**Supporting Information for
Ruthenium-Catalyzed Hydrogenation of Alkynylstannanes
with Migration of the Stannyl Group**

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General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a Varian Gemini 2000 (^1H , 300 MHz; ^{13}C , 75 MHz) or a Varian UNITY 500 plus (^{119}Sn , 186 MHz; ^{31}P , 202 MHz; ^{13}C , 126 MHz) spectrometer using tetramethylsilane (^1H and ^{13}C) as an internal standard as well as tetrabutyltin (^{119}Sn) and phosphoric acid (^{31}P) as an external standard. Preparative recycling gel permeation chromatography was performed with JAI LC-908 equipped with JAIGEL-1H and -2H using chloroform as an eluent. High-resolution mass spectra were obtained with a Bruker Bio APEX 70e spectrometer. Unless otherwise noted, reagents were commercially available and used without further purification. Anhydrous DMSO was purchased from Aldrich Chemical Co. and used as received. Toluene and 1,4-dioxane were distilled from sodium/benzophenone ketyl. Alkynylstannanes **1d** and **1e** were prepared by the reaction of the corresponding terminal alkyne with tributyltin methoxide.¹ **1h**, **1l** and **1m** were synthesized from the corresponding alkynyl(trimethyl)silane and bis(tributyltin)oxide.² Other alkynylstannanes were prepared by the reaction of the corresponding alkynyllithium with tributyltin chloride. Their data of ^1H NMR are as follows.

1-(Tributylstannyl)oct-1-yne (1a). A colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 0.82–1.08 (m, 18 H), 1.24–1.68 (m, 20 H), 2.24 (t, J = 7.2 Hz, 2 H).

3-Methyl-1-(tributylstannyl)but-1-yne (1b). A colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 0.83–1.07 (m, 15 H), 1.17 (d, J = 6.6 Hz, 6 H), 1.24–1.40 (m, 6 H), 1.43–1.70 (m, 6 H), 2.59 (sept, J = 6.6 Hz, 1 H).

6-(Tributylstannyl)hex-5-yn-1-ol (1c). A colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 0.80–1.16 (m, 15 H), 1.33 (sext, J = 7.2 Hz, 6 H), 1.49–1.75 (m, 11 H), 2.29 (t, J = 6.9 Hz, 2 H), 3.68 (q, J = 6.0 Hz, 2 H).

Methyl 7-(tributylstannyl)hept-6-ynoate (1d). A colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 0.80–1.14 (m, 15 H), 1.33 (sext, J = 7.2 Hz, 6 H), 1.44–1.65 (m, 8 H), 1.69–1.81 (m, 2 H), 2.27 (t, J = 6.9 Hz, 2 H), 2.34 (t, J = 7.2 Hz, 2 H), 3.67 (s, 3 H).

***N,N*-Dimethyl-7-(tributylstannyl)hept-6-ynamide (1e).** A colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 0.80–1.14 (m, 15 H), 1.32 (sext, J = 7.2 Hz, 6 H), 1.46–1.80 (m, 10 H), 2.20–2.40 (m, 4 H), 2.93 (s, 3 H), 3.00 (s, 3 H).

6-(Tributylstannyl)hex-5-yne nitrile (1f). A colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 0.80–1.15 (m, 15 H), 1.32 (sext, $J = 7.2$ Hz, 6 H), 1.40–1.69 (m, 6 H), 1.85 (quint, $J = 7.2$ Hz, 2 H), 2.42 (t, $J = 6.6$ Hz, 2 H), 2.51 (t, $J = 7.2$ Hz, 2 H).

2-Ethoxy-1-(tributylstannyl)ethyne (1g). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.82–1.06 (m, 15 H), 1.20–1.70 (m, 15 H), 4.10 (q, $J = 7.2$ Hz, 2 H).

1,4-Bis(tributylstannyl)-1,3-butadiyne (1h). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.82–1.13 (m, 12 H), 1.32 (sext, $J = 7.2$ Hz, 12 H), 1.40–1.72 (m, 12 H).

2-Phenyl-1-(tributylstannyl)ethyne (1i). A colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 0.84–1.20 (m, 15 H), 1.37 (sext, $J = 7.2$ Hz, 6 H), 1.48–1.80 (m, 6 H), 7.24–7.30 (m, 3 H), 7.43–7.47 (m, 2 H).

2-(4-Methoxyphenyl)-1-(tributylstannyl)ethyne (1j). A colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 0.82–1.10 (m, 15 H), 1.37 (sext, $J = 7.2$ Hz, 6 H), 1.42–1.78 (m, 6 H), 3.80 (s, 3 H), 6.80 (dt, $J = 8.7, 2.4$ Hz, 2 H), 7.39 (dt, $J = 8.7, 2.4$ Hz, 2 H).

1-(Tributylstannyl)-2-(4-trifluoromethylphenyl)ethyne (1k). A colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 0.82–1.20 (m, 15 H), 1.37 (sext, $J = 7.2$ Hz, 6 H), 1.45–1.75 (m, 6 H), 7.53 (s, 4 H).

2-(4-Bromophenyl)-1-(tributylstannyl)ethyne (1l). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.82–1.18 (m, 15 H), 1.36 (sext, $J = 7.2$ Hz, 6 H), 1.44–1.74 (m, 6 H), 7.30 (dt, $J = 8.7, 2.1$ Hz, 2 H), 7.41 (dt, $J = 8.7, 2.1$ Hz, 2 H).

2-(*o*-Tolyl)-1-(tributylstannyl)ethyne (1m). A colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 0.84–1.18 (m, 15 H), 1.38 (sext, $J = 7.2$ Hz, 6 H), 1.46–1.79 (m, 6 H), 2.45 (s, 3 H), 7.06–7.15 (m, 1 H), 7.16–7.21 (m, 2 H), 7.40–7.47 (m, 1 H).

2-(Thien-3-yl)-1-(tributylstannyl)ethyne (1n). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.84–1.17 (m, 15 H), 1.36 (sext, $J = 7.2$ Hz, 6 H), 1.44–1.76 (m, 6 H), 7.11 (dd, $J = 4.8, 1.2$ Hz, 1 H), 7.21 (dd, $J = 4.8, 3.0$ Hz, 1 H), 7.42 (dd, $J = 3.0, 1.2$ Hz, 1 H).

2-(Cyclohexen-1-yl)-1-(tributylstannyl)ethyne (1o). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.84–1.14 (m, 15 H), 1.33 (sext, $J = 7.2$ Hz, 6 H), 1.40–1.70 (m, 10 H), 2.03–2.17 (m, 4 H), 6.09–6.14 (m, 1 H).

Ruthenium-Catalyzed Hydrogenation of Alkynylstannanes. A General Procedure. A solution of an alkynylstannane (0.40 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (18.4 mg, 0.020 mmol) and a ligand [tributylphosphine: 24.3 mg, 0.120 mmol or *N,N*-dimethyl-2-diphenylphosphinobenzylamine (PN): 12.8 mg, 0.0401 mmol] in DMSO (0.30

mL) was degassed by three freeze-thaw cycles. The solution was again frozen to be substituted by a hydrogen gas. The mixture was stirred at 80 °C under a hydrogen atmosphere. After the time specified in Table 2, water (5 mL) was added and the resulting mixture was extracted with ether (20 mL x 3). The combined organic layer was washed with brine (10 mL), and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by purification by gel permeation chromatography gave the corresponding 2-stannyl-1-alkene. Yields are listed in Table 2.

2-(Tributylstannyl)oct-1-ene (2a). A pale yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 0.74–1.00 (m, 18 H), 1.24–1.62 (m, 20 H), 2.12–2.34 (m, 2 H), 5.08 (dt, *J* = 3.0, 1.2 Hz, 1 H), 5.66 (dt, *J* = 3.0, 1.5 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 9.5, 13.6, 14.0, 22.6, 27.3, 28.9, 29.1, 29.6, 31.7, 41.4, 124.6, 156.0. ¹¹⁹Sn{¹H} NMR (186 MHz, CDCl₃): δ –47.5. HRMS (EI): Calcd for C₁₆H₃₃Sn [M–Bu]⁺, 345.1603; found, 345.1598.

3-Methyl-2-(tributylstannyl)but-1-ene (2b). A pale yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 0.78–0.99 (m, 15 H), 1.00 (d, *J* = 6.6 Hz, 6 H), 1.32 (sext, *J* = 7.2 Hz, 6 H), 1.39–1.60 (m, 6 H), 2.34–2.60 (m, 1 H), 5.03 (dd, *J* = 2.4, 0.9 Hz, 1 H), 5.67 (dd, *J* = 2.4, 1.2 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 10.0, 13.6, 23.0, 27.3, 29.0, 38.7, 42.7, 121.9, 162.8. ¹¹⁹Sn{¹H} NMR (186 MHz, CDCl₃): δ –46.6. HRMS (EI): Calcd for C₁₃H₂₇Sn [M–Bu]⁺, 303.1133; found, 303.1143.

5-(Tributylstannyl)hex-5-en-1-ol (2c). A pale yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 0.76–1.00 (m, 15 H), 1.30 (sext, *J* = 7.2 Hz, 6 H), 1.36–1.72 (m, 11 H), 2.15–2.36 (m, 2 H), 3.58–3.68 (m, 2 H), 5.10 (dt, *J* = 3.0, 0.9 Hz, 1 H), 5.66 (dt, *J* = 3.0, 1.2 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 9.4, 13.5, 25.5, 27.3, 29.0, 32.3, 40.8, 62.7, 125.0, 155.3. ¹¹⁹Sn{¹H} NMR (186 MHz, CDCl₃): δ –47.2. HRMS (EI): Calcd for C₁₄H₂₉OSn [M–Bu]⁺, 333.1239; found, 333.1223.

Methyl 6-(tributylstannyl)hept-6-enoate (2d). A pale yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 0.76–1.00 (m, 15 H), 1.30 (sext, *J* = 7.2 Hz, 6 H), 1.38–1.67 (m, 10 H), 2.12–2.37 (m, 2 H), 2.31 (t, *J* = 7.5 Hz, 2 H), 3.66 (s, 3 H), 5.10 (dt, *J* = 3.0, 1.2 Hz, 1 H), 5.66 (dt, *J* = 3.0, 1.5 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 9.4, 13.5, 24.5, 27.3, 28.9, 29.0, 33.8, 40.7, 51.4, 125.1, 155.0, 174.3. ¹¹⁹Sn{¹H} NMR (186 MHz, CDCl₃): δ –47.0. HRMS (EI): Calcd for C₁₆H₃₁O₂Sn [M–Bu]⁺, 375.1344; found, 375.1318.

***N,N*-Dimethyl-6-(tributylstannyl)hept-6-enamide (2e).** A pale yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 0.76–1.00 (m, 15 H), 1.24–1.78 (m, 16 H), 2.14–2.37 (m, 4 H), 2.94 (s, 3 H), 3.00 (s, 3 H), 5.10 (dt, *J* = 2.7, 0.9 Hz, 1 H), 5.67 (dt, *J* = 2.7, 1.5 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 9.4, 13.6, 24.8, 27.3, 29.0, 29.2, 33.2, 35.3, 37.2, 40.9, 125.0, 155.3, 173.2. ¹¹⁹Sn{¹H} NMR (186 MHz, CDCl₃): δ –47.2. HRMS (EI): Calcd for C₁₇H₃₄NOSn [M–Bu]⁺, 388.1661; found, 388.1666.

5-(Tributylstannyl)hex-5-enenitrile (2f). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.75–1.02 (m, 15 H), 1.31 (sext, $J = 7.2$ Hz, 6 H), 1.40–1.60 (m, 6 H), 1.74 (quint, $J = 7.2$ Hz, 2 H), 2.24–2.50 (m, 4 H), 5.20 (dt, $J = 2.4, 1.2$ Hz, 1 H), 5.72 (dt, $J = 2.4, 1.2$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ 9.4, 13.5, 16.2, 24.8, 27.3, 29.0, 39.6, 119.7, 127.0, 152.9. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –45.8. HRMS (EI): Calcd for $\text{C}_{14}\text{H}_{26}\text{NSn}$ $[\text{M}-\text{Bu}]^+$, 328.1086; found, 328.1069.

1-Ethoxy-1-(tributylstannyl)ethene (2g). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.76–1.00 (m, 15 H), 1.21 (t, $J = 6.9$ Hz, 3 H), 1.30 (sext, $J = 7.2$ Hz, 6 H), 1.38–1.65 (m, 6 H), 3.77 (q, $J = 6.9$ Hz, 2 H), 4.50 (d, $J = 7.2$ Hz, 1 H), 6.77 (d, $J = 7.2$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ 9.9, 13.6, 15.2, 27.2, 29.1, 66.7, 97.7, 157.2. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –49.9. HRMS (EI): Calcd for $\text{C}_{12}\text{H}_{25}\text{OSn}$ $[\text{M}-\text{Bu}]^+$, 305.0926; found, 305.0906.

2,4-Bis(tributylstannyl)but-1-en-3-yne (2h). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.80–1.14 (m, 30 H), 1.24–1.40 (m, 12 H), 1.41–1.70 (m, 12 H), 6.50 (s, 2 H). ^{13}C NMR (75 MHz, CDCl_3): δ 9.9, 10.8, 13.5, 13.6, 27.0, 27.2, 28.8, 29.1, 94.2, 111.4, 127.5, 145.9. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –57.8, –43.4. HRMS (ESI): Calcd for $\text{C}_{28}\text{H}_{56}\text{Sn}_2\text{Na}$ $[\text{M}+\text{Na}]^+$, 655.2329; found, 655.2286.

1-Phenyl-1-(tributylstannyl)ethene (2i). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.78–1.09 (m, 15 H), 1.29 (sext, $J = 7.2$ Hz, 6 H), 1.42–1.54 (m, 6 H), 5.42 (d, $J = 2.4$ Hz, 1 H), 6.03 (d, $J = 2.4$ Hz, 1 H), 7.14–7.23 (m, 3 H), 7.26–7.33 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 10.1, 13.5, 27.2, 28.9, 126.26, 126.35, 126.9, 128.3, 146.5, 154.8. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –40.1. HRMS (EI): Calcd for $\text{C}_{16}\text{H}_{25}\text{Sn}$ $[\text{M}-\text{Bu}]^+$, 337.0977; found, 337.0955.

1-(4-Methoxyphenyl)-1-(tributylstannyl)ethene (2j). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.78–1.09 (m, 15 H), 1.32 (sext, $J = 7.2$ Hz, 6 H), 1.39–1.62 (m, 6 H), 3.82 (s, 3 H), 5.35 (d, $J = 2.4$ Hz, 1 H), 6.02 (d, $J = 2.4$ Hz, 1 H), 6.86 (dt, $J = 8.6, 2.6$ Hz, 2 H), 7.15 (dt, $J = 8.6, 2.6$ Hz, 2 H). ^{13}C NMR (75 MHz, CDCl_3): δ 10.1, 13.5, 27.2, 28.9, 55.2, 113.8, 125.3, 127.5, 138.8, 153.7, 158.5. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –40.3. HRMS (EI): Calcd for $\text{C}_{17}\text{H}_{27}\text{OSn}$ $[\text{M}-\text{Bu}]^+$, 367.1083; found, 367.1045.

1-(Tributylstannyl)-1-(4-trifluoromethylphenyl)ethene (2k). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.76–1.10 (m, 15 H), 1.29 (sext, $J = 7.2$ Hz, 6 H), 1.36–1.60 (m, 6 H), 5.50 (d, $J = 2.4$ Hz, 1 H), 6.03 (d, $J = 2.4$ Hz, 1 H), 7.22 (d, $J = 8.1$ Hz, 2 H), 7.54 (d, $J = 8.1$ Hz, 2 H). ^{13}C NMR (126 MHz, CDCl_3): δ 10.4, 13.6, 27.2, 29.0, 124.5 (q, $J = 271$ Hz), 125.2 (q, $J = 3.8$ Hz), 126.5, 128.2 (q, $J = 32.2$ Hz), 128.5, 150.6, 154.1. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –38.4. HRMS (EI): Calcd for $\text{C}_{17}\text{H}_{24}\text{F}_3\text{Sn}$ $[\text{M}-\text{Bu}]^+$, 405.0851; found, 405.0832.

1-(4-Bromophenyl)-1-(tributylstannyl)ethene (2l). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.80–1.08 (m, 15 H), 1.29 (sext, $J = 7.2$ Hz, 6 H), 1.37–1.62 (m, 6 H), 5.43 (d, $J = 2.4$ Hz, 1 H), 6.00 (d, $J = 2.4$ Hz, 1 H), 7.02 (dt, $J = 8.7, 2.1$ Hz, 1 H), 7.41 (dt, $J = 8.7, 2.1$ Hz, 2 H). ^{13}C NMR (75 MHz, CDCl_3): δ 10.1, 13.5, 27.2, 28.9, 120.1, 127.5, 128.0, 131.4, 145.6, 153.8. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –38.6. HRMS (EI): Calcd for $\text{C}_{16}\text{H}_{24}\text{BrSn} [\text{M}-\text{Bu}]^+$, 415.0082; found, 415.0097.

1-(*o*-Tolyl)-1-(tributylstannyl)ethene (2m). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.70–1.10 (m, 15 H), 1.26 (sext, $J = 7.2$ Hz, 6 H), 1.33–1.62 (m, 6 H), 2.20 (s, 3 H), 5.52 (d, $J = 3.3$ Hz, 1 H), 5.75 (d, $J = 3.3$ Hz, 1 H), 6.83–6.89 (m, 1 H), 7.01–7.14 (m, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 10.1, 13.5, 20.2, 27.2, 28.8, 125.46, 125.51, 126.7, 127.7, 129.8, 133.1, 147.3, 156.2. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –44.8. HRMS (EI): Calcd for $\text{C}_{17}\text{H}_{27}\text{Sn} [\text{M}-\text{Bu}]^+$, 351.1133; found, 351.1140.

1-(Thien-3-yl)-1-(tributylstannyl)ethene (2n). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.74–1.07 (m, 15 H), 1.31 (sext, $J = 7.2$ Hz, 6 H), 1.42–1.59 (m, 6 H), 5.37 (d, $J = 2.5$ Hz, 1 H), 6.12 (d, $J = 2.5$ Hz, 1 H), 6.97 (dd, $J = 2.9, 1.4$ Hz, 1 H), 7.10 (dd, $J = 5.0, 1.4$ Hz, 1 H), 7.25 (dd, $J = 5.0, 2.9$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ 10.2, 13.6, 27.3, 29.0, 120.0, 125.3, 125.7, 125.8, 147.4, 147.5. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –39.4. HRMS (EI): Calcd for $\text{C}_{14}\text{H}_{23}\text{SSn} [\text{M}-\text{Bu}]^+$, 343.0541; found, 343.0514.

1-(Cyclohexen-1-yl)-1-(tributylstannyl)ethene (2o). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.76–1.03 (m, 15 H), 1.31 (sext, $J = 7.2$ Hz, 6 H), 1.42–1.72 (m, 10 H), 2.09–2.22 (m, 4 H), 5.11 (d, $J = 2.1$ Hz, 1 H), 5.56 (t, $J = 3.9$ Hz, 1 H), 5.81 (d, $J = 2.1$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ 10.2, 13.6, 22.4, 22.8, 25.9, 26.1, 27.3, 29.0, 121.5, 128.6, 141.2, 155.9. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –42.3. HRMS (EI): Calcd for $\text{C}_{16}\text{H}_{29}\text{Sn} [\text{M}-\text{Bu}]^+$, 341.1290; found, 341.1283.

1,1-Dideuterio-2-(tributylstannyl)oct-1-ene (2'a). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.76–1.00 (m, 18 H), 1.20–1.70 (m, 20 H), 2.23 (t, $J = 7.4$ Hz, 2 H). ^{13}C NMR (126 MHz, CDCl_3): δ 9.6, 13.6, 14.1, 22.7, 27.4, 29.0, 29.2, 29.7, 31.8, 41.3, 124.0 (quint, $J = 22.2$ Hz), 155.6. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –47.5. HRMS (EI): Calcd for $\text{C}_{16}\text{H}_{31}\text{D}_2\text{Sn} [\text{M}-\text{Bu}]^+$, 347.1726; found, 347.1709.

2,2-Dideuterio-1-phenyl-1-(tributylstannyl)ethene (2'i). A pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 0.78–1.10 (m, 15 H), 1.29 (sext, $J = 7.2$ Hz, 6 H), 1.42–1.60 (m, 6 H), 7.13–7.23 (m, 3 H), 7.24–7.33 (m, 2 H). ^{13}C NMR (126 MHz, CDCl_3): δ 10.3, 13.6, 27.3, 29.0, 126.2, 126.3, 128.3, 146.5, 154.5; The resonance of CD_2 , which should have appeared at ca. 126.2 ppm as a quintet, was not detected due to its low intensity as well as overlap with that of carbon atoms of the phenyl group. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ –39.6. HRMS (EI): Calcd for $\text{C}_{16}\text{H}_{23}\text{D}_2\text{Sn} [\text{M}-\text{Bu}]^+$, 339.1101; found, 339.1082.

The Coupling Reaction of 1,1-Dideuterio-2-(tributylstannyl)oct-1-ene (2'a) with Iodobenzene. A solution of **2'a** (80.7 mg, 0.200 mmol), iodobenzene (40.8 mg, 0.200 mmol), Pd(PPh₃)₄ (11.6 mg, 0.0100 mmol), CuCl (19.8 mg, 0.200 mmol) and LiCl (12.7 mg, 0.300 mmol) in DMSO (1.0 mL) was degassed by three freeze-thaw cycle. After the solution was stirred at 60 °C for 48 h, water (10 mL) was added and the resulting mixture was extracted with ether (20 mL x 3). The combined organic layer was washed with brine (10 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by purification by gel permeation chromatography gave 1,1-dideuterio-2-phenyl-1-octene (31.6 mg, 83%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 0.87 (t, *J* = 6.9 Hz, 3 H), 1.23–1.52 (m, 8 H), 2.49 (t, *J* = 7.4 Hz, 2 H), 7.27–7.36 (m, 3 H), 7.38–7.43 (m, 2 H). ¹³C NMR (126 MHz, CDCl₃): δ 14.0, 22.6, 28.3, 29.0, 31.7, 35.3, 113.4 (quint, *J* = 23.2 Hz), 126.1, 127.2, 128.2, 141.6, 148.7. HRMS (EI): Calcd for C₁₄H₁₈D₂ [M]⁺, 190.1688; found, 190.1680.

Hydroxymethylation of 1,1-Dideuterio-2-(tributylstannyl)oct-1-ene (2'a). To a solution of **2'a** (80.7 mg, 0.200 mmol) in THF (1.0 mL) was added BuLi (1.58 M in hexane, 127 μL, 0.200 mmol) at –78 °C and the resulting solution was stirred at –78 °C for 2 h. To this was added benzaldehyde (21.2 mg, 0.200 mmol) and the solution was stirred at 0 °C for 3 h. Water (5 mL) was added and the resulting mixture was extracted with diethyl ether (10 mL x 3). The combined organic layer was washed with brine (10 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by purification by gel permeation chromatography gave 3,3-dideuterio-2-hexyl-1-phenyl-2-propen-1-ol (36.9 mg, 84%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 0.85 (t, *J* = 6.9 Hz, 3 H), 1.16–1.45 (m, 8 H), 1.76–2.01 (m, 3 H), 5.15 (d, *J* = 3.6 Hz, 1 H) 7.26–7.39 (m, 5 H). ¹³C NMR (126 MHz, CDCl₃): δ 14.0, 22.6, 27.8, 29.1, 31.7, 31.8, 77.4, 109.1 (quint, *J* = 23.4 Hz), 126.7, 127.7, 128.4, 142.3, 151.1. HRMS (EI): Calcd for C₁₅H₂₀D₂O [M]⁺, 220.1793; found, 220.1798.

Deuteriolysis of 1,1-Dideuterio-2-(tributylstannyl)oct-1-ene (2'a). To a solution of **2'a** (80.7 mg, 0.200 mmol) in THF (1.0 mL) was added DCl (20 wt% in D₂O, 200 μL) and stirred at room temperature for 2 h. The resulting mixture was treated with a saturated NaHCO₃ aqueous solution (5 mL) and extracted with diethyl ether (10 mL x 3). The combined organic layer was washed with brine (10 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by distillation (125 °C/760 mmHg) gave 1,1,2-(trideuterio)oct-1-ene (18.4 mg, 80%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 0.88 (t, *J* = 6.8 Hz, 3 H), 1.20–1.45 (m, 8 H), 2.04 (t, *J* = 7.3 Hz, 2 H). ¹³C NMR (126 MHz, CDCl₃): δ 14.1, 22.6, 28.8, 28.9, 31.7, 33.6; The resonances of –CD=CD₂, which should had appeared at ca. 138.9 ppm and 113.7 ppm, were not detected due to their low intensity. MS (EI) *m/z* (rel intensity): 115 (7), 100 (2), 86 (23), 70 (57), 56 (100).

Preparation of RuH₂(CO)(PBU₃)₃.³ A suspension of NaBH₄ (1.59 g, 42.0 mmol) in EtOH (40 mL) was added to a mixture of RuCl₃·*n*H₂O (1.00 g, 3.80 mmol) and PBU₃ (6.27 g, 31.0 mmol) in ethanol (40 mL) at 70 °C. After being stirred for 1 h, the mixture was cooled to 20 °C and the solvent was removed in vacuo. To this was added benzene (50 mL) and the

suspension was stirred at room temperature for 30 min followed by filtration under N₂. The filtrate was bubbled with CO gas at 60 °C. After 24 h, the solution was cooled to 20 °C and the volatile was pumped up under vacuum. Hexane (50 mL) was added to the resulting brown oil and stirred for 30 min successively. Filtration under N₂ followed by evaporation of hexane gave RuH₂(CO)(PBU₃)₃ (1.10 g, 40%) as a brown oil. ¹H NMR (300 MHz, CDCl₃): δ -9.70 (dtd, *J* = 75.3, 29.4, 6.0 Hz, 1 H), -8.23 (tdd, *J* = 25.8, 24.0, 6.0 Hz, 1 H), 0.90–1.80 (m, 81 H). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 20.7 (t, *J* = 20.4 Hz, 1 P), 32.8 (d, *J* = 20.4 Hz, 2 P). HRMS (ESI): Calcd for C₃₇H₈₂OP₃¹¹²Ru [M-H]⁺, 737.4618, found, 737.4582.

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