



S4 Fig. β -Galactosyltransferase (GalT) experiment on hCG1 samples. MALDI-TOF MS spectra of permethylated N-glycans derived from (A) EP-hCG1 sample (top panel, control, same as Fig. 1A; lower panel, after GalT) and (B) LP-hCG1 sample (top panel, control, same as Fig. 1B; lower panel, after GalT). Note that on EP-hCG1 and LP-hCG1 spectra before the GalT experiment (A and B, top panels), the molecular ions at m/z 2315, 2489, 2663, 2837, 2938, 3112, 3286, 3460, 3473 and 3647 which correspond to complex mature N-glycans with a single terminal GlcNAc residue. The same ions were also detected on the EP-hCG1 and LP-hCG1 spectra after the GalT experiment (A and B, lower panels), indicating that those terminal GlcNAc residues are not subject to a GalT experiment. Therefore, the above molecular ions correspond to bisected N-glycan structures. On the contrary, on

EP-hCG1 and LP-hCG1 spectra before the GalT experiment (**A** and **B**, top panels), the molecular ions at m/z 1835 and 1865 correspond to agalactosylated N-glycans (GlcNAc terminated residues on mannose arms). These ions are not present in GalT samples (**A** and **B** lower panels) indicating that these ions are subject to the β -galactosyltransferase experiment further indicating that they do not correspond to bisected N-glycans. Putative structures are based on composition, tandem MS and knowledge of biosynthetic pathways. All molecular ions are $[M+Na]^+$.