

Supporting Information

Highly Regio- and Stereoselective Hydrostannylation of Alkynols with A New Lewis Acidic Hydrostannane

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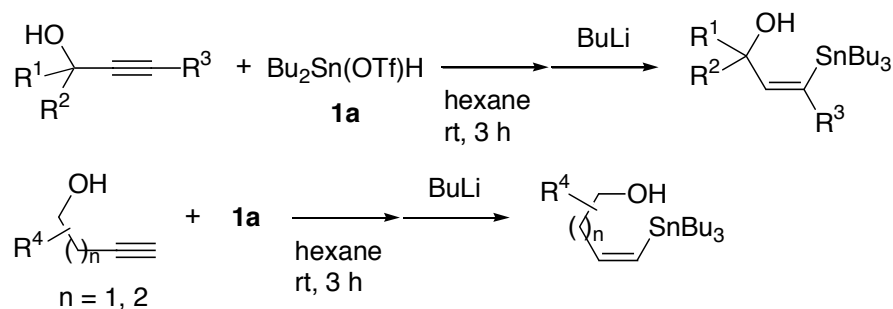


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1. General Method

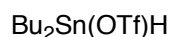
Unless otherwise noted, all reactions and distillation of solvents were carried out under N₂. Solvents were dried by distillation from sodium metal/benzophenone ketyl (THF, Et₂O) and CaH₂ (hexane, DMF). Alkynes were distilled simply or from CaH₂. Boiling points determined with Kugelrohr distillation apparatus are indicated by air-bath temperature (bath temp.). ¹H, ¹³C, and ¹¹⁹Sn NMR were recorded in CDCl₃, C₆D₆, CD₂Cl₂, or THF-d₈ at 270, 67.8, and 101 MHz, respectively. The chemical shifts (δ) are reported with reference at 0.00 ppm (Me₄Si), 7.15 ppm (C₆HD₅), 7.26 ppm (CHCl₃), 5.30 ppm (CHDCl₂), or 3.58 ppm (2,3,3,4,4,5,5-heptadeuterio-THF) for the proton, at 77.00 ppm (CDCl₃), 128.00 ppm (C₆D₆), 53.80 ppm (CD₂Cl₂), or 67.40 ppm (2-C of THF-d₈) for the carbon, and at 0.00 ppm (Me₄Sn) for the tin. The coupling constants between ^ySn (y = 119, 117) and ¹H or ¹³C are designated by ^xJ (^ySn–¹H) or ^xJ (^ySn–¹³C) where "x" denotes the number of bonds intervening between the nuclei. When the splitting between ¹¹⁹Sn and ¹¹⁷Sn satellites is not resolved, "y" is omitted.

2. Substrates and Reagents

2. 1. Hydrostannanes

Bu₂Sn(OTf)H (**1a**) was prepared by the reaction of Bu₂SnH₂ with TfOH as shown below. Bu₂SnH₂ was obtained by the reduction of Bu₂SnCl₂ with LiAlH₄.¹ According to the reported procedure,² Bu₂SnClH (**1b**) was prepared from Bu₂SnCl₂ and Bu₂SnH₂, and directly used for the hydrostannylation in the same flask. Bu₃SnH is commercially available.

Dibutyl(trifluoromethanesulfoxy)stannane (**1a**)



TfOH was dropwise added to an equimolar amount of Bu₂SnH₂ at 0 °C. The mixture was stirred for 2 h. The ¹H NMR analysis of the resultant mixture indicated quantitative formation of the title compound. The dehydrogenative reaction of Bu₃SnH with TfOH leading to Bu₃SnOTf was reported by Corey et al.³ The Bu₂Sn(OTf)H (**1a**) obtained was pure enough to be used for the hydrostannylation of alkynes. It was stored under N₂ in a refrigerator and used within a week after preparation. Similar to other Bu₂SnXH-type hydrostannanes (X = halogen, oxy group), **1a** trends to decompose to the corresponding

distannane at room temperature (see ref 9b in the text). An attempt to distill **1a** was unsuccessful because of the formation of Bu_2SnH_2 by disproportionation. **1a**: IR (neat) 2960, 2927, 2862, 1903 (Sn-H), 1323, 1209, 1016 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.93 (t, $J = 7.3$ Hz, 6H), 1.15–1.93 (m, 12H), 8.99 (br s, 1J ($^{119}\text{Sn}-^1\text{H}$) = 2336 Hz, 1J ($^{117}\text{Sn}-^1\text{H}$) = 2233 Hz, 1H); ^{13}C NMR (C_6D_6) δ 13.60 ($\text{CH}_3 \times 2$), 21.02 (br, $\text{CH}_2 \times 2$, 1J (Sn- ^{13}C) = 435 Hz), 26.71 ($\text{CH}_2 \times 2$, 3J ($^{119}\text{Sn}-^{13}\text{C}$) = 83.3 Hz, 3J ($^{117}\text{Sn}-^{13}\text{C}$) = 79.9 Hz), 27.88 (br, $\text{CH}_2 \times 2$, 2J (Sn- ^{13}C) = 30 Hz), 119.30 (q, 1J ($^{19}\text{F}-^{13}\text{C}$) = 317 Hz); ^{119}Sn NMR (C_6D_6) δ 22.7. Anal. Calcd for $\text{C}_9\text{H}_{19}\text{F}_3\text{O}_3\text{SSn}$: C, 28.22; H, 5.00. Found: C, 28.28; H, 5.27. A solution of **1a** (0.30 mmol) in C_6D_6 (0.6 mL) was used as the sample for NMR analyses.

Dibutylchlorostannane (**1b**) [2602-56-4]²



The title compound was prepared by mixing Bu_2SnCl_2 and Bu_2SnH_2 at 0 °C for 10 min and immediately used for the hydrostannylation of alkynes. Bu_2SnClH exists in equilibrium with the reactants Bu_2SnCl_2 and Bu_2SnH_2 . The percentage of Bu_2SnClH is 88% at 22 °C in C_6D_6 . **1b**: IR (neat) 2956, 2924, 2856, 1857 (Sn-H) cm^{-1} ; ^1H NMR (C_6D_6) δ 0.71–1.67 (m, 18H) including 0.80 (t, $J = 7.3$ Hz), 4.74 (quint, $J = 2.1$ Hz, 0.24H), 7.21 (s, 1J ($^{119}\text{Sn}-^1\text{H}$) = 1986 Hz, 1J ($^{117}\text{Sn}-^1\text{H}$) = 1898 Hz, 0.88H); ^{13}C NMR (C_6D_6) δ 13.67 ($\text{CH}_3 \times 2$), 16.92 ($\text{CH}_2 \times 2$, 1J ($^{119}\text{Sn}-^{13}\text{C}$) = 391 Hz, 1J ($^{117}\text{Sn}-^{13}\text{C}$) = 374 Hz), 26.71 ($\text{CH}_2 \times 2$, 3J (Sn- ^{13}C) = 70 Hz), 28.16 ($\text{CH}_2 \times 2$, 2J (Sn- ^{13}C) = 27 Hz); ^{119}Sn NMR (C_6D_6) δ 47.8. The ^{119}Sn NMR analysis was performed in the range from –100 to 100 ppm. The ^{119}Sn NMR signals of Bu_2SnCl_2 and Bu_2SnH_2 were not observed in this range.^{1b} A solution of **1b** (0.30 mmol) in C_6D_6 (0.6 mL) was used as the sample for NMR analyses.

NMR Studies on Hydrostannanes **1a** and **1b**

To gain some insight into the structures and Lewis acidity of **1a** and **1b**, ^1H , ^{13}C , and ^{119}Sn NMR analyses of these hydrostannanes were performed in C_6D_6 , CD_2Cl_2 , and THF-d_8 . The NMR data are summarized in Table S1.

In respect of the proton and carbons bound to tin, their NMR signals of **1a** appeared at lower fields than those of **1b**. These results indicate that the Sn–O bond of **1a** is highly polarized by the CF_3SO_2 group, therefore that **1a** has higher Lewis acidity than **1b**. The 1J values of Sn–H and Sn–C bonds in

1a were much larger than those in **1b**. The increased coupling constants also are attributable to the highly polarized Sn–O bond of **1a**, which increases the s character of the Sn–H and Sn–C bonds along with a structural change approaching a trigonal bipyramidal arrangement.^{4,5} ¹¹⁹Sn NMR analysis revealed that the ¹¹⁹Sn signal of **1a** appears at higher field than that of **1b**. This observation does not seem to be agreement with the higher Lewis acidity of **1a**. According to the report by Kuivila et al.,⁶ the ¹¹⁹Sn chemical shift of Bu₃SnOTf and its coupling constant ¹J (¹¹⁹Sn–¹³C) in CDCl₃ (168.43 ppm, 375.7 Hz) are larger than those of Bu₃SnCl (155.06 ppm, 336.9 Hz). In this case, the lower field shift of Bu₃SnOTf is consistent with its higher Lewis acidity. On the other hand, the ¹¹⁹Sn chemical shift of Me₃SnOTf (165.3 ppm) is quite similar to that of Me₃SnCl (164 ppm).^{4,7} Additionally, the Lewis acidity of R_{4-n}SnCl_n increases with an increase of the number "n"; however, their ¹¹⁹Sn signals are shifted to higher fields as the number increases.⁴ Thus it is difficult to correlate the ¹¹⁹Sn chemical shifts of organostannanes with their Lewis acidity.

When the solvent was changed from C₆D₆ and CD₂Cl₂ to THF-d₈, the values of ¹J (Sn–¹H) and ¹J (Sn–¹³C) increased,⁸ and the ¹¹⁹Sn signals appeared at considerably higher fields. These changes in NMR spectra clearly indicate that THF-d₈, a donative solvent, interacts with the Lewis acidic tin centers of **1a** and **1b**. In THF-d₈ these tin hydrides are likely pentacoordinate. The increments of the coupling constants ¹J in **1a** were less than those in **1b**. This result bears out that the structure of **1a** in non-coordinating solvents (C₆D₆ and CD₂Cl₂) is close to a trigonal bipyramid with a vacant site. The solvent change also brought about an upper field shift of the hydrogen bound to tin. The larger shift in **1a** implies that the coordination of **1a** with THF-d₈ is stronger than that of **1b**.

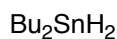
The effect of concentration on the NMR spectra of **1a** was also examined. When the concentration of **1a** (0.3 mmol of **1a** in 0.6 mL of C₆D₆) was reduced to 0.05 M (0.03 mmol of **1a** in 0.6 mL of C₆D₆), the selected NMR data are as follows: ¹H NMR for Sn–H δ 9.00 (s, ¹J (¹¹⁹Sn–¹H) = 2308 Hz, ¹J (¹¹⁷Sn–¹H) = 2207 Hz); ¹³C NMR for Sn–C δ 20.89; ¹¹⁹Sn NMR δ 18.3. The signals of the proton and carbons bound to tin were sharpened, and the tin appeared at slightly higher field. When the concentration was raised (0.6 mmol of **1a** in 0.6 mL of C₆D₆), two sets of ¹H and ¹³C NMR signals were observed: ¹H NMR for Sn–H δ 8.99 (br), 8.88 (br) (these peaks were unresolved); ¹³C NMR for Sn–C δ 21.05, 21.23; ¹¹⁹Sn NMR δ 22.9 (br). These results support a weak self-interaction of **1a** at high concentration.

Table S1. NMR Data for Hydrostannanes **1a** and **1b**^a

	C ₆ D ₆		CD ₂ Cl ₂		THF-d ₈	
	1a	1b	1a	1b	1a	1b
¹ H NMR						
δ (Sn–H) / ppm	8.99 (br)	7.21	8.59 (br)	7.35	8.14	7.17
¹ J (¹¹⁹ Sn– ¹ H) / Hz	2336	1986	2303	1973	2412	2208
¹ J (¹¹⁷ Sn– ¹ H) / Hz	2233	1898	2209	1885	2305	2111
¹³ C NMR						
δ (C _α) / ppm	21.02 (br)	16.92	20.73 (br)	17.71	19.42	18.87
δ (C _β) / ppm	27.88 (br)	28.16	26.77	28.38	28.57	29.02
δ (C _γ) / ppm	26.71	26.71	27.88	26.93	27.35	27.45
δ (C _δ) / ppm	13.60	13.67	13.61	13.80	13.87	14.15
¹ J (Sn– ¹³ C _α) / Hz ^b	435	391, 374	432	392, 374	481, 460	463, 442
² J (Sn– ¹³ C _β) / Hz	30	27	31	26	32	30
³ J (Sn– ¹³ C _γ) / Hz ^b	83.3, 79.9	70	84.0, 80.6	70.4,	86	76.6,
¹¹⁹ Sn NMR						
δ (Sn) / ppm	22.7	47.8	24.7	51.5	–31.3	–30.9
¹ J (¹¹⁹ Sn– ¹ H) / Hz	2328	1992	2340	1972	2392	2203

^a In all cases, a solution of **1** (0.3 mmol) in solvent (0.6 mL) was used as the analytical sample. ^b When the splitting between ¹¹⁹Sn and ¹¹⁷Sn satellites is resolved, both *J* (¹¹⁹Sn–¹³C) and *J* (¹¹⁷Sn–¹³C) are shown in this order.

Dibutylstannane [1002-53-5]^{1b}



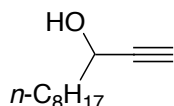
A solution of Bu₂SnCl₂ (26.4 g, 87 mmol) in Et₂O (80 mL) was dropwise added to a suspension of

LiAlH₄ (6.62 g, 174 mmol) in Et₂O (160 mL) over 2 h via a dropping funnel at room temperature, then the mixture was heated to reflux. After being stirred for 12 h at reflux, the resultant mixture was cooled with an ice-water bath and *p*-methoxyphenol (5 mol%) was added to the cooled mixture. The mixture was slowly poured into ice water (300 mL). After addition of 20% aqueous potassium sodium tartrate (270 mL), the mixture was extracted with *t*-BuOMe (2 × 100 mL). The combined organic layer was dried over Na₂SO₄ and evaporated. Purification of the residual oil by distillation gave the title compound (7.07 g, 60.0 mmol) in 69% yield. In some cases, the purification was unsuccessful due to the contamination with *p*-methoxyphenol. However, it could be easily removed by cooling the distillate to -78 °C followed by filtration. Bp 48–50 °C (10 Torr). ¹H NMR (C₆D₆) δ 0.76–1.09 (m, 10H) including 0.86 (t, *J* = 7.3 Hz), 1.21–1.64 (m, 8H), 4.76 (quint, *J* = 2.1 Hz, ¹*J* (¹¹⁹Sn–¹H) = 1669 Hz, ¹*J* (¹¹⁷Sn–¹H) = 1595 Hz, 2H); ¹³C NMR (C₆D₆) δ 7.10 (CH₂ × 2, ¹*J* (¹¹⁹Sn–¹³C) = 373 Hz, ¹*J* (¹¹⁷Sn–¹³C) = 357 Hz), 13.82 (CH₃ × 2), 27.17 (CH₂ × 2, ³*J* (Sn–¹³C) = 57.5 Hz), 30.69 (CH₂ × 2, ²*J* (Sn–¹³C) = 23.4 Hz).

2. 2. Alkynols

Propargyl alcohols **2a** and **2b** were prepared by the reactions of ethynyl magnesium bromide with nonanal and cyclohexanecarbaldehyde, respectively.⁹ For the syntheses of **2f** and **2h**, 1-dodecyne and 1-octyne were lithiated with BuLi and treated with paraformaldehyde and acetaldehyde, respectively.⁹ Propargyl alcohol **2g** was obtained from **2c** by lithiation with BuLi and subsequent silylation with chlorotrimethylsilane.¹⁰ Homopropargyl alcohol **5b** was prepared by propargylation of benzaldehyde with allenyl zinc bromide.¹¹ Bishomopropargyl alcohol **8b** were derived from methyl 3-methylbutanoate by propargylation of the carbon α to the carbonyl group and subsequent reduction with LiAlH₄.¹² For the preparation of **8c**, 1-octyne underwent dilithiation with BuLi followed by alkylation with ethylene oxide.^{9,12} Alkynyl alcohols **2c-e**, **5a**, **5c**, **8a**, and **10** are commercially available.

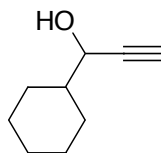
1-Undecyn-3-ol (**2a**) [53735-49-2]¹³



Acetylene (ethyne) was bubbled into THF (200 mL) at a rate of 5 mL/s. A THF solution of EtMgBr (1.28 M, 250 mL, 320 mmol) was slowly added to the THF bubbled with acetylene over 3.5 h at room

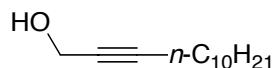
temperature. After addition of EtMgBr, introduction of acetylene was stopped. The reaction mixture was stirred for 20 min and cooled to 0 °C. Nonanal (54.8 mL, 320 mmol) was added to the acetylide solution over 30 min. The mixture was warmed to room temperature and stirred overnight. The resultant mixture was poured into a mixture of ice (50 g) and 2 M aqueous HCl (250 ml). The aqueous layer was extracted with *t*-BuOMe (100 mL). The combined organic layer was washed with saturated aqueous NaHCO₃, dried over Na₂SO₄, and evaporated. Purification of the residual oil by distillation gave the title compound (39.3 g, 234 mmol) in 73% yield. **2a**: Bp 143 °C (28 Torr). IR (neat) 3311 (br s, OH), 2925, 2856, 1466 cm⁻¹; ¹H NMR (CDCl₃) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.23–1.52 (m, 12H), 1.67–1.76 (m, 3H), 2.46 (d, *J* = 2.1 Hz, 1H), 4.37 (td, *J* = 6.6, 2.1 Hz, 1H); ¹³C NMR (CDCl₃) δ 13.99 (CH₃), 22.57 (CH₂), 24.97 (CH₂), 29.16 (CH₂), 29.18 (CH₂), 29.41 (CH₂), 31.78 (CH₂), 37.53 (CH₂), 62.11 (CH), 72.66 (CH), 85.08 (C).

1-Cyclohexyl-2-propyn-1-ol (2b) [4187-88-6]¹⁴



The title compound was prepared by a similar method as used for the synthesis of **2a**. **2b**: Bp 115 °C (0.2 Torr, bath temp.). IR (neat) 3307 (br s, OH), 2925, 2852, 1450, 1024 cm⁻¹; ¹H NMR (CDCl₃) δ 1.00–1.34 (m, 5H), 1.50–1.89 (m, 7H), 2.46 (d, *J* = 2.1 Hz, 1H), 4.13–4.19 (m, 1H); ¹³C NMR (CDCl₃) δ 25.76 (CH₂), 25.80 (CH₂), 26.28 (CH₂), 27.90 (CH₂), 28.35 (CH₂), 43.84 (CH), 66.97 (CH), 73.59 (CH), 83.92 (C); MS *m/z* (relative intensity) 137 (M⁺ – H, 0.43), 83 (39), 55 (100). Anal. Calcd for C₉H₁₄O: C, 78.21; H, 10.21. Found: C, 78.04; H, 10.48.

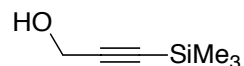
2-Tridecyn-1-ol (2f) [51887-25-3]¹⁵



BuLi (1.6 M in hexane, 6.6 mL, 10.5 mmol) was dropwise added to a THF (10 mL) solution of 1-dodecyne (1.66 g, 10.0 mmol) at 0 °C. After 30 min, dry paraformaldehyde (0.36 g, 12 mmol) was added to the mixture. The reaction was carried out at 0 °C for 1 h, then at room temperature overnight. The resultant mixture was poured into a mixture of saturated aqueous NH₄Cl and water (1:1, 30 mL)

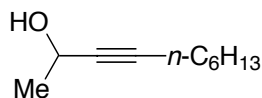
and extracted with AcOEt (2 × 20 mL). The extract was dried over Na₂SO₄ and evaporated. Purification of the residual oil by silica gel column chromatography (hexane-AcOEt 5:1) gave the title compound (1.79 g, 9.1 mmol) in 91% yield. Bp 100 °C (1 Torr, bath temp.). IR (neat) 3373 (br s, OH), 2927, 1214, 1011, 757 cm⁻¹; ¹H NMR (CDCl₃) δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.27–1.59 (m, 17H), 2.21 (tt, *J* = 7.1, 2.1 Hz, 2H), 4.25 (dt, *J* = 6.1, 2.1 Hz, 2H). ¹³C NMR (CDCl₃) δ 13.97 (CH₃), 18.62 (CH₂), 22.57 (CH₂), 28.54 (CH₂), 28.80 (CH₂), 29.66 (CH₂), 29.23 (CH₂), 29.43 (CH₂), 29.50 (CH₂), 31.80 (CH₂), 51.03 (CH₂), 78.23 (C), 86.26 (C).

3-Trimethylsilyl-2-propyn-1-ol (**2g**) [5272-36-6]¹⁶



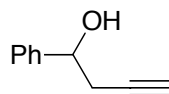
The title compound was prepared by the reported procedure. Bp 91 °C (28 Torr). IR (neat) 3342 (br s, OH), 2960, 2177 (C≡C), 1252, 1043, 845 cm⁻¹; ¹H NMR (CDCl₃) δ 0.18 (s, 9H), 1.61 (br s, 1H), 4.27 (s, 2H); ¹³C NMR (CDCl₃) δ -0.29 (CH₃ × 3), 51.37 (CH₂), 90.44 (C), 103.89 (C).

3-Decyn-2-ol (**2h**) [69668-93-5]¹⁷



The title compound was prepared from 1-octyne and acetaldehyde by a similar method as used for the synthesis of **2f**. 44% yield. **2h**: IR (neat) 3340 (br s, OH), 2931, 2858, 2246 (weak, C≡C) cm⁻¹; ¹H NMR (CDCl₃) δ 0.89 (t, *J* = 6.7 Hz, 3H), 1.26–1.55 (m, 12H) including 1.43 (d, *J* = 6.4 Hz), 2.19 (td, *J* = 7.3, 1.8 Hz, 2H), 4.51 (qt, *J* = 6.4, 1.8 Hz, 1H); ¹³C NMR (CDCl₃) δ 13.98 (CH₃), 18.58 (CH₂), 22.48 (CH₂), 24.69 (CH₃), 28.48 (CH₂), 28.57 (CH₂), 31.28 (CH₂), 58.52 (CH), 82.19 (C), 84.66 (C); MS *m/z* (relative intensity) 139 (M⁺ – CH₃, 2.6), 55 (100).

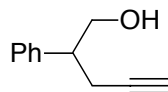
1-Phenyl-3-butyn-1-ol (**5b**) [1743-36-8]¹⁸



A mixture of zinc powder (3.60 g, 55.0 mmol), THF (3 mL), and 1,2-dibromoethane (0.17 mL, 2.0 mmol) was stirred for 1 h at reflux, then cooled to room temperature. After addition of TMSCl (0.17

mL, 2.0 mmol) and THF (30 mL), a solution of 3-bromo-1-propyne (6.00 g, 50.5 mmol) in THF (20 mL) was dropwise added to the mixture over 1 h at $-10\text{ }^{\circ}\text{C}$. After 1 h, benzaldehyde (5.1 mL, 50 mmol) was added to the mixture. Then, the resulting mixture was warmed to $0\text{ }^{\circ}\text{C}$ and stirred for 36 h, then poured into 1 M aqueous HCl (100 mL). The organic layer was washed with brine (50 mL) and the aqueous layer was extracted with AcOEt ($2 \times 25\text{ mL}$). The combined organic layer was dried and evaporated. Purification by silica gel column chromatography (hexane-AcOEt 5:1) gave the title compound (5.76 g, 39.4 mmol) in 79% yield. **5b**: IR (neat) 3390 (br s, OH), 2119 (weak, $\text{C}\equiv\text{C}$), 1051, 756, 700 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 2.08 (t, $J = 2.6\text{ Hz}$, 1H), 2.41 (d, $J = 3.0\text{ Hz}$, 1H), 2.65 (dd, $J = 6.3, 2.3\text{ Hz}$, 2H), 4.88 (td, $J = 6.3, 3.0\text{ Hz}$, 1H), 7.29–7.42 (m, 5H); $^{13}\text{C NMR}$ (CDCl_3) δ 29.30 (CH_2), 70.90 (CH), 72.23 (CH), 80.64 (C), 125.69 (CH \times 2), 127.90 (CH), 128.39 (CH \times 2), 142.38 (C). Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}$: C, 82.16; H, 6.89. Found: C, 81.31; H, 7.04.

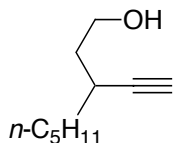
2-Phenyl-4-pentyn-1-ol (**8b**) [65351-11-3]¹²



To a THF (60 mL) solution of *i*-Pr₂NH (10.8 mL, 77 mmol) was dropwise added BuLi (1.64 M in hexane, 47 mL, 77 mmol) at $0\text{ }^{\circ}\text{C}$. After being stirred for 30 min, the mixture was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of methyl phenylacetate (10.8 mL, 75.0 mmol) in THF (20 mL) was dropwise added over 20 min. After 30 min, a solution of 3-bromo-1-propyne (6.2 mL, 83 mmol) in THF (10 mL) was dropwise added. The mixture was warmed to $0\text{ }^{\circ}\text{C}$ over 5 h, stirred at rt for 1 h, and poured into H₂O (100 mL). After extraction with AcOEt ($2 \times 50\text{ mL}$), the combined organic layer was dried over Na₂SO₄ and concentrated *in vacuo*. Purification by distillation gave methyl 2-phenyl-4-pentynoate in 82% yield (11.6 g). Methyl 2-phenyl-4-pentynoate: Bp $97\text{--}100\text{ }^{\circ}\text{C}$ (0.5 Torr); IR (neat) 3270, 1727, 1425, 1160 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.96 (t, $J = 2.6\text{ Hz}$, 1H), 2.64 (ddd, $J = 16.8, 7.3, 2.6\text{ Hz}$, 1H), 2.94 (ddd, $J = 16.8, 8.3, 2.6\text{ Hz}$, 1H), 3.70 (s, 3H), 3.82 (dd, $J = 8.3, 7.3\text{ Hz}$, 1H), 7.26–7.38 (m, 5H); $^{13}\text{C NMR}$ (CDCl_3) δ 22.93 (CH_2), 50.59 (CH), 52.10 (CH_3), 70.06 (CH), 81.30 (C), 127.69 (CH \times 3), 128.68 (CH \times 2), 137.48 (C), 172.76 (C); MS m/z (relative intensity) 187 ($\text{M}^+ - \text{H}$, 0.3), 157 (1.9), 129 (100). Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$: C, 76.57; H, 6.43. Found: C, 76.54; H, 6.37. A solution of methyl 2-phenyl-4-pentynoate (11.6 g, 61.4 mmol) in Et₂O (10 mL) was dropwise added to a suspension of LiAlH₄ (1.63

g, 43.0 mmol) in Et₂O (90 mL) over 20 min at 0 °C. After 1 h, potassium sodium tartrate (20% aqueous solution, 160 mL) and NaOH (2 M, 50 mL) were slowly added to the reaction mixture. After being stirred for 30 min, the organic layer was removed, and the aqueous layer was extracted with Et₂O (50 mL). The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification by distillation gave the title compound in 98% yield (9.64 g, 60.2 mmol). **8b**: Bp 135 °C (5.0 Torr, bath temp.); IR (neat) 3275 (br s, OH), 2905, 1060, 1019 cm⁻¹; ¹H NMR (CDCl₃) δ 1.52 (br s, 1H), 1.99 (t, *J* = 2.7 Hz, 1H), 2.56 (ddd, *J* = 16.9, 6.8, 2.7 Hz, 1H), 2.65 (ddd, *J* = 16.9, 7.1, 2.7 Hz, 1H), 3.00–3.11 (m, 1H), 3.83–3.99 (m, 2H), 7.23–7.39 (m, 5H); ¹³C NMR (CDCl₃) δ 21.49 (CH₂), 46.52 (CH), 65.55 (CH₂), 69.88 (CH), 82.23 (C), 126.90 (CH), 127.64 (CH × 2), 128.41 (CH × 2), 140.88 (C); MS *m/z* (relative intensity) 160 (M⁺, 11), 142 (11), 129 (100). Anal. Calcd for C₁₁H₁₂O: C, 82.46; H, 7.55. Found: C, 82.36; H, 7.36.

3-Pentyl-4-pentyn-1-ol (**8c**) [320399-93-7]¹²



BuLi (1.65 M in hexane, 133 mL, 219 mmol) was added to THF (70 mL) at -40 °C. A solution of 1-octyne (14.5 mL, 98.3 mmol) in THF (30 mL) was dropwise added to the solution of BuLi over 10 min. The mixture was immediately warmed to rt, and stirred at rt for 1 h, then at 35 °C for 2 h. After the yellow solution obtained was cooled to -40 °C, a solution of ethylene epoxide in THF, which was prepared from ethylene chlorohydrin (7.98 mL, 119 mmol) and BuLi (1.65 M in hexane, 73.0 mL, 120 mmol) in THF (60 mL) at 0 °C for 2.5 h, was added. The reaction mixture was gradually warmed to rt overnight, and poured into iced water (500 mL). The aqueous layer was extracted with Et₂O (2 × 50 mL). The combined organic layer was washed with brine, dried, and evaporated. Purification by distillation gave the title compounds in 63% yield (9.54 g, 61.8 mmol). **8c**: Bp 72–75 °C (0.90 Torr). IR (neat) 3285 (br s, OH), 2915, 1456, 1048 cm⁻¹; ¹H NMR δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.21–1.82 (m, 11H), 2.09 (d, *J* = 2.4 Hz, 1H), 2.46–2.58 (m, 1H), 3.82 (t, *J* = 5.9 Hz, 2H); ¹³C NMR δ 14.49 (CH₃), 23.02 (CH₂), 27.28 (CH₂), 28.79 (CH), 32.06 (CH₂), 35.49 (CH₂), 38.04 (CH₂), 61.53 (CH₂), 77.95 (CH), 87.85 (C); MS *m/z* (relative intensity) 154 (M⁺, 0.9), 43 (100). Anal. Calcd for C₁₀H₁₈O: C, 77.87; H,

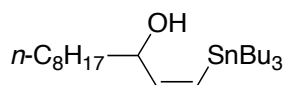
11.76. Found: C, 77.96; H, 11.86.

3. Hydrostannylation

Typical Procedure

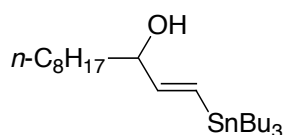
Hydrostannane **1a** (421 mg, 1.10 mmol) was added to a solution of **2a** (168 mg, 1.00 mmol) in hexane (2 mL) at room temperature. After being stirred for 3 h, the reaction mixture was diluted with Et₂O (2 mL), cooled to 0 °C, and treated with BuLi (1.60 M in hexane, 1.56 mL, 2.50 mmol). After 20 min, the resultant mixture was poured into a 1:1 mixture of saturated aqueous NH₄Cl and water. The extract with *t*-BuOMe was dried over Na₂SO₄ and evaporated. Purification of the residual oil by silica gel column chromatography (hexane-*t*-BuOMe 20:1) gave (*Z*)-**3a** ((*Z*)-**3a**:**4a** = >99:1) in 89% yield. A trace amount (<1%) of (*E*)-**3a** also was isolated. Since the ¹H NMR analysis of the crude product indicated no inclusion of (*E*)-**3a**, the formation of (*E*)-**3a** is attributable to the isomerization of (*Z*)-**3a** during the purification by column chromatography.

(*Z*)-1-Tributylstannyl-1-undecen-3-ol ((*Z*)-**3a**)



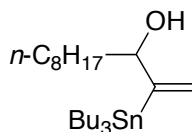
Bp 125 °C (0.5 Torr, bath temp.). IR (neat) 3419 (br s, OH), 2956, 2925, 2854, 1601 (weak, C=C), 1464 cm⁻¹; ¹H NMR (CDCl₃) δ 0.78–1.03 (m, 18H), 1.24–1.64 (m, 27H), 3.85–3.94 (m, 1H), 5.99 (dd, *J* = 12.7, 0.8 Hz, ²*J* (¹¹⁹Sn–¹H) = 65.6 Hz, ²*J* (¹¹⁷Sn–¹H) = 63.5 Hz, 1H), 6.49 (dd, *J* = 12.7, 7.5 Hz, ³*J* (¹¹⁹Sn–¹H) = 137 Hz, ³*J* (¹¹⁷Sn–¹H) = 131 Hz, 1H); ¹³C NMR (CDCl₃) δ 10.82 (CH₂ × 3), 13.66 (CH₃ × 3), 14.08 (CH₃), 22.66 (CH₂), 25.54 (CH₂), 27.32 (CH₂ × 3), 29.18 (CH₂ × 3), 29.25 (CH₂), 29.55 (CH₂), 29.70 (CH₂), 31.87 (CH₂), 37.35 (CH₂), 75.73 (CH), 130.73 (CH), 150.43 (CH). Anal. Calcd for C₂₃H₄₈OSn: C, 60.14; H, 10.53. Found: C, 60.09; H, 10.79.

(*E*)-1-Tributylstannyl-1-undecen-3-ol ((*E*)-**3a**)



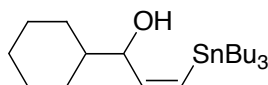
Bp 125 °C (0.5 Torr, bath temp.). IR (neat) 3336 (br s, OH), 2956, 2925, 2854, 1601 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.77–1.02 (m, 18H), 1.24–1.65 (m, 27H), 4.02–4.10 (m, 1H), 5.99 (dd, $J = 19.2, 5.1$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 64.5$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 61.8$ Hz, 1H), 6.12 (d, $J = 19.2$ Hz, $^2J(\text{Sn}-^1\text{H}) = 71$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 9.45 ($\text{CH}_2 \times 3$), 13.68 ($\text{CH}_3 \times 3$), 14.08 (CH_3), 22.66 (CH_2), 25.36 (CH_2), 27.24 ($\text{CH}_2 \times 3$), 29.07 ($\text{CH}_2 \times 3$), 29.25 (CH_2), 29.56 (CH_2), 29.60 (CH_2), 31.87 (CH_2), 36.99 (CH_2), 75.63 (CH), 127.59 (CH), 151.15 (CH); MS m/z (relative intensity) 403 ($\text{M}^+ - \text{Bu}$, 56), 401 ($\text{M}^+ - 2 - \text{Bu}$, 48), 399 ($\text{M}^+ - 4 - \text{Bu}$, 28), 207 (100). Anal. Calcd for $\text{C}_{23}\text{H}_{48}\text{OSn}$: C, 60.14; H, 10.53. Found: C, 60.26; H, 10.70.

2-Tributylstannyl-1-undecen-3-ol (4a)

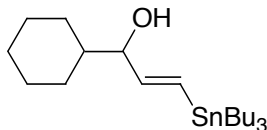


Bp 125 °C (0.5 Torr, bath temp.). IR (neat) 3392 (br s, OH), 2956, 2925, 2854, 1463 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.80–1.05 (m, 18H), 1.19–1.64 (m, 27H), 4.18 (br s, $^3J(\text{Sn}-^1\text{H}) = 50$ Hz, 1H), 5.20 (br s, $^3J(\text{Sn}-^1\text{H}) = 62$ Hz, 1H), 5.78 (br s, $^3J(\text{Sn}-^1\text{H}) = 132$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.14 ($\text{CH}_2 \times 3$), 13.67 ($\text{CH}_3 \times 3$), 14.09 (CH_3), 22.66 (CH_2), 25.67 (CH_2), 27.40 ($\text{CH}_2 \times 3$), 29.11 ($\text{CH}_2 \times 3$), 29.27 (CH_2), 29.57 ($\text{CH}_2 \times 2$), 31.88 (CH_2), 37.59 (CH_2), 79.43 (CH), 123.86 (CH_2), 159.33 (C). Anal. Calcd for $\text{C}_{23}\text{H}_{48}\text{OSn}$: C, 60.14; H, 10.53. Found: C, 60.32; H, 10.20.

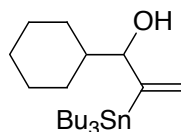
(Z)-1-Cyclohexyl-3-tributylstannyl-2-propen-1-ol ((Z)-3b)



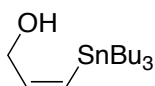
Bp 115 °C (0.5 Torr, bath temp.). IR (neat) 3460 (br s, OH), 2954, 2924, 2815, 1599 (weak, C=C), 1450 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.78–1.79 (m, 38H), 1.90 (br d, $J = 12.7$ Hz, 1H), 3.63 (td, $J = 6.9, 3.6$ Hz, 1H), 6.04 (d, $J = 12.8$ Hz, $^2J(\text{Sn}-^1\text{H}) = 65$ Hz, 1H), 6.52 (dd, $J = 12.8, 7.6$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 138$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 131$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.86 ($\text{CH}_2 \times 3$), 13.69 ($\text{CH}_3 \times 3$), 26.12 (CH_2), 26.27 (CH_2), 26.54 (CH_2), 27.34 ($\text{CH}_2 \times 3$), 28.43 (CH_2), 29.18 ($\text{CH}_2 \times 3$), 29.28 (CH_2), 43.79 (CH), 79.89 (CH), 131.86 (CH), 149.02 (CH). Anal. Calcd for $\text{C}_{21}\text{H}_{42}\text{OSn}$: C, 58.76; H, 9.86. Found: C, 58.92; H, 10.12.

(E)-1-Cyclohexyl-3-tributylstannyl-2-propen-1-ol ((E)-3b) [126531-28-0]¹⁹

Bp 115 °C (0.5 Torr, bath temp.). IR (neat) 3357 (br s, OH), 2954, 2924, 2852, 1600 (weak, C=C), 1450 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.77–1.86 (m, 39H), 3.82 (td, $J = 5.5, 4.4$ Hz, 1H), 5.99 (dd, $J = 19.1, 5.4$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 65.1$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 61.8$ Hz, 1H), 6.10 (d, $J = 19.1$ Hz, $^2J(\text{Sn}-^1\text{H}) = 72$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 9.50 ($\text{CH}_2 \times 3$), 13.70 ($\text{CH}_3 \times 3$), 26.15 (CH_2), 26.21 (CH_2), 26.57 (CH_2), 27.26 ($\text{CH}_2 \times 3$), 28.37 (CH_2), 28.85 (CH_2), 29.12 ($\text{CH}_2 \times 3$), 43.48 (CH), 80.11 (CH), 128.65 (CH), 149.68 (CH); MS m/z (relative intensity) 373 ($\text{M}^+ - \text{Bu}$, 24), 371 ($\text{M}^+ - 2 - \text{Bu}$, 19), 369 ($\text{M}^+ - 4 - \text{Bu}$, 11), 55 (100). Anal. Calcd for $\text{C}_{21}\text{H}_{42}\text{OSn}$: C, 58.76; H, 9.86. Found: C, 58.85; H, 10.02.

1-Cyclohexyl-2-tributylstannyl-2-propen-1-ol (4b)

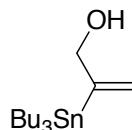
Bp 110 °C (0.5 Torr, bath temp.). IR (neat) 3481 (br s, OH), 2954, 2924, 2852, 1450 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.80–1.82 (m, 38H), 1.94 (br d, $J = 13.0$ Hz, 1H), 3.85 (dd, $J = 7.2, 3.1$ Hz, $^3J(\text{Sn}-^1\text{H}) = 55$ Hz, 1H), 5.25 (d, $J = 2.5$ Hz, $^3J(\text{Sn}-^1\text{H}) = 62$ Hz, 1H), 5.74 (d, $J = 1.3$ Hz, $^3J(\text{Sn}-^1\text{H}) = 133$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.14 ($\text{CH}_2 \times 3$), 13.68 ($\text{CH}_3 \times 3$), 26.09 (CH_2), 26.19 (CH_2), 26.48 (CH_2), 27.43 ($\text{CH}_2 \times 3$), 28.10 (CH_2), 29.10 ($\text{CH}_2 \times 3$), 30.02 (CH_2), 42.90 (CH), 84.34 (CH), 125.03 (CH_2), 158.16 (C); MS m/z (relative intensity) 373 ($\text{M}^+ - \text{Bu}$, 3.4), 371 ($\text{M}^+ - 2 - \text{Bu}$, 2.9), 369 ($\text{M}^+ - 4 - \text{Bu}$, 1.8), 55 (100). Anal. Calcd for $\text{C}_{21}\text{H}_{42}\text{OSn}$: C, 58.76; H, 9.86. Found: C, 59.04; H, 10.02.

(Z)-3-Tributylstannyl-2-propen-1-ol ((Z)-3c) [74141-13-2]²⁰

Bp 105 °C (0.5 Torr, bath temp.). IR (neat) 3330 (br s, OH), 2956, 2924, 2871, 2852, 1598 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.63–1.04 (m, 15H), 1.19–1.64 (m, 13H), 4.07–4.16 (m, 2H),

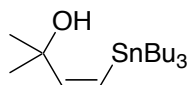
6.08 (d, $J = 12.8$ Hz, $^2J(^{119}\text{Sn}-^1\text{H}) = 64.9$ Hz, $^2J(^{117}\text{Sn}-^1\text{H}) = 62.4$ Hz, 1H), 6.69 (dt, $J = 12.8, 5.9$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 135$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 129$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.64 ($\text{CH}_2 \times 3$), 13.66 ($\text{CH}_3 \times 3$), 27.26 ($\text{CH}_2 \times 3$), 29.14 ($\text{CH}_2 \times 3$), 66.10 (CH_2), 131.76 (CH), 146.21 (CH). Anal. Calcd for $\text{C}_{15}\text{H}_{32}\text{OSn}$: C, 51.90; H, 9.29. Found: C, 51.83; H, 9.57.

2-Tributylstannyl-2-propen-1-ol (4c) [84666-30-8]^{21,22}



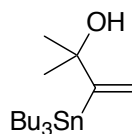
IR (neat) 3303 (br s, OH), 2956, 2925, 2852, 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.81–1.06 (m, 15H) including 0.89 (t, $J = 7.3$ Hz), 1.25–1.62 (m, 13H), 4.28 (dt, $J = 5.9, 1.8$ Hz, $^3J(\text{Sn}-^1\text{H}) = 29$ Hz, 2H), 5.24 (dt, $J = 2.2, 1.8$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 62.9$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 59.8$ Hz, 1H), 5.88 (dt, $J = 2.2, 1.8$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 131$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 127$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 9.41 ($\text{CH}_2 \times 3$), 13.64 ($\text{CH}_3 \times 3$), 27.31 ($\text{CH}_2 \times 3$), 29.08 ($\text{CH}_2 \times 3$), 69.47 (CH_2), 122.76 (CH_2), 154.70 (C); MS m/z (relative intensity) 291 ($\text{M}^+ - \text{Bu}$, 41), 289 ($\text{M}^+ - 2 - \text{Bu}$, 33), 287 ($\text{M}^+ - 4 - \text{Bu}$, 32), 251 (100). Anal. Calcd for $\text{C}_{15}\text{H}_{32}\text{OSn}$: C, 51.90; H, 9.29. Found: C, 52.09; H, 9.25.

(Z)-2-Methyl-4-tributylstannyl-3-buten-2-ol ((Z)-3d) [79970-79-9]²³



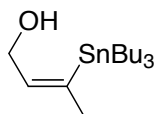
IR (neat) 3473 (br s, OH), 2956, 2921, 1603 (weak, C=C), 1461, 1359 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.73–0.98 (m, 15H), 1.11 (s, 1H), 1.23–1.60 (m, 18H) including 1.28 (s), 5.80 (d, $J = 13.2$ Hz, $^2J(^{119}\text{Sn}-^1\text{H}) = 68.5$ Hz, $^2J(^{117}\text{Sn}-^1\text{H}) = 65.4$ Hz, 1H), 6.59 (d, $J = 13.2$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 144$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 137$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 12.02 ($\text{CH}_2 \times 3$), 13.73 ($\text{CH}_3 \times 3$), 27.41 ($\text{CH}_2 \times 3$), 29.32 ($\text{CH}_2 \times 3$), 30.77 ($\text{CH}_3 \times 2$), 72.65 (C), 124.88 (CH), 153.26 (CH). Anal. Calcd for $\text{C}_{17}\text{H}_{36}\text{OSn}$: C, 54.43; H, 9.67. Found: C, 54.64; H, 9.41.

2-Methyl-3-tributylstannyl-3-buten-2-ol (4d) [87836-16-6]²⁴



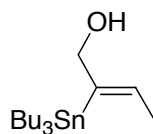
IR (neat) 3460 (br s, OH), 2956, 2925 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.79–1.04 (m, 15H), 1.25–1.63 (m, 19H) including 1.31 (s), 5.14 (d, $J = 1.5$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 69.4$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 66.4$ Hz, 1H), 5.72 (d, $J = 1.5$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 142$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 135$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.65 ($\text{CH}_2 \times 3$), 13.70 ($\text{CH}_3 \times 3$), 27.42 ($\text{CH}_2 \times 3$), 29.13 ($\text{CH}_2 \times 3$), 30.62 ($\text{CH}_3 \times 2$), 75.68 (C), 120.86 (CH_2), 164.92 (CH).

(Z)-3-Tributylstannyl-2-buten-1-ol ((Z)-3e) [121882-41-5]²⁵



Bp 170 $^\circ\text{C}$ (1.8 Torr, bath temp.). IR (neat) 3325 (br s, OH), 2956, 2925, 2852, 1626 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.81–1.06 (m, 15H) including 0.89 (t, $J = 7.2$ Hz), 1.15–1.60 (m, 13H), 1.95 (dt, $J = 1.6, 1.0$ Hz, $^3J(\text{Sn}-^1\text{H}) = 41$ Hz, 3H), 4.02 (ddq, $J = 6.8, 5.6, 1.0$ Hz, 2H), 6.27 (tq, $J = 6.8, 1.6$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 127$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 121$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.18 ($\text{CH}_2 \times 3$), 13.67 ($\text{CH}_3 \times 3$), 26.95 (CH_3), 27.35 ($\text{CH}_2 \times 3$), 29.16 ($\text{CH}_2 \times 3$), 65.08 (CH_2), 138.75 (CH), 144.54 (C); MS m/z (relative intensity) 305 ($\text{M}^+ - \text{Bu}$, 100), 303 ($\text{M}^+ - 2 - \text{Bu}$, 68), 301 ($\text{M}^+ - 4 - \text{Bu}$, 45). Anal. Calcd for $\text{C}_{16}\text{H}_{34}\text{OSn}$: C, 53.21; H, 9.49. Found: C, 52.94; H, 9.30.

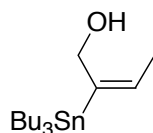
(Z)-2-Tributylstannyl-2-buten-1-ol ((Z)-4e) [79970-55-1]^{23,26}



Bp 170 $^\circ\text{C}$ (1.8 Torr, bath temp.). IR (neat) 3307 (br s, OH), 2956, 2925, 2852, 1626 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.84–1.09 (m, 15H) including 0.89 (t, $J = 7.3$ Hz), 1.18 (t, $J = 5.9$ Hz, 1H), 1.25–1.56 (m, 12H), 1.74 (dt, $J = 6.6, 1.2$ Hz, $^4J(\text{Sn}-^1\text{H}) = 11$ Hz, 3H), 4.17 (ddq, $J = 5.9, 1.3, 1.2$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 40.4$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 38.1$ Hz, 2H), 6.32 (qt, $J = 6.6, 1.3$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 125$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 120$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.04 ($\text{CH}_2 \times 3$), 13.69 ($\text{CH}_3 \times 3$), 19.53 (CH_3), 27.38 ($\text{CH}_2 \times 3$), 29.22 ($\text{CH}_2 \times 3$), 70.65 (CH_2), 136.06 (CH), 144.36 (C); MS m/z (relative intensity)

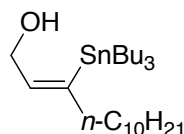
305 ($M^+ - \text{Bu}$, 46), 303 ($M^+ - 2 - \text{Bu}$, 41), 301 ($M^+ - 4 - \text{Bu}$, 21), 251 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{34}\text{OSn}$: C, 53.21; H, 9.49. Found: C, 53.30; H, 9.14.

(E)-2-Tributylstannyl-2-buten-1-ol ((E)-4e) [79970-54-0]^{21,26}



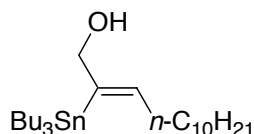
Bp 170 °C (1.8 Torr, bath temp.). IR (neat) 3384 (br s, OH), 2956, 2924, 2852, 1614 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.76–1.01 (m, 15H), 1.25–1.55 (m, 13H), 1.69 (dt, $J = 6.7, 1.2$ Hz, 4J (Sn– ^1H) = 11 Hz, 3H), 4.38 (ddq, $J = 5.3, 2.1, 1.2$ Hz, 3J ($^{119}\text{Sn}-^1\text{H}$) = 41.1 Hz, 3J ($^{117}\text{Sn}-^1\text{H}$) = 39.1 Hz, 2H), 5.62 (qt, $J = 6.7, 2.1$ Hz, 3J ($^{119}\text{Sn}-^1\text{H}$) = 70.3 Hz, 3J ($^{117}\text{Sn}-^1\text{H}$) = 66.8 Hz, 1H); ^{13}C NMR (CDCl_3) δ 9.96 ($\text{CH}_2 \times 3$), 13.69 ($\text{CH}_3 \times 3$), 15.12 (CH_3), 27.40 ($\text{CH}_2 \times 3$), 29.20 ($\text{CH}_2 \times 3$), 63.42 (CH_2), 134.01 (CH), 146.58 (C); MS m/z (relative intensity) 305 ($M^+ - \text{Bu}$, 27), 303 ($M^+ - 2 - \text{Bu}$, 24), 301 ($M^+ - 4 - \text{Bu}$, 21), 57 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{34}\text{OSn}$: C, 53.21; H, 9.49. Found: C, 52.89; H, 9.21.

(Z)-3-Tributylstannyl-2-tridecen-1-ol ((Z)-3f)



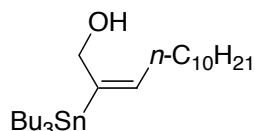
Bp 210 °C (1.3 Torr, bath temp.). IR (neat) 3327 (br s, OH), 2956, 2924, 2852, 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.82–1.04 (m, 18H), 1.12 (t, $J = 5.7$ Hz, 1H), 1.17–1.58 (m, 28H), 2.20 (t, $J = 5.9$ Hz, 3J (Sn– ^1H) = 48 Hz, 2H), 4.04 (dd, $J = 6.7, 5.7$ Hz, 4J (Sn– ^1H) = 9 Hz, 2H), 6.22 (tt, $J = 6.7, 1.2$ Hz, 3J ($^{119}\text{Sn}-^1\text{H}$) = 129 Hz, 3J ($^{117}\text{Sn}-^1\text{H}$) = 124 Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.52 ($\text{CH}_2 \times 3$), 13.65 ($\text{CH}_3 \times 3$), 14.10 (CH_3), 22.68 (CH_2), 27.39 ($\text{CH}_2 \times 3$), 29.20 ($\text{CH}_2 \times 3$), 29.30 (CH_2), 29.33 (CH_2), 29.53 (CH_2), 29.62 ($\text{CH}_2 \times 3$), 30.27 (CH_2), 31.90 (CH_2), 40.67 (CH_2), 138.10 (CH), 149.77 (C). Anal. Calcd for $\text{C}_{25}\text{H}_{52}\text{OSn}$: C, 61.61; H, 10.75. Found: C, 61.70; H, 10.72.

(Z)-2-Tributylstannyl-2-tridecen-1-ol ((Z)-4f)



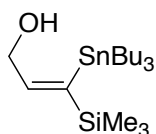
Bp 210 °C (1.3 Torr, bath temp.). IR (neat) 3313 (br s, OH), 2956, 2924, 2852, 1622 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.82–1.07 (m, 18H), 1.17 (t, $J = 6.0$ Hz, 1H), 1.26–1.59 (m, 28H), 2.02 (dt, $J = 7.2, 6.9$ Hz, 2H), 4.17 (dd, $J = 6.0, 1.2$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 39.9$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 37.9$ Hz, 2H), 6.23 (tt, $J = 7.2, 1.3$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 126$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 120$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.18 ($\text{CH}_2 \times 3$), 13.65 ($\text{CH}_3 \times 3$), 14.08 (CH_3), 22.67 (CH_2), 27.40 ($\text{CH}_2 \times 3$), 29.23 ($\text{CH}_2 \times 3$), 29.32 (CH_2), 29.49 (CH_2), 29.60 ($\text{CH}_2 \times 3$), 30.02 (CH_2), 31.90 (CH_2), 34.61 (CH_2), 70.48 (CH_2), 141.99 (CH), 142.89 (C). Anal. Calcd for $\text{C}_{25}\text{H}_{52}\text{OSn}$: C, 61.61; H, 10.75. Found: C, 61.44; H, 10.45.

(E)-2-Tributylstannyl-2-tridecen-1-ol ((E)-4f)

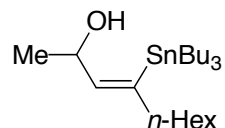


Bp 210 °C (1.3 Torr, bath temp.). IR (neat) 3411 (br s, OH), 2954, 2924, 2854, 1610 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.77–1.05 (m, 18H), 1.26–1.55 (m, 29H), 2.07 (dt, $J = 6.9, 6.6$ Hz, 2H), 4.36 (dd, $J = 5.4, 1.3$ Hz, $^3J(\text{Sn}-^1\text{H}) = 40$ Hz, 2H), 5.55 (tt, $J = 6.9, 1.8$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 71.6$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 67.4$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.00 ($\text{CH}_2 \times 3$), 13.72 ($\text{CH}_3 \times 3$), 14.10 (CH_3), 22.68 (CH_2), 27.39 ($\text{CH}_2 \times 3$), 29.22 ($\text{CH}_2 \times 3$), 29.25 (CH_2), 29.34 (CH_2), 29.45 (CH_2), 29.52 (CH_2), 29.57 (CH_2), 29.62 ($\text{CH}_2 \times 2$), 31.90 (CH_2), 63.64 (CH_2), 140.66 (CH), 145.11 (C). Anal. Calcd for $\text{C}_{25}\text{H}_{52}\text{OSn}$: C, 61.61; H, 10.75. Found: C, 61.62; H, 10.43.

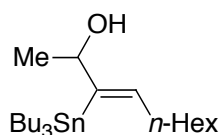
(Z)-3-Tributylstannyl-3-trimethylsilyl-2-propen-1-ol ((Z)-3g) [138407-96-2]²⁷



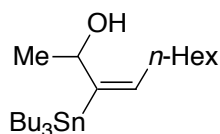
IR (neat) 3307 (br s, OH), 2956, 2925, 2871, 2854, 1572 (weak, C=C), 1464, 1246 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.08 (s, 9H), 0.82–1.05 (m, 15H) including 0.89 (t, $J = 7.2$ Hz), 1.25–1.57 (m, 13H), 4.15 (dd, $J = 5.8, 5.6$ Hz, 2H), 6.87 (t, $J = 5.6$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 170$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 162$ Hz, 1H); ^{13}C NMR (CDCl_3) δ -0.44 ($\text{CH}_3 \times 3$), 11.39 ($\text{CH}_2 \times 3$), 13.61 ($\text{CH}_3 \times 3$), 27.35 ($\text{CH}_2 \times 3$), 29.15 ($\text{CH}_2 \times 3$), 67.53 (CH_2), 146.49 (C), 152.94 (CH). Anal. Calcd for $\text{C}_{18}\text{H}_{40}\text{OSiSn}$: C, 51.56; H, 9.62. Found: C, 51.51; H, 9.81.

(Z)-4-Tributylstannyl-3-decen-2-ol ((Z)-3h)

Bp 180 °C (1.9 Torr, bath temp.). IR (neat) 3356 (br s, OH), 2956, 2924, 2854, 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.79–1.04 (m, 18H), 1.25–1.58 (m, 24H), 2.05–2.25 (m, 2H), 4.08 (dq, $J = 8.6, 6.1, 2.8$ Hz, 1H), 6.01 (dt, $J = 8.6, 1.2$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 130$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 124$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.58 ($\text{CH}_2 \times 3$), 13.61 ($\text{CH}_3 \times 3$), 14.04 (CH_3), 22.61 (CH_2), 23.49 (CH_3), 27.40 ($\text{CH}_2 \times 3$), 28.90 (CH_2), 29.23 ($\text{CH}_2 \times 3$), 30.22 (CH_2), 31.73 (CH_2), 40.42 (CH_2), 70.86 (CH), 143.56 (CH), 147.02 (C). Anal. Calcd for $\text{C}_{22}\text{H}_{46}\text{OSn}$: C, 59.34; H, 10.41. Found: C, 59.38; H, 10.26.

(Z)-3-Tributylstannyl-3-decen-2-ol ((Z)-4h) [144425-52-5]²⁸

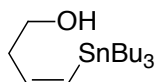
IR (neat) 3372 (br s, OH), 2956, 2925, 2854, 1618 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.85–1.08 (m, 18H), 1.21 (d, $J = 6.3$ Hz, 3H), 1.24–1.60 (m, 21H), 2.00 (dt, $J = 7.2, 6.8$ Hz, 2H), 4.34 (qdd, $J = 6.3, 3.6, 1.0$ Hz, 1H), 6.17 (td, $J = 7.2, 1.0$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 129$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 123$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 11.02 ($\text{CH}_2 \times 3$), 13.65 ($\text{CH}_3 \times 3$), 14.05 (CH_3), 22.61 (CH_2), 24.26 (CH_3), 27.41 ($\text{CH}_2 \times 3$), 29.18 (CH_2), 29.23 ($\text{CH}_2 \times 3$), 30.05 (CH_2), 31.83 (CH_2), 34.20 (CH_2), 75.57 (CH), 139.64 (CH), 148.79 (C); MS m/z (relative intensity) 389 ($\text{M}^+ - \text{Bu}$, 7.0), 387 ($\text{M}^+ - 2 - \text{Bu}$, 8.0), 385 ($\text{M}^+ - 4 - \text{Bu}$, 4.8), 251 (100). Anal. Calcd for $\text{C}_{22}\text{H}_{46}\text{OSn}$: C, 59.34; H, 10.41. Found: C, 59.32; H, 10.59.

(E)-3-Tributylstannyl-3-decen-2-ol ((E)-4h) [124582-45-2]²⁴

Bp 180 °C (1.9 Torr, bath temp.). IR (neat) 3371 (br s, OH), 2956, 2925, 2854, 1618 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.83–1.07 (m, 18H), 1.21 (d, $J = 6.3$ Hz, 3H), 1.26–1.58 (m, 21H),

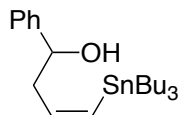
2.00 (dt, $J = 7.3, 6.5$ Hz, 2H), 4.35 (qdm, $J = 6.3, 3.5$ Hz, 1H), 6.17 (td, $J = 7.3, 1.0$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 129$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 123$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.98 ($\text{CH}_2 \times 3$), 13.65 ($\text{CH}_3 \times 3$), 14.05 (CH_3), 22.61 (CH_2), 24.23 (CH_3), 27.41 ($\text{CH}_2 \times 3$), 29.18 (CH_2), 29.23 ($\text{CH}_2 \times 3$), 30.04 (CH_2), 31.82 (CH_2), 34.20 (CH_2), 75.58 (CH), 139.63 (CH), 148.74 (C); MS m/z (relative intensity) 371 ($\text{M}^+ - \text{Bu} - \text{H}_2\text{O}$, 13), 369 ($\text{M}^+ - 2 - \text{Bu} - \text{H}_2\text{O}$, 8.9), 367 ($\text{M}^+ - 4 - \text{Bu} - \text{H}_2\text{O}$, 5.3), 68 (100).

(Z)-4-Tributylstannyl-3-buten-1-ol ((Z)-6a) [107711-42-2]^{29,30}



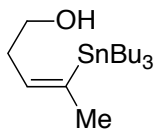
Bp 100 °C (0.5 Torr, bath temp.). IR (neat) 3327 (br s, OH), 2956, 2925, 1599 (C=C), 1464, 1045 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.80–1.05 (m, 15H) including 0.89 (t, $J = 7.3$ Hz), 1.24–1.65 (m, 13H), 2.26–2.38 (m, 2H), 3.68 (dt, $J = 6.3, 6.1$ Hz, 2H), 6.01 (dt, $J = 12.5, 1.1$ Hz, $^2J(^{119}\text{Sn}-^1\text{H}) = 69.8$ Hz, $^2J(^{117}\text{Sn}-^1\text{H}) = 66.8$ Hz, 1H), 6.51 (dt, $J = 12.5, 7.1$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 139$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 133$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.28 ($\text{CH}_2 \times 3$), 13.65 ($\text{CH}_3 \times 3$), 27.27 ($\text{CH}_2 \times 3$), 29.15 ($\text{CH}_2 \times 3$), 40.06 (CH_2), 62.12 (CH_2), 132.36 (CH), 144.36 (CH); MS m/z (relative intensity) 305 ($\text{M}^+ - \text{Bu}$, 73), 303 ($\text{M}^+ - 2 - \text{Bu}$, 55), 301 ($\text{M}^+ - 4 - \text{Bu}$, 26), 57 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{34}\text{OSn}$: C, 53.21; H, 9.49. Found: C, 53.34; H, 9.14.

(Z)-1-Phenyl-4-tributylstannyl-3-buten-1-ol ((Z)-6b) [251645-20-2]³¹



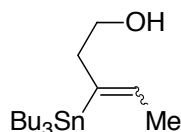
Bp 152 °C (1.0 Torr, bath temp.). IR (neat) 3373 (OH), 1597 (C=C) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.80–1.04 (m, 15H) including 0.88 (t, $J = 7.2$ Hz), 1.23–1.64 (m, 12H), 2.00 (d, $J = 3.0$ Hz, 1H), 2.37–2.59 (m, 2H), 4.74 (m, 1H), 6.04 (d, $J = 12.5$ Hz, 1H), 6.49–6.59 (m, 1H), 7.26–7.37 (m, 5H); ^{13}C NMR (CDCl_3) δ 10.30 ($\text{CH}_2 \times 3$), 13.66 ($\text{CH}_3 \times 3$), 27.29 ($\text{CH}_2 \times 3$), 29.15 ($\text{CH}_2 \times 3$), 46.69 (CH_2), 73.61 (CH), 125.76 (CH $\times 2$), 127.48 (CH), 128.39 (CH $\times 2$), 133.08 (CH), 144.01 (CH), 144.24 (C). Anal. Calcd for $\text{C}_{22}\text{H}_{38}\text{OSn}$: C, 60.43; H, 8.76. Found: C, 60.69; H, 8.51.

(Z)-4-Tributylstannyl-3-penten-1-ol ((Z)-6c) [651713-92-7]³²



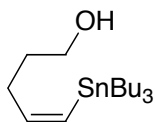
IR (neat) 3323 (br s, OH), 2956, 2925, 1624 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.82–1.06 (m, 15H) including 0.89 (t, $J = 7.3$ Hz), 1.24–1.64 (m, 13H), 1.92 (dt, $J = 1.6, 1.3$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 42.8$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 40.2$ Hz, 3H), 2.26 (dtq, $J = 7.2, 6.4, 1.2$ Hz, 2H), 3.64 (td, $J = 6.4, 5.7$ Hz, 2H), 6.02 (tq, $J = 7.2, 1.6$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 132$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 126$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 9.95 ($\text{CH}_2 \times 3$), 13.65 ($\text{CH}_3 \times 3$), 27.13 (CH_3), 27.36 ($\text{CH}_2 \times 3$), 29.18 ($\text{CH}_2 \times 3$), 37.99 (CH_2), 62.44 (CH_2), 136.02 (CH), 142.63 (C); MS m/z (relative intensity) 319 ($\text{M}^+ - \text{Bu}$, 82), 317 ($\text{M}^+ - 2 - \text{Bu}$, 70), 315 ($\text{M}^+ - 4 - \text{Bu}$, 46), 55 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{36}\text{OSn}$: C, 54.42; H, 9.67. Found: C, 54.17; H, 9.50.

(Z, E)-3-Tributylstannyl-3-penten-1-ol (7c, Z:E = 93:7)



IR (neat) 3327 (br s, OH), 2956, 2925, 1620 (weak, C=C), 1464, 1041 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.81–1.05 (m, 15H) including 0.89 (t, $J = 7.3$ Hz), 1.25–1.62 (m, 13H), 1.71–1.78 (m, 3H), 2.44 (t, $J = 6.2$ Hz, $^3J(\text{Sn}-^1\text{H}) = 50$ Hz, 1.86H), 2.57 (t, $J = 6.4$ Hz, 0.14H), 3.50–3.63 (m, 2H) including 3.53 (q, $J = 6.1$ Hz), 5.84 (qt, $J = 6.4, 1.2$ Hz, 0.07H), 6.21 (qt, $J = 6.6, 1.2$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 131$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 125$ Hz, 0.93H); ^{13}C NMR (CDCl_3) for the major isomer δ 10.06 ($\text{CH}_2 \times 3$), 13.63 ($\text{CH}_3 \times 3$), 19.99 (CH_3), 27.36 ($\text{CH}_2 \times 3$), 29.17 ($\text{CH}_2 \times 3$), 43.44 (CH_2), 61.57 (CH_2), 138.40 (CH), 140.49 (C); MS m/z (relative intensity) for the major isomer, 319 ($\text{M}^+ - \text{Bu}$, 100), 317 ($\text{M}^+ - 2 - \text{Bu}$, 73), 315 ($\text{M}^+ - 4 - \text{Bu}$, 44). Anal. Calcd for $\text{C}_{17}\text{H}_{36}\text{OSn}$: C, 54.42; H, 9.67. Found: C, 54.24; H, 9.46.

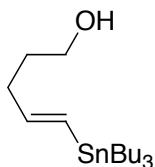
(Z)-5-Tributylstannyl-4-penten-1-ol ((Z)-9a) [211422-65-0]³³



Bp 105 °C (0.5 Torr, bath temp.). IR (neat) 3325 (br s, OH), 2956, 2925, 1599 (C=C), 1464, 1061 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.79–1.03 (m, 15H) including 0.89 (t, $J = 7.2$ Hz), 1.23–1.59 (m, 13H), 1.62–1.73 (m, 2H), 2.05–2.18 (m, 2H), 3.67 (td, $J = 6.5, 5.6$ Hz, 2H), 5.83 (dt, $J = 12.4, 1.0$ Hz, $^2J(^{119}\text{Sn}-^1\text{H})$)

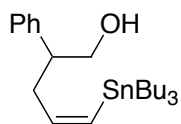
= 71.8 Hz, $^2J(^{117}\text{Sn}-^1\text{H}) = 69.0$ Hz, 1H), 6.53 (dt, $J = 12.4, 6.9$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 142$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 136$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 9.38 ($\text{CH}_2 \times 3$), 13.67 ($\text{CH}_3 \times 3$), 27.24 ($\text{CH}_2 \times 3$), 29.09 ($\text{CH}_2 \times 3$), 31.78 (CH_2), 34.08 (CH_2), 62.54 (CH_2), 128.20 (CH), 148.62 (CH); MS m/z (relative intensity) 319 ($\text{M}^+ - \text{Bu}, 58$), 317 ($\text{M}^+ - 2 - \text{Bu}, 45$), 315 ($\text{M}^+ - 4 - \text{Bu}, 28$), 121 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{36}\text{OSn}$: C, 54.42; H, 9.67. Found: C, 54.39; H, 9.57.

(E)-5-Tributylstannyl-4-penten-1-ol ((E)-9a) [123314-19-2]^{33,34}

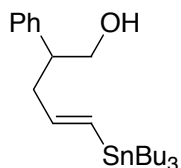


Bp 105 °C (0.5 Torr, bath temp.). IR (neat) 3327 (br s, OH), 2956, 2925, 1599 (C=C), 1464, 1070 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.74–0.98 (m, 15H), 1.24–1.62 (m, 13H), 1.64–1.74 (m, 2H), 2.17–2.27 (m, 2H), 3.66 (td, $J = 6.4, 5.8$ Hz, 2H), 5.81–6.09 (m, 2H); ^{13}C NMR (CDCl_3) δ 10.20 ($\text{CH}_2 \times 3$), 13.66 ($\text{CH}_3 \times 3$), 27.28 ($\text{CH}_2 \times 3$), 29.17 ($\text{CH}_2 \times 3$), 32.80 (CH_2), 33.35 (CH_2), 62.67 (CH_2), 128.76 (CH), 148.25 (CH); MS m/z (relative intensity) 319 ($\text{M}^+ - \text{Bu}, 79$), 317 ($\text{M}^+ - 2 - \text{Bu}, 62$), 315 ($\text{M}^+ - 4 - \text{Bu}, 37$), 121 (100).

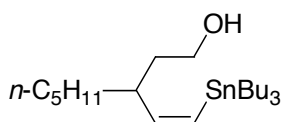
(Z)-2-Phenyl-5-tributylstannyl-4-penten-1-ol ((Z)-9b)



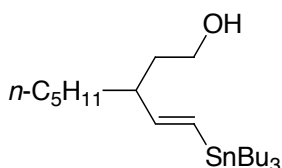
Bp 140 °C (1.0 Torr, bath temp.). IR (neat) 3359 (br s, OH), 2956, 2924, 1599 (C=C), 1454, 1068, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.78–1.03 (m, 15H) including 0.89 (t, $J = 7.2$ Hz), 1.23–1.63 (m, 13H), 2.36–2.45 (m, 2H), 2.90 (qd, $J = 7.4, 5.8$ Hz, 1H), 3.76 (ddd, $J = 10.9, 7.7, 5.1$ Hz, 1H), 3.82 (ddd, $J = 10.9, 7.6, 5.8$ Hz, 1H), 5.84 (dt, $J = 12.5, 1.2$ Hz, $^2J(^{119}\text{Sn}-^1\text{H}) = 70.7$ Hz, $^2J(^{117}\text{Sn}-^1\text{H}) = 67.7$ Hz, 1H), 6.44 (dt, $J = 12.5, 6.9$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 141$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 135$ Hz, 1H), 7.19–7.37 (m, 5H); ^{13}C NMR (CDCl_3) δ 10.21 ($\text{CH}_2 \times 3$), 13.67 ($\text{CH}_3 \times 3$), 27.29 ($\text{CH}_2 \times 3$), 29.18 ($\text{CH}_2 \times 3$), 39.60 (CH_2), 48.80 (CH), 66.99 (CH_2), 126.83 (CH), 127.98 (CH $\times 2$), 128.66 (CH $\times 2$), 130.03 (CH), 141.95 (C), 146.39 (CH); MS m/z (relative intensity) 395 ($\text{M}^+ - \text{Bu}, 34$), 393 ($\text{M}^+ - 2 - \text{Bu}, 21$), 391 ($\text{M}^+ - 4 - \text{Bu}, 12$), 91 (100). Anal. Calcd for $\text{C}_{23}\text{H}_{40}\text{OSn}$: C, 61.21; H, 8.93. Found: C, 61.48; H, 8.87.

(E)-2-Phenyl-5-tributylstannyl-4-penten-1-ol ((E)-9b)

IR (neat) 3352 (br s, OH), 2954, 2924, 2871, 2852, 1599 (weak, C=C), 1454 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.68–0.93 (m, 15H) including 0.87 (t, $J = 7.3$ Hz), 1.20–1.52 (m, 13H), 2.48 (ddd, $J = 13.6, 7.8, 5.1$ Hz, 1H), 2.52 (ddd, $J = 13.6, 6.9, 5.3$ Hz, 1H), 2.87–2.98 (m, 1H), 3.76 (ddd, $J = 10.9, 7.6, 5.3$ Hz, 1H), 3.82 (ddd, $J = 10.9, 7.4, 5.8$ Hz, 1H), 5.86 (ddd, $J = 10.2, 5.3, 5.1$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 67.0$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 64.7$ Hz, 1H), 5.92 (d, $J = 18.8$ Hz, $^2J(^{119}\text{Sn}-^1\text{H}) = 75.7$ Hz, $^2J(^{117}\text{Sn}-^1\text{H}) = 72.6$ Hz, 1H), 7.20–7.35 (m, 5H); ^{13}C NMR (CDCl_3) δ 9.34 ($\text{CH}_2 \times 3$), 13.67 ($\text{CH}_3 \times 3$), 27.21 ($\text{CH}_2 \times 3$), 29.01 ($\text{CH}_2 \times 3$), 40.91 (CH_2), 48.16 (CH), 66.84 (CH_2), 126.65 (CH), 128.01 (CH $\times 2$), 128.52 (CH $\times 2$), 130.21 (CH), 142.04 (C), 146.57 (CH). Anal. Calcd for $\text{C}_{23}\text{H}_{40}\text{OSn}$: C, 61.21; H, 8.93. Found: C, 61.30; H, 8.87.

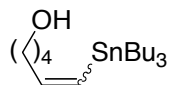
(Z)-3-Pentyl-5-tributylstannyl-4-penten-1-ol ((Z)-9c)

IR (neat) 3324 (br s, OH), 2954, 2925, 2854, 1597 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.79–1.04 (m, 18H), 1.19–1.61 (m, 22H), 1.63–1.75 (m, 1H), 1.90 (br s, 1H), 3.56–3.73 (m, 2H), 5.79 (d, $J = 12.5$ Hz, $^2J(^{119}\text{Sn}-^1\text{H}) = 69.2$ Hz, $^2J(^{117}\text{Sn}-^1\text{H}) = 66.2$ Hz, 1H), 6.29 (dd, $J = 12.5, 9.6$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 144$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 137$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.33 ($\text{CH}_2 \times 3$), 13.67 ($\text{CH}_3 \times 3$), 14.04 (CH_3), 22.62 (CH_2), 26.89 (CH_2), 27.37 ($\text{CH}_2 \times 3$), 29.18 ($\text{CH}_2 \times 3$), 32.24 (CH_2), 35.76 (CH_2), 38.05 (CH_2), 44.63 (CH), 61.74 (CH_2), 127.73 (CH), 154.01 (CH). Anal. Calcd for $\text{C}_{22}\text{H}_{46}\text{OSn}$: C, 59.34; H, 10.41. Found: C, 59.50; H, 10.62.

(E)-3-Pentyl-5-tributylstannyl-4-penten-1-ol ((E)-9c)

IR (neat) 3323 (br s, OH), 2956, 2925, 2854, 1597 (weak, C=C), 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.74–0.99 (m, 18H), 1.20–1.71 (m, 23H), 2.12 (br s, 1H), 3.57–3.73 (m, 2H), 5.67 (dd, $J = 18.9, 8.2$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 65.2$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 62.3$ Hz, 1H), 5.87 (d, $J = 18.9$ Hz, $^2J(^{119}\text{Sn}-^1\text{H}) = 79.2$ Hz, $^2J(^{117}\text{Sn}-^1\text{H}) = 75.2$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 9.46 ($\text{CH}_2 \times 3$), 13.70 ($\text{CH}_3 \times 3$), 14.05 (CH_3), 22.62 (CH_2), 26.78 (CH_2), 27.21 ($\text{CH}_2 \times 3$), 29.12 ($\text{CH}_2 \times 3$), 31.86 (CH_2), 35.17 (CH_2), 37.91 (CH_2), 45.48 (CH), 61.62 (CH_2), 127.90 (CH), 153.67 (CH).

6-Tributylstannyl-5-hexen-1-ol (11, Z:E = 76:24) [150599-59-0]³⁵ for *Z*-isomer; [122593-90-2]³⁶ for *E*-isomer



IR (neat) 3332 (br s, OH), 2956, 2925, 1599 (C=C), 1462, 1070 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.73–1.02 (m, 15H) including 0.89 (t, $J = 7.2$ Hz), 1.21–1.65 (m, 17H), 2.06 (tdd, $J = 7.3, 7.1, 1.0$ Hz, 1.52H), 2.17 (td, $J = 7.4, 4.8$ Hz, 0.48H), 3.65 (td, $J = 6.4, 5.6$ Hz, 2H), 5.80 (dt, $J = 12.4, 1.1$ Hz, $^2J(^{119}\text{Sn}-^1\text{H}) = 73.2$ Hz, $^2J(^{117}\text{Sn}-^1\text{H}) = 70.6$ Hz, 0.76H), 5.83–6.05 (m, 0.48 H), 6.50 (dt, $J = 12.4, 7.1$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 144$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 137$ Hz, 0.76H); ^{13}C NMR (CDCl_3) for the major isomer δ 10.19 ($\text{CH}_2 \times 3$), 13.67 ($\text{CH}_3 \times 3$), 25.99 (CH_2), 27.29 ($\text{CH}_2 \times 3$), 29.17 ($\text{CH}_2 \times 3$), 32.44 (CH_2), 36.71 (CH_2), 62.83 (CH_2), 128.27 (CH), 148.65 (CH), for the minor isomer (only resolved peaks) δ 9.34 ($\text{CH}_2 \times 3$), 24.97 (CH_2), 27.24 ($\text{CH}_2 \times 3$), 29.09 ($\text{CH}_2 \times 3$), 32.18 (CH_2), 37.48 (CH_2), 127.60 (CH), 149.10 (CH); MS m/z (relative intensity) for the major isomer 333 ($\text{M}^+ - \text{Bu}$, 100), 331 ($\text{M}^+ - 2 - \text{Bu}$, 77), 329 ($\text{M}^+ - 4 - \text{Bu}$, 45). Anal. Calcd for $\text{C}_{18}\text{H}_{38}\text{OSn}$: C, 55.55; H, 9.84. Found: C, 55.27; H, 9.71.

4. Mechanistic Aspect

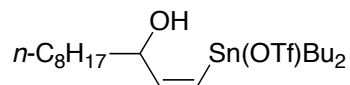
4. 1. NMR Analysis of (Trifluoromethanesulfoxy)vinylstannane (*Z*)-3a'

As described in the text, the present high stereo- and regioselectivity are probably due to the Sn-O coordination in vinyl radical intermediates **12** and products (*Z*)-**13a** (Scheme 2 in the text). To ascertain the presence of the Sn-O coordination, (trifluoromethanesulfoxy)vinylstannane (*Z*)-**3a'** prepared from **1a** and **2a** was subjected to NMR analysis. The ^1H NMR analysis disclosed that the allylic proton (4.63

ppm) appeared at a lower field than that of tributylvinylstannane (*Z*)-**3a** (3.90 ppm). The coupling constant between the allylic proton and the vicinal sp^2 -proton (1.7 Hz) was much smaller than that of (*Z*)-**3a** (7.5 Hz). These facts clearly shows the presence of the Sn-O coordination in (*Z*)-**3a'**. In addition, a broad singlet for one proton was observed at 7.04 ppm. Since addition of an excess amount of CD_3OD (5 equiv.) brought about both a downfield shift of the signal and a significant reduction of the integral value (8.65 ppm, 0.18H), the broad singlet is certainly corresponding to the hydroxy proton. In the case of (*Z*)-**3a**, its hydroxy proton was not observed at such a low field, and the signal was probably buried in the multiplet from 1.24 to 1.64 ppm. Accordingly, the remarkable downfield shift of the hydroxy proton in (*Z*)-**3a'** supports the Sn-O coordination.

To gain further evidence for the internal coordination, we prepared (*E*)-1-dibutyl(trifluoromethanesulfoxy)stannyl-1-dodecene (**15**) by the reaction of 1-dodecyne with **1a**, and compared (*Z*)-**3a'** with (*E*)-**15** in one bond coupling constant ($^1J(^{119}Sn-^{13}C)$) and ^{119}Sn chemical shift. The coupling constants of (*Z*)-**3a'** (448 Hz for $^{119}Sn-^{13}C_{CH_2}$; 575 Hz for $^{119}Sn-^{13}C_{CH}$) were found to be larger than those of (*E*)-**15** (430 Hz for $^{119}Sn-^{13}C_{CH_2}$; 534 Hz for $^{119}Sn-^{13}C_{CH}$). The increase of the coupling constant between tin and an adjacent nucleus is known to be related to the change in the hybridization around tin on changing from the tetrahedral sp^3 state in normally coordinated organotin compounds to a trigonal bipyramidal state in the corresponding pentacoordinated complexes.^{4,5} In ^{119}Sn NMR, (*Z*)-**3a'** (55.8 ppm) was observed at a higher field than (*E*)-**15** (81.2 ppm). This result is also indicative of the internal coordination in (*Z*)-**3a'**.

(*Z*)-1-Dibutyl(trifluoromethanesulfoxy)stannyl-1-undecen-3-ol ((*Z*)-**3a'**)



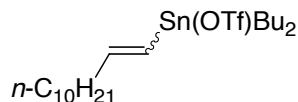
The sample of (*Z*)-**3a'** was obtained by the reaction of **2a** with **1a** (hexane, rt, 3 h) followed by evaporation. A solution of (*Z*)-**3a'** (0.15 mmol) in $CDCl_3$ (0.6 mL) was used for the NMR analysis. 1H NMR ($CDCl_3$) δ 0.85–0.99 (m, 9H), 1.26–1.77 (m, 26H), 4.64 (br s, 1H), 6.42 (dd, $J = 11.5, 2.3$ Hz, $^2J(^{119}Sn-^1H) = 133$ Hz, $^2J(^{117}Sn-^1H) = 128$ Hz, 1H), 6.71 (dd, $J = 11.5, 1.6$ Hz, $^3J(^{119}Sn-^1H) = 211$ Hz, $^3J(^{117}Sn-^1H) = 202$ Hz, 1H), 7.04 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.44 ($CH_3 \times 2$), 14.04 (CH_3), 20.27 ($CH_2 \times 2$, $^1J(^{119}Sn-^{13}C) = 448$ Hz, $^1J(^{117}Sn-^{13}C) = 426$ Hz), 22.62 (CH_2), 24.23 (CH_2), 26.41 ($CH_2 \times 2$, $^3J(Sn-^{13}C) = 78$ Hz), 27.26 ($CH_2 \times 2$, $^2J(Sn-^{13}C) = 31$ Hz), 29.19 (CH_2), 29.37 (CH_2), 29.51 (CH_2),

31.81 (CH₂), 36.38 (CH₂), 76.83 (CH), 119.31 (CF₃, q, $^1J(^{13}\text{C}-^{19}\text{F}) = 318$ Hz), 128.64 (CH, $^1J(^{119}\text{Sn}-^{13}\text{C}) = 575$ Hz, $^1J(^{117}\text{Sn}-^{13}\text{C}) = 549$ Hz), 146.65 (CH); ^{119}Sn NMR (CDCl₃) δ 55.8.

NMR Spectra for (Z)-**3a'** in the Presence of CD₃OD

A mixture of (Z)-**3a'** (0.15 mmol), CD₃OD (0.75 mmol), and CDCl₃ (0.6 mL) was used for the NMR analysis. ^1H NMR (CDCl₃) δ 0.80–0.92 (m, 9H), 1.22–1.70 (m, 26H), 4.10 (br s, 0.82 H), 4.52–4.56 (m, 1H), 6.28 (dd, $J = 11.5, 2.3$ Hz, $^2J(^{119}\text{Sn}-^1\text{H}) = 138$ Hz, $^2J(^{117}\text{Sn}-^1\text{H}) = 133$ Hz, 1H), 6.72 (dd, $J = 11.5, 2.1$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 212$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 203$ Hz, 1H), 8.65 (br s, 0.18H); ^{13}C NMR (CDCl₃) δ 13.32 (CH₃ \times 2), 13.93 (CH₃), 18.79 (CH₂ \times 2, $^1J(^{119}\text{Sn}-^{13}\text{C}) = 464$ Hz, $^1J(^{117}\text{Sn}-^{13}\text{C}) = 443$ Hz), 22.52 (CH₂), 24.21 (CH₂), 26.39 (CH₂ \times 2, $^3J(^{119}\text{Sn}-^{13}\text{C}) = 82.2$ Hz, $^3J(^{117}\text{Sn}-^{13}\text{C}) = 78.8$ Hz), 27.30 (CH₂ \times 2, $^2J(\text{Sn}-^{13}\text{C}) = 30$ Hz), 29.09 (CH₂), 29.28 (CH₂), 29.41 (CH₂), 31.71 (CH₂), 36.36 (CH₂), 75.66 (CH), 119.90 (CF₃, q, $^1J(^{13}\text{C}-^{19}\text{F}) = 319$ Hz), 126.25 (CH), 147.96 (CH); ^{119}Sn NMR (CDCl₃) δ 31.8.

1-Dibutyl(trifluoromethanesulfoxy)stannyl-1-dodecene (**15**, *E:Z* = 91:9)



The sample was prepared by the Et₃B-air-initiated reaction of 1-dodecyne with **1a** (hexane, 0 °C, 3 h) followed by evaporation. A solution of the crude product (0.30 or 0.15 mmol) in CDCl₃ (0.6 mL) was used for the NMR analysis in CDCl₃, which disclosed that the sample contained *E*- and *Z*-isomers (*E:Z* = 91:9) of the title compound and a small amount of 1-dodecene within 1 h. The ratio of 1-dodecene to the vinylstannane increased with time, and the latter almost disappeared after 3 days. The title compound seems to be easily destannylated to 1-dodecyne with adventitious water. ^1H NMR (CDCl₃) for the *E*-isomer δ 0.85–0.94 (m, 9H), 1.15–1.90 (m, 28H), 2.13–2.20 (m, 2H), 5.95 (d, $J = 18.6$ Hz, $^2J(^{119}\text{Sn}-^1\text{H}) = 127$ Hz, $^2J(^{117}\text{Sn}-^1\text{H}) = 123$ Hz, 1H), 6.28 (dt, $J = 18.6, 6.3$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 94.6$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 90.7$ Hz, 1H) for the *Z*-isomer (only well-resolved signals) δ 5.98 (d, $J = 11.9$ Hz, 1H), 6.64 (dt, $J = 11.9, 7.0$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 223$ Hz, $^3J(^{117}\text{Sn}-^1\text{H}) = 213$ Hz, 1H); ^{13}C NMR (CDCl₃) δ 13.46 (CH₃ \times 2), 14.07 (CH₃), 21.53 (CH₂ \times 2, $^1J(^{119}\text{Sn}-^{13}\text{C}) = 430$ Hz, $^1J(^{117}\text{Sn}-^{13}\text{C}) = 412$ Hz), 22.69 (CH₂), 26.56 (CH₂ \times 2, $^3J(\text{Sn}-^{13}\text{C}) = 82$ Hz), 27.22 (CH₂ \times 2, $^2J(\text{Sn}-^{13}\text{C}) = 30$ Hz), 28.42 (CH₂), 29.25 (CH₂), 29.37 (CH₂), 29.54 (CH₂), 29.65 (CH₂ \times 2), 31.93 (CH₂), 37.38 (CH₂), 118.80 (CF₃, q, $^1J(^{13}\text{C}-^{19}\text{F}) =$

317 Hz), 127.26 (CH, $^1J (^{119}\text{Sn}-^{13}\text{C}) = 534$ Hz, $^1J (^{117}\text{Sn}-^{13}\text{C}) = 511$ Hz), 153.39 (CH); ^{119}Sn NMR (CDCl_3) δ 81.2.

4. 2. ^1H NMR Analysis of A Mixture of $\text{Bu}_2\text{Sn}(\text{OTf})\text{H}$ and EtOH

A mixture of hydrostannane **1a** (0.3 mmol) and EtOH (0.4 mmol) in C_6D_6 (0.6 mL) was subjected to ^1H , ^{13}C , and ^{119}Sn NMR analyses at 22 °C. The results are shown below. In the presence of EtOH, the proton and carbons bound to tin ($\underline{\text{C}}-\text{Sn}-\underline{\text{H}}$) appeared at higher fields, and their coupling constants 1J with the tin nucleus increased (*cf.* Table S1). The ^{119}Sn signal shifted from 22.7 ppm to -21.6 ppm. Concerning the NMR data for EtOH, the hydroxy proton underwent a remarkable shift to a lower field (from 2.04 ppm to 6.11 ppm) in the presence of **1a**. The α -carbon ($\underline{\text{C}}-\text{O}$) also appeared at a lower field. These spectral changes in **1a** and EtOH clearly indicate the formation of an Sn–O coordinate bond. In this experiment, the formation of $\text{Bu}_2\text{Sn}(\text{OEt})\text{H}$ was not observed at all.

A Mixture of $\text{Bu}_2\text{Sn}(\text{OTf})\text{H}$ and EtOH (molar ratio = 1:1.3)

^1H NMR (C_6D_6) for **1a** δ 0.98 (t, $J = 7.3$ Hz, 6H), 1.37–1.98 (m, 12H), 8.30 (s, $^1J (^{119}\text{Sn}-^1\text{H}) = 2377$ Hz, $^1J (^{117}\text{Sn}-^1\text{H}) = 2272$ Hz, 1H), for EtOH δ 1.01 (t, $J = 7.1$ Hz, 3H), 3.42 (q, $J = 7.1$ Hz, 2H), 6.11 (br s, 1H); ^{13}C NMR (C_6D_6) for **1a** δ 13.67 ($\text{CH}_3 \times 2$), 19.48 ($\text{CH}_2 \times 2$, $^1J (^{119}\text{Sn}-^{13}\text{C}) = 477$ Hz, $^1J (^{117}\text{Sn}-^{13}\text{C}) = 455$ Hz), 26.83 ($\text{CH}_2 \times 2$, $^3J (\text{Sn}-^{13}\text{C}) = 84$ Hz), 27.99 ($\text{CH}_2 \times 2$, $^2J (\text{Sn}-^{13}\text{C}) = 32$ Hz), 120.35 (q, $^1J (^{13}\text{C}-^{19}\text{F}) = 319$ Hz), for EtOH δ 17.12 (CH_3), 60.51 (CH_2); ^{119}Sn NMR (C_6D_6) δ -21.6 ($^1J (^{119}\text{Sn}-^1\text{H}) = 2377$).

Ethanol in the Absence of $\text{Bu}_2\text{Sn}(\text{OTf})\text{H}$

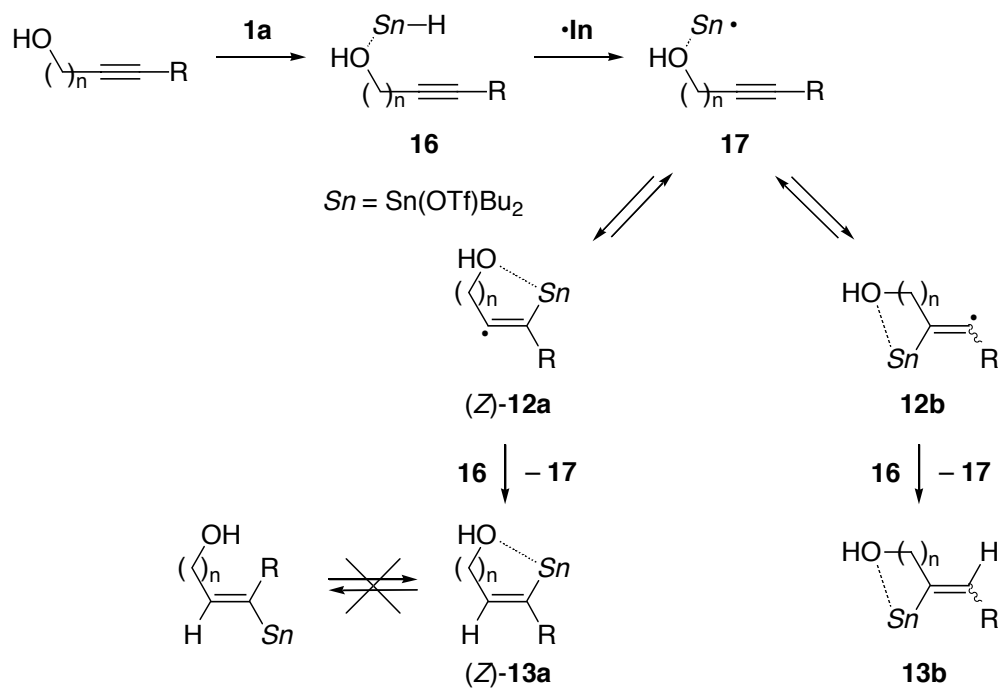
^1H NMR (C_6D_6) δ 1.00 (t, $J = 7.1$ Hz, 3H), 2.04 (br s, 1H), 3.41 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (C_6D_6) δ 18.42 (CH_3), 57.86 (CH_2).

4. 3. Further Discussion on Reaction Mechanism

As shown above, **1a** and EtOH readily formed a coordination compound. This fact implies that the present hydrostannylation of alkynols proceeds via pre-coordination of **1a** with the hydroxy group, that

is, the formation of **16** (Scheme S1). Vinyl radical intermediates **12** could be formed by intramolecular addition of stannyl radical **17** arising from **16**.

Scheme S1. A Plausible Mechanism Involving Pre-coordination of $\text{Bu}_2\text{Sn}(\text{OTf})\text{H}$

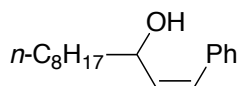


5. Hydrostannylation Followed by Pd-Catalyzed Cross-Coupling

Typical Procedure³⁷

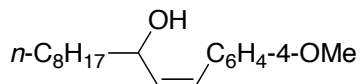
Hydrostannane **1a** (215 mg, 0.561 mmol) was added to a solution of **2a** (84.7 mg, 0.503 mmol) in hexane (1 mL) at room temperature. After being stirred for 3 h, the reaction mixture was concentrated *in vacuo*. A solution of Bu_4NF (70-75% in H_2O , 565 mg, 1.51–1.62 mmol) in DMF (2.5 mL), Ph_3P (13.2 mg, 0.050 mmol), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (10 mg, 0.010 mmol), and PhI (113 mg, 0.554 mmol) were successively added to the crude hydrostannylation product. The mixture was stirred at 70 °C for 5 h. The resultant mixture was cooled to room temperature and diluted with *t*-BuOMe (10 mL). After addition of DBU (0.5 mL), the mixture was stirred for 5-10 min, passed through a short silica gel column, and evaporated. Purification of the residual oil by silica gel column chromatography (hexane-AcOEt 7:1) gave (*Z*)-1-phenyl-1-undecen-3-ol (102 mg, 0.415 mmol, 82%).

(*Z*)-1-Phenyl-1-undecen-3-ol ((*Z*)-14a)



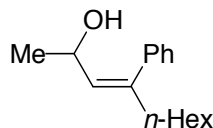
Bp 130 °C (0.8 Torr, bath temp.). IR (neat) 3334 (br s, OH), 2925, 2854, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87 (t, $J = 6.7$ Hz, 3H), 1.20–1.70 (m, 15H), 4.52–4.61 (m, 1H), 5.66 (dd, $J = 11.5, 9.2$ Hz, 1H), 6.55 (d, $J = 11.5$ Hz, 1H), 7.23–7.37 (m, 5H); ^{13}C NMR (CDCl_3) δ 14.07 (CH_3), 22.61 (CH_2), 25.33 (CH_2), 29.21 (CH_2), 29.50 (CH_2), 29.54 (CH_2), 31.81 (CH_2), 37.57 (CH_2), 67.80 (CH), 127.12 (CH), 128.21 (CH \times 2), 128.69 (CH \times 2), 130.83 (CH), 134.72 (CH), 136.64 (C); MS m/z (relative intensity) 246 (M^+ , 0.5), 228 ($\text{M}^+ - \text{H}_2\text{O}$, 3.6), 55 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}$: C, 82.87; H, 10.64. Found: C, 82.83; H, 10.35.

(Z)-1-(4-Methoxyphenyl)-1-undecen-3-ol ((Z)-14b)



Bp 210 °C (1.3 Torr, bath temp.). IR (neat) 3350 (br s, OH), 2925, 2854, 1608, 1510, 1252 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87 (t, $J = 6.7$ Hz, 3H), 1.20–1.73 (m, 15H), 3.82 (s, 3H), 4.56–4.61 (m, 1H), 5.58 (dd, $J = 11.5, 9.2$ Hz, 1H), 6.49 (d, $J = 11.5$ Hz, 1H), 6.85–6.91 (m, 2H), 7.23–7.28 (m, 2H); ^{13}C NMR (CDCl_3) δ 14.07 (CH_3), 22.62 (CH_2), 25.39 (CH_2), 29.22 (CH_2), 29.51 (CH_2), 29.56 (CH_2), 31.82 (CH_2), 37.70 (CH_2), 55.18 (CH_3), 67.88 (CH), 113.65 (CH \times 2), 129.23 (C), 130.02 (CH \times 2), 130.51 (CH), 133.20 (CH), 158.72 (C); MS m/z (relative intensity) 258 ($\text{M}^+ - \text{H}_2\text{O}$, 80), 173 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2$: C, 78.21; H, 10.21. Found: C, 78.19; H, 9.95.

(Z)-4-Phenyl-3-decen-2-ol ((Z)-14c)



IR (neat) 3332 (br s, OH), 2958, 2927, 1057, 702 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.86 (t, $J = 6.7$ Hz, 3H), 1.14–1.60 (m, 11H), 2.32 (t, $J = 6.8$ Hz, 3H), 4.23 (dq, $J = 9.1, 6.2$ Hz, 1H), 5.47 (d, $J = 9.1$ Hz, 1H), 7.11–7.15 (m, 2H), 7.23–7.36 (m, 3H); ^{13}C NMR (CDCl_3) δ 14.03 (CH_3), 22.54 (CH_2), 23.71 (CH_3), 27.69 (CH_2), 28.79 (CH_2), 31.58 (CH_2), 39.08 (CH_2), 65.31 (CH), 126.84 (CH), 128.06 (CH \times 4), 130.54 (CH), 140.57 (C), 143.17 (C); MS m/z (relative intensity) 232 (M^+ , 0.7), 214 ($\text{M}^+ - \text{H}_2\text{O}$, 11), 129 (100).

Anal. Calcd for C₁₆H₂₄O: C, 82.70; H, 10.41. Found: C, 82.37; H, 10.37.

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