Electronic Supporting Information.

1. Line-shape analysis by g-NMR best-fitting

Was achieved in order to confirm 2D-EXSY results albeit the large number of variables makes this method less accurate. Here we show a good best-fitting guess obtained by feeding the g-NMR with the EXSY results.

![Experimental and Calculated Spectra](image)

2. ESI-MS Spectra of 1 and 2 in H$_2$O$^{18}$

Were recorded in order to rule out the dominating effect of an external water nucleophilic attack in 2 (the enhancement, respect to 1, does not justify the $10^4$ overall rate increase).

![ESI-MS Spectra of 1 in H$_2$O$^{18}$](image)
Tables listing mutarotation rate constants vs. temperatures used for thermodynamic calculations; table of the $k_{(\alpha p-\beta p)}$ vs. pD referred to 1.

Table S1. Mutarotation rate constants at variable temperature for the activation parameter calculation.

<table>
<thead>
<tr>
<th>GalAH$_2$ (I)</th>
<th>$k_{(\alpha p-\beta p)}$ (s$^{-1}$)</th>
<th>$k_{(\alpha \alpha-\beta \beta)}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pD = 4.5</td>
<td>$3.9 \times 10^{-3}$ (285K)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$18 \times 10^{-5}$ (298K)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$70 \times 10^{-5}$ (315K)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$300 \times 10^{-5}$ (330K)</td>
<td>-</td>
</tr>
<tr>
<td>[Sn(CH$_3$)$_2$(GalA)(H$_2$O)$_2$] (2)</td>
<td>1.4 (298K)</td>
<td>2.64 (298K)</td>
</tr>
<tr>
<td>pD = 4.5</td>
<td>3.6 (311K)</td>
<td>10.3 (311K)</td>
</tr>
<tr>
<td></td>
<td>207.5 (368K)</td>
<td>135 (345K)</td>
</tr>
</tbody>
</table>

Table S2. Mutarotation rate constant $k_{(\alpha p-\beta p)}$ for 1 vs. pD.

<table>
<thead>
<tr>
<th>pD*</th>
<th>6.5</th>
<th>6.1</th>
<th>5.2</th>
<th>4.5</th>
<th>4.0</th>
<th>3.7</th>
<th>3.3</th>
<th>2.3</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{(\alpha p-\beta p)} \cdot 10^4$ (s$^{-1}$)</td>
<td>6.0</td>
<td>3.8</td>
<td>1.9</td>
<td>1.7</td>
<td>1.7</td>
<td>1.8</td>
<td>1.8</td>
<td>2</td>
<td>2.3</td>
</tr>
</tbody>
</table>