Supporting Information

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Bisstannylation of Strained Carbon–Carbon Triple Bonds Catalyzed by a Palladium Complex

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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 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz) spectrometer or a JEOL Lambda-400 (^{1}H, 400 MHz; ^{13}C, 99.5 MHz; ^{119}Sn, 147.5 MHz) spectrometer using residual chloroform (^{1}H) 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 (benzene 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. 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.

Aryne Precursors. 2-(Trimethylsilyl)phenyl triflate (**2a**),[1] 4-methyl-2-(trimethylsilyl)phenyl triflate (**2b**),[2] 4-methoxy-2-(trimethylsilyl)phenyl triflate (**2c**),[3] 4-phenyl-2-(trimethylsilyl)phenyl triflate (**2d**),[3] 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**2f**),[4] 6-(trimethylsilyl)-5-indanyl triflate (**2g**),[4] 6-methyl-2-(trimethylsilyl)phenyl triflate (**2h**),[3] 3-methoxy-2-(trimethylsilyl)phenyl triflate (**2i**),[5] 3,6-dimethoxy-2-(trimethylsilyl)phenyl triflate (**2j**),[4] 1-(trimethylsilyl)-2-naphthyl triflate (**2k**),[6] 6-phenyl-2-(trimethylsilyl)phenyl triflate (**2l**)[7] and 10-(trimethylsilyl)-9-phenanthryl triflate (**2m**)[6] were prepared according to literature procedures. 4-Fluoro-2-(trimethylsilyl)phenyl triflate (**2e**) was prepared from 2-bromo-4-fluorophenol (WAKO Chemical) in a similar manner as reported.[8]

Bisaryne Precursors. 3,3'-bis(trimethylsilyl)-4,4'-bis(trifluoromethanesulfonate)diphenyl ether (**2n**) was synthesized from 3,3'-dibromo-4,4'-dihydroxydiphenyl ether[9] similarly to the preparation of **2a**.

Cyclohexyne Precursors. All cyclohexyne precursors (**2o**–**2q**) were synthesized from 2-halogenated-1-(trimethylsiloxy)cyclohexenes (Cl for **2o**; Br for **2p**

and **2q**),[10] derived from 2-chlorocyclohexanone,[11] 2-bromo-4-methylcyclohexanone[12] or 2-bromotetralone,[13] respectively, in a similar manner as the preparation of **2a**.

Bisstannylation of Arynes or Cyclohexynes. ***A General Procedure.*** To a THF solution (1.0 mL) of 1,1,3,3-tetramethylbutyl isocyanide (9.2 mg, 0.066 mmol), $Pd(OAc)_2$ (1.0 mg, 4.4 mmol), KF (0.038 g, 0.66 mmol) and 18-crown-6 (0.17 g, 0.66 mmol) were added **1** (0.22 mmol) and a precursor (0.33 mmol), and the resulting mixture was stirred at 20 ℃. After the time specified in Table 1 or 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 (benzene as an eluent) gave the corresponding product.

1,2-Bis(tributylstannyl)benzene (3aa). Isolated in 73% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.1 Hz, 18 H), 1.01-1.07 (m, 12 H), 1.27-1.53 (m, 24 H), 7.19-7.22 (m, 2 H), 7.42-7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 13.6, 27.5, 29.2, 127.1, 137.5, 151.9; ^{119}Sn NMR ($CDCl_3$) δ -43.2; Anal. Calcd for $C_{30}H_{58}Sn_2$: C, 54.91; H, 8.91. Found: C, 55.18; H, 8.97.

3,4-Bis(tributylstannyl)toluene (3ab). Isolated in 71% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.85-1.07 (m, 30 H), 1.29-1.53 (m, 24 H), 2.30 (s, 3 H), 7.03-7.05 (m, 2 H), 7.32-7.35 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 13.6, 21.4, 27.5, 29.2, 128.0, 136.3 137.4, 147.6, 151.6; ^{119}Sn NMR ($CDCl_3$) δ -43.8, -42.6; Anal. Calcd for $C_{31}H_{60}Sn_2$: C, 55.55; H, 9.02. Found: C, 55.62; H, 9.00.

3,4-Bis(tributylstannyl)anisole (3ac). Isolated in 55% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.87-1.09 (m, 30 H), 1.30-1.55 (m, 24 H), 3.80 (s, 3 H), 6.78 (dd, *J* = 8.1, 2.8 Hz, 1 H), 7.07 (d, *J* = 2.8 Hz, 1 H), 7.38 (d, *J* = 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 13.7, 27.4, 27.5, 29.1, 54.7, 111.9, 124.0, 138.2, 141.5, 153.1, 158.3; ^{119}Sn NMR ($CDCl_3$) δ -40.7, -40.0; Anal. Calcd for $C_{31}H_{60}OSn_2$: C, 54.26; H, 8.81. Found: C, 54.51; H, 8.79.

3,4-Bis(tributylstannyl)biphenyl (3ad). Isolated in 40% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.89-0.95 (m, 18 H), 1.08-1.15 (m, 12 H), 1.31-1.59 (m, 24 H), 7.35-7.70 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 10.93, 10.96, 13.7, 27.49, 27.50, 29.2, 125.7 127.06, 127.10, 128.7, 136.0, 137.7, 139.3, 141.5, 150.7, 152.3; ^{119}Sn NMR ($CDCl_3$) δ -41.7, -41.1; Anal. Calcd for $C_{36}H_{62}Sn_2$: C, 59.05; H, 8.53. Found: C, 59.13; H, 8.50.

1-Fluoro-3,4-bis(tributylstannyl)benzene (3ae). Isolated in 26% yield as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 0.85-1.15 (m, 30 H), 1.26-1.54 (m, 24 H), 6.87-6.95 (m, 1 H), 7.16-7.25 (m, 1 H), 7.40-7.42 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 11.0, 13.6, 27.4, 29.0, 29.1, 113.9 (d, $J_{C\text{-}F}$ = 18.3 Hz), 123.8 (d, $J_{C\text{-}F}$ = 13.5 Hz), 138.4, 146.3, 154.6, 162.3 (d, $J_{C\text{-}F}$ = 251.5 Hz); ^{119}Sn NMR (CDCl$_3$) δ -39.2 (d, $J_{Sn\text{-}F}$ = 13.5 Hz), -38.6 (d, $J_{Sn\text{-}F}$ = 21.6 Hz); Anal. Calcd for $C_{30}H_{57}FSn_2$: C, 53.44; H, 8,52. Found: C, 53.73; H, 8.45.

1,2-Dimethyl-4,5-Bis(tributylstannyl)benzene (3af). Isolated in 73% yield as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 0.86-1.06 (m, 30 H), 1.29-1.54 (m, 24 H), 2.22 (s, 6 H), 7.20 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ 10.9, 13.6, 19.5, 27.5, 29.2, 135.3, 139.1, 148.3; ^{119}Sn NMR (CDCl$_3$) δ -44.1; Anal. Calcd for $C_{32}H_{62}Sn_2$: C, 56.17; H, 9.13. Found: C, 56.14; H, 9.17.

5,6-Bis(tributylstannyl)indan (3ag). Isolated in 64% yield as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 0.86-1.06 (m, 30 H), 1.29-1.53 (m, 24 H), 2.02 (quintet, J = 7.5 Hz, 2 H), 2.89 (t, J = 7.5 Hz, 4 H), 7.35 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ 11.1, 13.6, 24.8, 27.5, 29.2, 32.9, 133.8, 143.2, 148.3; ^{119}Sn NMR (CDCl$_3$) δ -42.1; Anal. Calcd for $C_{33}H_{62}Sn_2$: C, 56.93; H, 8.98. Found: C, 56.90; H, 9.00.

2,3-Bis(tributylstannyl)toluene (3ah). Isolated in 55% yield as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 0.86-1.09 (m, 30 H), 1.27-1.54 (m, 24 H), 2.43 (s, 3 H), 7.09-7.26 (m, 3 H); ^{13}C NMR (CDCl$_3$) δ 12.2, 12.4, 13.6, 26.2, 27.0, 27.5, 29.0, 29.1, 29.2, 127.0, 129.0, 134.8, 145.2, 152.4, 152.5; ^{119}Sn NMR (CDCl$_3$) δ -52.8, -41.2; Anal. Calcd for $C_{31}H_{60}Sn_2$: C, 55.55; H, 9.02. Found: C, 55.75; H, 9.12.

2,3-Bis(tributylstannyl)anisole (3ai). Isolated in 59% yield as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 0.85-1.07 (m, 30 H), 1.25-1.53 (m, 24 H), 3.74 (s, 3 H), 6.71-6.74 (m, 1 H), 7.04-7.08 (m, 1 H), 7.19-7.21 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 11.5, 11.7, 13.6, 13.7, 27.5, 29.2, 29.3, 29.4, 54.9, 108.6, 128.3, 130.4, 140.7, 152.6, 163.1; ^{119}Sn NMR (CDCl$_3$) δ -51.6, -41.6; Anal. Calcd for $C_{31}H_{60}OSn_2$: C, 54.26; H, 8.81. Found: C, 54.17; H, 8.81.

1,4-Dimethoxy-2,3-bis(tributylstannyl)benzene (3aj). Isolated in 63% yield as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 0.85-1.03 (m, 30 H), 1.27-1.55 (m, 24 H), 3.70 (s, 6 H), 6.68 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ 12.5, 13.7, 27.5, 29.3, 55.4, 108.7, 142.3 158.3; ^{119}Sn NMR (CDCl$_3$) δ -52.0; Anal. Calcd for $C_{32}H_{62}O_2Sn_2$: C, 53.66; H, 8.72. Found: C, 53.66; H, 8.75.

1,2-Bis(trimethylstannyl)benzene (3ba).[14] Isolated in 56% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 18 H), 7.25-7.28 (m, 2 H), 7.50-7.54 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -7.1, 127.6, 136.9, 151.9; ^{119}Sn NMR ($CDCl_3$) δ -32.6.

1,2-Bis(trimethylstannyl)naphthalene (3bk). Isolated in 61% yield as a white solid: mp 39.8-41.2 ℃; ^{1}H NMR ($CDCl_3$) δ 0.43 (s, 9 H), 0.52 (s, 9 H), 7.47-7.97 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ -5.5, -4.3, 125.4, 125.5, 127.2, 128.9, 129.9, 133.1, 133.2, 139.0, 152.0, 153.9; ^{119}Sn NMR ($CDCl_3$) δ -46.3, -31.6; Anal. Calcd for $C_{16}H_{24}Sn_2$: C, 42.35; H, 5.33. Found: C, 42.29; H, 5.21.

2,3-Bis(trimethylstannyl)biphenyl (3bl). Isolated in 39% yield as a white solid: mp 107.4-110.2 ℃; ^{1}H NMR ($CDCl_3$) δ -0.03 (s, 9 H), 0.41 (s, 9 H), 7.32-7.57 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ -5.6, -4.7, 127.1, 127.2, 128.4, 129.0, 129.4, 135.9, 146.2, 151.2, 151.8, 153.8; ^{119}Sn NMR ($CDCl_3$) δ -40.6, -30.7; Anal. Calcd for $C_{18}H_{26}Sn_2$: C, 45.08; H, 5.46. Found: C, 45.21; H, 5.52.

9,10-Bis(trimethylstannyl)phenanthrene (3bm). Isolated in 27% yield as a white solid: mp 72.8-74.5 ℃; ^{1}H NMR ($CDCl_3$) δ 0.47 (s, 18 H), 7.56-7.62 (m, 4 H), 7.83-7.90 (m, 2 H), 8.66-8.69 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -5.5, 123.2, 126.0, 126.1, 129.9, 130.7, 136.4, 156.6; ^{119}Sn NMR ($CDCl_3$) δ -41.6; Anal. Calcd for $C_{20}H_{26}Sn_2$: C, 47.68; H, 5.20. Found: C, 47.51; H, 5.44.

1,2-Bis(tributylstannyl)cyclohexene (3ao). Isolated in 70% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.85-0.93 (m, 30 H), 1.26-1.59 (m, 28 H), 2.23 (brs, 4 H); ^{13}C NMR ($CDCl_3$) δ 10.6, 13.7, 24.0, 27.6, 29.3, 36.8, 153.2; ^{119}Sn NMR ($CDCl_3$) δ -66.9; Anal. Calcd for $C_{30}H_{62}Sn_2$: C, 54.57; H, 9.47. Found: C, 54.70; H, 9.50.

1,2-Bis(trimethylstannyl)-4-methylcyclohexene (3bp). Isolated in 60% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 18 H), 0.89 (d, , $J = 6.5$ Hz, 3 H), 1.13-1.55 (m, 1 H), 1.63-1.66 (m, 2 H), 1.85-1.92 (m, 1 H), 2.28-2.32 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ -7.6, -7.5, 22.2, 29.2, 31.8, 36.5, 44.7, 152.6, 152.7; ^{119}Sn NMR ($CDCl_3$) δ -58.9, -57.6; Anal. Calcd for $C_{13}H_{28}Sn_2$: C, 37.02; H, 6.69. Found: C, 37.30; H, 6.79.

1,2-Bis(trimethylstannyl)-3,4-dihydronaphthalene (3bq). Isolated in 90% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.27 (s, 9 H), 0.30 (s, 9 H), 2.29-

2.35 (m, 2 H), 2.58-2.63 (m, 2 H), 6.95-7.20 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -7.0, -5.3, 28.5, 33.4, 126.0, 127.1, 127.2, 127.3, 136.3, 138.7, 153.8, 160.0; ^{119}Sn NMR ($CDCl_3$) δ -50.3, -47.3; Anal. Calcd for $C_{16}H_{26}Sn_2$: C, 42.16; H, 5.75. Found: C, 42.11; H, 5.79.

Tetrastannylation using 2n. To a THF solution (1.0 mL) of 1,1,3,3-tetramethylbutyl isocyanide (0.014 g, 0.099 mmol), $Pd(OAc)_2$ (1.5 mg, 6.6 mmol), KF (0.038 g, 0.66 mmol) and 18-crown-6 (0.17 g, 0.66 mmol) were added **1a** (0.39 g, 0.66 mmol) and **2n** (0.10 g, 0.17 mmol), and the resulting mixture was stirred at 20 °C for 24 h. 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 (benzene as an eluent) gave 3,3',4,4'-Tetrakis(tributylstannyl)diphenyl ether (**3an**) (0.066 g, 30% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.88-1.54 (m, 108 H), 6.85 (dd, *J* = 8.0, 2.6 Hz, 2 H), 7.17 (d, *J* = 2.6 Hz, 2 H), 7.39 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 11.0, 13.7, 27.4, 27.5, 29.1, 29.2, 117.2, 127.9, 138.2, 144.9, 153.6, 156.1; ^{119}Sn NMR ($CDCl_3$) δ -40.8, -40.0; Anal. Calcd for $C_{60}H_{114}OSn_4$: C, 54.33; H, 8.66. Found: C, 54.63; H, 8.61.

Synthesis of 4a. To a benzene solution (1.0 mL) of Pd(*t*-OcNC)$_2$, prepared from $Pd(C_5H_5)(C_3H_5)$ (0.10 g, 0.50 mmol) and 1,1,3,3-tetramethylbutyl isocyanide (0.28 g, 2.0 mmol),[15] was added **1a** (0.29 g, 0.50 mmol), and the mixture was stirred at 20 °C for 1.5 h. Evaporation of the solvent gave analytically pure bis(tributylstannyl)bis(1,1,3,3-tetramethylbutyl isocyanide)palladium (**4a**) as a brown oil: ^{1}H NMR (C_6D_6) δ 0.85 (s, 18 H), 0.94 (t, *J* = 7.2 Hz, 18 H), 1.10 (s, 12 H), 1.17 (br, 12 H), 1.26 (s, 4 H), 1.46 (br, 12 H), 1.73 (br, 12 H); ^{13}C NMR (C_6D_6) δ 13.2, 14.3, 28.7, 31.1, 31.75, 31.83, 53.8, 59.0, 152.1; ^{119}Sn NMR (C_6D_6) δ -1.9; Anal. Calcd for $C_{42}H_{88}N_2PdSn_2$: C, 52.27; H, 9.19; N, 2.90. Found: C, 52.37; H, 9.16; N, 2.77.

Stoichiometric reaction using 4a. To a THF solution (1.0 mL) of **4a** (0.50 mmol) were added KF (0.087 g, 1.5 mmol), 18-Crown-6 (0.40 g, 1.5 mmol) and **1a** (0.22 g, 0.75 mmol), and the resulting mixture was stirred at 20 °C for 1 h. 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 (benzene as an eluent) gave **3aa** (0.24 g, 74% yield).

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