SUPPORTING INFORMATION

A Promising General Solution to the Problem of Ligating Peptides and Glycopeptides

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Here we provide an expanded bibliography as to the total use of thio-intermediate in amide bond construction including simple peptide kinds:

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Materials and methods

All commercial materials (Aldrich, Fluka, Nova) were used without further purification. All solvents were reagent grade or HPLC grade (Fisher). Anhydrous THF, diethyl ether, CH_2Cl_2, toluene, and benzene were obtained from a dry solvent system (passed through column of alumina) and used without further drying. All reactions were performed under an atmosphere of pre-purified dry Ar (g). NMR spectra (^1H and ^{13}C) were recorded on a Bruker Advance DRX-600 MHz, referenced to TMS or residual solvent. Low-resolution mass spectral analyses were performed with a JOEL JMS-DX-303-HF mass spectrometer or Waters Micromass ZQ mass spectrometer. Analytical TLC was performed on E. Merck silica gel 60 F254 plates and flash column chromatography was performed on E. Merck silica gel 60 (40–63 mm). Yields refer to chromatographically pure compounds.

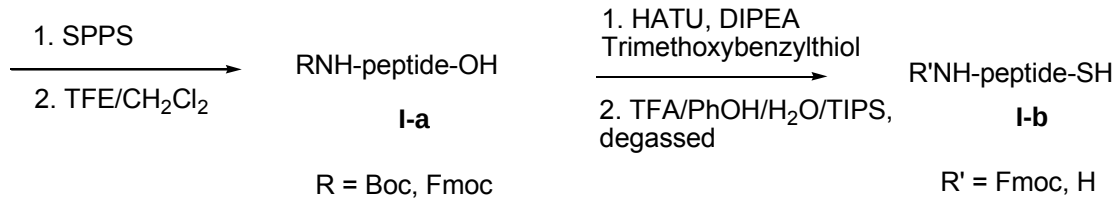
HPLC: All separations of peptides and glycopeptides involved a mobile phase of 0.05% TFA (v/v) in water (solvent A)/0.04% TFA in acetonitrile(solvent B). Preparative and analytical HPLC separations were performed using a Rainin HPXL solvent delivery system equipped with a Rainin UV-1 detector. LC-MS chromatographic separations were performed using a Waters Acquity Ultra Performance LC system equipped with acquity UPLC®BEN C18 column (1.7 µm, 2.1 x 100.0 mm) or acquity UPLC®BEN C8 column (1.7 µm, 2.1 x 100.0 mm) at a flow rate of 0.3 mL/min, Waters 2695 Separations Module and a Waters 996 Photodiode Array Detector equipped with Xbridge™ C18 column (5.0 µm, 2.1 x 150 mm), X-Terra™ MS C18 column (3.5 µm, 2.1 x 100.0 mm) or Varian Microsorb C18 column (2 x 150 mm) at a flow rate of 0.2 mL/min**.** HPLC separations were performed using: X-Bridge™ Prep C18 column OBDTM (5.0 µm, 19 x 150 mm) at a flow rate of 16 mL/min, Microsorb 100-5 C18 column at a flow rate of 16.0 mL/min, or Microsorb 300-5 C4 column at a flow rate of 16.0 mL/min.

Solid-phase peptide synthesis according to Fmoc-strategy

Automated peptide synthesis was performed on an Applied Biosystems Pioneer continuous flow peptide synthesizer. Peptides were synthesized under standard automated Fmoc protocols. The deblock mixture was a mixture of 100/5/5 of DMF/piperidine/DBU. The following Fmoc amino acids from NovaBiochem were employed: Fmoc-Ala-OH,

Fmoc-Arg(Pbf)-OH, Fmoc-Asn(Trt)-OH, Fmoc-Asp(O*t*Bu)-OH, Fmoc-Cys(*t*Buthio)-OH, Fmoc-Cys(Trt)-OH, Fmoc-Glu(O*t*Bu)-OH, Fmoc-Gln(Trt)-OH, Fmoc-Gly-OH, Fmoc-His(Boc)-OH, Fmoc-Ile-OH, Fmoc-Leu-OH, Fmoc-Lys(Boc)-OH, Fmoc-Met-OH, Fmoc-Phe-OH, Fmoc-Pro-OH, Fmoc-Ser(*t*Bu)-OH, Fmoc-Thr(*t*Bu)-OH, Fmoc-Trp(Boc)-OH, Fmoc-Tyr(*t*Bu)-OH, Fmoc-Val-OH, Fmoc-Ile-Thr($\psi^{Me,Me}$Pro)-OH, Fmoc-Ser(*t*Bu)-Ser($\psi^{Me,Me}$Pro)-OH. Upon completion of automated synthesis on a 0.05 mmol scale, the peptide resin was washed into a peptide synthesis vessel with DCM. The resin cleavage was effected by treatment with AcOH/TFE/DCM (1:1:4) for 3 x 25 min to yield peptidyl acids in good yield.

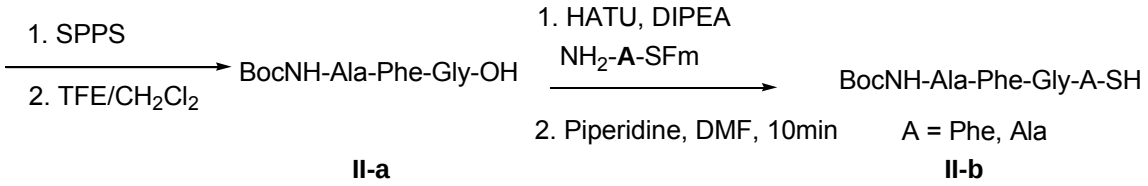
General Procedure I for thioacid **7**, **12**, **17**, **19**.



Following the general procedure for SPPS, peptides was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Gly(or Pro)-NovaSyn® TGT resin, and other standard Fmoc, Boc amino acids.

To a solution of **I-a** (0.02 mmol), 2, 4, 6-trimethoxybenzylthiol (0.1 mmol) in anhydrous DMF (200 uL) was added HATU (0.1 mmol) and DIPEA (0.08 mmol), and stirred overnight. The reaction was concentrated under a stream of nitrogen and the residue was passed through short silica gel column (10% MeOH/CH_2Cl_2) to give a white solid. Next the solid was treated with degassed cocktail TFA (30.0 mg of phenol, 0.1 ml of water, 0.07 ml of triisopropylsilane, and 1.5 ml TFA) for one hour. The solution was diluted with water (10 mL) and lyophilized immediately. The residue was triturated with diethyl ether to give a white suspension, which was centrifuged and the ether subsequently decanted. The resulting solid was purified by HPLC to give thioacid **I-b**.

General Procedure II for thioacid **21**, **24**, **26**.

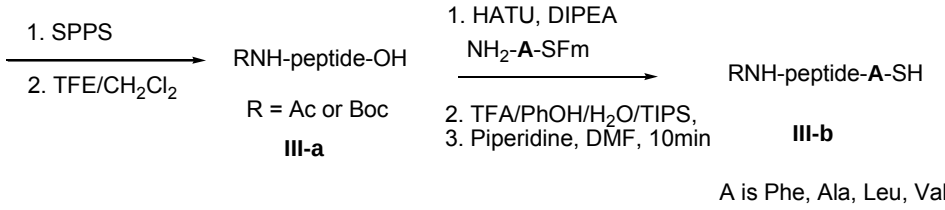


Following the general procedure for SPPS, peptide was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Gly-NovaSyn® TGT resin, Boc-Ala-OH, Boc-Val-OH, Ac-Gly-OH and other standard Fmoc amino acids.

To a solution of **II-a** (0.02 mmol) and NH_2-A-SFm (0.04 mmol) in anhydrous DMF (300 uL) was added HATU (0.04 mmol) and DIPEA (0.03 mmol) at rt. The reaction mixture was stirred at rt for 12 h. The solution was diluted with CH_2Cl_2. This organic phase was washed with H_2O, 1N HCl solution, brine and dried over Na_2SO_4. The solution was filtered, concentrated.

To a solution of the residue in anhydrous DMF (200 uL) was added piperidine (20 uL) at rt. The reaction mixture was stirred at rt for 15 min. The solution was diluted with EtOAc. The organic phase was washed with H_2O, 1N HCl solution, brine and dried over Na_2SO_4. The solution was filtered, concentrated. The resulting solid was purified by HPLC to give thioacid **II-b**.

General Procedure III for thioacid **28**, **31**, **33**.



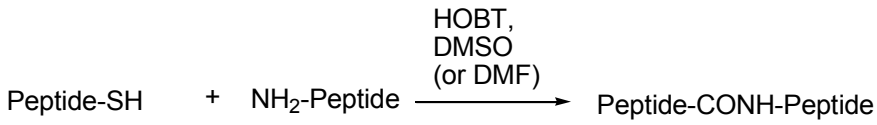
Following the general procedure for SPPS, peptide was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Gly-NovaSyn® TGT resin, Boc-Ala-OH, Boc-Val-OH, Ac-Gly-OH and other standard Fmoc amino acids.

To a solution of **III-a** (0.02 mmol) and NH_2-A-SFm (0.04 mmol) in anhydrous DMF (300 uL) was added HATU (0.04 mmol) and DIPEA (0.03 mmol) at rt. The reaction mixture was stirred at rt for 12 h. The solution was diluted with CH_2Cl_2. This

organic phase was washed with H_2O, 1N HCl solution, brine and dried over Na_2SO_4. The solution was filtered, concentrated. Next the residue was treated with cocktail TFA (30.0 mg of phenol, 0.1 ml of water, 0.07 ml of triisopropylsilane, and 1.5 ml TFA) for one hour. The reaction was concentrated under a stream of nitrogen and the residue was triturated with diethyl ether to give a white suspension, which was centrifuged and the ether subsequently decanted.

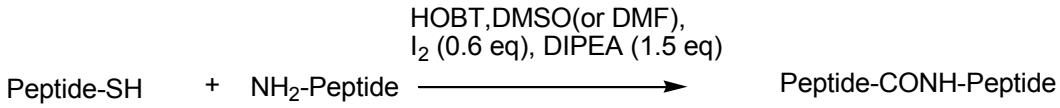
To a solution of the residue in anhydrous DMF (200 uL) was added piperidine (15 uL) at rt. The reaction mixture was stirred at rt for 20min. The reaction was concentrated under a stream of nitrogen and the residue was triturated with diethyl ether to give a white suspension, which was centrifuged and the ether subsequently decanted. The resulting solid was purified by HPLC to give thioacid **III-b**.

General procedure IV for HOBT-mediated Ligation:



To a mixture of thioacid (1.2 eq), NH_2-peptide (1.0 eq) and 4Å MS (2 mg) was added 30 uL DMSO (or DMF, containing 2.0 eq HOBT). The reaction mixture was stirred at room temperature for 3-6 h. The reactions were monitored by LC-MS and purified directly by HPLC upon complete consumption of the starting material.

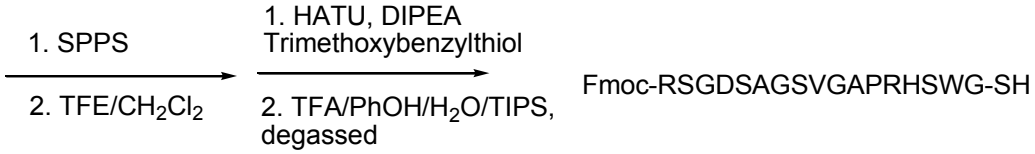
General procedure V for I_2/HOBT-mediated Ligation:



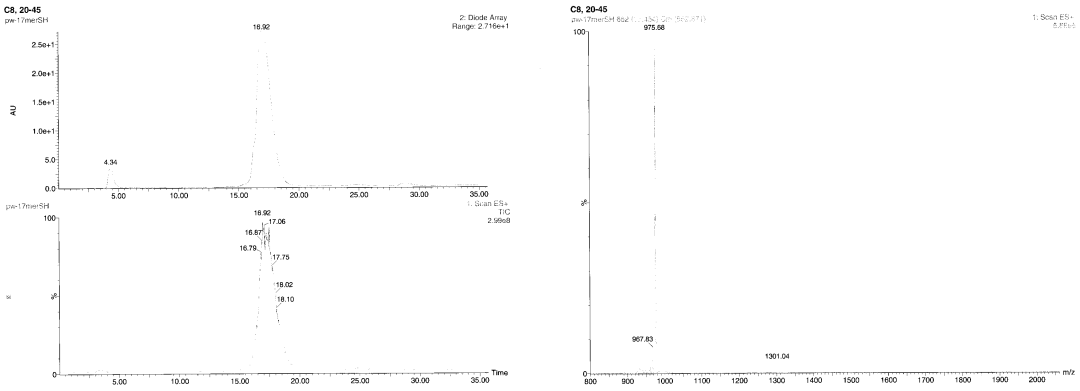
To an oven-dried vial were charged thioacid (1.2 eq), NH_2-peptide (1.0 eq) and 4Å MS (2 mg). A stock solution of DIPEA/HOBT (1.5 eq DIPEA, 2.0 eq HOBT in DMSO or DMF) and I_2 (0.6 eq in DMSO or DMF) was added to the vial. The reactions were monitored by LC-MS and purified directly by HPLC upon complete consumption of the starting material.

Preparation of thioacid..

Fmoc-RSGDSAGSVGAPRHSWG-SH **7**

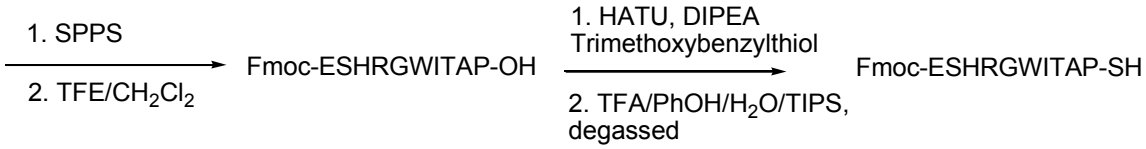


Following the general procedure for SPPS and I, peptide **7** (0.02 mmol) was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Gly-NovaSyn® TGT resin and other standard Fmoc amino acids. According to the general procedure, thioacid **7** (13.0 mg, 33% over two steps) was obtained as a white powder after HPLC (20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) purification and lyophilization.

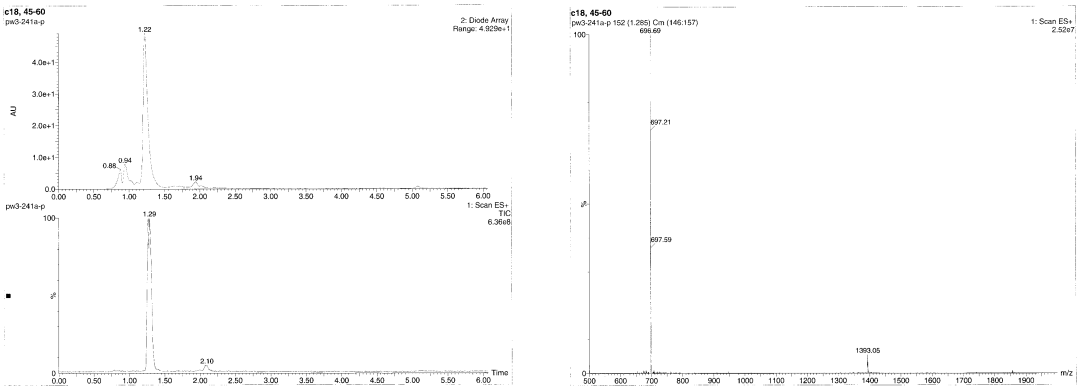


a) UV and MS traces from LC-MS analysis of thioacid **7**: gradient 20-45% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C4 column. (b) ESI-MS of compound**.** ESI calcd for $C_{86}H_{121}N_{26}O_{25}S$ $[M+H]^+$ *m/z* = 1949.86, $[M+2H]^{2+}$ *m/z* = 975.43, found: 975.68.

Fmoc-ESHRGWITAP-SH **12**

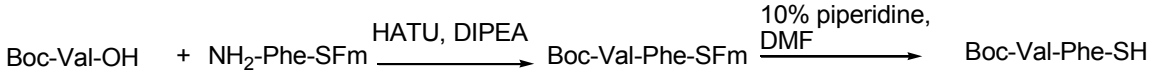


Following the general procedure for SPPS and I, peptide **12** (0.02 mmol) was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Pro-NovaSyn® TGT resin and other standard Fmoc amino acids. According to the general procedure, thioacid **12** (9.0 mg, 32% over two steps) was obtained as a white powder after HPLC (30-50% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 265 nm) purification and lyophilization.



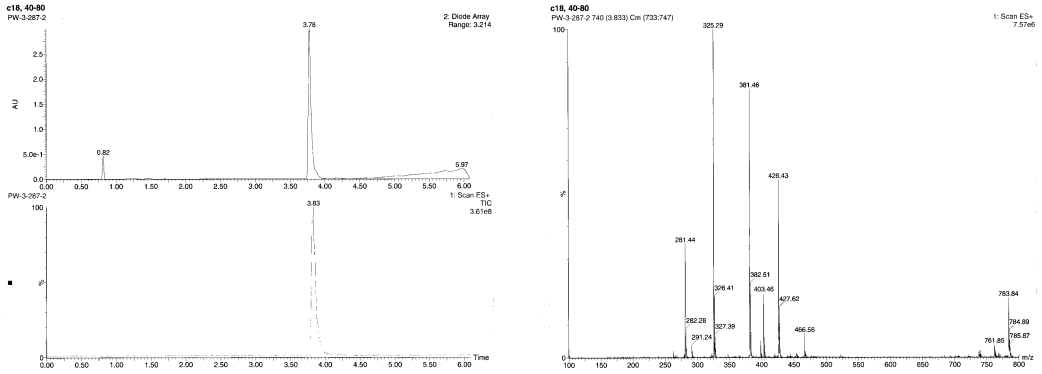
a) UV and MS traces from UPLC-MS analysis of thioacid **12**: gradient 45-60% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{66}H_{87}N_{16}O_{16}S$ $[M+H]^+$ *m/z* = 1391.61, $[M+2H]^{2+}$ *m/z* = 696.31, found: 1391.93, 696.69.

Boc-Val-Phe-SH **21**



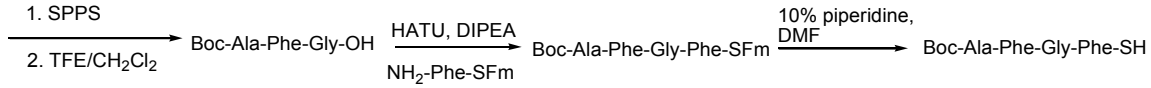
To a solution of Boc-Val-OH (10 mg, 0.046 mmol) and NH_2-Ala-SFm (17 mg, 0.047 mmol) in anhydrous CH_2Cl_2 (200 uL) was added HATU (28 mg, 0.073 mmol) and DIPEA (15 uL) at rt. The reaction mixture was stirred at rt for 12 h. The solution was diluted with CH_2Cl_2. This organic phase was washed with H_2O, 1N HCl solution, brine and dried over Na_2SO_4. The solution was filtered, concentrated.

To a solution of the residue in anhydrous DMF (200 uL) was added piperidine (20 uL) at rt. The reaction mixture was stirred at rt for 15 min. The solution was diluted with EtOAc. The organic phase was washed with H_2O, 1N HCl solution, brine and dried over Na_2SO_4. The solution was filtered, concentrated. Thioacid **21 (**12 mg, 67% over two steps) was obtained as a white powder after HPLC (50-90% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) purification and lyophilization. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (t, 2 H, *J* = 7.5 Hz), 7.27-7.23 (m, 1 H), 7.10 (d, 2 H, *J* = 7.5 Hz), 6.38 (br, s, 1 H), 4.91-4.88 (m, 1 H), 4.83 (br, s, 1 H), 4.58 (br, s, 1 H), 3.85-3.83 (dd, 1 H, *J* = 6.0, 8.4 Hz), 3.13-3.07 (m, 2 H), 2.12-2.08 (m, 1 H), 1.41 (s, 9 H), 0.88 (d, 3 H, *J* = 6.7 Hz), 0.79 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.7, 135.2, 129.3, 128.9, 127.4, 60.5, 37.6, 30.2, 28.3, 19.3; HR-ESIMS (*m/z*) Calcd for $C_{19}H_{28}N_2O_4SNa$: $[M+Na]^+$ *m/z* = 403.1668; Found: 403.1655.

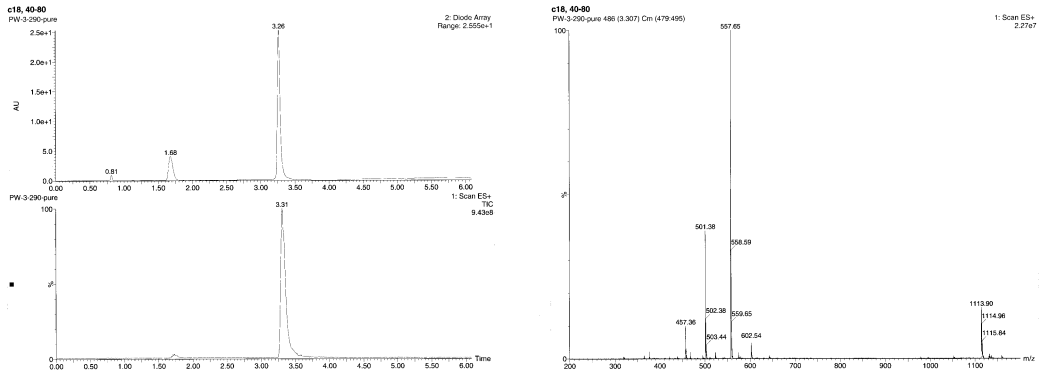


a) UV and MS traces from UPLC-MS analysis of thioacid **21**: gradient 40-80% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{19}H_{29}N_2O_4S$ $[M+H]^+$ *m/z* = 381.18, found: 381.46.

Boc-Ala-Phe-Gly-Phe-SH **24**

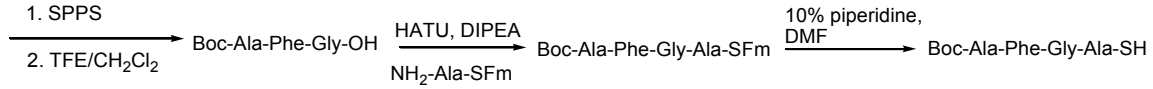


Following the general procedure for SPPS and II, peptide **24** (0.02 mmol)was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Gly-NovaSyn® TGT resin and other standard amino acids. According to the general procedure, thioacid **24** (7.3 mg, 66% over two steps) was obtained as a white powder after HPLC (50-80% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) purification and lyophilization. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25-7.23 (m, 3 H), 7.20-7.15 (m, 3 H), 7.16-7.11 (m, 3 H), 7.08 (d, 1 H, *J* = 7.1 Hz), 6.53 (d, 1 H, *J* = 8.4 Hz), 4.82 (s, 1 H), 4.74-4.71 (m, 1 H), 4.48-4.47 (m, 1 H), 4.00-3.96 (m, 1 H), 3.82-3.81 (m, 1 H), 3.57-3.54 (m, 1 H), 3.19-3.16 (m, 1 H), 3.10-3.06 (m, 2 H), 2.94 (dd, 1 H, *J* = 9.2, 14.4 Hz), 1.26 (s, 9 H), 1.20 (d, 3 H, *J* = 7.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.4, 173.7, 171.3, 169.4, 156.4, 136.3, 135.9, 129.3, 129.04, 129.01, 128.5, 127.4, 126.9, 81.5, 61.4, 54.7, 51.9, 43.1, 37.1, 36.6, 28.2, 17.5; HR-ESIMS (*m/z*) Calcd for $C_{28}H_{36}N_4O_6SNa$: $[M+Na]^+$ *m/z* = 579.2254; Found: 579.2242.

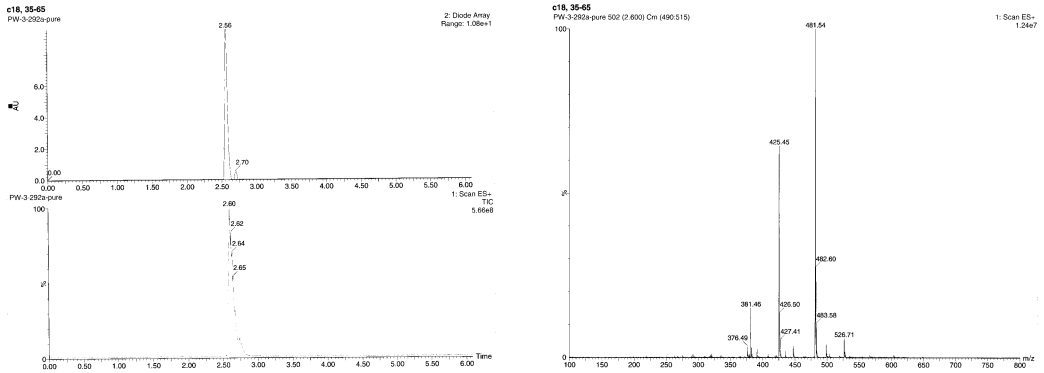


b) UV and MS traces from UPLC-MS analysis of compound **24**: gradient 40-80% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{28}H_{37}N_4O_6S$ $[M+H]^+$ *m/z* = 557.24, found: 557.65.

Boc-Ala-Phe-Gly-Ala-SH **26**

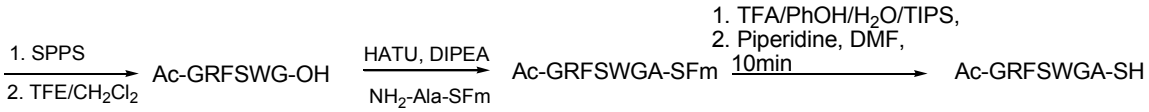


Following the general procedure for SPPS and II, peptide **26** (0.02 mmol) was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Gly-NovaSyn® TGT resin other standard amino acids. According to the general procedure, thioacid **26** (6.8 mg, 71% over two setps) was obtained as a white powder after HPLC (35-65% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) purification and lyophilization; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27-7.25 (m, 3 H), 7.24-7.22 (m, 1 H), 7.20 (br, s, 1 H), 6.48 (s, 1 H), 4.78 (s, 1 H), 4.50-4.46 (m, 2 H), 4.10-4.07 (m, 1 H), 3.85-3.84 (m, 1 H), 3.66 (d, 1 H, *J* = 5.1 Hz), 3.15-3.12 (m, 2 H), 1.37 (d, 3 H, *J* = 7.1 Hz);1.27 (s, 9 H), 1.23 (d, 3 H, *J* = 7.2 Hz); HR-ESIMS (*m/z*) Calcd for $C_{22}H_{32}N_4O_6SNa$: $[M+Na]^+$ *m/z* = 503.1941; Found: 503.1926.

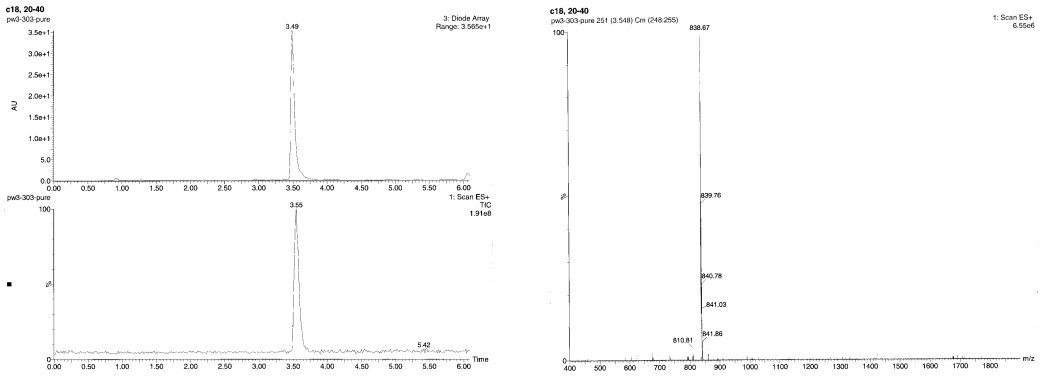


a) UV and MS traces from UPLC-MS analysis of thioacid **26**: gradient 35-65% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{22}H_{33}N_4O_6S$ $[M+H]^+$ *m/z* = 481.20, found: 481.54.

Ac-GRFSWGA-SH **28**

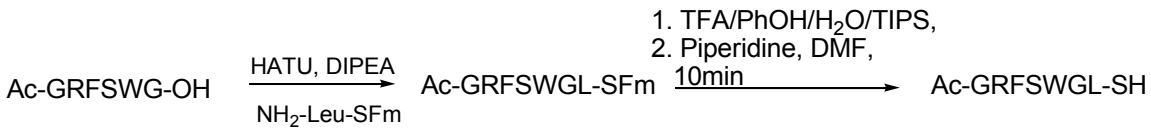


Following the general procedure for SPPS and III, peptide **28** (0.02 mmol) was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Gly-NovaSyn® TGT resin and other standard Fmoc amino acids. According to the general procedure, thioacid 28 (8.8 mg, 53% over three steps) was obtained as a white powder after HPLC (20-40% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) purification and lyophilization. HR-ESIMS (*m/z*) Calcd for $C_{38}H_{52}N_{11}O_9S$: $[M+H]^+$ *m/z* = 838.3672; Found: 838.3704.

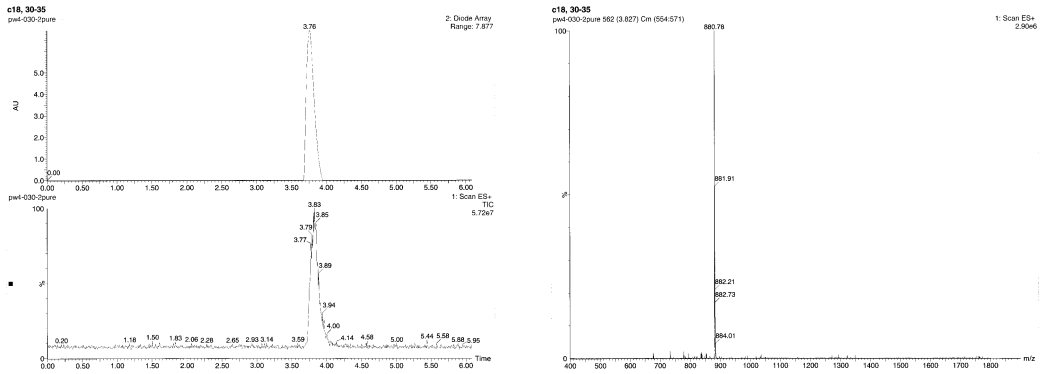


a) UV and MS traces from UPLC-MS analysis of thioacid **28**: gradient 20-40% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{38}H_{52}N_{11}O_9S$ $[M+H]^+$ *m/z* = 838.36, found: 838.67.

Ac-GRFSWGL-SH **31**

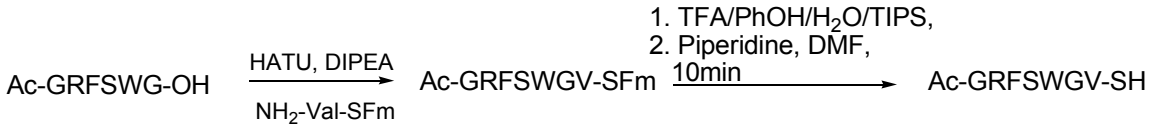


Following the general procedure for SPPS and III, peptide **31** (0.02 mmol) was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Gly-NovaSyn® TGT resin and other standard amino acids. According to the general procedure, thioacid **31** (8.5 mg, 48% over three steps) was obtained as a white powder after HPLC (30-35% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) purification and lyophilization. HR-ESIMS (*m/z*) Calcd for $C_{41}H_{58}N_{11}O_9S$: $[M+H]^+$ *m/z* = 880.4141; Found: 880.4132.

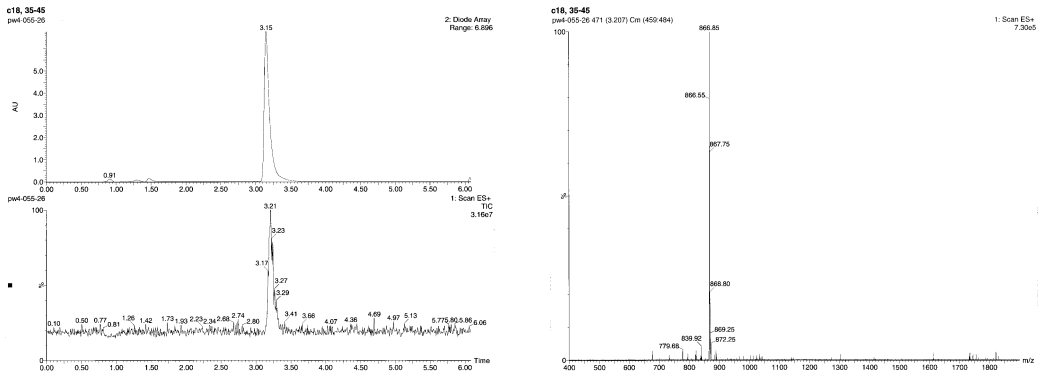


a) UV and MS traces from UPLC-MS analysis of thioacid **31**: gradient 30-35% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{41}H_{58}N_{11}O_9S$ $[M+H]^+$ *m/z* = 880.41, found: 880.78.

Ac-GRFSWGV-SH **33**

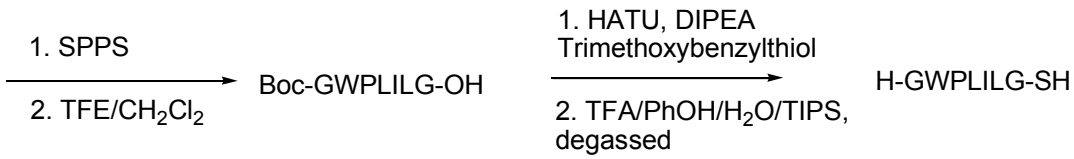


Following the general procedure for SPPS and III, peptide **33** was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Gly-NovaSyn® TGT resin and other standard amino acids. According to the general procedure, thioacid **33** (8.8 mg, 51% over three steps) was obtained as a white powder after HPLC (35-45% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) purification and lyophilization. HR-ESIMS (*m/z*) Calcd for $C_{40}H_{56}N_{11}O_9S$: $[M+H]^+$ *m/z* = 866.3985; Found: 866.3984.

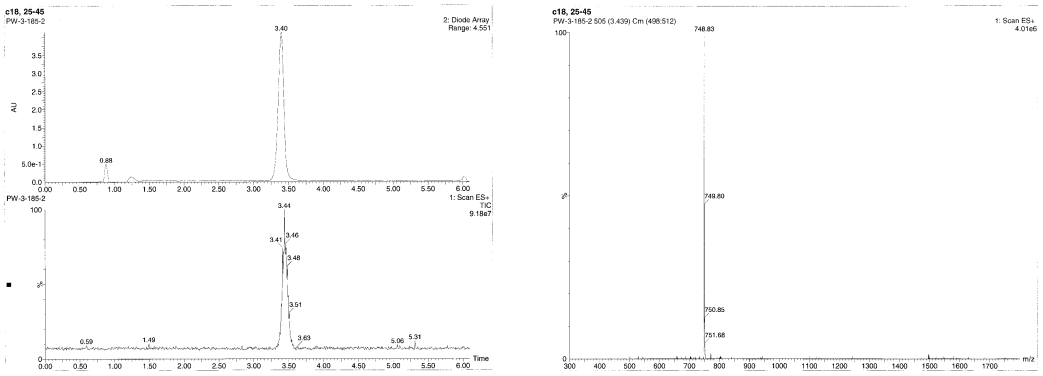


a) UV and MS traces from UPLC-MS analysis of thioacid **33**: gradient 35-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{40}H_{56}N_{11}O_9S$ $[M+H]^+$ *m/z* = 866.39, found: 866.55.

H-GWPLILG-SH **17**

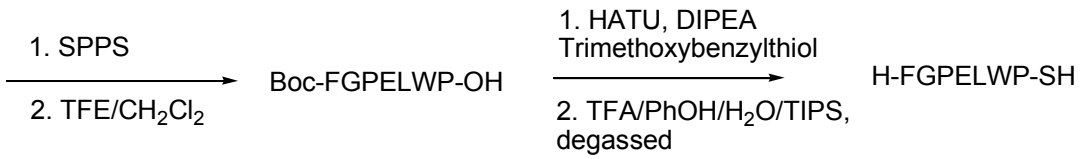


Following the general procedure for SPPS and I, peptide **17** (0.02 mmol) was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Gly-NovaSyn® TGT resin other standard amino acids. According to the general procedure, thioacid **17** (9.0 mg, 60% over two steps) was obtained as a white powder after HPLC (25-45% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) purification and lyophilization. HR-ESIMS (*m/z*) Calcd for $C_{36}H_{58}N_7O_8S$: $[M+H]^+$ *m/z* = 748.4069; Found: 748.4037.

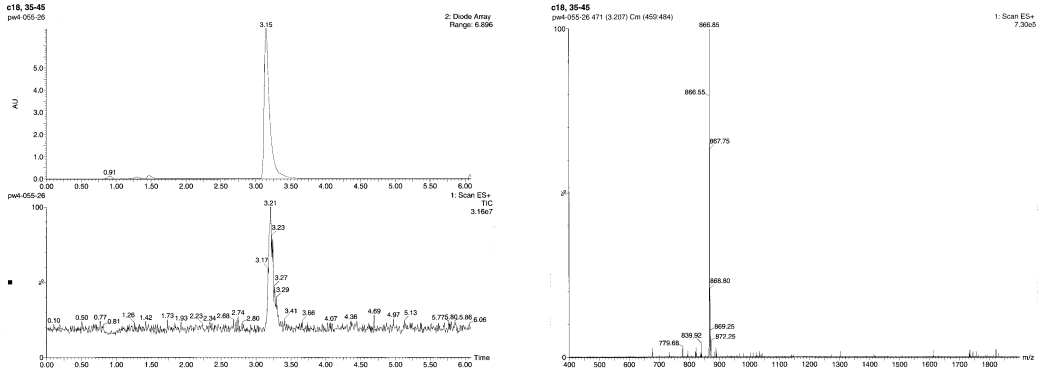


a) UV and MS traces from UPLC-MS analysis of thioacid **17**: gradient 25-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{36}H_{58}N_7O_8S$ $[M+H]^+$ *m/z* = 748.40, found: 748.83.

H-FGPELWP-SH **19**



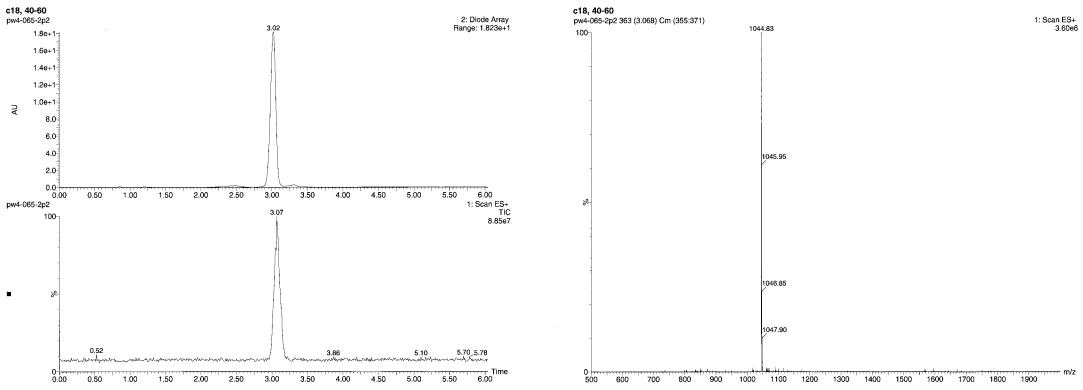
Following the general procedure for SPPS and I, peptide **19** (0.02 mmol) was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Pro-NovaSyn® TGT resin and other standard amino acids. According to the general procedure, thioacid **19** (8.2 mg, 48% over two steps) was obtained as a white powder after HPLC (30-50% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) purification and lyophilization. HR-ESIMS (*m/z*) Calcd for $C_{43}H_{57}N_8O_9S$: $[M+H]^+$ *m/z* = 861.3969; Found: 861.3950.



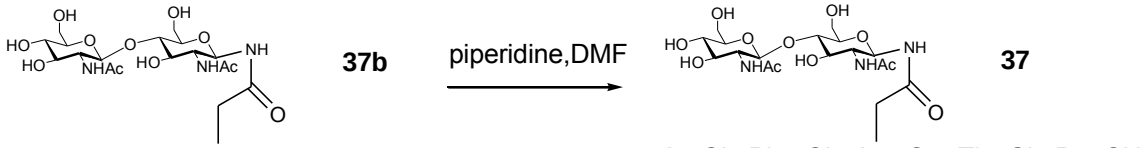
a) UV and MS traces from UPLC-MS analysis of thioacid **19**: gradient 30-50% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{43}H_{57}N_8O_9S$ $[M+H]^+$ *m/z* = 861.39, found: 861.80.

Ac-Gly-Phe-Gln-Asn-Ser-Thr-Gly-Pro-SFm **37a**

Following the general procedure for SPPS and III (SFm will be cleaved after aspartylation), peptide **37a** (0.02 mmol) was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Pro-NovaSyn® TGT resin and other standard amino acids. According to the general procedure, **37a** (12.8 mg, 61% over two steps) was obtained as a white powder after HPLC (30-60% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) purification and lyophilization.



a) UV and MS traces from UPLC-MS analysis of compound **37a**: gradient 40-60% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESIMS (*m/z*) Calcd for $C_{50}H_{62}N_9O_{14}S$: $[M+H]^+$ *m/z* = 1044.41; Found: 1044.83.



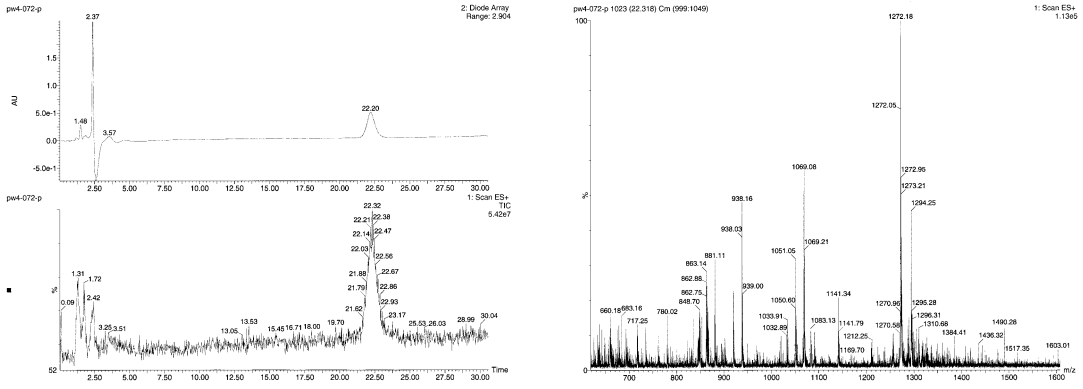
Ac-Gly-Phe-Gln-Asn-Ser-Thr-Gly-Pro-SFm

Ac-Gly-Phe-Gln-Asn-Ser-Thr-Gly-Pro-SH

To an oven-dried vial were charged **37a** (2.0 mg, 1.92 µmol), disaccharide (1.6 mg, 3.8 µmol). A stock solution of DIPEA (10 uL in 200 uL DMSO) 20 µL and HATU (33 mg in 200 uL DMSO) 20 uL was added to the vial. The solution was stirred at room temperature for 1 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (20-50% MeCN/H_2O over 30 min,

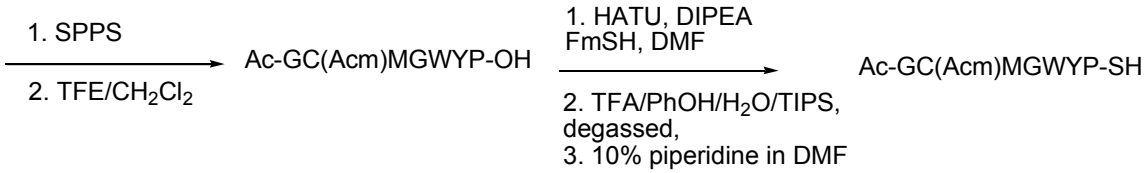
Microsorb 100-5 C18 column, 16 mL/min, 265 nm) and lyophilization afforded glycopeptide **37b** (1.9 mg, 68%).

To a solution of the glycopeptides **37b** (1.7 mg, 1.17 umol) in anhydrous DMF (60 uL) was added piperidine (10 uL) at rt. The reaction mixture was stirred at rt for 20 min. The reaction was concentrated under a stream of nitrogen and the residue was purified by HPLC purification (5-20% MeCN/H_2O over 30 min, Microsorb 100-5 C18 xbridge column, 16 mL/min, 230 nm) to give thioacid **37** (1.3 mg, 87%).

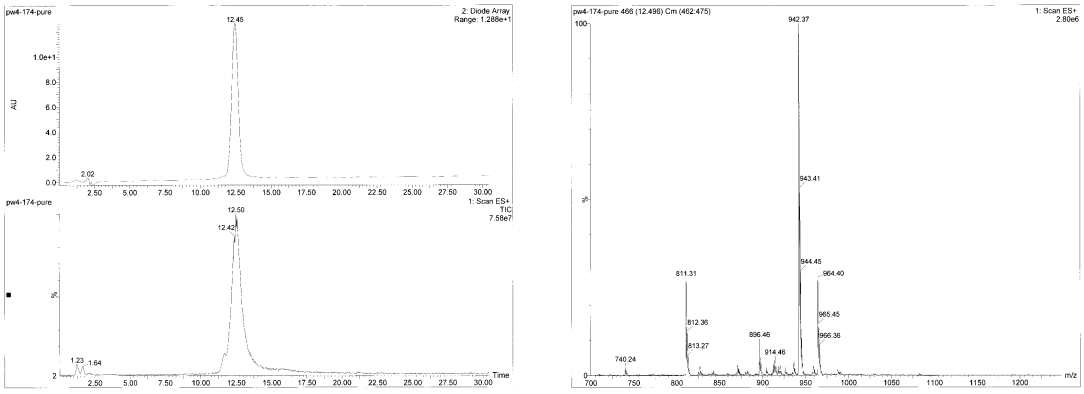


a) UV and MS traces from LC-MS analysis of glycopeptide **37**: gradient 5-20% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C18 xbridge column. (b) ESI-MS of compound**.** ESIMS (*m/z*) Calcd for $C_{52}H_{79}N_{12}O_{23}S$: $[M+H]^+$ *m/z* = 1271.50; Found: 1272.05.

Ac-GC(Acm)MGWYP-SH **46**



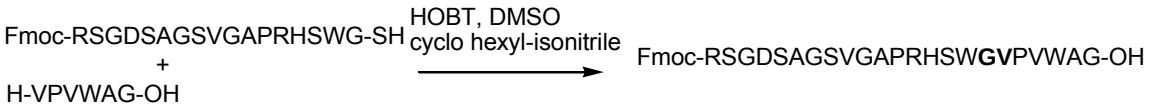
Following the general procedure for SPPS and III (FmSH replace NH2-AA-COSFm), peptide **46** (0.02 mmol) was synthesized by automated Applied Biosystems Pioneer continuous flow peptide synthesizer, employing Fmoc-Pro-NovaSyn® TGT resin and other standard Fmoc amino acids. According to the general procedure, thioacid **46** (10.0 mg, 53% over three steps) was obtained as a white powder after HPLC (25-50% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) purification and lyophilization. HR-ESIMS (*m/z*) Calcd for $C_{42}H_{55}N_9O_{10}S_3Na$: $[M+Na]^+$ *m/z* = 964.3132; Found: 964.3107.



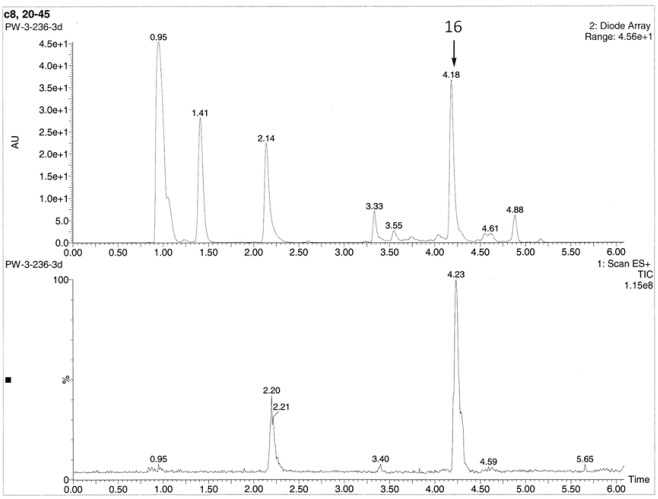
a) UV and MS traces from LC-MS analysis of thioacid **46**: gradient 25-50% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{42}H_{56}N_9O_{10}S_3$ $[M+H]^+$ *m/z* = 942.32, $[M+Na]^+$ *m/z* = 964.31, found: 942.37, 964.40.

Peptide Ligation

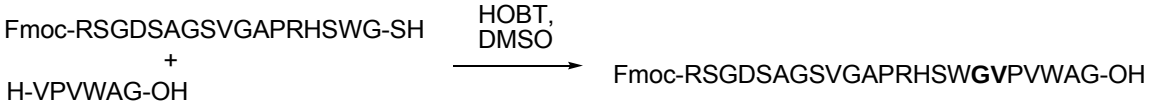
16



To an oven-dried vial were charged thioacid **7** (1.3 mg, 0.67 µmol), amine **13** (0.6 mg, 0.96 µmol) and 4Å MS (2 mg). A stock solution of HOBT/cyclo hexyl-isonitrile (1.8 mg HOBT/6 uL cyclo hexyl-isonitrile in 400 uL DMSO) 40 µL was added to the vial. The solution was stirred at room temperature for 48 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) and lyophilization afforded peptide **16 (**as a white powder (1.4 mg, 82%).

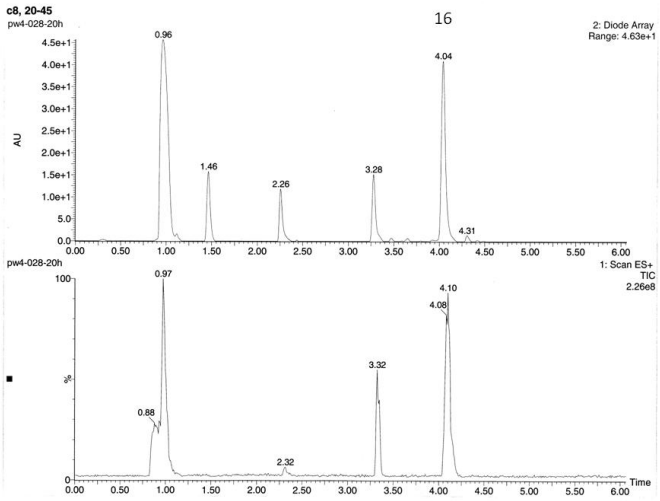


UPLC-MS traces of reaction mixture: gradient 20-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column.

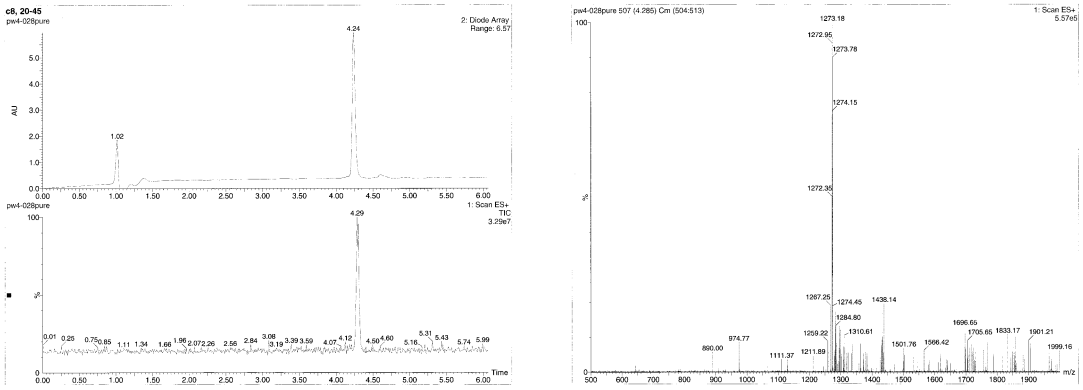


To an oven-dried vial were charged thioacid **7** (0.6 mg, 0.31 µmol), amine **13** (0.3 mg, 0.48 µmol) and 4Å MS (2 mg). A stock solution of HOBT (1.2 mg in 2.0 mL DMSO) 20 µL was added to the vial. The solution was stirred at room temperature for 20 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was

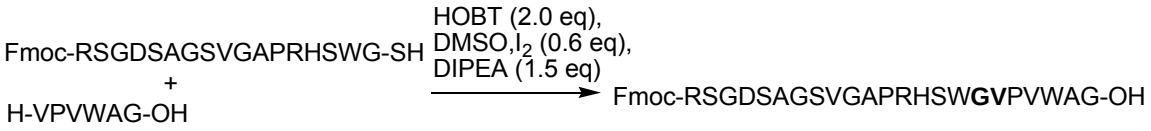
subject to HPLC purification (20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) and lyophilization afforded peptide **16 (**as a white powder (0.6 mg, 77%).



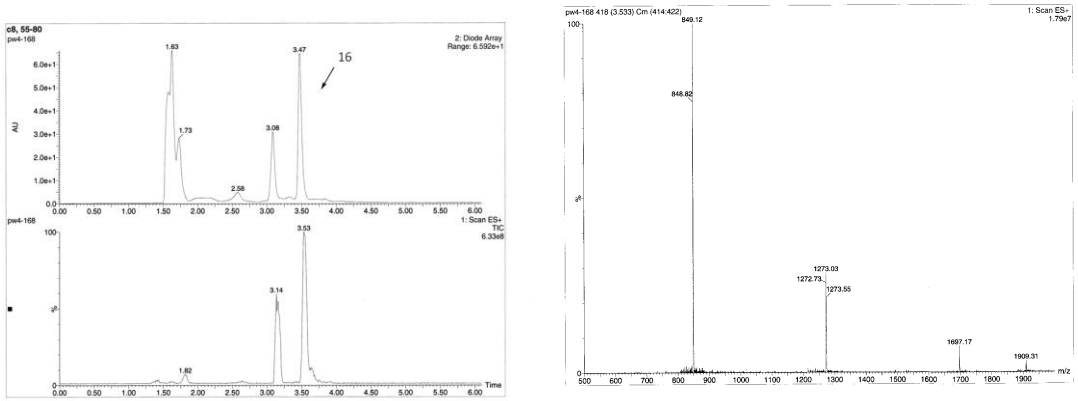
UPLC-MS traces of reaction mixture: gradient 20-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column.



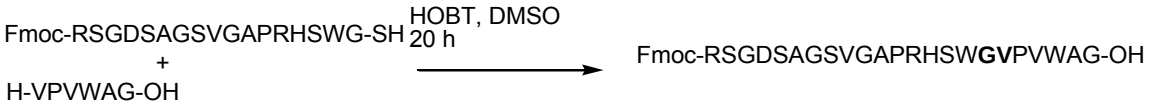
a) UV and MS traces from UPLC-MS analysis of peptide **16**: gradient 20-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column. (b) ESI-MS of compound**.** ESI calcd for $C_{117}H_{165}N_{34}O_{31}$ $[M+H]^+$ *m/z* = 2542.23, $[M+2H]^{2+}$ *m/z* = 1272.12; found: 1272.35.



To an oven-dried vial were charged thioacid **7** (0.8 mg, 0.41 µmol), amine **13** (0.2 mg, 0.32 µmol), HOBT (0.1 mg, 2.0 eq) and 4Å MS (2 mg). A stock solution of DIPEA (10 uL in 1.0 mL DMSO) 10 uL and I_2 (6.3 mg in 1.0 mL DMSO) 10 µL was added to the vial. The solution was stirred at room temperature for 30 min and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) and lyophilization afforded peptide **16 (**as a white powder (0.6 mg, 75%).

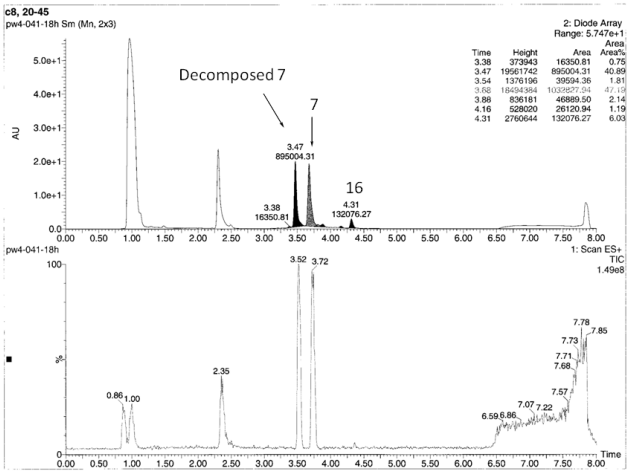


a) UV and MS traces from UPLC-MS analysis of peptide **16**: gradient 55-80% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column. (b) ESI-MS of compound**.** ESI calcd for $C_{117}H_{165}N_{34}O_{31}$ $[M+H]^+$ *m/z* = 2542.23, $[M+2H]^{2+}$ *m/z* = 1272.12; found: 1272.65.



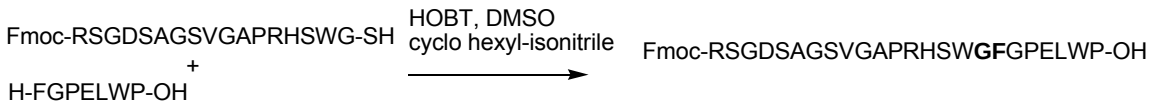
To an oven-dried vial were charged thioacid **7** (0.6 mg, 0.31 µmol), amine **13** (0.3 mg, 0.48 µmol) and 4Å MS (2 mg), the mixture was degassed with Argon carefully. 40 uL DMSO (degassed with Argon) was added to the vial. The reaction was run in glove box

at an atmosphere of nitrogen for 20 h, quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to UPLC, the conversion of **16** is 7%.

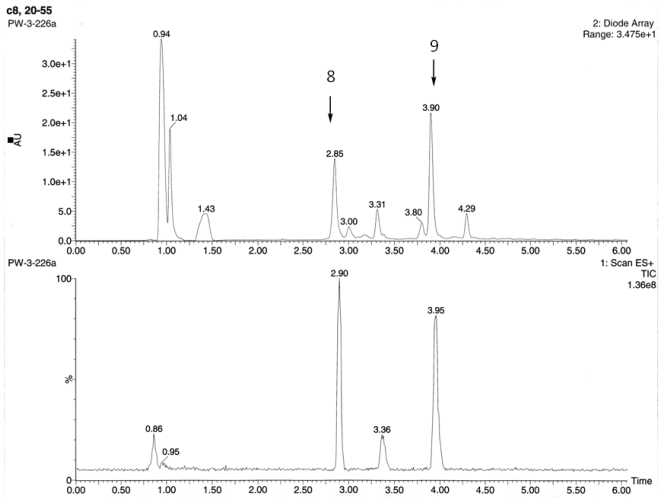


UPLC-MS traces of reaction mixture at 6 h: gradient 20-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. The conversion of **16** is 7%.

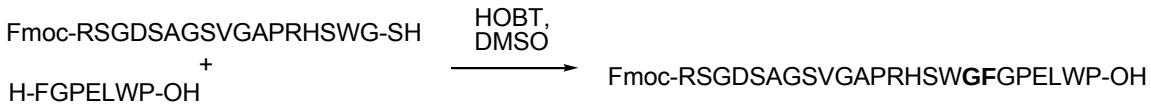
9



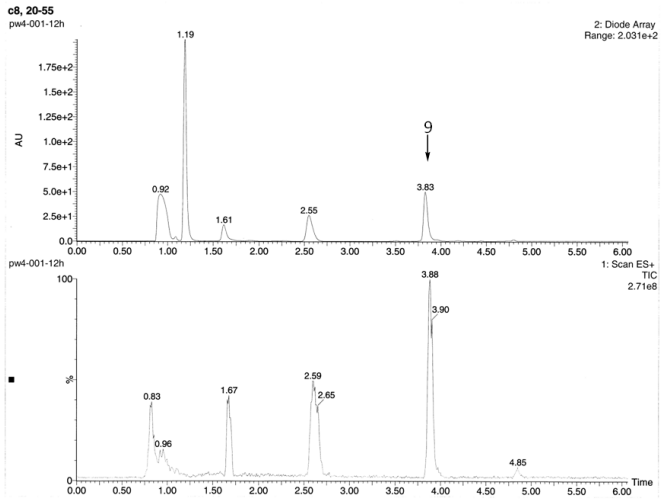
To an oven-dried vial were charged thioacid **7** (1.3 mg, 0.67 µmol), amine **8** (0.6 mg, 0.71 µmol) and 4Å MS (2 mg). A stock solution of HOBT/cyclo hexyl-isonitrile (0.6 mg HOBT/4 uL cyclo hexyl-isonitrile in 250 uL DMSO) 25 µL was added to the vial. The solution was stirred at room temperature for 20h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) and lyophilization afforded peptide **9 (**as a white powder (1.1 mg, 60%).



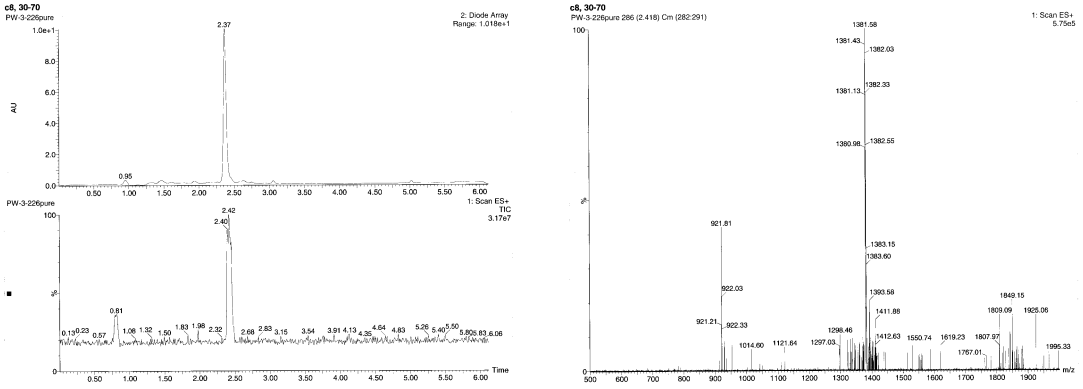
UPLC-MS traces of reaction mixture: gradient 20-55% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column.



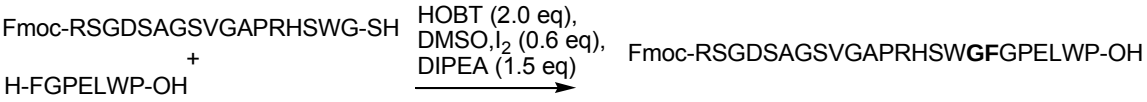
To an oven-dried vial were charged thioacid **7** (0.8 mg, 0.41 µmol), peptide **8** (0.3 mg, 0.36 µmol) and 4Å MS (2 mg). A stock solution of HOBT (1.0 mg in 300 uL DMSO) 30 µL was added to the vial. The solution was stirred at room temperature for 12 h and quenched by addition of 2 mL $MeCN/H_2O$ =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% $MeCN/H_2O$ over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) and lyophilization afforded glycopeptide **9** as a white powder (0.8 mg, 82%).



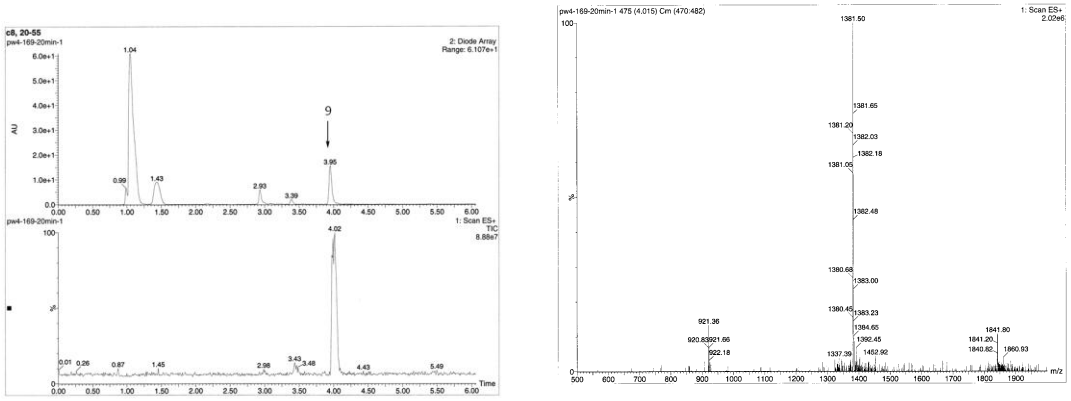
UPLC-MS traces of reaction mixture: gradient 20-55% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column.



a) UV and MS traces from UPLC-MS analysis of peptide **9**: gradient 30-70% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column. (b) ESI-MS of compound**.** ESI calcd for $C_{129}H_{175}N_{34}O_{35}$ $[M+H]^+$ *m/z* = 2760.29, $[M+2H]^{2+}$ *m/z* = 1380.65, $[M+3H]^{3+}$ *m/z* = 920.76; found: 921.06.



To an oven-dried vial were charged thioacid **7** (0.6 mg, 0.31 µmol), amine **8** (0.2 mg, 0.24 µmol) and 4Å MS (2 mg). A stock solution of DIPEA/HOBT (8 uL DIPEA/8 mg HOBT in 1.0 mL DMF) 10 uL and I_2 (4 mg in 1.0 mL DMF) 10 µL was added to the vial. The solution was stirred at room temperature for 30 min and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) and lyophilization afforded peptide **9 (**as a white powder (0.5 mg, 77%).

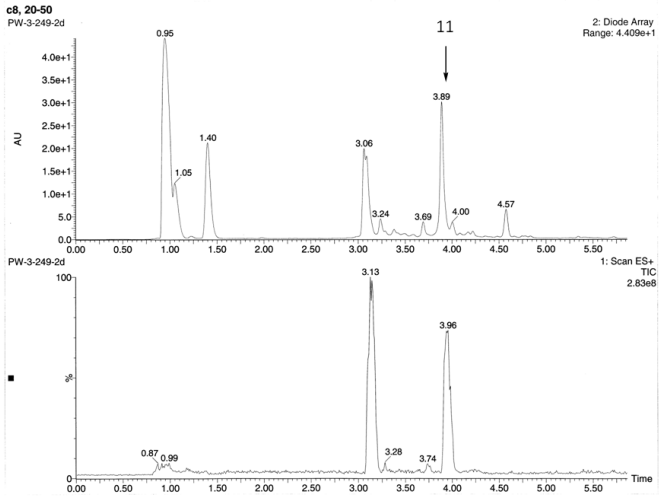


a) UV and MS traces from UPLC-MS analysis of peptide **9**: gradient 20-55% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column. (b) ESI-MS of compound**.** ESI calcd for $C_{129}H_{175}N_{34}O_{35}$ $[M+H]^+$ *m/z* = 2760.29, $[M+2H]^{2+}$ *m/z* = 1380.65, $[M+3H]^{3+}$ *m/z* = 920.76; found: 1380.68, 920.83.

11

Fmoc-RSGDSAGSVGAPRHSWG-SH + H-LYTGRLFWSAQASLG-OH $\xrightarrow[\text{cyclo hexyl-isonitrile}]{\text{HOBT, DMSO}}$ Fmoc-RSGDSAGSVGAPRHSW**GL**YTGRLFWSAQASLG-OH

To an oven-dried vial were charged thioacid **7** (0.9 mg, 0.46 µmol), amine **10** (1.0 mg, 0.60 µmol) and 4Å MS (2 mg). A stock solution of HOBT/cyclo hexyl-isonitrile (1.3 mg HOBT/6 uL cyclo hexyl-isonitrile in 300 uL DMSO) 30 µL was added to the vial. The solution was stirred at room temperature for 20h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) and lyophilization afforded peptide **11 (**as a white powder (1.2 mg, 73%).

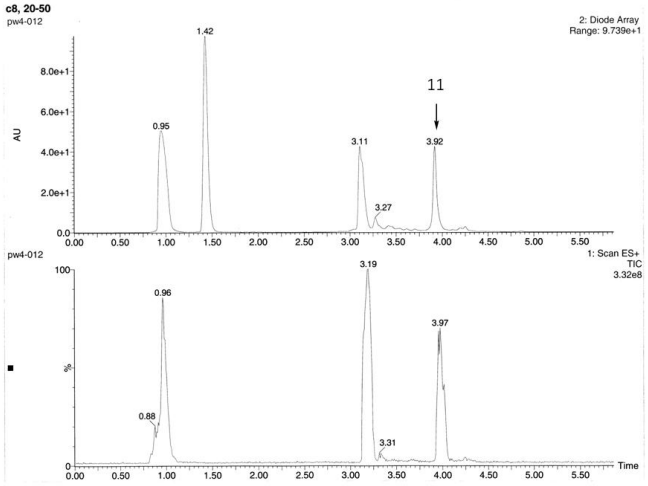


UPLC-MS traces of reaction mixture: gradient 20-50% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column.

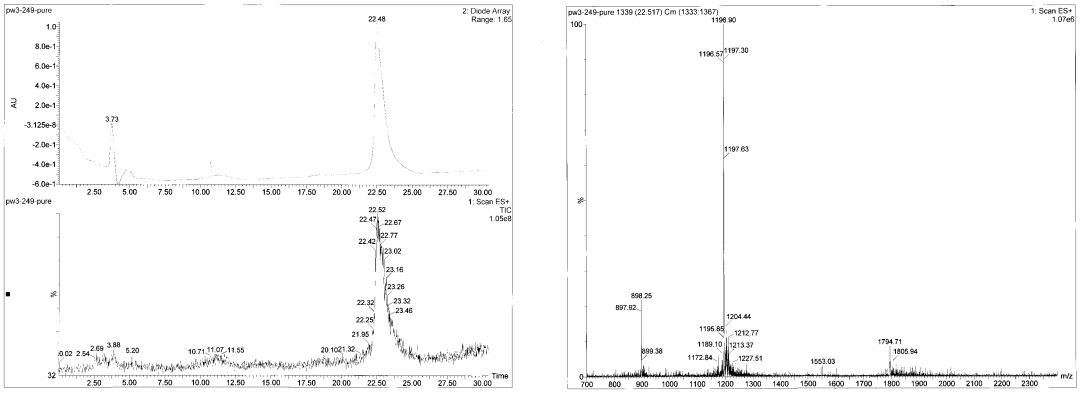
Fmoc-RSGDSAGSVGAPRHSWG-SH + H-LYTGRLFWSAQASLG-OH $\xrightarrow[\text{DMSO}]{\text{HOBT,}}$ Fmoc-RSGDSAGSVGAPRHSW**GL**YTGRLFWSAQASLG-OH

To an oven-dried vial were charged thioacid **7** (1.0 mg, 0.51 µmol), amine **10** (0.7 mg, 0.42 µmol) and 4Å MS (2 mg). A stock solution of HOBT (1.4 mg in 300 uL DMSO) 30 µL was added to the vial. The solution was stirred at room temperature for 12 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (20-50% MeCN/H_2O over 30 min, Microsorb 100-5 C4

column, 16 mL/min, 265 nm) and lyophilization afforded peptide **11** (1.2 mg, 80%) as a white powder.

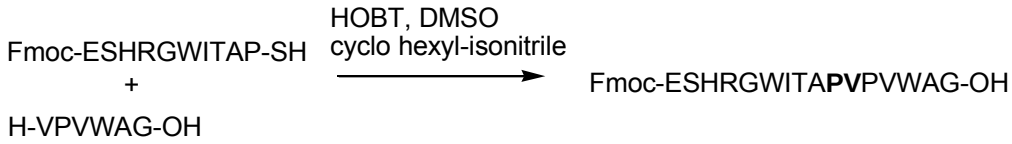


UPLC-MS traces of reaction mixture: gradient 20-50% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column.

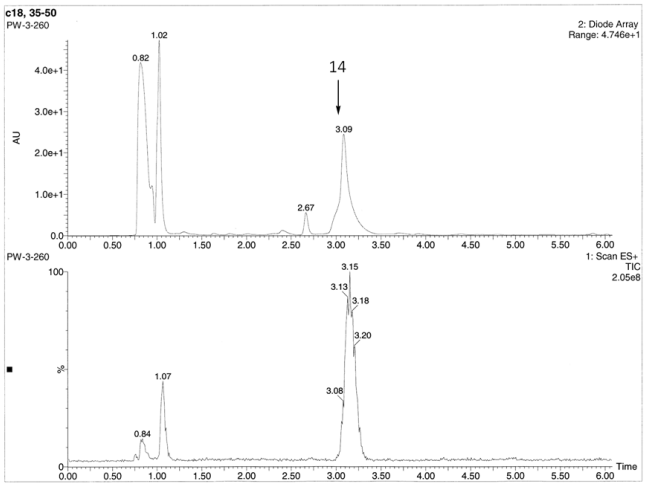


a) UV and MS traces from UPLC-MS analysis of peptide **11**: gradient 20-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column. (b) ESI-MS of compound**.** ESI calcd for $C_{164}H_{234}N_{46}O_{46}$ $[M+H]^+$ *m/z* = 3584.74, $[M+2H]^{2+}$ *m/z* = 1793.37, $[M+3H]^{3+}$ *m/z* = 1195.58; found: 1195.85.

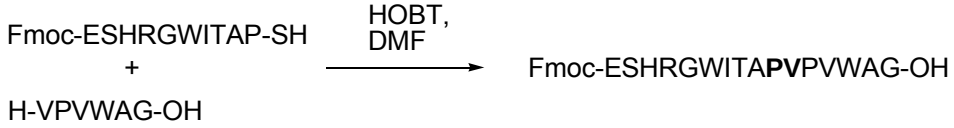
14



To an oven-dried vial were charged thioacid **12** (0.7 mg, 0.50 µmol), amine **13** (0.5 mg, 0.80 µmol) and 4Å MS (2 mg). A stock solution of HOBT/cyclo hexyl-isonitrile (1.4 mg HOBT/5 uL cyclo hexyl-isonitrile in 400 uL DMSO) 40 µL was added to the vial. The solution was stirred at room temperature for 48h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) and lyophilization afforded peptide **14 (**as a white powder (0.8 mg, 80%).

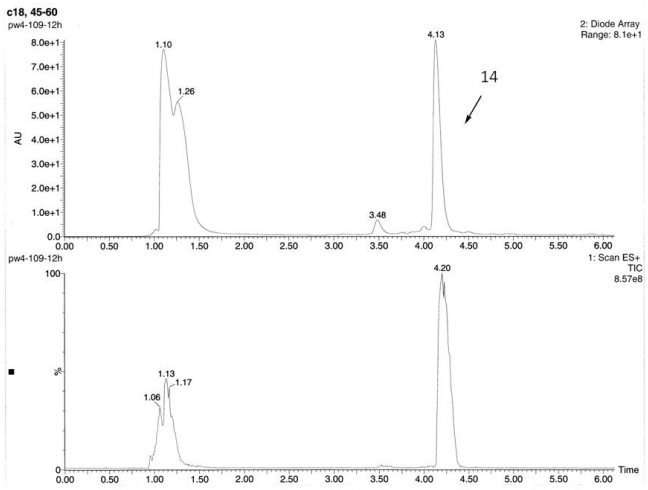


UPLC-MS traces of reaction mixture: gradient 35-50% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column.

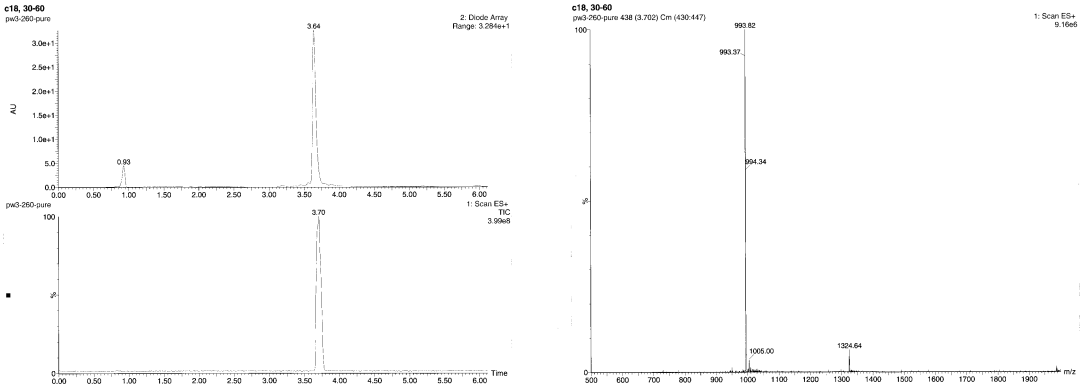


To an oven-dried vial were charged thioacid **12** (0.8 mg, 0.57 µmol), peptide **13** (0.4 mg, 0.69 µmol) and 4Å MS (2 mg). A stock solution of HOBT (1.4 mg in 250 uL DMF) 25 µL was added to the vial. The solution was stirred at room temperature for 6 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was

subject to HPLC purification (45-60% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 265 nm) and lyophilization afforded peptide **14** (1.0 mg, 87%) as a white powder.

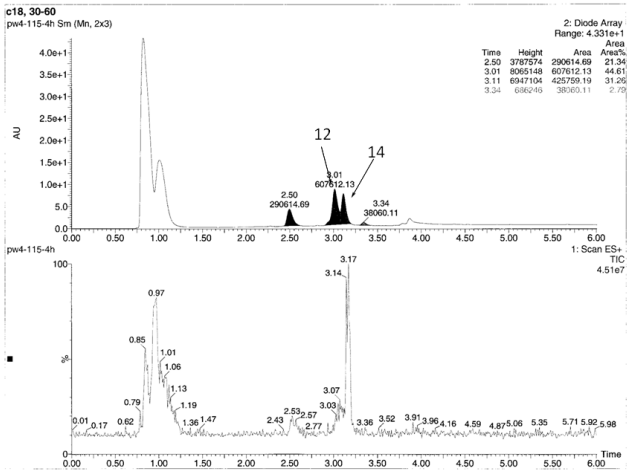


UPLC-MS traces of reaction mixture: gradient 45-60% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column.



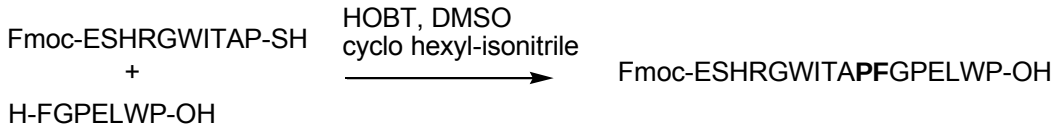
a) UV and MS traces from UPLC-MS analysis of peptide **14**: gradient 20-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column. (b) ESI-MS of compound**.** ESI calcd for $C_{97}H_{129}N_{23}O_{23}$ $[M+H]^+$ *m/z* = 1984.96, $[M+2H]^{2+}$ *m/z* = 992.93; found: 993.37.

To an oven-dried vial were charged thioacid **12** (0.7 mg, 0.50 µmol), amine **13** (0.5 mg, 0.80 µmol) and 4Å MS (2 mg), the mixture was degassed with Argon carefully. A stock solution of HOBT (1.4 mg HOBT in 400 uL DMSO, degassed with Argon) 40 µL was added to the vial. The solution was stirred at glove box at an atmosphere of nitrogen for 4 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to UPLC, the conversion of 14 is 30%.

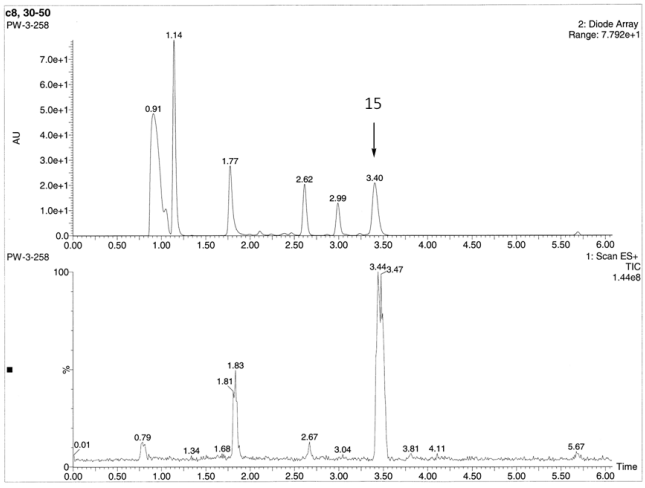


UPLC-MS traces of reaction mixture at 4 h: gradient 30-60% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column.

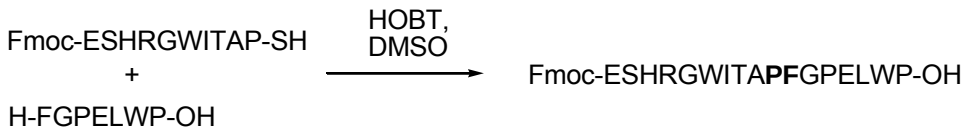
15



To an oven-dried vial were charged thioacid **12** (0.6 mg, 0.43 µmol), amine **8** (0.3 mg, 0.36 µmol) and 4Å MS (2 mg). A stock solution of HOBT/cyclo hexyl-isonitrile (1.2 mg HOBT/4 uL cyclo hexyl-isonitrile in 400 uL DMSO) 40 µL was added to the vial. The solution was stirred at room temperature for 48h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) and lyophilization afforded peptide **15 (**as a white powder (0.6 mg, 78%).

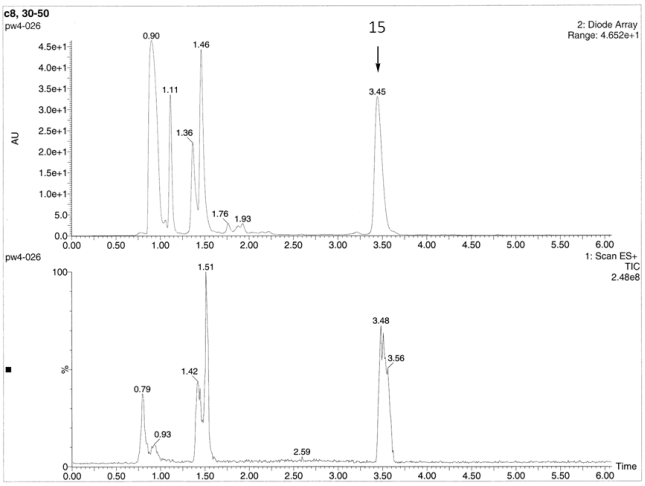


UPLC-MS traces of reaction mixture: gradient 30-50% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column.

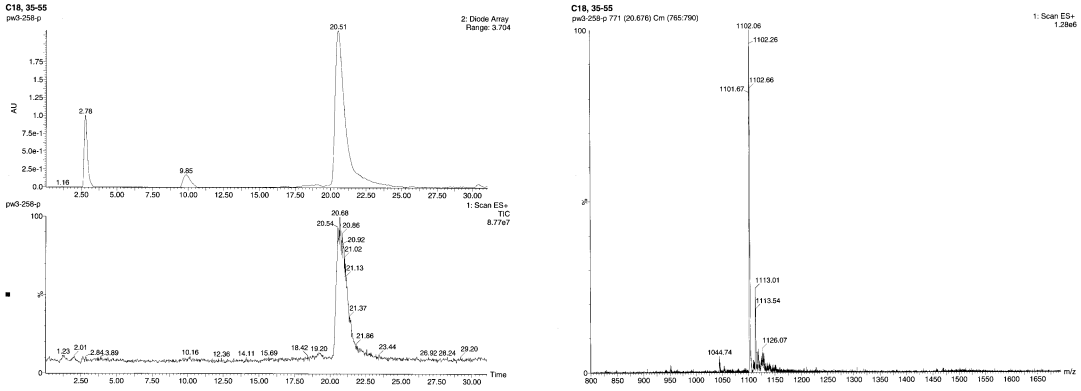


To an oven-dried vial were charged peptide **12** (1.0 mg, 0.72 µmol), amine **8** (0.5 mg, 0.59 µmol) and 4Å MS (2 mg). A stock solution of HOBT (2.9 mg in 3 mL DMSO) 30 µL was added to the vial. The solution was stirred at room temperature for 20 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was

subject to HPLC purification (30-50% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) and lyophilization afforded peptide **15** (0.9 mg, 70%) as a white powder.

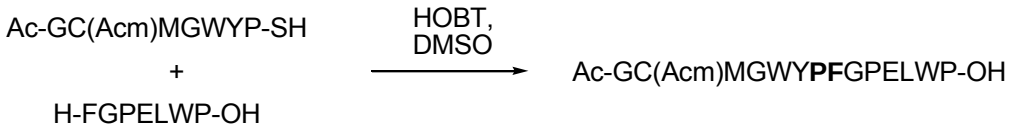


UPLC-MS traces of reaction mixture: gradient 30-50% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column.

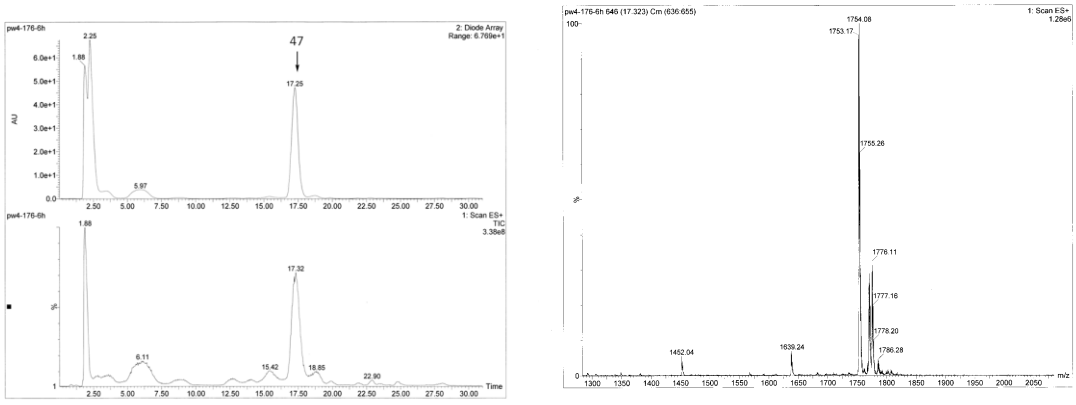


a) UV and MS traces from UPLC-MS analysis of peptide **15**: gradient 35-55% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{109}H_{140}N_{24}O_{26}$ $[M+H]^+$ *m/z* = 2202.04, $[M+2H]^{2+}$ *m/z* = 1101.52; found: 1101.67.

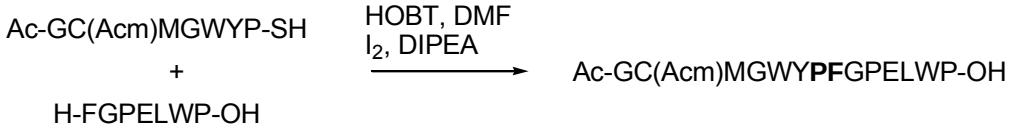
47



To an oven-dried vial were charged peptide **46** (0.6 mg, 0.64 µmol), peptide **8** (0.4 mg, 0.47 µmol) and 4Å MS (1 mg). A stock solution of HOBT (1.7 mg in 250 uL DMSO) 25 µL was added to the vial. The solution was stirred at room temperature for 6 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (35-50% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) and lyophilization afforded peptide **47** (0.7 mg, 85%) as a white powder.

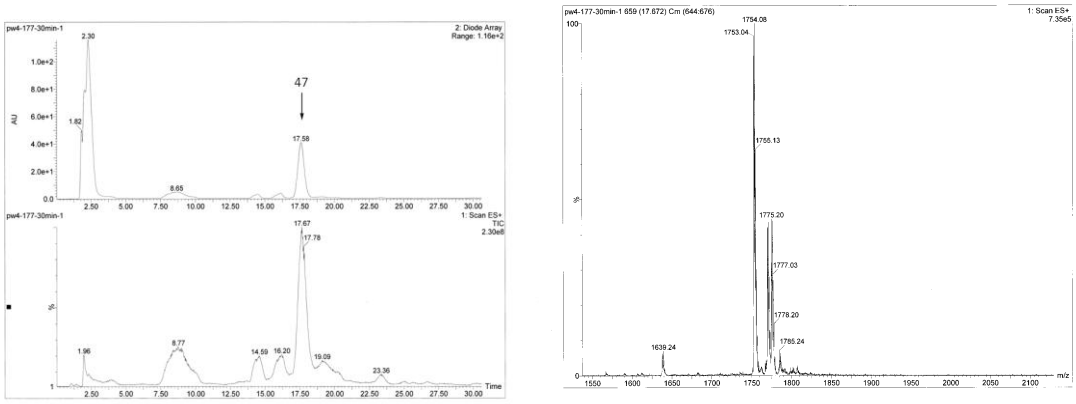


LC-MS traces of reaction mixture: gradient 25-50% CH_3CN/H_2O over 3 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI calcd for $C_{85}H_{110}N_{17}O_{20}S_2$ $[M+H]^+$ *m/z* = 1752.75; found: 1753.17.

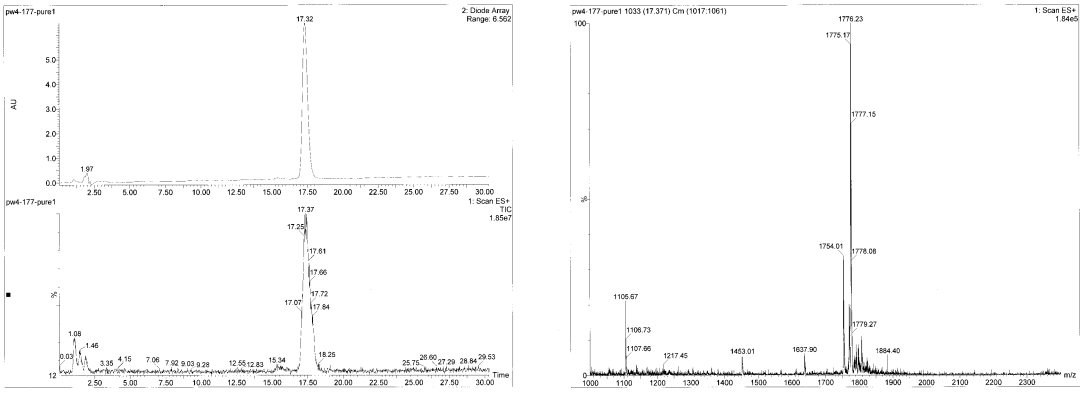


To an oven-dried vial were charged thioacid **46** (0.8 mg, 0.85 µmol), amine **8** (0.6 mg, 0.71 µmol) and 4Å MS (1 mg). A stock solution of DIPEA/HOBT (17 uL DIPEA/1.7 mg HOBT in 1.0 mL DMF) 10 uL and I_2 (9 mg in 1.0 mL DMF) 10 µL was added to the vial. The solution was stirred at room temperature for 30 min and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification

(20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) and lyophilization afforded peptide **47 (**as a white powder (1.0 mg, 80%).

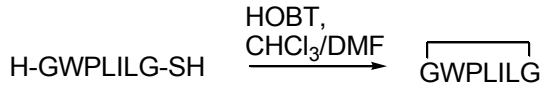


UPLC-MS traces of reaction mixture: gradient 25-50% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C8 column.

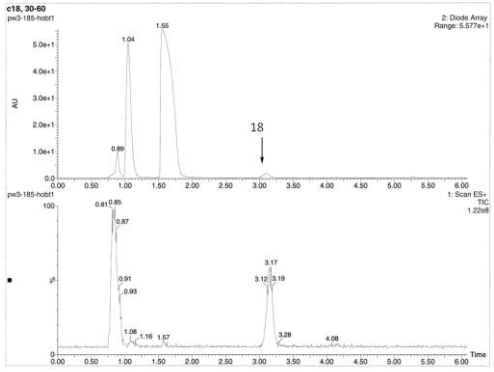


a) UV and MS traces from LC-MS analysis of peptide **47**: gradient 25-50% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{85}H_{110}N_{17}O_{20}S_2$ $[M+H]^+$ *m/z* = 1752.75; found: 1753.04.

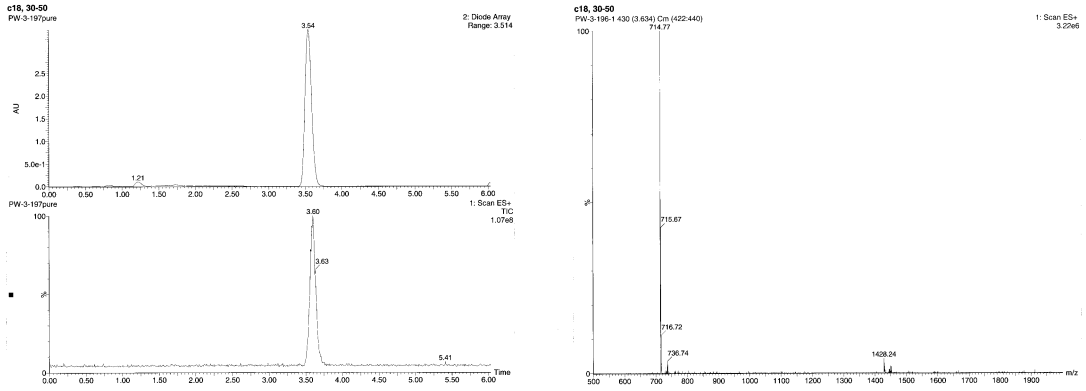
18



To an oven-dried vial were charged thioacid **17** (0.9 mg, 1.2 µmol) and 4Å MS (10 mg). A stock solution of HOBT (0.3 mg in 1 mL DMF/$CHCl_3$ 1:1, v/v) was added to the vial. The solution was stirred at room temperature for 48 h. The reaction was concentrated under a stream of nitrogen. The residue was subject to HPLC purification (30-60% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 225 nm) and lyophilization afforded cyclopeptide **18** (0.7 mg, 81%) as a white powder. HR-ESIMS (*m/z*) Calcd for $C_{36}H_{55}N_7O_8Na$: $[M+Na]^+$ *m/z* = 736.4010; Found: 736.3994.

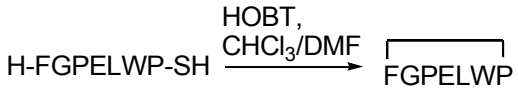


UPLC-MS traces of reaction mixture: gradient 30-60% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column.

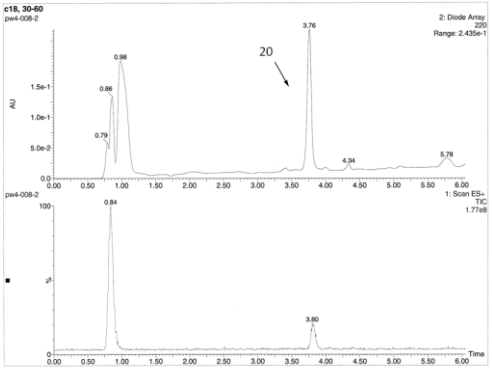


a) UV and MS traces from UPLC-MS analysis of peptide **18**: gradient 30-50% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{36}H_{57}N_7O_8$ $[M+H]^+$ *m/z* = 714.41; found: 714.77.

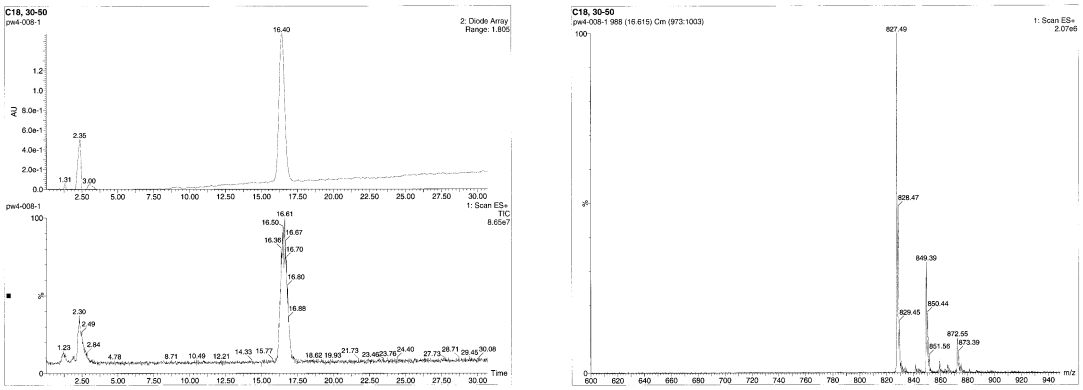
20



To an oven-dried vial were charged thioacid **19** (1.3 mg, 1.4 µmol) and 4Å MS (10 mg). A stock solution of HOBT (0.3 mg in 1 mL DMF/$CHCl_3$ 1:1, v/v) was added to the vial. The solution was stirred at room temperature for 48 h. The reaction was concentrated under a stream of nitrogen. The residue was subject to HPLC purification (30-60% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 225 nm) and lyophilization afforded cyclopeptide **20** (1.0 mg, 80%) as a white powder. HR-ESIMS (*m/z*) Calcd for $C_{43}H_{54}N_8O_9Na$: $[M+Na]^+$ *m/z* = 849.3911; Found: 849.3904.



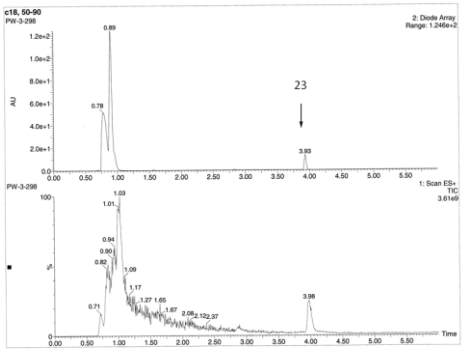
UPLC-MS traces of reaction mixture: gradient 30-60% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column.

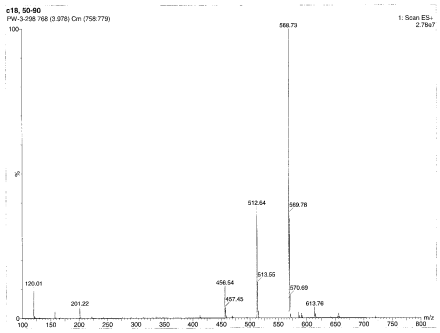


a) UV and MS traces from LC-MS analysis of cyclopeptide **20**: gradient 30-50% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{43}H_{55}N_8O_9$ $[M+H]^+$ *m/z* = 827.40; found: 827.49.

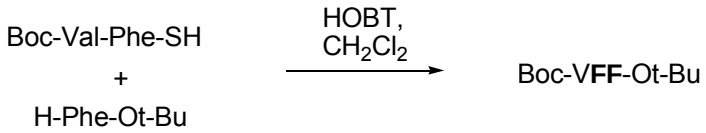
23

To an oven-dried vial were charged thioacid **21** (0.6 mg, 1.6 µmol), amine **22** (0.4 mg, 1.8 µmol) and 4Å MS (2 mg). A stock solution of HOBT (3.5 mg in 500 uL DMF) 50 µL was added to the vial. The solution was stirred at room temperature for 6 h. The reaction mixture was subject to a silica gel column and eluted with hexanes/ethyl acetate (3:1-2:1) to give peptide **23** (0.8 mg, 90%, L/D mixture, L/D = 9:1) as a white powder.

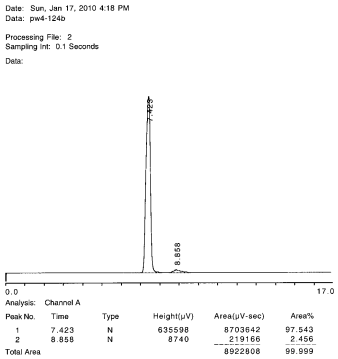




a) UPLC-MS traces of reaction mixture: gradient 50-90% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{32}H_{46}N_3O_6$: $[M+H]^+$ *m/z* = 568.34; Found: 568.73.

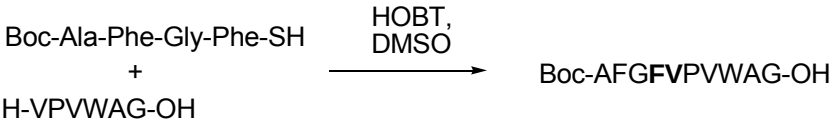


To an oven-dried vial were charged thioacid **21** (3.0 mg, 7.9 µmol), amine **22** (2.1 mg, 9.5 µmol) and 4Å MS (2 mg). A stock solution of HOBT (2 mg in 150 uL CH_2Cl_2) 150 µL was added to the vial. The solution was stirred at room temperature for 3 h. The reaction mixture was subject to a silica gel column and eluted with hexanes/ethyl acetate (3:1-2:1) to give peptide **23** (4.0 mg, 89%) as a white powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26-7.24 (m, 2 H), 7.18-7.16 (m, 6 H), 6.99 (d, 2 H, *J* = 6.7 Hz), 6.40 (d, 1 H, *J* = 6.6 Hz), 6.10 (d, 1 H, *J* = 6.0 Hz), 4.87 (d, 1 H, *J* = 6.1 Hz), 4.60-4.55 (m, 2 H), 3.86 (d, 1 H, *J* = 6.1 Hz), 3.09-3.06 (m, 1 H), 3.99-3.96 (m, 3 H), 2.08-2.05 (m, 1 H), 1.41 (s, 9 H), 1.33 (s, 9 H), 0.86 (d, 3 H, *J* = 6.7 Hz), 0.77 (d, 3 H, *J* = 6.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.3, 169.74, 169.72, 136.3, 135.9, 129.4, 129.3, 128.7, 128.4, 127.1, 127.0, 82.4, 54.3, 53.8, 38.3, 38.0, 30.7, 29.7, 28.3, 27.9, 19.2, 17.4; HR-ESIMS (*m/z*) Calcd for $C_{32}H_{46}N_3O_6$: $[M+H]^+$ *m/z* = 568.3387; Found: 568.3376.

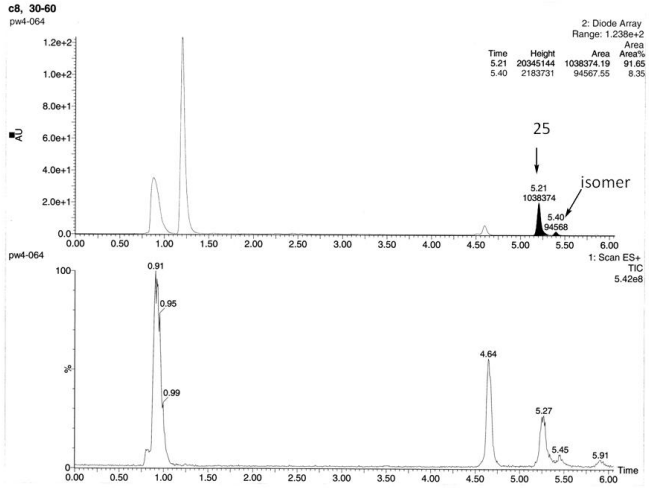


LC traces of **23**: gradient 1-3% isopropanol/hexane over 20 min at a flow rate of 0.5 mL/min, Chiralcel OD-H column.

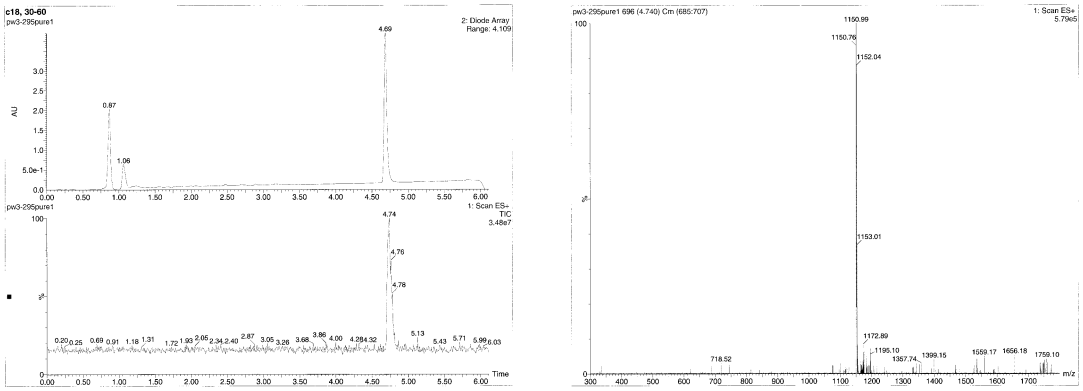
25



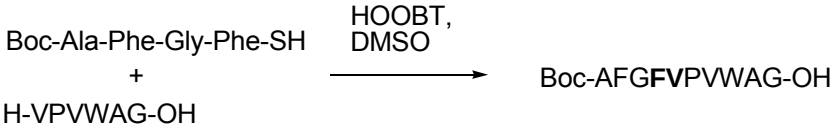
To an oven-dried vial were charged thioacid **24** (1.2 mg, 2.2 µmol), amine **13** (0.9 mg, 1.4 µmol) and 4Å MS (2 mg). A stock solution of HOBT (4.8 mg in 500 uL DMSO) 50 µL was added to the vial. The solution was stirred at room temperature for 12 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (35-50% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) and lyophilization afforded peptide **25** (1.4 mg, 85%) as a white powder. HR-ESIMS (*m/z*) Calcd for $C_{59}H_{79}N_{11}O_{13}Na$: $[M+Na]^+$ *m/z* = 1172.5757; Found: 1172.5811.



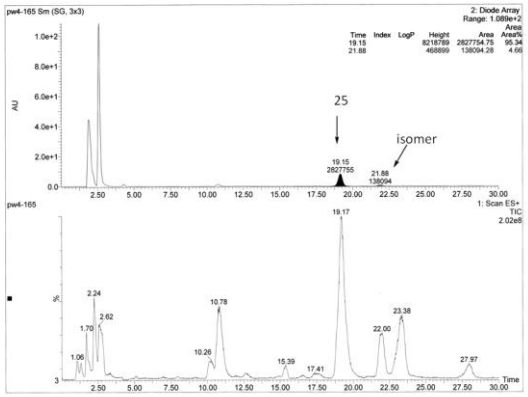
UPLC-MS traces of reaction mixture: gradient 30-60% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column.



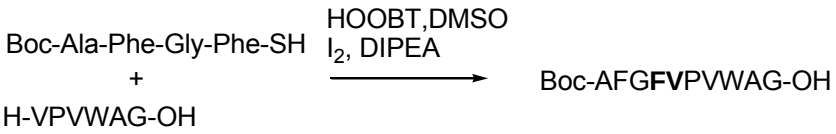
a) UV and MS traces from UPLC-MS analysis of peptide **25**: gradient 20-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column. (b) ESI-MS of compound**.** ESI calcd for $C_{59}H_{79}N_{11}O_{13}$ $[M+H]^+$ *m/z* = 1150.56; found: 1150.99.



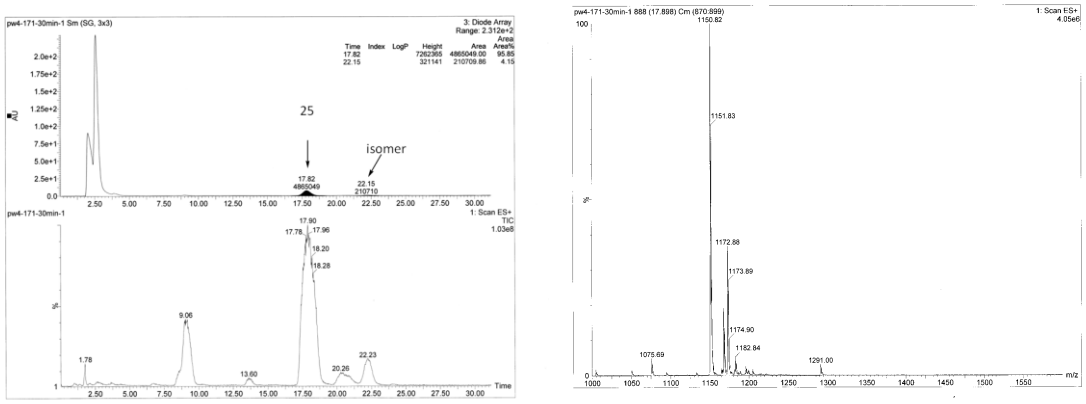
To an oven-dried vial were charged thioacid **24** (0.7 mg, 1.3 µmol), amine **13** (0.6 mg, 0.96 µmol) and 4Å MS (2 mg). A stock solution of HOOBT (4.0 mg in 300 uL DMSO) 30 µL was added to the vial. The solution was stirred at room temperature for 6 h and quenched by addition of 2 mL $MeCN/H_2O$ =1/1. The quenched reaction mixture was subject to HPLC purification (35-50% $MeCN/H_2O$ over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 230 nm) and lyophilization afforded peptide **25** (0.9 mg, 82%) as a white powder.



LC-MS traces of reaction mixture: gradient 20-45% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C18 Xbridge column.

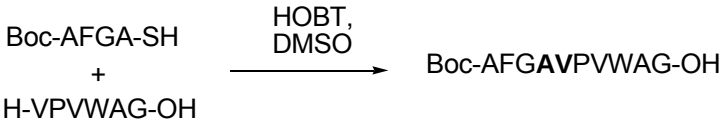


To an oven-dried vial were peptide **24** (0.6 mg, 1.1 µmol), amine **13** (0.4 mg, 0.64 µmol) and 4Å MS (2 mg). A stock solution of DIPEA/HOOBT (28 uL DIPEA/40 mg HOOBT in 1.5 mL DMF) 15 uL and I_2 (16 mg in 1.5 mL DMF) 15 µL was added to the vial. The solution was stirred at room temperature for 30 min and quenched by addition of 2 mL $MeCN/H_2O$ =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% $MeCN/H_2O$ over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 265 nm) and lyophilization afforded peptide **25 (**as a white powder (0.6 mg, 82%).

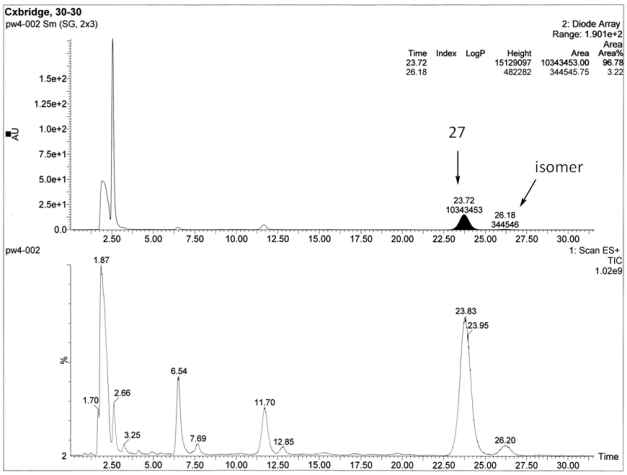


a) UV and MS traces from LC-MS analysis of peptide **25**: gradient 20-45% CH_3CN/H_2O over 6 min at a flow rate of 0.2 mL/min, C18 Xbridge column. (b) ESI-MS of compound**.** ESI calcd for $C_{59}H_{79}N_{11}O_{13}$ $[M+H]^+$ *m/z* = 1150.56; found: 1150.82.

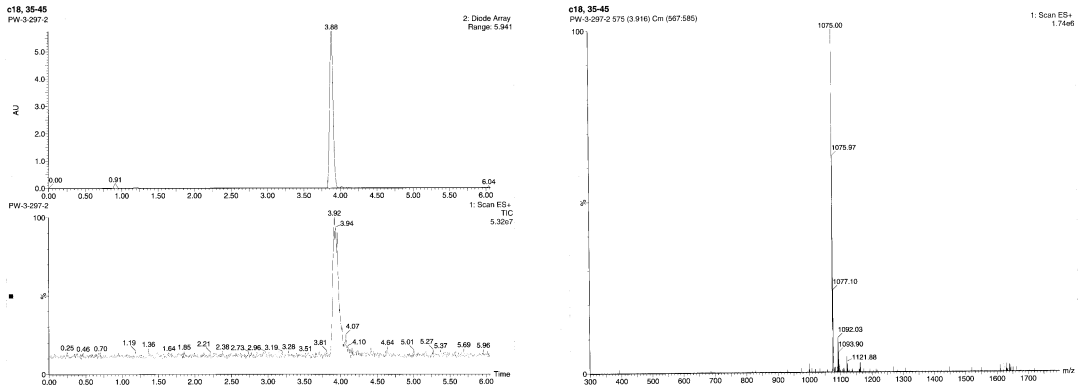
27



To an oven-dried vial were charged thioacid **26** (0.8 mg, 1.7 µmol), peptide **13** (1.0 mg, 1.6 µmol) and 4Å MS (2 mg). A stock solution of HOBT (4.5 mg in 500 uL DMSO) 50 µL was added to the vial. The solution was stirred at room temperature for 12 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (30-45% MeCN/H_2O over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 225 nm) and lyophilization afforded peptide **27** (1.4 mg, 80%) as a white powder. HR-ESIMS (*m/z*) Calcd for $C_{53}H_{75}N_{11}O_{13}Na$: $[M+Na]^+$ *m/z* = 1096.5444; Found: 1096.5450.

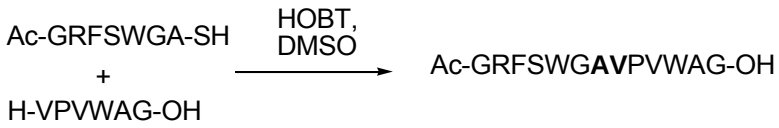


LC-MS traces of reaction mixture: gradient 30-30% CH_3CN/H_2O over 6 min at a flow rate of 0.2 mL/min, C18 column.

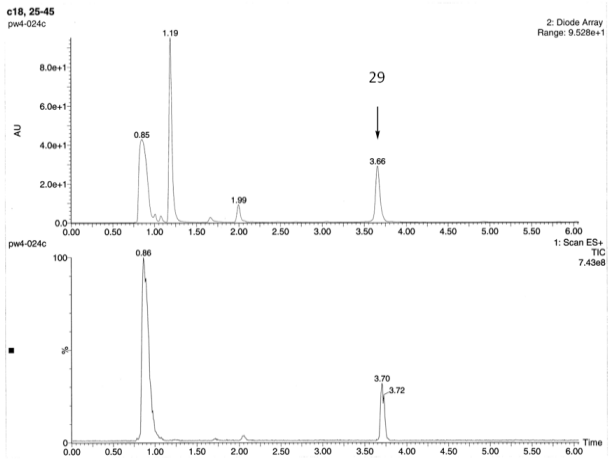


a) UV and MS traces from UPLC-MS analysis of peptide **27**: gradient 35-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{53}H_{76}N_{11}O_{13}$ $[M+H]^+$ *m/z* = 1074.55; found: 1075.00.

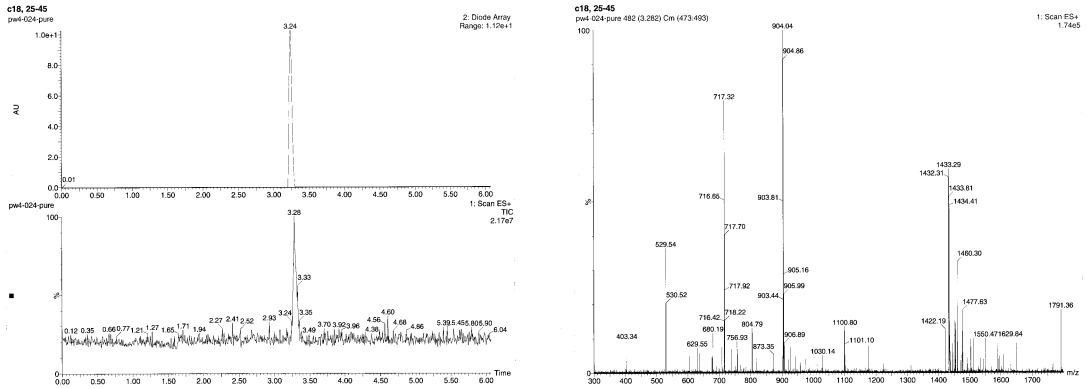
29



To an oven-dried vial were charged thioacid **28** (1.0 mg, 1.2 µmol), peptide **13** (0.7 mg, 1.1 µmol) and 4Å MS (2 mg). A stock solution of HOBT (3.2 mg in 400 uL DMSO) 40 µL was added to the vial. The solution was stirred at room temperature for 12 h and quenched by addition of 2 mL $MeCN/H_2O$ =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% $MeCN/H_2O$ over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 225 nm) and lyophilization afforded peptide **29** (1.3 mg, 81%) as a white powder.

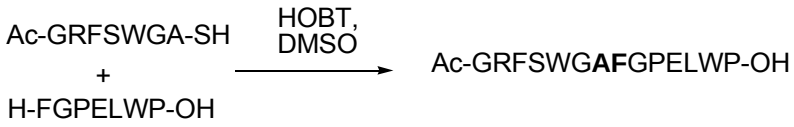


UPLC-MS traces of reaction mixture: gradient 25-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column.

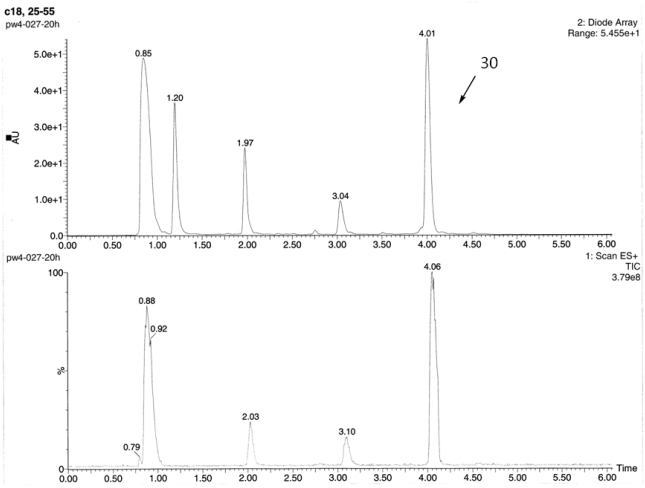


a) UV and MS traces from UPLC-MS analysis of peptide **29**: gradient 25-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{69}H_{95}N_{18}O_{16}$ $[M+H]^+$ *m/z* = 1431.71, $[M+2H]^{2+}$ *m/z* = 716.36; found: 1432.31, 716.65.

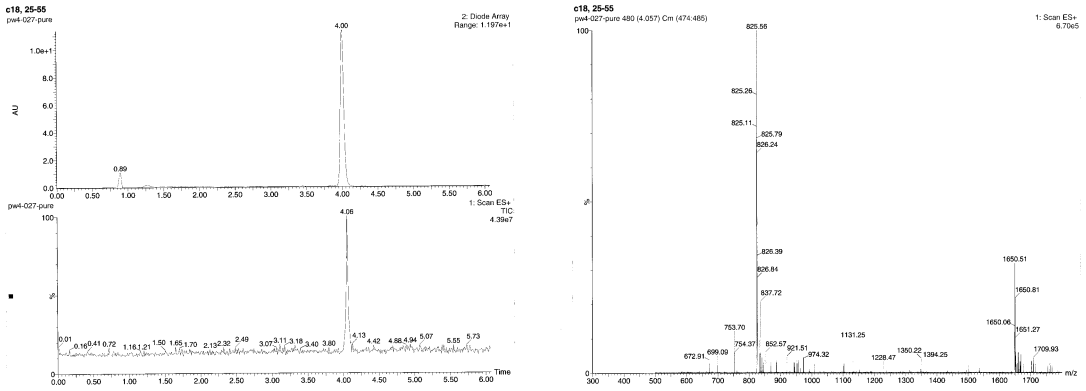
30



To an oven-dried vial were charged thioacid **28** (0.6 mg, 0.72 µmol), peptide **8** (0.5 mg, 0.60 µmol) and 4Å MS (2 mg). A stock solution of HOBT (1.9 mg in 300 uL DMSO) 30 µL was added to the vial. The solution was stirred at room temperature for 12 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 225 nm) and lyophilization afforded peptide **30** (0.8, 82%) as a white powder.

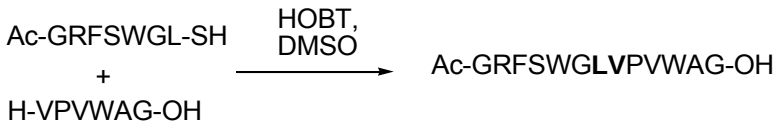


UPLC-MS traces of reaction mixture: gradient 25-55% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column.

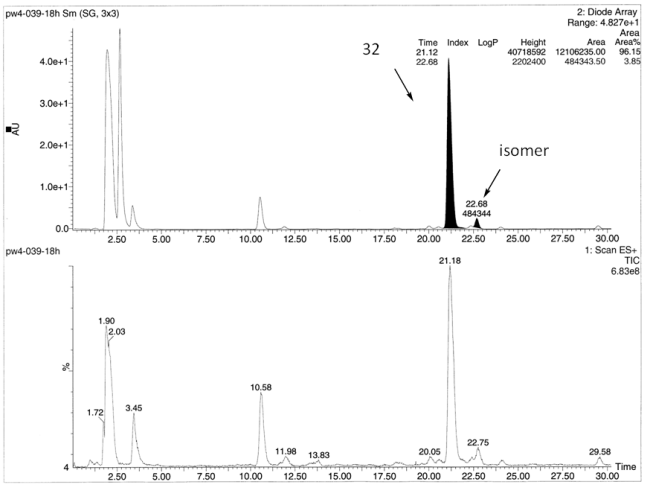


a) UV and MS traces from UPLC-MS analysis of peptide **30**: gradient 25-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{81}H_{106}N_{19}O_{19}$ $[M+H]^+$ *m/z* = 1648.78, $[M+2H]^{2+}$ *m/z* = 824.89; found: 825.11.

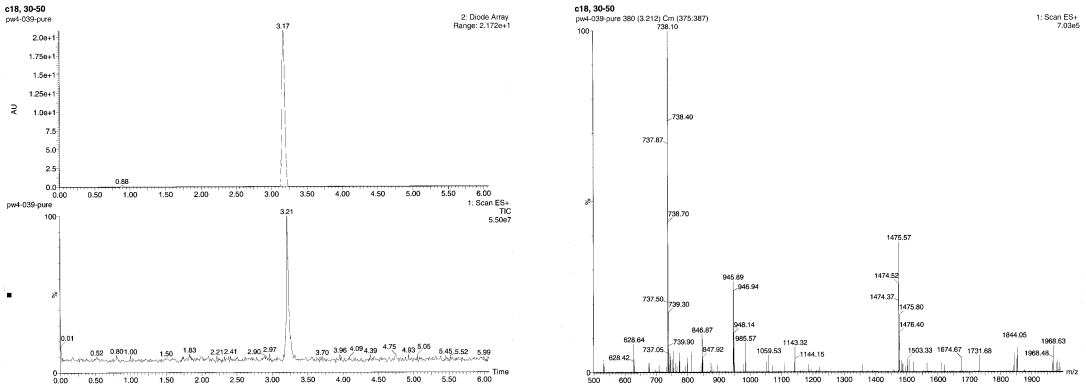
32



To an oven-dried vial were charged thioacid **31** (0.9 mg, 1.0 µmol), peptide **13** (0.7 mg, 1.1 µmol) and 4Å MS (2 mg). A stock solution of HOBT (2.8 mg in 400 uL DMSO) 40 µL was added to the vial. The solution was stirred at room temperature for 12 h and quenched by addition of 2 mL $MeCN/H_2O$ =1/1. The quenched reaction mixture was subject to HPLC purification (25-40% $MeCN/H_2O$ over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 225 nm) and lyophilization afforded peptide **32** (1.2 mg, 80%) as a white powder.

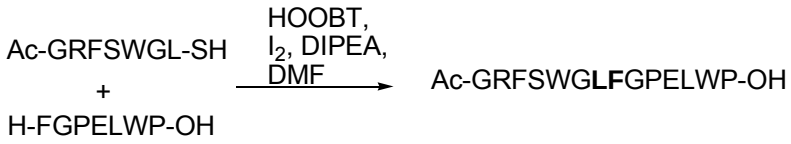


LC-MS traces of reaction mixture: gradient 30-50% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C18 column.

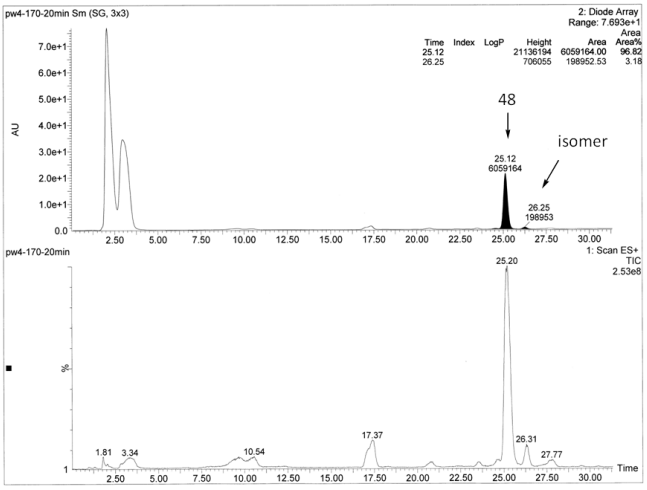


a) UV and MS traces from UPLC-MS analysis of peptide **32**: gradient 20-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column. (b) ESI-MS of compound**.** ESI calcd for $C_{72}H_{101}N_{18}O_{18}$ $[M+H]^+$ *m/z* = 1473.76, $[M+2H]^{2+}$ *m/z* = 737.38; found: 1474.37, 737.50.

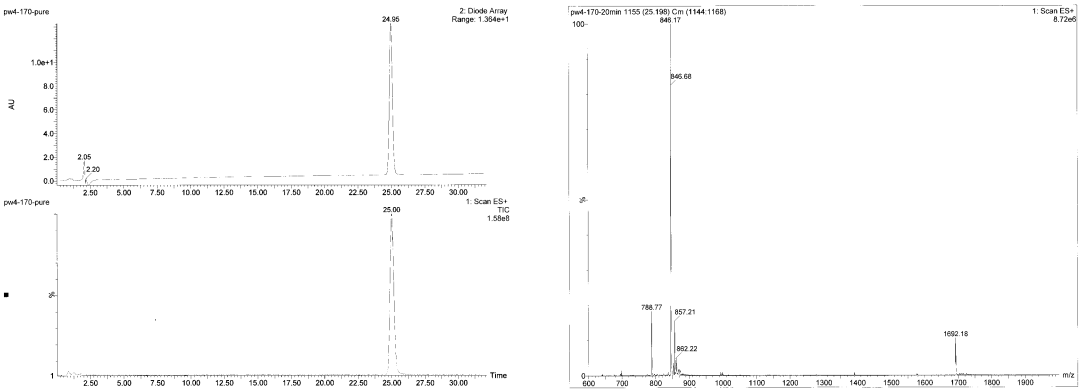
48



To an oven-dried vial were charged thioacid **31** (1.0 mg, 1.1 µmol), amine **8** (0.8 mg, 0.95 µmol) and 4Å MS (2 mg). A stock solution of DIPEA/HOOBT (3 uL DIPEA/4 mg HOOBT in 200 uL DMF) 20 uL and I_2 (16 mg in 1.5 mL DMF) 15 µL was added to the vial. The solution was stirred at room temperature for 30 min and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (25-45% MeCN/H_2O over 30 min, Microsorb 100-5 Xbridge C18 column, 16 mL/min, 230 nm) and lyophilization afforded peptide **48 (**as a white powder (1.4 mg, 82%).

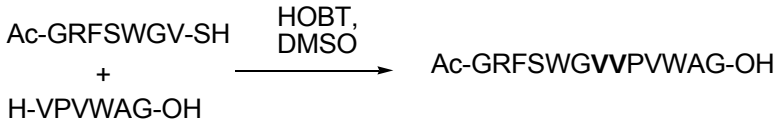


LC-MS traces of reaction mixture: gradient 25-45% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, Xbridge C18 column.

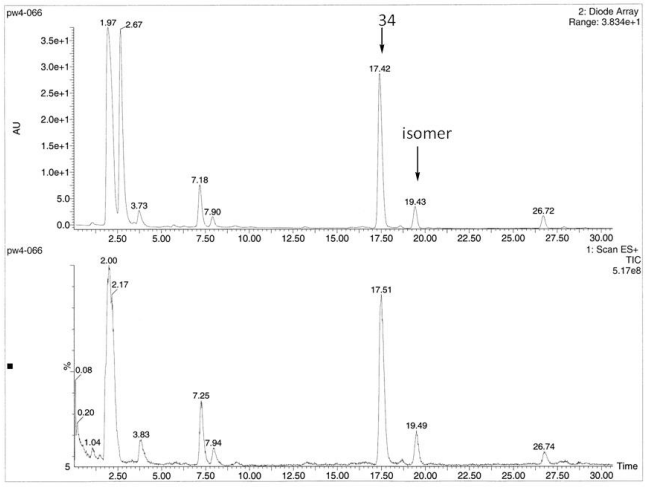


a) UV and MS traces from UPLC-MS analysis of peptide **48**: gradient 25-45% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, Xbridge C18 column. (b)) ESI-MS of compound**.** ESI calcd for $C_{84}H_{112}N_{19}O_{19}$ $[M+H]^+$ *m/z* = 1690.83, $[M+2H]^{2+}$ *m/z* = 845.9; found: 846.17.

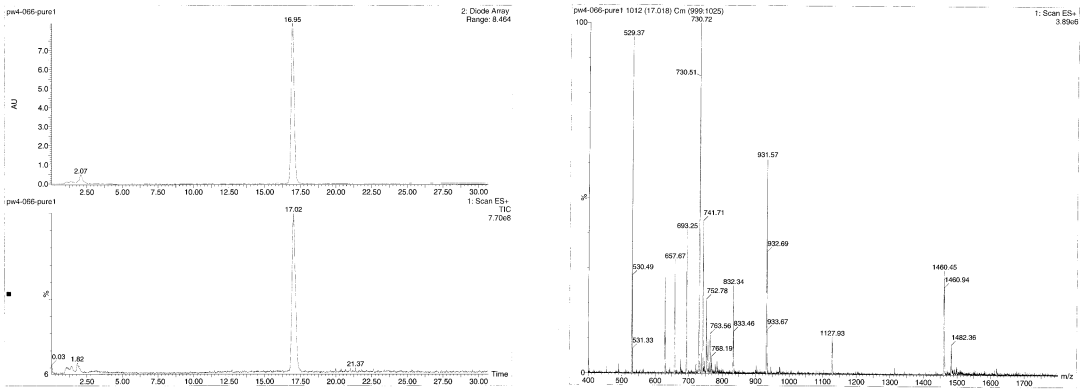
34



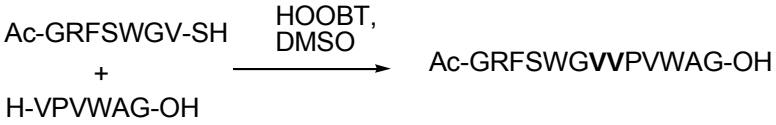
To an oven-dried vial were charged thioacid **33** (1.1 mg, 1.3 µmol), peptide **13** (0.6 mg, 0.96 µmol) and 4Å MS (2 mg). A stock solution of HOBT (3.4 mg in 400 uL DMSO) 40 µL was added to the vial. The solution was stirred at room temperature for 12 h and quenched by addition of 2 mL MeCN/H_2O =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% MeCN/H_2O over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 225 nm) and lyophilization, afforded peptide **34** (1.0 mg, 72%) as a white powder.



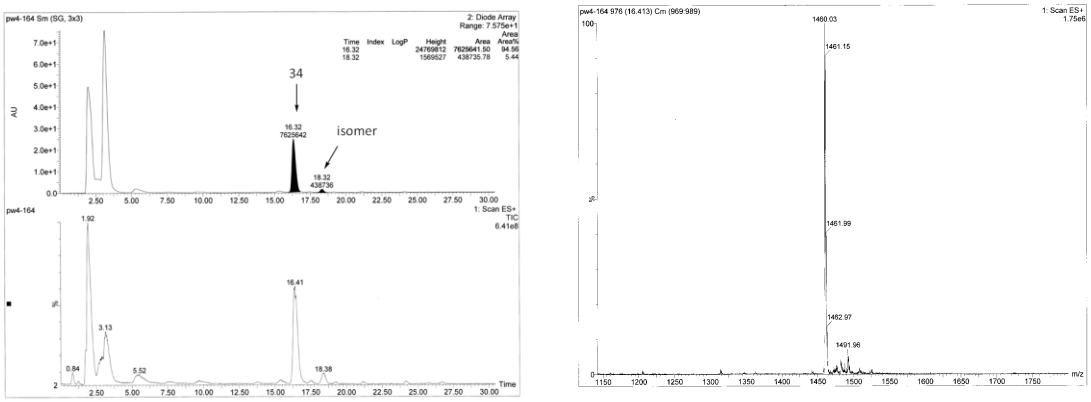
UPLC-MS traces of reaction mixture: gradient 30-50% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C18 column.



a) UV and MS traces from UPLC-MS analysis of peptide **34**: gradient 20-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{71}H_{99}N_{18}O_{16}$ $[M+H]^+$ *m/z* = 1459.74, $[M+2H]^{2+}$ *m/z* = 730.37; found: 1460.33, 730.51.

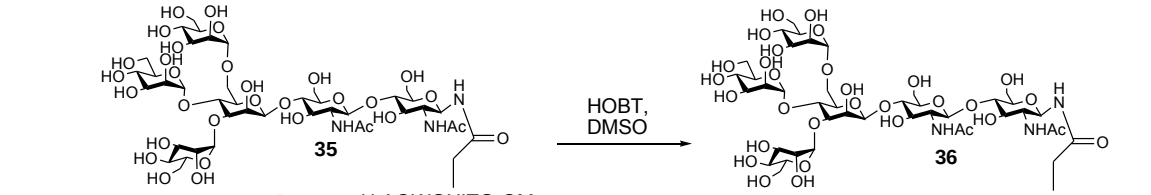


To an oven-dried vial were charged thioacid **33** (0.7 mg, 0.81 μmol), peptide **13** (0.4 mg, 0.64 μmol) and 4Å MS (2 mg). A stock solution of HOOBT (3.0 mg in 300 uL DMSO) 30 μL was added to the vial. The solution was stirred at room temperature for 6 h and quenched by addition of 2 mL $MeCN/H_2O$ =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% $MeCN/H_2O$ over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 225 nm) and lyophilization, afforded peptide **34** (0.8 mg, 86%) as a white powder.

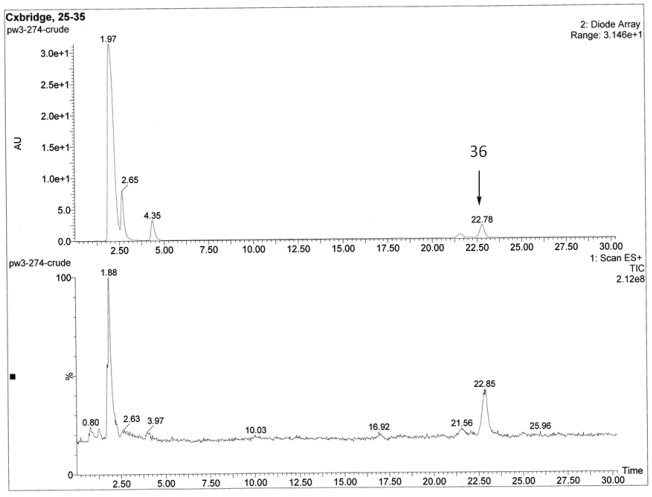


a) UV and MS traces from UPLC-MS analysis of peptide **34**: gradient 20-45% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{71}H_{99}N_{18}O_{16}$ $[M+H]^+$ *m/z* = 1459.74, $[M+2H]^{2+}$ *m/z* = 730.37; found: 1460.03.

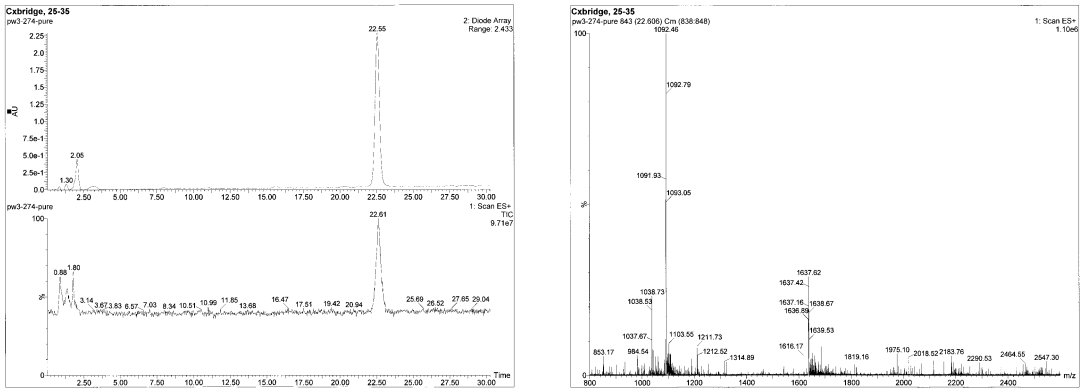
36



To an oven-dried vial were charged thioacid **12** (0.7 mg, 0.50 µmol), glycopeptide **35** (0.8 mg, 0.42 µmol) and 4Å MS (2 mg). A stock solution of HOBT (1.4 mg in 300 uL DMSO) 30 µL was added to the vial. The solution was stirred at room temperature for 12 h and quenched by addition of 2 mL $MeCN/H_2O$ =1/3. The quenched reaction mixture was subject to HPLC purification (25-35% $MeCN/H_2O$ over 30 min, Microsorb 100-5 C18 column, 16 mL/min, 265 nm) and lyophilization afforded glycopeptide **36** (1.1 mg, 80%) as a white powder.

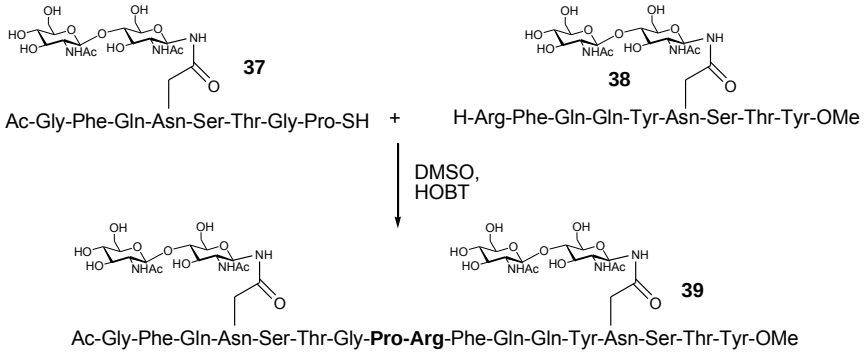


UPLC-MS traces of reaction mixture: gradient 25-35% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C18 column.

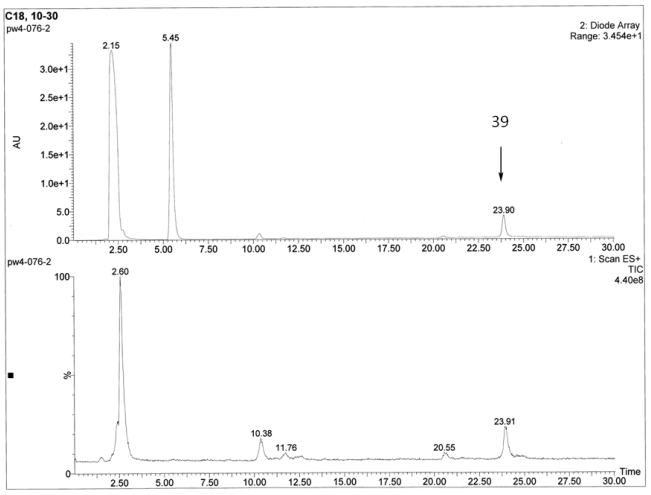


a) UV and MS traces from UPLC-MS analysis of glycopeptide **36**: gradient 20-35% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C8 column. (b) ESI-MS of compound**.** ESI calcd for $C_{144}H_{208}N_{29}O_{58}$ $[M+H]^+$ *m/z* = 3271.41, $[M+2H]^{2+}$ *m/z* = 1636.2, $[M+3H]^{3+}$ *m/z* = 1091.14; found: 1636.89, 1091.93.

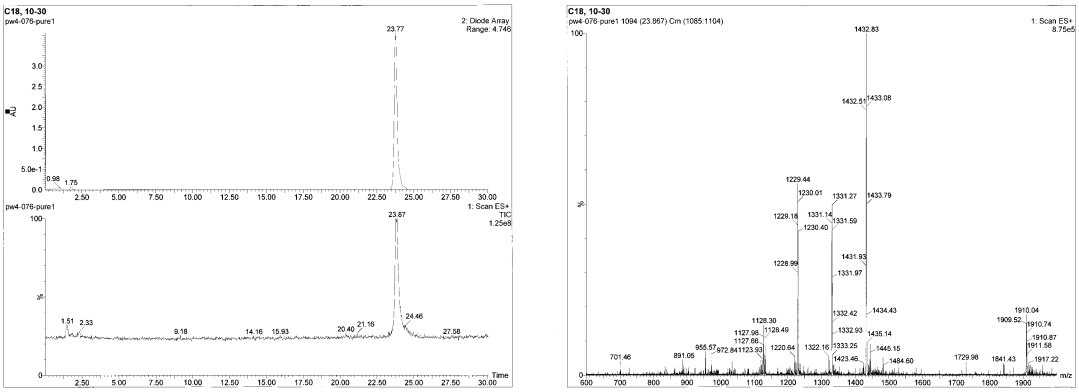
39



To an oven-dried vial were charged thioacid **37** (0.7 mg, 0.55 µmol), peptide **38** (0.7 mg, 0.43 µmol) and 4Å MS (2 mg). A stock solution of HOBT (1.5 mg in 250 uL DMSO) 25 µL was added to the vial. The solution was stirred at room temperature for 12 h and quenched by addition of 2 mL $MeCN/H_2O$ =1/1. The quenched reaction mixture was subject to HPLC purification (20-45% $MeCN/H_2O$ over 30 min, Microsorb 100-5 C4 column, 16 mL/min, 225 nm) and lyophilization afforded glycopeptide **39** (1.0 mg, 81%) as a white powder.

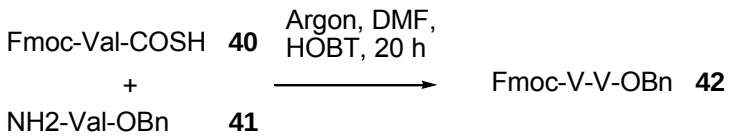


LC-MS traces of reaction mixture: gradient 10-30% CH_3CN/H_2O over 30 min at a flow rate of 0.2 mL/min, C18 column.



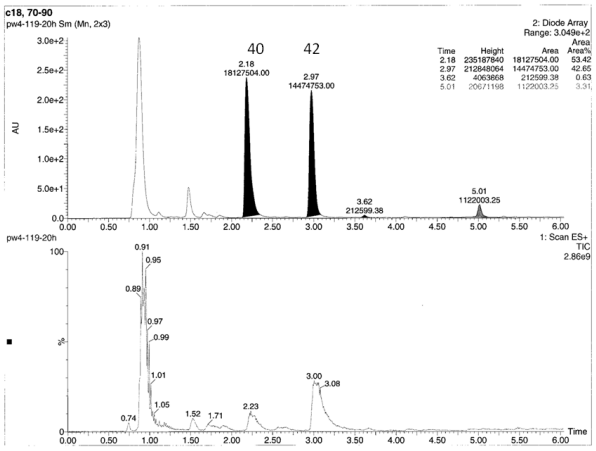
a) UV and MS traces from UPLC-MS analysis of glycopeptide **39**: gradient 10-30% CH_3CN/H_2O over 30 min at a flow rate of 0.3 mL/min, C18 column. (b) ESI-MS of compound**.** ESI calcd for $C_{123}H_{180}N_{29}O_{50}$ $[M+H]^+$ *m/z* = 2863.24, $[M+2H]^{2+}$ *m/z* = 1432.12; found: 1432.51.

42

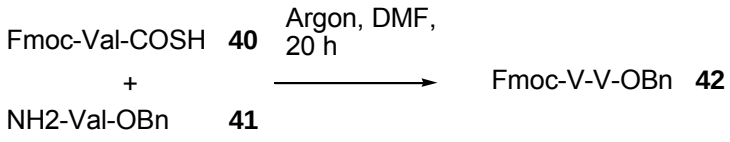


To an oven-dried vial were charged thioacid **40** (140 mg, 0.39 mmol), amine NH_2-Val-OBn (80 mg, 0.39 mmol) and 4Å MS (50 mg), the mixture was degassed with Argon

carefully. A stock solution of HOBT (53 mg in 500 uL DMF, degassed with Argon) was added to the vial. The reaction was run in glove box at an atmosphere of nitrogen. The solution was stirred at room temperature for 20 h. The reaction mixture was subject to a silica gel column and eluted with hexanes/ethyl acetate (4:1-2:1) to give peptide **42** (85 mg, 41%) as a white powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63-7.62 (m, 2 H), 7.50-7.46 (m, 2 H), 7.26-7.16 (m, 9 H), 6.78 (d, 1 H, *J* = 8.5 Hz), 5.63 (d, 1 H, *J* = 9.0 Hz), 5.05 (d, 1 H, *J* = 12.2 Hz), 4.95 (d, 1 H, *J* = 12.2 Hz), 4.53-4.51 (m, 1 H), 4.34-4.32 (m, 1 H), 4.23-4.21 (m, 1 H), 4.11-4.07 (m, 2 H), 2.07-2.04 (m, 1 H), 1.99-1.96 (m, 1 H), 0.85-0.82 (m, 6 H), 0.77 (d, 3 H, *J* = 6.8 Hz), 0.71 (d, 3 H, *J* = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.7, 171.6, 156.5, 143.9, 143.8, 141.3, 135.4, 128.6, 128.5, 128.47, 128.41, 127.7, 127.1, 125.2, 125.1, 120.0, 119.9, 67.2, 67.0, 60.3, 57.2, 47.2, 31.4, 31.2, 19.2, 19.0, 18.2, 17.7; ESIMS (*m/z*) Calcd for $C_{32}H_{37}N_2O_5$: $[M+H]^+$ *m/z* = 529.26; Found: 529.58.

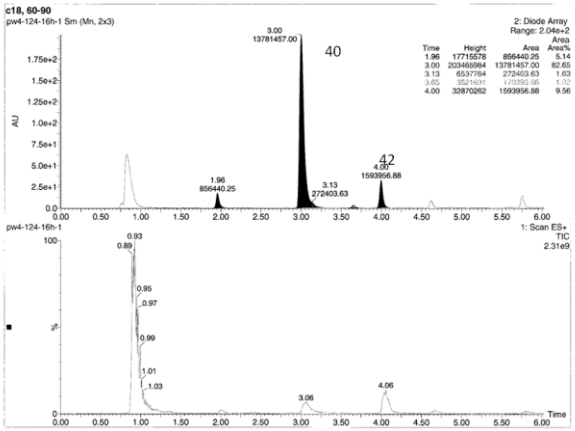


UPLC-MS traces of reaction mixture at 20 h: gradient 70-90% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column.



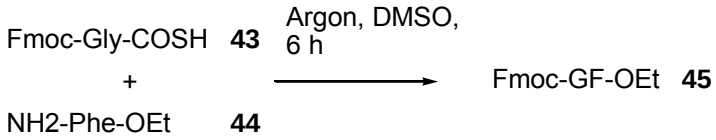
To an oven-dried vial were charged thioacid **40** (140 mg, 0.39 mmol), amine NH_2-Val-OBn (80 mg, 0.39 mmol) and 4Å MS (50 mg), the mixture was degassed with Argon carefully. A solution of DMF (500 uL, degassed with Argon) was added to the vial. The

reaction was run in glove box at an atmosphere of nitrogen. The solution was stirred at room temperature for 20 h.

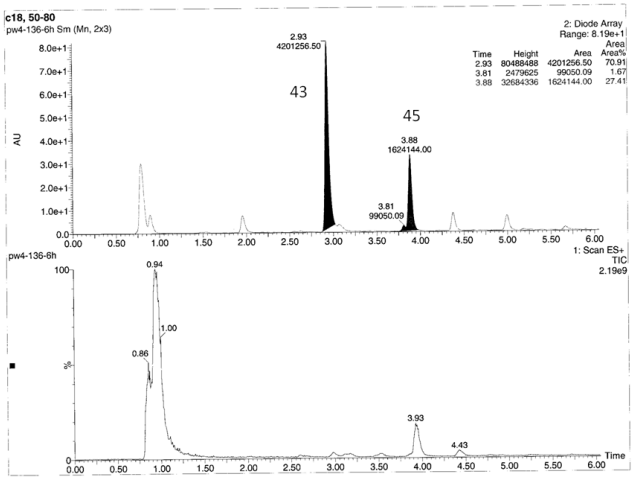


UPLC-MS traces of reaction mixture at 20 h: gradient 60-90% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column.

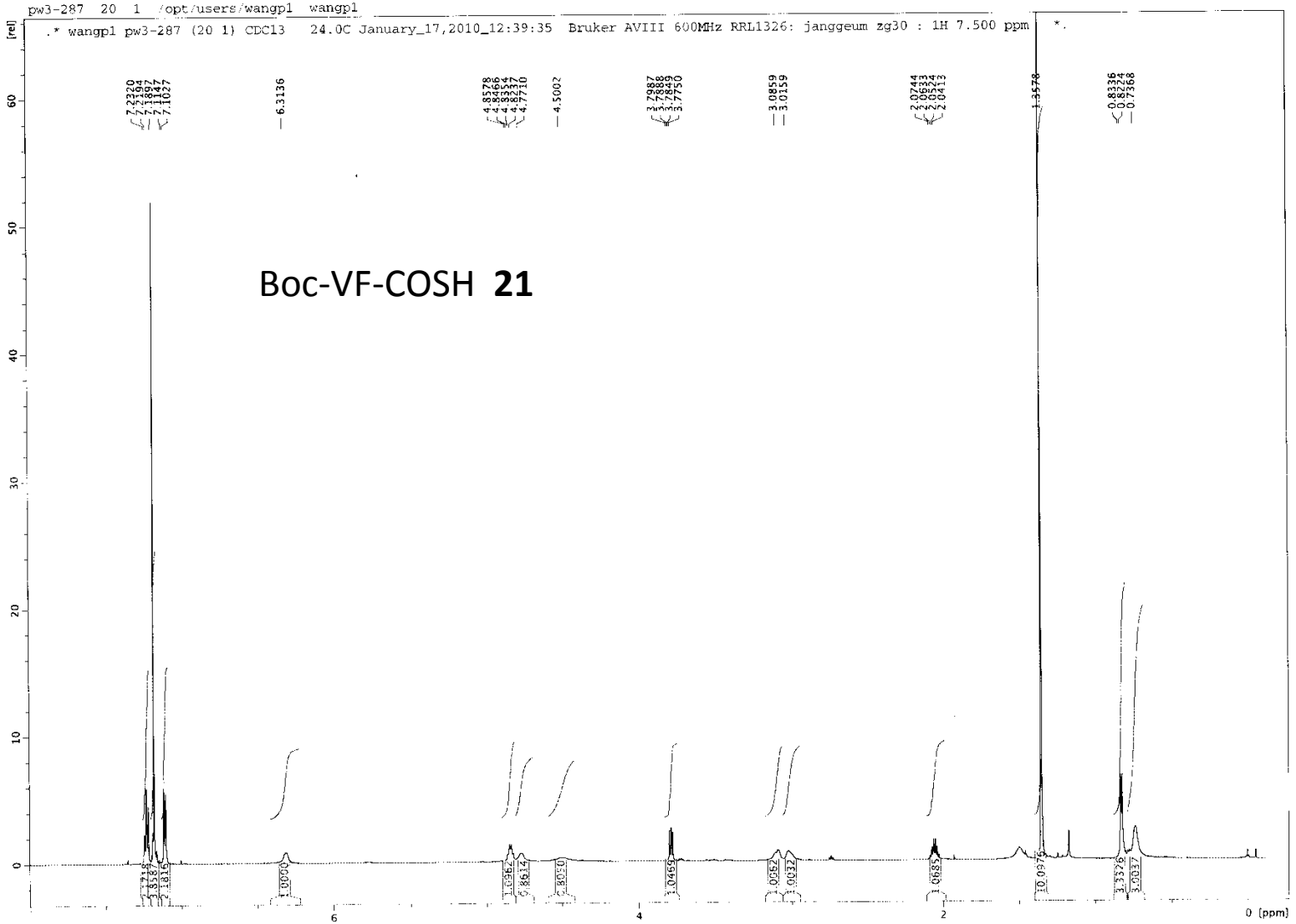
45



To an oven-dried vial were charged thioacid **43** (200 mg, 0.64 mmol), amine NH_2-Val-OBn (123 mg, 0.64 mmol) and 4Å MS (50 mg), the mixture was degassed with Argon carefully. 1.6 mL DMF (degassed with Argon) was added to the vial. The reaction was run in glove box at an atmosphere of nitrogen for 6 h. The reaction mixture was subject to a silica gel column and eluted with hexanes/ethyl acetate (4:1-2:1) to give peptide **45** (81 mg, 27%) as a white powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, 2 H, *J* = 7.6 Hz), 7.62 (d, 2 H, *J* = 7.2 Hz), 7.42-7.41 (m, 2 H), 7.34-7.31 (m, 2 H), 7.25-7.13 (m, 7 H), 6.94 (d, 1 H, *J* = 7.6 Hz), 5.87 (t, 1 H, *J* = 5.2 Hz), 4.94-4.90 (m, 1 H), 4.42-4.39 (m, 2 H), 4.25-4.22 (m, 1 H), 4.19-4.16 (m, 2 H), 3.93-3.91 (m, 2 H), 3.18-3.10 (m, 2 H), 1.25 (t, 3 H, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.4, 168.9, 156.7, 143.9, 143.8, 141.32, 143.31, 135.8, 129.3, 128.6, 127.8, 127.1, 125.2, 125.1, 120.0, 67.3, 61.6, 53.5, 53.4, 47.1, 44.4, 38.0, 14.1; ESIMS (*m/z*) Calcd for $C_{28}H_{29}N_2O_5$: $[M+H]^+$ *m/z* = 473.20; Found: 473.45.



UPLC-MS traces of reaction mixture at 6 h: gradient 50-80% CH_3CN/H_2O over 6 min at a flow rate of 0.3 mL/min, C18 column. The conversion of **45** is 28%.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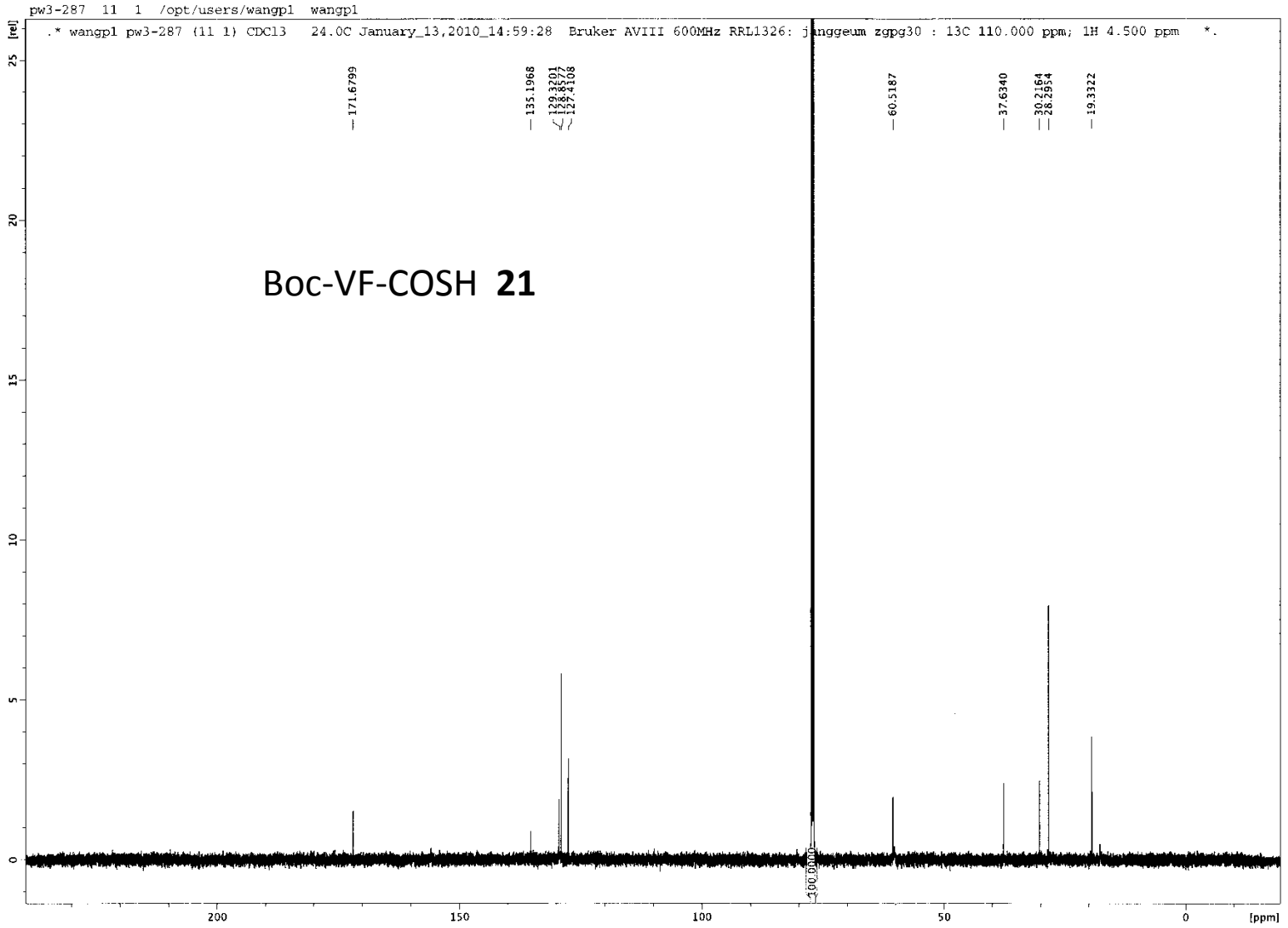
Boc-VF-COSH 21
[rel]
0 (ppm)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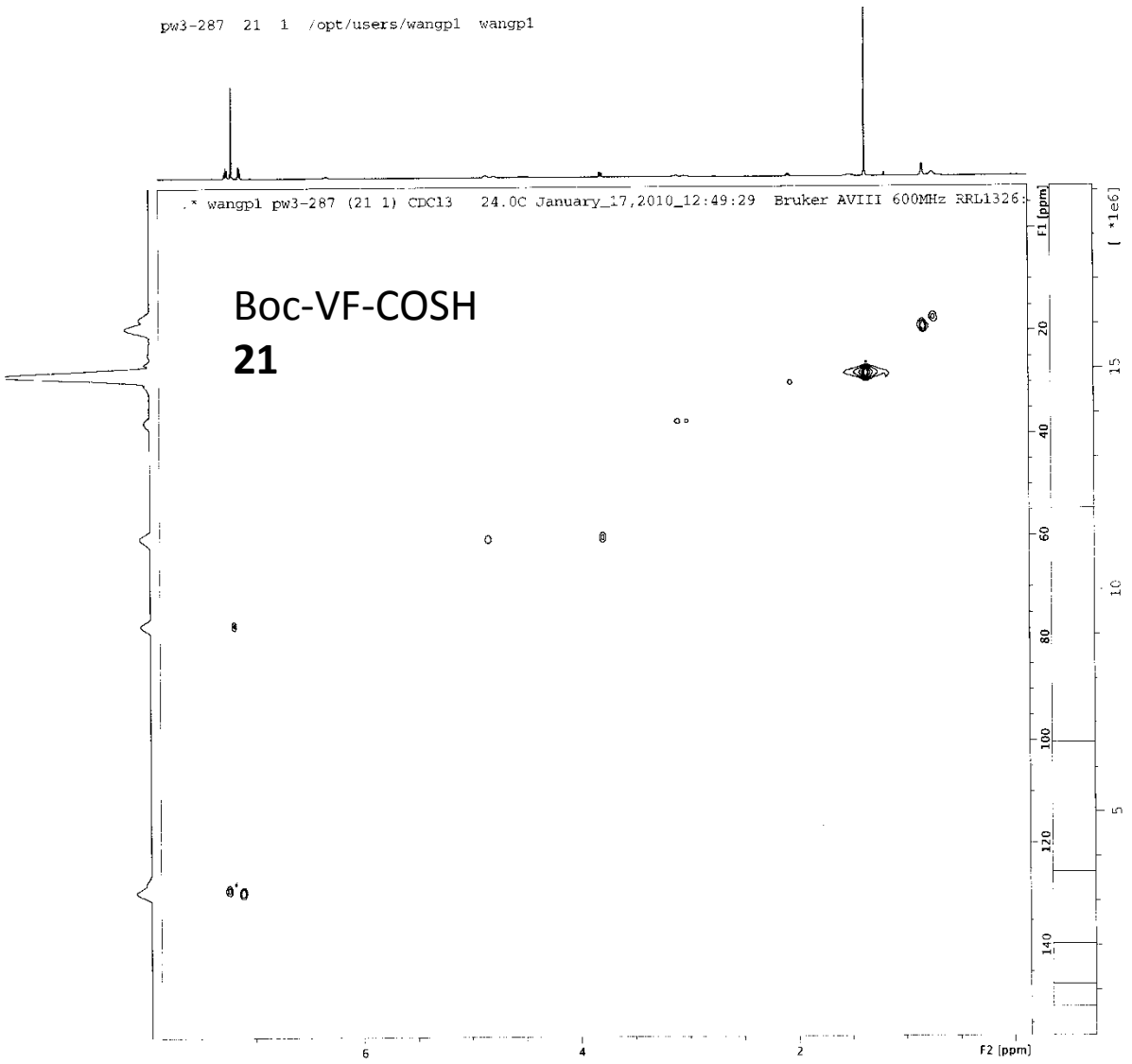
135.1968
129.3201
128.8577
128.7127
127.4108
60.5187
37.6340
30.2164
28.2934
19.3322
77.0000
Boc-VF-COSH 21
[rel]
25
20
15
10
5
0
200
150
100
50
0
[ppm]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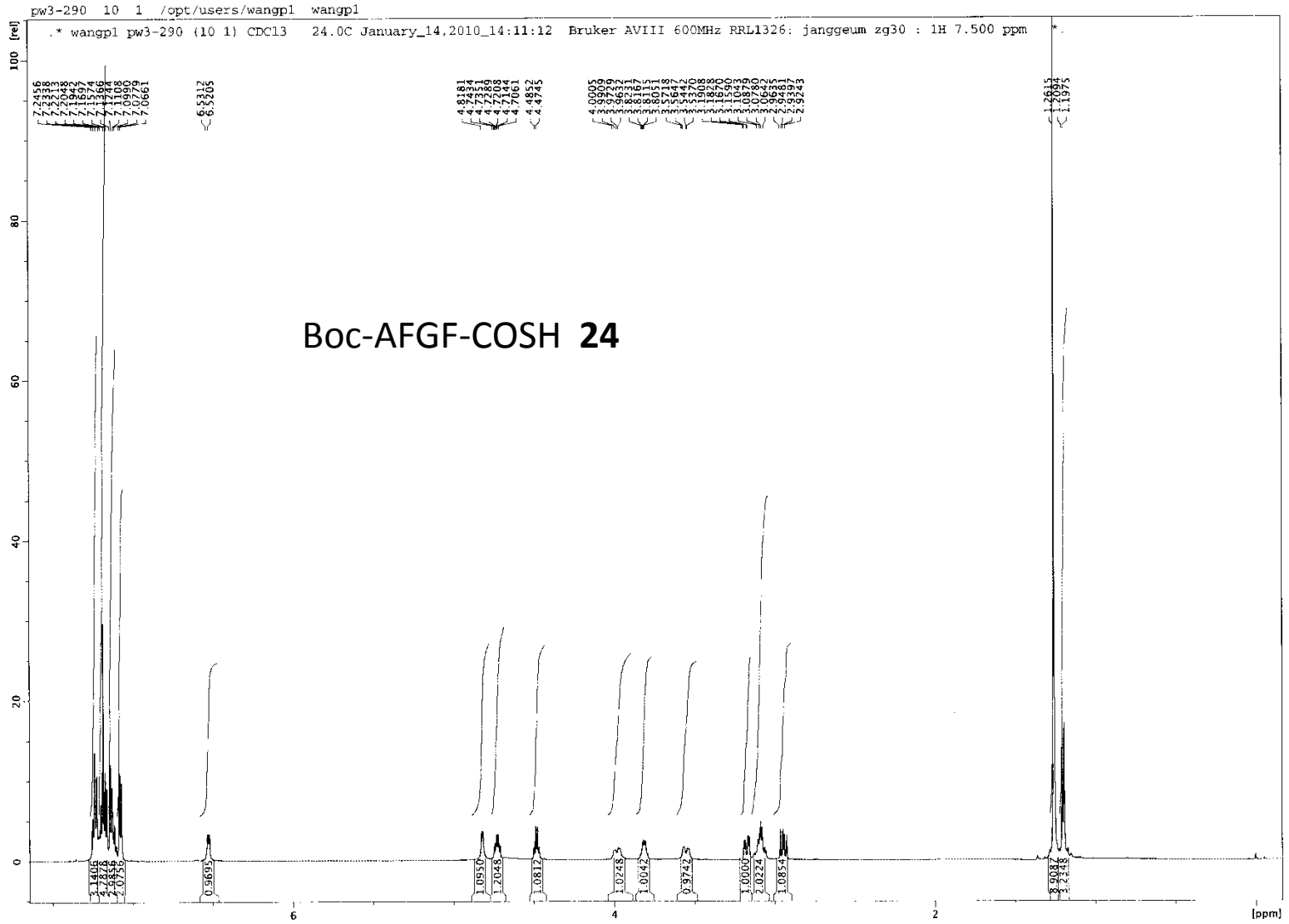
Boc-VF-COSH
21
F1 [ppm]
[*1e6]
F2 [ppm]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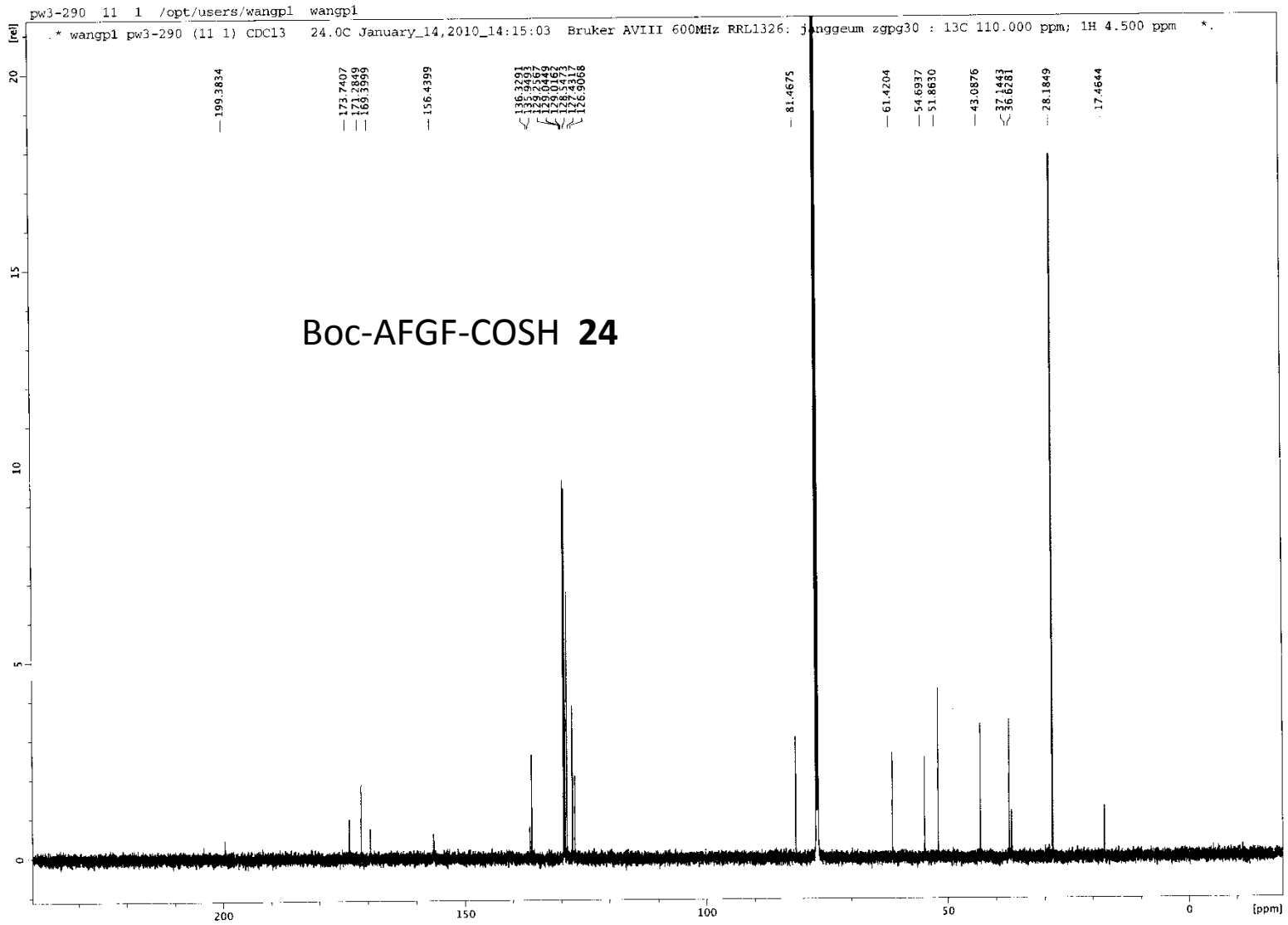
Boc-AFGF-COSH 24
[rel]
[ppm]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[rel]
199.3834
173.7407
171.2849
169.3999
156.4399
136.3291
135.9493
129.2367
129.0449
129.0162
128.5473
127.4317
126.9068
81.4675
61.4204
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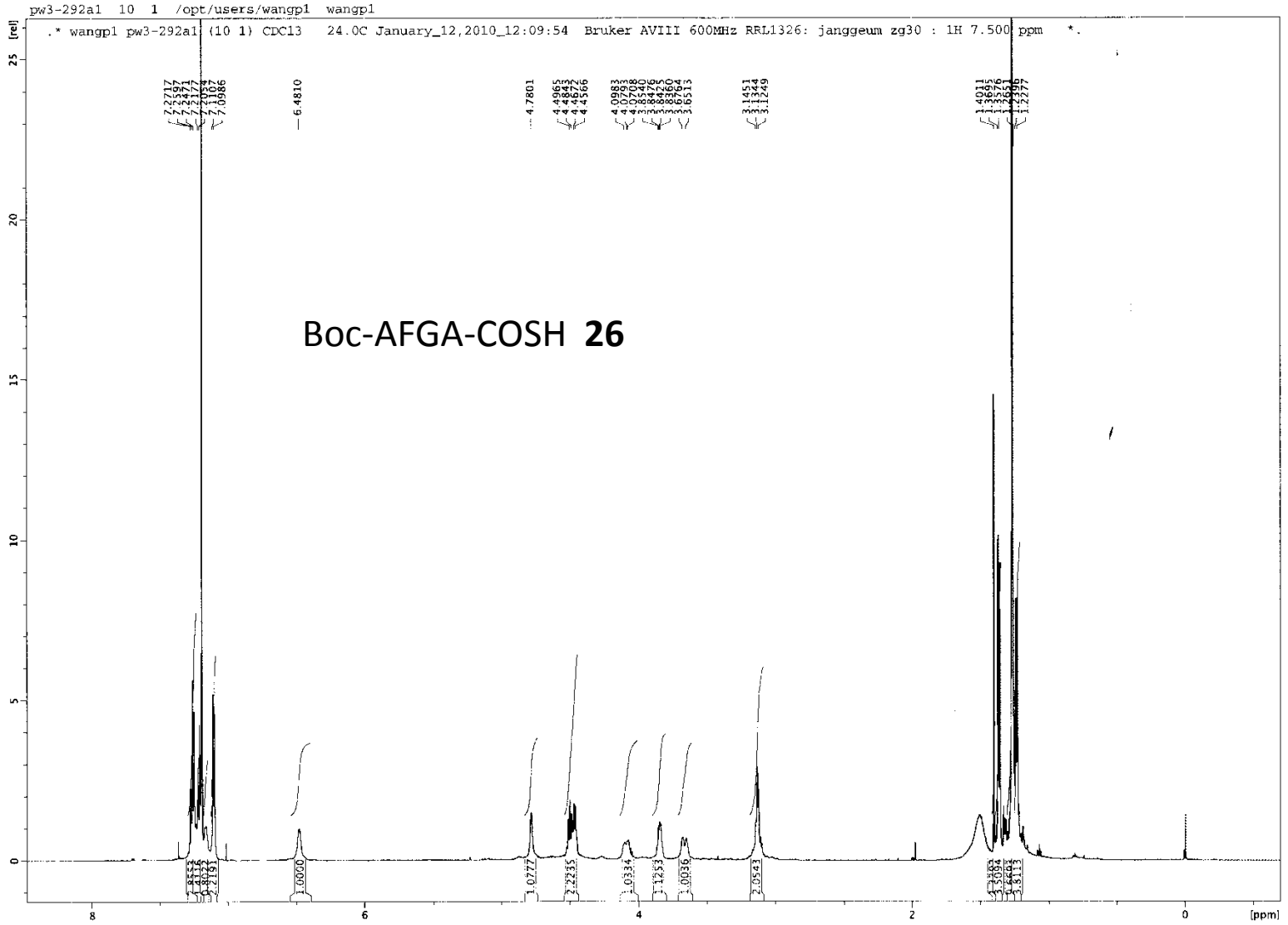
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Boc-AFGA-COSH 26
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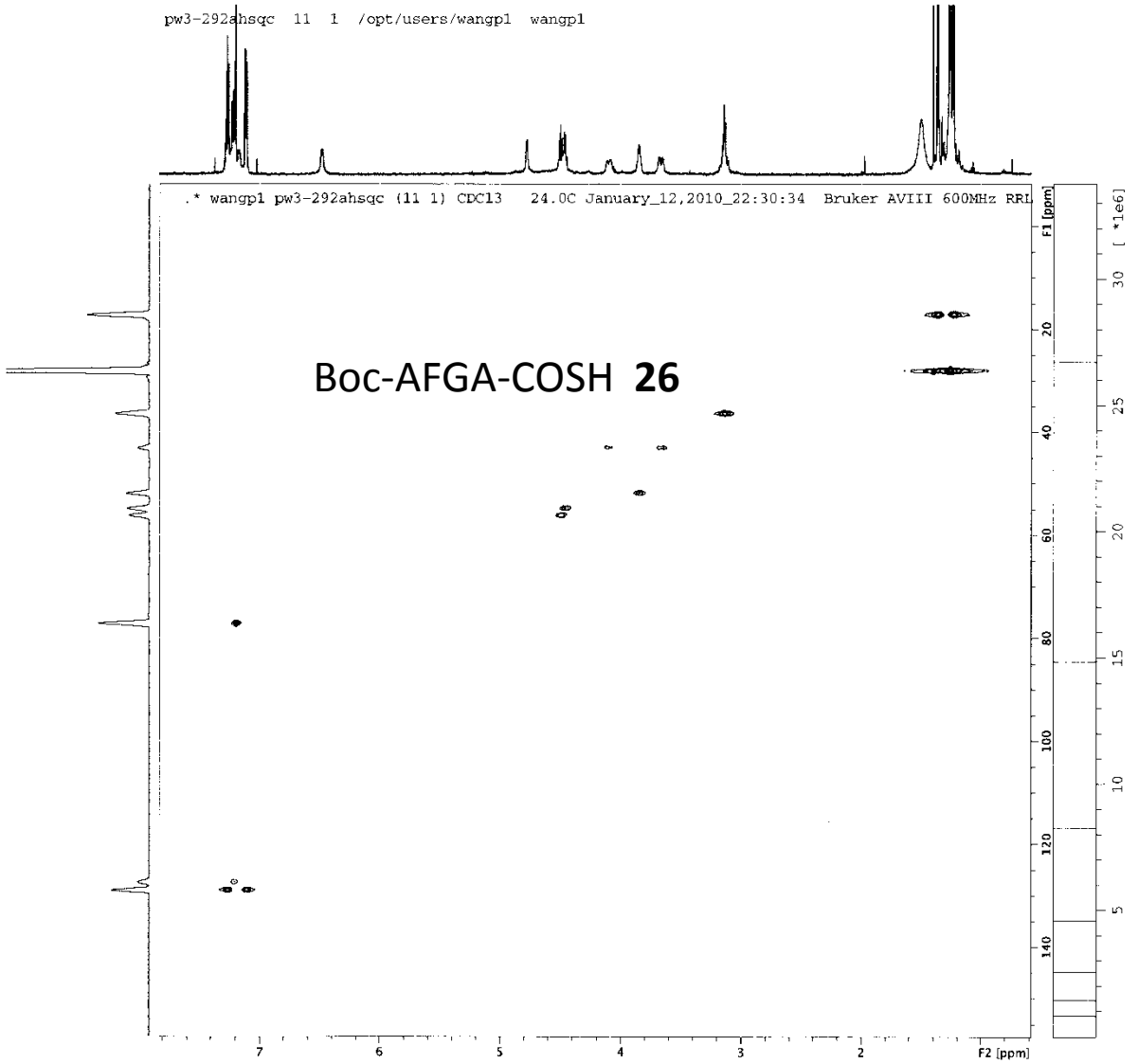
[ppm]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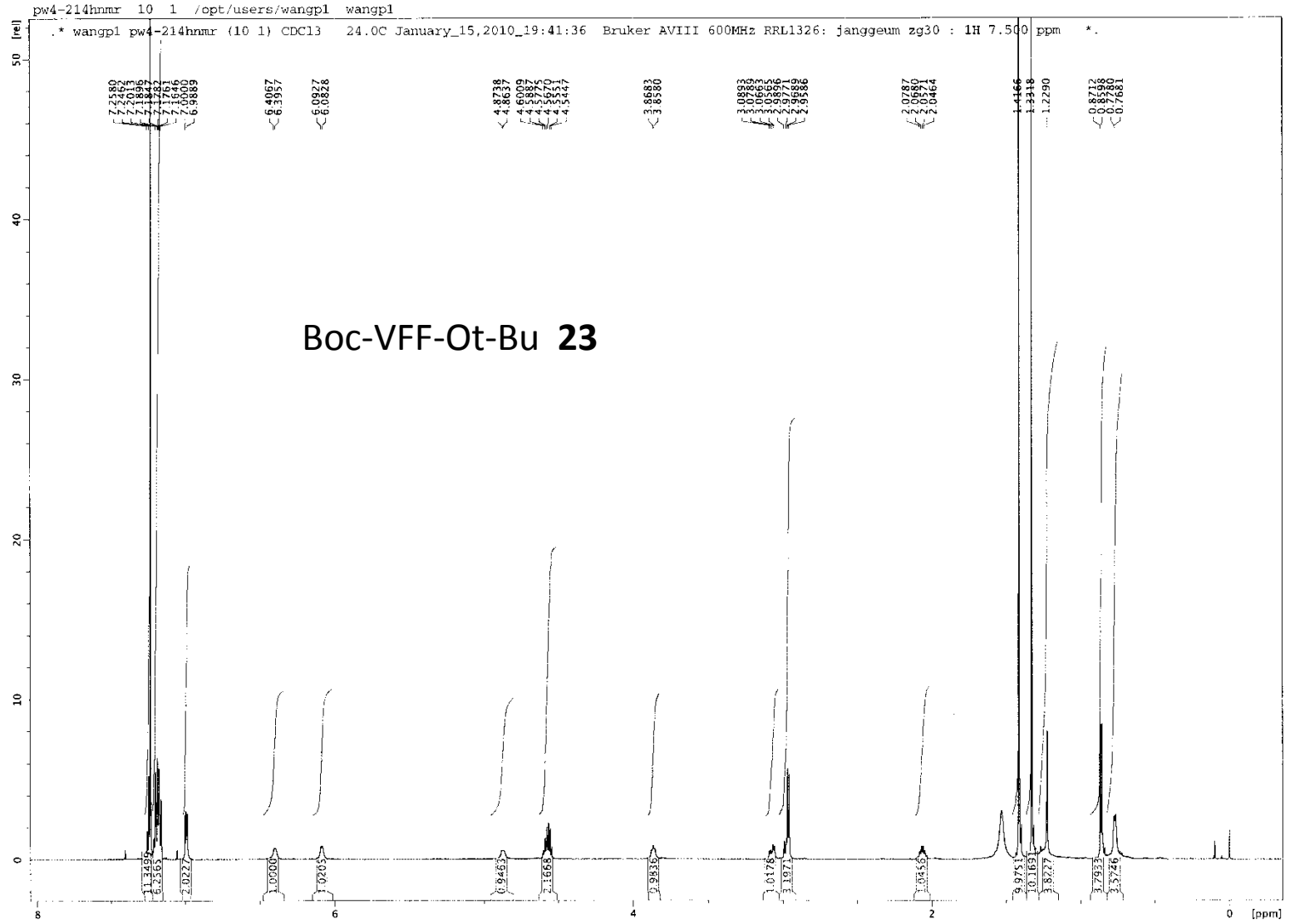
F1 [ppm]
F2 [ppm]
[*1e6]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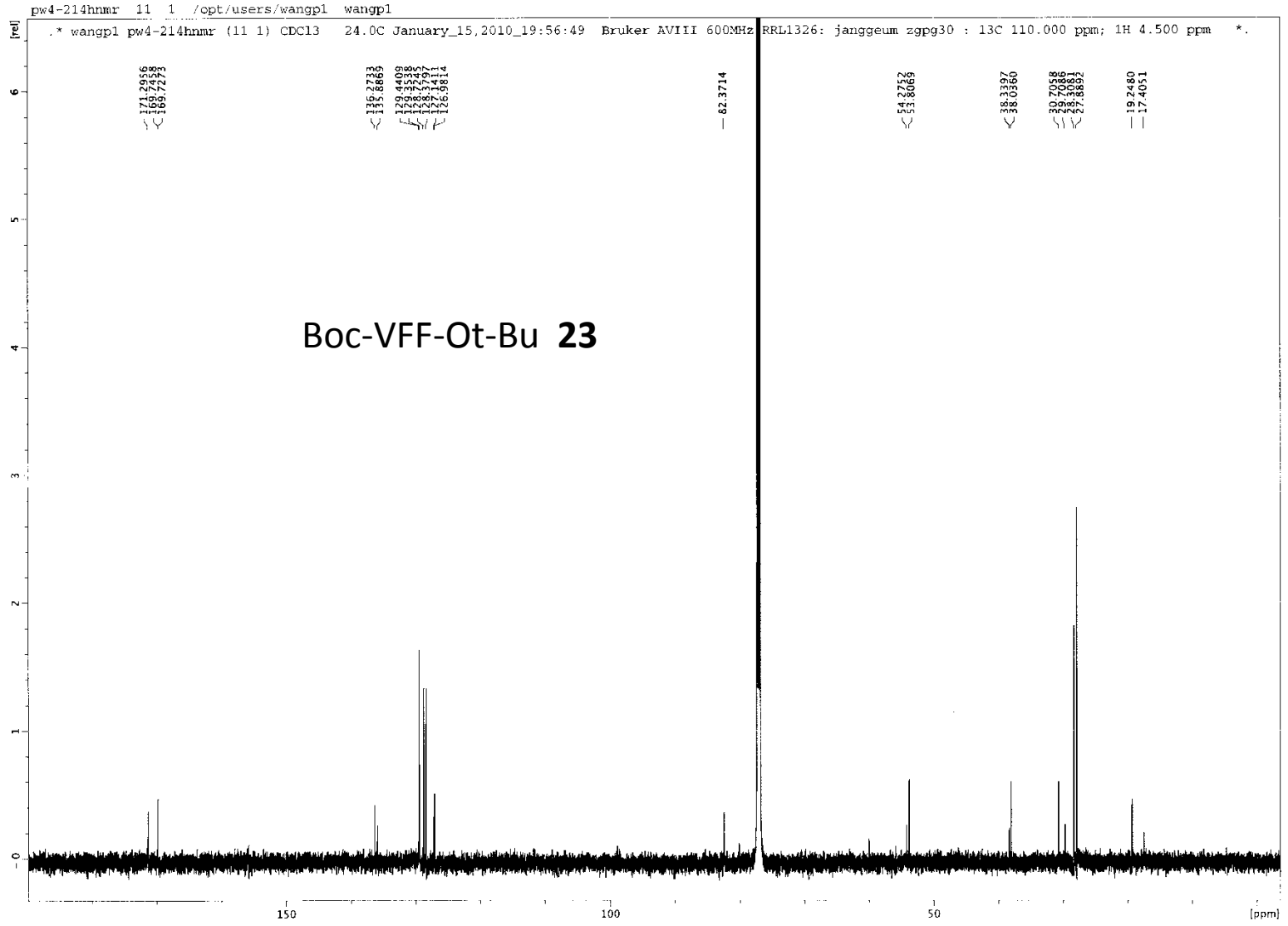
.* wangp1 pw4-214hnmr (10 1) CDCl3 24.0C January_15,2010_19:41:36 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm *.
Boc-VFF-Ot-Bu 23
[rel]
[ppm]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171.2956
169.7458
169.7273
136.2733
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129.4409
128.5328
128.3345
128.3797
127.1411
126.9814
82.3714
54.2752
53.8069
38.3397
38.0360
30.7058
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27.8892
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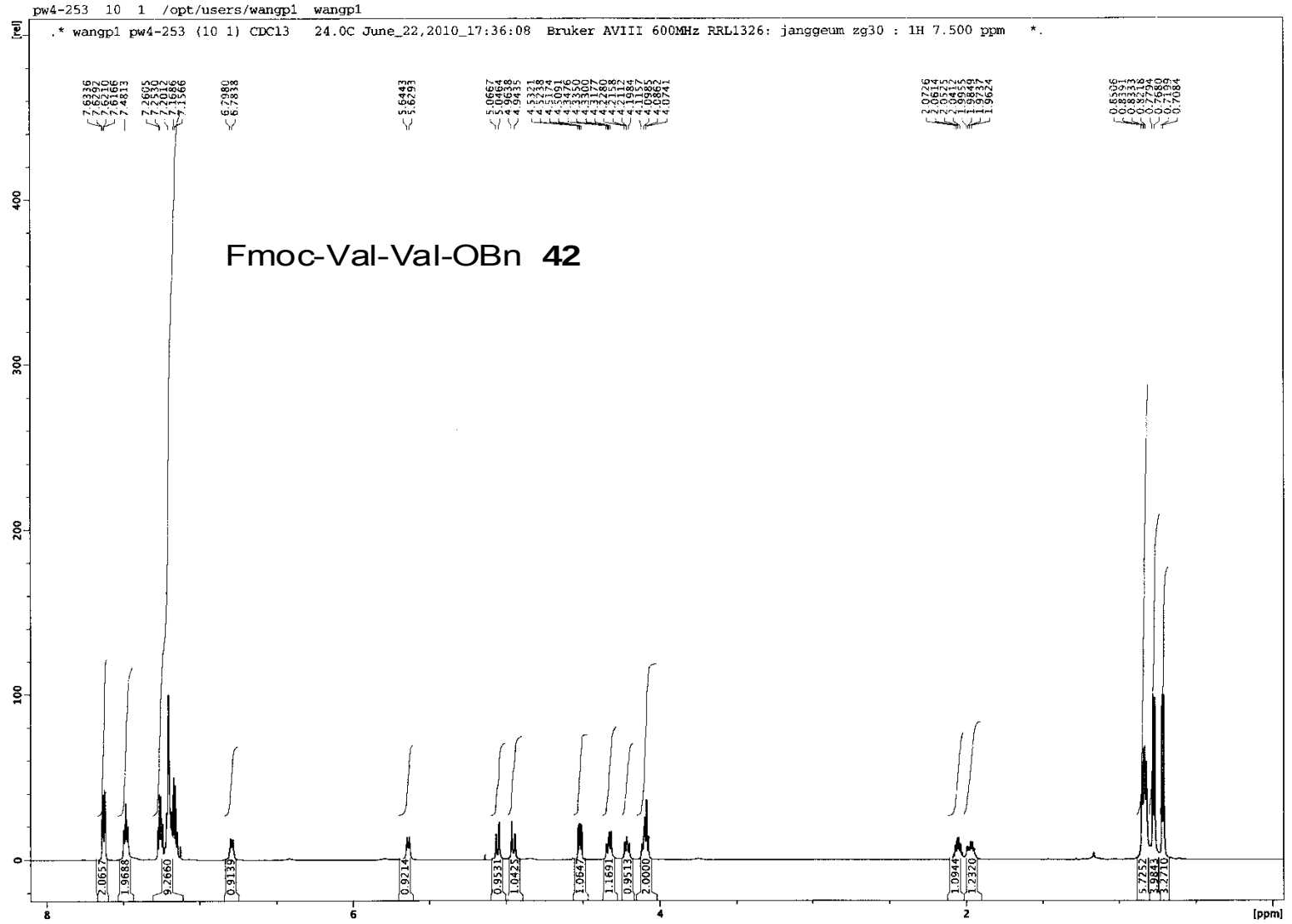
17.4051
Boc-VFF-Ot-Bu 23
[rel]
150
100
50
[ppm]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Fmoc-Val-Val-OBn 42
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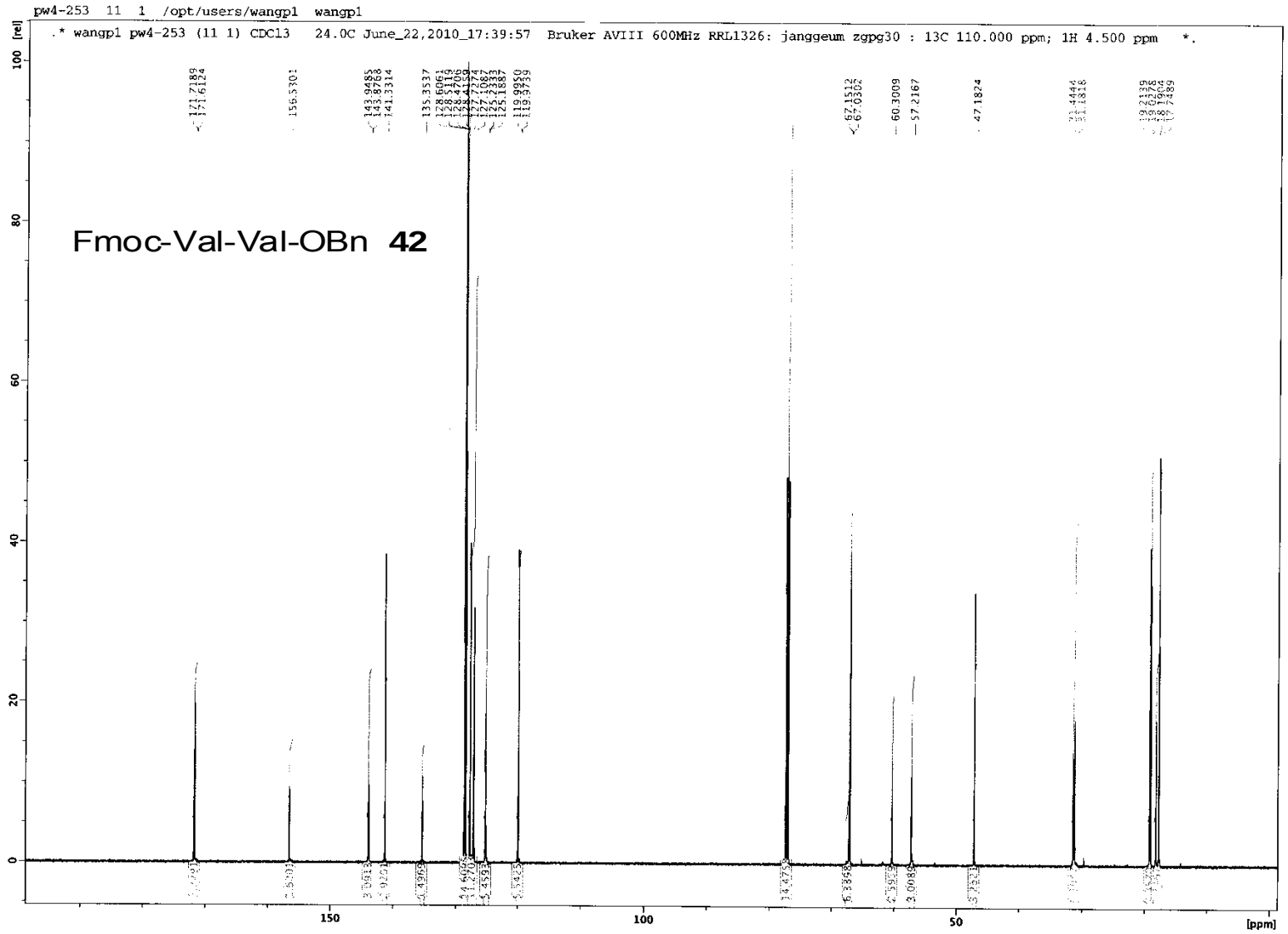
[ppm]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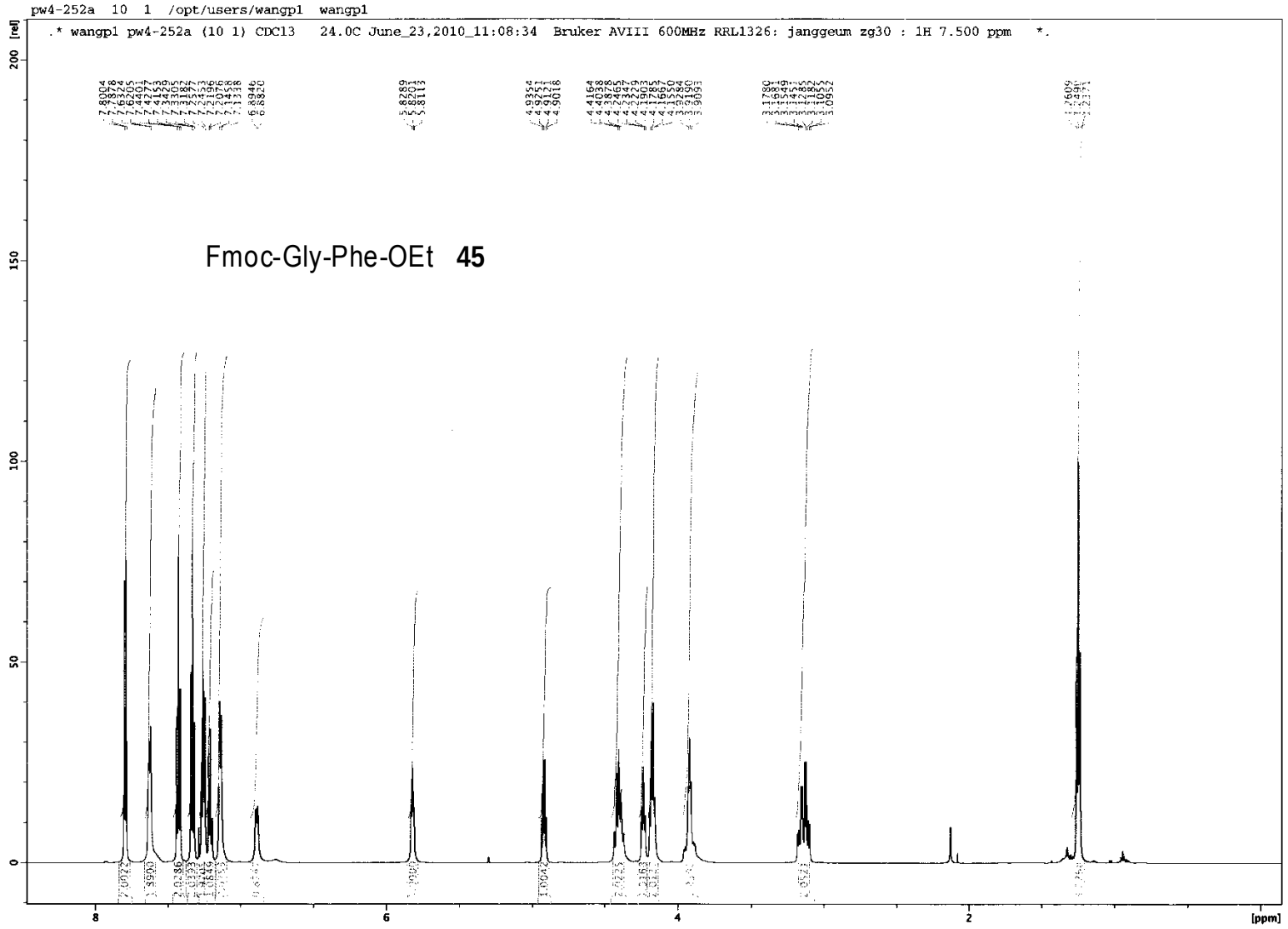
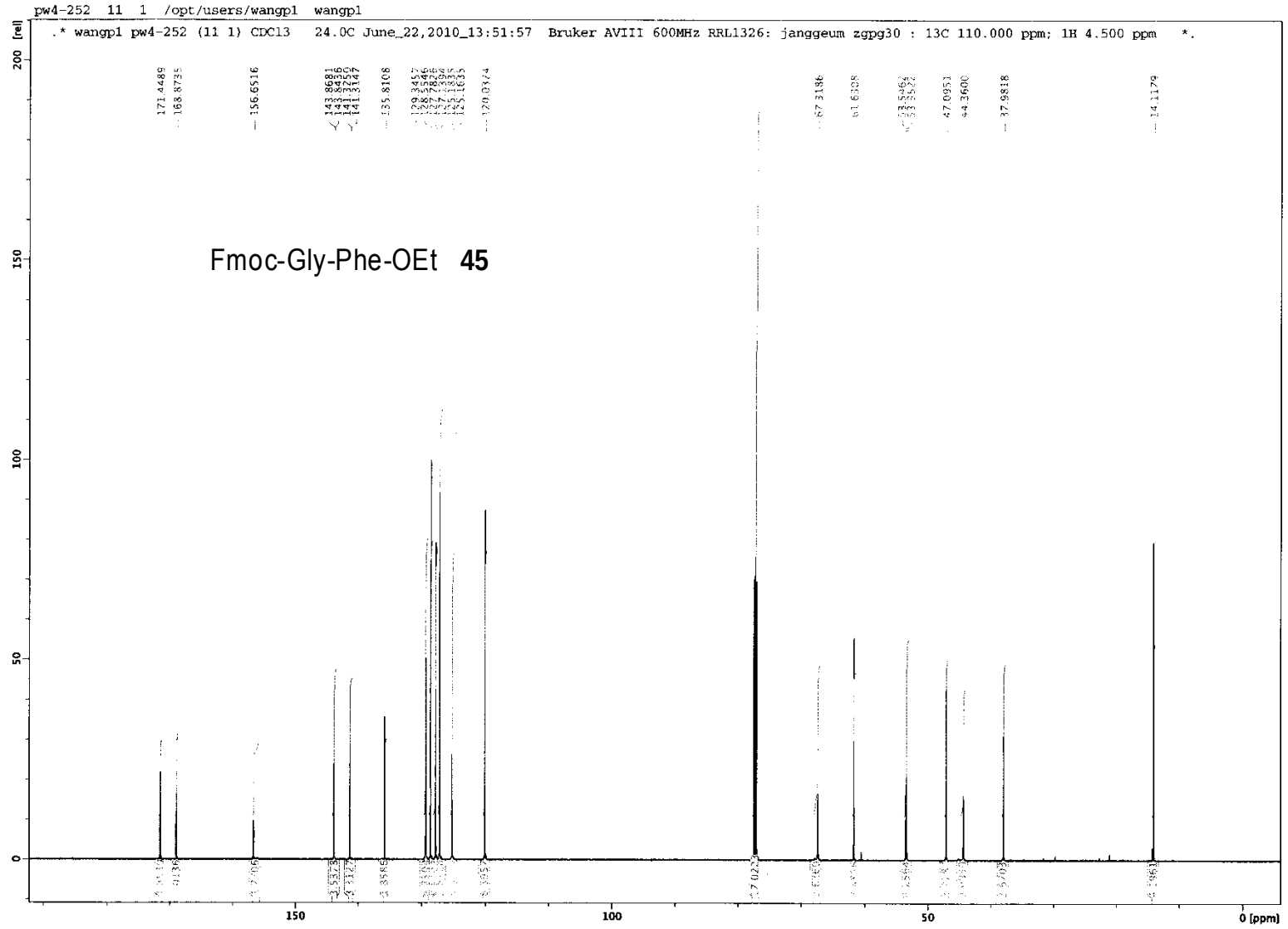
Fmoc-Val-Val-OBn 42
[rel]
[ppm]


pw4-252a 10 1 /opt/users/wangp1 wangp1
.* wangp1 pw4-252a (10 1) CDCl3 24.0C June_23,2010_11:08:34 Bruker AVIII 600MHz RRL1326: janggeum zg30 : 1H 7.500 ppm *.
Fmoc-Gly-Phe-OEt 45
[rel]
[ppm]


pw4-252 11 1 /opt/users/wangp1 wangp1
.* wangp1 pw4-252 (11 1) CDCl3 24.0C June_22,2010_13:51:57 Bruker AVIII 600MHz RRL1326: janggeum zgpg30 : 13C 110.000 ppm; 1H 4.500 ppm *.
Fmoc-Gly-Phe-OEt 45
171.4489
168.8735
156.6516
143.8681
141.3147
135.8168
129.3457
128.5546
127.7826
127.1336
125.1635
120.0374
67.3184
61.6328
53.5462
53.3522
47.0951
44.3600
37.9818
14.1179
200 [rel]
150
100
50
0
150
100
50
0 [ppm]