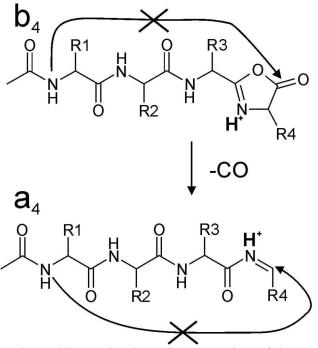
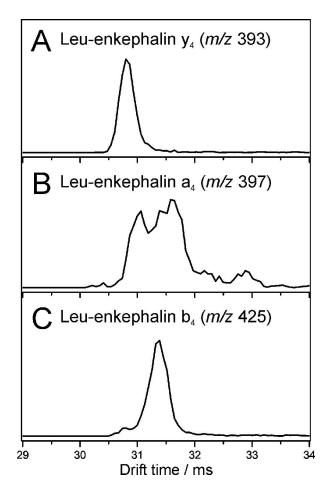
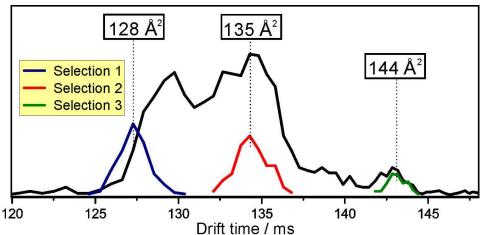
## On the dynamics of fragment isomerization in collision-induced dissociation of peptides



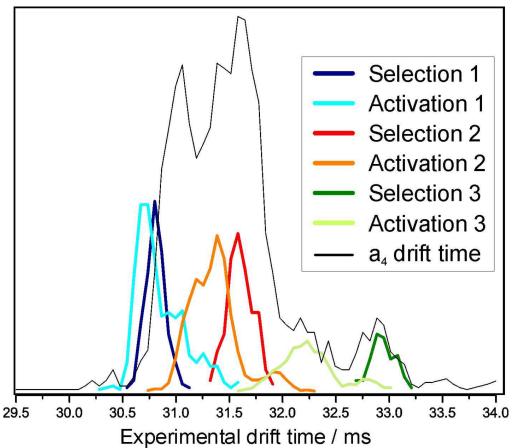
Scheme S1. Reaction scheme illustrating how the protection of the N-terminus with an acetyl group prevents formation of cyclic structures for  $b_4$  and  $a_4$ . The favored sites of proton attachment are indicated.



**Figure S2**. Drift time distributions of the most abundant CID fragment ions of protonated Leu-enkephalin: (A) y<sub>4</sub>, (B) a<sub>4</sub> and (C) b<sub>4</sub>. (230 V activation energy)



**Figure S3**. Drift time distributions for  $a_4$  (same as Fig S2 B) and for mobility selections of  $a_4$  at the end of the second drift tube. The experimentally derived collision cross sections are indicated. Note that the intensities of the mobility selections are multiplied by a factor of 20.



**Figure S4**. Drift time distributions of mobility-selected ions prior to and after collisional activation. The drift time distribution of the whole  $a_4$  distribution is indicated with a fine line as a reference.