Supplementary Information

Copper-catalyzed \( \alpha \)-selective hydrostannylation of alkynes for synthesis of branched alkenylstannanes

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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 Varian 400-MR ($^1$H, 400 MHz; $^{13}$C, 100 MHz) spectrometer or a Varian System 500 ($^1$H, 500 MHz; $^{13}$C, 125 MHz; $^{119}$Sn, 186 MHz) spectrometer using residual chloroform ($^1$H, $\delta$ = 7.26) or CDCl$_3$ ($^{13}$C, $\delta$ = 77.0) as an internal standard, and tetramethylditin ($^{119}$Sn, $\delta$ = 0) as an external standard. $^1$H NMR data are reported as follows: chemical shift, multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, quint = quintet, sext = sextet, $m$ = multiplet), coupling constants (Hz), integration. High-resolution mass spectra (ESI or APCI/FTMS; Negative Mode) were obtained with Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Preparative recycling gel permeation chromatography was performed with JAI LC-908 or JAI LC-9201 equipped with JAI GEL-1H and -2H columns (chloroform or toluene as an eluent). Column chromatography was carried out using Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. Toluene was distilled from sodium/benzophenone ketyl. DMF was distilled from calcium hydride.
Hydrostannylation of alkynes with Me₃SnSnMe₃: a general procedure.

A Schlenk tube equipped with a magnetic stirring bar was charged with Cu(OAc)₂ (0.015 mmol), tri-tert-butyolphosphine (20 wt% solution in toluene, 0.053 mmol) and MeOH (2.5 mL). After the mixture was stirred at 80 °C for 0.5 h, the solvent was removed in vacuo at room temperature. To the residue were added toluene (0.2 mL), hexamethyldistannane (0.39 mmol), an alkyne (0.30 mmol) and water (0.90 mmol), and the resulting mixture was stirred at 110 °C for the period as specified in Table 1. The mixture was diluted with ethyl acetate and filtered through a Celite plug before evaporation of the solvent. Then the residue was diluted with toluene and filtered through neutral alumina (activity = IV). Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

Trimethyl(tetradec-1-en-2-yl)stannane (2a)

A colorless oil: ¹H NMR (CDCl₃) δ 0.13 (s, 2J₁₁₉Sn-H = 53.9 Hz, 2J₁₁₇Sn-H = 51.6 Hz, 9H), 0.88 (t, J = 6.7 Hz, 3H), 1.20-1.42 (m, 20H), 2.26 (t, 3J₁₁₇Sn-H = 53.2 Hz, J =7.2 Hz, 2H), 5.12 (dt, 3J₁₁₉Sn-H = 71.9 Hz, J = 2.8, 1.0 Hz 1H), 5.64 (dt, 3J₁₁₇Sn-H = 155.0 Hz, J = 2.8, 1.5 Hz, 1H); ¹³C NMR (CDCl₃) δ -9.48, 14.13, 22.70, 29.21, 29.36, 29.48, 29.63, 29.65, 29.67, 31.93, 124.15, 156.17; ¹¹⁹Sn NMR (CDCl₃) δ -35.6; HRMS Calcd for C₁₆H₃₃Sn: [M-Me]⁺, 345.15987. Found: m/z 345.15985.

Dodec-1-en-2-yltrimethylstannane (2b)

A colorless oil: ¹H NMR (CDCl₃) δ 0.13 (s, 2J₁₁₉Sn-H = 53.9 Hz, 2J₁₁₇Sn-H = 51.5 Hz, 9H), 0.88 (t, J = 6.5 Hz, 3H), 1.20-1.41 (m, 16H), 2.27 (t, 3J₁₁₇Sn-H = 53.2 Hz, J =7.4 Hz, 2H), 5.12 (dt, 3J₁₁₉Sn-H = 73.3 Hz, J = 2.9, 1.0 Hz, 1H), 5.64 (dt, 3J₁₁₇Sn-H = 155.0 Hz, J = 2.9, 1.0 Hz, 1H); ¹³C NMR (CDCl₃) δ -9.48, 14.14, 22.70, 29.21, 29.36, 29.49, 29.64, 29.67, 31.93, 124.16, 156.15; ¹¹⁹Sn NMR (CDCl₃) δ -35.6; HRMS Calcd for C₁₀H₂₃Sn: [M-Me]⁺, 317.12857. Found: m/z 317.12854.

2-[5-(Trimethylstannyl)hex-5-enyl]isoindoline-1,3-dione (2c)
A green oil: $^1$H NMR (CDCl$_3$) δ 0.11 (s, $^2$J$_{119}\text{Sn-H} = 54.0$ Hz, $^2$J$_{117}\text{Sn-H} = 51.6$ Hz, 9H), 1.43 (quint, $J = 7.5$ Hz, 2H), 1.66 (quint, $J = 7.5$ Hz, 2H), 2.31 (t, $^3$J$_{119}\text{Sn-H} = 51.7$ Hz, $J = 1.3$ Hz, 2H), 3.68 (t, $J = 7.5$ Hz, 2H) 5.13 (dt, $^3$J$_{119}\text{Sn-H} = 71.0$ Hz, $J = 2.7$, 1.3 Hz, 1H), 5.78 (dt, $^3$J$_{119}\text{Sn-H} = 151.7$ Hz, $J = 2.7$, 1.4 Hz, 1H), 7.68-7.73 (m, 2H), 7.81-7.86 (m, 2H)；$^{13}$C NMR (CDCl$_3$) δ -9.53, 26.66, 28.03, 37.80, 40.16, 123.14, 124.93, 132.14, 144.84, 155.08, 168.41；$^{119}$Sn NMR (CDCl$_3$) δ -34.6；HRMS Calcd for C$_{17}$H$_{24}$O$_2$NSn: [M+H]$^+$, 374.08235. Found: m/z 374.08235.

Trimethyl[6-(tetrahydro-2H-pyran-2-yloxy)hex-1-en-2-yl]stannane (2d)

A colorless oil: $^1$H NMR (CDCl$_3$) δ 0.13 (s, $^2$J$_{119}\text{Sn-H} = 54.0$ Hz, $^2$J$_{117}\text{Sn-H} = 51.7$, 9H), 1.41-1.63 (m, 8H), 1.66-1.75 (m, 1H), 1.77-1.88 (m, 1H), 2.30 (t, $^3$J$_{119}\text{Sn-H} = 53.4$ Hz, $^3$J$_{117}\text{Sn-H} = 51.5$, $J =7.5$ Hz, 2H), 3.38 (dt, $J = 9.6$ Hz, 6.4 Hz, 1 H), 3.47-3.54 (m, 1H), 3.73 (dt, $J = 9.6$, 6.6 Hz, 1H), 3.86 (dd, $J = 11.2$, 7.9, 3.5 Hz, 1H), 4.58 (t, $J = 2.7$ Hz, 1H), 5.14 (s, $^3$J$_{119}\text{Sn-H} = 71.4$ Hz, 1H), 5.65 (s, $^3$J$_{119}\text{Sn-H} = 153.15$ Hz, 1H)；$^{13}$C NMR (CDCl$_3$) δ -9.53, 19.52, 25.46, 26.17, 29.19, 30.69, 40.54, 62.12, 67.23, 98.67, 124.53, 155.61；$^{119}$Sn NMR (CDCl$_3$) δ -35.1；HRMS Calcd for C$_{14}$H$_{28}$O$_2$NaSn: [M+Na]$^+$, 371.1004. Found: m/z 371.1005.

$\text{tert-Butyldimethyl[3-(trimethylstannyl)but-3-enyloxy]silane (2e)}$

A colorless oil: $^1$H NMR (CDCl$_3$) δ 0.06 (s, 6H), 0.14 (s, $^2$J$_{119}\text{Sn-H} = 54.2$ Hz, $^2$J$_{117}\text{Sn-H} = 51.8$ Hz, 9H), 0.89 (s, 9H), 0.89 (s, 9H), 2.49 (t, $^3$J$_{119}\text{Sn-H} = 53.1$ Hz, $^3$J$_{117}\text{Sn-H} = 51.0$ Hz, $J = 7.3$ Hz, 2H), 3.63 (t, $J = 7.2$ Hz, 2H), 5.21 (s, $^3$J$_{119}\text{Sn-H} = 71.0$ Hz, 1H), 5.76 (s, $^3$J$_{119}\text{Sn-H} = 151.1$ Hz, 1H)；$^{13}$C NMR (CDCl$_3$) δ -9.34, -5.18, 18.46, 26.02, 44.15, 63.41, 126.72, 151.65；$^{119}$Sn NMR (CDCl$_3$) δ -33.2；HRMS Calcd for C$_{12}$H$_{29}$O$_2$SiSn: [M-Me]$^+$, 335.08477. Found: m/z 335.08469.

$[4-(Benzzyloxy)but-1-en-2-yl]trimethylstannane (2f)$
A yellow oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.13 (s, $^2$J$_{Sn-H}$ = 53.1 Hz, 9H), 2.61 (t, $^3$J$_{Sn-H}$ = 50.9 Hz, J = 6.4 Hz, 2H), 3.52 (t, $J$ = 6.9 Hz, 2H), 4.52 (s, 2H), 5.25 (dt, $^3$J$_{Sn-H}$ = 70.13 Hz, $J$ = 2.7, 1.4 Hz., 1H), 5.76 (dt, $^3$J$_{Sn-H}$ = 129.75 Hz, $J$ = 2.8, 1.4 Hz, 1H), 7.27-7.39 (m, 5H); $^{13}$C NMR (CDCl$_3$) $\delta$ -9.24, 40.88, 70.16, 72.95, 126.41, 127.51, 127.73, 128.29, 138.29, 152.26; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -33.7; HRMS Calcd for C$_{13}$H$_{19}$OSn: [M-Me]$^+$, 311.04524. Found: m/z 311.04517.

9-(Trimethylstannyl)dec-9-en-1-ol (2g)

A brown oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.12 (s, $^2$J$_{Sn-H}$ = 52.8 Hz, 9H), 1.21 (m, 12H), 2.25 (t, $J$ = 7.6 Hz, 2H), 3.62 (dt, $J$ = 6.4 Hz, 5.3 Hz, 2H), 5.11 (s, $^3$J$_{Sn-H}$ = 72.1 Hz, 1H), 5.76 (s, $^3$J$_{Sn-H}$ = 154.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ -9.50, 25.69, 29.07, 29.36, 29.39, 29.59, 32.75, 40.80, 63.00, 124.20, 156.04; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -35.5; HRMS Calcd for C$_{12}$H$_{25}$OSn: [M-Me]$^+$, 305.09219. Found: m/z 305.0921.

(10-Bromodec-1-en-2-yl)trimethylstannane (2h)

A yellow oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.13 (s, $^2$J$_{Sn-H}$ = 53.9 Hz, $^2$J$_{Sn-H}$ = 51.6 Hz, 9H), 1.20-1.48 (m, 12H), 1.85 (quint, $J$ = 7.1 Hz), 2.26 (t, $^3$J$_{Sn-H}$ = 53.9 Hz, $^3$J$_{Sn-H}$ = 51.8, $J$ = 7.1 Hz, 2H), 5.12 (s, $^3$J$_{Sn-H}$ = 71.8 Hz, 1H), 5.76 (s, $^3$J$_{Sn-H}$ = 154.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ -9.48, 28.14, 28.71, 29.03, 29.23, 29.55, 32.80, 34.02, 40.78, 124.25, 156.00; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -35.5; HRMS Calcd for C$_{12}$H$_{24}$BrSn: [M-Me]$^+$, 367.00779. Found: m/z 367.00677.

1-[(2-(Trimethylstannyl)allyl)piperidin-4-one (2i)

A yellow oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.16 (s, $^2$J$_{Sn-H}$ = 54.8 Hz, $^2$J$_{Sn-H}$ = 52.4 Hz, 9H), 2.41 (t, $J$ = 6.2 Hz, 4H), 2.68 (t, $J$ = 5.8 Hz, 4H), 3.19 (t, $^3$J$_{Sn-H}$ = 49.8 Hz, $J$ = 1.3 Hz, 2H), 5.28 (dt, $^3$J$_{Sn-H}$ = 70.0 Hz, $J$ = 2.5, 1.4 Hz, 1H), 5.78 (dt, $^3$J$_{Sn-H}$ = 149.6 Hz, $J$ = 2.5, 1.5 Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ -9.38, 41.25, 53.00, 67.14, 125.77, 154.92, 209.41; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -38.5; HRMS Calcd for C$_{11}$H$_{22}$ONSn: [M+H]$^+$, 304.07169. Found: m/z 304.07166.
[3-(Benzyloxy)prop-1-en-2-yl]trimethylstannane (2j)

A brown oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.17 (s, $^2J_{\text{Sn-H}}$ = 55.4 Hz, $^2J_{\text{Sn-H}}$ = 52.9 Hz, 9H), 4.20 (t, $^3J_{\text{Sn-H}}$ = 39.5 Hz, $^3J_{\text{Sn-H}}$ = 1.4 Hz, 2H), 4.50 (s, 2H), 5.33 (dt, $^3J_{\text{Sn-H}}$ = 144.96 Hz, $^3J_{\text{Sn-H}}$ = 2.5 Hz, 0.9 Hz, 1H), 5.87 (dt, $^3J_{\text{Sn-H}}$ = 70.2 Hz, $^3J_{\text{Sn-H}}$ = 2.5 Hz, 1H), 7.27-7.79 (m, 5H); $^{13}$C NMR (CDCl$_3$) $\delta$ 9.97, 72.02, 77.05, 124.65, 127.44, 127.64, 128.26, 138.38, 153.32; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -35.0; HRMS Calcd for C$_{12}$H$_{17}$OSn: [M-Me]$^+$, 297.02959. Found: m/z 297.02939.

2-[1-(Trimethylstannyl)vinyl]pyridine (2k)

A brown oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.22 (s, $^3J_{\text{Sn-H}}$ = 55.7 Hz, $^3J_{\text{Sn-H}}$ = 53.2 Hz, 9H), 7.51 (d, $^3J_{\text{Sn-H}}$ = 72.0 Hz, $^3J_{\text{Sn-H}}$ = 1.7 Hz, 1H), 6.48 (d, $^3J_{\text{Sn-H}}$ = 145.1 Hz, $^3J_{\text{Sn-H}}$ = 1.8 Hz, 1H), 7.07 (ddd, $^3J_{\text{Sn-H}}$ = 7.3, 0.9 Hz, 1H), 7.50 (dt, $^3J_{\text{Sn-H}}$ = 7.3, 0.9 Hz, 1H), 7.60 (td, $^3J_{\text{Sn-H}}$ = 7.3, 1.8 Hz, 1H), 8.50 (ddd, $^3J_{\text{Sn-H}}$ = 7.3, 1.8, 0.9 Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ -9.47, 72.02, 77.05, 124.65, 127.44, 127.64, 128.26, 138.38, 153.32; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -35.0; HRMS Calcd for C$_9$H$_{12}$NSn: [M-Me]$^+$, 253.99862. Found: m/z 253.99835.

[1-(6-Methoxynaphthalen-2-yl)vinyl]trimethylstannane (2l)

A yellow needle: mp = 64.2 °C; $^1$H NMR (CDCl$_3$) $\delta$ 0.27 (s, $^3J_{\text{Sn-H}}$ = 54.4 Hz, $^2J_{\text{Sn-H}}$ = 52.0 Hz, 9H), 3.92 (s, 3H), 5.51 (d, $^3J_{\text{Sn-H}}$ = 69.2 Hz, $^3J_{\text{Sn-H}}$ = 2.3 Hz 1H), 6.16 (d, $^3J_{\text{Sn-H}}$ = 142.0 Hz, $^3J_{\text{Sn-H}}$ = 2.3 Hz 1H), 7.10-7.16 (m, 2H), 7.39 (dd, $^3J_{\text{Sn-H}}$ = 8.5, 1.9 Hz, 1H), 7.53-7.56 (m, 1H), 7.64-7.63 (m, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ -9.56, -8.54, 55.31, 105.61, 105.80, 123.70, 124.90, 125.34, 125.93, 126.08, 126.79, 126.94, 129.03, 129.08, 129.44, 129.66, 133.40, 140.64, 145.71, 154.40, 157.42; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -28.1; HRMS Calcd for C$_{16}$H$_{21}$OSn: [M+H]$^+$, 349.06089. Found: m/z 349.06079.

[1-(4-Butyphenyl)vinyl]trimethylstannane (2m)
A yellow oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.24 (s, $^3J_{Sn-H} = 54.3$ Hz, $^2J_{Sn-H} = 52.1$ Hz, 9H), 0.94 (t, $J = 7.3$ Hz, 3H), 1.38 (sext, $J = 7.2$ Hz, 2H), 1.56-1.66 (m, 2H), 2.60 (t, $J = 7.7$ Hz, 2H), 5.42 (d, $^3J_{Sn-H} = 69.8$ Hz, $J = 2.1$ Hz, 1H), 6.07 (d, $^3J_{Sn-H} = 144.4$ Hz, $J = 2.2$ Hz, 1H), 7.10-7.18 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ -8.62, 13.97, 22.39, 33.59, 35.26, 125.45, 126.14, 128.43, 141.28, 142.47, 154.11; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -28.8; HRMS Calcd for C$_{15}$H$_{25}$Sn: [M+H]$^+$, 325.09727. Found: m/z 325.09729.

Trimethyl[1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl]stannane (2n)

A white powder: mp = 47.4 °C; $^1$H NMR (CDCl$_3$) $\delta$ 0.15 (s, $^3J_{Sn-H} = 54.1$ Hz, $^2J_{Sn-H} = 51.8$ Hz, 9H), 1.25 (s, 6H), 1.27 (s, 6H), 1.66 (m, 4H), 2.16 (s, 3H), 5.56 (d, $^3J_{Sn-H} = 71.9$ Hz, $J = 3.2$ Hz 1H), 5.77 (d $^3J_{Sn-H} = 148.2$ Hz, $J = 3.0$ Hz 1H), 6.78 (s, 1H), 7.04 (s, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ -8.89, 20.11, 31.88, 31.93, 33.80, 35.23, 35.26, 124.82, 127.38, 127.69, 130.08, 140.91, 141.71, 141.84, 143.17, 156.05; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -78.1; HRMS Calcd for C$_{20}$H$_{33}$Sn: [M+H]$^+$, 393.15987. Found: m/z 393.15988.

(E)-(1,2-Diphenylvinyl)trimethylstannane (2o)$^1$

A green oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.18 (s, $^3J_{Sn-H} = 54.2$ Hz, $^2J_{Sn-H} = 51.8$ Hz, 9H), 6.67 (s, $^3J_{Sn-H} = 76.1$ Hz, 1H), 6.95-7.03 (m, 4H), 7.06-7.18 (m, 4H), 7.24-7.31 (m, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ -9.23, 125.17, 126.15, 126.73, 127.90, 128.70, 129.13, 137.29, 137.74, 145.02, 149.75; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -17.4.

Hydrostannylation of alkynes with Me$_3$SiSnBu$_3$: a general procedure.

A Schlenk tube equipped with a magnetic stirring bar was charged with Cu(OAc)$_2$(0.030 mmol), tricyclohexylphosphine (20 wt% solution in toluene, 0.105 mmol) and MeOH (5
mL). After the mixture was stirred at 80 °C for 0.5 h, the solvent was removed in vacuo at room temperature. To the residue were added toluene (0.2 mL), tributyl(trimethylsilyl)stannane (0.30 mmol), an alkyne (0.45 mmol) and water (0.45 mmol), and the resulting mixture was stirred at 30 °C for the period as specified in Table 2. The mixture was diluted with ethyl acetate and filtered through a Celite plug before drying over MgSO₄. Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

**Tributyl(oct-1-en-2-yl)stannane (3p)**

A colorless oil: ¹H NMR (CDCl₃) δ 0.79-0.98 (m, 16H), 1.21-1.62 (m, 22H), 2.23 (t, ³Jₜₜ= 47.9 Hz, J = 7.1 Hz, 2H), 5.09 (s, ³Jₜₜ= 63.5 Hz, 1H), 5.66 (s, ³Jₜₜ= 141.8 Hz, 1H); ¹³C NMR (CDCl₃) δ 9.56, 13.69, 14.11, 22.66, 27.43, 29.00, 29.14, 29.67, 31.77, 41.46, 124.50, 155.84; ¹¹⁹Sn NMR (CDCl₃) δ -47.3; HRMS Calcd for C₂₀H₄₂Sn: [M]+, 402.23085. Found: m/z 402.23115.

**Tributyl(dec-1-en-2-yl)stannane (3q)**

A pale yellow oil: ¹H NMR (CDCl₃) δ 0.77-1.00 (m, 18H), 1.20-1.40 (m, 18H), 1.41-1.57 (m, 6H), 2.23 (t, ³Jₜₜ= 47.8 Hz, J = 7.3 Hz, 2H), 5.08 (d, ³Jₜₜ= 63.8 Hz, J = 3.1 Hz, 1H), 5.65 (dt, ³Jₜₜ= 141.3 Hz, J = 3.1, 1.3 Hz, 1H); ¹³C NMR (CDCl₃) δ 9.57, 13.71, 14.12, 22.72, 27.45, 29.16, 29.35, 29.52, 29.74, 31.93, 41.48, 124.53, 155.78; ¹¹⁹Sn NMR (CDCl₃) δ -47.3; HRMS Calcd for C₂₂H₄₆Sn: [M]+, 430.26215. Found: m/z 430.26294.

**Tributyl(hex-1-en-2-yl)stannane (3r)**

A colorless oil: ¹H NMR (CDCl₃) δ 0.81-0.97 (m, 18H), 1.25-1.40 (m, 10H), 1.41-1.58 (m, 6H), 2.25 (t, ³Jₜₜ= 48.2 Hz, J = 7.1 Hz, 2H), 5.09 (d, ³Jₜₜ= 64.9 Hz, J = 2.9 Hz, 1H), 5.66 (dt, ³Jₜₜ= 141.1 Hz, J = 2.9, 1.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 9.56, 13.70, 13.99, 22.35, 27.43, 29.15, 31.88, 41.11, 124.53, 155.73; ¹¹⁹Sn NMR (CDCl₃) δ -47.2; HRMS Calcd for C₁₈H₃₈Sn: [M]+, 374.19955. Found: m/z 374.19984.
**Tributyl(5-methylhex-1-en-2-yl)stannane (3s)**

A colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.79-0.98 (m, 18H), 1.18-1.37 (m, 8H), 1.38-1.59 (m, 7H), 2.24 (t, $^3$J$_{Sn-H}$ = 48.3 Hz, $J$ = 8.1 Hz, 2H), 5.07 (d, $^3$J$_{Sn-H}$ = 64.7 Hz, $J$ = 2.9 Hz, 1H), 5.66 (dt, $^3$J$_{Sn-H}$ = 141.8 Hz, $J$ = 2.9, 1.5 Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 9.58, 13.70, 22.53, 27.42, 27.62, 29.14, 39.03, 39.22, 124.38, 155.95; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -46.9; HRMS Calcd for C$_{15}$H$_{40}$Sn: [M]$^+$, 388.21520. Found: m/z 388.21520.

**Tributyl(4-methylpent-1-en-2-yl)stannane (3t)**

A colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.78-0.98 (m, 23H), 1.25-1.37 (m, 6H), 1.39-1.65 (m, 7H), 2.12 (d, $^3$J$_{Sn-H}$ = 52.1 Hz, $J$ = 7.1 Hz, 2H), 5.13 (d, $^3$J$_{Sn-H}$ = 64.3 Hz, $J$ = 3.1 Hz, 1H), 5.62 (dt, $^3$J$_{Sn-H}$ = 141.7 Hz, $J$ = 3.1, 1.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 9.59, 13.70, 22.45, 27.42, 27.85, 29.11, 51.39, 125.72, 154.98; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -47.2; HRMS Calcd for C$_{14}$H$_{38}$Sn: [M]$^+$, 374.19955. Found: m/z 374.20060.

**5-(Tributylstanny)hex-5-enenitrile (3u)**

A colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.80-1.00 (m, 15H), 1.22-1.38 (m, 6H), 1.39-1.58 (m, 6H), 1.67-1.81 (m, 2H), 2.31 (t, $J$ = 7.2 Hz, 2H), 2.38 (t, $^3$J$_{Sn-H}$ = 44.6 Hz, $J$ = 7.3 Hz, 2H), 5.20 (s, $^3$J$_{Sn-H}$ = 61.5 Hz, 1H), 5.72 (s, $^3$J$_{Sn-H}$ = 133.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 9.53, 13.64, 16.32, 24.86, 27.33, 29.06, 39.64, 119.56, 126.87, 152.70; $^{119}$Sn NMR (CDCl$_3$) $\delta$ -45.5; HRMS Calcd for C$_{14}$H$_{39}$NSn: [M-Bu]$^+$, 328.10872. Found: m/z 328.10805.

**Tributyl(5-chloropent-1-en-2-yl)stannane (3v)**

A pale yellow oil: $^1$H NMR (CDCl$_3$) $\delta$ 0.82-0.98 (m, 15H), 1.26-1.36 (m, 6H), 1.40-1.57 (m, 6H), 1.85 (quint, $J$ = 7.5 Hz, 2H), 2.38 (t, $^3$J$_{Sn-H}$ = 45.0 Hz, $J$ = 7.5 Hz, 2H), 3.52 (t, $J$ = 6.7 Hz, 2H), 5.16 (dt, $^3$J$_{Sn-H}$ = 63.1 Hz, $J$ = 2.7, 1.1 Hz, 1H), 5.71 (dt, $^3$J$_{Sn-H}$ = 136.9 Hz, $J$ = 2.7, 1.5 Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 9.54, 13.69, 27.39, 29.10, 32.20, 38.09, 44.41, 89.
126.04, 153.51; $^{119}$Sn NMR (CDCl$_3$) δ -45.9; HRMS Calcd for C$_{13}$H$_{26}$ClSn: [M-Bu]$^+$, 337.07450. Found: m/z 337.07361.

[4-(Benzyloxy)but-1-en-2-yl]tributylstannane (3f)

![Structure](image)

A pale yellow oil: $^1$H NMR (CDCl$_3$) δ 0.80-1.00 (m, 15H), 1.25-1.35 (m, 6H), 1.39-1.55 (m, 6H), 2.58 (t, $^3$J$_{Sn-H} = 45.1$ Hz, $J = 7.0$ Hz, 2H), 3.50 (t, $J = 7.2$ Hz, 2H), 4.52 (s, 2H), 5.20 (d, $^3$J$_{Sn-H} = 63.0$ Hz, $J = 2.8$ Hz, 1H), 5.76 (dt, $^3$J$_{Sn-H} = 137.1$ Hz, $J = 2.8$, 1.5 Hz, 1H), 7.26-7.38 (m, 5H); $^{13}$C NMR (CDCl$_3$) δ 9.61, 13.69, 27.39, 29.08, 41.28, 70.21, 72.97, 126.86, 127.51, 127.72, 128.30, 138.38, 151.48; $^{119}$Sn NMR (CDCl$_3$) δ -45.1; HRMS Calcd for C$_{19}$H$_{31}$O$_2$Sn: [M-Bu]$^+$, 395.13969. Found: m/z 395.14076.

Tributyl(3-phenylprop-1-en-2-yl)stannane (3w)

![Structure](image)

A colorless oil: $^1$H NMR (CDCl$_3$) δ 0.54-0.71 (m, 6H), 0.77 (t, $J = 7.2$ Hz, 9H), 1.10-1.20 (m, 6H), 1.21-1.35 (m, 6H), 3.50 (s, $^3$J$_{Sn-H} = 46.0$ Hz, 2H), 5.15 (s, $^3$J$_{Sn-H} = 60.9$ Hz, 1H), 5.65 (s, $^3$J$_{Sn-H} = 134.3$ Hz, 1H), 7.04-7.14 (m, 3H), 7.19 (t, $J = 7.7$ Hz, 2H); $^{13}$C NMR (CDCl$_3$) δ 9.45, 13.69, 27.36, 28.97, 47.72, 126.00, 126.05, 128.22, 129.08, 140.23, 154.20; $^{119}$Sn NMR (CDCl$_3$) δ -44.1; HRMS Calcd for C$_{17}$H$_{25}$Sn: [M-Bu]$^+$, 351.11347. Found: m/z 351.11257.

Dideuteriostannylation of 1-tetradecyne.

A Schlenk tube equipped with a magnetic stirring bar was charged with Cu(OAc)$_2$ (0.015 mmol), tri-tert-butylphosphine (20 wt% solution in toluene, 0.053 mmol) and MeOH (2.5 mL). After the mixture was stirred at 80 °C for 0.5 h, the solvent was removed in vacuo at room temperature. To the residue were added toluene (0.2 mL), hexamethyldistannane (0.39 mmol), 1-tetradecyne (0.30 mmol) and deuterium oxide (0.90 mmol), and the resulting mixture was stirred at 110 °C for 2 h. The mixture was diluted with ethyl acetate and filtered through a Celite plug before evaporation of the solvent. Then the residue was diluted with toluene and filtered through neutral alumina (activity = IV). Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave the products. The ratio of the products was determined by $^1$H NMR.

Hydrogen–deuterium exchange of 1-tetradecyne.
A Schlenk tube equipped with a magnetic stirring bar was charged with Cu(OAc)$_2$ (0.015 mmol), tri-tert-butylphosphine (20 wt% solution in toluene, 0.053 mmol) and MeOH (2.5 mL). After the mixture was stirred at 80 °C for 0.5 h, the solvent was removed in vacuo at room temperature. To the residue were added toluene (0.2 mL), 1-tetradecyne (0.30 mmol) and deuterium oxide (0.90 mmol), and the resulting mixture was stirred at 110 °C for 12 h. The mixture was diluted with ethyl acetate and filtered through a Celite plug before evaporation of the solvent. The hydrogen–deuterium exchange ratio was determined by $^1$H NMR.

**Cross-coupling of 2n: Synthesis of ethyl 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (4).**

A Schlenk tube equipped with a magnetic stirring bar was charged with CsF (0.60 mmol). After CsF was dried with a heat gun in vacuo, Pd(dba)$_2$ (0.030 mmol), XPhos (0.060 mmol), CuI (0.060 mmol), 2n (0.30 mmol) and DMF (5.1 mL) were added. To this solution was added a DMF solution (1.5 mL) of ethyl 4-iodobenzoate (0.36 mmol) over 15 min, and the resulting mixture was stirred at 100 °C for 15 h before dilution with ethyl acetate. The solution was washed with sat.NH$_4$Cl (twice) and brine (twice), and the organic layer was dried over MgSO$_4$. Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave 4.$^2$

**Hydrolysis of 4: Synthesis of 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoic acid (bexarotene, 5).**

A MeOH solution (5 mL) of 4 (0.270 mmol) and 5M NaOHaq (125 mL) was stirred at reflux temperature overnight before the mixture was acidified with 5N HCl and extracted with ethyl acetate. After the organic extract was washed with water, the solvent was removed in vacuo to give 5.$^3$
Optimization of reaction conditions for hydrostannylation with Me₅SnSnMe₃ (Table S1).

Table S1

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<th>entry</th>
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<th>time (h)</th>
<th>NMR yield (%)</th>
<th>a:b</th>
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<td>2ᵃ</td>
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<td>PrBu₃</td>
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ᵃ H₂O = 10 equiv. ᵇ MeOH was used instead of H₂O. ᶜ Solvent = THF. ᵈ Solvent = MeCN. ᵉ Solvent = DMF. ᶠ (PPh₃)₃CuOAc (10 mol %) was used. Temperature = 60 °C. ᵍ Ad = 1-adamantyl. ʰ Temperature = 110 °C. ⁱ alkyn:distannane:H₂O = 1:1.3:3.
Optimization of reaction conditions for hydrostannylation with Me₃SiSnBu₃ (Table S2).

Table S2

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<th>a:b</th>
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</table>

<sup>a</sup> Cyp = cyclopentyl.  
<sup>b</sup> Ad = 1-admantyl.  
<sup>c</sup> Temperature = 50 °C.  
<sup>d</sup> Temperature = 80 °C.  
<sup>e</sup> tBuMe₂Si–SnBu₃ was used instead of Me₃Si–SnBu₃. Temperature = 80 °C.
Formation of a distannane from a silylstannane (Schemes S1 and S2)

Treatment of a silylstannane (PhMe₂SiSnBu₃) with a proton source (tBuOH) in the presence of Cu(OAc)₂–PCy₃ catalyst was found to produce a distannane (Bu₃SnSnBu₃) and a disiloxane (PhMe₂SiOSiMe₂Ph) (Scheme S1, eq. a), whereas the reaction without the proton source (eq. b) or the copper catalyst (eq. c) did not give the distannane at all. Accordingly, this transformation should proceed through a pathway, which includes dehydrogenative coupling of tributyltin hydride, as depicted in Scheme S2.

Scheme S1

Scheme S2
References
$n\text{Oct} \quad \text{SnBu}_3 \quad 3q$
SnBu₃
$\text{BnO} - \text{SnBu}_3$