Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information
Synthesis and biological studies of neopetrosiamides as inhibitors of tumour cell invasion in cancer metastasis

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All commercially available reagents and solvents were purchased from the Aldrich Chemical Company Inc. (Madison, WI), Sigma Chemical Company (St. Louis, MO), Fisher Scientific Ltd. (Ottawa, ON) or Caledon (Georgetown, ON). All protected amino acids and SPPS resins were purchased from the Calbiochem-Novabiochem Corporation (San Diego, CA), Sigma-Aldrich Canada Ltd. (Oakville, ON), Chem Impex International Inc. (Wood Dale, IL) or VWR International (Mississauga, ON). All reagents and solvents were of American Chemical Society (ACS) grade and used without further purification. Reagents used in cell biology were purchased from Mediatech Inc. (Manassas, VA), ATCC (Manassas, VA) and GIBCO (Grand Island, NY).

Mass spectrometry analysis was done on an Applied Biosystems Voyager Elite MALDI-TOF. All MALDI MS were acquired on an Applied Biosystems Voyager Elite MALDI-TOF with delayed extraction in reflectron mode. A two layer method using 3,5-dimethoxy-4-hydroxycinnamic acid (sinapinic acid) as the matrix was used.

Linear Peptide formation of M(O)24O-methyl HSE (16)
Linear peptide M*(O)*24*O*-methyl HSE was synthesized on a preloaded H_2N-Cys(Trt)-2-ClTrt resin (0.62 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 3, 26-Acm; Cys 12, 28-Trt; Cys 7, 18- *t*-Bu. The crude peptide (150 mg 45.4% relative to resin loading) was used in the next step without further purification. Calculated molecular weight for $C_{143}H_{216}N_{37}O_{41}S_6$ $(M + H)^+$ 3299.4 Found 3299.5 $(M + H)^+$.

Bis-disulfide formation of M(O)24O-methyl HSE (17)
Peptide **(17)** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **(16).** The crude peptide was purified by semi-prep RP-HPLC using the general method (t_R = 24.8 min) to give **(17)** as an off- white powder (22 mg, 23.2% relative to 100 mg of crude **(16)**). Calculated molecular weight for $C_{137}H_{202}N_{35}O_{39}S_6$ $(M + H)^+$ 3153 Found $(M + H)^+$ 3153

Tris-disulfide formation of residue 24 substitution with O-methyl homoserine (1) (M(O)24O-methyl HSE)
The introduction of the third disulfide bond was achieved by DMSO oxidation of the bicyclic peptide (**16)** according to the general method for tris-disulfide bond formation. The crude peptide was purified by semi-preparative RP-HPLC using the general method (t_R = 24.9 min, 1.0mg, 26.3% relative to 4 mg of bicyclic peptide purified). MALDI-TOF MS Calculated molecular weight for $C_{129}H_{184}N_{35}O_{39}S_6$ $(M + H)^+$ 3039 Found $(M + H)^+$ 3039.

Linear Peptide formation of M(O)24Gln (18)
Linear peptide M*(O)*24Gln was synthesized on a preloaded H_2N-Cys(Trt)-2-ClTrt resin (0.62 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 3, 26-Acm; Cys 12, 28-Trt; Cys 7, 18- *t*-Bu. The crude peptide (160 mg, 48.3% relative to resin loading) was used in the next step without further purification. MALDI-TOF MS calculated molecular weight for $C_{143}H_{215}N_{38}O_{41}S_6$ $(M + H)^+$ 3312 Found $(M + H)^+$ 3312.

Bis-disulfide formation of M(O)24Gln (19)
Peptide **(19)** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **(18).** The crude peptide was purified by semi-prep RP-HPLC using the general method (t_R = 24.0 min) to give **(19)** as an off- white powder (7.6 mg, 5.3% relative to 150 mg of crude **(18)**). Calculated molecular weight for $C_{137}H_{201}N_{36}O_{39}S_6$ $(M + H)^+$ 3166 Found $(M + H)^+$ 3166.

Tris-disulfide formation of residue 24 substitution with glutamine (2) (M(O)24Gln)
The introduction of the third disulfide bond was achieved by DMSO oxidation of the bicyclic peptide (**19)** according to the general method for tris-disulfide bond formation. The crude peptide **(2)** was purified by semi-preparative RP-HPLC using the general method (t_R = 21.1 min, 1.2mg, 27.0% relative to 4.6 mg of bicyclic peptide purified). MALDI-TOF MS Calculated molecular weight for $C_{129}H_{13}N_{36}O_{39}S_6$ $(M + H)^+$ 3052.1 Found $(M + H)^+$ 3052.

Linear Peptide formation of M(O)24Glu (20)
Linear peptide M*(O)*24Glu was synthesized on a preloaded H_2N-Cys(Trt)-2-ClTrt resin (0.62 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 3, 26-Acm; Cys 12, 28-Trt; Cys 7, 18- *t*-Bu. The crude peptide (152.9 mg, 45.9% relative to resin loading) was used in the next step without further purification. MALDI-TOF MS calculated molecular weight for $C_{143}H_{213}N_{37}O_{42}S_6$ $(M + H)^+$ 3315 Found $(M + H)^+$ 3315.

Bis-disulfide formation of M(O)24Glu (21)
Peptide **(21)** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **(20).** The crude peptide was purified by semi-prep RP-HPLC using the general method (t_R = 24.0 min) to give **(21)** as

an off- white powder (12 mg, 24% relative to 50 mg of crude **(20)**). Calculated molecular weight for $C_{137}H_{199}N_{35}O_{40}S_6$ $(M + H)^+$ 3169 Found $(M + H)^+$ 3169.

Tris-disulfide formation of residue 24 substitution with glutamic acid (3) (M(O)24Glu)
The introduction of the third disulfide bond was achieved by DMSO oxidation of the bicyclic peptide (**21**) according to the general method for tris-disulfide bond formation. The crude peptide **(3)** was purified by semi-preparative RP-HPLC using the general method (t_R = 17.5 min, 5.6 mg, 46.7% relative to 12 mg of bicyclic peptide purified). MALDI-TOF MS Calculated molecular weight for $C_{129}H_{181}N_{35}O_{40}S_6$ $(M + H)^+$ 3055 Found $(M + H)^+$ 3055.

Linear Peptide formation of M(O)24Asn (22)
Linear peptide M*(O)*24Asn was synthesized on a preloaded H_2N-Cys(Trt)-2-ClTrt resin (0.62 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 3, 26-Acm; Cys 12, 28-Trt; Cys 7, 18- *t*-Bu. The crude peptide (133 mg, 40.3% relative to resin loading* large impurity present at 2874 m/z) was used in the next step without further purification. MALDI-TOF MS calculated molecular weight for $C_{142}H_{212}N_{38}O_{41}S_6$ $(M + H)^+$ 3300 Found $(M + H)^+$ 3300.

Bis-disulfide formation of M(O)24Asn (23)
Peptide **(23)** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **(22).** The crude peptide was used without further purification giving an orange-yellow solid (8 mg, 40% relative to 20 mg of crude **(22)**). Calculated molecular weight for $C_{136}H_{198}N_{36}O_{39}S_6$ $(M + H)^+$ 3154 Found $(M + H)^+$ 3154.

Tris-disulfide formation of residue 24 substitution with asparagine (4) (M(O)24Asn)
The introduction of the third disulfide bond was achieved by DMSO oxidation of the bicyclic peptide (**23**) according to the general method for tris-disulfide bond formation. The crude peptide **(4)** was purified by semi-preparative RP-HPLC using the general method (t_R = 18.7 min, 2.1 mg, 26.3 % relative to 8 mg of crude bicyclic peptide). MALDI-TOF MS Calculated molecular weight for $C_{128}H_{180}N_{36}O_{39}S_6$ $(M + H)^+$ 3040 Found $(M + H)^+$ 3039.

Linear Peptide formation of M(O)24Ala (24)
Linear peptide M*(O)*24Ala was synthesized on a preloaded H_2N-Cys(Trt)-2-ClTrt resin (0.62 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 3, 26-Acm; Cys 12, 28-Trt; Cys 7, 18- *t*-Bu. The crude peptide (50 mg, 15 % isolated yield relative to resin loading) was used in the next step without further purification. MALDI-TOF MS calculated molecular weight for $C_{140}H_{211}N_{37}O_{40}S_6$ $(M + H)^+$ 3257 Found $(M + H)^+$ 3255.

Bis-disulfide formation of M(O)24Ala (25)
Peptide **(25)** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **(24).** The crude peptide was used without further purification giving an orange-yellow solid (35 mg, 74% relative to 50 mg of crude **(24)**). Calculated molecular weight for $C_{135}H_{197}N_{35}O_{38}S_6$ $(M + H)^+$ 3111 Found $(M + H)^+$ 3111.

Tris-disulfide formation of residue 24 substitution with alanine (5) (M(O)24Ala)
The introduction of the third disulfide bond was achieved by DMSO oxidation of the bicyclic peptide (**25**) according to the general method for tris-disulfide bond formation. The crude peptide **(5)** was purified by semi-preparative RP-HPLC using the general method (t_R = 23.2 min, 1.47 mg, 4 % isolated yield relative to 35 mg of crude bicyclic peptide). MALDI-TOF MS Calculated molecular weight for $C_{129}H_{13}N_{36}O_{39}S_6$ $(M + H)^+$ Found $(M + H)^+$ 2997.

Linear Peptide formation of M(O)24Leu (26)
Linear peptide M*(O)*24Leu was synthesized on a preloaded H_2N-Cys(Trt)-2-ClTrt resin (0.62 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 3, 26-Acm; Cys 12, 28-Trt; Cys 7, 18- *t*-Bu. The crude peptide (123 mg, 37.3% relative to resin loading) was used in the next step without further purification. MALDI-TOF MS calculated molecular weight for $C_{143}H_{215}N_{38}O_{41}S_6$ $(M + H)^+$ 3299 Found $(M + H)^+$ 3299.

Bis-disulfide formation of M(O)24Leu (27)
Peptide **(27)** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **(26).** The crude peptide was used without further purification giving an orange-yellow solid (8 mg, 40% relative to 20 mg of crude **(26)**). Calculated molecular weight for $C_{137}H_{201}N_{36}O_{39}S_6$ $(M + H)^+$ 3153 Found $(M + H)^+$ 3153.

Tris-disulfide formation of residue 24 substitution with leucine (6) (M(O)24Leu)
The introduction of the third disulfide bond was achieved by DMSO oxidation of the bicyclic peptide (**27**) according to the general method for tris-disulfide bond formation. The crude peptide **(6)** was purified by semi-preparative RP-HPLC

using the general method (t_R = 24.9 min, 2.1 mg, 26.3% relative to 8 mg of crude bicyclic peptide). MALDI-TOF MS Calculated molecular weight for $C_{129}H_{13}N_{36}O_{39}S_6$ $(M + H)^+$ 3039 Found $(M-2H)^+$ 3037.

Linear Peptide formation of M(O)24Ile (28)

Linear peptide M*(O)*24Ile was synthesized on a preloaded H_2N-Cys(Trt)-2-ClTrt resin (0.62 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 3, 26-Acm; Cys 12, 28-Trt; Cys 7, 18- *t*-Bu. The crude peptide (177 mg, 54 % relative to resin loading) was used in the next step without further purification. MALDI-TOF MS calculated molecular weight for $C_{144}H_{217}N_{37}O_{40}S_6$ $(M + H)^+$ 3299 Found $(M + H)^+$ 3299.

Bis-disulfide formation of M(O)24Ile (29)

Peptide **(29)** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **(28).** The crude peptide was used without further purification giving an orange-yellow solid (30 mg, 64% isolated yield relative to 50 mg of crude **(28)**). Calculated molecular weight for $C_{138}H_{203}N_{35}O_{38}S_6$ $(M + H)^+$ 3153 Found $(M + H)^+$ 3152.

Tris-disulfide formation of residue 24 substitution with isoleucine (7) (M(O)24Ile)

The introduction of the third disulfide bond was achieved by DMSO oxidation of the bicyclic peptide (**29**) according to the general method for tris-disulfide bond formation. The crude peptide **(7)** was purified by semi-preparative RP-HPLC using the general method (t_R = 20.6 min, 1.94mg, 7% isolated yield relative to 30 mg of crude bicyclic peptide). MALDI-TOF MS Calculated molecular weight for $C_{130}H_{185}N_{35}O_{38}S_6$ $(M + H)^+$ 3039 Found $(M + 2H)^+$ 3040.

Linear Peptide formation of M(O)24His (30)

Linear peptide M*(O)*24His was synthesized on a preloaded H_2N-Cys(Trt)-2-ClTrt resin (0.62 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 3, 26-Acm; Cys 12, 28-Trt; Cys 7, 18- *t*-Bu. The crude peptide (133 mg, 40% relative to resin loading) was used in the next step without further purification. MALDI-TOF MS calculated molecular weight for $C_{144}H_{213}N_{39}O_{40}S_6$ $(M + H)^+$ 3323 Found $(M + H)^+$ 3323.

Bis-disulfide formation of M(O)24His (31)

Peptide **(31)** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **(30).** The crude peptide was used without further purification giving an orange-yellow solid (35 mg, 74 % isolated yield relative to 50 mg of crude **(30)**). Calculated molecular weight for $C_{138}H_{199}N_{37}O_{38}S_6$ $(M + H)^+$ 3177 Found $(M + H)^+$ 3177.

Tris-disulfide formation of residue 24 substitution with histidine (8) (M(O)24His)

The introduction of the third disulfide bond was achieved by DMSO oxidation of the bicyclic peptide **(41)** according to the general method for tris-disulfide bond formation. The crude peptide **(8)** was purified by semi-preparative RP-HPLC using the general method (t_R = 23.7 min, 2.91 mg, 8.8 % isolated yield relative to 35 mg of crude bicyclic peptide). MALDI-TOF MS Calculated molecular weight for $C_{133}H_{183}N_{35}O_{38}S_6$ $(M + H)^+$ 3063 Found $(M)^+$ 3062.

Linear Peptide formation of M(O)24Phe (32)

Linear peptide M*(O)*24Phe was synthesized on a preloaded H_2N-Cys(Trt)-2-ClTrt resin (0.62 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 3, 26-Acm; Cys 12, 28-Trt; Cys 7, 18- *t*-Bu. The crude peptide (124 mg, 37% relative to resin loading) was used in the next step without further purification. MALDI-TOF MS calculated molecular weight for $C_{147}H_{215}N_{37}O_{40}S_6$ $(M + H)^+$ 3331 Found $(M + H)^+$ 3335.

Bis-disulfide formation of M(O)24Phe (33)

Peptide **(33)** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **(32).** The crude peptide was used without further purification giving an orange-yellow solid (35 mg, 74 % isolated yield relative to 50 mg of crude **(32)**). Calculated molecular weight for $C_{141}H_{201}N_{35}O_{38}S_6$ $(M + H)^+$ 3187 Found $(M + H)^+$ 3186.

Tris-disulfide formation of residue 24 substitution with phenylalanine (9) (M(O)24Phe)

The introduction of the third disulfide bond was achieved by DMSO oxidation of the bicyclic peptide **(33)** according to the general method for tris-disulfide bond formation. The crude peptide **(9)** was purified by semi-preparative RP-HPLC using the general method (t_R = 15.6 min, 1.96 mg isolated, 5.9 % isolated yield relative to 35 mg of crude bicyclic peptide). MALDI-TOF MS Calculated molecular weight for $C_{133}H_{183}N_{35}O_{38}S_6$ $(M + H)^+$ 3071 Found $(M + H)^+$ 3071.

Linear peptide formation of C3L, C26L (34)

Linear peptide C3L, C26L was synthesized on a preloaded H_2N-Cys(Acm)-2-ClTrt resin (0.62 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 7, 18-Trt, Cys 12, 28 -Acm. The crude peptide was used directly in the next reaction. MALDI-TOF (MS): cald. for $C_{141}H_{211}N_{37}O_{40}S_5$ $(M + H)^+$ 3223 found $(M + H)^+$ 3323.

Bis-disulfide peptide formation of C3L, C26L (11)
Peptide **11** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **34.** The crude peptide was purified by the semi-preparative RP-HPLC using the general method, t_R = 23.8 min. MALDI-TOF (MS): cald. for $C_{135}H_{197}N_{35}O_{38}S_5$ $(M + H)^+$ 3077. Found $(M + H)^+$ 3077.

Linear peptide formation of C7L, C18L (35)
Linear peptide C7L, C18L (**35)** was synthesized on a preloaded H_2N-Cys(Trt)-2-ClTrt resin (0.62 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 12, 28-Trt, Cys 3, 26-Acm. The crude peptide was used directly in the next reaction. MALDI-TOF (MS): cald. for $C_{141}H_{211}N_{37}O_{40}S_5$ $(M + H)^+$ 3223. found $(M + H)^+$ 3223.

***Bis-disulfide peptide formation of C7L, C18L* (13)**
Peptide **13** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **35**. The crude peptide was purified by the semi-preparative RP-HPLC using the general method, t_R = 24.9 min. MALDI-TOF (MS): cald. for $C_{135}H_{197}N_{35}O_{38}S_5$ $(M + H)^+$ 3077. Found $(M + 2H)^+$ 3078.

Linear peptide formation of C12L, C28L (36)
Linear peptide C12L, C28L **(36)** was synthesized on a preloaded Fmoc-Leu-Wang resin (0.52 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 7, 18-Trt, Cys 3, 26 (Acm). The crude peptide was used directly in the next reaction. MALDI-TOF (MS): cald. for $C_{141}H_{211}N_{37}O_{40}S_5$ $(M + H)^+$ 3223. found $(M + H)^+$3223

Bis-disulfide peptide formation of C12L, C28L (15)
Peptide **15** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **36.** The crude peptide was purified by the semi-preparative RP-HPLC using the general method, t_R = 28.1 min, (sulfoxide 27.5 min). MALDI-TOF (MS): cald. for $C_{135}H_{197}N_{35}O_{38}S_5$ $(M + H)^+$ 3077. Found $(M + 2H)^+$ 3078.

Linear peptide formation of C3F, C26F (37)
Linear peptide C3F, C26F **(37)** was synthesized on a preloaded H_2N-Cys(Acm)-2-ClTrt resin (0.82 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 7, 18-Trt, Cys 12, 28 -Acm. The crude peptide was used directly in the next reaction. MALDI-TOF (MS): cald. for $C_{147}H_{209}N_{37}O_{40}S_5$ $(M + H)^+$ 3291 found $(M + H)^+$ 3291.

Bis-disulfide peptide formation of C3F, C26F (10)
Peptide **10** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **37.** The crude peptide was purified by the semi-preparative RP-HPLC using the general method, t_R = 22.2 min (4.1 mg, 14.3% isolated yield relative to 30 mg of crude **(37)**). MALDI-TOF (MS): cald. for $C_{141}H_{194}N_{35}O_{38}S_5$ $(M + H)^+$ 3145. Found $(M + 2H)^+$ 3146.

Linear peptide formation of C7F, C18F (38)
Linear peptide C7F, C18F **(38)** was synthesized on a preloaded H_2N-Cys(Acm)-2-ClTrt resin (0.32 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 12, 28-Acm, Cys 3, 26 (Trt). The crude peptide was used directly in the next reaction. MALDI-TOF (MS): cald. for $C_{147}H_{209}N_{37}O_{40}S_5$ $(M + H)^+$ 3291. found $(M + H)^+$ 3291.

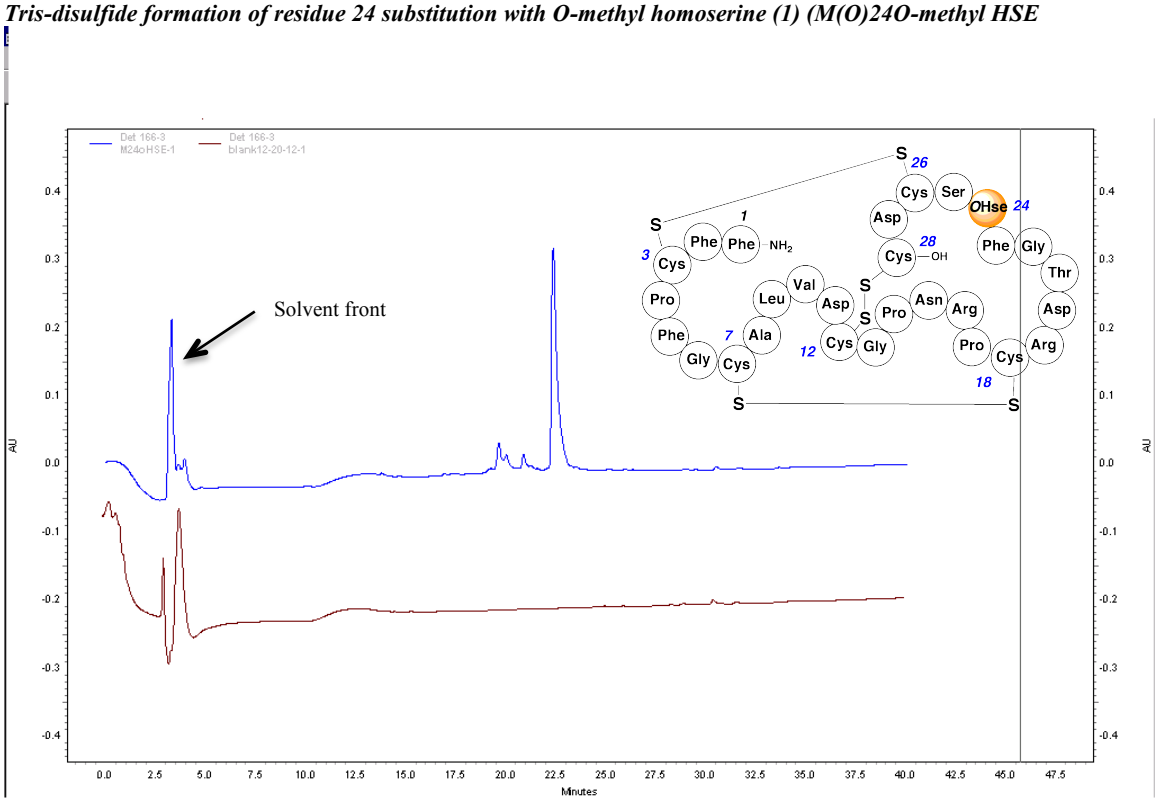
Bis-disulfide peptide formation of C7F, C18F (12)
Peptide **12** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **38**. The crude peptide was purified by the semi-preparative RP-HPLC using the general method, t_R = 25.6 min (4.8 mg, 3.3% isolated yield relative to 150 mg of crude **(38)**). MALDI-TOF (MS): cald. for $C_{141}H_{194}N_{35}O_{38}S_5$ $(M + H)^+$ 3145. Found $(M + 2H)^+$ 3146.

Linear peptide formation of C12F, C28F (39)
Linear peptide C12F, C28F **()** was synthesized on a preloaded Fmoc-Phe-Wang resin (0.60 mmol/g) on a 0.1 mmol scale using the automated peptide synthesizer according to the general method for solid phase peptide synthesis. Protection of the cysteine residues was Cys 7, 18-Trt, Cys 3, 26-Acm. The crude peptide was used directly in the next reaction. MALDI-TOF (MS): cald. for $C_{147}H_{209}N_{37}O_{40}S_5$ $(M + H)^+$ 3291. found $(M + H)^+$3291.

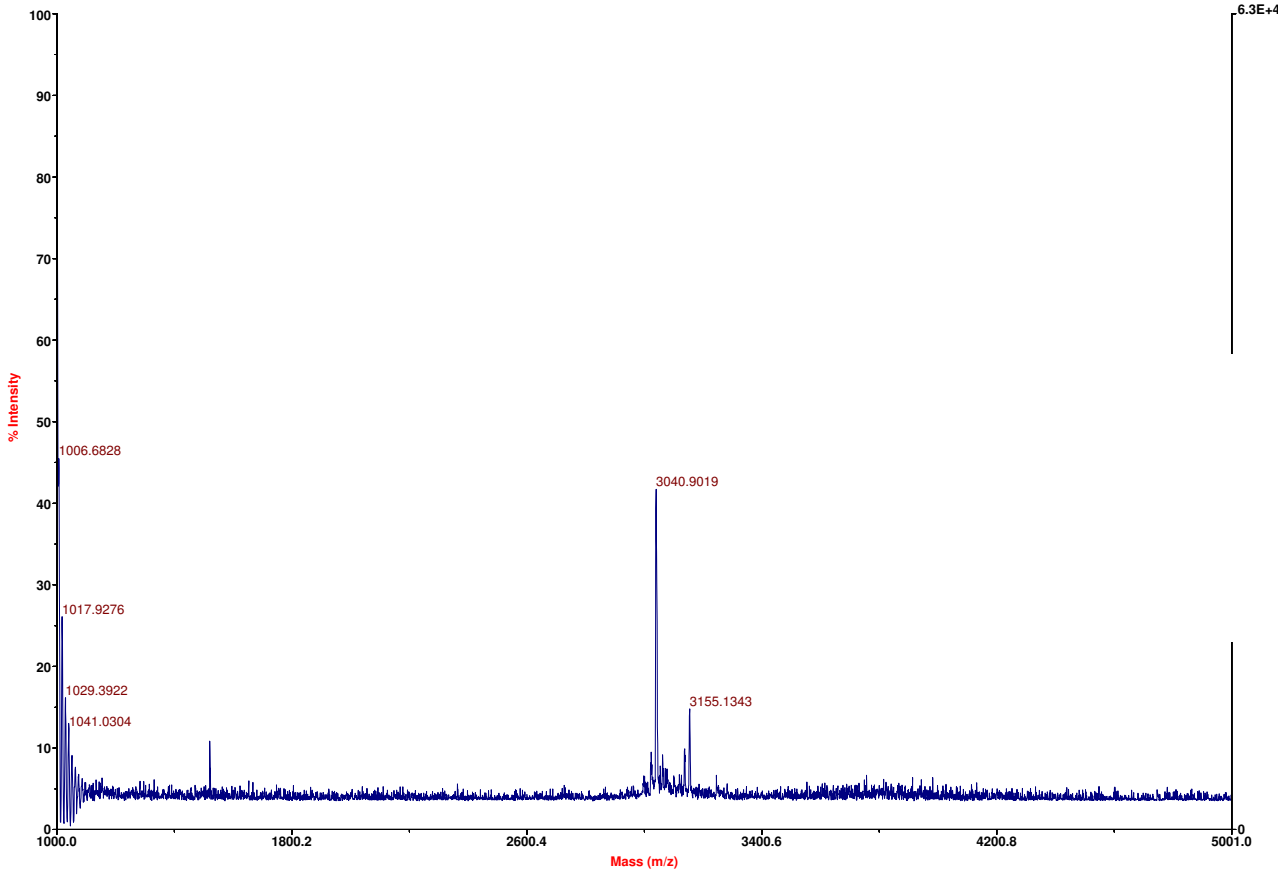
Bis-disulfide peptide formation of C12F, C28F (14)

Peptide **14** was synthesized according to the general method for bis-disulfide bond formation from the linear peptide **39.** The crude peptide was purified by the semi-preparative RP-HPLC using the general method, t_R = 29.6 min (3.7 mg, 28.6% isolated yield relative to 30 mg of crude **(39)**). MALDI-TOF (MS): cald. for $C_{141}H_{194}N_{35}O_{38}S_5$ $(M + H)^+$ 3145. Found $(M + 2H)^+$ 3146.

Tris-disulfide formation of residue 24 substitution with O-methyl homoserine (1) (M(O)24O-methyl HSE



Voyager Spec #1[BP = 1000.1, 63286]



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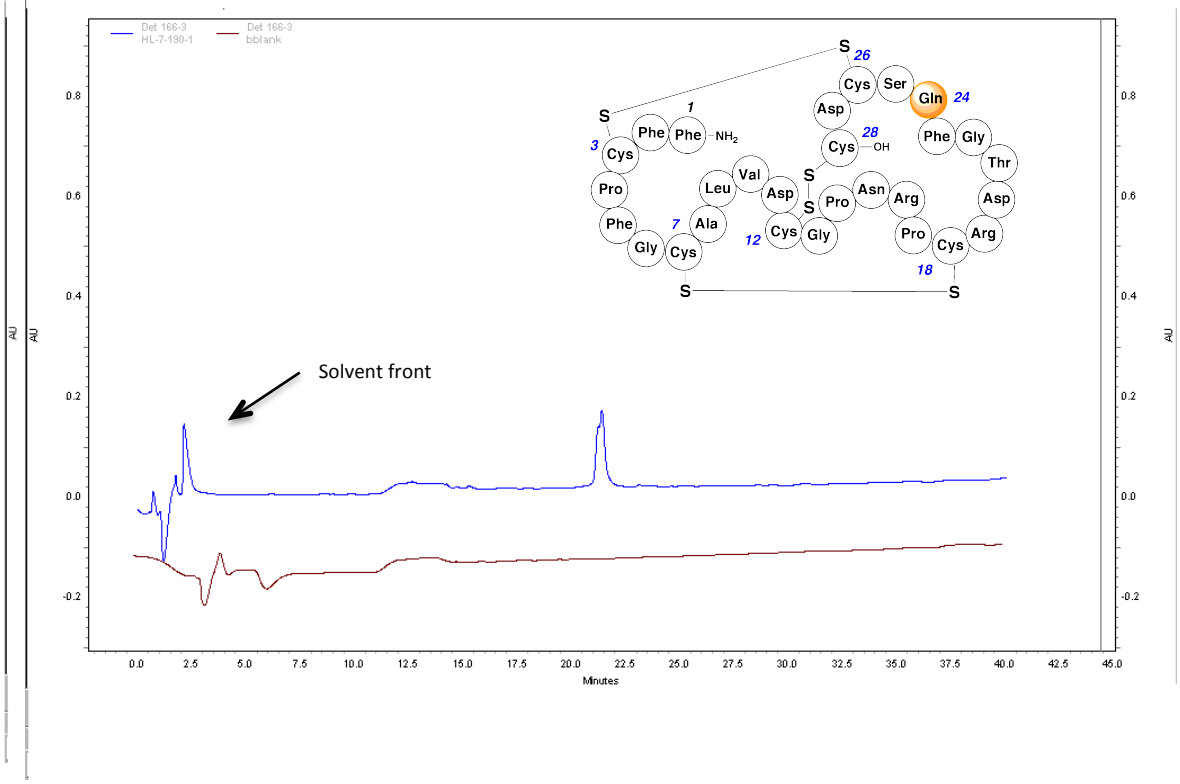
Tris-disulfide formation of residue 24 substitution with glutamine (2) (M(O)24Gln)



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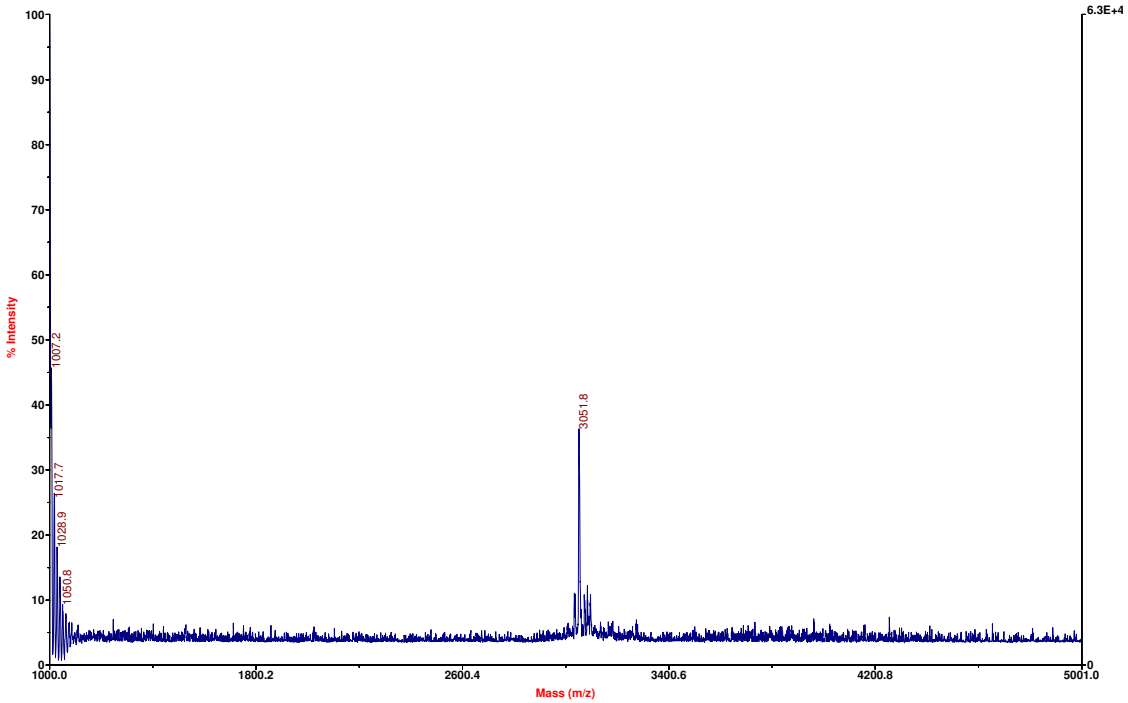

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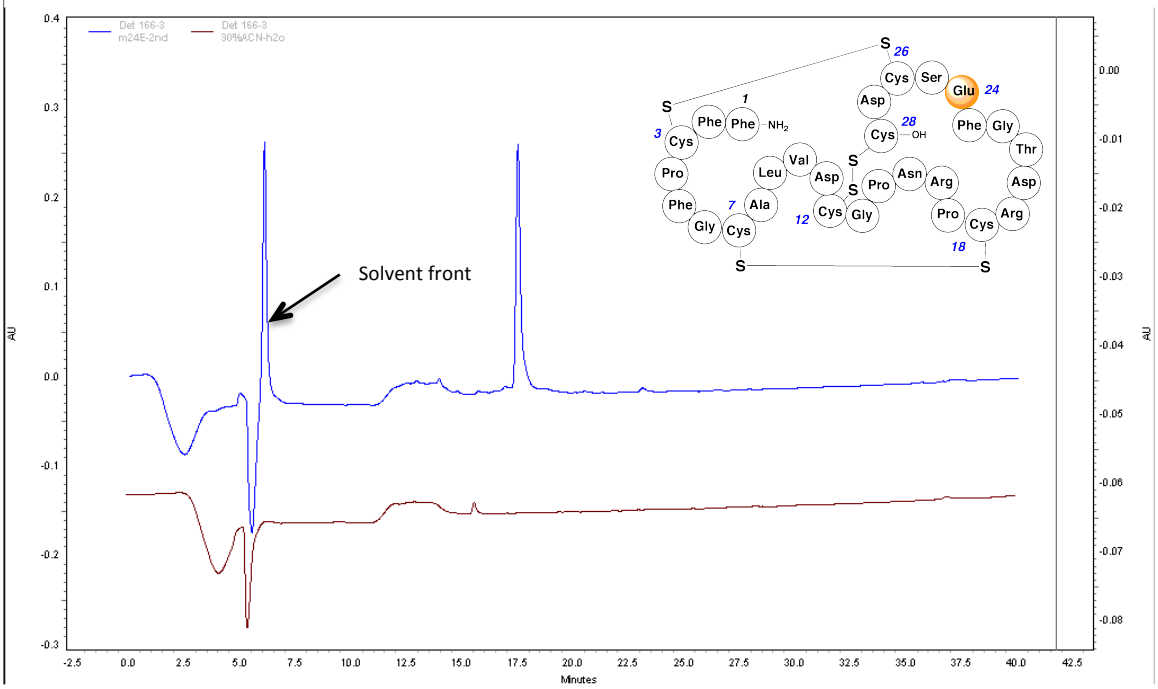
Tris-disulfide formation of residue 24 substitution with glutamic acid (3) (M(O)24Glu)



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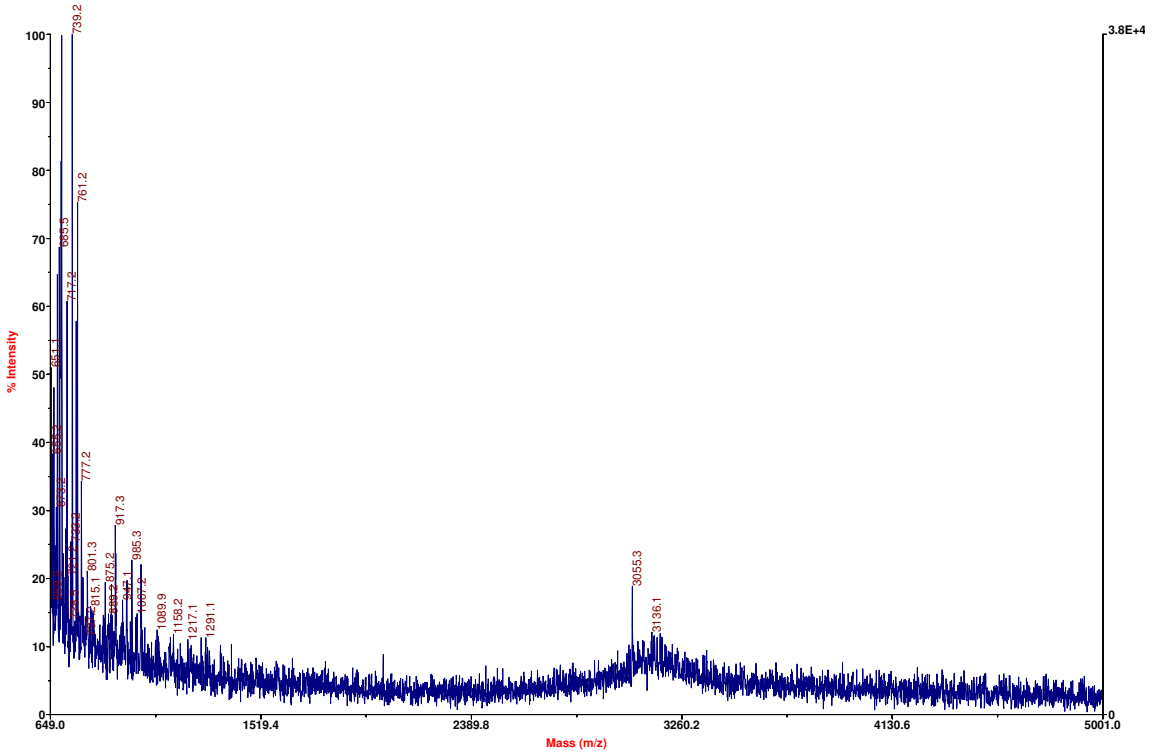

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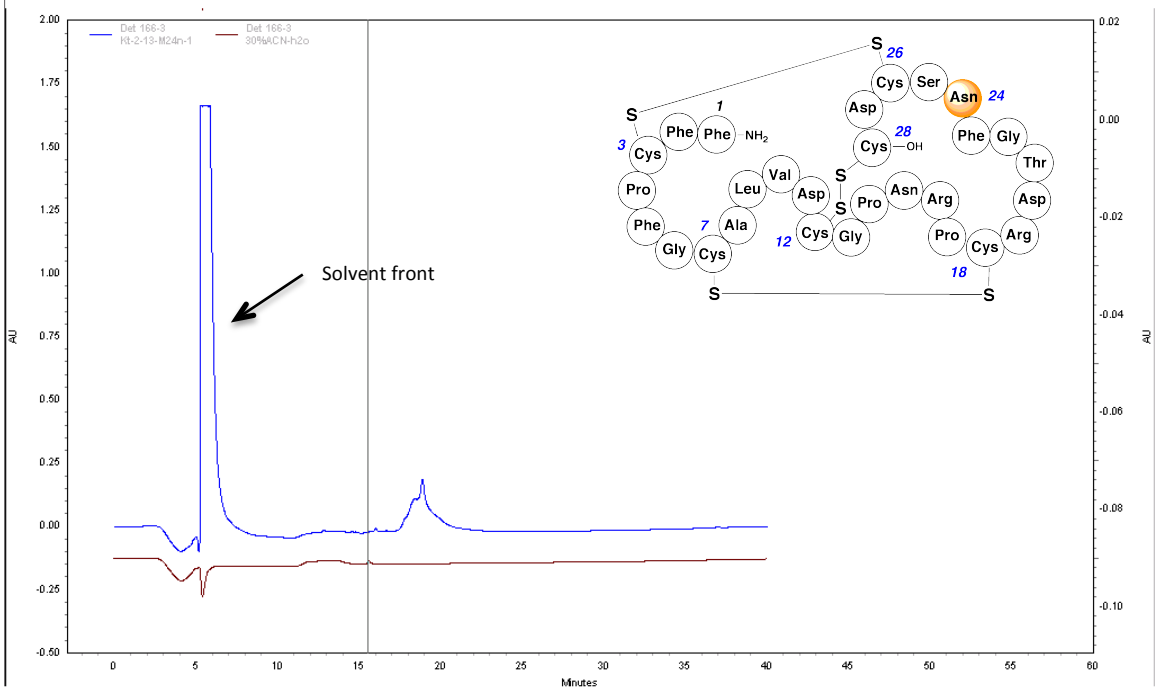
Tris-disulfide formation of residue 24 substitution with asparagine (4) (M(O)24Asn)



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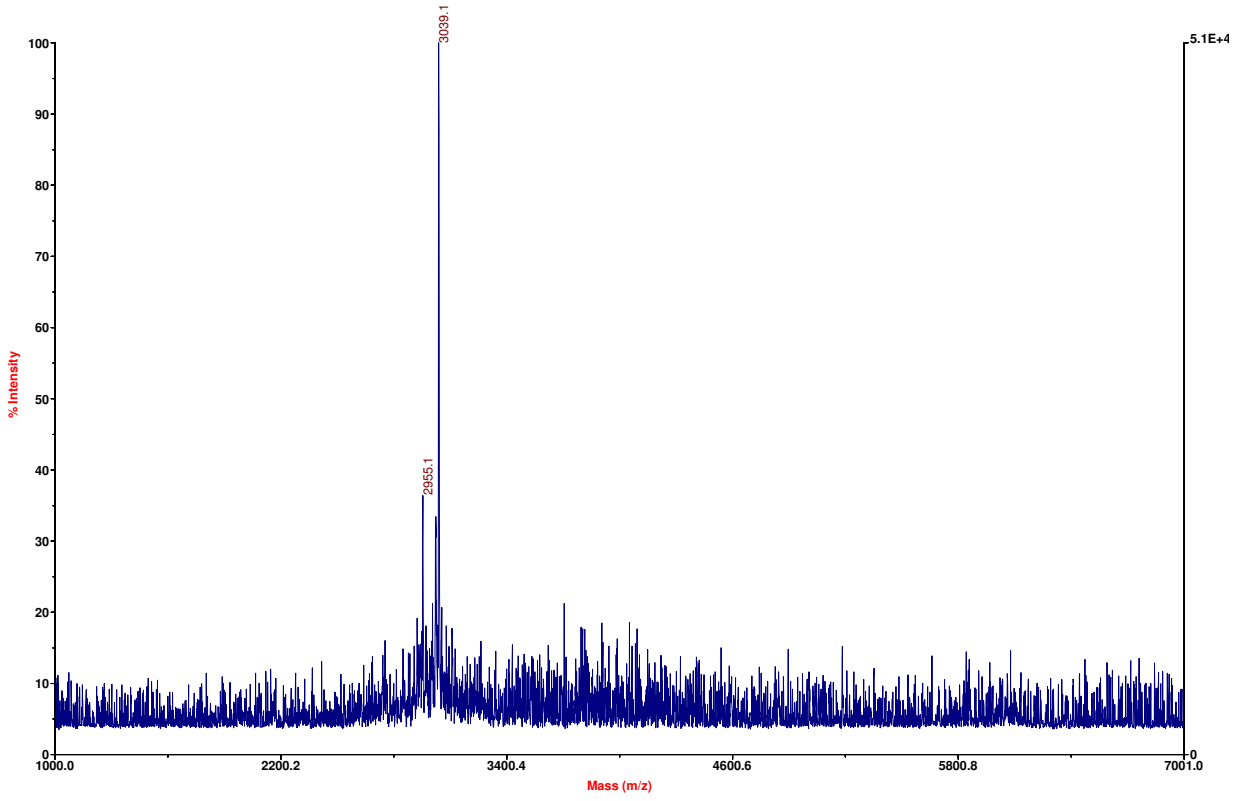

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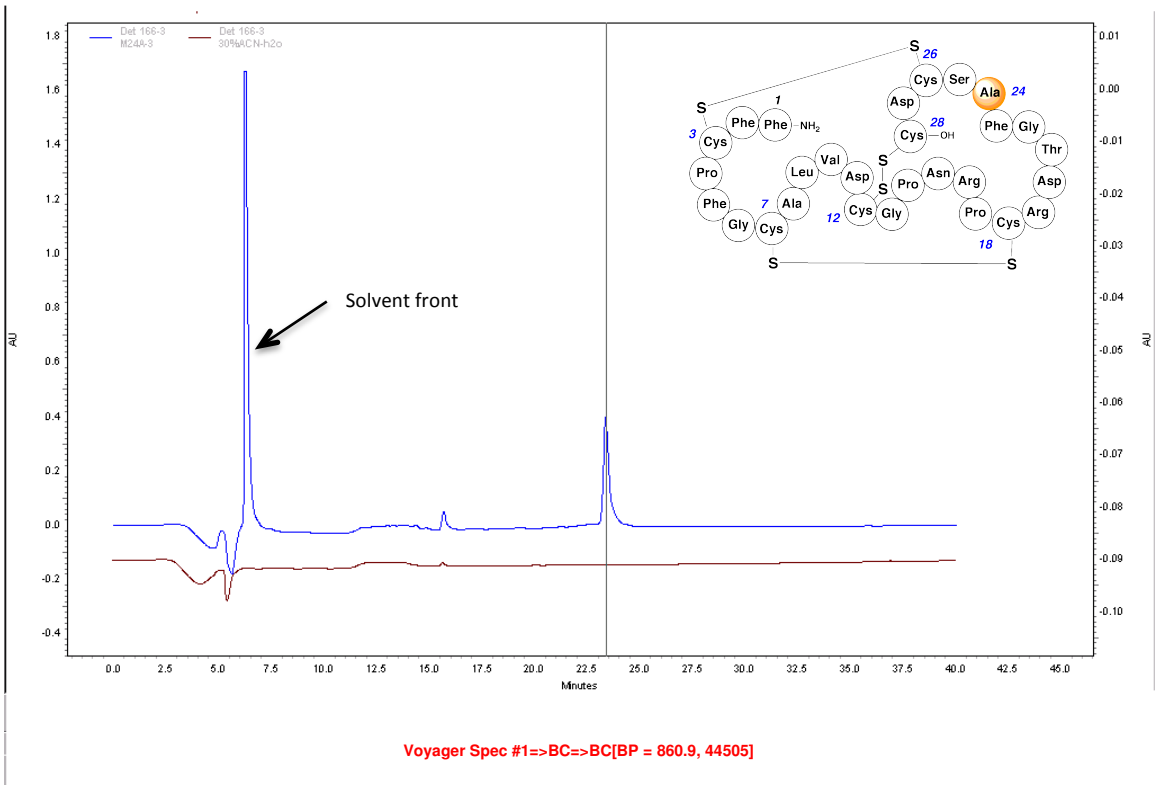
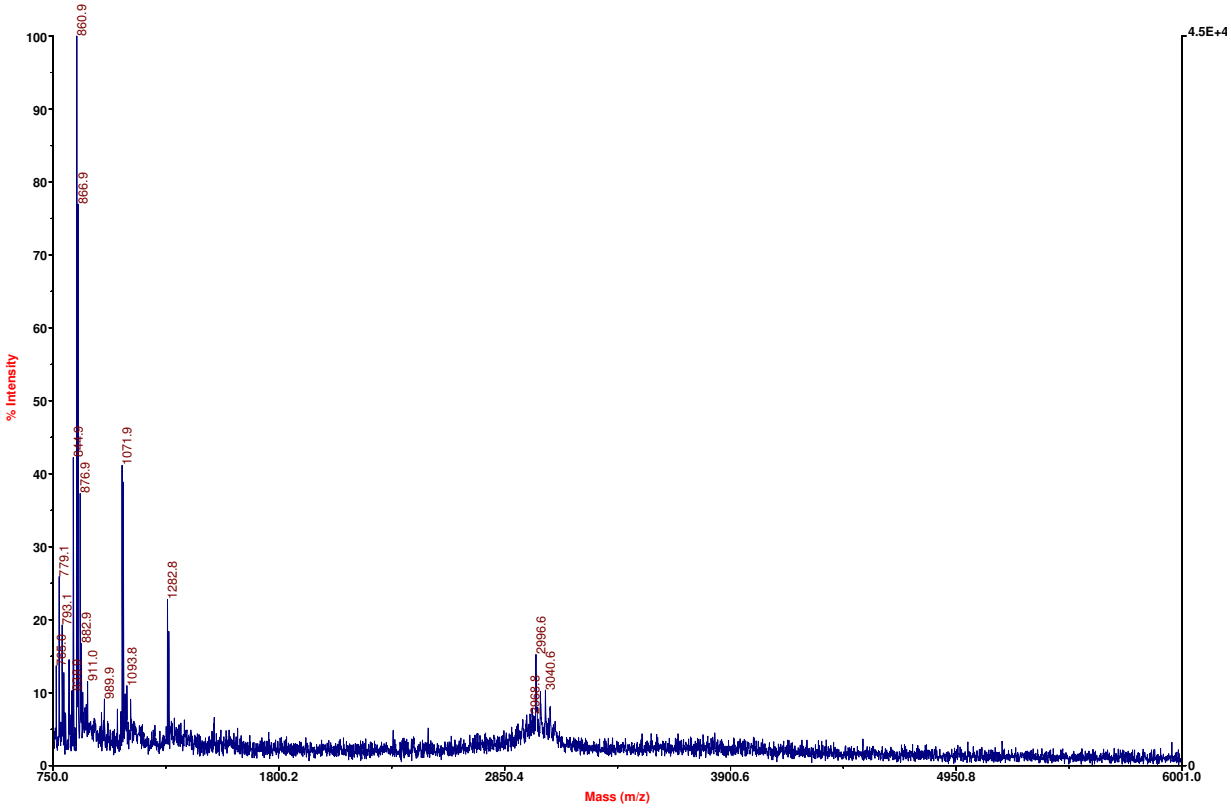
Acquired: 09:06:00, March 01, 2012

Tris-disulfide formation of residue 24 substitution with alanine (5) (M(O)24Ala)

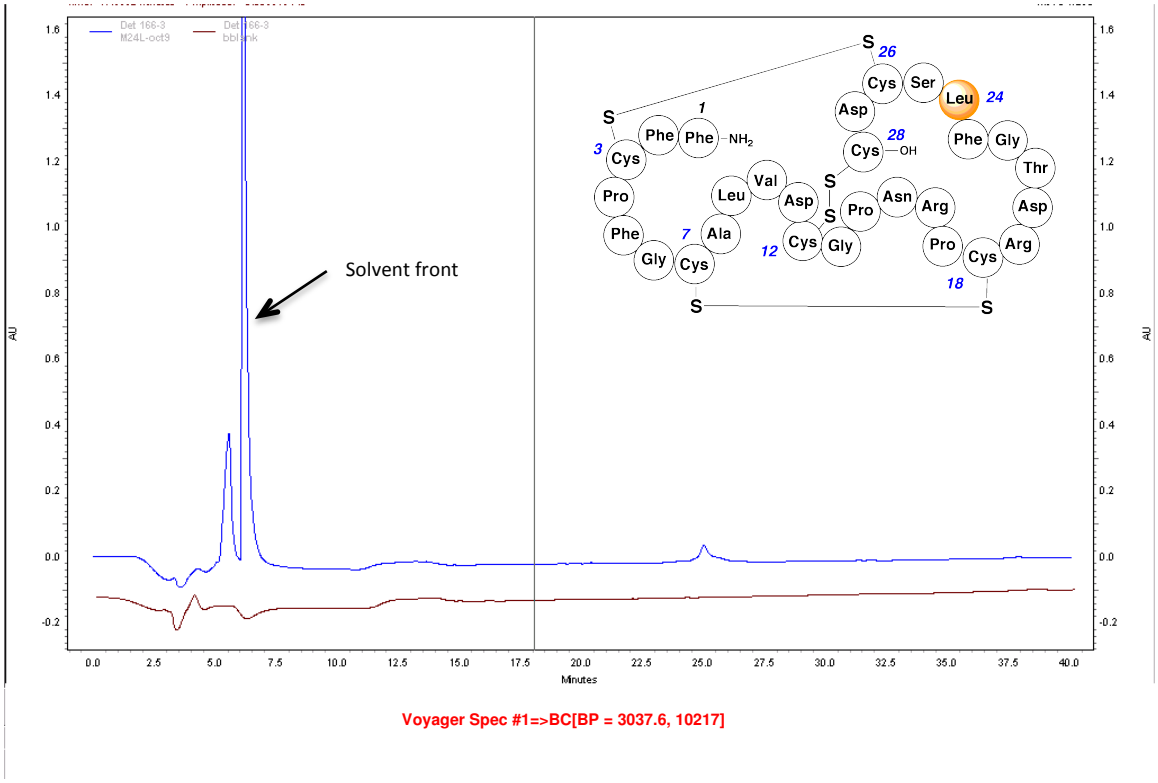


Voyager Spec #1=>BC=>BC[BP = 860.9, 44505]

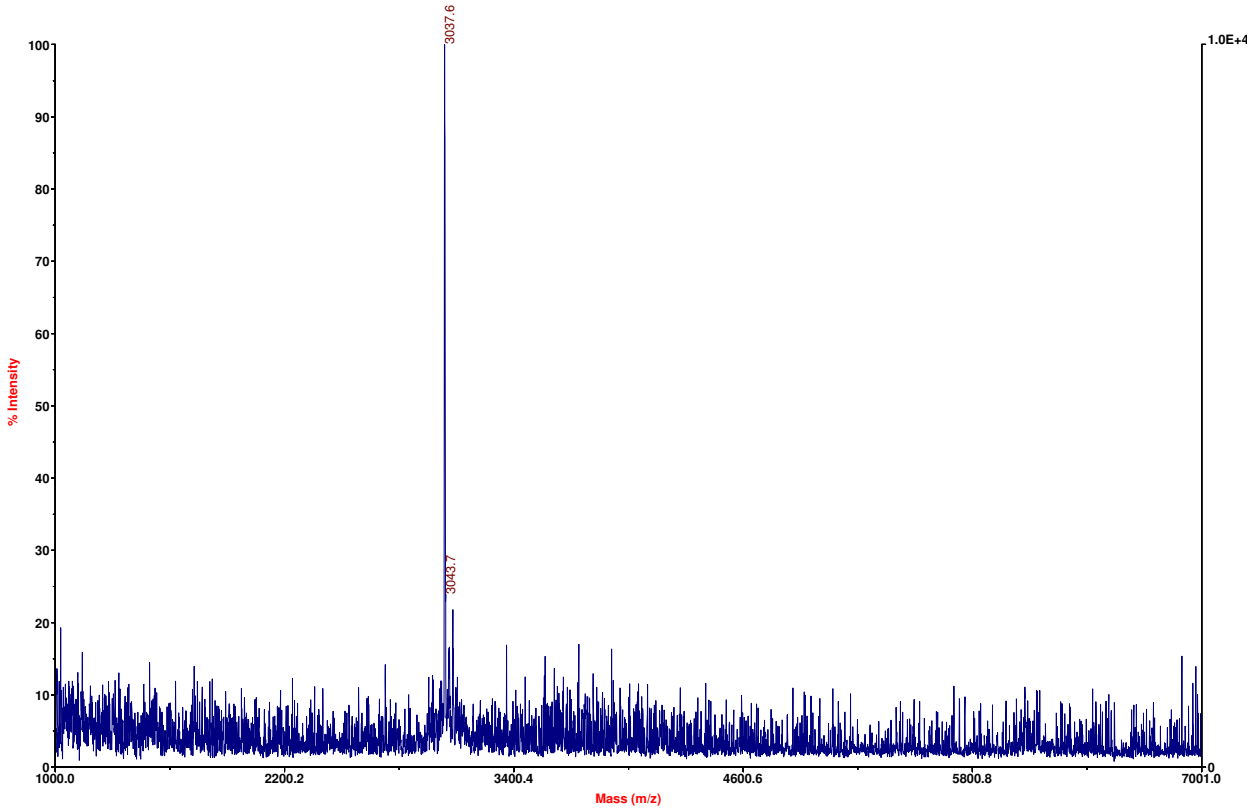


U:\...\M24A-2-26min_0001.dat
Acquired: 13:31:00, July 27, 2012

Tris-disulfide formation of residue 24 substitution with leucine (6) (M(O)24Leu)

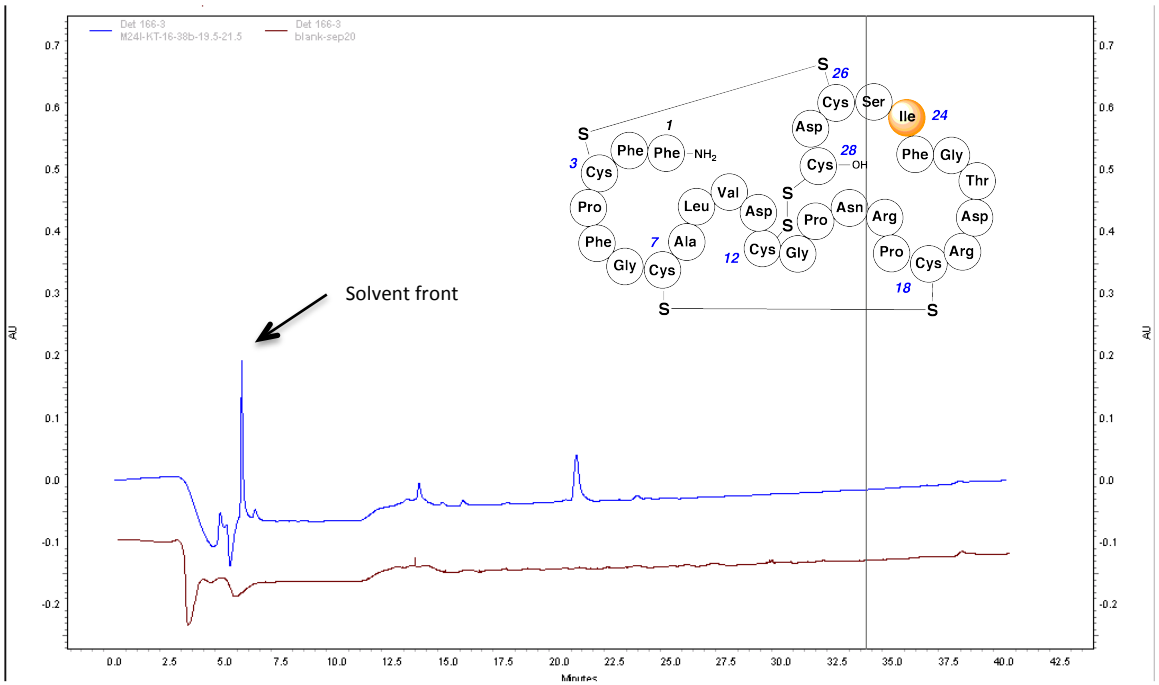


Voyager Spec #1=>BC[BP = 3037.6, 10217]

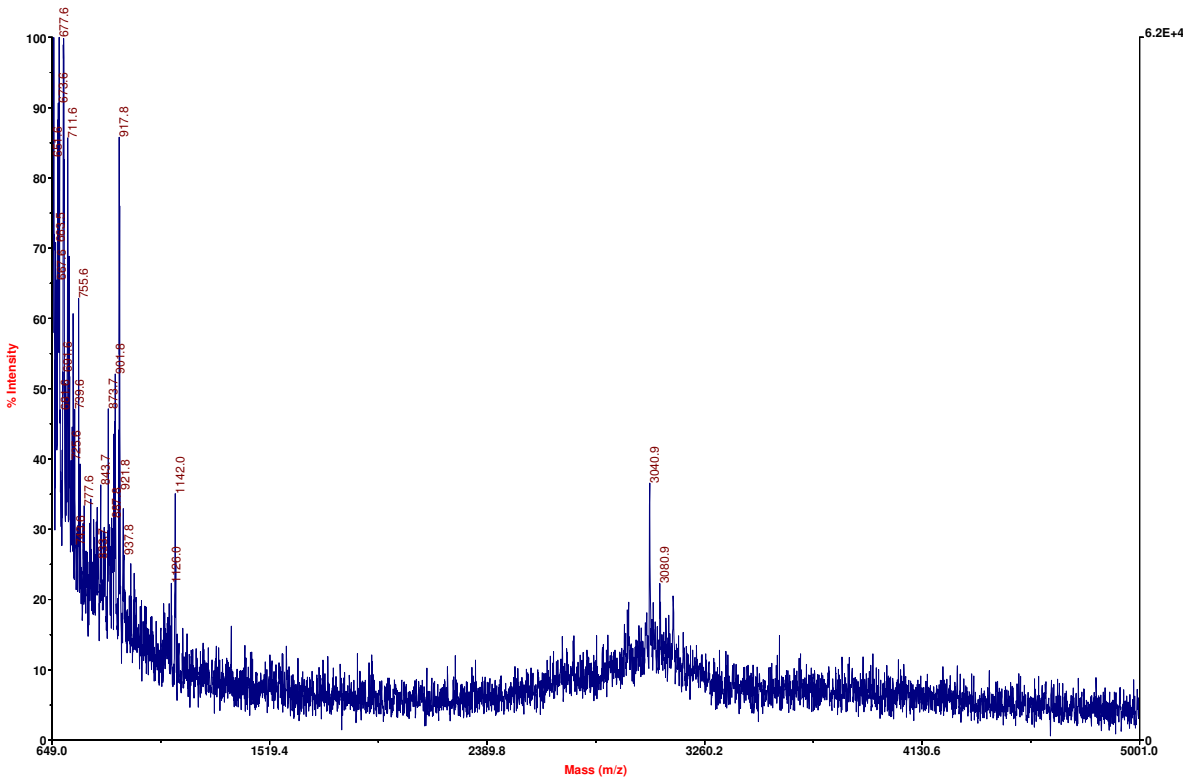


U:\...\M24L-24.4-25.1_0001.dat
Acquired: 14:03:00, October 04, 2012

Tris-disulfide formation of residue 24 substitution with isoleucine (7) (M(O)24Ile)

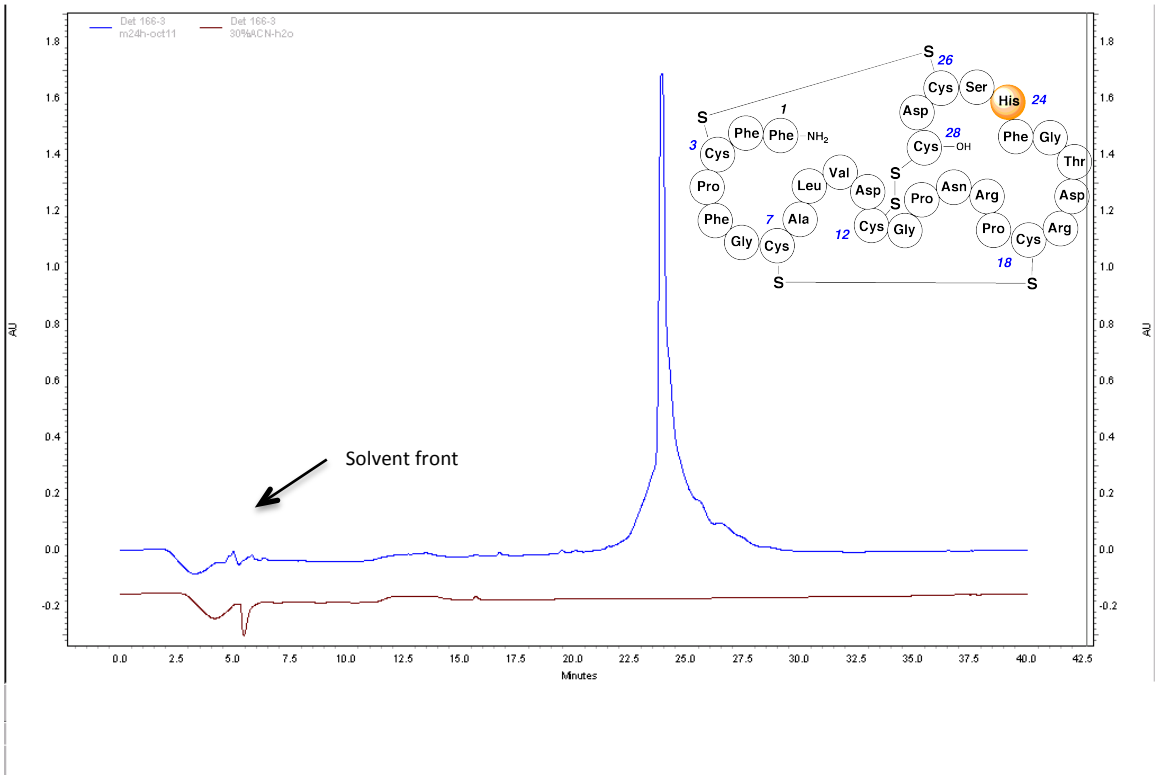


Voyager Spec #1=>BC[BP = 677.6, 61924]

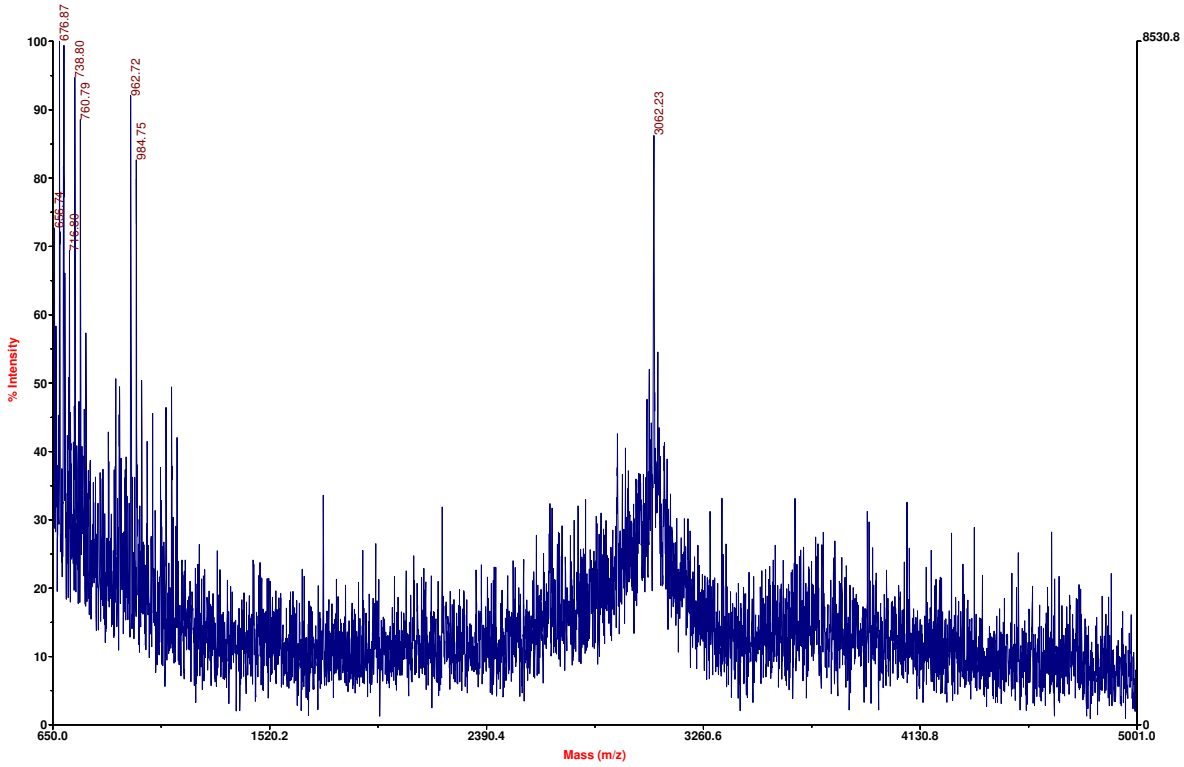


U:\...\M24Ile-trisdisulfide-Nov30-Kt-16-38a-pure_0001.dat
Acquired: 13:45:00, November 30, 2010

Tris-disulfide formation of residue 24 substitution with histidine (8) (M(O)24His)

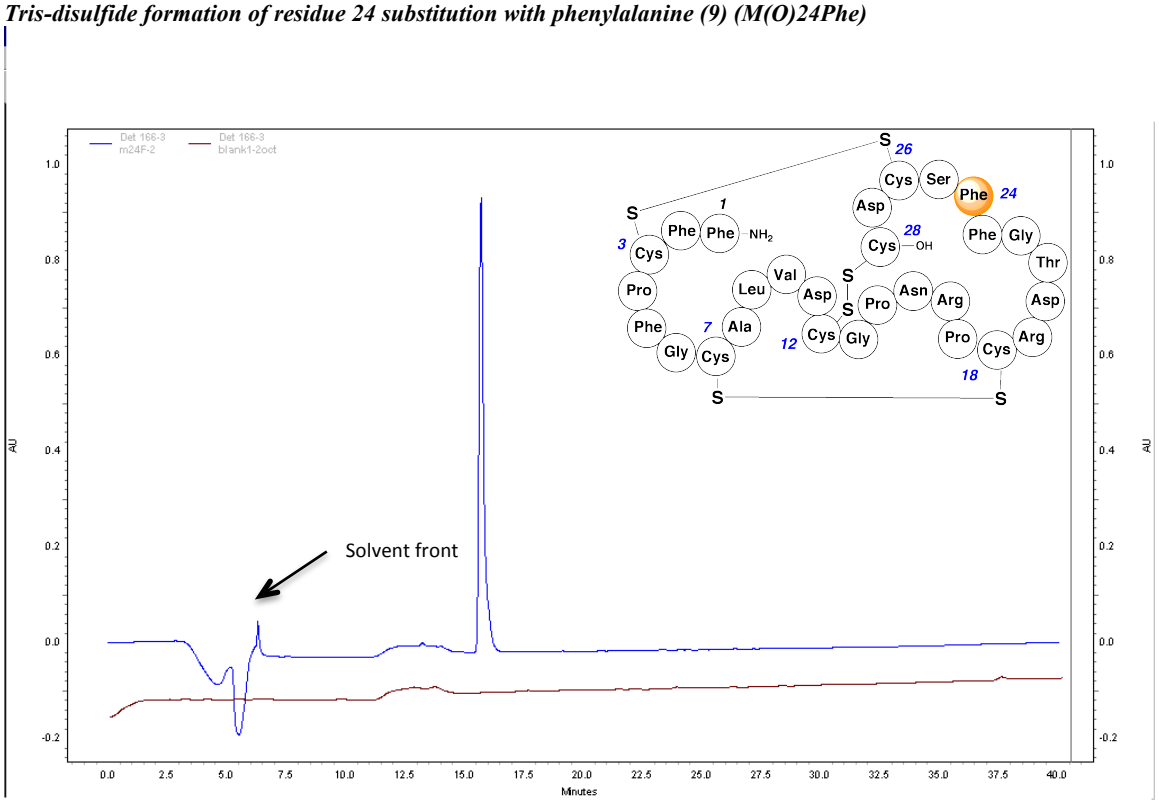


Voyager Spec #1=>BC[BP = 676.9, 8531]

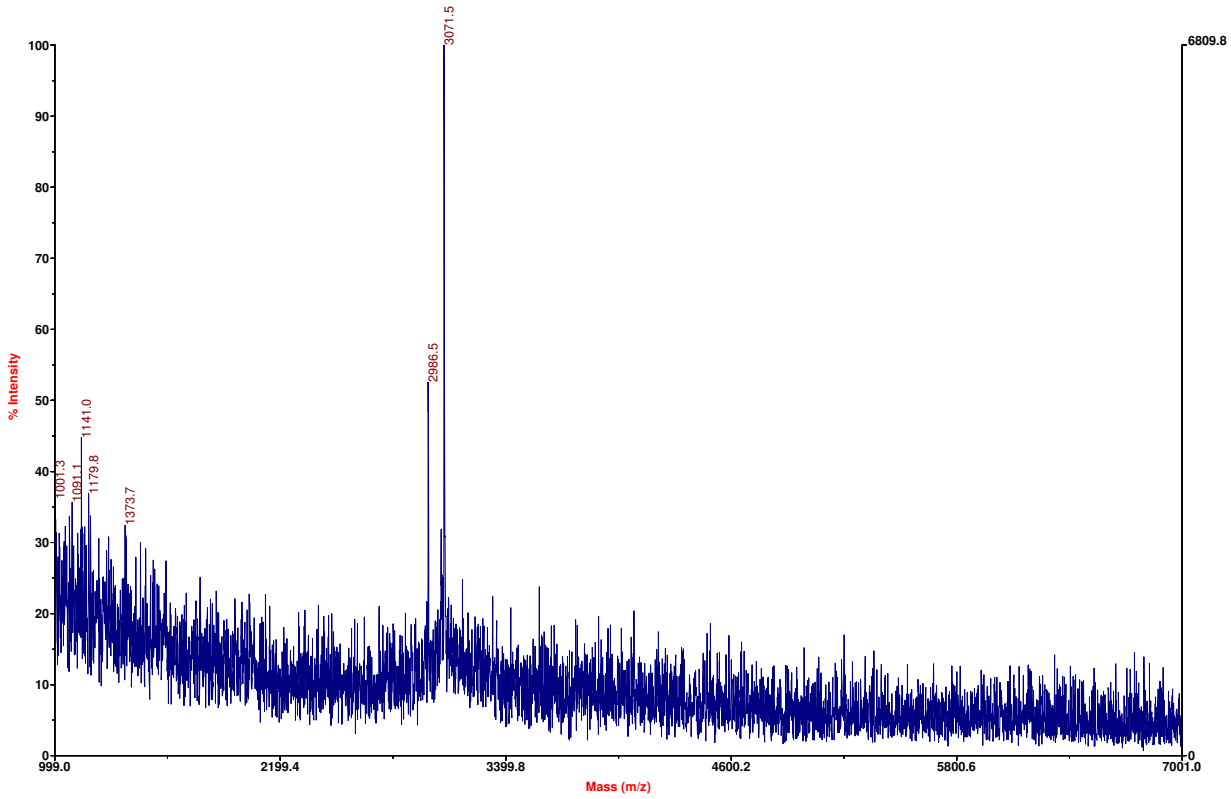


U:\...\JLC2-181_14.5-15.5min_1_0001.dat
Acquired: 23:15:00, January 22, 2012

Tris-disulfide formation of residue 24 substitution with phenylalanine (9) (M(O)24Phe)

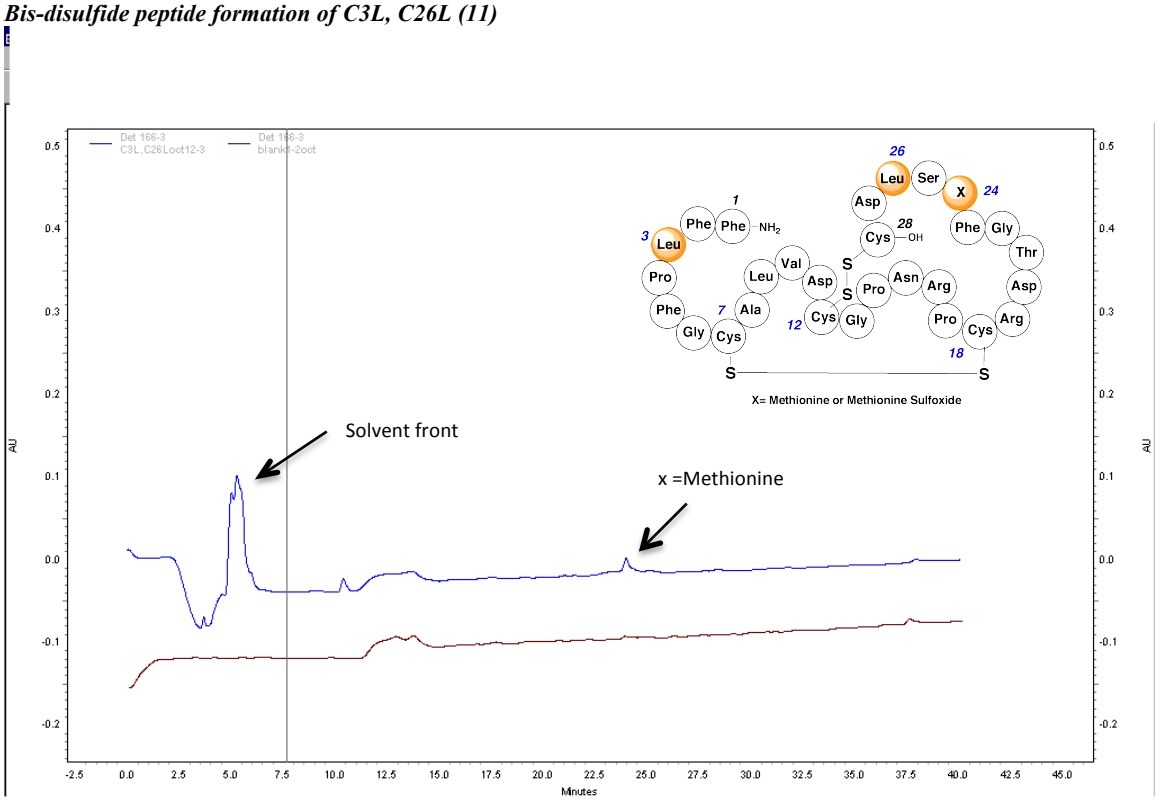


Voyager Spec #1=>BC[BP = 3071.5, 6810]

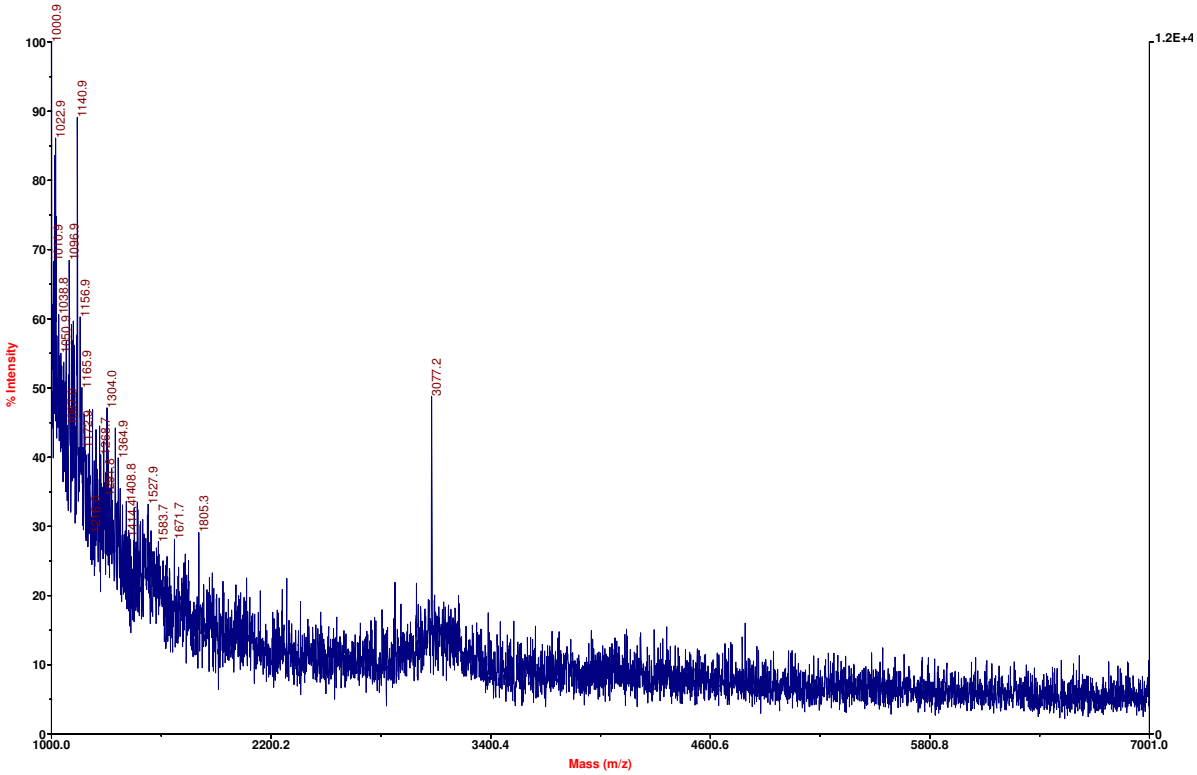


U:\...\M24F-trisdisulfide-22min_0001.dat
Acquired: 21:18:00, January 08, 2012

Bis-disulfide peptide formation of C3L, C26L (11)

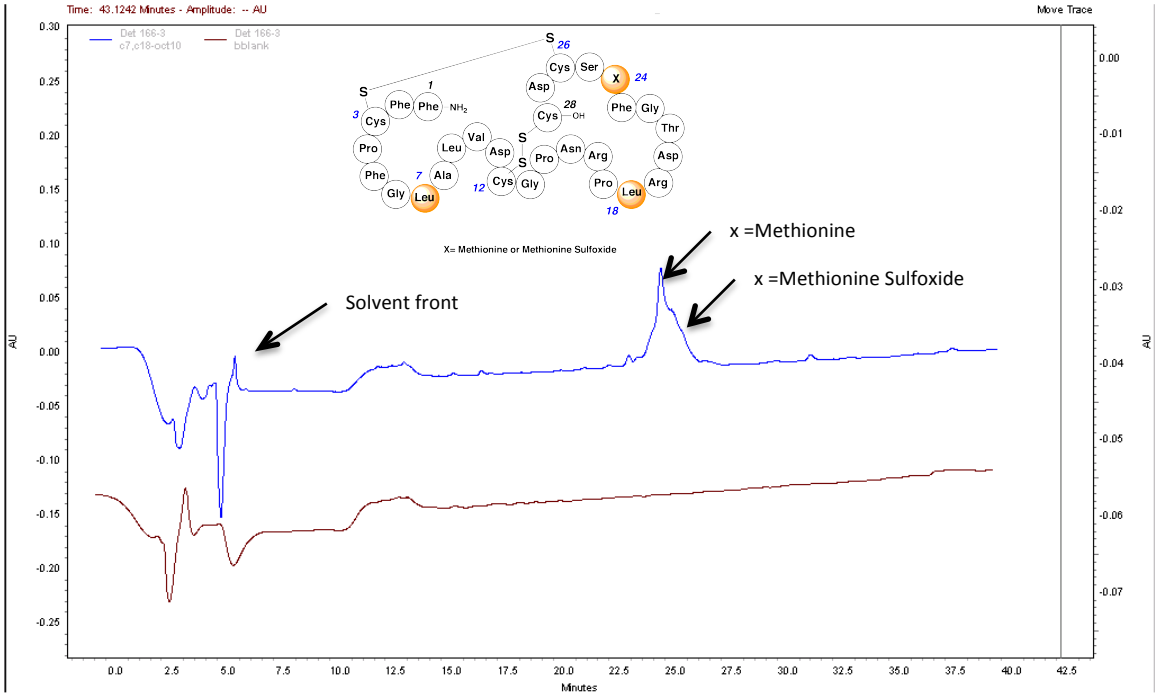


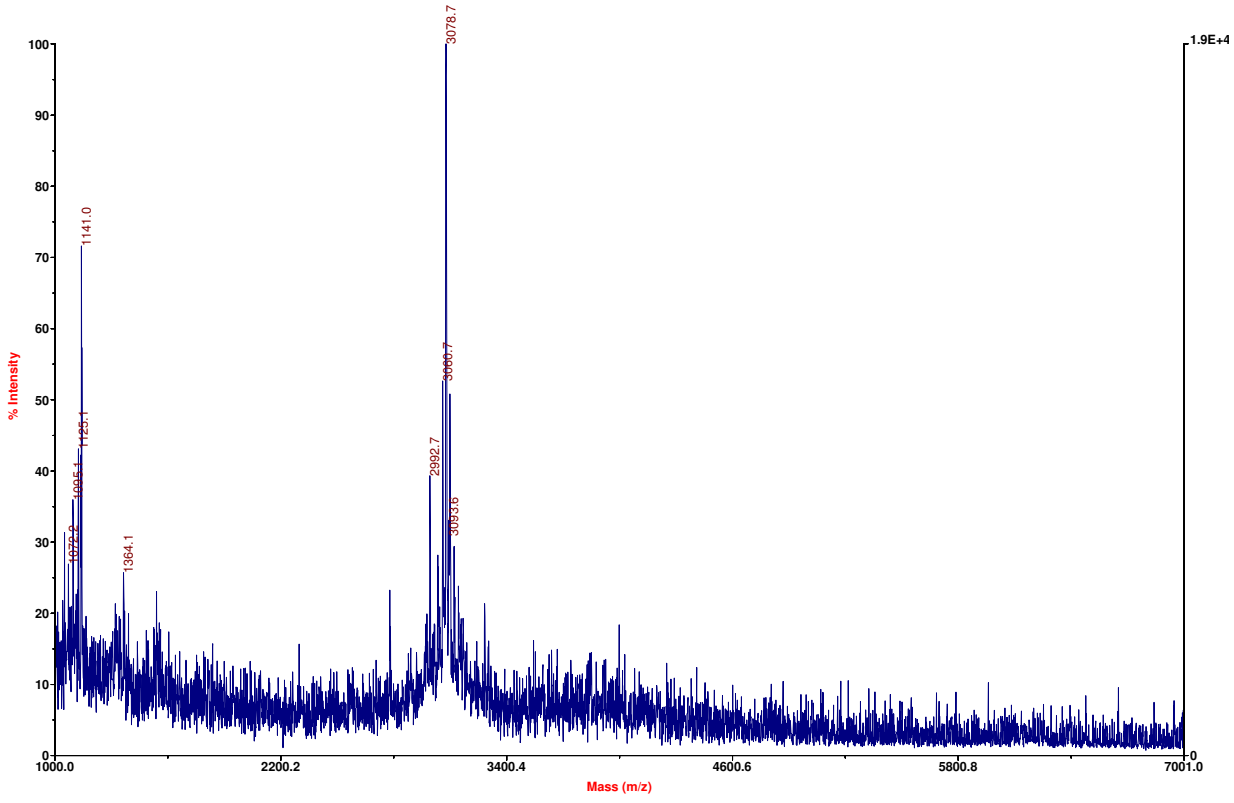
Voyager Spec #1=>BC[BP = 1000.9, 11997]



U:\...\C3l,C26L-oct12_0001.dat
Acquired: 13:51:00, October 12, 2012

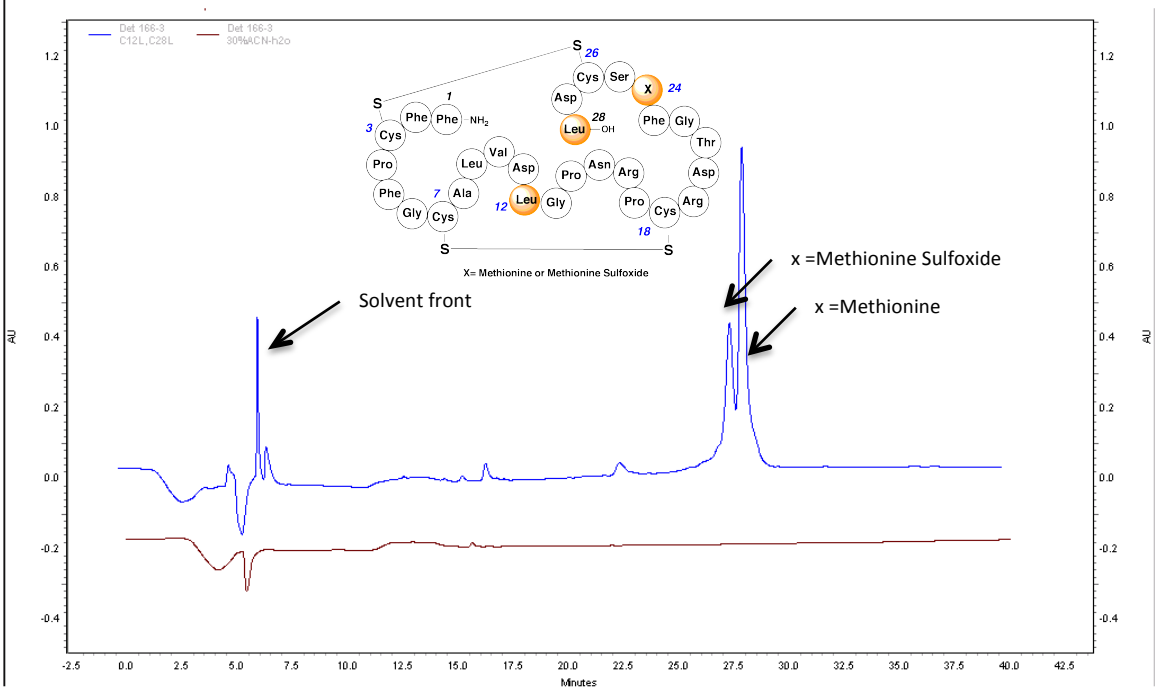
***Bis-disulfide peptide formation of C7L, C18L* (13)**



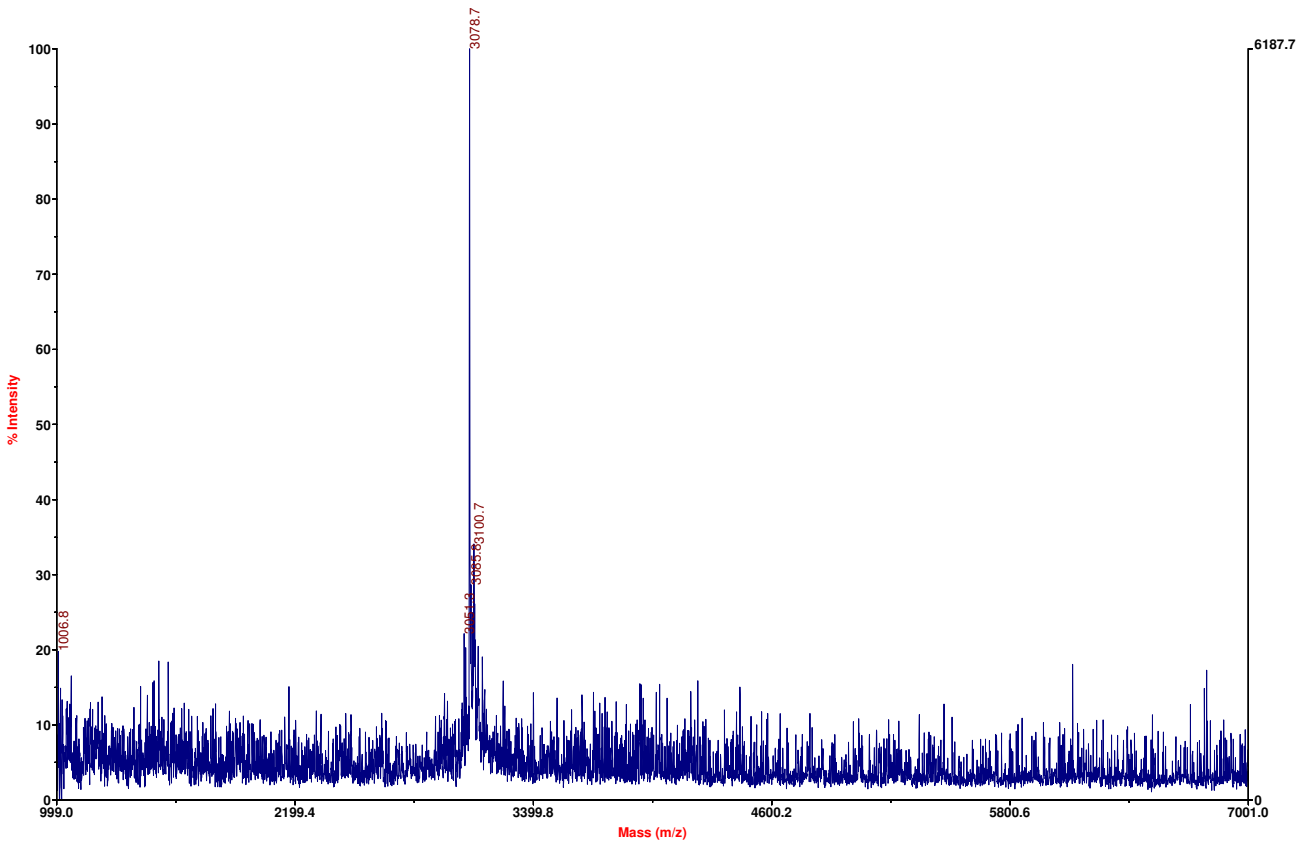


U:\...\24.6-26.1_0001.dat
Acquired: 14:17:00, October 04, 2012

Bis-disulfide peptide formation of C12L, C28L (15)

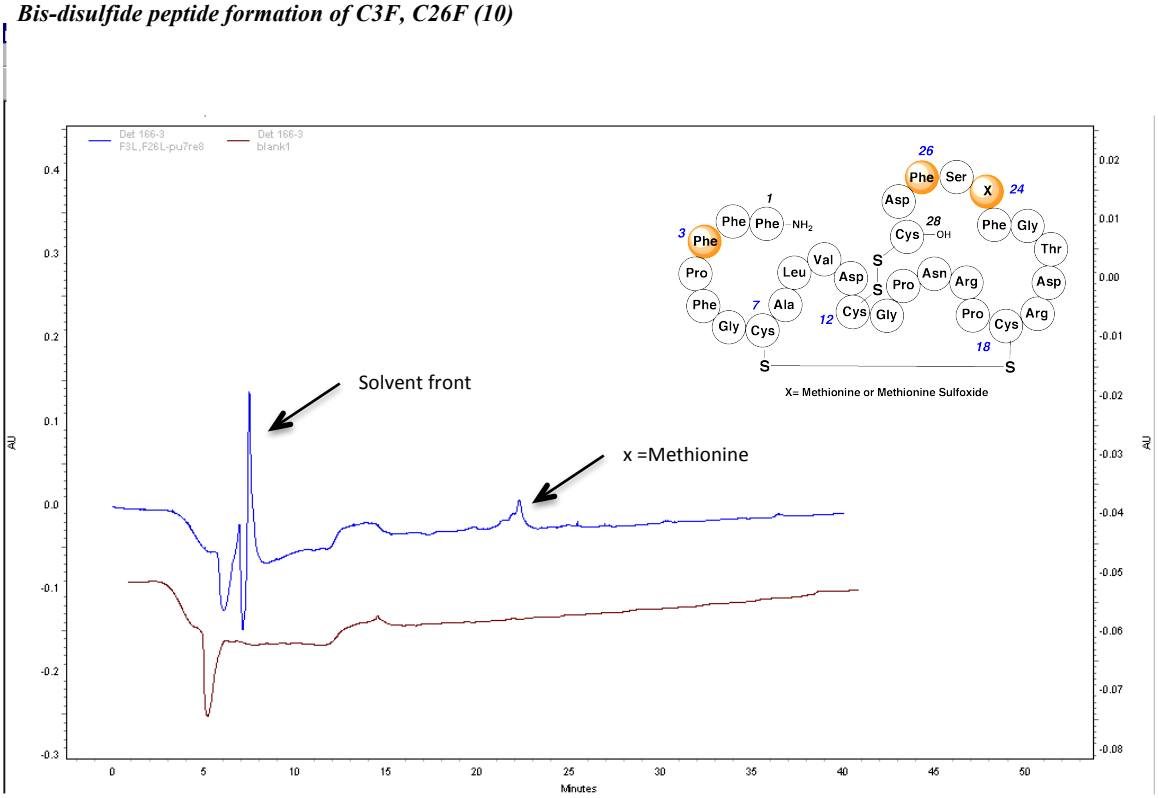


Voyager Spec #1=>BC[BP = 3078.7, 6188]

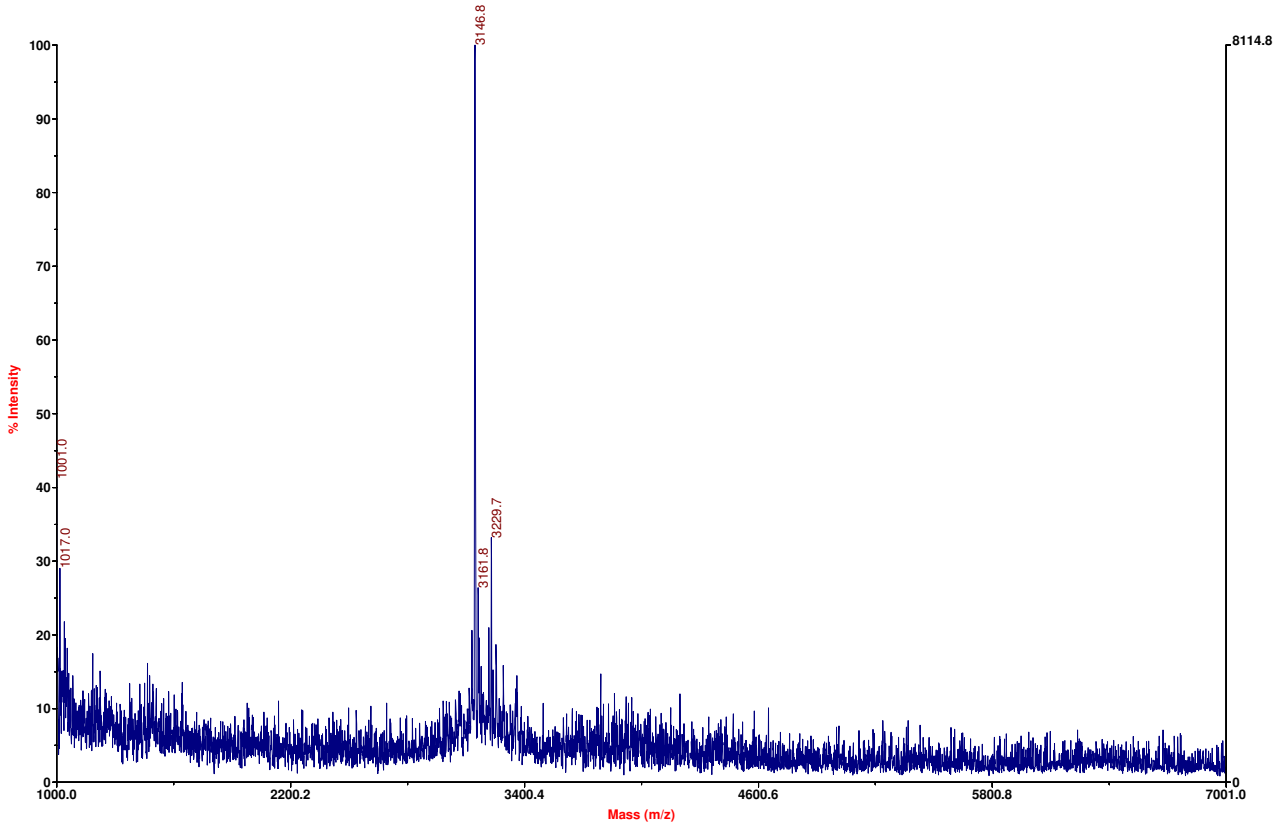


U:\...\JCL1-039-21-22min_0001.dat
Acquired: 00:38:00, January 03, 2012

Bis-disulfide peptide formation of C3F, C26F (10)

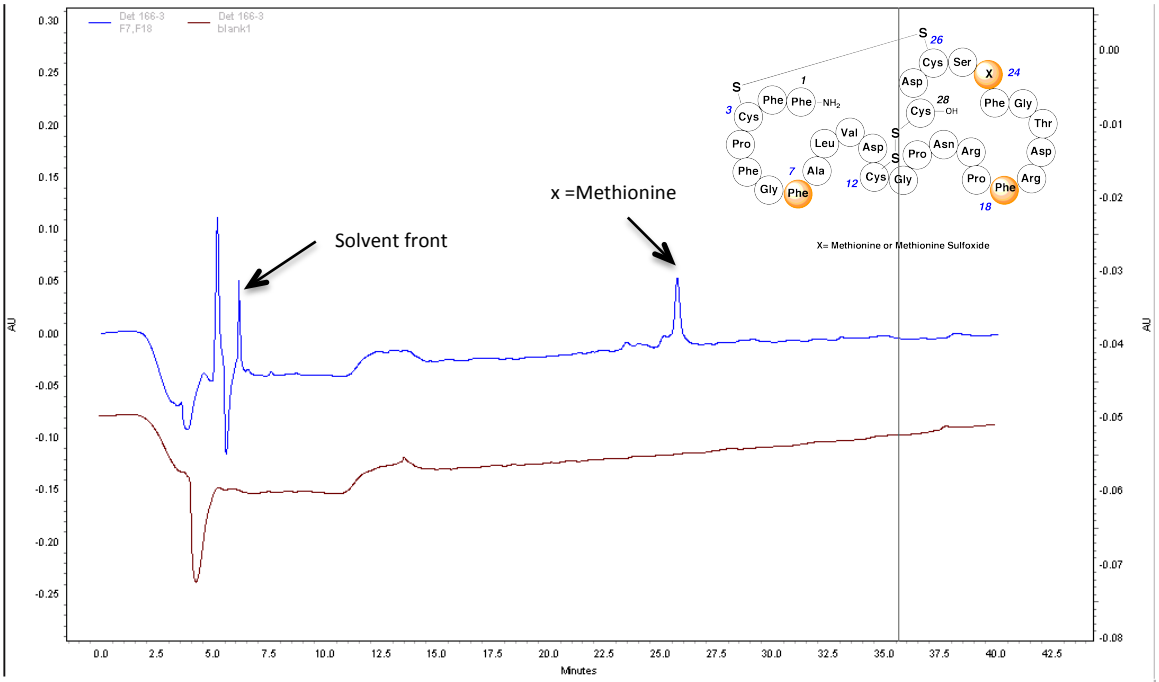


Voyager Spec #1=>BC[BP = 3146.8, 8115]

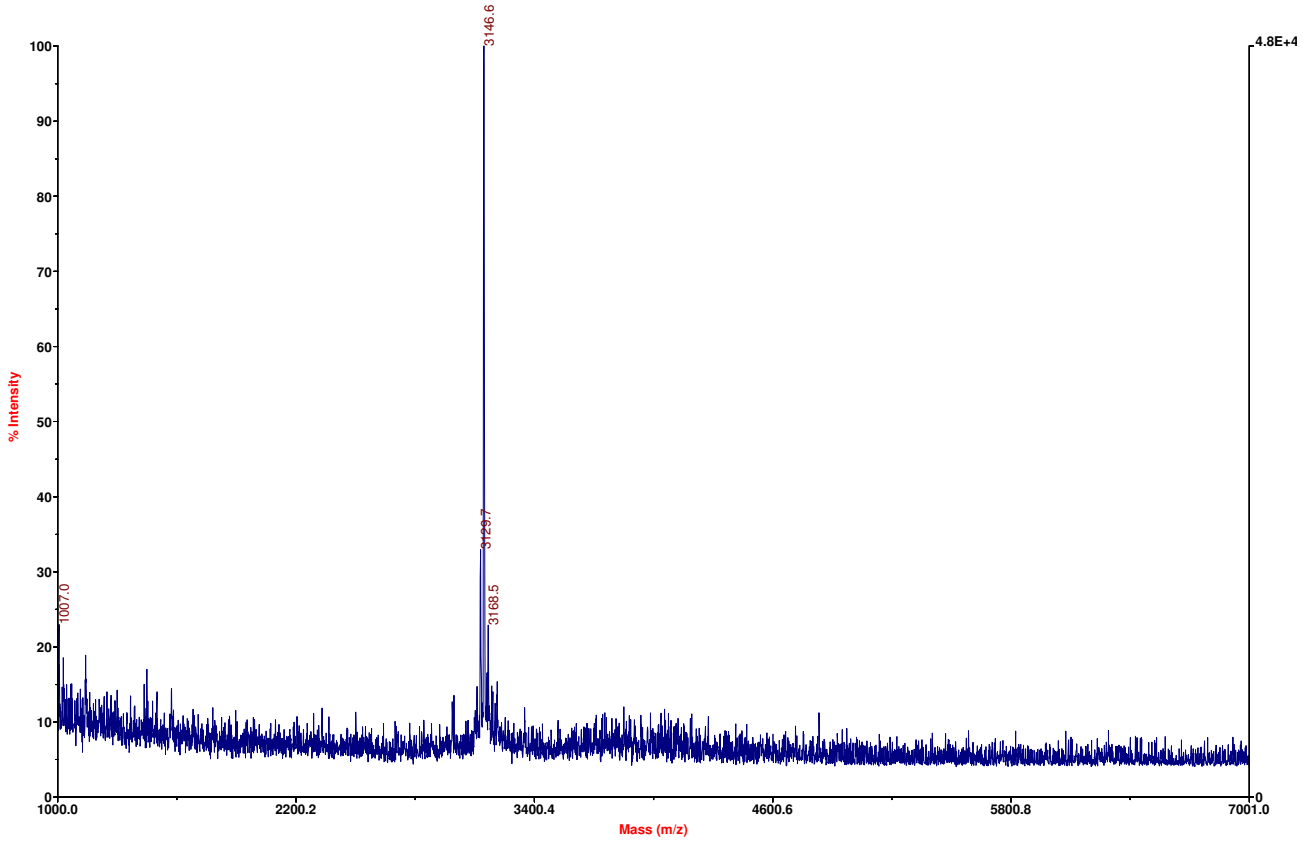


U:\...\F3C,F26C,23.3_0001.dat
Acquired: 14:06:00, September 18, 2012

Bis-disulfide peptide formation of C7F, C18F (12)

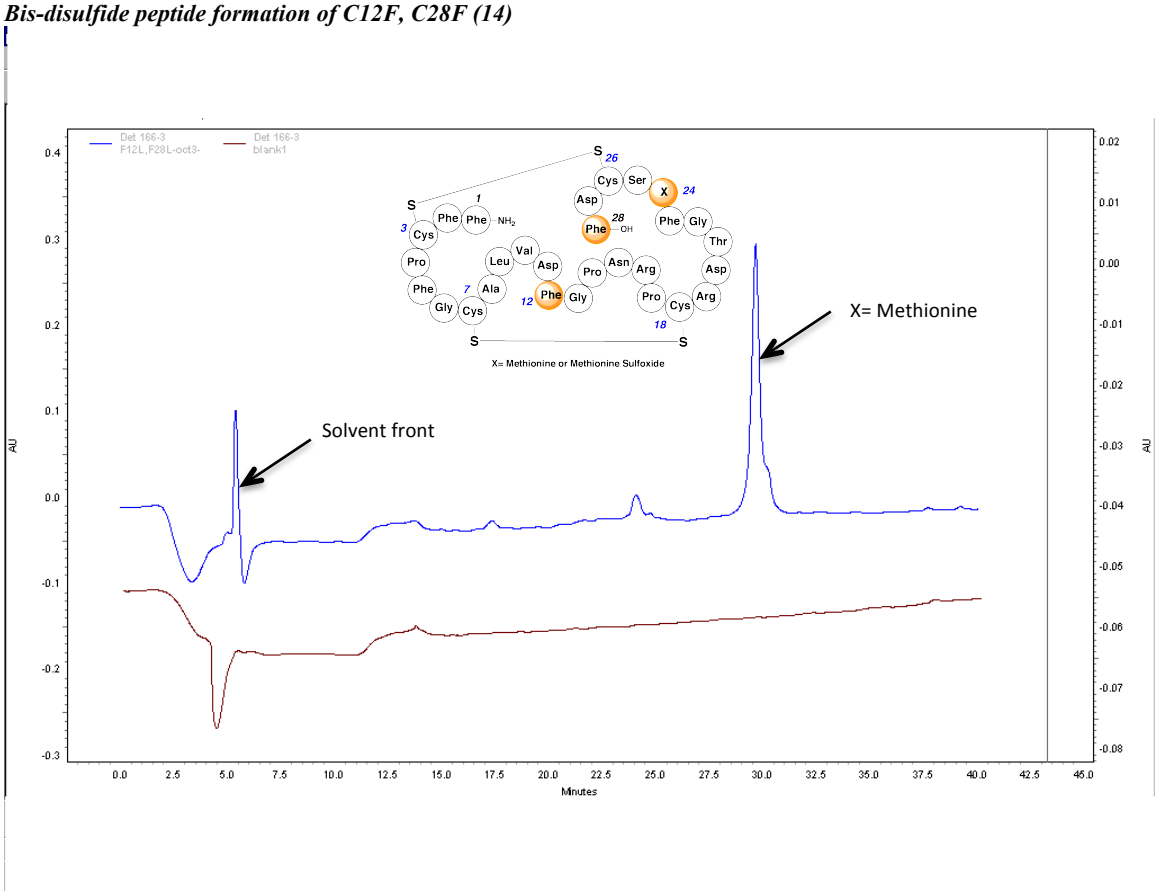


Voyager Spec #1[BP = 3146.6, 47972]

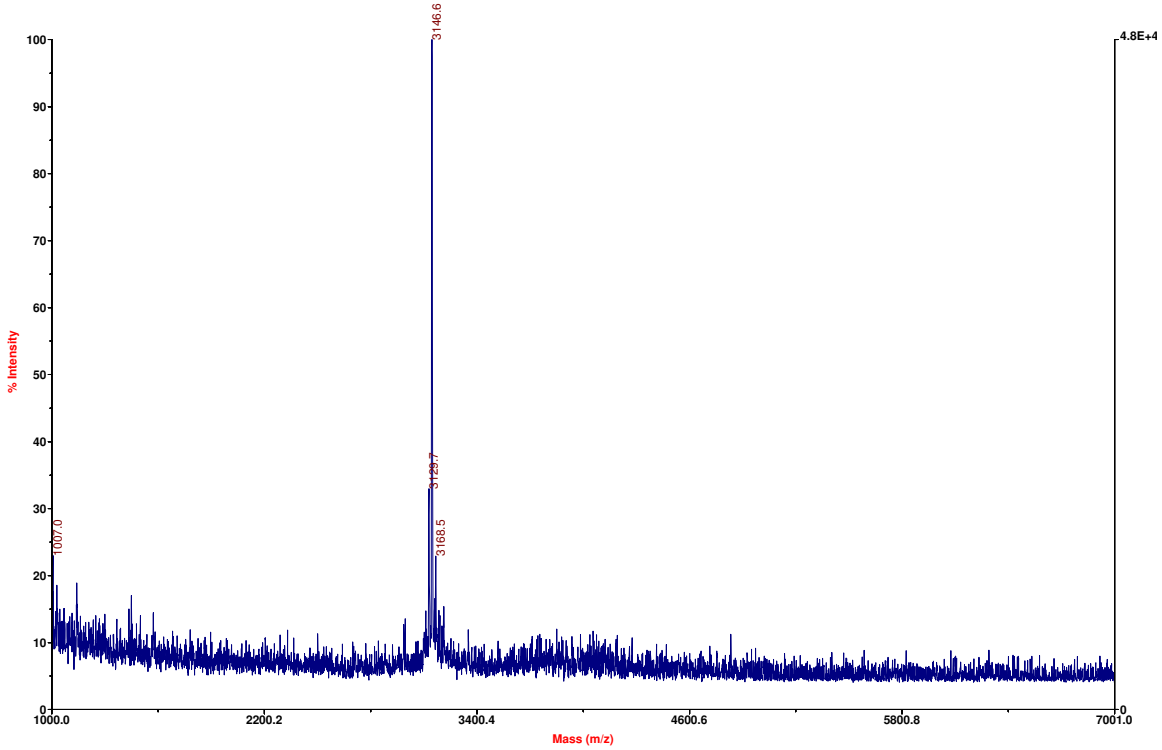


U:\...\29-30_0002.dat
Acquired: 14:19:00, October 04, 2012

Bis-disulfide peptide formation of C12F, C28F (14)



Voyager Spec #1[BP = 3146.6, 47972]



U:\...\29-30_0002.dat
Acquired: 14:19:00, October 04, 2012