

Supplementary figures

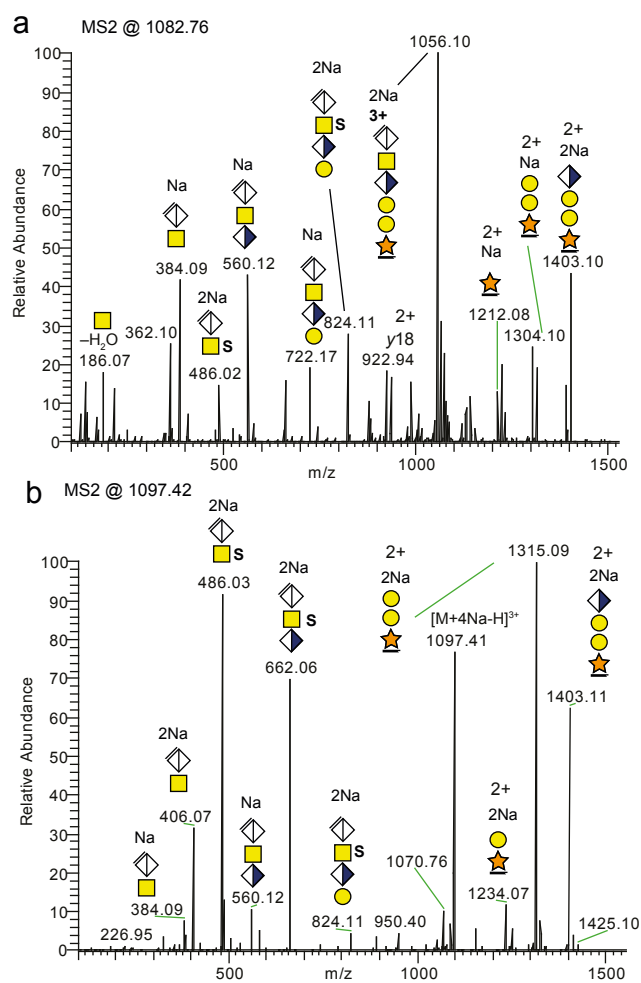
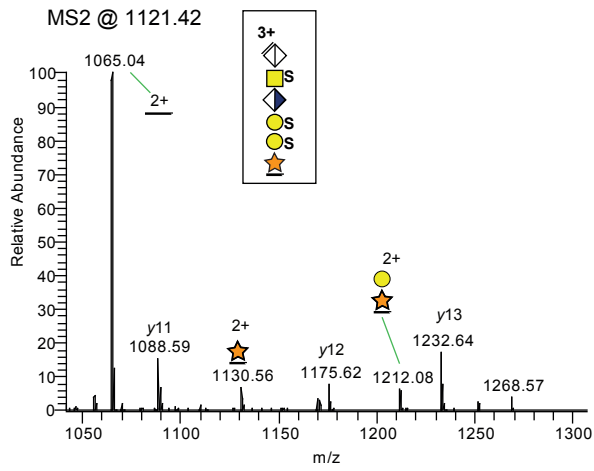


Fig. S1. HCD-MS2 spectra of mono-sulfated bikunin CS-glycopeptides at 100 mM Na⁺ ions. (a) HCD-MS2 spectrum of the [M+2Na+H]³⁺ precursor and (b) the [M+4Na-H]³⁺ precursor. The MS1 survey scan is presented in Fig. 3 of the main text. A NCE of 20% was used. All major fragment ions are annotated with charges > 1, m/z values, n.o of Na⁺-adducts and glycan structures.

a



b

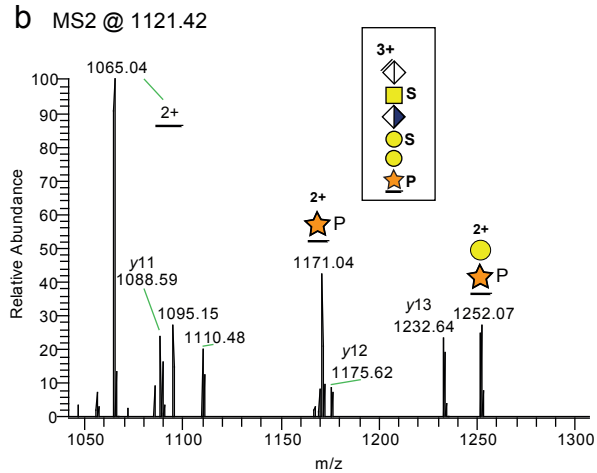


Fig. S2. HCD-MS2 of protonated bikunin CS-glycopeptides. (a) disulfated/phosphorylated (SSP-form) and **(b)** trisulfated (SSS-form). The precursor structures are shown in the boxes. A NCE of 30% was used. Peptide backbone fragmented y-ions, carrying an intact C-terminal, of the AVLPQEEEGSGGGQLVTEVTK sequence are annotated.

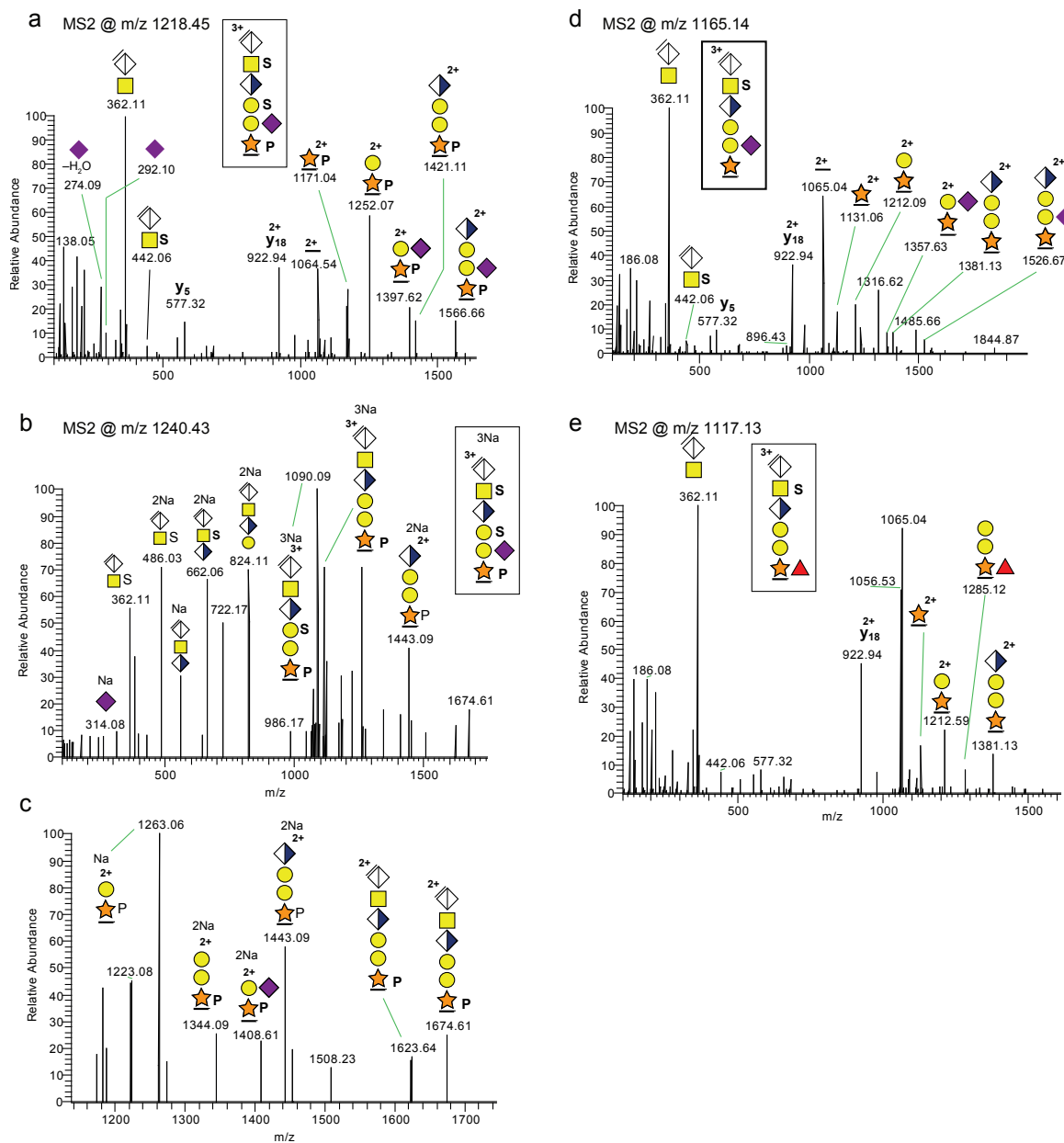


Fig. S3. Additional glycoforms of bikunin CS-glycopeptides. (a) HCD-MS2 spectra of a protonated precursor of the sialylated, phosphorylated and di-sulfated glycoform of the bikunin CS-glycopeptide. (b) The corresponding $[M+3Na]^+$ precursor and (c) the m/z 1100-1700 region. (d) A sialylated and mono-sulfated and (e) a fucosylated and mono-sulfated glycoform of the bikunin CS-glycopeptide. The precursor ion structures and charge states are indicated in the boxes. A NCE of 20% was used. The m/z values of precursor ions are that of the largest isotope peak. The monoisotopic masses of protonated precursor ions are presented in Table 1.