SUPPLEMENTARY DATA

Increasing Fragmentation of Disulfide-Bonded Proteins for Top-Down Mass Spectrometry by Supercharging

Jiang Zhang[1], Rachel R. Ogorzalek Loo[2,3], and Joseph A. Loo[1,2,3,*]

[1]Department of Chemistry and Biochemistry, University of California-Los Angeles, Los Angeles, California, 90095, United States

[2]Department of Biological Chemistry, David Geffen School of Medicine at UCLA, University of California-Los Angeles, Los Angeles, California, 90095, United States

[3]UCLA/DOE Institute for Genomics and Proteomics, University of California-Los Angeles, Los Angeles, California, 90095, United States

* Corresponding author. Tel.: +1 310 794 7023; fax: +1 310 206 4038.
E-mail address: JLoo@chem.ucla.edu (J.A. Loo).

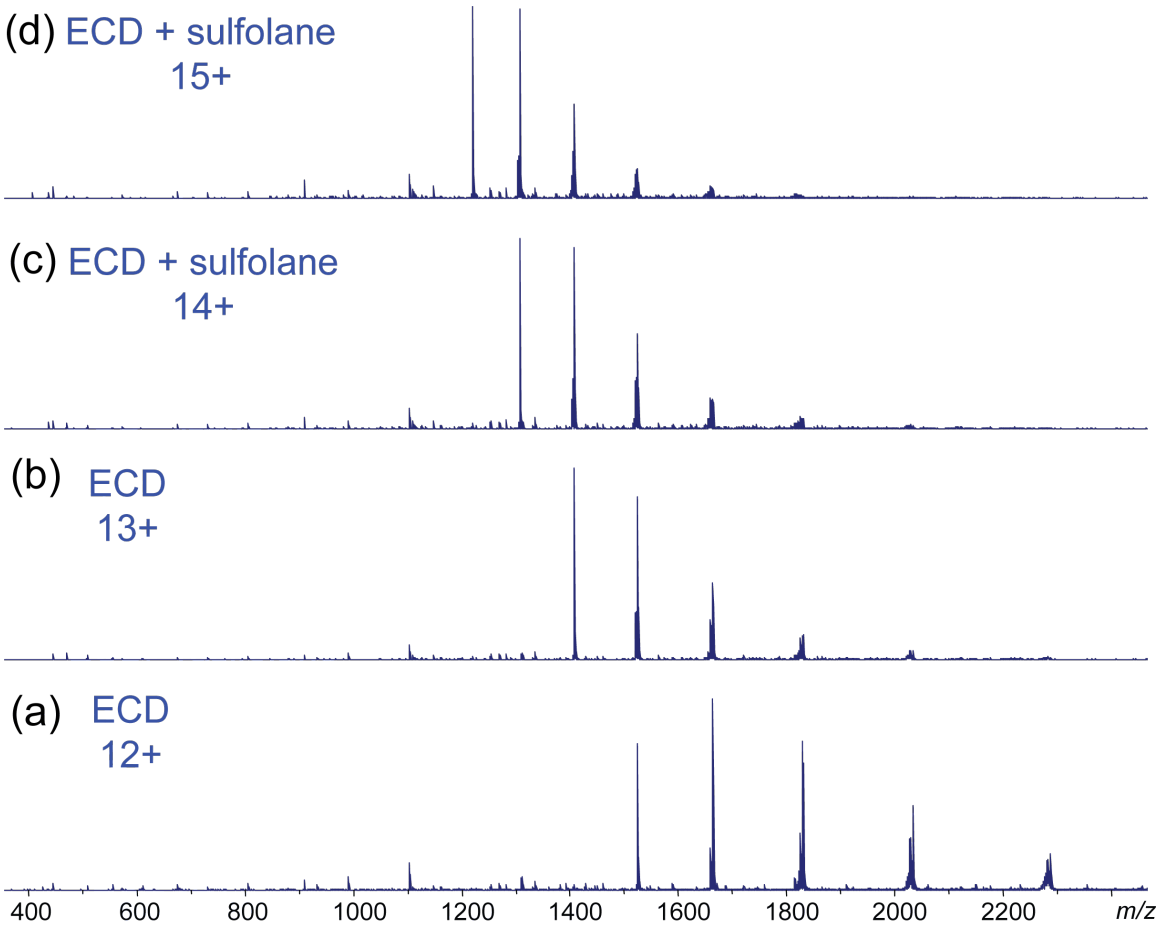

Figure S1. ECD mass spectra of β-lactoglobulin (0.5 µM) in (a-b) 50:50:0.1 ACN: H_2O: FA and (c-d) with 150 mM sulfolane.

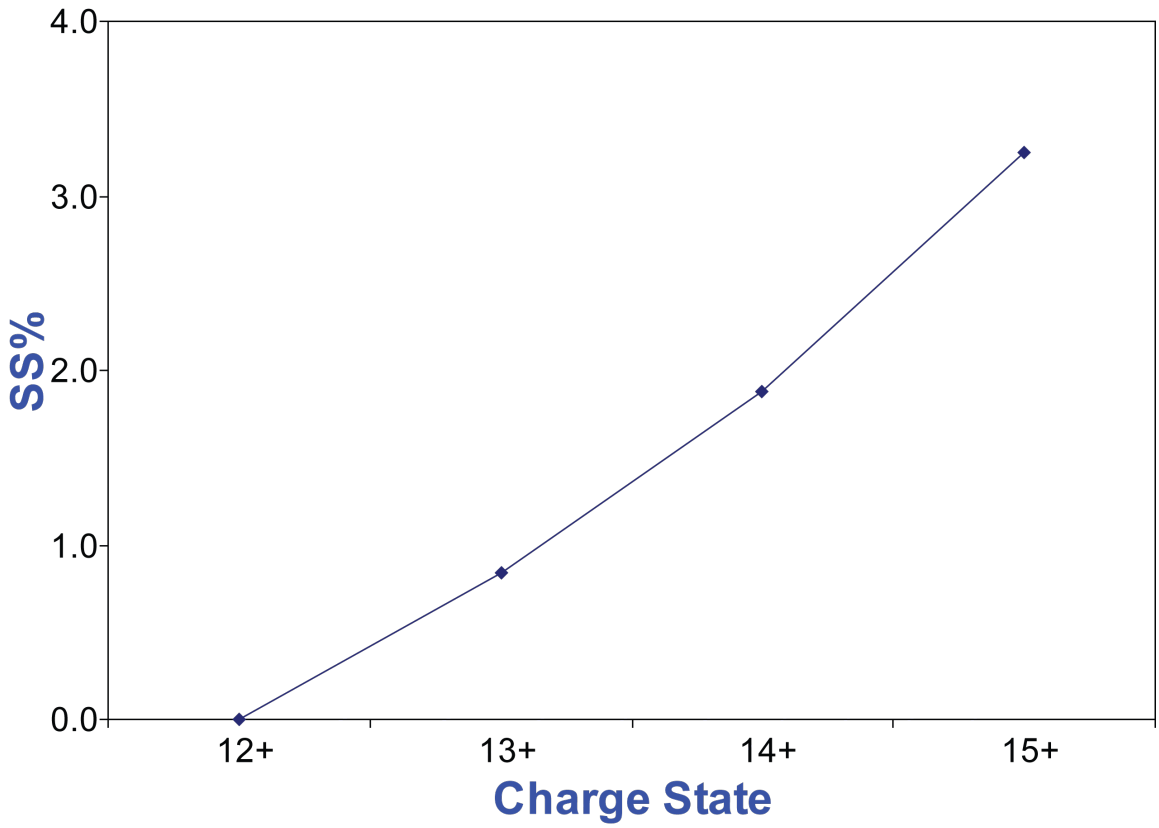

Figure S2. Relative fraction of product ions showing disulfide bond cleavage as a function of precursor charge for ECD of β-lactoglobulin.

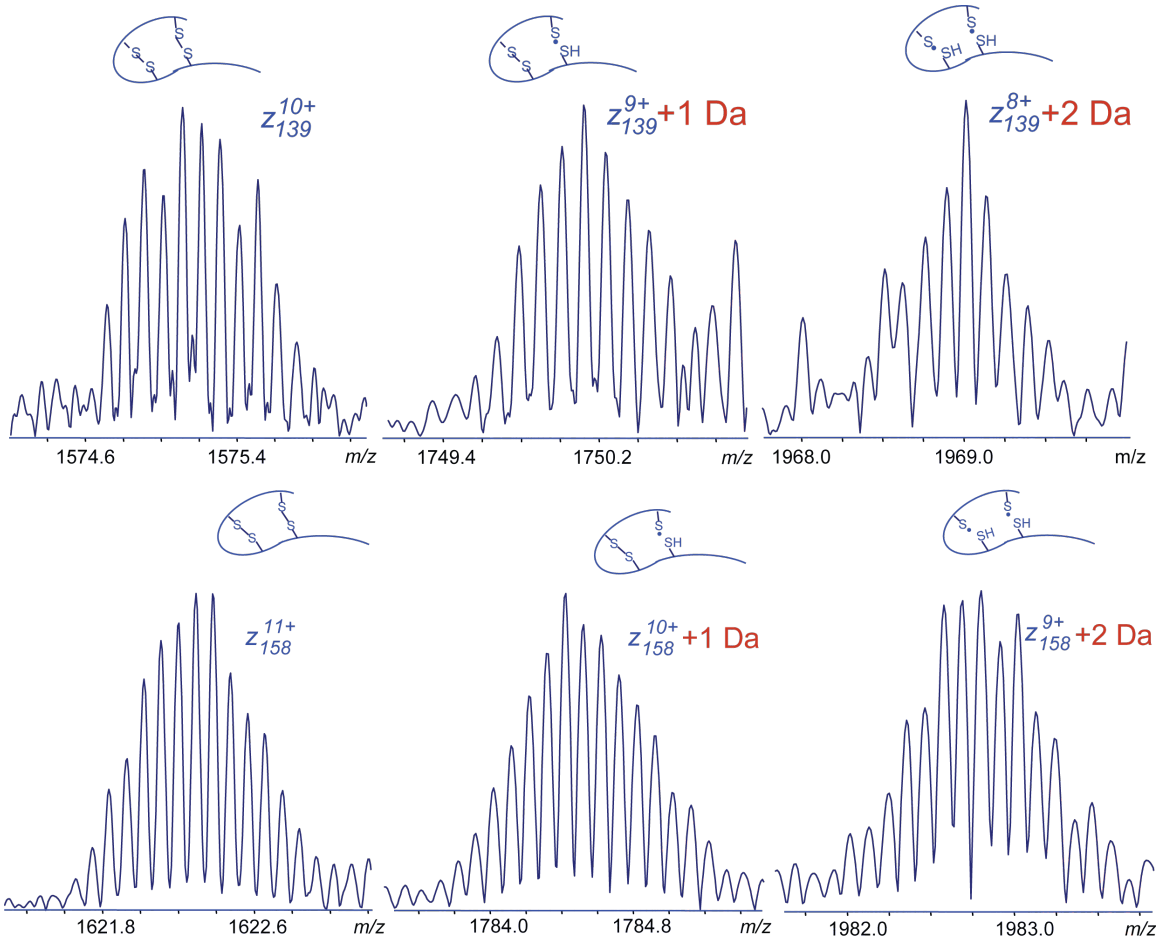

Figure S3. ECD product ions of β-lactoglobulin (bovine) containing potential disulfide cleavage by hydrogen radical capture, while the protein backbone inside the disulfide bond remain intact.

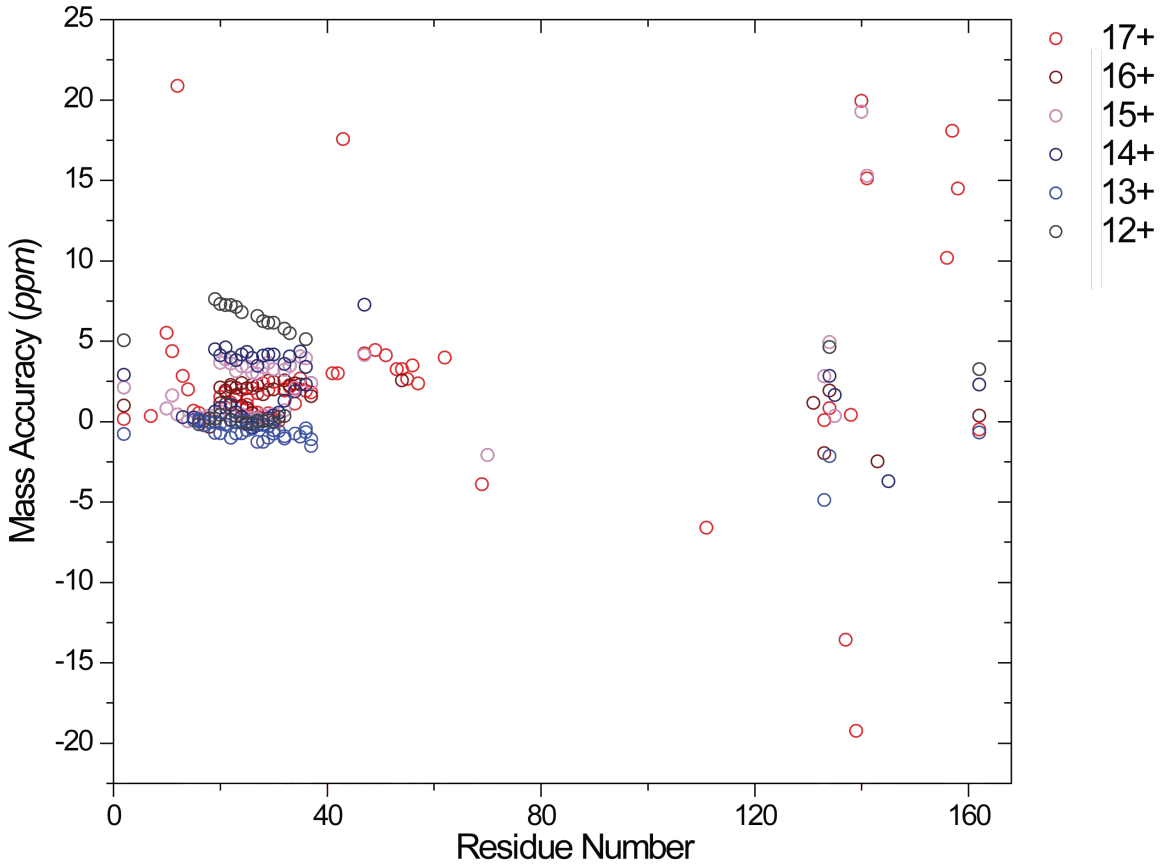

Figure S4. Mass accuracy of CAD-derived product ions of β-lactoglobulin for the 15+-17+ charge states (with sulfolane) and 12+-14+ charge states (without sulfolane).

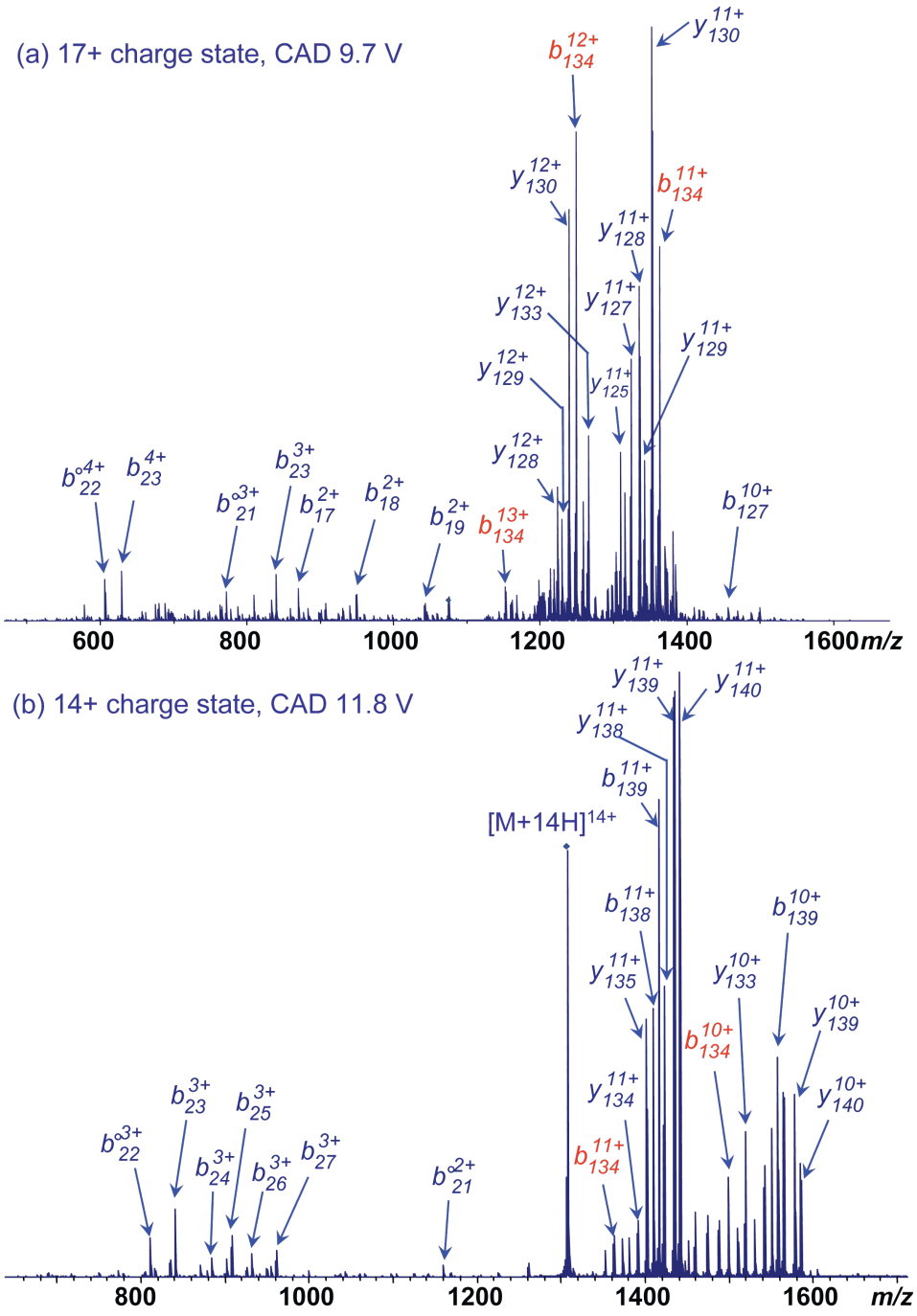

Figure S5. CAD mass spectra of β-lactoglobulin (bovine) (0.5 µM) for the (a) 17+ and (b) 14+ precursors. High abundance product ions with disulfide cleavages are labeled in red.

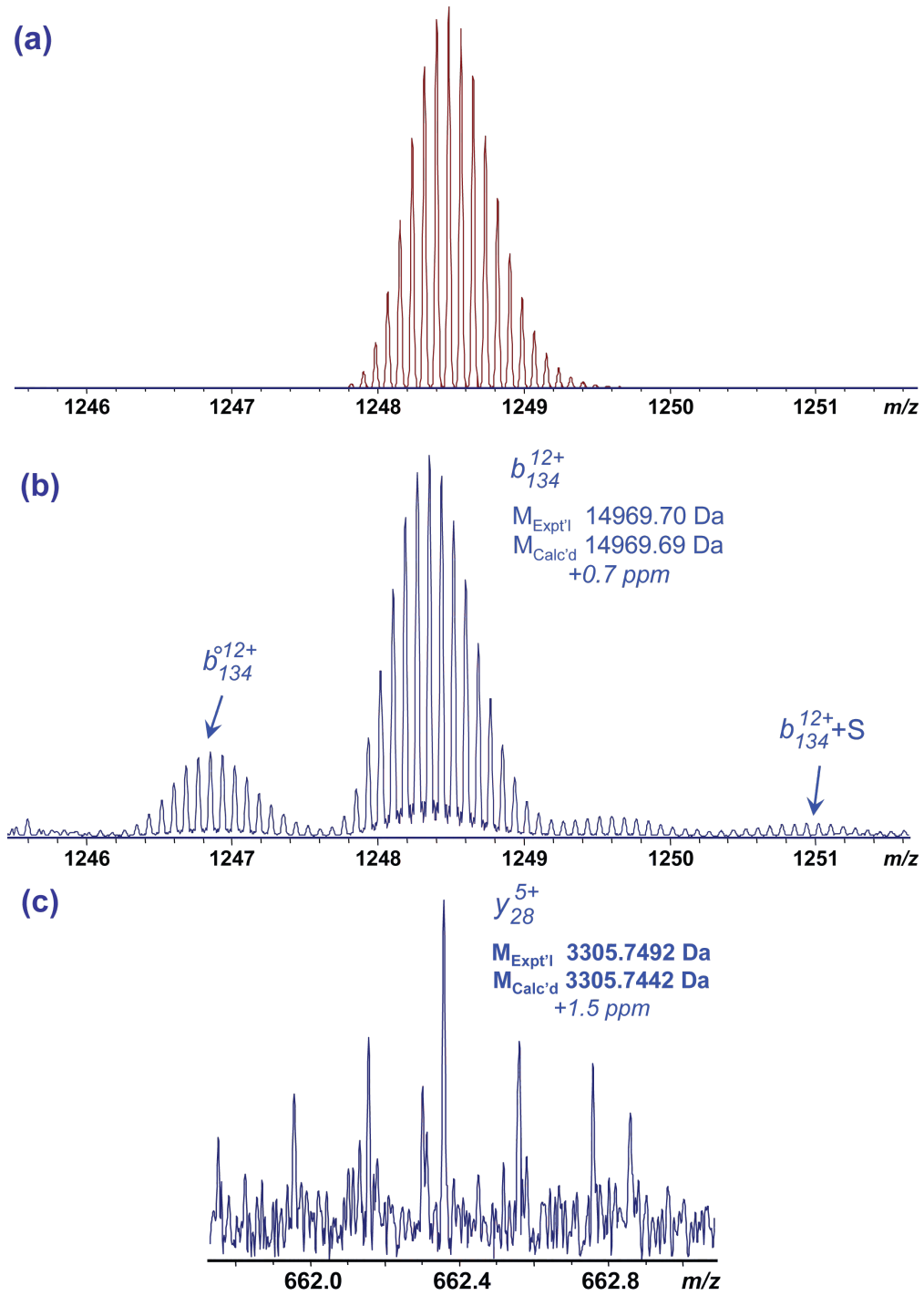

Figure S6. CAD mass spectra of β-lactoglobulin product ions with disulfide bond cleavage: (a) theoretical isotopic calculation of b_{134}, (b) experimental data for charge state 17+, (c) complementary y_{28} ion. The circle sign in superscript denotes water loss.

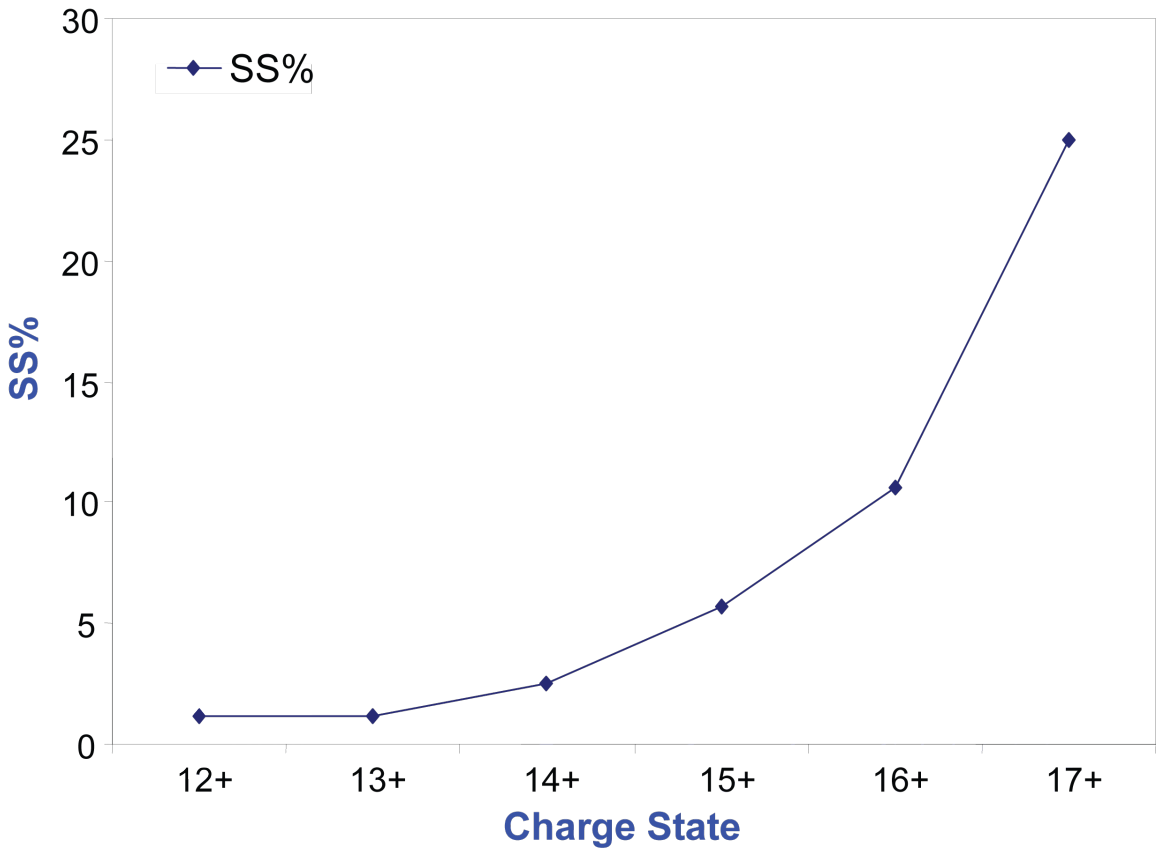

Figure S7. Relative fraction of product ions showing disulfide bond cleavage as a function of precursor charge for CAD of β-lactoglobulin.

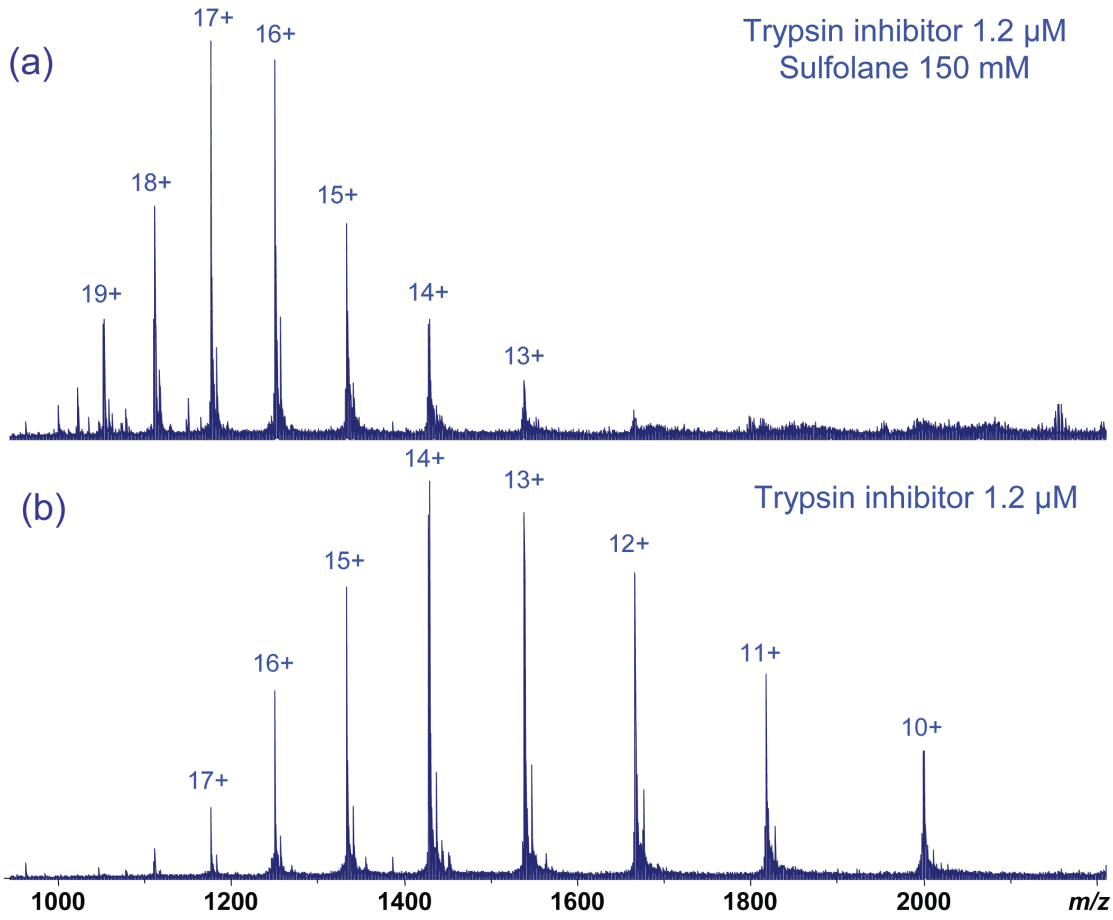

Figure S8. ESI mass spectra of trypsin inhibitor (soybean) (1.2 µM) in (a) 150 mM sulfolane in 50:50:0.1 ACN: H_2O: FA and (b) without sulfolane.

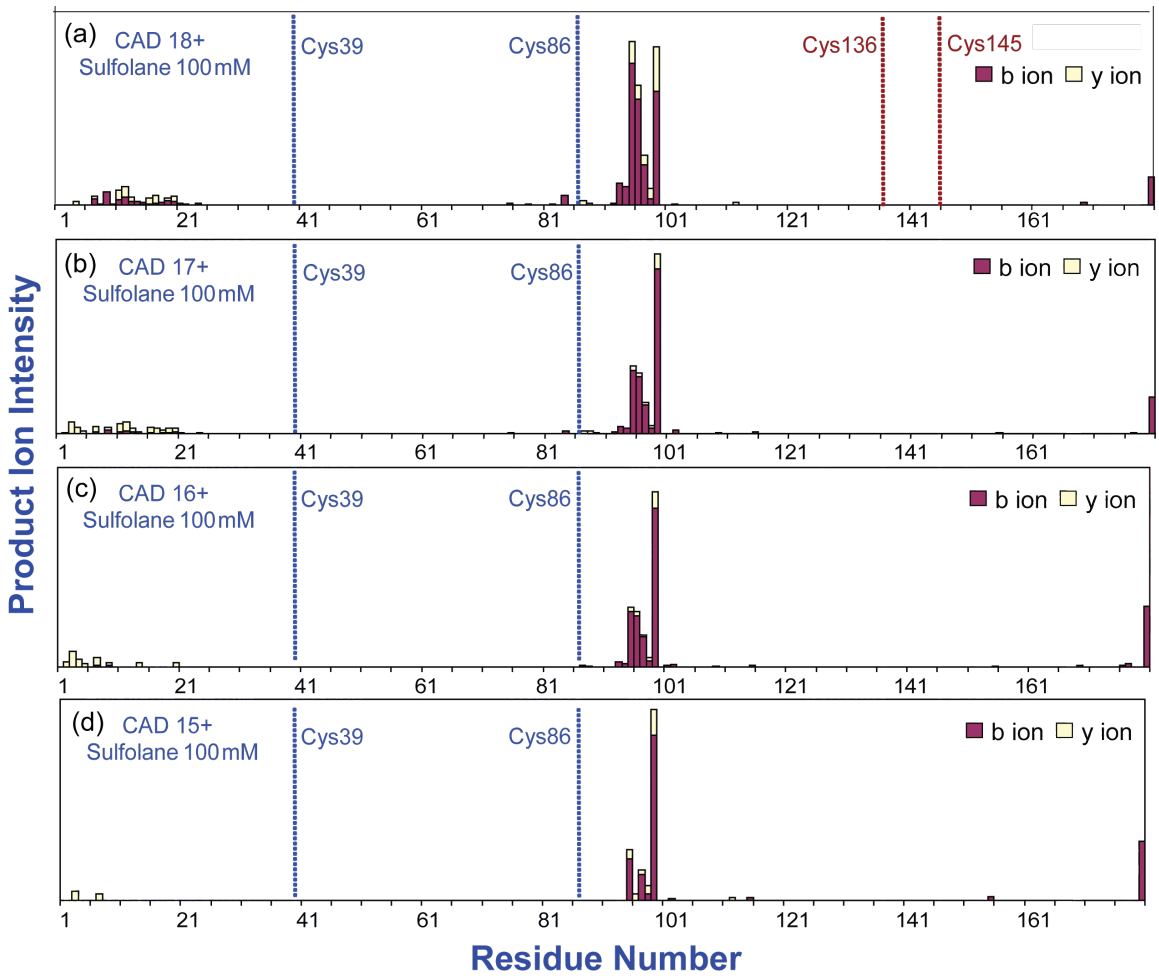

Figure S9. CAD product ion map of trypsin inhibitor (soybean) in 100 mM sulfolane.

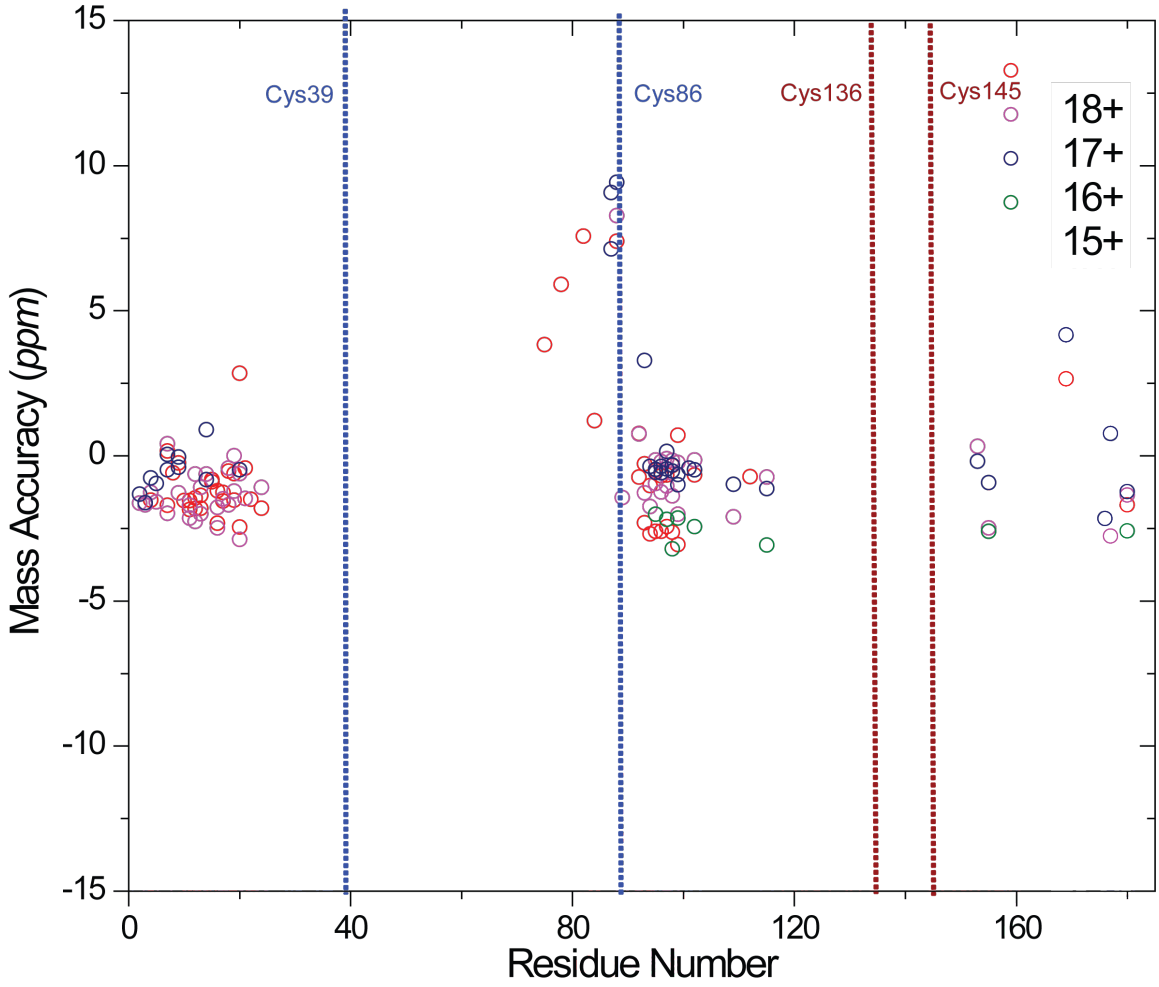

Figure S10. Mass accuracy of CAD-derived product ions of trypsin inhibitor for the 15+-18+ charge states. Product ions corresponding to disulfide bond cleavage Cys39-Cys86 were observed.

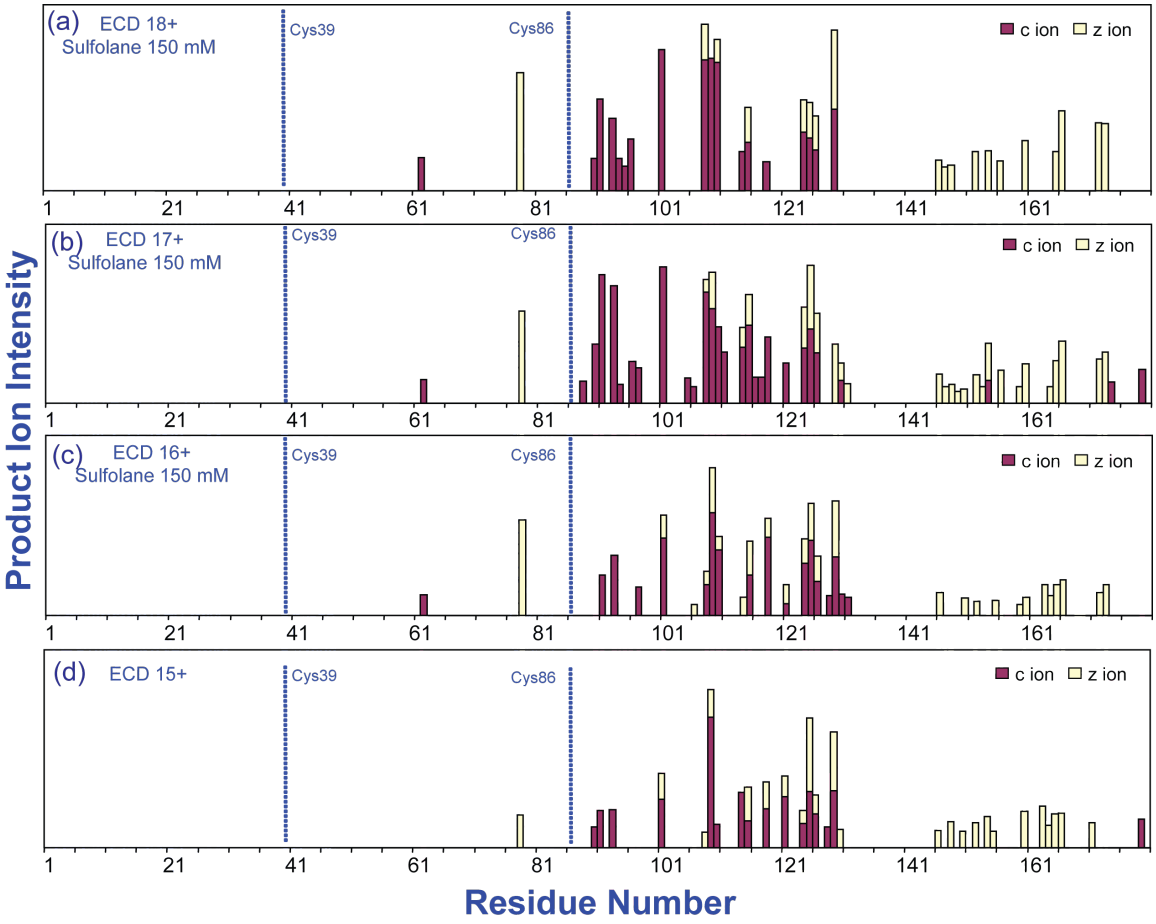

Figure S11. ECD product ion map of trypsin inhibitor (soybean) for charge states (a) 18+, (b) 17+ and (c) 16+ under supercharging conditions, and (d) 15+ without sulfolane.

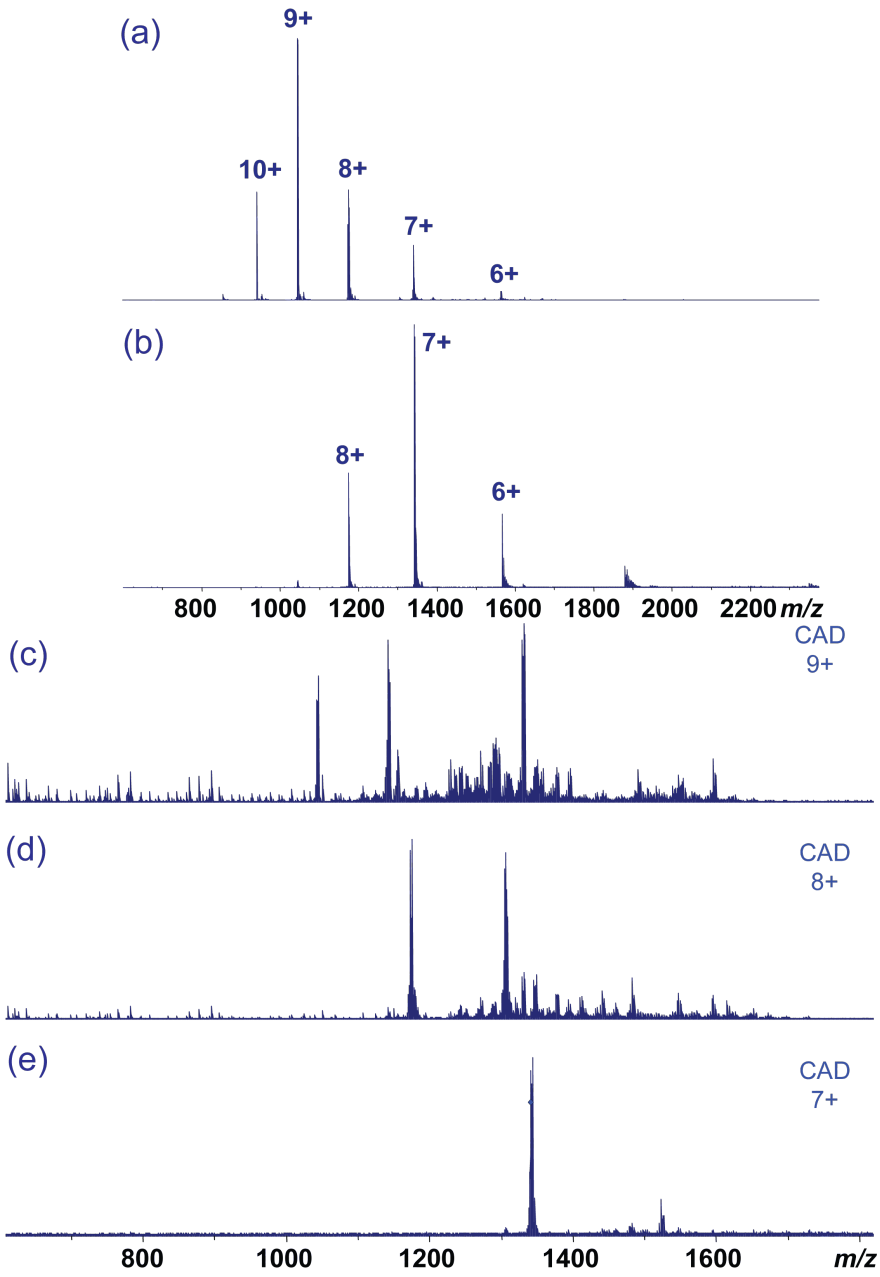

Figure S12. ESI mass spectrum of human proinsulin (a) with 150 mM sulfolane, and (b) without sulfolane. CAD mass spectra for charge states (c) 9+ and (d) 8+ with sulfolane, and (e) 7+ without sulfolane are shown.

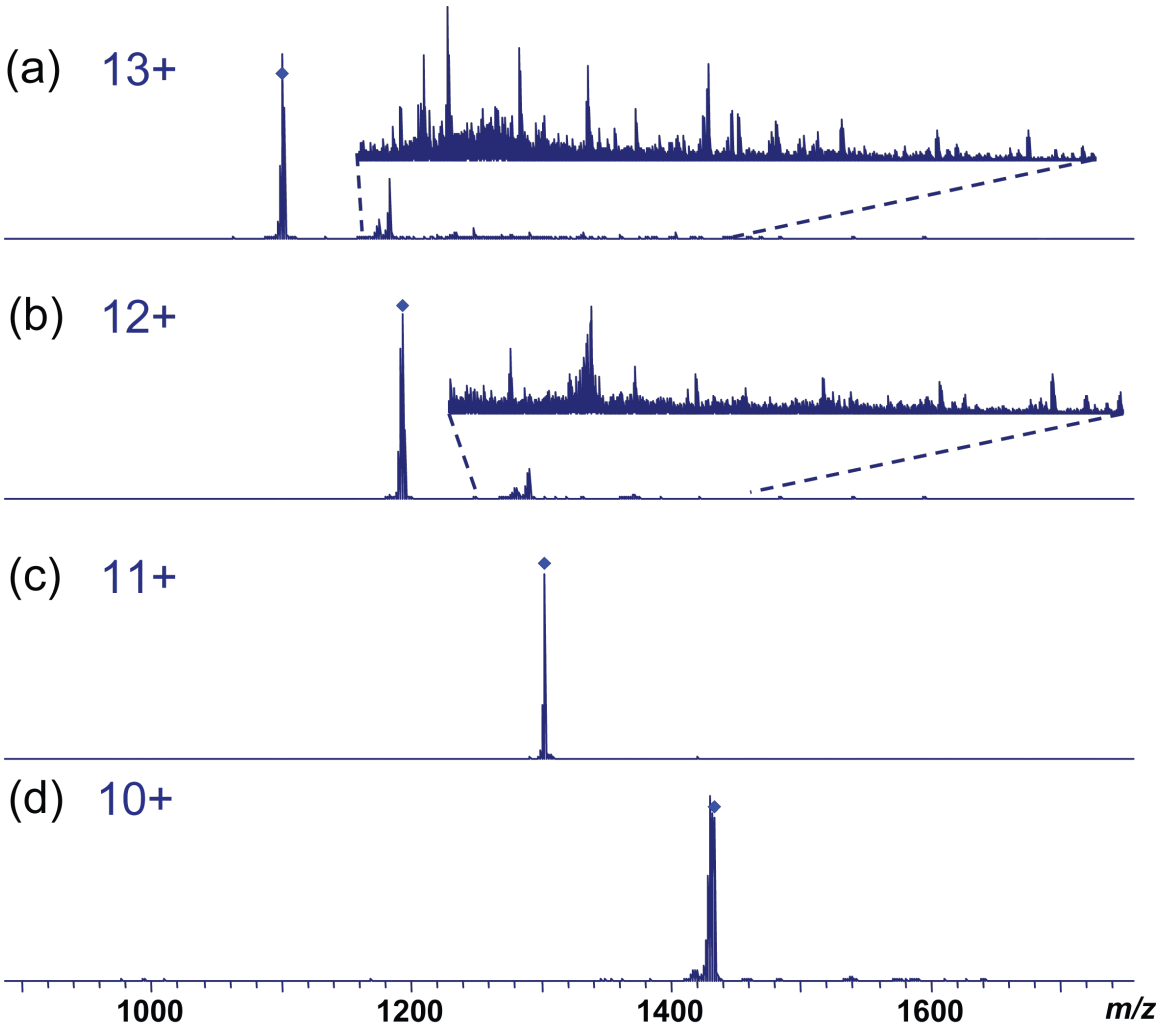

Figure S13. CAD mass spectra of chicken lysozyme for supercharged (a) 13+ and (b) 12+ precursors, and (c) 11+ and (d) 10+ precursors without sulfolane added.

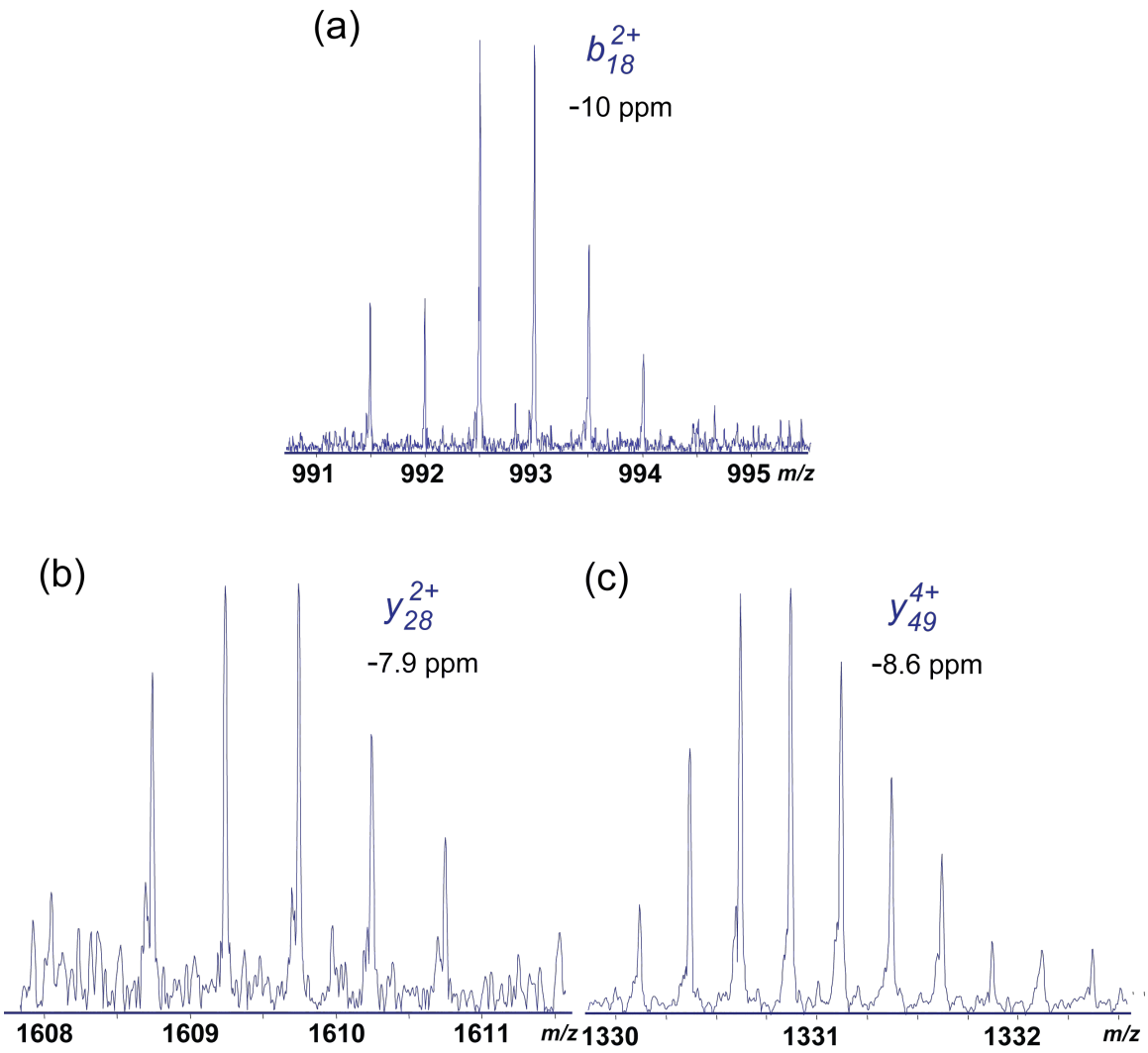

Figure S14. CAD product ions of chicken lysozyme: (a) b_{18}^{2+}, one disulfide bond cleavage; (b) y_{28}^{2+}, two disulfide bond cleavages; (c) y_{49}^{4+}, three disulfide bond cleavages.