

Reductive Aromatization of Quinols: Synthesis of the C-Arylglycoside Nucleus of the Papulacandins and Chaetiacandin

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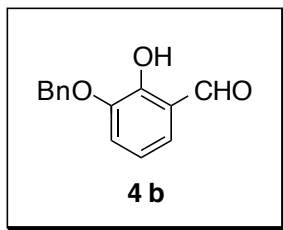
General Methods

Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer 1600 Series FT-IR spectrophotometer. Nuclear magnetic resonance spectra were recorded with a Bruker 300 or 400 MHz spectrometer and are reported in parts per million. Proton nuclear magnetic resonance spectra were taken in deuteriochloroform using tetramethylsilane (0.00 ppm) as the internal standard. The following abbreviations are used in the experimental section: singlet (s), doublet (d), triplet (t), quartet (q), quintet (qn), multiplet (m), doublet of doublets (dd), triplet of doublets (td), doublet of triplets (dt), doublet of doublets of doublets (ddd), broad singlet (bs), and broad doublet (bd). Values of the coupling constant, J, are given in Hertz (Hz). For complex multiplets, the chemical shift is given for the center of the multiplet. Carbon nuclear magnetic resonance spectra were taken in deuteriochloroform and the central peak of chloroform (77.0 ppm) was used as the internal standard. High resolution mass spectra were recorded with a Kratos MS-80 spectrometer under e.i. or c.i. conditions.

Thin layer chromatography (tlc) was performed on EM Science precoated silica gel 60 F-254 glass supported plates with 0.25mm thickness. Spots were visualized by exposure to ultraviolet light or to iodine vapor, or by dipping in a 10% solution of phosphomolybdenic acid (PMA) in ethanol followed by heating. Flash chromatography was performed with Fisher brand silica gel (170-400 mesh).

Ether refers to diethyl ether. Both ether and tetrahydrofuran were distilled from sodium-benzophenone ketyl. Benzene and dichloromethane were distilled from calcium hydride and stored over molecular sieves. Dimethyl sulfoxide and N,N'-dimethyl formamide were dried over molecular sieves (4 Å) prior to use. All reactions were conducted under an inert atmosphere of argon or nitrogen (N₂) as indicated.

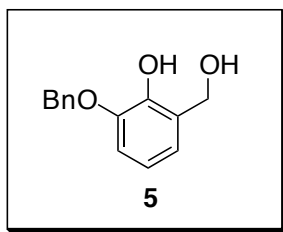
Experimental Procedures



2-Hydroxy-3-(phenylmethoxy)benzaldehyde (4b). To a suspension of dry NaH (6.30 g, 261 mmol) in THF (100 mL) was added a solution of 2,3-dihydroxybenzaldehyde (14.4 g, 104 mmol) in THF (50 mL) at 25 °C. After 1 h of stirring, a solution of benzyl bromide (17.1 g, 104 mmol) in THF (25 mL) was added at 25 °C, and stirring was continued for 24 h, whereupon the mixture was poured into water (500 mL) and extracted with CHCl₃ (3 x 100 mL). The aqueous layer was acidified with 3 N HCl to adjust the pH to 2-4 and was again extracted with CHCl₃ (3 x 150 mL). The latter CHCl₃ extracts were washed with 1 N HCl (2 x 150 mL) and dried over MgSO₄, and filtered through silica gel. Crystallization from EtOH gave 17.3 g (73%) of yellow needles; mp 89-90 °C (reported 86-87 °C).¹²

¹H NMR (CDCl₃) δ 11.09 (s, 1 H), 9.92 (s, 1H, OH), 7.46-7.29 (m, 5H), 7.20 (dd, J=7.8, 1.4 Hz, 1H), 7.13 (dd, J=7.8, 1.4 Hz, 1H), 6.90 (t, J=7.8 Hz, 1H), 5.20 (s, 2H).

IR (CDCl₃) 3250, 3060, 2938, 1657 cm⁻¹



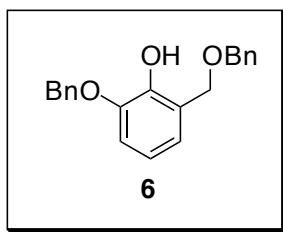
2-Hydroxymethyl-6-(phenylmethoxy)phenol (5). To a solution of 2-hydroxy-3-(phenylmethoxy)benzaldehyde **4b** (5.02 g, 21.9 mmol) in MeOH (200 mL) was added NaBH₄ (3.34 g, 87.7 mmol) at 0 °C. The reaction mixture was stirred for 4 h at ambient temperature and then concentrated. The residual white solid was dissolved in 3 N HCl and the resulting solution was extracted with CHCl₃ (3 x 100 mL). The organic solution was washed with water (3 x 100 mL) and brine (1 x 100 mL) and dried over MgSO₄. Removal of the solvent afforded 4.94 g (98%) of a colorless syrup.

¹H NMR (CDCl₃) δ 7.42-6.79 (m, 8H), 6.00 (bs, 1H, OH), 5.12 (s, 2H), 4.74 (d, J=6.1 Hz, 2H), 2.22 (t, J=6.1 Hz, 1H, OH).

¹³C NMR (CDCl₃) δ 145.7, 144.0, 136.4, 128.8, 128.4, 127.8, 126.9, 121.3, 119.8, 112.0, 71.3, 61.8.

IR (CDCl₃) 3369, 2876 cm⁻¹

HRMS (EI) calc'd. for C₁₄H₁₄O₃: 230.0943. Found: 230.0950.



2-(Phenylmethoxy)-6-(phenylmethoxymethyl)-phenol (6). To a suspension of dry NaH (421 mg, 16.4 mmol) in DMSO (8 mL) was added dropwise a solution of 2-

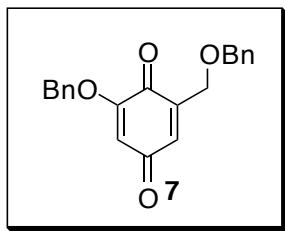
hydroxymethyl-6-(phenylmethoxy)phenol **5** (1.26 g, 5.47 mmol) in DMSO (4 mL) at 25 °C. After the reaction mixture had stirred for 1 h, a solution of benzyl bromide (932 mg, 5.47 mmol) in DMSO (2 mL) was added at 25 °C. Stirring was continued for 24 h and then the mixture was poured into water (150 mL) and extracted with CHCl₃ (2 x 50 mL). The aqueous layer was acidified with 3 N HCl to adjust the pH to 2-4 and was again extracted with CHCl₃ (3 x 50 mL). The latter CHCl₃ extracts were washed with 1 N HCl (1 x 50 mL), water (5 x 50 mL), and brine (1 x 50 mL), and dried over MgSO₄. Column chromatography (3:1 Hex/EtOAc) gave 1.28 g (68%) of a pale yellow viscous oil.

¹H NMR (CDCl₃) δ 7.44-7.25 (m, 10H), 6.95 (dd, J=8.0, 1.0 Hz, 1H), 6.88 (dd, J=8.0, 1.0 Hz, 1H), 6.81 (t, J=8.0 Hz, 1H), 6.23 (s, 1H), 5.11 (s, 2H), 4.67 (s, 2H), 4.60 (s, 2H).

¹³C NMR (CDCl₃) δ 146.8, 145.2, 139.0, 137.4, 129.5, 129.2, 129.1, 128.7, 128.6, 128.5, 124.9, 122.6, 120.3, 113.0, 73.2, 72.1, 68.5.

IR (CDCl₃) 3525, 3032, 2860 cm⁻¹

HRMS (FAB) calc'd. for: C₂₁H₂₀O₃Na ([M+Na]⁺): 343.1310. Found: 343.1319.



2-(Phenylmethoxy)-6-(phenylmethoxymethyl)-1,4-benzoquinone (7). To a solution of 2-(phenylmethoxy)-6-(phenylmethoxymethyl)-phenol **6** (283 mg, 0.825 mmol) in DMF (2 mL) was added a catalytic amount of salcomine (N,N'-bis(salicylidene)-ethylenediiminocobalt(II)) (143 mg, 0.044 mmol). The solution was stirred for 2 days with a slow stream of O₂ bubbling through it, protected from light. The reaction was quenched with cold water (50 mL) and the mixture was extracted with CHCl₃ (5 x 25 mL).

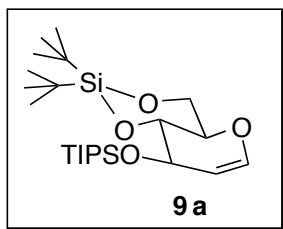
The combined organic solution was washed with water (5 x 50 mL) and brine (1 x 50 mL) and then dried over MgSO_4 . Column chromatography (3:1 Hex/EtOAc) and recrystallization from EtOH afforded 189 mg (64%) of bright yellow needles: mp 82-83 °C.

^1H NMR (CDCl_3) δ 7.40-7.30 (m, 10H), 6.81 (dt, $J=4.2, 2.4$ Hz, 1H), 5.95 (d, $J=2.4$ Hz, 1H), 5.04 (s, 2H), 4.64 (s, 2H), 4.41 (d, $J=4.2$ Hz, 2H).

^{13}C NMR (CDCl_3) δ 187.4, 181.4, 157.5, 143.7, 137.4, 134.0, 132.0, 128.9, 128.8, 128.5, 128.0, 127.7, 127.6, 108.6, 73.3, 71.1, 65.2.

IR (KBr) 1653, 1600 cm^{-1}

HRMS (FAB) calc'd. for: $\text{C}_{21}\text{H}_{18}\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 357.1103. Found: 357.1111.



Silylated glycal (9a). To a solution of commercially available tri-*O*-acetyl-D-glucal **8** (5.01 g, 18.4 mmol) in methanol (25 mL) was added K_2CO_3 (967 mg, 7.00 mmol). The reaction mixture was stirred for 24 h at room temperature and then filtered through silica gel. The silica gel was washed with methanol and the combined filtrate was concentrated to afford 2.64 g (98%) of a colorless syrup which was carried on to the next reaction without further purification.

To a solution of crude D-glucal (1.67 g, 11.4 mmol) in DMF (20 mL) at -50 °C was added 2,6-lutidine (3.67 g, 34.3 mmol) and the resulting solution was stirred for 30 min. Di-*tert*-butylsilylditriplate (6.03 g, 13.7 mmol) was added dropwise to the reaction mixture over a 30 min. period and stirring was continued for an additional 10 h at -50 °C. The reaction was quenched with water and warmed to ambient temperature, then extracted with ether (3 x 50 mL). The resulting organic solution was washed with water (5 x 50

mL), aq. NaHCO₃ (1 x 50 mL), and brine (1 x 50 mL) and then dried over MgSO₄. Column chromatography (9:1 Hex/EtOAc) gave 297 mg (91%) of colorless crystals: mp 48-49°C.

¹H NMR (CDCl₃) δ 6.27 (dd, J_{1,2}=6.0, J_{1,3}=1.6 Hz, H-1), 4.76 (dd, J_{1,2}=6.0, J_{2,3}=1.6 Hz, H-2), 4.30 (bd, J_{3,4}=7.2 Hz, H-3), 4.18 (dd, J_{6eq.,6ax.}=10.0, J_{5,6eq.}=4.8 Hz, H-6eq.), 3.97 (dd, J_{5,6ax.}=10.0, J_{6eq.,6ax.}=10.0 Hz, H-6ax.), 3.92 (dd, J_{4,5}=10.0, J_{3,4}=7.2 Hz, H-4), 3.84 (ddd, J_{4,5}=10.0, J_{5,6ax.}=10.0, J_{5,6eq.}=4.8 Hz, H-5), 2.43 (bs, 1H), 1.07 (s, 9H), 0.99 (s, 9H).

¹³C NMR (CDCl₃) δ 143.6, 102.9, 72.2, 70.2, 65.7, 27.4, 26.9, 22.7, 19.8.

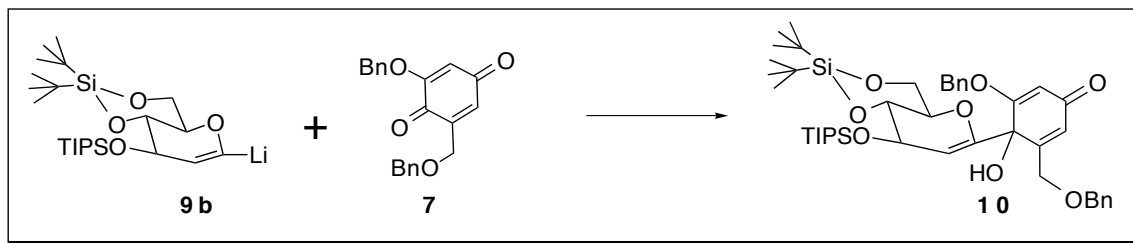
IR (CDCl₃) 3376, 2935, 2860 cm⁻¹

To a solution of the di-*tert*-butylsilylene derivative of D-glucal (550 mg, 1.92 mmol) in DMF (20 mL) was added imidazole (327 mg, 4.80 mmol) and triisopropylsilylchloride (482 mg, 2.50 mmol). The reaction mixture was stirred for 10 h at 45 °C, then cooled to room temperature and quenched with water (50 mL). Extraction with ether (3 x 50 mL) provided a combined organic solution which was washed with water (5 x 50 mL) and brine (1 x 50 mL) and then dried over MgSO₄. Column chromatography (5% EtOAc/Hex) gave 816 mg (96%) of colorless crystals: mp 54-55°C.

¹H NMR (CDCl₃) δ 6.23 (dd, J_{1,2}=6.0, J_{1,3}=1.6 Hz, H-1), 4.68 (dd, J_{1,2}=6.0, J_{2,3}=1.6 Hz, H-2), 4.42 (dd, J_{2,3}=1.6, J_{3,4}=6.8 Hz, H-3), 4.15 (dd, J_{6eq.,6ax.}=10.4, J_{5,6eq.}=4.8 Hz, H-6eq.), 4.00, (dd, J_{4,5}=10.4, J_{3,4}=6.8 Hz, H-4), 3.96 (dd, J_{5,6ax.}=10.4, J_{6eq.,6ax.}=10.4 Hz, H-6ax.), 3.80 (ddd, J_{4,5}=10.4, J_{5,6ax.}=10.4, J_{5,6eq.}=4.8 Hz, H-5), 1.18-0.90 (m, 39H).

¹³C NMR (CDCl₃) δ 142.7, 105.3, 72.8, 26.9, 22.8, 19.8, 18.1, 12.4.

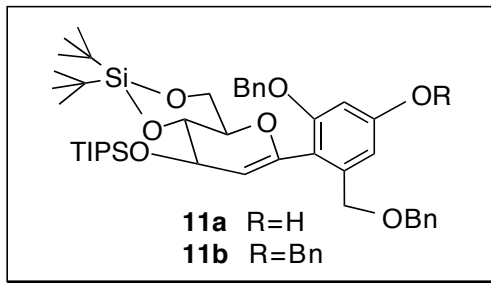
IR (CDCl₃) 2942, 2864 cm⁻¹



Quinol (10). To a solution of fully protected glycal **9a** (180 mg, 0.407 mmol) in THF (0.15 mL) at $-78\text{ }^{\circ}\text{C}$ (dry ice/acetone bath) was added *t*-BuLi (1.7M in hexanes, 0.48 mL, 0.82 mmol). The reaction mixture immediately turned bright yellow. After 5 min. of stirring at $-78\text{ }^{\circ}\text{C}$, the reaction mixture was allowed to warm to $0\text{ }^{\circ}\text{C}$ (ice bath) and was then stirred for an additional 105 min. The resulting solution, having now turned a pale yellow color, was cooled to $-100\text{ }^{\circ}\text{C}$ (N_2 /pentanes bath) and was added via cannula to a solution of quinone **7** (750 mg, 0.225 mmol) and $\text{BF}_3\text{-Et}_2\text{O}$ (0.03 mL, 0.225 mmol) in THF (1.5 mL) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for another 8 h and quenched with water and allowed to warm to ambient temperature. The reaction mixture was extracted with ether (3 x 25 mL) and the resulting organic solution was washed with water (3 x 25 mL) and brine (1 x 25 mL) and then dried over Na_2SO_4 . Column chromatography (3:1 Hex/EtOAc with 0.1% Et_3N) afforded 59 mg (33%) of **10** a pale yellow syrup and 46 mg (58%) of recovered quinone **7**.

^1H NMR (CDCl_3) δ 7.41-7.25 (m, 10H), 6.54 (s, 1H), 6.36 (s, 1H), 5.84 (bs, 1H), 5.10 (s, 2H), 4.93 (d, $J_{2,3}=2.4\text{ Hz}$, H-2), 4.72, 4.60 (2d, $J=12.0\text{ Hz}$, AB, 2H), 4.55 (d, $J=1.6\text{ Hz}$, 2H), 4.46 (dd, $J_{2,3}=2.4$, $J_{3,4}=6.8\text{ Hz}$, H-3), 4.14-4.09 (m, H-6eq.), 4.06 (dd, $J_{4,5}=10.0$, $J_{3,4}=6.8\text{ Hz}$, H-4), 3.96 (dd, $J_{5,6\text{ax.}}=10.0$, $J_{6\text{eq.},6\text{ax.}}=10.0\text{ Hz}$, H-6ax.), 3.85 (ddd, $J_{4,5}=10.0$, $J_{5,6\text{ax.}}=10.0$, $J_{5,6\text{eq.}}=4.8\text{ Hz}$, H-5), 1.13-0.99 (m, 39H).

IR (CDCl_3) 3424, 2942, 2864, 1658 cm^{-1}



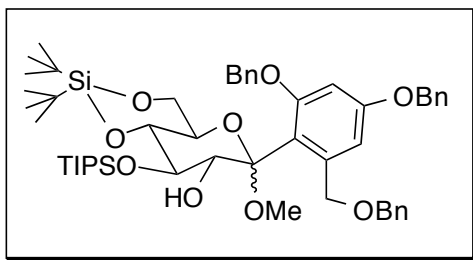
C-Arylglycoside (11b). To a solution of quinol **10** (200 mg, 0.026 mmol) in THF/H₂O (5:2, 0.7 mL) was added Na₂S₂O₄ (360 mg, 0.206 mmol). The reaction mixture was stirred at room temperature for 10 h and then concentrated. The resulting residue was dissolved in ether (5 mL) and this solution was washed with water (2 x 5 mL) and then dried over Na₂SO₄. Solvent was removed *in vacuo* and crude **11a** was redissolved in THF (1 mL). This solution was cooled to -78 °C, NaH (2 mg, 0.083 mmol) was added, and the reaction mixture was warmed to ambient temperature. Benzyl bromide was added (44 mg, 0.026 mmol) and the reaction mixture was stirred overnight and then quenched with cold water (3 mL). Extraction with CHCl₃ (3 x 15 mL) gave a combined organic solution that was washed with water (3 x 15 mL) and brine (1 x 15 mL) and then dried over MgSO₄. Column chromatography (6:1 Hex/EtOAc) gave 23 mg (85%) of a colorless syrup.

¹H NMR (CDCl₃) δ 7.43-7.26 (m, 15H), 6.79 (d, J=3.0 Hz, 1H), 6.53 (d, J=3.0 Hz, 1H), 5.05 (s, 2H), 5.02 (s, 2H), 4.74 (d, J_{2,3}=2.1 Hz, H-2), 4.60 (d, J=3.0 Hz, 2H), 4.54 (d, J=3.0 Hz, 2H), 4.50 (dd, J_{2,3}=2.1, J_{3,4}=6.0 Hz, H-3), 4.16-4.01 (m, H-6eq., H-4), 3.92 (dd, J_{5,6ax.}=10.2, J_{6eq.,6ax.}=10.2 Hz, H-6ax.), 3.89 (ddd, J_{4,5}=10.2, J_{5,6ax.}=10.2, J_{5,6eq.}=4.2 Hz, H-5), 1.15-0.88 (m, 39H).

¹³C NMR (CDCl₃) δ 160.20, 158.0, 147.1, 139.9, 138.3, 137.1, 136.8, 128.6, 128.4, 128.3, 128.0, 127.7, 127.6, 127.5, 126.9, 117.3, 107.0, 105.1, 100.2, 73.1, 72.3, 71.9, 70.4, 70.1, 69.4, 66.1, 27.5, 27.0, 22.7, 19.9, 18.2, 12.5.

IR (CDCl₃) 2938, 2863 cm⁻¹

HRMS (FAB) calc'd. for: C₅₁H₇₀O₇Si₂Na ([M+Na]⁺): 873.4558. Found: 873.4583.



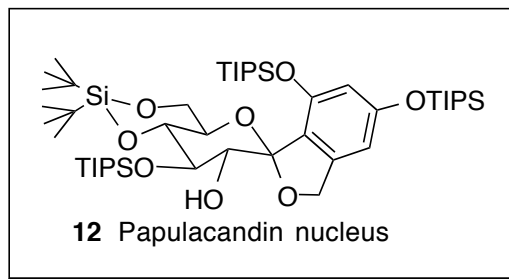
Methyl glycoside. C-arylglycoside intermediate **11b** (15 mg, 0.017 mmol) was dissolved in 10:1 MeOH/THF (1 mL) and 3-chloroperoxybenzoic acid (69 mg, 0.04 mmol) was added. The reaction mixture was stirred for 2 days and then the solvent was removed *in vacuo*. The residue was dissolved in EtOAc and the resulting organic solution was washed with 10% NaHCO₃ and brine and then dried over Na₂SO₄. Removal of the solvent *in vacuo* and column chromatography (10% EtOAc/Hex) afforded 15 mg (84%) of a colorless syrup.

¹H NMR (CDCl₃) δ 7.46-7.27 (m, 15H), 7.10 (d, J=2.7 Hz, 1H), 6.61 (d, J=2.7 Hz, 1H), 5.07 (s, 2H), 5.02 (dd, J=22.5, 12.3 Hz, 2H), 4.61 (s, 2H), 4.55 and 4.41 (2d, J=12.3 Hz, AB, 2H), 4.01 (dd, J_{6eq.,6ax.} =9.6, J_{5,6eq.} =4.5 Hz, H-6eq.), 3.92 (t, J_{3,4} =8.4, J_{2,3} =8.4 Hz, H-3), 3.78 (t, J_{6eq.,6ax.} =9.6, J_{5,6ax.} =9.6 Hz, H-6ax.), 3.64 (ddd, J_{5,6ax.} =9.6, J_{4,5} =9.6, J_{5,6eq.} =4.5 Hz, H-5), 3.52 (dd, J_{4,5} =9.6, J_{3,4} =8.4 Hz, H-4), 3.41 (t, J_{2,3} =8.4, J_{2,OH} =8.1 Hz, H-2), 3.15 (d, J_{2,OH} =8.1 Hz, OH, exchangeable in D₂O), 3.08 (s, 3H), 1.17-0.09 (m, 39H).

¹³C NMR (CDCl₃) δ 159.5, 157.7, 142.0, 138.2, 136.8, 136.4, 128.7, 128.6, 128.5, 128.1, 128.0, 127.7, 127.6, 127.5, 127.2, 116.4, 106.2, 103.7, 100.0, 78.3, 78.1, 72.0, 70.9, 70.0, 67.5, 66.7, 49.2, 27.7, 27.0, 22.8, 19.9, 18.5, 12.9.

IR (CDCl₃) 3526, 2934, 2862 cm⁻¹

HRMS (FAB) calc'd. for: C₅₂H₇₄O₉Si₂Na ([M+Na]⁺): 921.4769. Found: 921.4794.



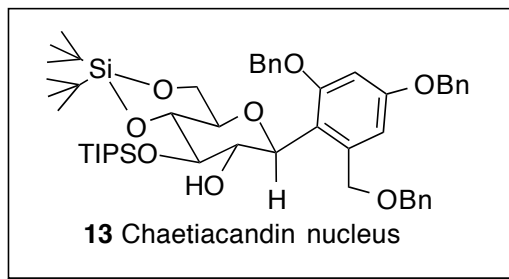
Papulacandin nucleus (12). A suspension of methyl glycoside (15 mg, 0.016 mmol) in EtOAc/MeOH (2:1, 3 mL) under H₂ in the presence of Pd/C (10%, 4 mg) was stirred at room temperature for 10 h. The reaction mixture was then filtered through a pad of Celite. The Celite was washed with methanol and the combined filtrate was concentrated *in vacuo*. The residue was dissolved in CH₂Cl₂ (0.2 mL) and treated first with 2 eq. of triisopropylsilylchloride (6 mg, 0.03 mmol) and then with 2 eq. of triethylamine (3 mg, 0.03 mmol). The reaction mixture was stirred overnight at ambient temperature and then diluted with CH₂Cl₂. The resulting solution was washed with water (3 x 3 mL) and brine (1 x 3 mL) and then dried over MgSO₄. Column chromatography (6:1 Hex/ EtOAc) afforded 16 mg (86%) of a colorless syrup.

¹H NMR (CDCl₃) δ 6.30 (d, J=1.8 Hz, 1H), 6.22 (d, J=1.8 Hz, 1H), 5.11 and 4.99 (2d, J=12.6 Hz, AB, 2H), 4.31 (t, J=8.0 Hz), 4.09 (dd, J=9.6, 4.8 Hz, H-2, loses coupling with D₂O exchange), 3.97-3.83 (t, 3.95, J=8.0 Hz, 1H, overlapping m, 2H, centered at 3.92), 3.79 (t, J=9.6 Hz), 1.32-0.95 (m, 81H).

¹³C NMR (CDCl₃) δ 158.8, 152.3, 143.3, 119.8, 110.9, 109.6, 104.9, 73.8, 73.2, 68.7, 67.1, 27.7, 27.2, 23.0, 20.1, 18.6, 18.5, 18.2, 18.1, 13.4, 13.2, 12.9.

IR (CDCl₃) 2932, 2862, 1603 cm⁻¹

HRMS (FAB) calc'd. for: C₄₈H₉₂O₈Si₄ ([M+H]⁺): 908.5869. Found: 908.5842.



Chaetiacandin nucleus (13). To a solution of C-aryl glycoside intermediate **11b** (5 mg, 6 μ mol) in THF (0.1 mL) at 0 °C was added BH_3 -THF (1M in THF, 8.0 eq., 50 μ L, 0.05 mmol). The reaction mixture was stirred at ambient temperature for 24 h and then treated with a solution of 3 N NaOH/30% H_2O_2 (1:1, 1.2 mL). The reaction mixture was stirred for 24 h then diluted with CH_2Cl_2 , washed with aqueous 20% sodium hydrogensulfite (1 x 10 mL), saturated aqueous ammonium chloride (1 x 10 mL), water (1 x 10 mL) and brine (1 x 10 mL) and then dried over Na_2SO_4 . Solvent was evaporated and column chromatography (3:1 Hex/EtOAc) of the residue afforded 4 mg (approximately 80%) of a colorless syrup.

^1H NMR [$(\text{CD}_3)_2\text{SO}$, 140 °C] δ 7.48-7.24 (m, 15H), 6.76 (d, J = 2.4 Hz, 1H), 6.74 (d, J = 2.4 Hz, 1H), 5.12 (s, 2H), 5.05 (s, 2H), 4.74, 4.55 (2d, J = 12.4 Hz, AB, 2H), 4.67 (d, $J_{1,2}$ =10.0 Hz, H-1), 4.54 (s, 2H), 4.02-3.96 (dd, centered at 4.00, $J_{1,2}$ =10.0, $J_{2,3}$ =5.2 Hz, H-2, overlapping m, 3.99, H-3), 3.69 (t, J =8.0 Hz, H-6, coupled to H-5 and to geminal H-6 with the same coupling constant), 3.63 (m, $J_{4,5}$ =10.0 Hz, H-4), 3.62 (t, J =8.0 Hz, H-6, coupled to H-5 and to geminal H-6 with the same coupling constant), 3.38 (m, H-5), 1.23-0.87 (s, 39H).

IR (CDCl_3) 3453, 2938, 2862 cm^{-1}

HRMS (FAB) calc'd. for: $\text{C}_{51}\text{H}_{72}\text{O}_8\text{Si}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$): 891.4664. Found: 891.4645.