

**Cyclocarbopalladation:  
5-exo-dig Cyclization *Versus* Direct Stille Cross Coupling Reaction.  
The Influence of the  $\alpha,\beta$ -Propargylic Substitution**

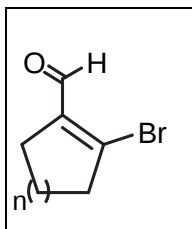
Bahaâ Salem, Estelle, Delort, Philippe Klotz, Jean Suffert\*

*Université Loris Pasteur de Strasbourg (UMR 7081 CNRS/ULP),  
Faculté de Pharmacie, 74, route du Rhin 67401 Illkirch-Cedex, France*

**General Methods.** Reactions were run under an atmosphere of argon in oven-dried glassware using standard syringe, cannula, and septa apparatus. Et<sub>2</sub>O 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% Et<sub>3</sub>N treated silica gel was used to avoid decomposition. Analytical TLC was carried out on Merck (60F-254) silica gel plates. <sup>1</sup>H spectra were recorded at 200 or 300 MHz using the residual solvent signal as internal reference (CDCl<sub>3</sub>, 7.27 ppm ; C<sub>6</sub>D<sub>6</sub>, 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). <sup>13</sup>C NMR spectra were recorded at 50 or 75 MHz at ambient temperature in CDCl<sub>3</sub> with  $\delta$  (CDCl<sub>3</sub>) 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 $\beta$ -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  $\text{CH}_2\text{Cl}_2$  (90 mL) cooled at  $0^\circ\text{C}$ . After one hour stirring at  $0^\circ\text{C}$ , the mixture turns yellow. Then a solution of cyclopentanone (8.85 mL, 100 mmol, 1 equiv.) in dry  $\text{CH}_2\text{Cl}_2$  (40 mL) is added dropwise at  $0^\circ\text{C}$  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  $\text{NaHCO}_3$  (sat.) and  $\text{NaHCO}_3(\text{s})$ . The mixture is extracted with ethylacetate and the combined organic phases are washed with distilled water ( $3 \times 200$  mL) and brine ( $1 \times 250$  mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated to an oil stored at  $-20^\circ\text{C}$  in etheral solution (12.2 g, 75%).

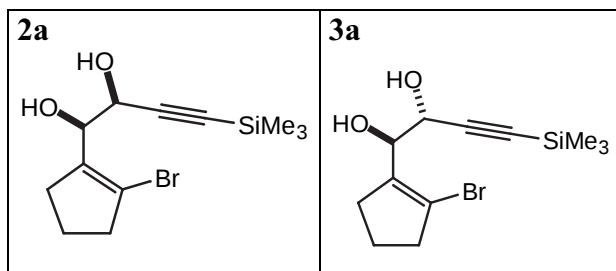
#### **Method B :**

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 $\beta$ -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

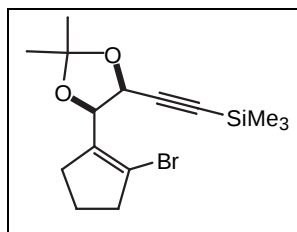


*n*-BuLi (30.9 mL, 1.55 M in hexane, 47.9 mmol, 1.3 equiv.) is added dropwise to a solution of 3-[(1-methoxy-1-methyl-ethoxy)-prop-1-ynyl]trimethylsilane (9.6 g, 47.9 mmol, 1.3 equiv.)

in dry THF (60 mL) cooled at  $-78^{\circ}\text{C}$  under argon. The yellow solution is stirred during 15 min. at  $-78^{\circ}\text{C}$ , and added at  $-78^{\circ}\text{C}$  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,  $\text{KMnO}_4$ ) and quenched after 35 minutes with saturated  $\text{NaHCO}_3$  solution (40 mL). The mixture is diluted in diethylether. After 3 extractions with diethylether ( $3 \times 40$  mL), the combined organic phases are washed with distilled water ( $2 \times 40$  mL). Then the organic phase is treated with  $\text{HCl}$  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 ( $2 \times 80$  mL). The combined organic phases are washed with distilled water ( $2 \times 250$  mL) and brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$  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 ( $3 \times 25$  mL), and the combined organic phases are washed with distilled water (25 mL),  $\text{NaHCO}_3$  sat (25 mL) and brine (25 mL), dried over  $\text{Na}_2\text{SO}_4$  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%).

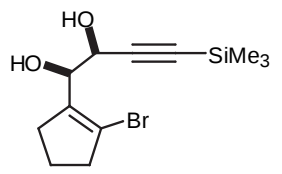
## 4-General procedure for the cyclocarbopalladation of $\delta$ -bromopropargylic diols and dioxolanes

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(PPh<sub>3</sub>)<sub>4</sub> (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 (Et<sub>2</sub>O/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 NEt<sub>3</sub> (5%) (Et<sub>2</sub>O/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"><li>- Rf: 0.39 (Et<sub>2</sub>O/Hexane : 40/60)</li><li>- Eluant of chromatography : 10/90 (Et<sub>2</sub>O/Hexane)</li><li>- Aspect : white solid</li><li>- mp = 70 °C</li><li>- Yield = 40 %</li><li>- C<sub>12</sub>H<sub>19</sub>BrO<sub>2</sub>Si</li><li>- MW = 303.27</li></ul> |
|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

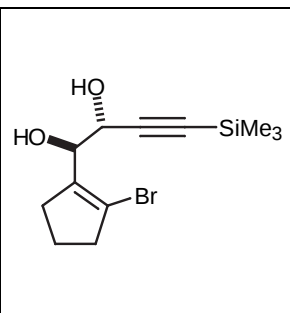
<sup>1</sup>**H-RMN** (300 MHz, CDCl<sub>3</sub>):  $\delta$  4.63 (dd, 1H,  $J = 4.9$  Hz,  $J = 5.8$  Hz, CHOH-CH<sub>2</sub>OH-C $\equiv$ C-TMS), 4.46 (m, 1H,  $J = 4.9$  Hz,  $J = 6.8$  Hz, CHOH-CH<sub>2</sub>OH-C $\equiv$ C-TMS), 2.74-2.62 (m, 2H, allylic CH<sub>2</sub>), 2.60-2.47 (m, 2H, allylic CH<sub>2</sub>), 2.38-2.24 (superposed doublets, 2H, 2\*OH), 1.96 (quint,  $J = 7.5$  Hz, 2H, CH<sub>2</sub>), 0.21 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>**C-NMR** (50 MHz, CDCl<sub>3</sub>) :  $\delta$  138.59, 119.4, 103.03, 91.83, 72.53, 64.91, 40.27, 31.08, 21.84, -0.34.

**IR** (FTIR, KBr) :  $\nu$  = 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<sup>-1</sup>.

**HRMS** (ESI, positive ion 180 eV) calcd for (C<sub>12</sub>H<sub>19</sub>BrO<sub>2</sub>SiNa)<sup>+</sup> 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"> <li>- R<sub>f</sub> : 0.29 (Et<sub>2</sub>O/Hexane : 40/60)</li> <li>- Eluant of chromatography : 10/90 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : white solid</li> <li>- mp = 62 °C</li> <li>- Yield = 17 %</li> <li>- C<sub>12</sub>H<sub>19</sub>BrO<sub>2</sub>Si</li> <li>- MW = 303.27</li> </ul> |
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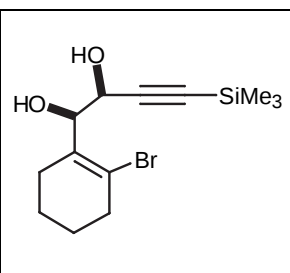
**<sup>1</sup>H-NMR** (200 MHz, CDCl<sub>3</sub>) : δ 4.62 (d, 1H, *J* = 7.1 Hz, CHOH-CH<sub>2</sub>OH-C≡C-TMS), 4.38 (d, 1H, *J* = 7.1 Hz, CH<sub>2</sub>OH-CHOH- C≡C-TMS), 2.73- 2.18 (m, 8H, 2 allylic CH<sub>2</sub> and 1 CH<sub>2</sub> and 2 OH), 0.17 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>) : δ 138.02, 120.73, 102.36, 91.63, 73.13, 65.10, 40.28, 30.38, 21.85, -0.35.

**IR** (CH<sub>2</sub>Cl<sub>2</sub>) : 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<sup>-1</sup>.

**HRMS** (ESI, positive ion 180 eV) calcd for (C<sub>12</sub>H<sub>19</sub>BrO<sub>2</sub>SiNa)<sup>+</sup> 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"> <li>- R<sub>f</sub> : 0.18 (Et<sub>2</sub>O/Hexane : 30/70)</li> <li>- Eluant of chromatography : 10/90 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellowish solid</li> <li>- mp = 80 °C</li> <li>- Yield = 25 %</li> <li>- C<sub>13</sub>H<sub>21</sub>BrO<sub>2</sub>Si</li> <li>- MW = 317.30</li> </ul> |
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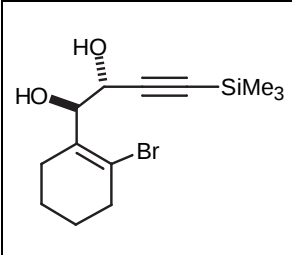
**<sup>1</sup>H NMR** (200 MHz, CDCl<sub>3</sub>) : δ 4.80 (dd, 1H, <sup>1</sup>*J* = <sup>2</sup>*J* = 5.1 Hz, CHOH-CH<sub>2</sub>OH-C≡C-TMS), 4.58 (dd, 1H, *J* = 6.8 Hz, *J* = 4.6 Hz, CH<sub>2</sub>OH-CHOH- C≡C-TMS), 2.56-2.32 (m, 6H, 2 allylic CH<sub>2</sub> + 2 d, 2H, *J* = 7.1 Hz, *J* = 5.6 Hz, 2 OH), 1.73-1.69 (m, 4H, 2 CH<sub>2</sub>), 0.20 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>) : 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) :  $\nu$  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<sup>-1</sup>.

**HRMS** (ESI, positive ion 130 eV) calcd for (C<sub>13</sub>H<sub>21</sub>BrO<sub>2</sub>SiNa)<sup>+</sup> 339.0392; found 339.0443

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

|                                                                                   |                                                                                                                                                                                                                                                                                                                                                  |
|-----------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.10 (Et<sub>2</sub>O/Hexane : 30/70)</li> <li>- Eluant of chromatography : 10/90 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellowish solid</li> <li>- mp = 84 °C</li> <li>- Yield = 15 %</li> <li>- C<sub>13</sub>H<sub>21</sub>BrO<sub>2</sub>Si</li> <li>- MW = 317.30</li> </ul> |
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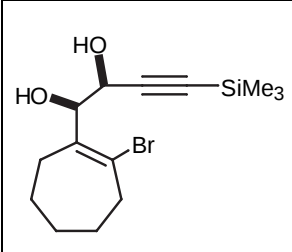
**<sup>1</sup>H-NMR** (200 MHz, CDCl<sub>3</sub>) :  $\delta$  4.80 (d, 1H, *J* = 7.3 Hz, CHOH-CH $\underline{\text{O}}$ H-C $\equiv$ C-TMS), 4.42 (d, 1H, *J* = 7.3 Hz, CH $\underline{\text{O}}$ H-CHOH- C $\equiv$ C-TMS), 2.57-1.56 (m, 8H, 2 allylic CH<sub>2</sub> et 2 CH<sub>2</sub>), 0.21 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (50 MHz, CDCl<sub>3</sub>) :  $\delta$  133.62, 122.77, 102.61, 90.97, 77.52, 64.72, 36.92, 25.71, 24.41, 21.94, -0.45.

**IR** (CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$  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<sup>-1</sup>.

**HRMS** (ESI, positive ion 100 eV) calcd for (C<sub>13</sub>H<sub>21</sub>BrO<sub>2</sub>SiNa)<sup>+</sup> 339.0392; found 339.0391

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

|                                                                                     |                                                                                                                                                                                                                                                                                                                                               |
|-------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.22 (Et<sub>2</sub>O/Hexane : 40/60)</li> <li>- Eluant of chromatography : 10/90 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow solid</li> <li>- mp = 80 °C</li> <li>- Yield = 36 %</li> <li>- C<sub>14</sub>H<sub>23</sub>BrO<sub>2</sub>Si</li> <li>- MW = 331.32</li> </ul> |
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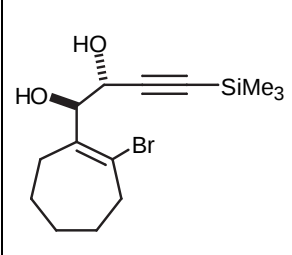
**<sup>1</sup>H NMR** (200 MHz, CDCl<sub>3</sub>) :  $\delta$  4.79 (broad s, 1H, CHOH-CH $\underline{\text{O}}$ H-C $\equiv$ C-TMS), 4.42 (m, 1H, CH $\underline{\text{O}}$ H-CHOH- C $\equiv$ C-TMS), 2.85-2.79 (m, 2H, allylic CH<sub>2</sub>), 2.42-2.26 (m, 3H, allylic CH<sub>2</sub> + 1 OH), 1.82-1.52 (m, 7H, 3 CH<sub>2</sub> + 1 OH), 0.19 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**$^{13}\text{C}$ -NMR** (50 MHz,  $\text{CDCl}_3$ ) :  $\delta$  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** ( $\text{CH}_2\text{Cl}_2$ ) :  $\nu$  3616 s (O-H), 2958 s ( $\text{CH}_3, \text{CH}_2$  or C-H), 2924 s, 2852 s, 2695 w, 2176 m ( $\text{C}\equiv\text{C}$ ), 1947 w, 1715 w, 1638 m ( $\text{C}=\text{C}$ ), 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  $\text{cm}^{-1}$ .

**HRMS** (ESI, positive ion 130 eV) calcd for  $(\text{C}_{14}\text{H}_{23}\text{BrO}_2\text{SiNa})^+$  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"> <li>- R<sub>f</sub> : 0.16 (<math>\text{Et}_2\text{O}/\text{Hexane}</math> : 40/60)</li> <li>- Eluant of chromatography : 10/90 (<math>\text{Et}_2\text{O}/\text{Hexane}</math>)</li> <li>- Aspect : yellow oil</li> <li>- Yield = 17 %</li> <li>- <math>\text{C}_{14}\text{H}_{23}\text{BrO}_2\text{Si}</math></li> <li>- MW = 331.32</li> </ul> |
|-----------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**$^1\text{H}$  NMR** (200 MHz,  $\text{CDCl}_3$ ) :  $\delta$  4.84 (dd, 1H,  $J = 8.2$  Hz,  $J = 1.9$  Hz,  $\text{CHOH}-\text{CHOH}-\text{C}\equiv\text{C}-\text{TMS}$ ), 4.42 (m, 1H,  $\text{CHOH}-\text{CHOH}-\text{C}\equiv\text{C}-\text{TMS}$ ), 2.87-2.77 (m, 2H, allylic  $\text{CH}_2$ ), 2.50-2.28 (m, 4H, allylic  $\text{CH}_2 + 2$  OH), 1.94-1.50 (m, 6H, 3  $\text{CH}_2$ ), 0.19 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ).

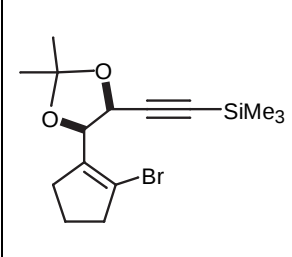
**$^{13}\text{C}$ -NMR** (50 MHz,  $\text{CDCl}_3$ ) :  $\delta$  138.57, 126.83, 102.59, 91.35, 78.53, 64.59, 41.69, 31.66, 27.79, 25.78, 24.77, -0.36.

**IR** ( $\text{CH}_2\text{Cl}_2$ ) :  $\nu$  3390 s (broad, OH), 2925 s, 2849 s, 2180 m ( $\text{C}\equiv\text{C}$ ), 1731 w, 1645 m ( $\text{C}=\text{C}$ ), 1446 m, 1249 s, 1061 s, 840 s, 761 s, 700 m  $\text{cm}^{-1}$ .

**HRMS** (ESI, positive ion 120 eV) calcd for  $(\text{C}_{14}\text{H}_{23}\text{BrO}_2\text{SiNa})^+$  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)**

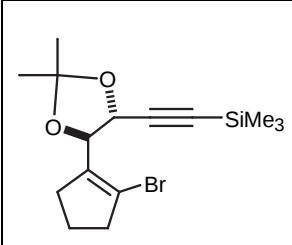
|                                                                                     |                                                                                                                                                                                                                                                                                                                                                                                              |
|-------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.65 (<math>\text{Et}_2\text{O}/\text{Hexane}</math> : 10/90)</li> <li>- Eluant of chromatography : 10/90 (<math>\text{Et}_2\text{O}/\text{Hexane}</math>)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 78 %</li> <li>- <math>\text{C}_{15}\text{H}_{23}\text{BrO}_2\text{Si}</math></li> <li>- MW = 340.32</li> </ul> |
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**<sup>1</sup>H NMR** (300 MHz, neutralised CDCl<sub>3</sub>) : δ 4.95 (m, 2H, -OCH<sub>2</sub>-C≡C-TMS et Br-C=C-CH<sub>2</sub>O), 2.74-2.44 (m, 4H, 2 allylic CH<sub>2</sub>), 2.00-1.87 (m, 2H, CH<sub>2</sub>), 1.56 (s, 3H, Me), 1.37 (s, 3H, Me), 0.15 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, neutralised CDCl<sub>3</sub>) : 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** (CH<sub>2</sub>Cl<sub>2</sub>) : ν 2986 m, 2960 m, 2900 m (CH<sub>3</sub>,CH<sub>2</sub> 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<sup>-1</sup>.

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

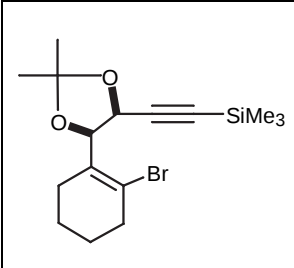
|                                                                                    |                                                                                                                                                                                                                                                                                                                                              |
|------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.55 (Et<sub>2</sub>O/Hexane : 10/90)</li> <li>- Eluant of chromatography : 10/90 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect :white solid</li> <li>- mp = 104 °C</li> <li>- Yield = 87 %</li> <li>- C<sub>15</sub>H<sub>23</sub>BrO<sub>2</sub>Si</li> <li>- MW = 340.32</li> </ul> |
|------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (300 MHz, neutralized CDCl<sub>3</sub>) : δ 4.95 (d, 1H, *J* = 7.8 Hz, -OCH<sub>2</sub>-C≡C-TMS), 4.35 (d, 1H, *J* = 8.1 Hz, -CBr=CH<sub>2</sub>O-), 2.70-2.65 (m, 2H, allylic CH<sub>2</sub>), 2.55-2.22 (m, 2H, allylic CH<sub>2</sub>), 2.01-1.91 (m, 2H, CH<sub>2</sub>), 1.50 (s, 3H, Me), 1.40 (s, 3H, Me), 0.16 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, neutralized CDCl<sub>3</sub>) : 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** (CH<sub>2</sub>Cl<sub>2</sub>) : 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<sup>-1</sup>.

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

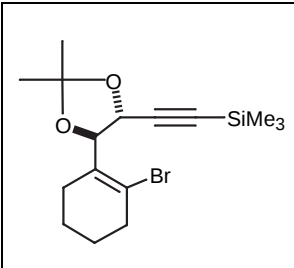
|                                                                                   |                                                                                                                                                                                                                                                                                                                              |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- 0.60 (Et<sub>2</sub>O/Hexane : 10/90)</li> <li>- Eluant of chromatography : 10/90 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : white solid</li> <li>- mp = 68 °C</li> <li>- Yield = 73 %</li> <li>- C<sub>16</sub>H<sub>25</sub>BrO<sub>2</sub>Si</li> <li>- MW = 357.36</li> </ul> |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (200 MHz, neutralised CDCl<sub>3</sub>) : δ 5.08 (2d, 2H, *J* = 6.8 Hz, *J* = 6.6 Hz, -OCH-C≡C-TMS et -CBr=CH-O-), 2.62-2.13 (m, 4H, 2 allylic CH<sub>2</sub>), 1.80-1.64 (m, 4H, 2 CH<sub>2</sub>), 1.57 (s, 3H, Me), 1.37 (s, 3H, Me), 0.16 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (50 MHz, neutralised CDCl<sub>3</sub>) : 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** (CH<sub>2</sub>Cl<sub>2</sub>) : ν 2982 w, 2936 m, 2864 w, 2358 w, 2179 w (C≡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<sup>-1</sup>.

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

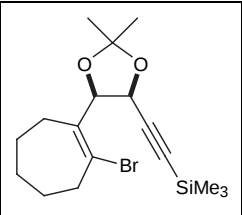
|                                                                                     |                                                                                                                                                                                                                                                                                                                               |
|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.47 (Et<sub>2</sub>O/Hexane : 10/90)</li> <li>- Eluant of chromatography : 10/90 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 82 %</li> <li>- C<sub>16</sub>H<sub>25</sub>BrO<sub>2</sub>Si</li> <li>- MW = 357.36</li> </ul> |
|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (300 MHz, neutralized CDCl<sub>3</sub>) : δ 5.27 (d, 1H, *J* = 7.5 Hz, -OCH-C≡C-TMS), 4.35 (d, 1H, *J* = 7.5 Hz, -CBr=CH-O-), 2.57-2.52 (m, 2H, allylic CH<sub>2</sub>), 2.34-1.95 (m, 2H, allylic CH<sub>2</sub>), 1.76-1.59 (m, 4H, 2 CH<sub>2</sub>), 1.52 (s, 3H, Me), 1.43 (s, 3H, Me), 0.17 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, neutralized CDCl<sub>3</sub>) : 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** (CH<sub>2</sub>Cl<sub>2</sub>) : ν 2990 m, 2942 s, 2860 m, 2341 w, 2179 w (C≡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)**

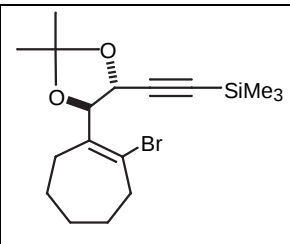
|                                                                                   |                                                                                                                                                                                                                                                                                                                     |
|-----------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> = 0.72 (70/30 Et<sub>2</sub>O/Hexane)</li> <li>- Eluant of chromatography : 30/70 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow oil</li> <li>- Yield = 68 %</li> <li>- C<sub>17</sub>H<sub>27</sub>BrO<sub>2</sub>Si</li> <li>- MW = 371.39</li> </ul> |
|-----------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$ : 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*<sub>AX</sub> = 7.2 Hz, *J*<sub>BX</sub> = 7.2 Hz, *J*<sub>AB</sub> = 16.2 Hz); 2.51 and 2.34 (ABX system dd, *J*<sub>AX</sub> = 7.6 Hz, *J*<sub>BX</sub> = 10.6 Hz, *J*<sub>AB</sub> = 16.2 Hz); 1.95-1.55 (m, 8H); 1.50-1.20 (m, 4H); 0.16 (s, 9H).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**  $\delta$ : 137.99 (C<sub>quat</sub>); 137.99 (C<sub>quat</sub>); 125.57 (C<sub>quat</sub>); 110.15 (C<sub>quat</sub>); 102.10 (C<sub>quat</sub>); 92.15 (C<sub>quat</sub>); 82.44 (+); 68.24 (+); 41.79 (-); 31.19 (-); 29.11 (-); 27.09 (+); 25.73 (-); 25.58 (+); 25.45 (-); -0.32 (+).

**IR (FTIR, CCl<sub>4</sub>)** :  $\nu$  = 3323, 2927, 2854, 2361, 2176, 1593, 1445, 1376, 1332, 1248, 1232, 1160, 1092, 1049, 846, 759 cm<sup>-1</sup>.

**{{(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"> <li>- R<sub>f</sub> : 0.46 (Et<sub>2</sub>O/Hexane : 10/90)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 70 %</li> <li>- C<sub>17</sub>H<sub>27</sub>BrO<sub>2</sub>Si</li> <li>- MW = 371.39</li> </ul> |
|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR (200 MHz, neutralized CDCl<sub>3</sub>)** :  $\delta$  5.22 (d, 1H, *J* = 7.6 Hz, -OCH-C $\equiv$ C-TMS), 4.24 (d, 1H, *J* = 7.8 Hz, -CBr=CH-), 2.81 (t, 2H, allylic CH<sub>2</sub>), 2.84-2.78 (m, 2H, allylic CH<sub>2</sub>), 2.26-2.21 (m, 2H, allylic CH<sub>2</sub>), 1.84-1.55 (m, 6H, 3 CH<sub>2</sub>), 1.52 (s, 3H, Me), 1.45 (s, 3H, Me), 0.17 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

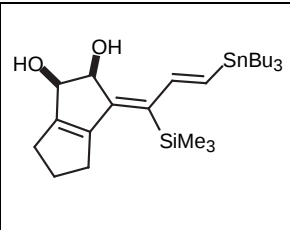
**<sup>13</sup>C-NMR (50 MHz, neutralized CDCl<sub>3</sub>)** :  $\delta$  135.83, 128.16, 110.43, 101.84, 91.90, 84.36, 68.21, 41.98, 31.59, 27.62, 26.75, 26.18, 25.05, -0.37.

**IR (CH<sub>2</sub>Cl<sub>2</sub>)** :  $\nu$  2990 m, 2925 s, 2855 m, 2180 w (C $\equiv$ C), 1648 w (C=C), 1446 w, 1380 w, 1380 m, 1249 w, 1049 s, 844 s, 760 f cm<sup>-1</sup>.

### 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)

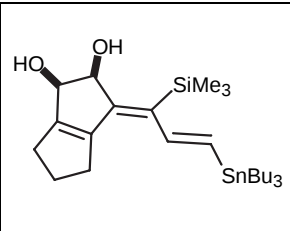
|                                                                                    |                                                                                                                                                                                                                                                                                                                              |
|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.47 (Et<sub>2</sub>O/Hexane : 50/50)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 16 %</li> <li>- C<sub>26</sub>H<sub>46</sub>O<sub>2</sub>SiSn</li> <li>- MW = 537.44</li> </ul> |
|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

<sup>1</sup>H NMR (300 MHz, neutralized CDCl<sub>3</sub>) : δ 6.83 (d, 1H, *J* = 19.8 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.92 (d, 1H, *J* = 19.8 Hz, -CH=CH(SnBu<sub>3</sub>)), 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 CH<sub>2</sub> + 2 OH), 1.62-1.22 (m, 12H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.96-0.86 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.17 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>C-NMR (50 MHz, neutralized CDCl<sub>3</sub>) : 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 (CH<sub>2</sub>Cl<sub>2</sub>) : 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)

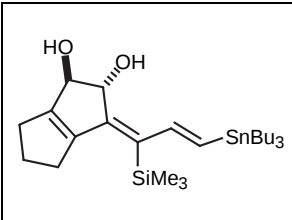
|                                                                                     |                                                                                                                                                                                                                                                                                                                              |
|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.33 (Et<sub>2</sub>O/Hexane : 50/50)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 59 %</li> <li>- C<sub>26</sub>H<sub>46</sub>O<sub>2</sub>SiSn</li> <li>- MW = 537.44</li> </ul> |
|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (300 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  6.75 (d, 1H,  $J$  = 19.6 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.82 (d, 1H,  $J$  = 19.6 Hz, -CH=CH(SnBu<sub>3</sub>)), 4.83 (s, 1H, CHOH-CHOH-C=C-TMS), 4.51 (s, 1H, CHOH-CHOH-C=C-TMS), 2.87-2.12 (m, 8H, 3 CH<sub>2</sub> + 2 OH), 1.63-1.08 (m, 12H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.93-0.78 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.23 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub> neutralized) :  $\delta$  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** (CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$  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<sup>-1</sup>.

**(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)**

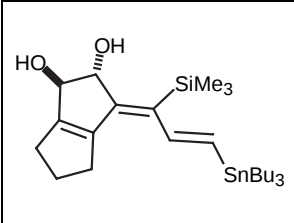
|                                                                                    |                                                                                                                                                                                                                                                                                                                              |
|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.35 (Et<sub>2</sub>O/Hexane : 50/50)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 16 %</li> <li>- C<sub>26</sub>H<sub>46</sub>O<sub>2</sub>SiSn</li> <li>- MW = 537.44</li> </ul> |
|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (200 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  6.82 (d, 1H,  $J$  = 19.8 Hz, -CH=CH(SnBu<sub>3</sub>)), 6.02 (d, 1H,  $J$  = 19.8 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.01 (s, 1H, CHOH-CHOH-C=C-TMS), 4.57 (s, 1H, CHOH-CHOH-C=C-TMS), 2.85-2.00 (m, 8H, 3 CH<sub>2</sub> + 2 OH), 1.70-1.18 (m, 12H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 1.07-0.77 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.17 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (50 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  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** (CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$  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<sup>-1</sup>.

**(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)**

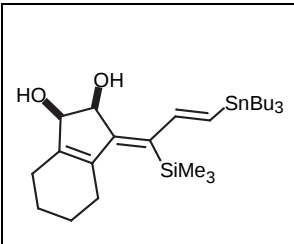
|                                                                                   |                                                                                                                                                                                                                                                                                                                      |
|-----------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.18 (Et<sub>2</sub>O/Hexane : 50/50)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow oil</li> <li>- Yield = 38 %</li> <li>- C<sub>26</sub>H<sub>46</sub>O<sub>2</sub>SiSn</li> <li>- MW = 537.44</li> </ul> |
|-----------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (300 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  6.77 (d, 1H,  $J$  = 19.7 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.83 (d, 1H,  $J$  = 19.7 Hz, -CH=CH(SnBu<sub>3</sub>)), 4.74 (d, 1H,  $J$  = 6.2 Hz, CHOH-CH<sub>2</sub>OH-C=C-TMS), 4.48 (s, 1H, CHOH-CH<sub>2</sub>OH-C=C-TMS), 2.53-2.15 (m, 8H, 3 CH<sub>2</sub> + 2 OH), 1.65-1.14 (m, 12H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.99-0.80 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.22 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub> neutralized) :  $\delta$  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** (CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$  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<sup>-1</sup>.

**(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)**

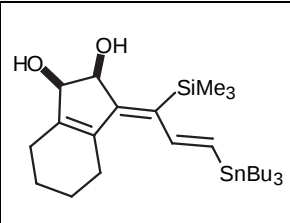
|                                                                                     |                                                                                                                                                                                                                                                                                                                              |
|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.64 (Et<sub>2</sub>O/Hexane : 70/30)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 24 %</li> <li>- C<sub>27</sub>H<sub>48</sub>O<sub>2</sub>SiSn</li> <li>- MW = 553.48</li> </ul> |
|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (300 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  6.82 (d, 1H,  $J$  = 19.9 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.90 (d, 1H,  $J$  = 19.6 Hz, -CH=CH(SnBu<sub>3</sub>)), 4.43 (s, 1H, CHOH-CH<sub>2</sub>OH-C=C-TMS), 4.30 (m, 1H, CHOH-CH<sub>2</sub>OH-C=C-TMS), 2.75-2.10 (m, 6H, 2 CH<sub>2</sub> + 2 OH), 1.65-1.19 (m, 16H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub> + 2 CH<sub>2</sub>), 1.02-0.74 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.17 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (50 MHz, CDCl<sub>3</sub> neutralized) :  $\delta$  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** (CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$  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)**

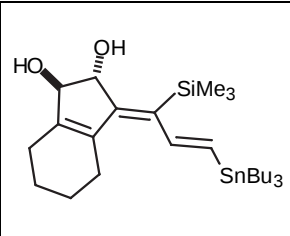
|                                                                                   |                                                                                                                                                                                                                                                                                                                              |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.52 (Et<sub>2</sub>O/Hexane : 70/30)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 47 %</li> <li>- C<sub>27</sub>H<sub>48</sub>O<sub>2</sub>SiSn</li> <li>- MW = 553.48</li> </ul> |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (300 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  6.75 (d, 1H,  $J$  = 19.6 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.75 (d, 1H,  $J$  = 19.6 Hz, -CH=CH(SnBu<sub>3</sub>)), 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 CH<sub>2</sub> + 2 OH), 1.68-1.21 (m, 16H, 2 CH<sub>2</sub> + Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 1.00-0.77 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.22 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  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** (CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$  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<sup>-1</sup>.

**(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"> <li>- R<sub>f</sub> : 0.17 (Et<sub>2</sub>O/Hexane : 70/30)</li> <li>- Eluant of chromatography : 70/30 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 52 %</li> <li>- C<sub>27</sub>H<sub>48</sub>O<sub>2</sub>SiSn</li> <li>- MW = 553.48</li> </ul> |
|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

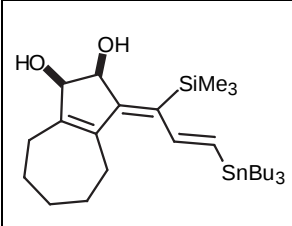
**<sup>1</sup>H NMR** (300 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  6.76 (d, 1H,  $J$  = 19.6 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.76 (d, 1H,  $J$  = 19.6 Hz, -CH=CH(SnBu<sub>3</sub>)), 4.44 (s, 1H, CHOH-CHOH-C=C-TMS), 4.35 (s, 1H, CHOH-CHOH-C=C-TMS), 2.38-2.00 (m, 6H, 2 CH<sub>2</sub> + 2 OH), 1.70-1.19 (m, 16H,

Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub> + 2 CH<sub>2</sub>), 0.93-0.87 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.20 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>C-NMR (75 MHz, neutralized CDCl<sub>3</sub>) : 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 (CH<sub>2</sub>Cl<sub>2</sub>) : 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<sup>-1</sup>.

**(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)**

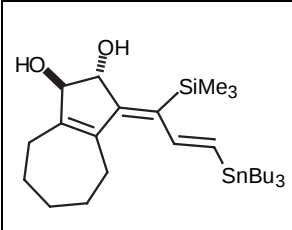
|                                                                                   |                                                                                                                                                                                                                                                                                                                              |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.44 (Et<sub>2</sub>O/Hexane : 60/40)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 45 %</li> <li>- C<sub>28</sub>H<sub>50</sub>O<sub>2</sub>SiSn</li> <li>- MW = 567.51</li> </ul> |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> neutralized) : δ 6.70 (d, 1H, *J* = 19.7 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.71 (d, 1H, *J* = 19.7 Hz, -CH=CH(SnBu<sub>3</sub>)), 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 CH<sub>2</sub> + 2 OH), 1.80-1.26 (m, 18H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub> + 3 CH<sub>2</sub>), 0.98-0.81 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.20 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub> 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 (CH<sub>2</sub>Cl<sub>2</sub>) : 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<sup>-1</sup>.

**(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"> <li>- R<sub>f</sub> : 0.24 (Et<sub>2</sub>O/Hexane : 60/40)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 31 %</li> <li>- C<sub>28</sub>H<sub>50</sub>O<sub>2</sub>SiSn</li> <li>- MW = 567.51</li> </ul> |
|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

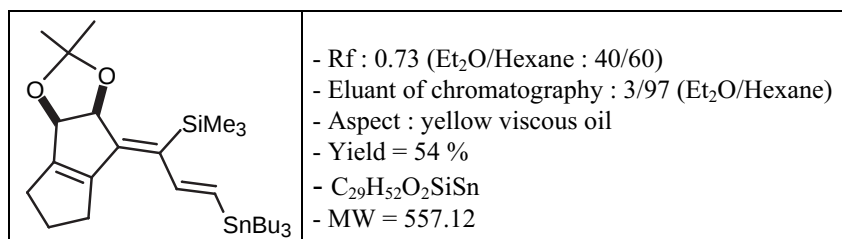
**<sup>1</sup>H NMR** (200 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  6.74 (d, 1H,  $J$  = 19.3 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.72 (d, 1H,  $J$  = 19.3 Hz, -CH=CH(SnBu<sub>3</sub>)), 4.42 (m, 1H, CHOH-CHOH-C=C-TMS), 4.32 (s, 1H, CHOH-CHOH-C=C-TMS), 2.45-2.01 (m, 6H, 2 CH<sub>2</sub> + 2 OH), 1.90-1.23 (m, 18H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub> + 3 CH<sub>2</sub>), 1.07-0.87 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.19 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (50 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  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** (CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$  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<sup>-1</sup>.

### 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)**



**<sup>1</sup>H NMR** (300 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  6.78 (d, 1H,  $J$  = 19.7 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.75 (d, 1H,  $J$  = 19.7 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.27 (d, 1H,  $J$  = 5.6 Hz, -O-CH=C=C-TMS), 4.89 (d, 1H,  $J$  = 5.6 Hz, -C=C-CH-O-), 2.52-2.10 (m, 6H, 3 CH<sub>2</sub>), 1.65-1.15 (m, 12H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 1.41 (s, 3H, Me), 1.38 (s, 3H, Me), 1.10-0.66 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.25 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  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** (CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$  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<sup>-1</sup>.

**[((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"> <li>- R<sub>f</sub> : 0.73 (Et<sub>2</sub>O/Hexane : 20/80)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 38 %</li> <li>- C<sub>29</sub>H<sub>52</sub>O<sub>2</sub>SiSn</li> <li>- MW = 557.12</li> </ul> |
|--|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (200 MHz, neutralized CDCl<sub>3</sub>) : δ 7.03 (d, 1H, *J* = 19.1 Hz, -CH=CH(SnBu<sub>3</sub>)), 6.24 (d, 1H, *J* = 19.1 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.04 (d, 1H, *J* = 8.1 Hz, -O-CH-C≡C-TMS), 4.45 (d, 1H, *J* = 8.1 Hz, C=C-CHO-), 2.70-2.40 (m, 4H, 2 CH<sub>2</sub>), 1.93-1.75 (m, 2H, CH<sub>2</sub>), 1.68-1.22 (m, 12H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 1.53 (s, 3H, Me), 1.45 (s, 3H, Me), 0.97-0.87 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.17 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, neutralized CDCl<sub>3</sub>) : 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** (CH<sub>2</sub>Cl<sub>2</sub>) : ν 2945 s, 2926 s, 2849 m, 2355 w (C≡C), 1455 m (C=C), 1379 m, 1250 m, 1052 m, 979 w, 844 s, 762 s, 504 m cm<sup>-1</sup>.

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

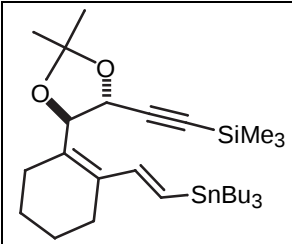
|  |                                                                                                                                                                                                                                                                                                                              |
|--|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.65 (Et<sub>2</sub>O/Hexane : 20/80)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 64 %</li> <li>- C<sub>30</sub>H<sub>54</sub>O<sub>2</sub>SiSn</li> <li>- MW = 593.55</li> </ul> |
|--|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (300 MHz, neutralized CDCl<sub>3</sub>) : δ 6.78 (d, 1H, *J* = 19.7 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.76 (d, 1H, *J* = 19.7 Hz, -CH=CH(SnBu<sub>3</sub>)), 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 CH<sub>2</sub>), 1.74-1.43 (m, 8H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub> + 1 CH<sub>2</sub>), 1.40-1.17 (m, 12H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub> + 2 Me), 1.01-0.79 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.21 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, neutralized CDCl<sub>3</sub>) : 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** (CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$  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<sup>-1</sup>.

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

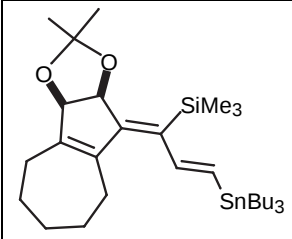
|                                                                                   |                                                                                                                                                                                                                                                                                                                              |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.58 (Et<sub>2</sub>O/Hexane : 20/80)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 56 %</li> <li>- C<sub>30</sub>H<sub>54</sub>O<sub>2</sub>SiSn</li> <li>- MW = 593.55</li> </ul> |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub> neutralized) :  $\delta$  7.11 (d, 1H,  $J$  = 19.2 Hz, -CH=CH(SnBu<sub>3</sub>)), 6.31 (d, 1H,  $J$  = 19.2 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.29 (d, 1H,  $J$  = 7.5 Hz, -O-CH-C $\equiv$ C-TMS), 4.48 (d, 1H,  $J$  = 7.5 Hz, C=C-CH-O-), 2.35-1.97 (m, 4H, 2 CH<sub>2</sub>), 1.65-1.26 (m, 16H, 2 CH<sub>2</sub> + Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 1.52 (s, 3H, Me), 1.46 (s, 3H, Me), 0.95-0.87 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.17 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub> neutralized) :  $\delta$  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** (CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$  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<sup>-1</sup>.

**[(1*Z*,2*E*)-1-[(*3aR\*,9aS\**)-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"> <li>- R<sub>f</sub> : 0.51 (Et<sub>2</sub>O/Hexane : 10/90)</li> <li>- Eluant of chromatography : 3/97 (Et<sub>2</sub>O/Hexane)</li> <li>- Aspect : yellow viscous oil</li> <li>- Yield = 48 %</li> <li>- C<sub>31</sub>H<sub>56</sub>O<sub>2</sub>SiSn</li> <li>- MW = 607.58</li> </ul> |
|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

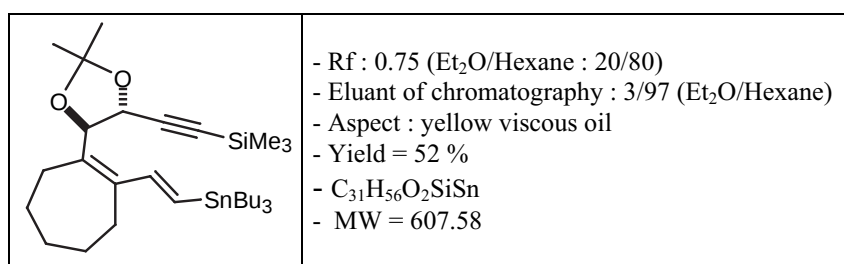
**<sup>1</sup>H NMR** (300 MHz, neutralized CDCl<sub>3</sub>) :  $\delta$  6.74 (d, 1H,  $J$  = 19.6 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.72 (d, 1H,  $J$  = 19.6 Hz, -CH=CH(SnBu<sub>3</sub>)), 4.88 (d, 1H,  $J$  = 5.1 Hz, -O-CH-C $\equiv$ C-TMS), 4.79 (d, 1H,  $J$  = 4.6 Hz, -C=C-CH-O-), 2.45-2.21 (m, 4H, 2 allylic CH<sub>2</sub>), 1.80-1.23 (m, 18H, 3

CH<sub>2</sub> et Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>, 1.40 (s, 3H, Me), 1.38 (s, 3H, Me), 0.94-0.86 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.21 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>C-NMR (50 MHz, neutralized CDCl<sub>3</sub>) : 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 (CH<sub>2</sub>Cl<sub>2</sub>) : 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<sup>-1</sup>.

**[(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)**

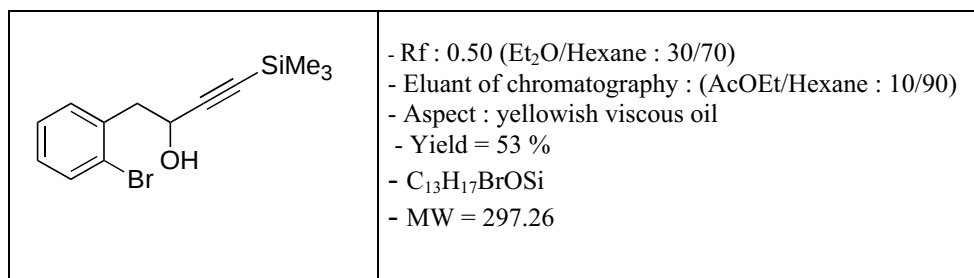


<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub> neutralized) : δ 7.03 (d, 1H, *J* = 19.1 Hz, -CH=CH(SnBu<sub>3</sub>)), 6.33 (d, 1H, *J* = 19.3 Hz, -CH=CH(SnBu<sub>3</sub>)), 5.28 (d, 1H, *J* = 7.8 Hz, -O-CH-C≡C-TMS), 4.39 (d, 1H, *J* = 7.8 Hz, C=C-CHO-), 2.54-2.17 (m, 4H, 2 CH<sub>2</sub>), 1.90-1.26 (m,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

<sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub> 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 (CH<sub>2</sub>Cl<sub>2</sub>) : 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<sup>-1</sup>.

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



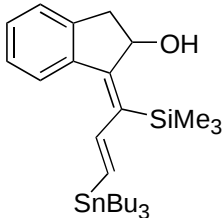
To a stirred solution of trimethylsilylacetylene (0.48 mL, 3.397 mmol) in dry THF (5 mL) at  $-78\text{ }^{\circ}\text{C}$  was added *n*-BuLi (1.5 M in hexane, 2.43 mL, 3.669 mmol). The mixture was stirred at this temperature for 15 min and dry  $\text{CeCl}_3$  (solid, 0.903 g, 3.664 mmol) was added 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  $\text{NH}_4\text{Cl}$ , filtered through Celite and extracted with AcOEt. The organic extract was washed with water, brine and dried over  $\text{MgSO}_4$ . The crude was purified by silica gel flash column chromatography to give a yellowish viscous oil (0.442 g, 53 %)

**$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$  neutralized) :  $\delta$  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,  $J = 7.0\text{ Hz}$ ,  $J = 5.31\text{ Hz}$ ,  $\text{CH}_2\text{OH}$ ), 3.22 (ABX part B, dd, 1H,  $J = 13.4\text{ Hz}$ ,  $J = 7.5\text{ Hz}$ ,  $\text{CH}_2$ ), 3.15 (ABX part A, dd, 1H,  $J = 13.9\text{ Hz}$ ,  $J = 7.0\text{ Hz}$ ,  $\text{CH}_2$ ), 1.9 (d, 1H,  $J = 5.62\text{ Hz}$ , OH), 0.17 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ).

**$^{13}\text{C}$ -NMR** (50 MHz,  $\text{CDCl}_3$  neutralized) :  $\delta$  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) :  $\nu$  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  $\text{cm}^{-1}$ .

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

|                                                                                     |                                                                                                                                                                                                                                                                                                                                                                |
|-------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- Rf : 0.39 (<math>\text{Et}_2\text{O}</math>/Hexane : 20/80)</li> <li>- Eluant of chromatography : (<math>\text{Et}_2\text{O}</math>/Hexane : 5/95)</li> <li>- Aspect : yellowish viscous oil</li> <li>- Yield = 61 %</li> <li>- <math>\text{C}_{27}\text{H}_{46}\text{OSiSn}</math></li> <li>- MW = 533.45</li> </ul> |
|-------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

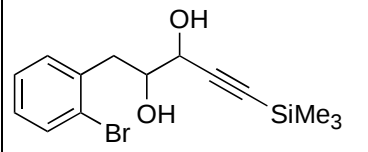
**$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$  neutralized) :  $\delta$  7.90 (d, 1H,  $J = 7.91\text{ Hz}$ , H arom.), 7.31-7.11 (m, 3H, H arom.), 6.89 (d, 1H,  $J = 20.0\text{ Hz}$ ,  $-\text{CH}=\text{CH}(\text{SnBu}_3)$ ), 6.04 (d, 1H,  $J = 20.0\text{ Hz}$ ,  $-\text{CH}=\text{CH}(\text{SnBu}_3)$ ), 4.98 (t, 1H,  $J = 5.7\text{ Hz}$ ,  $\text{CH}_2\text{OH}$ ), 3.23 (dd, 1H,  $J = 17.0\text{ Hz}$ ,  $J = 5.7\text{ Hz}$ ,  $\text{CH}_2$ ), 2.91 (d, 1H,  $J = 16.6\text{ Hz}$ ,  $\text{CH}_2$ ), 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-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 1.04-0.89 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.31 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub> 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<sup>-1</sup>.

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

|                                                                                   |                                                                                                                                                                                                                                                                                                                                     |
|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"> <li>- R<sub>f</sub> : 0.49 (Et<sub>2</sub>O/Hexane : 70/30)</li> <li>- Eluant of chromatography : (Et<sub>2</sub>O /Hexane : 30/70)</li> <li>- Aspect : yellowish viscous oil</li> <li>- Yield = 30 %</li> <li>- C<sub>14</sub>H<sub>19</sub>BrO<sub>2</sub>Si</li> <li>- MW = 327.29</li> </ul> |
|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

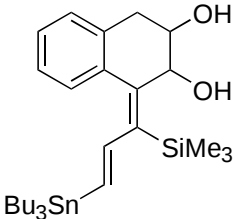
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> neutralized) : δ 7.56 (d, 1H, *J* = 7.8 Hz, H arom.), 7.36-7.24 (m, 2H, H arom.) 7.11 (t, 1H, *J* = 7.7 Hz, H arom.), 4.40 (d, 1H, *J* = 3.42 Hz -CH<sub>2</sub>OH-C≡C major), 4.25 (d, 1H, *J* = 6.12 Hz -CH<sub>2</sub>OH-C≡C minor) 4.08-3.91 (ABX part X, m, 1H, major + minor, -CH<sub>2</sub>-CH<sub>2</sub>OH), 3.27 (ABX part B, dd, 1H, minor, *J* = 13.9 Hz, *J* = 3.9 Hz, CH<sub>2</sub>), 3.16 (ABX part B, dd, 1H, major, *J* = 14.1 Hz, *J* = 4.4 Hz, CH<sub>2</sub>), 2.99 (ABX part Ar, dd, 1H, major, *J* = 14.0 Hz, *J* = 9.1 Hz, CH<sub>2</sub>), 2.87 (ABX part A, dd, 1H, minor, *J* = 13.9 Hz, *J* = 8.9 Hz, CH<sub>2</sub>), 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(CH<sub>3</sub>)<sub>3</sub> major), 0.19 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub> minor).

<sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub> 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<sup>-1</sup>.

HRMS (ESI, positive ion 180 eV) calcd for (C<sub>14</sub>H<sub>19</sub>BrO<sub>2</sub>SiNa)<sup>+</sup> 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"> <li>- Rf : 0.20 (Et<sub>2</sub>O/Hexane : 60/40)</li> <li>- Eluant of chromatography : (Et<sub>2</sub>O/Hexane : 50/50)</li> <li>- Aspect : yellowish solidl</li> <li>- Yield = 30 %</li> <li>- C<sub>28</sub>H<sub>48</sub>O<sub>2</sub>SiSn</li> <li>- MW = 563.48</li> </ul> |
|-----------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**<sup>1</sup>H NMR** (200 MHz, CDCl<sub>3</sub> neutralized) :  $\delta$  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(SnBu<sub>3</sub>)), 5.85 (d, 1H,  $J$  = 20.1 Hz, -CH=CH(SnBu<sub>3</sub>)), 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, CH<sub>2</sub>), 2.90 (dd, 1H,  $J$  = 16.6 Hz,  $J$  = 9.5 Hz, CH<sub>2</sub>), 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-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.97-0.83 (m, 15H, Sn-(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 0.29 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (50 MHz, CDCl<sub>3</sub> neutralized) :  $\delta$  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** (CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$  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<sup>-1</sup>.