

Figure S3. MALDI-Ion Trap-TOF MS, MS/MS and MS<sup>3</sup> mass spectra of O-glycans released from the Rabbit Duodenum Sample 4. The sample was kindly analyzed by Shimadzu Ltd, by their MALDI-Ion Trap-TOF instrument “Axima Resonance”.

A: MS spectrum of sample 4. The annotation of the structure at  $m/z$  1373 takes into account the information emerging from fragmentation data obtained through MS/MS and MS<sup>3</sup> analysis.

B: MS/MS spectrum of peak at  $m/z$  1373. Theoretical fragments, shown at the top- right corner of the figure, match the observed ones obtained by Ion trap-MS/MS analysis, reported on the annotated peaks. Peaks marked with the symbol “X” are due to the matrix used for MALDI analysis.

C: MS<sup>3</sup> spectra of the ion at  $m/z$  1079 obtained after fragmentation of the parent ion at  $m/z$  1373. Theoretical fragments, shown at the top- right corner of the figure, match the observed fragments obtained by Ion trap-MS<sup>3</sup> fragmentation, reported on the annotated peaks. Peaks marked with the symbol “X” are due to the matrix used for MALDI analysis.

