Addition of Organometallic Compounds to Tin-containing Cyclic Ketones. Remote Stereocontrol Induced by the Stannyl Group

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SUPPORTING INFORMATION

Conjugate addition of stannylvinylcuprates to enones.

Z-4-phenyl-6-tributylstannyl-5-hexen-2-one (8): Yellow pale oil (88%). IR (film) 1710, 1590 cm^{-1} . ^1H NMR (CDCl_3) 7.25 (m, 5H, Ph); 6.70 (dd, $^3J_{\text{Sn-H}} = 160$ Hz, $J = 12$, 8 Hz, 1H); 5.90 (d, $^2J_{\text{Sn-H}} = 80$ Hz, $J = 12$ Hz, 1H); 3.70 (m, 1H); 2.95 (dd, $J = 15$, 7 Hz, 1H); 2.75 (dd, $J = 15$, 4 Hz, 1H); 2.03 (s, 3H); 1.5-0.8 (m, 27H, Bu_3Sn). ^{13}C NMR (CDCl_3) 206.2, 150.1, 143.5, 128.5, 127.1, 126, 51.1, 48.3, 31.2, 29.1, 27.2, 13.6, 10.3; MS (EI) m/z 407 ($\text{M}^+ - \text{Bu}$, 100%), 177 (62%). HRMS (M/z): calc for $\text{C}_{20}\text{H}_{31}\text{OSn}$ (M-Bu) 407.1397, found 407.1357.

3-methyl-3-(Z-2-trimethylstannylvinyl)cyclopentan-1-one (9b): Yellow pale oil (87%). IR (film) 1745, 1590 cm^{-1} . ^1H NMR (CDCl_3) 6.70 (d, $^3J_{\text{Sn-H}} = 175$ Hz, $J = 14$ Hz 1H); 5.80 (d, $^2J_{\text{Sn-H}} = 75$ Hz, $J = 14$ Hz, 1H); 2.31 (d, $J = 16$ Hz, 1H), 2.30 (t, $J = 8$ Hz, 2H); 2.10 (d, $J = 16$ Hz, 1H); 2.0 (m, 1H), 1.85 (m, 1H), 1.17 (s, 3H), 0.19 (s, $^2J_{\text{Sn-H}} = 54$ Hz, 9H, Me_3Sn). ^{13}C NMR (CDCl_3) 217.9, 155.1, 127.3, 51.8, 43.9, 36.5, 36.1, 26.2, -7.1. MS (EI) m/z 273 ($\text{M}^+ - \text{CH}_3$, 92%), 135 (100%). Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{OSn}$: C, 46.04; H, 7.02. Found: C, 46.31; H, 7.21.

3-(Z-2-tributylstannylvinyl)ciclohexan-1-one (10a): Yellow pale oil (96%). IR (film) 1710, 1595 cm^{-1} . ^1H NMR (CDCl_3) 6.35 (dd, $^3J_{\text{Sn-H}} = 140$ Hz, $J = 12$, 10 Hz, 1H); 5.80 (d, $^2J_{\text{Sn-H}} = 70$ Hz, $J = 12$

Hz, 1H); 2.4-2.0 (m, 5H, 2CH₂, CH); 1.8-0.8 (m, 31H, 2CH₂, Bu₃Sn). ¹³C NMR (CDCl₃) 209.8, 151.2, 128.3, 47.8, 47.3, 41.1, 31.8, 29.5, 27.2, 25.2, 13.6, 10.2. MS (EI) m/z 357 (M⁺-Bu, 100%), 177 (20%). Anal. Calcd for C₂₀H₃₈OSn: C, 58.14; H, 9.27. Found: C, 58.02; H, 9.38.

3-(Z-2-trimethylstannylvinyl)cyclohexan-1-one (10b) Yellow pale oil (78%). IR (film) 1715, 1600 cm⁻¹. ¹H NMR (CDCl₃) 6.30 (dd, ³J_{Sn-H} = 140 Hz, J = 12, 7 Hz, 1H); 5.80 (d, ²J_{Sn-H} = 70 Hz, J = 12 Hz, 1H); 2.4-1.6 (m, 9H, 4CH₂, CH); 0.15 (s, ²J_{Sn-H} = 55 Hz, 9H, Me₃Sn). ¹³C NMR (CDCl₃) 210.1, 151.2, 128.9, 47.7, 46.5, 41.2, 32.0, 25.2, -8.5. MS (EI) m/z 287 (M⁺-1, 18%), 273 (M⁺-Me, 100%).

3,4-dihydro-4-(Z-2-tributylstannylvinyl)-2H-benzopiran-2-one (12): Yellow pale oil (75%). IR (film) 1770, 1590 cm⁻¹. ¹H NMR (CDCl₃) 7.3-7.05 (m, 4H); 6.40 (dd, ³J_{Sn-H} = 140 Hz, J = 15.0, 8 Hz, 1H); 6.2 (d, ²J_{Sn-H} = 60 Hz, J = 15.0 Hz, 1H); 3.5 (m, 1H); 2.82 (dd, J = 15.0, 6.0 Hz, 1H); 2.60 (dd, J = 15.0, 10.0 Hz, 1H); 1.5-0.9 (m, 27H, Bu₃Sn). ¹³C NMR (CDCl₃) 167.1, 152.3, 146.2, 134.4, 132.2, 129.3, 127.5, 125.3, 116.8, 42.2, 36.9, 29.4, 27.3, 13.9, 11.2. MS (EI) m/z 463 (M⁺-1, 5%), 407 (M⁺-Bu, 30%), 175 (100%).

(1S,4S,5R)-4,6,6-trimethyl-4-(Z-2-tributylstannylvinyl)bicyclo [3.1.1] heptan-2-one and (1S*,4S*,5R*)-4,6,6-trimethyl-4-(Z-2-tributylstannylvinyl)bicyclo [3.1.1] heptan-2-one (13): Yellow pale oil (82-84%). IR (film) 1715, 1580 cm⁻¹. ¹H NMR (CDCl₃) 6.60 (d, ³J_{Sn-H} = 140 Hz, J = 15 Hz, 1H); 5.75 (d, ²J_{Sn-H} = 40 Hz, J = 15 Hz, 1H); 2.82 (d, J = 20 Hz, 1H); 2.52 (t, J = 6 Hz, 1H); 2.45 (m, 1H); 2.37 (d, J = 20 Hz, 1H); 2.05 (t, J = 6 Hz, 1H); 1.5-0.90 (m, 28H, Bu₃Sn, CH); 1.38 (s, 3H); 1.25 (s, 3H); 1.05 (s, 3H). ¹³C NMR (CDCl₃) 213.2, 160.1, 125.2, 57.3, 53.4, 47.2, 41.1, 40.2, 29.5, 28.6, 27.1 (2 C), 26, 25.7, 14.2, 12.1; MS (EI) m/z 411 (M⁺-Bu, 100%), 177 (28%). [²⁵D] -22.6 (c 1.03, HCCl₃). Anal. Calcd for C₂₄H₄₄OSn: C, 61.69; H, 9.49. Found: C, 61.97; H, 9.71.

3-methyl-3-(E-2-tributylstannylvinyl)cyclopentan-1-one (23) (the addition of BF₃·Et₂O was not necessary). Yellow pale oil (98%). ¹H NMR (CDCl₃) 5.96 (d, ³J_{Sn-H} = 61 Hz, J = 20 Hz, 1H), 5.84 (d, ²J_{Sn-H} = 68, 20 Hz, 1H); 2.35 (d, J = 20 Hz, 1H); 2.12 (t, J = 8 Hz, 2H); 2.0 (d, J = 20 Hz, 1H); 1.95 (m, 1H); 1.77 (m, 1H); 1.5-0.9 (m, 27H, Bu₃Sn); 1.18 (s, 3H). ¹³C NMR (CDCl₃) 219.1, 155.2, 123.8,

51.2, 44.4, 37.3, 34.9, 29.4, 27.2, 25.8, 13.9, 9.1. MS (EI) m/z 357 (M^+ -Bu, 54%), 123 (100%). Anal. Calcd for $C_{20}H_{38}OSn$: C, 58.14; H, 9.27. Found: C, 58.43; H, 9.44.

Preparation of α -stannylated ketones: General procedure.

A solution of 2.2 mmol of the corresponding tin-cuprates^{22,23a}, was cooled to -78°C and then $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.55 ml, 625 mg, 4.4 mmol) was added dropwise. The resulting mixture was stirred at this temperature for 5 min and a solution of the corresponding enones (2 mmol) in 1 ml of THF was added very slowly through syringe. The well-stirred solution was warmed to 0°C over 2 h and quenched with 1 ml of CH_3OH . The reaction mixture was warmed to room temperature, diluted with 10 ml of Et_2O and washed thoroughly with 15 ml of NH_4Cl sat./ NH_4OH (10%) solution. The aqueous layer was extracted with diethyl ether (2x15 ml), the combined organic extracts were dried over anhydrous MgSO_4 , filtered, and the solvent was evaporated under reduced pressure. The residue was chromatographed to afford the corresponding conjugated addition products **34-36** in high yields.

3-methyl-3-(2-methyl-1-trimethylstannyl-1-propenyl)cyclopentan-1-one (34): Yellow pale oil (60%). ^1H NMR (CDCl_3) 2.55 (dd, $J = 17.7, 1.8$ Hz, 1H); 2.34 (d, $J = 17.7$ Hz, 1H); 2.2-2.3 (m, 4H); 1.79 (s, $^4J_{\text{Sn-H}} = 13.2$ Hz, 3H); 1.77 (s, $^4J_{\text{Sn-H}} = 8.8$ Hz, 3H); 1.14 (s, 3H); 0.21 (s, $^3J_{\text{Sn-H}} = 50$ Hz, 9H, Me_3Sn). ^{13}C NMR (CDCl_3) 220.2, 147.9, 140.3, 55.4, 47.3, 38.3, 35.8, 29.8, 24.7, 23.6, -4. MS (EI) m/z 301 (M^+ - CH_3 , 27%), 133 (100%). Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{OSn}$: C, 49.57; H, 7.68. Found: C, 49.84; H, 7.81.

3-methyl-3-tributylstannylmethylcyclopentan-1-one (35): Yellow pale oil (79%). IR (film) 1730 cm^{-1} . ^1H NMR (CDCl_3) 2.32 (t, $J = 6.6$ Hz, 2H); 2.09 (d, $J = 13.7$ Hz, 1H); 2.06 (d, $J = 13.7$ Hz, 1H); 1.92-1.75 (m, 2H); 1.12 (s, $^2J_{\text{Sn-H}} = 19$ Hz, 2H); 1.09 (s, 3H); 1.5-0.9 (m, 27H). ^{13}C NMR (CDCl_3) 220.2, 56.3, 39.8, 39.2, 37.3, 29.1, 28.5, 27.4, 25.8, 13.6, 10.1. MS (EI) m/z 345 (M^+ -Bu, 41%), 41 (100%). Anal. Calcd for $\text{C}_{19}\text{H}_{38}\text{OSn}$: C, 56.88; H, 9.55. Found: C, 57.10; H, 9.81.

3-tributylstannylmethylcyclohexan-1-one (36): Yellow pale oil (92%). IR (film) 1710 cm^{-1} . ^1H NMR (CDCl_3) 2.45-2.2 (m, 8H); 2.1-0.8 (m, 3H); 1.5-0.9 (m, 27H, Bu_3Sn). ^{13}C NMR (CDCl_3)

212.2, 52.3, 41.1, 38.4, 35.3, 28.7, 27.3, 25.2, 18.4, 13.6, 9.2. MS (EI) m/z 345 (M^+ -Bu, 100%). Anal. Calcd for $C_{19}H_{38}OSn$: C, 56.88; H, 9.55. Found: C, 57.11; H, 9.77.

Preparation of α -stannylated ketones: General procedure.

A solution of 4.4 mmol of the corresponding stannylcuprates^{20b,c,24}, was cooled at -78°C and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.1 ml, 1.250 g, 8.8 mmol) was added dropwise. The resulting mixture was stirred at this temperature for 5 min and a solution of 3-methyl-2-cyclopenten-1-one (4 mmol) in 2 ml of THF was slowly added through syringe. The well-stirred mixture was kept at -78°C for 30 minutes, then warmed to 0°C over 1 h and quenched with 2 ml. of CH_3OH . The reaction mixture was warmed to room temperature, diluted with 20 ml. of Et_2O and washed thoroughly with 30 ml of NH_4Cl sat./ NH_4OH (10%) solution. The aqueous layer was extracted with diethyl ether (2x25 ml), the ethereal extracts were combined, dried over anhydrous MgSO_4 , filtered, and the solvent was evaporated under reduced pressure. The residue was chromatographed under appropriate conditions to afford the corresponding conjugated addition products **27** and **28** in high yields.

3-methyl-3-tributylstannylcyclopentan-1-one (27a): Yellow pale oil (95%). IR (film) 1730 cm^{-1} . ^1H NMR (CDCl_3) 2.40 (d, $J = 18.4\text{ Hz}$, 1H); 2.35-2.0 (m, 3H); 1.8 (m, 1H); 2.05 (d, $J = 18.4\text{ Hz}$, 1H); 1.5, 1.3, 0.90 (m, 27H, Bu_3Sn); 1.29 (s, 3H). ^{13}C NMR (CDCl_3) 221.1, 52.4, 37.2, 36.3, 29.8, 29.3, 27.5, 26.7, 14, 8.2. MS (EI) m/z 313 (M^+ -Bu- H_2O , 5%), 269 (100%).

3-methyl-3-trimethylstannylcyclopentan-1-one (27b): Yellow pale oil (96%). ^1H NMR (CDCl_3) 2.4 (d, $J = 20\text{ Hz}$, 1H); 2.35-2.15 (m, 3H); 2.0 (d, $J = 20\text{ Hz}$, 1H); 1.8 (m, 1H); 1.3 (s, $^3J_{\text{Sn-H}} = 60\text{ Hz}$, 3H); 0.05 (s, $^2J_{\text{Sn-H}} = 50\text{ Hz}$, 9H, Me_3Sn). ^{13}C NMR (CDCl_3) 220.2, 52.3, 37.3, 35.9, 28.8, 26.3, -11.2. MS (EI) m/z 262 (M^+), 165 (100%). Anal. Calcd for $C_{18}H_{36}OSn$: C, 55.84; H, 9.37. Found: C, 56.05; H, 9.57.

[2S, 3R, 5S]-5-(isopropenyl)-2-methyl-3-tributylstannylcyclohexan-1-one (28) Yellow pale oil (80%). IR (film) $1710, 1650\text{ cm}^{-1}$. ^1H NMR (CDCl_3) 4.79 (s, 1H), 4.74 (s, 1H); 2.8 (m, 1H); 2.5-2.1 (m, 6H); 1.75 (s, 3H); 1.07 (d, $J = 6.6\text{ Hz}$, 3H); 1.5-0.8 (m, 27H, Bu_3Sn); 0.98 (d, $J = 6.5\text{ Hz}$, 3H). ^{13}C

NMR (CDCl₃) 212.3, 147.1, 110.2, 48.6, 47.3, 45.8, 35.2, 32.5, 29.4, 27.4, 20.7, 15.8, 13.6, 9.7. MS (EI) m/z 385 (M⁺-Bu, 9%), 55 (100%). [α]_D²⁵ -30.9 (c 0.69, HCCl₃). Anal. Calcd for C₂₂H₄₂OSn: C, 59.88; H, 9.59. Found: C, 59.99; H, 9.71. NOE enhancements were found between the following signals: a) 2.5-2.1 (C₅-H_{ax}) to 1.07 (C₂-Me), b) 1.07 (C₂-Me) to 1.5-0.8 (SnBu₃).

Addition of organolithium reagents to stannylated ketones.

[1S*, 3S*]-1-butyl-3-methyl-3-(Z-2-tributylstannylvinyl)cyclopentan-1-ol (14b) Yellow pale oil (91%). IR (film) 3370, 1580 cm⁻¹. ¹H NMR (CDCl₃) 6.74 (d, ³J_{Sn-H} = 170 Hz, J = 14 Hz, 1H); 5.61 (d, ²J_{Sn-H} = 70 Hz, J = 14 Hz, 1H); 1.82 (d, J = 13.6 Hz, 1H); 1.81-1.7 (m, 4H); 1.60 (d, J = 13.6 Hz, 1H); 1.5, 1.3, 0.9 (m, 37H, Bu₃Sn, Bu and -OH); 1.23 (s, 3H). ¹³C NMR (CDCl₃) 158.9, 123.3, 83.2, 54.1, 46.2, 43.4, 39.9, 39.6, 30.2, 29.6, 28.7, 27.2, 23.1, 14.5, 14.1, 12.0. MS (EI) m/z 415 (M⁺-Bu, 54%), 41 (100%). Anal. Calcd for C₂₄H₄₈OSn: C, 61.16; H, 10.26. Found: C, 61.48; H, 10.44.

[1S*, 3S*]-3-methyl-1-phenyl-3-(Z-2-tributylstannylvinyl)cyclopentan-1-ol (14c-syn). Yellow pale oil (67%). IR (film) 3480, 3050, 1600, 1580 cm⁻¹. ¹H NMR (CDCl₃) 7.5-7.2 (m, 5H); 6.85 (d, ³J_{Sn-H} = 170 Hz, J = 15 Hz, 1H); 5.70 (d, ²J_{Sn-H} = 70 Hz, J = 15 Hz, 1H); 2.35-1.95 (m, 6H); 1.65 (s, -OH); 1.5, 1.3, 0.9 (m, 27H, Bu₃Sn); 1.32 (s, 3H). ¹³C NMR (CDCl₃) 160.2, 147.3, 129.1, 126.9, 125.2, 123.1, 84.2, 57.2, 46.3, 42.1, 40.4, 29.2 (2 C), 27.2, 13.4, 11.1. MS (EI) m/z 435 (M⁺-Bu, 27%), 105 (100%). HRMS (EI) calcd for [C₂₆H₄₃OSn] ([M - H]⁺) 491.2414, found 491.2336. Anal. Calcd for C₂₆H₄₄OSn: C, 63.56; H, 9.03. Found: C, 63.83; H, 9.17.

[1R*, 3S*]-3-methyl-1-phenyl-3-(Z-2-tributylstannylvinyl)cyclopentan-1-ol (14c-anti). Yellow pale oil (7%). IR (film) 3490, 3050, 1600, 1580 cm⁻¹. ¹H NMR (CDCl₃) 7.55-7.2 (m, 5H); 7.02 (d, ³J_{Sn-H} = 170 Hz, J = 15 Hz, 1H); 5.75 (d, ²J_{Sn-H} = 70 Hz, J = 15 Hz, 1H); 2.70-1.95 (m, 6H); 1.80 (s, -OH); 1.6, 1.4, 0.95 (m, 27H, Bu₃Sn); 1.23 (s, 3H). ¹³C NMR (CDCl₃) 160.1, 147.2, 128.1, 126.9, 125.2, 123.1, 84.0, 56.8, 46.2, 41.1, 39.0, 29.5, 28.5, 27.1, 15.2, 11.1; MS (EI) m/z 491 (M⁺-1, 5%), 435 (M⁺-Bu, 21%), 417 (100%). HRMS (EI) calcd for [C₂₆H₄₃OSn] ([M - H]⁺) 491.2414, found 491.2336.

[1S*, 3S*]-1,3-dimethyl-3-(Z-2-trimethylstannylvinyl)cyclopentan-1-ol (14d) (prepared at -90°C). Yellow pale oil (92%). IR (film) 3590, 3350, 1580 cm^{-1} . ^1H NMR (CDCl_3) 6.71 (d, $^3J_{\text{Sn-H}} = 170$ Hz, $J = 13.7$ Hz, 1H); 5.81 (d, $^2J_{\text{Sn-H}} = 70$ Hz, $J = 13.7$ Hz, 1H); 1.87 (d, $J = 13.6$ Hz, 1H); 1.81-1.75 (m, 4H); 1.67 (d, $J = 13.6$ Hz, 1H); 1.35 (s, 3H); 1.25 (s, -OH); 1.23 (s, 3H); 0.30 (s, $^2J_{\text{Sn-H}} = 55$ Hz, 9H, Me_3Sn). ^{13}C NMR (CDCl_3) 160.2, 125.3, 80.1, 54.8, 47.2, 41.3, 40.2, 29.8, 29.2, -7. MS (EI) m/z 289 ($\text{M}^+ - \text{CH}_3$, 72%), 135 (100%).

[1S*, 3S*]-1-butyl-3-methyl-3-(Z-2-trimethylstannylvinyl)cyclopentan-1-ol (14e) (prepared at -90°C). Yellow pale oil (78%). IR (film) 3400, 1580 cm^{-1} . ^1H NMR (CDCl_3) 6.70 (d, $^3J_{\text{Sn-H}} = 170$ Hz, $J = 13.7$ Hz, 1H); 5.81 (d, $^2J_{\text{Sn-H}} = 70$ Hz, $J = 13.7$ Hz, 1H); 1.85 (d, $J = 13.7$ Hz, 1H); 1.82-1.71 (m, 4H); 1.63 (d, $J = 13.7$ Hz, 1H); 1.59 (s, -OH); 1.55 (t, $J = 7$ Hz, 2H); 1.4-1.3 (m, 4H); 1.24 (s, 3H); 0.91 (t, $J = 7.1$ Hz, 3H); 0.20 (s, $^2J_{\text{Sn-H}} = 55$ Hz, 9H, Me_3Sn). ^{13}C NMR (CDCl_3) 160.1, 125.3, 80.9, 54.2, 45.7, 42.1, 40.2, 38.0, 29.4, 26.2, 23.2, 14.7, -7.1. MS (EI) m/z 331 ($\text{M}^+ - \text{CH}_3$, 100%). Anal. Calcd for $\text{C}_{15}\text{H}_{30}\text{OSn}$: C, 52.21; H, 8.76. Found: C, 52.02; H, 8.88.

[1S*, 3S*]-3-methyl-1-phenyl-3-(Z-2-trimethylstannylvinyl)cyclopentan-1-ol (14f-syn) (prepared at -90°C). Yellow pale oil (75%). IR (film) 3600, 3440, 1590 cm^{-1} . ^1H NMR (CDCl_3) 7.5-7.2 (m, 5H); 6.85 (d, $^3J_{\text{Sn-H}} = 170$ Hz, $J = 15$ Hz, 1H); 5.75 (d, $^2J_{\text{Sn-H}} = 50$ Hz, $J = 15$ Hz, 1H); 2.35-2.0 (m, 6H); 1.87 (s, -OH); 1.40 (s, 3H); 0.20 (s, $^2J_{\text{Sn-H}} = 50$ Hz, 9H, Me_3Sn). ^{13}C NMR (CDCl_3) 160.1, 147.2, 127.9, 127.2, 125.4, 124.8, 84.2, 57.3, 47.1, 41.9, 40.1, 29.8, -7.1. MS (EI) m/z 351 ($\text{M}^+ - \text{CH}_3$, 53%), 105 (100%).

[1R*, 3S*]-1-phenyl, 3-methyl-3-(Z-2-trimethylstannylvinyl)cyclopentan-1-ol (14f-anti) (prepared at -90°C). Yellow pale oil (10%). IR (film) 3600, 3470, 1590 cm^{-1} . ^1H NMR (CDCl_3) 7.5-7.25 (m, 5H); 7.0 (d, $^3J_{\text{Sn-H}} = 170$ Hz, $J = 15$ Hz, 1H); 5.78 (d, $^2J_{\text{Sn-H}} = 50$ Hz, $J = 15$ Hz, 1H); 2.35-2.0 (m, 6H); 1.80 (s, -OH); 1.23 (s, 3H); 0.20 (s, $^2J_{\text{Sn-H}} = 50$ Hz, 9H, Me_3Sn). ^{13}C NMR (CDCl_3) 160.2, 147.1, 128.2, 127.1, 125.5, 124.8, 83.2, 57.4, 47.1, 42.4, 39.3, 29.3, -7. MS (EI) m/z 333 ($\text{M}^+ - \text{CH}_3 - \text{H}_2\text{O}$, 98%), 135 (100%).

[1S*, 3S*]-1-methyl, 3-(Z-2-tributylstannylvinyl)cyclohexa-1-ol (15a). Yellow pale oil (87%). IR (film) 3600, 3500, 1590 cm^{-1} . ^1H NMR (CDCl_3) 6.27 (dd, $^3J_{\text{Sn-H}} = 140$ Hz, $J = 12, 10$ Hz, 1H); 5.70 (d, $^2J_{\text{Sn-H}} = 70$ Hz, $J = 12$ Hz, 1H); 2.2 (m, 1H); 1.22 (s, 3H), 1.6-0.9 (m, 36H, 4CH_2 , Bu_3Sn , OH). ^{13}C NMR (CDCl_3) 154.1, 125.9, 69.1, 45.4, 41.8, 37.8, 32.4, 31.9, 29.2, 27.3, 21.0, 13.7, 10.3. MS (EI) m/z 355 ($\text{M}^+ - \text{Bu} - \text{H}_2\text{O}$, 75%), 121 (100%). Anal. Calcd for $\text{C}_{21}\text{H}_{42}\text{OSn}$: C, 58.76; H, 9.86. Found: C, 59.03; H, 10.11.

[1S*, 3S*]-1-methyl-3-(Z-2-trimethylstannylvinyl)cyclohexan-1-ol (15c) (prepared at -90°C). Yellow pale oil 80%). ^1H NMR (CDCl_3) 6.25 (dd, $^3J_{\text{Sn-H}} = 140$ Hz, $J = 12, 8$ Hz, 1H); 5.70 (d, $^2J_{\text{Sn-H}} = 80$ Hz, $J = 12$ Hz, 1H); 1.9 (m, 1H); 1.8-1.3 (m, 9H); 1.25 (s, 3H); 0.16 (s, $^2J_{\text{Sn-H}} = 55$ Hz, 9H, Me_3Sn).

[1R, 2R, 3R, 5R]-1,2-dimethyl-5-isopropenyl-3-(Z-2-tributylstannylvinyl)cyclohexan-1-ol (16a). Yellow pale oil (78%). IR (film) 3640, 1650, cm^{-1} . ^1H NMR (CDCl_3) 7.13 (dd, $^3J_{\text{Sn-H}} = 145$ Hz, $J = 12.3, 10.5$ Hz, 1H); 5.83 (dd, $^2J_{\text{Sn-H}} = 73$ Hz, $J = 12.3$ Hz, 1H); 4.72 (s, 1H); 4.70 (s, 1H); 2.54 (tt, $J = 12.6, 2.5$ Hz, 1H); 2.20-2.14 (m, 1H); 1.81 (dt, $J = 13.4, 2.7$ Hz, 1H); 1.73 (s, 3H); 1.76-1.68 (m, 1H); 1.23 (s, 3H); 1.12 (s, -OH); 1.65-0.82 (m, 30H, CH , CH_2 , Bu_3Sn); 0.9 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (CDCl_3) 151.3, 150.2, 128.3, 108.3, 72.6, 48.7, 45.7, 41.4, 39.1, 35.2, 30.4, 29.2, 27.3, 21.0, 13.6, 13.3, 10.2. MS (EI) m/z 409 ($\text{M}^+ - \text{Bu} - \text{H}_2\text{O}$, 43%), 43 (100%). $[\alpha]_{\text{D}}^{25} -29.5$ (c 0.40, HCCl_3). Anal. Calcd for $\text{C}_{25}\text{H}_{48}\text{OSn}$: C, 62.12; H, 10.01. Found: C, 62.41; H, 10.20. NOE enhancements were found between the following signals: a) 2.54 ($\text{C}_5\text{-H}_{\text{ax}}$) to 7.13 ($-\text{CH}=\text{CSn}$), b) 1.23 ($\text{C}_1\text{-CH}_3$) to 0.9 ($\text{C}_2\text{-CH}_3$).

(1S, 2S, 4S, 5R)-2,4,6,6-tetramethyl-4-(Z-2-tributylstannylvinyl)bicyclo [3.1.1] heptan-2-ol (17a) and **(1S*, 2S*, 4S*, 5R*)-2,4,6,6-tetramethyl-4-(Z-2-tributylstannylvinyl)bicyclo [3.1.1] heptan-2-ol (17b).** Yellow pale oil (79-80%). IR (film) 3570, 3460, 1580 cm^{-1} . ^1H NMR (CDCl_3) 6.70 (d, $^3J_{\text{Sn-H}} = 150$ Hz, $J = 14$ Hz, 1H); 5.70 (d, $^2J_{\text{Sn-H}} = 50$ Hz, $J = 14$ Hz, 1H); 2.20 (d, $J = 15$ Hz, 1H); 2.25 (m, 1H); 2.05 (d, $J = 15$ Hz, 1H); 1.82 (dd, $J = 8, 2$ Hz, 1H); 1.80 (dd, $J = 8$ Hz, $J = 2$ Hz, 1H); 1.6-0.90 (m, 27H, Bu_3Sn); 1.30 (s, 3H); 1.27 (s, 3H); 1.26 (s, 3H); 1.13 (s, 3H). ^{13}C NMR (CDCl_3) 163.1, 124.4, 75.6, 53.1, 52.8, 41.5, 39.5, 31.6, 30.2, 29.4 (2 C), 28.9, 27.3, 26.0, 13.6, 11.1. MS (EI)

m/z 427 (M^+ -Bu, 72%), 409 (M^+ -Bu- H_2O , 96%), 175 (100%). $[\eta]_D^{25}$ -4.5 (c 1.02, $CHCl_3$). Anal. Calcd for $C_{25}H_{48}OSn$: C, 62.12; H, 10.01. Found: C, 62.25; H, 10.13.

(1S*, 2S*, 4S*, 5R*)-2-butyl-4,6,6-trimethyl-4-(Z-2-tributylstannylvinyl)bicyclo [3.1.1] heptan-2-ol (17c). Yellow pale oil (74%). IR (film) 3430, 1570 cm^{-1} . 1H NMR ($CDCl_3$) 6.70 (d, $^3J_{Sn-H} = 160$ Hz, $J = 15$ Hz, 1H); 5.68 (d, $^2J_{Sn-H} = 50$ Hz, $J = 15$ Hz, 1H); 2.20-2.05 (m, 4H); 1.90 (t, $J = 6$ Hz, 1H); 1.80 (t, $J = 6$ Hz, 1H); 1.6-0.90 (m, 36H); 1.30 (s, 3H); 1.25 (s, 3H); 1.10 (s, 3H). ^{13}C NMR ($CDCl_3$) 163.0, 124.0, 75.0, 52.8, 49.5, 49.0, 44.0, 41.5, 39.3, 32.0, 30.2, 29.1 (2 C), 27.5, 26.0, 25.5, 23.0, 14.5, 14.0, 11.1. MS (EI) m/z 526 (M^+ , 7%), 469 (M^+ -Bu, 66%).

[1S*, 3S*]-1,3-dimethyl-3-trimethylstannylcyclopentan-1-ol (29a-syn). Yellow pale oil (41%). IR (film) 3400 cm^{-1} . 1H NMR ($CDCl_3$) 2.0 (d, $J = 14$ Hz, 1H); 1.92-1.8 (m, 3H); 1.60 (d, $J = 14$ Hz, 1H); 1.55 (m, 1H); 1.45 (br. s, -OH); 1.33 (s, 3H); 1.31 (s, 3H); 0.02 (s, $^2J_{Sn-H} = 50$ Hz, 9H, Me_3Sn).

[1R*, 3S*]-1,3-dimethyl-3-trimethylstannylcyclopentan-1-ol (29a-anti). Liquid (41%). IR (film) 3500, 3450 cm^{-1} . 1H NMR ($CDCl_3$) 2.1-1.95 (m, 3H); 1.8-1.6 (m, 2H); 1.45-1.4 (m, 2H); 1.35 (s, 3H); 1.15 (s, 3H); 0.02 (s, $^2J_{Sn-H} = 50$ Hz, 9H, Me_3Sn). MS (EI) m/z 263 (M^+ - CH_3 , 6%), 245 (M^+ - CH_3 - H_2O , 11%), 165 (100%).

[1S*, 3S*]-1,3-dimethyl-3-tributylstannylcyclopentan-1-ol (29b-syn). Yellow pale oil (43%). IR (film) 3360, 1460 cm^{-1} . 1H NMR ($CDCl_3$) 2.0 (d, $J = 15$ Hz, 1H); 1.90-1.55 (m, 5H, $2 \times CH_2$, OH); 1.65 (d, $J = 15$ Hz, 1H); 1.45 (s, 3H); 1.43 (s, 3H); 1.5-0.90 (m, 27H, Bu_3Sn). ^{13}C NMR ($CDCl_3$) 81.1, 55.2, 41.9, 39.2, 32.3, 29.3, 29.1, 29.0, 27.6, 13.9, 7.9. MS (EI) m/z 347 (M^+ -Bu, 42%), 43 (100%). Anal. Calcd for $C_{19}H_{40}OSn$: C, 56.60; H, 10.00. Found: C, 56.90; H, 10.21.

[1R*, 3S*]-1,3-dimethyl-3-tributylstannylcyclopentan-1-ol (29b-anti). Yellow pale oil (43%). IR (film) 3580, 3390, 1450 cm^{-1} . 1H NMR ($CDCl_3$) 2.15-1.58 (m, 4H); 2.05 (d, $J = 14$ Hz, 1H); 1.75 (d, $J = 14$ Hz, 1H); 1.55-0.8 (m, 28H, Bu_3Sn , -OH); 1.40 (s, 3H); 1.20 (s, 3H). ^{13}C NMR ($CDCl_3$) 80.5, 56.2, 39.1, 31.5, 30.1, 29.7, 29.3, 28.3, 27.7, 13.8, 9.1. MS (EI) m/z 347 (M^+ -Bu, 31%), 43 (100%).

[1R*, 3S*]-1-allyl-3-methyl-3-tributylstannylcyclopentan-1-ol (30) Yellow pale oil (77%). IR (film) 3440, 1635 cm^{-1} . ^1H NMR (CDCl_3) 5.89 (ddt, $J = 16.3, 11, 7.5$ Hz, 1H); 5.15 (d, $J = 16.3$ Hz, 1H); 5.13 (d, $J = 11$ Hz, 1H); 2.32 (d, $J = 7.5$ Hz, 2H); 2.00 (d, $J = 14.2$ Hz, 1H); 1.94-1.73 (m, 3H); 1.66-1.6 (m, 2H); 1.49 (s, -OH); 1.6-0.8 (m, 27H, Bu_3Sn); 1.35 (s, 3H, CH_3). ^{13}C NMR (CDCl_3) 134.3, 118.7, 81.9, 52.7, 46.7, 39.9, 38.9, 31.5, 29.3, 28.9, 27.6, 13.6, 8.3. MS (EI) m/z 373 ($\text{M}^+ - \text{Bu}$, 7%), 41 (100%). Anal. Calcd for $\text{C}_{21}\text{H}_{42}\text{OSn}$: C, 58.76; H, 9.86. Found: C, 58.98; H, 9.98.

[1S, 2S, 3R, 5S]-1, 2-dimethyl-5-isopropenyl-3-tributylstannylcyclohexan-1-ol (31). Yellow pale oil (88%). IR (film) 3617, 3482, 1644 cm^{-1} . ^1H NMR (CDCl_3) 4.68 (s, 2H); 2.26 (tt, $J = 11.8, 4.0$ Hz, 1H); 1.96-1.91 (m, 1H); 1.80-1.76 (m, 1H); 1.73 (s, 3H); 1.67 (s, 1H, OH); 1.69-1.64 (m, 1H); 1.51-0.82 (m, 33H); 1.18 (s, 3H). ^{13}C NMR (CDCl_3) 150.2, 108.4, 71.3, 45.8, 44.3, 40.1, 36.8, 32.7, 29.4, 29.3, 27.8, 21.0, 16.5, 13.7, 11.3. MS (EI) m/z 401 ($\text{M}^+ - \text{Bu}$ 57%). $[\alpha]_{\text{D}}^{25} -26.9$ (c 1.96, HCCl_3). Anal. Calcd for $\text{C}_{23}\text{H}_{46}\text{OSn}$: C, 60.41; H, 10.14. Found: C, 60.63; H, 10.22. NOE enhancements were found between the following signals: a) 1.73 (Me-C=) to 1.8-1.76 ($\text{C}_2\text{-H}_{\text{ax}}$), b) 1.18 ($\text{C}_1\text{-CH}_3$) to 1.8-1.76 ($\text{C}_2\text{-H}_{\text{ax}}$) and to 1.69-1.64 ($\text{C}_6\text{-H}_{\text{ax}}$), c) 2.26 ($\text{C}_5\text{-H}_{\text{ax}}$) to 1.51-0.82 (SnBu_3).

[1R, 2S, 3R, 5S]-1-allyl-2-methyl-5-isopropenyl-3-tributylstannylcyclohexan-1-ol (32). Yellow pale oil (73%). IR (film) 3570, 1640, cm^{-1} . ^1H NMR (CDCl_3) 5.86 (ddt, $J = 16.4, 10.6, 7.5$ Hz, 1H); 5.13 (d, $J = 10.6$ Hz, 1H); 5.12 (d, $J = 16.4$ Hz, 1H); 4.7 (s, 1H); 4.68 (s, 1H); 2.3-2.22 (m, 3H); 1.93-1.82 (m, 2H); 1.72 (s, 3H); 1.71-1.52 (m, 3H); 1.1 (s, -OH); 1.5-0.82 (m, 31H, CH , CH_3 , Bu_3Sn). ^{13}C NMR (CDCl_3) 150.3, 133.7, 118.6, 108.2, 72.7, 45.8, 42.6, 42.4, 39.7, 39.6, 32.6, 29.3, 27.7, 21.0, 16.3, 13.7, 11.2. MS (EI) m/z 409 ($\text{M}^+ - \text{Bu-H}_2\text{O}$, 7%), 41 (100%). $[\alpha]_{\text{D}}^{25} -28.6$ (c 0.50, HCCl_3). Anal. Calcd for $\text{C}_{25}\text{H}_{48}\text{OSn}$: C, 62.12; H, 10.01. Found: C, 62.31; H, 10.12. NOE enhancements were found between the signals 1.72 (Me-C=) and 1.1 (OH).

[1S*, 3S*]-1,3-dimethyl-3-(tributylstannylmethyl)cyclopentan-1-ol (38-syn). Yellow pale oil (57%). IR (film) 3360, 1450 cm^{-1} . ^1H NMR (CDCl_3) 1.8-1.6 (m, 5H, $2\text{CH}_2\text{,OH}$); 1.68 (d, $J = 14$ Hz, 1H); 1.55 (d, $J = 14$ Hz, 1H); 1.38 (s, 3H); 1.16 (s, 3H); 1.1 (d, $J = 13$ Hz, 1H); 1.05 (d, $J = 13$ Hz, 1H).

1H); 1.5-0.9 (m, 29H, CH₂, Bu₃Sn). ¹³C NMR (CDCl₃) 81.1, 59.2, 43.1, 42.8, 41.7, 32.0, 30.1, 29.8, 28.4, 27.4, 13.9, 10.2. MS (EI) m/z 361 (M⁺-Bu, 6%), 43 (100%). Anal. Calcd for C₂₀H₄₂OSn: C, 57.57; H, 10.15. Found: C, 57.89; H, 10.37.

[1R*, 3S*]-1,3-dimethyl-3-(tributylstannylmethyl)cyclopentan-1-ol (38-anti). Yellow pale oil (14%). IR (film) 3360, 1450 cm⁻¹. ¹H NMR (CDCl₃) 1.8-1.73 (m, 3H, CH₂, OH); 1.64 (d, *J* = 15 Hz, 1H); 1.61 (d, *J* = 15 Hz, 1H); 1.34 (s, 3H); 1.21 (s, 2H); 1.00 (s, 3H); 1.5-0.9 (m, 29H, CH₂, Bu₃Sn). ¹³C NMR (CDCl₃) 81.1, 59.2, 43.0, 41.5, 31.3, 29.8, 29.6, 29.1, 28.7, 27.4, 13.9, 10.1. MS (EI) m/z 361 (M⁺-Bu, 5%), 43 (100%).

[1S*, 3S*]-1-methyl-3-(tributylstannylmethyl)cyclohexan-1-ol (39-syn). Yellow pale oil (65%). ¹H NMR (CDCl₃) 1.8-1.5 (m, 7H); 1.5-0.8 (m, 32H, Bu₃Sn, 2xCH₂, OH); 1.20 (s, 3H). ¹³C NMR (CDCl₃) 70.2, 49.8, 38.2, 36.2, 31.6, 31.5, 29.2, 27.4, 22.0, 18.3, 13.6, 9.3. MS (EI) m/z 361 (M⁺-Bu, 42%), 343 (M⁺-Bu-H₂O, 41%), 235 (100%). Anal. Calcd for C₂₀H₄₂OSn: C, 57.57; H, 10.15. Found: C, 57.80; H, 10.26.

[1R*, 3S*]-1-methyl-3-(tributylstannylmethyl)cyclohexan-1-ol (39-anti). Yellow pale oil (22%). IR (film) 3600, 3330, 1450 cm⁻¹. ¹H NMR (CDCl₃) 1.75-1.65 (m, 5H); 1.6-0.8 (m, 34H); 1.25 (s, 3H). ¹³C NMR (CDCl₃) 71.5, 51.5, 40.1, 37.2, 33.9, 29.2, 27.3, 25.9, 24.1, 18.3, 13.6, 9.3.

Addition of Grignard reagents to -vinylstannyl ketones.

Typically to a solution of the ketone **9a** (275 mg, 0.66 mmol) in 2 ml of THF cooled to 0°C, was added dropwise MeMgI, BuMgI, or PhMgBr (0.73 mmol). The mixture was stirred for 1 hour at this temperature and quenched with saturated solution of NH₄Cl (5 ml). The aqueous layer was extracted with ether (2 x 5 ml) and the combined organic extracts were washed with brine (5 ml), dried over anhydrous MgSO₄, filtered, and the solvent evaporated in vacuo. The residue was chromatographed in silica, to afford the alcohols **14a-c** respectively (Table 1).

Assignment of the stereochemistry of **14a** (scheme 3).

To a solution of the ketone **18** (5 mmol, 628 mg) in 5 ml of THF, cooled to -78°C , was added 10 mmol of MeLi. The yellow solution was stirred for 1 h at this temperature and quenched with 2 ml of CH_3OH . The solution was warmed to room temperature, diluted with 10 ml of ether and washed successively with saturated solution of NH_4Cl (5 ml) and brine (5 ml). The organic layer was dried over anhydrous MgSO_4 , filtered, and the solvent was evaporated under reduced pressure. The residue was chromatographed in silica gel to afford the corresponding alcohols **19** and **20** in high yields.

[1R*, 3S*]-1,3-dimethyl-3-vinylcyclopentanol (19). Yellow pale oil (45%). IR (film) 3600, 3300, 1630 cm^{-1} . ^1H NMR (CDCl_3) 6.05 (dd, $J = 15, 10$ Hz, 1H); 5.05 (dd, $J = 15, 1$ Hz, 1H); 4.91 (dd, $J = 10, 1$ Hz, 1H); 1.90 (d, $J = 15$ Hz, 1H); 1.6-1.5 (m, 5H); 1.55 (d, $J = 15$ Hz, 1H); 1.45 (s, 3H); 1.10 (s, 3H). ^{13}C NMR (CDCl_3) 148.9, 110.1, 81.2, 55.3, 45.4, 40.9, 38.2, 29.3, 27.1. MS (EI) m/z 122 ($\text{M}^+ - \text{H}_2\text{O}$, 10%), 43 (100%).

[1S*, 3S*]-1,3-dimethyl-3-vinylcyclopentanol (20). Yellow pale oil (46%). IR (film) 3600, 3350, 1630 cm^{-1} . ^1H NMR (CDCl_3) 5.87 (dd, $J = 17, 11$ Hz, 1H); 4.93 (dd, $J = 17, 1$ Hz, 1H); 4.87 (dd, $J = 11, 1$ Hz, 1H); 1.83 (d, $J = 15$ Hz, 1H); 1.8-1.68 (m, 5H); 1.62 (d, $J = 15$ Hz, 1H); 1.35 (s, 3H); 1.23 (s, 3H). ^{13}C NMR (CDCl_3) 149.0, 109.1, 81.2, 54.3, 45.2, 42.1, 39.2, 30.3, 27.9. MS (EI) m/z 122 ($\text{M}^+ - \text{H}_2\text{O}$, 28%), 43 (100%).

Cyclization of vinylcyclopentanol **19**

Ozonolysis of vinylcyclopentanol **19**

(Caution: ozone is very toxic and special careful must be taken). Typically, a solution of the alcohol **19** (1 mmol) in 3 ml of CH_2Cl_2 was cooled at -78°C and bubbled with ozone for 10 minutes. The clear blue solution was purged with argon to eliminate the excess of ozone (negative test in oxidation of a IK solution) and a great excess of Me_2S (6 mmol) was added. The solution was stirred at room temperature overnight and then washed with 10 ml of brine. The aqueous layer was extracted with ether and the organic extracts were dried over MgSO_4 , filtered, and evaporated in vacuo. Suitable

chromatography of the residue afforded the corresponding hydroxyaldehyde **21**. (δ_{H} s, 9.6 ppm, HCO mixed with their hemiacetalic tautomer (δ_{H} br. s, 4.7 ppm O-CH-OH).

Oxidation of the hydroxyaldehyde **21**

Typically, the lactone **22** was obtained by adding PCC (323 mg, 1.5 mmol) to a solution of the hydroxyaldehyde **21** (0.5 mmol) in 4 ml of CH_2Cl_2 at room temperature. The mixture was stirred for 5 hours and filtered through a short pad of celite. The filtered solution was treated with 5 ml of brine and the organic layer was extracted with ether. The organic extracts were dried over MgSO_4 , filtered, and evaporated in vacuo. Suitable chromatography of the residue afforded the corresponding lactone **22** in excellent yield.

[1S*, 4R*]-1,4-dimethyl-2-oxabicyclo [2.2.1] heptan-3-one (22). Liquid (92%). IR (film) 1760 cm^{-1} . ^1H NMR (CDCl_3) 1.85 (d, $J = 8\text{ Hz}$, 1H); 1.70 (d, $J = 8\text{ Hz}$, 1H); 1.9-1.75 (m, 4H); 1.55 (s, 3H); 1.30 (s, 3H). ^{13}C NMR (CDCl_3) 180.1, 88.2, 53.4, 49.3, 35.3, 32.0, 19.1, 14.4. MS (EI) m/z 126 ($\text{M}^+ + 1 - \text{CH}_3$, 9%), 43 (100%).

[1S*, 3S*]-1-butyl-3-(cis-2-tributylstannylvinyl)cyclohexan-1-ol phenylurethane. Phenyl isocyanate (0.54 ml, 595 mg, 5 mmol) was added, under N_2 , to a solution of the alcohol **15b** in 2.5 ml of dry pyridine at room temperature. The mixture was heated at 60°C for 2 h and then was diluted with 10 ml ether at room temperature. The mixture was washed thoroughly several times with brine and the combined organic extracts were dried over MgSO_4 , filtered, and evaporated in vacuo.. The residue was chromatographed in silica to afford the phenylurethane (88%) and recrystallized from hexane (cubes, m.p. $50\text{--}51^\circ\text{C}$). IR (film) 3440, 1740, 1610, 1600 cm^{-1} . ^1H NMR (CDCl_3) 7.4-7.05 (m, 5H, Ph); 6.5 (br s, $-\text{NH}-$); 6.3 (dd, $^3J_{\text{Sn-H}} = 150\text{ Hz}$, $J = 12, 10\text{ Hz}$, 1H); 5.75 (d, $^2J_{\text{Sn-H}} = 75\text{ Hz}$, $J = 12\text{ Hz}$, 1H); 2.55 (m, 1H); 2.15-0.9 (m, 44H, 4CH_2 , Bu and Bu_3Sn). ^{13}C NMR (CDCl_3) 153.6, 152.1, 138.2, 129.3, 126.5, 123.0, 117.9, 84.2, 41.6, 41.2, 38.7, 33.5, 32.4, 29.2, 27.3, 25.3, 23.3, 21.1, 14.2, 13.7, 10.4; MS (EI) m/z 592 ($\text{M}^+ + 1$, 7%), 120 (100). Anal. calcd. for $\text{C}_{31}\text{H}_{53}\text{NO}_2\text{Sn}$: C, 63.06; H, 9.05; N 2.37. Found: C, 63.17; H, 8.73; N, 2.48.