S1: $^1$H-NMR spectrum of compound 1 (CDCl$_3$, 400 MHz).
S2: $^{13}$C-NMR spectrum of compound 1 (CDCl$_3$, 100 MHz).
S3: DEPT spectrum of compound 1 (CDCl₃, 100 MHz).
S4: $^1$H-NMR spectrum of compound 2 (CDCl$_3$, 400 MHz).
S5: $^{13}$C-NMR spectrum of compound 2 (CDCl$_3$, 100 MHz).
S6: DEPT spectrum of compound 2 (CDCl₃, 100 MHz).
S7: COSY spectrum of compound 2 (CDCl₃, 400 MHz).
S8: HMQC spectrum of compound 2 (CDCl₃, 100 MHz).
S9: $^1$H-NMR spectrum of compound 2 (D$_6$-DMSO, 400 MHz).
S10: $^{13}$C-NMR spectrum of compound 2 (D$_6$-DMSO, 100 MHz).
S11: DEPT spectrum of compound 2 (D$_6$-DMSO, 100 MHz).
S12: COSY spectrum of compound 2 (D$_6$-DMSO, 400 MHz).
S13: HMQC spectrum of compound 2 (D$_6$-DMSO, 100 MHz).
S14: $^1$H-NMR spectrum of compound 2 after deuterium exchange (D$_6$-DMSO, 400 MHz).
S15: $^1$H-NMR spectrum of compound 3 (CDCl$_3$, 300 MHz).
S16: $^{13}$C-NMR spectrum of compound 3 (CDCl$_3$, 125 MHz).
S17: APT spectrum of compound 3 (CDCl₃, 125 MHz).
S18: COSY spectrum of compound 3 (CDCl₃, 300 MHz).
S19: HSQC spectrum of compound 3 (CDCl$_3$, 300 MHz).
S20: HMBC spectrum of compound 3 (CDCl₃, 300 MHz).
S21: $^1$H-NMR spectrum of compound 4 (D$_6$-DMSO, 300 MHz).
S22: $^{13}$C-NMR spectrum of compound 4 (D$_6$-DMSO, 125 MHz).
S23: DEPT spectrum of compound 4 (D$_6$-DMSO, 125 MHz).
S24: COSY spectrum of compound 4 (D$_6$-DMSO, 300 MHz).
S25: HSQC spectrum of compound 4 (D$_6$-DMSO, 300 MHz).
S26: $^1$H-NMR spectrum of compound 4 after deuterium exchange (D$_6$-DMSO, 300 MHz).
S27: Physico-chemical data of Compounds 1, 2 and 4.

*Henriciaontane* (1): White solid; $R_f = 0.94$ (hexane–CHCl$_3$, 1:1); m. p. 67 °C, 68 °C; IR (ATR): $v_{\text{max}} = 2956, 2916, 2848, 1413, 1463, 1378, 730, 720$ cm$^{-1}$; EI-MS (70 eV): $m/z$ (%) = 436 [M]$^+$ (10), 323 (5), 253 (6), 183 (10), 141 (12), 113 (17), 99 (25), 85 (59), 71 (79), 57 (100), 43 (50).

(+)-13S,14R,15-Trihydroxy-ent-labd-7-ene (2). Colorless oil; $R_f = 0.25$ (CHCl$_3$–EtOAc, 1:1); [α]$^D_{20}$: +2 (c 4.22, CHCl$_3$); IR (ATR): $v_{\text{max}} = 3370, 2915, 1640, 1372, 1018, 720$ cm$^{-1}$; DCI-MS (NH$_3$): $m/z = 342$ [M + NH$_4]^+$; EI-MS (70 eV): $m/z$ (%) = 324 [M]$^+$ (5), 306 (1), 245 (10), 204 (100), 161 (12), 135 (11), 121 (23), 109 (26), 95 (15), 69 (7), 55 (2).

*D-Glycero-D-galacto-heptitol* (4). White solid; m. p. 185.6 °C; [α]$^D_{20}$: +14 (c 0.4, in 5% aq. ammoniumheptamolybdate); +72 (c ca. 0.4 in acidified 5% aq. ammoniumheptamolybdate); the foregoing solution was diluted with 25% 1N H$_2$SO$_4$, according to Richtmeyer *et al.* (Richtmeyer, N.K.; Hudson, C.S. The rotation of polyols in ammonium molybdate solutions. *J. Am. Chem. Soc.* 1951 73, 2249–2250); IR (ATR): $v_{\text{max}} = 3240, 2925, 1410, 1305, 1210, 1100, 1005, 890, 630$ cm$^{-1}$; The $^1$H- and $^{13}$C-NMR spectra in DMSO-d$_6$ were identical with those in the literature; ESI-MS (+)-mode: $m/z = 235$ [M + Na]$^+$, (-)-mode: $m/z = 211$ [M − H]$^-$; (+)-ESI-HR-MS: $m/z$ 235.07886 [M + Na]$^+$ (calcd. for C$_7$H$_{16}$O$_7$Na: 235.07882).

S28: $^1$H-(400 MHz) and $^{13}$C-NMR (100 MHz) data of compound 1 (CDCl$_3$).

<table>
<thead>
<tr>
<th>Position</th>
<th>$\delta$ (DEPT)</th>
<th>$\delta$, mult. ($J$ in Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 31</td>
<td>14.1</td>
<td>CH$_3$, 0.89 t (6.8)</td>
</tr>
<tr>
<td>2, 30</td>
<td>22.7</td>
<td>CH$_2$</td>
</tr>
<tr>
<td>3, 29</td>
<td>31.9</td>
<td>CH$_2$</td>
</tr>
<tr>
<td>4, 28</td>
<td>29.4</td>
<td>CH$_2$</td>
</tr>
<tr>
<td>5-27</td>
<td>29.7</td>
<td>CH$_3$, 1.27 m</td>
</tr>
</tbody>
</table>
S29: $^1$H-(400 MHz) and $^{13}$C-NMR (100 MHz) data of compound 2 (CDCl$_3$).

<table>
<thead>
<tr>
<th>Position</th>
<th>$^1$H (DEPT)</th>
<th>$^{13}$C</th>
<th>$^1$H, mult. ($J$ in Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39.2 CH$_2$</td>
<td>0.94 m, 1.79 br d (11)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>18.8 CH$_2$</td>
<td>1.44 m, 1.51 m</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>42.2 CH$_2$</td>
<td>1.14 m, 1.41 m</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>32.9 C$_q$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>50.1 CH</td>
<td>1.16 dd (12, 4.9)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>23.7 CH$_2$</td>
<td>1.87 m, 1.97 m</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>122.3 CH</td>
<td>5.37 br s</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>135.0 C$_q$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>55.2 CH</td>
<td>1.54 m</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>36.9 C$_q$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>20.7 CH$_2$</td>
<td>1.26 m, 1.43 m</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>40.7 CH$_2$</td>
<td>1.31 m, 1.85 m</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>75.0 C$_q$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>76.2 CH</td>
<td>3.48 dd (5.7, 3.65)</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>63.1 CH$_2$</td>
<td>3.74 d (5.7)</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>23.3 CH$_3$</td>
<td>1.22 s</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>22.2 CH$_3$</td>
<td>1.68 s</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>33.1 CH$_3$</td>
<td>0.84 s</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>21.8 CH$_3$</td>
<td>0.86 s</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>13.5 CH$_3$</td>
<td>0.75 s</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td></td>
<td>3.60 br s</td>
<td></td>
</tr>
</tbody>
</table>
**S30:** $^1$H-(400 MHz) and $^{13}$C-NMR (100 MHz) data of compound 2 (DMSO-$d_6$).

<table>
<thead>
<tr>
<th>Position</th>
<th>$^{13}$C</th>
<th>$^1$H (DEPT)</th>
<th>δ, mult, (J in Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.6</td>
<td>CH$_2$</td>
<td>0.91 m, 1.86 m</td>
</tr>
<tr>
<td>2</td>
<td>18.4</td>
<td>CH$_2$</td>
<td>1.40 m, 1.47 m</td>
</tr>
<tr>
<td>3</td>
<td>42.0</td>
<td>CH$_2$</td>
<td>1.17 m, 1.72 m</td>
</tr>
<tr>
<td>4</td>
<td>32.7</td>
<td>C$_q$</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>49.8</td>
<td>CH</td>
<td>1.11 m</td>
</tr>
<tr>
<td>6</td>
<td>23.3</td>
<td>CH$_2$</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>121.3</td>
<td>CH</td>
<td>5.32 s</td>
</tr>
<tr>
<td>8</td>
<td>135.6</td>
<td>C$_q$</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>55.0</td>
<td>CH</td>
<td>1.46 m</td>
</tr>
<tr>
<td>10</td>
<td>36.6</td>
<td>C$_q$</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>20.0</td>
<td>CH$_2$</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>41.9</td>
<td>CH$_2$</td>
<td>1.13 m, 1.37 m</td>
</tr>
<tr>
<td>13</td>
<td>73.1</td>
<td>C$_q$</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>76.0</td>
<td>CH</td>
<td>3.28 m</td>
</tr>
<tr>
<td>15</td>
<td>62.6</td>
<td>CH$_2$</td>
<td>3.31 m, 3.60 d (8)</td>
</tr>
<tr>
<td>16</td>
<td>22.3</td>
<td>CH$_3$</td>
<td>0.97 s</td>
</tr>
<tr>
<td>17</td>
<td>22.1</td>
<td>CH$_3$</td>
<td>1.64 s</td>
</tr>
<tr>
<td>18</td>
<td>33.0</td>
<td>CH$_3$</td>
<td>0.83 s</td>
</tr>
<tr>
<td>19</td>
<td>21.7</td>
<td>CH$_3$</td>
<td>0.85 s</td>
</tr>
<tr>
<td>20</td>
<td>13.5</td>
<td>CH$_3$</td>
<td>0.72 s</td>
</tr>
<tr>
<td>OH</td>
<td></td>
<td></td>
<td>4.09 br s, 4.46 br m</td>
</tr>
</tbody>
</table>

**S31:** $^1$H-(300 MHz) and $^{13}$C-NMR (125 MHz) data of compound 4 (DMSO-$d_6$).

<table>
<thead>
<tr>
<th>Position</th>
<th>$^{13}$C</th>
<th>$^1$H (DEPT)</th>
<th>δ, mult, (J in Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>63.9</td>
<td>CH$_2$</td>
<td>3.39 m, 3.61 m</td>
</tr>
<tr>
<td>2</td>
<td>71.6</td>
<td>CH</td>
<td>3.48 m</td>
</tr>
<tr>
<td>3</td>
<td>68.6</td>
<td>CH</td>
<td>3.69 m</td>
</tr>
<tr>
<td>4</td>
<td>69.2</td>
<td>CH</td>
<td>3.45 m</td>
</tr>
<tr>
<td>5</td>
<td>69.7</td>
<td>CH</td>
<td>3.57 m</td>
</tr>
<tr>
<td>6</td>
<td>70.2</td>
<td>CH</td>
<td>3.72 m</td>
</tr>
<tr>
<td>7</td>
<td>63.3</td>
<td>CH$_2$</td>
<td>3.42 m</td>
</tr>
<tr>
<td>OH</td>
<td></td>
<td></td>
<td>3.92 d, 3.99 m, 4.02 m, 4.07 m, 4.29 t, 4.34 m, 4.35 m</td>
</tr>
</tbody>
</table>