SUPPORTING INFORMATION

Chain Elongation of Aldoses by Indium-Mediated Coupling with 3-Bromopropenyl Esters

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General methods: All reagents were used from commercial sources without further purification. Dioxane was distilled from sodium/benzophenone.

Thin-layer chromatography (TLC) was carried out on aluminum plates coated with 0.25 mm silica gel 60. The plates were developed with UV-light or by dipping in a Cemol solution (ammonium molybdate (6.25 g) and cerium(IV) sulphate (2.50 g) in 10% sulphuric acid (250 mL)) followed by heating with a heatgun.

Flash column chromatography was performed on silica gel 60 (particle size 0.040-0.063 mm). Macherey-Nagel silica gel 60 C_{18} (particle size 0.040-0.063 mm) was used for reverse phase flash column chromatography. Water was used as the eluent for reverse phase chromatography.

^{1}H NMR were recorded at 500 or 300 MHz in $CDCl_3$ or D_2O. ^{1}H NMR data on literature compounds were within 0.01 ppm of the reported value and coupling constants within 0.3 Hz.

^{13}C NMR were recorded at 126 or 75 MHz in $CDCl_3$ or D_2O. ^{13}C NMR data on literature compounds were within 0.1 ppm of the reported value.

Melting points are uncorrected.

1,2-Dideoxy-D-*glycero*-D-*gulo*-oct-1-enitol (1). ^{1}H NMR (500 MHz, D_2O): δ 5.95 (ddd, *J* = 17.5, 10.7, 7.3 Hz, 1H), 5.36 (dt, *J* = 17.5, 1.3 Hz, 1H), 5.32 (dt, *J* = 10.7, 1.3 Hz, 1H), 4.21 (tt, *J* = 6.0, 1.3 Hz, 1H), 3.92 (dd, *J* = 4.7, 2.6 Hz, 1H), 3.80 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.79-3.75 (m, 1H), 3.73 (dd, *J* = 6.0, 4.7 Hz, 1H), 3.68 (dd, *J* = 7.7, 2.6 Hz, 1H), 3.63 (dd, *J* = 11.5, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, D_2O): δ 136.6, 119.0, 75.3, 73.2, 72.6, 71.7, 69.6, 63.4; Anal. Calcd for $C_8H_{16}O_6$: C, 46.15; H, 7.75. Found: C, 45.81, H, 7.82.

1,2-Dideoxy-D-*glycero*-L-*manno*-oct-1-enitol (2). ^{1}H NMR (500 MHz, D_2O): δ 6.01 (ddd, *J* = 17.4, 10.5, 6.8 Hz, 1H), 5.37 (dt, *J* = 17.4, 1.4 Hz, 1H), 5.31 (dt, *J* = 10.5, 1.4 Hz, 1H), 4.19 (ddt, *J* = 8.0, 6.8, 1.4 Hz, 1H), 3.97 (dt, *J* = 6.0, 1.7 Hz, 1H), 3.93 (dd, *J* = 9.0, 1.3 Hz, 1H), 3.74 (dd, *J* = 8.0, 1.3 Hz, 1H), 3.69 (d, *J* = 6.0 Hz, 2H), 3.67 (dd, *J* = 9.0, 1.7 Hz, 1H); ^{13}C NMR (75 MHz, D_2O): δ 138.3, 118.3, 73.2, 72.2, 70.9, 70.1, 69.1, 63.9; Anal. Calcd for $C_8H_{16}O_6$: C, 46.15; H, 7.75. Found: C, 46.09; H, 7.85.

3,4,5,6,7,8-Hexa-*O*-acetyl-1,2-dideoxy-D-*glycero*-D-*manno*-oct-1-enitol (3a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.69 (ddd, *J* = 17.1, 9.2, 7.7 Hz, 1H), 5.42 (dd, *J* = 9.2, 2.6 Hz, 1H), 5.36 (dt, *J* = 17.1, 0.9 Hz, 1H), 5.29-5.24 (m, 3H), 5.21 (t, *J* = 7.7 Hz, 1H), 5.14 (dt, *J* = 7.7, 3.0 Hz, 1H), 4.34 (dd, *J* = 11.9, 3.0 Hz, 1H), 4.20 (dd, *J* = 11.9, 7.7 Hz, 1H), 2.14 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 170.1, 170.1, 170.0, 169.6, 169.6, 132.3, 121.3, 71.9, 70.2, 69.8,

68.7, 67.8, 61.7, 21.1, 20.9, 20.9, 20.8, 20.8 (2C); Anal. Calcd for $C_{20}H_{28}O_{12}$: C, 52.17; H, 6.13. Found: C, 52.13; H, 6.17.

1,2-Dideoxy-D-*glycero*-D-*manno*-oct-1-enitol (3b). ^{1}H NMR (500 MHz, D_2O): δ 6.07 (ddd, *J* = 17.5, 10.7, 6.8 Hz, 1H), 5.45 (dt, *J* = 17.5, 1.3 Hz, 1H), 5.38 (dt, *J* = 10.7, 1.3 Hz, 1H), 4.25 (tt, *J* = 7.9, 1.3 Hz, 1H), 4.00 (ddd, *J* = 8.1, 5.1, 3.0 Hz, 1H), 3.98 (dd, *J* = 8.1, 1.3 Hz, 1H), 3.91-3.86 (m, 2H), 3.81 (dd, *J* = 7.9, 1.5 Hz, 1H), 3.76 (dd, *J* = 11.9, 7.3 Hz, 1H); ^{13}C NMR (125 MHz, D_2O): δ 138.1, 118.5, 73.3, 73.0, 72.5, 72.2, 70.4, 62.7; HRMS calcd for $C_8H_{16}O_6Na$ $[M + Na]^+$ *m*/*z* 231.0839, found *m*/*z* 231.0841; Anal. Calcd for $C_8H_{16}O_6$: C, 46.15; H, 7.75. Found: C, 45.70; H, 7.55.

3,4,5,6,7,8-Hexa-*O*-acetyl-1,2-dideoxy-D-*glycero*-L-*gulo*-oct-1-enitol (4a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.78 (ddd, *J* = 17.4, 10.2, 7.8 Hz, 1H), 5.40 (d, *J* = 17.4 Hz, 1H), 5.35-5.27 (m, 5H), 5.22 (dd, *J* = 7.7, 6.4 Hz, 1H), 4.25 (dd, *J* = 12.0, 4.3 Hz, 1H), 3.98 (dd, *J* = 12.0, 5.5 Hz, 1H), 2.10 (s, 6H), 2.09 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 170.1, 170.0, 169.9, 169.8, 169.6, 131.7, 121.5, 72.3, 70.7, 69.0, 68.7, 68.3, 61.8, 21.0, 20.8, 20.8, 20.8, 20.7, 20.7; Anal. Calcd for $C_{20}H_{28}O_{12}$: C, 52.17; H, 6.13. Found: C, 52.20; H, 6.03.

1,2-Dideoxy-D-*glycero*-L-*gulo*-oct-1-enitol (4b). ^{1}H NMR (500 MHz, D_2O): δ 5.97 (ddd, *J* = 17.5, 10.4, 7.3 Hz, 1H), 5.36 (dt, *J* = 17.5, 1.3 Hz, 1H), 5.31 (dt, *J* = 10.4, 1.3 Hz, 1H), 4.21 (t, *J* = 6.8 Hz, 1H), 3.89 (dd, *J* = 5.6, 3.4 Hz, 1H), 3.82 (dt, *J* = 7.3, 3.8 Hz,

1H), 3.75 (dd, *J* = 5.6, 3.8 Hz, 1H), 3.70 (dd, *J* = 11.5, 4.3 Hz, 1H), 3.68 (dd, *J* = 6.8, 3.4 Hz, 1H), 3.63 (dd, *J* = 11.5, 6.8 Hz, 1H); ^{13}C NMR (75 MHz, D_2O): δ 137.3, 118.9, 73.8, 73.1, 72.2, 72.1, 70.8, 63.4. Anal. Calcd for $C_8H_{16}O_6$: C, 46.15; H, 7.75. Found: C, 46.01; H, 7.77.

D-*glycero*-D-*gulo*-heptose (5). ^{1}H NMR (300 MHz, D_2O): δ 4.85 (d, *J* = 8.4 Hz, 1H), 4.10 (t, *J* = 3.4 Hz, 1H), 3.96 (d, *J* = 3.6 Hz, 1H), 3.83-3.79 (m, 3H), 3.70-3.64 (m, 1H), 3.62 (dd, *J* = 8.4, 3.5 Hz, 1H); ^{13}C NMR (75 MHz, D_2O): δ 94.6, 72.8, 71.7, 69.6, 69.5, 69.0, 63.6. ^{13}C NMR data are in agreement with literature values.[1]

D-*glycero*-L-*manno*-heptose (6). ^{1}H NMR (500 MHz, D_2O, 3:7 mixture of α and β, anomeric protons only): δ 5.24 (d, *J* = 1.7 Hz, H-1β), 4.94 (d, *J* = 0.9 Hz, H-1α); ^{13}C NMR (125 MHz, D_2O): α-anomer: δ 95.1, 75.8, 74.2, 72.4, 69.9, 67.1, 64.0, β-anomer: δ 95.4, 72.2, 71.9, 71.8, 70.0, 67.4, 64.2. NMR data are in accordance with literature data.[2]

D-*glycero*-D-*manno*-heptose (7). ^{1}H NMR (500 MHz, D_2O, 3:2 mixture of α and β, anomeric protons only): δ 5.15 (d, *J* = 2.1 Hz, H-1α), 4.85 (d, *J* = 1.3 Hz, H-1β); ^{13}C NMR (75 MHz, D_2O): δ 94.7, 94.6, 77.1, 73.9, 73.3, 72.5, 72.4, 71.6, 71.2, 71.1, 68.1, 67.9, 62.5, 62.3. NMR data are in accordance with literature values.[2]

D-*glycero*-L-*gulo*-heptose (8). ^{1}H NMR (500 MHz, D_2O): δ 4.93 (d, *J* = 8.5 Hz, 1H), 4.12 (t, *J* = 3.5 Hz, 1H), 3.98 (dd, *J* = 5.5, 3.0 Hz, 1H), 3.94 (dd, *J* = 7.5, 1.5 Hz, 1H),

3.90 (dd, *J* = 3.5, 1.0 Hz, 1H), 3.82 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.71 (dd, *J* = 8.0, 3.5 Hz, 1H), 3.68 (dd, *J* = 12.0, 5.5 Hz, 1H); ^{13}C NMR (125 MHz, D_2O): δ 94.7, 74.3, 72.0, 71.9, 70.2, 69.7, 62.6; Anal. Calcd for $C_7H_{14}O_7$: C, 40.00; H, 6.71. Found: C, 40.20; H, 6.45. The structure was confirmed by reduction with $NaBH_4$ in MeOH/water mixture to give D-*glycero*-L-*gulo*-heptitol. ^{13}C NMR (75 MHz, D_2O): δ 73.3, 72.5, 72.3, 72.1, 71.2, 64.3, 64.2. These data are in accordance with literature values.[3]

3,4,5,6,7,8,9-Hepta-*O*-acetyl-1,2-dideoxy-D-*threo*-L-*gulo*-non-1-enitol (9a). Isolated as a 3.5:1 mixture of diastereomers, which could not be separated by flash chromatography. The major isomer **9a** had the following analytical data: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.86 (ddd, *J* = 17.5, 10.2, 7.7 Hz, 1H), 5.45 (d, *J* = 17.5 Hz, 1H), 5.41-5.38 (m, 2H), 5.29-5.24 (m, 3H), 5.20-5.17 (m, 2H), 4.26 (dd, *J* = 11.5, 4.7 Hz, 1H), 3.85 (dd, *J* = 11.5, 6.8 Hz, 1H), 2.14 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.3, 170.2, 170.0, 170.0, 169.9, 169.7, 131.1, 121.8, 72.9, 70.9, 68.1, 68.0, 67.7, 67.2, 62.1, 20.9, 20.9, 20.8, 20.8, 20.8, 20.7, 20.7; Anal. Calcd for $C_{23}H_{32}O_{14}$: C, 51.88; H, 6.06. Found: C, 51.85; H, 5.85.

1,2-Dideoxy-D-*threo*-L-*gulo*-non-1-enitol (9b). ^{1}H NMR (500 MHz, D_2O): δ 6.01 (ddd, *J* = 17.5, 10.7, 7.3 Hz, 1H), 5.42 (dt, *J* = 17.5, 1.2 Hz, 1H), 5.37 (dt, *J* = 10.7, 1.2 Hz, 1H), 4.28 (dd, *J* = 6.8, 6.0 Hz, 1H), 4.01-3.98 (m, 2H), 3.84-3.81 (m, 2H), 3.75-3.71 (m, 3H); ^{13}C NMR (125 MHz, D_2O): δ 137.5, 120.0, 76.6, 74.2, 72.5, 71.7, 71.2, 70.4, 64.8; Anal. Calcd for $C_9H_{18}O_7$: C, 45.37; H, 7.62. Found: C, 45.27; H, 7.49.

3,4,5,6,7,8,9-Hepta-*O*-acetyl-1,2-dideoxy-D-*erythro*-L-*gulo*-non-1-enitol (10a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.73 (ddd, J = 17.1, 10.1, 7.7 Hz, 1H), 5.44 (d, J = 8.0 Hz, 2H), 5.37 (d, J = 17.1 Hz, 1H), 5.30 (d, J = 10.1 Hz, 1H), 5.26 (s, 2H), 5.20 (t, J = 7.7 Hz, 1H), 4.99 (ddd, J = 8.6, 4.6, 2.7 Hz, 1H), 4.22 (dd, J = 12.4, 2.5 Hz, 1H), 4.14 (dd, J = 12.4, 4.4 Hz, 1H), 2.17 (s, 3H), 2.13 (s, 3H), 2.08 (s, 3H), 2.04 (s, 6H), 2.04 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 170.0, 170.0, 169.9, 169.8, 169.8, 169.6, 132.3, 121.3, 71.7, 70.2, 68.4, 68.1, 67.9, 67.7, 61.4, 21.0, 20.9, 20.8 (2C), 20.7, 20.6, 20.6; Anal. Calcd for $C_{23}H_{32}O_{14}$: C, 51.88; H, 6.06. Found: C, 51.77; H, 6.05.

1,2-Dideoxy-D-*erythro*-L-*gulo*-non-1-enitol (10b). ^{1}H NMR (500 MHz, D_2O): δ 6.02 (ddd, J = 17.1, 10.2, 6.8 Hz, 1H), 5.42 (dt, J = 17.1, 1.2 Hz, 1H), 5.36 (dt, J = 10.2, 1.2 Hz, 1H), 4.26 (tt, J = 6.8, 1.2 Hz, 1H), 4.02-3.98 (m, 2H), 3.88-3.81 (m, 2H), 3.73-3.67 (m, 3H); ^{13}C NMR (125 MHz, D_2O): δ 137.7, 118.9, 73.3, 73.2, 71.7, 71.5, 71.3, 70.9, 63.6; Anal. Calcd for $C_9H_{18}O_7$: C, 45.37; H, 7.62. Found: C, 45.28; H, 7.53.

3,4,5,6,7,8,9-Hepta-*O*-acetyl-1,2-dideoxy-D-*erythro*-L-*manno*-non-1-enitol (11a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.73-5.66 (m, 1H), 5.42 (s, 2H), 5.32 (d, J = 17.0 Hz, 1H), 5.27-5.23 (m, 2H), 5.13-5.11 (m, 2H), 4.99 (ddd, J = 8.4, 5.6, 2.9 Hz, 1H), 4.22 (dd, J = 12.3, 2.9 Hz, 1H), 4.00 (dd, J = 12.3, 5.6 Hz, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 170.2, 170.1, 170.1, 169.8, 169.8, 169.7, 132.3, 121.2, 72.5, 69.4, 68.4, 67.5, 66.9,

66.6, 62.0, 21.2, 21.1, 21.1, 20.9, 20.9, 20.8, 20.8; Anal. Calcd for $C_{23}H_{32}O_{14}$: C, 51.88; H, 6.06. Found: C, 51.97; H, 5.86.

1,2-Dideoxy-D-*erythro*-L-*manno*-non-1-enitol (11b). ^{1}H NMR (500 MHz, D_2O): δ 6.10 (ddd, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.46 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.39 (dt, *J* = 11.5, 0.8 Hz, 1H), 4.27 (dt, *J* = 6.8, 1.3 Hz, 1H), 4.02-3.98 (m, 2H), 3.95 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.91 (d, *J* = 8.5 Hz, 1H), 3.86-3.83 (m, 2H), 3.75 (dd, *J* = 11.5, 6.0 Hz, 1H); ^{13}C NMR (125 MHz, D_2O): δ 138.4, 118.4, 73.3, 72.4, 71.8, 70.0, 69.1, 69.1, 64.0; Anal. Calcd for $C_9H_{18}O_7$: C, 45.37; H, 7.62. Found: C, 45.26; H, 7.59.

D-*threo*-L-*gulo*-octose (12). ^{1}H NMR (500 MHz, D_2O): δ 4.89 (d, *J* = 8.4 Hz, 1H), 4.12 (t, *J* = 3.5 Hz, 1H), 3.99 (d, *J* = 3.4 Hz, 1H), 3.96-3.92 (m, 2H), 3.80 (d, *J* = 9.5 Hz, 1H), 3.70 (d, *J* = 6.2 Hz, 2H), 3.64 (dd, *J* = 8.4, 3.4 Hz, 1H); ^{13}C NMR (75 MHz, D_2O): δ 94.6, 72.2, 71.8, 70.8, 69.7, 68.9, 68.2, 63.7.

D-*erythro*-L-*gulo*-octose (13). ^{1}H NMR (500 MHz, D_2O): δ 4.88 (d, *J* = 8.5 Hz, 1H), 4.03 (t, *J* = 3.6 Hz, 1H), 3.98 (dd, *J* = 5.1, 0.9 Hz, 1H), 3.91-3.88 (m, 2H), 3.82-3.78 (m, 1H), 3.76 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.67-3.63 (m, 2H); ^{13}C NMR (75 MHz, D_2O): δ 94.7, 73.1, 72.4, 71.9, 71.7, 71.5, 69.6, 62.6; Anal. Calcd for $C_8H_{16}O_8$: C, 40.00; H, 6.71. Found: C, 39.93; H, 6.53. The structure was confirmed by reduction with $NaBH_4$ in MeOH/water mixture to give D-*erythro*-L-*gulo*-octitol. ^{13}C NMR (75 MHz, D_2O): δ 71.6, 71.0, 70.5, 63.5.

D-*erythro*-L-*manno*-octose (14). ^{1}H NMR (500 MHz, D_2O, 3:7 mixture of α and β, anomeric protons only): δ 5.21 (s, H-1β), 4.92 (s, H-1α); ^{13}C NMR (75 MHz, D_2O): α-anomer: δ 94.6, 74.3, 74.0, 71.9, 71.2, 68.6, 66.4, 63.9, β-anomer: δ 95.0, 71.4, 71.4, 71.3, 70.7, 68.7, 66.8, 64.0. ^{13}C NMR data are in accordance with literature values.[4]

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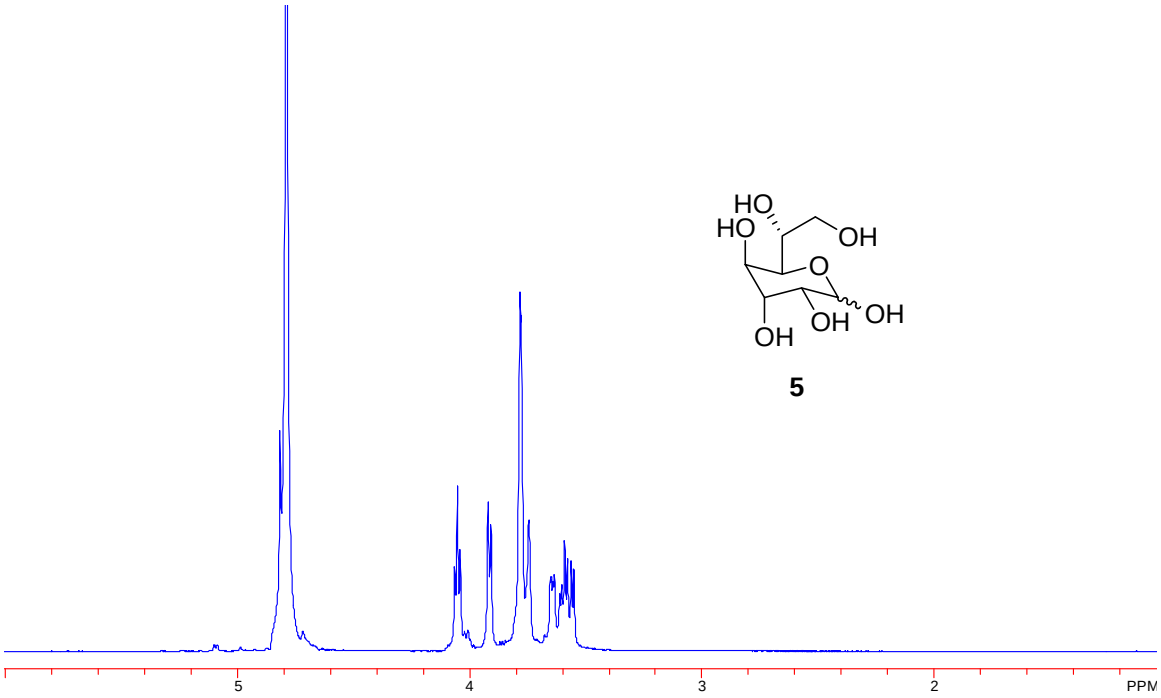
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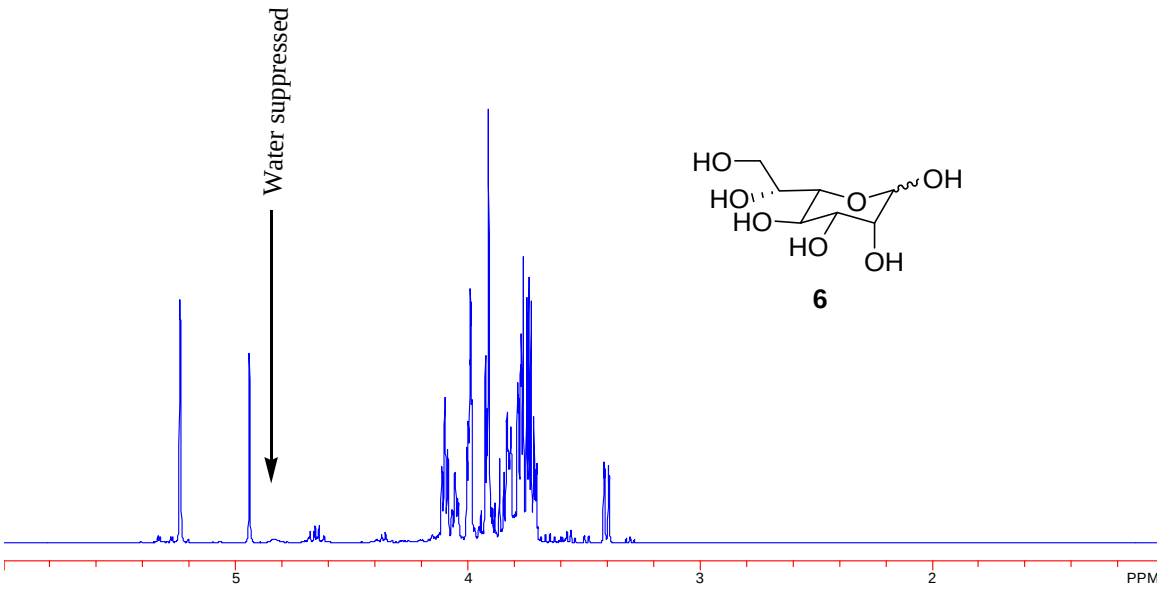
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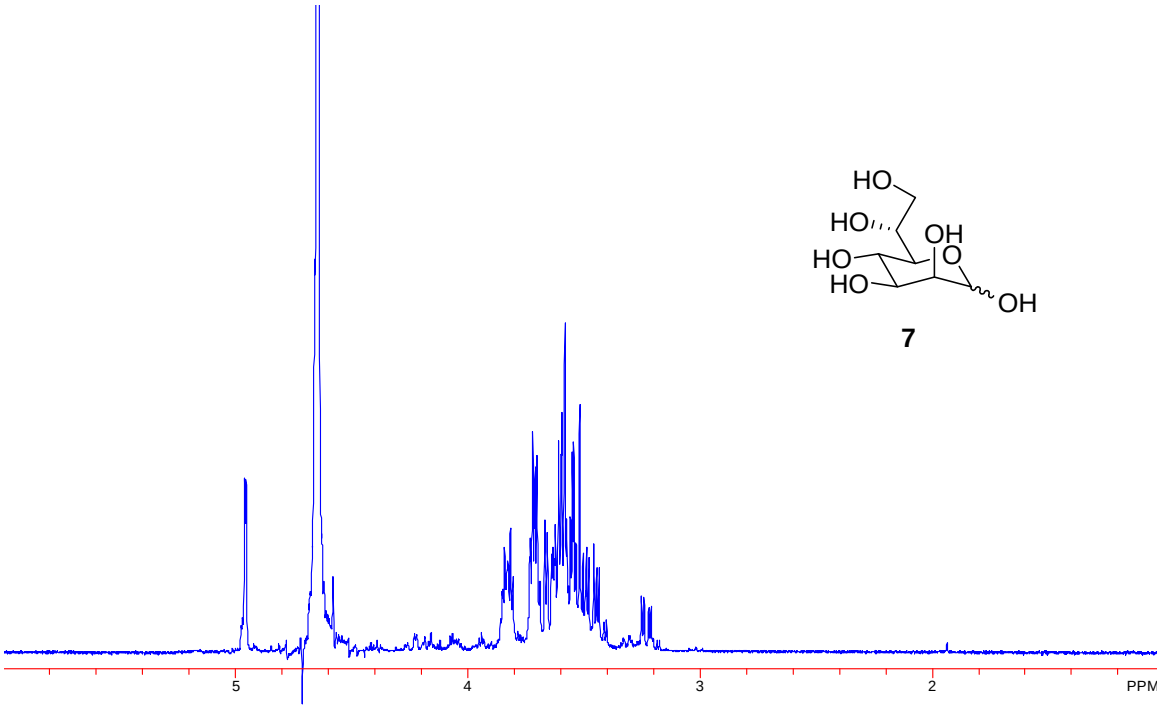
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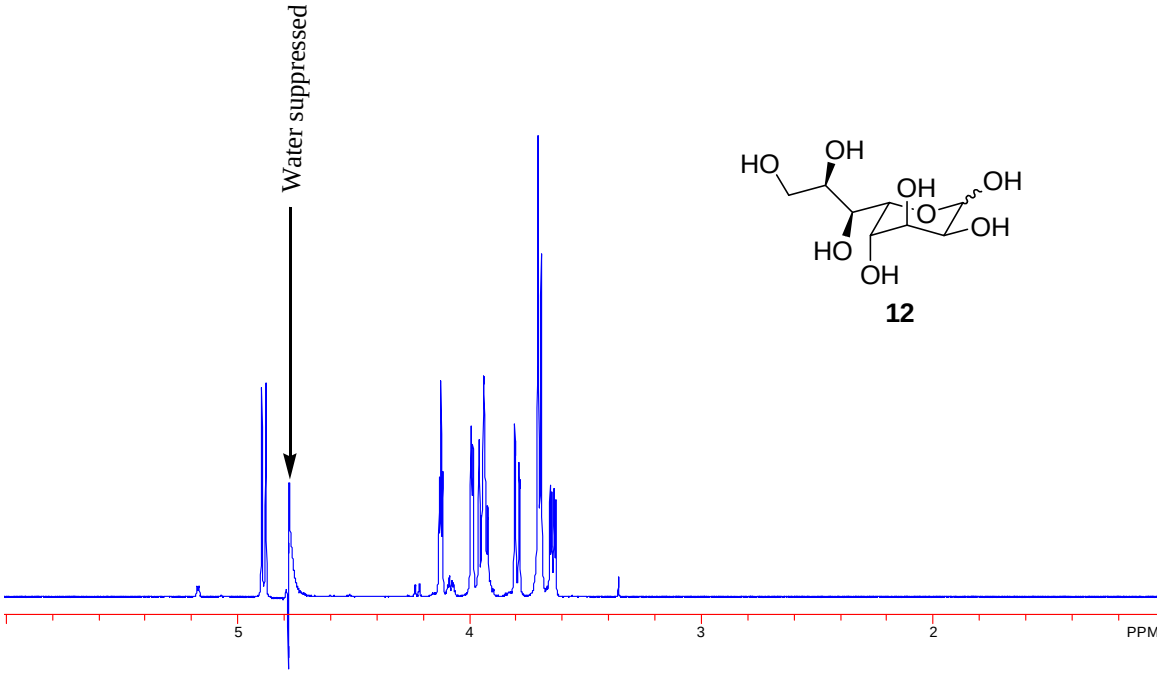
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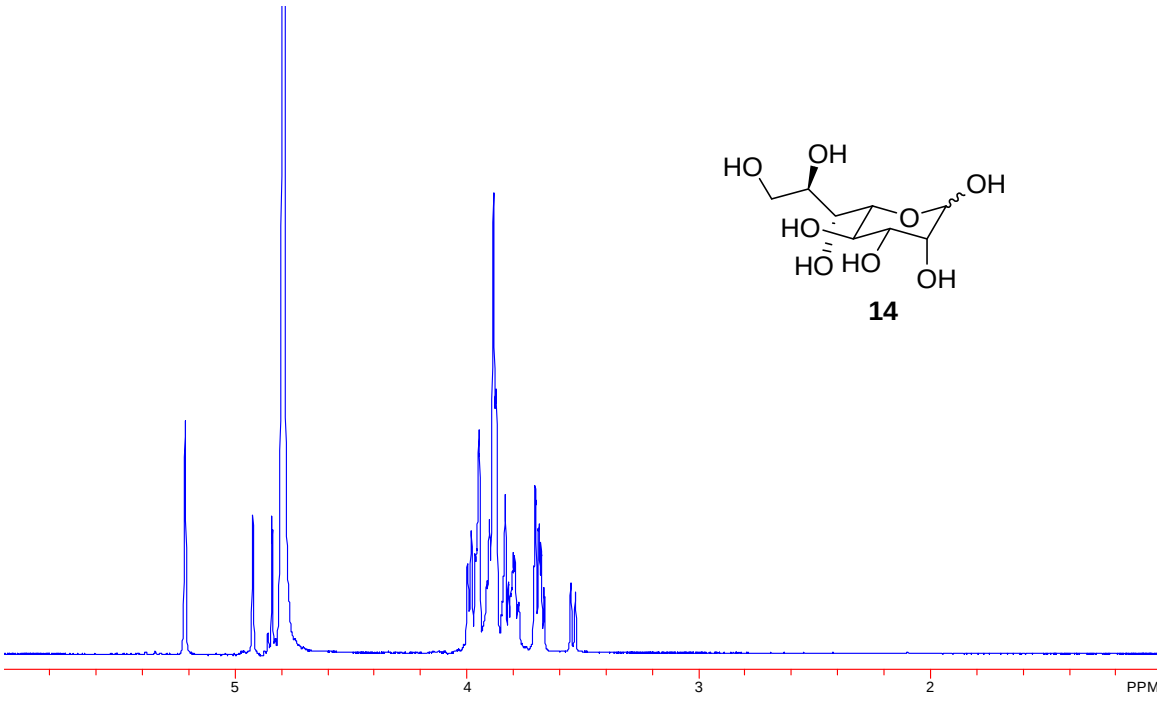

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