Supporting Information

for

Stereoselective syntheses of 3-aminocyclooctanetriols and halocyclooctanetriols

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A. Experimental section

General information

Melting points are uncorrected. Infrared spectra were obtained from solution in 0.1 mm cells or KBr pellets on an FTIR Mattson 1000 instrument. The $^1$H and $^{13}$C NMR spectra were recorded on 400 (100) MHz Varian or 400 (100) MHz Bruker spectrometer and are reported in $\delta$ units with SiMe$_4$ as internal standard. Elemental analyses were carried out on a LECO’s CHNS-932 instrument. Melting points were determined on a GallenKamp MPD 350. Column chromatography was performed on silica gel (60 mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F$_{254}$ analytical aluminium plates.

7,8-Dioxabicyclo[4.2.2]deca-9-ene (5), cis-2-cyclooctene-1,4-diol (6a), cis-1,4-diacetoxy-2-cyclooctene (6b) and (1$R$(S),2$R$(S),3$S$(R),4$S$(R))-2,3-dihydroxycyclooctane-1,4-diyldiacetate (7) were prepared as described in the literature [1].

(2$s$,3$aR$(S),4$S$(R),9$R$(S),9$aS$(R))-2-Oxidoctahydrocycloocta[d][1,3,2]dioxathiole-4,9-diyldiacetate (8): To a cooled (at 0 °C), magnetically stirred solution of diacetate diol 7 (1.60 g, 6.15 mmol) and pyridine (1.46 g, 18.51 mmol) in CH$_2$Cl$_2$ (20 mL) was added a dichloromethane solution (5 mL) of thionyl chloride (2.20 g, 18.51 mmol) dropwise over a period of 10 min. Stirring was continued for 2 h at 0 °C and stirred at room temperature for 19 h (the reaction was followed by TLC). To the reaction mixture was added water (25 mL) and extracted with ethyl acetate (4 × 30 mL). The combined organic extracts were washed with 1 N HCl solution (50 mL) and saturated NaHCO$_3$ solution (20 mL) and NaCl solution (20 mL). The organic solution was dried over Na$_2$SO$_4$. Evaporation of the solvents gave pure 8 (1.79 g, 95%). Sulfite 8 was recrystallized from CH$_2$Cl$_2$/n-hexane (9:1) as a colourless crystal; mp 146-147 °C. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 5.30-5.20 (m, 2H, CH$_{-}$OAc), 5.00-4.93 (m, 2H, CH$_{-}$SO$_3$), 2.07 (s, 6H, 2xOAc), 2.06-1.48 (series of m, 8H, CH$_2$). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 170.1, 82.2, 69.6, 32.3, 22.6, 21.2; IR (KBr, cm$^{-1}$): 2951, 2877, 1744, 1465, 1451, 1429, 1374, 1323, 1235, 1205, 1029, 996, 969, 955. Anal. Calcd for C$_{12}$H$_{18}$O$_7$S (306.08): C 47.05; H 5.92; S 10.47; found C 46.89; H 5.81; S 10.47.

(3$aR$(S),4$S$(R),9$R$(S),9$aS$(R))-2,2-Dioxidoctahydrocycloocta[d][1,3,2]dioxathiole-4,9-diyldiacetate (9): The sulfite 8 (1.81 g, 5.91 mmol) was dissolved in CCl$_4$ (20 mL). To mixture
was added NaIO₄ (1.90 g, 8.88 mmol) and acetonitrile (20 mL) and water (20 mL) and RuCl₃·3H₂O (15 mg). The reaction mixture was stirred 2.5 h at room temperature. The mixture was extracted with ethyl acetate (4 × 30 mL). The organic solution was dried over Na₂SO₄. Evaporation of the solvents gave pure 9 (1.80 g, 95%). Sulfate 9 was recrystallized from CH₂Cl₂/n-hexane (9:1) as a colourless crystal; mp 130-131 °C. ¹H-NMR (400 MHz, CDCl₃): δ 5.52-5.41 (m, 2H, CH- OAc), 5.12-5.05 (m, 2H, CH-SO₄), 2.09 (s, 6H, 2xOAc), 2.09-1.46 (series of m, 8H, CH₂). ¹³C-NMR (100 MHz, CDCl₃): δ 169.6, 84.5, 69.5, 31.4, 22.6, 21.1; IR (KBr, cm⁻¹): 2950, 2900, 1753, 1477, 1390, 1232, 1106, 1030, 957. Anal. Calcd for C₁₂H₁₈O₈S (322.07): C 44.72; H 5.63; S 9.95; found C 44.91; H 5.48; S 10.04.

(1S(R),2S(R),3R(S),4R(S))-3-Azidocyclooctane-1,2,4-triol (10): A mixture of the sulfate 9 (1.00 g, 3.10 mmol) and NaN₃ (1.00 g, 15.38 mmol) in absolute DMF (10 mL) was stirred under nitrogen for 24 h at 80 °C. The mixture was cooled to room temperature and THF (20 mL) was added. Then concentrated H₂SO₄ (4 drops) and water (4 drops) were added to the stirred suspension. After 40 min NaHCO₃ (400 mg) was added and the reaction mixture was stirred for 40 min. Filtration through a Celite and silica gel bed and concentration of the filtrate under reduced pressure provided a viscous oil. Column chromatography (silica gel, 100 g) eluting with MeOH/CH₂Cl₂ (3:97) gave azidosulfate diacetate (0.8 g, 70%) as a white solid. Absolute methanol (10 mL) containing 20% HCl gas was added into the azidosulfate diacetate (220 mg, 0.60 mmol). The mixture was stirred at room temperature for 2.5 h. Evaporation of solvent gave 118 mg (97% yield) of azidotriol 10 as a colourless oil. ¹H-NMR (400 MHz, D₂O): δ 4.07 (dt, J = 8.7, 2.3 Hz, 1H, H₄), 3.68-3.59 (m, 2H, H₁ and H₂), 3.59-3.52 (m, 1H, H₃), 1.90-1.30 (series of m, 8H, CH₂). ¹³C-NMR (100 MHz, D₂O): δ 73.4, 72.1, 70.0, 69.8, 31.8, 30.7, 23.6, 20.5; IR (KBr, cm⁻¹): 3407, 2934, 1420, 1365, 1284, 1230, 1068, 1038, 959.

Anal. Calcd for C₈H₁₅N₃O₅ (201.11): C 47.75; H 7.51; N 20.88; found C 47.76; H 7.35; N 20.71.

(1S(R),2S(R),3R(S),4R(S))-3-Azidocyclooctane-1,2,4-triyl triacetate (11). General procedure for the acetylation of hydroxyl groups: In a similar manner as described in the literature [2], the azidotriol 10 (280 mg, 1.39 mmol) was dissolved in anhydrous pyridine (3 mL) and the solution was cooled 0 °C. Ac₂O (0.7 mL, 8.35 mmol) and 4-(dimethylamino)pyridine (DMAP) (2.8 mg) were added and the solution was stirred for 2.5 day at room temperature. The mixture was cooled to 0 °C and 2 N HCl (70 mL) solution was
added. The mixture was extracted with ether (6 × 30 mL). The combined organic extracts were washed with saturated NaHCO₃ solution (70 mL) and water (3 × 10 mL) and then dried (Na₂SO₄). After evaporation of solvent, chromatography of the mixture on a silica gel column eluting with EtOAc/n-hexane (3:97) gave 350 mg (76%) of triacetate 11 as a colourless oil.

1H-NMR (400 MHz, CDCl₃): δ 5.24-5.15 (m, 2H, H-4 and H-2), 5.04-4.97 (m, 1H, H-1), 3.87 (dd, J = 8.8, 2.7 Hz, 1H, H-3), 2.06 (s, 3H), 2.05 (s, 3H) 1.98 (s, 3H), 2.10-1.58 (series of m, 8H, CH₂).

13C-NMR (100 MHz, CDCl₃): δ 170.1, 170.0, 169.8, 72.7, 72.1, 71.3, 65.6, 31.2, 28.6, 23.5, 21.8, 21.1, 21.0, 20.8; IR (KBr, cm⁻¹): 2941, 2870, 2106, 1744, 1433, 1371, 1238, 1028, 974, 906. Anal. Calcd for C₁₄H₂₁N₃O₆ (327.14): C 51.37; H 6.47; N 12.84; found C 51.52; H 6.52; N 12.99.

(1S(R),2S(R),3R(S),4R(S))-3-Aminocyclooctane-1,2,4-triol (12). General procedure for hydrogenation: In a similar manner as described in the literature [2], into a 50 mL flask was placed palladium on charcoal (30 mg, 10%) and azidotriol 10 (250 mg, 1.24 mmol) in absolute methanol (30 mL). The reaction mixture was flushed with hydrogen gas (the air in the solvent was removed under vacuum, and then the flask was filled with hydrogen gas; this process was repeated three times). The resulting mixture was stirred at room temperature for 2 h under the hydrogen atmosphere. The catalyst was removed by filtration. Evaporation of the solvent gave pure aminotriol 12 (207 mg, 95%) as a colourless viscous oil.

1H-NMR (400 MHz, CD₃OD): δ 3.99-3.91 (m, 1H, H-4), 3.75 (t, J = 8.4, 1H, H-2), 3.54-3.47 (m, H-1), 3.08 (dd, J = 7.9, 2.8 Hz, H-3), 1.96-1.34 (series of m, 8H, CH₂). 13C-NMR (100 MHz, CD₃OD): δ 74.8, 69.8, 69.5, 55.1, 30.2, 30.1, 21.7, 20.8; IR (KBr, cm⁻¹): 3390, 2935, 1466, 1386, 1123, 1037. Anal. Calcd for C₈H₁₇NO₃ (175.12): C 54.84; H 9.78; N 7.99; found C 54.74; H 9.71; N 7.88.

(1R(S),2S(R),7R(S),8S(R))-9-Oxabicyclo[6.1.0]nonane-2,7-diol (13): Compound 13 was prepared as described in the literature [1].

(1S(R),2R(S),3R(S),4R(S))-3-Bromocyclooctane-1,2,4-triol (14): Absolute methanol (25 mL) containing 35% HBr gas was added into trans-epoxide 13 (1.30 g, 8.22 mmol) and stirred at 0 °C for 30 min. Then, the reaction mixture was stirred for 19 h at room temperature. After removal of the solvent, crude product was dissolved in 25 mL of methanol and added into excess BaCO₃ (10 g) for neutralization (pH = 8), and stirred magnetically at room temperature for 4 h. The solvent was removed under reduced pressure and the residue
was dissolved in acetone and stirred for 5 min. The solid was filtered off. Evaporation of the solvent gave bromotriol 14 (1.89 g, 96%) as a colourless oil. 1H-NMR (400 MHz, CD3OD): δ 4.25 (dd, J = 8.7, 2.2 Hz, 1H, H-3), 4.05-3.97 (m, H-4), 3.93 (t, J = 8.6 Hz, 1H, H-2), 3.76-3.64 (m, H-1), 2.00-1.40 (series of m, 8H, CH2). 13C-NMR (100 MHz, CD3OD): δ 76.6, 71.5, 69.1, 68.1, 35.1, 33.2, 23.3, 21.8; IR (KBr, cm\(^{-1}\)): 3418, 2986, 2930, 2866, 1456, 1371, 1216, 1171, 1055, 1019, 949. Anal. Calcd for C8H15BrO3 (238.02): C 40.19; H 6.32; found C 40.09; H 6.40.

(1S(R),2R(S),3R(S),4R(S))-3-Bromocyclooctane-1,2,4-triyl triacetate (15): The bromotriol 14 (3.0 g, 12.55 mmol) was submitted to acetylation with Ac2O and DMAP in pyridine following the method described above for the acetylation of 10 to give 15: 3.75 g, 81%. Bromotriacetate 15 was recrystallized from CH2Cl2/hexane as colourless crystals; mp 92-94 °C. 1H-NMR (400 MHz, CDCl3): δ 5.46 (t, J = 9.0 Hz, 1H, H-2), 5.21-5.15 (m, 1H, H-4), 5.07 (ddd, J = 8.5, 7.3, 3.9 Hz, 1H, H-1), 4.42 (dd, J = 9.3, 2.4 Hz, 1H, H-3), 2.08 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H), 1.99-1.58 (series of m, 8H, CH2). 13C-NMR (100 MHz, CDCl3): δ 170.2, 169.8, 169.7, 74.3, 71.8, 71.0, 57.3, 32.5, 31.8, 23.3, 21.9, 21.3, 21.0, 20.8; IR (KBr, cm\(^{-1}\)): 2938, 2882, 1743, 1469, 1447, 1380, 1233, 1090, 1033, 975. Anal. Calcd for C14H21BrO6 (364.05): C 46.04; H 5.80; found C 46.06; H 5.66.

(1S(R),2S(R),3S(R),4R(S))-3-Azidocyclooctane-1,2,4-triyl triacetate (16): To a magnetically stirred solution of 15 (1.26 g, 5.27 mmol) in DMF (15 mL) to the mixture was added NaN3 (2.74 g, 42.16 mmol) and the mixture heated to 100 °C and was stirred at 100 °C for 28 h. The reaction mixture was filtered with methanol through a pad of silica gel in a sintered glass funnel. After evaporation of the solvents, chromatography of the mixture on a silica gel (100 g) column eluting with MeOH/CH2Cl2 (4:96) gave the azidotriol 16 (0.83 g, 78%) as a colourless oil. 1H-NMR (400 MHz, D2O): δ 3.90 (dd, J = 8.7, 2.5 Hz, H-2), 3.88-3.76 (m, 2H, H-1 and H-4), 3.69 (dd, J = 9.2, 2.5 Hz, 1H, H-3), 1.96-1.48 (series of m, 8H, CH2). 13C-NMR (100 MHz, D2O): δ 74.9, 72.4, 71.7, 70.0, 32.5, 31.4, 23.8, 23.2; IR (KBr, cm\(^{-1}\)): 3399, 2932, 2872, 2114, 1453, 1416, 1359, 1260, 1161, 1092, 1053, 1001, 982. Anal. Calcd for C14H15N3O3 (201.11): C 47.75; H 7.51; N 20.88; found C 47.60; H, 7.41; N 20.79.

(1S(R),2S(R),3S(R),4R(S))-3-Azidocyclooctane-1,2,4-triyl triacetate (17): The azidotriol 16 (200 mg, 0.99 mmol) was submitted to acetylation with Ac2O and DMAP in pyridine following the method described above for the acetylation of 10 to give 17: 243 mg, 74%; as a
colourless oil. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 5.47 (dd, $J_{2,1} = 9.4$ Hz, $J_{2,3} = 2.2$ Hz, 1H, H-2), 5.28-5.21 (m, 1H, H-1), 4.96 (t, $J = 7.8$ Hz, 1H, H-4), 3.95 (dd, $J = 8.6$ Hz, $J_{3,2} = 2.2$ Hz, H-3), 2.10 (s, 6H, 2xOAc) 2.02 (s, 3H, OAc) 2.10-1.55 (series of m, 8H, CH$_2$).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 170.0, 169.9, 169.7, 75.3, 72.6, 71.9, 65.4, 30.3, 28.4, 24.6, 21.7, 21.1, 21.0, 20.7; IR (KBr, cm$^{-1}$): 2943, 2887, 2118, 1742, 1472, 1445, 1371, 1253, 1201, 1094, 1033 960.

Anal. Calcd for C$_{14}$H$_{21}$N$_3$O$_6$ (327.14): C 51.37; H, 6.47; N, 12.84; found C 51.43; H 6.33; N, 12.73.

(1S(R),2S(R),3S(R),4R(S))-3-Aminocyclooctane-1,2,4-triol (18): The azidotriol 16 (200 mg, 0.99 mmol) was hydrogenated with Pd (10% on activated carbon; 25 mg) as described above for the synthesis of 12 to give aminotriol 18 (170 mg, 97%); as a colourless oil.

$^1$H-NMR (400 MHz, D$_2$O): $\delta$ 3.74 (ddd, $J = 8.2$, 6.6, 1.4 Hz, 1H, H-1), 3.61 (dd, $J = 8.8$, $J_{3,4} = 2.8$ Hz, H-3), 3.60-3.54 (m, 1H, H-4) 2.90 (dd, $J_{3,4} = 9.4$, $J_{3,2} = 2.7$ Hz, 1H, H-3), 1.90-1.32 (series of m, 8H, CH$_2$).

$^{13}$C-NMR (100 MHz, D$_2$O): $\delta$ 76.5, 73.4, 72.8, 56.7, 32.9, 32.2, 24.7, 23.3; IR (KBr, cm$^{-1}$): 3390, 2935, 1466, 1386, 1123, 1037. Anal. Calcd for C$_8$H$_{17}$NO$_3$ (175.12): C 54.84; H 9.78; N 7.99; found C 54.74; H 9.66; N 7.89.

(1S(R),2R(S),3R(S),4R(S))-3-Chlorocyclooctane-1,2,4-triol (19): To a magnetically stirred solution of the trans-epoxide 13 (2.0 g, 12.64 mmol) in absolute methanol (5 mL) was cooled to 0 °C. Then, absolute methanol (30 mL) containing 20% HCl gas was added into the reaction mixture and stirred at room temperature for 19 h. Evaporation of the solvent under reduced pressure and crystallization of the residue from MeOH/ether (8:2) gave chlorotriol 19 as colourless crystals (2.37 g, 96%), mp 117-119 °C. $^1$H-NMR (400 MHz, D$_2$O): $\delta$ 4.14 (dt, $J = 9.0$, $J_{3,4} = 2.8$ Hz, H-4), 4.07 (dd, $J = 8.6$, $J_{3,4} = 2.8$ Hz, H-3), 3.74 (t, $J = 8.8$ Hz, H-2), 3.60 (ddd, $J = 9.3$, 5.7, 4.0 Hz, H-1), 1.90-1.34 (series of m, 8H, CH$_2$).

$^{13}$C-NMR (100 MHz, D$_2$O): $\delta$ 74.8, 71.8, 71.4, 69.4, 33.0, 31.2, 23.6, 20.9; IR (KBr, cm$^{-1}$): 3292, 2934, 2875, 1459, 1402, 1322, 1295, 1256, 1234, 1215, 1144, 1040, 975. Anal. Calcd for C$_8$H$_{15}$ClO$_3$ (194.07): C 49.36; H 9.78; N 7.99; found C 49.42; H 9.66; N 7.89.

(1S(R),2R(S),3R(S),4R(S))-3-Chlorocyclooctane-1,2,4-triy triacetate (20): The chlorotriol 19 (2.5 g, 12.84 mmol) was submitted to acetylation with Ac$_2$O and DMAP in pyridine following the method described above for the acetylation of 10 to give 20: 3.76 g, 91%. Chlorotriacetate 20 was recrystallized from CH$_2$Cl$_2$/hexane (9:1) as colourless crystals, mp 75-76 °C. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 5.39 (t, $J = 8.8$ Hz, H-2), 5.35 (dt, $J = 9.7$, $J_{3,4} = 2.5$ Hz, H-3), 4.90 (dd, $J = 8.6$, 2.8 Hz, H-4), 3.74 (t, $J = 8.8$ Hz, H-2), 3.60 (ddd, $J = 9.3$, 5.7, 4.0 Hz, H-1), 1.90-1.34 (series of m, 8H, CH$_2$).
(1S(R),2S(R),3R(S),4R(S))-4-Chlorocyclooctane-1,2,3-triyl triacetate (25): $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 5.62 (dd, $J = 9.7, 8.1$ Hz, H-3), 5.25 (dt, $J = 7.3, J_{1,2} = 2.3$ Hz, H-1), 5.05 (dd, $J = 8.0, J_{1,2} = 2.3$ Hz, H-2) 4.26 (dddd, $J = 13.1, 8.7, 3.3$ Hz, H-4), 2.09 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.25-1.50 (series of m, 8H, CH$_2$). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 170.2, 169.7, 169.0, 71.9, 71.4, 70.6, 62.3, 30.0, 27.5, 21.5, 20.9, 20.5, 19.8; IR (KBr, cm$^{-1}$): 2937, 1740, 1645, 1435, 1370, 1239, 1092, 1035, 963. Anal. Calcd for C$_{14}$H$_{21}$ClO$_6$ (320.10): C 52.42; H 6.60; found C 52.35; H 6.64.

(1S(R),2S(R),3R(S),4S(R))-3-Chlorocyclooctane-1,2,4-triyl triacetate (26): $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 5.71 (t, $J = 2.3$ Hz, H-2), 5.25-5.18 (m, H-4) 5.15-5.09 (m, H-1) 4.34 (dd, $J = 9.5, 1.9$ Hz, H-3), 2.18 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.00-1.34 (series of m, 8H, CH$_2$). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 170.2, 169.9, 169.7, 75.5, 74.0, 73.6, 62.5, 29.7, 27.1, 22.7, 22.2, 21.0, 21.0, 20.7; IR (KBr, cm$^{-1}$): 2937, 1740, 1645, 1435, 1370, 1239, 1092, 1035, 963. Anal. Calcd for C$_{14}$H$_{21}$ClO$_6$ (320.10): C 52.42; H 6.60; found C 52.30; H 6.64.

Acetylation and reaction of epoxy-diol 22 with HCl(g)-MeOH: To a magnetically stirred solution of epoxy-diol 22 (500 mg, 3.16 mmol) in absolute methanol (5 mL) was cooled to 0 °C. Then, Absolute methanol (15 mL) containing 40% HCl gas was added into the reaction mixture and stirred at room temperature for 2.5 h. Evaporation of the solvent gave a mixture of chlorotriol 23 and chlorotriol 24 (590 mg, total yield 96%). From $^1$H NMR spectroscopy, it was observed that the mixture of 23 and 24 was in an 85:15 ratio. But these isomers could not be obtained in pure form, although all chromatographic purification methods were employed. Then, 450 mg (2.31 mmol) of the resultant mixture was submitted to acetylation with Ac$_2$O and DMAP in pyridine following the method described above for the acetylation of 10 to give a mixture of the diacetate isomer (670 mg), total yield 90%. Chromatography of the mixture on a silica gel column (80 g) eluting with EtOAc/hexane (10:90) gave the first fraction of chlorotriacetate 26 (90 mg, 12%, as a colourless oil) and the second chlorotriacetate 25 (0.55 g, 74%, as a colourless oil).
(1R(S),2R(S),3S(R),4S(R))-4-Chlorocyclooctane-1,2,3-triol (23): To a magnetically stirred solution of chlorotriacetate 25 (200 mg, 0.62 mmol) in absolute methanol (3 mL) was cooled to 0 °C. Then, Absolute methanol (15 mL) containing 20% HCl gas was added into the reaction mixture and stirred at room temperature for 2.5 h. Evaporation of the solvent gave chlorotriol 23 (118 mg, yield 97%). The chlorotriol 23 was recrystallized from CH$_2$Cl$_2$/hexane (9:1) as colourless crystals, mp 107-108 °C. $^1$H-NMR (400 MHz, CDCl$_3$): δ 4.03-3.96 (m, H-1), 3.89 (dt, J = 7.8, 2.6 Hz, H-4), 3.85 (dd, J = 9.6, J$_{3,2}$ = 7.9 Hz, H-3) 3.54 (dd, J$_{2,3}$ = 7.9, 2.7 Hz, H-2), 2.00-1.20 (series of m, 8H, CH$_2$). $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 72.5, 72.0, 71.2, 67.9, 30.5, 28.9, 21.5, 20.3; IR (KBr, cm$^{-1}$): 3400, 2925, 2878, 2863, 2731, 1467, 1458, 1392, 1372, 1284, 1267, 1221, 1067, 980, 959. Anal. Calcd for C$_8$H$_{15}$ClO$_3$ (194.07): C 49.36; H 7.77; found C 49.43; H 7.66.

(1R(S),2R(S),3S(R),4R(S))-3-Chlorocyclooctane-1,2,4-triol (24): The chlorotriacetate 26 (300 mg, 0.93 mmol) was submitted to hydrolysis with HCl(g)-MeOH following the method described above for the hydrolysis of 25 to give 24: 173 mg, 95%, as a colourless oil. $^1$H-NMR (400 MHz, CDCl$_3$): δ 4.17 (dd, J = 3.0, 1.6 Hz, H-2), 4.04 (dd, J$_{3,4}$ = 9.2, J = 1.4 Hz, H-3), 3.92-3.86 (m, H-4), 3.64 (dt, J = 11.9, 3.6 Hz, 1H), 2.00-0.95 (series of m, 8H, CH$_2$). $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 75.7, 74.5, 74.4, 69.7, 30.9, 28.4, 22.8, 21.9; IR (KBr, cm$^{-1}$): 3410, 2983, 2934, 1466, 1370, 1254, 1218, 1163, 1121, 1051, 961. Anal. Calcd for C$_8$H$_{15}$ClO$_3$ (194.07): C 49.36; H 7.77; found C 49.26; H 7.69.

References

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B. NMR Spectra

(25,3aR(S),4S(R),9R(S),9aS(R))-2-Oxidoctahydrocycloocta[\[1,3,2\]dioxathiole-4,9-diyl diacetate (8): CDCl₃ (¹H NMR and ¹³C NMR)
(2s,3aR(S),4S(R),9R(S),9aS(R))-2-Oxidoctahydrocycloocta[d][1,3,2]dioxathiole-4,9-diyl diacetate (8): CDCl₃-HMQC
(2s,3aR(S),4S(R),9R(S),9aS(R))-2-Oxidoctahydrocycloocta[d][1,3,2]dioxathiole-4,9-diyl diacetate (8): CDCl₃-COSY
(3aR,4S(R),9R(S),9aS(R))-2,2-Dioxidoctahydrocycloocta[d][1,3,2]dioxathiole-4,9-diyl diacetate (9): CDCl₃ (¹H NMR and ¹³C NMR)
1S(R),2S(R),3R(S),4R(S))-3-Azidocyclooctane-1,2,4-triol (10): D$_2$O ($^1$H NMR and $^{13}$C NMR)
(1S(R),2R(S),3R(S),4R(S))-3-Azidocyclooctane-1,2,4-triyl triacetate (11): CDCl$_3$ ($^1$H NMR and Double Resonance)
(1S(R),2S(R),3R(S),4R(S))-3-Azidocyclooctane-1,2,4-triyl triacetate (11): CDCl$_3$ ($^{13}$C NMR)
(1S(R),2S(R),3R(S),4R(S))-Azidocyclooctane-1,2,4-triyl triacetate (11): NOE-Dif spectra

a)

b)
(1S(R),2S(R),3R(S),4R(S))-3-Azidocyclooctane-1,2,4-triyl triacetate (11): HMOC
(1S(R),2S(R),3R(S),4R(S))-3-Azidocyclooctane-1,2,4-triyl triacetate (11): COSY
(1S(R),2S(R),3R(S),4R(S))-3-Aminocyclooctane-1,2,4-triol (12): CD$_3$OD ($^1$H NMR and $^{13}$C NMR)
(1S(R),2R(S),3R(S),4R(S))-3-Bromocyclooctane-1,2,4-triol (14): CD3OD ($^1$H NMR and $^{13}$C NMR)
(1S(R),2R(S),3R(S),4R(S))-3-Bromocyclooctane-1,2,4-triyl triacetate (15): CDCl₃ (¹H NMR and double resonance)
(1S(R),2R(S),3R(S),4R(S))-3-Bromocyclooctane-1,2,4-triyl triacetate (15): CDCl$_3$ ($^{13}$C NMR)
(1S(R),2S(R),3S(R),4R(S))-3-Azidocyclooctane-1,2,4-triol (16): D$_2$O ($^1$H NMR and $^{13}$C NMR)
(1S(R),2S(R),3S(R),4R(S))-3-Azidocyclooctane-1,2,4-triy triacetate (17): CDCl$_3$ (¹H NMR and double resonance)
(1S(R),2S(R),3S(R),4R(S))-3-Azidocyclooctane-1,2,4-triyl triacetate (17): CDCl₃ (¹³C NMR)
(1S(R),2S(R),3S(R),4R(S))-3-Azidocyclooctane-1,2,4-triyl triacetate (17): CDCl₃-HMQC
(1S(R),2S(R),3S(R),4R(S))-3-Azidocyclooctane-1,2,4-triyl triacetate (17): CDCl₃-COSY
(1S(R),2S(R),3S(R),4R(S))-3-Aminocyclooctane-1,2,4-triol (18): D$_2$O ($^1$H NMR and $^{13}$C NMR)
(1S(R),2R(S),3R(S),4R(S))-3-Chlorocyclooctane-1,2,4-triol (19): D$_2$O ($^1$H NMR and $^{13}$C NMR)
(1S(R),2R(S),3R(S),4R(S))-3-Chlorocyclooctane-1,2,4-triy1 triacetate (20): CDCl₃ (¹H NMR and double resonance)
(1S(R),2R(S),3R(S),4R(S))-3-Chlorocyclooctane-1,2,4-triyl triacetate (20): CDCl₃ (¹³C NMR)
(1S(R),2R(S),3R(S),4R(S))-3-Chlorocyclooctane-1,2,4-triyl triacetate (20): CDCl$_3$-HMQC
1S(R),2R(S),3R(S),4R(S))-3-Chlorocyclooctane-1,2,4-triyl triacetate (20): CDCl₃-COSY
(1R(S),2R(S),3S(R),4S(R))-4-Chlorocyclooctane-1,2,3-triol (23): D2O (1H NMR and 13C NMR)
(1R(S),2R(S),3S(R),4R(S))-3-Chlorocyclooctane-1,2,4-triol (24): D$_2$O ($^1$H NMR and $^{13}$C NMR)
(1R(S),2R(S),3S(R),4S(R))-4-Chlorocyclooctane-1,2,3-triyl triacetate (25): CDCl₃ ('H NMR and ¹³C NMR)
1R(S),2R(S),3S(R),4S(R)-4-Chlorocyclooctane-1,2,3-triyl triacetate (25): CDCl₃-HMQC
(1R(S),2R(S),3S(R),4S(R))-4-Chlorocyclooctane-1,2,3-triyl triacetate (25): CDCl₃-COSY
(1R(S),2R(S),3S(R),4R(S))-3-Chlorocyclooctane-1,2,4-triyyl triacetate (26): CDCl₃ (¹H NMR and ¹³C NMR)
(1R(S),2R(S),3S(R),4R(S))-3-Chlorocyclooctane-1,2,4-triyl triacetate (26): CDCl₃-HMQC
$(1R(S),2R(S),3S(R),4R(S))$-3-Chlorocyclooctane-1,2,4-triyl triacetate (26): CDCl$_3$-COSY