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Highly Stereoselective Addition of Stannylcuprates to Alkynones

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The addition of stannylcuprate reagents such as $(Bu_3Sn)(PhS)CuLi$ to alkynones has been found to proceed in high yield and with excellent stereoselectivity for the *Z* isomer of the product (>95%). The behavior of the stannylcuprates is thus very different from that of their "carbocuprate" counterparts such as Me_2CuLi or $Me_2Cu(CN)Li_2$ which are nonstereoselective. Furthermore, in contrast to the reactions of $(R_3Sn)(PhS)CuLi$ with the corresponding alkynoates, the presence of a proton source in the reaction medium has no effect on the stereoselectivity of the reaction of alkynones.

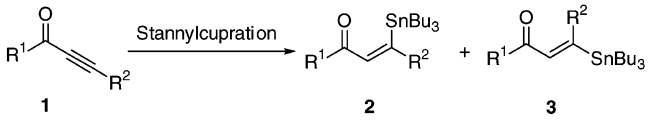
Introduction

Organocopper reagents provide one of the most reliable and versatile tools for carbon−carbon or carbon−heteroatom bond formation, either by substitution, conjugate addition, or carbocupration reactions.[1] As is often the case with organometallics, detailed mechanistic insight that is essential to the development of even more efficient reagents can be gleaned only with difficulty and not without some controversy.[2] However, recent theoretical, kinetic, and spectroscopic studies have gone some way to improving the "black box" reputation of organocopper chemistry.[3] An important mechanistic study by Ullenius and co-workers[4] recently highlighted the opportunities and difficulties associated with addition of organocuprates to alkynoates[5] and alkynones. Our interest in stereoselective stannylcupration of the latter substrates (Scheme 1) was awakened during the course of a total synthesis program,[6] and was further prompted by the pioneering work of Piers[7] on the addition of stannylcuprates to acetylenic esters. In the present paper we describe unusually high stereoselectivity (>95%) in the addition of stannylcuprates to alkynones **1**.

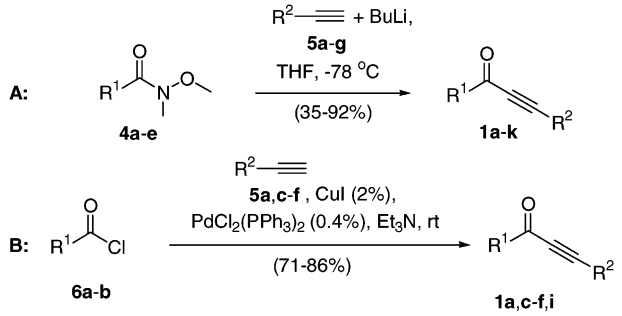
Results and Discussion

The alkynones[8] **1a**−**k** chosen for the present study were prepared by two simple and complementary methods: (A) addition of lithium acetylides to Weinreb amides, and (B) Sonogashira coupling of terminal alkynes with acid chlorides (Scheme 2 and Experimental Section).

SCHEME 1



SCHEME 2



Alkynone **1d** was chosen for the initial studies, using three different stannylcuprate reagents under the conditions shown in Table 1. We were initially most interested to investigate if the *Z*/*E* ratio of the products could be affected by variation of the reaction temperature and the presence (or absence) of a proton source (methanol) in the reaction medium.[7] In contrast to the corresponding alkynoates[7,9] and contrary to previous studies[10] involving "carbocuprates" the alkynones delivered *exclusively* the *Z* isomer of the product under all reaction conditions tested. The *E* isomer, if present at all, could not be detected in the high-field ^1H NMR spectra of the crude products. The stereochemistry of the product **2d** was determined[11] by NMR spectroscopy, where the coupling constant from the vinyl proton to tin, $J(Sn-H)$, was found to be 110 Hz. As indicated in footnote *d* in Table 1, trapping[12] of the presumed organocopper intermediate

(1) Lipshutz, B. H.; Sengupta, S. *Org. React.* **1992**, *41*, 135.
(2) Nakamura, E.; Mori, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3750.
(3) Woodward, S. *Chem. Soc. Rev.* **2000**, *9*, 393.
(4) Nilsson, K.; Andersson, T.; Ullenius, C.; Gerold, A.; Krause, N. *Chem. Eur. J.* **1998**, *4*, 2051.
(5) For a recent example, see: Williams, D. R.; Fromhold, M. G.; Earley, J. D. *Org. Lett.* **2001**, *3*, 2721.
(6) Tanner, D.; Tedenborg, L.; Somfai, P. *Acta Chem. Scand.* **1997**, *51*, 1217.
(7) Piers, E.; Morton, H. E. *J. Org. Chem.* **1980**, *45*, 4263.
(8) For leading references, see: Kel'in, A.; Gevorgyan, V. *J. Org. Chem.* **2002**, *67*, 95.
(9) Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron* **1989**, *45*, 363.
(10) For leading references, see ref 4.
(11) For typical $J(Sn-H)$ values, see refs 9 and 14.

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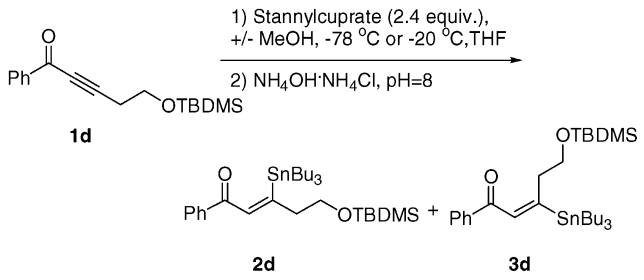
TABLE 1. Stannylcupration of Alkynones I



entry	stannylcuprate	MeOH (+/−)[a]	temp (°C)	product yield of **2d** (%)[b,c]
1	$(Bu_3Sn)(PhS)CuLi$	−	−78	>95
2[d]	$(Bu_3Sn)(PhS)CuLi$	−	−78	>95
3	$(Bu_3Sn)(PhS)CuLi$	+	−78	75
4	$(Bu_3Sn)(PhS)CuLi$	+	−20	58
5	$(Bu_3Sn)(CN)CuLi$	−	−78	>95
6	$(Bu_3Sn)(CN)CuLi$	+	−78	77
7	$Bu_3SnCu{\cdot}Me_2S$	−	−78	44
8	$Bu_3SnCu{\cdot}Me_2S$	+	−78	36

[a] (+) indicates that MeOH (1.7 equiv) *and* alkynone **1d** were dissolved in the same THF solution and added to the stannylcuprate, and (−) indicates that alkynone **1d** was added to the stannylcuprate in the absence of methanol. [b] Isolated yield after flash column chromatography. [c] None of the *E* isomer **3d** could be detected. [d] When TLC indicated complete conversion of the substrate, MeI (10 equiv) was added to the mixture, followed by stirring for 1 h at −78 °C to afford none of the methylated product.

by electrophiles other than a proton was unfortunately not possible.

On the basis of these encouraging results, we performed some further screening of stannylcuprates (Table 2).

Again, exclusive *Z*-selectivity was observed, with the $(Bu_3Sn)(PhS)CuLi$ reagent[13] generally providing the highest yields. THF was much superior to diethyl ether as solvent (entry 2) and it is interesting to note that one of the cuprates survived in the presence of 10 equiv of water (entry 5).

The $(Bu_3Sn)(PhS)CuLi$ reagent was then selected for the screening of acetylenic ketones summarized in Table 3. With the exception of entry 2, isolated yields were uniformly excellent and the *Z* isomers were the exclusive products which could be purified easily and with minimal decomposition (protodestannylation) by conventional flash chromatography. The configuration of the products was determined by ^{1}H NMR spectroscopy, where the coupling constants of the vinyl proton to tin, J(Sn−H), of products **2a**−**k** were measured to be within the range of 101−114 Hz, and NOE measurements (Figure 1).

That the high *Z*-selectivity is peculiar to the stannylcuprates is shown by the results gathered in Table 4. In line with previous work[4,14] a selection of Gilman (R_2CuLi) or Lipshutz ($R_2Cu(CN)Li_2$) reagents gave essentially 1:1 mixtures of the *E* and *Z* products, as determined by ^{1}H NMR spectroscopy.

Ullenius[4] and others[14] have noted that it is in general difficult to control the stereoselectivity of organocuprate additions to acetylenic ketones. Our results obviously have mechanistic implications worthy of further study, and we are currently investigating this reaction by a combination of experimental, spectroscopic, and theoretical techniques. Results will be published in due course.

Conclusions

We have demonstrated that stannylcuprates add to alkynones in high yield and with unprecedentedly high stereoselectivity (>95%), the *Z* isomer being the exclusive product. In our experience, the present method generally gives higher yields than can be obtained by alternative routes[15] and gives convenient access to functionalized trisubstituted alkenes which are useful building blocks for further synthesis (e.g. via cross-coupling reactions).[16] A solution to the problem of obtaining the corresponding *E* isomers is given elsewhere.[17]

Experimental Section

General Methods. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR, and ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded by 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. IR spectra were obtained for thin films on AgCl plates, and only the strongest/structurally most important peaks (ν_{max}/cm^{-1}) are listed. Microanalyses were performed by the Microanalysis Laboratory, Department of Physical Chemistry, University of Vienna, Austria. HRMS was performed at the Department of Chemistry, University of Copenhagen, Denmark. Molecular mass determinations (high-resolution mass spectrometry) for substances containing R_3Sn (Bu_3Sn or Me_3Sn) groups are based on ^{120}Sn and typically made on the $[M - R]^+$, unless otherwise stated. All compounds on which HRMS were performed exhibited clean ^{1}H proton 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. All chromatography was performed with use of Merck silica gel (40−63 μm). All solvents were distilled prior to use. THF and diethyl ether were distilled under nitrogen from Na-benzophenone. Diisopropylamine was dried over calcium hydride and distilled under nitrogen. Commercially available compounds were used as received unless otherwise indicated. Saturated ammonium chloride (pH ~8) was prepared by addition of 60 mL of aqueous ammonia (25%) to 950 mL of saturated ammonium chloride. Phenylthiocopper(I) was prepared according to Posner,[18] copper(I) bromide−dimethyl sulfide complex and copper(I) iodide were prepared according to House,[19] and commercial copper(I) cyanide was oven-dried overnight at 150 °C and used without any further purification. All reactions were carried out under

(12) Barbero, A.; Cuadrado, P.; Fleming, I.; González, A. M.; Pulido, F. J. *J. Chem. Soc., Chem. Commun.* **1992**, 351. Cuadrado, P.; González-Nogal, A. M.; Sánchez, A. *J. Org. Chem.* **2001**, *66*, 1961.

(13) For preparation of such reagents, see: Piers, E.; Chong, J. M.; Gustafson, K.; Andersen, R. J. *Can. J. Chem.* **1984**, *62*, 1.

(14) For examples, see: (a) Marino, J. P.; Browne, L. J. *Tetrahedron Lett.* **1976**, 3245. (b) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Org. Chem.* **1979**, *44*, 1744. (c) Fleming, I.; Perry, D. A. *Tetrahedron* **1981**, *37*, 4027 (stereoselective addition to a β-silyl alkynone). (d) Hashimoto, S.; Sonegawa, M.; Sakata, S.; Ikegami, S. *J. Chem. Soc., Chem. Commun.* **1987**, 24. (e) Degl'Innocenti, A.; Stucchi, E.; Capperucci, A.; Mordini, A.; Reginato, G.; Ricci, A. *Synlett* **1992**, 332 (stereoselective addition to a silyl alkynone with a terminal alkyne). (f) Houghton, T. J.; Choi, S.; Rawal, V. H. *Org. Lett.* **2001**, *3*, 3615.

(15) Piers, E.; Tillyer, R. D. *Can. J. Chem.* **1996**, *74*, 2048.

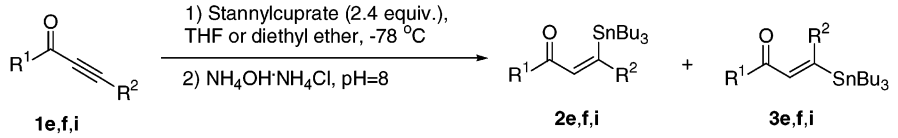
(16) Takeda, T.; Kabasawa, Y.; Fujiwara, T. *Tetrahedron* **1995**, *51*, 2515.

(17) Nielsen, T. E.; Tanner, D. *J. Org. Chem.* **2002**, *67*, 6366.

(18) Posner, G. H.; Brunelle, D. J. *Synthesis* **1974**, 662.

(19) House, H. O.; Chu, C.-Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460−1467.

TABLE 2. Stannylcupration of Alkynones II



entry	alkynone (R^1, R^2)	stannylcuprate	product (yield %)[a,b]
1	**1e** (Ph, $(CH_2)_3$OTBDMS)	$(Bu_3Sn)(PhS)CuLi$	**2e** (92)
2[c]	**1e**	$(Bu_3Sn)(PhS)CuLi$	**2e** (11)
3	**1f** (Ph, $(CH_2)_4$OTBDMS)	$(Bu_3Sn)(PhS)CuLi$	**2f** (>95)
4	**1f**	$(Bu_3Sn)(Bu)Cu(CN)Li_2$	**2f** (86)
5[d]	**1f**	$(Bu_3Sn)(Bu)Cu(CN)Li_2$	**2f** (62)
6	**1i** (*t*-Bu, $(CH_2)_2$OTBDMS)	$(Bu_3Sn)(PhS)CuLi$	**2i** (>95)
7[e]	**1i**	$(Me_3Sn)(PhS)CuLi$	**7** (79)

[a] Isolated yield after flash column chromatography. [b] None of the *E* isomers **3e**,**f**,**i** and **8** could be detected. [c] The reaction was performed in diethyl ether. [d] Reaction performed with H_2O (10 equiv) to quench the formed cuprate in situ. [e] Me_3SnLi required for the cuprate formation was generated by cleavage of hexamethylditin with MeLi (amine free reaction conditions).

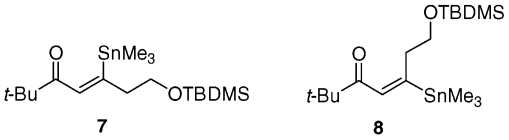
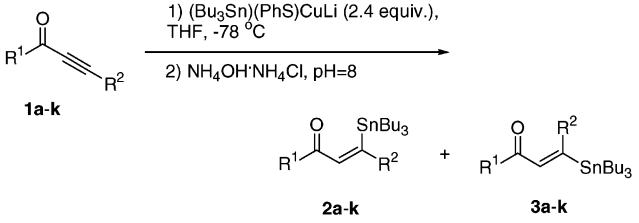


TABLE 3. Stannylcupration of Alkynones III



entry	alkynone (R^1, R^2)	product (yield %)[a,b]
1	**1a** (Ph, Bu)	**2a** (95)
2	**1b** (Ph, Ph)	**2b** (92)
3	**1c** (Ph, CH_2OTBDMS)	**2c** (78)
4[c]	**1d** (Ph, $(CH_2)_2$OTBDMS)	**2d** (>95)
5	**1e** (Ph, $(CH_2)_3$OTBDMS)	**2e** (92)
6	**1f** (Ph, $(CH_2)_4$OTBDMS)	**2f** (>95)
7	**1g** (Ph, CH(1-naphthyl)OTBDMS)	**2g** (41)
8[c]	**1h** (cyclohexyl, $(CH_2)_2$OTBDMS)	**2h** (>95)
9[c]	**1i** (*t*-Bu, $(CH_2)_2$OTBDMS)	**2i** (>95)
10[c]	**1j** (*i*-Pr, $(CH_2)_2$OTBDMS)	**2j** (>95)
11[c]	**1k** (Et, $(CH_2)_2$OTBDMS)	**2k** (>95)

[a] None of the (*E*)-stereoisomers **3a**−**k** could be detected. [b] Isolated yield after flash column chromatography. [c] Reactions were also performed with methanol (1.7 equiv) to quench the formed cuprate in situ, affording the *Z*-isomers **2d**,**h**−**k** exclusively, although in lower yields.

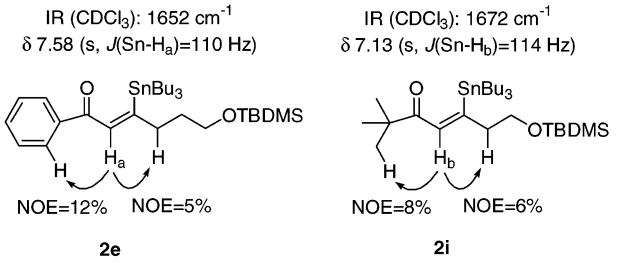
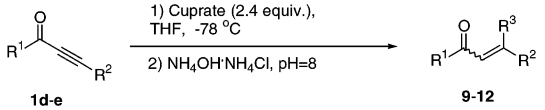
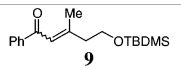
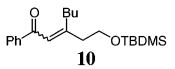
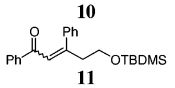
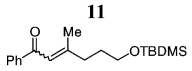


FIGURE 1. Spectroscopic data for (*Z*)-β-tributylstannyl-α,β-unsaturated ketones.

TABLE 4. Reactions of Common Cuprates with α,β-Acetylenic Ketones



entry	alkynone	cuprate	product (yield %)[a]
1[b,c]	**1d**	Me_2CuLi	 **9** (~75)[b,c]
2[b,c]	**1d**	Bu_2CuLi	 **10** (~80)[b,c]
3	**1d**	Ph_2CuLi	 **11** (0)
4	**1e**	$Me_2Cu(CN)Li_2$	 **12** (quant.)

[a] The products **9**, **10**, and **12** were obtained as *E*:*Z* = ∼1:1 mixtures of isomers. [b] Isolated yield after flash column chromatography. [c] The products **9** and **10** could not be separated from the substrate **1d**, and the yields were therefore indicated by ^{1}H NMR.

an atmosphere of dry argon in carefully flame-dried glassware. Argon gas was dried by passage through phosphorus pentoxide and silica gel. Stannylcupration reactions were routinely performed in Schlenk tubes, cautiously excluding oxygen from the reaction mixture (important: the quality of the tributyltin hydride batch was essential for the outcome of these reactions).

General Procedure for Addition of Lithium Acetylides to Weinreb Amides (A).[20] The terminal alkyne (2.4 mmol) was dissolved with stirring under nitrogen in THF (12 mL) and cooled to −78 °C before addition of *n*-butyllithium (1.6 M in hexanes, 1.6 mL, 2.6 mmol). The resultant solution was stirred for 1 h at −78 °C, and a solution of the Weinreb amide (1.2 mmol) in dry THF (2 mL) was added via a syringe. After 1 h, the reaction was brought to room temperature and stirred for an additional hour. Water was added and the phases were separated. The aqueous phase was extracted with diethyl ether (2 × 5 mL) and the combined organics were washed with water (5 mL) and brine (2 × 5 mL), dried over magnesium sulfate, and evaporated to dryness. The residue was purified by flash

(20) Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, *22*, 3815.

column chromatography on silica gel (hexane:ethyl acetate) to give the alkynones **1a**−**k** as colorless oils.

General Procedure for Sonogashira Coupling of Terminal Alkynes with Acid Chlorides (B).[21] To a Schlenk tube charged with freshly prepared copper(I) iodide (10 mg, 0.05 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.01 mmol), and the terminal alkyne (2.5 mmol) was added triethylamine (5 mL), followed by dropwise addition of the acid chloride (3.25 mmol) at room temperature. The resulting dark solution turned yellow/orange within a few hours of stirring with the formation of a large precipitate. This was stirred overnight, whereafter water (5 mL) was added to the reaction mixture. The aqueous phase was extracted with pentane (3 × 50 mL), and the combined organics were washed with water (5 mL) and brine (5 mL), dried over magnesium sulfate, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography on silica gel (hexane:ethyl acetate) to give the alkynones **1a**,**c**−**f**,**i** as colorless oils.

General Procedure for Stannylcupration of Alkynones. A solution of diisopropylamine (142 mg, 1.4 mmol) in THF (7 mL) was cooled to 0 °C and *n*-butyllithium (1.6 M in hexanes, 0.9 mL, 1.4 mmol) was added dropwise via syringe. After 30 min of stirring, tributyltin hydride (349 mg, 1.2 mmol) was added dropwise via syringe and stirring was continued at 0 °C for 30 min. The solution was cooled to −30 °C and solid phenylthiocopper(I) (208 mg, 1.2 mmol) was added in one portion. The mixture was stirred for 20 min at −30 °C to afford a dark red solution of lithium (phenylthio)(tributylstannyl)-cuprate. The reaction mixture was cooled to −78 °C before dropwise addition of the alkynone (0.5 mmol) in THF (1.5 mL). The reaction mixture was monitored by TLC, and when all the starting material had reacted the reaction was quenched by addition of saturated ammonium chloride (adjusted to pH ∼8 by addition of ammonium hydroxide) (10 mL) and diethyl ether (50 mL). The mixture was washed several times with saturated ammonium chloride (pH ∼8). The organic phase was washed with brine, dried over magnesium sulfate, and filtered. The solvent was evaporated and the residue purified by flash chromatography on silica gel (hexane:ethyl acetate) to give the (*Z*)-*β*-tributylstannyl-α,*β*-unsaturated ketones **2a**−**k** as colorless oils. **Addition of MeOH:** Following the general procedure, with the modification that MeOH (0.85 mmol) and the alkynone (0.5 mmol) dissolved in the same THF solution (1.5 mL) were added dropwise to the stannylcuprate reaction mixture.

Analytical data for compounds **2a**−**k** and **7**:

(*Z*)-1-Phenyl-3-tributylstannanyl-hept-2-en-1-one (2a). Yield 95%; IR ($CDCl_3$) 2956, 2872, 1651, 1560, 1464, 1234 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.03−7.97 (m, 2H), 7.59−7.43 (m, 3H), 7.56 (m, J(Sn−H) = 110 Hz, 1H), 2.56 (t, J = 7 Hz, J(Sn−H) = 44 Hz, 2H), 1.71−1.19 (m, 16H), 1.12−0.82 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 180.1, 138.4, 132.4, 132.1, 128.4, 128.3, 40.8, 31.6, 29.4, 27.5, 22.5, 14.0, 13.7, 11.2; HRMS (FAB) calcd for $C_{21}H_{33}OSn$ [M − C_4H_9]$^+$ 421.1557, found 421.1548.

(*Z*)-1,3-Diphenyl-3-tributylstannanyl-propenone (2b). Yield 92%; IR ($CDCl_3$) 2956, 1647, 1597, 1402, 1341 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.07−8.02 (m, 2H), 7.66 (s, J(Sn−H) = 101 Hz, 1H), 7.61−7.10 (m, 8H), 1.54−1.16 (m, 12H), 1.08−0.75 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.0, 176.6, 146.6, 138.2, 134.0, 132.7, 128.6, 128.5, 128.1, 126.9, 126.2, 29.2, 27.4, 13.7, 12.1; HRMS (FAB) calcd for $C_{23}H_{29}OSn$ [M − C_4H_9]$^+$ 441.1245, found 441.1269.

(*Z*)-4-(*tert*-Butyl-dimethyl-silanyloxy)-1-phenyl-3-tributylstannanyl-but-2-en-1-one (2c). Yield 78%; IR ($CDCl_3$) 2955, 2927, 1652, 1464, 1254 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.07−7.93 (m, 2H), 7.99 (s, J(Sn−H) = 104 Hz, 1H), 7.63−7.40 (m, 3H), 4.63 (br s, 2H), 1.57−1.38 (m, 6H), 1.35−1.20 (m, 6H), 1.08−0.78 (m, 15H), 0.95 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.9, 175.6, 138.5, 132.6, 128.5 (two peaks), 127.7, 69.3, 29.3, 27.2, 26.0, 18.5, 13.7, 11.0, −5.2; HRMS (FAB) calcd for $C_{24}H_{41}O_2SiSn$ [M − C_4H_9]$^+$ 509.1902, found 509.1891.

(*Z*)-5-(*tert*-Butyl-dimethyl-silanyloxy)-1-phenyl-3-tributylstannanyl-pent-2-en-1-one (2d). Yield >95%; IR ($CDCl_3$) 2955, 2928, 1652, 1234 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94−7.90 (m, 2H), δ 7.76 (m, 1H), 7.58 (s, J(Sn−H) = 110 Hz, 1H), 7.51−7.36 (m, 2H), 3.65 (t, J = 7 Hz, 2H), 2.71 (t, J = 7 Hz, J(Sn−H) = 43 Hz, 2H), 1.46−1.36 (m, 6H), 1.29−1.16 (m, 6H), 0.96−0.90 (m, 6H), 0.93 (t, J = 8 Hz, 3H), 0.82 (s, 9H), 0.80 (t, J = 7 Hz, 3H), 0.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 175.3, 138.3, 134.0, 132.5, 128.5, 128.4, 62.2, 43.8, 29.3, 27.5, 25.9, 18.3, 13.7, 11.2, −5.2; HRMS (FAB) calcd for $C_{25}H_{43}O_2SiSn$ [M − C_4H_9]$^+$ 523.2059, found 523.2075.

(*Z*)-6-(*tert*-Butyl-dimethyl-silanyloxy)-1-phenyl-3-tributylstannanyl-hex-2-en-1-one (2e). Yield 92%; IR ($CDCl_3$) 2955, 2929, 1652, 1560, 1463, 1233 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 (m, 2H), 7.61 (s, J(Sn−H) = 110 Hz, 1H), 7.59−7.53 (m, 1H), 7.51−7.43 (m, 2H), 3.67 (t, J = 7 Hz, 2H), 2.63 (t, J = 8 Hz, 2H), 1.70 (m, J = 7, 8 Hz, 2H), 1.57−1.42 (m, 6H), 1.35−1.25 (m, 6H), 1.10−0.80 (m, 15H), 0.93 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 179.6, 138.4, 132.4, 132.1, 128.4 (two peaks), 62.5, 37.3, 29.4, 27.5, 25.9, 18.4, 13.8, 11.2, −5.3; HRMS (FAB) calcd for $C_{26}H_{45}O_2SiSn$ [M − C_4H_9]$^+$ 537.2215, found 537.2224; Anal. Calcd for $C_{30}H_{54}O_2SiSn$: C, 60.70; H, 9.19. Found: C, 60.99; H, 9.19.

(*Z*)-6-(*tert*-Butyl-dimethyl-silanyloxy)-1-phenyl-3-tributylstannanyl-hept-2-en-1-one (2f). Yield >95%; IR ($CDCl_3$) 2955, 2958, 1652, 1463, 1255 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02−7.97 (m, 2H), 7.58 (s, J(Sn−H) = 111 Hz, 1H), 7.61−7.38 (m, 3H), 3.66 (t, J = 6 Hz, 2H), 2.58 (t, J = 6 Hz, J(Sn−H) = 43 Hz, 2H), 1.75−1.23 (m, 24H), 1.13−0.82 (m, 15H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.6, 179.9, 138.5, 132.4, 132.1, 128.5, 128.4, 63.0, 40.9, 32.7, 29.4, 27.5, 26.0, 18.4, 13.7, 11.2, −5.2; HRMS (FAB) calcd for $C_{27}H_{47}O_2SiSn$ [M − C_4H_9]$^+$ 551.2372, found 551.2377.

(*Z*)-4-(*tert*-Butyl-dimethyl-silanyloxy)-4-naphthalen-1-yl-1-phenyl-3-tributylstannanyl-but-2-en-1-one (2g). Yield 41%; IR ($CDCl_3$) 2954, 2927, 1653, 1464, 1229 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, J(Sn−H) = 103 Hz, 1H), 8.32−8.24 (m, 1H), 8.14−8.05 (m, 2H), 7.92−7.72 (m, 2H), 7.64−7.20 (m, 7H), 6.32 (s, J(Sn−H) = 19 Hz, 1H), 1.24−0.96 (m, 12H), 0.91 (s, 9H), 0.80−0.60 (m, 15H), 0.12 (s, 3H), −0.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 177.8, 136.7, 134.3, 132.7, 131.3, 130.8, 129.1, 128.8, 128.7, 128.6, 127.6, 127.1, 125.6, 125.4, 125.0, 124.5, 78.4, 29.0, 27.3, 26.0, 18.4, 13.6, 11.0, −4.1, −4.5; HRMS (FAB) calcd for $C_{34}H_{47}O_2SiSn$ [M − C_4H_9]$^+$ 635.2374, found 635.2385.

(*Z*)-7-(*tert*-Butyl-dimethyl-silanyloxy)-1-cyclohexyl-3-tributylstannanyl-pent-2-en-1-one (2h). Yield >95%; IR ($CDCl_3$) 2928, 1675, 1569, 1464, 1256 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, J(Sn−H) = 114 Hz, 1H), 3.64 (t, J = 7 Hz, 2H), 2.65 (t, J(Sn−H) = 43 Hz, 2H), 2.40 (m, J = 11, 4 Hz, 1H), 1.87−1.76 (m, 2H), 1.74−1.57 (m, 2H), 1.50−1.19 (m, 18H), 1.05−0.80 (m, 15H), 0.91 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.7, 171.5, 136.4, 62.2, 50.6, 43.2, 29.3, 28.5, 27.5, 26.0, 25.9, 25.7, 18.3,13.7, 11.1, −5.3; HRMS (FAB) calcd for $C_{25}H_{49}O_2SiSn$ [M − C_4H_9]$^+$ 529.2528, found 529.2548. Anal. Calcd for $C_{29}H_{58}O_2SiSn$: C, 59.47; H, 10.00. Found: C, 59.54; H, 9.87.

(*Z*)-7-(*tert*-Butyl-dimethyl-silanyloxy)-2,2-dimethyl-5-tributylstannanyl-hept-4-en-3-one (2i). Yield >95%; IR ($CDCl_3$) 2955, 2928, 1672, 1566, 1464, 1256 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (s, J(Sn−H) = 114 Hz), 1H), 3.67 (t, J = 7 Hz, 2H), 2.67 (t, J = 7 Hz, J(Sn−H) = 44 Hz, 2H), 1.54−1.23 (m, 12H), 1.17 (s, 9H), 1.03−0.82 (m, 15H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.5, 171.3, 133.5, 67.4, 48.7, 47.7, 29.3, 27.5, 26.4, 25.9, 18.3, 13.7, 11.1, −5.2; HRMS (FAB) calcd for $C_{23}H_{47}O_2SiSn$ [M − C_4H_9]$^+$ 503.2371, found 503.2373. Anal. Calcd for $C_{27}H_{56}O_2SiSn$: C, 57.95; H, 10.11. Found: C, 58.07; H, 9.84.

(*Z*)-7-(*tert*-Butyl-dimethyl-silanyloxy)-2-methyl-5-tributylstannanyl-hept-4-en-3-one (2j). Yield >95%; IR ($CDCl_3$)

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2956, 1680, 1457, 1256 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, J(Sn−H)=114 Hz, 1H), 3.65 (t, J = 7 Hz, 2H), 2.66 (m, J = 7, 7 Hz, J(Sn−H) = 43 Hz, 3H), 1.53−1.20 (m, 12H), 1.12 (d, J = 7 Hz, 6H), 1.01−0.81 (m, 15H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.4, 171.7, 136.1, 62.1, 43.2, 40.5, 29.3, 27.4, 25.9, 18.2 (two peaks), 13.7, 11.0, −5.3; HRMS (FAB) calcd for $C_{22}H_{45}O_2SiSn$ $[M - C_4H_9]^+$ 489.2214, found 489.2242.

(*Z*)-7-(*tert*-Butyl-dimethyl-silanyloxy)-5-tributylstannanyl-hept-4-en-3-one (2k). Yield >95%; IR ($CDCl_3$) 2956, 2927, 1684, 1570, 1464, 1256 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, J(Sn−H) = 111 Hz, 1H), 3.64 (t, J = 7 Hz, 2H), 2.65 (t, J = 7 Hz, J(Sn−H) = 43 Hz, 2H), 2.49 (q, J = 7 Hz, 2H), 1.56−1.20 (m, 12H), 1.11 (t, J = 7 Hz, 3H), 1.01−0.80 (m, 15H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9, 171.1, 136.9, 62.1, 43.1, 36.2, 29.3, 27.5, 26.0, 18.3, 13.7, 11.0, 8.3, −5.3; HRMS (FAB) calcd for $C_{21}H_{43}O_2SiSn$ $[M - C_4H_9]^+$ 475.2058, found 475.2075.

(*Z*)-7-(*tert*-Butyl-dimethyl-silanyloxy)-2,2-dimethyl-5-trimethylstannanyl-hept-4-en-3-one (7). Yield 79%; IR ($CDCl_3$) 2958, 1667, 1568, 1472, 1256 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.12 (s, J(Sn−H) = 123 Hz, 1H), 3.67 (t, J = 7 Hz, 3H), 2.69 (t, J = 7 Hz, 2H), 1.17 (s, 9H), 0.89 (s, 9H), 0.13 (s, J(Sn−H) = 54 Hz, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 171.6, 133.2, 62.2, 43.1, 42.5, 26.4, 26.0, 18.3, −5.2, −7.4; HRMS (FAB) calcd for $C_{14}H_{29}O_2SiSn$ $[M - CH_3]^+$ 419.1431, found 419.1424.

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Supporting Information Available: Analytical data for compounds **1c**−**k** and ^1H and ^{13}C NMR spectra for compounds **2a**−**k** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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