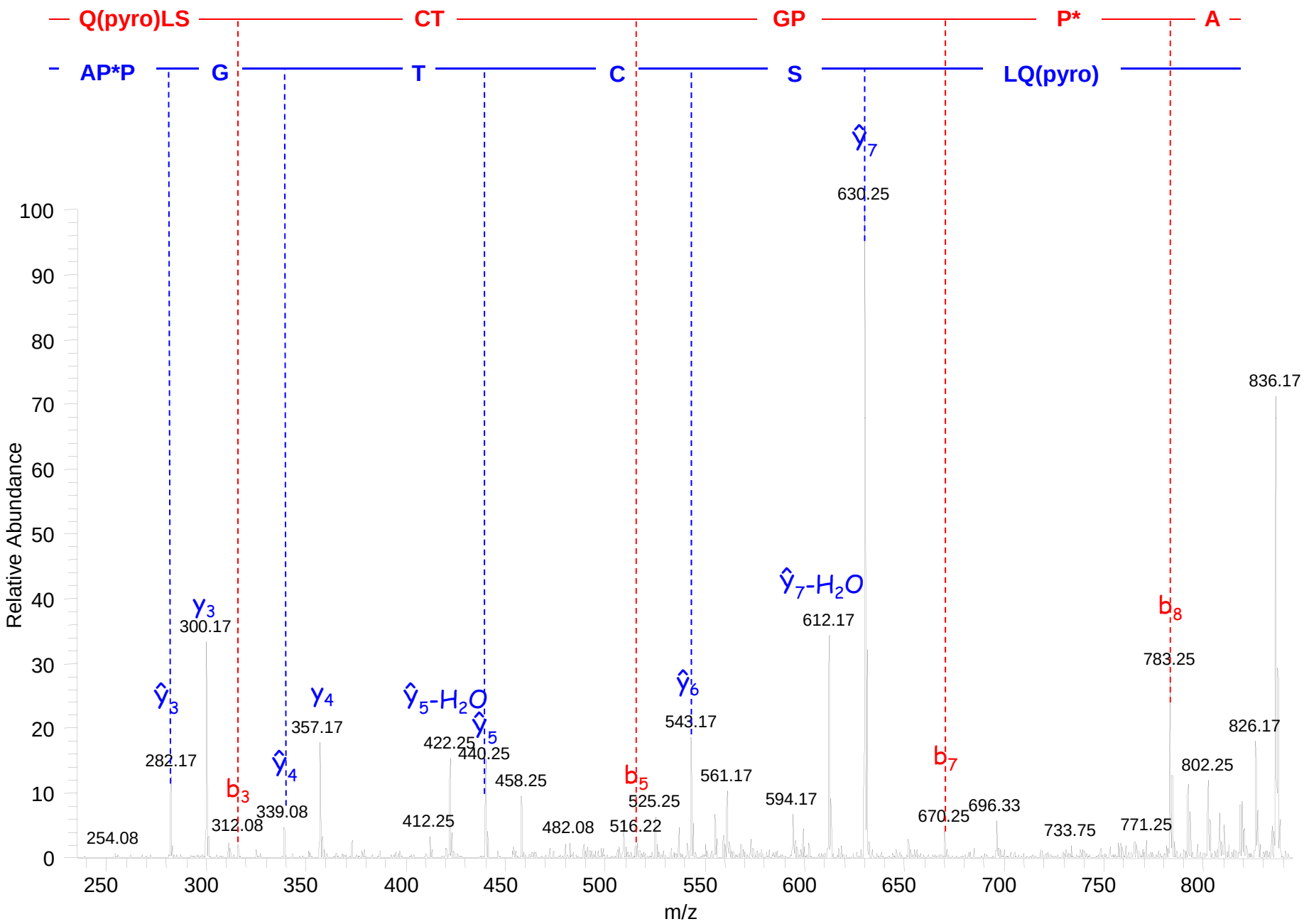
Interpretation of MS^3 and MS^4 spectra acquired during top down analysis of CLR chains.

The nomenclature for fragment ions defined by Macek et al in [Mol Cell Proteomics. 5(5):949-958] was adopted.

We thus marked as $\hat{y}$, the fragment ions containing the C-terminal residue of the b-type fragment selected for MS^3 or MS^4.

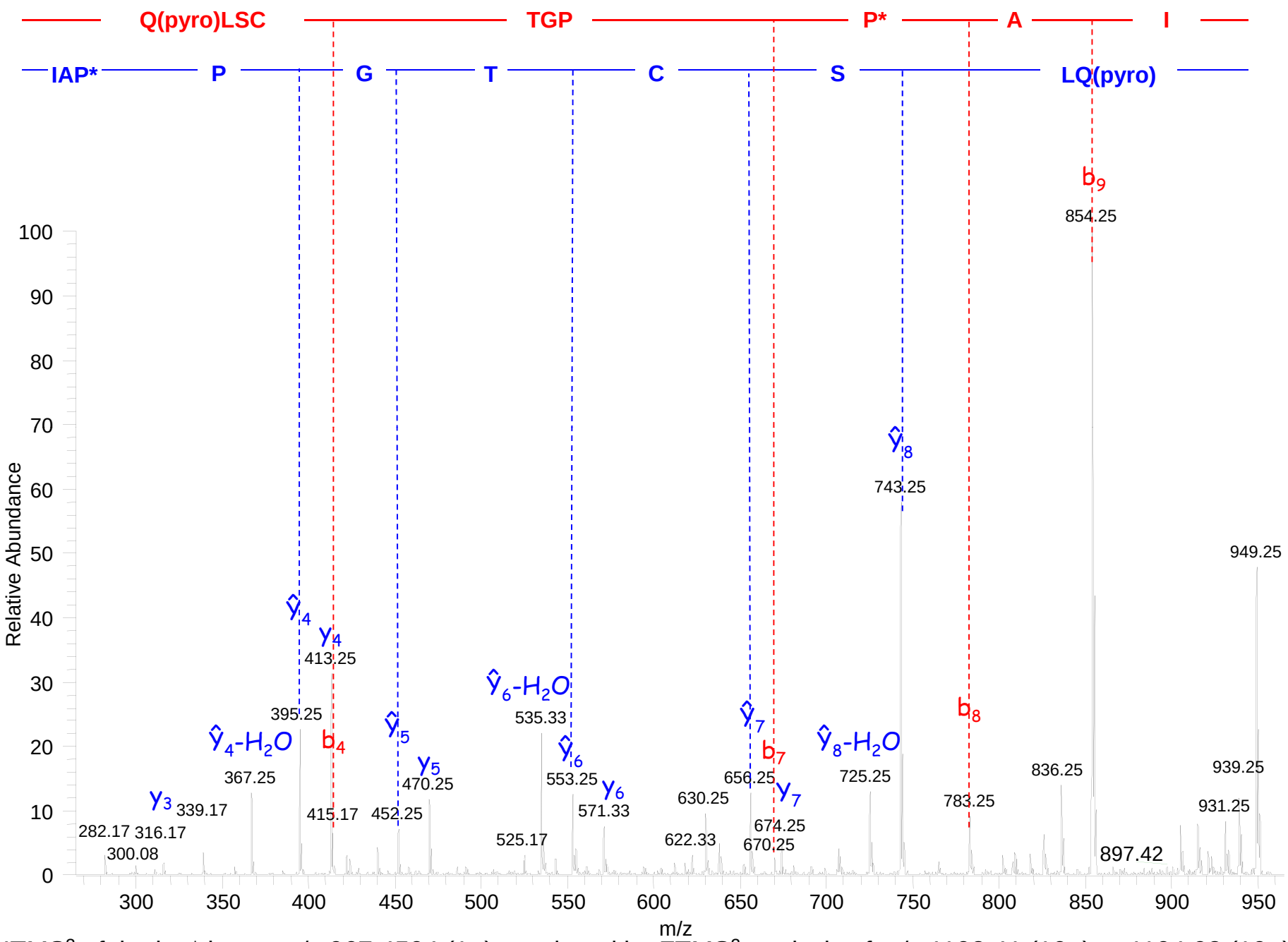
We marked as $\hat{b}$, the fragment ions containing the N-terminal residue of the y-type fragment selected for MS^3 or MS^4.

We chose to label as ‘y’ the fragments whose mass matched the theoretical m/z of y-type fragment ions, even though they came from MS^3 or MS^4 fragmentation of b ions.



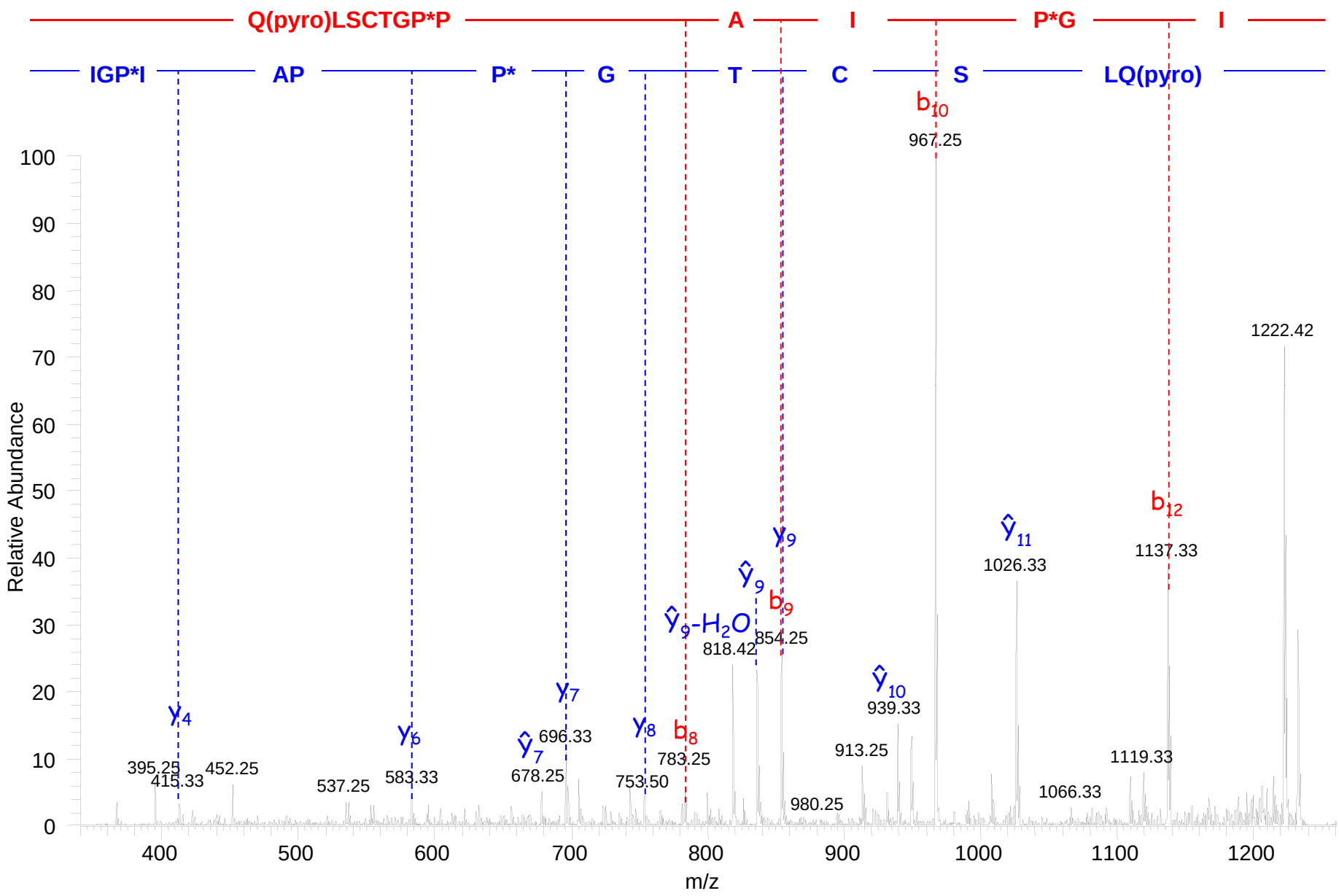
ITMS^3 of the b_9^+ ion at m/z 854.3670 (1+), produced by FTMS^2 analysis of m/z 1102.41 (10+) or 1104.02 (10+) (CLR-B)

Q(pyro)LSCTGPP*A



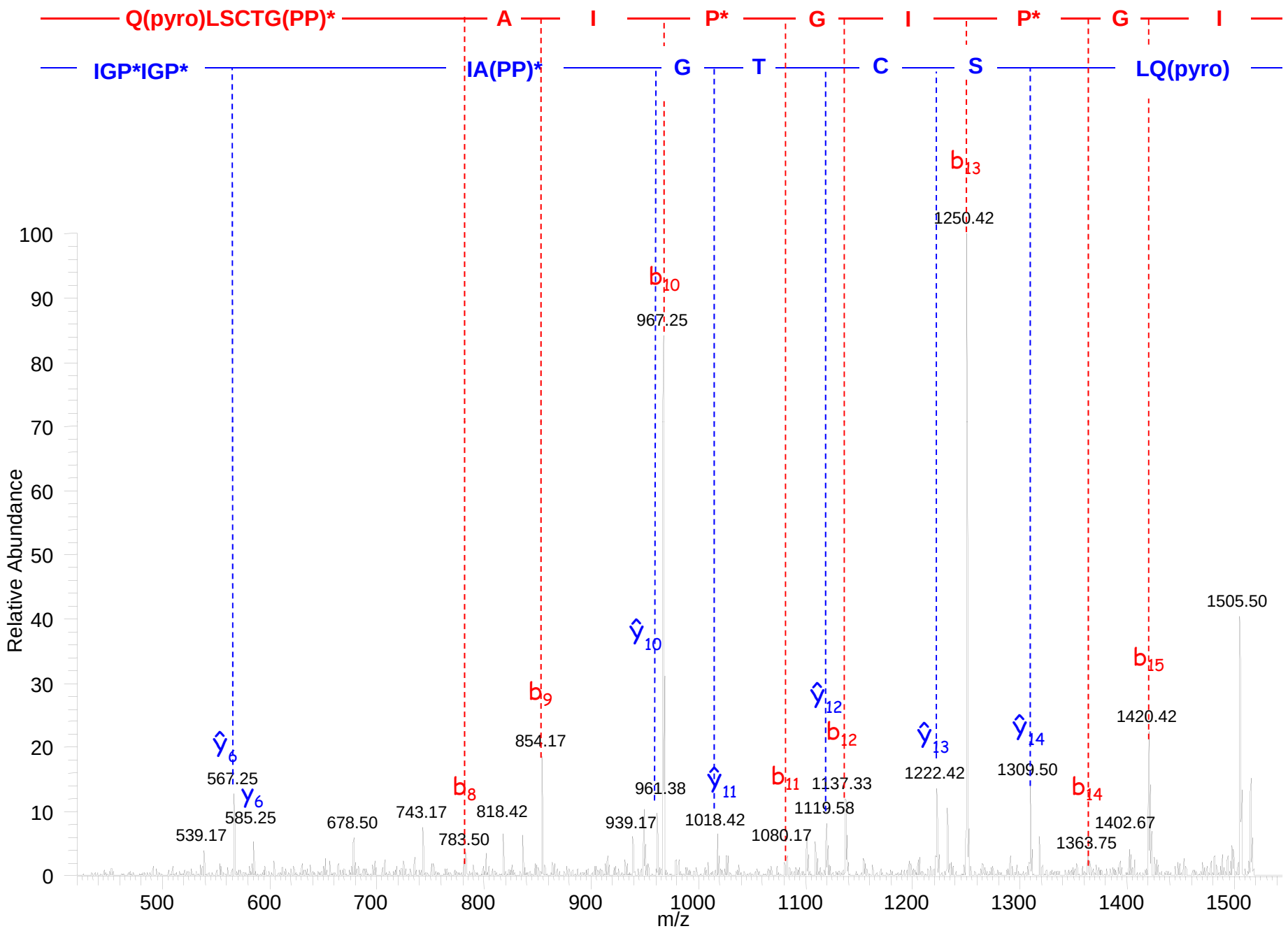
ITMS^3 of the b_{10}^+ ion at m/z 967.4504 (1+), produced by FTMS^2 analysis of m/z 1102.41 (10+) or 1104.02 (10+) (CLR-B)

Q(pyro)LSCTGPP*AI



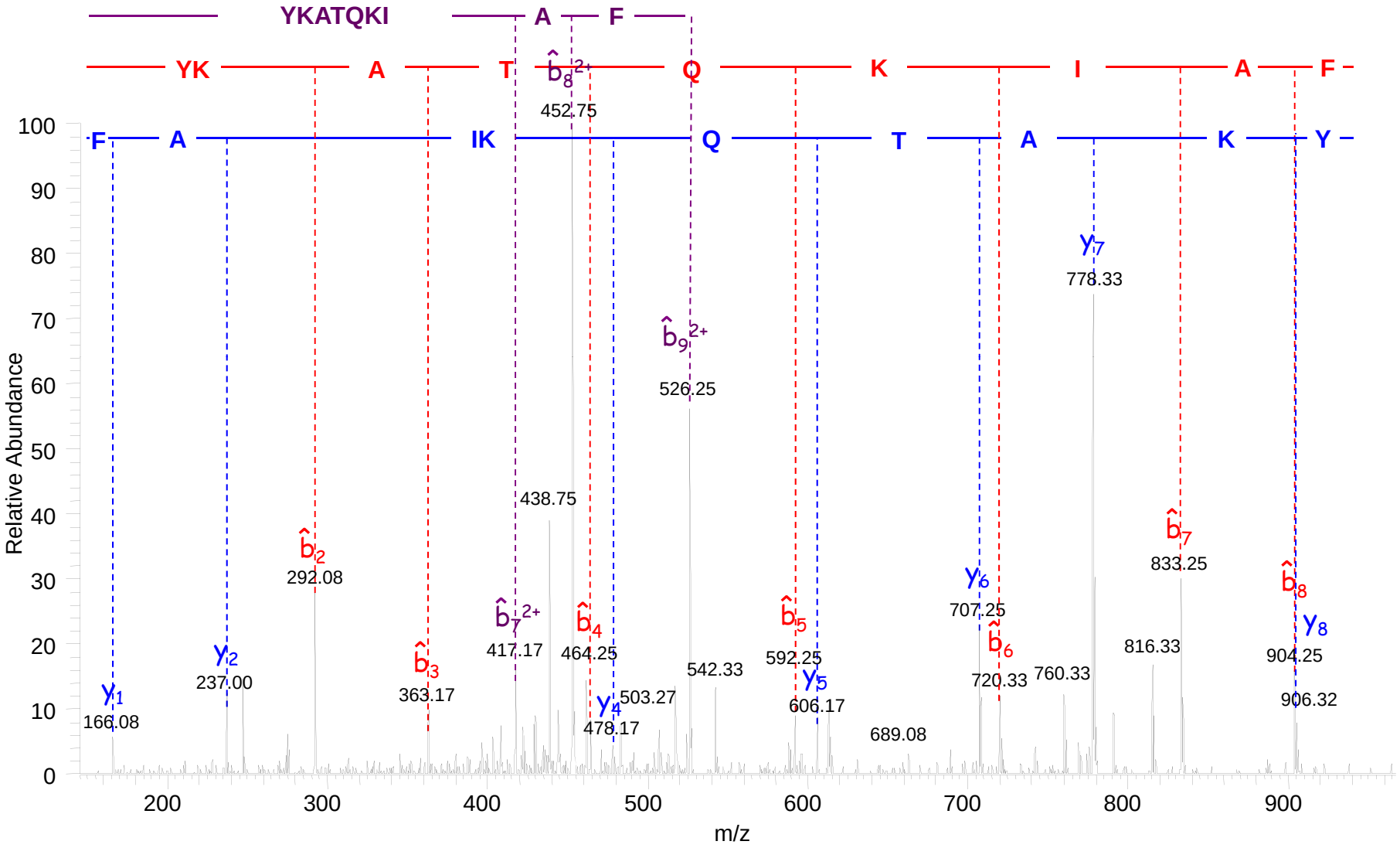
ITMS^3 of the b_{13}^+ ion at m/z 1250.6014 (1+), produced by FTMS^2 analysis of m/z 1102.41 (10+) or 1104.02 (10+) (CLR-B)

Q(pyro)LSCTGP*PAIP*GI



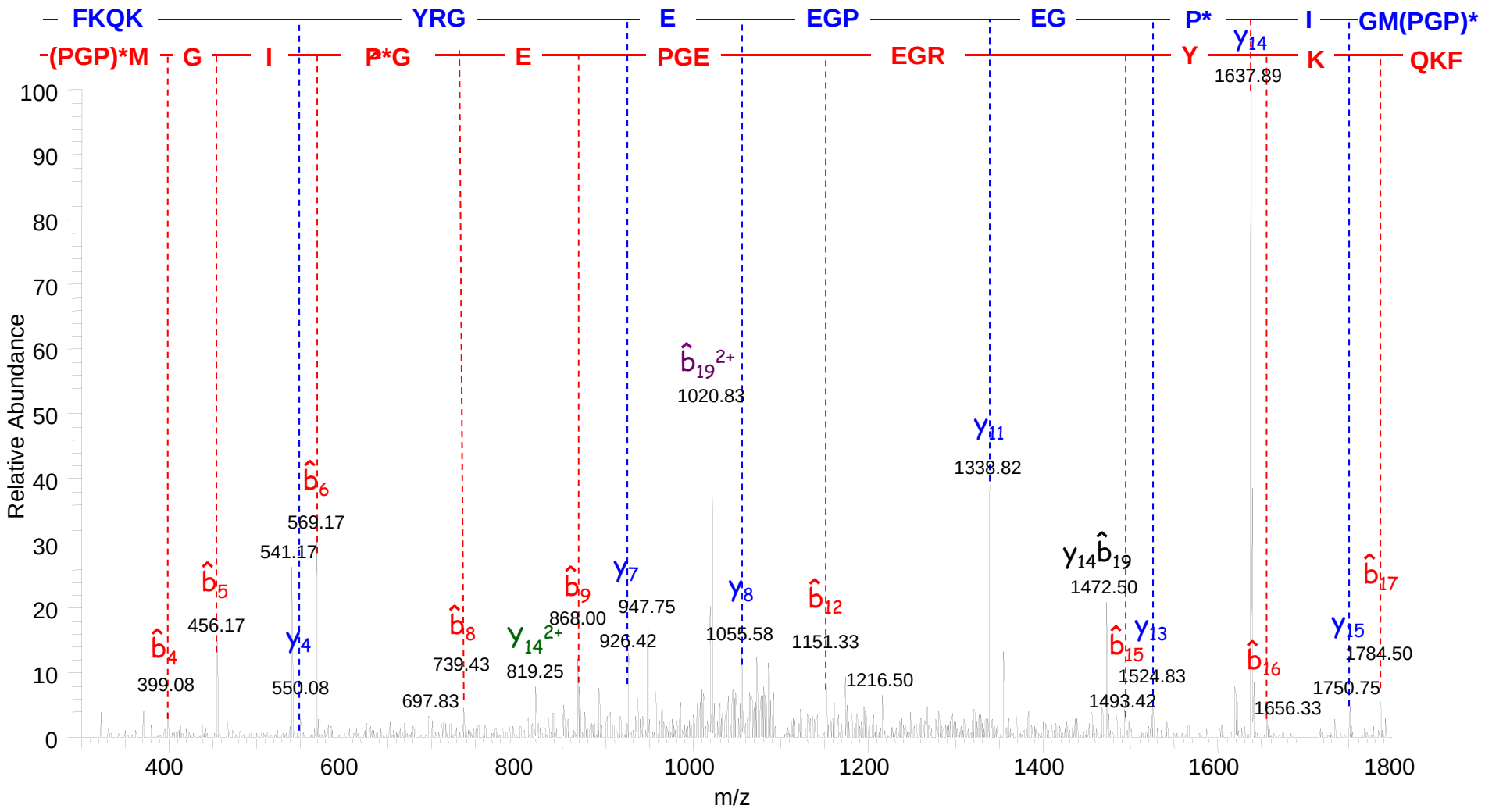
ITMS^3 of the b_{16}^+ ion at m/z 1533.7533 (1+), produced by FTMS^2 analysis of m/z 1102.41 (10+) or 1104.02 (10+) (CLR-B)

Q(pyro)LSCTG(PP)*AIP*GIP*GI



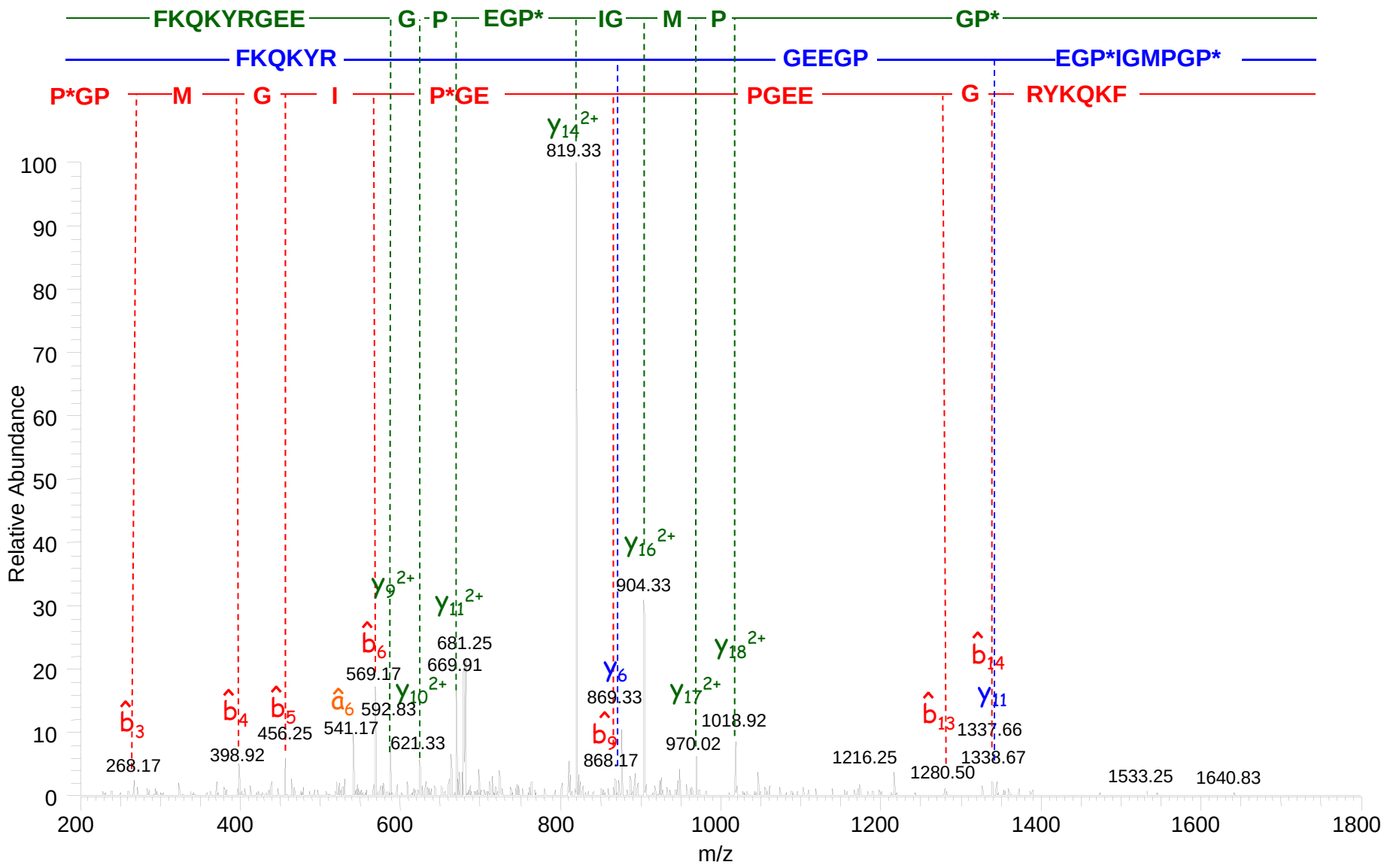
ITMS^3 of the y_9^{2+} ion at m/z 535.3027 (2+), produced by FTMS^2 analysis of m/z 1102.41 (10+) or 1104.02 (10+) (CLR-B, 1-97)

YKATQKIAF



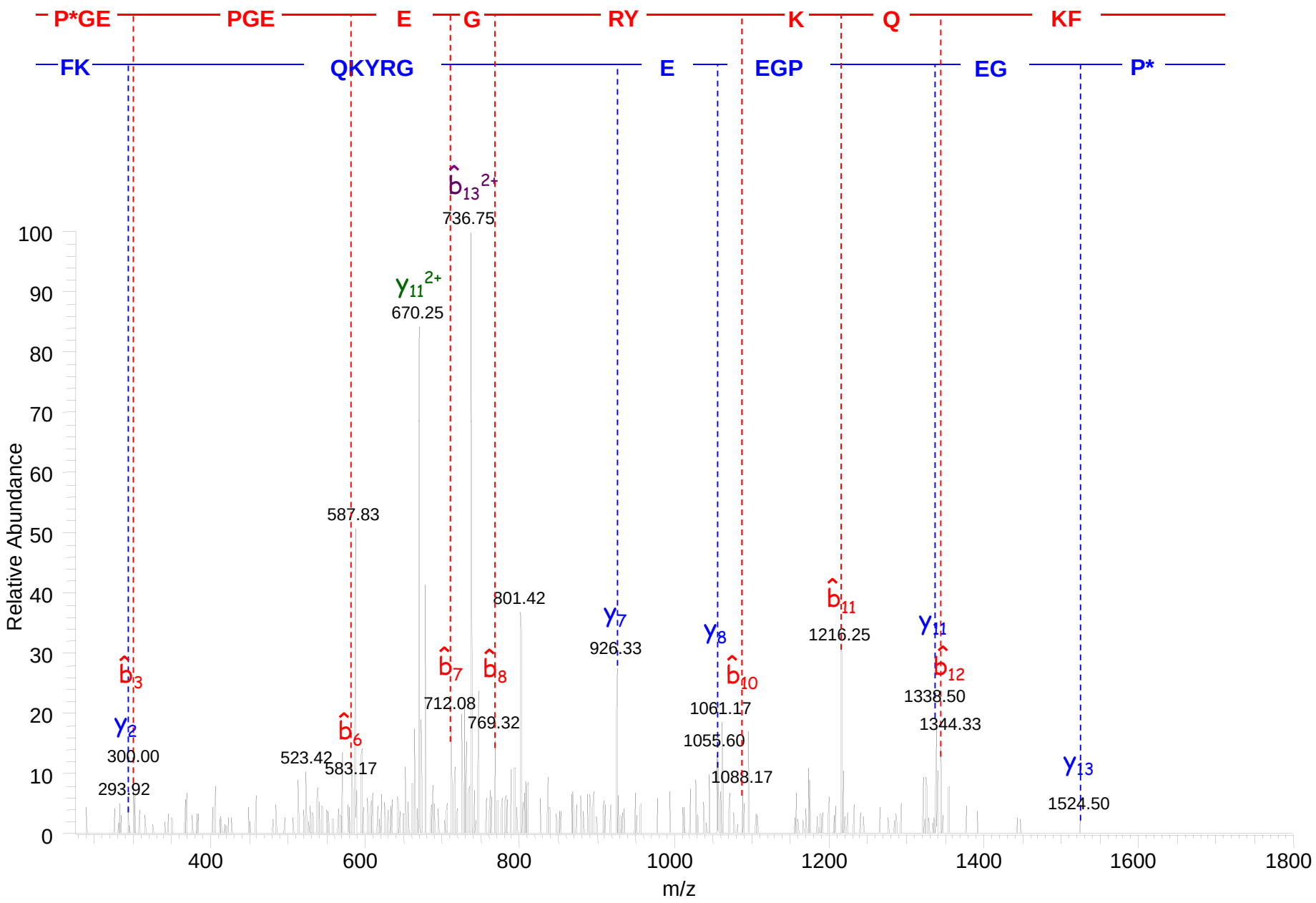
ITMS^3 of the y_{20}^{2+} ion at m/z 1103.5312 (2+), produced by FTMS^2 analysis of m/z 1256.71 (8+) (CLR-C, 1-90)

(PGP)*MGIP*GEPGEEGRYKQKF



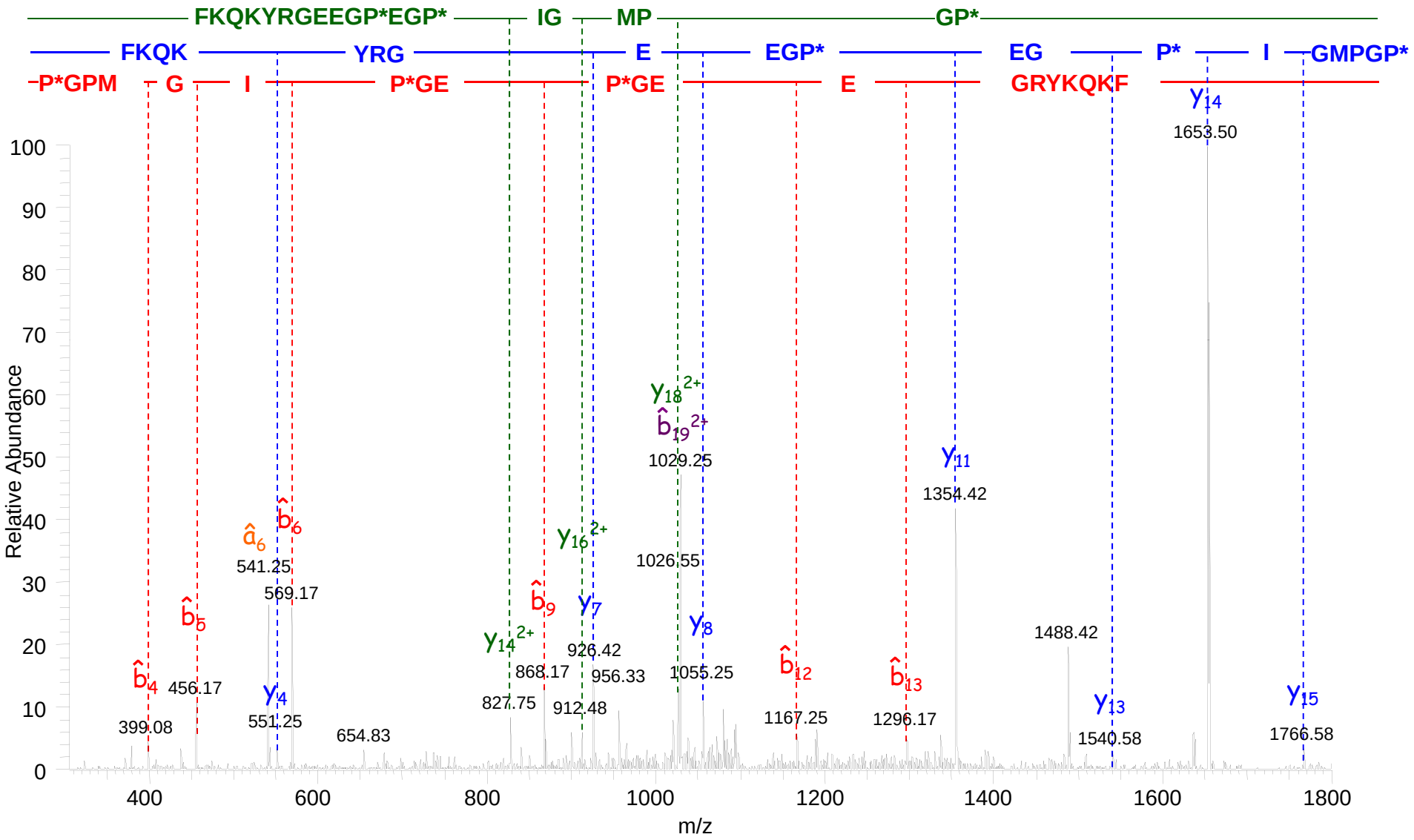
ITMS^3 of the y_{20}^{3+} ion at m/z 736.0229 (3+), produced by FTMS^2 analysis of m/z 1256.71 (8+) (CLR-C, 1-90)

P*GPMGIP*GEPGEEGRYKQKF



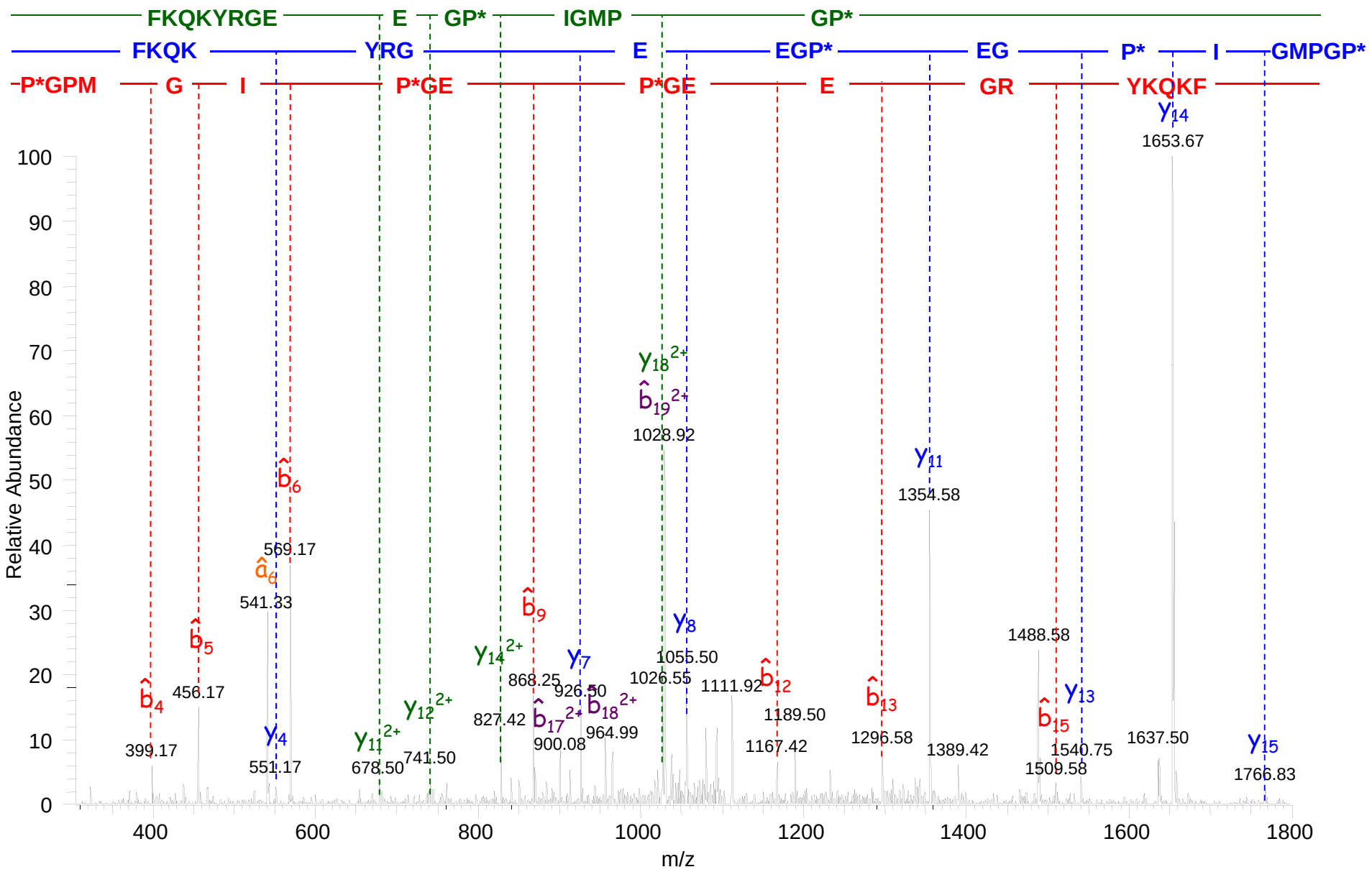
ITMS^3 of the y_{14}^{2+} ion at m/z 819.3975 (2+), produced by FTMS^2 analysis of m/z 1256.71 (8+) (CLR-C, 1-90)

P*GEPGEEGRYKQKF



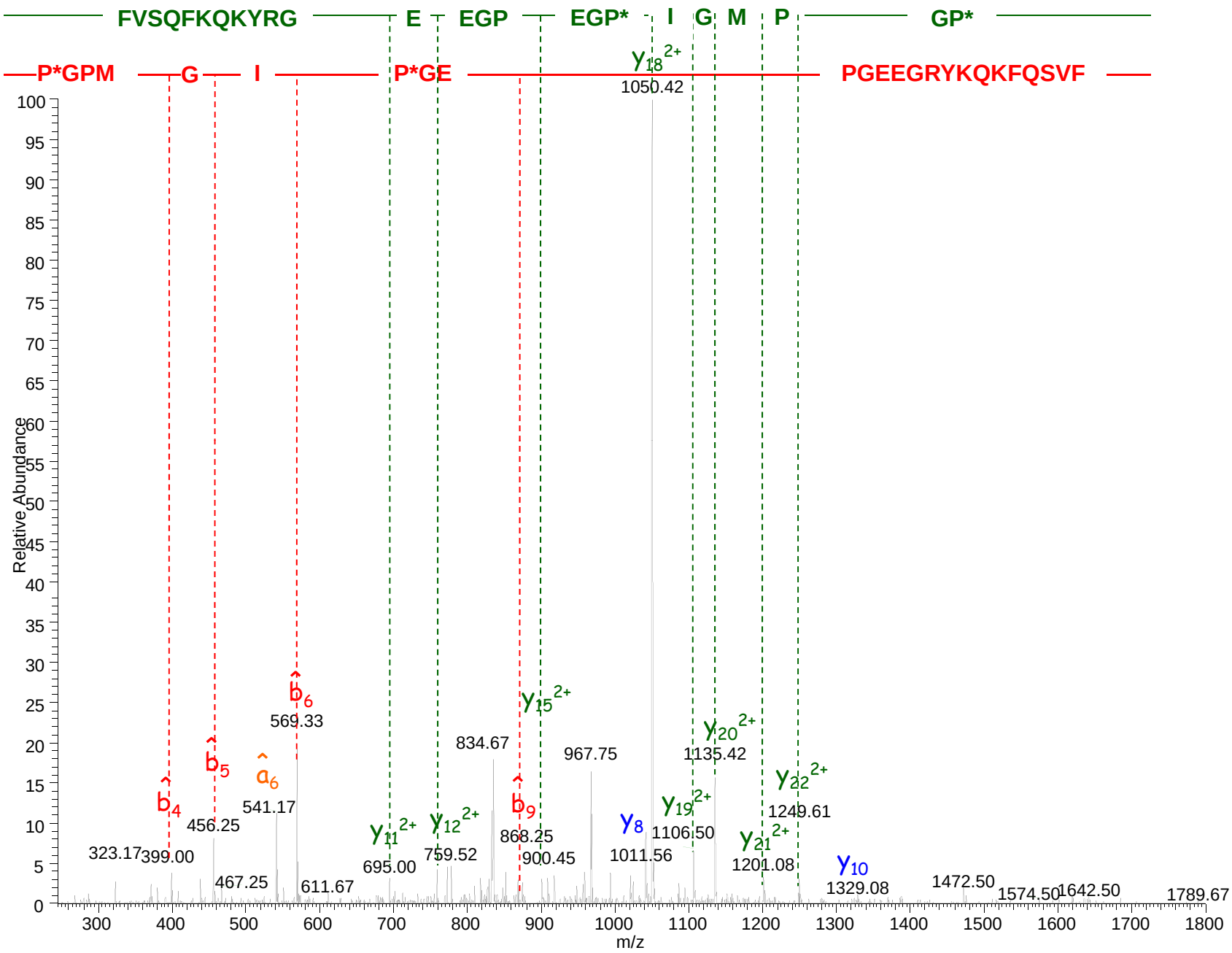
ITMS^3 of the y_{20}^{2+} ion at m/z 1111.5269 (2+), produced by FTMS^2 analysis of m/z 1258.71 (8+) (CLR-C, 1-90)

P*GPMGIP*GEP*GEEGRYKQKF



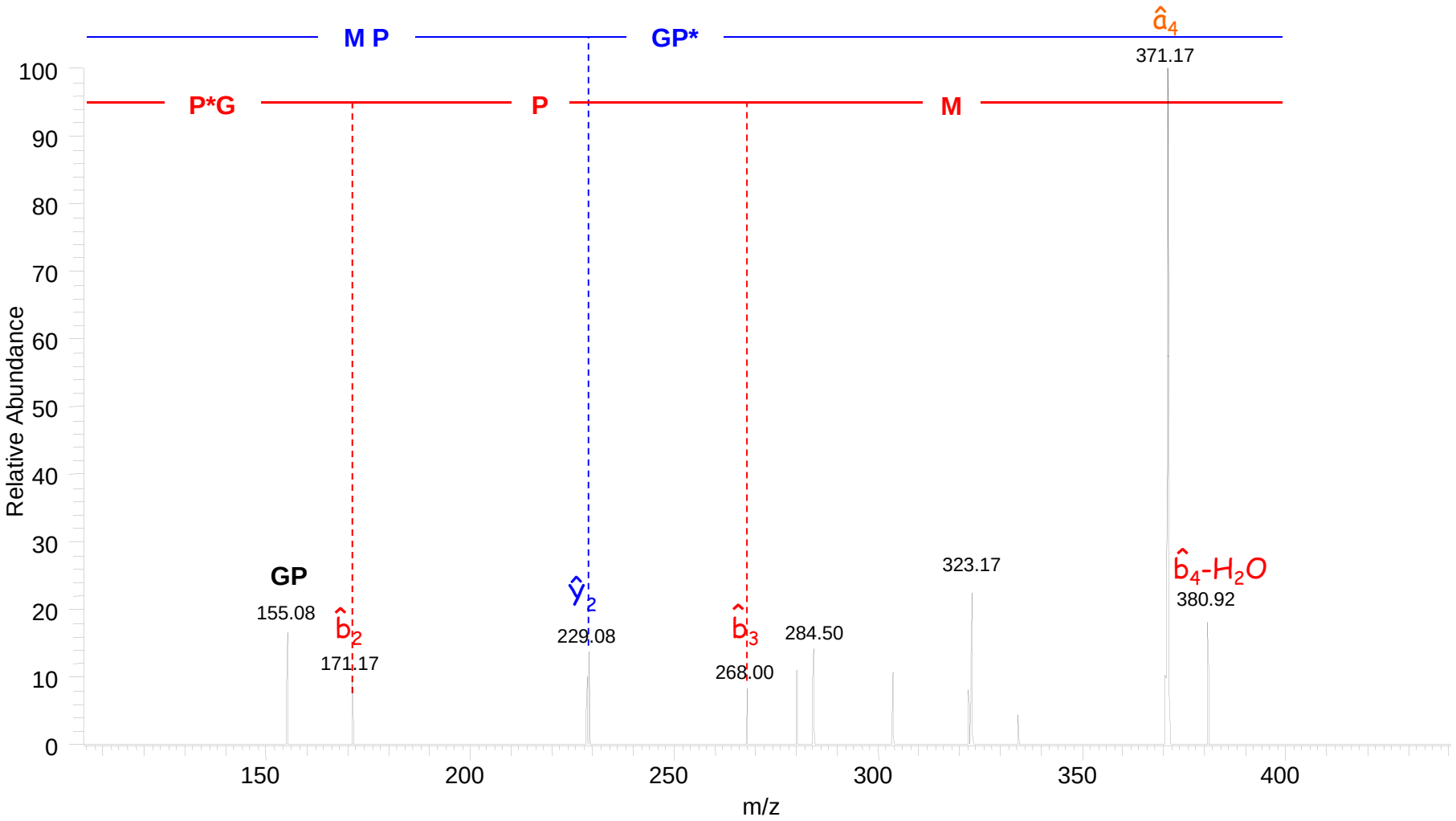
ITMS^3 of the y_{20}^{3+} ion at m/z 741.3538 (3+), produced by FTMS^2 analysis of m/z 1258.71 (8+) (CLR-C, 1-90)

P*GPMGIP*GEP*GEEGRYKQKF



ITMS^3 of the y_{24}^{3+} ion at m/z 889.7638 (3+), produced by FTMS^2 analysis of m/z 1314.23 (8+) (CLR-C, 1-94)

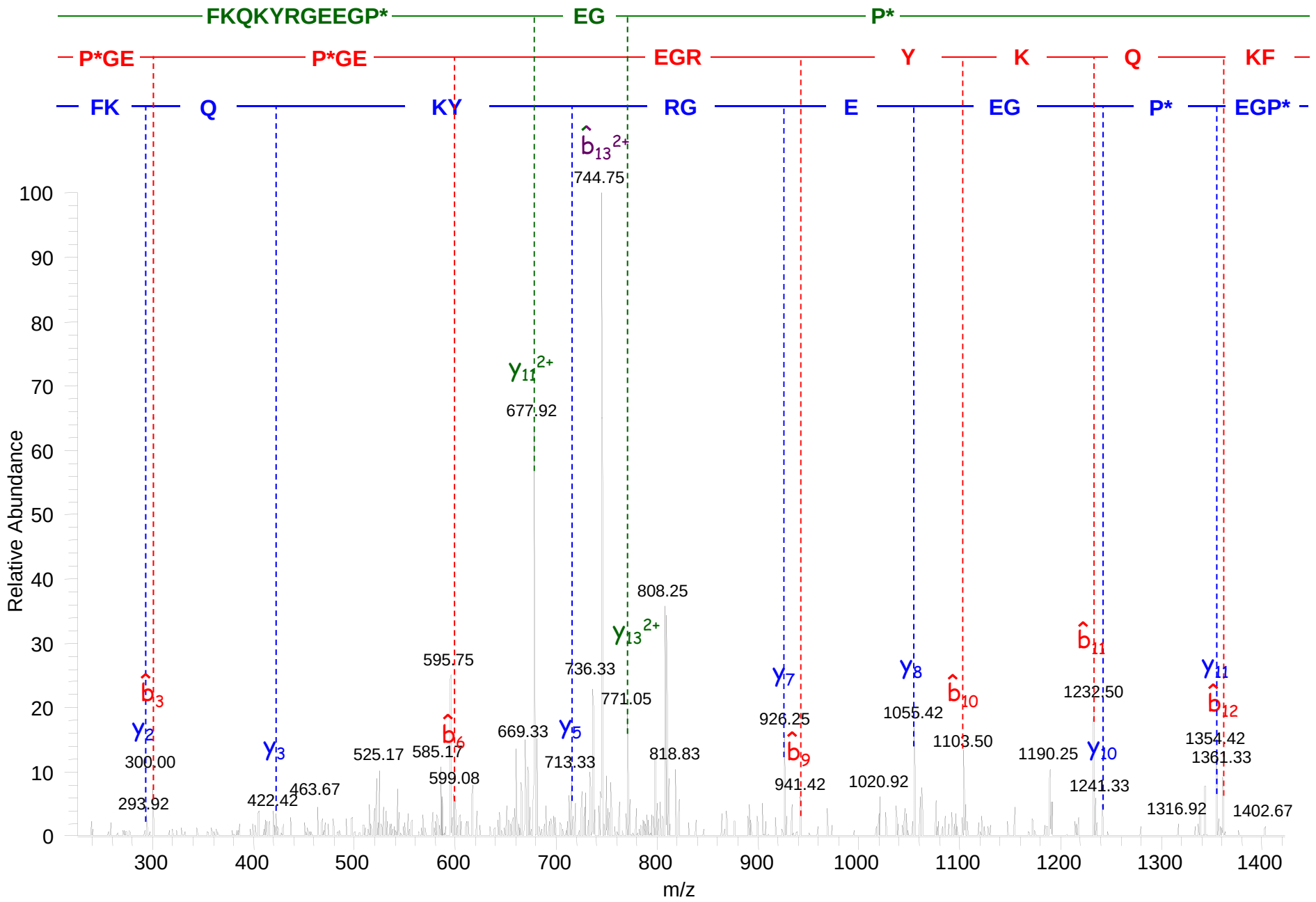
P*GPMGIP*GEPGEEGRYKQKFQSVF



ITMS^4 of the fragment at m/z 399.17 (1+), produced by ITMS^3 analysis of m/z 889.7638 (3+) (CLR-C, 1-94)

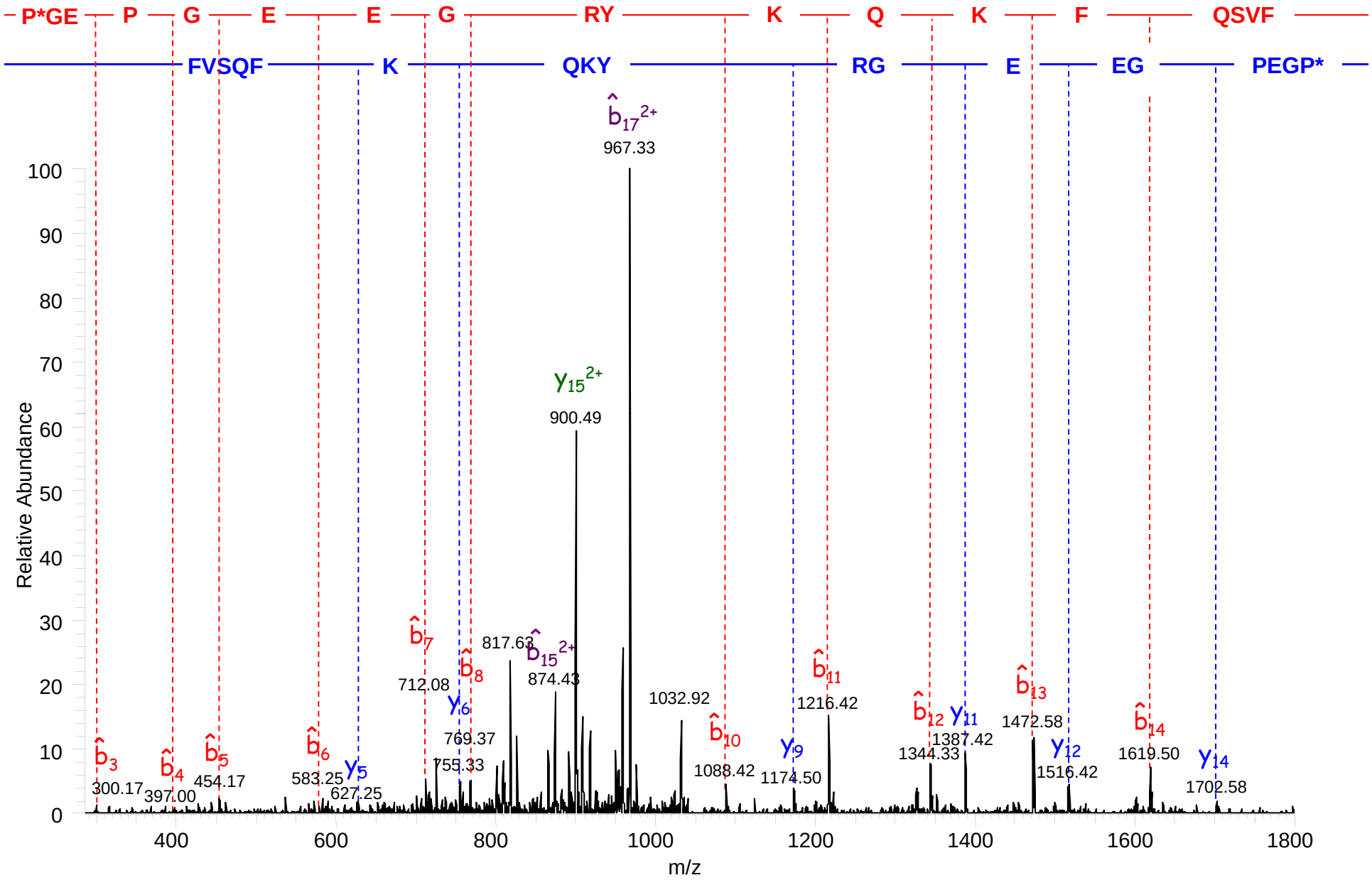
This ion corresponds to fragment b_4 produced from sequence P*GPMGIP*GEP*GEEGRYKQKFQSVF.

P*GPM



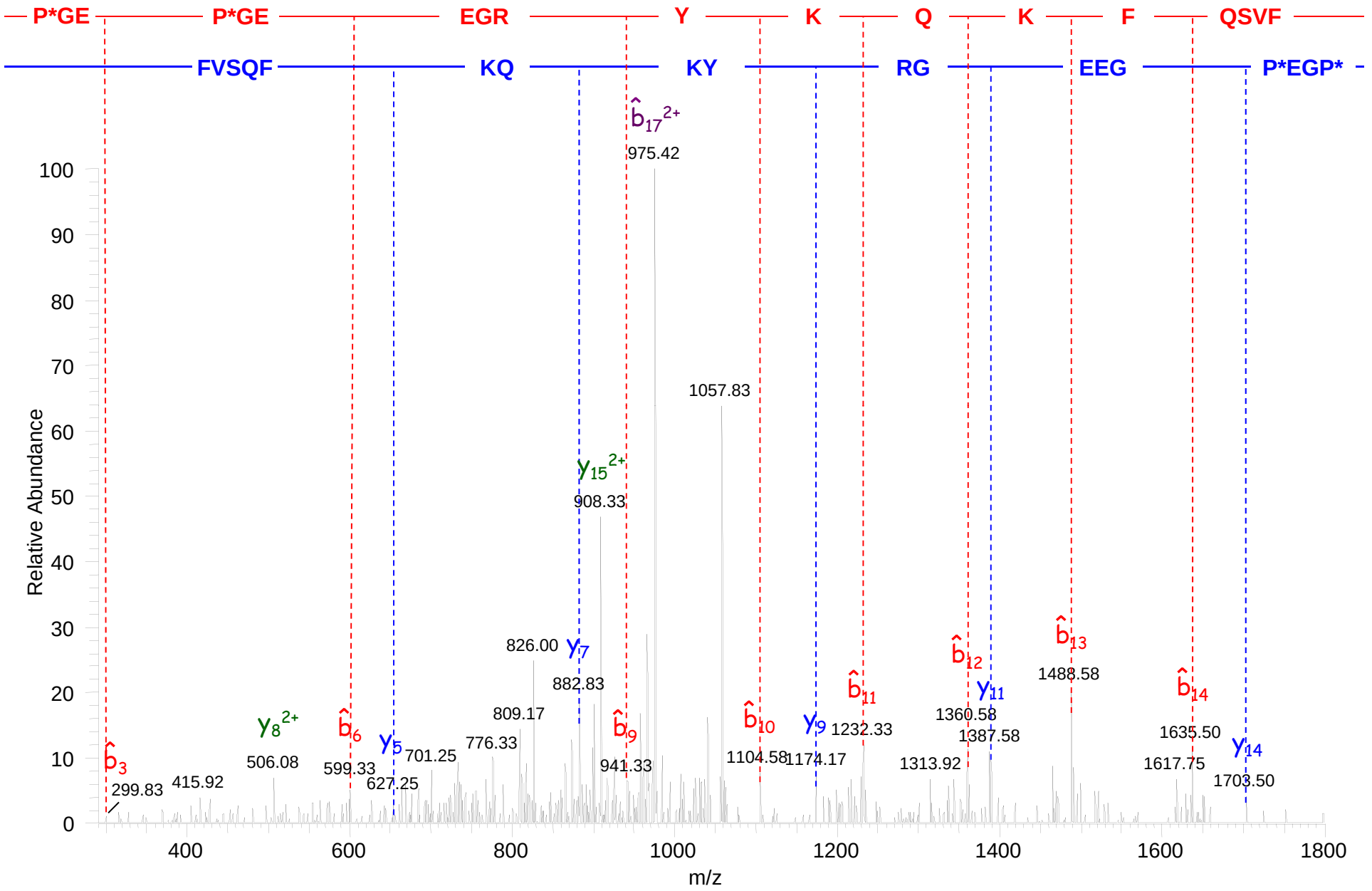
ITMS^3 of the y_{14}^{2+} ion at m/z 827.3938 (2+), produced by FTMS^2 analysis of m/z 1258.71 (8+) (CLR-C, 1-90)

P*GEP*GEEGRYKQK



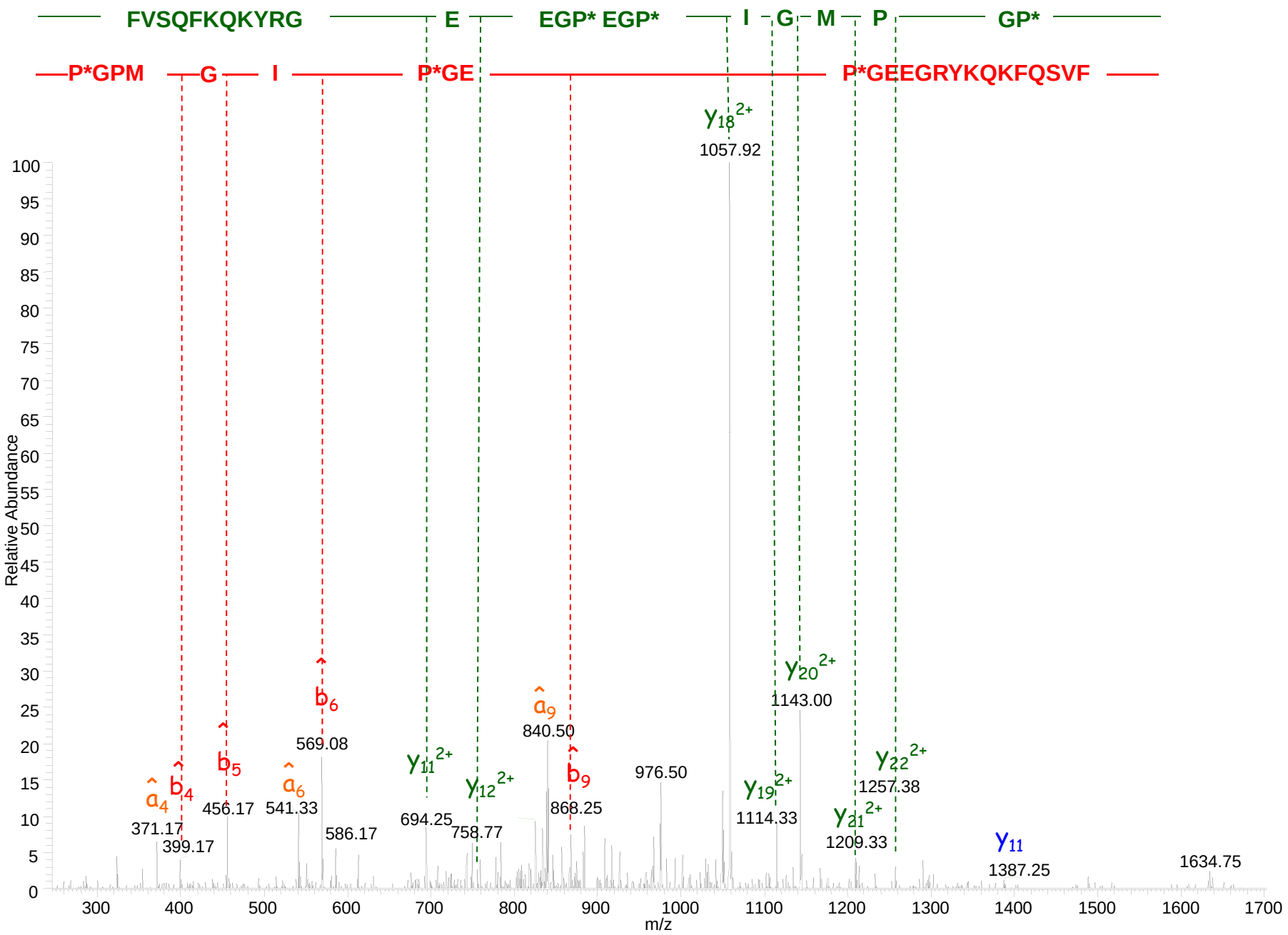
ITMS^3 of the y_{18}^{2+} ion at m/z 1050.0091 (2+), produced by FTMS^2 analysis of m/z 1314.36 (8+) (CLR-C, 1-94)

P*GEPGEEGRYKQKFQSVF



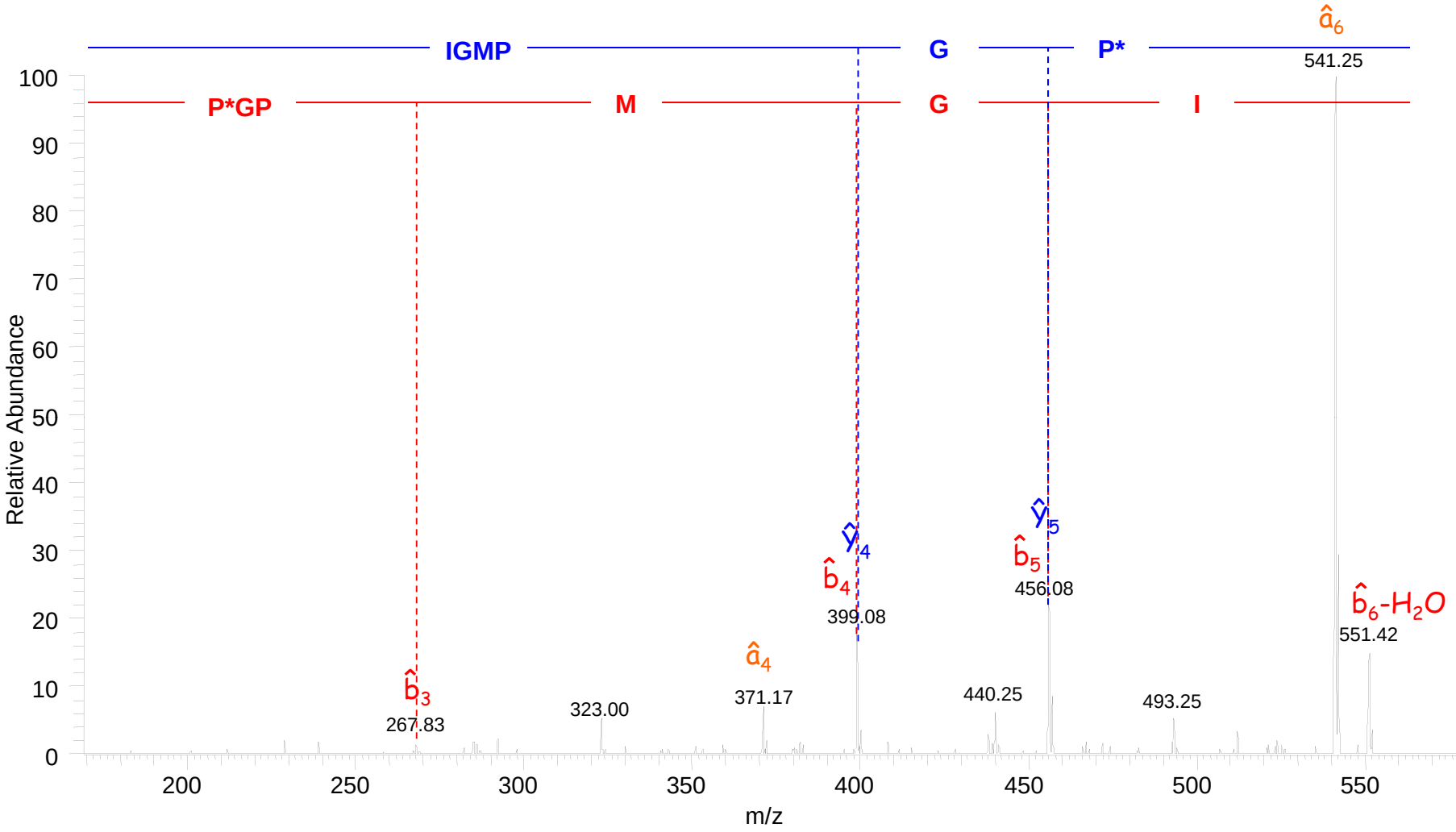
ITMS^3 of the y_{18}^{2+} ion at m/z 1058.0063 (2+), produced by FTMS^2 analysis of m/z 1316.38 (8+) (CLR-C, 1-94)

P*GEP*GEEGRYKQKFQSVF



ITMS^3 of the y_{24}^{3+} ion at m/z 895.0957 (3+), produced by FTMS^2 analysis of m/z 1316.38 (8+) (CLR-C, 1-94)

P*GPMGIP*GEP*GEEGRYKQKFQSVF



ITMS^4 of m/z 569.33 (1+), produced by ITMS^3 analysis of m/z 895.0957 (3+) (CLR-C, 1-94)

This ion corresponds to fragment $\hat{b}_6$ produced from sequence P*GPMGIP*GEP*GEEGRYKQKFQSVF

P*GPMGI