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

Supporting Information for the article:

Tandem mass spectrometry and infrared spectroscopy as a help to identify peptide oxidized residues

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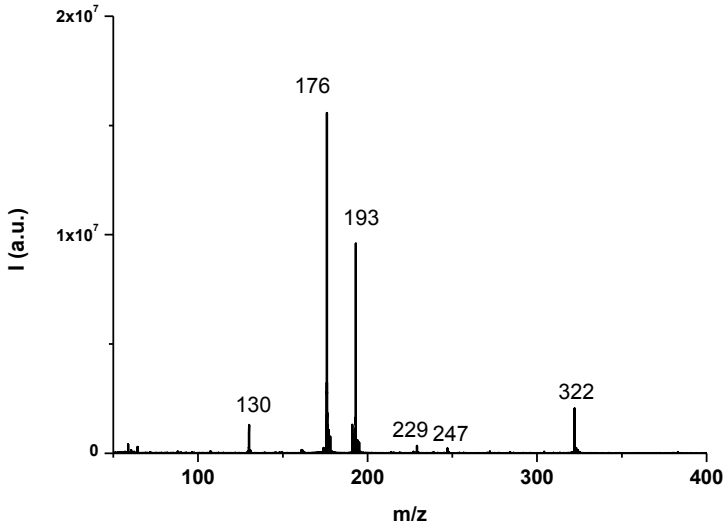

Figure 1SI: CID-MS^2 fragmentation mass spectrum of (GS-Me)H^+ (*m/z* 322).

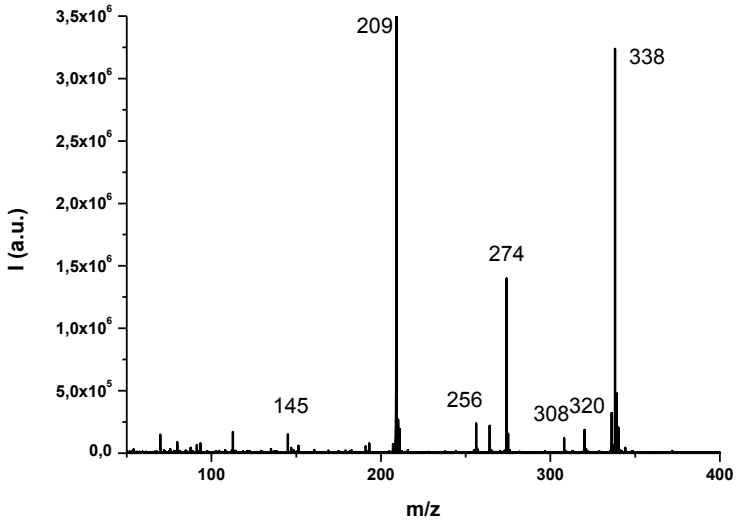

Figure 2SI: CID-MS^2 fragmentation mass spectrum of GS-Me(O)H^+ (*m/z* 338).

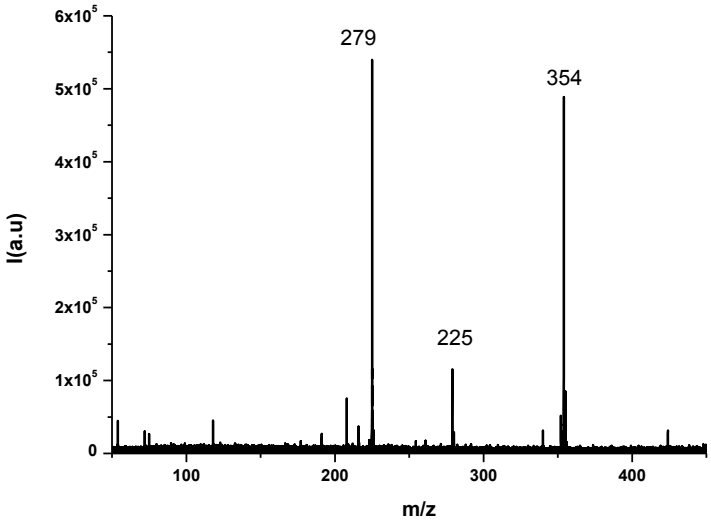

Figure 3SI: CID-MS^2 fragmentation mass spectrum of GS-$Me(O)_2H^+$ (*m/z* 354).

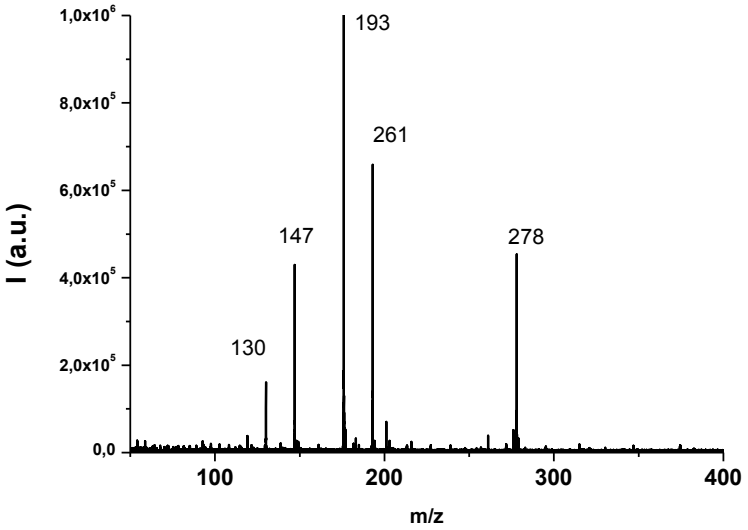

Figure 4SI: CID-MS^2 fragmentation mass spectrum of (GS-Me)H^+-CO_2 (*m/z* 278).

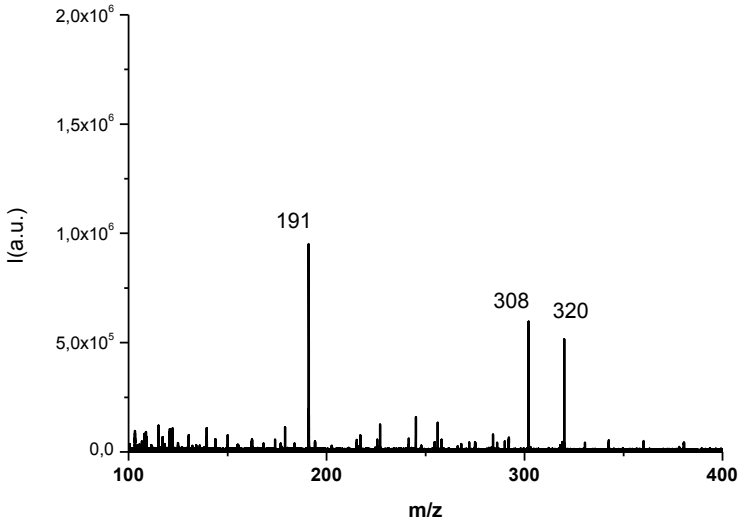

Figure 5 SI: CID-MS^2 fragmentation mass spectrum of (GS-Me)H^+-H_2 (*m/z* 320).

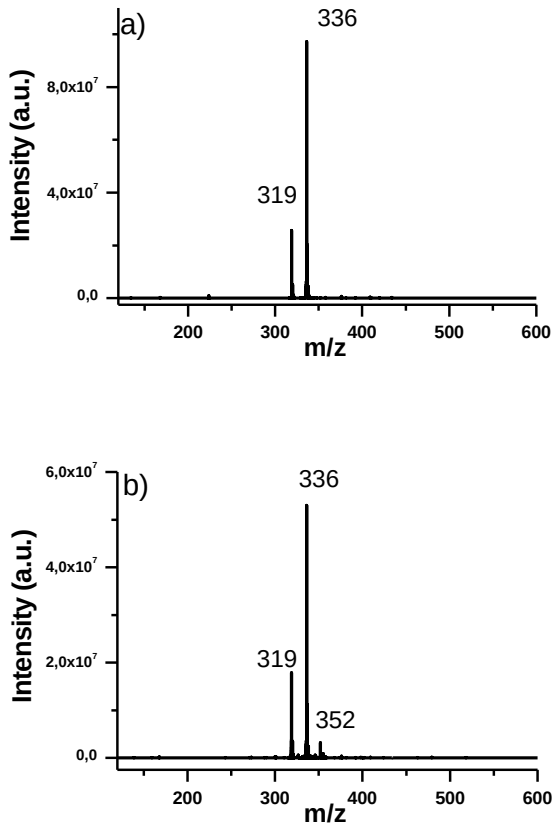

Figure 6SI: Mass spectra of non-irradiated **(a)** and irradiated Trp-Met **(b)** (irradiation dose 800 Gy).

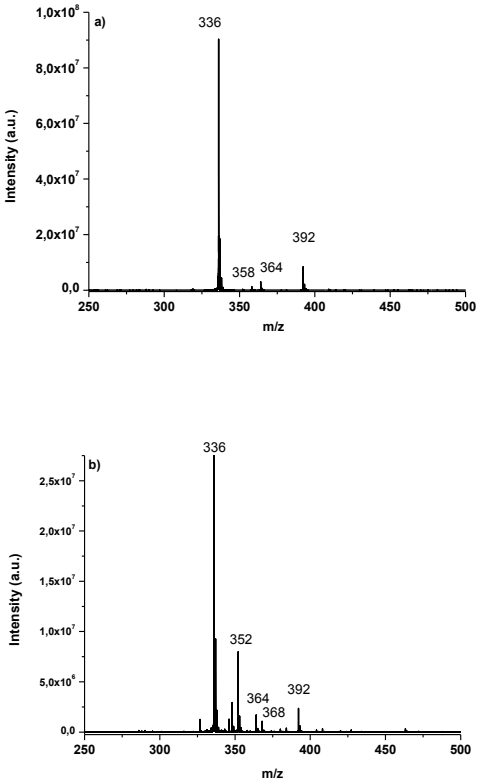

Figure 7SI: Mass spectra of non-irradiated **(a)** and irradiated Met-Trp **(b)** (irradiation dose 900 Gy).

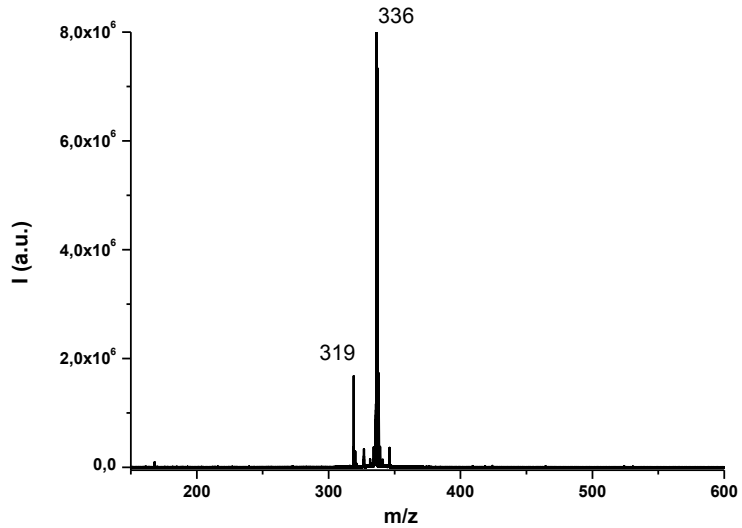

Figure 8SI: CID-MS^2 fragmentation mass spectrum $(Trp\text{-}Met)H^+$ (m/z 336).

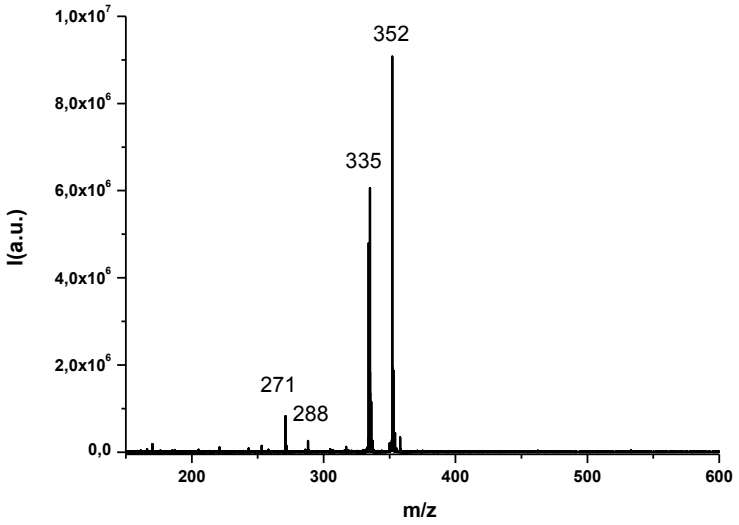

Figure 9SI: CID-MS^2 fragmentation mass spectrum of (Trp-Met)O_2H^+ (*m/z* 352).

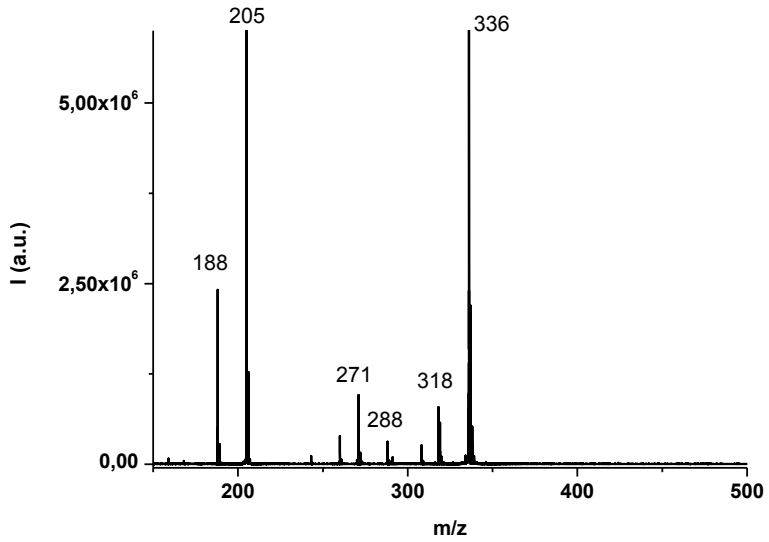

Figure 10SI: CID-MS^2 fragmentation mass spectrum of (Met-Trp)H^+ (*m/z* 336).

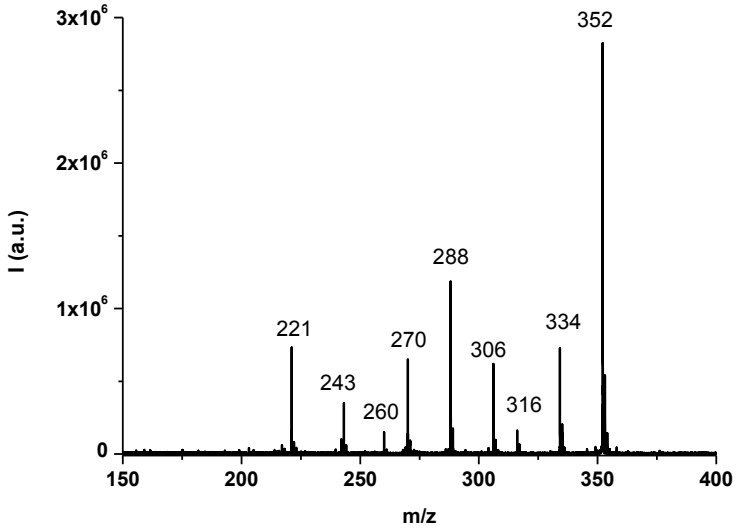

Figure 11SI: CID-MS^2 fragmentation mass spectrum of (Met-Trp)OH^+ (*m/z* 352).

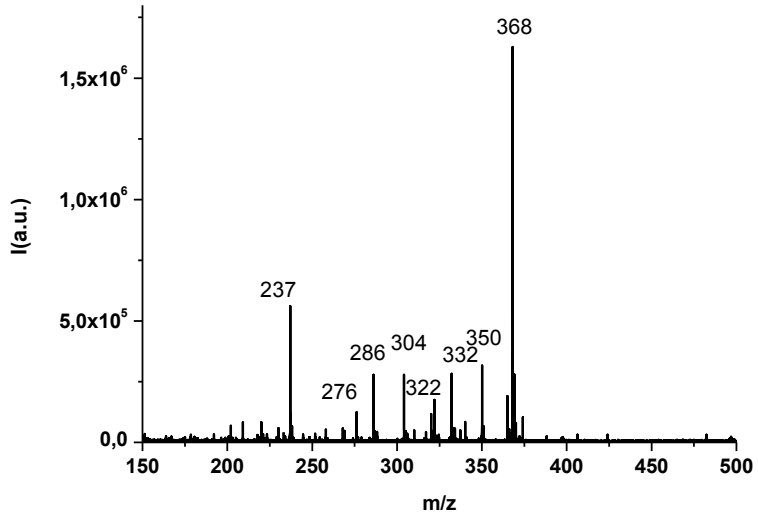

Figure 12SI: CID-MS^2 fragmentation mass spectrum of (Met-Trp)O_2H^+ (*m/z* 368).

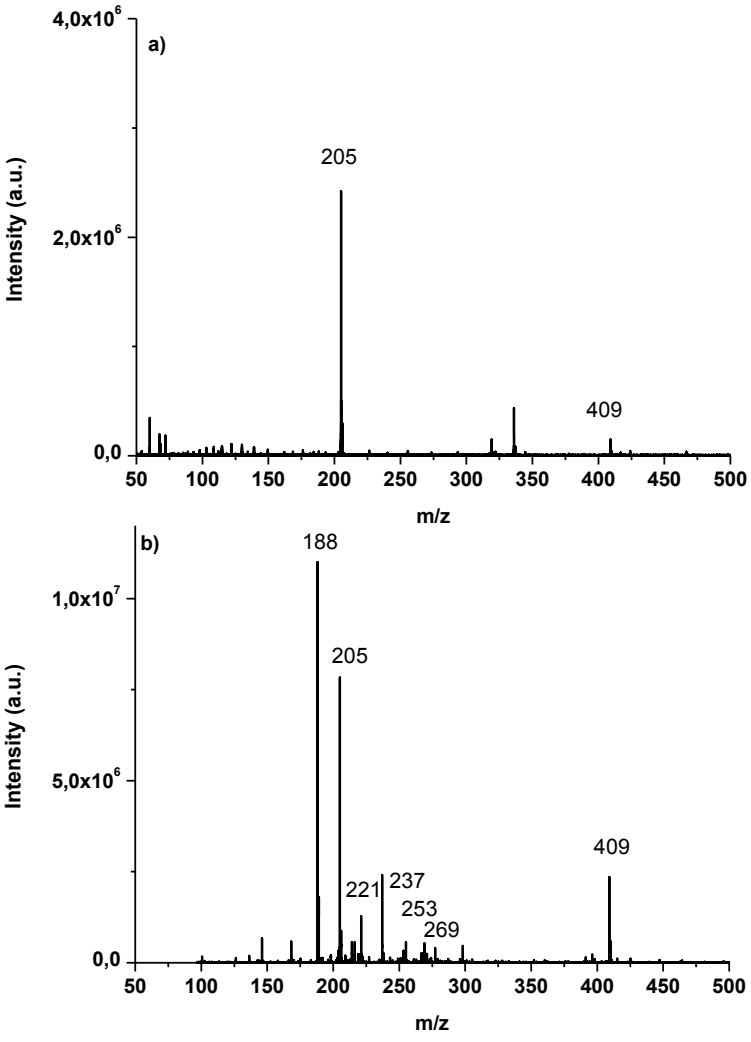

Figure 13SI: Mass spectrum of non-irradiated **(a)** and irradiated **(b)** Trp (irradiation dose 900 Gy).

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Compound	m/z, z=+1
(GS-Me)H^+-CO_2	278 (parent ion)
	261 (-NH_3)
	193(y2)
	147 (y2-H_2O-CO)
	130 (y2-H_2O-CO-NH_3)
(GS-Me)H^+-H2	320 (parent ion)
	308 (-H_2O)
	191 (y2)
(GS-Me)H^+	322 (parent ion)
	247(b2)
	229 (b_2-H_2O)
	193(y2)
	176 (y2-NH_3)
	130 (b1 ou y2-17-H_2O-CO)
(GS-Me)OH^+	338(parent ion)
	320(-H_2O)
	274(-CH_3SHO)
	256(-H2O-CH_3SOH)
	209 (y2)
	145 (y2-CH_3SOH)
(GS-Me)O_2H^+	354 (parent ion)
	279 (b2)
	225 (y2)
	208 (y2- NH_3)
	130 (b1)

Table 1SI. Most intense peaks in the CID-MS^2 fragmentation mass spectra of the products of GS-Me.

Compound	m/z, z=+1
(Trp-Met)H+	336 (parent ion)
	319 (Trp-Met)H^+-NH_3
(Trp-Met)OH+	352 (parent ion)
	335 (Trp-Met)OH^+-NH_3
	288 (Met-Trp)OH^+-CH_3SOH
	271 (Met-Trp)OH^+-NH_3-CH_3SOH

Table 2SI. Most intense peaks observed in the CID-MS^2 fragmentation mass spectra of the products of oxidation of Trp-Met.

Compound	m/z, z=+1
(Met-Trp)H+	336 (parent ion)
	318 (Met-Trp)H^+-H_2O
	288 (Met-Trp)H^+-CH_3SH
	271 (Met-Trp)H^+-NH_3
	205 (y)
	188 (y-NH_3)
(Met-Trp)OH+	352 (parent ion)
	334 (Met-Trp)OH^+-H_2O
	316 (Met-Trp)OH^+-$2H_2O$
	306 (Met-Trp)OH^+-H_2O-CO
	288 (Met-Trp)OH^+-CH_3SOH
	270 (Met-Trp)OH^+-H_2O -CH_3SOH
	243 (Met-Trp)OH^+-H_2O -CH_3SOH-NH_3
	221 (y)
(Met-Trp)O_2H+	368 (parent ion)
	350 (Trp-Met)O_2H^+-H_2O
	332 (Trp-Met)OH^+-$2H_2O$
	304 (Trp-Met)O_2H^+-CH_3SOH
	286 (Trp-Met)OH^+-CH_3SOH-H_2O
	276 (Trp-Met)OH^+-CH_3SOH-CO
	237 yO_2

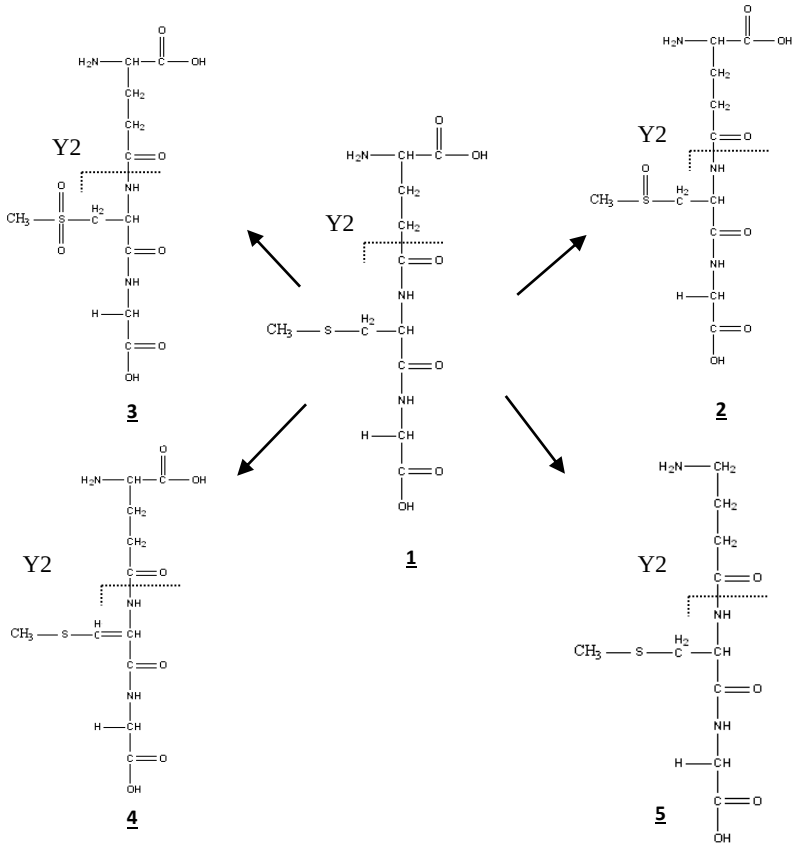
Table 3SI. Most intense peaks observed in the CID-MS^2 fragmentation mass spectra of the products of oxidation of Met-Trp.

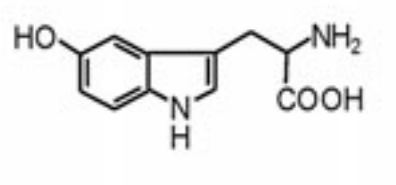
m/z, z=+1	***compound***
237	$(Trp)O_2H^+$
220	$(Trp)O_2H^+$-NH_3
219	$(Trp)O_2H^+$-H_2O
202	$(Trp)O_2H^+$-NH_3-H_2O
192	$(Trp)O_2H^+$ -NH_3-CO
174	$(Trp)O_2H^+$ -NH_3-CO-H_2O

Table 4SI: Most intense peaks observed in the CID-MS^2 fragmentation mass spectrum of ions at *m/z* 237 and their attribution.

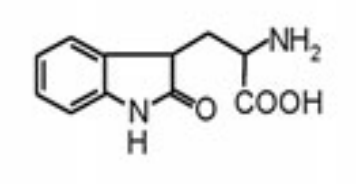
Scheme 1SI: Schematic representation of y2 fragments for each oxidation product of GS-Me according the Roepstorff-Fohlman nomenclature.

b)





a)



b)

Scheme 2SI: Structures of 5hydroxytrypthophan **(a)** and oxindolylalanine **(b)** corresponding to the addition of an oxygen atom to the tryptophan.