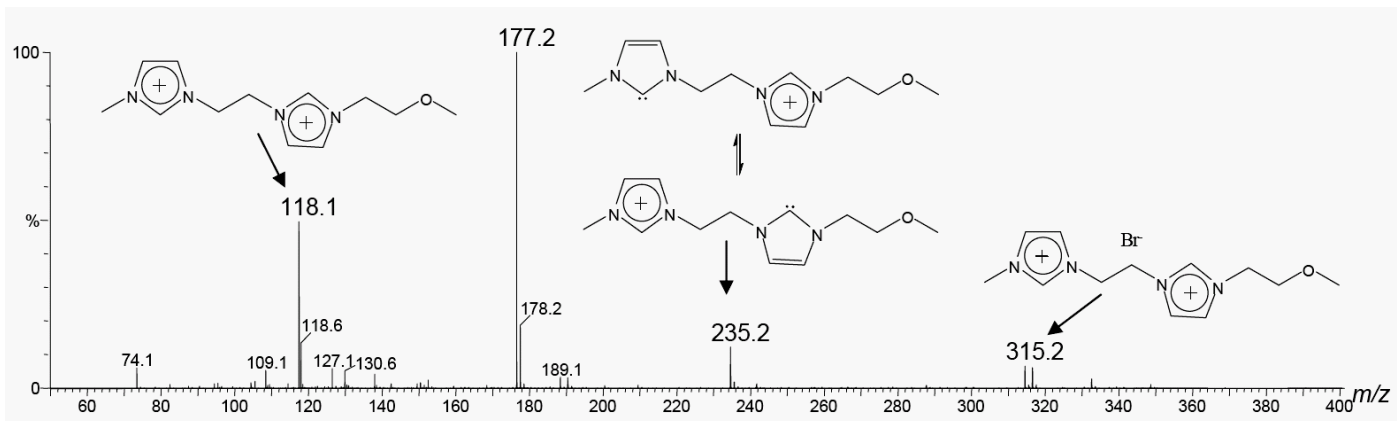


## Charge-Tagged *N*-Heterocyclic Carbenes

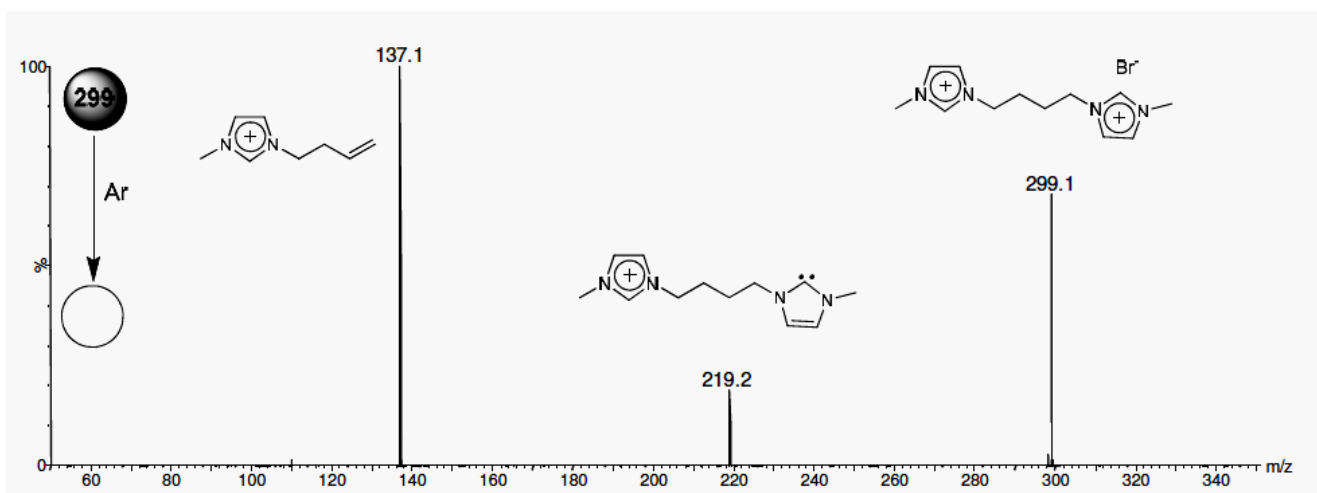
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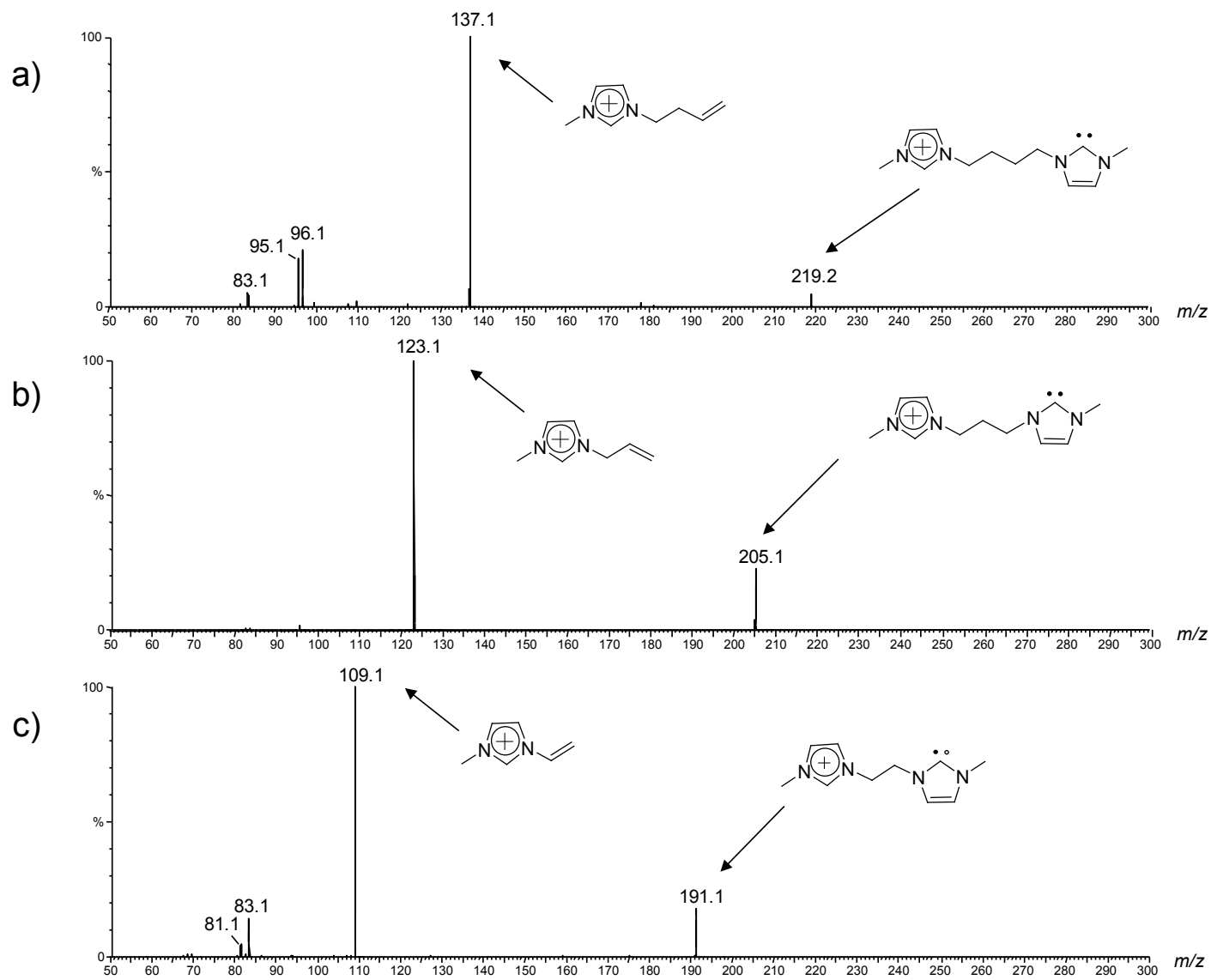
Supplementary Material



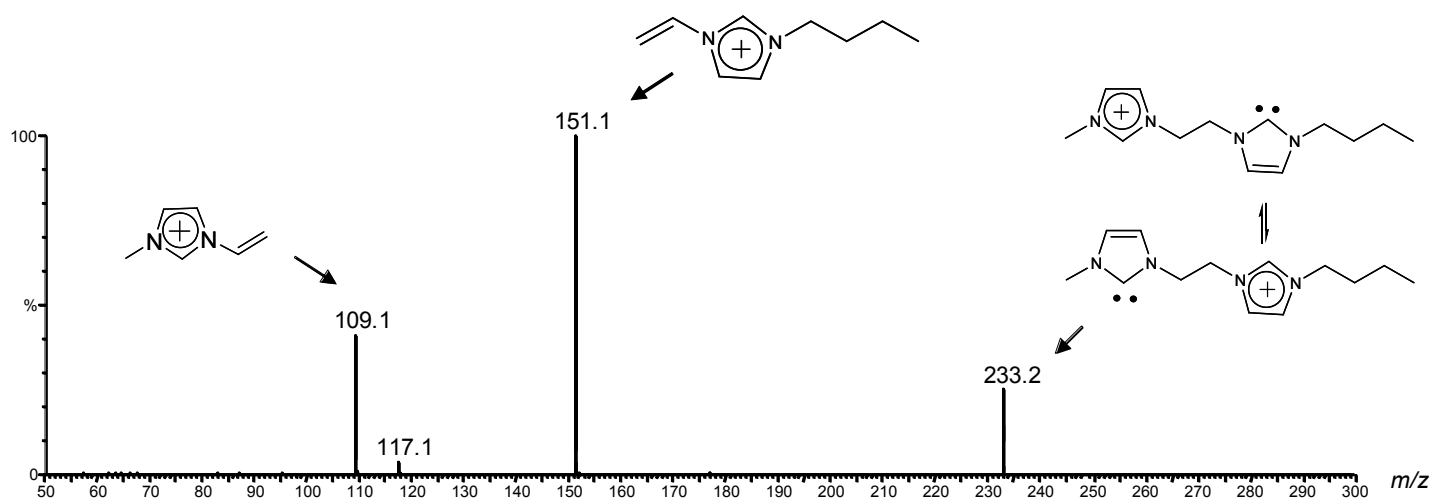
**Figure S1** - ESI(+)-MS of a methanolic solution of **3f**.Br<sub>2</sub>. Note the detection of the doubly charged imidazolium ion **3f**<sup>2+</sup> of *m/z* 118.1 (as well as the isotopologue ion of *m/z* 118.6) and the singly charged [3f.Br]<sup>+</sup> of *m/z* 313/315, and the unprecedented charge-tagged carbene **4f**<sup>+</sup> of *m/z* 219 directly sampled from solution (or formed via in-source CID of [3f.Br]<sup>+</sup>).



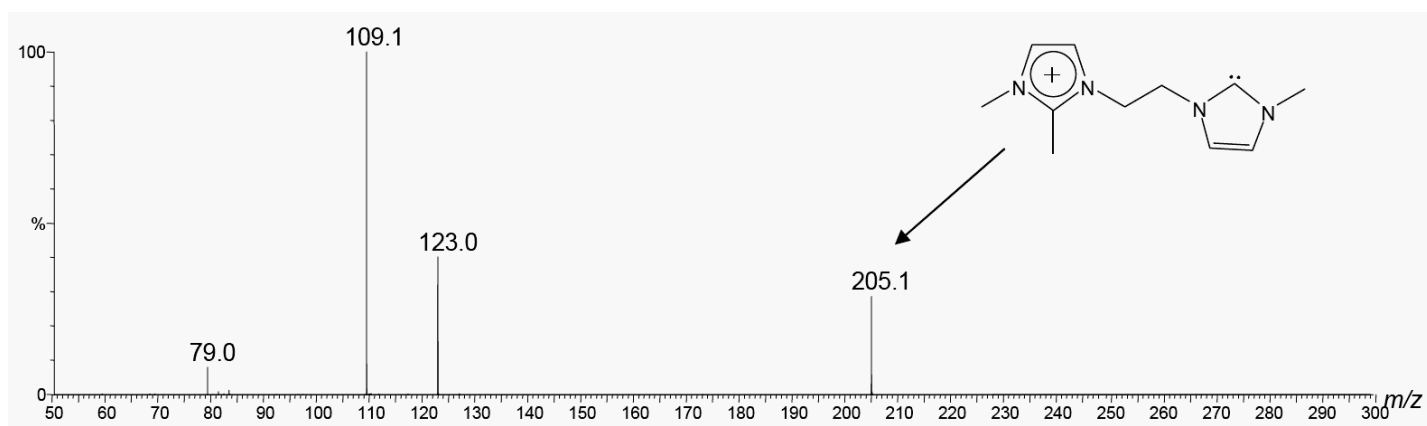
**Figure S2** – ESI(+)-MS/MS of  $[3a.Br]^+$  of  $m/z$  299.



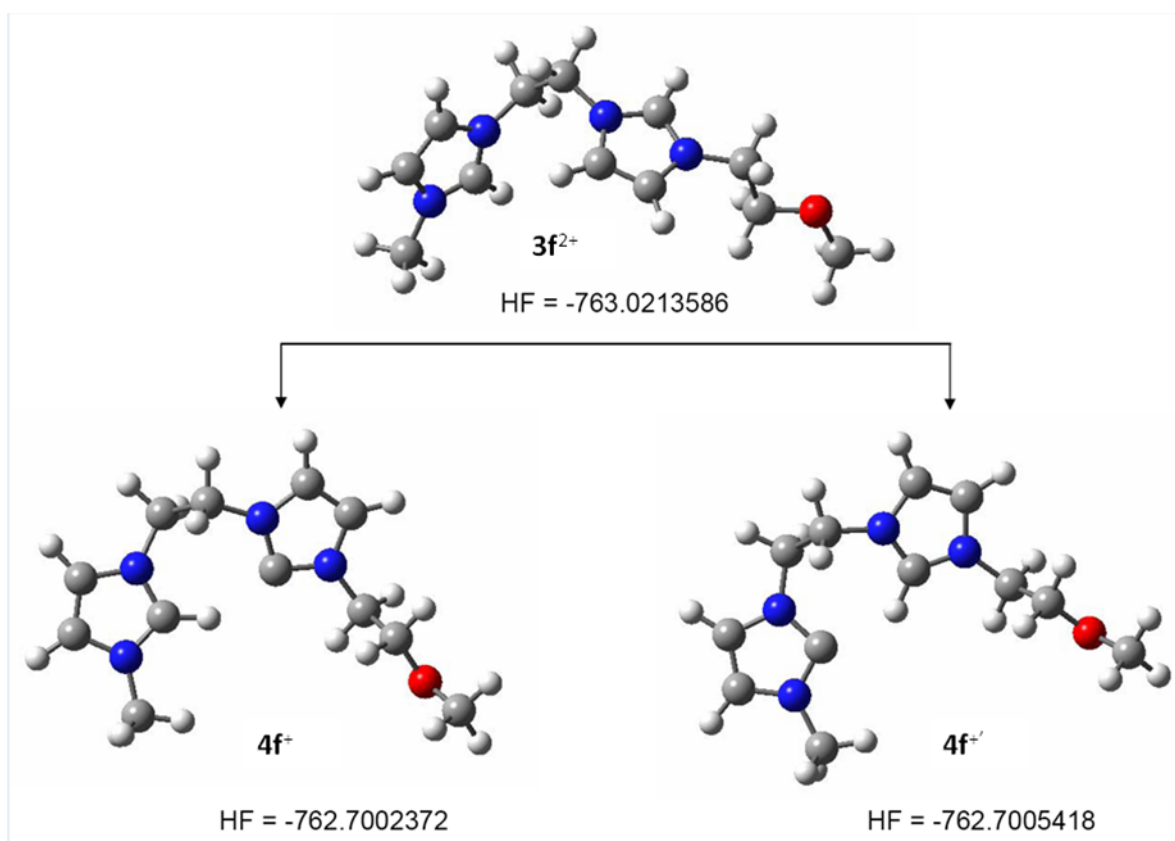
**Figure S3** – ESI(+)-MS/MS for the charge-tagged carbenes a) **4a**<sup>+</sup> of  $m/z$  219 b) **4b**<sup>+</sup> of  $m/z$  205 and c) **4c**<sup>+</sup> of  $m/z$  191.



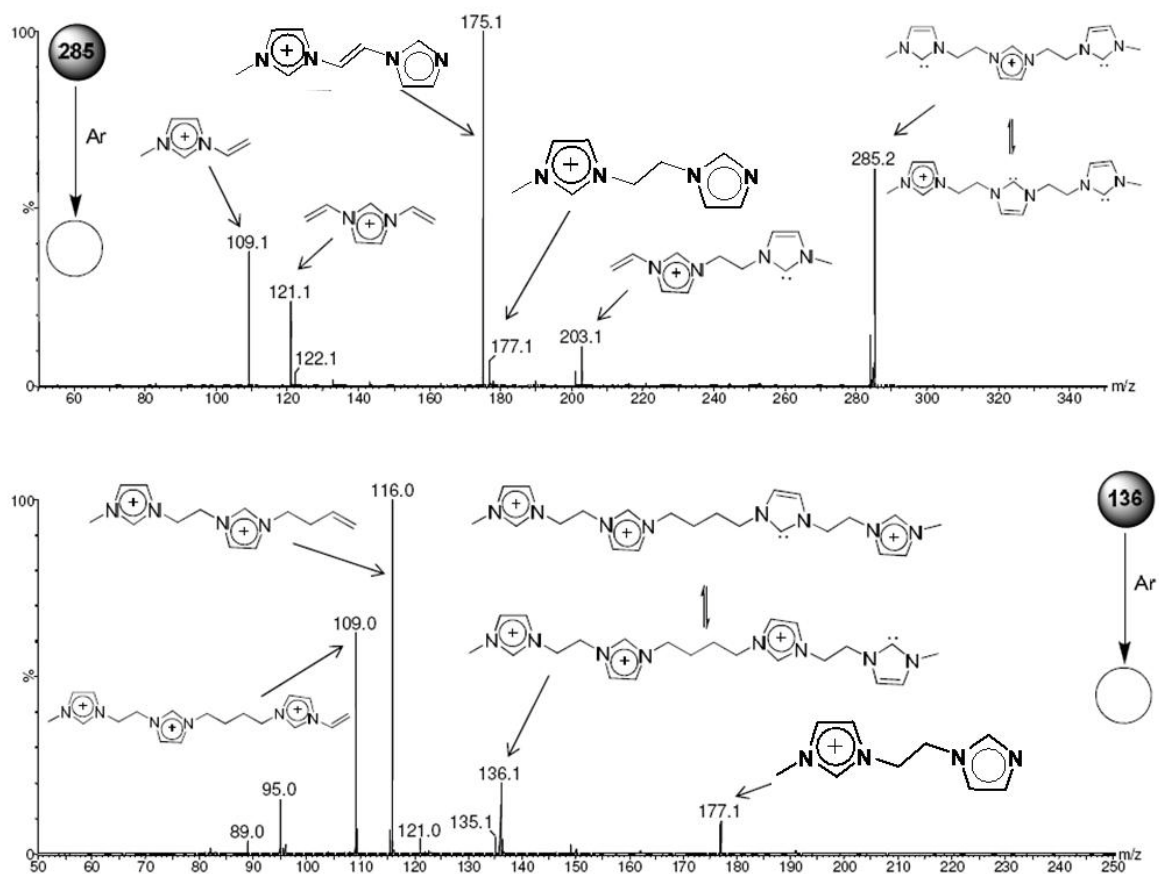
**Figure S4** - ESI(+)-MS/MS of the asymmetric charge-tagged carbene **4e<sup>+</sup>** of *m/z* 233.



**Figure S5** – ESI(+)-MS/MS for the charge-tagged carbene **4d**<sup>+</sup> of *m/z* 205.

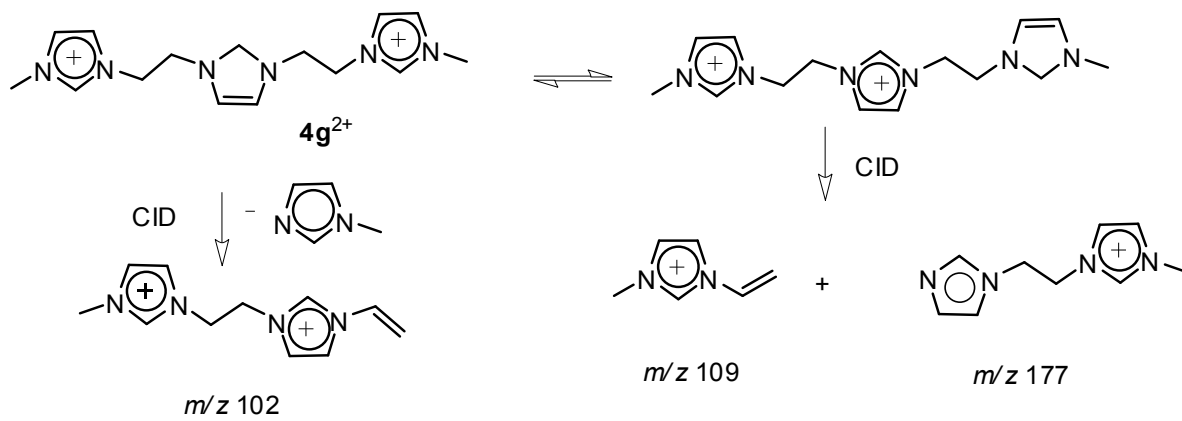


**Figure S6.** Beck3LYP 6-31G+(d,p) energies (HF energies in hartrees) and optimized structures for the isomeric  $4f^+$  and  $4f^{+'}$ .



**Figure S7** – ESI(+)-MS/MS of a) the singly charged di-carbene **4h**<sup>+</sup> of *m/z* 285 and b) the triply charged mono-carbene **4j**<sup>3+</sup> of *m/z* 136.





**Scheme S1**