Stereoselective Synthesis of (*E*)-Vinylstannanes from Aldehydes

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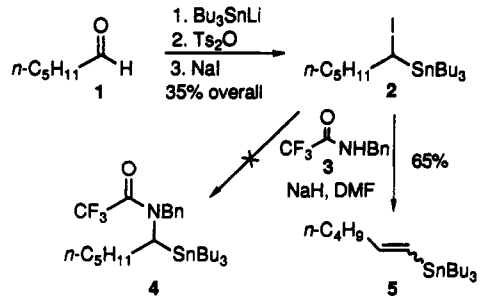
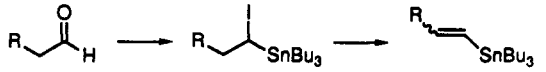
Vinylstannanes are useful intermediates in organic synthesis.[1] They serve as stable stereochemically defined alkenyl units that may be used for carbon–carbon bond formation reactions via Li,[2] Cu,[3] and Pd[4] chemistry. Vinylstannanes are most commonly prepared by hydrostannation[5] or stannylmetalation (with R_3SnMX_n-type reagents were M = Al,[6a] B,[6] Cu,[6-8] Mg,[9] Si,[10] Zn[9,11]) of alkynes. They have also been prepared by treatment of vinylorganometallics (often generated by hydrometalation or carbometalation of alkynes) with Bu_3SnOTf[12] or R_3SnCl.[13] While there have been recent advances in controlling the regio- and stereochemistry of hydrostannation,[5c,d] mixtures of isomers are commonly observed. The preparation of vinylstannanes via elimination of HBr from α-bromostannanes (as intermediates in a route to convert aldehydes to alkynes) has been noted.[14] We now report that α-iodostannanes may be employed in place of α-bromostannanes to prepare vinylstannanes in higher yields and with higher stereoselectivities.

As part of an investigation into the chemistry of α-aminoorganostannanes,[15] we treated α-iodostannane **2** with the anion of amide **3** (Scheme I). We were disappointed to find that none of the desired α-amidostannane **4** was formed[16] but instead the major reaction product

Scheme I



Scheme II



was vinylstannane **5**. However, it was noticed that **5** was formed as a mixture of stereoisomers with *E*:*Z* = ~10:1. It has previously been shown that such mixtures may, in fact, be sources of pure (*E*)-vinyllithiums since (*E*)-vinylstannanes undergo Sn–Li exchange much more rapidly than the corresponding *Z* isomers.[18] In addition, the stereoselectivity observed is comparable to or slightly better than that often observed (*E*:*Z* = ~85:15) in the hydrostannation of simple alkynes, and the formation of regioisomers (which are often observed in hydrostannations) is very unlikely. We thus decided to further investigate the elimination of HI from α-iodostannanes as a route to vinylstannanes.

There are relatively few examples of α-iodostannanes in the literature. The first α-iodostannanes reported were primary iodides R_3SnCH_2I[19] [R = Bu (**6a**), Me (**6b**), Ph (**6c**)]. More recently, the secondary iodide $Bu_3SnCH(CH_3)I$ (**7**) was reported.[17] These iodides are prepared by reaction of a Simmons–Smith reagent with R_3SnCl; **6a** has also been made by reaction of Bu_3SnCH_2Cl with NaI.[20] The only other examples of α-iodostannanes were prepared from α-hydroxystannanes in 50–60% yield using Ph_3P/DEAD/MeI (C_6H_6, rt, 48 h).[21] A more efficient general route to α-iodostannanes from α-hydroxystannanes was needed since it was already known that aldehydes may be transformed into α-hydroxystannanes in very high yields by reaction with Bu_3SnLi;[22] coupled with a stereoselective elimination, such a route would be part of a simple protocol for the conversion of aldehydes to (*E*)-vinylstannanes (Scheme II). Although there are many methods for the conversion of alcohols to iodides,[23] those that require long reaction times at rt or higher would be expected to give only modest yields with α-hydroxystannanes due to the instability[22] of stannylcarbinols. Reactions of α-(tosyloxy)-

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(16) It is interesting to note that the less-sterically hindered "methyl-substituted" iodostannane **7** reacted with the sodium salt of benzyl *N*-benzylcarbamate to afford a modest yield (42%) of the desired carbamatostannane.[17]
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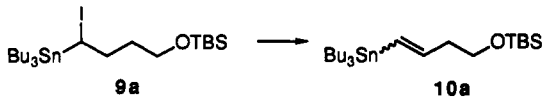
Table I. Conversion of Iodide 9a to Vinylstannane 10a[a]

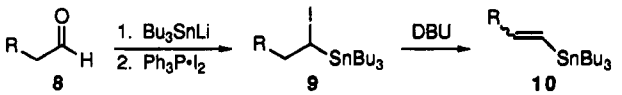


9a 10a

entry	base	solvent	temp (°C)	time (h)	E:Z[b]
1	DBU	THF	reflux	14	9:1
2	DBU	THF	rt	72	9.5:1
3	DBU	benzene	reflux	14	8.5:1
4	DBU	DME	reflux	14	7.5:1
5	DBU	CH_2Cl_2	reflux	36	9:1[c]
6	KO-*t*-Bu	THF	rt	3	2:1
7	2,6-lutidine	THF	reflux	72	*d*
8	LDA	THF	−78 → 0	12	*e*

[a] Reactions were run with 3 equiv of base. Yields of recovered materials were >90% in all cases. [b] Determined by GC analysis. [c] The reaction mixture contained 60% of the α-chlorostannane resulting from displacement of iodide with chloride. [d] Only starting iodide **9a** was recovered. [e] Starting iodide was consumed but no vinylstannane was isolated.

Table II. Stereoselective Synthesis of (*E*)-Vinylstannanes via α-Iodostannanes



8 9 10

entry	R	iodide (% yield)[a]	alkene (% yield)[a]	E:Z[b]
1	$TBSO(CH_2)_3$	**9a** (75)	**10a** (100)	9:1
2	$PhCH_2$	**9b** (72)	**10b** (95)	16:1
3	$Me_3SiC{\equiv}CCH_2CH_2$	**9c** (50)	**10c** (94)	10:1
4	$(CH_3)_2CH$	**9d** (85)	**10d** (95)	53:1
5	n-$C_5H_{11}CH(OTBS)$	**9e** (80)	**10e** (96)	150:1
6	n-$C_5H_{11}CH(OMOM)$	**9f** (56)	**10f** (100)	32:1

[a] Isolated yields. [b] Determined by GC.

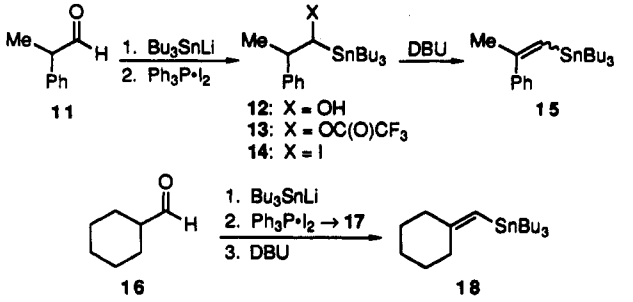
or α-(mesyloxy)stannanes with NaI provided α-iodostannanes as major products, but isolated yields (based on starting aldehyde) were typically 35–45%. Fortunately, the method recently reported by Lange and Gottardo[24] for the conversion of primary and secondary alcohols to iodides using Ph_3P/imidazole/I_2 in CH_2Cl_2 proved to be very effective, furnishing α-iodostannanes in good (typically 70–80% from aldehydes) yields.

The stereoselectivity of the conversion of iodide **9a** to vinylstannane **10a** was then examined (Table I). DBU proved to be an effective base, consistently providing >90% isolated yields of vinylstannane **10a** with *E*:*Z* = 9:1 and very little dependence on solvent and temperature.

Reactions of other iodides with DBU were carried out in THF at reflux since selectivities were marginally better than with other systems showing comparable (convenient) reaction times. Results are shown in Table II. Under these reaction conditions, excellent yields (94–100%) of elimination products were observed. With unbranched systems (entries 1–3), stereoselectivities were *E*:*Z* = ≈10:1. Branching lead to increased selectivity: With the isopropyl-substituted system (**9d** → **10d**), <2% of the *Z*-isomer was observed while the prostaglandin side-chain precursor (*E*)-**10e**[17b] was formed with <1% of the *Z*-isomer.

Leaving groups other than iodide were much less successful. Treatment of α-(tosyloxy)- and α-(mesyloxy)-stannanes with DBU (THF, reflux) did not afford vinylstannanes but only unidentified materials. Bromides were much less reactive, and only traces of vinylstannanes were produced after 12 h in refluxing THF. Reactions in refluxing toluene were complete after 24 h but isolated yields were mediocre (60%) and stereoselectivities were lower (e.g., *E*:*Z* = 5:1 for **10a** compared with 9:1 using iodide **9a**; *E*:*Z* = 15:1 for **10d** compared with 53:1 using iodide **9d**). The preparation of vinylstannanes from α-bromostannanes using DBU has previously been noted but selectivities were reported for only 2 compounds: a straight-chain system gave *E*:*Z* = 8:1 while a branched system showed ~10:1 selectivity.[14] The lower selectivities observed for bromides is consistent with the findings of Wolkoff who studied the elimination of HX from 2-halohexanes with DBU: the ratio of 2-hexenes formed for X = Cl, Br, and I were *E*:*Z* = 4.9, 5.5, and 9.1, respectively.[25]

Scheme III



The preparation of trisubstituted vinylstannanes was also investigated (Scheme III). Addition of Bu_3SnLi to aldehyde **11** resulted in a 6:1 mixture of diastereomeric alcohols **12** which were separable by flash chromatography as their trifluoroacetates **13**. Treatment of a 15:1 diastereomeric mixture of alcohols with Ph_3P/imidazole/I_2 provided (somewhat surprisingly) a 1:1 mixture of iodides **14**. Elimination of HI from these iodides (DBU, THF) then gave (even more surprisingly) a 7:1 mixture of vinylstannanes **15** with the *Z* isomer being the major one.[26] These results indicate that neither of the conversions from alcohol **12** to iodide **14** or from iodide **14** to alkene **15** is stereospecific. This lack of specificity may be explained by the occurrence of iodide exchange (Finkelstein) reactions during both conversions coupled with unequal rates of HI elimination from the diastereomeric iodides. It has been reported previously that the corresponding bromides may be stereospecifically converted to vinylstannanes **15** (DBU, toluene),[14] but since halide exchange occurs less readily with bromides than with iodides, equilibration of diastereomers may not be a problem with the bromides. With aldehyde **16**, stereochemistry is not an issue and the overall conversion to vinylstannane **18** occurs in good yield.

The results described above show that vinylstannanes may be prepared in good overall yields from aldehydes via the intermediacy of α-iodostannanes. The overall conversion shown in Table II provides vinylstannanes with stereoselectivities of ~10–100:1 in 50–80% overall yield from aldehydes and could be a useful alternative to hydrostannation chemistry.

Experimental Section

All reactions were carried out with dry glassware under an atmosphere of argon unless otherwise noted. Tributyltin hydride was prepared according to Szammer and Otvos and was freshly

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(26) The major isomer was identified as *Z* by ^1H NMR analysis: the vinyl proton of the *Z* isomer resonates at δ 5.87 while that of the *E* isomer appears at δ 6.27.[14]

distilled before use.[27] Other reagents were purchased (Aldrich) or prepared by modification of literature methods; aldehydes were usually chromatographed or distilled before use. Infrared spectra were recorded as neat liquids between NaCl plates. ^1H and ^{13}C NMR spectra were recorded using $CDCl_3$ as solvent; tetramethylsilane (^1H, δ 0.0) or $CDCl_3$ (^{13}C, δ 77.0) was used as internal reference. ^1H NMR data are presented as follows: chemical shift (multiplicity, integration, J in Hz, assignment). For ^{13}C NMR signals, coupling constants for satellites due to $^{117/119}Sn$ (where discernible) are reported in parentheses in Hz; an asterisk (*) indicates signals that could be unequivocally attributed to the major diastereomer of mixtures. Mass spectra were recorded in CI mode using CH_4. Gas chromatography (GC) analyses were performed with a 7% DB-1701 (30 m × 0.25 mm) column; the temperature program used was as follows: 200 °C, 13 min/10 deg·min^{-1}/240 °C, 20 min. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

General Procedure A: Preparation of α-Iodostannanes. To a cooled (0 °C) solution of diisopropylamine (0.5 M in THF) was added *n*-BuLi (1 equiv, 1.6 M in hexanes). After the solution was stirred for 10 min, Bu_3SnH (1 equiv) was added and stirring was continued for a further 20 min. The mixture was then cooled (−78 °C), and the appropriate aldehyde (1 equiv, 5 M solution in THF) was added dropwise. After 10 min the reaction was quenched with dilute $NH_4Cl_{(aq)}$. The mixture was diluted with ether, washed with H_2O, dried over $MgSO_4$, filtered, and concentrated in vacuo to provide crude α-hydroxystannane.

To a 1 M solution of Ph_3P (1.5 equiv) in CH_2Cl_2 was added imidazole (1.5 equiv), and the mixture was stirred until the imidazole had completely dissolved. Iodine (1.5 equiv) was then added, and the mixture was stirred for 5 min. The mixture was cooled (0 °C), and the crude alcohol (1 equiv, 1 M solution in CH_2Cl_2) was added dropwise. The ice bath was removed, and the mixture was stirred at rt until TLC indicated the reaction was complete (0.5–2.0 h). The solution was then diluted with 15 reaction volumes of hexane and two reaction volumes of CH_3CN. The two phases were separated, and the hexane layer was concentrated in vacuo. The resulting oil was then purified by flash chromatography (20 g of silica/g of substrate; hexane) to provide the iodides as colorless oils.

General Procedure B: Preparation of Vinylstannanes. To a 0.1 M solution of α-iodostannane in THF was added DBU (3 equiv), and the resulting mixture was stirred at reflux for 14 h. The mixture was diluted with hexane, washed twice with 1 M HCl, washed once with H_2O, dried over $MgSO_4$, filtered, and concentrated in vacuo to afford the vinylstannane as a colorless oil.

1-(*tert*-Butyldimethylsiloxy)-4-iodo-4-(tributylstannyl)-butane (9a) was prepared from 4-(*tert*-butyldimethylsiloxy)-butanal (available by monosilylation of 1,4-butanediol[28] followed by PCC oxidation[29]) according to General Procedure A in 75% yield: IR (neat) 1464, 1254, 1101, 837, 776 cm^{-1}; ^1H NMR (200 MHz) δ 3.63 (t, 2 H, J = 5.6 Hz, CH_2O), 3.38 (dd, 1 H, J = 6.5, 8.1 Hz, CHI), 1.92 (m, 2 H, CH_2CH_2O), 1.7–1.2 (m, 14 H, $SnCH_2CH_2CH_2CH_3$ and $CHCH_2$), 1.0–0.8 (m, 24 H, $SnCH_2CH_2CH_2CH_3$ and *t*-BuSi, 0.52 (s, 6 H, $SiCH_3$); ^{13}C NMR (50 MHz) δ 61.9, 35.4 (^3J = 30 Hz), 34.3, 28.9 (^3J = 20 Hz), 27.4 (^2J = 56, 58 Hz), 25.9, 18.2, 13.7, 12.6 (^1J = 244, 255 Hz), 10.7 (^1J = 317, 332 Hz), −5.3 ($^1J_{CSi}$ = 56 Hz); MS *m/z* (rel intensity) 547 ($M^+ - C_4H_9$, 19), 491 (12), 425 (13), 359 (32), 287 (100). Anal. Calcd for $C_{22}H_{49}IOSiSn$: C, 43.80; H, 8.19. Found: C, 44.08; H, 8.06.

1-Iodo-3-phenyl-1-(tributylstannyl)propane (9b) was prepared from 3-phenylpropanal according to General Procedure A in 72% yield: IR (neat) 1496, 1456, 1376, 1073, 698 cm^{-1}; ^1H NMR (200 MHz) δ 7.3–7.1 (m, 5 H, Ar-H), 3.28 (dd, 1 H, J = 4.1, 10.5 Hz, CHI), 2.87 (ddd, 1 H, J = 4.7, 8.8, 13.5 Hz, CH_2Ph), 2.70 (m, 1 H, CH_2Ph), 2.15 (m, 2 H, CH_2CHI), 1.6–1.2 (m, 12 H, $SnCH_2CH_2CH_2CH_3$), 1.0–0.8 (m, 15 H, $SnCH_2CH_2CH_2CH_3$); ^{13}C NMR (50 MHz) δ 140.8, 128.6, 128.3, 125.9, 39.4, 38.1, 28.85 (^2J = 20 Hz), 27.3 (^3J = 57 Hz), 13.6, 11.4, 10.6 (^1J = 331 Hz); MS *m/z* (rel intensity) 479 ($M^+ - C_4H_9$, 9), 423 (25), 357 (38), 291 (33), 247 (49), 235 (26), 91 (100). Anal. Calcd for $C_{21}H_{37}ISn$: C, 47.14; H, 6.97. Found: C, 47.26; H, 6.93.

6-Iodo-6-(tributylstannyl)-1-(trimethylsilyl)-1-hexyne (9c) was prepared from 6-(trimethylsilyl)hex-5-ynal[30] according to General Procedure A in 50% yield: IR (neat) 1464, 1254, 1101, 837, 776 cm^{-1}; ^1H NMR (200 MHz) δ 3.31 (dd, 1 *H*, J = 6.7, 7.9 Hz, CHI), 2.22 (t, 2 H, J = 6.8 Hz, CH_2CC), 1.95 (m, 2 H, CH_2CHI), 1.7–1.2 (m, 14 H, $SnCH_2CH_2CH_2CH_3$ and CH_2CH_2CHI), 0.95–0.8 (m, 15 H, $SnCH_2CH_2CH_2CH_3$), 0.10 [s, 9 H, $Si(CH_3)_3$]; ^{13}C NMR (50 MHz) δ 106.7, 84.9, 36.4, 30.9 (^3J = 32 Hz), 28.9 (^2J = 20 Hz), 27.4 (^3J = 57 Hz), 18.7, 13.7, 11.5, 10.7 (^1J = 318, 332 Hz), 0.1; MS *m/z* (rel intensity) 513 ($M^+ - C_4H_9$, 2), 385 (19), 361 (43), 287 (46), 235 (31). Anal. Calcd for $C_{21}H_{43}ISiSn$: C, 44.31; H, 7.61. Found: C, 44.38; H, 7.43.

1-Iodo-3-methyl-1-(tributylstannyl)butane (9d) was prepared from 3-methylbutanal according to General Procedure A in 85% yield: IR (neat) 1461, 1378, 1251, 670 cm^{-1}; ^1H NMR (200 MHz) δ 3.37 (dd, 1 H, J = 4.4, 12.1 Hz, CHI), 2.1–1.3 (m, 15 H, $SnCH_2CH_2CH_2CH_3$ and $CHCH_2CHI$), 1.0–0.8 [m, 21 H, $SnCH_2CH_2CH_2CH_3$ and $CH(CH_3)_2$]; ^{13}C NMR (50 MHz) δ 46.6 (^2J = 6 Hz), 29.6 (^3J = 33 Hz), 28.9 (^2J = 20 Hz), 27.4 (^3J = 55, 57 Hz), 22.8, 20.3, 13.7, 10.6 (^1J = 316, 332 Hz), 10.4 (^1J = 248, 259 Hz); MS *m/z* (rel intensity) 431 ($M^+ - C_4H_9$, 11), 359 (55), 291 (100), 236 (24). Anal. Calcd for $C_{17}H_{37}ISn$: C, 41.92; H, 7.66. Found: C, 42.16; H, 7.77.

3-(*tert*-Butyldimethylsiloxy)-1-iodo-1-(tributylstannyl)-octane (9e) was prepared from 3-(*tert*-butyldimethylsiloxy)-octanal[31] (hexanal, $LiCH_2CO_2Et$;[32] TBSCl, imidazole; DIBAL) according to General Procedure A in 80% yield as a 2:1 mixture of diastereomers: IR (neat) 1462, 1253, 1064, 835, 774 cm^{-1}; ^1H NMR (200 MHz) δ 3.84 (m, 1 H, CHO), 3.49 (dd, 0.65 H, J = 2.4, 12.7 Hz, CHI), 3.09 (dd, 0.35 H, J = 2.4, 12.8 Hz, CHI), 2.0 (m, 1 H, CH_2CHI), 1.1 (m, 1 H, CH_2CHI), 1.6–1.2 [m, 20 H, $SnCH_2CH_2CH_2CH_3$ and $CH_3(CH_4)_2$], 1.0–0.8 [m, 27 H, $SnCH_2CH_2CH_2CH_3$, $CH_3(CH_2)_4$, and $C(CH_3)_3$], 0.16 (s, 2 H, $SiCH_3$), 0.10 (s, 2 H, $SiCH_3$), 0.09 (s, 2 H, $SiCH_3$); ^{13}C NMR (50 MHz) δ 73.8 *72.2, *44.5, 44.4, *37.7, 34.7, *32.2, 32.0, 28.9(6), *28.9(3) (^2J = 21 Hz), 27.4(4), *27.4(0) (^3J = 56 Hz), 26.0, 24.5, 22.7(1), *22.6(7), 18.1, 14.1, *13.7, 10.6 (^1J = 318, 332 Hz), *10.5 (^1J = 318, 332 Hz); MS *m/z* (rel intensity) 603 ($M^+ - C_4H_9$, 11), 547 (2), 475 (12), 361 (38), 291 (72), 215 (100). Anal. Calcd for $C_{26}H_{57}IOSiSn$: C, 47.36; H, 8.71. Found: C, 47.42; H, 8.46.

1-Iodo-3-(methoxymethoxy)-1-(tributylstannyl)octane (9f) was prepared from 3-(methoxymethoxy)octanal[33] according to General Procedure A in 56% yield as a 1.5:1 mixture of diastereomers: IR (neat) 1460, 1099, 1041, 919 cm^{-1}; ^1H NMR (200 MHz) δ 4.75 (ABq, 2 H, $\Delta\delta$ = 0.025, J = 6.7 Hz, CH_2O), 3.8 (m, 1 H, CHO), 3.53 (dd, 0.6 H, J = 2.9, 12.6 Hz, CHI), 3.42 (s, 1.8 H, CH_3O), 3.39 (s, 1.2 H, CH_3O), 3.15 (dd, 0.4 H, J = 4.1, 11.8 Hz, CHI), 1.9 (m, 2 H, CH_2CHI), 1.7–1.3 [m, 20 H, $SnCH_2CH_2CH_2CH_3$ and $CH_3(CH_2)_4$], 1.1–0.9 [m, 18 H, $SnCH_2CH_2CH_2CH_3$ and $CH_3(CH_2)_4$]; ^{13}C NMR (50 MHz) δ *96.7, 96.0, 79.4 (^3J = 31 Hz), *78.5 (^3J = 36 Hz), *55.5, 55.4, *43.5, 42.6, *35.0, 33.3, *32.5, 32.4, 29.4 (^2J = 20 Hz), *29.3 (^2J = 20 Hz), 27.8(5) (^3J = 58 Hz), *27.7-(9) (^3J = 56 Hz), *25.1, 24.8, *23.1, 23.0, 14.4, *14.0, 11.3 (^1J = 318, 334 Hz), *10.4 (^1J = 318, 334 Hz), *7.6 (^1J = 252, 261 Hz), 6.0; MS *m/z* (rel intensity) 533 ($M^+ - C_4H_9$, 31), 361 (66), 359 (48), 291 (100). Anal. Calcd for $C_{22}H_{47}IO_2Sn$: C, 44.85; H, 8.04. Found: C, 44.83; H, 8.12.

(*E*)-4-(*tert*-Butyldimethylsiloxy)-1-(tributylstannyl)-1-butene (10a) was prepared from iodide **9a** according to General Procedure B in 100% yield. GC analysis indicated a 9:1 mixture of diasteromers (elution times: major, 11.79 min; minor, 11.94 min): IR (neat) 1463, 1253, 1100, 835, 775 cm^{-1}; ^1H NMR (250 MHz) δ 6.1 (m, 2 H, CH=CH), 3.77 (t, 2 H, J = 7.5 Hz, CH_2O), 2.47 (m, 2 H, CH_2CH), 1.7–1.3 (m, 12 H, $SnCH_2CH_2CH_2CH_3$), 1.00 [s, 9 H, $C(CH_3)_3$], 1.1–0.9 (m, 15 H, $SnCH_2CH_2CH_2CH_3$), 0.16 (s, 6 H, $SiCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$), δ *145.9 (^2J = 5 Hz), 145.2, 130.3, *129.8 (^1J = 377, 395 Hz), 63.2, *62.9, *41.5 (^3J = 64

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Hz), 40.5, 29.3, *29.2, (^2J = 20 Hz), 27.3 (^3J = 54 Hz), 26.0 ($^3J_{CSi}$ = 31 Hz), 18.4, 13.7, 10.2, *9.4 (^1J = 327, 341 Hz), -5.2 ($^1J_{CSi}$ = 43); MS *m/z* (rel intensity) 419 ($M^+ - C_4H_9$, 32), 363 (6), 307 (4), 193 (29), 91 (100). Anal. Calcd for $C_{22}H_{47}OSiSn$: C, 55.58; H, 9.96. Found: C, 55.76; H, 9.72.

(*E*)-3-Phenyl-1-(tributylstannyl)-1-propene (10b) was prepared from iodide **9b** according to General Procedure B in 95% yield. GC analysis indicated a 16:1 mixture of diastereomers (elution times: major, 12.53 min; minor, 13.40 min): IR (neat) 1595, 1458, 990, 696 cm^{-1}; ^1H NMR (250 MHz) δ 7.31–7.1 (m, 5 H, Ar-H), 6.09 (A part of ABX, 1 H, J_{AB} = 18.9 Hz, J_{AX} = 5.4 Hz), 5.96 (B part of ABX, 1 H, J_{AB} = 18.9 Hz, J_{BX} = 0, $^2J_{HSn}$ = 76 Hz, CHSn), 3.48 (d, 2 H, J = 5.4 Hz, CH_2CH=C), 1.6–1.2 (m, 12 H, $SnCH_2CH_2CH_2CH_3$), 1.0–0.8 [m, 15 H, $SnCH_2CH_2CH_2CH_3$]; ^{13}C NMR (50 MHz) δ *147.3, 147.1, 140.3, 129.6, *129.5 (^1J = 370, 387 Hz), 128.7, 128.4, 128.3, 125.9, *44.5, (^3J = 63 Hz), 29.2, *29.1 (^2J = 21 Hz), 27.3(2), *27.2(7) (^3J = 53 Hz), 13.7, 10.4, *9.5 (^1J = 327, 342 Hz); MS *m/z* (rel intensity) 303 ($M^+ - C_4H_9$, 100), 291 ($M^+ - C_5H_9$, 18), 247 (28), 191 (23). Anal. Calcd for $C_{17}H_{36}Sn$: C, 56.85; H, 10.04. Found: C, 56.83; H, 9.94.

The *Z* isomer exhibits discernible ^{13}C NMR signals at δ 147.1, 129.6, 43.0, 29.2, 27.3, 10.4.

(*E*)-6-(Tributylstannyl)-1-(trimethylsilyl)hex-5-en-1-yne (10c) was prepared from iodide **9c** according to General Procedure B in 94% yield. GC analysis indicated a 10:1 mixture of diastereomers (elution times: major, 9.63 min; minor, 9.26 min): IR (neat) 2176, 1600, 1459, 1249, 847 cm^{-1}; ^1H NMR (250 MHz) δ 6.0 (m, 2 H, CH=CH), 2.37 (m, 4 H, $C{\equiv}CCH_2CH_2$-CH=CH), 1.6–1.3 (m, 12 H, $SnCH_2CH_2CH_2CH_3$), 1.0–0.8 (m, 15 H, $SnCH_2CH_2CH_2CH_3$), 0.17 (s, 9 H, $SiCH_3$); ^{13}C NMR (50 MHz) δ *147.0, 146.8, 129.8, *128.9 (^1J = 372, 390 Hz), *107.0, 106.5, 84.7, *36.6 (^3J = 63 Hz), 35.9, 29.2, *29.1 (^2J = 21 Hz), 27.2 (^3J = 53 Hz), 20.4, *19.7, 13.7, 10.3, *9.4 (^1J = 327, 342 Hz), 0.2 ($^1J_{CSi}$ = 56 Hz); MS *m/z* (rel intensity) 427 ($M^+ - CH_3$, 4), 385 ($M^+ - C_4H_9$, 100), 329 (25), 273 (36). Anal. Calcd for $C_{21}H_{42}SiSn$: C, 57.15; H, 9.59. Found: C, 56.99; H, 9.41.

(*E*)-3-Methyl-1-(tributylstannyl)-1-butene (10d) was prepared from iodide **9d** according to General Procedure B in 95% yield. GC analysis indicated a 53:1 mixture of diastereomers (elution times: major, 7.76 min; minor, 7.86 min): IR (neat) 1596, 1460, 1377, 990 cm^{-1}; ^1H NMR (250 MHz) δ 5.94 (A part of ABX, 1 H, J_{AB} = 19.0 Hz, J_{AX} = 5.0 Hz, $^3J_{HSn}$ = 67, 70 Hz, CH=CHSn], 5.79 (B part of ABX, 1 H, J_{AB} = 19.0 Hz, J_{BX} = 0, $^2J_{HSn}$ = 74, 78 Hz, CHSn], 2.3 (m, 1 H, CHCH=CH), 1.6–1.2 (m, 12 H, $SnCH_2CH_2CH_2CH_3$), 1.0–0.8 [m, 21 H, $SnCH_2CH_2CH_2CH_3$ and $CH(CH_3)_2$]; ^{13}C NMR (50 MHz) δ 156.5, 123.0 (^1J = 384, 403 Hz), 35.5 (^3J = 60 Hz), 35.9, 29.2 (^2J = 21 Hz), 27.3 (^3J = 52 Hz), 22.1, 9.5 (^1J = 325, 341 Hz); MS *m/z* (rel intensity) 303 ($M^+ - C_4H_9$, 100), 291 ($M^+ - C_5H_9$, 18), 247 (28), 191 (23). Anal. Calcd for $C_{17}H_{36}Sn$: C, 56.85; H, 10.04. Found: C, 56.83; H, 9.94.

The ^1H NMR signals for the vinyl protons of the *Z* isomer appear at δ 6.30 (dd, J = 9.5, 12.0 Hz, CH=CHSn) and 5.63 (d, J = 12.0 Hz, CHSn).

(*E*)-3-(*tert*-Butyldimethylsiloxy)-1-(tributylstannyl)-1-octene (10e) was prepared from iodide **9e** according to General Procedure B in 96% yield. GC analysis indicated a 150:1 mixture of diastereomers (elution times: major, 16.73 min; minor, 16.80 min): IR (neat) 1462, 1252, 1073, 835, 775 cm^{-1}; ^1H NMR (200 MHz) δ 6.05 (A part of ABX, 1 H, J_{AB} = 19.0 Hz, J_{AX} = 0, $^2J_{HSn}$ = 72, 75 Hz, CHSn], 5.92 (B part of ABX, 1 H, J_{AB} = 19.0, J_{BX} = 4.8, $^3J_{HSn}$ = 64, 67 Hz, CH=CHSn), 4.05 (m, 1 H, CHO), 1.6–1.2 [m, 20 H, $SnCH_2CH_2CH_2CH_3$ and $CH_3(CH_2)_4$], 0.97 [s, 9 H, $C(CH_3)_3$], 1.0–0.8 [m, 18 H, $SnCH_2CH_2CH_2CH_3$ and CH_3-$(CH_2)_4$], 0.10 (s, 3 H, $SiCH_3$), 0.07 (s, 3 H, $SiCH_3$); ^{13}C NMR (50 MHz) δ 152.1, 126.2 (^1J = 368, 385 Hz), 76.9 (^3J = 65 Hz), 53.3, 38.1, 31.9, 29.2 (^2J = 20 Hz), 27.3 (^3J = 53 Hz), 25.9, 25.0, 22.7, 18.3, 14.0, 13.7, 9.4 (^1J = 327, 342 Hz); MS *m/z* (rel intensity) 475 ($M^+ - C_4H_9$, 35), 399 (100), 365 (15), 291 (15). Anal. Calcd for $C_{26}H_{56}OSiSn$: C, 58.76; H, 10.62. Found: C, 58.88; H, 10.55.

The ^1H NMR signals for the vinyl protons of the *Z* isomer appear at δ 5.74 (d, J = 9.5 Hz, CHSn) and 5.63 (d, J = 12.0 Hz, CHSn).

(*E*)-3-(Methoxymethoxy)-1-(tributylstannyl)-1-octene (10f) was prepared from iodide **9f** according to General Procedure B in 100% yield. GC analysis indicated a 33:1 mixture of diastereomers (elution times: major, 14.58 min; minor, 13.13 min): IR (neat) 1461, 1154, 1098, 1040 cm^{-1}; ^1H NMR (200 MHz) δ 6.10 (A part of ABX, 1 H, J_{AB} = 19.1 Hz, J_{AX} = 0, $^2J_{HSn}$ = 74, CHSn), 5.76 (B part of ABX, 1 H, J_{AB} = 19.1 Hz, J_{BX} = 7.1 Hz, $^3J_{HSn}$ = 61, 64 Hz, CH=CHSn), 4.71 (d, 1 H, J = 6.6 Hz, CH_2O), 4.53 (d, 1 H, J = 6.6 Hz, CH_2O), 3.93 (m, 1 H, CHO), 3.37 (s, 3 H, CH_3), 1.6–1.2 [m, 20 H, $SnCH_2CH_2CH_2CH_3$ and $CH_3(CH_2)_4$], 1.0–0.8 [m, 18 H, $SnCH_2CH_2CH_2CH_3$ and $CH_3(CH_2)_4$], 0.10 (s, 3 H, $SiCH_3$), 0.07 (s, 3 H, $SiCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.5, 131.1, 93.7, 80.2, 55.3, 35.3, 31.8, 29.1 (^2J = 21 Hz), 27.2 (^3J = 53 Hz), 25.1, 22.6, 14.0, 13.6, 9.5 (^1J = 329, 344 Hz); MS *m/z* (rel intensity) 405 ($M^+ - C_4H_9$, 15), 375 (85), 141 (100), 92 (72). Anal. Calcd for $C_{22}H_{46}O_2Sn$: C, 57.28; H, 10.05. Found: C, 57.49; H, 9.84.

The *Z* isomer exhibits distinguishable ^1H NMR signals at δ 6.33 (dd, J = 8.5, 13.0 Hz, CHSn) and 3.35 (s, OCH_3).

2-Phenyl-1-(tributylstannyl)propyl Trifluoroacetate (13). Crude α-hydroxystannane **12** was prepared from 2-phenylpropanal (**11**) as described in General Procedure A. To a 2.5 M solution of **12** in CH_2Cl_2 was added pyridine (2.5 equiv), and the resulting mixture was cooled (0 °C). A 5 M solution of TFAA (1.5 equiv) in CH_2Cl_2 was added dropwise, and the mixture was stirred for 1 h. The reaction mixture was diluted with H_2O (200 mL) and hexane (400 mL). The two phases were separated, and the hexane layer was washed with H_2O (2 × 100 mL), saturated $CuSO_4$ (aq, 3 × 50 mL), and H_2O (2 × 10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting oil was purified by flash chromatography (10 g of silica/g of substrate, hexane) to provide equal weights of a 15:1 mixture (elutes first) and a 3:1 mixture of the diastereomeric esters as colorless oils (total 65% yield from **11**); IR (neat) 1771, 1218, 1160 cm^{-1}; ^1H NMR (200 MHz), δ 7.35–7.10 (m, 5 H, Ar-H), 5.33 (d, 0.25 H, J = 10.0 Hz, CHO), 5.29 (d, 0.75 H, J = 10.0 Hz, CHO), 3.35 (m, 1 H, $CHCH_3$), 1.5–1.2 (m, 15 H, $SnCH_2CH_2CH_2CH_3$ and CH_3CH), 0.9–0.6 (m, 15 H, $SnCH_2CH_2CH_2CH_3$); ^{13}C NMR (50 MHz) δ *157.4 ($^2J_{CF}$ = 41 Hz), 157.1 ($^2J_{CF}$ = 41 Hz), 143.3, *142.8, *128.7, 128.4, 127.4, 127.2, 126.7, *114.8 ($^1J_{CF}$ = 286 Hz), 114.6 ($^1J_{CF}$ = 286 Hz), 80.7 (^1J = 279, 292 Hz), *43.5, 43.2, 28.8, *27.2 (^3J = 60 Hz), 19.9 (^3J = 27 Hz), 18.7, 13.4, 9.5 (^1J = 316, 330 Hz), 4.8 (^1J = 313, 327 Hz); MS *m/z* (rel intensity) 465 ($M^+ - C_4H_9$, 6), 347 (28), 291 (100). Anal. Calcd for $C_{23}H_{37}F_3O_2Sn$: C, 53.00; H, 7.15. Found: C, 52.88; H, 7.03.

1-Iodo-2-phenyl-1-(tributylstannyl)propane (14). Trifluoroacetate **13** (15:1 mixture of diastereomers, 400 mg, 0.77 mmol) was stirred in a mixture of EtOH (4 mL) and 2 M NaOH (1 mL) for 10 min. The mixture was diluted with hexane (25 mL), washed with H_2O (3 × 5 mL), dried over $MgSO_4$, filtered, and concentrated. The resulting α-hydroxystannane **12** was converted to iodide **14** (as a 1:1 mixture of diastereomers) as described in General Procedure A in 65% yield from **11**: IR (neat) 1493, 1455, 1074, 699 cm^{-1}; ^1H NMR (200 MHz) δ 7.35–7.10 (m, 5 H, Ar-H), 3.72 (d, 0.5 H, J = 7.2 Hz, CHI), 3.56 (d, 0.5 H, J = 8.5 Hz, CHI), 3.16 (quintet, 0.5 H, J = 7.0 Hz, $CHCH_3$), 2.96 (overlapping dq, 0.5 H, J = 6.7, 8.5 Hz, $CHCH_3$), 1.5–1.2 (m, 15 H, $SnCH_2CH_2CH_2CH_3$ and CH_3CH), 0.95–0.6 (m, 15 H, $SnCH_2$-$CH_2CH_2CH_3$); ^{13}C NMR (50 MHz) δ 145.7 (^3J = 20 Hz), 145.4 (^3J = 20 Hz), 128.5, 128.2, 127.1, 126.9, 126.8, 126.7, 46.0, 45.3, 28.8 (9) (^2J = 20 Hz), 28.8(6) (^2J = 20 Hz), 27.4 (^3J = 60 Hz), 27.3 (^3J = 60 Hz), 24.4 (^3J = 23 Hz), 23.4 (^1J = 237, 249 Hz), 22.8 (^3J = 18 Hz), 22.1 (^1J = 228, 238 Hz), 13.6, 11.9 (^1J = 318, 334 Hz); MS *m/z* (rel intensity) 501 (56), 351 (19), 201 (100). Anal. Calcd for $C_{21}H_{37}ISn$: C, 47.14; H, 6.97. Found: C, 47.26; H, 6.93.

(*Z*)-2-Phenyl-1-(tributylstannyl)propene (15) was prepared as a 7:1 mixture of isomers from iodide **14** in 100% yield. The reaction was carried out as described in General Procedure A except that the reaction was run at rt for 14 h: IR (neat) 2851, 1590, 1491, 1452, 1375 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.5–7.2 (m, 5 H, Ar-H), 6.27 (d, 0.125 H, J = 0.5 Hz, CHSn), 5.87 (q, 0.875 H, J = 1.4 Hz, $^2J_{HSn}$ = 64, 67 Hz, CHSn), 2.26 (d, 2.6 H, J = 1.4 Hz, CH_3CH=C), 2.21 (d, 0.4 H, J = 0.5 Hz, CH_3C=C), 1.7–0.8 [m, 27 H, $Sn(CH_2CH_2CH_2CH_3)$]; ^{13}C NMR (50 MHz) δ *155.7, 151.8, *146.2, 143.9, 128.0(5), 127.9(9), 127.8 (^1J = 377, 395 Hz), 127.0, 126.9, 125.5, 29.2, *29.0 (^2J = 20 Hz), 27.8, *27.3 (^3J = 57 Hz), 26.8, 17.5 *13.6, *10.4 (^1J = 325, 343 Hz), 10.2; MS *m/z* (rel intensity) 351 ($M^+ - C_4H_9$, 91), 291 (59), 269 (65), 235 (20), 91 (100). Anal. Calcd for $C_{21}H_{36}Sn$: C, 61.94; H, 8.91. Found: C, 61.90; H, 8.88.

1-Cyclohexyl-1-iodo-1-(tributylstannyl)methane (17) was prepared from cyclohexanecarboxaldehyde according to General Procedure A in 81% yield: IR (neat) 2923, 2861, 1453 cm^{-1}; ^1H NMR (200 MHz) δ 3.42 (d, 1 H, J = 3.7 Hz, CHI), 1.8–0.8 (m, 38 H, $SnCH_2CH_2CH_2CH_3$ and C_6H_{11}); ^{13}C NMR (50 MHz) δ 43.7, 35.4 (^3J = 19 Hz), 34.8 (^3J = 13 Hz), 29.0 (^2J = 20 Hz), 27.4 (^2J = 57 Hz), 26.3, 26.2, 25.9, 24.4 (^1J = 251 Hz), 13.6, 11.7 (^1J = 316, 332 Hz); MS m/z (rel intensity) 457 ($M^+ - C_4H_9$, 2), 329 (32), 291 (100). Anal. Calcd for $C_{19}H_{39}ISn$: C, 44.48; H, 7.66. Found: C, 44.55; H, 7.36.

((Tributylstannyl)methylene)cyclohexane (18) was prepared from iodide 17 according to General Procedure B in 95% yield. Limited spectral data have been reported previously:[34] IR (neat) 1607, 1454, 1073 cm^{-1}; ^1H NMR (250 MHz) δ 5.52 (s, 1 H, J_{HSn} = 73 Hz, CHSn), 2.24 (m, 2 H, $CH_2C{=}C$), 2.10 (m, 2 H, $CH_2C{=}C$), 1.6–1.2 (m, 18 H, $SnCH_2CH_2CH_2CH_3$ and 3 × CH_2 of c-C_6H_{10}), 1.0–0.8 (m, 15 H, $SnCH_2CH_2CH_2CH_3$); ^{13}C NMR (63 MHz) δ 159.3, 118.4, (^1J = 399, 420 Hz), 40.2 (^3J = 61 Hz), 37.8 (^3J = 36 Hz), 29.3 (^2J = 20 Hz), 28.9, 27.3 (^3J = 65 Hz), 26.4, 17.4, 13.6, 10.2 (^1J = 322, 337 Hz).

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