SUPPORTING INFORMATION: Experimental, Analytical, and Spectral data for compounds 7-17, 19-24, 26a-b, 27a-b, and 28.

*Bis-(6-[(1R, 2S, 3S, 6S)-4-bromo-2,3-O-isopropylidenecyclohex-4-ene-1,2,3-triol]) amine (7)*

A 2-neck round-bottom flask equipped with a dry-ice condenser was charged with epoxide 6 (1.934 g; 7.833 mmol) and Yb(OTf)\(_3\) (971 mg; 1.566 mmol). Ammonia (approx. 20 mL) was condensed into the reaction vessel and allowed to reflux for 8 hours, after which it was allowed to evaporate. To the solid residue was added a solution of epoxide 6 (2.1 g; 8.505 mmol) in 1,4-dioxane (20 mL) and the mixture was heated to reflux for 24 hours. After cooling to room temperature the solvent was removed under reduced pressure and the residue purified by flash-chromatography (1:1 hexanes/ethyl acetate) to yield 7 (3.136 g; 78%) as a yellow foam.

\[\alpha\]\(_D\)\(^{27}\) = +52.3 (c=0.90, CHCl\(_3\)); IR (KBr-pellet) 3448, 2987, 2934, 1382, 1219, 1073 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 6.21 (d, \(J = 1.9\) Hz, 2H), 4.68 (d, \(J = 6.5\) Hz, 2H), 4.16 (dd, \(J = 8.7\), 6.5 Hz, 2H), 3.49 (t, \(J = 8.8\) Hz, 3H), 3.20 (dt, \(J = 8.8, 1.5\) Hz, 2H), 1.54 (s, 6H), 1.42 (s, 6H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 133.9, 119.4, 110.9, 78.3, 77.2, 71.9, 57.2, 28.3, 26.0; HRMS calcd. for C\(_{18}\)H\(_{26}\)NBr\(_2\)O\(_6\) (M+H): 512.0108; Found: 512.0278; Anal. Calcd. for C\(_{18}\)H\(_{25}\)Br\(_2\)NO\(_6\): C, 42.29; H, 4.93; N, 2.74. Found: C, 42.22; H, 4.94; N, 2.60.

*Bis-(6-[(1R, 2S, 3R, 6S)-2,3-O-isopropylidenecyclohex-4-ene-1,2,3-triol]) amine (8)*
Compound 7 (407 mg; 0.796 mmol) was dissolved in dry THF and degassed with argon for 20 min. AIBN (13 mg; 0.079 mmol) was added and the mixture heated to reflux after which Bu₃SnH (514 µL; 1.911 mmol) was added. The reaction was allowed to reflux for 4.5 hours and then cooled to room temperature. The solvent was removed \textit{in vacuo} and the residue purified by flash-chromatography (ethyl acetate) to yield 232 mg (83%) of the title compound as a white solid.

mp = 159 – 160 ºC; $\lbrack \alpha \rbrack_D^{30} = -13.8$ (c=1.6, CHCl₃); IR (KBr-pellet) 3424, 2989, 2926, 1381, 1258, 1210, 1068 cm⁻¹; $^1$H NMR (CDCl₃, 300 MHz) $\delta$ 5.90 (m, 4H), 4.63 (dd, $J = 6.8, 2.0$ Hz, 2H), 4.13 (dd, $J = 8.8, 6.7$ Hz, 2H), 3.72 (s, 3H), 3.48 (dd, $J = 9.0$ Hz, 2H), 3.22 (d, $J = 9.2$ Hz, 2H), 1.51 (s, 6H), 1.39 (s, 6H); $^{13}$C NMR (CDCl₃, 75 MHz) $\delta$ 132.8, 124.0, 110.0, 78.1, 72.4, 72.3, 55.5, 28.1, 25.6; HRMS calcd. for C₁₈H₂₈NO₆ (M+H)$^+$: 354.1917; Found: 354.1925; Anal. Calcd. for C₁₈H₂₇NO₆: C, 61.17; H, 7.70; N, 3.96. Found: C, 60.88; H, 7.92; N, 3.87.

(1$S$, 4$R$, 5$R$, 6$R$)-N,N-(Bis-(4,5,6-trihydroxy-cyclohex-2-enyl)-amine hydrochloride (9)

Compound 8 (99 mg; 0.280 mmol) was dissolved in MeOH (2 mL) and conc. HCl (50 µL) was added. The solution was stirred for 5 minutes and then allowed to stand at r.t. for 22 hours. To the mixture was added ether (20 mL) upon which a white precipitate formed. The precipitate was removed by centrifugation and washed with ether. The mother liquor was concentrated, the residue dissolved in MeOH (1 mL) and additional fractions of precipitate were obtained by adding ether and subsequent evaporation. The
combined solid was dissolved in water (5 mL) and lyophilized to yield dimer 9 (84 mg; 92%) as the monohydrate of its HCl salt.

\[ \alpha \]D^29 = +10.7 (c=0.38, MeOH); IR (KBr-pellet) 3365, 1594, 1418, 1101 cm\(^{-1}\); \(^1\)H NMR (MeOH-\(d_4\), 300 MHz) \(\delta\) 6.11 (ddd, \(J = 10.2, 4.4, 2.0\) Hz, 2H), 5.91 (dd, \(J = 10.2, 2.4\) Hz, 1H), 4.29 (dd, \(J = 4.2\) Hz, 2H), 3.99 (dd, \(J = 8.5, 7.1\) Hz, 2H), 3.84 – 3.91 (m, 2H), 3.68 (dd, \(J = 8.5, 4.2\) Hz, 2H); \(^1\)C NMR (MeOH-\(d_4\), 75 MHz) \(\delta\) 135.2, 122.7, 72.5, 69.2, 67.3, 59.2; HRMS calcd. for C\(_{12}\)H\(_{20}\)NO\(_6\) (M\(^+\)): 274.1291; Found: 274.1313; Anal. Calcd. for C\(_{12}\)H\(_{20}\)ClNO\(_6\)\(\cdot\)H\(_2\)O: C, 43.97; H, 6.77; N, 4.27; Found: C, 44.25; H, 6.97; N, 4.44;

**Bis-(6-[\((1R, 2R, 3R, 6S)\)-1-O-acetyl-2,3-O-iso-propyldienecyclohex-4-ene-1,2,3-triol]) acetamide (10)**

Dimer 8 (165 mg, 0.467 mmol) was dissolved in dry 1,4-dioxane (15 mL) in a flame-dried flask under argon and a spatula tip of DMAP was added. Pyridine (1.70 mL, 21.016 mmol) and acetic anhydride (1.33 mL, 14.011 mmol) were added and the mixture heated to reflux until TLC monitoring showed that complete conversion had occurred (usually 24 hours). The mixture was allowed to cool down, quenched with excess methanol and stirred for 15 min. The solvent was removed under reduced pressure and the residue dissolved in 20 ml ethyl acetate. The organic layer was extracted three times with 0.1 M HCl (10 ml each) and washed with a saturated aqu. NaHCO\(_3\)-solution (5 mL). The organic layer was dried (MgSO\(_4\)) and concentrated on a rotary evaporator to give 10 (196 mg, 88 %) as a slightly yellow foam.
mp = 172-174 °C; $[\alpha]_D^{26} = +12.6$ (c=0.95, CHCl$_3$); IR (KBr-pellet) 3448, 2988, 2936, 2871, 1751, 1654, 1381, 1229, 1064 cm$^{-1}$; $^1$H NMR (acetone-$d_6$, 300 MHz) $\delta$ 7.74 (t, 4.7 Hz, 1H), 6.06 (dt, $J = 10.1$, 3.5 Hz, 1H), 5.95 (m, 1H), 5.77 – 5.59 (m, 2H), 5.35 (t, $J = 9.9$ Hz, 1H), 4.63 (m, 3H), 4.33 (dd, $J = 9.23$, 6.01 Hz, 1H), 4.23 (d, $J = 10.2$ Hz, 1H), 4.14 (dd, $J = 9.4$, 6.0 Hz, 1H), 3.76 (d, $J = 9.4$ Hz, 1H), 3.45 (bs, 1H), 2.1 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H), 1.25 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 171.3, 170.5, 170.2, 134.5, 124.5, 111.0, 110.6, 77.4, 72.3, 28.2, 26.5, 26.4, 21.7, 21.5; HRMS calcd. for C$_{24}$H$_{34}$NO$_9$ (M+H)$^+$: 480.2233; Found: 480.2242; Anal. Calcd. for C$_{24}$H$_{32}$NO$_9$: C, 60.11; H, 6.94; N, 2.92. Found: C, 60.18; H, 6.97; N, 2.88;

(1$S$, 4$R$, 5$R$, 6$R$)-$N$,$N$-(Bis-(4,5,6-trihydroxy-cyclohex-2-enyl)-acetamide (11)

Dimer 10 (188 mg; 0.392 mmol) was dissolved in a 0.1 M solution of NaOMe in MeOH (10 mL) and stirred at room temperature for 12 hours. The mixture was concentrated under reduced pressure and the residue redissolved in ethyl acetate and filtered through a plug of silica. The filtrate was concentrated in vacuo to provide 135 mg of a white solid. This precipitate (122 mg; 0.308 mmol) was dissolved in a 2:1:1 mixture of THF/TFA/H$_2$O (12 mL total) and stirred at room temperature for 1 hour. The solution was concentrated and the residue re-dissolved in MeOH (2 mL). Upon addition of ether (20 mL) a white precipitate formed. The mother liquor was concentrated and the crystallization process repeated two more times. The combined precipitates were dissolved in H$_2$O (5 mL) and lyophilized to yield the title compound (96 mg; 85% for two steps) as a white powder.
\[ [\alpha]_D^{27} = +37.7 \text{ (c=0.70, MeOH); IR (KBr-pellet) 3351, 1619, 1432, 1297, 1132 cm}^{-1}; \]

\(^1\text{H NMR (MeOH-}d_4, 300 \text{ MHz)} \delta 6.05 - 5.6 \text{ (m, 4H), } 4.50 - 4.05 \text{ (m, 6H), } 3.7 - 3.45 \text{ (m, 2H), } 2.21 \text{ (s, 3H); } \ ^{13}\text{C NMR (MeOH-}d_4, 75 \text{ MHz)} \delta 174.5, 133.6, 132.0, 130.8, 127.4, 74.6, 73.0, 70.2, 69.3, 68.6, 68.0, 65.6, 60.5, 23.6; \text{ HRMS calcd. for } C_{14}H_{22}NO_7 (M+H)^+: 316.1396; \text{ Found: 316.1398;}

Bis-(6-\{(1R, 2S, 3R, 6S)-1-O-acetyl-2,3,4,5-di-O-isopropyl-idenecyclohex-4-ene-1,2,3,4,5-pentol\}) acetamide (12)

Dimer 10 was dissolved in acetone / H\textsubscript{2}O (10:1, 23 mL), then NMNO (1.513 g, 12.91 mmol) and one crystal of OsO\textsubscript{4} were added. The reaction was stirred under argon for 16 hours. The dark mixture was quenched with excess solid NaHSO\textsubscript{3} and allowed to stir for \(\frac{1}{2}\) hour. The mixture was then put on a rotary evaporator to remove most of the acetone. To the residue was added 0.1 M HCl (50 mL) and the aqueous layer was extracted 8x with ethyl acetate (200 mL each). The combined organic layers were washed with a saturated aqu. NaHCO\textsubscript{3}-solution (50 mL), dried (MgSO\textsubscript{4}) and concentrated \textit{in vacuo} to give the crude tetrol (1.48 g) as a yellow semi-solid. The latter was dissolved in acetone (30 mL) and DMP (30 mL) and a small spatula tip of \(p\)-TsOH were added. The reaction mixture was stirred for 19 hours under argon. After quenching with excess solid NaHCO\textsubscript{3} and stirring for 10 min. the mixture was concentrated and loaded directly on a flash-chromatography column and eluted with hexanes – ethyl acetate (1:1) to yield 12 (1.359 g, 60% for both steps) as a white foam. mp = 96-98 °C; \([\alpha]_D^{26} = -54.5 \text{ (c=1.0, CHCl}_3\); IR (KBr-pellet) 3508, 2989, 2940, 1759, 1663, 1456, 1385, 1220, 1165, 1048 cm\textsuperscript{-1}; \(^1\text{H NMR (CDCl}_3, 300 \text{ MHz)} \delta 5.87 \text{ (dd, } J = 10.7, 9.1 \text{ Hz, } 1\text{H), } 4.95 \text{ (dd, } J = 11.7, 6.5 \text{ Hz, } 1\text{H),}
4.81 (dd, $J = 8.6$, 7.0 Hz, 1H), 4.73 (dd, $J = 5.8$, 5.1 Hz, 1H), 4.50 (t, $J = 5.9$ Hz, 1H), 4.45 – 4.34 (m, 3H), 4.23 (dd, $J = 7.3$, 5.4 Hz, 1H), 4.12 (m, 1H), 3.98 (dd, $J = 11.3$, 8.8 Hz, 1H), 3.22 (dd, $J = 10.7$, 5.1 Hz, 1H), 2.18 (s, 6H), 2.08 (s, 3H), 1.65 (s, 3H), 1.53 (s, 3H), 1.50 (s, 9H), 1.37 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 173.2, 171.1, 169.6, 110.3, 110.1, 109.5, 109.1, 78.9, 78.0, 77.5, 77.2, 77.0, 76.3, 76.2, 75.3, 70.4, 69.9, 28.2, 27.7, 27.6, 27.5, 25.7, 25.6, 25.0, 23.3, 22.0, 21.9, 21.6; HRMS calcd. for C$_{30}$H$_{46}$NO$_{13}$ (M+H)$^+$: 628.2969; Found: 628.2962; Anal. Calcd. for C$_{30}$H$_{45}$NO$_{13}$: C, 57.41; H, 7.23; N, 2.23. Found: C, 57.28; H, 7.21; N, 2.29.

**Bis-(6-[(1R, 2S, 3R, 6S)-cyclohexa-1,2,3,4,5-pentol]) acetamide (13)**

Compound 12 (128 mg; 0.204 mmol) was dissolved in a 0.1 M solution of NaOMe in MeOH (7 mL) and stirred at room temperature for 2.5 hours. The mixture was concentrated under reduced pressure and the residue was dissolved in CH$_2$Cl$_2$ / EtOAc (1:1) and filtered through a plug of silica. The filtrate was evaporated to yield an off-white foam (110 mg; 99%). The latter (249 mg; 0.458 mmol) was dissolved in MeOH (30 mL) and conc. HCl (100 $\mu$L) was added. The mixture was stirred for 24 hours and then concentrated under reduced pressure. The solid residue was dissolved in MeOH and acetone added until precipitation occurred. The amorphous precipitate was removed by centrifugation and washed with acetone to give the title compound (101 mg; 57% for both steps) as an off-white, amorphous solid.

mp = 259-262 °C (decomp.); $[\alpha]_D^{28} = -40.4$ (c=1.0, MeOH); IR (KBr-pellet) 3393, 2915, 1699, 1624, 1447, 1388, 1301, 1032 cm$^{-1}$; $^1$H NMR (MeOH-d$_4$, 300 MHz) $\delta$ 4.90 – 4.98 (m, 1H), 4.70 (dd, $J = 10.0$ Hz, 1H), 4.08 (dd, $J = 10.4$, 2.5 Hz, 2H), 3.70 – 3.90 (m,
6H), 3.62 (dd, \( J = 9.7, 3.1 \) Hz, 1H), 3.43 (dd, \( J = 10.4 \) Hz, 1H), 2.23 (s, 3H); \(^{13}\)C NMR (MeOH-\( d_4 \), 75 MHz) \( \delta \) 177.4, 72.5, 72.0, 71.4, 71.2, 71.0, 70.3, 67.8, 67.6, 65.7, 65.4, 64.4, 56.9, 23.4; HRMS calcd. for \( \text{C}_{14}\text{H}_{26}\text{NO}_{11} \) (M+H): 384.1505; Found: 384.1506; Anal. Calcd. for \( \text{C}_{14}\text{H}_{25}\text{NO}_{11} \cdot\text{H}_2\text{O} \): C, 41.90; H, 6.78; N, 3.49. Found: C, 41.81; H, 6.70; N, 3.18;

**Bis-(6-\( \{1R, 2R, 3R, 6S\}\)-1-O-acetyl-2,3-\( O \)-isopropylidenecyclohex-4-ene-1,2,3-trioli] trifluoroacetamide (14)**

Dimer 8 (323 mg; 0.914 mmol) was dissolved in dry CH\(_2\)Cl\(_2\) in a flame-dried flask under a static argon atmosphere and a spatula tip of DMAP was added. The reaction mixture was cooled to 0°C followed by addition of pyridine (211 \( \mu\)L; 2.61 mmol) and acetic anhydride (185 \( \mu\)L; 1.94 mmol). The reaction mixture was stirred at 0°C for 1 hour and then slowly allowed to warm to room temperature. After 10 hours, the mixture was quenched with MeOH (0.3 mL), stirred for 20 min. and concentrated in vacuo. The resulting yellow oil was purified by flash chromatography (hexanes / ethyl acetate = 3:2) to yield the free amine (356 mg; 89%) as a white solid. The latter (910 mg; 2.08 mmol) was dissolved in dry pyridine (20 mL) in a flame-dried thick-wall tube under argon atmosphere and trifluoroacetic anhydride (1.5 mL) was added. The tube was sealed and heated in an oil-bath to 100°C for two hours. The mixture was allowed to cool to room temperature, diluted with MeOH (50 mL) and concentrated under reduced pressure. The residue was co-evaporated several times with toluene and the resulting brown oil purified by flash-chromatography (3:2 hexanes / ethyl acetate) to yield amide 14 (980 mg; 78% for two steps) as an off-white foam.
$\alpha \text{D}^{28} = +52.4 \text{ (c=0.75, CHCl}_3)$; IR (film on NaCl) 2988, 2935, 2360, 1752, 1703, 1373, 1223, 1064 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 6.01 (dt, $J = 10.2$, 2.5 Hz, 1H), 5.91 (dt, $J = 10.0$, 3.2 Hz, 1H), 5.87 (dd, $J = 9.4$ Hz, 1H), 5.64 (d, $J = 10.4$ Hz, 1H), 5.58 (dd, $J = 10.4$, 2.4 Hz, 1H), 5.19 (bs, 1H), 4.64 (bs, 1H), 4.57 (m, 2H), 4.44 (dd, $J = 5.2$ Hz, 1H), 4.17 (d, $J = 9.8$ Hz, 1H), 4.10 (dd, $J = 9.1$, 6.1 Hz, 1H), 2.18 (s, 3H), 2.06 (s, 3H), 1.49 (s, 3H), 1.40 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 170.5, 169.8, 157.0 (q, $J = 36$ Hz), 132.7, 130.9, 126.0, 124.2, 115.9 (q, $J = 288$ Hz), 111.1, 110.7, 77.5, 72.8, 72.7, 71.4, 70.2, 69.2, 57.4, 57.3, 28.2, 28.0, 26.7, 26.4, 21.3, 21.1; HRMS calcd. for C$_{23}$H$_{27}$NO$_9$F$_3$ (M-CH$_3$)$^+$: 518.1638; Found: 518.1657; Anal. Calcd. for C$_{24}$H$_{30}$NO$_9$F$_3$: C, 54.03; H, 5.67; N, 2.63. Found: C, 54.28; H, 5.73; N, 2.55;

**Bis-(6-[(1R, 2S, 3R, 6S)-1-O-acetyl-2,3,4,5-di-O-isopropylidenecyclohex-4-ene-1,2,3,4,5-pentol)] trifluoro acetamide (15)**

Amide 14 (893 mg; 1.674 mmol) was dissolved in a mixture (15 mL) of acetone / H$_2$O / t-BuOH (100 : 10 : 1), followed by addition of NMNO (706 mg; 6.026 mmol) and a small crystal of solid OsO$_4$. After 48 hours, an additional portion of NMNO (400 mg; 3.414 mmol) was added. The reaction was quenched after 50 hours by addition of excess 10% aqu. sodium bisulfite and allowed to stir for 15 min. After adjusting the pH value to ~3 with 1M HCl, the mixture was extracted with ethyl acetate (4 x 200 mL) and the combined organic layers washed with saturated aqueous NaHCO$_3$ (20 mL), dried (MgSO$_4$) and concentrated in vacuo to yield 780 mg of a brown semi-solid of the corresponding tetrol.
This material was dissolved in CH$_2$Cl$_2$ (30 mL) and DMP (4 mL) and a catalytic amount of p-TsOH was added. The reaction was allowed to stir at room temperature for 14 hours. The mixture was diluted with ethyl acetate (100 mL), washed with sat. aqu. NaHCO$_3$ (10 mL), dried and concentrated under reduced pressure to give the tetraacetonide 15 (559 mg; 53% over two steps) as an off-white foam.

$[\alpha]_D^{27} = -71.2$ (c=0.80, CHCl$_3$); IR (KBr - pellet) 2989, 2941, 1762, 1701, 1457, 1374, 1220, 1054 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 5.76 (dd, $J = 11.0, 8.9$ Hz, 1H), 5.15 (dd, $J = 10.6, 7.1$ Hz, 1H), 4.92 (dd, $J = 7.9$ Hz, 1H), 4.84 (dd, $J = 6.1, 1$ H), 4.46 (m, 3H), 4.05 – 4.30 (m, 3H), 3.89 (dd, $J = 9.9$ Hz, 1H), 3.48 (dd, $J = 11.3, 5.6$ Hz, 1H), 2.18 (s, 3H), 2.07 (s, 3H), 1.61 (s, 3H), 1.53 (s, 3H), 1.51 (s, 3H), 1.49 (s, 3H), 1.45 (s, 3H), 1.36 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 170.9, 169.1, 159.1 (q, $J = 36$ Hz), 116.1 (q, $J = 290$ Hz), 110.7, 109.9, 109.7, 109.6, 78.4, 77.5, 76.7, 76.2, 75.8, 73.8, 68.5, 67.8, 60.2, 57.8, 28.1, 27.5, 27.4, 26.6, 25.6, 25.3, 24.8, 21.8, 21.1; HRMS calcd. for C$_{30}$H$_{43}$NO$_{13}$ (M+H)$^+$: 682.2686; Found: 682.2647; Anal. Calcd. for C$_{30}$H$_{42}$F$_3$NO$_{13}$: C, 53.86; H, 6.21; N, 2.05; Found: C, 53.09; H, 6.22; N, 1.98;

**Bis-(6-[(1R, 2S, 3R, 6S)-cyclohexa-1,2,3,4,5-pentol] amine hydrochloride (16)**

Compound 15 (444 mg; 0.707 mmol) was dissolved in a 0.1 M solution of NaOMe in MeOH (10 mL) and stirred at room temperature for 4 hours. The mixture was concentrated under reduced pressure and the residue loaded on a flash-chromatography column (3:1 ethyl acetate / hexanes) to yield an off-white foam (310 mg; 88%), which was dissolved in MeOH (9 mL) and conc. HCl (500 µL) was added. The mixture was allowed to stand at room temperature for 20 hours after which a white precipitate had
formed. The crystals were filtered off and washed with MeOH / acetone (1:1). Concentration and crystallization of the mother liquor gave additional precipitate that was combined with the former to yield hydrochloride 16 (200 mg; 75% over 2 steps) as white crystals.

$[\alpha]_D^{30} = -61.9 \ (c=1.0, \ H_2O)$; IR (KBr-pellet) 3444, 3321, 1577, 1440, 1383, 1333, 1207, 1091 cm$^{-1}$; $^1$H NMR (D$_2$O, 300 MHz) $\delta$ 4.19 (dd, $J = 10.6, 2.3 \ Hz, 2H), 4.09 (m, 4H), 3.99 (dd, $J = 10.2 \ Hz, 2H), 3.92 (dd, J = 10.3 \ Hz, 2H), 3.84 (dd, J = 9.1, 2.0 \ Hz, 2H); $^{13}$C NMR (D$_2$O, 75 MHz) $\delta$ 71.8, 71.1, 71.0, 69.6, 67.7, 62.4; HRMS calcd. for C$_{12}$H$_{24}$NO$_{10}$ (M$^+$): 342.1400; Found: 342.1410; Anal. Calcd. for C$_{12}$H$_{24}$ClNO$_{10}$: C, 38.15; H, 6.40; N, 3.71. Found: C, 38.21; H, 6.66; N, 3.60;

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\text{N-}[7\text{-Bromo-5S-}(7\text{-bromo-4S-hydroxy-2,2-dimethyl-3Ra,4S,5S,7a-tetrahydrobenzo[1S,3R]dioxol-5S-ylamino)-2,2-dimethyl-3Ra,4S,5S,7a-tetrahydrobenzo[1S,3R]dioxol-4S-yl]-4-methyl-benzenesulfonamide (19)}
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In a flame-dried sealed tube (30 x 5 cm) was condensed ammonia gas (~ 20 mL) at −78°C. To the liquid ammonia solution was added aziridine 18 (3.1 g, 7.75 mmol) and ytterbium triflate (830 mg, 1.34 mmol) as solids to the reaction mixture. To this mixture was then added of methylene chloride (10 mL) and the tube was sealed and heated to 50 °C. After 30 minutes, the mixture was homogenous and TLC monitoring showed no more starting material. The ammonia was allowed to evaporate and the residue concentrated under reduced pressure. To the residue was added freshly distilled dioxane (25 ml) and epoxide 6 (2.19g; 8.85 mmol). The tube was again sealed and heated to 60-70 °C with an oil bath for 3 hours. The dioxane was then removed under reduced
pressure, and the crude mixture was purified by flash column chromatography using a
gradient elution (hexanes -> ethyl acetate) to yield 19 (78-94%) as a white solid.

mp 158-158.5 °C; [α]D26 = + 41.7 (c=0.36, CHCl3); IR (KBr) 3905, 3822, 3752, 3677,
3651, 3589, 3504, 2346, 1846, 1794, 1752, 1735, 1710, 1702, 1654, 1638, 1560, 1508,
1458, 1382, 1330, 1220, 1161, 1074, 866, 814, 791, 669, 575, 544 cm⁻¹; ¹H NMR
(CDCl3, 300 MHz) δ 7.79 (d, J = 8.0 Hz, 2H); 7.36 (d, J = 8.0 Hz, 2H), 6.22 (d, J = 3.9
Hz, 1H), 5.93 (s, 1H); 4.86 (m, 1H, exchanges with D₂O), 4.64 (d, J = 6.6 Hz, 2H), 4.37
(d, J = 5.3 Hz, 1H), 4.26 (t, J = 5.8 Hz, 1H), 4.05 (m, 1H), 3.62 (m, 1H), 3.34 (t, J = 8.8
Hz, 1H), 3.03 (s, 1H), 2.92 (d, J = 8.8 Hz, 1H), 2.70 (s, 1H), 2.46 (s, 3H), 1.55 (s, 3H),
1.42 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H); ¹H NMR (DMSO, 300 MHz) δ 8.01 (d, J = 7.5
Hz, 1H), 7.71 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 6.31 (d, J = 3.5 Hz, 1H), 5.77
(s, 1H), 5.27 (d, J = 5.5 Hz, 1H), 4.62 (d, J = 5.7 Hz, 1H), 4.57 (d, J = 6.2 Hz, 1H), 4.03
(m, 2H), 3.28 (q, J = 6.4 Hz, 1H), 3.01 (m, 3H), 2.39 (s, 3H), 2.19 (dd, J = 9.9, 3.3 Hz,
1H), 1.40 (s, 3H), 1.30 (s, 3H), 1.27 (s, 3H), 1.22 (s, 3H); ¹³C NMR (CDCl3, 75 MHz) δ
144.2, 136.9, 133.4, 131.3, 130.0, 127.3, 122.8, 118.8, 111.4, 110.7, 78.2, 76.7, 75.7,
72.3, 57.8, 56.7, 54.0, 28.1, 27.4, 26.0, 25.8, 21.7; HRMS calcd. for C25H33O7N2Br2S:
663.0375; Found: 663.0372. Anal. Calcd.: C 45.19, H 4.85, N 4.22; Found: C 45.49, H
5.04, N 3.94.

Acetic acid 7-bromo-5S-[7-bromo-2,2-dimethyl-4S-(toluene-4-sulfonlamino)-
3Ra,4S,5S,7a-tetrahydro-benzo[1S,3R]dioxol-5S-ylamino]-2,2-dimethyl-
3Ra,4S,5S,7a-tetrahydro-benzo[1S,3R]dioxol-4S-yl ester (20)
To a solution of dimer 19 (2.025 g, 3.05 mmol) in methylene chloride (10 ml), was added a spatula tip of DMAP. The solution was stirred, and pyridine (2.5 mL, 30.5 mmol) was added, followed by addition of acetic anhydride (300 µL; 3.35 mmol). The solution was stirred at room temperature for 5 hours. The excess acetic anhydride was then quenched with of methanol (15 mL), and the solution was concentrated under reduced pressure. The resulting solution in pyridine was then dissolved in diethyl ether (200 mL), and washed with hydrochloric acid (1% vol; 4 x 15 mL), and brine (2 x 20 mL). The solution was dried with anhydrous magnesium sulfate, and concentrated to afford a yellow solid, which was purified using flash column chromatography (gradient elution: CH₂Cl₂ to CH₂Cl₂ : EtOAc [1:1]) to give 20 (1.996 g; 93 %) as a white solid.

mp 105.5-107 ºC; [α]D²⁸.⁵ = +31.8 (c=0.33, CHCl₃); IR (Neat) 3530, 3261, 2988, 2935, 1742, 1644, 1598, 1454, 1373, 1334, 1223, 1162, 1076, 1040, 989, 911, 860, 814, 793, 732, 6666, 574, 546 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.81 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.25 (d, J = 3.9 Hz, 1H), 5.99 (d, J = 3.6 Hz, 1H), 5.20 (d, J = 8.1 Hz, 1H), 5.00 (t, J = 6.0 Hz, 1H), 4.56 (dd, J = 8.8, 5.5 Hz, 2H), 4.21 (m, 1H), 3.05 (bs, 2H), 2.45 (s, 3H), 2.01 (s, 3H), 1.49 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 170.3, 145.2, 144.0, 137.1, 132.4, 131.9, 129.9, 129.7, 128.3, 127.3, 122.3, 120.6, 111.2, 76.2, 75.5, 75.4, 71.1, 58.4, 57.5, 54.6, 31.8, 29.0, 27.8, 27.5, 26.3, 16.1, 23.5, 22.7, 21.7, 21.6, 21.1, 14.1; HRMS calcd. for C₂₇H₃₅O₈N₂SBr₂: 705.0481; Found: 705.0454. Anal. Calcd.: C 45.91, H 4.85, N 3.97; Found: C 46.33, H 4.80, N 4.14.
Acetic acid 7-bromo-5S-[[7-bromo-2,2-dimethyl-4S-(toluene-4-sulfonylamino)-3Ra,4S,5S,7a-tetrahydro-benzo[1S,3R]dioxol-5S-yl]-2,2,2-trifluoro-acetyl-amino]-2,2-dimethyl-3Ra,4S,5S,7a-tetrahydro-benzo[1S,3R]dioxol-4S-yl ester (21)

To a solution of dimer 20 (1.996 g, 2.83 mmol) in methylene chloride (12 mL), was added a spatula tip of DMAP. The solution was stirred, and pyridine (2.3 mL; 28.3 mmol) was added, followed by trifluoroacetic anhydride (600 µL; 4.25 mmol). The solution was heated to reflux for three hours. After allowing the mixture to cool to room temperature the excess trifluoroacetic anhydride was quenched with methanol (15 mL) and concentrated under reduced pressure. The resulting solution in pyridine was then dissolved in diethyl ether (200 mL), and washed four times with hydrochloric acid (1% vol; 4 x 15 mL) and brine (2 x 20 mL). The solution was dried with anhydrous magnesium sulfate, concentrated and the residue purified using flash column chromatography (gradient elution: CH₂Cl₂ to CH₂Cl₂ : EtOAc [1:1]) to give 21 (92-98%) as a white solid.

mp 108-110 ºC; \([\alpha]_D^{28.5} = + 99.6\) (c=0.10, CHCl₃); IR (Neat) 3522, 3275, 2989, 2926, 2855, 1747, 1705, 1455, 1376, 1337, 1217, 1161, 1079, 989, 869, 795, 729, 665, 575.4 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.76 (d, \(J = 8.2\) Hz, 2H), 7.25 (d, \(J = 8.2\) Hz, 2H), 6.54 (d, \(J = 3.5\) Hz, 1H), 6.01 (s, 1H), 5.94 (d, \(J = 2.7\) Hz, 1H), 5.17 (d, \(J = 8.3\) Hz, 1H), 4.67 (s, 1H), 4.58 (m, 2H), 4.44 (dd, \(J = 5.1, 4.0\) Hz, 1H), 4.05 (m, 3H), 3.85 (dd, \(J = 9.1, 6.4\) Hz, 1H), 2.38 (s, 3H), 2.16 (s, 3H), 1.49 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.4, 147.4, 143.6, 137.1, 134.2, 129.5, 128.3, 126.5, 117.7, 111.6, 110.8, 76.81, 74.24, 74.0, 68.2, 52.2, 29.9, 28.1, 16.7, 26.6, 25.5, 21.7, 21.0; ¹⁹F NMR (CDCl₃, 282 MHz) δ -69.4; HRMS calcd. for C₂₆H₂₈O₈N₂SF₃Br₂:
Acetic acid 5S-[[2,2-dimethyl-4S-(toluene-4-sulfonylamino)-3Ra,4S,5S,7a-tetrahydro-benzo[1S,3R]dioxol-5S-yl]-(2,2,2-trifluoro-acetyl)-amino]-2,2-dimethyl-3Ra,4S,5S,7a-tetrahydro-benzo[1S,3R]dioxol-4-yl ester (22)

To a flame-dried 100 mL flask, was added the dibromide (1.874 g, 2.3 mmol) and 40 mL of THF. The solution was stirred and degassed with argon for 30 minutes. Tri-n-butyltinhydride (1.4 mL, 5.1 mmol) was then added to the solution, and it was heated to reflux. Upon reflux, a spatula tip of AIBN was added, and the solution was stirred at reflux for 2 hours. The resulting solution was concentrated under reduced pressure, and purified using flash column chromatography (gradient elution: CH₂Cl₂ to CH₂Cl₂ : EtOAc [1:1]) to yield compound 22 (56-73%).

mp 219-220 °C (decomposes); [α]D²⁹ = + 29.9 (c=0.98, CHCl₃); IR (KBr) 3270, 3049, 2988, 2935, 2873, 1748, 1702, 1599, 1455, 1374, 1338, 1217, 1161, 1065, 971, 915, 868, 735, 664, 573, 549 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.78 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 6.04 (dt, J = 10.3, 2.6 Hz, 1H), 5.84 (dt, J = 9.9, 2.9 Hz, 1H), 5.75 (m, 2H), 5.03 (d, J = 8.7 Hz, 2H), 4.67 (s, 1H), 4.56 (m, 2H), 4.32 (t, J = 5.3 Hz, 1H), 4.08 (dd, J = 9.6, 9.1 Hz, 1H), 3.83 (m, 2H), 2.37 (s, 3H), 2.17 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H), 1.18 (s, 3H), 0.84 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 170.1, 158.2, 157.7, 142.9, 137.4, 133.5, 130.3, 129.1, 128.1, 126.3, 123.9, 111.5, 117.8, 115.0, 114.0, 110.8, 110.0, 78.0, 73.7, 72.4, 70.3, 68.7, 57.3, 52.6, 31.9, 29.7, 29.0, 26.6, 26.5, 25.2, 22.7, 21.4, 21.2;
Acetic acid 2,2,7-trimethyl-5-[[2,2,7,7-tetramethyl-5S-(toluene-4-sulfonylamino)-hexahydro-benzo[1,2-d;3,4-d']bis[1S,3R]dioxol-4S-yl]-{(2,2,2-trifluoro-acetyl)-amino]-hexahydro-benzo[1,2-d;3,4-d']bis[1S,3R]dioxol-4S-y1 ester (23)

To a solution of dimer 22 (2.996 g; 4.6 mmol) in acetone (35 mL) was added N-methylmorpholine-N-oxide monohydrate (1.57 g; 11.6 mmol) and the solution was stirred at room temperature. A small crystal of osmium(VIII) tetroxide was then added, and the solution was stirred under argon overnight. The following day, the solution, now black, was quenched with excess saturated sodium bisulfite, and the pH was adjusted to 2 with concentrated sulfuric acid. The aqueous layer was extracted ten times with ethyl acetate (10 x 150 mL), and the organic fractions were dried with anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting dark oil was then redissolved in methylene chloride (25 mL) and 2,2-dimethoxypropane (25 mL), to which a crystal of p-toluenesulfonic acid was added. The solution was heated to reflux for three hours, after which aqueous saturated sodium bicarbonate (25 mL) was added, and the aqueous layer was extracted with diethyl ether (6 x 100 mL). The organic layers were then washed with saturated sodium bicarbonate (2 x 25 mL), and a saturated sodium carbonate solution (2 x 25 mL). The organic fractions were dried with anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to afford a crude oil (2.523 g), which was purified using flash column chromatography (gradient elution:
CH$_2$Cl$_2$: hexanes [1:1] to CH$_2$Cl$_2$ : EtOAc [1:1]) to afford 23 (26-61%) as an amorphous solid.

$[\alpha]_D^{29} = -34.3$ (c=0.28, CHCl$_3$); IR (KBr) 3545, 3284, 2988, 2938, 1744, 1697, 1457, 1383, 1373, 1342, 1217, 1162, 1057, 858, 815, 666 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.76 (d, $J = 8.0$ Hz, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 5.96 (s, 2H), 5.52 (t, $J = 4.9$ Hz, 1H), 5.16 (d, $J = 9.7$ Hz, 1H), 4.94 (t, $J = 7.0$ Hz, 1H), 4.64 (d, $J = 3.9$ Hz, 1H), 4.58 (d, $J = 5.4$ Hz, 1H), 4.28 (m, 3H), 4.08 (t, $J = 6.8$ Hz, 1H), 3.24 (dd, $J = 11.8$, 7.5 Hz, 1H), 2.39 (s, 3H), 2.19 (s, 3H), 1.59 (s, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.42 (s, 3H), 1.30 (s, 3H), 1.26 (s, 3H), 1.16 (s, 3H), 1.06 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 143.0, 129.2, 128.3, 128.0, 111.3, 109.9, 79.2, 77.0, 74.1, 73.7, 70.7, 69.5, 60.0, 29.9, 28.2, 27.8, 27.2, 26.7, 25.5, 24.9, 21.6, 21.5; HRMS calcd. for C$_{33}$H$_{48}$O$_{13}$N$_2$F$_3$S: 793.2829; Found: 793.2843.

6-(2-Amino-3,4,5,6-tetrahydroxy-cyclohexylamino)-cyclohexane-1,2,3,4,5-pentaol hydrochloride (17)

Fully hydroxylated dimer 23 (1.106 g; 1.39 mmol) was dissolved in a 0.2 M solution of NaOMe in MeOH (25 mL) and the solution was stirred at room temperature overnight. The mixture was then concentrated under reduced pressure and the residue purified by Flash column chromatography (gradient elution: hexanes -> EtOAc) to afford the aminoalcohol (518 mg) as a pale yellow powder. Ammonia (25 mL) was then condensed into a 2-neck flask, followed by addition of sodium (172 mg; 7.5 mmol) and the aminoalcohol (460 mg; 0.58 mmol) was added as a solution in THF (20 mL). After one minute, the reaction was quenched with excess 2-propanol. The crude solution was then
concentrated under reduced pressure, and redissolved in deionized water (25 mL) and diethyl ether (150 mL). The layers were separated, and the aqueous layer was then further extracted with diethyl ether (8 x 125 mL). The ethereal layer was dried (magnesium sulfate) and filtered, followed by concentration under reduced pressure to give a light yellow solid (222 mg). The latter was then dissolved in methanol (7.5 mL) at room temperature, and concentrated hydrochloric acid (1 mL) was added. The solution was stirred for 5 minutes and then allowed to stand overnight. To this solution was added ether (30 mL), which resulted in precipitation of the hydrochloride, which was filtered and washed with diethyl ether, affording the pure hydrochloride \textbf{17} (136 mg; 27\% for three steps) as off-white crystals.

\text{mp} > 250 ^\circ \text{C}; [\alpha]_D^{28.5} = -51.5 \text{ (c=0.32, CH}_2\text{OH)}; \text{IR (neat) 3341 (very broad, 2931, 1624, 1501, 1401, 1321, 1068, 664 cm}^{-1}; \text{^1H NMR (CD}_3\text{OD, 300 MHz)} \delta 4.22 \text{ (dd, } J = 11.1, 2.4 \text{ Hz, } 1\text{H), 4.11 \text{ (dd, } J = 9.4, 2.8 \text{ Hz, } 1\text{H), 4.05-3.85 \text{ (m, } 6\text{H), 3.73 \text{ (dd, } J = 9.4, 3.5 \text{ Hz, } 1\text{H), 3.70-3.58 \text{ (m, } 2\text{H), 3.41 \text{ (t, } J = 10.6 \text{ Hz, } 1\text{H); } \text{^1H NMR (D}_2\text{O, 500 MHz)} \delta 4.09 \text{ (t, } J = 3.5 \text{ Hz, } 1\text{H), 4.04 \text{ (t, } J = 3.7 \text{ Hz, } 1\text{H), 4.01 \text{ (m, } 2\text{H), 3.99 \text{ (dd, } J = 10.8, 3.1 \text{ Hz, } 1\text{H), 3.86 \text{ (dd, } J = 10.3, 3.2 \text{ Hz, } 1\text{H), 3.76 \text{ (dd, } J = 10.1, 2.7 \text{ Hz, } 1\text{H), 3.74 \text{ (dd, } J = 10.6, 2.7 \text{ Hz, } 1\text{H), 3.56 \text{ (t, } J = 9.9 \text{ Hz, } 1\text{H), 3.16 \text{ (t, } J = 11.0 \text{ Hz, } 1\text{H), 2.97 \text{ (t, } J = 10.5 \text{ Hz, } 1\text{H), 2.78 \text{ (t, } J = 10.1 \text{ Hz, } 1\text{H) Note: }} \text{Chemical shifts will change with concentration; } \text{^13C NMR (CD}_3\text{OD, 75 MHz)} \delta 73.33, 73.29, 73.15, 72.65, 72.30, 71.78, 69.86, 69.35, 69.23, 63.49, 62.42, 53.40; \text{HRMS calcd. for C}_{12}\text{H}_{25}\text{O}_9\text{N}_2: 341.1560; \text{Found: 341.1561. Anal. Calcd. for C}_{12}\text{H}_{24}\text{N}_2\text{O}_9 \cdot 1.3 \text{ HCl: C 37.18, H 6.58, N 7.23; Found: C 36.82, H 6.94, N 6.87.}
N-[7-Bromo-5-(7-bromo-4-hydroxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-5-yloxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-4-yl]-4-methyl-benzenesulfonamide (26a)

mp = 131-133°C; [α]D<sup>25</sup> = +47.4 (c = 1.0, CHCl<sub>3</sub>); IR (KBr pellet) 3480, 3272, 2987, 1495, 1382, 1247, 1055 cm<sup>-1</sup>; H NMR (CDCl<sub>3</sub>, 300 MHz) δ; HRMS calcd. for C<sub>25</sub>H<sub>32</sub>Br<sub>2</sub>NO<sub>8</sub>S (M+H)<sup>+</sup>: 664.0215; Found 664.0213; Anal. Calcd. for C<sub>25</sub>H<sub>31</sub>Br<sub>2</sub>NO<sub>8</sub>S: C, 45.13; H, 4.70. Found C, 45.08, H, 4.88.

N-[7-Bromo-5-(7-bromo-5-hydroxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-4-yloxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-4-yl]-4-methyl-benzenesulfonamide (26b)

mp = 224-225°C; [α]D<sup>25</sup> = +64.9 (c = 1.0, CHCl<sub>3</sub>); IR (KBr pellet) 3469, 3260, 2987, 2932, 1454, 1382, 1219, 1076 cm<sup>-1</sup>; HRMS calcd. for C<sub>25</sub>H<sub>32</sub>Br<sub>2</sub>NO<sub>8</sub>S (M+H)<sup>+</sup>: 664.0215; Found 664.0216; Anal. Calcd. for C<sub>25</sub>H<sub>31</sub>Br<sub>2</sub>NO<sub>8</sub>S: C, 45.13; H, 4.70. Found C, 45.00, H, 4.63.

N-[5-(4-hydroxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-5-yloxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-4-yl]-4-methyl-benzenesulfonamide (27a)

To a degassed solution of alcohol 26a (780 mg, 1.1 mmol) in THF (20 mL), was added tributyltin hydride (1.27 mL, 4.7 mmol) and the solution heated to reflux for 1 hour. To the mixture was then added AIBN (19 mg, 0.011 mmol) and the solution continued to reflux for 12 hours. The solvent was removed under reduced pressure and the residue
purified by flash chromatography (3:1 hexane: ethyl acetate) to give diene 27a (551 mg, 92%) as a white solid.

mp = 198-199 °C; [α]D<sup>25</sup> = +27.6 (c = 1.0, CHCl<sub>3</sub>); IR (KBr pellet) 3504, 3204, 2983, 1599, 1287, 1051 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.86 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 6.04 (d, J = 9.9 Hz, 2H), 5.87-5.77 (m, 2H), 5.55 (d, J = 6.9 Hz, 1H), 4.57 (s, 2H), 4.19 (d, J = 9.9, 1H), 4.05-3.90 (m, 4H), 3.62 (dd, J = 16.8 Hz, 1H), 3.30 (dd, J = 8.7 Hz, 1H), 2.51 (d, J = 3.3 Hz, 1H), 2.40 (s, 3H), 1.48 (s, 3H), 1.44 (s, 3H); 1.39 (s, 3H), 1.30 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz) δ 142.6, 139.4, 133.2, 133.1, 128.9, 127.4, 110.5, 110.3, 82.6, 77.0, 76.5, 72.9, 72.2, 68.5, 58.0, 27.8, 27.6, 25.9, 25.4, 21.3; HRMS Calcd. for C<sub>25</sub>H<sub>34</sub>NO<sub>8</sub>S (M+H)<sup>+</sup>: 508.2005, Found 508.2006; Anal. Calcd. for C<sub>25</sub>H<sub>33</sub>NO<sub>8</sub>S: C, 59.16; H, 6.55. Found C, 59.06; H, 6.44.

N-[5-(5-hydroxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-4-yloxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-4-yl]-4-methyl-benzenesulfonamide (27b)

Procedure analogous to the preparation of 27a. Diene 27b (86 %) was obtained as a white solid.

mp = 218-225 °C (decomp); [α]D<sup>25</sup> = +15.6 (c = 1.0, CHCl<sub>3</sub>); IR (KBr pellet) 3516, 3212, 2984, 1618, 1247, 1050 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.78 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.01 (d, J = 9.9 Hz, 1H), 5.87 (d, J = 8.1 Hz, 1H), 5.68 (s, 2H), 5.00 (d, J = 7.5 Hz, 1H), 4.55 (d, J = 6.3 Hz, 2H), 4.09-3.03 (m, 3H), 3.85 (d, J = 8.7 Hz, 1H), 3.52-3.37 (m, 2H), 2.60 (bs, 1H), 2.38 (s, 3H), 1.51 (s, 3H), 1.35 (d, J = 3.6 Hz, 6H); 1.27 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 Hz), δ 142.6, 139.4, 133.2, 133.1, 128.9,
N-[5-(5-Hydroxy-2,2,7,7-tetramethyl-hexahydro-benzo[1,2-d;3,4-d]bis[1,3]dioxol-4-yloxy)-2,2,7,7-tetramethyl-hexahydro-benzo[1,2-d;3,4-d]bis[1,3]dioxol-4-yl]-4-methyl-benzenesulfonamide (28)

To a solution of diene 27b (213 mg, 0.42 mmol) in a 10:1 mixture of acetone and water (10 mL), was added NMNO (295 mg, 2.5 mmol). A crystal of solid OsO4 was added and the reaction mixture was stirred overnight. The reaction was quenched with excess sodium sulfite and stirring was continued for 15 minutes. The pH was adjusted to 3 with 1N HCl (10 mL) and the mixture extracted (10 x 20 mL) with CH2Cl2. The combined organic layers were dried with NaSO4 and concentrated in vacuo to yield a brown solid. The crude mixture was dissolved in acetone (10 mL) and DMP (0.11mL, 0.90 mmol) was added, followed by a catalytic amount of pTsOH. The solution was stirred at room temperature for 4 hrs. The mixture was diluted with CH2Cl2 (20 mL) and washed with 10% NaOH (25 mL). The aqueous layer was extracted with CH2Cl2 (3 x 15 mL), dried with MgSO4, and the solvent removed under reduced pressure. Flash chromatography gave 28 (178 mg; 65% for two steps).

mp = 198-199 °C; [α]D25 = –44.6 (c = 1.0, CHCl3); IR (KBr pellet) 3449, 2990, 2937, 1495, 1374, 1217, 1054, 858, 754 cm⁻¹; ¹H NMR (CDCl3, 300 MHz) δ: 7.81 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 6.39 (d, J = 4.4 Hz, 1H), 4.31 (m, 3H), 4.17 (m, 3H), 4.11 (m, 3H), 4.02 (dd, J = 7.4, 6.5 Hz, 1H), 3.49-3.25 (m, 4H), 2.41 (s, 3H), 1.57 (s,
3H), 1.49 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H), 1.22 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 143.1, 137.8, 129.1, 127.6, 110.1, 110.0, 109.5, 85.4, 80.3, 79.0, 78.5, 78.3, 77.6, 76.1, 75.5, 71.9, 56.7, 27.7, 27.5, 27.1, 26.1, 25.4, 25.2, 25.1, 24.7, 21.4; HRMS Calcd. for C$_{31}$H$_{46}$NO$_{12}$S (M+H)$^+$: 656.2740; Found 656.2748; Anal. Calcd. for C$_{31}$H$_{45}$NO$_{12}$S: C, 56.78; H, 6.92. Found C, 56.66, H, 6.78.

6-(2,3,4,5-Tetrahydroxy-6-methyl-cyclohexyoxy)-cyclohexane-1,2,3,4,5-pentaol (24)

A flame dried round bottom flask, was charged with sodium pieces (12 mg, 0.05 mmol) under argon. Liquid ammonia was bubbled through and liquefied via a cold finger. A solution of 28 (120 mg, 0.01 mmol) dissolved in THF (3 mL) was added dropwise, allowed to stir for 5 minutes, and opened up to air to release the remaining ammonia. Water (5mL) was added slowly to quench the excess sodium and the mixture was extracted with diethyl ether (3x 10ml). The solution was dried with sodium sulfate and the solvent removed under reduced pressure to give a brown oil. The crude residue was dissolved in methanol (5 mL). Two drops of concentrated hydrochloric acid was added and the solution left to stand for 24 hours. A white precipitate appeared, which was removed by filtration and washed with MeOH (10 ml). The white solid was recrystallized from MeOH and ether to yield the title compound (39 mg; 52% over 2 steps).

$\left[\alpha\right]_{D}^{30} = -72.8$ (c=1.0, H$_2$O); IR (KBr-pellet) 3444, 2932, 1567, 1420, 1375, 1320, 1210, 1085, 900 cm$^{-1}$; $^1$H NMR (D$_2$O, 300 MHz) δ 4.18-3.91 (m, 8H), 3.82-3.77 (m, 3H), 3.42 (dd, $J = 10.2$ Hz, 1H); $^{13}$C NMR (D$_2$O, 75 MHz) δ 87.2, 83.1, 75.6, 74.3, 74.1, 74.0,
73.7, 73.6, 73.3, 72.9, 69.9, 57.9; HRMS calcd. for C_{12}H_{24}NO_{10} (M+): 342.1400; Found: 324.1402; Anal. Calcd. for C_{12}H_{23}NO_{10} \cdot 0.5\text{HCl} \cdot 0.5\text{H}_{2}\text{O}: \text{C}, 39.11; \text{H}, 6.70; \text{Found \ C},\ 38.67, \text{H}, 6.79.