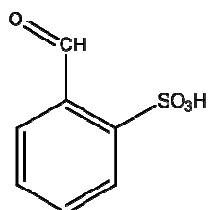


Supplementary information:  
Selective Covalent Bond Formation in Polypeptide Ions via Gas-Phase Ion/Ion Reaction  
Chemistry by Han and McLuckey

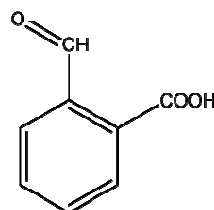
Reference 3(b): Ross, P.L.; Huang, Y.L.N.; Marchese, J.N.; Williamson, B.; Parker, K.; Hattan, S.; Khainovski, N.; Pillai, S.; Dey, S.; Daniels, S.; Purkayastha, S.; Juhasz, P.; Martin, S.; Bartlet-Jones, M.; He, F.; Jacobson, A.; Pappin, D.J. *Mol. and Cell. Proteomics*, **2004**, 3, 1154-1169.

Supplementary information Scheme 1: Other examined reagents.



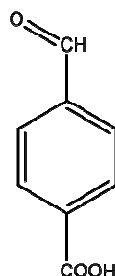
(a)

**2-formyl-benzenesulfonic acid**



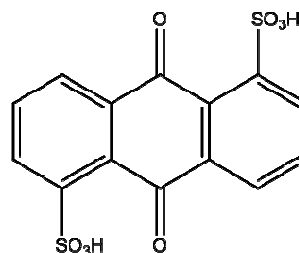
(b)

**2-formyl-benzoic acid**



(c)

**4-formyl-benzoic acid**



(d)

**Anthraquinone-1,5-disulfonic acid**

Deprotonated forms of the reagents a)-d) were also examined with triply protonated RGAGGKGAGGRL. Deprotonated a) showed evidence for Schiff base formation but a lesser degree of adduct formation than deprotonated 4-formyl-1,3-benzenedisulfonic acid. Deprotonated forms of reagents b)-d) showed exclusive proton transfer.

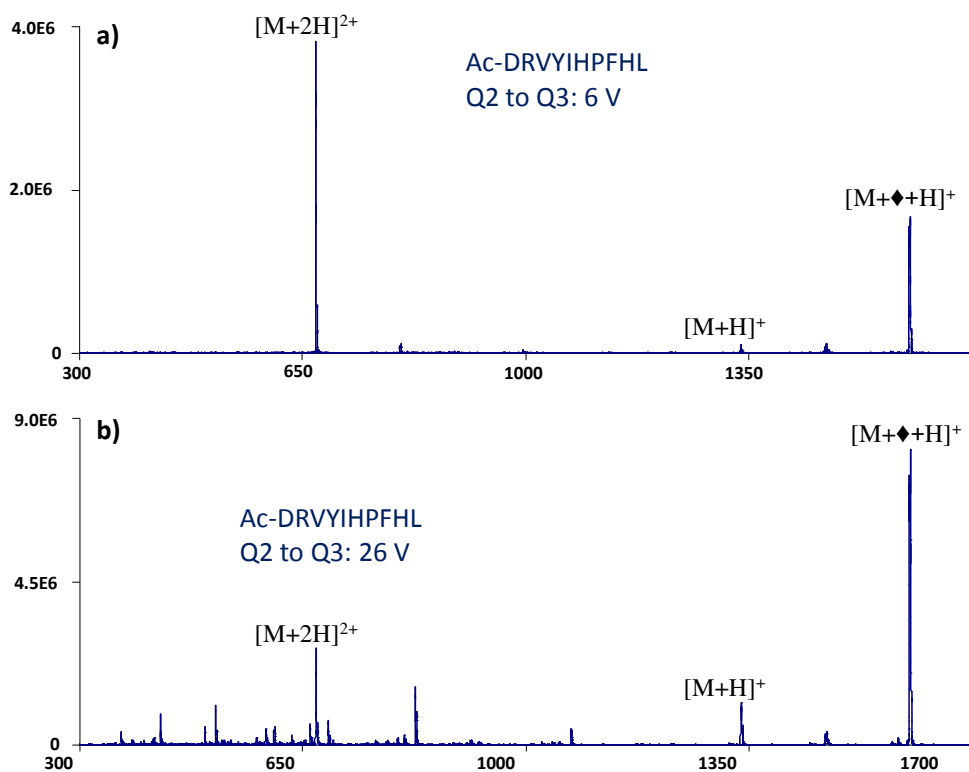


Figure S1 – a) Post-ion/ion reaction spectrum following reaction of deprotonated 4-formyl-1,3-benzenedisulfonic acid with doubly protonated N-terminally acetylated angiotensin and transfer to the analyzer quadrupole with a voltage difference of 6 V. b) Same as in a) except the transfer voltage was 26 V.

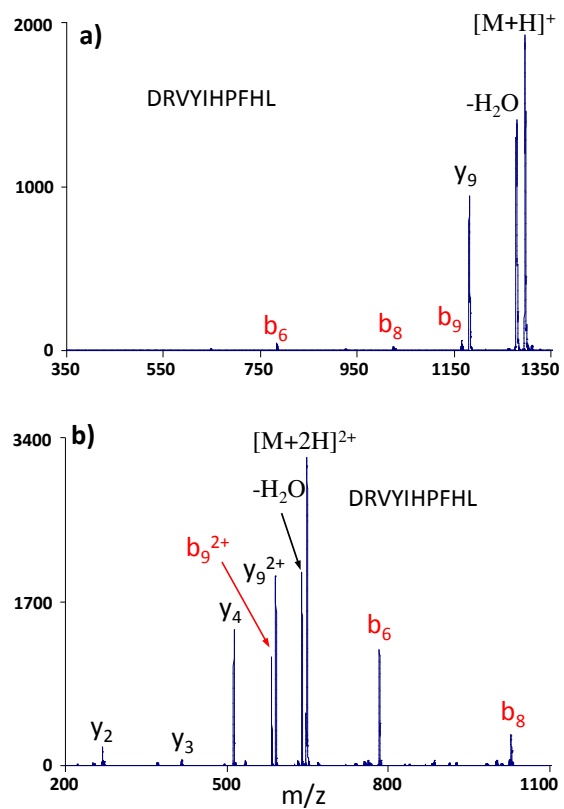


Figure S2 – Ion trap CID product ion spectra of a) singly- and b) doubly-protonated angiotensin I.