Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

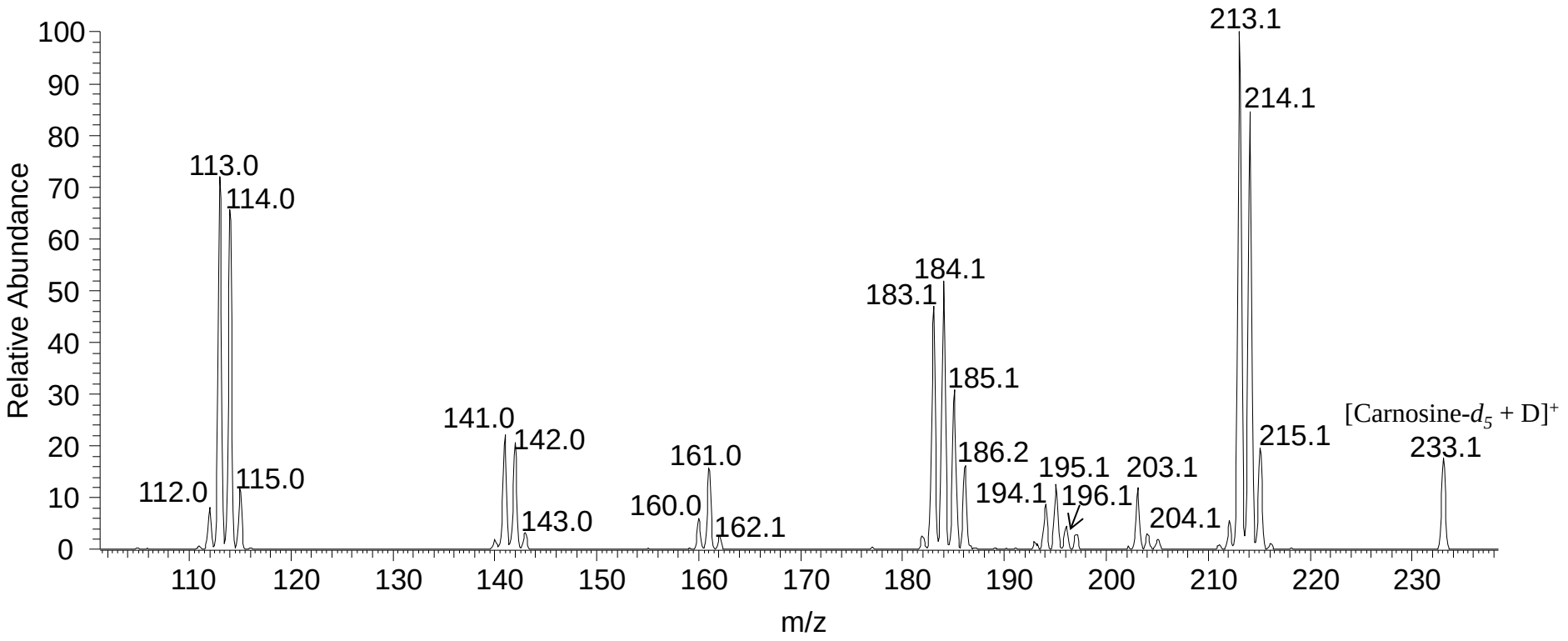

Figure S1: MS^2 spectrum of the ion [Carnosine-d_5 + D]$^+$ generated at 25 eV in the lab frame produced from a 1mM of Carnosine in a (1:1) (v/v) D_2O/MeOD solution without allowing for incubation time.

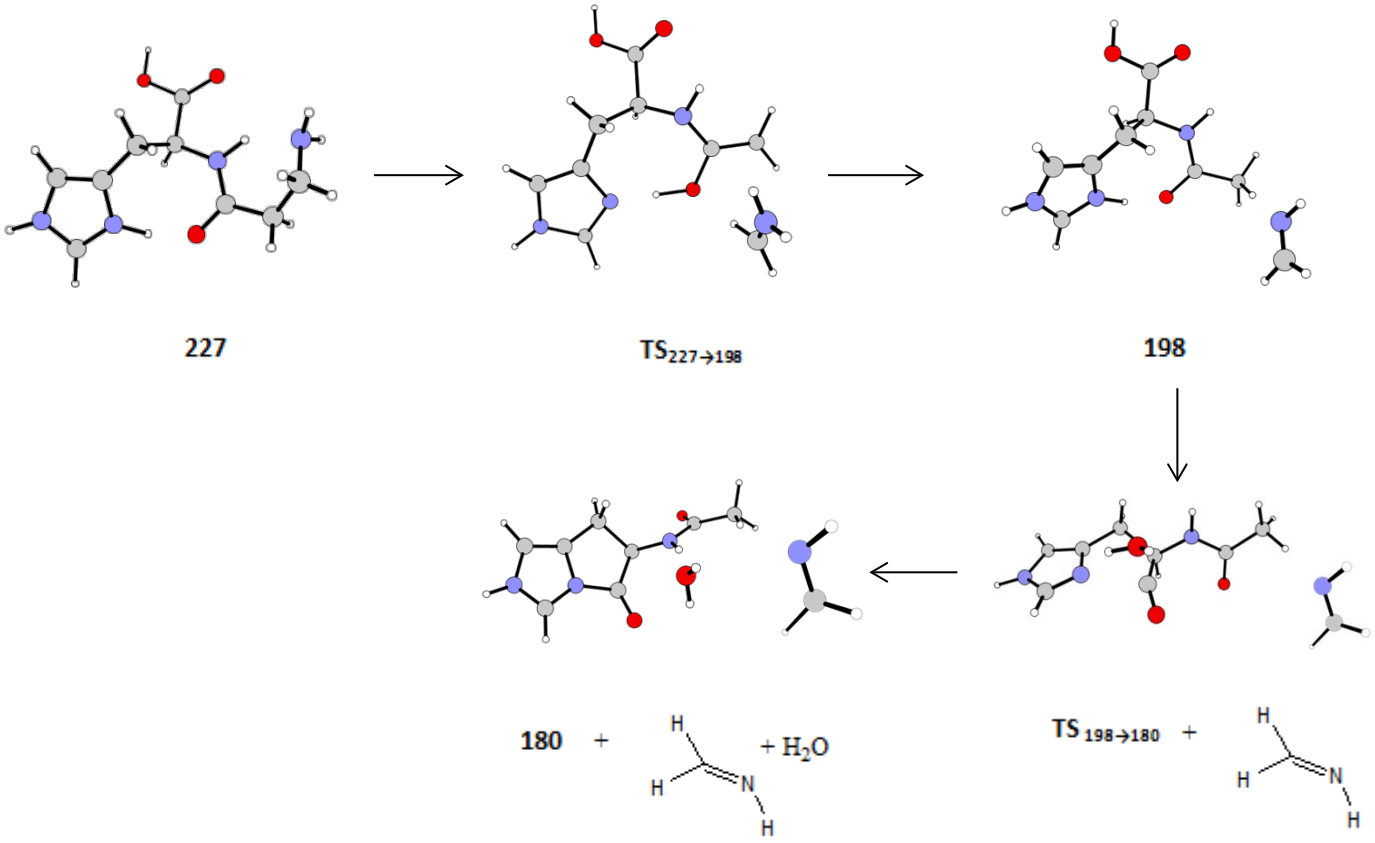

Figure S2: Proposed mechanism for the collision induced fragmentation of [Carnosine + H]$^+$ to produce the fragments observed at m/z 198 and 180. Gaussian output files from the B3LYP/6-311++G(d,p) calculations are depicted. The colors grey, white, red and blue refer to carbon, hydrogen, oxygen and nitrogen atoms respectively

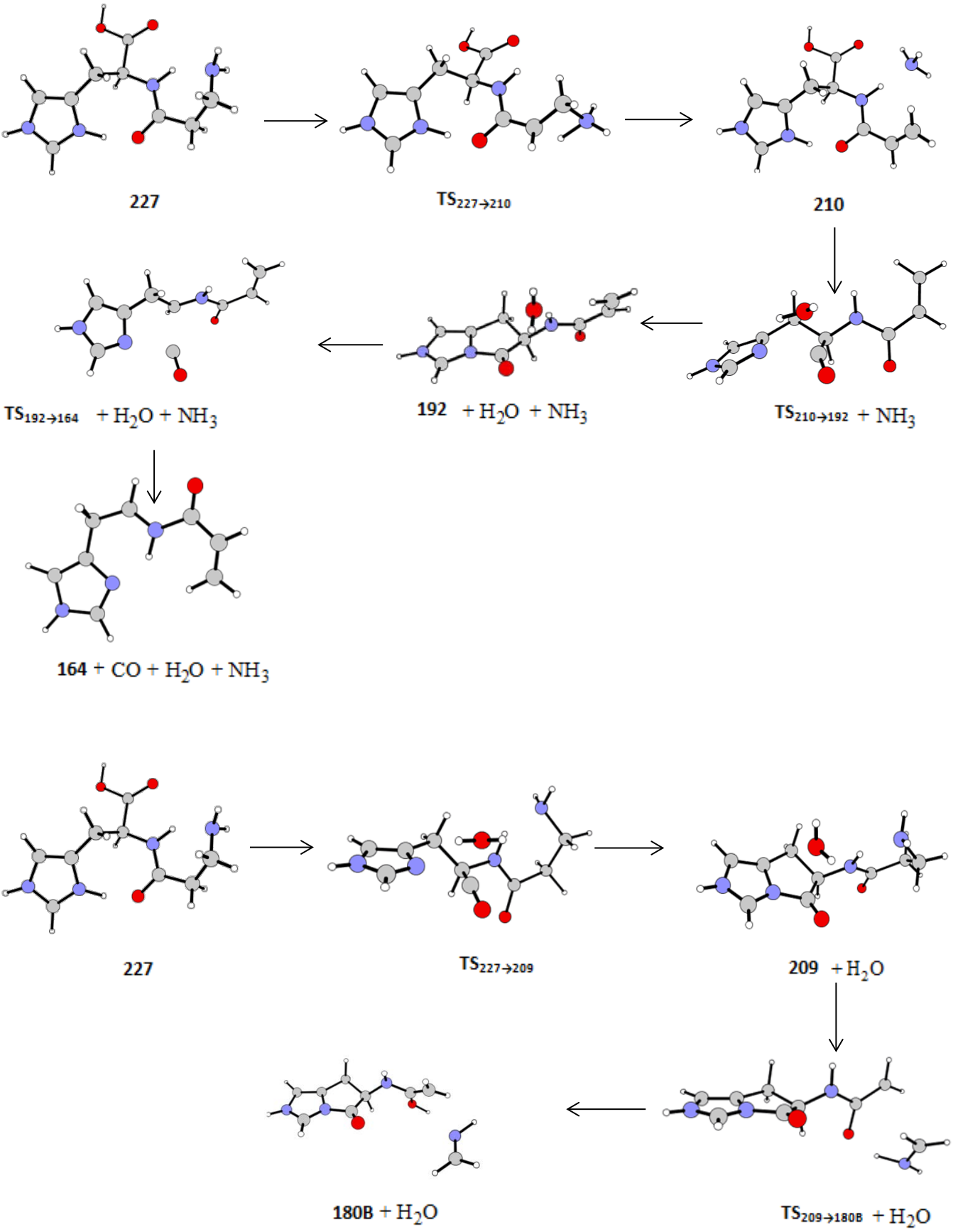

Figure S3: Proposed mechanism for the collision induced fragmentation of [Carnosine + H]$^+$ to produce the fragments observed at m/z 210, 192 and 164. Gaussian output files from the B3LYP/6-311++G(d,p) calculations are depicted. The colors grey, white, red and blue refer to carbon, hydrogen, oxygen and nitrogen atoms respectively.

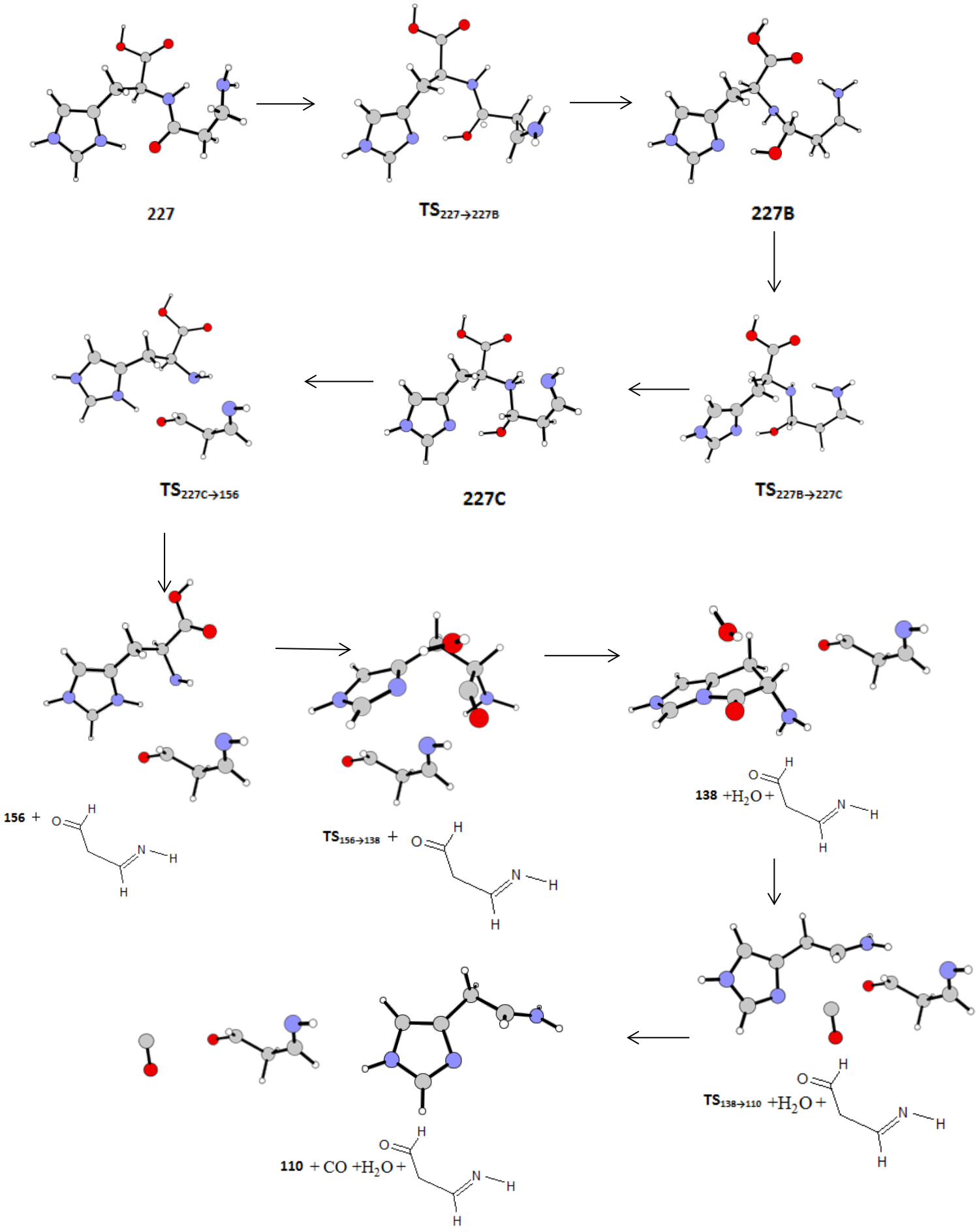

Figure S4: Proposed mechanism for the collision induced fragmentation of [Carnosine + H]$^+$ to produce the fragment ion observed at m/z 156, 138 and 110. Gaussian output files from the B3LYP/6-311++G(d,p) calculations are depicted. The colors grey, white, red and blue refer to carbon, hydrogen, oxygen and nitrogen atoms respectively

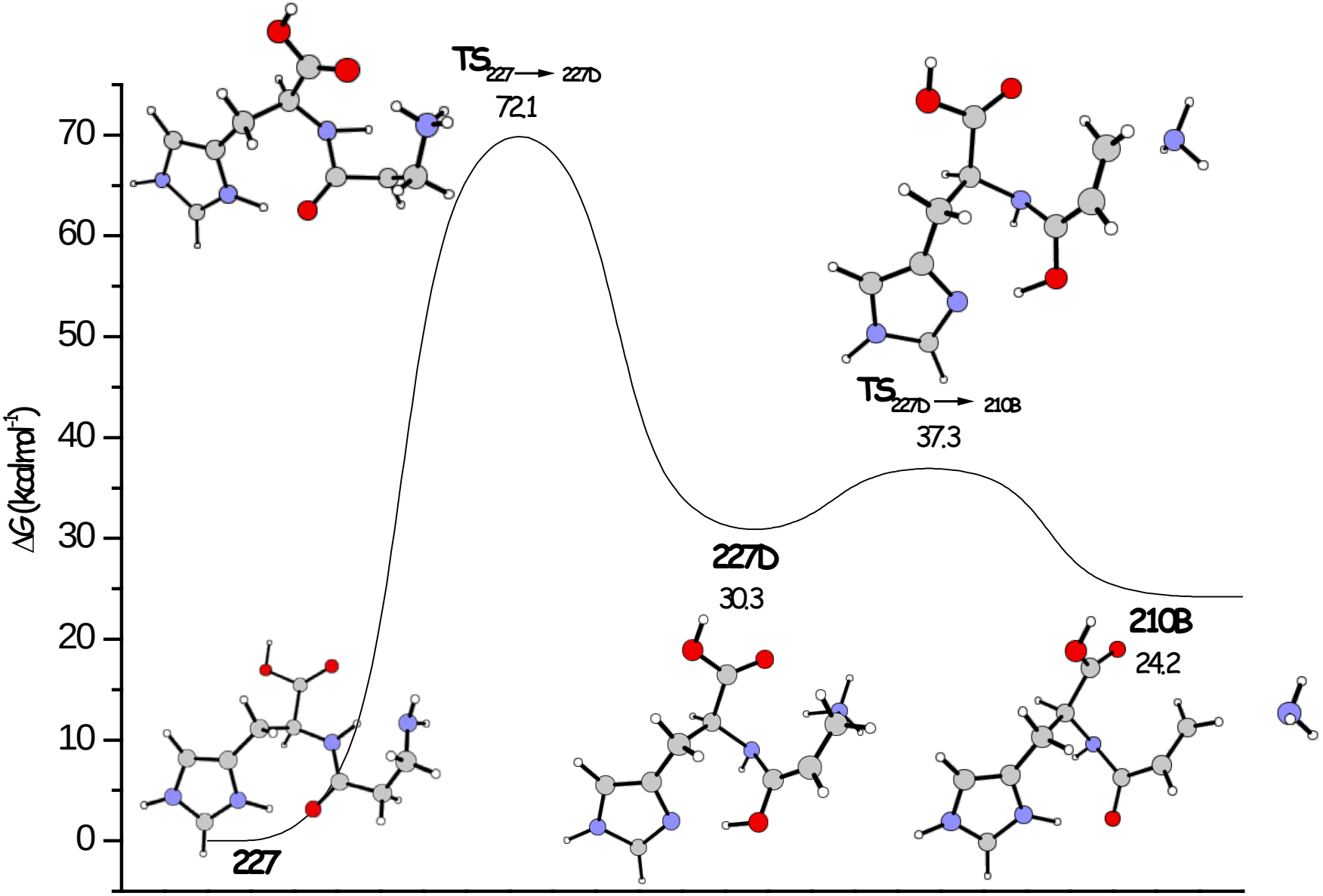

Figure S5: B3LYP free energy profile for an alternative fragmentation mechanism of [Carnosine + H]$^+$ to give the ion at m/z 210. Relative free energies at 298 K are in kcal mol^{-1} and calculated with respect to the most stable conformer, **227**, of protonated carnosine.

Table S1: Electronic energies, Zero-Point Vibrational Energies, Thermal Energies, Entropies and relative free energies for species calculated at B3LYP\6-311++G(d,p).

Structure	Electronic energy (Hartrees)	ZPE (kcal mol^{-1})	$\mathbf{H^o_{298} - H^o_0}$ (kcal mol^{-1})	Entropy (cal mol^{-1} K^{-1})	Relative free energy at 298 K (kcal mol^{-1})
227	-796.7420143	161.7	10.2	127.3	0.0
TS227to198	-796.6543187	158.7	11.1	137.9	49.7
198	-796.7143147	158.0	12.0	149.2	8.8
TS198to180	-796.6280855	154.1	12.1	177.0	51.0
180	-796.66763	155.0	12.6	184.7	25.2

Table S2: Electronic energies, Zero-Point Vibrational Energies, Thermal Energies, Entropies and relative free energies for species calculated at B3LYP\6-311++G(d,p).

Structure	Electronic energy (Hartrees)	ZPE (kcal mol^{-1})	$\mathbf{H^o_{298} - H^o_0}$ (kcal mol^{-1})	Entropy (cal mol^{-1} K^{-1})	Relative free energy at 298 K (kcal mol^{-1})
227	-796.7420143	161.7	10.2	127.3	0.0
TS227to210	-796.6614534	157.9	10.1	125.2	47.1
210	-796.7265001	158.9	11.6	138.3	5.0
TS210to192	-796.6353449	154.1	12.5	170.4	48.7
192	-796.6738943	154.9	12.9	177.3	23.7
TS192to164	-796.609968	150.4	13.8	210.7	50.3
164	-796.6354981	148.7	14.5	245.6	22.7

Table S3: Electronic energies, Zero-Point Vibrational Energies, Thermal Energies, Entropies and relative free energies for species calculated at B3LYP\6-311++G(d,p).

Structure	Electronic energy (Hartrees)	ZPE (kcal mol^{-1})	$\mathbf{H_{298}^{o} - H_{0}^{o}}$ (kcal mol^{-1})	Entropy (cal mol^{-1} K^{-1})	Relative free energy at 298 K (kcal mol^{-1})
227	-796.7420143	161.7	10.2	127.3	0.0
TS227to209	-796.6678158	158.8	10.9	131.6	43.0
209	-796.6678158	159.5	11.6	138.2	20.7
TS209to180B	-796.6099956	152.8	11.9	167.2	63.6
180B	-796.6090982	153.2	12.6	207.4	53.4

Table S4: Electronic energies, Zero-Point Vibrational Energies, Thermal Energies, Entropies and relative free energies for species calculated at B3LYP\6-311++G(d,p).

Structure	Electronic energy (Hartrees)	ZPE (kcal mol^{-1})	$\mathbf{H^o_{298} - H^o_0}$ (kcal mol^{-1})	Entropy (cal mol^{-1} K^{-1})	Relative free energy at 298 K (kcal mol^{-1})
227	-796.7420143	161.7	10.2	127.3	0.0
TS227to227B	-796.6448864	158.3	10.1	126.2	57.7
227B	-796.6970513	161.4	10.1	126.4	28.1
TS227Bto227C	-796.6891332	158.4	10.9	130.9	31.4
227C	-796.6993917	162.4	10.1	125.4	27.8
TS227Cto156	-796.680308	158.9	10.2	127.0	36.0
156	-796.6731828	158.2	11.0	175.0	26.1
TS156to138	-796.6063602	154.8	11.5	176.3	64.9
138	-796.6414835	155.4	12.3	184.6	41.7
TS138to110	-796.590918	151.6	12.8	214.8	61.2
110	-796.619971	149.7	13.6	251.1	30.8