

Legends

For ETD data

In the spectra

- $z^* = z+1$;
- $c^* = c-1$;
- ❖ = charge-reduced precursor ions
- * = harmonic = 2x precursor ion
- neutral sugar losses indicated as “-SA” or “-Gal” or “-GalNAc”
- a common neutral loss of ~42 Da was detected in most ETD spectra as indicated

In the sequences

- residue in bold = corresponding z[·] ion detected;
- residue underlined = corresponding c ion detected;
- residue in italic = corresponding b or y ion detected

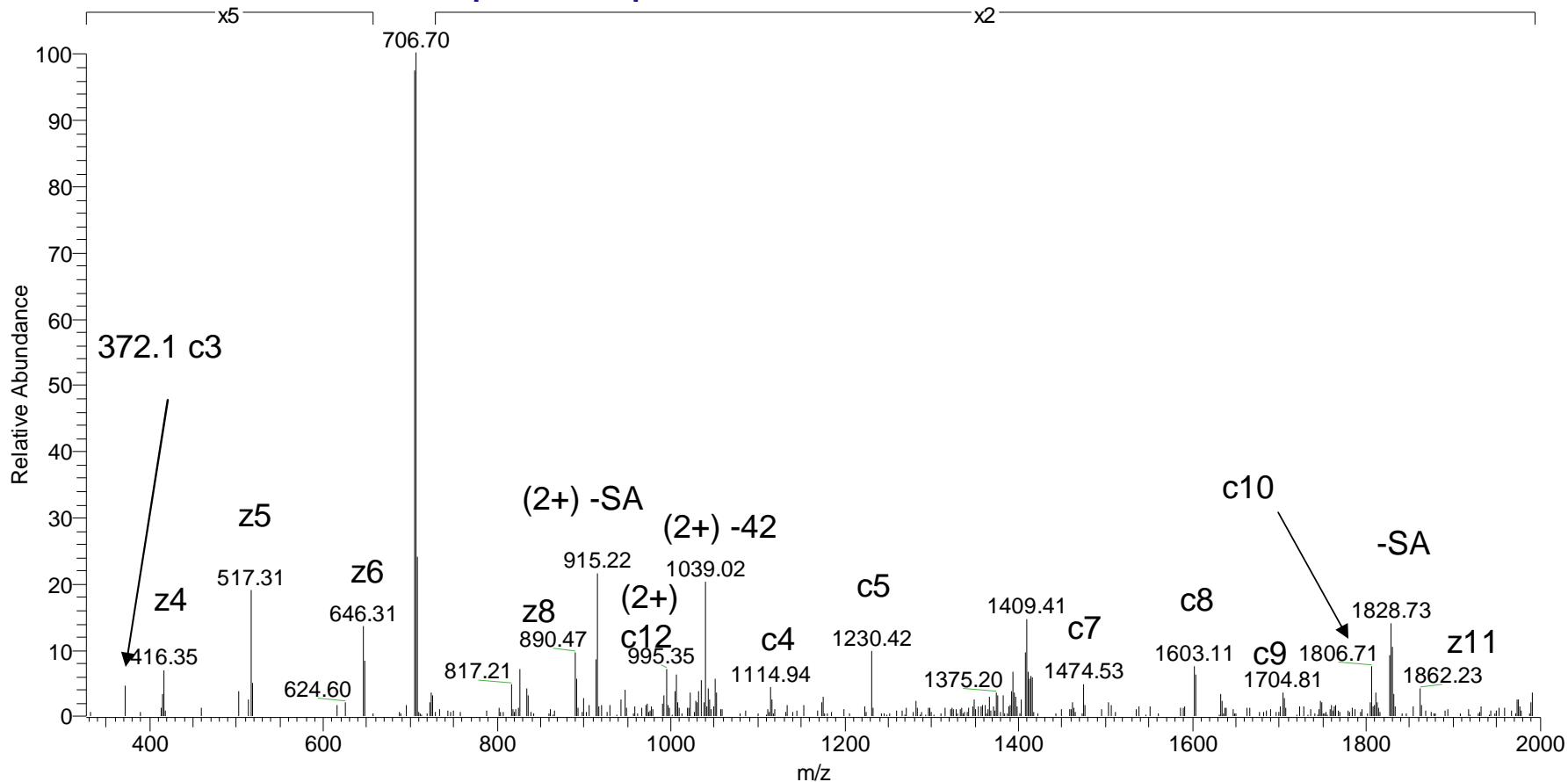
For CID data

- glycosylated CID fragments are labeled with “G”; the number of Gs indicates to the number of sugar units

P01044 = Kininogen-1 precursor

707.0082 (3+)

Katalin_Szuszanna_49 #2821 RT: 31.59 AV: 1 NL: 1.13E3
T: ITMS + c NSI d sa Full ms2 707.01 @etd90.00 [150.00-2000.00]

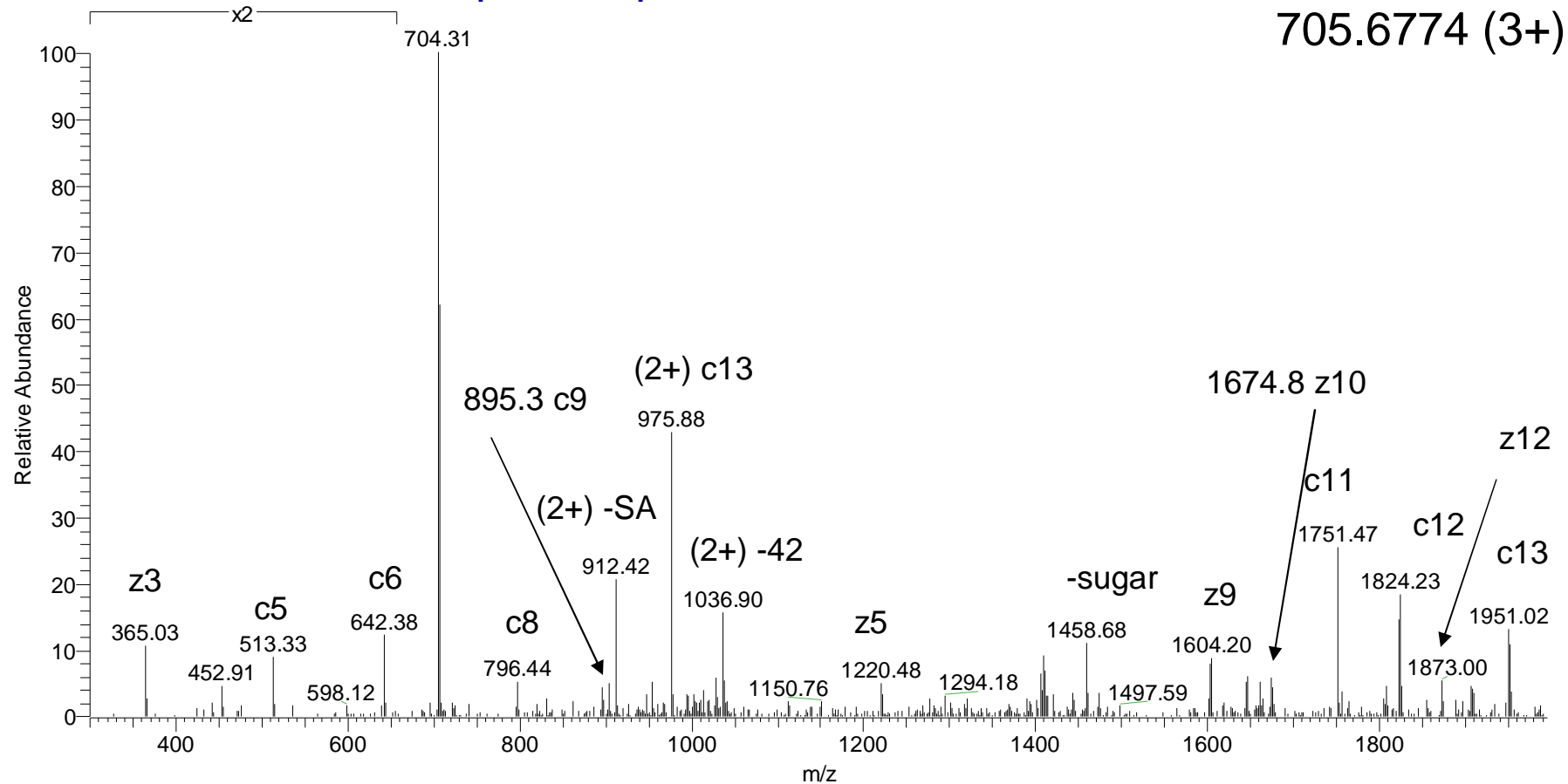


⁵⁷⁸KLIS(GalNAcGalSA)DFPETTSPK⁵⁹⁰

Supplementary Figure 1

P01044 = Kininogen-1 precursor

Katalin_Szuszanna_53 #4153 RT: 45.30 AV: 1 NL: 9.23E2
T: ITMS + c NSI d sa Full ms2 706.01 @etd90.00 [150.00-2000.00]



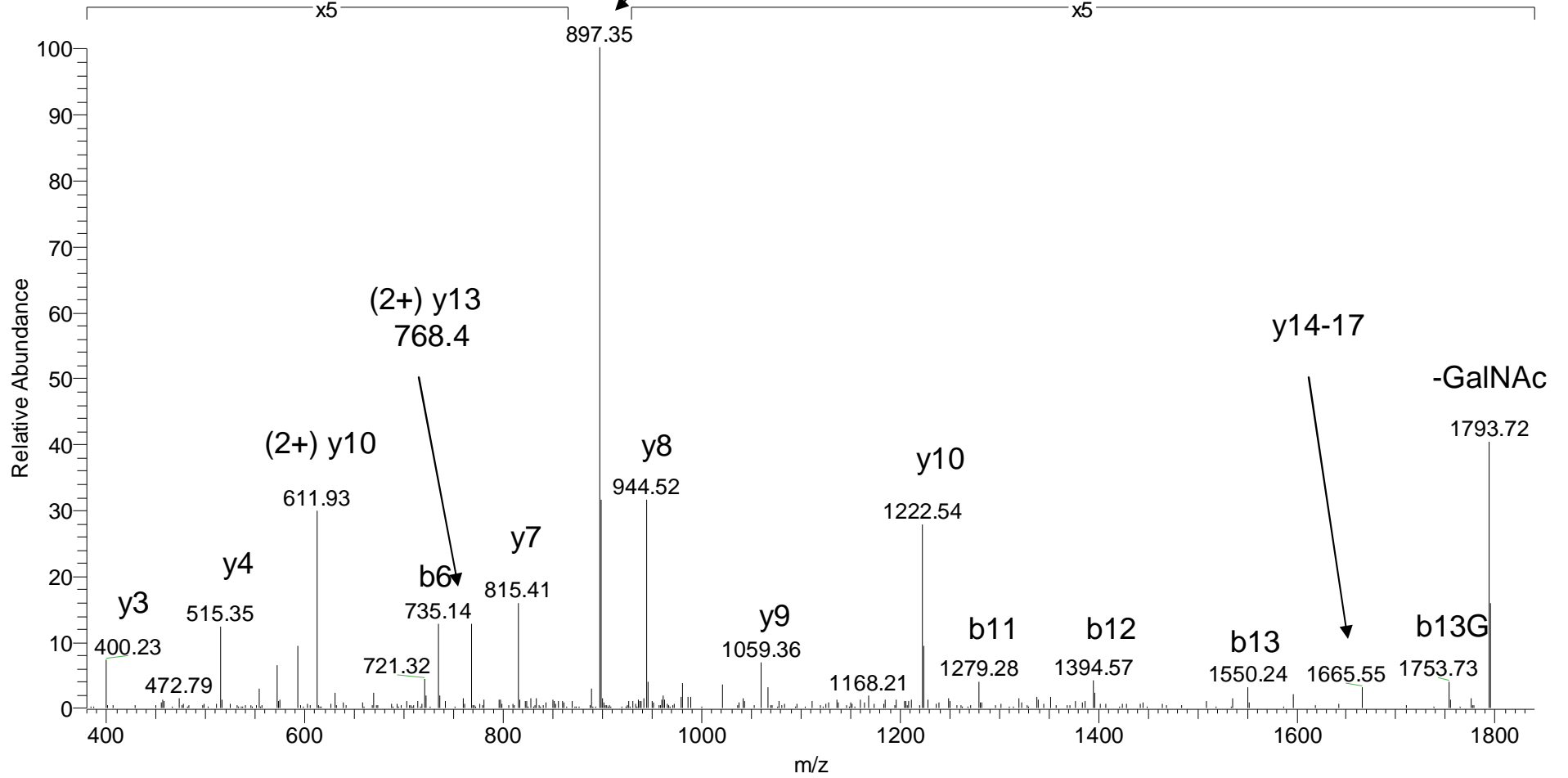
Supplementary Figure 2

P02676 = Fibrinopeptide B (Fibrinogen beta chain precursor)

T8102002 #2271 RT: 27.70 AV: 1 NL: 3.44E4
T: ITMS + c NSI d Full ms2 998.92@cid35.00 [265.00-2000.00]

(2+) -GalNAc

998.9212 (2+)



¹Q(Gln->pyro-Glu)FPT(GalNAc)DYDEGQDDRPK¹⁵

CID spectrum!

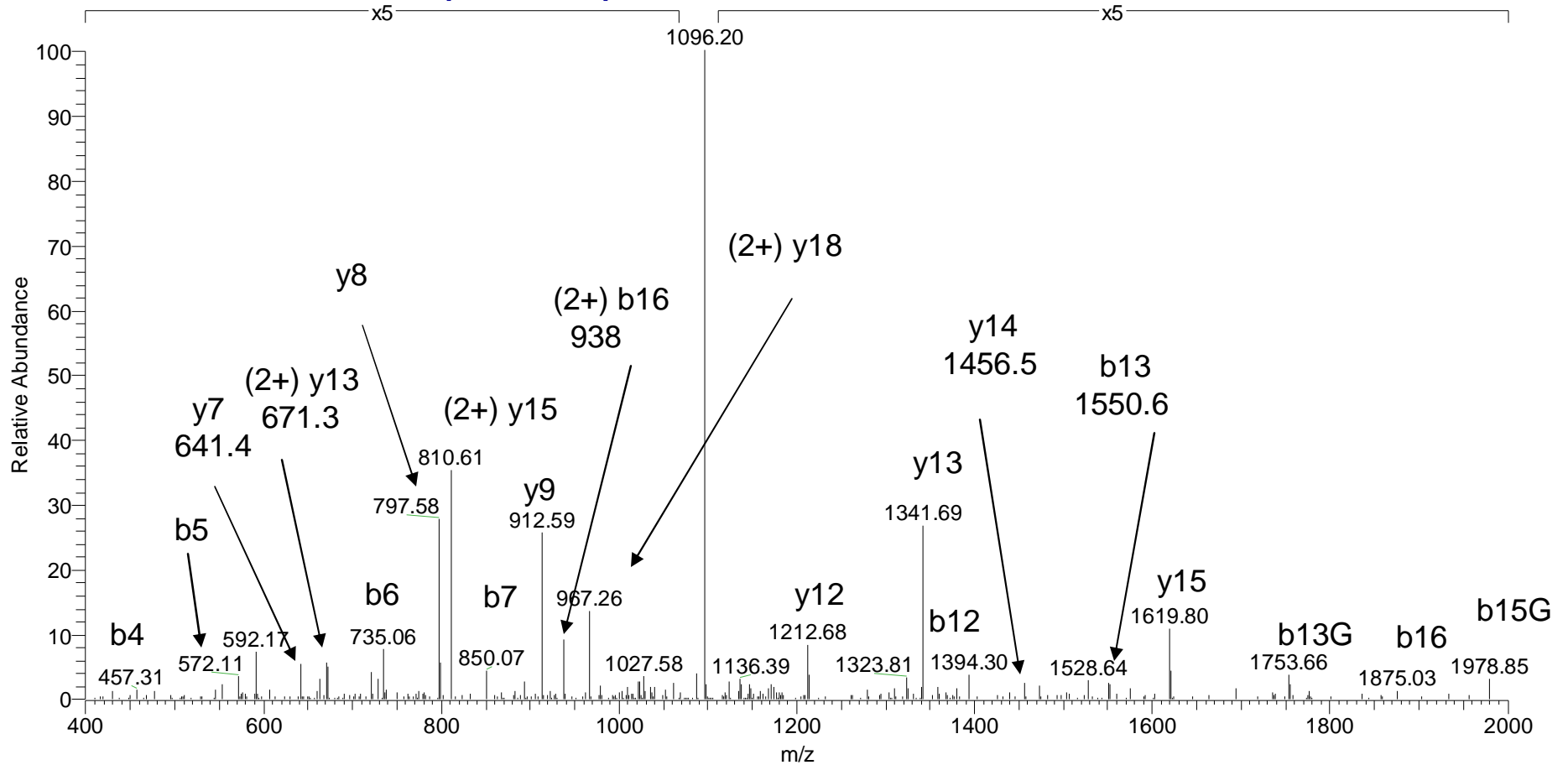
Supplementary Figure 3

P02676 = Fibrinopeptide B (Fibrinogen beta chain precursor)

1197.5413 (2+)

T8102002 #2909 RT: 32.51 AV: 1 NL: 3.67E4
T: ITMS + c NSI d Full ms2 1198.04 @cid35.00 [315.00-2000.00]

(2+) -GalNAc



$^1\text{Q}(\text{Gln} \rightarrow \text{pyro-Glu})\text{FPT}(\text{GalNAc})\text{DYDEGQDDRPKVGLGA}^{20}$

CID spectrum!

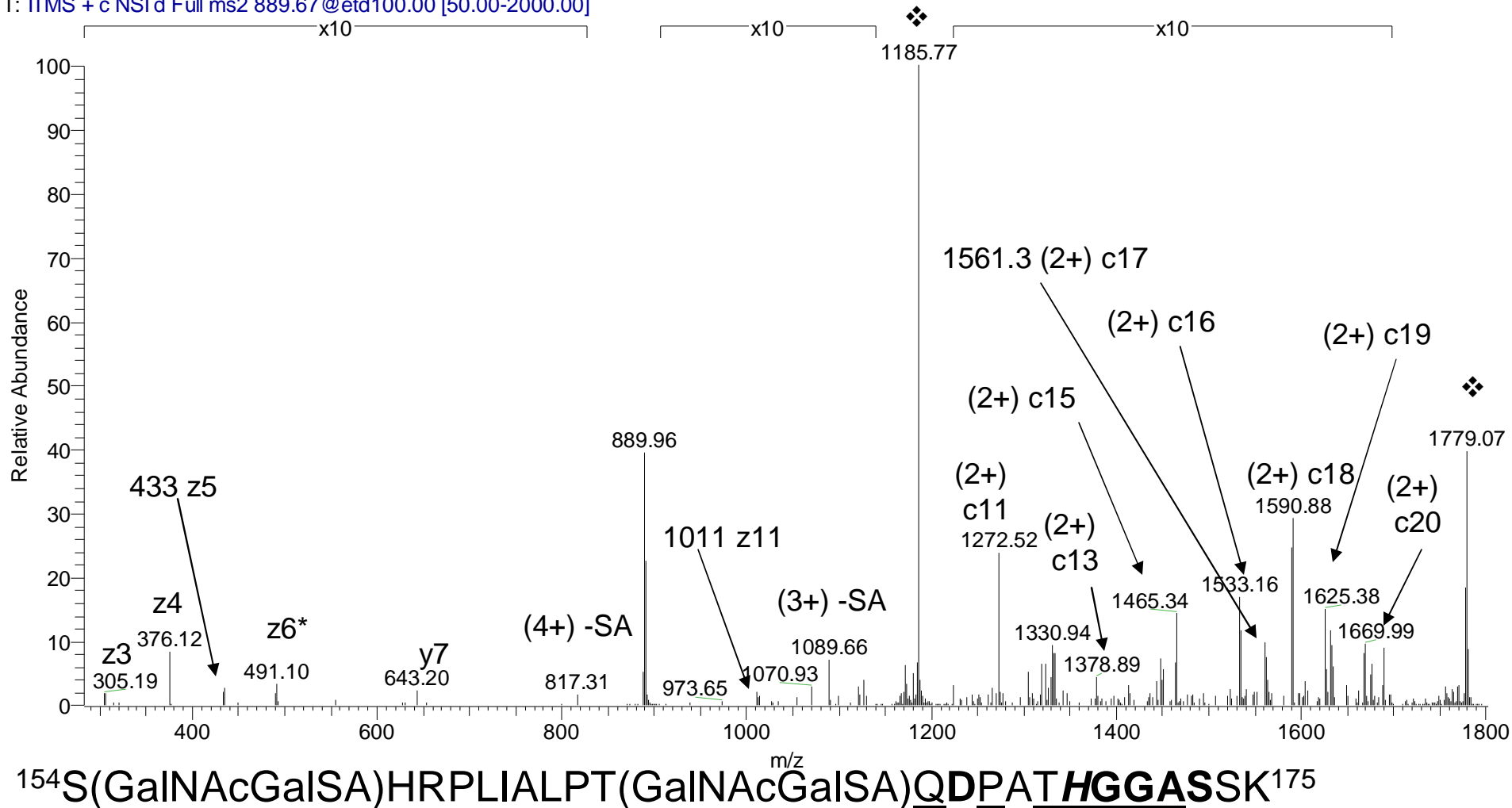
Supplementary Figure 4

P07456 = Insulin-like growth factor II

889.1648 (4+)

T8110314 #1981 RT: 29.45 AV: 1 NL: 3.36E4

T: ITMS + c NSI d Full ms2 889.67@etd100.00 [50.00-2000.00]

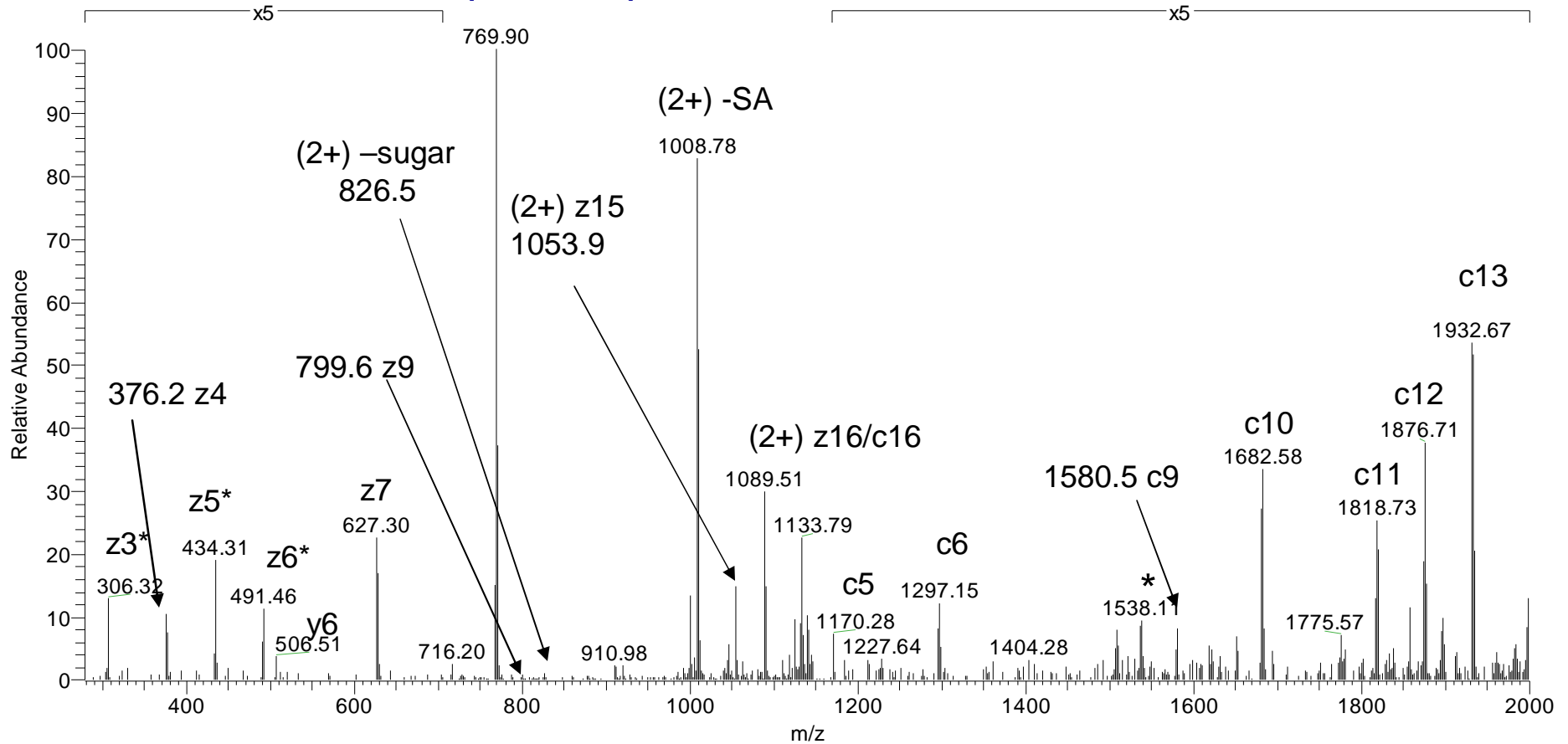


Supplementary Figure 5

P07456 = Insulin-like growth factor II

769.6972 (3+)

Katalin_Szuszanna_55 #2411 RT: 27.73 AV: 1 NL: 3.38E3
T: ITMS + c NSI d sa Full ms2 770.03@etd90.00 [150.00-2000.00]

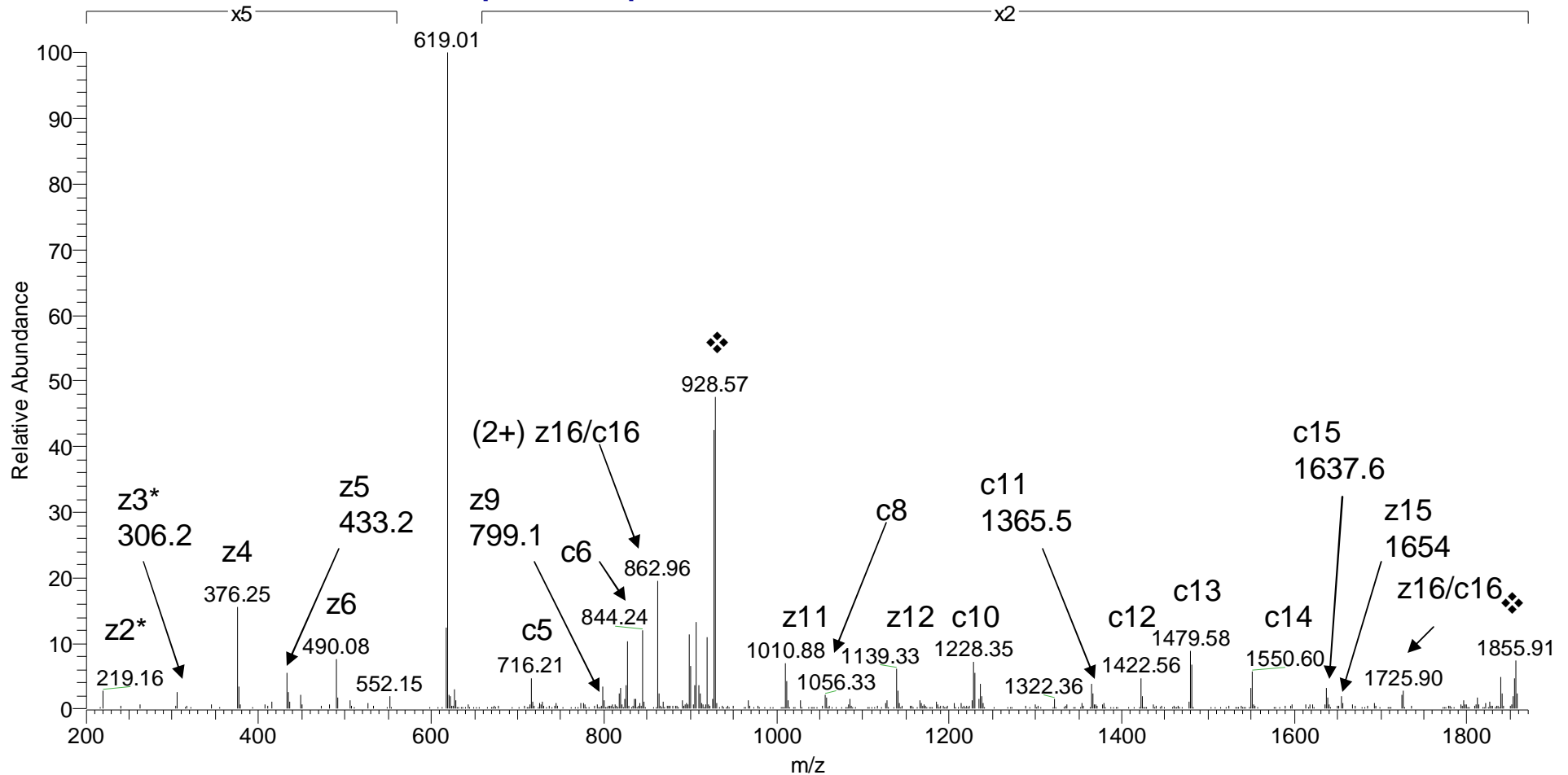


¹⁵⁹IALPT(GalNAcGalSA)QDPATHGGASSK¹⁷⁵

P07456 = Insulin-like growth factor II

618.6443 (3+)

T8102002 #1686 RT: 23.29 AV: 1 NL: 2.85E4
T: ITMS + c NSI d sa Full ms2 618.98@etd100.00 [50.00-1870.00]



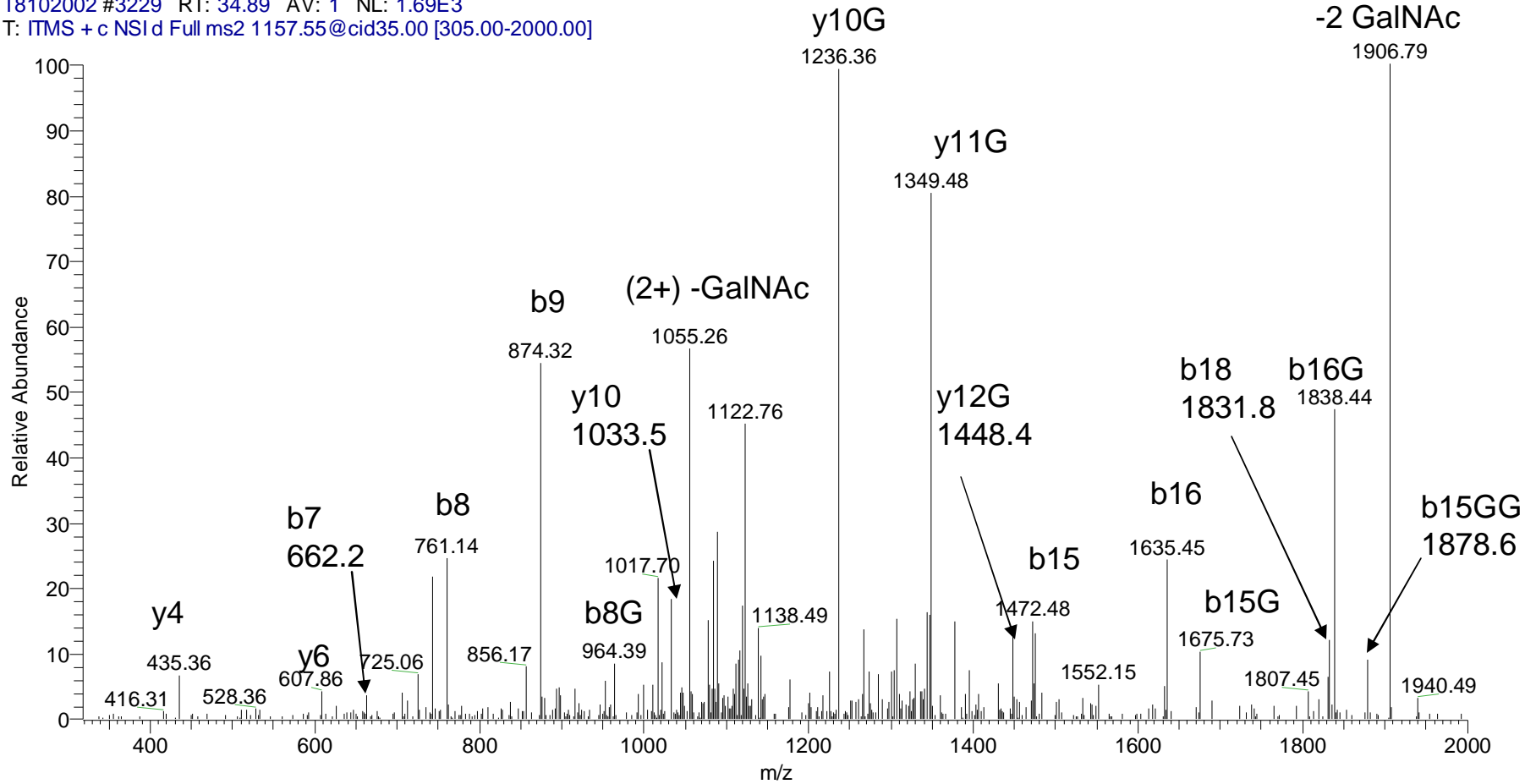
¹⁵⁹IALPT(GalNAc)QDPATHGGASSK¹⁷⁵

Supplementary Figure 7

P07456 = Insulin-like growth factor II

1157.0476 (2+)

T8102002 #3229 RT: 34.89 AV: 1 NL: 1.69E3
T: ITMS + c NSI d Full ms2 1157.55@cid35.00 [305.00-2000.00]



$^{93}\text{DVSASTTVLPDDVT}(\text{GalNAc})\text{AYPVG}^{111}+\text{GalNAc}$ CID spectrum!

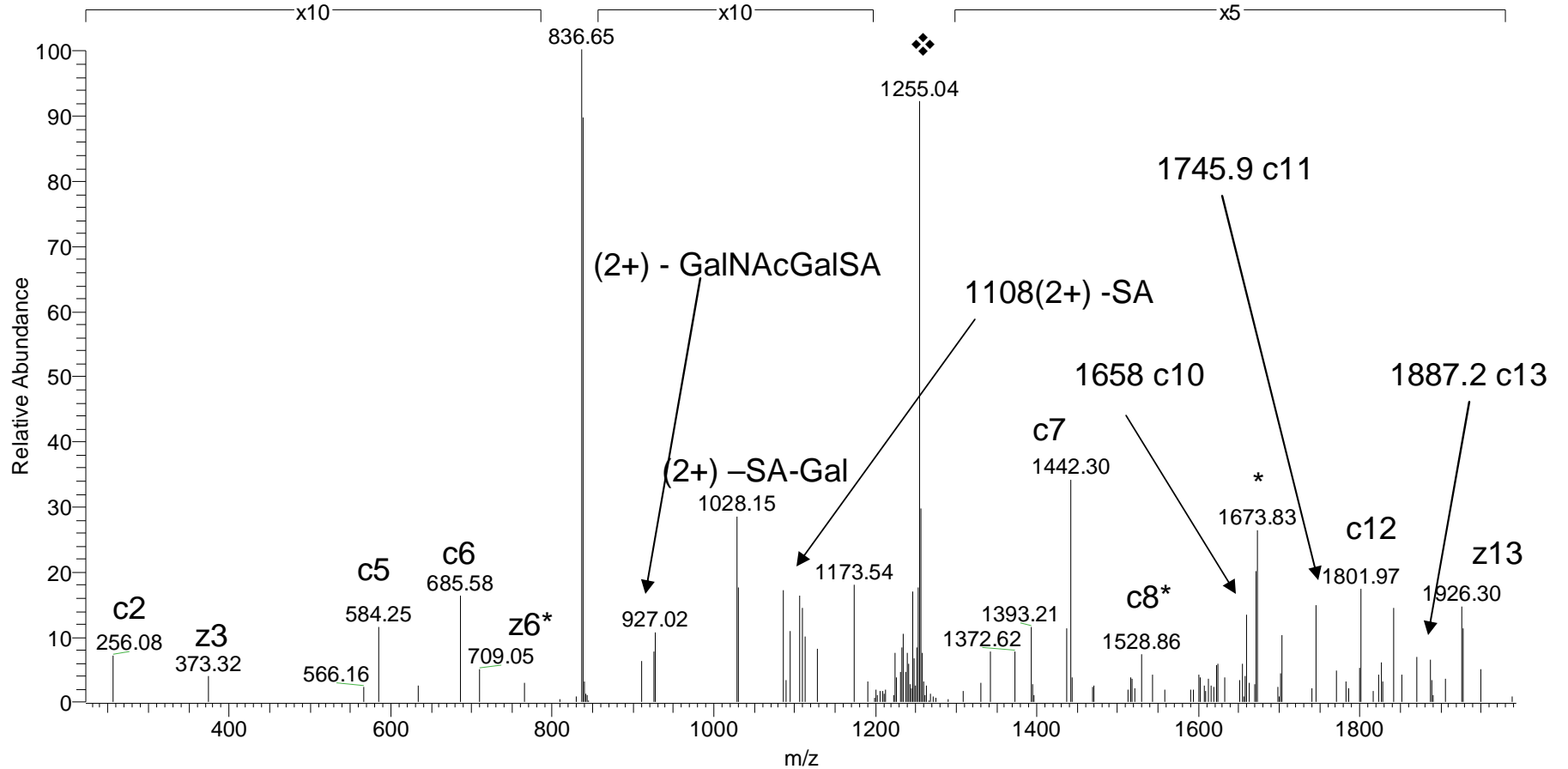
One of Ser-95,-97 or Thr-98,-99

Supplementary Figure 8

P07589 = **Fibronectin**

836.7081 (3+)

T8110316 #1564 RT: 26.02 AV: 1 NL: 1.55E3
T: ITMS + c NSI d Full ms2 837.04 @etd100.00 [50.00-2000.00]

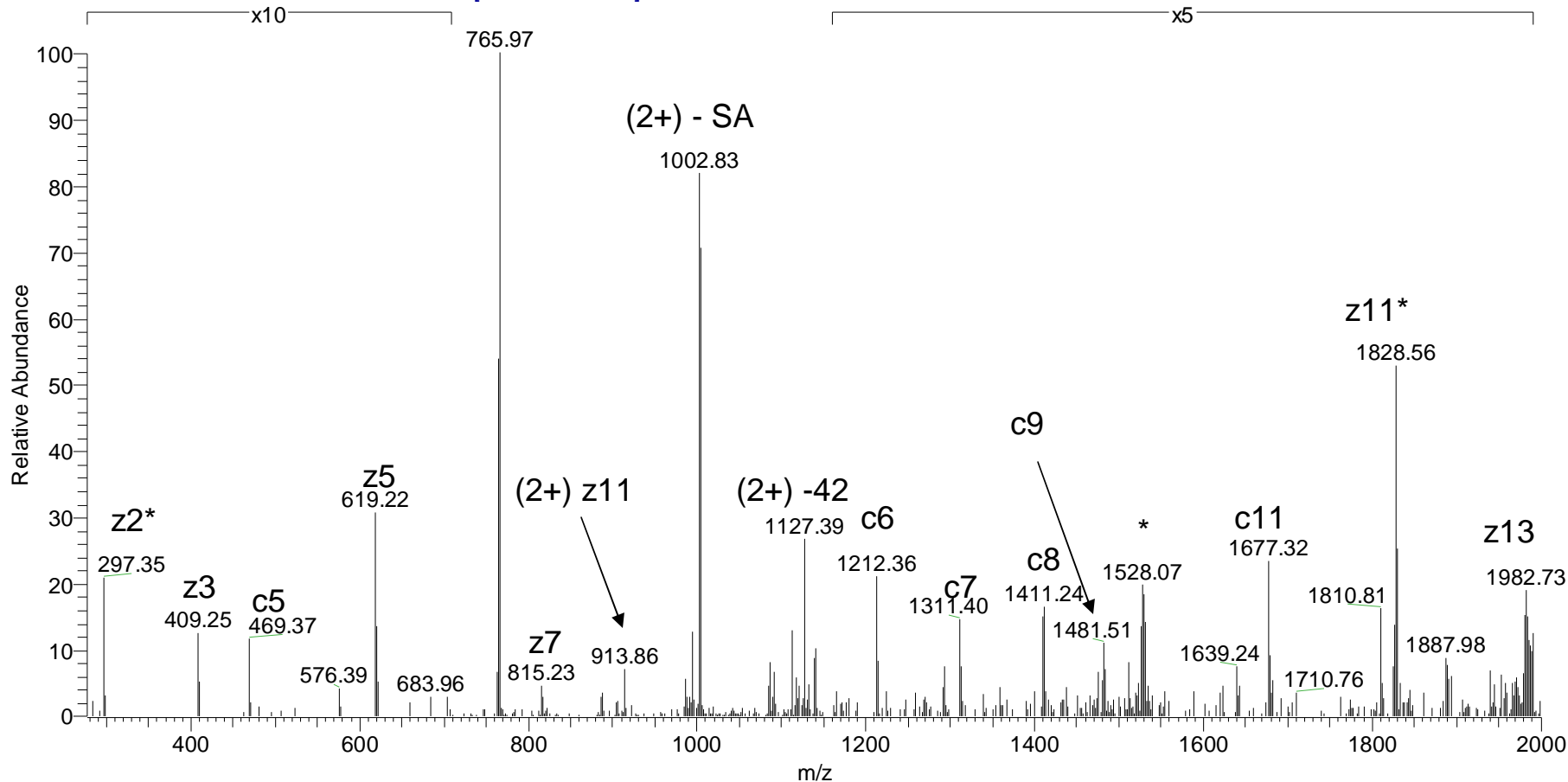


274HTSLQTT(GalNAcGalSA)SAGSGSFTDVR²⁹¹

P12763 = Alpha-2-HS-glycoprotein precursor (Fetuin)

765.7520 (3+)

Katalin_Szuszanna_51 #4649 RT: 51.00 AV: 1 NL: 1.47E3
T: ITMS + c NSI d sa Full ms2 766.09@etd90.00 [150.00-2000.00]



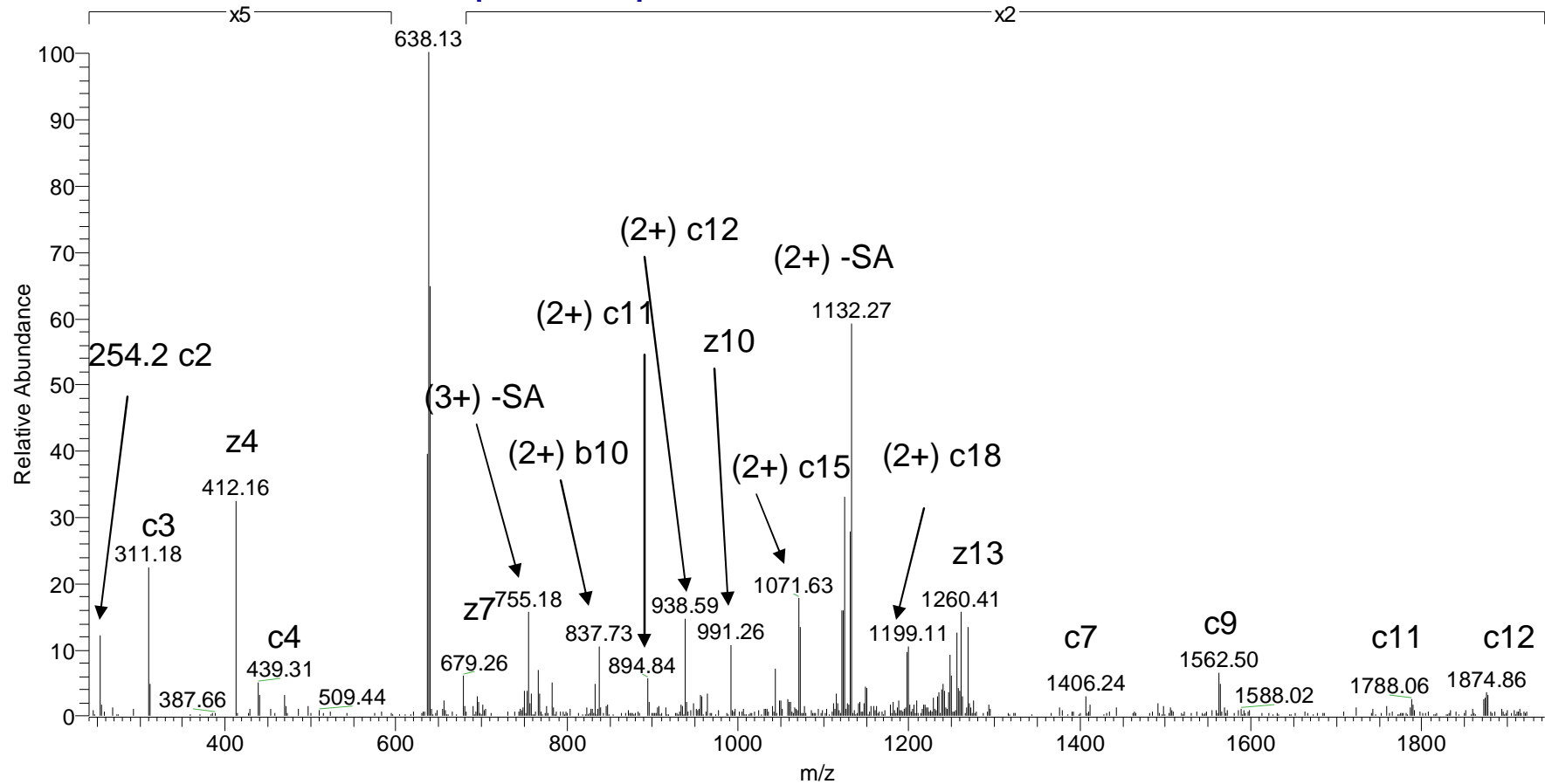
291VVVGPS(GalNAcGalSA)VVAVPLPLHR306

Supplementary Figure 10

P12763 = Alpha-2-HS-glycoprotein precursor (Fetuin)

638.8342(4+)

Katalin_Szuszanna_57 #2427 RT: 29.47 AV: 1 NL: 2.42E3
 T: ITMS + c NSI d sa Full ms2 639.08@etd90.00 [150.00-2000.00]

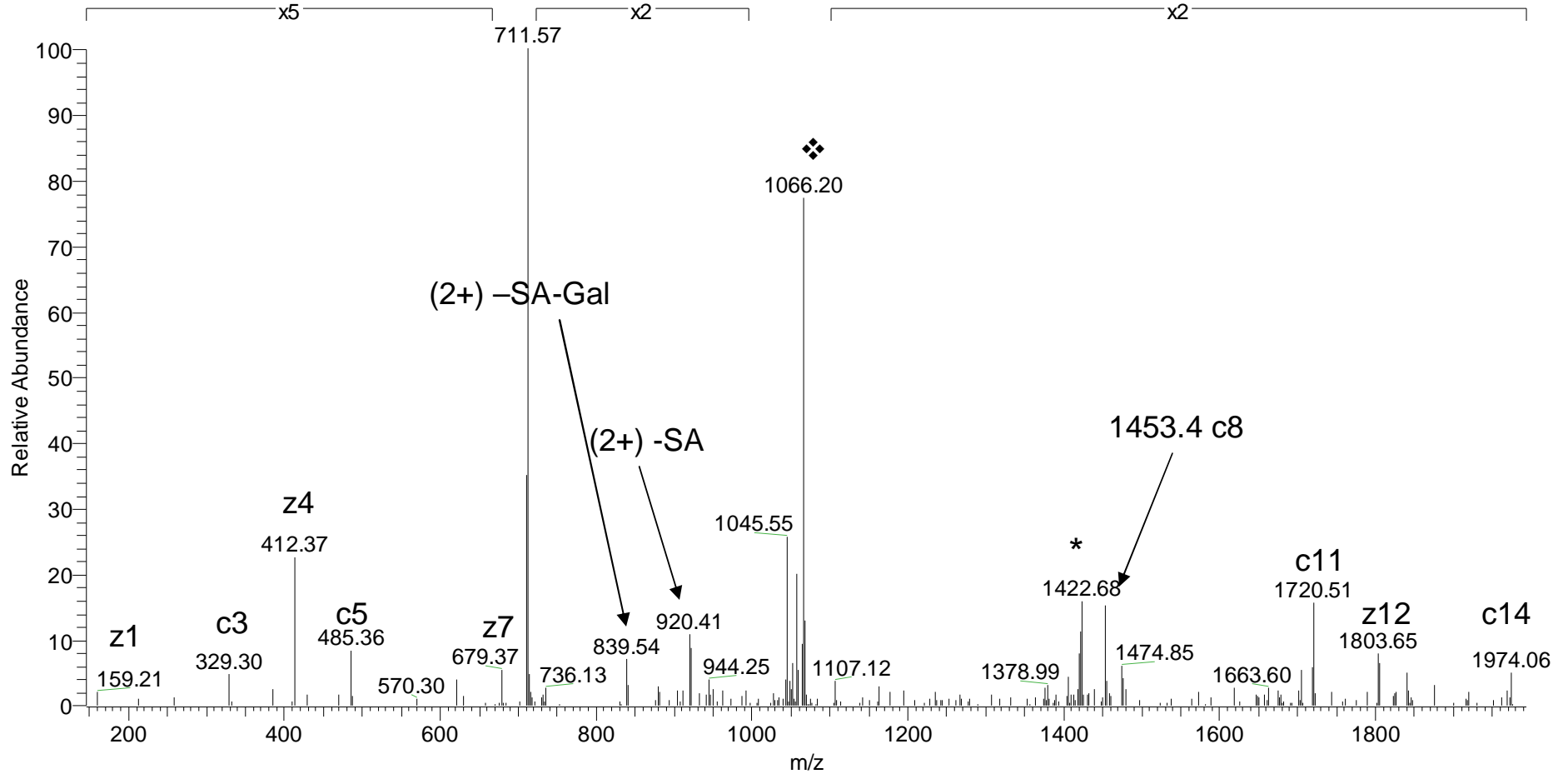


³³⁰HVGKT(GaINAcGalSA)PIVGQPSIPGGPVR³⁴⁸

P12763 = Alpha-2-HS-glycoprotein precursor (Fetuin)

711.0283 (3+)

T8110311 #1907 RT: 31.25 AV: 1 NL: 2.84E3
T: ITMS + c NSI d Full ms2 711.36@etd100.00 [50.00-2000.00]



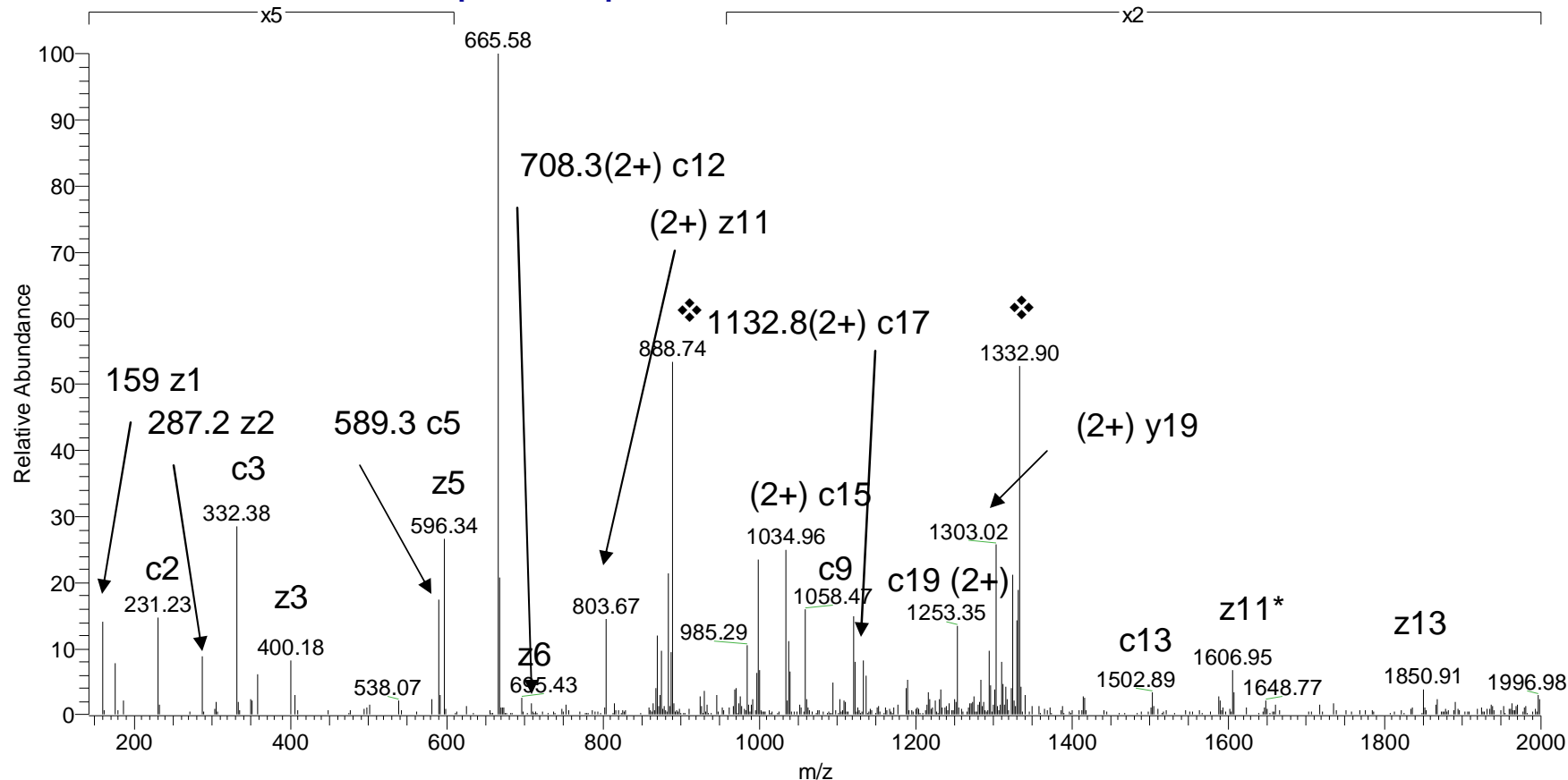
334 TPIVGQPS(GalNAcGalSA)IPGGPVR 341

Supplementary Figure 12

P17690 = Beta-2-glycoprotein 1 precursor

666.3536(4+)

T8110316 #2419 RT: 32.19 AV: 1 NL: 6.77E3
 T: ITMS + c NSI d Full ms2 666.60@etd100.00 [50.00-2000.00]

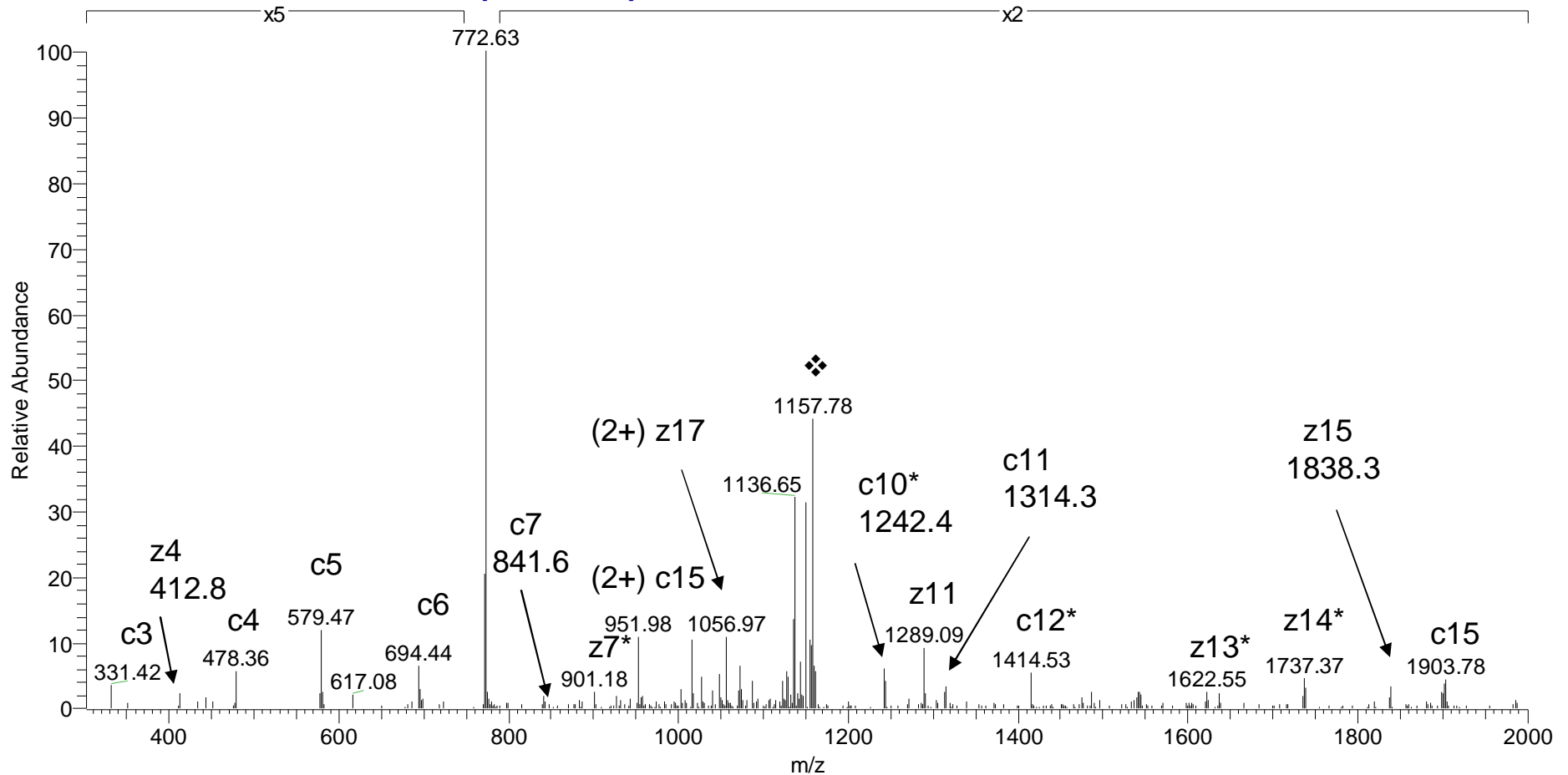


²⁰GRTC(Carbamidomethyl)PKPDELPFST(GalNAcGal)VVPLKR³⁹

P19035 = Apolipoprotein C-III precursor

772.0337 (3+)

T8102002 #2961 RT: 32.90 AV: 1 NL: 1.88E4
T: ITMS + c NSI d sa Full ms2 772.37@etd100.00 [50.00-2000.00]



⁷⁸KGKFTDFWESATSPT(GaINAc)QSPP⁹⁶

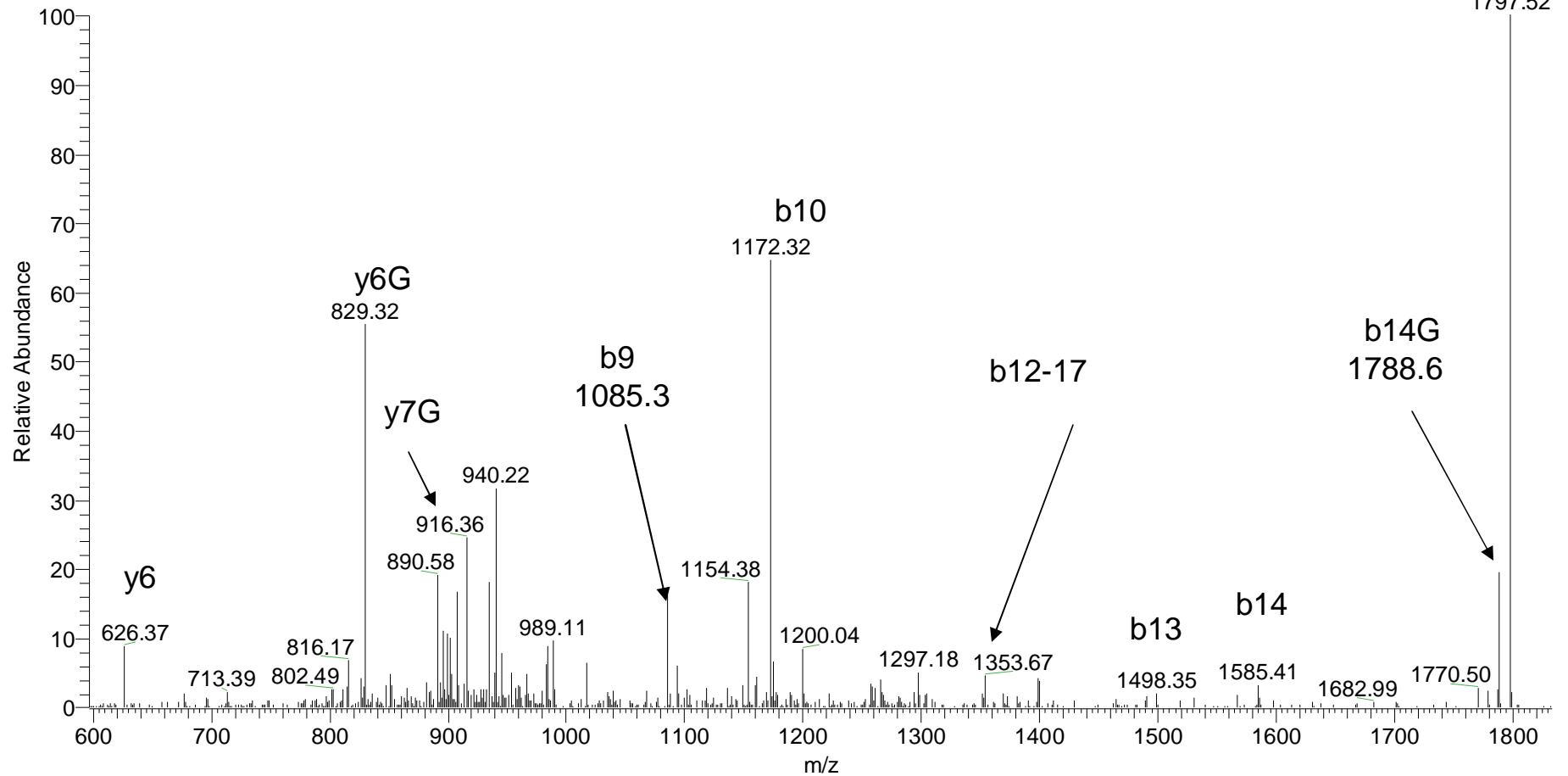
Ser-90 or Thr-92

Supplementary Figure 14

P19035 = Apolipoprotein C-III precursor

1000.9410 (2+)

T8102002 #3522 RT: 37.05 AV: 1 NL: 1.94E4
T: ITMS + c NSI d Full ms2 1001.44@cid35.00 [265.00-2000.00]



$^{78}\text{FTDFWESATSPTQSP}^{96} + \text{GalNAc}$

Thr-92 or Ser-94

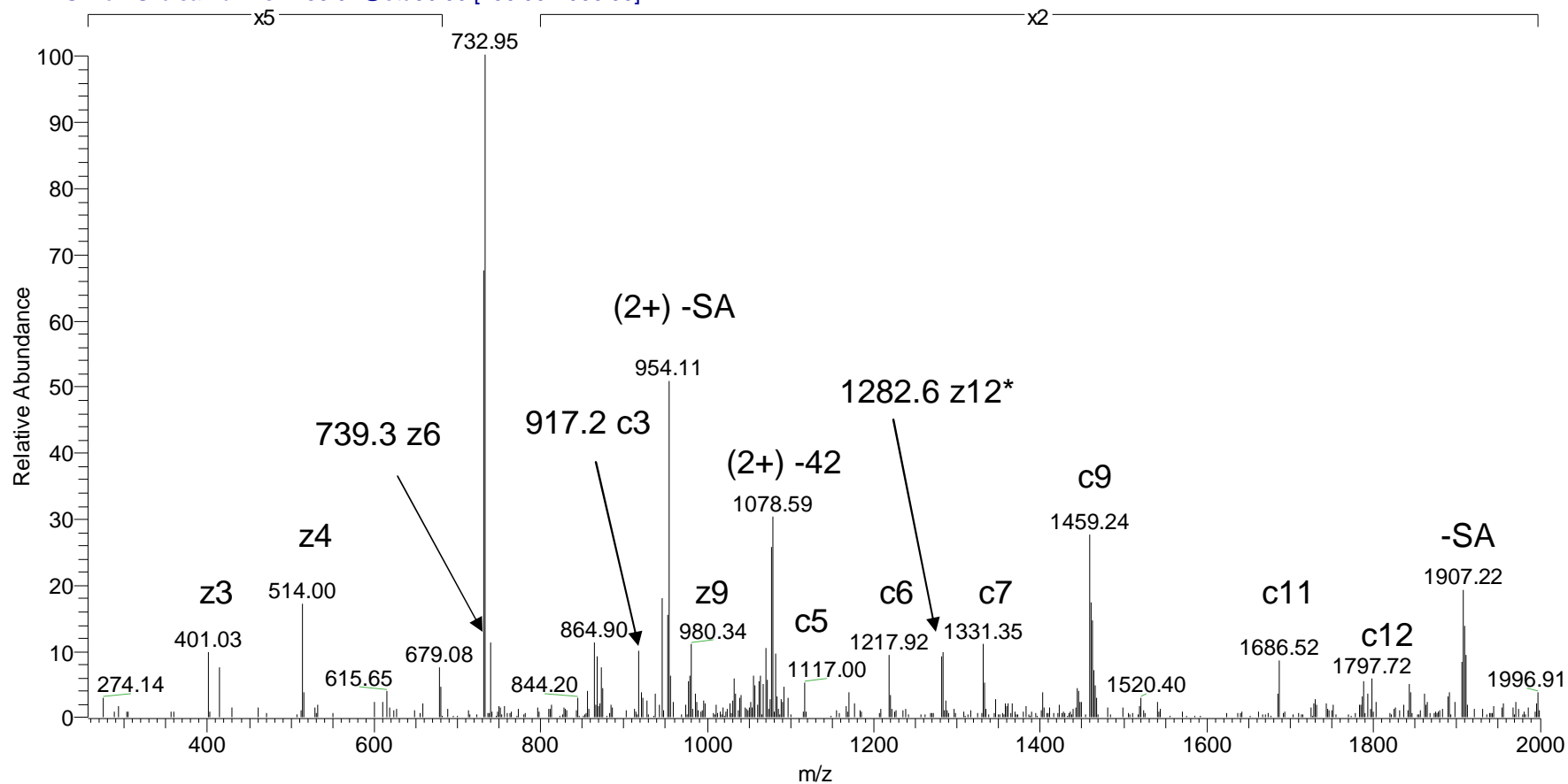
CID spectrum!

Supplementary Figure 15

Q03247 = Apolipoprotein E precursor

733.0369 (3+)

Katalin_Szuszanna_49 #4261 RT: 47.22 AV: 1 NL: 1.19E3
T: ITMS + c NSI d sa Full ms2 733.04@etd90.00 [150.00-2000.00]

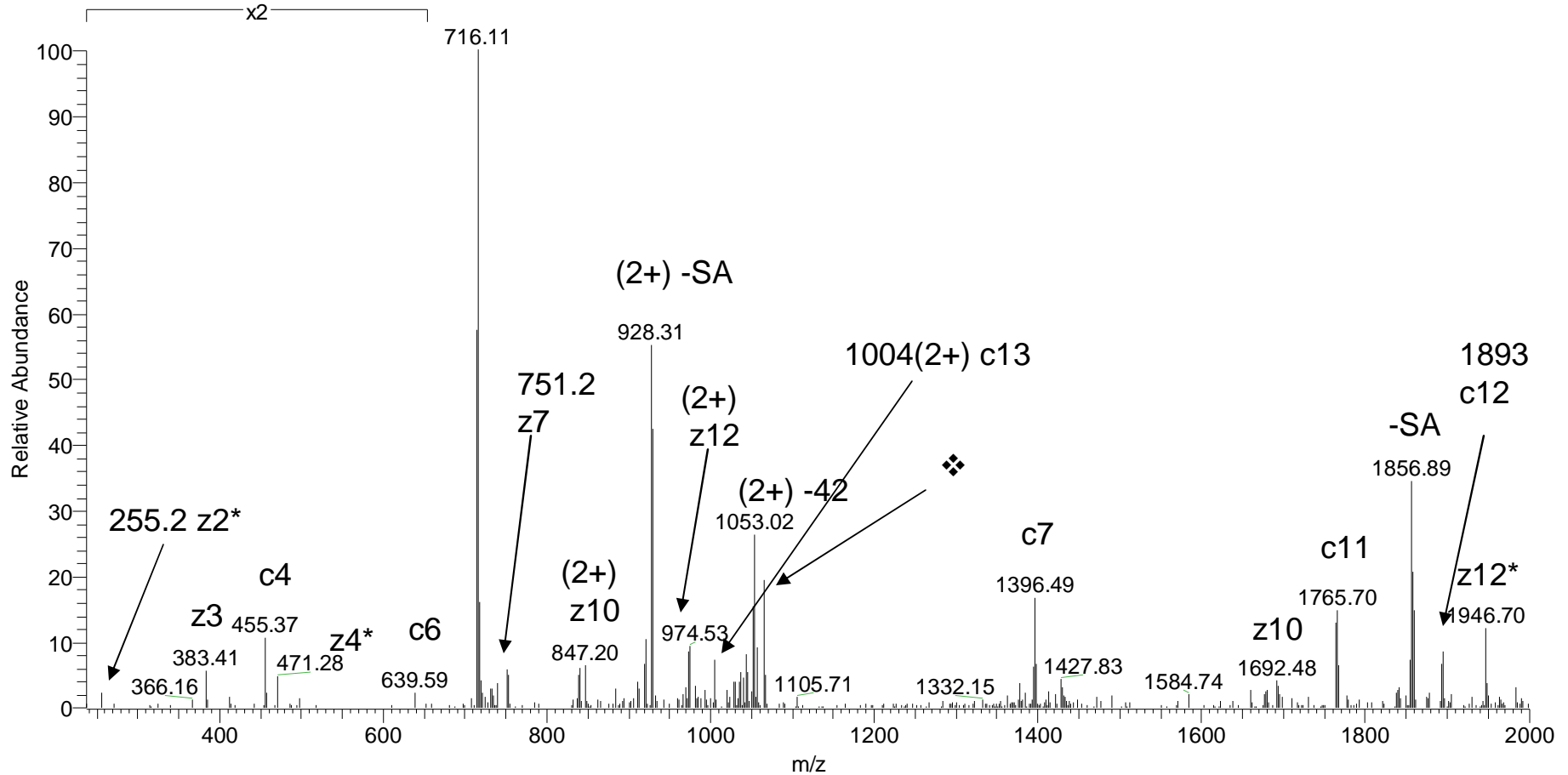


²⁰⁹AAT(GaINAcGalSA)LSTLAGQPLLER²²³

Q03247 = Apolipoprotein E precursor

Katalin_Szuszanna_55 #1170 RT: 14.29 AV: 1 NL: 8.23E2
T: ITMS + c NSI d sa Full ms2 716.33@etd90.00 [150.00-2000.00]

715.9969 (3+)



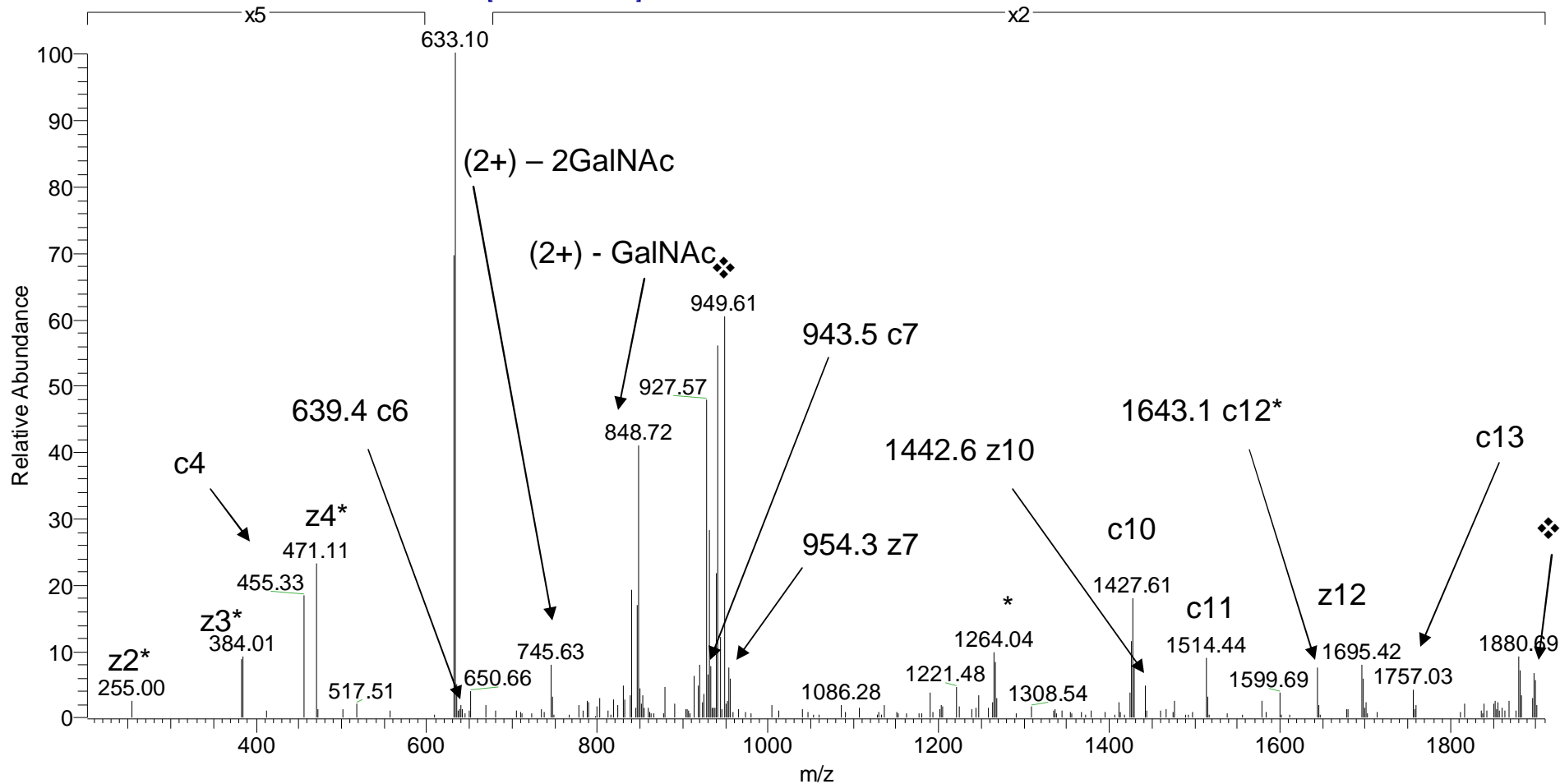
303 ALRSPT(GalNAcGalSA)SPPSENH 316

Supplementary Figure 17

Q03247 = Apolipoprotein E precursor

632.6347 (3+)

T8102002 #997 RT: 17.45 AV: 1 NL: 2.56E3
T: ITMS + c NSI d sa Full ms2 632.97@etd100.00 [50.00-1910.00]



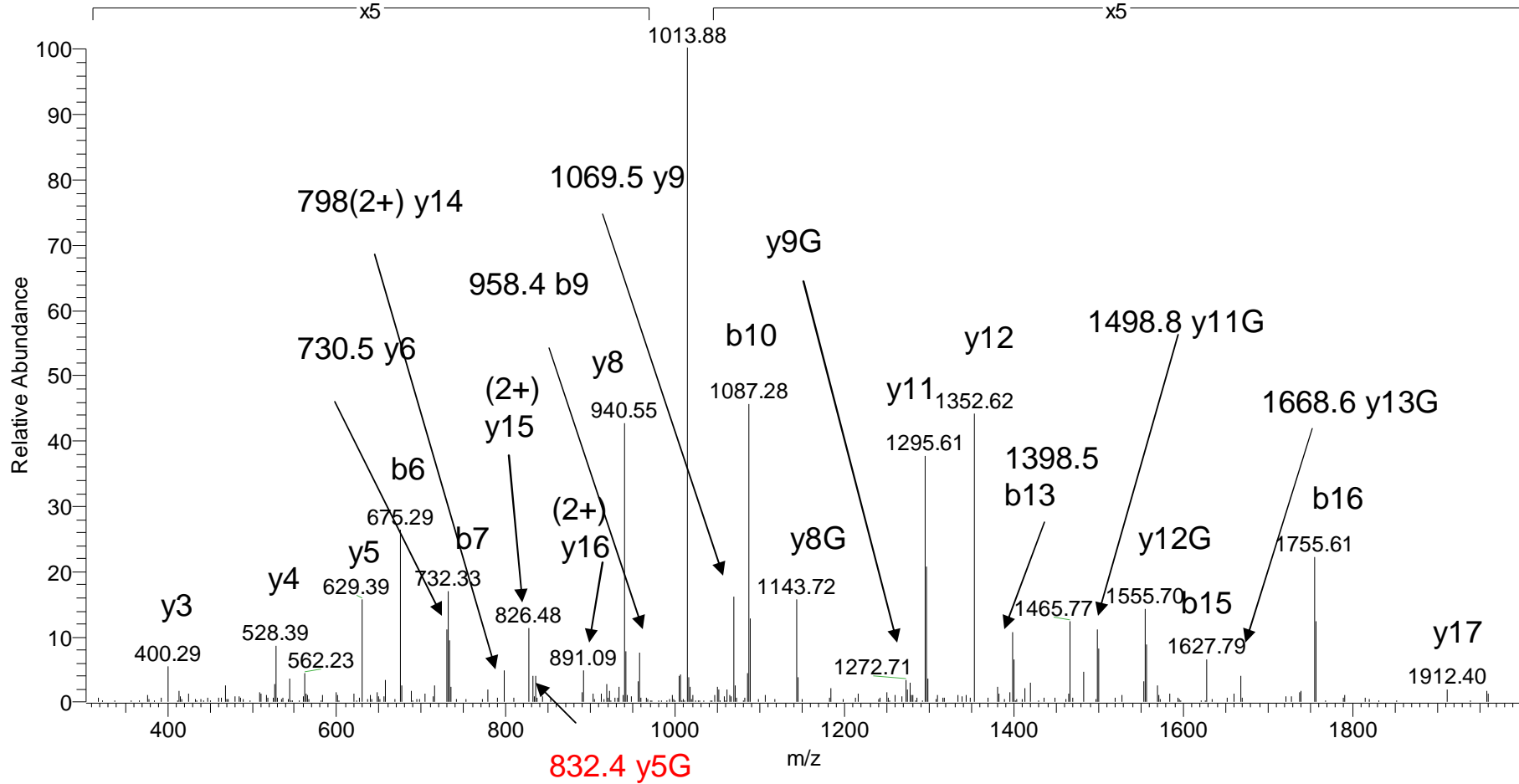
$^{303}\text{ALRPSPT}(\text{GalNAc})\text{S}(\text{GalNAc})\text{PPSENH}^{316}$

Supplementary Figure 18

Q03247 = Apolipoprotein E precursor

1115.5117 (2+)

T8102002 #2491 RT: 29.37 AV: 1 NL: 2.99E4
T: ITMS + c NSI d Full ms2 1116.01@cid35.00 [295.00-2000.00]



$^{19}\text{DMEGELGPEEPLTT(GaINAc)QQPR}^{36}$

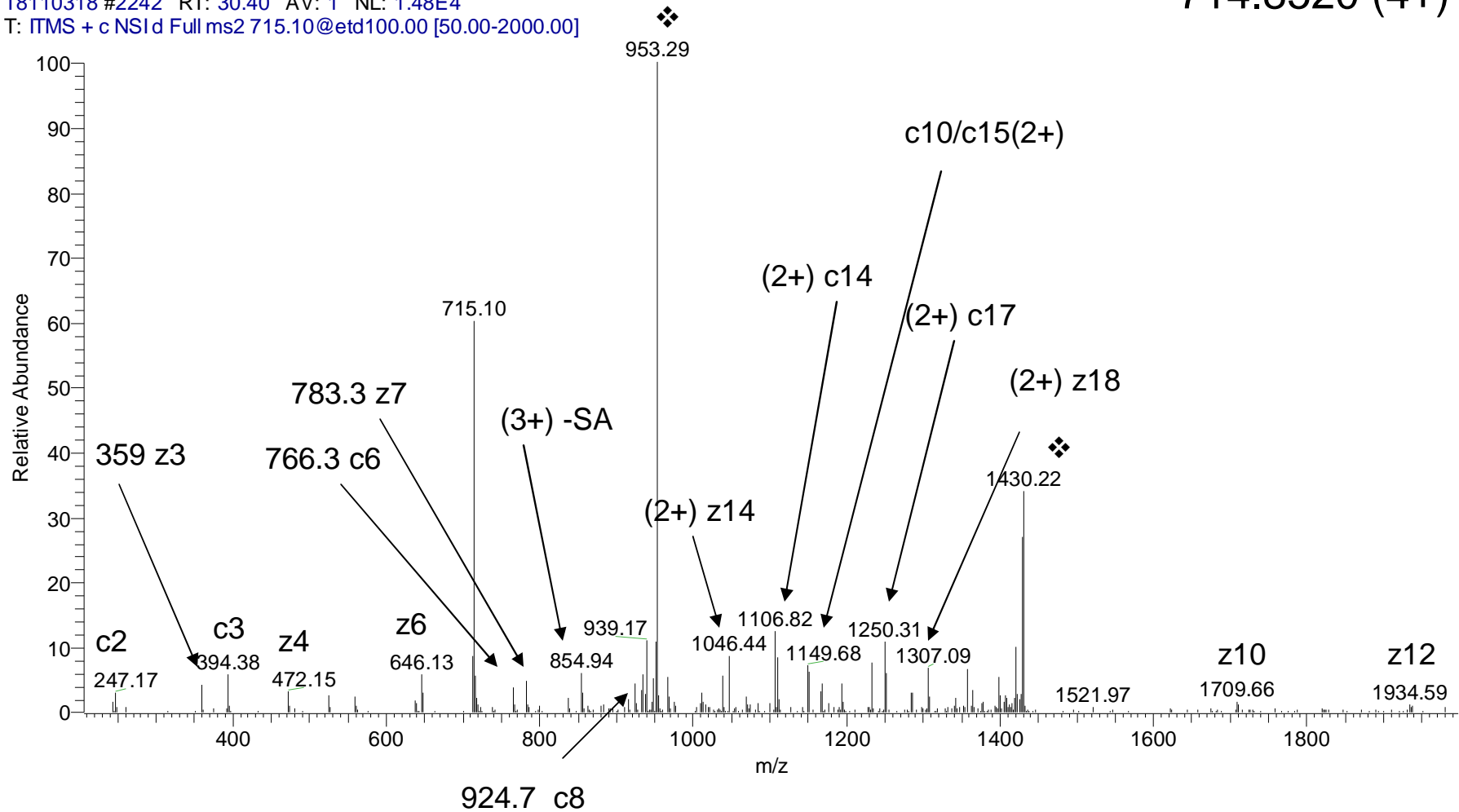
CID spectrum!

Supplementary Figure 19

Q0VCM5 = Inter-alpha-trypsin inhibitor heavy chain H1 precursor

T8110318 #2242 RT: 30.40 AV: 1 NL: 1.48E4
T: ITMS + c NSI d Full ms2 715.10@etd100.00 [50.00-2000.00]

714.8520 (4+)



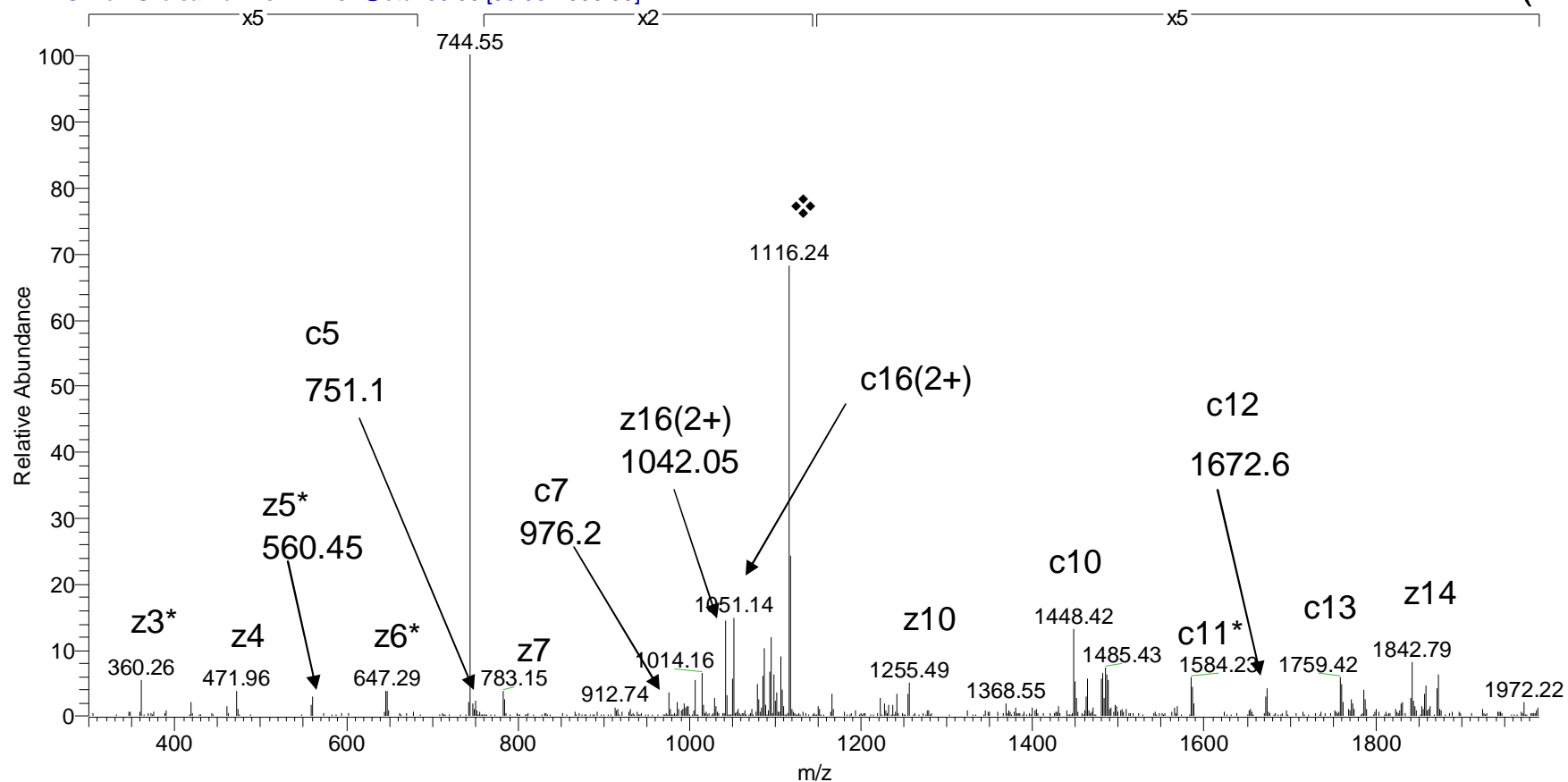
⁶³⁶KTFMLQASQPAPT(GaNAcGalSA)HSSLDIK⁶⁵⁵

Supplementary Figure 20

Q0VCM5 = Inter-alpha-trypsin inhibitor heavy chain H1 precursor

T8102002 #1799 RT: 24.16 AV: 1 NL: 6.12E4
T: ITMS + c NSI d sa Full ms2 744.37@etd100.00 [50.00-2000.00]

744.0329 (3+)



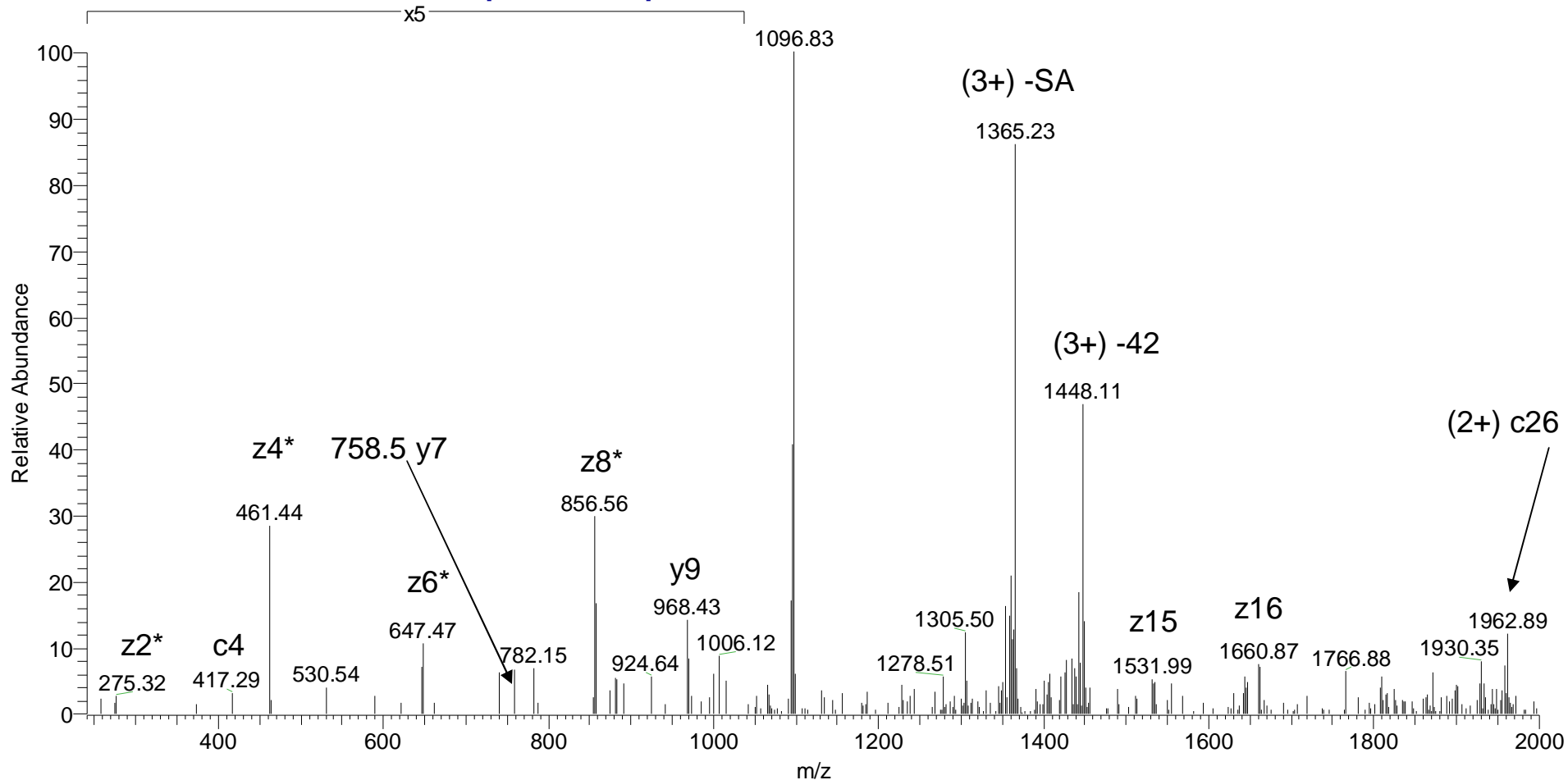
⁶³⁹MLQAS(GaINAc)QPAPT(GaINAc)HSSLDIK⁶⁵⁵

Supplementary Figure 21

Q3T052 = Inter-alpha-trypsin inhibitor heavy chain H4 precursor

1096.5561 (4+)

Katalin_Szuszanna_53 #6202 RT: 66.98 AV: 1 NL: 3.81E2
T: ITMS + c NSI d sa Full ms2 1097.31 @etd90.00 [150.00-2000.00]



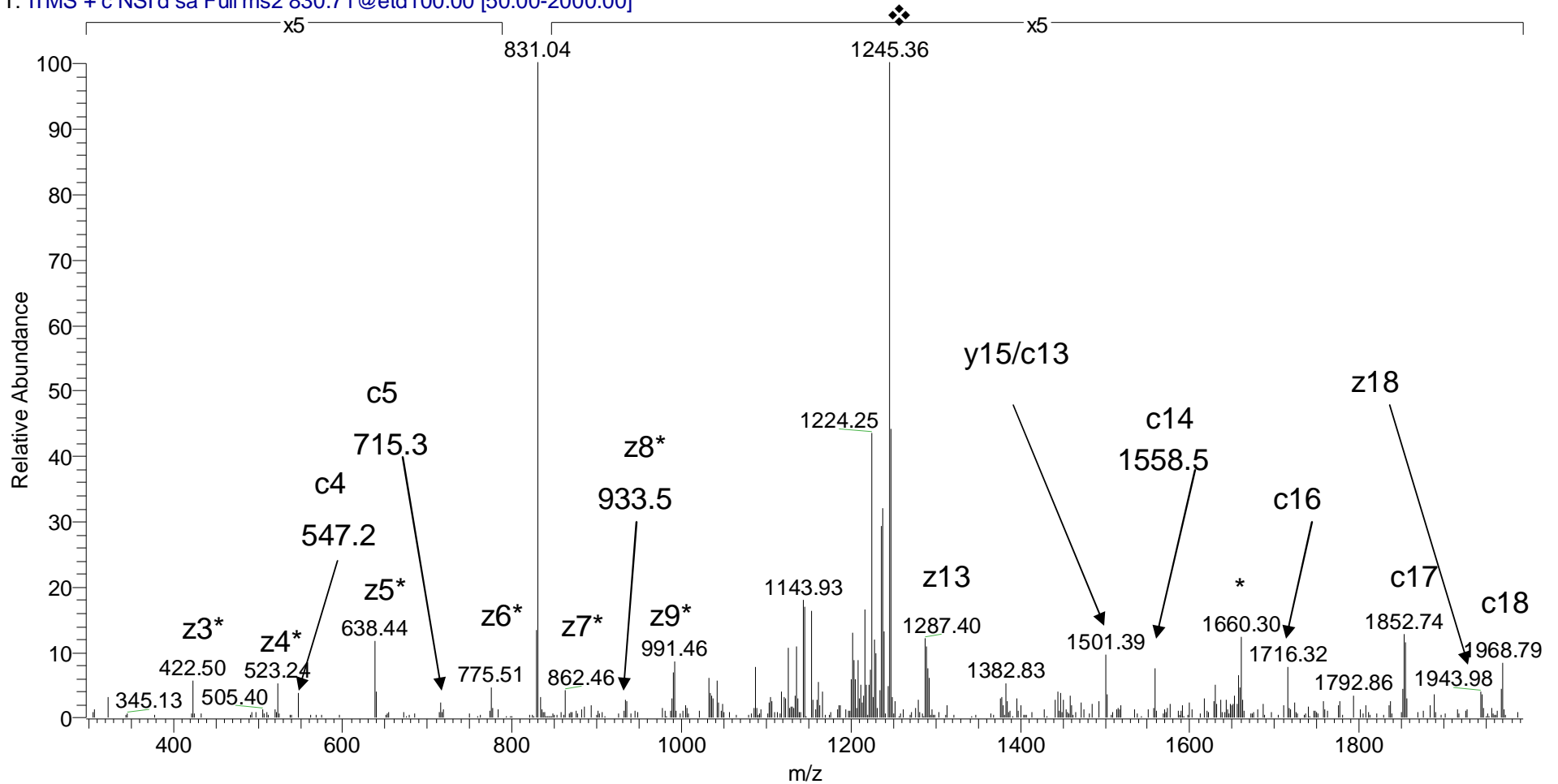
⁷⁰²IKGIT(GaINAcGaISA)PT(GaINAcGaISA)ALPFAPVQAPSVILPLPGQSVDR⁷³¹

Supplementary Figure 22

Q3T052 = Inter-alpha-trypsin inhibitor heavy chain H4 precursor

830.3722 (3+)

T8102002 #1402 RT: 21.10 AV: 1 NL: 1.05E4
T: ITMS + c NSI d sa Full ms2 830.71 @etd100.00 [50.00-2000.00]



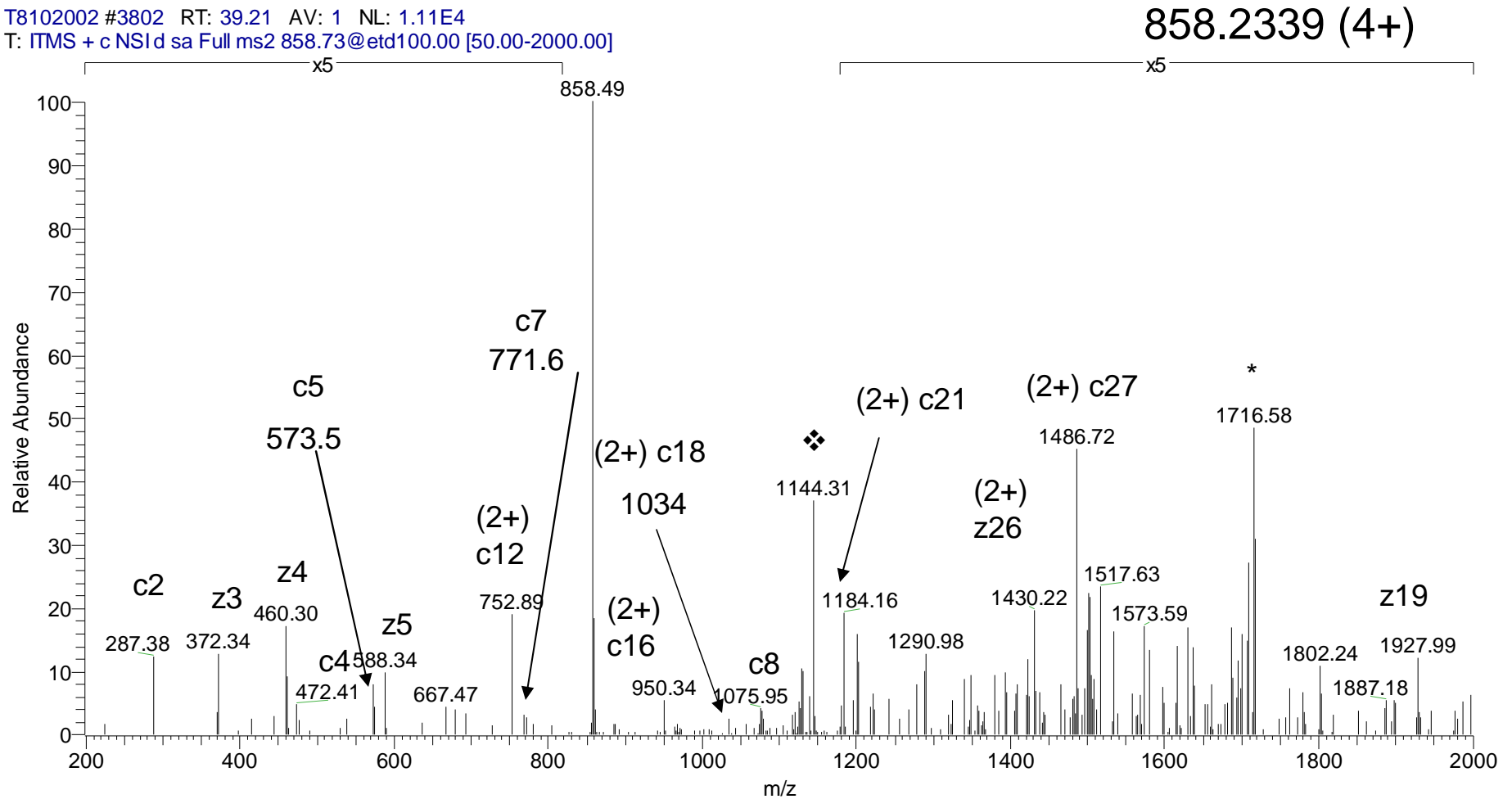
⁶⁸⁰APAS(GaINAc)APS(GaINAc)PTSGPGGASHDTDFR⁷⁰¹

Ser-683 & Ser-686 or Thr-688

Supplementary Figure 23

Q3T052 = Inter-alpha-trypsin inhibitor heavy chain H4 precursor

T8102002 #3802 RT: 39.21 AV: 1 NL: 1.11E4
T: ITMS + c NSI d sa Full ms2 858.73@etd100.00 [50.00-2000.00]

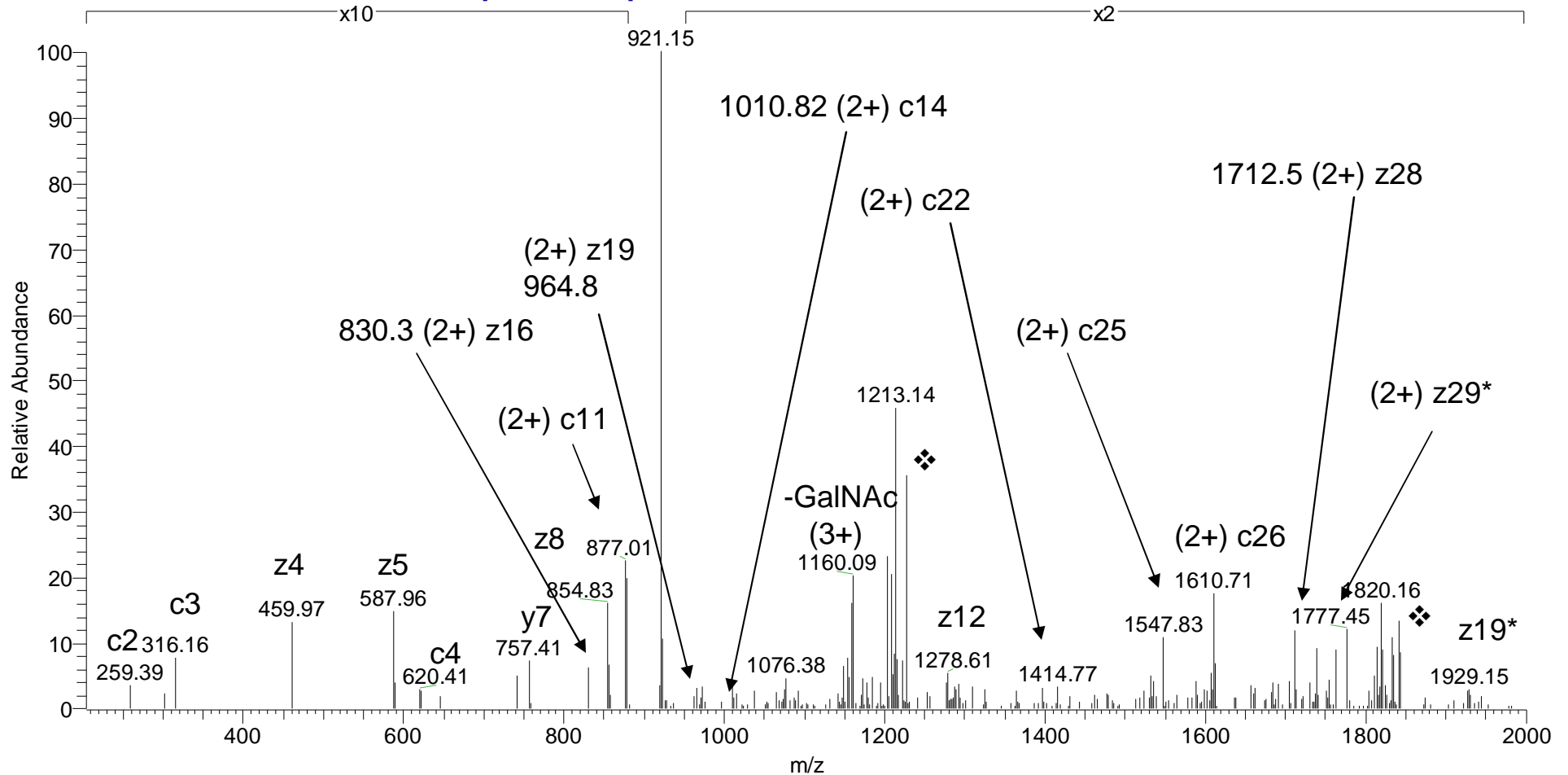


701RIKGTTPT(GaNAc)ALPFAPVQAPSVILPLPGQSVDR731

Q3T052 = Inter-alpha-trypsin inhibitor heavy chain H4 precursor

920.7469 (4+)

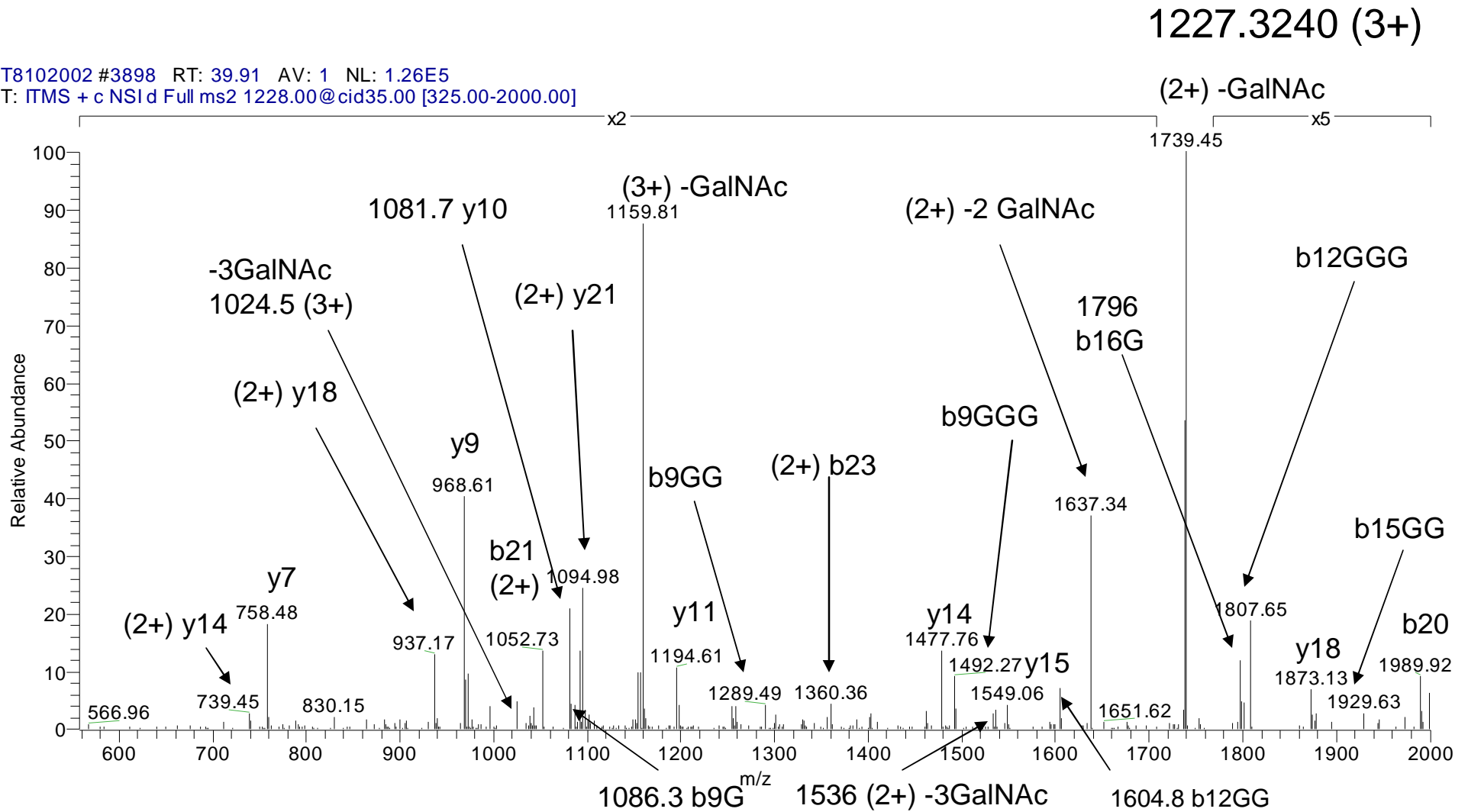
T8102002 #3913 RT: 40.02 AV: 1 NL: 4.67E4
T: ITMS + c NSI d sa Full ms2 921.25@etd100.00 [50.00-2000.00]



⁷⁰²IKGT(GalNAc)T(GalNAc)PT(GalNAc)ALPFAPVQAPSVILPLPGQSVDR⁷³¹

Q3T052 = Inter-alpha-trypsin inhibitor heavy chain H4 precursor

T8102002 #3898 RT: 39.91 AV: 1 NL: 1.26E5
 T: ITMS + c NSI d Full ms2 1228.00@cid35.00 [325.00-2000.00]



⁷⁰²IKGT(GalNAc)T(GalNAc)PT(GalNAc)ALPFAPVQAPSVILPLPGQSVD⁷³¹

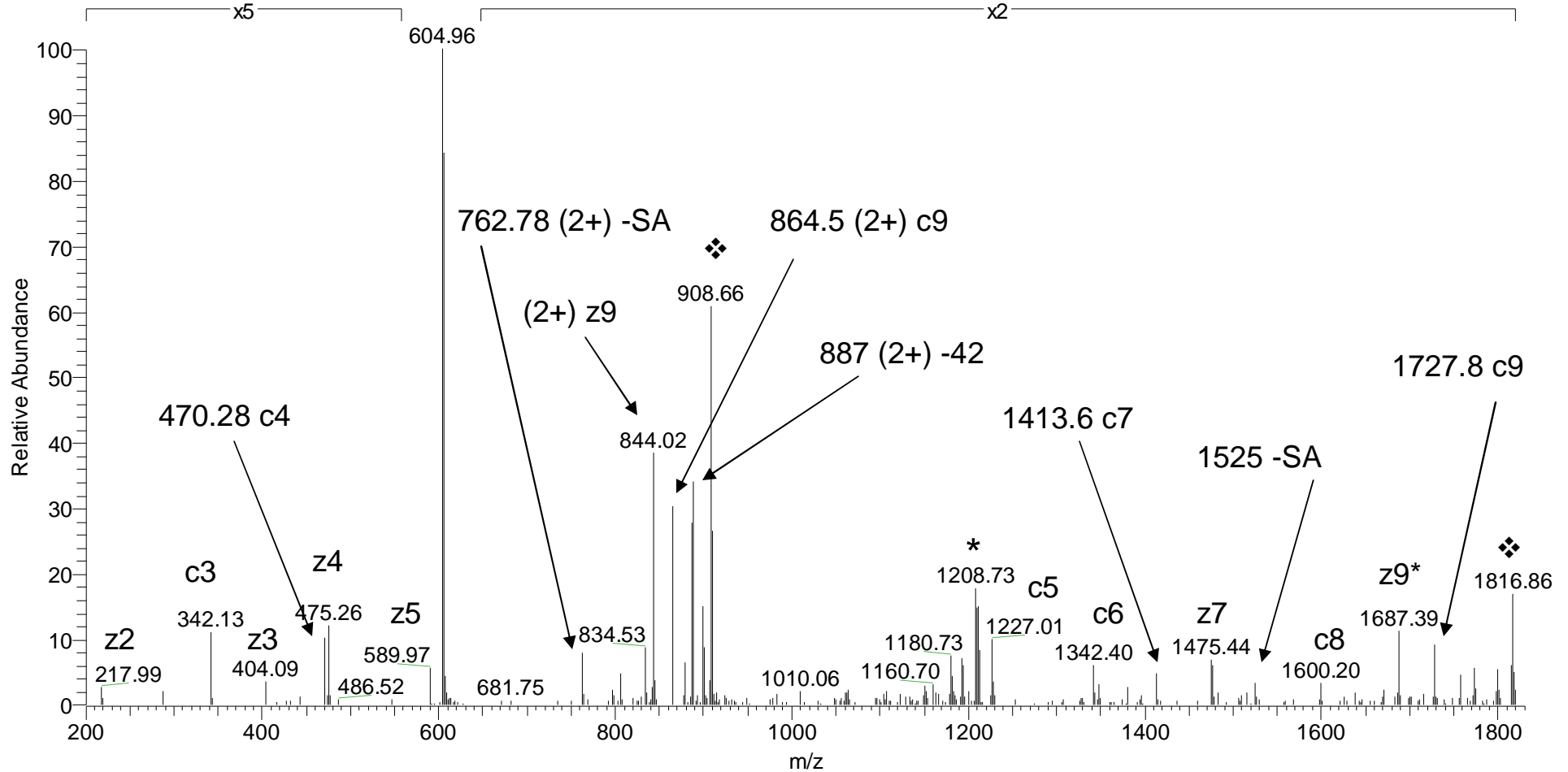
CID spectrum!

Supplementary Figure 26

Q58CQ9 = Pantetheinase precursor

605.9525 (3+)

T8110317 #1201 RT: 22.88 AV: 1 NL: 3.85E3
T: ITMS + c NSI d Full ms2 605.95@etd100.00 [50.00-1830.00]

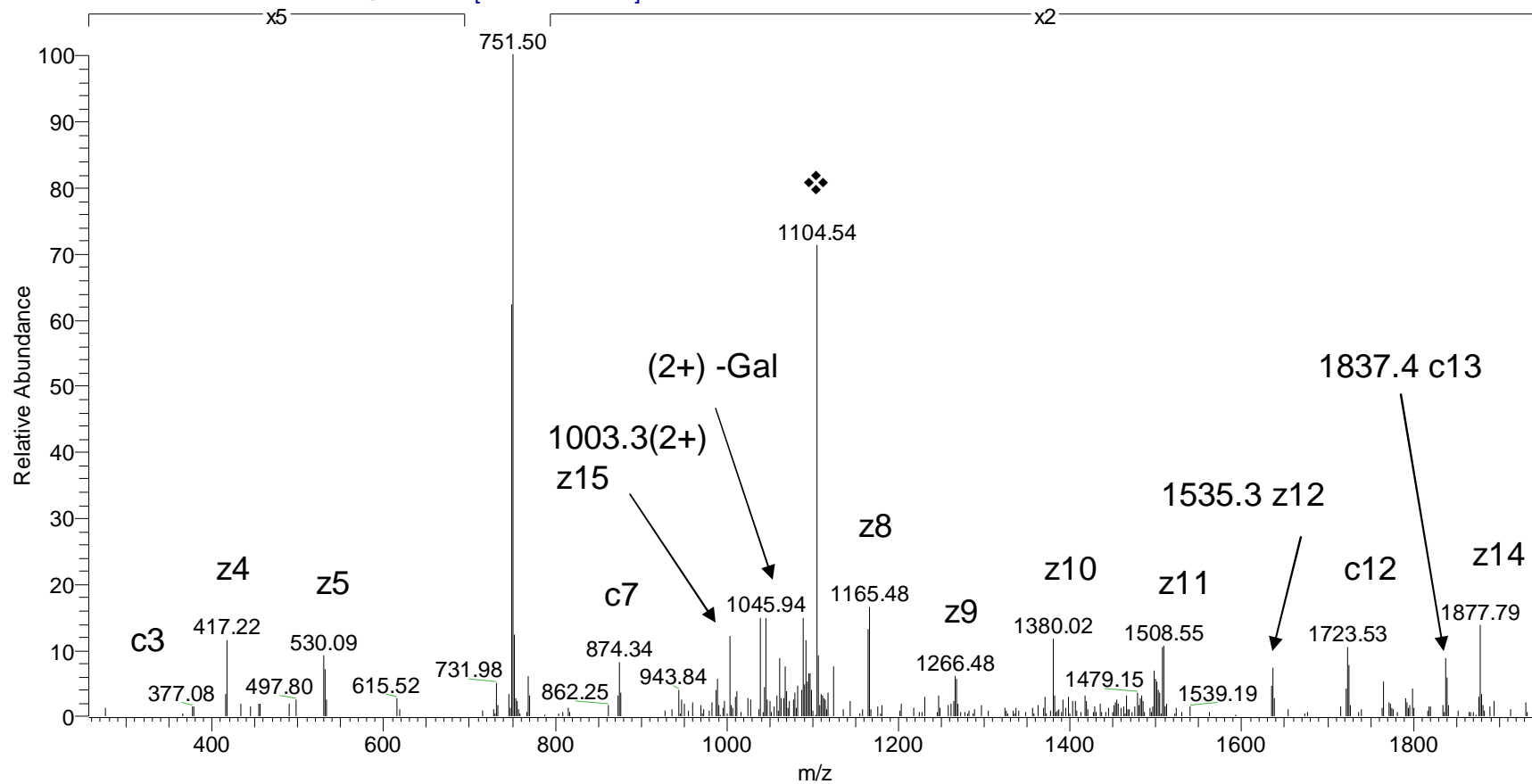


⁵⁰⁰LNPKT(GalNAcGalSA)DAWKS⁵¹⁰

Q58D62 = Fetuin B

Katalin_Szuszanna_53 #1205 RT: 14.70 AV: 1 NL: 7.84E2
T: ITMS + c NSI d sa Full ms2 751.35@etd90.00 [150.00-2000.00]

751.3538 (3+)



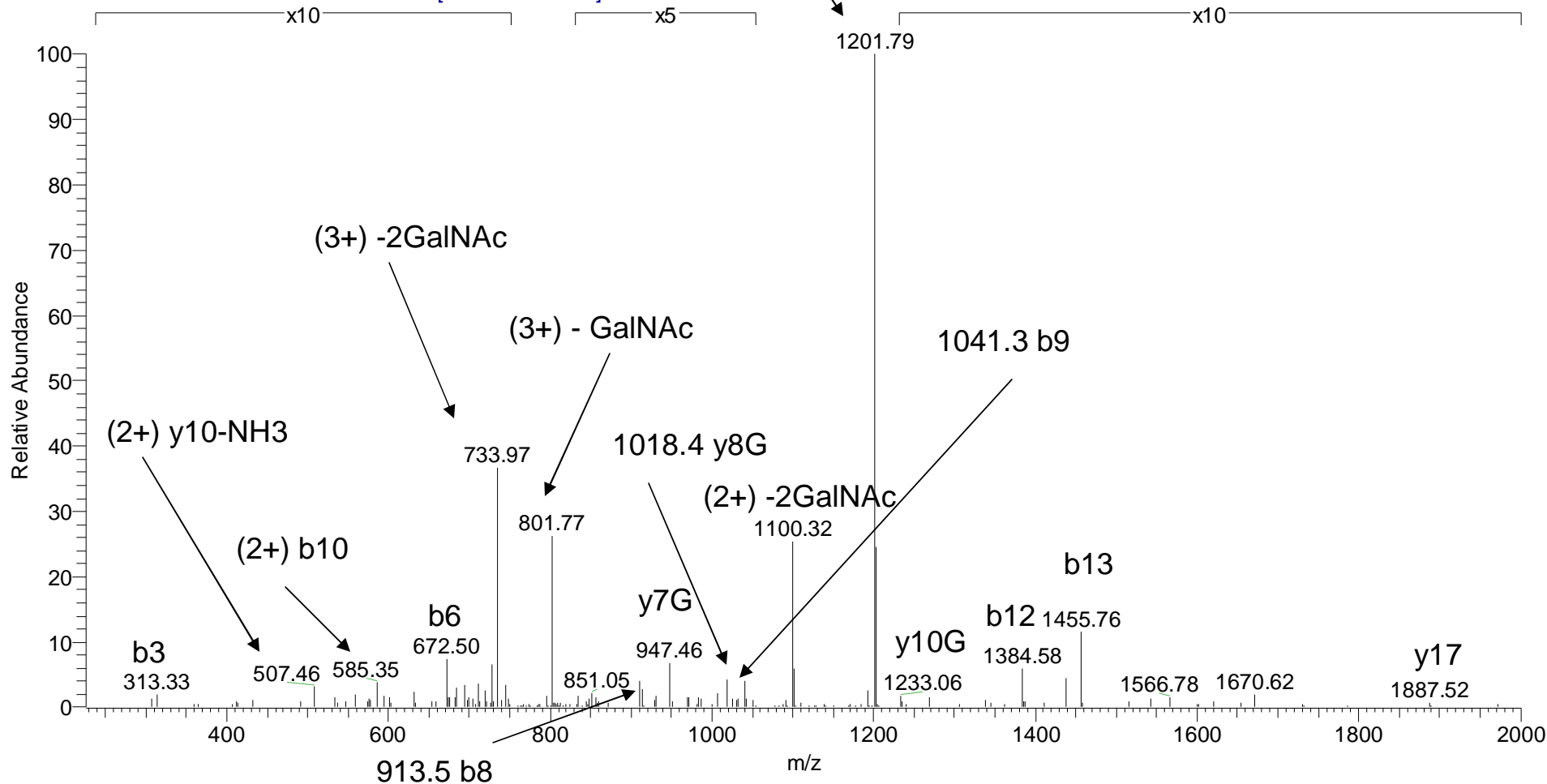
284TEELQQNTAPT(GalNAcGal)NSPTK300

Supplementary Figure 28

Q58D62 = Fetuin B

869.0856 (3+)

T8102002 #1076 RT: 18.21 AV: 1 NL: 1.44E4
T: ITMS + c NSI d Full ms2 869.42@cid35.00 [225.00-2000.00]



$^{281}\text{PSKTEELQQNTAPTNSPTK}^{300} + 2\text{GalNAc}$

CID spectrum!

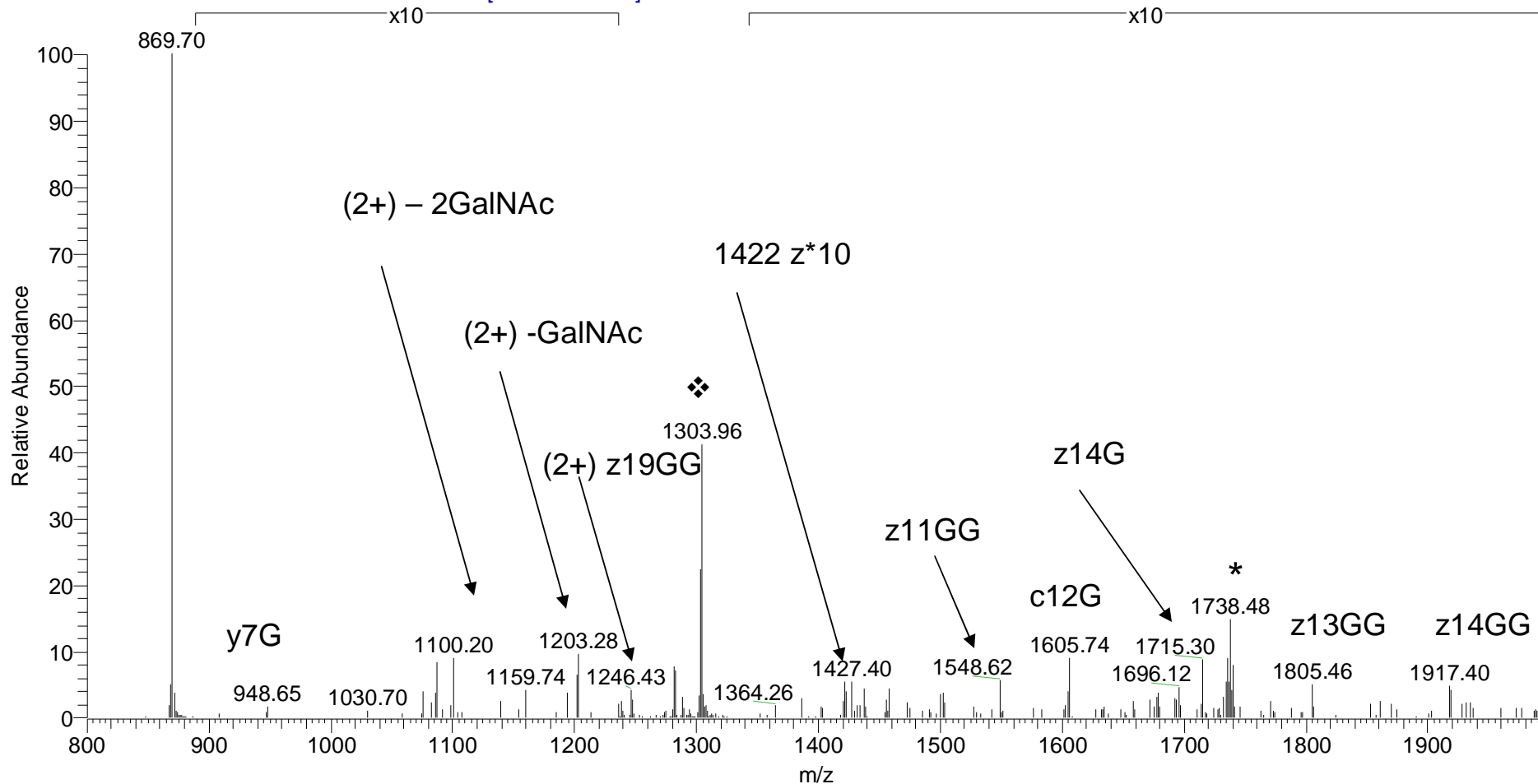
One of the sites is: Thr-295 or Ser-297 or Thr-299

Supplementary Figure 29

Q58D62 = Fetuin B

869.0856 (3+)

T8102002 #1077 RT: 18.22 AV: 1 NL: 1.27E4
T: ITMS + c NSI d sa Full ms2 869.42@etd100.00 [50.00-2000.00]



$^{281}\text{PSKTEELQQNI}(\text{GalNAc})\text{APTNSPTK}^{300} + \text{GalNAc}$

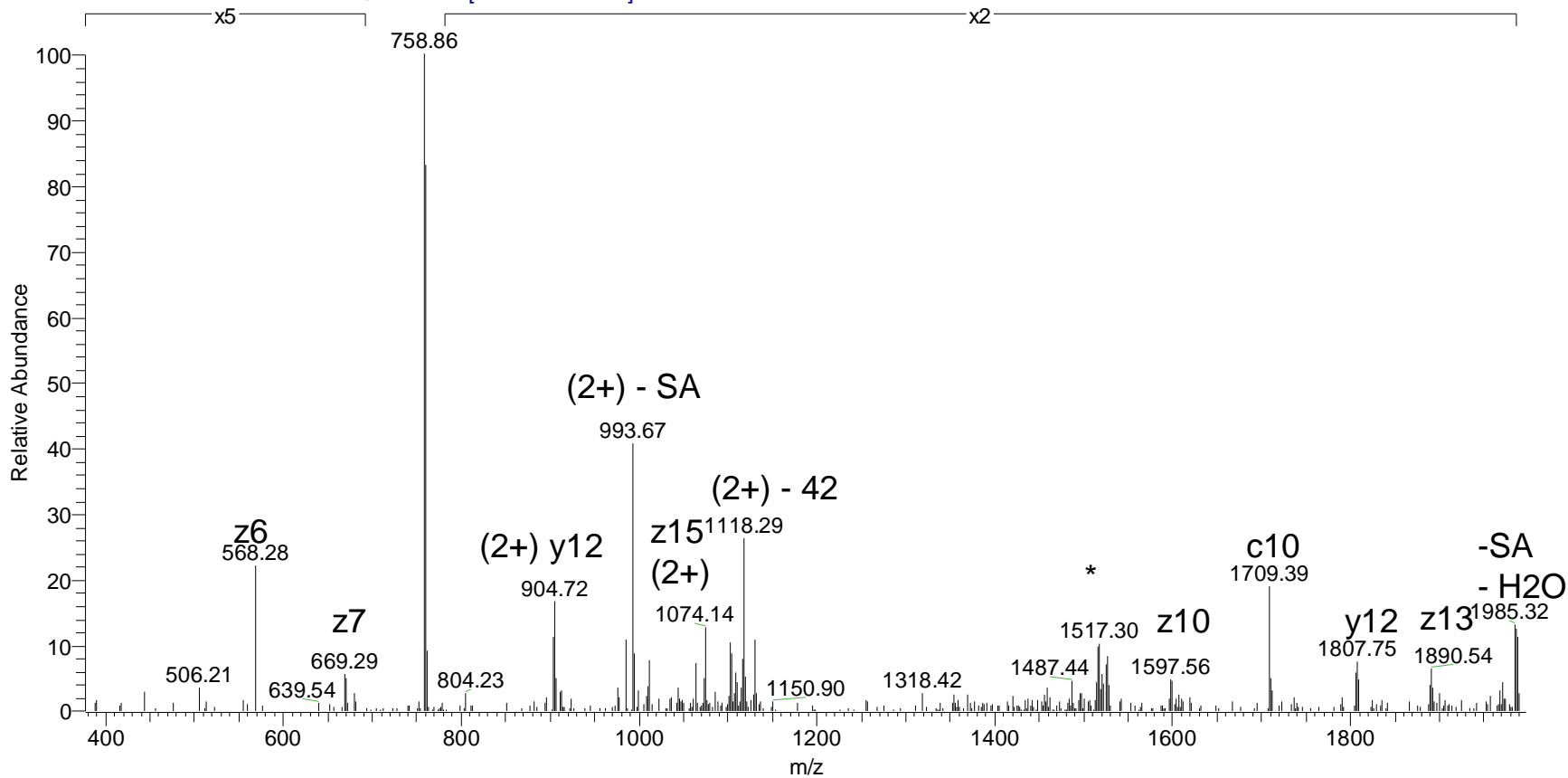
Thr-292 & Thr-295 or Ser 297 or Thr-299

Supplementary Figure 30

Q9N2I2 = Plasma serine protease inhibitor precursor

759.3746 (3+)

Katalin_Szuszanna_53 #2344 RT: 26.81 AV: 1 NL: 1.22E3
T: ITMS + c NSI d sa Full ms2 759.71 @etd90.00 [150.00-2000.00]

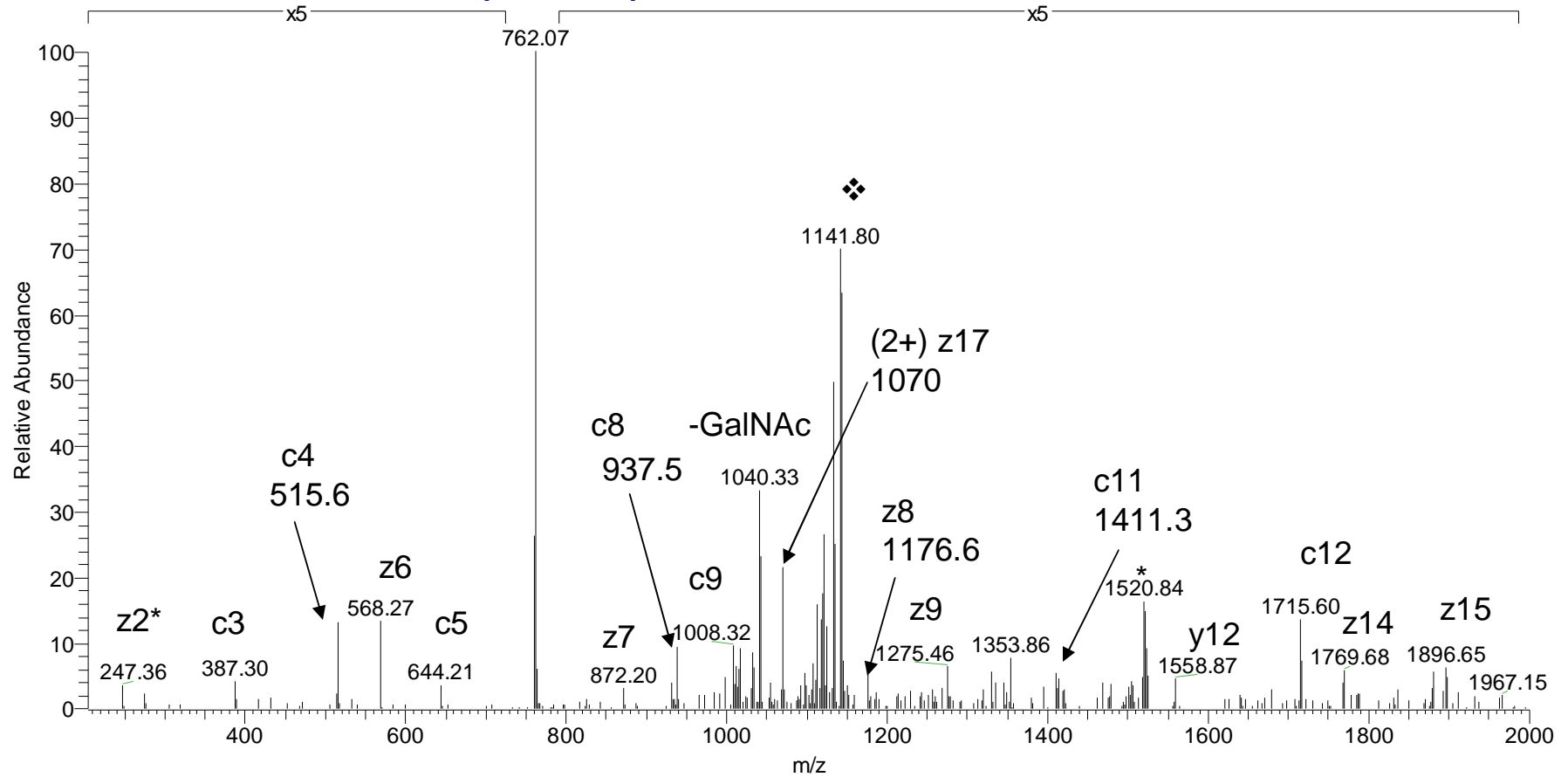


²⁷**IQEVP**PAVT(GaINAcGaISA)IAPPGSR⁴²

Q9N2I2 = Plasma serine protease inhibitor precursor

T8102002 #1317 RT: 20.40 AV: 1 NL: 6.09E3
 T: ITMS + c NSI d sa Full ms2 761.74@etd100.00 [50.00-2000.00]

761.4082 (3+)



²⁵KKIQEVPPAVT(GalNAc)I(GalNAc)APPGSR⁴²

Supplementary Figure 32