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Electronic Supplementary Information

Solid Phase Synthesis of Peptide Selenoesters *via* a Side Chain Anchoring Strategy

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General Methods and Materials

All reactions were carried out under an argon atmosphere and at room temperature (22 ^{o}C) unless otherwise specified. Reactions undertaken at -12 ^{o}C utilised a bath of ice, sodium chloride salt and water. Reactions carried out at 0 ^{o}C employed a bath of water and ice. Anhydrous CH_2Cl_2 and DMF were obtained using a PureSolv® solvent purification system with water detectable only in low ppm levels. Reactions were monitored by thin layer chromatography (TLC) on aluminium backed silica plates (Merck Silica Gel 60 F254). Visualisation of TLC plates was undertaken with an ultraviolet (UV) light at λ = 254 nm and staining with solutions of vanillin, ninhydrin, phosphomolybdic acid (PMA), potassium permanganate or sulfuric acid, followed by exposure of the stained plates to heat. Silica flash column chromatography (Merck Silica Gel 60 40 – 63 μm) was undertaken to purify crude reaction mixtures using solvents as specified. All commercially available reagents were used as obtained from Sigma-Aldrich, Merck or Acros Organics. Amino acids, coupling reagents and HMPB-ChemMatrix® resin were obtained from NovaBiochem or GL Biochem and peptide synthesis grade DMF was obtained from Merck or Labscan. All non-commercially available reagents were synthesised according to literature procedures as referenced. Unless otherwise stated, all amino acids used are L-configured.

^{1}H NMR spectra were obtained using a Bruker DRX 300, DRX 400 or DRX 500 at frequencies of 400 MHz or 500 MHz, respectively in $CDCl_3$, acetone-d^6 or DMSO-d^6. Chemical shifts are reported in parts per million (ppm) and coupling constants in Hertz (Hz). The residual solvent peaks were used as internal standards without the use of tetramethylsilane (TMS). ^{1}H NMR data is reported as follows: chemical shift values (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) and relative integral. ^{13}C NMR spectra were obtained using a Bruker DRX 400 or DRX 500 at 100 MHz or 125 MHz in $CDCl_3$, MeOD, acetone-d^6 or DMSO-d^6 unless otherwise specified. ^{13}C NMR data is reported as chemical shift values (ppm).

Low resolution mass spectra for novel compounds were recorded on a Bruker amaZon SL mass spectrometer (ESI) operating in positive mode or on a Shimadzu 2020 (ESI) mass spectrometer operating in positive mode for previously reported compounds.

High resolution mass spectra were recorded on a BrukerDaltronics Apex Ultra 7.0T Fourier transform (FTICR) mass spectrometer.

LC-MS was performed either on a Shimadzu LC-MS 2020 instrument consisting of a LC-M20A pump and a SPD-20A UV/Vis detector coupled to a Shimadzu 2020 mass spectrometer (ESI) operating in positive mode or a Shimadzu UPLC-MS equipped with the same modules as the LC-MS system except for an SPD-M30A diode array detector. Separations were performed on the LC-MS system either on a Waters Sunfire 5 μm, 2.1 x 150 mm column (C-18), or wide-pore equivalent operating at a flow rate of 0.2 mL min^{-1}. Separations on the UPLC-MS system were performed using a Waters Acquity UPLC BEH 1.7 μm 2.1 x 50 mm column (C-18) at a flow rate of 0.6 mL min^{-1}. Separations were performed using a mobile phase of 0.1% formic acid in water (Solvent A) and 0.1% formic acid in acetonitrile (Solvent B). Circular

dichroism spectra were obtained on a JASCO J-815 circular dichroism spectrometer.

Analytical HPLC was performed on either a Waters Acquity UPLC system equipped with PDA eλ detector (λ = 210 – 400 nm), Sample Manager FAN and Quaternary Solvent Manager (H-class) modules or a Waters System 2695 separations module with a 2996 photodiode array detector. Peptides were analysed using a Waters Sunfire 5 μm, 2.1 x 150 mm column (C-18) or a Sunfire 5 μm, 2.1 x 150 mm wide-pore column (C-18) at a flow rate of 0.2 mL min^{-1} on the HPLC system or Waters Acquity UPLC BEH 1.7 μm 2.1 x 50 mm column (C-18) at a flow rate of 0.6 mL min^{-1} on the UPLC system. Both instruments were run using a mobile phase composed of 0.1% trifluoroacetic acid in H_2O (Solvent A) and 0.1% trifluoroacetic acid in acetonitrile (Solvent B). The analysis of the chromatograms was conducted using Empower 3 Pro software (2010).

Preparative reverse-phase HPLC was performed using a Waters 600 Multisolvent Delivery System and Waters 500 pump with 2996 photodiode array detector or Waters 490E Programmable wavelength detector operating at 230 and 280 nm. Peptides were purified on a Waters Sunfire 5 μm (C-18) preparative column operating at a flow rate of 7 mL min^{-1} or the wide-pore equivalent using a mobile phase of 0.1% trifluoroacetic acid in water (Solvent A) and 0.1% trifluoroacetic in acetonitrile (Solvent B).

Solid Phase Peptide Synthesis (SPPS)

Preloading Rink Amide resin (for side chain anchoring Fmoc-Glu-OAll, Fmoc-Asp-OAll, Fmoc-GluAla-OAll, Fmoc-GluPhe-OAll, Fmoc-GluLeu-OAll): Rink amide resin was initially washed with CH_2Cl_2 (5 × 3 mL) and DMF (5 × 3 mL), followed by Fmoc deprotection with 20% piperidine/DMF (2 × 5 min). The resin was washed with DMF (5 × 3 mL), CH_2Cl_2 (5 × 3 mL) and DMF (5 × 3 mL). PyBOP (4 eq.) and NMM (8 eq.) were added to a solution of Fmoc-AA(OH)-OAll (4 eq.) in DMF. After 5 min of pre-activation, the mixture was added to the resin. After 2 h the resin was washed with DMF (5 × 3 mL), CH_2Cl_2 (5 × 3 mL) and DMF (5 × 3 mL), capped with acetic anhydride/pyridine (1:9 v/v) (2 × 3 min) and washed with DMF (5 × 3 mL), CH_2Cl_2 (5 × 3 mL) and DMF (5 × 3 mL).

Preloading Wang Resin (for side chain anchoring Fmoc-Tyr-OAll, Fmoc-Ser-OAll, Fmoc-TyrAla-OAll, Fmoc-TyrPhe-OAll, Fmoc-TyrLeu-OAll): Wang resin was swollen in dry CH_2Cl_2 for 30 min and then washed with CH_2Cl_2 (5 x 3 mL). Fmoc-AA(OH)-OAll (1 eq.) and triphenylphosphine (1.1 eq.) were dissolved in CH_2Cl_2 and the solution was added to the resin. A solution of diisopropyl azodicarboxylate (1.1 eq.) was diluted 5 fold in CH_2Cl_2 and added dropwise to the resin at 0 ^oC. The resin was shaken at rt for 16 h, and then washed with CH_2Cl_2 (5 × 3 mL), DMF (5 × 3 mL), and CH_2Cl_2 (5 × 3 mL).

Preloading 2-chloro-trityl chloride resin (for side chain anchoring Fmoc-SerAla-OAll, Fmoc-SerPhe-OAll, Fmoc-SerLeu-OAll, Fmoc-GluGly-OAll): 2-chloro-trityl chloride resin (1.22 mmol/g loading) was swollen in dry CH_2Cl_2 for 30 min then washed with CH_2Cl_2 (5 × 3 mL). A solution of Fmoc-AA-OH (0.5 eq. relative to resin functionalisation) and iPr_2NEt (2.0 eq. relative to resin functionalisation) in CH_2Cl_2 (final amino acid concentration 0.1 M of amino acid) was added and the resin was shaken at rt for 16 h. The resin was washed with DMF (5 × 3 mL) and CH_2Cl_2 (5 × 3

mL). The resin was treated with a solution of CH_2Cl_2/CH_3OH/*i*Pr_2NEt (17:2:1 v/v/v, 3 mL) for 1 h and washed with DMF (5 × 3 mL), CH_2Cl_2 (5 × 3 mL), and DMF (5 × 3 mL).

Estimation of amino acid loading: The resin was treated with 20% piperidine/DMF (2 x 3 mL, 3 min) and 50 µL of the combined deprotection solution was diluted to 10 mL using 20% piperidine/DMF in a volumetric flask. The UV absorbance of the resulting piperidine-fulvene adduct was measured (λ = 301 nm, ε = 7800 M^{-1} cm^{-1}) to estimate the amount of amino acid loaded onto the resin.

Iterative Peptide Assembly

General amino acid coupling: A solution of protected amino acid (4 eq.), PyBOP (4 eq.) and NMM (8 eq.) in DMF (final amino acid concentration 0.1 M) was added to the resin. After 1 h, the resin was washed with DMF (5 × 3 mL), CH_2Cl_2 (5 × 3 mL) and DMF (5 × 3 mL).

Deprotection: The resin was treated with 20% piperidine/DMF (2 x 3 mL, 3 min) and washed with DMF (5 × 3 mL), CH_2Cl_2 (5 × 3 mL) and DMF (5 × 3 mL).

Capping: Acetic anhydride/pyridine (1:9 v/v) was added to the resin (3 mL). After 3 min the resin was washed with DMF (5 × 3 mL), CH_2Cl_2 (5 × 3 mL) and DMF (5 × 3 mL).

On-Resin Selenoester Formation Procedure:

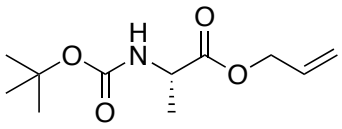
General procedure for the direct selenoesterification on solid phase: 25 µmol of resin was swollen in dry CH_2Cl_2 (5 mL) for 30 min, followed by the addition of a solution of $Pd(PPh_3)_4$ (25 mg, 22 µmol) and $PhSiH_3$ (123 µL, 1 mmol) in dry CH_2Cl_2 (2 mL). The resin was shaken for 1 h and the procedure was repeated. Afterwards, the resin was washed with CH_2Cl_2 (10 x 5 mL), DMF (5 x 5 mL) and CH_2Cl_2 (5 x 5 mL). A solution of diphenyldiselenide (DPDS) (30 eq.) and tri-*n*-butylphosphine (30 eq.) in DMF (2-3 mL) was added to the resin. The resin was shaken at rt, 0 ^oC, or -12 ^oC (as specified for each peptide) for 3 h. Afterwards, the resin was washed with CH_2Cl_2 (10 x 5 mL), DMF (5 x 5 mL) and CH_2Cl_2 (5 x 5 mL). Cleavage: A mixture of TFA : triisopropylsilane : water (90:5:5 v/v/v) was added. After 2 h, the resin was washed with TFA (2 x 2 mL) Work-up: The combined solutions were concentrated under a stream of nitrogen. The residue was dissolved in water containing 30% MeCN + 0.1% TFA, purified by preparative HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired peptide selenoester.

Initial Resin Loadings

Resin Number	Ac-LYRANX-Resin X =	Resin type	Resin Loading (mmol/g)
R1	Q	Rink Amide	0.40
R2	N	Rink Amide	0.46
R3	S	Wang	0.20
R4	Y	Wang	0.46
R5	QA	Rink Amide	0.41
R6	QF	Rink Amide	0.43
R7	QL	Rink Amide	0.27
R8	YA	Wang	0.23
R9	YF	Wang	0.26
R10	YL	Wang	0.27
R11	SA	2-CTC	0.31
R12	SF	2-CTC	0.30
R13	SL	2-CTC	0.28
R14	EG	2-CTC	0.61

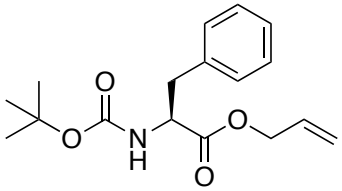
Dipeptide Synthesis

Boc-Ala-OAll



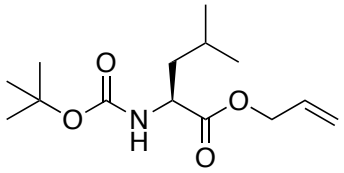
Boc-protected alanine (566 mg, 3.0 mmol) was dissolved in DMF (10 mL) and cooled to 0 ^{o}C in an ice-bath. $^{i}Pr_2NEt$ (1.57 mL, 9 mmol) was added slowly, followed by allyl bromide (280 µL, 3.3 mmol). The solution was allowed to warm to room temperature, and was left to stir for 16 h. The reaction mixture was diluted with EtOAc (40 mL) and then washed with water (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified via flash column chromatography; R_f = 0.4 (EtOAc/hexane: 1:2 v/v). Yield (685 mg, 99%). ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 5.92 (ddt, *J* = 5.7, 11.0, 16.2 Hz, 1H), 5.33, (dq, *J* = 2.0, 17.3 Hz, 1H), 5.25 (dd, *J* = 2.0, 10.5 Hz, 1H), 4.64 (t, *J* = 5.1 Hz, 1H), 1.45 (s, 9H), 1.40 (d, *J* = 7.2 Hz, 3H). ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 172.0, 154.0, 130.6, 117.6, 78.8, 64.8, 48.3, 27.3, 17.7. These data are in agreement with those previously reported by Lang *et al*.[1]

Boc-Phe-OAll



Boc-protected phenylalanine (799 mg, 3.0 mmol) was dissolved in DMF (10 mL) and cooled to 0 ^{o}C in an ice-bath. $^{i}Pr_2NEt$ (1.57 mL, 9 mmol) was added slowly, followed by allyl bromide (280 µL, 3.3 mmol). The solution was allowed to warm to room temperature, and was left to stir for 16 h. The reaction mixture was diluted with EtOAc (40 mL) and then washed with water (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified via flash column chromatography; R_f = 0.35 (EtOAc/hexane: 1:2 v/v). Yield (905 mg, 99%). ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.33-7.13 (m, 5H), 5.88 (ddt, *J* = 5.7, 11.0, 16.2 Hz, 1H), 5.32 (dq, *J* = 2.0, 17.3 Hz, 1H), 5.26 (dd, *J* = 2.0, 10.5 Hz, 1H), 4.62 (dt, *J* = 1.5, 6.0 Hz, 2H), 3.18-3.05 (m, 2H), 1.44 (s, 9H). ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 171.6, 155.1, 135.9, 131.5, 129.4, 128.5, 127.2, 118.9, 79.9, 65.9, 54.5, 38.4, 28.3. These data are in agreement with those previously reported by Lang *et al*.[1]

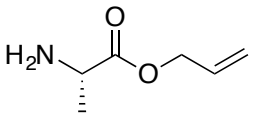
Boc-Leu-OAll



Boc-protected leucine (693 mg, 3.0 mmol) was dissolved in DMF (10 mL) and cooled to 0 ^{o}C in an ice-bath. $^{i}Pr_2NEt$ (1.57 mL, 9 mmol) was added slowly, followed by allyl bromide (280 µL, 3.3 mmol). The solution was allowed to warm to room temperature, and was left to stir for 16 h. The reaction mixture was diluted with EtOAc (40 mL)

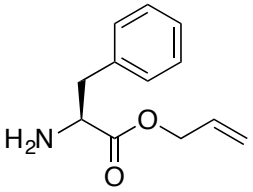
and then washed with water (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified via flash column chromatography; R_f = 0.33 (EtOAc/hexane: 1:2 v/v). Yield (799 mg, 98%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 5.89 (ddt, *J* = 5.7, 11.0, 16.2 Hz, 1H), 5.39-5.26 (m, 2H), 4.67 (d, *J* = 5.3 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 1H), 1.80 (m 2H), 0.96 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 173.2, 155.4, 131.7, 118.5, 79.8, 65.7, 52.1, 41.8, 28.3, 24.7, 22.8, 21.8. These data are in agreement with those previously reported by Lang *et al*.[1]

H-Ala-OAll



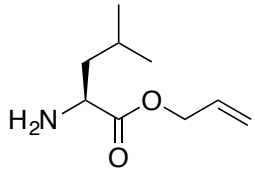
Boc alanine-allylester (655 mg, 2.86 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was removed under a gentle stream of nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$ and then concentrated in *vacuo* to afford a yellow oil. Yield (351 mg, 95%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 5.79 (ddt, *J* = 5.7, 11.0, 16.2 Hz, 1H), 5.25, (dq, *J* = 2.0, 17.3 Hz, 1H), 5.58 (t, *J* = 5.5 Hz, 2H), (dd, *J* = 7.2, 14.7 Hz, 1H), 1.51 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 169.9, 130.5, 119.7, 67.2, 49.2, 15.6. These data are in agreement with those previously reported by Treder *et al*.[2]

H-Phe-OAll



Boc phenylalanine-allylester (885 mg, 2.90 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was removed under a gentle stream of nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$ and then concentrated in *vacuo* to afford a yellow oil. Yield (592 mg, 99%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.27-7.07 (m, 5H), 5.70 (ddt, *J* = 5.7, 11.0, 16.2 Hz, 1H), 5.20-5.16 (m, 2H), 4.49 (d, *J* = 6.1 Hz, 2H), 4.20 (t, *J* = 7.0 Hz, 1H), 3.24-3.11 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 168.6, 132.9, 130.2, 129.3, 128.2, 120.2, 67.4, 54.3, 36.2. These data are in agreement with those previously reported by Lang *et al*.[1]

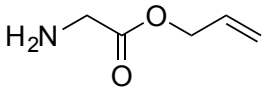
H-Leu-OAll



Boc leucine-allylester (769 mg, 2.83 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1

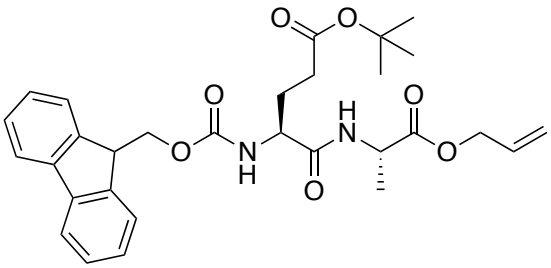
h, after which the TFA/CH_2Cl_2 solvent mixture was removed under a gentle stream of nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$ and then concentrated in *vacuo* to afford a yellow oil. Yield (454 mg, 94%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 5.80 (ddt, *J* = 5.7, 11.0, 16.2 Hz, 1H), 5.30-5.20 (m, 2H), 4.63-4.53 (m, 2H), 3.95 (m, 1H) 1.72 (m, 2H), 0.90-0.86 (m, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 169.9, 130.5, 119.9, 67.2, 51.7, 39.5, 24.4, 21.9, 21.7. These data are in agreement with those previously reported by Treder *et al*.[2]

H-Gly-OAll



Boc-protected glycine (2.0 g, 11.4 mmol) was dissolved in DMF (40 mL) and cooled to 0 ^oC in an ice-bath. $^iPr_2NEt$ (6.0 mL, 34.2 mmol) was added slowly, followed by allyl bromide (1.1 mL, 12.6 mmol). The solution was allowed to warm to room temperature, and was left to stir for 16 h. The reaction mixture was diluted with EtOAc (120 mL) and then washed with water (2 x 60 mL) and brine (60 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was concentrated in *vacuo* to afford a yellow oil. Yield (1.30 g, quant). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ (ppm): 5.90 (ddt, *J* = 5.9, 10.8, 16.7 Hz, 1H), 5.25, (m, 2H), 4.69 (d, *J* = 5.7 Hz, 2H), 3.82 (s, 2H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ (ppm): 167.5, 130.6, 120.1, 67.2, 40.6. These data are in agreement with those previously reported by Imhof *et al.*[3]

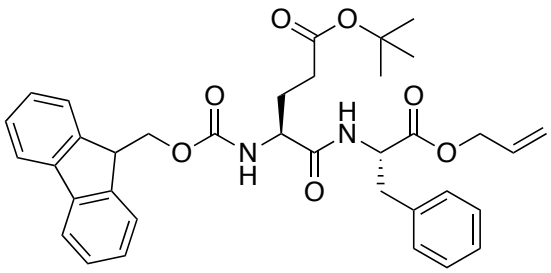
Fmoc-Glu(O*t*Bu)Ala-OAll



A solution of Fmoc-Glu(O*t*Bu)-OH (1.17 g, 2.7 mmol), HATU (1.04 mg, 2.7 mmol) and NMM (1 mL, 9.2 mmol) in DMF (final amino acid concentration 0.1 M) was added to a reaction vessel containing alanine-allylester (330 mg, 2.3 mmol). The reaction was stirred for 2 h, after which the solvent was removed under a stream of nitrogen. The residue was dissolved into CH_2Cl_2, washed with water (2 x 30 mL), 2 M HCl (20 mL), saturated aqueous $NaHCO_3$ solution (20 mL), and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.4 (EtOAc/hexane: 3:7). Yield (1.01 g, 83%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.67 (d, *J* = 8 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.3 (dd, *J* = 7.2, 7.5 Hz, 2H), 7.2 (dd, *J* = 1.0, 7.5 Hz, 2H), 6.87 (d, *J* = 6.7 Hz, 1H), 5.81 (ddt, *J* = 6.0, 11.2, 16 Hz, 1H), 5.69 (d, *J* = 7.7 Hz, 1H), 5.24 (d, *J* = 17.1 Hz, 1H), 5.16 (d, *J* = 10 Hz, H), 4.55-4.47 (m, 3H), 4.29 (d, *J* = 7.0 Hz, 2H),

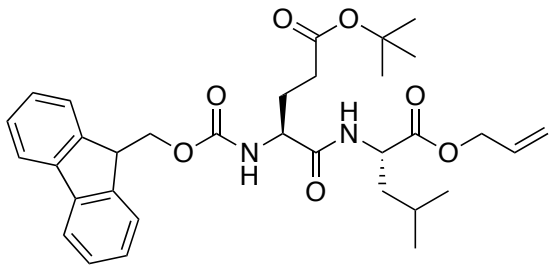
4.20 (q, *J* = 7.2 Hz, 1H), 4.12 (dd, *J* = 7.2, 7.8 Hz, 1H), 2.34 (m, 2H), 2.05-1.84 (m, 2H), 1.38 (s, 9H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 172.9, 172.2, 170.9, 156.1, 143.8, 141.3, 131.5, 127.7, 127.0, 125.1, 119.9, 118.8, 81.1, 67.1, 65.9, 53.9, 48.3, 47.1, 31.5, 28.5, 18.1; **HRMS**: (+ESI) Calc. for 559.2415 $[M+Na]^+$, Found: 559.2409 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3310, 3066, 2924, 2853, 2976, 1727, 1661, 1535, 1450, 1367, 1247, 1202, 1150, 1048, 740, 759 cm^{-1}; **[α]$_D$**: -5.4^o (c 1.0, CH_2Cl_2).

Fmoc-Glu(O*t*Bu)Phe-OAll



A solution of Fmoc-Glu(O*t*Bu)-OH (1.20 g, 2.8 mmol), HATU (1.06 mg, 2.8 mmol) and NMM (1 mL, 9.2 mmol) in DMF (final amino acid concentration 0.1 M) was added to a reaction vessel containing phenylalanine-allylester (513 mg, 2.5 mmol). The reaction was stirred for 2 h, after which the solvent was removed under a stream of nitrogen. The residue was dissolved into CH_2Cl_2, washed with water (2 x 30 mL), 2 M HCl (20 mL), saturated aqueous $NaHCO_3$ solution (20 mL), and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.45 (EtOAc/hexane: 3:7). Yield (1.20 g, 78%). ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.67 (d, *J* = 8 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.3 (dd, *J* = 7.2, 7.5 Hz, 2H), 7.2 (dd, *J* = 1.0, 7.5 Hz, 2H), 6.87 (d, *J* = 6.7 Hz, 1H), 5.81 (ddt, *J* = 6.0, 11.2, 16 Hz, 1H), 5.69 (d, *J* = 7.7 Hz, 1H), 5.24 (d, *J* = 17.1 Hz, 1H), 5.16 (d, *J* = 10 Hz, H), 4.55-4.47 (m, 3H), 4.29 (d, *J* = 7.0 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 1H), 4.12 (dd, *J* = 7.2, 7.8 Hz, 1H), 2.34 (m, 2H), 2.05-1.84 (m, 2H), 1.38 (s, 9H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 172.9, 172.2, 170.9, 156.1, 143.8, 141.3, 131.5, 127.7, 127.0, 125.1, 119.9, 118.8, 81.1, 67.1, 65.9, 53.9, 48.3, 47.1, 31.5, 28.5, 18.1; **HRMS**: (+ESI) Calc. for 635.2728 $[M+Na]^+$, Found: 635.2722 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3306, 2924, 2853, 1728, 1662, 1533, 1450, 1367, 1249, 1154, 740 cm^{-1}; **[α]$_D$**: +6.25^o (c 1.0, CH_2Cl_2).

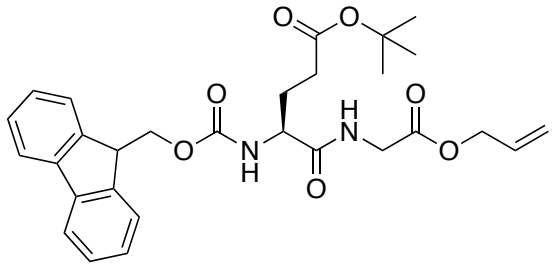
Fmoc-Glu(O*t*Bu)Leu-OAll



A solution of Fmoc-Glu(O*t*Bu)-OH (1.20 g, 2.8 mmol), HATU (1.06 mg, 2.8 mmol) and NMM (1 mL, 9.2 mmol) in DMF (final amino acid concentration 0.1 M) was added to a reaction vessel containing leucine-allylester (445 mg, 2.6 mmol). The

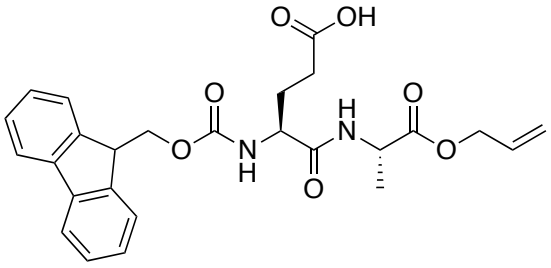
reaction was stirred for 2 h, after which the solvent was removed under a stream of nitrogen. The residue was dissolved into CH_2Cl_2, washed with water (2 x 30 mL), 2 M HCl (20 mL), saturated aqueous $NaHCO_3$ solution (20 mL), and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.43 (EtOAc/hexane: 3:7). Yield (1.34 g, 89%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.66 (d, *J* = 7.7 Hz, 2H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.29 (dd, *J* = 7.5, 7.7 Hz, 2H), 7.20 (dd, *J* = 7.5, 7.7 Hz, 2H), 6.85 (m, 1H), 5.77 (m, 2H), 5.23 (d, *J* = 17.4 Hz, 1H), 5.14 (d, *J* = 10.5 Hz, 1H), 4.52 (m, 3H), 4.27 (d, *J* = Hz, H), 4.28-4.22 (m, 3H), 4.11 (dd, *J* = 7.0, 7.3 Hz, 1H), 2.35-2.32 (m, 2H), 2.01-1.88 (m, 2H) 1.60-1.47 (m, 1H), 1.37 (s, 9H), 0.83 (d, *J* = 6.0 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 172.0, 171.2, 170.0, 155.1, 142.8, 142.7, 140.3, 130.5, 126.7, 126.0, 124.1, 118.9, 117.7, 80.0, 66.1, 64.7, 52.8, 50.0, 46.0, 40.1, 30.6, 27.0, 23.8, 21.7, 20.8; **HRMS**: (+ESI) Calc. for 601.2884 $[M+Na]^+$, Found: 601.2884 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3309, 3067, 2958, 2926, 1729, 1661, 1535, 1450, 1367, 1248, 1151, 1049, 759, 740 cm^{-1}; **$[\alpha]_D$**: -7.5^o (c 1.0, CH_2Cl_2).

Fmoc-Glu(O*t*Bu)Gly-OAll



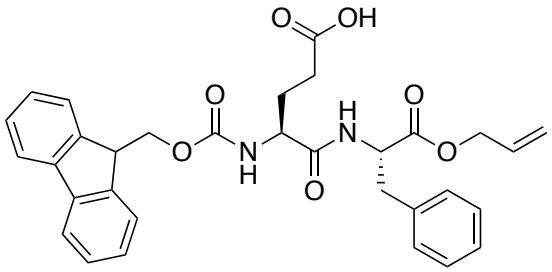
A solution of Fmoc-Glu(O*t*Bu)-OH (4.38 g, 10.3 mmol), HATU (3.92 g, 10.3 mmol) and NMM (4.6 mL, 41.2 mmol) in DMF (final amino acid concentration 0.1 M) was added to a reaction vessel containing glycine-allylester (1.30 g, 8.6 mmol). The reaction was stirred for 2 h, after which the solvent was removed under a stream of nitrogen. The residue was dissolved into CH_2Cl_2 (400 mL), washed with water (2 x 30 mL), 2 M HCl (200 mL), saturated aqueous $NaHCO_3$ solution (200 mL), and brine (300 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.16 (EtOAc/hexane: 1:3). Yield (2.93 g, 65%). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ (ppm): 7.76 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.4 (dd, *J* = 1.0, 7.2 Hz, 2H), 7.31 (dd, *J* = 1.0, 7.5 Hz, 2H), 5.87 (ddt, *J* = 6.0, 11.2, 16 Hz, 1H), 5.77 (d, *J* = 7.7 Hz, 1H), 5.33 (d, *J* = 17.7 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 4.65 (d, *J* = 5.4 Hz, 2H), 4.39 (d, *J* = 7.0 Hz, 2H), 4.27 (m, 1H), 4.24 (d, *J* = 7.5Hz, 1H), 4.07 (m, 1H), 2.40 (m, 2H), 2.05-1.94 (m, 2H), 1.46 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ (ppm): 175.5, 170.9, 168.2, 163.0, 142.8, 142.8, 140.3, 140.3, 132.0, 126.7, 126.7, 126.1, 126.1, 124.1, 124.1, 119.0, 118.1, 109.2, 82.3, 66.7, 65.1, 46.2, 46.1, 27.1 (x5), 13.4; **HRMS:** (+ESI) Calc. for 545.2264 $[M+Na]^+$, Found: 545.2258 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3314, 1726, 1532, 1450, 1154, 741cm^{-1}; **$[\alpha]_D$:** -7.7° (*c* 3.0, CH_2Cl_2);

Fmoc-GluAla-OAll (5)



The protected dipeptide (904 mg, 1.5 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was removed under a gentle stream of nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water (2 x 30 mL), saturated aqueous $NaHCO_3$ solution (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.32 (EtOAc/hexane: 1:2 v/v). Yield (655 mg, 91%). ^{1}**H NMR** (Acetone-d^6, 400 MHz) δ (ppm): 7.78 (d, *J* = 7.7 Hz, 2H), 7.66 (t, *J* = 6.4 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 5.92 (ddt, *J* = 5.5, 10.9, 16.5 Hz, 1H), 5.31 (d, *J* = 17.5 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 4.66-4.55 (m, 2H), 4.43 (q, *J* = 7.4 Hz, 1H), 4.36 (m, 2H), 4.25-4.15 (m, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.07 (ddd, *J* = 7.6, 13.8 Hz, 2H), 1.91 (ddd, *J* = 7.7, 15.2 Hz, 2H), 1.40 (d, *J* = 7.3 Hz, 6H); ^{13}**C NMR** (Acetone-d^6, 100 MHz) δ (ppm): 172.7, 172.2, 156.9, 143.9, 143.7, 141.2, 131.9, 127.4, 126.8, 124.8, 119.5, 117.3, 66.6, 65.4, 54.0, 29.7, 27.3, 15.8; **HRMS**: (+ESI) Calc. for 503.1789 $[M+Na]^+$, Found: 503.1783 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3305, 3060, 2915, 2866, 1719, 1659, 1534, 1451, 1367, 1249, 1202, 1150, 1046, 741 cm^{-1}; $[\alpha]_D$: -16^o (c 1.0, CH_2Cl_2).

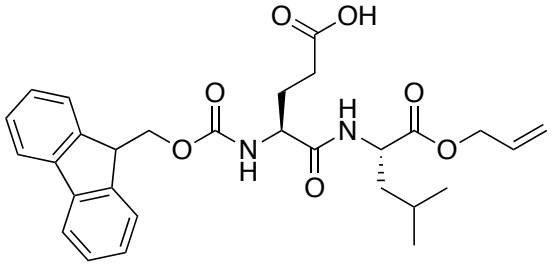
Fmoc-GluPhe-OAll (6)



The protected dipeptide (918 mg, 1.5 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/ CH_2Cl_2 solvent mixture was removed under a gentle stream of nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water (2 x 30 mL), saturated aqueous $NaHCO_3$ solution (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.41 (EtOAc/hexane: 1:2 v/v). Yield (767 mg, 92%). ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.75 (d, *J* = 7.4 Hz, 2H), 7.57 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 (m, 6H), 6.98 (d, *J* = 7.8 Hz, 1H), 5.82 (ddt, *J* = 5.5, 10.9, 16.5 Hz, 1H), 5.70 (d, *J* = 8.1 Hz, 1H), 5.27 (d, *J* = 17.5 Hz, 1H), 5.22 (d, *J* = 10.5 Hz, 1H), 4.86 (m, 1H), 4.57 (m, 2H), 4.42-4.28 (m,

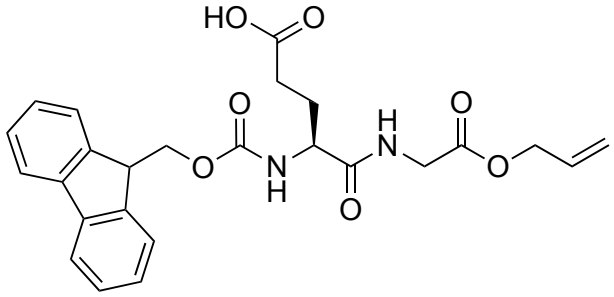
3H), 4.18 (t, *J* = 7.0 Hz, 1H), 3.15 (dd, *J* = 5.8, 14.0 Hz, 1H), 3.05 (d, *J* = 6.7, 14.3 Hz, 1H), 2.44 (m, 2H), 2.07 (m, 1H), 1.93 (p, *J* = 7.5 Hz, 1H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 175.8, 171.1, 156.3, 143.7, 141.3, 135.6, 131.3, 129.2, 128.5, 127.7, 127.1, 127.1, 125.1, 119.9, 119.1, 67.3, 66.2, 53.6, 47.1, 37.8, 30.9, 29.5, 28.0; **HRMS**: (+ESI) Calc. for 579.2102 $[M+Na]^+$, Found: 579.2098 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3299, 3064, 3031, 2924, 2854, 1710, 1661, 1531, 1449, 1248, 1210, 1049, 738, 700 cm^{-1}; **[α]$_D$**: +10^o (c 1.0, CH_2Cl_2).

Fmoc-GluLeu-OAll (7)



The protected dipeptide (1.10 g, 1.9 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was removed under a gentle stream of nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water (2 x 30 mL), saturated aqueous $NaHCO_3$ solution (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.38 (EtOAc/hexane: 1:1). Yield (882 mg, 89%). ^{1}**H NMR** (Acetone-d^6, 400 MHz) δ (ppm): 7. 73 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.27 (m, 2H), 7.15 (d, *J* = 7.7 Hz, 1H), 6.03 (d, *J* = 8.4 Hz, 1H), 5.87 (ddt, *J* = 5.8, 10.9, 16.4 Hz, 1H), 5.30 (d, *J* = 14.3 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H), 4.63-4.53 (m, 2H), 4.52-4.28 (m, 3H), 4.21-4.14 (m, 1H), 2.51 (t, *J* = 6.8 Hz, 2H), 2.13 (p, *J* = 6.7 Hz, 1H), 1.98 (p, *J* = 6.7 Hz, 1H), 1.69-1.52 (m, 2H), 0.87 (d, *J* = 5.8 Hz, 6H); ^{13}**C NMR** (Acetone-d^6, 100 MHz) δ (ppm): 176.4, 172.2, 171.7, 156.5, 143.6, 141.3, 131.5, 127.7, 127.1, 125.1, 119.9, 118.8, 67.5, 65.9, 53.5, 51.1, 47.0, 40.8, 29.6, 28.2, 24.8, 22.7, 21.7; **HRMS**: (+ESI) Calc. for 545.2258 $[M+Na]^+$, Found: 545.2258 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3310, 3078, 2957, 1712, 1660, 1536, 1449, 1250, 1051, 739 cm^{-1}; **[α]$_D$**: -11^o (c 1.0, CH_2Cl_2).

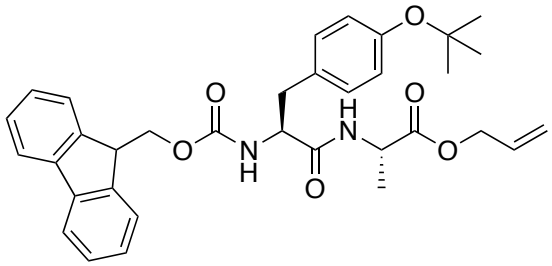
Fmoc-GluGly-OAll



The protected dipeptide (2.93 mg, 5.6 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (16 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was concentrated in *vacuo*. Azeotroping with toluene afforded the desired product as a yellow oil. Yield (2.50 g,

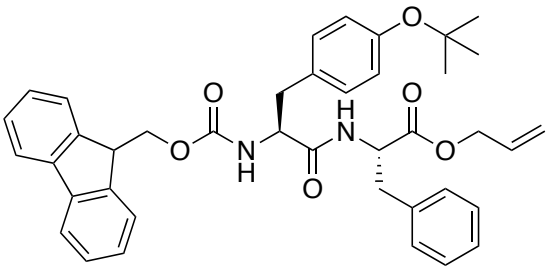
96%). ^{1}**H NMR** (DMSO, 500 MHz) δ (ppm): 7.80 (d, *J* = 7.5 Hz, 2H), 7.65 (t, *J* = 6.4 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 8.7 Hz, 2H), 5.92 (ddt, *J* = 5.5, 10.9, 16.5 Hz, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 5.22 (d, *J* = 9.9 Hz, 1H), 4.62 (m, 2H), 4.39 (m, 2H), 4.21 (m, 2H), 3.98 (q, *J* = 13.8 Hz, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 2.14 (ddd, *J* = 7.6, 13.8 Hz, 2H), 1.92 (ddd, *J* = 7.7, 15.2 Hz, 2H); ^{13}**C NMR** (DMSO, 125 MHz) δ (ppm): 176.8, 174.9, 170.9, 158.1, 145.6, 145.5, 142.6, 142.5, 133.3, 128.8, 128.7, 128.2, 128.1, 126.3, 126.2, 121.0, 120.9, 118.7, 68.0, 66.8, 55.7, 47.2, 42.0, 31.1, 28.5; **HRMS:** (+ESI) Calc. for 489.1638 $[M+Na]^+$, Found: 489.1633 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3307, 3069, 2935, 1711, 1670, 1534, 1202, 741 cm^{-1}; **$[\alpha]_D$:** -4.3 (*c* 3.0, CH_2Cl_2);

Fmoc-Tyr(O*t*Bu)Ala-OAll



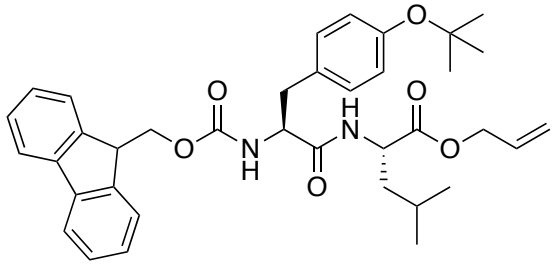
A solution of Fmoc-Tyr(O*t*Bu)-OH (1.51 g, 3.3 mmol), HATU (1.25 g, 3.3 mmol) and NMM (1.2 mL, 11 mmol) in DMF (final amino acid concentration 0.1 M) was added to a reaction vessel containing alanine-allylester (355 mg, 2.75 mmol). The reaction was stirred for 2 h, after which the solvent was removed under a stream of nitrogen. The residue was dissolved into CH_2Cl_2, washed with water (2 x 30 mL), 2 M HCl (20 mL), saturated aqueous $NaHCO_3$ solution (20 mL), and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.45 (EtOAc/hexane: 3:7). Yield (1.2 g, 76%). ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.65 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 2H), 5.79 (ddt, *J* = 5.8, 10.9, 16.8 Hz, 1H), 5.22 (d, *J* = 17.0 Hz, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 4.57-4.48 (m, 2H), 4.30 (d, *J* = 7.0 Hz, 1H), 4.13 (t, *J* = 7.0 Hz, 1H), 3.72 (m, 1H), 3.31 (t, *J* = 8.2 Hz, 1H), 1.34 (d, *J* = 7.1 Hz, 3H), 1.14 (s, 9H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 171.1, 168.9, 154.9, 142.8, 142.7, 140.2, 130.5, 126.6, 126.0, 124.2, 119.2, 117.0, 73.3, 66.1, 65.0, 64.8, 60.7, 53.1, 47.3, 46.1, 26.3, 17.4; **HRMS**: (+ESI) Calc. for 593.2628 $[M+Na]^+$, Found: 593.2627 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3288, 3063, 2926, 1645, 1511, 1473, 1259, 1164, 740 cm^{-1}; **$[\alpha]_D$**: +4^o (c 1.0, CH_2Cl_2).

Fmoc-Tyr(O*t*Bu)Phe-OAll



A solution of Fmoc-Tyr(O*t*Bu)-OH (1.23 g, 2.7 mmol), HATU (1.02 g, 2.7 mmol) and NMM (1 mL, 8.96 mmol) in DMF (final amino acid concentration 0.1 M) was added to a reaction vessel containing phenylalanine-allylester (459 mg, 2.24 mmol). The reaction was stirred for 2 h, after which the solvent was removed under a stream of nitrogen. The residue was dissolved into CH_2Cl_2, washed with water (2 x 30 mL), 2 M HCl (20 mL), saturated aqueous $NaHCO_3$ solution (20 mL), and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.55 (EtOAc/hexane: 1:2 v/v). Yield (1.10 g, 78%). ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.76 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.19 (m, 2H), 7.02 (m, 3H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.22, (m, 1H) 5.82 (ddt, *J* = 5.8, 10.9, 16.8 Hz, 1H), 5.30 (d, *J* = 17.3 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H), 4.78 (dd, *J* = 6.3, 12.6 Hz, 1H), 4.55 (m, 2H), 4.40 (m, 3H), 4.18 (t, *J* = 7.4 Hz, 1H), 3.10 (dd, *J* = 6.1, 13.9 Hz, 1H), 3.00 (dd, *J* = 6.1, 13.9 Hz, 2H), 1.31 (s, 9H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 169.5, 154.7, 153.5, 142.7, 140.3, 134.5, 130.3, 129.8, 128.8, 127.5, 126.7, 126.1, 126.0, 124.0, 123.2, 118.9, 118.1, 77.3, 66.1, 65.0, 55.0, 52.3, 46.1, 36.9, 28.6, 27.8; **HRMS**: (+ESI) Calc. for 669.2941 $[M+Na]^+$, Found: 669.2935 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3294, 3062, 3028, 2925, 2853, 1743, 1697, 1656, 1506, 1450, 1365, 1259, 1162, 1035, 740 cm^{-1}; $[\alpha]_D$: +9.7° (c 1.0, CH_2Cl_2).

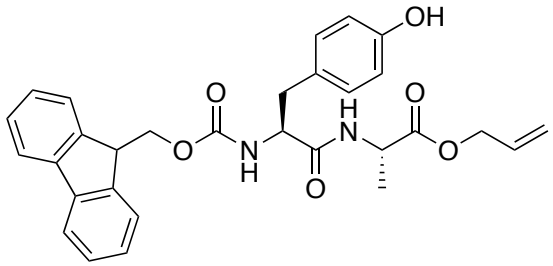
Fmoc-Tyr(O*t*Bu)Leu-OAll



A solution of Fmoc-Tyr(O*t*Bu)-OH (1.22 g, 2.6 mmol), HATU (1.03 g, 2.7 mmol) and NMM (1 mL, 8.96 mmol) in DMF (final amino acid concentration 0.1 M) was added to a reaction vessel containing leucine-allylester (379 mg, 2.2 mmol). The reaction was stirred for 2 h, after which the solvent was removed under a stream of nitrogen. The residue was dissolved into CH_2Cl_2, washed with water (2 x 30 mL), 2 M HCl (20 mL), saturated aqueous $NaHCO_3$ solution (20 mL), and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.48 (EtOAc/hexane: 1:2 v/v). Yield (998 mg, 74%). ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.71 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 6.6 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 5.86 (ddt, *J* = 5.8, 10.9, 16.8 Hz, 1H), 5.75 (m, 1H),

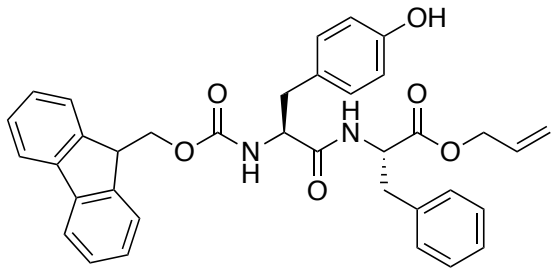
5.30 (d, *J* = 17.2 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 2H), 4.62-4.50 (m, 3H), 4.38 (dd, *J* = 7.4, 10.2 Hz, 1H), 4.24 (m, 1H), 4.14 (m, 1H), 3.02 (d, *J* = 5.7 Hz, 2H), 1.63 (m, 3H), 1.41 (s, 9H), 1.26 (d, *J* = 6.2 Hz, 6H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 172.1, 171.0, 156.0, 154.4, 143.8, 143.8, 141.3, 131.6, 129.9, 127.7, 127.1, 125.1, 124.1, 119.9, 118.7, 78.3, 67.2, 65.8, 56.1, 50.9, 47.1, 41.4, 38.0, 28.8, 24.8, 22.7, 21.9; **HRMS**: (+ESI) Calc. for 635.3097 $[M+Na]^+$, Found: 635.3097 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3291, 3066, 2957, 2926, 1744, 1655, 1542, 1506, 1449, 1365, 1238, 1160, 739 cm^{-1}; **$[\alpha]_D$:** -2.6° (c 1.0, CH_2Cl_2).

Fmoc-TyrAla-OAll (8)



The protected dipeptide (799 mg, 1.4 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was removed under a gentle stream of nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water (2 x 30 mL), saturated aqueous $NaHCO_3$ solution (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.26 (EtOAc/hexane: 1:2 v/v). Yield (668 mg, 93%). ^{1}**H NMR** (Acetone-d^6, 400 MHz) δ (ppm): 8.12 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.67-7.58 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 2H) 7.31 (t, *J* = 7.5 Hz, 2H), 7.11 (m, 2H), 6.74 (m, 2H), 6.51 (m, 1H), 5.93 (ddt, *J* = 5.8, 10.9, 16.8 Hz, 1H), 5.35 (dd, *J* = 17.3, 9.9 Hz, 1H), 5.30 (dd, *J* = 1.3, 9.9 Hz, 1H), 5.19 (t, *J* = 10.5 Hz, 1H), 4.63-4.56 (m, 2H), 4.49 , 4.52-4.14 (m, 5H), 3.07 (td, *J* = 4.8, 14.0 Hz, 1H), 2.85 (m, 1H), 1.38 (d, *J* = 7.3 Hz, 3H); ^{13}**C NMR** (Acetone-d^6, 100 MHz) δ (ppm): 172.8, 172.0, 156.9, 145.0, 142.1, 133.3, 131.3, 129.1, 129.0, 128.5, 127.9, 126.2, 126.1, 120.8, 118.1, 115.9, 67.2, 65.9, 57.2, 48.9, 47.9, 38.1, 17.9; **HRMS**: (+ESI) Calc. for 537.2002 $[M+Na]^+$, Found: 537.1999 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3293, 3065, 2927, 1655, 1514, 1448, 1260, 1042, 758, 736, 539 cm^{-1}; **$[\alpha]_D$**: +7° (c 1.0, CH_2Cl_2).

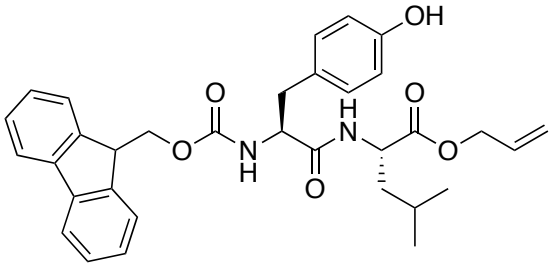
Fmoc-TyrPhe-OAll (9)



The protected dipeptide (906 mg, 1.4 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was removed under a gentle stream of

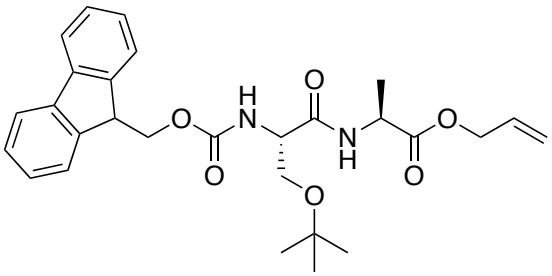
nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water (2 x 30 mL), saturated aqueous $NaHCO_3$ solution (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.35 (EtOAc/hexane: 1:2 v/v). Yield (793 mg, 96%). **^{1}H NMR** (Acetone-d^6, 400 MHz) δ (ppm): 8.21 (s, 1H), 7.78 (d, *J* = 7.7 Hz, 2H) 7.63 (dd, *J* = 7.4, 17.0 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.30-7.06 (m, 5H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.63 (d, *J* = 8.1 Hz, 1H), 5.93 (ddt, *J* = 5.8, 10.9, 16.8 Hz, 1H), 5.34 (d, *J* = 17.3 Hz, 1H), 5.22 (d, *J* = 17.3 Hz, 1H), 4.84 (m, 1H), 4.64 (d, *J* = 4.9 Hz, 2H), 4.53-4.44 (m, 1H), 4.40-4.32 (m, 1H), 4.26-4.18 (m, 1 2H), 3.023.23-2.85 (m, 5H); **^{13}C NMR** (Acetone-d^6, 100 MHz) δ (ppm): 171. 2, 170.7, 156.1, 155.9, 144.1, 141.2, 136.8, 132.2, 130.4, 129.3, 128.3, 127.6, 127.1, 126.7, 126.6, 125.3, 125.2, 119.9, 117.6, 115.1, 66.4, 65.3, 56.4, 53.7, 47.0, 37.4, 37.0. **HRMS**: (+ESI) Calc. for 613.2315 $[M+Na]^+$, Found: 613.2311 $[M+Na]^+$; **IR** (ATR): v_{max} = 3306, 3064, 2923, 2853, 1656, 1514, 1448, 1259, 1031, 803, 737, 700 cm^{-1}; **$[\alpha]_D$**: +14.4^o (c 1.0, CH_2Cl_2).

Fmoc-TyrLeu-OAll (10)



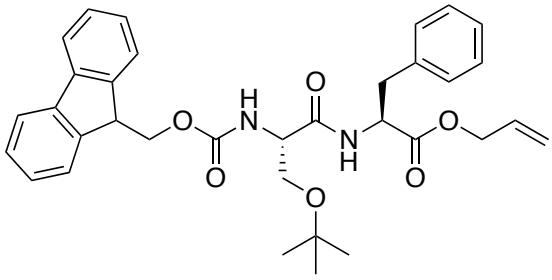
The protected dipeptide (920 mg, 1.5 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was removed under a gentle stream of nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water (2 x 30 mL), saturated aqueous $NaHCO_3$ solution (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.35 (EtOAc/hexane: 1:2 v/v). Yield (774 mg, 93%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.75 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.01 (m, 2H), 6.73 (d, *J* = 8.1 Hz, 2H), 6.26 (m, 1H), 5.92-5.80 (m, 1H), 5.38-5.23 (m, 2H), 4.61-4.50 (m, 3H), 4.45 (m, 2H), 4.20 (m, 1H), 3.05 (m, 2H), 1.62-1.32 (m, 2H), 0.90 (d, *J* = 6.2 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 172.0, 170.8, 155.0, 143.6, 141.3, 131.5, 130.5, 127.7, 127.1, 125.0, 120.0, 118.9, 115.6, 77.2, 67.2, 65.9, 51.0, 47.0, 41.5, 37.7, 24.7, 22.7, 21.9; **HRMS**: (+ESI) Calc. for 579.2471 $[M+Na]^+$, Found: 579.2477 $[M+Na]^+$; **IR** (ATR): v_{max} = 3287, 3063, 2955, 2931, 1657, 1520, 1449, 1363, 1239, 739, 700 cm^{-1}; **$[\alpha]_D$**: -4.3^o (c 1.0, CH_2Cl_2).

Fmoc-Ser(O*t*Bu)Ala-OAll



A solution of Fmoc-Ser(O*t*Bu)-OH (1.22 g, 2.6 mmol), HATU (1.03 g, 2.7 mmol) and NMM (1 mL, 8.96 mmol) in DMF (final amino acid concentration 0.1 M) was added to a reaction vessel containing alanine allylester (265 mg, 2.0 mmol). The reaction was stirred for 2 h, after which the solvent was removed under a stream of nitrogen. The residue was dissolved into CH_2Cl_2, washed with water (2 x 30 mL), 2 M HCl (20 mL), saturated aqueous $NaHCO_3$ solution (20 mL), and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.35 (EtOAc/hexane: 1:2 v/v). Yield (875 mg, 86%). ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.75 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 5.96-5.78 (m, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 4.67-4.58 (m, 3H) , 4.40 (d, *J* = 7.2 Hz, 2H), 4.31-4.20 (m, 2H), 3.85-3.78 (m, 1H), 3.44-3.37 (m, 1H), 1.44 (d, *J* = 7.2 Hz, 3H), 1.24 (s, 9H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 171.2, 168.9, 168.7, 155.0, 142.8, 140.3, 130.5, 126.6, 126.0, 124.1, 118.9, 117.6, 73.3, 66.1, 64.7, 60.7, 53.2, 47.3, 46.1, 26.4, 17.4; **HRMS**: (+ESI) Calc. for 517.2315 $[M+Na]^+$, Found: 517.2304 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3315, 3066, 2973, 2875, 1726, 1663, 1524, 1450, 1364, 1194, 1146, 1083, 759, 740, 621 cm^{-1}; $\mathbf{[\alpha]_D}$: +9.7^o (c 1.0, CH_2Cl_2).

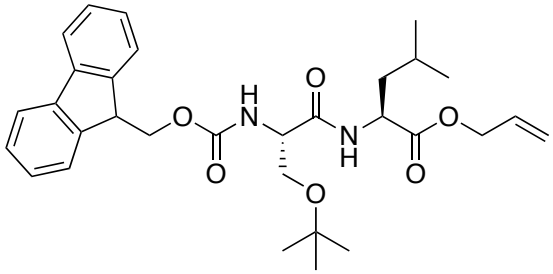
Fmoc-Ser(O*t*Bu)Phe-OAll



A solution of Fmoc-Ser(O*t*Bu)-OH (873 mg, 2.28 mmol), HATU (866 mg, 2.28 mmol) and NMM (0.83 mL, 7.6 mmol) in DMF (final amino acid concentration 0.1 M) was added to a reaction vessel containing phenylalanine-allylester (387 mg, 1.9 mmol). The reaction was stirred for 2 h, after which the solvent was removed under a stream of nitrogen. The residue was dissolved into CH_2Cl_2, washed with water (2 x 30 mL), 2 M HCl (20 mL), saturated aqueous $NaHCO_3$ solution (20 mL), and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.4 (EtOAc/hexane: 1:2 v/v). Yield (904 mg, 84%). ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.76 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.19-7.16 (m, 3H), 7.09-6.96 (m, 3H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.25-6.19 (m, 1H), 5.88 (m, 1H), 5.33-5.21 (m, 3H), 4.78 (q, *J* = 7.3 Hz, 1H), 4.59-4.53 (m, 2H), 4.43-4.26 (m, 3H),

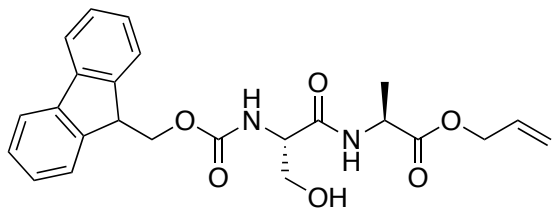
4.18 (t, *J* = 7.1 Hz, 1H), 3.12-2.91 (m, 4H), 1.31 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 170.7, 170.5, 154.6, 143.8, 141.4, 135.6, 131.5, 129.9, 129.4, 128.6 127.8, 127.3, 127.2, 125.2, 124.4, 120.1, 119.3 78.5, 77.3, 67.3, 66.2, 56.2, 53.5, 47.3, 38.1, 28.9; **HRMS**: (+ESI) Calc. for 593.2628 $[M+Na]^+$, Found: 593.2620 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3316, 3064, 2971, 2928, 1726, 1670, 1496, 1259, 1190, 1019, 796, 736, 700 cm^{-1}; **$[\alpha]_D$**: +24.1° (c 1.0, CH_2Cl_2).

Fmoc-Ser(O*t*Bu)Leu-OAll



A solution of Fmoc-Ser(O*t*Bu)-OH (919 mg, 2.4 mmol), HATU (911 mg, 2.4 mmol) and NMM (0.87, 8 mmol) in DMF (final amino acid concentration 0.1 M) was added to a reaction vessel containing leucine-allylester (338 mg, 2.0 mmol). The reaction was stirred for 2 h, after which the solvent was removed under a stream of nitrogen. The residue was dissolved into CH_2Cl_2, washed with water (2 x 30 mL), 2 M HCl (20 mL), saturated aqueous $NaHCO_3$ solution (20 mL), and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.4 (EtOAc/hexane: 1:2 v/v). Yield (945 mg, 89%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.71 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.07 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.92-5.70 (m, 2H), 5.29 (d, *J* = 17.4 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 4.62-4.46 (m, 3H), 4.38 (dd, *J* = 10.3, 7.6 Hz, 1H), 4.27-4.19 (m, 1H), 4.14 (t, *J* = 7.0 Hz, 1H), 3.05-2.96 (m, 2H), 1.64-1.38 (m, 3H), 1.26 (s, 9H), 0.84 (d, *J* = 6.4 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 172.1, 171.1, 156.0, 154.4, 143.8, 143.7, 141.3, 131.6, 131.2, 129.9, 127.7, 127.1, 125.2, 125.1, 124.2, 119.9, 118.7, 78.3, 77.5, 77.1, 76.8, 67.2, 65.8, 56.1, 50.9, 47.1, 41.4, 38.0, 28.8, 24.7, 22.7, 21.9, 21.0; **HRMS**: (+ESI) Calc. for 559.2784 $[M+Na]^+$, Found: 559.2773 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3314, 3066, 2958, 2927, 2871, 1735, 1666, 1527, 1450, 1364, 1193, 1085, 759, 740 cm^{-1}; **$[\alpha]_D$**: 1° (c 1.0, CH_2Cl_2).

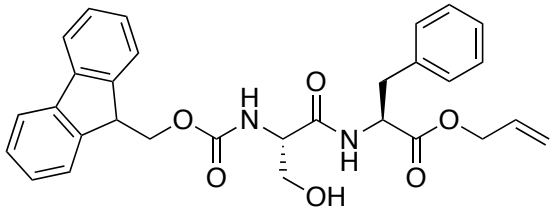
Fmoc-SerAla-OAll (11)



The protected dipeptide (751 mg, 1.5 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was removed under a gentle stream of nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water

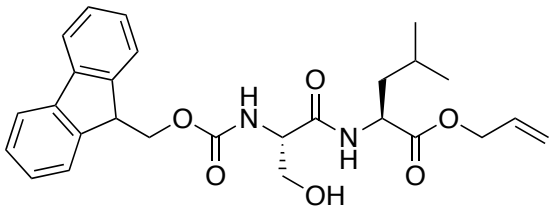
(2 x 30 mL), saturated aqueous $NaHCO_3$ solution (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.30 (EtOAc/hexane: 1:2 v/v). Yield (645 mg, 97%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.75 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.07 (m, 1H), 5.88 (ddt, *J* = 5.8, 10.9, 16.6 Hz, 1H), 5.34-5.20 (m, 2H), 4.67- 4.54 (m, 3H), 4.41 (m, 2H), 4.29 (m, 1H), 4.21 (m, 1H), 4.07 (m, 1H), 3.68 (d, *J* = 7.0 Hz, 1H), 1.42 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 172.6, 172.4, 170.7, 170.6, 156.5, 143.7, 141.3, 131.4, 127.8, 127.1, 125.0, 120.0, 118.9, 67.4, 66.2, 63.1, 55.4, 48.5, 47.1, 17.7; **HRMS**: (+ESI) Calc. for 461.1689 $[M+Na]^+$, Found: 461.1680 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3312, 2973, 2933, 2874, 1726, 1663, 1523, 1450, 1364, 1194, 1146, 1083, 759, 740 cm^{-1}; **$[\alpha]_D$**: 15^o (c 1.0, CH_2Cl_2).

Fmoc-SerPhe-OAll (12)



The protected dipeptide (846 mg, 1.5 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was removed under a gentle stream of nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water (2 x 30 mL), saturated aqueous $NaHCO_3$ solution (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.36 (EtOAc/hexane: 1:2 v/v). Yield (724 mg, 95%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.76 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 5.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.25-7.06 (m, 3H), 5.85 (m, 1H), 5.33-5.20 (m, 2H), 4.91-4.84 (m, 1H), 4.59 (m, 2H), 4.42-4.15 (m, 4H), 3.97 (m, 1H), 3.62 (m, 1H), 3.17 (dd, *J* = 5.6, 14.2 Hz, 1H), 3.05 (dd, *J* = 7.3, 14.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 171.1, 156.5, 143.7, 141.3, 135.6, 131.3, 129.2, 128.6, 127.8, 127.2, 127.1, 125.1, 120.0, 119.2, 67.4, 66.3, 62.9, 62.8, 55.4, 53.5, 53.3, 47.0, 37.7; **HRMS**: (+ESI) Calc. for 537.2002 $[M+Na]^+$, Found: 537.1993 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3302, 3064, 2923, 2853, 1729, 1650, 1530, 1449, 1261, 1018, 737, 699 cm^{-1}; **$[\alpha]_D$**: 3.8^o (c 1.0, CH_2Cl_2).

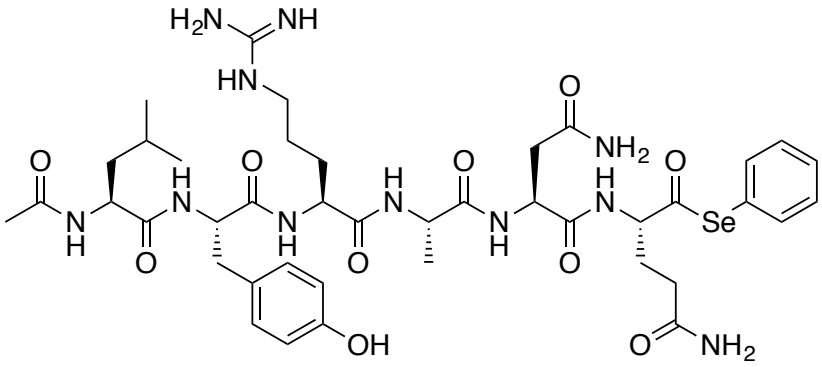
Fmoc-SerLeu-OAll (13)



The protected dipeptide (795 mg, 1.5 mmol) was treated with a 1:1 v/v mixture of TFA in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the TFA/CH_2Cl_2 solvent mixture was removed under a gentle stream of nitrogen. The reaction mixture was diluted into CH_2Cl_2 and then washed with water (2 x 30 mL), saturated aqueous $NaHCO_3$ solution (2 x 30 mL) and brine (30 mL). The organic phase was dried with anhydrous $MgSO_4$, concentrated in *vacuo*, and purified by flash column chromatography; R_f = 0.35 (EtOAc/hexane: 1:2 v/v). Yield (655 mg, 92%). ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.76 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 5.95-5.80 (m, 2H), 5.36-5.21 (m, 2H), 4.66-4.56 (m, 3H), 4.45-4.37 (m, 2H), 4.33-4.18 (m, 2H), 4.17-4.02 (m, 1H) , 3.71-3.62 (m, 1H), 1.71-1.52 (m, 3H), 0.92 (m, 6H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 171.6, 170.0, 155.6, 142.7, 140.3, 130.4, 126.7, 126.1, 124.0, 119.0, 118.0, 66.4, 65.2, 62.0, 50.2, 46.0, 39.8, 28.6, 23.9, 21.7, 20.6; **HRMS**: (+ESI) Calc. for 503.2158 $[M+Na]^+$, Found: 503.2147 $[M+Na]^+$; **IR** (ATR): ν_{max} = 3306, 3066, 2956, 2923, 1726, 1660, 1525, 1449, 1259, 1055, 798, 758, 738 cm^{-1}; $[\alpha]_D$: -4.5^o (c 10.0, CH_2Cl_2).

Synthesis of Model Peptide Selenoesters

Ac-LYRANQ-SePh (1)



Side chain anchored Ac-LYRANQ-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on Rink amide resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at room temperature and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (17.7 mg, 75% yield).

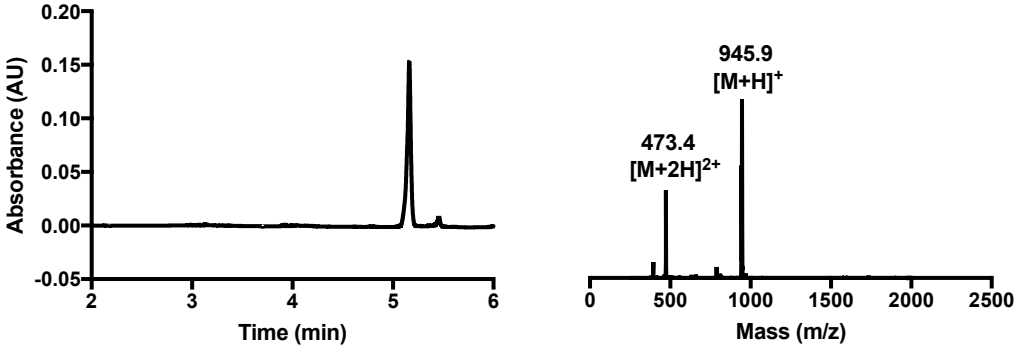
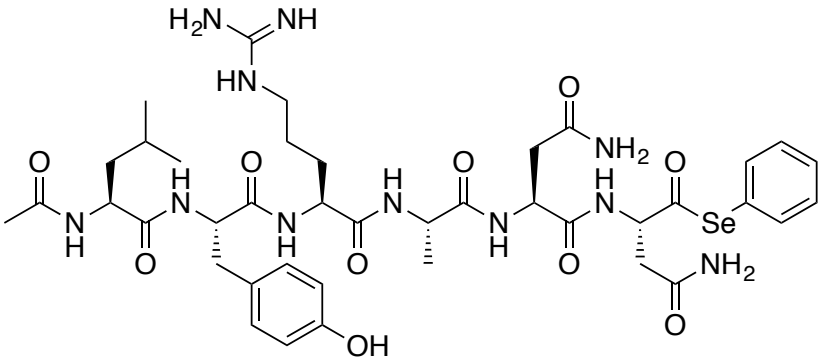


Figure S1. Analytical UPLC trace of HPLC purified Ac-LYRANQ-SePh (**1**); R_t 5.16 min (0-60% B over 5 min, λ = 230 nm); Calc. Mass $[M+H]^+$: 945.3, $[M+2H]^{2+}$: 473.2; Found; $[M+H]^+$: 945.9, $[M+2H]^{2+}$: 473.4.

Ac-LYRANN-SePh (2)



Side chain anchored Ac-LYRANN-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on Rink amide resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at room temperature and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (17.0 mg, 73% yield).

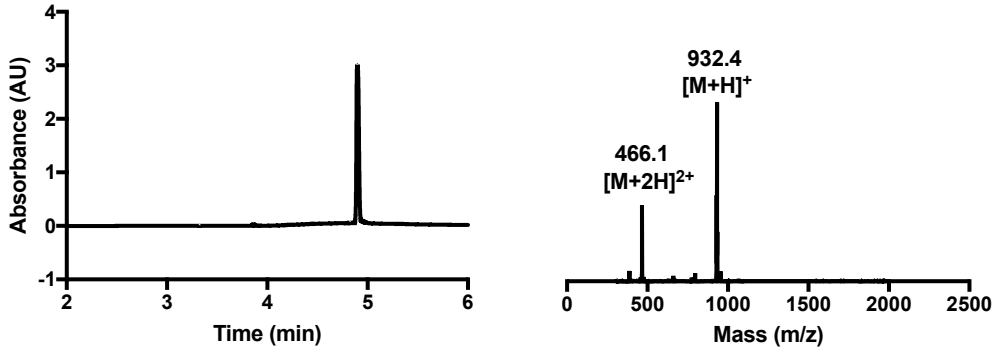
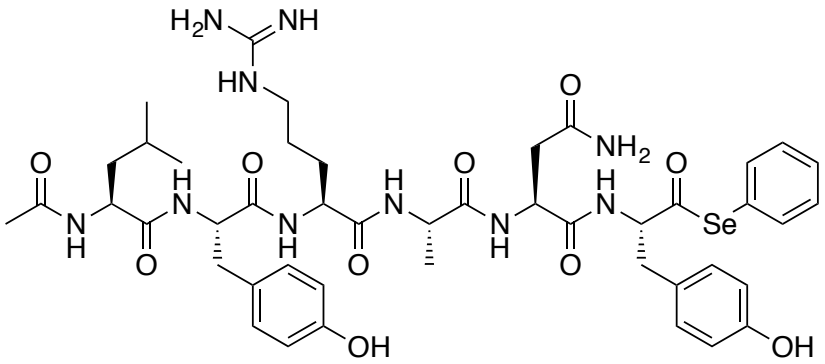


Figure S2. Analytical UPLC trace of HPLC purified Ac-LYRANN-SePh (**2**); R_t 4.90 min (0-60% B over 5 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 932.3, $[M+2H]^{2+}$: 466.7; Found; $[M+H]^+$: 932.4, $[M+2H]^{2+}$: 466.1.

Ac-LYRANY-SePh (3)



Side chain anchored Ac-LYRANY-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on Wang resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at room temperature and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (17.4 mg, 71% yield).

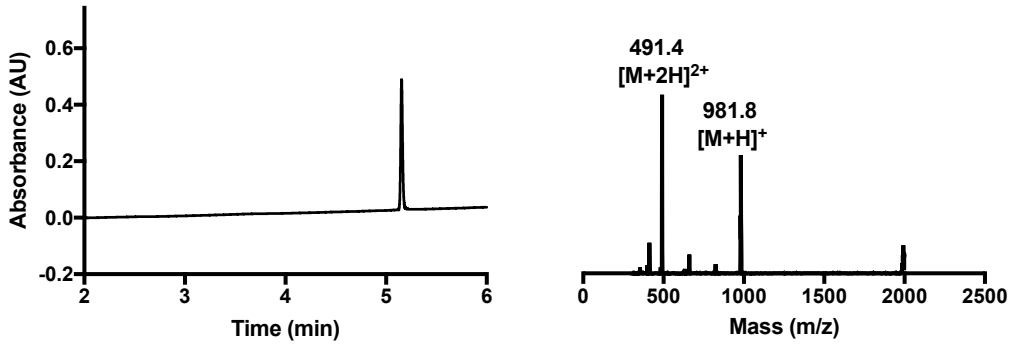
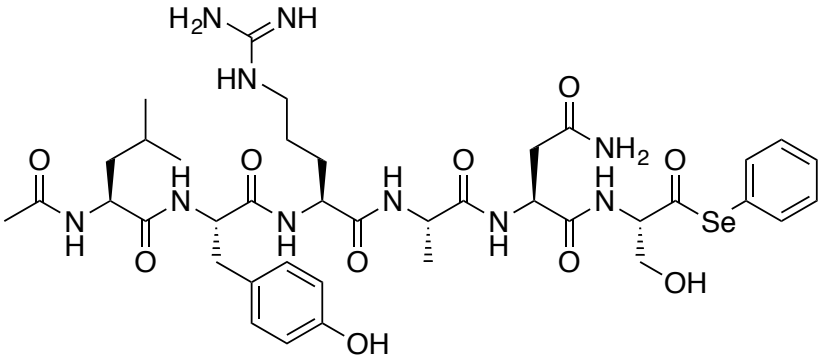


Figure S3. Analytical UPLC trace of HPLC purified Ac-LYRANY-SePh (**3**); R_t 5.15 min (0-60% B over 8 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 981.4, $[M+2H]^{2+}$: 491.2; Found; $[M+H]^+$: 981.8, $[M+2H]^{2+}$: 491.4.

Ac-LYRANS-SePh (4)



Side chain anchored Ac-LYRANS-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on Wang resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at room temperature and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (15.1 mg, 67% yield).

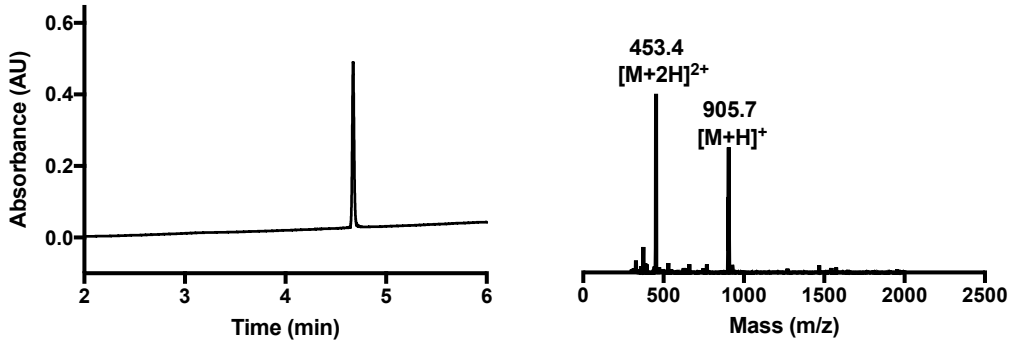
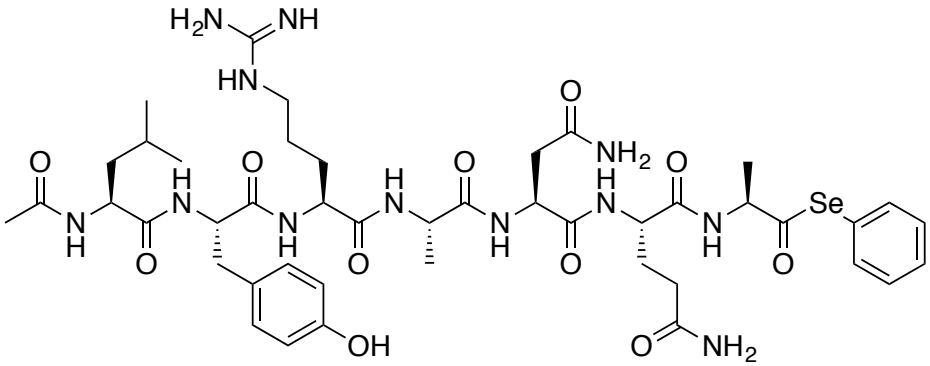


Figure S4. Analytical UPLC trace of HPLC purified Ac-LYRANS-SePh (**4**); R_t 4.67 min (0-60% B over 5 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 905.3, $[M+2H]^{2+}$: 453.2; Found; $[M+H]^+$: 905.7, $[M+2H]^{2+}$: 453.4.

Ac-LYRANQA-SePh (14)



Side chain anchored Ac-LYRANQA-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on Rink amide resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at 0 ^{o}C and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (17.7 mg, 70% yield).

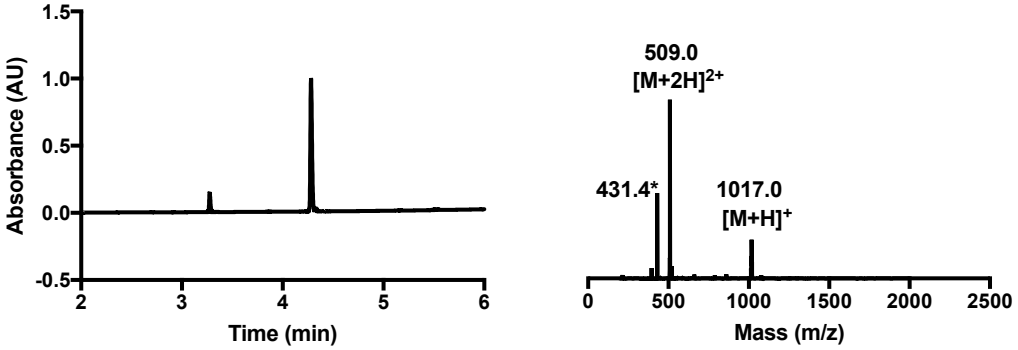
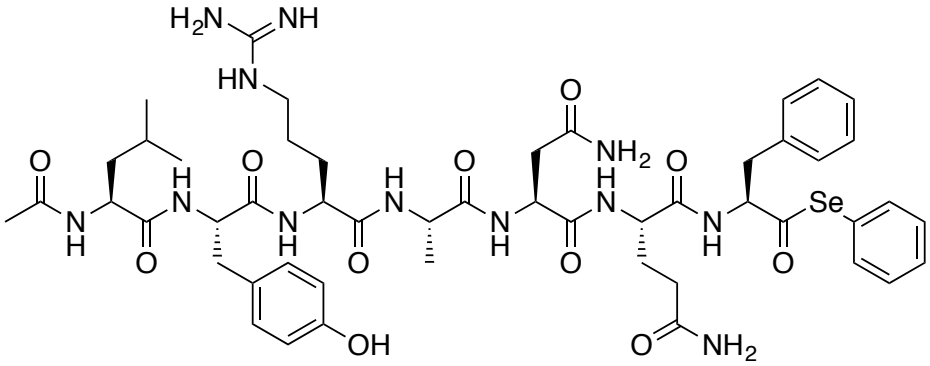


Figure S5. Analytical UPLC trace of HPLC purified Ac-LYRANQA-SePh (**14**); R_t 4.28 min (0-60% B over 5 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1017.4, $[M+2H]^{2+}$: 509.2; Found; $[M+H]^+$: 1017.0, $[M+2H]^{2+}$:509.0, *$[M(-SePh)+2H]^{2+}$: 431.4 (artefact ion).

Ac-LYRANQF-SePh (15)



Side chain anchored Ac-LYRANQF-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on Rink amide resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at 0 ^{o}C and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (17.1 mg, 63% yield).

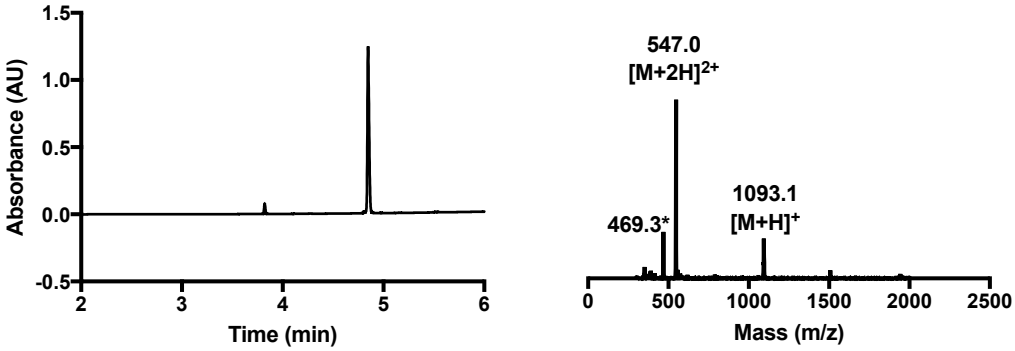
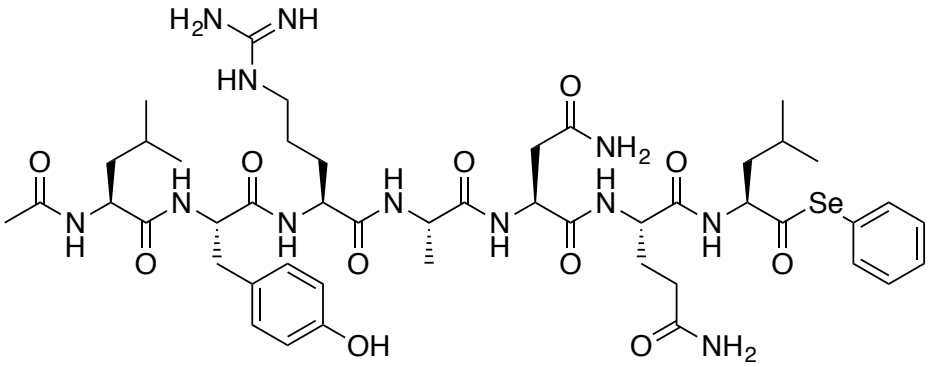


Figure S6. Analytical UPLC trace of HPLC purified Ac-LYRANQF-SePh (**15**); R_t 4.84 min (0-60% B over 5 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1093.4, $[M+2H]^{2+}$: 547.2; Found; $[M+H]^+$: 1093.1, $[M+2H]^{2+}$: 547.0. *$[M(-SePh)+2H]^{2+}$: 469.3 (artefact ion).

Ac-LYRANQL-SePh (16)



Side chain anchored Ac-LYRANQL-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on Rink amide resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at 0 ^{o}C and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (16.4 mg, 62% yield).

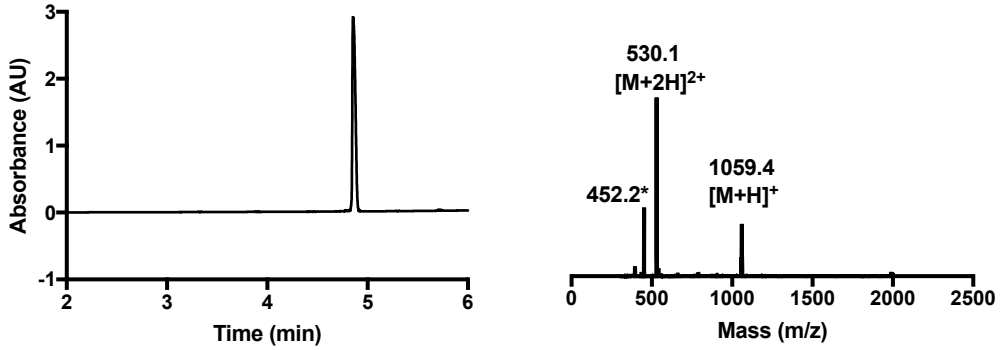
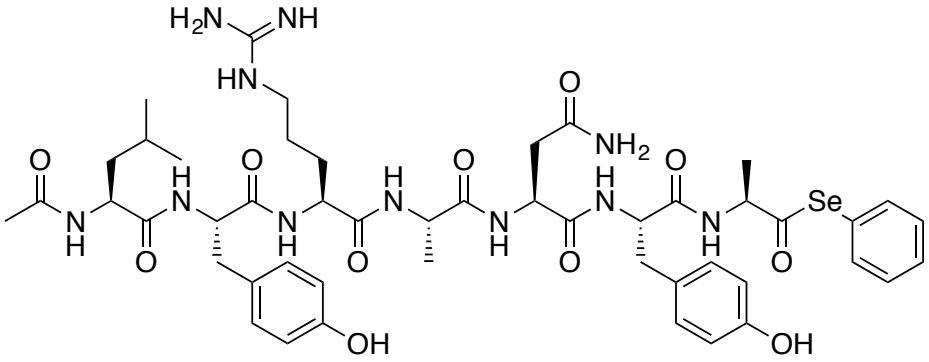


Figure S7. Analytical UPLC trace of HPLC purified Ac-LYRANQL-SePh (**16**); R_t 4.90 min (0-60% B over 5 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1059.5, $[M+2H]^{2+}$: 530.2; Found; $[M+H]^+$: 1059.4, $[M+2H]^{2+}$: 530.1. *$[M(-SePh)+2H]^{2+}$: 452.2 (artefact ion).

Ac-LYRANYA-SePh (17)



Side chain anchored Ac-LYRANYA-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on Wang resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at 0 ^{o}C and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (19.1 mg, 71% yield).

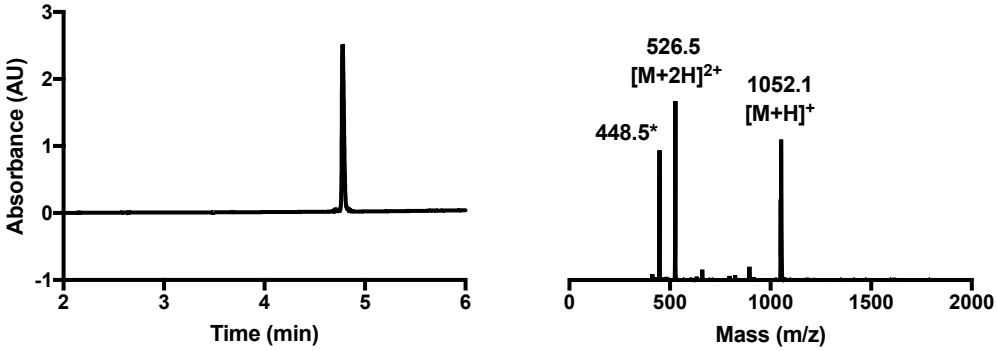
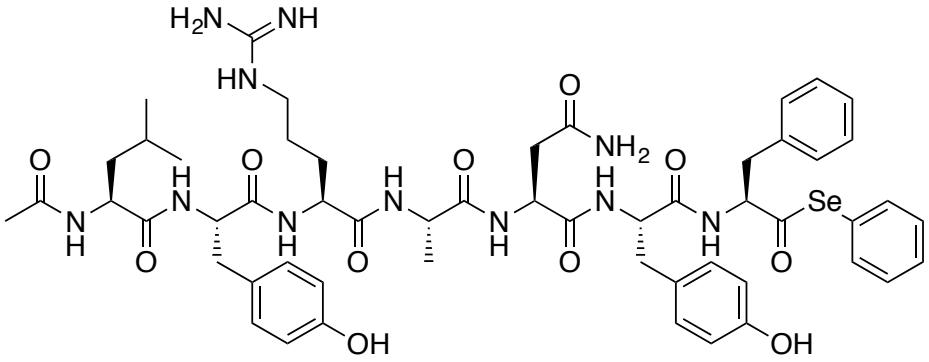


Figure S8. Analytical UPLC trace of HPLC purified Ac-LYRANYA-SePh (**17**); R_t 4.78 min (0-60% B over 5 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1052.4, $[M+2H]^{2+}$: 526.7; Found; $[M+H]^+$: 1052.1, $[M+2H]^{2+}$: 526.5. *$[M(-SePh)+2H]^{2+}$: 448.5 (artefact ion).

Ac-LYRANYF-SePh (18)



Side chain anchored Ac-LYRANYF-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on Wang resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at 0 ^{o}C and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (20.3 mg, 72% yield).

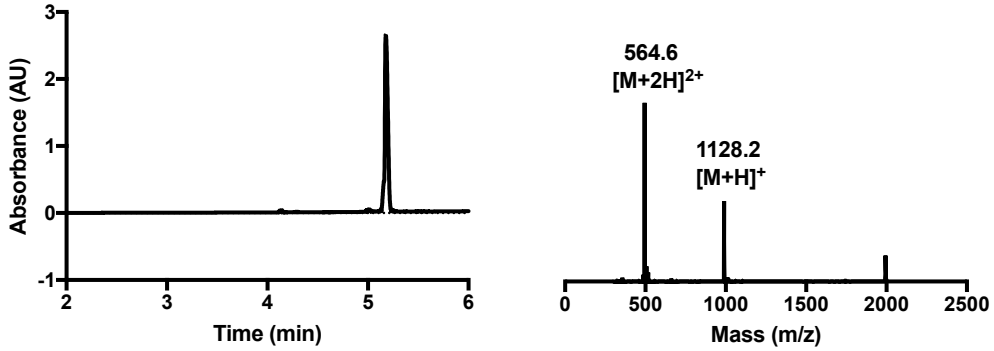
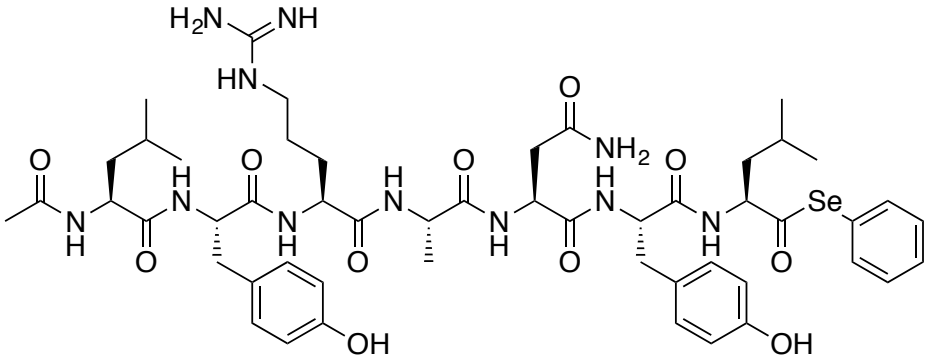


Figure S9. Analytical UPLC trace of HPLC purified Ac-LYRANYF-SePh (**18**); R_t 5.18 min (0-60% B over 5 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1128.4, $[M+2H]^{2+}$: 564.7; Found; $[M+H]^+$: 1128.2, $[M+2H]^{2+}$: 564.6.

Ac-LYRANYL-SePh (19)



Side chain anchored Ac-LYRANYL-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on Wang resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at 0 ^{o}C and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (19.1 mg, 70% yield).

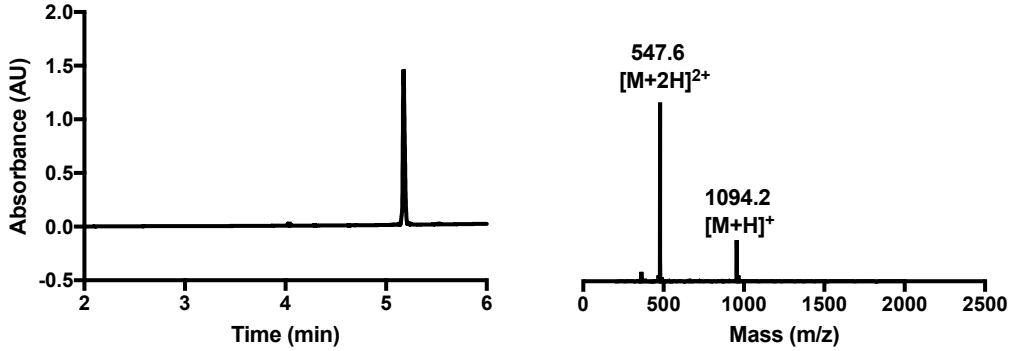
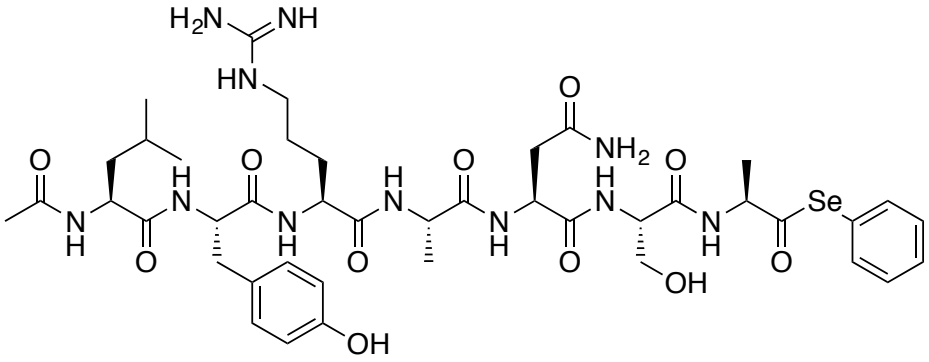


Figure S10. Analytical UPLC trace of HPLC purified Ac-LYRANYL-SePh (**19**); R_t 5.17 min (0-60% B over 5 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1094.5 $[M+2H]^{2+}$: 547.7; Found; $[M+H]^+$: 1094.2, $[M+2H]^{2+}$: 547.6.

Ac-LYRANSA-SePh (20)



Side chain anchored Ac-LYRANSA-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on 2-CTC resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at -12 ^{o}C and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (15.8 mg, 65%)

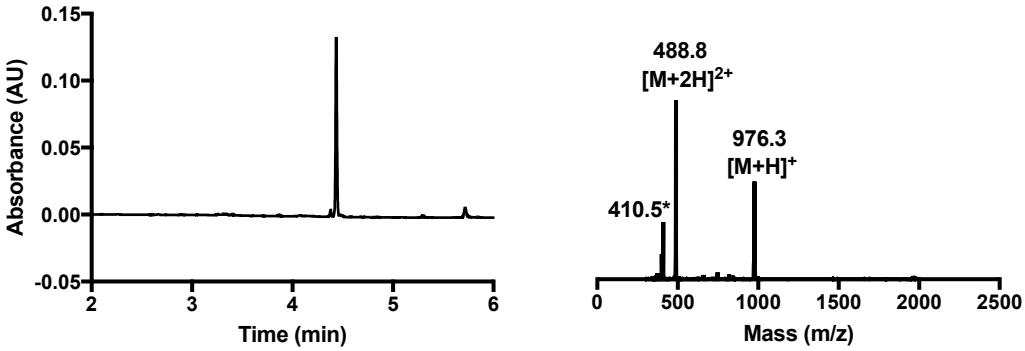
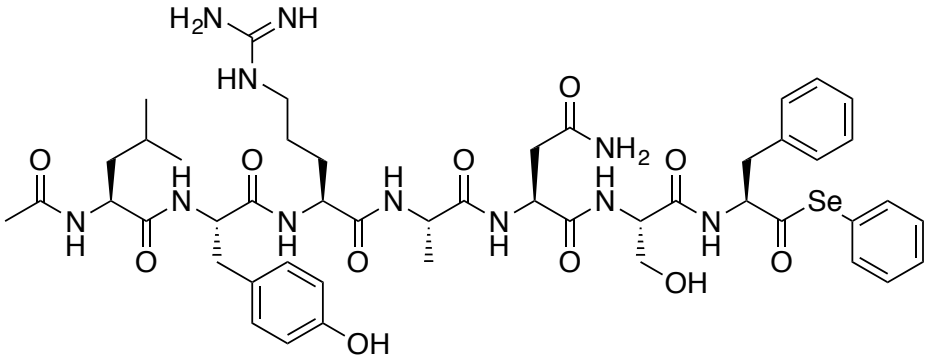


Figure S11. Analytical UPLC trace of HPLC purified Ac-LYRANSA-SePh (**20**); R_t 4.44 min (0-60% B over 5 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 976.4, $[M+2H]^{2+}$: 488.7; Found; $[M+H]^+$: 976.3, $[M+2H]^{2+}$: 488.8. *$[M(-SePh)+2H]^{2+}$: 410.5 (artefact ion).

Ac-LYRANSF-SePh (21)



Side chain anchored Ac-LYRANSF-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on 2-CTC resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at 0 ^{o}C and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (18.4 mg, 70% yield).

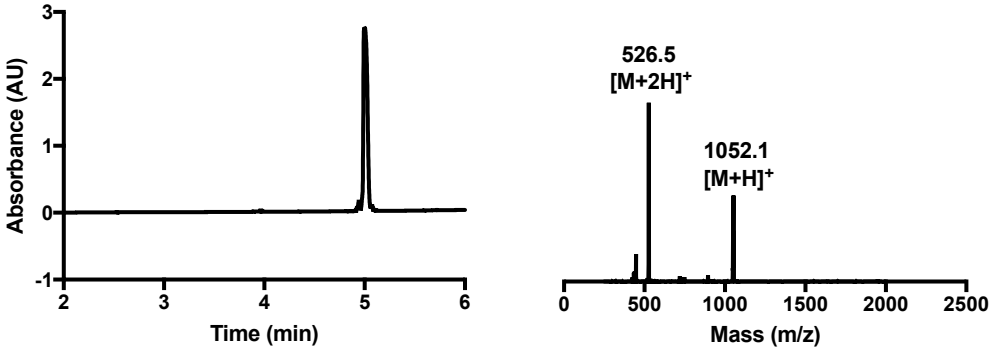
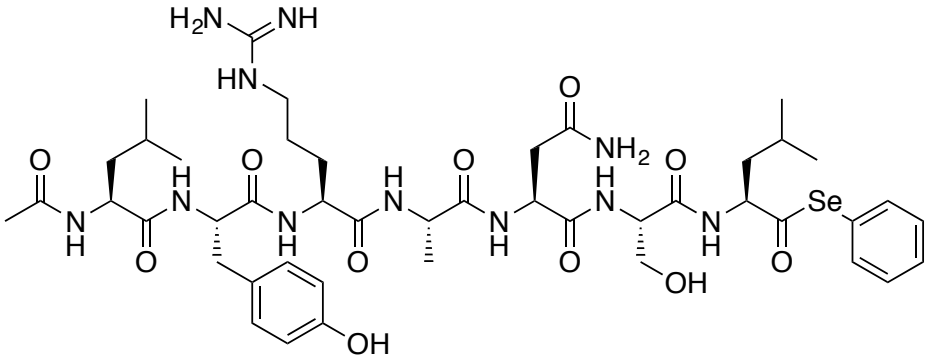


Figure S12. Analytical UPLC trace of HPLC purified Ac-LYRANSF-SePh (**21**); R_t 5.01 min (0-60% B over 5 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1052.4, $[M+2H]^{2+}$: 526.7; Found; $[M+H]^+$: 1052.1, $[M+2H]^{2+}$: 526.5.

Ac-LYRANSL-SePh (22)



Side chain anchored Ac-LYRANSL-OAll was synthesised via solid phase peptide synthesis as outlined in the general methods section on 2-CTC resin. 25 μmol of the protected peptide was allyl deprotected, selenoesterified at 0 ^{o}C and cleaved from the resin as outlined in the general methods section. The crude peptide was purified by preparative reverse-phase HPLC (0 to 60% B over 30 min, 0.1% TFA) and lyophilised to afford the desired selenoester (18.9 mg, 74% yield).

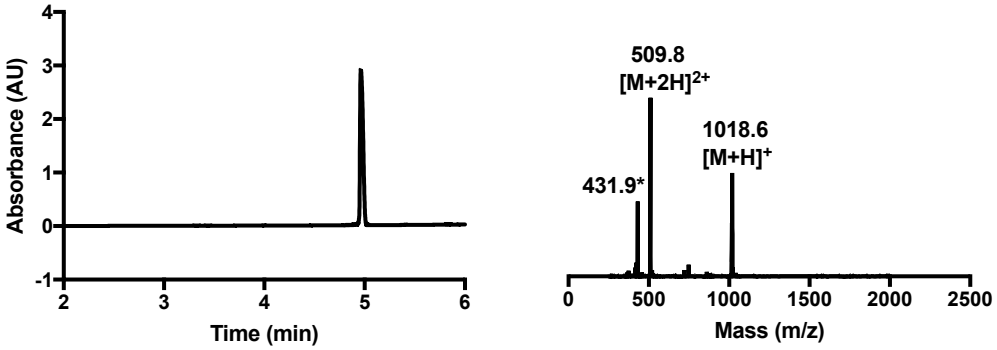


Figure S13. Analytical UPLC trace of HPLC purified Ac-LYRANSL-SePh (**22**); R_t 4.98 min (0-60% B over 5 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1018.4, $[M+2H]^{2+}$: 509.7; Found; $[M+H]^+$: 1018.6, $[M+2H]^{2+}$: 509.8. *$[M(-SePh)+2H]^{2+}$: 431.9 (artefact ion).

UPLC Epimerisation Studies:

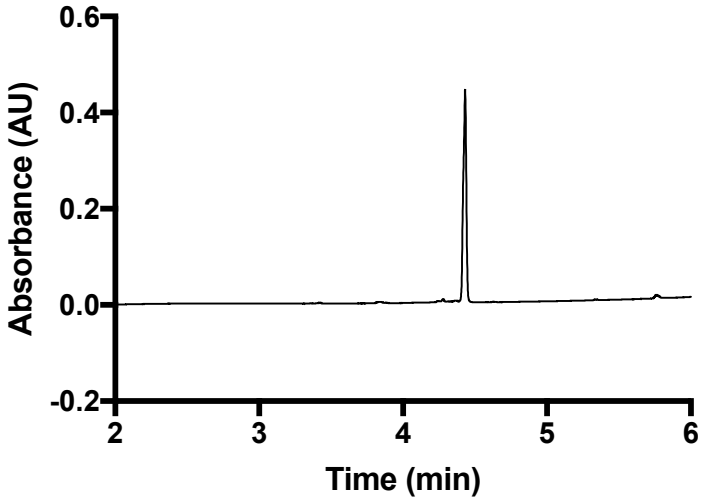


Figure S14. Analytical UPLC trace of HPLC purified Ac-LYRAN**L**Q-SePh; Rt 4.43 min (0-60% B over 5 min, λ = 230 nm)

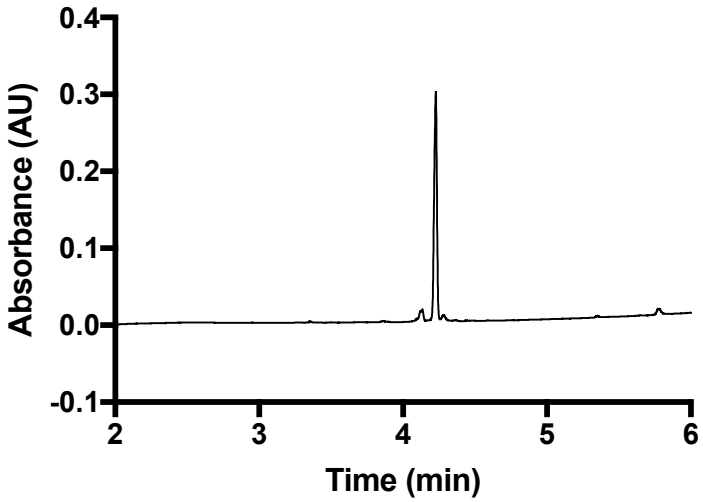


Figure S15. Analytical UPLC trace of HPLC purified Ac-LYRAN**D**Q-SePh; R_t 4.26 min (0-60% B over 5 min, λ = 230 nm)

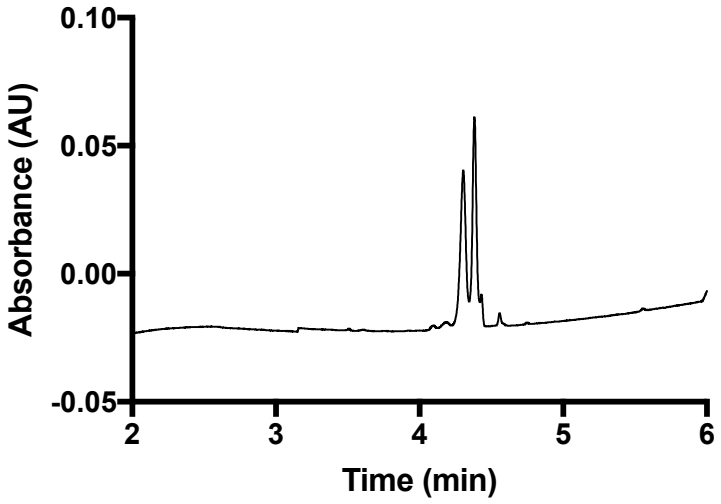


Figure S16. Analytical UPLC trace of HPLC purified Ac-LYRAN**L**Q-SePh and Ac-LYRAN**D**Q-SePh co-injected; R_t 4.30 and 4.47 min (0-60% B over 5 min, λ = 230 nm)

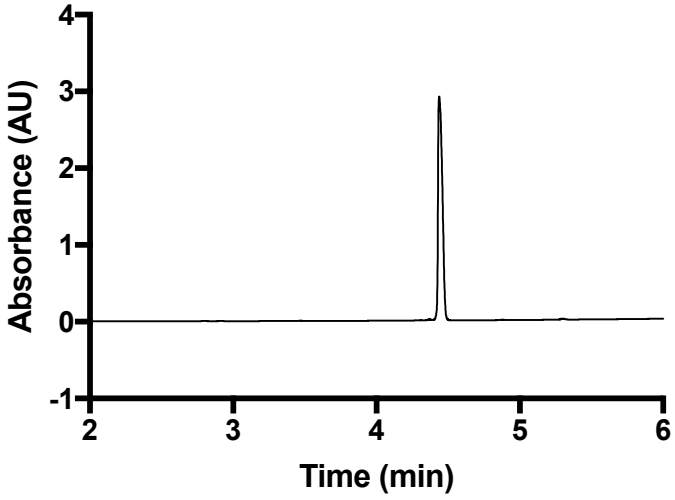


Figure S17. Analytical UPLC trace of HPLC purified Ac-LYRANS**L**A-SePh; R_t 4.43 min (0-60% B over 5 min, λ = 230 nm)

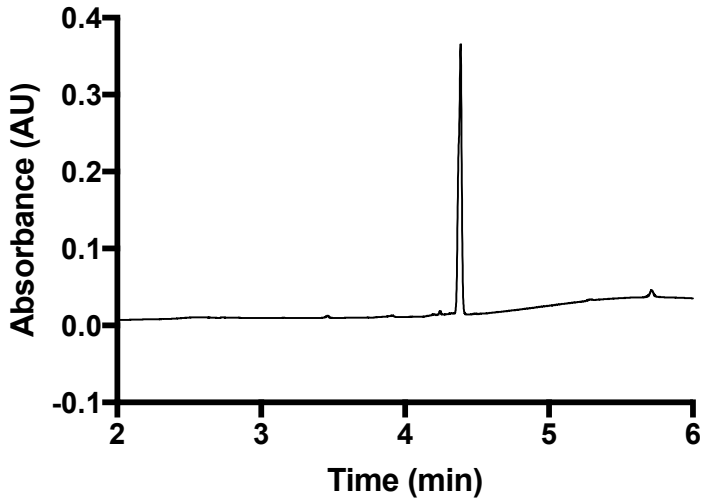


Figure S18. Analytical UPLC trace of HPLC purified Ac-LYRANS**D**A-SePh; R_t 4.38 min (0-60% B over 5 min, λ = 230 nm)

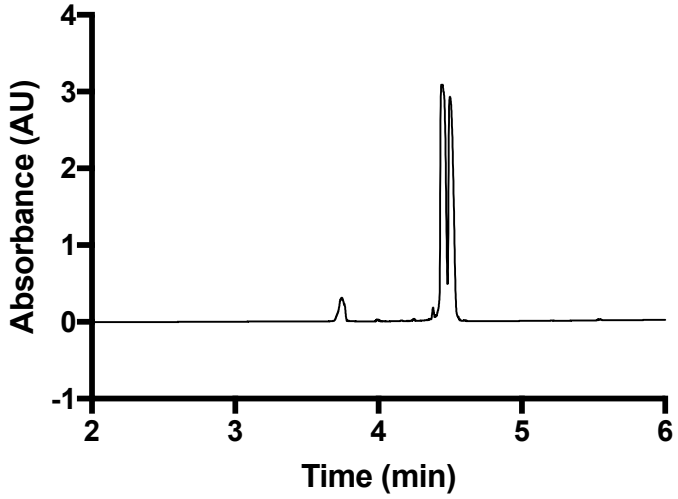
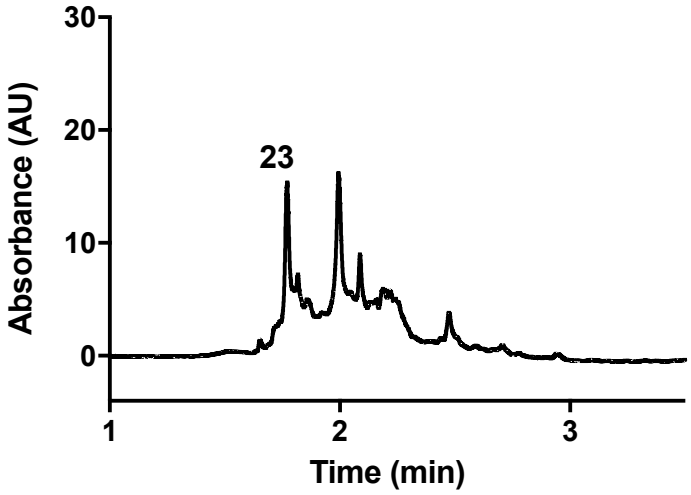


Figure S19. Analytical UPLC trace of HPLC purified Ac-LYRANS**L**A-SePh and Ac-LYRANS**D**A-SePh co-injected; R_t 4.45 and 4.50 min (0-60% B over 5 min, λ = 230 nm)

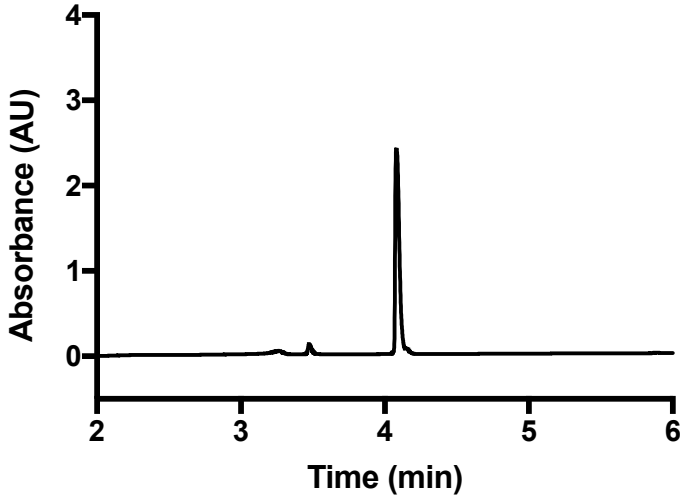
Hyalomin-1 N Terminal Fragment (K1-N25) (23) Synthesis

Peptide selenoester **23** was prepared by side-chain anchoring Fmoc-Asp-OAll to Rink amide resin (24 μmol) and extended via Fmoc-SPPS. The final lysine residue was coupled as the *N*-Boc-protected amino acid. On-resin allyl ester deprotection and on-resin selenoesterification were then completed as outlined in the general procedures. Global cleavage was achieved upon treatment of the resin-bound peptide selenoester with a solution of TFA/TIS/H_2O (90:5:5 v/v/v, 4 mL) for 2 h at room temperature. The deprotection solution was then concentrated under nitrogen flow and the crude selenoester precipitated from ice-cold diethyl ether. Purification of the crude peptide by preparative RP-HPLC (0 to 50% B over 40 min, 0.1% TFA) afforded peptide **23** as a white solid after lyophilisation (16.7 mg, 23% yield).

A



B



C

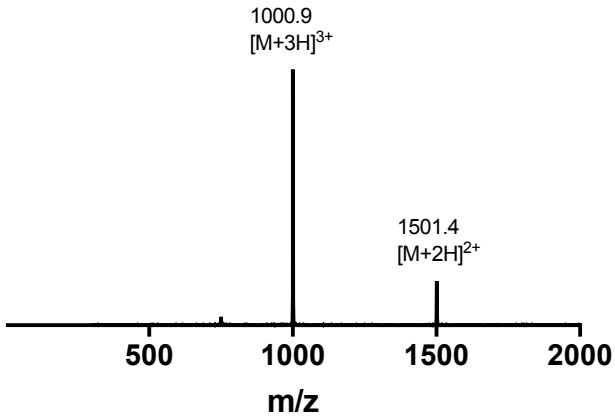
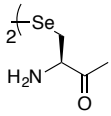


Figure S20. A: UPLC-MS trace of crude hyalomin 1 fragment (**23**). **B:** Analytical UPLC trace of HPLC purified hyalomin 1 fragment (**23**); Rt 4.10 min (0-50% B over 5 min, λ = 214 nm). **C:** Low resolution mass spectrum of HPLC purified Hyalomin 1 fragment (**23**): Calc. Mass $[M+2H]^{2+}$: 1500.4, $[M+3H]^{3+}$: 1000.6; Found; $[M+2H]^{2+}$: 1501.4, $[M+3H]^{3+}$: 1000.9.

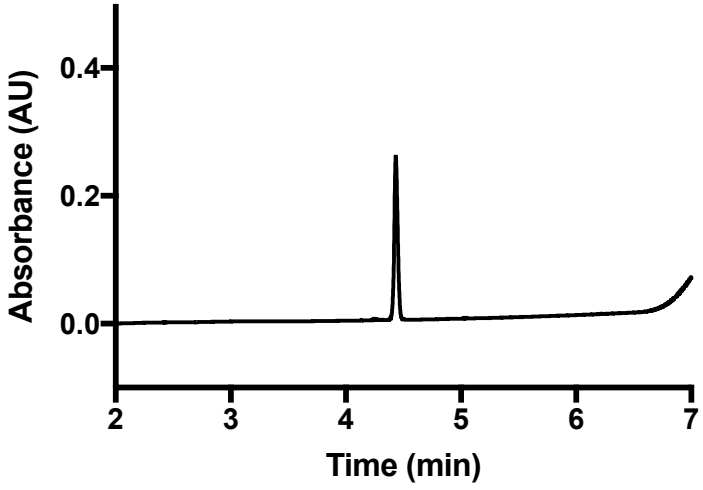
Hyalomin 1 C Terminal Fragment Mutant (U26-D59) (26) Synthesis



DSGERNGGSEPAKPRLPVPGSGRDSERIPVPVD-OH

The C-terminal fragment of hyalomin-1 (26-59) (**26**) was synthesised via standard Fmoc SPPS as outlined in the general methods section. For the N-terminal residue, a solution of Boc-Sec(Pmb)-OH (1.2 eq.), HOAt (1.2 eq.) and DIC (1.2 eq.) in DMF (final amino acid concentration 0.1 M) was added to the resin (1.0 eq.) and shaken. It should be noted that this protected selenocysteine (Sec) residue was incorporated in place of a native Asp-26 residue in hyalomin-1. After 16 h, the resin was washed with DMF (5 x 3 mL), DCM (5 x 3 mL), and DMF (5 x 3 mL). The Pmb-protected selenopeptide (1.0 eq.) was then treated with a solution of 10% DMSO in TFA:ligation buffer (3:1 v/v) (ligation buffer = 6 M Gn•HCl, 1 M HEPES, pH 7.2). The reaction mixture was stirred at room temperature for 45 min, at which point UPLC-MS analysis indicated complete consumption of starting material. The mixture was concentrated under a stream of nitrogen, reconstituted in water containing 0.1% TFA, and immediately subjected to purification by reverse-phase HPLC (0 to 50% B over 50 min, 0.1% TFA) followed by lyophilisation to yield the desired product exclusively as the diselenide dimer peptide. (6.5 mg, 7% yield).

A



B

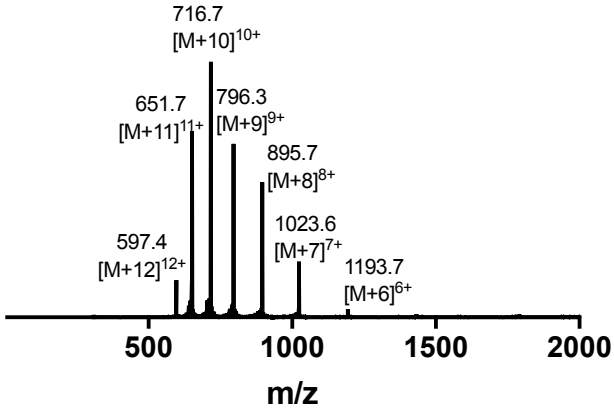
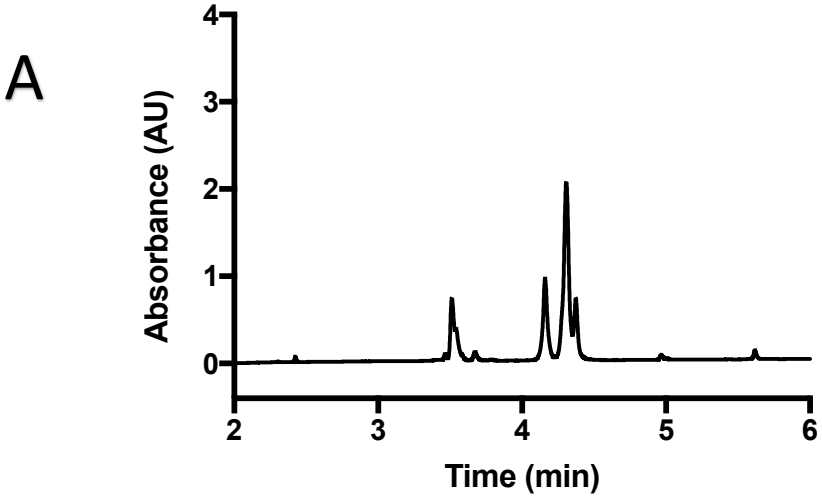


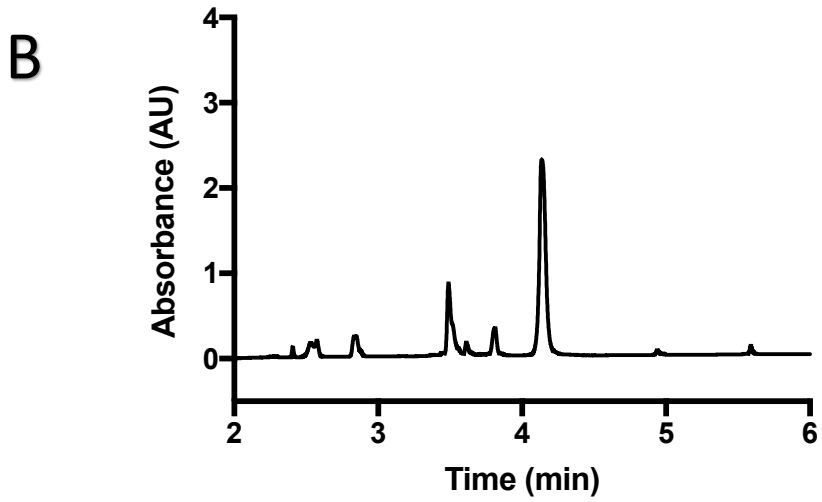
Figure S21. A: Analytical UPLC trace of HPLC purified mutant hyalomin-1 C-terminal fragment (**26**); R_t 4.43 min (0-50% B over 5 min, λ = 230 nm). **B:** Low resolution mass spectrum of HPLC purified hyalomin-1 fragment (**26**): Calc. Mass $[M+7H]^{7+}$: 1022.9, $[M+8H]^{8+}$: 895.1, $[M+9H]^{9+}$: 795.8, $[M+10H]^{10+}$: 716.3, $[M+11H]^{11+}$: 651.3; Found; $[M+7H]^{7+}$: 1023.6, $[M+8H]^{8+}$: 895.7, $[M+9H]^{9+}$: 796.3, $[M+10H]^{10+}$: 716.7, $[M+11H]^{11+}$: 651.7.

Hyalomin-1 (1-59 D26A) (27) Synthesis *via* Ligation of (23) and (26)

H-KPNLQSRSDDGVDESDYDTYPDDNNADSGERNGGSEPAKPRLPVPGSGRDSERIPVPVD-OH

Selenoester **23** (1.2 mg, 0.40 μmol, 1.5 eq.) was dissolved in ligation buffer (6 M Gn•HCl, 0.1 M Na_2HPO_4, pH 7.2) to a final concentration of 7.5 mM. Diselenide **26** (0.9 mg, 0.27 μmol, 1.0 eq.) was dissolved in ligation buffer to a final diselenide concentration of 5 mM (with respect to the monomer) and added to the selenoester solution and the pH adjusted using 1 M NaOH to a final pH of 6.0. The reaction was allowed to proceed for 15 min at room temperature, with reaction completion judged by UPLC-MS. The reaction mixture was subsequently extracted with hexane (6 x 150 μL) before being sparged with argon for 10 min. To the reaction was added an equal volume of deselenization buffer (250 mM TCEP, 25 mM DTT in ligation buffer) and the reaction was further sparged with argon. The deselenization reaction was allowed to proceed at room temperature overnight, with completion again judged by UPLC-MS monitoring. Purification via reverse phase HPLC (0 to 50% B over 40 min, 0.1% TFA) followed by lyophilisation afforded final protein **27** as a white solid (1.20 mg, 71%).





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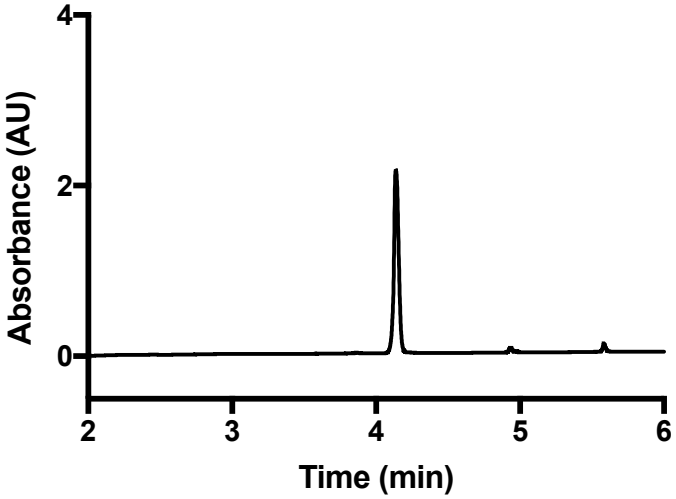
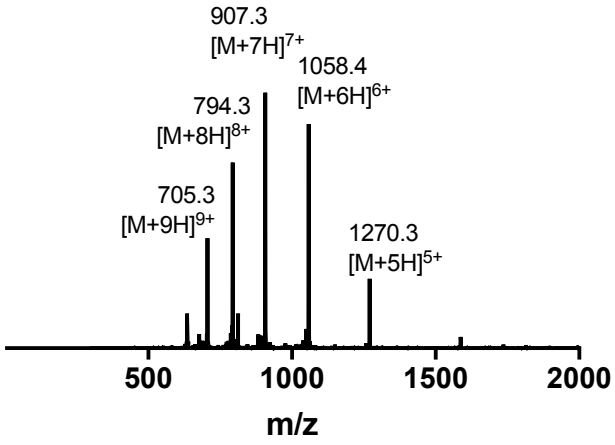

Absorbance (AU)
4
2
0
2
3
4
5
6
Time (min)

D


907.3
[M+7H]7+
1058.4
[M+6H]6+
794.3
[M+8H]8+
705.3
[M+9H]9+
1270.3
[M+5H]5+
500
1000
1500
2000
m/z

E

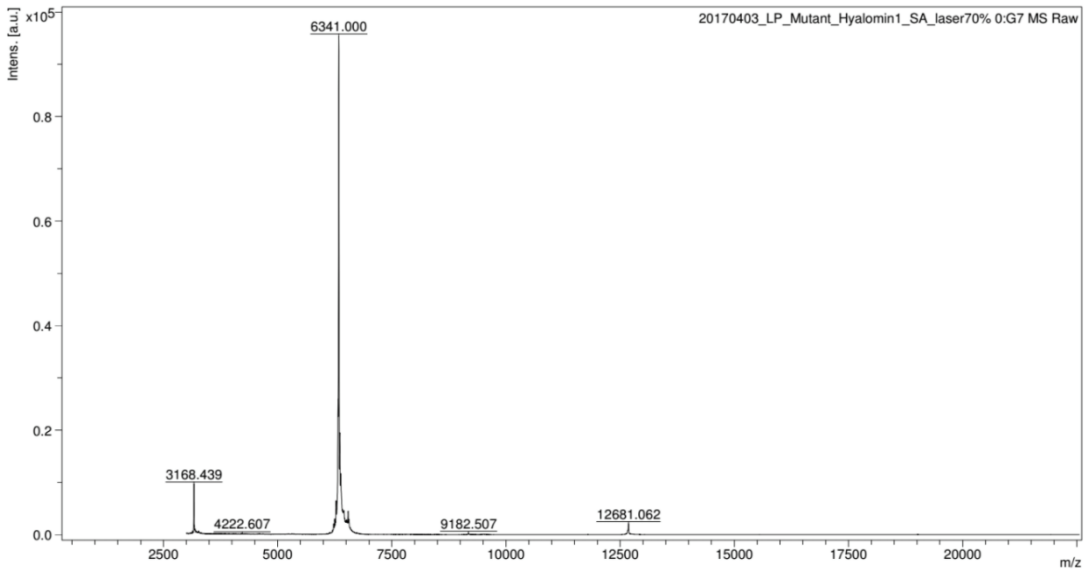
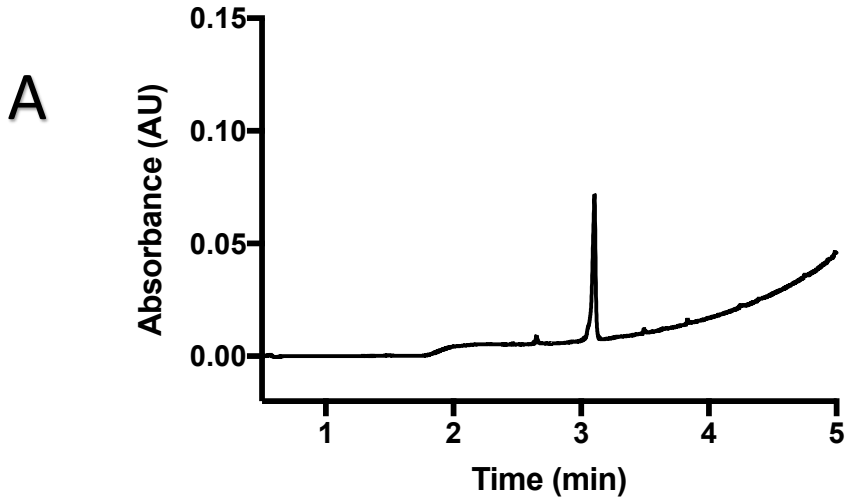

20170403_LP_Mutant_Hyalomin1_SA_laser70% 0:G7 MS Raw
Intens. [a.u.]
x10^5
0.8
0.6
0.4
0.2
0.0
6341.000
3168.439
4222.607
9182.507
12681.062
2500
5000
7500
10000
12500
15000
17500
20000
m/z

Figure S22. A: Analytical UPLC trace of the crude reaction mixture after ligation. **B:** Analytical UPLC trace of crude hyalomin-1 after deselenization. **C:** Analytical UPLC trace of HPLC purified yalomin-1 (**27**); Rt 4.14 min (0-50% B over 5 min, λ = 230 nm). **D:** Low resolution mass spectrum of HPLC purified hyalomin-1 (**27**) Calc. Mass $[M+5H]^{5+}$: 1268.6, $[M+6H]^{6+}$: 1057.3, $[M+7H]^{7+}$: 906.4, $[M+8H]^{8+}$: 793.2, $[M+9H]^{9+}$: 705.2. Mass Found (ESI) $[M+5H]^{5+}$: 1270.3, $[M+6H]^{6+}$: 1058.4, $[M+7H]^{7+}$: 907.3, $[M+8H]^{8+}$: 794.3, $[M+9H]^{9+}$: 705.3. **E:** MALDI-TOF mass spectrum: Calc. Mass: 6341.62. Mass Found: 6341.00

***Dermacentor andersoni* 240 N Terminal (K1-Q34) (24) Synthesis**

Peptide selenoester **24** was prepared by side-chain anchoring Fmoc-Glu-OAll to Rink amide resin (10 μmol) and extended *via* Fmoc-SPPS. The final lysine residue was coupled as the Boc-protected amino acid. On-resin allyl ester deprotection and on-resin selenoesterification was completed as outlined in the general procedures. Global cleavage was achieved on treatment of the resin-bound peptide selenoester with a solution of TFA/TIS/H_2O (90:5:5 v/v/v, 4 mL) for 2 h at room temperature. The cleavage solution was then concentrated under nitrogen flow and the crude selenoester precipitated from ice-cold diethyl ether. Purification of the crude peptide by preparative reverse phase HPLC (0 to 50% B over 40 min, 0.1% TFA) afforded peptide **24** as a white solid after lyophilisation (7.2 mg, 18% yield).



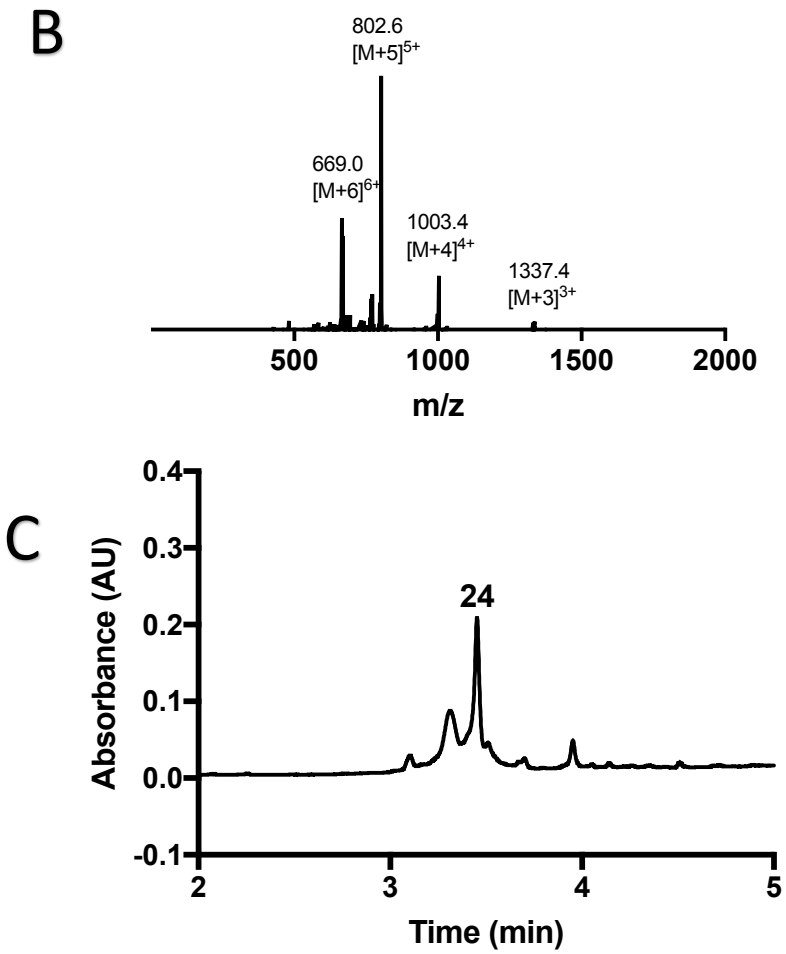
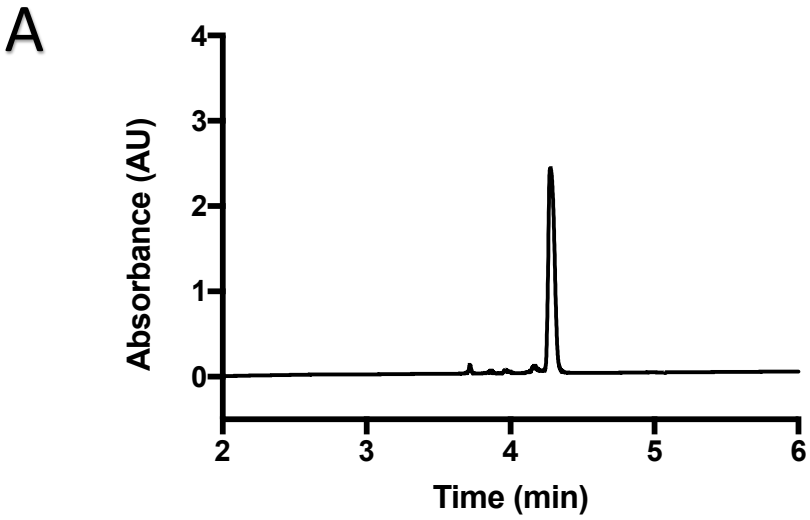
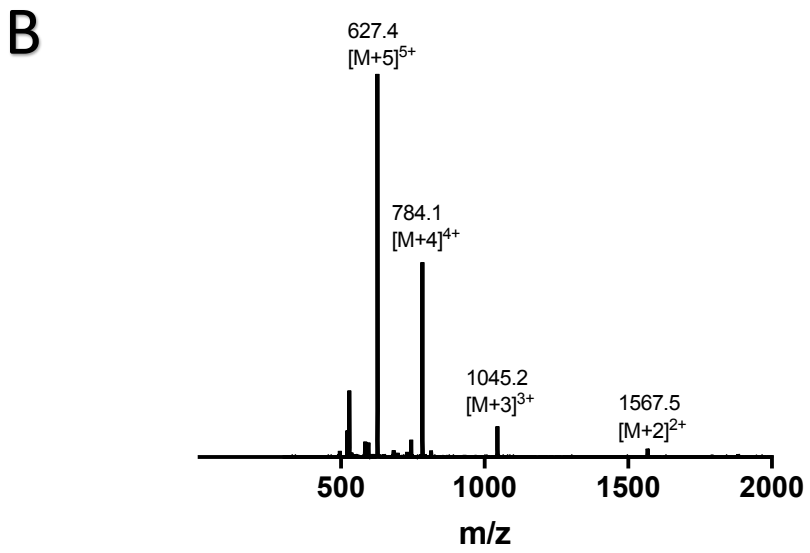


Figure S23. A: Analytical UPLC trace of HPLC purified *D. andersoni* 240 fragment (**24**); Rt 3.10 min (0-50% B over 5 min, λ = 230 nm); **B**: Low resolution mass spectrum of HPLC purified (**24**): Calc. Mass $[M+4H]^{4+}$: 1002.4, $[M+5H]^{5+}$: 802.1, $[M+6H]^{6+}$: 668.6; Found; $[M+4H]^{4+}$: 1003.4, $[M+5H]^{5+}$: 802.6, $[M+6H]^{6+}$: 669.0. **C**: UPLC trace of crude *D. andersoni* fragment (**24**).

***Dermacentor andersoni* 310 N-Terminal (K1-E25) (25) Synthesis**

Peptide selenoester **25** was prepared by side-chain anchoring dipeptide Fmoc-AspGly-OAll to 2-CTC resin (25 μmol) and extended *via* Fmoc-SPPS. The final lysine residue was coupled as the Boc-protected amino acid. On-resin allyl ester deprotection and on-resin selenoesterification was completed as outlined in the general procedures. Global cleavage was achieved on treatment of the resin-bound peptide selenoester with a solution of TFA/TIS/H_2O (90:5:5 v/v/v, 4 mL) for 2 h at room temperature. The cleavage solution was then concentrated under nitrogen flow and the crude selenoester precipitated from ice-cold diethyl ether. Purification of the crude peptide by preparative RP-HPLC (0 to 50% B over 40 min, 0.1% TFA) afforded peptide **25** as a fluffy white solid after lyophilisation (25.2 mg, 15% yield).





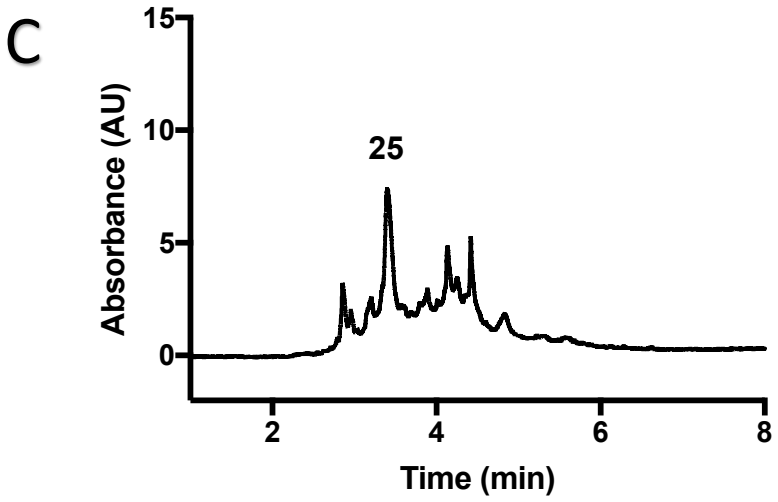
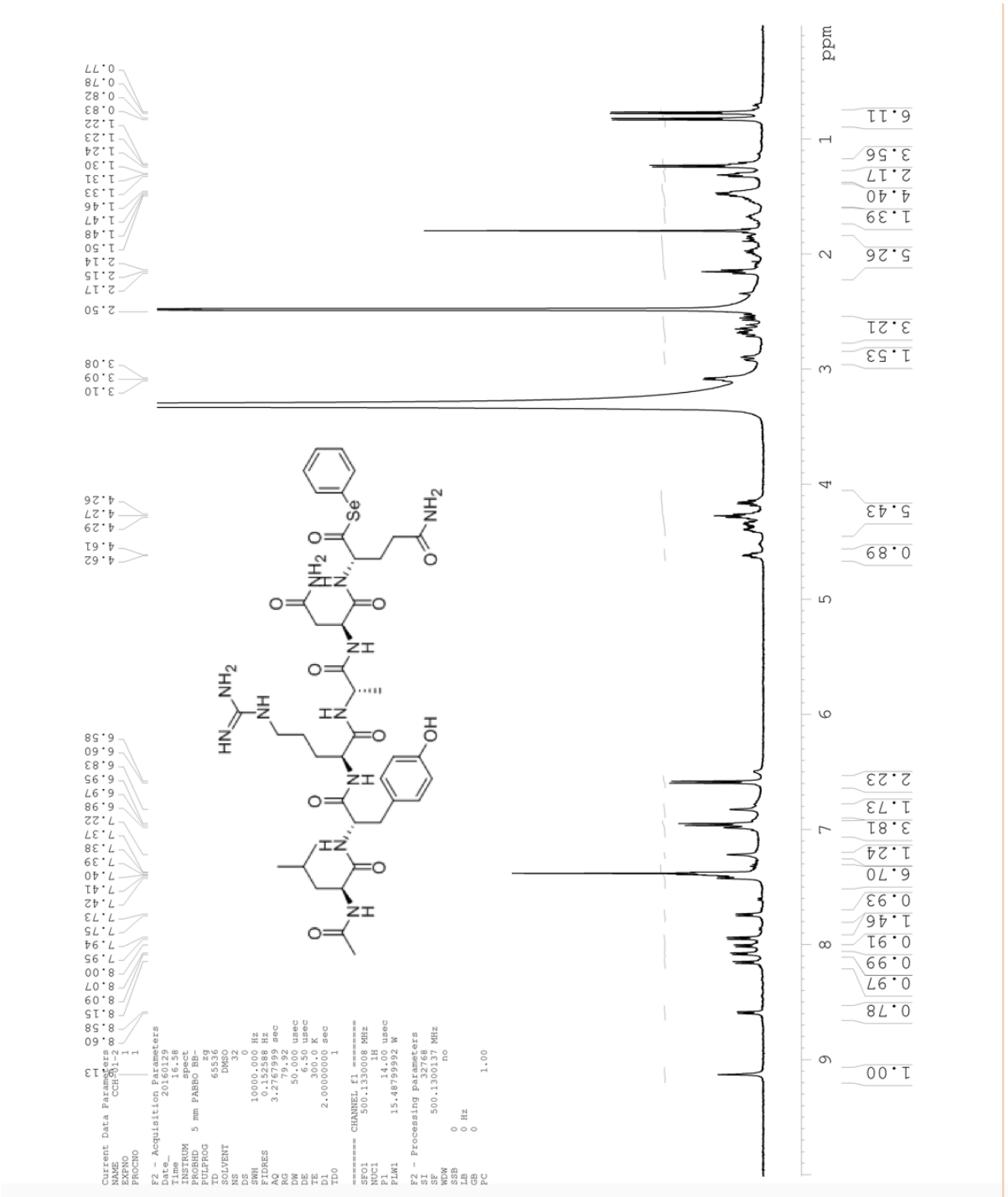


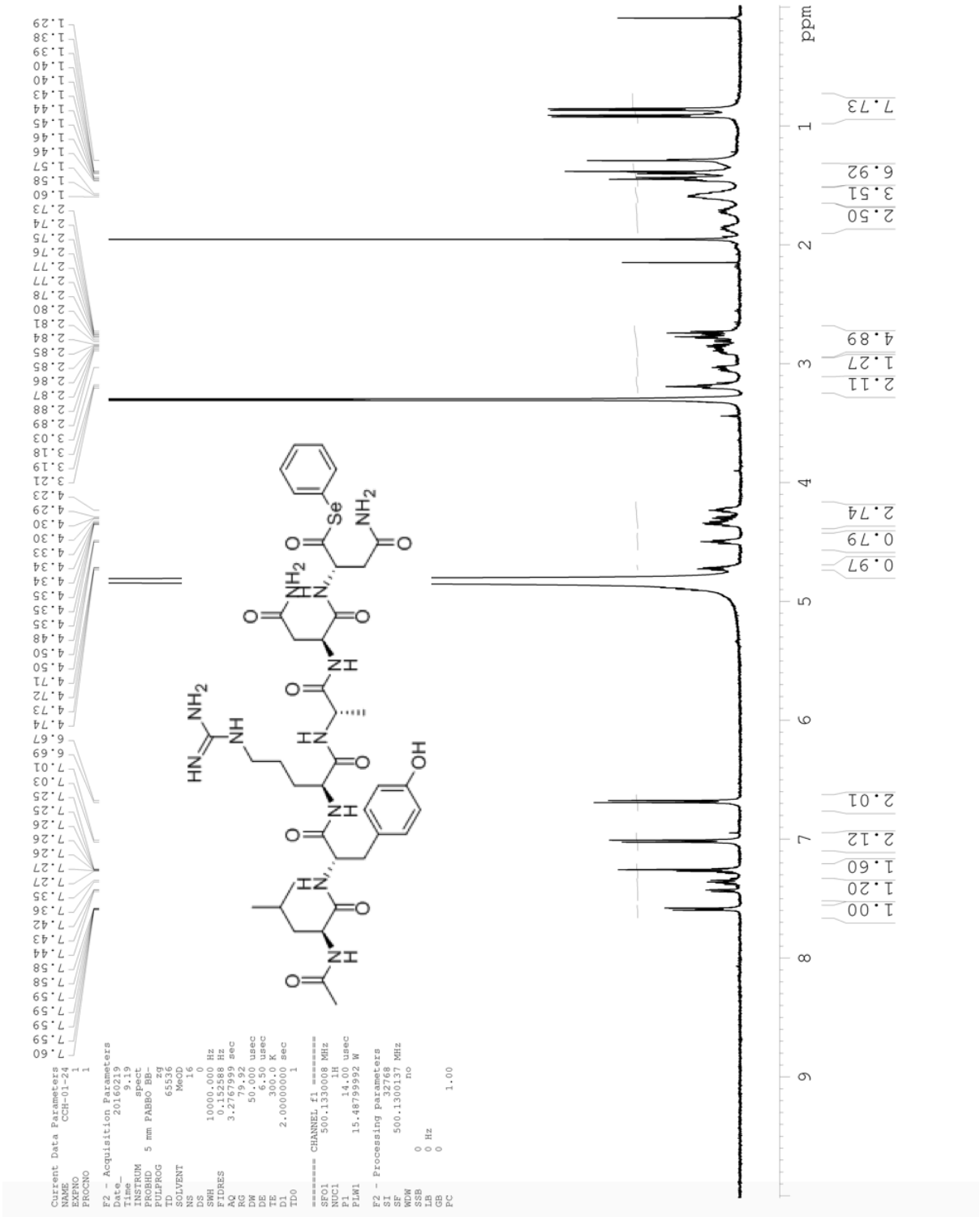
Figure S24. A: Analytical UPLC trace of HPLC purified *D. andersoni* 310 Fragment (**25**); Rt 4.28 min (0-50% B over 5 min, λ = 230 nm); **B**: Low resolution mass spectrum of HPLC purified (**25**): Calc. Mass $[M+3H]^{3+}$: 1044.5, $[M+4H]^{4+}$: 783.6, $[M+5H]^{5+}$: 627.0; Found: $[M+3H]^{3+}$: 1045.2, $[M+4H]^{4+}$: 784.1, $[M+5H]^{5+}$: 627.4. C: UPLC-MS trace of crude *D. andersoni* fragment (**25**).

Model Peptide NMR Data

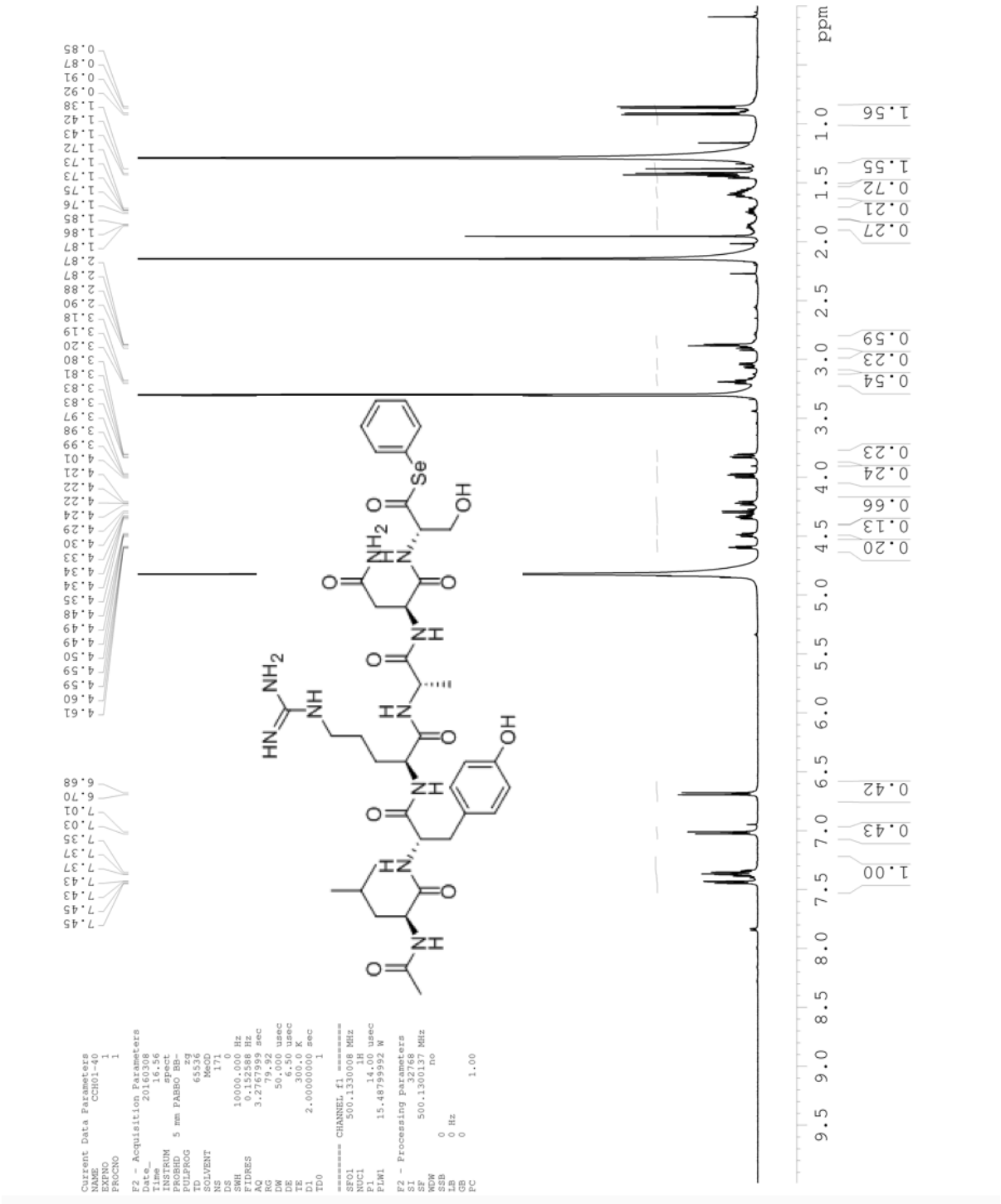
Ac-LYRANQ-SePh (1) (selenoesterified at room temperature)



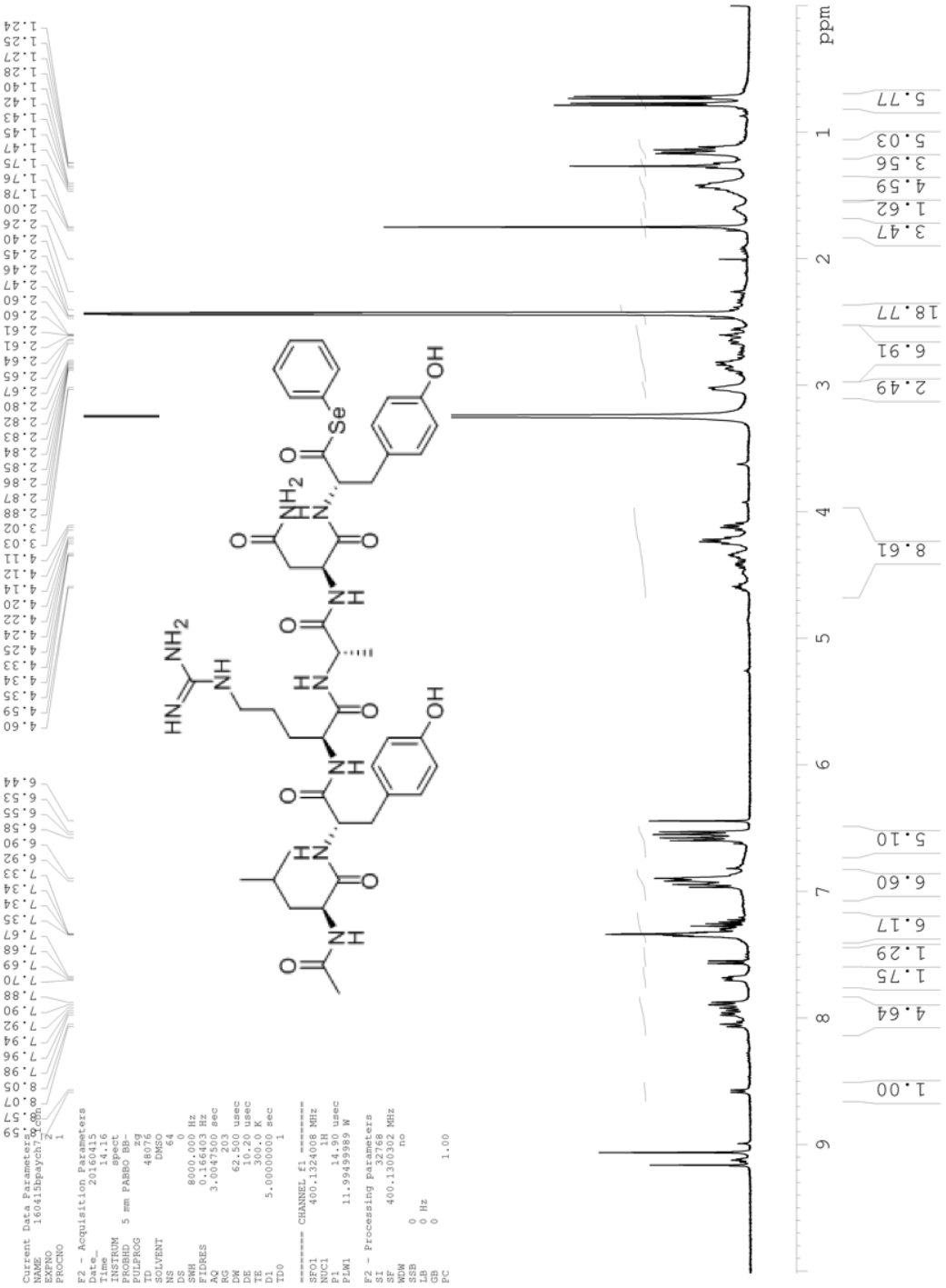
Ac-LYRANN-SePh (2) (selenoesterified at room temperature)



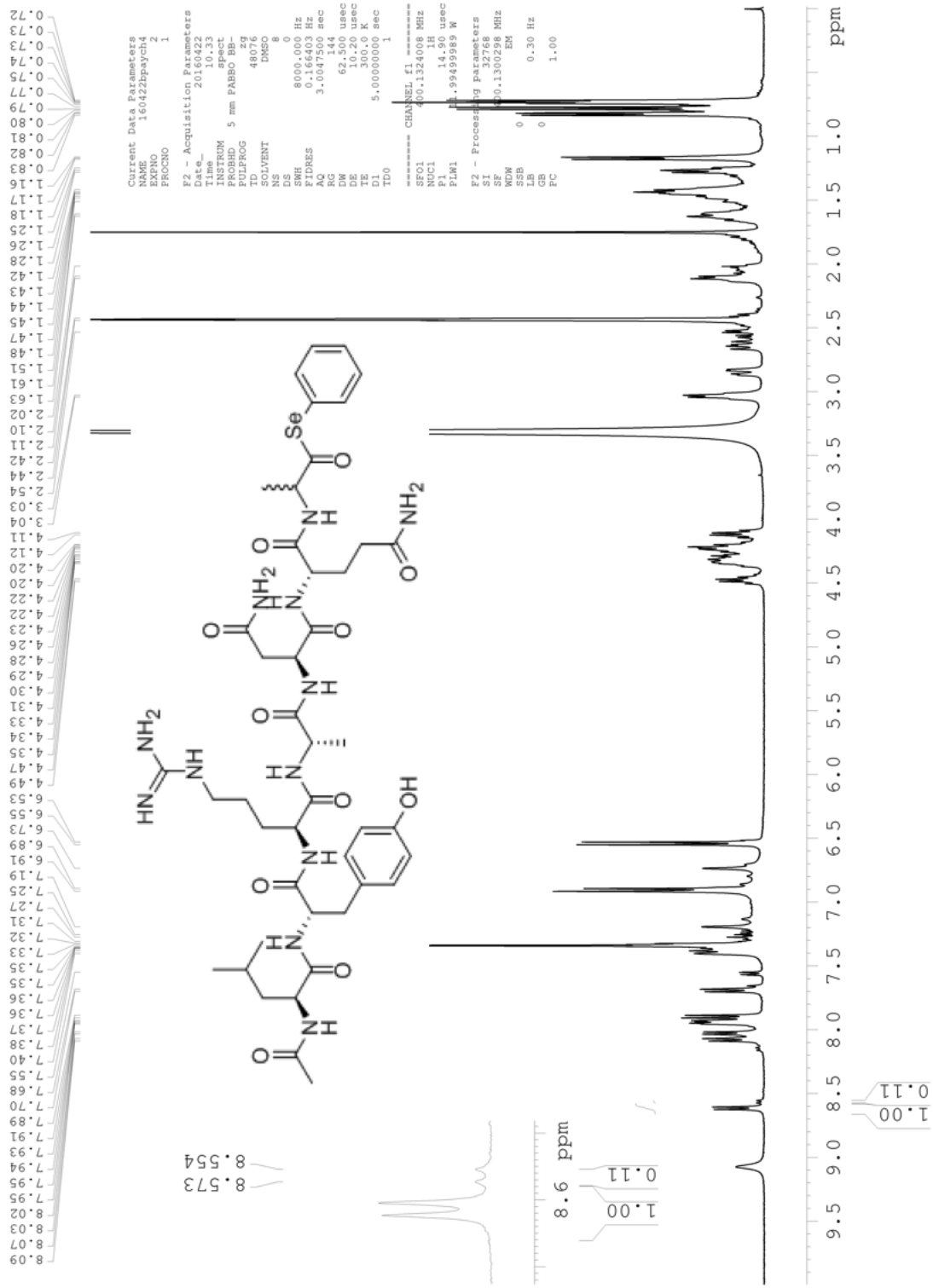
Ac-LYRANS-SePh (4) (selenoesterified at room temperature)



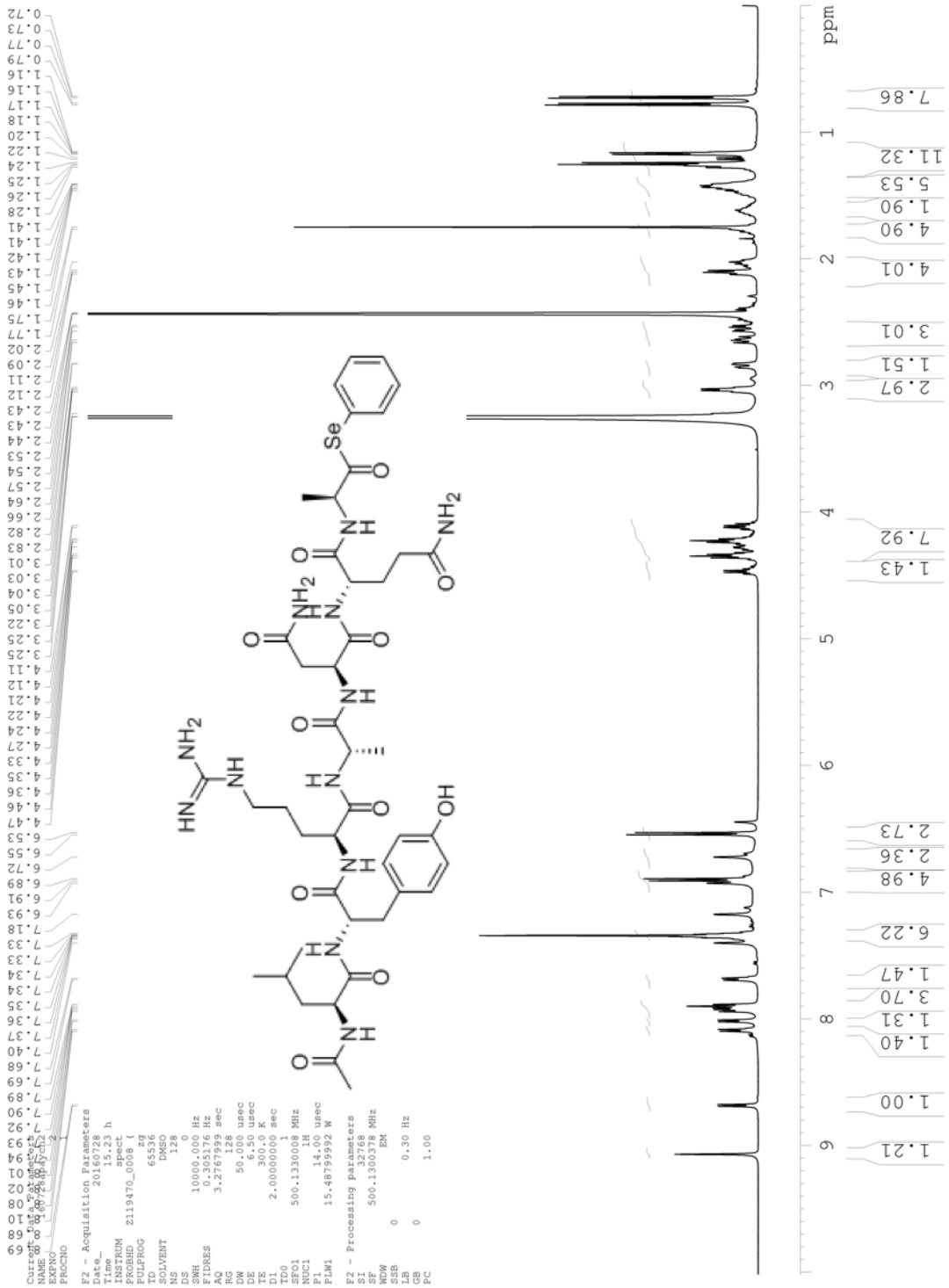
Ac-LYRANY-SePh (3) (selenoesterified at room temperature)



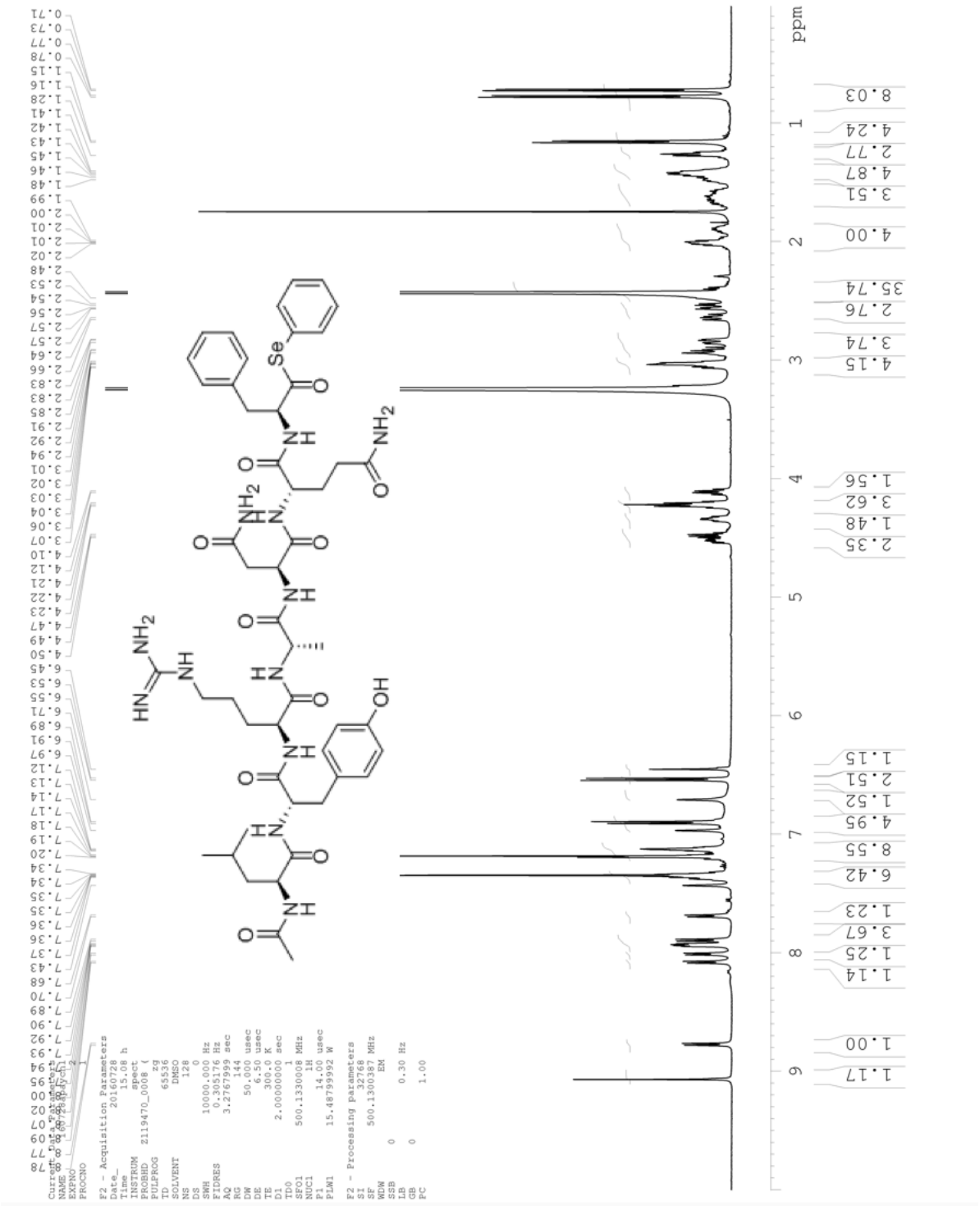
Ac-LYRANQA-SePh (14) (selenoesterified at room temperature)



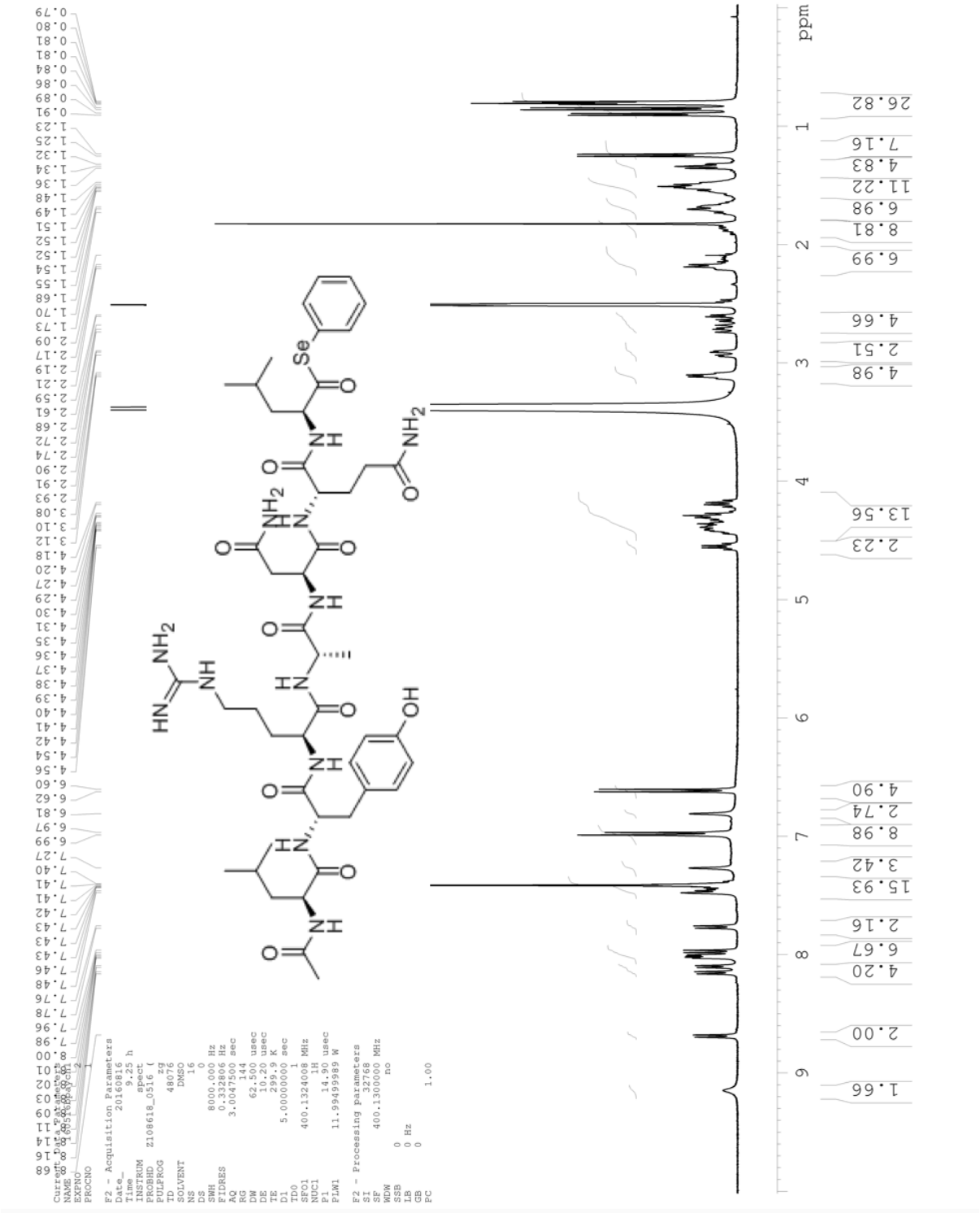
Ac-LYRANQA-SePh (14) (selenoesterified at 0^{o}C)



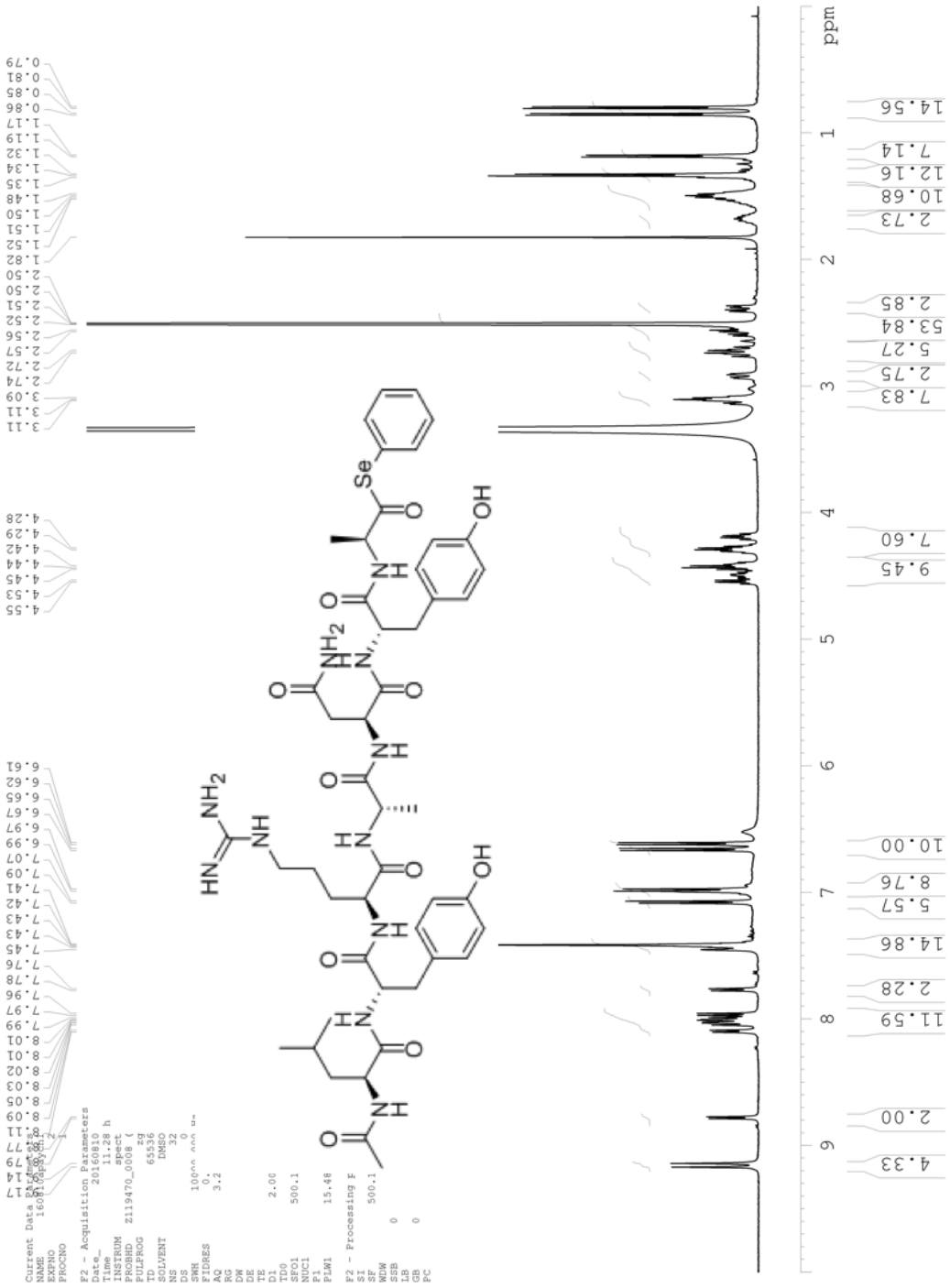
Ac-LYRANQF-SePh (15) (selenoesterified at 0°C)



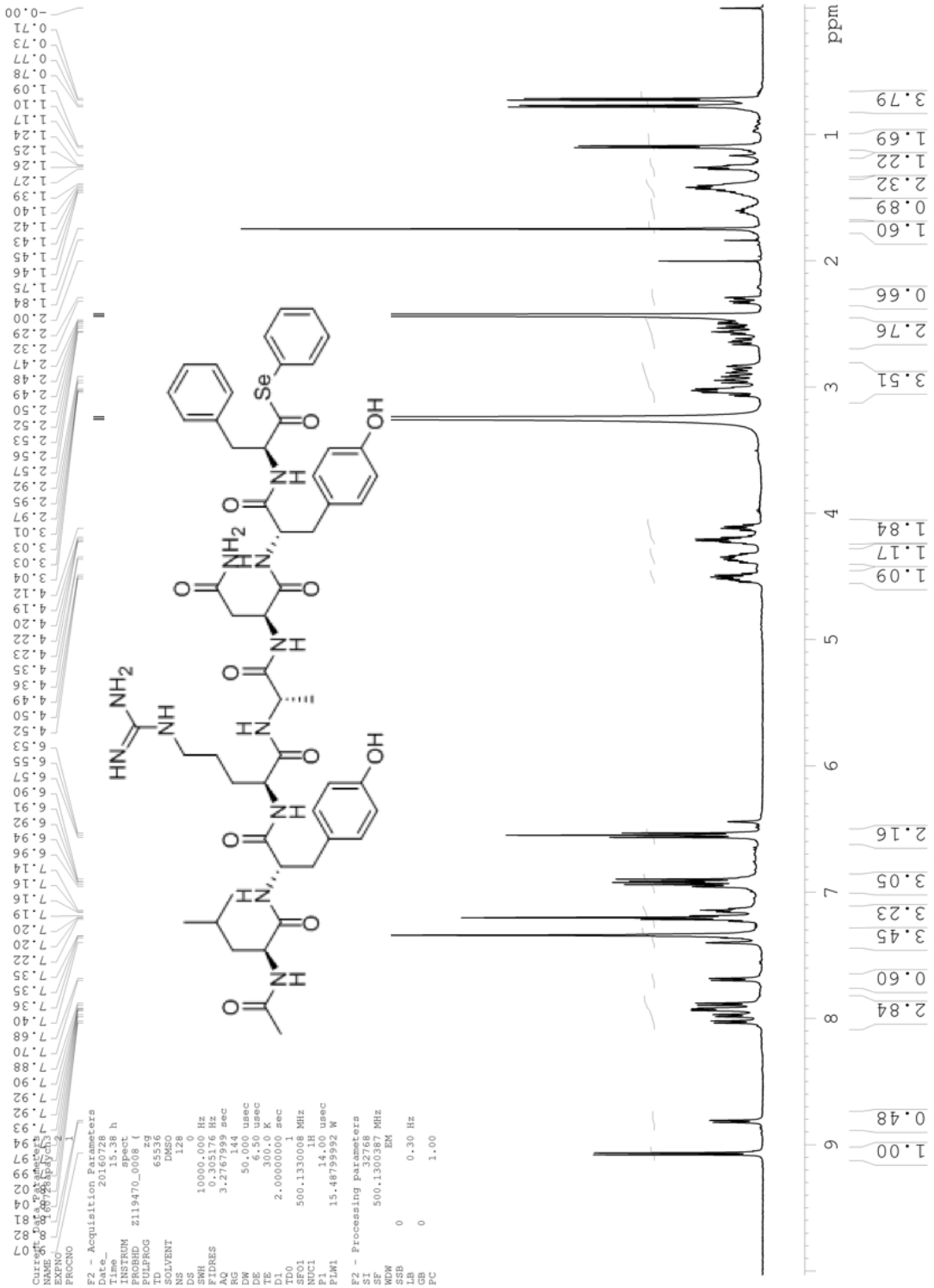
Ac-LYRANQL-SePh (16) (selenoesterified at 0°C)



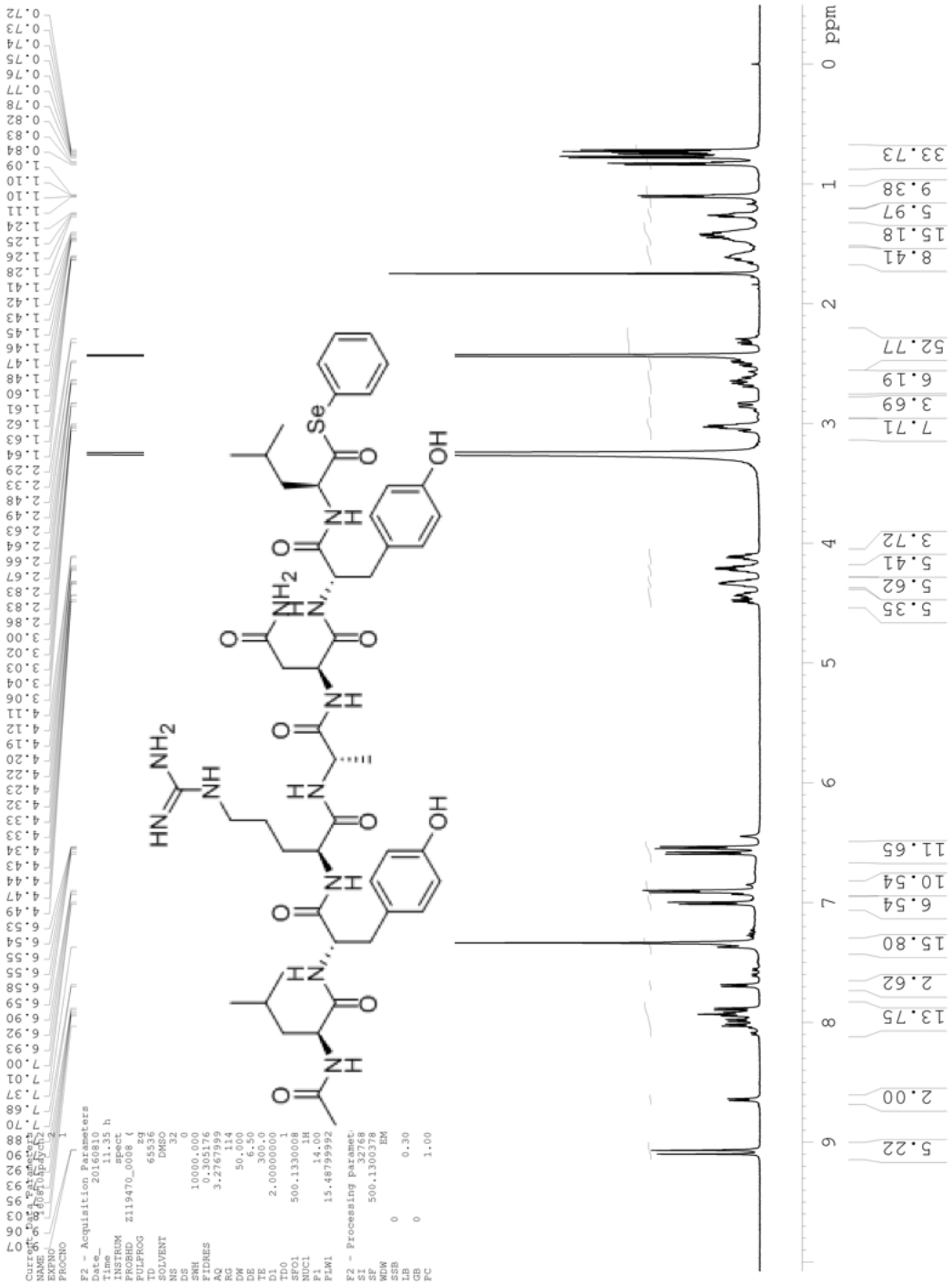
Ac-LYRANYA-SePh (17) (selenoesterified at 0^{o}C)



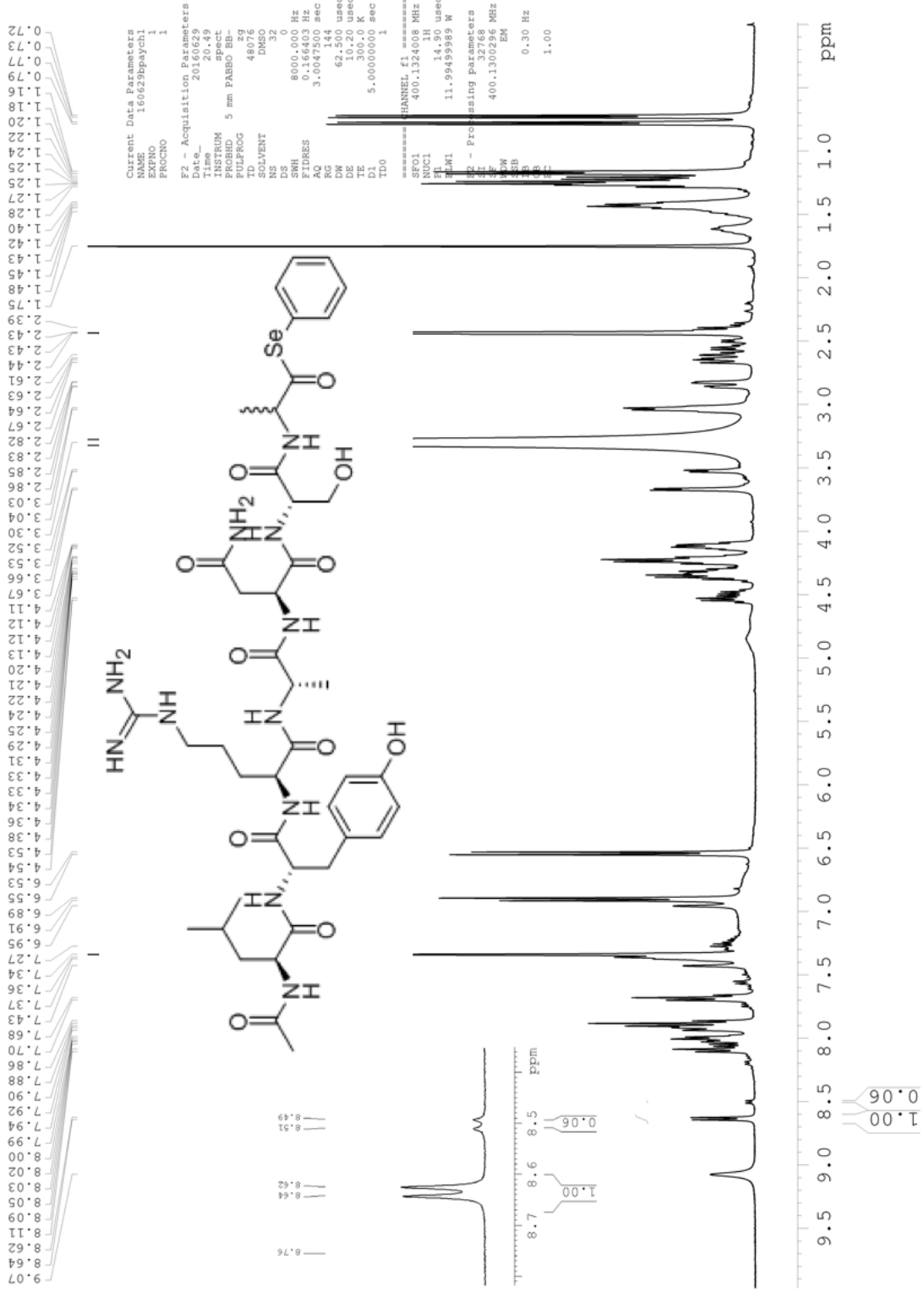
Ac-LYRANYF-SePh (18) (selenoesterified at 0^{o}C)



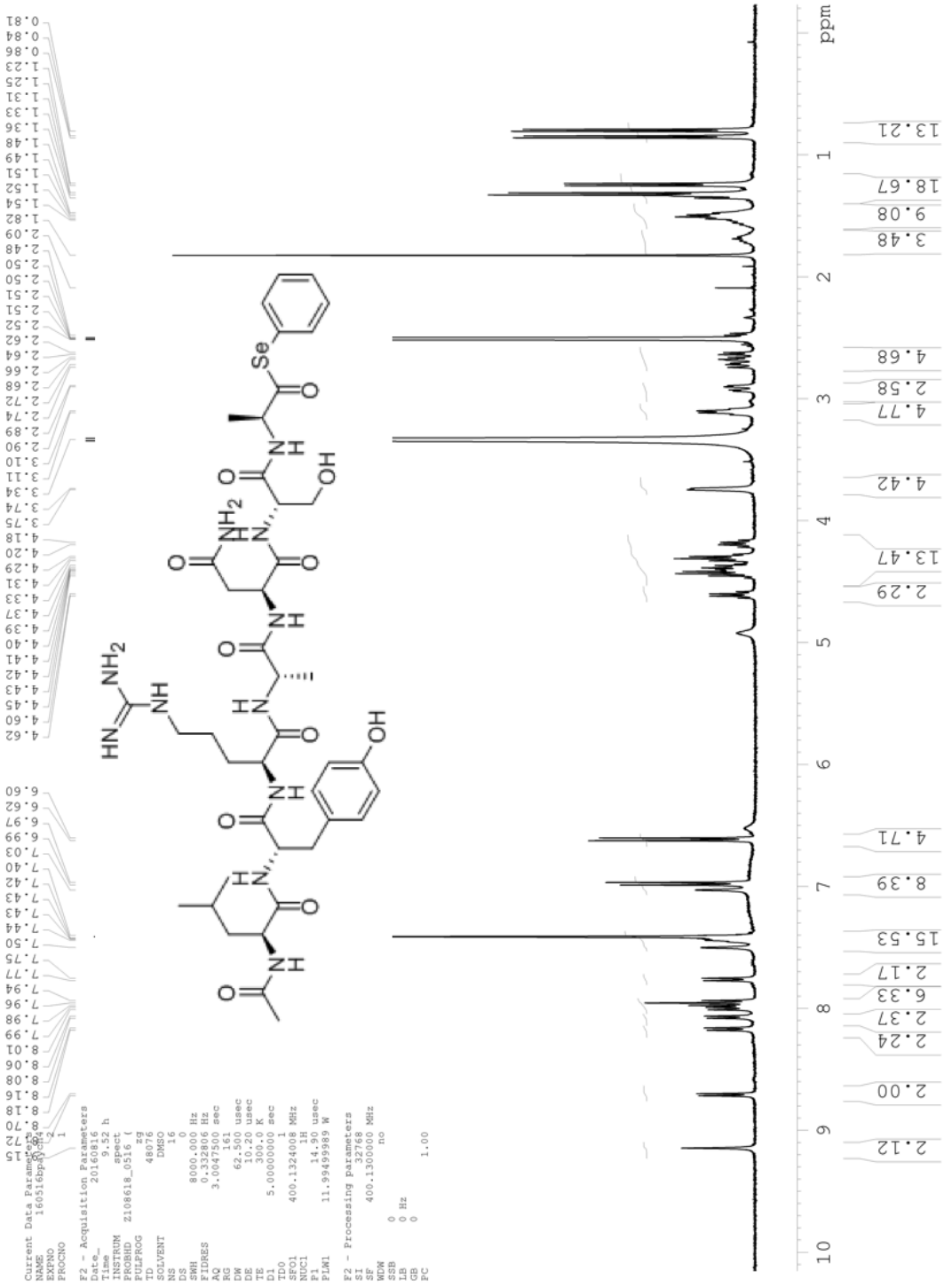
Ac-LYRANYL-SePh (19) (selenoesterified at 0°C)



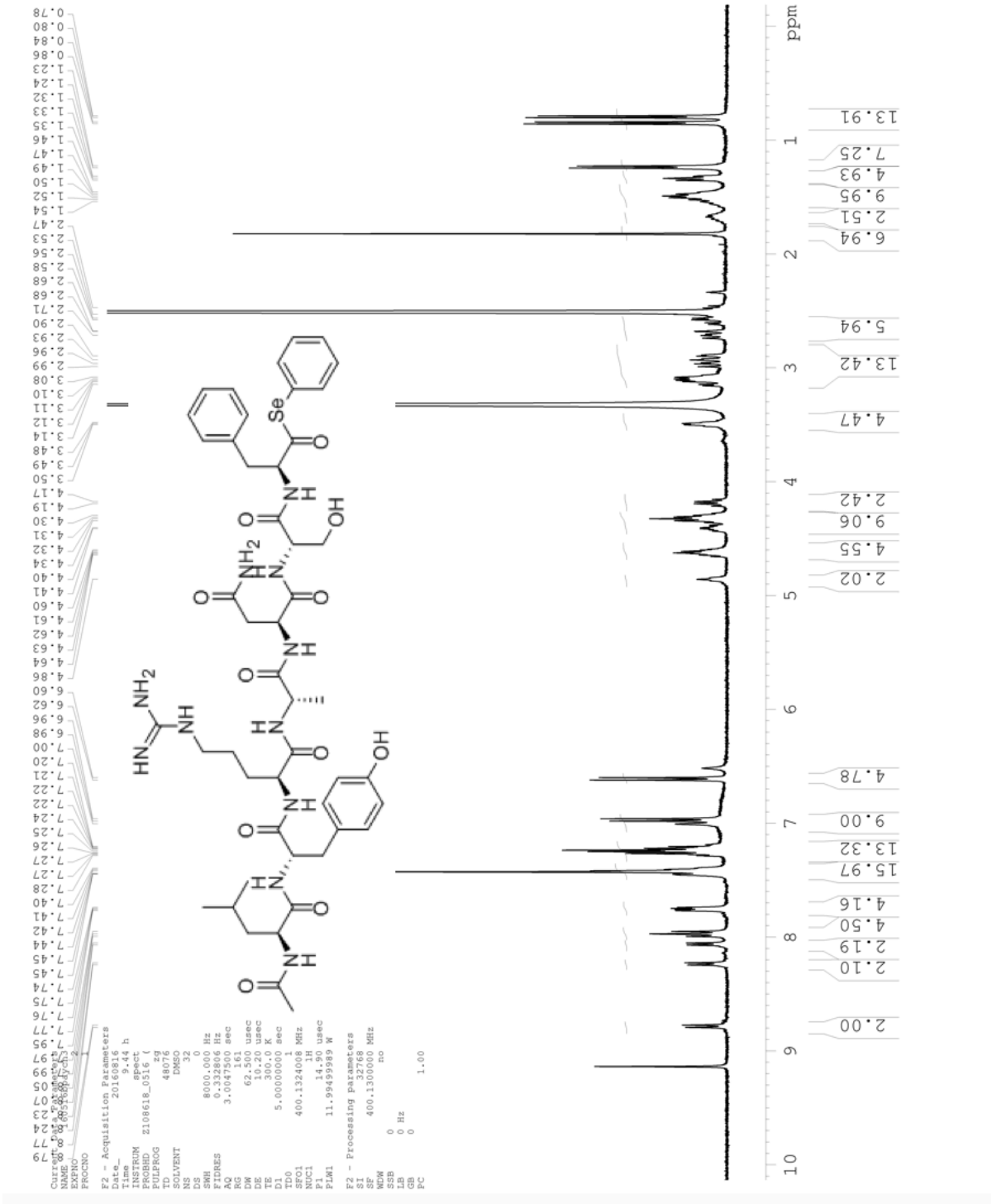
Ac-LYRANSA-SePh (20) (selenoesterified at 0°C)



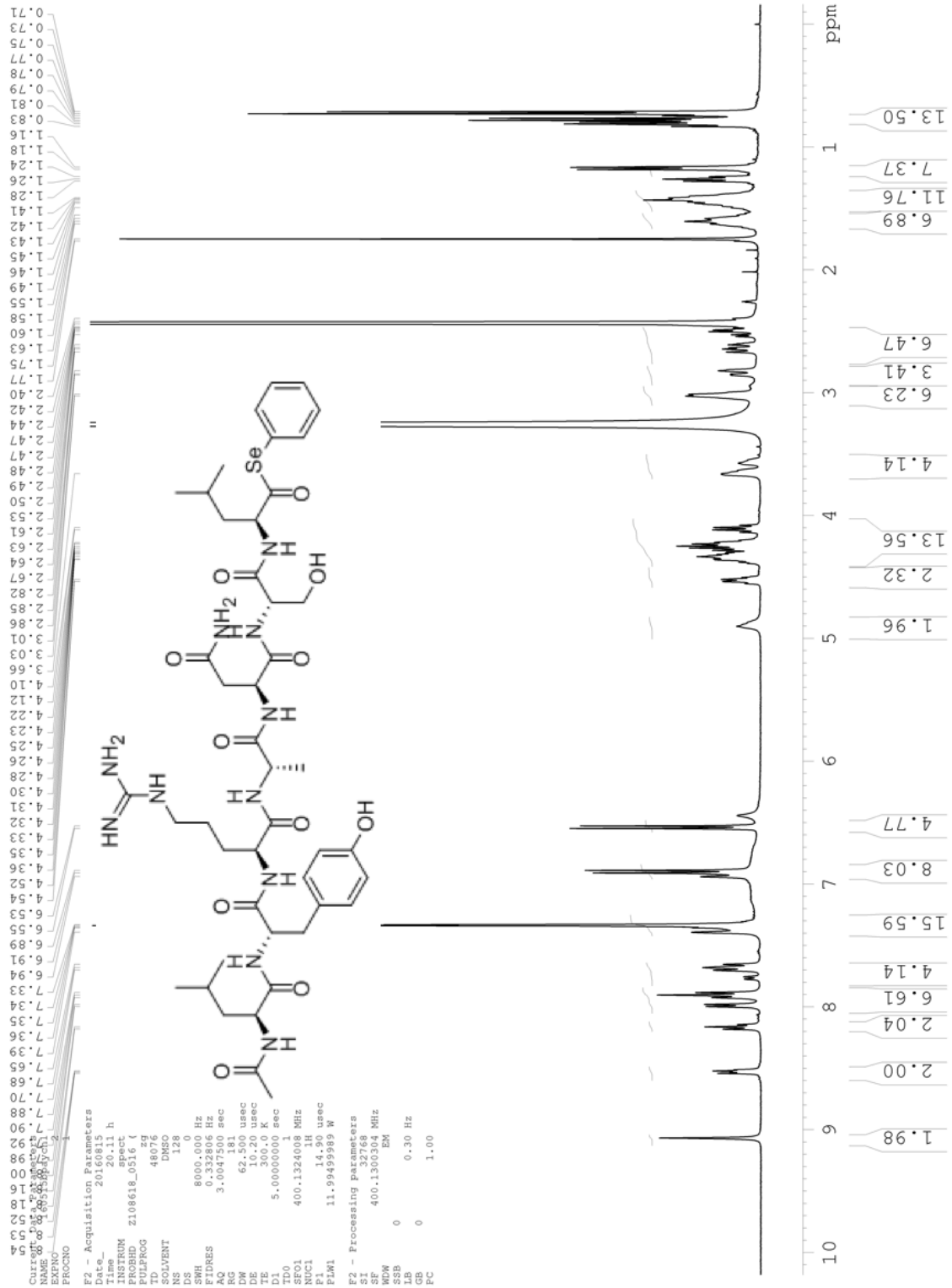
Ac-LYRANSA-SePh (20) (selenoesterified at -12°C)



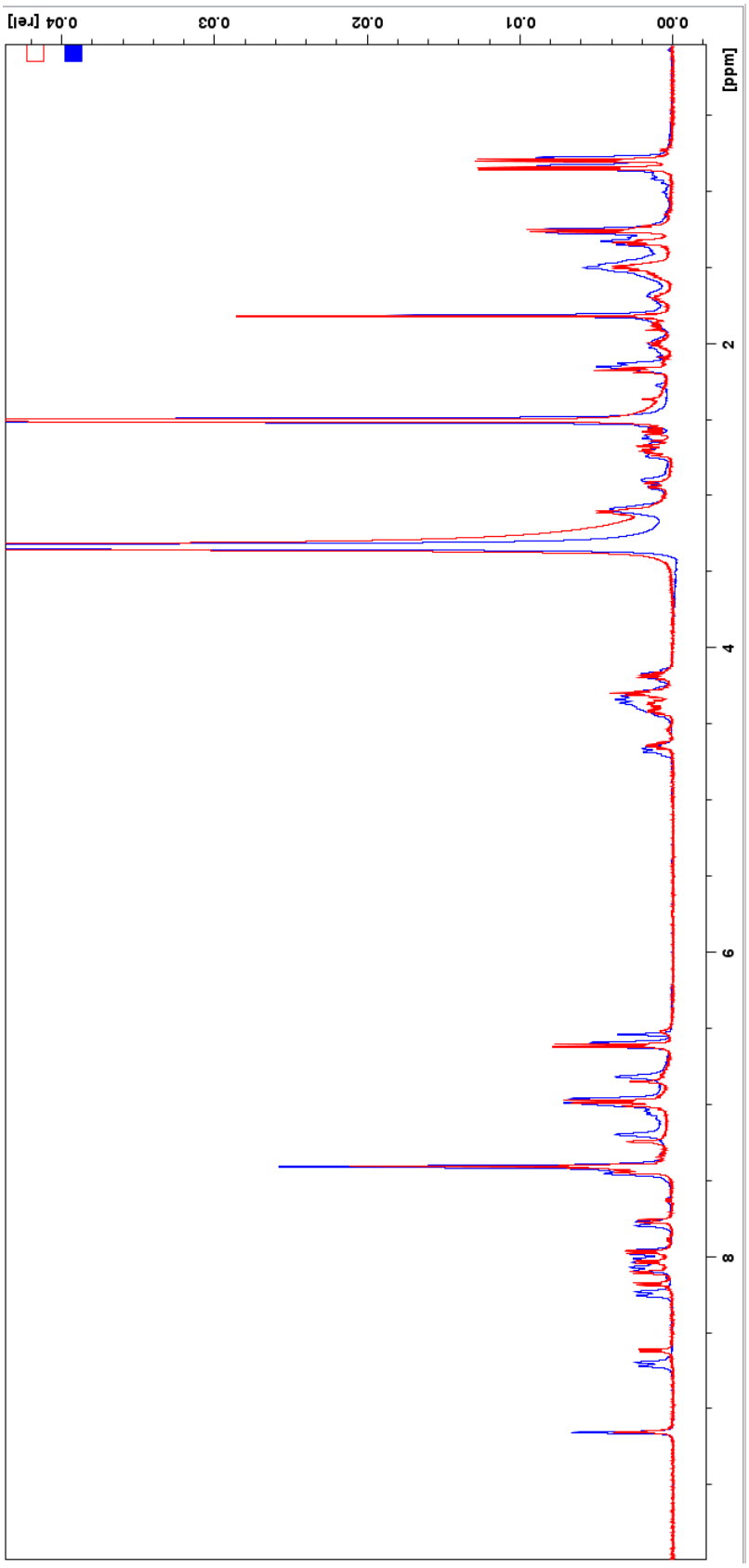
Ac-LYRANSF-SePh (21) (selenoesterified at 0°C)



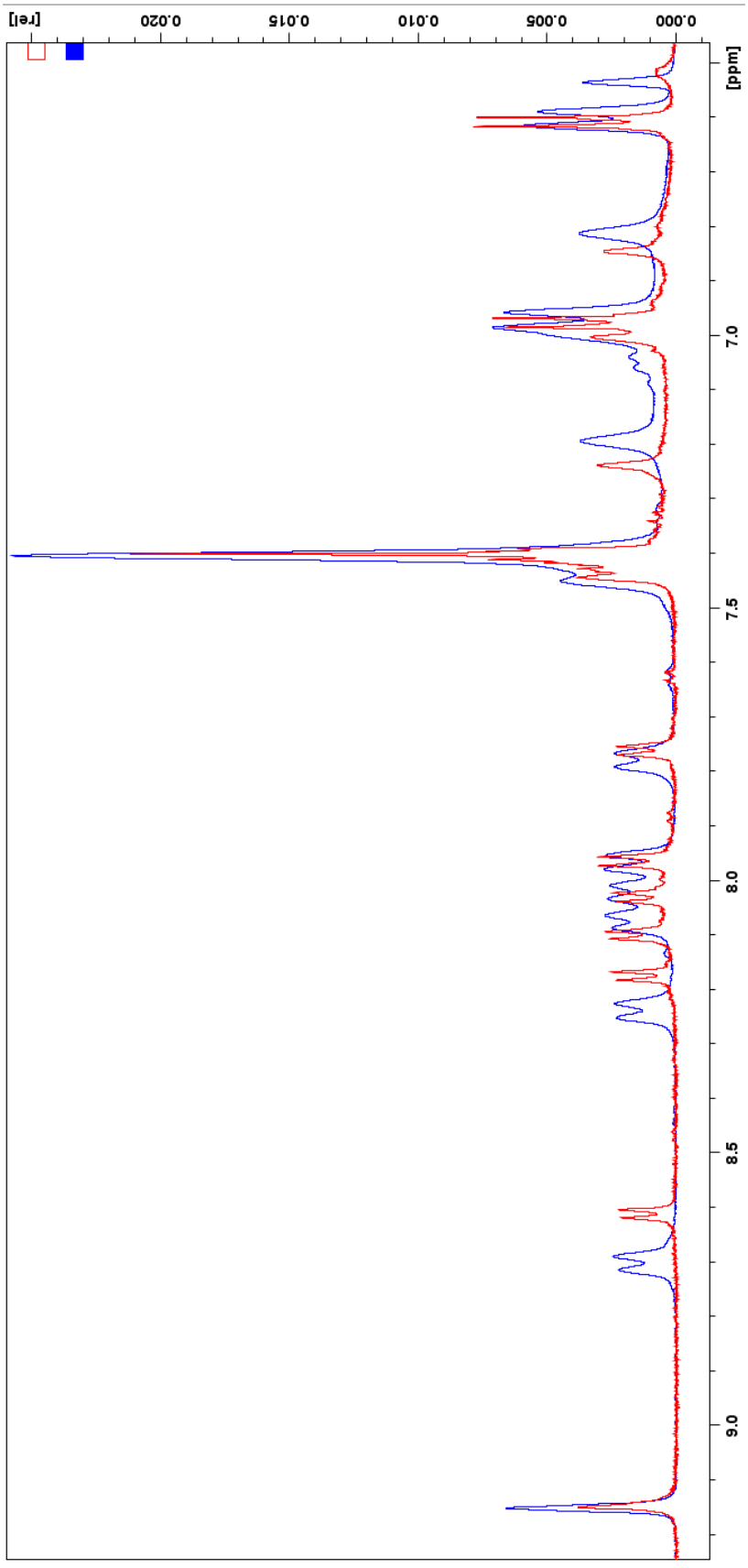
Ac-LYRANSL-SePh (22) (selenoesterified at 0^{o}C)



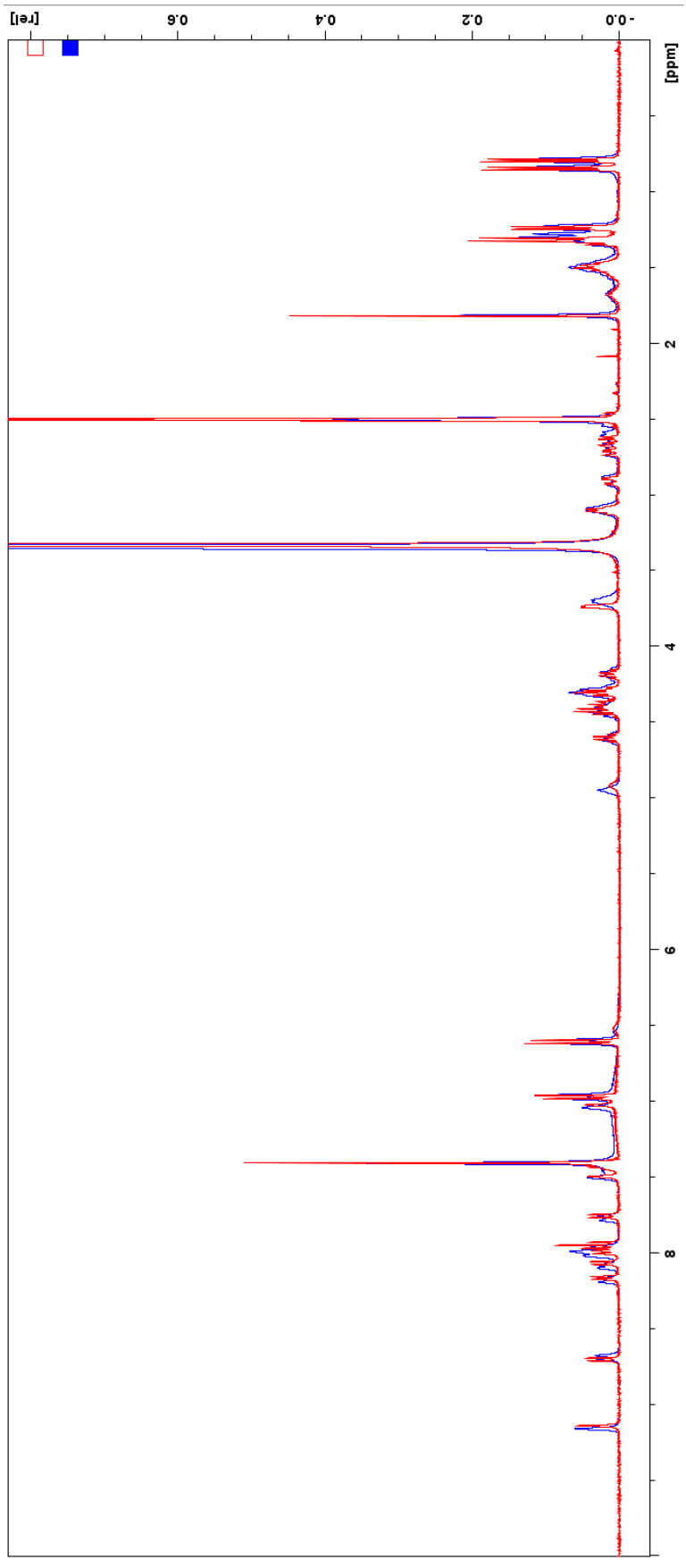
Ac-LYRANLQ-SePh (1) and Ac-LYRANDQ-SePh ^{1}H NMR Overlay
Red = Ac-LYRANLQ-SePh, Blue = Ac-LYRANDQ-SePh



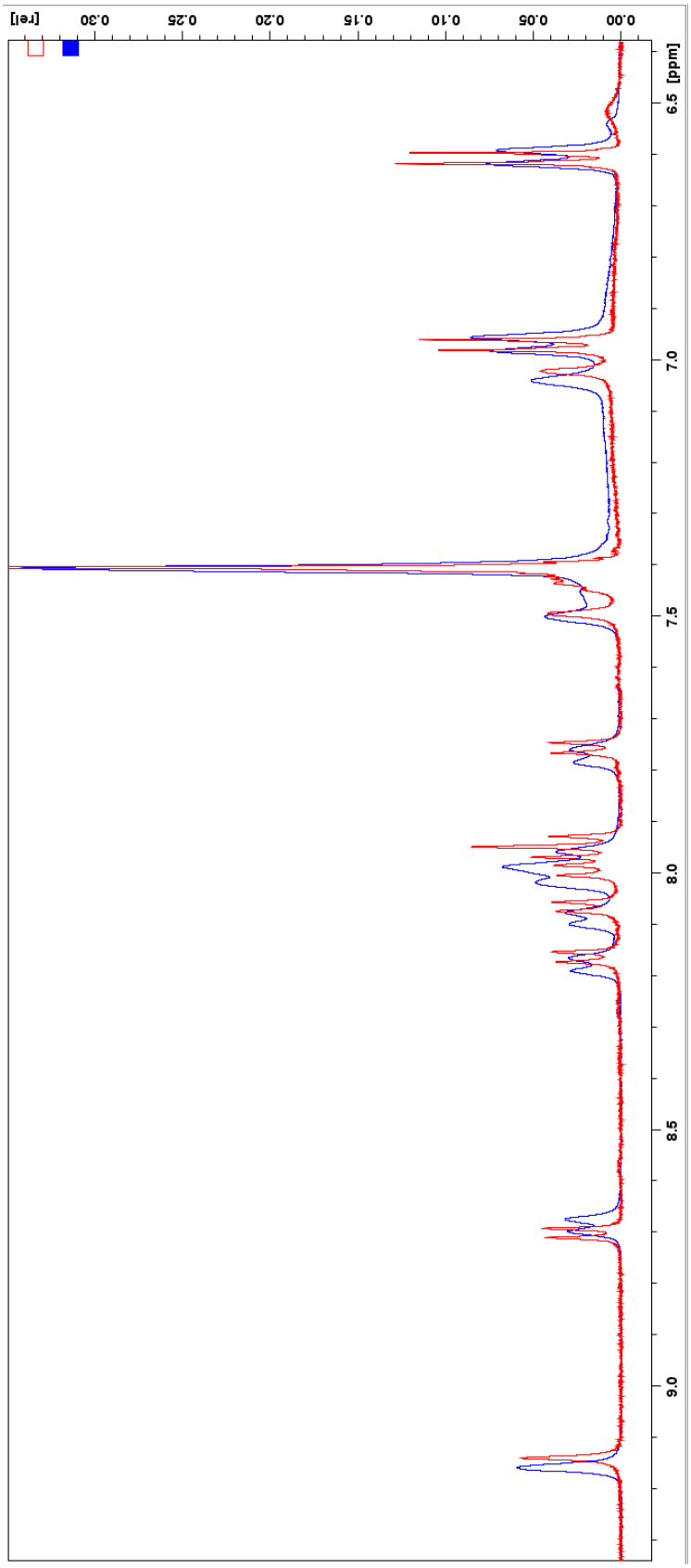
Ac-LYRANLQ-SePh (1) and Ac-LYRANDQ-SePh ^{1}H NMR Overlay
Red = Ac-LYRANLQ-SePh, Blue = Ac-LYRANDQ-SePh
Zoomed in between 6.5-9.2 ppm.



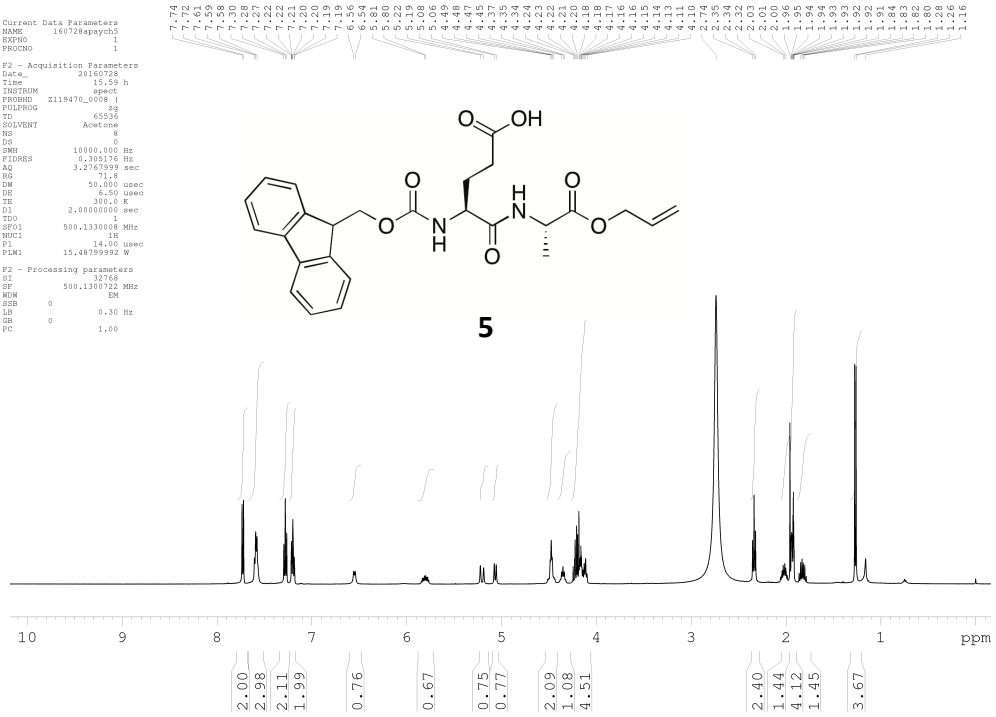
Ac-LYRANSLA-SePh (20) and Ac-LYRANSDA-SePh ^{1}H NMR Overlay
Red = Ac-LYRANSLA-SePh, Blue = Ac-LYRANSDA-SePh

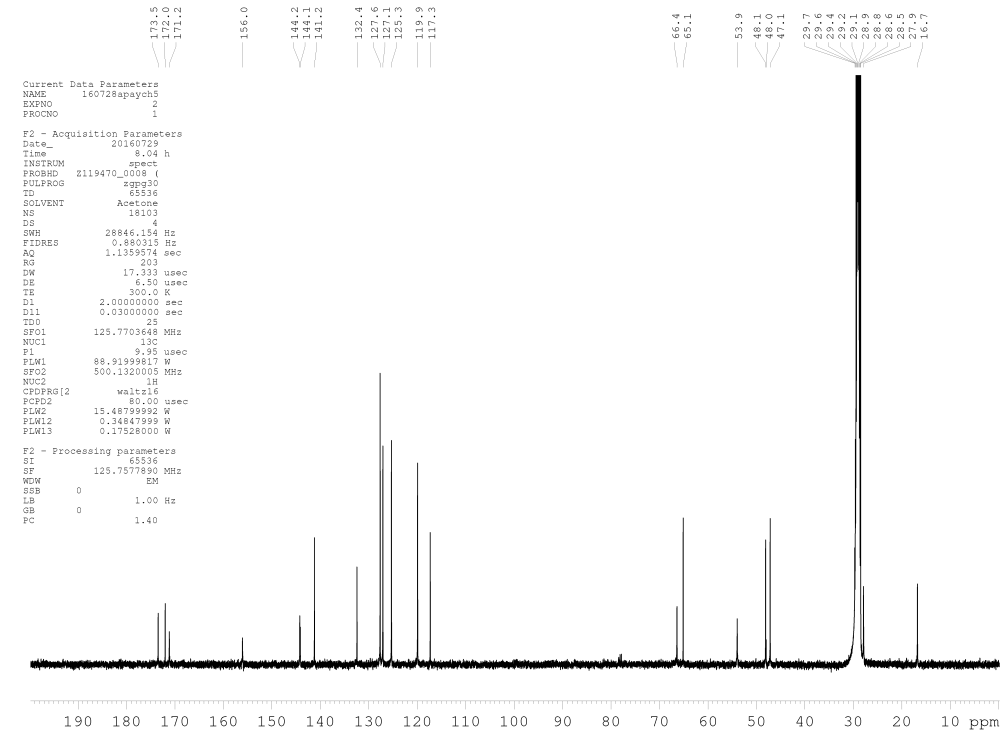


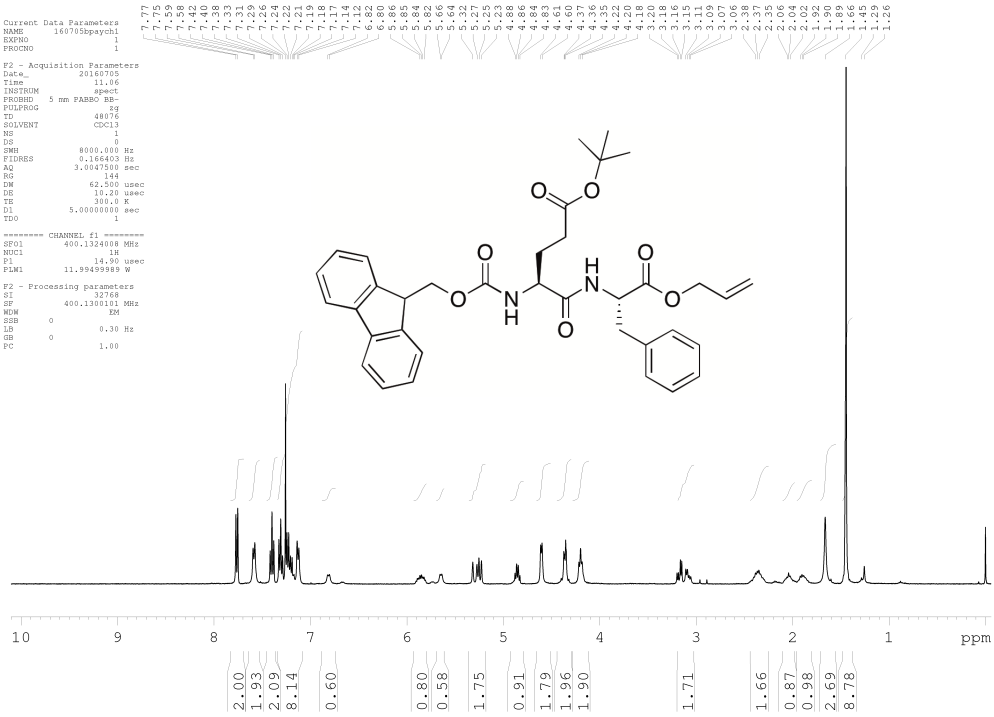
Ac-LYRANSLA-SePh (20) and Ac-LYRANSDA-SePh ^{1}H NMR Overlay
Red = Ac-LYRANSLA-SePh, Blue = Ac-LYRANSDA-SePh
Zoomed in between 6.5-9.2 ppm.



Dipeptide Building Blocks NMR Data



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PROCNO 1
F2 - Acquisition Parameters
Date_ 20160705
Time 11.06
INSTRUM spect
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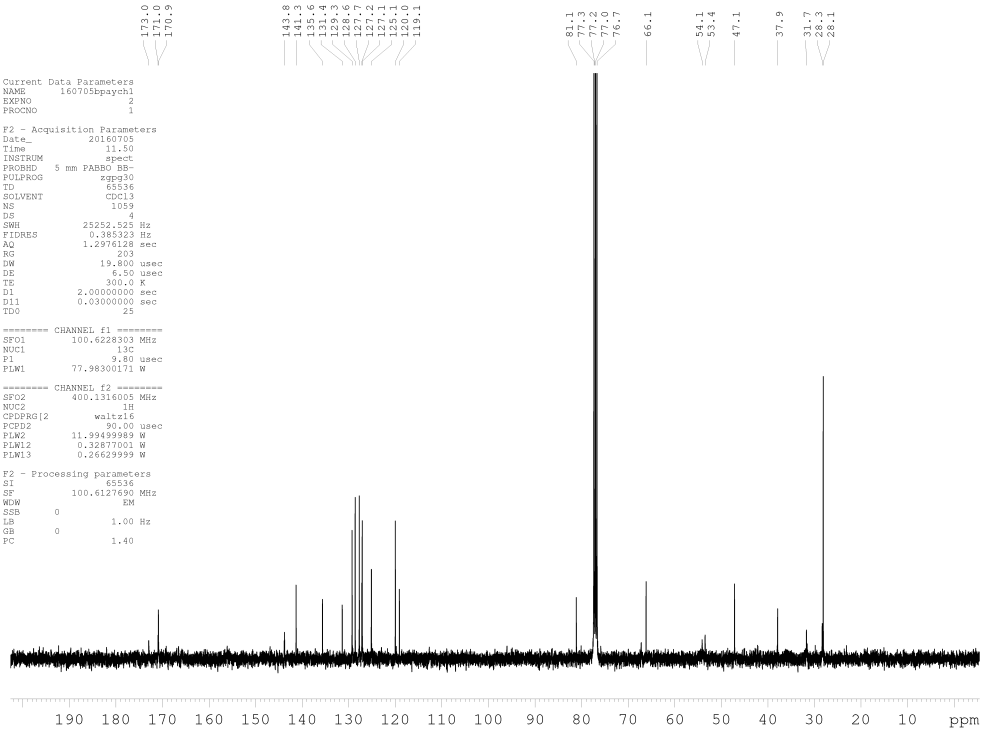
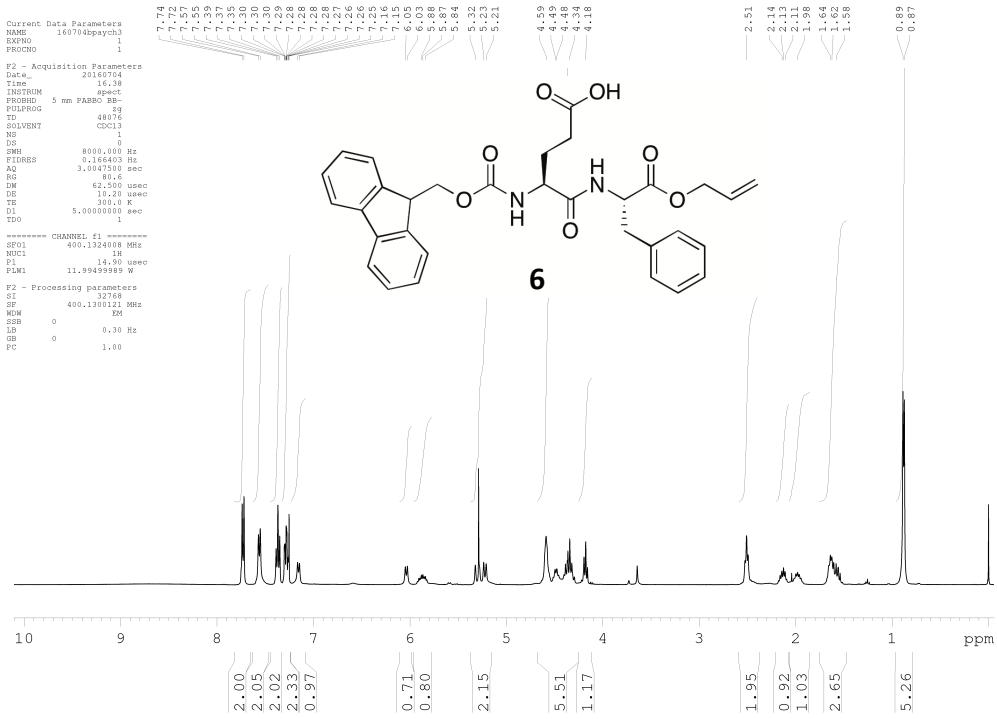
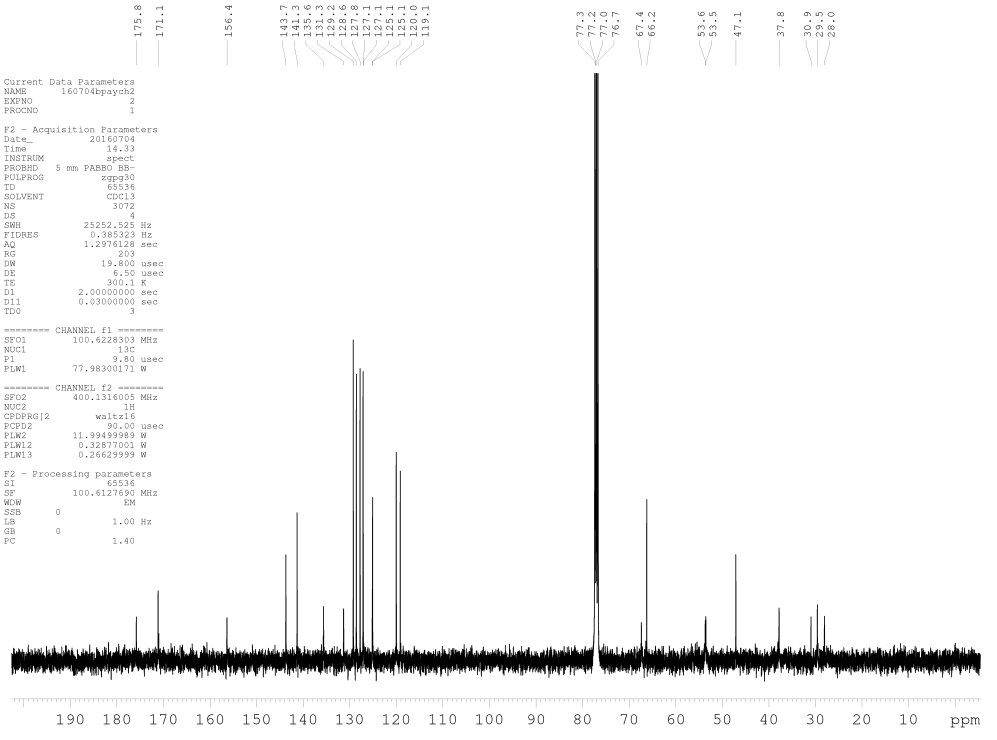
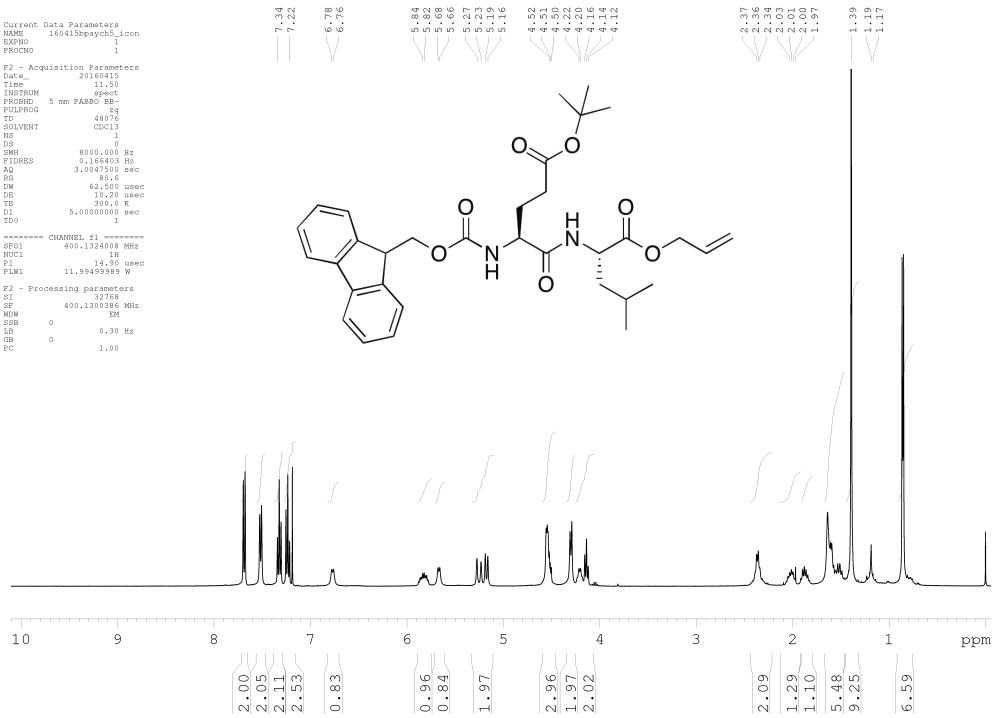
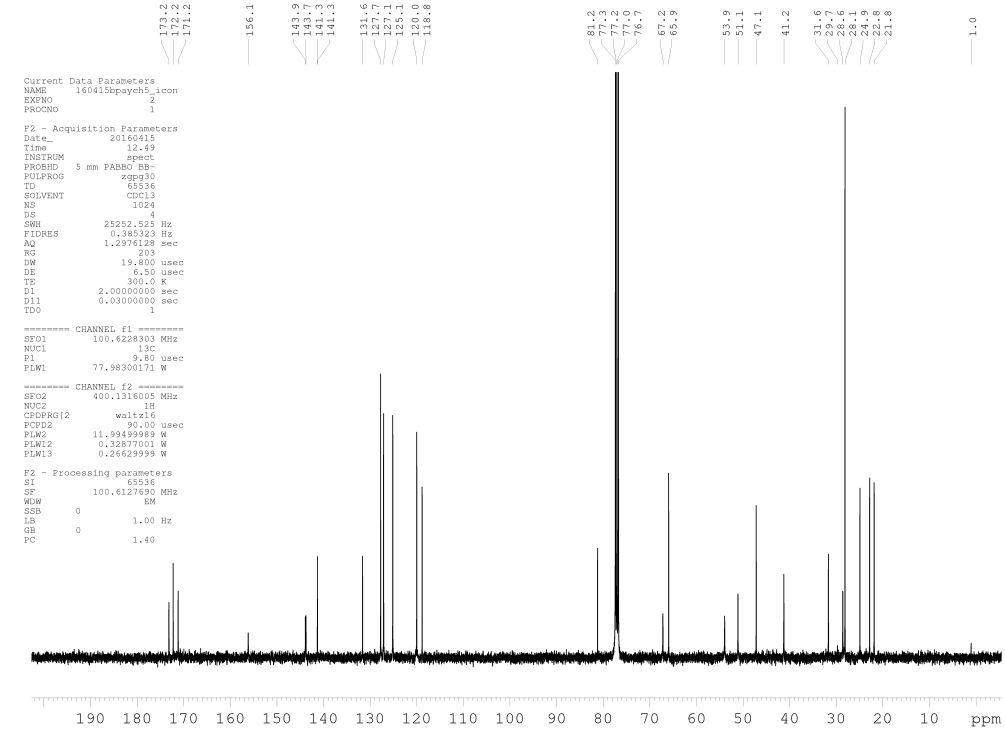
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 1
DS 0
SWH 8000.000 Hz
FIDRES 0.166403 Hz
AQ 3.0047500 sec
RG 144
DW 62.500 usec
DE 10.20 usec
TE 300.0 K
D1 5.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
SI 32768
SF 400.1300101 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.77 7.75 7.59 7.58 7.42 7.40 7.38 7.33 7.31 7.29 7.26 7.24 7.22 7.21 7.19 7.18 7.17 7.14 7.12 6.82 6.80 6.80 5.85 5.84 5.82 5.66 5.64 5.32 5.27 5.25 5.23 4.88 4.86 4.84 4.83 4.61 4.60 4.37 4.36 4.35 4.22 4.20 4.18 3.20 3.18 3.16 3.15 3.11 3.09 3.07 3.06 2.38 2.37 2.35 2.06 2.04 2.02 1.92 1.90 1.89 1.66 1.45 1.29 1.26
10 9 8 7 6 5 4 3 2 1 ppm
2.00 1.93 2.09 8.14 0.60 0.80 0.58 1.75 0.91 1.79 1.96 1.90 1.71 1.66 0.87 0.98 2.69 8.78

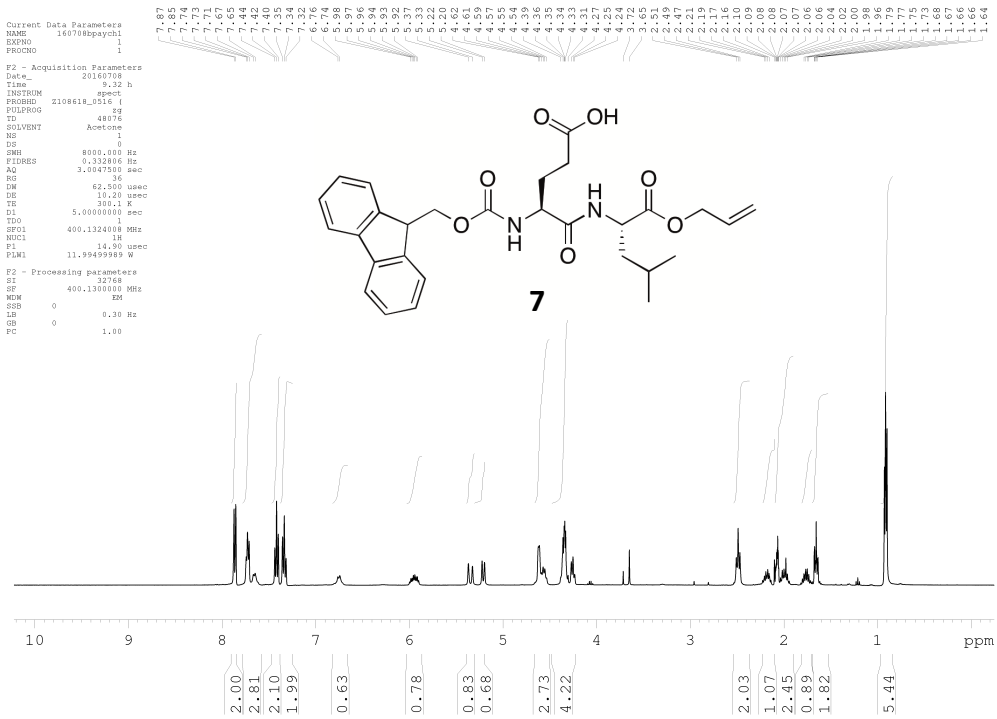

173.0 171.0 170.9 143.8 141.3 141.2 131.4 129.3 128.6 127.7 127.2 127.1 125.1 120.0 119.1 81.1 77.3 77.2 77.0 76.7 66.1 54.1 53.4 47.1 37.9 31.7 28.3 28.1
Current Data Parameters
NAME 160705bpaych1
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160705
Time 11.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1059
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 25
======== CHANNEL f1 ========
SFO1 100.6228303 MHz
NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.26629999 W
F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.74 7.72 7.57 7.55 7.39 7.37 7.35 7.30 7.30 7.29 7.28 7.28 7.28 7.27 7.26 7.25 7.16 7.15 6.05 6.03 5.88 5.87 5.84 5.32 5.23 5.21 4.59 4.49 4.48 4.34 4.18 2.51 2.14 2.13 2.11 1.98 1.64 1.62 1.58 0.89 0.87
Current Data Parameters
NAME 160704bpaych3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160704
Time 16.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 1
DS 0
SWH 8000.000 Hz
FIDRES 0.166403 Hz
AQ 3.0047500 sec
RG 80.6
DW 62.500 usec
DE 10.20 usec
TE 300.0 K
D1 5.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
SI 32768
SF 400.1301121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
OH
O
O
N
H
O
O
N
H
O
O
6
10 9 8 7 6 5 4 3 2 1 ppm
2.00 2.05 2.02 2.33 0.97 0.71 0.80 2.15 5.51 1.17 1.95 0.92 1.03 2.65 5.26


175.8 171.1 156.4 143.7 141.3 135.6 131.3 129.2 128.6 127.8 127.1 127.1 125.1 125.1 120.0 119.1 77.3 77.2 77.0 76.7 67.4 66.2 53.6 53.5 47.1 37.8 30.9 29.5 28.0
Current Data Parameters
NAME 160704bpaych2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160704
Time 14.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3072
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 3
======== CHANNEL f1 ========
SFO1 100.6228303 MHz
NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.26629999 W
F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Current Data Parameters
NAME 160415bpaych5_icon
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160415
Time 11.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 1
DS 0
SWH 8000.000 Hz
FIDRES 0.166403 Hz
AQ 3.0047500 sec
RG 80.6
DW 62.500 usec
DE 10.20 usec
TE 300.0 K
D1 5.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
SI 32768
SF 400.1300386 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.34
7.22
6.78
6.76
5.84
5.82
5.68
5.66
5.27
5.23
5.18
5.16
4.52
4.51
4.50
4.22
4.20
4.16
4.14
4.12
2.37
2.36
2.34
2.03
2.01
2.00
1.97
1.39
1.19
1.17
O
O
O
N
H
O
N
H
O
O
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.05
2.11
2.53
0.83
0.96
0.84
1.97
2.96
1.97
2.02
2.09
1.29
1.10
5.48
9.25
6.59


173.2
172.2
171.2
156.1
143.9
143.7
141.3
141.3
131.6
127.7
127.1
125.1
120.0
118.8
81.2
71.3
77.2
77.0
76.7
67.2
65.9
53.9
51.1
47.1
41.2
31.6
28.7
28.6
28.1
24.9
22.8
21.8
1.0
Current Data Parameters
NAME 160415bpaych5_icon
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160415
Time 12.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228303 MHz
NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.26629999 W
F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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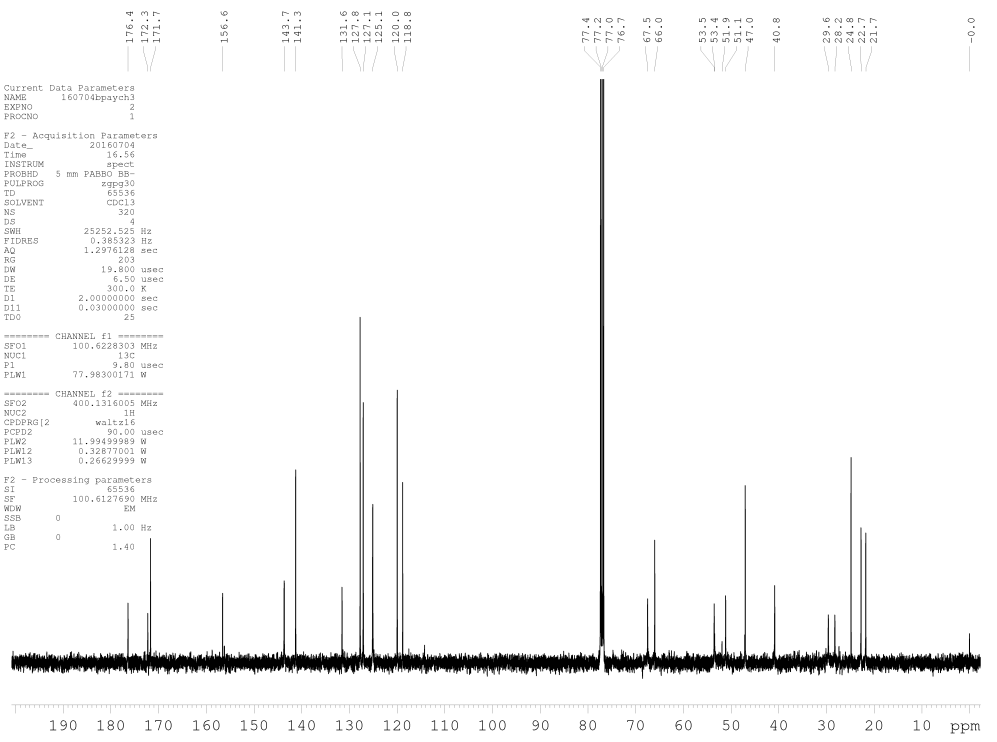
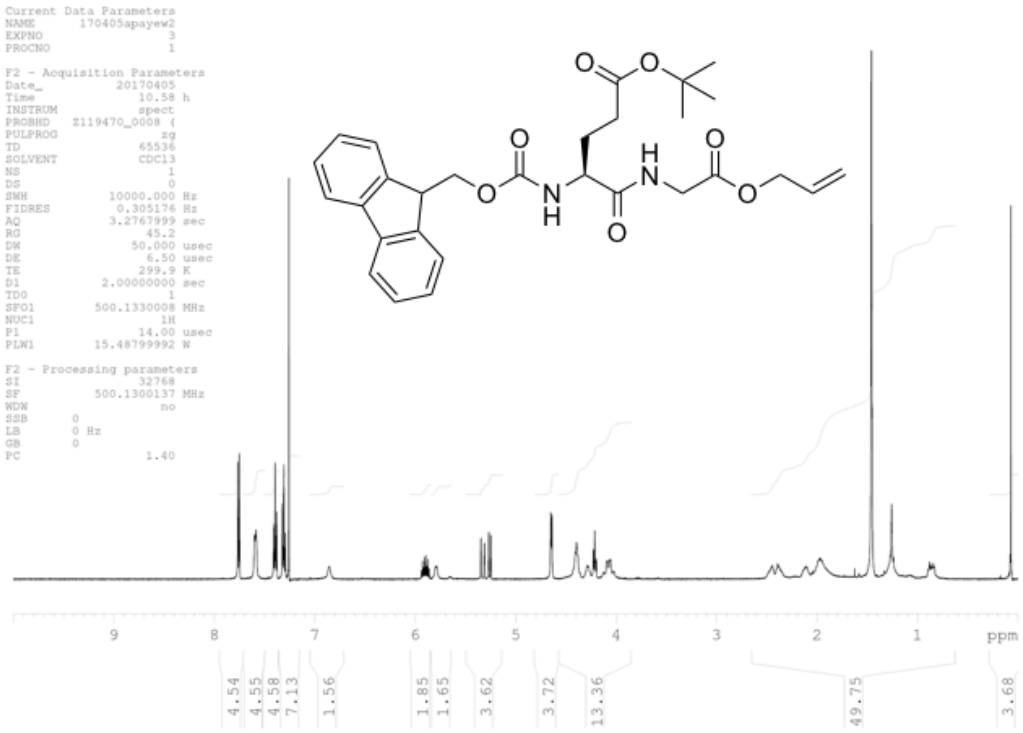
NAME 160708bpaych1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160708
Time 9.32 h
INSTRUM spect
PROBHD Z108618_0516 (
PULPROG zg
TD 48076
SOLVENT Acetone
NS 1
DS 0
SWH 8000.000 Hz
FIDRES 0.332806 Hz
AQ 3.0047500 sec
RG 16
DW 62.500 usec
DE 10.20 usec
TE 300.1 K
D1 5.00000000 sec
TD0 1
SFO1 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.87 7.85 7.74 7.73 7.71 7.67 7.65 7.44 7.42 7.40 7.35 7.34 7.32 6.76 6.74 5.98 5.97 5.96 5.94 5.93 5.92 5.37 5.33 5.22 5.20 4.62 4.61 4.59 4.57 4.55 4.54 4.39 4.36 4.35 4.34 4.33 4.31 4.27 4.25 4.24 3.72 3.65 2.51 2.49 2.47 2.21 2.19 2.17 2.16 2.10 2.09 2.08 2.08 2.07 2.07 2.06 2.06 2.04 2.02 2.00 1.98 1.96 1.79 1.79 1.77 1.75 1.73 1.68 1.67 1.66 1.66 1.64
O
OH
O
N
H
O
H
N
O
O
O
7
10 9 8 7 6 5 4 3 2 1 ppm
2.00 2.81 2.10 1.99 0.63 0.78 0.83 0.68 2.73 4.22 2.03 1.07 2.45 0.89 1.82 5.44


176.4 172.3 171.7 156.6 143.7 141.3 131.6 127.8 127.1 125.1 120.0 118.8 77.4 77.2 77.0 76.7 67.5 66.0 53.5 53.4 51.9 51.1 47.0 40.8 29.6 28.2 24.8 22.7 21.7 -0.0
Current Data Parameters
NAME 160704bpaych3
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160704
Time 16.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 320
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 25
======== CHANNEL f1 ========
SFO1 100.6228303 MHz
NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.26629999 W
F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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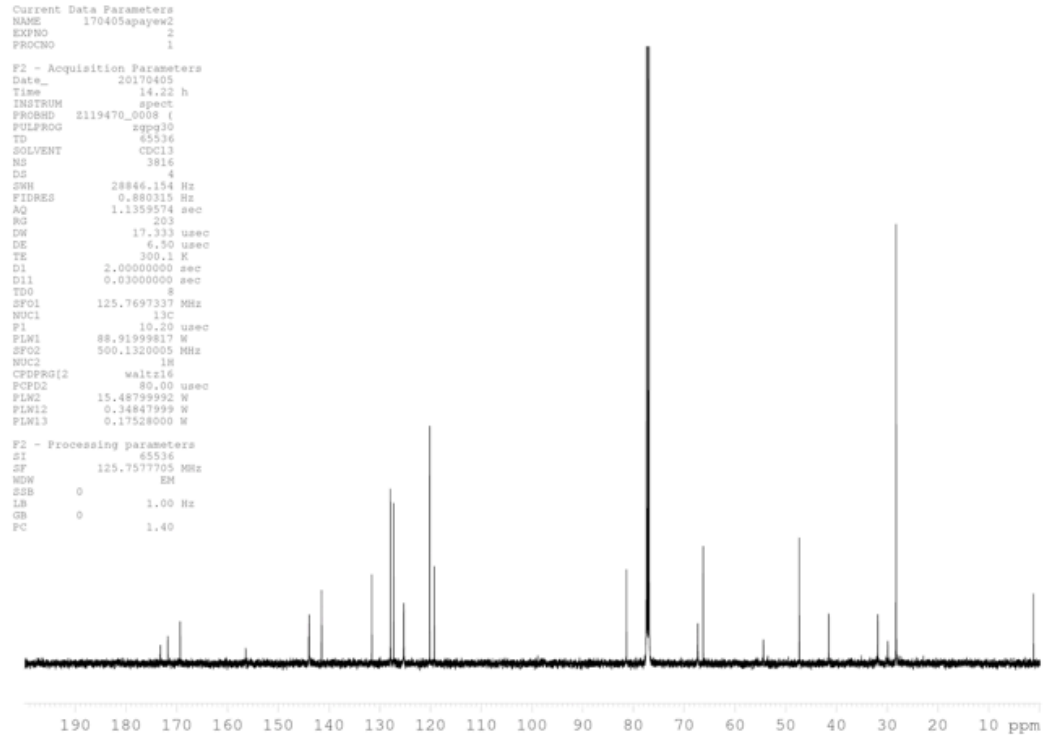
NAME 170405apayew2
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170405
Time 10.58 h
INSTRUM spect
PROBHD Z119470_0008 (
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 1
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 45.2
DW 50.000 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 14.00 usec
PLW1 15.48799992 W
F2 - Processing parameters
SI 32768
SF 500.1300137 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40
O
O
O
N
H
H
N
O
O
O
9
8
7
6
5
4
3
2
1
ppm
4.54
4.55
4.58
7.13
1.56
1.85
1.65
3.62
3.72
13.36
49.75
3.68


Current Data Parameters
NAME 170405apayew2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170405
Time 14.22 h
INSTRUM spect
PROBHD Z119470_0008 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3816
DS 4
SWH 28846.154 Hz
FIDRES 0.880315 Hz
AQ 1.1359574 sec
RG 203
DW 17.333 usec
DE 6.50 usec
TE 300.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 8
SFO1 125.7697337 MHz
NUC1 13C
P1 10.20 usec
PLW1 88.91999817 W
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.48799992 W
PLW12 0.34847999 W
PLW13 0.17528000 W
F2 - Processing parameters
SI 65536
SF 125.7577705 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190
180
170
160
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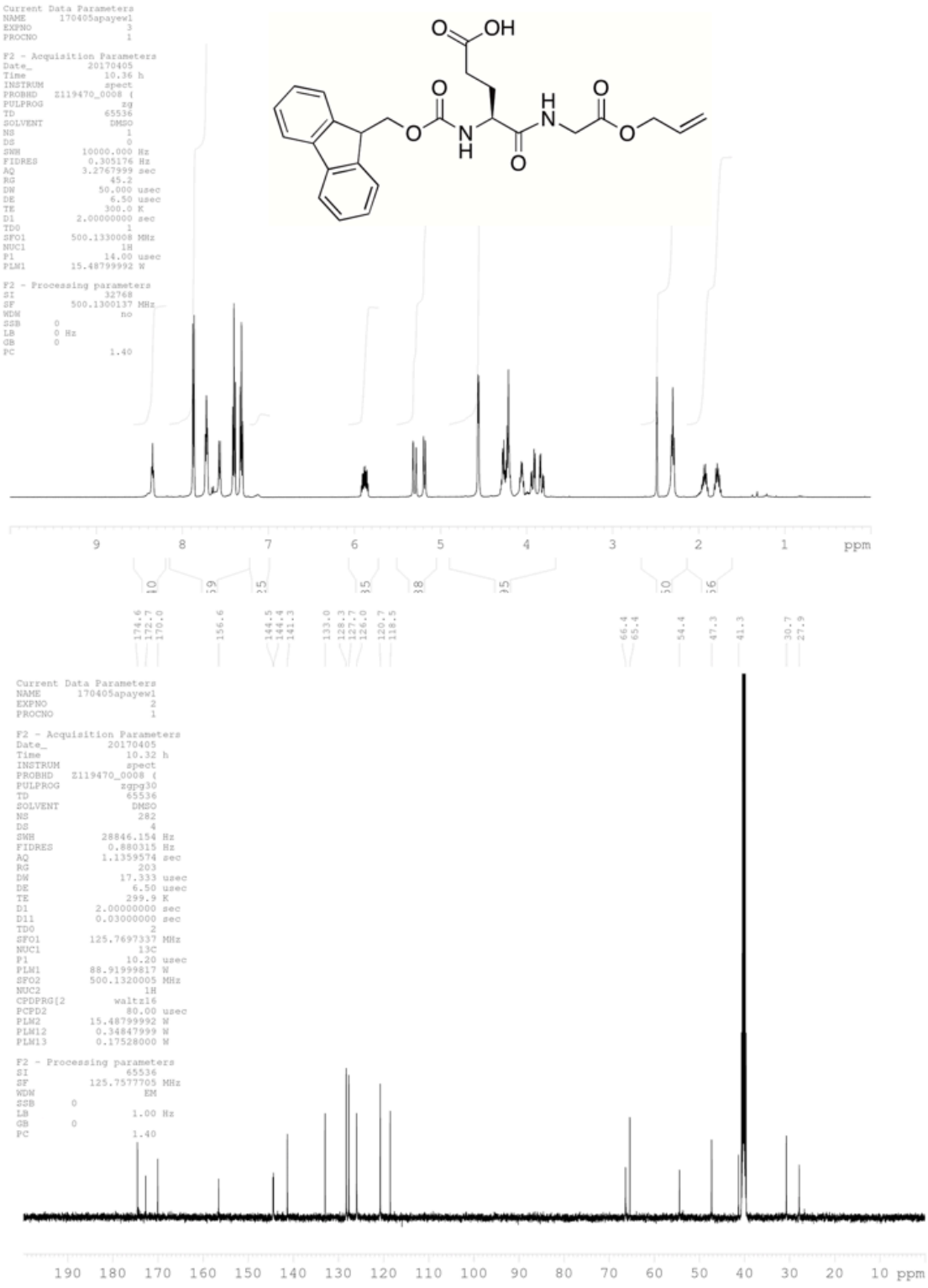
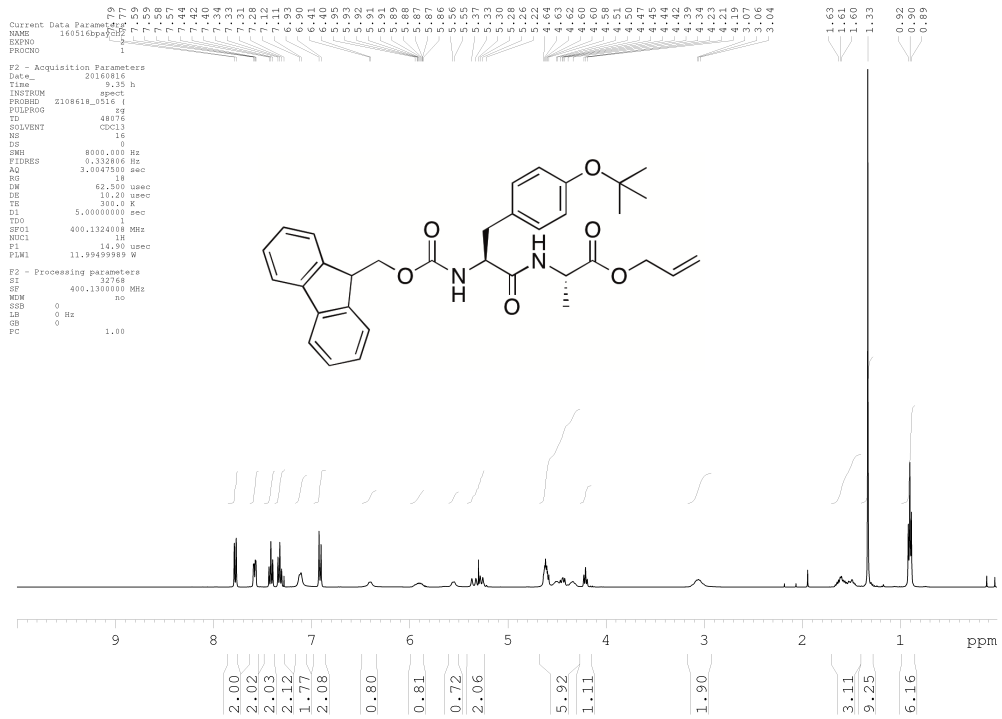
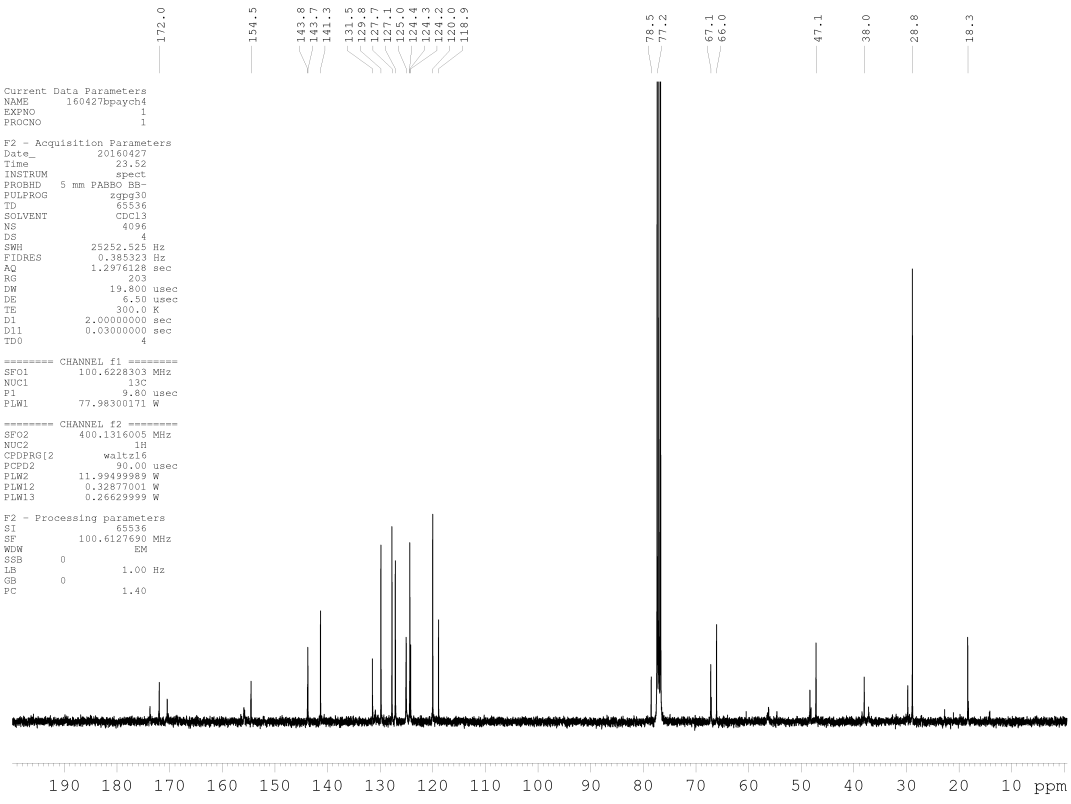
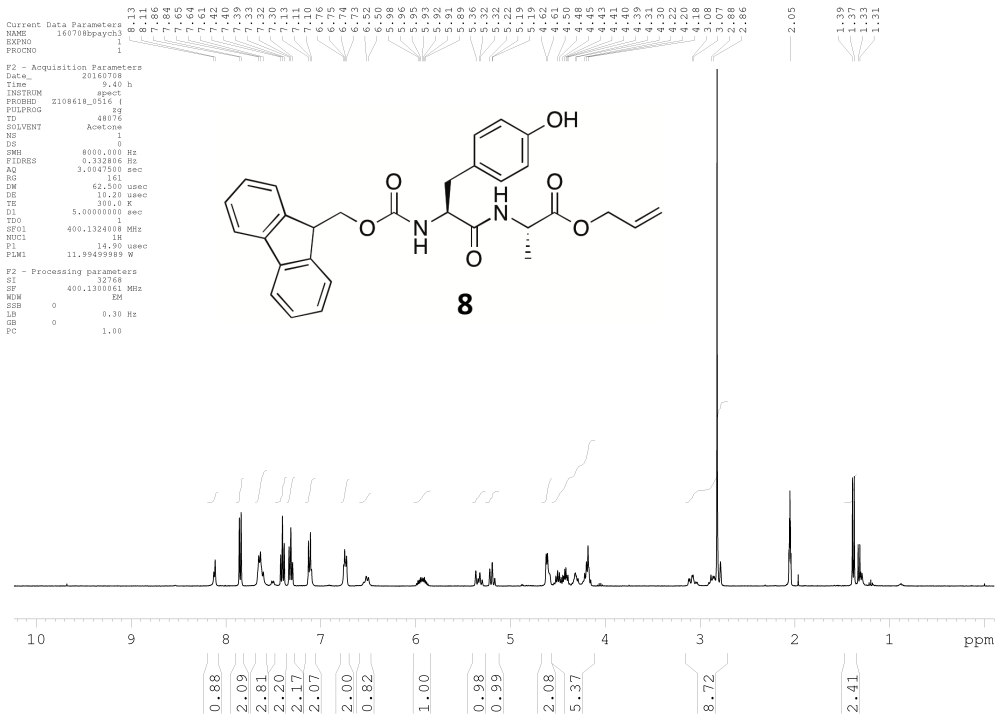
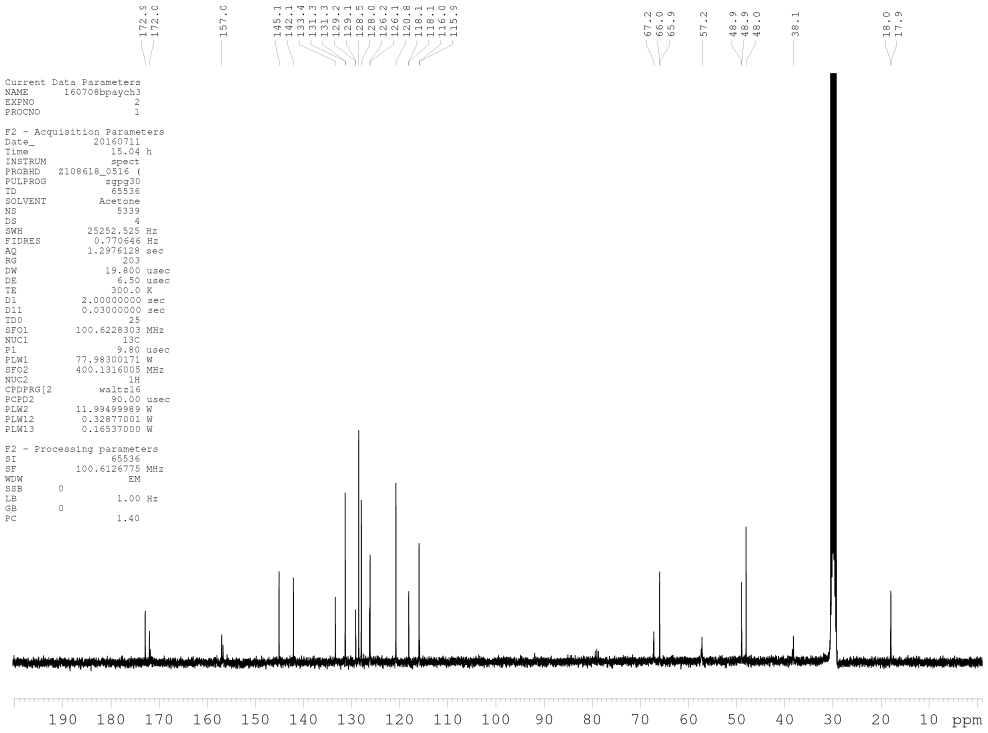
90
80
70
60
50
40
30
20
10
ppm

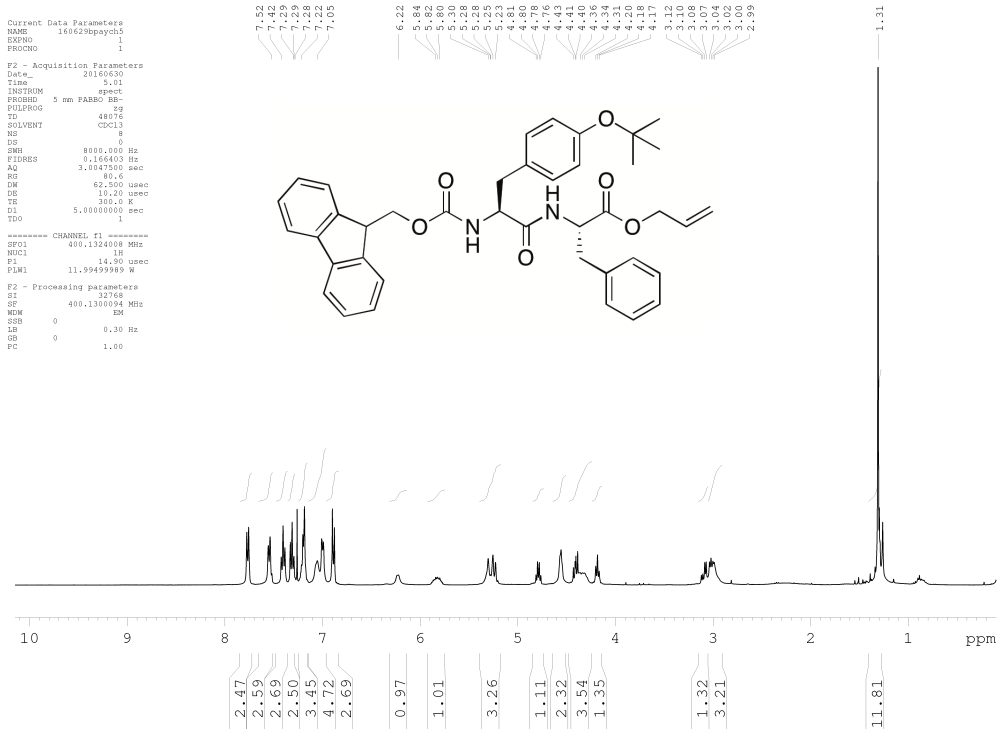

Current Data Parameters
NAME 170405apayew1
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170405
Time 10.36 h
INSTRUM spect
PROBHD Z119470_0008 (
PULPROG zg
TD 65536
SOLVENT DMSO
NS 1
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 45.2
DW 50.000 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 14.00 usec
PLW1 15.48799992 W
F2 - Processing parameters
SI 32768
SF 500.1300137 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40
O
OH
O
N
H
O
H
N
O
O
9 8 7 6 5 4 3 2 1 ppm
174.6
172.7
170.0
156.6
144.5
144.4
141.3
133.0
128.3
127.7
126.0
120.7
118.5
66.4
65.4
54.4
47.3
41.3
30.7
27.9
Current Data Parameters
NAME 170405apayew1
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170405
Time 10.32 h
INSTRUM spect
PROBHD Z119470_0008 (
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 282
DS 4
SWH 28846.154 Hz
FIDRES 0.880315 Hz
AQ 1.1359574 sec
RG 203
DW 17.333 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 2
SFO1 125.7697337 MHz
NUC1 13C
P1 10.20 usec
PLW1 88.91999817 W
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.48799992 W
PLW12 0.34847999 W
PLW13 0.17528000 W
F2 - Processing parameters
SI 65536
SF 125.7577705 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

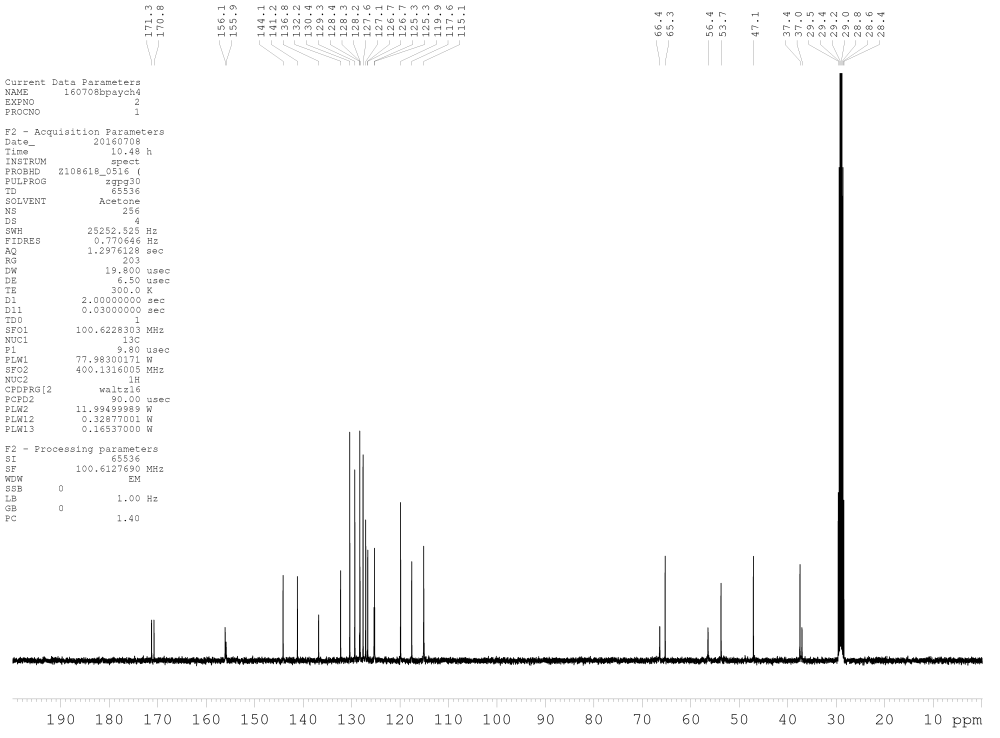

Current Data Parameters
NAME 160516bpaych2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160816
Time 9.35 h
INSTRUM spect
PROBHD Z108618_0516 (
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 16
DS 0
SWH 8000.000 Hz
FIDRES 0.332806 Hz
AQ 3.0047500 sec
RG 18
DW 62.500 usec
DE 10.20 usec
TE 300.0 K
D1 5.00000000 sec
TD0 1
SFO1 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
2.00
2.02
2.03
2.12
1.77
2.08
0.80
0.81
0.72
2.06
5.92
1.11
1.90
3.11
9.25
6.16

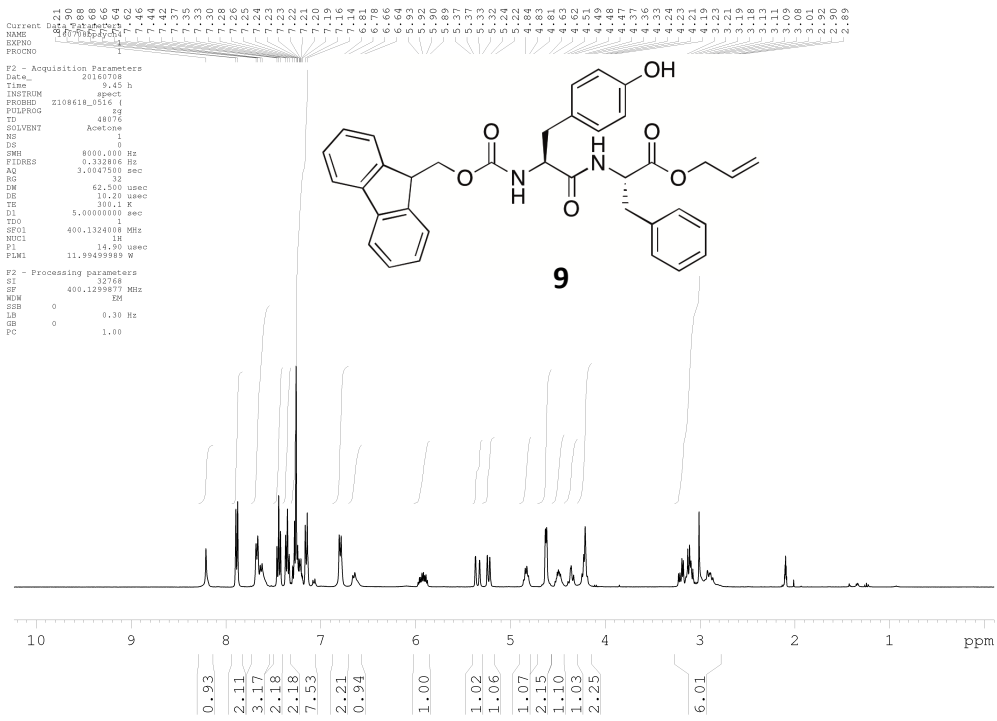

172.0
154.5
143.8
143.7
141.3
131.5
129.8
127.7
127.1
125.0
124.4
124.3
124.2
120.0
118.9
78.5
77.2
67.1
66.0
47.1
38.0
28.8
18.3
Current Data Parameters
NAME 160427bpaych4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160427
Time 23.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4096
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 4
======== CHANNEL f1 ========
SFO1 100.6228303 MHz
NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.26629999 W
F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

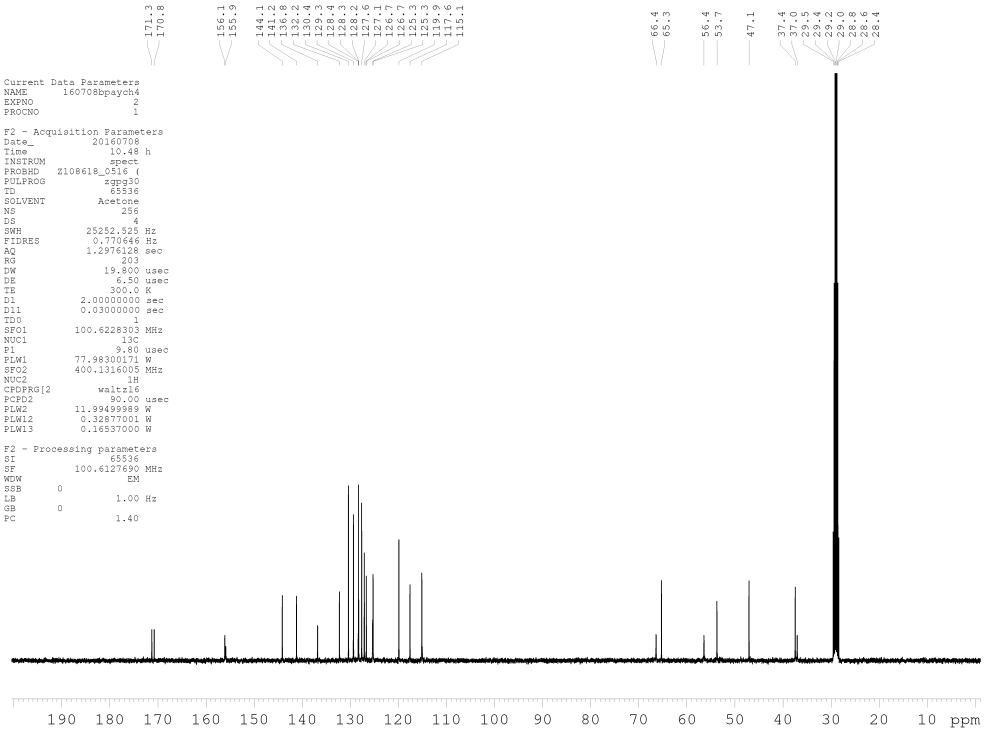

8.13
8.11
7.86
7.84
7.65
7.64
7.61
7.42
7.40
7.39
7.33
7.32
7.30
7.13
7.11
7.10
6.76
6.75
6.74
6.73
6.52
6.50
5.98
5.96
5.95
5.93
5.92
5.91
5.89
5.36
5.32
5.22
5.22
5.19
4.62
4.61
4.50
4.48
4.46
4.45
4.43
4.41
4.40
4.39
4.31
4.30
4.22
4.20
4.18
3.08
3.07
2.88
2.86
2.05
1.39
1.37
1.33
1.31
Current Data Parameters
NAME 160708bpaych3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160708
Time 9.40 h
INSTRUM spect
PROBHD Z108618_0516 (
PULPROG zg
TD 48076
SOLVENT Acetone
NS 1
DS 0
SWH 8000.000 Hz
FIDRES 0.332806 Hz
AQ 3.0047500 sec
RG 161
DW 62.500 usec
DE 10.20 usec
TE 300.0 K
D1 5.00000000 sec
TD0 1
SFO1 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
SI 32768
SF 400.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
O
O
N
H
H
N
O
O
O
8
10
9
8
7
6
5
4
3
2
1
ppm
0.88
2.09
2.81
2.20
2.17
2.07
2.00
0.82
1.00
0.98
0.99
2.08
5.37
8.72
2.41

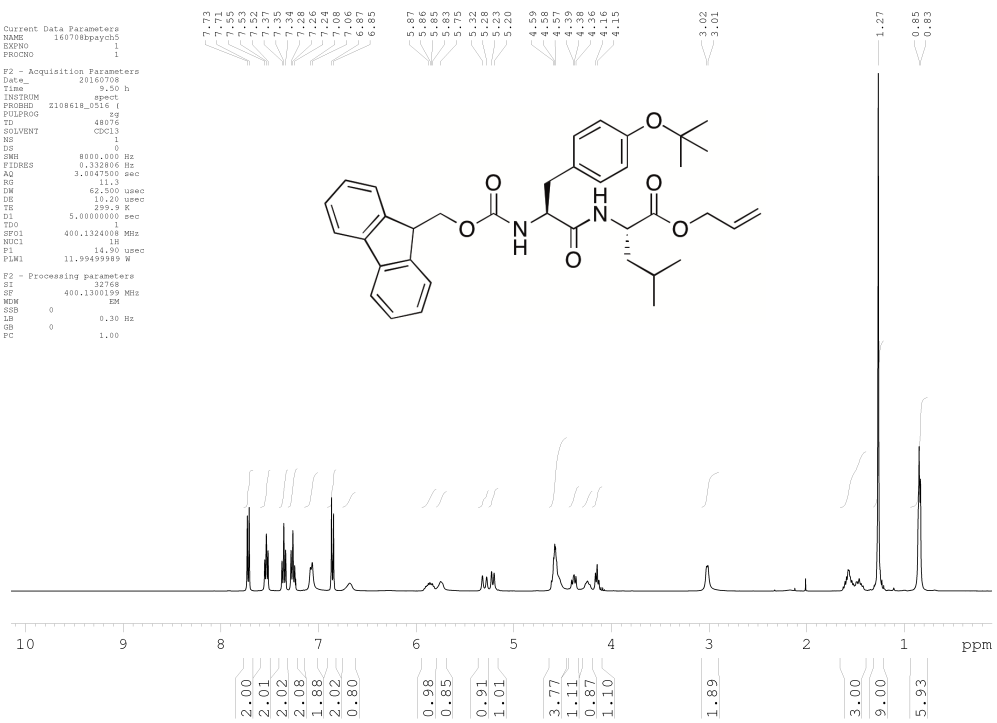

172.9
172.0
157.0
145.1
142.1
133.4
131.3
131.3
129.2
129.1
128.5
128.0
126.2
126.1
120.8
118.1
118.1
116.0
115.9
67.2
66.0
65.9
57.2
48.9
48.9
48.0
38.1
18.0
17.9
Current Data Parameters
NAME 160708bpaych3
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160711
Time 15.04 h
INSTRUM spect
PROBHD Z108618_0516 (
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 5339
DS 4
SWH 25252.525 Hz
FIDRES 0.770646 Hz
AQ 1.2976128 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 25
SFO1 100.6228303 MHz
NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.16537000 W
F2 - Processing parameters
SI 65536
SF 100.6126775 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

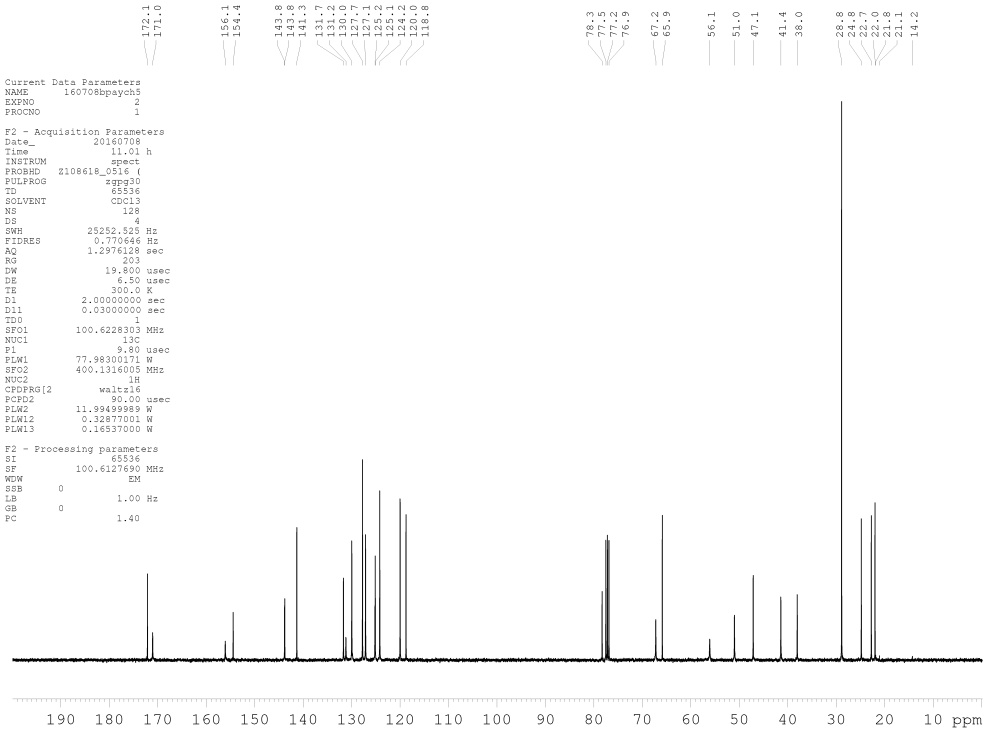

Current Data Parameters
NAME 160629bpaych5
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160630
Time 5.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 8
DS 0
SWH 8000.000 Hz
FIDRES 0.166403 Hz
AQ 3.0047500 sec
RG 80.6
DW 62.500 usec
DE 10.20 usec
TE 300.0 K
D1 5.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.52
7.42
7.29
7.29
7.28
7.22
7.05
6.22
5.84
5.82
5.80
5.30
5.28
5.25
5.23
4.81
4.80
4.78
4.76
4.43
4.41
4.40
4.36
4.34
4.31
4.20
4.18
4.17
3.12
3.10
3.08
3.07
3.04
3.02
3.00
2.99
1.31
O
O
O
N
H
O
N
H
O
O
10
9
8
7
6
5
4
3
2
1
ppm
2.47
2.59
2.69
2.50
3.45
4.72
2.69
0.97
1.01
3.26
1.11
2.32
3.54
1.35
1.32
3.21
11.81

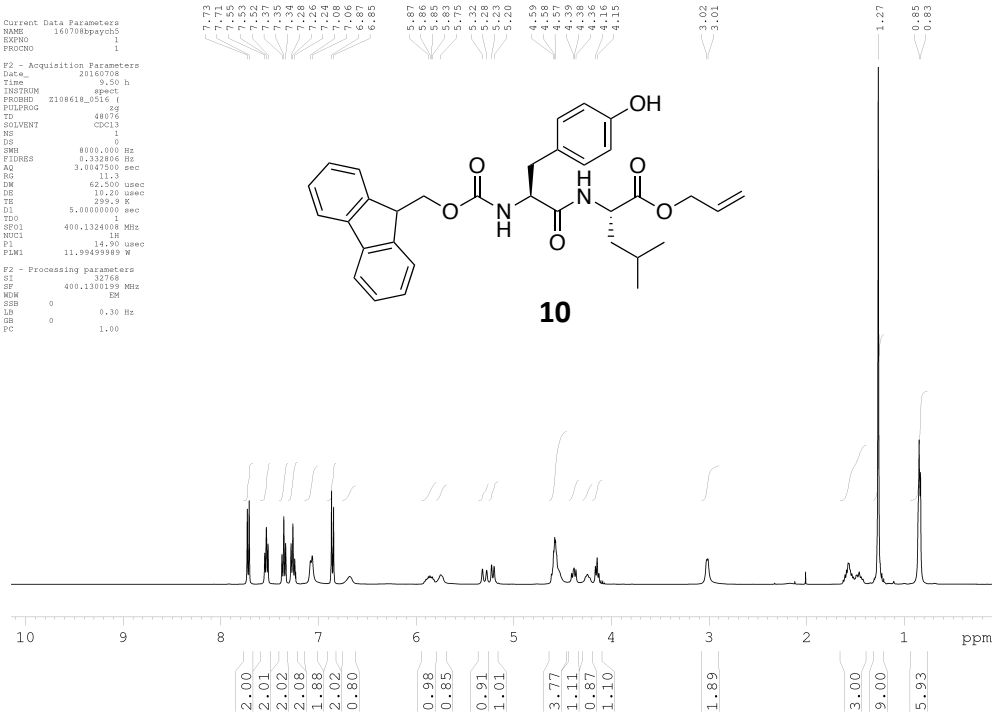

Current Data Parameters
NAME 160708bpaych4
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160708
Time 10.48 h
INSTRUM spect
PROBHD Z108618_0516 (
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 256
DS 4
SWH 25252.525 Hz
FIDRES 0.770646 Hz
AQ 1.2976128 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228303 MHz
NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.16537000 W
F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
171.3
170.8
156.1
155.9
144.1
141.2
136.8
132.2
130.4
129.3
128.4
128.3
128.2
127.6
127.1
126.7
125.7
125.3
119.9
117.6
115.1
66.4
65.3
56.4
53.7
47.1
37.4
37.0
29.5
29.4
29.2
29.0
28.8
28.6
28.4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

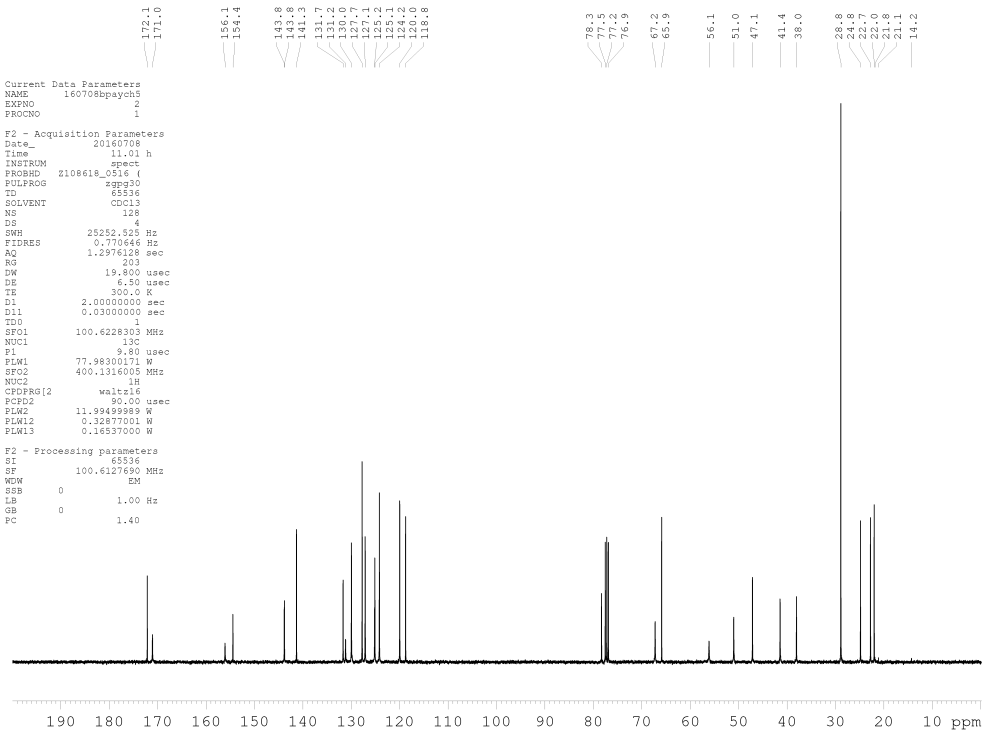

Current Data Parameters
NAME 160708bpaych4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160708
Time 9.45 h
INSTRUM spect
PROBHD Z108618_0516 (
PULPROG zg
TD 48076
SOLVENT Acetone
NS 1
DS 0
SWH 8000.000 Hz
FIDRES 0.332806 Hz
AQ 3.0047500 sec
RG 32
DW 62.500 usec
DE 10.20 usec
TE 300.1 K
D1 5.00000000 sec
TD0 1
SFO1 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
SI 32768
SF 400.1299877 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
O
N
H
O
O
O
N
H
O
O
9
10
9
8
7
6
5
4
3
2
1
ppm
0.93
2.11
3.17
2.18
2.18
7.53
2.21
0.94
1.00
1.02
1.06
1.07
2.15
1.10
1.03
2.25
6.01

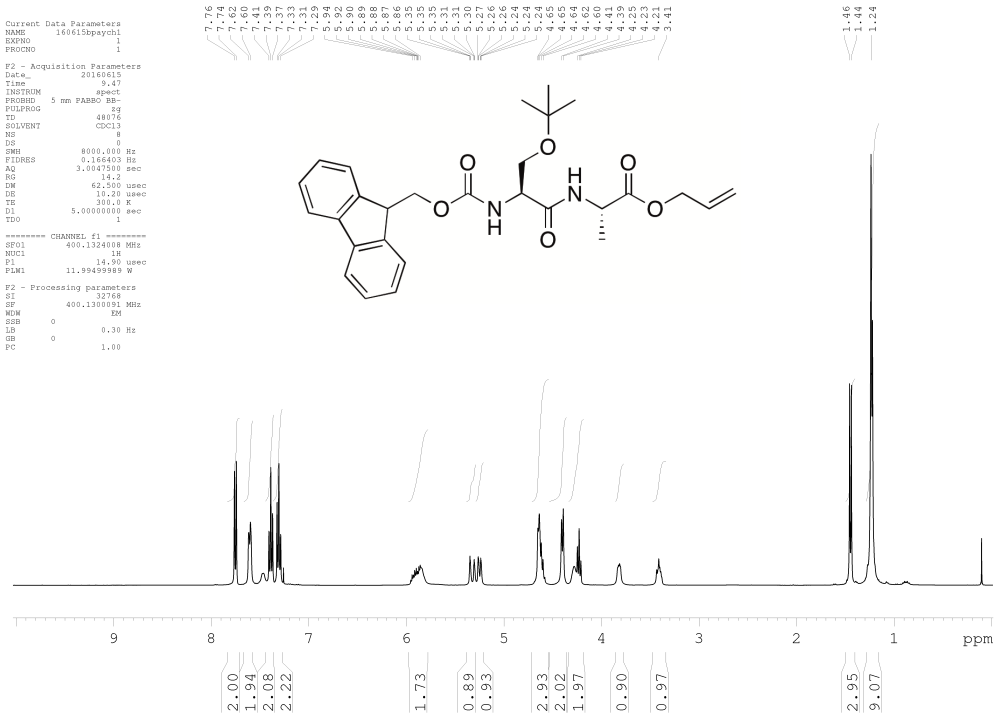

Current Data Parameters
NAME 160708bpaych4
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160708
Time 10.48 h
INSTRUM spect
PROBHD Z108618_0516 (
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 256
DS 4
SWH 25252.525 Hz
FIDRES 0.770646 Hz
AQ 1.2976128 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228303 MHz
NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.16537000 W
F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
171.3
170.8
156.1
155.9
144.1
141.2
141.8
132.2
130.4
129.3
128.4
128.3
128.2
127.6
127.1
126.7
126.7
125.3
125.3
119.9
117.6
115.1
66.4
65.3
56.4
53.7
47.1
37.4
37.0
29.5
29.4
29.2
29.0
28.8
28.6
28.4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Current Data Parameters
NAME 160708bpaych5
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160708
Time 9.50 h
INSTRUM spect
PROBHD Z108618_0516 (
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 1
DS 0
SWH 8000.000 Hz
FIDRES 0.332806 Hz
AQ 3.0047500 sec
RG 11.3
DW 62.500 usec
DE 10.20 usec
TE 299.9 K
D1 5.00000000 sec
TD0 1
SFO1 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
SI 32768
SF 400.1300199 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.73
7.71
7.55
7.53
7.52
7.37
7.35
7.34
7.28
7.26
7.24
7.08
7.06
6.87
6.85
5.87
5.86
5.85
5.83
5.75
5.32
5.28
5.23
5.20
4.59
4.58
4.57
4.39
4.38
4.36
4.16
4.15
3.02
3.01
1.27
0.85
0.83
ppm
2.00
2.01
2.02
2.08
1.88
2.02
0.80
0.98
0.85
0.91
1.01
3.77
1.11
0.87
1.10
1.89
3.00
9.00
5.93


Current Data Parameters
NAME 160708bpaych5
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160708
Time 11.01 h
INSTRUM spect
PROBHD Z108618_0516 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 25252.525 Hz
FIDRES 0.770646 Hz
AQ 1.2976128 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228303 MHz
NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.16537000 W
F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
172.1
171.0
156.1
154.4
143.8
143.8
141.3
131.7
131.2
130.0
127.7
127.1
125.2
125.1
124.2
120.0
118.8
78.3
77.5
77.2
76.9
67.2
65.9
56.1
51.0
47.1
41.4
38.0
28.8
24.8
22.7
22.0
21.8
21.1
14.2
ppm


Current Data Parameters
NAME 160708bpaych5
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160708
Time 9.50 h
INSTRUM spect
PROBHD Z108618_0516 (
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 1
DS 0
SWH 8000.000 Hz
FIDRES 0.332806 Hz
AQ 3.0047500 sec
RG 11.3
DW 62.500 usec
DE 10.20 usec
TE 299.9 K
D1 5.00000000 sec
TD0 1
SF01 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
SI 32768
SF 400.1300199 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.73 7.71 7.55 7.53 7.52 7.37 7.35 7.34 7.28 7.26 7.24 7.08 7.06 6.87 6.85
5.87 5.86 5.85 5.83 5.75 5.22 5.20 5.23 5.20
4.59 4.58 4.57 4.39 4.38 4.36 4.16 4.15
3.02 3.01
1.27
0.85 0.83
OH
O
N
H
O
O
N
H
O
O
10
10 9 8 7 6 5 4 3 2 1 ppm
2.00 2.01 2.02 2.08 1.88 2.02 0.80
0.98 0.85
0.91 1.01
3.77 1.11 0.87 1.10
1.89
3.00 9.00
5.93


172.1 171.0
156.1 154.4
143.8 143.8 141.3
131.7 131.2 130.0 127.7 127.1 125.2 125.1 124.2 120.0 118.8
78.3 77.5 77.2 76.9
67.2 65.9
56.1
51.0
47.1
41.4
38.0
28.8 24.8 22.7 22.0 21.8 21.1
14.2
Current Data Parameters
NAME 160708bpaych5
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160708
Time 11.01 h
INSTRUM spect
PROBHD Z108618_0516 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 25252.525 Hz
FIDRES 0.770646 Hz
AQ 1.2976128 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SF01 100.6228303 MHz
NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
SF02 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.16537000 W
F2 - Processing parameters
SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Current Data Parameters
NAME 160615bpaych1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160615
Time 9.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 8
DS 0
SWH 8000.000 Hz
FIDRES 0.166403 Hz
AQ 3.0047500 sec
RG 14.2
DW 62.500 usec
DE 10.20 usec
TE 300.0 K
D1 5.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.76
7.74
7.62
7.60
7.41
7.39
7.37
7.33
7.31
7.29
5.94
5.92
5.90
5.89
5.88
5.87
5.86
5.35
5.35
5.31
5.31
5.30
5.27
5.26
5.24
5.24
5.24
4.65
4.64
4.62
4.60
4.41
4.39
4.25
4.23
4.21
3.41
1.46
1.44
1.24
O
O
O
N
H
O
H
N
O
O
9
8
7
6
5
4
3
2
1
ppm
2.00
1.94
2.08
2.22
1.73
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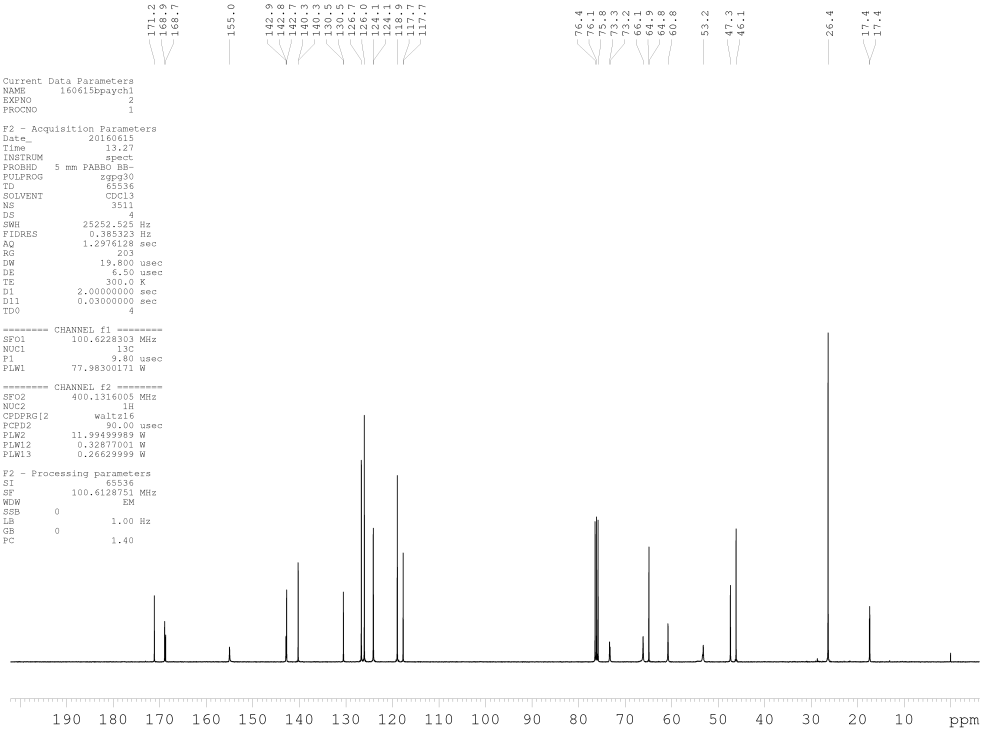
2.93
2.02
1.97
0.90
0.97
2.95
9.07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124.1
118.9
117.7
117.7
76.4
76.1
75.8
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26.4
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SOLVENT CDCl3
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FIDRES 0.385323 Hz
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RG 203
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DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 4
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P1 9.80 usec
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======== CHANNEL f2 ========
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PLW13 0.22629999 W
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PC 1.40
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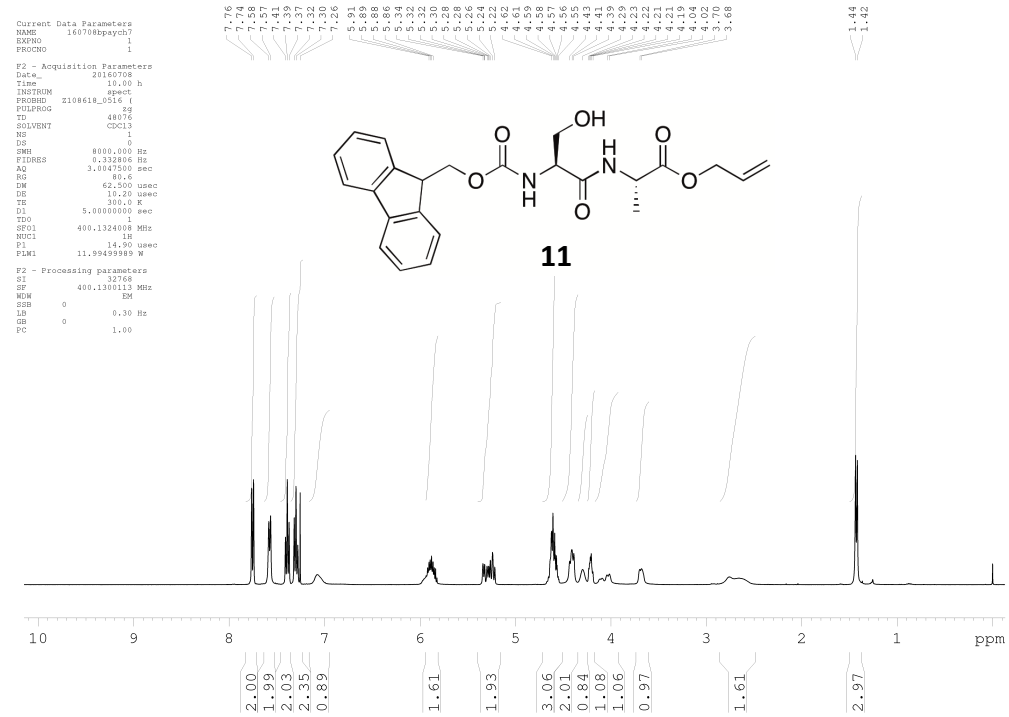
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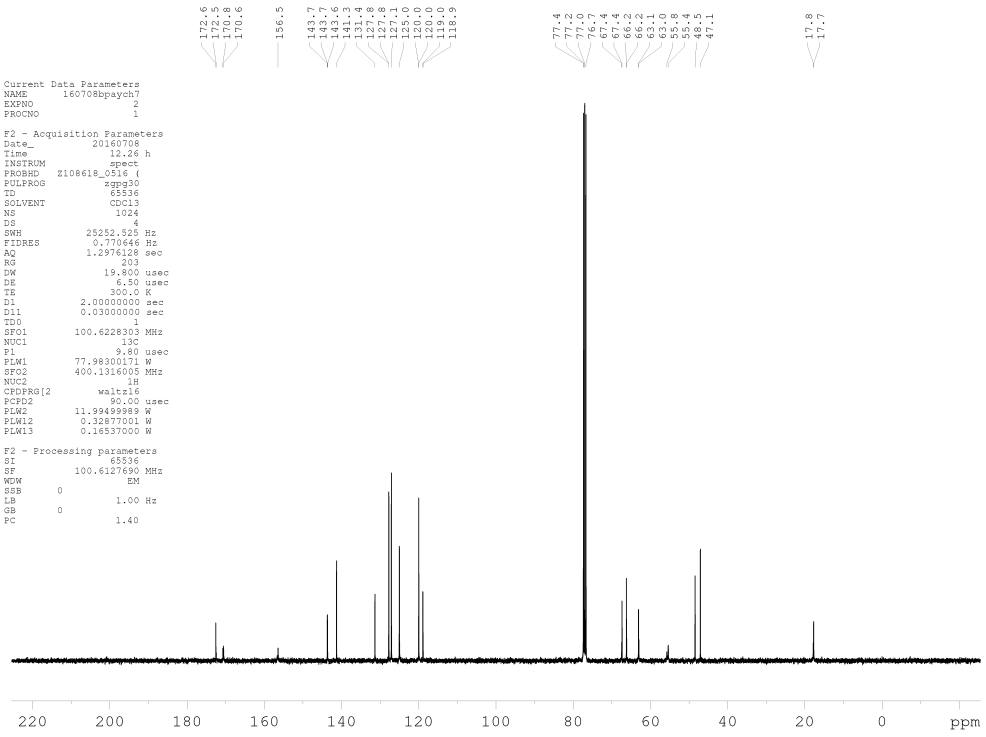
2.97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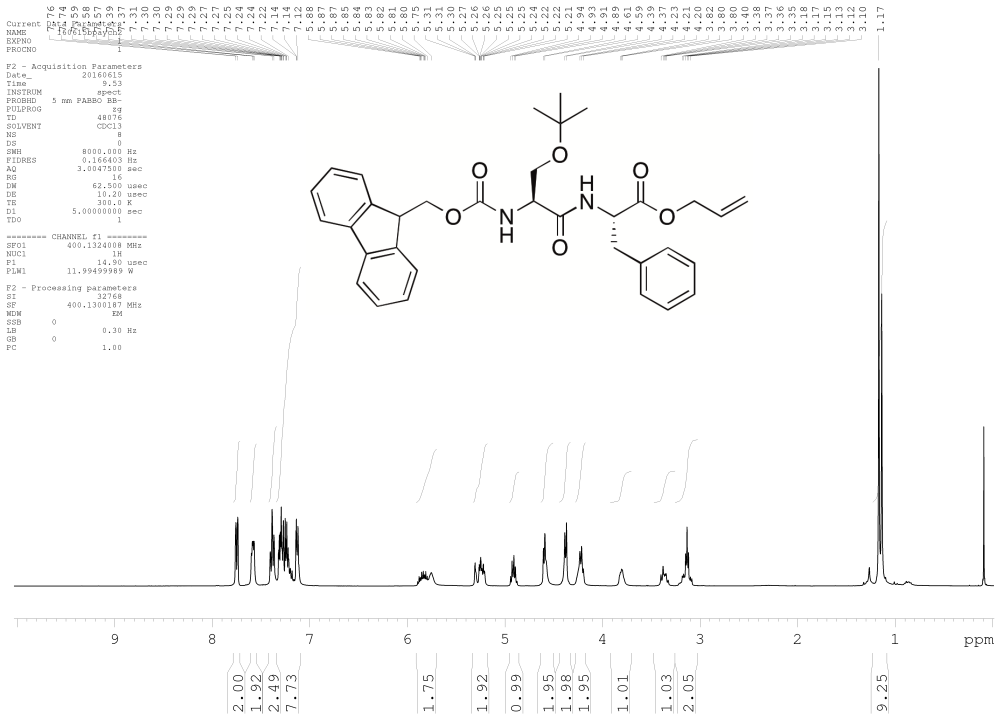

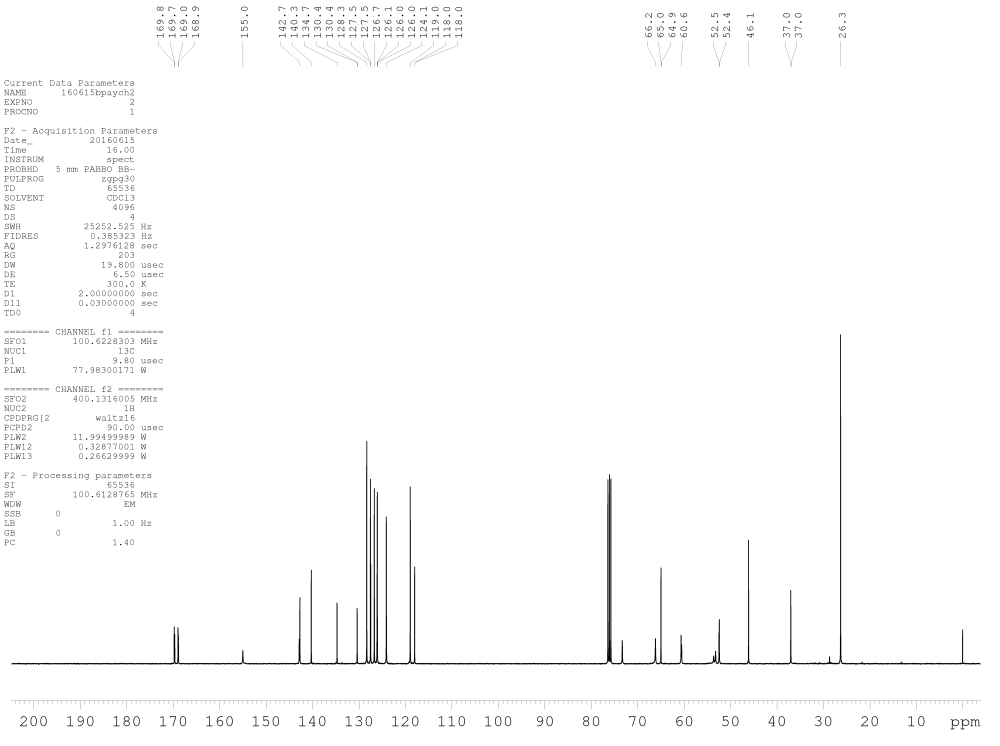

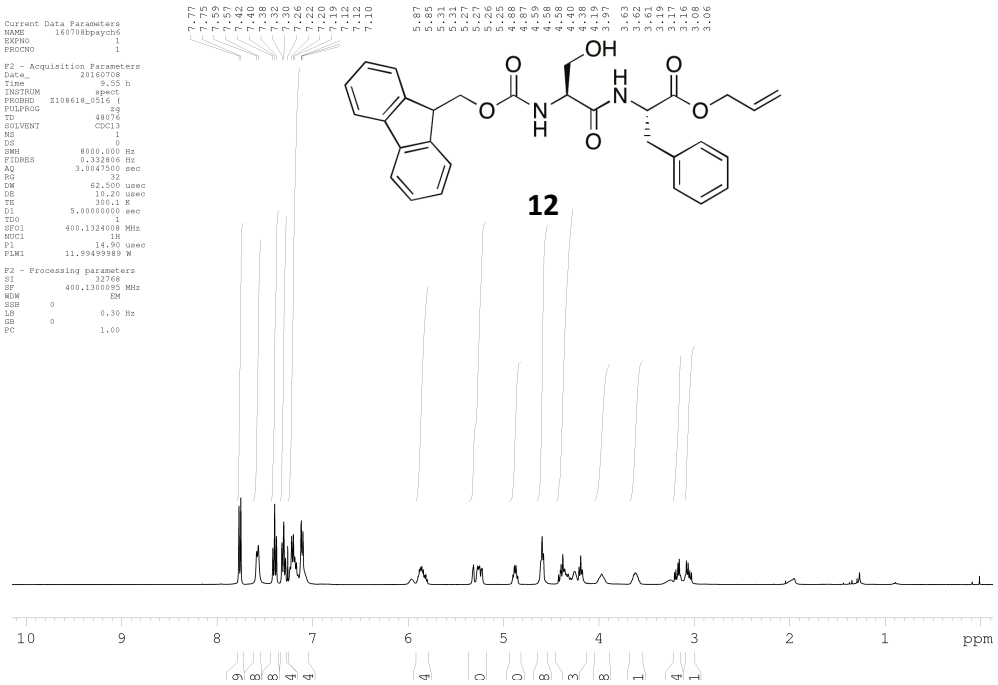
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D1 5.00000000 sec
TD0 1
SFO1 400.1324008 MHz
NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
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WDW EM
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LB 0.30 Hz
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PC 1.00
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5.87 5.85 5.31 5.31 5.27 5.27 5.26 5.26 4.88 4.87 4.59 4.58 4.56 4.40 4.38 4.19 3.97 3.63 3.62 3.61 3.19 3.17 3.15 3.08 3.06
OH
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N
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O
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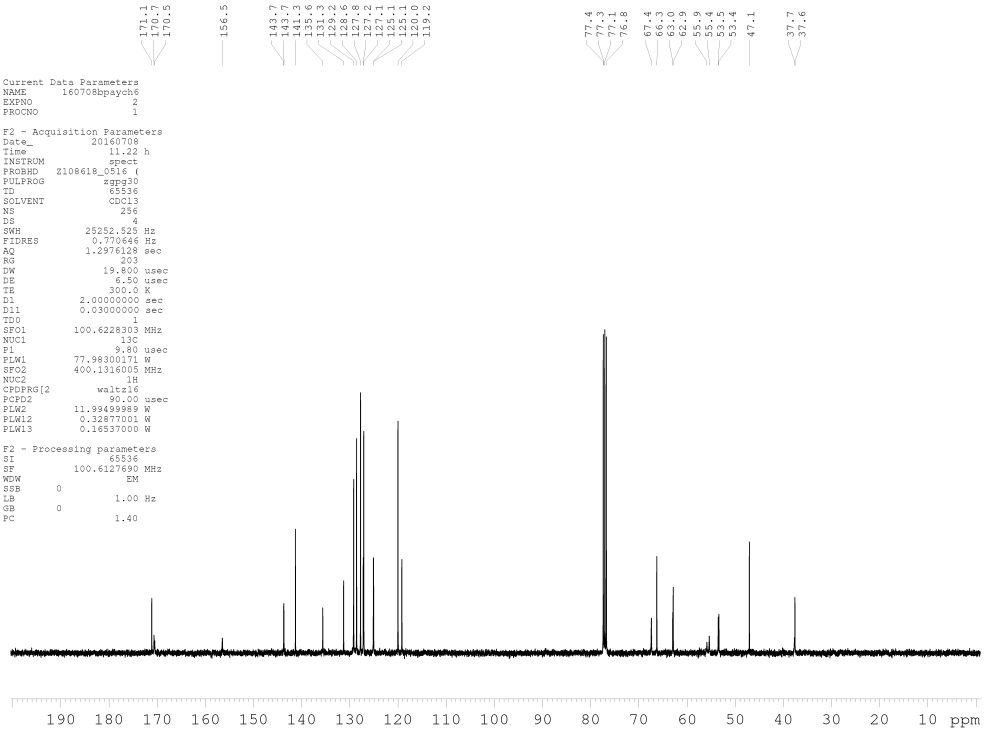
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D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.16537000 W
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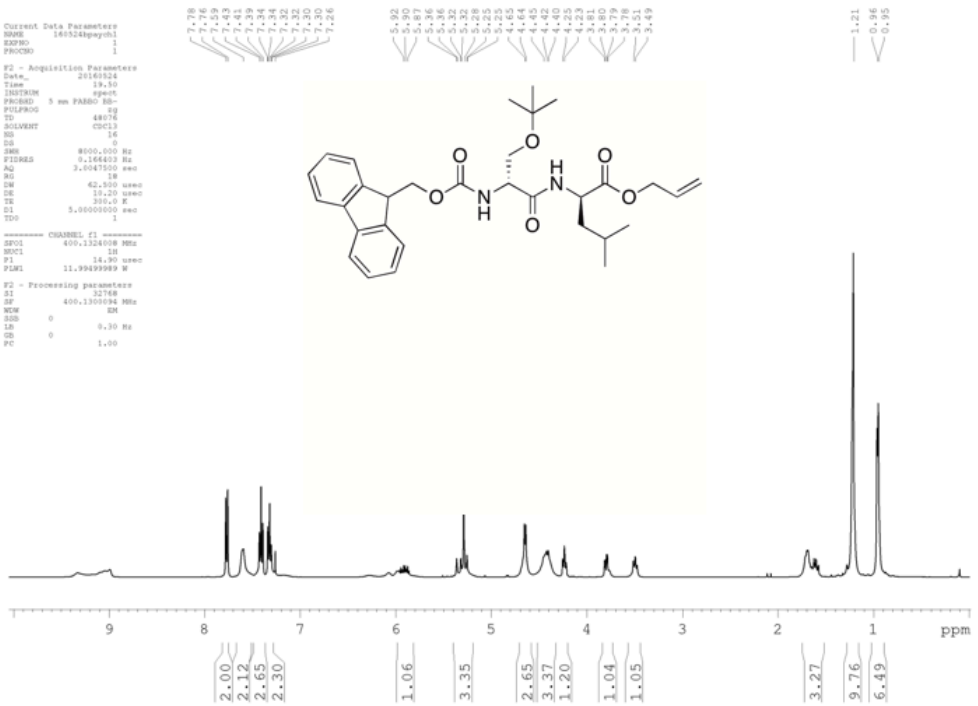
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SOLVENT CDCl3
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DW 62.500 usec
DE 10.20 usec
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D1 5.00000000 sec
TD0 1
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NUC1 1H
P1 14.90 usec
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LB 0.30 Hz
GB 0
PC 1.00
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5.92 5.90 5.87 5.36 5.35 5.32 5.28 5.25 5.25 4.64 4.45 4.42 4.40 4.25 4.23 3.81 3.80 3.79 3.78 3.71 3.49
1.21 0.96 0.95
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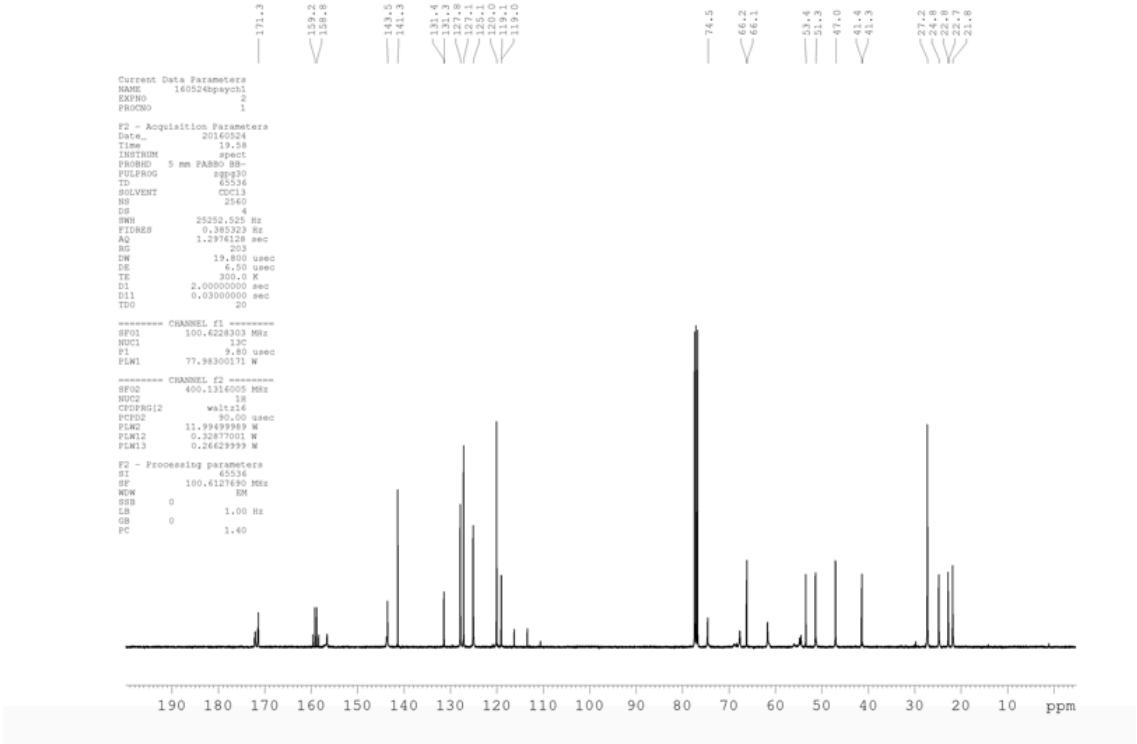
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SOLVENT CDCl3
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D11 0.03000000 sec
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NUC1 13C
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======== CHANNEL f2 ========
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NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
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PLW12 0.32877001 W
PLW13 0.26629999 W
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SSB 0
LB 1.00 Hz
GB 0
PC 1.40
171.3 159.2 158.8 143.5 141.3 131.4 131.3 127.8 127.1 125.1 120.0 119.1 119.0 74.5 66.2 66.1 53.4 51.3 47.0 41.4 41.3 27.2 24.8 22.9 22.7 21.8
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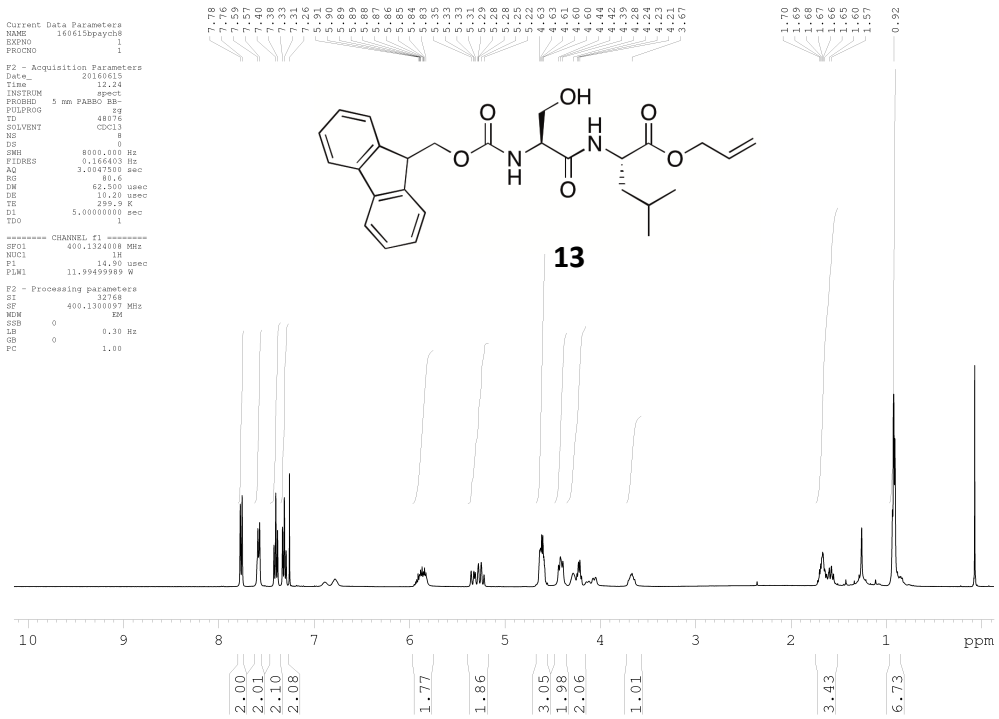
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PROCNO 1
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SOLVENT CDCl3
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FIDRES 0.166403 Hz
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NUC1 1H
P1 14.90 usec
PLW1 11.99499989 W
F2 - Processing parameters
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SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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O
N
H
O
O
O
13
10
9
8
7
6
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3
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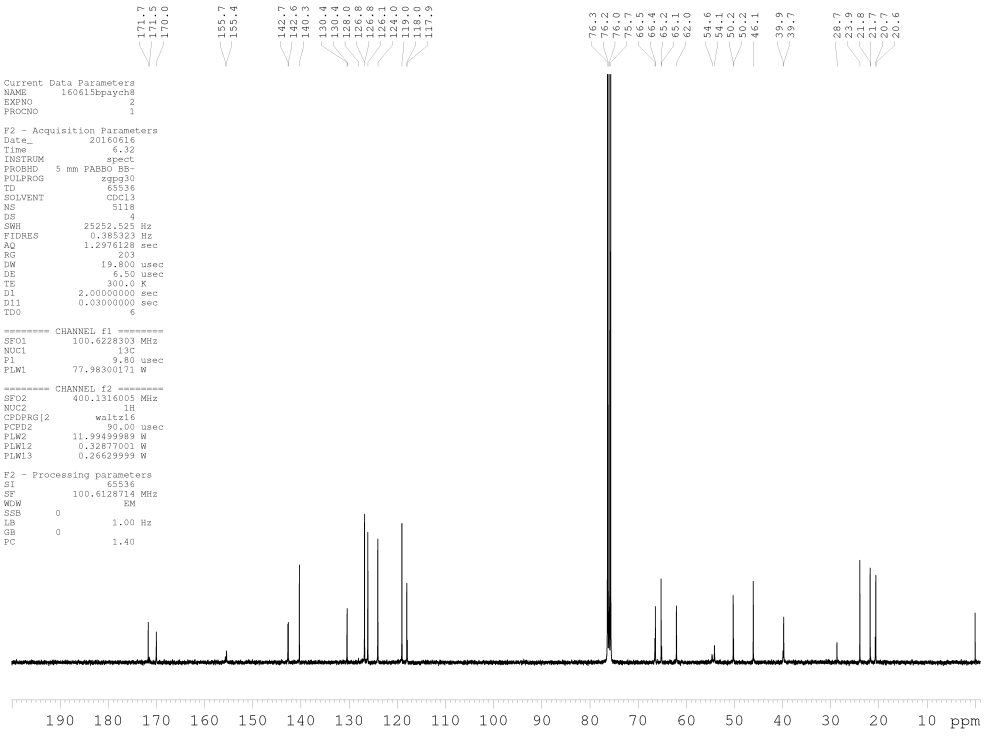
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SOLVENT CDCl3
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TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 6
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NUC1 13C
P1 9.80 usec
PLW1 77.98300171 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.99499989 W
PLW12 0.32877001 W
PLW13 0.26629999 W
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160
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120
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40
30
20
10
ppm

Synthesis of Model Peptide Selenoesters: Crude Data

Ac-LYRANQ-SePh (1)

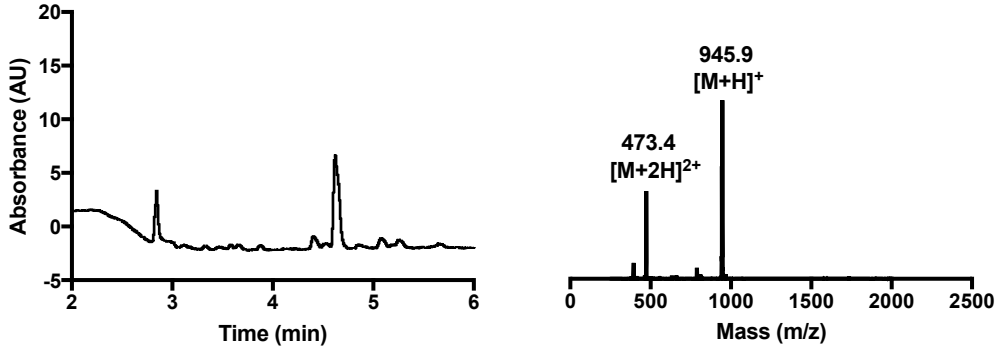

Figure S26. UPLC-MS trace of crude Ac-LYRANQ-SePh (**1**) esterified at rt; R_t 4.71 min (0-60% B over 8 min, λ = 230 nm); Calc. Mass $[M+H]^+$: 945.3, $[M+2H]^{2+}$: 473.2; Found; $[M+H]^+$: 945.9, $[M+2H]^{2+}$: 473.4.

Ac-LYRANN-SePh (2)

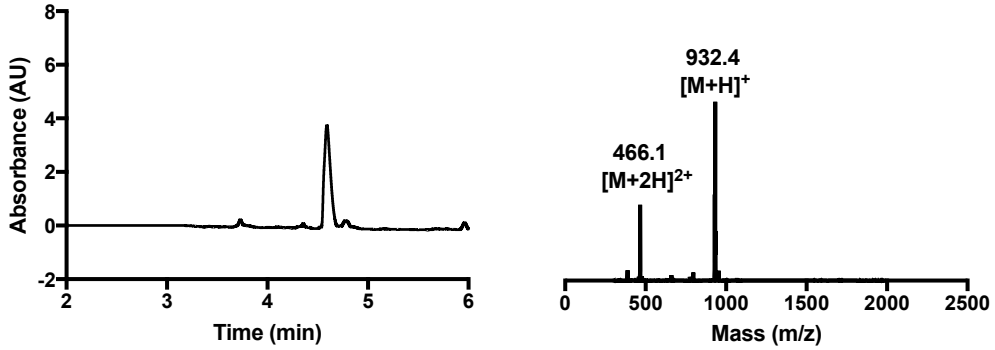

Figure S27. UPLC-MS trace of crude Ac-LYRANN-SePh (**2**) esterified at rt; R_t 4.60 min (0-60% B over 8 min, λ = 230 nm); Calc. Mass $[M+H]^+$: 932.3, $[M+2H]^{2+}$: 466.7; Found; $[M+H]^+$: 932.4, $[M+2H]^{2+}$: 466.1.

Ac-LYRANY-SePh (3)

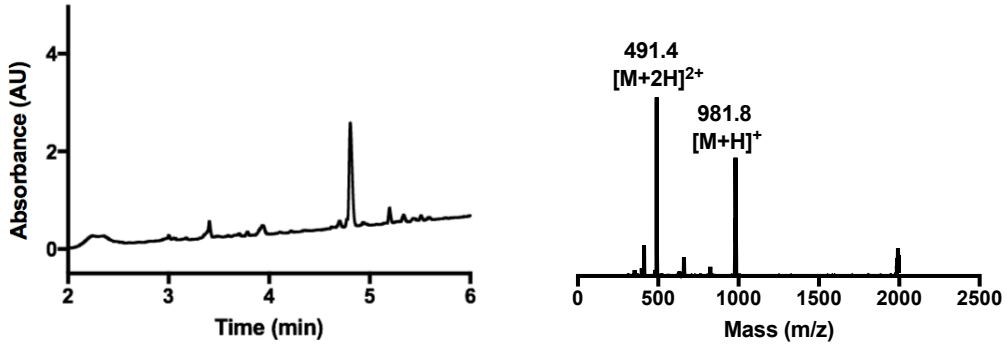

Figure S28. UPLC-MS trace of crude Ac-LYRANY-SePh (**3**) esterified at rt; R_t 4.81 min (0-60% B over 8 min, λ = 230 nm); Calc. Mass $[M+H]^+$: 981.4, $[M+2H]^{2+}$: 491.2; Found; $[M+H]^+$: 981.8, $[M+2H]^{2+}$: 491.4.

Ac-LYRANS-SePh (4)

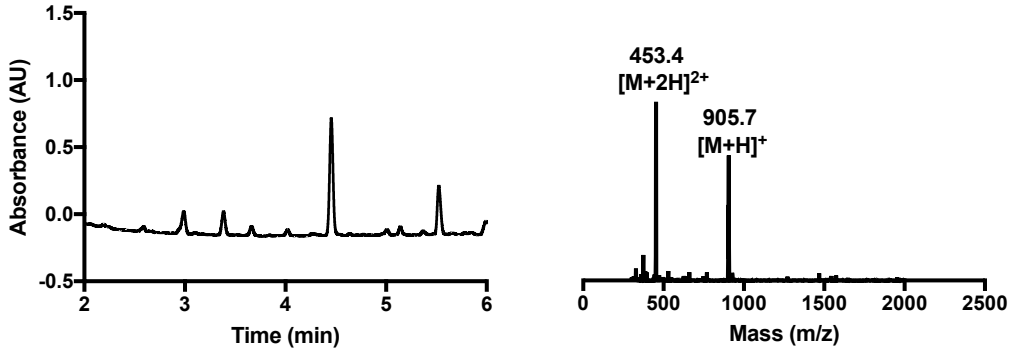

Figure S29. UPLC-MS trace of crude Ac-LYRANS-SePh (**4**) esterified at rt; R_t 4.46 min (0-60% B over 8 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 905.3, $[M+2H]^{2+}$: 453.2; Found; $[M+H]^+$: 905.7, $[M+2H]^{2+}$: 453.4.

Ac-LYRANQA-SePh (14)

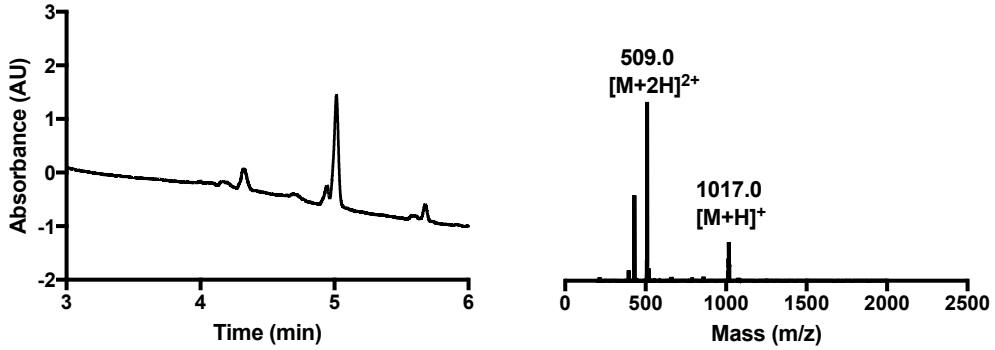

Figure S30. UPLC-MS trace of crude Ac-LYRANQA-SePh (**14**) esterified at rt; R_t 4.94 min (0-40% B over 8 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1017.4, $[M+2H]^{2+}$: 509.2; Mass Found (ESI^+); $[M+H]^+$: 1017.0, $[M+2H]^{2+}$:509.0.

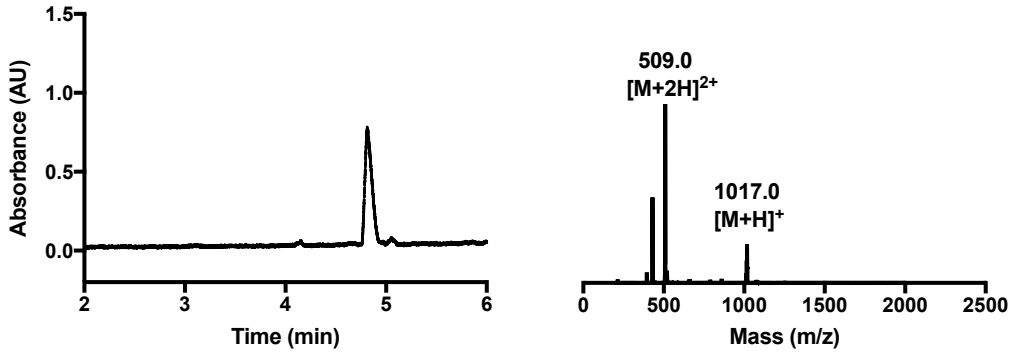

Figure S31. UPLC-MS trace of crude Ac-LYRANQA-SePh (**14**), esterified at 0 °C; R_t 4.91 min (0-40% B over 8 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1017.4, $[M+2H]^{2+}$: 509.2; Found; $[M+H]^+$: 1017.0, $[M+2H]^{2+}$:509.0.

Ac-LYRANQF-SePh (15)

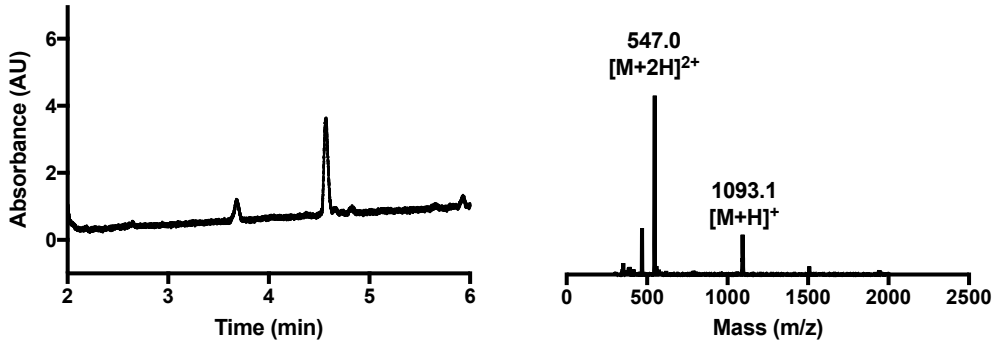

Figure S32. UPLC-MS trace of crude Ac-LYRANQF-SePh (**15**) esterified at 0 °C; R_t 4.57 min (0-60% B over 8 min, λ = 230 nm); Calc. Mass $[M+H]^+$: 1093.4, $[M+2H]^{2+}$: 547.2; Found; $[M+H]^+$: 1093.1, $[M+2H]^{2+}$: 547.0.

Ac-LYRANQL-SePh (16)

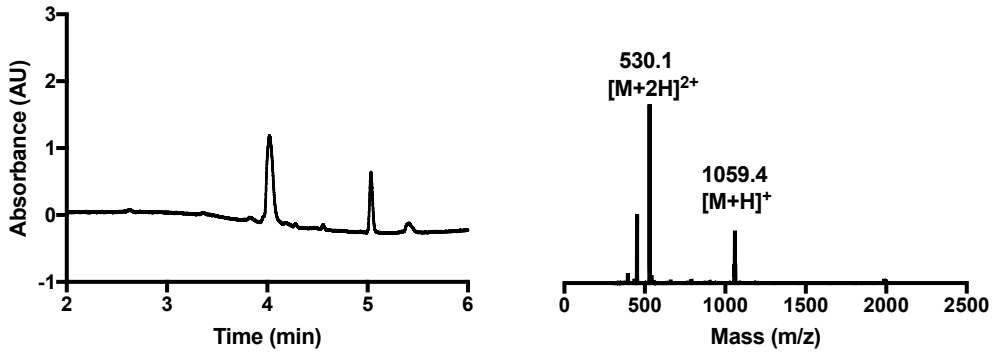

Figure S33. UPLC-MS trace of crude Ac-LYRANQL-SePh (**16**) esterified at 0 °C; R_t 4.04 min (0-80% B over 8 min, λ = 230 nm); Calc. Mass $[M+H]^+$: 1059.5, $[M+2H]^{2+}$: 530.2; Found; $[M+H]^+$: 1059.4, $[M+2H]^{2+}$: 530.1.

Ac-LYRANYA-SePh (17)

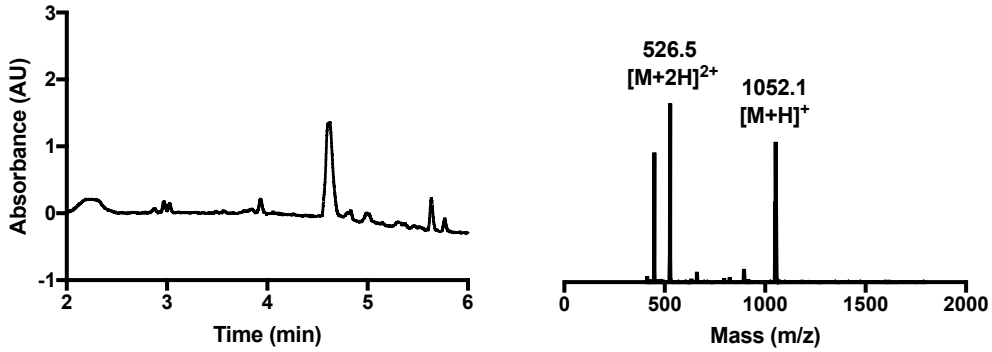

Figure S34. UPLC-MS trace of crude Ac-LYRANYA-SePh (**17**) esterified at 0 °C; R_t 4.63 min (0-60% B over 8 min, λ = 230 nm); Calc. Mass $[M+H]^+$: 1052.4, $[M+2H]^{2+}$: 526.7; Found; $[M+H]^+$: 1052.1, $[M+2H]^{2+}$: 526.5.

Ac-LYRANYF-SePh (18)

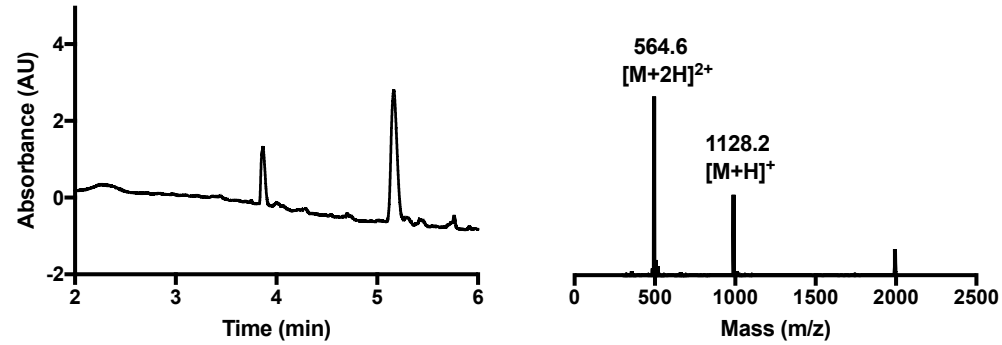

Figure S35. UPLC-MS trace of crude Ac-LYRANYF-SePh (**18**) esterified at 0 °C; R_t 5.17 min (0-50% B over 8 min, λ = 230 nm); Calc. Mass $[M+H]^+$: 1128.4, $[M+2H]^{2+}$: 564.7; Found; $[M+H]^+$: 1128.2, $[M+2H]^{2+}$: 564.6.

Ac-LYRANYL-SePh (19)

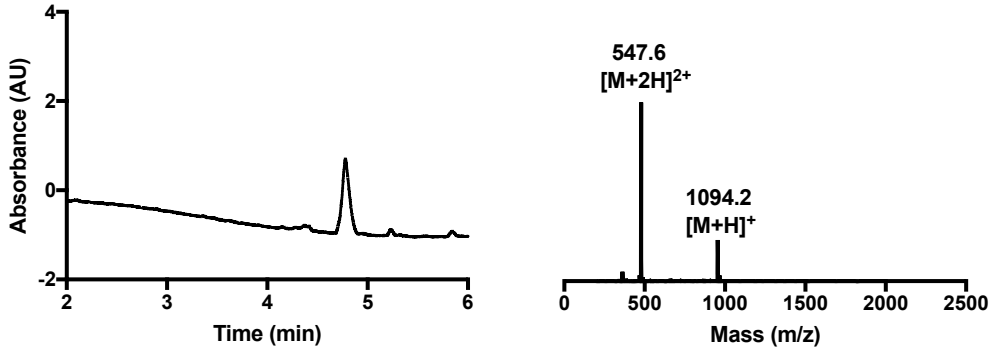

Figure S36. UPLC-MS trace of crude Ac-LYRANYL-SePh (**19**) esterified at 0 °C; R_t 4.81 min (0-60% B over 8 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1094.5 $[M+2H]^{2+}$: 547.7; Found; $[M+H]^+$: 1094.2, $[M+2H]^{2+}$: 547.6.

Ac-LYRANSA-SePh (20)

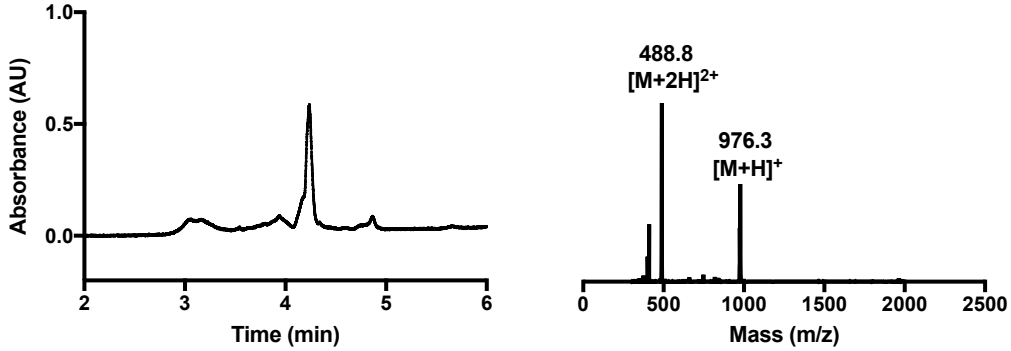

Figure S37. UPLC-MS trace of crude Ac-LYRANSA-SePh (**20**) esterified at 0 °C; R_t 4.23 min (0-60% B over 8 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 976.4, $[M+2H]^{2+}$: 488.7; Found; $[M+H]^+$: 976.3, $[M+2H]^{2+}$: 488.8

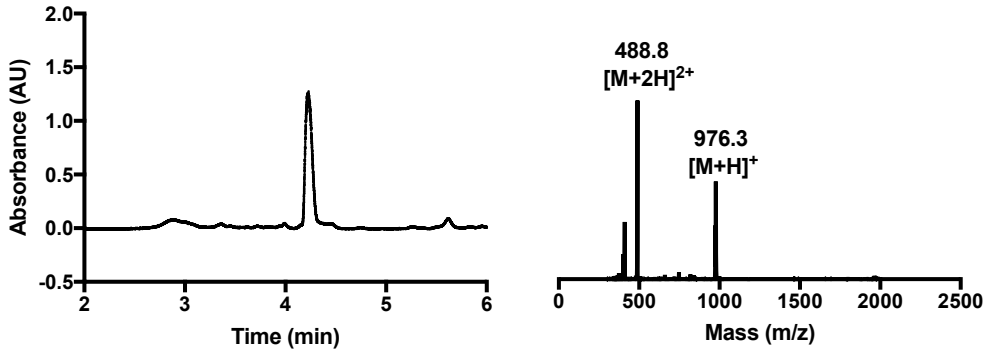

Figure S38. UPLC-MS trace of crude Ac-LYRANSA-SePh (**20**) esterified at -12 °C; R_t 4.24 min (0-60% B over 8 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 976.4, $[M+2H]^{2+}$: 488.7; Found; $[M+H]^+$: 976.3, $[M+2H]^{2+}$: 488.8

Ac-LYRANSF-SePh (21)

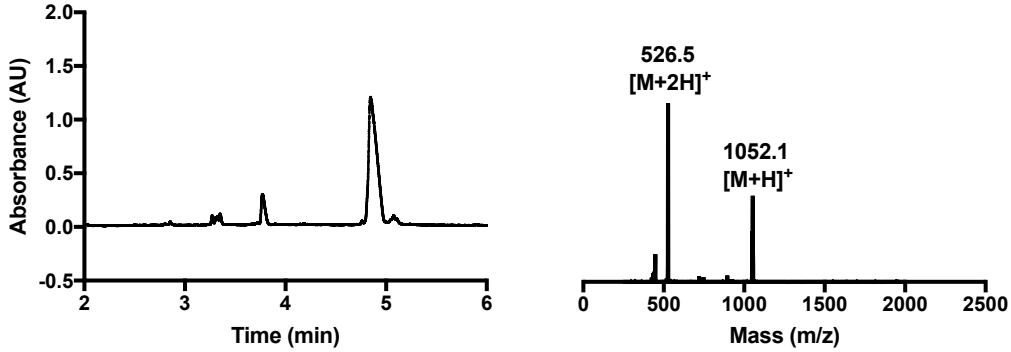

Figure S39. UPLC-MS trace of crude Ac-LYRANSF-SePh (**21**) esterified at 0 °C; R_t 4.84 min (0-60% B over 8 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1052.4, $[M+2H]^{2+}$: 526.7; Found; $[M+H]^+$: 1052.1, $[M+2H]^{2+}$: 526.5.

Ac-LYRANSL-SePh (22)

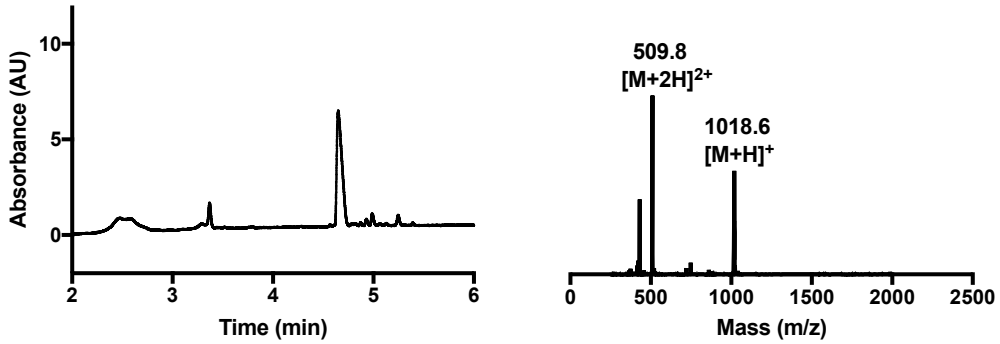

Figure S40. UPLC-MS trace of crude Ac-LYRANSL-SePh (**22**) esterified at 0 ^{o}C; R_t 4.65 min (0-70% B over 8 min, λ = 214 nm); Calc. Mass $[M+H]^+$: 1018.4, $[M+2H]^{2+}$: 509.7; Found; $[M+H]^+$: 1018.6, $[M+2H]^{2+}$: 509.8.

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