Supporting Information

Palladium Pincer-Complex Catalyzed Trimethyltin Substitution of Functionalized Propargylic Substrates. An Efficient Route to Propargyl- and Allenyl-Stannanes

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Experimental Procedures and Characterization of the Products

All solvents used in the reactions were freshly distilled prior to use. The NMR spectra were recorded on Varian spectrometers. ^1H -NMR spectra was recorded at either 300 or 400 MHz, ^{13}C -NMR spectra was recorded at either 75 or 100.5 MHz and ^{119}Sn -NMR spectra was recorded at 149.1 MHz. Unless otherwise stated CDCl_3 was used as solvent for the NMR-measurements using CHCl_3 ($\delta[^1\text{H}] = 7.26$ ppm, $\delta[^{13}\text{C}] = 77.0$ ppm) as internal standard. The stoichiometric reactions of **1b** with hexamethylditin (**3**) were conducted in THF-d_8 and the reactions were monitored by ^1H - and ^{119}Sn -NMR spectroscopy. In these measurements THF ($\delta[^1\text{H}] = 1.85$ ppm) and hexamethylditin ($\delta[^{119}\text{Sn}] = -109$ ppm)¹ was used as internal standard. Complex **1a** was prepared according to the procedure published by van Koten and co-workers² except that the final product was purified by column chromatography using CH_2Cl_2 :ether 20:1 as eluent. The propargyl chloride derivatives were prepared using standard literature procedures.³⁻⁶ All reactions were conducted under argon atmosphere by employing standard manifold techniques. For column chromatography silica gel (230-400 mesh) was used. All eluents for silica gel chromatography are given in volume:volume ratios.

General procedure for catalytic substitution of propargylic substrates with 3. The corresponding propargylic substrate **4a-k** (0.16 mmol) and catalyst **1a** (0.004 mmol, 2.5 mol%) was dissolved in THF (0.25 mL). To this mixture hexamethylditin **3** (0.168 mmol) was added resulting in a dark-yellow solution. Thereafter, the reaction mixture was stirred for the allotted temperatures and times given in Table 1. The solvent was evaporated and the products were purified by column chromatography. To avoid decomposition of the allenyl and propargyl stannane products a rapid chromatography procedure was applied. Accordingly, we used a short silica-gel column (5-10 cm long and 3 cm in diameter) with a relatively fast eluent system given below for the corresponding products. It was found that the allenyl stannane products are usually more stable than their propargyl counterparts.

Warning. In these catalytic transformations toxic organometallic tin compounds, such as trimethyltin chloride, are formed. Please, consult the Material Safety Data Sheet (MSDS, www.msdssearch.com) before performing these reactions.

Reaction of 4a with 3 (entry 1). The reaction mixture was purified by column chromatography using pentane: ether 10:1 as eluent giving an 8:1 mixture of **5a** and **6a**. NMR data for trimethyl(3-phenylprop-2-ynyl)stannane **5a**. ^1H NMR: 0.27 (s, 9H, $^3J(\text{H}-^{117}\text{Sn}) = 26.4$ Hz, $^3J(\text{H}-^{119}\text{Sn}) = 27.7$ Hz), 1.81 (s, 2H, $^3J(\text{H}-\text{Sn}) = 28.4$ Hz, 29.9 Hz), 7.14-7.38 (m, 5H). ^{13}C NMR: -9.33 ($^2J(\text{C}-^{117}\text{Sn}) = 164.1$ Hz, $^2J(\text{C}-^{119}\text{Sn}) = 170.5$ Hz), -0.84 ($^2J(\text{C}-^{117}\text{Sn}) = 126.2$ Hz, $^2J(\text{C}-^{119}\text{Sn}) = 131.6$ Hz), 79.02, 90.98, 125.11, 126.74, 128.12, 131.29.

Reaction of 4c with 3 (entry 5). The reaction mixture was purified by column chromatography using pentane: ether 10:1 as eluent giving a 10:1 mixture of **5a** and **6a**. NMR data for trimethyl(oct-2-ynyl)stannane **5b**: ^1H NMR: 0.18 (s, 9H, $^3J(\text{H}-^{117}\text{Sn}) = 26.2$ Hz, $^3J(\text{H}-^{119}\text{Sn}) = 27.4$ Hz), 0.85-0.93 (m, 3H), 1.24-1.38 (m, 4H), 1.40-1.50 (m, 2H), 1.54 (t, 2H, $^3J(\text{H}-\text{H}) = 2.7$ Hz), 2.08-2.19 (m, 2H). ^{13}C NMR: -9.66 ($^2J(\text{C}-^{117}\text{Sn}) = 163.0$ Hz, $^2J(\text{C}-^{119}\text{Sn}) = 170.1$ Hz), -1.97 ($^2J(\text{C}-^{117}\text{Sn}) = 135.8$ Hz, $^2J(\text{C}-^{119}\text{Sn}) = 142.6$ Hz), 14.03, 19.00, 22.26, 29.29, 31.10, 78.29, 79.53.

Reaction of 4d with 3 (entry 6). This reaction was conducted in THF- d_8 and the progress of the reaction was monitored by ^1H -NMR spectroscopy. The product **6c** was not isolated because of its volatility. NMR data for trimethyl(propa-1,2-dienyl)stannane **6c**. ^1H NMR(THF- d_8): 0.21 (s, 9H), 4.12 (d, 2H, $^3J(\text{H}-\text{H}) = 7.1$ Hz), 5.02 (t, 1H, $^3J(\text{H}-\text{H}) = 7.1$ Hz). ^{13}C NMR: -9.12, 63.64, 79.79, 210.89.

Reaction of 4e with 3 (entry 7). The reaction mixture was purified by column chromatography using pentane: ether 10:1 as eluent giving **6d** as product. NMR data for ethyl 2-(1,1,1-trimethylstannyl)buta-2,3-dienoate **6d**: ^1H NMR: 0.26 (s, 9H, $^3J(\text{H}-^{117}\text{Sn}) = 27.4$ Hz, $^3J(\text{H}-^{119}\text{Sn}) = 28.5$ Hz), 1.27 (t, 3H, $^3J(\text{H}-\text{H}) = 7.0$ Hz), 4.16 (q, 2H, $^3J(\text{H}-\text{H}) =$

7.3, 15.6 Hz), 4.67 (s, 2H, $^3J(\text{H-Sn}) = 16.0$ Hz). ^{13}C NMR: -8.43 ($^2J(\text{C-}^{117}\text{Sn}) = 177.7$ Hz, $^2J(\text{C-}^{119}\text{Sn}) = 185.4$ Hz), 14.21, 61.09, 69.18 ($^2J(\text{C-Sn}) = 18.3$ Hz), 91.56, 168.25, 213.56.

Reaction of 4f with 3 (entry 8). The reaction mixture was purified by column chromatography using pentane: ether 2:1 as eluent giving **6e** as product. NMR data for 2-(1,1,1-trimethylstannyl)buta-2,3-dien-1-ol **6e**: ^1H NMR: 0.23 (s, 9H, $^3J(\text{H-}^{117}\text{Sn}) = 27.1$ Hz, $^3J(\text{H-}^{119}\text{Sn}) = 27.9$ Hz), 1.61 (t, 1H, $^3J(\text{H-H}) = 5.6$ Hz), 4.24 (dt, 2H, $^3J(\text{H-H}) = 3.7$ Hz, 5.9 Hz), 4.39 (t, 2H, $^3J(\text{H-H}) = 3.7$ Hz). ^{13}C NMR: -9.08 ($^2J(\text{C-}^{117}\text{Sn}) = 170.3$ Hz, $^2J(\text{C-}^{119}\text{Sn}) = 178.0$ Hz), 62.78 ($^2J(\text{C-Sn}) = 12.2$ Hz), 68.51 ($^2J(\text{C-Sn}) = 21.3$ Hz), 94.11, 202.62.

Reaction of 4g with 3 (entry 9). The reaction mixture was purified by column chromatography using pentane: ether 10:1 as eluent giving **6f** as product. NMR data for 1-phenyl-4-(1,1,1-trimethylstannyl)buta-2,3-dienyl acetate **6f**: ^1H NMR: 0.09 (s, 9H, $^3J(\text{H-}^{117}\text{Sn}) = 26.7$ Hz, $^3J(\text{H-}^{119}\text{Sn}) = 27.9$ Hz), 2.10 (s, 3H), 4.40 (dd, 2H, $^3J(\text{H-H}) = 3.1$, 6.6 Hz), $^3J(\text{H-}^{117}\text{Sn}) = 12.6$ Hz, $^3J(\text{H-}^{119}\text{Sn}) = 15.4$ Hz), 6.41 (t, 1H, $^3J(\text{H-H}) = 3.3$ Hz, $^3J(\text{H-Sn}) = 14.9$ Hz), 7.27-7.36 (m, 5H). ^{13}C NMR: -8.58 ($^2J(\text{C-}^{117}\text{Sn}) = 173.4$ Hz, $^2J(\text{C-}^{119}\text{Sn}) = 180.8$ Hz), 21.19, 68.62 ($^2J(\text{C-Sn}) = 20.2$ Hz), 76.24 ($^2J(\text{C-}^{117}\text{Sn}) = 10.1$ Hz), 95.37, 126.94, 127.98, 128.32, 140.03, 169.78, 204.68.

Reaction of 4h with 3 (entry 10). The reaction mixture was purified by column chromatography using pentane: ether 15:1 as eluent giving **6g** as product. NMR data for trimethyl-1-[phenyl(tetrahydro-2H-pyran-2-yloxy)methyl]propa-1,2-dienylstannane **6g**: ^1H NMR: -0.01 (s, 9H, $^3J(\text{H-}^{117}\text{Sn}) = 26.8$ Hz, $^3J(\text{H-}^{119}\text{Sn}) = 28.0$ Hz), 1.45-1.66 (m, 3H), 1.67-1.84 (m, 2H), 1.87-2.01 (m, 1H), 3.47 (dt, 1H, $^3J(\text{H-H}) = 11.4$, 4.2, 1.3 Hz), 3.77 (m, 1H), 4.40 (t, 2H, $^3J(\text{H-H}) = 1.7$, 18.3 Hz, $^3J(\text{H-}^{117}\text{Sn}) = 10.8$ Hz, $^3J(\text{H-}^{119}\text{Sn}) = 12.2$ Hz), 4.99 (t, 1H, $^3J(\text{H-H}) = 3.3$ Hz), 5.56 (s, 1H, $^3J(\text{H-}^{117}\text{Sn}) = 20.2$ Hz, $^3J(\text{H-}^{119}\text{Sn}) = 23.1$ Hz), 7.18-7.47 (m, 5H). ^{13}C NMR: -8.57 ($^2J(\text{C-}^{117}\text{Sn}) = 169.2$ Hz, $^2J(\text{C-}^{119}\text{Sn}) = 178.2$

Hz), 19.09, 25.56, 30.44, 61.66, 66.70 ($^2J(\text{C}-^{117}\text{Sn}) = 21.0 \text{ Hz}$, $^2J(\text{C}-^{119}\text{Sn}) = 26.3 \text{ Hz}$), 77.58, 94.94, 95.85, 126.21, 126.92, 128.00, 142.76, 206.36.

Reaction of 4i with 3 (entry 11). The reaction mixture was purified by column chromatography using $\text{CH}_2\text{Cl}_2 : \text{NEt}_3$ 10:1 as eluent giving a 2:3 mixture of **5c** and **6h**. Subsequently, this mixture was further purified by column chromatography using ($\text{CH}_2\text{Cl}_2 : \text{MeOH}$ 15:1) as eluent to obtain pure **6h**. (Under this second chromatography propargyl derivative **5c** was completely decomposed.) NMR data for 4-[2-(1,1,1-trimethylstannyl)buta-2,3-dienyl]morpholine **6h**: ^1H NMR: δ 0.18 (s, 9H, $^3J(\text{H}-^{117}\text{Sn}) = 26.40 \text{ Hz}$, $^3J(\text{H}-^{119}\text{Sn}) = 27.97 \text{ Hz}$), 2.44 (m, 4H), 3.07 (t, 2H, $^3J(\text{H}-\text{H}) = 3.30 \text{ Hz}$), $^3J(\text{H}-^{119}\text{Sn}) = 23.57$), 3.67 (t, 4H, $^3J(\text{H}-\text{H}) = 5.14 \text{ Hz}$), 4.23 (t, 2H, $^3J(\text{H}-\text{H}) = 3.21 \text{ Hz}$), $^3J(\text{H}-^{119}\text{Sn}) = 19.83$). ^{13}C NMR: δ - 8.71, 53.80, 61.40, 65.84, 67.33, 92.00, 205.09. ^1H -NMR data for 4-[4-(1,1,1-trimethylstannyl)but-2-ynyl]morpholine **5c** (determined from the 2:3 mixture of **5c** and **6h**): δ 0.20 (s, 9H, $^3J(\text{H}-^{117}\text{Sn}) = 25.72 \text{ Hz}$, $^3J(\text{H}-^{119}\text{Sn}) = 25.47 \text{ Hz}$), 1.58 (t, 2H $^3J(\text{H}-\text{H}) = 2.99 \text{ Hz}$, $^3J(\text{H}-^{119}\text{Sn}) = 26.17$), 2.53 (m, 2H), 3.25 (t, 2H, $^3J(\text{H}-\text{H}) = 2.88 \text{ Hz}$, $^3J(\text{H}-^{119}\text{Sn}) = 8.65$), 3.73 (t, 2H $^3J(\text{H}-\text{H}) = 4.55 \text{ Hz}$).

Reaction of 4j with 3 (entry 12). The reaction mixture was purified by column chromatography using CH_2Cl_2 : ether 15:1 as eluent giving a 1:2 mixture of **5d** and **6i**. Subsequently, this mixture was further purified by column chromatography using (pentane : ether 15:1) as eluent to obtain pure **6i**. (Under this second chromatography propargyl derivative **5e** was decomposed.) NMR data for *N*1-phenyl-*N*1-[2-(1,1,1-trimethylstannyl)buta-2,3-dienyl]acetamide **6i**: ^1H NMR: -0.21 (s, 9H, $^3J(\text{H}-^{117}\text{Sn}) = 26.5 \text{ Hz}$, $^3J(\text{H}-^{119}\text{Sn}) = 27.9 \text{ Hz}$), 1.55 (s, 3H), 4.20 (t, 2H, $^3J(\text{H}-\text{H}) = 2.5 \text{ Hz}$, $^3J(\text{H}-\text{Sn}) = 18.3 \text{ Hz}$), 4.36 (t, 2H, $^3J(\text{H}-\text{H}) = 2.3 \text{ Hz}$, $^3J(\text{H}-\text{Sn}) = 17.1 \text{ Hz}$), 7.16-7.46 (m, 5H). ^{13}C NMR: - 8.77 ($^2J(\text{C}-^{117}\text{Sn}) = 170.9 \text{ Hz}$, $^2J(\text{C}-^{119}\text{Sn}) = 177.8 \text{ Hz}$), 22.52, 51.25 ($^2J(\text{C}-\text{Sn}) = 14.9 \text{ Hz}$), 67.03 ($^2J(\text{C}-\text{Sn}) = 21.3 \text{ Hz}$), 89.06, 127.69, 128.18, 129.39, 143.29, 169.94, 206.39. The ^1H NMR data for *N*1-phenyl-*N*1-[4-(1,1,1-trimethylstannyl)but-2-ynyl]acetamide **5d** (determined from the 1:2 mixture of **5d** and **6i**): 0.18 (s, 9H), 1.50 (t, 2H, $^3J(\text{H}-\text{H}) = 2.9 \text{ Hz}$), 1.55 (s, 3H), 4.46 (t, 2H, 2.6 Hz), 7.06-7.46 (m, 5H).

Reaction of 4k with 3 (entry 13). The reaction mixture was purified by column chromatography using CH₂Cl₂: ether 10:1 as eluent giving a 1:6 mixture of **5e** and **6j**. Subsequently, this mixture was further purified by column chromatography using pure CH₂Cl₂ as eluent to obtain pure **6i**. (Under this second chromatography propargyl derivative **5e** was decomposed.) NMR data for *N*1-phenyl-*N*1-[2-(1,1,1-trimethylstannyl)buta-2,3-dienyl]-4-methylbenzene-1-sulfonamide **6j**: ¹H NMR: δ 0.20 (s, 9H, ³*J*(H-¹¹⁷Sn) = 27.08 Hz, ³*J*(H-¹¹⁹Sn) = 28.16 Hz), 2.40 (s, 3H), 4.06 (t, 2H ³*J*(H-H) = 2.47 Hz), ³*J*(H-¹¹⁹Sn) = 17.67), 4.24 (t, 4H, ³*J*(H-H) = 2.26 Hz), ³*J*(H-¹¹⁹Sn) = 17.91), 7.04 (m, 2H), 7.24 (m, 5H), 7.40 (m, 2H). ¹³C NMR: δ -8.83, 21.51, 52.41, 66.50, 88.96, 127.27, 127.76, 128.38, 128.41, 129.28, 134.57, 138.68, 143.39, 207.42. ¹H NMR data for *N*1-phenyl-*N*1-[4-(1,1,1-trimethylstannyl)but-2-ynyl]-4-methylbenzene-1-sulfonamide **5e** (determined from the 1:2 mixture of **5e** and **6j**): 0.07 (s, 9H), 1.38 (t, 2H, 2.7 Hz), 2.40 (s, 3H), 4.42 (t, 2H, 2.7 Hz), 7.01-7.55 (m, 9H).

Reaction of Complex **1b** with **3** monitored by ^{119}Sn NMR.

The chloride counter ion of **1a** was exchanged to acetate (**1b**) by using the following procedure. Complex **1a** (12 mg 0.032 mmol) was added to AgOAc (8 mg, 0.048 mmol) suspended in CHCl_3 at 0 °C. This mixture was stirred 1h at 0 °C and then an additional hour at 25 °C in a dark reaction vessel. The AgBr precipitation was separated by centrifugation and the solvent was evaporated to yield **1b**. Complex **1b** was dissolved in 0.7 mL THF-d_8 , and then hexamethylditin (63 mg, 0.192 mmol) was added to the solution. The progress of the reaction was monitored by an array experiment using ^{119}Sn -NMR spectroscopy (Figure 1).

Figure 1. ^{119}Sn -NMR spectrum of the reaction of **1b** with **3** in THF-d_8 . The sampling times are given in minutes.

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