Supplementary Material

Osmium Catalysed Dihydroxylation of 1,2-Dioxines: A New Entry for Stereoselective Sugar Synthesis.

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¹H NMR

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General Methods. Solvents were dried by appropriate methods wherever needed. Thin-layer chromatography (TLC) used aluminium sheets coated with silica gel 60 F₂₅₄ (40 x 80 mm) and visualized under 254 nm light, or developed in vanillin or permanganate dip. Flash chromatography was conducted using silica gel 60 of particle size 0.040-0.063 mm. Melting points were uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on either a 300 MHz or 600 MHz instrument. NMR spectra were recorded in CDCl₃ solution using TMS (0 ppm) and CDCl₃ (77.0 ppm) as internal standards, and D₂O using 3-(Trimethylsilyl)propionic acid sodium salt (TMSPSA) as an external zero for both ¹H and ¹³C NMR. NMR spectra recorded in CD₃OD were calibrated to CD₃OD (3.31 and 49.0 ppm), and those in *d*₆-DMSO were calibrated to *d*₆-DMSO (2.50 and 39.5 ppm). All yields refer to isolated material judged to be homogeneous by TLC and NMR spectroscopy.

General procedure for the synthesis of 1,2-dioxines 1. A solution of 1,3-butadiene in CH₂Cl₂ (30 mL / g) was irradiated with 3 x 500 W halogen lamps in the presence of Rose Bengal *bis*(triethylammonium) salt (100 mg) and oxygen for 6 hours. The reaction was performed in a Pyrex flask fitted with an external cooling jacket. The solution was concentrated *in vacuo* and the resulting residue purified by flash chromatography.

TABLE S1. Yields for known 1,2-dioxines **1a-k**.

1,2-dioxine	yield	reference
1a	4.00 g, 41%	1
1c	3.12 g, 52%	2
1e	3.93 g, 55%	2
1f	2.51 g, 52%	3
1g	3.50 g, 51%	4
1h	2.50 g, 61%	2
1k	6.32 g, 91%	5

(±)-*tert*-Butyl(dimethyl)[(3*R*,6*R*)-6-methyl-3,6-dihydro-1,2-dioxin-3-yl]methoxysilane (**1b**). colorless oil (6.67 g, 82%); R_f 0.35 (2:3 CH₂Cl₂/hexane); IR (neat) 1472, 1362, 1256, 1128, 837, 778 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 0.09 (s, 3H), 0.10 (s, 3H), 0.91 (s, 9H), 1.21 (d, J = 6.6 Hz, 3H), 3.68 (dd, J = 11.0, 4.8, Hz, 1H), 3.89 (dd, J = 11.0, 7.2 Hz, 1H), 4.40-4.45 (m, 1H), 4.74 (dq, J = 6.6, 2.1 Hz, 1H), 5.92 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ -5.5, -5.2, 17.8, 18.4, 25.9, 63.8, 74.2, 79.7, 124.2, 130.7; MS m/z (+EI): 245 (M⁺ + H, 100), 211 (32), 185 (9), 142 (18), 57 (53). HRMS calcd. for (M⁺ + Na) C₁₂H₂₄O₃SiNa: 267.1392; Found: 267.1388

(±)-*tert*-Butyl(dimethyl)3-[(3*S*,6*R*)-6-methyl-3,6-dihydro-1,2-dioxin-3-yl]propoxysilane (**1d**). colorless oil (500 mg, 50%); R_f 0.41 (1:1 CH₂Cl₂/hexane); IR (neat): 1464, 1389, 1255, 1100, 836, 776 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 0.05 (s, 6H), 0.89 (s, 9H), 1.27 (d, J = 6.6 Hz, 3H), 1.56-1.77 (m, 4H), 3.58-3.70 (m, 2H), 4.42-4.49 (m, 1H), 4.60-4.69 (m, 1H), 5.83-5.91 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ -5.3, 18.3, 18.4, 25.9, 28.6, 29.5, 62.8, 74.3, 78.1, 127.5, 129.0; MS m/z

(+EI): 273 ($M^+ + H$, 100), 255 (21), 197 (8), 173 (10), 141 (10), 123 (67). HRMS calcd. for ($M^+ + Na$) $C_{14}H_{28}O_3SiNa$: 295.1705; Found: 295.1703.

(±)-*tert*-Butyl[(3*S*,6*R*)-6-([1-(*tert*-butyl)-1,1-dimethylsilyl]oxymethyl)-3,6-dihydro-1,2-dioxin-3-yl]methoxydimethylsilane (1i). colourless oil (2.5 g, 92%), R_f 0.32 (1:1 CH_2Cl_2 /hexane); IR (neat): 1472, 1256, 1131, 1076, 837, 777 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 0.07 (s, 6H), 0.08 (s, 6H), 0.89 (s, 18H), 3.64 (dd, $J = 11.1, 4.2$ Hz, 2H), 3.80 (dd, $J = 11.1, 6.9$ Hz, 2H), 4.55-4.60 (m, 2H), 5.98-6.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.4, -5.2, 18.3, 25.8, 63.3, 79.6, 126.2; MS m/z (+EI): 376 ($M^+ + H$, 2), 342 (10), 318 (15), 300 (50), 73 (100); HRMS calcd. for ($M^+ + Na$) $C_{18}H_{38}O_4SiNa$: 397.2206; Found: 397.2200.

(±)-(3*R*,6*S*)-3,6-Di(bromomethyl)-3,6-dihydro-1,2-dioxine (1j). colourless solid (2.20 g, 63%); mp 101-102 °C; R_f 0.26 (3:7 $CHCl_3$ / hexane); IR (nujol): 1416, 1281, 1225, 1075, 1011, 941 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 3.45 (dd, $J = 10.8, 4.8$ Hz, 2H), 3.56 (dd, $J = 10.8, 6.6$ Hz, 2H), 4.74-4.78 (m, 2H), 6.14 (d, $J = 0.9$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.5, 77.4, 127.1; MS m/z (+EI): 272 (M^+ , 2), 241 (39), 178 (53), 162 (66), 95 (82), 79 (90), 39 (100); Anal. Calcd. for $C_6H_8O_2Br_2$: C, 26.50; H, 2.97; Found: C, 26.75; H, 3.25.

meso-(4R,5R,6S,7S)Decane-4,5,6,7-tetraol (3f). **Figure S1**

Molecular Structure of **3f** showing crystallographic numbering scheme employed. The molecule is disposed about a crystallographic center of inversion; the symmetry operator for *i* is $-x, -y, 1-z$. Selected bond distances and angles: C4-O4 1.4386(11), C5-O5 1.4285(10), C5-C5i 1.5314(16) Å; O4-C4-C3 108.94(7), O4-C4-C5 108.23(7), C3-C4-C5 114.57(7), O5-C5-C4 111.78(7), O5-C5-C5i 106.56(8), C4-C5-C5i 113.75(9)°.

Crystallographic data for 3f.

Intensity data for a colorless crystal were measured at 223(2) K on a Bruker AXS SMART CCD using Mo K α radiation so that $\theta_{\max} = 30.0^\circ$. The structure was solved by direct-methods and refined (anisotropic displacement parameters, H atoms in their calculated positions and a weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.0785P^2 + 0.071P]$ where $P = (F_o^2 + 2F_c^2)/3$ on F^2 with SHELXL-97. The molecular structure (ORTEP, 50% displacement parameters) is shown in Fig. 1 of the Supplementary Material.

Crystal data: $C_{10}H_{22}O_4$, $M = 206.28$, monoclinic, $P2_1/c$, $a = 8.547(3)$, $b = 6.899(2)$, $c = 9.743(3)$ Å, $\beta = 101.650(7)^\circ$, $V = 562.7(3)$ Å³, $Z = 4$, $D_x = 1.218$, $F(000) = 228$, $\mu = 0.092$ mm⁻¹, no. of unique data = 1619, no. of parameters = 66, R (all data) = 0.050, wR (all data) = 0.128, $\rho = 0.53$ e Å⁻³. CCDC deposition number: 606229.

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