Palladium-Catalyzed Distannylation of *ortho*-Quinodimethanes

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Supporting Information

General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^1H , 270 MHz; ^{13}C , 67.8 MHz) spectrometer or a JEOL Lambda-400 (^1H , 400 MHz; ^{13}C , 99.5 MHz; ^{119}Sn , 147.5 MHz) spectrometer using residual chloroform (^1H) or CDCl_3 (^{13}C) as an internal standard and tetramethyltin (^{119}Sn) as an external standard. The preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (chloroform as an eluent). Column chromatography was carried out using Merck Aluminium oxide 90, activated, neutral. Unless otherwise noted, commercially available reagents were used without purification. THF was distilled from sodium/benzophenone ketyl and purified by passing through activated aluminium oxide column (5 g/8 mL of THF) prior to use. MeCN was distilled from phosphorus pentoxide. 18-Crown-6 was recrystallized from distilled MeCN. KF (spray-dried) was vacuum dried at 100 °C for 12 h.

Diels-Alder Reaction of *ortho*-Quinodimethane Using **1a as a Precursor.** Generation of *ortho*-quinodimethane from **1a** has been confirmed by the Diels-Alder reaction with methyl acrylate.

Distannylation Using Various Precursors or Ligands. Distannylation of *o*-quinodimethane with **2** using various precursors or ligands was examined. The results were summarized in Table A.

Table A

$ \begin{array}{c} \text{SiMe}_3 \\ \\ \text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{X} + \text{Bu}_3\text{Sn-SnBu}_3 \xrightarrow[\text{THF, 50 } ^\circ\text{C}]{\text{KF/18-crown-6, Pd(dba)}_2 \text{ (5 mol\%), Ligand (5 mol\%)}} \text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{SnBu}_3 \\ \text{X} \qquad \qquad \qquad \text{2} \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \text{3a} \end{array} $			
X	Ligand	time (h)	yield (%) ^a
OCO ₂ Me	none	4	8
OCOCF ₃	none	18	13
OPO(OEt) ₂	none	19	8
OCO ₂ CH ₂ CCl ₃	none	14	trace
OCO ₂ Ph (1a)	none	7	42
OCO ₂ Ph (1a)		12	60
OCO ₂ Ph (1a)		24	14
OCO ₂ Ph (1a)		25	27
OCO ₂ Ph (1a)		25	48
OCO ₂ Ph (1a)		7	59
OCO ₂ Ph (1a)	PPh ₃ ^b	5	53
OCO ₂ Ph (1a)		5	52
OCO ₂ Ph (1a)		5	28
OCO ₂ Ph (1a)		7	18
OCO ₂ Ph (1a)		5	16
OCO ₂ Ph (1a)		18	12

^a Yields were determined by ¹H NMR spectroscopic analysis with anisole as an internal standard. ^b Ligand = 10 mol%.

***o*-Quinodimethane Precursors.** *o*-Quinodimethane precursors were synthesized from 2-(hydroxymethyl)-1-[(trimethylsilyl)methyl]arenes^{1,2} as follows.

Synthesis of Benzyl phenyl carbonate 1. To a CH₂Cl₂ solution (20 mL) of a 2-(hydroxymethyl)-1-[(trimethylsilyl)methyl]arene (0.010 mol) were added pyridine (1.6 g, 0.020 mol) and phenyl chloroformate (2.3 g, 0.015 mol) at 0 °C, and the mixture was stirred at 0 °C. After the completion of the reaction, the mixture was washed with water, and the resulting organic phase was dried over anhydrous MgSO₄. Evaporation of the solvent followed by column chromatography gave **1**.

2-[(Trimethylsilyl)methyl]benzyl phenyl carbonate (1a). Isolated in 95% yield as a colorless oil: ¹H NMR (CDCl₃) δ 0.03 (s, 9 H), 2.23 (s, 2 H), 5.24 (s, 2 H), 7.06 (d, *J* = 7.7 Hz, 1 H), 7.12 (t, *J* = 7.5 Hz, 1 H), 7.18 (d, *J* = 8.5 Hz, 2 H), 7.21-7.32 (m, 2 H), 7.38 (t, *J* = 7.5 Hz, 3 H); ¹³C NMR (CDCl₃) δ -1.4, 23.3, 68.8, 121.1, 124.5, 126.0, 128.8, 129.4, 129.5, 130.2, 131.1, 140.0, 151.2, 153.8; Anal. Calcd for C₁₈H₂₂O₃Si: C, 68.75; H, 7.05. Found: C, 68.58; H, 7.00.

{2-[(Trimethylsilyl)methyl]naphth-1-yl}methyl phenyl carbonate (1b). Isolated in 81% yield as a pale yellow oil: ¹H NMR (CDCl₃) δ 0.04 (s, 9 H), 2.53 (s, 2 H), 5.75 (s, 2 H), 7.10-7.32 (m, 4 H), 7.32-7.50 (m, 3 H), 7.56 (td, *J* = 8.5, 1.4 Hz, 1 H), 7.75 (d, *J* = 8.4 Hz, 1 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 8.11 (d, *J* = 8.7 Hz, 1 H); ¹³C NMR (CDCl₃) δ -1.5, 25.2, 64.4, 121.1, 123.4, 124.6, 126.0, 126.9, 128.5, 128.7, 129.4, 129.4, 129.6, 131.6, 133.2, 139.8, 151.2, 154.0; Anal. Calcd for C₂₂H₂₄O₃Si: C, 72.49; H, 6.64. Found: C, 72.20; H, 6.50.

3-Phenyl-2-[(trimethylsilyl)methyl]benzyl phenyl carbonate (1c). Isolated in 88% yield as a pale yellow oil: ¹H NMR (CDCl₃) δ -0.27 (s, 9 H), 2.42 (s, 2 H), 5.30 (s, 2 H), 7.09-7.55 (m, 13 H); ¹³C NMR (CDCl₃) δ -0.7, 19.5, 69.5, 121.1, 124.0, 126.0, 126.9, 128.2, 129.2, 129.5, 129.8, 131.1, 131.7, 138.5, 141.6, 142.5, 151.2, 153.8; Anal. Calcd for C₂₄H₂₆O₃Si: C, 73.81; H, 6.71. Found: C, 73.61; H, 6.45.

6-Methyl-2-[(trimethylsilyl)methyl]benzyl phenyl carbonate (1d). Isolated in 91% yield as a colorless oil: ¹H NMR (CDCl₃) δ 0.02 (s, 9 H), 2.30 (s, 2 H), 2.45 (s, 3 H), 5.34 (s, 2 H), 6.91 (d, *J* =

7.5 Hz, 1 H), 6.98 (d, $J = 7.5$ Hz, 1 H), 7.08-7.33 (m, 4 H), 7.34-7.46 (m, 2 H); ^{13}C NMR (CDCl_3) δ -1.5, 20.0, 23.9, 65.3, 121.0, 126.0, 126.7, 127.5, 128.8, 129.2, 129.4, 139.0, 141.2, 151.2, 153.9; Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3\text{Si}$: C, 69.47; H, 7.36. Found: C, 69.38; H, 7.37.

5-Methyl-2-[(trimethylsilyl)methyl]benzyl phenyl carbonate (1e). Isolated in 88% yield as a colorless oil: ^1H NMR (CDCl_3) δ 0.02 (s, 9 H), 2.29 (s, 2 H), 2.44 (s, 3 H), 5.33 (s, 2 H), 6.90 (d, $J = 7.7$ Hz, 1 H), 6.97 (d, $J = 7.5$ Hz, 1 H), 7.07-7.33 (m, 4 H), 7.33-7.47 (m, 2 H); ^{13}C NMR (CDCl_3) δ -1.5, 20.7, 22.6, 68.8, 121.0, 125.9, 129.3, 129.4, 129.5, 130.8, 133.7, 136.6, 151.2, 153.7; Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3\text{Si}$: C, 69.47; H, 7.36. Found: C, 69.31; H, 7.54.

4,6-Dimethyl-2-[(trimethylsilyl)methyl]benzyl phenyl carbonate (1f). Isolated in 91% yield as a pale yellow oil: ^1H NMR (CDCl_3) δ 0.04 (s, 9 H), 2.28 (s, 2 H), 2.29 (s, 3 H), 2.42 (s, 3 H), 5.32 (s, 2 H), 6.74 (s, 1 H), 6.82 (s, 1 H), 7.10-7.34 (m, 3 H), 7.34-7.49 (m, 2 H); ^{13}C NMR (CDCl_3) δ -1.5, 19.9, 21.1, 23.8, 65.2, 121.1, 125.9, 126.4, 127.7, 128.1, 129.4, 138.5, 138.8, 141.0, 151.2, 154.0; Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_3\text{Si}$: C, 70.13; H, 7.65. Found: C, 70.40; H, 7.69.

4-Fluoro-2-[(trimethylsilyl)methyl]benzyl phenyl carbonate (1g). Isolated in 96% yield as a pale yellow crystal: ^1H NMR (CDCl_3) δ 0.55 (s, 9 H), 2.24 (s, 2 H), 5.20 (s, 2 H), 6.67-6.87 (m, 2 H), 7.10-7.22 (m, 2 H), 7.22-7.32 (m, 1 H), 7.32-7.47 (m, 3 H); ^{13}C NMR (CDCl_3) δ -1.5, 23.7, 68.0, 111.3 (d, $J_{\text{C-F}} = 22.0$ Hz), 115.7 (d, $J_{\text{C-F}} = 20.7$ Hz), 121.0, 126.0, 129.5, 132.3 (d, $J_{\text{C-F}} = 0.34$ Hz), 143.1, 143.2, 153.7, 151.1, 162.9 (d, $J_{\text{C-F}} = 246.6$ Hz); Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{FO}_3\text{Si}$: C, 65.03; H, 6.37. Found: C, 65.22; H, 6.32.

α -Methyl-2-[(trimethylsilyl)methyl]benzyl phenyl carbonate (1h). Isolated in 98% yield as a pale yellow oil: ^1H NMR (CDCl_3) δ 0.03 (s, 9 H), 1.66 (d, $J = 6.5$ Hz, 3 H), 2.13 (d, $J = 14.0$ Hz, 1 H), 2.31 (d, $J = 14.0$ Hz, 1 H), 6.02 (q, $J = 6.5$ Hz, 1 H), 7.01 (dd, $J = 7.2, 1.9$ Hz, 1 H), 7.12-7.32 (m, 5 H), 7.32-7.46 (m, 2 H), 7.49 (dd, $J = 7.2, 1.9$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ -1.4, 21.7, 23.1, 74.3, 121.1, 124.8, 125.9, 126.1, 127.9, 129.4, 129.6, 136.9, 137.7, 151.2, 153.2; Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3\text{Si}$: C, 69.47; H, 7.36. Found: C, 69.30; H, 7.40.

3-[(Trimethylsilyl)methyl]benzyl phenyl carbonate (1i).

Isolated in 94% yield as a yellow oil: ^1H NMR (CDCl_3) δ 0.02 (s, 9 H), 2.13 (s, 2 H), 5.25 (s, 2 H), 7.02 (d, $J = 7.7$ Hz, 1 H), 7.09 (s, 1 H), 7.16-7.34 (m, 5 H), 7.34-7.48 (m, 2 H); ^{13}C NMR (CDCl_3) δ -1.9, 27.0, 70.6, 121.1, 124.2, 126.0, 128.1, 128.4, 128.5, 129.5, 134.6, 141.1, 151.2, 153.7; Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3\text{Si}$: C, 68.75; H, 7.05. Found: C, 68.60; H, 7.09.

4-[(Trimethylsilyl)methyl]benzyl phenyl carbonate (1j).

Isolated in 97% yield as a orange crystal: ^1H NMR (CDCl_3) δ -0.01 (s, 9 H), 2.10 (s, 2 H), 5.21 (s, 2 H), 7.02 (d, $J = 7.9$ Hz, 2 H), 7.09-7.45 (m, 7 H); ^{13}C NMR (CDCl_3) δ -2.0, 27.0, 70.5, 121.0, 126.0, 128.2, 128.8, 129.4, 130.1, 141.5, 151.2, 153.7; Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3\text{Si}$: C, 68.75; H, 7.05. Found: C, 69.00; H, 7.12.

2-[(Trimethylsilyl)methyl]benzyl methyl carbonate.

Synthesized from 2-[(trimethylsilyl)methyl]benzyl alcohol according to a literature method.³ Isolated in 73% yield as a colorless oil: b.p. 120 °C (bath temp., 1 mmHg); ^1H NMR (CDCl_3) δ 0.02 (s, 9 H), 2.10 (s, 3 H), 2.17 (s, 2 H), 5.07 (s, 2 H), 7.03 (d, $J = 7.4$ Hz, 1 H), 7.09 (td, $J = 7.4, 1.3$ Hz, 1 H), 7.22 (td, $J = 7.4, 1.7$ Hz, 1 H), 7.33 (d, $J = 7.4$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ -1.5, 23.1, 54.8, 68.0, 124.3, 128.5, 129.3, 129.8, 131.4, 139.7, 155.8; Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}_3\text{Si}$: C, 61.87; H, 7.99. Found: C, 61.64; H, 8.05.

2-[(Trimethylsilyl)methyl]benzyl trifluoroacetate.

To a CH_2Cl_2 solution (20 mL) of 2-[(trimethylsilyl)methyl]benzyl alcohol (0.010 mol) were added triethylamine (2.0 g, 0.020 mol) and trifluoroacetic anhydride (3.2 g, 0.015 mol) at 0 °C, and the mixture was stirred at room temperature for 3 h before evaporation of the solvent. The residue was treated with hexane and the insoluble material was removed by filtration. Evaporation of the solvent gave 2-[(trimethylsilyl)methyl]benzyl trifluoroacetate (**3**), which was used for the reaction without further purification. Isolated in 95% yield as a pale yellow oil: ^1H NMR (CDCl_3) δ 0.04 (s, 9 H), 2.20 (s, 2 H), 5.35 (s, 2 H), 7.08 (d, $J = 7.6$ Hz, 1 H), 7.14 (td, $J = 7.6, 1.2$ Hz, 1 H), 7.28 (td, $J = 7.6, 1.5$ Hz, 1 H), 7.34 (dd, $J = 7.6, 1.2$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ -1.6, 23.2, 68.0, 114.6 (q, $J_{\text{C-F}} = 285.5$ Hz), 124.6, 129.3, 129.6, 130.3, 140.2,

157.5 (q, $J_{\text{C-F}} = 41.8$ Hz); Anal. Calcd for $\text{C}_{13}\text{H}_{17}\text{F}_3\text{O}_2\text{Si}$: C, 53.78; H, 5.90. Found: C, 53.78; H, 5.94.

Diethyl 2-[(trimethylsilyl)methyl]benzyl phosphate. To a CH_2Cl_2 solution (5 mL) of 2-[(trimethylsilyl)methyl]benzyl alcohol (0.39 g, 2.0 mmol) were added pyridine (0.24 g, 3.0 mmol) and diethyl chlorophosphate (0.52 mg, 3.0 mmol) at 0 °C, and the mixture was stirred at 0 °C for 3 h. After the reaction mixture was washed with water, the resulting organic phase was dried over anhydrous MgSO_4 , filtered, and concentrated in vacuo. Silica gel column chromatography gave diethyl 2-[(trimethylsilyl)methyl]benzyl phosphate (**4**) in 54% yield as a colorless oil: ^1H NMR (CDCl_3) δ -0.01 (s, 9 H), 1.26 (td, $J = 7.5, 1.0$ Hz, 6 H), 2.04 (s, 2 H), 4.00-4.17 (m, 4 H), 5.09 (d, $J = 7.5$ Hz, 2 H), 7.01 (d, $J = 7.7$ Hz, 1 H), 7.09 (td, $J = 7.5, 1.0$ Hz, 1 H), 7.21 (td, $J = 7.5, 1.2$ Hz, 1 H), 7.36 (d, $J = 7.5$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ -1.6, 16.0 (d, $J_{\text{C-P}} = 6.6$ Hz), 22.9, 63.7 (d, $J_{\text{C-P}} = 5.7$ Hz), 67.3 (d, $J_{\text{C-P}} = 5.7$ Hz), 124.3, 128.4, 129.2, 129.2, 132.3 (d, $J_{\text{C-P}} = 7.4$ Hz), 139.3; Anal. Calcd for $\text{C}_{15}\text{H}_{27}\text{O}_4\text{PSi}$: C, 54.52; H, 8.24. Found: C, 54.40; H, 8.22

2,2,2-Trichloroethyl 2-[(trimethylsilyl)methyl]benzyl carbonate. To a CH_2Cl_2 solution (5 mL) of 2-[(trimethylsilyl)methyl]benzyl alcohol (0.39 g, 2.0 mmol) were added pyridine (0.24 g, 3.0 mmol) and 2,2,2-trichloroethyl chloroformate (0.51 g, 2.4 mmol) at 0 °C, and the mixture was stirred at 0 °C for 3 h. After the reaction mixture was washed with sat. NaHCO_3 aq, the resulting organic phase was dried over anhydrous MgSO_4 , filtered, and concentrated in vacuo. Silica gel column chromatography gave 2,2,2-trichloroethyl 2-[(trimethylsilyl)methyl]benzyl carbonate (**5**) in 80% yield as a colorless oil: ^1H NMR (CDCl_3) δ 0.02 (s, 9 H), 2.20 (s, 2 H), 4.78 (s, 2 H), 5.22 (s, 2 H), 7.04 (d, $J = 7.5$ Hz, 1 H), 7.10 (td, $J = 7.5, 1.0$ Hz, 1 H), 7.18-7.32 (m, 1 H), 7.35 (d, $J = 7.7$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ -1.5, 23.2, 69.2, 76.8, 94.4, 124.4, 128.9, 129.4, 130.2, 130.8, 140.1, 154.0; Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{Cl}_3\text{O}_3\text{Si}$: C, 45.48; H, 5.18. Found: C, 45.51; H, 5.16.

Distannylation of *o*-Quinodimethanes. A General Procedure. A THF solution (1.0 mL) of 18-crown-6 (0.16 g, 0.60 mmol), diphenyl-2-pyridylphosphine (2.6 mg, 0.010 mmol) and $\text{Pd}(\text{dba})_2$ (5.8 mg, 0.010 mmol) was degassed by two freeze-thaw cycles. To this solution were added **1** (0.30 mmol), **2** (0.12 g, 0.20 mmol) and KF (0.035 g, 0.60 mmol), and the resulting mixture was stirred at 50 °C. After the time specified in Scheme 2, the mixture was diluted with ethyl acetate, filtered through a Celite plug, and concentrated. Alumina column chromatography (hexane as an eluent, Activity IV)

followed by gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

α,α' -Bis(tributylstannyl)-*o*-xylene (3a). Isolated in 55% yield as a pale yellow oil: ^1H NMR (CDCl_3) δ 0.65-1.04 (m, 30 H), 1.16-1.59 (m, 24 H), 2.14 (s, 4 H), 6.73-6.97 (m, 4 H); ^{13}C NMR (CDCl_3) δ 9.7, 13.7, 16.8, 27.4, 29.1, 123.2, 127.4, 138.7; ^{119}Sn NMR (CDCl_3) δ -12.4. Anal. Calcd for $\text{C}_{32}\text{H}_{62}\text{Sn}_2$: C, 56.17; H, 9.13. Found: C, 56.21; H, 9.13.

1,2-Bis[(tributylstannyl)methyl]naphthalene (3b). Isolated in 63% yield as a pale yellow oil: ^1H NMR (CDCl_3) δ 0.50-0.99 (m, 30 H), 1.02-1.61 (m, 24 H), 2.37 (s, 2 H), 2.60 (s, 2 H), 7.11 (d, $J = 8.3$ Hz, 1 H), 7.23-7.47 (m, 3 H), 7.72 (d, $J = 7.6$ Hz, 1 H), 7.85 (d, $J = 8.6$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 9.9, 10.3, 13.0, 13.6, 18.4, 27.4, 29.1, 29.1, 123.1, 123.3, 124.9, 127.8, 128.5, 131.4, 132.5, 135.4; ^{119}Sn NMR (CDCl_3) δ -10.4, -7.1; Anal. Calcd for $\text{C}_{36}\text{H}_{64}\text{Sn}_2$: C, 58.88; H, 8.78. Found: C, 58.70; H, 8.80.

α,α' -Bis(tributylstannyl)-3-phenyl-*o*-xylene (3c). Isolated in 59% yield as a pale yellow oil: ^1H NMR (CDCl_3) δ 0.48-0.68 (m, 6 H), 0.72-0.98 (m, 24 H), 1.08-1.56 (m, 24 H), 2.18 (s, 2 H), 2.21 (s, 2 H), 6.76 (dd, $J = 7.1, 1.6$ Hz, 1 H), 6.81-6.78 (m, 2 H), 7.16-7.33 (m, 2 H), 7.38 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR (CDCl_3) δ 9.9, 10.2, 13.6, 13.7, 14.6, 18.0, 27.3, 27.5, 28.9, 29.1, 122.6, 125.1, 126.3, 126.5, 128.0, 129.4, 136.5, 139.4, 139.7, 143.8; ^{119}Sn NMR (CDCl_3) δ -13.3, -13.1; Anal. Calcd for $\text{C}_{38}\text{H}_{66}\text{Sn}_2$: C, 60.03; H, 8.75. Found: C, 60.07; H, 8.53.

α,α' -Bis(tributylstannyl)-3-methyl-*o*-xylene (3d). Isolated in 62% yield as a pale yellow oil: ^1H NMR (CDCl_3) δ 0.66-1.06 (m, 30 H), 1.14-1.60 (m, 24 H), 2.12 (s, 2 H), 2.14-2.27 (m, 5 H), 6.69-6.85 (m, 3 H); ^{13}C NMR (CDCl_3) δ 9.7, 10.3, 13.7, 13.9, 17.5, 21.2, 27.4, 29.1, 122.7, 125.0, 125.3, 133.1, 137.2, 138.6; ^{119}Sn NMR (CDCl_3) δ -13.5, -13.0; Anal. Calcd for $\text{C}_{33}\text{H}_{64}\text{Sn}_2$: C, 56.76; H, 9.24. Found: C, 56.70; H, 9.15.

α,α' -Bis(tributylstannyl)-4-methyl-*o*-xylene (3e). Isolated in 59% yield as a pale yellow oil: ^1H NMR (CDCl_3) δ 0.57-1.02

(m, 30 H), 1.14-1.59 (m, 24 H), 2.11 (s, 4 H), 2.20 (s, 3 H), 6.64 (d, $J = 7.6$ Hz, 1 H), 6.70 (s, 1 H), 6.77 (d, $J = 7.6$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 9.7, 9.7, 13.7, 16.1, 16.7, 20.9, 27.4, 29.1, 124.0, 127.4, 128.2, 132.3, 135.4, 138.5; ^{119}Sn NMR (CDCl_3) δ -13.6, -12.9; Anal. Calcd for $\text{C}_{33}\text{H}_{64}\text{Sn}_2$: C, 56.76; H, 9.24. Found: C, 56.70; H, 9.28.

α,α' -Bis(tributylstannyl)-3,5-dimethyl-*o*-xylene (3f).

Isolated in 53% yield as a pale yellow oil: ^1H NMR (CDCl_3) δ 0.66-1.04 (m, 30 H), 1.16-1.54 (m, 24 H), 2.07 (s, 2 H), 2.10-2.23 (m, 8 H), 6.57 (s, 1 H), 6.59 (s, 1 H); ^{13}C NMR (CDCl_3) δ 9.7, 10.3, 13.4, 13.6, 13.7, 17.4, 20.8, 21.1, 27.4, 29.1, 125.9, 125.0, 126.1, 131.6, 132.9, 138.4; ^{119}Sn NMR (CDCl_3) δ -14.1; Anal. Calcd for $\text{C}_{34}\text{H}_{66}\text{Sn}_2$: C, 57.33; H, 9.34. Found: C, 57.54; H, 9.50.

α,α' -Bis(tributylstannyl)-4-fluoro-*o*-xylene (3g).

Isolated in 50% yield as a pale yellow oil: ^1H NMR (CDCl_3) δ 0.67-0.96 (m, 30 H), 1.07-1.56 (m, 24 H), 2.08 (s, 2 H), 2.12 (s, 2 H), 6.53 (td, $J = 8.4, 2.7$ Hz, 1 H), 6.60 (dd, $J = 10.4, 2.7$ Hz, 1 H), 6.80 (dd, $J = 8.4, 6.0$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 9.7, 9.8, 13.6, 15.8, 17.4, 27.4, 29.0, 29.2, 109.8 (d, $J_{\text{C-F}} = 20.8$ Hz), 113.3 (d, $J_{\text{C-F}} = 20.7$ Hz), 128.2 (d, $J_{\text{C-F}} = 8.6$ Hz), 134.2, 141.0 (d, $J_{\text{C-F}} = 7.3$ Hz), 159.8 (d, $J_{\text{C-F}} = 239.2$ Hz); ^{119}Sn NMR (CDCl_3) δ -12.8 (d, $J_{\text{Sn-F}} = 21.6$ Hz), -10.6 (d, $J_{\text{Sn-F}} = 10.8$ Hz); Anal. Calcd for $\text{C}_{32}\text{H}_{61}\text{FSn}_2$: C, 54.73; H, 8.76. Found: C, 54.71; H, 8.72.

α,α' -Bis(tributylstannyl)- α -methyl-*o*-xylene (3h).

Isolated in 63% yield as a pale yellow oil: ^1H NMR (CDCl_3) δ 0.50-1.05 (m, 30 H), 1.05-1.80 (m, 24 H), 2.11 (s, 1 H), 2.15 (s, 2 H), 2.16 (s, 3 H), 6.73-6.76 (m, 4 H); ^{13}C NMR (CDCl_3) δ 9.1, 9.5, 13.7, 13.7, 16.8, 17.5, 23.5, 27.4, 27.5, 29.1, 29.1, 123.0, 123.5, 123.9, 127.4, 138.1, 143.9; ^{119}Sn NMR (CDCl_3) δ -14.4, -6.6; Anal. Calcd for $\text{C}_{33}\text{H}_{64}\text{Sn}_2$: C, 56.76; H, 9.24. Found: C, 56.64; H, 9.08.

Iododestannylation of 3a. To a CH_2Cl_2 solution (1 mL) of **3a** (0.023 g, 0.034 mmol) was added iodine (0.018 g, 0.071 mmol), and the mixture was stirred at r.t. for 1.5 h before evaporation of the solvent. Silica gel column chromatography (hexane as an eluent) gave **7** (5.2 mg, 43% yield)⁴ as a pale yellow solid:

^1H NMR (CDCl_3) δ 4.58 (s, 4 H), 7.16-7.35 (m, 4 H); ^{13}C NMR (CDCl_3) δ 1.7, 129.0, 130.8, 137.4.

Synthesis of 8. Meldrum's acid (0.014 g, 0.095 mmol) was added to a suspension of NaH (4.2 mg, 0.095 mmol, 55% dispersion in mineral oil) in DMSO (0.2 mL), and the mixture was stirred at r.t. for 0.5 h. To this mixture was added a DMSO solution (1 mL) of crude **7**, prepared as above [from **3a** (0.030 g, 0.043 mmol) and I₂ (0.023 g, 0.091 mmol)], and the resulting mixture was stirred at 50 °C for 13 h. The mixture was poured into 0.04 M aqueous HCl (25 mL) and extracted with chloroform (3 times). The combined extracts were washed with H₂O, dried over MgSO₄ and concentrated. Gel permeation chromatography gave **8** (2.9 mg, 27% yield based on **3a**)⁵ as a white solid: ¹H NMR (CDCl₃) δ 1.83 (s, 6 H), 3.74 (s, 4 H), 7.23 (brs, 4 H); ¹³C NMR (CDCl₃) δ 29.0, 45.6, 52.4, 105.2, 124.0, 127.6, 138.8, 170.5.

Synthesis of 9. Diethyl malonate (0.021 g, 0.13 mmol) was added to a suspension of NaH (5.7 mg, 0.13 mmol, 55% dispersion in mineral oil) in DMSO (0.4 mL), and the mixture was stirred at r.t. for 0.5 h. To this mixture was added a DMSO solution (1 mL) of crude **7**, prepared as above [from **3a** (0.036 g, 0.052 mmol) and I₂ (0.028 g, 0.11 mmol)], and the resulting mixture was stirred at r.t. for 19 h. The mixture was poured into 0.04 M aqueous HCl (25 mL) and extracted with ether (3 times). The combined extracts were washed with H₂O, dried over MgSO₄ and concentrated. Gel permeation chromatography gave **9** (3.2 mg, 15% yield based on **3a**)⁶ as a pale yellow oil: ¹H NMR (CDCl₃) δ 1.20 (t, *J* = 7.3 Hz, 12 H), 3.28 (d, *J* = 7.6 Hz, 4 H), 3.69 (t, *J* = 7.6 Hz, 2 H), 4.15 (q, *J* = 7.3 Hz, 8 H), 7.14 (s, 4 H); ¹³C NMR (CDCl₃) δ 13.9, 31.1, 52.9, 61.5, 127.0, 129.6, 136.1, 168.9.

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- (2) (a) Lan, A. J. Y.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 2738. (b) Lenihan, B. D.; Shechter, H. *J. Org. Chem.* **1998**, *63*, 2072.
- (3) (a) Minami, I.; Tsuji, J. *Tetrahedron* **1987**, *43*, 3903. (b) Oppolzer, W.; Robyr, C. *Tetrahedron* **1994**, *50*, 415.
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031016-15-1-recycle, 4

Date : Thu Oct 16 14:59:31 2003

File Name : LoadingFID.nmdata
 Comment : 031016-15-1-recycle, 4
 SliceHistory :
 EXMODE : non

POINT : 32768 points
 SAMP0 : 32768 points
 FREQ : 7917.7 Hz
 FILTR : 3950 Hz
 DELAY : 50.6 usec
 DEADT : 73.2 usec
 INTVL : 126.3 usec
 TIMES : 8 times
 DUMMY : 2 times
 PD : 2.8614 sec
 ACQTM : 4138.5986 msec
 PREDL : 0.01000 msec
 INTWT : 1000.0000 msec
 RESOL : 0.24 Hz
 PW1 : 5.50 usec
 1H : 395.75 MHz
 OBFRQ : 134498.00 Hz
 OBSET : 13
 RGAIN : 8 times
 SCANS : 8 times
 SLVNT : CDCL3
 SPINNING : 16 Hz
 TEMP : 23.7 C

1H Line

Date : Tue Jan 17 01:41:37 2006

FileName : .LoadingFID.nmdata
 Comment : 1H Line
 SliceHistory :
 EXMODE : bcm
 POINT : 32768 points
 SAMPO : 32768 points
 FREQU : 26881.7 Hz
 FILTR : 13450 Hz
 DELAY : 14.9 usec
 DEADT : 19.1 usec
 INTVL : 37.2 usec
 TIMES : 20000 times
 DUMMY : 1 times
 PD : 1.7810 sec
 ACQTM : 1218.9696 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.82 Hz
 PW1 : 6.50 usec
 13C :
 OBNUC : 99.45 MHz
 OBFRQ : 104750.00 Hz
 OBSET : 28
 1H :
 IRNUC : 395.75 MHz
 IRFRO : 134498.00 Hz
 IRSET : 45.0 usec
 IRRPW : 0
 IRRNS :
 SCANS : 370 times
 SLVNT : CDCL3
 SPINNING : 8 Hz
 TEMP : 19.3 C

05-FEB-04 21:06:33

205-17-4-RECYCLE

1.000
0.996
0.874
0.850
1.024

4.156

24.215

31.489

PPM

7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9

8 7 6 5 4 3 2 1 0
PPM

3b

DFILE JJJ
OBNUC 1H
EXMOD NON
OFR 270.05 MHZ
OBSET 112.00 KHZ
OBFIN 5800.0 HZ
POINT 32768
FREQU 5405.4 HZ
SCANS 16
ACQTM 3.031 sec
PD 3.969 sec
PW1 5.2 us
IRNUC 1H
CTEMP 18.5 C
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.16 HZ
RGAIN 11
OPERATOR :

OFFILE	JJJJ
ORNUC	13C
EXMOD	BCM

QFR	67.80 MHz
OBSET	135.00 kHz
OBFIN	5200.0 Hz
POINT	32768
FREQU	20000.0 Hz
SCANS	11996
ACQTM	0.819 sec
PD	2.181 sec
PW1	3.8 us
IRNUC 1H	
CTEMP	0.0 c
SLVNT CDCL3	
EXREF	77.00 ppm
BF	1.22.Hz
RGAIN	24
OPERATOR :

३६

ԵՐԵՎԱՆԻ ՄԱՐԶԻ
 ԵՐԵՎԱՆԻ ՄԱՐԶԻ
 ԵՐԵՎԱՆԻ ՄԱՐԶԻ

031211-16-5-recycle, 3

Date : Thu Dec 11 17:35:20 2003

FileName : loadingfid.nmdata
 Comment : 031211-16-5-recycle, 3
 SliceHistory :
 EXMODE : non

POINT 32768 points
 SAMPO 32768 points
 FREQU 7917.7 Hz
 FILTR 3950 Hz
 DELAY 50.6 usec
 DEADT 73.2 usec
 INTVL 126.3 usec
 TIMES 16 times
 DUMMY 4 times
 PD 2.8614 sec
 ACQTM 4138.5986 msec
 PREDL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 0.24 Hz
 PW1 5.50 usec
 1H
 OBNUC 395.75 MHz
 OBFRQ 134498.00 Hz
 OBSET 12
 RGAIN 16 times
 SCANS :
 SLVNT : CDCL3
 SPINNING 11 Hz
 TEMP 21.3 C

031211-16-5-recycle.3

Date : Thu Dec 11 17:58:45 2003

File Name : .LoadingFID.nmdata
Comment : 031211-16-5-recycle.3
Slice History :
EXMODE : bcmPOINT : 32768 points
SAMP0 : 32768 points
FREQU : 26881.7 Hz
FILTR : 13450 Hz
DELAY : 14.9 usec
DEADT : 19.7 usec
INTVL : 37.2 usec
TIMES : 15000 times
DUMMY : 1 times
PD : 1.7810 sec
ACQTM : 1218.9696 msec
PREDL : 0.01000 msec
INIWT : 1000.0000 msec
RESOL : 0.82 Hz
PW1 : 5.25 usec
OBNUC : ¹³C
OBFRQ : 99.45 MHz
OBSET : 104750.00 Hz
RGAIN : 29
IRNUC : ¹H
IRFRQ : 395.75 MHz
IRSET : 134498.00 Hz
IRPW : 75.0 usec
IRNS : 0
SCANS : 102 times
SLVNT : CDCL₃
SPINNING : 11 Hz
TEMP : 22.3 C

031222-16-9-afterrecycle

Date : Mon Dec 22 16:14:25 2003

FileName : LoadingFID.nmdata
 Comment : 031222-16-9-afterrecycle
 SliceHistory :
 EXMODE : non

POINT 32768 points
 SAMPO 32768 points
 FREQU 7917.7 Hz
 FILTR 3950 Hz
 DELAY 50.6 usec
 DEADT 73.2 usec
 INTVL 126.3 usec
 TIMES 16 times
 DUMMY 4 times
 PD 2.8614 sec
 ACQTM 4138.5986 msec
 PREDL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 0.24 Hz
 PW1 5.50 usec
 OBNJC 1H
 OBFRQ 395.75 MHz
 OBSET 134498.00 Hz
 RGAIN 12

SCANS : 16 times

SLVNT : CDCL3
 SPINNING 12 Hz
 TEMP 18.7 C

Chemical structure: Cc1ccc(cc1)C(Sn(C)(C)C)C(Sn(C)(C)C) **3d**

031222-16-9-afterrecycle

Date : Mon Dec 22 16:45:45 2003

FileName : .LoadingFID.nmdata
Comment : 031222-16-9-afterrecycle
SliceHistory :
EXMODE : bcm

POINT : 32768 points
SAMP0 : 32768 points
FREQ0 : 26881.7 Hz
FILTR : 13450 Hz
DELAY : 14.9 usec
DEADT : 19.7 usec
INTVL : 37.2 usec
TIMES : 1000 times
DUMMY : 1 times
PD : 1.7810 sec
ACQTM : 1218.9696 msec
PREDL : 0.01000 msec
INIWT : 1000.0000 msec
RESOL : 0.82 Hz
PW1 : 5.25 usec
OBNUC : ¹³C
OBFRQ : 99.45 MHz
OBSET : 104750.00 Hz
RGAIN : 28
IRNUC : ¹H
IRFRQ : 395.75 MHz
IRSET : 134498.00 Hz
IRRPW : 75.0 usec
IRRNS : 0
SCANS : 445 times
SLVNT : CDCl₃
SPINNING : 13 Hz
TEMP : 20.1 C

40208-17-5-RECYCLE

OBNUC 1H

EXMOD NON

OFR 270.05 MHz

112.00 KHZ

001380 170300
5800 0 H3
111:00 H12

00TINT 7CZEO
JUNO V HZ

POINT 32/08
E 405 4 11

FREQ(HZ) 5405.4 HZ

SCANS
16

ACQTM 3.031 sec

04 3.969 sec

PW1 5.2 us

IR (KBr) 1710 (C=O), 1600 (C=C), 1510 (C=C), 1450 (C=C), 1380 (C=C), 1280 (C=C), 1180 (C=C), 1100 (C=C), 1050 (C=C), 1000 (C=C), 950 (C=C), 900 (C=C), 850 (C=C), 800 (C=C), 750 (C=C), 700 (C=C), 650 (C=C), 600 (C=C), 550 (C=C), 500 (C=C), 450 (C=C), 400 (C=C), 350 (C=C), 300 (C=C), 250 (C=C), 200 (C=C), 150 (C=C), 100 (C=C), 50 (C=C), 0 (C=C).

CTEMP 18.0 C

91 VNT C001 3

EXFEE 7 36 00M

0.15 Hz

0.10 Hz

AGAIN 12

OPERATION :

7.260

DFILE JJJ

OBNUC 13C

EXMOD BCM

QFR

OBSET

OBFIN

POINT

FREQU

SCANS

ACQTM

PD

PW1

IRNUC 1H

CTEMP

SLVNT CDCL3

EXREF

BF

RGAIN 24

OPERATOR :

67.80 MHz

135.00 KHZ

5200.0 HZ

32768

20000.0 HZ

4022

0.819 sec

2.181 sec

3.8 us

0.0 C

77.00 ppm

1.22 HZ

040208-17-5-RECYCLE

031202-15-31-recycle

Date : Tue Dec 2 13:14:43 2003
 FileName : LoadingFID.nmdata
 Comment : 031202-15-31-recycle
 SliceHistory :
 EXMODE : non

POINT : 32768 points
 SAMPO : 32768 points
 FREQU : 7917.7 Hz
 FILTR : 3950 Hz
 DELAY : 50.6 usec
 DEATH : 73.2 usec
 INTVL : 126.3 usec
 TIMES : 4 times
 DUMMY : 1 times
 PD : 2 8614 sec
 ACQTM : 4138.5986 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.24 Hz
 PW1 : 5.50 usec
 1H :
 OBNUC : 395.75 MHz
 OBFRQ : 134498.00 Hz
 OBSET : 12
 RGAIN : 12
 SCANS : : 4 times
 SLVNT : CDCL3
 SPINNING : 12 Hz
 TEMP : 23.3 C

031202-15-31-recycle

Date : Tue Dec 2 13:53:07 2003

File Name : .LoadingFID.nmdata
 Comment : 031202-15-31-recycle
 Slice History :
 EXMODE : bcm

POINT : 32768 points
 SAMPO : 32768 points
 FREQ : 26881.7 Hz
 FILTR : 13450 Hz
 DELAY : 14.9 usec
 DEADT : 19.7 usec
 INTVL : 37.2 usec
 TIMES : 5000 times
 DUMMY : 1 times
 PD : 1.7810 sec
 ACQTM : 1218.9696 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.82 Hz
 PW1 : 5.25 usec
 13C : 99.45 MHz
 OBFRQ : 104750.00 Hz
 OBSET : 29
 RGAIN :
 1H : 395.75 MHz
 IRFRQ : 134498.00 Hz
 IRSET : 75.0 usec
 IRRPW : 0
 IRFNS :
 SCANS : 751 times
 SLVNT : CDCL3
 SPINNING : 12 Hz
 TEMP : 24.6 C

040202-16-12-recycle

Date : Mon Feb 2 13:31:52 2004

FileName : LoadingFID.nmdata
 Comment : 040202-16-12-recycle
 SliceHistory :
 EXMODE : non

POINT : 32768 points
 SAMPO : 32768 points
 FREQU : 7917.7 Hz
 FILTR : 3950 Hz
 DELAY : 50.6 usec
 DEATH : 73.2 usec
 INTVL : 126.3 usec
 TIMES : 16 times
 DUMMY : 1 times
 PD : 2.8614 sec
 ACQTM : 4138.5986 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.24 Hz
 PW1 : 5.50 usec
 1H : 395.75 MHz
 OBFRQ : 134498.00 Hz
 OBSET : 17
 RGAIN :
 SCANS : 16 times
 SLVNT : CDCL3
 SPINNING : 0 Hz
 TEMP : 19.4 C

202-16-12-RECYCLE

3g

EXPANSION OF THE ALIPHATIC REGION OF THE 13C NMR SPECTRUM OF 3g. THE PEAKS CORRESPOND TO THE BUTYL CHAINS OF THE DIALLYL DIBUTYL STANNANE DERIVATIVE.

DFILE JJJ
OBNUC 13C
EXMOD BCM
OFR 67.80 MHz
OBSET 135.00 KHZ
OBFIN 5200.0 HZ
POINT 32768
FREQU 20000.0 HZ
SCANS 12831
ACQTM 0.819 sec
PD 2.181 sec
PW1 3.8 us
IRNUC 1H
CTEMP 0.0°C
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.22 HZ
HGA IN 24
OPERATOR :

Date :	Mon May 23 04:22:24 2005
FileName	: .LoadingFID.nmdata
Comment	: 1H Line
SliceHistory	:
EXMODE	: non
POINT	: 32768 points
SSAMPO	: 32768 points
FREQU	: 7917.7 Hz
FILTR	: 3950 Hz
OELAY	: 50.6 usec
DEADT	: 73.4 usec
INTVL	: 126.3 usec
TIMES	: 16 times
TDUMY	: 1 times
POPO	: 2.8614 sec
ACGTM	: 4138.5986 msec
PPREDL	: 0.01000 msec
INTIWT	: 1000.0000 msec
RESOL	: 0.24 Hz
PW1	: 5.05 usec
ORNUC	: 1H
OBFRQ	: 395.75 MHz
DBSET	: 134498.00 Hz
RGAIN	: 17
SSCANS	: ; 16 times
SELVNT	: COCL3
SPINNING	: 14 Hz
TEMP	: 20.9 C

```

: .LoadingFID.nmdata
: 1H Line
:
: SliceHistory
: EXMODE
: non

```

POINT	:	32768	points
SSAMPO	:	32768	points
FFREQU	:	7917.7	Hz
FILTR	:	3950	Hz
ODELAY	:	50.6	usec
DEADT	:	73.4	usec
INTVL	:	126.3	usec
TIMES	:	15	times
DUMMY	:	1	times
PO	:	2	8614 sec
ACOTM	:	4138.5986	msec
PREDL	:	0.01000	msec
INIWT	:	1000.0000	msec
RESOL	:	0.24	Hz
PW1	:	5.05	usec
OBNUC	:	1H	
OBFRQ	:	395.75	MHz
OBSET	:	134498.00	Hz
RGAIN	:	17	

SCANS : 16 times

```

SLVNT      : COCL3
SPINNING   : 14 HZ
TEMP       : 20.9 C

```

[illegible]

21-54-1

21-48-GPC

21-50-GPC-RE