JOC Article

Stereoselective Synthesis of (*E*)-*β*-Tributylstannyl-α,*β*-unsaturated Ketones: Construction of a Key Intermediate for the Total Synthesis of Zoanthamine

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(*E*)-*β*-Trialkylstannyl-α,*β*-unsaturated ketones are readily available from secondary propargylic alcohols via a two-step sequence involving highly regio- and stereoselective Pd(0)-catalyzed hydrostannation followed by mild oxidation (TPAP). The methodology has been applied to the synthesis of enantiomerically pure enone **12** which is a key intermediate for the total synthesis of zoanthamine, a structurally complex marine natural product.

Introduction

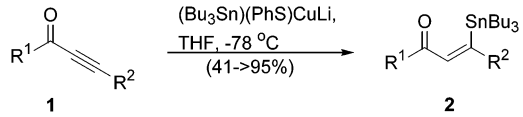
Previously,[1] we described the highly stereoselective synthesis of (*Z*)-*β*-tributylstannyl-α,*β*-unsaturated ketones **2** via addition of stannylcuprates to alkynones **1** (Scheme 1).

Our work thus complements that of Takeda[2] who has described an alternative route to these useful intermediates and has demonstrated their use in Pd(0)-catalyzed cross-coupling reactions. Piers has published yet another route which leads to the *Z* isomers of the corresponding trimethylstannyl enones.[3] A drawback with all three approaches is that (*E*)-*β*-trialkylstannyl-α,*β*-unsaturated ketones are not directly available. For example, in contrast to earlier work by Piers on the addition reactions of stannylcuprates to alkynoates[4] we were unable to find reaction conditions which would allow access to the *E* isomers of the corresponding ketones. This was of major concern for a project dealing with the total synthesis of the natural product zoanthamine **3**, a simplified retrosynthetic analysis of which[5] is shown in Figure 1.

The proposed convergent route calls for stereoselective synthesis of (*E*)-*β*-trialkylstannyl species **C** prior to cross-coupling with **B**. Since the stannylcupration route proved untenable, we turned our attention to the work of Greeves[6] who has described the regio- and stereoselective hydrostannation[7] of certain secondary propargylic alcohols **5** (Scheme 2).

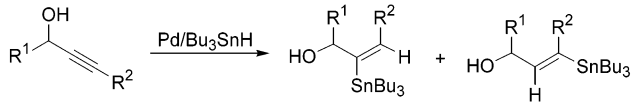
Greeves reported regioselectivities which varied widely (from 0 to 100%), but in cases of nonzero regioselectivity,

SCHEME 1



1 **2**

SCHEME 2



5 **6** (α) **7** (β)

the *β*-stannylated product always dominated.[6] We deemed this reaction worthy of further investigation, and we now wish to report (i) an extension of the Greeves work which demonstrates uniformly excellent *β*-regioselectivity; (ii) that *β*-stannyl allylic alcohols such as **7a**−**j** can be smoothly oxidized in high yields to the desired (*E*)-*β*-trialkylstannyl-α,*β*-unsaturated ketones **8a**−**j**; (iii) an application of this methodology to the synthesis of an advanced key intermediate **12** for the total synthesis of zoanthamine (cf. structure **C** in Figure 1).

Results and Discussion

We first prepared a series of propargylic secondary alcohols **5a**−**l** (Table 1) by reaction of aldehydes with lithiated acetylenes. These were then subjected to Pd-catalyzed hydrostannation according to the method of Greeves,[6] and the results are collected in Table 1.

With the exception of the reactions of the two terminal alkyne substrates (entries 11 and 12), isolated yields of product were generally very satisfactory. Furthermore, in most cases, the desired *β*-regioisomer was the *exclusive* product; in those cases (entries 5, 8−10) for which the α isomer could be detected in the crude product, it was present to the extent of <10% according to ^{1}H NMR

(1) Nielsen, T. E.; Cubillo de Dios, M. A.; Tanner, D. Submitted for publication.
(2) Takeda, T.; Kabasawa, Y.; Fujiwara, T. *Tetrahedron* **1995**, *51*, 2515.
(3) Piers, E.; Tillyer, R. D. *Can. J. Chem.* **1996**, *74*, 2048.
(4) Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron* **1989**, *45*, 363.
(5) Tanner, D.; Tedenborg, L.; Somfai, P. *Acta Chem. Scand.* **1997**, *51*, 1217.
(6) Greeves, N.; Torode, J. S. *Synlett.* **1994**, 537.
(7) Review: Smith, N. D.; Mancuso, J.; Lautens, M. *Chem. Rev.* **2000**, *100*, 3257.

10.1021/jo025902s CCC: $22.00
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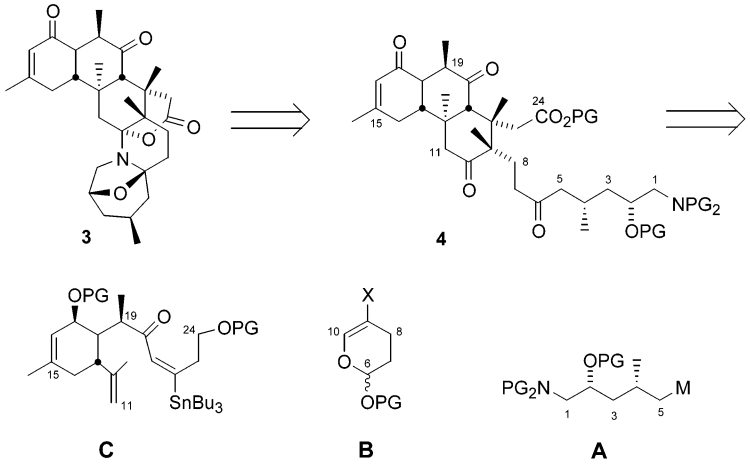
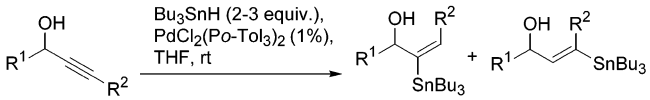


FIGURE 1. Simplified retrosynthesis of zoanthamine **3**.

TABLE 1. Hydrostannation of Propargylic Alcohols



entry	propargylic alcohol	R^1, R^2	product (yield %)[a]
1	**5a**	Cy[b], CH_2(OTBDMS)	**7a** (75)
2	**5b**	Cy, $(CH_2)_2$(OTBDMS)	**7b** (71)
3	**5c**	Cy, $(CH_2)_3$(OTBDMS)	**7c** (73)
4	**5d**	Cy, Bu	**7d** (82)
5	**5e**	*i*-Pr, $(CH_2)_2$(OTBDMS)	**7e** (70)[c]
6	**5f**	*i*-Pent, $(CH_2)_2$(OTBDMS)	**7f** (76)
7	**5g**	*t*-Bu, $(CH_2)_2$(OTBDMS)	**7g** (86)
8	**5h**	Ph, $(CH_2)_2$(OTBDMS)	**7h** (82)[c]
9	**5i**	Mes, $(CH_2)_2$(OTBDMS)	**7i** (74)[c]
10	**5j**	1-naphthyl, $(CH_2)_2$(OTBDMS)	**7j** (71)[c]
11	**5k**	*t*-Bu, H	**7k** (54)
12	**5l**	Cy, H	**7l** (40)

[a] Isolated yield of the pure *E*-*β* isomer after flash chromatography. [b] Cy = cyclohexyl. [c] Minor amounts of the α isomers **6e**, **h**-**j** (<10%) were also isolated.

spectroscopy. Pure regioisomers were obtained after flash chromatography in all cases.

The next task was to oxidize the *β*-stannyl allylic alcohols **7a**−**j** to the desired (*E*)-*β*-trialkylstannyl-α,*β*-unsaturated ketones **8a**−**j**, without isomerization to the *Z* isomers.[8] We found that this could be accomplished in excellent yield by TPAP[9] and the results are shown in Table 2.

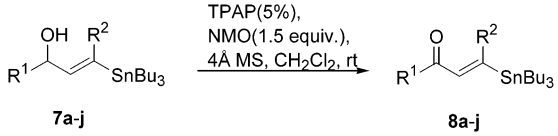
The desired products were isolated after flash chromatography and were shown to be stereoisomerically pure by ^{1}H NMR spectroscopy. Some typical data are shown in Figure 2, which allows comparison with the spectroscopic characteristics of the earlier prepared[1] *Z* isomers.

Having secured an efficient route to the desired *E* isomers, we applied the methodology to compound **12**, a projected intermediate for the zoanthamine total synthesis (Scheme 3).

(8) The *Z* isomers may well be the thermodynamically more stable, due to a stabilizing interaction between the lone pair of the carbonyl oxygen and the tin (cf. ref 3).

(9) Review: Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639.

TABLE 2. Oxidation of *β*-Stannyl Allylic Alcohols



entry	*β*-stannyl allylic alcohol	product (yield %)[a]
1	**7a**	**8a** (79)
2	**7b**	**8b** (89)
3	**7c**	**8c** (92)
4	**7d**	**8d** (76)
5	**7e**	**8e** (90)
6	**7f**	**8f** (94)
7	**7g**	**8g** (74)
8	**7h**	**8h** (92)
9	**7i**	**8i** (91)
10	**7j**	**8j** (88)

[a] Isolated yield after flash chromatography.

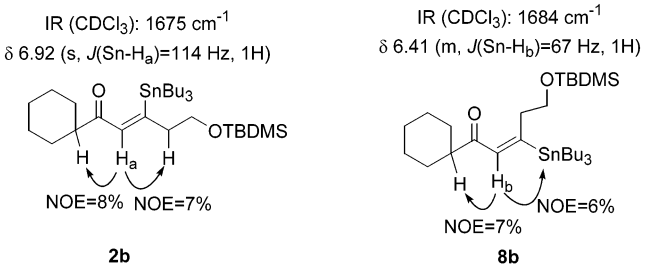
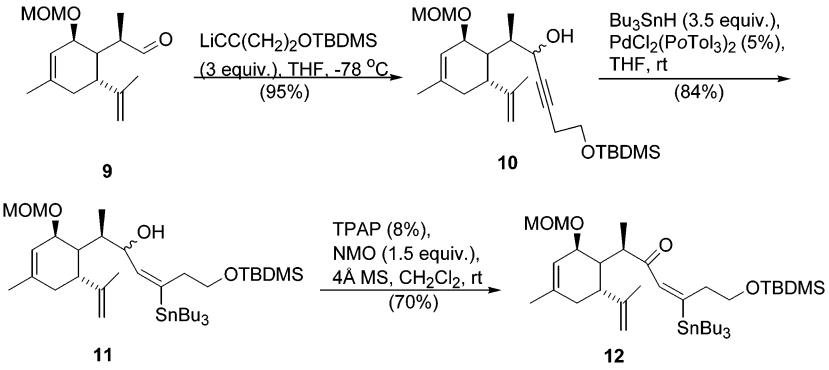


FIGURE 2. Spectroscopic data for (*Z*)- and (*E*)-*β*-(tributylstannyl)-α,*β*-unsaturated ketones.

The enantiomerically pure aldehyde **9** was transformed to the previously reported[5] propargylic alcohol **10** in standard fashion, affording a 2:1 mixture of diastereomers. Since the newly formed stereogenic center is later destroyed, the mixture of alcohols was used in the hydrostannation reaction which proceeded in excellent yield and with complete *β*-regioselectivity. The hydrostannylated products could be separated chromatographically and fully characterized (see Experimental Section). The mixture of vinylstannanes **11** was oxidized cleanly by TPAP to a single ketone **12** in good yield, thus completing the synthesis of a substantial portion of the target molecule. With intermediates corresponding to all three

SCHEME 3



major fragments in Scheme 1 now at hand, the zoanthamine end-game can commence and details will be reported separately.

Conclusions

We have described a convenient route to (*E*)-*β*-trialkylstannyl-α,*β*-unsaturated ketones **8a**−**j**, which relies on regio- and stereoselective Pd(0)-catalyzed hydrostannation of secondary propargylic alcohols **6a**−**j** followed by TPAP oxidation. In conjunction with our earlier work,[1] the present study means that both the *E* and *Z* isomers of these versatile building blocks are now readily available in regio- and stereoisomerically pure form. The present methodology has been applied to the preparation of an advanced key intermediate **12** for the total synthesis of the marine alkaloid zoanthamine **3**.

Experimental Section

General Methods. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded using $CDCl_3$ as the solvent, and signal positions (*δ*-values) were measured relative to the signals for $CHCl_3$ (7.27) and $CDCl_3$ (77.0), respectively. Tin−hydrogen coupling constants, *J*(Sn−H), are given as the average of the ^{117}Sn and ^{119}Sn values, due to overlap of the satellite peaks. IR spectra were obtained for thin films on AgCl plates, and only the strongest/structurally most important peaks (ν_{max}/cm^{-1}) are listed. Optical rotations were measured at ambient temperature. Microanalyses were performed by the Microanalysis Laboratory, Department of Physical Chemistry, University of Vienna, Austria, and at the Department of Chemistry, University of Bath, England. HRMS was performed at the Department of Chemistry, University of Copenhagen, Denmark, and the Department of Chemistry, University of Bath, England. Molecular mass determinations (high-resolution mass spectrometry) for substances containing a Bu_3Sn group are based on ^{120}Sn and typically made on the $[M - Bu]^+$, unless otherwise stated. All compounds on which HRMS was performed exhibited clean ^{1}H NMR spectra and showed one spot on TLC analysis. TLC analyses were performed on Merck aluminum-backed F254 silica gel plates, using UV light, and a solution of 5−10% phosphomolybdic acid in ethanol for visualization. Column chromatography was performed using Amicon Matrex silica gel (35−70 *μ*m). All solvents were distilled prior to use. THF was distilled under nitrogen from Na−benzophenone. Dichloromethane was dried over calcium hydride and distilled under nitrogen. Commercially available compounds were used as received unless otherwise indicated (important: the quality of the tributyltin hydride batch was essential for the outcome of the hydrostannation reactions). All reactions were carried out under an atmosphere of dry argon using carefully flame-dried glassware. Argon gas was dried by passage through phosphorus pentoxide and silica gel.

General Procedure for Preparation of Propargylic Alcohols 5a−**l.** To a solution of the freshly distilled alkyne, or acetylene gas, (30.0 mmol) in THF (100 mL) was added dropwise *n*-butyllithium (1.6 M in hexanes, 18.75 mL, 30.0 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min and then at −30 °C for 30 min, before recooling to −78 °C and dropwise addition of the aldehyde (30.0 mmol). After being stirred for 1 h at −78 °C, the reaction mixture was allowed to reach rt. A mixture of ether (125 mL) and sat. sodium bicarbonate (200 mL) was added, and the organic layer was separated, washed with brine (2 × 100 mL), dried over magnesium sulfate, filtered, and rotary evaporated. The residue was purified by flash column chromatography on silica gel (hexane:ethyl acetate, 15:1−5:1) to give the propargylic alcohols **5a**−**l** as colorless oils.

Analytical data for compounds **5a**−**l**:

4-(*tert*-Butyldimethylsilanyloxy)-1-cyclohexylbut-2-yn-1-ol (5a).[10] Yield: 83%; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 4.36 (dd, *J* = 1 Hz, *J* = 2 Hz, 2H), 4.22−4.15 (m, 1H), 1.91−1.47 (m, 7H), 1.35−0.82 (m, 4H), 0.92 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 84.8, 84.3, 67.2, 51.7, 44.1, 28.5, 28.1, 26.4, 25.9 (two signals), 25.8, 18.3, −5.1.

5-(*tert*-Butyldimethylsilanyloxy)-1-cyclohexylpent-2-yn-1-ol (5b). Yield: 87%; IR ($CDCl_3$): 2939, 1472, 1378, 1252, 1102, 1004; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 4.13 (m, 1H), 3.73 (t, *J* = 7 Hz, 2H), 2.45 (dt, *J* = 2 Hz, *J* = 7 Hz, 2H), 1.91−0.80 (m, 11H), 0.91 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 83.0, 81.3, 67.3, 61.9, 44.3, 28.6, 28.2, 26.4, 25.9 (three signals), 23.2, 18.3, −5.3; Anal. Calcd for $C_{17}H_{32}O_2Si$: C, 68.86; H, 10.88. Found: C, 68.62; H, 10.64.

6-(*tert*-Butyldimethylsilanyloxy)-1-cyclohexylhex-2-yn-1-ol (5c).[11] Yield: 81%; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 4.17−4.09 (m, 1H), 3.70 (t, *J* = 6 Hz, 2H), 2.31 (dt, *J* = 2 Hz, *J* = 7 Hz, 2H), 1.72−1.45 (m, 9H), 1.40−0.82 (m, 4H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 85.7, 80.3, 67.4, 61.6, 44.4, 31.7, 28.6, 28.1, 26.4, 25.9 (two signals), 18.3, 15.1, −5.3.

1-Cyclohexylhept-2-yn-1-ol (5d).[12] Yield: 91%; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 4.15−4.09 (m, 1H), 2.20 (dt, *J* = 2 Hz, *J* = 7 Hz, 2H), 1.95−0.85 (m, 15H), 0.90 (t, *J* = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 86.2, 80.1, 67.4, 44.4, 30.8, 28.6, 28.1, 26.5, 25.9 (two signals), 21.9, 18.4, 13.5.

7-(*tert*-Butyldimethyl-3silanyloxy)-2-methylhept-4-yn-3-ol (5e).[3] Yield: 83%; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 4.18−4.11 (m, 1H), 3.72 (t, *J* = 7 Hz, 2H), 2.44 (dt, *J* = 2 Hz, *J* = 7 Hz, 2H), 1.92−1.74 (m, 1H), 0.99 (d, *J* = 7 Hz, 3H), 0.98 (d, *J* = 7 Hz, 3H), 0.92 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 82.9, 81.0, 68.0, 61.9, 34.6, 25.9, 23.1, 18.1, 17.5, −5.3.

7-(*tert*-Butyldimethylsilanyloxy)-2,2-dimethylhept-4-yn-3-ol (5f). Yield: 96%; IR ($CDCl_3$): 3406, 2960, 1464, 1382, 1256, 1105, 1006, 912, 836, 776, 735; ^{1}H NMR (300 MHz,

(10) Frantz, D. E.; Faessler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 1806.

(11) Fournier-Nguefack, C.; Lhoste, P.; Sinou, D. *J. Chem. Res. Miniprint* **1998**, *3*, 614.

$CDCl_3$) δ 4.42−4.36 (m, 1H), 3.71 (t, J = 7 Hz, 2H), 2.43 (dt, J = 2 Hz, J = 7 Hz, 2H), 1.67−1.25 (m, 5H), 0.98−0.88 (m, 6H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 82.9, 81.4, 64.9, 61.9, 47.5, 25.9, 23.2, 22.0, 21.8, 18.3, 11.6, 11,5, −5.3; Anal. Calcd for $C_{16}H_{32}O_2Si$: C, 67.54; H, 11.34. Found: C, 67.65; H, 11.26.

7-(*tert*-Butyldimethylsilanyloxy)-2,2-dimethylhept-4-yn-3-ol (5g).[13] Yield: 94%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.98 (bs, 1H), 3.71 (t, J = 7 Hz, 2H), 2.43 (dt, J = 2 Hz, J = 7 Hz, 2H), 0.98 (s, 9H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.0, 80.9, 71.5, 61.9, 35.7, 25.9, 25.3, 23.1, 18.3, −5.3.

5-(*tert*-Butyldimethylsilanyloxy)-1-phenylpent-2-yn-1-ol (5h).[14] Yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58−7.51 (m, 2H), 7.41−7.28 (m, 3H), 5.45 (bs, 1H), 3.76 (t, J = 7 Hz, 2H), 2.50 (dt, J = 2 Hz, J = 7 Hz, 2H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 128.4, 128.1, 126.6, 84.3, 81.1, 64.6, 61.7, 25.8, 23.2, 18.3, −5.3.

5-(*tert*-Butyldimethylsilanyloxy)-1-(2,4,6-trimethylphenyl)pent-2-yn-1-ol (5i). Yield: 82%; IR ($CDCl_3$): 3414, 2928, 1611, 1472, 1256, 1106, 1006; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (s, 2H), 5.90−5.85 (m, 1H), 3.71 (t, J = 7 Hz, 2H), 2.49 (s, 6H), 2.43 (dt, J = 2 Hz, J = 7 Hz, 2H), 2.25 (s, 3H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 136.3, 133.9, 129.9, 83.2, 80.8, 61.7, 60.4, 25.8, 23.3, 20.8, 20.2, 18.3, −5.3; Anal. Calcd for $C_{20}H_{32}O_2Si$: C, 72.23; H, 9.70. Found: 72.13, 9.75.

5-(*tert*-Butyldimethylsilanyloxy)-1-naphthalen-1-ylpent-2-yn-1-ol (5j). Yield: 74%; IR ($CDCl_3$): 3398, 2928, 2856, 1472, 1388, 1256, 1105, 1057; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34−8.27 (m, 1H), 7.92−7.81 (m, 3H), 7.60−7.44 (m, 3H), 6.12 (s, 1H), 3.77 (t, J = 7 Hz, 2H,), 2.52 (dt, J = 1 Hz, J = 7 Hz, 2H), 2.25 (bs, 1H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0, 134.0, 130.5, 129.1, 128.6, 126.2, 125.7, 125.2, 124.4, 124.0, 85.1, 80.8, 62.9, 61.7, 25.9, 23.3, 18.3, −5.3; Anal. Calcd for $C_{21}H_{28}O_2Si$: C, 74.07; H, 8.29. Found: 73.82, 8.21.

4,4-Dimethylpent-1-yn-3-ol (5k).[15] Yield: 68%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.04 (d, J = 2 Hz, 1H), 2.48 (d, J = 2 Hz, 1H), 1.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.6, 73.6, 70.9, 35.4, 25.0.

1-Cyclohexylprop-2-yn-1-ol (5l).[16] Yield: 69%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.23−4.10 (m, 1H), 2.48 (d, J = 2 Hz, 1H), 1.85−0.90 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.9, 73.6, 67.0, 43.9, 28.3, 27.9, 26.4, 25.8 (two signals).

Preparation of $PdCl_2(P(o\text{-}Tol)_3)_2$. To a solution of $PdCl_2(MeCN)_2$ (426 mg, 1.64 mmol) in benzene (25 mL) was added in one portion solid tri-*o*-tolylphosphine (1.00 g, 3.29 mmol). The reaction mixture was stirred overnight at room temperature to afford a suspension of a yellow solid, which was cautiously filtered, and washed with several portions of benzene. The product was dried under high vacuum, affording the title compound (1.25 g, 97%) as a yellow powder.

General Procedure for Hydrostannation of Propargylic Alcohols 7a−l. To a solution of $PdCl_2(P(o\text{-}Tol)_3)_2$ (8 mg, 0.01 mmol) and the propargylic alcohol (1.0 mmol) in THF (2.0 mL) was added *dropwise* tributyltin hydride (364 mg, 1.25 mmol) during 0.5 h. The reaction mixture was stirred at room temperature for 1 h, and another amount of tributyltin hydride (364 mg, 1.25 mmol) was *dropwise* added during 0.5 h, followed by stirring overnight. The reaction mixture was added to ether (50 mL) and filtered through a pad of Celite. The volatiles were removed in vacuo, and the residue was purified by flash column chromatography on silica gel (hexane:ethyl acetate, 25:1−15:1) giving the β-stannyl allylic alcohols **7a−l** as colorless oils.

(12) Tzalis, D.; Knochel, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1463.
(13) Maynard, D. F.; Okamura, W. H. *J. Org. Chem.* **1995**, *60*, 1763.
(14) Edwards, N.; Macritchie, J. A.; Parsons, P. J.; Drew, M. G. B.; Jahans, A. W. *Tetrahedron* **1997**, *53*, 12651.
(15) Henderson, M. A.; Heathcock, C. H. *J. Org. Chem.* **1988**, *53*, 4736.
(16) Feldman, K. S.; Bruendl, M. M.; Schildknegt, K.; Bohnstedt, A. C. *J. Org. Chem.* **1996**, *61*, 5440.

Analytical data for compounds **5a−l**:

(*E*)-4-(*tert*-Butyldimethylsilanyloxy)-1-cyclohexyl-3-(tributylstannyl)but-2-en-1-ol (7a). Yield: 75%; IR (neat): 3381, 2926, 1462, 1254, 1073; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.48 (d, J = 8 Hz, J(Sn−H) = 71 Hz, 1H), 4.48 (dd, J = 2 Hz, J = 13 Hz, J(Sn−H) = 53 Hz, 1H), 4.26 (dd, J = 1 Hz, J = 13 Hz, J(Sn−H) = 43 Hz, 1H), 4.10−3.97 (m, 1H), 1.94−1.04 (m, 22H), 1.04−0.75 (m, 15H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 138.9, 72.9, 64.6, 44.0, 29.2, 28.8, 28.4, 27.4, 26.5, 26.1, 26.0, 18.5, 13.7, 10.2, −5.3 (two signals); Anal. Calcd for $C_{28}H_{58}O_2SiSn$: C, 58.63; H, 10.19. Found: C, 59.05; H, 10.24; HRMS (FAB) calcd for $C_{24}H_{49}O_2SiSn$ [M − C_4H_9]$^+$ 517.2524, found 517.2515.

(*E*)-5-(*tert*-Butyldimethylsilanyloxy)-1-cyclohexyl-3-tributylstannylpent-2-en-1-ol (7b). Yield: 71%; IR ($CDCl_3$): 3461, 2926, 1464, 1256, 1088, 1004; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (d, J = 8 Hz, J(Sn−H) = 70 Hz, 1H), 4.18−4.06 (m, 1H), 3.71−3.58 (m, 1H), 3.58−3.44 (m, 1H), 2.93−2.54 (m, 1H), 2.52−2.33 (m, 1H), 2.26 (bs, 1H), 2.01−1.90 (m, 1H), 1.81−1.09 (m, 22H), 1.04−0.76 (m, 15H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 143.6, 70.9, 62.7, 43.5, 36.9, 29.2, 29.0, 28.8, 27.4, 26.7, 26.2, 26.1 (two signals), 18.6, 13.7, 9.8, −5.3 (two signals); Anal. Calcd for $C_{29}H_{60}O_2SiSn$: C, 59.28; H, 10.29. Found: C, 59.38; H, 10.08; HRMS (FAB) calcd for $C_{25}H_{51}O_2SiSn$ [M − C_4H_9]$^+$ 529.2680, found 529.2682.

(*E*)-6-(*tert*-Butyldimethylsilanyloxy)-1-cyclohexyl-3-(tributylstannyl)hex-2-en-1-ol (7c). Yield: 73%; IR ($CDCl_3$): 3454, 2930, 1464, 1377, 1256, 1096, 1005; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 (d, J = 9 Hz, J(Sn−H) = 72 Hz, 1H), 4.25−4.12 (m, 1H), 3.61 (t, J = 7 Hz, 2H), 2.68−2.36 (m, 1H), 2.3 6−2.12 (m, 1H), 2.01−1.91 (m, 1H), 1.88 (d, J = 3 Hz, 1H), 1.81−1.05 (m, 24H), 1.00−0.76 (m, 15H), 0.90 (s, 9H), 0.06 (2×s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 142.9, 70.9, 62.3, 43.8, 33.3 29.7, 29.2, 29.0, 28.9, 27.4, 26.2, 26.1, 25.9, 18.3, 13.7, 9.8, −5.2, −5.3.; Anal. Calcd for $C_{30}H_{62}O_2SiSn$: C, 59.89; H, 10.39. Found: C, 60.13; H, 10.48; HRMS (FAB) calcd for $C_{26}H_{53}O_2SiSn$ [M − C_4H_9]$^+$ 543.2837, found 543.2884.

(*E*)-Cyclohexyl-3-(tributylstannyl)hept-2-en-1-ol (7d). Yield: 82%; IR ($CDCl_3$): 3386, 2924, 1451, 1376, 1079, 1012; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.49 (d, J = 9 Hz, J(Sn−H) = 71 Hz, 1H), 4.26−4.14 (m, 1H), 2.43−2.12 (m, 2H), 1.99−1.88 (m, 1H), 1.82−1.07 (m, 26H), 1.03−0.76 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 141.6, 71.5, 44.1, 33.5, 32.9, 29.2, 28.9, 28.8, 27.4, 26.7, 26.3, 26.1, 22.8, 14.0, 13.7, 9.9; Anal. Calcd for $C_{25}H_{50}OSn$: C, 61.86; H, 10.38. Found: C, 61.86; H, 10.56 (FAB) calcd for $C_{21}H_{41}OSn$ [M − C_4H_9]$^+$ 427.2179, found 427.2192.

(*E*)-7-(*tert*-Butyldimethylsilanyloxy)-2-methyl-5-(tributylstannyl)hept-4-en-3-ol (7e). Yield: 70%; IR ($CDCl_3$): 3449, 2957, 1464, 1377, 1256, 1081, 1006; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73 (d, J = 8 Hz, J(Sn−H) = 71 Hz, 1H), 4.20−4.05 (m, 1H), 3.80−3.62 (m, 1H), 3.60−3.46 (m, 1H), 2.98−2.60 (m, 1H), 2.52−2.27 (m, 1H), 2.45 (d, J = 4 Hz, 1H), 1.80−1.62 (m, 1H), 1.61−1.22 (m, 12H), 0.97 (d, J = 7 Hz, 6H), 0.97−0.76 (m, 15H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 143.9, 71.6, 62.6, 36.9, 33.6, 29.1, 27.4, 26.1, 18.6, 18.4, 18.3, 13.7, 9.8, −5.3 (two signals); Anal. Calcd for $C_{26}H_{56}O_2SiSn$: C, 57.04; H, 10.31. Found: C, 57.33; H, 10.37; HRMS (FAB) calcd for $C_{22}H_{47}O_2SiSn$ [M − C_4H_9]$^+$ 489.2367, found 489.2349.

(*E*)-8-(*tert*-Butyldimethylsilanyloxy)-3-ethyl-6-(tributylstannyl)oct-5-en-4-ol (7f). Yield: 76%; IR ($CDCl_3$): 3448, 2958, 2927, 1465, 1377, 1256, 1089, 1005; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75 (d, J = 8 Hz, J(Sn−H) = 70 Hz, 1H), 4.45−4.28 (m, 1H), 3.80−3.59 (m, 1H), 3.58−3.46 (m, 1H), 2.95−2.62 (m, 1H), 2.50−2.26 (m, 1H), 2.40 (d, J = 2 Hz, 1H,), 1.63−1.12 (m, 16H), 1.02−0.77 (m, 15H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 142.9, 128.3, 74.0, 62.6, 36.9, 34.5, 29.1, 27.4, 26.0, 25.6, 18.5, 13.7, 9.8, −5.3; Anal. Calcd for $C_{28}H_{60}O_2SiSn$: C, 58.43; H, 10.51. Found: C,

58.63; H, 10.68; HRMS (FAB) calcd for $C_{24}H_{51}O_2SiSn$ [M − C_4H_9]$^+$ 517.2680, found 517.2685.

(*E*)-7-(*tert*-Butyldimethylsilanyloxy)-2,2-dimethyl-5-(tributylstannyl)hept-4-en-3-ol (7g). Yield: 86%; IR (neat): 3468, 1463, 1254, 1089, 1002; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (d, J = 8 Hz, J(Sn−H) = 71 Hz, 1H), 4.13−4.05 (m, 1H), 3.72−3.60 (m, 1H), 3.59−3.46 (m, 1H), 2.92−2.61 (m, 1H), 2.55−2.26 (m, 1H), 2.19 (d, J = 3 Hz, 1H), 1.63−1.20 (m, 12H), 1.01−0.77 (m, 15H), 0.92 (s, 9H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 142.9, 128.3, 74.0, 62.6, 34.5, 29.1, 27.4, 26.0, 25.6, 18.5, 13.7, 9.8, −5.3; Anal. Calcd for $C_{27}H_{58}O_2SiSn$: C, 57.75; H, 10.41. Found: C, 57.80; H, 10.25; HRMS (FAB) calcd for $C_{23}H_{49}O_2SiSn$ [M − C_4H_9]$^+$ 503.2524, found 503.2534.

(*E*)-5-(*tert*-Butyldimethylsilanyloxy)-1-phenyl-3-(tributylstannyl)pent-2-en-1-ol (7h). Yield: 82%; IR (neat): 3421, 2926, 1461, 1254, 1086, 1013; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.19 (m, 5H), 5.92 (d, J = 8 Hz, J(Sn−H) = 67 Hz, 1H), 5.53 (dd, J = 2 Hz, J = 8 Hz, 1H), 3.80−3.67 (m, 1H), 3.65−3.51 (m, 1H), 3.14 (d, J = 2 Hz, 1H), 3.06−2.76 (m, 1H), 2.64−2.31 (m, 1H), 1.54−1.18 (m, 12H), 0.99−0.76 (m, 15H), 0.91 (s, 9H), 0.09 (2 × s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 144.2, 144.1, 128.3, 126.9, 126.1, 68.5, 62.3, 36.8, 29.0, 27.4, 26.1, 18.6, 13.7, 9.7, −5.4 (two signals); Anal. Calcd for $C_{29}H_{54}O_2SiSn$: C, 59.90; H, 9.36. Found: C, 59.55; H, 9.37; HRMS (FAB) calcd for $C_{25}H_{45}O_2SiSn$ [M − C_4H_9]$^+$ 523.2211, found 523.2204.

(*E*)-5-(*tert*-Butyldimethylsilanyloxy)-3-(tributylstannyl)1-(2,4,6-trimethylphenyl)-pent-2-en-1-ol (7i). Yield: 74%; IR ($CDCl_3$): 3420, 2957, 2928, 1464, 1376, 1256, 1004; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 2H), 6.13 (d, J = 6 Hz, J(Sn−H) = 68 Hz, 1H), 5.85 (dd, J = 1 Hz, J = 6 Hz, 1H), 3.81−3.71 (m, 1H), 3.63−3.52 (ddd [app. dt], J = 4 Hz, J = 10 Hz, 1H), 3.43 (d, J = 2 Hz, 1H), 3.06−2.92 (m, 1H), 2.46−2.35 (m, 1H), 2.40 (s, 6H), 2.25 (s, 3H), 1.60−1.21 (m, 12H), 1.00−0.75 (m, 15H), 0.91 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 145.0, 136.7, 136.5, 136.3, 129.8, 66.1, 62.2, 37.0, 29.1, 27.4, 26.1, 20.8, 18.5, 13.7, 9.8, −5.4 (two signals); Anal. Calcd for $C_{32}H_{60}O_2SiSn$: C, 61.63; H, 9.70. Found: C, 61.85; H, 9.71; HRMS (FAB) calcd for $C_{28}H_{51}O_2SiSn$ [M − C_4H_9]$^+$ 565.2680, found 565.2669.

(*E*)-5-(*tert*-Butyldimethylsilanyloxy)-1-naphthalen-1-yl-3-tributylstannylpent-2-en-1-ol (7j). Yield: 71%; IR ($CDCl_3$): 3423, 2925, 1464, 1376, 1256, 1081, 1005; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07−7.98 (m, 1H), 7.90−7.73 (m, 3H), 7.54−7.39 (m, 3H), 6.19−6.07 (m, 1H), 6.06 (d, J = 7 Hz, J(Sn−H) = 66 Hz, 1H), 3.95−3.82 (m, 1H), 3.83 (d, J = 2 Hz, 1H), 3.71−3.58 (m, 1H), 3.42−3.05 (m, 1H), 2.65−2.42 (m, 1H), 1.58−1.34 (m, 12H), 0.96 (s, 9H), 0.96−0.74 (m, 15H), 0.14 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4, 145.2, 139.6, 133.9, 130.6, 128.6, 127.5, 125.5, 125.4, 125.2, 124.2, 123.2, 66.4, 62.2, 36.9, 29.1, 27.4, 26.1, 18.7, 13.6, 9.8, −5.3 (two signals); Anal. Calcd for $C_{33}H_{56}O_2SiSn$: C, 62.75; H, 8.94. Found: C, 62.80; H, 8.83; HRMS (FAB) calcd for $C_{29}H_{47}O_2SiSn$ [M − C_4H_9]$^+$ 573.2367, found 573.2382.

(*E*)-4,4-Dimethyl-1-(tributylstannyl)pent-1-en-3-ol (7k). Yield: 54%; IR (neat): 3423, 2956, 2926, 1594, 1461, 1376, 1075; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32−5.95 (m, 2H), 3.73 (t, J = 5 Hz, 1H), 1.67−1.05 (m, 12H), 1.03−0.77 (m, 15H), 0.92 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 129.6, 83.5, 34.8, 29.1, 27.2, 25.7, 13.7, 9.6; HRMS (FAB) calcd for $C_{15}H_{31}OSn$ [M − C_4H_9]$^+$ 347.1397, found 347.1432.

(*E*)-Cyclohexyl-3-(tributylstannyl)prop-2-en-1-ol (7l). Yield: 40%; IR (neat): 3428, 2923, 1642, 1451, 1376, 1260, 1072, 1017; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.29−5.84 (2H, m), 3.83 (1H, dd, J = 5 Hz, J = 10 Hz), 3.28−3.15 (1H, m), 1.90−0.65 (37H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 128.7, 80.1, 43.5, 29.2, 28.9, 28.4, 27.3, 26.6, 26.2 (two signals), 13.7, 9.6; HRMS (FAB) calcd for $C_{17}H_{33}OSn$ [M − C_4H_9]$^+$ 373.1553, found 373.1611.

General Procedure for Oxidation of β-Stannyl Allylic Alcohols 7a−j. To a slurry of freshly activated and finely pulverized 4 Å molecular sieves (1 g) in dichloromethane (2 mL) were added 4-methylmorpholine *N*-oxide (22 mg, 0.19 mmol) and a solution of the β-stannyl allylic alcohol (0.105 mmol) in dichloromethane (1 mL). The reaction mixture was stirred for 10 min, before the addition of tetrapropylammonium perruthenate (2.1 mg, 0.006 mmol). The reaction mixture was stirred overnight and diluted with dichloromethane (50 mL) before filtering off the molecular sieves, which were washed with further amounts of dichloromethane (3 × 25 mL). The combined organic phases were concentrated, and then was added the minimum amount of dichloromethane to redissolve the thick, dark oil, which was purified by flash column chromatography on silica gel (petroleum ether:ethyl acetate, 50:1−35:1) to give the oxidation products **8a−j** as colorless oils.

(*E*)-4-(*tert*-Butyldimethylsilanyloxy)-1-cyclohexyl-3-(tributylstannyl)but-2-en-1-one (8a). Yield: 79%; IR (CH_2Cl_2): 2928, 1677, 1574, 1463, 1254, 1070; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.35 (m, J(Sn−H) = 66 Hz, 1H), 4.82 (d, J = 3 Hz, J(Sn−H) = 28 Hz, 2H), 2.50−2.33 (m, 1H), 1.97−1.10 (m, 25H), 1.10−0.80 (m, 12H), 0.92 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8, 179.9, 130.1, 68.9, 50.8, 29.1, 28.5, 27.4, 26.3, 25.9, 25.8, 18.7, 13.7, 11.0, −5.2; Anal. Calcd for $C_{28}H_{56}O_2SiSn$: C, 58.84; H, 9.88. Found: C, 58.49; H, 10.10; HRMS (FAB) calcd for $C_{24}H_{47}O_2SiSn$ [M − C_4H_9]$^+$ 513.2367, found 513.2401.

(*E*)-5-(*tert*-Butyldimethylsilanyloxy)-1-cyclohexyl-3-(tributylstannyl)pent-2-en-1-one (8b). Yield: 89%; IR ($CDCl_3$): 2929, 1684, 1569, 1464, 1255, 1087; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.41 (m, J(Sn−H) = 67 Hz, 1H), 3.66 (t, J = 7 Hz, 2H), 2.99 (t, J = 7 Hz, J(Sn−H) = 55 Hz, 2H), 2.40−2.25 (m, 1H), 1.90−1.12 (m, 22H), 1.00−0.82 (m, 15H), 0.88 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.3, 167.1, 137.2, 63.1, 51.2, 39.4, 29.1, 28.6, 27.4, 26.1, 26.0, 25.8, 18.5, 13.7, 10.2, −5.2; Anal. Calcd for $C_{29}H_{58}O_2SiSn$: C, 59.48; H, 9.98. Found: C, 59.24; H, 9.78; HRMS (FAB) calcd for $C_{25}H_{49}O_2SiSn$ [M − C_4H_9]$^+$ 527.2524, found 527.2527.

(*E*)-6-(*tert*-Butyldimethylsilanyloxy)-1-cyclohexyl-3-(tributylstannyl)hex-2-en-1-one (8c). Yield: 92%; IR (CH_2Cl_2): 2928, 1681, 1568, 1457, 1377, 1252, 1096; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.34 (bs, J(Sn−H) = 67 Hz, 1H), 3.62 (t, J = 7 Hz, 2H), 2.77 (m, J(Sn−H) = 58 Hz, 2H), 2.33 (m, 1H), 1.90−1.11 (m, 24H), 1.09−0.83 (m, 15H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 171.5, 135.5, 63.2, 51.1, 32.9, 32.4, 28.9, 28.5, 27.3, 25.9, 25.8, 18.3, 13.7, 10.0, −5.3; Anal. Calcd for $C_{30}H_{60}O_2SiSn$: C, 60.09; H, 10.09. Found: C, 59.68; H, 9.81; HRMS (FAB) calcd for $C_{26}H_{51}O_2SiSn$ [M − C_4H_9]$^+$ 541.2680, found 541.2688.

(*E*)-1-Cyclohexyl-3-(tributylstannyl)hept-2-en-1-one (8d). Yield: 76%; IR (CH_2Cl_2): 2927, 1682, 1568, 1455, 1374, 1145, 1070; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.33 (bs, J(Sn−H) = 68 Hz, 1H), 2.76 (m, J(Sn−H) = 59 Hz, 2H), 2.34 (m, 1H), 1.91−1.10 (m, 26H), 1.06−0.83 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.6, 172.0, 135.3, 51.2, 35.5, 32.0, 29.0, 28.5, 27.3, 26.0, 25.8, 22.9, 14.0, 13.7, 10.0; Anal. Calcd for $C_{25}H_{48}OSn$: C, 62.12; H, 10.01. Found: C, 62.01; H, 9.99; HRMS (FAB) calcd for $C_{21}H_{39}OSn$ [M − C_4H_9]$^+$ 425.2023, found 425.2024.

(*E*)-7-(*tert*-Butyldimethylsilanyloxy)-2-methyl-5-(tributylstannyl)hept-4-en-3-one (8e). Yield: 90%; IR (CH_2Cl_2): 2927, 1686, 1569, 1463, 1380, 1254, 1088; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.42 (bs, J(Sn−H) = 66 Hz, 1H), 3.66 (t, J = 7 Hz, 2H), 3.01 (dt, J = 7 Hz, J = 1 Hz, J(Sn−H) = 55 Hz, 2H), 2.62 (hept, J = 7 Hz, 1H), 1.64−1.19 (m, 12H), 1.02−0.83 (m, 15H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.9, 167.8, 136.7, 63.0, 41.2, 39.3, 29.0, 27.4, 26.0, 18.4, 18.2, 13.7, 10.1, −5.2; Anal. Calcd for $C_{26}H_{54}O_2SiSn$: C, 57.25; H, 9.98. Found: C, 57.21; H, 9.96; HRMS (FAB) calcd for $C_{22}H_{45}O_2SiSn$ [M − C_4H_9]$^+$ 487.2211, found 487.2218.

(*E*)-8-(*tert*-Butyldimethylsilanyloxy)-3-ethyl-6-(tributylstannyl)oct-5-en-4-one (8f). Yield: 94%; IR (CH_2Cl_2): 2927, 1681, 1567, 1462, 1380, 1254, 1089. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.41 (bs, J(Sn−H) = 66 Hz, 1H), 3.67 (t, J = 7 Hz, 2H), 3.03 (dt, J = 7 Hz, J = 1 Hz, J(Sn−H) = 55 Hz, 2H), 2.30

(m, 1H), 1.71−1.22 (m, 16H), 1.10−0.80 (m, 21H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.8, 167.8, 137.5, 63.1, 55.9, 39.4, 29.0, 27.4, 26.0, 24.4, 18.5, 13.7, 11.9, 10.1, −5.2; Anal. Calcd for $C_{28}H_{58}O_2SiSn$: C, 58.63; H, 10.19. Found: C, 58.26; H, 9.84; HRMS (FAB) calcd for $C_{24}H_{49}O_2SiSn$ $[M - C_4H_9]^+$ 515.2524, found 515.2539.

(*E*)-7-(*tert*-Butyldimethylsilanyloxy)-2,2-dimethyl-5-(tributylstannyl)hept-4-en-3-one (8g). Yield: 74%; IR (CH_2Cl_2): 2942, 1680, 1568, 1465, 1370, 1255, 1077, 1004; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.62 (m, J(Sn−H) = 68 Hz, 1H), 3.66 (t, J = 7 Hz, 2H), 2.94 (dt, J = 1 Hz, J = 7 Hz, J(Sn−H) = 56 Hz, 2H), 1.60−1.24 (m, 15H), 1.15 (s, 9H), 1.07−0.84 (m, 12H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.6, 166.4, 134.4, 63.1, 43.5, 39.3, 29.1, 27.4, 26.5, 26.0, 18.5, 13.7, 10.2, −5.2; Anal. Calcd for $C_{27}H_{56}O_2SiSn$: C, 57.96; H, 10.09. Found: C, 57.99; H, 10.12; HRMS (FAB) calcd for $C_{23}H_{47}O_2SiSn$ $[M - C_4H_9]^+$ 501.2367, found 501.2355.

(*E*)-5-(*tert*-Butyldimethylsilanyloxy)-1-phenyl-3-(tributylstannyl)pent-2-en-1-one (8h). Yield: 92%; IR (CH_2Cl_2): 2927, 1660, 1571, 1462, 1252, 1229, 1087; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98−7.88 (m, 2H), 7.58−7.41 (m, 3H), 6.97 (m, J(Sn−H) = 66, 1H), 3.71 (t, J = 7 Hz, 2H), 2.98 (dt, J = 7 Hz, J = 1 Hz, J(Sn−H) = 54 Hz, 2H), 1.69−1.22 (m, 15H), 1.15−0.82 (m, 12H), 0.85 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 167.1, 138.6, 136.2, 132.5, 128.6, 128.5, 63.0, 39.6, 29.1, 27.4, 26.0, 18.4, 13.7, 10.2, −5.2; Anal. Calcd for $C_{29}H_{52}O_2SiSn$: C, 60.10; H, 9.04. Found: C, 59.99; H, 9.10; HRMS (FAB) calcd for $C_{25}H_{43}O_2SiSn$ $[M - C_4H_9]^+$ 521.2054, found 521.2077.

(*E*)-5-(*tert*-Butyldimethylsilanyloxy)-3-(tributylstannyl)1-(2,4,6-trimethyl-phenyl)-pent-2-en-1-one (8i). Yield: 91%; IR (CH_2Cl_2): 2927, 1660, 1571, 1462, 1379, 1252, 1229, 1087, 1004; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (s, 2H), 6.56 (m, J(Sn−H) = 64 Hz, 1H), 3.72 (t, J = 7 Hz, 2H), 3.11 (dt, J = 7 Hz, J = 1 Hz, J(Sn−H) = 55 Hz, 2H), 2.28 (s, 3H), 2.21 (s, 6H), 1.62−1.21 (m, 15H), 1.12−0.83 (m, 12H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 170.8, 140.2, 139.2, 138.1, 133.4, 128.5, 62.9, 39.5, 29.0, 27.4, 26.0, 21.1, 19.3, 18.5, 13.7, 10.2, −5.2; Anal. Calcd for $C_{32}H_{58}O_2SiSn$: C, 61.83; H, 9.40. Found: C, 61.77; H, 9.53; HRMS (FAB) calcd for $C_{28}H_{49}O_2SiSn$ $[M - C_4H_9]^+$ 563.2524, found 563.2511.

(*E*)-5-(*tert*-Butyldimethylsilanyloxy)-1-naphthalen-1-yl-3-(tributylstannyl)pent-2-en-1-one (8j). Yield: 88%; IR (CH_2Cl_2): 2926, 1658, 1565, 1462, 1253, 1231, 1093; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60−8.52 (m, 1H), 8.01−7.78 (m, 3H), 7.61−7.44 (m, 4H), 6.88 (m, J(Sn−H) = 65 Hz, 1H), 3.77 (t, J = 7 Hz, 2H), 3.09 (dt, J = 7 Hz, J = 1 Hz, J(Sn−H) = 54 Hz, 2H), 1.68−1.62 (m, 15H), 1.13−0.82 (m, 12H), 0.87 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.6, 168.4, 139.2, 137.5, 133.9, 132.0, 130.3, 128.4, 128.1, 127.5, 126.3, 125.8, 124.5, 63.0, 39.6, 29.1, 27.4, 26.0, 18.5, 13.7, 10.2, −5.2; Anal. Calcd for $C_{33}H_{54}O_2SiSn$: C, 62.96; H, 8.65. Found: C, 62.38; H, 8.63; HRMS (FAB) calcd for $C_{29}H_{45}O_2SiSn$ $[M - C_4H_9]^+$ 571.2211, found 571.2216.

Hydrostannation of Propargylic Alcohol 10. To the 2:1 diastereomeric mixture of propargylic alcohols **10** (44 mg, 0.10 mmol) and $PdCl_2(P(o\text{-}Tol)_3)_2$ (4 mg, 0.005 mmol) in THF (1 mL) was added dropwise tributyltin hydride (116 mg, 0.40 mmol) during 3.5 h, at which time TLC showed a complete conversion. The mixture was added 1 mL of eluent and subjected to flash column chromatography on silica gel (hexane:ethyl acetate, 12:1) to give the separated two diastereomers of the title compound **11** (*minor diastereomer*: 19 mg, 26%, *major diastereomer*: 42 mg, 58%; 84% total yield, *dr* = 2:1), each as colorless oils: *Minor diastereomer*; $[\alpha]^{25}_D$ −28.6 (*c* 1.8, CH_2Cl_2); IR ($CDCl_3$): 2927, 1464, 1255, 1149, 1094, 1041; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (s, 1H), 5.62 (d, J = 9 Hz, J(Sn−H) = 69 Hz, 1H), 4.89 (s, 1H). 4.88 (s, 1H), 4.79 (d, J = 7 Hz, 1H), 4.67 (d, J = 7 Hz, 1H), 4.40−4.28 (m, 1H), 4.12 (m, 1H), 3.71−3.60 (m, 1H), 3.57−3.45 (m, 1H), 3.41 (s, 3H), 2.95 (d, J = 2 Hz, 1H), 2.89−2.65 (m, 2H), 2.44−2.30 (m, 1H), 2.21−2.14 (m, 1H), 2.07−1.98 (m, 2H), 1.89−1.78 (m, 1H), 1.79 (s, 3H), 1.71 (s, 3H), 1.60−1.41 (m, 6H), 1.40−1.24 (m, 6H), 0.96 (d, J = 7 Hz, 3H), 1.00−0.78 (m, 15H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 146.6, 142.6, 138.2, 121.6, 112.8, 95.4, 74.3, 68.9, 62.8, 55.7, 40.9, 40.6, 40.5, 37.3, 37.1, 29.2, 27.5, 26.1, 23.2, 19.6, 18.6, 14.6, 13.7, 9.8, −5.2; HRMS (FAB) calcd for $C_{33}H_{63}O_4SiSn$ $[M - C_4H_9]^+$ 669.3518, found 669.3519. *Major diastereomer*: $[\alpha]^{25}_D$ −40.9 (*c* 2.8, CH_2Cl_2); IR ($CDCl_3$): 2926, 1464, 1253, 1151, 1092, 1028; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (d, J = 7 Hz, J(Sn−H) = 72 Hz, 1H), 5.68 (s, 1H), 4.95−4.89 (m, 2H), 4.88 (d, J = 7 Hz, 1H), 4.72 (m, 1H), 4.63 (d, J = 7 Hz, 1H), 4.55 (s, 1H), 4.25 (m, 1H), 3.59−3.49 (m, 2H), 3.43 (s, 3H), 2.90−2.74 (m, 1H), 2.74−2.60 (m, 1H), 2.50−2.37 (m, 1H), 2.19−1.76 (m, 4H), 1.74 (s, 3H), 1.72 (s, 3H), 1.50−1.42 (m, 6H), 1.38−1.24 (m, 6H), 1.07 (d, J = 7 Hz, 3H), 0.94−0.76 (m, 15H), 0.92 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 145.8, 140.3, 139.6, 120.3, 113.7, 94.2, 69.3, 66.1, 63.4, 56.3, 45.0, 40.2, 39.8, 37.6, 37.4, 30.9, 29.2, 27.5, 26.1, 23.1, 19.2, 18.4, 13.7, 11.8, 9.9, −5.2; HRMS (FAB) calcd for $C_{33}H_{63}O_4SiSn$ $[M - C_4H_9]^+$ 669.3518, found 669.3536.

Oxidation of β-Stannyl Allylic Alcohol 11. A 2:1 diastereomeric mixture of β-stannyl allylic alcohols **11** (20 mg, 0.027 mmol), 4 Å molecular sieves (0.5 g), and *N*-methylmorpholine *N*-oxide (5.2 mg. 0.044 mmol) were slurried in dichloromethane (2 mL) and stirred for 15 min before the addition of tetrapropylammonium peruthenate (0.4 mg, 0.0011 mmol). After the reaction mixture was stirred for 1 h, another portion of tetrapropylammonium perruthenate (0.4 mg, 0.0011 mmol) was added, and the reaction mixture was stirred overnight. The reaction mixture was diluted with dichloromethane (50 mL) and filtered through a pad of Celite. The organic phase was concentrated by rotary evaporation, and the residue was purified by flash column chromatography (hexane:ethyl acetate, 15:1) to give the oxidation product **12** (14 mg, 70%) as a colorless oil: $[\alpha]^{25}_D$ −23.4 (*c* 0.8, CH_2Cl_2); IR ($CDCl_3$): 2927, 1684, 1459, 1256, 1097, 1040; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.38 (s, J(Sn−H) = 68 Hz, 1H), 5.34 (bs, 1H), 4.82 (bs, 1H), 4.67 (bs, 1H), 4.41 (d, J = 7 Hz, 1H), 4.32 (d, J = 7 Hz, 1H), 4.04 (bs, 1H), 3.76−3.58 (m, 2H), 3.21 (s, 3H), 3.13−2.99 (m, 1H), 2.98−2.82 (m, 1H), 2.75−2.40 (m, 3H), 2.13−1.88 (m, 2H), 1.80 (s, 3H), 1.73 (s, 3H), 1.64−1.41 (m, 6H), 1.40−1.23 (m, 6H), 1.05 (d, J = 7 Hz, 3H), 1.00−0.84 (m, 15H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.1, 163.9, 147.0, 139.5, 135.4, 122.2, 111.0, 95.1, 72.3, 63.3, 55.3, 31.9, 29.1, 27.4, 26.1, 23.0, 21.5, 18.5, 15.6, 13.7, 10.2, −5.1; HRMS (FAB) calcd for $C_{33}H_{61}O_4SiSn$ $[M - C_4H_9]^+$ 667.3361, found 667.3381.

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Supporting Information Available: ^{1}H NMR spectra for compounds **7a**−**l**, **8a**−**j**, **10**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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