

Supporting Information

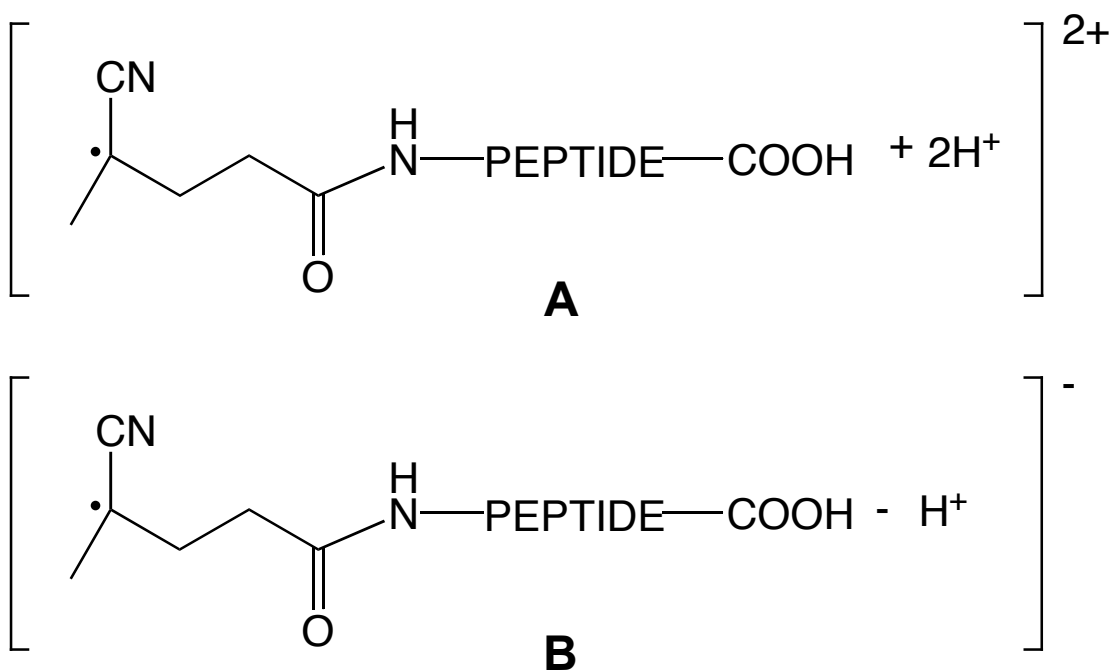
Figure S1. FRIPS and CAD spectra of positively charged bradykinin.

Figure S2. FRIPS and CAD spectra of positively charged anxiety peptide.

Figure S3. FRIPS and CAD spectra of negatively charged met-enkephalin.

Scheme S1. Possible mechanism for FRIPS fragmentation.

The peptide fragment ion nomenclature used in the communication and supporting information is that of Biemann, from “Appendix 5. Nomenclature for Peptide Fragment Ions (Positive Ions)” in *Methods in Enzymology*, 1990, Volume 193, 886-887.



Radical peptide conjugates referred to in the Supporting Information.

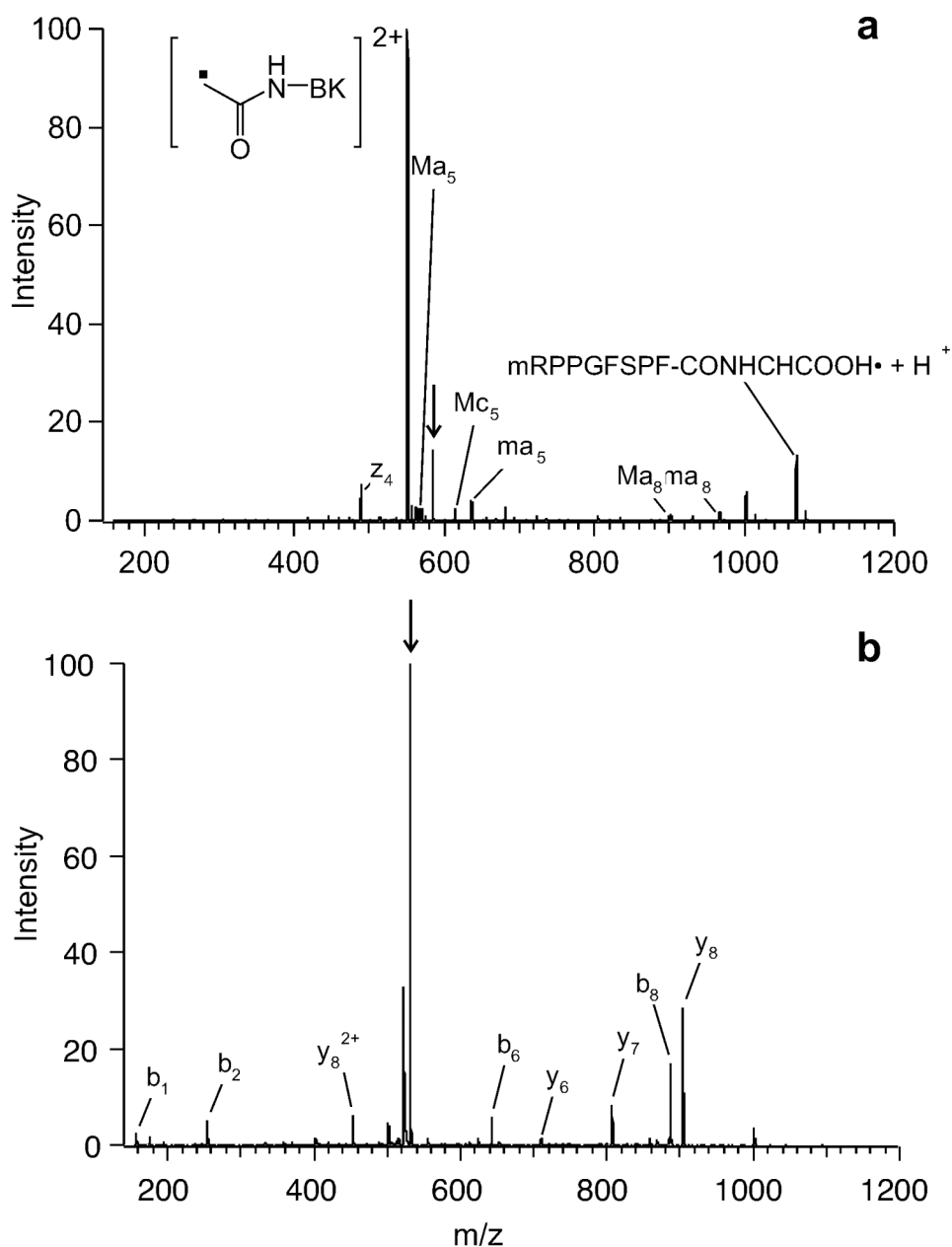


Figure S1. (a) Spectrum resulting from CAD of doubly protonated A, where the peptide is bradykinin. The “m” refers to a peptide fragment with a Vazo 68 radical fragment ($-\text{COCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CN}$) attached to the N terminus; “M” refers to a peptide fragment with $-\text{COCH}_3$ attached to the N terminus. (b) Spectrum resulting from CAD of doubly protonated unmodified bradykinin. Arrows point to the dissociated species.

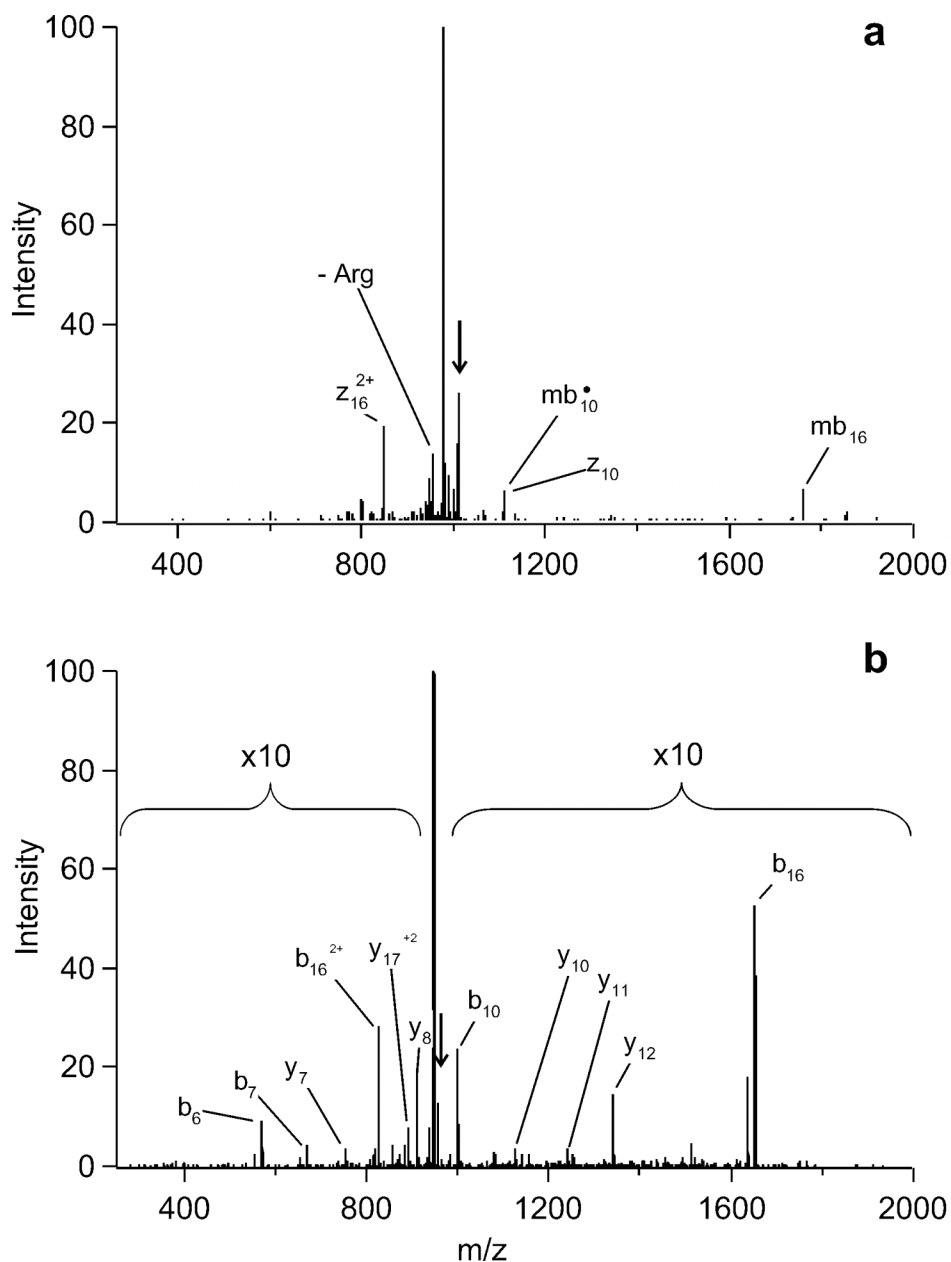


Figure S2. (a) Spectrum resulting from CAD of doubly protonated A, where the peptide is anxiety peptide, QATVGDVNTDRPGLLDLK. The “m” refers to a peptide fragment with a Vazo 68 radical fragment ($-\text{COCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CN}$) attached to the N terminus; “M” refers to a peptide fragment with $-\text{COCH}_3$ attached to the N terminus. (b) Spectrum resulting from CAD of doubly protonated unmodified anxiety peptide. Arrows point to the dissociated species.

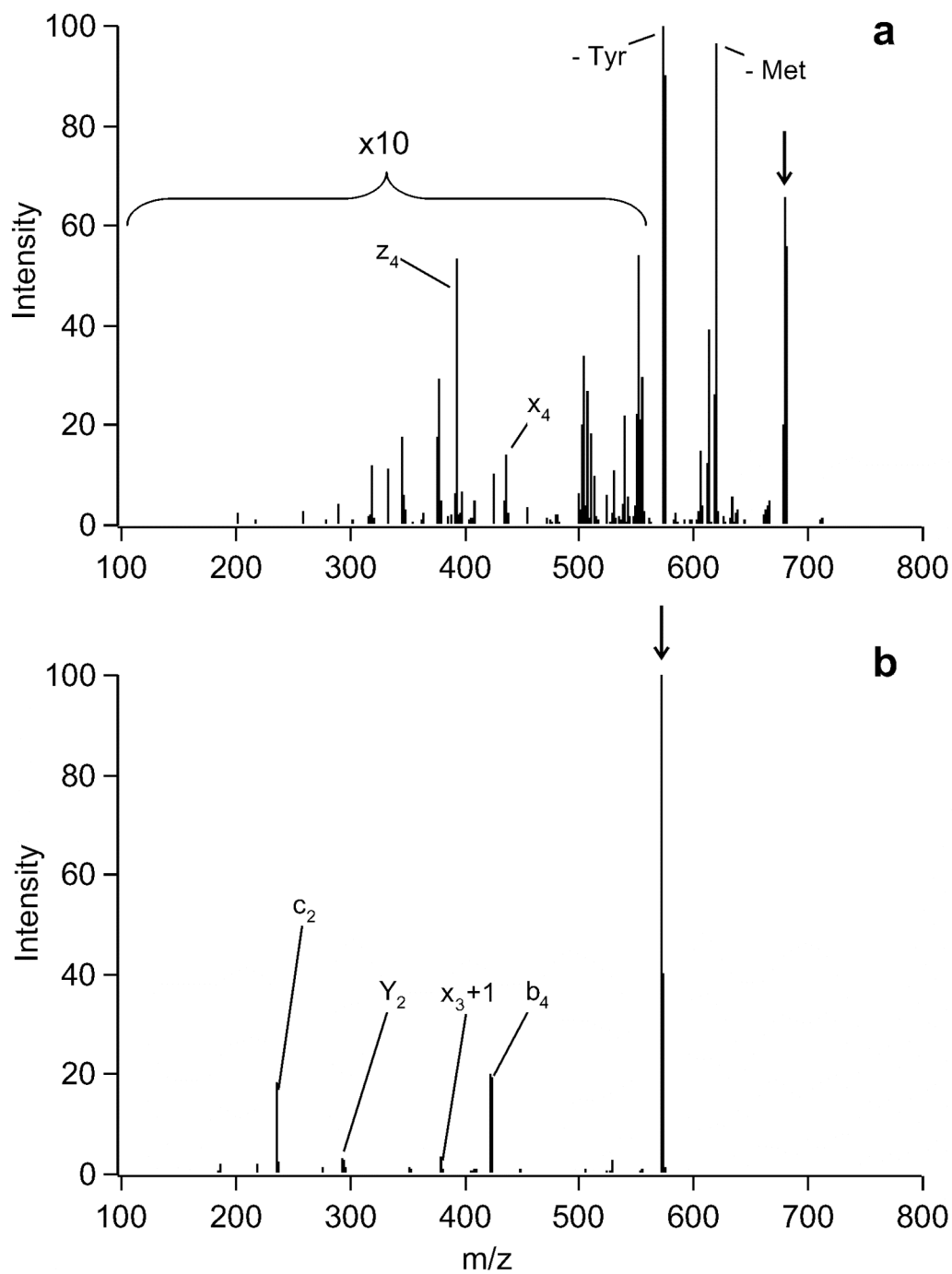
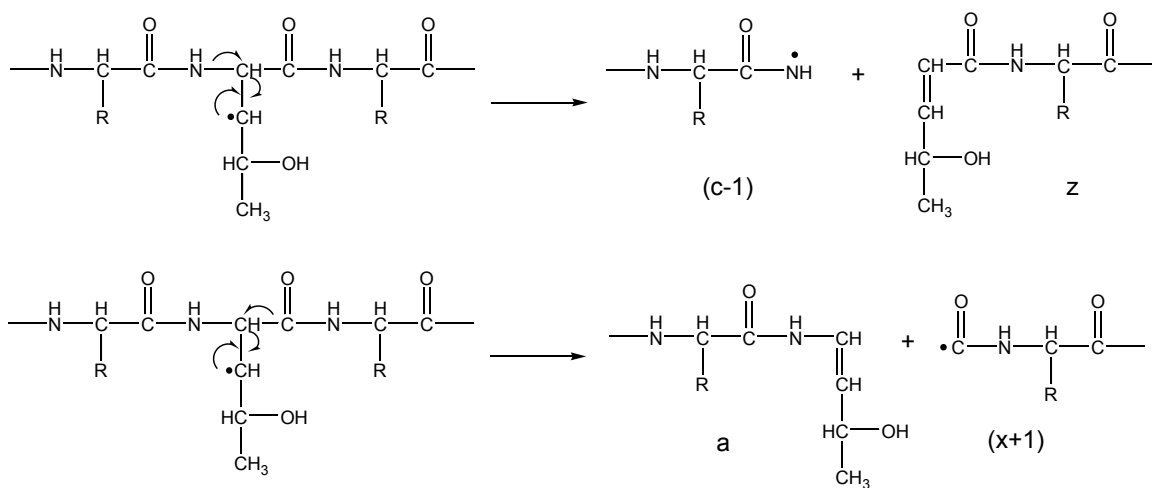


Figure S1. (a) Spectrum resulting from CAD of B, where the peptide is met-enkephalin, YGGFM. (b) Spectrum resulting from CAD of singly negatively charged unmodified met-enkephalin. Arrows point to the dissociated species.



Scheme S1. Possible FRIPS mechanisms, explaining the observation of c , z , x , and a type fragments.