**Cyclocarbopalladation:
5-exo-dig Cyclization *Versus* Direct Stille Cross Coupling Reaction.
The Influence of the α,β -Propargylic Substitution**

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General Methods. Reactions were run under an atmosphere of argon in oven-dried glassware using standard syringe, cannula, and septa apparatus. Et₂O and THF were distilled from sodium benzophenone. Benzene and DMF were distilled from KOH. Crude products were purified by flash column chromatography on Merck 230-400 mesh silica gel. For some compounds, 5% Et₃N treated silica gel was used to avoid decomposition. Analytical TLC was carried out on Merck (60F-254) silica gel plates. ¹H spectra were recorded at 200 or 300 MHz using the residual solvent signal as internal reference (CDCl₃, 7.27 ppm ; C₆D₆, 7.16 ppm). Chemical shifts are quoted in ppm, coupling constants (*J*) are given in Hz. The following abbreviations are used to describe peak patterns when appropriate : s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), ap (apparent), br (broad). ¹³C NMR spectra were recorded at 50 or 75 MHz at ambient temperature in CDCl₃ with δ (CDCl₃) at 77.0 as internal standard. Multiplicities were determined by DEPT pulse. Melting points were determined with a glass capillary apparatus and are uncorrected. Mass Spectral Analysis by Electro-Spray were performed using a Mariner ESI-Tof instrument from Applied Bio-System /Perking Elmer.

1-Typical procedure for the synthesis of β -bromoaldehyde

Synthesis of 2-bromo-cyclopent-1-ene-1-carbaldehyde (6a)

Method A :

Phosphore tribromide (23.7 mL, 250 mmol, 2.5 equiv.) is dropwise added to a solution of dry DMF (23.2 mL, 300 mmol, 3 equiv.) in dry CH_2Cl_2 (90 mL) cooled at 0°C . After one hour stirring at 0°C , the mixture turns yellow. Then a solution of cyclopentanone (8.85 mL, 100 mmol, 1 equiv.) in dry CH_2Cl_2 (40 mL) is added dropwise at 0°C to the suspension and stirred overnight at room temperature. The solution is powered on ice while the pH is maintained at pH 7-8 by regular addition of NaHCO_3 (sat.) and $\text{NaHCO}_3(\text{s})$. The mixture is extracted with ethylacetate and the combined organic phases are washed with distilled water (3×200 mL) and brine (1×250 mL), dried over Na_2SO_4 and concentrated to an oil stored at -20°C in etheral solution (12.2 g, 75%).

Method B :

The procedure is the same except that 3 equiv. of phosphore tribromide were used and that the solution is stirred 1h30 at reflux ($T = 45^\circ\text{C}$) instead of one night at room temperature.

2-General procedure for the preparation of the diols from the β -bromoaldehyde

(2a *anti*) (1*R*,2*S**)-1-(2-bromocyclopent-1-en-yl)-4-(trimethylsilyl)but-3-yne-1,2-diol and

(3a *syn*) (1*R**,2*R**)-1-(2-bromocyclopent-1-en-yl)-4-(triméthylsilyl)but-3-yne-1,2-diol

n-BuLi (30.9 mL, 1.55 M in hexane, 47.9 mmol, 1.3 equiv.) is added dropwise to a solution of 3-[(1-methoxy-1-methyl-ethoxy)-prop-1-ynyl]trimethylsilane (9.6 g, 47.9 mmol, 1.3 equiv.)

in dry THF (60 mL) cooled at -78°C under argon. The yellow solution is stirred during 15 min. at -78°C , and added at -78°C through a cannula to a solution of 2-bromo-cyclopent-1-en carbaldehyde **6a** (6.0 g, 36.8 mmol, 1 equiv.) in dry THF (15 mL). The brown solution is allowed to warm to room temperature. The reaction is followed by TLC ($\text{Et}_2\text{O}/\text{Hexane}$: 20/80, KMnO_4) and quenched after 35 minutes with saturated NaHCO_3 solution (40 mL). The mixture is diluted in diethylether. After 3 extractions with diethylether (3×40 mL), the combined organic phases are washed with distilled water (2×40 mL). Then the organic phase is treated with HCl 1N (30 mL). The deprotection is followed by TLC ($\text{Et}_2\text{O}/\text{Hexane}$: 60/40, anisaldehyde). After 2h30, the mixture is extracted with diethylether (2×80 mL). The combined organic phases are washed with distilled water (2×250 mL) and brine (50 mL), dried over Na_2SO_4 and concentrated to an oil. The mixture of the 2 diastereoisomers is separated by flash chromatography on silica gel ($\text{Et}_2\text{O}/\text{Hexane}$: 30/70) to give 3.55 g of diol **2a anti** and 1.54 g of dia **3a syn** (overall yield 57 %).

3-General procedure for the preparation of the dioxolane derivatives

{{(4*S,5*R**)-5-(2-bromocyclopent-1-en-yl)-2,2-diméthyl-1,3-dioxolan-4-yl}ethynyl} trimethylsilane (23)**

(1*R**,2*S**)-1-(2-bromocyclopent-1-en-yl)-4-(trimethylsilyl)but-3-yne-1,2-diol (900 mg, 2.97 mmol, 1 equiv.), a large excess of 2,2-dimethoxypropane (1.54 g, 14.8 mmol, 5 equiv.), *p*-TsOH (56 mg, 0.29 mmol, 10 %) and acetone (16 mL) are vigorously stirred at room temperature during 30 minutes. The mixture is treated with brine (25 mL), extracted with diethylether (3×25 mL), and the combined organic phases are washed with distilled water (25 mL), NaHCO_3 sat (25 mL) and brine (25 mL), dried over Na_2SO_4 and concentrated to dryness. The residue is purified by flash chromatography on silica gel ($\text{Et}_2\text{O}/\text{Hexane}$: 10/90) to give 880 mg of cetal *anti* (78%).

4-General procedure for the cyclocarbopalladation of δ -bromopropargylic diols and dioxolanes

The reaction is carried out in an oven-dried 25 mL-bicol, equipped with a reflux condenser, under argon atmosphere. Trans-1,2-bis-(tributylstannyl)ethylene (1.286 mmol, 780 mg, 1.3 equiv.) and Pd(PPh₃)₄ (0.099 mmol, 114 mg, 10 %) are added to a solution of diol *anti* (0.989 mmol, 1 equiv) in benzene (6.6 mL). The mixture is purged with argon and heated at 95°C under argon. The reaction is followed by TLC (Et₂O/Hexane : 50/50, anisaldehyde). After the time indicated in Table 1 and 2 at 95°C, the mixture is cooled to room temperature, diluted in diethylether (30 mL), treated with active charcoal, filtrated over *Celite* and concentrated to dryness. The residue is purified by flash chromatography on silica gel treated with NEt₃ (5%) (Et₂O/Hexane : see detail on the description of products) to give the *syn* or *anti* cyclocarbopalladated or the *trans* Stille product and in some cases the other isomer *anti*.

5-Analytical description of the products

a-Starting propargylic diols

(1*R**,2*S**)-1-(2-bromocyclopent-1-en-1-yl)-4-(trimethylsilyl)but-3-yne-1,2-diol (2a)

<ul style="list-style-type: none">- Rf: 0.39 (Et₂O/Hexane : 40/60)- Eluant of chromatography : 10/90 (Et₂O/Hexane)- Aspect : white solid- mp = 70 °C- Yield = 40 %- C₁₂H₁₉BrO₂Si- MW = 303.27
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¹**H-RMN** (300 MHz, CDCl₃): δ 4.63 (dd, 1H, $J = 4.9$ Hz, $J = 5.8$ Hz, CHOH-CHOH-C $\equiv$ C-TMS), 4.46 (m, 1H, $J = 4.9$ Hz, $J = 6.8$ Hz, CHOH-CHOH-C $\equiv$ C-TMS), 2.74-2.62 (m, 2H, allylic CH₂), 2.60-2.47 (m, 2H, allylic CH₂), 2.38-2.24 (superposed doublets, 2H, 2*OH), 1.96 (quint, $J = 7.5$ Hz, 2H, CH₂), 0.21 (s, 9H, Si(CH₃)₃).

¹³**C-NMR** (50 MHz, CDCl₃) : δ 138.59, 119.4, 103.03, 91.83, 72.53, 64.91, 40.27, 31.08, 21.84, -0.34.

IR (FTIR, KBr) : ν = 3318 s (O-H), 2958 s, 2899 s, 2853 s, 2177 m (C $\equiv$ C), 1646 m (C=C), 1444 s, 1422 s, 1356 m, 1342 m, 1318 m, 1293 m, 1249 s, 1171 m, 1103 s, 1043 s, 1027 s, 1013 s, 905 m, 918 m, 844 s, 779 s, 762 s, 733 m, 701 m, 638 m, 540 f cm⁻¹.

HRMS (ESI, positive ion 180 eV) calcd for (C₁₂H₁₉BrO₂SiNa)⁺ 325.0235; found 325.0236

(1*R,2*R**)-1-(2-bromocyclopent-1-en-1-yl)-4-(trimethylsilyl)but-3-yne-1,2-diol (3a)**

<ul style="list-style-type: none"> - R_f : 0.29 (Et₂O/Hexane : 40/60) - Eluant of chromatography : 10/90 (Et₂O/Hexane) - Aspect : white solid - mp = 62 °C - Yield = 17 % - C₁₂H₁₉BrO₂Si - MW = 303.27
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¹H-NMR (200 MHz, CDCl₃) : δ 4.62 (d, 1H, *J* = 7.1 Hz, CHOH-CH₂OH-C≡C-TMS), 4.38 (d, 1H, *J* = 7.1 Hz, CH₂OH-CHOH- C≡C-TMS), 2.73- 2.18 (m, 8H, 2 allylic CH₂ and 1 CH₂ and 2 OH), 0.17 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, CDCl₃) : δ 138.02, 120.73, 102.36, 91.63, 73.13, 65.10, 40.28, 30.38, 21.85, -0.35.

IR (CH₂Cl₂) : ν 3388 s (OH), 2959 s, 2899 m, 2853 m, 2177 m (C≡C), 1654 m (C=C), 1442 m, 1408 m, 1319 m, 1250 s, 1134 w, 1088 s, 1054 s, 1002 s, 969 s, 845 s, 761 s cm⁻¹.

HRMS (ESI, positive ion 180 eV) calcd for (C₁₂H₁₉BrO₂SiNa)⁺ 325.0235; found 325.0239

(1*R,2*S**)-1-(2-bromocyclohex-1-en-1-yl)-4-(trimethylsilyl)but-3-yne-1,2-diol (2b)**

<ul style="list-style-type: none"> - R_f : 0.18 (Et₂O/Hexane : 30/70) - Eluant of chromatography : 10/90 (Et₂O/Hexane) - Aspect : yellowish solid - mp = 80 °C - Yield = 25 % - C₁₃H₂₁BrO₂Si - MW = 317.30
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¹H NMR (200 MHz, CDCl₃) : δ 4.80 (dd, 1H, ¹*J* = ²*J* = 5.1 Hz, CHOH-CH₂OH-C≡C-TMS), 4.58 (dd, 1H, *J* = 6.8 Hz, *J* = 4.6 Hz, CH₂OH-CHOH- C≡C-TMS), 2.56-2.32 (m, 6H, 2 allylic CH₂ + 2 d, 2H, *J* = 7.1 Hz, *J* = 5.6 Hz, 2 OH), 1.73-1.69 (m, 4H, 2 CH₂), 0.20 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, CDCl₃) : δ 134.11, 121.67, 103.42, 91.59, 75.29, 64.31, 36.85, 26.41, 24.56, 21.93, -0.33.

IR (KBr) : ν 3326 s (OH), 2956 s, 2934 s, 2897 m, 2853 m, 2177 w (C $\equiv$ C), 1652 w (C=C), 1448 m, 1337 m, 1250 s, 1168 w, 1114 s, 1068 m, 1037 s, 1014 m, 970 m, 953 w, 903 w, 840 s, 761 s, 700 m, 640 w, 504 w cm⁻¹.

HRMS (ESI, positive ion 130 eV) calcd for (C₁₃H₂₁BrO₂SiNa)⁺ 339.0392; found 339.0443

(1R*,2R*)-1-(2-bromocyclohex-1-en-1-yl)-4-(trimethylsilyl)but-3-yne-1,2-diol (3b)

<ul style="list-style-type: none"> - R_f : 0.10 (Et₂O/Hexane : 30/70) - Eluant of chromatography : 10/90 (Et₂O/Hexane) - Aspect : yellowish solid - mp = 84 °C - Yield = 15 % - C₁₃H₂₁BrO₂Si - MW = 317.30
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¹H-NMR (200 MHz, CDCl₃) : δ 4.80 (d, 1H, *J* = 7.3 Hz, CHOH-CH $\underline{\text{O}}$ H-C $\equiv$ C-TMS), 4.42 (d, 1H, *J* = 7.3 Hz, CH $\underline{\text{O}}$ H-CHOH- C $\equiv$ C-TMS), 2.57-1.56 (m, 8H, 2 allylic CH₂ et 2 CH₂), 0.21 (s, 9H, Si(CH₃)₃).

¹³C-NMR (50 MHz, CDCl₃) : δ 133.62, 122.77, 102.61, 90.97, 77.52, 64.72, 36.92, 25.71, 24.41, 21.94, -0.45.

IR (CH₂Cl₂) : ν 3389 s (O-H), 2937 s, 2898 s, 2861 s, 2841 s, 2663 w, 2177 m (C $\equiv$ C), 1682 w, 1652 w (C=C), 1448 s, 1436 m, 1408 m, 1333 m, 1250 s, 1148 m, 1140 m, 1101 m, 1063 s, 972 s, 944 m, 840 s, 805 m, 761 s, 712 m, 671 m cm⁻¹.

HRMS (ESI, positive ion 100 eV) calcd for (C₁₃H₂₁BrO₂SiNa)⁺ 339.0392; found 339.0391

(1R*,2S*)-1-(2-bromocyclohept-1-en-1-yl)-4-(trimethylsilyl)but-3-yne-1,2-diol (2c)

<ul style="list-style-type: none"> - R_f : 0.22 (Et₂O/Hexane : 40/60) - Eluant of chromatography : 10/90 (Et₂O/Hexane) - Aspect : yellow solid - mp = 80 °C - Yield = 36 % - C₁₄H₂₃BrO₂Si - MW = 331.32
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¹H NMR (200 MHz, CDCl₃) : δ 4.79 (broad s, 1H, CHOH-CH $\underline{\text{O}}$ H-C $\equiv$ C-TMS), 4.42 (m, 1H, CH $\underline{\text{O}}$ H-CHOH- C $\equiv$ C-TMS), 2.85-2.79 (m, 2H, allylic CH₂), 2.42-2.26 (m, 3H, allylic CH₂ + 1 OH), 1.82-1.52 (m, 7H, 3 CH₂ + 1 OH), 0.19 (s, 9H, Si(CH₃)₃).

¹³C-NMR (50 MHz, CDCl₃) : δ 139.23, 125.82, 103.28, 91.85, 77.23, 64.56, 41.78, 31.51, 27.77, 26.20, 25.10, -0.30.

IR (CH₂Cl₂) : ν 3616 s (O-H), 2958 s (CH₃,CH₂ or C-H), 2924 s, 2852 s, 2695 w, 2176 m (C $\equiv$ C), 1947 w, 1715 w, 1638 m (C=C), 1448 s, 1407 s, 1332 m, 1250 s, 1215 m, 1101 s, 1041 s, 994 m, 970 m, 952 m, 870 s, 844 s, 761 s, 699 m cm⁻¹.

HRMS (ESI, positive ion 130 eV) calcd for (C₁₄H₂₃BrO₂SiNa)⁺ 353.0548; found 353.0532

(1*R,2*R**)-1-(2-bromocyclohept-1-en-1-yl)-4-(trimethylsilyl)but-3-yne-1,2-diol (3c)**

<ul style="list-style-type: none"> - R_f : 0.16 (Et₂O/Hexane : 40/60) - Eluant of chromatography : 10/90 (Et₂O/Hexane) - Aspect : yellow oil - Yield = 17 % - C₁₄H₂₃BrO₂Si - MW = 331.32
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¹H NMR (200 MHz, CDCl₃) : δ 4.84 (dd, 1H, *J* = 8.2 Hz, *J* = 1.9 Hz, CHOH-CHOH-C $\equiv$ C-TMS), 4.42 (m, 1H, CHOH-CHOH- C $\equiv$ C-TMS), 2.87-2.77 (m, 2H, allylic CH₂), 2.50-2.28 (m, 4H, allylic CH₂ + 2 OH), 1.94-1.50 (m, 6H, 3 CH₂), 0.19 (s, 9H, Si(CH₃)₃).

¹³C-NMR (50 MHz, CDCl₃) : δ 138.57, 126.83, 102.59, 91.35, 78.53, 64.59, 41.69, 31.66, 27.79, 25.78, 24.77, -0.36.

IR (CH₂Cl₂) : ν 3390 s (broad, OH), 2925 s, 2849 s, 2180 m (C $\equiv$ C), 1731 w, 1645 m (C=C), 1446 m, 1249 s, 1061 s, 840 s, 761 s, 700 m cm⁻¹.

HRMS (ESI, positive ion 120 eV) calcd for (C₁₄H₂₃BrO₂SiNa)⁺ 353.0548; found 353.0537

b-dioxolanes

{[(4*S,5*R**)-5-(2-bromocyclopent-1-en-1-yl)-2,2-dimethyl-1,3-dioxolan-4-yl]ethynyl} (trimethyl)silane (23)**

<ul style="list-style-type: none"> - R_f : 0.65 (Et₂O/Hexane : 10/90) - Eluant of chromatography : 10/90 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 78 % - C₁₅H₂₃BrO₂Si - MW = 340.32
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¹H NMR (300 MHz, neutralised CDCl₃) : δ 4.95 (m, 2H, -OCH₂-C≡C-TMS et Br-C=C-CH₂O), 2.74-2.44 (m, 4H, 2 allylic CH₂), 2.00-1.87 (m, 2H, CH₂), 1.56 (s, 3H, Me), 1.37 (s, 3H, Me), 0.15 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, neutralised CDCl₃) : δ 137.74, 119.07, 110.17, 101.24, 92.12, 76.58, 68.52, 40.40, 32.11, 27.06, 25.45, 21.80, -0.43.

IR (CH₂Cl₂) : ν 2986 m, 2960 m, 2900 m (CH₃,CH₂ or C-H), 2855 m, 2176 w (C≡C), 1656 f (C=C), 1455 w, 1408 w, 1380 m, 1302 w, 1319 , 1250 s, 1233 s, 1211 m, 1159 m, 1097 s, 1057 s, 930 w, 844 s, 760 s, 700 w, 638 w, 580 w, 503 m cm⁻¹.

{[(4*R,5*R**)-5-(2-bromocyclopent-1-en-1-yl)-2,2-dimethyl-1,3-dioxolan-4-yl] ethynyl} (trimethyl)silane (29)**

<ul style="list-style-type: none"> - R_f : 0.55 (Et₂O/Hexane : 10/90) - Eluant of chromatography : 10/90 (Et₂O/Hexane) - Aspect : white solid - mp = 104 °C - Yield = 87 % - C₁₅H₂₃BrO₂Si - MW = 340.32
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¹H NMR (300 MHz, neutralized CDCl₃) : δ 4.95 (d, 1H, *J* = 7.8 Hz, -OCH₂-C≡C-TMS), 4.35 (d, 1H, *J* = 8.1 Hz, -CBr=CH₂O-), 2.70-2.65 (m, 2H, allylic CH₂), 2.55-2.22 (m, 2H, allylic CH₂), 2.01-1.91 (m, 2H, CH₂), 1.50 (s, 3H, Me), 1.40 (s, 3H, Me), 0.16 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, neutralized CDCl₃) : δ 135.32, 122.05, 110.37, 101.11, 92.10, 78.86, 68.13, 40.71, 29.96, 26.65, 26.19, 21.45, -0.43.

IR (CH₂Cl₂) : ν 2990 w, 2965 m, 2849 w, 2359 w, 2179 w (C≡C), 1654 w (C=C), 1373 w, 1320 w, 1250 m, 1163 w, 1095 w, 1053 m, 844 s, 762 s cm⁻¹.

{[(4*S,5*R**)-5-(2-bromocyclohex-1-en-1-yl)-2,2-dimethyl-1,3-dioxolan-4-yl]ethynyl} (trimethyl)silane (24)**

<ul style="list-style-type: none"> - 0.60 (Et₂O/Hexane : 10/90) - Eluant of chromatography : 10/90 (Et₂O/Hexane) - Aspect : white solid - mp = 68 °C - Yield = 73 % - C₁₆H₂₅BrO₂Si - MW = 357.36
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¹H NMR (200 MHz, neutralised CDCl₃) : δ 5.08 (2d, 2H, $J = 6.8$ Hz, $J = 6.6$ Hz, -OCH-C $\equiv$ C-TMS et -CBr=CH-), 2.62-2.13 (m, 4H, 2 allylic CH₂), 1.80-1.64 (m, 4H, 2 CH₂), 1.57 (s, 3H, Me), 1.37 (s, 3H, Me), 0.16 (s, 9H, Si(CH₃)₃).

¹³C-NMR (50 MHz, neutralised CDCl₃) : δ 133.11, 121.40, 110.04, 101.57 91.64, 80.47, 68.41, 36.77, 27.57, 26.93, 25.55, 24.55, 21.89, -0.34.

IR (CH₂Cl₂) : ν 2982 w, 2936 m, 2864 w, 2358 w, 2179 w (C $\equiv$ C), 1648 w, 1446 w, 1380 m, 1332 m, 1249 s, 1232 m, 1210 m, 1160 m, 1108 m, 11052 s, 975 m, 902 m, 843 s, 760 f cm⁻¹.

{{(4*R,5*R**)-5-(2-bromocyclohex-1-en-1-yl)-2,2-dimethyl-1,3-dioxolan-4-yl}ethynyl} (trimethyl)silane (30)**

<ul style="list-style-type: none"> - R_f : 0.47 (Et₂O/Hexane : 10/90) - Eluant of chromatography : 10/90 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 82 % - C₁₆H₂₅BrO₂Si - MW = 357.36
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¹H NMR (300 MHz, neutralized CDCl₃) : δ 5.27 (d, 1H, $J = 7.5$ Hz, -OCH-C $\equiv$ C-TMS), 4.35 (d, 1H, $J = 7.5$ Hz, -CBr=CH-), 2.57-2.52 (m, 2H, allylic CH₂), 2.34-1.95 (m, 2H, allylic CH₂), 1.76-1.59 (m, 4H, 2 CH₂), 1.52 (s, 3H, Me), 1.43 (s, 3H, Me), 0.17 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, neutralized CDCl₃) : δ 130.90, 124.17, 110.49, 102.16, 92.1, 83.02, 68.39, 37.20, 26.60, 26.03, 25.37, 24.54, 21.92, -0.37.

IR (CH₂Cl₂) : ν 2990 m, 2942 s, 2860 m, 2341 w, 2179 w (C $\equiv$ C), 1654 w, 1449 w, 1380 m, 1334 m, 1249 w, 1208 m, 1163 m, 1108 s, 1048 s, 974 m, 946 w, 843 s, 761 s, 504 w.

{{(4*S,5*R**)-5-(2-bromocyclohept-1-en-1-yl)-2,2-dimethyl-1,3-dioxolan-4-yl}}ehynyl (trimethyl)silane (25)**

<ul style="list-style-type: none"> - R_f = 0.72 (70/30 Et₂O/Hexane) - Eluant of chromatography : 30/70 (Et₂O/Hexane) - Aspect : yellow oil - Yield = 68 % - C₁₇H₂₇BrO₂Si - MW = 371.39
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¹H NMR (300 MHz, CDCl₃) δ : 5.10 (d, 1H, *J* = 6.6 Hz); 4.99 (d, 1H, *J* = 6.6 Hz); 2.85 and 2.73 (ABX system dd, *J*_{AX} = 7.2 Hz, *J*_{BX} = 7.2 Hz, *J*_{AB} = 16.2 Hz); 2.51 and 2.34 (ABX system dd, *J*_{AX} = 7.6 Hz, *J*_{BX} = 10.6 Hz, *J*_{AB} = 16.2 Hz); 1.95-1.55 (m, 8H); 1.50-1.20 (m, 4H); 0.16 (s, 9H).

¹³C NMR (75 MHz, CDCl₃) δ : 137.99 (C_{quat}); 137.99 (C_{quat}); 125.57 (C_{quat}); 110.15 (C_{quat}); 102.10 (C_{quat}); 92.15 (C_{quat}); 82.44 (+); 68.24 (+); 41.79 (-); 31.19 (-); 29.11 (-); 27.09 (+); 25.73 (-); 25.58 (+); 25.45 (-); -0.32 (+).

IR (FTIR, CCl₄) : ν = 3323, 2927, 2854, 2361, 2176, 1593, 1445, 1376, 1332, 1248, 1232, 1160, 1092, 1049, 846, 759 cm⁻¹.

{{(4*R,5*R**)-5-(2-bromocyclohept-1-en-1-yl)-2,2-dimethyl-1,3-dioxolan-4-yl}ethynyl} (trimethyl)silane (31)**

<ul style="list-style-type: none"> - R_f : 0.46 (Et₂O/Hexane : 10/90) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 70 % - C₁₇H₂₇BrO₂Si - MW = 371.39
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¹H NMR (200 MHz, neutralized CDCl₃) : δ 5.22 (d, 1H, *J* = 7.6 Hz, -OCH-C≡C-TMS), 4.24 (d, 1H, *J* = 7.8 Hz, -CBr=CH-), 2.81 (t, 2H, allylic CH₂), 2.84-2.78 (m, 2H, allylic CH₂), 2.26-2.21 (m, 2H, allylic CH₂), 1.84-1.55 (m, 6H, 3 CH₂), 1.52 (s, 3H, Me), 1.45 (s, 3H, Me), 0.17 (s, 9H, Si(CH₃)₃).

¹³C-NMR (50 MHz, neutralized CDCl₃) : δ 135.83, 128.16, 110.43, 101.84, 91.90, 84.36, 68.21, 41.98, 31.59, 27.62, 26.75, 26.18, 25.05, -0.37.

IR (CH₂Cl₂) : ν 2990 m, 2925 s, 2855 m, 2180 w (C≡C), 1648 w (C=C), 1446 w, 1380 w, 1380 m, 1249 w, 1049 s, 844 s, 760 f cm⁻¹.

c- Bicyclic stannylated diols

HRMS of all the stannylated compounds have been performed without success due to the rapid decomposition of the products during the analyses. Microanalyses as well didn't give good results due to the highly viscous oil always contaminated with a small amount of solvent. Nevertheless the other analyses are in good agreement with the proposed structures.

(1*R**,2*S**,3*E*)-3-[(2*E*)-3-(tributylstannyl)-1-(trimethylsilyl)prop-2-enylidene]-1,2,3,4,5,6-hexahydropentalene-1,2-diol : minor isomer (14b)

<ul style="list-style-type: none"> - R_f : 0.47 (Et₂O/Hexane : 50/50) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 16 % - C₂₆H₄₆O₂SiSn - MW = 537.44
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¹H NMR (300 MHz, neutralized CDCl₃) : δ 6.83 (d, 1H, *J* = 19.8 Hz, -CH=CH(SnBu₃)), 5.92 (d, 1H, *J* = 19.8 Hz, -CH=CH(SnBu₃)), 5.00 (m, 1H, CHOH-CHOH-C=C-TMS), 4.53 (s, 1H, CHOH-CHOH-C=C-TMS), 2.90-2.22 (m, 8H, 3 CH₂ + 2 OH), 1.62-1.22 (m, 12H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.96-0.86 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.17 (s, 9H, Si(CH₃)₃).

¹³C-NMR (50 MHz, neutralized CDCl₃) : δ 159.58, 150.73, 149.90, 147.79, 137.03, 130.29, 76.90, 70.24, 30.44, 29.17, 27.89, 27.63, 27.27, 13.68, 9.68, 1.91.

IR (CH₂Cl₂) : ν 3392 w (broad, OH), 2955 i, 2925 i, 2854 m, 2362 w, 1731 m, 1566 w (C=C), 1463 w, 1376 w, 1248 m, 1077 m, 836 m, 800 w, 750 w, 691 w.

(1*R**,2*S**,3*Z*)-3-[(2*E*)-3-(tributylstannyl)-1-(trimethylsilyl)prop-2-enylidene]-1,2,3,4,5,6-hexahydropentalene-1,2-diol : major isomer (14a)

<ul style="list-style-type: none"> - R_f : 0.33 (Et₂O/Hexane : 50/50) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 59 % - C₂₆H₄₆O₂SiSn - MW = 537.44
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¹H NMR (300 MHz, neutralized CDCl₃) : δ 6.75 (d, 1H, $J = 19.6$ Hz, $-\underline{\text{CH}}=\text{CH}(\text{SnBu}_3)$), 5.82 (d, 1H, $J = 19.6$ Hz, $-\text{CH}=\underline{\text{CH}}(\text{SnBu}_3)$), 4.83 (s, 1H, $\text{CHOH}-\underline{\text{CHOH}}-\text{C}=\text{C}-\text{TMS}$), 4.51 (s, 1H, $\underline{\text{CHOH}}-\text{CHOH}-\text{C}=\text{C}-\text{TMS}$), 2.87-2.12 (m, 8H, 3 CH_2 + 2 $\underline{\text{OH}}$), 1.63-1.08 (m, 12H, $\text{Sn}-(\text{CH}_2-\underline{\text{CH}}_2-\underline{\text{CH}}_2-\text{CH}_3)_3$), 0.93-0.78 (m, 15H, $\text{Sn}-(\underline{\text{CH}}_2-\text{CH}_2-\text{CH}_2-\underline{\text{CH}}_3)_3$), 0.23 (s, 9H, $\text{Si}(\underline{\text{CH}}_3)_3$).

¹³C-NMR (75 MHz, CDCl₃ neutralized) : δ 156.04, 150.27, 148.38, 137.50, 130.59, 76.50, 70.63, 31.52, 29.22, 27.50, 27.32, 27.20, 13.68, 9.54, 0.76.

IR (CH₂Cl₂) : ν 3286 m (broad, OH), 2956 s, 2925, 2871 m, 2852 m, 1731 m, 1560 w (C=C), 1463 m, 1376 w, 1275 m, 1244 m, 1118 m, 1073 w, 985 w, 861 m, 838 s, 750 m, 689 w, 614 w, 506 w cm⁻¹.

(1*R,2*R**,3*E*)-3-[(2*E*)-3-(tributylstannyl)-1-(trimethylsilyl)prop-2-enylidene]-1,2,3,4,5,6-hexahydropentalene-1,2-diol: minor isomer (18b)**

<ul style="list-style-type: none"> - R_f : 0.35 (Et₂O/Hexane : 50/50) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 16 % - C₂₆H₄₆O₂SiSn - MW = 537.44
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¹H NMR (200 MHz, neutralized CDCl₃) : δ 6.82 (d, 1H, $J = 19.8$ Hz, $-\underline{\text{CH}}=\text{CH}(\text{SnBu}_3)$), 6.02 (d, 1H, $J = 19.8$ Hz, $-\text{CH}=\underline{\text{CH}}(\text{SnBu}_3)$), 5.01 (s, 1H, $\text{CHOH}-\underline{\text{CHOH}}-\text{C}=\text{C}-\text{TMS}$), 4.57 (s, 1H, $\underline{\text{CHOH}}-\text{CHOH}-\text{C}=\text{C}-\text{TMS}$), 2.85-2.00 (m, 8H, 3 CH_2 + 2 $\underline{\text{OH}}$), 1.70-1.18 (m, 12H, $\text{Sn}-(\text{CH}_2-\underline{\text{CH}}_2-\underline{\text{CH}}_2-\text{CH}_3)_3$), 1.07-0.77 (m, 15H, $\text{Sn}-(\underline{\text{CH}}_2-\text{CH}_2-\text{CH}_2-\underline{\text{CH}}_3)_3$), 0.17 (s, 9H, $\text{Si}(\underline{\text{CH}}_3)_3$).

¹³C-NMR (50 MHz, neutralized CDCl₃) : δ 156.49, 151.20, 150.30, 148.29, 136.47, 130.77, 86.50, 77.62, 30.62, 29.14, 27.68 (2C), 27.26, 13.65, 9.69, 1.74.

IR (CH₂Cl₂) : ν 3372 m (broad, OH), 2956 et 2924 s, 1566 w (C=C), 1456 w, 1370 w, 1275 s, 1260 s, 1000 m, 838 s, 808 m, 764 s, 750 s, 693 m, 504 m cm⁻¹.

(1*R,2*R**,3*Z*)-3-[(2*E*)-3-(tributylstannyl)-1-(trimethylsilyl)prop-2-enylidene]-1,2,3,4,5,6-hexahydropentalene-1,2-diol : major isomer b (18a)**

<ul style="list-style-type: none"> - R_f : 0.18 (Et₂O/Hexane : 50/50) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow oil - Yield = 38 % - C₂₆H₄₆O₂SiSn - MW = 537.44
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¹H NMR (300 MHz, neutralized CDCl₃) : δ 6.77 (d, 1H, J = 19.7 Hz, -CH=CH(SnBu₃)), 5.83 (d, 1H, J = 19.7 Hz, -CH=CH(SnBu₃)), 4.74 (d, 1H, J = 6.2 Hz, CHOH-CH₂OH-C=C-TMS), 4.48 (s, 1H, CHOH-CH₂OH-C=C-TMS), 2.53-2.15 (m, 8H, 3 CH₂ + 2 OH), 1.65-1.14 (m, 12H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.99-0.80 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.22 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, CDCl₃ neutralized) : δ 154.45, 150.65, 148.59, 148.27, 138.04, 130.90, 86.16, 79.75, 31.69, 29.22, 27.32 (3C), 13.70, 9.54, 0.61.

IR (CH₂Cl₂) : ν 3343 s (broad, OH), 2956 s, 2925 s, 2871 s, 2852 s, 1727 m, 1560 m (C=C), 1458 m, 1418 m, 1376 m, 1291 m, 1244 s, 1173 m, 1130 m, 1070 s, 1022 s, 986 s, 966 s cm⁻¹.

(1R*,2S*,3E)-3-[(2E)-3-(tributylstannyl)-1-(trimethylsilyl)prop-2-enylidene]-2,3,4,5,6,7-hexahydro-1H-indene-1,2-diol anti C6-diol : minor isomer (15b)

<ul style="list-style-type: none"> - R_f : 0.64 (Et₂O/Hexane : 70/30) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 24 % - C₂₇H₄₈O₂SiSn - MW = 553.48
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¹H NMR (300 MHz, neutralized CDCl₃) : δ 6.82 (d, 1H, J = 19.9 Hz, -CH=CH(SnBu₃)), 5.90 (d, 1H, J = 19.6 Hz, -CH=CH(SnBu₃)), 4.43 (s, 1H, CHOH-CH₂OH-C=C-TMS), 4.30 (m, 1H, CHOH-CH₂OH-C=C-TMS), 2.75-2.10 (m, 6H, 2 CH₂ + 2 OH), 1.65-1.19 (m, 16H, Sn-(CH₂-CH₂-CH₂-CH₃)₃ + 2 CH₂), 1.02-0.74 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.17 (s, 9H, Si(CH₃)₃).

¹³C-NMR (50 MHz, CDCl₃ neutralized) : δ 148.81, 146.92, 143.88, 139.92, 131.59, 128.80, 77.20, 72.08, 30.43, 29.27, 27.34, 22.56, 21.02, 20.53, 13.74, 9.60, 0.31.

IR (CH₂Cl₂) : ν 3390 w (broad, OH), 2955 s, 2931 s, 2929 s, 2355 w, 1731 w, 1693 m (C=C), 1588 w, 1462 w, 1275 m, 1260 m, 1120 w, 1068 w, 985 w, 840 m, 764 s, 750 s, 505 w.

(1*R,2*S**,3*Z*)-3-[(2*E*)-3-(tributylstannyl)-1-(trimethylsilyl)prop-2-enylidene]-2,3,4,5,6,7-hexahydro-1*H*-indene-1,2-diol : major isomer (15a)**

<ul style="list-style-type: none"> - R_f : 0.52 (Et₂O/Hexane : 70/30) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 47 % - C₂₇H₄₈O₂SiSn - MW = 553.48
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¹H NMR (300 MHz, neutralized CDCl₃) : δ 6.75 (d, 1H, J = 19.6 Hz, -CH=CH(SnBu₃)), 5.75 (d, 1H, J = 19.6 Hz, -CH=CH(SnBu₃)), 4.56 (d, 1H, J = 6.0 Hz, CHOH-CHOH-C=C-TMS), 4.39 (m, 1H, CHOH-CHOH-C=C-TMS), 2.57-2.08 (m, 6H, 2 CH₂ + 2 OH), 1.68-1.21 (m, 16H, 2 CH₂ + Sn-(CH₂-CH₂-CH₂-CH₃)₃), 1.00-0.77 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.22 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, neutralized CDCl₃) : δ 151.73, 149.19, 146.35, 139.60, 138.46, 129.80, 75.12, 71.62, 29.23, 28.34, 27.33, 24.15, 23.02, 21.94, 13.68, 9.52, 0.59.

IR (CH₂Cl₂) : ν 3316 m (broad, OH), 2956 s, 2926 s, 2871 s, 2855 s, 1581 w (C=C), 1463 m, 1376 w, 1275 s, 1260 s, 1119 m, 1070 m, 1019 w, 986 w, 838 s, 764 s, 750 s, 688 w, 619 w, 592 w, 504 w cm⁻¹.

(1*R,2*R**,3*Z*)-3-[(2*E*)-3-(tributylstannyl)-1-(trimethylsilyl)prop-2-enylidene]-2,3,4,5,6,7-hexahydro-1*H*-indene-1,2-diol (19)**

<ul style="list-style-type: none"> - R_f : 0.17 (Et₂O/Hexane : 70/30) - Eluant of chromatography : 70/30 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 52 % - C₂₇H₄₈O₂SiSn - MW = 553.48
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¹H NMR (300 MHz, neutralized CDCl₃) : δ 6.76 (d, 1H, J = 19.6 Hz, -CH=CH(SnBu₃)), 5.76 (d, 1H, J = 19.6 Hz, -CH=CH(SnBu₃)), 4.44 (s, 1H, CHOH-CHOH-C=C-TMS), 4.35 (s, 1H, CHOH-CHOH-C=C-TMS), 2.38-2.00 (m, 6H, 2 CH₂ + 2 OH), 1.70-1.19 (m, 16H,

Sn-(CH₂-CH₂-CH₂-CH₃)₃ + 2 CH₂), 0.93-0.87 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.20 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, neutralized CDCl₃) : δ 152.08, 149.13, 144.89, 140.31, 139.06, 129.83, 83.76, 80.37, 29.24, 28.47, 27.34, 24.16, 22.83, 21.96, 13.70, 9.53, 0.38.

IR (CH₂Cl₂) : ν 3356 f (broad, OH), 2956 s, 2927 s, 2863 m, 2366 w, 1728 m, 1582 w (C=C), 1463 w, 1370 w, 1275 m, 1128 w, 985 w, 880 w, 838 s, 749 s, 681 w, 503 s cm⁻¹.

(1*R,2*S**,3*Z*)-3-[(2*E*)-3-(tributylstannyl)-1-(trimethylsilyl)prop-2-enylidene]-1,2,3,4,5,6,7,8-octahydroazulene-1,2-diol (16)**

<ul style="list-style-type: none"> - R_f : 0.44 (Et₂O/Hexane : 60/40) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 45 % - C₂₈H₅₀O₂SiSn - MW = 567.51
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¹H NMR (300 MHz, CDCl₃ neutralized) : δ 6.70 (d, 1H, *J* = 19.7 Hz, -CH=CH(SnBu₃)), 5.71 (d, 1H, *J* = 19.7 Hz, -CH=CH(SnBu₃)), 4.52 (d, 1H, *J* = 5.0 Hz, CHOH-CHOH-C=C-TMS), 4.35 (s, 1H, CHOH-CHOH-C=C-TMS), 2.70-2.10 (m, 6H, 2 CH₂ + 2 OH), 1.80-1.26 (m, 18H, Sn-(CH₂-CH₂-CH₂-CH₃)₃ + 3 CH₂), 0.98-0.81 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.20 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, CDCl₃ neutralized) : δ 152.14, 150.69, 149.79, 144.59, 137.83, 129.61, 76.27, 73.17, 31.19, 30.03, 29.22, 27.36, 26.39, 26.28, 13.70, 9.54, 0.51.

IR (CH₂Cl₂) : ν 3375 w (broad OH), 2955 m, 2923 m, 2850 m, 1559 s (C=C), 1458 w, 1376 w, 1275 m, 1260 m, 1112 w, 1070 w, 986 w, 838 m, 764 s, 750 s, 690 w, 663 w, 504 m cm⁻¹.

(1*R,2*R**,3*Z*)-3-[(2*E*)-3-(tributylstannyl)-1-(trimethylsilyl)prop-2-enylidene]-1,2,3,4,5,6,7,8-octahydroazulene-1,2-diol (20)**

<ul style="list-style-type: none"> - R_f : 0.24 (Et₂O/Hexane : 60/40) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 31 % - C₂₈H₅₀O₂SiSn - MW = 567.51
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¹H NMR (200 MHz, neutralized CDCl₃) : δ 6.74 (d, 1H, J = 19.3 Hz, -CH=CH(SnBu₃)), 5.72 (d, 1H, J = 19.3 Hz, -CH=CH(SnBu₃)), 4.42 (m, 1H, CHOH-CH₂-C=C-TMS), 4.32 (s, 1H, CHOH-CH₂-C=C-TMS), 2.45-2.01 (m, 6H, 2 CH₂ + 2 OH), 1.90-1.23 (m, 18H, Sn-(CH₂-CH₂-CH₂-CH₃)₃ + 3 CH₂), 1.07-0.87 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.19 (s, 9H, Si(CH₃)₃).

¹³C-NMR (50 MHz, neutralized CDCl₃) : δ 152.84, 149.99, 149.31, 145.11, 138.55, 129.71, 84.81, 81.18, 31.00, 29.98, 29.25, 27.74, 27.37, 26.40, 25.98, 13.73, 9.59, -0.26.

IR (CH₂Cl₂) : ν 3352 m (broad, OH), 2955 s, 2923 s, 2851 s, 2180 w, 1556 m (C=C), 1455 m, 1376 m, 1244 s, 1049 m, 985 s, 859 s, 839 s, 766 m, 681 m, 505 w cm⁻¹.

d-bicyclic ketals

[(1Z,2E)-1-[(3a*R,7a*S**)-2,2-dimethyl-3a,5,6,7a-tetrahydropentaleno[1,2-*d*][1,3]dioxol-7(4*H*)-ylidene]-3-(tributylstannyl)prop-2-enyl](trimethyl)silane (26)**

¹H NMR (300 MHz, neutralized CDCl₃) : δ 6.78 (d, 1H, J = 19.7 Hz, -CH=CH(SnBu₃)), 5.75 (d, 1H, J = 19.7 Hz, -CH=CH(SnBu₃)), 5.27 (d, 1H, J = 5.6 Hz, -O-CH₂-C=C-TMS), 4.89 (d, 1H, J = 5.6 Hz, -C=C-CH₂-O-), 2.52-2.10 (m, 6H, 3 CH₂), 1.65-1.15 (m, 12H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 1.41 (s, 3H, Me), 1.38 (s, 3H, Me), 1.10-0.66 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.25 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, neutralized CDCl₃) : δ 154.89, 150.23, 148.32, 145.63, 138.18, 130.65, 110.88, 85.00, 78.41, 31.33, 29.23, 29.17, 27.48, 27.33, 25.79, 13.71, 9.53, 0.61.

IR (CH₂Cl₂) : ν 2956 s, 2942 s, 2926 s, 2872 s, 2849 s, 1561 f (C=C), 1463 w, 1378 m, 1244 s, 1242 m, 1111 w, 1050 m, 985 w, 875 m, 840 s, 755 w, 690 w, 510 w cm⁻¹.

[((4*R,5*R**)-2,2-dimethyl-5-{2-[(*E*)-2-(tributylstannyl)vinyl]cyclopent-1-en-1-yl}-1,3-dioxolan-4-yl)ethynyl](trimethyl)silane (29)**

<ul style="list-style-type: none"> - R_f : 0.73 (Et₂O/Hexane : 20/80) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 38 % - C₂₉H₅₂O₂SiSn - MW = 557.12
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¹H NMR (200 MHz, neutralized CDCl₃) : δ 7.03 (d, 1H, J = 19.1 Hz, -CH=CH(SnBu₃)), 6.24 (d, 1H, J = 19.1 Hz, -CH=CH(SnBu₃)), 5.04 (d, 1H, J = 8.1 Hz, -O-CH-C $\equiv$ C-TMS), 4.45 (d, 1H, J = 8.1 Hz, C=C-CHO-), 2.70-2.40 (m, 4H, 2 CH₂), 1.93-1.75 (m, 2H, CH₂), 1.68-1.22 (m, 12H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 1.53 (s, 3H, Me), 1.45 (s, 3H, Me), 0.97-0.87 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.17 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, neutralized CDCl₃) : δ 142.85, 139.62, 132.70, 132.14, 110.06, 101.62, 91.93, 78.07, 68.98, 33.38, 32.71, 29.12, 27.27, 26.79, 26.20, 21.28, 13.69, 9.49, -0.25 .

IR (CH₂Cl₂) : ν 2945 s, 2926 s, 2849 m, 2355 w (C $\equiv$ C), 1455 m (C=C), 1379 m, 1250 m, 1052 m, 979 w, 844 s, 762 s, 504 m cm⁻¹.

[(1Z,2E)-1-[(3aR*,8aS*)-2,2-dimethyl-3a,4,5,6,7,8a-hexahydro-8H-indeno[1,2-d][1,3]dioxol-8-ylidene]-3-(tributylstannyl)prop-2-enyl](trimethyl)silane (27)

<ul style="list-style-type: none"> - R_f : 0.65 (Et₂O/Hexane : 20/80) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 64 % - C₃₀H₅₄O₂SiSn - MW = 593.55
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¹H NMR (300 MHz, neutralized CDCl₃) : δ 6.78 (d, 1H, J = 19.7 Hz, -CH=CH(SnBu₃)), 5.76 (d, 1H, J = 19.7 Hz, -CH=CH(SnBu₃)), 4.95 (d, 1H, J = 5.6 Hz, -O-CH-C=C-TMS), 4.80 (m, 1H, -C=C-CH-O-), 2.40-2.05 (m, 4H, 2 CH₂), 1.74-1.43 (m, 8H, Sn-(CH₂-CH₂-CH₂-CH₃)₃ + 1 CH₂), 1.40-1.17 (m, 12H, Sn-(CH₂-CH₂-CH₂-CH₃)₃ + 2 Me), 1.01-0.79 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.21 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, neutralized CDCl₃) : δ 149.18, 148.69, 145.26, 139.51, 139.38, 129.64, 110.54, 83.46, 79.25, 29.24, 28.42, 27.75, 27.34, 26.21, 24.32, 22.96, 21.95, 13.7, 9.52, 0.40.

IR (CH₂Cl₂) : ν 2957 s, 2929 s, 2855 m, 2349 w (C $\equiv$ C), 1589 w (C=C), 1456 m, 1377 m, 1244 s, 1206 m, 1056 m, 985 w, 875 m, 840 s, 764 m, 688 m cm⁻¹.

[[((4*R,5*R**)-2,2-dimethyl-5-{2-[(*E*)-2-(tributylstannyl)vinyl]cyclohex-1-en-1-yl}-1,3-dioxolan-4-yl)ethynyl](trimethyl)silane (33)**

<ul style="list-style-type: none"> - R_f : 0.58 (Et₂O/Hexane : 20/80) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 56 % - C₃₀H₅₄O₂SiSn - MW = 593.55
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¹H NMR (300 MHz, CDCl₃ neutralized) : δ 7.11 (d, 1H, *J* = 19.2 Hz, -CH=CH(SnBu₃)), 6.31 (d, 1H, *J* = 19.2 Hz, -CH=CH(SnBu₃)), 5.29 (d, 1H, *J* = 7.5 Hz, -O-CH=C-TMS), 4.48 (d, 1H, *J* = 7.5 Hz, C=C-CH-O-), 2.35-1.97 (m, 4H, 2 CH₂), 1.65-1.26 (m, 16H, 2 CH₂ + Sn-(CH₂-CH₂-CH₂-CH₃)₃), 1.52 (s, 3H, Me), 1.46 (s, 3H, Me), 0.95-0.87 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.17 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, CDCl₃ neutralized) : δ 143.11, 136.90, 128.90, 128.68, 109.86, 102.31, 91.78, 79.33, 68.60, 29.15, 27.31, 26.70, 26.04, 25.96, 24.14, 22.50, 22.46, 13.71, 9.53, -0.23

IR (CH₂Cl₂) : ν 2939 s, 2929 s, 2179 f (C $\equiv$ C), 1554 f (C=C), 1456 m, 1379 m, 1250 s, 1160 w, 1044 s, 979 w, 844 s, 760 m, 684 w cm⁻¹.

[(1*Z*,2*E*)-1-[(3*aR,9*aS**)-2,2-dimethyl-3*a*,5,6,7,8,9*a*-hexahydroazuleno[1,2-*d*][1,3]dioxol-9(4*H*)-ylidene]-3-(tributylstannyl)prop-2-enyl](trimethyl)silane (28)**

<ul style="list-style-type: none"> - R_f : 0.51 (Et₂O/Hexane : 10/90) - Eluant of chromatography : 3/97 (Et₂O/Hexane) - Aspect : yellow viscous oil - Yield = 48 % - C₃₁H₅₆O₂SiSn - MW = 607.58
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¹H NMR (300 MHz, neutralized CDCl₃) : δ 6.74 (d, 1H, *J* = 19.6 Hz, -CH=CH(SnBu₃)), 5.72 (d, 1H, *J* = 19.6 Hz, -CH=CH(SnBu₃)), 4.88 (d, 1H, *J* = 5.1 Hz, -O-CH=C-TMS), 4.79 (d, 1H, *J* = 4.6 Hz, -C=C-CH-O-), 2.45-2.21 (m, 4H, 2 allylic CH₂), 1.80-1.23 (m, 18H, 3

CH₂ et Sn-(CH₂-CH₂-CH₂-CH₃)₃, 1.40 (s, 3H, Me), 1.38 (s, 3H, Me), 0.94-0.86 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.21 (s, 9H, Si(CH₃)₃).

¹³C-NMR (50 MHz, neutralized CDCl₃) : δ 150.26, 149.97, 149.76, 144.43, 139.70, 129.73, 110.77, 85.14, 80.10, 31.36, 30.54, 29.66, 28.53, 28.38, 27.78, 27.09, 26.70, 26.54, 14.14, 9.99, 0.64.

IR (CH₂Cl₂) : ν 2956 s, 2925 s, 2872 s, 2852 s, 1738 w, 1585 m (C=C), 1455 s, 1377 s, 1368 s, 1310 w, 1244 s, 1207 m, 1054 s, 986 m, 926 w, 839 s, 804 m cm⁻¹.

[(4*R,5*R**)-2,2-dimethyl-5-{2-[(*E*)-2-(tributylstannyl)vinyl]cyclohept-1-en-1-yl}-1,3-dioxolan-4-yl)ethynyl](trimethyl)silane (34)**

¹H NMR (200 MHz, CDCl₃ neutralized) : δ 7.03 (d, 1H, *J* = 19.1 Hz, -CH=CH(SnBu₃)), 6.33 (d, 1H, *J* = 19.3 Hz, -CH=CH(SnBu₃)), 5.28 (d, 1H, *J* = 7.8 Hz, -O-CH-C≡C-TMS), 4.39 (d, 1H, *J* = 7.8 Hz, C=C-CHO-), 2.54-2.17 (m, 4H, 2 CH₂), 1.90-1.26 (m, 18H, 3 CH₂ + Sn-(CH₂-CH₂-CH₂-CH₃)₃), 1.51 (s, 3H, Me), 1.46 (s, 3H, Me), 1.01-0.80 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.17 (s, 9H, Si(CH₃)₃).

¹³C-NMR (50 MHz, CDCl₃ neutralized) : δ 143.39, 133.06, 129.62, 109.86, 102.22, 79.72, 68.67, 32.33, 29.49, 29.16, 27.82, 27.31, 26.98, 26.82, 26.06, 13.7, 9.59, -0.25.

IR (CH₂Cl₂) : ν 2956 m, 2923 s, 2852 m, 2180 w (C≡C), 1552 w (C=C), 1459 w, 1378 w, 1275 m, 1250 m, 1160 w, 1045 m, 979 w, 843 s, 750 s, 670 w, 506 w cm⁻¹.

***rac*-1-(2-bromophenyl)-4-(trimethylsilyl)but-3-yn-2-ol (12)**

To a stirred solution of trimethylsilylacetylene (0.48 mL, 3.397 mmol) in dry THF (5 mL) at $-78\text{ }^{\circ}\text{C}$ was added *n*-BuLi (1.5 M in hexane, 2.43 mL, 3.669 mmol). The mixture was stirred at this temperature for 15 min and dry CeCl_3 (solid, 0.903 g, 3.664 mmol) was added at ones. The obtained white suspension was stirred for one hour at $-78\text{ }^{\circ}\text{C}$ and then a solution of 2-bromo-phenetaldehyde (0.560 g, 2.814 mmol) in dry THF (6 mL) was added. The resulting mixture was stirred over night with the temperature coming to rt. The reaction was next quenched with a solution of NH_4Cl , filtered through Celite and extracted with AcOEt. The organic extract was washed with water, brine and dried over MgSO_4 . The crude was purified by silica gel flash column chromatography to give a yellowish viscous oil (0.442 g, 53 %)

^1H NMR (300 MHz, CDCl_3 neutralized) : δ 7.56 (dd, 1H, $J = 8.1\text{ Hz}$, $J = 1.3\text{ Hz}$, H arom.), 7.35 (dd, 1H, $J = 7.7\text{ Hz}$, $J = 1.7\text{ Hz}$, H arom.), 7.26 (td, 1H, $J = 8.7\text{ Hz}$, $J = 1.3\text{ Hz}$, H arom.), 7.12 (td, 1H, $J = 7.5\text{ Hz}$, $J = 1.9\text{ Hz}$, H arom.), 4.68 (ABX part X, td, 1H, $J = 7.0\text{ Hz}$, $J = 5.31\text{ Hz}$, CH_2OH), 3.22 (ABX part B, dd, 1H, $J = 13.4\text{ Hz}$, $J = 7.5\text{ Hz}$, CH_2), 3.15 (ABX part A, dd, 1H, $J = 13.9\text{ Hz}$, $J = 7.0\text{ Hz}$, CH_2), 1.9 (d, 1H, $J = 5.62\text{ Hz}$, OH), 0.17 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

^{13}C -NMR (50 MHz, CDCl_3 neutralized) : δ 136.2, 132.8, 132.3, 128.5, 127.2, 125.0, 105.6, 90.6, 62.2, 44.1, -0.3.

IR (thin film) : ν 3355 m, 3063 w, 2960 m, 2901 w, 2362 w, 2174 w, 1719 w, 1592 w, 1587 w, 1470 m, 1440 m, 1329 w, 1251 s, 1164 w, 1034 s, 974 w, 882 m, 845 s, 786 m, 756 s, 701 w, 659 w cm^{-1} .

(1Z)-1-[(2E)-3-(tributylstannyl)-1-(trimethylsilyl)prop-2-enylidene]indan-2-ol (21)

<ul style="list-style-type: none"> - R_f : 0.39 (Et_2O/Hexane : 20/80) - Eluant of chromatography : (Et_2O/Hexane : 5/95) - Aspect : yellowish viscous oil - Yield = 61 % - $\text{C}_{27}\text{H}_{46}\text{OSiSn}$ - MW = 533.45
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^1H NMR (300 MHz, CDCl_3 neutralized) : δ 7.90 (d, 1H, $J = 7.91\text{ Hz}$, H arom.), 7.31-7.11 (m, 3H, H arom.), 6.89 (d, 1H, $J = 20.0\text{ Hz}$, $-\text{CH}=\text{CH}(\text{SnBu}_3)$), 6.04 (d, 1H, $J = 20.0\text{ Hz}$, $-\text{CH}=\text{CH}(\text{SnBu}_3)$), 4.98 (t, 1H, $J = 5.7\text{ Hz}$, CH_2OH), 3.23 (dd, 1H, $J = 17.0\text{ Hz}$, $J = 5.7\text{ Hz}$, CH_2), 2.91 (d, 1H, $J = 16.6\text{ Hz}$, CH_2), 1.60-1.52 (m, 6H, $\text{Sn}-(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3)_3$), 1.41-

1.31 (m, 6H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 1.04-0.89 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.31 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, CDCl₃ neutralized) : δ 149.16, 144.30, 139.52, 130.67, 128.30, 127.35, 125.99, 125.69, 73.43, 40.70, 29.28, 27.39, 13.74, 9.58, 1.02.

IR (thin film) : ν 3326 w, 3065 w, 2956 s, 2924 s, 2852 m, 1579 w, 1460 m, 1419 w, 1377 w, 1340 w, 1296 w, 1249 m, 1157 w, 1072 w, 1024 w, 992 w, 867 m, 839, 786 s, 765 s, 687 w, 597 w cm⁻¹.

***rac*-1-(2-bromophenyl)-5-(trimethylsilyl)pent-4-yne-2,3-diol (13)**

<ul style="list-style-type: none"> - R_f : 0.49 (Et₂O/Hexane : 70/30) - Eluant of chromatography : (Et₂O /Hexane : 30/70) - Aspect : yellowish viscous oil - Yield = 30 % - C₁₄H₁₉BrO₂Si - MW = 327.29
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¹H NMR (300 MHz, CDCl₃ neutralized) : δ 7.56 (d, 1H, *J* = 7.8 Hz, H arom.), 7.36-7.24 (m, 2H, H arom.) 7.11 (t, 1H, *J* = 7.7 Hz, H arom.), 4.40 (d, 1H, *J* = 3.42 Hz -CH₂OH-C≡C major), 4.25 (d, 1H, *J* = 6.12 Hz -CH₂OH-C≡C minor) 4.08-3.91 (ABX part X, m, 1H, major + minor, -CH₂-CH₂OH), 3.27 (ABX part B, dd, 1H, minor, *J* = 13.9 Hz, *J* = 3.9 Hz, CH₂), 3.16 (ABX part B, dd, 1H, major, *J* = 14.1 Hz, *J* = 4.4 Hz, CH₂), 2.99 (ABX part Ar, dd, 1H, major, *J* = 14.0 Hz, *J* = 9.1 Hz, CH₂), 2.87 (ABX part A, dd, 1H, minor, *J* = 13.9 Hz, *J* = 8.9 Hz, CH₂), 2.56 (s broad, 2H, OH major), 2.41 (s broad, 1H, OH minor) 2.14 (s broad, 1H, OH minor), 0.23 (s, 9H, Si(CH₃)₃ major), 0.19 (s, 9H, Si(CH₃)₃ minor).

¹³C-NMR (50 MHz, CDCl₃ neutralized) : δ 137.31, 132.84, 131.74, 128.25, 127.36, 124.83 103.54 minor, 102.62 major, 92.42 major, 91.69 minor, 73.91 minor, 73.22 major, 66.15 major, 65.99 minor, 39.06 minor, 38.92 major, -0.19.

IR (thin film) : ν 3382 s, 3065 m, 2959 s, 2927 s, 2176 w, 1951 w, 1720 w, 1593 w, 1567 w, 1470 m, 1439 m, 1252 s, 1169 w, 1053 s, 995 m, 847 s, 757 s, 702 w, 660 w cm⁻¹.

HRMS (ESI, positive ion 180 eV) calcd for (C₁₄H₁₉BrO₂SiNa)⁺ 349.0235; found 349.0233

(1*Z*)-1-[(2*E*)-3-(tributylstannyl)-1-(trimethylsilyl)prop-2-enylidene]-1,2,3,4-tetrahydronaphthalene-2,3-diol (22)

<ul style="list-style-type: none"> - Rf : 0.20 (Et₂O/Hexane : 60/40) - Eluant of chromatography : (Et₂O/Hexane : 50/50) - Aspect : yellowish solidl - Yield = 30 % - C₂₈H₄₈O₂SiSn - MW = 563.48
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¹H NMR (200 MHz, CDCl₃ neutralized) : δ 7.66 (d, 1H, J = 7.6 Hz, H arom.), 7.19-7.00 (m, 3H, H arom.), 6.69 (d, 1H, J = 20.1 Hz, -CH=CH(SnBu₃)), 5.85 (d, 1H, J = 20.1 Hz, -CH=CH(SnBu₃)), 4.82 (s broad, 1H, J = 5.7 Hz, CHOH-CHOH-C=C-TMS), 4.19-4.05 (m, 1H, CHOH-CHOH-C=C-TMS), 3.20 (dd, 1H, J = 16.9 Hz, J = 7.1 Hz, CH₂), 2.90 (dd, 1H, J = 16.6 Hz, J = 9.5 Hz, CH₂), 2.42 (d broad, 1H, J = 8.1 Hz, OH), 1.96 (d broad, 1H, J = 3.9 Hz, OH) 1.53-1.27 (m, 12H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.97-0.83 (m, 15H, Sn-(CH₂-CH₂-CH₂-CH₃)₃), 0.29 (s, 9H, Si(CH₃)₃).

¹³C-NMR (50 MHz, CDCl₃ neutralized) : δ 149.79, 145.02, 144.80, 135.63, 132.66, 132.35, 131.31, 128.44, 127.47, 124.80, 73.99, 70.02, 34.53, 29.16, 27.30, 13.67, 9.48, 1.34.

IR (CH₂Cl₂) : ν 3366 s, 3335 m, 3062 w, 2956 s, 2924 s, 2854 m, 1729 w, 1579 w, 1458 w, 1414 w, 1376 w, 1299 w, 1268 w, 1183 w, 1119 w, 1073 m, 990 w, 953 w, 906 w, 839 m, 786 m, 783 m, 713 w, 686 w cm⁻¹.