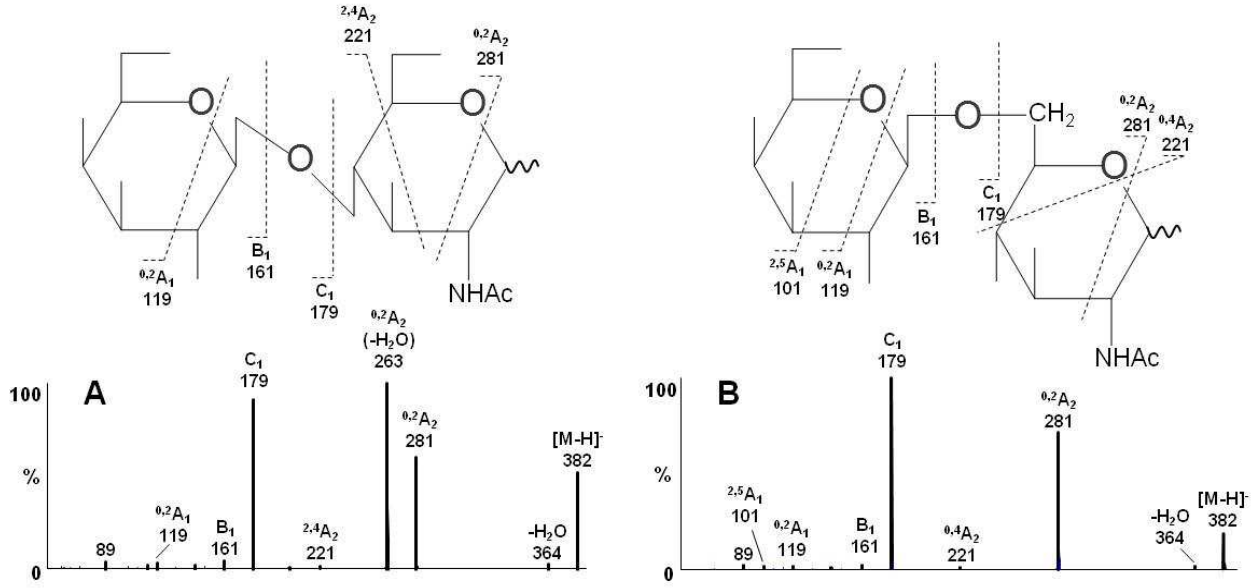
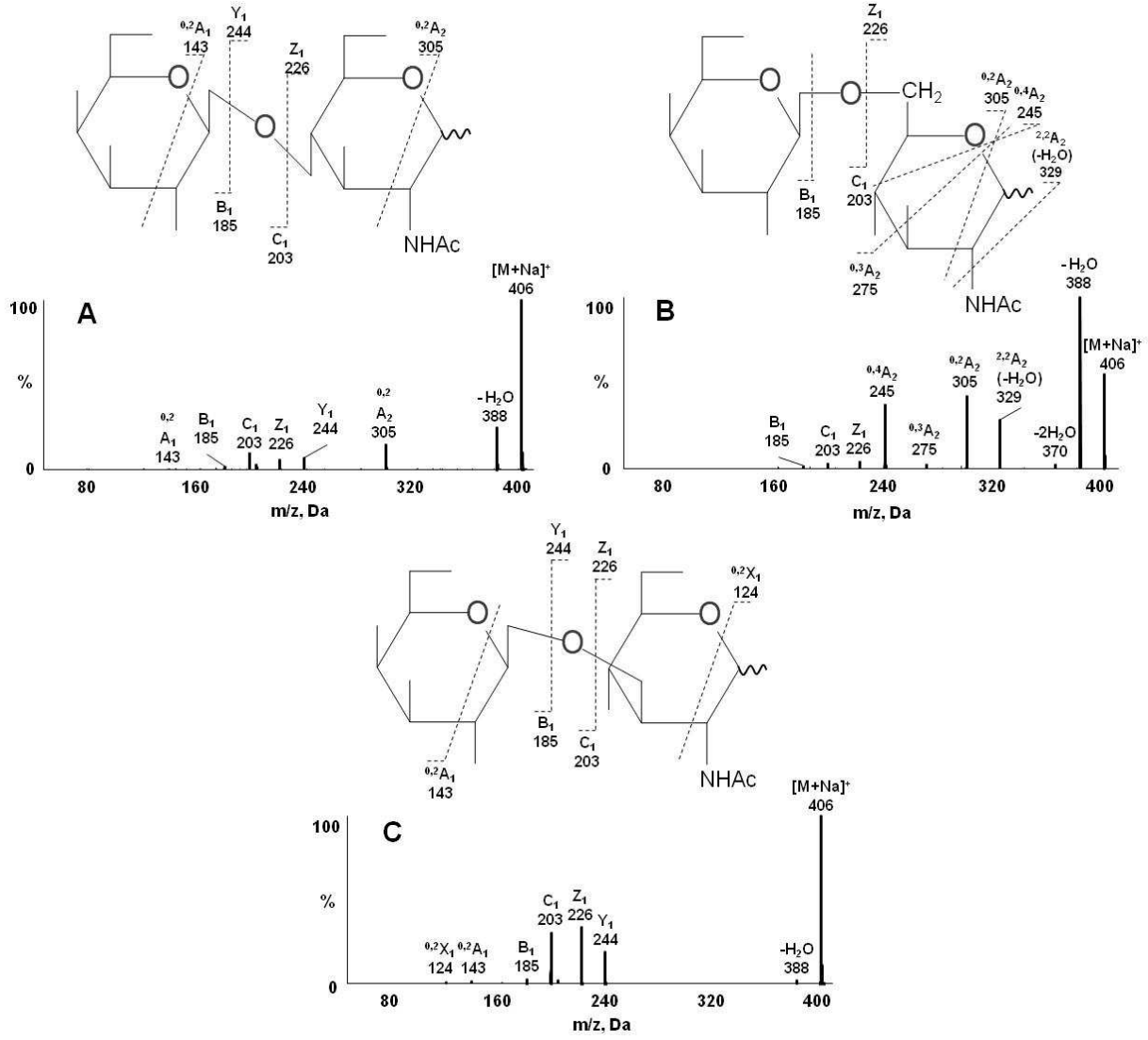
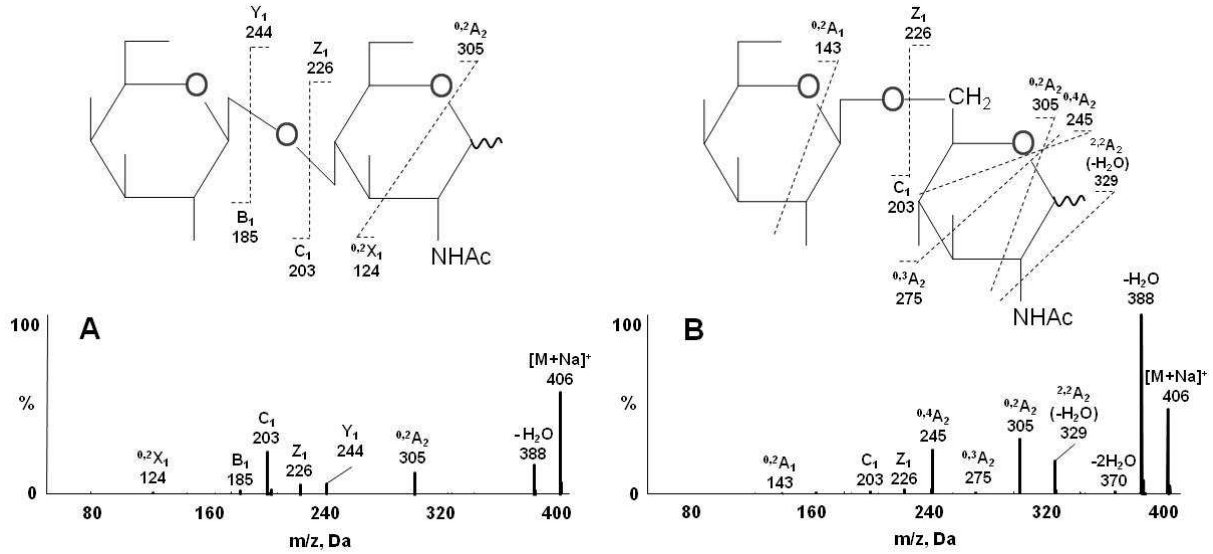


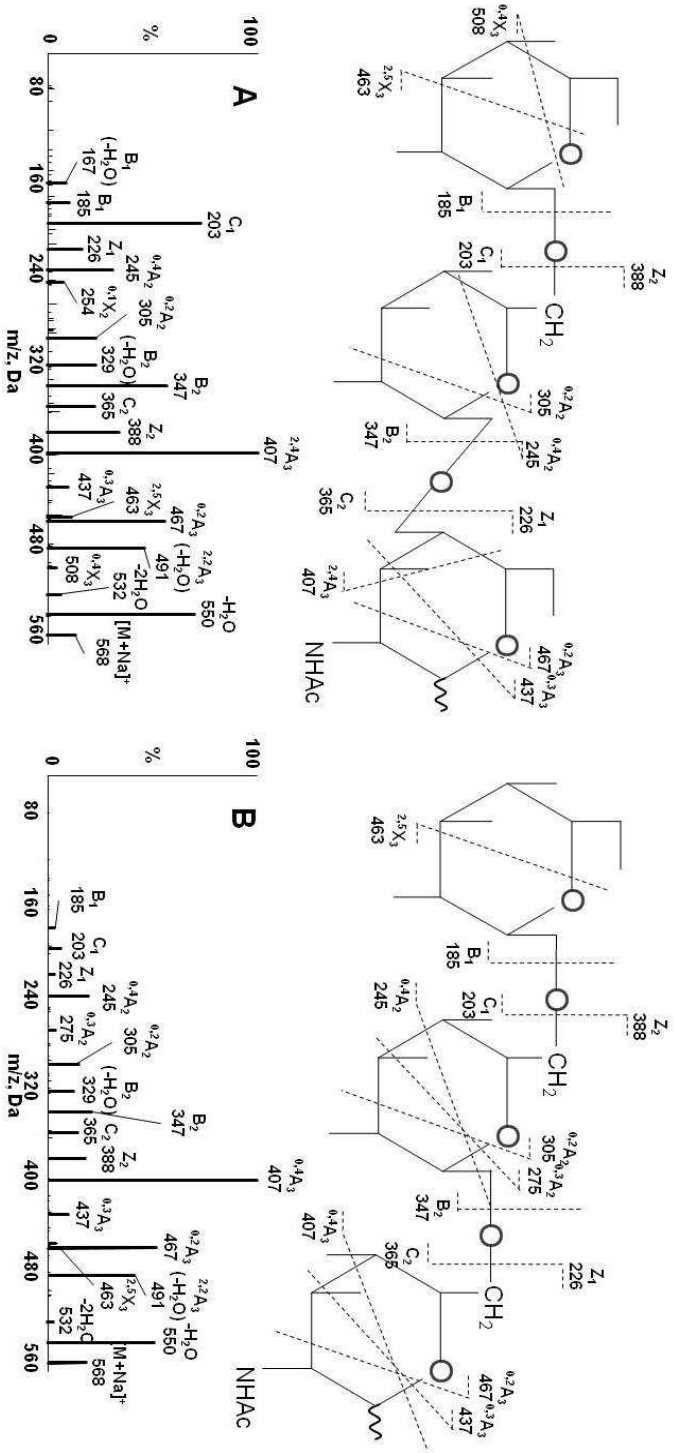
Supplemental Figure 1. ESI-MS/MS spectra of $[M-H]^-$ ions of the Gal-GlcNAc isomers. (A) Sample compound, Gal-GlcNAc peak 1; (B) Sample compound, Gal-GlcNAc peak 2.



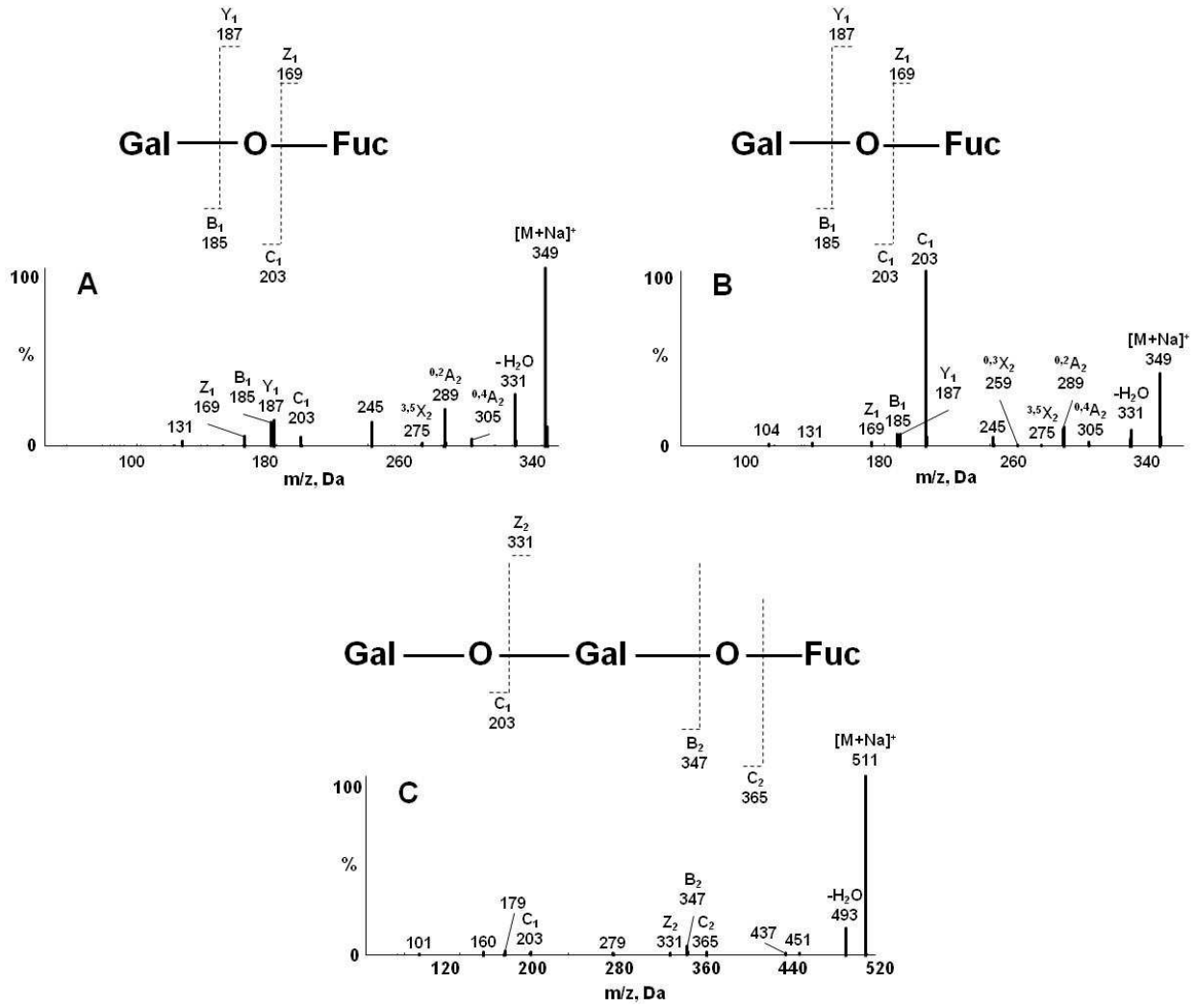
Supplemental Figure 2. ESI-MS/MS sodiated spectra of Gal-GlcNAc standards, $[M+Na]^+$ at *m/z* 406. (A) Galβ-(1→4)-GlcNAc standard; (B) Galβ-(1→6)-GlcNAc standard; (C) Galβ-(1→3)-GlcNAc standard. Structures are shown to indicate proposed fragmentation.



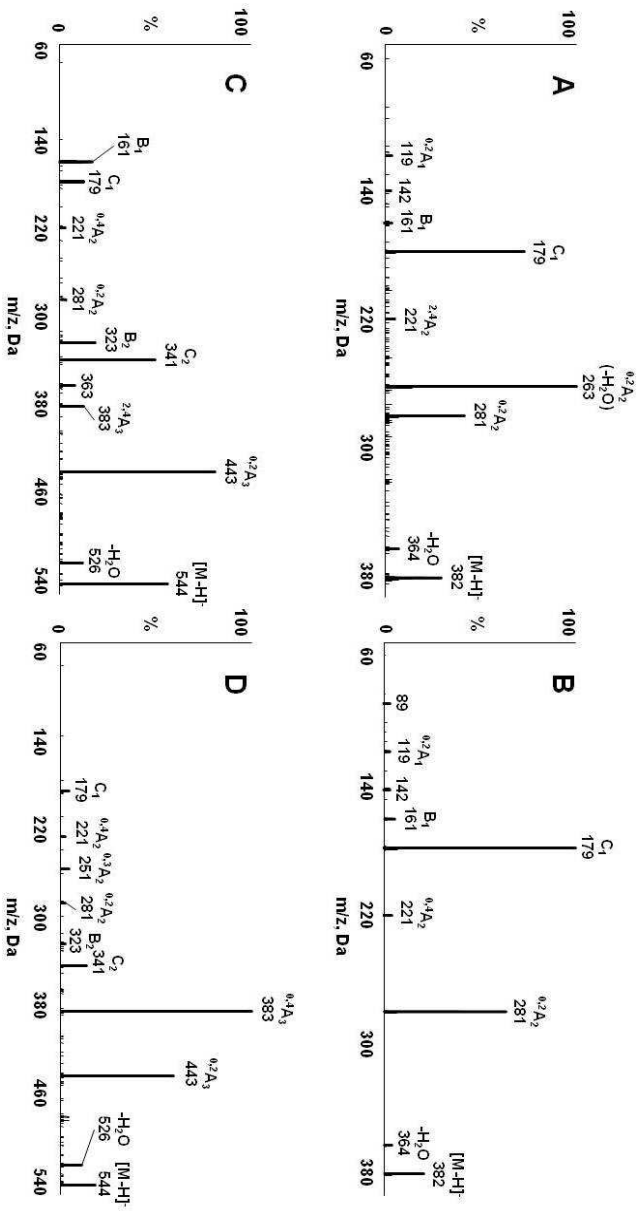
Supplemental Figure 3. ESI-MS/MS sodiated spectra of Gal-GlcNAc sample compounds, $[M+Na]^+$ at *m/z* 406. (A) Gal-GlcNAc peak 1; (B) Gal-GlcNAc peak 2; Structures are shown to indicate proposed fragmentation.



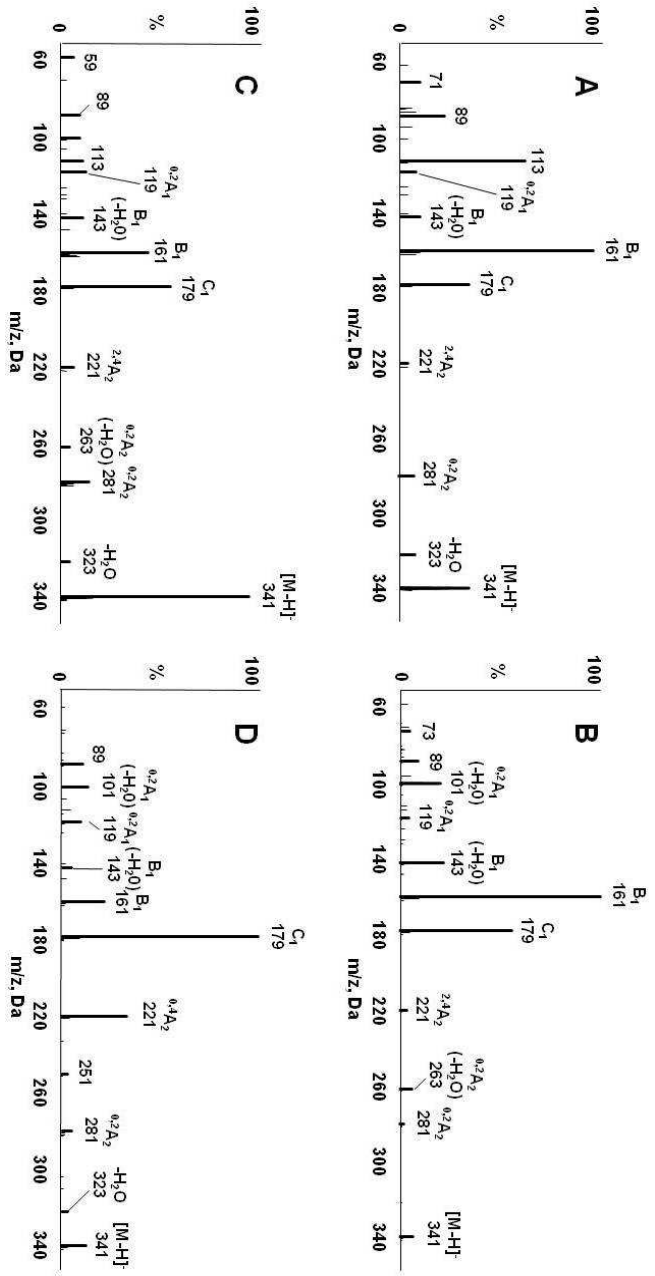
Supplemental Figure 4. ESI-MS/MS sodiated spectra of Gal-Gal-GlcNAc sample compounds, $[M+Na]^+$ at *m/z* 568. (A) Gal-Gal-GlcNAc peak 1; (B) Gal-Gal-GlcNAc peak 2; Structures are shown to indicate proposed fragmentation.



Supplemental Figure 5. ESI-MS/MS sodiated spectra of sample compounds. (A) Gal-Fuc peak 1, $[M+Na]^+$ at *m/z* 349; (B) Gal-Fuc peak 2, $[M+Na]^+$ at *m/z* 349; (C) Representative of sample compound Gal-Gal-Fuc peak 1, 2 and 3, $[M+Na]^+$ at *m/z* 511; Structures are shown to indicate proposed fragmentation.



Supplemental Figure 6. ESI-MS/MS spectra of $[M-H]^-$ ions of galactosylated GlcNAc formed by CCE of *Lactococcus lactis* MG1363 expressing LacLM of *L. plantarum* FUA3112. (A) Gal-GlcNAc *m/z* 382 with a retention time of 18.1 minutes; (B) Gal-GlcNAc *m/z* 382 with a retention time of 22.9 minutes; (C) Gal-Gal-GlcNAc *m/z* 544 with a retention time of 54.8 minutes; (D) Gal-Gal-GlcNAc *m/z* 544 with a retention time of 66.8 minutes.



Supplemental Figure 7. ESI-MS/MS spectra of $[M-H]^-$ ions of galacto-oligosaccharides formed by CCE of *Lactococcus lactis* MG1363 expressing LacLM of *L. plantarum* FUA3112. (A) Gal-β-(1→3)Glc/Gal *m/z* 341 with a retention time of 15.5 minutes; (B) Lactose *m/z* 341 with a retention time of 17.5 minutes; (C) Gal-β-(1→4)-Gal *m/z* 341 with a retention time of 20.1 minutes; (D) Gal-β-(1→6)Glc/Gal *m/z* 341 with a retention time of 22.0 minutes.