Supplementary Information

Activation-Free Sulfonyl Fluoride Probes for Fragment Screening

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Table S1. Characterization of the sulfonyl fluoride library

ID	^{13}C NMR measured [ppm]	^{13}C NMR calculated [ppm]	Nonapeptide labelling conversion [%]	TYROSINE labelling conversion [%]	LYSINE labelling conversion [%]	Measured Fluorescence Intensity in DPF-assay [-]
1	131.09	147.34	83%	79%	4%	6465428
2	132.54	149.40	84%	70%	14%	12979003
3	114.38	128.80	0%	0%	0%	6762316
4	132.3 [24]	153.64	65%	65%	0%	4682278
5	135.0 [24]	148.55	79%	79%	0%	4788817
6	132.40	150.87	59%	58%	1%	11413202
7	132.39	152.21	67%	64%	3%	14500736
8	132.43	152.82	47%	46%	1%	9887691
9	122.55	140.99	5%	5%	0%	8446817
10	122.55	141.16	7%	7%	0%	7763602
11	122.55	141.97	0%	0%	0%	7083526
12	132.40	150.57	94%	72%	22%	19124365
13	132.37	149.09	83%	79%	4%	15615169
14	132.46	150.33	96%	59%	36%	20431421
15	122.93	139.16	70%	67%	2%	5602622
16	122.90	136.92	52%	49%	3%	7351058
17	123.01	134.73	16%	16%	0%	8187924
18	130.04	145.42	48%	47%	1%	8761611
19	130.01	149.21	25%	25%	0%	8650134
20	130.10	149.99	46%	41%	5%	8115745

Figure S1. Correlation between calculated and measured ^{13}C NMR shifts

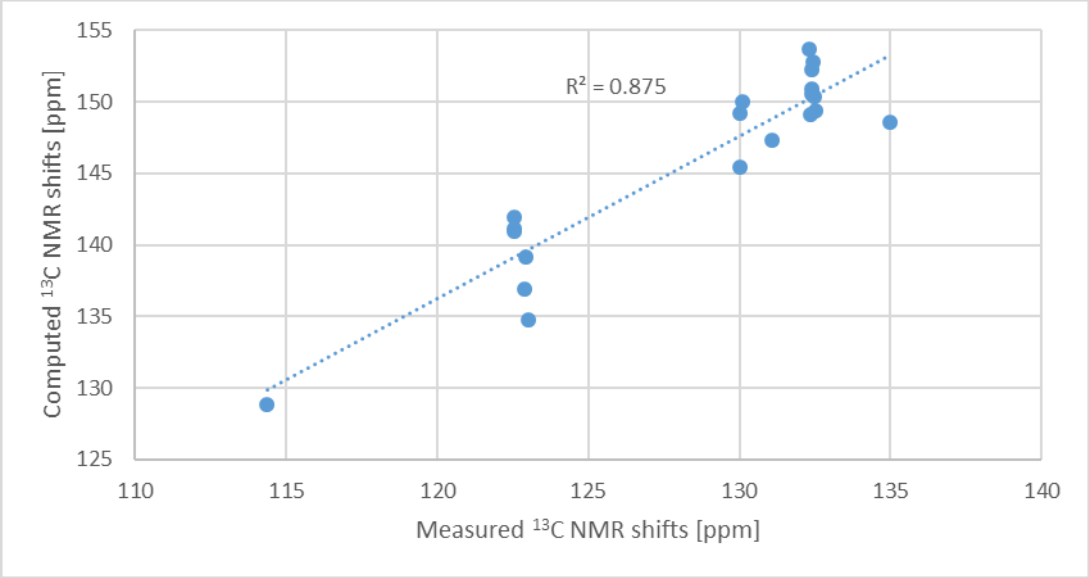
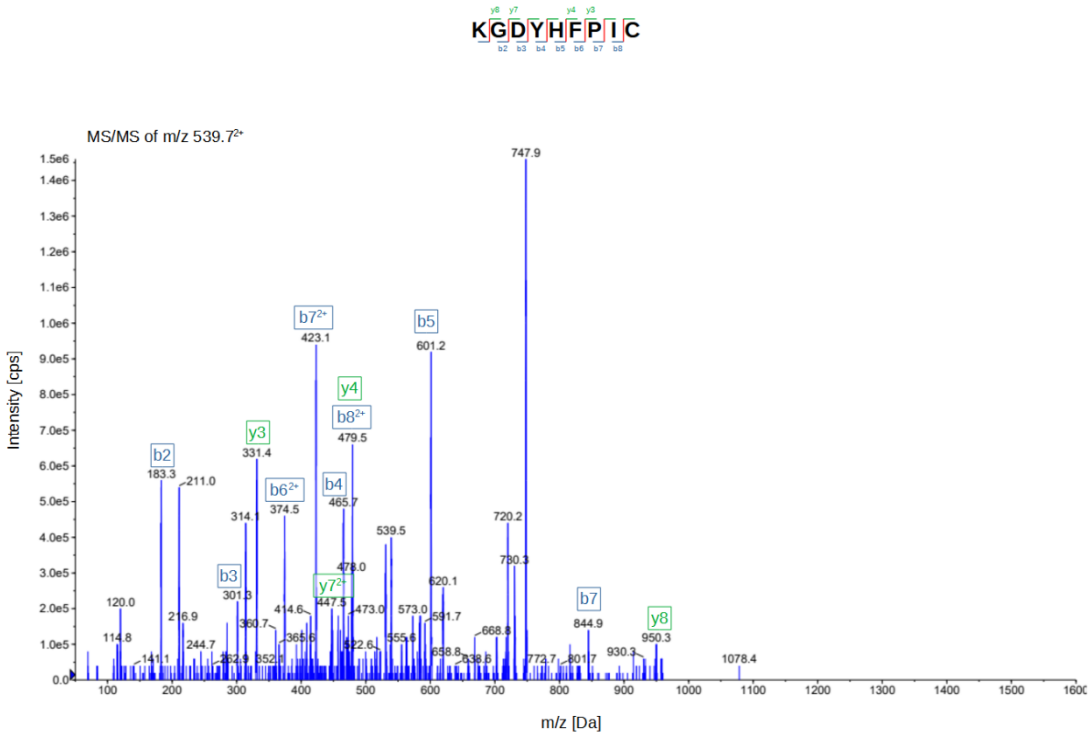


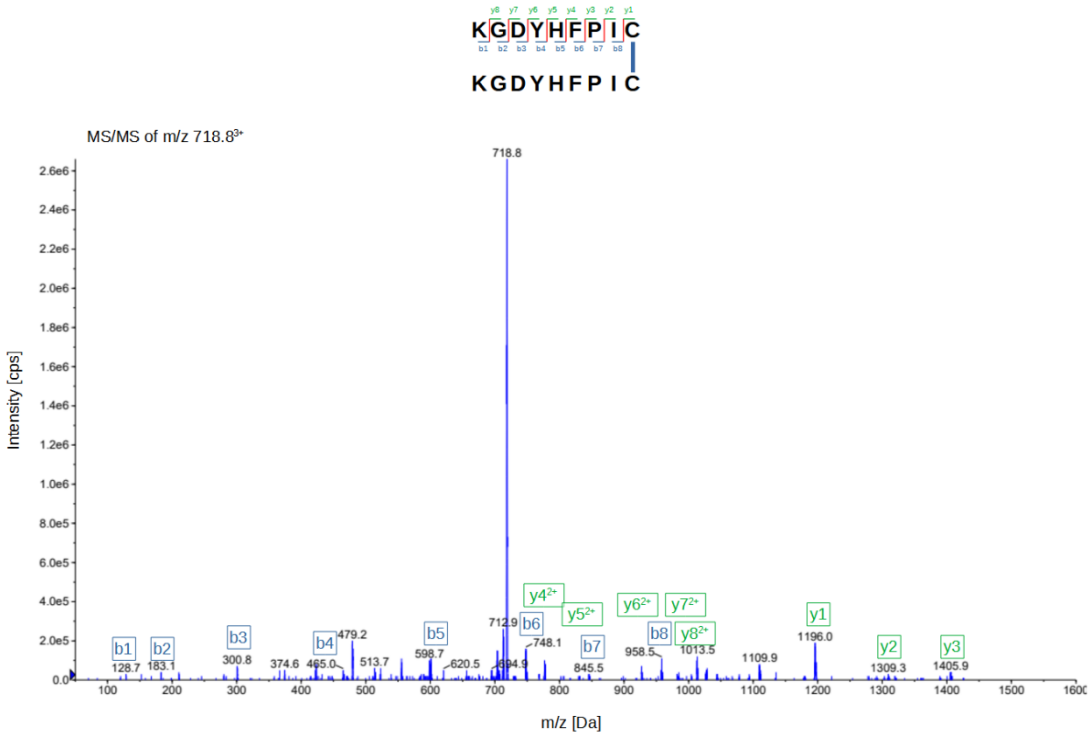
Figure S2. MS/MS spectrum of nonapeptide assay

Representative TIC is presented for compound **12**.

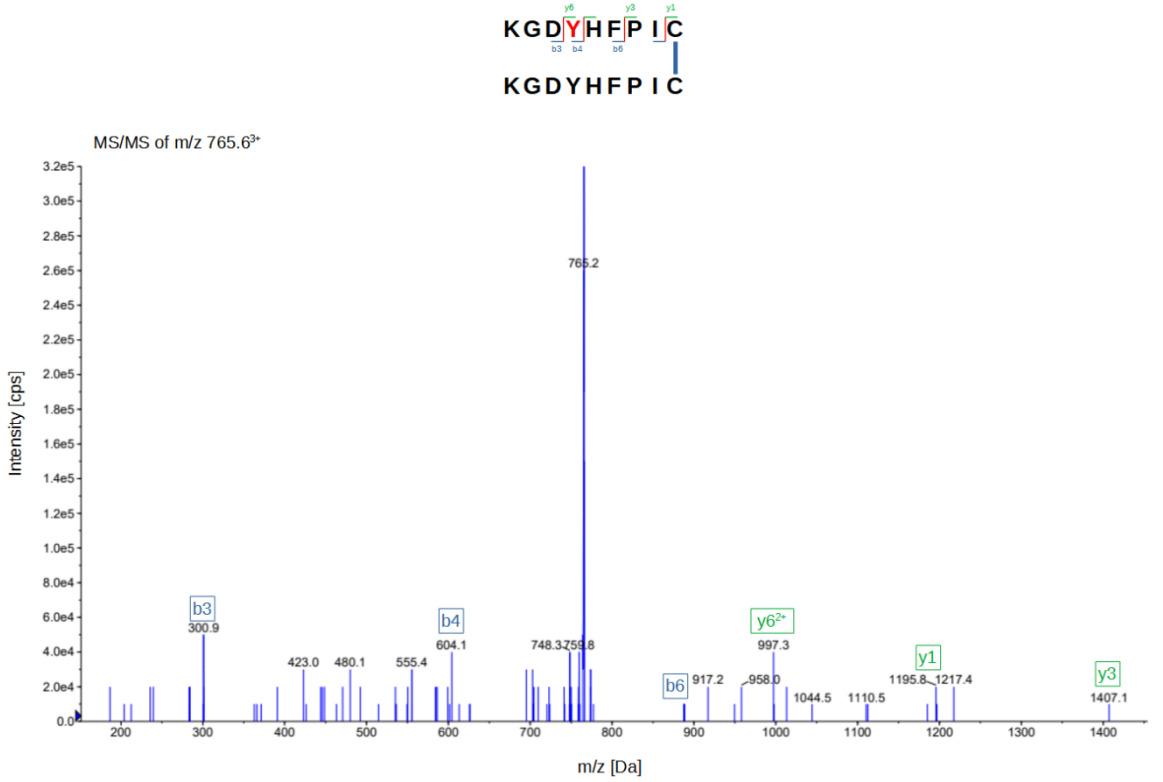
Nonapeptide

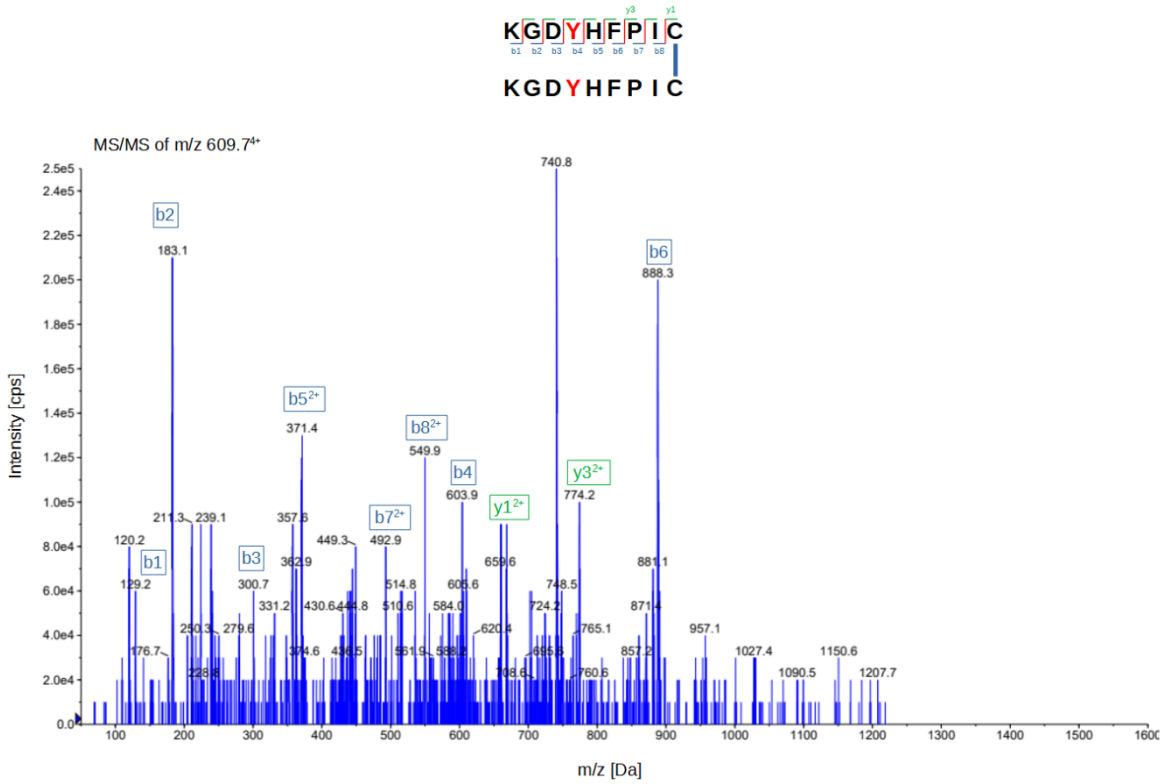


Nonapeptide dimer

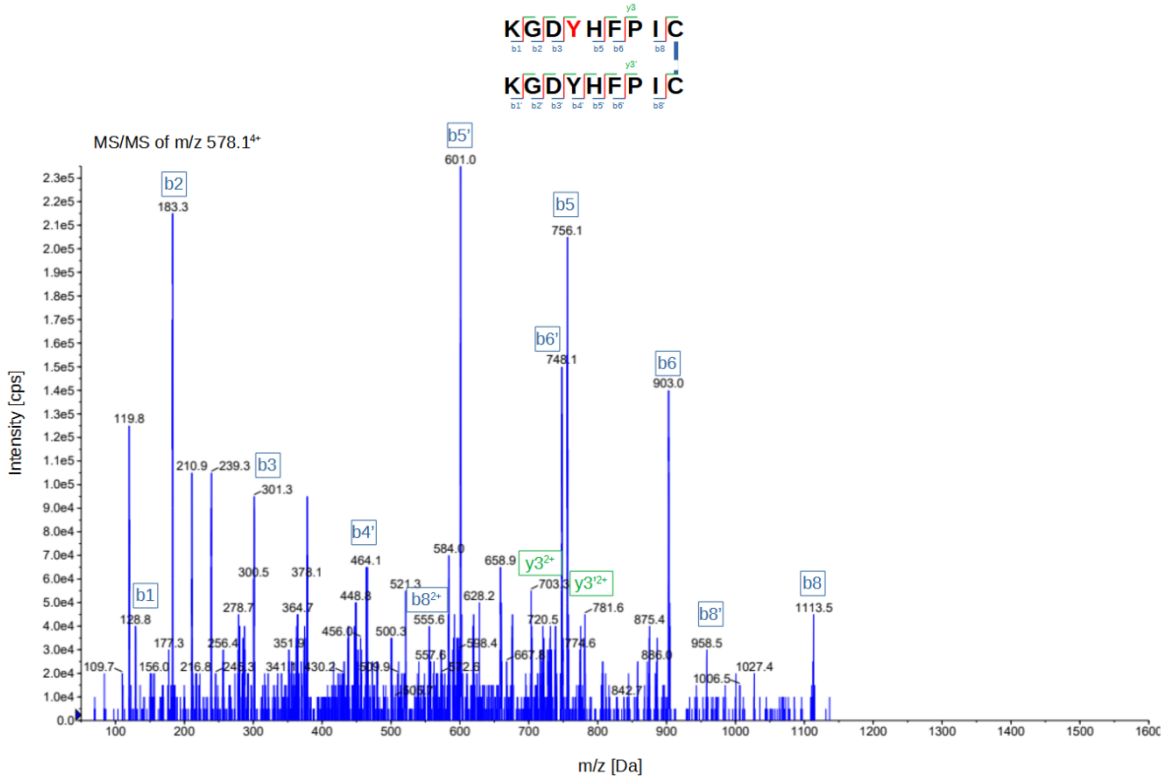


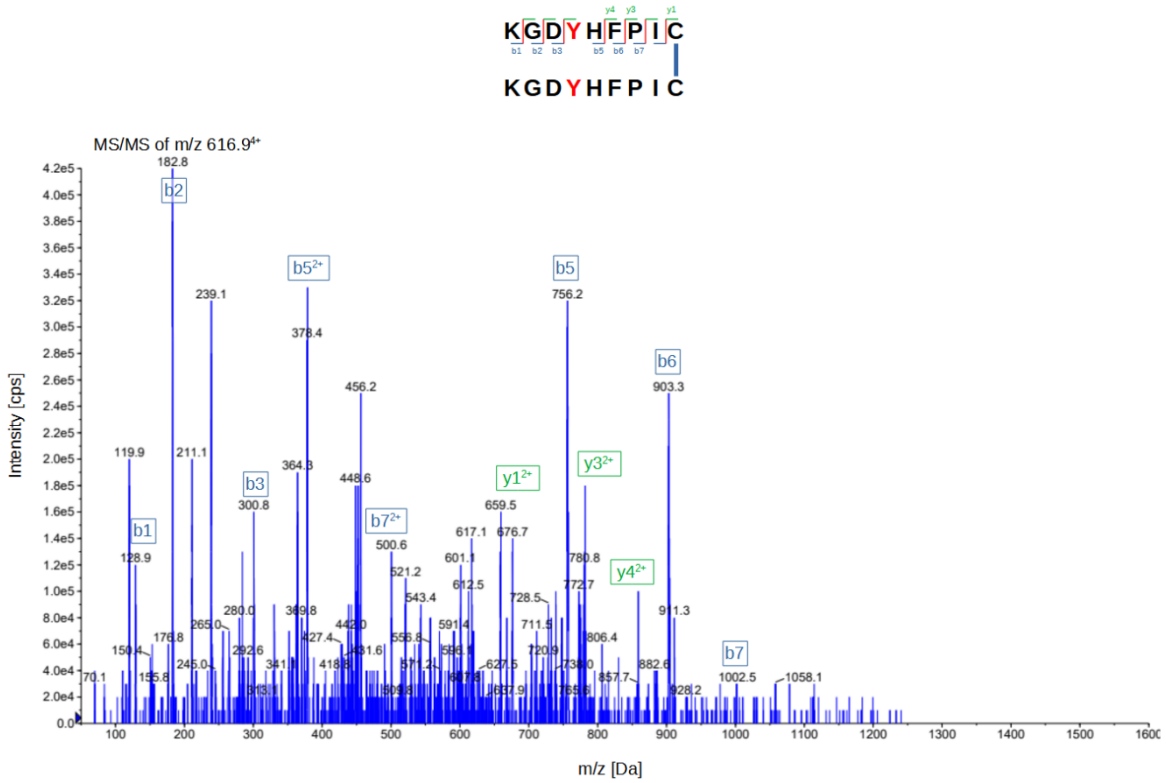
NP+1


KGDYHFPIC
MS/MS of m/z 765.6^3+
Intensity [cps]
m/z [Da]
765.2
b3
300.9
b4
604.1
y6^2+
997.3
y1
1195.8
1217.4
y3
1407.1
b6
917.2
423.0
480.1
555.4
748.3
759.8
958.0
1044.5
1110.5

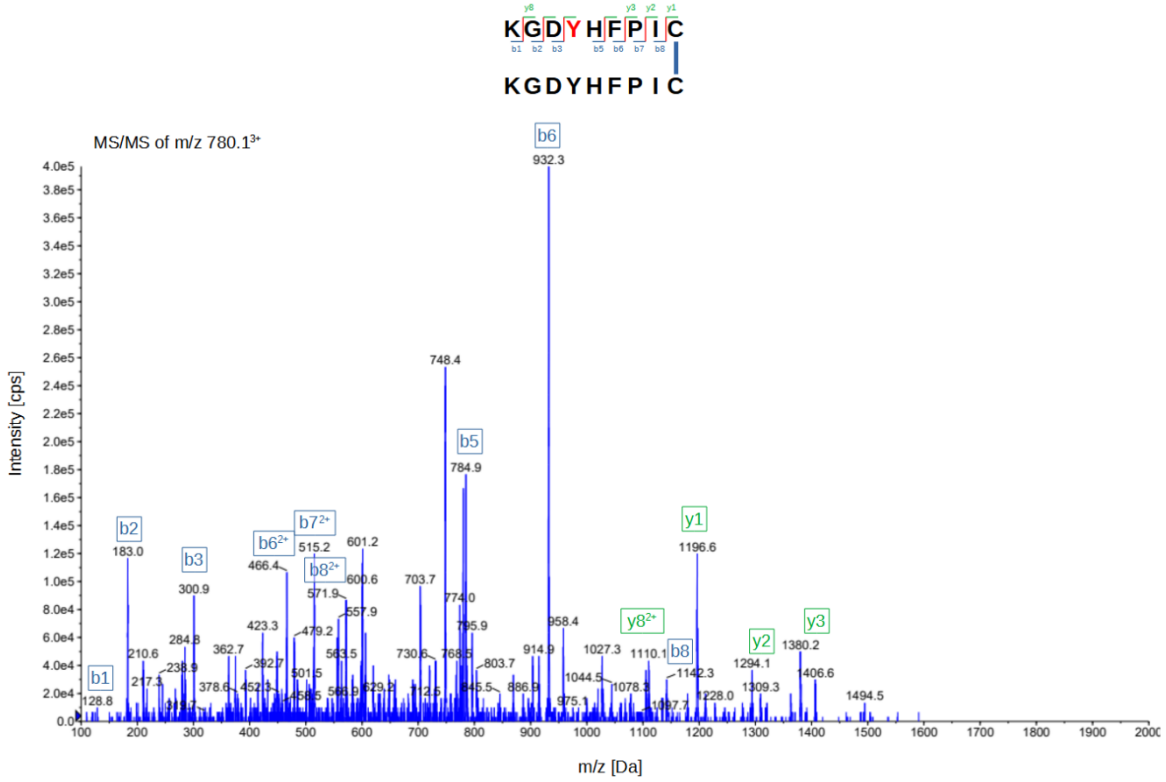

KGDYHFPIC
MS/MS of m/z 609.7^4+
Intensity [cps]
m/z [Da]
740.8
b2
183.1
b6
888.3
b5^2+
371.4
b8^2+
549.9
b4
603.9
y3^2+
774.2
y1^2+
b7^2+
492.9
b1
b3
300.7
881.1
957.1
1027.4
1150.6
1090.5
1207.7

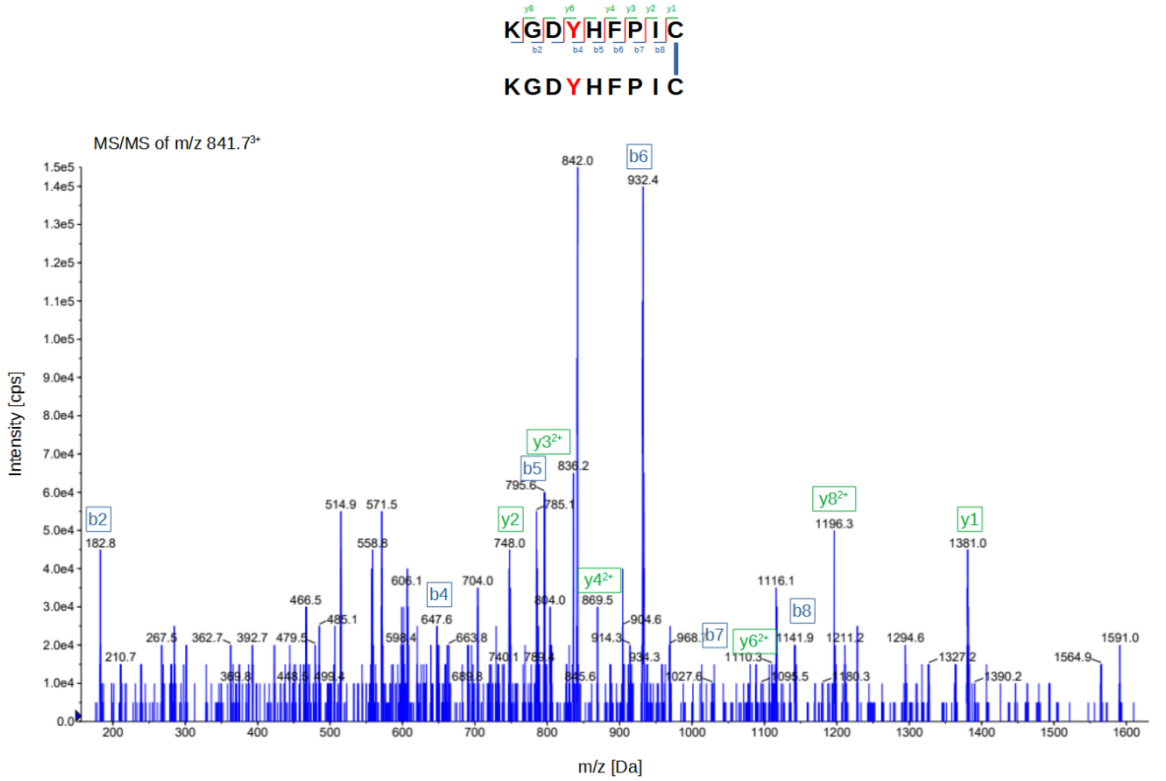
NP+2


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 578.1⁴⁺
Intensity [cps]
m/z [Da]
b2
183.3
b5'
601.0
b5
756.1
b6'
748.1
b6
903.0
b3
301.3
b4'
464.1
b1
128.8
b8²⁺
555.6
y3²⁺
658.9
y3'²⁺
703.3
b8
1113.5
b8'
958.5

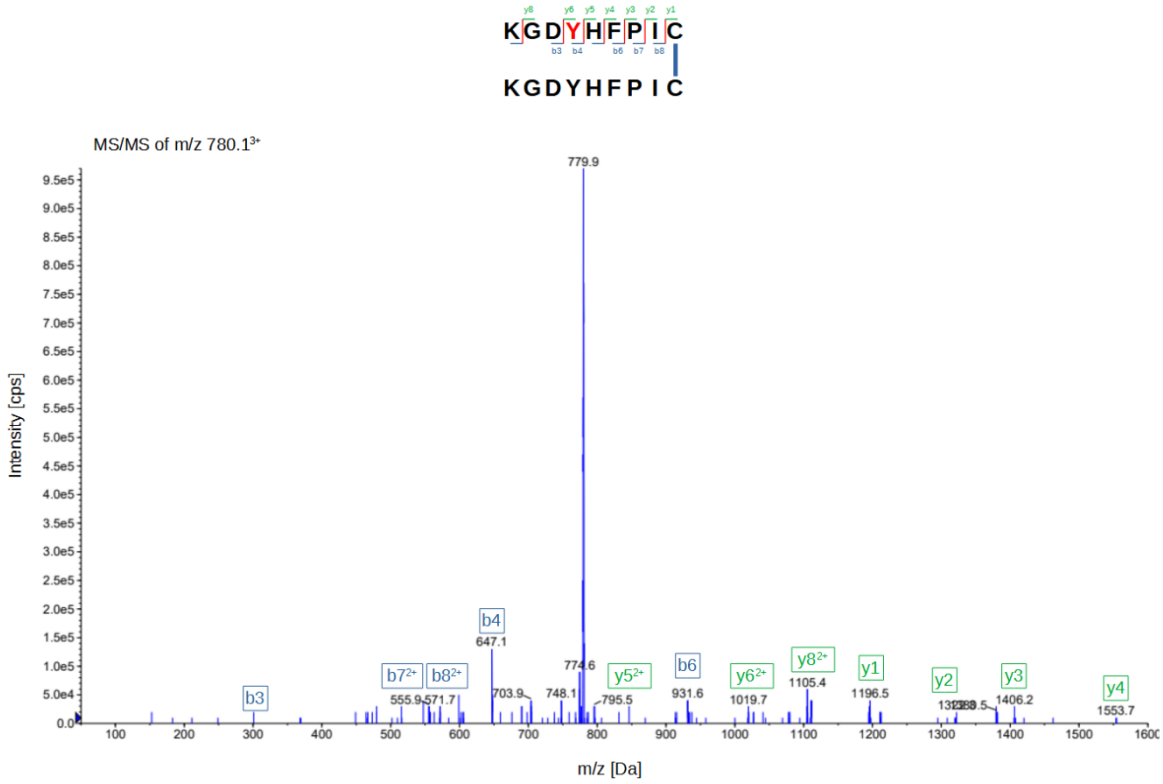

KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 616.9⁴⁺
Intensity [cps]
m/z [Da]
b2
182.8
b5²⁺
378.4
b5
756.2
b6
903.3
b3
300.8
b1
128.9
b7²⁺
500.6
y1²⁺
659.5
y3²⁺
y4²⁺
b7
1002.5

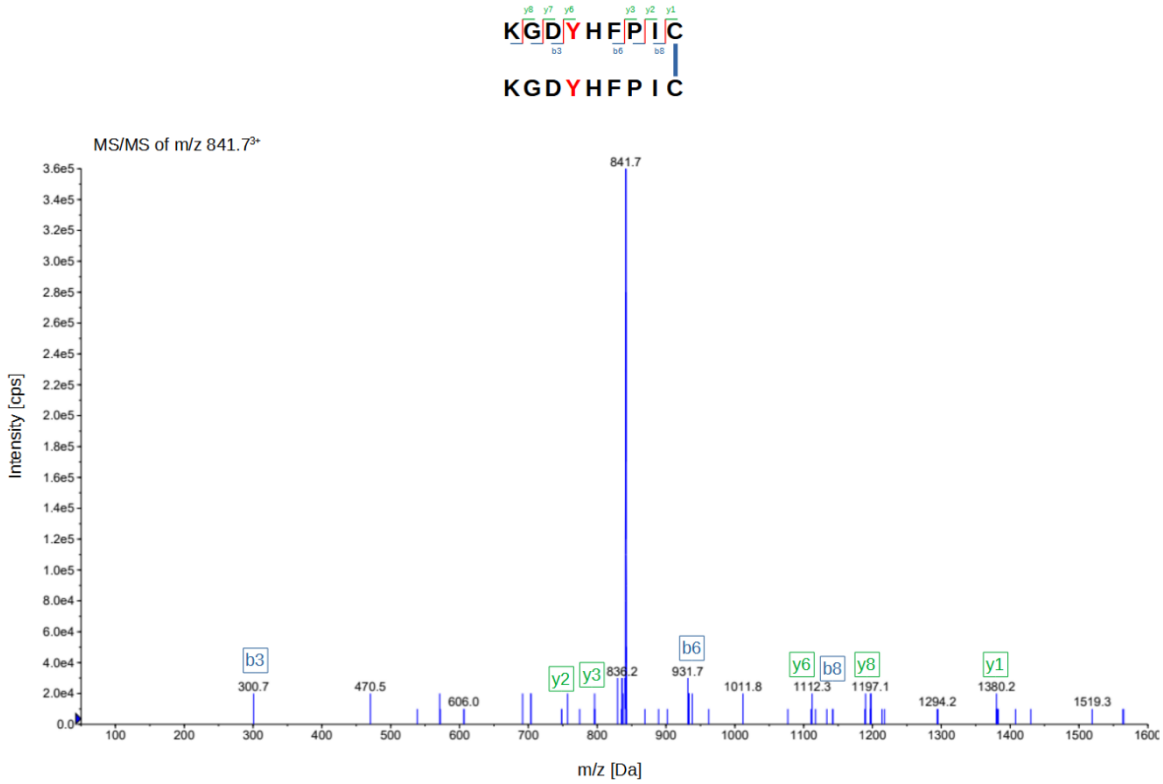
NP+4


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 780.1³⁺
Intensity [cps]
m/z [Da]
b6
932.3
748.4
b5
784.9
y1
1196.6
b2
183.0
b3
300.9
b6²⁺
515.2
b7²⁺
601.2
b8²⁺
600.6
y8²⁺
y3
1380.2
y2
1294.1
b8
1142.3
b1
128.8
1494.5

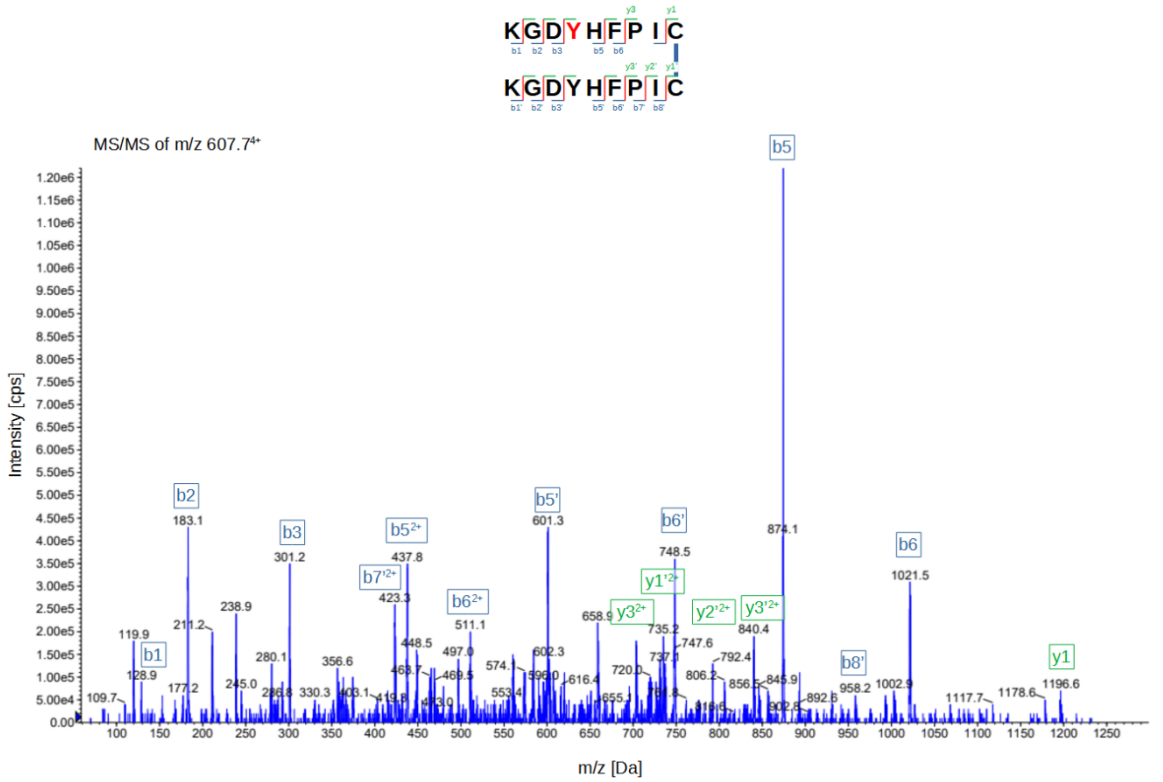

KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 841.7³⁺
Intensity [cps]
m/z [Da]
842.0
b6
932.4
y3²⁺
b5
836.2
y8²⁺
1196.3
y1
1381.0
b2
182.8
y2
748.0
y4²⁺
869.5
b4
b8
b7
y6²⁺
1591.0

NP+5


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 780.1³⁺
Intensity [cps]
m/z [Da]
779.9
b4
647.1
b3
b7²⁺
b8²⁺
y5²⁺
b6
y6²⁺
y8²⁺
1105.4
y1
1196.5
y2
y3
1406.2
y4
1553.7


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 841.7³⁺
Intensity [cps]
m/z [Da]
841.7
b3
300.7
470.5
606.0
y2
y3
836.2
b6
931.7
1011.8
y6
b8
y8
1112.3
1197.1
1294.2
y1
1380.2
1519.3

NP+6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KGDYHFPIC
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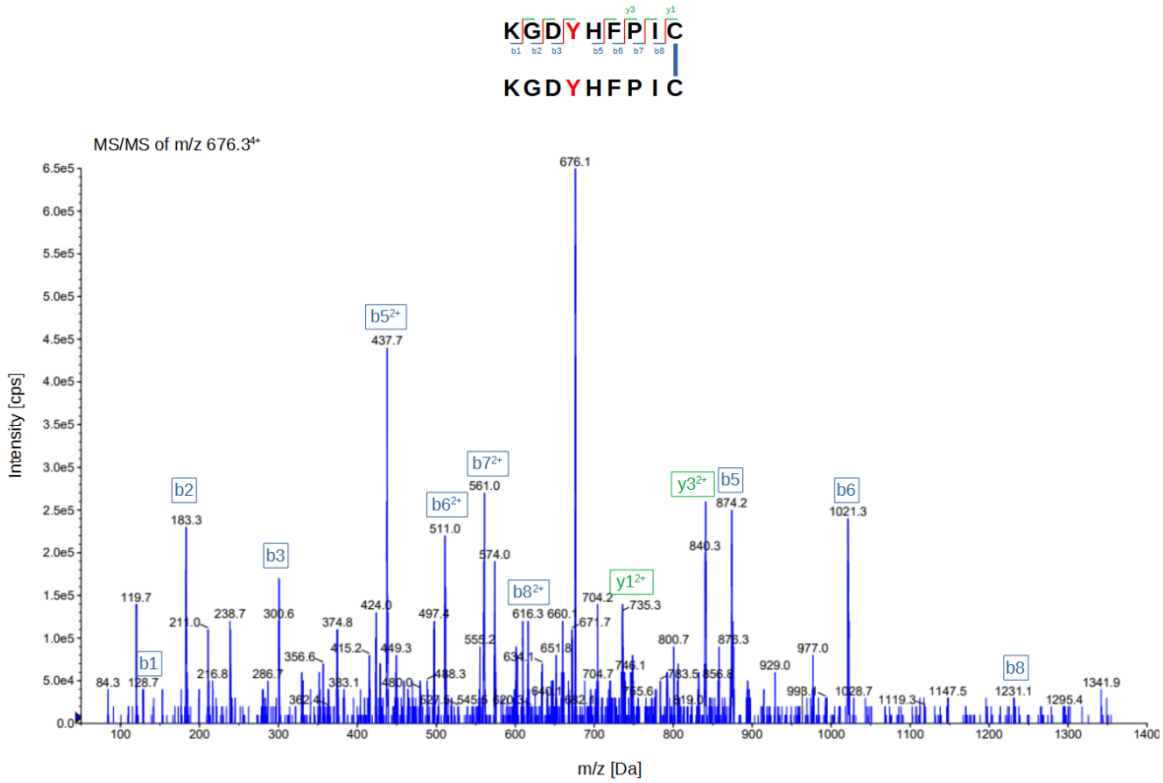
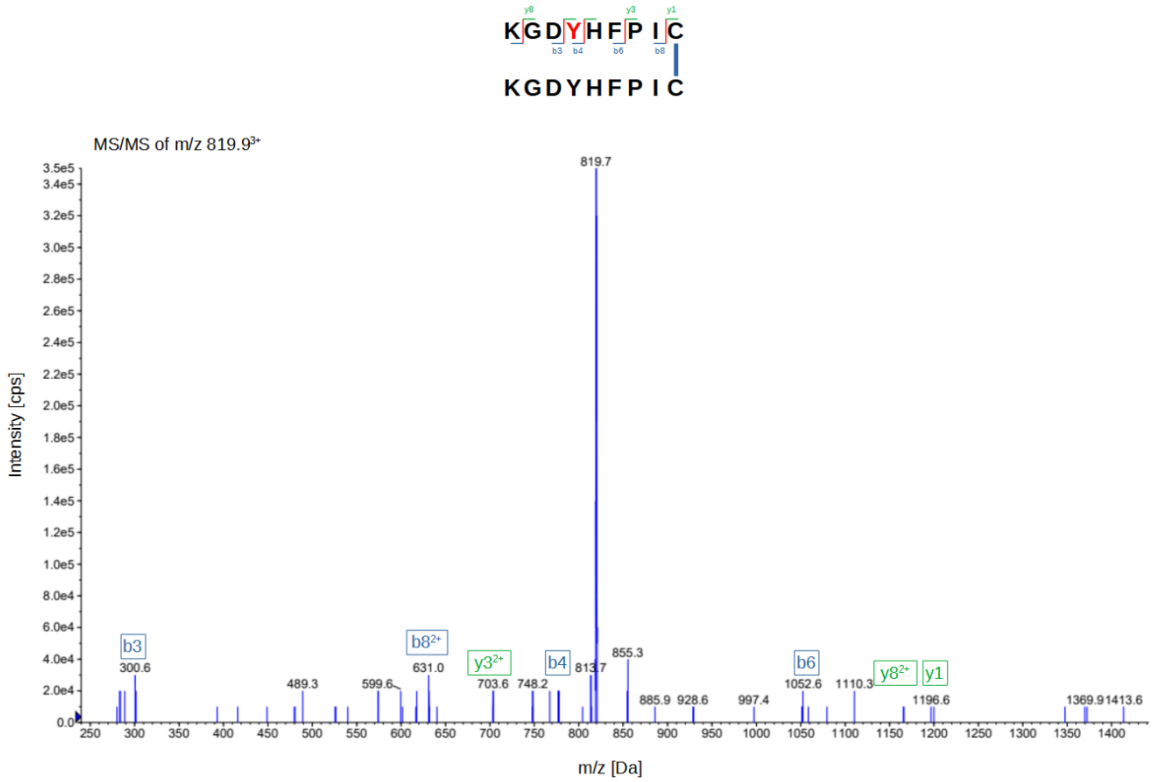
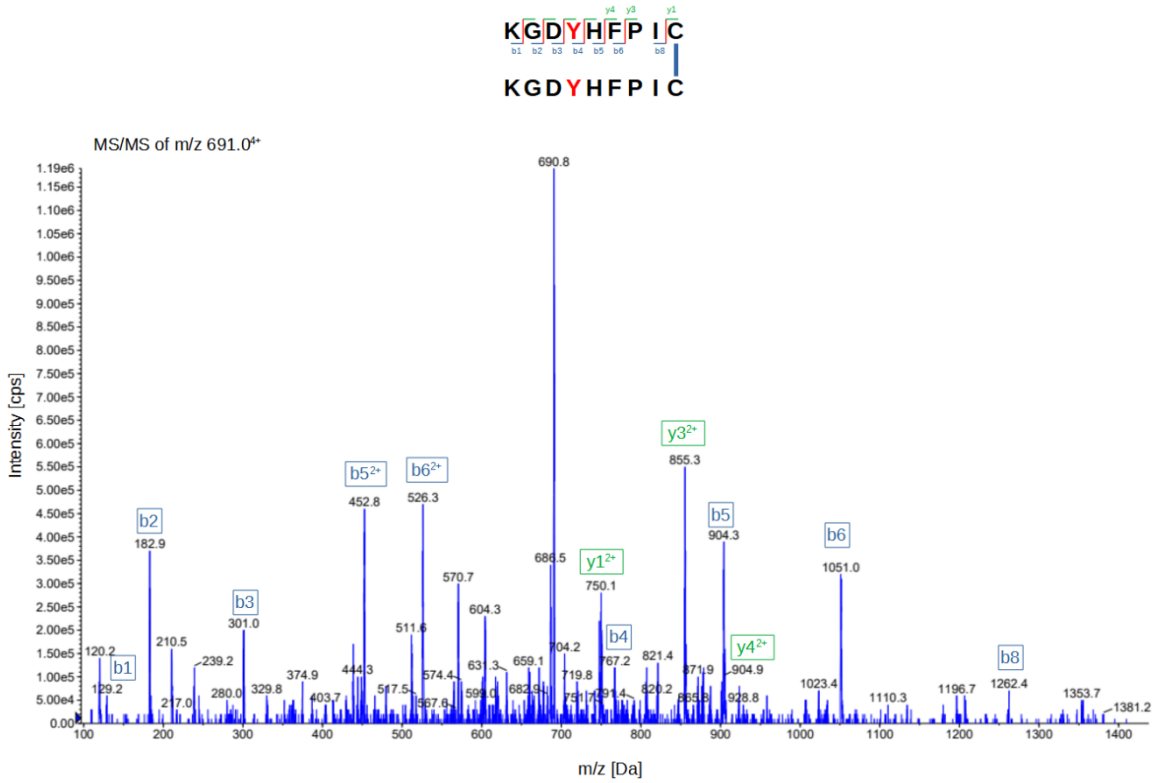
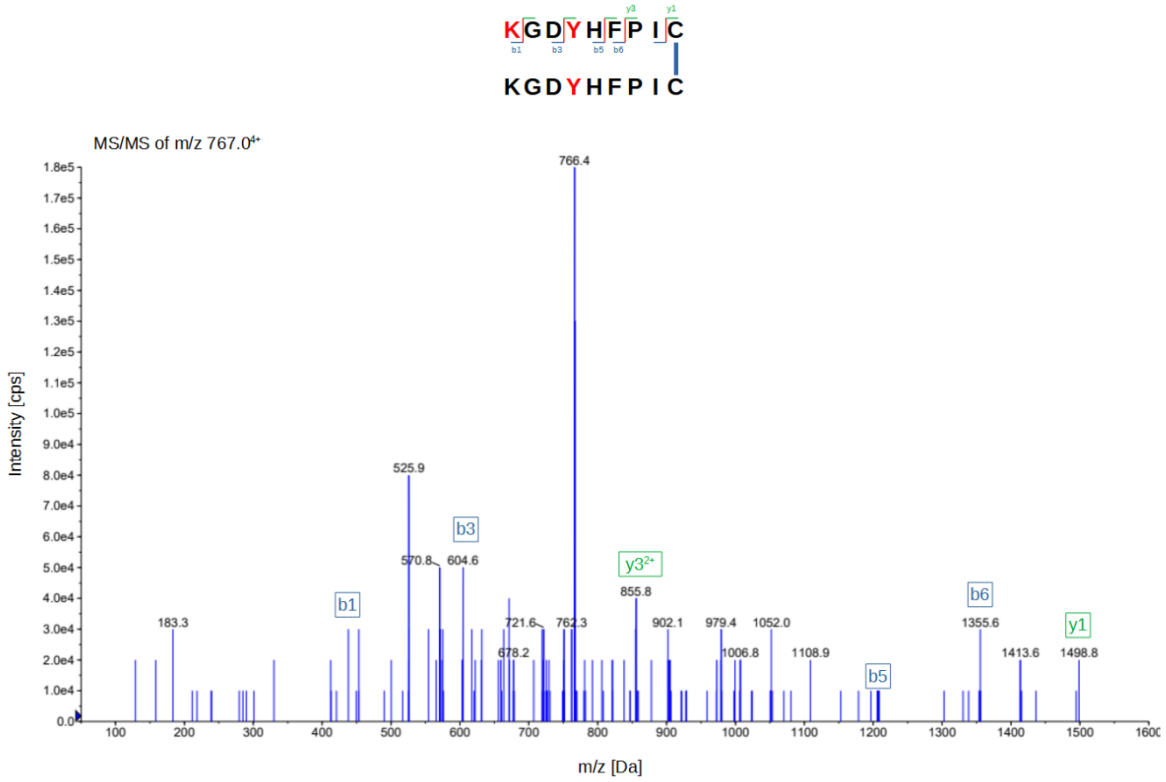
Intensity [cps]
m/z [Da]


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 676.3⁴⁺
Intensity [cps]
m/z [Da]

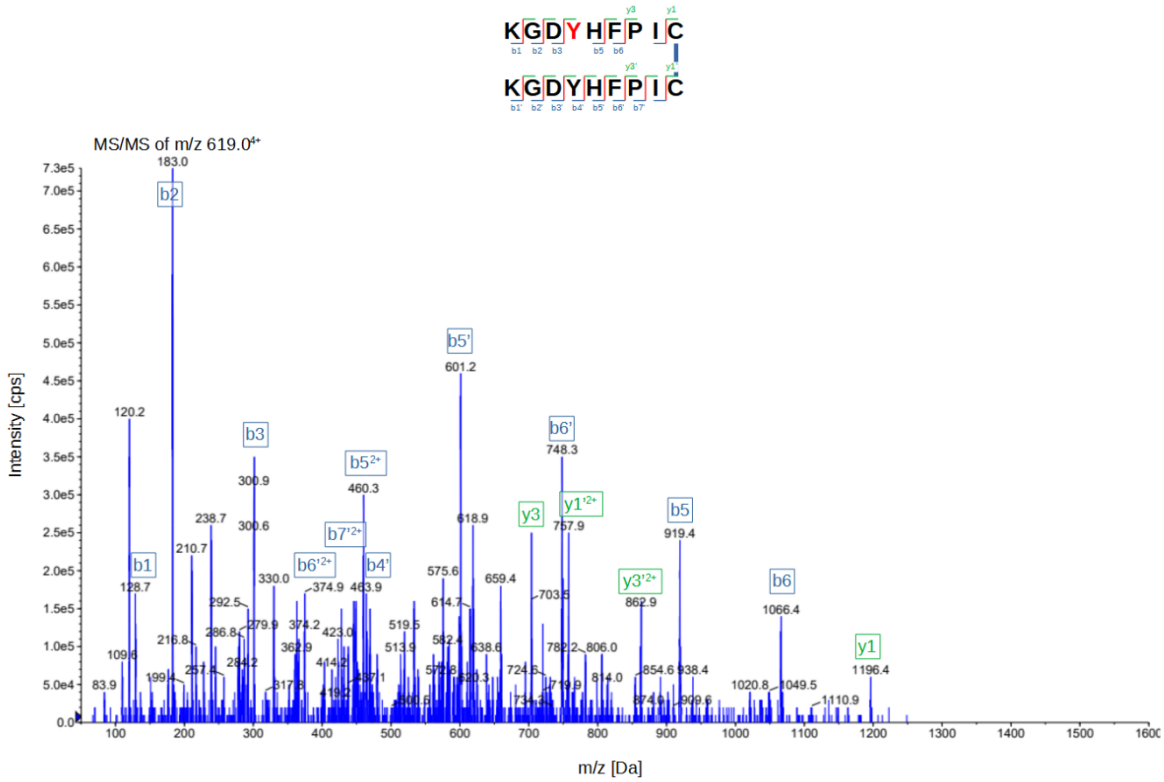
NP+7


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 819.9³⁺
Intensity [cps]
m/z [Da]
819.7
b3
300.6
b8²⁺
631.0
y3²⁺
703.6
b4
748.2
855.3
b6
1052.6
y8²⁺
y1
1196.6
1369.9
1413.6


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 691.0⁴⁺
Intensity [cps]
m/z [Da]
690.8
y3²⁺
855.3
b5²⁺
452.8
b6²⁺
526.3
b2
182.9
b5
904.3
b6
1051.0
y1²⁺
750.1
b3
301.0
b1
y4²⁺
b8
1262.4


KGDYHFPIC
b1 b3 b5 b6 y3 y1
KGDYHFPIC
MS/MS of m/z 767.04+
Intensity [cps]
m/z [Da]
766.4
525.9
b3
570.8
604.6
y32+
855.8
b1
183.3
721.6
762.3
678.2
902.1
979.4
1006.8
1052.0
1108.9
b6
1355.6
1413.6
y1
1498.8
b5

NP+8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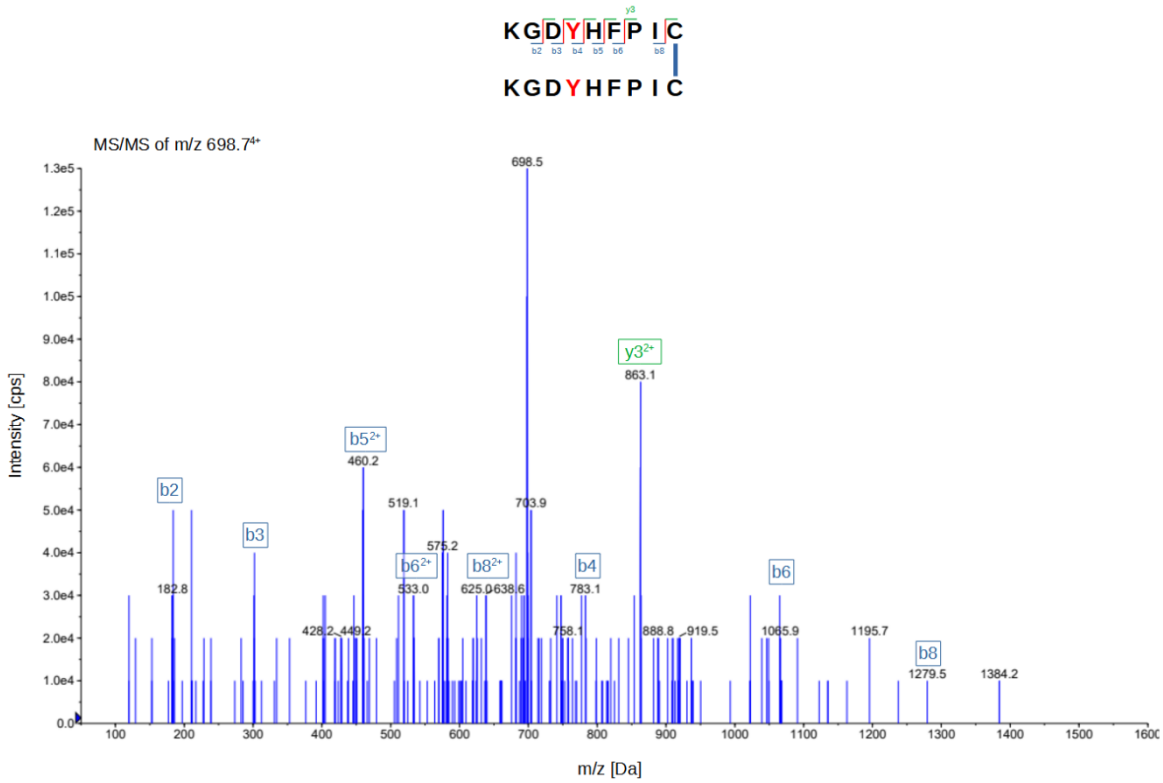
MS/MS of m/z 619.0^4+
Intensity [cps]
m/z [Da]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KGDYHFPIC
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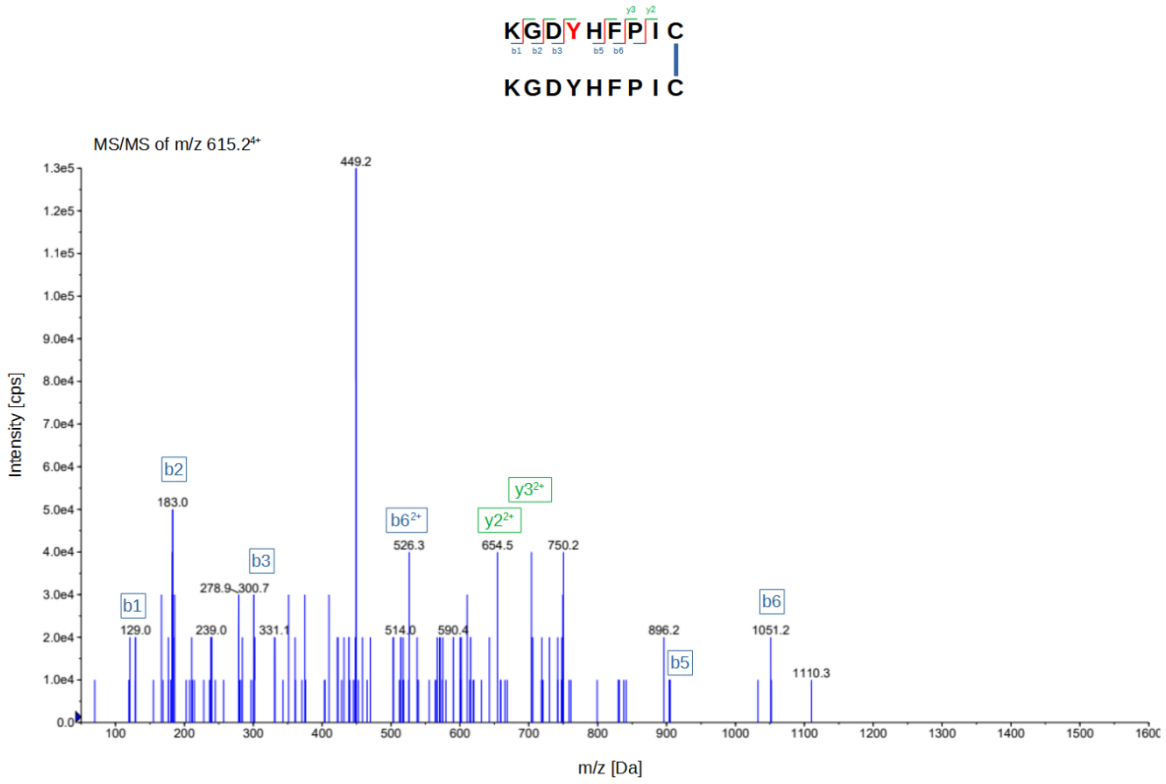
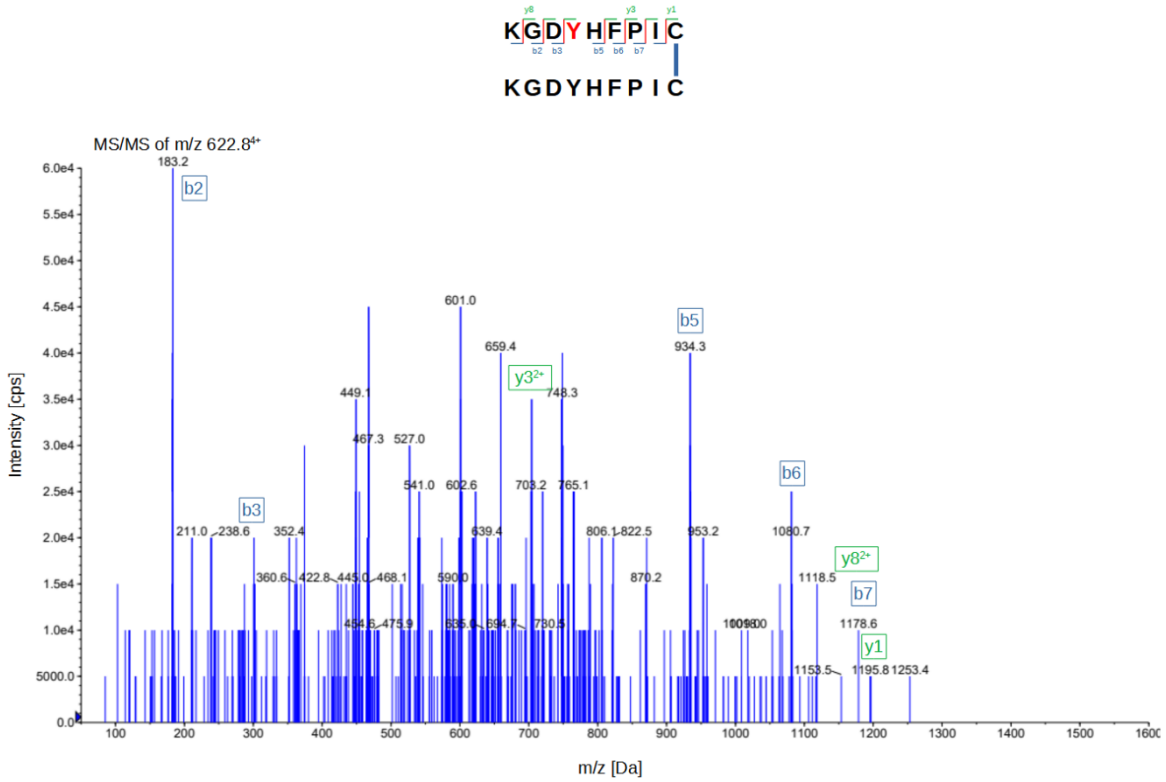
Intensity [cps]
m/z [Da]

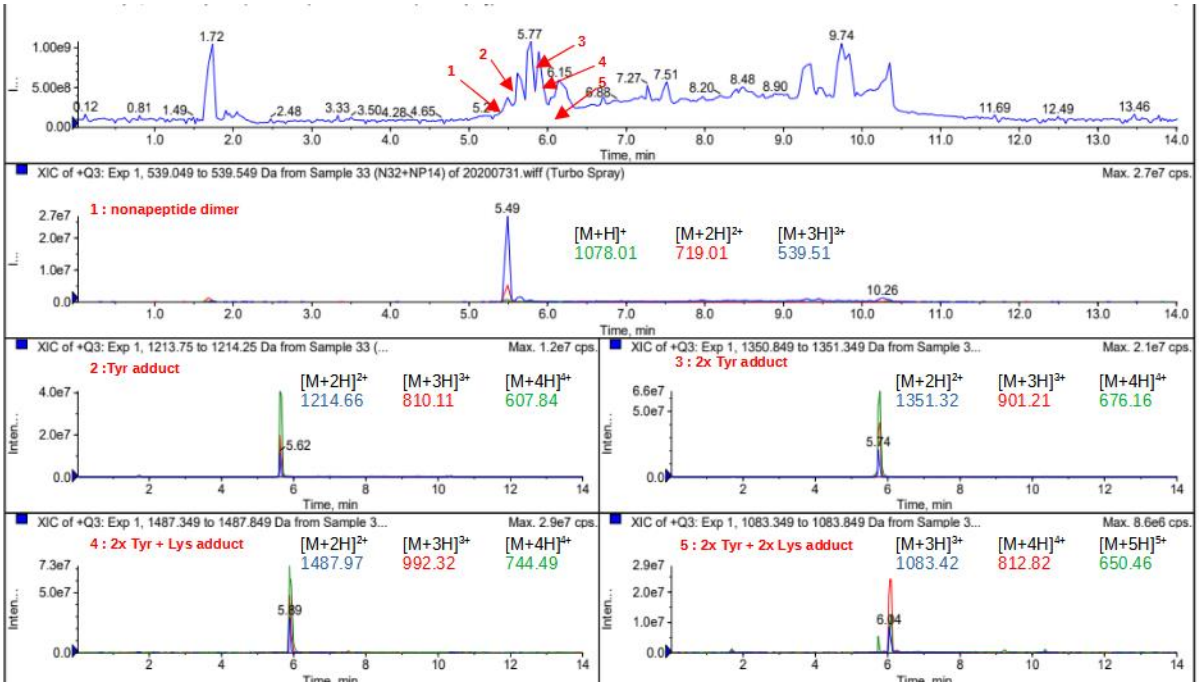
NP+9

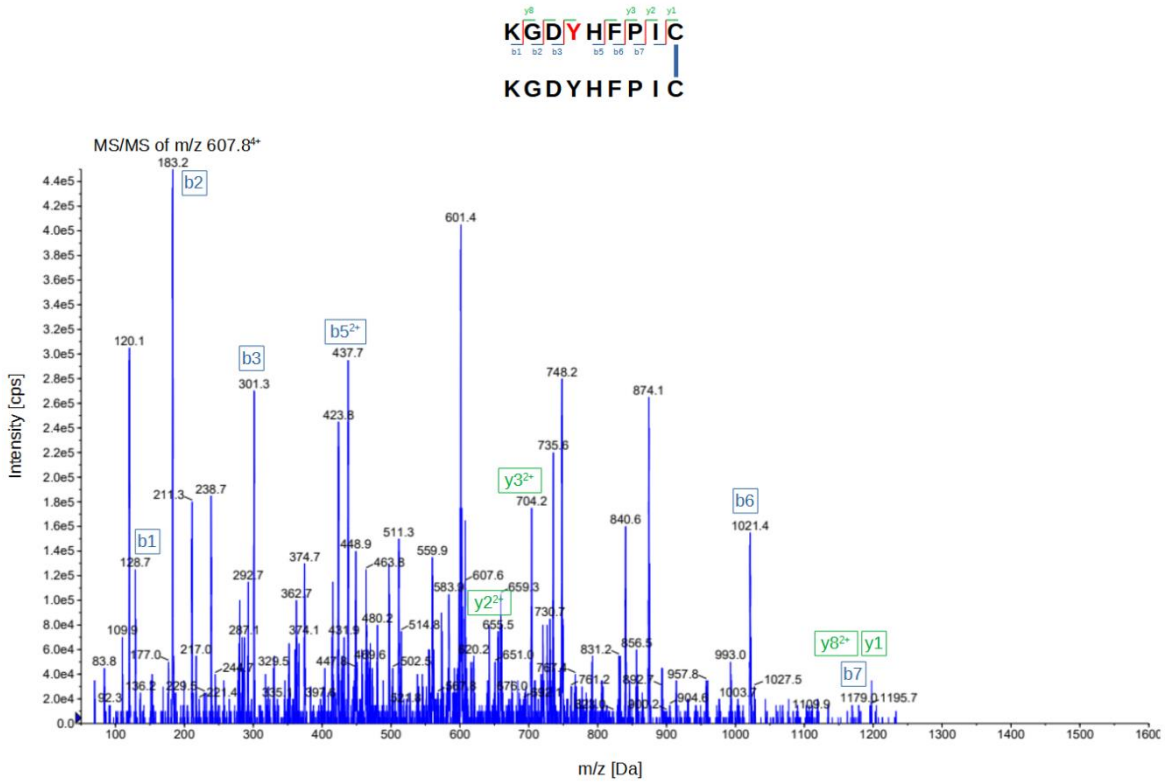

KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 615.2^4+
Intensity [cps]
m/z [Da]
449.2
183.0
526.3
654.5
750.2
278.9
300.7
129.0
239.0
331.1
514.0
590.4
896.2
1051.2
1110.3
b1
b2
b3
b5
b6
b6^2+
y2^2+
y3^2+

NP+10


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 622.8⁴⁺
Intensity [cps]
m/z [Da]
b2
b3
b5
b6
b7
y1
y3²⁺
y8²⁺

NP+12


Time, min
XIC of +Q3: Exp 1, 539.049 to 539.549 Da from Sample 33 (N32+NP14) of 20200731.wiff (Turbo Spray)
Max. 2.7e7 cps.
1 : nonapeptide dimer
[M+H]⁺ 1078.01
[M+2H]²⁺ 719.01
[M+3H]³⁺ 539.51
XIC of +Q3: Exp 1, 1213.75 to 1214.25 Da from Sample 33 (...
Max. 1.2e7 cps.
2 :Tyr adduct
[M+2H]²⁺ 1214.66
[M+3H]³⁺ 810.11
[M+4H]⁴⁺ 607.84
XIC of +Q3: Exp 1, 1350.849 to 1351.349 Da from Sample 3...
Max. 2.1e7 cps.
3 : 2x Tyr adduct
[M+2H]²⁺ 1351.32
[M+3H]³⁺ 901.21
[M+4H]⁴⁺ 676.16
XIC of +Q3: Exp 1, 1487.349 to 1487.849 Da from Sample 3...
Max. 2.9e7 cps.
4 : 2x Tyr + Lys adduct
[M+2H]²⁺ 1487.97
[M+3H]³⁺ 992.32
[M+4H]⁴⁺ 744.49
XIC of +Q3: Exp 1, 1083.349 to 1083.849 Da from Sample 3...
Max. 8.6e6 cps.
5 : 2x Tyr + 2x Lys adduct
[M+3H]³⁺ 1083.42
[M+4H]⁴⁺ 812.82
[M+5H]⁵⁺ 650.46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KGDYHFPIC
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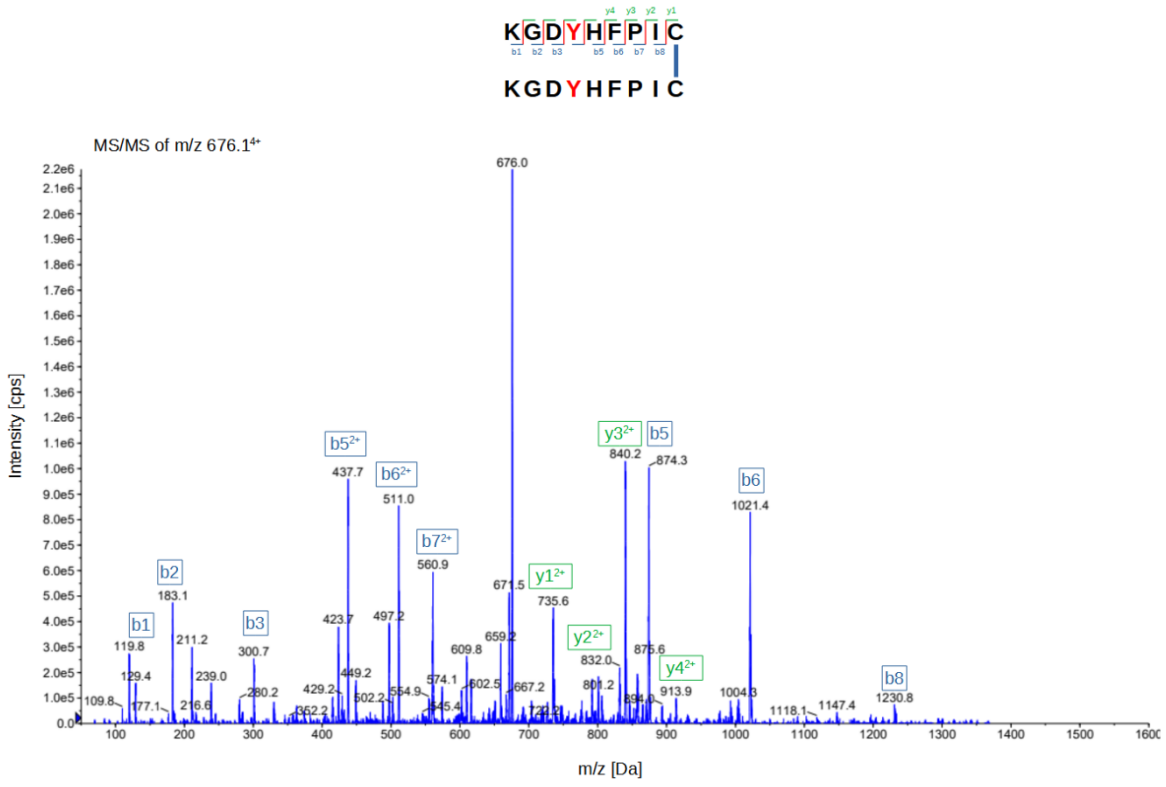
Intensity [cps]
m/z [Da]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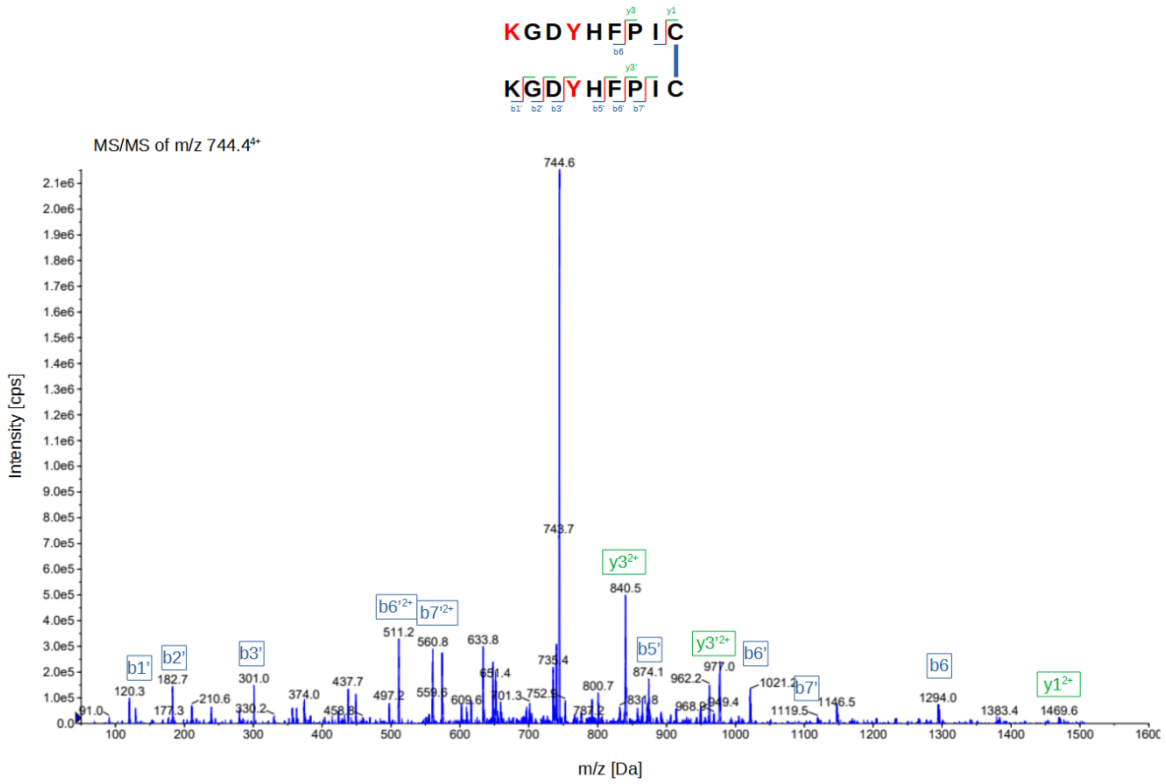
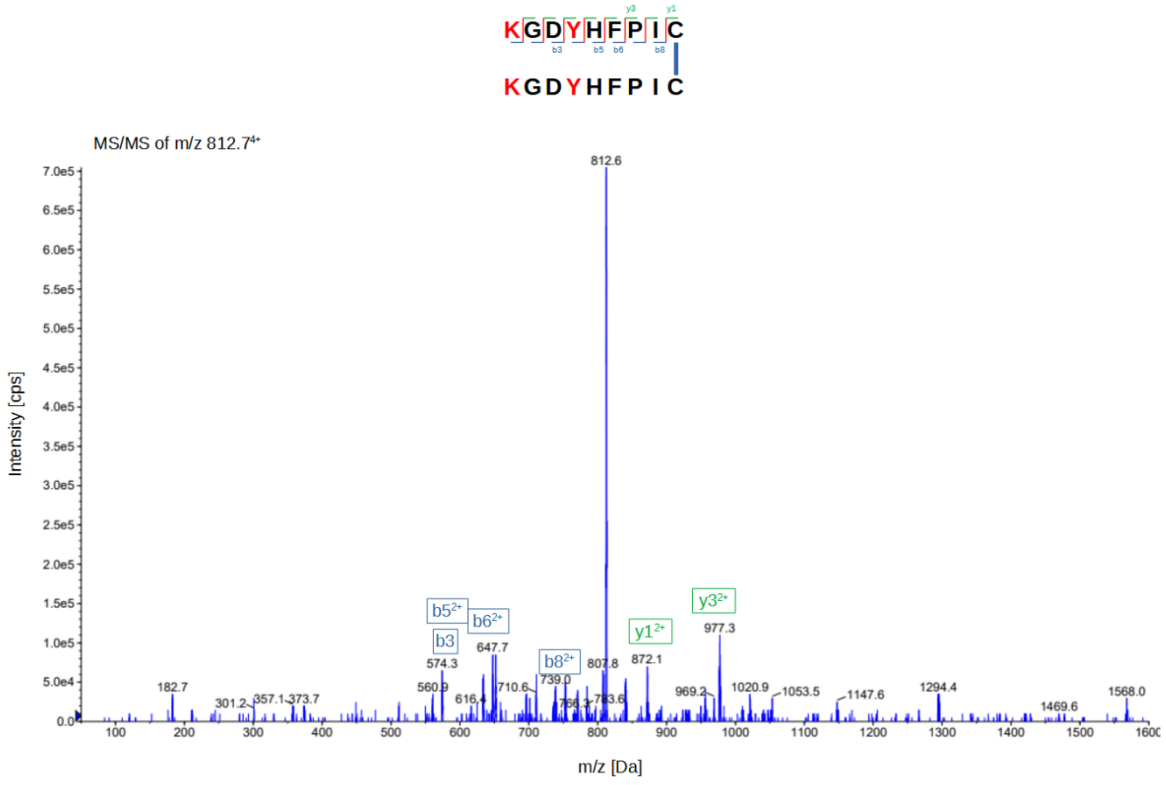
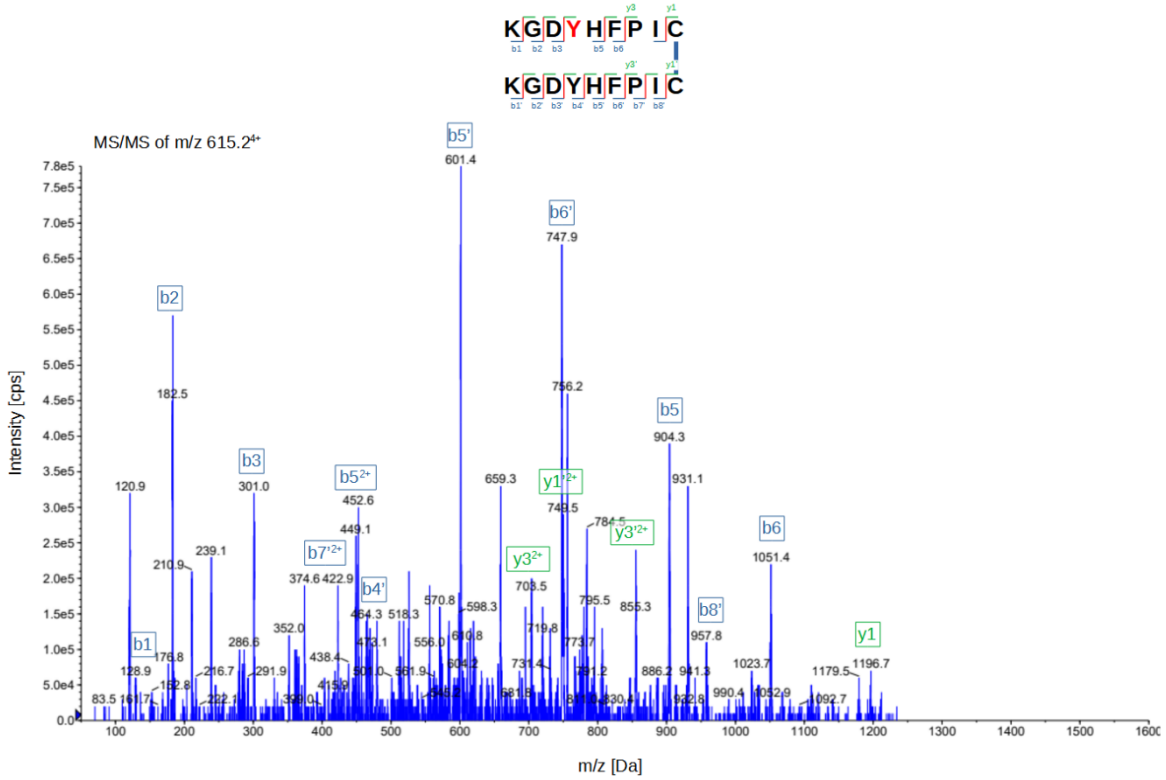
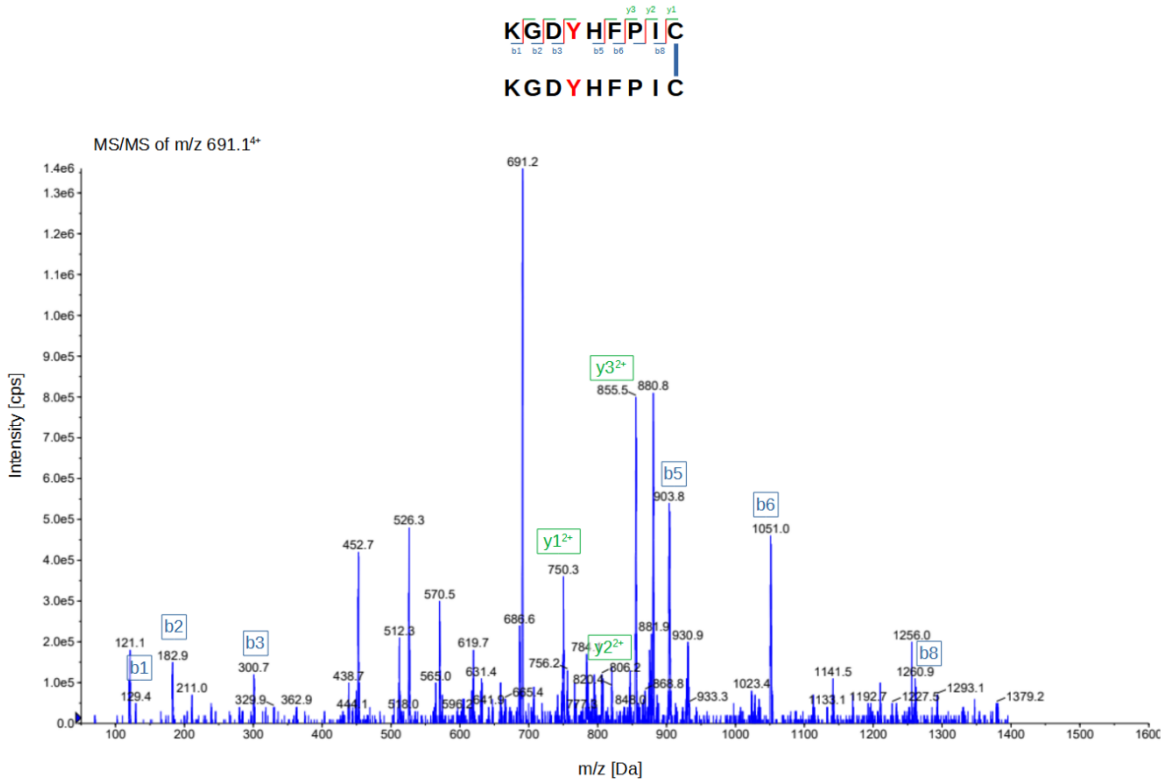
Intensity [cps]
m/z [Da]

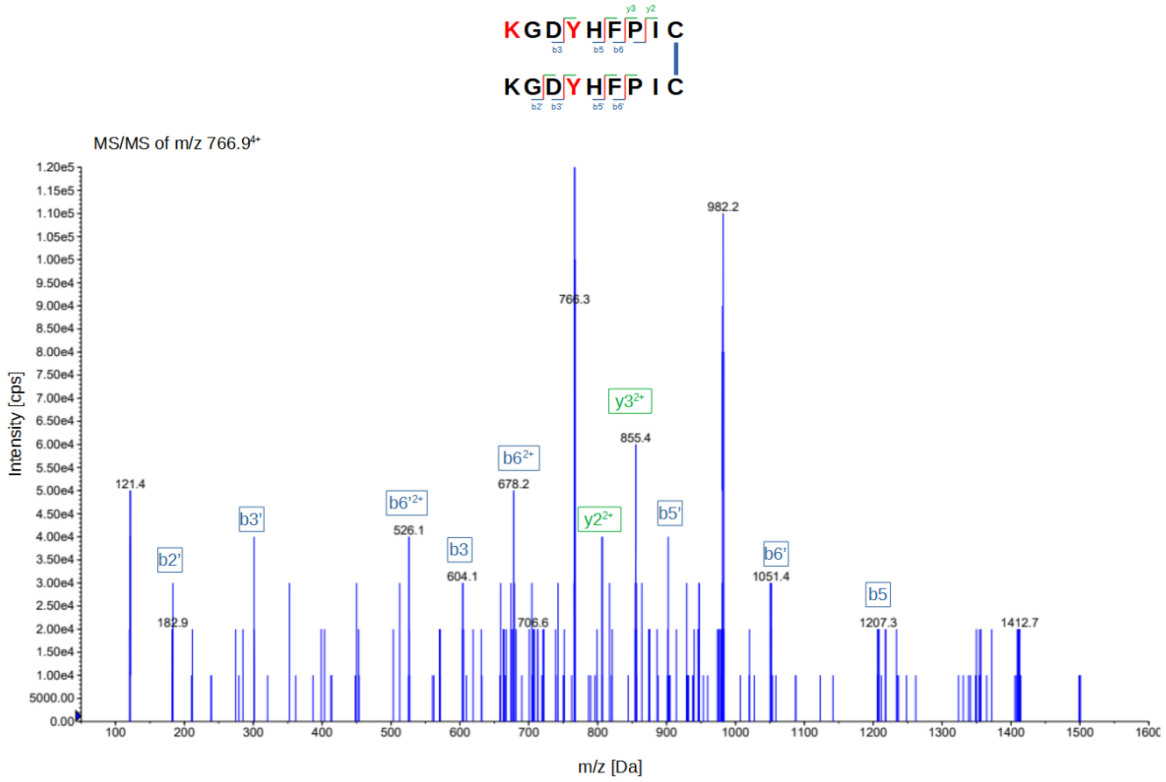

KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 744.4⁴⁺
Intensity [cps]
m/z [Da]
744.6
743.7
y3²⁺
840.5
b6'²⁺
b7'²⁺
511.2
560.8
633.8
b1'
b2'
b3'
b5'
y3'²⁺
b6'
b6
b7'
y1²⁺
182.7
301.0
874.1
977.0
1294.0
1469.6


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 812.7⁴⁺
Intensity [cps]
m/z [Da]
812.6
b5²⁺
b6²⁺
b3
y3²⁺
977.3
y1²⁺
872.1
b8²⁺
647.7
574.3
739.0
807.8
182.7
1294.4
1568.0
1469.6

NP+13


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 615.2⁴⁺
Intensity [cps]
m/z [Da]


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 691.1⁴⁺
Intensity [cps]
m/z [Da]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KGDYHFPIC
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Intensity [cps]
m/z [Da]
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855.4
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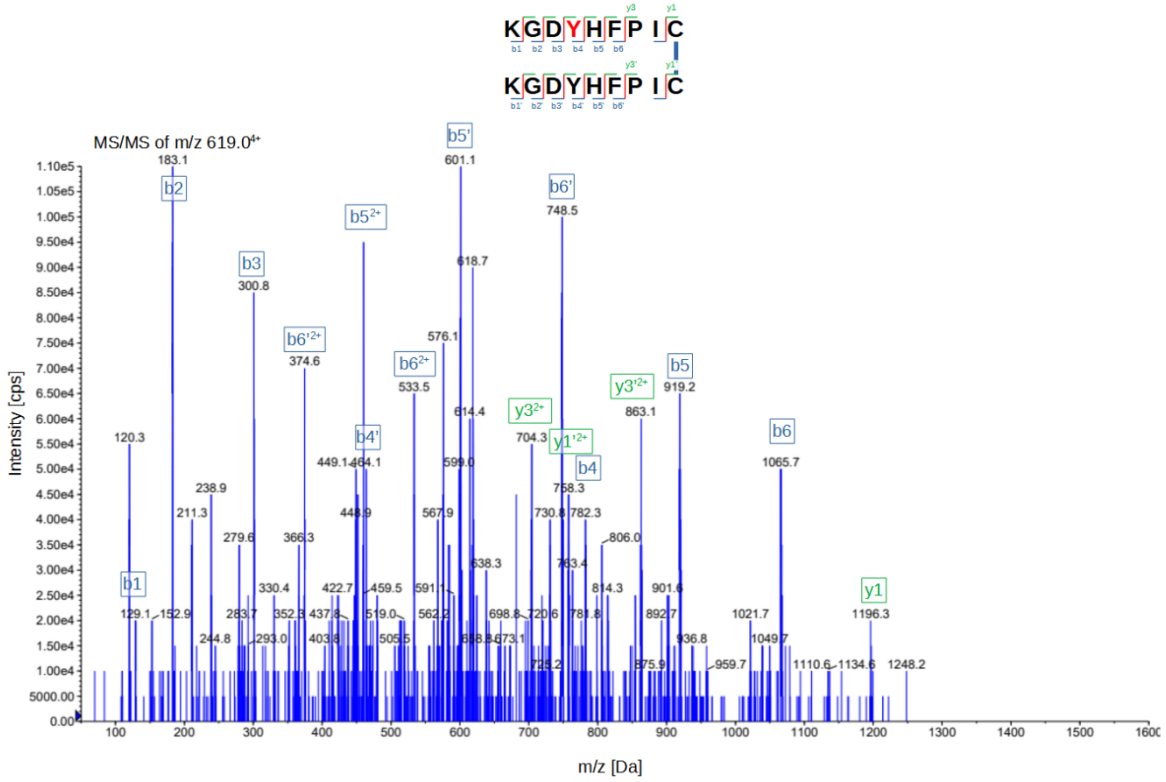
526.1
604.1
1051.4
1207.3
1412.7
121.4
182.9
706.6

NP+14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KGDYHFPIC
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m/z [Da]
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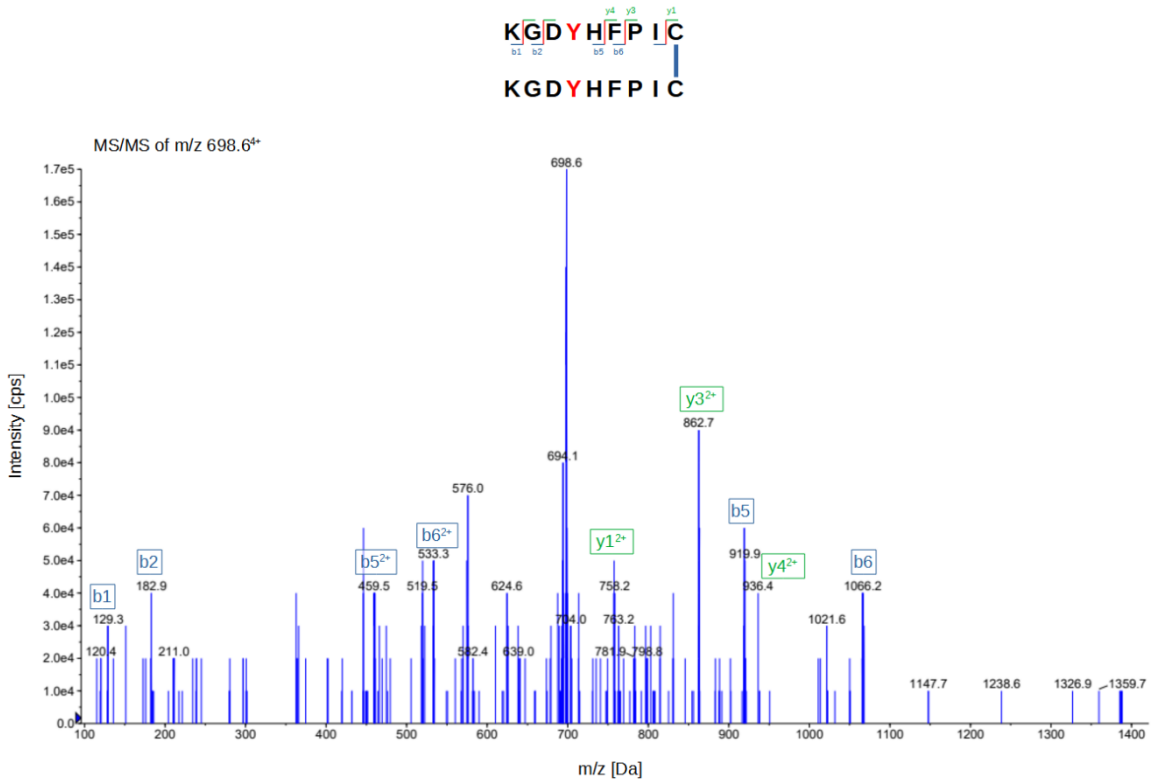
374.6
533.5
919.2
863.1
704.3
1065.7
1196.3
183.1
120.3
129.1
238.9
211.3
279.6
366.3
330.4
422.7
459.5
591.1
698.8
720.6
781.8
892.7
1021.7
1049.7
1110.6
1134.6
1248.2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KGDYHFPIC
MS/MS of m/z 698.6^4+
Intensity [cps]
m/z [Da]
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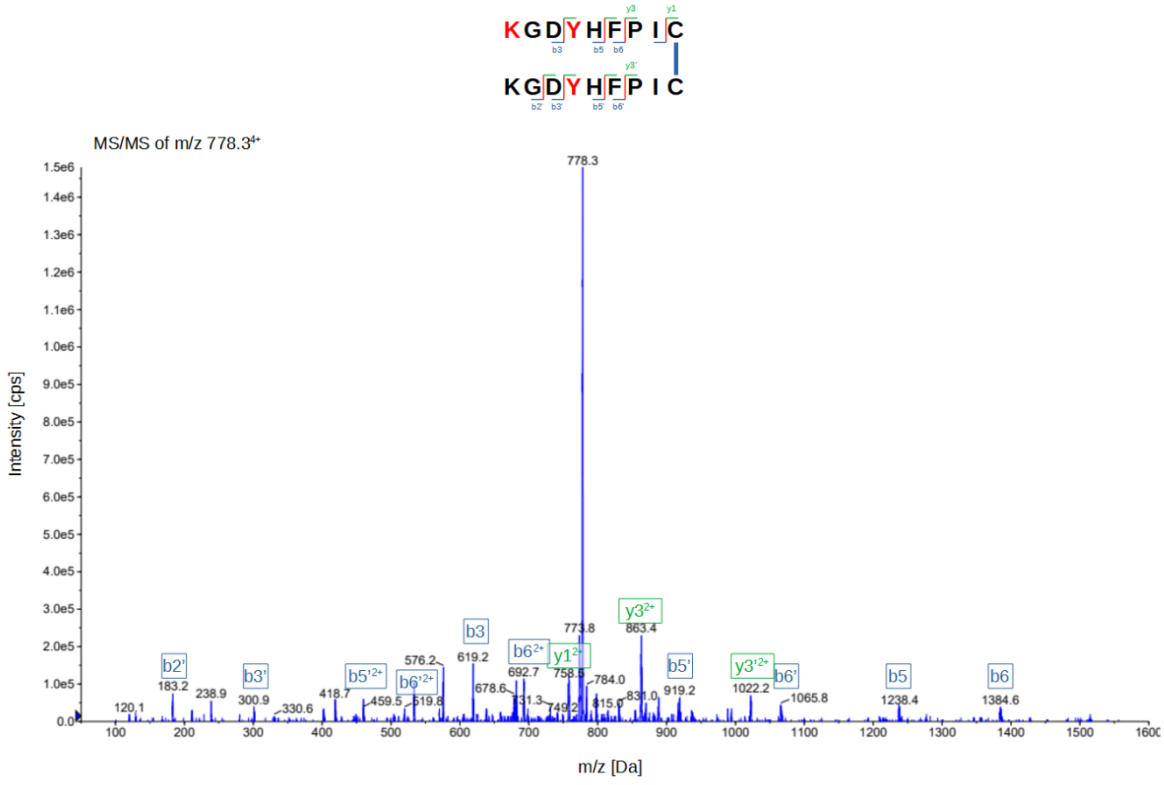
694.1
862.7
576.0
533.3
459.5
519.5
624.6
758.2
784.0
763.2
919.9
936.4
1066.2
1021.6
1147.7
1238.6
1326.9
1359.7
129.3
120.4
211.0
182.9
582.4
639.0
781.9
798.8
y3^2+
b5
y1^2+
y4^2+
b6
b2
b1
b6^2+
b5^2+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KGDYHFPIC
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m/z [Da]
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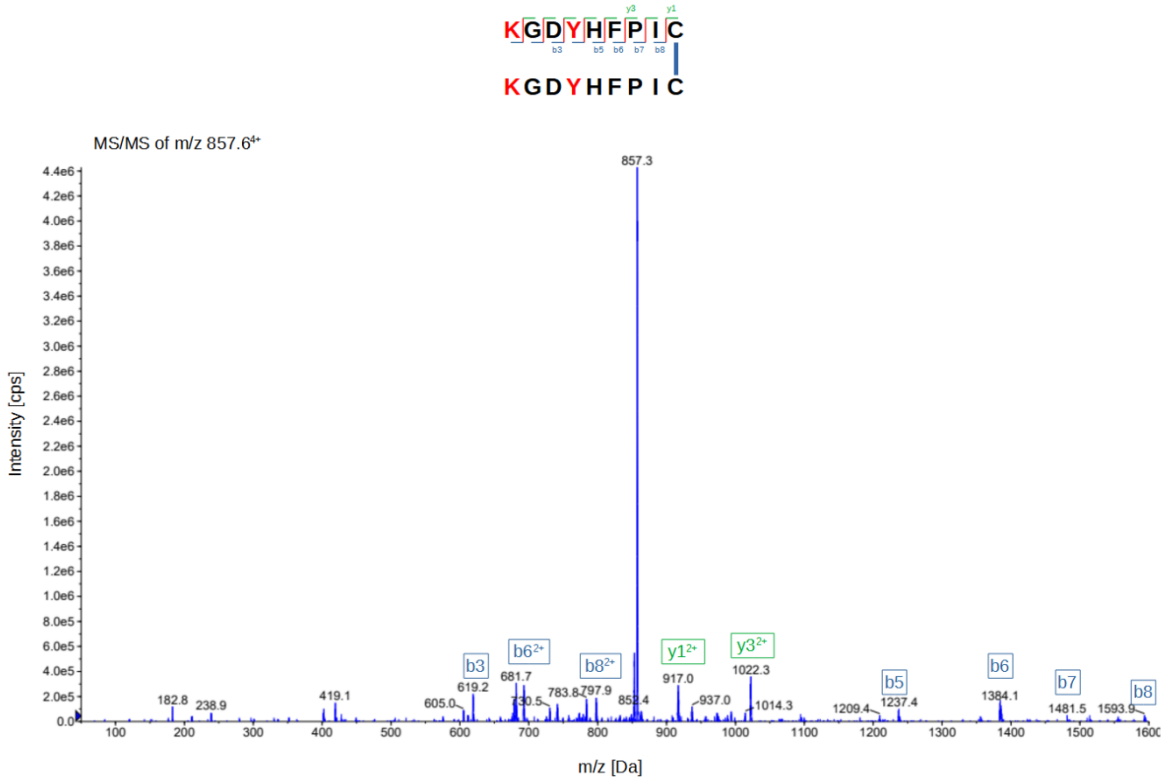
863.4
619.2
576.2
692.7
758.5
784.0
678.6
731.3
749.2
815.0
831.0
919.2
1022.2
1065.8
1238.4
1384.6
183.2
238.9
300.9
330.6
418.7
459.5
519.8
120.1
y3^2+
b3
b6^2+
y1^2+
b5'
y3'^2+
b6'
b5
b6
b2'
b3'
b5'^2+
b6'^2+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Intensity [cps]
m/z [Da]
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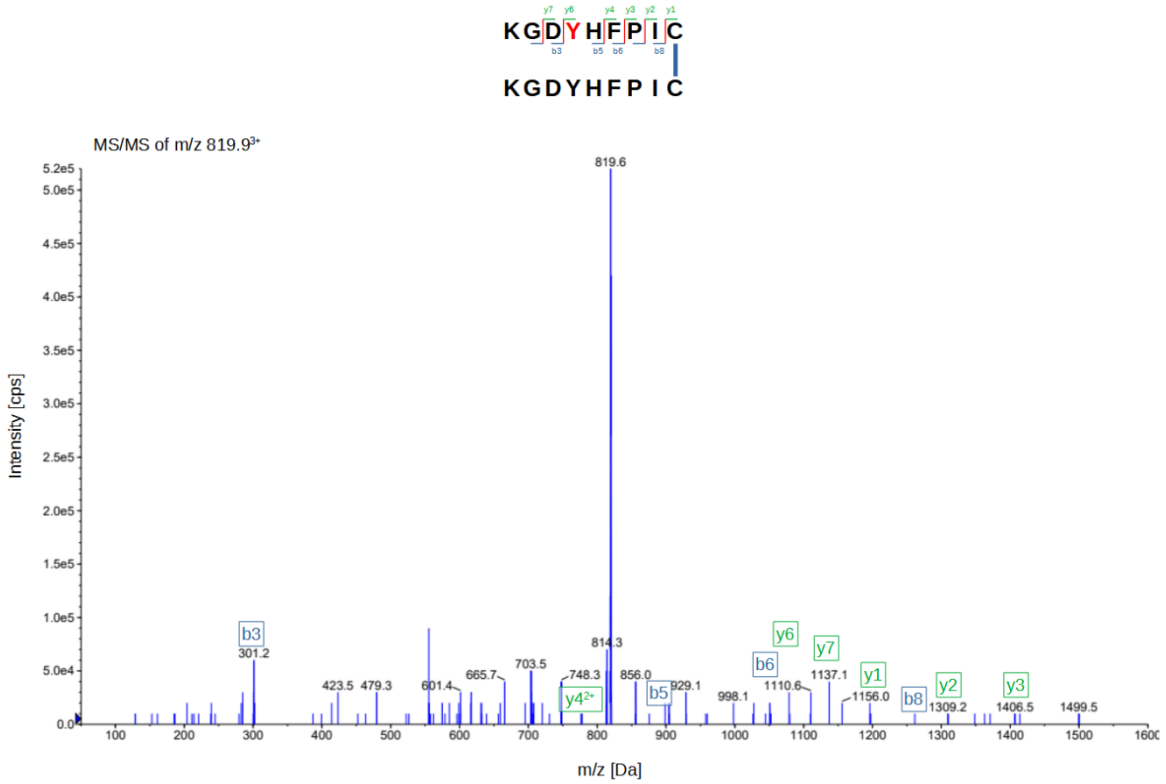
b6²⁺
b8²⁺
y1²⁺
y3²⁺
b5
b6
b7
b8

NP+15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Intensity [cps]
m/z [Da]
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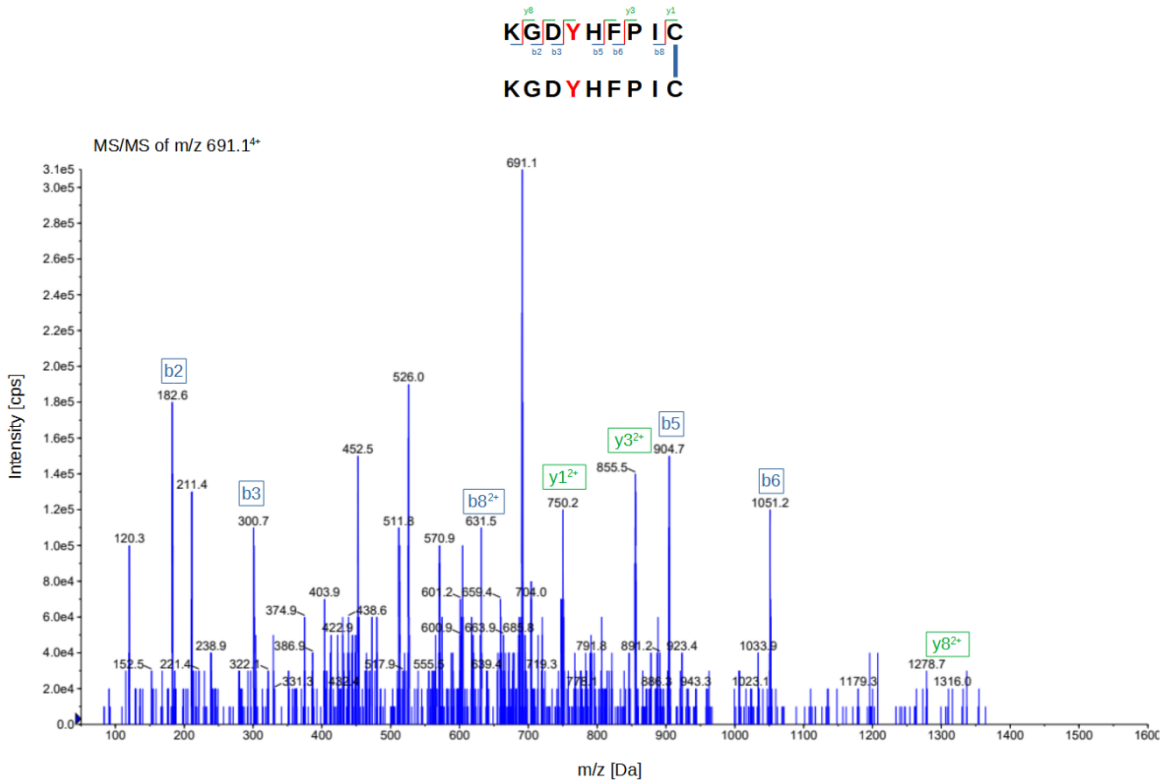
b3
814.3
y4²⁺
y6
y7
b6
y1
b5
b8
y2
y3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KGDYHFPIC
MS/MS of m/z 691.1^4+
Intensity [cps]
m/z [Da]
b2
b3
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b6
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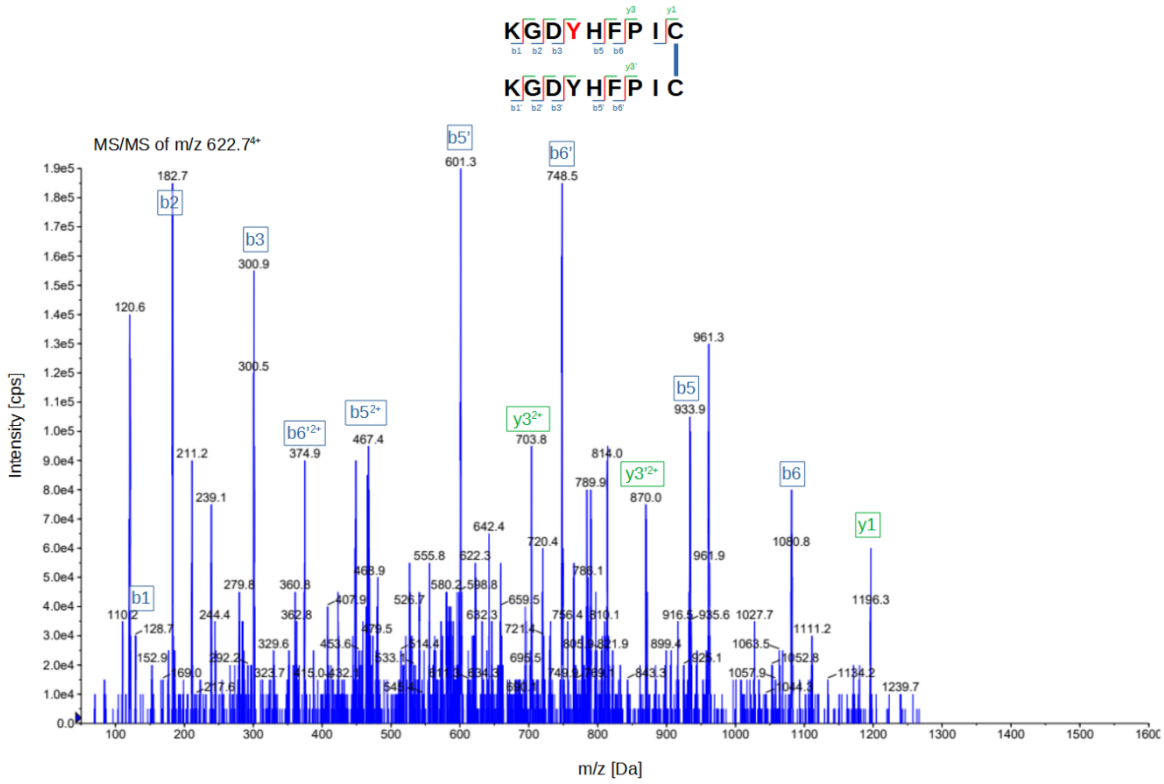
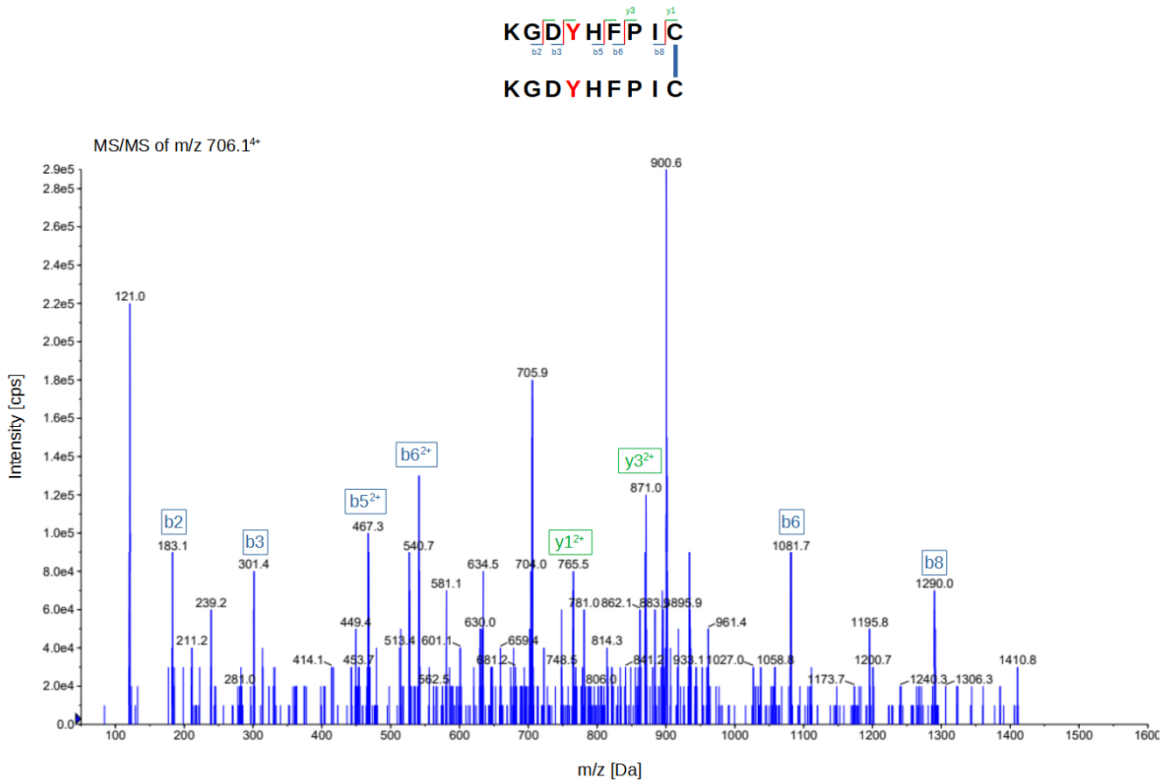
y1^2+
y3^2+
y8^2+

NP+16


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 622.7^4+
Intensity [cps]
m/z [Da]
b1
b2
b3
b5'
b6'
b6'^2+
b5^2+
y3^2+
y3'^2+
b5
b6
y1


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 706.1⁴⁺
Intensity [cps]
m/z [Da]
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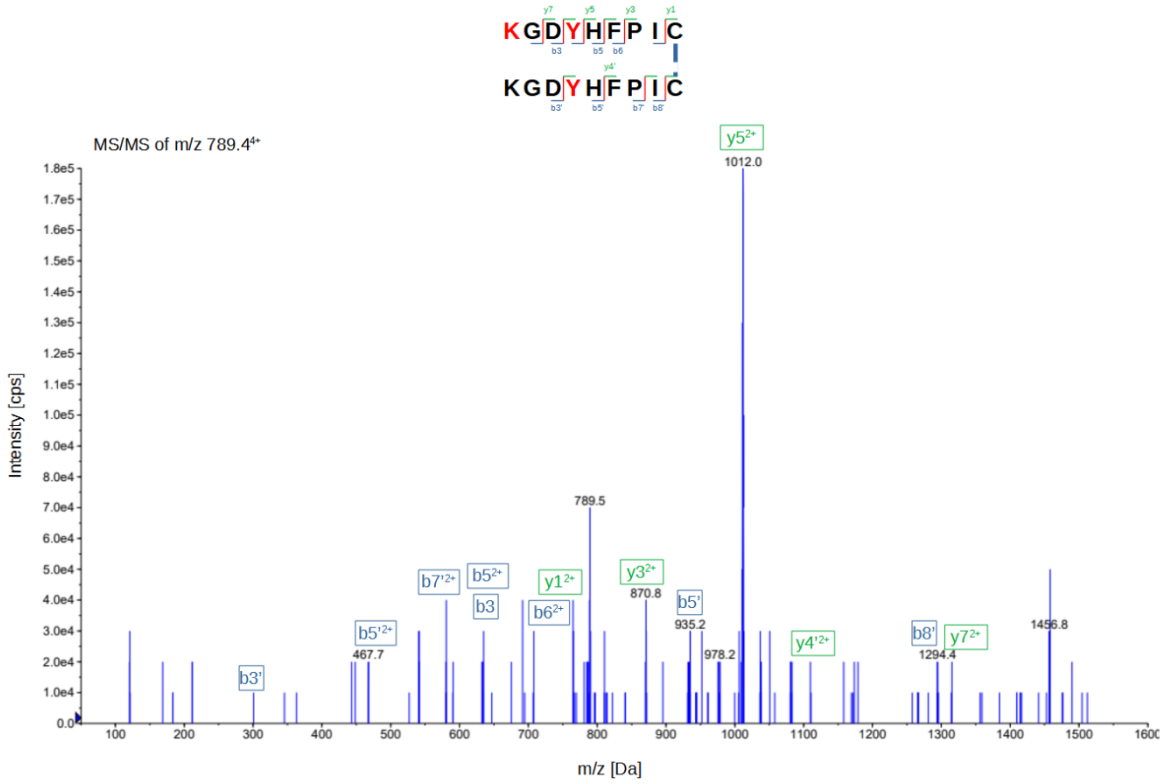
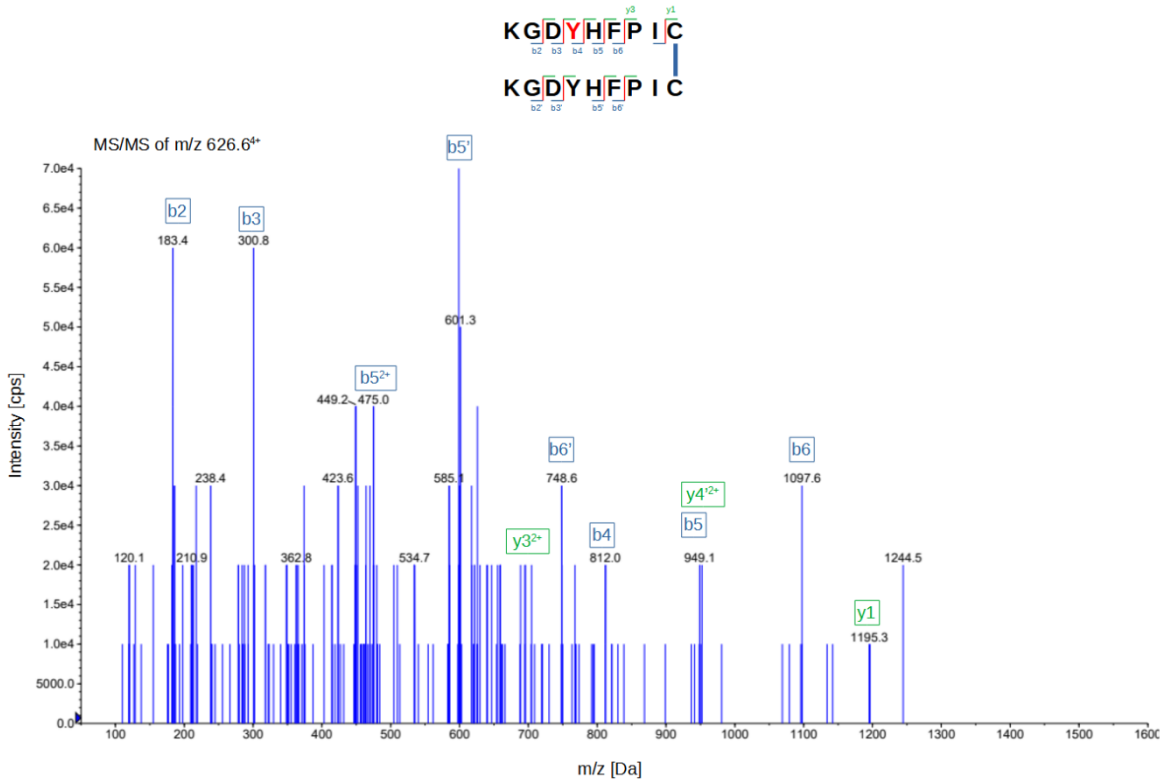
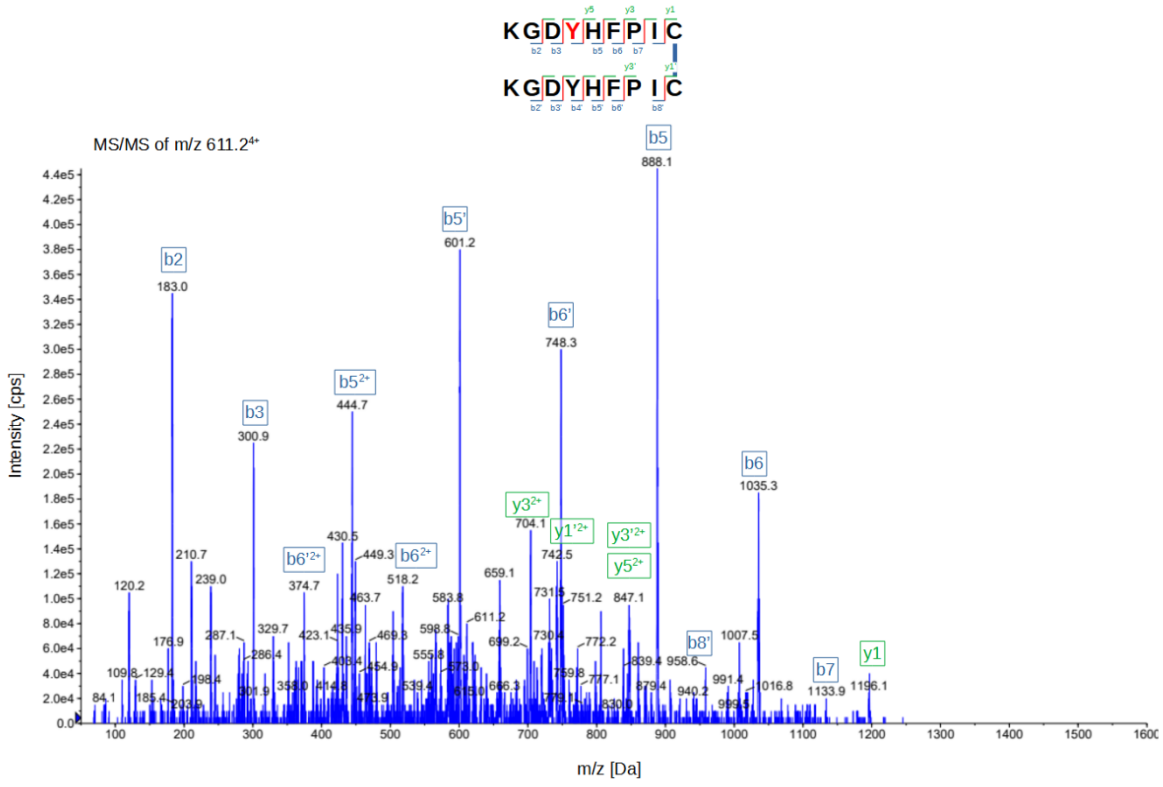
121.0
705.9
b6²⁺
y3²⁺
871.0
b5²⁺
467.3
b2
183.1
b3
301.4
540.7
y1²⁺
765.5
634.5
704.0
581.1
b6
1081.7
b8
1290.0
239.2
449.4
630.0
961.4
1195.8
211.2
513.4
601.1
659.4
814.3
1200.7
1410.8
414.1
453.7
748.5
1027.0
1058.8
281.0
542.5
806.0
1173.7
1240.3
1306.3


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 789.4⁴⁺
Intensity [cps]
m/z [Da]
y5²⁺
1012.0
789.5
b7'²⁺
b5²⁺
y1²⁺
y3²⁺
870.8
b3
b6²⁺
b5'
935.2
b5'²⁺
467.7
978.2
y4'²⁺
b8'
y7²⁺
1294.4
1456.8
b3'

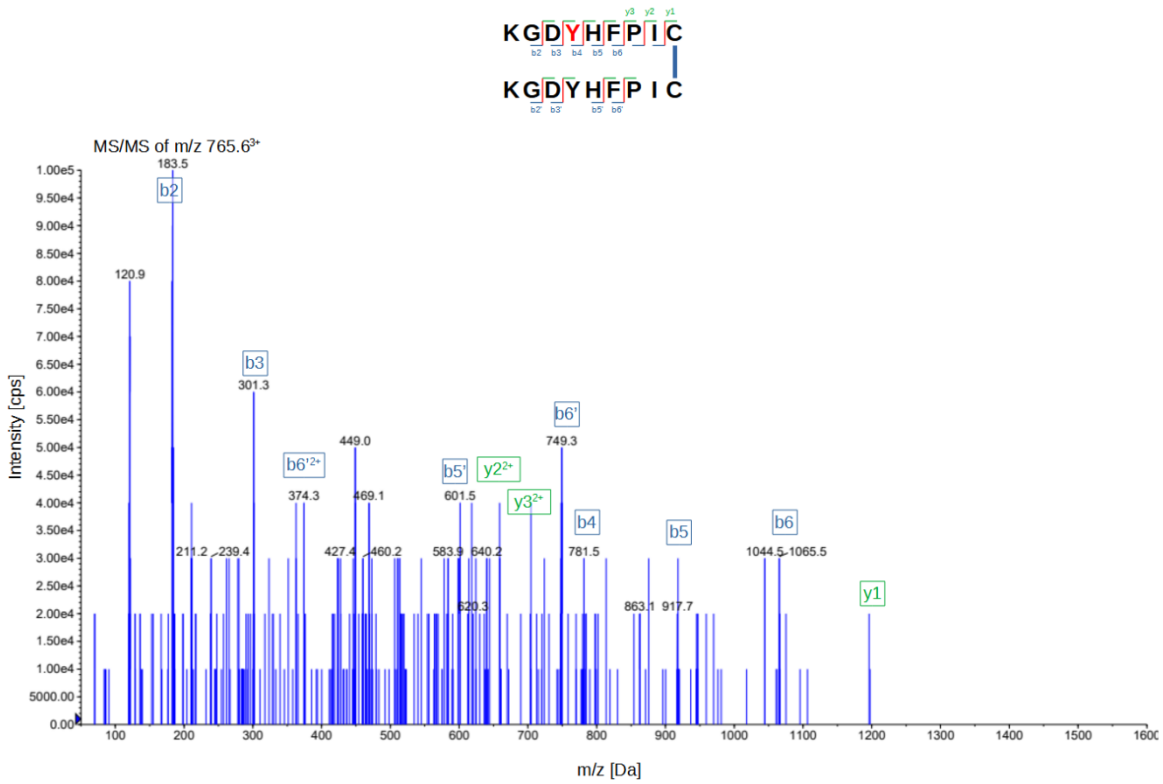
NP+17


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 626.6⁴⁺
Intensity [cps]
m/z [Da]
b5'
b2
b3
b5²⁺
b6'
b6
y4'²⁺
b5
y3²⁺
b4
y1
601.3
183.4
300.8
449.2
475.0
748.6
1097.6
949.1
812.0
1195.3
1244.5
120.1
210.9
238.4
362.8
423.6
534.7
585.1

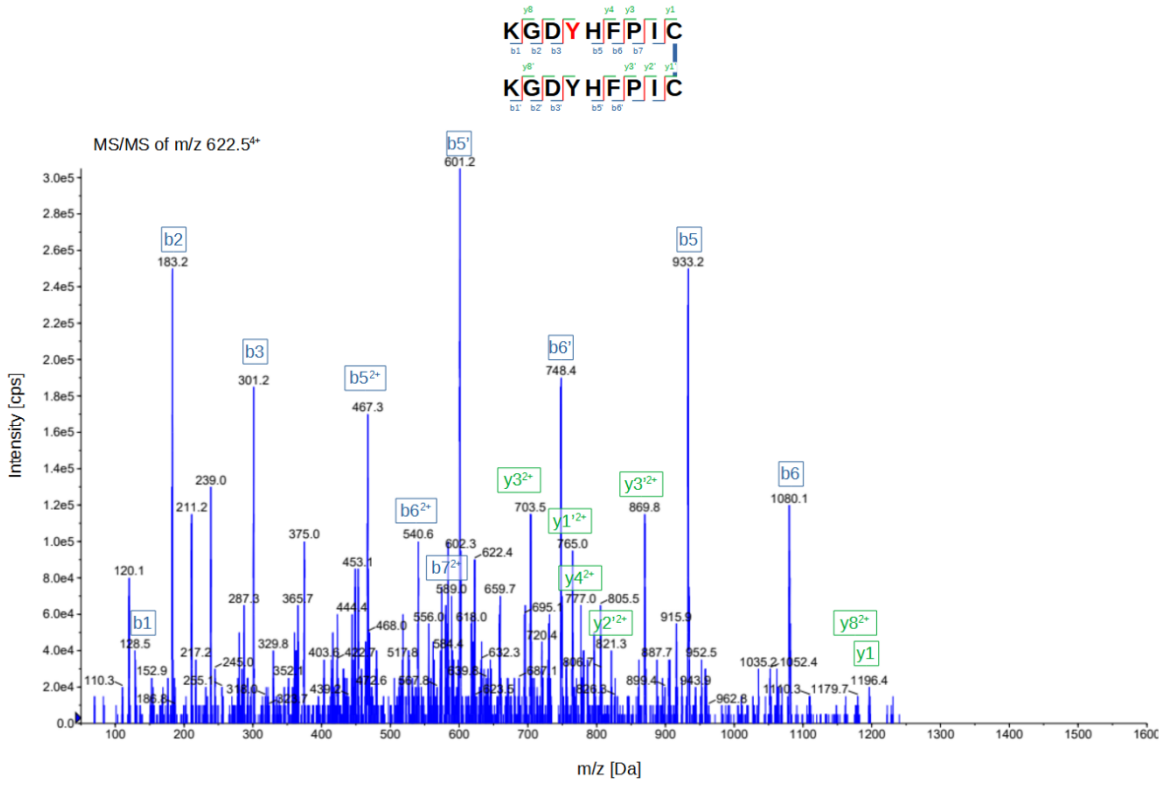
NP+18


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 611.2⁴⁺
Intensity [cps]
m/z [Da]
b5
888.1
b5'
601.2
b2
183.0
b6'
748.3
b5²⁺
444.7
b3
300.9
b6
1035.3
y3²⁺
704.1
y1'²⁺
742.5
y3'²⁺
y5²⁺
b6'²⁺
b6²⁺
b8'
b7
1133.9
y1
1196.1
1007.5
847.1
659.1
518.2
374.7
430.5
449.3
463.7
583.8
611.2
699.2
772.2
751.2
731.5
210.7
239.0
120.2
176.9
287.1
329.7
423.1
435.9
469.3
598.8
958.6
991.4
1016.8
940.2
879.4
839.4
777.1
759.8
666.3
555.8
454.9
403.4
286.4
198.4
129.4
109.8
84.1
185.4

NP+19


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 765.6³⁺
Intensity [cps]
m/z [Da]
b2
b3
b6'
b5'
y2²⁺
y3²⁺
b4
b5
b6
y1
b6'²⁺

NP+20


KGDYHFPIC
KGDYHFPIC
MS/MS of m/z 622.5⁴⁺
Intensity [cps]
m/z [Da]
b5'
b2
b5
b3
b6'
b5²⁺
y3²⁺
y3'²⁺
b6
b6²⁺
y1'²⁺
b7²⁺
y4²⁺
y2'²⁺
y8²⁺
y1
b1

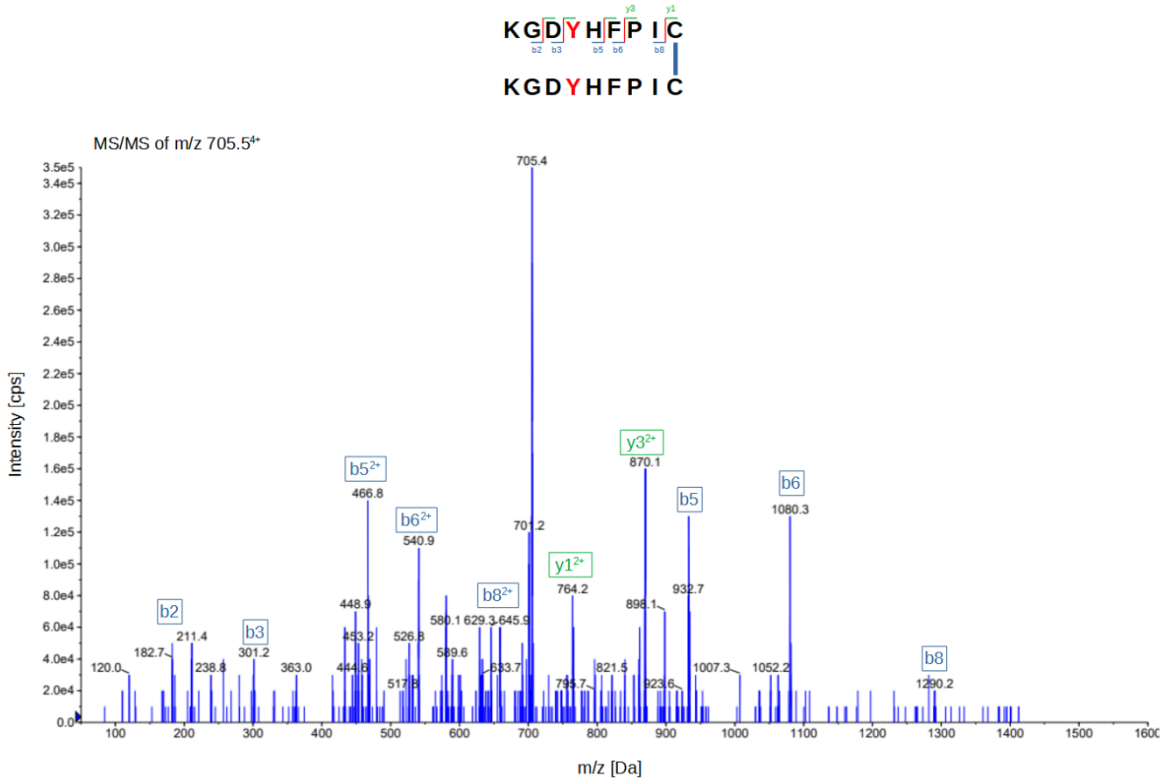


Table S2. Peptide mapping analysis for KRas^{G12D} labelled with 12 and 14 probes

Covalent probe	Modified Peptides	Position	RT (min)	Calculated Peptide Mass (Da)	Detected *m/z*	Measured Mass (Da)	Mass Error (ppm)
12	QGVDDAFYTLVR	150-161	47.5	1655.7290	828.8702	1655.7245	-2.7
	TRQGVDDAFYTLVR	148-161	40.1	1912.8778	638.6304	1912.8673	-5.5
14	QGVDDAFYTLVR	150-161	47.8	1700.7140	851.3618	1700.7078	-3.6
	TRQGVDDAFYTLVR	148-161	40.4	1957.8628	653.6249	1957.8511	-6.0

Figure S3. Mass spectrum of KRas^{G12D} 150-161 tryptic peptide modified with probe 12 and 14

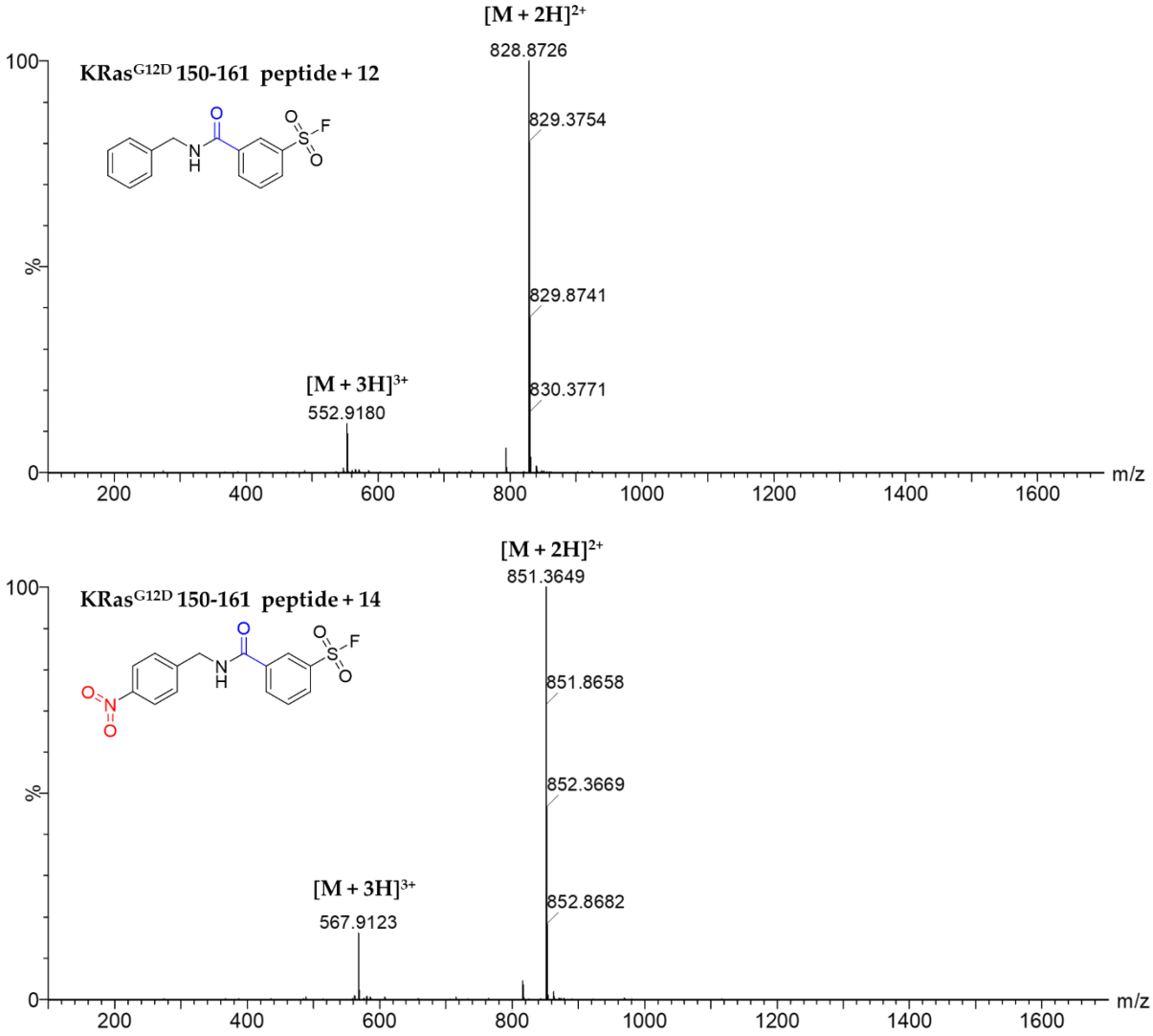


Figure S4. Mass spectrum of KRasG12D 150-161 tryptic peptide modified with probe 14

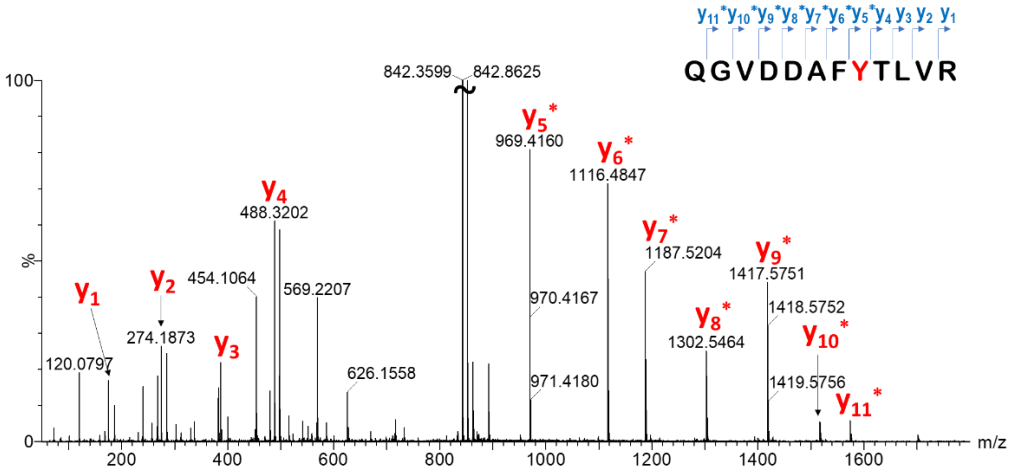


Table S3. Results of PANC-1 lysate labelling experiments analysed by mass spectrometry

Protein		Labelling site
Name	Uniprot	
40S ribosomal protein S16	P62249	N-term
60S ribosomal protein L14	P50914	K79
40S ribosomal protein S14	P62263	K106
Actin, cytoplasmic 1	P60709	Y53; Y240
Vimentin	P08670	Y30; Y38
Heterogeneous nuclear ribonucleoproteins A2/B1	P22626	T176; Y324; Y336
X-ray repair cross-complementing protein 6	P12956	S222
T-complex protein 1 subunit delta	P50991	T69
Heterogeneous nuclear ribonucleoprotein A1	P09651	Y357; S365 / Y366
60S ribosomal protein L4	P36578	Y122
60S ribosomal protein L3	P39023	Y307
40S ribosomal protein S3a	P61247	S154
60S ribosomal protein L8	P62917	Y133
60S ribosomal protein L7	P18124	Y82
60S ribosomal protein L34	P49207	S17
60S ribosomal protein L17	P18621	Y4
60S ribosomal protein L28	P46779	Y25
60S ribosomal protein L36	Q9Y3U8	Y5

Supplementary Methods

General

Reagents and solvents were purchased from commercial suppliers and were used without further purification. The reactions were monitored using thin layer chromatography (TLC) (which was carried out on Merck aluminum sheets, silica gel 60 F_{254}) or HPLC-MS (Shimadzu LCMS2020). Flash column chromatography was carried out on Teledyne ISCO Combi Flash Lumen+ Rf using silica gel 60 F_{254}. The NMR experiments were performed at 500 MHz on a Varian VNMR SYSTEM spectrometer for ^{1}H and 126 MHz for ^{13}C.

Synthesis of 2-oxo-2H-chromen-7-yl acetate (S1)

To a solution of 7-hydroxycoumarin (5 mmol, 1 eq.) in ethyl-acetate (10 ml) were added pyridine (1.1 eq.) and acetic anhydride (3.7 eq.). The resulting mixture was stirred for 2 h at room temperature. The reaction was quenched with water (20 ml) and stirred for further 30 min. The aqueous phase was separated and extracted with ethyl-acetate (3x10 ml). The combined organic phases were washed with 1M aq. HCl, saturated $NaHCO_3$ solution, water and brine then dried on Na_2SO_4. After filtration the solvent was evaporated resulting the product (**S1**) (0,961 g, 95%) as a white solid which doesn't required further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.68 (dd, *J* = 9.5, 0.7 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 2.2 Hz, 1H), 7.06 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.39 (d, *J* = 9.6 Hz, 1H), 2.34 (s, 3H). [43]

Synthesis of 7-hydroxy-2-oxo-2H-chromene-8-carbaldehyde (S2)

The solution of (**S1**) (4.7 mmol, 1 eq.) and trifluoroacetic acid (6,4 ml) was cooled down to 0 °C and hexamethylenetetramine (7.05 mmol, 1.5 eq.) was added. The resulting mixture was refluxed for 16 h. After completion of the reaction the TFA was evaporated under vacuum then 20 ml of water was added to the residue. The resulting mixture was stirred at 60 °C for 30 min then cooled down to 20 °C. The yellow precipitate was filtered off and dried in high vacuum to give **S2** (0,191 g, 21%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.89 (s, 1H), 10.44 (s, 1H), 8.02 (d, J = 9.6 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 6.96 (d, J = 8.7 Hz, 1H), 6.38 (d, J = 9.6 Hz, 1H). [44]

Synthesis of ethyl 4-((tert-butyldiphenylsilyl)oxy)benzoate (S3)

Tert-butylchlorodiphenylsilane (5,3 mmol, 1.1 eq.) was added dropwise to the mixture of ethyl 4-hydroxybenzoate (4.81 mmol, 1 eq.) and diisopropylethylamine (5.78 mmol, 1.2 eq.) in chloroform (20 ml). The resulting mixture was stirred at room temperature for 5 h then quenched with water (20 ml). The aqueous phase was washed with chloroform (2x10 ml). The combined organic phases were dried on Na_2SO_4. After evaporation of the chloroform the crude product was purified by normal-phase flash chromatography using hexane/ethyl-acetate 0-10% eluent to furnish the desired product (**S3**) (0,788 g, 41%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.72 – 7.68 (m, 4H), 7.45 – 7.41 (m, 2H), 7.39 – 7.35 (m, 4H), 6.79 – 6.76 (m, 2H), 4.30 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.11 (s, 9H). [45]

Syntesis of (4-((tert-butyldiphenylsilyl)oxy)phenyl)methanol (S4)

Under argon diethyl ether (5 ml) was cooled down to -10 °C then $LiAlH_4$ (1.87 mmol, 2 eq.) was added. To the resulting mixture (**S3**) (0.93 mmol, 1 eq.) in DEE (3 ml) was added dropwise via syringe in 10 minutes then stirred for 1,5 h keeping the temperature below 0 °C. The reaction was quenched with saturated Na_2SO_4 solution (10 ml) at 0 °C and warmed up to room temperature. The resulting white precipitate was filtered off and washed with cold water following by ethyl-acetate. The aqueous phase was separated and washed with ethyl-acetate (3x10 ml). The combined organic phases were extracted with brine, separated and dried on Na_2SO_4 then evaporated in vacuum. The resulting white solid (**S4**) (0,271 g, 81 %) required no further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 4H), 7.44 – 7.40 (m, 2H), 7.38 – 7.34 (m, 4H), 7.11 – 7.07 (m, 2H), 6.78 – 6.72 (m, 2H), 4.54 (s, 2H), 1.10 (s, 9H). [46]

Synthesis of tert-butyl(4-(chloromethyl)phenoxy)diphenylsilane (S5)

Compound **S4** (0.60 mmol, 1 eq.) was dissolved in dichloromethane (5 ml) and cooled to 0 °C. Thionyl chloride (0.1 ml, 2,1 eq.) was added dropwise to the solution. The resulting mixture was warmed up to room temperature then stirred for 2 h. The mixture was poured on ice then extracted with EtOAc (3x5 ml). The organic layers were combined and washed with saturated aqueous solution of $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The product (**S5**) was obtained as a white solid (0.114 g, 50 %) and was used without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.73 – 7.68 (m, 4H), 7.45 – 7.40 (m, 2H), 7.37 (dd, J = 7.9, 6.5 Hz, 4H), 7.13 – 7.09 (m, 2H), 6.75 – 6.71 (m, 2H), 4.48 (s, 2H), 1.10 (s, 9H). [47]

Synthesis of 7-((4-((tert-butyldiphenylsilyl)oxy)benzyl)oxy)-2-oxo-2H-chromene-8-carbaldehyde (S6)

Under argon tert-butyl(4-(chloromethyl)phenoxy)diphenylsilane (**S5**) (0.85 mmol, 1.23 eq.), 7-hydroxy-8-formylcoumarin (**2**) (0.69 mmol, 1 eq.), KI (1.71 mmol, 2.47 eq.) and K_2CO_3 (6.83 mmol, 9.88 eq.) were dissolved in dry DMF (6 ml) and stirred at room temperature for 16h. The mixture was diluted with

water then the aqueous phase was extracted with EtOAc (3x10 ml). The combined organic phases were dried on Na_2SO_4 then evaporated in vacuum. The crude product was purified by normal-phase flash chromatography using hexane/ethyl-acetate 0-50% eluent to furnish the desired product (**S6**) (0.125 g, 34%) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.71 (dt, J = 6.8, 1.5 Hz, 4H), 7.61 (d, J = 9.5 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.34 (m, 4H), 7.20 – 7.15 (m, 2H), 6.93 (d, J = 8.8 Hz, 1H), 6.81 – 6.77 (m, 2H), 6.32 (d, J = 9.6 Hz, 1H), 5.14 (s, 2H), 1.10 (s, 9H). [31]

Synthesis of 7-((4-((tert-butyldiphenylsilyl)oxy)benzyl)oxy)-8-(difluoromethyl)-2H-chromen-2-one (DPF sensor: S7)

Under argon (**S6**) (0.24 mmol, 1 eq.) was dissolved in DCM (5 ml), cooled down to -20 °C then N,N-diethylaminosulfur trifluoride (DAST, 0.40 mmol, 1.7 eq.) was added dropwise via a syringe. The resulting mixture was warmed up to -5 °C and stirred for 4 h. After completion of the reaction the mixture was cooled to -78 °C and quenched with water (10 ml). The resulting solution was warmed up to room temperature and extracted with dichloromethane (2x5 ml). The combined organic phases were dried on Na_2SO_4 and evaporated in vacuum. The crude product was purified by normal-phase flash chromatography using hexane/ethyl-acetate 0-35% eluent to furnish the desired DPF sensor (**S7**) (0.035 g, 27%) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 4H), 7.60 (d, J = 9.6 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.40 – 7.34 (m, 4H), 7.27 (s, 1H), 7.18 – 7.13 (m, 2H), 6.90 (d, J = 8.8 Hz, 1H), 6.81 – 6.77 (m, 2H), 6.29 (d, J = 9.5 Hz, 1H), 5.10 (s, 2H), 1.12 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.48, 155.76, 143.00, 135.49, 132.73, 131.22, 129.94, 128.44, 127.80, 127.78, 119.99, 113.92, 112.82, 110.01, 109.47, 71.01, 26.50, 19.45.

Supplementary References

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