Organic Letters

Supporting Information to Accompany°:

Cyclocarbopalladation°: Formation of Bicyclic 1,2-Cyclobutandiols through a Rare 4-exo-dig Cyclization

Baha Salem, Philippe Klotz, Jean Suffert

*Laboratoire de Pharmacochimie de la Communication Cellulaire
(UMR 7081, CNRS/ULP), Facult de Pharmacie, 64 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. 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 sequence and are given as follow°: + = CH or CH₃, - = CH₂, C_{quat} = C. Melting points were determined with a glass capillary apparatus and are uncorrected. Mass spectra were obtained from the Service de spectrometrie de masse of the Institute de Chimie of Strasbourg (France).

General Procedure. Carbocyclopalladation of γ -bromopropargylic diol :

The reaction is carried out in an oven-dried 25 mL-bicol, equipped with a reflux condenser, under argon atmosphere. To a solution of the substrate (**1**, **2**, **3**, **4**, **17**, or **18**) (100 mg, 1 eq) in 10 mL dried benzene, was added $\text{Pd}(\text{PPh}_3)_4$ (0.1 eq), followed by the stannylated reagent (1.3 eq). The reaction mixture was stirred for 1-17 hours in a preheated 90°C oil bath. The reaction is followed by TLC. Then, the reaction mixture was concentrated *in vacuo* and immediately purified by flash chromatography, leading to the different bicyclic cyclobutan-1,2-diols.

(1*R*,7*Z*,8*S*)-7-[3-phenyl-1-(trimethylsilyl)prop-2-ynylidene]bicyclo[4.2.0]oct-5-ene-1,8-diol (**1a**)

<ul style="list-style-type: none">- Time of heating°: 3 hours- R_f = 0.43 (50/50 Et₂O/Hexane)- Eluant of chromatography°: 10/90 (Et₂O/Hexane)- Aspect°: yellow solid- mp = 98 °C- Yield = 69 %
---	---

¹H-NMR (300 MHz, CDCl₃)°: δ 7.50-7.20 (m, 5H); 6.45 (ap t, 1H); 4.44 (d, 1H, J = 9.5 Hz); 3.11 (d, 1H, J = 9.5 Hz); 2.57-2.42 (m, 1H)°; 2.38-2.12 (m, 2H); 2.07-1.78 (m, 3H); 1.50-1.32 (m, 1H); 0.34 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃)°: 162.95 (C_{quat}), 139.40 (C_{quat}), 131.32 (+), 128.28 (+), 127.74 (+), 126.93 (+), 124.36 (C_{quat}), 118.23 (C_{quat}), 98.31 (C_{quat}), 90.86 (C_{quat}), 76.11 (+), 75.17 (C_{quat}), 30.86 (-), 25.90 (-), 18.11 (-), -0.92 (+).

IR (FTIR, film)°: ν = 3382, 3030, 2946, 2856, 2174, 1942, 1871, 1723, 1648, 1596, 1486, 1439, 1338, 1250, 1194, 1149, 1100, 998, 843, 784, 762, 691, 629 cm⁻¹.

HRMS (ESI, positive ion 130 eV) calcd for (C₂₀H₂₄O₂SiNa)⁺ 347.1443; found 347.1442.

(1*R*,7*Z*,8*S*)-7-[2-furyl(trimethylsilyl)methylene]bicyclo[4.2.0]oct-5-ene-1,8-diol (**1b**)

<ul style="list-style-type: none">- Time of heating°: 2 hours- R_f = 0.47 (50/50 Et₂O/Hexane)- Eluant of chromatography°: 20/80 (Et₂O/Hexane)- Aspect°: brown oil-Yield = 84 %
---	--

¹H-NMR (300 MHz, CDCl₃)°: δ 7.37 (s, 1H); 6.38 (br t, 1H); 6.24 (br s, 2H); 4.43 (br s, 1H); 3.18 (br s, 1H); 2.50-2.12 (m, 3H); 2.13-1.73 (m, 3H); 1.57-1.32 (m, 1H); 0.30 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃)°: δ 155.53 (C_{quat}), 155.32 (C_{quat}), 140.70 (+), 138.69 (C_{quat}), 127.37 (+), 125.42 (C_{quat}), 110.96 (+), 108.06 (+), 75.76 (+), 74.66 (C_{quat}), 31.16 (-), 26.19 (-), 17.69 (-), 0.32 (+).

IR (FTIR, film): $\nu = 3379, 2943, 1720, 1650, 1607, 1424, 1390, 1330, 1249, 1192, 1126, 1089, 1024, 1000, 934, 843, 762, 732, 694, 626, 596 \text{ cm}^{-1}$.

HRMS (ESI, positive ion 135 eV) calcd for $(\text{C}_{16}\text{H}_{22}\text{O}_3\text{SiNa})^+$ 313.1236; found 313.1237.

(1*R*,7*Z*,8*S*)-7-[(2*E*,4*E*)-6-hydroxy-4-methyl-1-(trimethylsilyl)hexa-2,4-dienylidene]bicyclo[4.2.0]oct-5-ene-1,8-diol (1c)

<ul style="list-style-type: none"> - Time of heating: 2 hours - Rf = (AcOEt/Hexane) - Eluant of chromatography: 40/60 (Et₂O/Hexane) - Aspect: yellow oil - Yield = 12 %
---	---

¹H-NMR (300 MHz, CDCl₃): δ 6.65 (d, 1H, $J = 16.4 \text{ Hz}$); 6.38 (d, 1H, $J = 16.4 \text{ Hz}$); 6.00 (ap t, 1H, $J = 3.4 \text{ Hz}$); 5.67 (t, 1H, $J = 6.8 \text{ Hz}$); 4.38 (d, 1H, $J = 9.4 \text{ Hz}$); 4.31 (d, 2H, $J = 7.1 \text{ Hz}$); 2.56-1.62 (m, 6H); 0.30 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃): δ 156.84 (C_{quat}), 139.47 (C_{quat}), 136.86 (C_{quat}), 135.32 (C_{quat}), 135.32 (+), 130.45 (+), 130.14 (+), 125.39 (+), 75.76 (+), 74.57 (C_{quat}), 59.45 (-), 31.66 (-), 26.04 (-), 17.84 (-), 12.31 (-), 0.56 (+).

IR (FTIR, film): $\nu = 3381, 2949, 2931, 2864, 1722, 1655, 1434, 1383, 1248, 1188, 1098, 1001, 837, 754, 687 \text{ cm}^{-1}$.

HRMS (ESI, positive ion 90 eV) calcd for $(\text{C}_{18}\text{H}_{28}\text{O}_3\text{SiNa})^+$ 343.1705; found 343.1706.

(1*S*,1*aR*)-7-(trimethylsilyl)-3,4,4*a*,5-tetrahydro-1*H*-cyclobuta[*de*]naphthalene-1,1*a*(2*H*)-diol (1d)

<ul style="list-style-type: none"> - Time of heating: 6 hours - Rf = 0.21 (30/70 Et₂O/Hexane) - Eluant of chromatography: 30/70 (Et₂O/Hexane) - Aspect: yellow oil - Yield = 35 %
---	--

¹H-NMR (300 MHz, CDCl₃): δ 5.90 (dd, 1H, $J = 2.2 \text{ Hz}, 5.3 \text{ Hz}$); 4.37 (s, 1H); 2.68-2.50 (m, 2H); 2.22-2.04 (m, 1H); 2.02 (dd, 1H, $J = 1.2 \text{ Hz}, 10.3 \text{ Hz}$); 1.74-1.47 (m, 3H); 1.35 (dt, 1H, $J = 3.4 \text{ Hz}, 13 \text{ Hz}$); 1.25 (m, 1H); 0.11 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃): δ 141.41 (C_{quat}), 139.52 (C_{quat}), 137.50 (+), 130.51 (C_{quat}), 82.16 (+), 38.93 (-), 33.65 (-), 31.30 (+), 29.83 (-), 22.50 (-), 1.36 (+).

IR (FTIR, CCl₄): $\nu = 3359, 2930, 2856, 1717, 1450, 1402, 1247, 1082, 1044, 836, 793 \text{ cm}^{-1}$.

HRMS (ESI, positive ion 90eV): calcd for $(\text{C}_{14}\text{H}_{22}\text{O}_2\text{SiK})^+$ 289.1026, found 289.1221.

(5*aS*,8*aS*,8*bS*)-3-(trimethylsilyl)-5*a*,7,8,8*b*-tetrahydro-2*H*-naphtho[1,8-*bc*]furan-8*a*(6*H*)-ol (1e)

<ul style="list-style-type: none"> - Time of heating°: 6 hours - Rf = 0.29 (50/50 Et₂O/Hexane) - Eluant of chromatography°: 30/70 (Et₂O/Hexane) - Aspect°: yellow solid - mp = 97 °C - Yield = 62 %
---	---

¹H-NMR (300 MHz, CDCl₃)°: δ 5.99 (d, *J* = 9.4 Hz); 5.76 (ddd, 1H, *J* = 1.2 Hz, 6.2 Hz, 9.4 Hz); 4.71 and 4.40 (ABX system, *J*_{AX} = 3.1 Hz, *J*_{BX} = 2.8 Hz, *J*_{AB} = 15 Hz); 2.93 (s, 1H), 2.67 (br d, 1H, *J* = 10 Hz); 2.40 (m, 1H); 1.87-1.73 (m, 1H); 1.67-1.26 (m, 4H); 0.94 (dq, 1H, *J* = 2.5 Hz, 12.5 Hz), 0.12 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃)°: δ 146.46, 127.22, 125.89, 124.21, 105.65, 67.83, 47.96, 33.75, 31.48, 26.57, 20.48, -1.31.

IR (FTIR, CCl₄)°: ν = 3334, 2982, 2856, 1632, 1573, 1445, 1242, 1151, 1087, 1051, 873, 839, 740 cm⁻¹.

HRMS (ESI, positive ion 90 eV)°: calcd for (C₁₄H₂₂O₂SiNa)⁺ 273.1287, found 273.1292.

X Ray analysis see supporting information JACS

(1R,7Z,8S)-7-[1-(trimethylsilyl)but-3-enylidene]bicyclo[4.2.0]oct-5-ene-1,8-diol (1f)

<ul style="list-style-type: none"> - Time of heating°: 5 hours - Rf = 0.42 (50/50 Et₂O/Hexane) - Eluant of chromatography°: 20/80 (Et₂O/Hexane) - Aspect°: yellow oil - Yield = 56 %
---	--

¹H-NMR (300 MHz, CDCl₃)°: δ 5.88 (ap t, 1H, *J* = 3.5 Hz); 5.87-5.70 (m, 1H); 4.99 (d, 1H, *J* = 15.1 Hz); 4.96 (s, 1H); 4.33 (s, 1H); 3.07 (dd, 1H, *J* = 5.8 Hz, 14.9 Hz); 2.94 (dd, 1H, *J* = 5.8 Hz, 14.9 Hz); 2.47-2.26 (m, 1H); 2.23-2.03 (m, 2H); 1.99-1.67 (m, 3H); 1.50-1.24 (m, 1H); 0.18 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃)°: δ 155.38 (C_{quat}), 138.54 (C_{quat}), 136.97 (+), 135.12 (C_{quat}), 124.51 (+), 115.05 (-), 75.61 (+), 74.70 (C_{quat}), 37.34 (-), 31.17 (-), 25.80 (-), 17.85 (-), -0.45 (+).

IR (FTIR, film)°: ν = 3380, 3078, 2945, 2895, 2824, 1655, 1636, 1426, 1409, 1327, 1301, 1243, 1192, 1155, 1094, 1059, 998, 946, 909, 854, 837, 805, 759, 689, 623, 555 cm⁻¹.

HRMS (ESI, positive ion) calcd for (C₁₅H₂₅O₂Si)⁺ 265.1624; found 265.1627.

→ Effect of the SiEt₃ substitution°:

(1R,7Z,8S)-7-[3-phenyl-1-(triethylsilyl)prop-2-ynylidene]bicyclo[4.2.0]oct-5-ene-1,8-diol (2a)

<ul style="list-style-type: none"> - Time of heating°: 8 hours - Rf = 0.38 (50/50 Et₂O/Hexane) - Eluant of chromatography°: 25/75 (Et₂O/Hexane) - Aspect°: yellow brown oil - Yield = 52 %
---	---

¹H-NMR (200 MHz, CDCl₃)°: δ 7.75-7.52 (m, 5H); 6.75 (ap t, 1H, *J* = 3.9 Hz); 4.66 (s, 1H); 3.46 (br s, 2H); 2.85-2.63 (m, 1H); 2.62-2.36 (m, 2H); 2.32-2.00 (m, 3H); 1.48-1.02 (m, 15H).

¹³C-NMR (75 MHz, CDCl₃)°: δ 163.48 (C_{quat}), 139.34 (C_{quat}), 130.98 (+), 128.02 (+), 127.40 (+), 126.53 (+), 124.28 (C_{quat}), 115.57 (C_{quat}), 97.47 (C_{quat}), 91.31 (C_{quat}), 76.03 (+), 74.76 (C_{quat}), 30.64 (-), 25.62 (-), 17.89 (-), 7.29 (+), 3.53 (-).

IR (FTIR, thin film)°: ν = 3515, 3270, 3060, 3030, 2950, 2869, 2730, 2249, 2182, 1879, 1810, 1718, 1658, 1597, 1580, 1488, 1454, 1440, 1392, 1339, 1271, 1234, 1190, 1144, 1098, 1060, 1004, 977, 941, 907, 890, 867, 846, 804, 755, 690, 654, 598, 518 cm⁻¹.

HRMS (ESI, positive ion 90 eV) calcd for (C₂₃H₃₀O₂SiNa)⁺ 389.1913; found 389.1915.

(1R,7Z,8S)-7-[2-furyl(triethylsilyl)methylene]bicyclo[4.2.0]oct-5-ene-1,8-diol (2b)

<ul style="list-style-type: none"> - Time of heating°: 2.5 hours - Rf = 0.55 (50/50 Et₂O/Hexane) - Eluant of chromatography°: 10/90 (Et₂O/Hexane) - Aspect°: yellow oil - yield = 30 %
---	---

¹H-NMR (300 MHz, CDCl₃)°: δ 7.35 (d, 1H, *J* = 1.9 Hz); 6.37 (dd, 1H, *J* = 1.9 Hz, 3.3 Hz); 6.18 (d, 1H, *J* = 3.3 Hz); 6.11 (t, 1H, *J* = 4.1 Hz); 4.37 (s, 1H); 3.17 (br s, 1H); 2.49-2.09 (m, 3H); 2.02-1.70 (m, 4H); 0.93 (t, 9H, *J* = 6.8 Hz); 0.83 (q, 6H, *J* = 6.8 Hz).

¹³C-NMR (50 MHz, CDCl₃)°: δ 157.53 (C_{quat}), 155.40 (C_{quat}), 140.51 (+), 138.48 (C_{quat}), 127.31 (+), 123.91 (C_{quat}), 110.82 (+), 107.51 (+), 75.97 (+), 74.45 (C_{quat}), 31.04 (-), 26.10 (-), 17.68 (-), 7.59 (+), 4.01 (-).

IR (FTIR, film)°: ν = 3426, 2955, 2875, 2173, 1786, 1726, 1665, 1456, 1415, 1379, 1238, 1153, 1057, 1019, 962, 808, 727 cm⁻¹.

HRMS (ESI, positive ion, 90 eV) calcd for (C₁₉H₂₈O₃SiNa)⁺ 355.1705; found 355.1709.

(1R)-2-(2-furyl)-1-[(1S)-1-hydroxy-3-(triethylsilyl)prop-2-ynyl]cyclohex-2-en-1-ol (2b)

<ul style="list-style-type: none"> - Time of heating°: 2.5 hours - Rf = 0.64 (50/50 Et₂O/Hexane) - Eluant of chromatography°: 10/90 (Et₂O/Hexane) - Aspect°: yellow oil - Yield = 15 %
---	---

¹H-NMR (300 MHz, CDCl₃)°: δ 7.36 (d, 1H, *J* = 1.9 Hz); 6.47 (dd, 1H, *J* = 3.0 Hz, 5.3 Hz); 6.42 (d, 1H, *J* = 4.5 Hz); 6.37 (dd, 1H, *J* = 1.9 Hz, 4.5 Hz); 4.67 (s, 1H); 2.64 (s, 1H); 2.39-2.06 (m, 3H); 2.03-1.64 (m, 3H); 1.00 (t, 9H, *J* = 7.0 Hz); 0.62 (q, 6H, *J* = 7.0 Hz).

¹³C-NMR (50 MHz, CDCl₃)°: δ 153.31 (C_{quat}), 141.37 (+), 134.31 (+), 129.44 (C_{quat}), 110.91 (+), 107.35 (+), 104.55 (C_{quat}), 89.53 (C_{quat}), 73.31 (C_{quat}), 68.55 (+), 32.51 (-), 25.84 (-), 18.33(-), 7.41 (+), 4.23 (-).

IR (FTIR, film)°: ν = 3426, 2955, 2875, 2173, 1786, 1666, 1456, 1415, 1379, 1238, 1153, 1057, 1019, 962, 808, 727 cm⁻¹.

HRMS (ESI, positive ion 90 eV) calcd for (C₁₉H₂₈O₃SiNa)⁺ 355.1705; found 355.1707.

(1R)-1-[(1S)-1-hydroxy-3-(triethylsilyl)prop-2-ynyl]-2-vinylcyclohex-2-en-1-ol (2d)

<ul style="list-style-type: none"> - Time of heating°: 6 hours - Rf = 0.39 (50/50 Et₂O/Hexane) - Eluant of chromatography°: 20/80 (Et₂O/Hexane) - Aspect°: yellow oil - Yield = 29 %
---	---

¹H-NMR (300 MHz, CDCl₃)°: δ 5.53 (dd, 1H, *J* = 10.9 Hz, 17.3 Hz); 6.13 (ap t, 1H, *J* = 3.7 Hz); 5.40 (dd, 1H, *J* = 1.9 Hz, 17.3 Hz); 5.05 (dd, 1H, *J* = 1.9 Hz, 10.9 Hz); 4.58 (d, 1H, *J* = 5.0 Hz); 2.25 (s, 1H); 2.14 (d, 1H); 2.10-1.95 (m, 2H); 1.85-1.66 (m, 4H); 0.99 (t, 9H, *J* = 6.9 Hz); 0.64 (q, 6H, *J* = 6.9 Hz).

¹³C-NMR (75 MHz, CDCl₃) : δ 137.31 (C_{quat}), 135.50 (+), 131.35 (+), 114.96 (+), 104.96 (C_{quat}), 89.80 (C_{quat}), 73.57 (C_{quat}), 68.39 (+), 32.57 (-), 25.76 (-), 18.47 (-), 7.39 (+), 4.17 (-).

IR (FTIR, film)°: ν = 3416, 3082, 2955, 2875, 2174, 1617, 1458, 1415, 1379, 1307, 1237, 1174, 1163, 1052, 1020, 999, 987, 965, 911, 820, 739, 728 cm⁻¹.

HRMS (ESI, positive ion 80 eV) calcd for (C₁₇H₂₈O₂SiK)⁺ 331.1496; found 331.1496.

(5aS,8aS,8bS)-3-(triethylsilyl)-5a,7,8,8b-tetrahydro-2H-naphtho[1,8-bc]furan-8a(6H)-ol (2e)

<ul style="list-style-type: none"> - Time of heating°: 4 hours - Rf = 0.27 (50/50 Et₂O/Hexane) - Eluant of chromatography°: 40/60 (Et₂O/Hexane) - Aspect°: brown oil - Yield = 63 %
---	--

¹H-NMR (300 MHz, CDCl₃)°: δ 5.98 (d, 1H, *J* = 9.3 Hz); 5.74 (dd, 1H, *J* = 5.9 Hz, 9.3 Hz); 4.69 and 4.40 (AB system, dd, 1H, *J* = 3.4 Hz, 15.2 Hz); 4.66 (br d, 1H, *J* = 9.4 Hz); 3.03

(s, 1H); 2.47-2.32 (m, 1H); 2.88-1.66 (m, 2H); 1.63-1.32 (m, 4H); 0.90 (t, 10H, $J = 6.8$ Hz); 0.64 (q, 6H, $J = 6.8$ Hz).

^{13}C -NMR (50 MHz, CDCl_3): δ 174.87 (C_{quat}), (+), 126.54 (+), 122.17 (C_{quat}), 105.48 (C_{quat}), 68.23 (-), 48.43 (+), 33.87, 31.55, 26.66, 20.59 (-), 7.35, 3.00 (-).

IR (FTIR, thin film): $\nu = 3390, 3026, 2951, 2871, 2733, 1698, 1632, 1574, 1455, 1416, 1378, 1338, 1299, 1278, 1234, 1181, 1156, 1116, 1054, 1016, 961, 906, 861, 731, 692, 586, 540, 510 \text{ cm}^{-1}$.

HRMS (ESI, positive ion 90 eV) calcd for $(\text{C}_{17}\text{H}_{29}\text{O}_2\text{Si})^+$ 293.1937; found 293.1938.

→ Effect of the protection of the diol:

{{(1Z)-1-[(3aS,8aR)-2,2-dimethyl-7,8-dihydro-3aH-benzo[1,4]cyclobuta[1,2-d][1,3]dioxol-4(6H)-ylidene]-3-phenylprop-2-ynyl}(trimethyl)silane (3a)}

<ul style="list-style-type: none"> - Time of heating: 3 hours - $R_f = 0.65$ (50/50 Et_2O/Hexane) - Eluant of chromatography: 5/95 (Et_2O/Hexane) - Aspect: brown oil - Yield = 53 %
--	--

^1H -NMR (300 MHz, CDCl_3): δ 7.46-7.29 (m, 5H); 6.47 (ap t, 1H, $J = 4.1$ Hz); 4.91 (s, 1H); 2.55-2.37 (m, 1H); 2.30-2.09 (m, 1H); 2.06-1.82 (m, 4H); 1.54 (s, 3H); 1.45 (s, 3H); 0.31 (s, 9H).

^{13}C -NMR (75 MHz, CDCl_3): δ 161.10 (C_{quat}), 140.54 (C_{quat}), 130.14 (+), 128.24 (+), 127.15 (+), 125.89 (+), 124.33 (C_{quat}), 118.94 (C_{quat}), 113.97 (C_{quat}), 98.96 (C_{quat}), 90.84 (C_{quat}), 86.01 (C_{quat}), 82.97 (+), 29.36 (-), 29.09 (+), 28.53 (+), 25.76 (-), 19.07 (-), -1.23 (+).

IR (FTIR, thin film): $\nu = 3421, 3056, 2951, 2365, 2336, 2183, 1720, 1600, 1489, 1448, 1378, 1250, 1202, 1147, 1092, 1036, 846, 759, 694 \text{ cm}^{-1}$.

[(Z)-[(3aS,8aR)-2,2-dimethyl-7,8-dihydro-3aH-benzo[1,4]cyclobuta[1,2-d][1,3]dioxol-4(6H)-ylidene](2-furyl)methyl](trimethyl)silane (3b)}

<ul style="list-style-type: none"> - Time of heating: 2 hours - $R_f = 0.76$ (50/50 Et_2O/Hexane) - Eluant of chromatography: 10/ 90 (Et_2O/Hexane) - Aspect: yellow oil - Yield = 83 %
---	---

^1H -NMR (200 MHz, CDCl_3): δ 7.38 (d, 1H, $J = 2.2$ Hz), 6.39 (dd, 1H, $J = 2.2$ Hz, 3.4 Hz); 6.34 (d, 1H, $J = 3.4$ Hz); 6.23 (ap t, 1H, $J = 3.9$ Hz); 4.95 (s, 1H); 2.52-2.32 (m, 1H); 2.27-1.97 (m, 3H); 1.95-1.78 (m, 2H); 1.52 (s, 3H); 1.45 (s, 3H); 0.30 (s, 9H).

^{13}C -NMR (50 MHz, CDCl_3): δ 155.12 (C_{quat}), 153.12 (C_{quat}), 140.83 (+), 139.72 (C_{quat}), 126.22 (C_{quat}), 125.42 (+), 113.73 (C_{quat}), 111.00 (+), 108.37 (+), 85.23 (C_{quat}), 29.90 (-), 29.33 (+), 28.71 (+), 25.86 (-), 18.66 (-), 0.18 (+).

HRMS (ESI, positive ion 200 eV) calcd for $(\text{C}_{19}\text{H}_{26}\text{O}_3\text{SiK})^+$ 369.1288; found 369.1253.

(2E,4E,6Z)-6-[(3aS,8aR)-2,2-dimethyl-7,8-dihydro-3aH-benzo[1,4]cyclobuta[1,2-d][1,3]dioxol-4(6H)-ylidene]-3-methyl-6-(trimethylsilyl)hexa-2,4-dien-1-ol (3c)

^1H -NMR (200 MHz, CDCl_3): δ 6.67 (d, 1H, J = 16.4 Hz); 6.40 (d, 1H, J = 16.4 Hz); 5.98 (ap t, 1H, J = 3.7 Hz); 5.68 (t, 1H, J = 6.6 Hz); 4.88 (s, 1H); 4.30 (d, 1H, J = 7.1 Hz); 2.52-2.30 (m, 1H); 2.28-1.68 (m, 5H); 1.47 (s, 3H); 1.43 (s, 3H); 1.42 (s, 3H); 0.28 (s, 9H).

^{13}C -NMR (50 MHz, CDCl_3): δ 155.67 (C_{quat}), 140.17 (C_{quat}), 136.82 (C_{quat}), 136.62 (C_{quat}), 135.53 (+), 130.51 (+), 130.41 (+), 124.59 (+), 113.70 (C_{quat}), 85.13 (C_{quat}), 85.16 (+), 59.37 (-), 30.27 (C_{quat}), 29.65 (-), 29.20 (+), 28.68 (+), 25.88 (-), 18.76 (-), 12.27 (+), 0.34 (+).

IR (FTIR, thin film): ν = 3430, 2943, 2856, 2247, 1722, 1666, 1445, 1376, 1250, 1201, 1147, 1107, 1073, 1042, 977, 912, 844, 759, 733, 694, 646, 528 cm^{-1} .

[(3aS,6bS,9aR)-8,8-dimethyl-2,3,3a,6b-tetrahydro-1H,4H-naphtho[1',8':2,3,4]cyclobuta[1,2-d][1,3]dioxol-6-yl](trimethyl)silane (3d)

^1H -NMR (200 MHz, CDCl_3): δ 5.89 (ap t, 1H, J = 3.9 Hz); 4.79 (s, 1H); 2.83-2.50 (m, 2H); 2.35-1.58 (m, 7H); 1.53 (s, 3H); 1.43 (s, 3H); 0.11 (s, 9H).

^{13}C -NMR (50 MHz, CDCl_3): δ 150.12 (C_{quat}), 141.81 (C_{quat}), 137.42 (+), 130.50 (C_{quat}), 115.26 (C_{quat}), 86.69 (+), 83.95 (C_{quat}), 34.99 (-), 34.00 (-), 30.33 (-), 29.48 (+), 28.85 (+), 28.74 (+), 23.14 (-), -1.16 (+).

IR (FTIR, thin film): ν = 3438, 2937, 2856, 1711, 1447, 1375, 1307, 1251, 1208, 1154, 1053, 842, 788, 757, 695, 627 cm^{-1} .

[(6bS,9aR)-8,8-dimethyl-2,3-dihydro-1H,6bH-naphtho[1',8':2,3,4]cyclobuta[1,2-d][1,3]dioxol-6-yl](trimethyl)silane (3e)

<ul style="list-style-type: none"> - Time of heating°: 17 hours - Rf = 0.81 (40/60 Et₂O/Hexane) - Eluant of chromatography°: 5/95 (Et₂O/Hexane) - Aspect°: yellow oil - Yield = 21 %
---	---

¹H-NMR (300 MHz, CDCl₃)°: δ 7.37 (d, 1H, *J* = 7.5 Hz); 7.03 (d, 1H, *J* = 7.5 Hz); 5.25 (s, 1H); 2.95 (dd, 1H, *J* = 6.4 Hz, 17.3 Hz); 2.49-1.95 (m, 5H); 1.53 (s, 3H), 1.38 (s, 3H), 0.30 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃)°: δ 153.77 (C_{quat}), 147.52 (C_{quat}), 136.52 (+), 135.67 (C_{quat}), 134.40 (C_{quat}), 127.07 (+), 114.24 (C_{quat}), 87.82 (C_{quat}), 85.92 (+), 29.38 (+), 29.11 (+), 28.26 (-), 25.49 (-), 22.14 (-), -0.91 (+).

IR (FTIR, thin film)°: ν = 3427, 2954, 2866, 1731, 1593, 1456, 1377, 1252, 1210, 1154, 1081, 908, 843, 756, 734, 692 cm⁻¹.

→ Effect of the ring size°:

(8Z)-8-[3-phenyl-1-(trimethylsilyl)prop-2-ynylidene]bicyclo[5.2.0]non-6-ene-1,9-diol (4a)

<ul style="list-style-type: none"> - Time of heating°: 1 hour - Rf = 0.38 (50/50 Et₂O/Hexane) - Eluant of chromatography°: 15/85 (Et₂O/Hexane) - Aspect°: yellow solid - mp = 114 °C - Yield = 61 %
---	---

¹H-NMR (300 MHz, CDCl₃)°: δ 7.50-7.29 (m, 5H); 6.96 (dd, 1H, *J* = 8.1 Hz, 4.7 Hz); 4.41 (d, 1H, *J* = 9.0 Hz); 2.85 (d, 1H, *J* = 9.0 Hz); 2.56-2.19 (m, 3H); 2.13-1.79 (m, 4H); 1.72-1.55 (m, 1H); 1.52-1.30 (m, 1H); 0.33 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃)°: δ 158.13 (C_{quat}), 146.29 (C_{quat}), 131.77 (+), 131.23 (+), 128.31 (+), 127.87 (+), 124.27 (C_{quat}), 119.46 (C_{quat}), 101.14 (C_{quat}), 91.14 (C_{quat}), 79.65 (C_{quat}), 76.18 (+), 35.79 (-), 29.25 (-), 28.19 (-), 26.25 (-), -1.04 (+).

IR (FTIR, CCl₄)°: ν = 3405, 3340, 2931, 2856, 2356, 2356, 2177, 1943, 1871, 1716, 1650, 1598, 1436, 1250, 1184, 1095, 1056, 991, 836, 784, 762, 680 cm⁻¹.

HRMS (ESI, positive ion 175 eV) calcd for (C₂₁H₂₆O₂SiNa)⁺ 361.1600; found 361.1602.

(8Z)-8-[2-furyl(trimethylsilyl)methylene]bicyclo[5.2.0]non-6-ene-1,9-diol (4b)

<ul style="list-style-type: none"> - Time of heating°: 3 hours - R_f = 0.35 (70/30 Et₂O/Hexane) - Eluant of chromatography°: 15/85 (Et₂O/Hexane) - Aspect°: orange solid - mp = 113 °C - Yield = 70 %
---	---

¹H-NMR (300 MHz, CDCl₃)°: δ 7.38 (d, 1H, *J* = 1.5 Hz); 6.39 (dd, 1H, *J* = 3.2 Hz, 1.5 Hz); 6.16 (d, 1H, *J* = 3.2 Hz); 6.10 (dd, 1H, *J* = 8.1 Hz, 4.7 Hz); 4.40 (d, 1H, *J* = 9.3 Hz); 2.95 (d, 1H, *J* = 9.3 Hz); 2.45-2.09 (m, 3H); 2.0-1.77 (m, 4H); 1.72-1.55 (m, 1H); 1.50-1.30 (m, 1H); 0.23 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃)°: δ 154.21 (C_{quat}), 153.03 (C_{quat}), 145.10 (C_{quat}), 140.63 (+), 130.96 (+), 128.69 (C_{quat}), 110.89 (+), 107.74 (+), 78.69 (C_{quat}), 75.73 (+), 35.88 (-), 29.09 (-), 27.98 (-), 26.18 (-), -0.23 (+).

IR (FTIR, CCl₄)°: ν = 3516, 3348, 2932, 2856, 1721, 1645, 1437, 1249, 1185, 1143, 1091, 1056, 1012, 930, 842, 788, 756, 693, 625 cm⁻¹.

HRMS (ESI, positive ion, 175 eV) calcd for (C₁₇H₂₄O₃SiNa)⁺ 327.1396; found 327.1392.

***anti*-(4*R*,4*aS*,9*R*,10*S*)-4-[(1*E*)-3-hydroxy-1-methylprop-1-enyl]-2-(trimethylsilyl)-4,4*a*,5,6,7,8-hexahydro-9*H*-1,9-methanobenzo[7]annulene-9,10-diol (4c)**

<ul style="list-style-type: none"> - Time of heating°: 4 hours - R_f = 0.11 (70/30 Et₂O/Hexane) - Eluant of chromatography°: 60/40 (Et₂O/Hexane) - Aspect°: yellow solid - mp = 93 °C - Yield = 60 %
---	--

¹H-NMR (300 MHz, CDCl₃)°: δ 6.04 (d, 1H, *J* = 2.5 Hz); 5.56 (t, 1H, *J* = 6.6 Hz); 4.48 (d, 1H, *J* = 5.9 Hz); 4.25 (AB system, ap t, 2H, *J* = 5.6 Hz); 3.26 (br d, 1H, *J* = 6.2 Hz); 2.71 (s, 1H); 2.53-2.35 (m, 2H); 2.12 (dd, 1H, *J* = 4.7 Hz, 14 Hz); 1.97-1.82 (m, 2H); 1.73 (s, 3H), 1.82-1.53 (m, 3H); 1.40-1.17 (m, 2H); 0.17 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃)°: δ 152.17 (C_{quat}), 145.45 (C_{quat}), 14.66 (+), 139.22 (C_{quat}), 132.82 (C_{quat}), 125.53 (+), 82.89 (C_{quat}), 75.86 (+), 59.63 (-), 48.85 (+), 36.44 (-), 35.88 (+), 29.14 (-), 27.38 (-), 25.64 (-), 17.03 (+), -1.49 (+).

IR (FTIR, CCl₄)°: ν = 3379, 2926, 2856, 1721, 1663, 1547, 1441, 1390, 1250, 1157, 1094, 1043, 837, 788, 755, 693 cm⁻¹.

HRMS (ESI, positive ion, 200 eV) calcd for (C₁₉H₃₀O₃SiNa)⁺ 357.1862; found 357.1863.

(4*aS*,9*R*,10*S*)-2-methyl-4,4*a*,5,6,7,8-hexahydro-9*H*-1,9-methanobenzo[7]annulene-9,10-diol

<ul style="list-style-type: none"> - Time of heating°: 2 hours - Rf = 0.17 (50/50 Et₂O/Hexane) - Eluant of chromatography°: 10/90 to 30/70 (Et₂O/Hexane) - Aspect°: yellow solid - mp = 90 °C - Yield = 62 %
---	--

¹H-NMR (300 MHz, CDCl₃)°: δ 6.03 (dd, 1H, *J* = 3.1 Hz, 5 Hz); 4.45 (br d, 1H, *J* = 4.4 Hz); 2.60-2.36 (m, 4H); 2.26-2.13 (m, 1H); 1.96-1.12 (m, 8H), 0.14 (s, 9H).

¹³C-NMR (50 MHz, CDCl₃)°: δ 151.53 (C_{quat}), 145.13 (C_{quat}), 137.39 (+), 132.29 (C_{quat}), 83.12 (C_{quat}), 77.31 (+), 37.36 (-), 33.01 (-), 31.13 (+), 30.82 (-), 28.17, 26.15 (-), -1.13 (+).

IR (FTIR, film)°: ν = 3335, 2912, 2846, 1718, 1654, 1549, 1440, 1417, 1244, 1060, 846, 692, 629 cm⁻¹.

HRMS (ESI, positive ion 130 eV)°: calcd for (C₁₅H₂₄O₂SiNa)⁺ 287.1443, found 287.1442

Xray structure : see supporting information of *J. Am. Chem. Soc.* **2001**, *123*, 12107.

(5aS,9aS,9bS)-3-(trimethylsilyl)-5a,6,7,8,9,9b-hexahydrocyclohepta[cd][2]benzofuran-9a(2H)-ol (4e)

<ul style="list-style-type: none"> - Time of heating°: 2 hours - Rf = 0.25 (50/50 Et₂O/Hexane) - Eluant of chromatography°: 20/80 (AcOEt/Hexane) - Aspect°: yellow solid - mp = 91 °C - Yield = 24 %
--	---

¹H-NMR (300 MHz, CDCl₃)°: δ 5.95 (d, 1H, *J* = 9.4 Hz); 5.73 (dd, 1H, *J* = 6.9 Hz, 9.4 Hz); 4.72 and 4.52 (ABX system, *J*_{AX} = 2.8 Hz, *J*_{BX} = 2.5 Hz, *J*_{AB} = 13.7 Hz); 2.38-2.26 (m, 1H); 2.19 (br s, 1H); 2.05-1.92 (m, 2H); 1.76-1.16 (m, 6H); 0.13 (s, 9H).

¹³C-NMR (50 MHz, CDCl₃)°: δ 148.25 (C_{quat}), 134.85 (+), 129.61 (+), 122.98 (C_{quat}), 108.00 (C_{quat}), 68.30 (-), 54.32 (+), 40.37 (-), 35.64 (+), 30.59 (-), 26.14 (-), 23.85 (-), -1.14 (+).

IR (FTIR, CCl₄)°: ν = 3380, 3027, 2920, 2846, 1627, 1445, 1242, 1034, 836, 793 cm⁻¹.

HRMS (ESI, positive ion 130 eV)°: calcd for (C₁₅H₂₄O₂SiNa)⁺ 287.1443, found 287.1441.

(1R,8Z,9S)-8-[1-(trimethylsilyl)but-3-enylidene]bicyclo[5.2.0]non-6-ene-1,9-diol (4f)

<ul style="list-style-type: none"> - Time of heating°: 7.5 hours - Rf = 0.47 (50/50 Et₂O/Hexane) - Eluant of chromatography°: 20/80 (Et₂O/Hexane) - Aspect°: yellow solid - mp = 95 °C - Yield = 71 %
---	---

¹H-NMR (300 MHz, CDCl₃)°: δ 6.10 (dd, 1H, *J* = 4.7 Hz, 8.1 Hz); 5.63-4.87 (m, 1H); 5.12-4.89 (m, 2H), 4.30 (br d, 1H, *J* = 7.2 Hz); 3.01 (br d, 1H, *J* = 5.3 Hz); 2.64 (br s, 1H); 2.48-2.13 (m, 3H); 2.08-1.77 (m, 4H), 1.72-1.51 (m, 1H); 1.50-1.30 (m, 1H); 0.18 (s, 9H).

^{13}C -NMR (75 MHz, CDCl_3): δ 150.73 (C_{quat}), 145.67 (C_{quat}), 138.37 (C_{quat}), 135.68 (+), 129.68 (+), 115.13 (-), 78.73 (C_{quat}), 75.47 (+), 36.28 (-), 36.07 (-), 29.14 (-), 28.19 (-), 26.21 (-), -0.64 (+)

IR (FTIR, CCl_4): ν = 3379, 3288, 2925, 2856, 1712, 1639, 1435, 1383, 1240, 1188, 1098, 1046, 986, 904, 837, 784, 762, 694 cm^{-1} .

HRMS (ESI, positive ion 90 eV) calcd for $(\text{C}_{16}\text{H}_{27}\text{O}_2\text{Si})^+$ 279.1780; found 279.1779.

→ Effect of the stereochemistry of the diol:

(1*R*,7*Z*,8*R*)-7-[3-phenyl-1-(trimethylsilyl)prop-2-ynylidene]bicyclo[4.2.0]oct-5-ene-1,8-diol (17a)

<ul style="list-style-type: none"> - Time of heating: 6 hours - R_f = 0.14 (20/80 Et_2O/Hexane) - Eluant of chromatography: 20/80 (AcOEt/hexane) - Aspect: yellow oil - Yield = 26 %
---	---

^1H -NMR (300 MHz, CDCl_3): δ 7.50-7.28 (m, 5H); 6.50 (dd, 1H, J = 4.4 Hz, 7.5 Hz); 4.75 (s, 1H); 2.53-2.38 (m, 1H); 2.35-1.58 (m, 5H); 0.34 (s, 9H).

^{13}C -NMR (75 MHz, CDCl_3): δ 159.80 (C_{quat}), 143.86 (C_{quat}), 131.51 (+), 131.32 (+), 128.29 (+), 127.88 (+), 126.40 (+), 124.19 (C_{quat}), 120.01 (C_{quat}), 103.00 (C_{quat}), 99.00 (C_{quat}), 81.68 (+), 77.67 (C_{quat}), 26.03 (-), 25.38 (-), 17.18 (-), -1.04 (+).

IR (FTIR, thin film): ν = 3380, 3060, 3029, 2950, 2871, 2246, 2178, 1948, 179, 1697, 1651, 1597, 1488, 1441, 1383, 1250, 1159, 1074, 984, 938, 904, 842, 7757, 694, 628, 528 cm^{-1} .

HRMS (ESI, positive ion 175 eV) calcd for $(\text{C}_{20}\text{H}_{24}\text{O}_2\text{SiNa})^+$ 347.1443; found 347.1445.

(1*R*)-1-[(1*R*)-1-hydroxy-3-(trimethylsilyl)prop-2-ynyl]-2-(phenylethynyl)cyclohex-2-en-1-ol (17 a)

<ul style="list-style-type: none"> - R_f = 0.17 (20/80 Et_2O/Hexane) - Aspect: brown oil - Yield = 24 %
---	--

^1H -NMR (300 MHz, CDCl_3): δ 7.54-7.40 (m, 2H); 7.37-7.28 (m, 3H); 6.48 (dd, 1H, J = 3.1 Hz, 5.2 Hz); 4.87 (s, 1H); 2.58 (br s, 2H); 2.37-2.21 (m, 1H); 2.20-2.03 (m, 2H); 1.98-1.65 (m, 3H); 0.16 (s, 9H).

^{13}C -NMR (75 MHz, CDCl_3): δ 140.88 (+), 131.51 (+), 128.24 (+), 128.16 (+), 123.09 (C_{quat}), 102.98 (C_{quat}), 92.14 (C_{quat}), 90.36 (C_{quat}), 73.43 (C_{quat}), 69.92 (+), 29.83 (-), 26.23 (-), 17.95 (-), -0.31 (+).

IR (FTIR, thin film): $\nu = 3412, 3059, 3028, 2955, 2871, 2176, 1951, 1883, 1711, 1629, 1598, 1488, 1440, 1308, 1252, 1166, 1136, 1089, 984, 963, 849, 759, 694 \text{ cm}^{-1}$.

HRMS (ESI, positive ion 180 eV) calcd for $(\text{C}_{20}\text{H}_{24}\text{O}_2\text{SiNa})^+$ 347.1443; found 347.1443.

(1*R*,7*Z*,8*R*)-7-[2-furyl(trimethylsilyl)methylene]bicyclo[4.2.0]oct-5-ene-1,8-diol (17b)

(1*R*)-2-(2-furyl)-1-[(1*R*)-1-hydroxy-3-(trimethylsilyl)prop-2-ynyl]cyclohex-2-en-1-ol (17b')

<p>17b</p>	<ul style="list-style-type: none"> - Time of heating°: 6 hours - Rf = 0.42 (70/30 Et₂O/Hexane) - Eluant of chromatography°: 20/80 (AcOEt/Hexane) <p>the 2 products are not separable by chromatography on silica gel. The NMR experiments are described as a mixture of 17b and 17b'</p>
<p>17b'</p>	<ul style="list-style-type: none"> -Overall yield : 60 % -Ration (17b/17b') : 66/34

¹H-NMR (300 MHz, CDCl₃): δ 7.37 (d, 2H, $J = 10.9 \text{ Hz}$); 6.49-6.32 (superposition of signals t and d, 5H); 6.19 (t, 1H, $J = 4.0 \text{ Hz}$); 4.72 (br d, 1H); 4.66 (s, 1H); 2.48-2.03 and 2.01-1.53 (m, 12H); 0.30 (s, 9H); 0.13 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃): δ 154.94 (C_{quat}), 153.59 (C_{quat}), 151.57 (+, 17b), 143.41 (+, 17b), 141.13 (C_{quat}), 140.78 (C_{quat}), 133.01 (+, 17b), 129.68 (C_{quat}), 127.42 (C_{quat}), 124.96 (+, 17b), 111.11 (+, 17b), 110.90 (+, 17b), 108.69 (+, 17b), 107.07 (+, 17b), 103.20 (C_{quat}, 17b), 91.99 (C_{quat}, 17b), 81.09 (+, 17b), 74.73, 69.14, 69.10, 31.25 (-, 17b), 26.14 (-, 17b), 25.92 (-, 17b), 25.49 (-, 17b), 18.43 (-, 17b), 17.00 (-, 17b), 0.34 (+, 17b), -0.35 (+, 17b).

IR (FTIR, thin film): $\nu = 333, 2950, 2871, 2175, 1943, 1876, 1719, 1644, 1592, 1554, 1427, 1382, 1315, 1248, 1188, 1150, 1121, 1061, 1016, 979, 844, 754, 732, 694, 627 \text{ cm}^{-1}$.

HRMS (ESI, positive ion 175 eV) calcd for $(\text{C}_{16}\text{H}_{22}\text{O}_3\text{SiNa})^+$ 313.1236; found 313.1238.

(1*R*,8*Z*,9*R*)-8-[3-phenyl-1-(trimethylsilyl)prop-2-ynylidene]bicyclo[5.2.0]non-6-ene-1,9-diol (18a)

<ul style="list-style-type: none"> - Time of heating°: 2 hours - Rf = 0.29 (70/30 Et₂O/Hexane) - Eluant of chromatography°: 5/95 (Et₂O/Hexane) - Aspect°: yellow solid - mp = 124 °C - Yield = 72 %
---	---

¹H-NMR (300 MHz, CDCl₃): δ 7.55-7.22 (m, 5H); 7.02 (dd, 1H, $J = 4.7 \text{ Hz}, 8.4 \text{ Hz}$); 4.60 (br s, 1H); 2.57-2.40 (m, 1H); 2.37-1.63 (m, 8H); 0.32 (s, 9H).

^{13}C -NMR (75 MHz, CDCl_3): δ 155.99 (C_{quat}), 147.22 (C_{quat}), 132.18 (+), 131.24 (+), 128.06 (+), 127.96 (+), 124.20 (C_{quat}), 120.41 (C_{quat}), 101.60 (C_{quat}), 91.32 (C_{quat}), 81.74 (C_{quat}), 81.37 (+), 30.30 (-), 28.52 (-), 27.84 (-), 25.92 (-), -0.98 (+).

IR (FTIR, CCl_4): ν = 3518, 3373, 3355, 3298, 2929, 2856, 2175, 1943, 1872, 1720, 1647, 1597, 1437, 1375, 1248, 1136, 1091, 1024, 986, 837, 784, 762, 695 cm^{-1} .

HRMS (ESI, positive ion 175 eV) calcd for $(\text{C}_{21}\text{H}_{26}\text{O}_2\text{SiNa})^+$ 361.1600; found 361.1595.

(1R)-1-[(1R)-1-hydroxy-3-(trimethylsilyl)prop-2-ynyl]-2-(phenylethynyl)cyclohept-2-en-1-ol (18a)

<ul style="list-style-type: none"> - Time of heating°: 2 hours - R_f = 0.43 (70/30 Et_2O/Hexane) - Eluant of chromatography°: 3/97 (Et_2O/Hexane) - Aspect°: yellow oil - Yield = 9 %
---	---

^1H -NMR (300 MHz, CDCl_3): δ 7.50-7.24 (m, 5H); 6.53 (dd, 1H, J = 5.9 Hz, 8.4 Hz); 4.70 (s, 1H); 2.90 (br s, 1H); 2.64 (br s, 1H); 2.55-2.15 (m, 4H); 2.02-1.50 (m, 4H); 0.20 (s, 9H).

^{13}C -NMR (75 MHz, CDCl_3): δ 140.66 (+), 131.46 (+), 128.29 (C_{quat}), 128.26 (+), 122.87 (C_{quat}), 102.85 (C_{quat}), 91.55 (C_{quat}), 90.30 (C_{quat}), 88.44 (C_{quat}), 77.42 (C_{quat}), 68.79 (+), 33.00 (-), 26.96 (-), 25.83 (-), 22.02 (-), -0.26 (+).

IR (FTIR, thin film): ν = 3413, 3060, 2939, 2861, 2361, 2335, 2175, 1951, 1887, 1719, 166, 1601, 1488, 1445, 1393, 1323, 1258, 1173, 1065, 1004, 847, 760, 695 cm^{-1} .

HRMS (ESI, positive ion 175 eV) calcd for $(\text{C}_{21}\text{H}_{26}\text{O}_2\text{SiNa})^+$ 361.1600; found 361.1602.

(1R,8Z,9R)-8-[2-furyl(trimethylsilyl)methylene]bicyclo[5.2.0]non-6-ene-1,9-diol (18b)

<ul style="list-style-type: none"> - Time of heating°: 2 hours - R_f = 0.37 (50/50 Et_2O/Hexane) - Eluant of chromatography°: 3/97 (Et_2O/Hexane) - Aspect°: yellow solid - mp = 109 °C - Yield = 40 %
---	---

^1H -NMR (300 MHz, CDCl_3): δ 7.39 (d, 1H, J = 1.7 Hz); 6.41 (ap t, 1H, J = 1.7 Hz), 6.23 (dd, 1H, J = 5.0 Hz, 6.5 Hz); 6.19 (d, 1H, J = 3.4 Hz); 4.59 (d, 1H, J = 8.1 Hz); 2.47-2.30 (m, 1H); 2.29-1.75 (m, 6H); 1.73-1.57 (m, 2H); 0.22 (s, 9H).

^{13}C -NMR (75 MHz, CDCl_3): δ 154.29 (C_{quat}), 150.39 (C_{quat}), 146.12 (C_{quat}), 140.71 (+), 130.46 (+), 129.84 (C_{quat}), 110.91 (+), 107.95 (+), 80.97 (+), 77.19 (C_{quat}), 30.28 (-), 28.35 (-), 27.68 (-), 25.84 (-), -0.25 (+).

IR (FTIR, CCl_4): ν = 3492, 3349, 2931, 2856, 1719, 1644, 1584, 1555, 1427, 1383, 1323, 1248, 1196, 1136, 1076, 1016, 979, 919, 837, 784, 762, 687, 620 cm^{-1} .

HRMS (ESI, positive ion 175 eV) calcd for $(\text{C}_{17}\text{H}_{24}\text{O}_3\text{SiNa})^+$ 327.1392; found 327.1393.

(2*E*,4*E*,6*Z*)-6-[(3*aS*,8*aR*)-2,2-dimethyl-7,8-dihydro-3*aH*-benzo[1,4]cyclobuta[1,2-*d*][1,3]dioxol-4(6*H*)-ylidene]-3-methyl-6-(trimethylsilyl)hexa-2,4-dien-1-ol (3c)

[(3a*S*,6b*S*,9a*R*)-8,8-dimethyl-2,3,3a,6b-tetrahydro-1*H*,4*H*-naphtho[1',8':2,3,4]cyclobuta[1,2-*d*][1,3]dioxol-6-yl](trimethyl)silane (3d)

[(6bS,9aR)-8,8-dimethyl-2,3-dihydro-1H,6bH-naphtho[1',8':2,3,4]cyclobuta[1,2-d][1,3]dioxol-6-yl)](trimethyl)silane (3e)