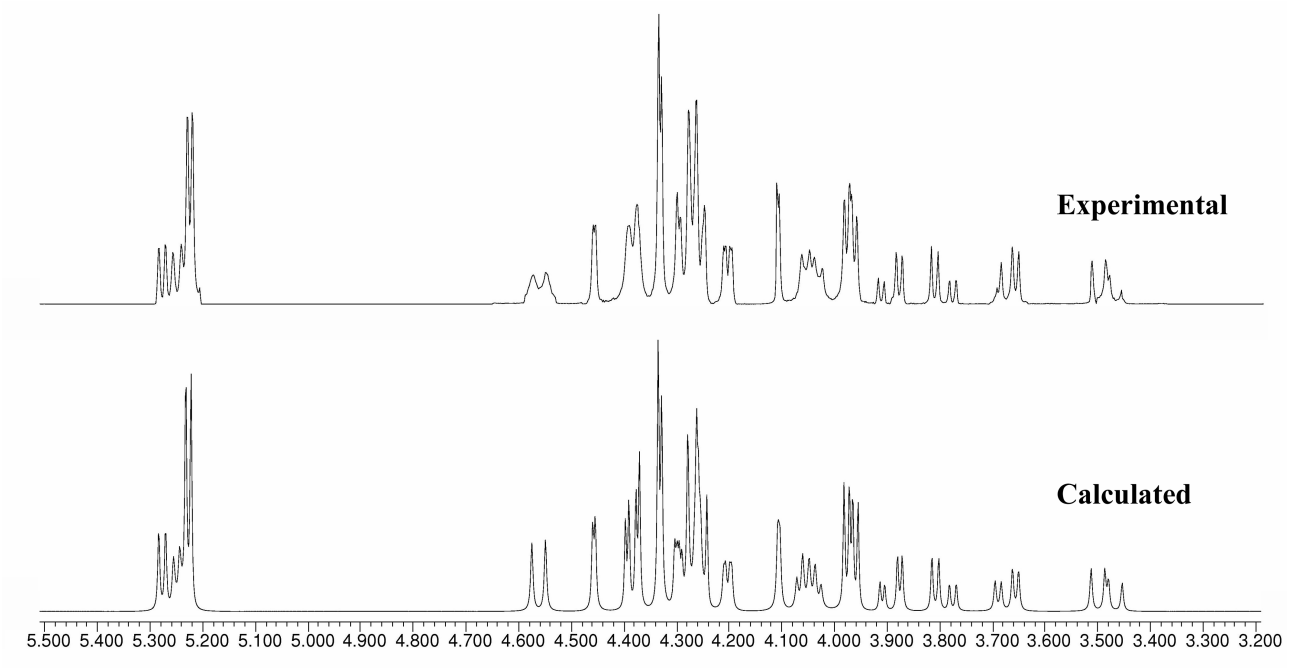
Electronic Supporting Information.

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.



*2. ESI-MS Spectra of **1** and **2** in H_2O^{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).

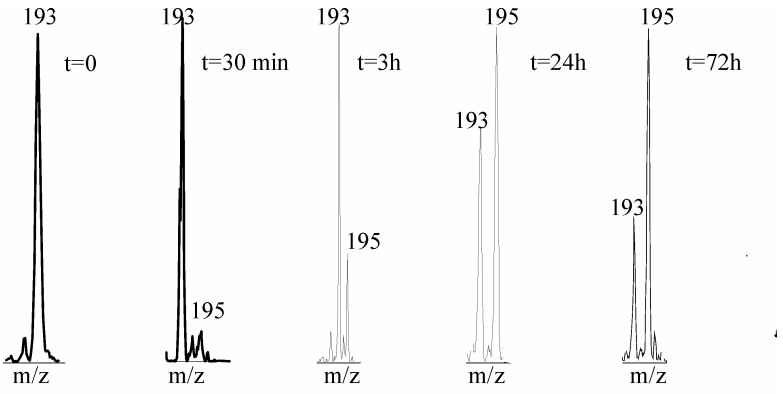


Fig.1 ESI-MS spectra of **1** in$H_2^{18}O$

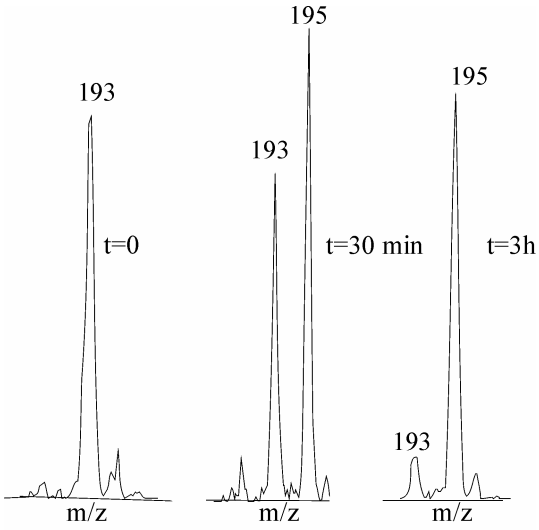


Fig.2 ESI-MS spectra of **2** in $H_2{}^{18}O$

*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.

	$k_{(\alpha p-\beta p)}(s^{-1})$	$k_{(\alpha f-\beta f)}$ (s^{-1})
$GalAH_2$	$3.9\cdot10^{-5}$ (285K)	-
(**1**)	$18\cdot10^{-5}$ (298K)	-
pD = 4.5	$70\cdot10^{-5}$ (315K)	-
	$300\cdot10^{-5}$ (330K)	-
$[Sn(CH_3)_2(GalA)(H_2O)_2]$	1.4 (298K)	2.64 (298K)
(**2**)	3.6 (311K)	10.3 (311K)
pD = 4.5	207.5 (368K)	135 (345K)

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

pD*	**6.5**	**6.1**	**5.2**	**4.5**	**4.0**	**3.7**	**3.3**	**2.3**	**2.0**
$k_{(\alpha p-\beta p)} \cdot 10^4$(s-1)	6.0	3.8	1.9	1.7	1.7	1.8	1.8	2	2.3