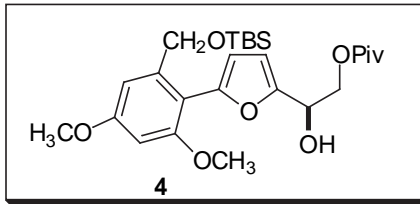


## Supplementary Material

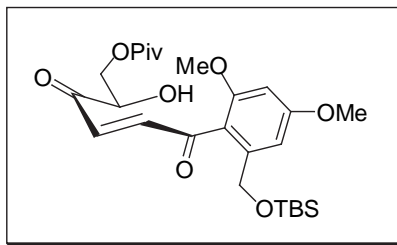
### **Experimental Section :**

**General Experimental :** Low reaction temperatures were recorded as bath temperatures unless otherwise stated. Column chromatography was carried out on E. Merck silica gel 230-400 mesh ASTM using flash chromatography techniques. Analytical thin-layer chromatography (TLC) was performed on E. Merck or precoated silica gel 60 F254 plates. Hexane, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), ethyl acetate (EtOAc), and diethyl ether ( $\text{Et}_2\text{O}$ ) when used as eluants were ACS reagent grade solvent. The following reaction solvents were purified by distillation: dimethylformamide (DMF) (from calcium hydride,  $\text{N}_2$  at reduced pressure), dichloromethane (from  $\text{CaH}_2$ ,  $\text{N}_2$ ), diethyl ether ( $\text{Et}_2\text{O}$ ) (from  $\text{Ph}_2\text{CONa}$ ,  $\text{N}_2$ ), dichloroethane (from  $\text{CaH}_2$ ,  $\text{N}_2$ ) and tetrahydrofuran (THF) (from  $\text{Ph}_2\text{CO-Na}$ ,  $\text{N}_2$ ). Organic extracts were dried over anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) or anhydrous magnesium sulfate ( $\text{MgSO}_4$ ), filtered and rotary evaporated at  $<25^\circ\text{C}$  bath temperature; involatile oils were further evaporated at  $<1\text{mm Hg}$ . NBS was recrystallized prior to use.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were acquired on Varian 200, 300 and 500 MHz spectrometers. Chemical shifts and coupling constants are reported in parts per million (ppm) and hertz (Hz) respectively. Chemical shifts are reported relative to internal tetramethylsilane ( $\delta$  0.00 ppm) or  $\text{CDCl}_3$  ( $\delta$  7.26 ppm) for  $^1\text{H}$ NMR and  $\text{CDCl}_3$  ( $\delta$  77.0 ppm) for  $^{13}\text{C}$ NMR. Melting Points are uncorrected. Combustion analysis was performed by M-H-W Laboratories, Phoenix, AZ.



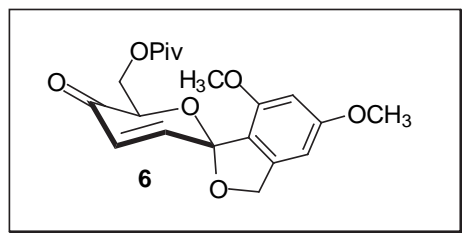
### Furfuryl alcohol (**4**)

To a  $\text{CH}_2\text{Cl}_2$  (150 mL) solution of diol **4** (7.48 g, 21 mmol) under  $\text{N}_2$  atmosphere at  $-78^\circ\text{C}$  was added  $\text{Et}_3\text{N}$  (11 mL, 5 eq) followed by a slow addition of a  $\text{CH}_2\text{Cl}_2$  (10 mL) solution of pivaloylchloride (2.64 mL, 1.3 mmol). After stirring for 3h at  $-78^\circ\text{C}$  the solution was warmed to room temperature and stirred overnight. The solution was diluted with  $\text{CH}_2\text{Cl}_2$  (100 mL) and quenched with 1M sodium bisulfate (aq) (25 mL) then washed with water, brine and dried ( $\text{Na}_2\text{SO}_4$ ). The crude product was purified by flash silica gel chromatography with hexane/ethylacetate (9:1) as eluent. Diol **4** (7.13 g) was isolated in a 69 % yield. m.p:  $46^\circ\text{C}$ .  $R_f = 0.5$  [Hexane/EtOAc (8:2)].  $[\alpha]_D = +9.1$  in  $\text{CH}_2\text{Cl}_2$  ( $c = 1$ ). IR (thin film,  $\text{cm}^{-1}$ ) 3446, 2953, 2851, 1728, 1600, 1584, 1461, 1323, 1282, 1251, 1200, 1154, 1067.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.87 (d,  $J=2.4\text{Hz}$ , 1H), 6.37-6.41 (m, 3H), 4.96 (t,  $J=6\text{ Hz}$ , 1H), 4.7 (s, 2H), 4.39 (d,  $J=2.1\text{ Hz}$ , 1H), 4.37 (d,  $J=0.9\text{ Hz}$ , 1H), 3.84 (s, 3H), 3.75 (s, 3H), 1.18 (s, 9H), 0.92 (s, 9H), 0.06 (s, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.7, 160.9, 158.5, 151.7, 148.8, 143.7, 110.9, 110.1, 108.5, 102.7, 97.2, 66.6, 66.5, 63.0, 55.8, 55.3, 38.8, 27.2, 25.9, 18.4, -5.3. HRMS ( $\text{CI}^+$ ) calcd for ( $\text{M}$ ) $^+$   $\text{C}_{26}\text{H}_{40}\text{O}_7\text{Si}$ : 492.254, found: 492.255.



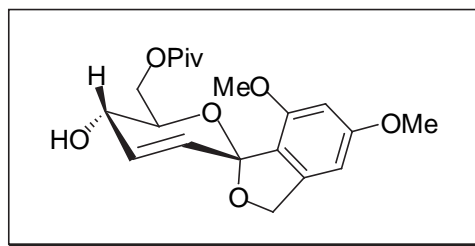
### Oxidative ring expansion of furan carbinol **4** (Not shown in the text)

To a 4:1 THF/H<sub>2</sub>O (14.6 mL: 3.6 mL) solution of furylalcohol **4** (1.74 g, 3.53 mmol) was added solid NaHCO<sub>3</sub> (0.6 g, 7.6 mmol) and NaOAc•3H<sub>2</sub>O (0.48 g, 3.53 mmol) at 0 °C. To the vigorously stirred heterogeneous solution was slowly added NBS (0.69 g, 3.8 mmol). The solution was stirred at 0 °C for 2 h, until TLC analysis showed the absence of starting material. The reaction was quenched by the addition of saturated NaHCO<sub>3(aq)</sub> (1 mL) and hexane (50 mL). The organic layer was separated and washed with brine and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was evaporated under reduced pressure followed by silica gel column chromatography, which resulted in 1.1 g of a light yellow viscous liquid (60.5 %).  $R_f = 0.4$  [Hexane/ EtOAc (7:3)]. IR (thin film, cm<sup>-1</sup>) 3463, 2956, 2856, 1732, 1602, 1462, 1424, 1370, 1325, 1284, 1255, 1201, 1156, 1067. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.02 (d,  $J=2.2$  Hz, 1H), 6.9 (d,  $J=11.8$  Hz, 1H), 6.33 (d,  $J=2.2$  Hz, 1H), 6.29 (d,  $J=12$  Hz, 1H), 4.97 (d,  $J=16$  Hz, 1H), 4.90 (d,  $J=16$  Hz, 1H), 4.53 (dd,  $J=9, 6$  Hz, 1H), 4.35 (m, 2H), 3.81 (s, 3H), 3.85 (s, 3H), 3.63 (d, 1H), 1.14 (s, 9H), 0.95 (s, 9H), 0.11 (s, 3H), 0.1 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 200.9, 193.3, 178.3, 163.8, 161.1, 148.2, 142.4, 127.6, 117.3, 103.4, 96.8, 75.1, 64.9, 62.9, 55.8, 55.4, 38.8, 27.1, 26.0, 18.4, -5.3. HRMS (CI<sup>+</sup>) calcd for (M+H)<sup>+</sup> C<sub>26</sub>H<sub>41</sub>O<sub>8</sub>Si: 509.2571, found: 509.2583.



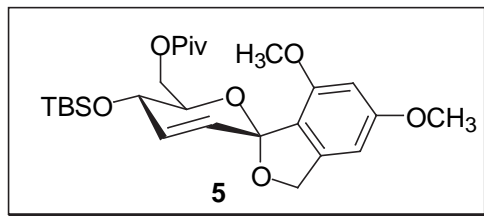
### Spiroenone (6)

To a THF/H<sub>2</sub>O (10:1 mL) solution of the above intermediate (0.8 g, 1.57 mmol) was added 1 M HCl<sub>(aq)</sub> (1M, 0.4 mL) at room temperature and stirred until TLC analysis showed the disappearance of starting material and appearance of a less polar compound (3 h). The solution was quenched with saturated K<sub>2</sub>CO<sub>3(aq)</sub> (0.5 mL). The reaction mixture was diluted with ether (20 mL), washed with brine and dried (Na<sub>2</sub>SO<sub>4</sub>). After filtration and evaporation under reduced pressure the crude product was purified by silica gel flash chromatography (10 %hexanes: ethyl acetate) yielding 0.32 g of a colorless oil (54 %). R<sub>f</sub>: 0.4 [hexanes:EtOAc (3:1)]. [α]<sub>D</sub> = +48.8 in CH<sub>2</sub>Cl<sub>2</sub> (c = 1.1). IR (thin film, cm<sup>-1</sup>) 2956, 1729, 1697, 1609, 1495, 1463, 1430, 1394, 1343, 1283, 1223, 1201, 1155, 1043, 1086, 1017. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.91 (d, *J*=10.2 Hz, 1H), 6.35 (s, 2H), 6.17 (d, *J*=10.2 Hz, 1H), 5.17 (d, *J*=12.6 Hz, 1H), 5.01 (d, *J*=12.6 Hz, 1H), 4.82 (dd, *J*=3.74, 2.7 Hz, 1H), 4.51 (dd, *J*=11.7, 3.9 Hz, 1H), 4.41 (dd, *J*=11.7, 3.9 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 1.13 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 194.2, 178.0, 163.4, 155.9, 147.6, 143.7, 126.6, 119.5, 104.3, 98.2, 96.9, 75.1, 72.5, 62.7, 55.7, 55.4, 39.0, 27.0. HRMS (CI<sup>+</sup>) calcd for (M+H)<sup>+</sup> C<sub>20</sub>H<sub>25</sub>O<sub>7</sub>: 377.1600, found: 377.1598.



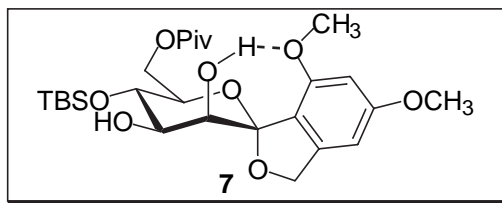
**Spiroenol** (Not shown in the text)

To an aqueous solution of sodium borohydride (4 mg, 0.1 mmol, in 0.8 mL of water) was added dropwise a THF (0.4 mL) solution of enone **6** (27 mg, 0.085 mmol) at 0 °C. The reaction mixture was stirred for 45 min at 0 °C, until TLC showed the absence of starting material. The reaction was quenched by the addition of a brine (5 mL) solution and the mixture was extracted with EtOAc (2x10 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). The organic phase was filtered, evaporated under reduced pressure and the crude product was purified by silica gel flash chromatography [ethyl acetate/hexane (4:6)] to yield 24 mg (88 %) of a colorless oil.  $R_f = 0.4$  [Hexanes :EtOAc (6:4)].  $[\alpha]_D^{25} = +31.2$  in CH<sub>2</sub>Cl<sub>2</sub> (c = 0.9). IR (thin film, cm<sup>-1</sup>) 3471, 2960, 1728, 1608, 1497, 1465, 1431, 1344, 1287, 1222, 1200, 1156, 1089, 1067, 1017. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.32 (s, 2H), 6.04 (dd,  $J=10.1, 1.8$  Hz, 1H), 5.71 (dd,  $J=10.1, 2.4$  Hz, 1H), 5.09(d,  $J=12.6$  Hz, 1H), 4.95(d,  $J=12.6$  Hz, 1H), 4.62 (dd,  $J=12.3, 3.6$  Hz, 1H), 4.2 (dd,  $J=12.3, 2.4$  Hz, 1H), 4.04 - 4.1 (br.m, 1H), 3.92 (ddd,  $J=10.2, 2.7, 2.7$  Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 2.68 (d,  $J=6$  Hz, 1H), 1.2 (s, 9H), <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  179.6, 162.9, 156.1, 143.6, 132.0, 128.4, 120.1, 105.9, 98.3, 96.8, 74.1, 71.8, 63.5, 63.4, 55.7, 55.4, 39.0, 27.2. HRMS (CI<sup>+</sup>) calcd for (M+H)<sup>+</sup> C<sub>20</sub>H<sub>27</sub>O<sub>7</sub>: 379.1757, found: 379.1770.



### Silylated spiroenol ether (**5**)

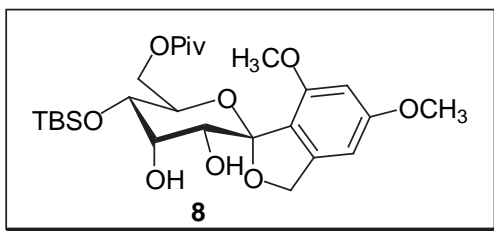
To a DMF (1 mL) solution of the spiroenol **5** (54 mg, 0.14 mmol) under a nitrogen atmosphere was added imidazole (19 mg, 0.28 mmol), DMAP (5 mg) and TBSCl (0.32 mg, 0.21 mmol) at room temperature. The solution was stirred overnight then poured into water (20 mL) and extracted it with Et<sub>2</sub>O (2x10 mL). The organic layer was washed with water, aqueous hydrochloric acid (1M), water, brine and dried (Na<sub>2</sub>SO<sub>4</sub>). After silica gel flash chromatography (hexanes: 10 % ethyl acetate) resulted in 45 mg of a white crystalline solid (64 %). m.p : 131 °C. *R*<sub>f</sub>: 0.6[hexanes:EtOAc (9:1)]. [α]<sub>D</sub> = +137.2 in CH<sub>2</sub>Cl<sub>2</sub> (c = 0.7). IR (thin film, cm<sup>-1</sup>) 2954, 2860, 1731, 1607, 1490, 1460, 1425, 1343, 1278, 1249, 1155, 1096, 1020. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.31 (br.s, 2H), 5.93 (dd, *J*=10.05, 1.8 Hz, 1H), 5.69 (dd, *J*=10.05, 2.1 Hz, 1H), 5.06 (d, *J*=12.9Hz, 1H), 4.92 (d, *J*=12.9Hz, 1H), 4.4 (dd, *J*=11.7, 1.8 Hz, 1H), 4.33 (ddd, *J*=9, 1.8, 1.8 Hz, 1H), 4.09 (dd, *J*=11.7 Hz, 1H), 4.01 (m, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 1.16 (s, 9H), 0.89 (s, 9H), 0.13 (s, 3H), 0.09 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 178.1, 162.7, 156.0, 143.8, 132.9, 127.8, 120.4, 105.6, 98.3, 96.8, 73.5, 71.7, 63.8, 63.1, 55.7, 55.6, 38.8, 27.2, 25.7, 17.9, -4.1, -4.8. FAB HRMS calcd for (M+ H)<sup>+</sup> C<sub>26</sub>H<sub>41</sub>O<sub>7</sub>Si: 493.2621, found: 493.2633. Anal. Calcd for C = 63.38 %, H = 8.19 %; Anal. found C = 63.19 %, H = 7.91 %.



### Mannopapulacandin pivaloate ester (**7**)

A round bottom flask containing a 0.1 M solution of protected alcohol **5** in *t*-butanol /H<sub>2</sub>O (5:1) (0.32 mg in 40 mL) was stirred at room temperature and a molar excess of 4-*N*-methyl morpholine-*N*-oxide<sub>(aq)</sub> (50 % w/w solution) was added. A catalytic amount ( 20 mol %) of OsO<sub>4</sub> (35 mg) was added to the reaction and the reaction was allowed to stir at room temperature for 2 h. The temperature of the bath was slowly raised to 80 °C and the reaction stirred at this temp for 20 hours. The solution was cooled to room temperature and quenched with 1 M NaHSO<sub>3</sub> (1 mL). After stirring an additional 10 minutes the mixture was extracted with ethyl acetate (10 mL) and washed with brine. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. Silica gel column chromatography (40 % EtOAc / Hexanes) afforded 0.32 g of two diols **7** and **8** in a 94 % combined yield. The major diol **7** was isolated as a white solid in 69 % yield.  $R_f = 0.5$  [hexanes: EtOAc (8:2)]. m.p : 55 °C.  $[\alpha]_D = +37.5$  in CH<sub>2</sub>Cl<sub>2</sub> (c = 0.9). IR (thin film, cm<sup>-1</sup>) 3460, 2942, 2860, 1731, 1607, 1601, 1490, 1466, 1461, 1431, 1396, 1343, 1284, 1249, 1219, 1202, 1155, 1108, 1090, 1026, 1008. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.41 (d, *J*=1.5 Hz, 1H), 6.39 (d, *J*=1.5 Hz, 1H), 5.09 (d, *J*=12.5 Hz, 1H), 5.01 (d, *J*=12.5 Hz, 1H), 4.74 (d, *J*=2.5 Hz, 1H), 4.35 (dd, *J*=12, 2 Hz, 1H), 4.22 (dd, *J*=12, 3 Hz, 1H), 4.04 (t, *J*=9.5 Hz, 1H), 3.95 (q, *J*=4.75, 1.2 Hz, 1H), 3.91 (dt, *J*=16.5, 2.5 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 2.41 (d, *J*=10 Hz, 1H), 1.21 (s, 9H), 0.89 (s, 9H), 0.2 (s, 3H), 0.1 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.9, 162.9, 154.5, 143.9, 118.7, 110.8, 98.9, 98.0, 74.1, 73.6, 73.2, 72.3, 69.1, 62.6, 56.0, 55.7, 38.9,

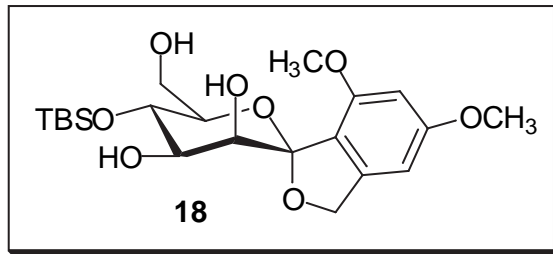
27.2, 25.9, 18.3, -3.8, -4.9. HRMS (CI<sup>+</sup>) calcd for (M+H)<sup>+</sup> C<sub>26</sub>H<sub>43</sub>O<sub>9</sub>Si: 527.2676, found: 527.2683. Anal. Calcd for C = 59.29 %, H = 8.04 %; Anal. found C = 59.32 %, H = 7.94 %.



### Allose nucleus (8)

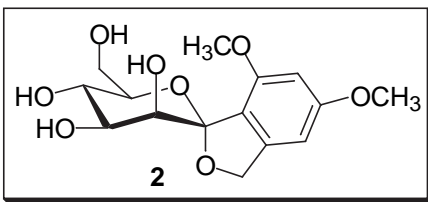
The allose isomer was obtained in the above reaction as a minor isomer in 25% yield. m.p : 69 °C.  $[\alpha]_D = +34.0$  in CH<sub>2</sub>Cl<sub>2</sub> (c = 0.3). IR (thin film, cm<sup>-1</sup>) 3500, 2952, 2932, 2855, 1726, 1610, 1495, 1466, 1427, 1394, 1360, 1341, 1284, 1255, 1197, 1154, 1096, 1024, 981, 836. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.35(d, *J*=1.5Hz, 1H), 6.33(d, *J*=1.5Hz, 1H), 5.16(d, *J*=12.5Hz, 1H), 5.07(d, *J*=12.5Hz, 1H), 4.47(br.s, 1H), 4.44(dd, *J*=12, 1.5Hz, 1H), 4.23(m, 1H), 4.13(dt, *J*=10, 3.5Hz, 1H), 4.09(dd, *J*=12, 3.5Hz, 1H), 3.9(dd, *J*=9.5, 3.5Hz, 1H), 3.79(s, 3H), 3.78(s, 3H), 2.78(br.s, 1H), 2.73(br.s, 1H), 1.18(s, 9H), 0.92(s, 9H), 0.17(s, 3H), 0.13(s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.9, 162.9, 155.7, 143.1, 117.9, 110.7, 98.3, 96.7, 73.5, 72.2, 68.0, 67.9, 67.8, 62.6, 55.6, 55.2, 38.8, 27.1, 25.6, 17.9, -4.2, -4.9. HRFAB calcd for (M+H)<sup>+</sup> C<sub>26</sub>H<sub>43</sub>O<sub>9</sub>Si: 527.2676, found: 527.2662.





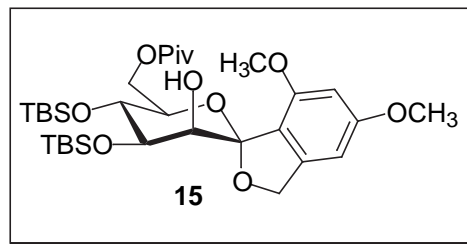
### Mannosetriol (**18**)

Under  $N_2$  atmosphere, DIBAL-H (0.25 mL, 1M in Hexane solution, 2equiv) was added dropwise over a 5 min period, to an ether (1.5 mL) solution of ester **7** (64 mg, 0.12 mmol) at  $-78\text{ }^\circ\text{C}$ . The reaction was stirred for 3 h at  $-78\text{ }^\circ\text{C}$  before being quenched with a 50 % aqueous ether (1 mL) solution. The cooling bath was removed and was stirred at room temperature for 0.5 h, diluted with ethyl acetate (5 mL) and filtered through plug of celite and silica gel using ethyl acetate as eluent. The organic filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography ( $\text{SiO}_2$ , 50% EtOAc/Hexanes) affording 50 mg (93%) of **13** as a white solid. m.p :  $159\text{ }^\circ\text{C}$ .  $R_f = 0.2$  [hexanes:EtOAc (8:2)].  $[\alpha]_D = +32.1$  in  $\text{CH}_2\text{Cl}_2$  ( $c = 0.76$ ). IR (thin film,  $\text{cm}^{-1}$ ): 3475, 2950, 2925, 2850, 1604, 1495, 1462, 1433, 1400, 1354, 1321, 1250, 1229, 1200, 1150, 1087, 1020, 975.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.42 (d,  $J=2.1$  Hz, 1H), 6.4 (d,  $J=2.1$  Hz, 1H), 5.1 (d,  $J=12.9$  Hz, 1H), 4.99 (d,  $J=12.9$  Hz, 1H), 4.69 (d,  $J=2.1$  Hz, 1H), 3.97-3.75 (m, 5H), 3.9 (s, 3H), 3.8 (s, 3H), 2.4 (d,  $J=9.6$  Hz, 1H), 1.9 (t,  $J=6.6$  Hz, 1H), 1.6 (br s, 1H), 0.9 (s, 9H), 0.19 (s, 3H), 0.13 (s, 3H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 154.4, 144.0, 118.6, 110.8, 98.6, 97.9, 75.2, 73.9, 73.4, 72.1, 69.3, 62.1, 56.1, 55.7, 25.9, 18.3, -3.8, -4.9. HRFAB calcd for  $(\text{M}+\text{H})^+ \text{C}_{21}\text{H}_{35}\text{O}_8\text{Si}$ : 443.2101, found: 443.2092.



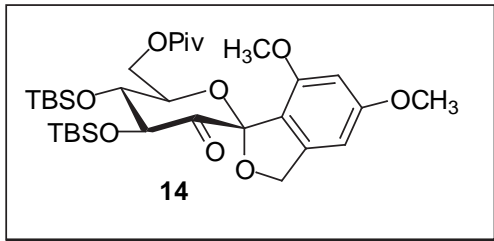
### Mannopapulacandin nucleus (2)

A THF (0.3 mL) solution of compound **18** (9 mg, 0.02 mmol) at room temperature was treated with tetrabutylammonium fluoride•3H<sub>2</sub>O (1.0M solution in THF, 40 μL, 0.04 mmol) under N<sub>2</sub> atmosphere. After 3h, the mixture was diluted with Et<sub>2</sub>O (1 mL) and filtered through a plug of celite and florisil using methanol as eluent. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography [florisil, CH<sub>2</sub>Cl<sub>2</sub>/MeOH(8:2)] affording 6 mg (93%) of **2**. m.p : 155 °C. R<sub>f</sub> = 0.5 [CH<sub>2</sub>Cl<sub>2</sub>/MeOH(8:2)]. [α]<sub>D</sub> = +30.6 in CH<sub>3</sub>OH (c = 0.6). IR (thin film, cm<sup>-1</sup>): 3389, 2931, 1613, 1601, 1490, 1461, 1431, 1337, 1296, 1225, 1196, 1155, 1090, 1067, 1026, 979, 908, 832. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 6.53 (s, 1H), 6.52 (s, 1H), 5.09 (d, *J*=12.9 Hz, 1H), 5.00 (d, *J*=12.9 Hz, 1H), 4.92 (s, 1H), 3.99-3.95 (m, 1H), 3.94-3.87 (m, 2H), 3.90 (s, 3H), 3.86 (m, 2H), 3.82 (s, 3H), 3.74-3.67 (m, 1H), 3.38-3.33 (m, 1H). <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ 164.7, 156.4, 145.7, 120.1, 112.5, 99.7, 99.3, 77.4, 75.7, 74.0, 73.2, 68.6, 63.4, 56.8, 56.3. HRFAB calcd for (M+Na)<sup>+</sup> C<sub>15</sub>H<sub>20</sub>O<sub>8</sub>Na: 351.1055, found: 351.1053.



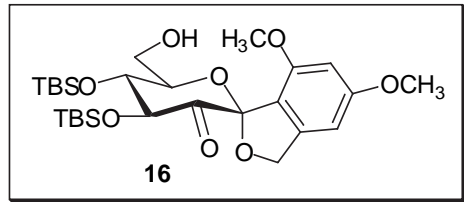
### Disilylated mannopapulacandin nucleus (15)

To a DMF (1 mL) solution of diol **7** (100 mg, 0.19 mmol) at room temperature and under a N<sub>2</sub> atmosphere was added imidazole (260 mg, 3.8 mmol) and DMAP (10 mg) followed by TBSCl (570 mg, 3.8 mmol). The solution was stirred overnight then poured into water (20 mL) and extracted with Et<sub>2</sub>O (2 x10 mL). The organic layer was washed with water, aqueous hydrochloric acid (1M), water, brine and dried (Na<sub>2</sub>SO<sub>4</sub>). Purification of the crude product by silica gel flash chromatography (9:1 hexanes/ethyl acetate) resulted in 115 mg of a white crystalline solid (95 %). m.p : 98 °C. [α]<sub>D</sub> = +18.7 in CH<sub>2</sub>Cl<sub>2</sub> (c = 1.2). IR (thin film, cm<sup>-1</sup>): 3491, 2956, 2929, 2856, 1731, 1614, 1496, 1472, 1432, 1396, 1347, 1323, 1284, 1255, 1224, 1200, 1159, 1122, 1093, 1031, 980, 938. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.39 (d, *J*=1.8Hz, 1H), 6.37(d, *J*=1.8Hz, 1H), 5.08(d, *J*=12.6Hz, 1H), 4.98 (d, *J*=12.6Hz, 1H), 4.59 (d, *J*=1.5Hz, 1H), 4.35 (dd, *J*=12.1, 2.4Hz, 1H), 4.28-4.2 (m, 2H), 4.12 (dd, *J*=12.1, 2.4Hz, 1H), 3.97(t, *J*=1.8Hz, 1H), 3.89-3.85(m, 1H), 3.83(s, 3H), 3.81(s, 3H), 1.19(s, 9H), 0.95(s, 9H), 0.89(s, 9H), 0.16(s, 3H), 0.16(s, 3H), 0.14(s, 3H), 0.05(s, 3H). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>) δ 178.2, 162.8, 154.7, 143.9, 118.9, 111.4, 98.7, 98.3, 97.8, 75.1, 74.9, 74.1, 72.2, 67.9, 62.5, 55.8, 55.7, 38.8, 27.3, 26.5, 26.1, 18.7, 18.1, -2.5, -3.0, -3.9, -4.9. HRFAB calcd for (M+H)<sup>+</sup> C<sub>32</sub>H<sub>57</sub>O<sub>9</sub>Si<sub>2</sub>: 641.3541, found: 641.3591.



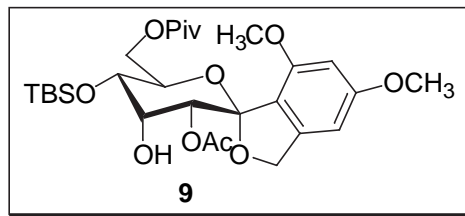
### Ketone (14)

To a room temperature  $\text{CH}_2\text{Cl}_2$  (1.5 mL) solution of alcohol **15** (90 mg, 0.14 mmol) and pyridine (0.3 mL) under a  $\text{N}_2$  atmosphere was added Dess-Martin periodinane (0.3 g, 0.7 mmol) in five portions. The reaction mixture was stirred for 3 h at 25 °C, after which time TLC analysis indicated that no starting material remained. The reaction mixture was diluted with ether (10 mL) and passed through a small plug of florisil and celite. The crude reaction mixture was purified by silica gel flash chromatography (9:1/hexanes: ethyl acetate) resulting in 87 mg of a white crystalline solid (98 %). m.p. = 75 °C.  $[\alpha]_D = +11.3$  in  $\text{CH}_2\text{Cl}_2$  ( $c = 0.7$ ). IR (thin film,  $\text{cm}^{-1}$ ): 2954, 2931, 2860, 1748, 1730, 1607, 1496, 1466, 1431, 1390, 1343, 1325, 1284, 1249, 1220, 1196, 1155, 1096, 1014, 937, 908, 838, 779, 732, 673.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.36(d,  $J=1.8\text{Hz}$ , 1H), 6.29(d,  $J=1.8\text{Hz}$ , 1H), 5.16(d,  $J=12.9\text{Hz}$ , 1H), 4.99(d,  $J=12.9\text{Hz}$ , 1H), 4.75(d,  $J=9.6\text{Hz}$ , 1H), 4.5(dd,  $J=11.7, 2.4\text{Hz}$ , 1H), 4.24(dt,  $J=9.6, 3\text{Hz}$ , 1H), 4.14-4.09(m, 1H), 3.98(t,  $J=9.3\text{Hz}$ , 1H), 3.79(s, 3H), 3.73(s, 3H), 1.17(s, 9H), 0.96(s, 9H), 0.92(s, 9H), 0.18(s, 3H), 0.12(s, 3H), 0.08(s, 3H), 0.03(s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  195.7, 178.0, 163.4, 156.7, 143.1, 115.6, 110.2, 98.5, 96.4, 79.5, 62.0, 55.6, 55.4, 38.8, 27.1, 26.3, 26.0, 18.6, 18.0, -2.6, -3.5, -4.7 (2 C). HRFAB calcd for  $(\text{M}+\text{H})^+$   $\text{C}_{32}\text{H}_{55}\text{O}_9\text{Si}_2$ : 639.3384, found: 639.3386.



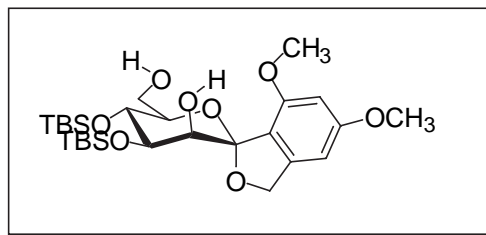
### Ketoalcohol (**16**)

Under anhydrous conditions, DIBAL-H (0.3 mL, 1M in hexane, 2equiv) was added dropwise over a 5 min period to an ether (1.5 mL) solution of ketone **14** (90 mg, 0.14 mmol) at -78 °C. The reaction was stirred for 3 h at -78 °C before it was quenched with a 50 % aqueous ether solution (1 mL). The cooling bath was removed and the solution was stirred for 0.5 h at room temperature. The solution was diluted with ethyl acetate (5 mL) and filtered through plug of celite and silica gel using ethyl acetate as eluent. The organic filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (SiO<sub>2</sub>, 20% EtOAc/hexanes) affording 76 mg of **16** (98 %). m.p : 102 °C.  $[\alpha]_D = -27.7$  in CH<sub>2</sub>Cl<sub>2</sub> (c = 0.26). IR (thin film, cm<sup>-1</sup>): 3483, 2931, 2860, 1748, 1607, 1495, 1460, 1431, 1390, 1349, 1249, 1220, 1202, 1143, 1084, 1008, 955, 890, 837, 779. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.39(d, *J*=1.5Hz, 1H), 6.31(d, *J*=1.8Hz, 1H), 5.19(d, *J*=12.6Hz, 1H), 5.0(d, *J*=12.9 Hz, 1H), 4.76(d, *J*=9Hz, 1H), 4.14-4.08(m, 1H), 3.96(t, *J*=9.6Hz, 1H), 3.88-3.72(m, 2H), 3.8(s, 3H), 3.78(s, 3H), 2.0(dd, *J*=8.1, 5.1Hz, 1H), 0.95(s, 9H), 0.92(s, 9H), 0.17(s, 3H), 0.15(s, 3H), 0.1(s, 3H), 0.02(s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 196.1, 163.5, 156.7, 143.0, 115.6, 110.3, 98.6, 96.5, 79.2, 75.6, 73.5, 73.4, 26.2, 26.0, 18.6, 18.0, -2.6, -3.7, -4.8, -4.9. HRFAB calcd for (M+H)<sup>+</sup> C<sub>27</sub>H<sub>47</sub>O<sub>8</sub>Si<sub>2</sub>: 555.2809, found: 555.2820.



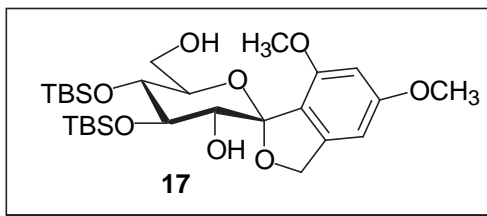
### Acetate (**9**)

To a pyridine (0.2 mL) solution of **8** (38 mg, 0.07 mmol) was added acetic anhydride (0.1 mL) at room temperature and under N<sub>2</sub> atmosphere. The solution was stirred overnight. Water (2 mL) was added to the reaction mixture and the solution was extracted with ether. The organic layer was washed with 1 M HCl (0.5 mL), water, brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Silica gel column chromatography (8:2 hexanes/EtOAc) afforded 26 mg (63 %) of monoacetate **9** as a colorless solid. m.p : 73 °C.  $[\alpha]_D = +33.7$  in CH<sub>2</sub>Cl<sub>2</sub> (c = 0.7). IR (thin film, cm<sup>-1</sup>): 3526, 2958, 2933, 2858, 1733, 1608, 1496, 1466, 1429, 1366, 1345, 1279, 1233, 1200, 1154, 1092, 1058, 1037, 983, 912. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.29(s, 2H), 5.66(d, *J*=3Hz, 1H), 5.15(d, *J*= 12.6Hz, 1H), 5.08(d, *J*= 12.6Hz, 1H), 4.42(dd, *J*=12, 2.1Hz, 1H), 4.29(dd, *J*=6, 3.3Hz, 1H), 4.25(ddd, *J*=9.9, 2.4, 2.4Hz, 1H), 4.14(dd, *J*=12.3, 3Hz, 1H), 3.96(dd, *J*=9.8, 3Hz, 1H), 3.79(s, 3H), 3.76(s, 3H), 3.33(d, *J*=6.3Hz, 1H), 1.88(s, 3H), 1.19(s, 9H), 0.91(s, 9H), 0.16(s, 3H), 0.12(s, 3H). <sup>13</sup>C NMR(75MHz, CDCl<sub>3</sub>) δ 178.1, 169.9, 163.1, 156.0, 143.1, 116.7, 109.6, 98.2, 96.6, 73.5, 70.7, 69.4, 68.6, 68.0, 62.5, 55.6, 55.3, 38.9, 27.2, 25.7, 20.9, 18.1, -4.1, -4.8. HRFAB calcd for (M+H)<sup>+</sup> C<sub>28</sub>H<sub>45</sub>O<sub>10</sub>Si: 569.2782, found: 569.2776.



**Disilylated mannopapulacandin** (Not shown in the text)

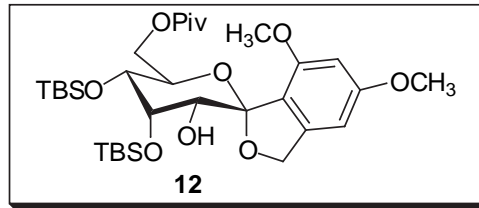
Under a N<sub>2</sub> atmosphere an anhydrous ether (1.5 mL) solution of alcohol **15** (25 mg, 0.14 mmol) was cooled to -78 °C, and 1M DIBALH (0.08 mL, in Hexane solution, 2 equiv) was added dropwise over 5 min. The reaction was stirred for 3 h at -78 °C and then quenched with a 50 % aqueous ether solution (1 mL). The cooling bath was removed and the reaction was stirred at room temperature for 0.5 h, diluted with ethyl acetate (5 mL) and filtered through plug of celite/silica gel using ethyl acetate as eluent. The organic filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (SiO<sub>2</sub>, 20% EtOAc/Hexanes) affording 22 mg of a colorless liquid (98%). m.p. = 128°C. R<sub>f</sub> = 0.2 [hexanes/EtOAc (3:1)]. IR (thin film, cm<sup>-1</sup>): 3482, 2953, 2928, 2856, 1612, 1495, 1471, 1432, 1347, 1252, 1224, 1200, 1156, 1092, 1028, 980, 938, 891, 860, 838, 779, 733. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.41(d, *J*=1.8Hz, 1H), 6.39(d, *J*=1.8Hz, 1H), 5.04(dd, *J*=33.9, 12.9, 2H), 4.47(d, *J*=1.2Hz, 1H), 4.21(dd, *J*=8.7, 1.5Hz, 1H), 4.12(t, *J*=8.7Hz, 1H), 3.95(t, *J*=2.1Hz, 1H), 3.88(s, 3H), 3.81(s, 3H), 3.8-3.7(m, 2H), 1.96(dd, *J*=6.9, 5.7Hz, 1H), 0.94(s, 9H), 0.89(s, 9H), 0.15(s, 3H), 0.14(s, 3H), 0.13(s, 3H), 0.12(s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 162.8, 154.6, 143.8, 118.7, 111.3, 98.6, 97.8, 76.1, 74.9, 74.9, 72.1, 67.8, 61.9, 56.0, 55.7, 26.3, 26.0, 18.5, -2.6, -3.2, -4.2, -4.9. HRFAB calcd for (M+H)<sup>+</sup> C<sub>27</sub>H<sub>49</sub>O<sub>8</sub>Si<sub>2</sub>: 557.2966, found: 557.2955.



### Disilylated glucopapulacandin nucleus (**17**)

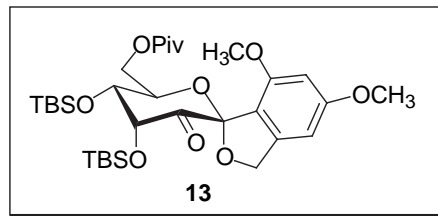
To a slurry of  $\text{LiAlH}_4$  (5 mg) in ether (0.5 mL), under a  $\text{N}_2$  atmosphere an anhydrous ether solution (0.5 mL) of ketoalcohol **16** (35 mg, 63  $\mu\text{mol}$ ) was added at  $-78^\circ\text{C}$ . The reaction was stirred for 12 h and quenched at  $-78^\circ\text{C}$  by adding ethyl acetate (0.5 ml) and followed by the addition of 50 % aqueous ether (1 mL). The cooling bath was removed and the reaction was stirred at room temperature for 0.5 h, diluted with ethyl acetate (5 mL) and filtered through plug of celite and silica gel using ethyl acetate as eluent. The organic filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography ( $\text{SiO}_2$ , 20% EtOAc/hexanes) affording 31 mg (89%) of **17** as a white solid. m.p. =  $118^\circ\text{C}$ .  $R_f = 0.3$  [Hexane/EtOAc (8:2)].  $[\alpha]_D = +24.6$  in  $\text{CH}_2\text{Cl}_2$  ( $c = 0.8$ ). IR (thin film,  $\text{cm}^{-1}$ ) 3500, 2923, 2856, 1610, 1495, 1461, 1430, 1356, 1341, 1250, 1221, 1197, 1149, 1086, 1038, 1019, 961, 889, 836, 779.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.36(d,  $J=1.2\text{Hz}$ , 1H), 6.33(d,  $J=1.2\text{Hz}$ , 1H), 5.12(d,  $J=12.6\text{Hz}$ , 1H), 5.01(d,  $J=12.6\text{Hz}$ , 1H), 4.16(t,  $J=9\text{Hz}$ , 1H), 3.9-3.6(m, 5H), 3.83(s, 3H), 3.79(s, 3H), 2.00(br.s, 1H), 0.94(s, 9H), 0.91(s, 9H), 0.17(s, 3H), 0.15(s, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 155.8, 143.4, 117.6, 110.7, 98.3, 96.8, 76.6, 74.8, 72.9, 72.6, 71.8, 61.8, 55.6, 55.4, 26.6, 26.2, 18.7, 18.1, -2.1, -2.3, -2.8, -4.2. HRFAB calcd for  $(\text{M}+\text{H})^+$   $\text{C}_{27}\text{H}_{49}\text{O}_8\text{Si}_2$ : 557.2966, found: 557.2970.





### Disilylated allose isomer (12)

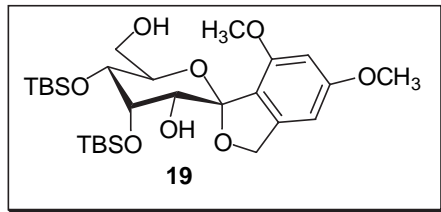
To a DMF (0.5 mL) solution of diol **8** (32 mg, 0.06 mmol) at room temperature and under a N<sub>2</sub> atmosphere was added imidazole (17 mg, 0.24 mmol), DMAP (5 mg), and TBSCl (37 mg, 0.24 mmol). The solution was stirred overnight then poured into water (2 mL) and extract with Et<sub>2</sub>O (2 x 10 mL). The organic layer was washed with water (2 mL), 1 M HCl<sub>(aq)</sub> (0.5 mL), saturated NaHCO<sub>3(aq)</sub> (1 mL), brine (5 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation of solvent under reduced pressure and flash chromatography over silica gel using hexanes: ethyl acetate (9:1) resulted in **18** mg of a white crystalline solid (50 %). m.p. = 44 °C. [α]<sub>D</sub> = +8.0 in CH<sub>2</sub>Cl<sub>2</sub> (c = 0.2). IR (thin film, cm<sup>-1</sup>) 3538, 2952, 2933, 2856, 1730, 1610, 1495, 1471, 1461, 1428, 1360, 1346, 1284, 1250, 1197, 1154, 1101, 1028, 981, 836, 774. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 6.21(d, *J*=1.8Hz, 1H), 5.86(d, *J*=1.5Hz, 1H), 4.85(d, *J*=12.6Hz, 1H), 4.76(d, *J*=12.6Hz, 1H), 4.74(dd, *J*=11.5, 2.1Hz, 1H), 4.46(m, 1H), 4.63(d, *J*=3.3Hz, 1H), 4.47(dd, *J*=11.5, 4.5Hz, 1H), 4.42-4.38(m, 1H), 4.03(dd, *J*=9.6, 2.7Hz, 1H), 3.81(d, *J*=6.6Hz, 1H), 3.23(s, 6H), 1.17(s, 9H), 1.01(s, 9H), 0.79(s, 9H), 0.25(s, 3H), 0.16(s, 3H), 0.1(s, 3H), -0.23(s, 3H). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 177.7, 163.6, 156.4, 144.2, 119.2, 112.7, 99.0, 96.7, 74.2, 74.1, 70.6, 70.5, 69.7, 63.9, 55.5, 55.1, 39.3, 27.7, 26.4, 25.9, 18.8, 18.4, -3.4, -4.0, -4.2, -5.0. HRFAB calcd for (M+H)<sup>+</sup> C<sub>32</sub>H<sub>57</sub>O<sub>9</sub>Si<sub>2</sub>: 641.3541, found: 641.3542.



### Ketone 13

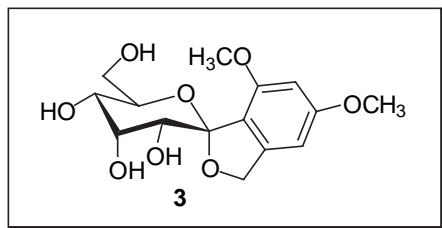
An anhydrous  $\text{CH}_2\text{Cl}_2$  (0.5 mL) solution of oxalyl chloride (6 mg, 0.05 mmol) under a  $\text{N}_2$  atmosphere was cooled to  $-60\text{ }^\circ\text{C}$  and DMSO (3.6 mg, 0.05 mmol) was added dropwise at a rapid rate with stirring. After 5 min. a  $\text{CH}_2\text{Cl}_2$  solution (0.1 mL) of alcohol **12** (10 mg, 0.015 mmol) was added dropwise at  $-60\text{ }^\circ\text{C}$ . After 30 min of stirring,  $\text{Et}_3\text{N}$  (8 mg, 0.08 mmol) was added dropwise and stirred for 5 minutes. The mixture was warm to room temperature and water (2 mL) was added. The aqueous layer was separated and extracted twice with  $\text{CH}_2\text{Cl}_2$  (5 mL). The organic phase was washed twice with brine and dried over  $\text{MgSO}_4$ . Column chromatography over silica gel (9:1 Hex/EtOAc) afforded 6 mg (61%) of **13**.  $[\alpha]_D = +4.7$  in  $\text{CH}_2\text{Cl}_2$  ( $c = 0.4$ ). IR (thin film,  $\text{cm}^{-1}$ ): 2954, 2931, 2860, 1748, 1731, 1607, 1496, 1466, 1460, 1431, 1361, 1343, 1284, 1249, 1196, 1155, 1096, 1043, 1026, 838, 779.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.33(d,  $J=1.8\text{Hz}$ , 1H), 6.29(d,  $J=1.8\text{Hz}$ , 1H), 5.08(d,  $J=12.6\text{Hz}$ , 1H), 5.01(d,  $J=12.6\text{Hz}$ , 1H), 4.93(d,  $J=1.5\text{Hz}$ , 1H), 4.51(dd,  $J=12, 2.1\text{Hz}$ , 1H), 4.42(dd,  $J=9.6, 1.5\text{Hz}$ , 1H), 4.21(dd,  $J=12, 2.7\text{Hz}$ , 1H), 4.14(ddd,  $J=9.3, 2.4, 2.4\text{Hz}$ , 1H), 3.79(s, 3H), 3.78(s, 3H), 1.2(s, 9H), 0.9(s, 9H), 0.62(s, 9H), 0.21(s, 3H), 0.05(s, 3H), 0.03(s, 3H), -0.23(s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  203.3, 170.1, 164.2, 163.2, 155.7, 143.8, 127.3, 98.1, 96.1, 73.9, 73.7, 62.4, 55.7, 55.0, 39.0, 27.2, 25.7, 25.3, 20.1, 18.8, -4.0, -4.4, -5.6, -6.0.\* HRFAB calcd for  $(\text{M}+\text{H})^+$   $\text{C}_{32}\text{H}_{55}\text{O}_9\text{Si}_2$ : 639.3384, found: 639.3361.

\* Due to lack of sample the  $^{13}\text{C}$  NMR is missing two carbons.



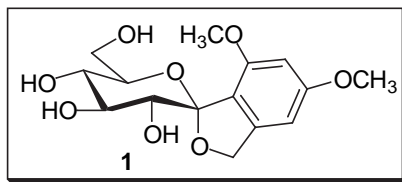
### Disilylated allose isomer (**19**)

An ether (0.5 mL) solution of alcohol **12** (13 mg, 0.14 mmol) was cooled to  $-78\text{ }^{\circ}\text{C}$ , and DIBAL-H (0.04 mL, 1M in Hexane solution, 2 equiv) was added dropwise over 5 min. The reaction was stirred for 3 h at  $-78\text{ }^{\circ}\text{C}$  before being quenched with 50 % aqueous ether (1 mL). The cooling bath was removed and the solution was stirred at room temperature for 0.5 h. The solution was then diluted with ethyl acetate (5 mL) and filtered through plug of celite and silica gel using ethyl acetate as eluent. The organic filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography ( $\text{SiO}_2$ , 20% EtOAc/Hexanes) affording 9 mg (81%) of **19** as a viscous liquid.  $[\alpha]_{\text{D}} = +10.3$  in  $\text{CH}_2\text{Cl}_2$  ( $c = 0.7$ ). IR (thin film,  $\text{cm}^{-1}$ ): 3518, 2942, 2931, 2860, 1607, 1496, 1466, 1460, 1425, 1361, 1343, 1325, 1302, 1249, 1196, 1149, 1102, 1032, 985, 932, 879, 832, 779.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.33(s, 1H), 6.31(s, 1H), 5.15(d,  $J=12.6\text{Hz}$ , 1H), 5.02(d,  $J=12.6\text{Hz}$ , 1H), 4.28(d,  $J=3\text{Hz}$ , 1H), 4.12(ddd,  $J=9.9, 3, 3\text{Hz}$ , 1H), 4.06(br.s, 1H), 3.83-3.7(m, 4H), 3.8(s, 3H), 3.79(s, 3H), 3.46(br.s, 1H), 0.94(s, 9H), 0.68(s, 9H), 0.17(s, 3H), 0.16(s, 3H), -0.02(s, 3H), -0.35(s, 3H).  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 155.5, 143.7, 117.9, 111.6, 98.0, 96.4, 73.8, 73.2, 70.2, 69.5, 68.7, 61.7, 55.7, 55.2, 25.8, 25.3, 18.1, 17.7, -4.2, -4.7 (2 C), -5.8. HRFAB calcd for  $(\text{M}+\text{H})^+$   $\text{C}_{27}\text{H}_{49}\text{O}_8\text{Si}_2$ : 557.2966, found: 557.2940.



### Allose papulacandin nucleus (**3**)

To a room temperature THF (0.3 mL) solution of TBS-ether **19** (7 mg, 0.012 mmol) was added with tetrabutylammonium fluoride•3H<sub>2</sub>O (1.0M solution in THF, 50 μL, 0.05 mmol) under N<sub>2</sub> atmosphere. After TLC-analysis indicated the disappearance of starting material (3 h), the mixture was diluted with Et<sub>2</sub>O (1 mL) and filtered through a plug of celite and florisil using methanol as eluent. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography [florisil, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (8:2)] affording 4 mg (93%) of **3**. m.p : 199 °C. [α]<sub>D</sub> = +6.3 in MeOH (c = 0.6). IR (thin film, cm<sup>-1</sup>): 3357, 2924, 2855, 1611, 1500, 1462, 1433, 1227, 1200, 1150, 1058, 1030, 975, 874. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 6.44(d, *J*=1.8Hz, 1H), 6.43(d, *J*=1.8Hz, 1H), 5.13(d, *J*=12.6Hz, 1H), 5.05(d, *J*=12.6Hz, 1H), 4.43(d, *J*=3.6Hz, 1H), 4.11(dd, *J*=3.3, 3.3Hz, 1H), 4.0(dddd, *J*=10.2, 6.0, 2.7, 2.7Hz, 1H), 3.84(m, 1H), 3.81(s, 3H), 3.79(s, 3H), 3.67(dd, *J*=12, 6Hz, 1H), 3.57(dd, *J*=10.2, 3.3Hz, 1H). <sup>13</sup>C NMR(75 MHz, CD<sub>3</sub>OD) δ 164.6, 157.4, 145.1, 119.4, 112.6, 99.0, 97.9, 74.2, 72.3, 69.1, 68.9, 63.2, 56.2, 56.0, 30.8. HRFAB calcd for (M+Na)<sup>+</sup> C<sub>15</sub>H<sub>20</sub>O<sub>8</sub>Na: 351.1056, found: 351.1069.



### Papulacandin nucleus (**1**)

A room temperature THF (0.2 mL) solution of bis-silylether **17** (5 mg, 0.02 mmol) was treated with tetrabutylammonium fluoride•3H<sub>2</sub>O (1.0 M solution in THF, 36 μL, 0.035 mmol) under N<sub>2</sub> atmosphere. After TLC analysis showed the disappearance of starting material (3 h), the mixture was diluted with Et<sub>2</sub>O (1 mL) and filtered through a plug of celite and florisil using methanol as eluent. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography [florisil, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (8:2)] affording 2 mg (67%) of **1**. m.p : 174 °C. [α]<sub>D</sub> = +25.2 in CH<sub>3</sub>OH (c = 0.8). IR (thin film, cm<sup>-1</sup>): 3380, 2924, 1609, 1498, 1466, 1431, 1343, 1226, 1200, 1154, 1066, 1011, 956, 832. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 6.43(s, 1H), 6.42(s, 1H), 5.1(d, *J*=12.6Hz, 1H), 5.01(d, *J*=12.6Hz, 1H), 4.2(d, *J*=9.6Hz, 1H), 3.84-3.6(m, 4H), 3.8(s, 6H), 3.4(t, *J*=9Hz, 1H). <sup>13</sup>C NMR (75MHz, CD<sub>3</sub>OD) δ 164.6, 157.5, 145.6, 119.3, 112.2, 99.0, 98.0, 76.5, 76.1, 73.8, 73.6, 72.2, 63.2, 56.2, 56.0. HRFAB calcd for (M+Na)<sup>+</sup> C<sub>15</sub>H<sub>20</sub>O<sub>8</sub>Na: 351.1056, found: 351.1032.