Supporting Information

D-Amino Acid-Containing Lipopeptides Derived from the Lead Peptide BP100 with Activity against Plant Pathogens

Àngel Oliveras [1], Luís Moll [2], Gerard Riesco-Llach [1], Arnau Tolosa-Canudas [1], Sergio Gil-Caballero [3], Esther Badosa [2], Anna Bonaterra [2], Emilio Montesinos [2], Marta Planas [1,*] and Lidia Feliu [1,*]

Table of contents:

1. Biological activity of lipopeptides

Table S1. Antimicrobial activity (MIC) of lipopeptides

Peptide[a]	MIC (µM)							
	Ea[b]	*Pss*[b]	*Xap*[b]	*Xf*[b]	*Psa*[b]	*Xav*[b]	*Pe*[b]	*Fo*[b]
BP367	3.1-6.2	3.1-6.2	3.1-6.2	3.1-6.2	3.1-6.2	3.1-6.2	12.5-25	1.6-3.1
BP472	3.1-6.2	3.1-6.2	1.6-3.1	1.6-3.1	1.6-3.1	1.6-3.1	>25	3.1-6.2
BP371	3.1-6.2	3.1- 6.2	3.1- 6.2	3.1-6.2	3.1-6.2	3.1-6.2	3.1-6.2	0.8-1.6
BP484	6.2-12.5	3.1-6.2	3.1-6.2	1.6-3.1	3.1-6.2	6.2-12.5	6.2-12.5	1.6-3.1
BP374	3.1-6.2	6.2-12.5	6.2-12.5	3.1-6.2	3.1-6.2	6.2-12.5	>25	0.8-1.6
BP494	6.2-12.5	3.1-6.2	6.2-12.5	12.5-25	3.1-6.2	6.2-12.5	0.8-1.6	3.1-6.2
BP378	3.1-6.2	6.2-12.5	3.1-6.2	3.1-6.2	3.1-6.2	3.1-6.2	3.1-6.2	0.8-1.6
BP495	3.1-6.2	3.1-6.2	3.1-6.2	6.2-12.5	1.6-3.1	6.2-12.5	0.8-1.6	1.6-3.1
BP379	3.1-6.2	3.1-6.2	3.1-6.2	3.1-6.2	3.1-6.2	3.1-6.2	6.2-12.5	3.1-6.2
BP485	6.2-12.5	3.1-6.2	1.6-3.1	1.6-3.1	3.1-6.2	1.6-3.1	3.1-6.2	1.6-3.1
BP381	3.1-6.2	3.1-6.2	3.1-6.2	1.6-3.1	3.1-6.2	1.6-3.1	1.6-3.1	0.8-1.6
BP486	6.2-12.5	12.5-25	3.1-6.2	3.1-6.2	6.2-12.5	6.2-12.5	6.2-12.5	0.8-1.6
BP384	3.1-6.2	6.2-12.5	3.1-6.2	1.6-3.1	6.2-12.5	1.6-3.1	12.5-25	1.6-3.1
BP498	6.2-12.5	6.2-12.5	1.6-3.1	3.1-6.2	6.2-12.5	1.6-3.1	1.6-3.1	0.8-1.6
BP385	6.2-12.5	6.2-12.5	0.8-1.6	1.6-3.1	6.2-12.5	0.8-1.6	6.2-12.5	1.6-3.1
BP473	3.1-6.2	6.2-12.5	1.6-3.1	1.6-3.1	3.1-6.2	1.6-3.1	>25	0.8-1.6
BP387	3.1-6.2	3.1-6.2	3.1-6.2	1.6-3.1	3.1-6.2	1.6-3.1	6.2-12.5	0.8-1.6
BP474	6.2-12.5	3.1-6.2	3.1-6.2	6.2-12.5	1.6-3.1	3.1-6.2	3.1-6.2	0.8-1.6
BP388	3.1-6.2	6.2-12.5	3.1-6.2	1.6-3.1	6.2-12.5	1.6-3.1	6.2-12.5	0.8-1.6
BP499	3.1-6.2	6.2-12.5	3.1-6.2	3.1-6.2	3.1-6.2	1.6-3.1	1.6-3.1	0.8-1.6
BP389	3.1-6.2	6.2-12.5	0.8-1.6	1.6-3.1	3.1-6.2	0.8-1.6	6.2-12.5	1.6-3.1
BP475	3.1-6.2	3.1-6.2	0.8-1.6	1.6-3.1	1.6-3.1	1.6-3.1	3.1-6.2	0.8-1.6
BP390	3.1-6.2	6.2-12.5	6.2-12.5	3.1-6.2	6.2-12.5	3.1-6.2	6.2-12.5	0.8-1.6
BP496	6.2-12.5	6.2-12.5	1.6-3.1	12.5-25	3.1-6.2	12.5-25	3.1-6.2	1.6-3.1
BP394	12.5-25	6.2-12.5	1.6-3.1	0.8- 1.6	6.2-12.5	1.6-3.1	12.5-25	6.2-12.5
BP500	6.2-12.5	3.1-6.2	1.6-3.1	1.6-3.1	3.1-6.2	0.8-1.6	6.2-12.5	3.1-6.2
BP395	12.5-25	3.1-6.2	1.6-3.1	1.6-3.1	3.1-6.2	1.6-3.1	12.5-25	6.2-12.5
BP488	6.2-12.5	3.1-6.2	1.6-3.1	1.6-3.1	3.1-6.2	1.6-3.1	12.5-25	>25
BP398	>25	3.1-6.2	1.6-3.1	3.1-6.2	3.1-6.2	0.8-1.6	>25	6.2-12.5
BP489	6.2-12.5	3.1-6.2	1.6-3.1	3.1-6.2	3.1-6.2	1.6-3.1	12.5-25	>25
BP399	>25	3.1-6.2	1.6-3.1	3.1-6.2	3.1-6.2	0.8-1.6	12.5-25	6.2-12.5
BP490	>25	6.2-12.5	1.6-3.1	1.6-3.1	3.1-6.2	1.6-3.1	12.5-25	>25
BP400	>25	>25	1.6-3.1	3.1-6.2	>25	1.6-3.1	>25	6.2-12.5
BP497	>25	>25	1.6-3.1	0.8-1.6	>25	1.6-3.1	12.5-25	>25
BP402	3.1-6.2	3.1-6.2	1.6-3.1	3.1-6.2	3.1-6.2	1.6-3.1	12.5-25	6.2-12.5
BP476	6.2-12.5	6.2-12.5	1.6-3.1	1.6-3.1	1.6-3.1	1.6-3.1	12.5-25	12.5-25

[a]For each group of peptides, the top sequence corresponds to the all-L derivative

[b]*Ea*, *Erwinia amylovora*; *Pss*, *Pseudomonas syringae* pv. syringae; *Xap*, *Xanthomonas arboricola* pv. pruni; *Xf*, *Xanthomonas fragariae*; *Psa*, *Pseudomonas syringae* pv. actinidiae; *Xav*, *Xanthomonas axonopodis* pv. vesicatoria; *Pe*, *Penicillium expansum*; *Fo*, *Fusarium oxysporum*.

Table S2. Hemolytic activity

Lipopeptide[a]	Hemolysis (%)[b]			
	50 µM	**150 µM**	**250 µM**	**375 µM**
BP367	89 ± 2	87 ± 14	83 ± 6	95 ± 13
BP472	21 ± 5	66 ± 3	78 ± 5	90 ± 3
BP371	22 ± 4	47 ± 2	75 ± 4	95 ± 3
BP484	3 ± 0.1	5 ± 0.9	10 ± 2	15 ± 4
BP374	4 ± 2	8 ± 0.4	19 ± 3	28 ± 2
BP494	0 ± 0.5	0.3 ± 0.8	0.2 ± 0.2	0.4 ± 0.5
BP378	15 ± 7	21 ± 2	26 ± 0.4	52 ± 6
BP495	0 ± 0.4	0 ± 0.4	0.6 ± 1	1 ± 2
BP379	60 ± 10	86 ± 2	93 ± 0.8	96 ± 1
BP485	9 ± 0.4	16 ± 4	24 ± 9	46 ± 5
BP381	11 ± 2	30 ± 3	54 ± 6	76 ± 2
BP486	3 ± 2	6 ± 2	14 ± 5	14 ± 2
BP384	41 ± 15	97 ± 10	100 ± 4	100 ± 2
BP498	6 ± 1	17 ± 2	21 ± 3	36 ± 2
BP385	42 ± 3	98 ± 8	100 ± 3	100 ± 4
BP473	7 ± 2	41 ± 4	84 ± 11	75 ± 12
BP387	4 ± 0.9	11 ± 5	14 ± 0.5	18 ± 1
BP474	0 ± 0	0 ± 0	0 ± 0	0 ± 0
BP388	10 ± 1	32 ± 3	38 ± 4	89 ± 10
BP499	3 ± 0.8	7 ± 0.3	11 ± 1	17 ± 1
BP389	9 ± 4	17 ± 0.7	22 ± 2	39 ± 3
BP475	0 ± 0	0 ± 0	0 ± 0	0 ± 0
BP390	1 ± 0.2	2 ± 0.2	5 ± 0.3	7 ± 0.9
BP496	0 ± 1	0 ± 0.2	1 ± 1	1 ± 0.5
BP394	100 ± 7	100 ± 7	100 ± 1	100 ± 2
BP500	74 ± 5	71 ± 2	71 ± 8	77 ± 5
BP395	100 ± 2	100 ± 2	100 ± 2	100 ± 2
BP488	71 ± 2	84 ± 9	86 ± 14	82 ± 7
BP398	70 ± 18	100 ± 9	100 ± 3	100 ± 5
BP489	50 ± 5	83 ± 15	100 ± 6	100 ± 1
BP399	94 ± 8	100 ± 5	100 ± 5	100 ± 6
BP490	100 ± 3	92 ± 17	100 ± 6	98 ± 2
BP400	43 ± 3	56 ± 1	99 ± 0.4	100 ± 14
BP497	88 ± 14	100 ± 2	100 ± 2	100 ± 4
BP402	95 ± 6	93 ± 13	100 ± 4	100 ± 0.5
BP476	69 ± 3	79 ± 7	94 ± 10	94 ± 67

[a]For each group of peptides, the top sequence corresponds to the all-L derivative

[b]Percent hemolysis plus confidence interval ($\alpha = 0.05$)

Table S3. Size of the lesion in infiltrated tobacco leaves

Lipopeptide[a]	Size of the lesion (mm)[b]		
	50 µM	**150 µM**	**250 µM**
BP367	6 ± 0.4	9 ± 2	15 ± 4
BP472	2 ± 1	4 ± 1	4 ± 1
BP371	2 ± 0.5	-	9 ± 2
BP484	0 ± 0	2 ± 2	7 ± 1
BP374	3 ± 0.6	9 ± 2	12 ± 3
BP494	1 ± 1	6 ± 1	8 ± 1
BP378	4 ± 0.7	12 ± 3	13 ± 5
BP495	3 ± 0	6 ± 2	11 ± 2
BP379	7 ± 1	13 ± 3	16 ± 3
BP485	4 ± 0.7	7 ± 0.7	12 ± 1
BP381	5 ± 2	11 ± 2	11 ± 2
BP486	4 ± 1	8 ± 1	17 ± 2
BP384	8 ± 1	11 ± 3	11 ± 2
BP498	4 ± 3	6 ± 2	6 ± 1
BP385	8 ± 1	13 ± 2	13 ± 2
BP473	2 ± 2	4 ± 0.9	5 ± 2
BP387	3 ± 0.7	8 ± 1	9 ± 1
BP474	0 ± 0	2 ± 2	4 ± 2
BP388	8 ± 2	11 ± 0.4	10 ± 3
BP499	6 ± 1	8 ± 2	8 ± 2
BP389	4 ± 1	7 ± 1	9 ± 3
BP475	5 ± 1	7 ± 2	10 ± 1
BP390	3 ± 0.7	7 ± 1	8 ± 2
BP496	3 ± 0.5	4 ± 0.5	10 ± 3
BP394	3 ± 0.7	12 ± 1	13 ± 0.6
BP500	3 ± 2	6 ± 2	9 ± 3
BP395	8 ± 0.7	11 ± 2	10 ± 3
BP488	4 ± 0.7	5 ± 1	13 ± 5
BP398	5 ± 0.5	9 ± 2	11 ± 4
BP489	2 ± 0.5	6 ± 2	11 ± 1
BP399	5 ± 0.8	8 ± 2	10 ± 3
BP490	4 ± 0.7	6 ± 2	11 ± 3
BP400	7 ± 1	11 ± 2	15 ± 4
BP497	5 ± 1	18 ± 1	18 ± 0
BP402	4 ± 1	10 ± 2	9 ± 2
BP476	3 ± 0.6	3 ± 0.5	5 ± 0.5

[a]For each group of peptides, the top sequence corresponds to the all-L derivative
[b]Effect on the size of the lesion in infiltrated tobacco leaves plus confidence interval

2. Synthesis of lipopeptides

$C_5H_{11}CO$-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP472)

This lipopeptide was prepared following the procedure described in the manuscript using hexanoic acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (75:25) afforded $C_5H_{11}CO$-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (**BP472**) in >99% purity. t_R = 6.14 min. MS (ESI) *m/z*: 760.1 $[M + 2H]^{2+}$, 1519.1 $[M + H]^+$; HRMS (ESI) *m/z*: calcd for $C_{78}H_{137}N_{17}O_{13}$ $[M + 2H]^{2+}$ 760.0285, found 760.0260; calcd for $C_{78}H_{136}N_{17}O_{13}$ $[M + H]^+$ 1519.0498, found 1519.0511.

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys(COC_3H_7)-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP473)

This lipopeptide was prepared following the procedure described in the manuscript using butyric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (75:25) afforded Ac-Lys-Lys-Leu-D-Phe-Lys-Lys(COC_3H_7)-Ile-Leu-Lys-Tyr-Leu-NH_2 (**BP473**) in >99% purity. t_R = 5.99 min. MS (ESI) *m/z*: 767.1 $[M + 2H]^{2+}$, 1533.1 $[M + H]^+$, 1555.1 $[M + Na]^+$; HRMS (ESI) *m/z*: calcd for $C_{78}H_{135}N_{17}O_{14}$ $[M + 2H]^{2+}$ 767.0182, found 767.0158; calcd for $C_{78}H_{134}N_{17}O_{14}$ $[M + H]^+$ 1533.0291, found 1533.0240.

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Lys(COC_3H_7)-Lys-Tyr-Leu-NH_2 (BP474)

This lipopeptide was prepared following the procedure described in the manuscript using butyric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (85:15) afforded Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Lys(COC_3H_7)-Lys-Tyr-Leu-NH_2 (**BP474**) in >99% purity. t_R = 5.36 min. MS (ESI) *m/z*: 774.6 $[M + 2H]^{2+}$, 1548.1 $[M + H]^+$, 1570.1 $[M + Na]^+$; HRMS (ESI) *m/z*: calcd for $C_{78}H_{136}N_{18}O_{14}$ $[M + 2H]^{2+}$ 774.5236, found 774.5208; calcd for $C_{78}H_{135}N_{18}O_{14}$ $[M + H]^+$ 1548.0400, found 1548.0381.

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Lys(COC_3H_7)-Leu-NH_2 (BP475)

This lipopeptide was prepared following the procedure described in the manuscript using butyric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (80:20) afforded

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Lys(COC_3H_7)-Leu-NH_2 (**BP475**) in >99% purity. t_R = 5.69 min. MS (ESI) *m/z*: 750.1 $[M + 2H]^{2+}$, 1498.2 $[M + H]^+$, 1520.1 $[M + Na]^+$; HRMS (ESI) *m/z*: calcd for $C_{75}H_{138}N_{18}O_{13}$ $[M + 2H]^{2+}$ 749.5340, found 749.5343; calcd for $C_{75}H_{137}N_{18}O_{13}$ $[M + H]^+$ 1498.0607, found 1498.0610; calcd for $C_{75}H_{136}N_{18}O_{13}Na$ $[M + Na]^+$ 1520.0426, found 1520.0424.

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Lys($COC_{11}H_{23}$)-NH_2 (BP476)

This lipopeptide was prepared following the procedure described in the manuscript using lauric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (80:20) afforded Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Lys($COC_{11}H_{23}$)-NH_2 (**BP476**) in >99% purity. t_R = 6.67 min. MS (ESI) *m/z*: 830.6 $[M + 2H]^{2+}$, 1660.3 $[M + H]^+$, 1682.2 $[M + Na]^+$; HRMS (ESI) *m/z*: calcd for $C_{86}H_{152}N_{18}O_{14}$ $[M + 2H]^{2+}$ 830.5862, found 830.5839; calcd for $C_{86}H_{151}N_{18}O_{14}$ $[M + H]^+$ 1660.1652, found 1660.1578.

Ac-Lys-Lys-Leu-D-Lys(COC_5H_{11})-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP484)

This lipopeptide was prepared following the procedure described in the manuscript using hexanoic acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (80:20) afforded Ac-Lys-Lys-Leu-D-Lys(COC_5H_{11})-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (**BP484**) in >99% purity. t_R = 6.45 min. MS (ESI) *m/z*: 771.5 $[M + 2H]^{2+}$, 1542.0 $[M + H]^+$; HRMS (ESI) *m/z*: calcd for $C_{77}H_{142}N_{18}O_{14}$ $[M + 2H]^{2+}$ 771.5471, found 771.5477; calcd for $C_{77}H_{141}N_{18}O_{14}$ $[M + H]^+$ 1542.0869, found 1542.0812.

C_3H_7CO-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP485)

This lipopeptide was prepared following the procedure described in the manuscript using butyric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (75:25) afforded C_3H_7CO-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (**BP485**) in >99% purity. t_R = 6.79 min. MS (ESI) *m/z*: 746.4 $[M + 2H]^{2+}$, 1491.0 $[M + H]^+$, 1513.1 $[M + Na]^+$; HRMS (ESI) *m/z*: calcd for $C_{76}H_{133}N_{17}O_{13}$ $[M + 2H]^{2+}$ 746.0129, found 746.0097; calcd for $C_{76}H_{132}N_{17}O_{13}$ $[M + H]^+$ 1491.0185, found 1491.0154.

Ac-Lys-Lys(COC$_3$H$_7$)-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH$_2$ (BP486)

This lipopeptide was prepared following the procedure described in the manuscript using butyric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (75:25) afforded Ac-Lys-Lys(COC$_3$H$_7$)-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH$_2$ (**BP486**) in >99% purity. t_R = 6.17 min. MS (ESI) *m/z*: 767.1 $[M + 2H]^{2+}$, 1533.1 $[M + H]^+$; HRMS (ESI) *m/z*: calcd for $C_{78}H_{134}N_{17}O_{14}$ $[M + H]^+$ 1533.0291, found 1533.0266; calcd for $C_{78}H_{133}N_{17}O_{14}Na$ $[M + Na]^+$ 1555.0110, found 1555.0071.

Ac-Lys-Lys-Leu-D-Lys(COC$_{11}$H$_{23}$)-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH$_2$ (BP488)

This lipopeptide was prepared following the procedure described in the manuscript using lauric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (75:25) afforded Ac-Lys-Lys-Leu-D-Lys(COC$_{11}$H$_{23}$)-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH$_2$ (**BP488**) in >99% purity. t_R = 6.80 min. MS (ESI) *m/z*: 814.1 $[M + 2H]^{2+}$, 1626.2 $[M + H]^+$; HRMS (ESI) *m/z*: calcd for $C_{83}H_{153}N_{18}O_{14}$ $[M + H]^+$ 1626.1808, found 1626.1787; calcd for $C_{83}H_{152}N_{18}O_{14}Na$ $[M + Na]^+$ 1648.1628, found 1648.1600.

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Lys(COC$_{11}$H$_{23}$)-Leu-Lys-Tyr-Leu-NH$_2$ (BP489)

This lipopeptide was prepared following the procedure described in the manuscript using lauric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (75:25) afforded Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Lys(COC$_{11}$H$_{23}$)-Leu-Lys-Tyr-Leu-NH$_2$ (**BP489**) in >99% purity. t_R = 6.76 min. MS (ESI) *m/z*: 554.4 $[M + 3H]^{3+}$, 831.1 $[M + 2H]^{2+}$, 1660.2 $[M + H]^+$; HRMS (ESI) *m/z*: calcd for $C_{86}H_{152}N_{18}O_{14}$ $[M + 2H]^{2+}$ 830.5862, found 830.5825; calcd for $C_{86}H_{151}N_{18}O_{14}$ $[M + H]^+$ 1660.1652, found 1660.1598.

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Lys(COC$_{11}$H$_{23}$)-Lys-Tyr-Leu-NH$_2$ (BP490)

This lipopeptide was prepared following the procedure described in the manuscript using lauric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (75:25) afforded Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Lys(COC$_{11}$H$_{23}$)-Lys-Tyr-Leu-NH$_2$ (**BP490**) in >99% purity. t_R

= 7.12 min. MS (ESI) *m/z*: 554.4 $[M + 3H]^{3+}$, 831.1 $[M + 2H]^{2+}$, 1660.2 $[M + H]^{+}$; HRMS (ESI) *m/z*: calcd for $C_{86}H_{151}N_{18}O_{14}$ $[M + H]^{+}$ 1660.1652, found 1660.1635; calcd for $C_{86}H_{150}N_{18}O_{14}Na$ $[M + Na]^{+}$ 1682.1471, found 1682.1449.

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Lys(COC_5H_{11})-Leu-Lys-Tyr-Leu-NH_2 (BP494)

This lipopeptide was prepared following the procedure described in the manuscript using hexanoic acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (80:20) afforded Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Lys(COC_5H_{11})-Leu-Lys-Tyr-Leu-NH_2 (**BP494**) in >99% purity. t_R = 5.42 min. MS (ESI) *m/z*: 788.6 $[M + 2H]^{2+}$, 1576.1 $[M + H]^{+}$; HRMS (ESI) *m/z*: calcd for $C_{80}H_{139}N_{18}O_{14}$ $[M + H]^{+}$ 1576.0713, found 1576.0683; calcd for $C_{80}H_{138}N_{18}O_{14}Na$ $[M + Na]^{+}$ 1598.0532, found 1598.0490.

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Lys(COC_5H_{11})-NH_2 (BP495)

This lipopeptide was prepared following the procedure described in the manuscript using hexanoic acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (80:20) afforded Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Lys(COC_5H_{11})-NH_2 (**BP495**) in >99% purity. t_R = 5.44 min. MS (ESI) *m/z*: 789.1 $[M + 2H]^{2+}$, 1576.1 $[M + H]^{+}$; HRMS (ESI) *m/z*: calcd for $C_{80}H_{139}N_{18}O_{14}$ $[M + H]^{+}$ 1576.0713, found 1576.0683; calcd for $C_{80}H_{138}N_{18}O_{14}Na$ $[M + Na]^{+}$ 1598.0532, found 1598.0499.

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Lys(COC_3H_7)-NH_2 (BP496)

This lipopeptide was prepared following the procedure described in the manuscript using butyric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (80:20) afforded Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Lys(COC_3H_7)-NH_2 (**BP496**) in >99% purity. t_R = 5.11 min. MS (ESI) *m/z*: 775.1 $[M + 2H]^{2+}$, 1548.2 $[M + H]^{+}$, 1570.1 $[M + Na]^{+}$; HRMS (ESI) *m/z*: calcd for $C_{86}H_{135}N_{18}O_{14}$ $[M + H]^{+}$ 1548.0400, found 1548.0367; calcd for $C_{78}H_{134}N_{18}O_{14}Na$ $[M + Na]^{+}$ 1570.0219, found 1570.0179.

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys($COC_{11}H_{23}$)-Tyr-Leu-NH_2 (BP497)

This lipopeptide was prepared following the procedure described in the manuscript using lauric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (75:25) afforded Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys($COC_{11}H_{23}$)-Tyr-Leu-NH_2 (**BP497**) in >99% purity. t_R = 7.21 min. MS (ESI) *m/z*: 823.1 $[M + 2H]^{2+}$, 1645.1 $[M + H]^+$; HRMS (ESI) *m/z*: calcd for $C_{86}H_{150}N_{17}O_{14}$ $[M + H]^+$ 1645.1543, found 1645.1516; calcd for $C_{86}H_{149}N_{17}O_{14}Na$ $[M + Na]^+$ 1667.1362, found 1667.1311.

Ac-Lys-Lys-Leu-D-Phe-Lys(COC_3H_7)-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP498)

This lipopeptide was prepared following the procedure described in the manuscript using butyric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (70:30) afforded Ac-Lys-Lys-Leu-D-Phe-Lys(COC_3H_7)-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (**BP498**) in >99% purity. t_R = 6.12 min. MS (ESI) *m/z*: 767.0 $[M + 2H]^{2+}$, 1533.1 $[M + H]^+$; HRMS (ESI) *m/z*: calcd for $C_{78}H_{135}N_{17}O_{14}$ $[M + 2H]^{2+}$ 767.0182, found 767.0147; calcd for $C_{78}H_{134}N_{17}O_{14}$ $[M + H]^+$ 1533.0291, found 1533.0225; calcd for $C_{78}H_{133}N_{17}O_{14}Na$ $[M + Na]^+$ 1555.0110, found 1555.0032.

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys(COC_3H_7)-Tyr-Leu-NH_2 (BP499)

This lipopeptide was prepared following the procedure described in the manuscript using butyric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (75:25) afforded Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys(COC_3H_7)-Tyr-Leu-NH_2 (**BP499**) in >99% purity. t_R = 5.89 min. MS (ESI) *m/z*: 766.8 $[M + 2H]^{2+}$, 1533.4 $[M + H]^+$, 1555.1 $[M + Na]^+$; HRMS (ESI) *m/z*: : calcd for $C_{78}H_{134}N_{17}O_{14}$ $[M + H]^+$ 1533.0291, found 1533.0269; calcd for $C_{78}H_{133}N_{17}O_{14}Na$ $[M + Na]^+$ 1555.0110, found 1555.0097.

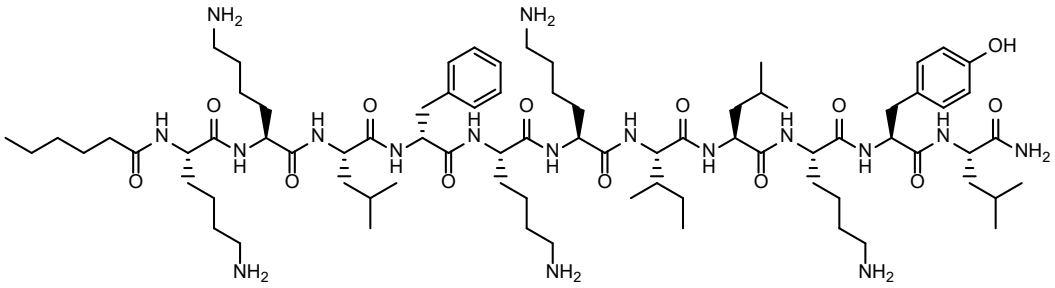
Ac-Lys-Lys-Lys($COC_{11}H_{23}$)-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP500)

This lipopeptide was prepared following the procedure described in the manuscript using lauric acid. Acidolytic cleavage of the resulting resin and purification eluting with H_2O/CH_3CN (70:30) afforded Ac-Lys-Lys-Lys($COC_{11}H_{23}$)-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (**BP500**) in >99% purity. t_R

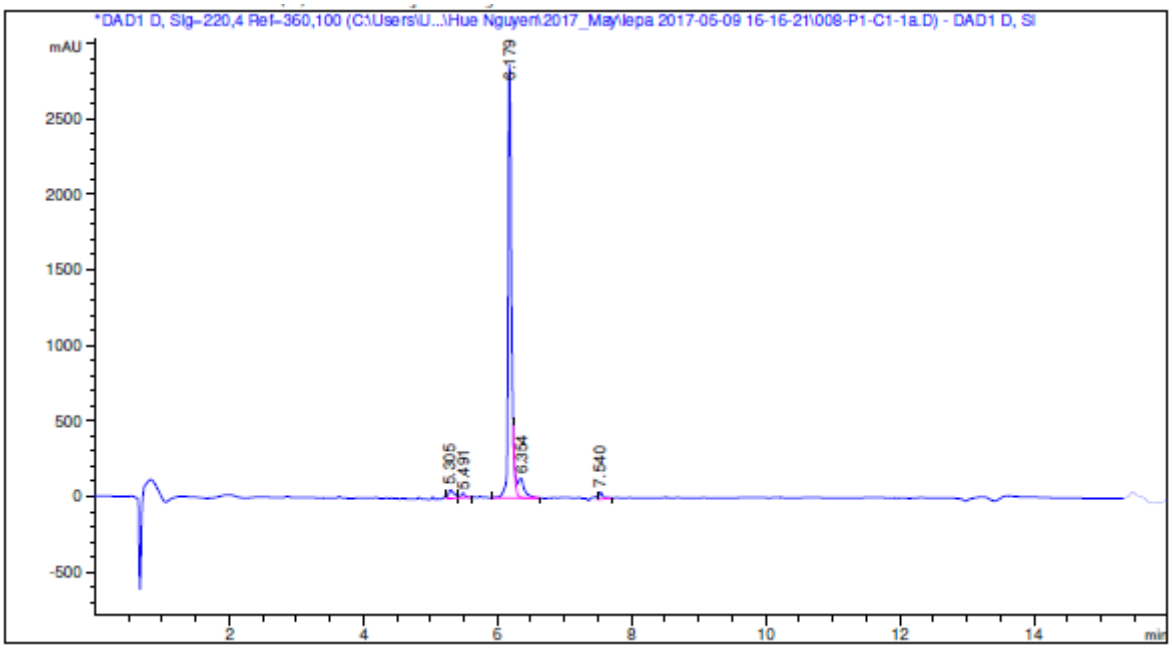
= 6.80 min. MS (ESI) *m/z*: 554.4 $[M + 3H]^{3+}$, 830.7 $[M + 2H]^{2+}$; HRMS (ESI) *m/z*: calcd for $C_{86}H_{151}N_{18}O_{14}$ $[M + H]^{+}$ 1661.1684, found 1661.1667; calcd for $C_{86}H_{150}N_{18}O_{14}Na$ $[M + Na]^{+}$ 1683.1503, found 1683.1487.

3. HPLC of crude and purified lipopeptides, ESI-MS and HRMS of purified lipopeptides

$C_5H_{11}CO$-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP472)

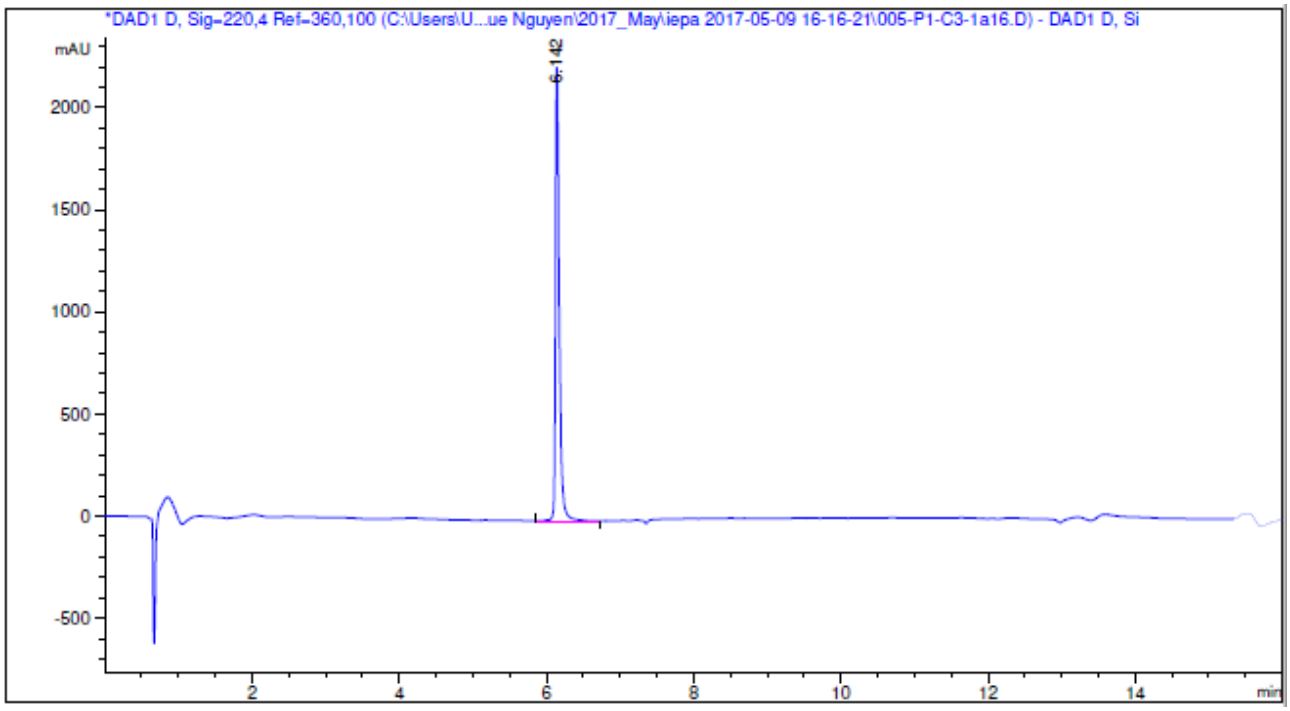


HPLC of crude peptide (λ=220 nm)



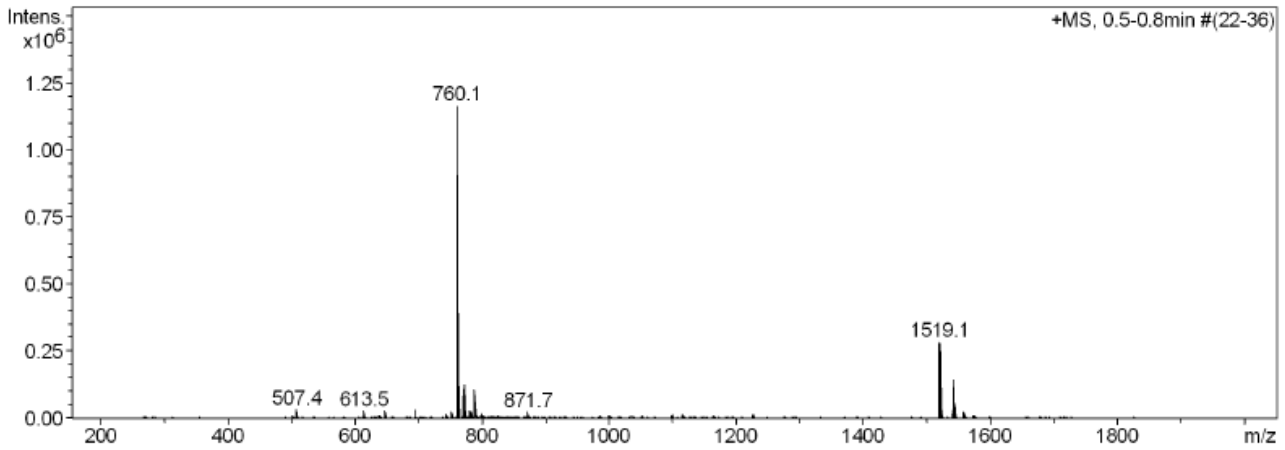
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.305	VV	0.0871	334.45099	54.91665	2.8671
2	5.491	VB	0.0577	135.30244	32.39536	1.1599
3	6.179	BV R	0.0529	1.00572e4	2871.68335	86.2160
4	6.354	VB E	0.0962	953.29431	126.04663	8.1722
5	7.540	VV R	0.0572	184.87265	46.71790	1.5848

HPLC of purified peptide (λ=220 nm)

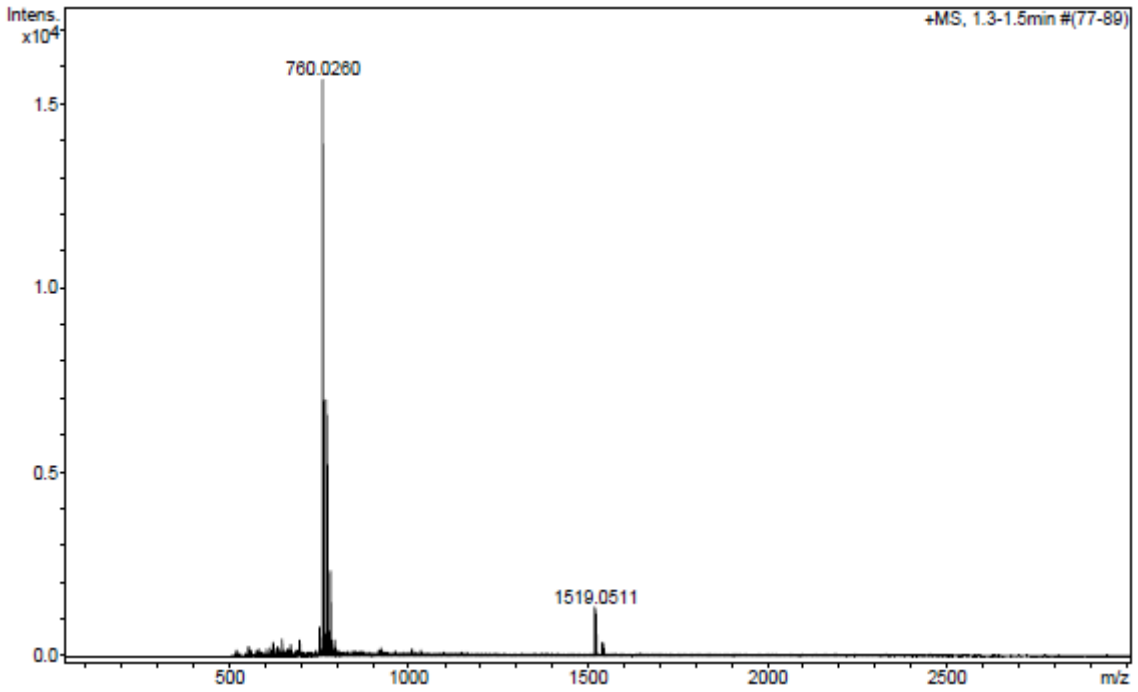


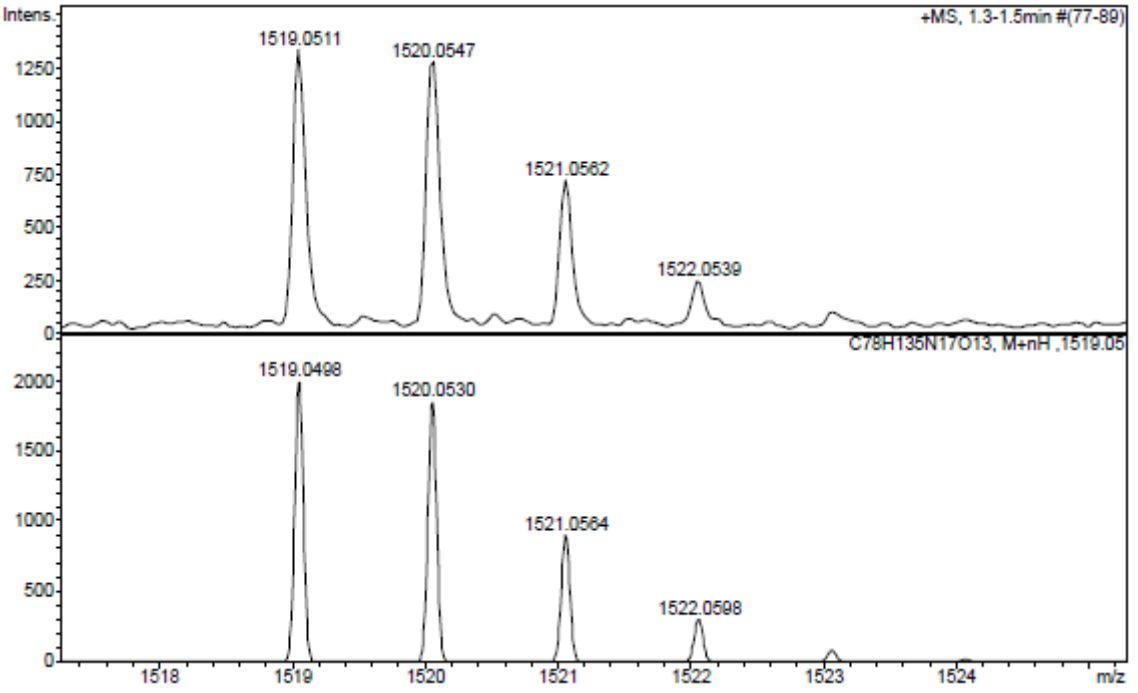
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.142	BB	0.0530	8007.58594	2222.06152	100.0000

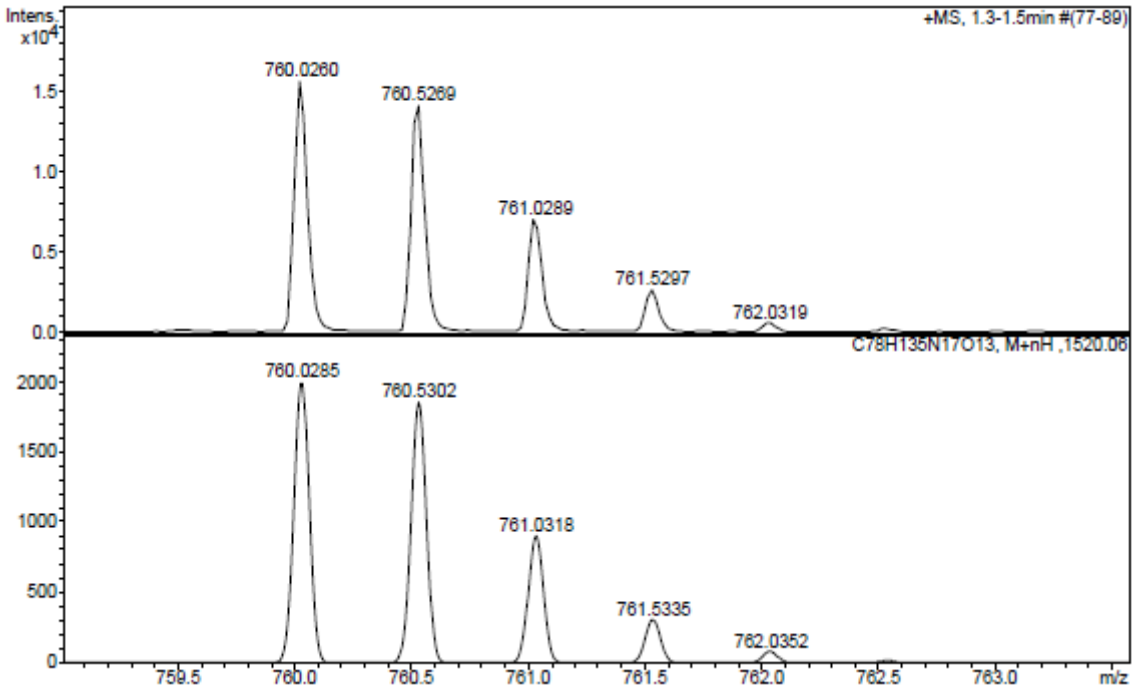
ESI-MS (*m/z*)



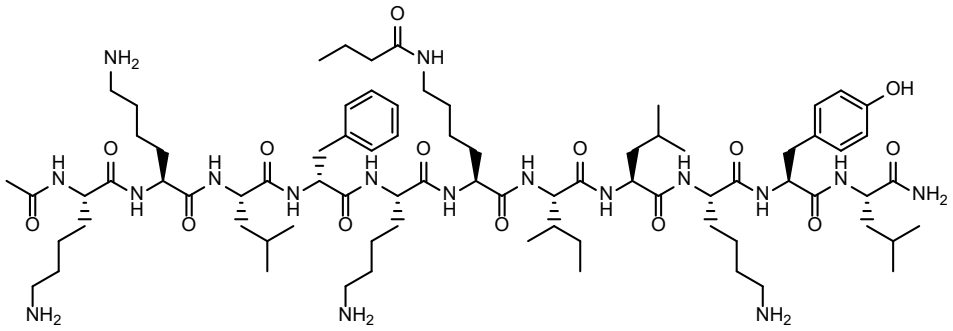
HRMS (*m/z*)


Intens.
x10^4
+MS, 1.3-1.5min #(77-89)
760.0260
1519.0511
1.5
1.0
0.5
0.0
500
1000
1500
2000
2500
m/z

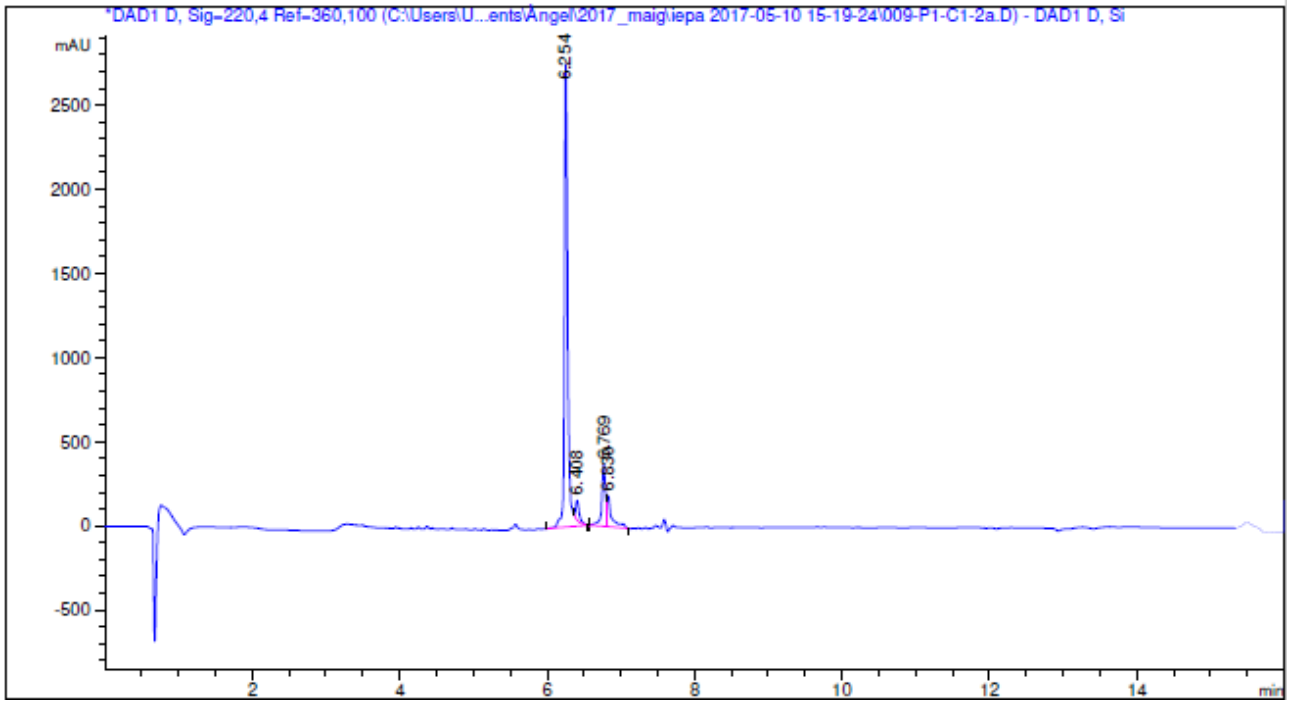

Intens.
+MS, 1.3-1.5min #(77-89)
1519.0511
1520.0547
1521.0562
1522.0539
1250
1000
750
500
250
0
C78H135N17O13, M+nH ,1519.05
1519.0498
1520.0530
1521.0564
1522.0598
2000
1500
1000
500
0
1518
1519
1520
1521
1522
1523
1524
m/z


Intens.
x10^4
+MS, 1.3-1.5min #(77-89)
760.0260
760.5269
761.0289
761.5297
762.0319
C78H135N17O13, M+nH ,1520.06
760.0285
760.5302
761.0318
761.5335
762.0352
m/z

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys(COC_3H_7)-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP473)

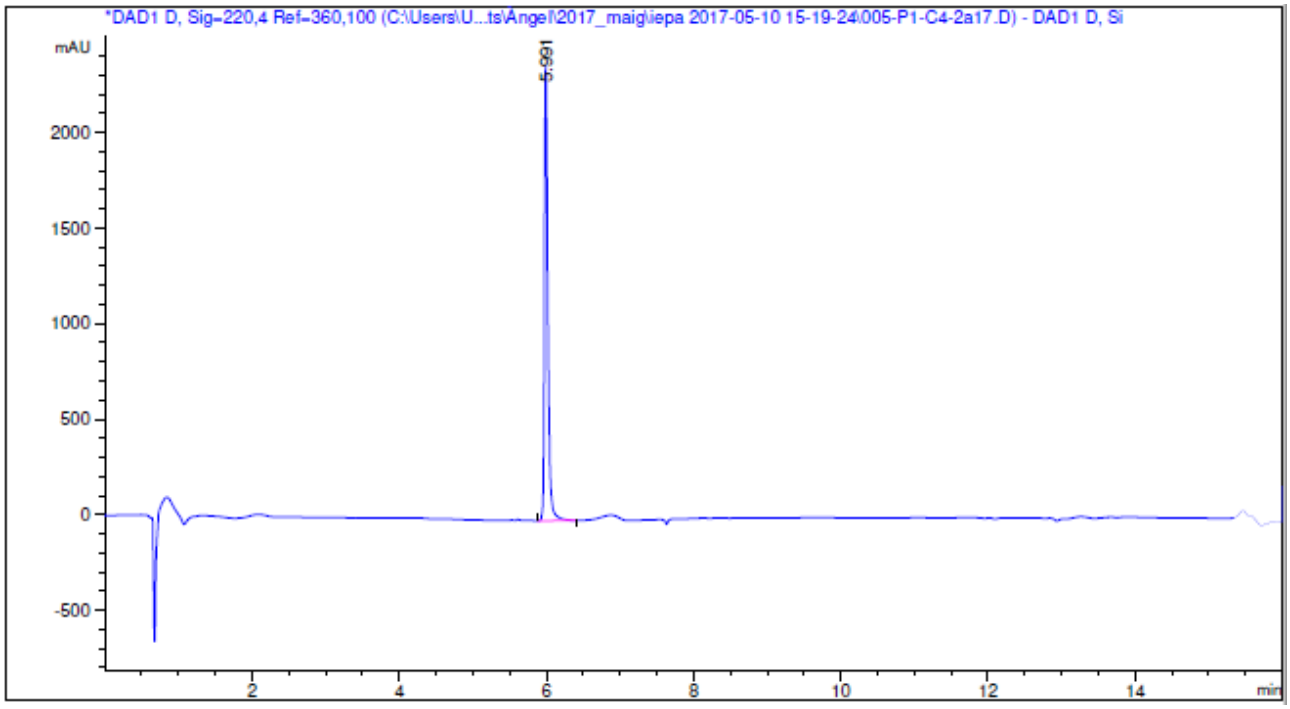


HPLC of crude peptide (λ=220 nm)



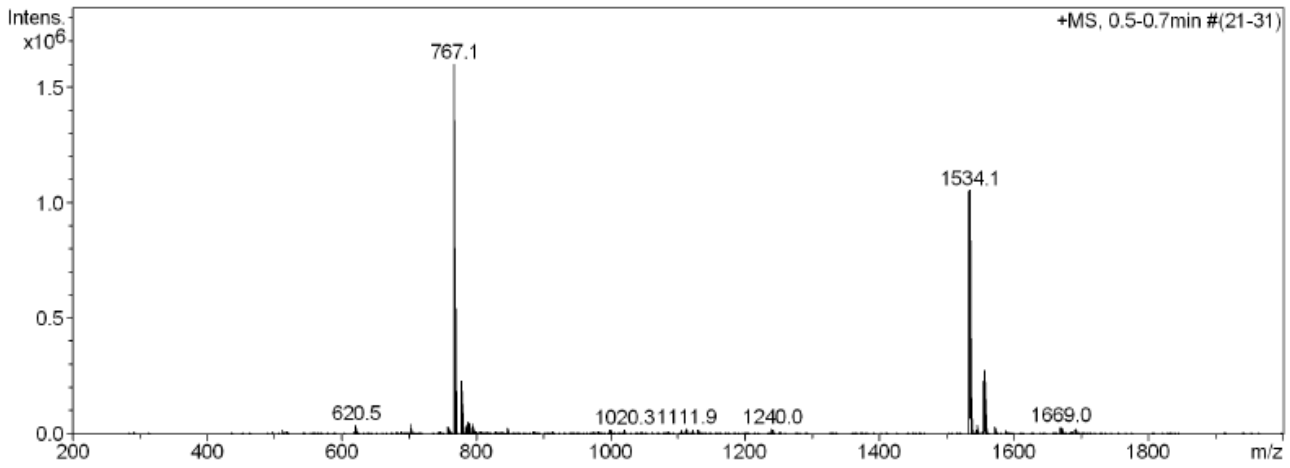
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.254	BV R	0.0464	8589.29297	2749.92847	77.4871
2	6.408	VB E	0.0496	383.71664	115.83309	3.4616
3	6.769	BV	0.0511	1300.70288	369.00027	11.7341
4	6.830	VV R	0.0589	811.08887	182.18036	7.3171

HPLC of purified peptide (λ=220 nm)

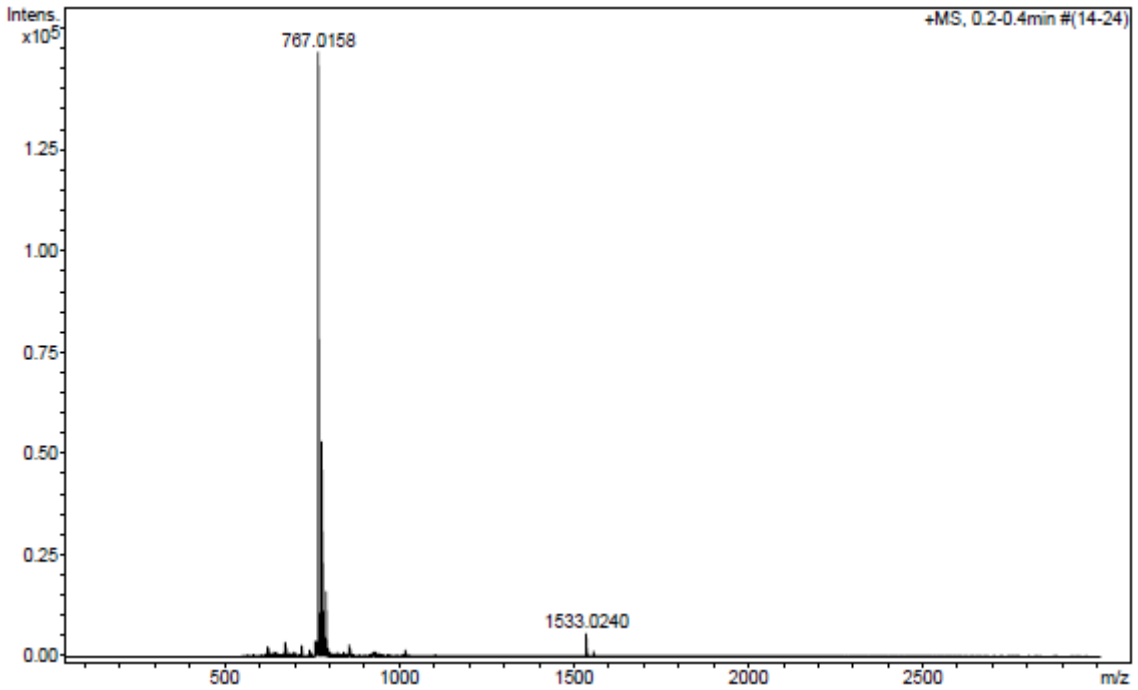


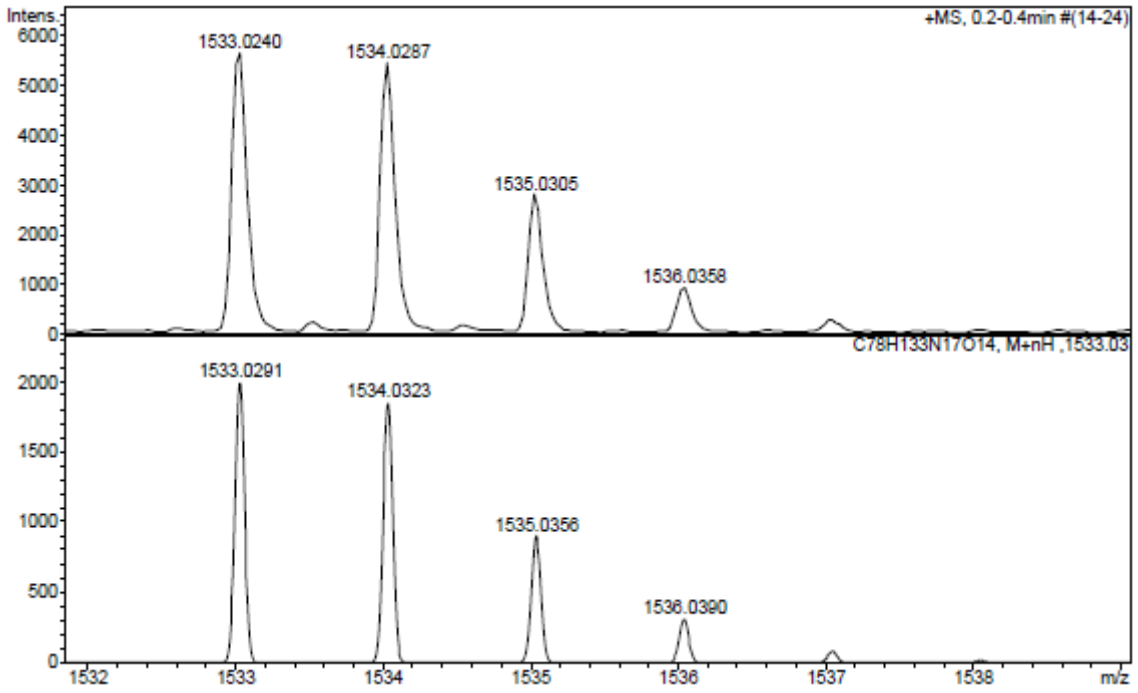
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.991	BB	0.0488	7708.68848	2381.31323	100.0000

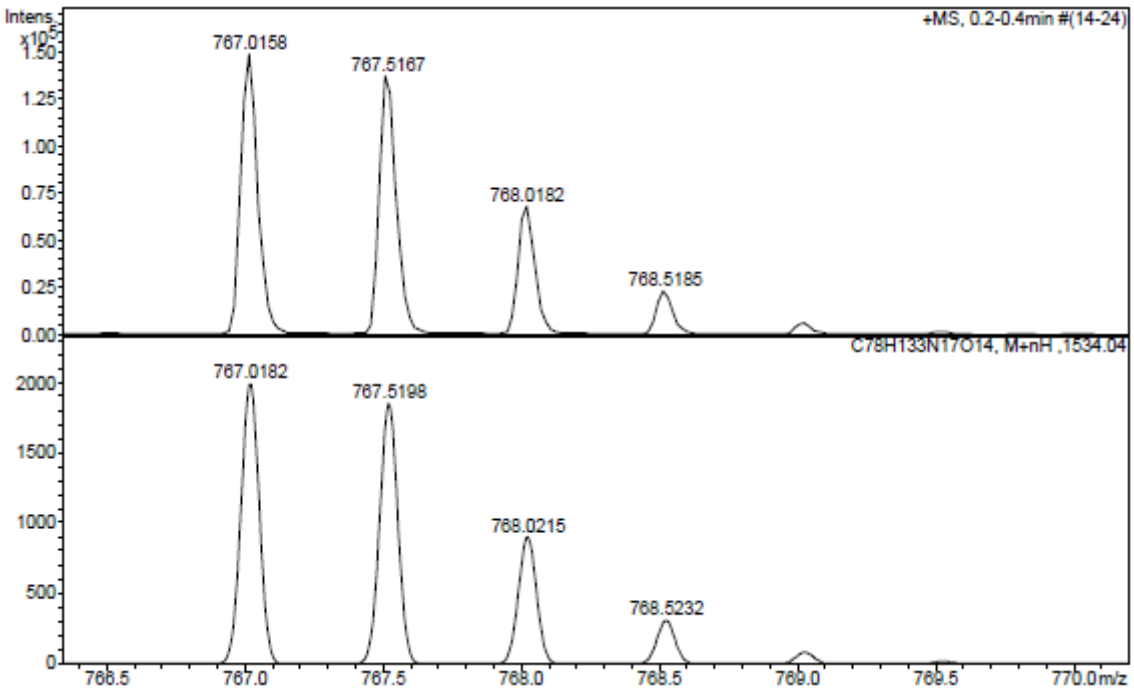
ESI-MS (*m/z*)



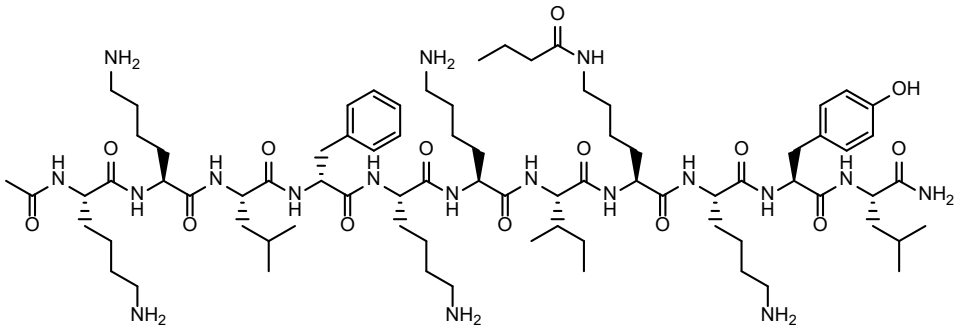
HRMS (*m/z*)


Intens.
x10^5
+MS, 0.2-0.4min #(14-24)
767.0158
1533.0240
1.25
1.00
0.75
0.50
0.25
0.00
500
1000
1500
2000
2500
m/z

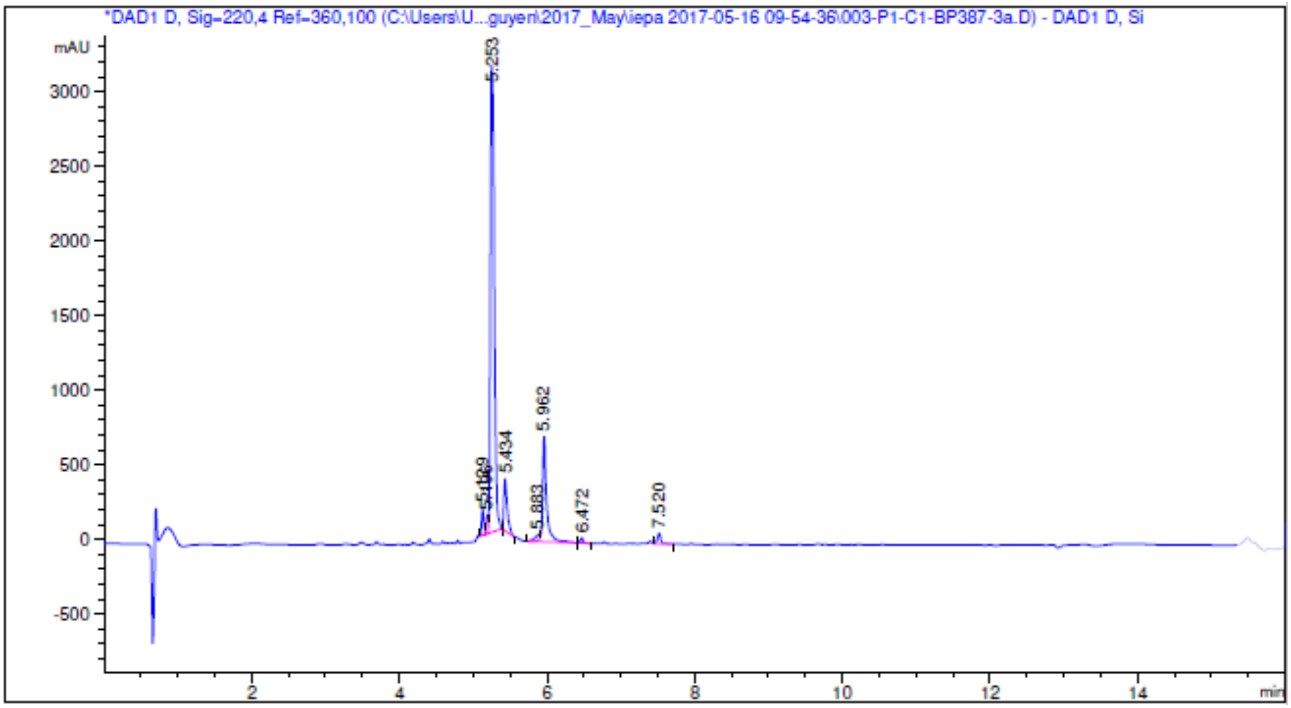

Intens.
6000
+MS, 0.2-0.4min #(14-24)
1533.0240
1534.0287
1535.0305
1536.0358
5000
4000
3000
2000
1000
0
C78H133N17O14, M+nH ,1533.03
1533.0291
1534.0323
1535.0356
1536.0390
2000
1500
1000
500
0
1532
1533
1534
1535
1536
1537
1538
m/z


Intens.
x10^5
1.50
1.25
1.00
0.75
0.50
0.25
0.00
+MS, 0.2-0.4min #(14-24)
767.0158
767.5167
768.0182
768.5185
C78H133N17O14, M+nH ,1534.04
2000
1500
1000
500
0
767.0182
767.5198
768.0215
768.5232
766.5
767.0
767.5
768.0
768.5
769.0
769.5
770.0m/z

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Lys(COC_3H_7)-Lys-Tyr-Leu-NH_2 (BP474)

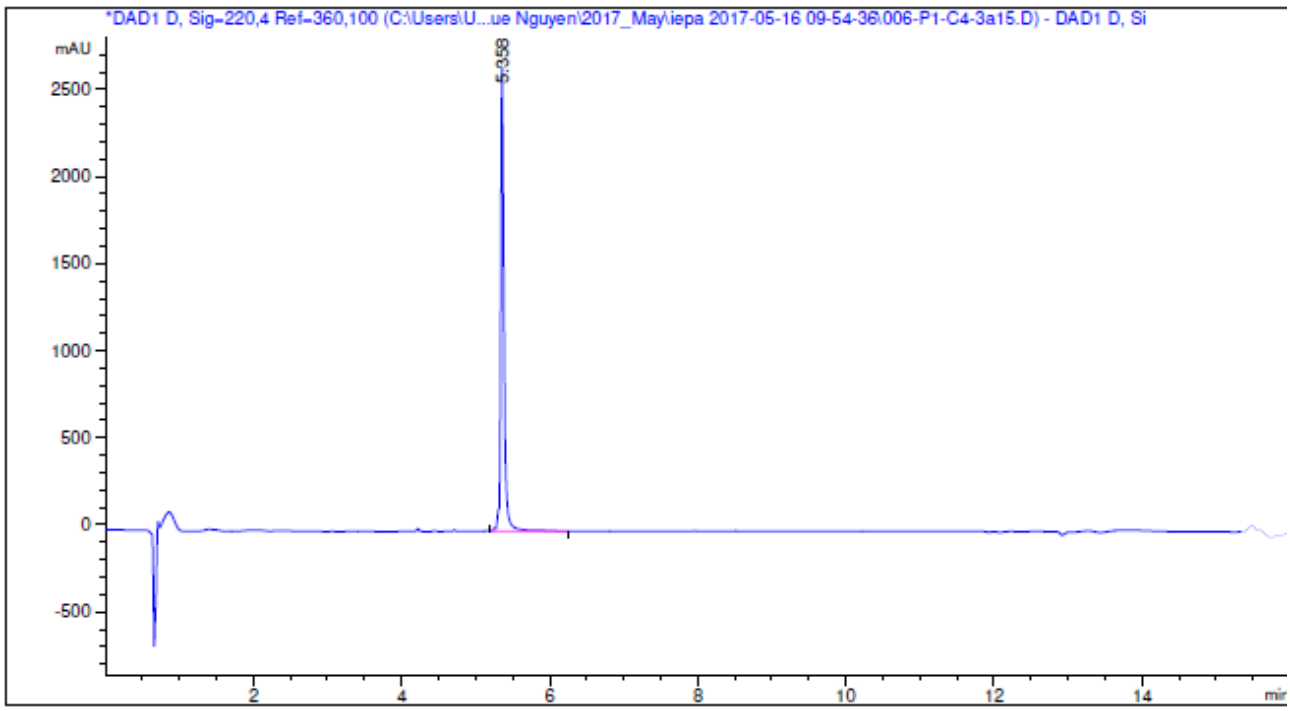


HPLC of crude peptide (λ=220 nm)



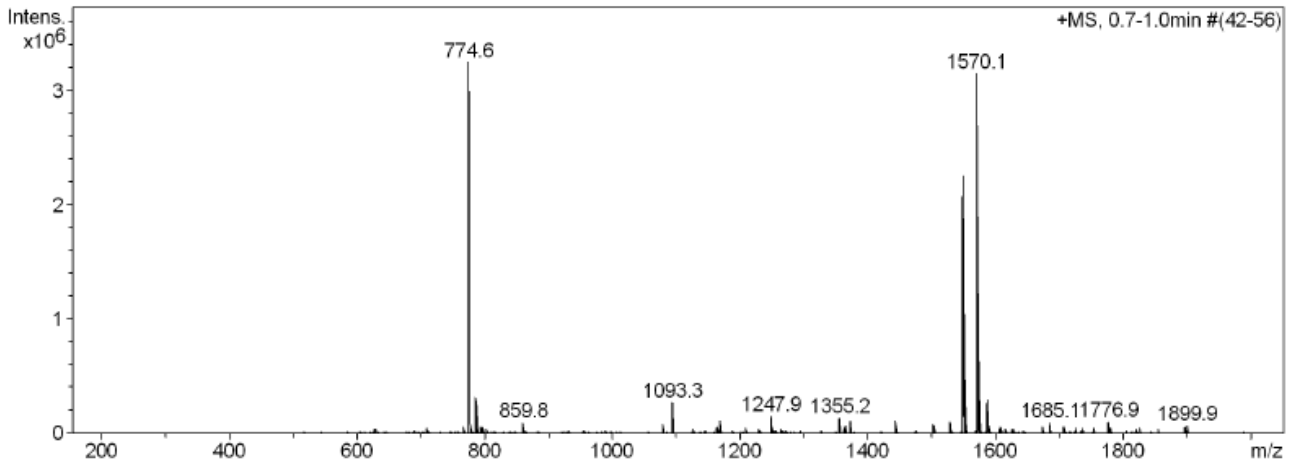
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.129	BV E	0.0323	377.93021	181.34412	2.2820
2	5.196	VV E	0.0268	212.25146	119.26482	1.2816
3	5.253	VB R	0.0595	1.16522e4	3125.37207	70.3588
4	5.434	BB	0.0460	1109.19092	349.34921	6.6976
5	5.883	BV E	0.0659	192.02771	38.04109	1.1595
6	5.962	VV R	0.0532	2679.02954	707.11737	16.1766
7	6.472	BB	0.0410	95.51791	34.79841	0.5768
8	7.520	VB R	0.0507	242.96144	71.34217	1.4671

HPLC of purified peptide (λ=220 nm)

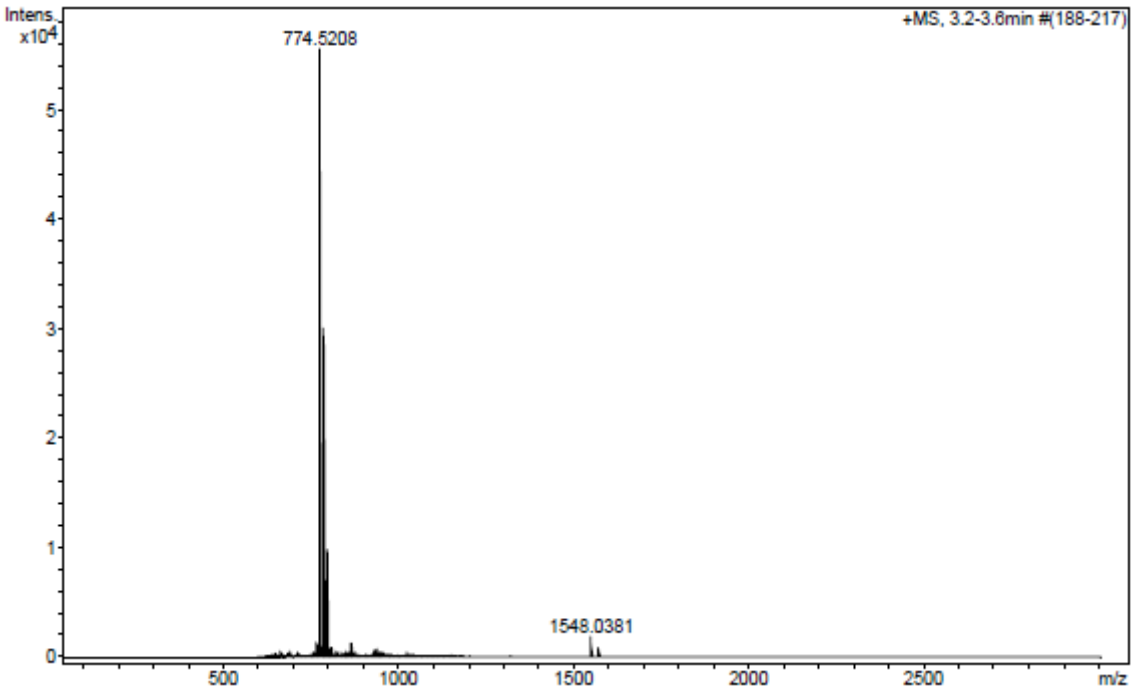


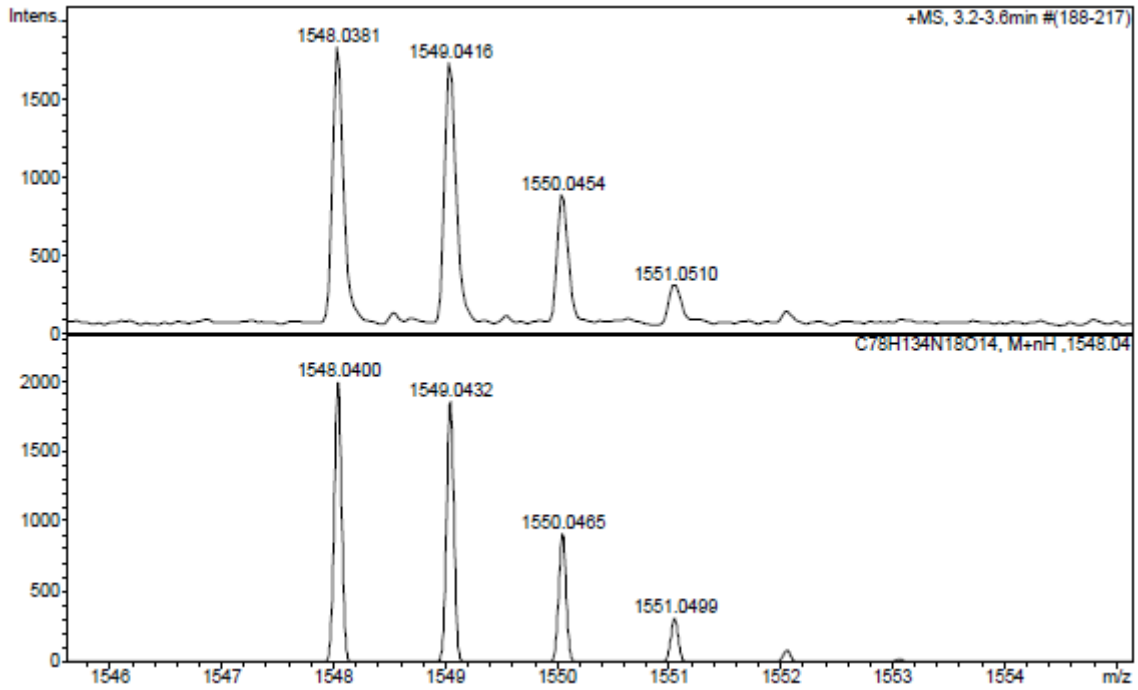
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.358	VB R	0.0460	8253.83496	2673.69556	100.0000

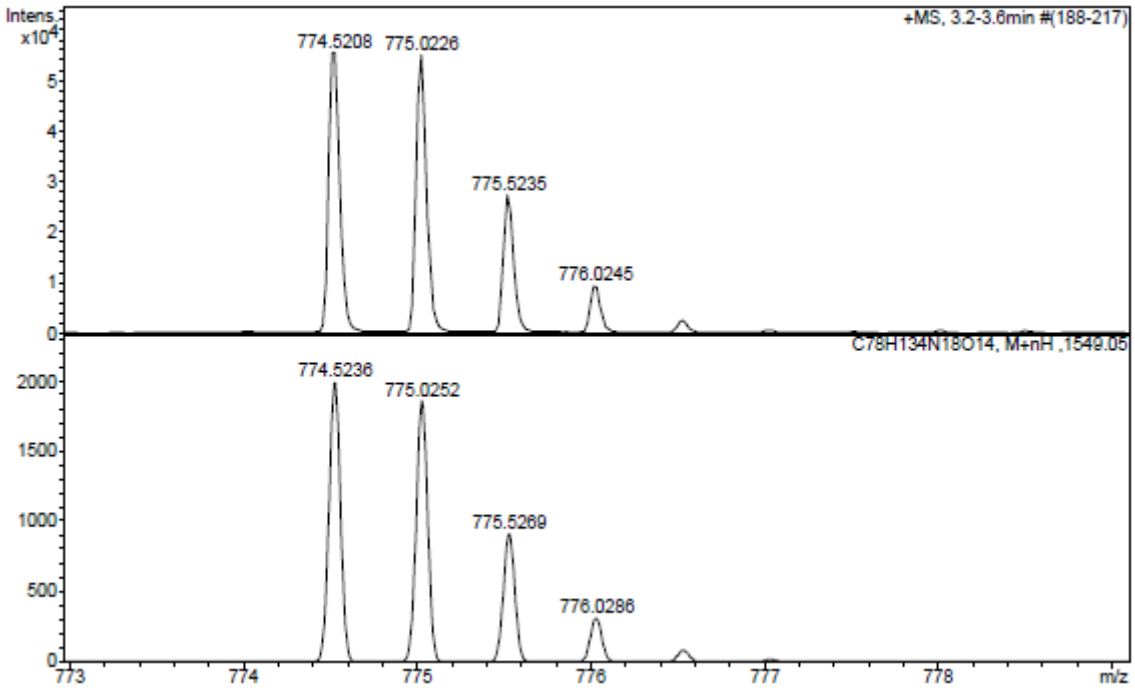
ESI-MS (*m/z*)



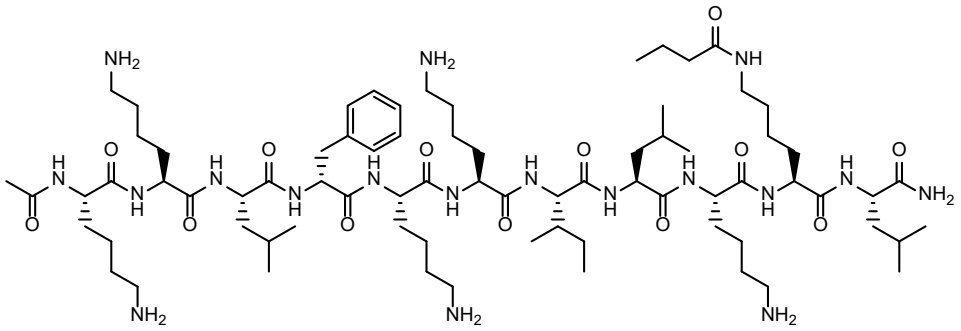
HRMS (*m/z*)


Intens.
x10^4
+MS, 3.2-3.6min #(188-217)
774.5208
1548.0381
m/z

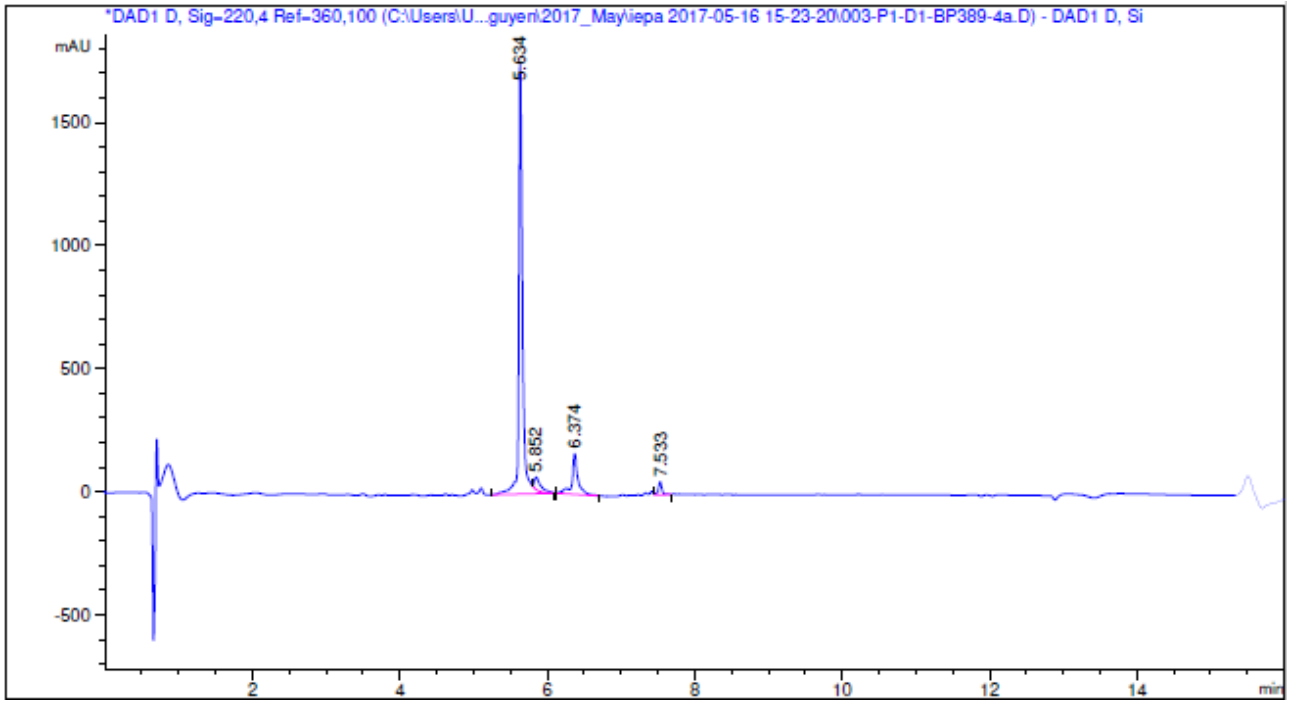

Intens.
+MS, 3.2-3.6min #(188-217)
1548.0381
1549.0416
1550.0454
1551.0510
C78H134N18O14, M+nH ,1548.04
1548.0400
1549.0432
1550.0465
1551.0499
m/z


Intens.
x10^4
+MS, 3.2-3.6min #(188-217)
774.5208
775.0226
775.5235
776.0245
C78H134N18O14, M+nH ,1549.05
774.5236
775.0252
775.5269
776.0286
773
774
775
776
777
778
m/z

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Lys(COC_3H_7)-Leu-NH_2 (BP475)

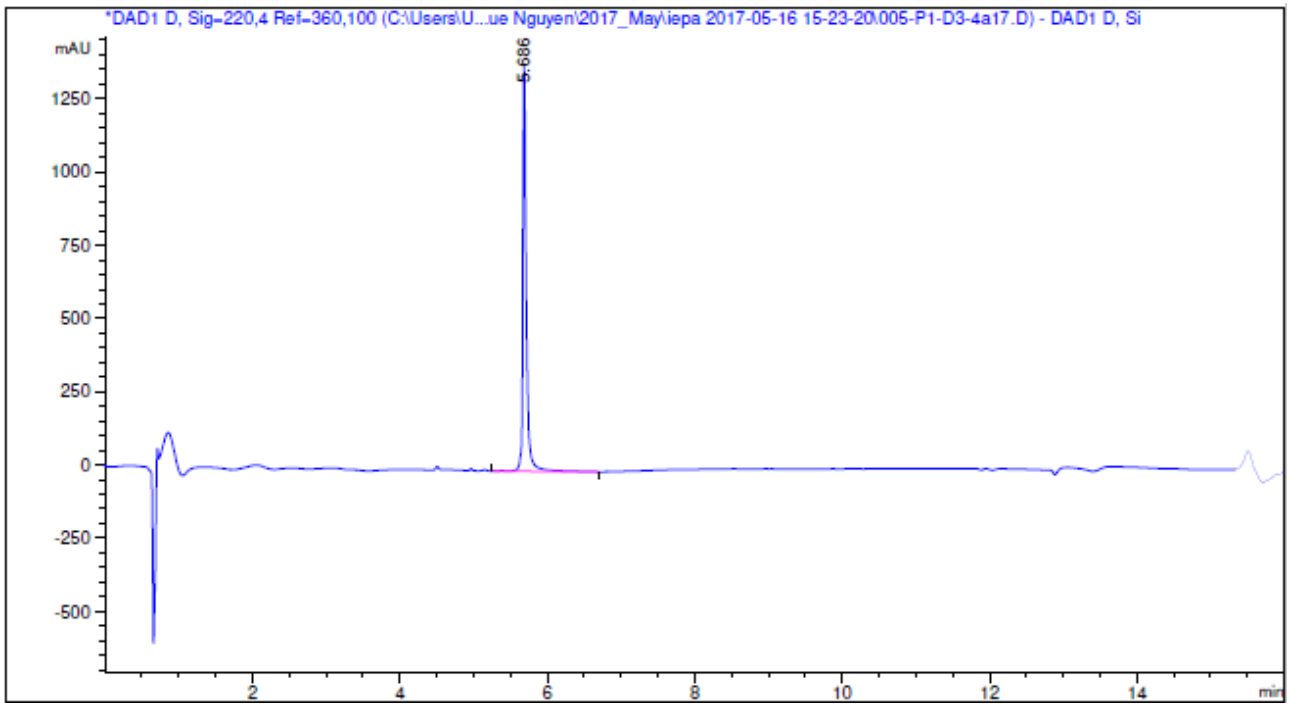


HPLC of crude peptide (λ=220 nm)



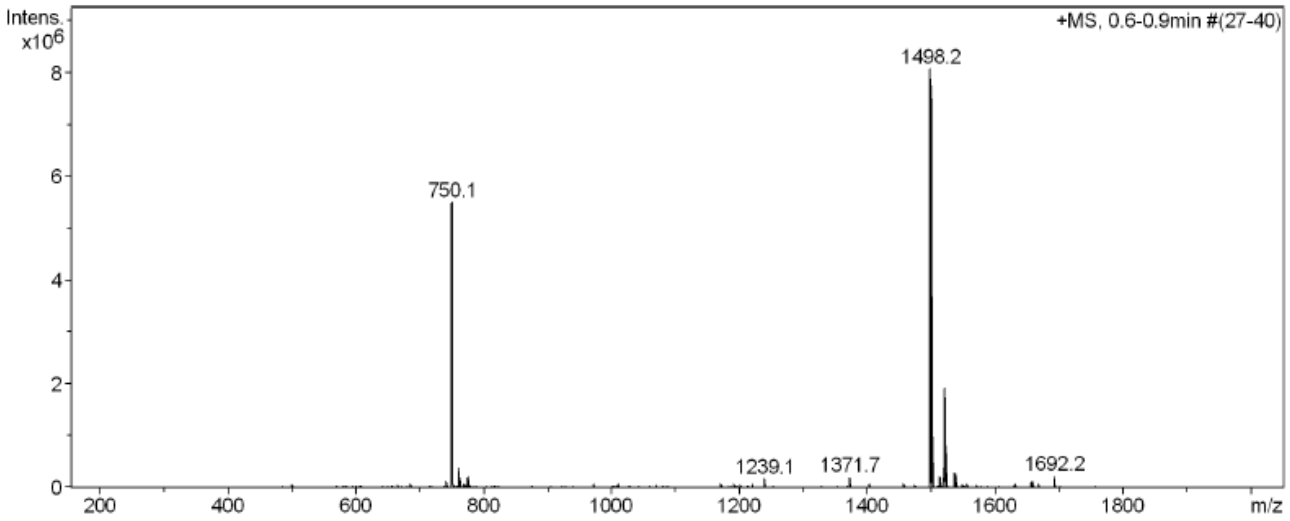
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.634	VV R	0.0514	6206.26611	1748.02429	81.1357
2	5.852	VB E	0.0914	327.03192	50.62853	4.2753
3	6.374	VB R	0.0767	938.12811	166.53392	12.2643
4	7.533	VV R	0.0512	177.81927	52.87458	2.3247

HPLC of purified peptide (λ=220 nm)

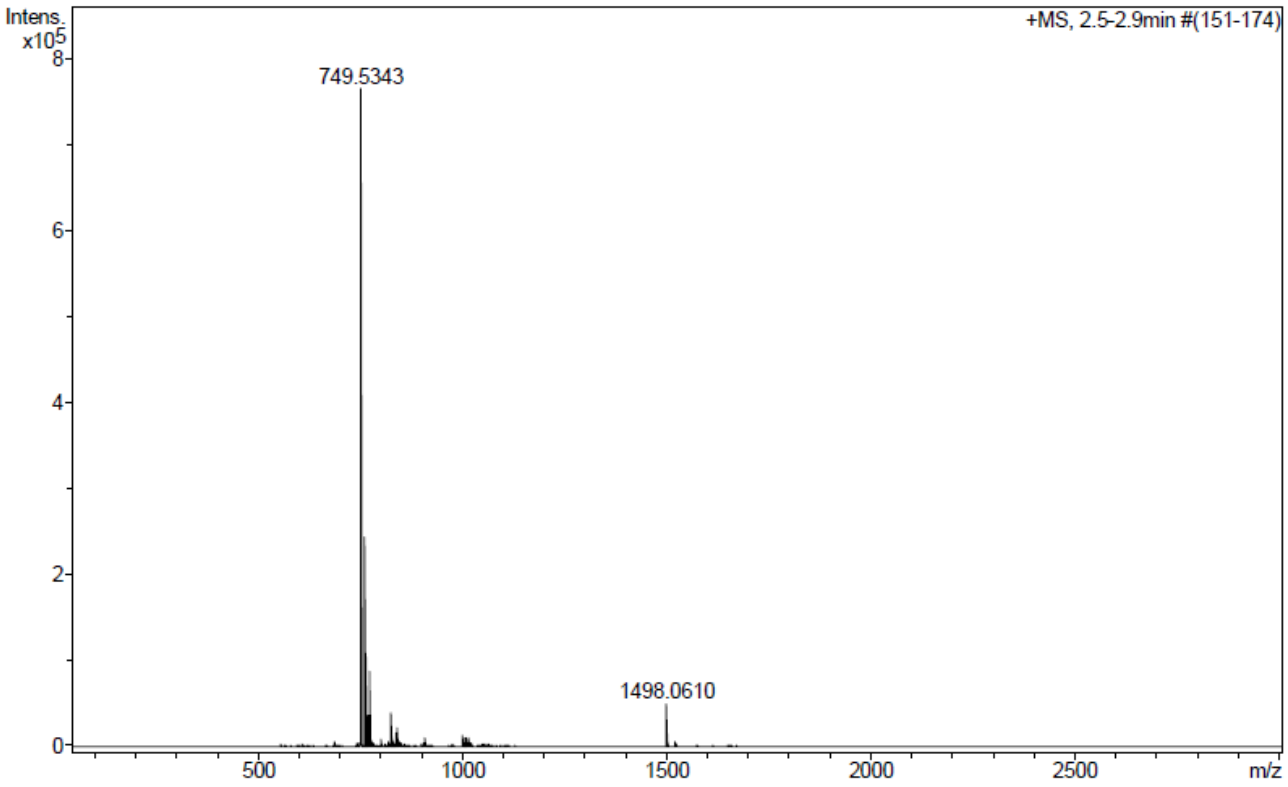


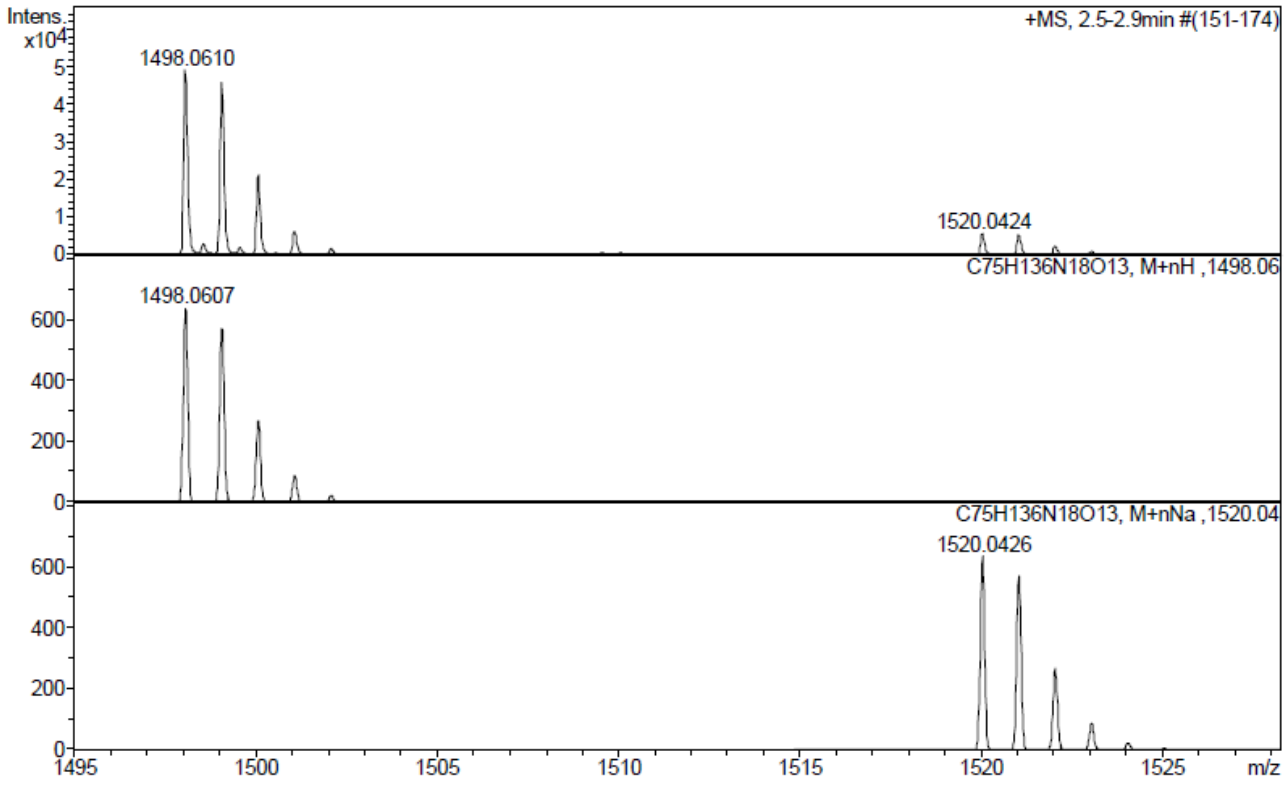
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.686	VB R	0.0485	4586.54346	1388.06421	100.0000

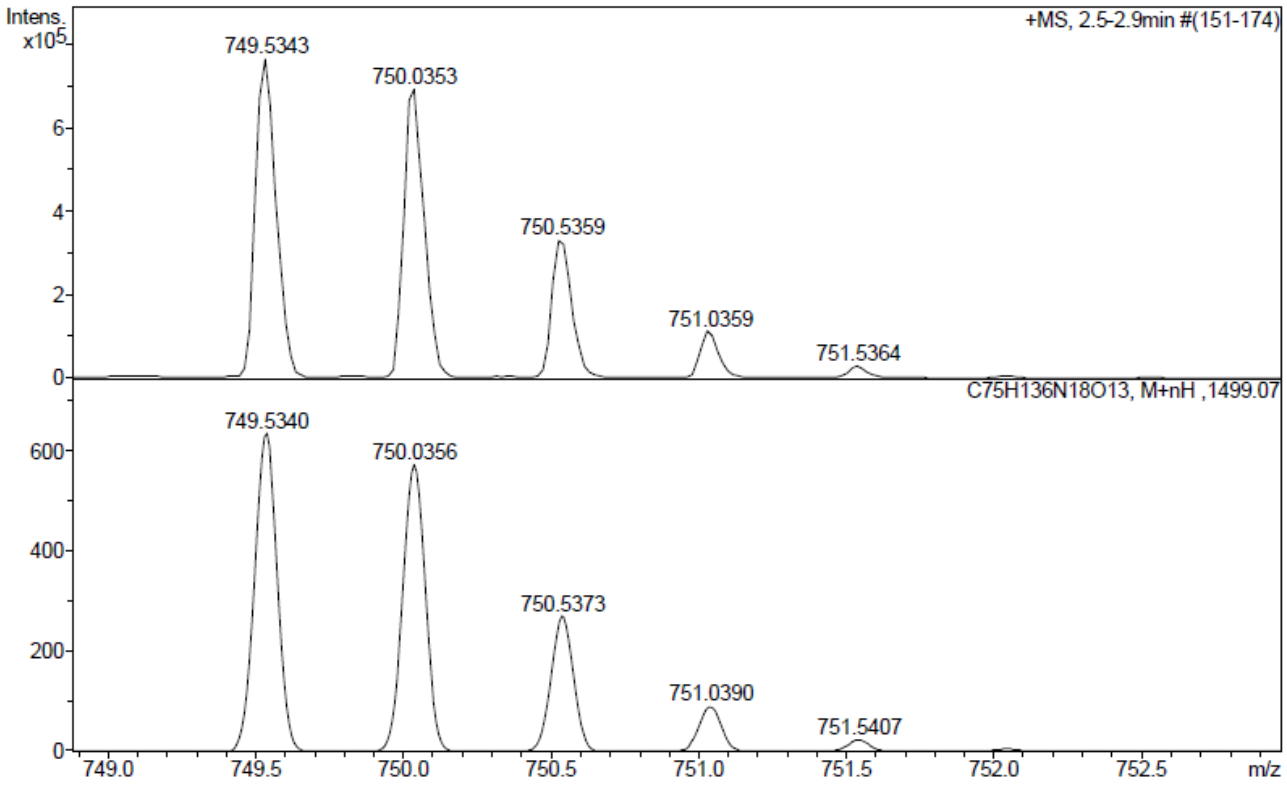
ESI-MS (*m/z*)



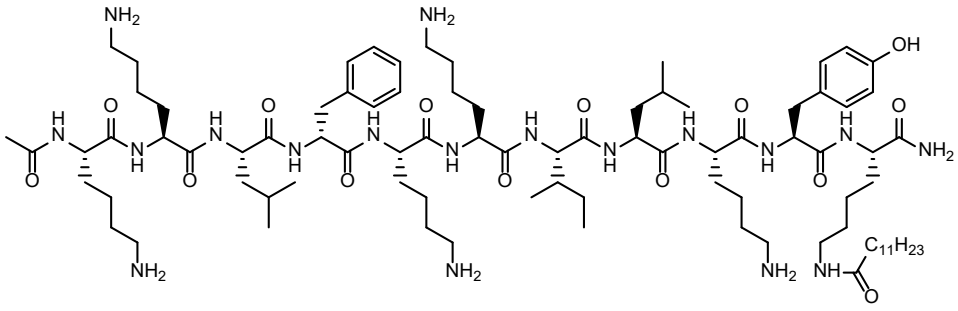
HRMS (*m/z*)


Intens.
x10^5
+MS, 2.5-2.9min #(151-174)
749.5343
1498.0610
m/z

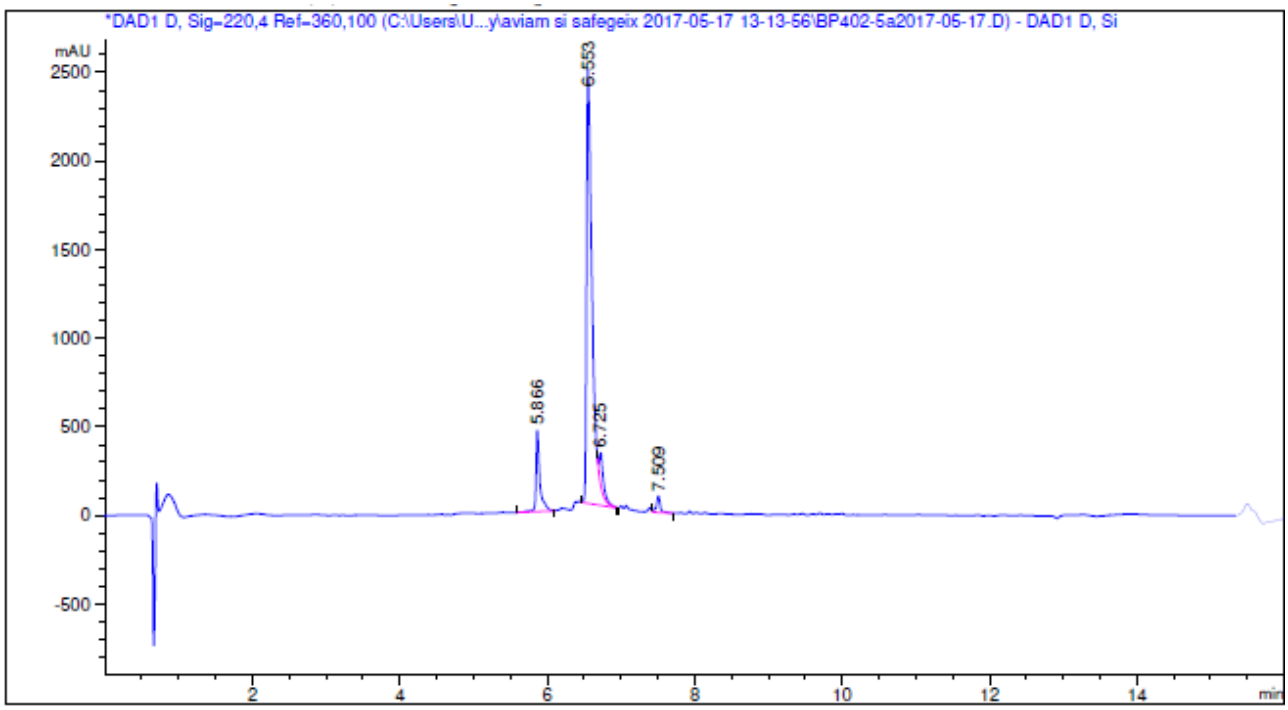

Intens.
x10^4
+MS, 2.5-2.9min #(151-174)
1498.0610
1520.0424
C75H136N18O13, M+nH ,1498.06
1498.0607
C75H136N18O13, M+nNa ,1520.04
1520.0426
m/z


Intens.
x10^5
+MS, 2.5-2.9min #(151-174)
749.5343
750.0353
750.5359
751.0359
751.5364
C75H136N18O13, M+nH ,1499.07
749.5340
750.0356
750.5373
751.0390
751.5407
m/z

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Lys($COC_{11}H_{23}$)-NH_2 (BP476)

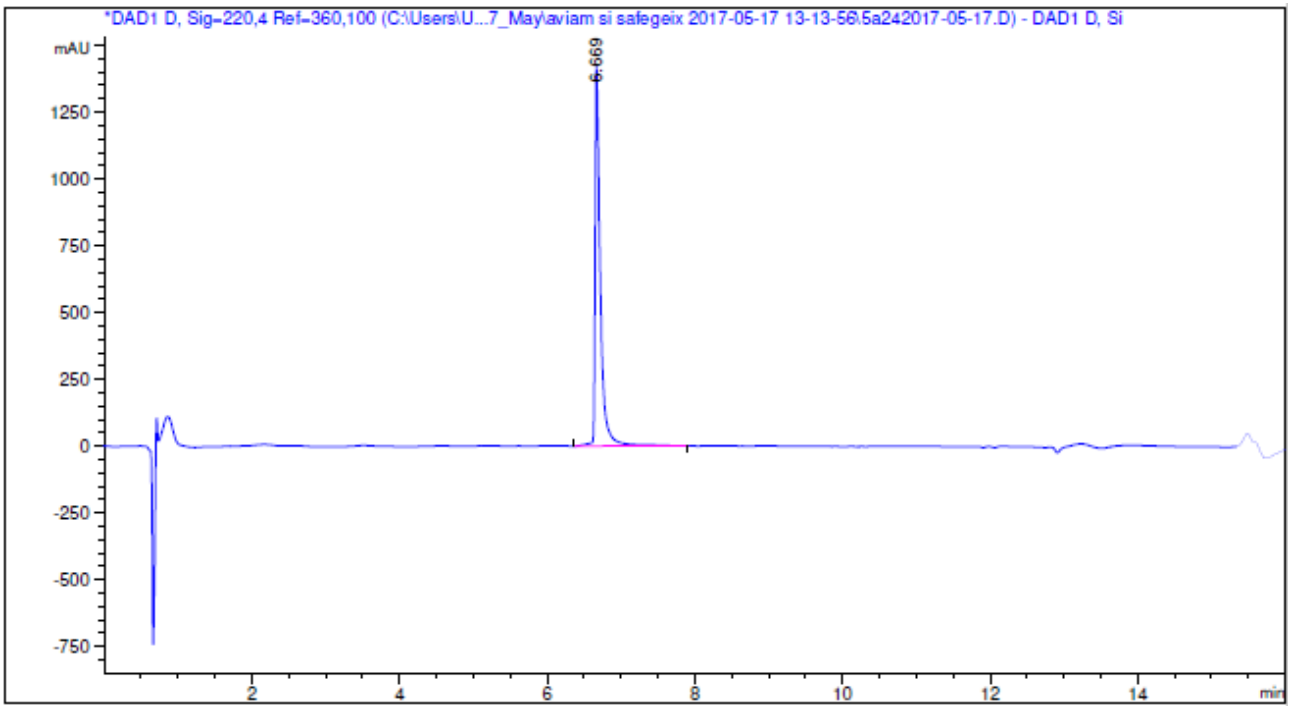


HPLC of crude peptide (λ=220 nm)



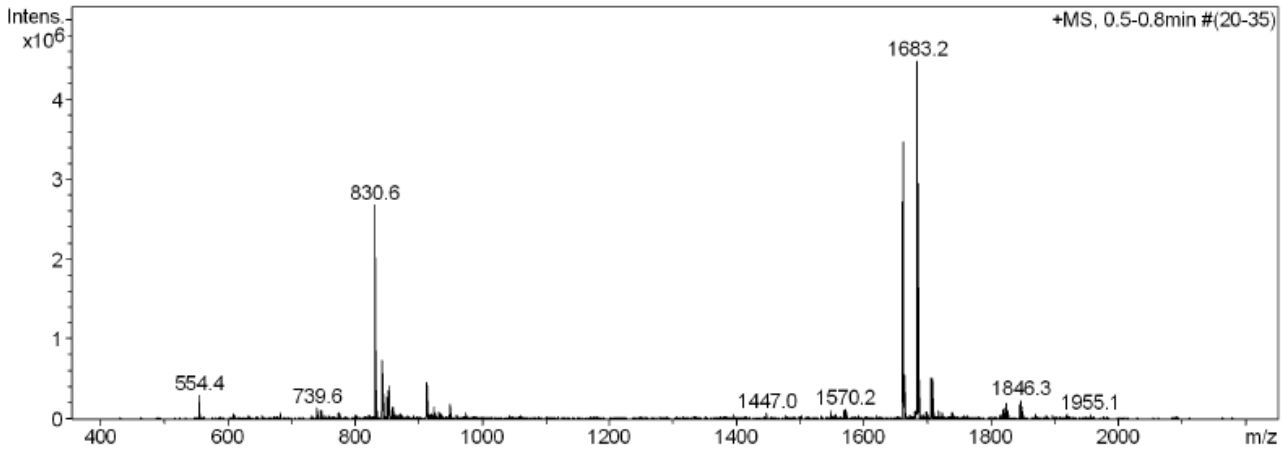
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.866	VB R	0.0513	1669.44141	460.88354	10.5820
2	6.553	VV R	0.0791	1.30655e4	2452.72852	82.8174
3	6.725	VB E	0.0570	698.40192	177.29459	4.4269
4	7.509	VB R	0.0537	342.92166	93.65472	2.1737

HPLC of purified peptide (λ=220 nm)

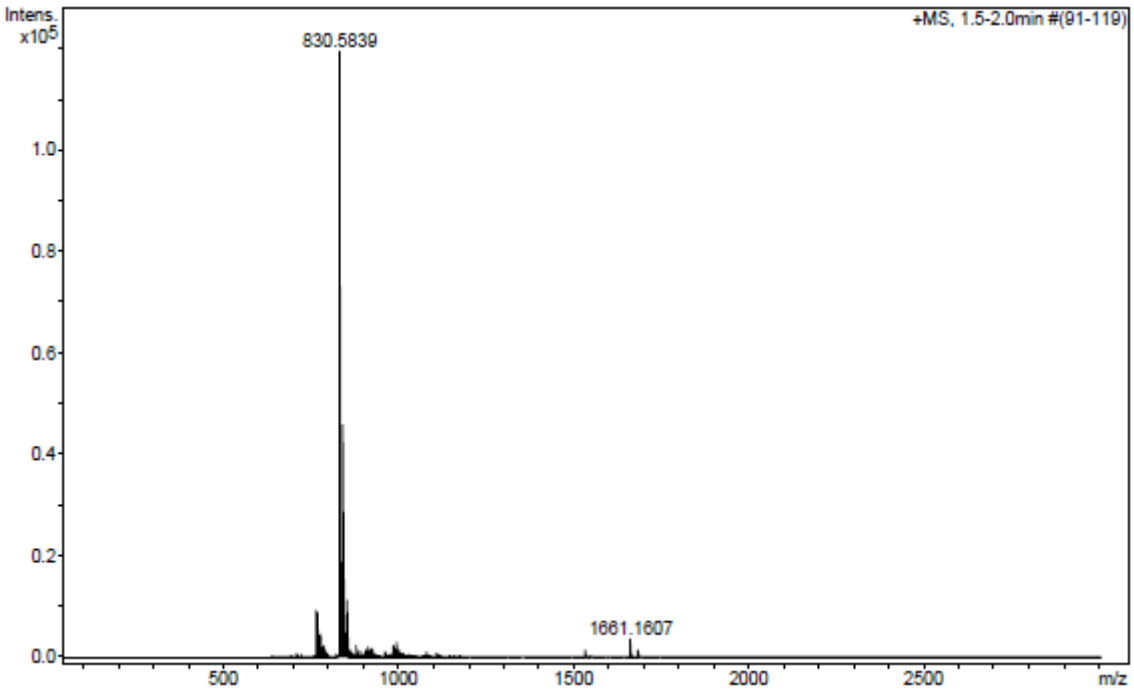


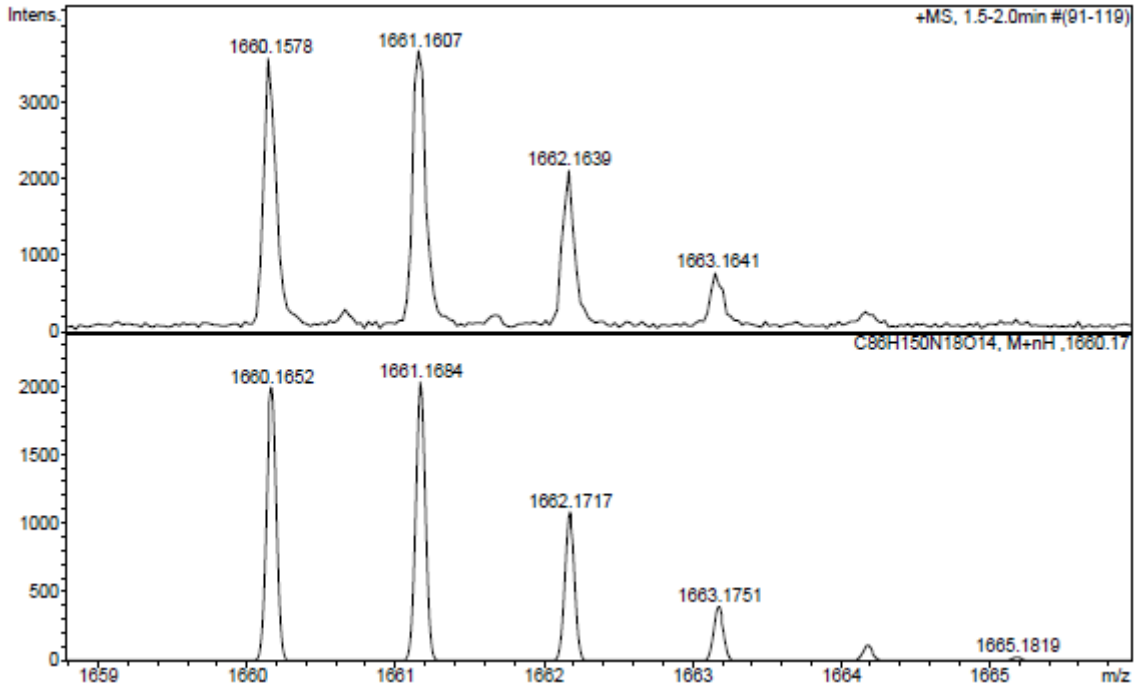
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.669	BB	0.0692	6972.58691	1421.61267	100.0000

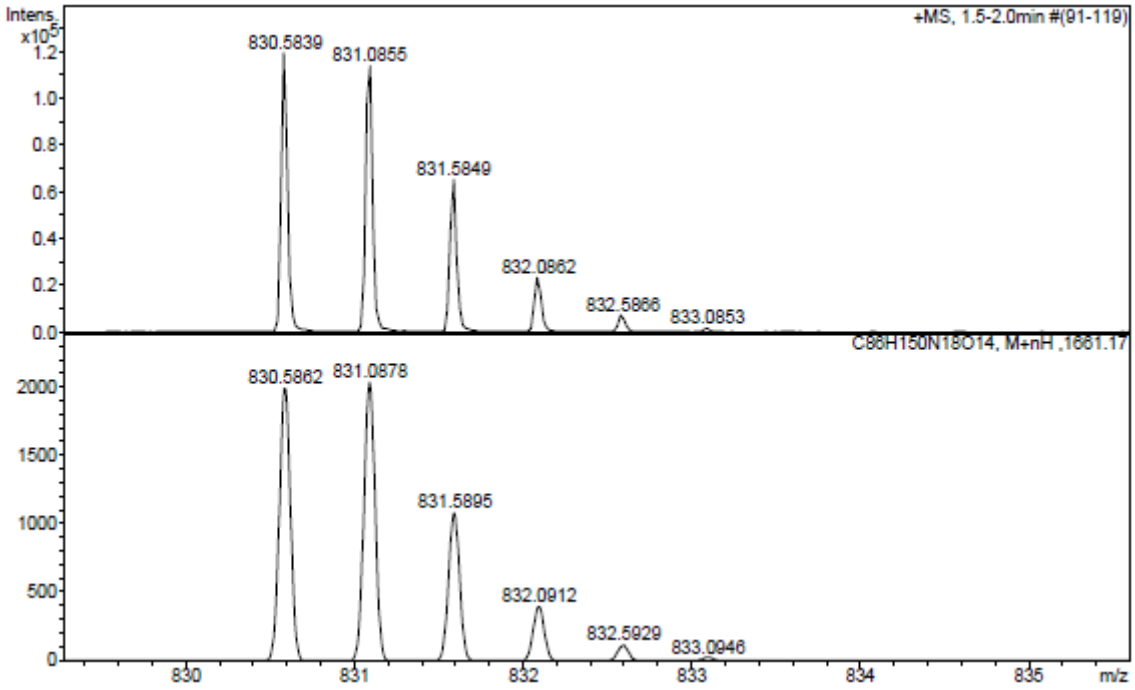
ESI-MS (*m/z*)



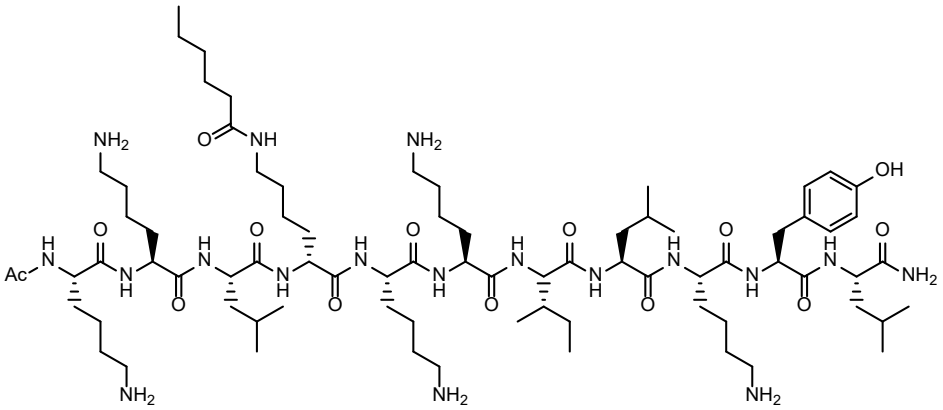
HRMS (*m/z*)


Intens.
x10^5
+MS, 1.5-2.0min #(91-119)
830.5839
1661.1607
1.0
0.8
0.6
0.4
0.2
0.0
500
1000
1500
2000
2500
m/z

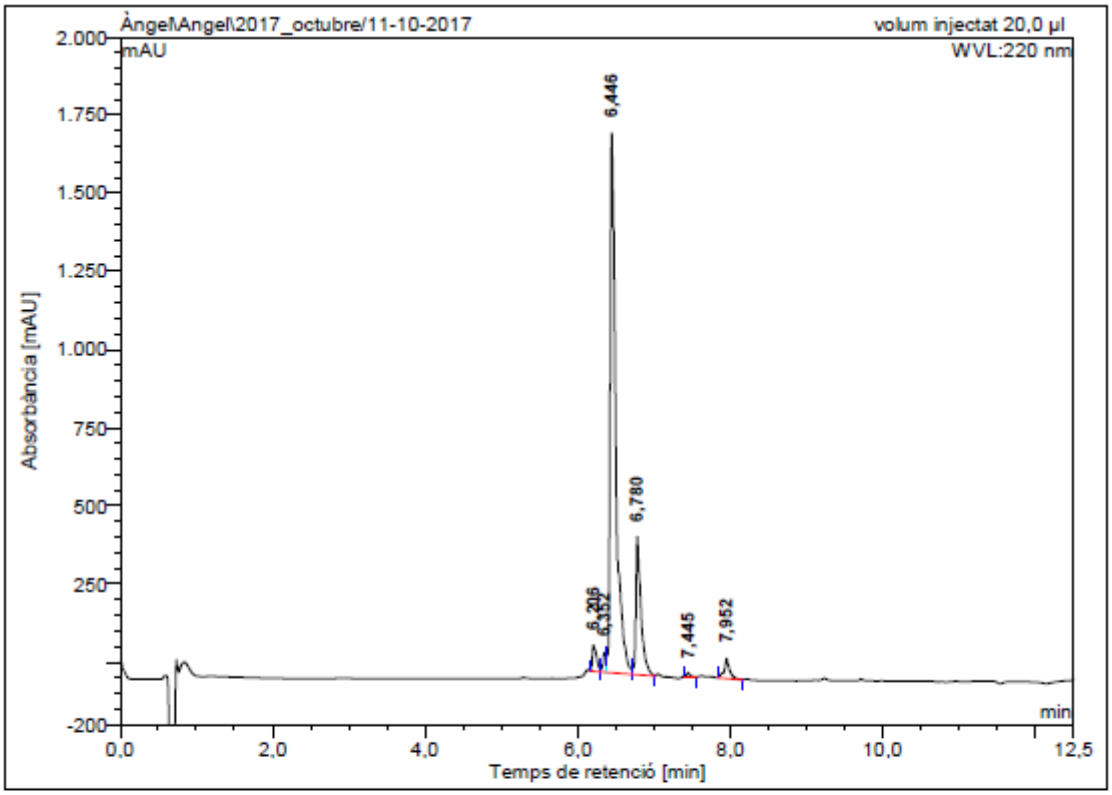

Intens.
+MS, 1.5-2.0min #(91-119)
1660.1578
1661.1607
1662.1639
1663.1641
3000
2000
1000
0
C88H150N18O14, M+nH ,1660.17
1660.1652
1661.1684
1662.1717
1663.1751
1665.1819
2000
1500
1000
500
0
1659
1660
1661
1662
1663
1664
1665
m/z


Intens.
x10^5
1.2
1.0
0.8
0.6
0.4
0.2
0.0
+MS, 1.5-2.0min #(91-119)
830.5839
831.0855
831.5849
832.0862
832.5866
833.0853
C88H150N18O14, M+nH ,1661.17
2000
1500
1000
500
0
830.5862
831.0878
831.5895
832.0912
832.5929
833.0946
830
831
832
833
834
835
m/z

Ac-Lys-Lys-Leu-D-Lys(COC_5H_{11})-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP484)

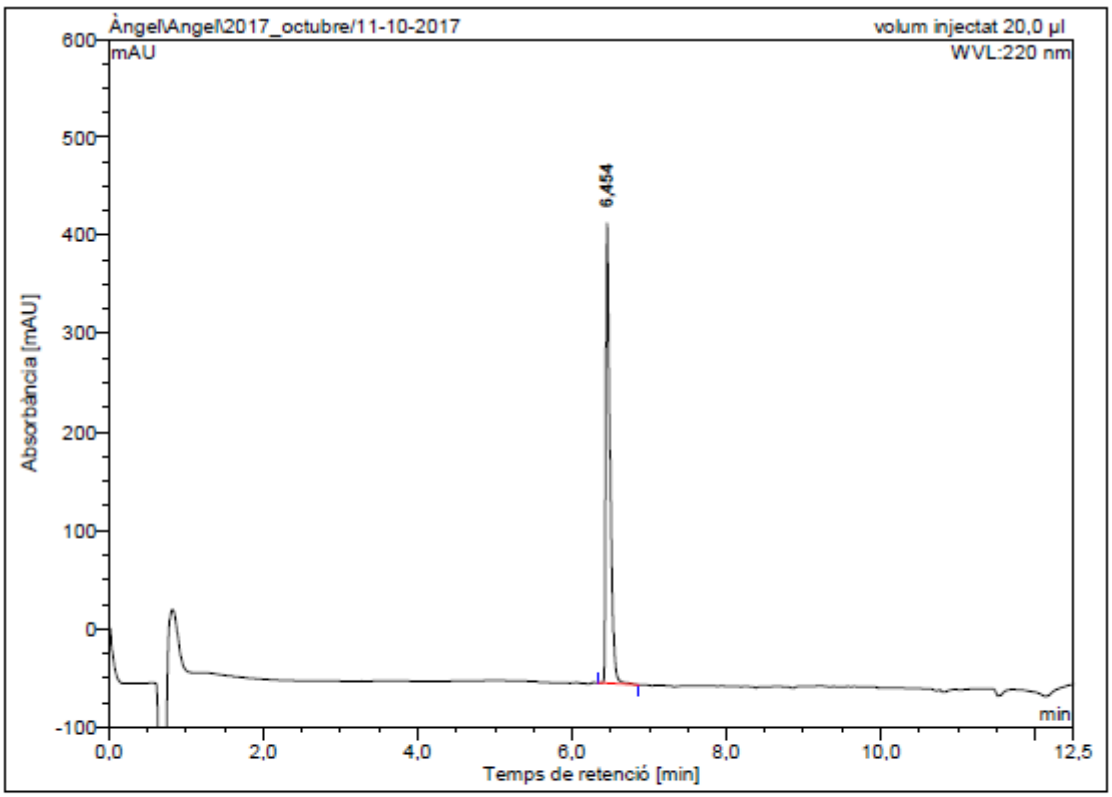


HPLC of crude peptide (λ=220 nm)



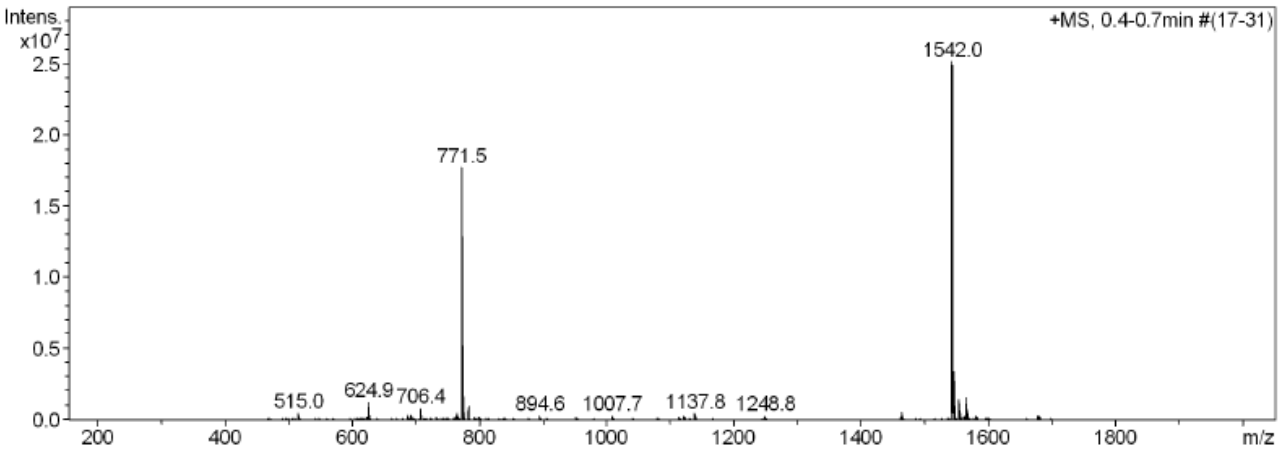
No.	Ret.Time (detected) min	Height mAU	Area mAU*min	Rel.Area %
1	6,21	83,361	5,410	2,75
2	6,35	62,693	3,161	1,61
3	6,45	1725,101	147,916	75,14
4	6,78	441,976	34,458	17,50
5	7,45	13,446	0,734	0,37
6	7,95	63,681	5,177	2,63
Total:		2390,257	196,857	100,00

HPLC of purified peptide (λ=220 nm)

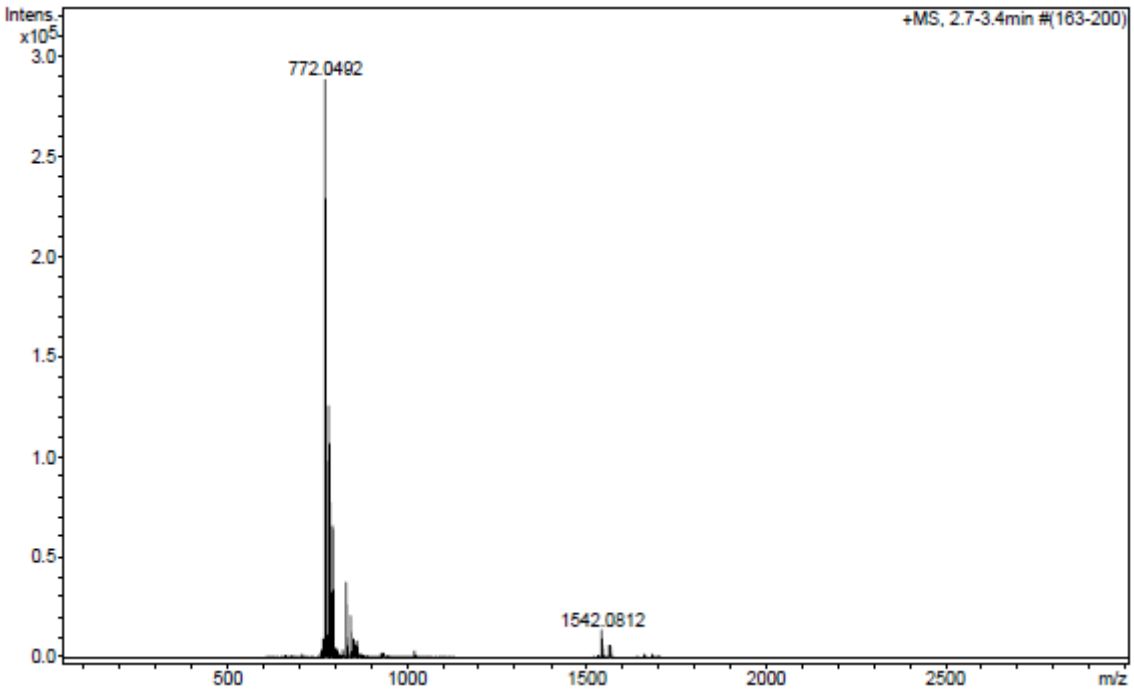


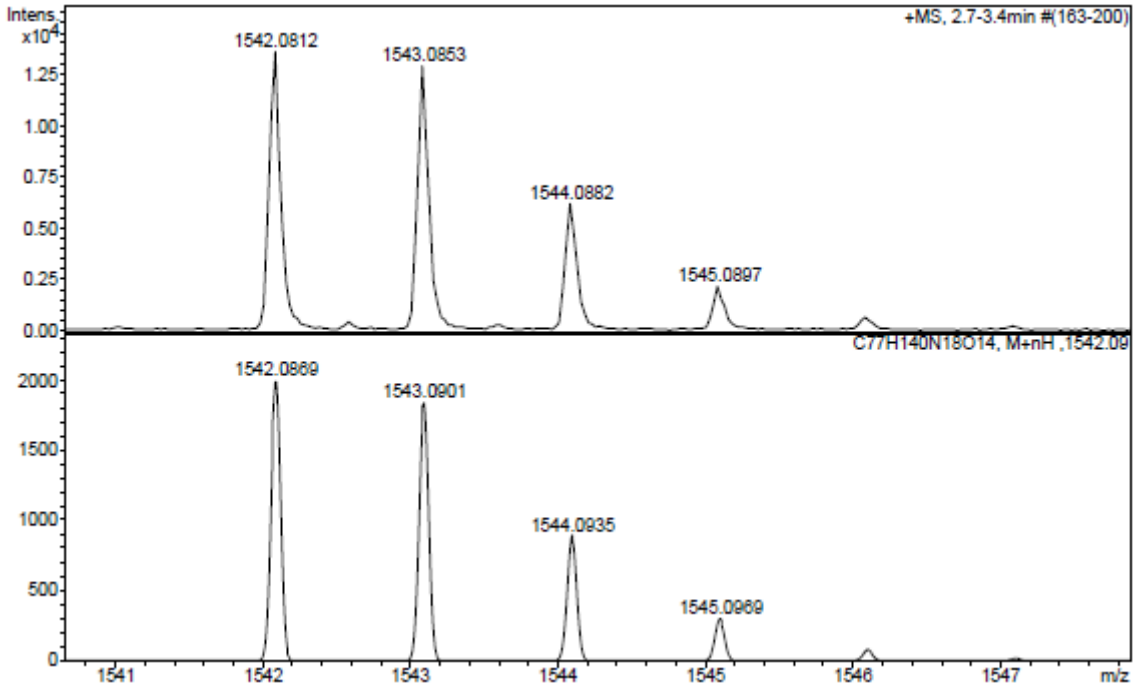
No.	Ret.Time (detected) min	Height mAU	Area mAU*min	Rel.Area %
1	6,45	467,768	30,006	100,00
Total:		467,768	30,006	100,00

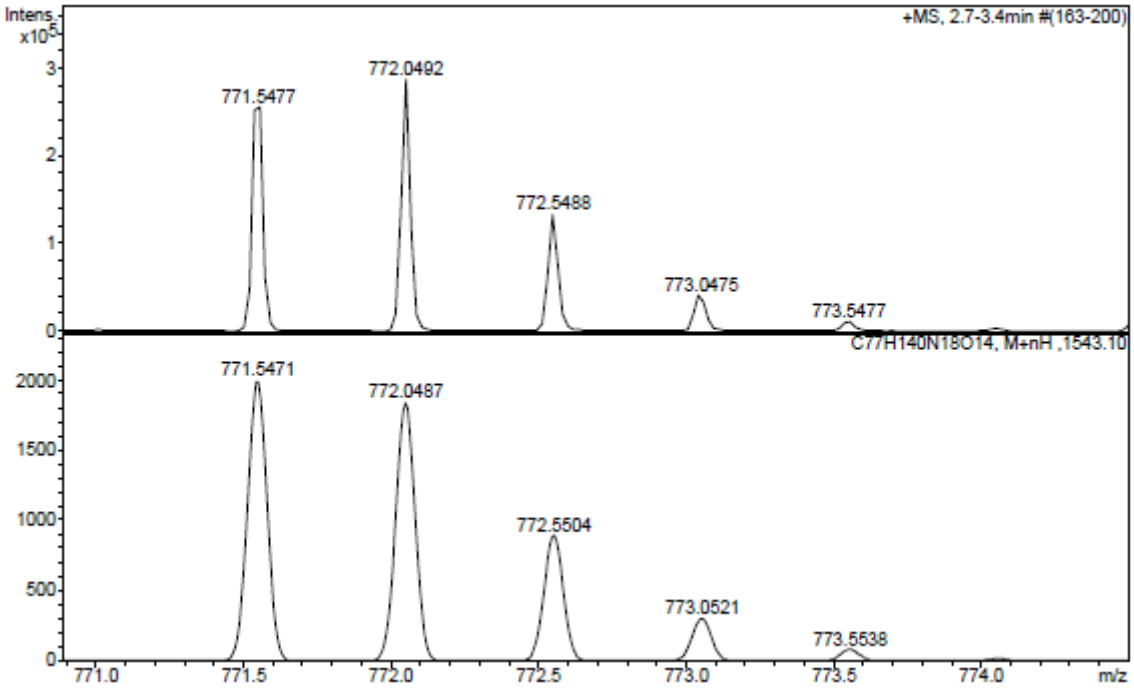
ESI-MS (*m/z*)



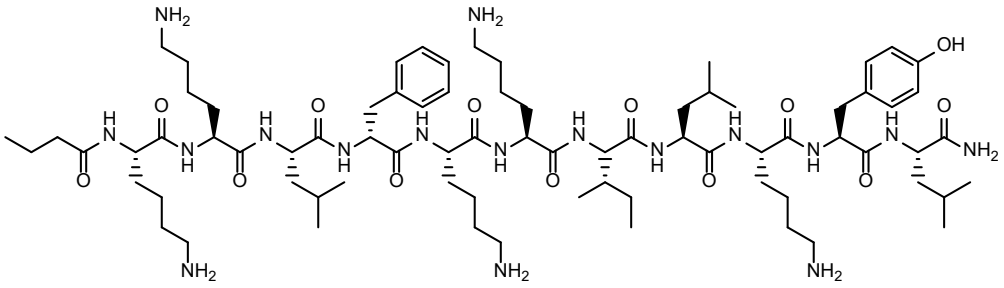
HRMS (*m/z*)


Intens.
x10^5
+MS, 2.7-3.4min #(163-200)
772.0492
1542.0812
m/z

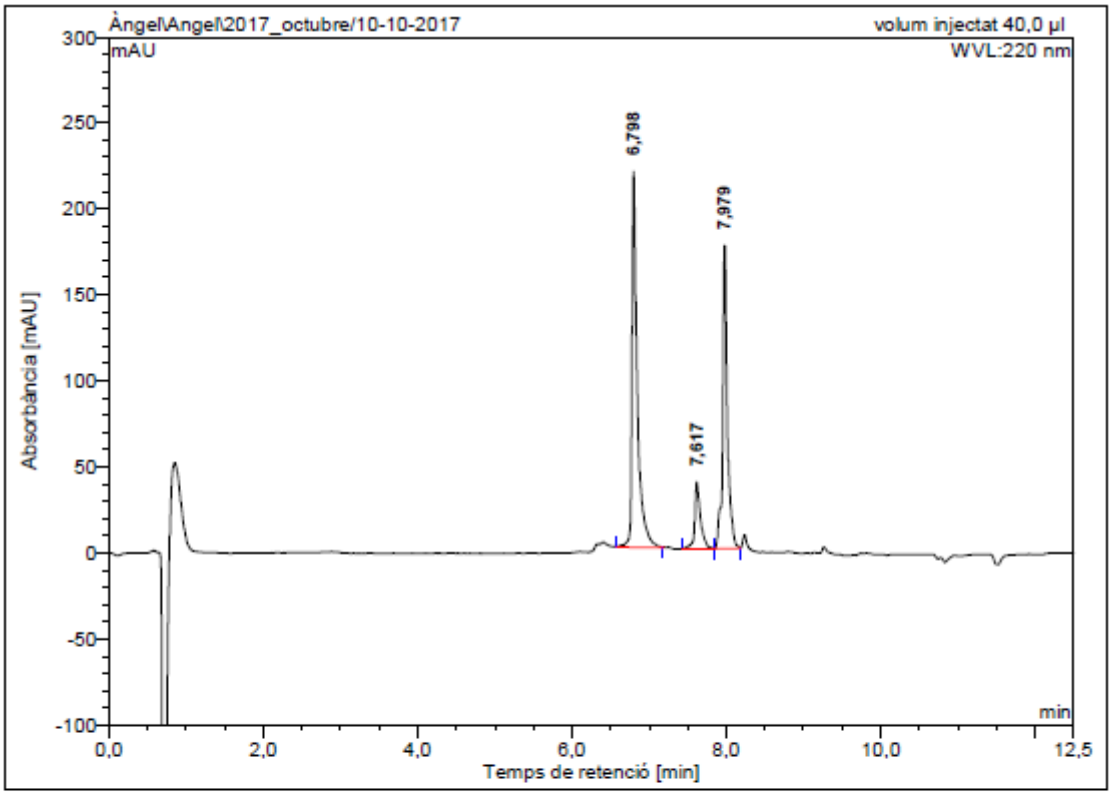

Intens.
x10^4
+MS, 2.7-3.4min #(163-200)
1542.0812
1543.0853
1544.0882
1545.0897
C77H140N18O14, M+nH ,1542.09
1542.0869
1543.0901
1544.0935
1545.0969
m/z


Intens.
x10^5
+MS, 2.7-3.4min #(163-200)
771.5477
772.0492
772.5488
773.0475
773.5477
C77H140N18O14, M+nH ,1543.10
771.5471
772.0487
772.5504
773.0521
773.5538
m/z

C_3H_7CO-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP485)

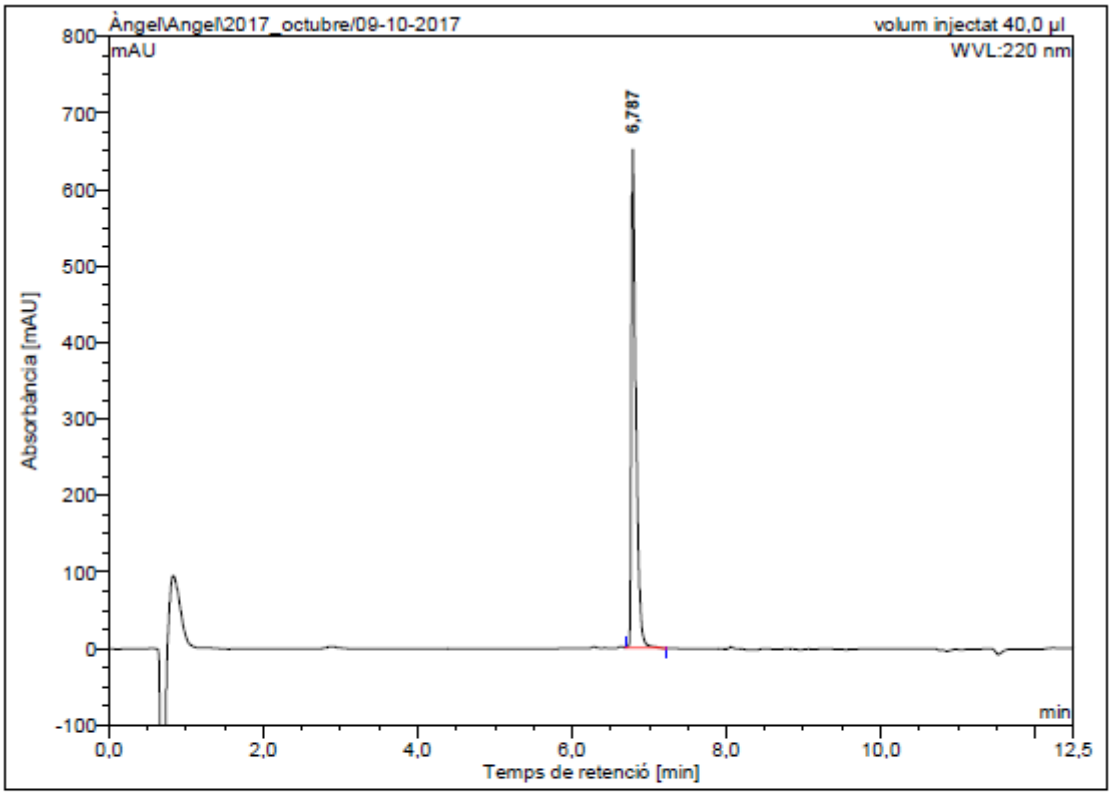


HPLC of crude peptide (λ=220 nm)



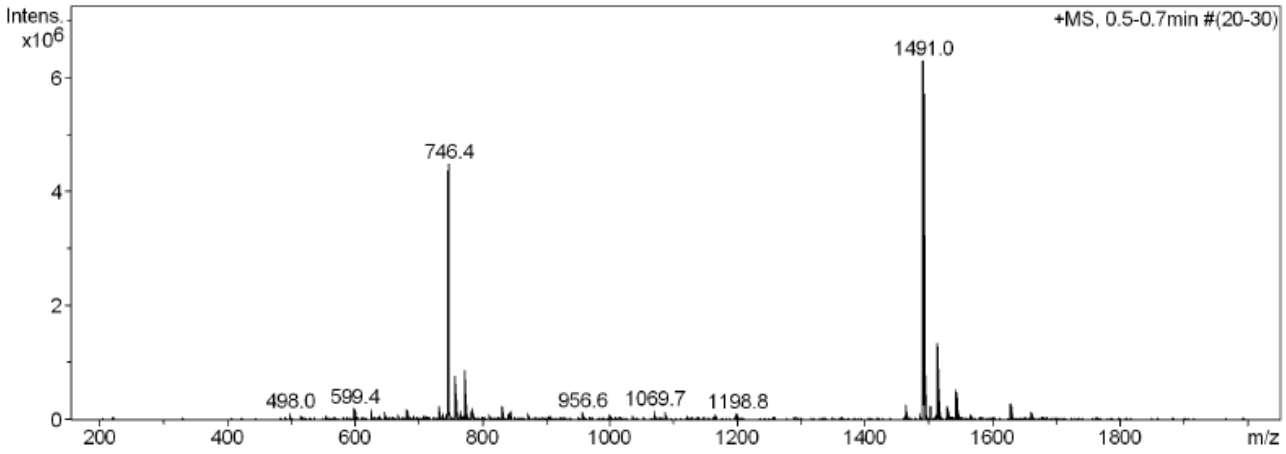
No.	Ret.Time (detected) min	Height mAU	Area mAU*min	Rel.Area %
1	6,80	218,320	17,258	52,25
2	7,62	38,563	3,368	10,20
3	7,98	176,249	12,401	37,55
Total:		433,132	33,026	100,00

HPLC of purified peptide (λ=220 nm)

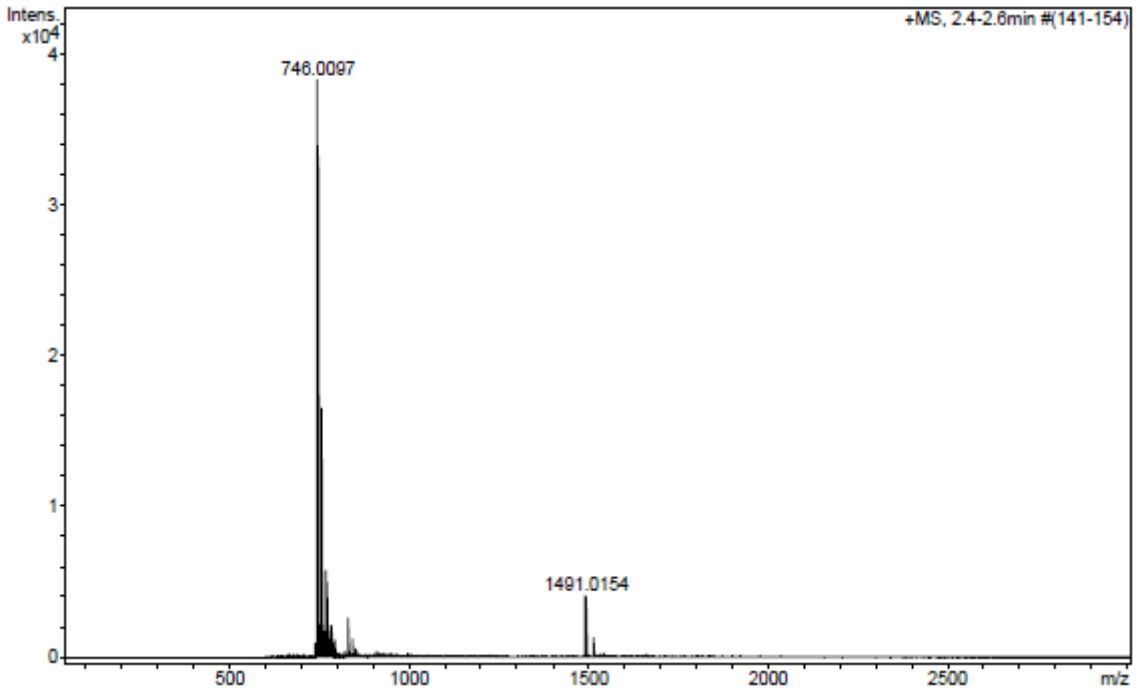


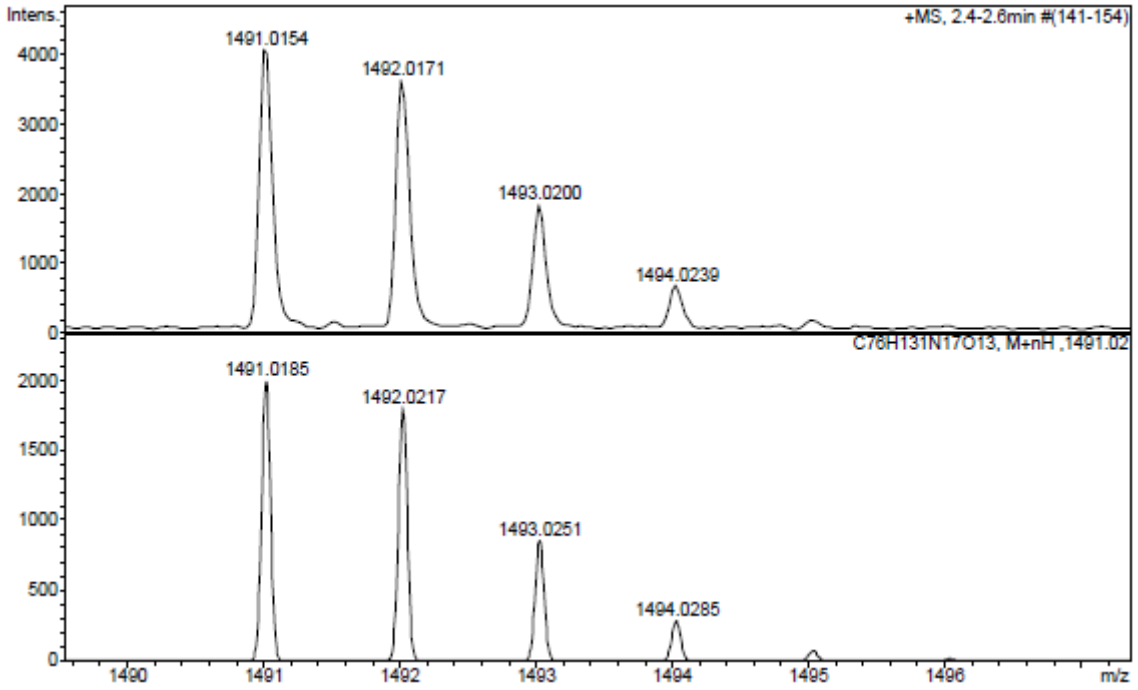
No.	Ret.Time (detected) min	Height mAU	Area mAU*min	Rel.Area %
1	6,79	651,352	44,377	100,00
Total:		651,352	44,377	100,00

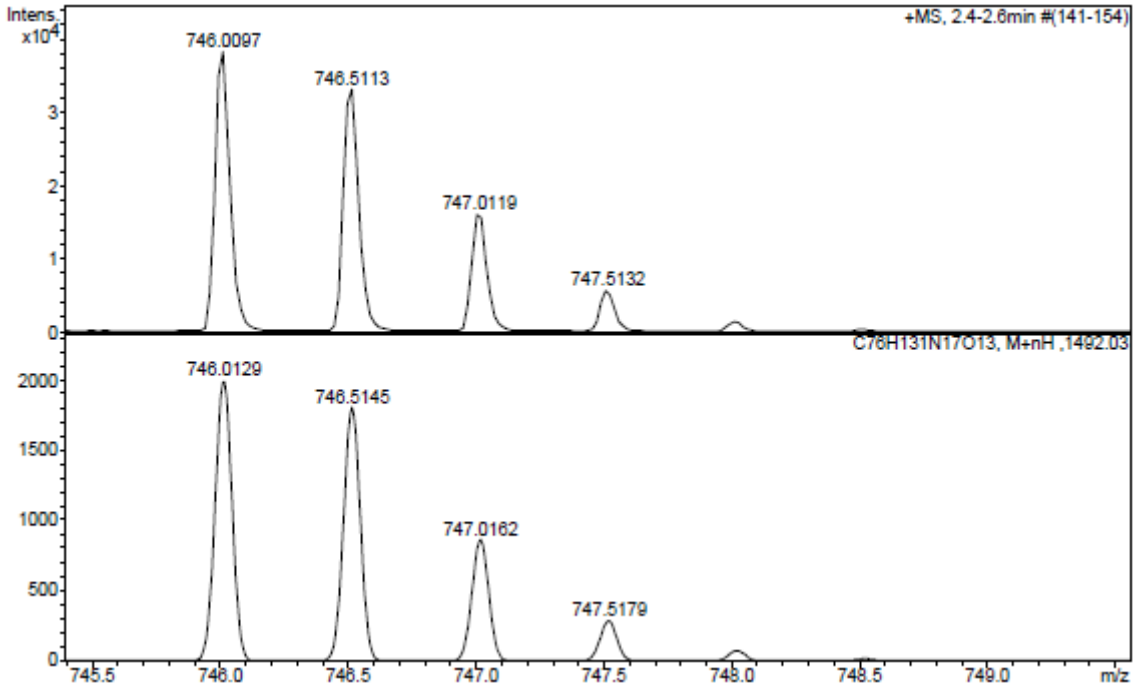
ESI-MS (*m/z*)



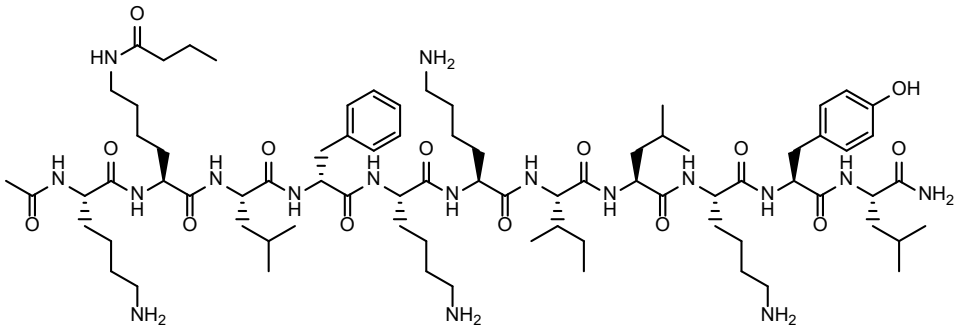
HRMS (*m/z*)


Intens.
x10^4
+MS, 2.4-2.6min #(141-154)
746.0097
1491.0154
m/z

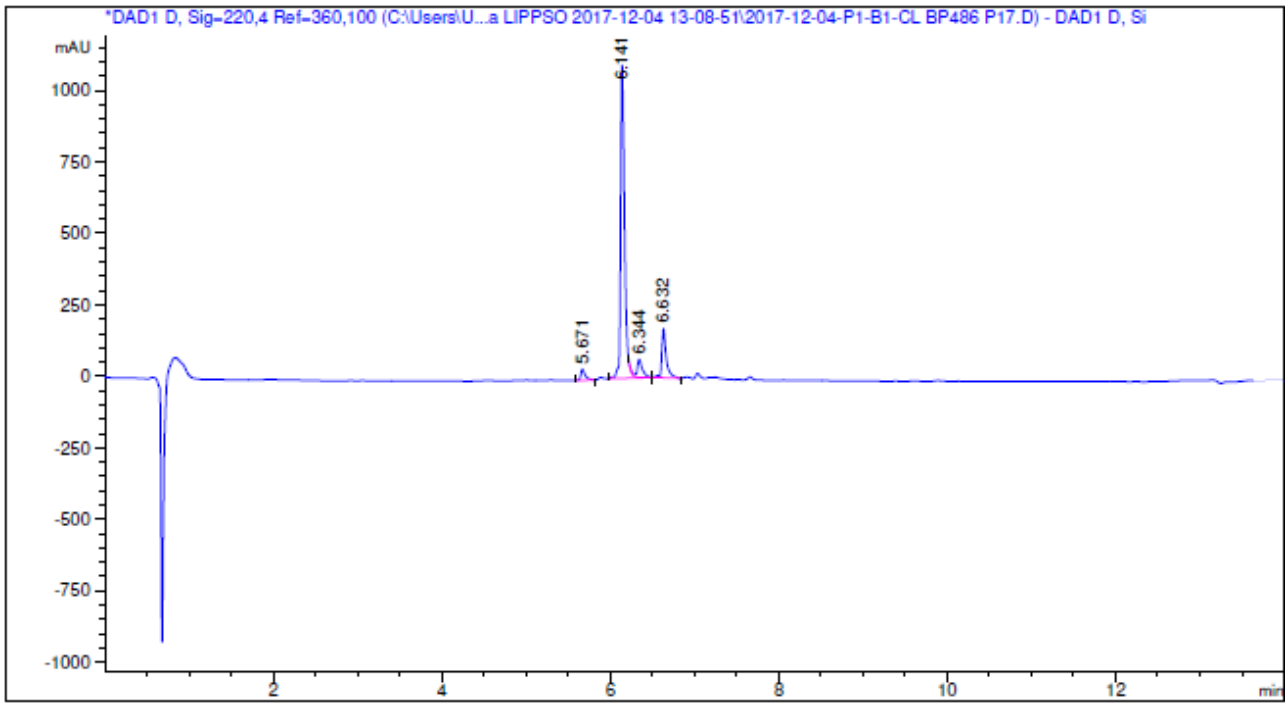

Intens.
+MS, 2.4-2.6min #(141-154)
1491.0154
1492.0171
1493.0200
1494.0239
C76H131N17O13, M+nH ,1491.02
1491.0185
1492.0217
1493.0251
1494.0285
m/z


Intens.
x10^4
+MS, 2.4-2.6min #(141-154)
746.0097
746.5113
747.0119
747.5132
C76H131N17O13, M+nH ,1492.03
746.0129
746.5145
747.0162
747.5179
745.5
746.0
746.5
747.0
747.5
748.0
748.5
749.0
m/z

Ac-Lys-Lys(COC_3H_7)-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP486)

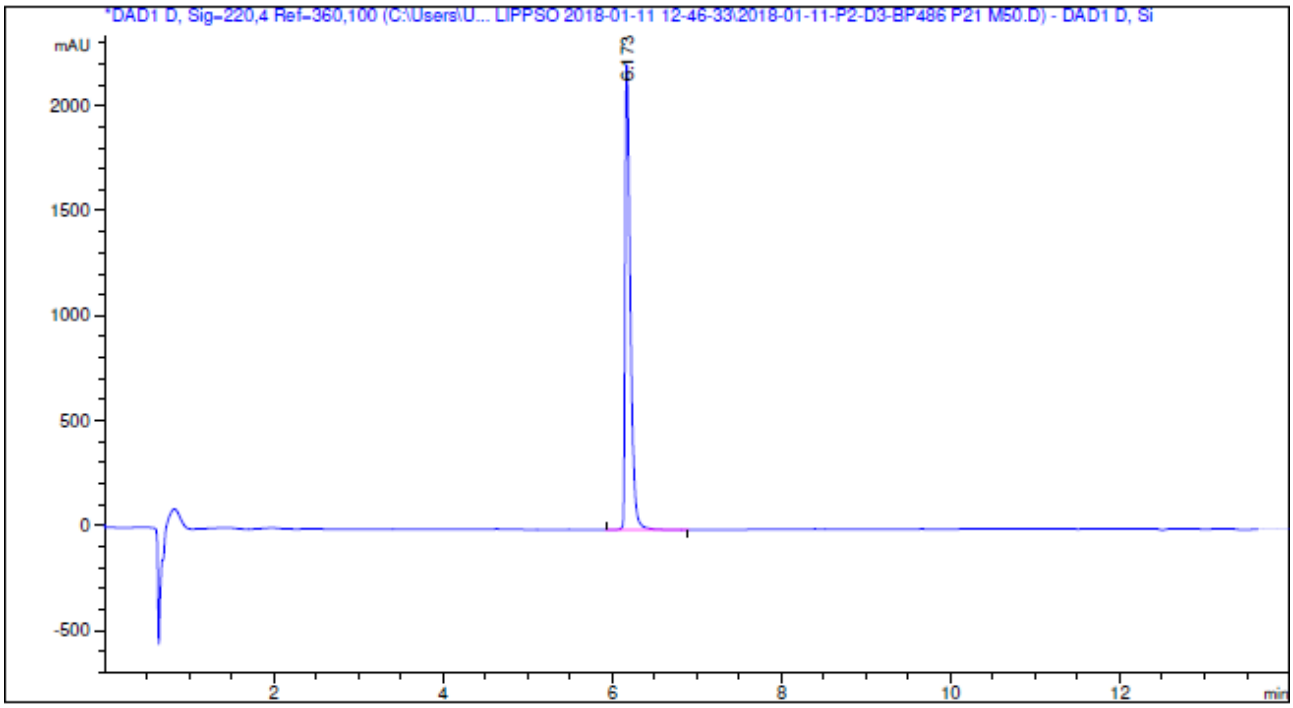


HPLC of crude peptide (λ=220 nm)



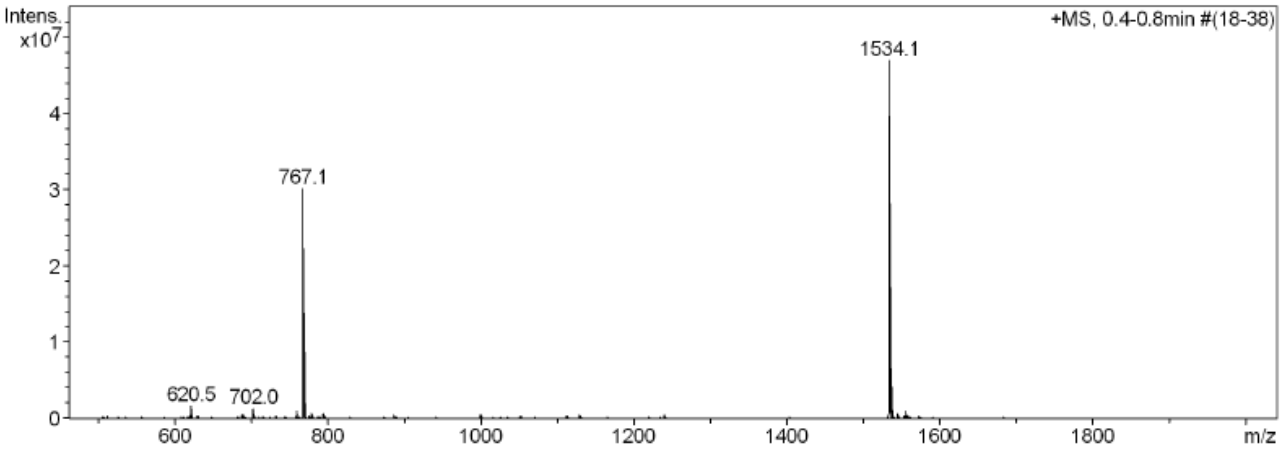
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.671	BB	0.0522	143.78764	39.70819	3.1093
2	6.141	VV R	0.0479	3568.24097	1098.94568	77.1617
3	6.344	VB E	0.0628	284.22037	63.95224	6.1461
4	6.632	VB R	0.0526	628.11932	172.08841	13.5828
Totals :				4624.36830	1374.69452	

HPLC of purified peptide (λ=220 nm)

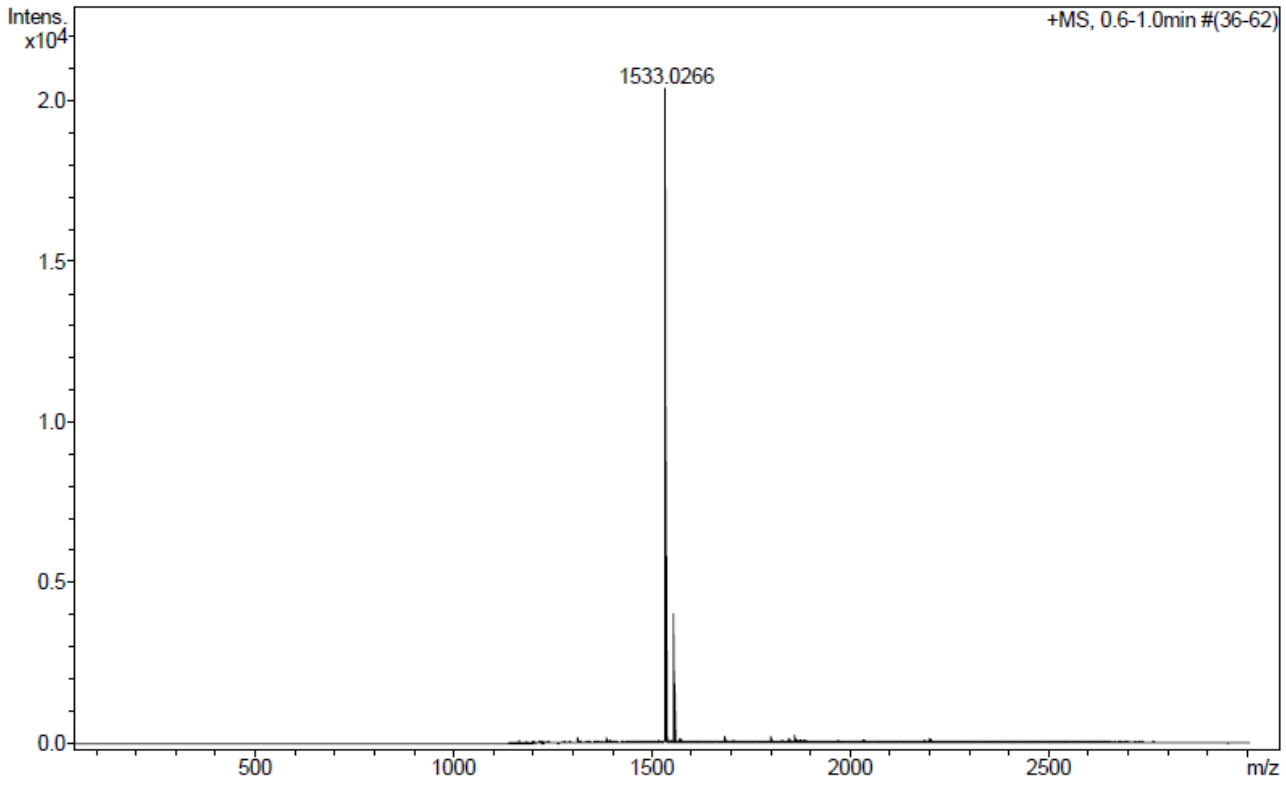


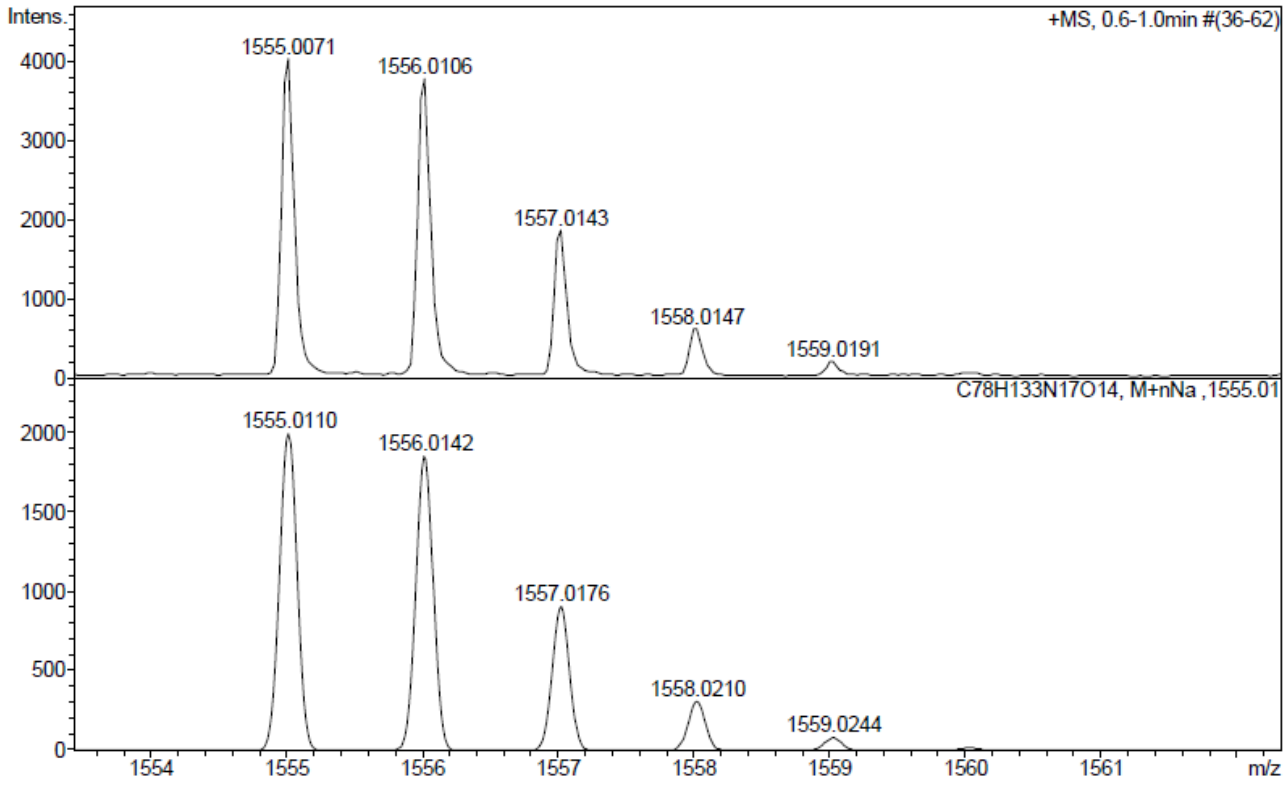
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.173	BB	0.0634	9405.44824	2219.42041	100.0000
Totals :				9405.44824	2219.42041	

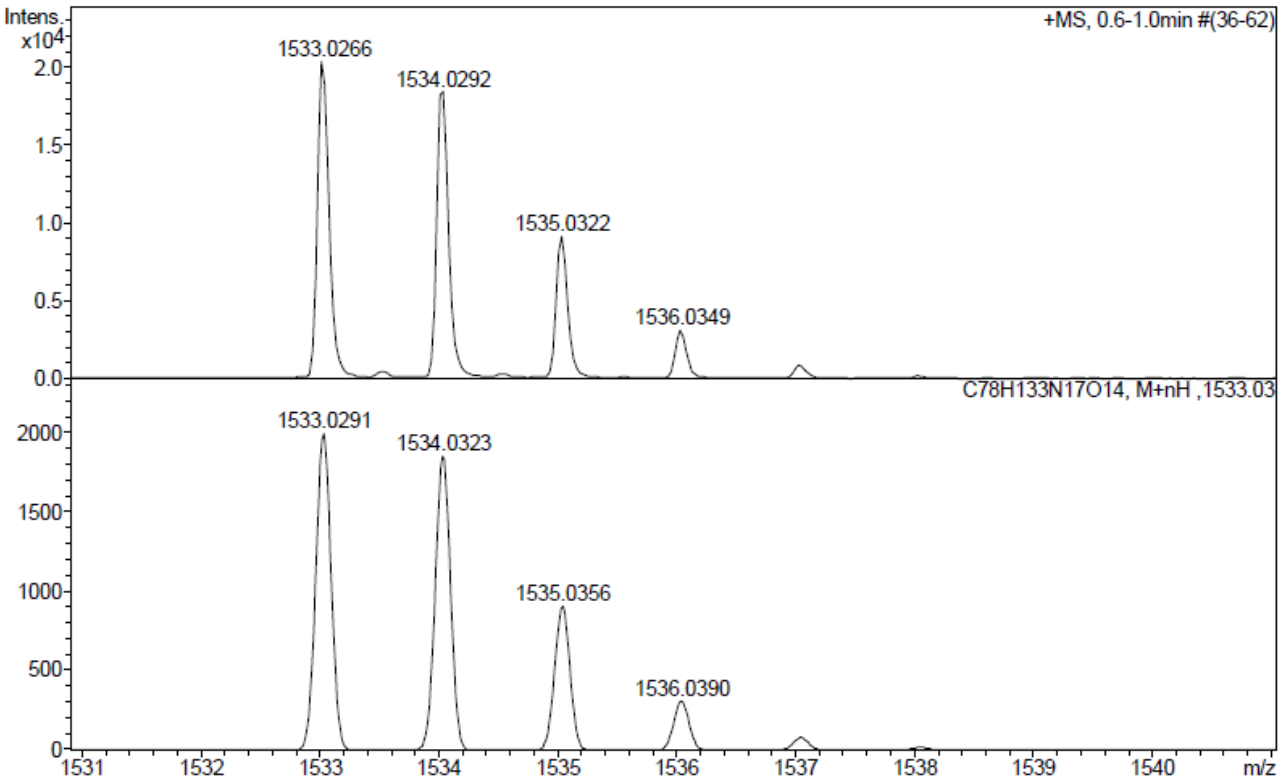
ESI-MS (*m/z*)



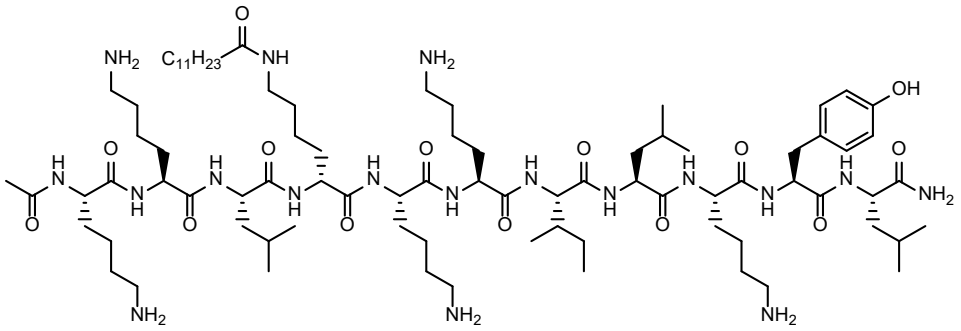
HRMS (*m/z*)


Intens.
x10^4
+MS, 0.6-1.0min #(36-62)
1533.0266
2.0
1.5
1.0
0.5
0.0
500
1000
1500
2000
2500
m/z

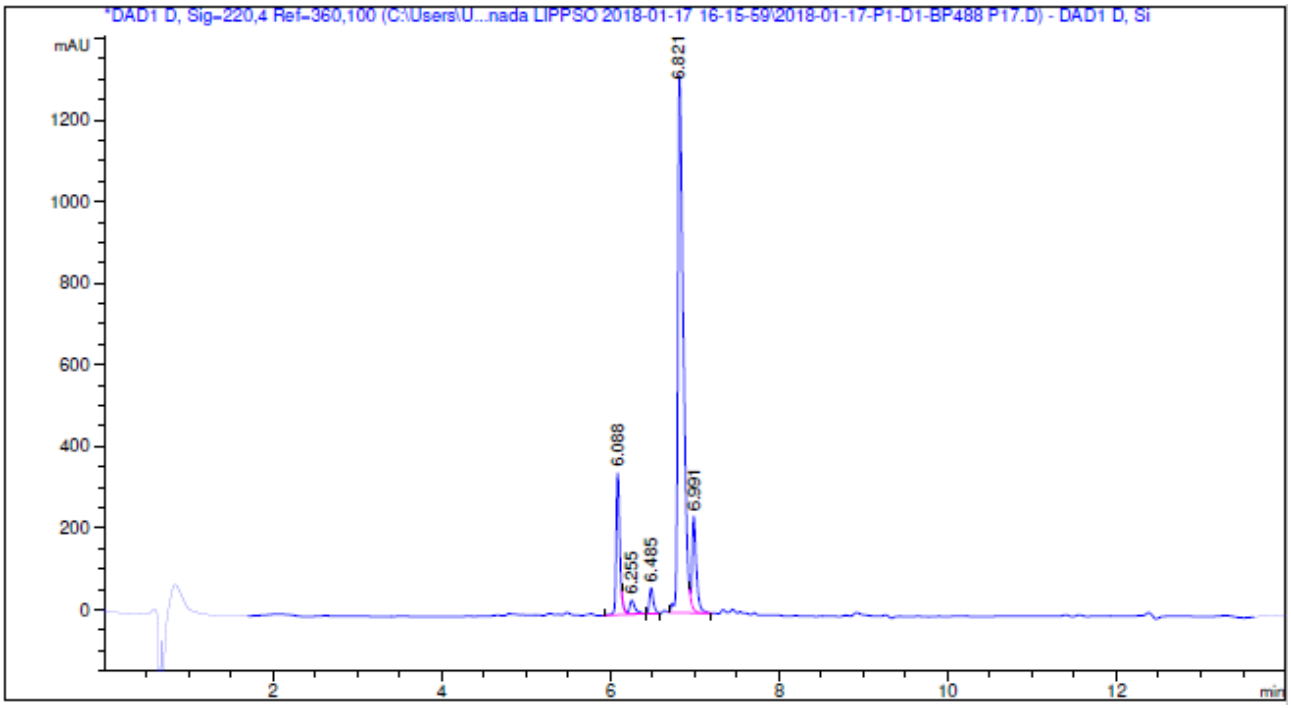

Intens.
+MS, 0.6-1.0min #(36-62)
1555.0071
1556.0106
1557.0143
1558.0147
1559.0191
4000
3000
2000
1000
0
C78H133N17O14, M+nNa ,1555.01
1555.0110
1556.0142
1557.0176
1558.0210
1559.0244
2000
1500
1000
500
0
1554
1555
1556
1557
1558
1559
1560
1561
m/z


Intens.
x10^4
2.0
1.5
1.0
0.5
0.0
+MS, 0.6-1.0min #(36-62)
1533.0266
1534.0292
1535.0322
1536.0349
C78H133N17O14, M+nH ,1533.03
2000
1500
1000
500
0
1533.0291
1534.0323
1535.0356
1536.0390
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
m/z

Ac-Lys-Lys-Leu-D-Lys($COC_{11}H_{23}$)-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP488)

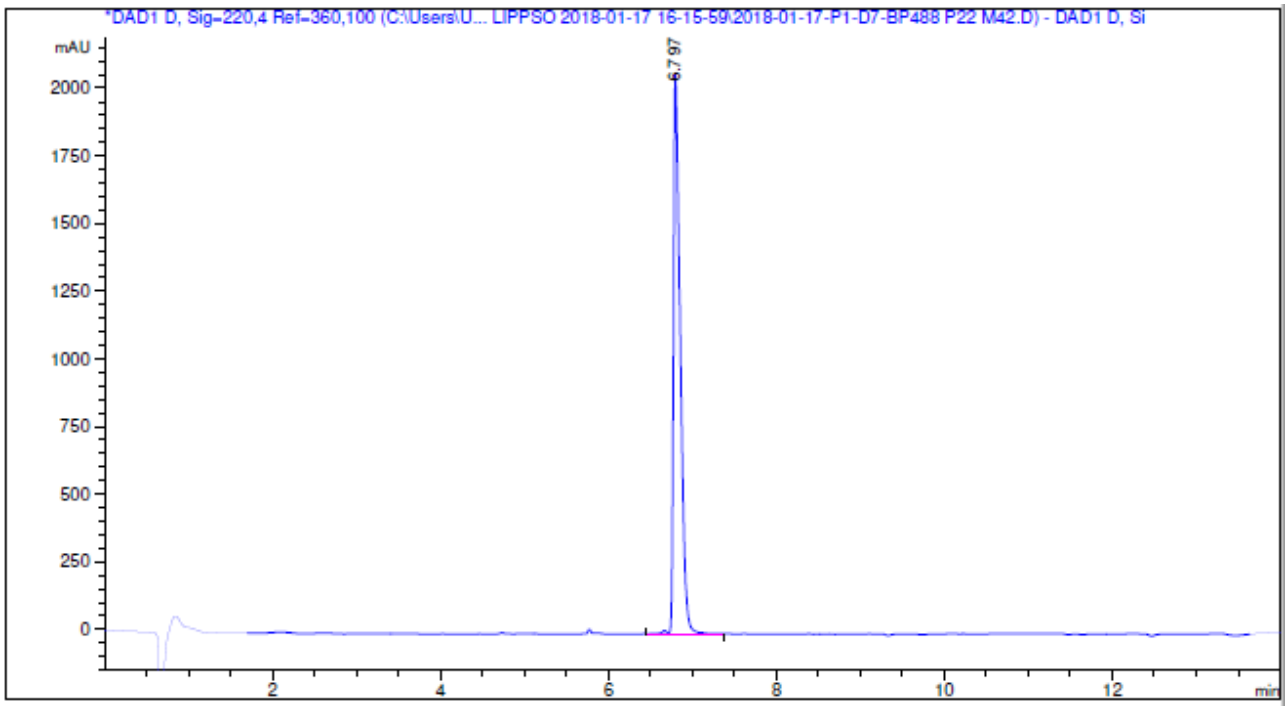


HPLC of crude peptide (λ=220 nm)



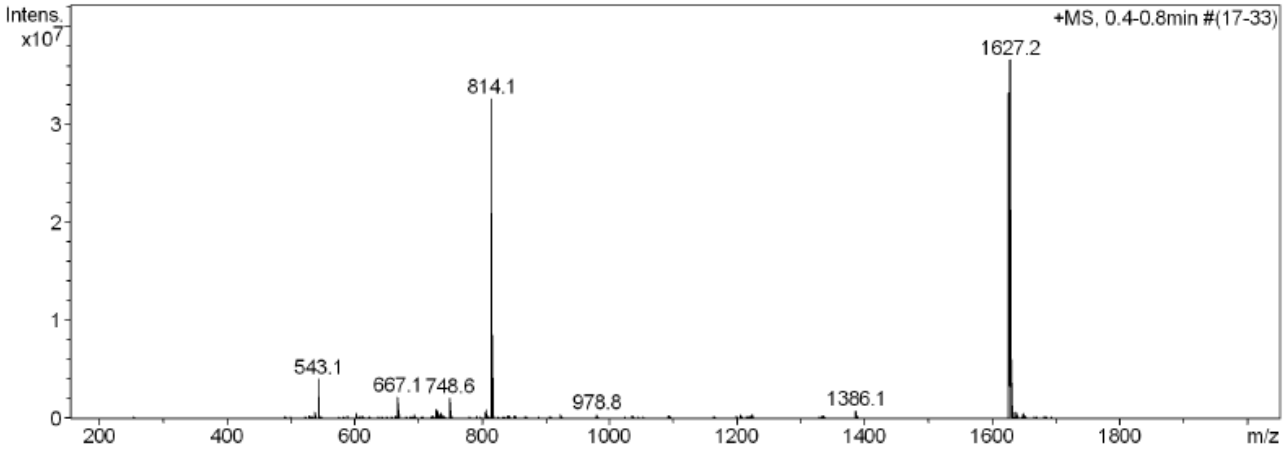
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.088	BV R	0.0441	1046.76038	347.67551	12.7178
2	6.255	VB E	0.0670	154.87279	33.46687	1.8817
3	6.485	BB	0.0487	202.15788	62.57148	2.4562
4	6.821	VV R	0.0686	6048.61426	1316.82983	73.4888
5	6.991	VB E	0.0507	778.25232	228.61604	9.4555
Totals :				8230.65762	1989.15973	

HPLC of purified peptide (λ=220 nm)

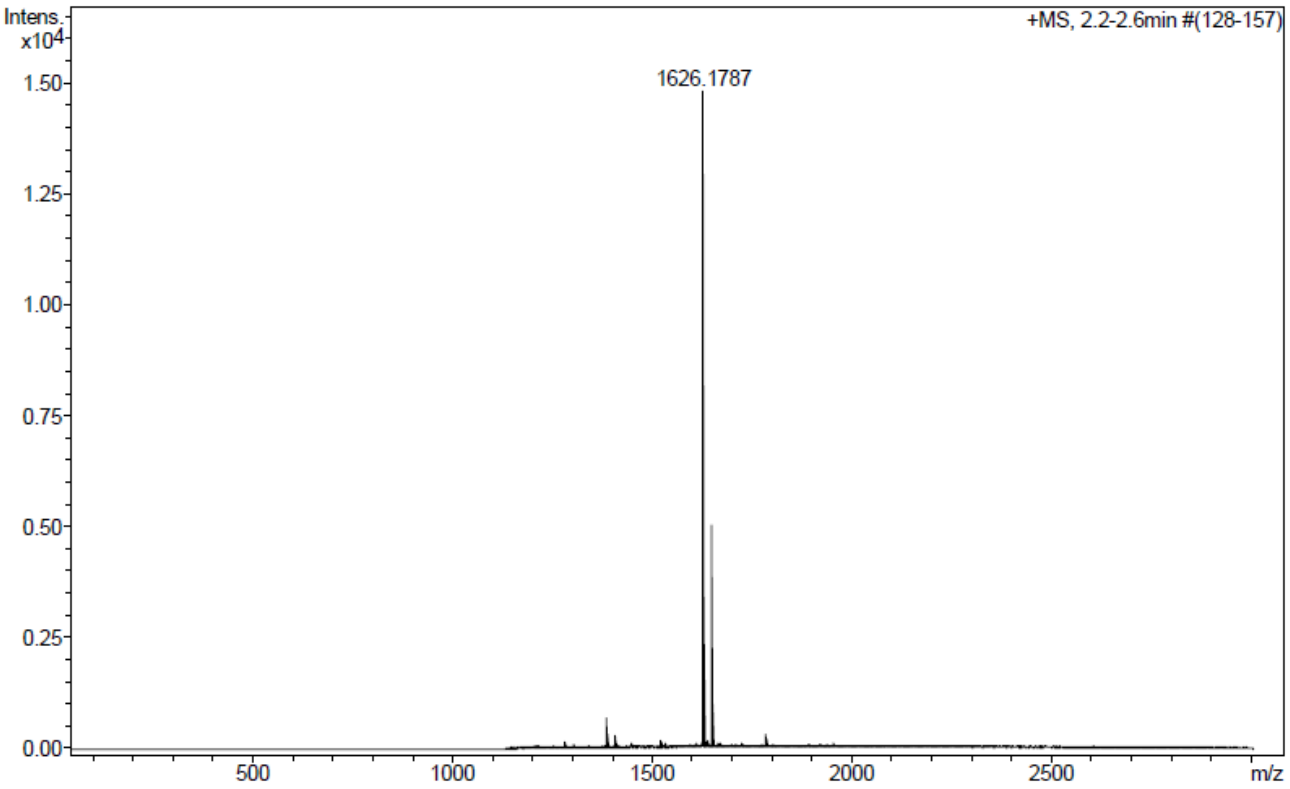


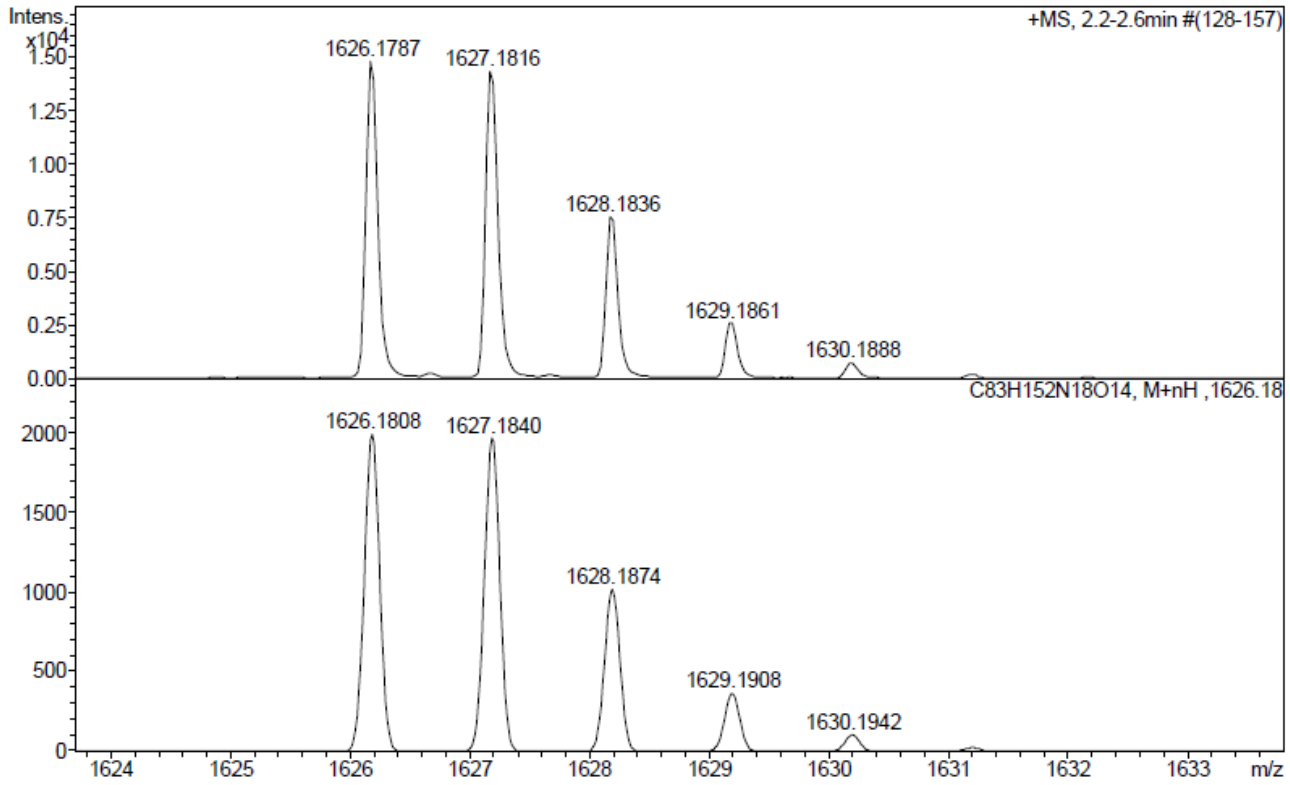
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.797	VB R	0.0858	1.14854e4	2066.89282	100.0000
Totals :				1.14854e4	2066.89282	

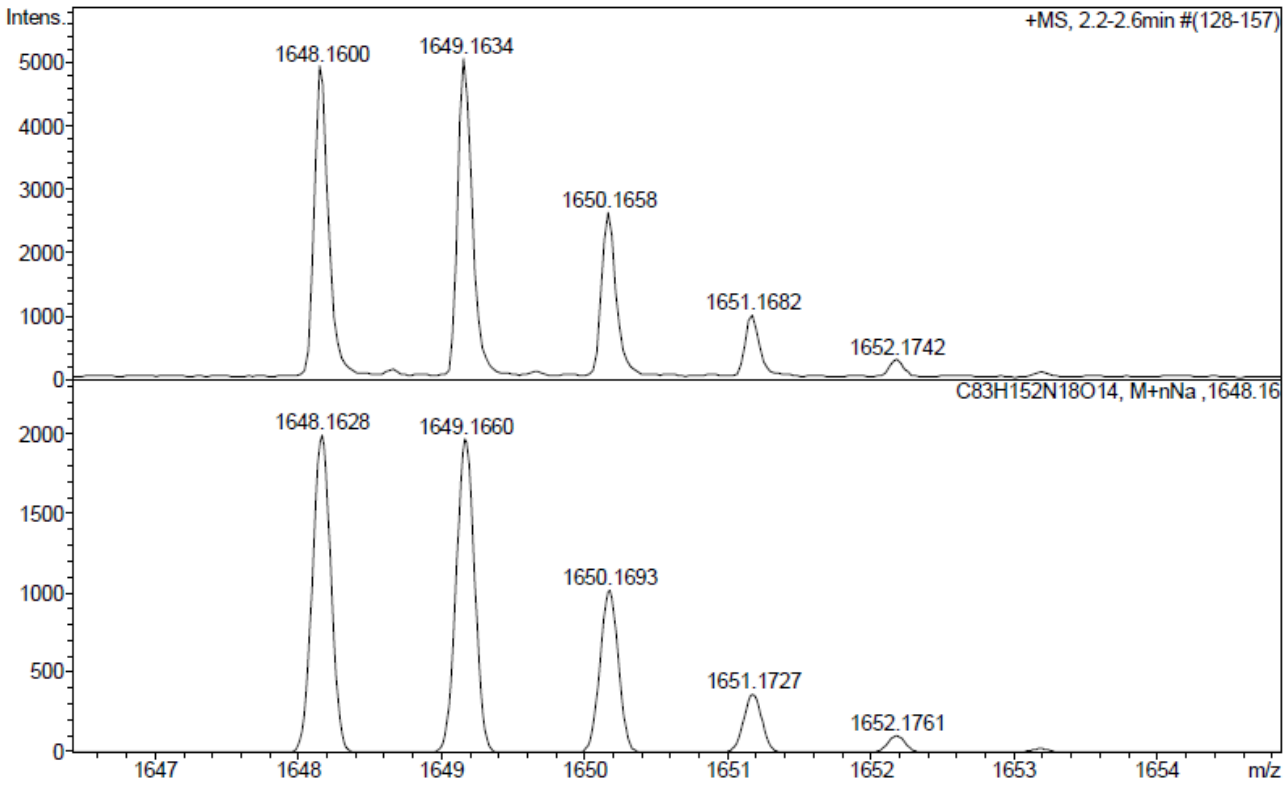
ESI-MS (*m/z*)



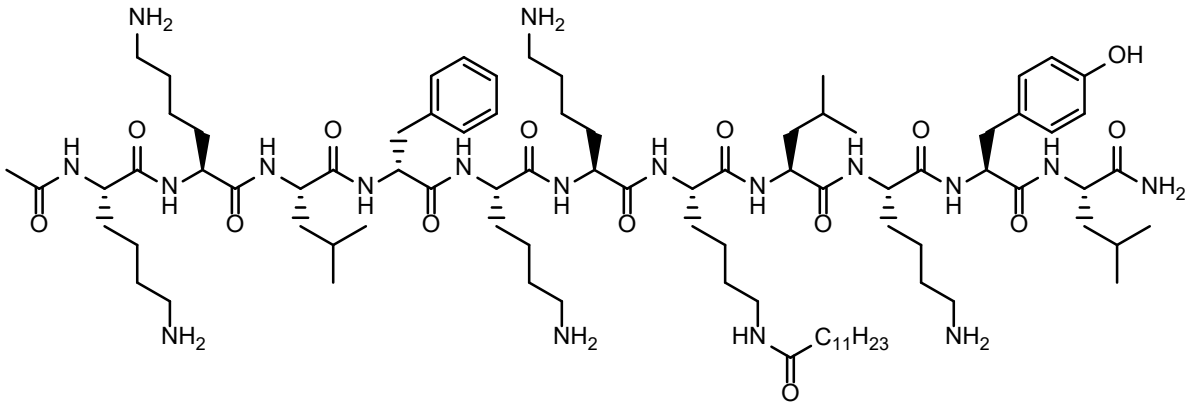
HRMS (m/z)


Intens.
x10^4
+MS, 2.2-2.6min #(128-157)
1626.1787
1.50
1.25
1.00
0.75
0.50
0.25
0.00
500
1000
1500
2000
2500
m/z

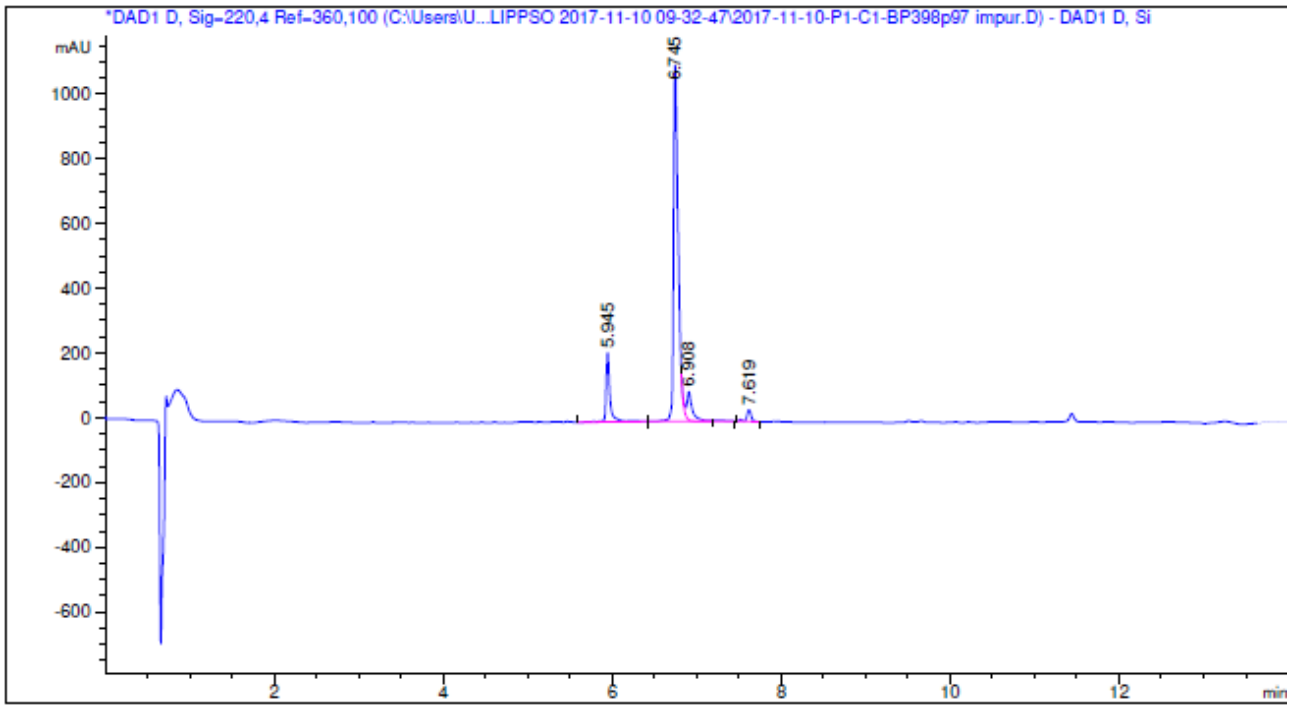

Intens.
x10^4
+MS, 2.2-2.6min #(128-157)
1626.1787
1627.1816
1628.1836
1629.1861
1630.1888
1.50
1.25
1.00
0.75
0.50
0.25
0.00
C83H152N18O14, M+nH ,1626.18
1626.1808
1627.1840
1628.1874
1629.1908
1630.1942
2000
1500
1000
500
0
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
m/z


Intens.
+MS, 2.2-2.6min #(128-157)
1648.1600
1649.1634
1650.1658
1651.1682
1652.1742
C83H152N18O14, M+nNa ,1648.16
1648.1628
1649.1660
1650.1693
1651.1727
1652.1761
m/z

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Lys($COC_{11}H_{23}$)-Leu-Lys-Tyr-Leu-NH_2 (BP489)

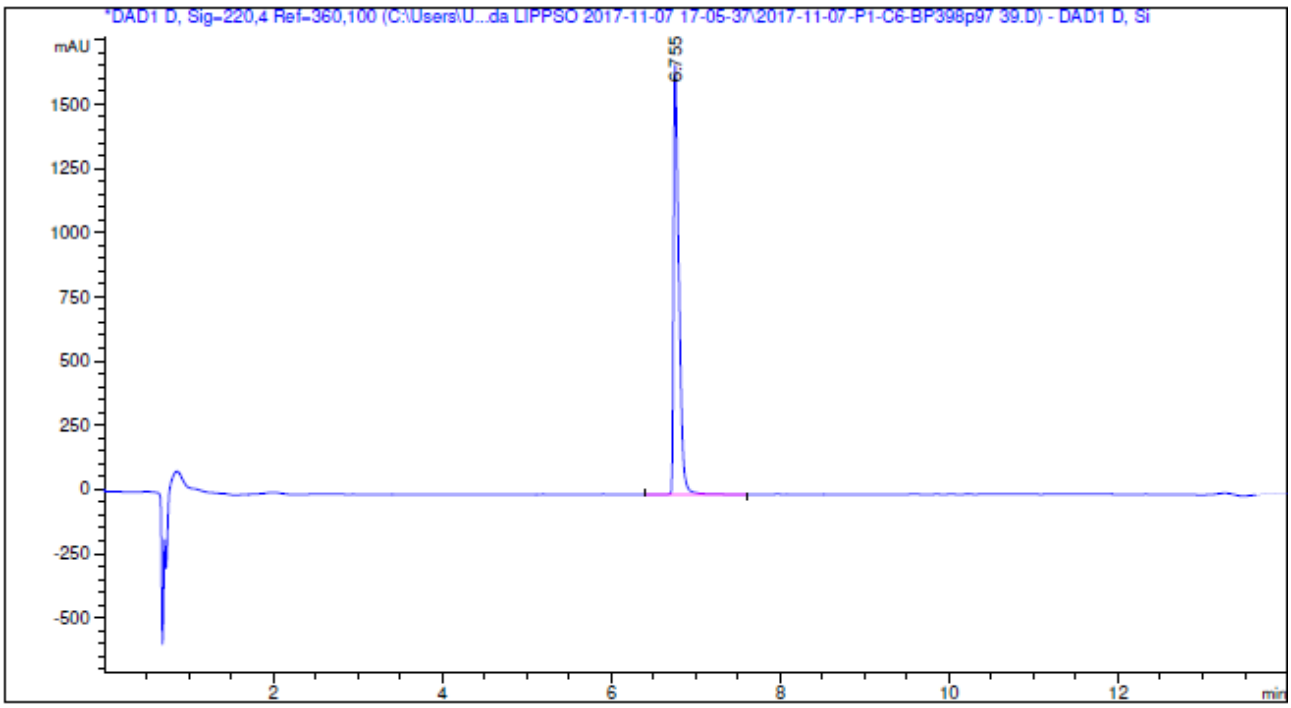


HPLC of crude peptide (λ=220 nm)



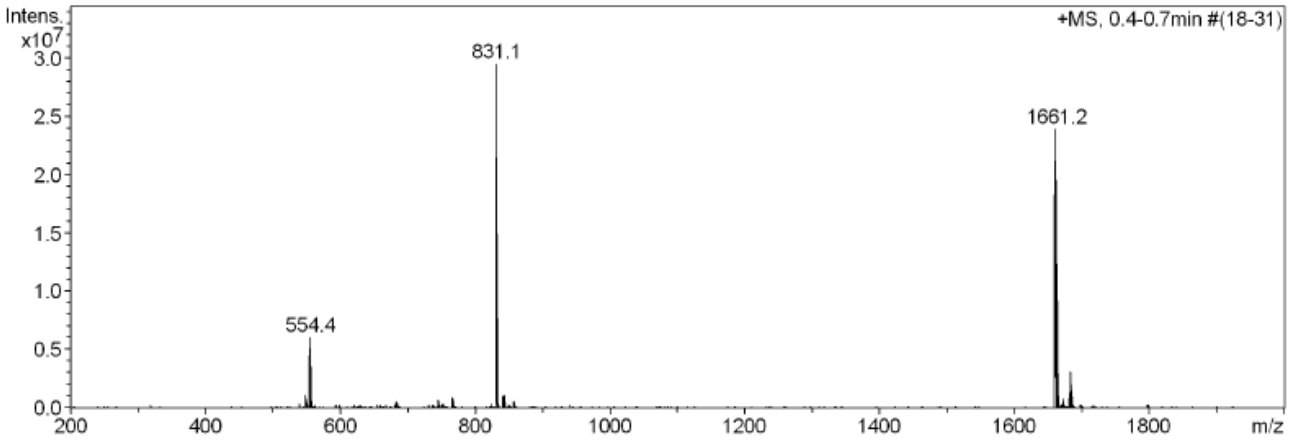
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.945	VV R	0.0468	694.77289	214.59721	12.4485
2	6.745	BV R	0.0579	4328.80762	1099.50281	77.5611
3	6.908	VV E	0.0672	426.74368	87.06355	7.6461
4	7.619	VB R	0.0553	130.83649	36.04453	2.3443
Totals :				5581.16068	1437.20810	

HPLC of purified peptide (λ=220 nm)

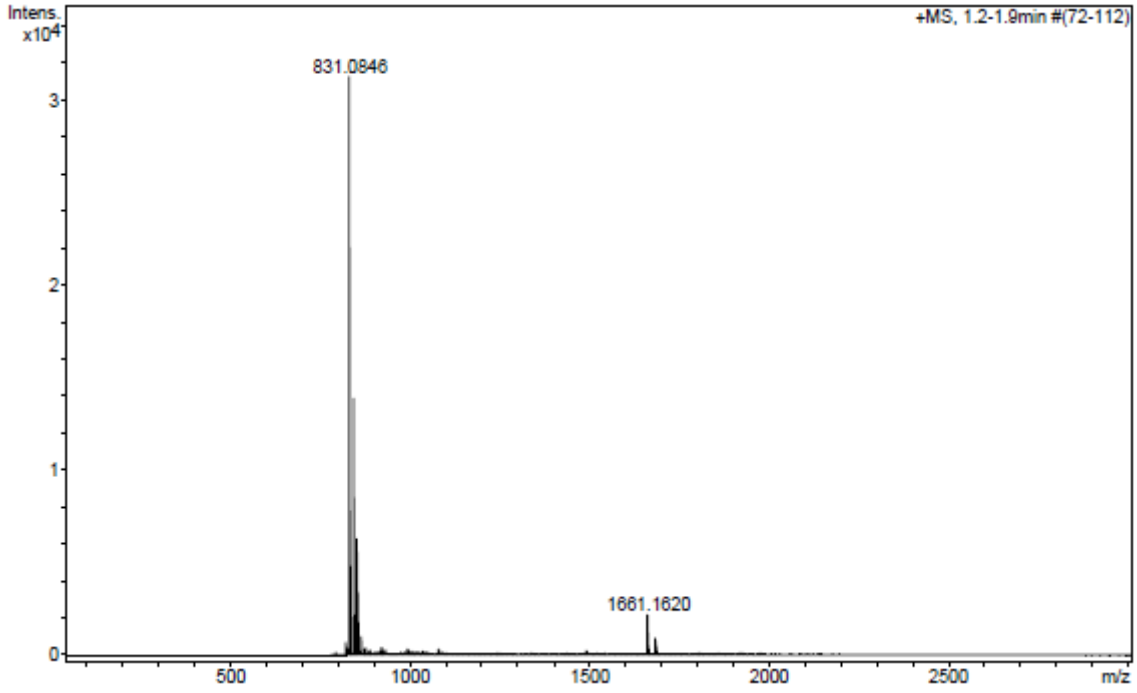


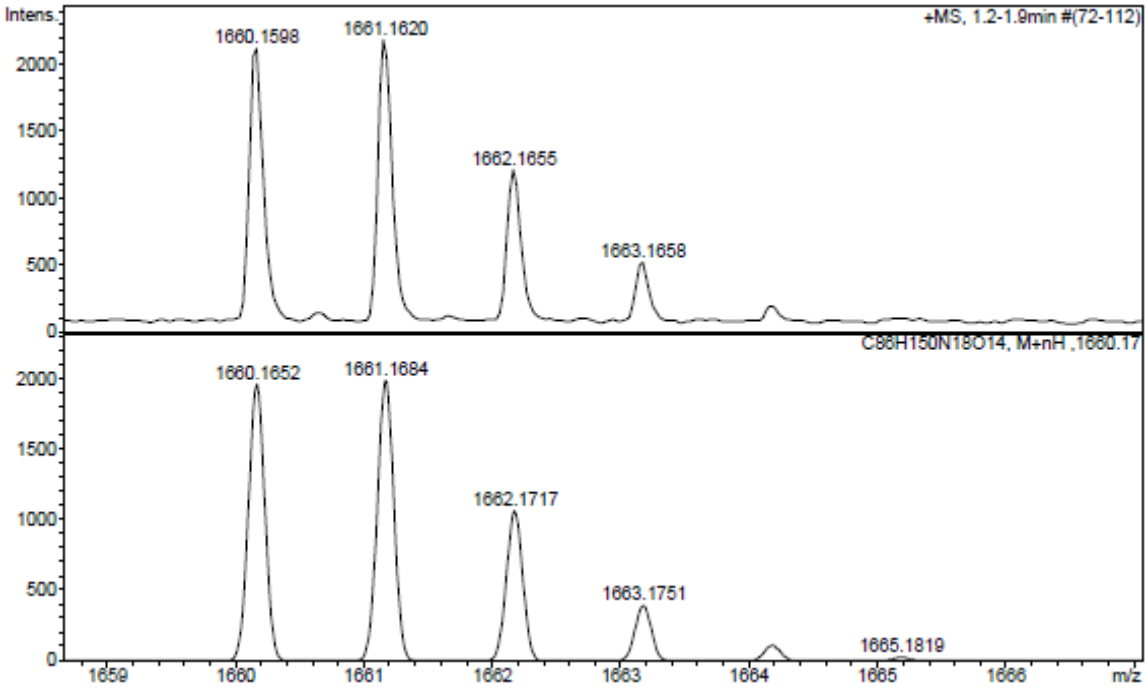
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.755	BB	0.0665	7391.91846	1673.21887	100.0000
Totals :				7391.91846	1673.21887	

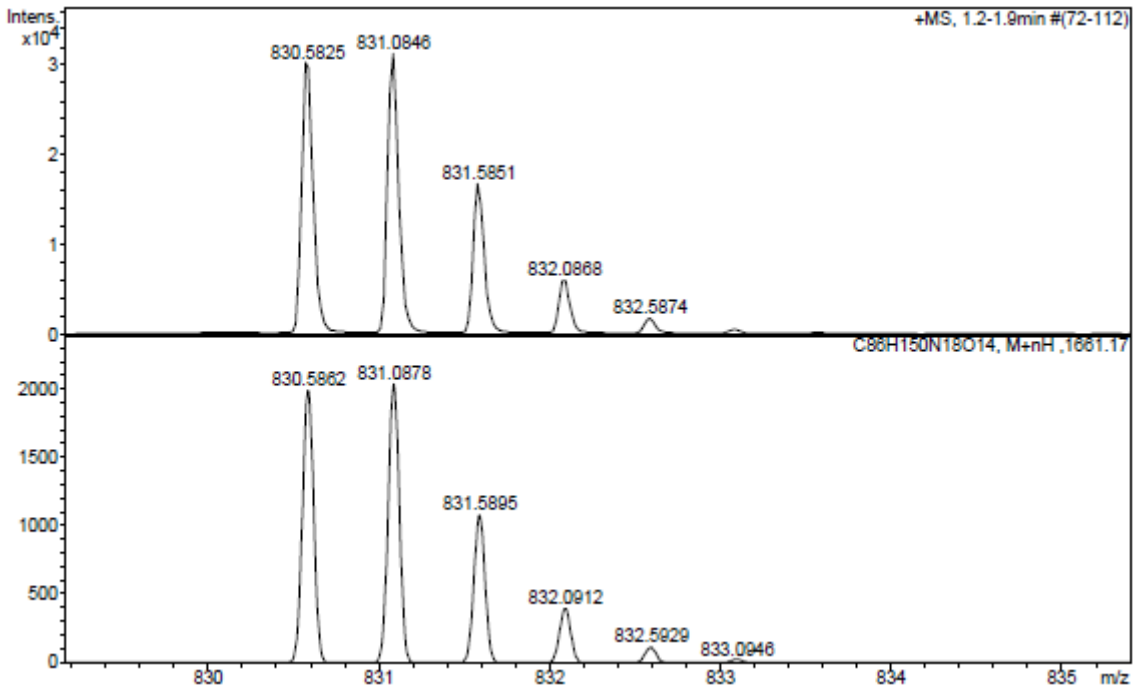
ESI-MS (*m/z*)



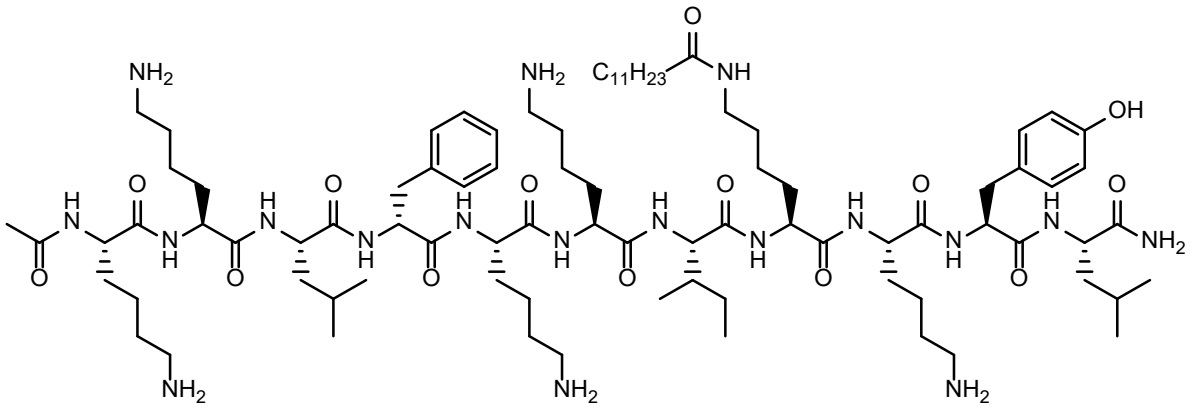
HRMS (*m/z*)


Intens.
x10^4
+MS, 1.2-1.9min #(72-112)
831.0846
1661.1620
0
1
2
3
500
1000
1500
2000
2500
m/z

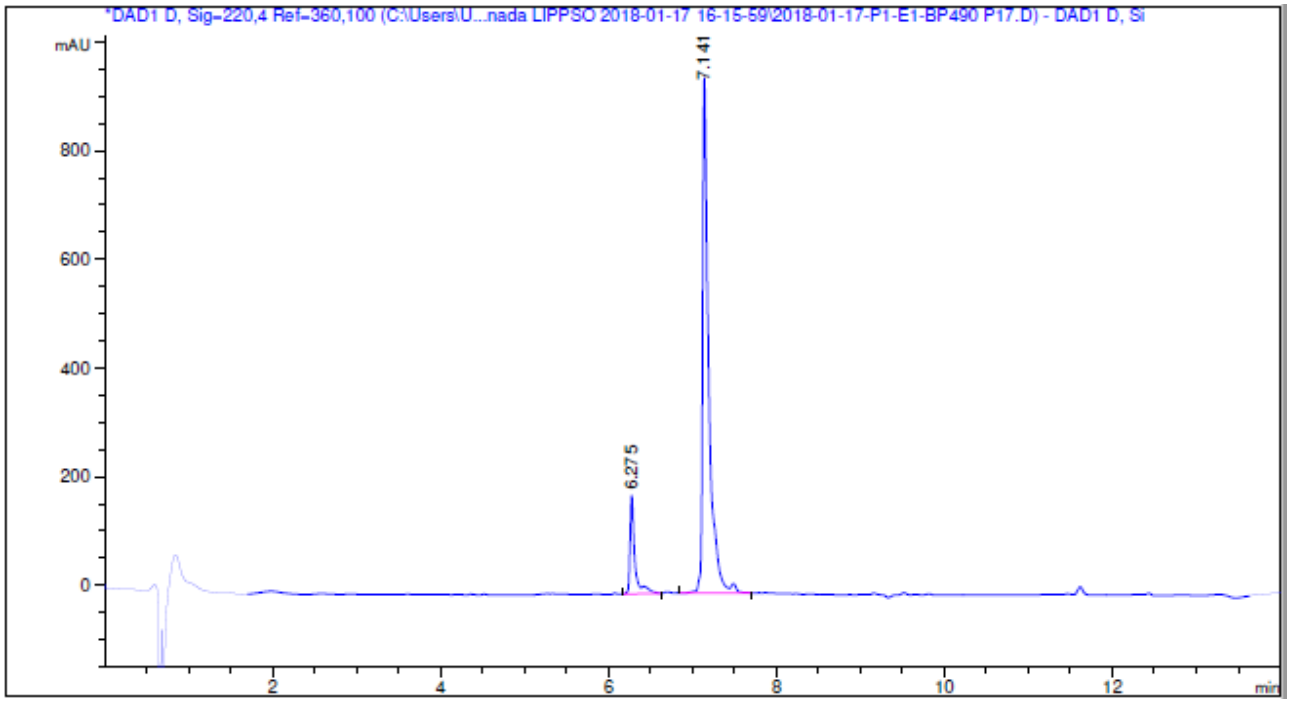

Intens.
+MS, 1.2-1.9min #(72-112)
1660.1598
1661.1620
1662.1655
1663.1658
0
500
1000
1500
2000
C88H150N18O14, M+nH ,1660.17
1660.1652
1661.1684
1662.1717
1663.1751
1665.1819
1659
1660
1661
1662
1663
1664
1665
1666
m/z


Intens.
x10^4
+MS, 1.2-1.9min #(72-112)
830.5825
831.0846
831.5851
832.0868
832.5874
C86H150N18O14, M+nH, 1661.17
830.5862
831.0878
831.5895
832.0912
832.5929
833.0946
m/z

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Lys($COC_{11}H_{23}$)-Lys-Tyr-Leu-NH_2 (BP490)

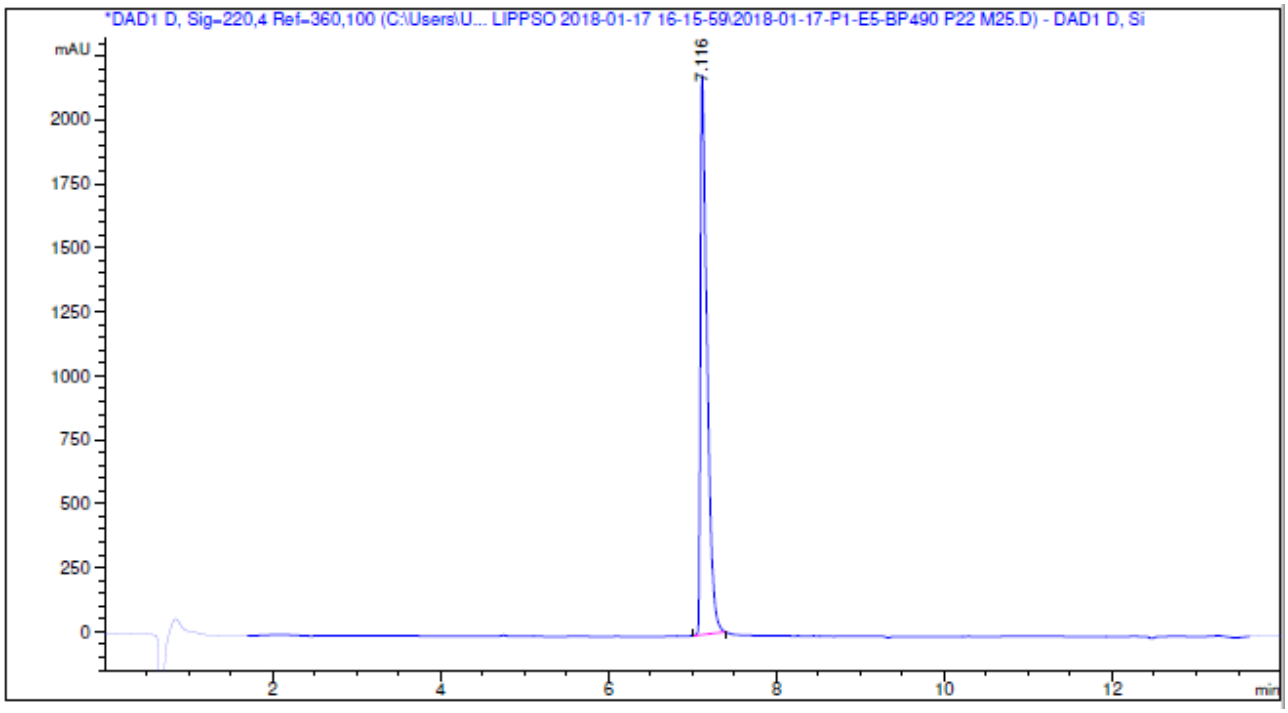


HPLC of crude peptide (λ=220 nm)



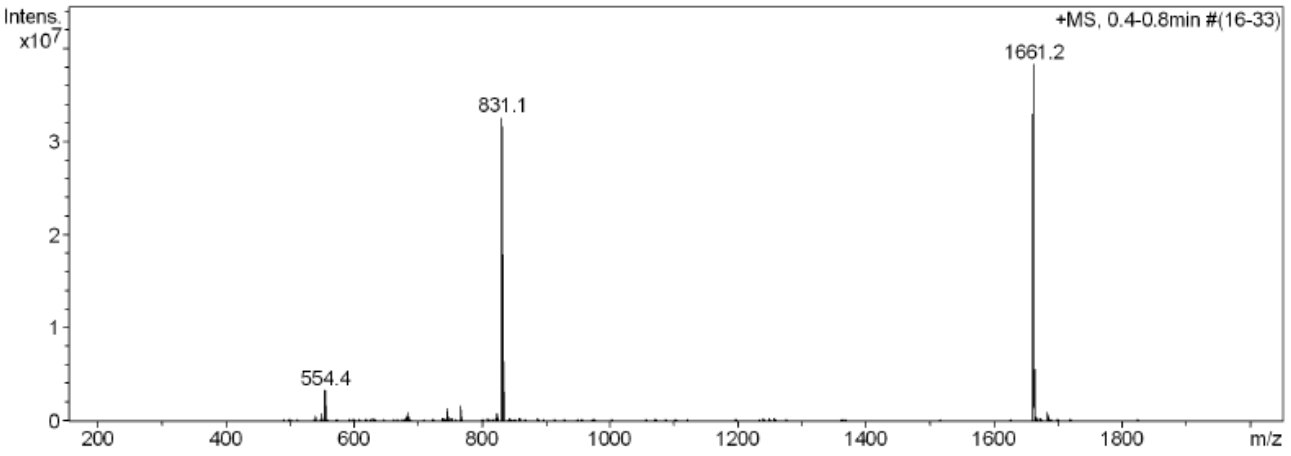
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.275	BV R	0.0575	723.08496	181.44606	12.9286
2	7.141	BV R	0.0729	4869.80566	948.12061	87.0714
Totals :				5592.89063	1129.56667	

HPLC of purified peptide (λ=220 nm)

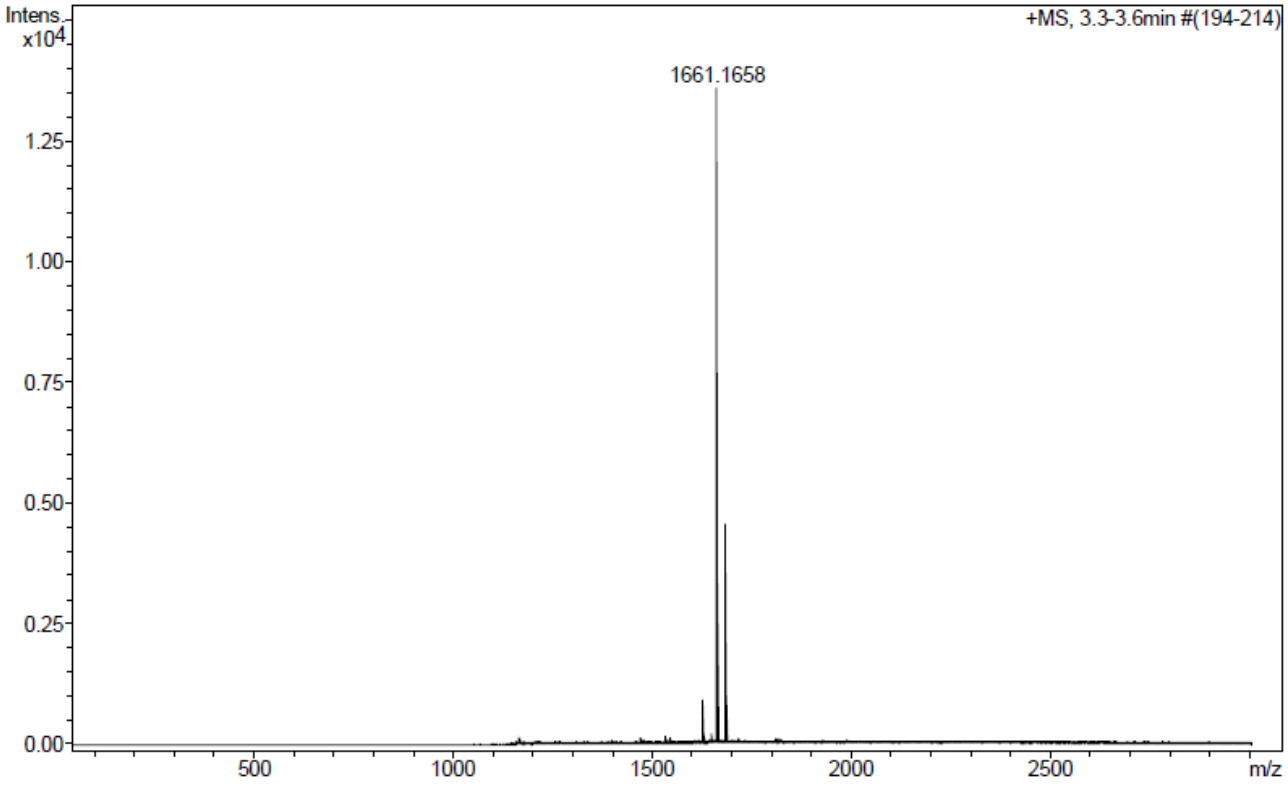


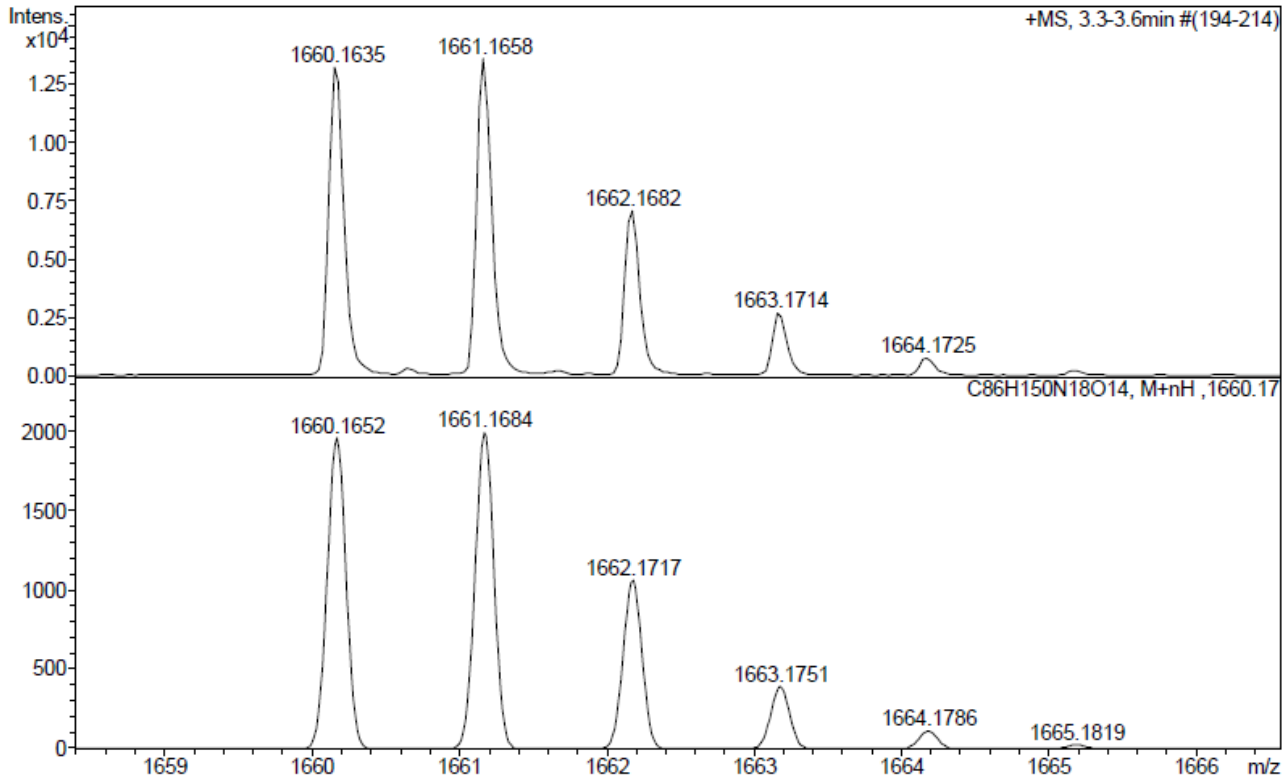
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.116	BBA	0.0821	1.20145e4	2186.71582	100.0000
Totals :				1.20145e4	2186.71582	

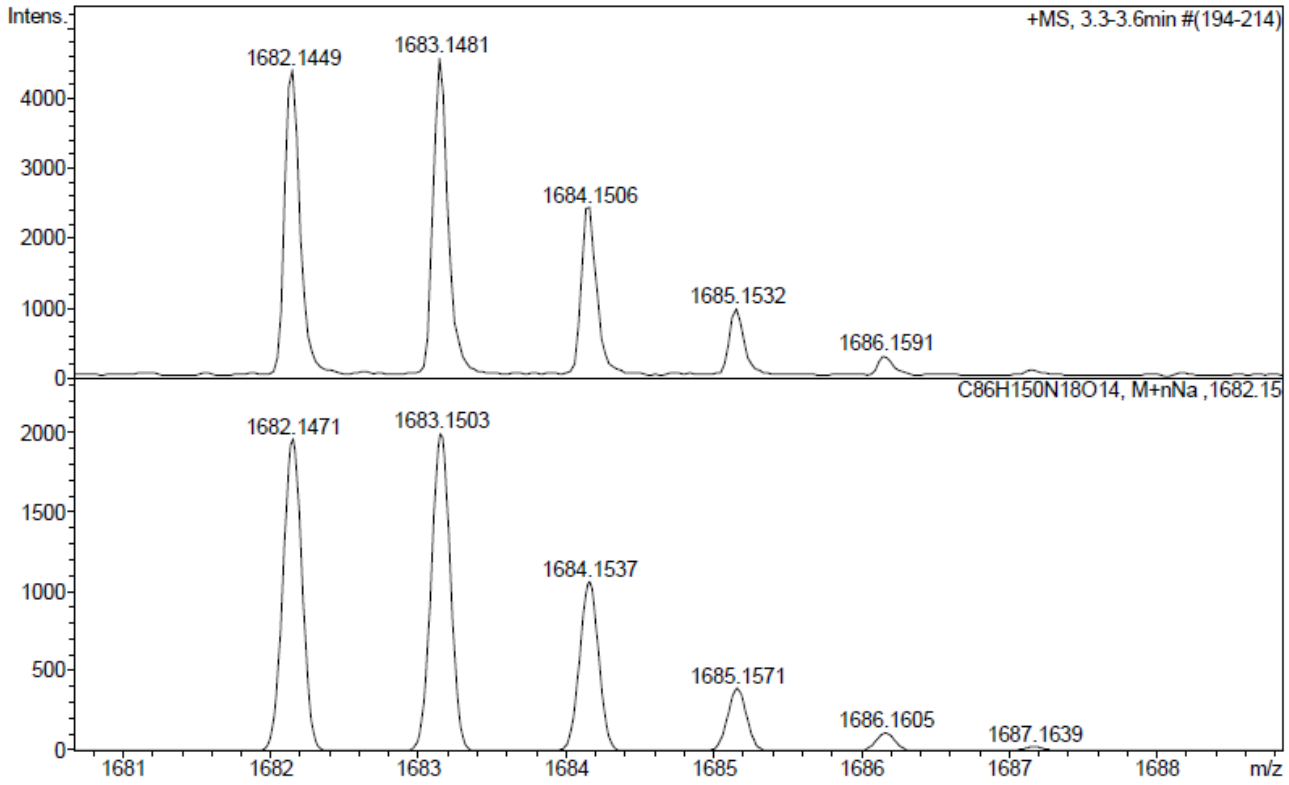
ESI-MS (*m/z*)



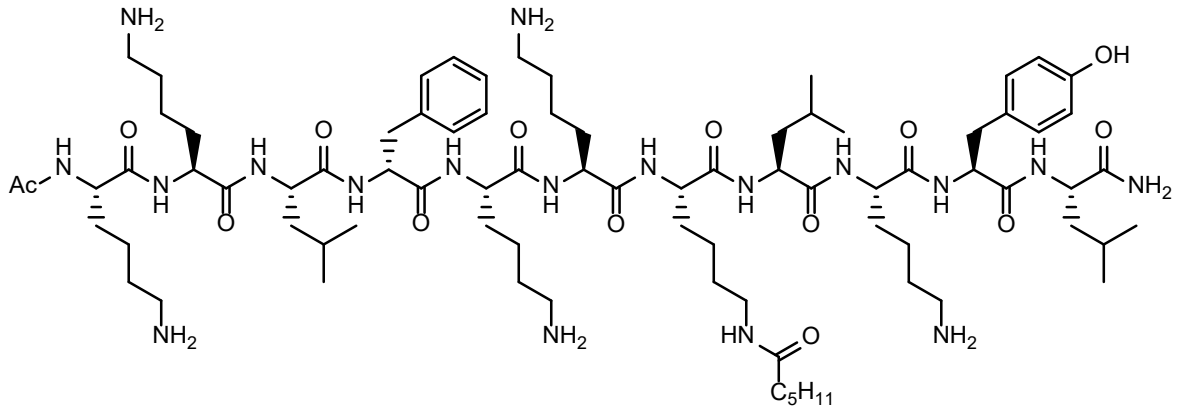
HRMS (*m/z*)


Intens.
x10^4
+MS, 3.3-3.6min #(194-214)
1661.1658
1.25
1.00
0.75
0.50
0.25
0.00
500
1000
1500
2000
2500
m/z

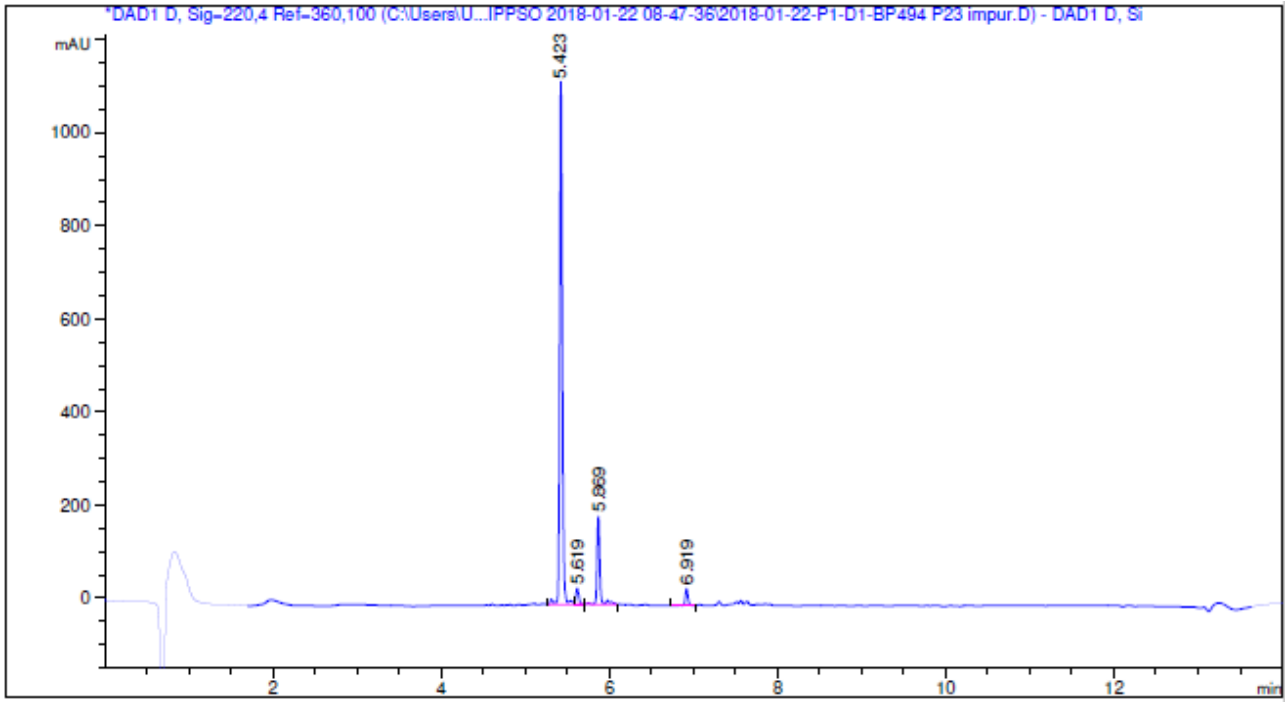

Intens.
x10^4
+MS, 3.3-3.6min #(194-214)
1660.1635
1661.1658
1662.1682
1663.1714
1664.1725
1.25
1.00
0.75
0.50
0.25
0.00
C86H150N18O14, M+nH ,1660.17
1660.1652
1661.1684
1662.1717
1663.1751
1664.1786
1665.1819
2000
1500
1000
500
0
1659
1660
1661
1662
1663
1664
1665
1666
m/z


Intens.
+MS, 3.3-3.6min #(194-214)
1682.1449
1683.1481
1684.1506
1685.1532
1686.1591
4000
3000
2000
1000
0
C86H150N18O14, M+nNa ,1682.15
1682.1471
1683.1503
1684.1537
1685.1571
1686.1605
1687.1639
2000
1500
1000
500
0
1681
1682
1683
1684
1685
1686
1687
1688
m/z

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Lys(COC_5H_{11})-Leu-Lys-Tyr-Leu-NH_2 (BP494)

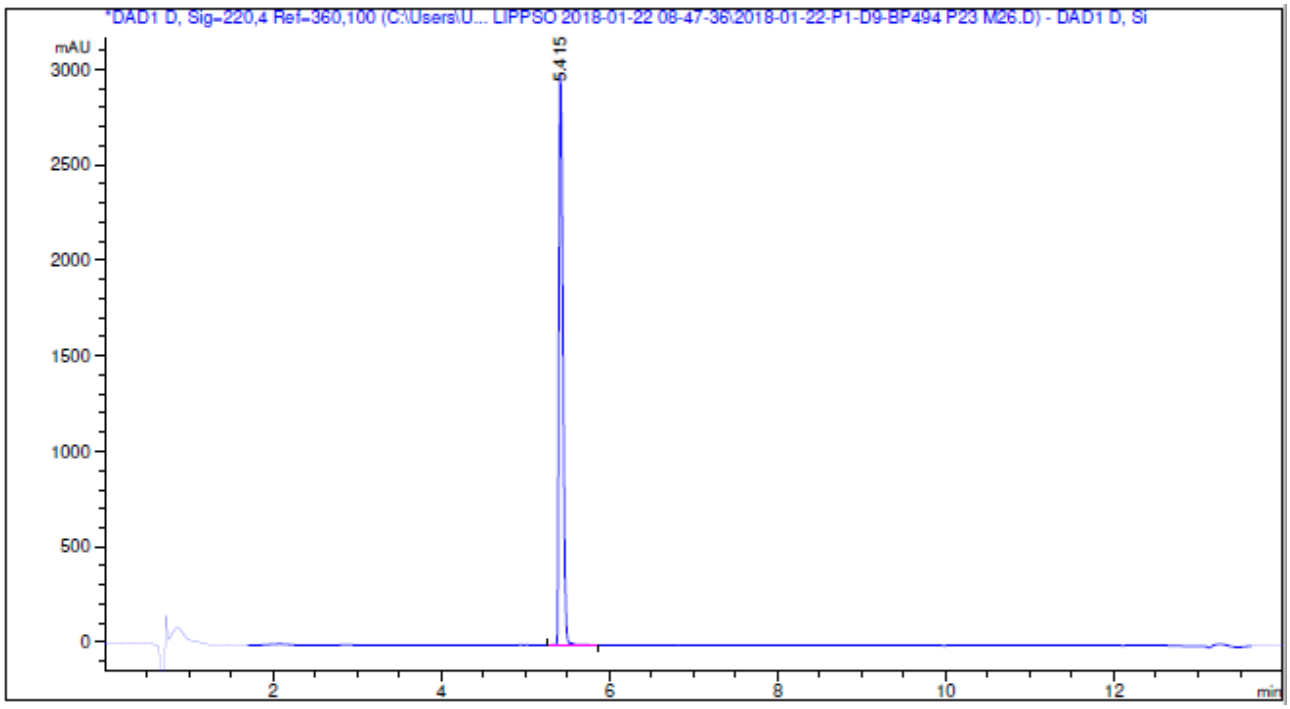


HPLC of crude peptide (λ=220 nm)



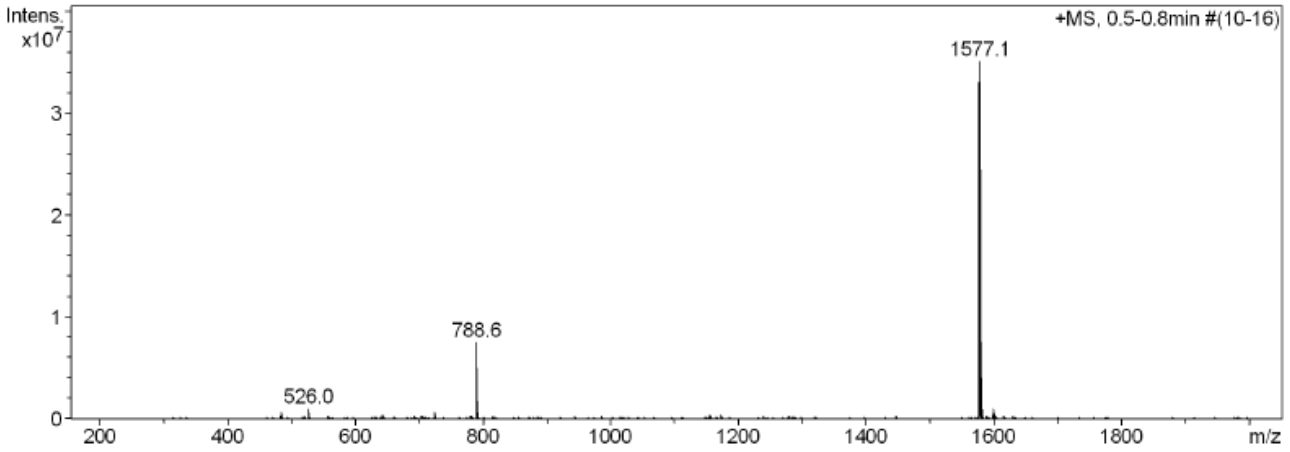
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.423	VV R	0.0340	2517.67651	1130.30176	80.8293
2	5.619	VB E	0.0374	84.14298	34.50963	2.7014
3	5.869	VV R	0.0346	432.04156	189.79099	13.8706
4	6.919	VV R	0.0340	80.94740	36.32489	2.5988
Totals :				3114.80846	1390.92727	

HPLC of purified peptide (λ=220 nm)

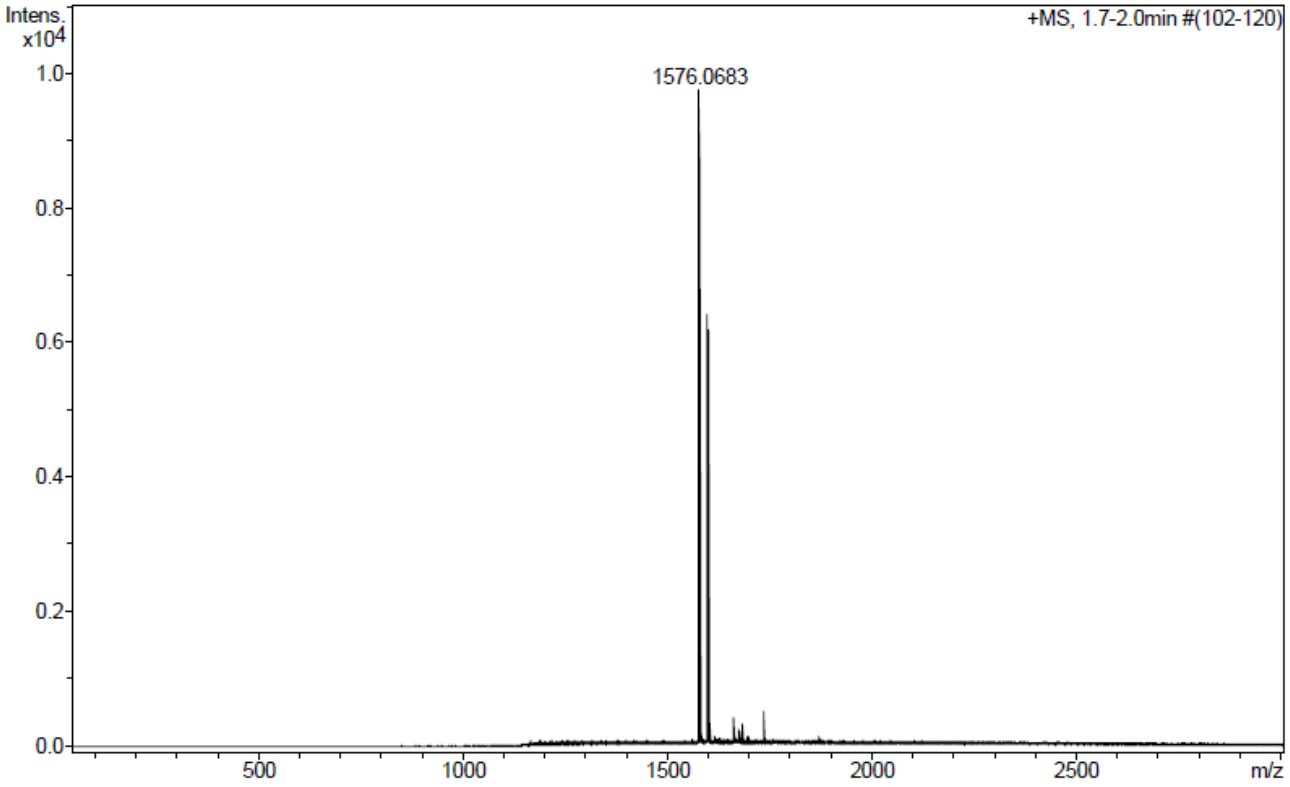


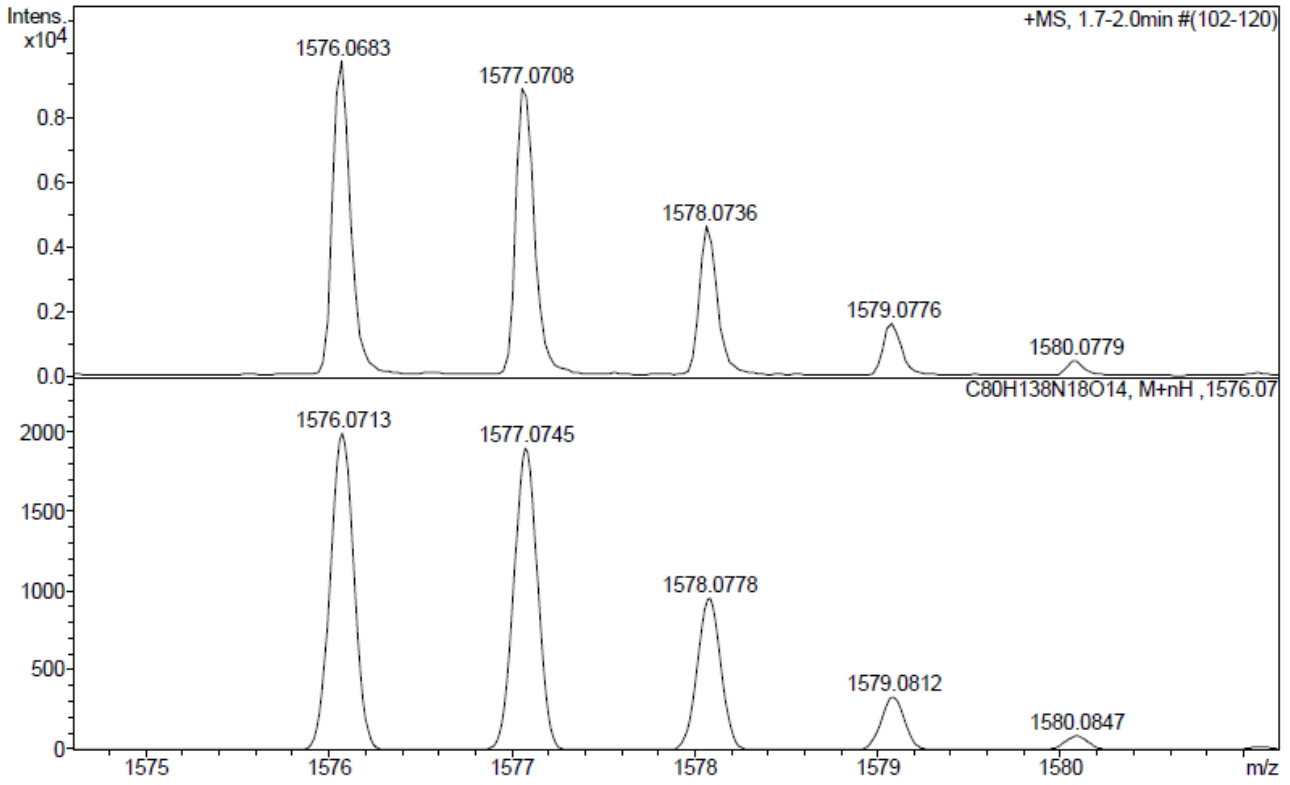
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.415	VV R	0.0536	9889.14844	2990.65039	100.0000
Totals :				9889.14844	2990.65039	

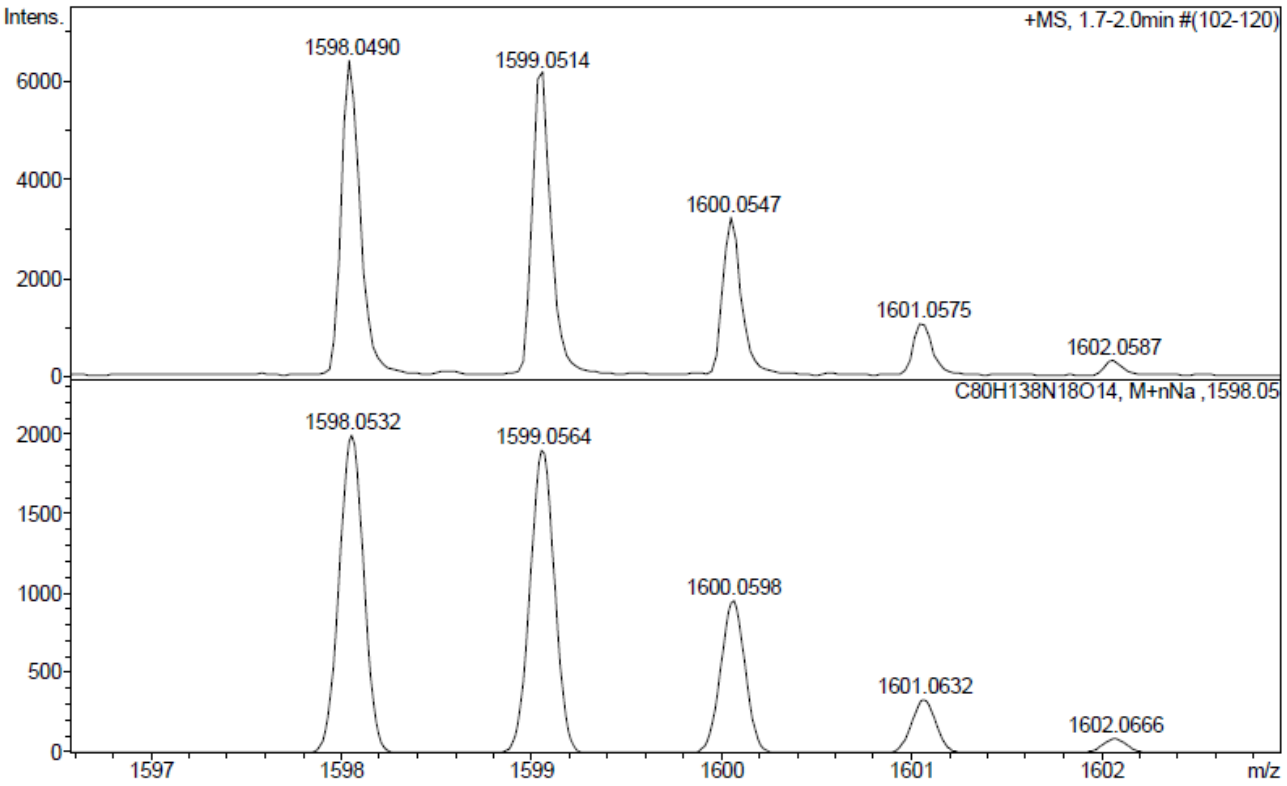
ESI-MS (*m/z*)



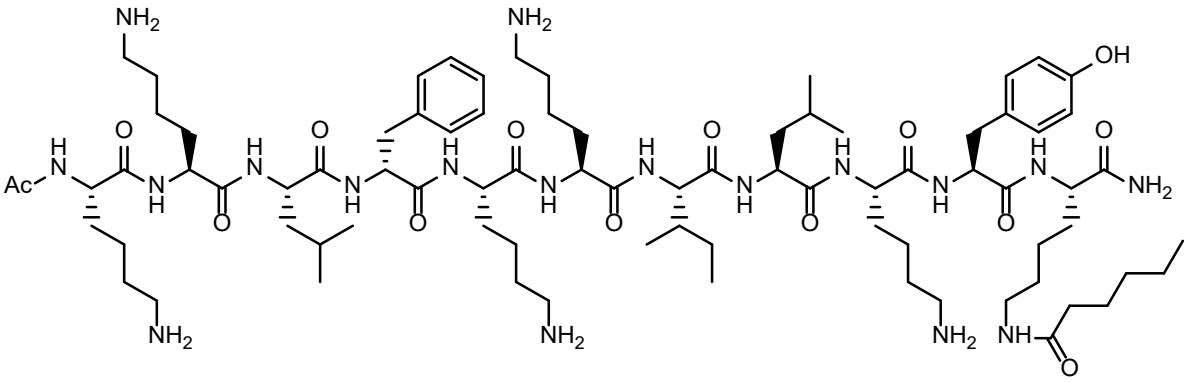
HRMS (*m/z*)


Intens.
x10^4
+MS, 1.7-2.0min #(102-120)
1576.0683
1.0
0.8
0.6
0.4
0.2
0.0
500
1000
1500
2000
2500
m/z

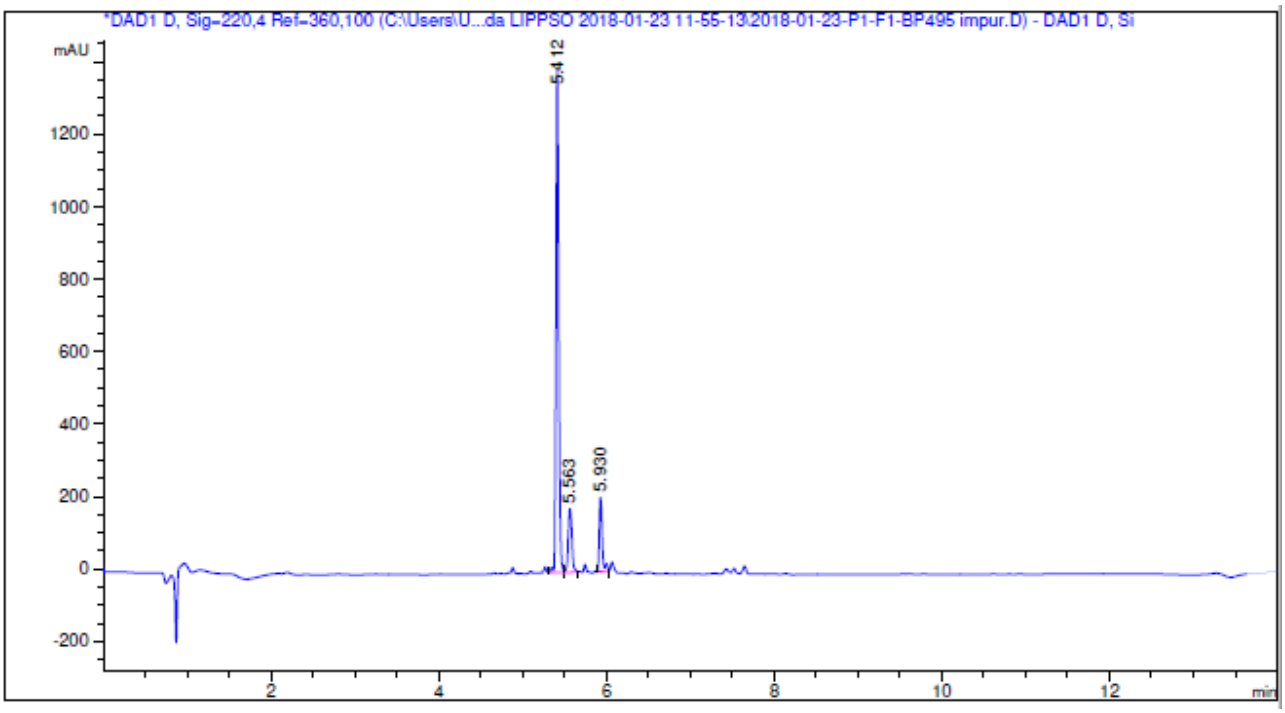

Intens.
x10^4
+MS, 1.7-2.0min #(102-120)
1576.0683
1577.0708
1578.0736
1579.0776
1580.0779
0.8
0.6
0.4
0.2
0.0
C80H138N18O14, M+nH ,1576.07
1576.0713
1577.0745
1578.0778
1579.0812
1580.0847
2000
1500
1000
500
0
1575
1576
1577
1578
1579
1580
m/z


Intens.
+MS, 1.7-2.0min #(102-120)
1598.0490
1599.0514
1600.0547
1601.0575
1602.0587
6000
4000
2000
0
C80H138N18O14, M+nNa ,1598.05
1598.0532
1599.0564
1600.0598
1601.0632
1602.0666
2000
1500
1000
500
0
1597
1598
1599
1600
1601
1602
m/z

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Lys(COC_5H_{11})-NH_2 (BP495)

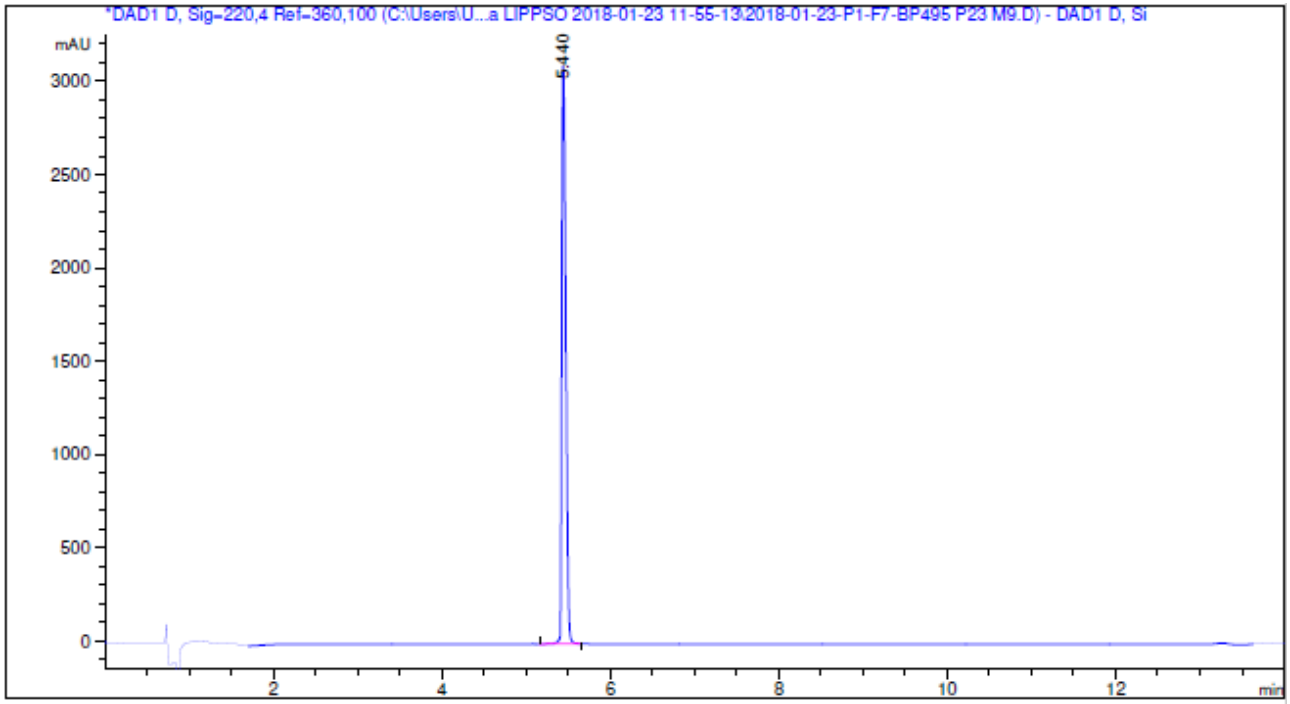


HPLC of crude peptide (λ=220 nm)



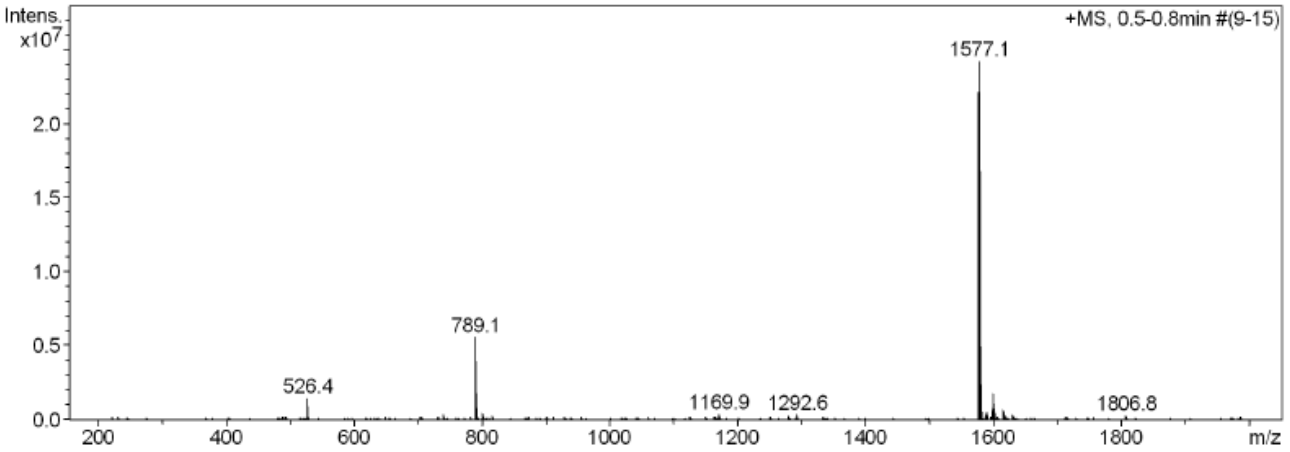
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.412	VV R	0.0356	3169.20239	1389.56665	75.7298
2	5.563	VB	0.0487	535.45313	174.93906	12.7949
3	5.930	BV R	0.0353	480.22589	204.92200	11.4753
Totals :				4184.88141	1769.42770	

HPLC of purified peptide (λ=220 nm)

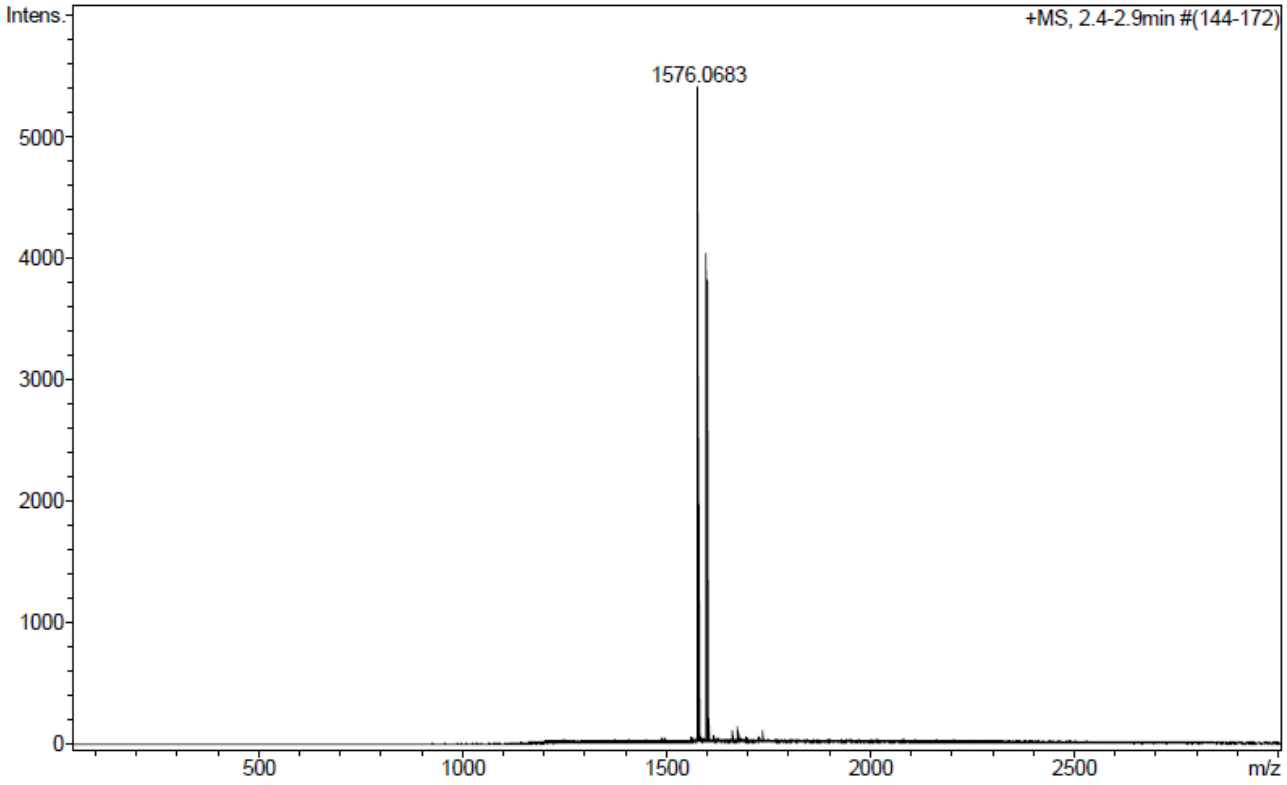


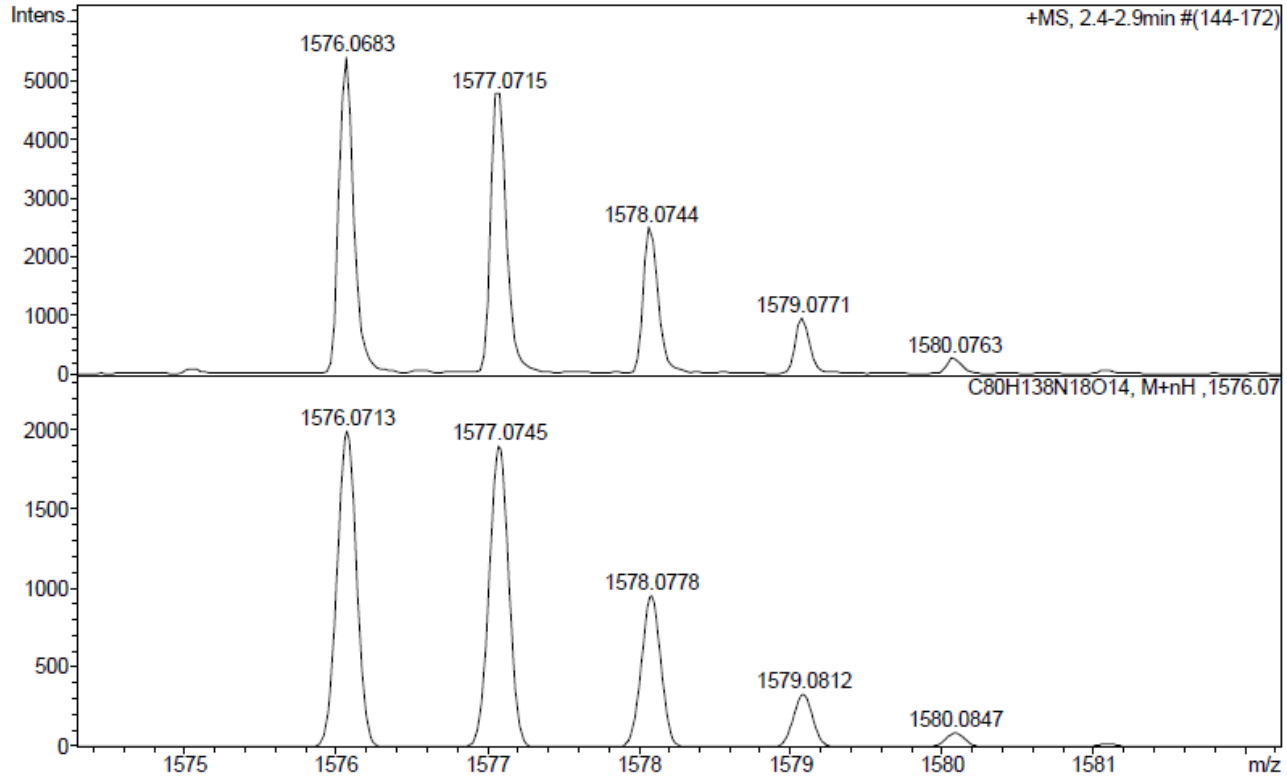
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.440	VB R	0.0545	1.04920e4	3101.66650	100.0000
Totals :				1.04920e4	3101.66650	

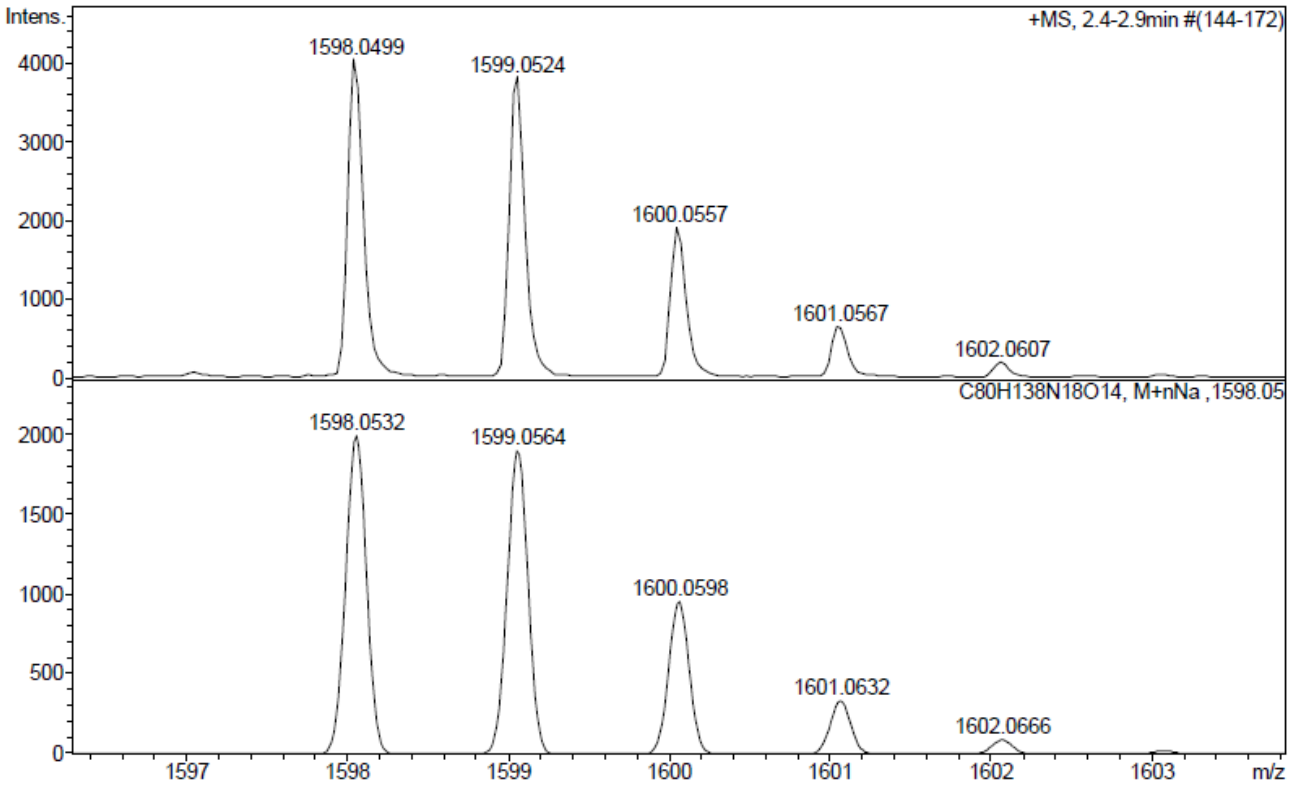
ESI-MS (*m/z*)



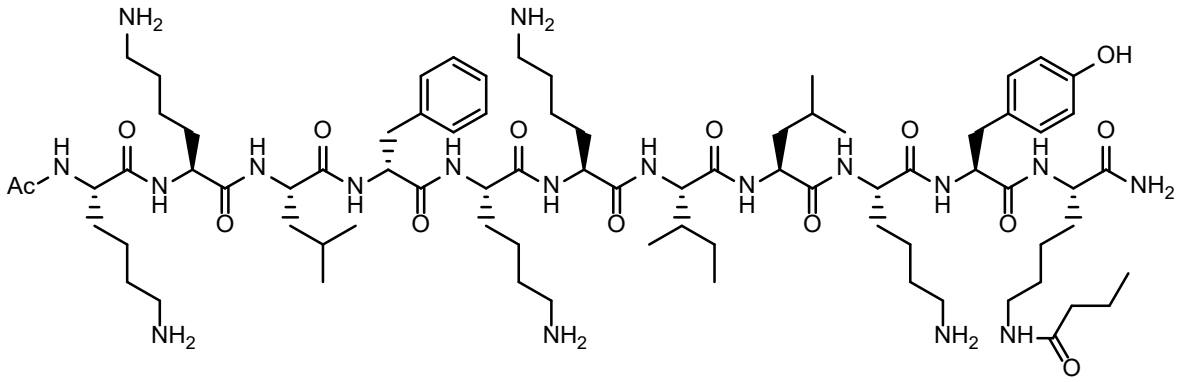
HRMS (*m/z*)


Intens.
+MS, 2.4-2.9min #(144-172)
1576.0683
5000
4000
3000
2000
1000
0
500
1000
1500
2000
2500
m/z

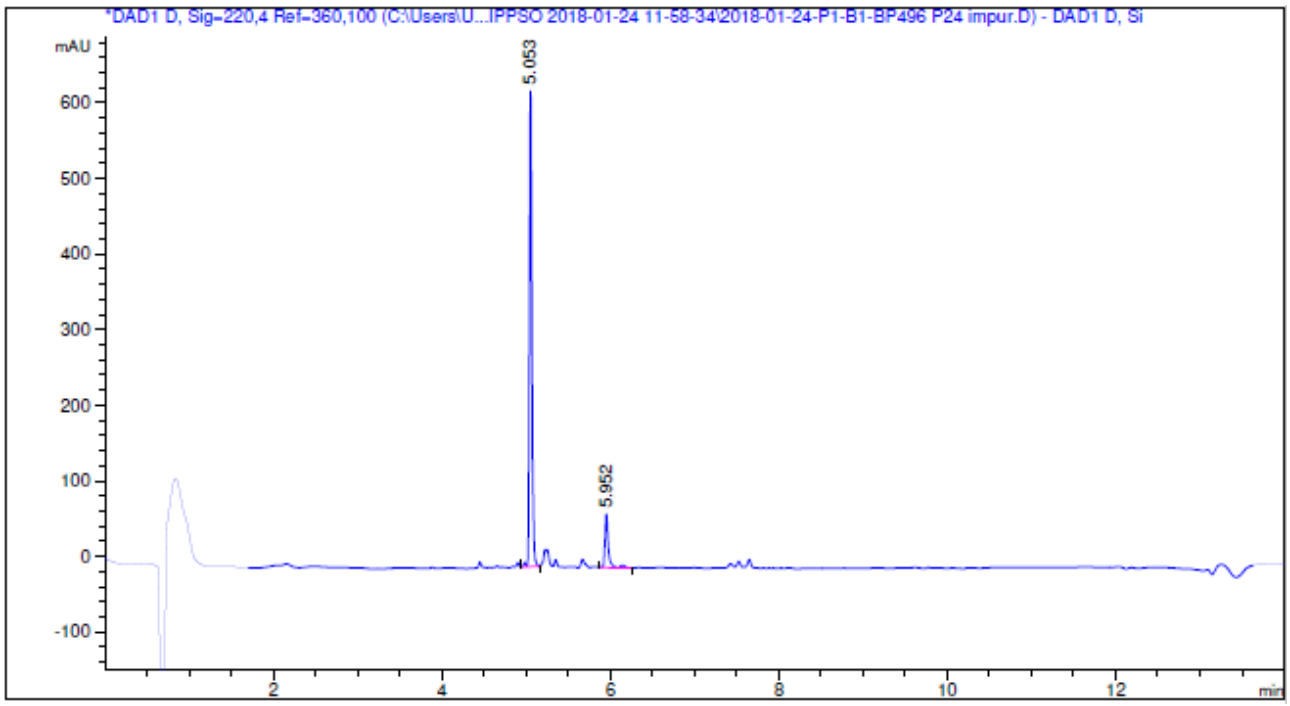

Intens.
+MS, 2.4-2.9min #(144-172)
1576.0683
1577.0715
1578.0744
1579.0771
1580.0763
5000
4000
3000
2000
1000
0
C80H138N18O14, M+nH ,1576.07
1576.0713
1577.0745
1578.0778
1579.0812
1580.0847
2000
1500
1000
500
0
1575
1576
1577
1578
1579
1580
1581
m/z


Intens.
+MS, 2.4-2.9min #(144-172)
1598.0499
1599.0524
1600.0557
1601.0567
1602.0607
4000
3000
2000
1000
0
C80H138N18O14, M+nNa ,1598.05
1598.0532
1599.0564
1600.0598
1601.0632
1602.0666
2000
1500
1000
500
0
1597
1598
1599
1600
1601
1602
1603
m/z

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Lys(COC_3H_7)-NH_2 (BP496)

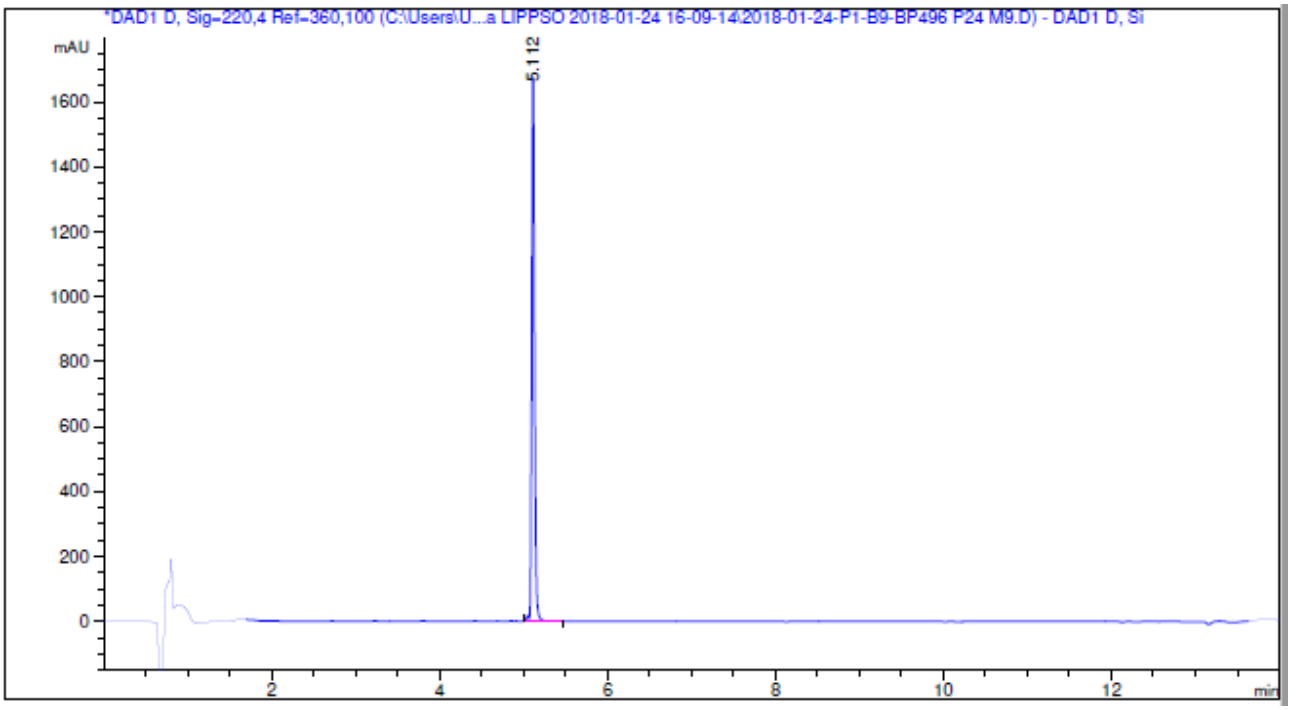


HPLC of crude peptide (λ=220 nm)



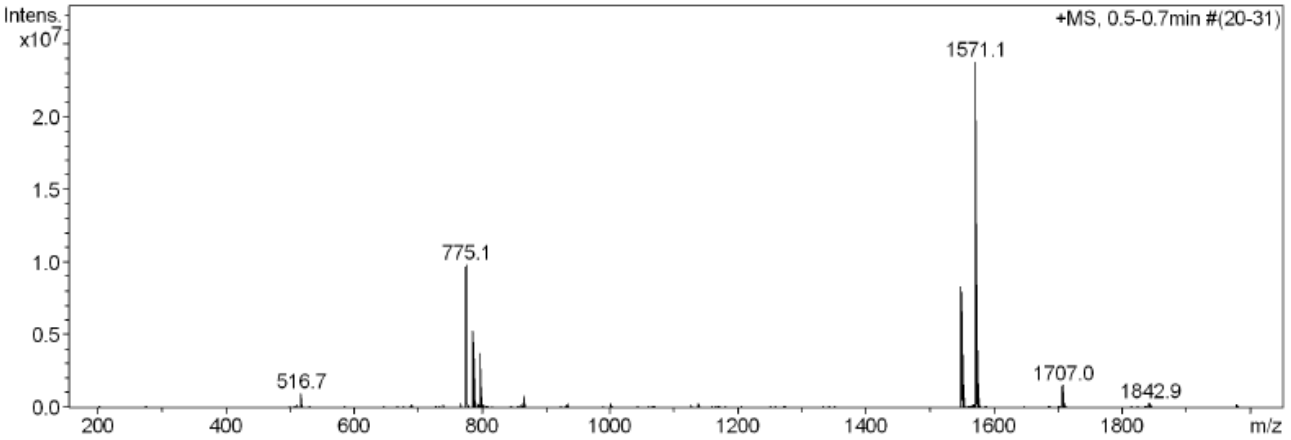
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.053	VB R	0.0325	1323.29224	630.92993	86.8886
2	5.952	VV R	0.0419	199.68292	70.85992	13.1114
Totals :				1522.97516	701.78985	

HPLC of purified peptide (λ=220 nm)

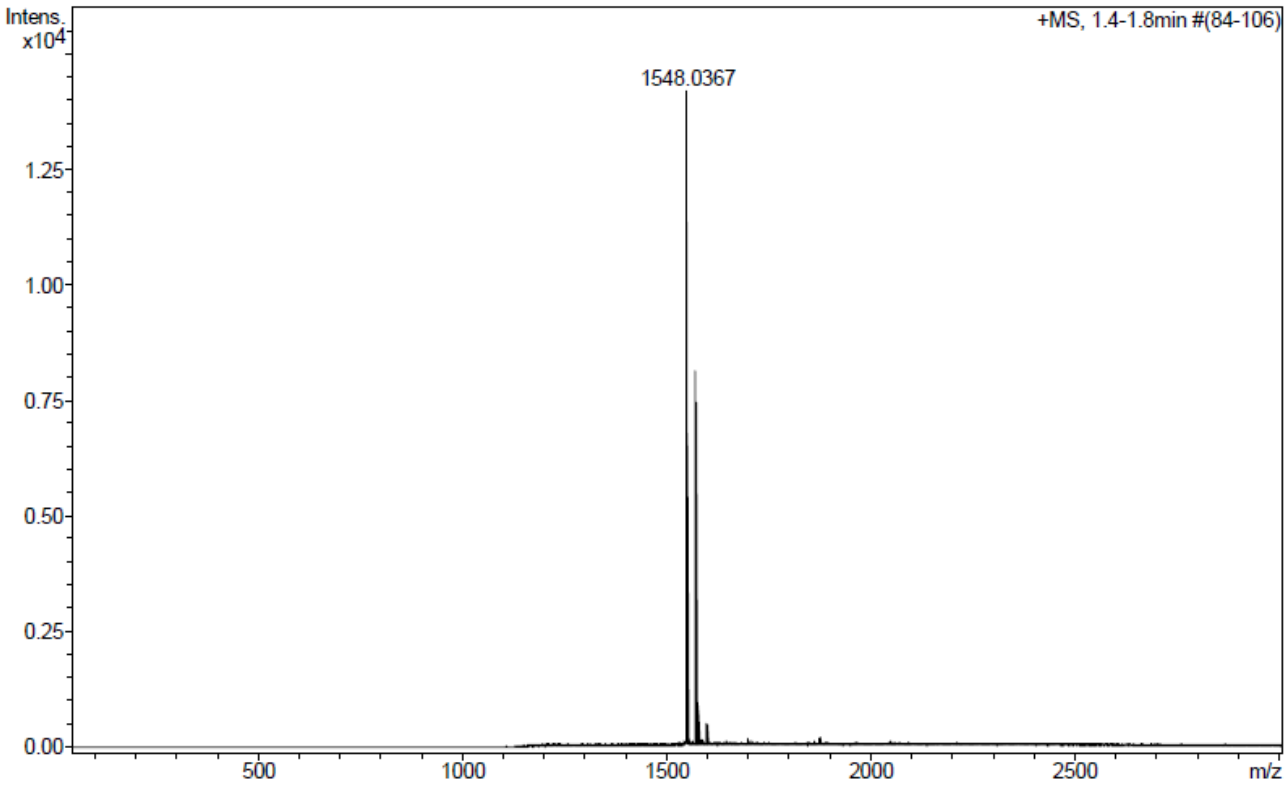


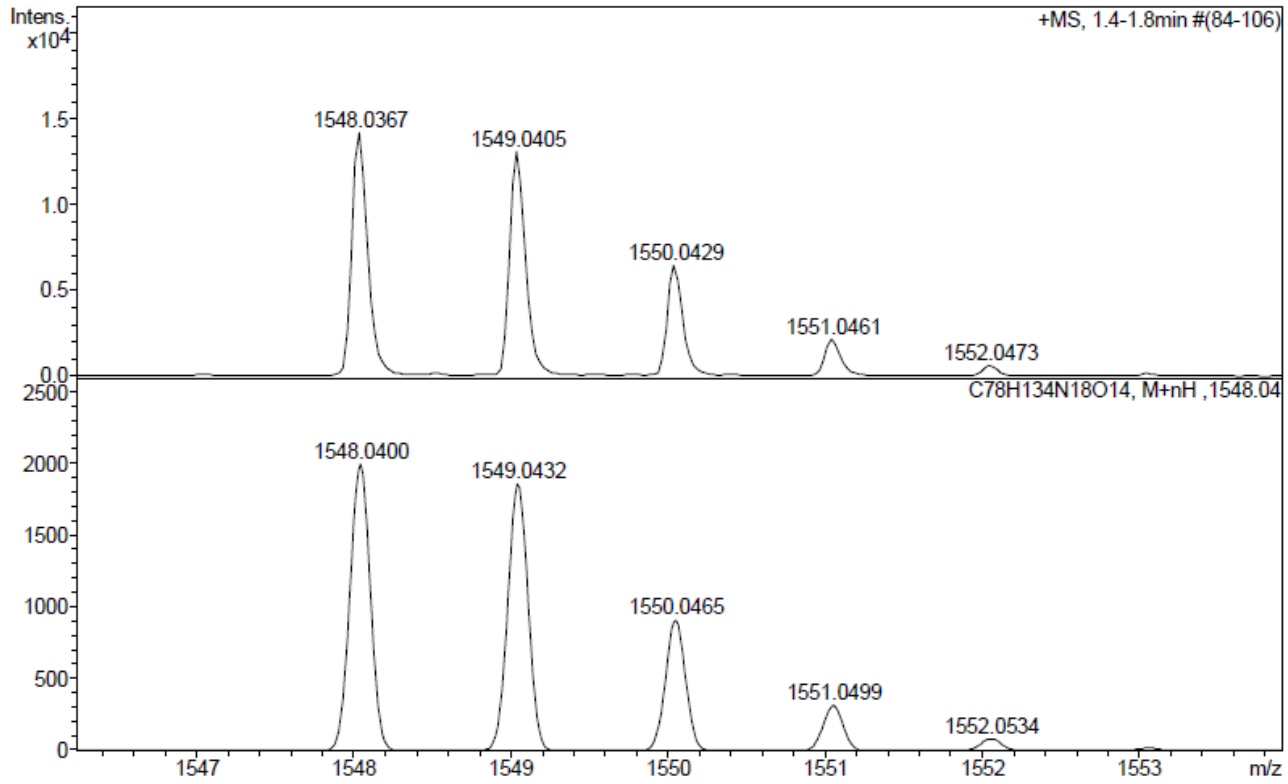
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.112	VV R	0.0361	3886.18408	1673.98193	100.0000
Totals :				3886.18408	1673.98193	

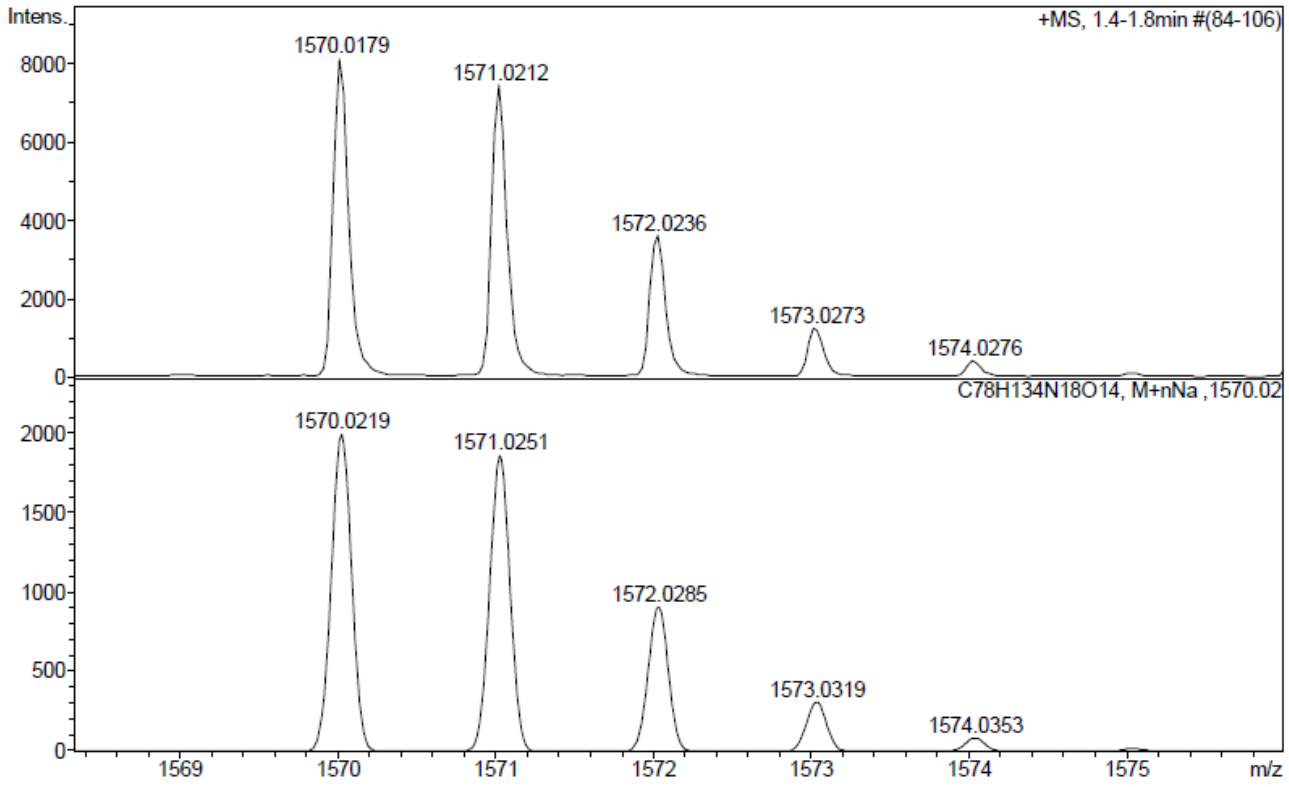
ESI-MS (*m/z*)



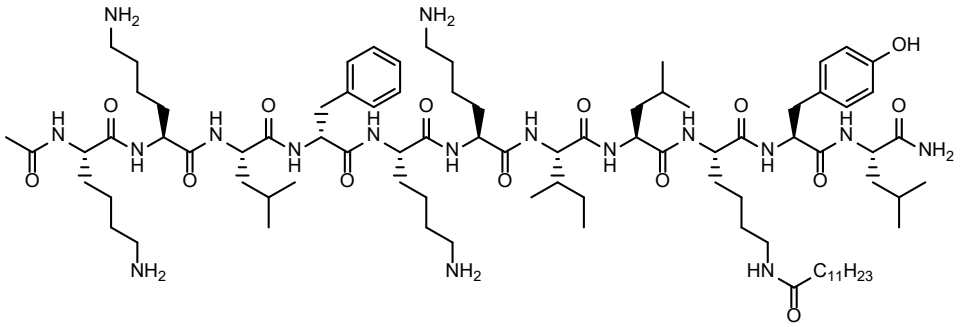
HRMS (*m/z*)


Intens.
x10^4
+MS, 1.4-1.8min #(84-106)
1548.0367
1.25
1.00
0.75
0.50
0.25
0.00
500
1000
1500
2000
2500
m/z

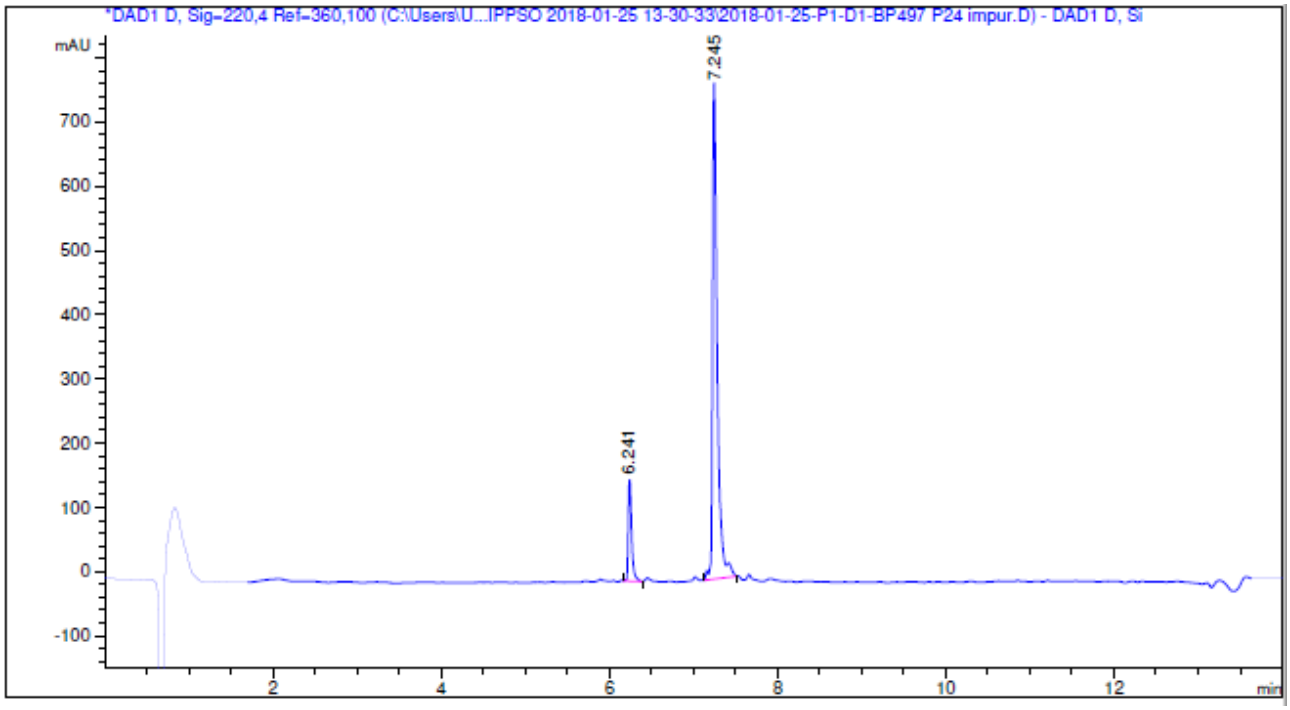

Intens.
x10^4
+MS, 1.4-1.8min #(84-106)
1548.0367
1549.0405
1550.0429
1551.0461
1552.0473
1.5
1.0
0.5
0.0
C78H134N18O14, M+nH ,1548.04
1548.0400
1549.0432
1550.0465
1551.0499
1552.0534
2500
2000
1500
1000
500
0
1547
1548
1549
1550
1551
1552
1553
m/z


Intens.
+MS, 1.4-1.8min #(84-106)
1570.0179
1571.0212
1572.0236
1573.0273
1574.0276
8000
6000
4000
2000
0
C78H134N18O14, M+nNa ,1570.02
1570.0219
1571.0251
1572.0285
1573.0319
1574.0353
2000
1500
1000
500
0
1569
1570
1571
1572
1573
1574
1575
m/z

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys($COC_{11}H_{23}$)-Tyr-Leu-NH_2 (BP497)

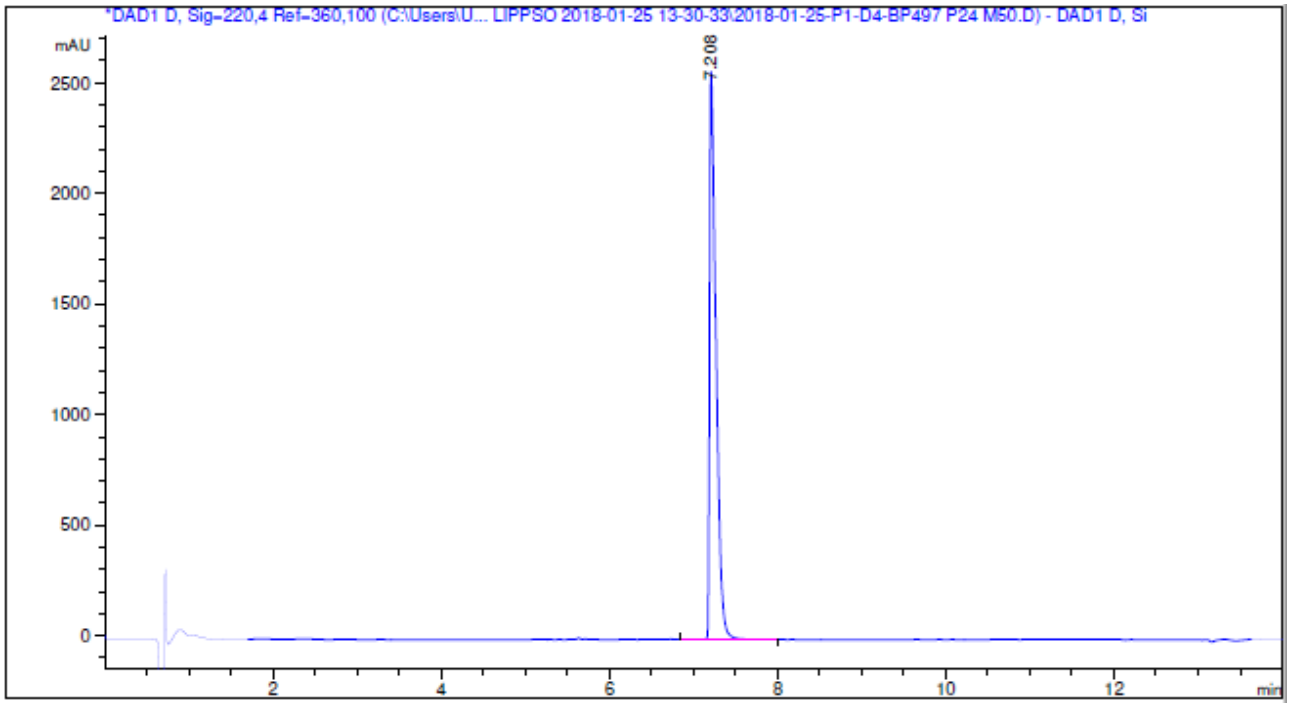


HPLC of crude peptide (λ=220 nm)



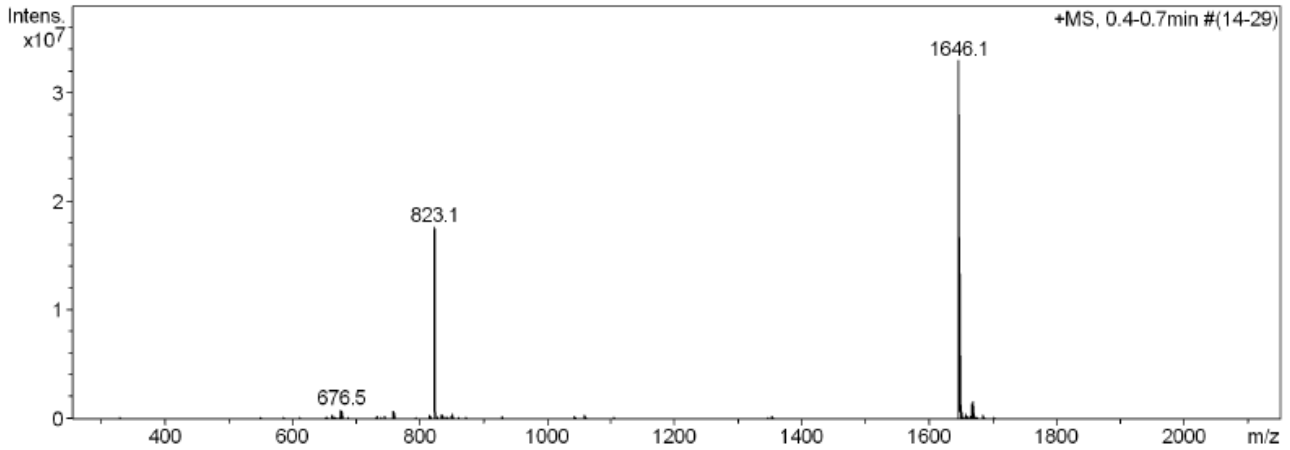
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.241	VB R	0.0399	431.05203	157.88124	12.7336
2	7.245	VV R	0.0556	2954.10278	772.97687	87.2664
Totals :				3385.15482	930.85811	

HPLC of purified peptide (λ=220 nm)

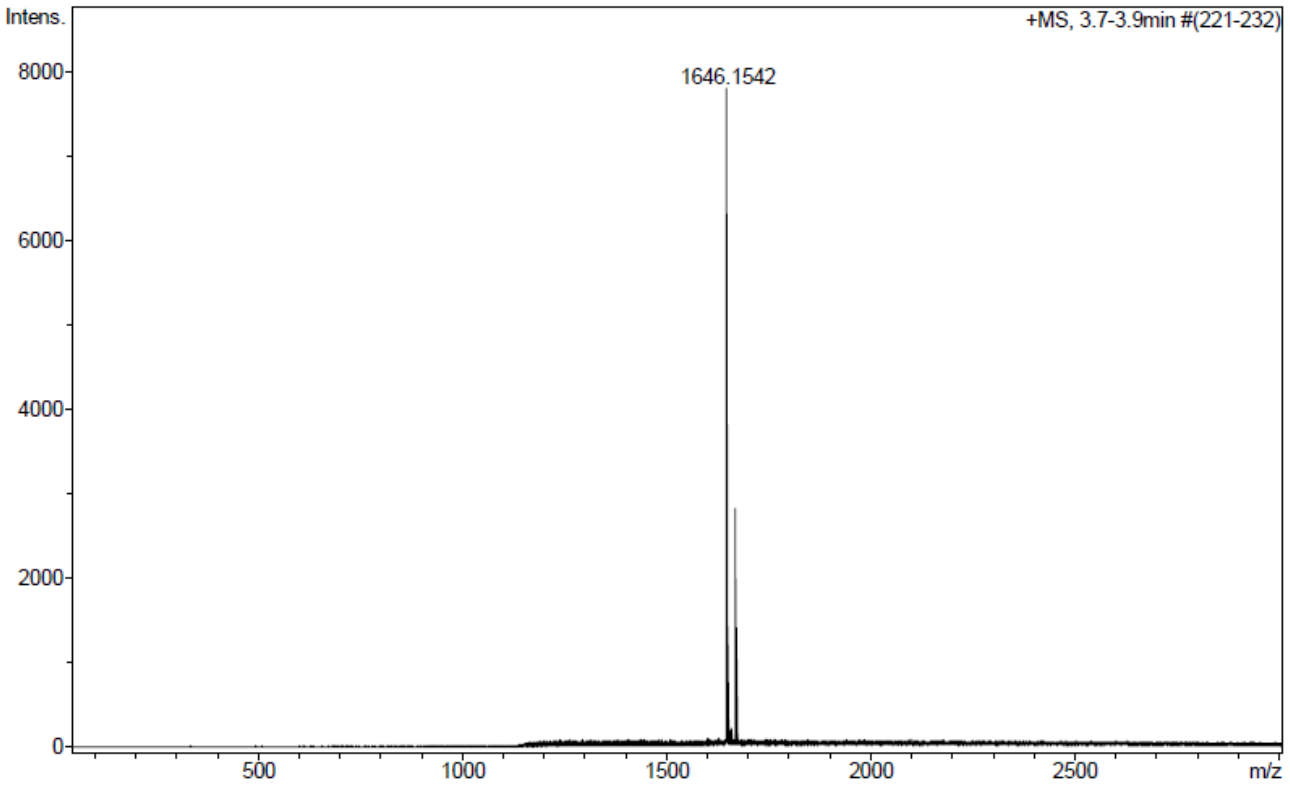


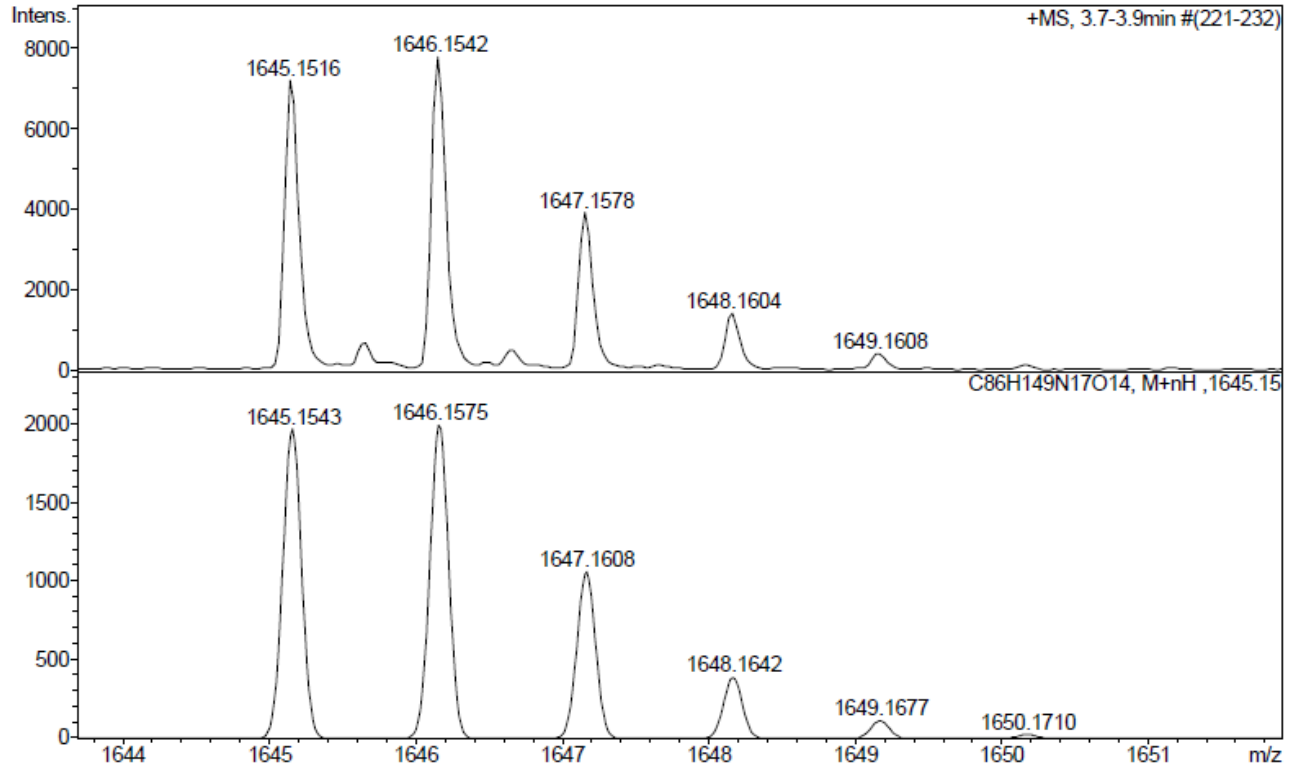
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.208	VB R	0.0804	1.37346e4	2568.37622	100.0000
Totals :				1.37346e4	2568.37622	

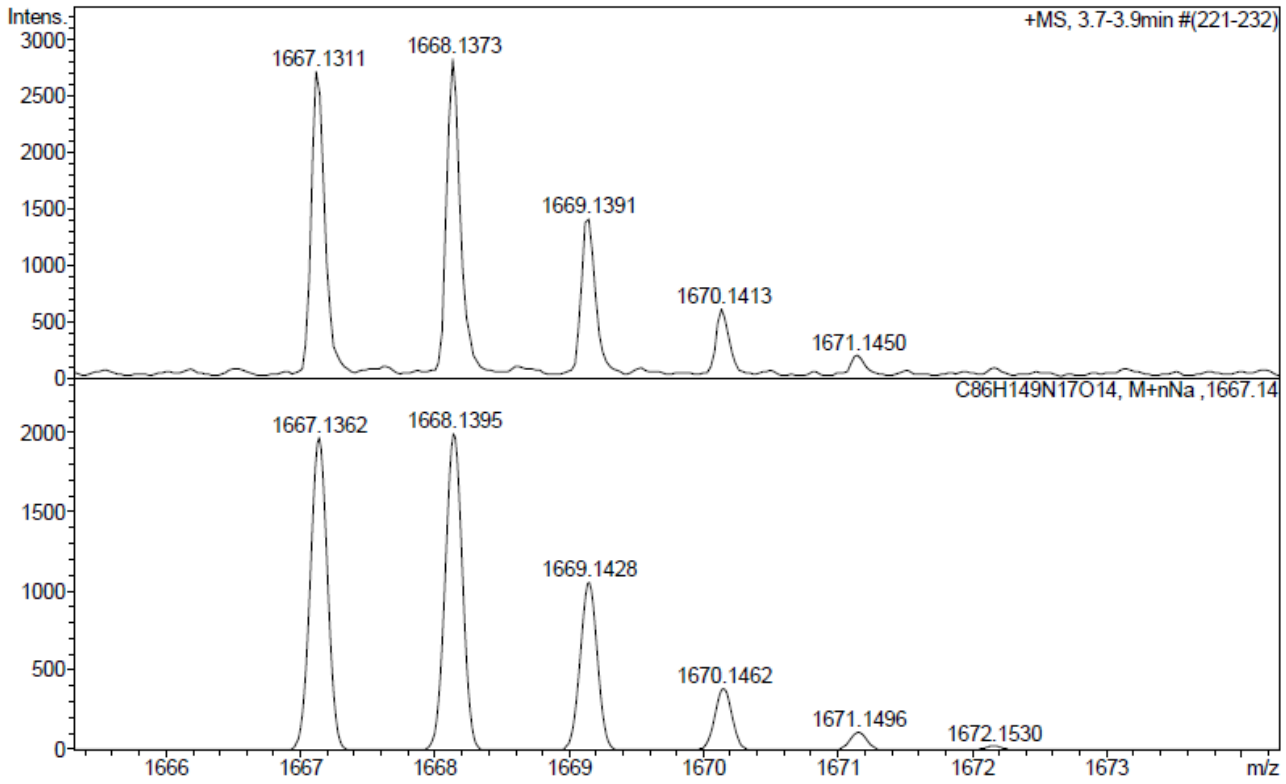
ESI-MS (*m/z*)



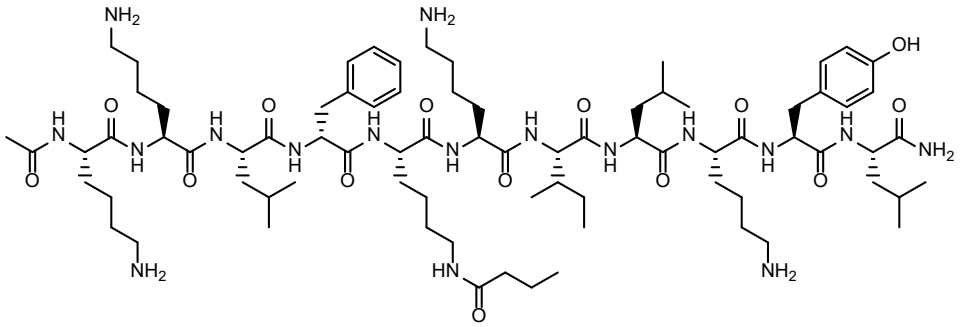
HRMS (*m/z*)


Intens.
+MS, 3.7-3.9min #(221-232)
8000
6000
4000
2000
0
1646.1542
500
1000
1500
2000
2500
m/z

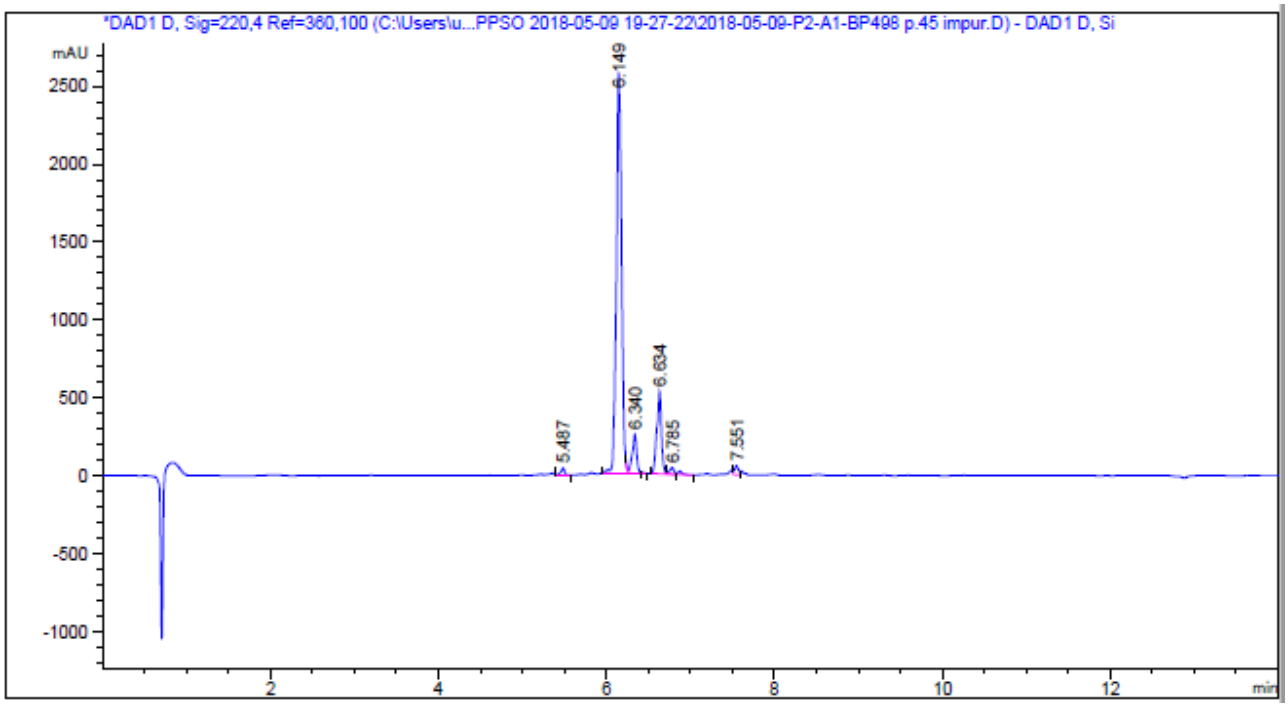

Intens.
+MS, 3.7-3.9min #(221-232)
8000
6000
4000
2000
0
1645.1516
1646.1542
1647.1578
1648.1604
1649.1608
C86H149N17O14, M+nH ,1645.15
2000
1500
1000
500
0
1645.1543
1646.1575
1647.1608
1648.1642
1649.1677
1650.1710
1644
1645
1646
1647
1648
1649
1650
1651
m/z


Intens.
+MS, 3.7-3.9min #(221-232)
1667.1311
1668.1373
1669.1391
1670.1413
1671.1450
C86H149N17O14, M+nNa ,1667.14
1667.1362
1668.1395
1669.1428
1670.1462
1671.1496
1672.1530
m/z

Ac-Lys-Lys-Leu-D-Phe-Lys(COC_3H_7)-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP498)

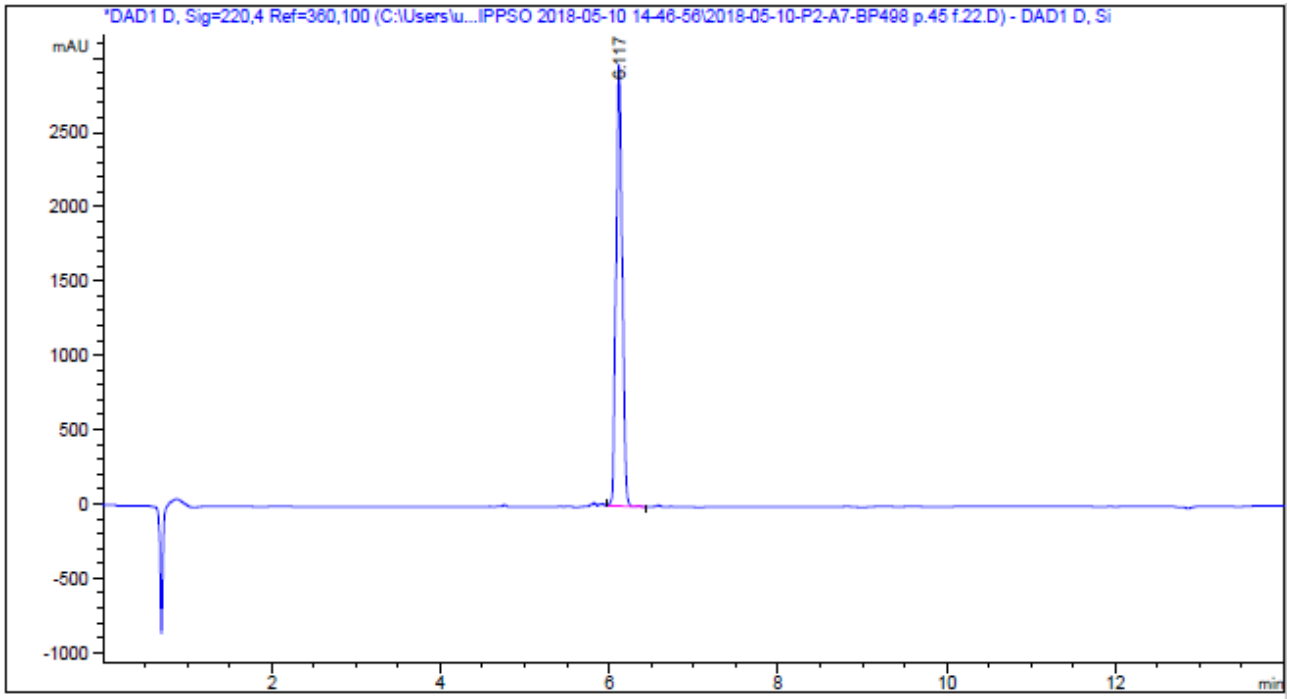


HPLC of crude peptide (λ=220 nm)



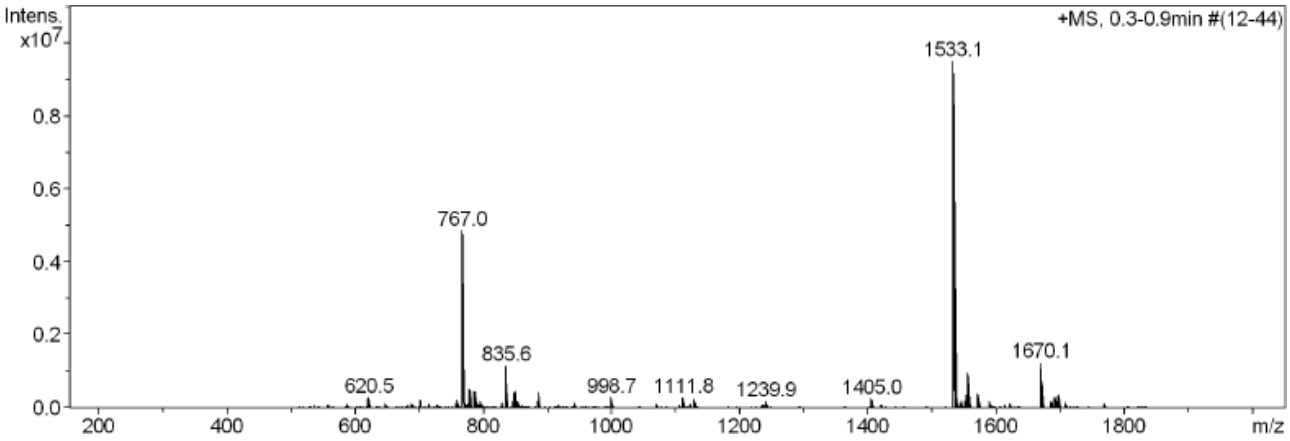
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.487	VB R	0.0464	148.45491	45.10777	1.0160
2	6.149	VV R	0.0632	1.10937e4	2578.84717	75.9247
3	6.340	VV E	0.0510	902.96692	250.56866	6.1799
4	6.634	BV R	0.0567	2112.34912	528.10651	14.4569
5	6.785	VV E	0.0489	152.63356	43.54723	1.0446
6	7.551	VV	0.0518	201.33051	57.53705	1.3779
Totals :				1.46114e4	3503.71439	

HPLC of purified peptide (λ=220 nm)

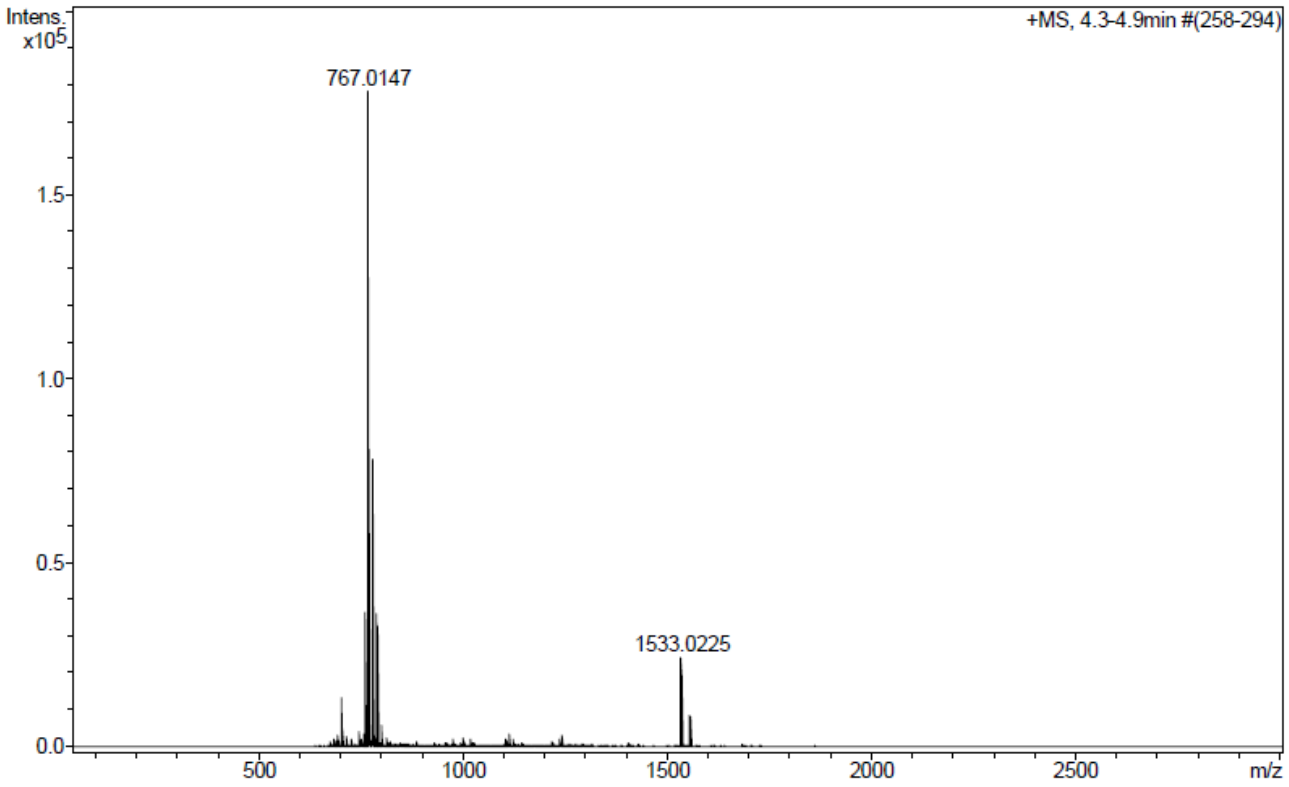


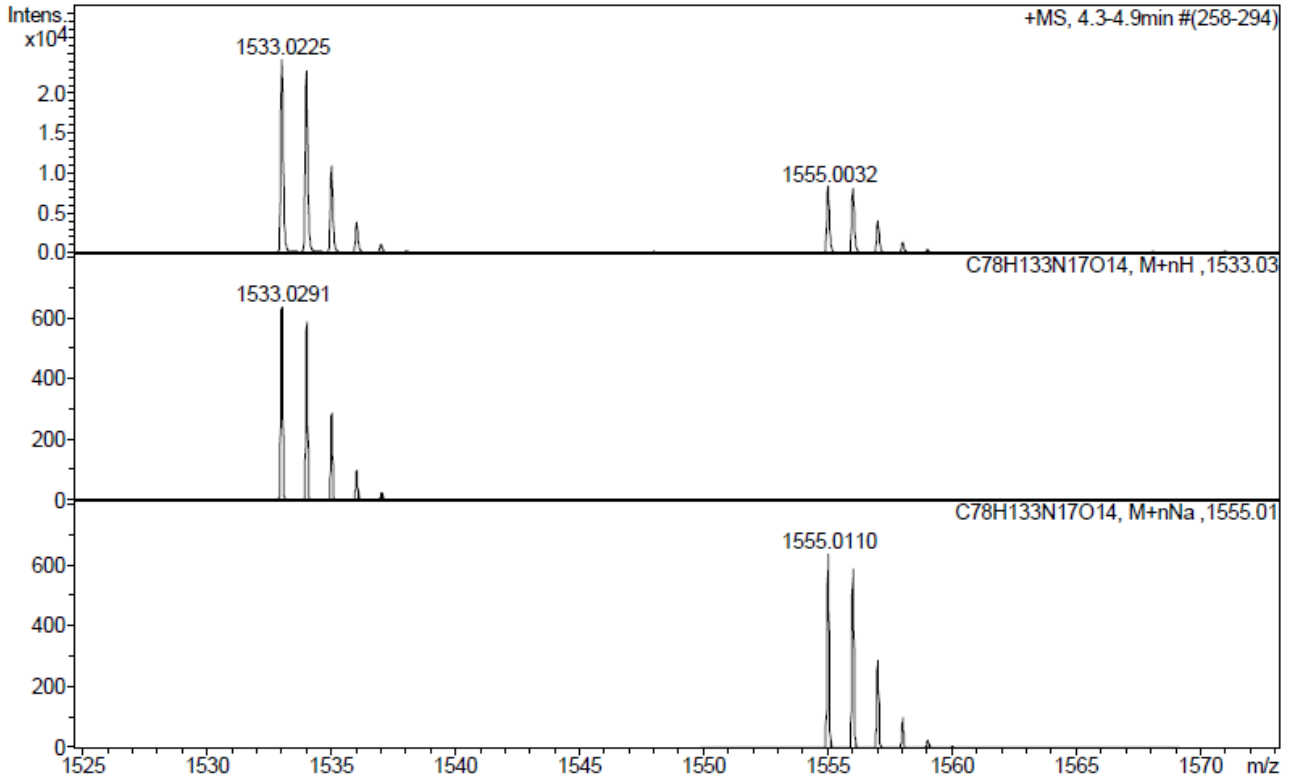
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.117	BV R	0.0755	1.51550e4	2973.04297	100.0000
Totals :				1.51550e4	2973.04297	

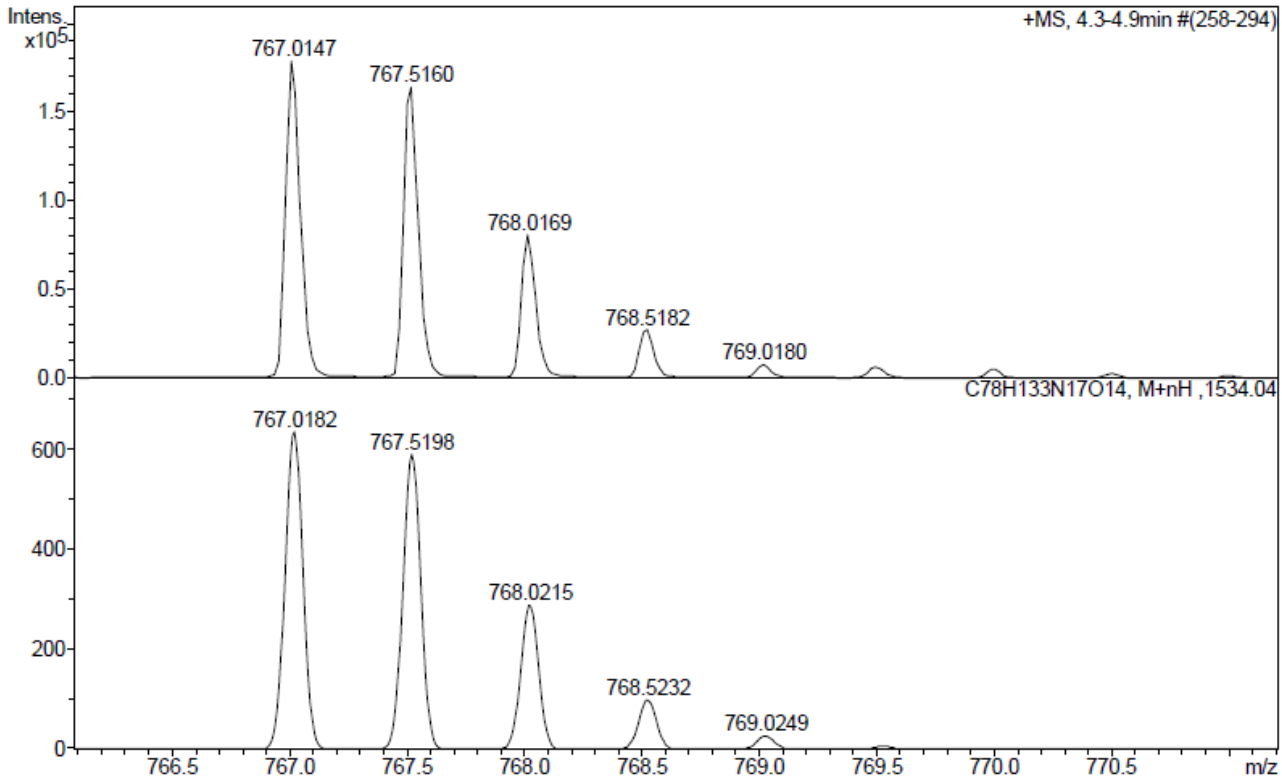
ESI-MS (*m/z*)



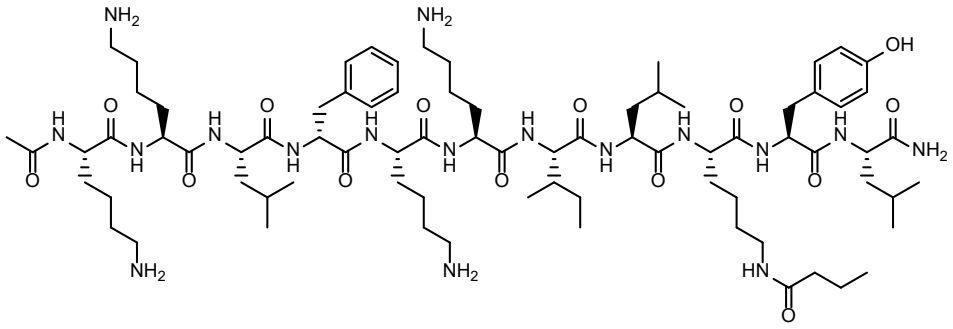
HRMS (*m/z*)


Intens.
x10^5
+MS, 4.3-4.9min #(258-294)
767.0147
1533.0225
1.5
1.0
0.5
0.0
500
1000
1500
2000
2500
m/z

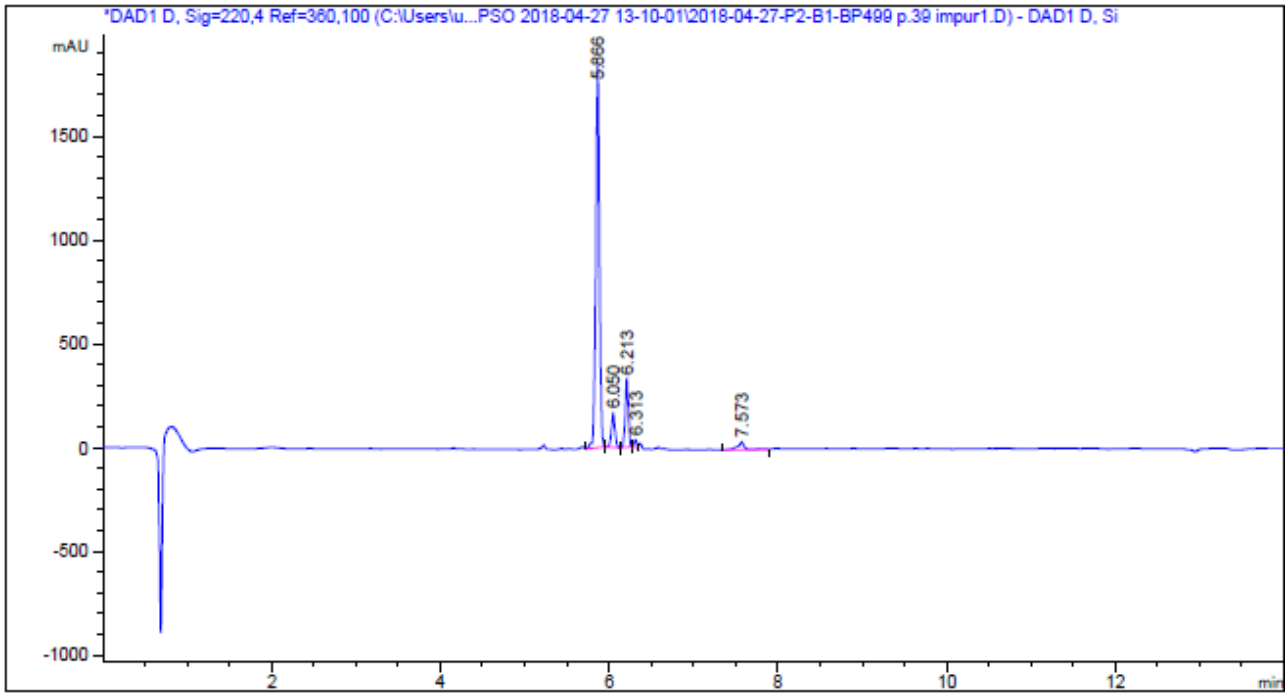

Intens.
x10^4
+MS, 4.3-4.9min #(258-294)
1533.0225
1555.0032
2.0
1.5
1.0
0.5
0.0
C78H133N17O14, M+nH ,1533.03
1533.0291
600
400
200
0
C78H133N17O14, M+nNa ,1555.01
1555.0110
600
400
200
0
1525
1530
1535
1540
1545
1550
1555
1560
1565
1570
m/z


Intens.
x10^5
+MS, 4.3-4.9min #(258-294)
767.0147
767.5160
768.0169
768.5182
769.0180
1.5
1.0
0.5
0.0
C78H133N17O14, M+nH ,1534.04
767.0182
767.5198
768.0215
768.5232
769.0249
600
400
200
0
766.5
767.0
767.5
768.0
768.5
769.0
769.5
770.0
770.5
m/z

Ac-Lys-Lys-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys(COC_3H_7)-Tyr-Leu-NH_2 (BP499)

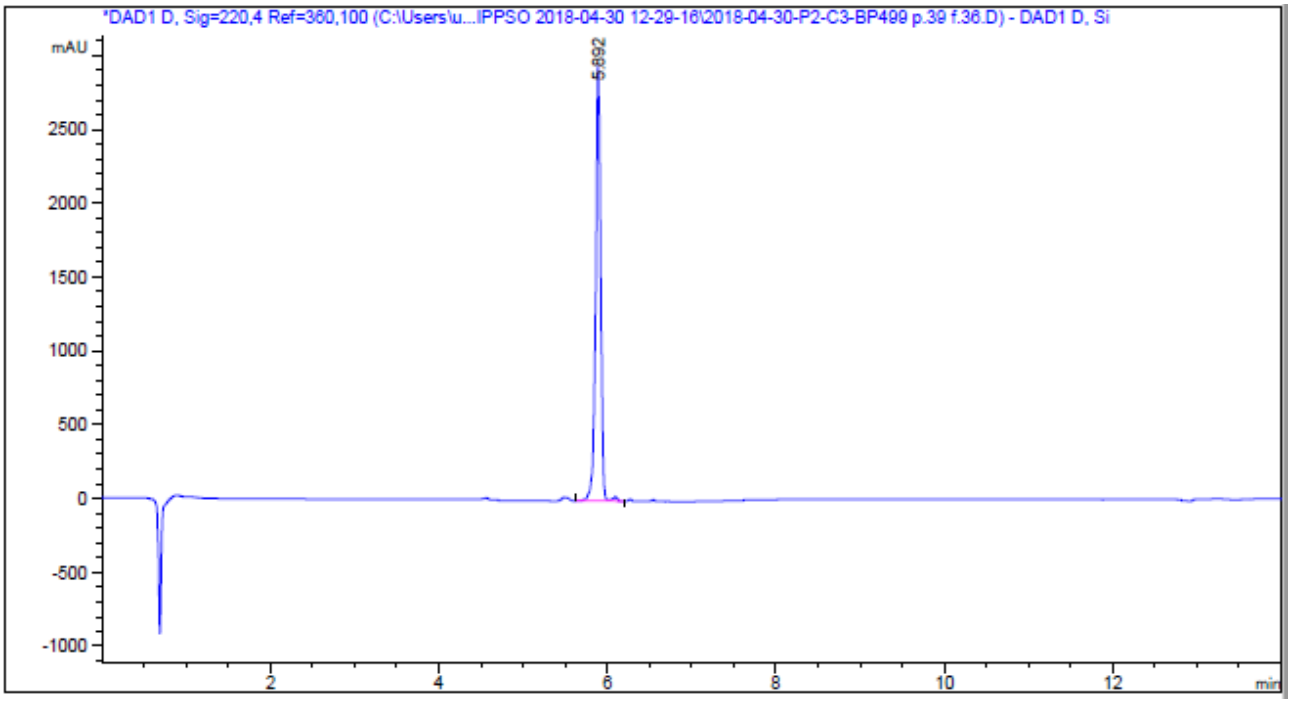


HPLC of crude peptide (λ=220 nm)



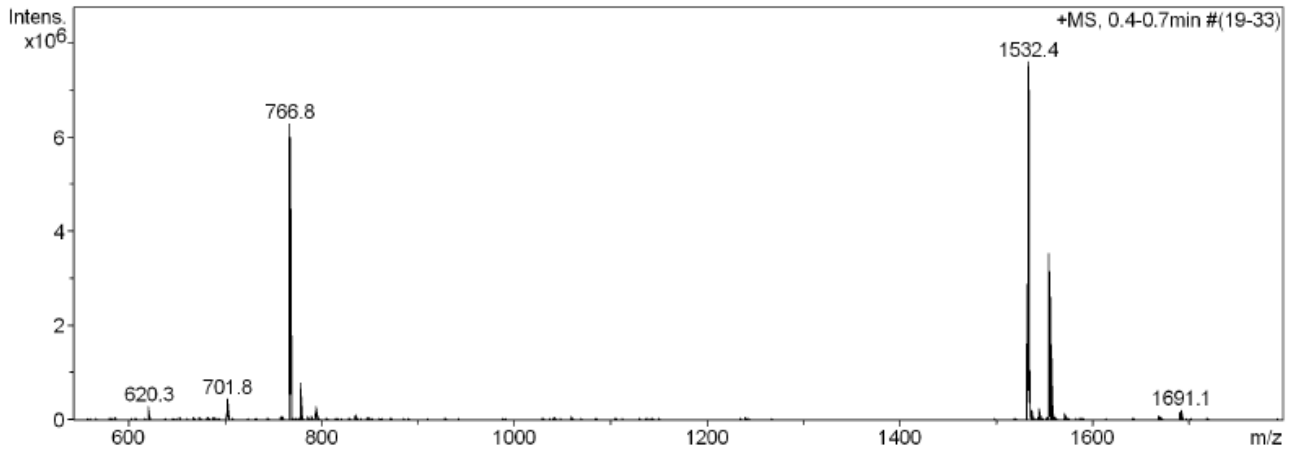
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.866	VB R	0.0443	5598.51953	1849.33667	77.5439
2	6.050	BB	0.0433	478.38898	162.94824	6.6261
3	6.213	BB	0.0390	849.00946	329.78500	11.7594
4	6.313	BV	0.0370	90.36411	37.69422	1.2516
5	7.573	BV R	0.0764	203.52594	36.29560	2.8190
Totals :				7219.80802	2416.05974	

HPLC of purified peptide (λ=220 nm)

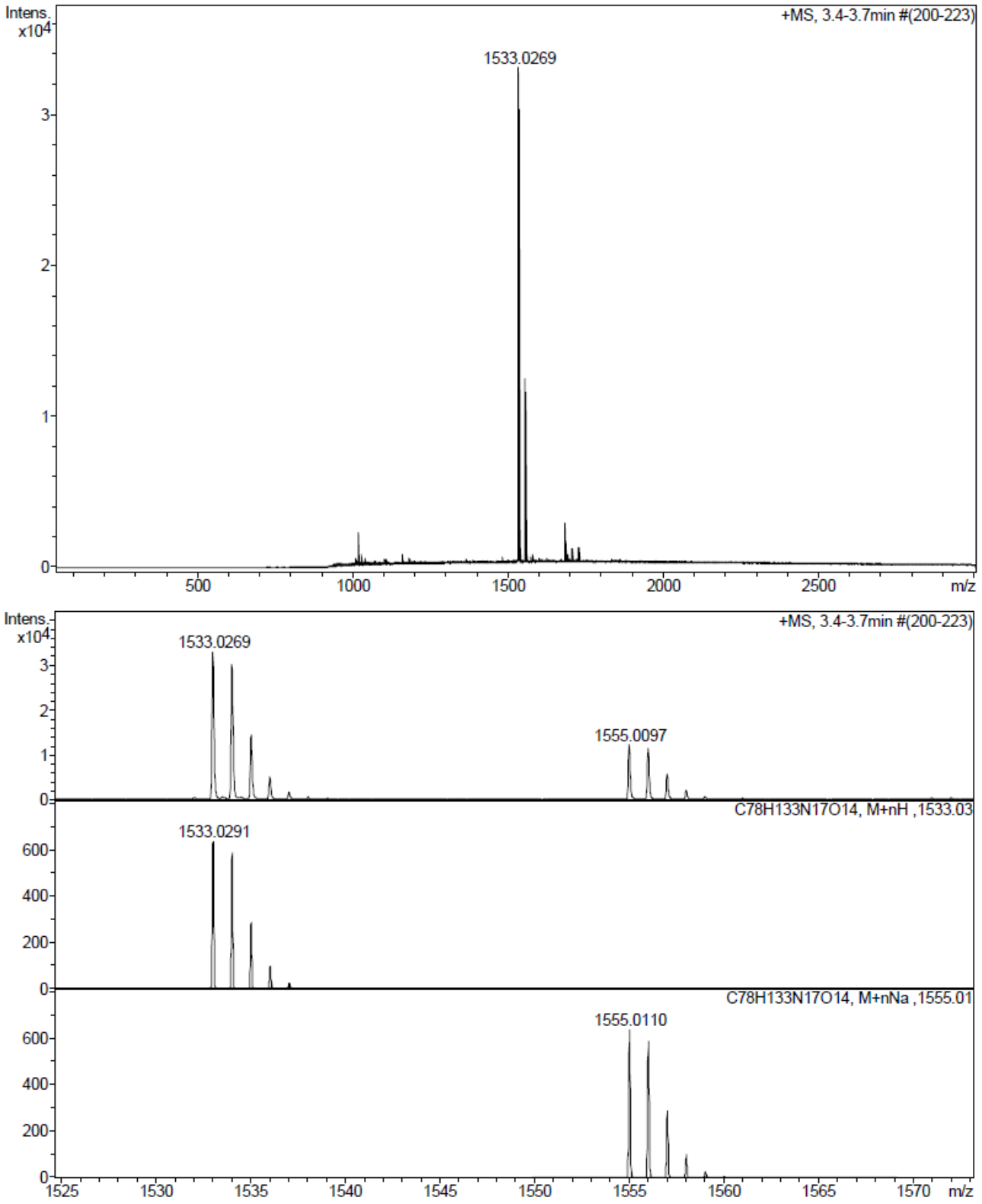


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.892	BV R	0.0617	1.23197e4	2951.55957	100.0000
Totals :				1.23197e4	2951.55957	

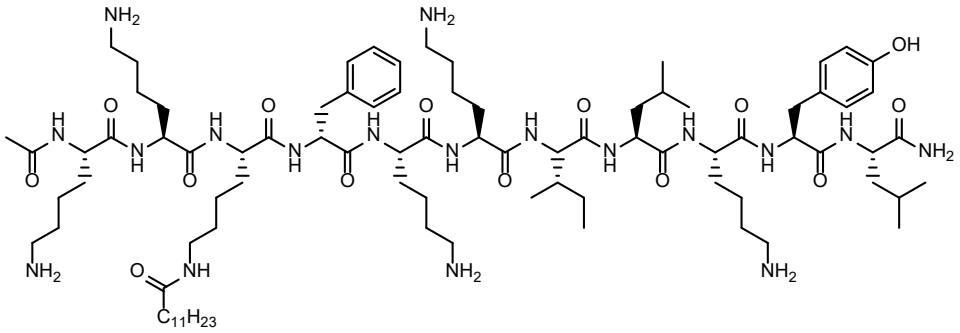
ESI-MS (*m/z*)



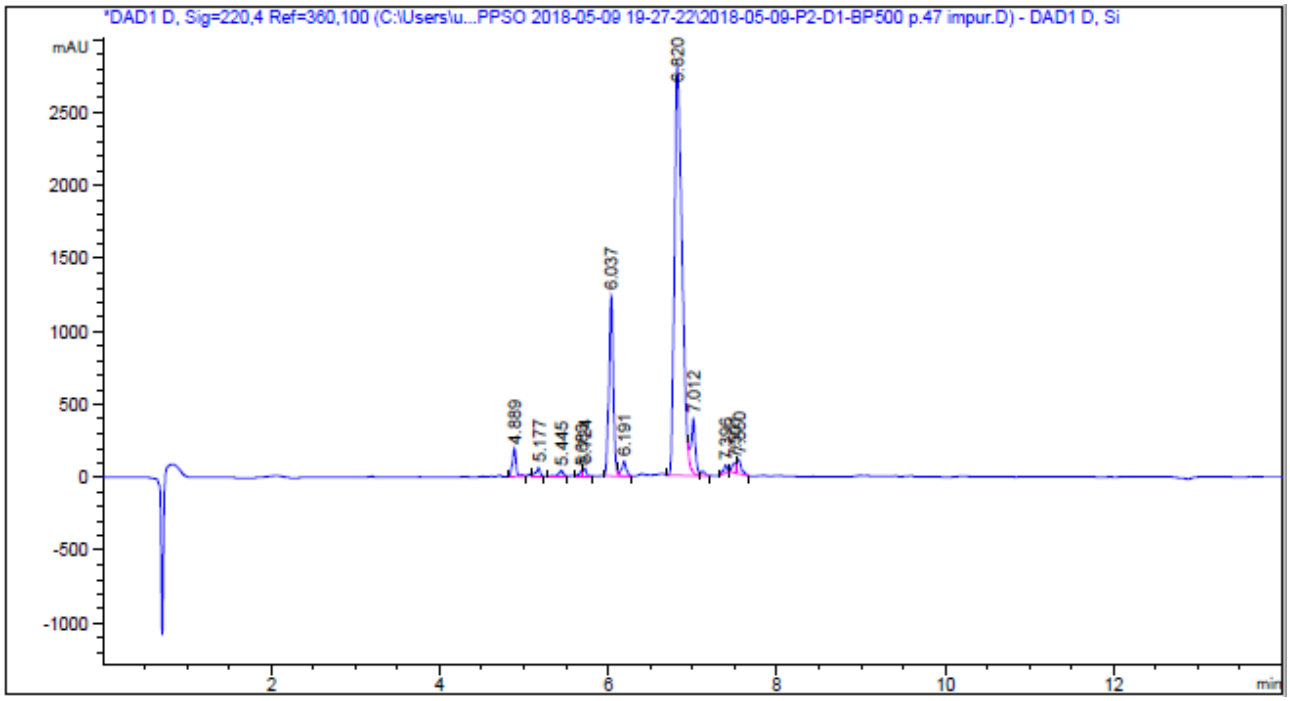
HRMS (m/z)


Intens.
x10^4
+MS, 3.4-3.7min #(200-223)
1533.0269
3
2
1
0
500
1000
1500
2000
2500
m/z
Intens.
x10^4
+MS, 3.4-3.7min #(200-223)
1533.0269
1555.0097
C78H133N17O14, M+nH ,1533.03
1533.0291
600
400
200
0
C78H133N17O14, M+nNa ,1555.01
1555.0110
1525
1530
1535
1540
1545
1550
1555
1560
1565
1570
m/z

Ac-Lys-Lys($COC_{11}H_{23}$)-Leu-D-Phe-Lys-Lys-Ile-Leu-Lys-Tyr-Leu-NH_2 (BP500)

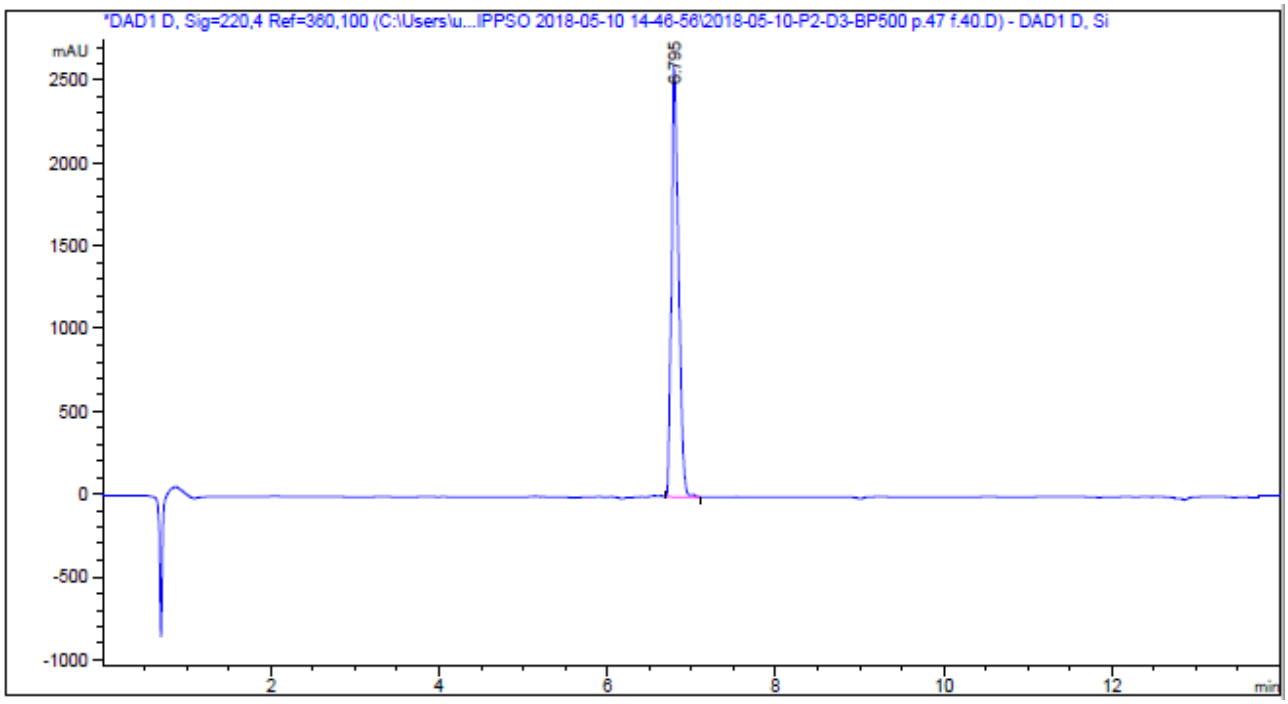


HPLC of crude peptide (λ=220 nm)



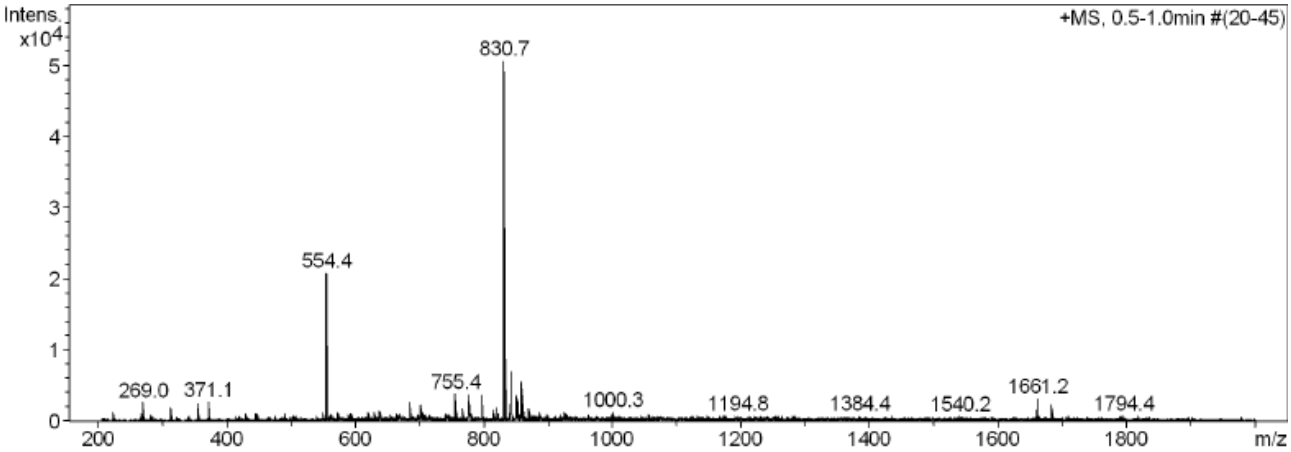
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.889	BV R	0.0428	573.98651	192.62531	2.2259
2	5.177	VB	0.0478	194.40025	56.93281	0.7539
3	5.445	VB R	0.0522	155.32494	41.03360	0.6023
4	5.683	BV	0.0402	88.94859	32.20647	0.3449
5	5.724	VB	0.0343	124.03711	52.92344	0.4810
6	6.037	BV R	0.0531	4459.11426	1236.56287	17.2920
7	6.191	VB E	0.0551	397.45981	102.88657	1.5413
8	6.820	BV R	0.0960	1.77881e4	2804.05859	68.9804
9	7.012	VV E	0.0503	1283.47070	371.63638	4.9772
10	7.396	BB	0.0442	159.22202	52.83167	0.6174
11	7.501	BV	0.0502	202.72284	65.27905	0.7861
12	7.550	VB	0.0532	360.41031	97.30477	1.3976
Totals :				2.57872e4	5106.28153	

HPLC of purified peptide (λ=220 nm)

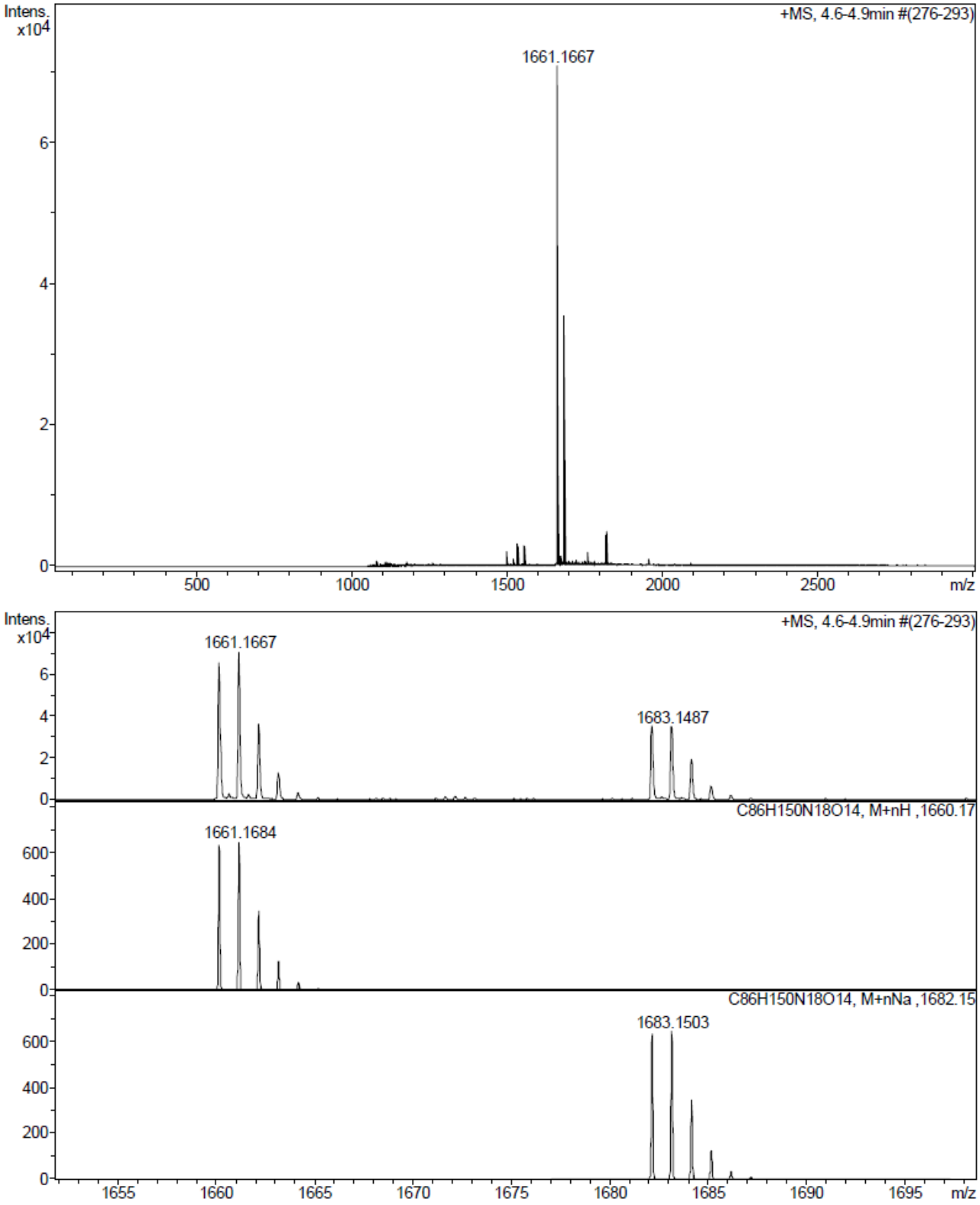


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.795	BV R	0.0854	1.51681e4	2586.43701	100.0000
Totals :				1.51681e4	2586.43701	

ESI-MS (*m/z*)



HRMS (*m/z*)


Intens.
x10^4
+MS, 4.6-4.9min #(276-293)
1661.1667
6
4
2
0
500
1000
1500
2000
2500
m/z
Intens.
x10^4
+MS, 4.6-4.9min #(276-293)
1661.1667
1683.1487
6
4
2
0
C86H150N18O14, M+nH ,1660.17
1661.1684
600
400
200
0
C86H150N18O14, M+nNa ,1682.15
1683.1503
600
400
200
0
1655
1660
1665
1670
1675
1680
1685
1690
1695
m/z

4. NMR experiments of lipopeptides BP389 and BP475

BP389

^{1}H-NMR (400 MHz, 20 mM phosphate buffer pH = 6.5 H_2O/D_2O (90:10)) *δ* (ppm): 0.77-0.89 (m, 29H, CH_3-butanoyl, δ-CH_3-Ile, 6 × δ-CH_3-Leu, γ-CH_3-Ile, δ-CH_2-Lys), 1.22-1.81 (m, 48 H, β-CH_2-butanoyl, β-CH_2-Ile, γ-CH_2-Ile, 3 × β-CH_2-Leu, 3 × γ-CH-Leu, 6 × β-CH_2-Lys, 6 × γ-CH_2-Lys, 5 × δ-CH_2-Lys), 1.97 (s, 3H, CH_3CO), 2.14 (t, *J* = 7.57 Hz, 2H, α-CH_2-butanoyl), 2.88-3.02 (m, 12H, 5 × ε-CH_2-Lys, β-CH_2-Phe), 3.09-3.16 (m, 2H, ε-CH_2-Lys^{10}), 4.03-4.07 (m, 1H, α-CH-Ile), 4.12-4.33 (m, 5H, 5 x α-CH-Lys, α-CH-Lys$^{10.}$ 3 × α-CH-Leu), 4.52-4.55 (m, α-CH-Phe), 7.09 (s, 1H, $CONH_2$), 7.18 (d, *J* = 6.96 Hz, 2H, 2 × *o*-CH-Phe$_{arom}$), 7.22-7.31 (m, 3H, 2 × *m*-CH-Phe$_{arom}$, *p*-CH-Phe$_{arom}$), 7.58 (s, 1H, $CONH_2$), 8.02 (t, *J* = 5.94 Hz, 1H, ζ-NH-Lys^{10}), 8.16-8.22 (m, 3H, α-NH-Phe, α-NH-Leu, α-NH-Lys), 8.29-8.36 (m, 6H, 4 × α-NH-Lys, α-NH-Ile, α-NH-Leu) 8.40-8.42 (m, 2H, α-NH-Lys^{10}, α-NH-Leu).

^{1}H-NMR (400 MHz, 20 mM phosphate buffer at pH = 6.5 with H_2O/D_2O (90:10) containing 30% CF_3CD_2OD) δ (ppm): 0.69-0.72 (m, 6H, 2 × δ-CH_3-Leu^8), 0.77-0.92 (m, 18H, 2 × δ-CH_3-Leu^{11}, δ-CH_3-Ile^7, δ-CH_3-Leu^3, CH_3-butanoyl, δ'-CH_3-Leu^3), 1.03-1.11 (m, 3H, γ-CH_3-Ile^7), 1.35-1.98 (m, 48H, γ-CH-Leu^8, δ-CH_2-Lys^1, δ-CH_2-Lys^2, δ-CH_2-Lys^5, δ-CH_2-Lys^6, δ-CH_2-Lys^9, δ-CH_2-Lys^{10}, γ-CH-Leu^{11}, β-CH_2-butanoyl, γ-CH-Leu^3, γ-CH_2-Lys^1, γ-CH_2-Lys^2, γ-CH_2-Lys^5, γ-CH_2-Lys^6, γ-CH_2-Lys^9, γ-CH_2-Lys^{10}, β-CH-Leu^8, γ-CH_2-Ile^7, β-CH-Leu^3, β-CH_2-Lys^1, β-CH_2-Lys^2, β-CH_2-Lys^5, β-CH_2-Lys^6, β-CH_2-Lys^9, β-CH_2-Lys^{10}, β-CH_2-Leu^{11}, β-CH-Ile^7), 2.03 (s, 3H, CH_3CO), 2.13 (t, *J* = 7.48 Hz, 2H, α-CH_2-butanoyl), 2.91-3.00 (m, 10 H, ε-CH_2-Lys^1, ε-CH_2-Lys^2, ε-CH_2-Lys^5, ε-CH_2-Lys^6, ε-CH_2-Lys^9), 3.08-3.16 (m, 4 H, ε-CH_2-Lys^{10}, β-CH_2-Phe^4), 3.59 (br, 1H, α-CH-Ile^7), 3.84-4.24 (m, 10H, α-CH-Lys^5, α-CH-Leu^8, α-CH-Lys^6, α-CH-Lys^1, α-CH-Lys^2, α-CH-Lys^9, α-CH-Lys^{10}, α-CH-Leu^{11}, α-CH-Leu^3, α-CH-Phe^4), 6.96 (s, 1H, $CONH_2$), 7.10 (d, *J* = 7.01 Hz, 2H, 2 × *o*-CH-Phe$_{arom}$), 7.16-7.21 (m, 4 H, *p*-CH-Phe$_{arom}$, 2 × *m*-CH-Phe$_{arom}$, $CONH_2$), 7.57 (br, 1H, α-NH-Leu^3), 7.59 (br, 1H, α-NH-Lys^6), 7.73 (br, 1H, α-NH-Lys^9), 7.83 (br, 1H, α-NH-Lys^{10}), 8.07-8.10 (m, 3H, α-NH-Leu^{11}, α-NH-Ile^7, α-NH-Phe^4), 8.13 (br, 1H, α-NH-Lys^5), 8.26 (br, 1H, α-NH-Leu^8), 8.36 (br, 1H, α-NH-Lys^1), 8.42 (br, 1H, α-NH-Lys^2).

BP475

^{1}H-NMR (400 MHz, 20 mM phosphate buffer pH = 6.5 H_2O/D_2O (90:10)) *δ* (ppm): 0.75-0.90 (m, 24H, CH_3-butanoyl, δ-CH_3-Ile, 6 × δ-CH_3-Leu), 0.99-1.16 (m, 5H, γ-CH_3-Ile, δ-CH_2-Lys), 1.25-1.82 (m, 48 H, β-CH_2-butanoyl, β-CH_2-Ile, γ-CH_2-Ile, 3 × β-CH_2-Leu, 3 × γ-CH-Leu, 6 × β-CH_2-Lys, 6 × γ-CH_2-Lys, 5 × δ-CH_2-Lys), 1.98 (s, 3H, CH_3CO), 2.15 (t, *J* = 7.48 Hz, 2H, α-CH_2-butanoyl), 2.85-3.00 (m, 11H, 5 × ε-CH_2-Lys, β-CH_2-Phe), 3.06-3.16 (m, 3H, ε-CH_2-Lys$^{10.}$ β-CH_2-Phe), 4.06-4.13 (m, 2H, α-CH-Ile, α-CH-Lys), 4.15-4.34 (m, 5H, 4 x α-CH-Lys, α-CH-Lys$^{10.}$ 3 × α-CH-Leu), 4.54-4.57 (m, α-CH-Phe), 7.11 (s, 1H, $CONH_2$), 7.21 (d, *J* = 7.16 Hz, 2H, 2 × *o*-CH-Phe$_{arom}$), 7.26-7.36 (m, 3H, 2 × *m*-CH-Phe$_{arom}$, *p*-CH-Phe$_{arom}$), 7.59 (s, 1H, $CONH_2$), 8.04 (t, *J* = 5.82Hz, 1H, ζ-NH-Lys^{10}), 8.21-8.29 (m, 3H, α-NH-Ile, α-NH-Leu, α-NH-Lys), 8.32-8.46 (m, 6H, α-NH-Lys^{10}, 4 × α-NH-Lys, α-NH-Phe, 2 × α-NH-Leu).

^{1}H-NMR (400 MHz, 20 mM phosphate buffer at pH = 6.5 with H_2O/D_2O (90:10) containing 30% CF_3CD_2OD)) *δ* (ppm): 0.82-0.94 (m, 24H, CH_3-butanoyl, 2 × δ-CH_3-Leu^3, 2 × δ-CH_3-Leu^8, 2 × δ-CH_3-Leu^{11}, δ-CH_3-Ile), 1.08-1.31 (m, 3H, γ-CH_3-Ile), 1.33-1.85 (m, 24H, β-CH_2-butanoyl, β-CH_2-Lys^6, β-CH_2-Leu^8, β-CH_2-Leu^{11}, δ-CH_2-Lys^1, δ-CH_2-Lys^2, δ-CH_2-Lys^6, δ-CH_2-Lys^{10}, γ-CH_2-Lys^1, γ-CH_2-Lys^2, γ-CH_2-Lys^6, γ-CH_2-Ile), 1.95 (s, 7H, β-CH_2-Lys^2, β-CH_2-Lys^{10}, CH_3CO), 2.14 (t, *J* = 7.66 Hz, 2H, α-CH_2-butanoyl), 2.90-2.99 (m, 7 H, ε-CH_2-Lys^1, ε-CH_2-Lys^2, ε-CH_2-Lys^6, β-CH_2-Phe), 3.15 (m, 3H, ε-CH_2-Lys^{10}, β-CH_2-Phe), 3.77 (br, 1H, α-CH-Ile), 3.85-4.19 (m, 8 H, α-CH-Lys^1, α-CH-Lys^2, α-CH-Lys^6, α-CH-Lys^{10}, α-CH-Leu^3, α-CH-Leu^8, α-CH-Leu^{11}, α-CH-Phe), 6.94 (s, 1H, $CONH_2$), 7.08 (d, *J* = 6.36 Hz, 2H, 2 × *o*-CH-Phe$_{arom}$), 7.27-7.18 (m, 4 H, *p*-CH-Phe$_{arom}$, 2 × *m*-CH-Phe$_{arom}$, $CONH_2$), 7.46-7.43 (m, 1H, ζ-NH-Lys^{10}), 7.64 (br, 1H, α-NH-Leu^3), 7.76 (br, 1H, α-NH-Lys^{10}), 7.81 (br, 1H, α-NH-Lys^6), 7.92 (br, 1H, α-NH-Lys^9), 8.03-8.11 (m, 3H, α-NH-Lys^5, α-NH-Ile, α-NH-Leu^{11}), 8.15-8.19 (m, 2H, α-NH-Phe, α-NH-Leu^8), 8.22 (br, 1H, α-NH-Lys^1), 8.30 (br, 1H, α-NH-Lys^2).

BP389

Table S4. NMR data of lipopeptide BP389 recorded at 400 MHz in 20 mM phosphate buffer, pH = 6.5 H_2O/D_2O (90:10)

Amino acid	δ (ppm)					
	CO-N*H*	CO-*N*H	α-C*H*	α-*C*H	β-C*H*	β-*C*H
Phe[4]	8.32	123.8	4.53	54.8	2.97 / 3.01	36.9
Ile[7]	8.34	124.1	4.06	57.9	1.78	35.7
Lys[10]	8.41	122.5	4.21	53.2	1.66	38.9
5 × Lys	8.30	123.0	4.19	53.1	1.61	30.5
	8.32	127.0	4.24	53.3	1.70	30.3
	8.32	121.9	4.18	53.5	1.67	30.2
	8.35	123.7	4.13	53.8	1.65	30.2
	8.17	124.0	4.20	53.6	1.46	30.3
3 × Leu	8.21	123.6	4.26	51.8	1.51	39.6
	8.34	124.1	4.29	52.0	1.54	39.6
	8.42	127.8	4.33	52.1	1.61	39.5

Table S5. NMR data of lipopeptide BP389 recorded at 400 MHz in 20 mM phosphate buffer, pH = 6.5 H_2O/D_2O (90:10), containing 30% CF_3CD_2OD

Amino acid	δ (ppm)					
	CO-N*H*	CO-*N*H	α-C*H*	α-*C*H	β-C*H*	β-*C*H
Lys[1]	8.36	126.1	4.00	56.6	1.82	29.4
Lys[2]	8.42	116.8	4.02	56.5	1.82	29.7
Leu[3]	7.57	124.6	4.15	54.3	1.73	26.6
Phe[4]	8.10	118.2	4.24	57.8	3.10	35.7
Lys[5]	8.13	116.0	3.84	57.0	1.88	29.4
Lys[6]	7.59	118.7	3.99	56.8	2.01	29.5
Ile[7]	8.10	120.2	3.59	62.2	1.92	34.8
Leu[8]	8.26	118.7	3.88	55.1	1.66	26.5
Lys[9]	7.73	117.9	4.02	55.7	1.95	29.2
Lys[10]	7.83	119.5	4.04	55.9	1.90	28.0
Leu[11]	8.07	118.4	4.12	53.0	1.79	

BP475

Table S6. NMR data of lipopeptide BP475 recorded at 400 MHz in 20 mM phosphate buffer, pH = 6.5 H_2O/D_2O (90:10)

Amino acid	δ (ppm)					
	CO-N*H*	CO-*N*H	α-C*H*	α-*C*H	β-C*H*	β-*C*H
Phe[4]	8.40	122.0	4.56	55.3	3.08 / 2.98	36.8
Ile[7]	8.26	122.3	4.08	57.9	1.79	35.6
Lys[10]	8.32	122.9	4.24	53.4	1.72	30.3
5 × Lys	8.27	122.7	4.22	53.5	1.68	30.2
	8.34	124.0	4.17	53.8	1.72	30.3
	8.38	124.2	4.10	53.4	1.49	30.1
	8.39	122.7	4.22	53.6	1.72	38.3
	8.45	122.3	4.29	53.2	1.68	30.1
3 × Leu	8.22	123.5	4.25	52.2	1.39	39.8
	8.34	121.0	4.27	52.0	1.62	39.6
	8.42	127.8	4.33	52.1	1.54	39.5

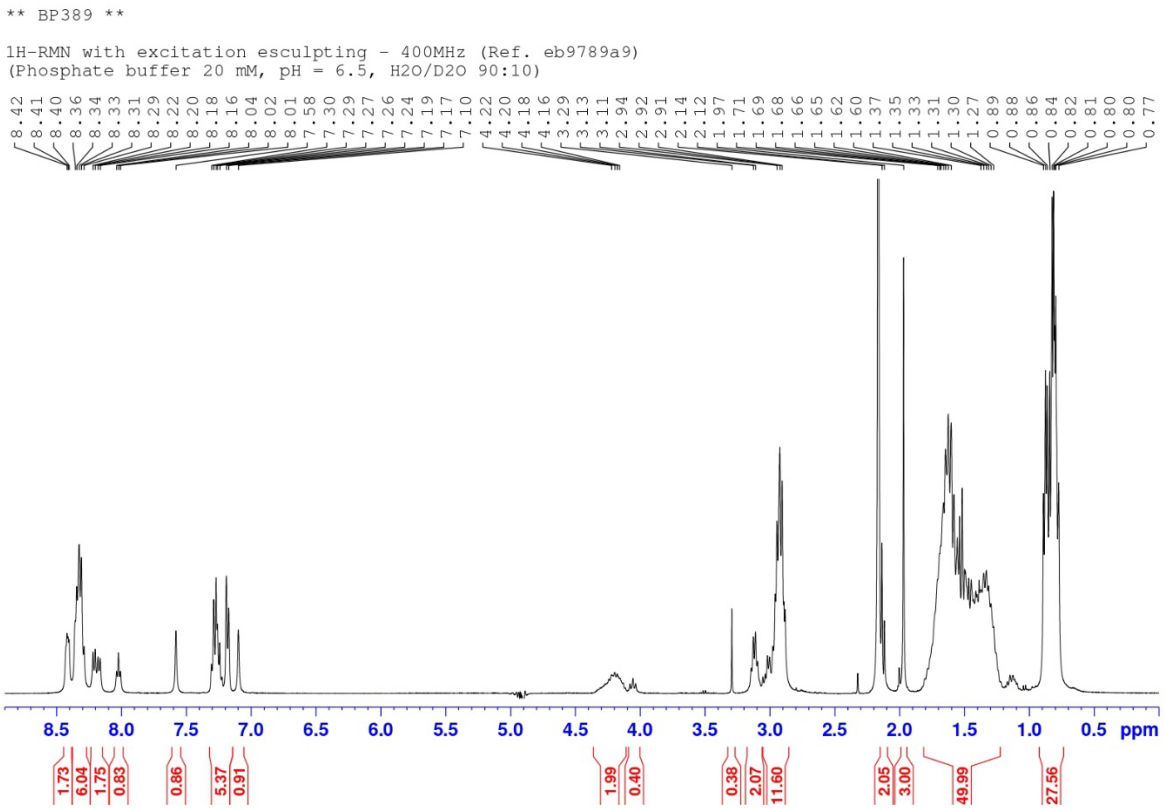
Table S7. NMR data of lipopeptide BP475 recorded at 400 MHz in 20 mM phosphate buffer, pH = 6.5 H_2O/D_2O (90:10), containing 30% CF_3CD_2OD

Amino acid	δ (ppm)					
	CO-N*H*	CO-*N*H	α-C*H*	α-*C*H	β-C*H*	β-*C*H
Lys[1]	8.22	125.7	3.89	55.8		
Lys[2]	8.30	117.5	4.10	55.5	1.94	29.3
Leu[3]	7.64	112.0	4.13	54.2		
Phe[4]	8.16	116.0	4.04	55.5	2.99 / 3.15	38.9
Lys[5]	8.07	119.4	4.03	55.1		
Lys[6]	7.81	118.8	4.01	56.6	1.78	29.2
Ile[7]	8.09	118.7	3.77	61.4	2.08	34.6
Leu[8]	8.18	119.0	4.01	56.6	1.71	
Lys[9]	7.92	117.8	4.06	55.55		
Lys[10]	7.76	119.4	4.08	55.9	1.95	30.1
Leu[11]	8.04	118.4	4.17	53.0	1.83	

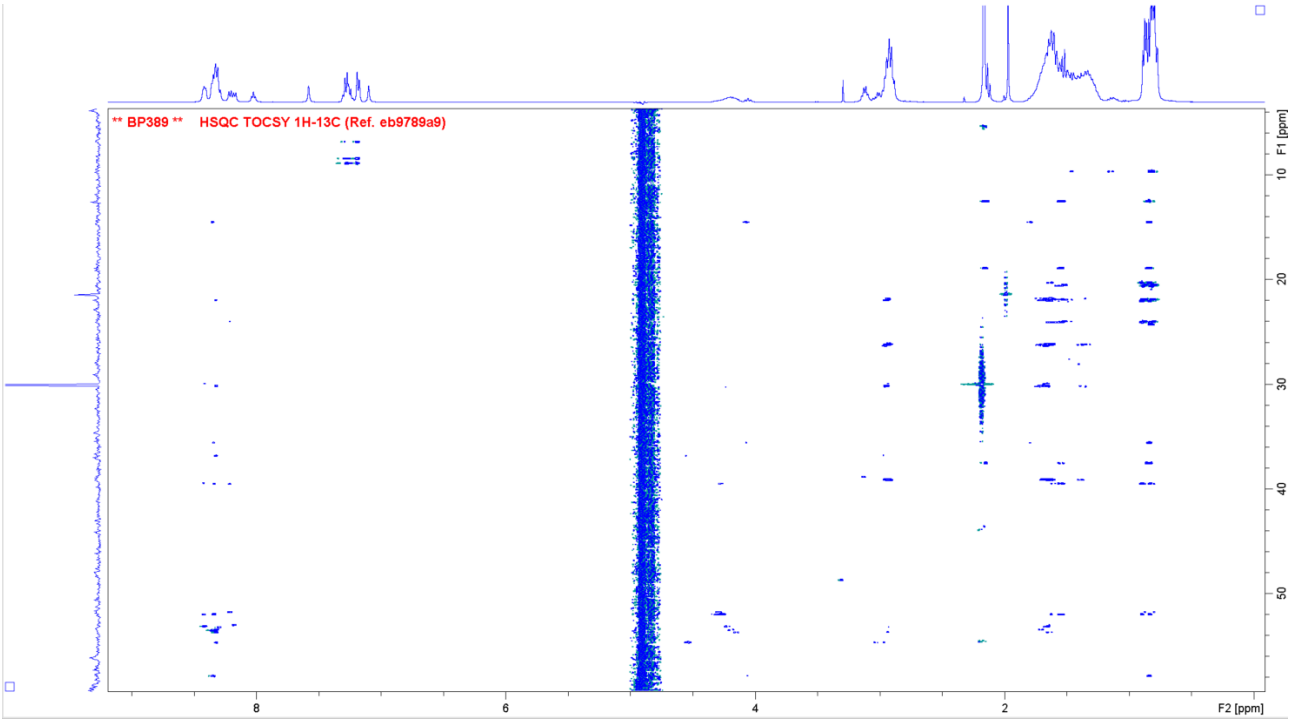
BP389

400 MHz. 20 mM phosphate buffer. pH = 6.5 H_2O/D_2O (90:10)

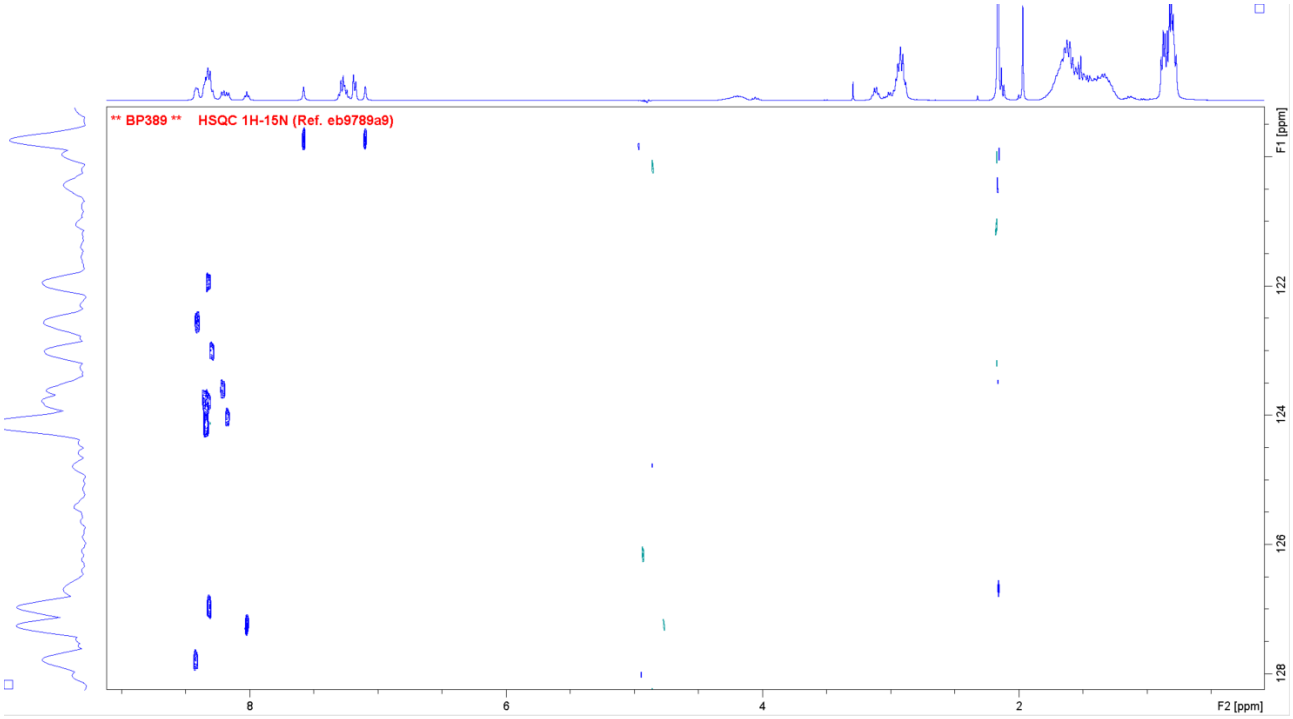
^{1}H-NMR



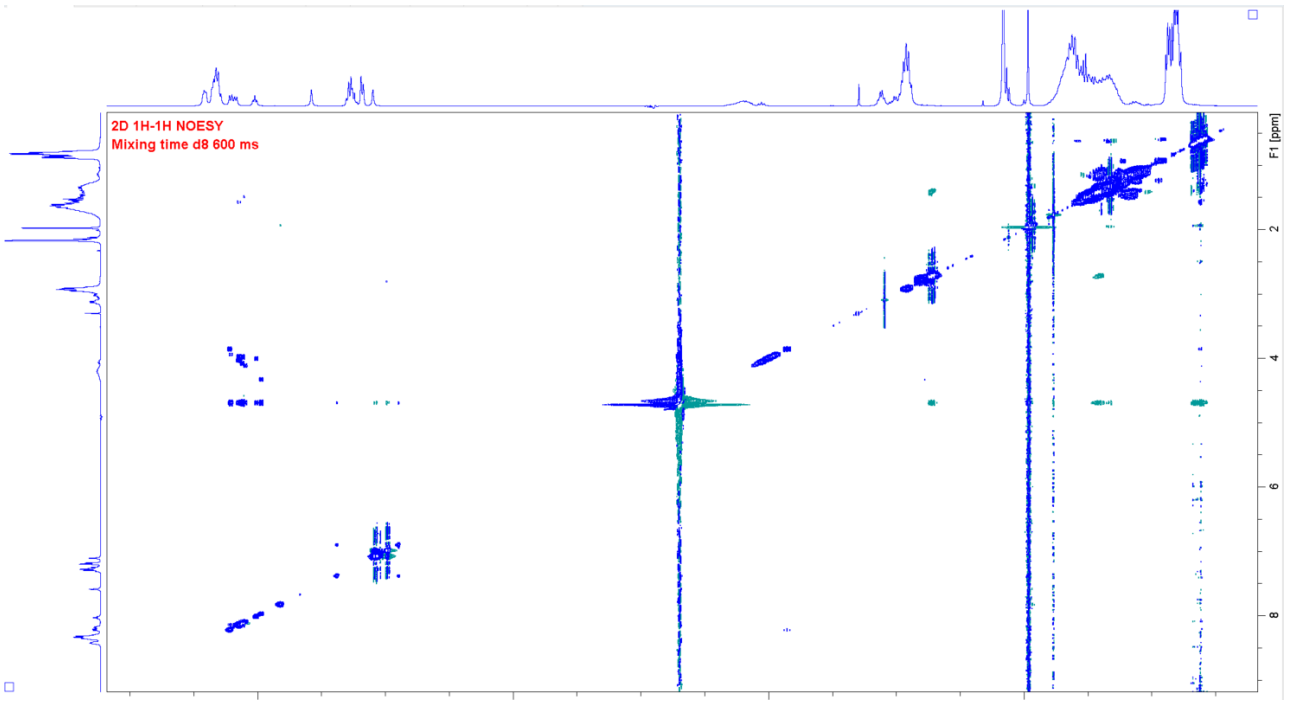
HSQC-TOCSY



HSQC ^{1}H-^{15}N



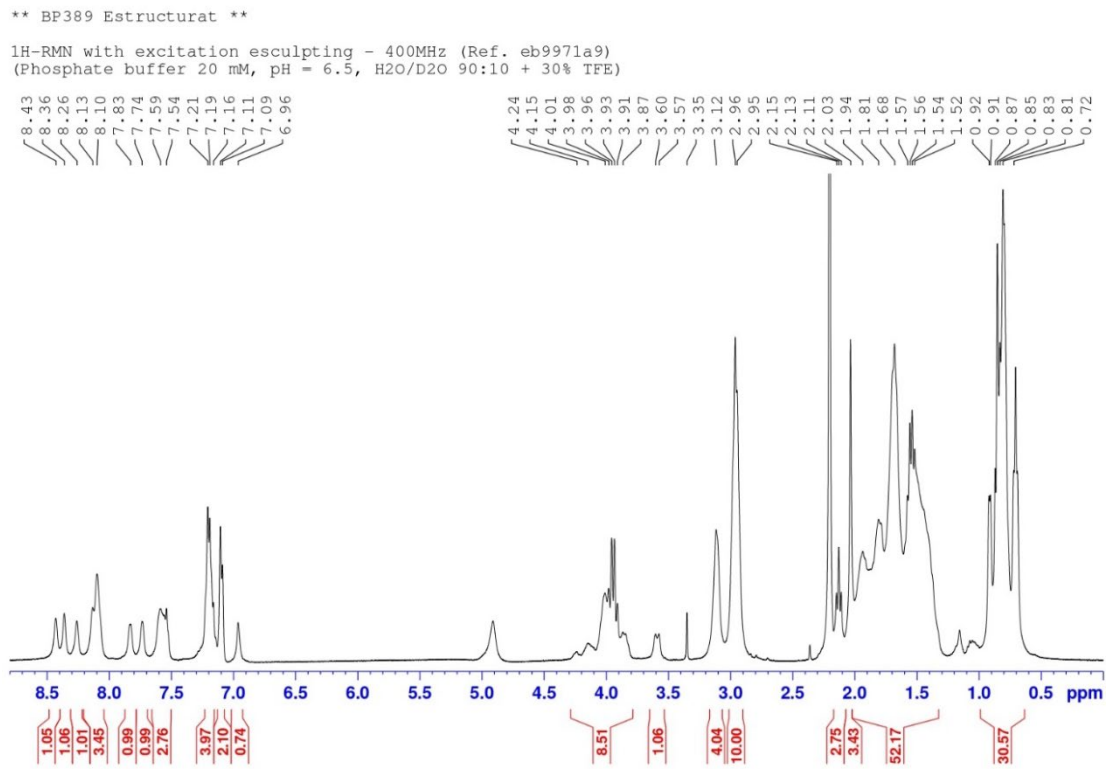
NOESY



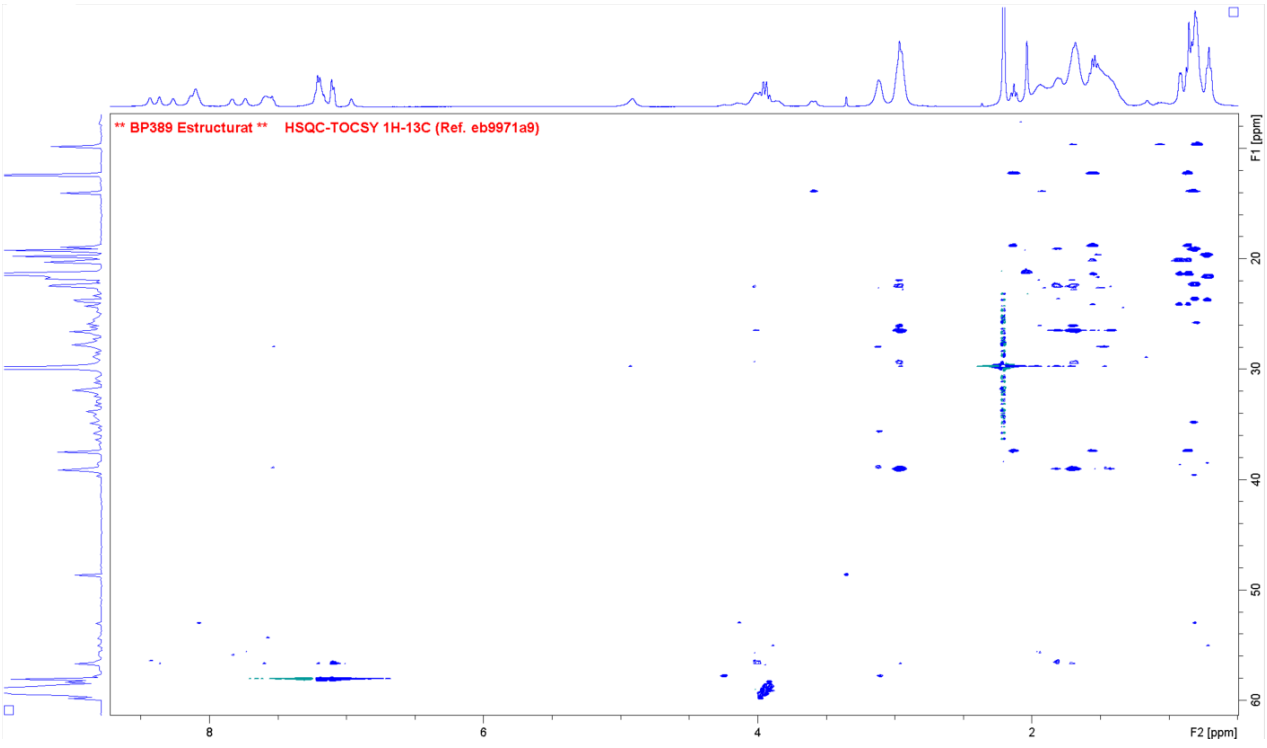
BP389

400 MHz. 20 mM phosphate buffer, pH = 6.5 H_2O/D_2O (90:10), containing 30% CF_3CD_2OD

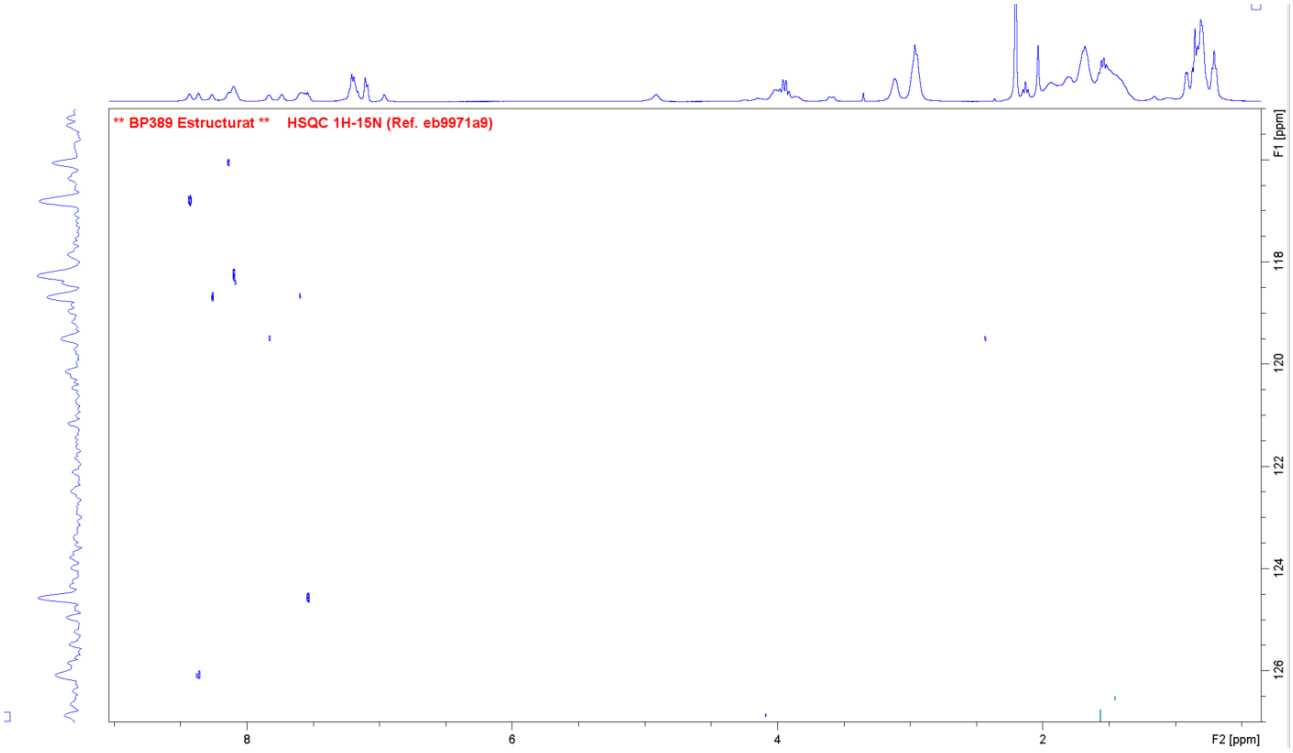
^{1}H-NMR



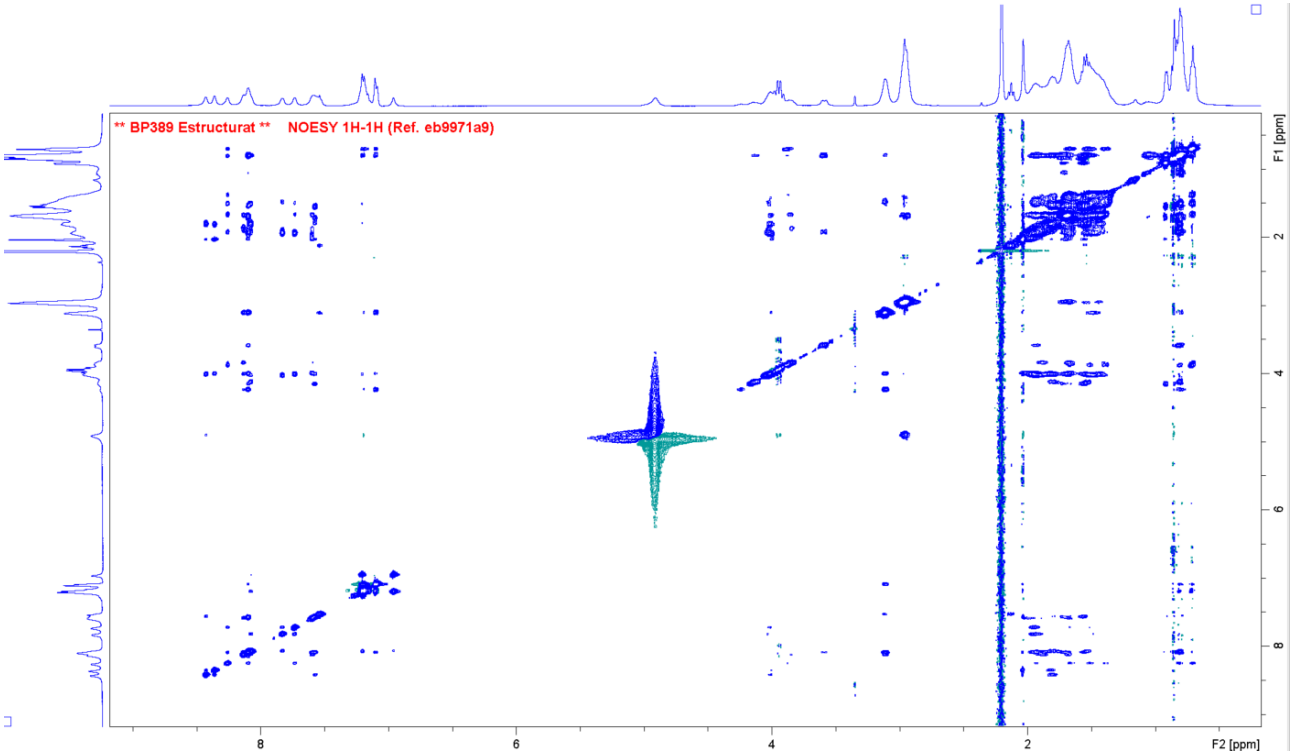
HSQC-TOCSY



HSQC ^{1}H-^{15}N



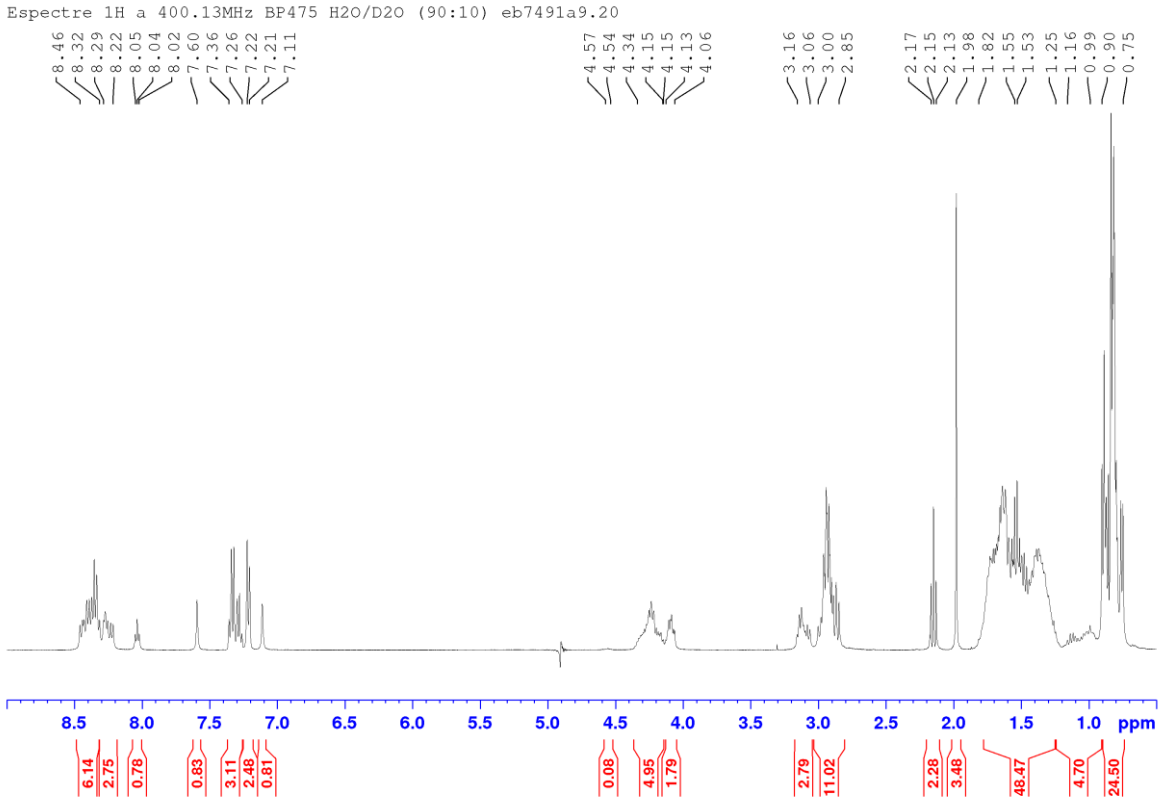
NOESY



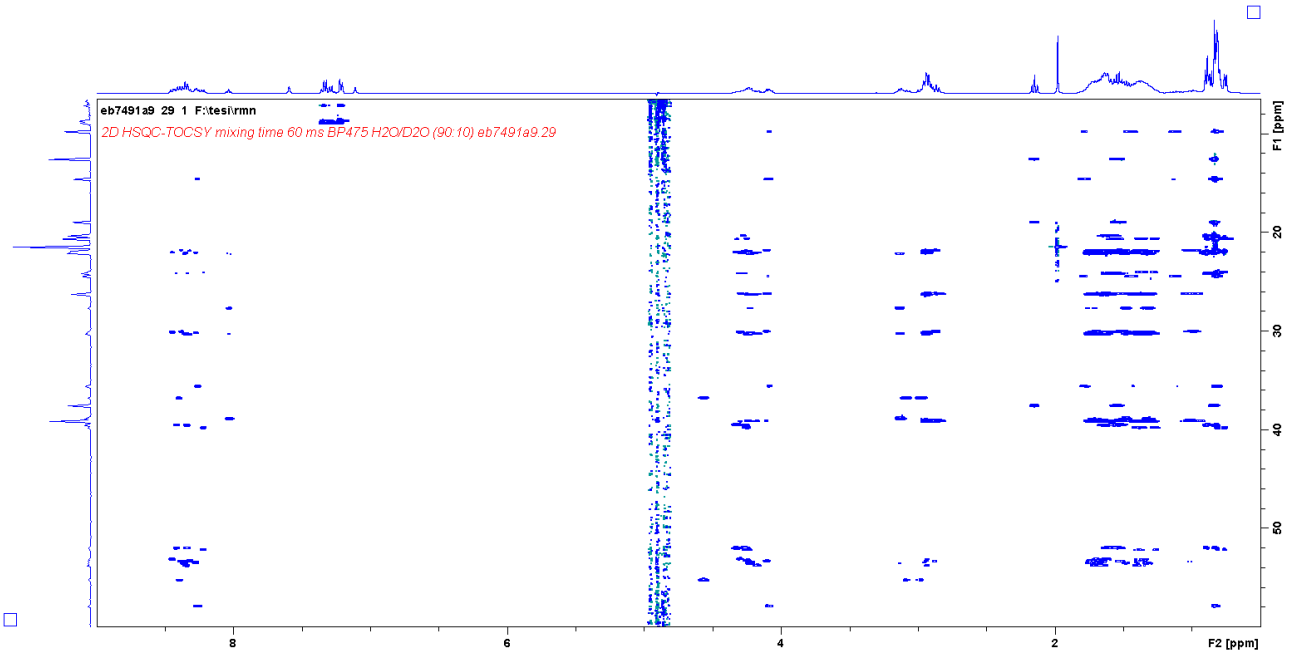
BP475

400 MHz. 20 mM phosphate buffer. pH = 6.5 H_2O/D_2O (90:10)

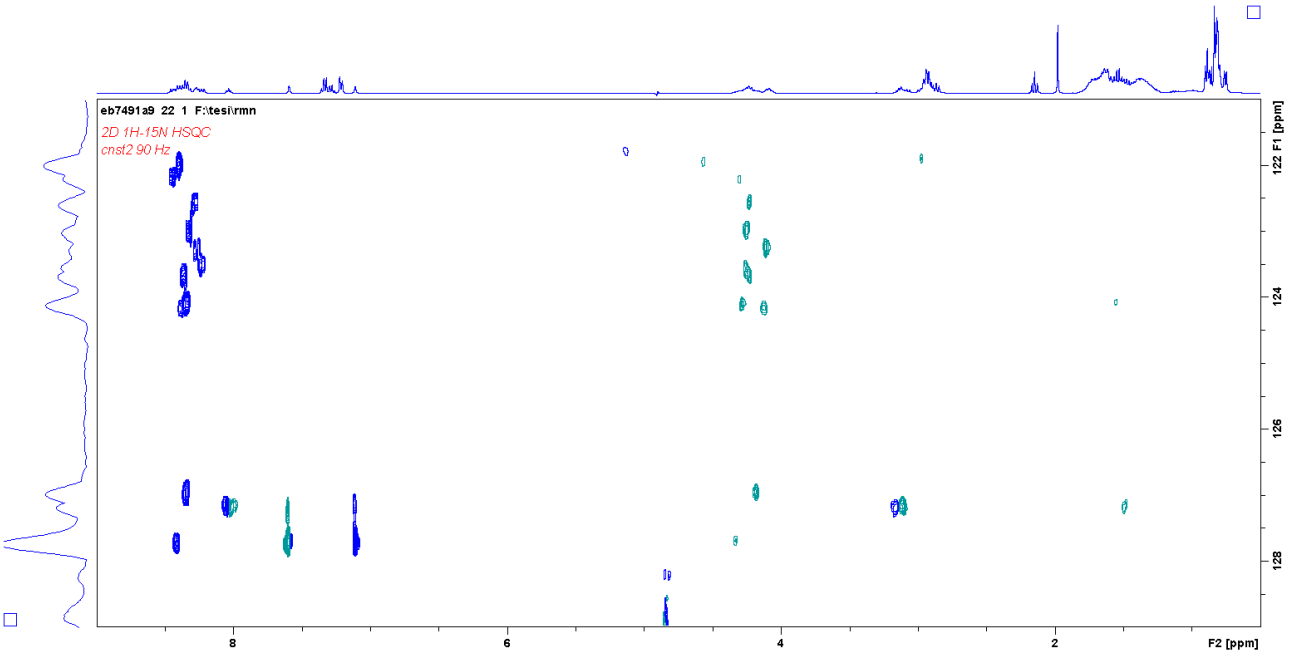
^{1}H-NMR



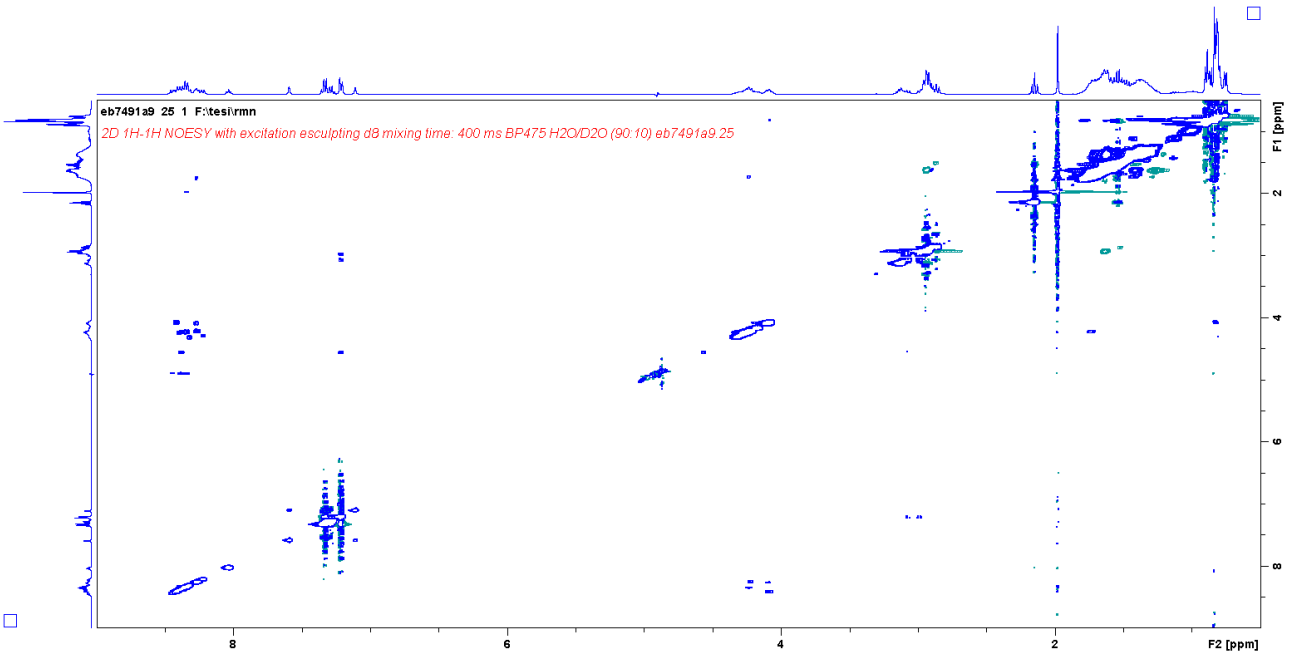
HSQC-TOCSY



HSQC ^{1}H-^{15}N



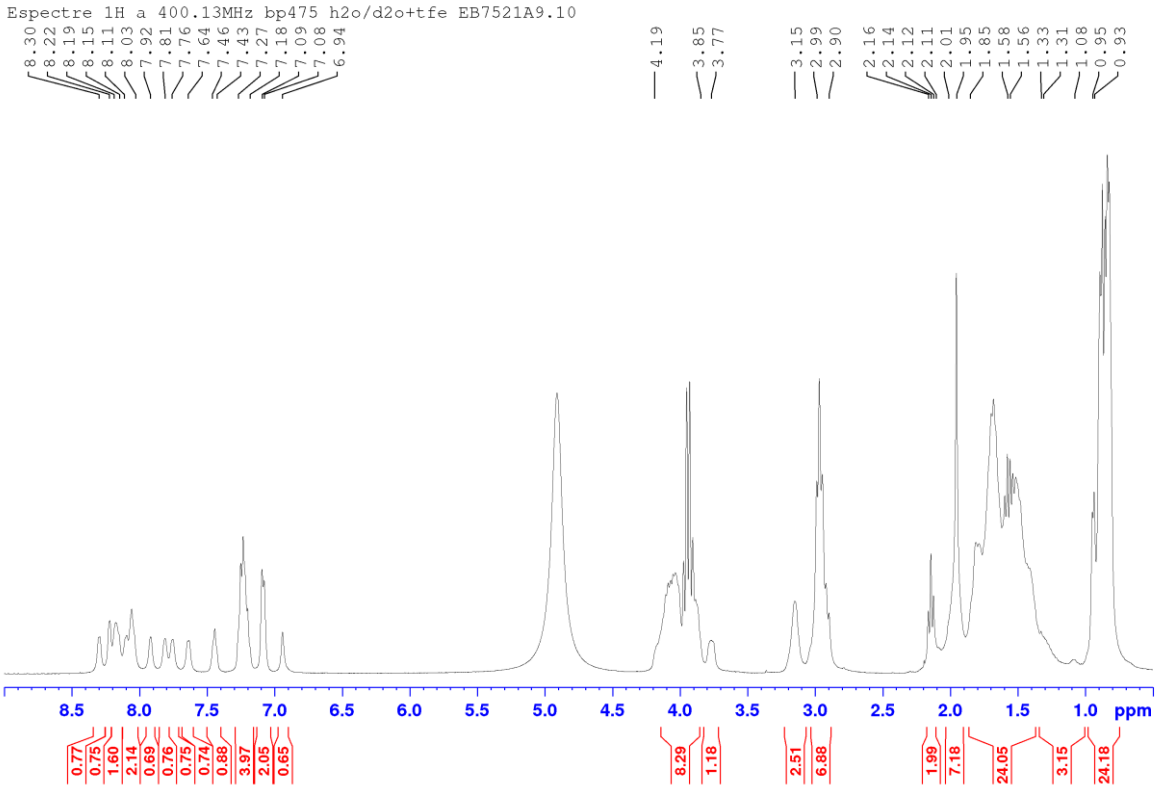
NOESY



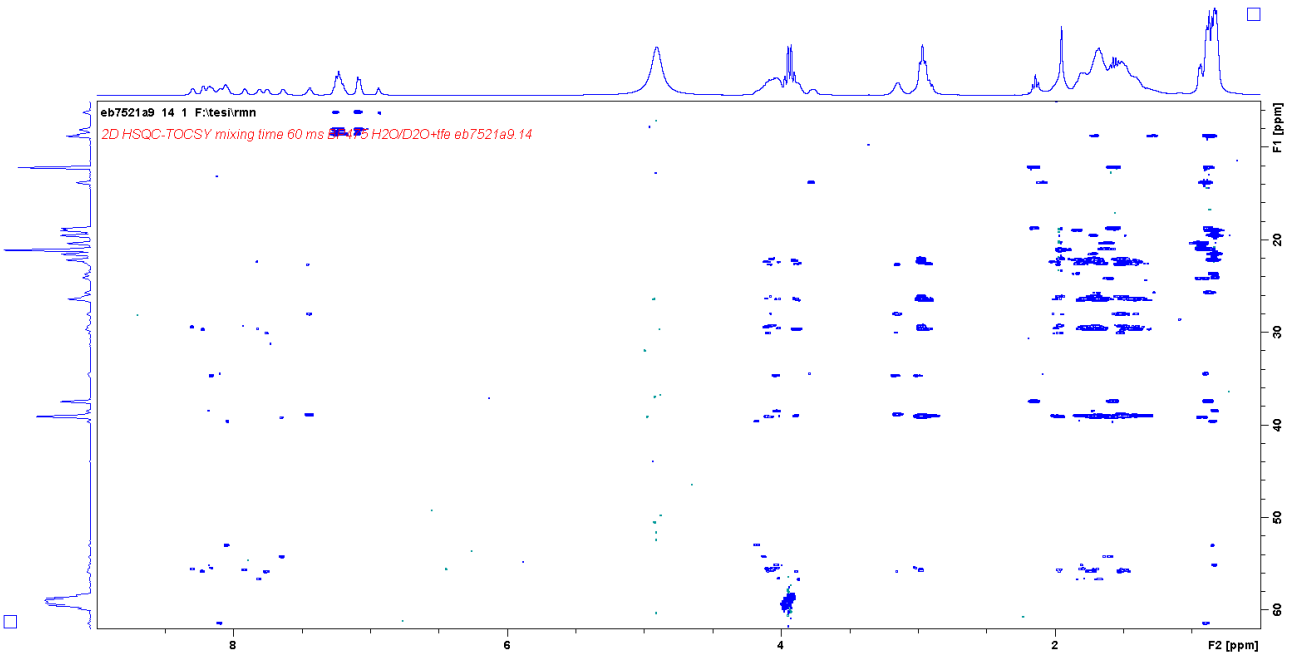
BP475

400 MHz. 20 mM phosphate buffer, pH = 6.5 H_2O/D_2O (90:10), containing 30% CF_3CD_2OD

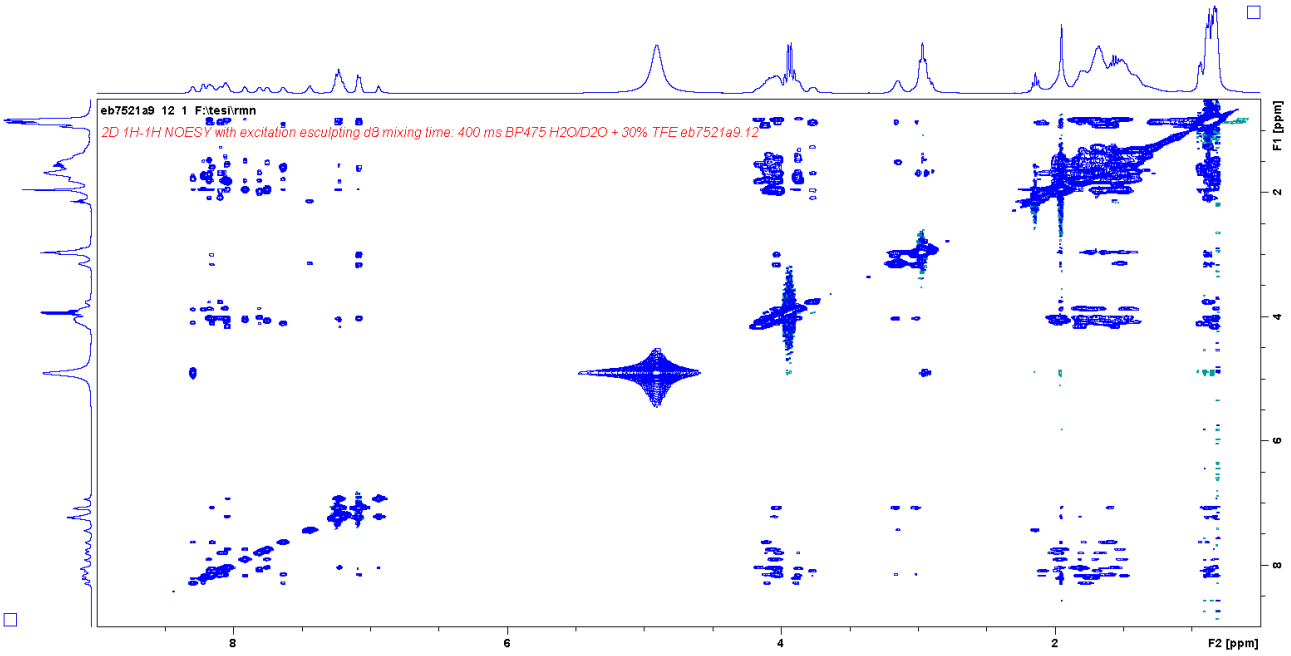
^{1}H-NMR



HSQC-TOCSY



NOESY


eb7521a9 12 1 F:\tesi\rmn
2D 1H-1H NOESY with excitation esculpting dB mixing time: 400 ms BP475 H2O/D2O + 30% TFE eb7521a9.12
F1 [ppm]
F2 [ppm]
2
4
6
8