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Conversion of D-Glucose to Cyclitol with hydroxymethyl Substituent via Intramolecular Silyl Nitronate Cycloaddition Reaction: Application to Total Synthesis of (+)-Cyclophellitol

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Instrumentation. IR spectra were recorded on a Horiba Fourier transform infrared spectrophotometer Model FT-210 instrument. ¹H NMR and ¹³C NMR spectra were recorded on Varian Mercury-300 (300 MHz for proton and 75 MHz for carbon-13) instrument. The chemical shifts are given in δ units relative to internal CHCl₃ (7.26 ppm for ¹H) or CDCl₃ (77 ppm for ¹³C). All NMR experiments were performed using deuteriochloroform as a solvent unless otherwise indicated. Optical rotations were measured on a digital polarimeter (Horiba SEPA-300) using a 3.5 mm x 0.5 dm pyrex cell. Mass spectra were obtained on a JEOL JMS-DX303 instrument relying on a JMA-DA5000 mass data system. Elemental analyses were made with a Perkin–Elmer 2400 CHN Elemental Analyzer.

Analytical Procedure and Data Presentation. Analytical thin layer chromatography was performed on Merck pre-coated silica gel 60 F-254 (0.25 mm thickness). ¹H NMR spectral data were indicated in the form: δ -value of signal (peak multiplicity, coupling constant (if any) and integrated number of protons). Splitting patterns are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

General Reaction Procedure. All reactions, unless otherwise noted, were conducted under a nitrogen or an argon atmosphere. Liquid reagents were transferred via a dry hypodermic syringe from sure seal bottles to a reaction flask through a rubber septa wired on to the reaction flask. The septa can also serve to permit evacuation to eliminate air and introduce the inert gas by means of a steady stream of inert gas flowing system. Organic extracts were concentrated by evaporation with a rotary evaporator evacuated at around 60 mmHg. Column chromatography, unless otherwise specified, was performed on a Merck silica gel 60 7734 using an appropriate ratio of ethyl acetate-hexane mixed solvent and abbreviated as CC.

Materials. Unless otherwise noted, materials were obtained from commercial suppliers and reagent grade materials were used without further purification. Toluene, triethylamine (Et_3N), dichloromethane (CH_2Cl_2), and acetonitrile (MeCN) were freshly distilled from CaH_2 prior to use. Methanol and Ethanol were distilled from magnesium turnings under argon. Tetrahydrofuran (THF) purchased from Kanto Chemical Co., Inc is dehydrated and stabilizer-free grade and was used as received.

Methyl-4,6-*O*-benzylidene-2,3-di-*O*-benzyl- α -D-glucopyranoside (2). To a solution of methyl- α -D-glucopyranoside (1.65 g, 8.51 mmol) in THF (30 mL) were added benzaldehyde dimethyl acetal (1.66 mL, 11.1 mmol) and *p*-toluenesulfonic acid (161 mg, 0.85 mmol) at room temperature. The mixture was stirred at room temperature for 2 days. The reaction was neutralized with Et_3N (0.24 mL) and concentrated to give a crude solid, which on CC, gave methyl-4,6-*O*-benzylidene- α -D-glucopyranoside (2.17 g, 91 %) as a colorless viscous gum.

To a solution of methyl-4,6-*O*-benzylidene- α -D-glucopyranoside (2.08 g, 7.42 mmol) in DMF (30 mL) was added NaH (60 % in oil, 742 mg, 18.6 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h followed by the addition of benzyl bromide (2.65 mL 18.6 mmol). The reaction was stirred at room temperature for 12 h, quenched by the addition of water, and extracted with hexane-AcOEt (3:1) mixed solvent (3 times). The combined extracts were dried over Na_2SO_4 and concentrated to give a crude viscous gum, which on CC, gave **2** as a colorless viscous gum (3.01 g, 88 %). ^1H NMR δ 7.58–7.22 (m, 15H), 5.55 (s, 1H), 4.92 and 4.83 (ABq, J = 11.3 Hz, 2H), 4.86 and 4.70 (ABq, J = 12.1 Hz, 2H), 4.60 (d, J = 3.8 Hz, 1H), 4.28 (dd, J = 9.9, 4.4 Hz, 1H), 4.05 (dd, J = 9.3, 9.1 Hz, 1H), 3.84 (ddd, J = 9.9, 9.3, 4.2 Hz, 1H), 3.71 (dd, J = 9.8, 9.5 Hz, 1H), 3.40 (s, 3H); ^{13}C NMR δ 138.6, 138.1, 137.3, 128.9, 128.4, 128.2, 128.1, 128.0, 127.9, 127.5, 125.9, 101.2, 99.2, 82.1, 79.1, 78.5, 75.3, 73.7, 68.9, 62.3, 55.3; $[\alpha]_{\text{D}}^{32}$ +15.7 (c 2.38, CHCl_3); IR (film) 3494, 1054 cm^{-1} ; R_f = 0.63 (hexane/AcOEt = 3:1).

Methyl-2,3,6-tri-*O*-benzyl- α -D-glucopyranoside (4) and Methyl-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (5). To a solution of **2** (1.41 g, 3.05 mmol) in CH_2Cl_2 (20 mL) was added borane-methyl sulfide complex (10 M in dimethyl sulfide, 0.34 mL, 3.4 mmol) at 0 °C. The mixture was stirred at room temperature for 3 h, followed by the addition of boron trifluoride diethyl etherate (0.43 mL 3.36 mmol) at 0 °C. The mixture was stirred at room temperature for 30 min, quenched by the addition of EtOH, and concentrated to give a crude solid, which on CC, gave **4** (288 mg, 20 %) and **5** (980 mg, 68 %) as a colorless viscous gum, respectively.

Data for **4**: ^1H NMR δ 7.38–7.18 (m, 15H), 4.78–4.45 (m, 7H), 3.75 (dd, $J = 9.3, 8.8$ Hz, 1H), 3.71–3.62 (m, 3H) 3.60 (dd, $J = 9.3, 8.8$ Hz, 1H), 3.50 (dd, $J = 9.3, 3.6$ Hz, 1H), 3.42 (s, 3H), 2.42 (br, 1H); ^{13}C -NMR δ 138.7, 137.9, 137.9, 128.5, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.6, 127.5, 98.0, 81.3, 79.5, 75.3, 73.5, 73.0, 70.5, 69.8, 69.3, 55.2; $[\alpha]_{\text{D}}^{22} +13.4$ (c 2.97, CHCl_3); IR (film) 3494, 1054 cm^{-1} ; $R_f = 0.66$ (hexane/AcOEt = 1:1); exact mass, m/z 464.21976 (calcd for $\text{C}_{28}\text{H}_{32}\text{O}_6$ m/z 464.21989).

Data for **5**: ^1H NMR δ 7.42–7.21 (m, 15H), 5.05–4.58 (m, 6H), 4.57 (d, $J = 3.6$ Hz, 1H), 4.02 (dd, $J = 9.3, 9.1$ Hz, 1H), 3.84–3.37 (m, 5H), 3.38 (s, 3H), 1.56 (t, $J = 6.0$ Hz 1H); ^{13}C NMR δ 138.6, 138.02, 138.00, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 98.1, 81.9, 79.9, 77.3, 75.7, 75.0, 73.4, 70.6, 61.7, 55.1; $[\alpha]_{\text{D}}^{19} +19.2$ (c 2.47, CHCl_3); IR (film) 3502, 1072 cm^{-1} ; $R_f = 0.53$ (hexane/AcOEt = 1:1).

(2S,3S,4S,5R)-2,3,4-tri-O-benzyl-1-nitrohept-6-ene-2,3,4,5-tetraol (6a) and **(2R,3S,4S,5R)-2,3,4-tri-O-benzyl-1-nitrohept-6-ene-2,3,4,5-tetraol (6b)**. To a solution of **5** (1.16 g, 2.41 mmol) and triphenylphosphine (944 mg, 3.62 mmol) in CH_2Cl_2 (15 mL) was added carbon tetrabromide (1.20 g 3.62 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h, quenched by the addition of water, and extracted with AcOEt (3 times). The combined extracts were dried with Na_2SO_4 and concentrated to give a crude oil, which on CC, gave a bromide (1.15 g, 90 %) as a colorless oil. To a solution of the bromide (1.21 g, 2.11 mmol) in 80 % EtOH (12 mL) was added zinc powder (500 mg, 7.64 mmol) at room temperature, and the mixture was stirred at 90 °C for 30 min. The mixture was filtered through a pad of celite using AcOEt, and the filtrate was concentrated to give crude aldehyde **3** as an oil. To a solution of crude **3** and nitromethane (0.23 mL, 4.22 mmol) in THF (10 mL) was added 1,1,3,3-tetramethylguanidine (0.05 mL, 0.40 mmol) at 0 °C. The mixture was stirred at room temperature for 12 h, quenched by the addition of saturated aqueous solution of NH_4Cl , and extracted with AcOEt (3 times). The combined extracts were dried with Na_2SO_4 and concentrated to give a crude oil, which on CC, gave an inseparable mixture of **6a** and **6b** (557 mg, 59 %) as a colorless oil. ^1H NMR δ 7.44–7.20 (m, 15H), 6.08–5.84 (m, 1H), 5.48–5.35 (m, 2H), 4.85–4.10 (m, 10H), 3.85 (dd, $J = 6.8, 3.6$ Hz, 1H), 3.72–3.62 (m, 2H), 3.62 (d, $J = 4.7$ Hz, 1H), 3.13 (d, $J = 5.8, 0.5$ H); IR (film) 3500, 1075 cm^{-1} ; $R_f = 0.50$ (hexane/AcOEt = 3:1).

(1R,2R,3S,4S,5S)-2,3,4-tris(benzyloxy)-5-hydroxy-7-aza-8-oxabicyclo[4.3.0]non-6-ene (9). To a solution of **6** (1.17 g, 2.61 mmol), DMAP (32 mg, 0.26 mmol) and Et_3N (1.8 mL, 13.0 mmol) in CH_3CN (10 mL) was added chlorotrimethylsilane (1.0 mL, 7.8 mmol) at 0 °C. The mixture was stirred at room temperature for 12 h, followed by the addition of *p*-

toluenesulfonic acid (50 mg, 0.26 mmol). The mixture was stirred at room temperature for 3 h and, then, neutralized with Et₃N (0.03 mL, 0.26 mol). To the mixture was added water, and the resulting mixture was extracted with AcOEt (3 times). The combined extracts were dried with Na₂SO₄ and concentrated to give a crude oil, which on CC, gave **9** (702 mg, 54 %) as a yellow oil and unchanged **6b** (93 mg, 8 %). Data for **9**: ¹H NMR δ 7.38–7.21 (m, 15H), 4.99–4.58 (m, 6H), 4.78 (d, *J* = 3.6 Hz, 1H), 4.41 (dd, *J* = 10.4, 8.8 Hz, 1H), 3.98 (dd, *J* = 9.6, 9.3 Hz, 1H), 3.90 (dd, *J* = 8.8, 7.9 Hz, 1H), 3.68 (ddd, *J* = 10.4, 9.6, 7.9 Hz, 1H), 3.53 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.36 (dd, *J* = 9.6, 9.3 Hz, 1H), 2.82 (br, 1H); ¹³C NMR δ 160.0, 138.2, 137.8, 137.1, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 82.0, 81.4, 81.3, 76.1, 74.5, 73.2, 73.0, 63.3, 50.2; [α]_D³⁰ –10.3 (c 2.41, CHCl₃); IR (film) 3450, 1734 cm^{–1}; *R*_f = 0.67 (hexane/AcOEt = 1:1); exact mass, *m/z* 459.20441 (calcd for C₂₈H₂₉NO₅ *m/z* 459.20457).

Data for **6b**: ¹H NMR δ 7.42–7.18 (m, 15H), 6.05–5.86 (m, 1H), 5.42–5.26 (m, 1H), 4.80–4.15 (m, 9H), 4.06 (dd, *J* = 7.1, 3.3 Hz, 7.9H), 3.80 (dd, *J* = 6.9, 3.6 Hz, 1H), 3.61 (dd, *J* = 6.9, 2.8 Hz, 1H), 3.20 (d, *J* = 6.9 Hz, 1H); ¹³C NMR δ 137.6, 137.4, 137.3, 134.5, 128.5, 128.4, 128.3, 128.2, 128.2, 128.0, 127.9, 127.6, 119.2, 80.9, 78.8, 78.5, 78.1, 74.8, 74.6, 70.8, 68.2; [α]_D²² –7.0 (1.03, CHCl₃); IR (film) 3398, 3031, 1725, 1560, 1063, 915 cm^{–1}; *R*_f = 0.87 (hexane/AcOEt = 1:1).

(1*R*,2*R*,3*S*,4*S*,5*S*)-2,3,4-tris(benzyloxy)-5-(*tert*-butyldimethylsiloxy)-7-aza-8-oxabicyclo[4.3.0]non-6-ene (10). To a solution of **9** (402 mg, 0.87 mmol) and Et₃N (0.36 mL, 2.61 mmol) in CH₂Cl₂ (5 mL) was added TBDMSOTf (0.24 mL, 1.04 mmol) at –78 °C. The mixture was stirred at room temperature for 12 h, quenched by the addition of water and extracted with AcOEt. The combined extracts were dried with Na₂SO₄ and concentrated to give an oil, which on CC, gave **10** (478 mg, 95 %) as yellow oil. ¹H NMR δ 7.58–7.36 (m, 15H), 5.08–4.66 (m, 7H), 4.41 (dd, *J* = 10.7, 8.5 Hz, 1H), 4.12 (t, *J* = 9.3, 9.1 Hz, 1H), 3.85 (dd, *J* = 8.5, 8.2 Hz, 1H), 3.71 (ddd, *J* = 10.2, 8.5, 8.2 Hz, 1H), 3.38–3.34 (m, 2H), 0.90 (s, 9H), 0.12 (s, 3H), 0.05 (s, 3H); ¹³C NMR δ 156.2, 140.0, 138.4, 137.9, 128.5, 128.3, 128.1, 128.0, 127.7, 127.6, 82.1, 82.0, 81.7, 75.9, 74.6, 73.2, 72.5, 64.4, 50.9, 25.6, 18.1, –3.6, –4.9; [α]_D¹⁹ +19.2 (c 3.40, CHCl₃); IR (film) 1738, 1099, 837 cm^{–1}; *R*_f = 0.83 (hexane/AcOEt = 2:1).

(1*S*,2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-Tris(benzyloxy)-6-(hydroxymethyl)cyclohexane-1,2-diol (12a) and **(1*R*,2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-(hydroxymethyl)cyclohexane-1,2-diol (12b)**. To a solution of **10** (29 mg, 0.049 mmol) in CH₃CN–H₂O (3:1, 4 mL) was added Mo(CO)₆ (20 mg, 0.076 mmol) at room temperature. The mixture was stirred at 90 °C for 1.5

h, filtered through a celite pad using AcOEt. The filtrate was concentrated to give an oil, which on CC, gave ketone **11** (20 mg) as a colorless oil. The ketone **11** (13 mg) was dissolved in toluene (2 mL) and was added DIBALH (1M in toluene, 0.02 mL) at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and carefully quenched at $0\text{ }^{\circ}\text{C}$ by the addition of water. The mixture was filtered through a celite pad using AcOEt and the filtrate was concentrated to give a crude solid, which on CC, gave a colorless oil. This oil was dissolved in THF (2 mL), and to this was added TBAF in THF (1 M, 0.04 mL, 0.04 mmol) at room temperature. The mixture was stirred at room temperature for 4 h, diluted with water, and extracted with AcOEt (3 times). The combined extracts were dried with Na_2SO_4 and concentrated to give a colorless gum, which on CC, gave **12a** (10 mg, 55 %) and **12b** (3 mg, 17 %) a colorless solid, respectively. Data for **12a**: ^1H NMR δ 7.28-7.12 (m, 15H), 4.88-4.45 (m, 6H), 4.06 (dd, $J = 2.8, 2.7\text{ Hz}$, 1H), 3.90-3.78 (m, 2H), 3.68 (dd, $J = 10.7, 4.7\text{ Hz}$, 1H), 3.45 (dd, $J = 11.0, 2.7\text{ Hz}$, 1H), 3.32 (dd, $J = 9.7, 2.7\text{ Hz}$, 1H), 3.18 (dd, $J = 9.7, 11.0\text{ Hz}$, 1H), 2.05–1.95 (ddt, $J = 10.7, 9.7, 4.7\text{ Hz}$, 1H); ^{13}C NMR δ 138.7, 138.2, 137.8, 128.6, 128.4, 128.3, 128.1, 128.0, 127.82, 127.79, 127.7, 127.6, 127.5, 82.8, 80.0, 77.6, 75.6, 75.1, 72.5, 70.3, 69.1, 60.6, 44.1; $[\alpha]_{\text{D}}^{24} +14.6$ (c 3.73, CHCl_3); IR (film) 3404, 2805 cm^{-1} ; $R_f = 0.36$ (AcOEt); exact mass, m/z 464.21965 (calcd for $\text{C}_{28}\text{H}_{32}\text{O}_6$ m/z 464.21989).

Data for **12b**: ^1H NMR δ 7.42-7.25 (m, 15H), 4.98-4.65 (m, 6H), 4.20 (dd, $J = 3.0, 2.5\text{ Hz}$, 1H), 4.05 (dd, $J = 10.8, 3.6\text{ Hz}$, 1H), 4.00 (dd, $J = 3.0, 2.8\text{ Hz}$, 1H), 3.98-3.05 (m, 3H), 3.80 (dd, $J = 10.8, 2.5\text{ Hz}$, 1H), 3.75 (br, 1H), 2.72 (br, 1H), 2.08-1.95 (m, 1H) ^{13}C NMR δ 138.8, 138.5, 138.1, 128.5, 128.4, 128.33, 128.30, 127.9, 127.8, 127.5, 83.9, 80.7, 75.7, 75.6, 74.9, 73.0, 72.9, 69.9, 62.8, 41.4; $[\alpha]_{\text{D}}^{19} +51.2$ (3.11, CHCl_3); IR (film) 3544, 2850 cm^{-1} ; $R_f = 0.46$ (AcOEt).

(3R,4R,5R,6S)-3-Hydroxymethyl-4, 5, 6-tris(benzyloxy)cyclohexene (14). A solution of **12a** (35 mg, 0.076 mmol) in triethyl orthformate (2 mL) was stirred at $130\text{ }^{\circ}\text{C}$ for 1 h. To the solution was added acetic anhydride (1.0 mL, 6.0 mmol) at room temperature and the reaction was stirred at $140\text{ }^{\circ}\text{C}$ for 4 days. The mixture was concentrated in vacuo to give an oil, which on CC, gave **13** (26 mg) as a colorless oil. To a solution of **13** (26 mg) in MeOH (2 mL) was added K_2CO_3 (2 mg, 0.015 mmol). The mixture was stirred at room temperature for 1.5 h, quenched by the addition of saturated aqueous solution of NH_4Cl , and extracted with AcOEt (3 times). The combined extracts were dried with Na_2SO_4 and concentrated to give a crude viscous gum, which on CC, gave **14** (18 mg, 57 % from **12a**) as a colorless viscous gum. ^1H NMR δ 7.40–7.22 (m, 15H), 5.76 (dt, $J = 10.0, 2.5\text{ Hz}$, 1H), 5.55 (dt, $J = 10.0, 1.8\text{ Hz}$, 1H),

5.01 and 4.66 (ABq, $J = 11.2$ Hz, 2H), 4.94 (s, 2H), 4.70 (s, 2H), 4.25 (m, 1H) 3.85 (dd, $J = 10.0$, 7.8 Hz, 1H), 3.70-3.66 (m, 3H), 2.52-2.42 (m 1H) 1.47 (br s, 1H), ^{13}C NMR δ 138.7, 138.2, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 85.1, 80.8, 78.5, 75.3, 75.1, 72.1, 63.3, 45.7 (^1H and ^{13}C -NMR data are completely consistent with those reported¹); $[\alpha]_{\text{D}}^{27} +103$ (c 0.566, CHCl_3) [lit.¹ $[\alpha]_{\text{D}}^{23} +104.5$ (c 1.92, CHCl_3)]; IR (film) 3442, 2878, 1454 cm^{-1} ; $R_f = 0.36$ (hexane/AcOEt = 2:1).

(1R,6R,7R,8S,9R,10R)-3,3-Dimethyl-7,8,9-tris(benzyloxy)-10-methansulfonyloxy-2,4-dioxabicyclo[4.4.0]decane (16). To a mixture of **12b** (90 mg, 0.19 mmol), 2,2-dimethoxypropane (0.03 mL, 0.24 mmol) and 4Å MS (10 mg) in CH_2Cl_2 (3 mL) was added *p*-toluenesulfonic acid (7 mg, 0.037 mmol). The mixture was stirred at room temperature for 30 min. The reaction was quenched by the addition of water and extracted with AcOEt (3 times). The combined extracts were dried with Na_2SO_4 and concentrated to give oil, which on CC, gave a acetonide product (81 mg, 92 %) as a colorless oil. To a solution of this acetonide product (21 mg, 0.043 mmol), Et_3N (0.03 mL, 0.21 mmol), and DMAP (1 mg, 0.008 mmol) in THF (2 mL) was added methanesulfonyl chloride (0.01 mL, 0.13 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h, quenched with water, and extracted with AcOEt (3 times). The combined extracts were dried with Na_2SO_4 and concentrated to give an oil, which on CC, gave **16** (24 mg, 96 %) as a colorless oil. ^1H NMR δ 7.42-7.22 (m, 15H), 5.14-4.68 (m, 7H), 4.35 (t, $J = 3.0$, Hz, 1H), 4.20-3.82 (m, 5H), 3.00 (s, 3H), 1.80 (d, $J = 10.1$ Hz, 1H); ^{13}C NMR δ 183.4, 138.3, 137.4, 128.43, 128.38, 128.36, 128.2, 128.0, 127.9, 127.7, 127.6, 99.4, 82.7, 78.8, 78.4, 76.9, 76.0, 75.7, 73.8, 68.9, 59.5, 38.6, 29.5, 18.8; $[\alpha]_{\text{D}}^{29} +5.73$ (c 2.66, CHCl_3); IR (film) 1174, 1101 cm^{-1} ; $R_f = 0.70$ (hexane/AcOEt = 1:1); exact mass, m/z 582.22861 (calcd for $\text{C}_{32}\text{H}_{38}\text{O}_8\text{S}$ m/z 582.22874).

(+)-2,3,4,-Tri-*O*-benzylcycophellitol (15) To a solution of **16** (72 mg, 0.12 mmol) in MeOH (2 mL) was added *p*-toluenesulfonic acid (1.3 mg, 0.078 mmol) at room temperature. The mixture was stirred at room temperature for 1.5 h, followed by the addition of Et_3N (0.01 mL, 0.078 mmol). The mixture was concentrated and purified by CC to afford a diol (63 mg, 0.12 mmol) as a colorless solid. To a solution of the diol (18 mg, 0.034 mmol) in CH_2Cl_2 (2 mL) was added NaOMe (5 mg, 0.093 mmol). The mixture was stirred at room temperature for 1 h, quenched by addition of NH_4Cl and extracted with AcOEt (3 times). The combined extracts were dried with Na_2SO_4 and concentrated to give a crystalline white solid, which on CC, gave **15** (14 mg, 94 %) as a crystalline white solid: mp 102–103.5 °C (recrystallized from diethyl ether/hexane) [lit.¹ mp 101 °C; lit.² mp 92–93 °C]; ^1H NMR δ 7.40–7.20 (m, 15H),

4.95 and 4.55 (Abq, $J = 11.0$ Hz, 2H), 4.88–4.85 (m, 2H), 4.81 and 4.73 (Abq, $J = 11.3$ Hz, 2H), 3.96 (dt, $J = 11.0$, 4.7 Hz, 1H), 3.92–3.82 (m, 2H), 3.59 (dd, $J = 10.2$, 8.0 Hz, 1H), 3.47 (dd, $J = 10.2$, 9.9 Hz, 1H), 3.36–3.32 (m, 1H), 3.17 (d, $J = 3.6$ Hz, 1H), 2.22–2.14 (m 1H), 2.45(br 1H). ^{13}C NMR δ 138.5, 138.0, 137.5, 128.53, 128.50, 128.3, 128.1, 128.8, 127.94, 127.90, 127.8, 127.6, 84.9, 79.8, 75.6, 75.5, 75.4, 73.1, 62.8, 55.9, 52.9, 43.9 (^1H and ^{13}C -NMR data are completely consistent with those reported¹); $[\alpha]_{\text{D}}^{30} +71.2$ (c 1.62, CHCl_3) [lit.¹ $[\alpha]_{\text{D}}^{23} +71.7$ (c 1.62, CHCl_3); lit.² $[\alpha]_{\text{D}} +71.0$ (c 0.9, CHCl_3); IR (film) 3029, 2894, 1454, 1062 cm^{-1} ; $R_f = 0.37$ (hexane/AcOEt = 1:1).

(+)-Cycophellitol (1). **1** was prepared from **14** via **15** after the reported procedure¹: **1** was also obtained from **16** via **15**: mp 147–148 °C (recrystallized from EtOAc) [lit.¹ mp 145 °C; lit.^{3,4} mp 149–151 °C]; ^1H NMR (CD_3OD) δ 4.00 (dd, $J = 10.4$, 4.4 Hz, 1H), 3.72–3.60 (m, 2H), 3.41 (m, 1H), 3.20 (dd, $J = 9.9$, 8.0 Hz, 1H), 3.10–3.00 (m 1H), 2.01–1.91 (m, 1H) (^1H -NMR data are completely consistent with those reported¹); ^{13}C NMR (CD_3OD) 78.5, 72.8, 68.8, 62.5, 57.4, 56.0, 45.9; $[\alpha]_{\text{D}}^{30} +103$ (c 0.80, H_2O) [lit.¹ $[\alpha]_{\text{D}}^{23} +102$ (c 0.70, H_2O); lit.² $[\alpha]_{\text{D}} +97.0$ (c 0.35, H_2O); lit.^{3,4} $[\alpha]_{\text{D}} +103$ (c 0.50, H_2O); IR (film) 3360, 2895, 1081 cm^{-1} ; $R_f = 0.63$ ($\text{CH}_2\text{Cl}_2/\text{MeOH} = 1:1$).

(2R,3R,4R,5S)-2-Hydroxymethyl-3,4,5-tris(benzyloxy)cyclohexanone (19). The compound **19** was prepared by the similar procedure as that for **11** from acetate **17** or mesylate **18**. ^1H NMR δ 7.38–7.23 (m, 15H), 4.98–4.82 (m, 3H), 4.68–4.60 (m, 3H), 4.07–3.95 (m, 2H), 3.84–3.62 (m, 3H), 2.78 (dd, $J = 4.9$, 14.7 Hz, 1H), 2.70 (ddd, $J = 3.0$, 3.6, 11.5 Hz, 1H), 2.60 (dd, $J = 14.7$, 9.9, Hz, 1H), 2.38 (br, 1H); ^{13}C NMR δ 207.6, 138.1, 137.8, 137.6, 128.5, 128.4, 128.0, 127.92, 127.86, 127.8, 85.6, 77.3, 75.9, 75.0, 74.8, 72.3, 58.2, 55.7, 44.8; $[\alpha]_{\text{D}}^{21} +12.8$ (c 0.570, CHCl_3); IR (film) 3467, 1716, 1070 cm^{-1} ; $R_f = 0.67$ (hexane/AcOEt = 1:1).

References:

- (1) Trost, B. M.; Patterson, D. E.; Hembre, E. J. *Chem. Eur. J.* **2001**, 7, 3768–3775; (2) Ziegler, F.; Wang, Y. *J. Org. Chem.* **1998**, 63, 7920–7930; (3) Tatsuta, K.; Niwata, Y.; Umezawa, K.; Toshima, K.; Nakata, M. *Carbohydr. Res.* **1991**, 222, 189–203. (4) Atsumi, S.; Umezawa, K.; Iinuma, H.; Naganawa, H.; Nakamura, H.; Iitaka, Y.; Takeuchi, T. *J. Antibiot.* **1990**, 43, 49–53.

<p>PULSE SEQUENCE</p> <p>Relax. delay 1.502 sec</p> <p>Pulse 45.0 degrees</p> <p>Acq. time 3.498 sec</p> <p>Width 4500.5 Hz</p> <p>32 repetitions</p>	<p>OBSERVE H1, 300.0836740</p>	<p>DATA PROCESSING</p> <p>FT size 32768</p> <p>Total time 2 minutes</p>	<p>YS-Kanngengob</p> <p>Pulse Sequence: s2pul</p> <p>Solvent: CDCl3</p> <p>Ambient temperature</p> <p>Mercury-300 "varian"</p>
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<p>PULSE SEQUENCE Relax. delay 0.501 sec Pulse 45.0 degrees Acq. time 1.499 sec Width 18865.6 Hz 160 repetitions</p>	<p>OBSERVE C13, 75.4561032 DECOUPLE H1, 300.0851346 Power 36 dB continuously on WALTZ-16 modulated</p>	<p>DATA PROCESSING Line broadening 1.0 Hz Ft size 65536 Total time 5 minutes</p>	<p>Chemical Structure: </p>	<p>YS-kanungenob Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"</p>
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<p>PULSE SEQUENCE</p> <p>Relax. delay 1.502 sec</p> <p>Pulse 45.0 degrees</p> <p>Acq. time 3.498 sec</p> <p>Width 4500.5 Hz</p> <p>12 repetitions</p>	<p>OBSERVE H1, 300.0836523</p>	<p>DATA PROCESSING</p> <p>FT size 32768</p> <p>Total time 1 minute</p>	<p>YS-II-74</p> <p>Pulse Sequence: s2pul</p> <p>Solvent: CDCl₃</p> <p>Ambient temperature</p> <p>Mercury-300 *varian*</p>
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<p>PULSE SEQUENCE Relax. delay 0.501 sec Pulse 45.0 degrees Acq. time 1.499 sec Width 18865.6 Hz 192 repetitions</p>	<p>OBSERVE C13, 75.4561004 DECOUPLE H1, 300.0851346 Power 36 dB continuously on WALTZ-16 modulated</p>	<p>DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 6 minutes</p>	<div data-bbox="1260 627 1388 896"> </div> <div data-bbox="1260 266 1388 627"> <p>OH</p> <p>Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"</p> </div>
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PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 32 repetitions	OBSERVE H1, 300.0836523	DATA PROCESSING FT size 32768 Total time 2 minutes	<div> <p>9</p> </div>	YS-II-73B Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"
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<p>PULSE SEQUENCE Relax. delay 0.501 sec Pulse 45.0 degrees Acq. time 1.499 sec Width 18865.6 Hz 192 repetitions</p>	<p>OBSERVE C13, 75.4561015 DECOUPLE H1, 300.0851346 Power 36 dB continuously on WALTZ-16 modulated</p>	<p>DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 6 minutes</p>	<p>Chemical structure of compound 9: </p>	<p>YS-II-103 Pulse sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"</p>
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PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 16 repetitions	OBSERVE H1, 300.0836525 DATA PROCESSING FT size 32768 Total time 1 minute	YS-III-26 Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"	10
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<p>PULSE SEQUENCE Relax. delay 0.501 sec Pulse 45.0 degrees Acq. time 1.499 sec Width 18655.6 Hz 144 repetitions</p>	<p>OBSERVE C13, 75.4560975 DECOUPLE H1, 300.0851346 Power 36 dB continuously on WALTZ-16 modulated</p>	<p>DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 4 minutes</p>	<p>YS-III-5</p> <div data-bbox="1252 600 1396 862"> </div> <p>Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"</p>
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PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 32 repetitions	OBSERVE H1, 300.0836823	DATA PROCESSING FT size 32768 Total time 2 minutes	YS-III-14 Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"
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PULSE SEQUENCE Relax. delay 0.501 sec Pulse 45.0 degrees Acq. time 1.499 sec Width 18865.6 Hz 160 repetitions	OBSERVE C13, 75.4560998 DECOUPLE H1, 300.0851346 Power 36 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 5 minutes	12a	YS-II-191C Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"
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PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 12 repetitions	OBSERVE H1, 300.0836523	DATA PROCESSING FT size 32768 Total time 1 minute	YS-II-191B Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"
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<p>PULSE SEQUENCE</p> <p>Relax. delay 0.501 sec</p> <p>Pulse 45.0 degrees</p> <p>Acq. time 1.499 sec</p> <p>Width 18865.6 Hz</p> <p>96 repetitions</p>	<p>OBSERVE C13, 75.4560998</p> <p>DECOUPLE H1, 300.0851346</p> <p>Power 36 dB</p> <p>continuously on</p> <p>WALTZ-16 modulated</p>	<p>DATA PROCESSING</p> <p>Line broadening 1.0 Hz</p> <p>FT size 65536</p> <p>Total time 3 minutes</p>	<div data-bbox="1276 627 1436 896"> <chem>O[C@H]1[C@@H](OC(=O)c2ccccc2)[C@H](O)[C@@H](OC(=O)c3ccccc3)[C@H](O)[C@H]1O</chem> <p>12b</p> </div>	<p>YS-II-191B</p> <p>Pulse Sequence: s2pul</p> <p>Solvent: CDCl3</p> <p>Ambient temperature</p> <p>Mercury-300 "varian"</p>
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<p>PULSE SEQUENCE</p> <p>Relax. delay 1.502 sec</p> <p>Pulse 45.0 degrees</p> <p>Acq. time 3.498 sec</p> <p>Width 4500.5 Hz</p> <p>28 repetitions</p>	<p>OBSERVE H1, 300.0836523</p>	<p>DATA PROCESSING</p> <p>FT size 32768</p> <p>Total time 2 minutes</p>	<p>Chemical structure of 14:</p>	<p>YS-III-25</p> <p>Pulse Sequence: s2pul</p> <p>Solvent: CDCl₃</p> <p>Ambient temperature</p> <p>Mercury-300 "varian"</p>
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PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 16 repetitions	OBSERVE H1, 300.0836523	DATA PROCESSING F1 size 32768 Total time 1 minute	16	YS-III-33A Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"
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PULSE SEQUENCE Relax. delay 0.501 sec Pulse 45.0 degrees Acq. time 1.499 sec Width 18865.6 Hz 176 repetitions	OBSERVE C13, 75.4561015 DECOUPLE H1, 300.0851346 Power 36 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 5 minutes	YS-III-33A Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"
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<p>PULSE SEQUENCE</p> <p>Relax. delay 1.502 sec</p> <p>Pulse 45.0 degrees</p> <p>Acq. time 3.498 sec</p> <p>Width 4500.5 Hz</p> <p>8 repetitions</p>	<p>OBSERVE H1, 300.0836531</p>	<p>DATA PROCESSING</p> <p>FT size 32768</p> <p>Total time 1 minute</p>	<p>YS-III-64</p> <p>Pulse Sequence: s2pul</p> <p>Solvent: CDCl3</p> <p>Ambient temperature</p> <p>Mercury-300 "varian"</p>	<p>15</p>
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<p>PULSE SEQUENCE Relax. delay 0.501 sec Pulse 45.0 degrees Acq. time 1.499 sec Width 18865.6 Hz 2128 repetitions</p>	<p>OBSERVE C13, 75.4560958 DECOUPLE H1, 300.0851346 Power 36 dB continuously on WALTZ-16 modulated</p>	<p>DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 70 minutes</p>
<p>YS-III-44B Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"</p>	<p>Chemical Structure 15</p>

<p>ULSE SEQUENCE</p> <p>Relax. delay 1.502 sec</p> <p>Pulse 45.0 degrees</p> <p>Acq. time 3.498 sec</p> <p>Width 4500.5 Hz</p> <p>16 repetitions</p>	<p>OBSERVE H1, 300.0848363</p>	<p>DATA PROCESSING</p> <p>FT size 32768</p> <p>Total time 1 minute</p>	<p>cyclophellitol</p> <p>Pulse Sequence: s2pul</p> <p>Solvent: CD3OD</p> <p>Ambient temperature</p> <p>Mercury-300 "varian"</p>
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<p>PULSE SEQUENCE Relax. delay 0.501 sec Pulse 45.0 degrees Acq. time 1.499 sec Width 18865.6 Hz 13648 repetitions</p>	<p>OBSERVE C13, 75.4562848 DECOUPLE H1, 300.0863170 Power 36 dB continuously on WALTZ-16 modulated</p>	<p>DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 7.6 hours</p>	<p>YS-III-45 Pulse Sequence: s2pul Solvent: CD3OD Ambient temperature Mercury-300 "varian"</p>
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PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 8 repetitions	OBSERVE H1, 300.0836523	DATA PROCESSING F1 size 32768 Total time 1 minute	<div> <p>19</p> </div>	YS-II-110B Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"
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PULSE SEQUENCE Relax. delay 0.501 sec Pulse 45.0 degrees Acq. time 1.499 sec Width 1865.6 Hz 272 repetitions	OBSERVE C13, 75.4560969 DECOUPLE H1, 300.0851346 Power 36 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 9 minutes	YS-II-110B Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"
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