

## SUPPORTING INFORMATION

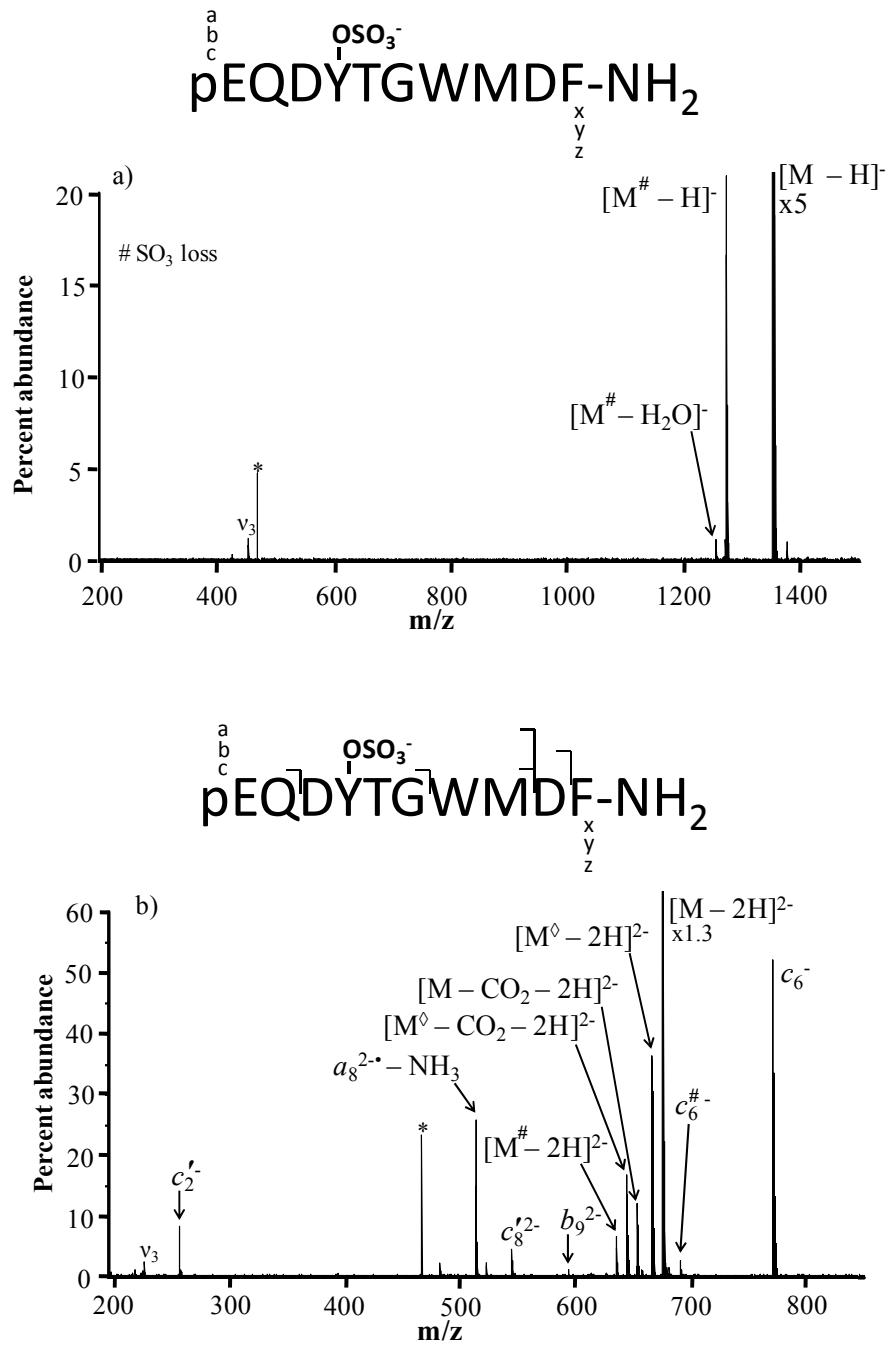
# Characterization of *O*-Sulfopeptides by Negative Ion Mode Tandem Mass Spectrometry: Superior Performance of Negative Ion Electron Capture Dissociation

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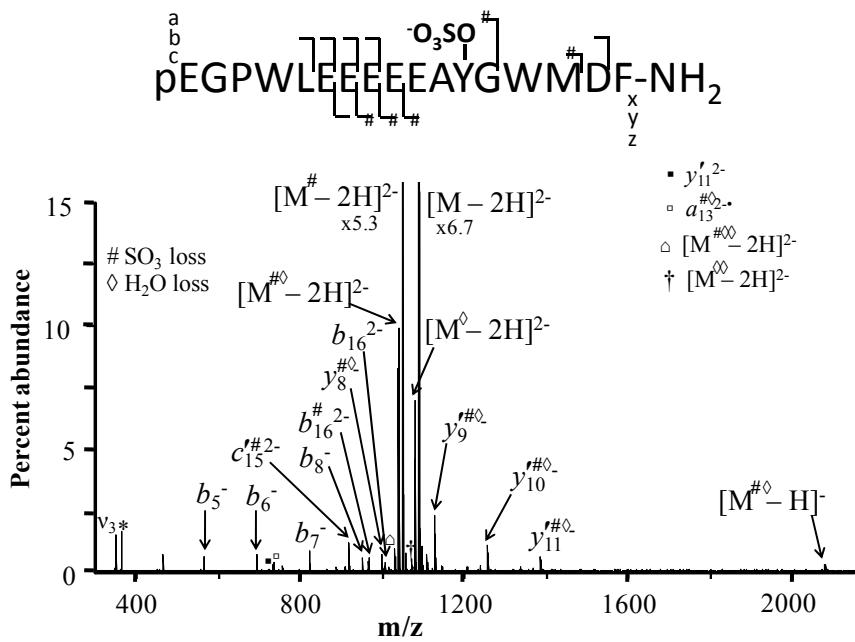
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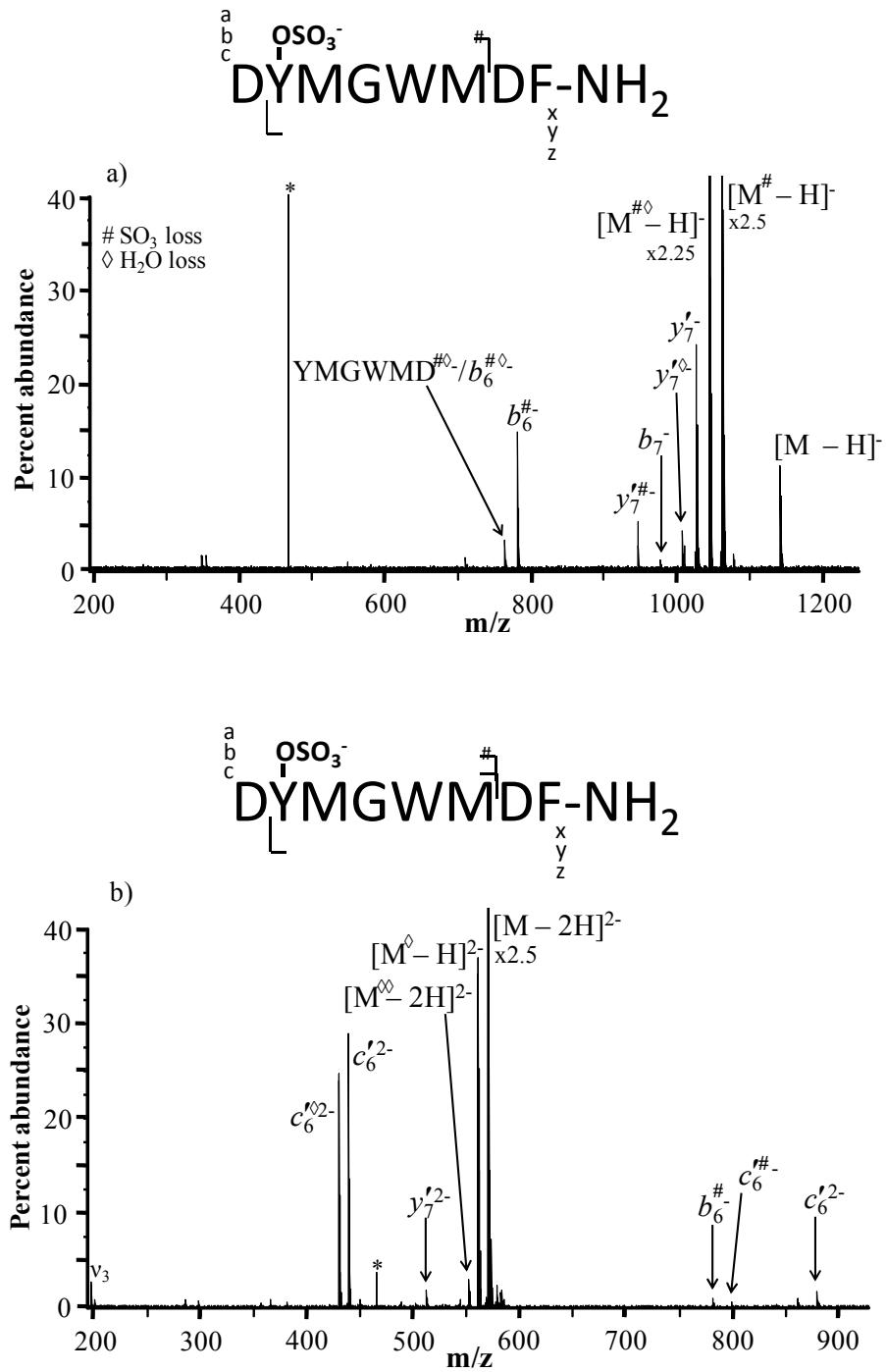
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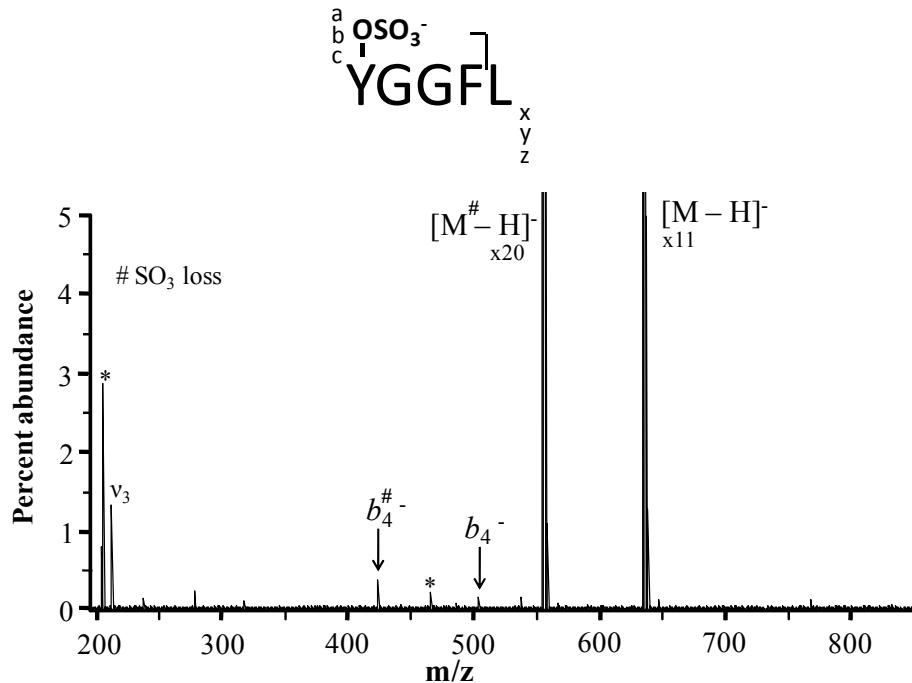
**Supplemental Figure S1.** Negative ion mode CAD of singly- (a) and doubly-deprotonated (b) sulfonated caerulein. Sulfonate loss is indicated by # while electronic noise is indicated by \*.



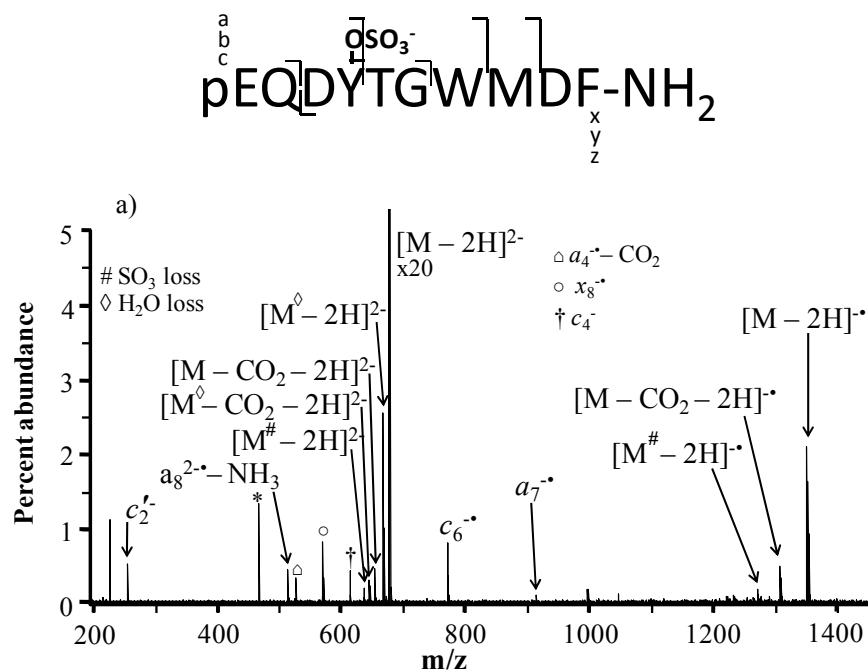
**Supplemental Figure S2.** Negative ion mode CAD of doubly-deprotonated sulfonated human gastrin II. Sulfonate loss and water loss are indicated by # and  $\diamond$ , respectively, while electronic noise is indicated by \*.

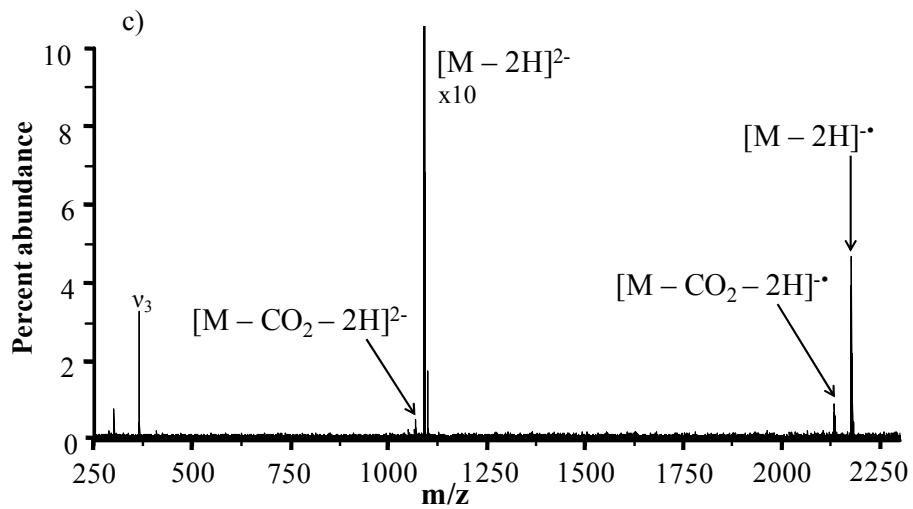
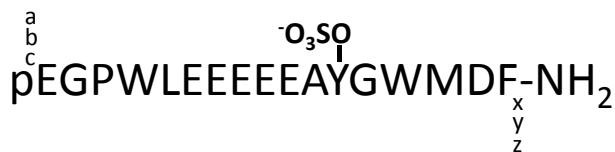
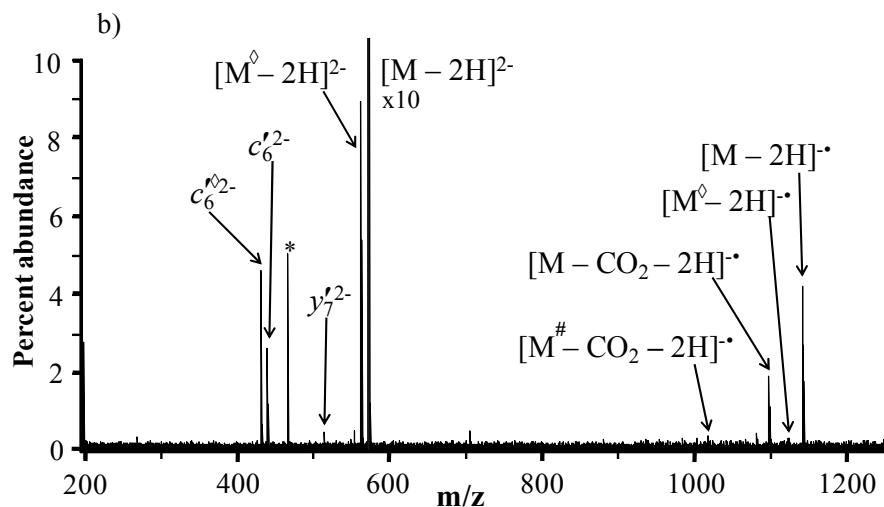


**Supplemental Figure S3.** Negative ion mode CAD of singly- (a) and doubly-deprotonated (b) sulfonated cholecystokinin (CCKS). Sulfonate loss and water loss are indicated by # and ◊, respectively, while electronic noise is indicated by \*.

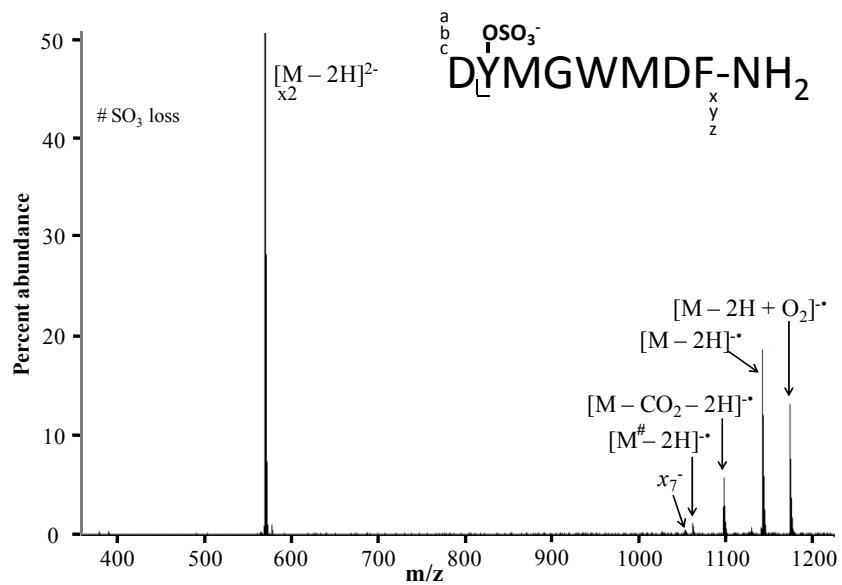


**Supplemental Figure S4.** Negative ion mode CAD of singly-deprotonated sulfonated leucine-enkephalin. Sulfonate loss is indicated by # while electronic noise is indicated by \*.



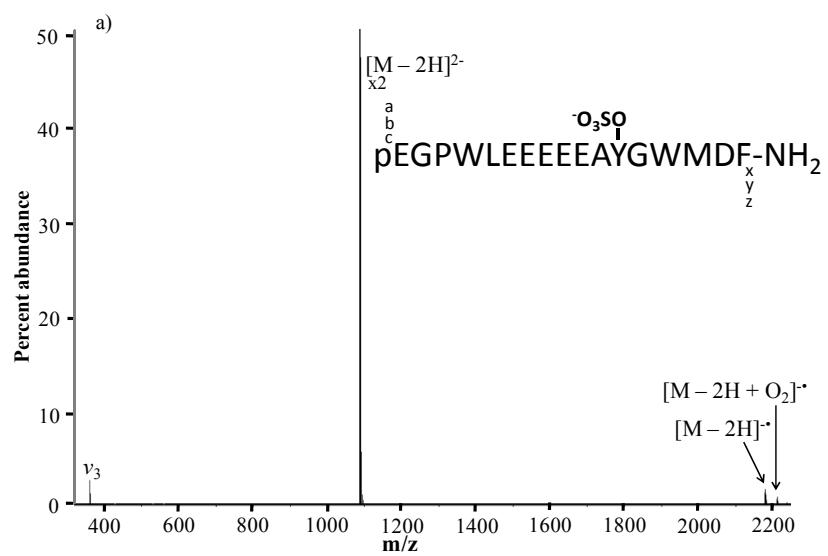


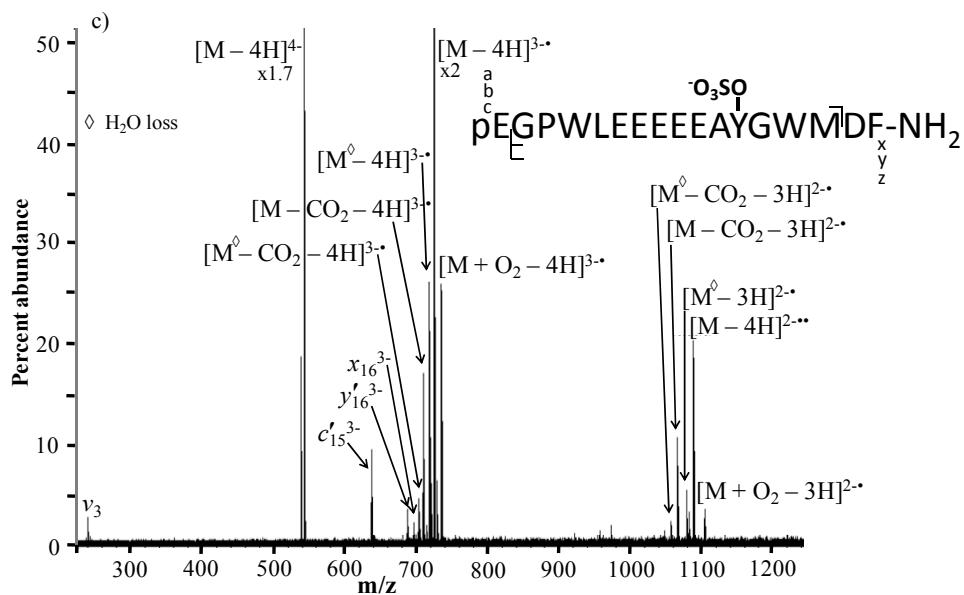
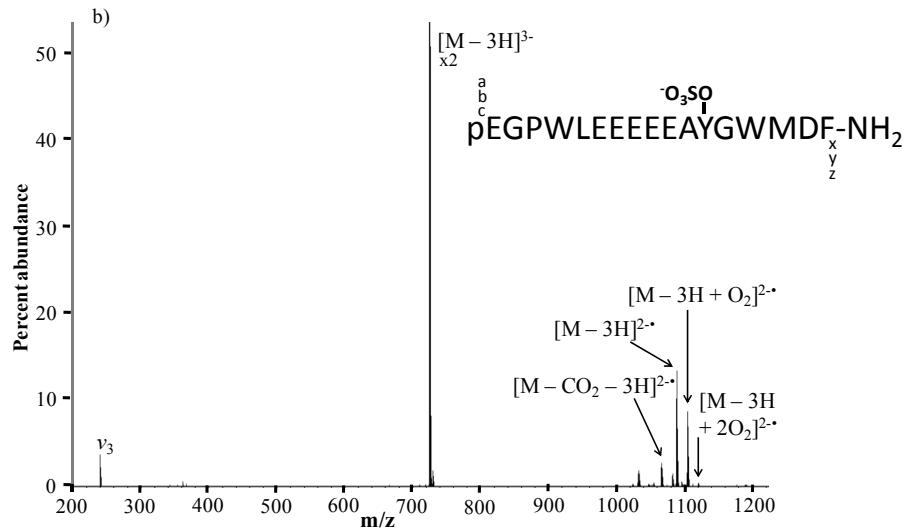
**Supplemental Figure S5.** EDD of doubly-deprotonated caerulein (a), CCKS (b), and gastrin II (c). Sulfonate loss and water loss are indicated by # and  $\diamond$ , respectively, while electronic noise is indicated by \*.



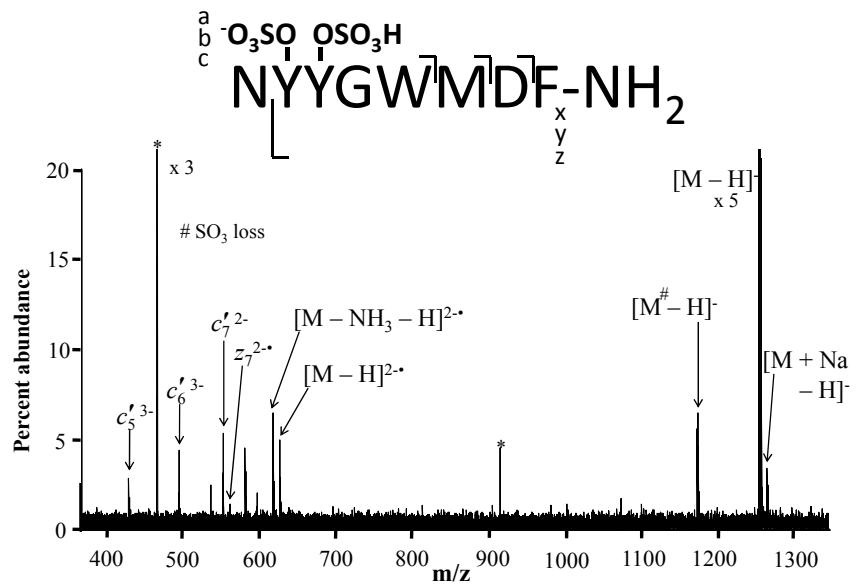
**Supplemental Figure S6.** NETD of doubly-deprotonated sulfonated cholecystokinin (CCKS).

Sulfonate loss is indicated by #.





**Supplemental Figure S7.** NETD of doubly- (a), triply- (b) and quadruply-deprotonated (c) sulfonated human gastrin II. No sulfonate loss was observed in any of these three spectra but sequence coverage is low. Water loss is indicated by  $\diamond$ .



**Supplemental Figure S8.** niECD of singly-deprotonated sulfonated cionin. Sulfonate loss is indicated by #. Electronic noise is indicated by \*. Charge location is arbitrarily assigned to the sulfonate residue.