SUPPLEMENTARY MATERIAL

A Novel 1,3-Stannyl Shift Promoted Intramolecular Cyclizations of α-Stannyl Radicals with Formyl Group

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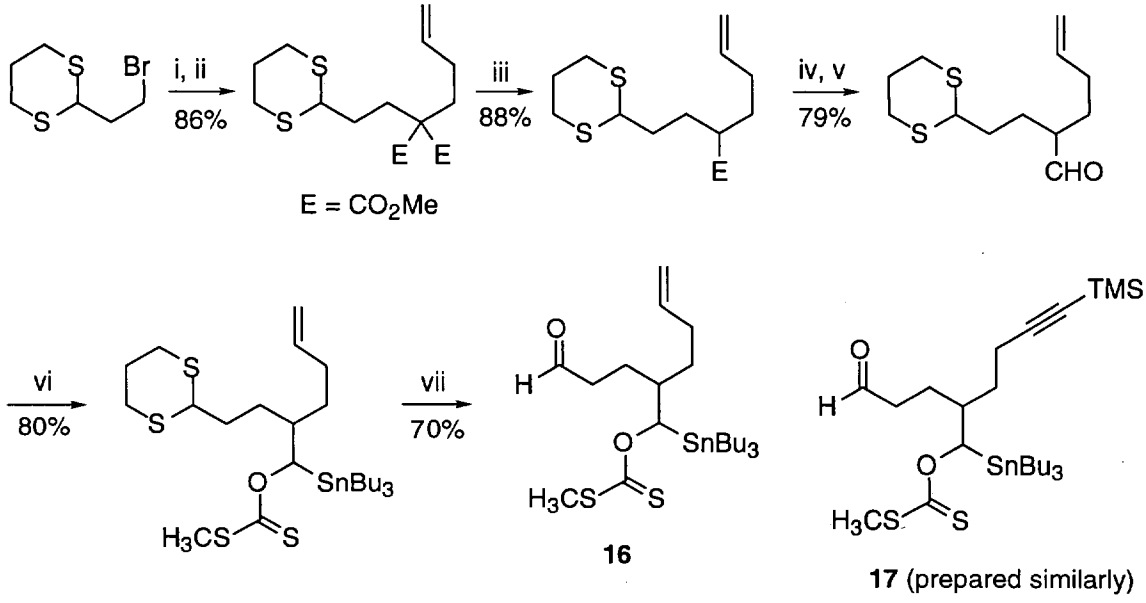
This supplementary material includes:

1. Scheme for the synthesis of **16** and **17**.
2. Details of compound characterization of **2a**, **b** , **4**, **12**, **13**, **15–20**, and **25–27**.

Scheme for the synthesis of 16 and 17



Reagents and conditions: i, $CH_2(CO_2Me)_2$, NaH, DMF, 80 °C. ii, NaH, DMF; $BrCH_2CH_2CH{=}CH_2$. iii, NaCN, DMF, 120 °C. iv, LAH, THF. v, Swern oxidation. vi, Bu_3SnLi, THF; CS_2,; MeI. vii, MeI (15 equiv), acetone/H_2O.

5-Bromo-5-(tributylstannyl)pentanal (2a). IR (neat) 1718 cm^{-1}; ^1H NMR (200 MHz) δ 0.80–1.17 (m, 15 H), 1.18–1.82 (m, 14 H), 1.82–2.12 (m, 2 H), 2.32–2.56 (m, 2 H), 3.58 (dd, J = 8.3, 5.5 Hz, 1 H), 9.74 (br s, 1 H); ^{13}C NMR (75 MHz) δ 9.9 ($J_{C\text{-}Sn}$ = 310 Hz), 13.6, 22.4, 27.3 ($J_{C\text{-}Sn}$ = 60 Hz), 28.9 ($J_{C\text{-}Sn}$ = 20 Hz), 36.8, 38.6, 42.8, 202.0. Anal. Calcd for $C_{17}H_{35}BrOSn$: C, 44.97; H, 7.77. Found: C, 45.37; H, 8.11.

6-Bromo-6-(tributylstannyl)hexanal (2b). IR (neat) 1718 cm^{-1}; ^1H NMR (200 MHz) δ 0.79–1.03 (m, 15 H), 1.18–2.10 (m, 18 H), 2.44 (td, J = 7.1, 1.6 Hz, 2 H), 3.60 (dd, J = 8.5, 5.9 Hz, 1 H), 9.76 (t, J = 1.6 Hz, 1 H); ^{13}C NMR (50 MHz) δ 9.9 (t; $J_{C\text{-}Sn}$ = 310 Hz), 13.6 (q), 21.2 (t), 27.3 (t; $J_{C\text{-}Sn}$ = 60 Hz), 28.9 (t; $J_{C\text{-}Sn}$ = 20 Hz), 29.3 (t), 37.3(t), 39.0 (d), 43.7 (t), 202.2 (d); HRMS Calcd for $C_{18}H_{37}{}^{81}BrO^{118}Sn$ *m/z* 468.1023, found *m/z* 468.1029.

5-(Tributylstannyl)pentanal (4). IR (neat) 1718 cm^{-1}; ^1H NMR (300 MHz) δ 0.65–1.00 (m, 17 H), 1.20–1.75 (m, 16 H), 2.41 (td, J = 7.2, 1.9 Hz, 2 H), 9.74 (t, J = 1.9 Hz, 1 H); ^{13}C NMR (75 MHz) δ 8.5 (t; $J_{C\text{-}Sn}$ = 310 Hz), 8.7 (t; $J_{C\text{-}Sn}$ = 310 Hz), 13.6 (q), 26.8 (t), 27.4 (t; $J_{C\text{-}Sn}$ = 60 Hz), 28.2 (t), 29.2 (t; $J_{C\text{-}Sn}$ = 20 Hz), 43.5 (t), 202.9 (d); HRMS Calcd for $C_{17}H_{35}O^{118}Sn$ (M^+–H) *m/z* 373.1704, found *m/z* 373.1706.

6-(Tributylstannyl)hexanal (12). IR (neat) 1720 cm^{-1}; ^1H NMR (300 MHz) δ 0.65–0.90 (m, 17 H), 1.20–1.69 (m overlapped with quintet, J = 7.5 Hz, at 1.61, 18 H), 2.38 (t, J = 7.4 Hz, 2 H), 9.73 (br s, 1 H); ^{13}C NMR (75 MHz) δ 8.6 (t; $J_{C\text{-}Sn}$ = 310 Hz), 8.7 (t; $J_{C\text{-}Sn}$ = 310 Hz), 13.7 (q), 21.6 (t), 26.7 (t), 27.4 (t; $J_{C\text{-}Sn}$ = 60 Hz), 29.2 (t; $J_{C\text{-}Sn}$ = 20 Hz), 33.9 (t; $J_{C\text{-}Sn}$ = 60 Hz), 43.9 (t), 202.8 (d); HRMS Calcd for $C_{18}H_{37}O^{120}Sn$ (M^+–H) *m/z* 389.1866, found *m/z* 389.1862.

6-(Tributylstannyl)hexanol (13). IR (neat) 3354 (br) cm^{-1}; ^1H NMR (300 MHz) δ 0.66–0.91 (m, 17 H), 1.20–1.60 (m, 20 H), 1.70 (s, 1 H), 3.62 (t, J = 6.6 Hz, 2 H); ^{13}C NMR (75 MHz) δ 8.7 ($J_{C\text{-}Sn}$ = 310 Hz), 8.9 ($J_{C\text{-}Sn}$ = 310 Hz), 13.7, 25.3, 26.9, 27.3 ($J_{C\text{-}Sn}$ = 60 Hz),

29.2 ($J_{C\text{-}Sn}$ = 20 Hz), 32.8, 34.2 (J = 60 Hz), 63.1; HRMS Calcd for $C_{18}H_{39}O^{120}Sn$ (M^+–H) *m/z* 391.2023, found *m/z* 391.2031.

2-[4-(Tributylstannyl)butyl]-4-pentenal (15). IR (neat) 1729, 1642 cm^{-1}; ^1H NMR (300 MHz) δ 0.62–0.92 (m, 17 H), 1.15–1.70 (m, 18 H), 2.13–2.45 (m, 3 H), 5.00–5.10 (m, 2 H), 5.63–5.10 (m, 1 H); ^{13}C NMR (75 MHz) δ 8.7 (t; $J_{C\text{-}Sn}$ = 310 Hz), 8.8 (t; $J_{C\text{-}Sn}$ = 310 Hz), 13.7 (q), 27.0 (t), 27.4 (t; $J_{C\text{-}Sn}$ = 60 Hz), 28.0 (t), 29.2 (t; $J_{C\text{-}Sn}$ = 20 Hz), 31.7 (t; J = 60 Hz), 33.1 (t), 51.3 (d), 117.1 (t), 135.0 (d), 204.7 (d). Anal. Calcd for $C_{21}H_{42}OSn$: C, 58.76; H, 9.86. Found: C, 58.66; H, 9.85.

***O*-[1-(Tributylstannyl)-2-(2-formylethyl)-5-hexenyl] *S*-methyl dithiocarbonate (16)**. A 1:1 mixture of two diatereomers. IR (neat) 1718, 1633 cm^{-1}; ^1H NMR (300 MHz) δ 0.82–1.12 (m overlapped with t, J = 7.7 Hz, at 0.87, 15 H), 1.28 (sixtet, J = 7.2 Hz, 6 H), 1.39–1.98 (m, 10 H), 1.98–2.34 (m, 3 H), 2.37–2.64 (m overlapped with s at 2.52, 5 H), 4.91–5.10 (m, 2 H), 5.67–5.86 (m, 1 H), 5.96 (d, J = 5.9 Hz, 0.5 H, OCH of one isomer), 6.04 (d, J = 4.1 Hz, 0.5 H, OCH of another isomer), 9.71–9.80 (two overlapped t, J = 1.5 Hz, at 9.75 and 9.76, 1 H). Anal. Calcd for $C_{23}H_{44}O_2S_2Sn$: C, 51.60; H, 8.28. Found: C, 51.21; H, 8.30.

***O*-[1-(Tributylstannyl)-2-(2-formylethyl)-6-trimethylsilyl-5-hexynyl] *S*-methyl dithiocarbonate (17)**. A 1:1 mixture of two diatereomers. IR (neat) 2715, 1728 cm^{-1}; ^1H NMR (200 MHz) δ 0.09–0.17 (two overlapped s at 0.11 and 0.12, 9 H), 0.80–1.09 (m overlapped with t, J = 7.2 Hz, at 0.87, 15 H), 1.28 (sixtet, J = 7.2 Hz, 6 H), 1.36–1.90 (m, 10 H), 1.93–2.18 (m, 1 H), 2.19–2.71 (m overlapped with t, J = 7.2 Hz at 0.27, and s at 2.51, 7 H), 5.95 (d, J = 4.9 Hz, 0.5 H, OCH of one isomer), 6.03 (d, J = 3.9 Hz, 0.5 H, OCH of another isomer), 9.75 (br s, 0.5 H, CHO of one isomer), 9.78 (br s, 0.5 H, CHO of another isomer). Anal. Calcd for $C_{26}H_{50}O_2S_2SiSn$: C, 51.57; H, 8.32. Found: C, 51.46; H, 8.40.

3-(3-Methyl-2-tributylstannylcyclopentyl)propanal (18). IR (neat) 1720 cm^{-1}; ^1H NMR (200 MHz) δ 0.70–2.20 (m, 39 H), 2.25–2.50 (m, 2 H), 9.70–9.75 (m, 1 H); HRMS Calcd for $C_{21}H_{42}O^{120}Sn$ *m/z* 430.2258, found *m/z* 430.2268.

3-(3-Methyl-2-tributylstannylcyclopentyl)propanol (19). IR (CH_2Cl_2) 3330 (br) cm^{-1}; ^1H NMR (200 MHz) δ 0.60–1.01 (m overlapped with t, *J* = 7.0 Hz, at 0.87, 19 H), 1.01–2.05 (m, 23 H), 3.60 (t, *J* = 6.5 Hz, 2 H); HRMS calcd for $C_{21}H_{44}O^{120}Sn$ *m/z* 432.2414, found *m/z* 432.2406.

3-*exo*-Hydroxy-8-*endo*-methyl-*cis*-bicyclo[3.3.0]octane (20). IR (CH_2Cl_2) 3350 (br) cm^{-1}; ^1H NMR (200 MHz) δ 0.75–2.19 (m overlapped with d, *J* = 6.7 Hz, at 1.07, 14 H), 2.61 (quintet, *J* = 7.1 Hz, 1 H), 3.96 (dt, *J* = 8.4, 5.8 Hz, 1 H); ^{13}C (50 MHz) δ 14.8 (q), 30.9 (t), 32.7 (t), 33.1 (t), 36.3 (t), 36.9 (d), 42.2 (d), 55.3 (d), 74.9 (d); HRMS calcd for C_9H_{14} ($M^+–H_2O$) *m/z* 122.1096, found *m/z* 122.1098.

2-*exo*-Hydroxy-8-(*Z*)-(trimethylsilyl)methylene-*cis*-bicyclo[3.3.0]octane (*Z*-25). mp 55.0–56.5 °C; IR (KBr) 3330 (br), 1619 cm^{-1}; ^1H NMR (200 MHz; C_6D_6) δ 0.26 (s, 9 H), 1.09–1.69 (m, 6 H), 1.88–2.34 (m, 3H), 2.66 (qt, *J* = 8.3, 3.0 Hz, 1 H), 2.92 (br d, *J* = 8.3 Hz, 1 H), 3.96 (dt, *J* = 4.3, 2.6 Hz, 1 H), 5.49 (q, *J* = 1.7 Hz, 1 H); ^{13}C NMR (75 MHz; C_6D_6) δ 0.4 (q), 31.6 (t), 32.3 (t), 36.0 (t), 38.3 (t), 42.9 (d), 57.0 (d), 81.7 (d), 120.8 (d), 164.5 (s); HRMS calcd for $C_{12}H_{22}OSi$ *m/z* 210.1440, found *m/z* 210.1443.

2-*exo*-Hydroxy-8-(*E*)-(trimethylsilyl)methylene-*cis*-bicyclo[3.3.0]octane (*E*-25). IR (neat) 3341 (br), 1620 cm^{-1}; ^1H NMR (300 MHz; C_6D_6) δ 0.16 (s, 9 H), 0.80–1.01 (m, 1 H), 1.06–1.29 (m, 2 H), 1.38–1.49 (m, 1 H), 1.49–1.72 (m, 2 H), 1.97 (dq, *J* = 12.6, 8.4 Hz, 1 H), 2.18 (t, *J* = 7.1 Hz, 2 H), 2.48–2.61 (m, 1 H), 2.71 (br d, *J* = 8.4 Hz, 1 H), 3.94 (br s, 1 H), 5.53 (br s, 1 H); ^{13}C NMR (75 Hz; C_6D_6) δ 0.0 (q), 30.7 (t), 32.6 (t), 33.3 (t), 35.1 (t), 41.6 (d), 61.4 (d), 81.4 (d), 119.6 (d), 165.1 (s); HRMS calcd for $C_{12}H_{22}OSi$ *m/z* 210.1440, found *m/z* 210.1443.

2-*endo*-Hydroxy-8-(*E*)-(trimethylsilyl)methylene-*cis*-bicyclo[3.3.0]octane (*E*-26). IR (neat) 3553 (br), 1618 cm^{-1}; ^1H NMR (300 MHz; C_6D_6) δ 0.10 (s, 9 H), 1.37–1.89 (m, 7 H), 2.13–2.40 (m, 3 H), 2.79 (br t, J = 7.8 Hz, 1 H), 4.09–4.16 (m, 1 H), 5.34 (q, J = 1.9 Hz, 1 H); ^{13}C NMR (75 MHz; C_6D_6) δ –0.1 (q), 30.7 (t), 33.6 (t), 35.4 (t), 36.5 (t), 42.8 (d), 58.8 (d), 74.2 (d), 122.3 (d), 163.7 (s); HRMS calcd for $C_{12}H_{21}OSi$ (M^+–1) *m/z* 209.1361, found *m/z* 209.1365.

2-*endo*-Hydroxy-8-(*Z*)-(trimethylsilyl)methylene-*cis*-bicyclo[3.3.0]octane (*Z*-26). IR (neat) 3557 (br), 1619 cm^{-1}; ^1H NMR (300 MHz; C_6D_6) δ 0.11 (s, 9 H), 1.32–1.72 (m, 6 H), 1.79–1.90 (m, 1 H), 2.09–2.21 (m, 1 H), 2.35–2.49 (m, 2 H), 2.91 (t, J = 8.6 Hz, 1 H), 4.11–4.21 (m, 1 H), 5.57 (br s, 1 H); ^{13}C NMR (75 MHz; C_6D_6) δ 0.0 (q), 30.9 (t), 31.0 (t), 36.6 (t), 40.1 (t), 45.1 (d), 53.8 (d), 74.7 (d), 122.7 (d), 163.0 (s); HRMS calcd for $C_{12}H_{22}OSi$ *m/z* 210.1440, found *m/z* 210.1454.

3-[3-(Trimethylsilylmethylene)-2-(tributylstannyl)cyclopentyl]propanol (27). A mixture of stereoisomers. IR (CH_2Cl_2) 3617 (br), 1619 cm^{-1}; ^1H NMR (200 MHz) δ –0.02 (s, 6.6 H), 0.12 (s, 2.4 H), 0.62–1.01 (m overlapped with t, J = 7.0 Hz, at 0.87, 15 H), 1.11–1.63 (m, 18 H), 1.83–2.28 (m overlapped with t, J = 7.4 Hz, at 2.18, 4 H), 2.49–2.67 (m, 1 H), 3.62 (t, J = 6.6 Hz, 2 H), 4.95 (br s, 1 H); HRMS calcd for $C_{24}H_{50}OSi^{120}Sn$ *m/z* 502.2653, found *m/z* 502.2656.