

SUPPLEMENTARY MATERIAL

Catalytic *cis*-dihydroxylation of *cis*-dihydrodiols **2b_S-d_S**

(1*S*,2*S*,3*S*,4*S*)-5-Chloro-5-cyclohexene-1,2,3,4-tetraol 6b.

Colourless oil (1.08 g, 75%); $[\alpha]_{\text{D}} -3.0$ (*c* 0.95, MeOH); (Found: $\text{M}^+ - \text{H}_2\text{O}$, $-\text{CHO}$, 133.0056. $\text{C}_5\text{H}_6\text{ClO}_2$ requires 133.0056); δ_{H} (500 MHz, D_2O) 4.00 (1 H, m, 3-H), 4.04 (1 H, m, 2-H), 4.25 (1 H, d, $J_{4,3}$ 4.6, 4-H), 4.34 (1 H, d, $J_{1,2}$ 3.6, 1-H), 6.04 (1 H, d, $J_{6,1}$ 3.6, 6-H); δ_{H} (75 MHz, D_2O) 68.05, 69.74, 70.05, 70.61, 127.32, 134.37; *m/z* (EI) 135 ($\text{M}^+ [^{37}\text{Cl}] - \text{H}_2\text{O}, -\text{CHO}$, 26%), 133 ($\text{M}^+ - \text{H}_2\text{O}, -\text{CHO}$, 66%), 122 (61), 120 (100), 93 (30), 91 (69), 55 (29), 41 (32), 29 (41).

(1*S*,2*S*,3*S*,4*S*)-5-Bromo-5-cyclohexene-1,2,3,4-tetraol 6c.

Colourless oil (1.385 g, 77%); $[\alpha]_{\text{D}} +4.9$ (*c* 0.52, MeOH) (lit.³⁷ $[\alpha]_{\text{D}} +4.4$); δ_{H} (300 MHz, D_2O) 3.96 (1 H, dd, $J_{3,4}$ 2.0, $J_{3,2}$ 5.2, 3-H), 4.03 (1 H, d, $J_{2,3}$ 2.9, 2-H), 4.25 (2 H, m, 1-H and 4-H), 6.25 (1 H, d, $J_{6,1}$ 5.1, 6-H).

(1*S*,2*S*,3*S*,4*S*)-5-Iodo-5-cyclohexene-1,2,3,4-tetraol 6d.

Colourless oil (1.545 g, 71%); $[\alpha]_{\text{D}} -3.0$ (*c* 0.45, MeOH); (Found: M^+ , 271.9555. $\text{C}_6\text{H}_9\text{IO}_4$ requires 271.9546); δ_{H} (500 MHz, D_2O) 3.96 (1 H, dd, $J_{3,4}$ 4.6, $J_{3,2}$ 2.2, 3-H), 4.02 (1 H, m, 2-H), 4.16 (1 H, m, 1-H), 4.21 (1 H, dd, $J_{4,3}$ 4.6, $J_{4,6}$ 0.6, 4-H), 6.54 (1 H, dd, $J_{6,1}$ 3.4, $J_{6,4}$ 0.6, 6-H); δ_{C} (75 MHz, D_2O) 68.41, 68.64, 68.89, 73.06, 101.60, 138.61; *m/z* 272 (M^+ , 46%), 254 (75), 225 (45), 212 (100), 85 (48), 57 (53).

Syntheses of *bis*-bromoacetates **7b-d**

(1*R*,2*R*,5*R*,6*S*)-6-(Acetyloxy)-2,5-dibromo-3-chloro-3-cyclohexenyl acetate 7b.

Colourless oil (1.02 g, 87%); $[\alpha]_{\text{D}} +26$ (*c* 0.68, CHCl_3); (Found: $\text{M}^+ - \text{Br}$, 308.9522. $\text{C}_{10}\text{H}_{11}\text{BrClO}_4$ requires 308.9528); δ_{H} (500 MHz, CDCl_3) 2.11 (3 H, s, Me), 2.13 (3H, s, Me), 4.49 (1 H, d, $J_{5,6}$ 3.6, 5-H), 4.78(1 H, dd, $J_{2,4}$ 3.3, $J_{2,1}$ 8.0, 2-H), 5.56 (1 H, dd, $J_{6,5}$ 3.6, $J_{6,1}$ 2.5, 6-H), 5.72 (1 H, dd, $J_{1,2}$ 8.0 $J_{1,6}$ 2.45, 1-H), 6.15 (1 H, d, $J_{4,2}$ 3.3, 4-H); δ_{C} (125 MHz, CDCl_3) 20.67, 20.79, 42.92, 46.03, 70.65, 72.40, 128.00, 132.28, 169.32,

169.45; m/z (EI) 393 (M^+ , 9%), 391 (M^+ , 14%), 331 (16), 311 (32), 309 (24), 251 (39), 249 (32), 209 (57), 207 (50), 128 (55), 43 (100).

(1R,2R,5R,6S)-6-(Acetyloxy)-2,3,5-tribromo-3-cyclohexenyl acetate 7c.

Yellow oil (1.12 g, 86%); $[\alpha]_D +3.0$ (c 1.38, CHCl_3); (Found: C 27.7; H 2.5. $\text{C}_{10}\text{H}_{11}\text{Br}_3\text{O}_4$ requires C 27.6; H 2.55%); δ_{H} (500 MHz, CDCl_3) 2.15 (3 H, s, Me), 2.13 (3 H, s, Me), 4.56 (1 H, d, $J_{5,6}$ 3.6, 5-H), 4.73 (1 H, dd, $J_{2,4}$ 3.2, $J_{2,1}$ 8.2, 2-H), 5.55 (1 H, dd, $J_{6,5}$ 3.6, $J_{6,1}$ 2.5, 6-H), 5.73 (1 H, dd, $J_{1,2}$ 8.2, $J_{1,6}$ 2.5, 1-H), 6.34 (1 H, d, $J_{4,2}$ 3.2, 4-H); δ_{C} (125 MHz, CDCl_3) 20.71, 20.80, 43.86, 48.08, 70.44, 72.53, 122.16, 132.02, 169.32, 169.43; m/z (EI) 357 (M^+ -Br, 7%), 355 (15), 353 (7), 297 (12), 295 (26), 293 (12), 255 (30), 253 (51), 251 (31).

(1R,2R,5R,6S)-6-(Acetyloxy)-2,5-dibromo-3-iodo-3-cyclohexenyl acetate 7d.

Colourless crystals (1.156 g, 80%); mp 94-96 °C (from MeOH); $[\alpha]_D -16.9$ (c 0.88, CHCl_3); (Found: C 24.9; H 2.1. $\text{C}_{10}\text{H}_{11}\text{Br}_2\text{IO}_4$ requires C 24.9, H 2.3%); δ_{H} (500 MHz, CDCl_3) 2.11 (3 H, s, Me), 2.12 (3 H, s, Me), 4.57 (1 H, d, $J_{5,6}$ 3.5, 5-H), 4.69 (1 H, dd, $J_{2,4}$ 3.0, $J_{2,1}$ 8.2, 2-H), 5.52 (1 H, d, $J_{1,6}$ 2.2, 6-H), 5.72 (1 H, dd, $J_{1,2}$ 8.2, $J_{1,6}$ 2.2, 1-H), 6.55 (1 H, d, $J_{4,2}$ 3.0, 4-H); δ_{C} (125 MHz, CDCl_3) 20.69, 20.68, 45.06, 52.35, 70.22, 72.20, 96.8, 139.7, 169.34, 169.42; m/z (EI) 483 (M^+ +1, 28%), 403 (15), 401 (15), 343 (40), 341 (40), 301 (57), 343 (40), 341 (40), 299 (62), 174 (69), 172 (69), 43 (100).

Syntheses of *syn*-benzene dioxides 8b_S-d_S

(1S,2S,4S,7S)-5-Chloro-3,8-dioxa-tricyclo[5.1.0.0^{2,4}]oct-5-ene 8b_S.

Colourless crystals (0.17 g, 78%); mp 36-38 °C; $[\alpha]_D -58.9$ (c 0.66, CHCl_3); (Found: M^+ , 143.9982. $\text{C}_6\text{H}_5\text{ClO}_2$ requires 143.9978); δ_{H} (500 MHz, CDCl_3) 3.52 (2 H, m, 4-H and 7-H), 3.72 (1 H, dd, $J_{1,2} = J_{1,7}$ 3.2, 1-H), 3.78 (1 H, dd, $J_{2,1} = J_{2,4}$ 3.2, 2-H), 6.51 (1 H, dd, $J_{6,7}$ 4.1, $J_{6,4}$ 2.2, 6-H); δ_{C} (125 MHz, CDCl_3) 46.73, 48.73, 48.89, 50.29, 125.73, 136.78; m/z (EI) 144 (M^+ , 11%), 117 (35), 115 (100), 81 (27), 51 (63).

(1S,2S,4S,7S)-5-Bromo-3,8-dioxa-tricyclo[5.1.0.0^{2,4}]oct-5-ene 8c_S.

Colourless crystals (0.224 g, 79%); mp 71-73 °C (lit.²⁷ mp 73 °C); $[\alpha]_D -55.6$ (c 0.4, CHCl_3); (Found: M^+ , 187.9476. $\text{C}_6\text{H}_5\text{BrO}_2$ requires 187.9473); δ_{H} (500 MHz, CDCl_3),

3.44 (1 H, m, 7-H), 3.64 (1 H, m, 4-H), 3.74 (1 H, dd, $J_{1,2} = J_{1,7}$ 3.1, 1-H), 3.77 (1 H, dd, $J_{2,1} = J_{2,4}$ 3.0, 2-H), 6.82 (1 H, dd, $J_{6,7}$ 4.3, $J_{6,4}$ 2.2, 6-H); δ_{C} (75 MHz, CDCl_3), 46.60, 48.82, 49.27, 51.50, 126.31, 130.17; m/z (EI) 188 (M^+ , 4%), 159 (90), 141 (44), 132 (57), 130 (56), 109 (58), 83 (65), 81 (95), 53 (94), 51 (100), 39 (70).

(1*S*,2*S*,4*S*,7*S*)-5-Iodo-3,8-dioxa-tricyclo[5.1.0.0^{2,4}]oct-5-ene 8*d*_S.

Colourless crystals (0.29 g, 82%); mp 102-104 °C (Et_2O /hexane); $[\alpha]_{\text{D}} -59$ (c 0.7, CHCl_3); (Found: M^+ , 235.9341. $\text{C}_6\text{H}_5\text{IO}_2$ requires 235.9334); δ_{H} (500 MHz, CDCl_3) 3.26 (1 H, dd, $J_{7,6} = J_{7,1}$ 3.8, 7-H), 3.74 (3 H, m, 1-H, 2-H, 4-H), 7.20 (1 H, dd, $J_{6,7}$ 3.8, $J_{6,4}$ 1.1, 6-H); δ_{C} (125 MHz, CDCl_3) 46.43, 48.17, 49.90, 54.33, 100.14, 138.77; m/z (EI) 236 (M^+ , 82%), 207 (89), 178 (23), 127 (29), 109 (29), 81 (77), 53 (100), 51 (84).

Synthesis of *cis*-dihydrodiols 4*b*_S-*d*_S

(1*S*,2*R*)-4-Chloro-3,5-cyclohexadiene-1,2-diol 4*b*_S.

Colourless crystals (0.065 g, 75%); mp 84-86 °C; R_{f} 0.25 (40% EtOAc in hexane); $[\alpha]_{\text{D}} +20$ (c 0.83, MeOH); >98% ee; (Found: M^+ , 146.0139. $\text{C}_6\text{H}_7\text{ClO}_2$ requires 146.0139); δ_{H} (500 MHz, CDCl_3) 4.27 (1 H, dd, $J_{2,1}$ 6.4, $J_{2,3}$ 4.8, 2-H), 4.33 (1 H, dd, $J_{1,2}$ 6.4, $J_{1,6}$ 3.4, 1-H), 5.91 (1 H, dd, $J_{5,6}$ 9.9, $J_{5,3}$ 1.9, 5-H), 6.01 (1 H, dd, $J_{6,5}$ 9.9, $J_{6,1}$ 3.4, 6-H), 6.03 (1 H, dd, $J_{3,2}$ 4.8, $J_{3,5}$ 1.9, 3-H); δ_{C} (125 MHz, CDCl_3) 67.24, 67.71, 124.29, 126.91, 130.80, 132.55; m/z (EI) 146 (M^+ , 41%), 130 (75), 128 (100), 119 (10), 117 (34), 111 (14), 102 (55), 100 (77), 81 (42), 63 (54), 53 (66), 39 (74).

(1*S*,2*R*)-4-Bromo-3,5-cyclohexadiene-1,2-diol 4*c*_S.

Colourless crystals (0.08 g, 70%); mp 59-60 °C; R_{f} 0.33 (50% EtOAc in hexane); $[\alpha]_{\text{D}} +28$ (c 0.79, MeOH); >98% ee; (Found: M^+ , 189.9632. $\text{C}_6\text{H}_7\text{BrO}_2$ requires 189.9629); δ_{H} (500 MHz, CDCl_3) 2.22 (2 H, br s, OH), 4.22 (1 H, br s, 2-H), 4.30 (1 H, br s, 1-H), 5.92 (1 H, dd, $J_{6,5}$ 10.0, $J_{6,1}$ 3.5, 6-H), 6.02 (1 H, dd, $J_{5,6}$ 9.9, $J_{5,3}$ 1.7, 5-H), 6.27 (1 H, dd, $J_{3,2}$ 4.6, $J_{3,5}$ 1.7, 3-H); δ_{C} (125 MHz, CDCl_3) 67.13, 68.96, 119.63, 129.23, 129.27, 132.33; m/z (EI) 190 (M^+ , 31%), 172 (40), 161 (24), 146 (50), 144 (48), 111 (21), 83 (38), 81 (34), 65 (100), 63 (17), 55 (53), 53 (43), 39 (57).

(1*S*,2*R*)-4-Iodo-3,5-cyclohexadiene-1,2-diol 4d₅.

Colourless crystals (0.11 g, 77%); mp 59-60 °C; R_f 0.38 (50% EtOAc in hexane); $[\alpha]_D^{25} +43$ (c 0.77, MeOH); >98% ee; (Found: M^+ , 237.9479. $C_6H_7IO_2$ requires 237.9491); δ_H (500 MHz, $CDCl_3$) 4.16 (1 H, dd, $J_{2,1}$ 6.2, $J_{2,3}$ 4.3, 2-H), 4.26 (1 H, dd, $J_{1,2}$ 6.2, $J_{1,6}$ 3.8, 1-H), 5.78 (1 H, dd, $J_{6,5}$ 9.8, $J_{6,1}$ 3.8, 6-H), 6.15 (1 H, dd, $J_{5,6}$ 9.8, $J_{5,3}$ 1.5, 5-H), 6.58 (1 H, dd, $J_{3,2}$ 4.3, $J_{3,5}$ 1.5, 3-H); δ_C (125 MHz, $CDCl_3$) 66.14, 69.45, 91.20, 130.80, 132.81, 137.89; m/z (EI) 238 (M^+ , 13%), 220 (100), 111 (18), 93 (51), 83 (24), 65 (74), 55 (30), 39 (46).