Supplemental Information for

A Mild Procedure for the Catalytic Bis(stannylation) of Alkynes with Hexaalkylditins

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Materials and Instrumentation

Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. Benzene was distilled from calcium hydride under nitrogen. Palladium(II) dichloride was purchased from Strem Chemicals, Inc. Bis(tributyltin), tributyltin hydride, and *tert*-butyl isocyanide were purchased from Aldrich, Inc. and used as received. Proton and carbon NMR spectra were acquired on a Varian UNITY 400 MHz spectrometer. ^{119}Sn -NMR spectra were acquired on a Varian Gemini 300 MHz spectrometer. Tin-hydrogen coupling constants are listed as an average of the ^{117}Sn and ^{119}Sn values. Infrared frequencies were acquired using a Perkin-Elmer Spectrum 1000 FT-IR spectrometer.

Preparation of $\text{Pd}(t\text{-BuNC})_2\text{Cl}_2$ (adapted from Otsuka et al, *J. Am. Chem. Soc.* **1971**, 93, 6705.): Palladium(II) chloride (308 mg, 1.73 mmol) was suspended in distilled benzene (10 mL) in a flame-dried round bottom flask under a nitrogen atmosphere. *Tert*-butyl isocyanide (10 eq., 17.3 mmol, 1.96 mL) was added and the dark brown suspension was allowed to stir at room temperature overnight. The solution became an opaque light orange suspension and the mixture was concentrated to half-volume. Cold hexanes was added to initiate precipitation of the product and the mixture was filtered, and the solids washed with cold hexanes. After drying on high vacuum, 457 mg (77%) of an air-stable, pale yellow powder was obtained whose spectral data was in agreement with the published IR and ^1H -NMR characterization data of *cis*- $\text{Pd}(t\text{-BuNC})_2\text{Cl}_2$.

General procedure for Bis(stannylation) of Alkynes with Hexabutylditin:

A flame-dried 3-dram glass vial was flushed under an atmosphere of nitrogen and charged with 8.5 mg of $\text{Pd}(t\text{-BuNC})_2\text{Cl}_2$ (0.025 mmol, 0.025 eq.). The vial was sealed with a rubber septum and 5 mL of distilled THF was added followed by addition of the alkyne (1 mmol). Bis(tributyltin) (0.56 mL, 1.1 mmol, 1.1 eq.) was added by syringe in one portion and left to stir at room temperature for 12-16h. Immediately after the addition of bis(tributyltin), the solution was yellow and changed over time to a dark orange or red solution. Reaction completion was monitored by TLC. The solvent was removed *in vacuo*, and the residue was immediately purified by silica gel column chromatography using a hexanes/ethyl acetate solvent mixture containing 0.5% triethylamine.

General procedure for Bis(stannylation) of Alkynes with Tributyltin Hydride:

A flame-dried 3-dram glass vial was flushed under an atmosphere of nitrogen and charged with 8.5 mg of $\text{Pd}(t\text{-BuNC})_2\text{Cl}_2$ (0.025 mmol, 0.025 eq.). The vial was sealed with a rubber septum and 3 mL of distilled THF was added followed by addition of the alkyne (1 mmol). Tributyltin hydride (0.59 mL, 2.2 mmol, 2.2 eq.) was dissolved in 2 mL distilled THF in a separate flame-dried round bottom flask under nitrogen and the solution was added dropwise to the reaction vial. The reaction mixture was left to stir at room temperature for 12-16h. Reaction completion was monitored by TLC. The solvent was removed *in vacuo*, and the residue was immediately purified by silica gel column chromatography using a hexanes/ethyl acetate solvent mixture containing 0.5% triethylamine.

(2,3-Bis-tributylstannanyl-allyl)-carbamic acid tert-butyl ester, 1: colorless oil. IR (neat): 3453, 3365, 2956, 1705, 1494, 1463, 1418, 1365, 1339, 1245, 1170, 1071, 1047, 1010, 959, 865, 773, 666 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 6.79 (1H, vinylic, s, $^2J_{\text{H-Sn}}$ = 68.8 Hz, $^3J_{\text{H-Sn}}$ = 169.8 Hz), 4.44 (1H, -NH, bs), 3.90 (2H, -CH₂-, bs), 2.43 (3H, tosyl CH₃, s), 1.45-1.51 (12H, -CH₂-, m), 1.45 (9H, t-Bu CH₃, s), 1.29-1.36 (12H, -CH₂-, m), 0.88-0.93 (30H, -CH₂CH₃, m). ^{13}C -NMR (100 MHz, CDCl_3) δ = 162.8, 155.3, 142.7, 79.0, 54.4, 29.3, 29.2, 29.1, 29.0, 28.4, 27.8, 27.7, 27.6, 27.4, 27.3, 27.1, 27.0, 26.8, 17.5, 13.6, 12.4, 12.3, 11.8, 11.7, 10.7, 10.2. ^{119}Sn NMR (112 MHz, CDCl_3) δ = -53.9 (terminal Sn), -66.2 (internal Sn). HRMS: m/z calcd for $\text{C}_{28}\text{H}_{58}\text{NO}_2\text{Sn}_2$ $[\text{M}-(\text{C}_4\text{H}_9)]^+$: 680.2524; found: 680.2511.

(2,3-Bis-tributylstannanyl-allyl)-dimethyl-amine, 3: colorless oil. IR (neat): 2923, 2854, 2769, 1458, 1375, 1337, 1267, 1169, 1145, 1069, 1045, 1015, 960, 866, 799, 665 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3) δ = 6.96 (1H, vinylic, s, $^2J_{\text{H-Sn}}$ = 70.4 Hz, $^3J_{\text{H-Sn}}$ = 186.8 Hz), 2.99 (2H, -CH₂-, bs), 2.11 (6H, -CH₃, s), 1.40-1.55 (12H, -CH₂-, m), 1.27-1.38 (12H, -CH₂-, m), 0.82-1.00 (30H, -CH₂CH₃, m). ^{13}C -NMR (100 MHz, CDCl_3) δ = 168.7, 142.0, 45.0, 29.4, 29.3, 29.2, 29.1, 27.9, 27.7, 27.6, 27.3, 27.0, 13.7, 13.6, 10.7, 10.6. ^{119}Sn -NMR (112 MHz, CDCl_3) δ = -60.4 (terminal Sn), -69.3 (internal Sn). HRMS: m/z calcd for $\text{C}_{25}\text{H}_{54}\text{NSn}_2$ $[\text{M}-(\text{C}_4\text{H}_9)]^+$: 608.2315; found: 608.2300.

N-(2,3-Bis-tributylstannanyl-allyl)-4-methyl-benzenesulfonamide, 4: light red oil. IR (neat): 3272, 2956, 1599, 1495, 1463, 1417, 1376, 1333, 1162, 1095, 1070, 960, 873, 813, 663 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3) δ = 7.74 (2H, aromatic, d, J = 8.2 Hz), 7.30 (2H, aromatic, d, J = 8.2 Hz), 6.72 (1H, vinylic, s, $^2J_{\text{H-Sn}}$ = 66.6 Hz, $^3J_{\text{H-Sn}}$ = 164.4 Hz), 4.18 (1H, -NH, bs), 3.70 (2H, -CH₂-, m), 2.43 (3H, tosyl CH₃, s), 1.41-1.49 (12H, -CH₂-, m), 1.25-1.36 (12H, -CH₂-, m), 0.85-0.95 (30H, -CH₂CH₃, m). ^{13}C -NMR (100 MHz, CDCl_3) δ = 160.3, 145.1, 143.3, 136.9, 129.6, 127.2, 56.8, 29.2, 29.2, 29.1, 29.0, 27.4, 27.3, 21.5, 17.5, 13.6, 10.7, 10.4. ^{119}Sn -NMR (112 MHz, CDCl_3) δ = -51.7 (terminal Sn), -65.2 (internal Sn). HRMS: m/z calcd for $\text{C}_{30}\text{H}_{56}\text{NO}_2\text{SSn}_2$ $[\text{M}-(\text{C}_4\text{H}_9)]^+$: 734.2082; found: 734.2075.

(2,3-Bis-tributylstannanyl-allyloxy)-methane, 5: red oil. (IR neat): IR (neat): 2955, 1524, 1463, 1417, 1375, 1291, 1191, 1151, 1109, 1071, 1001, 960, 873, 810, 667 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 6.86 (1H, vinylic, s, $^2J_{\text{H-Sn}}$ = 73.6 Hz, $^3J_{\text{H-Sn}}$ = 165.8

Hz), 4.00 (2H, -CH₂-, s), 3.28 (3H, -CH₃, s), 1.46-1.56 (12H, -CH₂-, m), 1.27-1.36 (12H, -CH₂-, m), 0.84-0.94 (30H, -CH₂CH₃, m). ¹³C-NMR (100 MHz, CDCl₃) δ = 164.8, 143.3, 84.9, 57.4, 29.3, 29.3, 29.2, 29.2, 29.1, 29.0, 27.8, 27.5, 27.4, 13.7, 10.7, 10.4. ¹¹⁹Sn-NMR (112 MHz, CDCl₃) δ = -56.6 (terminal Sn), -67.1 (internal Sn). HRMS: *m/z* calcd for C₂₄H₅₁OSn₂ [M-(C₄H₉)]⁺: 595.2001; found: 595.1983.

[3-(2,3-Bis-tributylstannanyl-allyloxy)-propenyl]-benzene, 6: red oil. IR (neat): 3027, 2955, 2853, 1524, 1496, 1463, 1417, 1376, 1340, 1291, 1073, 963, 873, 810, 743, 690 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.26-7.42 (5H, aromatic, m), 6.93 (1H, vinylic, s, ²*J*_{H-Sn} = 74.8 Hz, ³*J*_{H-Sn} = 175 Hz), 6.62 (1H, -CH=CHPh, d, *J* = 16 Hz), 6.33 (1H, -CH=CHPh, dt, *J* = 6 Hz, 16 Hz), 4.13 (4H, allylic, m), 1.49-1.57 (12H, -CH₂-, m), 1.31-1.40 (12H, -CH₂-, m), 0.87-1.02 (30H, -CH₂CH₃, m). ¹³C-NMR (100 MHz, CDCl₃) δ = 164.7, 143.6, 136.9, 132.0, 128.5, 127.5, 126.4, 126.4, 82.6, 70.3, 29.4, 29.3, 29.2, 27.6, 27.4, 13.7, 13.6, 10.8, 10.5. ¹¹⁹Sn NMR (112 MHz, CDCl₃) δ = -57.4 (terminal Sn), -67.2 (internal Sn). HRMS: *m/z* calcd for C₃₂H₅₇OSn₂ [M-(C₄H₉)]⁺: 697.2482; found: 697.2453.

2,3-Bis-tributylstannanyl-acrylic acid methyl ester, 7: light red oil. IR (neat): 2956, 2853, 1715, 1687, 1534, 1464, 1431, 1376, 1340, 1260, 1213, 1072, 1023, 960, 866, 768, 668 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.21 (1H, vinylic, s, ²*J*_{H-Sn} = 64.4 Hz, ³*J*_{H-Sn} = 154.8 Hz), 3.72 (3H, -OCH₃, s), 1.45-1.56 (12H, -CH₂-, m), 1.28-1.35 (12H, -CH₂-, m), 0.88-1.00 (30H, -CH₂CH₃, m). ¹³C-NMR (100 MHz, CDCl₃) δ = 170.4, 163.6, 157.1, 51.8, 29.0, 28.9, 27.6, 27.3, 27.0, 13.6, 11.1. ¹¹⁹Sn NMR (112 MHz, CDCl₃) δ = -47.0 (terminal Sn), -61.3 (internal Sn). HRMS: *m/z* calcd for C₂₄H₄₉O₂Sn₂ [M-(C₄H₉)]⁺: 609.1783; found: 609.1776.

2,3-Bis-trimethylstannanyl-acrylic acid methyl ester, 8: pale yellow oil. IR (neat): 2984, 2948, 2914, 1711, 1693, 1538, 1432, 1257, 1210, 1022, 871, 770 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.21 (1H, vinylic, s, ²*J*_{H-Sn} = 71.6 Hz, ³*J*_{H-Sn} = 166.4 Hz), 3.79 (3H, -OCH₃, s), 0.28 (9H, -Sn(CH₃)₃, m). ¹³C-NMR (100 MHz, CDCl₃) δ = 170.1, 163.8, 157.3, 51.8, -6.9, -7.5. ¹¹⁹Sn NMR (112 MHz, CDCl₃) δ = -38.7 (terminal Sn), -51.9 (internal Sn). HRMS: *m/z* calcd for C₉H₁₉O₂Sn₂ [M-(CH₃)]⁺: 398.9423; found: 398.9429.

(3,4-Bis-tributylstannanyl-but-3-enyloxy)-tert-butyl-dimethyl-silane, 9: colorless oil. IR (neat) 2955, 2855, 1541, 1463, 1376, 1254, 1099, 1005, 960, 835, 813, 774, 664 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃) δ = 6.70 (1H, vinylic, s, ²*J*_{H-Sn} = 75.2 Hz, ³*J*_{H-Sn} = 184 Hz), 3.56 (2H, -C=C-CH₂-, t, *J* = 7.4 Hz), 2.53 (2H, -CH₂-OTBDMS, t, *J* = 7.4 Hz), 1.44-1.53 (12H, -CH₂-, m), 1.28-1.35 (12H, -CH₂-, m), 0.83-1.00 (36H, -CH₂CH₃ and -SiCH₃, m), 0.06 (9H, -Si-C(CH₃)₃, s). ¹³C-NMR (100 MHz, CDCl₃) δ = 163.4, 145.5, 63.6, 63.5, 63.4, 50.5, 29.3, 29.0, 27.6, 27.5, 26.0, 18.3, 13.6, 10.6, 10.5, -5.1. ¹¹⁹Sn NMR (112 MHz, CDCl₃) δ = -55.9 (terminal Sn), -70.0 (internal Sn). HRMS: *m/z* calcd for C₃₀H₆₅OSiSn₂ [M-(C₄H₉)]⁺: 709.2866; found: 709.2848.

2-Methyl-3,4-bis-tributylstannanyl-but-3-en-2-ol, 10: colorless oil. IR (neat) 3614, 3470, 2956, 2921, 2853, 1463, 1375, 1359, 1339, 1291, 1149, 1105, 1071, 960, 912, 873, 828, 669 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃) δ = 6.63 (1H, vinylic, s, ²*J*_{H-Sn} = 78.8 Hz, ³*J*_{H-}

$\delta_{\text{Sn}} = 254$ Hz), 1.42-1.58 (13H, $-\text{CH}_2-$ and $-\text{OH}$, m), 1.27-1.39 (18H, $-\text{CH}_2-$ and $-\text{CH}_3$, m), 0.83-1.00 (30H, $-\text{CH}_2\text{CH}_3$, m). ^{13}C -NMR (100 MHz, CDCl_3) $\delta = 177.9, 136.5, 30.6, 29.4, 29.2, 27.6, 27.3, 13.7, 13.6, 12.1, 11.2$. ^{119}Sn NMR (112 MHz, CDCl_3) $\delta = -59.9$ (terminal Sn), -64.0 (internal Sn). HRMS: m/z calcd for $\text{C}_{25}\text{H}_{53}\text{OSn}_2$ $[\text{M}-(\text{C}_4\text{H}_9)]^+$: 609.2154; found: 609.2140.

2,3-Bis-tributylstannanyl-but-2-enedioic acid dimethyl ester, 11: colorless oil. IR (neat): 2954, 2854, 1709, 1458, 1433, 1375, 1319, 1221, 1073, 1025, 959, 874, 809, 675 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3) $\delta = 3.68$ (6H, $-\text{CH}_3$, s), 1.40-1.57 (12H, $-\text{CH}_2-$, m), 1.31-1.40 (12H, $-\text{CH}_2-$, m), 0.88-1.04 (30H, $-\text{CH}_2\text{CH}_3$, m). ^{13}C -NMR (100 MHz, CDCl_3) $\delta = 171.8, 158.0, 51.5, 28.9, 28.8, 28.7, 27.3, 13.6, 13.5, 11.8$. ^{119}Sn NMR (112 MHz, CDCl_3) $\delta = -38.6$. HRMS: m/z calcd for $\text{C}_{26}\text{H}_{51}\text{O}_4\text{Sn}_2$ $[\text{M}-(\text{C}_4\text{H}_9)]^+$: 667.1852; found: 667.1831.