hz, J ^{13}C−^{119}Sn^b = 423.2 Hz, J ^{13}C−^{117}Sn^a = J ^{13}C−^{119}Sn^a = 59.2 Hz), 74.3 (J ^{13}C−^{117}Sn^a = J ^{13}C−^{119}Sn^a = 68.4 Hz, J ^{13}C−^{117}Sn^b = J ^{13}C−^{119}Sn^b = 93.1 Hz), 29.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 18.0 Hz), 29.3 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 17.8 Hz), 27.8 (J ^{13}C−^{117}Sn = J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 60.3 Hz), 27.6 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 57.4 Hz), 13.8, 10.9 (J ^{13}C−^{117}Sn = 319.4, J ^{13}C−^{119}Sn = 333.7 Hz), 10.1 (J ^{13}C−^{117}Sn = 310.6, J ^{13}C−^{119}Sn = 324.7 Hz). IR (thin film) ν 3332, 2955, 2922, 2870, 2853, 2359, 1463, 1418, 1376, 1340, 1070, 1050, 960, 863, 811, 767, 668, 592 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 637 (MH^+, 2), 597 (15), 308 (100), 291 (40), 52 (2). Anal. Calcd for $C_{27}H_{58}OSn_2$, 636.13: C, 50.98; H, 9.19. Found : C, 51.29; H, 9.41.

Stannylations of Propargylic Derivatives 23a,b and 25. Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of propargyl derivative **23a** (R = H, 125 mg, 1.0 mmol) led to **24a** (R = H, 301 mg, 71%) as a colorless oil.

Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of propargyl derivative **23b** (R = MOM, 179 mg, 1.06 mmol) led to **24b** (R = MOM, 298 mg, 65%) as a colorless oil.

Pd(0)-Catalyzed Hydrostannylation. Using method **B**, stannylation of propargyl derivative **25** (100 mg, 0.397 mmol) led to **26** (151 mg, 70%) as a colorless oil.

(2*E*)-1-[2-(Tributylstannyl)ethenyl]cyclohexanol (24a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (d, 1 H, J = 19.5 Hz, J ^{1}H−^{117}Sn = 69.2 Hz, J ^{1}H−^{119}Sn = 72.2 Hz), 6.06 (d, 1 H, J = 19.5 Hz, J ^{1}H−^{117}Sn = 65.3 Hz, J ^{1}H−^{119}Sn = 68.2 Hz), 1.68−1.40 (m, 10 H), 1.50−1.40 (tt, 6 H, J = 8.1, 7.3 Hz), 1.32−1.24 (hex, 6 H, J = 7.3 Hz), 0.86 (t, 6 H, J = 8.1 Hz), 0.85 (t, 9 H, J = 7.3 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.8, 123.5 (J ^{13}C−^{117}Sn = 362.0 Hz, J ^{13}C−^{119}Sn = 380.0 Hz), 73.1 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 55.0 Hz), 37.8, 29.2 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 20.0 Hz), 27.3 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 53.0 Hz), 25.7, 22.4, 13.6, 9.6 (J ^{13}C−^{117}Sn = 326.0 Hz, J ^{13}C−^{119}Sn = 341.0 Hz). IR (thin film) ν 3373, 2926, 2852, 1597, 1464, 1376, 991, 959, 735 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 399 (MH^+ − 18, 15), 359 (80), 303 (50), 177 (50), 99 (70), 81 (90, 55 (100). Anal. Calcd for $C_{20}H_{40}OSn$, 415.23: C, 57.85; H, 9.71. Found: C, 57.90; H, 9.51.

(2*E*)-1-(Methoxymethoxy)-1-[2-(tributylstannyl)ethenyl]-cyclohexane (24b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (d, 1 H, J = 19.7 Hz, J ^{1}H−^{117}Sn = 70.3 Hz, J ^{1}H−^{119}Sn = 73.4 Hz), 5.82 (d, 1 H, J = 19.7 Hz, J ^{1}H−^{117}Sn = 65.2 Hz, J ^{1}H−^{119}Sn = 68.1 Hz), 4.59 (s, 2 H), 3.37 (s, 3 H), 1.75−1.40 (m, 10 H), 1.50−1.40 (tt, 6 H, J = 8.1, 7.3 Hz), 1.32−1.24 (hex, 6 H, J = 7.3 Hz), 0.86 (t, 6 H, J = 8.1 Hz), 0.85 (t, 9 H, J = 7.3 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.6, 128.3 (J ^{13}C−^{117}Sn = 363.0 Hz, J ^{13}C−^{119}Sn = 381.0 Hz), 91.7, 78.9 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 55.0 Hz), 55.7, 35.5, 25.9, 22.4, 29.2 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 20.0 Hz), 27.3 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 52.0 Hz) 13.8, 9.0 (J ^{13}C−^{117}Sn = 325.0 Hz, J ^{13}C−^{119}Sn = 340.0 Hz). IR (thin film) ν 2927, 2854, 1594, 1449, 1159, 1030, 998, 924 cm^{-1}. MS (DI, CI, NH_3) *m/z calculated from major ^{120}Sn isotope* 416 (30), 399 (50), 360 (25), 308 (75), 291 (20), 250 (20), 139 (100). Anal. Calcd for $C_{22}H_{44}O_2Sn$, 429.25: C, 57.53; H, 9.66. Found: C, 57.69; H, 9.54.

(2*E*)-3,3,7,7-Tetramethyl-8-[2-(tributylstannyl)ethenyl]-1,5-dioxaspiro[5.5]undecan-8-ol (26). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (d, 1 H, J = 19.3 Hz, J ^{1}H−^{117}Sn = 77.3 Hz, J ^{1}H−^{119}Sn = 80.8 Hz), 5.94 (d, 1 H, J = 19.3 Hz, J ^{1}H−^{117}Sn = J ^{1}H−^{119}Sn = 68.3 Hz), 3.67 (d, 1 H, J = 11.2 Hz), 3.64 (d, 1 H, J = 11.2 Hz), 3.37 (dd, 1 H, J = 11.2, 2.6 Hz), 3.26 (dd, 1 H, J = 11.2, 2.6 Hz), 2.55 (m, 1 H), 1.87 (td, 1 H, J = 13.4, 5.7 Hz), 1.60−1.20 (m, 16 H), 1.15 (s, 3 H), 1.06 (s, 3 H), 0.84 (m, 15 H), 0.97 (s, 3 H), 0.69 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.1, 126.7 (J ^{13}C−^{117}Sn = 379.0 Hz, J ^{13}C−^{119}Sn = 398.0 Hz), 102.6, 78.6 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 57.0 Hz), 70.1, 69.8, 45.8, 33.7, 30.1, 29.3 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 20.0 Hz), 27.4 (J ^{13}C−^{117}Sn = J ^{13}C−^{119}Sn = 52.0 Hz), 23.5, 22.4, 21.3, 15.8, 21.6, 17.6, 13.7, 9.8 (J ^{13}C−^{117}Sn = 323.0 Hz, J ^{13}C−^{119}Sn = 338.0 Hz). IR (thin film) ν 3501, 2955, 2927, 1599, 1464, 1394, 1377, 1136, 1117, 1094, 1001, 906 cm^{-1}. MS (DI, CI, NH_3) *m/z* 527 (MH^+ − 18, 5), 308 (20), 291 (45), 237 (100), 227 (25), 186 (10), 157 (10), 128 (7), 72 (15). Anal. Calcd for $C_{27}H_{52}O_3Sn$, 543.40: C: 59.68; H: 9.65. Found: C: 59.75; H: 9.58.

Acknowledgment. The CNRS, the Ecole Polytechnique and Rhône-Poulenc Rorer are acknowledged for financial support and fellowships for J.-F.B, F.D., and B.M. We would also thank Dr. J.-P. Férézou for fruitful discussions.

JO9710339