

Table S1. Identification of the proteins in the sample from the Cimitero Monumentale of Pisa by overnight trypsin digestion in heterogeneous phase and LCMSMS analysis^a. Proteins were identified searching UniprotSprot database, with *Chordata* as taxonomy restriction, with MSMS Ion search Mascot software (Matrix Science). Only identification of proteins with at least two peptides were considered as significative.

Identified protein (Accession number)	Total score ^a	Sequence coverage (%)	Matched sequence (individual peptide scores) (Only oxidation of methionine, hydroxylation of proline and lysine, pyro-Glu formation at Gln at the N-terminus of peptides were inserted as variable modifications in the MSMS Ion Search Program).
Beta-casein precursor (P02666)	1689	75	EMPFPK (33) VLPVPQK (31) AVPYPQR (12) VLPVPQKAVPYPQR (27) FQSEEQQTEDELQDK (83) DMPIQAFLLYQEPVLGPVR (117) DMPIQAFLLYQEPVLGPVRGPFPIIV (53) AVPYPQRDMPIQAFLLYQEPVLGPVR (53) IHPFAQTQSLVYPFGPIPNSLPQNIPPLTQTPVVVPPFLQPEVMGVSK (77) YPVEPFTESQSLTLTDVENLHLPLLLQSWMHQPHQPLPPTVMFPPQSVLSLSQSK (68)
Casein alpha-S1 (P02662)	1464	50	TTMPLW (19) EDVPSER (47) EKVNELSK (31) YLGYLEQLLR (76) HIQKEDVPSER (59) FFVAPFPEVFGK (69) VPQLEIVPNSAEER (43) FFVAPFPEVFGKEK (35) HQGLPQEVNLNENLLR (60) YKVPQLEIVPNSAEER (34) EDVPSERYLGYLEQLLR (31) HPIKHQGLPQEVNLNENLLR (30) EPMIGVNQELAYFYPELFR (130) EGIHAAQQKEPMIGVNQELAYFYPELFR (39)
Collagen alpha-1(I) chain (P02453)	780	35	GAAGLPGPK (48) GFSGLDGAK (36) GSEGPQGVR (34) GVVGLPGQR (31) GFPGADGVAGPK (41) GVQGPPEGAGPR (39) GVPGPAGVGPAGK (53) GQAGVMGFPGPK (31) GLTGSPPGSPGPDGK (76) GPSGPQGPPGPPGPK (66) GFPGLPGPSGEPGK (25) GEPGPAGLPGPPGER (59) GSAGPPGATGFPGAAGR (42) GETGPAGPAGPIGPVGAR (51) GLTGPAGPPGAGAPGDK (26) GSPGEAGRPGEAGLPGAK (16) EGAPGAEGSPGRDGSPPGAK (57) GPPGPMGPPGLAGPPGESGR (33) VGPPGPSGNAGPPGPPGAGK (24) GEPGPTGIQPPGPAGEEGK (34) SGDRGETGPAGPAGPIGPVGAR (52) GEPGPTGIQPPGPAGEEGKR (56) TGPPGPAGQDGRPGPPGPPGAR (40) GAPGADGPAGAPGTPGPQGIAGQR (19) GEPGPPGAGFAGPPGADGQPGAK (32) GETGPAGRPGEVGPMPGPPGAGEK (44) GAPGDRGEPGPPGAGFAGPPGADGQPGAK (57) GFSGLQGPPGPPGSPGEQGPSGASGPAGPR (99) GLTGPAGPPGAGAPGDKGEAGPSGPAGPTGAR (57) GVPPGPAGVGPAGKDGEGAGAQCPGPPGAGPAGER (34) GLPMPGAPGPQCFQGPPEGPEPGASGPMGPR (40)
Kappa-casein precursor (P02668)	646	26	YIPIQYVLSR (54) HHPHPLSFMALPPK (42)

Collagen alpha-2(I) chain (P02465)	592	30	HPHPHLSFMAIPPKK (42) SPAQILQWQVLSNTVPAK (143) GVVGPQGAR (31) GPSGPQGIR (38) VGAPGPAGAR (20) GLVGEPGPAGSK (39) GEPGNIGFPGPK (35) IGQPGAVGPAGIR (34) GPAGPSGPAGKDGR (32) GIPGPVGAAGATGAR (19) GFPGPSGNIGPAGK (46) GIPGEFGLPGPAGAR (52) GDGGPPGATGFPGAAGR (30) SGETGASGPPGFVGEK (68) GEPGPAGAVGPAGAVGPR (49) GAAGLPGVAGAPGLPGPR (36) GPPGESGAAGPTGPIGSR (53) GELGPVGNPAGPAGPR (28) GSTGEIGPAGPPGPPGLR (63) RGSTGEIGPAGPPGPPGLR (27) EGPVGLPGIDGRPGPIGPAGAR (21) GLPGVAGSVGEPGLGIAGPPGAR (76) GPPGASGAPGPQGFQPPGEPGQTGPAGAR (34)
Casein alpha-S2 (P02663)	275	46	VIPYVR (28) LNFLKK (21) NMAINPSK (34) FALPQYLK (42) VIPYVRYL (13) AMKPWIQPK (28) NAVPITPTLNR (35) RNAVPITPTLNR (38) ALNEINQFYQK (67) TVDMESTEVFTK (39) FALPQYLKTVYQHQQ (18) FPQYLQYLYQGPIVLNPWDQVK (53)
Beta-lactoglobulin (P02754)	129	33	ALPMHIR (10) IDALNENK (39) VLVLDTDYK (22) VLVLDTDYKK (23) TPEVDDEALEK (14) TPEVDDEALEKFDK (29) VYVEELKPTPEGDLEILLQK (67)
Lactadherin (Q95114)	52	9	VTGIITQGAR (40) QFQFIQVAGR (38) DFGHIQYVAAYR (19)

^a Ions score is $-10 \cdot \log(P)$, where P is the probability that the observed match is a random event. Individual ions scores > 31 indicate identity or extensive homology ($p < 0.05$). Protein scores are derived from ions scores as a non-probabilistic basis for ranking protein hits. (http://www.matrixscience.com/help/interpretation_help.html)

Table S2: Main series matches of the fragmentation spectra reported in Figure 1 and Figure 2. Those ions containing the deamidation site are highlighted reported in bold.

	YLGYLEQLLR	YLGYLEQ*LLR	FALPQYLK	FALPQ*YLK
Daughter ion	m/z	m/z	m/z	m/z
y ₁	175.1213	175.1188	147.1142	147.1164
y ₂	288.2069	288.2066	260.2044	260.1990
y ₃	401.2924	401.2823	423.2609	423.2469
y ₄	529.3491	530.3313	551.3244	552.2882
y ₅	658.3893	659.3660	648.3701	649.3549
y ₆	771.4714	772.4542	761.4525	762.4367
y ₇	934.5386	935.5100	832.4970	833.4685
y ₈	991.5664	992.5379		
y ₉	1104.6354	1105.6353		
b ₂	277.1605	277.1568	219.1142	219.1140
b ₃	334.1784	334.1803	332.2001	332.1984
b ₄	497.2403	497.2425	429.2483	
b ₅	610.3256	610.3282		
b ₆	739.3653		720.3621	
b ₇	867.4202			
b ₈	980.4983			
b ₉	1093.6009	1094.5944		

Figure S1: MSMS spectra of the doubly charged ions at m/z 490.28 (A) and 490.78 (B) of the peptide 189-FALPQYLK-196 from bovine alpha-S2 casein (P02663) and its deamidated form, respectively, identified in the analysis of the sample from Camposanto Monumentale of Pisa. The product ions are indicated with the observed masses.

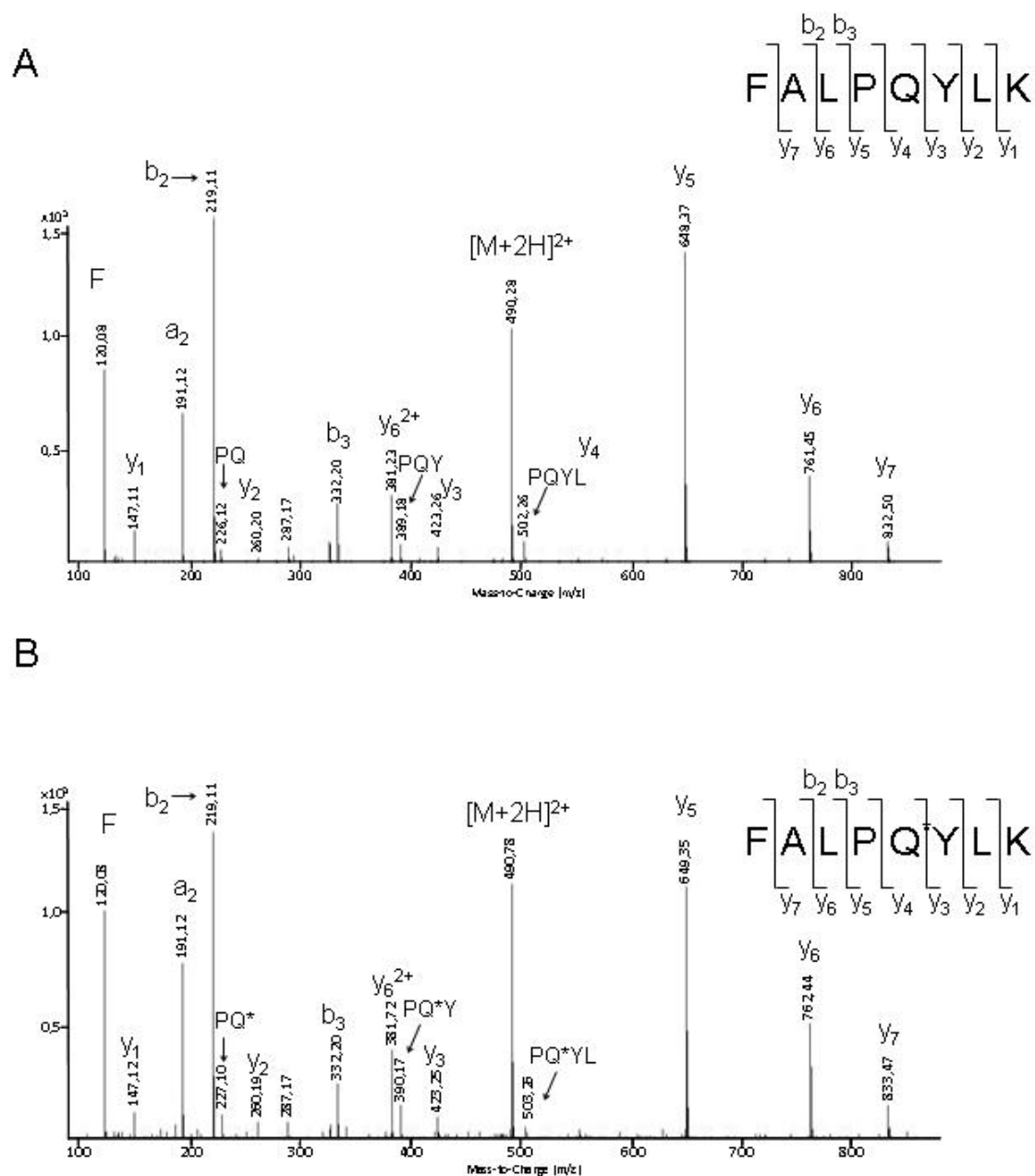


Figure S2: MSMS spectra of the doubly charged ions at m/z 653,84 (A) and 491,78 (B) of the deamidated peptide 106-YLGYLEQLLR-115 from alpha S1 casein (P02662) and of the deamidated peptide 189-FALPQYLK-196 from alpha-S2 casein (P02663), respectively, identified in the sample from Camposanto Monumentale of Pisa when trypsin digestion was carried out in $H_2^{18}O$. The product ions are indicated with the observed masses.

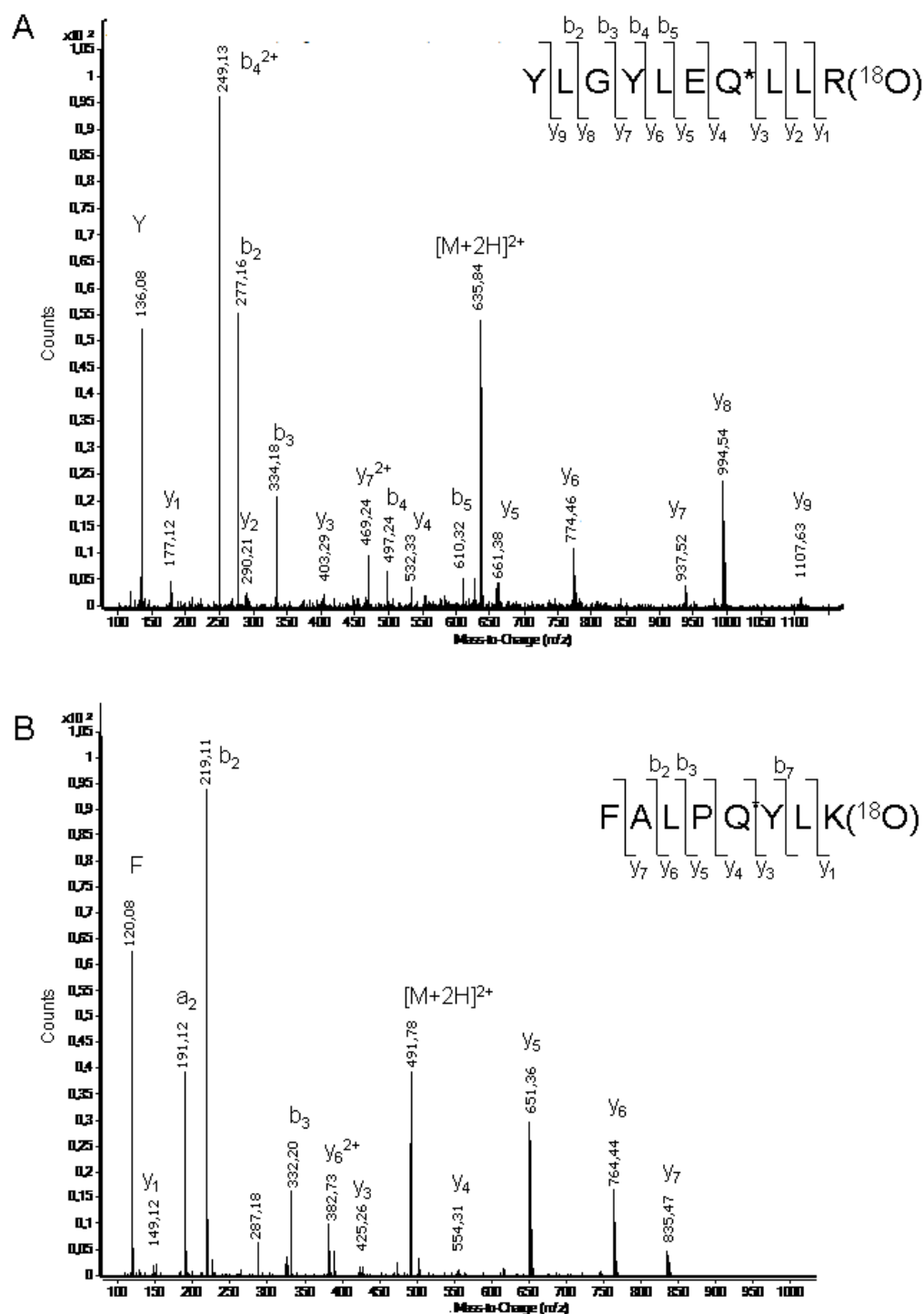


Figure S3: MSMS spectra of the doubly charged ions at m/z 390.75 (A) and 391.25 (B) of the peptide 185-VLPVPQK-191 from bovine beta casein (P02666) and its deamidated form, respectively, identified in the analysis of the sample from Camposanto Monumentale of Pisa. The product ions are indicated with the observed masses.

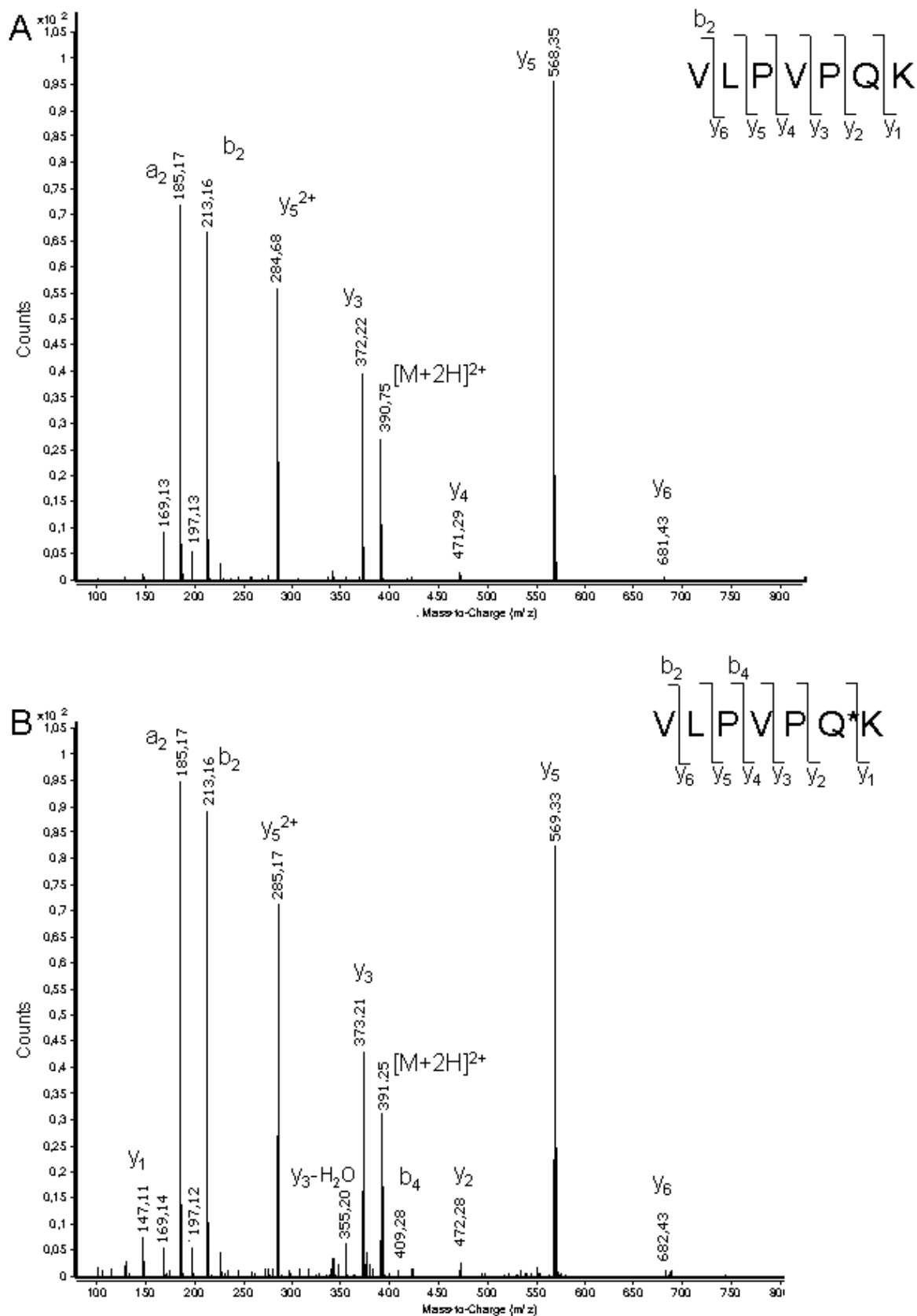


Figure S4: MSMS spectra of the doubly charged ions at m/z 626.34 (A) and 626.85 (B) of the peptide 46-YIPIQYVLSR-55 from bovine kappa casein (P02668) and its deamidated form, respectively, identified in the analysis of the sample from Camposanto Monumentale of Pisa. The product ions are indicated with the observed masses.

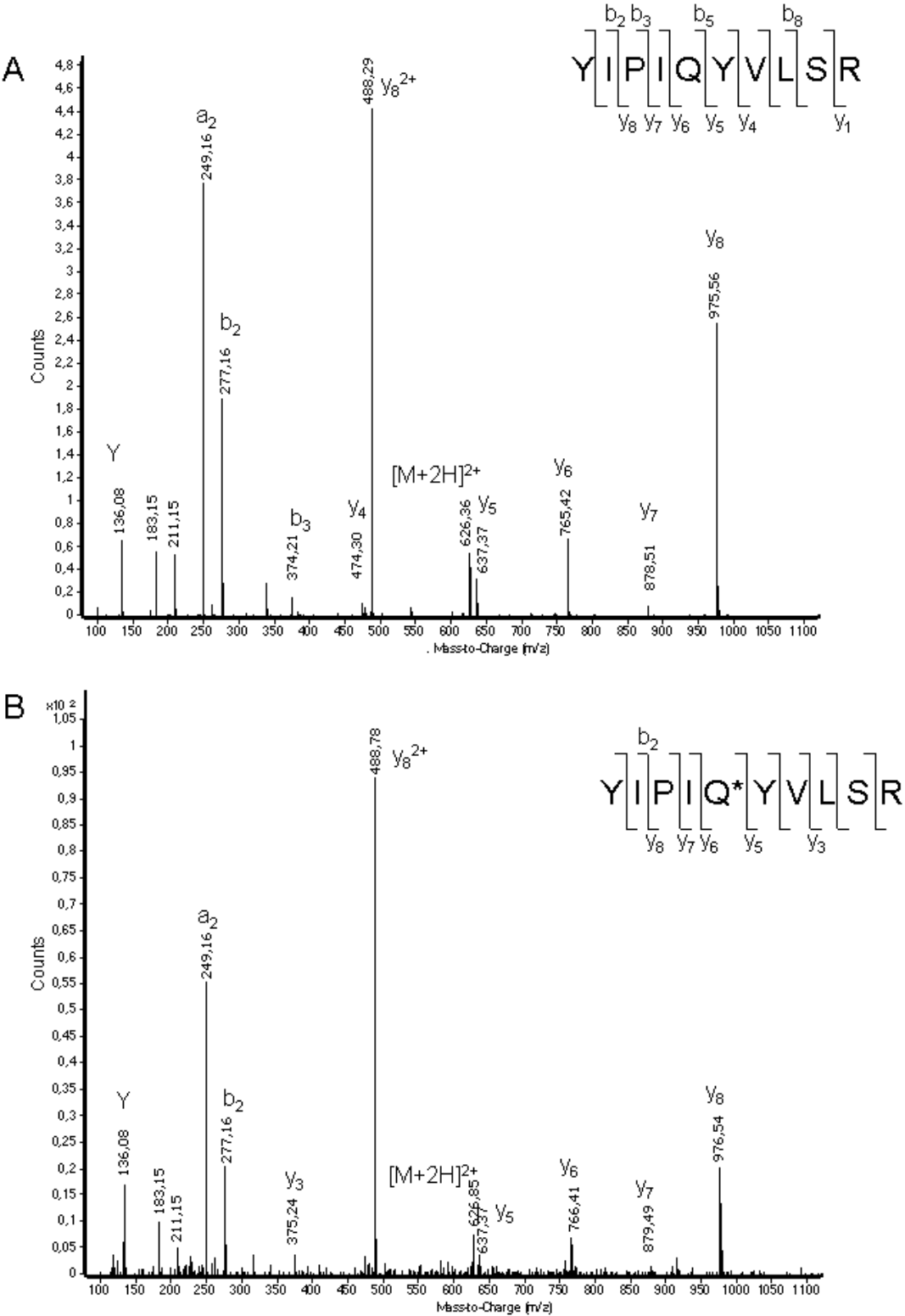


Figure S5: MSMS spectra of the triply charged ions at m/z 451.26 (A), 451.59 (B) and 451.92 (C) of the peptide 129-RNAVITPTLNR-140 from alpha-S2 casein (P02663), and its mono- and doubly deamidated forms, identified in the analysis of the sample from Camposanto Monumentale of Pisa. The product ions are indicated with the observed masses.

