

**Supporting Information for
Mechanistic Aspects of Palladium-Catalyzed Allylstannylation of Alkynes**

Eiji Shirakawa, Hiroto Yoshida, Yoshiaki Nakao and Tamejiro Hiyama

General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere (deoxygenated by passing through BASF-Catalyst R3-11 column at 80 °C). Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^1H , 270 MHz; ^{13}C , 67.8 MHz; ^{119}Sn , 101 MHz) spectrometer or a Varian Mercury 200 (^1H , 200 MHz) spectrometer using tetramethylsilane (^1H) as an internal standard and tetramethyltin (^{119}Sn) as an external standard. The preparative recycling gel permeation chromatography was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns (chloroform as an eluent). Unless otherwise noted, commercially available reagents were used without purification. Toluene and 1,4-dioxane were distilled from sodium/benzophenone ketyl. Allyl(tributyl)tin,¹ 1-buten-3-yl(tributyl)tin,² 2-methylallyl(tributyl)tin,³ (*E*)-2-buten-1-yl(tributyl)tin,⁴ (*Z*)-2-buten-1-yl(tributyl)tin,⁵ (*E*)-cinnamyl(tributyl)tin,⁶ 2-cyclohexen-1-yl(tributyl)tin,¹ 2-heptynenitrile,⁷ 3,3,3-trifluoro-1-phenyl-1-propyne,⁸ and phenylethynyl *p*-tolyl sulfone⁹ were prepared according to literature procedures.

Allylstannylation of Alkynes. A General Procedure. A solution (3 mL) of an organostannane (0.33 mmol), and an alkyne (0.99 mmol) was degassed by four freeze-thaw cycles. To this solution was added $\text{Pd}_2(\text{dba})_3$ (7.5 mg, 8.2 μmol) and the mixture was stirred at 50 °C. After the time specified in Table 1 or Schemes, evaporation of the solvent followed by gel permeation chromatography gave the corresponding carbostannylation product.

Ethyl (2*E*,5*E*)-3-phenyl-2-tributylstannyl-2,5-heptadienoate (3a). A yellow oil: ^1H NMR (CDCl_3) δ 0.75–1.70 (m, 33 H), 3.12 (d, J = 6.3 Hz, 2 H), 3.84 (q, J = 7.3 Hz, 2 H), 5.25 (dtq, J = 15.2, 6.3, 1.3 Hz, 1 H), 5.40 (dqt, J = 15.2, 6.3, 1.3 Hz, 1 H), 7.03–7.34 (m, 5 H); ^{13}C NMR (CDCl_3) δ 11.4, 13.7, 13.9, 17.9, 27.3, 28.9, 43.6, 59.8, 127.0, 127.2, 127.4, 127.5, 127.7, 136.9, 142.2, 154.4, 172.8; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -39.6; Anal. Calcd for $\text{C}_{27}\text{H}_{44}\text{O}_2\text{Sn}$: C, 62.44; H, 8.54. Found (as a mixture of 3a and 4a): C, 62.20; H, 8.30.

Ethyl (1*E*,4*E*)-1-phenyl-1-tributylstannyl-1,4-hexadiene-2-carboxylate (4a). A yellow oil: ^1H NMR (CDCl_3) δ 0.63–1.75 (m, 33 H), 3.11 (d, J = 4.6 Hz, 2 H), 3.81 (q, J = 7.3 Hz, 2 H), 5.43 (dtq, J = 15.2, 4.6, 1.3 Hz, 1 H), 5.56 (dqt, J = 15.2, 5.9, 1.3 Hz, 1 H), 6.73–7.36 (m, 5 H); ^{13}C NMR (CDCl_3) δ 11.2, 13.6, 18.0, 27.3, 28.9, 40.0,

59.9, 125.0, 125.8, 127.3, 127.4, 127.7, 142.0, 145.7, 152.9, 168.5; $^{119}\text{Sn}\{\text{H}\}$ NMR (CDCl_3) δ -45.1; Anal. Calcd for $\text{C}_{27}\text{H}_{44}\text{O}_2\text{Sn}$: C, 62.44; H, 8.54. Found (as a mixture of **3a** and **4a**): C, 62.20; H, 8.30.

(1E,4E)-2-Phenyl-1-(4-toluenesulfonyl)-1-tributylstannyl-1,4-hexadiene

((E)-**3b**). A yellow oil: ^1H NMR (CDCl_3) δ 0.70–1.79 (m, 30 H), 2.28 (s, 3 H), 3.02 (d, J = 6.3 Hz, 2 H), 5.09 (dtq, J = 15.2, 6.3, 1.3 Hz, 1 H), 5.27 (dq, J = 15.2, 6.3 Hz, 1 H), 6.55–7.11 (m, 9 H); ^{13}C NMR (CDCl_3) δ 13.7, 14.0, 17.9, 21.4, 27.3, 29.0, 45.4, 126.0, 127.0, 127.1, 127.2, 128.4, 128.5, 128.6, 139.6, 139.7, 141.7, 151.2, 162.7; $^{119}\text{Sn}\{\text{H}\}$ NMR (CDCl_3) δ -37.9.

(1E,4Z)-2-Phenyl-1-(4-toluenesulfonyl)-1-tributylstannyl-1,4-hexadiene

((Z)-**3b**). A yellow oil: ^1H NMR (CDCl_3) δ 0.54–1.93 (m, 30 H), 2.28 (s, 3 H), 3.09 (d, J = 6.8 Hz, 2 H), 5.13 (dt, J = 10.5, 6.8 Hz, 1 H), 5.40 (dq, J = 10.5, 6.5 Hz, 1 H), 6.54–7.11 (m, 9 H); $^{119}\text{Sn}\{\text{H}\}$ NMR (CDCl_3) δ -37.4.

**Dimethyl (1E,4E)-1-tributylstannyl-1,4-hexadiene-1,2-dicarboxylate ((E)-
3c).** A yellow oil: ^1H NMR (CDCl_3) δ 0.80–1.80 (m, 30 H), 3.01 (d, J = 4.8 Hz, 2 H), 3.71 (s, 3 H), 3.73 (s, 3 H), 5.38 (dt, J = 15.4, 4.8 Hz, 1 H), 5.51 (dq, J = 15.4, 5.4 Hz, 1 H); ^{13}C NMR (CDCl_3) δ 11.3, 13.6, 18.0, 27.2, 28.7, 38.2, 51.4, 52.0, 127.0, 127.6, 141.7, 149.9, 165.9, 172.9; $^{119}\text{Sn}\{\text{H}\}$ NMR (CDCl_3) δ -32.5; Anal. Calcd for $\text{C}_{22}\text{H}_{40}\text{O}_4\text{Sn}$: C, 54.23; H, 8.27. Found: C, 54.02; H, 8.45.

**Dimethyl (1E,4Z)-1-tributylstannyl-1,4-hexadiene-1,2-dicarboxylate ((Z)-
3c).** A yellow oil: ^1H NMR (CDCl_3) δ 0.76–1.75 (m, 30 H), 3.08 (d, J = 6.6 Hz, 2 H), 3.70 (s, 3 H), 3.73 (s, 3 H), 5.24 (dt, J = 10.7, 6.6 Hz, 1 H), 5.54 (dq, J = 10.7, 6.9 Hz, 1 H); ^{13}C NMR (CDCl_3) δ 11.3, 13.1, 13.6, 27.2, 28.7, 33.5, 51.5, 52.0, 126.3, 126.4, 142.0, 149.9, 166.0, 172.9; $^{119}\text{Sn}\{\text{H}\}$ NMR (CDCl_3) δ -32.2.

**Dimethyl (E)-3-methyl-1-tributylstannyl-1,4-pentadiene-1,2-dicarboxylate
(3'c).** A yellow oil: ^1H NMR (CDCl_3) δ 0.81–1.76 (m, 30 H), 2.96 (qd, J = 7.1, 5.9 Hz, 1 H), 3.69 (s, 3 H), 3.71 (s, 3 H), 5.06 (dd, J = 10.2, 1.1 Hz, 1 H), 5.07 (dq, J = 17.4, 1.1 Hz, 1 H), 5.98 (ddd, J = 17.4, 10.2, 5.9 Hz, 1 H); ^{13}C NMR (CDCl_3) δ 11.4, 13.6, 19.4, 27.2, 28.8, 45.9, 51.5, 51.7, 114.8, 139.9, 146.6, 148.6, 166.3, 172.3; $^{119}\text{Sn}\{\text{H}\}$ NMR (CDCl_3) δ -34.7; Anal. Calcd for $\text{C}_{22}\text{H}_{40}\text{O}_4\text{Sn}$: C, 54.23; H, 8.27. Found: C, 54.31; H, 8.55.

Tetramethyl (1*E*,3*Z*,6*E*)-1-tributylstannyl-1,3,6-octatriene-1,2,3,4-tetracarboxylate ((*E*)-3"*c*). A yellow oil: ^1H NMR (CDCl_3) δ 0.81–1.71 (m, 30 H), 2.81–3.21 (m, 2 H), 3.70 (s, 3 H), 3.72 (s, 3 H), 3.81 (s, 3 H), 3.81 (s, 3 H), 5.28 (dtd, J = 15.2, 6.8, 1.5 Hz, 1 H), 5.52 (dq, J = 15.2, 6.2 Hz, 1 H); ^{13}C NMR (CDCl_3) δ 10.9, 13.6, 17.9, 27.2, 28.6, 35.5, 51.6, 52.2, 52.4, 52.5, 123.7, 129.1, 129.5, 135.1, 146.7, 159.4, 163.4, 165.4, 168.7, 172.4; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -28.3; Anal. Calcd for $\text{C}_{28}\text{H}_{46}\text{O}_8\text{Sn}$: C, 53.43; H, 7.37. Found: C, 53.41; H, 7.64.

Tetramethyl (1*E*,3*Z*,6*Z*)-1-tributylstannyl-1,3,6-octatriene-1,2,3,4-tetracarboxylate ((*Z*)-3"*c*). A yellow oil: ^1H NMR (CDCl_3) δ 0.66–1.82 (m, 30 H), 2.89–3.27 (m, 2 H), 3.70 (s, 3 H), 3.71 (s, 3 H), 3.80 (s, 3 H), 3.81 (s, 3 H), 5.26 (dt, J = 10.3, 7.3 Hz, 1 H), 5.58 (dq, J = 10.3, 7.1 Hz, 1 H); ^{13}C NMR (CDCl_3) δ 10.9, 12.7, 13.6, 27.2, 28.7, 30.1, 51.6, 52.3, 52.45, 52.54, 122.9, 127.5, 128.8, 130.9, 135.1, 146.9, 168.8, 172.4; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -28.0.

Ethyl (*E*)-3-phenyl-2-tributylstannyl-2,5-hexadienoate (9a). A yellow oil: ^1H NMR (CDCl_3) δ 0.81–1.87 (m, 30 H), 3.20 (dt, J = 6.6, 1.5 Hz, 2 H), 3.85 (q, J = 7.0 Hz, 2 H), 4.96 (dtd, J = 10.2, 1.5, 1.3 Hz, 1 H), 5.00 (dtd, J = 17.2, 1.5, 1.3 Hz, 1 H), 5.65 (ddt, J = 17.2, 10.2, 6.6 Hz, 1 H), 7.13–7.46 (m, 5 H); ^{13}C NMR (CDCl_3) δ 11.5, 13.7, 13.9, 27.2, 28.9, 44.7, 59.8, 116.8, 127.1, 127.5, 127.8, 135.0, 137.7, 141.9, 153.5, 172.7; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -39.2; Anal. Calcd for $\text{C}_{26}\text{H}_{42}\text{O}_2\text{Sn}$: C, 61.80; H, 8.38. Found: C, 61.85; H, 8.10.

Ethyl (*E*)-1-phenyl-1-tributylstannyl-1,4-pentadiene-2-carboxylate (10a). A yellow oil: ^1H NMR (CDCl_3) δ 0.63–1.74 (m, 30 H), 3.12 (dt, J = 6.2, 1.5 Hz, 2 H), 3.74 (q, J = 7.1 Hz, 2 H), 5.01 (ddt, J = 10.1, 1.6, 1.5 Hz, 1 H), 5.09 (ddt, J = 17.1, 1.6, 1.5 Hz, 1 H), 5.78 (ddt, J = 17.1, 10.1, 6.2 Hz, 1 H), 6.76–7.45 (m, 5 H); ^{13}C NMR (CDCl_3) δ 11.2, 13.6, 27.3, 28.9, 40.9, 59.9, 116.7, 125.1, 125.7, 125.8, 127.8, 135.0, 141.1, 145.7, 154.2, 168.3; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -44.8; Anal. Calcd for $\text{C}_{26}\text{H}_{42}\text{O}_2\text{Sn}$: C, 61.80; H, 8.38. Found: C, 61.63; H, 8.60.

(*E*)-2-Phenyl-1-(4-toluenesulfonyl)-1-tributylstannyl-1,4-pentadiene (9b). A yellow oil: ^1H NMR (CDCl_3) δ 0.84–1.88 (m, 27 H), 2.27 (s, 3 H), 3.10 (d, J = 6.4 Hz, 2 H), 4.88 (d, J = 16.9 Hz, 1 H), 4.94 (d, J = 10.3 Hz, 1 H), 5.50 (ddt, J = 16.9, 10.3, 6.4 Hz, 1 H), 6.64–7.16 (m, 9 H); ^{13}C NMR (CDCl_3) δ 13.7, 14.0, 21.3, 27.3, 29.0, 46.3, 117.8, 127.1, 127.2, 128.36, 128.44, 133.6, 139.4, 139.5, 141.7, 152.1, 161.7; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -37.6; Anal. Calcd for $\text{C}_{30}\text{H}_{44}\text{O}_2\text{SSn}$: C, 61.34; H, 7.55. Found: C, 61.16; H, 7.58.

(E)-1-Phenyl-2-(4-toluenesulfonyl)-1-tributylstannyl-1,4-pentadiene

(10b). A yellow oil: ^1H NMR (CDCl_3) δ 0.63–1.72 (m, 27 H), 2.34 (s, 3 H), 3.48 (dt, J = 5.6, 1.6 Hz, 2 H), 5.26 (dtd, J = 10.1, 1.6, 1.6 Hz, 1 H), 5.36 (d, J = 17.1, 1.6, 1.6 Hz, 1 H), 6.05 (ddt, J = 17.1, 10.1, 5.6 Hz, 1 H), 6.47–6.61 (m, 2 H), 6.91–7.40 (m, 7 H); ^{13}C NMR (CDCl_3) δ 11.7, 13.5, 21.5, 27.2, 28.7, 39.3, 117.4, 125.2, 125.8, 127.48, 127.51, 128.8, 135.3, 139.6, 141.8, 142.7, 146.5, 162.1; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -29.0.

Dimethyl (E)-1-tributylstannyl-1,4-pentadiene-1,2-dicarboxylate (9c). A yellow oil: ^1H NMR (CDCl_3) δ 0.84–1.74 (m, 27 H), 3.08 (dt, J = 6.0, 1.6 Hz, 2 H), 3.71 (s, 3 H), 3.74 (s, 3 H), 5.07 (dtd, J = 10.3, 1.6, 1.5 Hz, 1 H), 5.09 (dtd, J = 17.0, 1.6, 1.5 Hz, 1 H), 5.81 (ddt, J = 17.0, 10.3, 6.0 Hz, 1 H); ^{13}C NMR (CDCl_3) δ 11.4, 13.6, 27.2, 28.7, 39.2, 51.5, 52.0, 116.8, 134.6, 140.7, 151.2, 165.7, 172.8; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -31.9; Anal. Calcd for $\text{C}_{21}\text{H}_{38}\text{O}_4\text{Sn}$: C, 53.30; H, 8.09. Found: C, 53.01; H, 7.90.

Dimethyl (1*E*,3*E*)-1-tributylstannyl-1,3-pentadiene-1,2-dicarboxylate (9'c). A yellow oil: ^1H NMR (CDCl_3) δ 0.83–1.70 (m, 27 H), 1.85 (d, J = 5.4 Hz, 3 H), 3.70 (s, 3 H), 3.79 (s, 3 H), 5.99 (dq, J = 15.8, 5.4 Hz, 1 H), 6.11 (d, J = 15.8 Hz, 1 H); ^{13}C NMR (CDCl_3) δ 11.9, 13.6, 19.0, 27.2, 28.8, 51.8, 52.1, 129.5, 135.1, 140.6, 149.0, 168.2, 171.6; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -34.9; Anal. Calcd for $\text{C}_{21}\text{H}_{38}\text{O}_4\text{Sn}$: C, 53.30; H, 8.09. Found: C, 53.38; H, 8.30.

(Z)-3-Butyl-2-tributylstannyl-2,5-hexadienenitrile (9d). A yellow oil: ^1H NMR (CDCl_3) δ 0.73–1.83 (m, 34 H), 2.52 (t, J = 7.5 Hz, 2 H), 2.88 (dt, J = 6.4, 1.5 Hz, 2 H), 5.11 (dtd, J = 16.5, 1.5, 1.5 Hz, 1 H), 5.13 (dtd, J = 10.7, 1.5, 1.5 Hz, 1 H), 5.69 (ddt, J = 16.5, 10.7, 1.5 Hz, 1 H); ^{13}C NMR (CDCl_3) δ 11.3, 13.6, 13.9, 22.5, 27.1, 28.8, 30.6, 36.7, 43.0, 109.2, 117.9, 121.0, 134.2, 174.3; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -37.8; Anal. Calcd for $\text{C}_{22}\text{H}_{41}\text{NSn}$: C, 60.29; H, 9.43. Found: C, 60.55; H, 9.35.

Ethyl (Z)-3-methyl-2-tributylstannyl-2,5-hexadienoate (9e). A yellow oil: ^1H NMR (CDCl_3) δ 0.76–1.71 (m, 30 H), 1.85 (s, 3 H), 2.80 (dt, J = 6.6, 1.5 Hz, 2 H), 4.15 (q, J = 7.1 Hz, 2 H), 5.09 (ddt, J = 10.1, 1.7, 1.5 Hz, 1 H), 5.11 (ddt, J = 16.9, 1.7, 1.5 Hz, 1 H), 5.75 (ddt, J = 16.9, 10.1, 6.6 Hz, 1 H); ^{13}C NMR (CDCl_3) δ 11.3, 13.6, 14.4, 20.5, 27.2, 28.9, 45.7, 60.0, 117.0, 133.8, 135.5, 151.0, 173.0; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -43.9; Anal. Calcd for $\text{C}_{21}\text{H}_{40}\text{O}_2\text{Sn}$: C, 56.90; H, 9.10. Found: C, 57.07; H, 9.31.

Ethyl (E)-5-tributylstannyl-1,4-hexadiene-4-carboxylate (10e). A yellow oil: ^1H NMR (CDCl_3) δ 0.79–1.70 (m, 30 H), 2.08 (s, 3 H), 3.03 (d, J = 6.1 Hz, 2 H), 4.19 (q, J = 7.1 Hz, 2 H), 5.00 (dd, J = 10.1, 1.6 Hz, 1 H), 5.05 (dd, J = 17.2, 1.6 Hz, 1 H), 5.76 (ddt, J = 17.2, 10.1, 6.1 Hz, 1 H); ^{13}C NMR (CDCl_3) δ 10.5, 13.6, 14.3, 23.2, 27.4, 29.1, 41.6, 60.0, 116.1, 135.7, 139.2, 150.4, 167.8; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -43.5; Anal. Calcd for $\text{C}_{21}\text{H}_{40}\text{O}_2\text{Sn}$: C, 56.90; H, 9.10. Found: C, 56.86; H, 9.05.

(E)-6,6,6-Trifluoro-4-phenyl-5-tributylstannyl-1,4-hexadiene (9f). A yellow oil: ^1H NMR (CDCl_3) δ 0.81–1.80 (m, 27 H), 3.18 (dq, J = 6.6, 1.5 Hz, 2 H), 4.95 (dq, J = 16.8, 1.5 Hz, 1 H), 4.99 (dq, J = 10.3, 1.5 Hz, 1 H), 5.59 (ddt, J = 16.8, 10.3, 6.6 Hz, 1 H), 6.98–7.40 (m, 5 H); ^{13}C NMR (CDCl_3) δ 11.9, 13.7, 27.2, 28.8, 46.8, 117.6, 124.4, 127.0, 127.2, 127.4, 127.6, 128.5, 131.8, 132.3, 133.9, 141.7, 158.6, 158.7, 158.8; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -36.8 (q, J = 16.6 Hz); Anal. Calcd for $\text{C}_{24}\text{H}_{37}\text{F}_3\text{Sn}$: C, 57.51; H, 7.44. Found: C, 57.21; H, 7.27.

(E)-1-Phenyl-1-tributylstannyl-2-trifluoromethyl-1,4-pentadiene (10f). A yellow oil: ^1H NMR (CDCl_3) δ 0.67–1.73 (m, 27 H), 3.11 (d, J = 5.8 Hz, 2 H), 5.16 (dtd, J = 10.2, 1.6, 1.5 Hz, 1 H), 5.21 (dtd, J = 17.2, 1.6, 1.5 Hz, 1 H), 5.89 (ddt, J = 17.2, 10.2, 5.8 Hz, 1 H), 6.76–7.44 (m, 5 H); ^{13}C NMR (CDCl_3) δ 11.3, 13.5, 27.2, 28.8, 39.3, 116.7, 120.6, 124.7, 125.1, 125.2, 127.7, 134.7, 135.1, 135.2, 143.8, 158.29, 158.34; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -40.8; Anal. Calcd for $\text{C}_{24}\text{H}_{37}\text{F}_3\text{Sn}$: C, 57.51; H, 7.44. Found: C, 57.37; H, 7.67.

Ethyl (2E,5E)-3,6-diphenyl-2-tributylstannyl-2,5-hexadienoate (12a). A yellow oil: ^1H NMR (CDCl_3) δ 0.83–1.78 (m, 30 H), 3.34 (dd, J = 6.6, 1.4 Hz, 2 H), 3.86 (q, J = 7.1 Hz, 2 H), 6.02 (dt, J = 15.8, 6.6 Hz, 1 H), 6.34 (dd, J = 15.8, 1.4 Hz, 1 H), 7.00–7.38 (m, 10 H); ^{13}C NMR (CDCl_3) δ 11.5, 13.7, 13.9, 27.3, 29.0, 43.9, 59.8, 126.0, 126.8, 127.1, 127.2, 127.5, 127.9, 128.4, 131.8, 137.3, 137.8, 142.0, 153.6, 172.7; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -39.3; Anal. Calcd for $\text{C}_{32}\text{H}_{46}\text{O}_2\text{Sn}$: C, 66.10; H, 7.97. Found: C, 66.06; H, 8.12.

Ethyl (1E,4E)-1,5-diphenyl-1-tributylstannyl-1,4-pentadiene-2-carboxylate (13a). A yellow oil: ^1H NMR (CDCl_3) δ 0.71–1.67 (m, 30 H), 3.35 (dd, J = 6.4, 1.3 Hz, 2 H), 3.80 (q, J = 7.1 Hz, 2 H), 6.20 (dt, J = 15.9, 6.4 Hz, 1 H), 6.50 (d, J = 15.9 Hz, 1 H), 6.84–7.34 (m, 10 H); ^{13}C NMR (CDCl_3) δ 11.3, 13.6, 27.3, 28.9, 40.2, 60.0, 125.1, 125.7, 126.1, 126.7, 127.1, 127.8, 128.4, 131.9, 137.4, 141.2, 145.6, 154.4, 168.2; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -44.6.

Dimethyl (1*E*,4*E*)-5-phenyl-1-tributylstannyl-1,4-pentadiene-1,2-dicarboxylate (12c). A yellow oil: ^1H NMR (CDCl_3) δ 0.77–1.79 (m, 27 H), 3.27 (d, J = 6.0 Hz, 2 H), 3.73 (s, 3 H), 3.78 (s, 3 H), 6.17 (dt, J = 15.9, 6.0 Hz, 1 H), 6.45 (d, J = 15.9 Hz, 1 H), 7.12–7.48 (m, 5 H); ^{13}C NMR (CDCl_3) δ 11.4, 13.6, 27.2, 28.7, 38.4, 51.5, 52.1, 126.1, 126.2, 127.3, 128.4, 132.0, 137.1, 140.6, 151.5, 165.6, 172.8; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -31.8.

Tetramethyl (1*E*,3*Z*,6*E*)-7-Phenyl-1-tributylstannylhepta-1,3,6-triene-1,2,3,4-tetracarboxylate (12"*c*). A brown oil: ^1H NMR (CDCl_3) δ 0.82–1.67 (m, 27 H), 3.60 (s, 3 H), 3.73 (s, 3 H), 3.82 (s, 3 H), 3.83 (s, 3 H), 6.04 (dt, J = 15.7, 7.0 Hz, 1 H), 6.43 (d, J = 15.7 Hz, 1 H), 7.14–7.39 (m, 5 H); ^{13}C NMR (CDCl_3) δ 11.0, 13.5, 27.2, 28.6, 35.6, 51.6, 52.3, 52.45, 52.54, 122.7, 126.2, 127.5, 128.4, 130.3, 133.5, 135.0, 136.8, 145.4, 159.7, 163.3, 165.4, 168.6, 172.3; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -28.3; Anal. Calcd for $\text{C}_{33}\text{H}_{48}\text{O}_8\text{Sn}$: C, 57.32; H, 7.00. Found: C, 57.07; H, 7.27.

Dimethyl (E)-4-methyl-1-tributylstannyl-1,4-pentadiene-1,2-dicarboxylate (14c). A yellow oil: ^1H NMR (CDCl_3) δ 0.80–1.95 (m, 30 H), 2.99 (s, 2 H), 3.69 (s, 3 H), 3.74 (s, 3 H), 4.67 (s, 1 H), 4.81 (s, 1 H); ^{13}C NMR (CDCl_3) δ 11.3, 13.6, 23.4, 27.2, 28.7, 42.3, 51.5, 52.1, 111.7, 141.3, 142.6, 151.4, 166.1, 172.8; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -32.6; Anal. Calcd for $\text{C}_{22}\text{H}_{40}\text{O}_4\text{Sn}$: C, 54.23; H, 8.27. Found: C, 54.43; H, 8.52.

Tetramethyl (1*E*,3*Z*)-6-methyl-1-tributylstannyl-1,3,6-heptatriene-1,2,3,4-tetracarboxylate (14"*c*). A yellow oil: ^1H NMR (CDCl_3) δ 0.75–1.84 (m, 30 H), 2.82–3.01 (m, 1 H), 3.09–3.27 (m, 1 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 3.79 (s, 3 H), 3.81 (s, 3 H), 4.76 (s, 1 H), 4.81 (s, 1 H); ^{13}C NMR (CDCl_3) δ 10.9, 13.6, 22.3, 27.2, 28.6, 40.6, 51.6, 52.1, 52.3, 52.4, 114.5, 130.4, 135.0, 140.0, 146.5, 159.7, 163.4, 165.2, 168.7, 172.4; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -27.6; Anal. Calcd for $\text{C}_{28}\text{H}_{46}\text{O}_8\text{Sn}$: C, 53.43; H, 7.37. Found: C, 53.64; H, 7.43.

Ethyl (E)-3-(2-cyclohexen-1-yl)-3-phenyl-2-tributylstannyl-2-propenoate (15a). A yellow oil: ^1H NMR (CDCl_3) δ 0.20–2.05 (m, 36 H), 2.89–3.12 (m, 1 H), 3.77 (q, J = 7.1 Hz, 2 H), 5.62–5.82 (m, 2 H), 7.00–7.52 (m, 5 H); ^{13}C NMR (CDCl_3) δ 11.4, 13.7, 13.9, 21.7, 24.5, 27.2, 28.2, 29.0, 48.2, 59.6, 126.6, 127.2, 128.5, 128.9, 129.2, 137.6, 140.3, 158.8, 172.5; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3) δ -43.4; Anal. Calcd for $\text{C}_{29}\text{H}_{46}\text{O}_2\text{Sn}$: C, 63.87; H, 8.50. Found: C, 63.96; H, 8.22.

- (1) Tanaka, H.; Hai, A. K. M. A.; Ogawa, H.; Torii, S. *Synlett* **1993**, 835–836.
- (2) Jephcote, V. J.; Thomas, E. J. *J. Chem. Soc. Perkin Trans. 1* **1991**, 429–434.
- (3) Naruta, Y.; Nishigaichi, Y.; Maruyama, K. *Chem. Lett.* **1986**, 1857–1860.
- (4) Weigand, S.; Brückner, R. *Synthesis* **1996**, 475–482.
- (5) Miyake, H.; Yamamura, K. *Chem. Lett.* **1992**, 507–508.
- (6) Trost, B. M.; Herndon, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 6835–6837.
- (7) Luo, F. -T.; Wang, M. -W.; Wang, R. -T. *Org. Synth.* **1998**, *75*, 146–152.
- (8) Hiyama, T.; Sato, K.; Fujita, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1352–1354.
- (9) Hanack, M.; Wilhelm, B.; Subramanian, L. R. *Synthesis* **1988**, 592–595.