Electronic Supplementary Material (ESI) for Analyst

SUPPORTING INFORMATION

for

Structural characterization of glycerophospholipids by combinations of ozone- and collision-induced dissociation mass spectrometry: The next step towards "top-down" lipidomics

Huong T. Pham[a§], Alan T. Maccarone[a], Michael C. Thomas[a¶], J. Larry Campbell[b], Todd W. Mitchell[c]* and Stephen J. Blanksby[a]*,

[a] ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, School of Chemistry, University of Wollongong, NSW, Australia

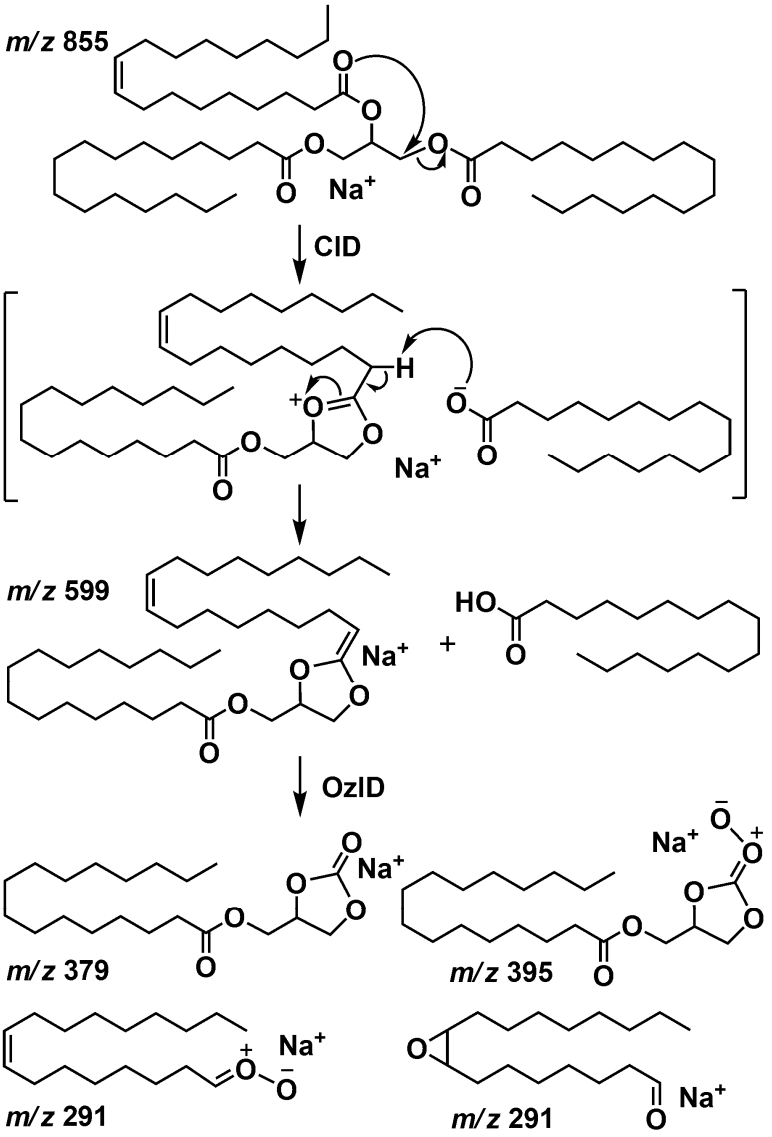
[b] AB SCIEX, Concord, Ontario, Canada

[c] School of Health Sciences, University of Wollongong, NSW, Australia

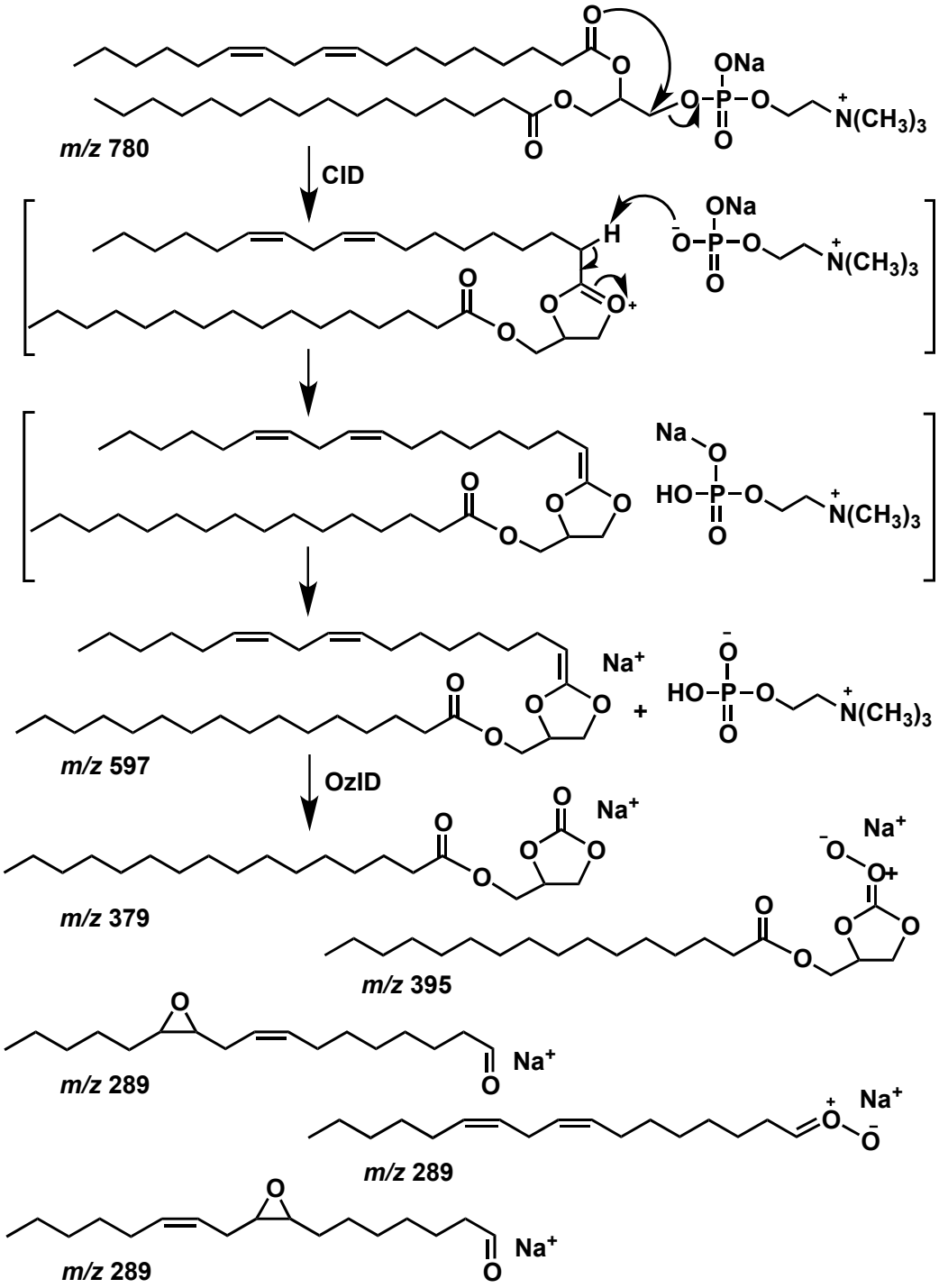
* Corresponding Author: Stephen J. Blanksby blanksby@uow.edu.au

Todd W. Mitchell toddm@uow.edu.au

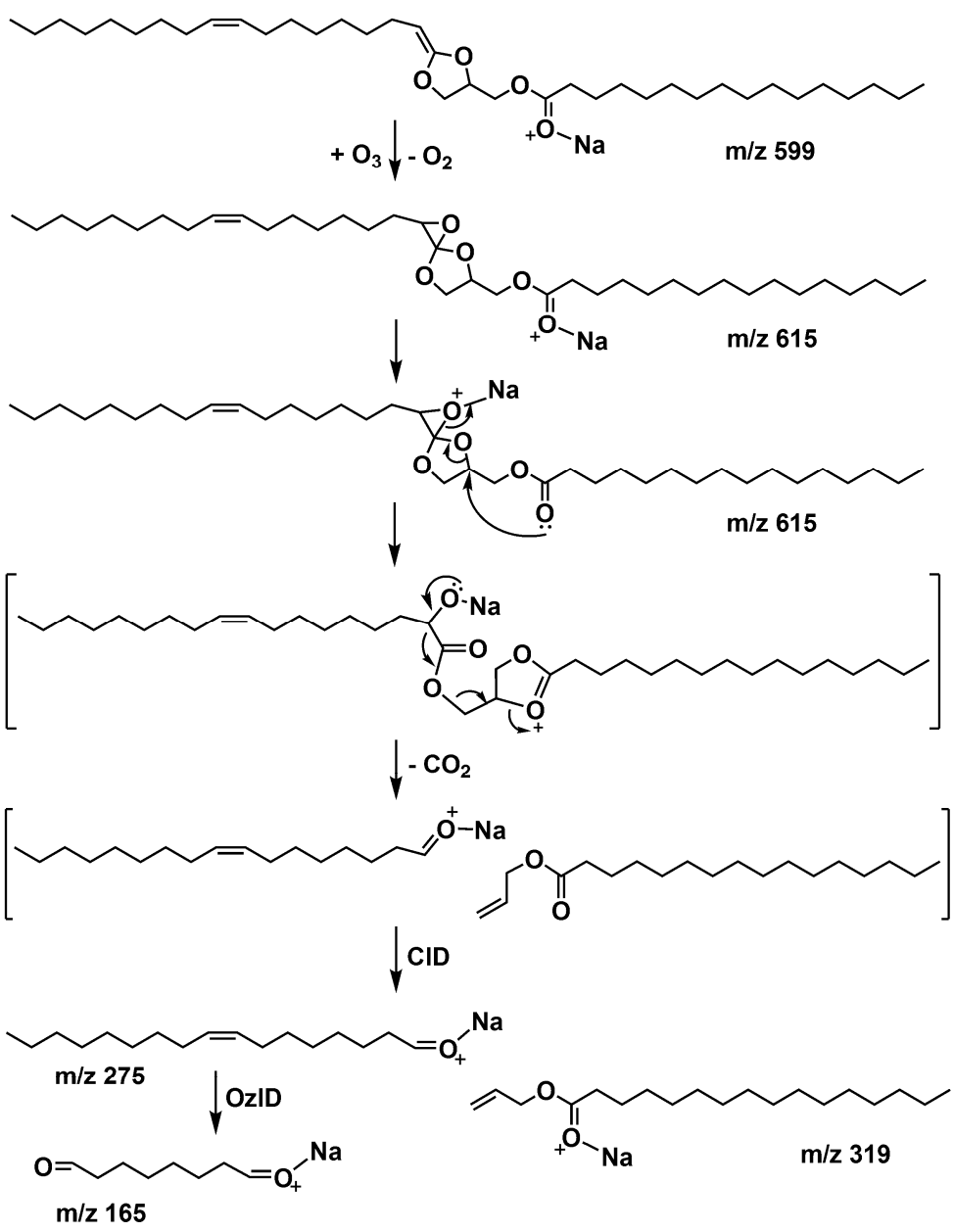
Scheme S-1: The substitution mechanism with a five-membered ring intermediate driven by the *sn*-2 fatty acyl chain during CID/OzID fragmentation of [TG 16:0/18:1/16:0 + Na]$^+$.



Scheme S-2: Proposed structures of major product ions forming in CID/OzID from [PC 16:0/18:2 + Na]$^+$.



Scheme S-3: A mechanism proposed for the formation and (CID/OzID)[2] fragmentation of the *m/z* 614/615 ion resulting from the PC 16:0/18:1(9*Z*) standard.



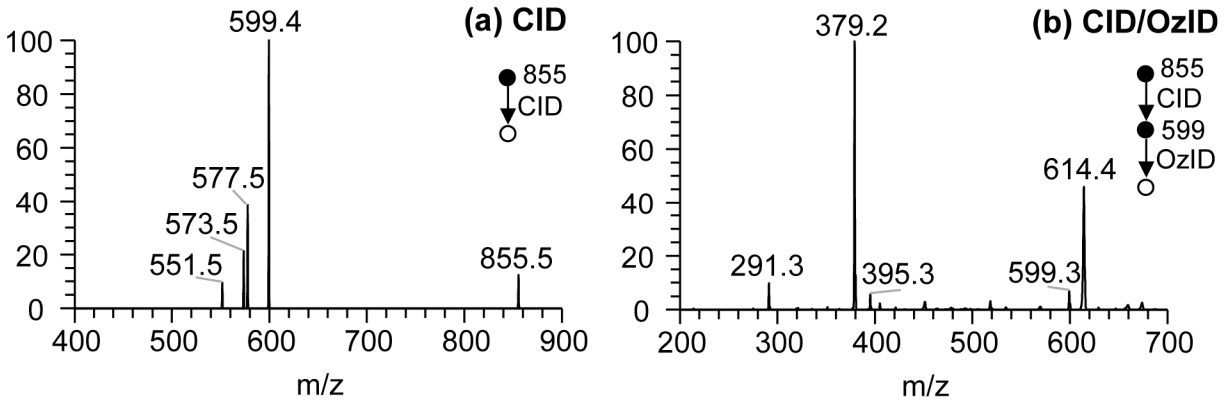


Figure S-1: (a) CID spectrum of [TG 16:0/18:1/16:0 + Na]$^+$ precursor ion at *m/z* 855, (b) CID/OzID spectrum of *m/z* 599 fragment ion [TG 16:0/18:1/16:0 + Na - 16:0]$^+$ formed in (a).

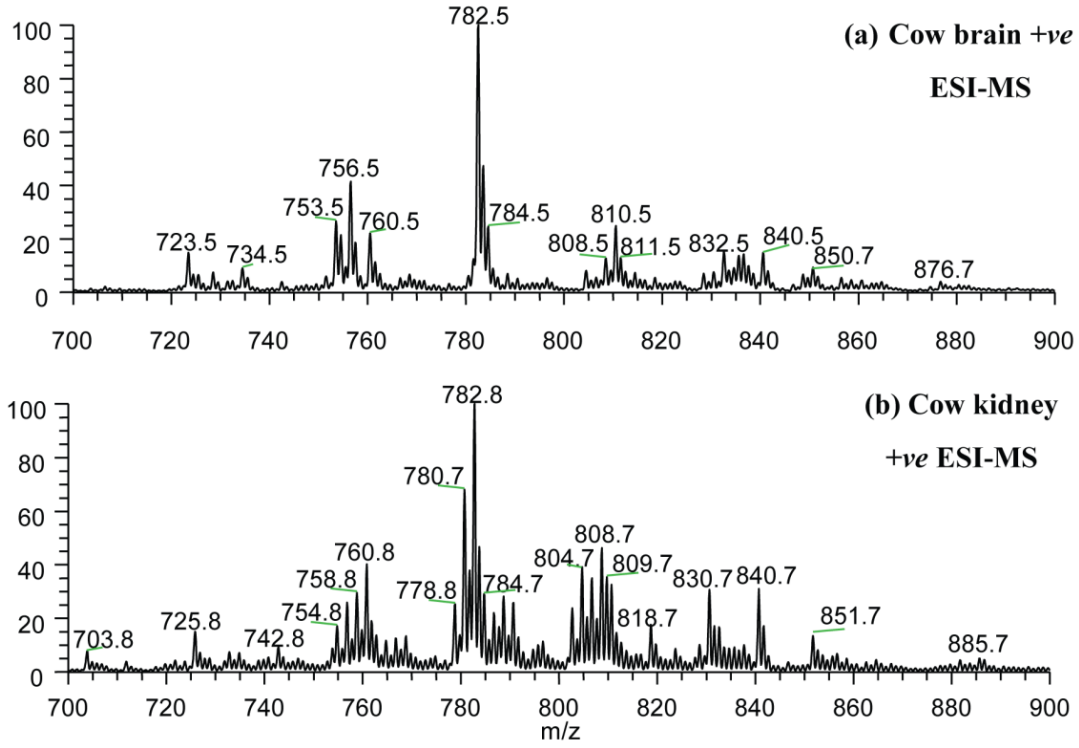


Figure S-2: ESI-MS mass spectra obtained in positive ion mode for lipids extracts from (a) cow brain and (b) cow kidney. The ions observed represent the [M + Na]$^+$ adducts of a wide range of phospholipids present in the samples.

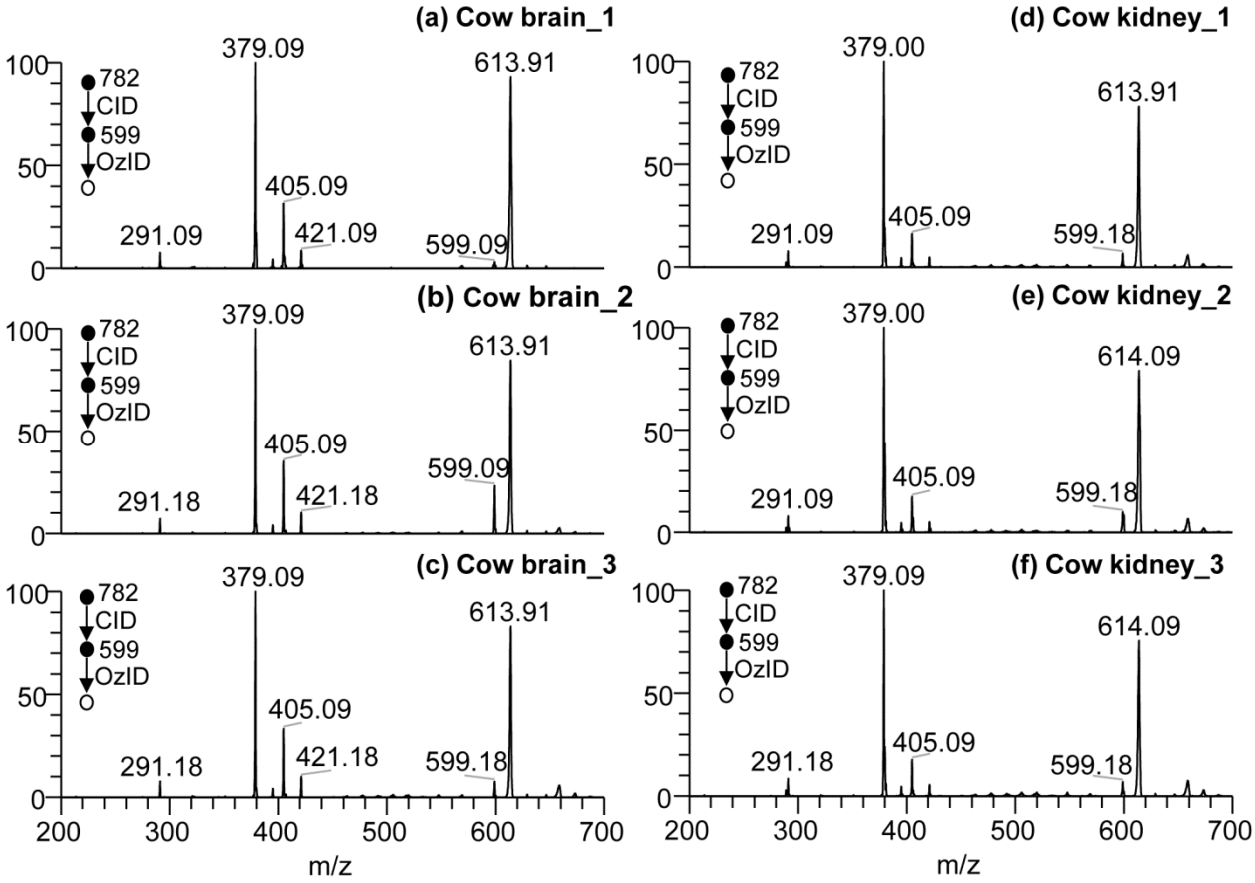


Figure S-3: Duplicate measurement of CID/OzID spectra generated by initially mass-selecting $[M + Na]^+$ adduct ions at *m/z* 782 from (a), (b) and (c) bovine brain and (d), (e), (f) bovine kidney extracts.

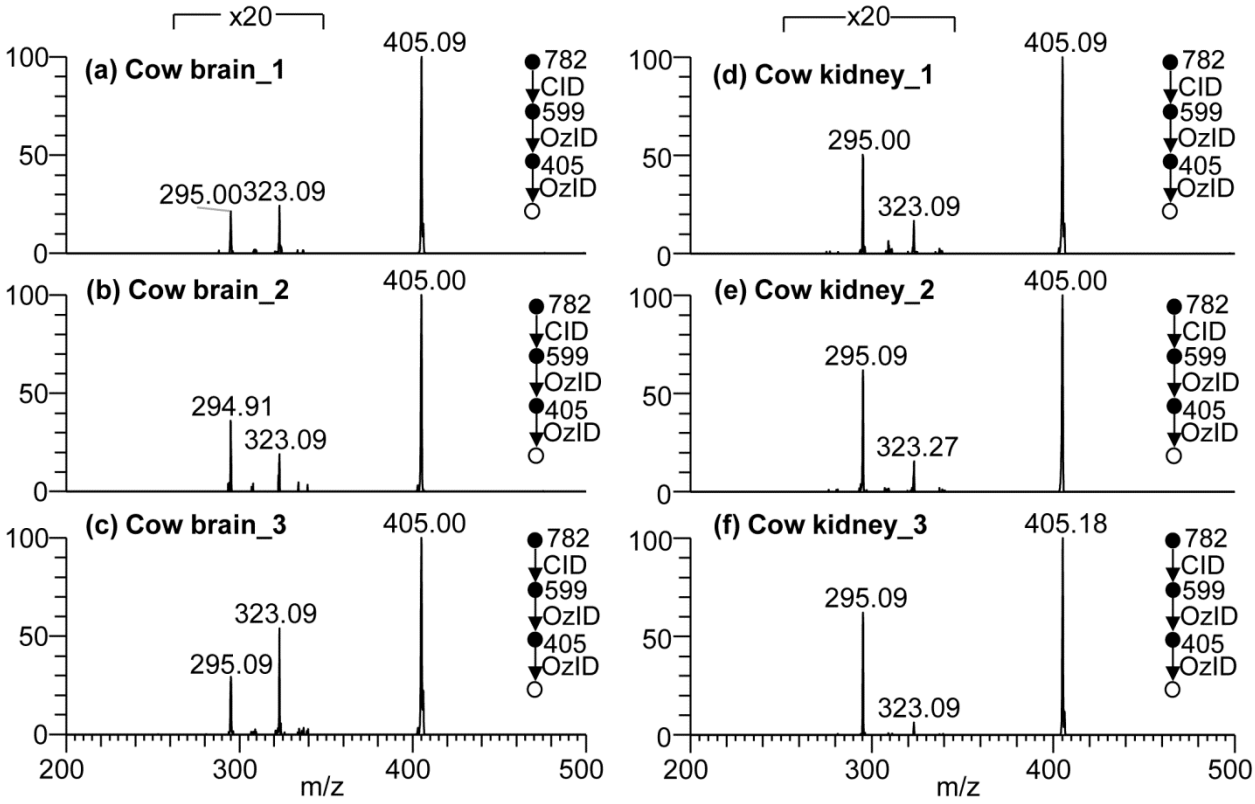


Figure S-4: Duplicate measurement of CID/OzID^2 spectra generated by initially mass-selecting $[M + Na]^+$ adduct ions at *m/z* 782 from (a), (b) and (c) bovine brain and (d), (e), (f) bovine kidney extracts. The magnifying factor of 20 times is the same for all spectra.

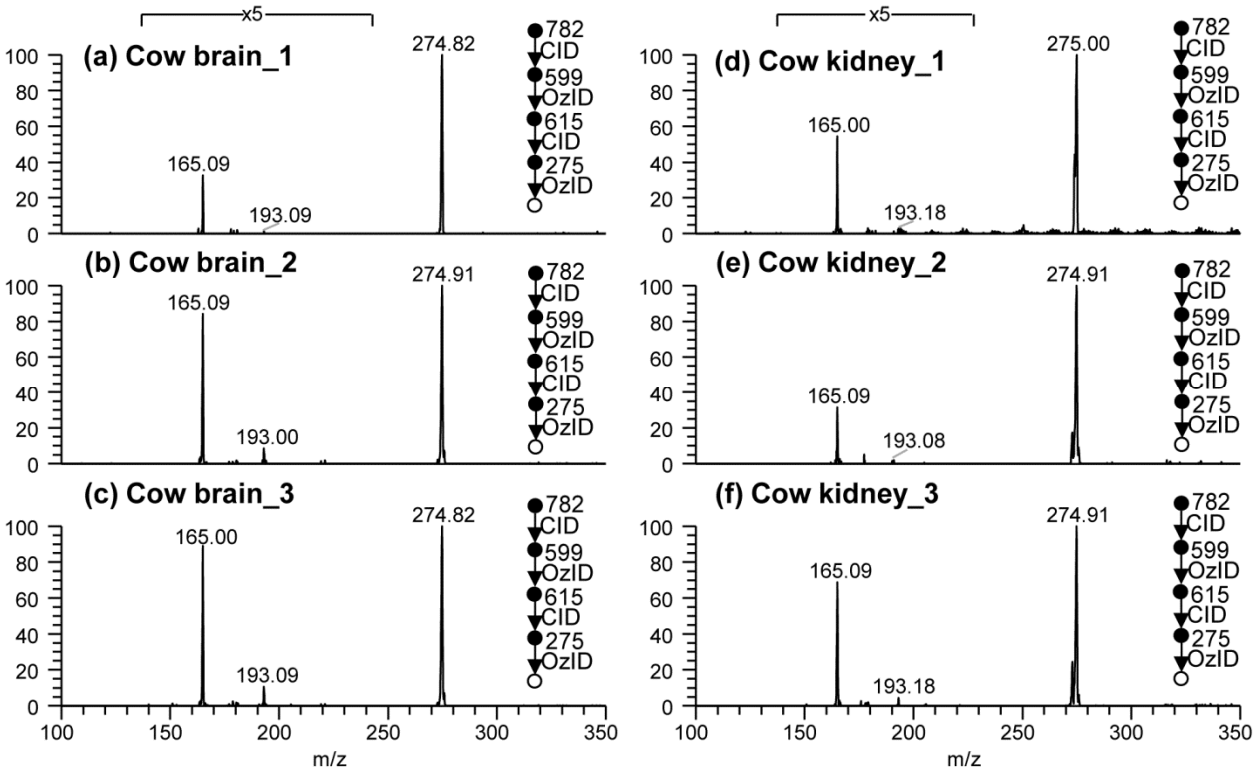


Figure S-5: Duplicate measurement of $(CID/OzID)^2$ spectra generated by initially mass-selecting $[M + Na]^+$ adduct ions at *m/z* 782 from (a), (b) and (c) bovine brain and (d), (e), (f) bovine kidney extracts. The magnifying factor of 5 times is the same for all spectra.