

Digital Supplementary

Sample ID	Sum Formula	Targeted Ion [M+2H] ²⁺ (m/z)	Charge	Optimal NCE
Py SA	C ₄₉ H ₇₂ N ₁₄ O ₁₉	581.26273	2	30
PAO1	C ₅₅ H ₈₃ N ₁₇ O ₂₂	667.80275	2	35
1-60	C ₄₅ H ₆₅ N ₁₃ O ₁₉	546.73381	2	25
206-12	C ₄₈ H ₆₇ N ₁₅ O ₂₀	587.74216	2	25
3A06	C ₅₂ H ₇₆ N ₁₄ O ₂₃	633.26821	2	25
3B19	C ₆₁ H ₉₃ N ₁₇ O ₂₂	708.84188	2	30
3C16	C ₄₄ H ₆₀ N ₁₂ O ₂₀	539.21017	2	25
3D19	C ₄₃ H ₅₇ N ₁₂ O ₂₂	562.21291	2	25
3F12	C ₅₅ H ₈₂ N ₁₆ O ₂₂	660.29730	2	30
3G07	C ₅₅ H ₈₁ N ₁₅ O ₂₁	644.79440	2	30
S3a05	C ₄₇ H ₆₉ N ₁₃ O ₁₈	552.75200	2	25
S3a20	C ₄₂ H ₅₉ N ₁₁ O ₁₇	495.71234	2	20
S3b09	C ₅₆ H ₈₃ N ₁₅ O ₂₄	675.79459	2	25
S3b16	C ₄₅ H ₆₆ N ₁₂ O ₁₇	524.24127	2	30
S3c13	C ₄₃ H ₅₉ N ₁₁ O ₂₀	525.70472	2	25
S3e20	C ₅₃ H ₇₉ N ₁₅ O ₂₃	647.78149	2	25
S3g01	C ₄₆ H ₆₄ N ₁₂ O ₂₂	569.22073	2	25

Table S1. Targeted ions and NCE values for MS/MS analysis used for pyoverdine structure elucidation.

Sample ID	RT (min) of			
	Glu-FerB	Suc-Py	Suca-Py	Glu-IsoPy
Py SA	-	3.28	2.63	-
PAO1	3.16	3.97	3.36	-
1-60	1.73	2.58	1.86	-
206-12	1.45	2.42	-	-
3A06	1.87	2.98	2.33	-
3B19	1.37	2.09	1.41	-
3C16	4.63	-	-	3.98
3D19	3.85	4.41	3.69	-
3F12	3.39	4.10	3.37	-
3G07	2.29	3.04	2.44	-
S3a05	3.58	4.18	3.48	-
S3a20	3.30 (H-FerB: 2.99)	4.27	3.55	-
S3b09	2.41	3.39	2.80	-
S3b16	3.39	3.91	3.33	-
S3c13	4.85	5.78	5.01	-
S3e20	3.08	3.84	3.21	-
S3g01	4.89	5.18	4.50	-

Table S2. Average retention times of identified pyoverdines and ferribactins found in the extracts of the investigated bacterial strains.

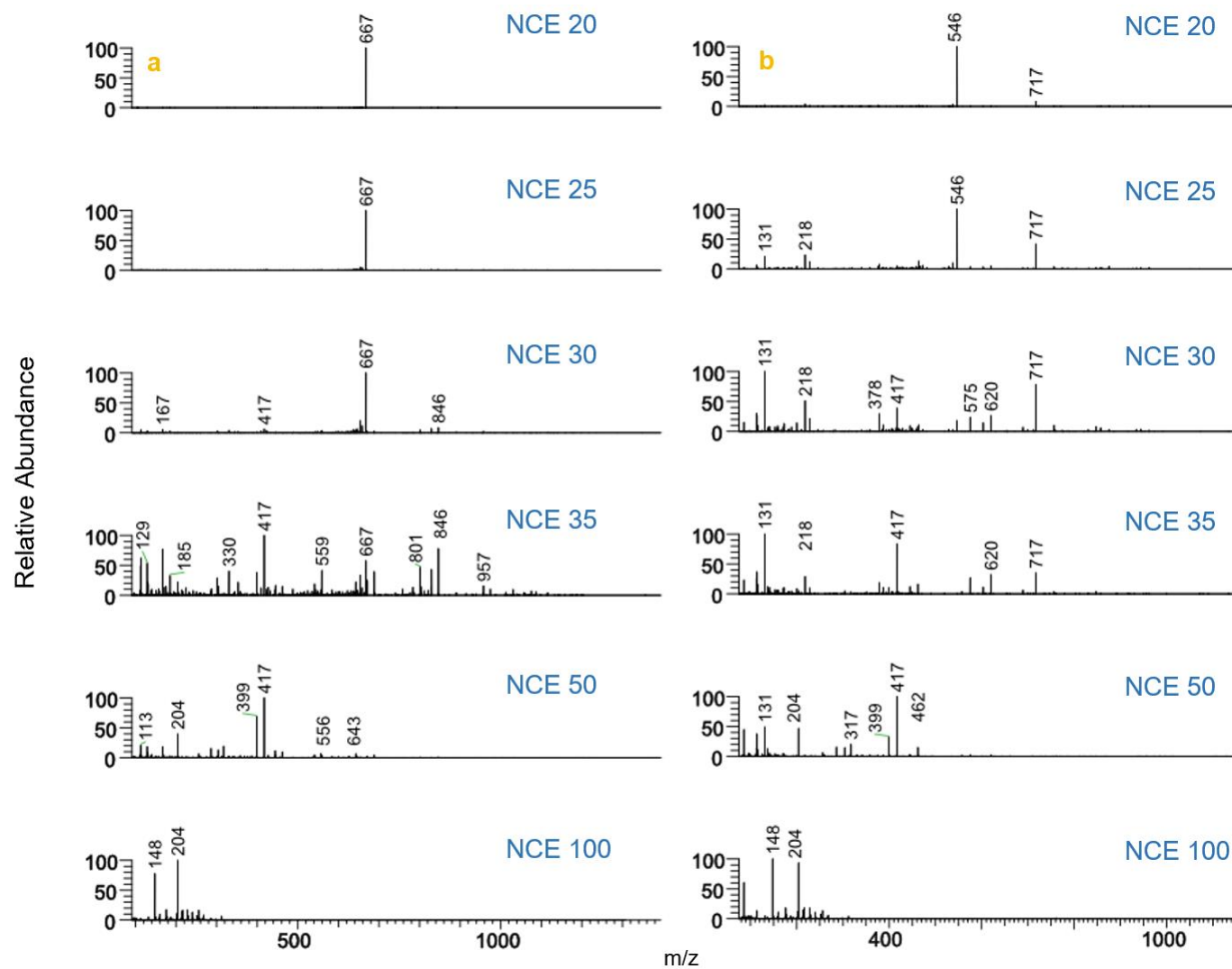


Fig. S1. Stepped MS/MS acquired of the doubly charged Suc-Py $[M+2H]^{2+}$ ions of the bacteria PAO1 (m/z 667.80275) (a) and 1-60 (m/z 546.73381) (b).

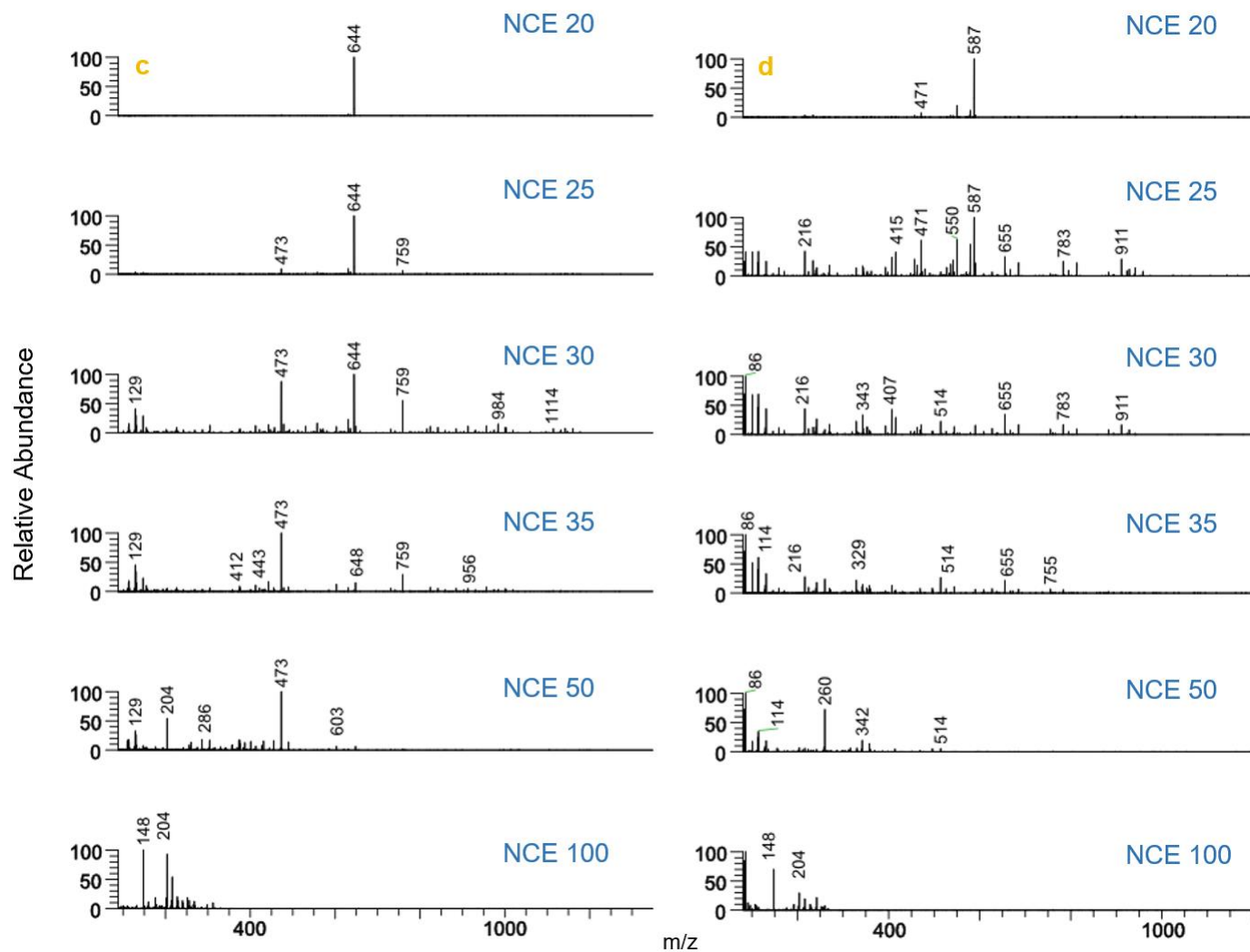
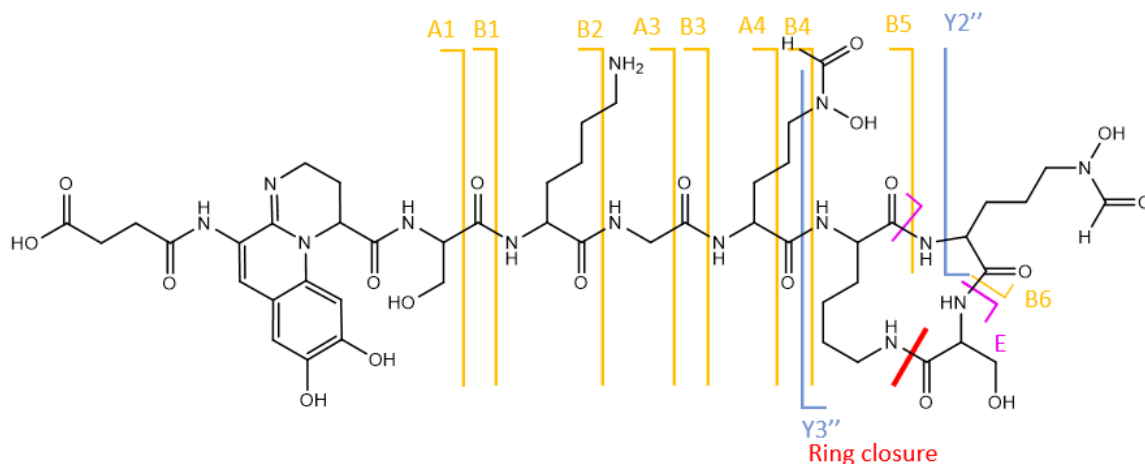


Fig. S2. Stepped MS/MS acquired of the doubly charged Suc-Py $[M+2H]^{2+}$ ions of the bacteria 3G07 (m/z 644.79440) (c) and 206-12 (m/z 587.74216) (d)

Table S3. Detected fragments in the MS/MS fragmentation of Suc-Py of Py SA compared to their theoretical value m/z value and their ppm deviation.



Name:	Py SA			
Sequence:	Ser-Lys-Gly-FoOHOrn-(Lys-FoOHOrn-Ser)			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₉ H ₇₃ N ₁₄ O ₁₉	1161.51764	1161.51704	-0.52
[M+2H]²⁺	C ₄₉ H ₇₄ N ₁₄ O ₁₉	581.26273	581.26216	-0.99
Fragment Type (NCE = 30)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₁₉ H ₂₁ N ₄ O ₇	417.14048	417.14066	0.44
A₀₁ - H₂O	C ₁₉ H ₁₉ N ₄ O ₆	399.12991	399.13060	1.73
A₀₃	C ₂₇ H ₃₆ N ₇ O ₉	602.25690	602.25637	-0.88
A₀₄	C ₃₃ H ₄₆ N ₉ O ₁₂	760.32604	760.32613	0.11
A₀₄ - H₂O	C ₃₃ H ₄₄ N ₉ O ₁₁	742.31548	742.31585	0.50
B₀₁	C ₂₀ H ₂₁ N ₄ O ₈	445.13539	445.13561	0.49
B₀₂	C ₂₆ H ₃₃ N ₆ O ₉	573.23035	573.23036	0.01
B₀₃	C ₂₈ H ₃₆ N ₇ O ₁₀	630.25182	630.25187	0.08
B₀₃ - H₂O	C ₂₈ H ₃₄ N ₇ O ₉	612.24125	612.24126	0.01
B₀₄	C ₃₄ H ₄₆ N ₉ O ₁₃	788.32096	788.32068	-0.35
B₀₄ - H₂O	C ₃₄ H ₄₄ N ₉ O ₁₂	770.31039	770.30967	-0.94
B₀₅ + H - H₂O	C ₄₀ H ₅₆ N ₁₁ O ₁₃	898.40536	898.40605	0.77
B₀₅ + H	C ₄₀ H ₅₈ N ₁₁ O ₁₄	916.41592	916.41545	-0.52
B₀₆ + H (NCE 25)	C ₄₆ H ₆₈ N ₁₃ O ₁₇	1074.4856	1074.4856	0.01
Y₀₂ + H	C ₉ H ₁₆ N ₃ O ₅	246.10845	246.10898	2.17
Y''₀₃	C ₁₅ H ₂₈ N ₅ O ₆	374.20341	374.20392	1.36
E + H	C ₄₃ H ₆₃ N ₁₂ O ₁₆	1003.44795	1003.44947	1.51

MS/MS of Suc-Py from Py
SA

(NCE = 30)

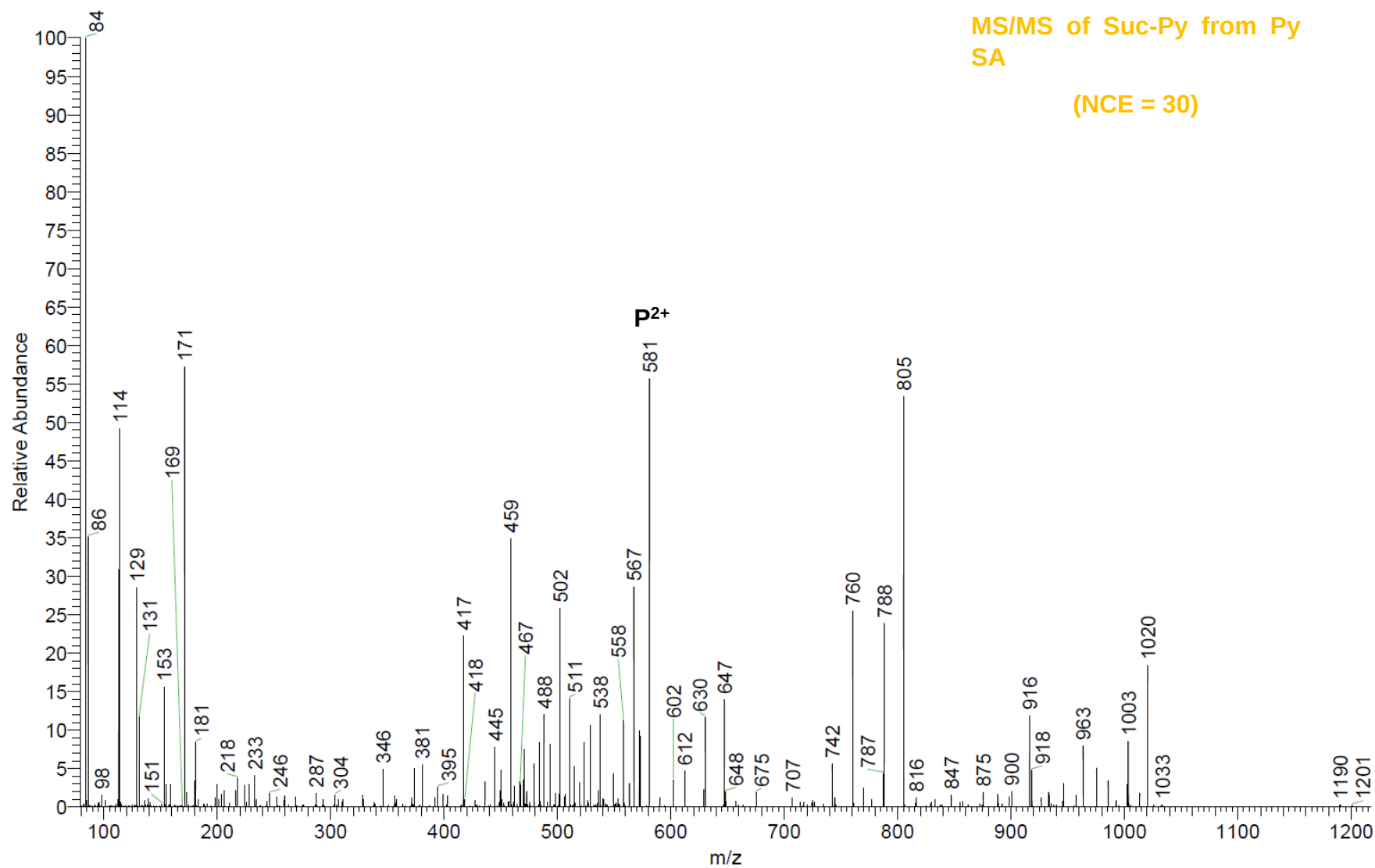
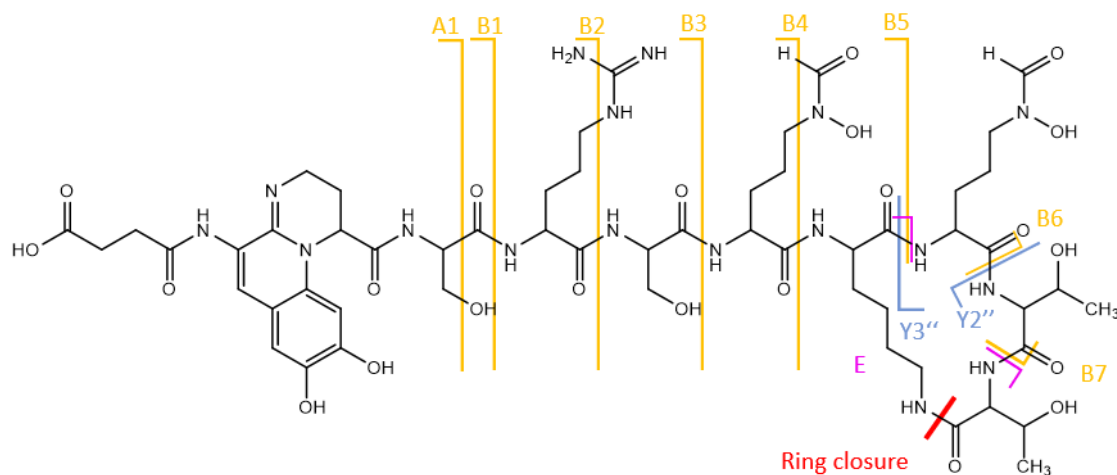


Table S4. Detected fragments in the MS/MS fragmentation of Suc-Py of PAO1 compared to their theoretical value m/z value and their ppm deviation.



Name:	PAO1			
Sequence:	Ser-Arg-Ser-FoHOrn-(Lys-FoHOrn-Thr-Thr)			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₅₅ H ₈₄ N ₁₇ O ₂₂	1334.59768	1334.59766	-0.02
[M+2H]²⁺	C ₅₅ H ₈₅ N ₁₇ O ₂₂	667.80275	667.80200	-1.13
Fragment Type (NCE = 35)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₁₉ H ₂₁ N ₄ O ₇	417.14048	417.13959	-2.12
A₀₁ - H₂O	C ₁₉ H ₁₉ N ₄ O ₆	399.12991	399.12898	-2.33
B₀₁ - H₂O	C ₂₀ H ₁₉ N ₄ O ₇	427.12483	427.12388	-2.22
B₀₂	C ₂₆ H ₃₃ N ₈ O ₉	601.23650	601.23458	-3.20
B₀₃	C ₂₉ H ₃₈ N ₉ O ₁₁	688.26853	688.26721	-1.92
B₀₃ - H₂O	C ₂₉ H ₃₆ N ₉ O ₁₀	670.25796	670.25632	-2.45
B₀₄	C ₃₅ H ₄₈ N ₁₁ O ₁₄	846.33767	846.33546	-2.61
B₀₄ - H₂O	C ₃₅ H ₄₆ N ₁₁ O ₁₃	828.32711	828.32543	-2.02
[B₀₅ + 2H]²⁺	C ₄₁ H ₆₁ N ₁₃ O ₁₅	487.7202	487.7186	-3.30
B₀₅ - H₂O	C ₄₁ H ₅₈ N ₁₃ O ₁₄	956.42207	956.41735	-4.94
[B₀₆ + 2H]²⁺ (NCE = 30)	C ₄₇ H ₇₁ N ₁₅ O ₁₈	566.7548	566.7535	-2.25
[B₀₇ + 2H]²⁺ (NCE = 30)	C ₅₁ H ₇₈ N ₁₆ O ₂₀	617.2786	617.2776	-1.70
Y''₀₂	C ₈ H ₁₅ N ₂ O ₄	203.10263	203.10256	-0.36
Y''₀₃	C ₁₄ H ₂₅ N ₄ O ₇	361.17178	361.17134	-1.21
E + H	C ₄₅ H ₆₇ N ₁₄ O ₁₇	1075.48031	1075.48038	0.06

MS/MS of Suc-Py from PAO1

(NCE = 35)

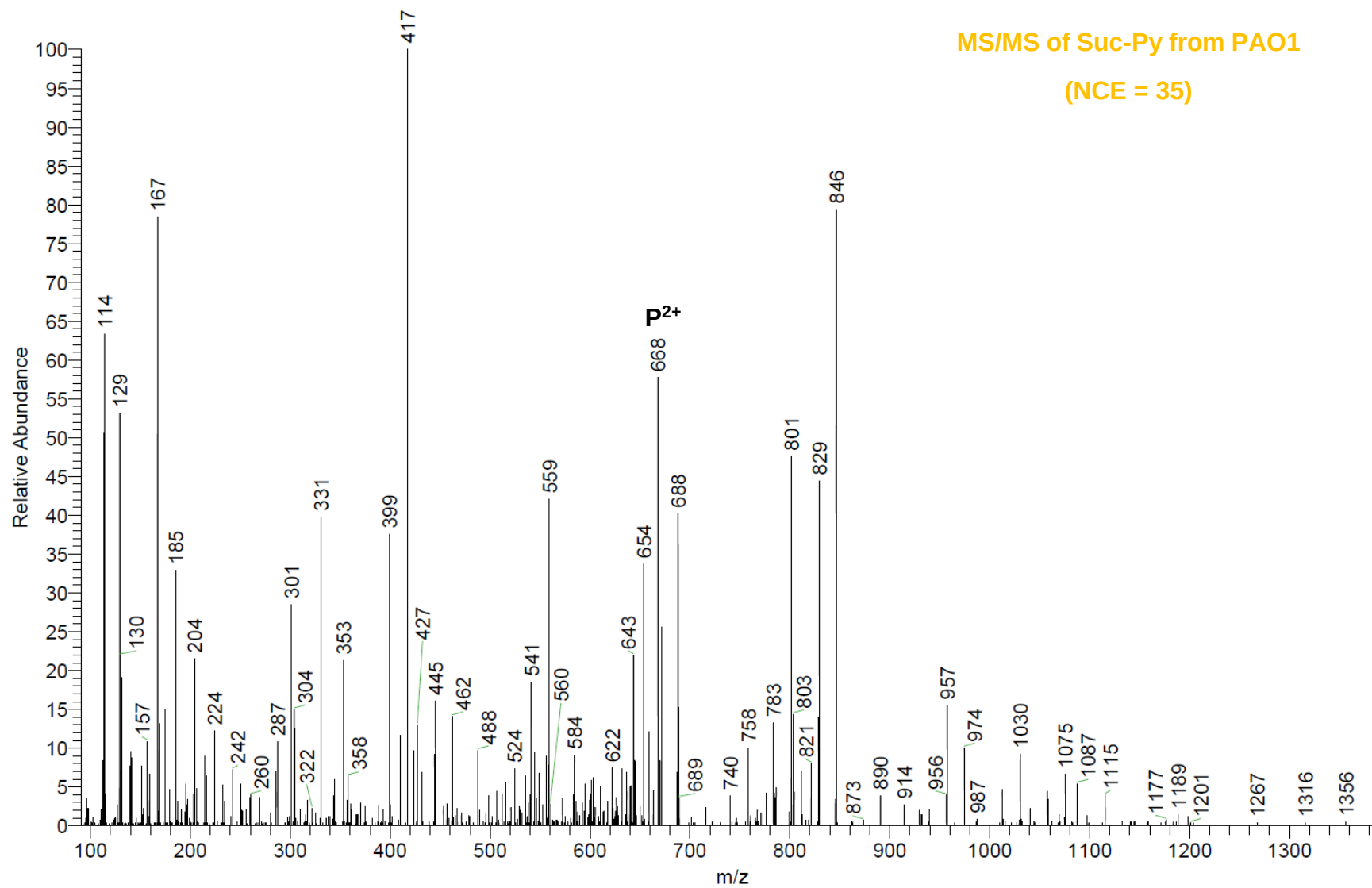
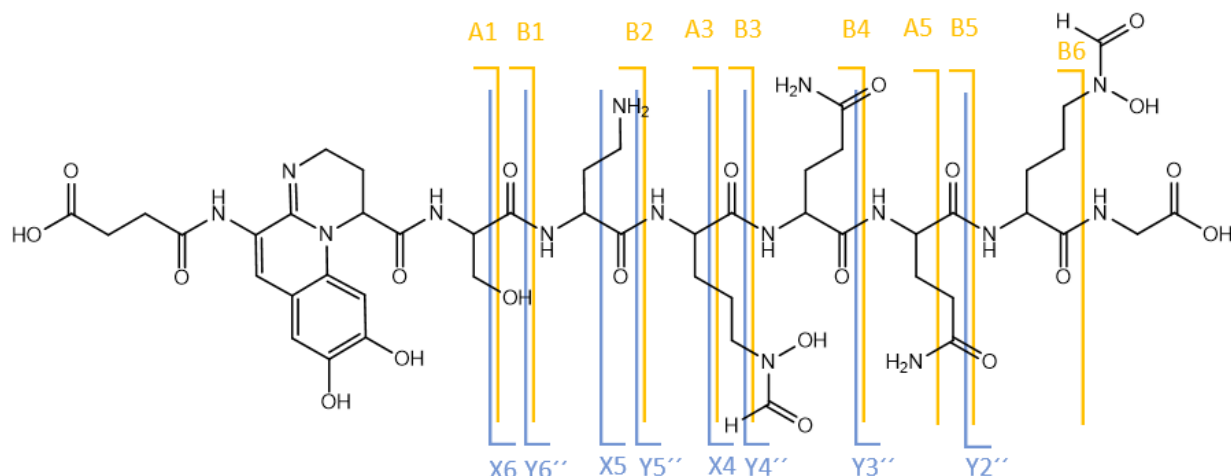


Table S5. Detected fragments in the MS/MS fragmentation of Suc-Py of 206-12 compared to their theoretical value m/z value and their ppm deviation.



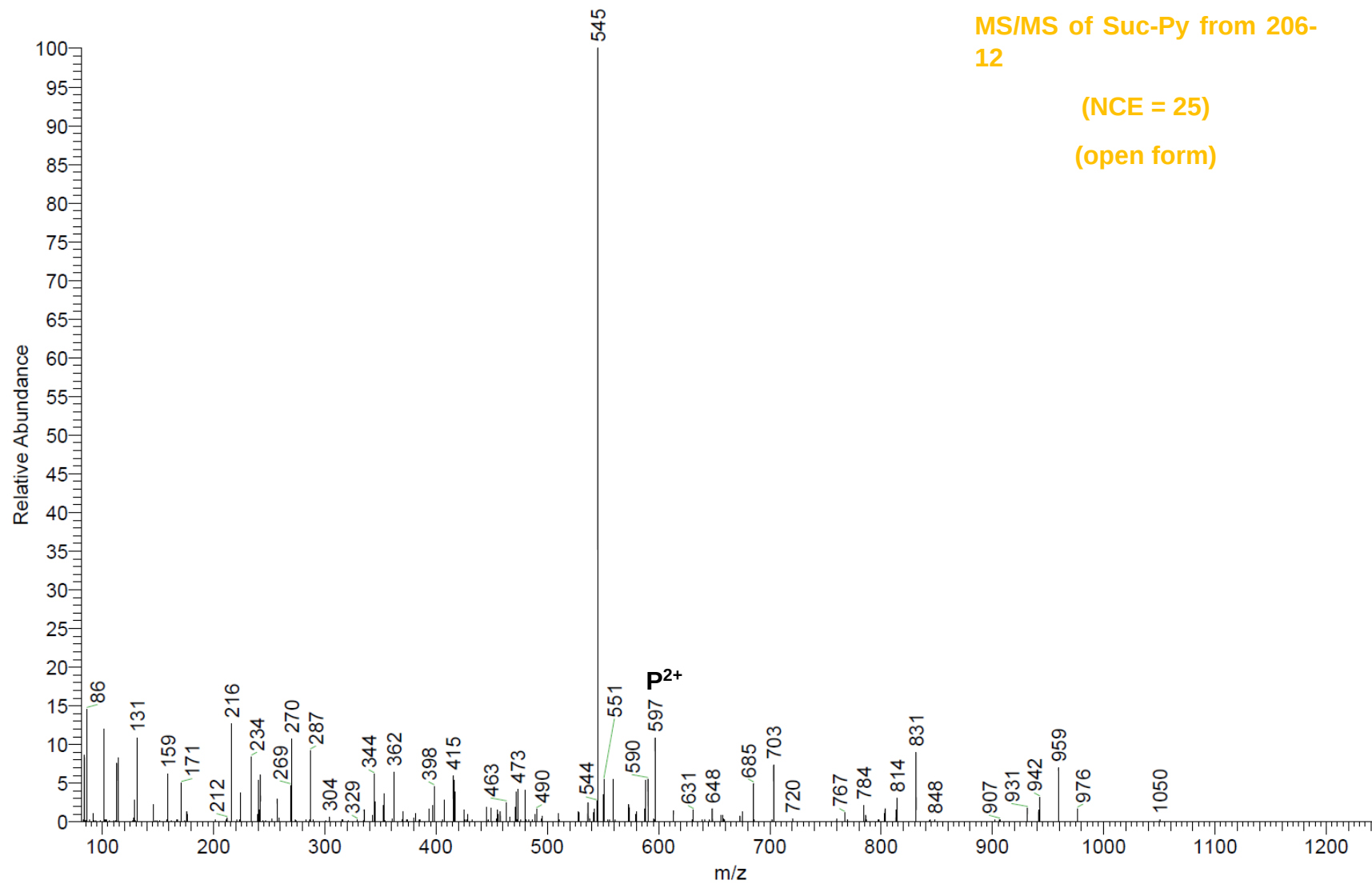
Name:	206-12			
Sequence:	Ser-Dab-FoOHOrn-Gln-Gln-FoOHOrn-Gly (open)			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₈ H ₇₀ N ₁₅ O ₂₁	1192.48707	1192.48609	-0.82
[M+2H]²⁺	C ₄₈ H ₇₁ N ₁₅ O ₂₁	596.74745	596.74659	-1.44
Fragment Type (NCE = 25)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₁₉ H ₂₁ N ₄ O ₇	417.14048	417.13961	-2.07
A₀₃	C ₂₉ H ₃₉ N ₈ O ₁₁	675.27328	675.27226	-1.51
A₀₅	C ₃₉ H ₅₅ N ₁₂ O ₁₅	931.39044	931.38649	-4.23
B₀₁	C ₂₀ H ₂₁ N ₄ O ₈	445.13539	445.13507	-0.72
B₀₂	C ₂₄ H ₂₉ N ₆ O ₉	545.19905	545.19879	-0.48
B₀₃	C ₃₀ H ₃₉ N ₈ O ₁₂	703.26820	703.26854	0.49
B₀₄	C ₃₅ H ₄₇ N ₁₀ O ₁₄	831.32677	831.32495	-2.19
B₀₅	C ₄₀ H ₅₅ N ₁₂ O ₁₆	959.38535	959.38145	-4.07
[B₀₆ + H]²⁺	C ₄₆ H ₆₆ N ₁₄ O ₁₉	559.2312	559.2298	-2.50
Y''₀₃	C ₈ H ₁₆ N ₃ O ₅	234.10845	234.10844	-0.03
Y''₀₄	C ₁₃ H ₂₄ N ₅ O ₇	362.16702	362.16641	-1.70
Y''₀₅	C ₁₈ H ₃₂ N ₇ O ₉	490.22560	490.22611	1.04
Y''₀₆	C ₂₄ H ₄₂ N ₉ O ₁₂	648.29474	648.29477	0.04
Z₀₄	C ₁₃ H ₂₁ N ₄ O ₇	345.14048	345.14057	0.27
Z₀₅	C ₁₈ H ₂₉ N ₆ O ₉	473.19905	473.19892	-0.28
Z₀₆	C ₂₄ H ₃₉ N ₈ O ₁₂	631.26820	631.26702	-1.86

Additional Data:				
Sequence: (Ser-Dab)-FoOHOrn-Gln-Gln-FoOHOrn-Gly (condensed)				
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₈ H ₆₈ N ₁₅ O ₂₀	1174.47650	1174.47598	-0.45
[M+2H]²⁺	C ₄₈ H ₆₉ N ₁₅ O ₂₀	587.74216	587.74134	-1.40
Fragment Type (NCE = 25)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
B₀₃	C ₃₀ H ₃₇ N ₈ O ₁₁	685.25763	685.25654	-1.59
B₀₄	C ₃₅ H ₄₅ N ₁₀ O ₁₃	813.31621	813.31532	-1.09
B₀₅	C ₄₀ H ₅₃ N ₁₂ O ₁₅	941.37479	941.37316	-1.73
[B₀₆ + H]²⁺	C ₄₆ H ₆₄ N ₁₄ O ₁₈	550.2259	550.2247	-2.13
Y''₀₃	C ₈ H ₁₄ N ₃ O ₄	216.09788	216.09797	0.41
Y''₀₄	C ₁₃ H ₂₂ N ₅ O ₆	344.15646	344.15670	0.70
Y''₀₅	C ₁₈ H ₃₀ N ₇ O ₈	472.21504	472.21503	-0.02

MS/MS of Suc-Py from 206-
12

(NCE = 25)

(open form)



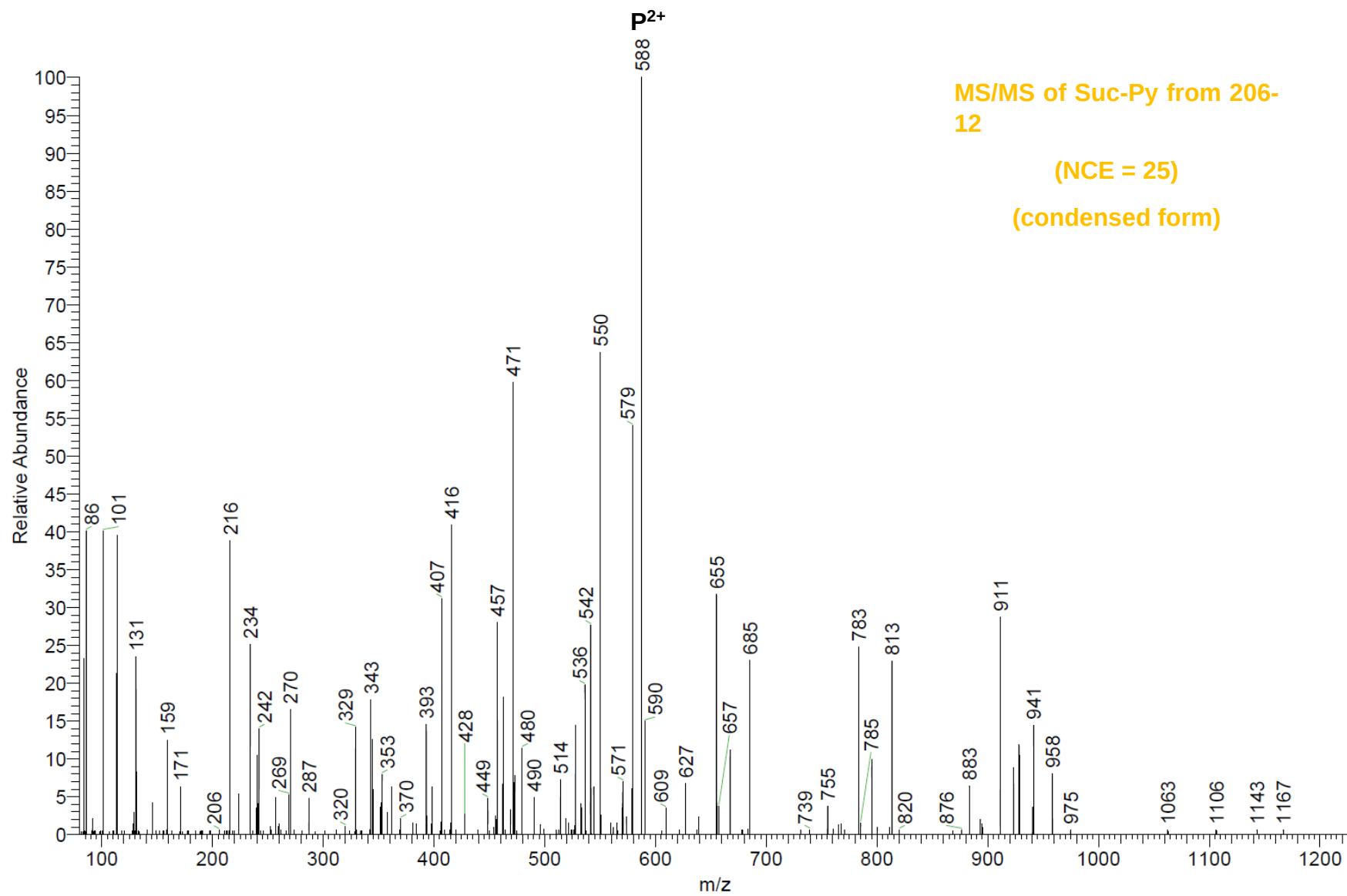
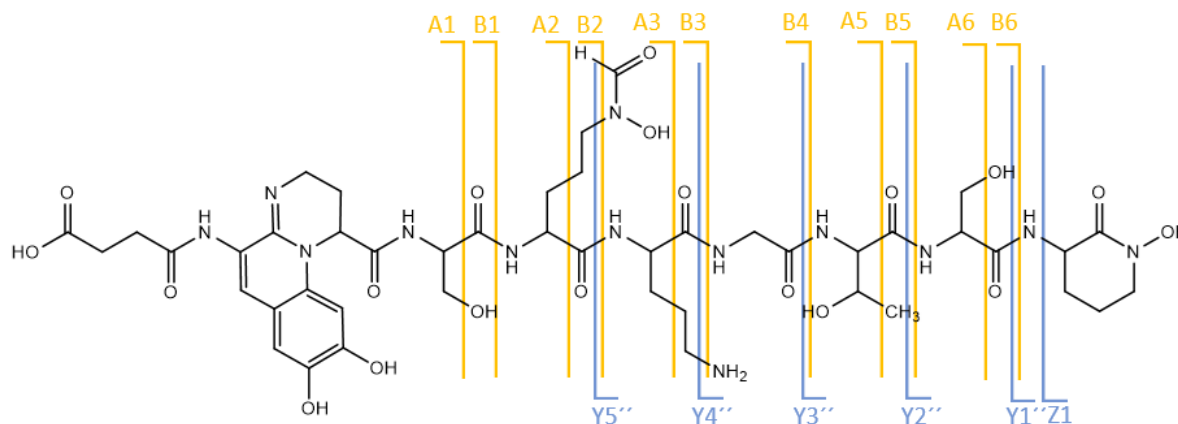


Table S6. Detected fragments in the MS/MS fragmentation of Suc-Py of 1-60 compared to their theoretical value m/z value and their ppm deviation.



Name:	1-60			
Sequence:	Ser-FoHOrn-Orn-Gly-aThr-Ser-cOHOrn			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₅ H ₆₆ N ₁₃ O ₁₉	1092.45979	1092.45855	-1.14
[M+2H]²⁺	C ₄₅ H ₆₇ N ₁₃ O ₁₉	546.73381	546.73270	-2.03
Fragment Type (NCE = 25)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₁₉ H ₂₁ N ₄ O ₇	417.14048	417.13998	-1.19
A₀₂	C ₂₅ H ₃₁ N ₆ O ₁₀	575.20962	575.20906	-0.97
A₀₃	C ₃₀ H ₄₁ N ₈ O ₁₁	689.28893	689.28904	0.16
A₀₅	C ₃₆ H ₅₁ N ₁₀ O ₁₄	847.35807	847.35746	-0.72
A₀₆	C ₃₉ H ₅₆ N ₁₁ O ₁₆	934.39010	934.38828	-1.95
B₀₁	C ₂₀ H ₂₁ N ₄ O ₈	445.13539	445.13465	-1.66
B₀₂	C ₂₆ H ₃₁ N ₆ O ₁₁	603.20453	603.20340	-1.88
B₀₃	C ₃₁ H ₄₁ N ₈ O ₁₂	717.28385	717.28310	-1.04
B₀₄	C ₃₃ H ₄₄ N ₉ O ₁₃	774.30531	774.30476	-0.71
B₀₅	C ₃₇ H ₅₁ N ₁₀ O ₁₅	875.35299	875.35105	-2.21
B₀₆	C ₄₀ H ₅₆ N ₁₁ O ₁₇	962.38502	962.38269	-2.42
Y''₀₁	C ₅ H ₁₁ N ₂ O ₂	131.08150	131.08141	-0.72
Y''₀₂	C ₈ H ₁₆ N ₃ O ₄	218.11353	218.11334	-0.88
Y''₀₃	C ₁₂ H ₂₃ N ₄ O ₆	319.16121	319.16072	-1.54
Y''₀₄	C ₁₄ H ₂₆ N ₅ O ₇	376.18267	376.18205	-1.66
Y''₀₅	C ₂₅ H ₄₆ N ₉ O ₁₁	648.33113	648.33030	-1.28
Z₀₁	C ₅ H ₈ N ₁ O ₂	114.05495	114.05513	1.53

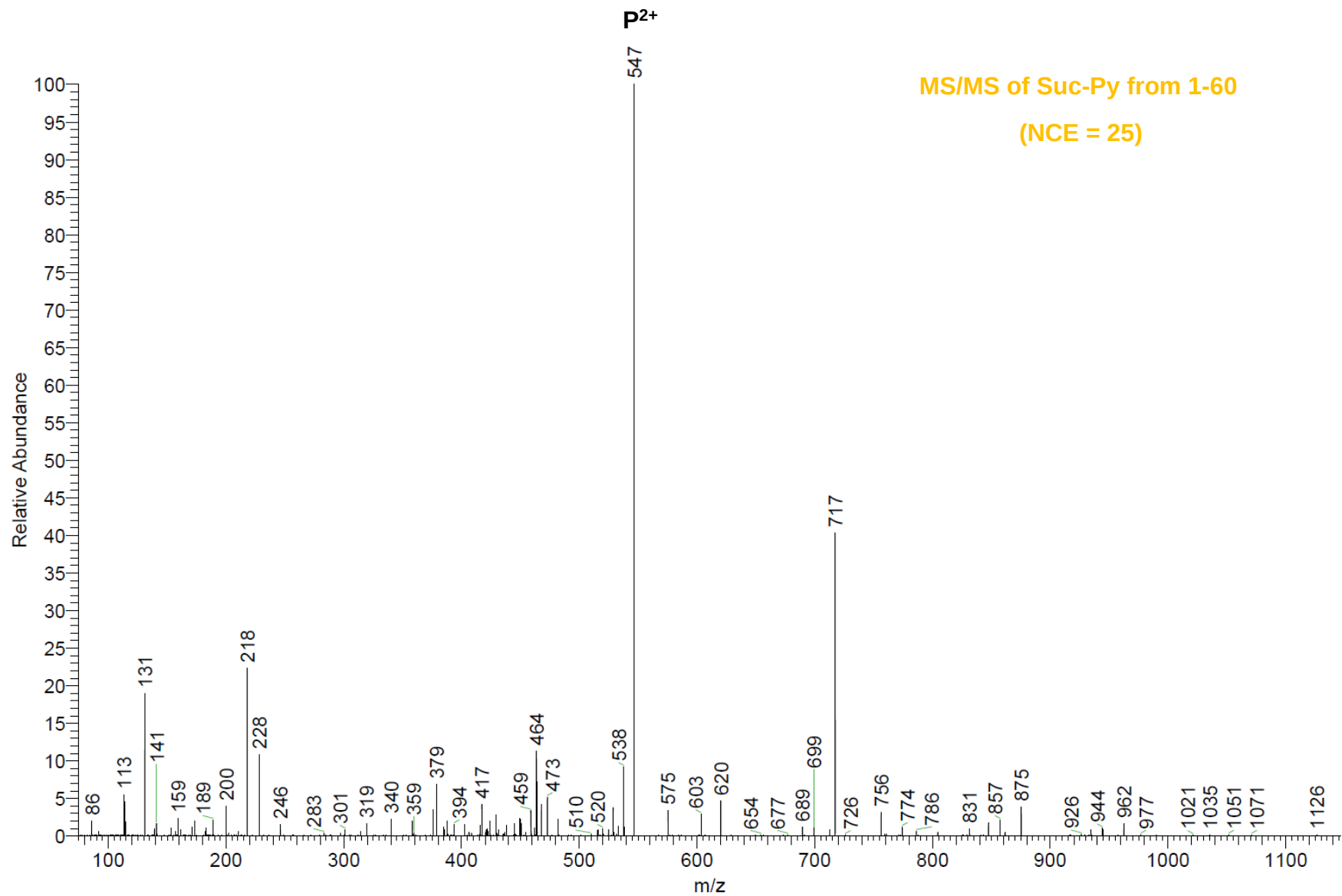
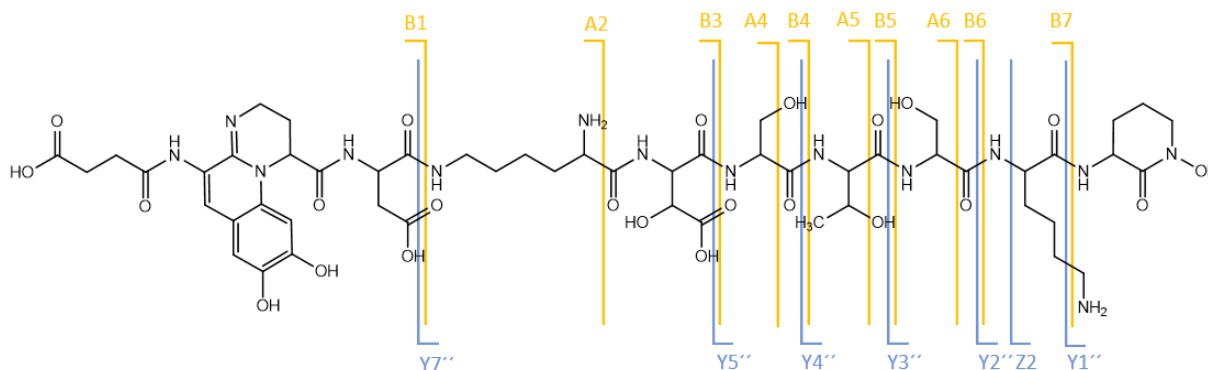


Table S7. Detected fragments in the MS/MS fragmentation of Suc-Py of 3A06 compared to their theoretical value m/z value and their ppm deviation.



Name:	3A06			
Sequence:	Asp-ε-Lys-OHAsp-Ser-Thr-Ser-Lys-cOHOrn			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₅₂ H ₇₇ N ₁₄ O ₂₃	1265.52860	1265.52727	-1.05
[M+2H]²⁺	C ₅₂ H ₇₈ N ₁₄ O ₂₃	633.26821	633.26699	-1.93
Fragment Type (NCE = 25)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₂	C ₂₆ H ₃₃ N ₆ O ₉	573.23035	573.23188	2.66
A₀₄	C ₃₃ H ₄₃ N ₈ O ₁₅	791.28424	791.28388	-0.45
A₀₅	C ₃₇ H ₅₀ N ₉ O ₁₇	892.33192	892.33267	0.84
A₀₆	C ₄₀ H ₅₅ N ₁₀ O ₁₉	979.36395	979.36458	0.65
B₀₁	C ₂₁ H ₂₁ N ₄ O ₉	473.13030	473.13006	-0.52
B₀₃	C ₃₁ H ₃₈ N ₇ O ₁₄	732.24713	732.24671	-0.57
B₀₄	C ₃₄ H ₄₃ N ₈ O ₁₆	819.27915	819.27946	0.37
B₀₅	C ₃₈ H ₅₀ N ₉ O ₁₈	920.32683	920.32572	-1.21
B₀₆	C ₄₁ H ₅₅ N ₁₀ O ₂₀	1007.35886	1007.35886	-0.00
B₀₇	C ₄₇ H ₆₇ N ₁₂ O ₂₁	1135.45382	1135.45068	-2.77
Y''₀₁	C ₅ H ₁₁ N ₂ O ₂	131.08150	131.08171	1.57
Y''₀₂	C ₁₁ H ₂₃ N ₄ O ₃	259.17647	259.17652	0.20
Y''₀₃	C ₁₄ H ₂₈ N ₅ O ₅	346.20850	346.20850	0.00
Y''₀₄	C ₁₈ H ₃₅ N ₆ O ₇	447.25617	447.25742	2.79
Y''₀₅	C ₂₁ H ₄₀ N ₇ O ₉	534.28820	534.28826	0.11
Y''₀₇	C ₃₁ H ₅₇ N ₁₀ O ₁₄	793.40502	793.40428	-0.94
Z₀₂	C ₁₁ H ₂₀ N ₃ O ₃	242.14992	242.14994	0.09

MS/MS of Suc-Py from 3A06
(NCE = 25)

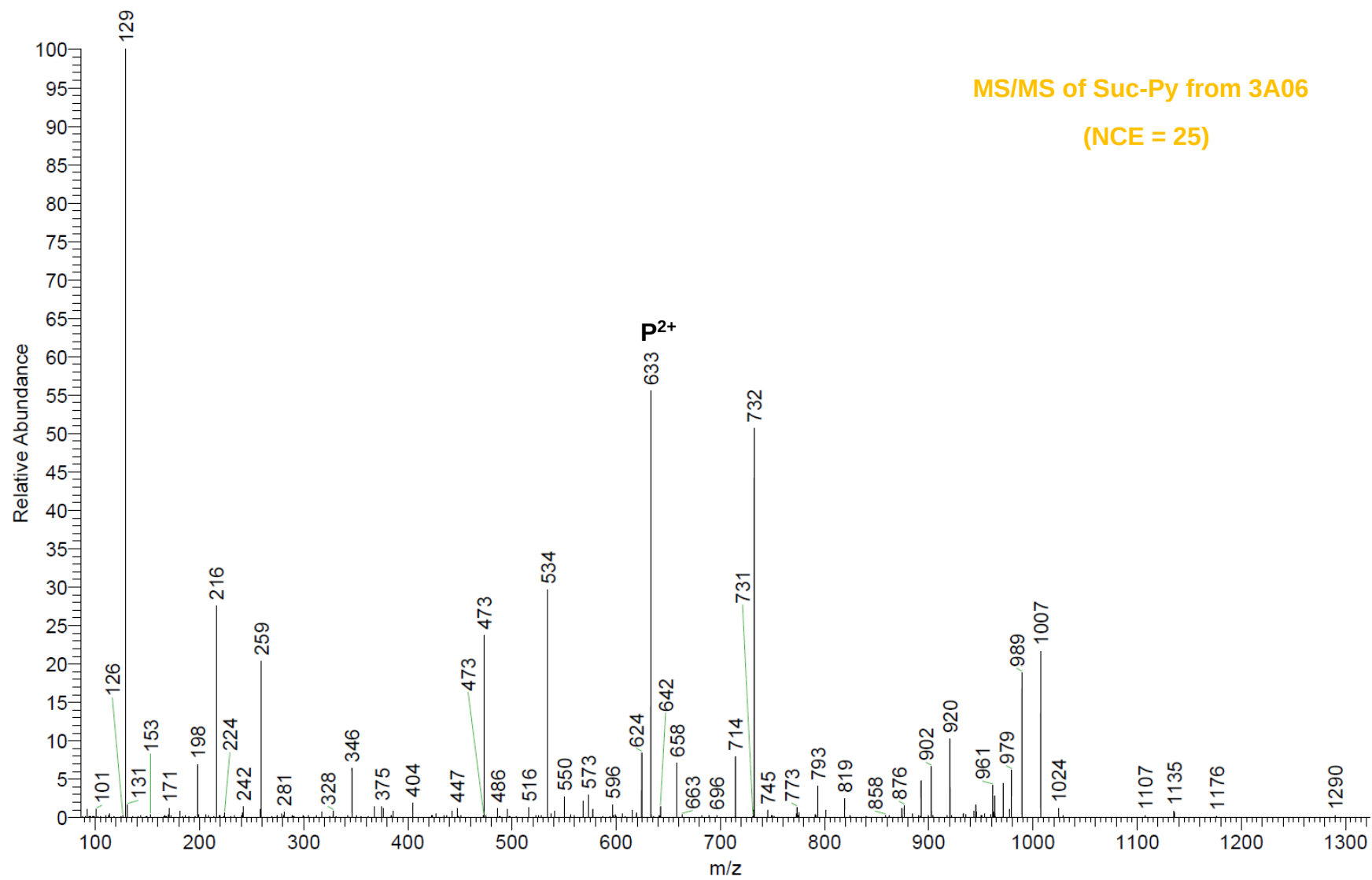
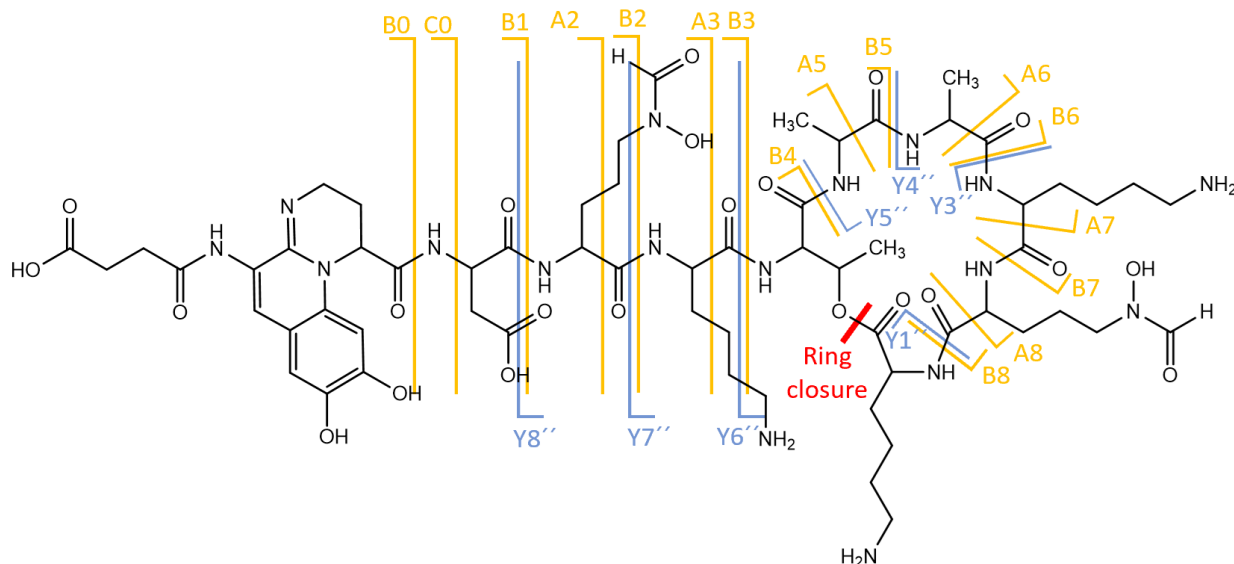


Table S8. Detected fragments in the MS/MS fragmentation of Suc-Py of 3B19 compared to their theoretical value m/z value and their ppm deviation.



Name:	3B19			
Sequence:	Asp-FoHOrn-Lys-(Thr-Ala-Ala-Lys-FoHOrn-Lys)			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₆₁ H ₉₄ N ₁₇ O ₂₂	1416.67593	1416.67291	-2.13
[M+2H]²⁺	C ₆₁ H ₉₅ N ₁₇ O ₂₂	708.84188	708.83988	-2.82
Fragment Type (NCE = 30)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₂	C ₂₆ H ₃₁ N ₆ O ₁₁	603.20453	603.20435	-0.30
A₀₃	C ₃₂ H ₄₃ N ₈ O ₁₂	731.29950	731.29854	-1.31
A₀₃ - H₂O	C ₃₂ H ₄₁ N ₈ O ₁₁	713.28893	713.28774	-1.67
A₀₅	C ₃₉ H ₅₅ N ₁₀ O ₁₅	903.38429	903.38208	-2.44
A₀₅ - H₂O	C ₃₉ H ₅₃ N ₁₀ O ₁₄	885.37372	885.37277	-1.08
A₀₆	C ₄₂ H ₆₀ N ₁₁ O ₁₆	974.42140	974.42055	-0.87
A₀₆ - H₂O	C ₄₂ H ₅₈ N ₁₁ O ₁₅	956.41084	956.40948	-1.42
A₀₇ - H₂O	C ₄₈ H ₇₀ N ₁₃ O ₁₆	1084.50580	1084.50235	-3.18
A₀₈	C ₅₄ H ₈₂ N ₁₅ O ₂₀	1260.58551	1260.58280	-2.15
B₀₀	C ₁₇ H ₁₆ N ₃ O ₆	358.10336	358.10336	0.00
B₀₁	C ₂₁ H ₂₁ N ₄ O ₉	473.13030	473.13030	-0.01
B₀₁ - H₂O	C ₂₁ H ₁₉ N ₄ O ₈	455.11974	455.11985	0.24
B₀₂	C ₂₇ H ₃₁ N ₆ O ₁₂	631.19945	631.19952	0.12
B₀₃	C ₃₃ H ₄₃ N ₈ O ₁₃	759.29441	759.29377	-0.84
B₀₃ - H₂O	C ₃₃ H ₄₁ N ₈ O ₁₂	741.28385	741.28109	-3.72
B₀₄ - H₂O	C ₃₇ H ₄₈ N ₉ O ₁₄	842.33152	842.33132	-0.24
B₀₅	C ₄₀ H ₅₅ N ₁₀ O ₁₆	931.37920	931.37483	-4.69
B₀₅ - H₂O	C ₄₀ H ₅₃ N ₁₀ O ₁₅	913.36864	913.36814	-0.54
B₀₆	C ₄₃ H ₆₀ N ₁₁ O ₁₇	1002.41632	1002.41426	-2.05
B₀₆ - H₂O	C ₄₃ H ₅₈ N ₁₁ O ₁₆	984.40575	984.40375	-2.03

B₀₇	C₄₉H₇₂N₁₃O₁₈	1130.51128	1130.51290	1.43
B₀₇ - H₂O	C₄₉H₇₀N₁₃O₁₇	1112.50071	1112.50077	0.05
B₀₈	C₅₅H₈₂N₁₅O₂₁	1288.58042	1288.57827	-1.67
C₀₀	C₁₇H₁₇N₄O₆	373.11426	373.11430	0.11
X₀₅	C₂₂H₃₈N₇O₇	512.28272	512.28188	-1.65
Y''₀₁	C₄₀H₇₄N₁₃O₁₃	944.55236	944.55145	-0.96
Y''₀₃	C₂₈H₅₂N₉O₉	658.38825	658.38827	0.03
Y''₀₄ + H₂O	C₂₄H₄₇N₈O₈	575.35114	575.35194	1.40
Y''₀₅ + H₂O	C₂₁H₄₂N₇O₇	504.31402	504.31550	2.93
Y''₀₆ + H₂O	C₁₈H₃₇N₆O₆	433.27691	433.27648	-0.99
Y''₀₆	C₁₈H₃₅N₆O₅	415.26634	415.26634	-0.01
Y''₀₇ + H₂O	C₁₂H₂₅N₄O₅	305.18195	305.18187	-0.25
Y''₀₇	C₁₂H₂₃N₄O₄	287.17138	287.17150	0.41
Y''₀₈ + H₂O	C₆H₁₅N₂O₂	147.11280	147.11278	-0.16
Y''₀₈	C₆H₁₃N₂O₁	129.10224	129.10241	1.32

MS/MS of Suc-Py from 3B19
(NCE = 30)

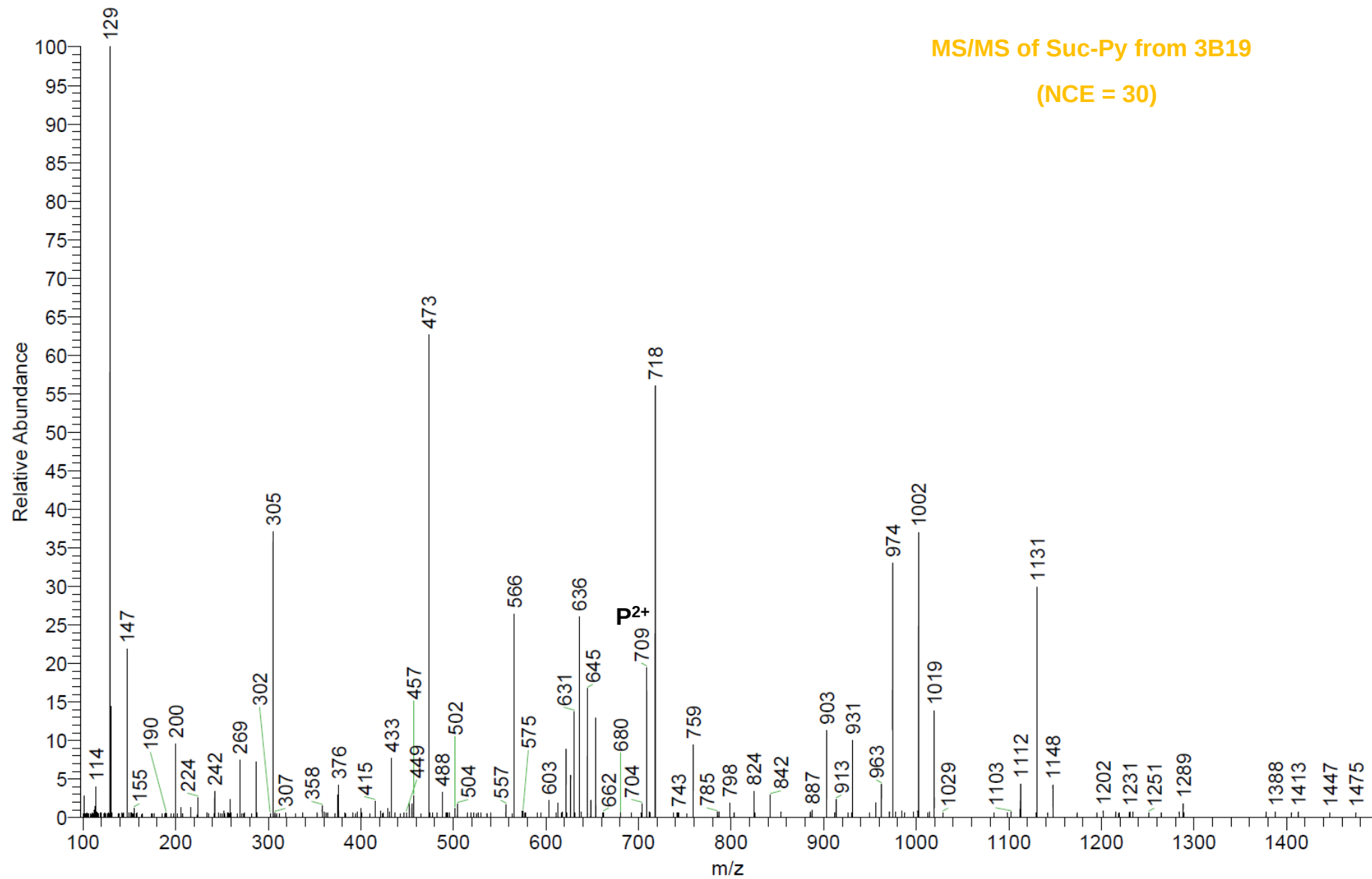
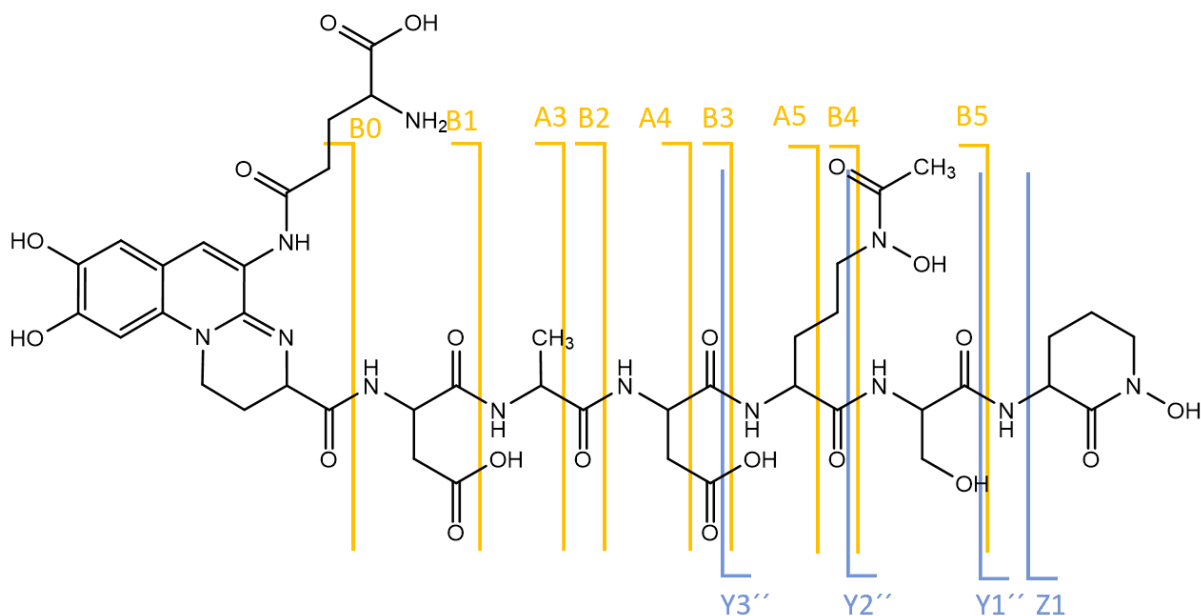


Table S9. Detected fragments in the MS/MS fragmentation of Glu-IsoPy of 3C16 compared to their theoretical value m/z value and their ppm deviation.



Name:	3C16			
Sequence:	Asp-Ala-Asp-AcOHOrn-Ser-cOHOrn			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₄ H ₆₁ N ₁₂ O ₂₀	1077.412508	1077.40998	-2.35
[M+2H]²⁺	C ₄₄ H ₆₂ N ₁₂ O ₂₀	539.2101663	539.20861	-2.89
Fragment Type (NCE = 25)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
B₀₀	C ₁₈ H ₁₉ N ₄ O ₆	387.12991	387.12869	-3.15
B₀₁	C ₂₂ H ₂₄ N ₅ O ₉	502.15685	502.15600	-1.70
B₀₂	C ₂₅ H ₂₉ N ₆ O ₁₀	573.19397	573.19337	-1.04
B₀₃	C ₂₉ H ₃₄ N ₇ O ₁₃	688.22091	688.22025	-0.96
B₀₄	C ₃₆ H ₄₆ N ₉ O ₁₆	860.30570	860.30416	-1.79
B₀₅	C ₃₉ H ₅₁ N ₁₀ O ₁₈	947.33773	947.33626	-1.55
Y''₀₃	C ₁₅ H ₂₈ N ₅ O ₇	390.19832	390.19763	-1.78
Y''₀₂	C ₈ H ₁₆ N ₃ O ₄	218.11353	218.11319	-1.57
Y''₀₁	C ₅ H ₁₁ N ₂ O ₂	131.08150	131.08142	-0.64
Z₀₁	C ₅ H ₈ N ₁ O ₂	114.05495	114.05508	1.10

MS/MS of Glu-IsoPy from 3C16

(NCE = 25)

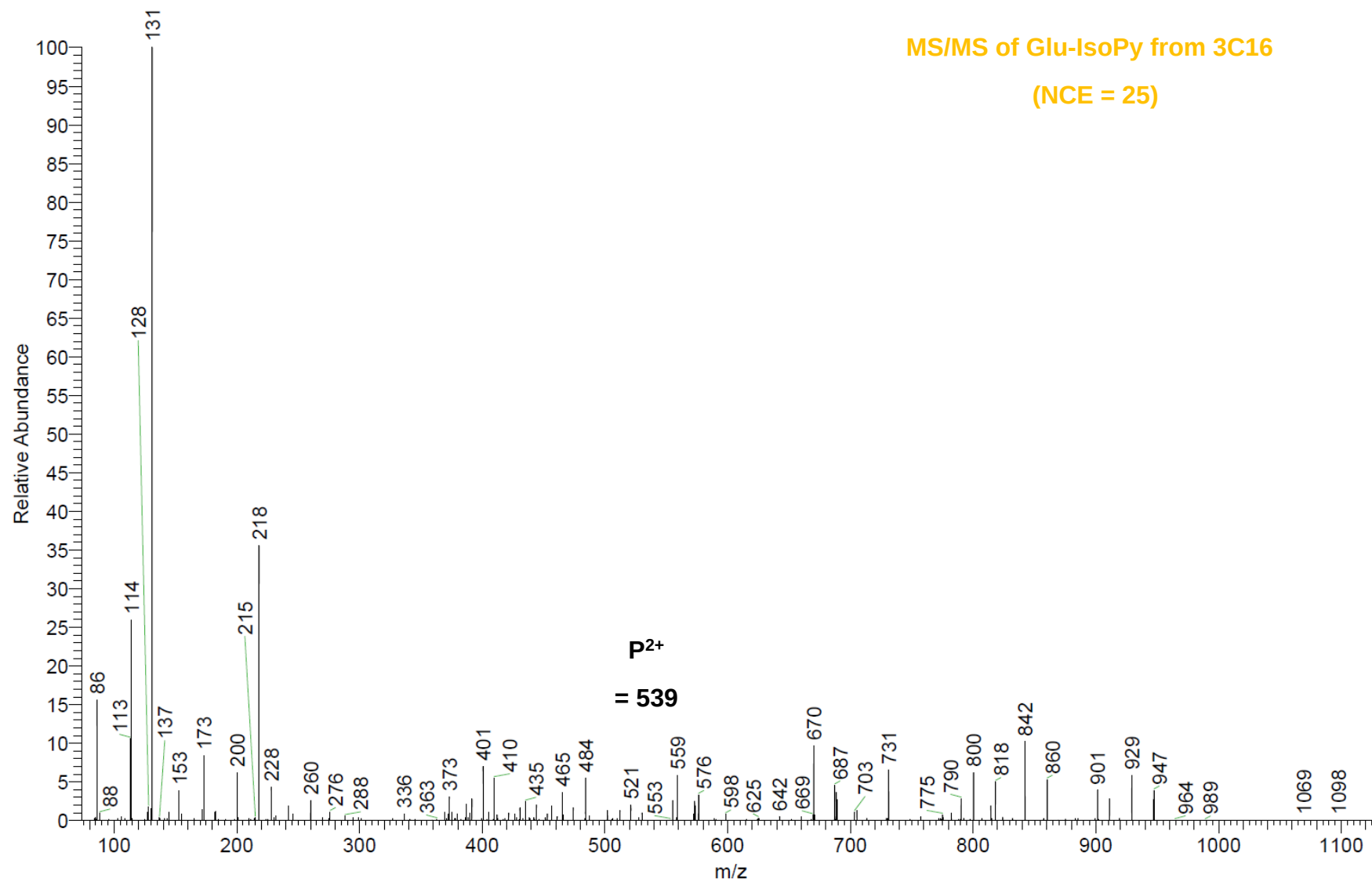
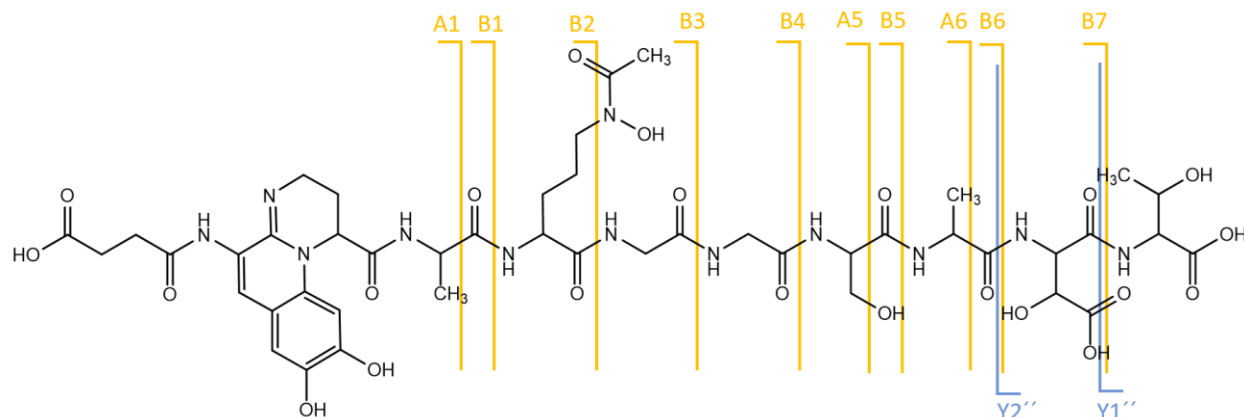


Table S10. Detected fragments in the MS/MS fragmentation of Suc-Py of 3D19 compared to their theoretical value m/z value and their ppm deviation.



Name:	3D19			
Sequence:	Ala-AcOHOrn-Gly-Gly-Ser-Ala-OHAsp-Thr			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₅ H ₆₃ N ₁₂ O ₂₂	1123.41799	1123.41840	0.37
[M+2H]²⁺	C ₄₅ H ₆₄ N ₁₂ O ₂₂	562.21291	562.21255	-0.63
Fragment Type (NCE = 25)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₁₉ H ₂₁ N ₄ O ₆	401.14556	401.14540	-0.40
A₀₅	C ₃₃ H ₄₄ N ₉ O ₁₃	774.30531	774.30328	-2.62
A₀₆	C ₃₆ H ₄₉ N ₁₀ O ₁₄	845.34242	845.34110	-1.56
B₀₁	C ₂₀ H ₂₁ N ₄ O ₇	429.14048	429.14058	0.24
B₀₂	C ₂₇ H ₃₃ N ₆ O ₁₀	601.22527	601.22670	2.38
B₀₃	C ₂₉ H ₃₆ N ₇ O ₁₁	658.24673	658.24372	-4.58
B₀₄	C ₃₁ H ₃₉ N ₈ O ₁₂	715.26820	715.26797	-0.31
B₀₅	C ₃₄ H ₄₄ N ₉ O ₁₄	802.30022	802.30008	-0.18
B₀₆	C ₃₇ H ₄₉ N ₁₀ O ₁₅	873.33734	873.33723	-0.12
B₀₇	C ₄₁ H ₅₄ N ₁₁ O ₁₉	1004.35920	1004.35544	-3.74
Y''₀₂	C ₈ H ₁₅ N ₂ O ₇	251.08738	251.08715	-0.91
Y''₀₁	C ₄ H ₁₀ N ₁ O ₃	120.06552	120.06578	2.17

MS/MS of Suc-Py from 3D19
(NCE = 25)

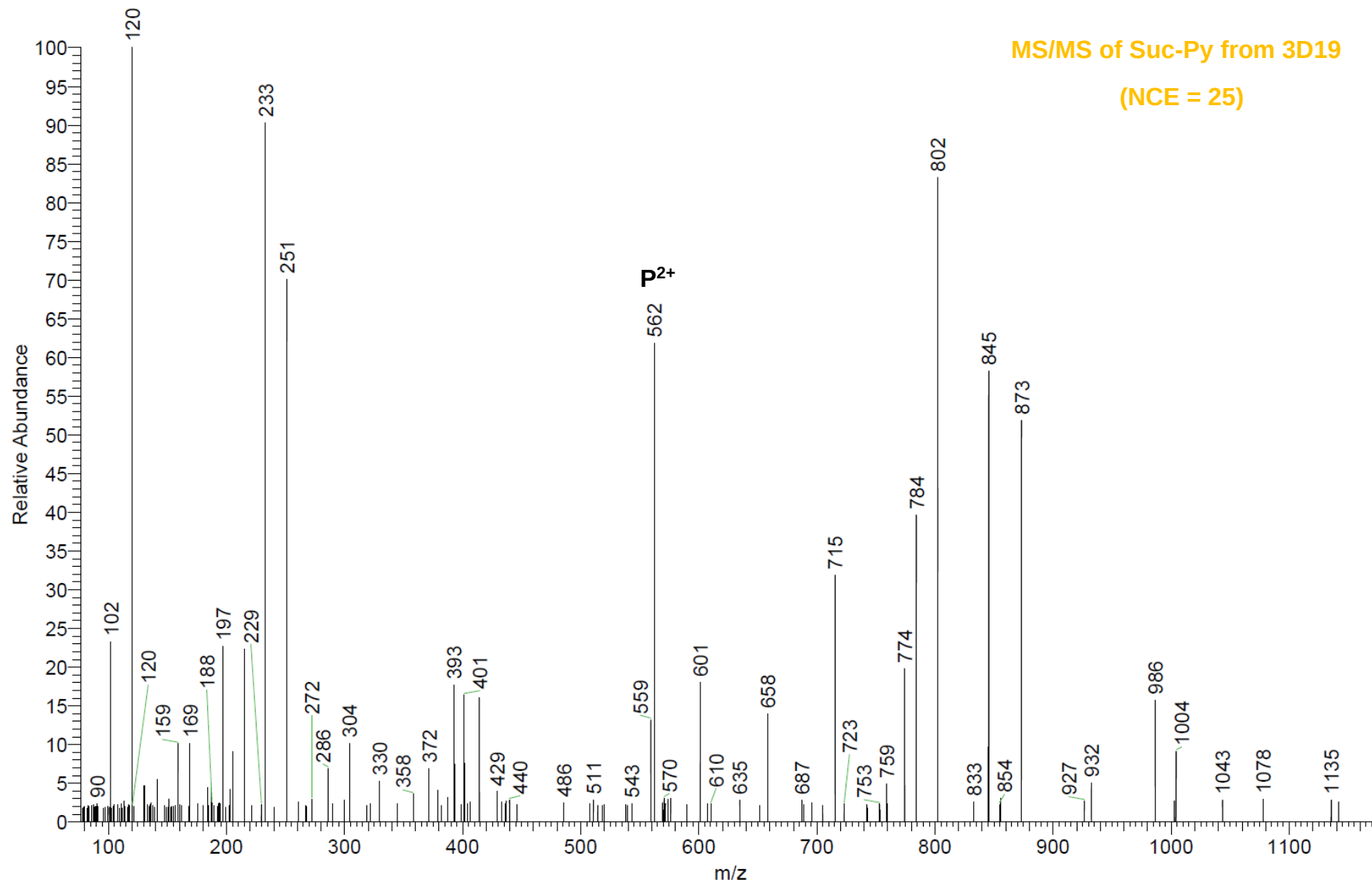
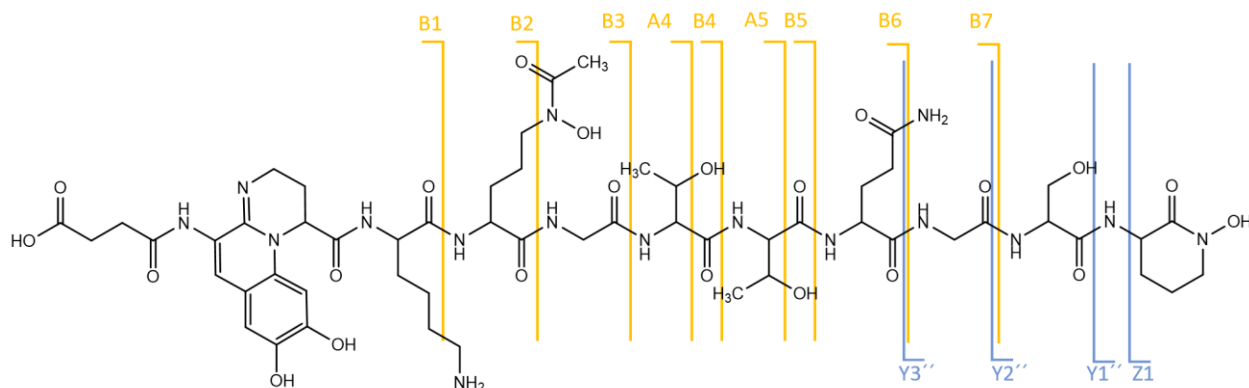


Table S11. Detected fragments in the MS/MS fragmentation of Suc-Py of 3F12 compared to their theoretical value m/z value and their ppm deviation.



Name:	3F12			
Sequence:	Lys-AcOHOrn-Gly-Thr-Thr-Gln-Gly-Ser-cOHOrn			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₅₅ H ₈₃ N ₁₆ O ₂₂	1319.58678	1319.58741	0.47
[M+2H]²⁺	C ₅₅ H ₈₄ N ₁₆ O ₂₂	660.29730	660.29664	-1.00
Fragment Type (NCE = 30)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₃	C ₃₁ H ₄₃ N ₈ O ₁₀	687.30967	687.30655	-4.53
A₀₄	C ₃₅ H ₅₀ N ₉ O ₁₂	788.35734	788.35401	-4.23
A₀₅	C ₃₉ H ₅₇ N ₁₀ O ₁₄	889.40502	889.40422	-0.90
B₀₁	C ₂₃ H ₂₈ N ₅ O ₇	486.19832	486.19770	-1.28
B₀₂	C ₃₀ H ₄₀ N ₇ O ₁₀	658.28311	658.28177	-2.05
B₀₃	C ₃₂ H ₄₃ N ₈ O ₁₁	715.30458	715.3024	-3.05
B₀₄	C ₃₆ H ₅₀ N ₉ O ₁₃	816.35226	816.35041	-2.27
B₀₅	C ₄₀ H ₅₇ N ₁₀ O ₁₅	917.39994	917.39858	-1.48
B₀₆	C ₄₅ H ₆₅ N ₁₂ O ₁₇	1045.45851	1045.45688	-1.56
B₀₇	C ₄₇ H ₆₈ N ₁₃ O ₁₈	1102.47998	1102.47896	-0.92
Y''₀₁	C ₅ H ₁₁ N ₂ O ₂	131.08150	131.08155	0.35
Y''₀₂	C ₈ H ₁₆ N ₃ O ₄	218.11353	218.11344	-0.42
Y''₀₃	C ₁₀ H ₁₉ N ₄ O ₅	275.13500	275.13510	0.38
Z₀₁	C ₅ H ₈ N ₁ O ₂	114.05495	114.05522	2.32

MS/MS of Suc-Py from 3F12
(NCE = 30)

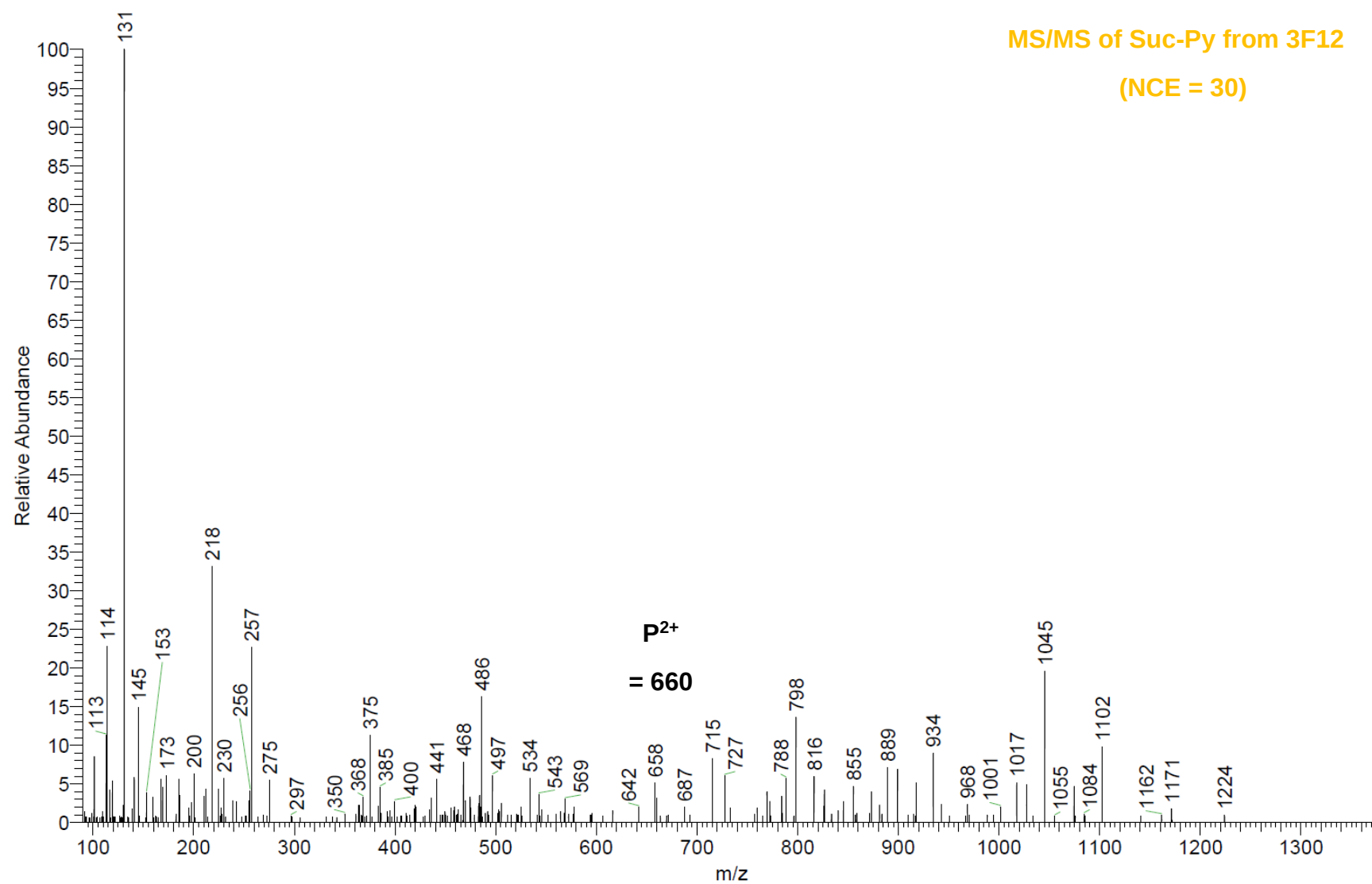
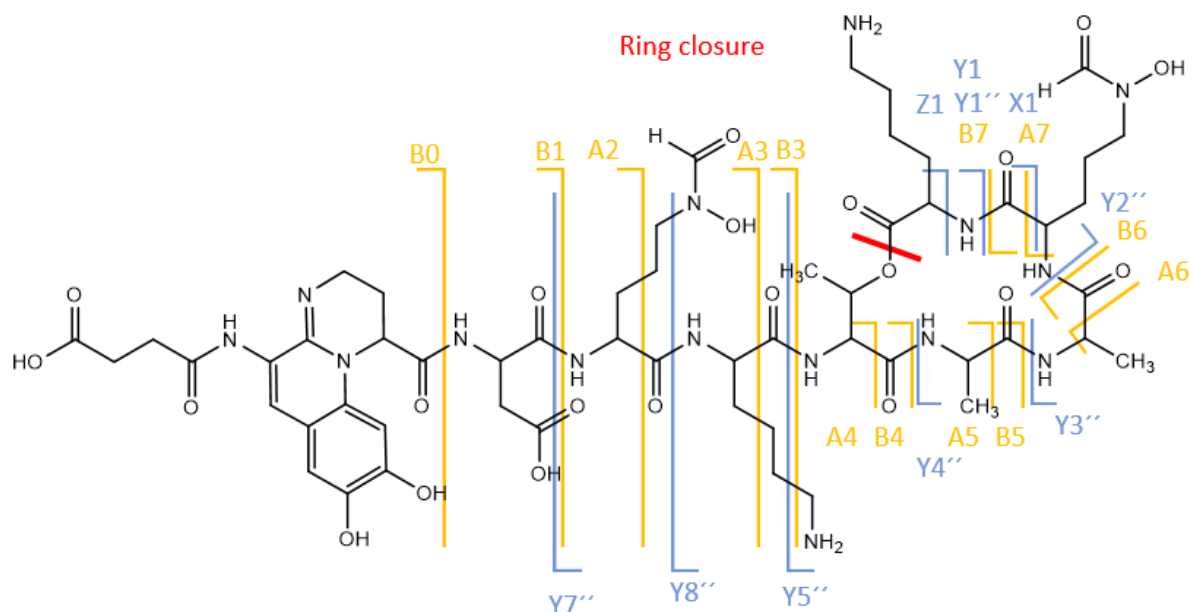


Table S12. Detected fragments in the MS/MS fragmentation of Suc-Py of 3G07 compared to their theoretical value m/z value and their ppm deviation.



Name:	3G07			
Sequence:	Asp-FoHOrn-Lys-(Thr-Ala-Ala-FoHOrn-Lys)			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₅₅ H ₈₂ N ₁₅ O ₂₁	1288.58097	1288.58102	0.04
[M+2H]²⁺	C ₅₅ H ₈₃ N ₁₅ O ₂₁	644.79440	644.79380	-0.93
Fragment Type (NCE = 30)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₂	C ₂₆ H ₃₁ N ₆ O ₁₁	603.20453	603.20410	-0.72
A₀₃	C ₃₂ H ₄₃ N ₈ O ₁₂	731.29950	731.29831	-1.62
A₀₄	C ₃₆ H ₅₀ N ₉ O ₁₄	832.34717	832.34713	-0.05
A₀₅	C ₃₉ H ₅₅ N ₁₀ O ₁₅	903.38429	903.38324	-1.16
A₀₆	C ₄₂ H ₆₀ N ₁₁ O ₁₆	974.42140	974.42072	-0.70
A₀₇	C ₄₈ H ₇₀ N ₁₃ O ₁₉	1132.49054	1132.49132	0.69
B₀₀	C ₁₇ H ₁₆ N ₃ O ₆	358.10336	358.10304	-0.90
B₀₁	C ₂₁ H ₂₁ N ₄ O ₉	473.13030	473.12982	-1.02
B₀₃	C ₃₃ H ₄₃ N ₈ O ₁₃	759.29441	759.29389	-0.68
B₀₄	C ₃₇ H ₅₀ N ₉ O ₁₅	860.34209	860.34121	-1.02
B₀₅	C ₄₀ H ₅₅ N ₁₀ O ₁₆	931.37920	931.37790	-1.40
B₀₆	C ₄₃ H ₆₀ N ₁₁ O ₁₇	1002.41632	1002.41518	-1.13
B₀₇	C ₄₉ H ₇₀ N ₁₃ O ₂₀	1160.48546	1160.48485	-0.52
X₀₁	C ₇ H ₁₁ N ₂ O ₂	155.08150	155.08140	-0.67
X₀₁ + H₂O	C ₇ H ₁₃ N ₂ O ₃	173.09207	173.09199	-0.45
Y₀₁	C ₆ H ₁₁ N ₂ O ₁	127.08659	127.08668	0.71
Y''₀₁	C ₆ H ₁₃ N ₂ O ₁	129.10224	129.10231	0.55
Y''₀₁ + H₂O	C ₆ H ₁₅ N ₂ O ₂	147.11280	147.11268	-0.84

Y''₀₂	C₁₂H₂₃N₄O₄	287.17138	287.17107	-1.09
Y''₀₂ + H₂O	C₁₂H₂₅N₄O₅	305.18195	305.18155	-1.30
Y''₀₃ + H₂O	C₁₅H₃₀N₅O₆	376.21906	376.21880	-0.69
Y''₀₄ + H₂O	C₁₈H₃₅N₆O₇	447.25617	447.25584	-0.75
Y''₀₅	C₂₂H₄₀N₇O₈	530.29329	530.29287	-0.79
Y''₀₆	C₂₈H₅₂N₉O₉	658.38825	658.38749	-1.16
Y''₀₇	C₃₄H₆₂N₁₁O₁₂	816.45739	816.45703	-0.44
Z₀₁ + H₂O	C₆H₁₀N₁O₁	112.07569	112.07592	2.05
Z₀₁ + H₂O	C₆H₁₂N₁O₂	130.08626	130.08633	0.58

MS/MS of Suc-Py from 3G07
(NCE = 30)

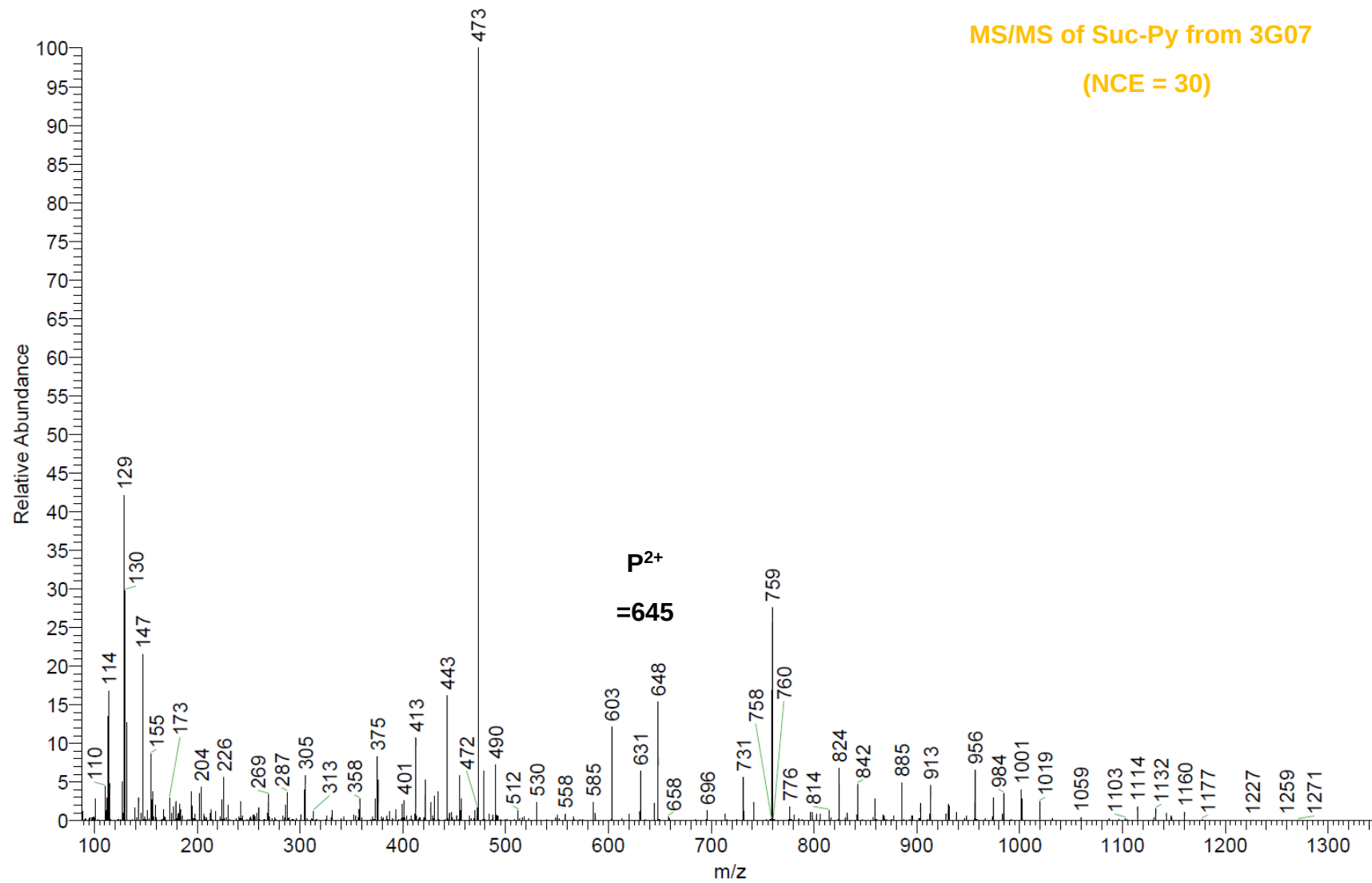
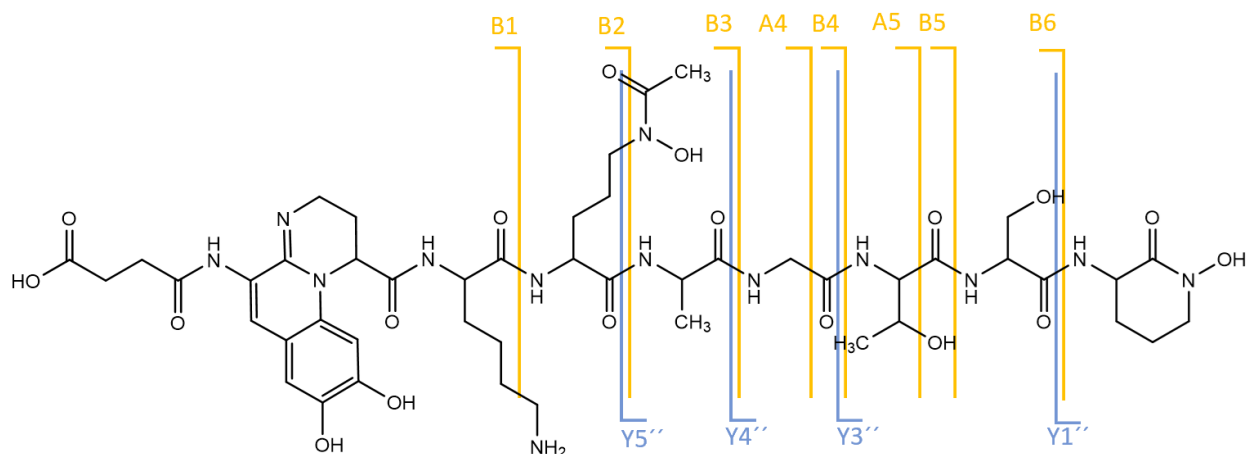


Table S13. Detected fragments in the MS/MS fragmentation of Suc-Py of S3a05 compared to their theoretical value m/z value and their ppm deviation.



Name:	S3a-05			
Sequence:	Lys-AcOHOrn-Ala-Gly-aThr-Ser-cOHOrn			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₇ H ₇₀ N ₁₃ O ₁₈	1104.49618	1104.49568	-0.45
[M+2H]²⁺	C ₄₇ H ₇₁ N ₁₃ O ₁₈	552.75200	552.75159	-0.74
Fragment Type (NCE = 25)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₄	C ₃₄ H ₄₈ N ₉ O ₁₁	758.34678	758.34384	-3.88
A₀₅	C ₃₈ H ₅₅ N ₁₀ O ₁₃	859.39446	859.39089	-4.15
B₀₁	C ₂₃ H ₂₈ N ₅ O ₇	486.19832	486.19708	-2.56
B₀₂	C ₃₀ H ₄₀ N ₇ O ₁₀	658.28312	658.28144	-2.55
B₀₃	C ₃₃ H ₄₅ N ₈ O ₁₁	729.32023	729.31786	-3.25
B₀₄	C ₃₅ H ₄₈ N ₉ O ₁₂	786.34169	786.33893	-3.52
B₀₅	C ₃₉ H ₅₅ N ₁₀ O ₁₄	887.38937	887.38634	-3.42
B₀₆	C ₄₂ H ₆₀ N ₁₁ O ₁₆	974.42140	974.41706	-4.46
Y''₀₁	C ₂₄ H ₄₃ N ₈ O ₁₁	619.30458	619.30226	-3.75
Y''₀₃	C ₁₄ H ₂₆ N ₅ O ₇	376.18267	376.18203	-1.71
Y''₀₄	C ₁₂ H ₂₃ N ₄ O ₆	319.16121	319.16056	-2.04
Y''₀₅	C ₈ H ₁₆ N ₃ O ₄	218.11353	218.11295	-2.67

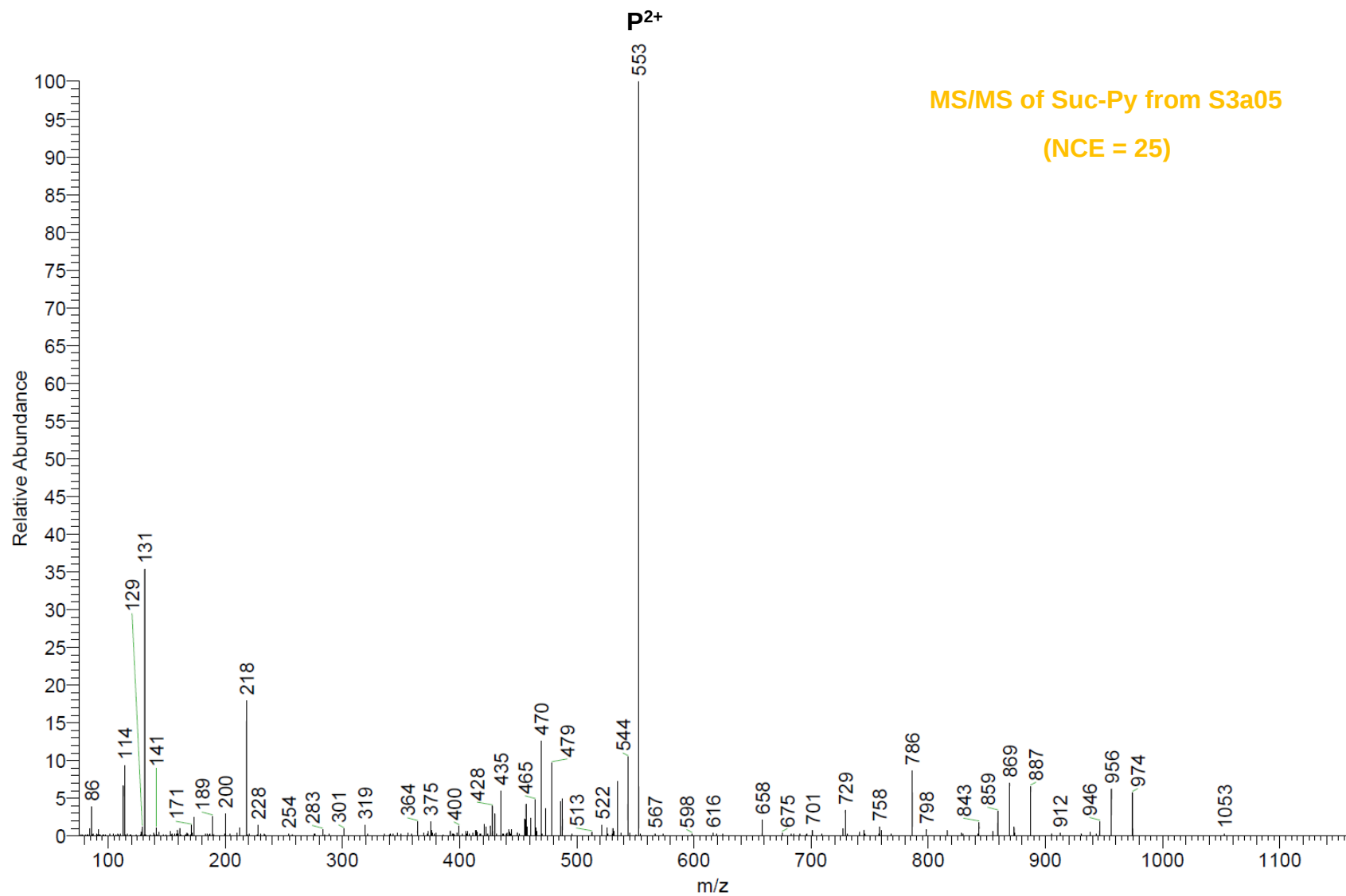
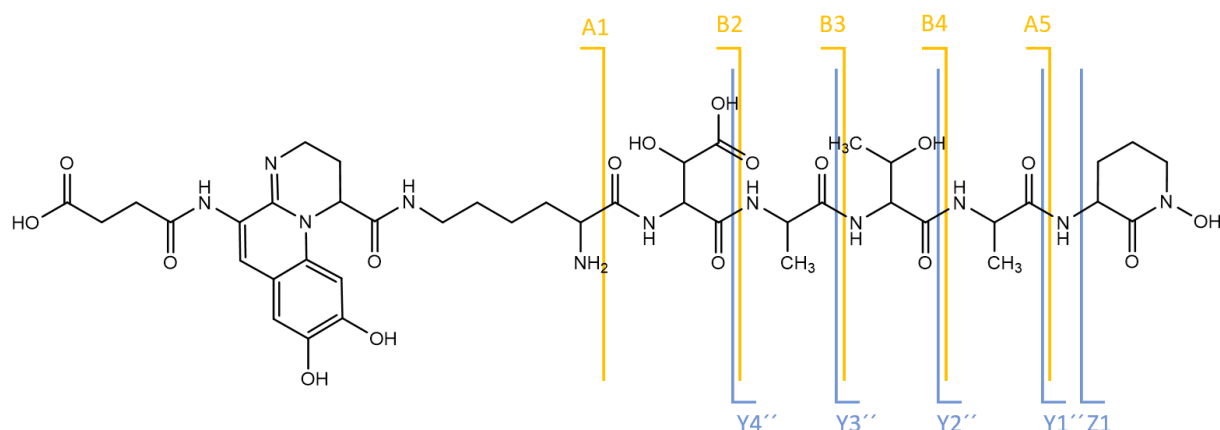


Table S14. Detected fragments in the MS/MS fragmentation of Suc-Py of S3a20 compared to their theoretical value m/z value and their ppm deviation. Additional spectral interpretation of H-FerB and Glu-FerB fragments are attached.

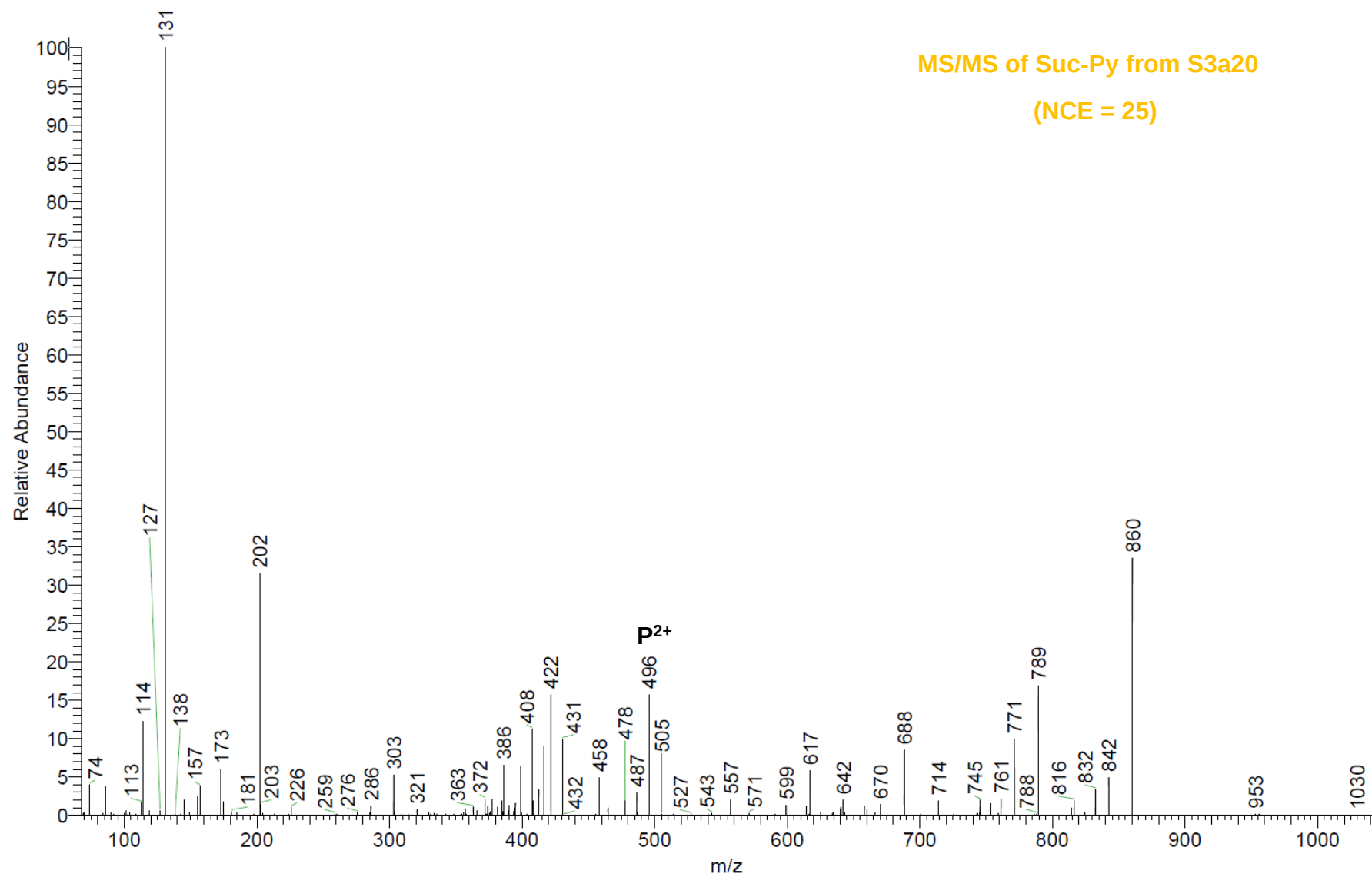


Name:	S3a-20			
Sequence:	ϵ -Lys-OHAsp-Ala-aThr-Ala-cOHOrn			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₂ H ₆₀ N ₁₁ O ₁₇	990.41686	990.41468	-2.21
[M+2H]²⁺	C ₄₂ H ₆₁ N ₁₁ O ₁₇	495.71234	495.71140	-1.91
Fragment Type (NCE = 20)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₂₂ H ₂₈ N ₅ O ₆	458.20341	458.20218	-2.68
B₀₂	C ₂₇ H ₃₃ N ₆ O ₁₁	617.22018	617.21892	-2.05
B₀₃	C ₃₀ H ₃₈ N ₇ O ₁₂	688.25730	688.25537	-2.80
B₀₄	C ₃₄ H ₄₅ N ₈ O ₁₄	789.30497	789.30309	-2.39
B₀₅	C ₃₇ H ₅₀ N ₉ O ₁₅	860.34209	860.33927	-3.28
Y''₀₄	C ₁₅ H ₂₈ N ₅ O ₆	374.20341	374.20268	-1.95
Y''₀₃	C ₁₂ H ₂₃ N ₄ O ₅	303.16630	303.16542	-2.89
Y''₀₂	C ₈ H ₁₆ N ₃ O ₃	202.11862	202.11808	-2.66
Y''₀₁	C ₅ H ₁₁ N ₂ O ₂	131.08150	131.08128	-1.71
Z₀₁	C ₅ H ₈ N ₁ O ₂	114.05550	114.05499	-4.50
Additional information				
Ferribactin	H-FerB			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₃₈ H ₆₀ N ₁₁ O ₁₃	878.43721	878.43576	-1.65
[M+2H]²⁺	C ₃₈ H ₆₁ N ₁₁ O ₁₃	439.72252	439.72191	-1.38
Fragment Type	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₁₈ H ₂₈ N ₅ O ₂	346.22375	346.22343	-0.93
A₀₃	C ₂₅ H ₃₈ N ₇ O ₇	548.28272	548.28148	-2.27
B₀₂	C ₂₃ H ₃₃ N ₆ O ₇	505.24052	505.24051	-0.03
B₀₃	C ₂₆ H ₃₈ N ₇ O ₈	576.27764	576.27706	-1.00

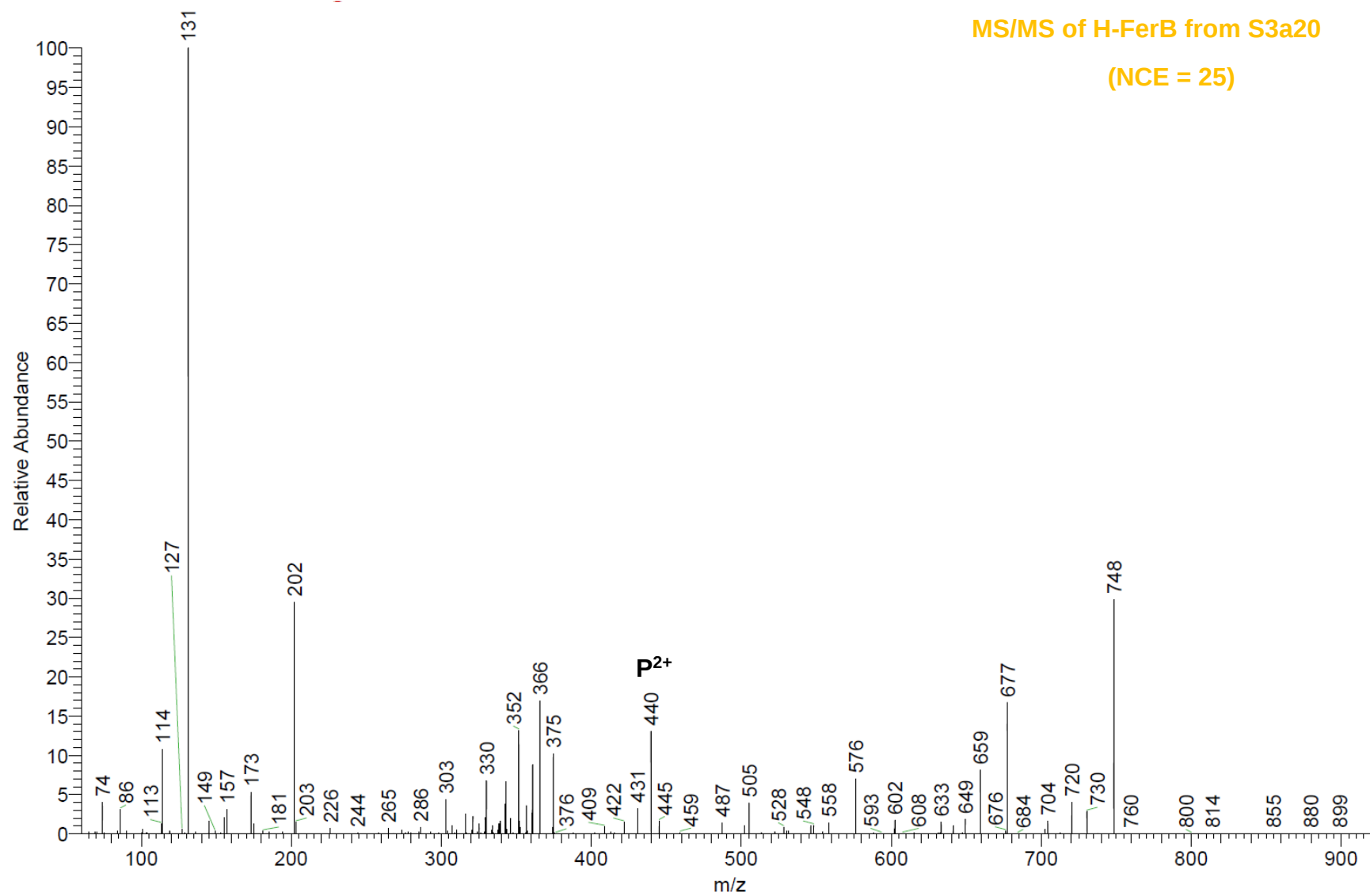
B₀₄	C ₃₀ H ₄₅ N ₈ O ₁₀	677.32532	677.32404	-1.88
B₀₅	C ₃₃ H ₅₀ N ₉ O ₁₁	748.36243	748.36101	-1.90
Y''₀₂	C ₁₅ H ₂₈ N ₅ O ₆	374.20341	374.20289	-1.39
Y''₀₃	C ₁₂ H ₂₃ N ₄ O ₅	303.16630	303.16586	-1.44
Y''₀₄	C ₈ H ₁₆ N ₃ O ₃	202.11862	202.11841	-1.03
Y''₀₅	C ₅ H ₁₁ N ₂ O ₂	131.08150	131.08145	-0.41
Z₀₅	C ₅ H ₈ N ₁ O ₂	114.05495	114.05510	1.27
Ferribactin	Glu-FerB			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₃ H ₆₇ N ₁₁ O ₁₆	1007.47980	1007.47939	-0.41
[M+2H]²⁺	C ₄₃ H ₆₈ N ₁₁ O ₁₆	504.24381	504.24334	-0.94
Fragment Type	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₂₃ H ₃₅ N ₆ O ₅	475.26634	475.26548	-1.82
A₀₃	C ₃₀ H ₄₅ N ₈ O ₁₀	677.32532	677.32471	-0.90
B₀₂	C ₂₈ H ₄₀ N ₇ O ₁₀	634.28312	634.28330	0.29
B₀₃	C ₃₁ H ₄₅ N ₈ O ₁₁	705.32023	705.31969	-0.77
B₀₄	C ₃₅ H ₅₂ N ₉ O ₁₃	806.36791	806.36696	-1.18
B₀₅	C ₃₈ H ₅₇ N ₁₀ O ₁₄	877.40502	877.40421	-0.93
Y''₀₂	C ₁₅ H ₂₈ N ₅ O ₆	374.20341	374.20342	0.03
Y''₀₃	C ₁₂ H ₂₃ N ₄ O ₅	303.16630	303.16583	-1.54
Y''₀₄	C ₈ H ₁₆ N ₃ O ₃	202.11862	202.11842	-0.98
Y''₀₅	C ₅ H ₁₁ N ₂ O ₂	131.08150	131.08150	-0.03
Z₀₅	C ₅ H ₈ N ₁ O ₂	114.05495	114.05518	1.97

MS/MS of Suc-Py from S3a20

(NCE = 25)



MS/MS of H-FerB from S3a20
(NCE = 25)



MS/MS of Glu-FerB from S3a20
(NCE = 25)

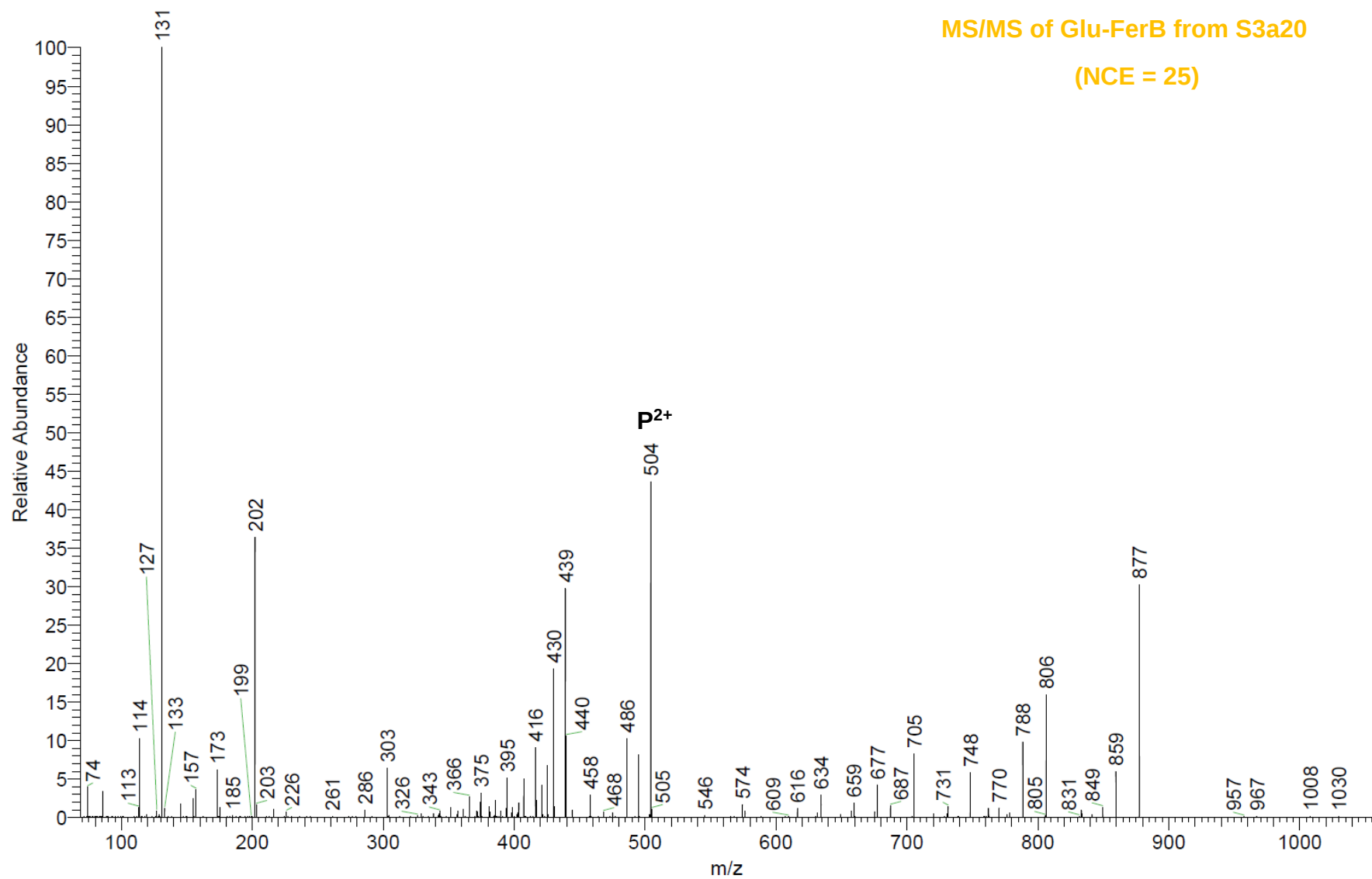
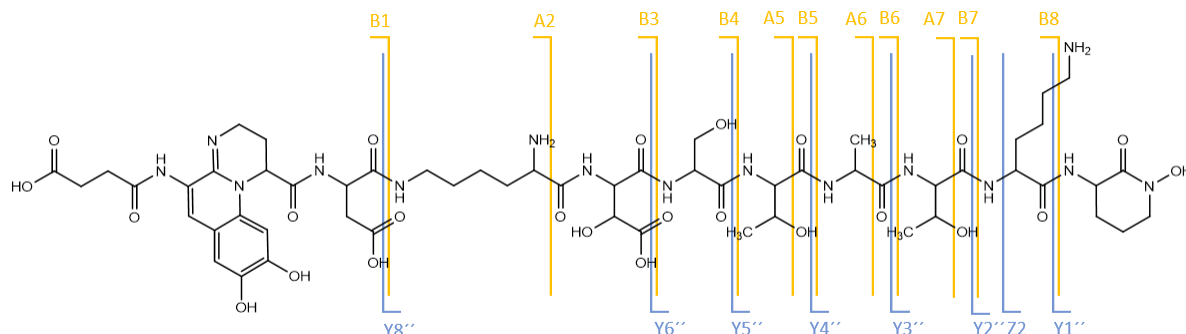


Table S15. Detected fragments in the MS/MS fragmentation of Suc-Py of S3b09 compared to their theoretical value m/z value and their ppm deviation.



Name:	S3b09			
Sequence:	Asp- ϵ -Lys-OHAsp-Ser-Thr-Ala-Thr-Lys-cOHO ^{rn}			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₅₆ H ₈₄ N ₁₅ O ₂₄	1350.58136	1350.57959	-1.31
[M+2H]²⁺	C ₅₆ H ₈₅ N ₁₅ O ₂₄	675.79459	675.79279	-2.67
Fragment Type (NCE = 25)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₂	C ₂₆ H ₃₃ N ₆ O ₉	573.23035	573.22840	-3.41
A₀₅	C ₃₇ H ₅₀ N ₉ O ₁₇	892.33192	892.32922	-3.02
A₀₆	C ₄₀ H ₅₅ N ₁₀ O ₁₈	963.36903	963.36594	-3.21
A₀₇	C ₄₄ H ₆₂ N ₁₁ O ₂₀	1064.41671	1064.41335	-3.16
B₀₁	C ₂₁ H ₂₁ N ₄ O ₉	473.13030	473.12848	-3.86
B₀₃	C ₃₁ H ₃₈ N ₇ O ₁₄	732.24713	732.24431	-3.85
B₀₄	C ₃₄ H ₄₃ N ₈ O ₁₆	819.27915	819.27658	-3.14
B₀₅	C ₃₈ H ₅₀ N ₉ O ₁₈	920.32683	920.32343	-3.70
B₀₆	C ₄₁ H ₅₅ N ₁₀ O ₁₉	991.36395	991.36126	-2.71
B₀₇	C ₄₅ H ₆₂ N ₁₁ O ₂₁	1092.41162	1092.40869	-2.69
B₀₈	C ₅₁ H ₇₄ N ₁₃ O ₂₂	1220.50659	1220.50242	-3.41
Y''₀₁	C ₅ H ₁₁ N ₂ O ₂	131.08150	131.08118	-2.47
Y''₀₂	C ₁₁ H ₂₃ N ₄ O ₃	259.17647	259.17566	-3.11
Y''₀₃	C ₁₅ H ₃₀ N ₅ O ₅	360.22415	360.22294	-3.35
Y''₀₄	C ₁₈ H ₃₅ N ₆ O ₆	431.26126	431.25966	-3.71
Y''₀₅	C ₂₂ H ₄₂ N ₇ O ₈	532.30894	532.30737	-2.95
Y''₀₆	C ₂₅ H ₄₇ N ₈ O ₁₀	619.34097	619.33848	-4.01
Y''₀₈	C ₃₅ H ₆₄ N ₁₁ O ₁₅	878.45779	878.45505	-3.12
Z₀₂	C ₁₁ H ₂₀ N ₃ O ₃	242.14992	242.14910	-3.38

MS/MS of Suc-Py from S3b09

(NCE = 25)

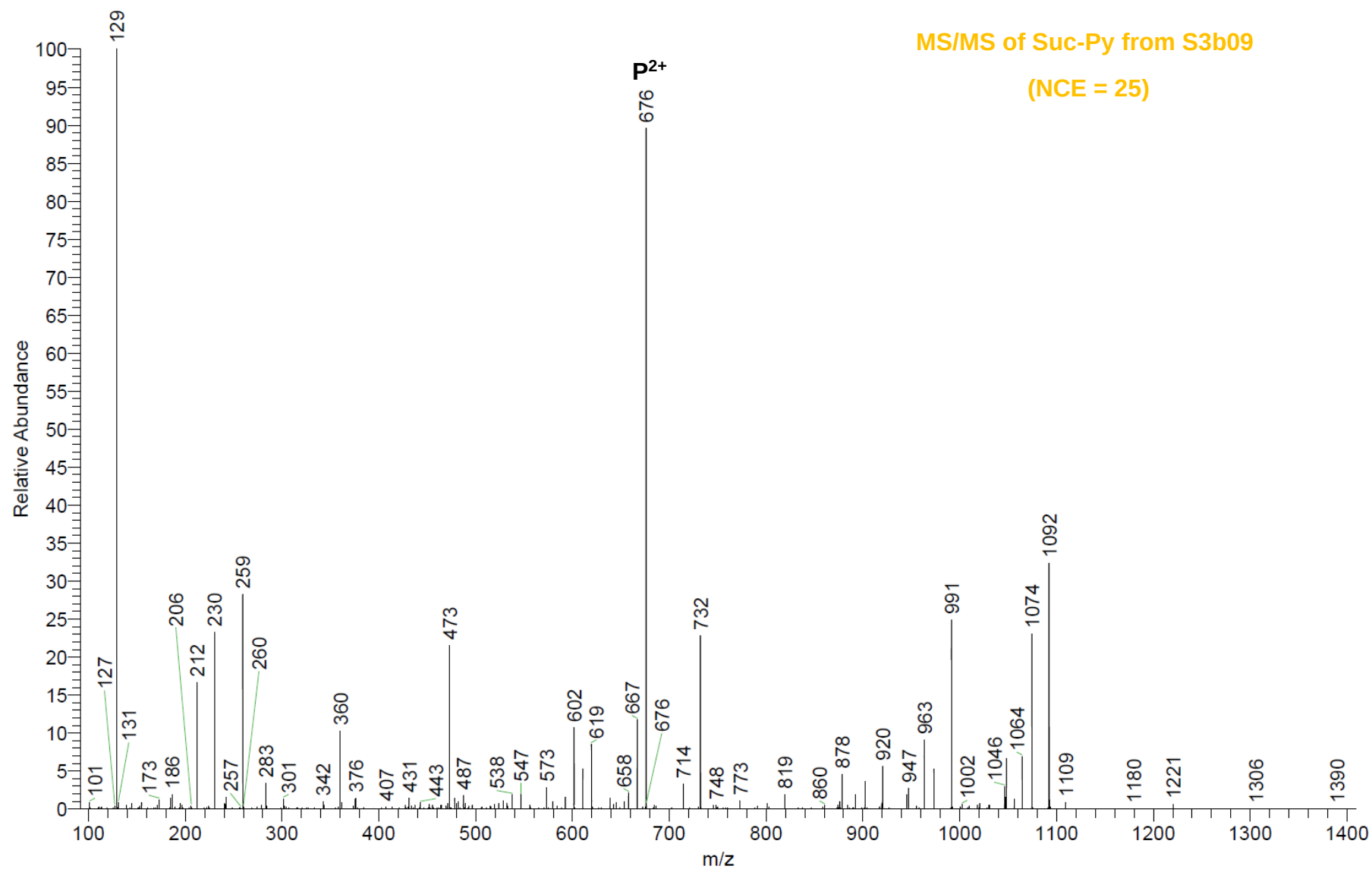
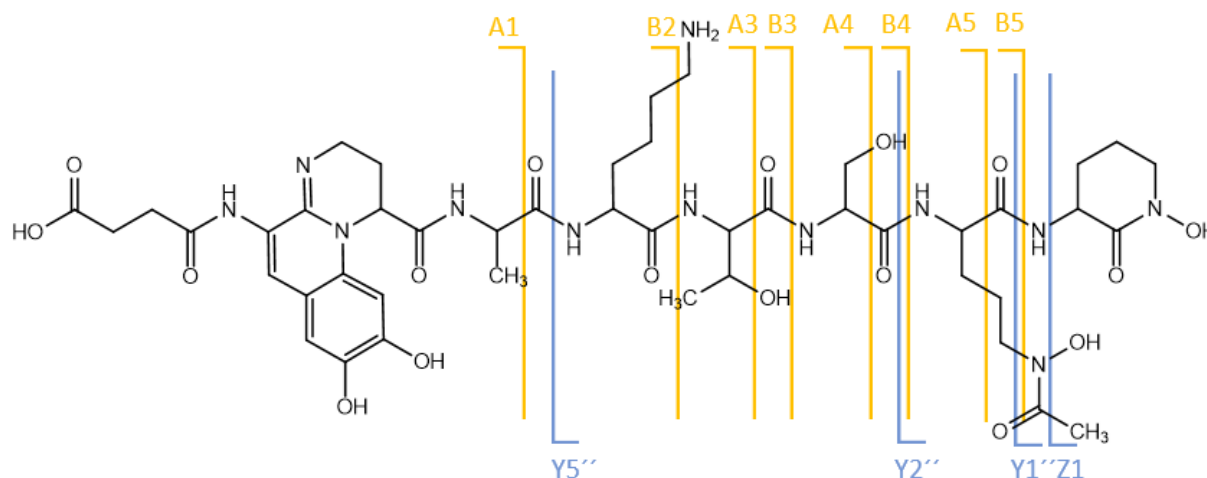


Table S16. Detected fragments in the MS/MS fragmentation of Suc-Py of S3b16 compared to their theoretical value m/z value and their ppm deviation.



Name:	S3b-16			
Sequence:	Ala-Lys-Thr-Ser-AcOHOrn-cOHOrn			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₅ H ₆₇ N ₁₂ O ₁₇	1047.47471	1047.47449	-0.21
[M+2H]²⁺	C ₄₅ H ₆₈ N ₁₂ O ₁₇	524.24127	524.24115	-0.23
Fragment Type (NCE = 30)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₁₉ H ₂₁ N ₄ O ₆	401.14556	401.14485	-1.77
A₀₃	C ₂₉ H ₄₀ N ₇ O ₉	630.28820	630.28728	-1.46
A₀₄	C ₃₂ H ₄₅ N ₈ O ₁₁	717.32023	717.31928	-1.33
A₀₅	C ₃₉ H ₅₇ N ₁₀ O ₁₄	889.40502	889.40180	-3.62
B₀₂	C ₂₆ H ₃₃ N ₆ O ₈	557.23544	557.23451	-1.67
B₀₃	C ₃₀ H ₄₀ N ₇ O ₁₀	658.28312	658.28346	0.52
B₀₄	C ₃₃ H ₄₅ N ₈ O ₁₂	745.31515	745.31419	-1.28
B₀₅	C ₄₀ H ₅₇ N ₁₀ O ₁₅	917.39994	917.39947	-0.51
Y''₀₁	C ₅ H ₁₁ N ₂ O ₂	131.08150	131.08146	-0.34
Y''₀₂	C ₁₂ H ₂₃ N ₄ O ₅	303.16630	303.16603	-0.88
Y''₀₅ (25 NCE)	C ₂₅ H ₄₇ N ₈ O ₁₀	619.34097	619.34042	-0.88
Z₀₁	C ₅ H ₈ N ₁ O ₂	114.05550	114.05515	-3.10

MS/MS of Suc-Py from S3b16
(NCE = 30)

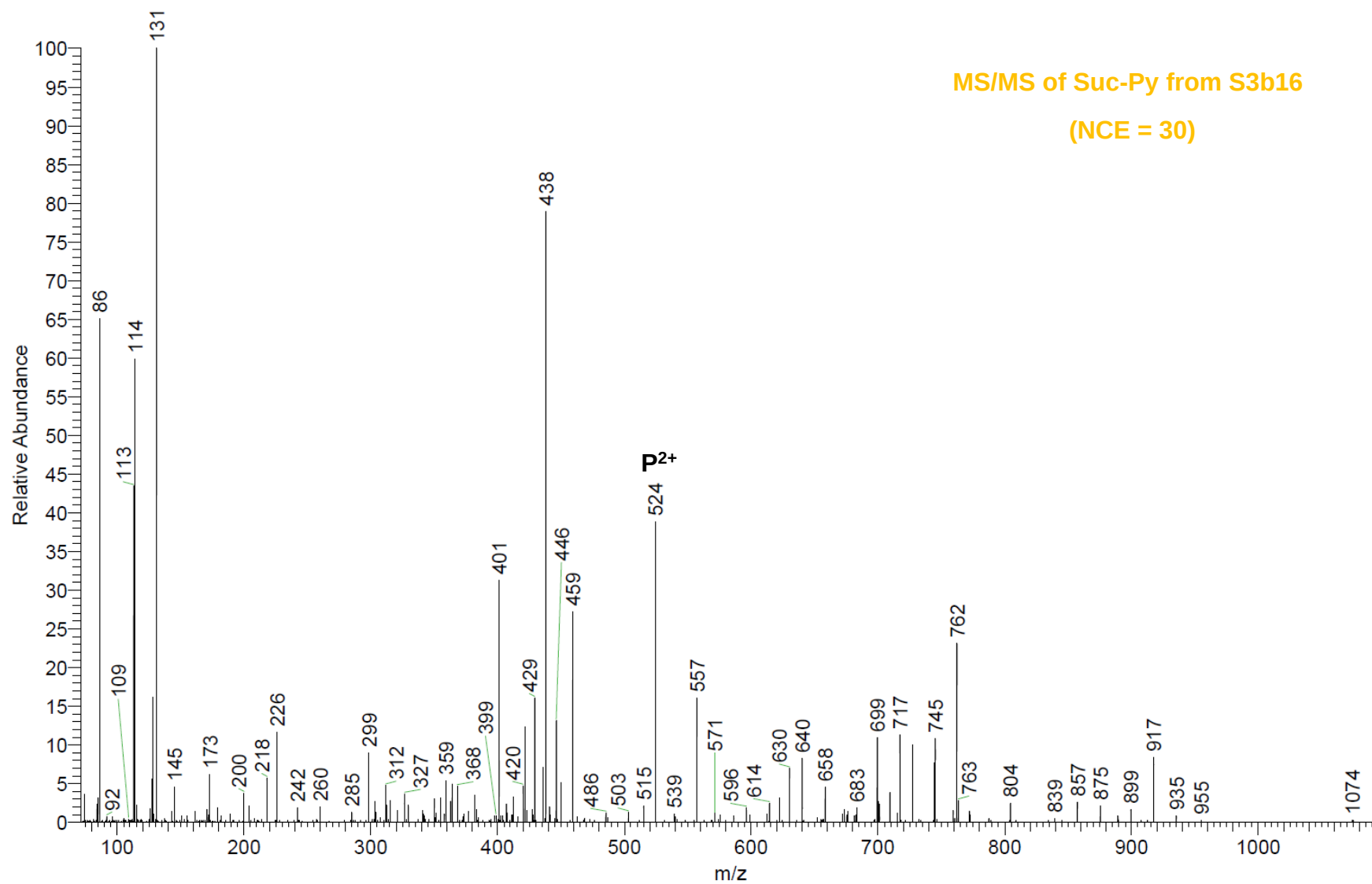
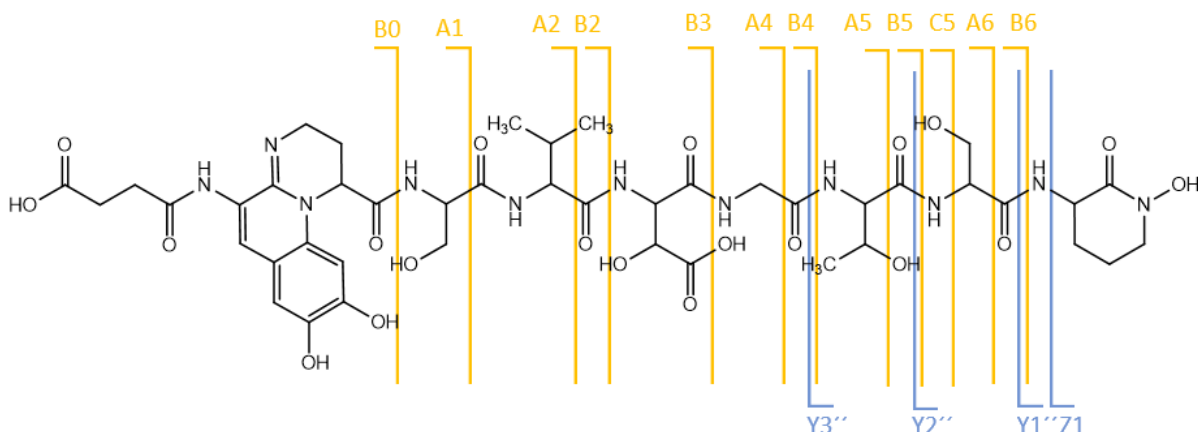


Table S17. Detected fragments in the MS/MS fragmentation of Suc-Py of S3c13 compared to their theoretical value m/z value and their ppm deviation.



Name:	S3c13			
Sequence:	Ser-Val-OHAsp-Gly-Thr-Ser-cOHO ^{rn}			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₃ H ₆₀ N ₁₁ O ₂₀	1050.40161	1050.40066	-0.90
[M+2H]²⁺	C ₄₃ H ₆₁ N ₁₁ O ₂₀	525.70472	525.70433	-0.74
Fragment Type (NCE = 25)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₁₉ H ₂₁ N ₄ O ₇	417.14048	417.13928	-2.87
A₀₂	C ₂₄ H ₃₀ N ₅ O ₈	516.20889	516.20891	0.04
A₀₄	C ₃₀ H ₃₈ N ₇ O ₁₃	704.25221	704.25092	-1.83
A₀₅	C ₃₄ H ₄₅ N ₈ O ₁₅	805.29989	805.29750	-2.97
A₀₆	C ₃₇ H ₅₀ N ₉ O ₁₇	892.33192	892.32904	-3.23
B₀₀	C ₁₇ H ₁₆ N ₃ O ₆	358.10336	358.10326	-0.28
B₀₂	C ₂₅ H ₃₀ N ₅ O ₉	544.20380	544.20288	-1.70
B₀₃	C ₂₉ H ₃₅ N ₆ O ₁₃	675.22566	675.22370	-2.91
B₀₄	C ₃₁ H ₃₈ N ₇ O ₁₄	732.24713	732.24523	-2.59
B₀₅	C ₃₅ H ₄₅ N ₈ O ₁₆	833.29480	833.29231	-2.99
B₀₆	C ₃₈ H ₅₀ N ₉ O ₁₈	920.32683	920.32477	-2.24
C₀₅	C ₃₅ H ₄₆ N ₉ O ₁₆	848.30570	848.30291	-3.29
Y''₀₁	C ₅ H ₁₁ N ₂ O ₂	131.08150	131.08138	-0.95
Y''₀₂	C ₈ H ₁₆ N ₃ O ₄	218.11353	218.11308	-2.07
Y''₀₃	C ₁₂ H ₂₃ N ₄ O ₆	319.16121	319.16083	-1.19
Z₀₁	C ₅ H ₈ N ₁ O ₂	114.05495	114.05502	0.57

MS/MS of Suc-Py from S3c13

(NCE = 25)

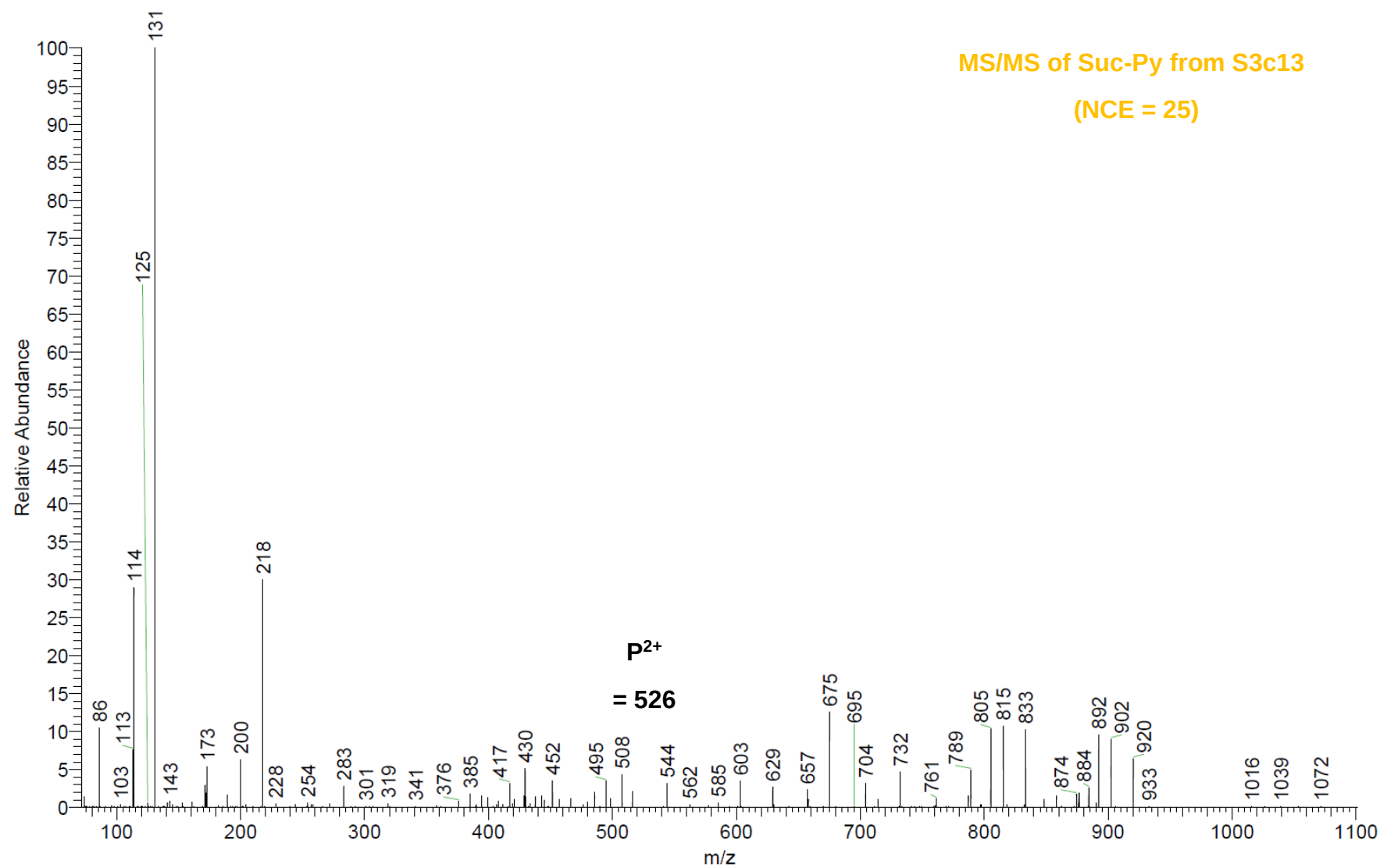
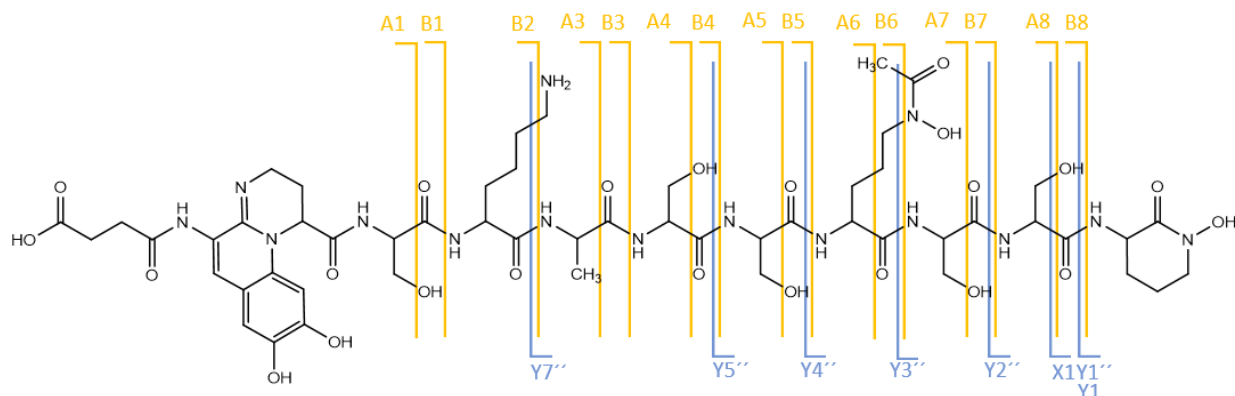


Table S18. Detected fragments in the MS/MS fragmentation of Suc-Py of S3e20 compared to their theoretical value m/z value and their ppm deviation.



Name:	S3e20			
Sequence:	Ser-Lys-Ala-Ser-Ser-AcOHOrn-Ser-Ser-cOHOrn			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₅₃ H ₈₀ N ₁₅ O ₂₃	1294.55515	1294.55323	-1.48
[M+2H]²⁺	C ₅₃ H ₈₁ N ₁₅ O ₂₃	647.78149	647.78015	-2.06
Fragment Type (NCE = 25)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₁₉ H ₂₁ N ₄ O ₇	417.14048	417.13957	-2.17
A₀₃	C ₂₈ H ₃₈ N ₇ O ₉	616.27255	616.27022	-3.78
A₀₄	C ₃₁ H ₄₃ N ₈ O ₁₁	703.30458	703.30288	-2.42
A₀₅	C ₃₄ H ₄₈ N ₉ O ₁₃	790.33661	790.33503	-2.00
A₀₆	C ₄₁ H ₆₀ N ₁₁ O ₁₆	962.42140	962.41979	-1.67
A₀₇	C ₄₄ H ₆₅ N ₁₂ O ₁₈	1049.45343	1049.45157	-1.77
A₀₈	C ₄₇ H ₇₀ N ₁₃ O ₂₀	1136.48546	1136.48263	-2.49
B₀₁	C ₂₀ H ₂₁ N ₄ O ₈	445.13539	445.13442	-2.18
B₀₂	C ₂₆ H ₃₃ N ₆ O ₉	573.23035	573.22843	-3.36
B₀₃	C ₂₉ H ₃₈ N ₇ O ₁₀	644.26747	644.26598	-2.31
B₀₄	C ₃₂ H ₄₃ N ₈ O ₁₂	731.29950	731.29768	-2.48
B₀₅	C ₃₅ H ₄₈ N ₉ O ₁₄	818.33152	818.33043	-1.34
B₀₆	C ₄₂ H ₆₀ N ₁₁ O ₁₇	990.41632	990.41480	-1.53
B₀₇	C ₄₅ H ₆₅ N ₁₂ O ₁₉	1077.44834	1077.44659	-1.63
B₀₈	C ₄₈ H ₇₀ N ₁₃ O ₂₁	1164.48037	1164.48036	-0.01
X₀₁	C ₆ H ₉ N ₂ O ₃	157.06077	157.06059	-1.14
Y₀₁	C ₅ H ₉ N ₂ O ₂	129.06585	129.06591	0.43
Y''₀₁	C ₅ H ₁₁ N ₂ O ₂	131.08150	131.08145	-0.41
Y''₀₂	C ₈ H ₁₆ N ₃ O ₄	218.11353	218.11334	-0.88
Y''₀₃	C ₁₁ H ₂₁ N ₄ O ₆	305.14556	305.14503	-1.74
Y''₀₄	C ₁₈ H ₃₃ N ₆ O ₉	477.23035	477.23121	1.80
Y''₀₇	C ₂₇ H ₄₈ N ₉ O ₁₄	722.33152	722.32902	-3.47
Z₀₈	C ₅ H ₈ N ₁ O ₂	114.05495	114.05519	2.06

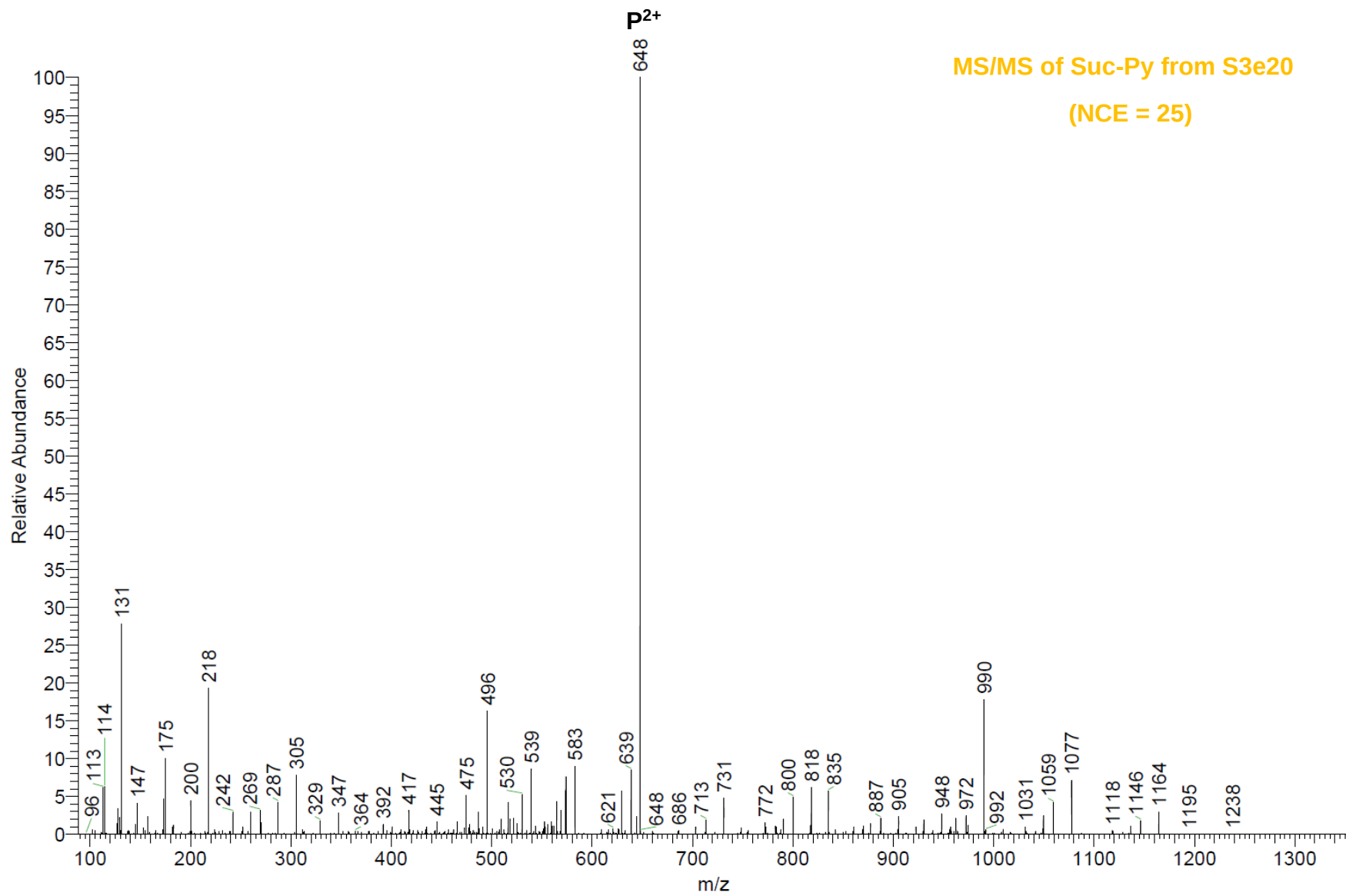
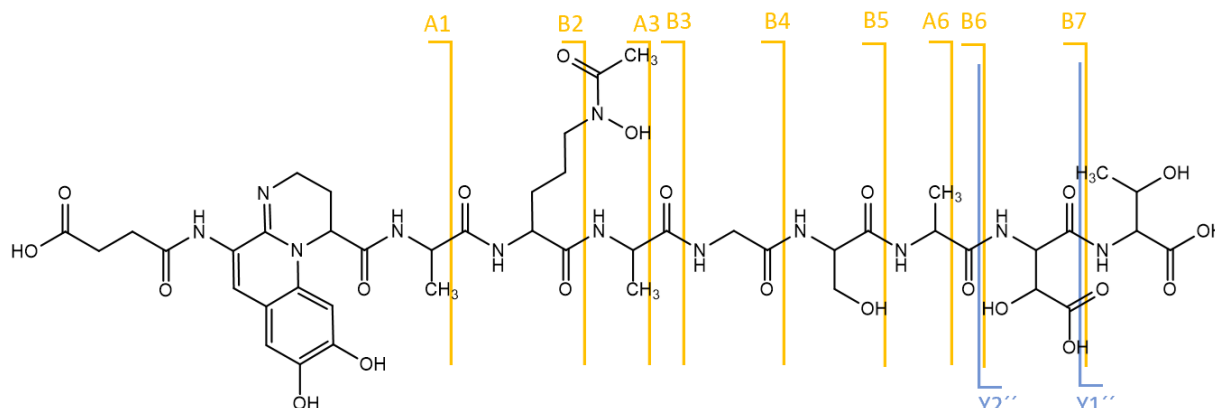


Table S19. Detected fragments in the MS/MS fragmentation of Suc-Py of S3g01 compared to their theoretical value m/z value and their ppm deviation.



Name:	S3g01			
Sequence:	Ala-AcOHorn-Ala-Gly-Ser-Ala-OHAsp-Thr			
	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
[M+H]⁺	C ₄₆ H ₆₅ N ₁₂ O ₂₂	1137.43364	1137.43391	0.24
[M+2H]²⁺	C ₄₆ H ₆₆ N ₁₂ O ₂₂	569.22073	569.22067	-0.11
Fragment Type (NCE = 25)	Formula	Mass (m/z)	Found Mass (m/z)	ppm Deviation
A₀₁	C ₁₉ H ₂₁ N ₄ O ₆	401.14556	401.14395	-4.02
A₀₃	C ₂₉ H ₃₈ N ₇ O ₁₀	644.26747	644.26653	-1.45
B₀₂	C ₂₇ H ₃₃ N ₆ O ₁₀	601.22527	601.22608	1.35
B₀₃	C ₃₀ H ₃₈ N ₇ O ₁₁	672.26238	672.26162	-1.13
B₀₄	C ₃₂ H ₄₁ N ₈ O ₁₂	729.28385	729.28398	0.18
B₀₅	C ₃₅ H ₄₆ N ₉ O ₁₄	816.31587	816.31578	-0.111
B₀₆	C ₃₈ H ₅₁ N ₁₀ O ₁₅	887.35299	887.35205	-1.06
B₀₇ (NCE = 20)	C ₄₂ H ₅₆ N ₁₁ O ₁₉	1018.3748	1018.37438	-0.46
Y''₀₂	C ₈ H ₁₅ N ₂ O ₇	251.08738	251.08682	-2.22
Y''₀₁	C ₄ H ₁₀ N ₁ O ₃	120.06552	120.06566	1.17

MS/MS of Suc-Py from S3g01
(NCE = 25)

