Copper-catalyzed hydrostannation of activated alkynes

Lai To Leung, Sze Kar Leung, and Pauline Chiu*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

pchiu@hku.hk

Table of Contents:

1. Experimental and characterizations for compounds **2e**, **7b-c**, **3a-f**, **8c-d** and **9a-d** (pp. S2-S10)
2. ¹H and ¹³C NMR spectra for compounds **2e**, **7b-c**, **3a-f**, and **9a-c** (pp. S11-S22)

General Experimental

All reactions were performed in oven-dried flasks under argon or nitrogen. All glassware and syringes were dried in oven for at least 4 hours. Dried syringes were stored in a dry box while the glassware was cooled under a stream of a dry argon or nitrogen. Solvents and solution reagents were transferred with syringes or cannulae using standard inert atmosphere techniques. Stryker's reagent, $[(\text{Ph}_3\text{P})\text{CuH}]_6$, (**1**) was stored and weighed inside a dry-box. Reactions were monitored by TLC using E. Merck 0.2 mm pre-coated silica gel plates (Kieselgel 60 F₂₅₄). Components were visualized by illumination with a short-wavelength UV light and staining in potassium permanganate solution or anisaldehyde followed by heating. Flash column chromatography was performed on E. Merck silica gel 60 (230-400 mesh ASTM).

Instrumental analysis

All ^1H and ^{13}C NMR spectra were recorded in deuteriochloroform (CDCl_3) unless otherwise specified, with tetramethylsilane (TMS) as an internal standard at ambient temperature on a Bruker DPX 300, 400 or 500 Fourier Transform Spectrometer operating at 300 MHz, 400 MHz or 500 MHz for ^1H and 75 MHz, 100 MHz or 125 MHz respectively for ^{13}C . All the spectra were calibrated at δ 7.26 or δ 0.00 ppm for ^1H and δ 77.03 for ^{13}C . Spectral features were designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Both $J(^{117}\text{SnH})$ and $J(^{119}\text{SnH})$, and $J(^{117}\text{SnC})$ and $J(^{119}\text{SnC})$ values are reported when the ^{117}Sn and ^{119}Sn satellite peaks are clearly distinct. Otherwise the indicated value of J_{SnH} and J_{SnC} values must be considered as an approximate mean value of $J(^{117}\text{SnH})$ and $J(^{119}\text{SnH})$ due to overlap of the satellite peaks. IR absorption spectra were recorded as a solution in CH_2Cl_2 on a Bio-Rad Fourier Transform 165 Spectrophotometer from 4000 cm^{-1} to 400 cm^{-1} with subtraction of peaks for the solvent. Mass Spectra were obtained from a Finnigan MAT 95 mass spectrometer for both low resolution and high resolution, with accurate mass reported for the molecular ion (M^+) or the next largest fragment thereof.

Chemicals:

Solvents and chemicals were purified according to the literature procedures.¹ Solvents were freshly distilled before use. THF was distilled over sodium benzophenone ketyl; toluene, benzene, cyclohexane, dichloromethane and acetonitrile were distilled over granular calcium hydride.

Tributyltin hydride, methyl 2-butynoate (**2b**), ethyl 2-heptynoate (**2c**), methyl 2-octynoate (**2d**), and 3-hexyn-2-one (**7a**) are commercially available and used as received. **1**², ethyl 4-(*tert*-butyldimethylsilyloxy)-2-butynoate (**2a**)³, 1-(1-oxo-2-butynyl)piperidine (**2f**)⁴ and 2,2-dimethylnon-4-yn-3-one (**7d**)⁵ were prepared according to literature procedures. *i*-Butyl 2-octynoate (**2e**), 3-decyn-2-one (**7b**) and 4-nonyl-3-one (**7c**) were prepared as described below.

Preparation of substrates

2e. A solution of 1-octyne (0.20 mL, 1.36 mmol) in 5 mL THF at -78 °C under argon, was treated with *n*-BuLi in hexane (1.6 M, 1.02 mL, 1.63 mmol). The reaction mixture was stirred for 1 h at -70°C and treated with freshly distilled isobutyl chloroformate (0.21 mL, 1.63 mmol). It was warmed to room temperature over 12 h. The reaction mixture was quenched with 3 M HCl and extracted with ether (3 x 3 mL). The combined organic layers were washed with saturated NaHCO₃ and brine, dried over anhydrous MgSO₄, and the volatiles were removed *in vacuo*. The residue was purified by flash chromatography (5% EtOAc/hexane) to give 0.2581 g (91% yield) of **2e** as a colorless oil. **2e:** R_f = 0.56 (10% EtOAc/hexane); ¹H NMR (CDCl₃, 300 Hz): δ 3.91 (d, J =6.7 Hz, 2H), 2.30 (t, J = 7.1 Hz, 2H), 1.95 (m, 1H), 1.51-1.58 (m, 2H), 1.33-1.43 (m, 2H), 1.21-1.31 (m, 4H), 0.93 (d, J = 6.7 Hz, 6H), 0.87 (t, J = 6.7 Hz, 3H). ¹³C NMR (CDCl₃, 75 Hz): δ 154.0 (C), 89.4 (C), 73.1 (C), 71.7 (CH₂), 31.2 (CH₂), 28.5 (CH₂), 27.6 (CH), 27.5 (CH₂), 22.4 (CH₂), 19.0 (CH₃), 18.7 (CH₂), 13.9 (CH₃); IR (CH₂Cl₂): 2962s, 2934s, 2875m, 2237s (C $\equiv$ C), 1703s (C=O), 1470m, 1396w, 1376m, 1303m, 1278s, 1273w, 1258w, 1253s cm⁻¹. LRMS (EI, 20 eV) m/z (relative intensity): 155 ([M⁺ - OC₄H₉], 56), 137 (100), 125 (11), 109 (8); HRMS (EI) m/z calcd for C₉H₁₃O [M⁺ - OC₄H₉]: 137.0966, found: 137.0968.

¹ Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory chemicals*. Butterworth: London, 1996.

² Chiu, P.; Li, Z.; Fung, C.M.; *Tetrahedron Lett.* **2003**, 44, 455.

³ Rossi, R.; Carpita, A.; Cossi, P.; *Tetrahedron*. **1992**, 48, 8801.

⁴ Ma, D.; Lu, X; *Tetrahedron*. **1990** 46, 3189.

⁵ Chopra, A. K.; Moss, G. P.; Weedon, B. C. L.; *J. Chem. Soc. Perkin Trans. I* **1988**, 1371.

7b. To a solution of 1-octyne (1.0 mL, 6.78 mmol) in 20 mL in THF at -78 °C was added *n*-BuLi in hexane (1.6 M, 5.5 mL, 8.80 mmol) under argon. The mixture was stirred for 1 h and then treated with N-methoxy-N-methylacetamide (0.87 mL, 8.17 mmol) in 2 mL THF. The reaction mixture was stirred at room temperature for 4 h, then quenched by the addition of 10 mL of 3 M HCl. The reaction mixture was extracted with ether (3 x 10 mL). The combined organic layers were washed with saturated NaHCO₃, brine, dried over anhydrous MgSO₄, and the volatiles were removed *in vacuo*. The residue was purified by flash chromatography (10% EtOAc/hexane) to afford 0.9636 g (93% yield) **7b** as a colorless oil. **7b**: *R*_f = 0.62 (20% EtOAc/hexane); ¹H NMR (CDCl₃, 400 Hz): δ2.34 (t, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.52-1.59 (m, 2H), 1.37-1.42 (m, 2H), 1.22-1.35 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (CDCl₃, 100 Hz): δ184.9 (C), 94.2 (C), 81.4 (C), 32.7 (CH₃), 31.2 (CH₂), 28.5 (CH₂), 27.6 (CH₂), 22.4 (CH₂), 18.9 (CH₂), 14.0 (CH₃); IR (CH₂Cl₂): 2960_s, 2934_s, 2855_m, 2211_s (C≡C), 1672_s (C=O), 1470_w, 1402_w, 1360_m, 12754_s, 1256_s cm⁻¹. LRMS (EI, 20eV) *m/z* (relative intensity): 137 ([M⁺ - CH₃], 100), 126 (16), 109 (12); HRMS (EI) *m/z* calcd for C₉H₁₃O [M⁺ - CH₃]: 137.0966, found: 137.0972 .

7c. *n*-BuLi in hexane (2.5 M, 4.9 mL, 12.25 mmol) was added slowly to a solution of 1-hexyne (1.4 mL, 12.25 mmol) in 30 mL THF at -78 °C under argon and stirred for 1 h. The mixture was then treated with N-methoxy-N-methylpropionamide⁶ (1.2 g, 10.24 mmol) in 5 mL THF at -55 °C. After stirring for 1.5 h at ambient temperature, the resulting solution was acidified to pH 1 with 3 M HCl. The aqueous layer was extracted with diethyl ether (3 x 10 mL). . The combined organic layers were washed with brine, dried over MgSO₄, and removed of solvent *in vacuo*. The residue was purified by flash chromatography (3% EtOAc/Hex) to give 1.2517 g (88% yield) of **7c** as a colorless oil. **7c**: *R*_f = 0.55 (10% EtOAc/Hex); ¹H NMR (CDCl₃, 400 Hz): δ2.50 (q, *J* = 7.4 Hz, 2H), 2.30 (t, *J* = 7.0 Hz, 2H), 1.46-1.55 (m, 2H), 1.34-1.46 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (CDCl₃, 100 Hz): δ188.7 (C), 94.1 (C), 80.5 (C), 38.7 (CH₂), 29.6 (CH₂), 21.8 (CH₂), 18.5 (CH₂), 13.3 (CH₃), 8.0 (CH₃); IR (CH₂Cl₂): 2969_s,

⁶ Wolberg, M.; Hummel, W.; Müller, M.; *Chem. Eur. J.* **2001**, *7*, 4562.

2937s, 2869m, 2217s (C≡C), 1664s (C=O), 1457m, 1402w, 1356m, 1303m, 1275s, 1203w cm⁻¹. LRMS (EI, 20eV) *m/z* (relative intensity): 109 ([M⁺ - C₂H₅], 100), 81 (7); HRMS (EI) *m/z* calcd for C₇H₉O [M⁺ - C₂H₅]: 109.0653, found: 109.0652.

General procedure for the hydrostannation of 2a catalyzed by 1. Stryker's reagent (**1**) (11 mg, 0.1 equiv) was dissolved in distilled and degassed toluene (1 mL) under argon at room temperature to give a bright red solution. To this solution was added **2a** (80 mg, 0.33 mmol) and Bu₃SnH (0.13 mL, 0.50 mol) in 1 mL toluene slowly via cannula. The color of the solution changed gradually from bright red to dark brown. The reaction mixture was stirred at room temperature. After the full consumption of **2a** as monitored by TLC, the solvent was removed in vacuo. The residue was dissolved in CDCl₃ and analyzed by ¹H and/or ¹³C NMR to obtain the ratio of the components. Then the crude mixture was purified quickly by flash chromatography using silica gel pretreated with 1% Et₃N. Residual tin hydride was removed by flushing with pure hexane. The mixture thus obtained was again analyzed by ¹H and/or ¹³C NMR to confirm the ratio of the components. Following this, the mixture was repurified carefully by flash chromatography using silica gel pretreated with 1% Et₃N eluting with 2% EtOAc in hexane to obtain analytically pure samples of vinylstannane **3a** (83% yield) and **5a**⁷.

3a: a colorless oil; *R_f* = 0.45 (5% EtOAc/Hex); ¹H NMR (400 MHz, CDCl₃): δ 6.29 (t, ³*J*_{HH} = 4.6 Hz, ³*J*_{SnH} = 61.2/58.6 Hz, 1H) (H-5), 4.61 (d, *J* = 4.6 Hz, 2H) (H-6), 4.12 (q, *J* = 7.1 Hz, 2H) (H-2), 1.38-1.57 (m, 6H) (H-11), 1.25-1.35 (m, 9H) (H-1, 12), 0.86-1.05 (m, 15H) (H-10, 13), 0.90 (s, 9H) (H-9), 0.07 (s, 6H) (H-7); ¹³C NMR (100 MHz, CDCl₃): δ 170.2 (C-3), 157.4 (C-5), 134.2 (C-4), 63.8 (³*J*_{SnC} = 44.4 Hz) (C-6), 60.2 (C-2), 28.9 (²*J*_{SnC} = 20.5 Hz) (C-11), 27.3 (³*J*_{SnC} = 58.7 Hz) (C-12), 25.9 (C-9), 18.3 (C-8), 14.3 (C-1),

⁷ ¹H and ¹³C NMR of **5a** is the same as reported in the literature: Guo, X.; Basu, K.; Cabral, J. A.; Paquette, L. A.; *Org. Lett.* **2003**, 5, 789.

13.7 (C-13), 10.3 ($^1J_{\text{SnC}} = 346.4/331.1$ Hz) (C-10), -5.16 (C-7); IR (CH₂Cl₂): 2937_s, 2873_s, 2851_s, 2738_w, 2711_w, 1699_s (C=O), 1602_w, 1465_s, 1418_m, 1389_m, 1365_s, 1275_m, 1259_w, 1253_s cm⁻¹; LRMS (EI, 20eV) m/z (relative intensity): 477 ([M⁺ - C₄H₉], 100), 475 (75), 473 (35), 433 (52), 431 (57), 315 (6), 313 (5); HRMS (EI) m/z calcd for C₂₀H₄₁SiSnO₃ [M⁺ - C₄H₉]: 477.1849, found: 477.1846.

3b: a colourless oil; $R_f = 0.76$ (10% EtOAc/Hex); ^1H NMR (300 MHz, CDCl₃): δ 6.18 (q, $^3J_{\text{HH}} = 6.8$ Hz, $^3J_{\text{SnH}} = 61.1/58.5$ Hz, 1H), 3.70 (s, 3H), 2.00 (d, $J = 6.8$ Hz, 3H), 1.43-1.56 (m, 6H), 1.25-1.35 (m, 6H), 0.91-1.02 (m, 6H), 0.88 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (125 MHz, CDCl₃): δ 171.7 ($^2J_{\text{SnC}} = 38.2$ Hz) (C), 148.1 ($^2J_{\text{SnC}} = 14.5$ Hz) (CH), 136.8 ($^1J_{\text{SnC}} = 331.0/316.1$ Hz) (C), 51.1 (CH₃), 29.0 ($^2J_{\text{SnC}} = 22.6$ Hz) (CH₂), 27.3 ($^3J_{\text{SnC}} = 58.4$ Hz) (CH₂), 18.3 ($^3J_{\text{SnC}} = 42.5$ Hz) (CH₃), 13.7 (CH₃), 10.3 ($^1J_{\text{SnC}} = 348.5 / 330.1$ Hz) (CH₂); IR (CH₂Cl₂): 2973_w, 2961_s, 2933_s, 2875_m, 2850_m, 1699_s (C=O), 1601_w, 1460_w, 1433_w, 1375_m, 1340_w, 1275_m, 1201_m cm⁻¹; LRMS (EI, 20eV) m/z (relative intensity): 333 ([M⁺ - C₄H₉], 100), 331 (74), 275 (25), 273 (15), 263 (16), 262 (77), 261 (15), 219 (19), 217 (13); HRMS (EI) m/z calcd for C₁₇H₃₄O₂Sn [M⁺ - C₄H₉]: 390.1583, found: 390.1538.

3c: a colourless oil; $R_f = 0.69$ (10% EtOAc/Hex); ^1H NMR (300 MHz, CDCl₃): δ 6.03 (t, $^3J_{\text{HH}} = 7.1$ Hz, $^3J_{\text{SnH}} = 61.4$ Hz, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 2.42 (dt, $J = 7.1$ Hz, 7.3 Hz, 2H), 1.24-1.52 (m, 19H), 0.91-0.96 (m, 9H), 0.88 (t, $J = 7.2$ Hz, 9H); ^{13}C NMR (75 MHz, CDCl₃): δ 171.3 (C), 153.6 (CH), 135.6 (C), 59.9 (CH₂), 31.8 ($^3J_{\text{SnC}} = 39.8$ Hz) (CH₂), 31.4 (CH₂), 28.9 ($^2J_{\text{SnC}} = 20.5$ Hz) (CH₂), 27.3 ($^3J_{\text{SnC}} = 58.4$ Hz) (CH₂), 22.3 (CH₂), 14.4 (CH₃), 13.9 (CH₃), 13.7 (CH₃), 10.3 ($^1J_{\text{SnC}} = 347.3/331.9$ Hz) (CH₂); IR (CH₂Cl₂): 2918_s, 2873_s, 1700_s (C=O), 1601_m, 1464_m, 1464_m, 1420_w, 1381_m, 1369_m, 1350_m cm⁻¹; LRMS (EI, 20eV) m/z (relative intensity): 389 ([M⁺ - C₄H₉], 100), 387 (78), 385 (45), 345 (42), 344 (15), 343 (33); HRMS (EI) m/z calcd for C₁₇H₃₃O₂Sn [M⁺ - C₄H₉]: 389.1505, found: 389.1500.

3d: a colorless oil; $R_f = 0.83$ (10% EtOAc/Hex); ^1H NMR (300 MHz, CDCl_3): δ 6.04 (t, $^3J_{\text{HH}} = 7.1$ Hz, $^3J_{\text{SnH}} = 61.8/59.3$ Hz, 1H), 3.69 (s, 3H), 2.40 (dt, $J = 7.3$ Hz, 7.1 Hz, 2H), 1.40-1.57 (m, 8H), 1.24-1.37 (m, 12H), 0.82-1.05 (m, 18H); ^{13}C NMR (500 MHz, C_6D_6): δ 170.8 ($^2J_{\text{SnC}} = 39.8$ Hz) (C), 153.9 ($^2J_{\text{SnC}} = 11.6$ Hz) (CH), 136.0 ($^1J_{\text{SnC}} = 341.2$ Hz) (C), 50.6 (CH_3), 32.2 ($^3J_{\text{SnC}} = 40.5$ Hz) (CH_2), 31.9 (CH_2), 29.5 (CH_2), 29.3 ($^2J_{\text{SnC}} = 20.3$ Hz) (CH_2), 29.1 (CH_2), 27.5 ($^3J_{\text{SnC}} = 56.9$ Hz) (CH_2), 22.8 (CH_2), 14.1 (CH_3), 13.8 (CH_3), 10.5 ($^1J_{\text{SnC}} = 346.4/331.1$ Hz) (CH_2); IR (CH_2Cl_2): 2960s, 2931s, 2875s, 2859s, 1700s (C=O), 1607w, 1466m, 1441m, 1377m, 1354w, 1274w, 1202s cm^{-1} ; LRMS (EI, 20eV) m/z (relative intensity): 403 ($[\text{M}^+ - \text{C}_4\text{H}_9]$, 60), 376 (47), 374 (18), 297 (100), 295 (95), 251 (10), 249 (19); HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{35}\text{O}_2\text{Sn}$ $[\text{M}^+ - \text{C}_4\text{H}_9]$: 403.1662, found: 403.1600.

3e: a colorless oil; $R_f = 0.41$ (5% EtOAc/Hex); ^1H NMR (300 MHz, CDCl_3): δ 6.02 (t, $^3J_{\text{HH}} = 7.1$ Hz, $^3J_{\text{SnH}} = 62.4/60.2$ Hz, 1H), 3.87 (d, $J = 6.6$ Hz, 2H), 2.40 (dt, $J = 7.2$ Hz, 7.2 Hz, 2H), 1.94 (m, 1H), 1.39-1.54 (m, 8H), 1.24-1.37 (m, 12H), 0.85-1.06 (m, 21H); ^{13}C NMR (75 MHz, C_6D_6): δ 171.4 (C), 153.9 (CH), 136.0 (C), 71.2 (CH_2), 33.3 ($^3J_{\text{SnC}} = 40.7$ Hz) (CH_2), 32.68 (CH_2), 30.4 (CH_2), 30.1 ($^2J_{\text{SnC}} = 20.1$ Hz) (CH_2), 30.0 (CH_2), 28.9 (CH), 28.4 ($^3J_{\text{SnC}} = 57.0$ Hz) (CH_2), 23.6 (CH_2), 20.0 (CH_3), 14.9 (CH_3), 14.6 (CH_3), 11.3 ($^1J_{\text{SnC}} = 345.7/330.2$ Hz) (CH_2); IR (CH_2Cl_2): 2963s, 2929s, 2875s, 2857s, 1694s (C=O), 1605m, 1466m, 1466m, 1399w, 1383w, 1354w, 1275m, 1256w cm^{-1} ; LRMS (EI, 20eV) m/z (relative intensity): 445 ($[\text{M}^+ - \text{C}_4\text{H}_9]$, 100), 443 (63), 441 (41), 389 (32), 387 (12), 373 (31), 371 (34); HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{41}\text{O}_2\text{Sn}$ $[\text{M}^+ - \text{C}_4\text{H}_9]$: 445.2132, found: 445.2131.

3f: a colorless oil; $R_f = 0.55$ (30% EtOAc/Hex); ^1H NMR (300 MHz, CDCl_3): δ 5.70 (q, $^3J_{\text{HH}} = 6.5$ Hz, $^3J_{\text{SnH}} = 60.7$ Hz, 1H) (H-2), 3.55 (dd, $J = 5.5$ Hz, 4.9 Hz, 2H) (H-5), 3.33 (dd, $J = 5.6$ Hz, 5.3 Hz, 2H) (H-9), 1.67 (d, $J = 6.5$ Hz, 3H) (H-1), 1.55-1.58 (m, 2H) (H-7), 1.34-1.54 (m, 10H) (H-6, 8, 12), 1.15-1.32 (m, 6H) (H-11), 0.88-1.06 (m, 6H) (H-10), 0.88 (t, $J = 7.3$ Hz, 9H) (H-13); ^{13}C NMR (75 MHz, CDCl_3): δ 172.0 (C-4), 141.2 (C-3), 136.0 (C-2), 46.9 (C-9), 41.67 (C-5), 28.9 ($^2J_{\text{SnC}} = 19.8$ Hz) (C-11), 27.2 ($^3J_{\text{SnC}} = 59.3$ Hz) (C-12), 26.9 (C-8), 25.7 (C-6), 24.6 (C-7), 17.8 ($^3J_{\text{SnC}} = 42.5$ Hz) (C-1), 13.6 (C-13), 10.1 ($^1J_{\text{SnC}} = 341.4/326.1$ Hz) (C-10); IR (CH_2Cl_2): 3046m, 2958s, 2932s, 2872m, 2856m, 1595s (C=O), 1466m, 1454m, 1430m, 1377w, 1353w, 1334w, 1269w, 1278m, 1254s cm^{-1} ; LRMS (EI, 20eV) m/z (relative intensity): 386 ($[\text{M}^+ - \text{C}_4\text{H}_9]$, 100), 384 (67), 382 (33) 303 (5), 301 (6), 272 (3), 270 (40), 247 (2), 245 (2); HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{32}\text{NOSn}$ $[\text{M}^+ - \text{C}_4\text{H}_9]$: 386.1509, found: 386.1505.

9a: a colorless oil; $R_f = 0.47$ (5% EtOAc/Hex); ^1H NMR (400 MHz, CDCl_3): δ 7.14 (t, $^3J_{\text{HH}} = 7.3$ Hz, $^3J_{\text{SnH}} = 116.4/111.3$ Hz, 1H), 2.26 (s, 3H), 2.22 (m, 2H), 1.41-1.49 (m, 6H), 1.25-1.34 (m, 6H), 1.07 (t, $J = 7.5$ Hz, 3H), 0.94-0.98 (m, 6H), 0.87 (t, $J = 7.2$ Hz, 9H); ^{13}C NMR (125 MHz, CDCl_3): δ 204.6 (C), 157.65 ($^2J_{\text{SnC}} = 16.4$ Hz) (CH), 148.6 ($^1J_{\text{SnC}} = 344.0/328.8$ Hz) (C), 29.1 ($^2J_{\text{SnC}} = 20.0$ Hz) (CH_2), 27.6 ($^2J_{\text{SnC}} = 27.6$ Hz) (CH_2), 27.3 ($^3J_{\text{SnC}} = 61.0$ Hz) (CH_2), 25.7 ($^3J_{\text{SnC}} = 10.5$ Hz) (CH_3), 13.71 (CH_3), 13.66 (CH_3), 11.5 ($^1J_{\text{SnC}} = 347.1/331.7$ Hz) (CH_2); IR (CH_2Cl_2): 2960s, 2930s, 2874s, 2856m, 1647s (C=O), 1600m, 1465m, 1377w, 1357w, 1274s, 1257s, 1232m cm^{-1} ; LRMS (EI, 20eV) m/z 331 $[\text{M}^+ - \text{C}_4\text{H}_9]$, 100], 329 (73), 327 (42), 217 (14), 215 (11); HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{27}\text{OSn}$ $[\text{M}^+ - \text{C}_4\text{H}_9]$: 331.1086, found: 331.1088.

9b: a colorless oil; $R_f = 0.83$ (10% EtOAc/Hex); ^1H NMR (300 MHz, CDCl_3): δ 7.17 (t, $^3J_{\text{HH}} = 7.3$ Hz, $^3J_{\text{SnH}} = 117.0/111.9$ Hz, 1H), 2.26 (s, 3H), 2.40 (dt, $J = 7.4$ Hz, 7.4 Hz, 2H), 1.50-1.65 (m, 8H), 1.23-1.49 (m, 12H), 0.78-1.10 (m, 18H); ^{13}C NMR (75 MHz, CDCl_3): δ 204.7 (C), 156.7 (CH), 149.9 (C), 34.4 ($^3J_{\text{SnC}} = 26.4$ Hz) (CH_2), 31.7 (CH_2), 29.31 (CH_2), 29.28 (CH_2), 29.1 ($^2J_{\text{SnC}} = 20.1$ Hz) (CH_2), 27.8 ($^3J_{\text{SnC}} = 61.1$ Hz) (CH_2), 25.8 (CH_3), 22.6 (CH_2), 14.1 (CH_3), 13.8 (CH_3), 11.5 ($^1J_{\text{SnC}} = 345.0/331.4$ Hz) (CH_2); IR (CH_2Cl_2): 2961 s , 2929 s , 2856 s , 2873 s , 1645 s (C=O), 1600 m , 1465 m , 1465 m , 1376 w , 1357 w , 1292 w , 1256 w , 1240 m cm^{-1} ; LRMS (EI, 20eV) m/z (relative intensity): 387 ($[\text{M}^+ - \text{C}_4\text{H}_9]$, 100), 386 (34), 385 (66), 384 (28), 383 (35), 273 (9), 271 (7); HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{35}\text{OSn}$ [$\text{M}^+ - \text{C}_4\text{H}_9$]: 387.1713, found: 387.1714.

8c: ^1H NMR (300 MHz, CDCl_3): δ 5.62 (t, $^3J_{\text{HH}} = 7.1$ Hz, $^3J_{\text{SnH}} = 64.9$ Hz, 1H)

9c: a colorless oil; $R_f = 0.66$ (10% EtOAc/Hex); ^1H NMR (400 MHz, CDCl_3): δ 6.03 (t, $^3J_{\text{HH}} = 7.3$ Hz, $^3J_{\text{SnH}} = 118.7/113.4$ Hz, 1H), 2.63 (q, $J = 7.3$ Hz, 2H), 2.20 (dt, $J = 7.3$ Hz, 7.3 Hz, 2H), 1.40-1.59 (m, 8H), 1.25-1.40 (m, 8H), 1.07 (t, $J = 7.3$ Hz, 3H), 0.91-1.02 (m, 9H) 0.88 (t, $J = 7.3$ Hz, 9H) ^{13}C NMR (100 MHz, CDCl_3): δ 207.7 (C), 154.2 (CH), 148.4 (C), 34.2 (CH_2), 31.7 (CH_2), 31.3 (CH_2), 29.1 ($^2J_{\text{SnC}} = 19.9$ Hz) (CH_2), 27.3 ($^3J_{\text{SnC}} = 61.5$ Hz) (CH_2), 22.3 (CH_2), 14.0 (CH_3), 13.9 (CH_3), 11.5 ($^1J_{\text{SnC}} = 345.5/330.2$ Hz) (CH_2), 8.9 (CH_3); IR (CH_2Cl_2): 2963 s , 2923 s , 2875 s , 2857 s , 1651 s (C=O), 1597 m , 1462 m , 1369 w , 1275 m , 1213 w cm^{-1} ; LRMS (EI, 20eV) m/z (relative intensity): 373 ($[\text{M}^+ - \text{C}_4\text{H}_9]$, 97), 372 (28), 371 (57), 370 (24), 369 (25), 135 (100); HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{33}\text{OSn}$ [$\text{M}^+ - \text{C}_4\text{H}_9$]: 373.1556, found: 373.1559.

8d: ^1H NMR (300 MHz, CDCl_3): δ 5.48 (t, $^3J_{\text{HH}} = 7.0$ Hz, $^3J_{\text{SnH}} = 65.5$ Hz, 1H)

9d: ^1H NMR (300 MHz, CDCl_3): δ 6.27 (t, $^3J_{\text{HH}} = 7.1$ Hz, $^3J_{\text{SnH}} = 116.2$ Hz, 1H)