# Photoaffinity Labeling of the Human $A_{2A}$ Adenosine Receptor and Cross-link Position Analysis by Mass Spectrometry

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## Supporting Information 1

## Experimental procedures and spectral characterization data

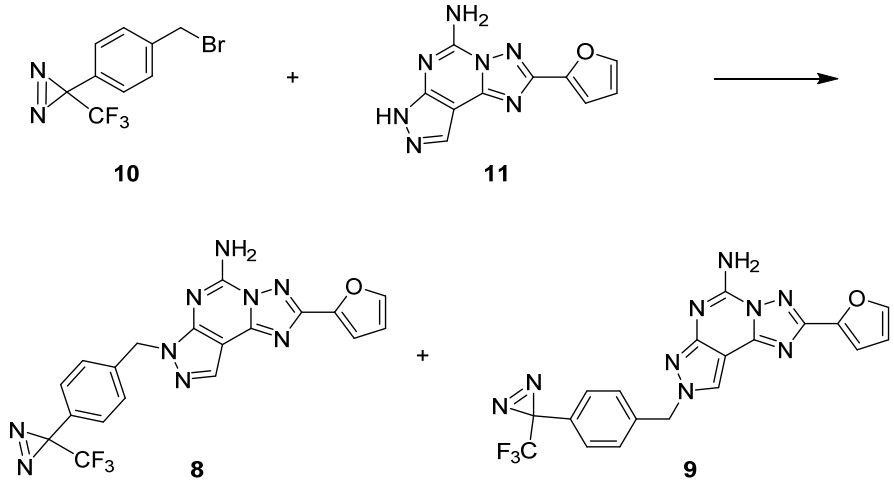
## Contents:

## 1. Materials and instruments.

All reagents and solvents were purchased from commercial sources and used without further purification. Flash column chromatography was performed on a Flash Master Personal equipped with GradMaster (Biotage, Charlotte, NC, USA). Reverse phase preparative HPLC was performed by using a preparative HPLC system (Gilson, Middleton, WI, USA). Analytical HPLC was performed on a LC-VP series instrument (Shimadzu, Kyoto, Japan). Melting points were determined on a MP-J3 micro melting point apparatus (Yanaco Co., Ltd., Kyoto, Japan). $^{1}$H, $^{13}$C and $^{15}$N NMR spectra were recorded on an AV600 spectrometers (Bruker, Billerica, MA, USA). Chemical shifts are reported in δ units (ppm) relative to sodium 3-(trimethylsilyl)propionate-2,2,3,3-*d*4 (TSP) in $D_2O$ or tetramethylsilane (TMS) in DMSO-*d*6 as internal standards for $^{1}$H NMR spectra. The central peak of the DMSO-*d*6 multiplet at 39.52 ppm was used as an internal reference for $^{13}$C NMR spectra and nitromethane was used as an external standard for $^{15}$N NMR spectra. Coupling constants (*J*) are reported in hertz (Hz). Characterization data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br s = broad singlet, m = multiplet), coupling constants, number of protons. Mass spectra were recorded on a 6520 Accurate-Mass Q-TOF instrument with a 1200 series HPLC (Agilent Technologies, Santa Clara, CA, USA). The internal standards at *m*/*z* = 121.050873 and 922.009798 in positive ion mode, while *m*/*z* = 112.985587 and 966.000725 in negative ion mode, were sprayed with a separate nebulizer. Fluorescence polarization (FP) experiments were performed with an Infinite M1000 plate reader (TECAN, Morrisville, NC, USA). Photoaffinity labeling was performed with a model B-100A UV lamp (UVP, Upland, CA, USA). The intensity of UV light was measured by a UV-37SD digital radiometer equipped with a UVA sensor (CUSTOM, Tokyo, Japan). Assay plates were prepared with a mosquito HTS liquid handler (TTP LabTech, Melbourn, UK).

## 2. Synthesis and spectral characterization data.

2.1 Synthesis of photoaffinity probes **8** and **9**.

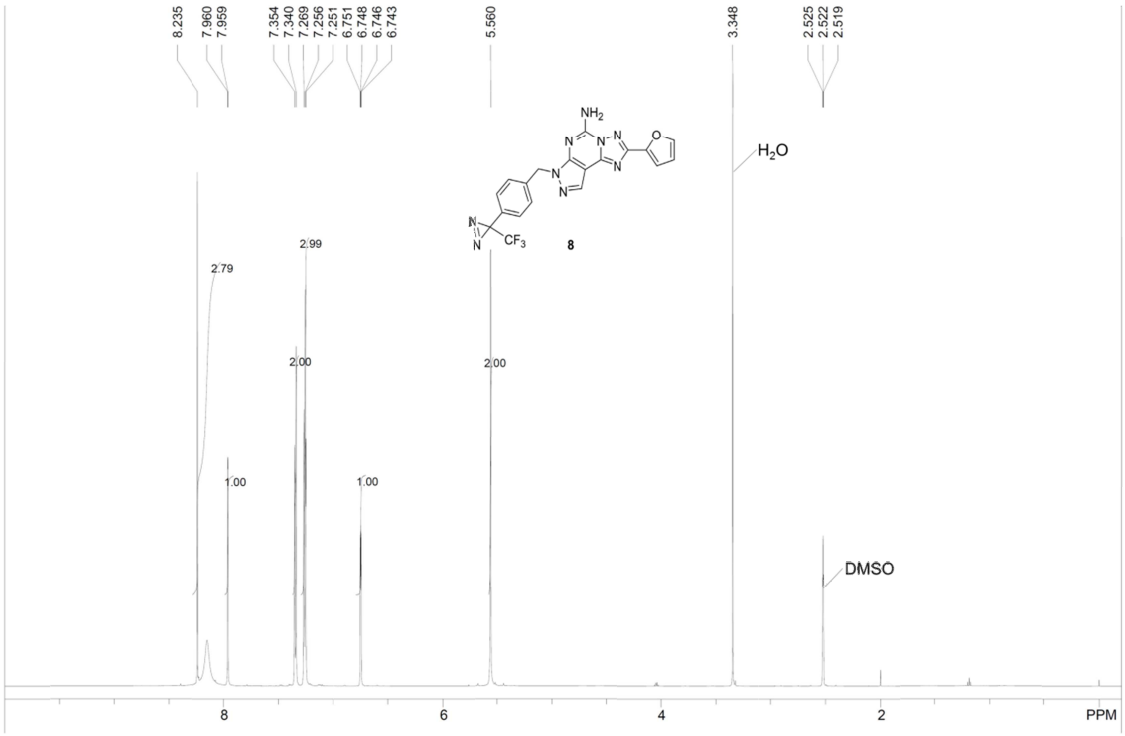



A mixture of a commercially available 3-(4-bromomethylphenyl)-3-(trifluoromethyl)-3*H*-diazirine **10** (245 mg, 0.88 mmol , TCI, Tokyo, Japan), 2-(2-furanyl)-7*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidin-5-amine **11** (193 mg, 0.80 mmol)[1] and potassium carbonate (166 mg, 1.20 mmol) in dry DMF (4.0 mL) was stirred at room temperature for 6 h. The mixture was diluted with ethyl acetate and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated with amino-silica gel powder. The adsorbed gel was packed into a pre-column cartridge and assembled with a Hi-Flash column cartridge (L, Amino, Yamazen, Osaka, Japan). The column was eluted with a linear gradient of ethyl acetate in *n*-hexane (20–100%) to obtain $N^7$-isomers **8** (139 mg, 39.6%) and $N^8$-isomers **9** (68 mg, 19.4%) as a white powder after washing with a small amount of dichloromethane, respectively.

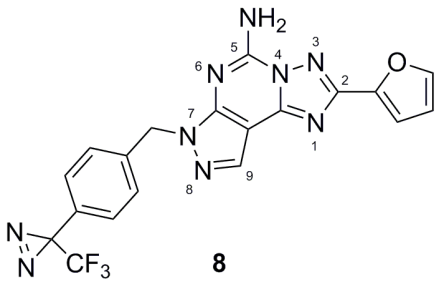
**Spectral characterization of 7-({4-[3-(trifluoromethyl)-3*H*-diazirin-3-yl]phenyl}methyl)-2-(2-furanyl)-7*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidin-5-amine (8)**

mp: 190–191 °C.

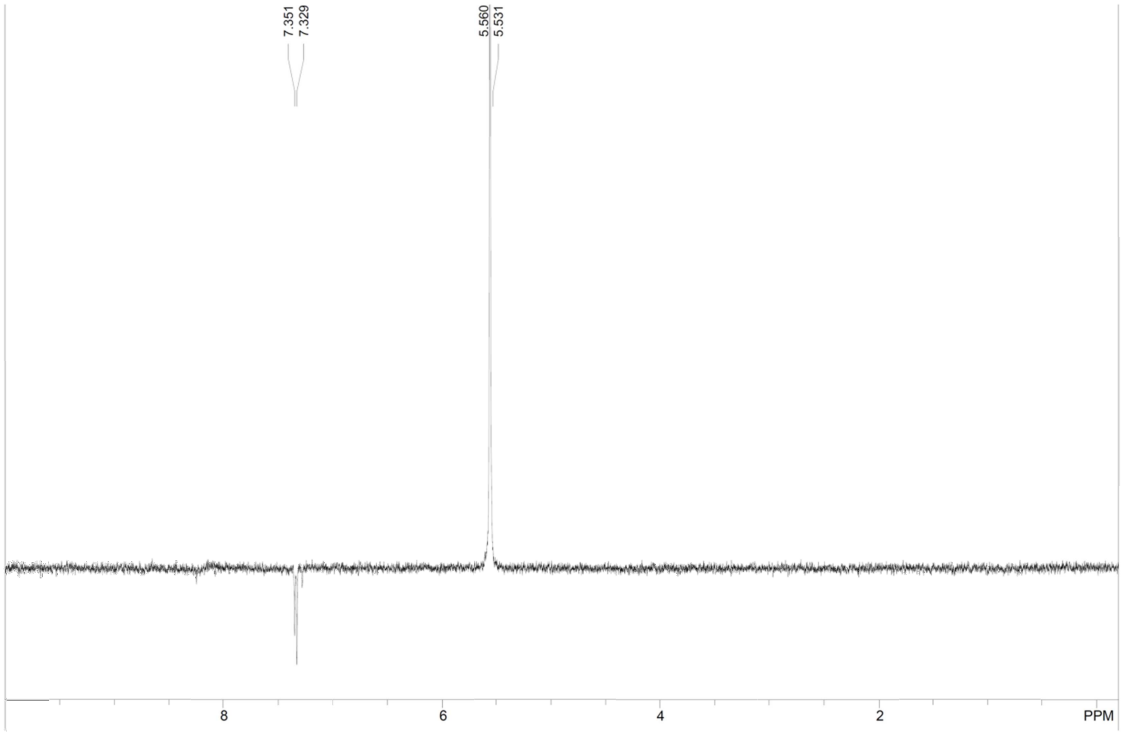
$^{1}$H NMR (600 MHz, DMSO-*d*6, δ): 5.56 (s, 2H), 6.73–6.77 (m, 1H), 7.23–7.29 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.93–7.98 (m, 1H), 8.15 (br s, 2H), 8.24 (s, 1H).



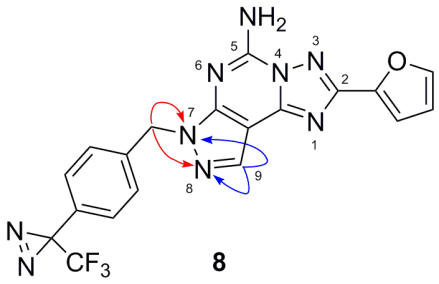
$^{1}$H NOE (600 MHz, DMSO-*d*6). No clear $^{1}$H NOE was observed between methylene protons (δ 5.56, s) and H-9 (δ 8.24, s).



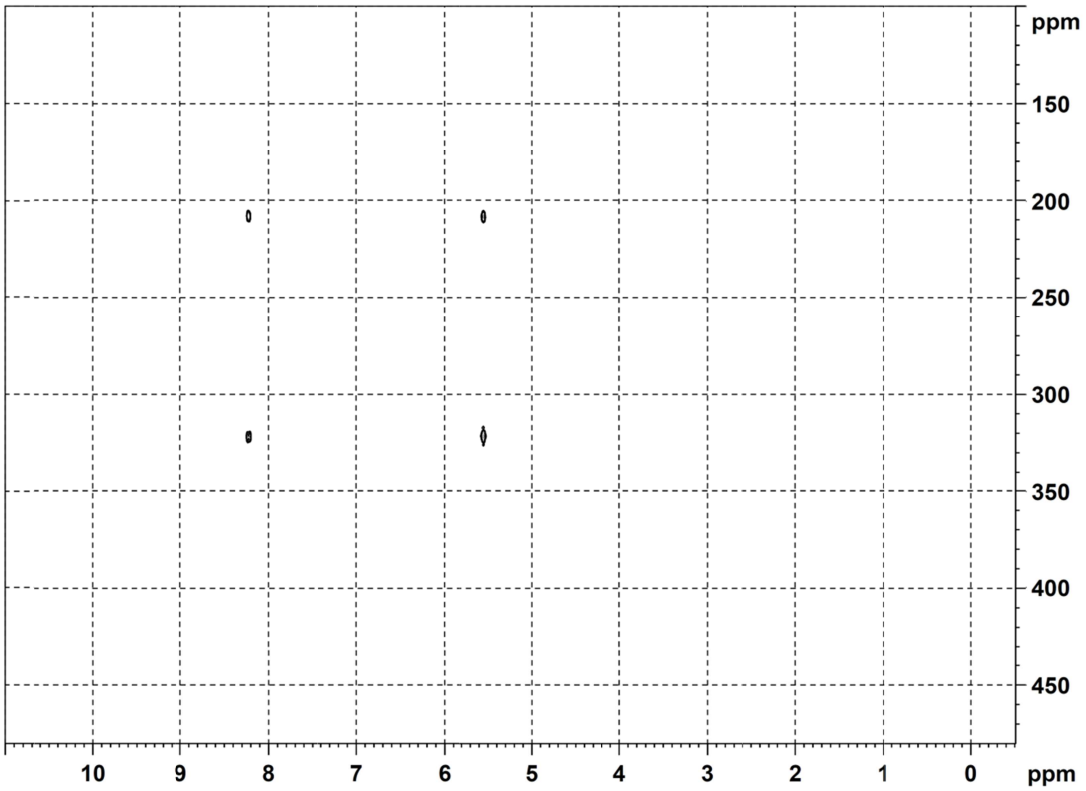

**8**



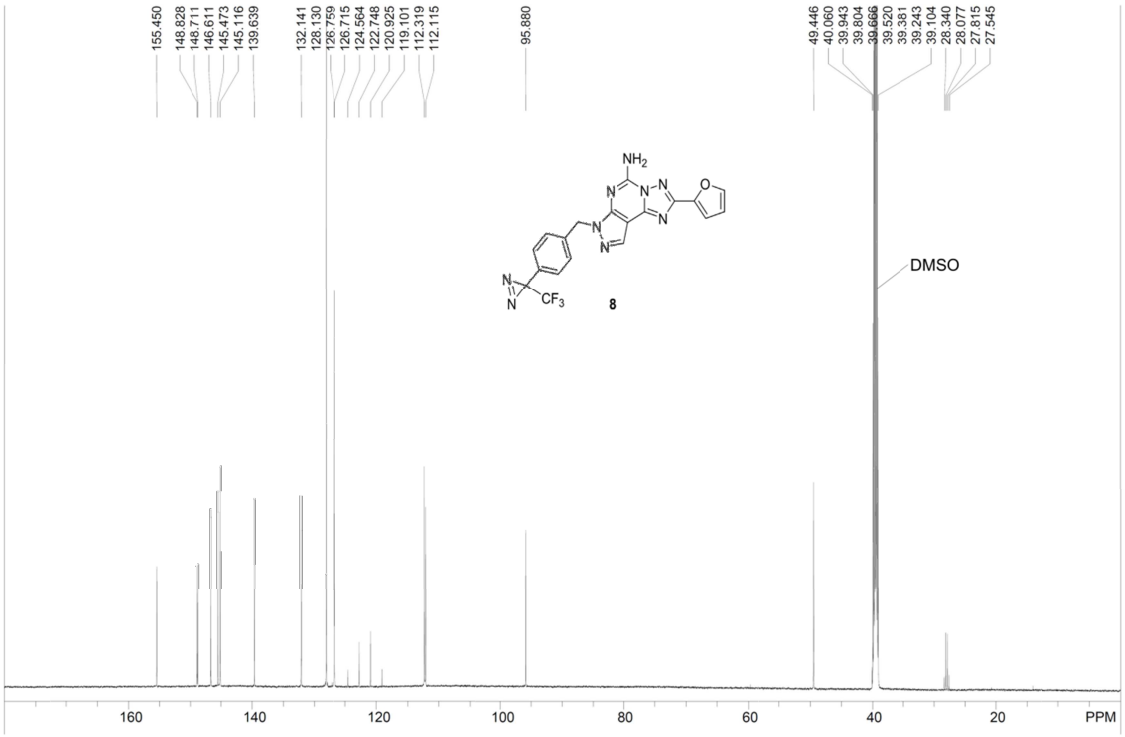
$^{1}$H–$^{15}$N HMBC (600MHz, DMSO-*d*6). Two-bond correlation ($^{2}J_{HN}$) and three-bond correlation ($^{3}J_{HN}$), denoted by the red arrowed lines, were observed from $CH_2$ (δ 5.56, s) to the pyrazolo-triazolo-pyrimidine (PTP) N-7 (δ 208.7 ppm) and N-8 (δ 321.8 ppm). Two-bond correlation ($^{2}J_{HN}$) and three-bond correlation ($^{3}J_{HN}$), denoted by the blue arrowed lines, were also observed from H-9 (δ 8.24, s) to the pyrazolo-triazolo-pyrimidine (PTP) N-8 (δ 321.8 ppm) and N-7 (δ 208.7 ppm).



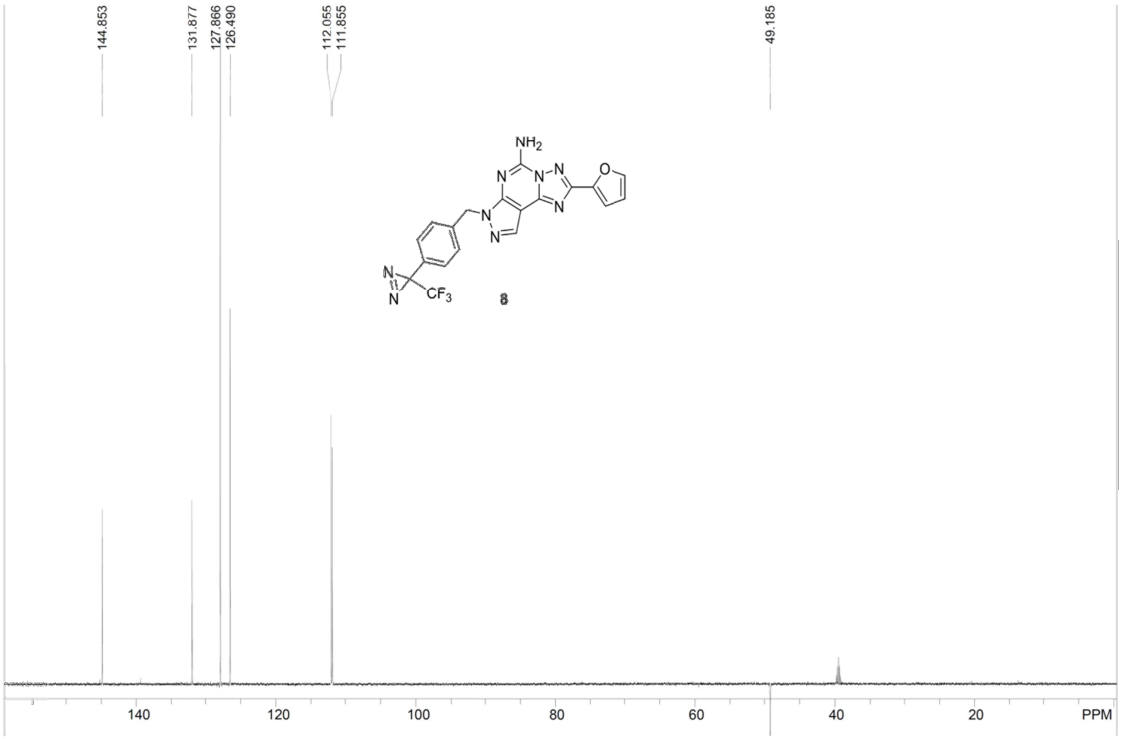

**8**



$^{13}$C NMR (600 MHz, DMSO-*d*6, δ): 27.9 (q, *J* = 39.5 Hz, diazirine-C), 49.5, 95.9, 112.1, 112.3, 121.8 (q, *J* = 275.7 Hz, $CF_3$), 126.7, 126.8, 128.1, 132.1, 139.6, 145.1, 145.5, 146.6, 148.7, 148.8, 155.5.

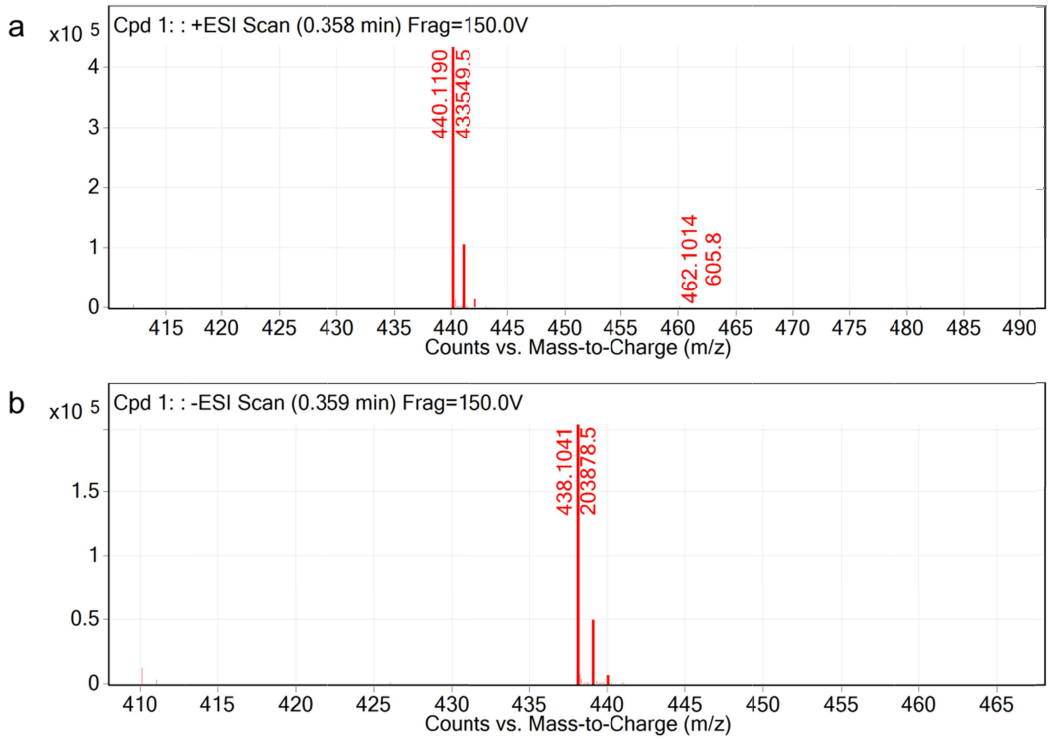


$^{13}$C DEPT NMR (600 MHz, DMSO-*d*6, δ): 49.2, 111.9, 112.1, 126.5, 127.9, 131.9, 144.9.



(a) HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{19}H_{13}F_3N_9O$, 440.1190; found 440.1190.

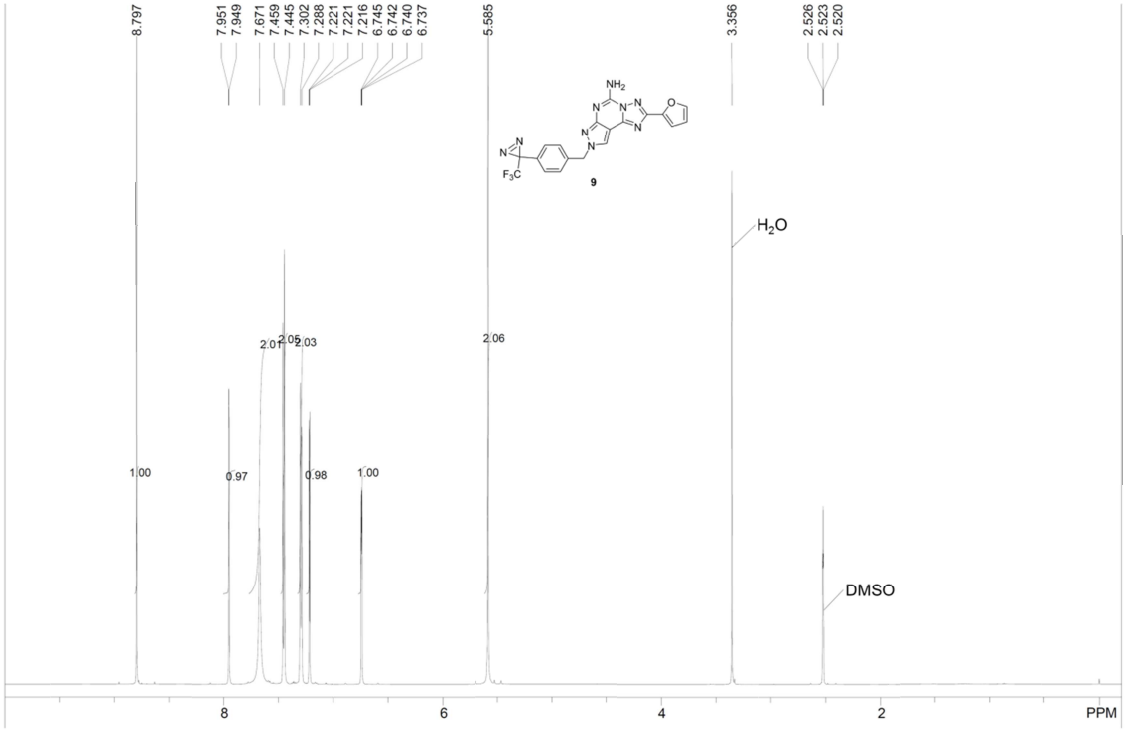
(b) HRMS–ESI (*m/z*): $[M - H]^-$ calcd for $C_{19}H_{11}F_3N_9O$, 438.1044; found 438.1041.



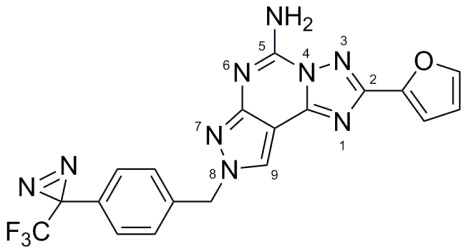
**Spectral characterization of 8-({4-[3-(trifluoromethyl)-3*H*-diazirin-3-yl]phenyl}methyl)-2-(2-furanyl)-8*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidin-5-amine (9)**

mp: 207–208 °C.

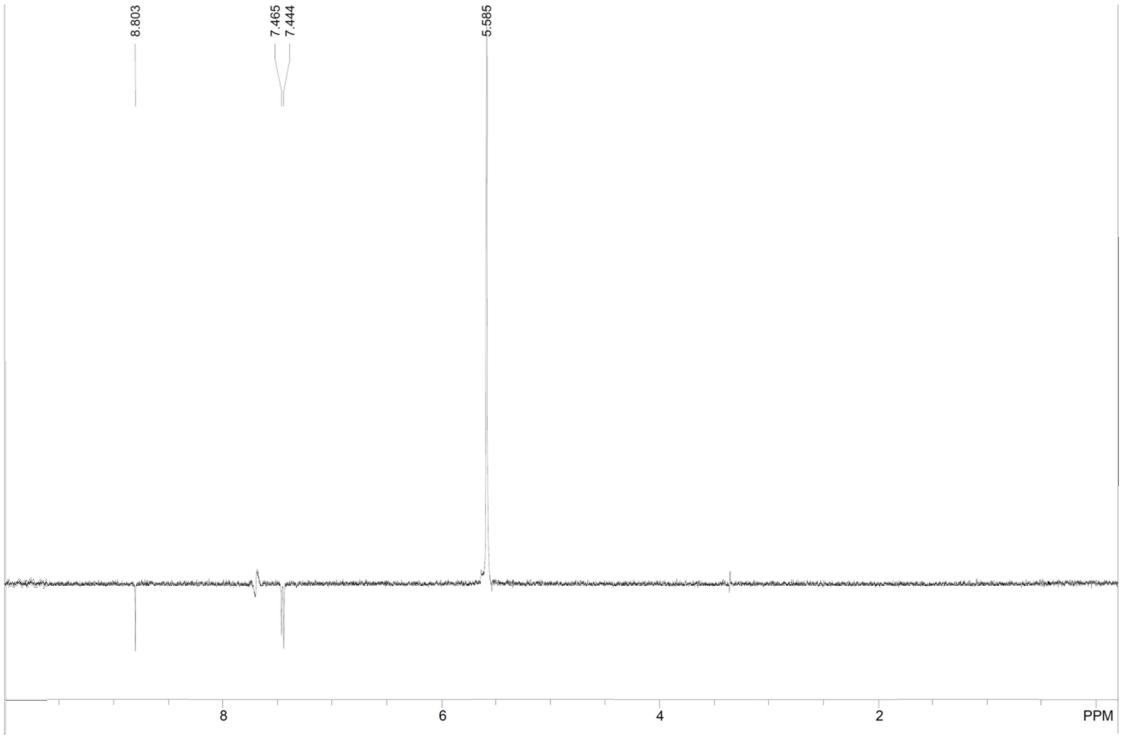
$^1$H NMR (600 MHz, DMSO-*d*6, δ): 5.59 (s, 2H), 6.72–6.77 (m, 1H), 7.19–7.24 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.67 (br s, 2H), 7.92–7.98 (m, 1H), 8.80 (s, 1H).



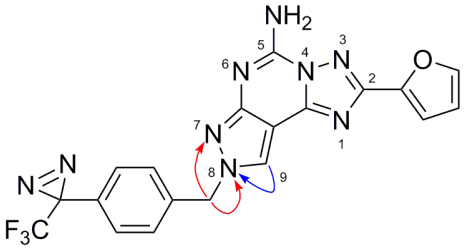
$^1$H NOE (600 MHz, DMSO-*d*6). $^1$H NOE was observed between methylene protons (δ 5.59, s) and H-9 (δ 8.80, s) of compound **9**.



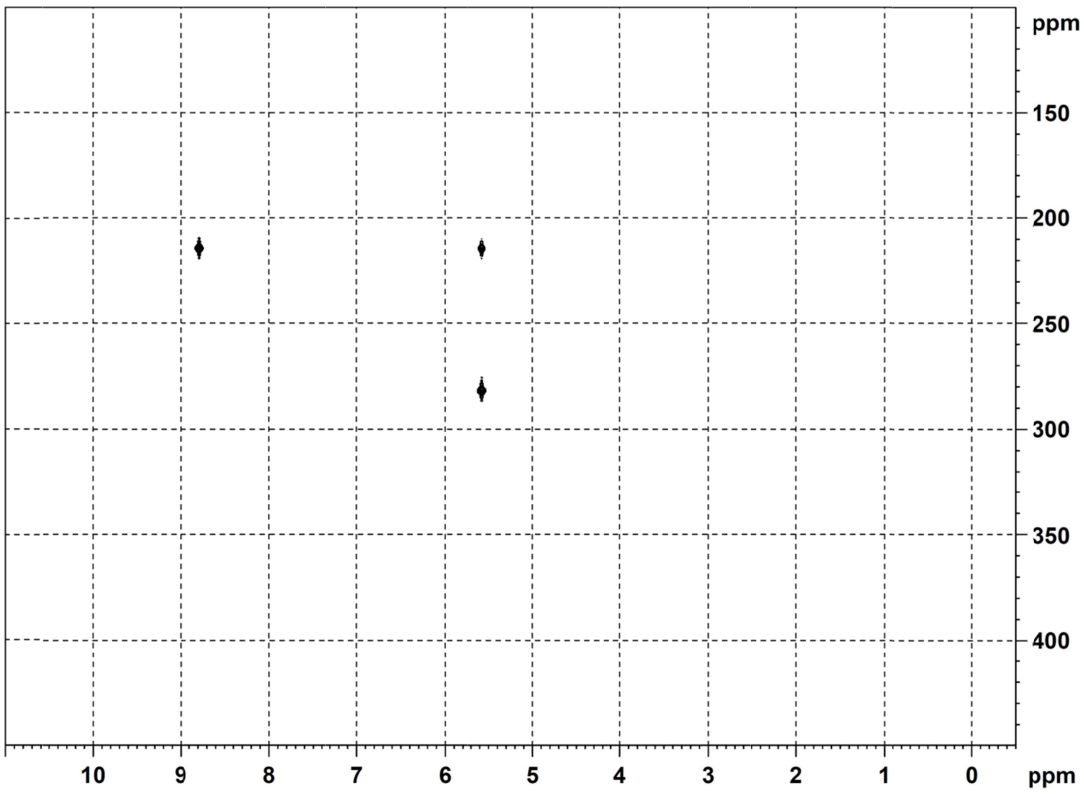

**9**



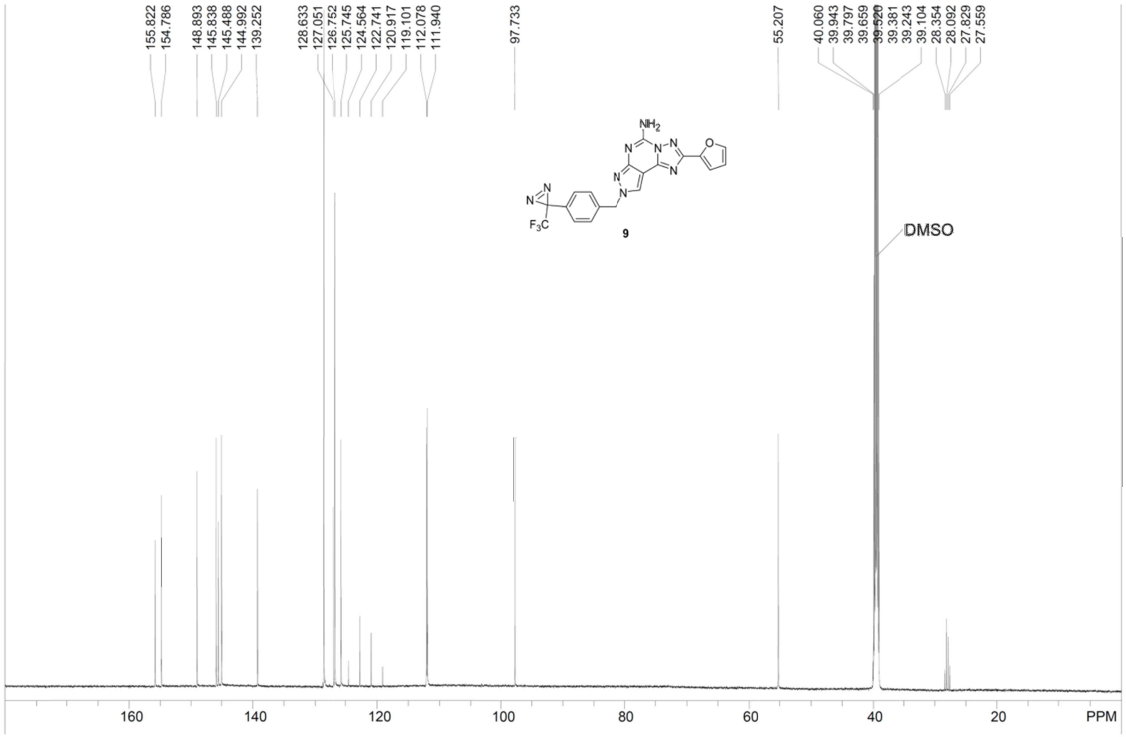
$^{1}H–^{15}N$ HMBC (600MHz, DMSO-*d*6). Two-bond correlation ($^{2}J_{HN}$) and three-bond correlation ($^{3}J_{HN}$), denoted by the red arrowed lines, were observed from $CH_2$ (δ 5.59, s) to the pyrazolo-triazolo-pyrimidine (PTP) N-8 (δ 214.5 ppm) and N-7 (δ 282.0 ppm) respectively. Two-bond correlation ($^{2}J_{HN}$), denoted by the blue arrowed line, was observed from H-9 (δ 8.80, s) to the pyrazolo-triazolo-pyrimidine (PTP) N-8 (δ 214.5 ppm).



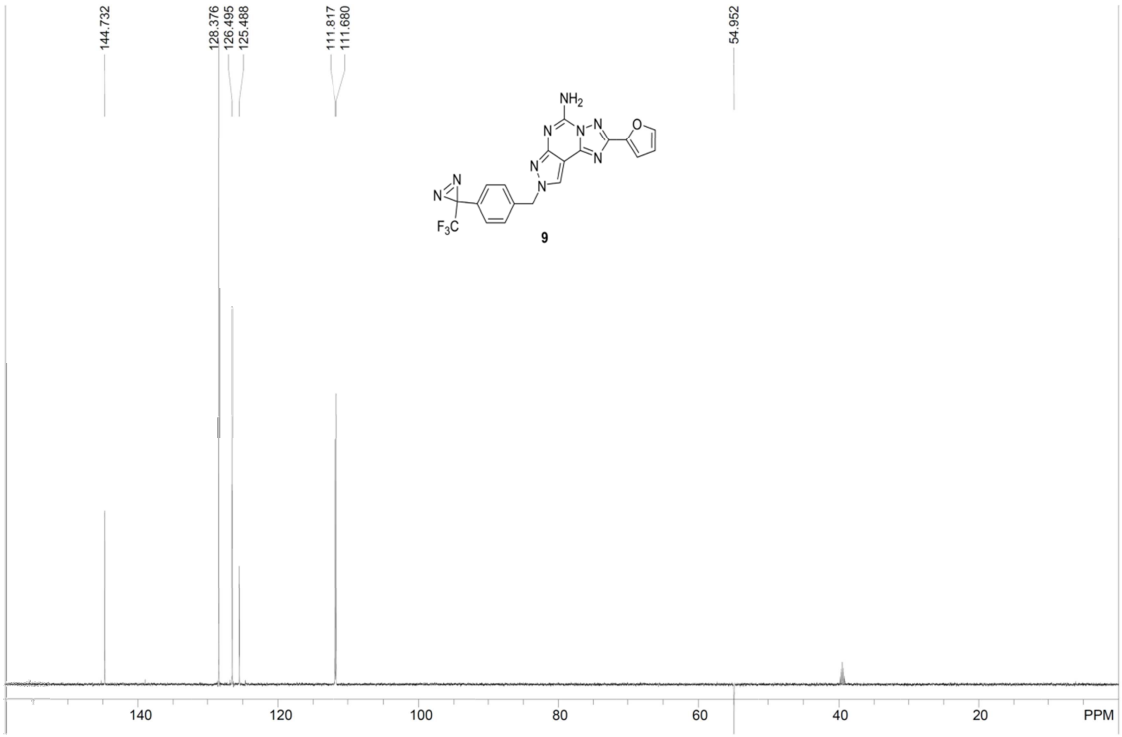

**9**



$^{13}$C NMR (600 MHz, DMSO-*d*6, δ): 28.0 (q, *J* = 40.2 Hz, diazirine-C), 55.2, 97.7, 111.9, 112.1, 121.8 (q, *J* = 274.6 Hz, $CF_3$), 125.8, 126.8, 127.1, 128.6, 139.3, 145.0, 145.5, 145.8, 148.9, 154.8, 155.8.

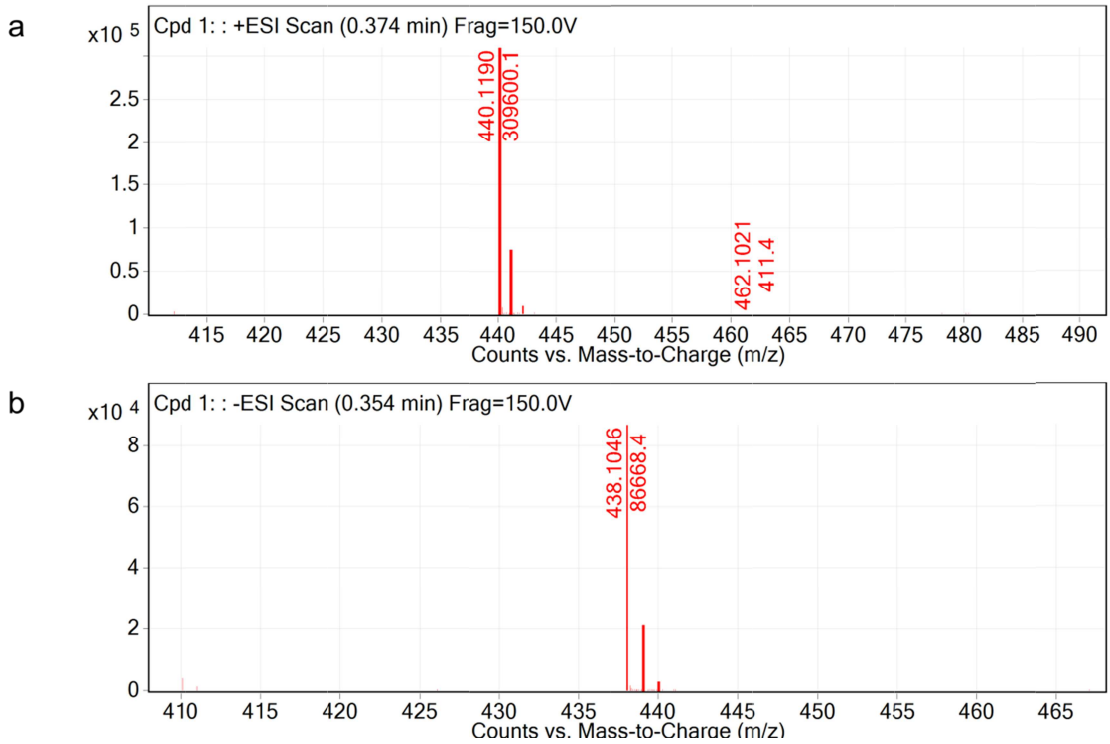


$^{13}$C DEPT NMR (600 MHz, DMSO-*d*6, δ): 55.0, 111.7, 111.8, 125.5, 126.5, 128.4, 144.7.

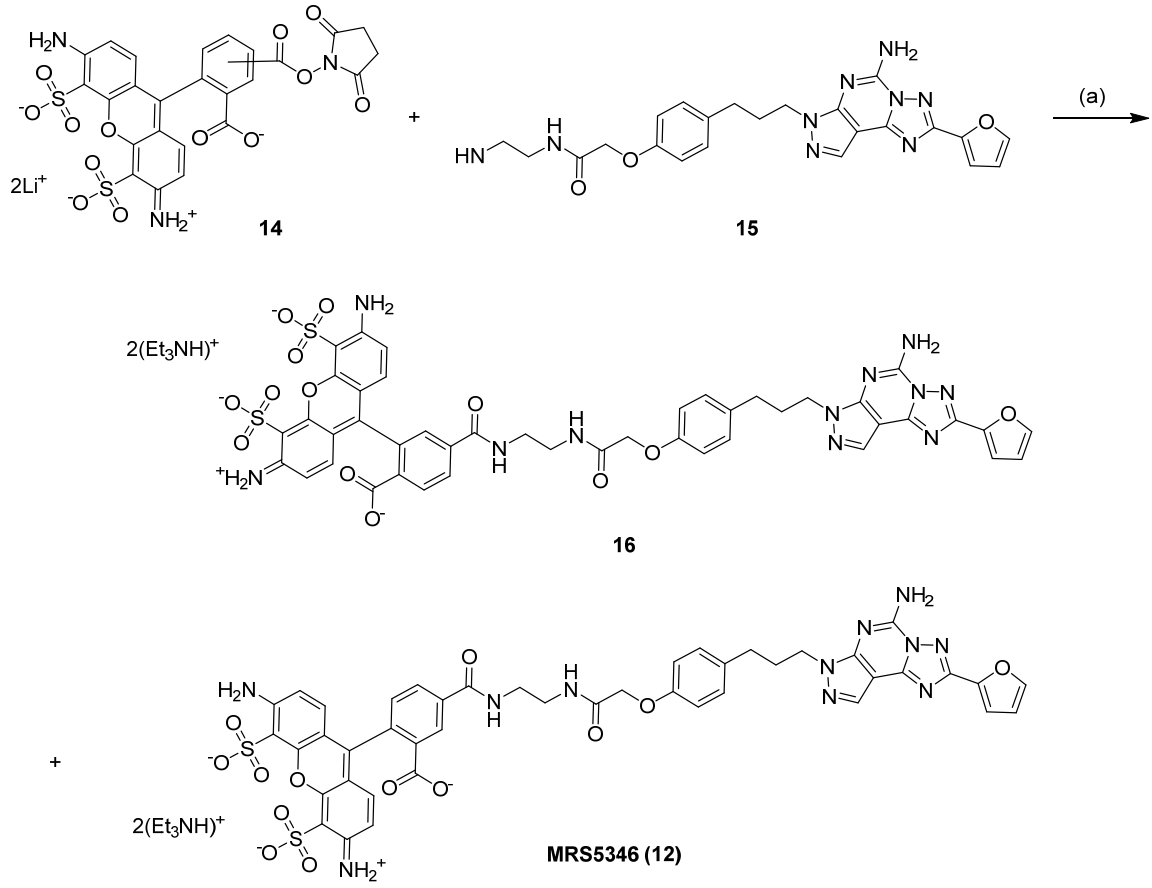


(a) HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{19}H_{13}F_3N_9O$, 440.1190; found 440.1190.

(b) HRMS–ESI (*m/z*): $[M - H]^-$ calcd for $C_{19}H_{11}F_3N_9O$, 438.1044; found 438.1046.



2.2 Synthesis of a fluorescent tracer MRS5346 (**12**).



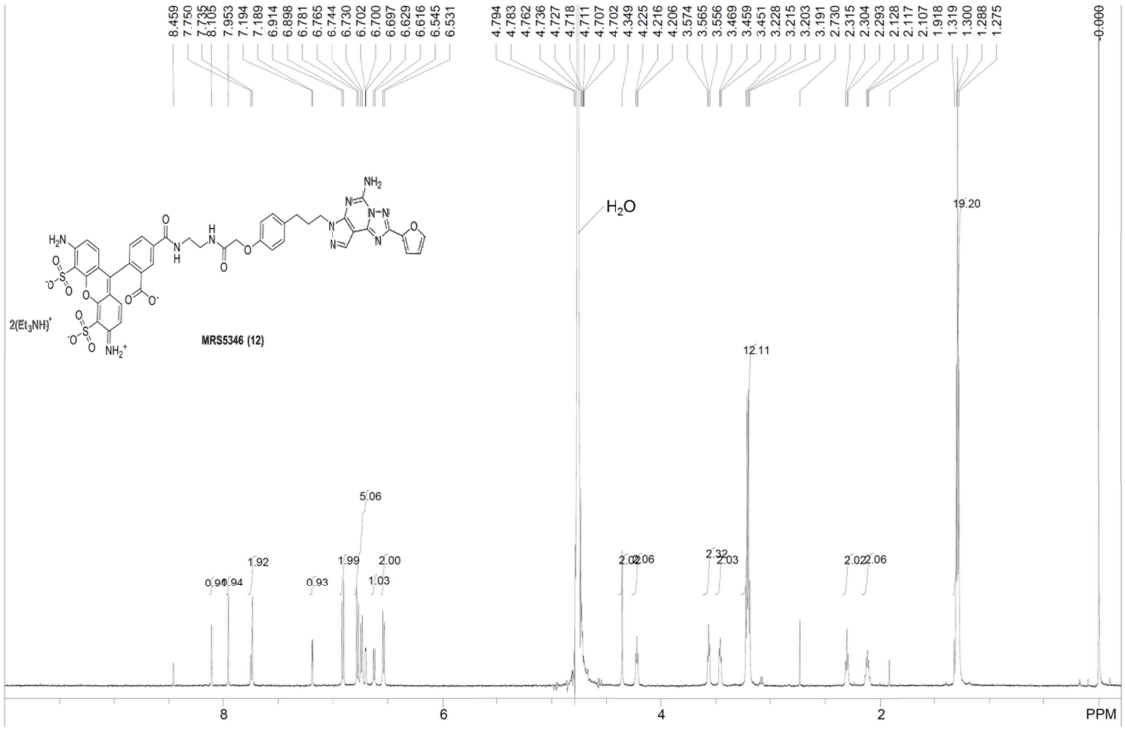

To the mixture of Alexa Fluor 488 carboxylic acid–succinimidyl ester **14** (2.9 mg, 4.5 μmol; Thermo Fisher Scientific Inc., Waltham, MA, USA) and amine **15** (2.3 mg, 4.8 μmol)[2] in dry DMF (150 μL) was added triethylamine (1.4 μL, 9.9 μmol) and the mixture was stirred at room temperature for overnight. The mixture was purified with reverse-phase preparative HPLC to give 6-isomers **16** (1.0 mg, 19%) and MRS5346 (**12**) (0.7 mg, 13%), respectively.

2.3 Reverse-phase preparative HPLC conditions.

- Column: YMC Triart C18 (20 × 50 mm, 5 μm particle size; YMC, Kyoto, Japan).
- Eluents: water (Solvent A)/0.1% triethylamine in acetonitrile (Solvent B), 0–20 min (linear gradient, A/B = 98/2 to 10/90).
- Flow rate: 30 mL/min.
- Detection wavelength: 254 nm.

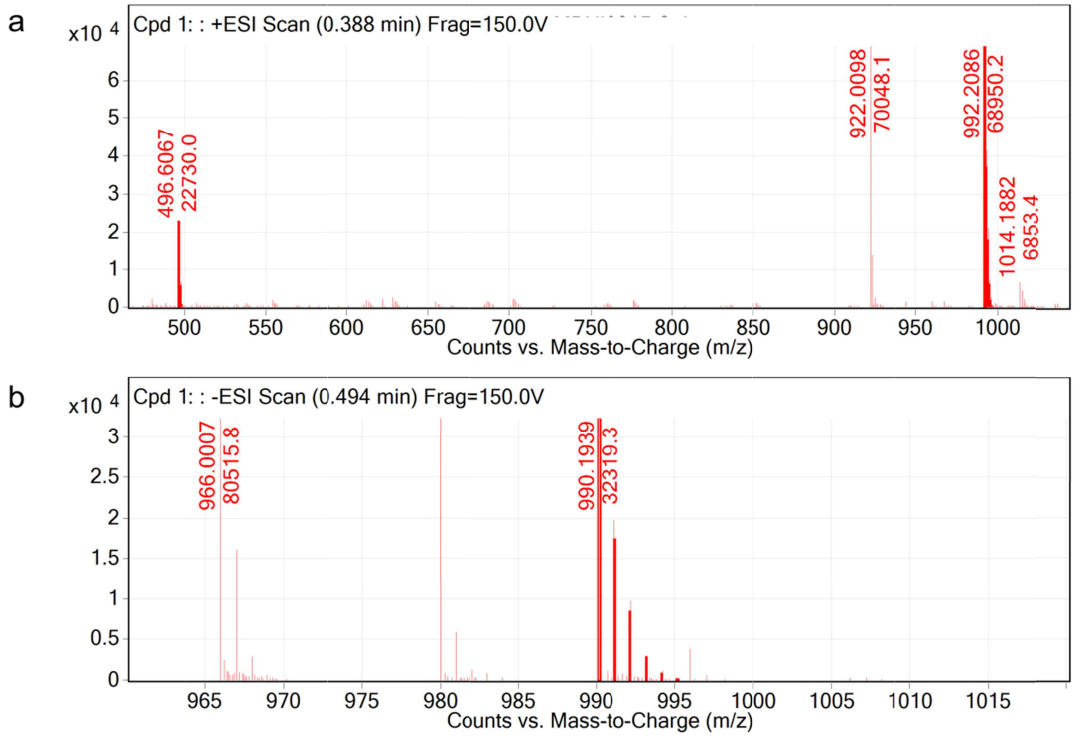
**Spectral characterization of ditriethylamine 5-({2-[2-(4-{3-[5-Amino-2-(2-furanyl)-7*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidin-7-yl]propyl}phenoxy)acetamido]ethyl}carbamoyl)-2-(6-amino-3-imino-4,5-disulfonato-3*H*-xanthen-9-yl)benzoate (12) (MRS5346)**[2,3]

$^1$H NMR (600 MHz, $D_2O$, δ): 1.29 (t, *J* = 7.4 Hz, 18H, triethylamine-$CH_3$), 2.06–2.18 (m, 2H), 2.30 (t, *J* = 6.9 Hz, 2H), 3.21 (q, *J* = 7.4 Hz, 12H, triethylamine-$CH_2$), 3.42–3.50 (m, 2H), 3.52–3.60 (m, 2H), 4.22 (t, *J* = 5.9 Hz, 2H), 4.35 (s, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 7.9 Hz, 1H), 6.68–6.72 (m, 1H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 9.3 Hz, 2H), 6.91 (d, *J* = 9.3 Hz, 2H), 7.19 (d, *J* = 3.5 Hz, 1H), 7.70–7.78 (m, 2H), 7.95 (s, 1H), 8.11 (s, 1H).



(a) HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{44}H_{38}N_{11}O_{13}S_2$ 992.2086, found 992.2086; $[M + 2H]^{2+}$ calcd for $C_{44}H_{39}N_{11}O_{13}S_2$ 496.6080, found 496.6067.

(b) HRMS–ESI (*m/z*): $[M - H]^-$ calcd for $C_{44}H_{36}N_{11}O_{13}S_2$ 990.1941, found 990.1939.



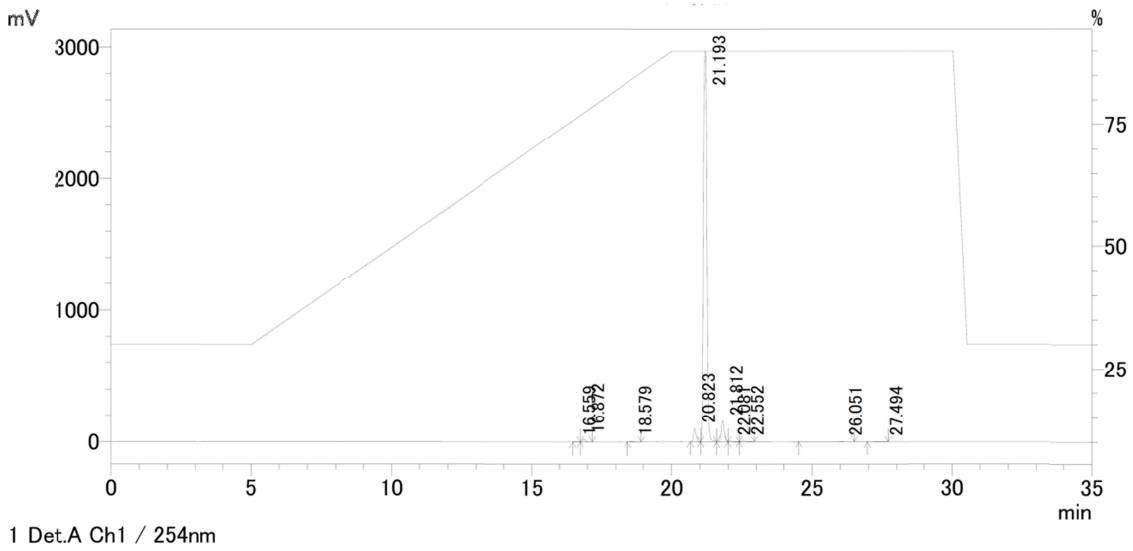
## 3. HPLC assessment of compound purity.

All compounds including compounds **8**, **9**, MRS5346 (**12**), and SCH442416 (**13**)[4] with a purity of >90% were used for the FP and photoaffinity labeling experiments.

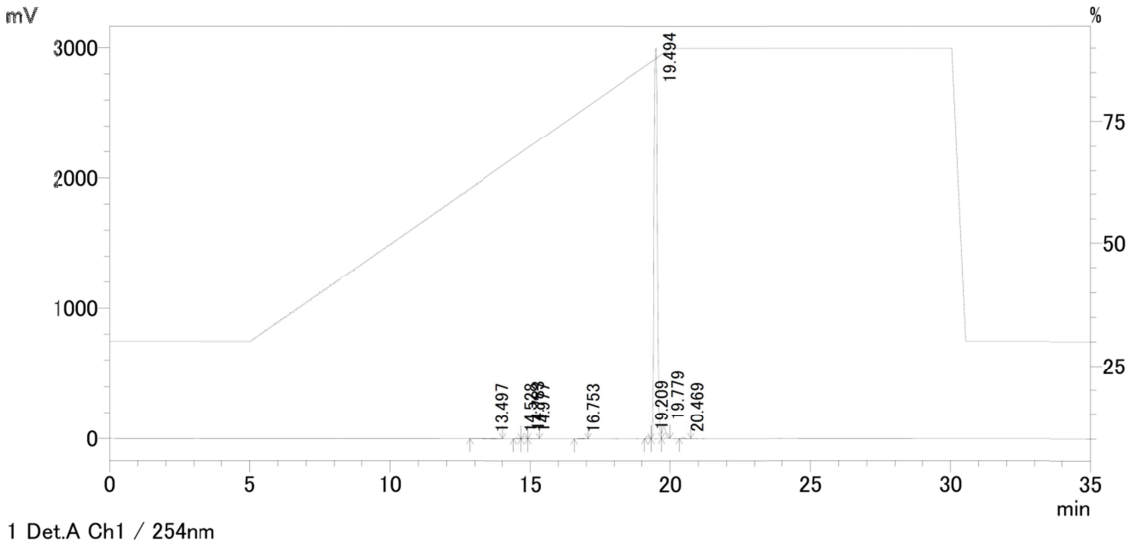
3.1 Analytical HPLC conditions for compounds **8**, **9** and SCH442416 (**13**).

- Column: InertSustain C18 (4.6 × 250 mm, 5 μm particle size, GL Sciences Inc., Tokyo, Japan).
- Column temperature: 35 °C.
- Eluent: 10 mM aqueous ammonium acetate (solvent A)/acetonitrile (solvent B), 0–5 min (A/B = 70/30), 5–20 min (linear gradient A/B = 70/30 to 10/90), 20–30 min (A/B = 10/90).
- Flow rate: 1.0 mL/min.
- Detection wavelength: 254 nm.

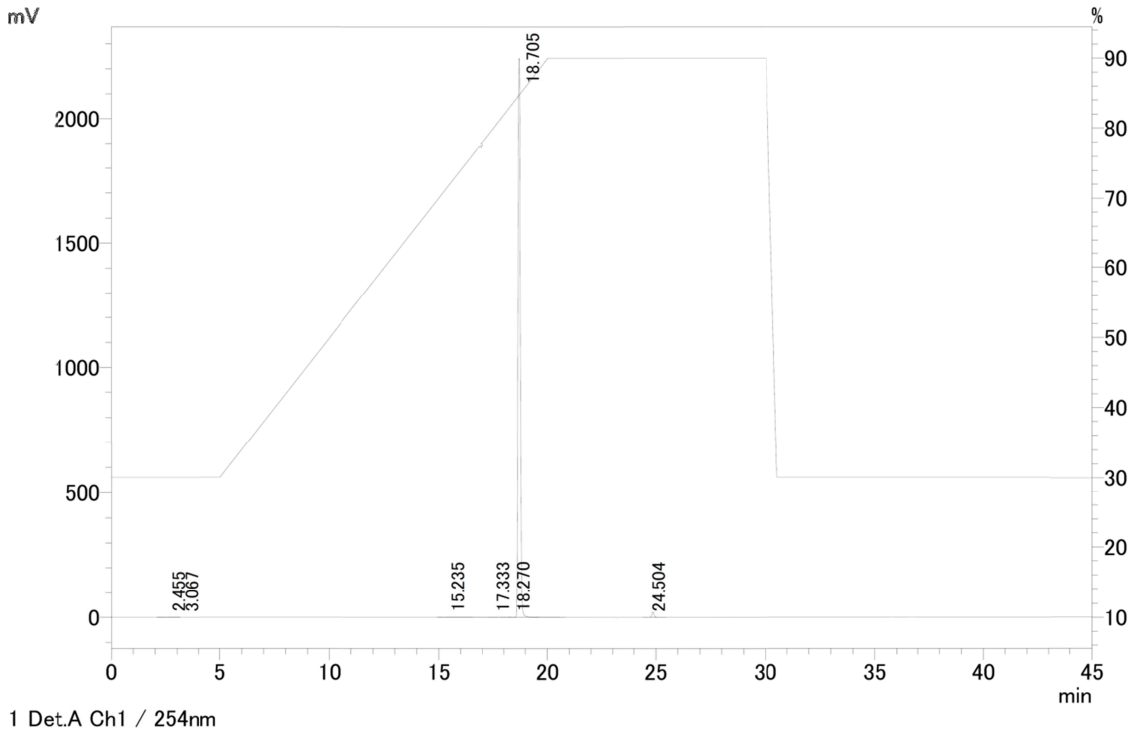
Compound **8**, 91.8% (Retention time: $t_R$ 21.193 min).




Compound **9**, 95.4% (Retention time: $t_R$ 19.494 min).



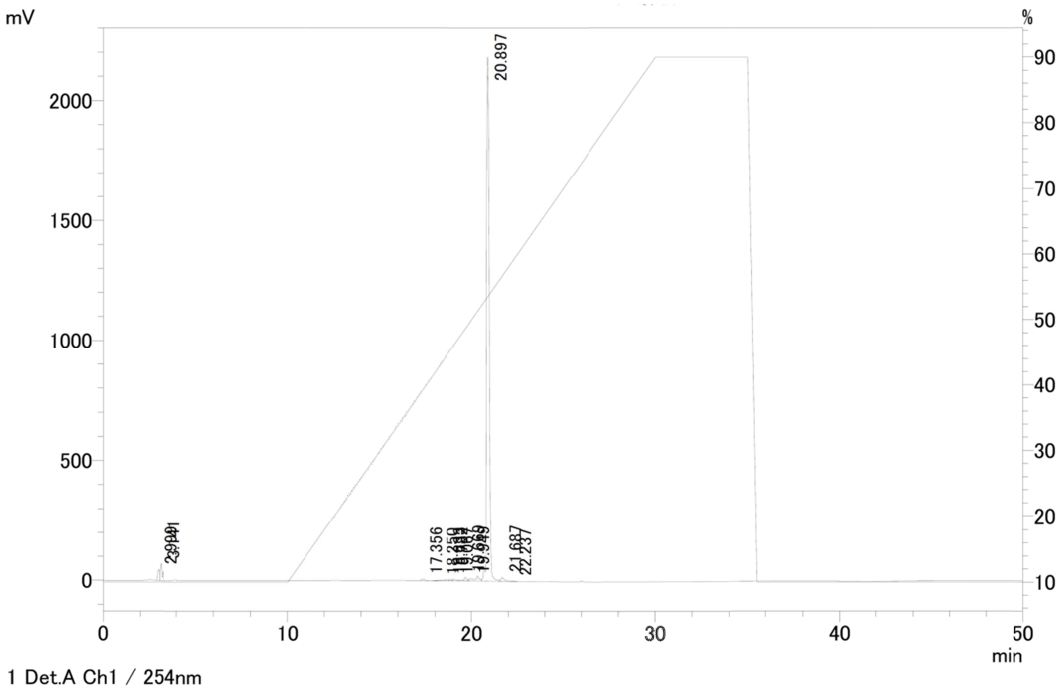
SCH442416 (**13**), 98.9% (Retention time: $t_R$ 18.705 min).



3.2 Analytical HPLC conditions for MRS5346 (**12**).

- Analytical column: InertSustain C18 (4.6 × 250 mm, 5 μm particle size, GL Sciences Inc., Tokyo, Japan).
- Column temperature: 35 °C.
- Eluent: 10 mM aqueous ammonium acetate (solvent A)/acetonitrile (solvent B), 0–10 min (A/B = 100/0), 10–30 min (linear gradient, 100/0 to 10/90), 30–35 min (10/90).
- Flow rate: 1.0 mL/min.
- Detection wavelength: 254 nm.

MRS5346 (**12**), 91.5% (Retention time: $t_R$ 20.897 min).



## 4. Protein expression and purification.

4.1 Protein expression.

The cDNA encoding the C-terminal-truncated human $A_{2A}$ adenosine receptor (1–316) with a C terminal 10× His tag followed by a 1D4 tag was kindly provided by Dr. I. Shimada (University of Tokyo) and subcloned into the pPinkα-HC expression vector (Thermo Fisher Scientific Inc., Waltham, MA, USA) downstream of the yeast α-mating factor secretion signal sequence. The resulting plasmid was linearized with PmeI and transformed into the *P. pastoris* strain PichiaPink Strain 1 (Thermo Fisher Scientific Inc., Waltham, MA, USA) by electroporation. Transformants harboring the receptor sequence were selected on SD (−Ade) ager plate. A single colony of transformants was grown into 10 ml of BMGY medium [1% (w/v) yeast extract, 2% (w/v) peptone, 1.34% (w/v) yeast nitrogen base without amino acids, 0.00004% (w/v) biotin, 1% (v/v) glycerol, 0.1 M phosphate buffer at pH 6.0] to saturation at 30 °C, and then transferred to 1 L of BMGY medium. After the culture was grown to an OD 600 over 15 h at 29 °C, cells were harvested by centrifugation and resuspended into 1 L of BMMY medium [1% (w/v) yeast extract, 2% (w/v) peptone, 1.34% (w/v) yeast nitrogen base without amino acids, 0.00004% (w/v) biotin, 1% (v/v) methanol, 0.1 M phosphate buffer at pH 6.0] containing 2.5% (v/v) DMSO and 10 mM theophylline. The culture was further grown for 24–36 h at 22 °C to induce receptor expression. Cells were harvested by centrifugation and resuspended in a buffer containing 20 mM Tris-HCl (pH 7.4), 150 mM NaCl.

4.2 Protein purification.

Receptor expressed cells were disrupted using 0.5 mm glass or zirconia beads. Undisrupted cells and cell debris were removed by centrifugation at 1,500 g for 5 min and at 10,000 g for 30 min. Cell membranes were isolated by ultracentrifugation at 100,000 g for 30 min and resupended in a buffer containing 20 mM Tris-HCl (pH 7.4), 150 mM NaCl. 10% DDM (*n*-dodecyl-β-D-maltoside)/2% CHS (cholesteryl hemisuccinate) stock solution was added to the membrane suspension to give a final concentration of 2% DDM/0.4% CHS. After overnight incubation at 4 °C, the solubilized membrane was separated by ultracentrifugation at 100,000 g for 30 min. Resulting supernatant was batch bound with TALON resin (Clontech Laboratories, Inc., Palo Alto, CA, USA) in a chromatography column for 2 h at 4 °C. After washing the resin with 10 bed volume of a buffer containing 20 mM Tris-HCl (pH 7.4), 150 mM NaCl, 10 mM imidazole, 0.05% DDM, and 0.01% CHS, receptor was eluted with a buffer containing 20 mM Tris-HCl (pH 7.4), 150 mM NaCl, 200 mM Imidazole, 0.05% DDM, and 0.01% CHS. Finally, the eluted receptor was concentrated by centrifugal filter device and buffer was exchanged into 20 mM Tris-HCl (pH 7.4), 150 mM NaCl, 0.05% DDM and 0.01% CHS by a PD-10 column (GE

Healthcare, Milwaukee, WI, USA).

## 5. Fluorescence polarization experiments.

5.1 Saturation binding expetiments.

Saturation binding expetiments were performed in triplicate in black, non-binding 384 well plates (Greiner; cat. no. 784900). To each well, four concentrations of the tracer **12** (final concentration: 1, 2, 4, and 8 nM) and increasing concentrations of $hA_{2A}AR$ (final concentration: 0–2000 nM) were added to a final volume 20 μL in the assay buffer (20 mM Tris-HCl, pH 7.4, 150 mM NaCl, 0.05% DDM, 0.01% CHS). To confirm the specific binding, another saturation binding experiment was performed with 2 nM (final concentration) of the tracer **12** in the presence of 10 μM (final concentration) of SCH442416 (**13**). The plate was incubated at room temperature for 1 h to reach equilibrium. The polarization values were measured at an excitation wavelength at 470 nm (5 nm bandwidth) and an emmision wavelength at 520 nm (20 nm bandwidth) using an Infinite M1000 plate reader. The compound concentration ($K_d$) at which 50% of the tracer **12** bound was dertermined using PRISM (version 4.03, GraphPad Software, La Jolla, CA, USA).

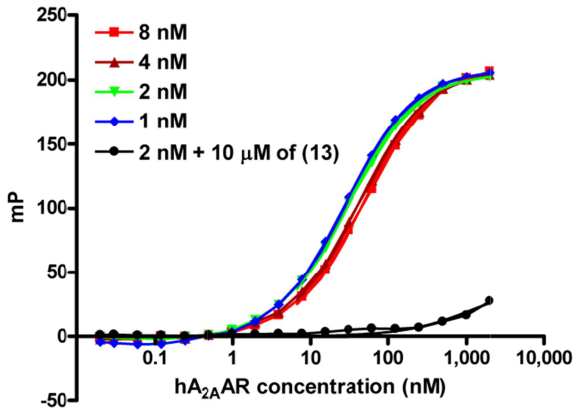



**Figure S1-1.** FP saturation binding experiments on solubilized $hA_{2A}AR$ with the tracer **12** at different concentrations: ■, 8 nM; ▲, 4 nM; ▼, 2 nM; ◆, 1 nM; ●, 2 nM in the presence of 10 μM of SCH442416 (**13**). Data is shown as mean ± SEM; $N = 3$.

**Table S1-1. $K_d$ values of the tracer 12 caliculated in different concentrations.**

| Concentration of tracer **12** | $K_d$ (nM) |
|---|---|
| 8 nM | 49.5 ± 0.3 |
| 4 nM | 42.4 ± 0.6 |
| 2 nM | 30.8 ± 0.5 |
| 1 nM | 29.0 ± 0.6 |

5.2 Competitive binding experiments.

Competitive binding experiments were performed in triplicate in black, non-binding 384-well plates (Greiner; cat. no. 784900). Two-fold serial dilutions of compounds ZM241385 (**1**), XAC (**2**), NECA (**5**), compounds **8**, and **9** were prepared as 100× solution in anhydrous DMSO and spotted into plate (200 nL) by a mosquito HTS liquid handler. 20 μL of the pre-mix solution of $hA_{2A}AR$ (final concentration, 25 nM) and the tracer **12** (final concentration, 2 nM) in assay buffer (20 mM Tris-HCl, pH 7.4, 150 mM NaCl, 0.05% DDM, 0.01% CHS) was added to the plate. The plate was incubated at room temperature for 1 h to reach equilibrium. The polarization values were measured as described above. Each plate included positive controls (corresponding to 100% inhibition) with only tracer **12** in assay buffer and negative controls (corresponding to 0% inhibition) containing tracer **12** and the $hA_{2A}AR$ in assay buffer to calcurate minimum and maximum binding. $IC_{50}$ values were dertermined from the plot using non linear least squares analysis. $K_i$ values of test compounds were calucurated using the Cheng-Prusoff equation. The curve fitting was performed by PRISM (version 4.03, GraphPad Software, La Jolla, CA, USA).

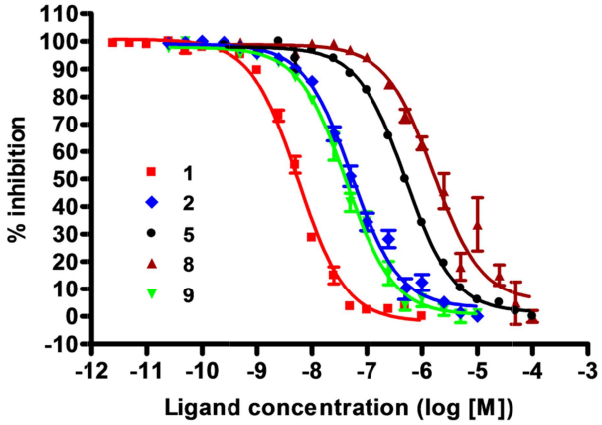



**Figure S1-2.** Normalized FP competitive binding experiments: ■, ZM241385 (**1**); ◆, XAC (**2**); ●, NECA (**5**); ▲, compound **8**; ▼, compound **9**. Data is shown as mean ± SEM; *N* = 3.

**Table S1-2. $K_i$ values of the adenosine antagonists and agonist together with photoaffinity probes.**

| Compounds | $K_i$ | Lit $K_i$[5] |
|---|---|---|
| ZM241385 (**1**) | 5.3 ± 0.03 nM | 3.3 ± 0.6 nM |
| XAC (**2**) | 50.1 ± 0.03 nM | 43.9 ± 0.4 nM |
| NECA (**5**) | 481 ± 0.02 nM | 1.3 ± 0.3 μM |
| Compound **8** | 1520 ± 0.06 nM | |
| Compound **9** | 39.7 ± 0.03 nM | |

## 6. Photoaffinity labeling and in-solution digestion.

6.1 Photoaffinity labeling.

The mixtures of the $hA_{2A}AR$ (75 μg, 2 nmol, final concentration 10 μM) and compound **9** (final concentration 20 μM) with/without ZM241385 (**1**) (final concentration 100 μM) in reaction buffer (200 μL, 50 mM Tris-HCl pH 7.4, 150 mM NaCl, 0.05% DDM, 0.01% CHS) were incubated at 30 °C for 30 min. Final DMSO concentration of mixtures were 1.0%. The each reaction mixtures were irradiated with a model B-100A UV lamp from a distance of 5 cm for 30 min on ice (measured light intensity: 5 $mW/cm^2$). Peak wavelength of the UV lamp was 365 nm and bandwidth was approximately 50 nm.

6.2 In-solution digestion.

The photolabeling samples were treated with 10% (v/v) TCA on ice for 25 min and sedimented at 12,000 × g for 5 min. The supernatants were discarded and suspended in 100 mM Tris-HCl (pH 8.0) and sedimented at 12,000 × g for 5 min. This washing step was repeated again. The supernatants were discarded and the pellet was suspended in buffer containing 10 mM $CaCl_2$, 0.05% CYMAL-5 (Anatrace, Maumee, OH, USA), 0.1% Rapigest (Waters, Milford, MA, USA) in 100 mM Tris-HCl (pH 8.0). The mixture was lysed by sonication in a Bioruptor UCD-200T sonicator (Toso, Tokyo, Japan) for 3 min under ice cooling. The samples were treated with 10% (v/v) of 50 mM TCEP-HCl (pH 7.0) and incubated at 30 °C for 1 h. After addition of 10% (v/v) of 500 mM iodoacetamide, the mixtures were incubated in darkness at room temperature for 1 h. Alkylation was stopped by the addition of 14% (v/v) of 500 mM DTT solution. The pH was adjusted (> 7.0) with addition of 11% (v/v) of 100 mM Tris-HCl (pH 8.0). To the mixture was added sequencing grade chymotrypsin (Promega, Madison, WI, USA) at a ratio of 1:20 chymotrypsin/$hA_{2A}AR$ and incubated at 25 °C for 13 h. Digestion was stopped by the acidification with 5% (v/v) of an acidic aqueous solution containing 10% trifluoroacetic acid and 40% acetonitrile in water, and incubated for 20 min at 37 °C. The pH was adjusted to pH 6 with 1 M Tris-HCl (pH 8.0) and the mixture was centrifuged at 12,000 × g for 5 min. The supernatants were subjected to LC–MS/MS analysis. The same procedure was performed to prepare tryptic peptides by using the sequencing grade trypsin instead of chymotrypsin (Promega, Madison, WI, USA).

## 7. LC–MS and LC–MS/MS analysis conditions.

7.1 LC–MS analysis of intact $hA_{2A}AR$ samples.

Purified and photolabeled $hA_{2A}AR$ samples were analyzed by a 6520 Accurate-Mass Q-TOF instrument with a 1200 series HPLC. The measurement conditions were described as follows.

LC–MS analysis conditions.

- Analytical column: PLRP-S (4.6 × 100 mm, 300 Å pore size, 5 μm particle size, Agilent)
- Column temperature: 60 °C
- First gradient: flow rate, 0.5 mL/min; eluent A (0.1% formic acid in water) and eluent B (0.1% formic acid in acetonitrile), 0–1 min (linear gradient, A/B = 70/30 to 0/100), 1–5 min (100% B).
- Second gradient: flow rate, 0.4 mL/min; eluent A (0.1% formic acid in water) and eluent B (0.1% formic acid in isopropyl alcohol), 0–1 min (linear gradient, A/B = 70/30 to 0/100), 1–5 min (100% B). The column was regenerated by repeated washing with both gradient conditions.
- MS parameters: Ion source, electron spray ionization (positive); drying gas temperature, 300 °C; drying gas flow, 13 L/min; nebulizer pressure, 60 psi; VCap, 3500 V; fragmentor, 200 V.

7.2 LC–MS/MS analysis of digested peptide samples.

Digested peptide samples from in-solution digestion with chymotrypsin and trypsin were analyzed by the same Q-TOF instruments. The measurement conditions were described as follows.

LC–MS/MS analysis conditions.

- Analytical column: XBridge BEH C18 column (2.1 × 100 mm, 130 Å pore size, 3.5 μm particle size, Waters).
- Column temperature: 60 °C.
- Flow rate: 0.5 mL/min.
- Gradient condition: eluent A (0.1% formic acid in water) and eluent B (0.1% formic acid in acetonitrile), 0–2 min (A/B = 98/2), 2–60 min (linear gradient, A/B = 98/2 to 30/70), 60–60.1 min (linear gradient, A/B = 30/70 to 10/90), 60.1–65 min (A/B = 10/90).
- MS parameters: Ion source, ESI-positive; drying gas temperature, 300 °C; drying gas flow, 12 L/min; nebulizer pressure, 50 psig; VCap, 3500 V; fragmentor, 150 V.
- MS/MS parameters: MS scan rate, (3 spectra/sec, $m/z$ = 100–2000); intensity threshold, 1000; max precursors per cycle, 10; isolation width, Medium; MS/MS scan rate, (2 spectra/sec, $m/z$ = 50–3000).

**Table S1-3. Collision energy ramp settings for auto MS/MS.**

| Charge | Slope | Offset |
|---|---|---|
| $z = 1$ | 3.1 | 6.7 |
| $z = 2$ | 3.1 | 6.7 |
| $z = 3$ | 3.6 | −4.8 |
| $z > 3$ | 3.6 | −4.8 |

7.3 LC–MS/MS analysis for the target peptide.

The target peptide ($m/z$ = 913.9227, $z$ = 4) detected from chymotryptic digests was analyzed by the same measurement conditions as 7.2 except for MS/MS parameters as follows.

• MS/MS parameters: target mass ($m/z$ = 913.9226, $z$ = 4); retention time, 35.7 min; delta retention time, 5 min; isolation width, medium; collision energy, (31, 34, and 37 V); acquisition time, 1500 ms/spec.

## 8. LC–MS and LC–MS/MS results.

8.1 LC–MS results of intact $hA_{2A}AR$.

All LC–MS data aquired by Q-TOF instrument were processed by Agilent MassHunter Workstation Software Qualitative Analysis with BioConfirm Software (Version B.06.00). MS spectrum was obtained by manual integration of the main peak in the total ion chromatogram (TIC). The multiply charged ions produced by ESI were deconvoluted to zero-charge molecular mass values by means of the Maximum Entropy deconvolution algorithm.

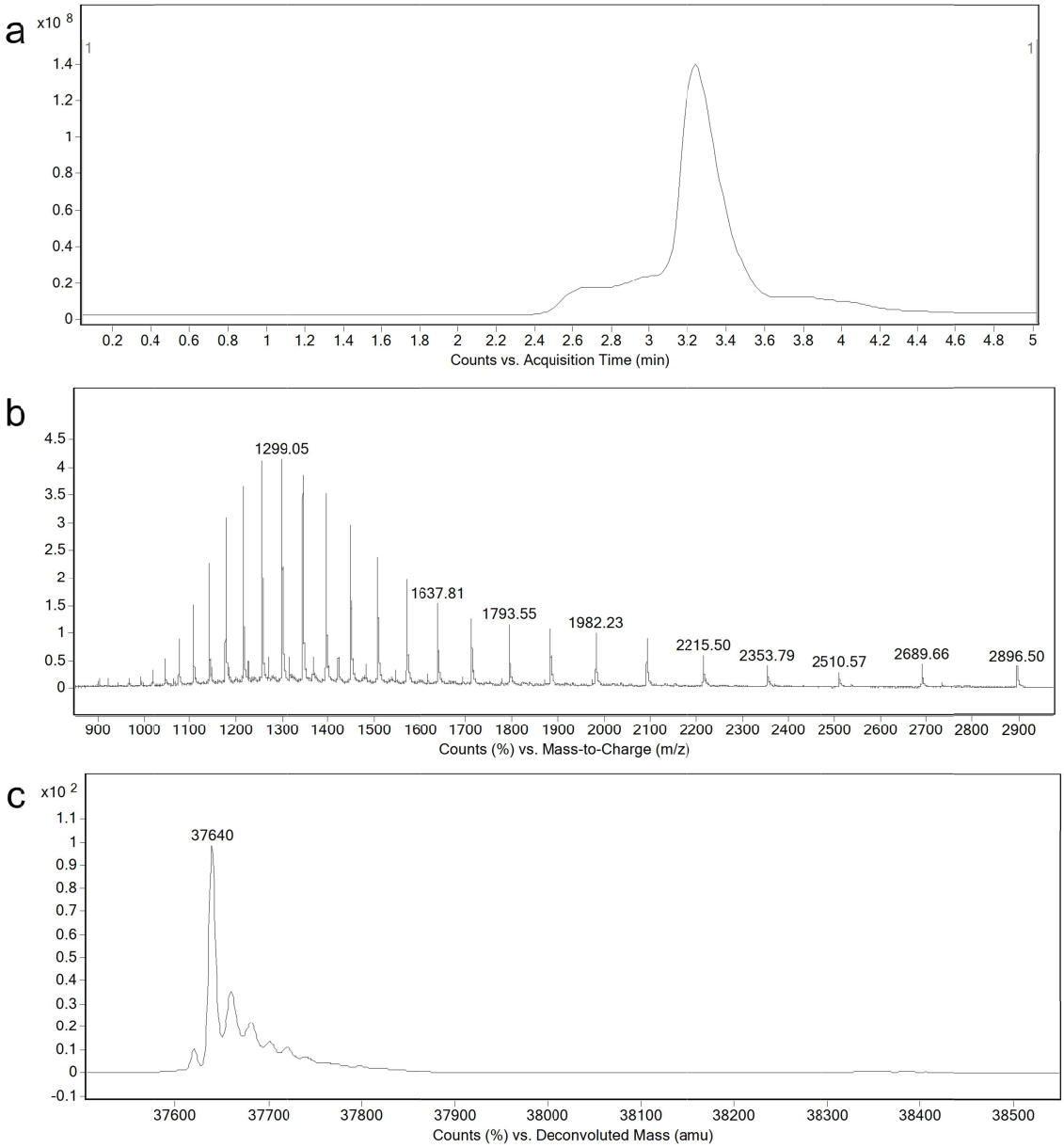



**Figure S1-3.** LC–MS results of purified $hA_{2A}AR$. (a) TIC of the second gradient. (b) An averaged mass spectrum (3.1–3.5 min). (c) Deconvoluted mass spectrum.

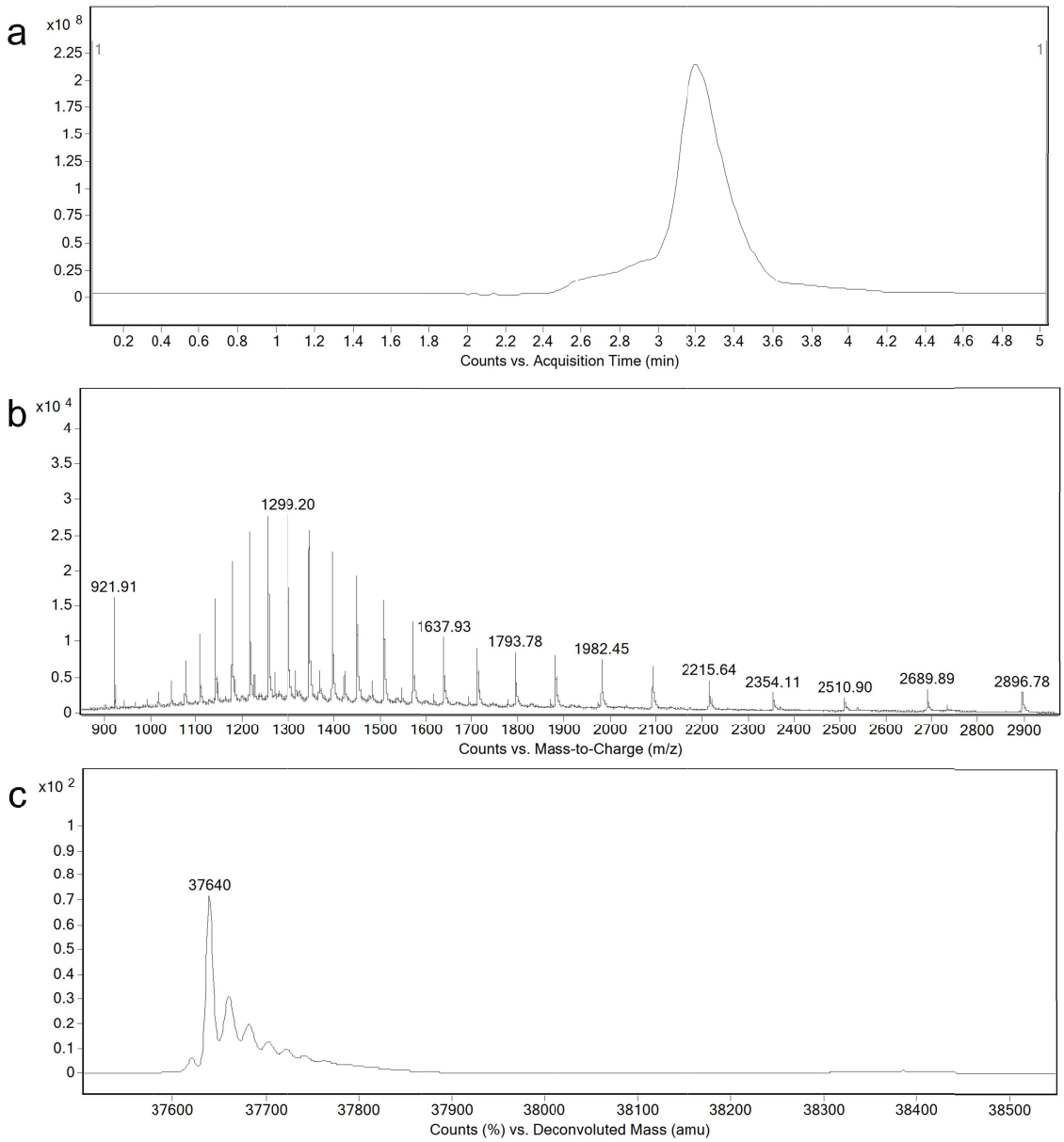



**Figure S1-4.** LC–MS results of the $hA_{2A}AR$ in DMSO control after UV irradiation. (a) TIC of the second gradient. (b) An averaged mass spectrum (3.1–3.5 min). (c) Deconvoluted mass spectrum.

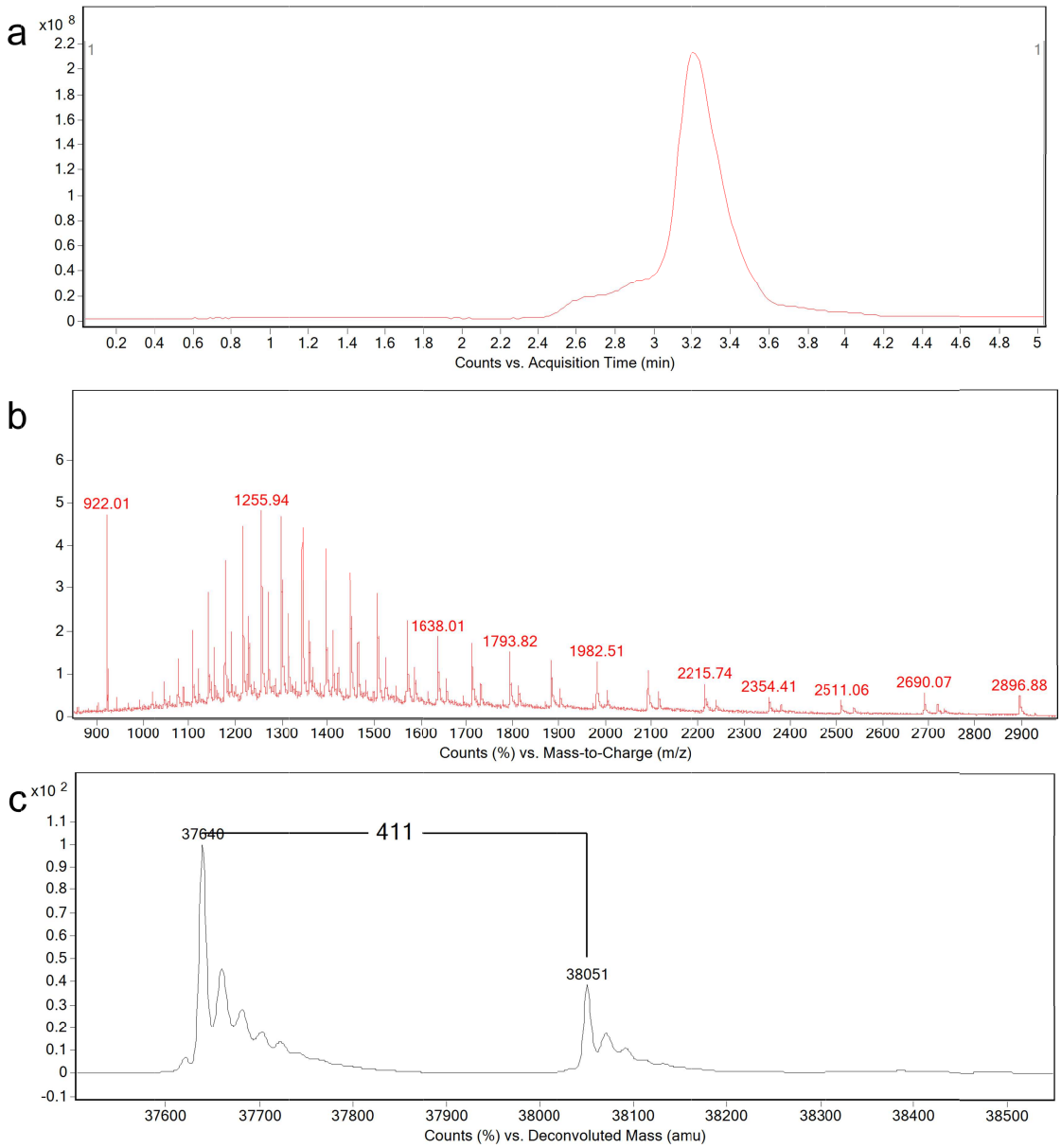



**Figure S1-5.** LC–MS results of the $hA_{2A}AR$ with compound **9** after UV irradiation. (a) TIC of the second gradient. (b) An averaged mass spectrum (3.1–3.5 min). (c) Deconvoluted mass spectrum.

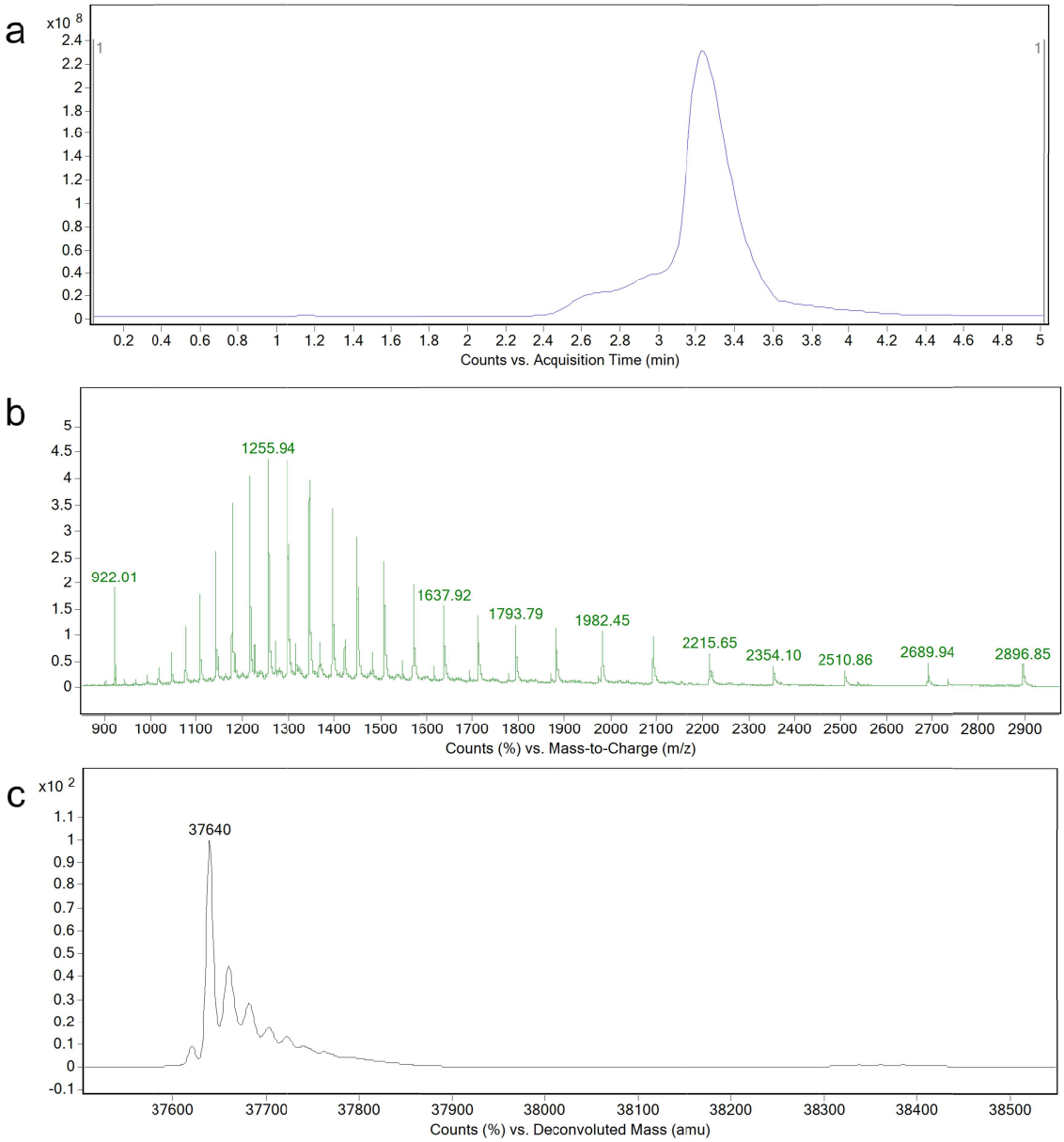



**Figure S1-6.** LC–MS results of the $hA_{2A}AR$ with compound **9** in the presence of a 5-fold molar excess of ZM241385 (**1**) after UV irradiation. (a) TIC of the second gradient. (b) An averaged mass spectrum (3.1–3.5 min). (c) Deconvoluted mass spectrum.

8.2 LC–MS/MS results of the digested peptides (peptide mapping).

Raw data were processed with PEAKS Studio (version 7.5, Bioinformatics Solutions Inc., Waterloo, Canada). Data refinement was done using following parameters: merge scans, 1.0 min, 5 ppm; correct precursor mass option, enabled; precursor charge states, minimum $z$ = 1 and maximum $z$ = 8. The following parameters were used for the PEAKS search: parent mass error tolerance, 10 ppm; fragment mass error tolerance, 0.05 Da; fixed modification, carbamidomethylation. The chymotrypsin cleavage sites were used with default settings at C-terminal side of F, L, M, W, Y (not before P) and maximum missed cleavages per peptides were set to 8. The trypsin cleavage sites were also used with default settings at C-terminal side of K, R (not before P) and allowed for up to 2 missed cleavage sites. The results of peptide mapping were shown in supporting information 2.

8.3 LC–MS/MS results of the digested peptides (cross-linked peptide search).

The personal compound database and library (PCDL) comprising theoretical digested-peptides formulae with fixed modification of cysteine carbamidomethylation ($C_2H_3NO$) and one molecule of compound **9** with a loss of $N_2$ ($C_{19}H_{12}F_3N_7O$) was created by in-house software. The chymotrypsin and trypsin cleavage sites were defined the same as described in section 8.2. Raw data were searched for potential matches against the PCDL database with Agilent MassHunter Find-by-Formula (FBF) algorithm with a 10 ppm mass tolerance. Isotopic distribution pattern and the presence of other multiply-charged ions were visually inspected. As a result of the search, tertiary charged peptide ions with $m/z$ = 913.9158 (calcd for $m/z$ = 913.9226, $z$ = 4) together with triply charged peptide ions with $m/z$ = 1218.2253 (calcd for $m/z$ = 1218.2278, $z$ = 3) that corresponded to the single cross-linked peptide (Cys259$^{6.61}$–Phe286$^{7.51}$) located near the extracellular start of TM7 were detected (Figure S1-7).

An additional LC–MS/MS analysis targeted to the quadruply charged cross-link peptide ion (m/z = 913.9226, $z$ = 4) was carried out to determine the cross-link position. MS/MS spectra for the unlabeled Cys259$^{6.61}$–Phe286$^{7.51}$ chymotryptic peptide were also acquired. Spectrum comparisons are shown in Figure S1-8. The same fragment ions (b11 and some smaller b-series ions) were observed in both spectra. On the other hand, similar patterns of fragment ions with a mass shift of compound 9 with a loss of $N_2$ (b13 and some larger b-series ions)were observed in the labeled peptides. These results supported the cross-link position of Tyr271$^{7.36}$ for the h$A_{2A}$AR.

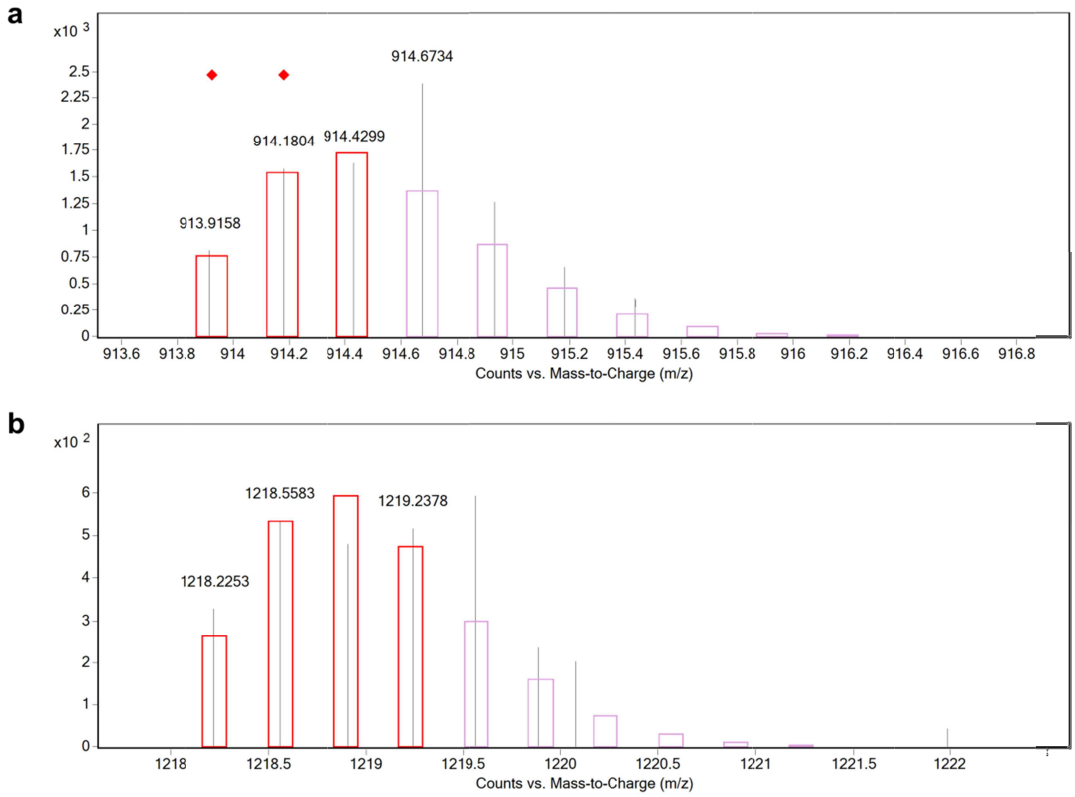



**Figure S1-7.** Results of FBF search. Both ions correspond to the Cys259$^{6.61}$–Phe286$^{7.51}$ peptide labeled with one molecule of compound **9** with a loss of $N_2$ ($C_{166}H_{233}F_3N_{44}O_{41}S_3$). (a) Quadruply charged peptide ions with *m*/*z* = 913.9158 (calcd for *m*/*z* = 913.9226, *z* = 4). (b) Triply charged peptide ions with *m*/*z* =1218.2253 (calcd for *m*/*z* = 1218.2278, *z* = 3). The numbering of amino acids is based on the human $A_{2A}$ adenosine receptor.

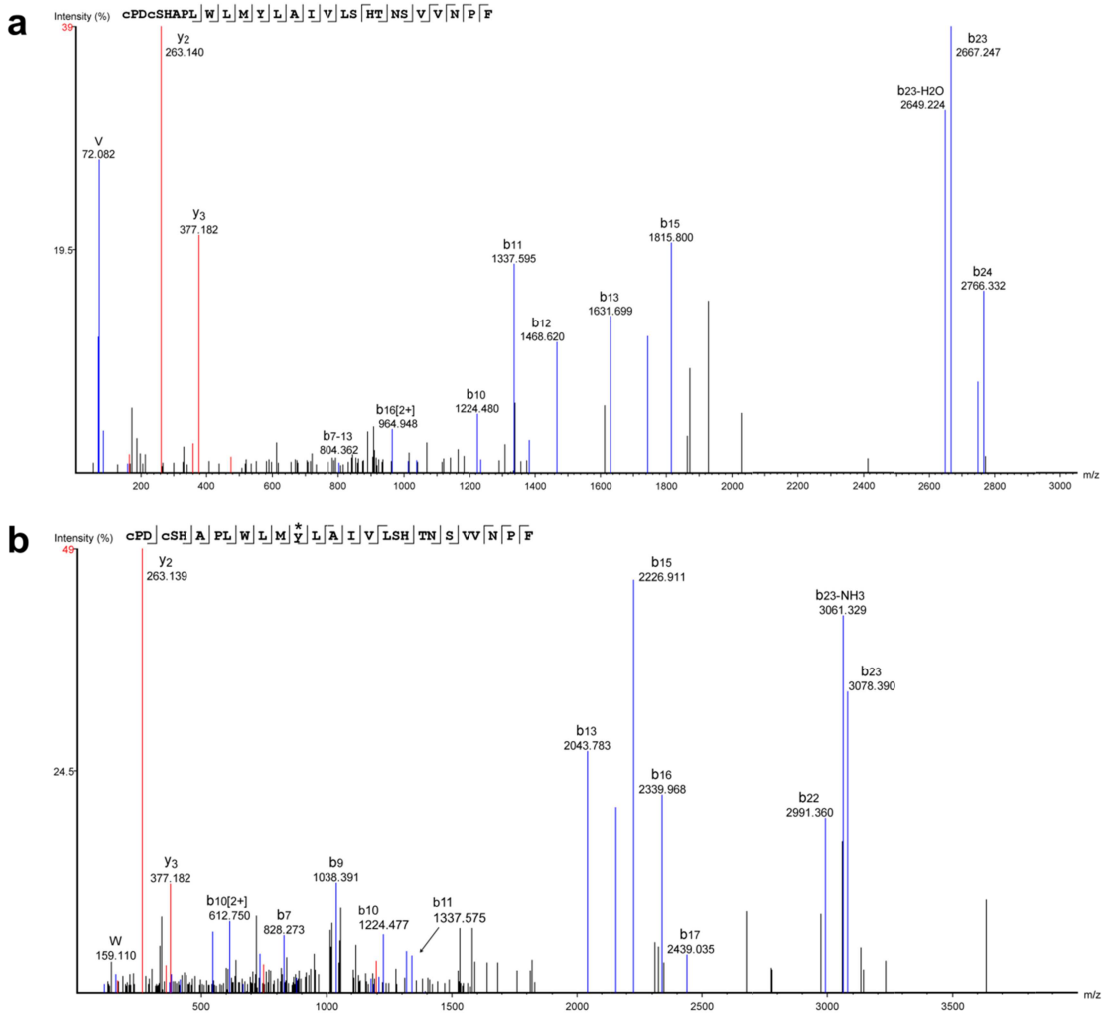



**Figure S1-8.** Comparison of MS/MS spectra of the Cys259$^{6.61}$–Phe286$^{7.51}$ chymotryptic peptides. (a) Unlabeled and (b) labeled with photoaffinity probe **9** with a loss of $N_2$. Carbamidomethylcysteines are designated in lower case. The asterisk indicates the cross-link position (Tyr271$^{7.36}$). The numbering of amino acids is based on the human $A_{2A}$ adenosine receptor.

**Table S1-4. MS/MS ion table of the chymotryptic peptide Cys259$^{6.61}$–Phe286$^{7.51}$ (unlabeled).**

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 133.043 | 161.038 | 143.028 | 144.011 | 81.019 | C(+57.02) | | | | | 28 |
| 2 | 70.064 | 258.091 | 240.081 | 241.064 | 129.546 | P | 3081.532 | 3063.522 | 3064.505 | 1541.266 | 27 |
| 3 | 88.040 | 373.118 | 355.108 | 356.091 | 187.059 | D | 2984.480 | 2966.469 | 2967.453 | 1492.740 | 26 |
| 4 | 133.043 | 533.149 | 515.138 | 516.122 | 267.074 | C(+57.02) | 2869.453 | 2851.442 | 2852.426 | 1435.226 | 25 |
| 5 | 60.045 | 620.181 | 602.170 | 603.154 | 310.590 | S | 2709.422 | 2691.412 | 2692.395 | 1355.211 | 24 |
| 6 | 110.072 | 757.240 | 739.229 | 740.213 | 379.120 | H | 2622.390 | 2604.380 | 2605.363 | 1311.695 | 23 |
| 7 | 44.050 | 828.277 | 810.266 | 811.250 | 414.638 | A | 2485.331 | 2467.321 | 2468.304 | 1243.166 | 22 |
| 8 | 70.066 | 925.330 | 907.319 | 908.303 | 463.165 | P | 2414.294 | 2396.283 | 2397.267 | 1207.647 | 21 |
| 9 | 86.097 | 1038.398 | 1020.403 | 1021.387 | 519.707 | L | 2317.241 | 2299.231 | 2300.214 | 1159.121 | 20 |
| 10 | 159.111 | 1224.480 | 1206.483 | 1207.466 | 612.747 | W | 2204.157 | 2186.147 | 2187.130 | 1102.579 | 19 |
| 11 | 86.097 | 1337.595 | 1319.567 | 1320.550 | 669.289 | L | 2018.078 | 2000.067 | 2001.051 | 1009.539 | 18 |
| 12 | 104.053 | 1468.620 | 1450.607 | 1451.591 | 734.809 | M | 1904.994 | 1886.983 | 1887.967 | 952.997 | 17 |
| 13 | 136.076 | 1631.699 | 1613.670 | 1614.654 | 816.340 | Y | 1773.953 | 1755.943 | 1756.926 | 887.477 | 16 |
| 14 | 86.097 | 1744.781 | 1726.754 | 1727.738 | 872.882 | L | 1610.890 | 1592.880 | 1593.863 | 805.945 | 15 |
| 15 | 44.050 | 1815.800 | 1797.792 | 1798.775 | 908.401 | A | 1497.806 | 1479.795 | 1480.779 | 749.403 | 14 |
| 16 | 86.097 | 1928.886 | 1910.876 | 1911.859 | 964.948 | I | 1426.769 | 1408.758 | 1409.742 | 713.884 | 13 |
| 17 | 72.082 | 2027.955 | 2009.944 | 2010.928 | 1014.477 | V | 1313.685 | 1295.674 | 1296.658 | 657.342 | 12 |
| 18 | 86.097 | 2141.039 | 2123.028 | 2124.011 | 1071.019 | L | 1214.616 | 1196.606 | 1197.589 | 607.808 | 11 |
| 19 | 60.045 | 2228.071 | 2210.060 | 2211.043 | 1114.535 | S | 1101.532 | 1083.522 | 1084.505 | 551.266 | 10 |
| 20 | 110.072 | 2365.130 | 2347.119 | 2348.103 | 1183.065 | H | 1014.477 | 996.490 | 997.473 | 507.750 | 9 |
| 21 | 74.061 | 2466.177 | 2448.167 | 2449.150 | 1233.583 | T | 877.441 | 859.431 | 860.414 | 439.221 | 8 |
| 22 | 87.056 | 2580.220 | 2562.210 | 2563.193 | 1290.610 | N | 776.394 | 758.383 | 759.367 | 388.697 | 7 |
| 23 | 60.045 | 2667.247 | 2649.224 | 2650.225 | 1334.126 | S | 662.351 | 644.340 | 645.324 | 331.675 | 6 |
| 24 | 72.081 | 2766.332 | 2748.339 | 2749.293 | 1383.673 | V | 575.319 | 557.308 | 558.292 | 288.159 | 5 |
| 25 | 72.081 | 2865.389 | 2847.378 | 2848.362 | 1433.194 | V | 476.262 | 458.240 | 459.223 | 238.625 | 4 |
| 26 | 87.056 | 2979.432 | 2961.421 | 2962.405 | 1490.216 | N | 377.182 | 359.170 | 360.159 | 189.091 | 3 |
| 27 | 70.066 | 3076.485 | 3058.474 | 3059.458 | 1538.742 | P | 263.140 | 245.128 | 246.112 | 132.069 | 2 |
| 28 | 120.081 | | | | | F | 166.086 | 148.076 | 149.059 | 83.543 | 1 |

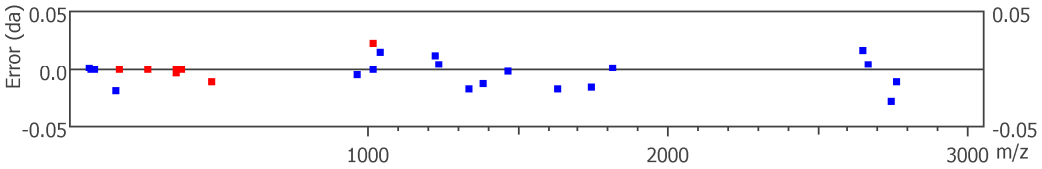
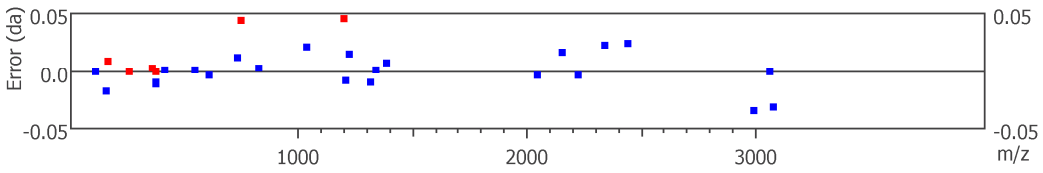


**Table S1-5. MS/MS ion table of the chymotryptic peptide Cys259$^{6.61}$–Phe286$^{7.51}$ (labeled with probe 9).**

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 133.043 | 161.038 | 143.028 | 144.011 | 81.019 | C(+57.02) | | | | | 28 |
| 2 | 70.066 | 258.091 | 240.081 | 241.064 | 129.546 | P | 3492.638 | 3474.627 | 3475.611 | 1746.819 | 27 |
| 3 | 88.040 | 373.128 | 355.108 | 356.091 | 187.059 | D | 3395.585 | 3377.575 | 3378.558 | 1698.293 | 26 |
| 4 | 133.043 | 533.149 | 515.138 | 516.122 | 267.074 | C(+57.02) | 3280.558 | 3262.548 | 3263.531 | 1640.779 | 25 |
| 5 | 60.045 | 620.181 | 602.170 | 603.154 | 310.590 | S | 3120.528 | 3102.517 | 3103.500 | 1560.764 | 24 |
| 6 | 110.073 | 757.240 | 739.229 | 740.213 | 379.132 | H | 3033.496 | 3015.485 | 3016.469 | 1517.248 | 23 |
| 7 | 44.050 | 828.273 | 810.266 | 811.250 | 414.636 | A | 2896.437 | 2878.426 | 2879.410 | 1448.718 | 22 |
| 8 | 70.066 | 925.330 | 907.319 | 908.303 | 463.165 | P | 2825.400 | 2807.389 | 2808.373 | 1413.200 | 21 |
| 9 | 86.097 | 1038.391 | 1020.403 | 1021.387 | 519.707 | L | 2728.347 | 2710.336 | 2711.320 | 1364.673 | 20 |
| 10 | 159.110 | 1224.477 | 1206.491 | 1207.466 | 612.750 | W | 2615.263 | 2597.252 | 2598.236 | 1308.131 | 19 |
| 11 | 86.097 | 1337.575 | 1319.577 | 1320.550 | 669.289 | L | 2429.183 | 2411.173 | 2412.156 | 1215.092 | 18 |
| 12 | 104.053 | 1468.618 | 1450.607 | 1451.591 | 734.796 | M | 2316.099 | 2298.089 | 2299.072 | 1158.550 | 17 |
| 13 | 547.180 | 2042.790 | 2024.776 | 2025.759 | 1021.893 | Y(+411.11) | 2185.059 | 2167.048 | 2168.032 | 1093.029 | 16 |
| 14 | 86.097 | 2155.852 | 2137.860 | 2138.843 | 1078.435 | L | 1610.890 | 1592.880 | 1593.863 | 805.945 | 15 |
| 15 | 44.050 | 2226.911 | 2208.897 | 2209.880 | 1113.954 | A | 1497.806 | 1479.795 | 1480.779 | 749.358 | 14 |
| 16 | 86.097 | 2339.968 | 2321.981 | 2322.965 | 1170.496 | I | 1426.769 | 1408.758 | 1409.742 | 713.884 | 13 |
| 17 | 72.081 | 2439.035 | 2421.050 | 2422.033 | 1220.030 | V | 1313.685 | 1295.674 | 1296.658 | 657.342 | 12 |
| 18 | 86.097 | 2552.144 | 2534.134 | 2535.117 | 1276.572 | L | 1214.616 | 1196.559 | 1197.589 | 607.808 | 11 |
| 19 | 60.045 | 2639.176 | 2621.166 | 2622.149 | 1320.088 | S | 1101.532 | 1083.522 | 1084.505 | 551.266 | 10 |
| 20 | 110.072 | 2776.235 | 2758.225 | 2759.208 | 1388.609 | H | 1014.500 | 996.490 | 997.473 | 507.750 | 9 |
| 21 | 74.061 | 2877.283 | 2859.272 | 2860.256 | 1439.141 | T | 877.441 | 859.431 | 860.414 | 439.221 | 8 |
| 22 | 87.056 | 2991.360 | 2973.315 | 2974.299 | 1496.163 | N | 776.394 | 758.383 | 759.367 | 388.697 | 7 |
| 23 | 60.045 | 3078.390 | 3060.347 | 3061.329 | 1539.679 | S | 662.351 | 644.340 | 645.324 | 331.675 | 6 |
| 24 | 72.081 | 3177.426 | 3159.416 | 3160.399 | 1589.213 | V | 575.319 | 557.308 | 558.292 | 288.159 | 5 |
| 25 | 72.081 | 3276.494 | 3258.484 | 3259.467 | 1638.747 | V | 476.250 | 458.240 | 459.223 | 238.625 | 4 |
| 26 | 87.056 | 3390.537 | 3372.527 | 3373.510 | 1695.769 | N | 377.182 | 359.167 | 360.155 | 189.091 | 3 |
| 27 | 70.066 | 3487.590 | 3469.580 | 3470.563 | 1744.295 | P | 263.139 | 245.128 | 246.112 | 132.069 | 2 |
| 28 | 120.081 | | | | | F | 166.077 | 148.076 | 149.059 | 83.543 | 1 |



## 9. Docking study.

The coordinates of $hA_{2A}AR$ for the docking study of compound **9** were prepared from the X-ray structure complexed with ZM241385 (PDB code: 3EML). The crystal water (HOH-565) was kept in the calculations. For the protein and water, hydrogen atoms were added using the Discovery Studio (version 4.5, BIOVIA, San Diego, CA, USA) with default settings (Glu and Asp are negatively charged, Arg and Lys are positively charged, and the other amino acids and water are neutral). Three-dimensional conformations of compound **9** were generated by OMEGA (version 3.141592-1.23.2.3, OpenEye Scientific Software, Santa Fe, NM, USA), and the docking was performed using FRED (version 3.0.1, OpenEye Scientific Software) with default settings, respectively. The displayed docking model was selected based on the position and orientation of compound **9** which were similar to ZM241385 (**1**).

## 10. References.


(1) Baraldi, P. G.; Cacciari, B.; Spalluto, G.; Pineda de las Infantas y Villatoro, M. J.; Zocchi, C.; Dionisotti, S.; Ongini, E. Pyrazolo[4,3-*e*]-1,2,4-triazolo[1,5-*c*]pyrimidine Derivatives: Potent and Selective $A_{2A}$ Adenosine Antagonists. *J. Med. Chem.* **1996**, *39*, 1164–1171.

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# Photoaffinity Labeling of the Human $A_{2A}$ Adenosine Receptor and Cross-link Position Analysis by Mass Spectrometry

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## Supporting Information 2

## Sequence coverage and MS/MS spectra of proteolytic digests of $hA_{2A}AR$

## Contents:

## 1. Supplementary Figures.

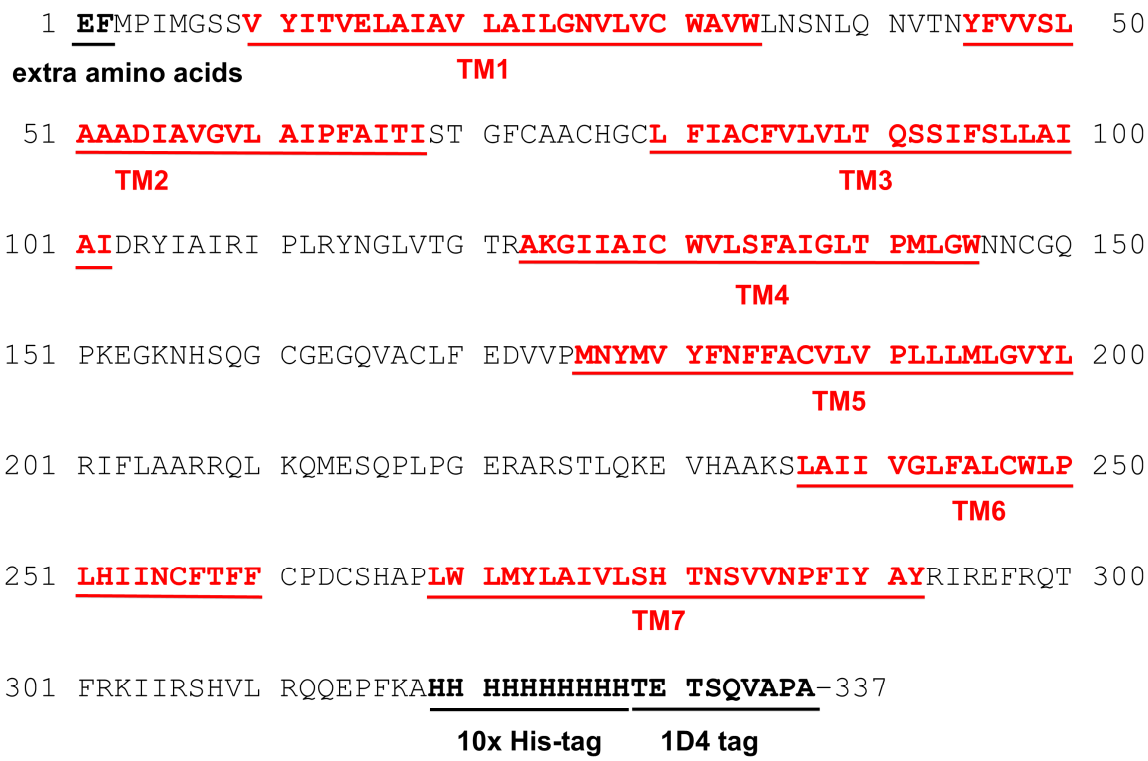



**Figure S2-1.** Amino acid sequence of C-terminal truncated $hA_{2A}AR$ (1–337) used in this study. Transmembrane domains (TMs) are red, bolded and underlined. Two extra amino acids (Glu, Phe) at the N-terminus and a 10× His-tag followed by a 1D4 tag at the C-terminal are black, bolded and underlined. The numbering of amino acids in supporting information 2 follows this sequence number.

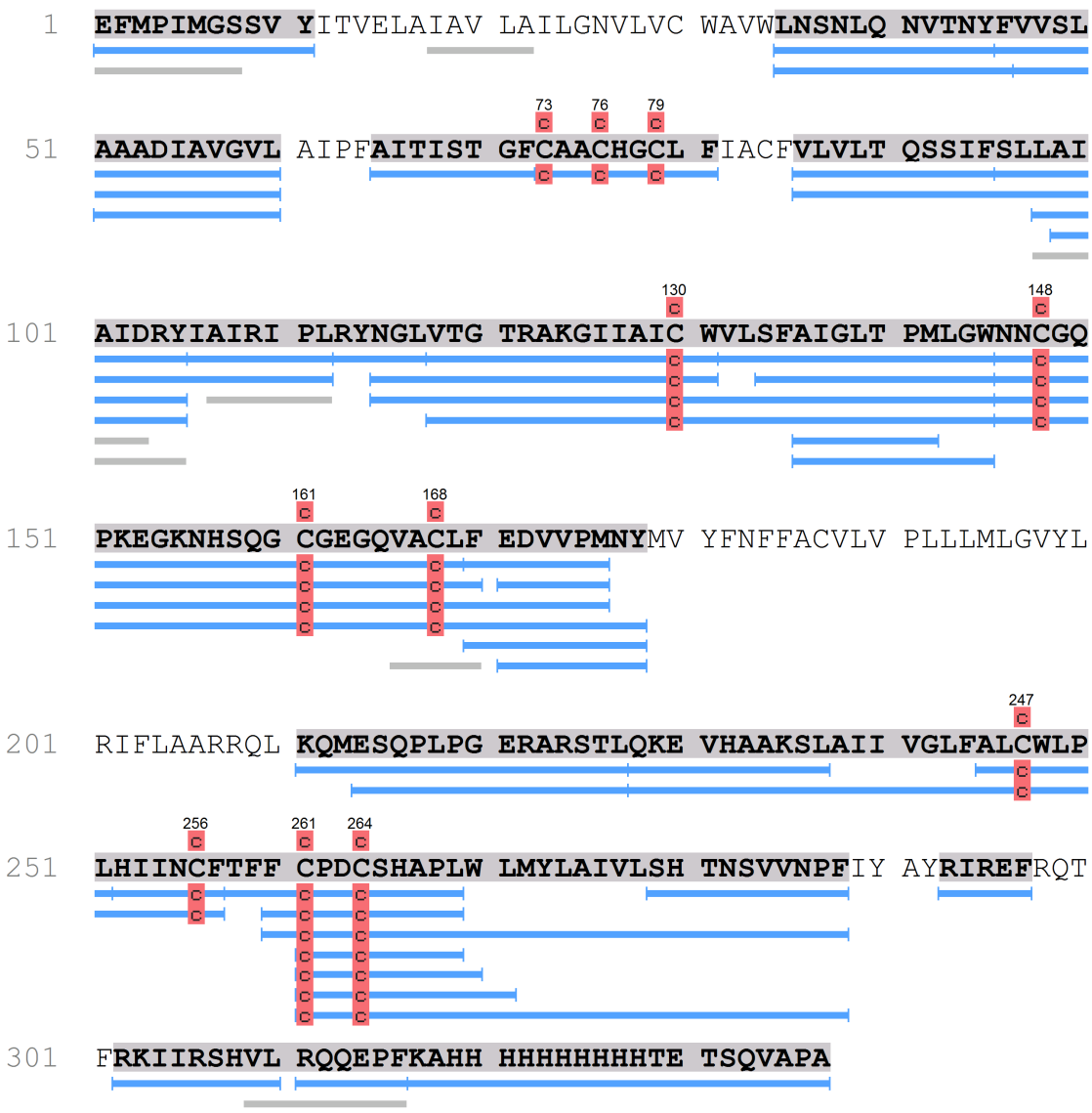



**Figure S2-2.** Sequence coverage map for chymotryptic peptides of $hA_{2A}AR$ obtained from LC–MS/MS and PEAKS Studio search.

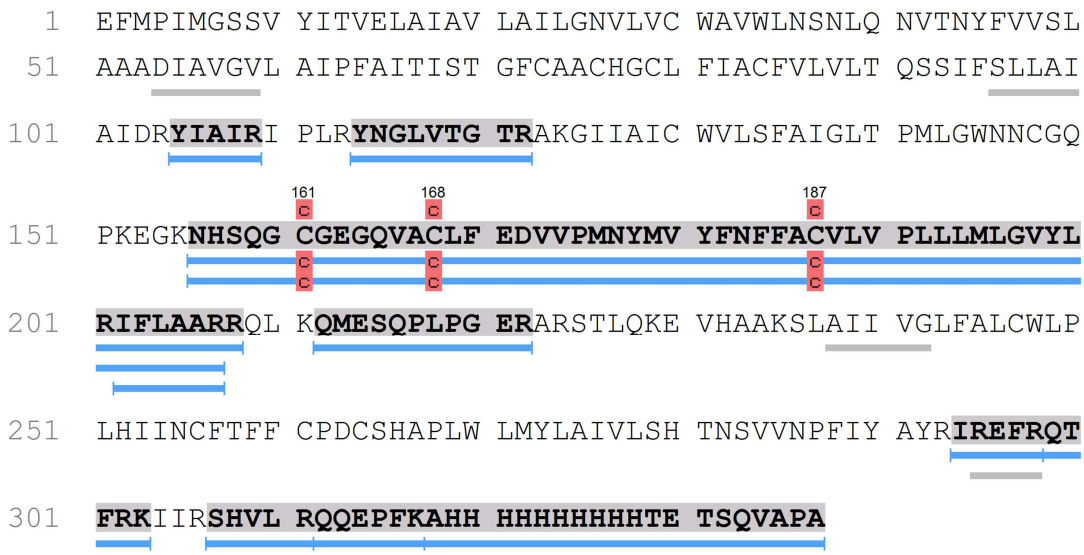



**Figure S2-3.** Sequence coverage map for tryptic peptides of $hA_{2A}AR$ obtained from LC–MS/MS and PEAKS Studio search.

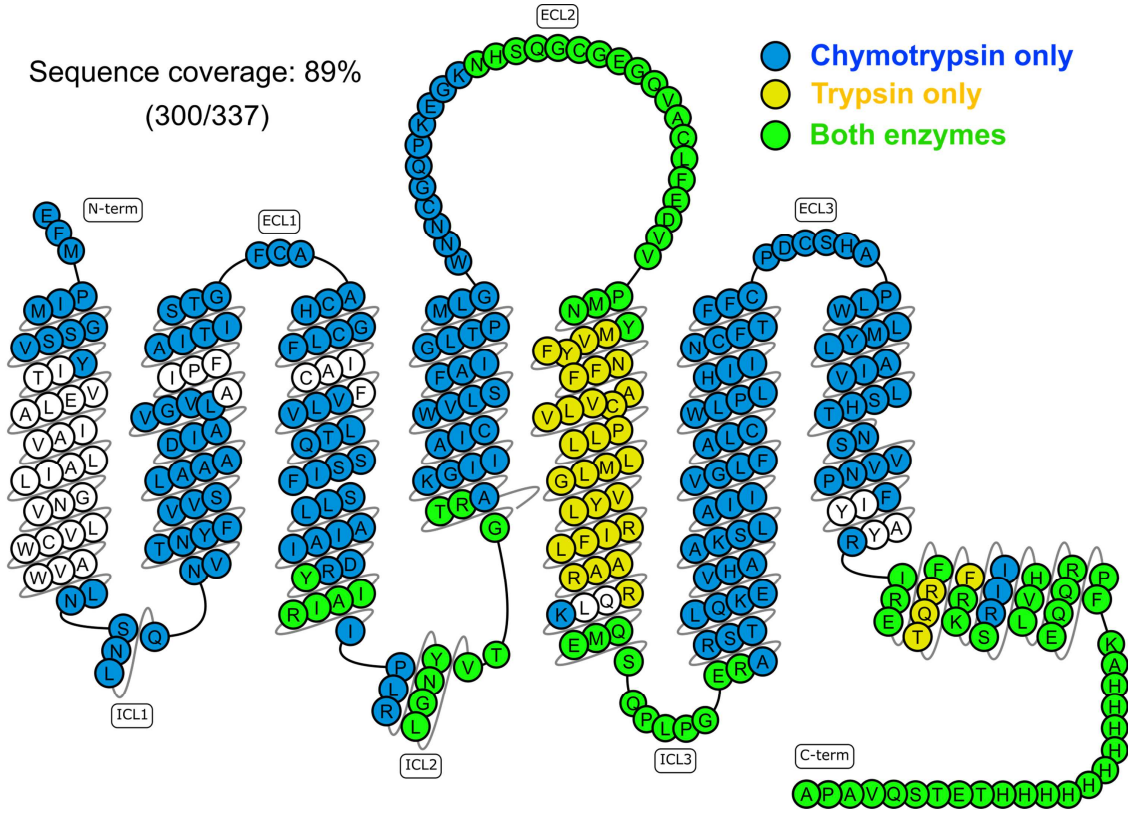



**Figure S2-4.** Combined sequence coverage map shown on a snake diagram of the $hA_{2A}AR$ taken from GCPRdb.[1] Amino acids are colored to indicate the enzyme used in their identification: blue, chymotrypsin; yellow, trypsin; green, both enzymes. The 37 amino acids in white were not identified. Chymotryptic sequence coverage was 79% (266 / 337) and tryptic sequence coverage was 35% (119 / 337) of the entire sequence respectively. The combined sequence coverage was as high as 89% (300 / 337).

## 2. Supplementary Tables.

**Table S2-1.** A list of chymotryptic peptides of $hA_{2A}AR$ identified by PEAKS Studio search.

| Sequence | Peptide | -10lgP | Mass | Length | ppm | m/z | RT (min) |
|---|---|---|---|---|---|---|---|
| 1–11 | EFMPIMGSSVY | 29.12 | 1259.5566 | 11 | 3.2 | 630.7876 | 21.96 |
| 35–45 | LNSNLQNVTNY | 22.12 | 1278.6205 | 11 | 1.2 | 640.3183 | 14.57 |
| 35–46 | LNSNLQNVTNYF | 17.66 | 1425.6888 | 12 | 4.1 | 713.8546 | 20.29 |
| 46–60 | FVVSLAAADIAVGVL | 20.5 | 1443.8336 | 15 | -0.4 | 722.9238 | 28.42 |
| 47–60 | VVSLAAADIAVGVL | 24.38 | 1296.7653 | 14 | 0.9 | 649.3905 | 25.44 |
| 51–60 | AAADIAVGVL | 14.34 | 898.5123 | 10 | 3.9 | 450.2652 | 19.61 |
| 65–72 | AITISTGF | 8.58 | 808.433 | 8 | 2 | 405.2246 | 18.13 |
| 73–81 | C(+57.02)AAC(+57.02)HGC(+57.02)LF | 21.2 | 1094.4095 | 9 | 0 | 548.212 | 13.23 |
| 86–112 | VLVLTQSSIFSLLAIAIDRYIAIRIPL | 36.12 | 2997.7993 | 27 | 4.9 | 1000.2786 | 39.38 |
| 86–95 | VLVLTQSSIF | 5.69 | 1105.6383 | 10 | 1 | 553.827 | 22.99 |
| 96–105 | SLLAIAIDRY | 17.25 | 1133.6444 | 10 | 1.5 | 567.8303 | 20.98 |
| 98–105 | LAIAIDRY | 9.54 | 933.5283 | 8 | 3.6 | 312.1845 | 2.64 |
| 99–105 | AIAIDRY | 13.96 | 820.4443 | 7 | 0.9 | 411.2298 | 12.66 |
| 106–112 | IAIRIPL | 12.16 | 794.5378 | 7 | 6.4 | 398.2787 | 21.34 |
| 113–117 | RYNGL | 7.24 | 621.3234 | 5 | -1.3 | 311.6686 | 7.28 |
| 115–145 | NGLVTGTRAKGIIAIC(+57.02)WVLSFAIGLTPMLGW | 33.49 | 3314.8035 | 31 | 3 | 1105.9451 | 38.23 |
| 115–131 | NGLVTGTRAKGIIAIC(+57.02)W | 27.04 | 1828.9982 | 17 | 2.1 | 610.6746 | 20.89 |
| 118–145 | VTGTRAKGIIAIC(+57.02)WVLSFAIGLTPMLGW | 19.18 | 3030.655 | 28 | -3.3 | 1011.2223 | 37.72 |
| 118–131 | VTGTRAKGIIAIC(+57.02)W | 9.18 | 1544.8497 | 14 | -0.8 | 515.9568 | 19.16 |
| 132–145 | VLSFAIGLTPMLGW | 7.16 | 1503.8159 | 14 | 1.4 | 752.9163 | 30.47 |
| 134–145 | SFAIGLTPMLGW | 20.97 | 1291.6635 | 12 | 6.4 | 646.8431 | 28.13 |
| 136–145 | AIGLTPMLGW | 17.45 | 1057.563 | 10 | 1.1 | 529.7894 | 25.66 |
| 136–142 | AIGLTPM | 6.43 | 701.3782 | 7 | 9.4 | 351.6997 | 16.87 |
| 146–170 | NNC(+57.02)GQPKEGKNHSQGC(+57.02)GEGQVAC(+57.02)LF | 43.49 | 2775.1912 | 25 | 1.8 | 926.0726 | 13.97 |
| 146–169 | NNC(+57.02)GQPKEGKNHSQGC(+57.02)GEGQVAC(+57.02)L | 39.12 | 2628.1228 | 24 | 0.6 | 877.0488 | 9.44 |
| 146–176 | NNC(+57.02)GQPKEGKNHSQGC(+57.02)GEGQVAC(+57.02)LFEDVVPM | 29.93 | 3445.4907 | 31 | 6.5 | 1149.5116 | 21.77 |
| 146–178 | NNC(+57.02)GQPKEGKNHSQGC(+57.02)GEGQVAC(+57.02)LFEDVVPMNY | 21.49 | 3722.5969 | 33 | -3.9 | 1241.868 | 21.96 |
| 170–178 | FEDVVPMNY | 20.35 | 1112.4849 | 9 | 0.7 | 557.2501 | 18.74 |
| 170–176 | FEDVVPM | 10.84 | 835.3785 | 7 | 1.9 | 418.6974 | 17.9 |
| 171–178 | EDVVPMNY | 19.11 | 965.4164 | 8 | 3.6 | 483.7173 | 15.71 |
| 171–176 | EDVVPM | 13.53 | 688.3102 | 6 | 4.3 | 345.1638 | 13.91 |
| 211–227 | KQMESQPLPGERARSTL | 5.86 | 1926.9945 | 17 | 2.4 | 643.3403 | 11.58 |
| 211–227 | KQMESQPLPGERARSTL | 98.32 | 1926.9945 | 17 | 2.8 | 482.7573 | 11.54 |
| 214–227 | ESQPLPGERARSTL | 35.95 | 1539.8004 | 14 | 2.2 | 514.2752 | 11.57 |
| 228–237 | QKEVHAAKSL | 19.36 | 1109.6193 | 10 | 1.3 | 555.8176 | 5.33 |
| 228–257 | QKEVHAAKSLAIVGLFALC(+57.02)WLPLHIINC(+57.02)F | 12.04 | 3460.8879 | 30 | -3.2 | 693.1826 | 36.22 |
| 245–251 | ALC(+57.02)WLPL | 5.11 | 871.4626 | 7 | 2.7 | 436.7397 | 25.6 |
| 252–257 | HIINC(+57.02)F | 16.35 | 802.3796 | 6 | 2.3 | 402.198 | 13.76 |
| 258–269 | TFFC(+57.02)PDC(+57.02)SHAPL | 16.8 | 1450.601 | 12 | -1.4 | 726.3068 | 17.87 |
| 260–288 | FC(+57.02)PDC(+57.02)SHAPLWLMYLAIVLSHTNSVVNPF | 26.96 | 3387.6243 | 29 | -1.3 | 1130.2139 | 34.35 |
| 260–269 | FC(+57.02)PDC(+57.02)SHAPL | 10.84 | 1202.4849 | 10 | -1.1 | 602.249 | 13.08 |
| 261–288 | C(+57.02)PDC(+57.02)SHAPLWLMYLAIVLSHTNSVVNPF | 50.8 | 3240.5559 | 28 | 1.3 | 811.1473 | 33.83 |
| 261–269 | C(+57.02)PDC(+57.02)SHAPL | 29.44 | 1055.4165 | 9 | 3.1 | 528.7172 | 9.76 |
| 261–271 | C(+57.02)PDC(+57.02)SHAPLWL | 5.78 | 1354.5798 | 11 | 4.5 | 678.3002 | 19.4 |
| 261–270 | C(+57.02)PDC(+57.02)SHAPLW | 5.2 | 1241.4957 | 10 | 3.5 | 621.7573 | 14.99 |
| 274–278 | LAIVL | 13.32 | 527.3683 | 5 | -0.5 | 528.3753 | 20.65 |
| 279–288 | SHTNSVVNPF | 44.09 | 1100.525 | 10 | 1.9 | 551.2708 | 14.56 |
| 293–297 | RIREF | 6.11 | 719.4078 | 5 | 2.4 | 360.7121 | 7.59 |
| 302–310 | RKIIRSHVL | 7.03 | 1120.7192 | 9 | 5.1 | 374.5822 | 8.18 |
| 311–316 | RQQEPF | 14.18 | 803.3926 | 6 | 3.3 | 402.7049 | 9.17 |
| 317–337 | KAHHHHHHHHHHTETSQVAPA | 35.94 | 2472.1558 | 21 | -1.6 | 495.4376 | 23.61 |

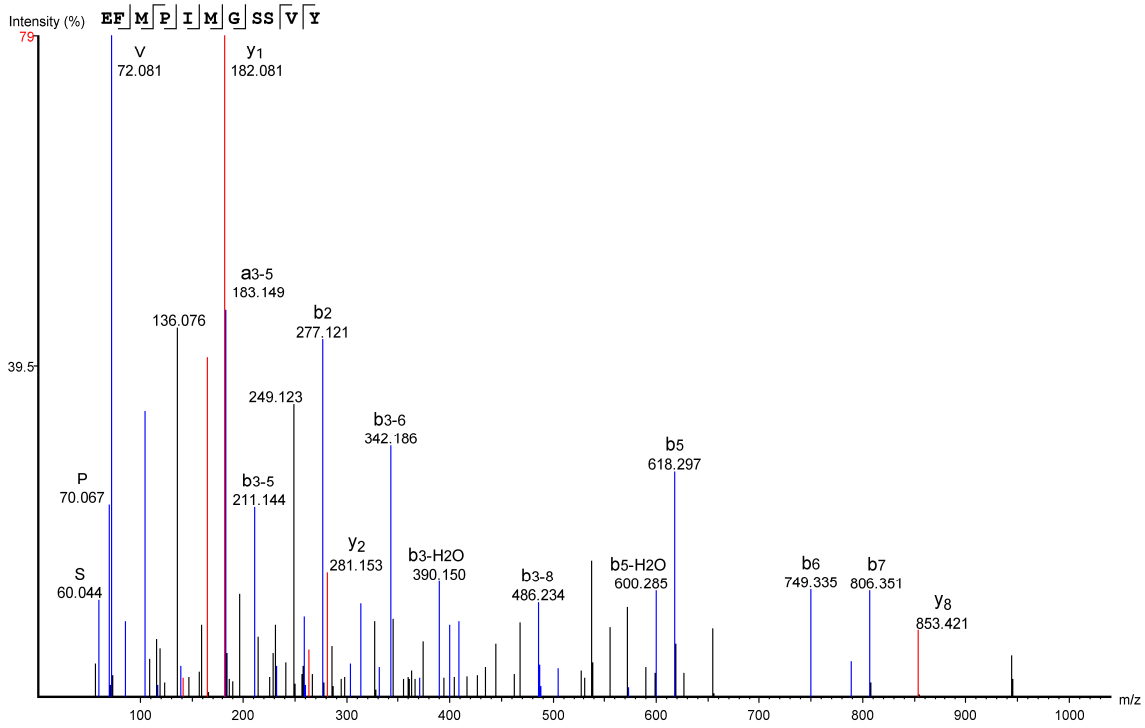
**Table S2-2.** A list of tryptic peptides of $hA_{2A}AR$ identified by PEAKS Studio search.

| Sequence | Peptide | -10lgP | Mass | Length | ppm | m/z | RT (min) |
|---|---|---|---|---|---|---|---|
| 105–109 | YIAIR | 10.62 | 634.3802 | 5 | 3.3 | 318.1985 | 10.31 |
| 114–122 | YNGLVTGTR | 38.47 | 979.5087 | 9 | 0.2 | 490.7617 | 10.03 |
| 156–207 | NHSQGC(+57.02)GEGQVAC(+57.02)LFEDVVPMNYMVYFNFFAC(+57.02)VLVPLLLMLGVYLRIFLAAR | 101.01 | 6040.9824 | 52 | -2.2 | 1511.2495 | 51.46 |
| 156–208 | NHSQGC(+57.02)GEGQVAC(+57.02)LFEDVVPMNYMVYFNFFAC(+57.02)VLVPLLLMLGVYLRIFLAARR | 93.74 | 6197.0835 | 53 | -7 | 1240.4153 | 47.67 |
| 202–207 | IFLAAR | 10.72 | 689.4224 | 6 | -5.1 | 345.7167 | 12.93 |
| 212–222 | QMESQPLPGER | 61.01 | 1270.5975 | 11 | 3.9 | 636.3085 | 10.38 |
| 294–298 | IREFR | 7.3 | 719.4078 | 5 | 1.2 | 360.7116 | 6.62 |
| 299–303 | QTFRK | 8.63 | 678.3813 | 5 | 5.5 | 340.1998 | 1.52 |
| 307–311 | SHVLR | 14.16 | 610.3551 | 5 | 2.6 | 306.1856 | 2 |
| 312–317 | QQEPFK | 21.25 | 775.3864 | 6 | 1.7 | 388.7011 | 7.3 |
| 318–337 | AHHHHHHHHHHTETSQVAPA | 37.18 | 2344.0608 | 20 | 4.7 | 469.8217 | 6.59 |

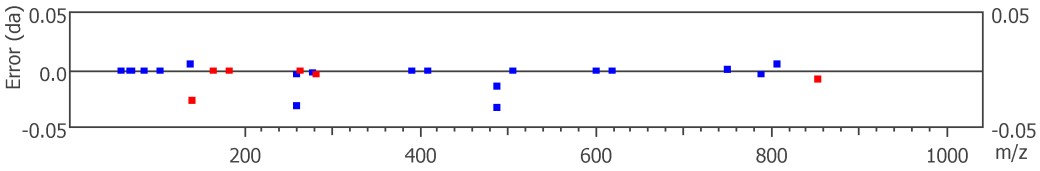
## 3. MS/MS Spectra for chymotryptic peptides of $hA_{2A}AR$.

Carbamidomethylcysteines are designated in lower case in all figures.

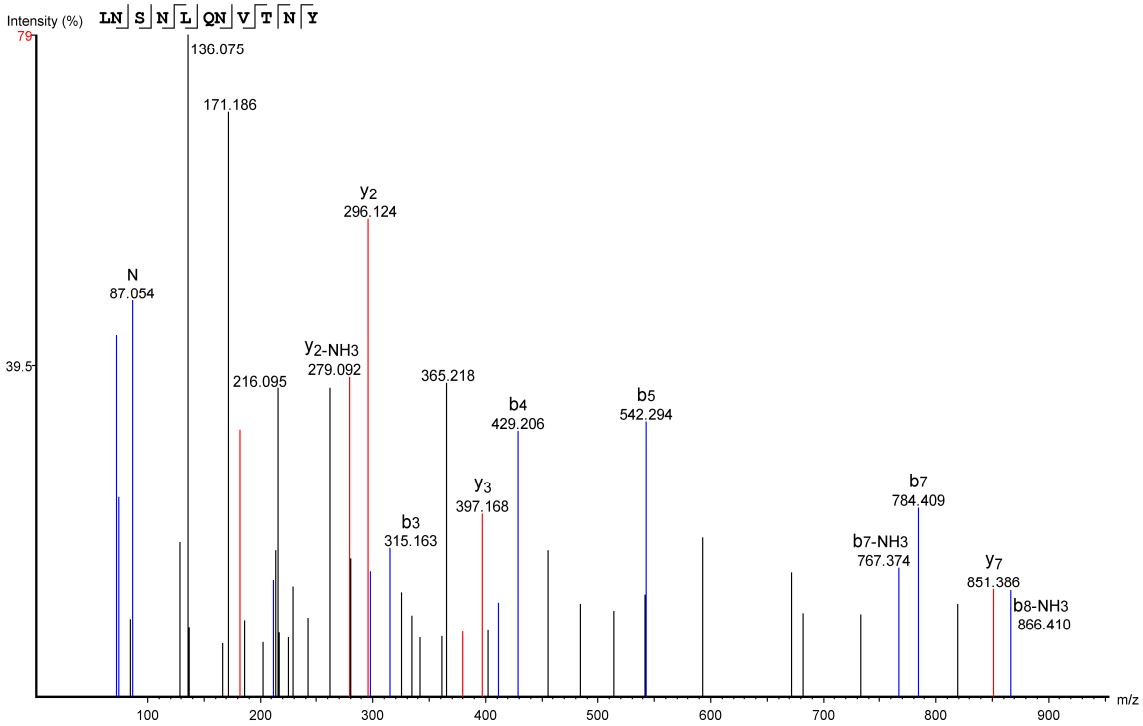
1–11, EFMPIMGSSVY



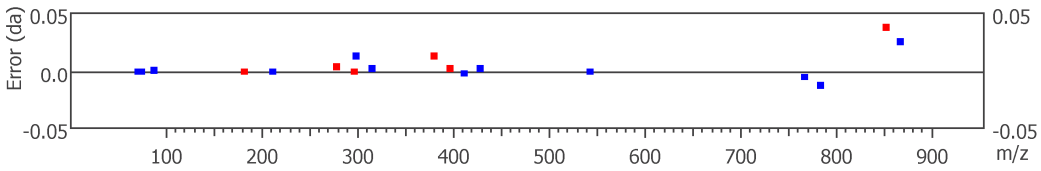

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 102.055 | 130.050 | 112.040 | 113.023 | 65.525 | E | | | | | 11 |
| 2 | 120.081 | 277.121 | 259.112 | 260.123 | 139.052 | F | 1131.521 | 1113.511 | 1114.494 | 566.261 | 10 |
| 3 | 104.052 | 408.160 | 390.150 | 391.132 | 204.580 | M | 984.453 | 966.442 | 967.426 | 492.726 | 9 |
| 4 | 70.067 | 505.213 | 487.235 | 488.199 | 253.106 | P | 853.421 | 835.402 | 836.385 | 427.206 | 8 |
| 5 | 86.098 | 618.297 | 600.285 | 601.269 | 309.648 | I | 756.360 | 738.349 | 739.333 | 378.680 | 7 |
| 6 | 104.053 | 749.335 | 731.326 | 732.310 | 375.168 | M | 643.276 | 625.265 | 626.249 | 322.138 | 6 |
| 7 | 30.034 | 806.351 | 788.352 | 789.331 | 403.679 | G | 512.235 | 494.225 | 495.208 | 256.618 | 5 |
| 8 | 60.044 | 893.390 | 875.380 | 876.363 | 447.195 | S | 455.214 | 437.203 | 438.187 | 228.107 | 4 |
| 9 | 60.045 | 980.422 | 962.412 | 963.395 | 490.711 | S | 368.182 | 350.171 | 351.155 | 184.591 | 3 |
| 10 | 72.081 | 1079.491 | 1061.480 | 1062.464 | 540.245 | V | 281.153 | 263.138 | 264.123 | 141.101 | 2 |
| 11 | 136.076 | | | | | Y | 182.081 | 164.071 | 165.054 | 91.541 | 1 |



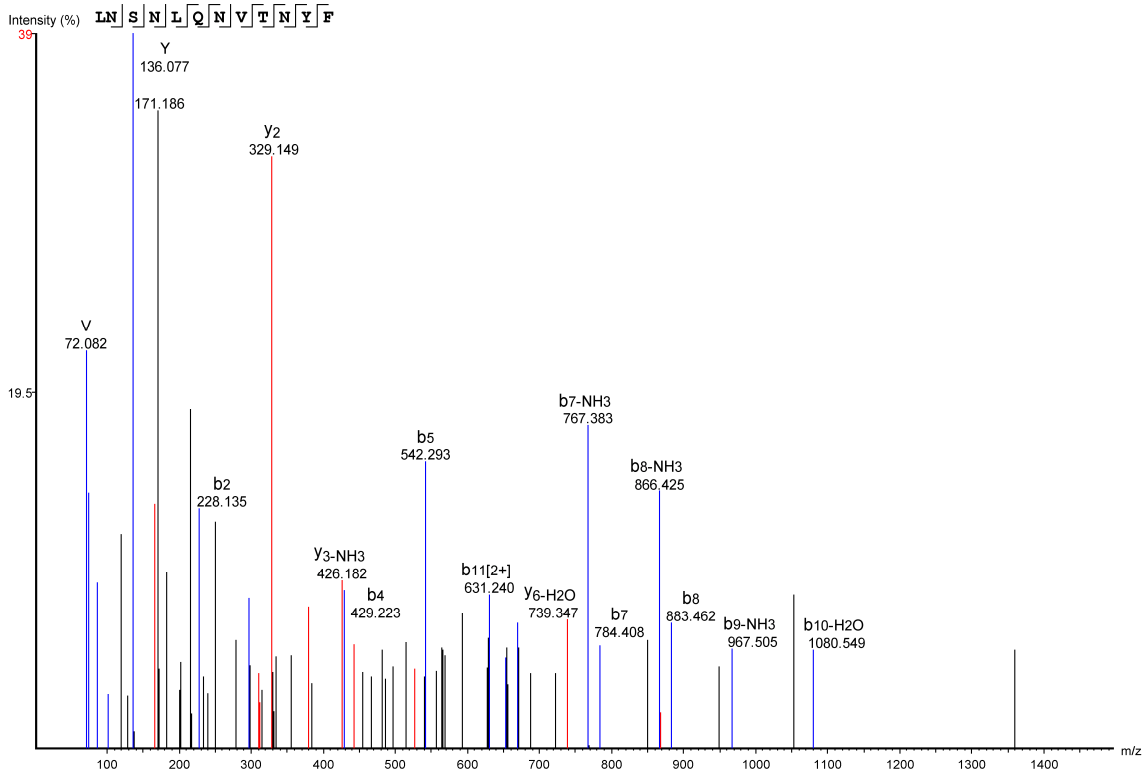
35–45, LNSNLQNVTNY



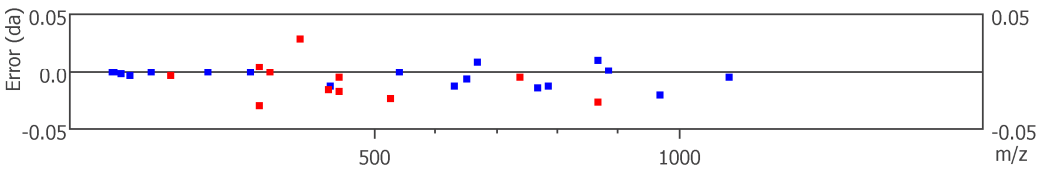

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 86.097 | 114.092 | 96.081 | 97.065 | 57.546 | L | | | | | 11 |
| 2 | 87.054 | 228.135 | 210.124 | 211.108 | 114.567 | N | 1166.544 | 1148.533 | 1149.517 | 583.772 | 10 |
| 3 | 60.045 | 315.163 | 297.156 | 298.126 | 158.083 | S | 1052.501 | 1034.490 | 1035.474 | 526.750 | 9 |
| 4 | 87.056 | 429.206 | 411.202 | 412.183 | 215.105 | N | 965.469 | 947.458 | 948.442 | 483.234 | 8 |
| 5 | 86.097 | 542.294 | 524.283 | 525.267 | 271.647 | L | 851.386 | 833.415 | 834.399 | 426.213 | 7 |
| 6 | 101.071 | 670.352 | 652.342 | 653.325 | 335.676 | Q | 738.342 | 720.331 | 721.315 | 369.671 | 6 |
| 7 | 87.056 | 784.409 | 766.385 | 767.374 | 392.698 | N | 610.283 | 592.273 | 593.256 | 305.642 | 5 |
| 8 | 72.082 | 883.464 | 865.453 | 866.410 | 442.232 | V | 496.240 | 478.230 | 479.213 | 248.620 | 4 |
| 9 | 74.060 | 984.511 | 966.501 | 967.484 | 492.756 | T | 397.168 | 379.161 | 380.130 | 199.086 | 3 |
| 10 | 87.056 | 1098.554 | 1080.544 | 1081.527 | 549.777 | N | 296.124 | 278.114 | 279.092 | 148.562 | 2 |
| 11 | 136.076 | | | | | Y | 182.081 | 164.071 | 165.054 | 91.541 | 1 |



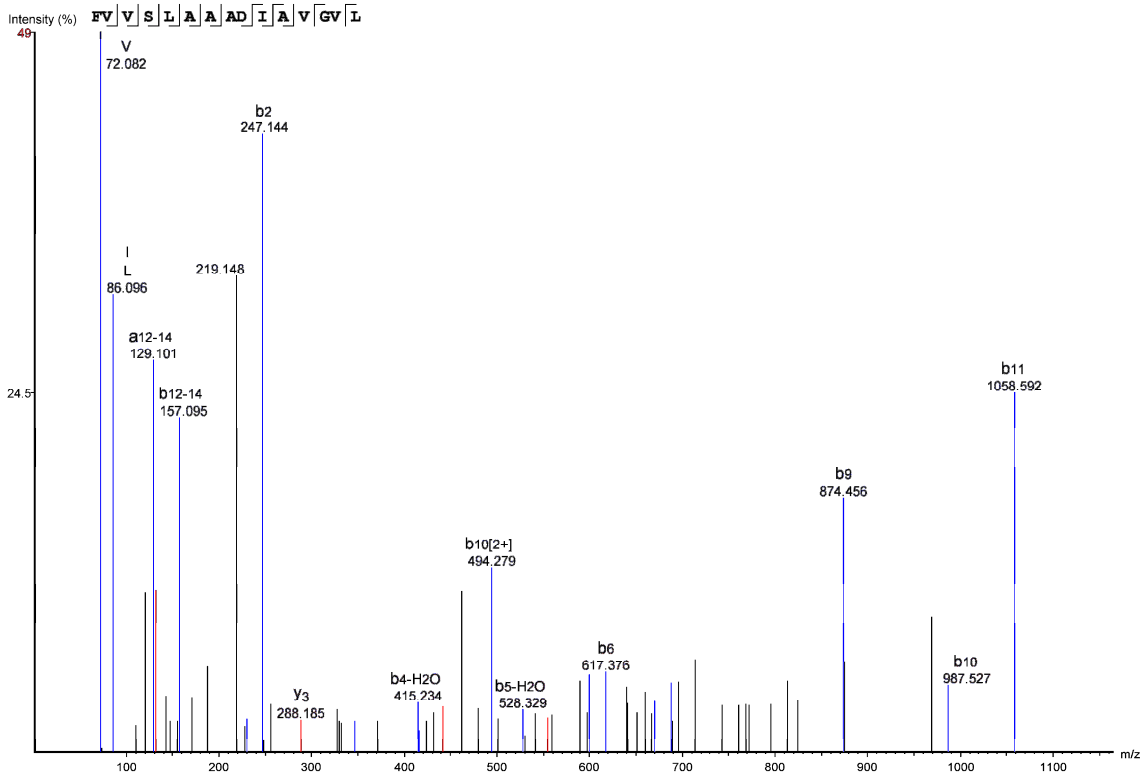
35–46, LNSNLQNVTNYF



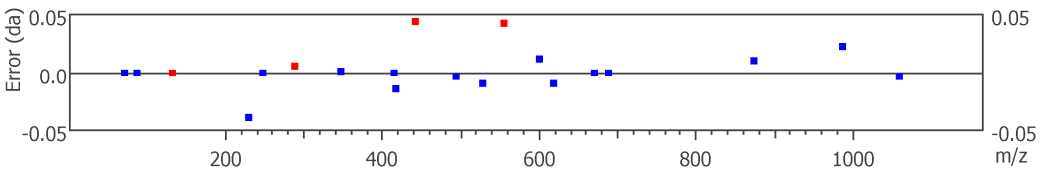

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 86.097 | 114.092 | 96.081 | 97.065 | 57.546 | L | | | | | 12 |
| 2 | 87.058 | 228.135 | 210.124 | 211.108 | 114.567 | N | 1313.612 | 1295.602 | 1296.585 | 657.306 | 11 |
| 3 | 60.045 | 315.167 | 297.155 | 298.140 | 158.083 | S | 1199.569 | 1181.559 | 1182.542 | 600.285 | 10 |
| 4 | 87.056 | 429.223 | 411.199 | 412.183 | 215.105 | N | 1112.537 | 1094.527 | 1095.510 | 556.769 | 9 |
| 5 | 86.097 | 542.293 | 524.283 | 525.267 | 271.647 | L | 998.494 | 980.484 | 981.467 | 499.747 | 8 |
| 6 | 101.075 | 670.342 | 652.342 | 653.332 | 335.676 | Q | 885.410 | 867.426 | 868.383 | 443.210 | 7 |
| 7 | 87.056 | 784.408 | 766.385 | 767.383 | 392.698 | N | 757.352 | 739.347 | 740.325 | 379.145 | 6 |
| 8 | 72.082 | 883.462 | 865.453 | 866.425 | 442.232 | V | 643.309 | 625.298 | 626.282 | 322.154 | 5 |
| 9 | 74.059 | 984.511 | 966.501 | 967.505 | 492.756 | T | 544.240 | 526.254 | 527.213 | 272.620 | 4 |
| 10 | 87.056 | 1098.554 | 1080.549 | 1081.527 | 549.777 | N | 443.210 | 425.182 | 426.182 | 222.096 | 3 |
| 11 | 136.077 | 1261.618 | 1243.607 | 1244.591 | 631.322 | Y | 329.149 | 311.134 | 312.153 | 165.075 | 2 |
| 12 | 120.081 | | | | | F | 166.090 | 148.076 | 149.059 | 83.543 | 1 |



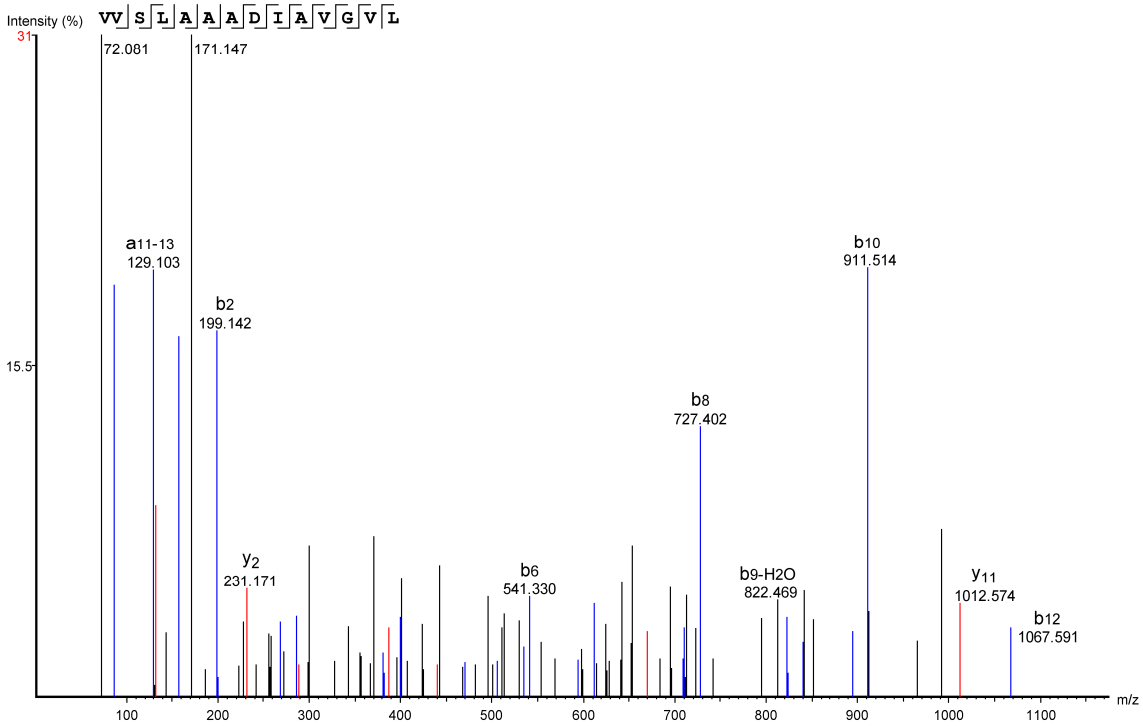
46–60, FVVSLAAADIAVGVL



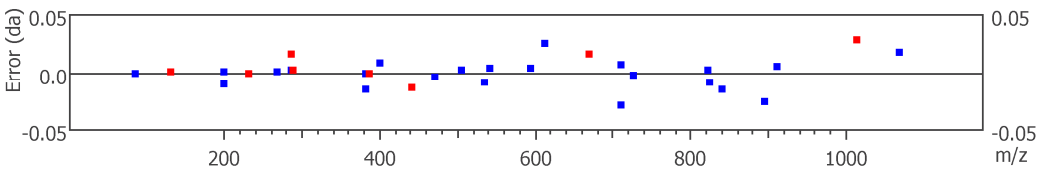

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 120.081 | 148.076 | 130.066 | 131.049 | 74.538 | F | | | | | 15 |
| 2 | 72.082 | 247.144 | 229.134 | 230.157 | 124.072 | V | 1297.772 | 1279.762 | 1280.745 | 649.386 | 14 |
| 3 | 72.081 | 346.211 | 328.202 | 329.186 | 173.607 | V | 1198.704 | 1180.694 | 1181.677 | 599.852 | 13 |
| 4 | 60.045 | 433.245 | 415.234 | 416.232 | 217.123 | S | 1099.636 | 1081.625 | 1082.609 | 550.318 | 12 |
| 5 | 86.096 | 546.329 | 528.329 | 529.302 | 273.665 | L | 1012.604 | 994.593 | 995.577 | 506.802 | 11 |
| 6 | 44.050 | 617.376 | 599.343 | 600.339 | 309.183 | A | 899.520 | 881.509 | 882.493 | 450.260 | 10 |
| 7 | 44.050 | 688.402 | 670.392 | 671.376 | 344.702 | A | 828.482 | 810.472 | 811.456 | 414.741 | 9 |
| 8 | 44.050 | 759.440 | 741.430 | 742.413 | 380.220 | A | 757.445 | 739.435 | 740.418 | 379.223 | 8 |
| 9 | 88.040 | 874.456 | 856.457 | 857.440 | 437.734 | D | 686.408 | 668.398 | 669.381 | 343.704 | 7 |
| 10 | 86.096 | 987.527 | 969.541 | 970.524 | 494.279 | I | 571.381 | 553.371 | 554.311 | 286.191 | 6 |
| 11 | 44.050 | 1058.592 | 1040.578 | 1041.562 | 529.794 | A | 458.297 | 440.287 | 441.225 | 229.649 | 5 |
| 12 | 72.081 | 1157.657 | 1139.646 | 1140.630 | 579.328 | V | 387.260 | 369.250 | 370.233 | 194.130 | 4 |
| 13 | 30.034 | 1214.678 | 1196.668 | 1197.651 | 607.839 | G | 288.185 | 270.181 | 271.165 | 144.596 | 3 |
| 14 | 72.081 | 1313.747 | 1295.736 | 1296.720 | 657.373 | V | 231.170 | 213.160 | 214.143 | 116.085 | 2 |
| 15 | 86.097 | | | | | L | 132.101 | 114.091 | 115.075 | 66.551 | 1 |



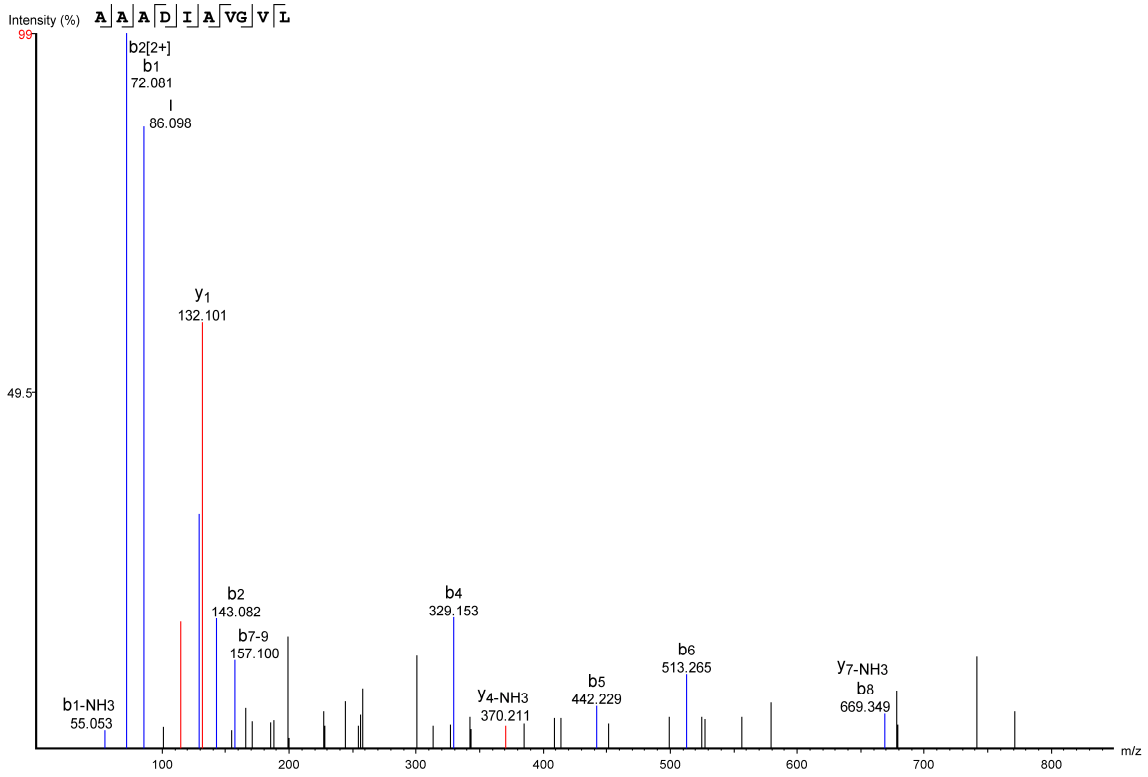
47–60, VVSLAAADIAVGVL



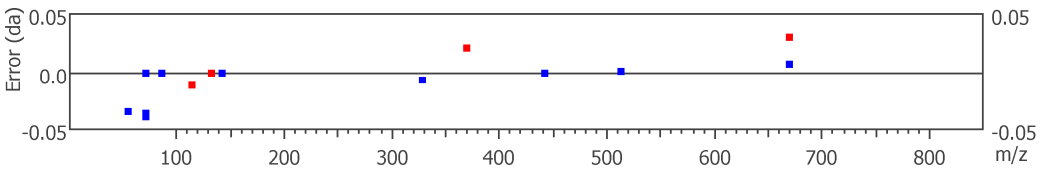

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 72.081 | 100.076 | 82.066 | 83.049 | 50.538 | V | | | | | 14 |
| 2 | 72.081 | 199.142 | 181.134 | 182.118 | 100.072 | V | 1198.704 | 1180.694 | 1181.677 | 599.852 | 13 |
| 3 | 60.045 | 286.173 | 268.164 | 269.150 | 143.588 | S | 1099.636 | 1081.625 | 1082.609 | 550.318 | 12 |
| 4 | 86.096 | 399.251 | 381.251 | 382.248 | 200.141 | L | 1012.574 | 994.593 | 995.577 | 506.802 | 11 |
| 5 | 44.050 | 470.302 | 452.287 | 453.271 | 235.649 | A | 899.520 | 881.509 | 882.493 | 450.260 | 10 |
| 6 | 44.050 | 541.330 | 523.324 | 524.308 | 271.167 | A | 828.482 | 810.472 | 811.456 | 414.741 | 9 |
| 7 | 44.050 | 612.345 | 594.356 | 595.345 | 306.686 | A | 757.445 | 739.435 | 740.418 | 379.223 | 8 |
| 8 | 88.040 | 727.402 | 709.380 | 710.401 | 364.199 | D | 686.408 | 668.398 | 669.363 | 343.704 | 7 |
| 9 | 86.096 | 840.498 | 822.469 | 823.464 | 420.742 | I | 571.381 | 553.371 | 554.354 | 286.173 | 6 |
| 10 | 44.050 | 911.514 | 893.510 | 894.518 | 456.260 | A | 458.297 | 440.300 | 441.270 | 229.649 | 5 |
| 11 | 72.081 | 1010.589 | 992.578 | 993.562 | 505.791 | V | 387.260 | 369.250 | 370.233 | 194.130 | 4 |
| 12 | 30.034 | 1067.591 | 1049.599 | 1050.583 | 534.313 | G | 288.188 | 270.181 | 271.165 | 144.596 | 3 |
| 13 | 72.081 | 1166.678 | 1148.668 | 1149.651 | 583.839 | V | 231.171 | 213.160 | 214.143 | 116.085 | 2 |
| 14 | 86.097 | | | | | L | 132.100 | 114.091 | 115.075 | 66.551 | 1 |



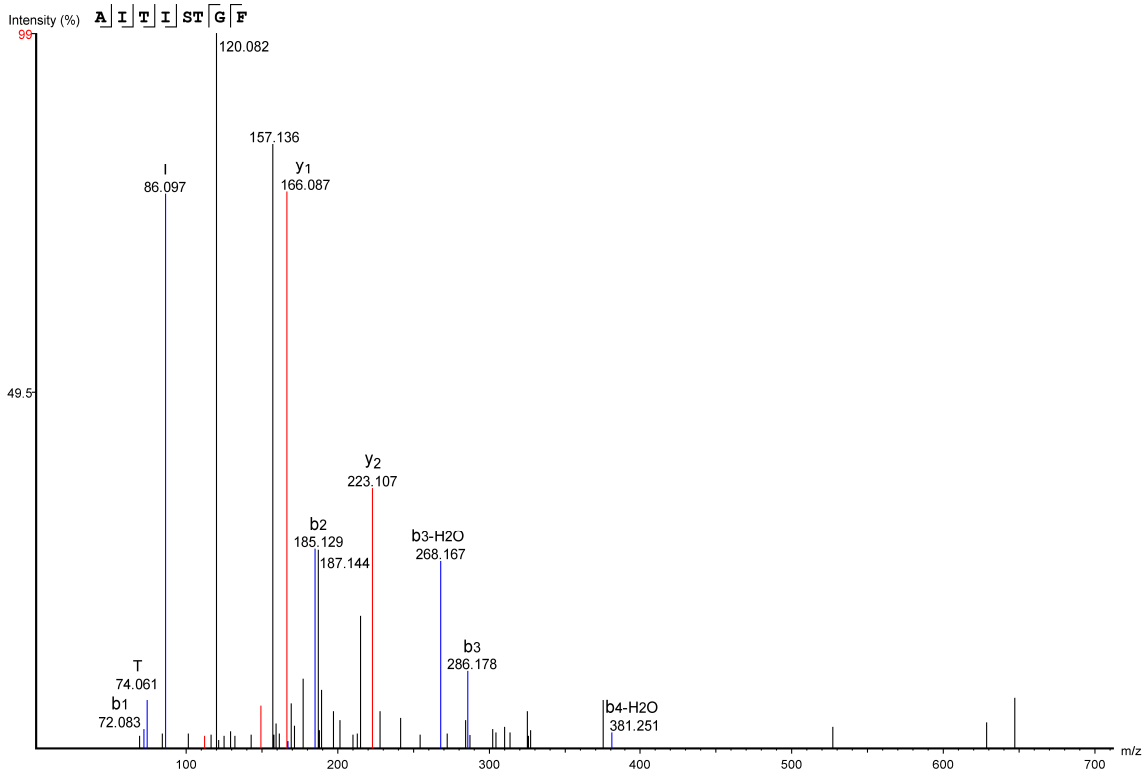
51–60, AAADIAVGVL



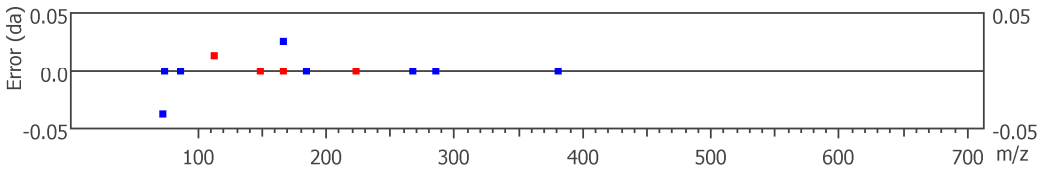

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 44.050 | 72.081 | 54.034 | 55.053 | 36.522 | A | | | | | 10 |
| 2 | 44.050 | 143.082 | 125.071 | 126.055 | 72.081 | A | 828.482 | 810.472 | 811.456 | 414.741 | 9 |
| 3 | 44.050 | 214.119 | 196.109 | 197.092 | 107.560 | A | 757.445 | 739.435 | 740.418 | 379.223 | 8 |
| 4 | 88.040 | 329.153 | 311.136 | 312.119 | 165.073 | D | 686.408 | 668.398 | 669.349 | 343.704 | 7 |
| 5 | 86.098 | 442.229 | 424.220 | 425.203 | 221.615 | I | 571.381 | 553.371 | 554.354 | 286.191 | 6 |
| 6 | 44.050 | 513.265 | 495.257 | 496.240 | 257.134 | A | 458.297 | 440.287 | 441.270 | 229.649 | 5 |
| 7 | 72.081 | 612.336 | 594.325 | 595.309 | 306.668 | V | 387.260 | 369.250 | 370.211 | 194.130 | 4 |
| 8 | 30.034 | 669.349 | 651.347 | 652.330 | 335.179 | G | 288.192 | 270.181 | 271.165 | 144.596 | 3 |
| 9 | 72.081 | 768.426 | 750.415 | 751.399 | 384.713 | V | 231.170 | 213.160 | 214.143 | 116.085 | 2 |
| 10 | 86.097 | | | | | L | 132.101 | 114.091 | 115.086 | 66.551 | 1 |



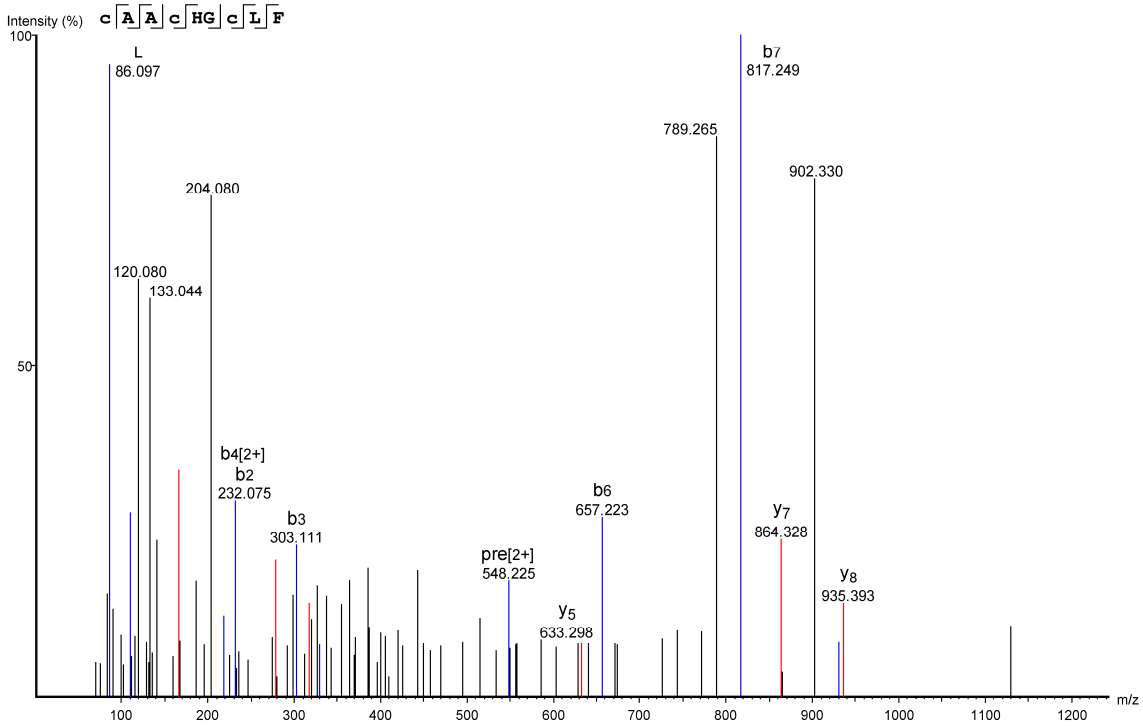
65–72, AITISTGF



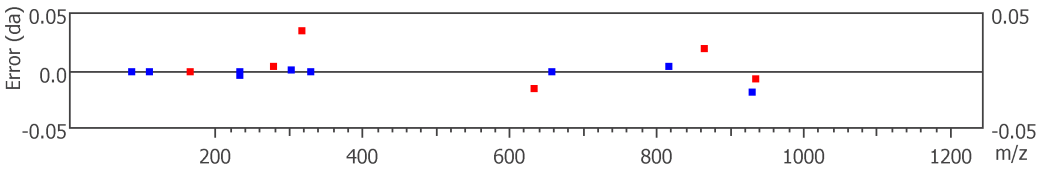

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 44.050 | 72.083 | 54.034 | 55.018 | 36.522 | A | | | | | 8 |
| 2 | 86.097 | 185.129 | 167.091 | 168.102 | 93.064 | I | 738.403 | 720.393 | 721.376 | 369.702 | 7 |
| 3 | 74.061 | 286.178 | 268.167 | 269.150 | 143.588 | T | 625.319 | 607.309 | 608.292 | 313.160 | 6 |
| 4 | 86.097 | 399.261 | 381.251 | 382.234 | 200.130 | I | 524.271 | 506.261 | 507.244 | 262.636 | 5 |
| 5 | 60.045 | 486.293 | 468.282 | 469.266 | 243.646 | S | 411.187 | 393.177 | 394.160 | 206.094 | 4 |
| 6 | 74.061 | 587.340 | 569.330 | 570.313 | 294.170 | T | 324.155 | 306.145 | 307.128 | 162.578 | 3 |
| 7 | 30.034 | 644.362 | 626.351 | 627.335 | 322.681 | G | 223.107 | 205.097 | 206.081 | 112.039 | 2 |
| 8 | 120.081 | | | | | F | 166.087 | 148.076 | 149.058 | 83.543 | 1 |



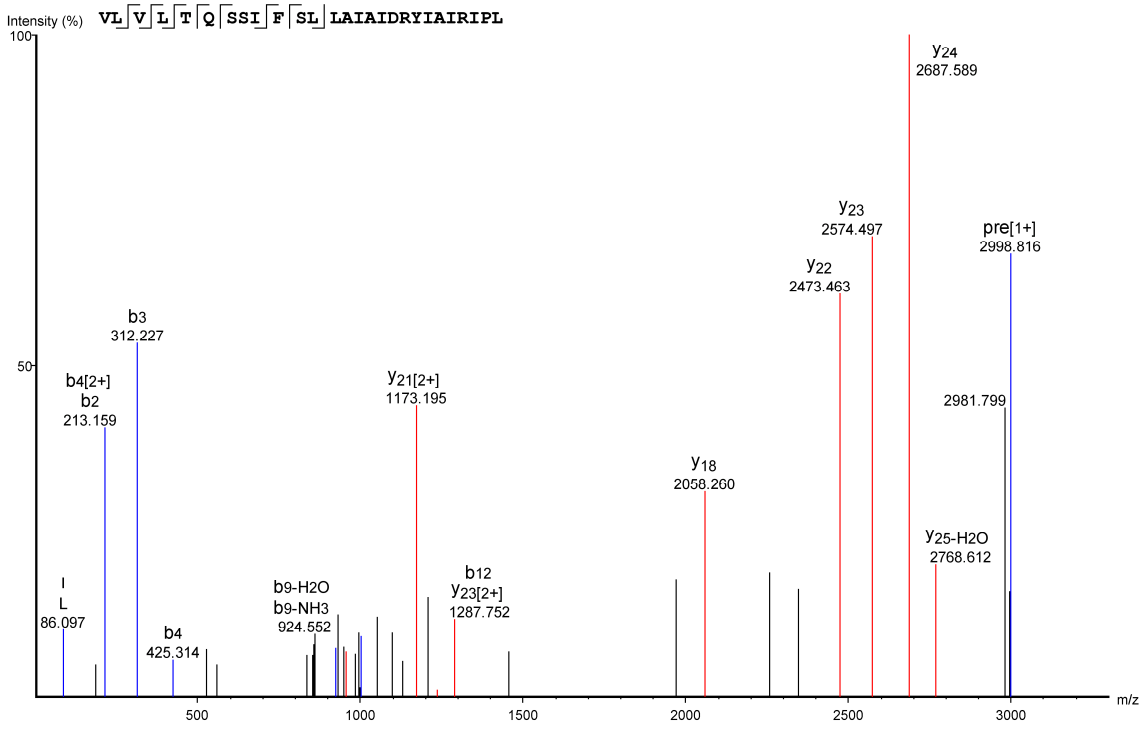
73–81, cAAcHGcLF



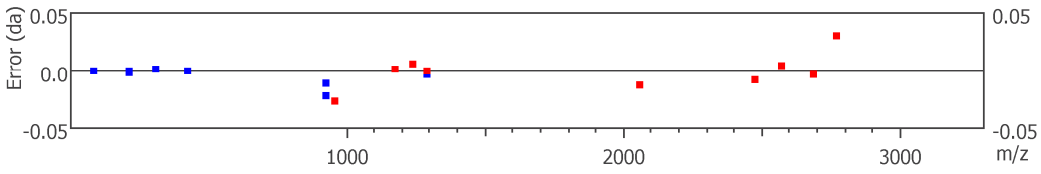

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 133.043 | 161.038 | 143.028 | 144.011 | 81.019 | C(+57.02) | | | | | 9 |
| 2 | 44.050 | 232.075 | 214.065 | 215.049 | 116.538 | A | 935.393 | 917.376 | 918.359 | 468.193 | 8 |
| 3 | 44.050 | 303.111 | 285.102 | 286.086 | 152.056 | A | 864.328 | 846.339 | 847.322 | 432.675 | 7 |
| 4 | 133.043 | 463.143 | 445.133 | 446.116 | 232.075 | C(+57.02) | 793.312 | 775.301 | 776.285 | 397.156 | 6 |
| 5 | 110.071 | 600.202 | 582.192 | 583.175 | 300.601 | H | 633.298 | 615.271 | 616.254 | 317.104 | 5 |
| 6 | 30.034 | 657.223 | 639.213 | 640.197 | 329.111 | G | 496.222 | 478.212 | 479.195 | 248.611 | 4 |
| 7 | 133.043 | 817.249 | 799.244 | 800.227 | 409.127 | C(+57.02) | 439.201 | 421.190 | 422.174 | 220.100 | 3 |
| 8 | 86.097 | 930.358 | 912.328 | 913.311 | 465.669 | L | 279.165 | 261.160 | 262.143 | 140.085 | 2 |
| 9 | 120.081 | | | | | F | 166.085 | 148.076 | 149.059 | 83.543 | 1 |



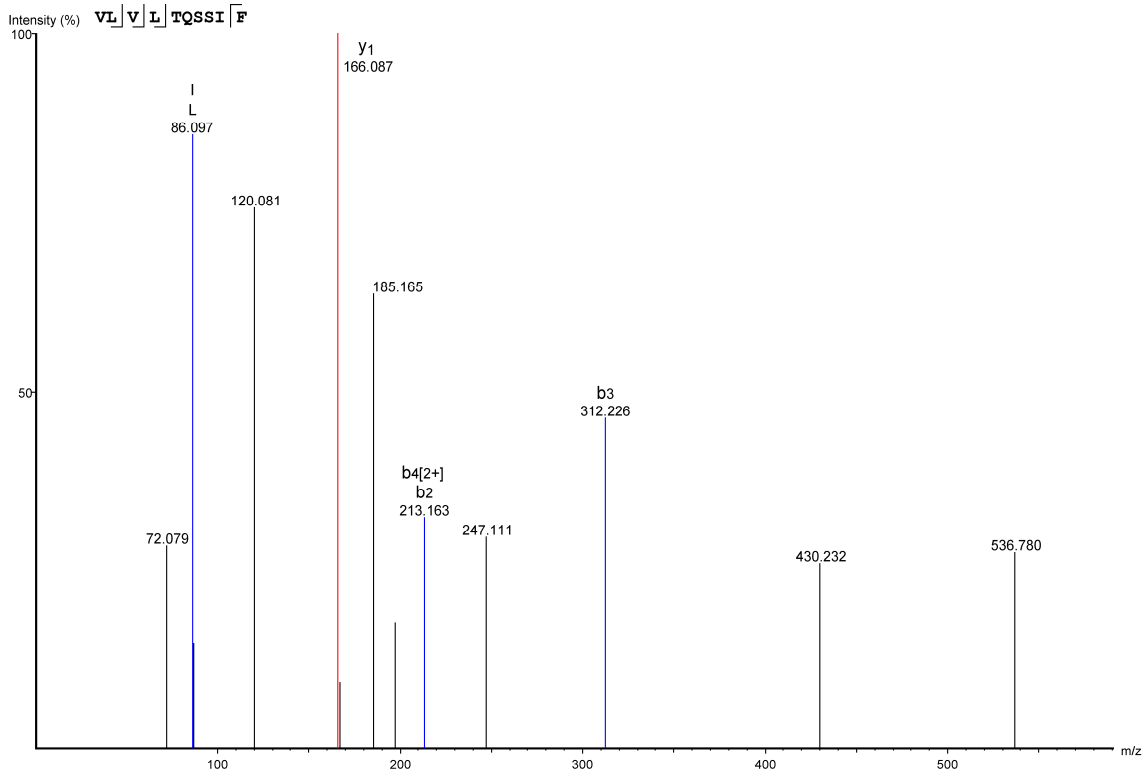
86–112, VLVLTQSSIFSLLAIAIDRYIAIRIPL



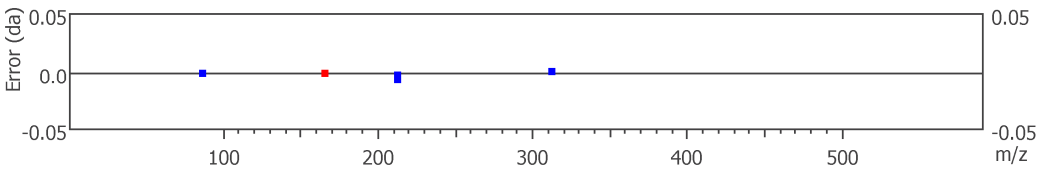
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 72.081 | 100.076 | 82.066 | 83.049 | 50.538 | V | | | | | 27 |
| 2 | 86.097 | 213.159 | 195.150 | 196.133 | 107.080 | L | 2899.738 | 2881.728 | 2882.711 | 1450.369 | 26 |
| 3 | 72.081 | 312.227 | 294.218 | 295.202 | 156.614 | V | 2786.654 | 2768.612 | 2769.627 | 1393.827 | 25 |
| 4 | 86.097 | 425.314 | 407.302 | 408.286 | 213.159 | L | 2687.589 | 2669.575 | 2670.559 | 1344.293 | 24 |
| 5 | 74.061 | 526.360 | 508.350 | 509.333 | 263.680 | T | 2574.497 | 2556.491 | 2557.475 | 1287.752 | 23 |
| 6 | 101.071 | 654.419 | 636.408 | 637.392 | 327.710 | Q | 2473.463 | 2455.444 | 2456.427 | 1237.220 | 22 |
| 7 | 60.045 | 741.451 | 723.440 | 724.424 | 371.226 | S | 2345.396 | 2327.385 | 2328.368 | 1173.195 | 21 |
| 8 | 60.045 | 828.483 | 810.473 | 811.456 | 414.742 | S | 2258.363 | 2240.353 | 2241.336 | 1129.682 | 20 |
| 9 | 86.097 | 941.567 | 923.579 | 924.552 | 471.284 | I | 2171.331 | 2153.321 | 2154.304 | 1086.166 | 19 |
| 10 | 120.081 | 1088.635 | 1070.625 | 1071.609 | 544.818 | F | 2058.260 | 2040.237 | 2041.220 | 1029.624 | 18 |
| 11 | 60.045 | 1175.668 | 1157.657 | 1158.641 | 588.334 | S | 1911.179 | 1893.168 | 1894.152 | 956.116 | 17 |
| 12 | 86.097 | 1288.755 | 1270.741 | 1271.725 | 644.876 | L | 1824.147 | 1806.136 | 1807.120 | 912.573 | 16 |
| 13 | 86.097 | 1401.836 | 1383.825 | 1384.809 | 701.418 | L | 1711.063 | 1693.052 | 1694.036 | 856.031 | 15 |
| 14 | 44.050 | 1472.873 | 1454.862 | 1455.846 | 736.936 | A | 1597.979 | 1579.968 | 1580.952 | 799.489 | 14 |
| 15 | 86.097 | 1585.957 | 1567.946 | 1568.930 | 793.478 | I | 1526.942 | 1508.931 | 1509.915 | 763.971 | 13 |
| 16 | 44.050 | 1656.994 | 1638.984 | 1639.967 | 828.997 | A | 1413.858 | 1395.847 | 1396.831 | 707.429 | 12 |
| 17 | 86.097 | 1770.078 | 1752.068 | 1753.051 | 885.539 | I | 1342.820 | 1324.810 | 1325.793 | 671.910 | 11 |
| 18 | 88.040 | 1885.105 | 1867.094 | 1868.078 | 943.052 | D | 1229.736 | 1211.726 | 1212.709 | 615.368 | 10 |
| 19 | 129.114 | 2041.206 | 2023.196 | 2024.179 | 1021.103 | R | 1114.709 | 1096.699 | 1097.682 | 557.855 | 9 |
| 20 | 136.076 | 2204.269 | 2186.259 | 2187.242 | 1102.635 | Y | 958.608 | 940.598 | 941.581 | 479.804 | 8 |
| 21 | 86.097 | 2317.354 | 2299.343 | 2300.326 | 1159.177 | I | 795.545 | 777.534 | 778.518 | 398.273 | 7 |
| 22 | 44.050 | 2388.391 | 2370.380 | 2371.364 | 1194.695 | A | 682.461 | 664.450 | 665.434 | 341.730 | 6 |
| 23 | 86.097 | 2501.475 | 2483.464 | 2484.448 | 1251.237 | I | 611.424 | 593.413 | 594.397 | 306.212 | 5 |
| 24 | 129.114 | 2657.576 | 2639.565 | 2640.549 | 1329.288 | R | 498.340 | 480.329 | 481.313 | 249.670 | 4 |
| 25 | 86.097 | 2770.660 | 2752.649 | 2753.633 | 1385.830 | I | 342.239 | 324.228 | 325.212 | 171.619 | 3 |
| 26 | 70.066 | 2867.713 | 2849.702 | 2850.686 | 1434.356 | P | 229.155 | 211.144 | 212.128 | 115.077 | 2 |
| 27 | 86.097 | | | | | L | 132.102 | 114.091 | 115.075 | 66.551 | 1 |



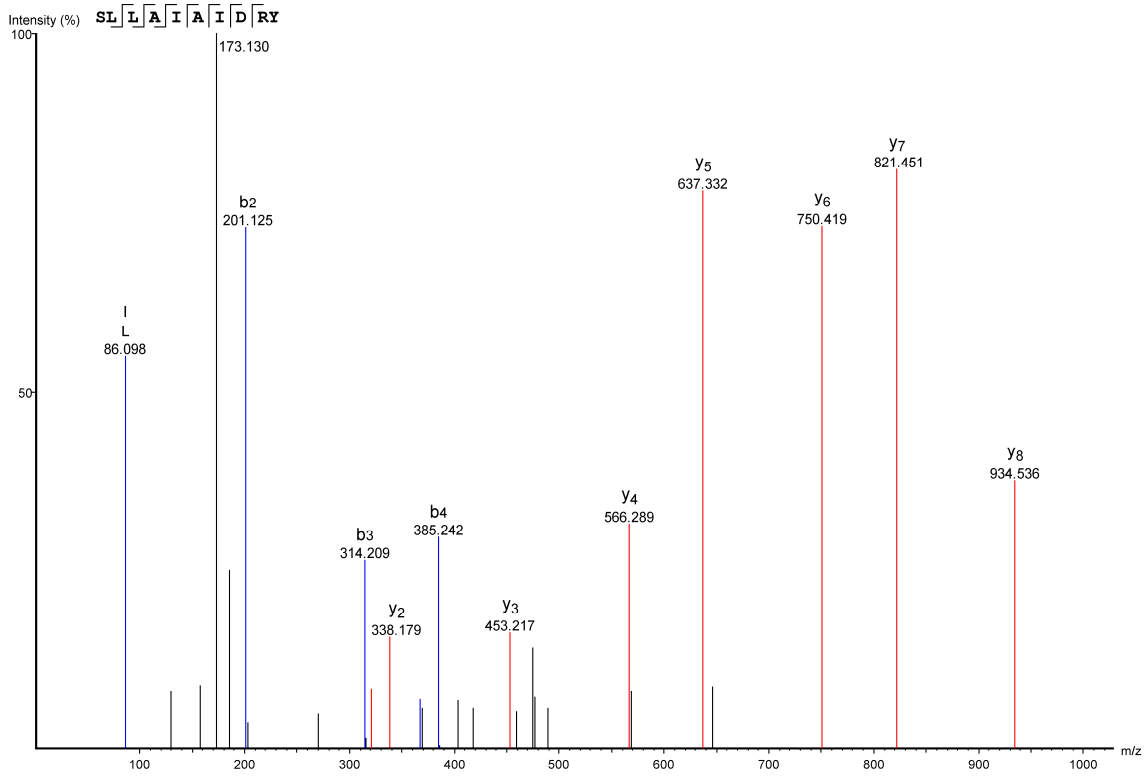
86–95, VLVLTQSSIF



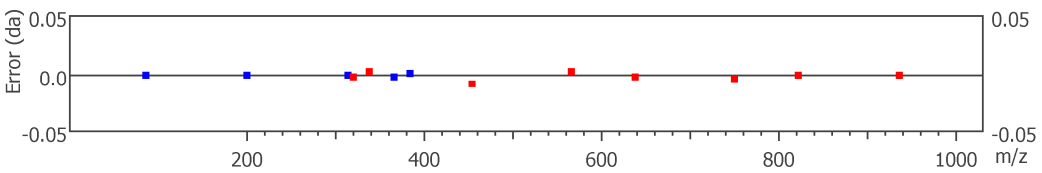

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 72.081 | 100.076 | 82.066 | 83.049 | 50.538 | V | | | | | 10 |
| 2 | 86.097 | 213.163 | 195.150 | 196.133 | 107.080 | L | 1007.577 | 989.567 | 990.550 | 504.289 | 9 |
| 3 | 72.081 | 312.226 | 294.218 | 295.202 | 156.614 | V | 894.493 | 876.483 | 877.466 | 447.747 | 8 |
| 4 | 86.097 | 425.313 | 407.302 | 408.286 | 213.163 | L | 795.425 | 777.414 | 778.398 | 398.212 | 7 |
| 5 | 74.061 | 526.360 | 508.350 | 509.333 | 263.680 | T | 682.341 | 664.330 | 665.314 | 341.670 | 6 |
| 6 | 101.071 | 654.419 | 636.408 | 637.392 | 327.710 | Q | 581.293 | 563.282 | 564.266 | 291.146 | 5 |
| 7 | 60.045 | 741.451 | 723.440 | 724.424 | 371.226 | S | 453.234 | 435.224 | 436.207 | 227.117 | 4 |
| 8 | 60.045 | 828.483 | 810.473 | 811.456 | 414.742 | S | 366.202 | 348.192 | 349.175 | 183.601 | 3 |
| 9 | 86.097 | 941.567 | 923.557 | 924.540 | 471.284 | I | 279.170 | 261.160 | 262.143 | 140.085 | 2 |
| 10 | 120.081 | | | | | F | 166.087 | 148.076 | 149.059 | 83.543 | 1 |



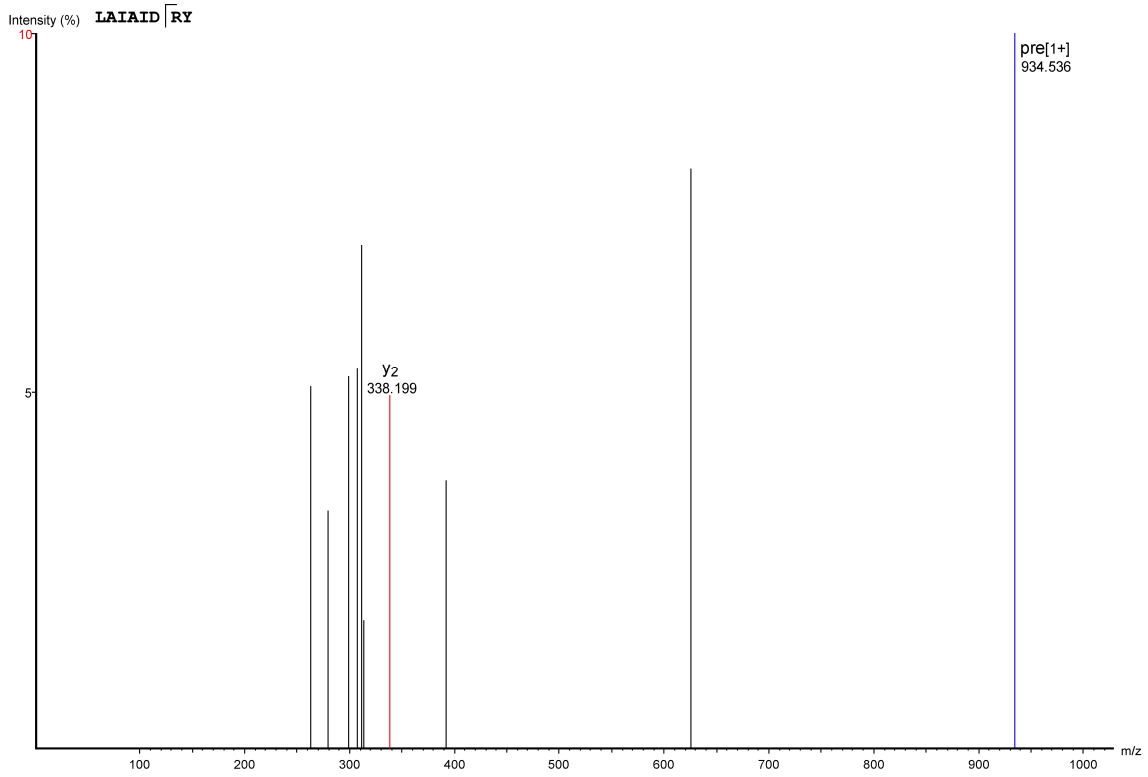
96–105, SLLAIAIDRY



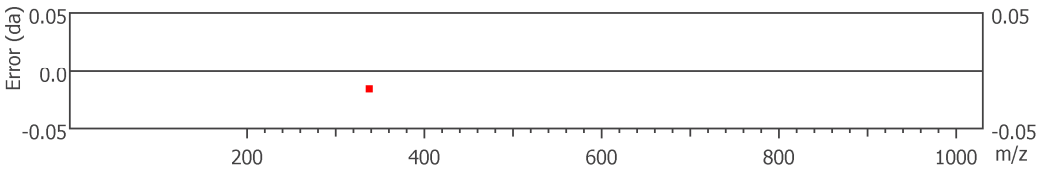

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 60.045 | 88.040 | 70.029 | 71.013 | 44.520 | S | | | | | 10 |
| 2 | 86.098 | 201.125 | 183.113 | 184.097 | 101.062 | L | 1047.620 | 1029.609 | 1030.593 | 524.310 | 9 |
| 3 | 86.097 | 314.209 | 296.197 | 297.181 | 157.604 | L | 934.536 | 916.525 | 917.509 | 467.768 | 8 |
| 4 | 44.050 | 385.242 | 367.237 | 368.218 | 193.123 | A | 821.451 | 803.441 | 804.425 | 411.226 | 7 |
| 5 | 86.098 | 498.329 | 480.319 | 481.302 | 249.665 | I | 750.419 | 732.404 | 733.387 | 375.707 | 6 |
| 6 | 44.050 | 569.366 | 551.356 | 552.339 | 285.183 | A | 637.332 | 619.320 | 620.303 | 319.165 | 5 |
| 7 | 86.097 | 682.450 | 664.440 | 665.423 | 341.725 | I | 566.289 | 548.283 | 549.266 | 283.647 | 4 |
| 8 | 88.040 | 797.477 | 779.467 | 780.450 | 399.239 | D | 453.217 | 435.199 | 436.182 | 227.105 | 3 |
| 9 | 129.114 | 953.578 | 935.568 | 936.551 | 477.289 | R | 338.179 | 320.172 | 321.157 | 169.591 | 2 |
| 10 | 136.076 | | | | | Y | 182.081 | 164.071 | 165.054 | 91.541 | 1 |



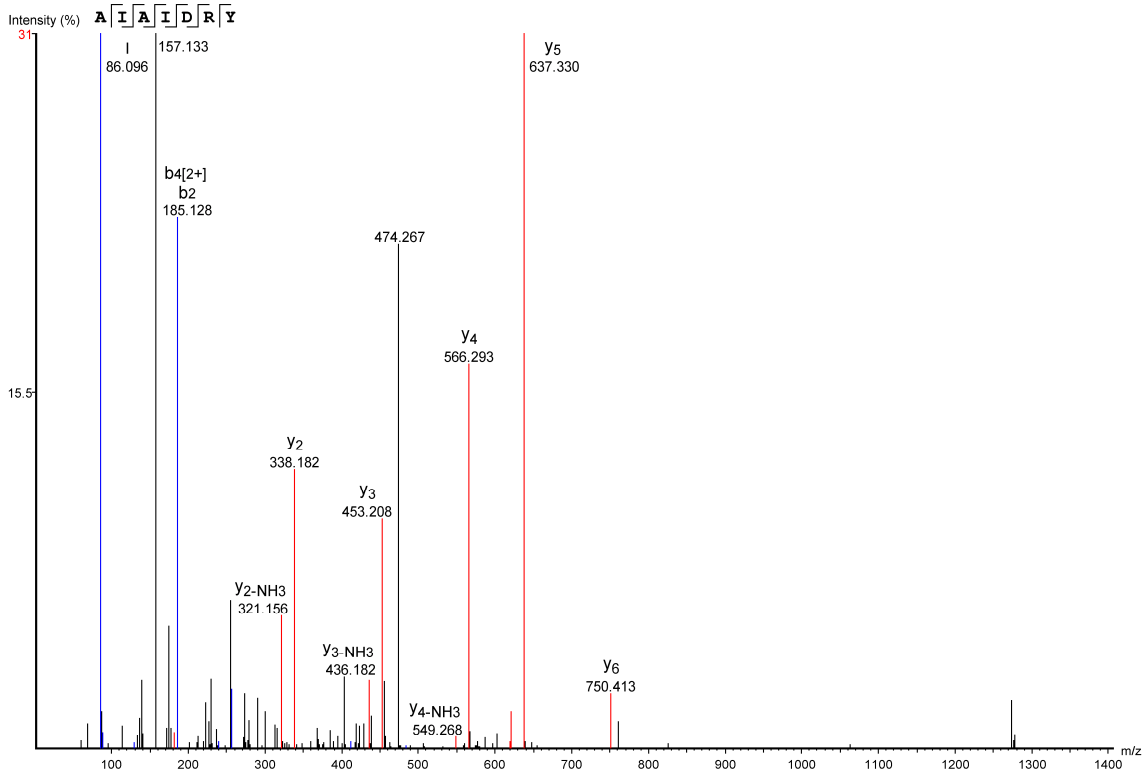
98–105, LAIAIDRY



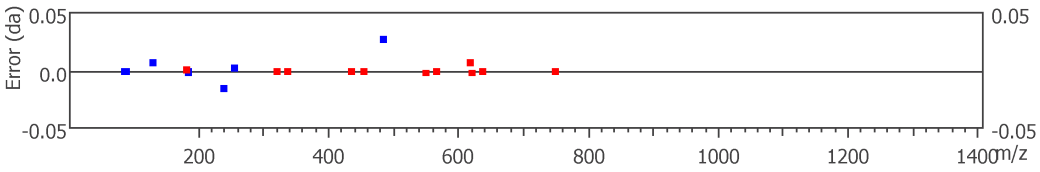

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 86.097 | 114.092 | 96.081 | 97.065 | 57.546 | L | | | | | 8 |
| 2 | 44.050 | 185.129 | 167.118 | 168.102 | 93.064 | A | 821.452 | 803.441 | 804.425 | 411.226 | 7 |
| 3 | 86.097 | 298.213 | 280.202 | 281.186 | 149.607 | I | 750.414 | 732.404 | 733.387 | 375.707 | 6 |
| 4 | 44.050 | 369.250 | 351.240 | 352.223 | 185.125 | A | 637.330 | 619.320 | 620.303 | 319.165 | 5 |
| 5 | 86.097 | 482.334 | 464.324 | 465.307 | 241.667 | I | 566.293 | 548.283 | 549.266 | 283.647 | 4 |
| 6 | 88.040 | 597.361 | 579.351 | 580.334 | 299.181 | D | 453.209 | 435.199 | 436.182 | 227.105 | 3 |
| 7 | 129.114 | 753.462 | 735.452 | 736.435 | 377.231 | R | 338.199 | 320.172 | 321.155 | 169.591 | 2 |
| 8 | 136.076 | | | | | Y | 182.081 | 164.071 | 165.054 | 91.541 | 1 |



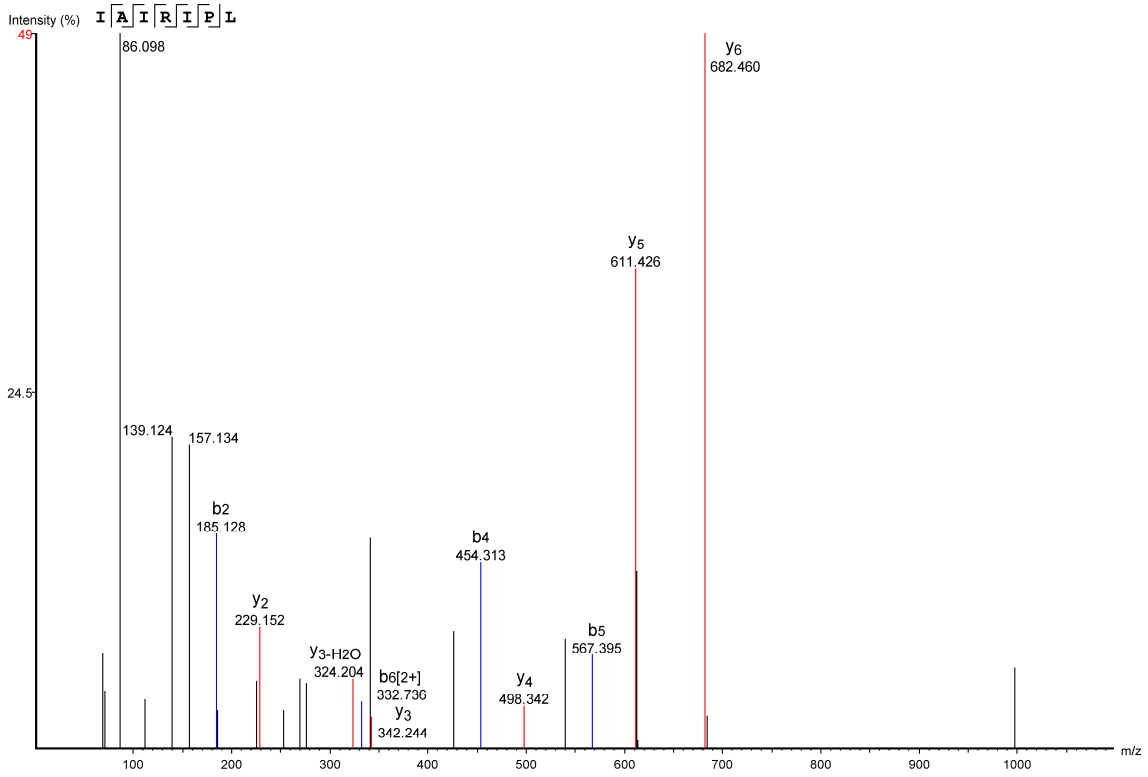
99–105, AIAIDRY



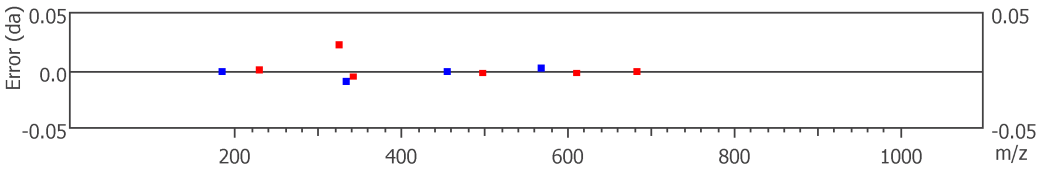

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 44.050 | 72.045 | 54.034 | 55.018 | 36.522 | A | | | | | 7 |
| 2 | 86.096 | 185.128 | 167.118 | 168.102 | 93.064 | I | 750.413 | 732.404 | 733.387 | 375.707 | 6 |
| 3 | 44.050 | 256.163 | 238.156 | 239.156 | 128.583 | A | 637.330 | 619.311 | 620.306 | 319.165 | 5 |
| 4 | 86.097 | 369.250 | 351.240 | 352.223 | 185.128 | I | 566.293 | 548.283 | 549.268 | 283.647 | 4 |
| 5 | 88.040 | 484.248 | 466.267 | 467.250 | 242.639 | D | 453.208 | 435.199 | 436.182 | 227.105 | 3 |
| 6 | 129.105 | 640.378 | 622.368 | 623.351 | 320.689 | R | 338.182 | 320.172 | 321.156 | 169.591 | 2 |
| 7 | 136.076 | | | | | Y | 182.079 | 164.071 | 165.054 | 91.541 | 1 |



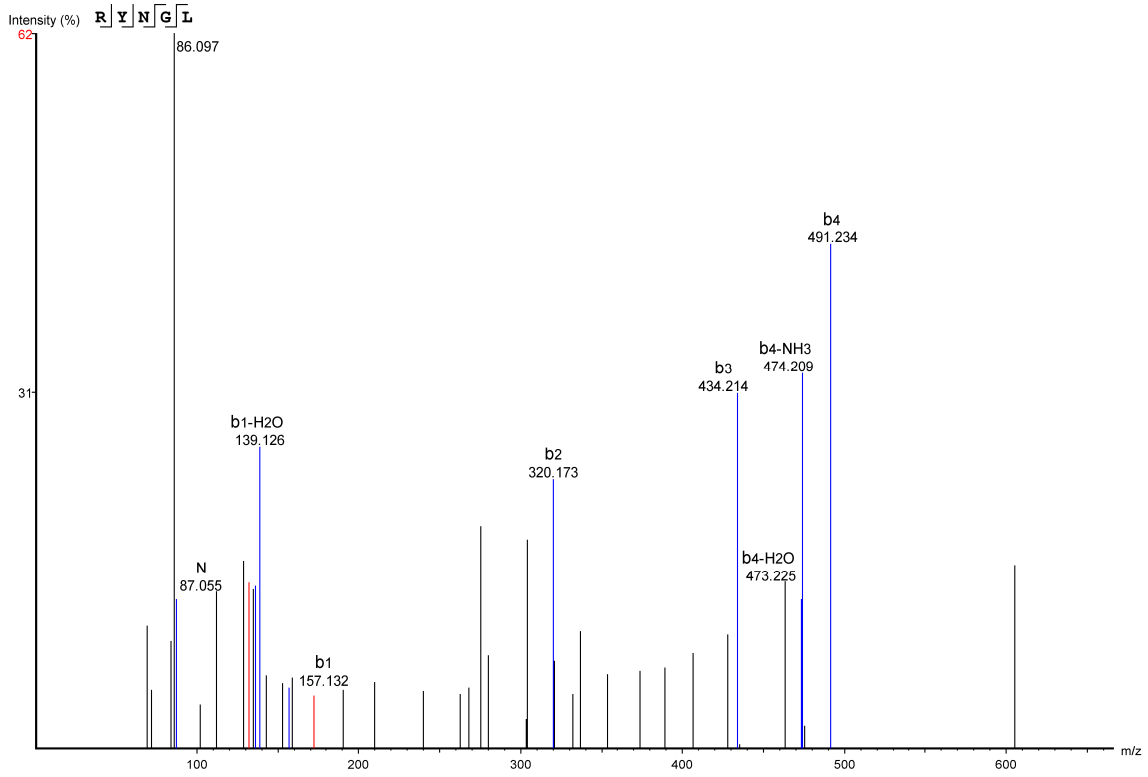
106–112, IAIRIPL



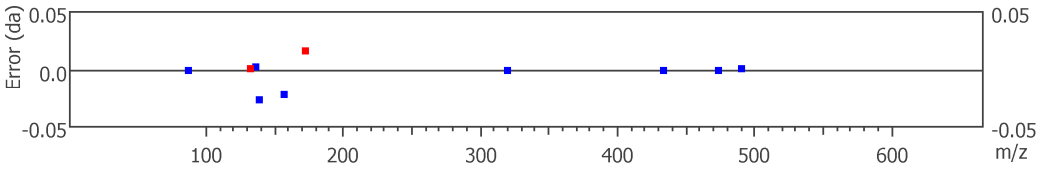

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 86.097 | 114.092 | 96.081 | 97.065 | 57.546 | I | | | | | 7 |
| 2 | 44.050 | 185.128 | 167.118 | 168.102 | 93.064 | A | 682.460 | 664.450 | 665.434 | 341.730 | 6 |
| 3 | 86.097 | 298.213 | 280.202 | 281.186 | 149.607 | I | 611.426 | 593.413 | 594.397 | 306.212 | 5 |
| 4 | 129.114 | 454.313 | 436.304 | 437.287 | 227.657 | R | 498.342 | 480.329 | 481.313 | 249.670 | 4 |
| 5 | 86.097 | 567.395 | 549.388 | 550.371 | 284.199 | I | 342.244 | 324.204 | 325.212 | 171.619 | 3 |
| 6 | 70.066 | 664.451 | 646.440 | 647.424 | 332.736 | P | 229.152 | 211.144 | 212.128 | 115.077 | 2 |
| 7 | 86.097 | | | | | L | 132.102 | 114.091 | 115.075 | 66.551 | 1 |



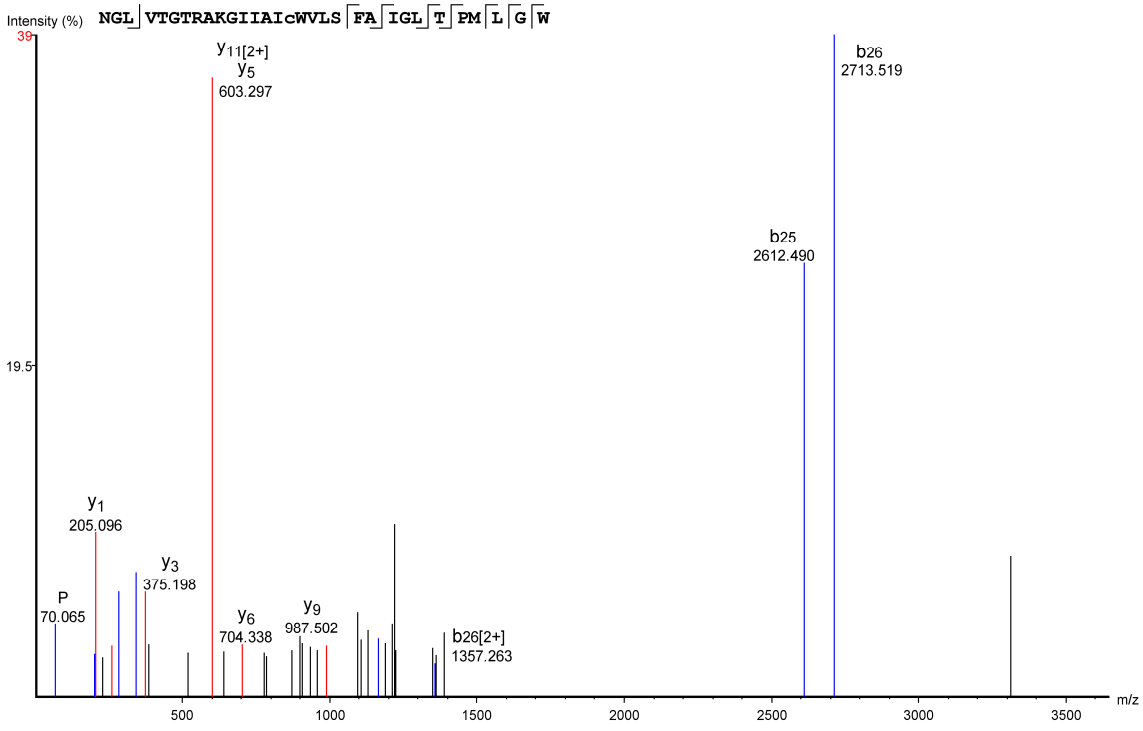
113–117, RYNGL



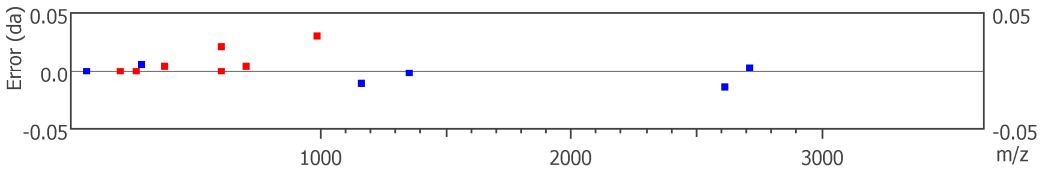

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 129.114 | 157.132 | 139.126 | 140.082 | 79.054 | R | | | | | 5 |
| 2 | 136.073 | 320.173 | 302.162 | 303.145 | 160.586 | Y | 466.230 | 448.219 | 449.203 | 233.615 | 4 |
| 3 | 87.055 | 434.214 | 416.205 | 417.188 | 217.608 | N | 303.166 | 285.156 | 286.139 | 152.083 | 3 |
| 4 | 30.034 | 491.234 | 473.225 | 474.209 | 246.118 | G | 189.123 | 171.113 | 172.078 | 95.062 | 2 |
| 5 | 86.097 | | | | | L | 132.100 | 114.091 | 115.075 | 66.551 | 1 |



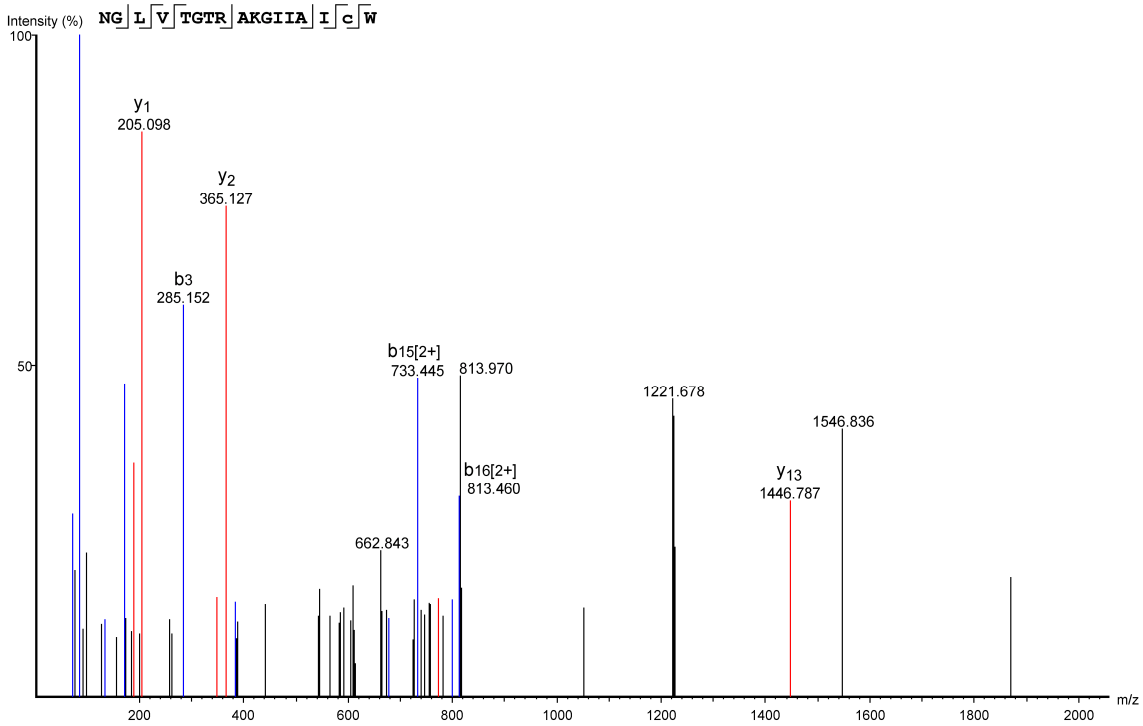
115–145, NGLVTGTRAKGIIAIcWVLSFAIGLTPMLGW



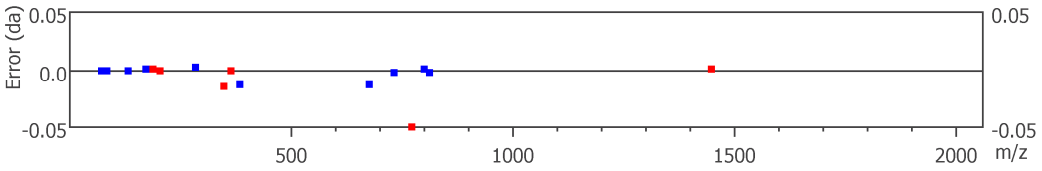
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 87.056 | 115.051 | 97.040 | 98.024 | 58.025 | N | | | | | 31 |
| 2 | 30.034 | 172.072 | 154.062 | 155.045 | 86.536 | G | 3201.768 | 3183.757 | 3184.741 | 1601.384 | 30 |
| 3 | 86.097 | 285.150 | 267.146 | 268.129 | 143.078 | L | 3144.746 | 3126.736 | 3127.719 | 1572.873 | 29 |
| 4 | 72.081 | 384.225 | 366.214 | 367.198 | 192.612 | V | 3031.662 | 3013.652 | 3014.635 | 1516.331 | 28 |
| 5 | 74.061 | 485.272 | 467.262 | 468.245 | 243.136 | T | 2932.594 | 2914.583 | 2915.567 | 1466.797 | 27 |
| 6 | 30.034 | 542.294 | 524.283 | 525.267 | 271.647 | G | 2831.546 | 2813.536 | 2814.519 | 1416.273 | 26 |
| 7 | 74.061 | 643.341 | 625.331 | 626.315 | 322.171 | T | 2774.525 | 2756.514 | 2757.498 | 1387.762 | 25 |
| 8 | 129.114 | 799.443 | 781.432 | 782.416 | 400.221 | R | 2673.477 | 2655.467 | 2656.450 | 1337.239 | 24 |
| 9 | 44.050 | 870.480 | 852.469 | 853.453 | 435.740 | A | 2517.376 | 2499.365 | 2500.349 | 1259.188 | 23 |
| 10 | 101.108 | 998.575 | 980.564 | 981.548 | 499.787 | K | 2446.339 | 2428.328 | 2429.312 | 1223.669 | 22 |
| 11 | 30.034 | 1055.596 | 1037.586 | 1038.569 | 528.298 | G | 2318.244 | 2300.233 | 2301.217 | 1159.622 | 21 |
| 12 | 86.097 | 1168.680 | 1150.670 | 1151.653 | 584.840 | I | 2261.222 | 2243.212 | 2244.195 | 1131.111 | 20 |
| 13 | 86.097 | 1281.764 | 1263.754 | 1264.737 | 641.382 | I | 2148.138 | 2130.128 | 2131.111 | 1074.569 | 19 |
| 14 | 44.050 | 1352.801 | 1334.791 | 1335.774 | 676.901 | A | 2035.054 | 2017.044 | 2018.027 | 1018.027 | 18 |
| 15 | 86.097 | 1465.885 | 1447.875 | 1448.858 | 733.443 | I | 1964.017 | 1946.007 | 1946.990 | 982.509 | 17 |
| 16 | 133.043 | 1625.916 | 1607.906 | 1608.889 | 813.458 | C(+57.02) | 1850.933 | 1832.923 | 1833.906 | 925.967 | 16 |
| 17 | 159.092 | 1811.995 | 1793.985 | 1794.968 | 906.498 | W | 1690.902 | 1672.892 | 1673.875 | 845.951 | 15 |
| 18 | 72.081 | 1911.064 | 1893.053 | 1894.037 | 956.032 | V | 1504.823 | 1486.813 | 1487.796 | 752.912 | 14 |
| 19 | 86.097 | 2024.148 | 2006.137 | 2007.121 | 1012.574 | L | 1405.755 | 1387.744 | 1388.728 | 703.377 | 13 |
| 20 | 60.045 | 2111.180 | 2093.169 | 2094.153 | 1056.090 | S | 1292.671 | 1274.660 | 1275.644 | 646.835 | 12 |
| 21 | 120.081 | 2258.248 | 2240.238 | 2241.221 | 1129.624 | F | 1205.639 | 1187.628 | 1188.612 | 603.297 | 11 |
| 22 | 44.050 | 2329.285 | 2311.275 | 2312.258 | 1165.154 | A | 1058.570 | 1040.560 | 1041.543 | 529.785 | 10 |
| 23 | 86.097 | 2442.369 | 2424.359 | 2425.342 | 1221.685 | I | 987.502 | 969.523 | 970.506 | 494.267 | 9 |
| 24 | 30.034 | 2499.391 | 2481.380 | 2482.364 | 1250.195 | G | 874.449 | 856.439 | 857.422 | 437.725 | 8 |
| 25 | 86.097 | 2612.490 | 2594.465 | 2595.448 | 1306.738 | L | 817.428 | 799.417 | 800.401 | 409.214 | 7 |
| 26 | 74.061 | 2713.519 | 2695.512 | 2696.496 | 1357.263 | T | 704.338 | 686.333 | 687.317 | 352.672 | 6 |
| 27 | 70.065 | 2810.575 | 2792.565 | 2793.548 | 1405.788 | P | 603.297 | 585.285 | 586.269 | 302.148 | 5 |
| 28 | 104.053 | 2941.616 | 2923.605 | 2924.589 | 1471.308 | M | 506.243 | 488.233 | 489.216 | 253.622 | 4 |
| 29 | 86.097 | 3054.700 | 3036.689 | 3037.673 | 1527.850 | L | 375.198 | 357.192 | 358.176 | 188.101 | 3 |
| 30 | 30.034 | 3111.721 | 3093.711 | 3094.694 | 1556.361 | G | 262.118 | 244.108 | 245.092 | 131.559 | 2 |
| 31 | 159.092 | | | | | W | 205.096 | 187.087 | 188.070 | 103.049 | 1 |



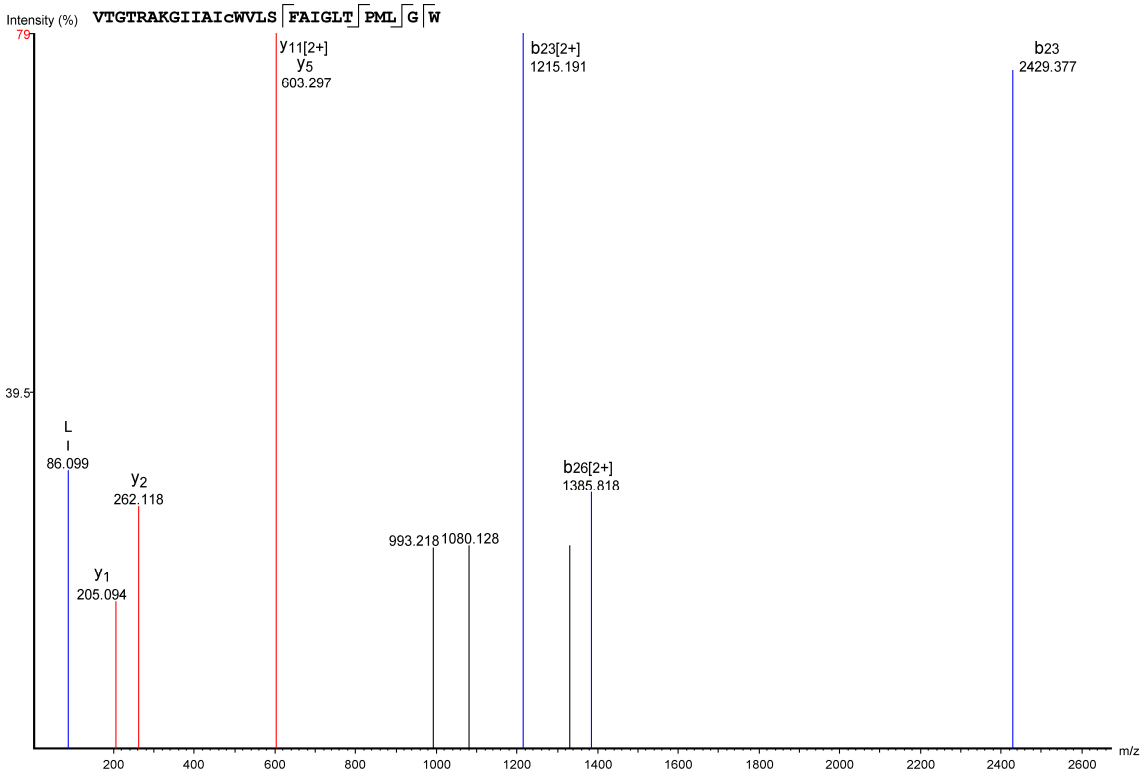
115–131, NGLVTGTRAKGIIAIcW



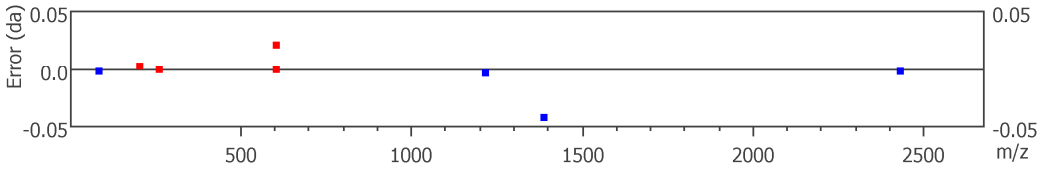

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 87.056 | 115.051 | 97.040 | 98.024 | 58.025 | N | | | | | 17 |
| 2 | 30.034 | 172.070 | 154.062 | 155.045 | 86.536 | G | 1715.963 | 1697.952 | 1698.936 | 858.481 | 16 |
| 3 | 86.098 | 285.152 | 267.146 | 268.129 | 143.078 | L | 1658.941 | 1640.931 | 1641.914 | 829.971 | 15 |
| 4 | 72.081 | 384.238 | 366.214 | 367.198 | 192.612 | V | 1545.857 | 1527.846 | 1528.830 | 773.478 | 14 |
| 5 | 74.061 | 485.272 | 467.262 | 468.245 | 243.136 | T | 1446.787 | 1428.778 | 1429.762 | 723.894 | 13 |
| 6 | 30.034 | 542.294 | 524.283 | 525.267 | 271.647 | G | 1345.741 | 1327.730 | 1328.714 | 673.370 | 12 |
| 7 | 74.061 | 643.341 | 625.331 | 626.315 | 322.171 | T | 1288.719 | 1270.709 | 1271.692 | 644.860 | 11 |
| 8 | 129.114 | 799.441 | 781.432 | 782.416 | 400.221 | R | 1187.672 | 1169.661 | 1170.645 | 594.336 | 10 |
| 9 | 44.050 | 870.480 | 852.469 | 853.453 | 435.740 | A | 1031.571 | 1013.560 | 1014.544 | 516.285 | 9 |
| 10 | 101.108 | 998.575 | 980.564 | 981.548 | 499.787 | K | 960.534 | 942.523 | 943.507 | 480.767 | 8 |
| 11 | 30.034 | 1055.596 | 1037.586 | 1038.569 | 528.298 | G | 832.439 | 814.428 | 815.412 | 416.719 | 7 |
| 12 | 86.098 | 1168.680 | 1150.670 | 1151.653 | 584.840 | I | 775.417 | 757.407 | 758.390 | 388.209 | 6 |
| 13 | 86.097 | 1281.764 | 1263.754 | 1264.737 | 641.382 | I | 662.333 | 644.322 | 645.306 | 331.667 | 5 |
| 14 | 44.050 | 1352.801 | 1334.791 | 1335.774 | 676.914 | A | 549.249 | 531.238 | 532.222 | 275.124 | 4 |
| 15 | 86.097 | 1465.885 | 1447.875 | 1448.858 | 733.445 | I | 478.212 | 460.201 | 461.185 | 239.606 | 3 |
| 16 | 133.044 | 1625.916 | 1607.906 | 1608.889 | 813.460 | C(+57.02) | 365.127 | 347.117 | 348.115 | 183.064 | 2 |
| 17 | 159.092 | | | | | W | 205.098 | 187.087 | 188.068 | 103.049 | 1 |



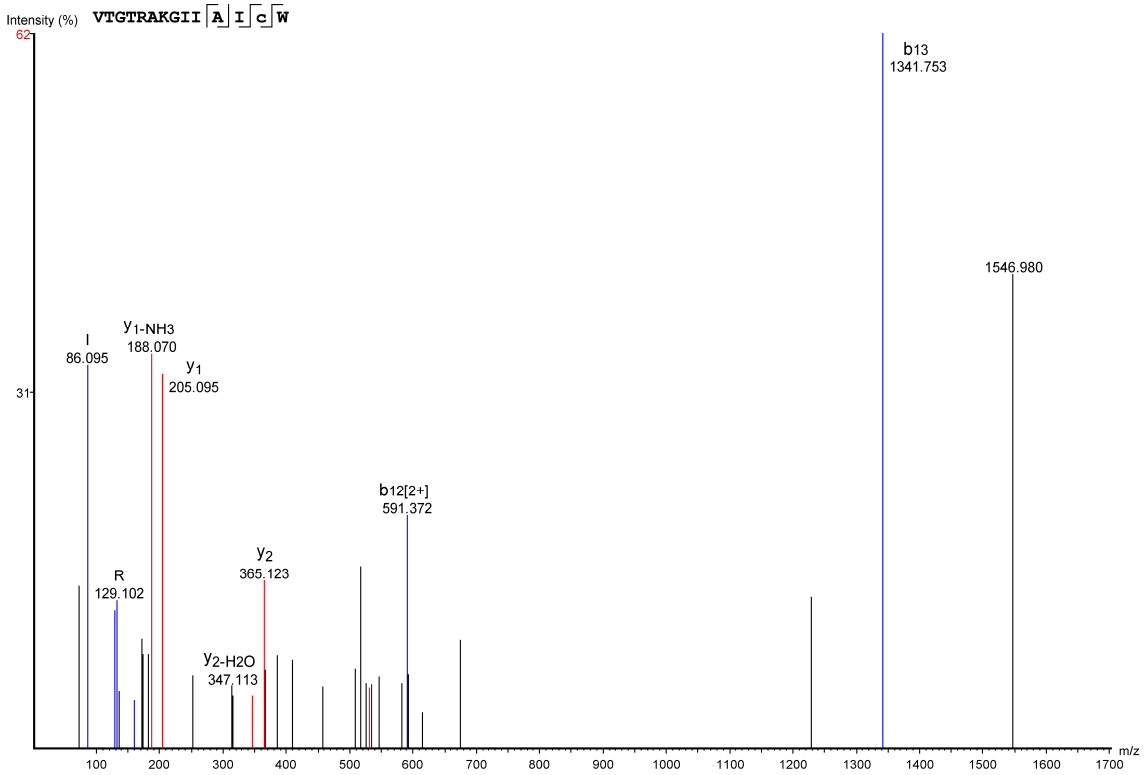
118–145, VTGTRAKGIIAIcWVLSFAIGLTPMLGW



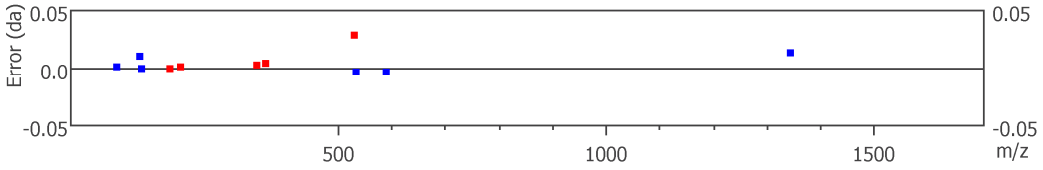
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 72.081 | 100.076 | 82.066 | 83.049 | 50.538 | V | | | | | 28 |
| 2 | 74.061 | 201.124 | 183.113 | 184.097 | 101.062 | T | 2932.594 | 2914.583 | 2915.567 | 1466.797 | 27 |
| 3 | 30.034 | 258.145 | 240.135 | 241.118 | 129.573 | G | 2831.546 | 2813.536 | 2814.519 | 1416.273 | 26 |
| 4 | 74.061 | 359.193 | 341.182 | 342.166 | 180.097 | T | 2774.525 | 2756.514 | 2757.498 | 1387.762 | 25 |
| 5 | 129.114 | 515.294 | 497.284 | 498.267 | 258.147 | R | 2673.477 | 2655.467 | 2656.450 | 1337.239 | 24 |
| 6 | 44.050 | 586.331 | 568.321 | 569.304 | 293.666 | A | 2517.376 | 2499.365 | 2500.349 | 1259.188 | 23 |
| 7 | 101.108 | 714.426 | 696.416 | 697.399 | 357.713 | K | 2446.339 | 2428.328 | 2429.312 | 1223.669 | 22 |
| 8 | 30.034 | 771.448 | 753.437 | 754.421 | 386.224 | G | 2318.244 | 2300.233 | 2301.217 | 1159.622 | 21 |
| 9 | 86.099 | 884.532 | 866.521 | 867.505 | 442.766 | I | 2261.222 | 2243.212 | 2244.195 | 1131.111 | 20 |
| 10 | 86.097 | 997.616 | 979.605 | 980.589 | 499.308 | I | 2148.138 | 2130.128 | 2131.111 | 1074.569 | 19 |
| 11 | 44.050 | 1068.653 | 1050.642 | 1051.626 | 534.826 | A | 2035.054 | 2017.044 | 2018.027 | 1018.027 | 18 |
| 12 | 86.097 | 1181.737 | 1163.726 | 1164.710 | 591.368 | I | 1964.017 | 1946.007 | 1946.990 | 982.509 | 17 |
| 13 | 133.043 | 1341.768 | 1323.757 | 1324.741 | 671.384 | C(+57.02) | 1850.933 | 1832.923 | 1833.906 | 925.967 | 16 |
| 14 | 159.092 | 1527.847 | 1509.836 | 1510.820 | 764.423 | W | 1690.902 | 1672.892 | 1673.875 | 845.951 | 15 |
| 15 | 72.081 | 1626.915 | 1608.905 | 1609.888 | 813.958 | V | 1504.823 | 1486.813 | 1487.796 | 752.912 | 14 |
| 16 | 86.099 | 1739.999 | 1721.989 | 1722.972 | 870.500 | L | 1405.755 | 1387.744 | 1388.728 | 703.377 | 13 |
| 17 | 60.045 | 1827.031 | 1809.021 | 1810.005 | 914.016 | S | 1292.671 | 1274.660 | 1275.644 | 646.835 | 12 |
| 18 | 120.081 | 1974.100 | 1956.089 | 1957.073 | 987.550 | F | 1205.639 | 1187.628 | 1188.612 | 603.297 | 11 |
| 19 | 44.050 | 2045.137 | 2027.126 | 2028.110 | 1023.068 | A | 1058.570 | 1040.560 | 1041.543 | 529.785 | 10 |
| 20 | 86.097 | 2158.221 | 2140.210 | 2141.194 | 1079.610 | I | 987.533 | 969.523 | 970.506 | 494.267 | 9 |
| 21 | 30.034 | 2215.242 | 2197.232 | 2198.215 | 1108.121 | G | 874.449 | 856.439 | 857.422 | 437.725 | 8 |
| 22 | 86.097 | 2328.327 | 2310.316 | 2311.300 | 1164.663 | L | 817.428 | 799.417 | 800.401 | 409.214 | 7 |
| 23 | 74.061 | 2429.377 | 2411.364 | 2412.347 | 1215.191 | T | 704.344 | 686.333 | 687.317 | 352.672 | 6 |
| 24 | 70.066 | 2526.427 | 2508.417 | 2509.400 | 1263.714 | P | 603.297 | 585.285 | 586.269 | 302.148 | 5 |
| 25 | 104.053 | 2657.468 | 2639.457 | 2640.440 | 1329.234 | M | 506.243 | 488.233 | 489.216 | 253.622 | 4 |
| 26 | 86.097 | 2770.552 | 2752.541 | 2753.524 | 1385.818 | L | 375.203 | 357.192 | 358.176 | 188.101 | 3 |
| 27 | 30.034 | 2827.573 | 2809.562 | 2810.546 | 1414.286 | G | 262.118 | 244.108 | 245.092 | 131.559 | 2 |
| 28 | 159.092 | | | | | W | 205.094 | 187.087 | 188.070 | 103.049 | 1 |



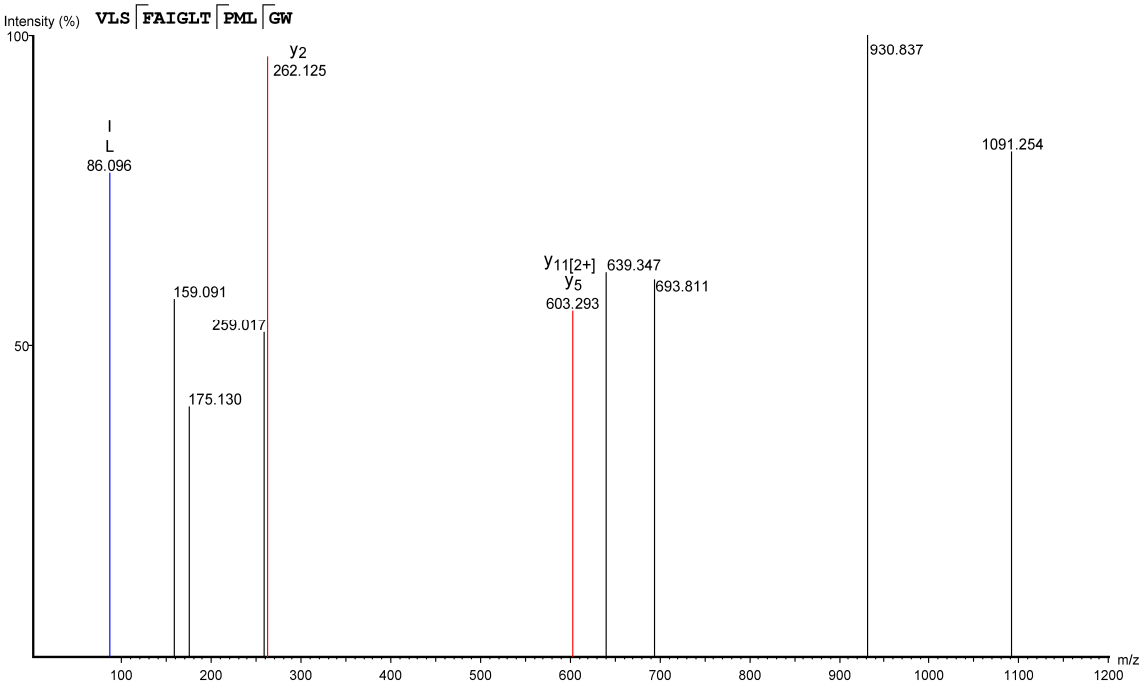
118–131, VTGTRAKGIIAIcW



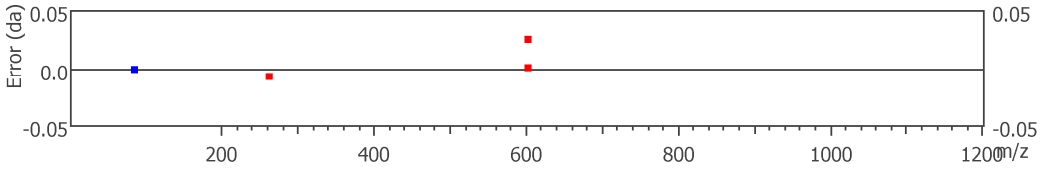

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 72.081 | 100.076 | 82.066 | 83.049 | 50.538 | V | | | | | 14 |
| 2 | 74.061 | 201.124 | 183.113 | 184.097 | 101.062 | T | 1446.789 | 1428.778 | 1429.762 | 723.894 | 13 |
| 3 | 30.034 | 258.145 | 240.135 | 241.118 | 129.573 | G | 1345.741 | 1327.730 | 1328.714 | 673.370 | 12 |
| 4 | 74.061 | 359.193 | 341.182 | 342.166 | 180.097 | T | 1288.719 | 1270.709 | 1271.692 | 644.860 | 11 |
| 5 | 129.102 | 515.294 | 497.284 | 498.267 | 258.147 | R | 1187.672 | 1169.661 | 1170.645 | 594.336 | 10 |
| 6 | 44.050 | 586.331 | 568.321 | 569.304 | 293.666 | A | 1031.571 | 1013.560 | 1014.544 | 516.285 | 9 |
| 7 | 101.108 | 714.426 | 696.416 | 697.399 | 357.713 | K | 960.534 | 942.523 | 943.507 | 480.767 | 8 |
| 8 | 30.034 | 771.448 | 753.437 | 754.421 | 386.224 | G | 832.439 | 814.428 | 815.412 | 416.719 | 7 |
| 9 | 86.095 | 884.532 | 866.521 | 867.505 | 442.766 | I | 775.417 | 757.407 | 758.390 | 388.209 | 6 |
| 10 | 86.097 | 997.616 | 979.605 | 980.589 | 499.308 | I | 662.333 | 644.322 | 645.306 | 331.667 | 5 |
| 11 | 44.050 | 1068.653 | 1050.642 | 1051.626 | 534.830 | A | 549.249 | 531.209 | 532.222 | 275.124 | 4 |
| 12 | 86.097 | 1181.737 | 1163.726 | 1164.710 | 591.372 | I | 478.212 | 460.201 | 461.185 | 239.606 | 3 |
| 13 | 133.043 | 1341.753 | 1323.757 | 1324.741 | 671.384 | C(+57.02) | 365.123 | 347.113 | 348.101 | 183.064 | 2 |
| 14 | 159.092 | | | | | W | 205.095 | 187.087 | 188.070 | 103.049 | 1 |



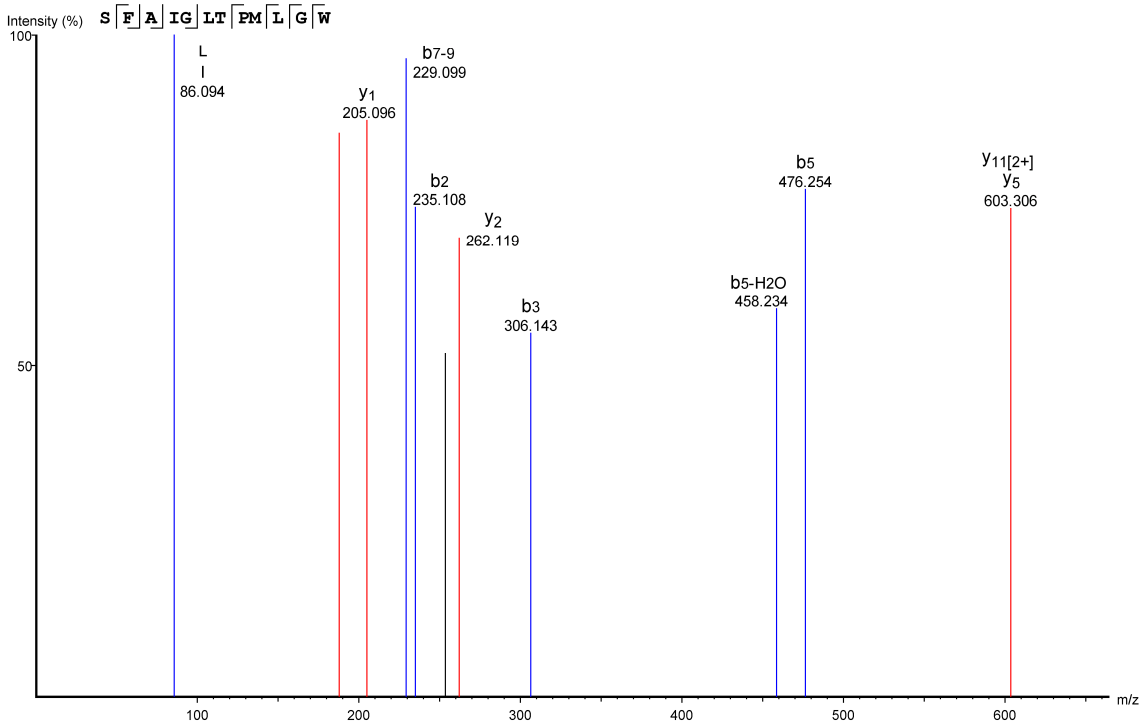
132–145, VLSFAIGLTPMLGW



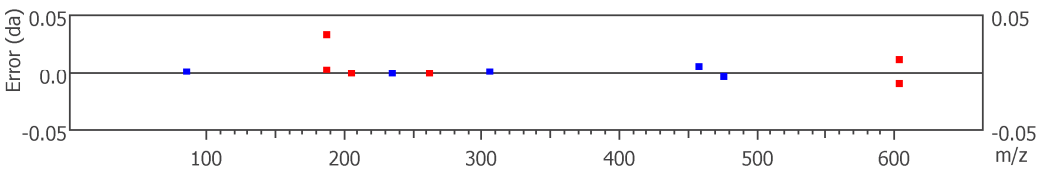

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 72.081 | 100.076 | 82.066 | 83.049 | 50.538 | V | | | | | 14 |
| 2 | 86.096 | 213.160 | 195.150 | 196.133 | 107.080 | L | 1405.755 | 1387.744 | 1388.728 | 703.377 | 13 |
| 3 | 60.045 | 300.192 | 282.182 | 283.165 | 150.596 | S | 1292.671 | 1274.660 | 1275.644 | 646.835 | 12 |
| 4 | 120.081 | 447.261 | 429.250 | 430.234 | 224.130 | F | 1205.639 | 1187.628 | 1188.612 | 603.293 | 11 |
| 5 | 44.050 | 518.298 | 500.287 | 501.271 | 259.649 | A | 1058.570 | 1040.560 | 1041.543 | 529.785 | 10 |
| 6 | 86.096 | 631.382 | 613.371 | 614.355 | 316.191 | I | 987.533 | 969.523 | 970.506 | 494.267 | 9 |
| 7 | 30.034 | 688.403 | 670.393 | 671.376 | 344.702 | G | 874.449 | 856.439 | 857.422 | 437.725 | 8 |
| 8 | 86.097 | 801.487 | 783.477 | 784.460 | 401.244 | L | 817.428 | 799.417 | 800.401 | 409.214 | 7 |
| 9 | 74.061 | 902.535 | 884.525 | 885.508 | 451.768 | T | 704.344 | 686.333 | 687.317 | 352.672 | 6 |
| 10 | 70.066 | 999.588 | 981.577 | 982.561 | 500.294 | P | 603.293 | 585.285 | 586.269 | 302.148 | 5 |
| 11 | 104.053 | 1130.628 | 1112.618 | 1113.601 | 565.814 | M | 506.243 | 488.233 | 489.216 | 253.622 | 4 |
| 12 | 86.097 | 1243.712 | 1225.702 | 1226.685 | 622.356 | L | 375.203 | 357.192 | 358.176 | 188.101 | 3 |
| 13 | 30.034 | 1300.734 | 1282.723 | 1283.707 | 650.867 | G | 262.125 | 244.108 | 245.092 | 131.559 | 2 |
| 14 | 159.092 | | | | | W | 205.097 | 187.087 | 188.070 | 103.049 | 1 |



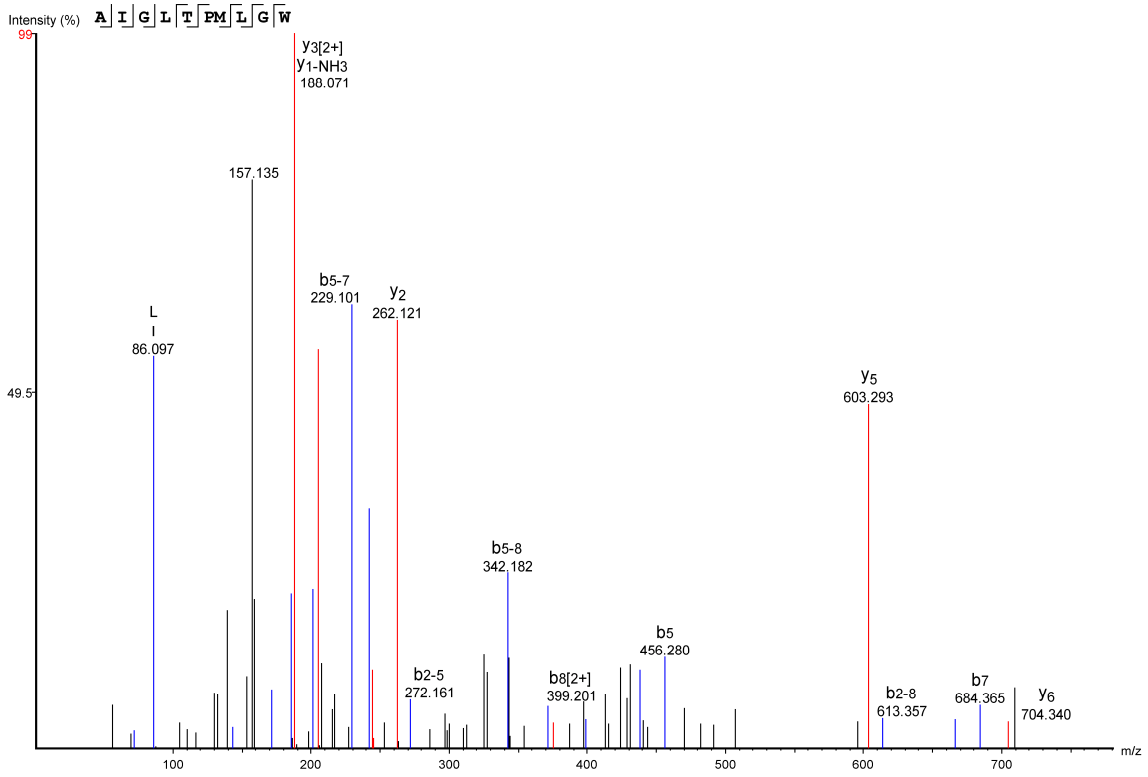
134–145, SFAIGLTPMLGW



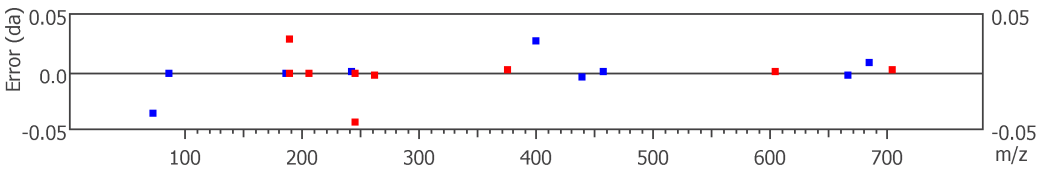

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 60.045 | 88.040 | 70.029 | 71.013 | 44.520 | S | | | | | 12 |
| 2 | 120.081 | 235.108 | 217.098 | 218.081 | 118.054 | F | 1205.639 | 1187.628 | 1188.612 | 603.306 | 11 |
| 3 | 44.050 | 306.143 | 288.135 | 289.118 | 153.573 | A | 1058.570 | 1040.560 | 1041.543 | 529.785 | 10 |
| 4 | 86.094 | 419.229 | 401.219 | 402.202 | 210.115 | I | 987.533 | 969.523 | 970.506 | 494.267 | 9 |
| 5 | 30.034 | 476.254 | 458.234 | 459.224 | 238.625 | G | 874.449 | 856.439 | 857.422 | 437.725 | 8 |
| 6 | 86.094 | 589.335 | 571.324 | 572.308 | 295.167 | L | 817.428 | 799.417 | 800.401 | 409.214 | 7 |
| 7 | 74.061 | 690.383 | 672.372 | 673.356 | 345.691 | T | 704.344 | 686.333 | 687.317 | 352.672 | 6 |
| 8 | 70.066 | 787.435 | 769.425 | 770.408 | 394.218 | P | 603.306 | 585.285 | 586.269 | 302.148 | 5 |
| 9 | 104.053 | 918.476 | 900.465 | 901.449 | 459.738 | M | 506.243 | 488.233 | 489.216 | 253.622 | 4 |
| 10 | 86.097 | 1031.560 | 1013.549 | 1014.533 | 516.280 | L | 375.203 | 357.192 | 358.176 | 188.067 | 3 |
| 11 | 30.034 | 1088.581 | 1070.571 | 1071.554 | 544.791 | G | 262.119 | 244.108 | 245.092 | 131.559 | 2 |
| 12 | 159.092 | | | | | W | 205.096 | 187.087 | 188.067 | 103.049 | 1 |



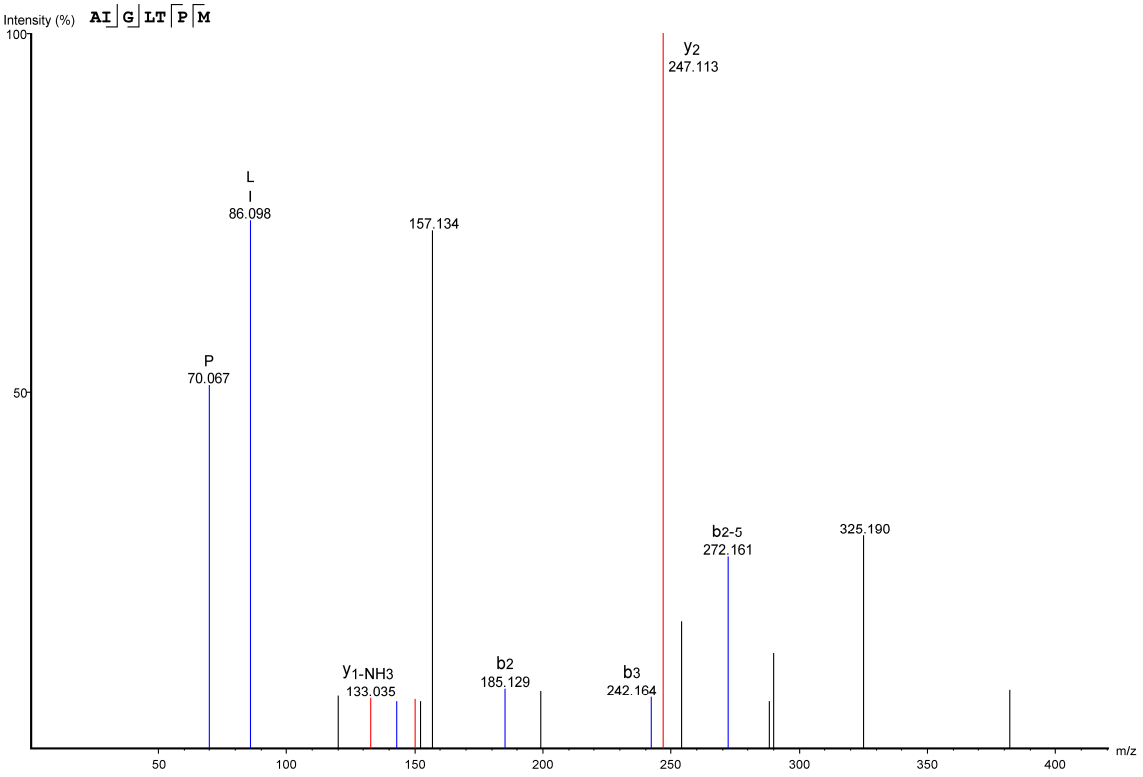
136–145, AIGLTPMLGW



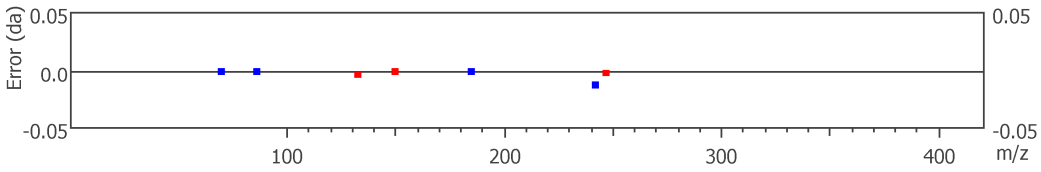

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 44.050 | 72.081 | 54.034 | 55.018 | 36.522 | A | | | | | 10 |
| 2 | 86.097 | 185.129 | 167.118 | 168.102 | 93.064 | I | 987.533 | 969.523 | 970.506 | 494.267 | 9 |
| 3 | 30.034 | 242.148 | 224.140 | 225.123 | 121.575 | G | 874.449 | 856.439 | 857.422 | 437.725 | 8 |
| 4 | 86.097 | 355.234 | 337.224 | 338.208 | 178.117 | L | 817.428 | 799.417 | 800.401 | 409.214 | 7 |
| 5 | 74.061 | 456.280 | 438.276 | 439.255 | 228.641 | T | 704.340 | 686.333 | 687.317 | 352.672 | 6 |
| 6 | 70.066 | 553.335 | 535.324 | 536.308 | 277.167 | P | 603.293 | 585.285 | 586.269 | 302.148 | 5 |
| 7 | 104.053 | 684.365 | 666.367 | 667.348 | 342.688 | M | 506.243 | 488.233 | 489.216 | 253.622 | 4 |
| 8 | 86.097 | 797.459 | 779.449 | 780.432 | 399.201 | L | 375.199 | 357.192 | 358.176 | 188.071 | 3 |
| 9 | 30.034 | 854.481 | 836.470 | 837.454 | 427.740 | G | 262.121 | 244.108 | 245.135 | 131.559 | 2 |
| 10 | 159.092 | | | | | W | 205.097 | 187.087 | 188.071 | 103.049 | 1 |



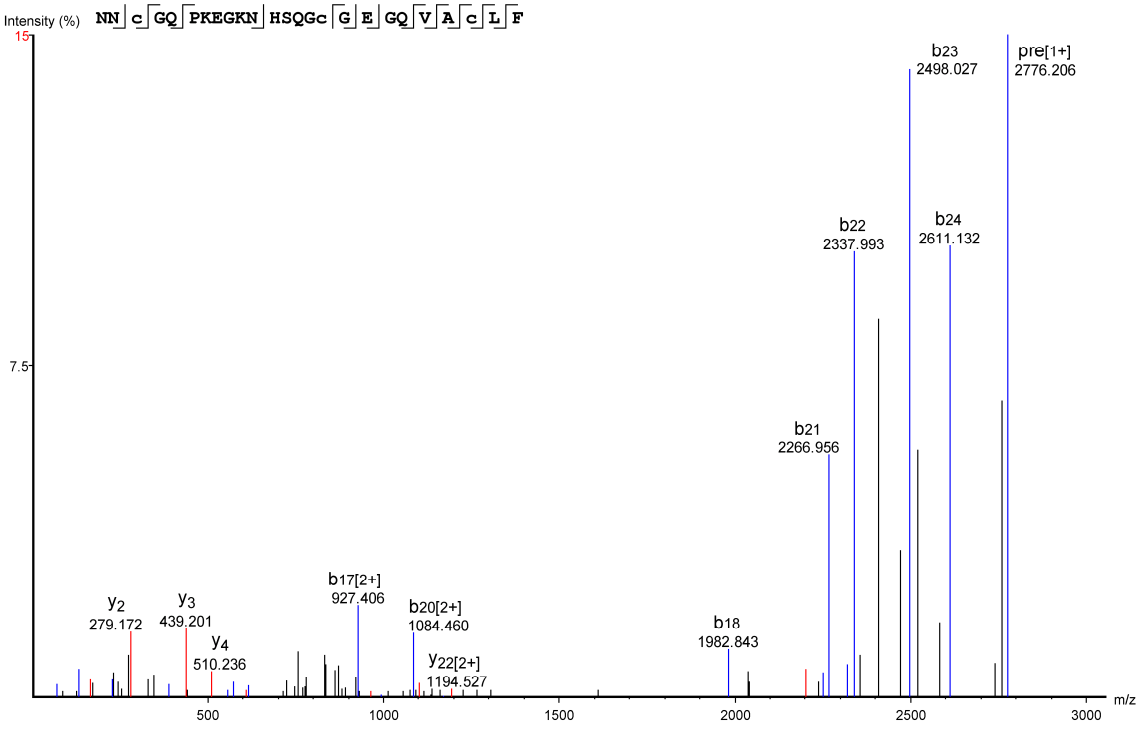
136–142, AIGLTPM



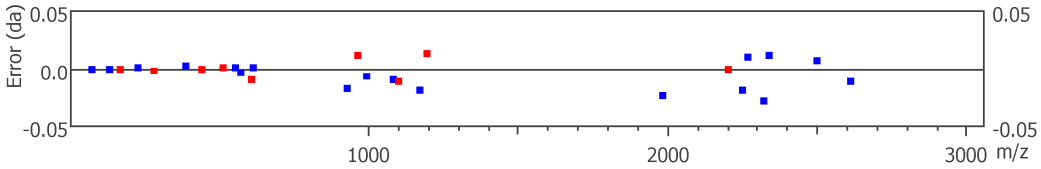

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 44.050 | 72.045 | 54.034 | 55.018 | 36.522 | A | | | | | 7 |
| 2 | 86.098 | 185.129 | 167.118 | 168.102 | 93.064 | I | 631.348 | 613.338 | 614.321 | 316.174 | 6 |
| 3 | 30.034 | 242.164 | 224.140 | 225.123 | 121.575 | G | 518.264 | 500.254 | 501.237 | 259.632 | 5 |
| 4 | 86.098 | 355.234 | 337.224 | 338.208 | 178.117 | L | 461.243 | 443.232 | 444.216 | 231.121 | 4 |
| 5 | 74.061 | 456.282 | 438.272 | 439.255 | 228.641 | T | 348.159 | 330.148 | 331.132 | 174.579 | 3 |
| 6 | 70.067 | 553.335 | 535.324 | 536.308 | 277.167 | P | 247.113 | 229.101 | 230.084 | 124.056 | 2 |
| 7 | 104.053 | | | | | M | 150.059 | 132.048 | 133.035 | 75.529 | 1 |



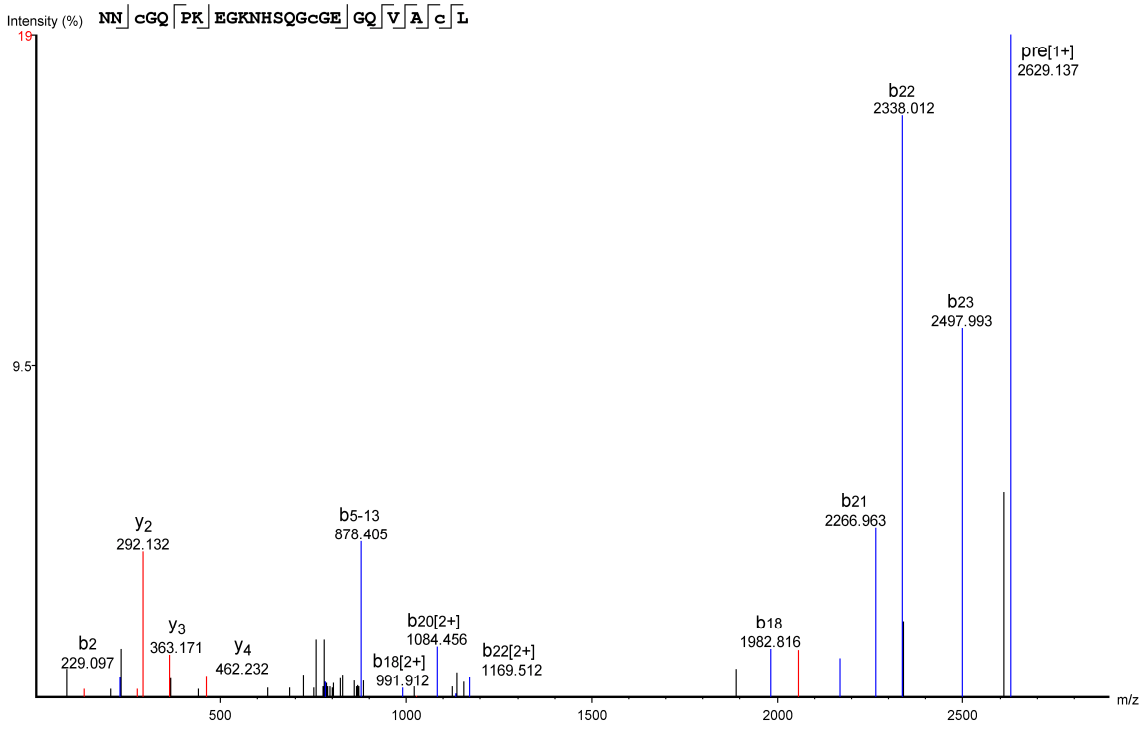
146–170, NNcGQPKEGKNHSQGcGEGQVAcLF



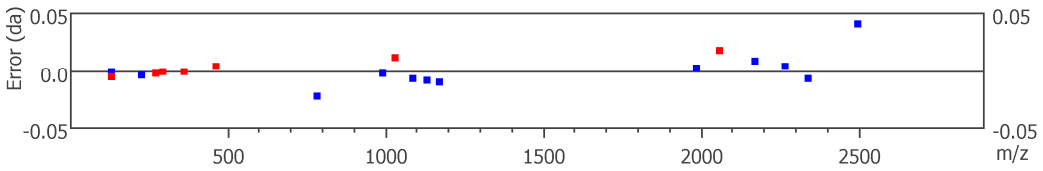
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 87.056 | 115.051 | 97.040 | 98.024 | 58.025 | N | | | | | 25 |
| 2 | 87.056 | 229.092 | 211.083 | 212.067 | 115.047 | N | 2662.156 | 2644.145 | 2645.128 | 1331.578 | 24 |
| 3 | 133.042 | 389.120 | 371.114 | 372.097 | 195.062 | C(+57.02) | 2548.113 | 2530.102 | 2531.085 | 1274.556 | 23 |
| 4 | 30.034 | 446.146 | 428.135 | 429.119 | 223.573 | G | 2388.082 | 2370.071 | 2371.055 | 1194.527 | 22 |
| 5 | 101.071 | 574.208 | 556.194 | 557.175 | 287.602 | Q | 2331.060 | 2313.050 | 2314.033 | 1166.030 | 21 |
| 6 | 70.066 | 671.257 | 653.247 | 654.230 | 336.129 | P | 2203.002 | 2184.991 | 2185.975 | 1102.012 | 20 |
| 7 | 101.108 | 799.352 | 781.341 | 782.325 | 400.176 | K | 2105.949 | 2087.938 | 2088.922 | 1053.474 | 19 |
| 8 | 102.055 | 928.395 | 910.384 | 911.368 | 464.697 | E | 1977.854 | 1959.844 | 1960.827 | 989.427 | 18 |
| 9 | 30.034 | 985.416 | 967.406 | 968.389 | 493.208 | G | 1848.812 | 1830.801 | 1831.785 | 924.906 | 17 |
| 10 | 101.108 | 1113.511 | 1095.501 | 1096.484 | 557.256 | K | 1791.790 | 1773.780 | 1774.763 | 896.395 | 16 |
| 11 | 87.056 | 1227.554 | 1209.543 | 1210.527 | 614.274 | N | 1663.695 | 1645.685 | 1646.668 | 832.348 | 15 |
| 12 | 110.072 | 1364.613 | 1346.602 | 1347.586 | 682.806 | H | 1549.652 | 1531.642 | 1532.625 | 775.326 | 14 |
| 13 | 60.045 | 1451.645 | 1433.635 | 1434.618 | 726.323 | S | 1412.593 | 1394.583 | 1395.566 | 706.797 | 13 |
| 14 | 101.071 | 1579.703 | 1561.693 | 1562.677 | 790.352 | Q | 1325.561 | 1307.551 | 1308.534 | 663.281 | 12 |
| 15 | 30.034 | 1636.725 | 1618.714 | 1619.698 | 818.862 | G | 1197.503 | 1179.492 | 1180.476 | 599.251 | 11 |
| 16 | 133.043 | 1796.756 | 1778.745 | 1779.729 | 898.878 | C(+57.02) | 1140.481 | 1122.471 | 1123.454 | 570.741 | 10 |
| 17 | 30.034 | 1853.777 | 1835.767 | 1836.750 | 927.406 | G | 980.451 | 962.440 | 963.410 | 490.725 | 9 |
| 18 | 102.055 | 1982.843 | 1964.809 | 1965.793 | 991.916 | E | 923.429 | 905.419 | 906.402 | 462.215 | 8 |
| 19 | 30.034 | 2039.841 | 2021.831 | 2022.814 | 1020.421 | G | 794.386 | 776.376 | 777.359 | 397.693 | 7 |
| 20 | 101.071 | 2167.900 | 2149.889 | 2150.873 | 1084.460 | Q | 737.365 | 719.354 | 720.338 | 369.183 | 6 |
| 21 | 72.082 | 2266.956 | 2248.958 | 2249.960 | 1133.984 | V | 609.317 | 591.296 | 592.279 | 305.153 | 5 |
| 22 | 44.050 | 2337.993 | 2319.995 | 2321.007 | 1169.522 | A | 510.236 | 492.227 | 493.211 | 255.619 | 4 |
| 23 | 133.043 | 2498.027 | 2480.025 | 2481.009 | 1249.518 | C(+57.02) | 439.201 | 421.190 | 422.174 | 220.100 | 3 |
| 24 | 86.097 | 2611.132 | 2593.109 | 2594.093 | 1306.060 | L | 279.172 | 261.160 | 262.143 | 140.085 | 2 |
| 25 | 120.081 | | | | | F | 166.086 | 148.076 | 149.059 | 83.543 | 1 |



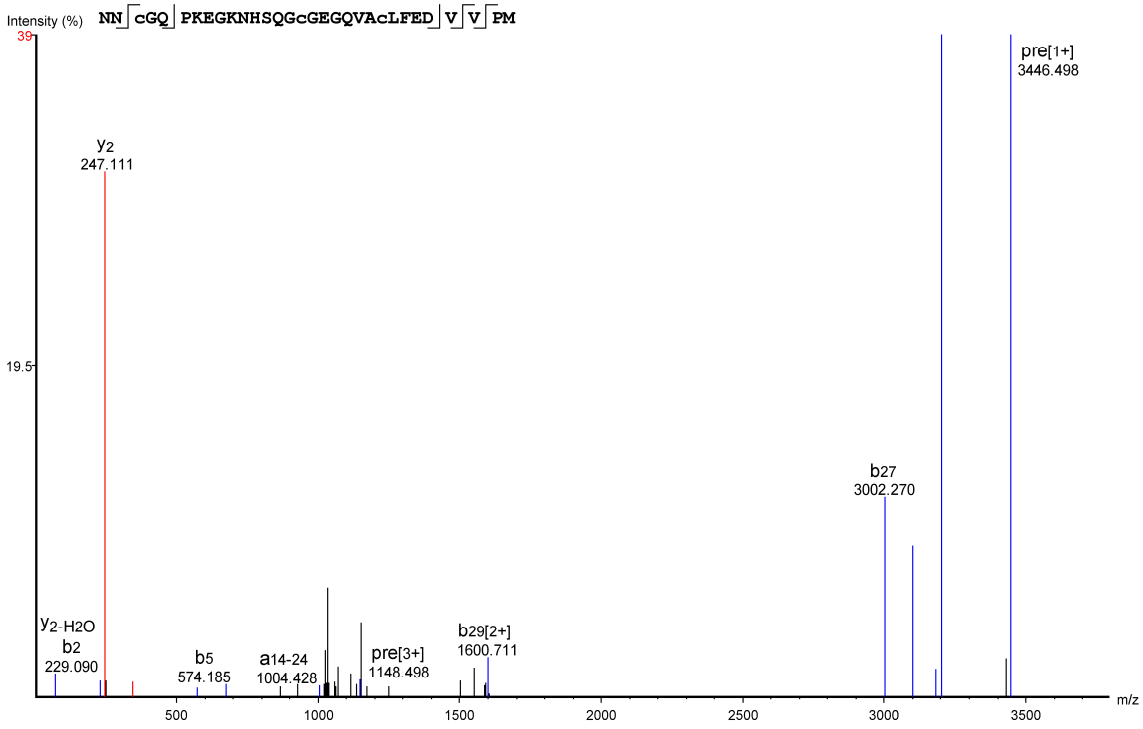
146–169, NNcGQPKEGKNHSQGcGEGQVAcL



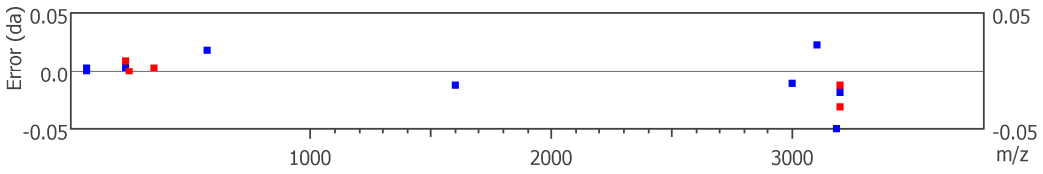
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 87.056 | 115.051 | 97.040 | 98.024 | 58.025 | N | | | | | 24 |
| 2 | 87.056 | 229.097 | 211.083 | 212.067 | 115.047 | N | 2515.087 | 2497.077 | 2498.060 | 1258.044 | 23 |
| 3 | 133.042 | 389.124 | 371.114 | 372.097 | 195.062 | C(+57.02) | 2401.044 | 2383.034 | 2384.017 | 1201.022 | 22 |
| 4 | 30.034 | 446.146 | 428.135 | 429.119 | 223.573 | G | 2241.013 | 2223.003 | 2223.986 | 1121.007 | 21 |
| 5 | 101.071 | 574.204 | 556.194 | 557.177 | 287.602 | Q | 2183.992 | 2165.981 | 2166.965 | 1092.496 | 20 |
| 6 | 70.066 | 671.257 | 653.247 | 654.230 | 336.129 | P | 2055.915 | 2037.923 | 2038.906 | 1028.454 | 19 |
| 7 | 101.108 | 799.352 | 781.364 | 782.325 | 400.176 | K | 1958.881 | 1940.870 | 1941.854 | 979.940 | 18 |
| 8 | 102.055 | 928.395 | 910.384 | 911.368 | 464.697 | E | 1830.786 | 1812.775 | 1813.759 | 915.893 | 17 |
| 9 | 30.034 | 985.416 | 967.406 | 968.389 | 493.208 | G | 1701.743 | 1683.733 | 1684.716 | 851.372 | 16 |
| 10 | 101.108 | 1113.511 | 1095.501 | 1096.484 | 557.256 | K | 1644.722 | 1626.711 | 1627.695 | 822.861 | 15 |
| 11 | 87.056 | 1227.554 | 1209.543 | 1210.527 | 614.277 | N | 1516.627 | 1498.616 | 1499.600 | 758.813 | 14 |
| 12 | 110.072 | 1364.613 | 1346.602 | 1347.586 | 682.806 | H | 1402.584 | 1384.573 | 1385.557 | 701.792 | 13 |
| 13 | 60.045 | 1451.645 | 1433.635 | 1434.618 | 726.323 | S | 1265.525 | 1247.514 | 1248.498 | 633.262 | 12 |
| 14 | 101.071 | 1579.703 | 1561.693 | 1562.677 | 790.352 | Q | 1178.493 | 1160.482 | 1161.466 | 589.746 | 11 |
| 15 | 30.034 | 1636.725 | 1618.714 | 1619.698 | 818.862 | G | 1050.434 | 1032.424 | 1033.407 | 525.717 | 10 |
| 16 | 133.043 | 1796.756 | 1778.745 | 1779.729 | 898.878 | C(+57.02) | 993.413 | 975.402 | 976.386 | 497.206 | 9 |
| 17 | 30.034 | 1853.777 | 1835.767 | 1836.750 | 927.389 | G | 833.382 | 815.372 | 816.355 | 417.191 | 8 |
| 18 | 102.055 | 1982.816 | 1964.809 | 1965.793 | 991.912 | E | 776.361 | 758.350 | 759.334 | 388.680 | 7 |
| 19 | 30.034 | 2039.841 | 2021.831 | 2022.814 | 1020.421 | G | 647.318 | 629.308 | 630.291 | 324.159 | 6 |
| 20 | 101.071 | 2167.889 | 2149.889 | 2150.873 | 1084.456 | Q | 590.297 | 572.286 | 573.270 | 295.648 | 5 |
| 21 | 72.081 | 2266.963 | 2248.958 | 2249.941 | 1133.992 | V | 462.232 | 444.228 | 445.211 | 231.619 | 4 |
| 22 | 44.050 | 2338.012 | 2319.995 | 2320.978 | 1169.512 | A | 363.171 | 345.159 | 346.143 | 182.085 | 3 |
| 23 | 133.043 | 2497.993 | 2480.025 | 2481.009 | 1249.518 | C(+57.02) | 292.132 | 274.122 | 275.108 | 146.566 | 2 |
| 24 | 86.097 | | | | | L | 132.107 | 114.091 | 115.075 | 66.551 | 1 |



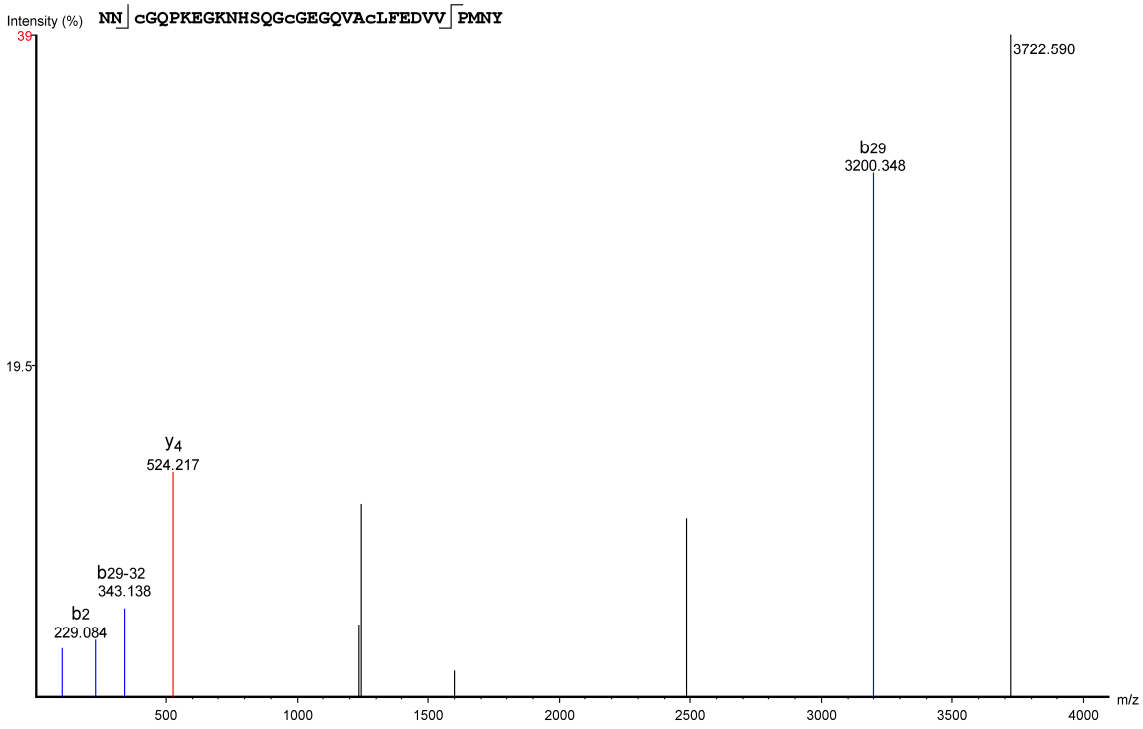
146–176, NNcGQPKEGKNHSQGcGEGQVAcLFEDVVPM



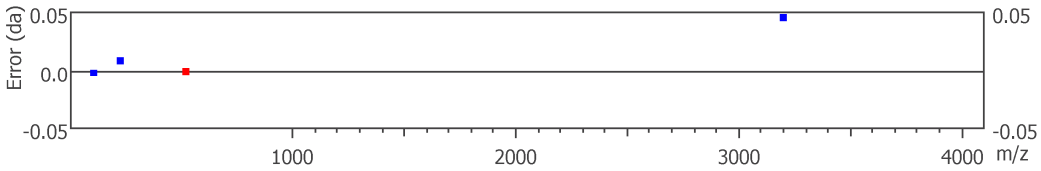
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 87.056 | 115.051 | 97.040 | 98.024 | 58.025 | N | | | | | 31 |
| 2 | 87.056 | 229.090 | 211.083 | 212.067 | 115.047 | N | 3332.455 | 3314.445 | 3315.428 | 1666.728 | 30 |
| 3 | 133.043 | 389.124 | 371.114 | 372.097 | 195.062 | C(+57.02) | 3218.412 | 3200.414 | 3201.417 | 1609.706 | 29 |
| 4 | 30.034 | 446.146 | 428.135 | 429.119 | 223.573 | G | 3058.382 | 3040.371 | 3041.354 | 1529.691 | 28 |
| 5 | 101.071 | 574.185 | 556.194 | 557.177 | 287.602 | Q | 3001.360 | 2983.350 | 2984.333 | 1501.180 | 27 |
| 6 | 70.065 | 671.257 | 653.247 | 654.230 | 336.129 | P | 2873.302 | 2855.291 | 2856.274 | 1437.151 | 26 |
| 7 | 101.108 | 799.352 | 781.341 | 782.325 | 400.176 | K | 2776.249 | 2758.238 | 2759.222 | 1388.624 | 25 |
| 8 | 102.055 | 928.395 | 910.384 | 911.368 | 464.697 | E | 2648.154 | 2630.143 | 2631.127 | 1324.577 | 24 |
| 9 | 30.034 | 985.416 | 967.406 | 968.389 | 493.208 | G | 2519.111 | 2501.101 | 2502.084 | 1260.056 | 23 |
| 10 | 101.108 | 1113.511 | 1095.501 | 1096.484 | 557.256 | K | 2462.090 | 2444.079 | 2445.062 | 1231.545 | 22 |
| 11 | 87.056 | 1227.554 | 1209.543 | 1210.527 | 614.277 | N | 2333.995 | 2315.984 | 2316.968 | 1167.497 | 21 |
| 12 | 110.072 | 1364.613 | 1346.602 | 1347.586 | 682.806 | H | 2219.952 | 2201.941 | 2202.925 | 1110.476 | 20 |
| 13 | 60.045 | 1451.645 | 1433.635 | 1434.618 | 726.323 | S | 2082.893 | 2064.882 | 2065.866 | 1041.946 | 19 |
| 14 | 101.071 | 1579.703 | 1561.693 | 1562.677 | 790.352 | Q | 1995.861 | 1977.850 | 1978.834 | 998.430 | 18 |
| 15 | 30.034 | 1636.725 | 1618.714 | 1619.698 | 818.862 | G | 1867.802 | 1849.792 | 1850.775 | 934.401 | 17 |
| 16 | 133.043 | 1796.756 | 1778.745 | 1779.729 | 898.878 | C(+57.02) | 1810.781 | 1792.770 | 1793.754 | 905.890 | 16 |
| 17 | 30.034 | 1853.777 | 1835.767 | 1836.750 | 927.389 | G | 1650.750 | 1632.740 | 1633.723 | 825.875 | 15 |
| 18 | 102.055 | 1982.820 | 1964.809 | 1965.793 | 991.910 | E | 1593.729 | 1575.718 | 1576.702 | 797.364 | 14 |
| 19 | 30.034 | 2039.841 | 2021.831 | 2022.814 | 1020.421 | G | 1464.686 | 1446.676 | 1447.659 | 732.843 | 13 |
| 20 | 101.071 | 2167.900 | 2149.889 | 2150.873 | 1084.450 | Q | 1407.665 | 1389.654 | 1390.638 | 704.332 | 12 |
| 21 | 72.078 | 2266.968 | 2248.958 | 2249.941 | 1133.984 | V | 1279.606 | 1261.596 | 1262.579 | 640.303 | 11 |
| 22 | 44.050 | 2338.005 | 2319.995 | 2320.978 | 1169.503 | A | 1180.538 | 1162.527 | 1163.511 | 590.769 | 10 |
| 23 | 133.043 | 2498.036 | 2480.025 | 2481.009 | 1249.518 | C(+57.02) | 1109.500 | 1091.490 | 1092.474 | 555.250 | 9 |
| 24 | 86.097 | 2611.120 | 2593.109 | 2594.093 | 1306.060 | L | 949.470 | 931.459 | 932.443 | 475.235 | 8 |
| 25 | 120.081 | 2758.188 | 2740.178 | 2741.161 | 1379.594 | F | 836.386 | 818.375 | 819.359 | 418.693 | 7 |
| 26 | 102.055 | 2887.231 | 2869.220 | 2870.204 | 1444.115 | E | 689.317 | 671.307 | 672.290 | 345.159 | 6 |
| 27 | 88.040 | 3002.270 | 2984.247 | 2985.231 | 1501.629 | D | 560.275 | 542.264 | 543.248 | 280.637 | 5 |
| 28 | 72.081 | 3101.303 | 3083.316 | 3084.299 | 1551.163 | V | 445.248 | 427.237 | 428.221 | 223.124 | 4 |
| 29 | 72.081 | 3200.414 | 3182.434 | 3183.368 | 1600.711 | V | 346.176 | 328.169 | 329.153 | 173.590 | 3 |
| 30 | 70.066 | 3297.448 | 3279.437 | 3280.420 | 1649.224 | P | 247.111 | 229.090 | 230.084 | 124.056 | 2 |
| 31 | 104.053 | | | | | M | 150.058 | 132.048 | 133.031 | 75.529 | 1 |



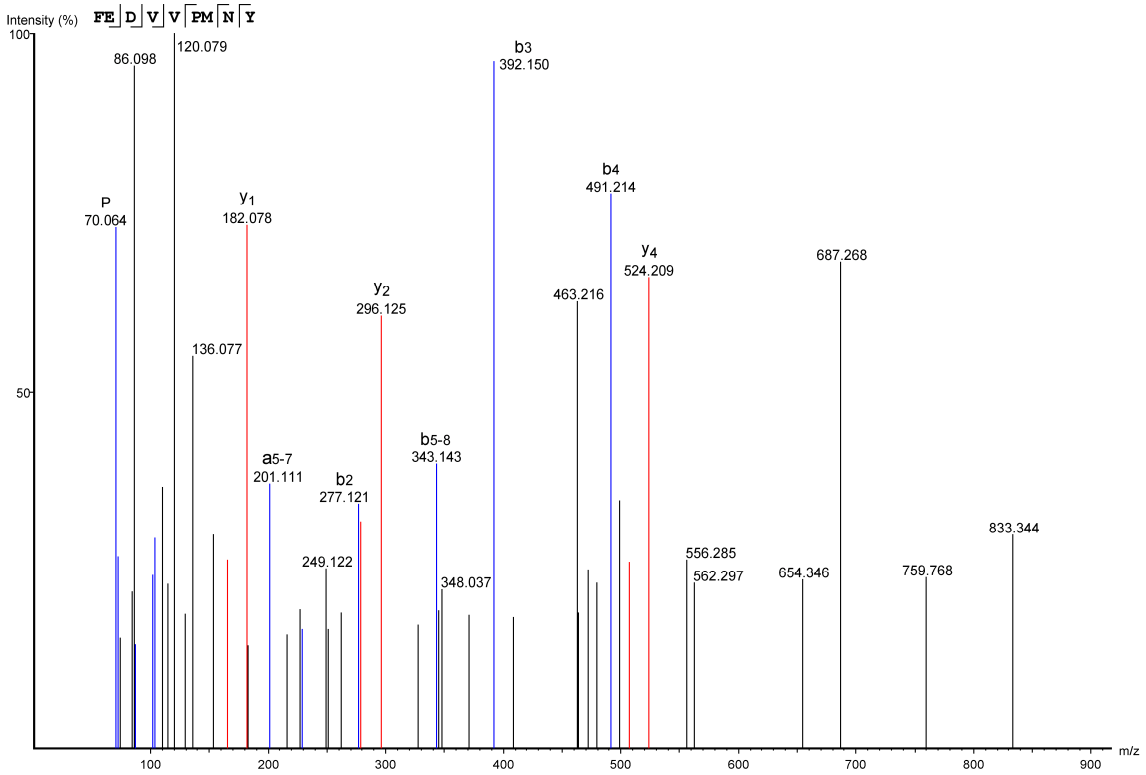
146–178, NNcGQPKEGKNHSQGcGEGQVAcLFEDVVPMNY



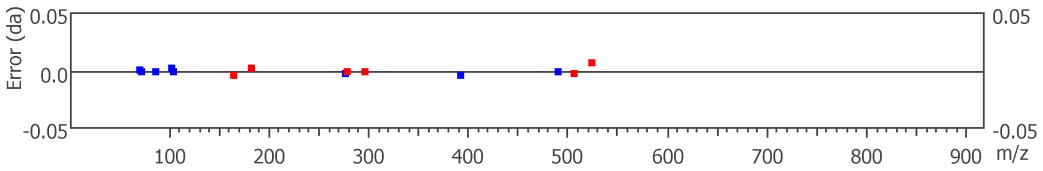
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 87.056 | 115.051 | 97.040 | 98.024 | 58.025 | N | | | | | 33 |
| 2 | 87.056 | 229.084 | 211.083 | 212.067 | 115.047 | N | 3609.561 | 3591.551 | 3592.534 | 1805.281 | 32 |
| 3 | 133.043 | 389.124 | 371.114 | 372.097 | 195.062 | C(+57.02) | 3495.518 | 3477.508 | 3478.491 | 1748.259 | 31 |
| 4 | 30.034 | 446.146 | 428.135 | 429.119 | 223.573 | G | 3335.488 | 3317.477 | 3318.461 | 1668.244 | 30 |
| 5 | 101.071 | 574.204 | 556.194 | 557.177 | 287.602 | Q | 3278.466 | 3260.456 | 3261.439 | 1639.733 | 29 |
| 6 | 70.066 | 671.257 | 653.247 | 654.230 | 336.129 | P | 3150.408 | 3132.397 | 3133.381 | 1575.704 | 28 |
| 7 | 101.108 | 799.352 | 781.341 | 782.325 | 400.176 | K | 3053.355 | 3035.344 | 3036.328 | 1527.177 | 27 |
| 8 | 102.055 | 928.395 | 910.384 | 911.368 | 464.697 | E | 2925.260 | 2907.250 | 2908.233 | 1463.130 | 26 |
| 9 | 30.034 | 985.416 | 967.406 | 968.389 | 493.208 | G | 2796.217 | 2778.207 | 2779.190 | 1398.609 | 25 |
| 10 | 101.108 | 1113.511 | 1095.501 | 1096.484 | 557.256 | K | 2739.196 | 2721.186 | 2722.169 | 1370.098 | 24 |
| 11 | 87.056 | 1227.554 | 1209.543 | 1210.527 | 614.277 | N | 2611.101 | 2593.091 | 2594.074 | 1306.051 | 23 |
| 12 | 110.072 | 1364.613 | 1346.602 | 1347.586 | 682.806 | H | 2497.058 | 2479.048 | 2480.031 | 1249.029 | 22 |
| 13 | 60.045 | 1451.645 | 1433.635 | 1434.618 | 726.323 | S | 2359.999 | 2341.989 | 2342.972 | 1180.500 | 21 |
| 14 | 101.071 | 1579.703 | 1561.693 | 1562.677 | 790.352 | Q | 2272.967 | 2254.957 | 2255.940 | 1136.984 | 20 |
| 15 | 30.034 | 1636.725 | 1618.714 | 1619.698 | 818.862 | G | 2144.908 | 2126.898 | 2127.881 | 1072.954 | 19 |
| 16 | 133.043 | 1796.756 | 1778.745 | 1779.729 | 898.878 | C(+57.02) | 2087.887 | 2069.876 | 2070.860 | 1044.443 | 18 |
| 17 | 30.034 | 1853.777 | 1835.767 | 1836.750 | 927.389 | G | 1927.856 | 1909.846 | 1910.829 | 964.428 | 17 |
| 18 | 102.055 | 1982.820 | 1964.809 | 1965.793 | 991.910 | E | 1870.835 | 1852.824 | 1853.808 | 935.917 | 16 |
| 19 | 30.034 | 2039.841 | 2021.831 | 2022.814 | 1020.421 | G | 1741.792 | 1723.782 | 1724.765 | 871.396 | 15 |
| 20 | 101.071 | 2167.900 | 2149.889 | 2150.873 | 1084.450 | Q | 1684.771 | 1666.760 | 1667.744 | 842.885 | 14 |
| 21 | 72.081 | 2266.968 | 2248.958 | 2249.941 | 1133.984 | V | 1556.712 | 1538.702 | 1539.685 | 778.856 | 13 |
| 22 | 44.050 | 2338.005 | 2319.995 | 2320.978 | 1169.503 | A | 1457.644 | 1439.633 | 1440.617 | 729.322 | 12 |
| 23 | 133.043 | 2498.036 | 2480.025 | 2481.009 | 1249.518 | C(+57.02) | 1386.607 | 1368.596 | 1369.580 | 693.803 | 11 |
| 24 | 86.097 | 2611.120 | 2593.109 | 2594.093 | 1306.060 | L | 1226.576 | 1208.566 | 1209.549 | 613.788 | 10 |
| 25 | 120.081 | 2758.188 | 2740.178 | 2741.161 | 1379.594 | F | 1113.492 | 1095.482 | 1096.465 | 557.246 | 9 |
| 26 | 102.055 | 2887.231 | 2869.220 | 2870.204 | 1444.115 | E | 966.424 | 948.413 | 949.397 | 483.712 | 8 |
| 27 | 88.040 | 3002.258 | 2984.247 | 2985.231 | 1501.629 | D | 837.381 | 819.371 | 820.354 | 419.191 | 7 |
| 28 | 72.081 | 3101.326 | 3083.316 | 3084.299 | 1551.163 | V | 722.354 | 704.344 | 705.327 | 361.677 | 6 |
| 29 | 72.081 | 3200.348 | 3182.384 | 3183.368 | 1600.697 | V | 623.286 | 605.275 | 606.259 | 312.143 | 5 |
| 30 | 70.066 | 3297.448 | 3279.437 | 3280.420 | 1649.224 | P | 524.217 | 506.207 | 507.190 | 262.609 | 4 |
| 31 | 104.056 | 3428.488 | 3410.478 | 3411.461 | 1714.744 | M | 427.165 | 409.154 | 410.138 | 214.082 | 3 |
| 32 | 87.056 | 3542.531 | 3524.521 | 3525.504 | 1771.766 | N | 296.124 | 278.114 | 279.097 | 148.562 | 2 |
| 33 | 136.076 | | | | | Y | 182.081 | 164.071 | 165.054 | 91.541 | 1 |



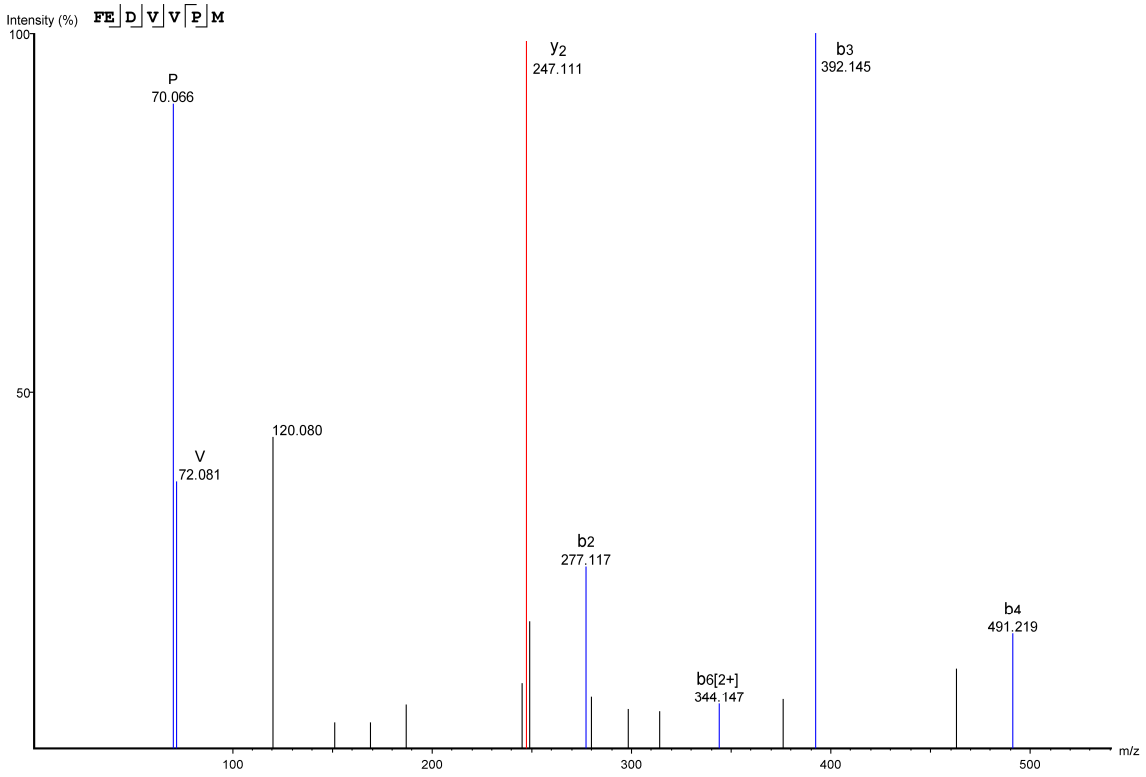
170–178, FEDVVPMNY



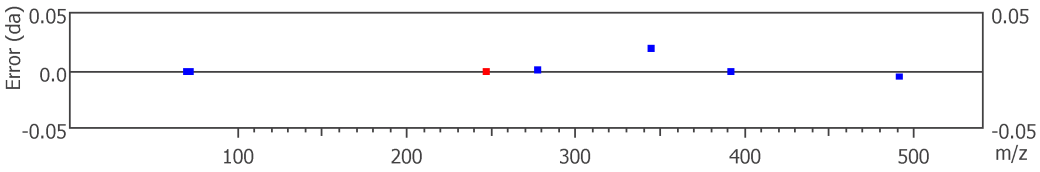

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 120.081 | 148.076 | 130.066 | 131.049 | 74.538 | F | | | | | 9 |
| 2 | 102.051 | 277.121 | 259.108 | 260.092 | 139.059 | E | 966.424 | 948.413 | 949.397 | 483.712 | 8 |
| 3 | 88.040 | 392.150 | 374.135 | 375.119 | 196.573 | D | 837.381 | 819.371 | 820.354 | 419.191 | 7 |
| 4 | 72.080 | 491.214 | 473.204 | 474.187 | 246.107 | V | 722.354 | 704.344 | 705.327 | 361.677 | 6 |
| 5 | 72.081 | 590.283 | 572.272 | 573.256 | 295.641 | V | 623.286 | 605.275 | 606.259 | 312.143 | 5 |
| 6 | 70.064 | 687.335 | 669.325 | 670.308 | 344.168 | P | 524.209 | 506.207 | 507.193 | 262.609 | 4 |
| 7 | 104.054 | 818.376 | 800.365 | 801.349 | 409.688 | M | 427.165 | 409.154 | 410.138 | 214.082 | 3 |
| 8 | 87.055 | 932.419 | 914.408 | 915.392 | 466.709 | N | 296.125 | 278.114 | 279.097 | 148.562 | 2 |
| 9 | 136.076 | | | | | Y | 182.078 | 164.071 | 165.058 | 91.541 | 1 |



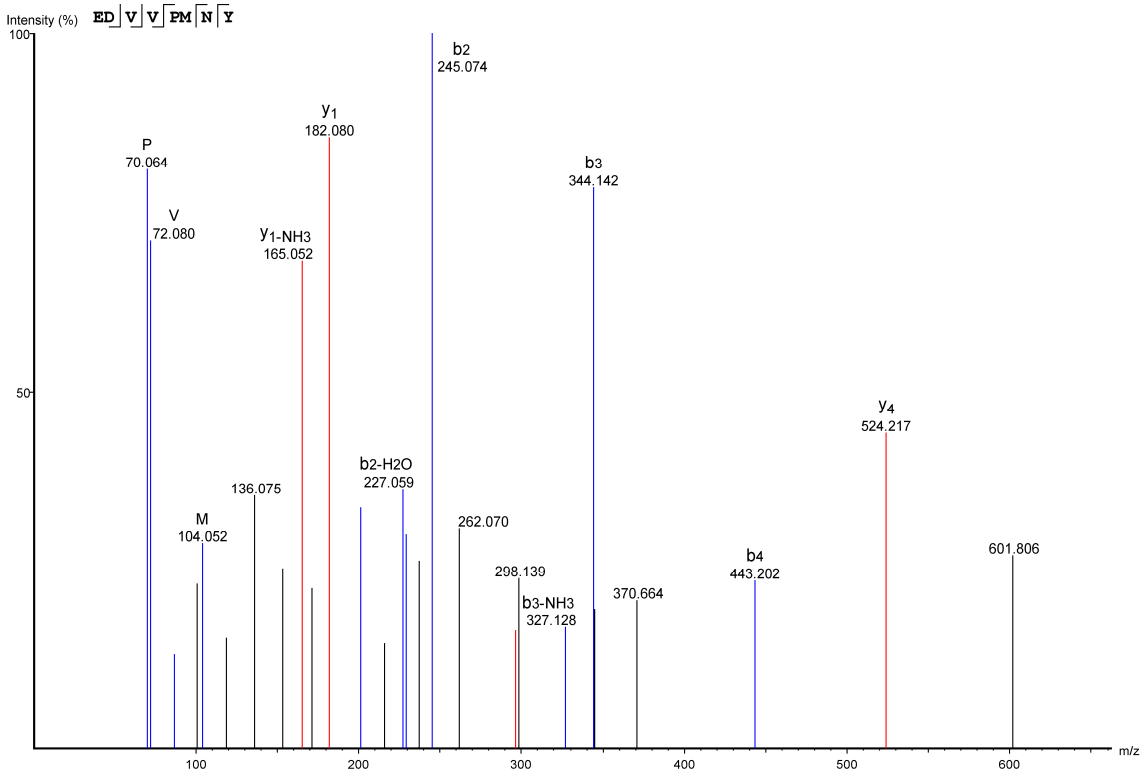
170–176, FEDVVPM



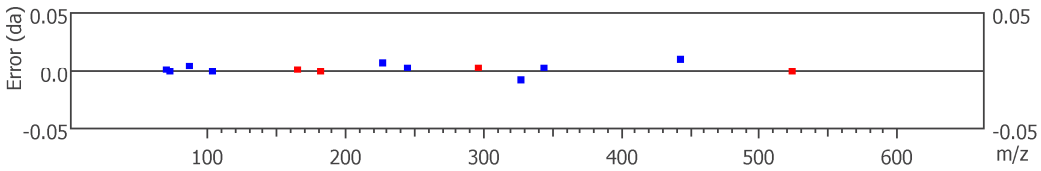

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 120.081 | 148.076 | 130.066 | 131.049 | 74.538 | F | | | | | 7 |
| 2 | 102.055 | 277.117 | 259.108 | 260.092 | 139.059 | E | 689.317 | 671.307 | 672.290 | 345.159 | 6 |
| 3 | 88.040 | 392.145 | 374.135 | 375.119 | 196.573 | D | 560.275 | 542.264 | 543.248 | 280.637 | 5 |
| 4 | 72.081 | 491.219 | 473.204 | 474.187 | 246.107 | V | 445.248 | 427.237 | 428.221 | 223.124 | 4 |
| 5 | 72.081 | 590.283 | 572.272 | 573.256 | 295.641 | V | 346.180 | 328.169 | 329.153 | 173.590 | 3 |
| 6 | 70.066 | 687.335 | 669.325 | 670.308 | 344.147 | P | 247.111 | 229.101 | 230.084 | 124.056 | 2 |
| 7 | 104.053 | | | | | M | 150.058 | 132.048 | 133.031 | 75.529 | 1 |



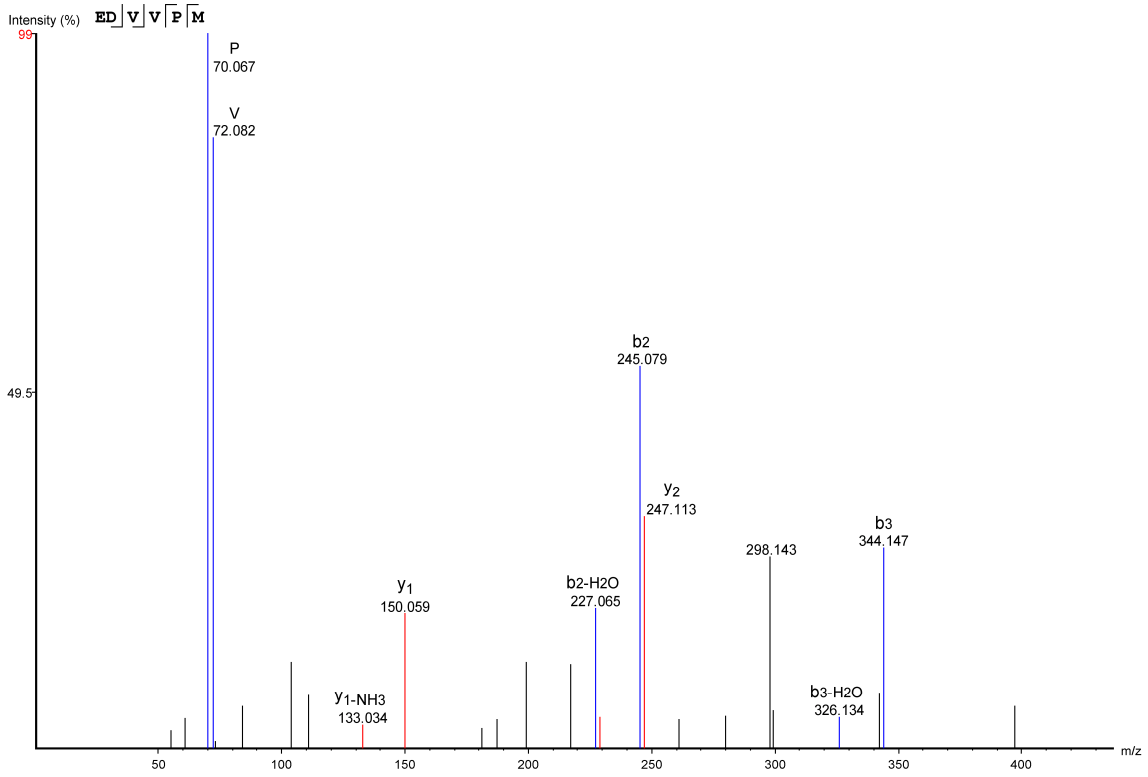
171–178, EDVVPMNY



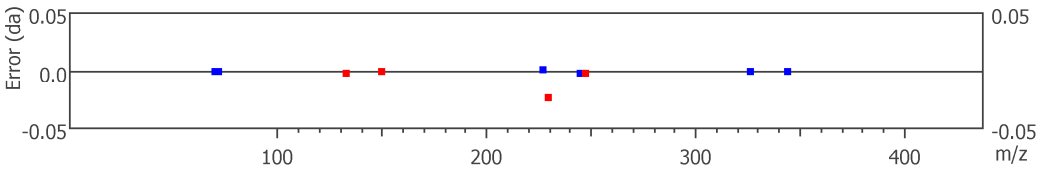

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 102.055 | 130.050 | 112.040 | 113.023 | 65.525 | E | | | | | 8 |
| 2 | 88.040 | 245.074 | 227.059 | 228.050 | 123.039 | D | 837.381 | 819.371 | 820.354 | 419.191 | 7 |
| 3 | 72.080 | 344.142 | 326.135 | 327.128 | 172.573 | V | 722.354 | 704.344 | 705.327 | 361.677 | 6 |
| 4 | 72.081 | 443.202 | 425.204 | 426.187 | 222.107 | V | 623.286 | 605.275 | 606.259 | 312.143 | 5 |
| 5 | 70.064 | 540.267 | 522.256 | 523.240 | 270.633 | P | 524.217 | 506.207 | 507.190 | 262.609 | 4 |
| 6 | 104.052 | 671.307 | 653.297 | 654.280 | 336.154 | M | 427.165 | 409.154 | 410.138 | 214.082 | 3 |
| 7 | 87.050 | 785.350 | 767.340 | 768.323 | 393.175 | N | 296.121 | 278.114 | 279.097 | 148.562 | 2 |
| 8 | 136.076 | | | | | Y | 182.080 | 164.071 | 165.052 | 91.541 | 1 |



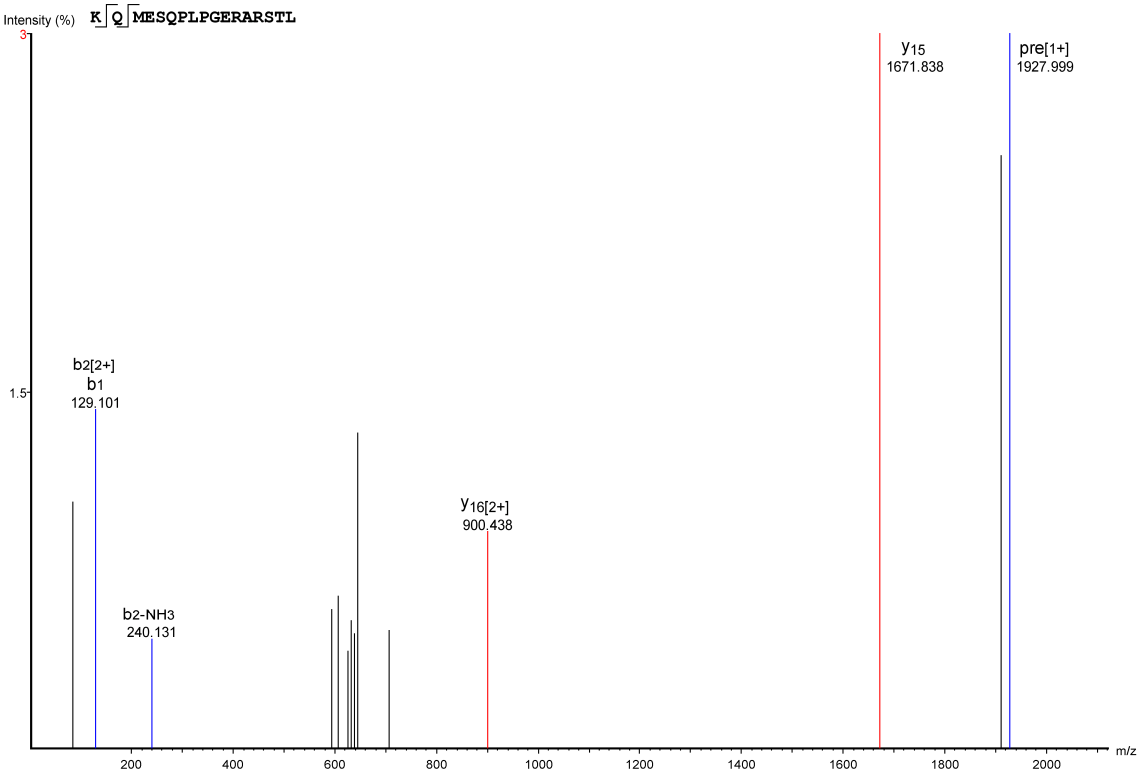
171–176, EDVVPM



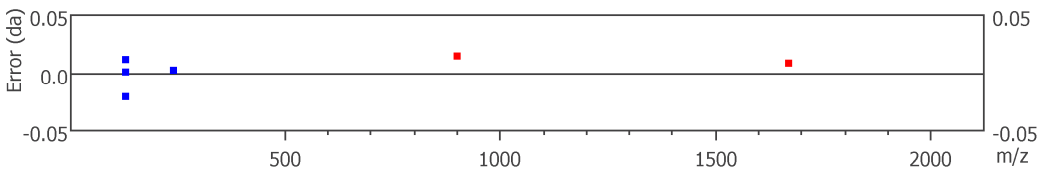

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 102.055 | 130.050 | 112.040 | 113.023 | 65.525 | E | | | | | 6 |
| 2 | 88.040 | 245.079 | 227.065 | 228.050 | 123.039 | D | 560.275 | 542.264 | 543.248 | 280.637 | 5 |
| 3 | 72.082 | 344.147 | 326.134 | 327.119 | 172.573 | V | 445.248 | 427.237 | 428.221 | 223.124 | 4 |
| 4 | 72.081 | 443.214 | 425.204 | 426.187 | 222.107 | V | 346.180 | 328.169 | 329.153 | 173.590 | 3 |
| 5 | 70.067 | 540.267 | 522.256 | 523.240 | 270.633 | P | 247.113 | 229.124 | 230.084 | 124.056 | 2 |
| 6 | 104.053 | | | | | M | 150.059 | 132.048 | 133.034 | 75.529 | 1 |



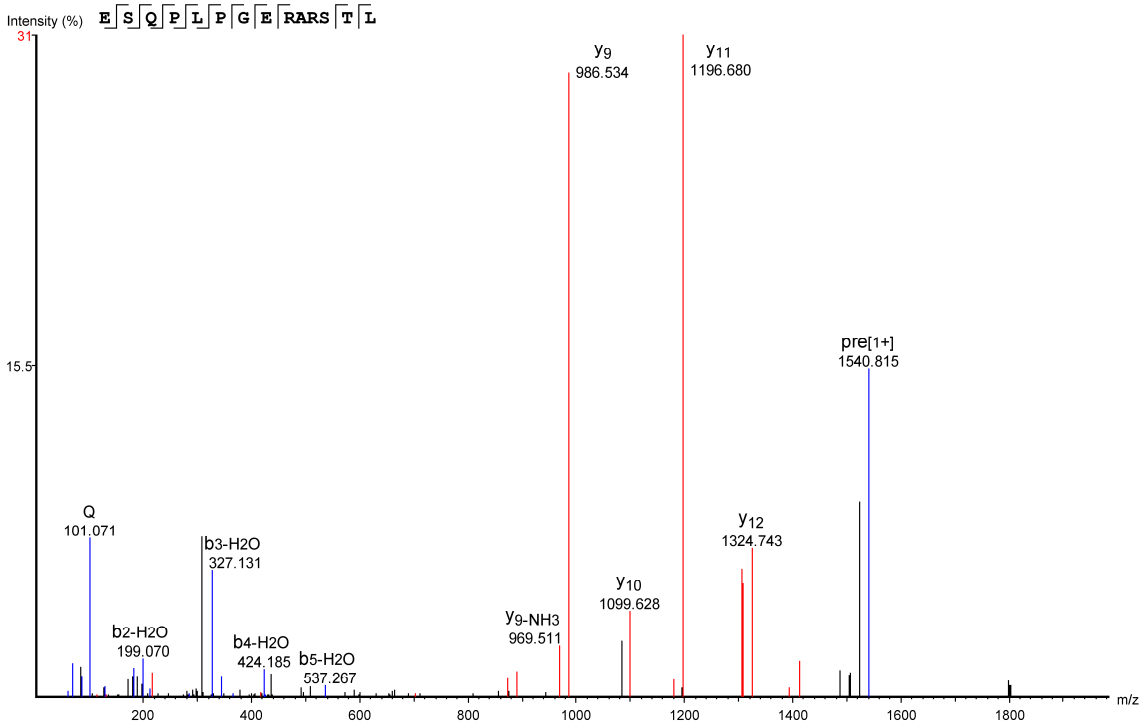
211–227, KQMESQPLPGERARSTL



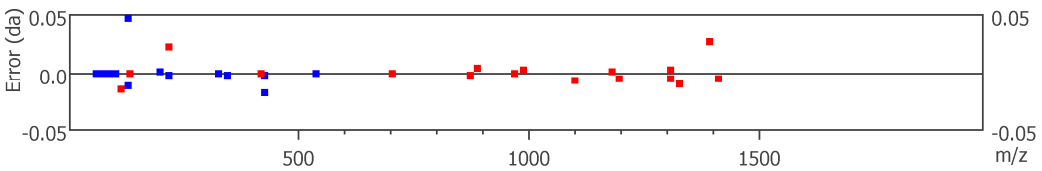

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 101.108 | 129.101 | 111.092 | 112.076 | 65.051 | K | | | | | 17 |
| 2 | 101.071 | 257.161 | 239.151 | 240.131 | 129.101 | Q | 1799.907 | 1781.896 | 1782.880 | 900.438 | 16 |
| 3 | 104.053 | 388.202 | 370.191 | 371.175 | 194.601 | M | 1671.838 | 1653.838 | 1654.821 | 836.424 | 15 |
| 4 | 102.055 | 517.244 | 499.234 | 500.217 | 259.122 | E | 1540.808 | 1522.797 | 1523.781 | 770.904 | 14 |
| 5 | 60.045 | 604.276 | 586.266 | 587.250 | 302.638 | S | 1411.765 | 1393.755 | 1394.738 | 706.383 | 13 |
| 6 | 101.071 | 732.335 | 714.324 | 715.308 | 366.668 | Q | 1324.733 | 1306.723 | 1307.706 | 662.867 | 12 |
| 7 | 70.066 | 829.388 | 811.377 | 812.361 | 415.194 | P | 1196.675 | 1178.664 | 1179.648 | 598.837 | 11 |
| 8 | 86.097 | 942.472 | 924.461 | 925.445 | 471.736 | L | 1099.622 | 1081.611 | 1082.595 | 550.311 | 10 |
| 9 | 70.066 | 1039.525 | 1021.514 | 1022.498 | 520.262 | P | 986.538 | 968.527 | 969.511 | 493.769 | 9 |
| 10 | 30.034 | 1096.546 | 1078.536 | 1079.519 | 548.773 | G | 889.485 | 871.474 | 872.458 | 445.242 | 8 |
| 11 | 102.055 | 1225.589 | 1207.578 | 1208.562 | 613.294 | E | 832.464 | 814.453 | 815.437 | 416.732 | 7 |
| 12 | 129.101 | 1381.690 | 1363.679 | 1364.663 | 691.345 | R | 703.421 | 685.410 | 686.394 | 352.210 | 6 |
| 13 | 44.050 | 1452.727 | 1434.716 | 1435.700 | 726.863 | A | 547.320 | 529.309 | 530.293 | 274.160 | 5 |
| 14 | 129.114 | 1608.828 | 1590.818 | 1591.801 | 804.914 | R | 476.283 | 458.272 | 459.256 | 238.641 | 4 |
| 15 | 60.045 | 1695.860 | 1677.849 | 1678.833 | 848.430 | S | 320.182 | 302.171 | 303.155 | 160.591 | 3 |
| 16 | 74.061 | 1796.908 | 1778.897 | 1779.881 | 898.954 | T | 233.150 | 215.139 | 216.123 | 117.075 | 2 |
| 17 | 86.097 | | | | | L | 132.102 | 114.091 | 115.075 | 66.551 | 1 |



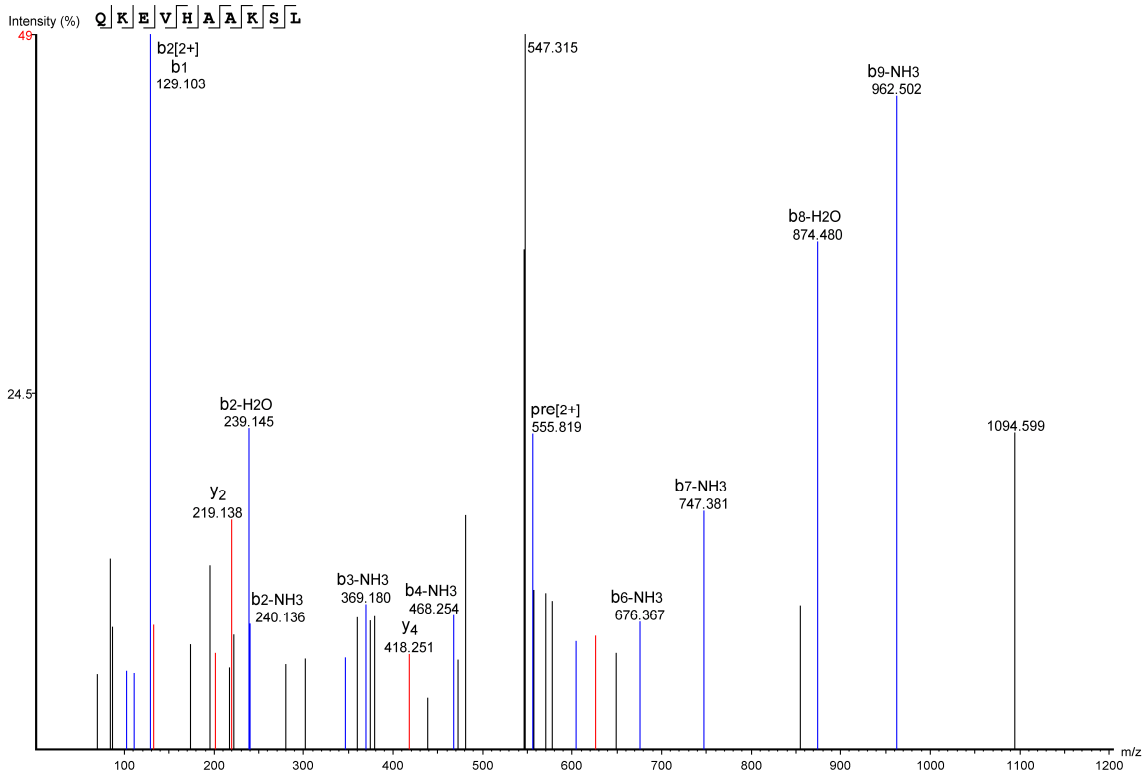
214–227, ESQPLPGERARSTL



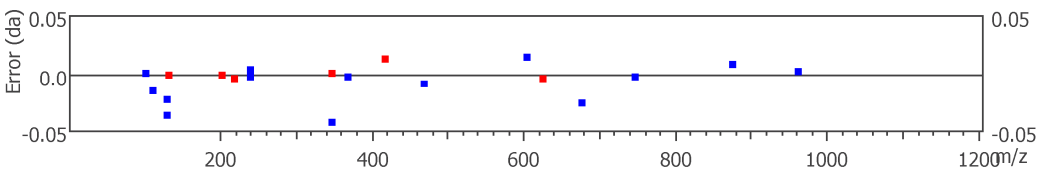

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 102.055 | 130.062 | 112.040 | 113.023 | 65.525 | E | | | | | 14 |
| 2 | 60.044 | 217.085 | 199.070 | 200.055 | 109.041 | S | 1411.770 | 1393.726 | 1394.738 | 706.383 | 13 |
| 3 | 101.071 | 345.143 | 327.131 | 328.114 | 173.070 | Q | 1324.743 | 1306.719 | 1307.712 | 662.867 | 12 |
| 4 | 70.066 | 442.194 | 424.185 | 425.184 | 221.597 | P | 1196.680 | 1178.664 | 1179.646 | 598.837 | 11 |
| 5 | 86.097 | 555.278 | 537.267 | 538.251 | 278.139 | L | 1099.628 | 1081.611 | 1082.595 | 550.311 | 10 |
| 6 | 70.066 | 652.331 | 634.320 | 635.304 | 326.665 | P | 986.534 | 968.527 | 969.511 | 493.769 | 9 |
| 7 | 30.034 | 709.352 | 691.341 | 692.325 | 355.176 | G | 889.480 | 871.474 | 872.461 | 445.242 | 8 |
| 8 | 102.055 | 838.395 | 820.384 | 821.368 | 419.697 | E | 832.464 | 814.453 | 815.437 | 416.731 | 7 |
| 9 | 129.066 | 994.496 | 976.485 | 977.469 | 497.748 | R | 703.422 | 685.410 | 686.394 | 352.210 | 6 |
| 10 | 44.050 | 1065.533 | 1047.522 | 1048.506 | 533.266 | A | 547.320 | 529.309 | 530.293 | 274.160 | 5 |
| 11 | 129.114 | 1221.634 | 1203.623 | 1204.607 | 611.317 | R | 476.283 | 458.272 | 459.256 | 238.641 | 4 |
| 12 | 60.045 | 1308.666 | 1290.656 | 1291.639 | 654.833 | S | 320.182 | 302.171 | 303.155 | 160.591 | 3 |
| 13 | 74.061 | 1409.714 | 1391.703 | 1392.687 | 705.357 | T | 233.150 | 215.139 | 216.098 | 117.075 | 2 |
| 14 | 86.097 | | | | | L | 132.102 | 114.091 | 115.090 | 66.551 | 1 |



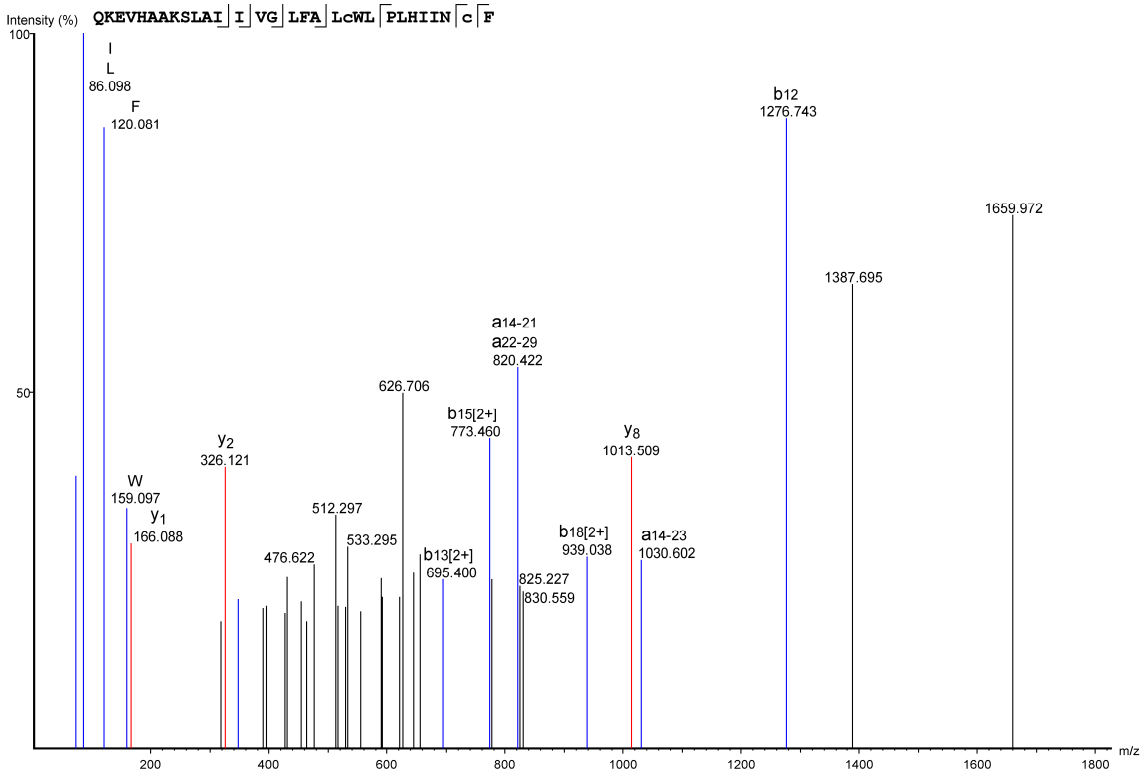
228–237, QKEVHAAKSL



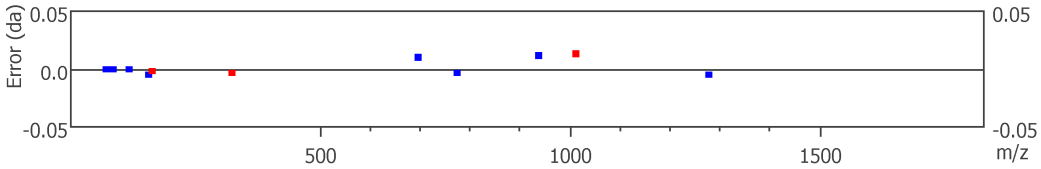

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 101.071 | 129.103 | 111.071 | 112.039 | 65.033 | Q | | | | | 10 |
| 2 | 101.108 | 257.161 | 239.145 | 240.136 | 129.103 | K | 982.568 | 964.557 | 965.541 | 491.784 | 9 |
| 3 | 102.053 | 386.204 | 368.193 | 369.180 | 193.602 | E | 854.473 | 836.462 | 837.446 | 427.737 | 8 |
| 4 | 72.081 | 485.272 | 467.262 | 468.254 | 243.136 | V | 725.430 | 707.420 | 708.403 | 363.215 | 7 |
| 5 | 110.072 | 622.331 | 604.305 | 605.304 | 311.666 | H | 626.366 | 608.351 | 609.335 | 313.681 | 6 |
| 6 | 44.050 | 693.368 | 675.358 | 676.367 | 347.227 | A | 489.303 | 471.293 | 472.276 | 245.152 | 5 |
| 7 | 44.050 | 764.405 | 746.395 | 747.381 | 382.703 | A | 418.251 | 400.255 | 401.239 | 209.633 | 4 |
| 8 | 101.108 | 892.500 | 874.480 | 875.473 | 446.750 | K | 347.227 | 329.218 | 330.202 | 174.114 | 3 |
| 9 | 60.045 | 979.532 | 961.522 | 962.502 | 490.266 | S | 219.138 | 201.122 | 202.107 | 110.067 | 2 |
| 10 | 86.097 | | | | | L | 132.102 | 114.091 | 115.075 | 66.551 | 1 |



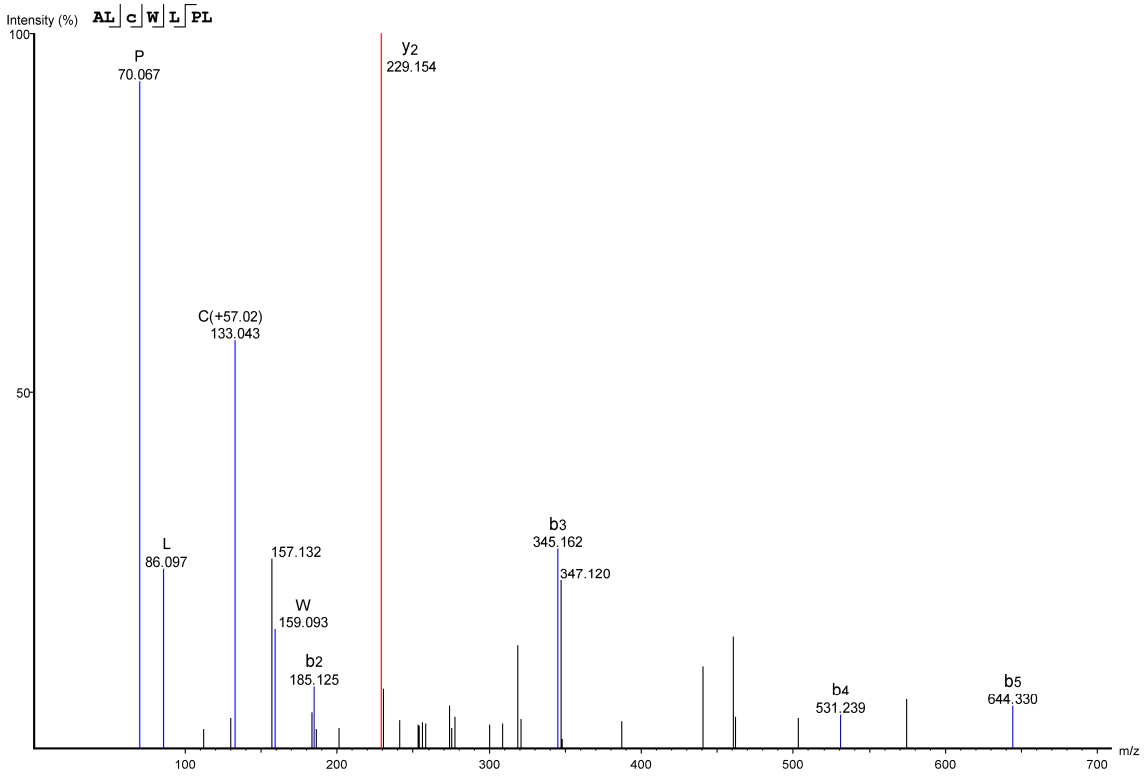
228–257, QKEVHAAKSLAIIVGLFALcWLPLHIINcF



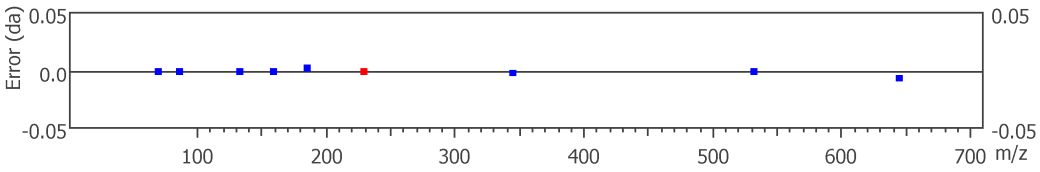
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 101.071 | 129.066 | 111.056 | 112.039 | 65.033 | Q | | | | | 30 |
| 2 | 101.108 | 257.161 | 239.151 | 240.134 | 129.081 | K | 3333.837 | 3315.826 | 3316.810 | 1667.418 | 29 |
| 3 | 102.055 | 386.204 | 368.193 | 369.177 | 193.602 | E | 3205.742 | 3187.731 | 3188.715 | 1603.371 | 28 |
| 4 | 72.081 | 485.272 | 467.262 | 468.245 | 243.136 | V | 3076.699 | 3058.688 | 3059.672 | 1538.849 | 27 |
| 5 | 110.072 | 622.331 | 604.321 | 605.304 | 311.666 | H | 2977.631 | 2959.620 | 2960.604 | 1489.315 | 26 |
| 6 | 44.050 | 693.368 | 675.358 | 676.341 | 347.184 | A | 2840.572 | 2822.561 | 2823.545 | 1420.786 | 25 |
| 7 | 44.050 | 764.405 | 746.395 | 747.378 | 382.703 | A | 2769.535 | 2751.524 | 2752.508 | 1385.267 | 24 |
| 8 | 101.108 | 892.500 | 874.490 | 875.473 | 446.750 | K | 2698.498 | 2680.487 | 2681.470 | 1349.749 | 23 |
| 9 | 60.045 | 979.532 | 961.522 | 962.505 | 490.266 | S | 2570.403 | 2552.392 | 2553.375 | 1285.701 | 22 |
| 10 | 86.098 | 1092.617 | 1074.606 | 1075.590 | 546.808 | L | 2483.371 | 2465.360 | 2466.344 | 1242.185 | 21 |
| 11 | 44.050 | 1163.654 | 1145.643 | 1146.627 | 582.327 | A | 2370.286 | 2352.276 | 2353.259 | 1185.643 | 20 |
| 12 | 86.098 | 1276.743 | 1258.727 | 1259.711 | 638.869 | I | 2299.249 | 2281.239 | 2282.222 | 1150.125 | 19 |
| 13 | 86.097 | 1389.822 | 1371.811 | 1372.795 | 695.400 | I | 2186.165 | 2168.155 | 2169.138 | 1093.583 | 18 |
| 14 | 72.081 | 1488.890 | 1470.880 | 1471.863 | 744.945 | V | 2073.081 | 2055.071 | 2056.054 | 1037.041 | 17 |
| 15 | 30.034 | 1545.912 | 1527.901 | 1528.885 | 773.460 | G | 1974.013 | 1956.002 | 1956.986 | 987.506 | 16 |
| 16 | 86.097 | 1658.996 | 1640.985 | 1641.969 | 829.998 | L | 1916.991 | 1898.981 | 1899.964 | 958.996 | 15 |
| 17 | 120.081 | 1806.064 | 1788.054 | 1789.037 | 903.532 | F | 1803.907 | 1785.897 | 1786.880 | 902.454 | 14 |
| 18 | 44.050 | 1877.101 | 1859.091 | 1860.074 | 939.038 | A | 1656.839 | 1638.828 | 1639.812 | 828.919 | 13 |
| 19 | 86.097 | 1990.185 | 1972.175 | 1973.158 | 995.593 | L | 1585.802 | 1567.791 | 1568.775 | 793.401 | 12 |
| 20 | 133.043 | 2150.216 | 2132.205 | 2133.189 | 1075.608 | C(+57.02) | 1472.718 | 1454.707 | 1455.691 | 736.859 | 11 |
| 21 | 159.097 | 2336.295 | 2318.285 | 2319.268 | 1168.648 | W | 1312.687 | 1294.677 | 1295.660 | 656.844 | 10 |
| 22 | 86.097 | 2449.379 | 2431.369 | 2432.352 | 1225.190 | L | 1126.608 | 1108.597 | 1109.581 | 563.804 | 9 |
| 23 | 70.066 | 2546.432 | 2528.422 | 2529.405 | 1273.716 | P | 1013.509 | 995.513 | 996.497 | 507.262 | 8 |
| 24 | 86.097 | 2659.516 | 2641.506 | 2642.489 | 1330.258 | L | 916.471 | 898.460 | 899.444 | 458.735 | 7 |
| 25 | 110.072 | 2796.575 | 2778.564 | 2779.548 | 1398.787 | H | 803.387 | 785.376 | 786.360 | 402.193 | 6 |
| 26 | 86.097 | 2909.659 | 2891.649 | 2892.632 | 1455.330 | I | 666.328 | 648.317 | 649.301 | 333.664 | 5 |
| 27 | 86.097 | 3022.743 | 3004.733 | 3005.716 | 1511.872 | I | 553.244 | 535.233 | 536.217 | 277.122 | 4 |
| 28 | 87.056 | 3136.786 | 3118.776 | 3119.759 | 1568.893 | N | 440.160 | 422.149 | 423.133 | 220.580 | 3 |
| 29 | 133.043 | 3296.817 | 3278.806 | 3279.790 | 1648.908 | C(+57.02) | 326.121 | 308.106 | 309.090 | 163.558 | 2 |
| 30 | 120.081 | | | | | F | 166.088 | 148.076 | 149.059 | 83.543 | 1 |



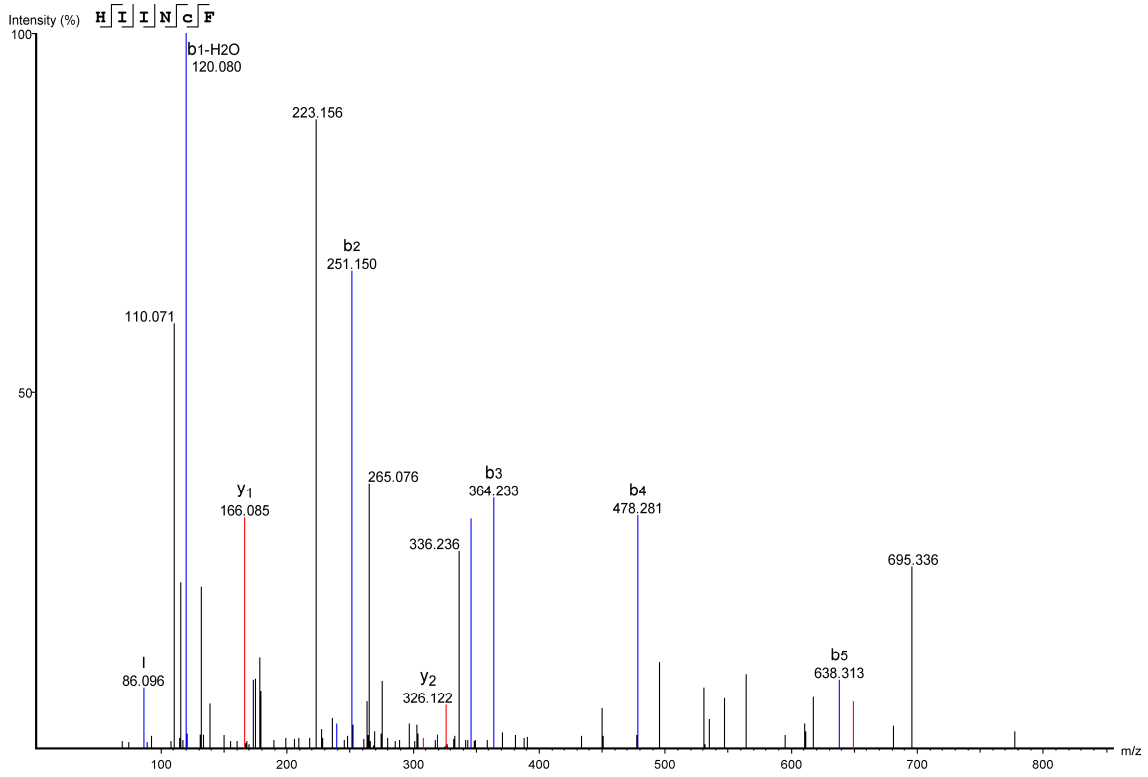
245–251, ALcWLPL



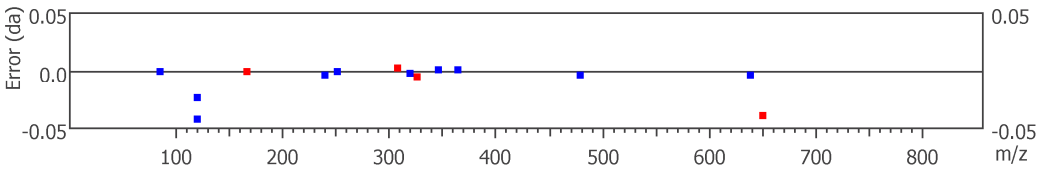

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 44.050 | 72.045 | 54.034 | 55.018 | 36.522 | A | | | | | 7 |
| 2 | 86.097 | 185.125 | 167.118 | 168.102 | 93.064 | L | 801.433 | 783.422 | 784.406 | 401.216 | 6 |
| 3 | 133.043 | 345.162 | 327.149 | 328.133 | 173.080 | C(+57.02) | 688.349 | 670.338 | 671.322 | 344.674 | 5 |
| 4 | 159.093 | 531.239 | 513.228 | 514.212 | 266.119 | W | 528.318 | 510.307 | 511.291 | 264.659 | 4 |
| 5 | 86.097 | 644.330 | 626.312 | 627.296 | 322.661 | L | 342.239 | 324.228 | 325.212 | 171.619 | 3 |
| 6 | 70.067 | 741.376 | 723.365 | 724.349 | 371.188 | P | 229.154 | 211.144 | 212.128 | 115.077 | 2 |
| 7 | 86.097 | | | | | L | 132.102 | 114.091 | 115.075 | 66.551 | 1 |



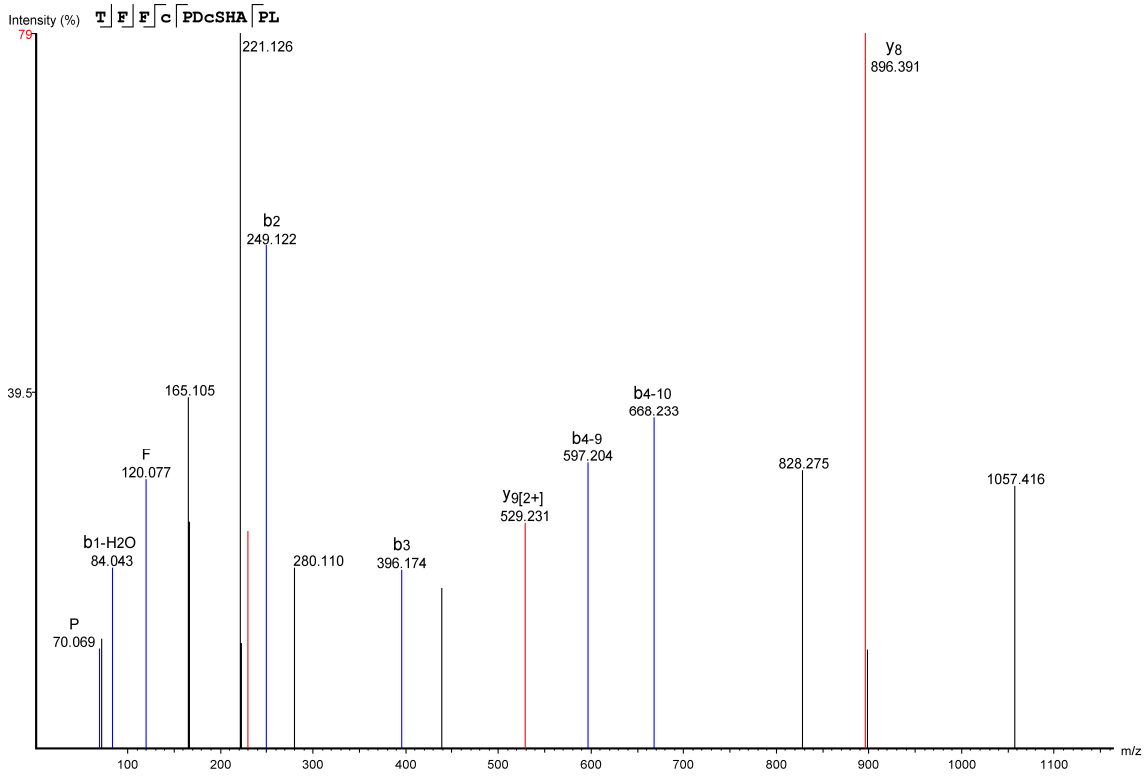
252–257, HIINcF



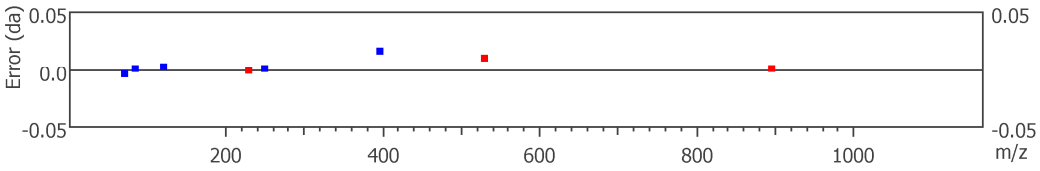

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 110.072 | 138.067 | 120.080 | 121.082 | 69.533 | H | | | | | 6 |
| 2 | 86.096 | 251.150 | 233.140 | 234.124 | 126.075 | I | 666.328 | 648.317 | 649.340 | 333.664 | 5 |
| 3 | 86.097 | 364.233 | 346.222 | 347.208 | 182.617 | I | 553.244 | 535.233 | 536.217 | 277.122 | 4 |
| 4 | 87.056 | 478.281 | 460.267 | 461.251 | 239.643 | N | 440.160 | 422.149 | 423.133 | 220.580 | 3 |
| 5 | 133.043 | 638.313 | 620.298 | 621.281 | 319.656 | C(+57.02) | 326.122 | 308.102 | 309.090 | 163.558 | 2 |
| 6 | 120.081 | | | | | F | 166.085 | 148.076 | 149.059 | 83.543 | 1 |



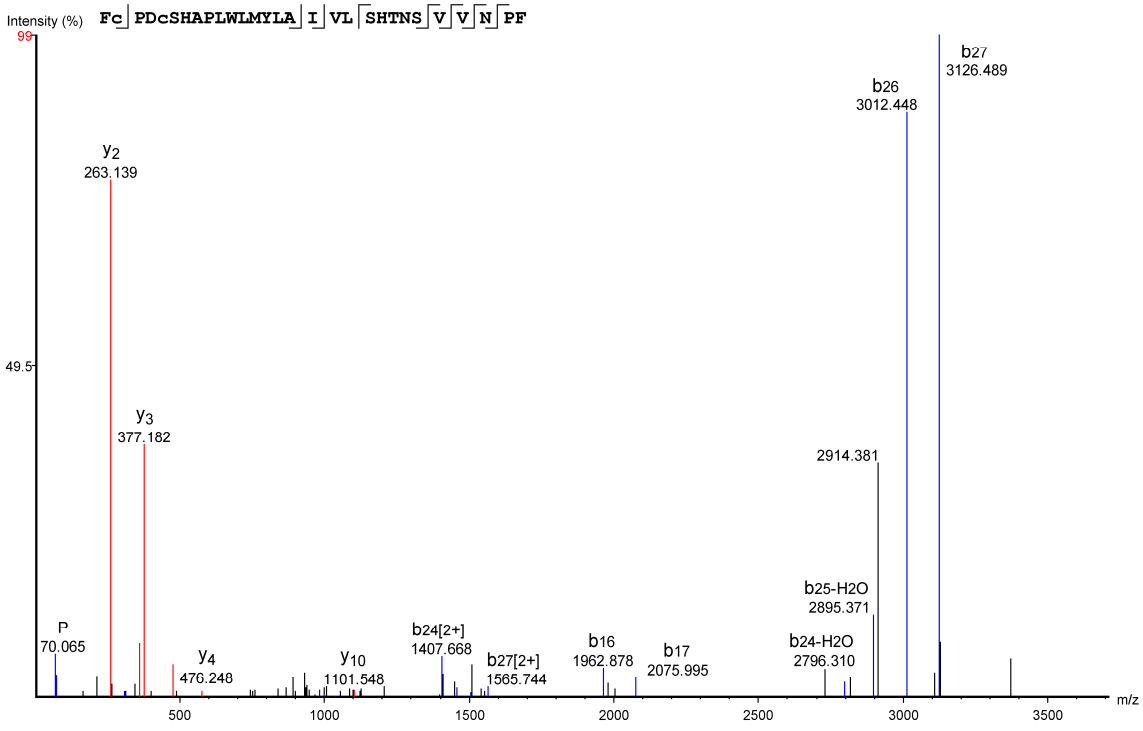
258–269, TFFcPDcSHAPL



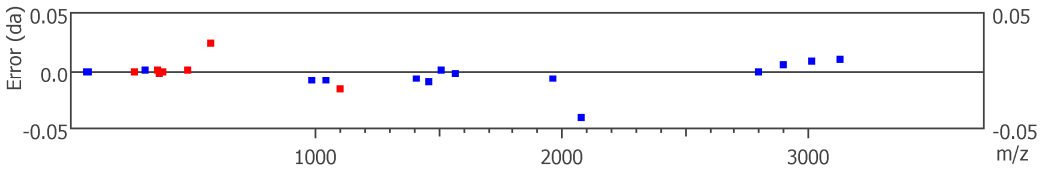

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 74.061 | 102.056 | 84.043 | 85.029 | 51.528 | T | | | | | 12 |
| 2 | 120.077 | 249.122 | 231.113 | 232.097 | 125.062 | F | 1350.561 | 1332.550 | 1333.534 | 675.780 | 11 |
| 3 | 120.081 | 396.174 | 378.182 | 379.165 | 198.596 | F | 1203.492 | 1185.482 | 1186.465 | 602.246 | 10 |
| 4 | 133.043 | 556.223 | 538.212 | 539.196 | 278.611 | C(+57.02) | 1056.424 | 1038.413 | 1039.397 | 528.701 | 9 |
| 5 | 70.069 | 653.276 | 635.265 | 636.249 | 327.138 | P | 896.391 | 878.383 | 879.366 | 448.697 | 8 |
| 6 | 88.040 | 768.303 | 750.292 | 751.276 | 384.651 | D | 799.340 | 781.330 | 782.313 | 400.170 | 7 |
| 7 | 133.043 | 928.333 | 910.323 | 911.306 | 464.667 | C(+57.02) | 684.313 | 666.303 | 667.286 | 342.657 | 6 |
| 8 | 60.045 | 1015.365 | 997.355 | 998.338 | 508.183 | S | 524.283 | 506.272 | 507.256 | 262.641 | 5 |
| 9 | 110.072 | 1152.424 | 1134.414 | 1135.397 | 576.712 | H | 437.251 | 419.240 | 420.224 | 219.125 | 4 |
| 10 | 44.050 | 1223.461 | 1205.451 | 1206.434 | 612.231 | A | 300.192 | 282.181 | 283.165 | 150.596 | 3 |
| 11 | 70.066 | 1320.514 | 1302.504 | 1303.487 | 660.757 | P | 229.156 | 211.144 | 212.128 | 115.077 | 2 |
| 12 | 86.097 | | | | | L | 132.102 | 114.091 | 115.075 | 66.551 | 1 |



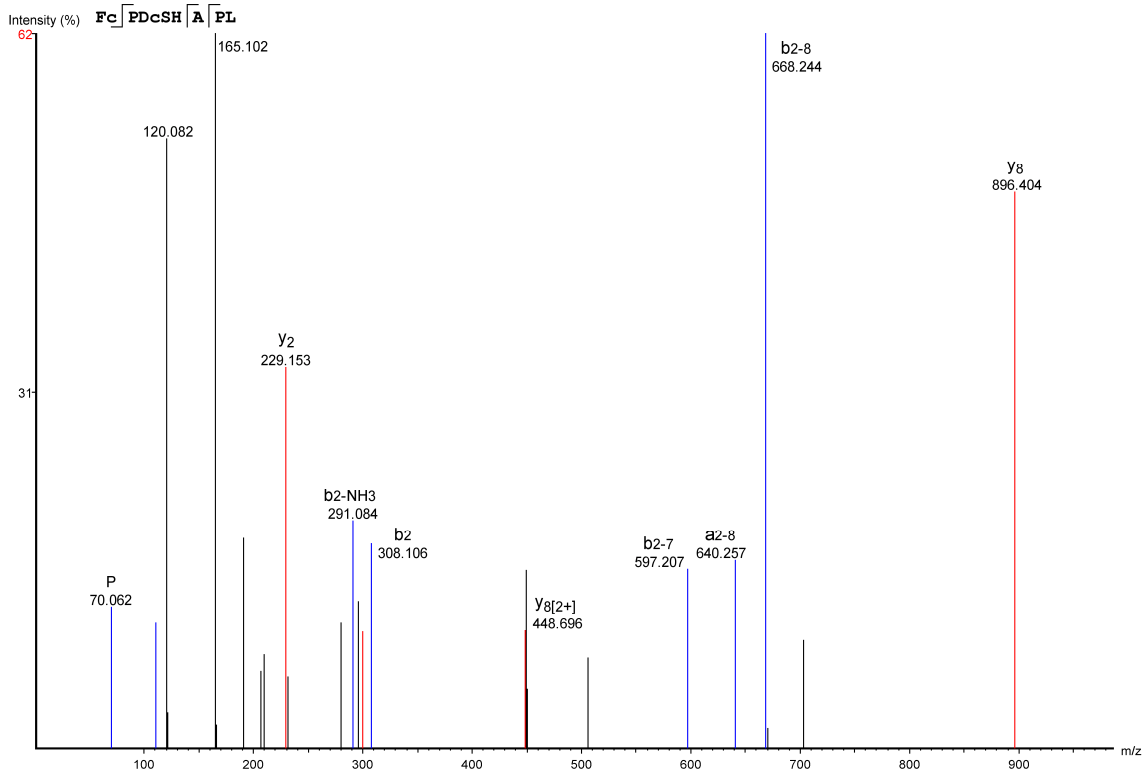
260–288, FcPDcSHAPLWLMYLAIVLSHTNSVVNPF



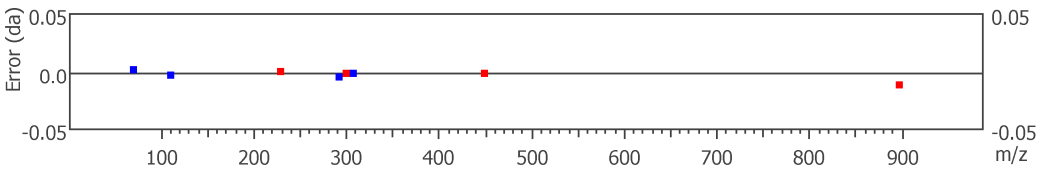
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 120.081 | 148.076 | 130.066 | 131.049 | 74.538 | F | | | | | 29 |
| 2 | 133.043 | 308.104 | 290.096 | 291.080 | 154.553 | C(+57.02) | 3241.563 | 3223.552 | 3224.536 | 1621.281 | 28 |
| 3 | 70.065 | 405.160 | 387.149 | 388.133 | 203.080 | P | 3081.532 | 3063.522 | 3064.505 | 1541.266 | 27 |
| 4 | 88.040 | 520.187 | 502.176 | 503.160 | 260.593 | D | 2984.480 | 2966.469 | 2967.453 | 1492.740 | 26 |
| 5 | 133.043 | 680.217 | 662.207 | 663.190 | 340.609 | C(+57.02) | 2869.453 | 2851.442 | 2852.426 | 1435.226 | 25 |
| 6 | 60.045 | 767.249 | 749.239 | 750.222 | 384.125 | S | 2709.422 | 2691.412 | 2692.395 | 1355.211 | 24 |
| 7 | 110.072 | 904.308 | 886.298 | 887.281 | 452.654 | H | 2622.390 | 2604.380 | 2605.363 | 1311.695 | 23 |
| 8 | 44.050 | 975.345 | 957.335 | 958.318 | 488.173 | A | 2485.331 | 2467.321 | 2468.304 | 1243.166 | 22 |
| 9 | 70.066 | 1072.398 | 1054.388 | 1055.371 | 536.699 | P | 2414.294 | 2396.283 | 2397.267 | 1207.647 | 21 |
| 10 | 86.097 | 1185.482 | 1167.472 | 1168.455 | 593.241 | L | 2317.241 | 2299.231 | 2300.214 | 1159.121 | 20 |
| 11 | 159.092 | 1371.561 | 1353.551 | 1354.534 | 686.281 | W | 2204.157 | 2186.147 | 2187.130 | 1102.579 | 19 |
| 12 | 86.097 | 1484.646 | 1466.635 | 1467.619 | 742.823 | L | 2018.078 | 2000.067 | 2001.051 | 1009.539 | 18 |
| 13 | 104.053 | 1615.686 | 1597.675 | 1598.659 | 808.343 | M | 1904.994 | 1886.983 | 1887.967 | 952.997 | 17 |
| 14 | 136.076 | 1778.749 | 1760.739 | 1761.722 | 889.875 | Y | 1773.953 | 1755.943 | 1756.926 | 887.477 | 16 |
| 15 | 86.097 | 1891.833 | 1873.823 | 1874.806 | 946.417 | L | 1610.890 | 1592.880 | 1593.863 | 805.945 | 15 |
| 16 | 44.050 | 1962.878 | 1944.860 | 1945.844 | 981.943 | A | 1497.806 | 1479.795 | 1480.779 | 749.403 | 14 |
| 17 | 86.097 | 2075.995 | 2057.944 | 2058.927 | 1038.486 | I | 1426.769 | 1408.758 | 1409.742 | 713.884 | 13 |
| 18 | 72.082 | 2175.023 | 2157.012 | 2157.996 | 1088.011 | V | 1313.685 | 1295.674 | 1296.658 | 657.342 | 12 |
| 19 | 86.097 | 2288.107 | 2270.096 | 2271.080 | 1144.553 | L | 1214.616 | 1196.606 | 1197.589 | 607.808 | 11 |
| 20 | 60.045 | 2375.139 | 2357.128 | 2358.112 | 1188.069 | S | 1101.548 | 1083.522 | 1084.505 | 551.266 | 10 |
| 21 | 110.072 | 2512.198 | 2494.188 | 2495.171 | 1256.599 | H | 1014.500 | 996.490 | 997.473 | 507.750 | 9 |
| 22 | 74.061 | 2613.246 | 2595.235 | 2596.219 | 1307.123 | T | 877.441 | 859.431 | 860.414 | 439.221 | 8 |
| 23 | 87.056 | 2727.289 | 2709.278 | 2710.261 | 1364.144 | N | 776.394 | 758.383 | 759.367 | 388.697 | 7 |
| 24 | 60.045 | 2814.321 | 2796.310 | 2797.293 | 1407.668 | S | 662.351 | 644.340 | 645.324 | 331.675 | 6 |
| 25 | 72.081 | 2913.389 | 2895.371 | 2896.362 | 1457.204 | V | 575.294 | 557.308 | 558.292 | 288.159 | 5 |
| 26 | 72.081 | 3012.448 | 2994.447 | 2995.430 | 1506.727 | V | 476.248 | 458.240 | 459.223 | 238.625 | 4 |
| 27 | 87.056 | 3126.489 | 3108.490 | 3109.473 | 1563.753 | N | 377.182 | 359.169 | 360.158 | 189.091 | 3 |
| 28 | 70.066 | 3223.553 | 3205.542 | 3206.526 | 1612.276 | P | 263.139 | 245.128 | 246.112 | 132.069 | 2 |
| 29 | 120.081 | | | | | F | 166.086 | 148.076 | 149.059 | 83.543 | 1 |



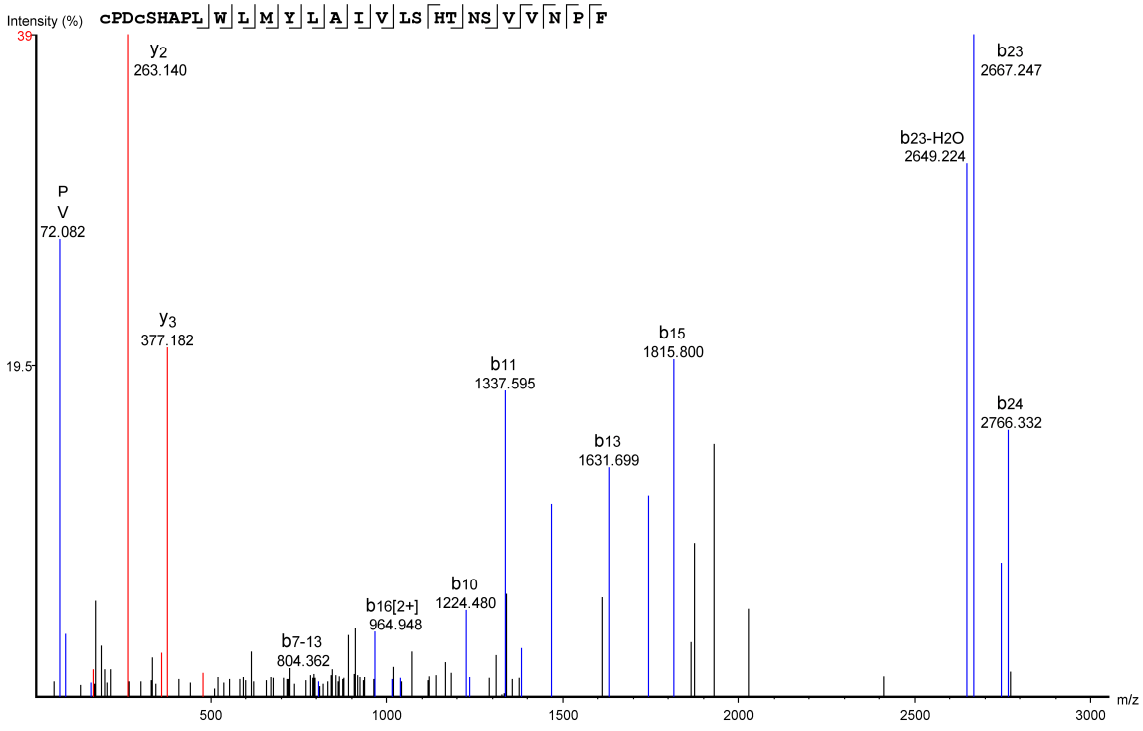
260–269, FcPDcSHAPL



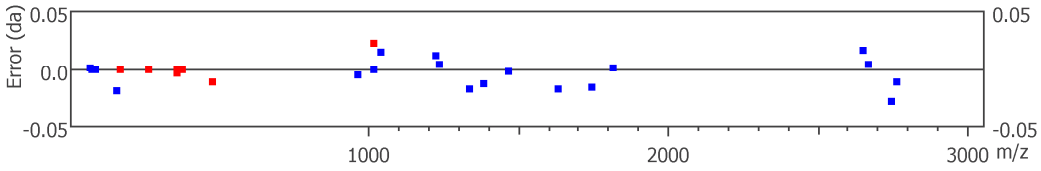

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 120.081 | 148.076 | 130.066 | 131.049 | 74.538 | F | | | | | 10 |
| 2 | 133.043 | 308.106 | 290.096 | 291.084 | 154.553 | C(+57.02) | 1056.424 | 1038.413 | 1039.397 | 528.712 | 9 |
| 3 | 70.062 | 405.160 | 387.149 | 388.133 | 203.080 | P | 896.404 | 878.383 | 879.366 | 448.696 | 8 |
| 4 | 88.040 | 520.187 | 502.176 | 503.160 | 260.593 | D | 799.340 | 781.330 | 782.313 | 400.170 | 7 |
| 5 | 133.043 | 680.217 | 662.207 | 663.190 | 340.609 | C(+57.02) | 684.313 | 666.303 | 667.286 | 342.657 | 6 |
| 6 | 60.045 | 767.249 | 749.239 | 750.222 | 384.125 | S | 524.283 | 506.272 | 507.256 | 262.641 | 5 |
| 7 | 110.074 | 904.308 | 886.298 | 887.281 | 452.654 | H | 437.251 | 419.240 | 420.224 | 219.125 | 4 |
| 8 | 44.050 | 975.345 | 957.335 | 958.318 | 488.173 | A | 300.192 | 282.181 | 283.165 | 150.596 | 3 |
| 9 | 70.066 | 1072.398 | 1054.388 | 1055.371 | 536.699 | P | 229.153 | 211.144 | 212.128 | 115.077 | 2 |
| 10 | 86.097 | | | | | L | 132.102 | 114.091 | 115.075 | 66.551 | 1 |



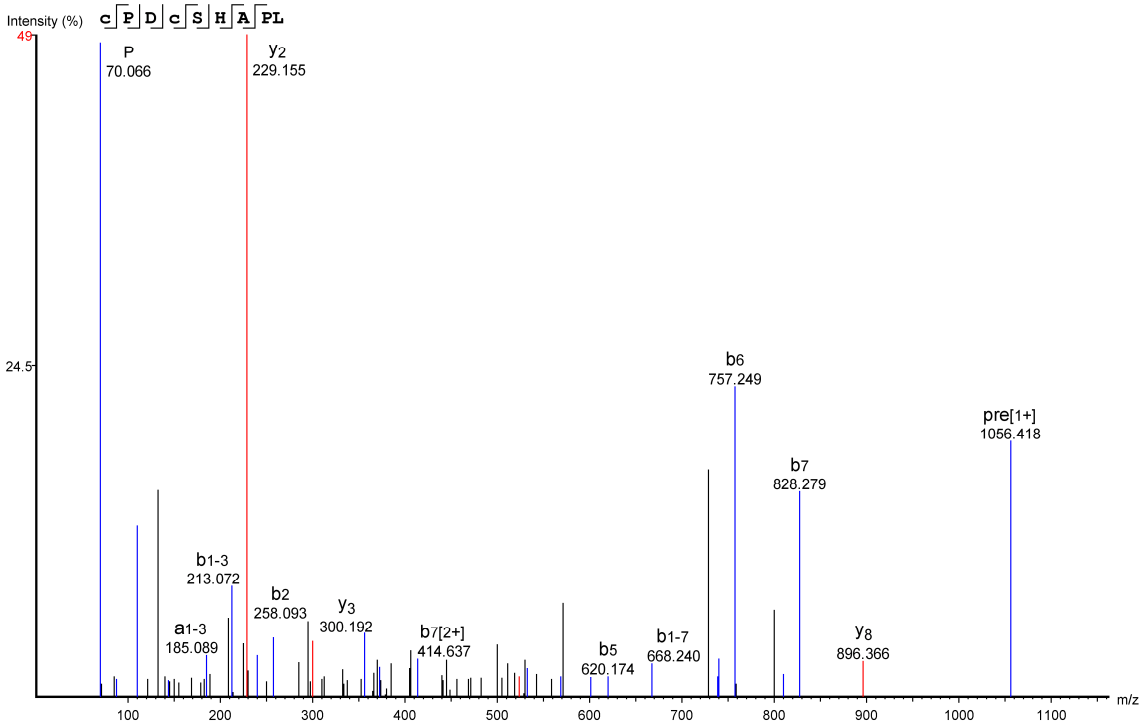
261–288, cPDcSHAPLWLMYLAIVLSHTNSVVNPF



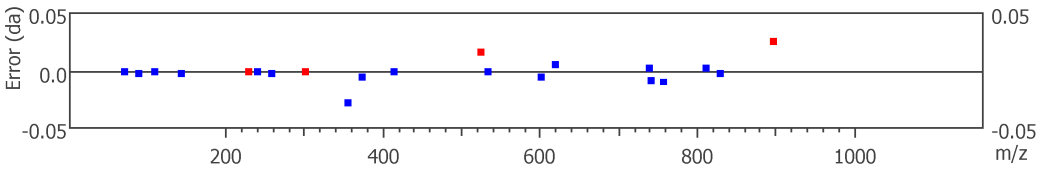
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 133.043 | 161.038 | 143.028 | 144.011 | 81.019 | C(+57.02) | | | | | 28 |
| 2 | 70.064 | 258.091 | 240.081 | 241.064 | 129.546 | P | 3081.532 | 3063.522 | 3064.505 | 1541.266 | 27 |
| 3 | 88.040 | 373.118 | 355.108 | 356.091 | 187.059 | D | 2984.480 | 2966.469 | 2967.453 | 1492.740 | 26 |
| 4 | 133.043 | 533.149 | 515.138 | 516.122 | 267.074 | C(+57.02) | 2869.453 | 2851.442 | 2852.426 | 1435.226 | 25 |
| 5 | 60.045 | 620.181 | 602.170 | 603.154 | 310.590 | S | 2709.422 | 2691.412 | 2692.395 | 1355.211 | 24 |
| 6 | 110.072 | 757.240 | 739.229 | 740.213 | 379.120 | H | 2622.390 | 2604.380 | 2605.363 | 1311.695 | 23 |
| 7 | 44.050 | 828.277 | 810.266 | 811.250 | 414.638 | A | 2485.331 | 2467.321 | 2468.304 | 1243.166 | 22 |
| 8 | 70.066 | 925.330 | 907.319 | 908.303 | 463.165 | P | 2414.294 | 2396.283 | 2397.267 | 1207.647 | 21 |
| 9 | 86.097 | 1038.398 | 1020.403 | 1021.387 | 519.707 | L | 2317.241 | 2299.231 | 2300.214 | 1159.121 | 20 |
| 10 | 159.111 | 1224.480 | 1206.483 | 1207.466 | 612.747 | W | 2204.157 | 2186.147 | 2187.130 | 1102.579 | 19 |
| 11 | 86.097 | 1337.595 | 1319.567 | 1320.550 | 669.289 | L | 2018.078 | 2000.067 | 2001.051 | 1009.539 | 18 |
| 12 | 104.053 | 1468.620 | 1450.607 | 1451.591 | 734.809 | M | 1904.994 | 1886.983 | 1887.967 | 952.997 | 17 |
| 13 | 136.076 | 1631.699 | 1613.670 | 1614.654 | 816.340 | Y | 1773.953 | 1755.943 | 1756.926 | 887.477 | 16 |
| 14 | 86.097 | 1744.781 | 1726.754 | 1727.738 | 872.882 | L | 1610.890 | 1592.880 | 1593.863 | 805.945 | 15 |
| 15 | 44.050 | 1815.800 | 1797.792 | 1798.775 | 908.401 | A | 1497.806 | 1479.795 | 1480.779 | 749.403 | 14 |
| 16 | 86.097 | 1928.886 | 1910.876 | 1911.859 | 964.948 | I | 1426.769 | 1408.758 | 1409.742 | 713.884 | 13 |
| 17 | 72.082 | 2027.955 | 2009.944 | 2010.928 | 1014.477 | V | 1313.685 | 1295.674 | 1296.658 | 657.342 | 12 |
| 18 | 86.097 | 2141.039 | 2123.028 | 2124.011 | 1071.019 | L | 1214.616 | 1196.606 | 1197.589 | 607.808 | 11 |
| 19 | 60.045 | 2228.071 | 2210.060 | 2211.043 | 1114.535 | S | 1101.532 | 1083.522 | 1084.505 | 551.266 | 10 |
| 20 | 110.072 | 2365.130 | 2347.119 | 2348.103 | 1183.065 | H | 1014.477 | 996.490 | 997.473 | 507.750 | 9 |
| 21 | 74.061 | 2466.177 | 2448.167 | 2449.150 | 1233.583 | T | 877.441 | 859.431 | 860.414 | 439.221 | 8 |
| 22 | 87.056 | 2580.220 | 2562.210 | 2563.193 | 1290.610 | N | 776.394 | 758.383 | 759.367 | 388.697 | 7 |
| 23 | 60.045 | 2667.247 | 2649.224 | 2650.225 | 1334.126 | S | 662.351 | 644.340 | 645.324 | 331.675 | 6 |
| 24 | 72.081 | 2766.332 | 2748.339 | 2749.293 | 1383.673 | V | 575.319 | 557.308 | 558.292 | 288.159 | 5 |
| 25 | 72.081 | 2865.389 | 2847.378 | 2848.362 | 1433.194 | V | 476.262 | 458.240 | 459.223 | 238.625 | 4 |
| 26 | 87.056 | 2979.432 | 2961.421 | 2962.405 | 1490.216 | N | 377.182 | 359.170 | 360.159 | 189.091 | 3 |
| 27 | 70.066 | 3076.485 | 3058.474 | 3059.458 | 1538.742 | P | 263.140 | 245.128 | 246.112 | 132.069 | 2 |
| 28 | 120.081 | | | | | F | 166.086 | 148.076 | 149.059 | 83.543 | 1 |



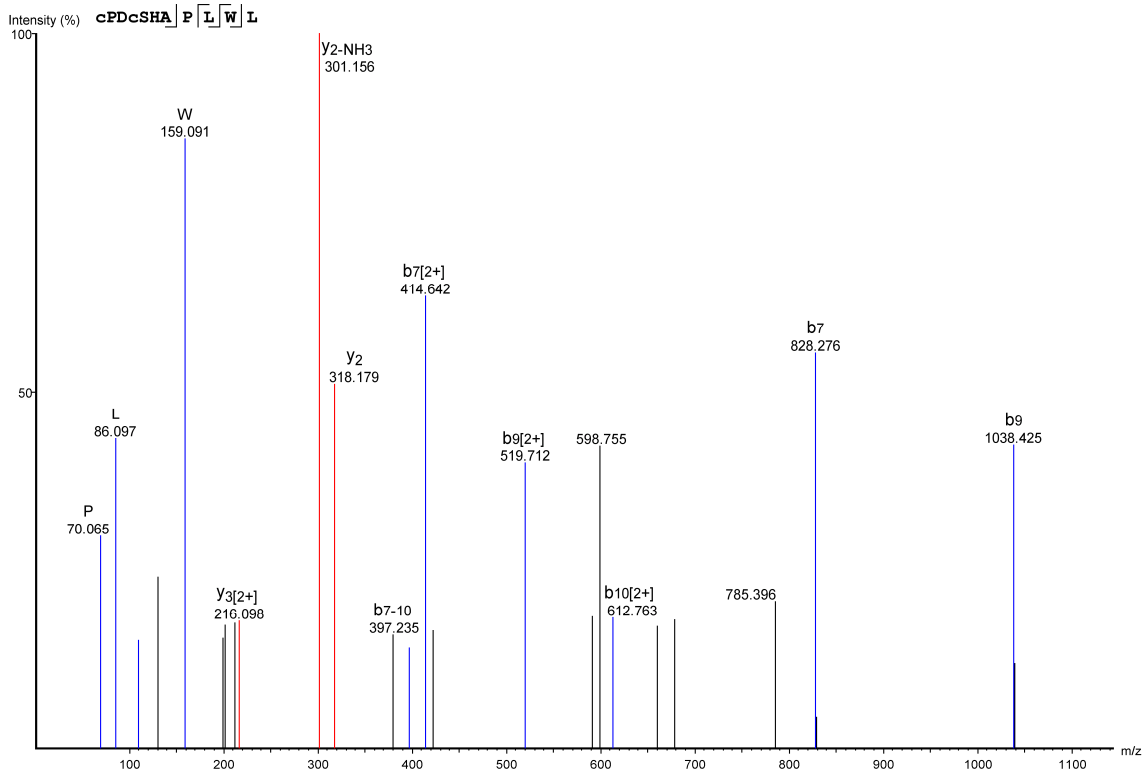
261–269, cPDcSHAPL



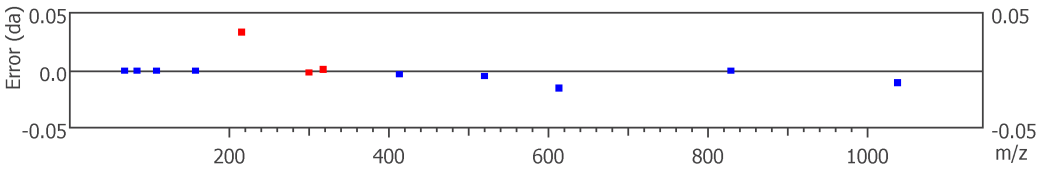

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 133.043 | 161.038 | 143.028 | 144.014 | 81.019 | C(+57.02) | | | | | 9 |
| 2 | 70.066 | 258.093 | 240.081 | 241.064 | 129.546 | P | 896.366 | 878.383 | 879.366 | 448.697 | 8 |
| 3 | 88.042 | 373.124 | 355.108 | 356.120 | 187.059 | D | 799.340 | 781.330 | 782.313 | 400.170 | 7 |
| 4 | 133.043 | 533.149 | 515.138 | 516.122 | 267.074 | C(+57.02) | 684.313 | 666.303 | 667.286 | 342.657 | 6 |
| 5 | 60.045 | 620.174 | 602.175 | 603.154 | 310.590 | S | 524.265 | 506.272 | 507.256 | 262.641 | 5 |
| 6 | 110.071 | 757.249 | 739.226 | 740.222 | 379.120 | H | 437.251 | 419.240 | 420.224 | 219.125 | 4 |
| 7 | 44.050 | 828.279 | 810.263 | 811.250 | 414.637 | A | 300.192 | 282.181 | 283.165 | 150.596 | 3 |
| 8 | 70.066 | 925.330 | 907.319 | 908.303 | 463.165 | P | 229.155 | 211.144 | 212.128 | 115.077 | 2 |
| 9 | 86.097 | | | | | L | 132.102 | 114.091 | 115.075 | 66.551 | 1 |



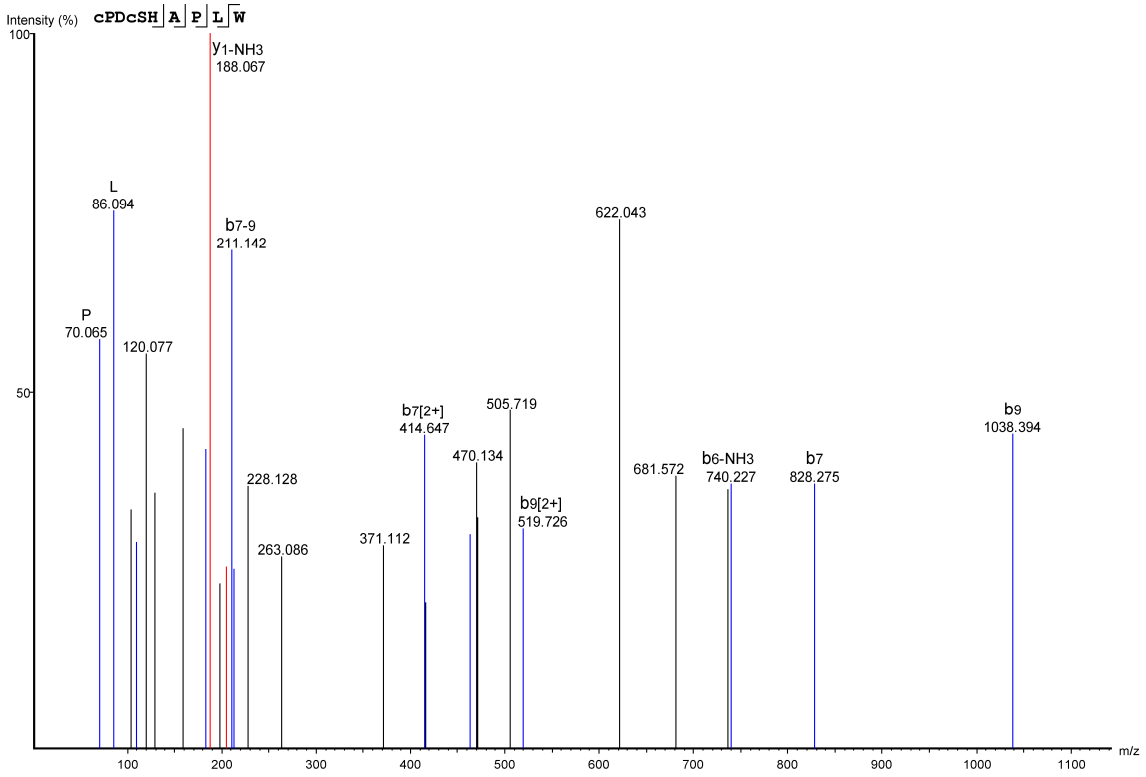
261–271, cPDcSHAPLWL



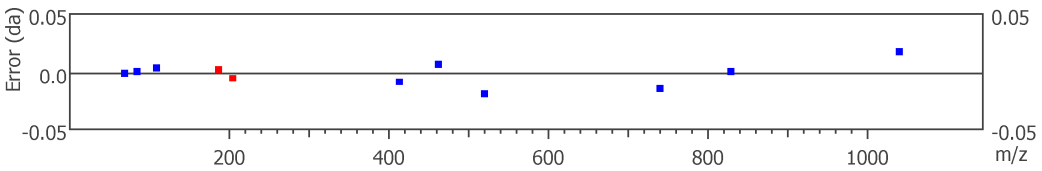

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 133.043 | 161.038 | 143.028 | 144.011 | 81.019 | C(+57.02) | | | | | 11 |
| 2 | 70.065 | 258.091 | 240.081 | 241.064 | 129.546 | P | 1195.556 | 1177.546 | 1178.529 | 598.278 | 10 |
| 3 | 88.040 | 373.118 | 355.108 | 356.091 | 187.059 | D | 1098.504 | 1080.493 | 1081.477 | 549.752 | 9 |
| 4 | 133.043 | 533.149 | 515.138 | 516.122 | 267.074 | C(+57.02) | 983.477 | 965.466 | 966.450 | 492.238 | 8 |
| 5 | 60.045 | 620.181 | 602.170 | 603.154 | 310.590 | S | 823.446 | 805.435 | 806.419 | 412.223 | 7 |
| 6 | 110.073 | 757.240 | 739.229 | 740.213 | 379.120 | H | 736.414 | 718.404 | 719.387 | 368.707 | 6 |
| 7 | 44.050 | 828.276 | 810.266 | 811.250 | 414.642 | A | 599.355 | 581.345 | 582.328 | 300.178 | 5 |
| 8 | 70.066 | 925.330 | 907.319 | 908.303 | 463.165 | P | 528.318 | 510.307 | 511.291 | 264.659 | 4 |
| 9 | 86.097 | 1038.425 | 1020.403 | 1021.387 | 519.712 | L | 431.265 | 413.255 | 414.238 | 216.098 | 3 |
| 10 | 159.091 | 1224.493 | 1206.483 | 1207.466 | 612.763 | W | 318.179 | 300.171 | 301.156 | 159.591 | 2 |
| 11 | 86.097 | | | | | L | 132.102 | 114.091 | 115.075 | 66.551 | 1 |



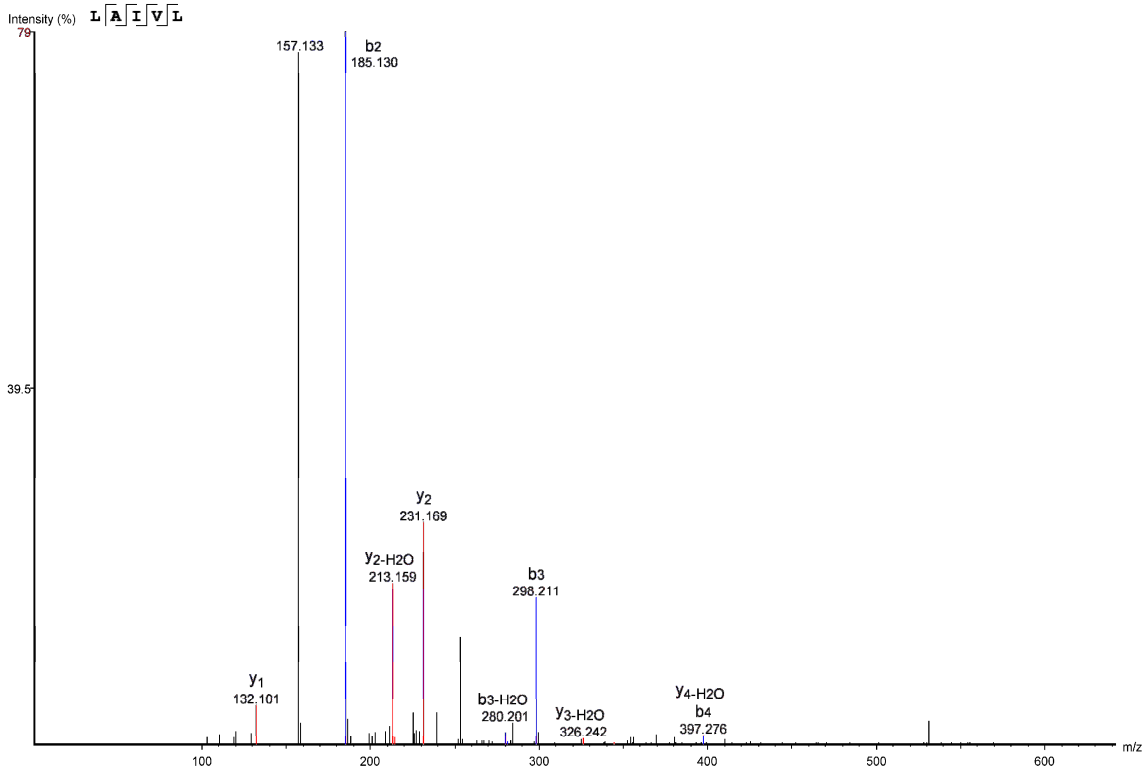
261–270, cPDcSHAPLW



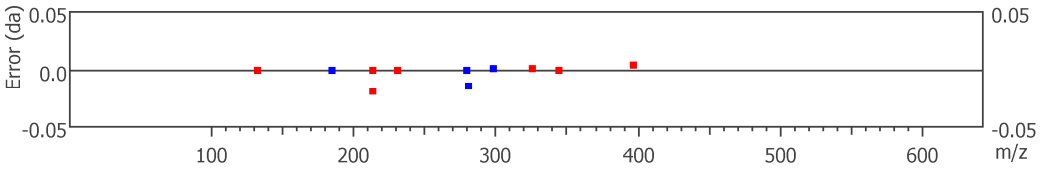

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 133.043 | 161.038 | 143.028 | 144.011 | 81.019 | C(+57.02) | | | | | 10 |
| 2 | 70.065 | 258.091 | 240.081 | 241.064 | 129.546 | P | 1082.472 | 1064.462 | 1065.445 | 541.736 | 9 |
| 3 | 88.040 | 373.118 | 355.108 | 356.091 | 187.059 | D | 985.420 | 967.409 | 968.393 | 493.210 | 8 |
| 4 | 133.043 | 533.149 | 515.138 | 516.122 | 267.074 | C(+57.02) | 870.393 | 852.382 | 853.366 | 435.696 | 7 |
| 5 | 60.045 | 620.181 | 602.170 | 603.154 | 310.590 | S | 710.362 | 692.351 | 693.335 | 355.681 | 6 |
| 6 | 110.066 | 757.240 | 739.229 | 740.227 | 379.120 | H | 623.330 | 605.319 | 606.303 | 312.165 | 5 |
| 7 | 44.050 | 828.275 | 810.266 | 811.250 | 414.647 | A | 486.271 | 468.260 | 469.244 | 243.636 | 4 |
| 8 | 70.066 | 925.330 | 907.319 | 908.303 | 463.157 | P | 415.234 | 397.223 | 398.207 | 208.117 | 3 |
| 9 | 86.094 | 1038.394 | 1020.403 | 1021.387 | 519.726 | L | 318.181 | 300.171 | 301.154 | 159.591 | 2 |
| 10 | 159.092 | | | | | W | 205.102 | 187.087 | 188.067 | 103.049 | 1 |



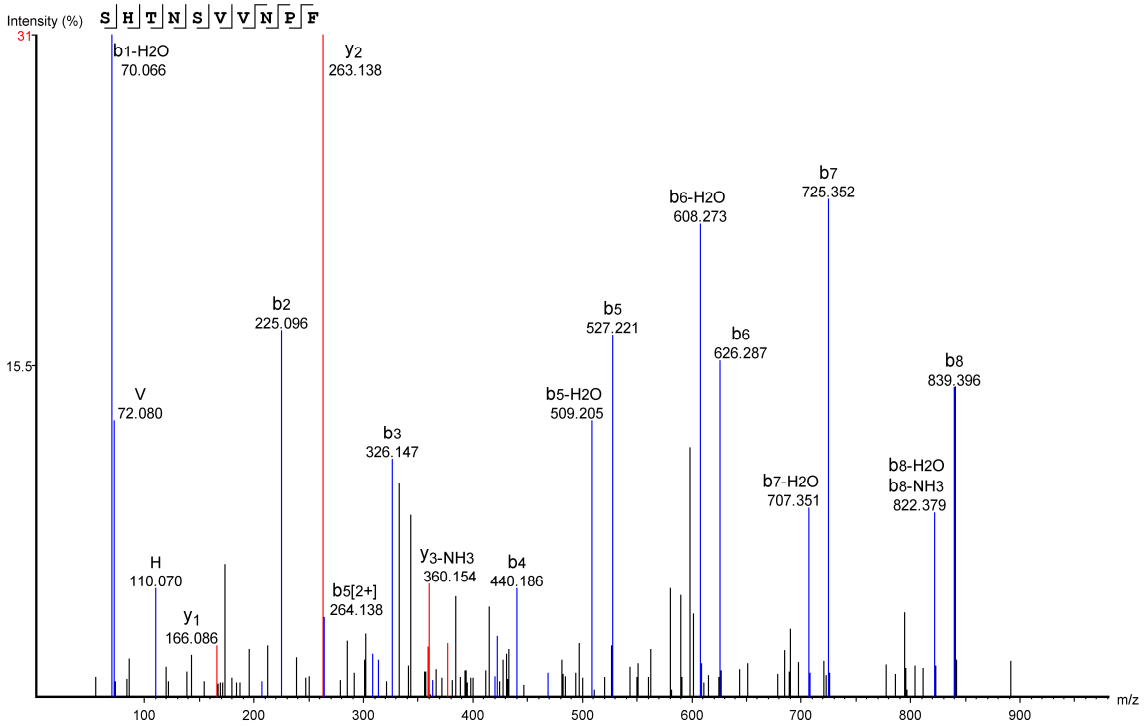
274–278, LAIVL



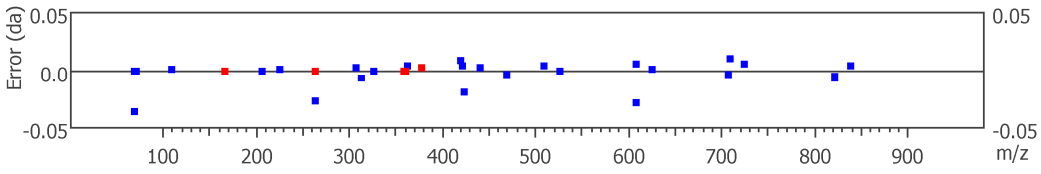

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 86.097 | 114.092 | 96.081 | 97.065 | 57.546 | L | | | | | 5 |
| 2 | 44.050 | 185.130 | 167.118 | 168.102 | 93.064 | A | 415.291 | 397.276 | 398.264 | 208.146 | 4 |
| 3 | 86.097 | 298.211 | 280.201 | 281.200 | 149.607 | I | 344.254 | 326.242 | 327.227 | 172.627 | 3 |
| 4 | 72.081 | 397.276 | 379.271 | 380.254 | 199.141 | V | 231.169 | 213.159 | 214.162 | 116.085 | 2 |
| 5 | 86.097 | | | | | L | 132.101 | 114.091 | 115.075 | 66.551 | 1 |



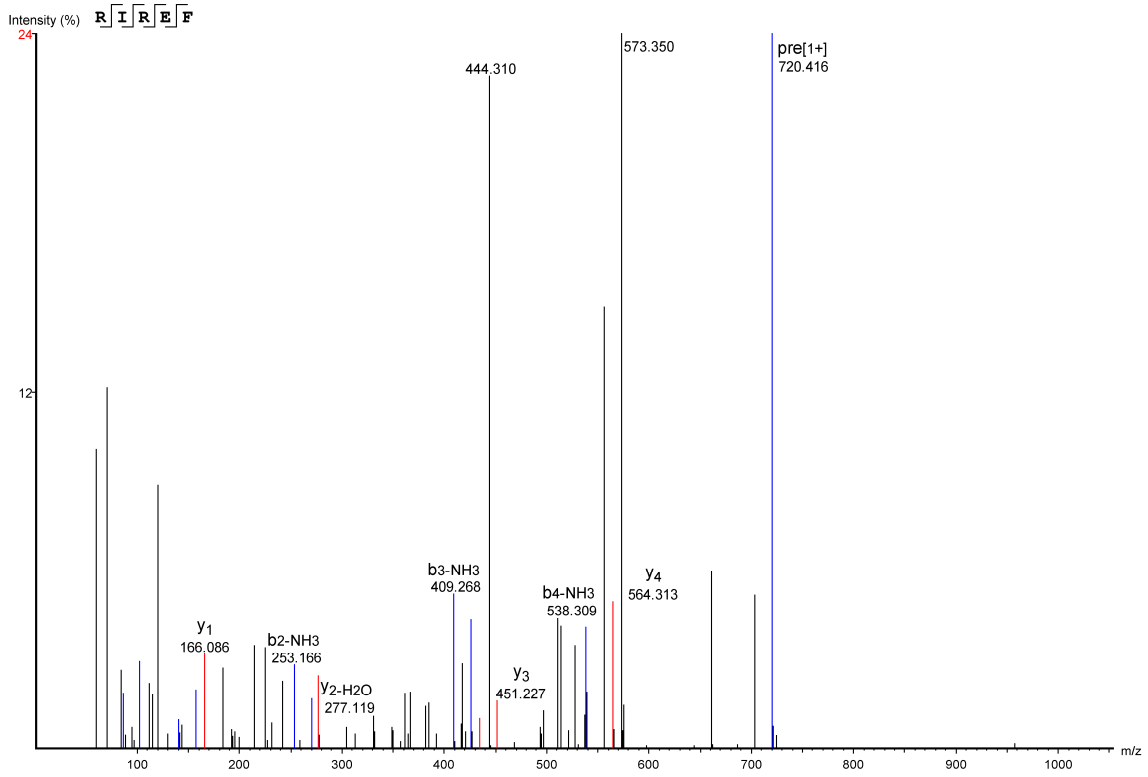
279–288, SHTNSVVNPF



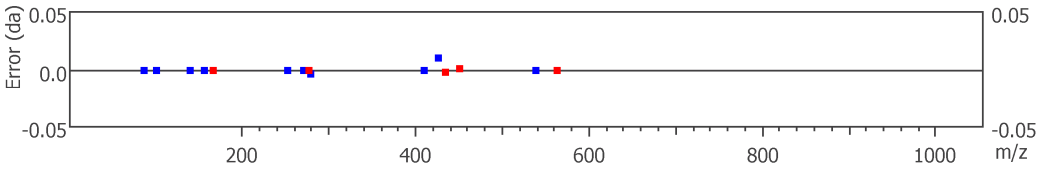

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 60.045 | 88.040 | 70.066 | 71.013 | 44.520 | S | | | | | 10 |
| 2 | 110.070 | 225.096 | 207.087 | 208.072 | 113.049 | H | 1014.500 | 996.490 | 997.473 | 507.750 | 9 |
| 3 | 74.061 | 326.147 | 308.132 | 309.119 | 163.573 | T | 877.441 | 859.431 | 860.414 | 439.221 | 8 |
| 4 | 87.056 | 440.186 | 422.174 | 423.181 | 220.595 | N | 776.394 | 758.383 | 759.367 | 388.697 | 7 |
| 5 | 60.045 | 527.221 | 509.205 | 510.194 | 264.138 | S | 662.351 | 644.340 | 645.324 | 331.675 | 6 |
| 6 | 72.080 | 626.287 | 608.273 | 609.291 | 313.652 | V | 575.319 | 557.308 | 558.292 | 288.159 | 5 |
| 7 | 72.081 | 725.352 | 707.351 | 708.319 | 363.173 | V | 476.250 | 458.240 | 459.223 | 238.625 | 4 |
| 8 | 87.056 | 839.396 | 821.398 | 822.379 | 420.190 | N | 377.178 | 359.170 | 360.154 | 189.091 | 3 |
| 9 | 70.066 | 936.454 | 918.443 | 919.427 | 468.731 | P | 263.138 | 245.128 | 246.112 | 132.069 | 2 |
| 10 | 120.081 | | | | | F | 166.086 | 148.076 | 149.059 | 83.543 | 1 |



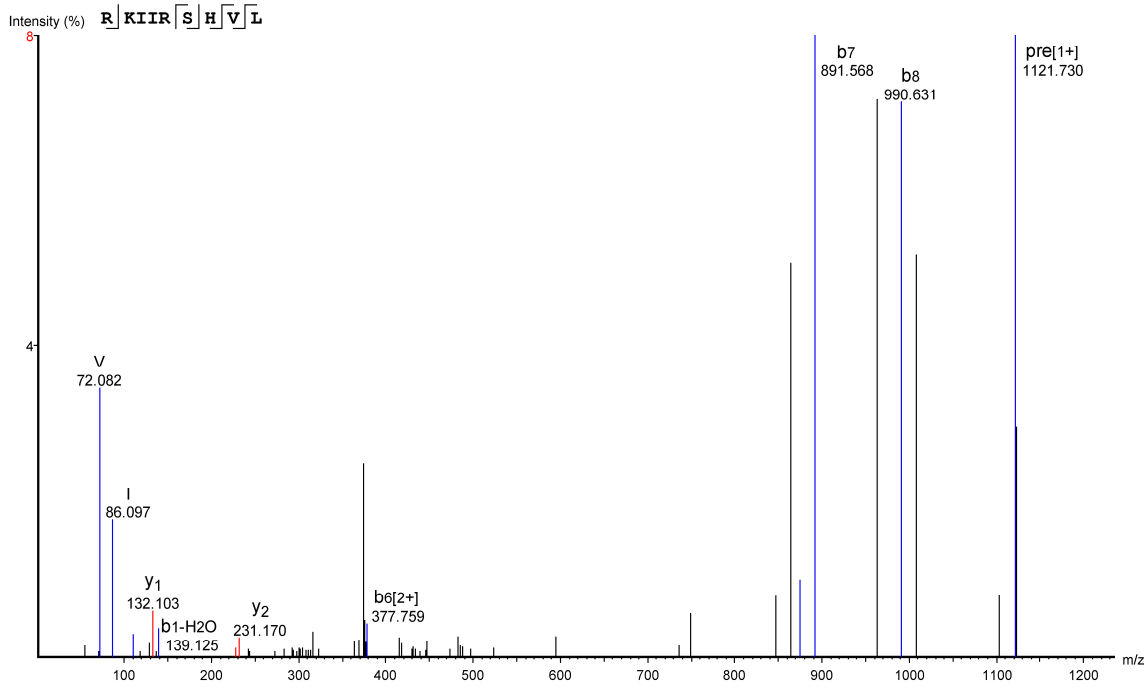
293–297, RIREF



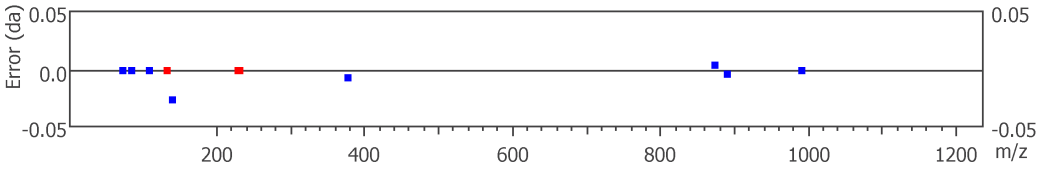

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 129.114 | 157.108 | 139.098 | 140.081 | 79.054 | R | | | | | 5 |
| 2 | 86.096 | 270.192 | 252.182 | 253.166 | 135.596 | I | 564.313 | 546.303 | 547.287 | 282.657 | 4 |
| 3 | 129.114 | 426.283 | 408.284 | 409.268 | 213.647 | R | 451.227 | 433.219 | 434.206 | 226.115 | 3 |
| 4 | 102.054 | 555.337 | 537.326 | 538.309 | 278.172 | E | 295.129 | 277.119 | 278.102 | 148.064 | 2 |
| 5 | 120.081 | | | | | F | 166.086 | 148.076 | 149.059 | 83.543 | 1 |



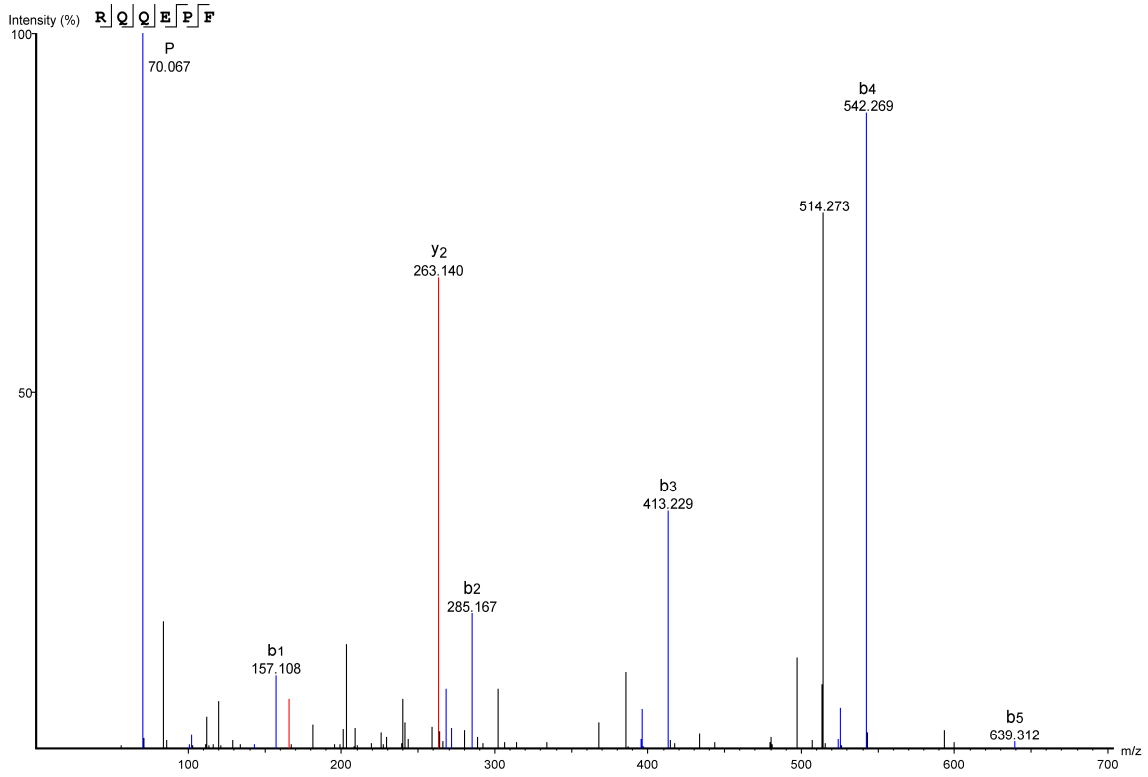
302–310, RKIIRSHVL



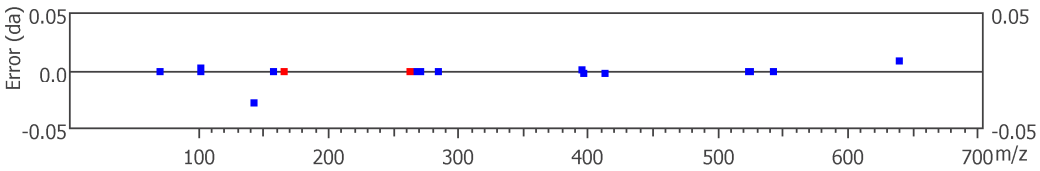

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 129.114 | 157.109 | 139.125 | 140.082 | 79.054 | R | | | | | 9 |
| 2 | 101.108 | 285.204 | 267.193 | 268.177 | 143.102 | K | 965.625 | 947.615 | 948.598 | 483.313 | 8 |
| 3 | 86.097 | 398.288 | 380.277 | 381.261 | 199.644 | I | 837.530 | 819.520 | 820.503 | 419.265 | 7 |
| 4 | 86.097 | 511.372 | 493.361 | 494.345 | 256.186 | I | 724.446 | 706.436 | 707.419 | 362.723 | 6 |
| 5 | 129.114 | 667.473 | 649.463 | 650.446 | 334.237 | R | 611.362 | 593.352 | 594.335 | 306.181 | 5 |
| 6 | 60.045 | 754.505 | 736.495 | 737.478 | 377.759 | S | 455.261 | 437.251 | 438.234 | 228.132 | 4 |
| 7 | 110.072 | 891.568 | 873.553 | 874.532 | 446.282 | H | 368.229 | 350.219 | 351.202 | 184.615 | 3 |
| 8 | 72.082 | 990.631 | 972.622 | 973.605 | 495.816 | V | 231.170 | 213.160 | 214.143 | 116.085 | 2 |
| 9 | 86.097 | | | | | L | 132.103 | 114.091 | 115.075 | 66.551 | 1 |



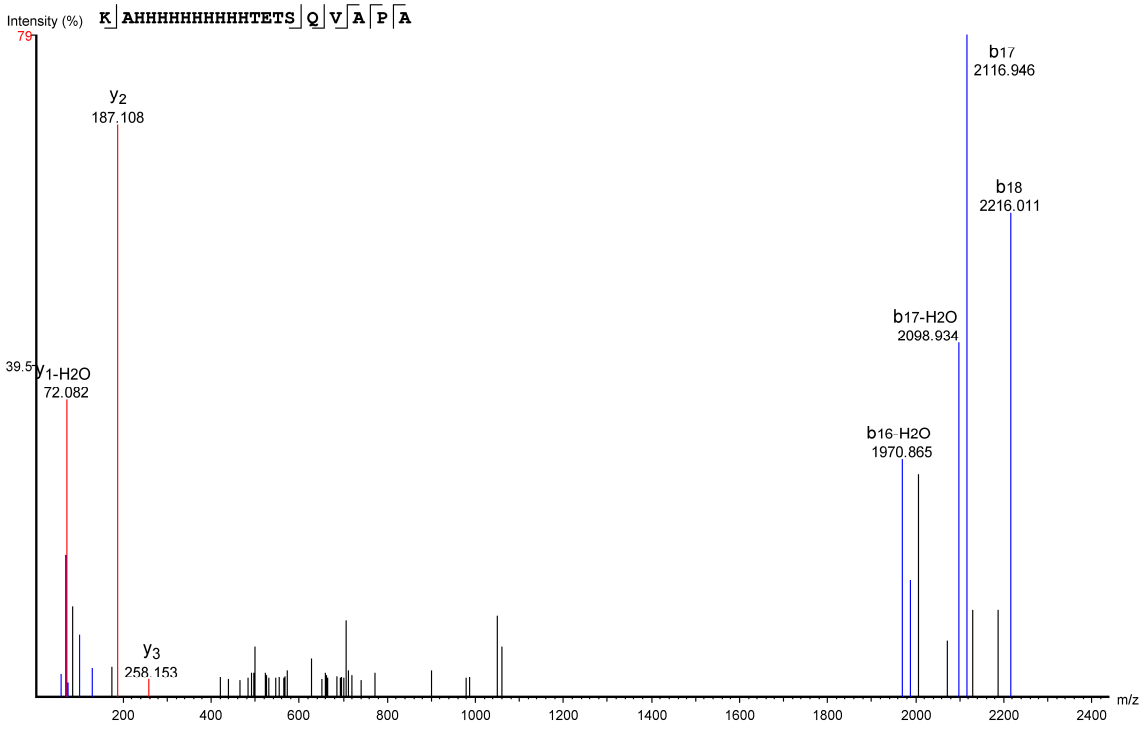
311–316, RQQEPF



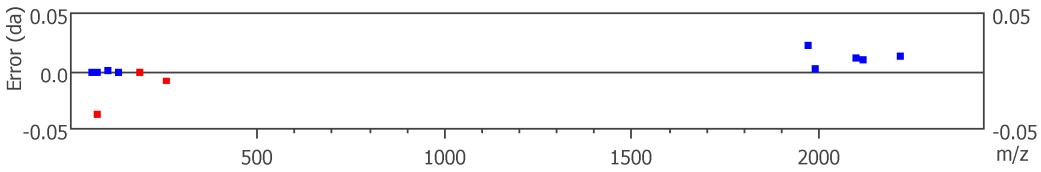

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 129.114 | 157.108 | 139.098 | 140.082 | 79.054 | R | | | | | 6 |
| 2 | 101.067 | 285.167 | 267.157 | 268.142 | 143.112 | Q | 648.299 | 630.288 | 631.272 | 324.649 | 5 |
| 3 | 101.071 | 413.229 | 395.213 | 396.202 | 207.113 | Q | 520.240 | 502.230 | 503.213 | 260.620 | 4 |
| 4 | 102.054 | 542.269 | 524.259 | 525.243 | 271.633 | E | 392.182 | 374.171 | 375.155 | 196.591 | 3 |
| 5 | 70.067 | 639.312 | 621.311 | 622.294 | 320.161 | P | 263.140 | 245.128 | 246.112 | 132.069 | 2 |
| 6 | 120.081 | | | | | F | 166.086 | 148.076 | 149.059 | 83.543 | 1 |



317–337, KAHHHHHHHHHHHTETSQVAPA



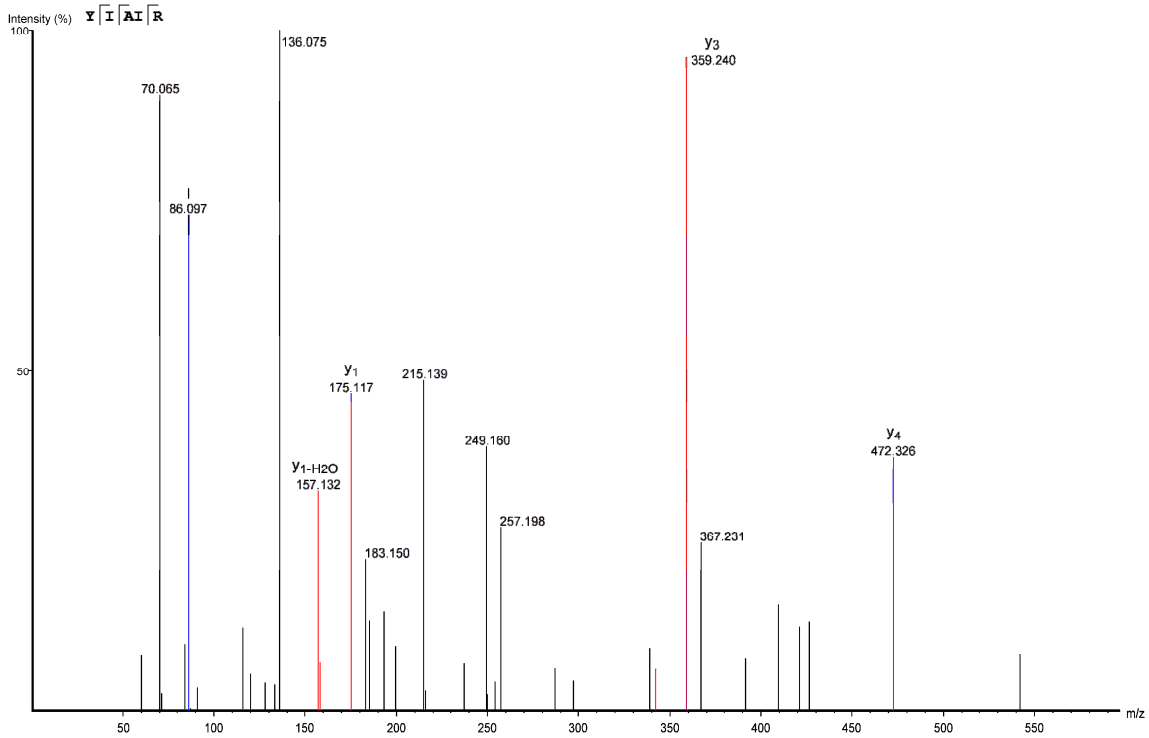
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 101.108 | 129.102 | 111.092 | 112.076 | 65.051 | K | | | | | 21 |
| 2 | 44.050 | 200.140 | 182.129 | 183.113 | 100.570 | A | 2345.068 | 2327.058 | 2328.041 | 1173.034 | 20 |
| 3 | 110.072 | 337.199 | 319.188 | 320.172 | 169.099 | H | 2274.031 | 2256.021 | 2257.004 | 1137.516 | 19 |
| 4 | 110.072 | 474.258 | 456.247 | 457.231 | 237.629 | H | 2136.972 | 2118.961 | 2119.945 | 1068.986 | 18 |
| 5 | 110.072 | 611.317 | 593.306 | 594.290 | 306.158 | H | 1999.913 | 1981.903 | 1982.886 | 1000.457 | 17 |
| 6 | 110.072 | 748.376 | 730.365 | 731.349 | 374.688 | H | 1862.854 | 1844.844 | 1845.827 | 931.927 | 16 |
| 7 | 110.072 | 885.434 | 867.424 | 868.407 | 443.217 | H | 1725.795 | 1707.785 | 1708.768 | 863.398 | 15 |
| 8 | 110.072 | 1022.493 | 1004.483 | 1005.466 | 511.747 | H | 1588.736 | 1570.726 | 1571.709 | 794.868 | 14 |
| 9 | 110.072 | 1159.552 | 1141.542 | 1142.525 | 580.276 | H | 1451.677 | 1433.667 | 1434.651 | 726.339 | 13 |
| 10 | 110.072 | 1296.611 | 1278.601 | 1279.584 | 648.806 | H | 1314.619 | 1296.608 | 1297.592 | 657.809 | 12 |
| 11 | 110.072 | 1433.670 | 1415.660 | 1416.643 | 717.335 | H | 1177.560 | 1159.549 | 1160.533 | 589.280 | 11 |
| 12 | 110.072 | 1570.729 | 1552.719 | 1553.702 | 785.865 | H | 1040.501 | 1022.490 | 1023.474 | 520.750 | 10 |
| 13 | 74.060 | 1671.777 | 1653.766 | 1654.750 | 836.388 | T | 903.442 | 885.431 | 886.415 | 452.221 | 9 |
| 14 | 102.055 | 1800.819 | 1782.809 | 1783.792 | 900.910 | E | 802.394 | 784.384 | 785.367 | 401.697 | 8 |
| 15 | 74.061 | 1901.867 | 1883.856 | 1884.840 | 951.433 | T | 673.352 | 655.341 | 656.325 | 337.176 | 7 |
| 16 | 60.045 | 1988.895 | 1970.865 | 1971.872 | 994.950 | S | 572.304 | 554.293 | 555.277 | 286.652 | 6 |
| 17 | 101.069 | 2116.946 | 2098.934 | 2099.930 | 1058.979 | Q | 485.272 | 467.261 | 468.245 | 243.136 | 5 |
| 18 | 72.082 | 2216.011 | 2198.015 | 2198.999 | 1108.513 | V | 357.213 | 339.203 | 340.186 | 179.107 | 4 |
| 19 | 44.050 | 2287.063 | 2269.052 | 2270.036 | 1144.031 | A | 258.153 | 240.134 | 241.118 | 129.572 | 3 |
| 20 | 70.065 | 2384.116 | 2366.105 | 2367.089 | 1192.558 | P | 187.108 | 169.097 | 170.081 | 94.054 | 2 |
| 21 | 44.050 | | | | | A | 90.055 | 72.082 | 73.028 | 45.527 | 1 |



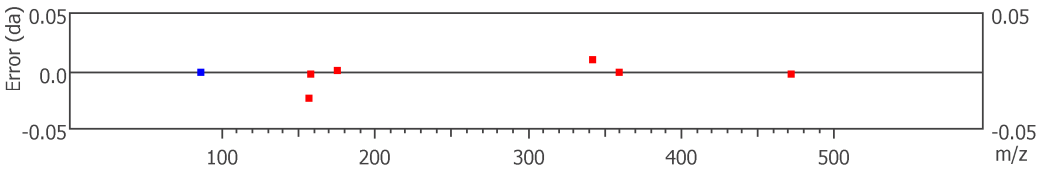
## 4. MS/MS Spectra for tryptic peptides of $hA_{2A}AR$.

Carbamidomethylcysteines are designated in lower case in all figures.

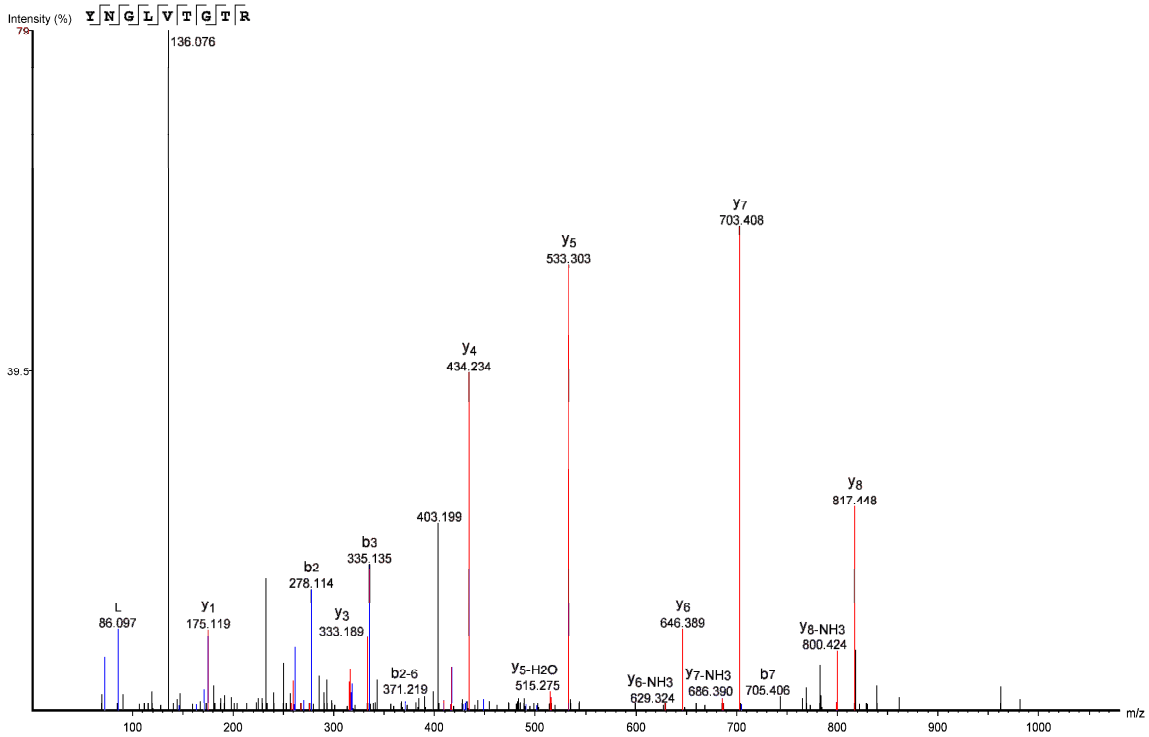
105–109, YIAIR



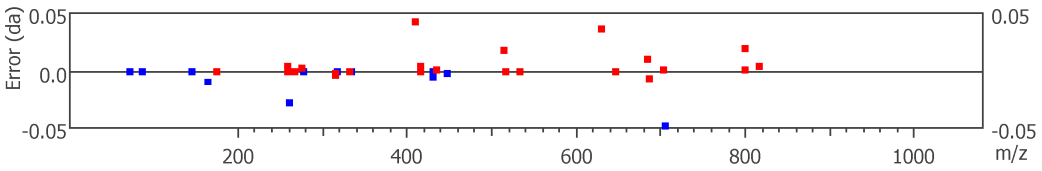

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 136.076 | 164.071 | 146.061 | 147.044 | 82.536 | Y | | | | | 5 |
| 2 | 86.097 | 277.155 | 259.145 | 260.128 | 139.078 | I | 472.326 | 454.314 | 455.297 | 236.662 | 4 |
| 3 | 44.050 | 348.192 | 330.182 | 331.165 | 174.596 | A | 359.240 | 341.230 | 342.202 | 180.120 | 3 |
| 4 | 86.097 | 461.276 | 443.266 | 444.249 | 231.138 | I | 288.203 | 270.192 | 271.176 | 144.602 | 2 |
| 5 | 129.114 | | | | | R | 175.117 | 157.132 | 158.095 | 88.059 | 1 |



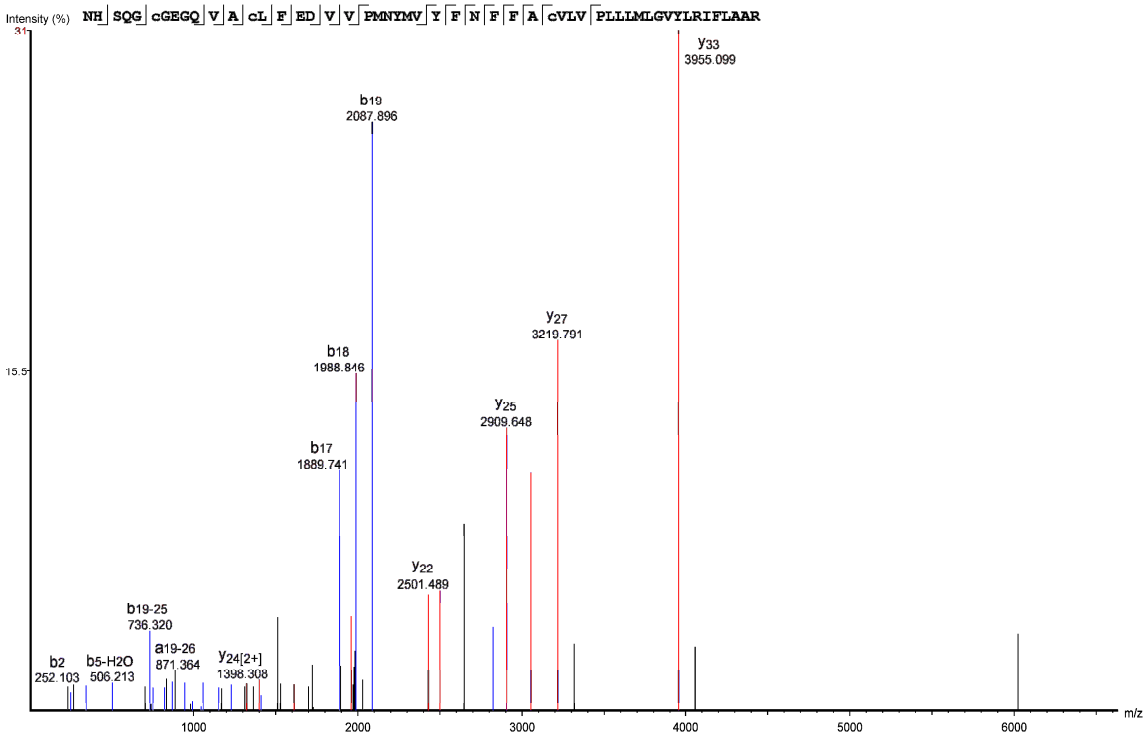
114–122, YNGLVTGTR



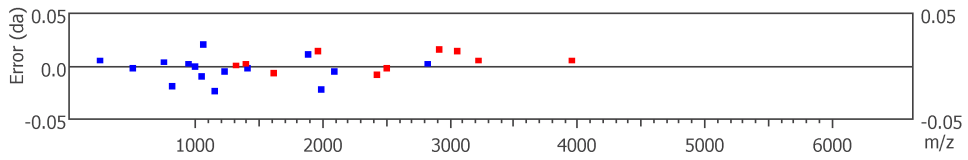

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 136.076 | 164.081 | 146.061 | 147.044 | 82.536 | Y | | | | | 9 |
| 2 | 87.056 | 278.114 | 260.132 | 261.087 | 139.557 | N | 817.448 | 799.421 | 800.424 | 409.182 | 8 |
| 3 | 30.034 | 335.135 | 317.126 | 318.110 | 168.068 | G | 703.408 | 685.387 | 686.390 | 352.205 | 7 |
| 4 | 86.097 | 448.222 | 430.214 | 431.192 | 224.610 | L | 646.389 | 628.378 | 629.324 | 323.694 | 6 |
| 5 | 72.082 | 547.288 | 529.277 | 530.261 | 274.144 | V | 533.303 | 515.275 | 516.278 | 267.151 | 5 |
| 6 | 74.061 | 648.336 | 630.325 | 631.309 | 324.668 | T | 434.234 | 416.220 | 417.208 | 217.618 | 4 |
| 7 | 30.034 | 705.406 | 687.347 | 688.330 | 353.179 | G | 333.189 | 315.182 | 316.163 | 167.094 | 3 |
| 8 | 74.061 | 806.405 | 788.394 | 789.378 | 403.702 | T | 276.163 | 258.150 | 259.140 | 138.583 | 2 |
| 9 | 129.114 | | | | | R | 175.119 | 157.108 | 158.092 | 88.059 | 1 |



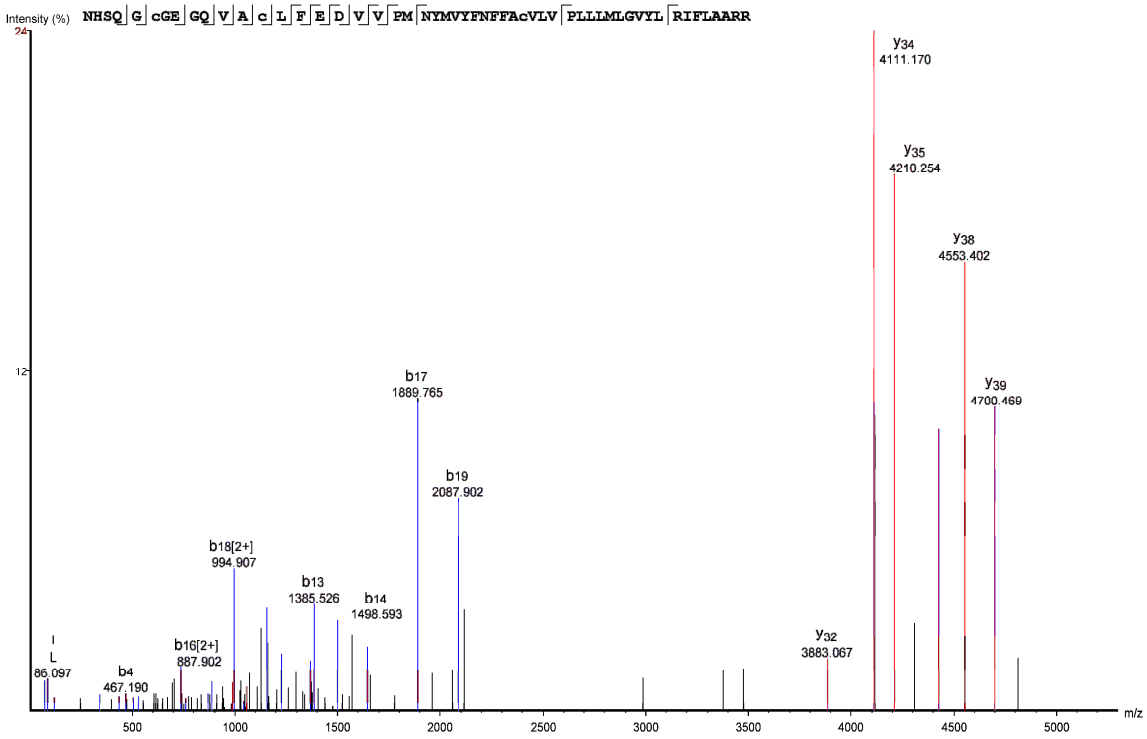
156–207, NHSQGcGEGQVAcLFEDVVPMNYMVYFNFFAcVLVPLLLMLGVYLRIFLAAR



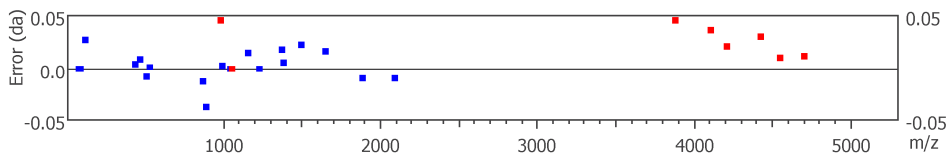
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 87.056 | 115.051 | 97.040 | 98.024 | 58.025 | N | | | | | 52 |
| 2 | 110.072 | 252.103 | 234.099 | 235.083 | 126.555 | H | 5927.947 | 5909.937 | 5910.920 | 2964.474 | 51 |
| 3 | 60.045 | 339.142 | 321.131 | 322.115 | 170.071 | S | 5790.888 | 5772.877 | 5773.861 | 2895.944 | 50 |
| 4 | 101.071 | 467.200 | 449.190 | 450.173 | 234.100 | Q | 5703.856 | 5685.845 | 5686.829 | 2852.428 | 49 |
| 5 | 30.034 | 524.222 | 506.213 | 507.195 | 262.611 | G | 5575.797 | 5557.787 | 5558.770 | 2788.399 | 48 |
| 6 | 133.043 | 684.252 | 666.242 | 667.225 | 342.626 | C(+57.02) | 5518.776 | 5500.765 | 5501.749 | 2759.888 | 47 |
| 7 | 30.034 | 741.274 | 723.263 | 724.247 | 371.137 | G | 5358.746 | 5340.735 | 5341.718 | 2679.873 | 46 |
| 8 | 102.055 | 870.316 | 852.306 | 853.289 | 435.658 | E | 5301.724 | 5283.713 | 5284.697 | 2651.362 | 45 |
| 9 | 30.034 | 927.338 | 909.327 | 910.311 | 464.169 | G | 5172.681 | 5154.670 | 5155.654 | 2586.841 | 44 |
| 10 | 101.071 | 1055.374 | 1037.386 | 1038.370 | 528.198 | Q | 5115.660 | 5097.649 | 5098.632 | 2558.330 | 43 |
| 11 | 72.081 | 1154.489 | 1136.454 | 1137.438 | 577.732 | V | 4987.601 | 4969.590 | 4970.574 | 2494.301 | 42 |
| 12 | 44.050 | 1225.507 | 1207.491 | 1208.475 | 613.251 | A | 4888.533 | 4870.522 | 4871.505 | 2444.766 | 41 |
| 13 | 133.043 | 1385.533 | 1367.522 | 1368.506 | 693.266 | C(+57.02) | 4817.496 | 4799.485 | 4800.468 | 2409.248 | 40 |
| 14 | 86.097 | 1498.617 | 1480.606 | 1481.590 | 749.803 | L | 4657.465 | 4639.455 | 4640.438 | 2329.233 | 39 |
| 15 | 120.081 | 1645.685 | 1627.675 | 1628.658 | 823.362 | F | 4544.381 | 4526.370 | 4527.354 | 2272.690 | 38 |
| 16 | 102.055 | 1774.728 | 1756.717 | 1757.701 | 887.864 | E | 4397.312 | 4379.302 | 4380.285 | 2199.156 | 37 |
| 17 | 88.040 | 1889.741 | 1871.744 | 1872.728 | 945.374 | D | 4268.270 | 4250.259 | 4251.243 | 2134.635 | 36 |
| 18 | 72.081 | 1988.846 | 1970.812 | 1971.796 | 994.910 | V | 4153.243 | 4135.232 | 4136.216 | 2077.122 | 35 |
| 19 | 72.081 | 2087.896 | 2069.881 | 2070.864 | 1044.455 | V | 4054.175 | 4036.164 | 4037.147 | 2027.587 | 34 |
| 20 | 70.066 | 2184.944 | 2166.934 | 2167.917 | 1092.972 | P | 3955.099 | 3937.095 | 3938.079 | 1978.053 | 33 |
| 21 | 104.053 | 2315.985 | 2297.974 | 2298.958 | 1158.492 | M | 3858.053 | 3840.043 | 3841.026 | 1929.527 | 32 |
| 22 | 87.056 | 2430.028 | 2412.017 | 2413.000 | 1215.514 | N | 3727.013 | 3709.002 | 3709.986 | 1864.006 | 31 |
| 23 | 136.076 | 2593.091 | 2575.081 | 2576.064 | 1297.046 | Y | 3612.970 | 3594.959 | 3595.943 | 1806.985 | 30 |
| 24 | 104.053 | 2724.131 | 2706.121 | 2707.104 | 1362.566 | M | 3449.906 | 3431.896 | 3432.879 | 1725.453 | 29 |
| 25 | 72.081 | 2823.196 | 2805.189 | 2806.173 | 1412.102 | V | 3318.866 | 3300.855 | 3301.839 | 1659.933 | 28 |
| 26 | 136.076 | 2986.263 | 2968.253 | 2969.236 | 1493.632 | Y | 3219.791 | 3201.787 | 3202.771 | 1610.406 | 27 |
| 27 | 120.081 | 3133.332 | 3115.321 | 3116.304 | 1567.166 | F | 3056.718 | 3038.724 | 3039.707 | 1528.867 | 26 |
| 28 | 87.056 | 3247.375 | 3229.364 | 3230.347 | 1624.187 | N | 2909.648 | 2891.656 | 2892.639 | 1455.333 | 25 |
| 29 | 120.081 | 3394.443 | 3376.432 | 3377.416 | 1697.721 | F | 2795.623 | 2777.613 | 2778.596 | 1398.308 | 24 |
| 30 | 120.081 | 3541.511 | 3523.501 | 3524.484 | 1771.256 | F | 2648.555 | 2630.544 | 2631.528 | 1324.775 | 23 |
| 31 | 44.050 | 3612.548 | 3594.538 | 3595.521 | 1806.774 | A | 2501.489 | 2483.476 | 2484.459 | 1251.243 | 22 |
| 32 | 133.043 | 3772.579 | 3754.569 | 3755.552 | 1886.790 | C(+57.02) | 2430.458 | 2412.438 | 2413.422 | 1215.724 | 21 |
| 33 | 72.081 | 3871.647 | 3853.637 | 3854.620 | 1936.324 | V | 2270.418 | 2252.408 | 2253.391 | 1135.709 | 20 |
| 34 | 86.097 | 3984.732 | 3966.721 | 3967.705 | 1992.866 | L | 2171.350 | 2153.340 | 2154.323 | 1086.175 | 19 |
| 35 | 72.081 | 4083.800 | 4065.790 | 4066.773 | 2042.400 | V | 2058.266 | 2040.255 | 2041.239 | 1029.633 | 18 |
| 36 | 70.066 | 4180.853 | 4162.842 | 4163.826 | 2090.926 | P | 1959.182 | 1941.187 | 1942.171 | 980.099 | 17 |
| 37 | 86.097 | 4293.937 | 4275.926 | 4276.910 | 2147.469 | L | 1862.145 | 1844.134 | 1845.118 | 931.572 | 16 |
| 38 | 86.097 | 4407.021 | 4389.010 | 4389.994 | 2204.010 | L | 1749.061 | 1731.050 | 1732.034 | 875.030 | 15 |
| 39 | 86.097 | 4520.105 | 4502.094 | 4503.078 | 2260.552 | L | 1635.977 | 1617.966 | 1618.950 | 818.488 | 14 |
| 40 | 104.053 | 4651.146 | 4633.135 | 4634.119 | 2326.073 | M | 1522.893 | 1504.882 | 1505.866 | 761.946 | 13 |
| 41 | 86.097 | 4764.229 | 4746.219 | 4747.203 | 2382.615 | L | 1391.852 | 1373.842 | 1374.825 | 696.426 | 12 |
| 42 | 30.034 | 4821.251 | 4803.240 | 4804.224 | 2411.125 | G | 1278.768 | 1260.758 | 1261.741 | 639.884 | 11 |
| 43 | 72.081 | 4920.319 | 4902.309 | 4903.292 | 2460.660 | V | 1221.747 | 1203.736 | 1204.720 | 611.373 | 10 |
| 44 | 136.076 | 5083.383 | 5065.372 | 5066.356 | 2542.191 | Y | 1122.678 | 1104.668 | 1105.651 | 561.839 | 9 |
| 45 | 86.097 | 5196.467 | 5178.456 | 5179.440 | 2598.733 | L | 959.615 | 941.604 | 942.588 | 480.307 | 8 |
| 46 | 129.114 | 5352.568 | 5334.557 | 5335.541 | 2676.784 | R | 846.531 | 828.520 | 829.504 | 423.765 | 7 |
| 47 | 86.097 | 5465.652 | 5447.641 | 5448.625 | 2733.326 | I | 690.430 | 672.419 | 673.403 | 345.715 | 6 |
| 48 | 120.081 | 5612.720 | 5594.709 | 5595.693 | 2806.860 | F | 577.346 | 559.335 | 560.319 | 289.173 | 5 |
| 49 | 86.097 | 5725.804 | 5707.793 | 5708.777 | 2863.402 | L | 430.277 | 412.267 | 413.250 | 215.639 | 4 |
| 50 | 44.050 | 5796.841 | 5778.831 | 5779.814 | 2898.921 | A | 317.193 | 299.183 | 300.166 | 159.097 | 3 |
| 51 | 44.050 | 5867.878 | 5849.868 | 5850.852 | 2934.439 | A | 246.156 | 228.145 | 229.129 | 123.578 | 2 |
| 52 | 129.114 | | | | | R | 175.119 | 157.108 | 158.092 | 88.059 | 1 |



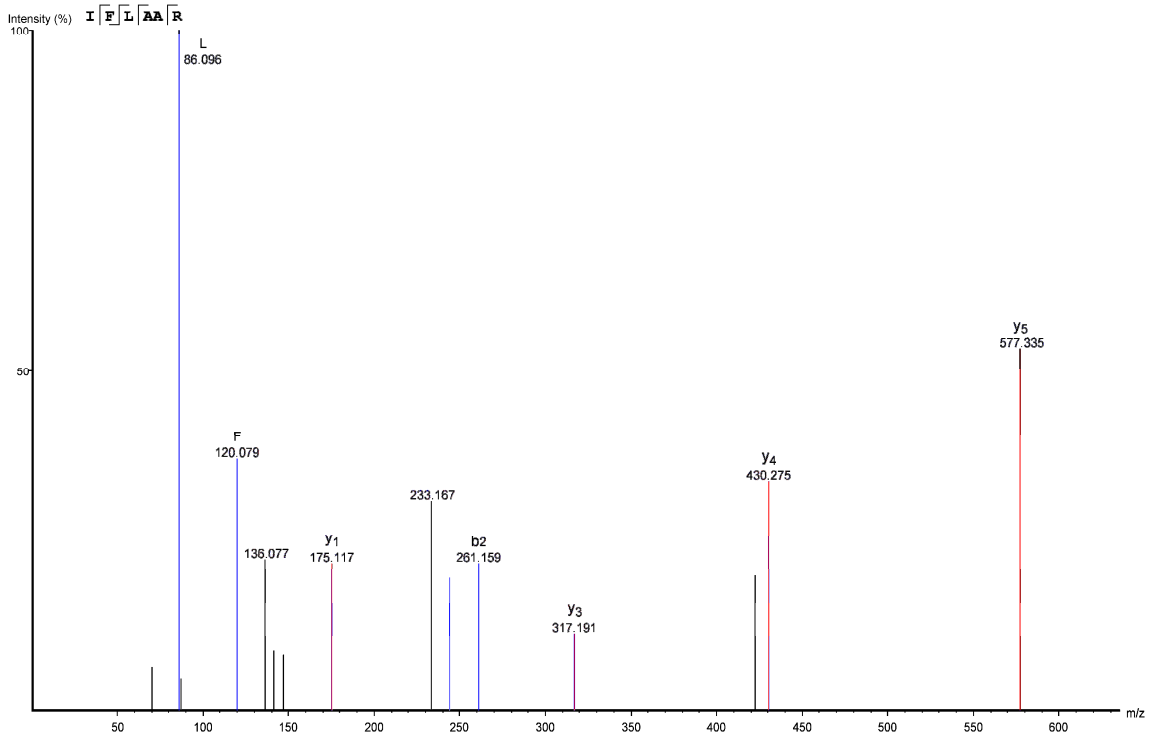
156–208, NHSQGcGEGQVAcLFEDVVPMNYMVYFNFFAcVLVPLLLMLGVYLRIFLAARR



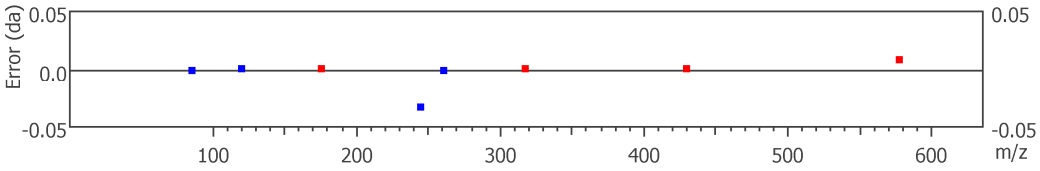
| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 87.056 | 115.051 | 97.040 | 98.024 | 58.025 | N | | | | | 53 |
| 2 | 110.072 | 252.110 | 234.099 | 235.083 | 126.555 | H | 6084.048 | 6066.038 | 6067.021 | 3042.524 | 52 |
| 3 | 60.045 | 339.142 | 321.131 | 322.115 | 170.071 | S | 5946.989 | 5928.979 | 5929.962 | 2973.995 | 51 |
| 4 | 101.071 | 467.190 | 449.190 | 450.173 | 234.100 | Q | 5859.957 | 5841.946 | 5842.930 | 2930.479 | 50 |
| 5 | 30.034 | 524.222 | 506.219 | 507.195 | 262.611 | G | 5731.898 | 5713.888 | 5714.871 | 2866.449 | 49 |
| 6 | 133.043 | 684.252 | 666.242 | 667.225 | 342.626 | C(+57.02) | 5674.877 | 5656.866 | 5657.850 | 2837.938 | 48 |
| 7 | 30.034 | 741.274 | 723.263 | 724.247 | 371.137 | G | 5514.847 | 5496.836 | 5497.819 | 2757.923 | 47 |
| 8 | 102.055 | 870.330 | 852.306 | 853.289 | 435.653 | E | 5457.825 | 5439.814 | 5440.798 | 2729.413 | 46 |
| 9 | 30.034 | 927.338 | 909.327 | 910.311 | 464.169 | G | 5328.782 | 5310.771 | 5311.755 | 2664.891 | 45 |
| 10 | 101.071 | 1055.396 | 1037.386 | 1038.370 | 528.196 | Q | 5271.761 | 5253.750 | 5254.734 | 2636.381 | 44 |
| 11 | 72.081 | 1154.448 | 1136.454 | 1137.438 | 577.732 | V | 5143.703 | 5125.692 | 5126.675 | 2572.351 | 43 |
| 12 | 44.050 | 1225.501 | 1207.491 | 1208.475 | 613.251 | A | 5044.634 | 5026.623 | 5027.606 | 2522.817 | 42 |
| 13 | 133.043 | 1385.526 | 1367.522 | 1368.486 | 693.266 | C(+57.02) | 4973.597 | 4955.586 | 4956.569 | 2487.298 | 41 |
| 14 | 86.097 | 1498.593 | 1480.606 | 1481.590 | 749.808 | L | 4813.566 | 4795.556 | 4796.539 | 2407.283 | 40 |
| 15 | 120.053 | 1645.668 | 1627.675 | 1628.658 | 823.343 | F | 4700.469 | 4682.471 | 4683.455 | 2350.741 | 39 |
| 16 | 102.055 | 1774.728 | 1756.717 | 1757.701 | 887.902 | E | 4553.402 | 4535.403 | 4536.386 | 2277.207 | 38 |
| 17 | 88.040 | 1889.765 | 1871.744 | 1872.728 | 945.377 | D | 4424.340 | 4406.360 | 4407.344 | 2212.686 | 37 |
| 18 | 72.081 | 1988.823 | 1970.812 | 1971.796 | 994.907 | V | 4309.344 | 4291.333 | 4292.317 | 2155.172 | 36 |
| 19 | 72.081 | 2087.902 | 2069.881 | 2070.864 | 1044.445 | V | 4210.254 | 4192.265 | 4193.249 | 2105.638 | 35 |
| 20 | 70.066 | 2184.944 | 2166.934 | 2167.917 | 1092.972 | P | 4111.170 | 4093.197 | 4094.180 | 2056.104 | 34 |
| 21 | 104.053 | 2315.985 | 2297.974 | 2298.958 | 1158.492 | M | 4014.155 | 3996.144 | 3997.127 | 2007.577 | 33 |
| 22 | 87.056 | 2430.028 | 2412.017 | 2413.000 | 1215.514 | N | 3883.067 | 3865.104 | 3866.087 | 1942.057 | 32 |
| 23 | 136.076 | 2593.091 | 2575.081 | 2576.064 | 1297.046 | Y | 3769.071 | 3751.061 | 3752.044 | 1885.036 | 31 |
| 24 | 104.053 | 2724.131 | 2706.121 | 2707.104 | 1362.566 | M | 3606.008 | 3587.997 | 3588.980 | 1803.504 | 30 |
| 25 | 72.081 | 2823.200 | 2805.189 | 2806.173 | 1412.100 | V | 3474.967 | 3456.957 | 3457.940 | 1737.984 | 29 |
| 26 | 136.076 | 2986.263 | 2968.253 | 2969.236 | 1493.632 | Y | 3375.899 | 3357.888 | 3358.872 | 1688.449 | 28 |
| 27 | 120.081 | 3133.332 | 3115.321 | 3116.304 | 1567.166 | F | 3212.835 | 3194.825 | 3195.808 | 1606.918 | 27 |
| 28 | 87.056 | 3247.375 | 3229.364 | 3230.347 | 1624.187 | N | 3065.767 | 3047.757 | 3048.740 | 1533.384 | 26 |
| 29 | 120.081 | 3394.443 | 3376.432 | 3377.416 | 1697.721 | F | 2951.724 | 2933.714 | 2934.697 | 1476.362 | 25 |
| 30 | 120.081 | 3541.511 | 3523.501 | 3524.484 | 1771.256 | F | 2804.656 | 2786.645 | 2787.629 | 1402.828 | 24 |
| 31 | 44.050 | 3612.548 | 3594.538 | 3595.521 | 1806.774 | A | 2657.587 | 2639.577 | 2640.560 | 1329.294 | 23 |
| 32 | 133.043 | 3772.579 | 3754.569 | 3755.552 | 1886.790 | C(+57.02) | 2586.550 | 2568.540 | 2569.523 | 1293.775 | 22 |
| 33 | 72.081 | 3871.647 | 3853.637 | 3854.620 | 1936.324 | V | 2426.520 | 2408.509 | 2409.492 | 1213.760 | 21 |
| 34 | 86.097 | 3984.732 | 3966.721 | 3967.705 | 1992.866 | L | 2327.451 | 2309.441 | 2310.424 | 1164.226 | 20 |
| 35 | 72.081 | 4083.800 | 4065.790 | 4066.773 | 2042.400 | V | 2214.367 | 2196.356 | 2197.340 | 1107.683 | 19 |
| 36 | 70.066 | 4180.853 | 4162.842 | 4163.826 | 2090.926 | P | 2115.299 | 2097.288 | 2098.271 | 1058.150 | 18 |
| 37 | 86.097 | 4293.937 | 4275.926 | 4276.910 | 2147.469 | L | 2018.246 | 2000.235 | 2001.219 | 1009.623 | 17 |
| 38 | 86.097 | 4407.021 | 4389.010 | 4389.994 | 2204.010 | L | 1905.162 | 1887.151 | 1888.135 | 953.081 | 16 |
| 39 | 86.097 | 4520.105 | 4502.094 | 4503.078 | 2260.552 | L | 1792.078 | 1774.067 | 1775.051 | 896.539 | 15 |
| 40 | 104.053 | 4651.146 | 4633.135 | 4634.119 | 2326.073 | M | 1678.994 | 1660.983 | 1661.967 | 839.997 | 14 |
| 41 | 86.097 | 4764.229 | 4746.219 | 4747.203 | 2382.615 | L | 1547.953 | 1529.943 | 1530.926 | 774.477 | 13 |
| 42 | 30.034 | 4821.251 | 4803.240 | 4804.224 | 2411.125 | G | 1434.869 | 1416.859 | 1417.842 | 717.935 | 12 |
| 43 | 72.081 | 4920.319 | 4902.309 | 4903.292 | 2460.660 | V | 1377.848 | 1359.837 | 1360.821 | 689.424 | 11 |
| 44 | 136.076 | 5083.383 | 5065.372 | 5066.356 | 2542.191 | Y | 1278.779 | 1260.769 | 1261.752 | 639.890 | 10 |
| 45 | 86.097 | 5196.467 | 5178.456 | 5179.440 | 2598.733 | L | 1115.716 | 1097.705 | 1098.689 | 558.358 | 9 |
| 46 | 129.114 | 5352.568 | 5334.557 | 5335.541 | 2676.784 | R | 1002.632 | 984.574 | 985.605 | 501.816 | 8 |
| 47 | 86.097 | 5465.652 | 5447.641 | 5448.625 | 2733.326 | I | 846.531 | 828.520 | 829.504 | 423.765 | 7 |
| 48 | 120.081 | 5612.720 | 5594.709 | 5595.693 | 2806.860 | F | 733.447 | 715.436 | 716.420 | 367.223 | 6 |
| 49 | 86.097 | 5725.804 | 5707.793 | 5708.777 | 2863.402 | L | 586.378 | 568.368 | 569.351 | 293.689 | 5 |
| 50 | 44.050 | 5796.841 | 5778.831 | 5779.814 | 2898.921 | A | 473.294 | 455.284 | 456.267 | 237.147 | 4 |
| 51 | 44.050 | 5867.878 | 5849.868 | 5850.852 | 2934.439 | A | 402.257 | 384.247 | 385.230 | 201.629 | 3 |
| 52 | 129.114 | 6023.979 | 6005.969 | 6006.953 | 3012.490 | R | 331.220 | 313.209 | 314.193 | 166.110 | 2 |
| 53 | 129.114 | | | | | R | 175.119 | 157.108 | 158.092 | 88.059 | 1 |



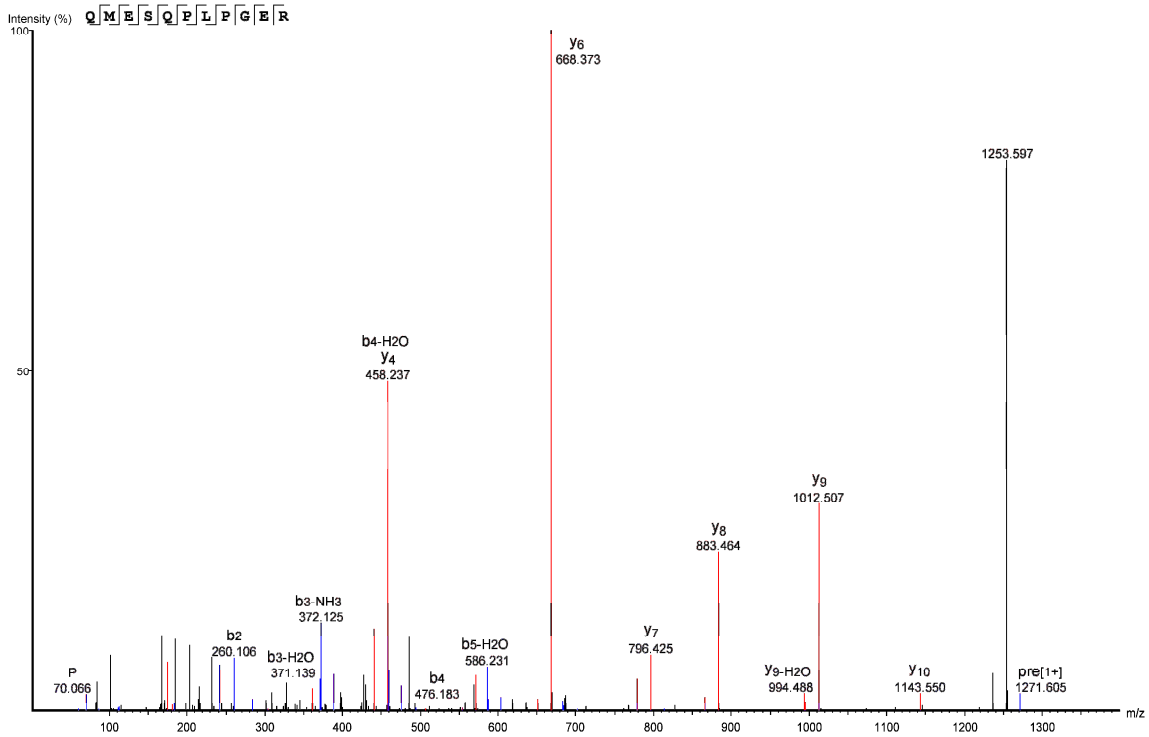
202–207, IFLAAR



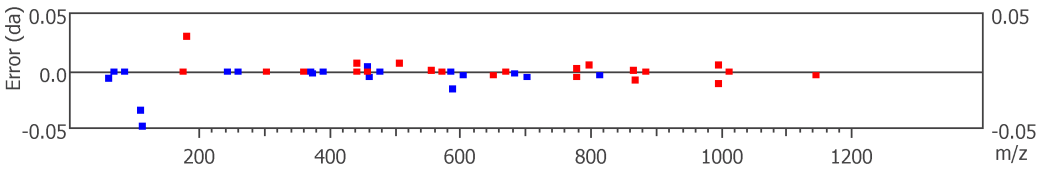

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 86.097 | 114.092 | 96.081 | 97.065 | 57.546 | I | | | | | 6 |
| 2 | 120.079 | 261.159 | 243.150 | 244.166 | 131.080 | F | 577.335 | 559.335 | 560.319 | 289.173 | 5 |
| 3 | 86.096 | 374.244 | 356.234 | 357.217 | 187.622 | L | 430.275 | 412.267 | 413.250 | 215.639 | 4 |
| 4 | 44.050 | 445.281 | 427.271 | 428.254 | 223.141 | A | 317.191 | 299.183 | 300.166 | 159.097 | 3 |
| 5 | 44.050 | 516.319 | 498.308 | 499.292 | 258.659 | A | 246.156 | 228.145 | 229.129 | 123.578 | 2 |
| 6 | 129.114 | | | | | R | 175.117 | 157.108 | 158.092 | 88.059 | 1 |



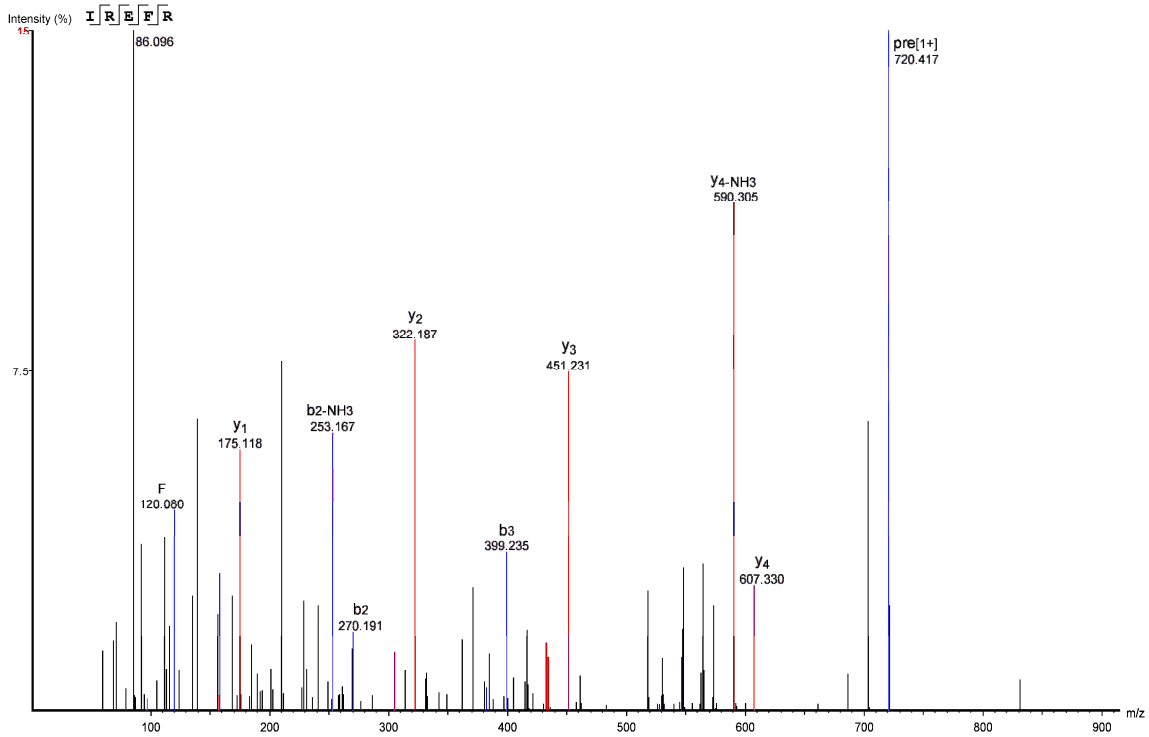
212–222, QMESQPLPGER



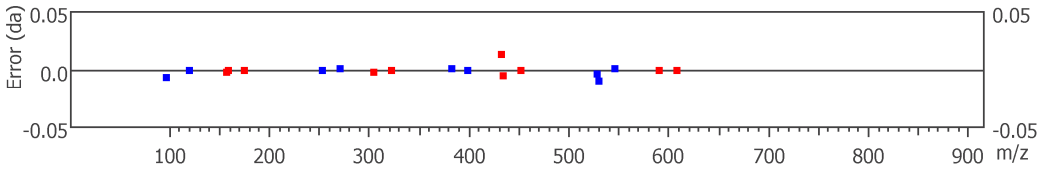

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 101.071 | 129.066 | 111.090 | 112.088 | 65.033 | Q | | | | | 11 |
| 2 | 104.053 | 260.106 | 242.096 | 243.080 | 130.553 | M | 1143.550 | 1125.536 | 1126.519 | 572.273 | 10 |
| 3 | 102.055 | 389.150 | 371.139 | 372.125 | 195.075 | E | 1012.507 | 994.488 | 995.491 | 506.744 | 9 |
| 4 | 60.052 | 476.183 | 458.166 | 459.160 | 238.591 | S | 883.464 | 865.451 | 866.445 | 442.232 | 8 |
| 5 | 101.071 | 604.244 | 586.231 | 587.230 | 302.620 | Q | 796.425 | 778.417 | 779.409 | 398.716 | 7 |
| 6 | 70.066 | 701.298 | 683.285 | 684.268 | 351.146 | P | 668.373 | 650.362 | 651.350 | 334.686 | 6 |
| 7 | 86.098 | 814.381 | 796.366 | 797.350 | 407.688 | L | 571.320 | 553.309 | 554.291 | 286.160 | 5 |
| 8 | 70.066 | 911.430 | 893.419 | 894.403 | 456.215 | P | 458.237 | 440.217 | 441.209 | 229.618 | 4 |
| 9 | 30.034 | 968.451 | 950.441 | 951.424 | 484.726 | G | 361.182 | 343.172 | 344.156 | 181.060 | 3 |
| 10 | 102.055 | 1097.494 | 1079.483 | 1080.467 | 549.247 | E | 304.162 | 286.151 | 287.135 | 152.581 | 2 |
| 11 | 129.114 | | | | | R | 175.118 | 157.108 | 158.092 | 88.059 | 1 |



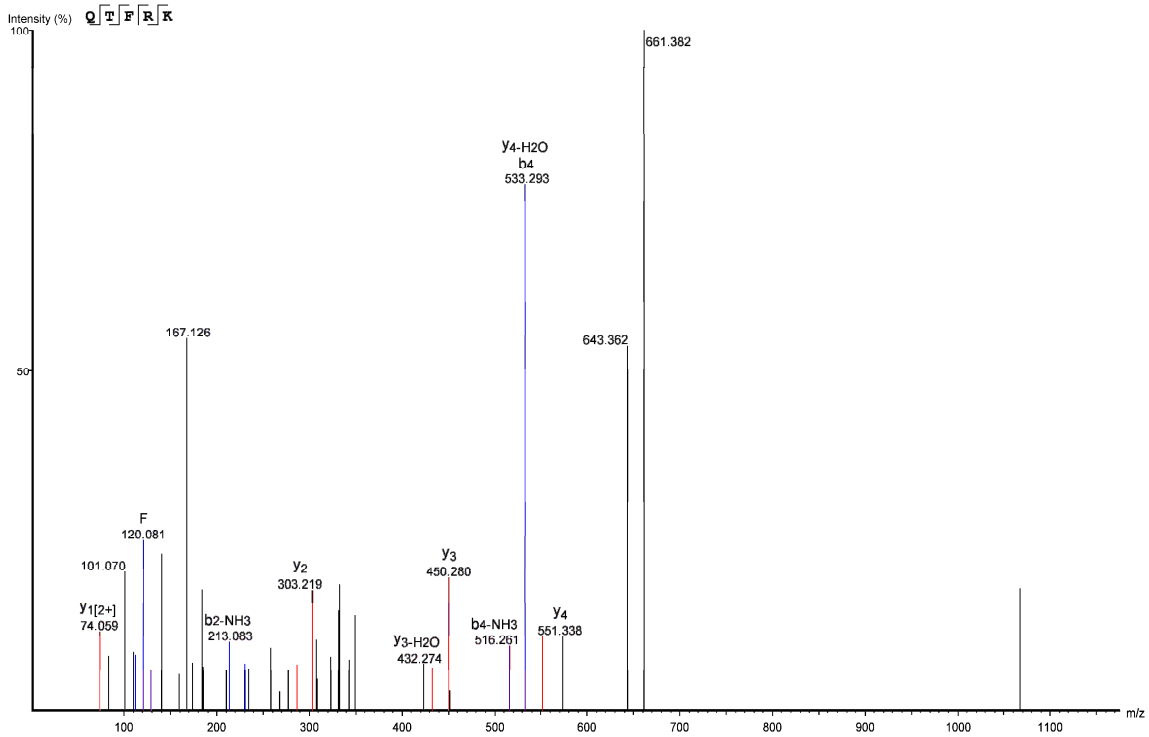
294–298, IREFR



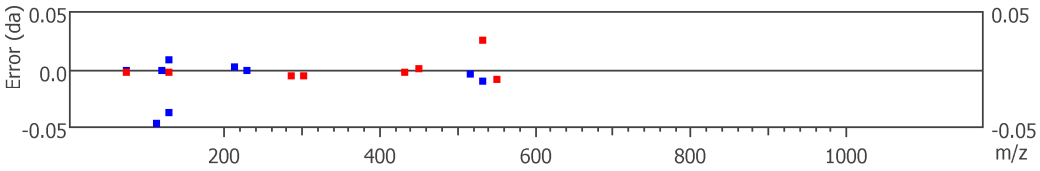

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 86.097 | 114.092 | 96.081 | 97.072 | 57.546 | I | | | | | 5 |
| 2 | 129.114 | 270.191 | 252.182 | 253.167 | 135.596 | R | 607.330 | 589.320 | 590.305 | 304.166 | 4 |
| 3 | 102.055 | 399.235 | 381.225 | 382.206 | 200.118 | E | 451.231 | 433.205 | 434.208 | 226.115 | 3 |
| 4 | 120.080 | 546.301 | 528.298 | 529.287 | 273.652 | F | 322.187 | 304.177 | 305.163 | 161.594 | 2 |
| 5 | 129.114 | | | | | R | 175.118 | 157.111 | 158.092 | 88.059 | 1 |



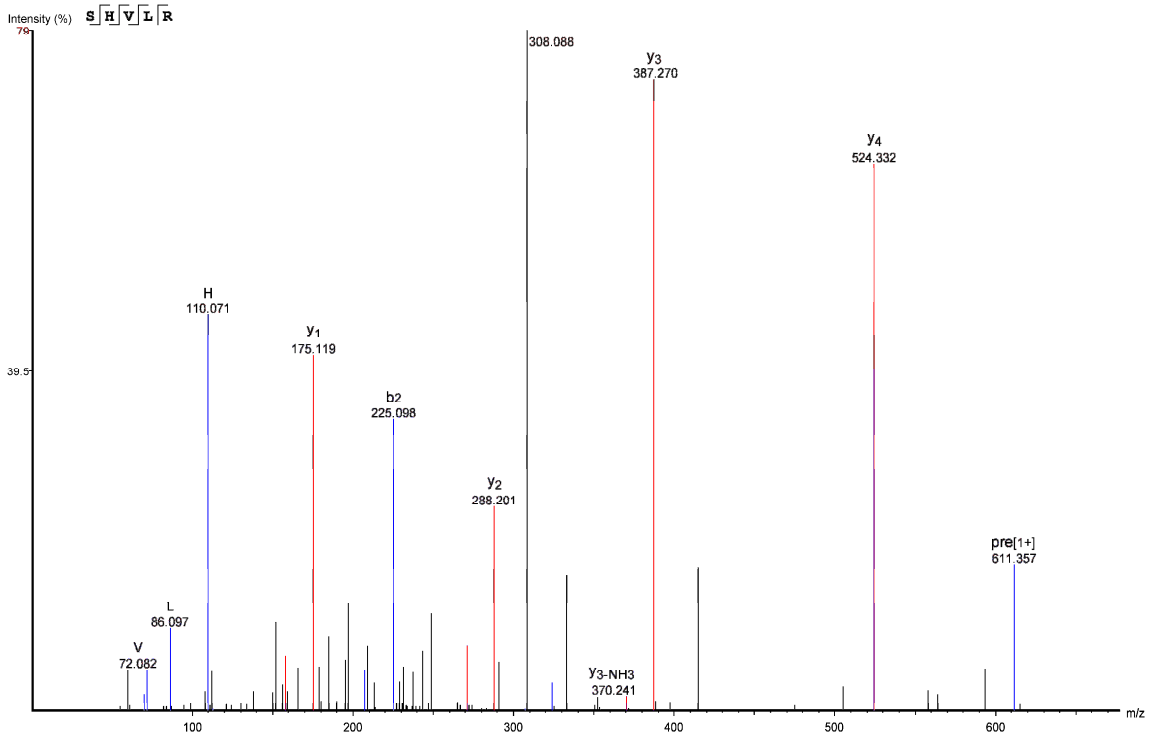
299–303, QTFRK



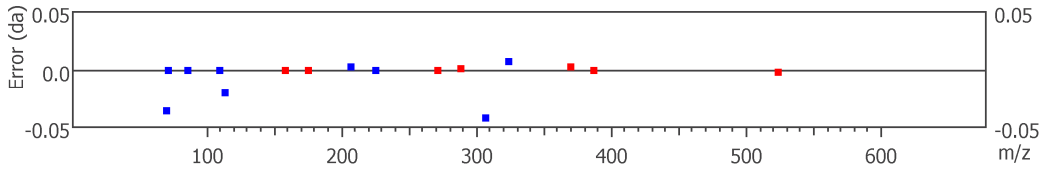

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 101.071 | 129.104 | 111.056 | 112.087 | 65.033 | Q | | | | | 5 |
| 2 | 74.059 | 230.113 | 212.104 | 213.083 | 115.557 | T | 551.338 | 533.293 | 534.303 | 276.165 | 4 |
| 3 | 120.081 | 377.182 | 359.172 | 360.156 | 189.091 | F | 450.280 | 432.274 | 433.255 | 225.641 | 3 |
| 4 | 129.104 | 533.293 | 515.273 | 516.261 | 267.142 | R | 303.219 | 285.203 | 286.193 | 152.107 | 2 |
| 5 | 101.108 | | | | | K | 147.113 | 129.104 | 130.086 | 74.059 | 1 |



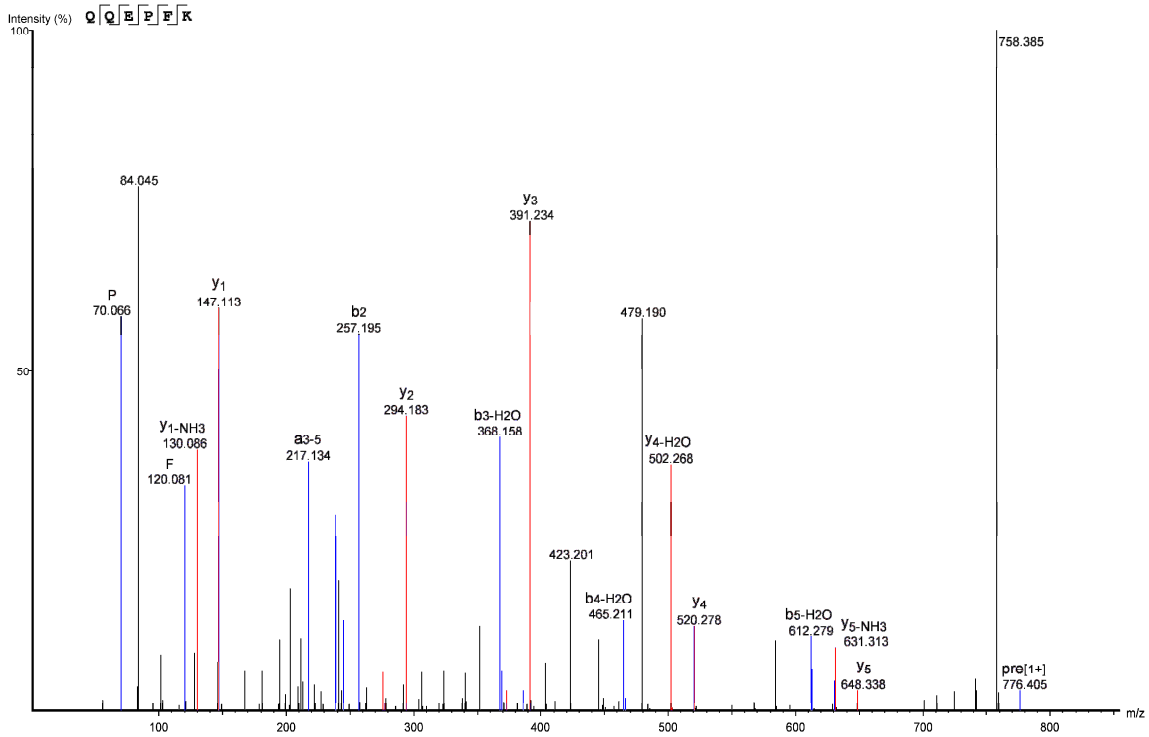
307–311, SHVLR



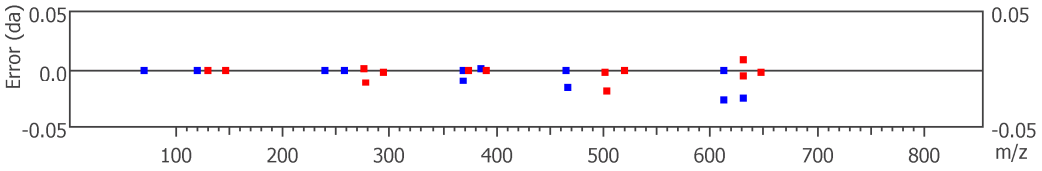

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 60.045 | 88.040 | 70.066 | 71.013 | 44.520 | S | | | | | 5 |
| 2 | 110.071 | 225.098 | 207.085 | 208.072 | 113.070 | H | 524.332 | 506.320 | 507.303 | 262.665 | 4 |
| 3 | 72.082 | 324.159 | 306.157 | 307.183 | 162.584 | V | 387.270 | 369.261 | 370.241 | 194.136 | 3 |
| 4 | 86.097 | 437.251 | 419.241 | 420.224 | 219.126 | L | 288.201 | 270.192 | 271.177 | 144.602 | 2 |
| 5 | 129.114 | | | | | R | 175.119 | 157.108 | 158.091 | 88.059 | 1 |



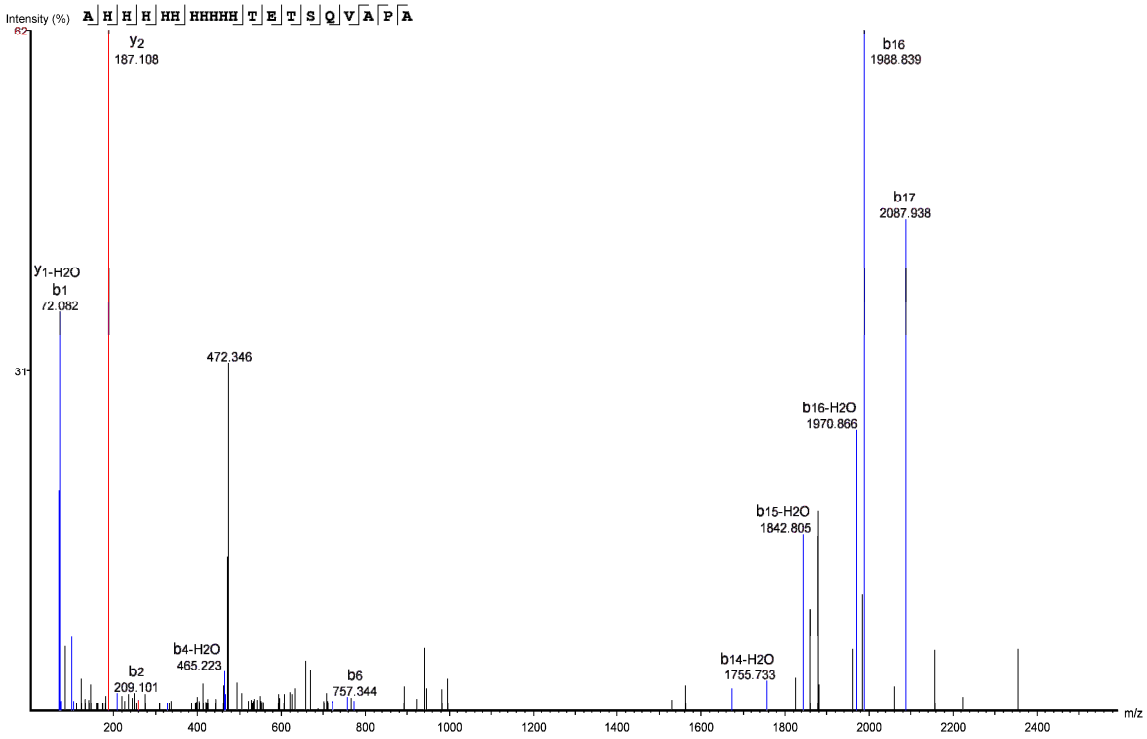
312–317, QQEPFK



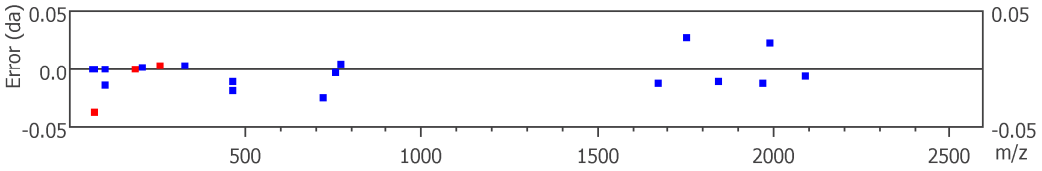

| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 101.071 | 129.066 | 111.056 | 112.039 | 65.033 | Q | | | | | 6 |
| 2 | 101.071 | 257.125 | 239.114 | 240.098 | 129.062 | Q | 648.338 | 630.314 | 631.313 | 324.668 | 5 |
| 3 | 102.055 | 386.165 | 368.158 | 369.150 | 193.584 | E | 520.278 | 502.268 | 503.269 | 260.638 | 4 |
| 4 | 70.066 | 483.220 | 465.211 | 466.209 | 242.110 | P | 391.234 | 373.222 | 374.207 | 196.117 | 3 |
| 5 | 120.081 | 630.314 | 612.279 | 613.289 | 315.644 | F | 294.183 | 276.169 | 277.165 | 147.591 | 2 |
| 6 | 101.108 | | | | | K | 147.113 | 129.102 | 130.086 | 74.056 | 1 |



318–337, AHHHHHHHHHHTETSQVAPA



| # | Immonium | b | b-H2O | b-NH3 | b (2+) | Seq | y | y-H2O | y-NH3 | y (2+) | # |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 44.050 | 72.082 | 54.034 | 55.018 | 36.522 | A | | | | | 20 |
| 2 | 110.072 | 209.101 | 191.093 | 192.077 | 105.066 | H | 2274.031 | 2256.021 | 2257.004 | 1137.516 | 19 |
| 3 | 110.072 | 346.163 | 328.148 | 329.136 | 173.581 | H | 2136.972 | 2118.961 | 2119.945 | 1068.986 | 18 |
| 4 | 110.072 | 483.222 | 465.223 | 466.214 | 242.111 | H | 1999.913 | 1981.903 | 1982.886 | 1000.457 | 17 |
| 5 | 110.072 | 620.281 | 602.270 | 603.254 | 310.640 | H | 1862.854 | 1844.844 | 1845.827 | 931.927 | 16 |
| 6 | 110.072 | 757.344 | 739.329 | 740.312 | 379.170 | H | 1725.795 | 1707.785 | 1708.768 | 863.398 | 15 |
| 7 | 110.072 | 894.398 | 876.388 | 877.371 | 447.699 | H | 1588.736 | 1570.726 | 1571.709 | 794.868 | 14 |
| 8 | 110.072 | 1031.457 | 1013.447 | 1014.430 | 516.229 | H | 1451.677 | 1433.667 | 1434.651 | 726.339 | 13 |
| 9 | 110.072 | 1168.516 | 1150.506 | 1151.489 | 584.758 | H | 1314.619 | 1296.608 | 1297.592 | 657.809 | 12 |
| 10 | 110.072 | 1305.575 | 1287.565 | 1288.548 | 653.288 | H | 1177.560 | 1159.549 | 1160.533 | 589.280 | 11 |
| 11 | 110.072 | 1442.634 | 1424.624 | 1425.607 | 721.842 | H | 1040.501 | 1022.490 | 1023.474 | 520.750 | 10 |
| 12 | 74.062 | 1543.682 | 1525.671 | 1526.655 | 772.336 | T | 903.442 | 885.431 | 886.415 | 452.221 | 9 |
| 13 | 102.055 | 1672.737 | 1654.714 | 1655.697 | 836.862 | E | 802.394 | 784.384 | 785.367 | 401.697 | 8 |
| 14 | 74.061 | 1773.772 | 1755.733 | 1756.745 | 887.386 | T | 673.352 | 655.341 | 656.325 | 337.176 | 7 |
| 15 | 60.045 | 1860.804 | 1842.805 | 1843.777 | 930.902 | S | 572.304 | 554.293 | 555.277 | 286.652 | 6 |
| 16 | 101.072 | 1988.839 | 1970.866 | 1971.836 | 994.931 | Q | 485.272 | 467.261 | 468.245 | 243.136 | 5 |
| 17 | 72.082 | 2087.938 | 2069.921 | 2070.904 | 1044.466 | V | 357.213 | 339.203 | 340.186 | 179.107 | 4 |
| 18 | 44.050 | 2158.968 | 2140.958 | 2141.941 | 1079.984 | A | 258.141 | 240.134 | 241.118 | 129.572 | 3 |
| 19 | 70.066 | 2256.021 | 2238.010 | 2238.994 | 1128.510 | P | 187.108 | 169.097 | 170.081 | 94.054 | 2 |
| 20 | 44.050 | | | | | A | 90.055 | 72.082 | 73.028 | 45.527 | 1 |




## 5. Reference.

(1) Isberg, V.; Mordalski, S.; Munk, C.; Rataj, K.; Harpsøe, K.; Hauser, A. S.; Vroling, B.; Bojarski, A. J.; Vriend, G.; Gloriam, D. E. GPCRdb: an Information System for G Protein-Coupled Receptors. *Nucleic Acids Res.* **2016**, *44*, D356–D364.