- Supporting information -

Oligoproline helices as structurally defined scaffolds for oligomeric G protein-coupled receptor ligands

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Experimental procedures

Measurement of CRE-induced luciferase activity

Materials. Recombinant human LH (recLH) and human recombinant FSH (recFSH) were synthesized at Schering-Plough Research Institute, Oss, The Netherlands. Luclite® was obtained from Packard. All cell culture supplies were obtained from Gibco/BRL unless indicated otherwise. The human LH receptor cDNA[1] and human FSH receptor cDNA[2] were kindly provided by Dr. A.J.W. Hsueh, Stanford University.

Luciferase assay. Chinese Hamster Ovary (CHO)-K1 cells stably expressing the CRE-luciferase reporter with the human LH receptor or human FSH receptor were grown to 80-90% confluency in Dulbecco's MEM/Nutrient Mix F12 containing 5% bovine calf serum and supplemented with penicillin G (80 units/mL) and streptomycin (0.08 mg/mL) in 5% CO_2 at 37 °C. Cells were harvested using cell dissociation solution (Sigma). Aliquots of the cells were cryopreserved in DMSO without a loss of functional activity on LH receptor or FSH receptor.[3] On the day of the experiment, cells were thawed, washed with assay medium (Dulbecco's MEM/Nutrient Mix F12 supplemented with 1 mg/L bovine insulin (Sigma), 5 mg/L apo-transferrin (Sigma), penicillin G (80 units/mL) and streptomycin (0.08 mg/mL)) and then resuspended in assay medium. The compounds were tested at 10 concentrations ranging from final concentrations of 10 μM to 0.316 nM with half log intervals. In the luciferase assays, 10 μL of assay medium containing test compound and 3% DMSO, 10 μL of assay medium containing 3% DMSO with recLH (final concentration of 1 nM) or recFSH (final concentration of 586 pM) or 10 μL of assay medium containing 3% DMSO alone were added to the wells of a 384-well white culture plate followed by the addition of 10 μL of assay medium. Then, 10 μL of cell suspension containing 7,500 cells was added to the wells. The final concentration of DMSO was 1%. After incubation for 4 h in a humidified atmosphere in

5% CO_2 at 37 °C, plates were allowed to adjust to room temperature for 1 h. Then, 15 µL of LucLite solution (Packard) was added to the incubation mixture. Following 60 min at room temperature in the dark, luciferase activity was measured in a Packard Topcount Microplate Scintillation and Luminescence Counter. Agonistic effects of the compounds were determined as percentage of the (maximal) effect induced by 1 nM recLH or 586 pM recFSH. The EC_{50} values (concentration of the test compound that elicits half-maximal (50%) luciferase stimulation compared to the compound's maximally attainable effect, respectively) and the efficacy values (maximal effect as percentage of the effect of recLH or recFSH) of the test compounds were determined using the software program MathIQ (version 2.0, ID Business Solutions Limited).

Chemical procedures

NMR spectra were recorded on a 400/100 MHz, 500/125 MHz or 600/150 MHz spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane as internal standard. Coupling constants (*J*) are given in Hz. All presented ^{13}C-APT spectra are proton decoupled. Where indicated, NMR peak assignments were made using COSY, NOESY (τ mix = 1 sec) and HMQC experiments. For LC-MS analysis, a HPLC-system (detection simultaneously at 214 and 254 nm) equipped with an analytical C_{18} column (4.6 mmD x 250 mmL, 5µ particle size) in combination with buffers A: H_2O, B: CH_3CN and C: 1% aq TFA and coupled to a mass instrument with an electro spray interface (ESI) was used. For RP-HPLC purifications, an automated HPLC system equipped with a semi-preparative C_{18} column (5 µm C_{18}, 10Å, 150 x 21.2 mm) was used. The applied buffers were A: H_2O + ammonium acetate (20 mM) and B: CH_3CN. High resolution mass spectra were recorded by direct injection (2 µL of a 2 µM solution in water/acetonitrile; 50/50; v/v and 0.1% formic acid) on a mass spectrometer (Thermo Finnigan LTQ Orbitrap) equipped with an electro spray ion source in positive mode (source voltage 3.5 kV, sheath gas flow 10, capillary temperature 250 °C) with resolution R =

60000 at *m/z* 400 (mass range *m/z* = 150-2000) and dioctylphthalate (*m/z* = 391.28428) as a lock mass. The high resolution mass spectrometer was calibrated prior to measurements with a calibration mixture (Thermo Finnigan). CD spectra were recorded using a spectral bandwidth of 1 nm, at 25 °C with a response time of 2 s. The spectra are the result of 2-3 accumulations. A peptide solution was measured in a concentration of 4E-5 M in 10% *i*-PrOH/phosphate buffer (10 mM, pH 7.2) in a quartz cell of 2 mm. CD data is given as mean residual molar ellipticities (Θ in deg cm^2 $dmol^{-1}$). All samples were equilibrated at least 12 h before measurement.

General procedure for SPPS of azido-containing polyprolines.

Rink amide MBHA resin (loading 0.64 mmol/g, 78 mg, 0.05 mmol) was preswollen in DMF for 30 min, drained and the Fmoc protecting group removed with 20% piperidine in NMP. After shaking for 30 min, the resin was drained, washed with NMP (3×), DCM (5×) and NMP (3×). Subsequently, Fmoc-Pro-OH or Fmoc-(*R/S*)Azp-OH (3 eq)[4,5] and HCTU (3 eq) are dissolved in NMP followed by DiPEA (9 eq). After standing for 5 min the mixture was added to the amino-functionalized resin (preswollen in NMP). After shaking for 3 h, the resin was drained, washed with NMP (3×), DCM (5×) and NMP (3×). Acetylation was accomplished by adding Ac_2O (5 eq) and DiPEA (5 eq) in DMF to the resin and shaken for 2 h. The resin was drained, washed with NMP (3×), DCM (5×) and NMP (3×). All couplings were monitored by the qualitative Chloranil test.[6] The polyproline peptide was cleaved from the resin by stirring in 95% TFA/H_2O (2 mL) for 2 h. The solution was then titrated in 40 mL of Et_2O and centrifuged. The solvent was decanted and the polyproline peptide dissolved in H_2O and purified by preparative HPLC (0 to 20 % B) to yield the compounds as white solids.

Monomeric azidoproline helix 1R-Azp. Yield after RP-HPLC purification: 16.0 mg (12.6 μmol, 25%). LC-MS analysis: t_R 5.07 min (gradient 10 to 50% B). ESI-MS *m/z*: 1265.7 [M +

H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.79 – 4.72 (m, 11H, Hα), 4.54 – 4.48 (m, 1H, Hγ-Azp), 4.42 (dd, *J* = 5.5, 8.4, 1H, Hα-Pro-NH_2), 3.94 – 3.82 (m, 12H, Hδ-Azp, Hδ), 3.74 – 3.59 (m, 12H, Hδ'), 2.57 (ddd, *J* = 1.5, 7.6, 11.4, 1H, Hβ-Azp), 2.44 – 2.30 (m, 11H, Hβ), 2.15 (s, 3H, CH_3), 2.23 – 2.03 (m, 24H, 1 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 2.01 – 1.92 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{68}N_{16}O_{13}$ + H^+: 1265.67895, obsd 1265.67892.

Monomeric azidoproline helix 2R-Azp. Yield after RP-HPLC purification: 37.8 mg (30.0 μmol, 60%). LC-MS analysis: t_R 5.05 min (gradient 10 to 50% B). ESI-MS *m/z*: 1265.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.78 – 4.70 (m, 11H, Hα), 4.59 – 4.52 (m, 1H, Hγ-Azp), 4.41 (dd, *J* = 5.5, 8.4, 1H, Hα-Pro-NH_2), 3.99 (d, *J* = 12.2, 1H, Hδ-Azp), 3.93 – 3.80 (m, 11H, Hδ), 3.74 – 3.52 (m, 12H, Hδ'), 2.53 (ddd, *J* = 2.5, 8.3, 12.2, 1H, Hβ-Azp), 2.44 – 2.29 (m, 11H, Hβ), 2.13 (s, 3H, CH_3), 2.18 – 2.01 (m, 24H, 1 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 2.02 – 1.87 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{68}N_{16}O_{13}$ + H^+: 1265.67895, obsd 1265.67897.

Monomeric azidoproline helix 3R-Azp. Yield after RP-HPLC purification: 43.8 mg (34.6 μmol, 69%). LC-MS analysis: t_R 5.00 min (gradient 10 to 50% B). ESI-MS *m/z*: 1265.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.88 – 4.69 (m, 11H, Hα), 4.59 – 4.51 (m, 1H, Hγ-Azp), 4.41 (dd, *J* = 5.3, 8.4, 1H, Hα-Pro-NH_2), 3.99 (d, *J* = 11.6, 1H, Hδ-Azp), 3.94 – 3.81 (m, 11H, Hδ), 3.74 – 3.65 (m, 12H, Hδ'), 2.53 (ddd, *J* = 1.5, 7.2, 10.2, 1H, Hβ-Azp), 2.45 – 2.28 (m, 11H, Hβ), 2.13 (s, 3H, CH_3), 2.12 – 2.01 (m, 24H, 1 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 2.01 – 1.86 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{68}N_{16}O_{13}$ + H^+: 1265.67895, obsd 1265.67870.

Monomeric azidoproline helix 4R-Azp. Yield after RP-HPLC purification: 8.7 mg (6.9 μmol, 14%). LC-MS analysis: t_R 4.94 min (gradient 10 to 50% B). ESI-MS *m/z*: 1265.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.91 – 4.68 (m, 11H, Hα), 4.60 – 4.52 (m, 1H, Hγ-Azp), 4.41 (dd, *J* = 5.4, 8.4, 1H, Hα-Pro-NH_2), 3.99 (d, *J* = 11.1, 1H, Hδ-Azp), 3.95 – 3.80 (m, 11H, Hδ), 3.73 – 3.52 (m, 12H, Hδ'), 2.54 (ddd, *J* = 3.1, 7.7, 10.4, 1H, Hβ-Azp), 2.46 – 2.26 (m, 11H, Hβ), 2.13 (s, 3H, CH_3), 2.19 – 2.02 (m, 24H, 1 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 2.02 – 1.84 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{68}N_{16}O_{13}$ + H^+: 1265.67895, obsd 1265.67898.

Dimeric azidoproline helix 5R-Azp$_2$. Yield after RP-HPLC purification: 33.2 mg (25.5 μmol, 51%). LC-MS analysis: t_R 5.56 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.8 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.82 (t, *J* = 8.1, 1H, Hα-Azp), 4.75 (t, *J* = 8.0, 1H, Hα-Azp), 4.72 – 4.66 (m, 9H, Hα), 4.45 (ddd, *J* = 3.0, 5.2, 7.5, 1H, Hγ-Azp), 4.46 (ddd, *J* = 2.9, 5.1, 7.8, 1H, Hγ-Azp), 4.35 (dd, *J* = 5.5, 8.6, 1H, Hα-Pro-NH_2), 4.02 (d, *J* = 12.3, 1H, Hδ-Azp), 3.86 – 3.76 (m, 12H, Hδ), 3.71 (d, *J* = 12.1, 1H, Hδ'), 3.65 – 3.56 (m, 10H, Hδ'), 2.51 – 2.44 (m, 2H, Hβ-Azp), 2.36 – 2.26 (m, 9H, Hβ), 2.13 – 2.07 (m, 2H, Hβ'-Azp), 2.09 (s, 3H, CH_3), 2.05 – 1.98 (m, 21H, 1 × Hβ-Pro-NH_2, Hγ), 1.92 – 1.85 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13}$ + H^+: 1306.68035, obsd 1306.68115.

Dimeric azidoproline helix 6R-Azp$_2$. Yield after RP-HPLC purification: 31.5 mg (24.1 μmol, 48%). LC-MS analysis: t_R 5.48 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.77 (t, *J* = 8.0, 1H, Hα-Azp), 4.74 – 4.67 (m, 10H, Hα), 4.49 (ddd, *J* = 2.8, 5.1, 7.6, 1H, Hγ-Azp), 4.46 (ddd, *J* = 2.8, 5.2, 7.8, 1H, Hγ-Azp), 4.35 (dd, *J* = 5.5, 8.6, 1H, Hα-Pro-NH_2), 3.93 (d, *J* = 12.3, 1H, Hδ-Azp), 3.86 – 3.78 (m, 12H, Hδ), 3.72 (d, *J* = 12.1, 1H, Hδ'), 3.66 – 3.57 (m, 10H, Hδ'), 2.54 – 2.47 (m, 2H, Hβ-Azp), 2.36 – 2.25

(m, 9H, Hβ), 2.15 – 2.09 (m, 2H, Hβ'-Azp), 2.09 (s, 3H, CH_3), 2.06 – 1.99 (m, 21H, 1 × Hβ-Pro-NH_2, Hγ), 1.95 – 1.86 (m, 10H, 1 × Hβ'Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13}$ + H^+: 1306.68035, obsd 1306.68115.

Dimeric azidoproline helix 7R-Azp$_2$. Yield after RP-HPLC purification: 37.5 mg (28.7 μmol, 57%). LC-MS analysis: t_R 5.70 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.77 (t, *J* = 7.6, 1H, Hα-Azp), 4.73 – 4.66 (m, 10H, Hα), 4.49 (ddd, *J* = 3.0, 5.3, 7.6, 1H, Hγ-Azp), 4.44 (ddd, *J* = 2.9, 5.3, 7.9, 1H, Hγ-Azp), 4.35 (dd, *J* = 5.5, 8.6, 1H, Hα-Pro-NH_2), 3.93 (d, *J* = 11.4, 1H, Hδ-Azp), 3.87 – 3.76 (m, 12H, Hδ), 3.71 (d, *J* = 11.8, 1H, Hδ'), 3.66 – 3.56 (m, 10H, Hδ'), 2.53 – 2.45 (m, 2H, Hβ-Azp), 2.36 – 2.24 (m, 9H, Hβ), 2.16 – 2.06 (m, 2H, Hβ'-Azp), 2.09 (s, 3H, CH_3), 2.06 – 1.97 (m, 21H, 1 × Hβ-Pro-NH_2, Hγ), 1.94 – 1.84 (m, 10H, 1 × Hβ'Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13}$ + H^+: 1306.68035, obsd 1306.68164.

Dimeric azidoproline helix 8R-Azp$_2$. Yield after RP-HPLC purification: 26.2 mg (20.1 μmol, 40%). LC-MS analysis: t_R 5.59 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.77 (t, *J* = 8.0, 1H, Hα-Azp), 4.74 – 4.68 (m, 10H, Hα), 4.50 (ddd, *J* = 3.0, 5.3, 7.8, 1H, Hγ-Azp), 4.46 (ddd, *J* = 3.1, 5.3, 8.0, 1H, Hγ-Azp), 4.36 (dd, *J* = 5.5, 8.6, 1H, Hα-Pro-NH_2), 3.94 (d, *J* = 12.1, 1H, Hδ-Azp), 3.87 – 3.78 (m, 12H, Hδ), 3.72 (d, *J* = 12.1, 1H, Hδ'), 3.66 – 3.57 (m, 10H, Hδ'), 2.54 – 2.46 (m, 2H, Hβ-Azp), 2.37 – 2.26 (m, 9H, Hβ), 2.16 – 2.07 (m, 2H, Hβ'-Azp), 2.09 (s, 3H, CH_3), 2.07 – 1.98 (m, 21H, 1 × Hβ-Pro-NH_2, Hγ), 1.95 – 1.85 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13}$ + H^+: 1306.68035, obsd 1306.68140.

Dimeric azidoproline helix 9R-Azp$_2$. Yield after RP-HPLC purification: 46.9 mg (35.9 μmol, 72%). LC-MS analysis: t_R 5.52 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.77 (t, *J* = 7.9, 1H, Hα-Azp), 4.73 (t, *J* = 8.0, 1H, Hα-Azp), 4.88 – 4.69 (m, 9H, Hα), 4.46 (ddd, *J* = 3.1, 5.3, 8.0, 1H, Hγ-Azp), 4.42 (ddd, *J* = 3.1, 5.4, 7.9, 1H, Hγ-Azp), 4.31 (dd, *J* = 5.3, 8.4, 1H, Hα-Pro-NH_2), 3.90 (d, *J* = 11.7, 1H, Hδ-Azp), 3.85 – 3.73 (m, 12H, Hδ), 3.68 (d, *J* = 11.7, 1H, Hδ'), 3.62 – 3.52 (m, 10H, Hδ'), 2.50 – 2.42 (m, 2H, Hβ-Azp), 2.34 – 2.21 (m, 9H, Hβ), 2.09 (ddd, *J* = 5.2, 7.9, 13.2, 1H, Hβ'-Azp), 2.06 – 2.02 (m, 1H, Hβ'-Azp), 2.05 (s, 3H, CH_3), 2.02 – 1.95 (m, 21H, 1 × Hβ-Pro-NH_2, Hγ), 1.91 – 1.81 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13}$ + H^+: 1306.68035, obsd 1306.68176.

Dimeric azidoproline helix 10R-Azp$_2$. Yield after RP-HPLC purification: 16.8 mg (10.5 μmol, 21%). LC-MS analysis: t_R 5.65 min (gradient 10 to 50% B). ESI-MS *m/z*: 1598.6 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.90 – 4.69 (m, 14H, Hα), 4.61 – 4.54 (m, 1H, Hγ-Azp), 4.54 – 4.48 (m, 1H, Hγ-Azp), 4.42 (dd, *J* = 5.3, 8.3, 1H, Hα-ProNH_2), 4.02 (d, *J* = 11.3, 1H, Hδ-Azp), 3.96 – 3.82 (m, 14H, Hδ-Azp, Hδ), 3.76 – 3.58 (m, 15H, Hδ'), 2.61-2.50 (m, 2H, Hβ-Azp), 2.48 – 2.25 (m, 13H, Hβ), 2.16 (s, 3H, CH_3), 2.23 – 2.02 (m, 29H, 1 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 2.02 – 1.83 (m, 12H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{77}H_{108}N_{22}O_{16}$ + H^+: 1597.83864, obsd 1597.83828.

Dimeric azidoproline helix 11R-Azp$_2$. Yield after RP-HPLC purification: 61.4 mg (32.5 μmol, 65%). LC-MS analysis: t_R 5.77 min (gradient 10 to 50% B). ESI-MS *m/z*: 1888.8 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.74 – 4.61 (m, 17H, Hα), 4.53 – 4.48 (m, 1H, Hγ-Azp), 4.48 – 4.41 (m, 1H, Hγ-Azp), 4.35 (dd, *J* = 5.3, 8.3, 1H, Hα-ProNH_2), 3.94 (d, *J* = 11.7, 1H, Hδ-Azp), 3.90 – 3.76 (m, 17H, Hδ-Azp, Hδ), 3.70 – 3.50 (m, 18H, Hδ'), 2.57 -2.44 (m, 2H,

Hβ-Azp), 2.41 – 2.16 (m, 16H, Hβ), 2.08 (s, 3H, CH_3), 2.15 – 1.96 (m, 35H, 1 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.96 – 1.80 (m, 15H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{92}H_{129}N_{25}O_{19} + H^+$: 1888.99693, obsd 1888.99568.

Dimeric azidoproline helix 12R-Azp$_2$. Yield after RP-HPLC purification: 58.8 mg (27.0 μmol, 54%). LC-MS analysis: t_R 5.86 min (gradient 10 to 50% B). ESI-MS *m/z*: 1091.7 $[M + 2H]^{2+}$. ^{1}H NMR (400 MHz, D_2O) δ 4.74 – 4.61 (m, 20H, Hα), 4.53 – 4.47 (m, 1H, Hγ-Azp), 4.47 – 4.41 (m, 1H, Hγ-Azp), 4.34 (dd, *J* = 5.6, 8.3, 1H, Hα-ProNH_2), 3.93 (d, *J* = 11.9, 1H, Hδ-Azp), 3.89 – 3.74 (m, 20H, Hδ-Azp, Hδ), 3.69 – 3.46 (m, 21H, Hδ'), 2.55 -2.41 (m, 2H, Hβ-Azp), 2.41 – 2.19 (m, 19H, Hβ), 2.08 (s, 3H, CH_3), 2.17 – 1.95 (m, 41H, 1 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.94 – 1.78 (m, 18H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{107}H_{150}N_{28}O_{22} + 2H^+$: 1090.58125, obsd 1090.58260.

Dimeric azidoproline helix 13R-Azp$_2$. Yield after RP-HPLC purification: 33.0 mg (25.3 μmol, 51%). LC-MS analysis: t_R 5.64 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 $[M + H]^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.74 – 4.65 (m, 11H, Hα), 4.51 – 4.47 (m, 2H, Hγ-Azp), 4.35 (dd, *J* = 5.5, 8.6, 1H, Hα-Pro-NH_2), 3.93 (d, *J* = 12.2, 1H, Hδ-Azp), 3.87 – 3.77 (m, 12H, Hδ), 3.67 – 3.57 (m, 11H, Hδ'), 2.48 (ddd, *J* = 2.3, 7.7, 11.0, 2H, Hβ-Azp), 2.38 – 2.25 (m, 9H, Hβ), 2.14 – 2.07 (m, 2H, Hβ'-Azp), 2.08 (s, 3H, CH_3), 2.06 – 1.96 (m, 21H, 1 × Hβ-Pro-NH_2, Hγ), 1.95 – 1.83 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13} + H^+$: 1306.68035, obsd 1306.68115.

Dimeric azidoproline helix 14R-Azp$_2$. Yield after RP-HPLC purification: 36.6 mg (28.0 μmol, 56%). LC-MS analysis: t_R 5.52 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.8 $[M + H]^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.72 – 4.66 (m, 11H, Hα), 4.51 – 4.47 (m, 2H, Hγ-Azp), 4.34 (dd, *J* = 5.3, 8.4, 1H, Hα-Pro-NH_2), 3.93 (d, *J* = 10.5, 1H, Hδ-Azp), 3.88 – 3.77 (m, 12H,

Hδ), 3.65 – 3.57 (m, 11H, Hδ'), 2.51 – 2.45 (m, 2H, Hβ-Azp), 2.37 – 2.25 (m, 9H, Hβ), 2.13 – 2.06 (m, 2H, Hβ'-Azp), 2.08 (s, 3H, CH_3), 2.06 – 1.97 (m, 21H, 1 × Hβ-Pro-NH_2, Hγ), 1.95 – 1.84 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13} + H^+$: 1306.68035, obsd 1306.68176.

Tetrameric azidoproline helix 15R-Azp$_4$. Yield after RP-HPLC purification: 14.3 mg (10.3 μmol, 21%). LCMS analysis: t_R 6.72 min (gradient 10 to 50% B). ESI-MS *m/z*: 1388.8 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.88 – 4.70 (m, 11H, Hα), 4.57 – 4.51 (m, 3H, Hγ-Azp), 4.51 – 4.46 (m, 1H, Hγ-Azp), 4.40 (dd, *J* = 5.5, 8.4, 1H, Hα-ProNH_2), 3.98 (d, *J* = 11.4, 3H, Hδ-Azp), 3.94 – 3.79 (m, 9H, Hδ-Azp, Hδ), 3.72 – 3.59 (m, 12H, Hδ'), 2.61 -2.47 (m, 4H, Hβ-Azp), 2.46 – 2.26 (m, 8H, Hβ), 2.14 (s, 3H, CH_3), 2.23 – 2.02 (m, 21H, 4 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 2.01 – 1.84 (m, 7H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{85}N_{25}O_{13} + H^+$: 1388.68314, obsd 1388.68314.

Monomeric azidoproline helix 1S-Azp. Yield after RP-HPLC purification: 50.0 mg (39.5 μmol, 79%). LC-MS analysis: t_R 4.74 min (gradient 10 to 50% B). ESI-MS *m/z*: 1265.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.82 – 4.67 (m, 11H, Hα), 4.46 (dt, *J* = 5.2, 10.6, 1H, Hγ-Azp), 4.38 (dd, *J* = 5.6, 8.7, 1H, Hα-Pro-NH_2), 3.97 (dd, *J* = 6.3, 11.2, 1H, Hδ-Azp), 3.89 – 3.77 (m, 11H, Hδ), 3.70 – 3.53 (m, 12H, Hδ', Hδ'-Azp), 2.73 (ddd, *J* = 6.2, 9.2, 13.2, 1H, Hβ-Azp), 2.41 – 2.24 (m, 11H, Hβ), 2.10 (s, 3H, CH_3), 2.09 – 1.98 (m, 24H, 1 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.98 – 1.84 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{68}N_{16}O_{13} + H^+$: 1265.67895, obsd 1265.67881.

Monomeric azidoproline helix 2S-Azp. Yield after RP-HPLC purification: 22.9 mg (18.0 μmol, 36%). LC-MS analysis: t_R 4.83 min (gradient 10 to 50% B). ESI-MS *m/z*: 1265.7 [M +

H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.82 – 4.68 (m, 11H, Hα), 4.46 (dt, *J* = 5.9, 12.0, 1H, Hγ-Azp), 4.40 (dd, *J* = 5.4, 8.5, 1H, Hα-Pro-NH_2), 4.19 (dd, *J* = 6.6, 10.9, 1H, Hδ-Azp), 3.92 – 3.79 (m, 11H, Hδ), 3.73 – 3.60 (m, 11H, Hδ'), 3.56 (dd, *J* = 5.7, 10.7, 1H, Hδ'-Azp), 2.76 (ddd, *J* = 6.8, 8.6, 14.0, 1H, Hβ-Azp), 2.44 – 2.27 (m, 11H, Hβ), 2.12 (s, 3H, CH_3), 2.11 – 2.00 (m, 24H, 1 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.99 – 1.87 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{68}N_{16}O_{13}$ + H^+: 1265.67895, obsd 1265.67888.

Monomeric azidoproline helix 3S-Azp. Yield after RP-HPLC purification: 23.6 mg (18.6 μmol, 37%). LC-MS analysis: t_R 4.79 min (gradient 10 to 50% B). ESI-MS *m/z*: 1265.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.76 – 4.66 (m, 11H, Hα), 4.46 (dt, *J* = 6.0, 11.9, 1H, Hγ-Azp), 4.39 (dd, *J* = 5.4, 8.5, 1H, Hα-Pro-NH_2), 4.19 (dd, *J* = 6.4, 11.0, 1H, Hδ-Azp), 3.90 – 3.79 (m, 11H, Hδ), 3.72 – 3.59 (m, 11H, Hδ'), 3.57 (dd, *J* = 5.7, 10.9, 1H, Hδ'-Azp), 2.75 (ddd, *J* = 6.3, 8.7, 14.0, 1H, Hβ-Azp), 2.42 – 2.27 (m, 11H, Hβ), 2.12 (s, 3H, CH_3), 2.10 – 1.99 (m, 24H, 1 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.99 – 1.84 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{68}N_{16}O_{13}$ + H^+: 1265.67895, obsd 1265.67897.

Monomeric azidoproline helix 4S-Azp. Yield after RP-HPLC purification: 22.3 mg (17.6 μmol, 35%). LC-MS analysis: t_R 4.80 min (gradient 10 to 50% B). ESI-MS *m/z*: 1265.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.93 – 4.67 (m, 11H, Hα), 4.46 (dt, *J* = 6.5, 12.6, 1H, Hγ-Azp), 4.30 (dd, *J* = 5.3, 8.5, 1H, Hα-Pro-NH_2), 4.22 (dd, *J* = 6.5, 10.9, 1H, Hδ-Azp), 3.93 – 3.81 (m, 11H, Hδ), 3.74 – 3.60 (m, 11H, Hδ'), 3.56 (dd, *J* = 5.5, 10.6, 1H, Hδ'-Azp), 2.78 (ddd, *J* = 6.6, 8.9, 13.5, 1H, Hβ-Azp), 2.46 – 2.26 (m, 11H, Hβ), 2.13 (s, 3H, CH_3), 2.11 – 1.01 (m, 24H, 1 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 2.01 – 1.84 (m, 10H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{68}N_{16}O_{13}$ + H^+: 1265.67895, obsd 1265.67961.

Dimeric azidoproline helix 5S-Azp$_2$. Yield after RP-HPLC purification: 31.8 mg (24.1 μmol, 48%). LC-MS analysis: t_R 5.23 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 $[M + H]^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.76 – 4.68 (m, 11H, Hα), 4.45 – 4.37 (m, 2H, Hγ-Azp), 4.36 (dd, *J* = 5.4, 8.6, 1H, Hα-Pro-NH_2), 4.13 (dd, *J* = 6.6, 10.9, 1H, Hδ-Azp), 3.95 (dd, *J* = 6.1, 11.2, 1H, Hδ-Azp), 3.87 – 3.77 (m, 10H, Hδ), 3.68 – 3.53 (m, 11H, Hδ', Hδ'-Azp), 3.49 (dd, *J* = 6.1, 10.9, 1H, Hδ'-Azp), 2.77 – 2.67 (m, 2H, Hβ-Azp), 2.37 – 2.27 (m, 10H, Hβ), 2.09 (s, 3H, CH_3), 2.08 – 1.98 (m, 23H, 2 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.97 – 1.85 (m, 9H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13} + H^+$: 1306.68035, obsd 1306.68140.

Dimeric azidoproline helix 6S-Azp$_2$. Yield after RP-HPLC purification: 37.5 mg (28.7 μmol, 57%). LC-MS analysis: t_R 5.06 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 $[M + H]^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.76 (dd, *J* = 3.5, 9.0, 2H, Hα-Azp), 4.74 – 4.67 (m, 9H, Hα), 4.46 – 4.38 (m, 2H, Hγ-Azp), 4.36 (dd, *J* = 5.4, 8.6, 1H, HαPro-NH_2), 4.18 (dd, *J* = 6.6, 11.0, 1H, Hδ-Azp), 3.94 (dd, *J* = 6.2, 11.3, 1H, Hδ-Azp), 3.87 – 3.74 (m, 10H, Hδ), 3.68 – 3.50 (m, 12H, Hδ', Hδ'-Azp), 2.76 – 2.67 (m, 2H, Hβ-Azp), 2.38 – 2.26 (m, 10H, Hβ), 2.09 (s, 3H, CH_3), 2.07 – 1.97 (m, 23H, 2 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.97 – 1.84 (m, 9H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13} + H^+$: 1306.68035, obsd 1306.68188.

Dimeric azidoproline helix 7S-Azp$_2$. Yield after RP-HPLC purification: 19.4 mg (14.8 μmol, 30%). LC-MS analysis: t_R 5.14 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 $[M + H]^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.77 – 4.66 (m, 11H, Hα), 4.74 – 4.67 (m, 9H, Hα), 4.46 – 4.38 (m, 2H, Hγ-Azp), 4.39 (dd, *J* = 5.4, 8.6, 1H, Hα-Pro-NH_2), 4.19 (dd, *J* = 6.4, 11.0, 1H, Hδ-Azp), 3.98 (dd, *J* = 6.3, 11.3, 1H, Hδ-Azp), 3.90 – 3.77 (m, 10H, Hδ), 3.71 – 3.53 (m, 12H, Hδ', Hδ'-Azp), 2.79 – 2.70 (m, 2H, Hβ-Azp), 2.41 – 2.28 (m, 10H, Hβ), 2.10 (s, 3H, CH_3), 2.10 – 2.00 (m, 23H, 2 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 2.00 – 1.86 (m, 9H, 1 × Hβ'-Pro-

NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13} + H^+$: 1306.68035, obsd 1306.68140.

Dimeric azidoproline helix 8S-Azp$_2$. Yield after RP-HPLC purification: 26.2 mg (20.1 μmol, 40%). LC-MS analysis: t_R 5.12 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 $[M + H]^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.79 – 4.64 (m, 11H, Hα), 4.42 (ddd, *J* = 6.3, 12.1, 18.1, 2H, Hγ-Azp), 4.37 (dd, *J* = 5.4, 8.6, 1H, Hα-Pro-NH_2), 4.16 (dd, *J* = 6.6, 11.3, 1H, Hδ-Azp), 3.96 (dd, *J* = 6.3, 11.2, 1H, Hδ-Azp), 3.87 – 3.75 (m, 10H, Hδ), 3.68 – 3.50 (m, 12H, Hδ', Hδ'-Azp), 2.77 – 2.68 (m, 2H, Hβ-Azp), 2.42 – 2.26 (m, 10H, Hβ), 2.10 (s, 3H, CH_3), 2.08 – 1.99 (m, 23H, 2 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.98 – 1.83 (m, 9H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13} + H^+$: 1306.68035, obsd 1306.68127.

Dimeric azidoproline helix 9S-Azp$_2$. Yield after RP-HPLC purification: 42.3 mg (32.4 μmol, 65%). LC-MS analysis: t_R 5.05 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 $[M + H]^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.75 – 4.67 (m, 11H, Hα), 4.44 (dt, *J* = 6.3, 12.8, 2H, Hγ-Azp), 4.39 (dd, *J* = 5.2, 8.6, 1H, Hα-Pro-NH_2), 4.19 (dd, *J* = 6.6, 11.0, 1H, Hδ-Azp), 3.97 (dd, *J* = 6.3, 11.3, 1H, Hδ-Azp), 3.89 – 3.75 (m, 10H, Hδ), 3.71 – 3.46 (m, 12H, Hδ', Hδ'-Azp), 2.74 (ddt, *J* = 6.6, 8.9, 13.6, 2H, Hβ-Azp), 2.42 – 2.25 (m, 10H, Hβ), 2.11 (s, 3H, CH_3), 2.09 – 1.99 (m, 23H, 2 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.99 – 1.85 (m, 9H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13} + H^+$: 1306.68035, obsd 1306.68127.

Dimeric azidoproline helix 10S-Azp$_2$. Yield after RP-HPLC purification: 35.3 mg (22.1 μmol, 44%). LC-MS analysis: t_R 5.32 min (gradient 10 to 50% B). ESI-MS *m/z*: 1597.6 $[M + H]^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.82 – 4.67 (m, 14H, Hα), 4.44 (dt, *J* = 6.6, 12.9, 2H, Hγ-Azp), 4.40 (dd, *J* = 5.3, 8.9, 1H, Hα-Pro-NH_2), 4.19 (dd, *J* = 6.6, 11.0, 1H, Hδ-Azp), 3.97 (dd, *J* = 6.3, 11.3, 1H, Hδ-Azp), 3.89 – 3.78 (m, 13H, Hδ), 3.69 – 3.57 (m, 14H, Hδ'), 3.54 (dd, *J*

= 5.7, 10.5, 1H, Hδ'-Azp), 2.74 (ddt, *J* = 6.7, 8.8, 13.6, 2H, Hβ-Azp), 2.40 – 2.25 (m, 12H, Hβ), 2.11 (s, 3H, CH_3), 2.10 – 1.99 (m, 29H, 2 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.98 – 1.85 (m, 13H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{77}H_{108}N_{22}O_{16} + H^+$: 1597.83864, obsd 1597.83844.

Dimeric azidoproline helix 11S-Azp$_2$. Yield after RP-HPLC purification: 57.9 mg (30.7 μmol, 61%). LC-MS analysis: t_R 5.44 min (gradient 10 to 50% B). ESI-MS *m/z*: 1888.7 $[M + H]^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.83 – 4.62 (m, 17H, Hα), 4.38 (dt, *J* = 6.7, 12.8, 2H, Hγ-Azp), 4.35 (dd, *J* = 5.3, 8.8, 1H, Hα-Pro-NH_2), 4.15 (dd, *J* = 6.4, 10.5, 1H, Hδ-Azp), 3.92 (dd, *J* = 6.2, 11.2, 1H, Hδ-Azp), 3.87 – 3.74 (m, 16H, Hδ), 3.67 – 3.55 (m, 17H, Hδ'), 3.49 (dd, *J* = 5.6, 10.3, 1H, Hδ'-Azp), 2.69 (ddt, *J* = 6.0, 7.5, 13.5, 2H, Hβ-Azp), 2.43 – 2.20 (m, 15H, Hβ), 2.06 (s, 3H, CH_3), 2.05 – 1.94 (m, 35H, 2 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.94 – 1.81 (m, 16H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{92}H_{129}N_{25}O_{19} + H^+$: 1888.99693, obsd 1888.99924.

Dimeric azidoproline helix 12S-Azp$_2$. Yield after RP-HPLC purification: 42.8 mg (19.6 μmol, 39%). LC-MS analysis: t_R 5.54 min (gradient 10 to 50% B). ESI-MS *m/z*: 1090.4 $[M + 2H]^{2+}$. ^{1}H NMR (400 MHz, D_2O) δ 4.80 – 4.60 (m, 20H, Hα), 4.40 (dt, *J* = 6.5, 12.8, 2H, Hγ-Azp), 4.36 (dd, *J* = 5.3, 8.9, 1H, Hα-Pro-NH_2), 4.16 (dd, *J* = 6.6, 11.0, 1H, Hδ-Azp), 3.94 (dd, *J* = 6.3, 11.2, 1H, Hδ-Azp), 3.86 – 3.75 (m, 19H, Hδ), 3.68 – 3.54 (m, 20H, Hδ'), 3.51 (dd, *J* = 5.6, 10.4, 1H, Hδ'-Azp), 2.71 (ddt, *J* = 5.6, 7.6, 13.2, 2H, Hβ-Azp), 2.43 – 2.23 (m, 18H, Hβ), 2.08 (s, 3H, CH_3), 2.06 – 1.95 (m, 41H, 2 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.95 – 1.80 (m, 19H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{107}H_{150}N_{28}O_{22} + 2H^+$: 1090.58125, obsd 1090.58221.

Dimeric azidoproline helix 13S-Azp$_2$. Yield after RP-HPLC purification: 21.2 mg (16.2 μmol, 32%). LC-MS analysis: t_R 5.21 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.80 – 4.65 (m, 11H, Hα), 4.44 (ddd, *J* = 6.0, 11.8, 18.2, 2H, Hγ-Azp), 4.38 (dd, *J* = 5.4, 8.5, 1H, Hα-Pro-NH_2), 4.17 (dt, *J* = 6.7, 11.4, 2H, Hδ-Azp), 3.89 – 3.76 (m, 10H, Hδ), 3.70 – 3.58 (m, 10H, Hδ'), 3.54 (ddd, *J* = 3.1, 5.0, 10.5, 2H, Hδ'-Azp), 2.78 – 2.69 (m, 2H, Hβ-Azp), 2.41 – 2.27 (m, 10H, Hβ), 2.10 (s, 3H, CH_3), 2.09 – 1.98 (m, 23H, 2 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 1.98 – 1.85 (m, 9H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13}$ + H^+: 1306.68035, obsd 1306.68127.

Dimeric azidoproline helix 14S-Azp$_2$. Yield after RP-HPLC purification: 40.6 mg (31.1 μmol, 62%). LC-MS analysis: t_R 5.14 min (gradient 10 to 50% B). ESI-MS *m/z*: 1306.7 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.78 – 4.62 (m, 11H, Hα), 4.43 (ddd, *J* = 5.8, 11.4, 17.1, 2H, Hγ-Azp), 4.37 (dd, *J* = 5.3, 8.7, 1H, Hα-Pro-NH_2), 4.16 (ddd, *J* = 6.5, 11.1, 14.1, 2H, Hδ-Azp), 3.86 – 3.75 (m, 10H, Hδ), 3.68 – 3.48 (m, 12H, Hδ', Hδ'-Azp), 2.72 (ddd, *J* = 6.2, 9.0, 13.4, 2H, Hβ-Azp), 2.36 – 2.25 (m, 10H, Hβ), 2.08 (s, 3H, CH_3), 2.07 – 1.97 (m, 23H, 2 × Hβ'-Azp, 1 × HβPro-NH_2, Hγ), 1.97 – 1.84 (m, 9H, 1 × Hβ'-Pro-NH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{87}N_{19}O_{13}$ + H^+: 1306.68035, obsd 1306.68176.

Tetrameric azidoproline helix 15S-Azp$_4$. Yield after RP-HPLC purification: 13.7 mg (9.9 μmol, 20%). LC-MS analysis: t_R 5.98 min (gradient 10 to 50% B). ESI-MS *m/z*: 1388.8 [M + H]$^+$. ^{1}H NMR (400 MHz, D_2O) δ 4.84 – 4.63 (m, 11H, Hα), 4.50 – 4.36 (m, 5H, Hγ-Azp, Hα-Pro-NH_2), 4.25 – 4.13 (m, 3H, Hδ-Azp), 3.97 (dd, *J* = 6.3, 11.2, 1H, Hδ-Azp), 3.92 – 3.76 (m, 8H, Hδ), 3.72 – 3.46 (m, 12H, Hδ'), 2.81 -2.67 (m, 4H, Hβ-Azp), 2.43 – 2.25 (m, 8H, Hβ), 2.12 (s, 3H, CH_3), 2.10 – 2.00 (m, 21H, 4 × Hβ'-Azp, 1 × Hβ-Pro-NH_2, Hγ), 2.00 – 1.87 (m, 7H, 1 × Hβ'-ProNH_2, Hβ). HRMS *m/z* calcd for $C_{62}H_{85}N_{25}O_{13}$ + H^+: 1388.68314, obsd

1388.68298.

General procedure for the functionalization of azidoproline peptides with LHA.

To a solution of the desired azidoproline peptide (5.0 μmol) and **LHA** (1.2 eq. per azide, 6 μmol, 2.9 mg) in a mixture of degassed *t*BuOH/MeCN/H_2O (2/2/1; v/v/v, 500 μL) were added sodium ascorbate (2.5 eq. per azide, 50 μL of a 0.25M solution in H_2O) and $CuSO_4$ (0.5 eq. per azide, 25 μL of a 0.1M solution in H_2O). The reaction mixture was stirred and heated at 60 °C for 3 h. The mixture was evaporated, redissolved H_2O/CH_3CN (1/1; v/v, 1 mL) and filtrated. The crude products were analyzed by LC-MS and purified by semi-preparative RP-HPLC (linear gradient of 5.0 CV; 40 to 80% B). Evaporation and lyophilization of the combined fractions from Dioxane/H_2O (1/1; v/v) furnished the ligands as yellow powders.

Monomeric ligand 1R-LHA. Yield after RP-HPLC purification: 2.0 mg (1.1 μmol, 21%). LC-MS analysis: t_R 6.58 min (gradient 10 to 90% B). ESI-MS *m/z*: 1747.6 $[M + H]^+$. HRMS *m/z* calcd for $C_{85}H_{114}N_{22}O_{15}S_2 + H^+$: 1747.83482, obsd 1747.83601.

Monomeric ligand 2R-LHA. Yield after RP-HPLC purification: 1.6 mg (0.9 μmol, 17%). LC-MS analysis: t_R 6.54 min (gradient 10 to 90% B). ESI-MS *m/z*: 1747.6 $[M + H]^+$. HRMS *m/z* calcd for $C_{85}H_{114}N_{22}O_{15}S_2 + H^+$: 1747.83482, obsd 1747.83581.

Monomeric ligand 3R-LHA. Yield after RP-HPLC purification: 1.1 mg (0.6 μmol, 12%). LC-MS analysis: t_R 6.40 min (gradient 10 to 90% B). ESI-MS *m/z*: 1747.6 $[M + H]^+$. HRMS *m/z* calcd for $C_{85}H_{114}N_{22}O_{15}S_2 + H^+$: 1747.83482, obsd 1747.83570.

Monomeric ligand 4R-LHA. Yield after RP-HPLC purification: 4.1 mg (2.2 μmol, 44%). LC-MS analysis: t_R 6.50 min (gradient 10 to 90% B). ESI-MS *m/z*: 1747.7 $[M + H]^+$. HRMS *m/z* calcd for $C_{85}H_{114}N_{22}O_{15}S_2 + H^+$: 1747.83482, obsd 1747.83561.

Dimeric ligand 5R-LHA$_2$. Yield after RP-HPLC purification: 2.2 mg (1.0 μmol, 19%). LC-MS analysis: t_R 8.24 min (gradient 10 to 90% B). ESI-MS *m/z*: 1136.4 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00061.

Dimeric ligand 6R-LHA$_2$. Yield after RP-HPLC purification: 2.7 mg (1.2 μmol, 24%). LC-MS analysis: t_R 8.20 min (gradient 10 to 90% B). ESI-MS *m/z*: 1136.5 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00098.

Dimeric ligand 7R-LHA$_2$. Yield after RP-HPLC purification: 2.1 mg (0.9 μmol, 19%). LC-MS analysis: t_R 8.17 min (gradient 10 to 90% B). ESI-MS *m/z*: 1136.5 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00012.

Dimeric ligand 8R-LHA$_2$. Yield after RP-HPLC purification: 2.5 mg (1.1 μmol, 22%). LC-MS analysis: t_R 7.94 min (gradient 10 to 90% B). ESI-MS *m/z*: 1136.4 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00110.

Dimeric ligand 9R-LHA$_2$. Yield after RP-HPLC purification: 2.8 mg (1.2 μmol, 25%). LC-MS analysis: t_R 7.94 min (gradient 10 to 90% B). ESI-MS *m/z*: 1135.7 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00159.

Dimeric ligand 10R-LHA$_2$. Yield after RP-HPLC purification: 1.9 mg (0.7 μmol, 14%). LC-

MS analysis: t_R 7.76 min (gradient 10 to 90% B). ESI-MS *m/z*: 1281.5 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{123}H_{160}N_{34}O_{20}S_4 + 2H^+$: 1281.57882, obsd 1281.57994.

Dimeric ligand 11R-LHA$_2$. Yield after RP-HPLC purification: 3.6 mg (1.2 μmol, 24%). LC-MS analysis: t_R 7.56 min (gradient 10 to 90% B). ESI-MS *m/z*: 1427.1 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{138}H_{181}N_{37}O_{23}S_4 + 2H^+$: 1427.15797, obsd 1427.15894.

Dimeric ligand 12R-LHA$_2$. Yield after RP-HPLC purification: 2.8 mg (0.8 μmol, 17%). LC-MS analysis: t_R 7.43 min (gradient 10 to 90% B). ESI-MS *m/z*: 1572.7 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{153}H_{202}N_{40}O_{26}S_4 + 2H^+$: 1572.73712, obsd 1572.73759.

Dimeric ligand 13R-LHA$_2$. Yield after RP-HPLC purification: 2.2 mg (1.0 μmol, 19%). LC-MS analysis: t_R 8.11 min (gradient 10 to 90% B ESI-MS *m/z*: 1136.5 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00110.

Dimeric ligand 14R-LHA$_2$. Yield after RP-HPLC purification: 3.0 mg (1.3 μmol, 26%). LC-MS analysis: t_R 8.03 min (gradient 10 to 90% B ESI-MS *m/z*: 1136.7 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00110.

Tetrameric ligand 15R-LHA$_4$. Yield after RP-HPLC purification: 1.4 mg (0.4 μmol, 7%). LC-MS analysis: t_R 10.91 min (gradient 10 to 90% B). ESI-MS *m/z*: 1659.6 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{154}H_{189}N_{49}O_{21}S_8 + 2H^+$: 1659.15694, obsd 1659.15793.

Monomeric ligand 1S-LHA. Yield after RP-HPLC purification: 2.2 mg (1.1 μmol, 24%). LC-MS analysis: t_R 6.48 min (gradient 10 to 90% B). ESI-MS *m/z*: 1747.7 $[M + H]^{2+}$. HRMS

m/z calcd for $C_{85}H_{114}N_{22}O_{15}S_2 + H^+$: 1747.83482, obsd 1747.83534.

Monomeric ligand 2S-LHA. Yield after RP-HPLC purification: 1.9 mg (1.0 μmol, 20%). LC-MS analysis: t_R 6.39 min (gradient 10 to 90% B). ESI-MS *m/z*: 1747.7 $[M + H]^{2+}$. HRMS *m/z* calcd for $C_{85}H_{114}N_{22}O_{15}S_2 + H^+$: 1747.83482, obsd 1747.83455.

Monomeric ligand 3S-LHA. Yield after RP-HPLC purification: 1.9 mg (1.0 μmol, 20%). LC-MS analysis: t_R 6.32 min (gradient 10 to 90% B). ESI-MS *m/z*: 1747.5 $[M + H]^{2+}$. HRMS *m/z* calcd for $C_{85}H_{114}N_{22}O_{15}S_2 + H^+$: 1747.83482, obsd 1747.83542.

Monomeric ligand 4S-LHA. Yield after RP-HPLC purification: 1.5 mg (0.8 μmol, 16%). LC-MS analysis: t_R 6.39 min (gradient 10 to 90% B). ESI-MS *m/z*: 1747.6 $[M + H]^{2+}$. HRMS *m/z* calcd for $C_{85}H_{114}N_{22}O_{15}S_2 + H^+$: 1747.83482, obsd 1747.83532.

Dimeric ligand 5S-LHA$_2$. Yield after RP-HPLC purification: 2.9 mg (1.3 μmol, 26%). LC-MS analysis: t_R 8.01 min (gradient 10 to 90% B). ESI-MS *m/z*: 1136.3 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1135.99915.

Dimeric ligand 6S-LHA$_2$. Yield after RP-HPLC purification: 4.7 mg (2.1 μmol, 41%). LC-MS analysis: t_R 7.97 min (gradient 10 to 90% B). ESI-MS *m/z*: 1136.5 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00085.

Dimeric ligand 7S-LHA$_2$. Yield after RP-HPLC purification: 3.5 mg (1.5 μmol, 31%). LC-MS analysis: t_R 8.08 min (gradient 10 to 90% B). ESI-MS *m/z*: 1136.5 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00012.

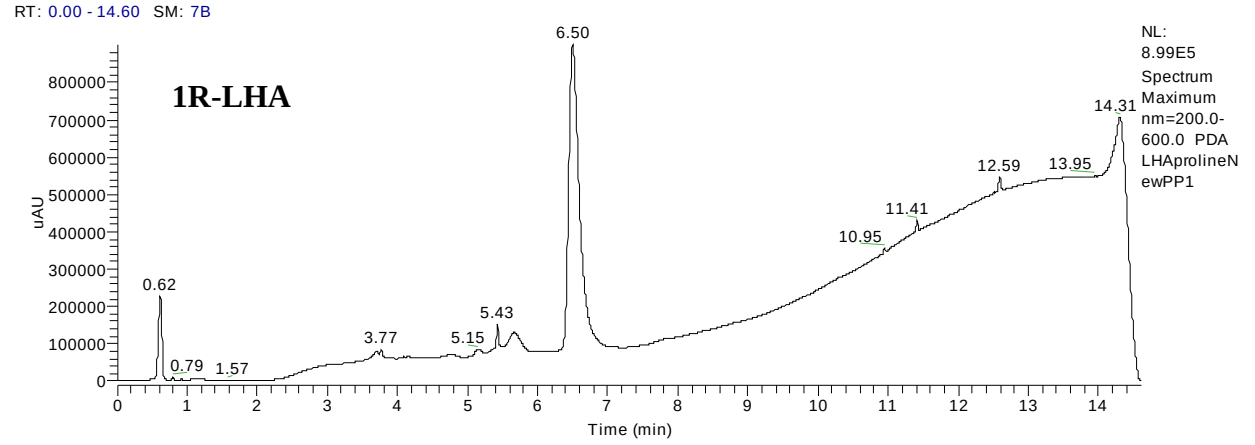
Dimeric ligand 8S-LHA$_2$. Yield after RP-HPLC purification: 4.1 mg (1.8 μmol, 36%). LC-MS analysis: t_R 7.92 min (gradient 10 to 90% B). ESI-MS *m/z*: 1136.3 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1135.99890.

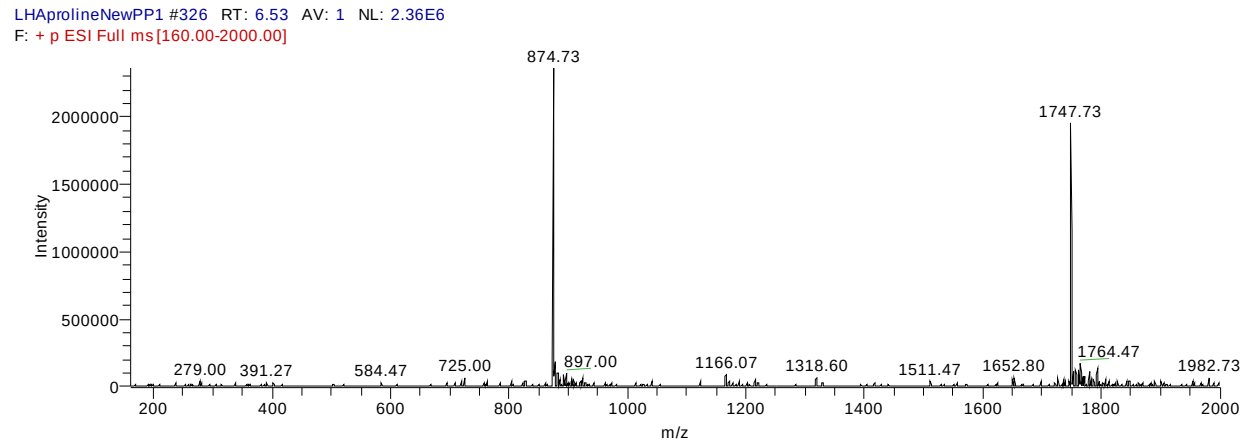
Dimeric ligand 9S-LHA$_2$. Yield after RP-HPLC purification: 3.5 mg (1.5 μmol, 31%). LC-MS analysis: t_R 8.00 min (gradient 10 to 90% B ESI-MS *m/z*: 1137.3 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00000.

Dimeric ligand 13S-LHA$_2$. Yield after RP-HPLC purification: 3.7 mg (1.6 μmol, 33%). LC-MS analysis: t_R 7.97 min (gradient 10 to 90% B). ESI-MS *m/z*: 1136.2 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00073.

Dimeric ligand 14S-LHA$_2$. Yield after RP-HPLC purification: 3.2 mg (1.4 μmol, 28%). LC-MS analysis: t_R 8.07 min (gradient 10 to 90% B). ESI-MS *m/z*: 1136.5 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{108}H_{139}N_{31}O_{17}S_4 + 2H^+$: 1135.99968, obsd 1136.00000.

Tetrameric ligand 15S-LHA$_4$. Yield after RP-HPLC purification: 1.5 mg (0.4 μmol, 8%). LC-MS analysis: t_R 10.9 min (gradient 10 to 90% B). ESI-MS *m/z*: 1659.6 $[M + 2H]^{2+}$. HRMS *m/z* calcd for $C_{154}H_{189}N_{49}O_{21}S_8 + 2H^+$: 1659.15694, obsd 1659.15774.


RT: 0.00 - 14.60 SM: 7B
1R-LHA
uAU
Time (min)
NL: 8.99E5 Spectrum Maximum nm=200.0-600.0 PDA LHAprolineNewPP1
6.50
14.31
12.59
13.95
11.41
10.95
0.62
5.43
3.77
5.15
0.79
1.57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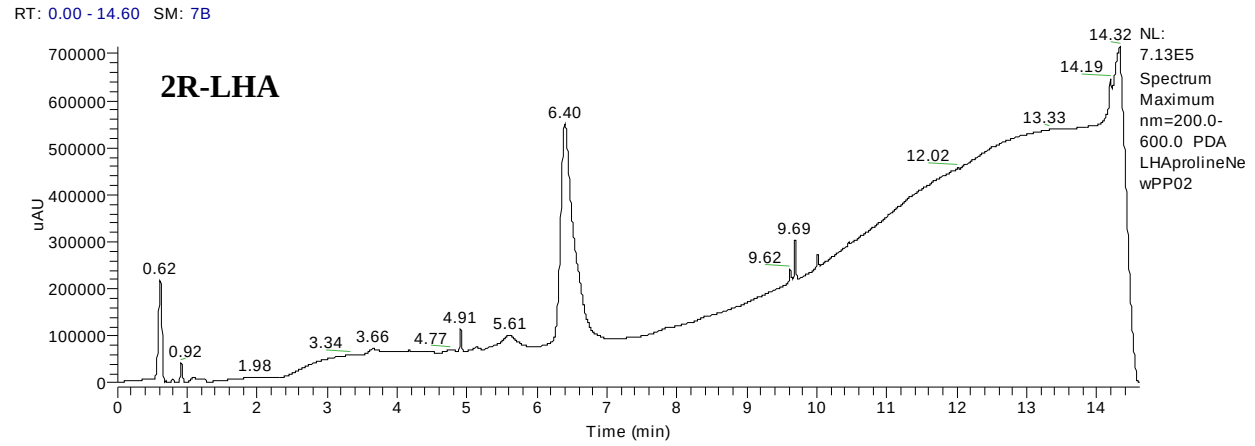
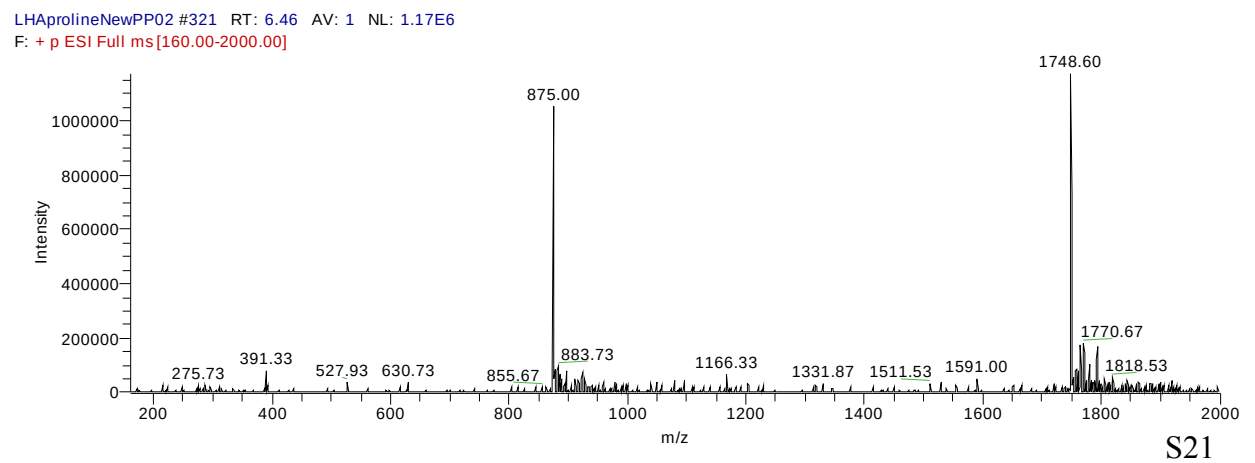
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
874.73
1747.73
279.00
391.27
584.47
725.00
897.00
1166.07
1318.60
1511.47
1652.80
1764.47
1982.73


RT: 0.00 - 14.60 SM: 7B
2R-LHA
uAU
Time (min)
NL: 7.13E5 Spectrum Maximum nm=200.0-600.0 PDA LHAprolineNewPP02
14.32
14.19
13.33
6.40
12.02
9.69
9.62
0.62
4.91
5.61
3.34
3.66
4.77
0.92
1.98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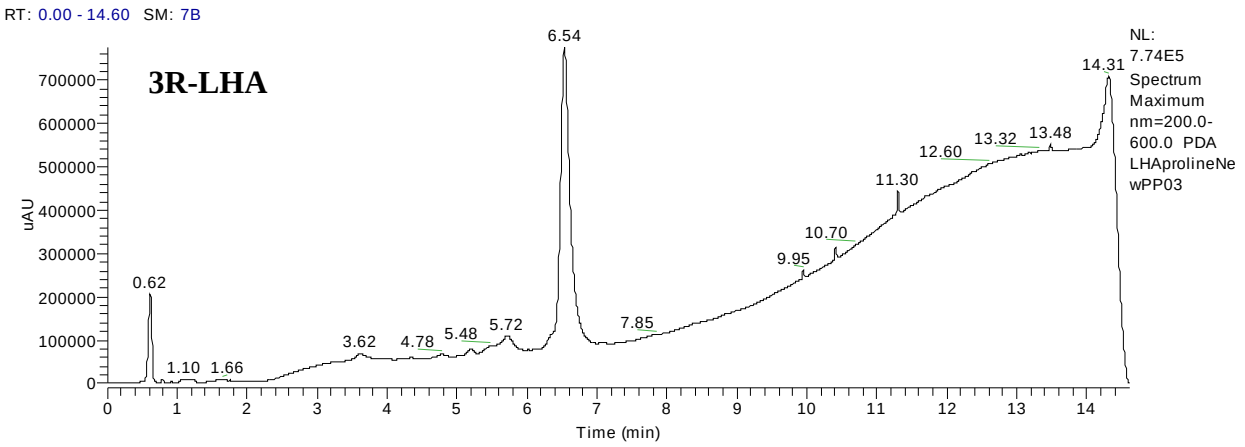
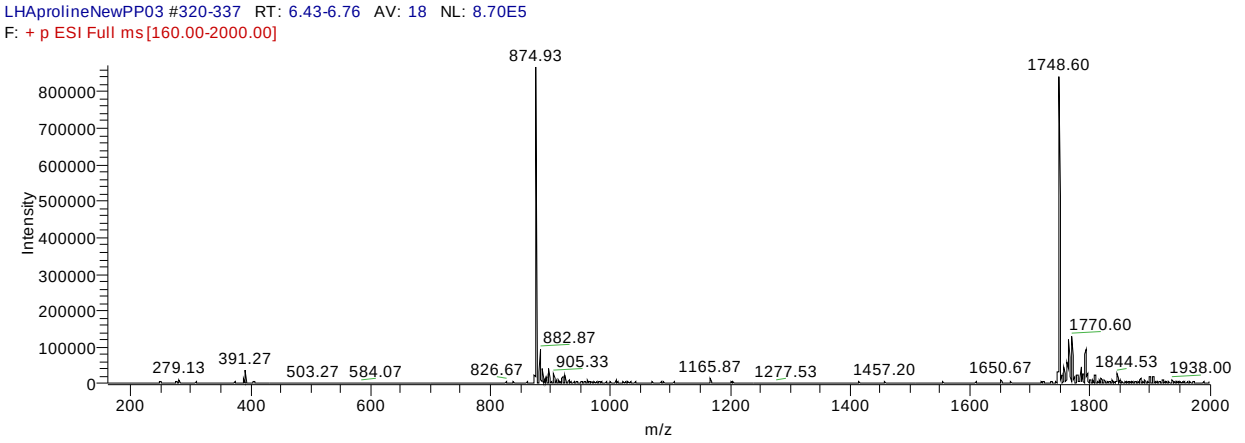
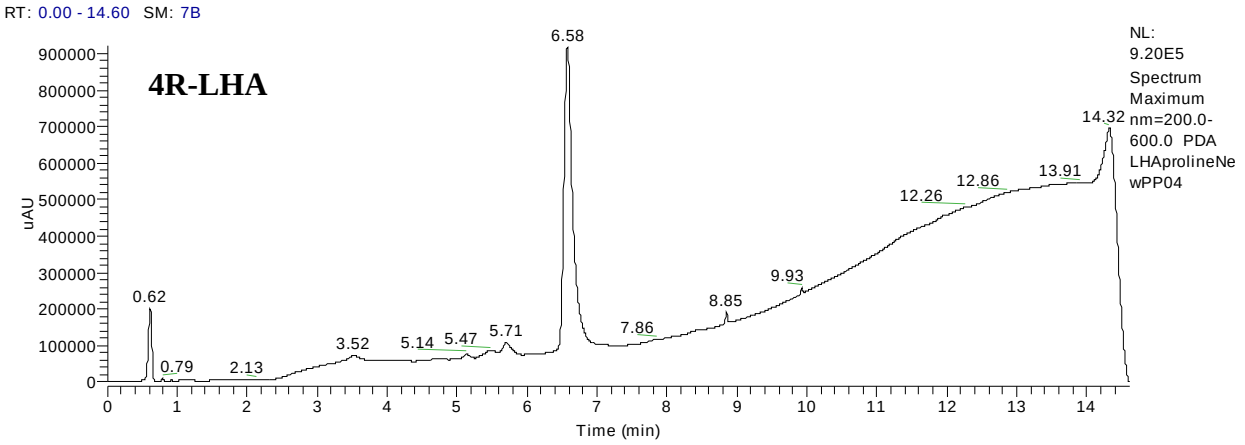
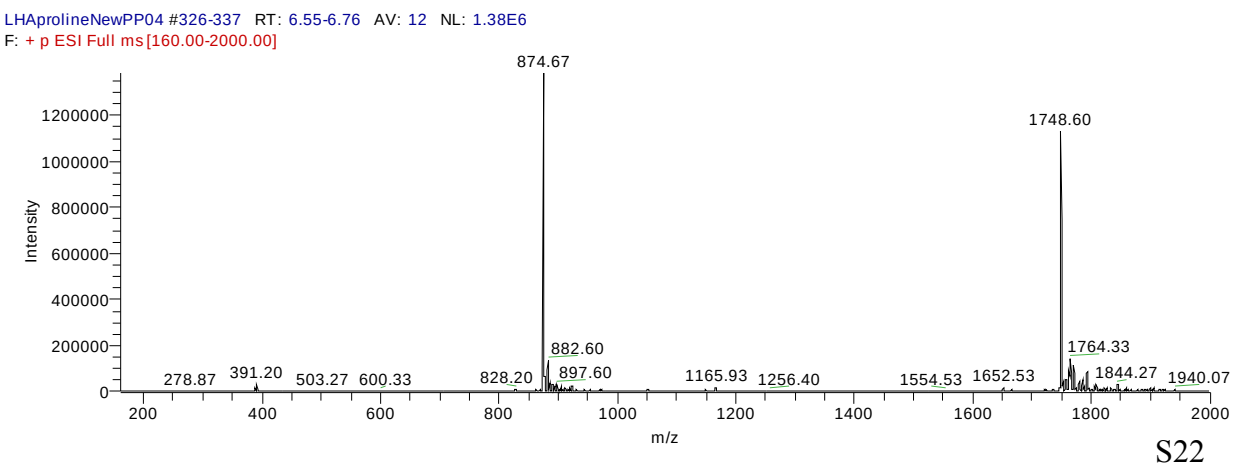
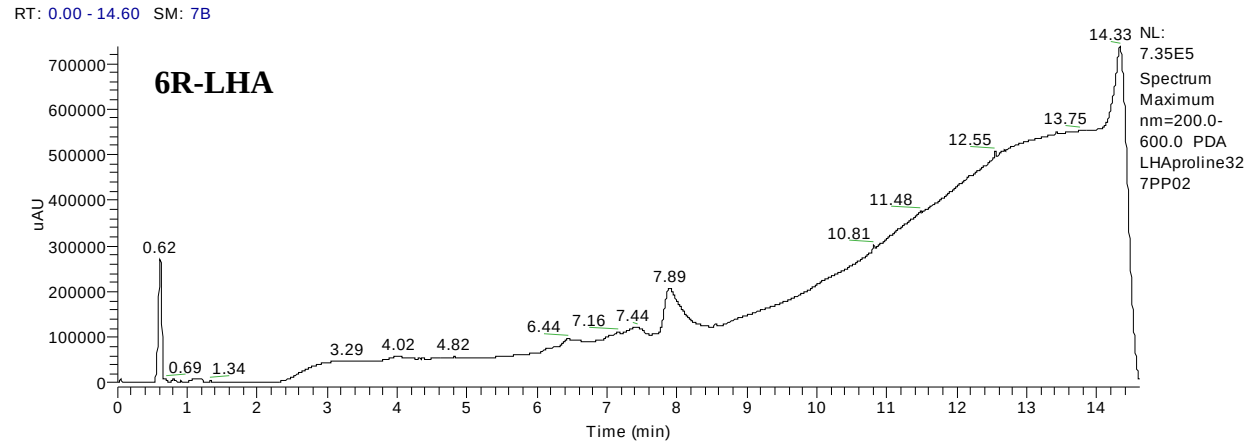
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
1748.60
875.00
1770.67
391.33
883.73
1166.33
1591.00
1818.53
275.73
527.93
630.73
855.67
1331.87
1511.53

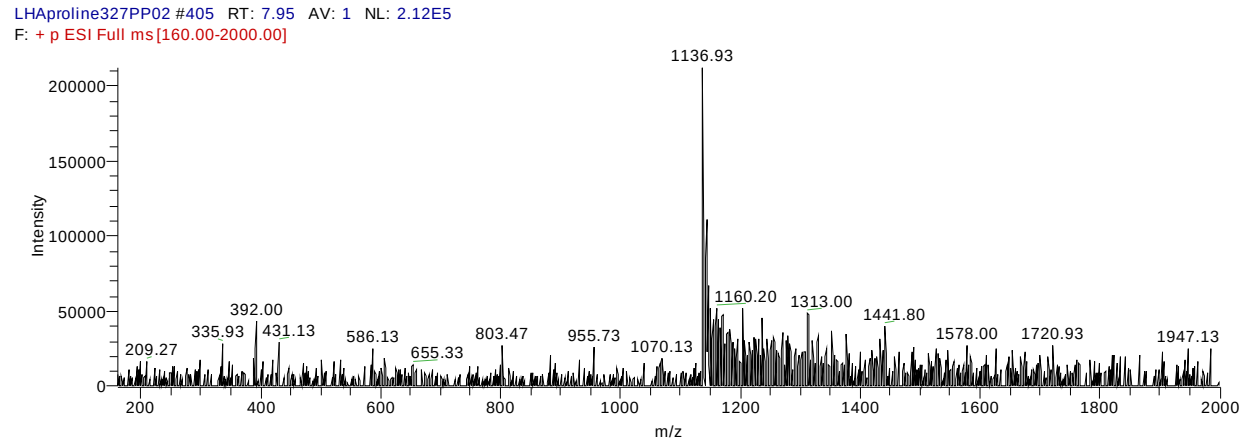

RT: 0.00 - 14.60 SM: 7B
3R-LHA
NL: 7.74E5 Spectrum Maximum nm=200.0-600.0 PDA LHAprolineNewPP03
uAU
Time (min)
0.62
1.10
1.66
3.62
4.78
5.48
5.72
6.54
7.85
9.95
10.70
11.30
12.60
13.32
13.48
14.31

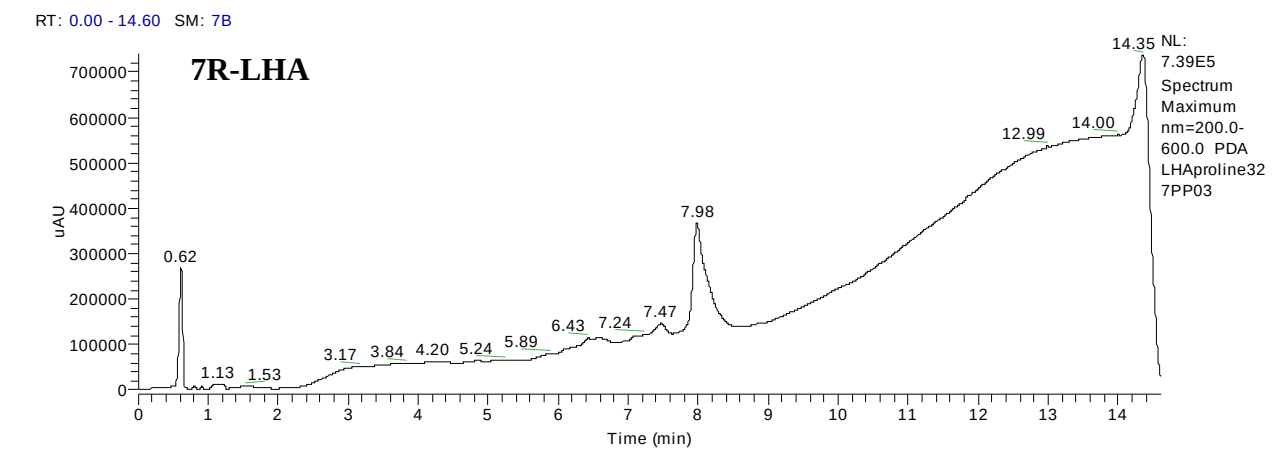

LHAprolineNewPP03 #320-337 RT: 6.43-6.76 AV: 18 NL: 8.70E5
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
279.13
391.27
503.27
584.07
826.67
874.93
882.87
905.33
1165.87
1277.53
1457.20
1650.67
1748.60
1770.60
1844.53
1938.00

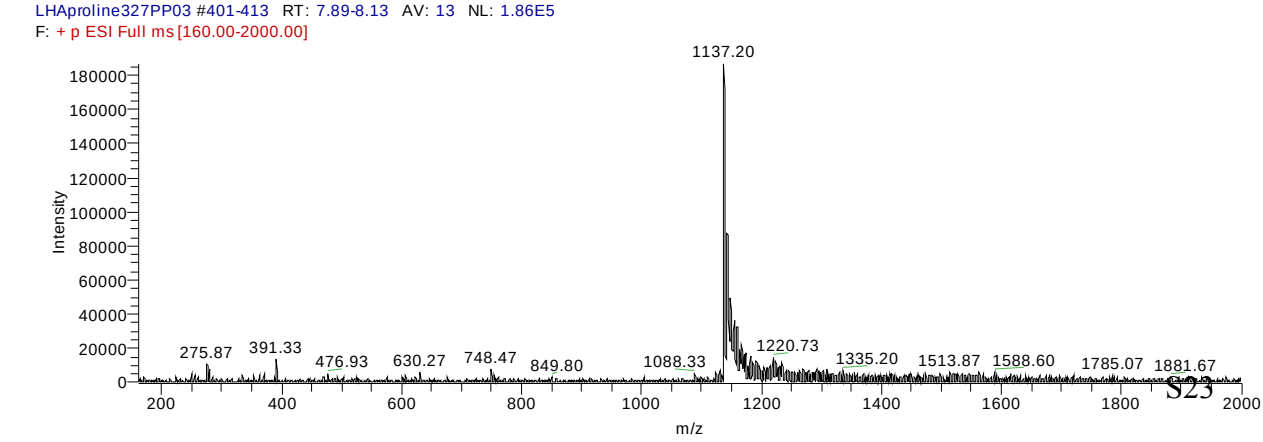

RT: 0.00 - 14.60 SM: 7B
4R-LHA
NL: 9.20E5 Spectrum Maximum nm=200.0-600.0 PDA LHAprolineNewPP04
uAU
Time (min)
0.62
0.79
2.13
3.52
5.14
5.47
5.71
6.58
7.86
8.85
9.93
12.26
12.86
13.91
14.32

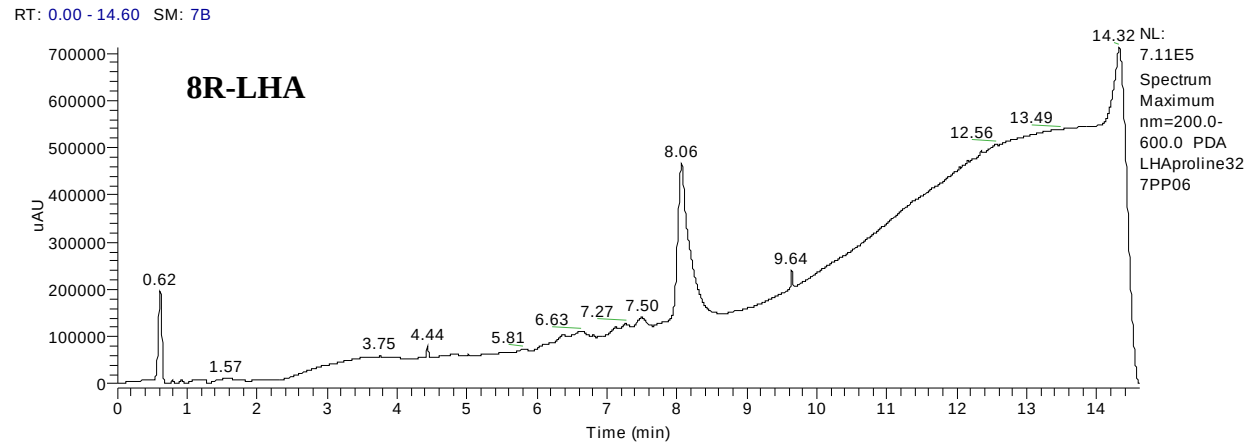

LHAprolineNewPP04 #326-337 RT: 6.55-6.76 AV: 12 NL: 1.38E6
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
278.87
391.20
503.27
600.33
828.20
874.67
882.60
897.60
1165.93
1256.40
1554.53
1652.53
1748.60
1764.33
1844.27
1940.07

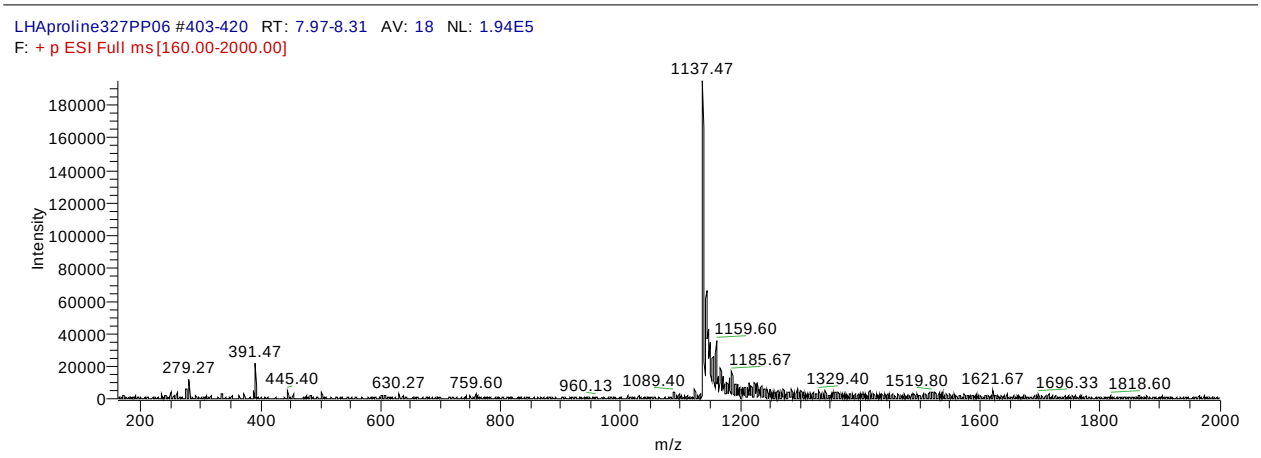

RT: 0.00 - 14.60 SM: 7B
6R-LHA
uAU
Time (min)
NL: 7.35E5 Spectrum Maximum nm=200.0-600.0 PDA LHAproline32 7PP02
0.62
0.69
1.34
3.29
4.02
4.82
6.44
7.16
7.44
7.89
10.81
11.48
12.55
13.75
14.33

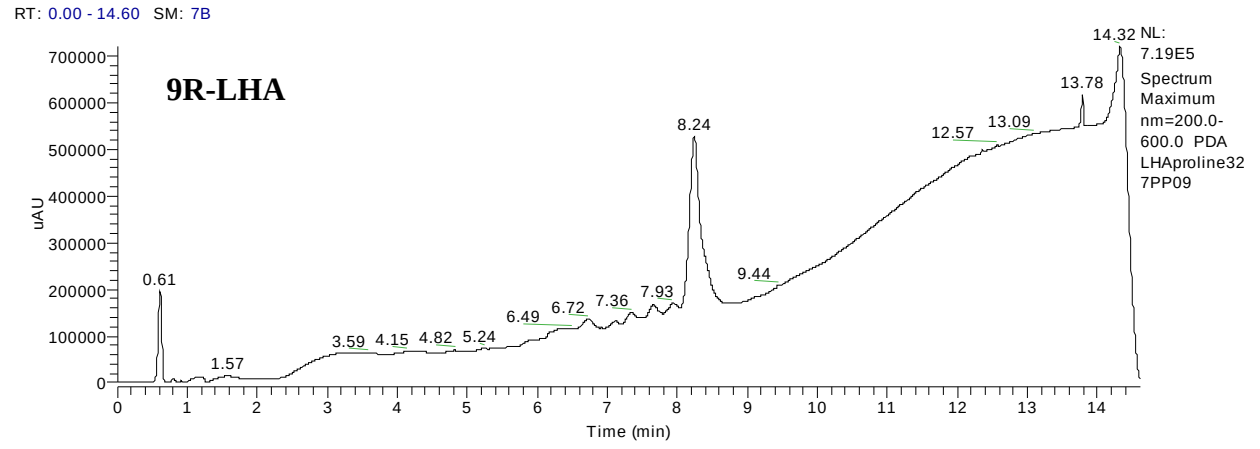

LHAproline327PP02 #405 RT: 7.95 AV: 1 NL: 2.12E5
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
1136.93
1160.20
1313.00
1441.80
1578.00
1720.93
1947.13
392.00
335.93
431.13
586.13
655.33
803.47
955.73
1070.13
209.27

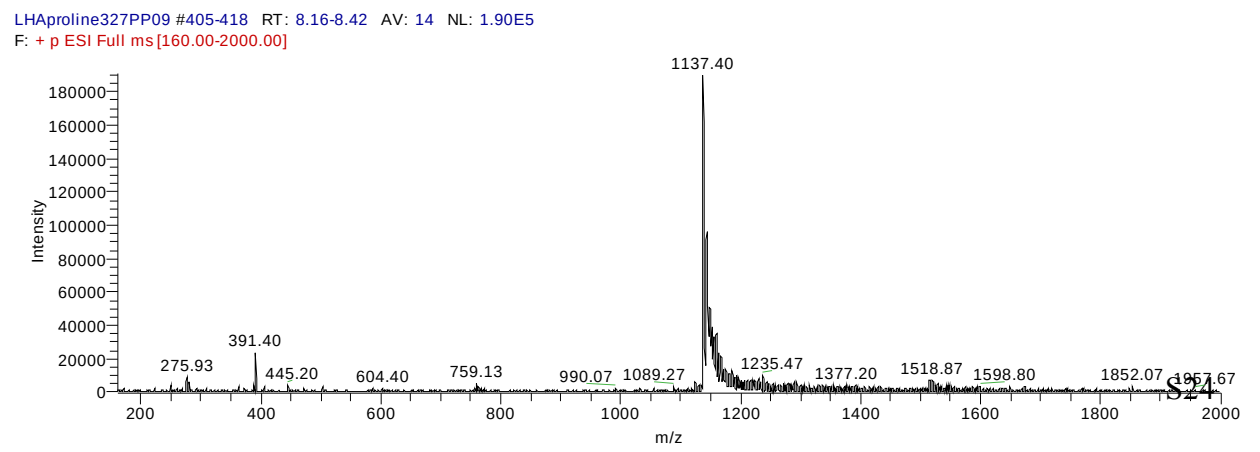

RT: 0.00 - 14.60 SM: 7B
7R-LHA
uAU
Time (min)
NL: 7.39E5 Spectrum Maximum nm=200.0-600.0 PDA LHAproline32 7PP03
0.62
1.13
1.53
3.17
3.84
4.20
5.24
5.89
6.43
7.24
7.47
7.98
12.99
14.00
14.35


LHAproline327PP03 #401-413 RT: 7.89-8.13 AV: 13 NL: 1.86E5
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
1137.20
1220.73
1335.20
1513.87
1588.60
1785.07
1881.67
275.87
391.33
476.93
630.27
748.47
849.80
1088.33


RT: 0.00 - 14.60 SM: 7B
8R-LHA
uAU
Time (min)
14.32 NL: 7.11E5 Spectrum Maximum nm=200.0-600.0 PDA LHAproline32 7PP06
0.62
1.57
3.75
4.44
5.81
6.63
7.27
7.50
8.06
9.64
12.56
13.49


LHAproline327PP06 #403-420 RT: 7.97-8.31 AV: 18 NL: 1.94E5
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
1137.47
1159.60
1185.67
391.47
279.27
445.40
630.27
759.60
960.13
1089.40
1329.40
1519.80
1621.67
1696.33
1818.60


RT: 0.00 - 14.60 SM: 7B
9R-LHA
uAU
Time (min)
14.32 NL: 7.19E5 Spectrum Maximum nm=200.0-600.0 PDA LHAproline32 7PP09
0.61
1.57
3.59
4.15
4.82
5.24
6.49
6.72
7.36
7.93
8.24
9.44
12.57
13.09
13.78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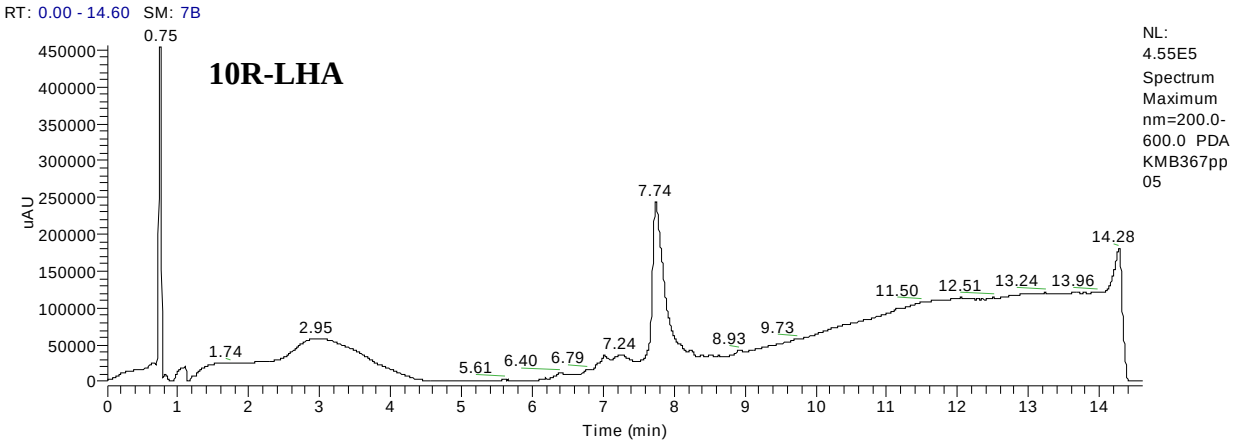
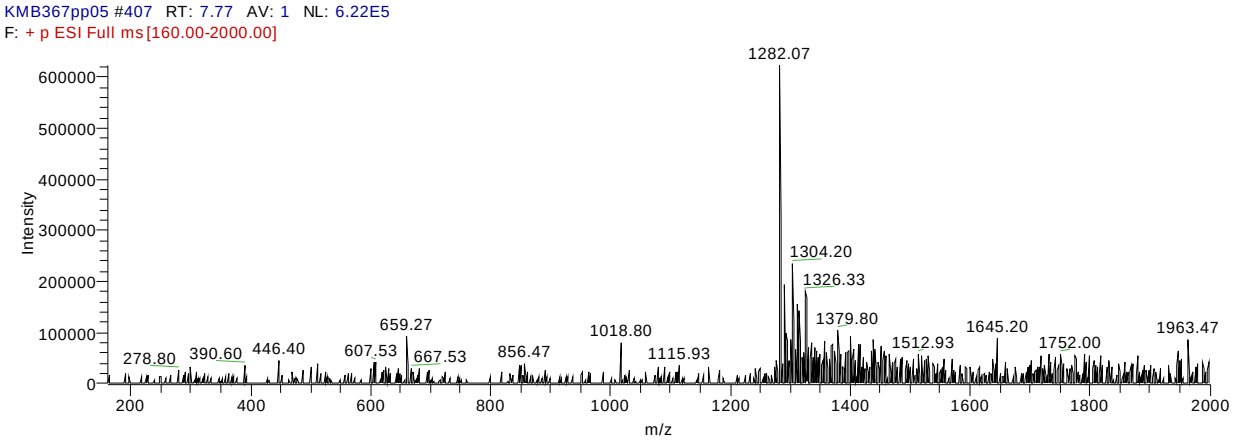
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
1137.40
391.40
275.93
445.20
604.40
759.13
990.07
1089.27
1235.47
1377.20
1518.87
1598.80
1852.07
1957.67


RT: 0.00 - 14.60 SM: 7B
10R-LHA
NL: 4.55E5 Spectrum Maximum nm=200.0-600.0 PDA KMB367pp 05
uAU
Time (min)
0.75
1.74
2.95
5.61
6.40
6.79
7.24
7.74
8.93
9.73
11.50
12.51
13.24
13.96
14.28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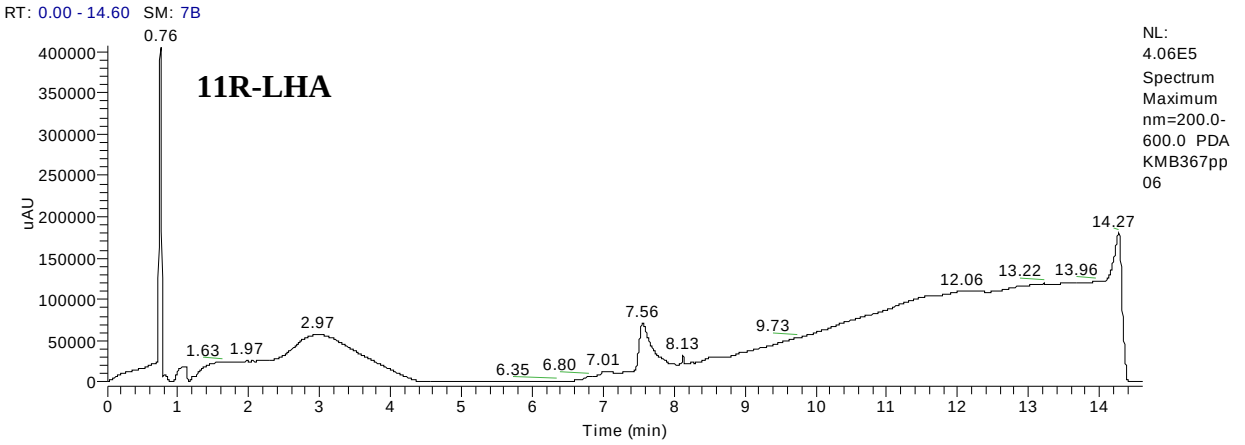
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
278.80
390.60
446.40
607.53
659.27
667.53
856.47
1018.80
1115.93
1282.07
1304.20
1326.33
1379.80
1512.93
1645.20
1752.00
1963.47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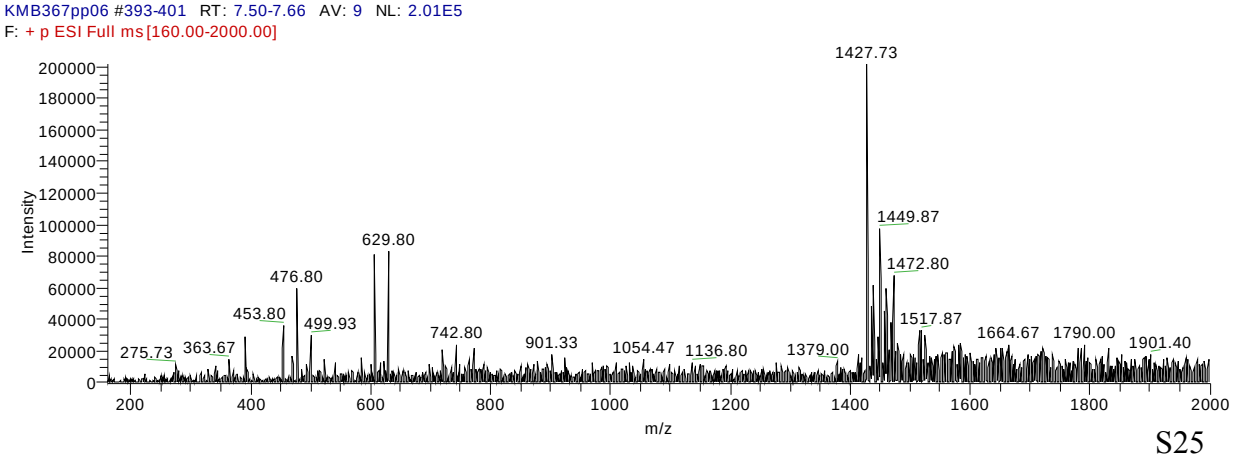
11R-LHA
NL: 4.06E5 Spectrum Maximum nm=200.0-600.0 PDA KMB367pp 06
uAU
Time (min)
0.76
1.63
1.97
2.97
6.35
6.80
7.01
7.56
8.13
9.73
12.06
13.22
13.96
14.27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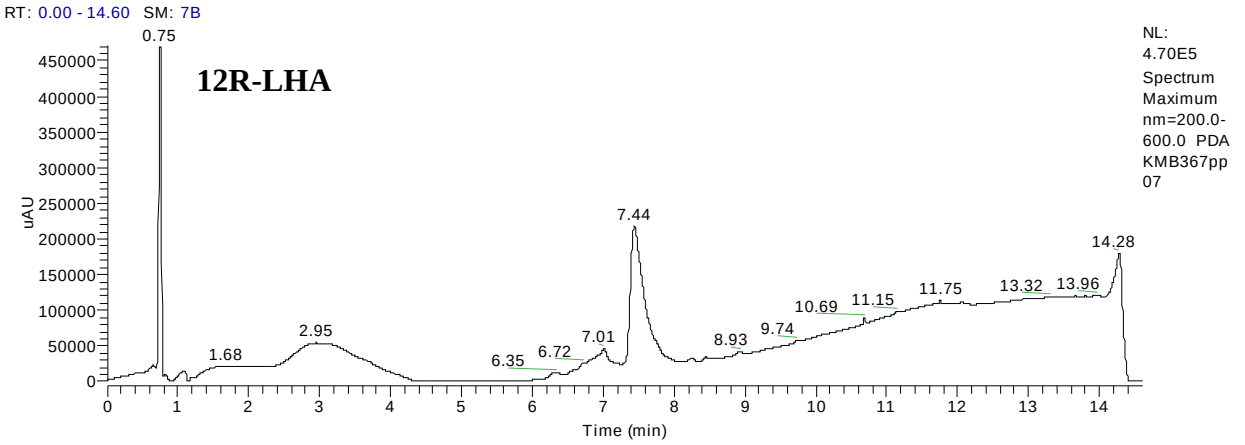
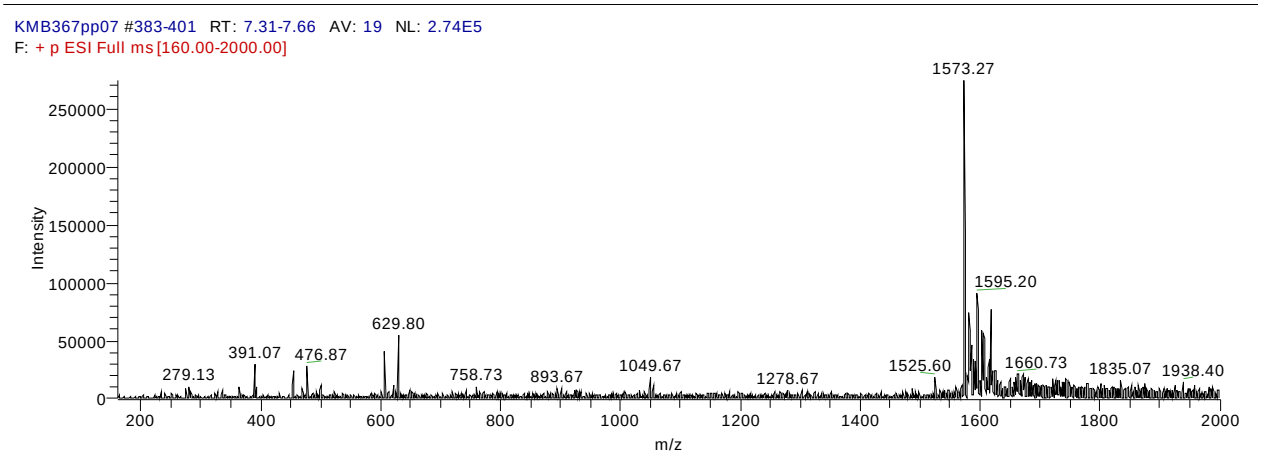
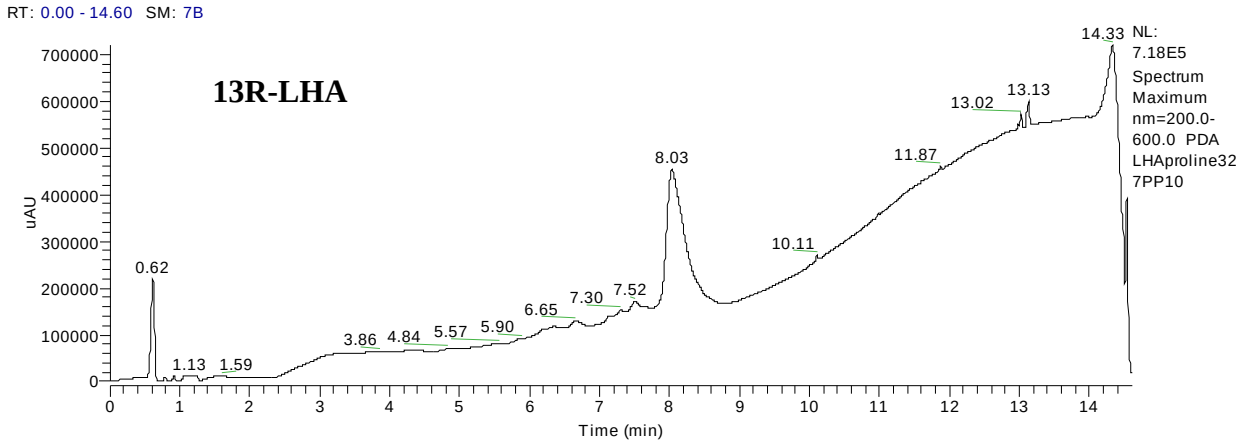
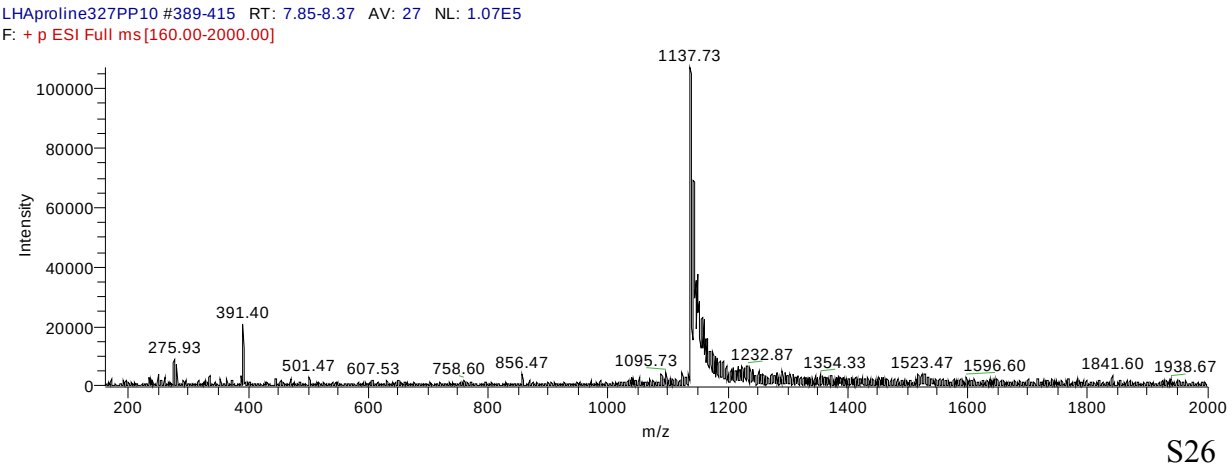
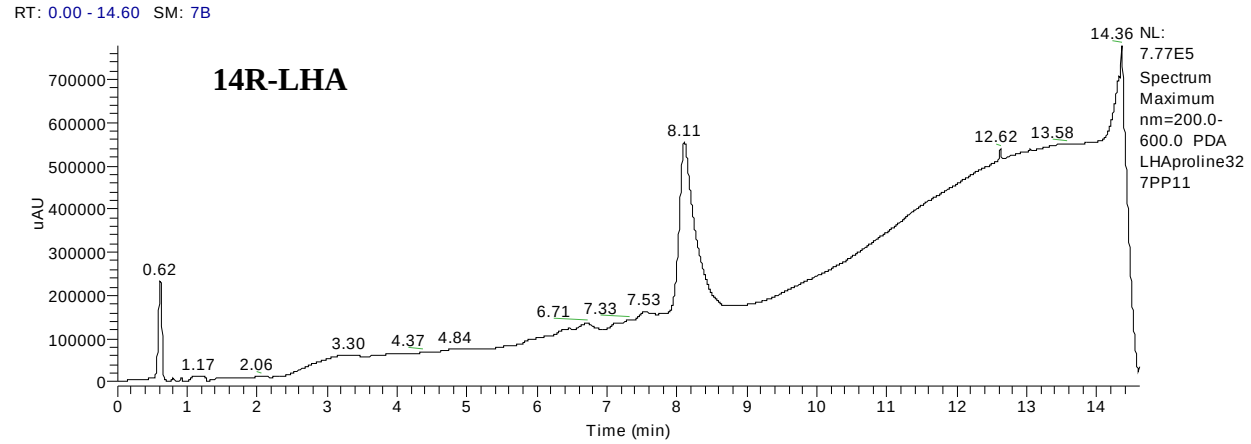
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
275.73
363.67
453.80
476.80
499.93
629.80
742.80
901.33
1054.47
1136.80
1379.00
1427.73
1449.87
1472.80
1517.87
1664.67
1790.00
1901.40

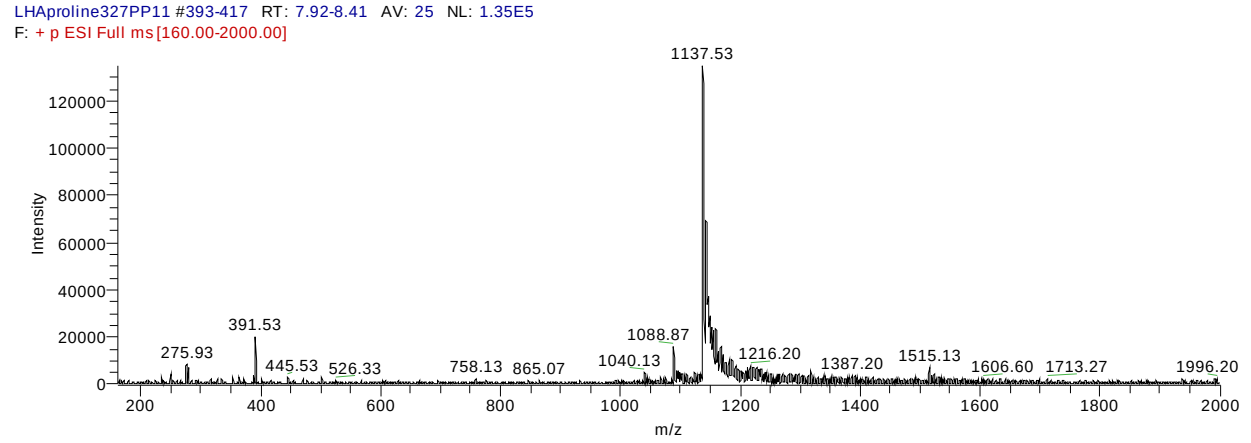

RT: 0.00 - 14.60 SM: 7B
12R-LHA
NL: 4.70E5
Spectrum Maximum nm=200.0-600.0 PDA KMB367pp07
uAU
Time (min)
0.75
1.68
2.95
6.35
6.72
7.01
7.44
8.93
9.74
10.69
11.15
11.75
13.32
13.96
14.28

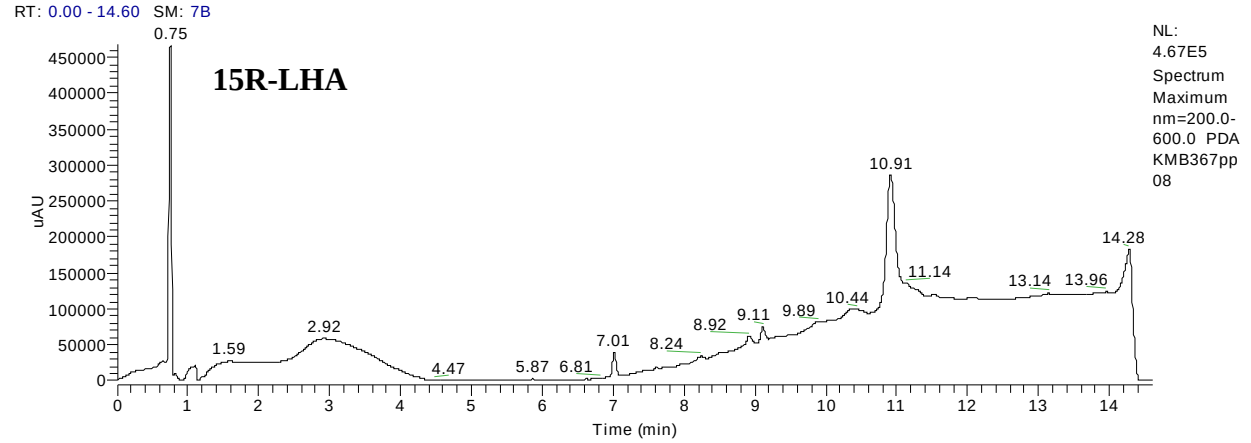

KMB367pp07 #383-401 RT: 7.31-7.66 AV: 19 NL: 2.74E5
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
279.13
391.07
476.87
629.80
758.73
893.67
1049.67
1278.67
1525.60
1573.27
1595.20
1660.73
1835.07
1938.40

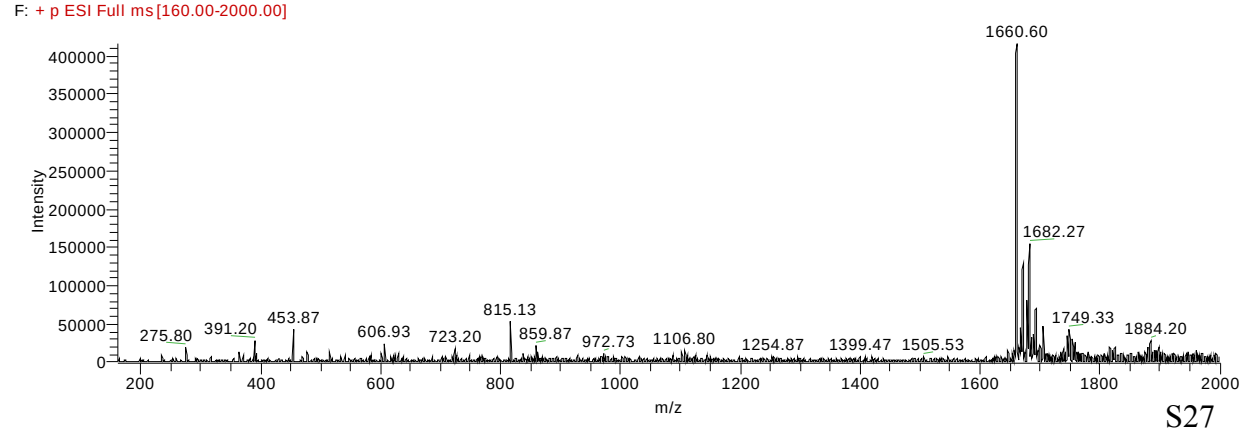

RT: 0.00 - 14.60 SM: 7B
13R-LHA
NL: 7.18E5
Spectrum Maximum nm=200.0-600.0 PDA LHAproline327PP10
uAU
Time (min)
0.62
1.13
1.59
3.86
4.84
5.57
5.90
6.65
7.30
7.52
8.03
10.11
11.87
13.02
13.13
14.33

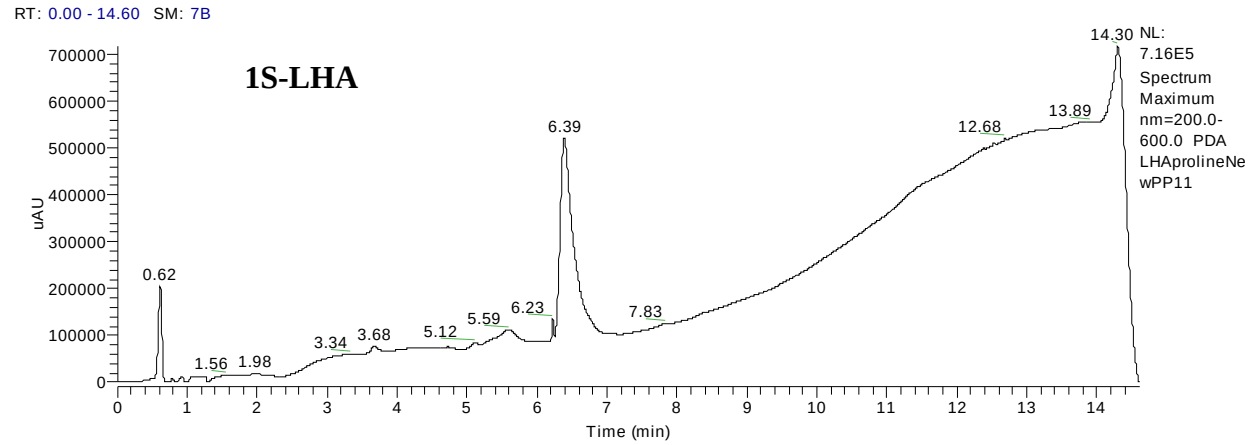

LHAproline327PP10 #389-415 RT: 7.85-8.37 AV: 27 NL: 1.07E5
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
275.93
391.40
501.47
607.53
758.60
856.47
1095.73
1137.73
1232.87
1354.33
1523.47
1596.60
1841.60
1938.67

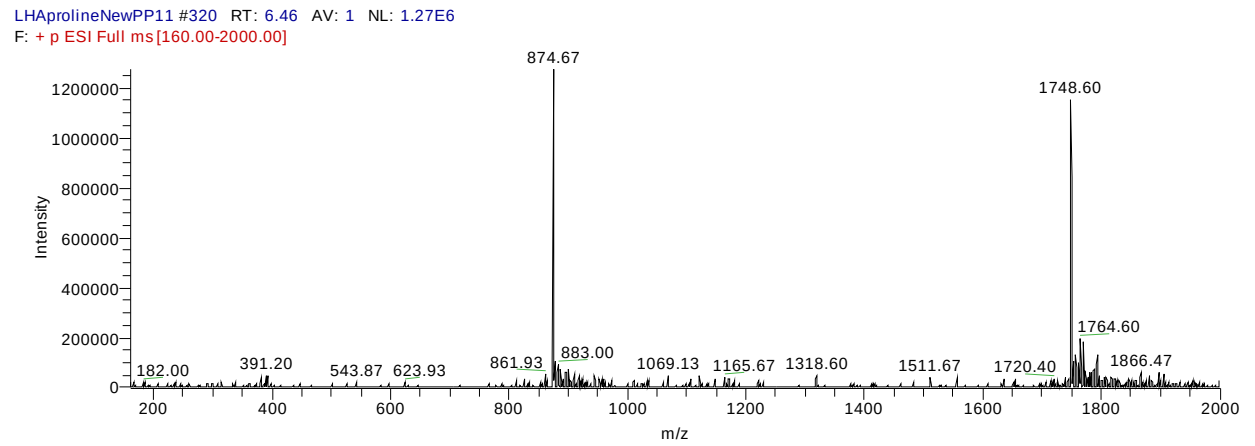

RT: 0.00 - 14.60 SM: 7B
14R-LHA
14.36 NL: 7.77E5 Spectrum Maximum nm=200.0-600.0 PDA LHAproline327PP11
8.11
12.62
13.58
0.62
1.17
2.06
3.30
4.37
4.84
6.71
7.33
7.53
uAU
Time (min)

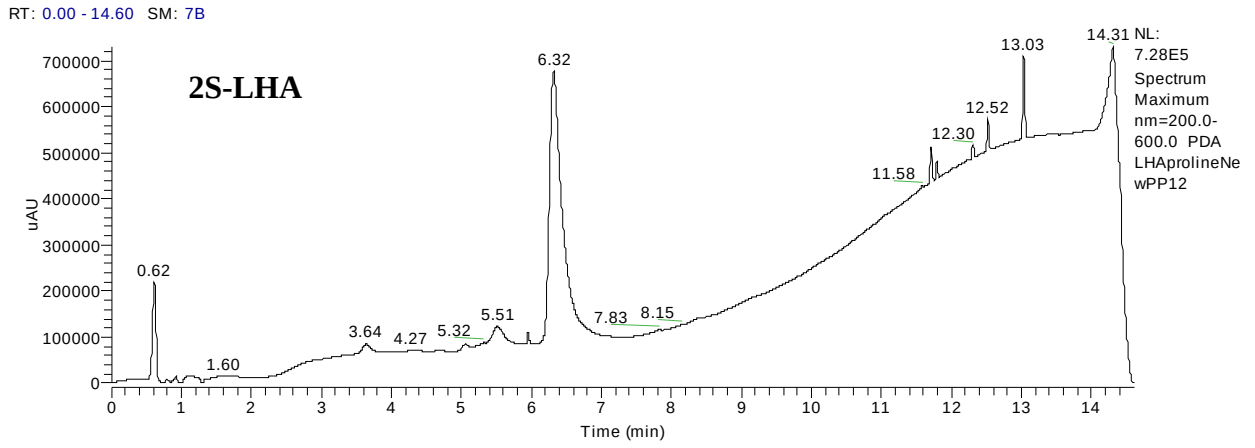

LHAproline327PP11 #393-417 RT: 7.92-8.41 AV: 25 NL: 1.35E5
F: + p ESI Full ms [160.00-2000.00]
1137.53
391.53
275.93
445.53
526.33
758.13
865.07
1088.87
1040.13
1216.20
1387.20
1515.13
1606.60
1713.27
1996.20
Intensity
m/z

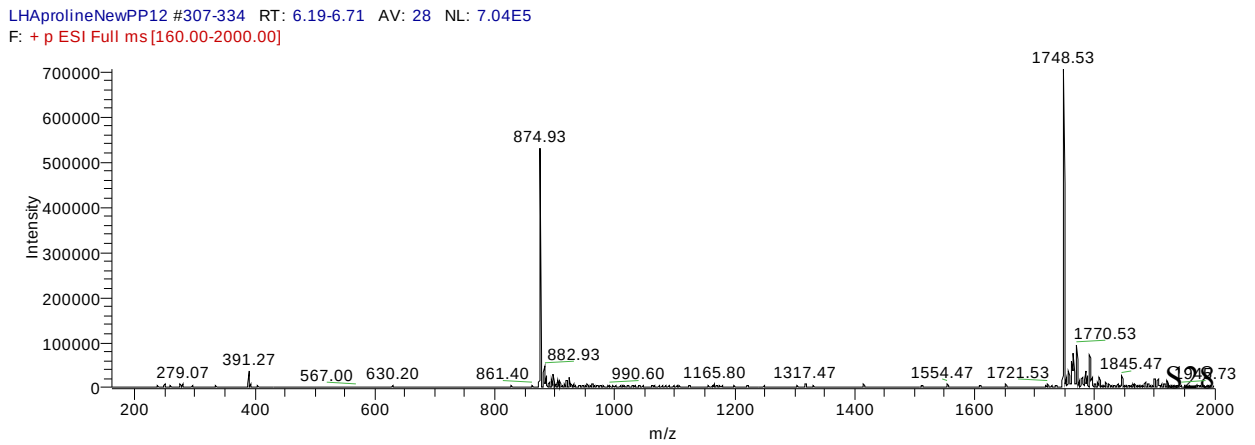

RT: 0.00 - 14.60 SM: 7B
15R-LHA
NL: 4.67E5 Spectrum Maximum nm=200.0-600.0 PDA KMB367pp08
0.75
10.91
14.28
11.14
13.14
13.96
10.44
8.92
9.11
9.89
2.92
1.59
7.01
8.24
4.47
5.87
6.81
uAU
Time (min)

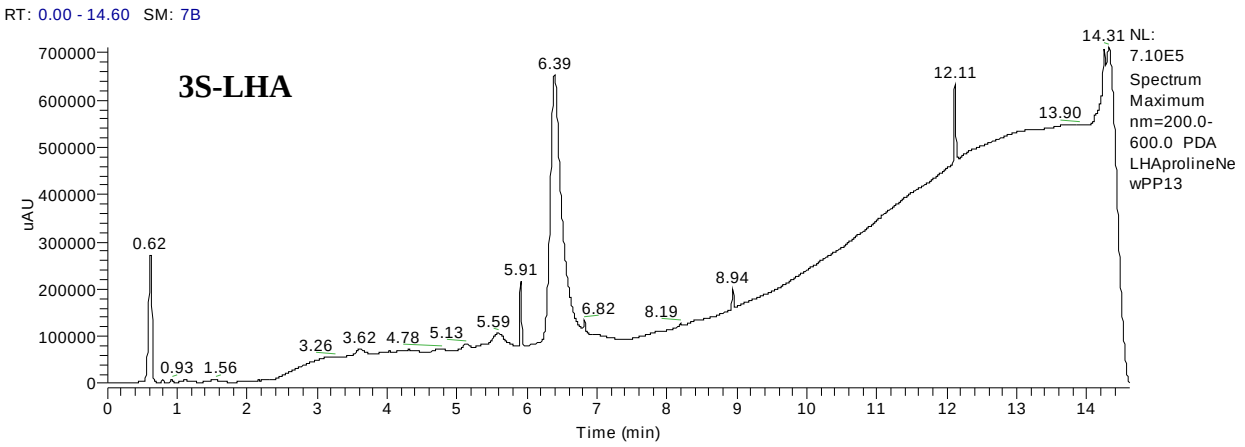

KMB367pp08 #569-578 RT: 10.86-11.03 AV: 10 NL: 4.15E5
F: + p ESI Full ms [160.00-2000.00]
1660.60
1682.27
1749.33
1884.20
815.13
453.87
391.20
275.80
606.93
723.20
859.87
972.73
1106.80
1254.87
1399.47
1505.53
Intensity
m/z

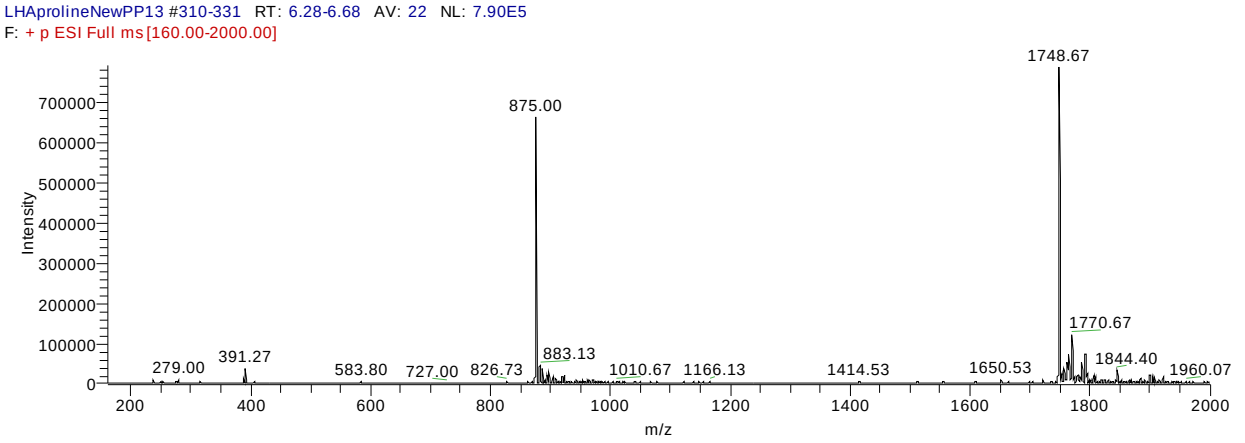

RT: 0.00 - 14.60 SM: 7B
1S-LHA
14.30 NL:
7.16E5
Spectrum
Maximum
nm=200.0-
600.0 PDA
LHAprolineNe
wPP11
6.39
12.68
13.89
0.62
1.56
1.98
3.34
3.68
5.12
5.59
6.23
7.83
uAU
Time (min)

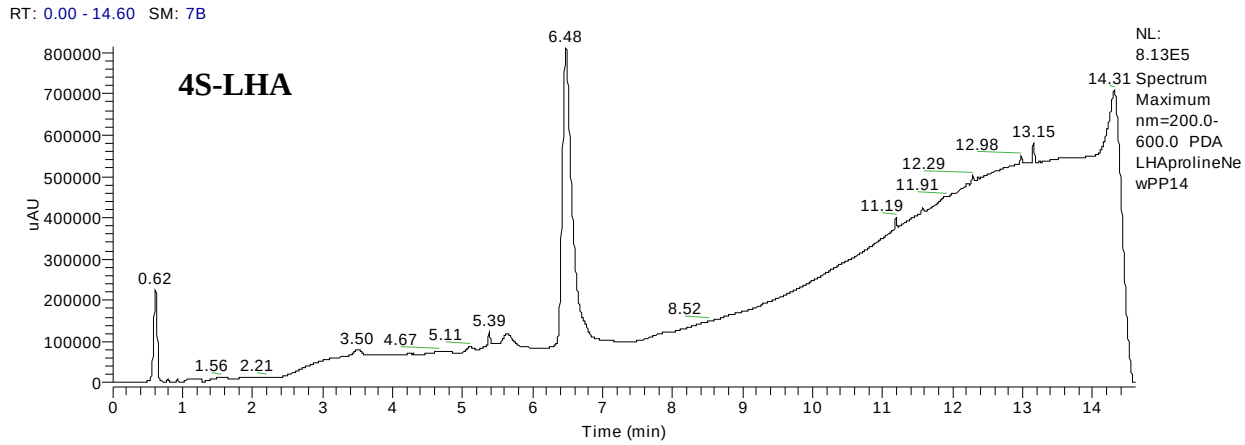

LHAprolineNewPP11 #320 RT: 6.46 AV: 1 NL: 1.27E6
F: + p ESI Full ms [160.00-2000.00]
874.67
1748.60
1764.60
182.00
391.20
543.87
623.93
861.93
883.00
1069.13
1165.67
1318.60
1511.67
1720.40
1866.47
Intensity
m/z

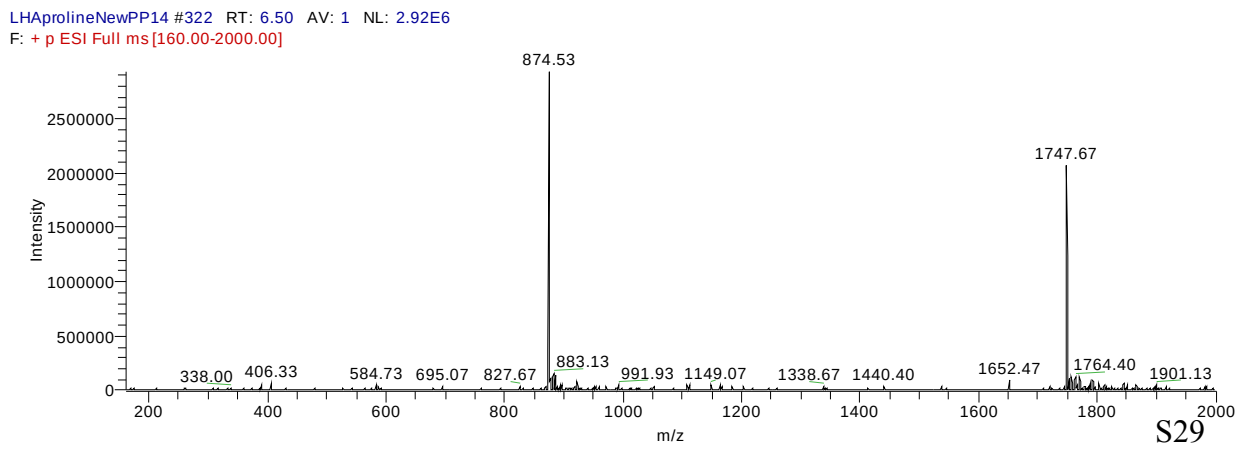

RT: 0.00 - 14.60 SM: 7B
2S-LHA
14.31 NL:
7.28E5
Spectrum
Maximum
nm=200.0-
600.0 PDA
LHAprolineNe
wPP12
6.32
13.03
12.52
12.30
11.58
0.62
1.60
3.64
4.27
5.32
5.51
7.83
8.15
uAU
Time (min)

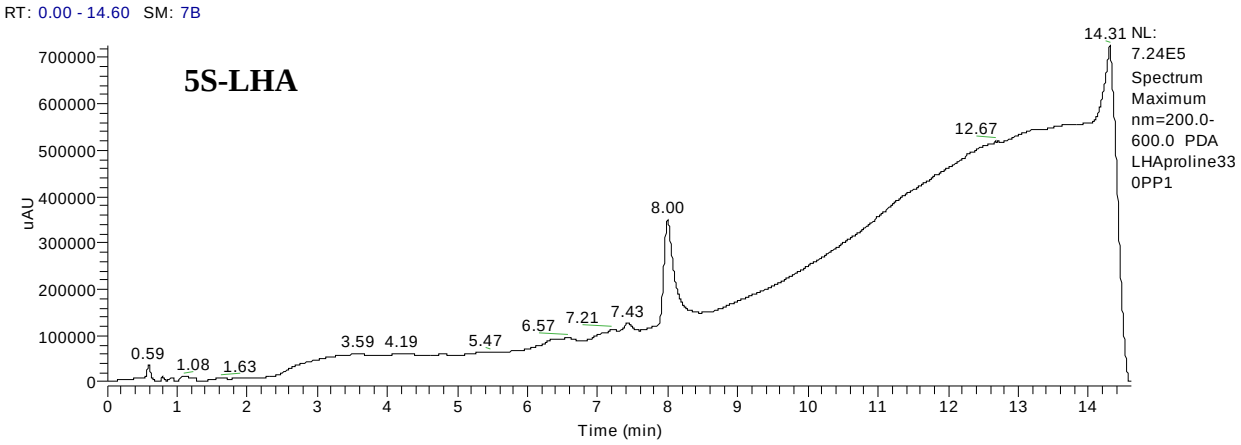

LHAprolineNewPP12 #307-334 RT: 6.19-6.71 AV: 28 NL: 7.04E5
F: + p ESI Full ms [160.00-2000.00]
1748.53
874.93
1770.53
279.07
391.27
567.00
630.20
861.40
882.93
990.60
1165.80
1317.47
1554.47
1721.53
1845.47
Intensity
m/z

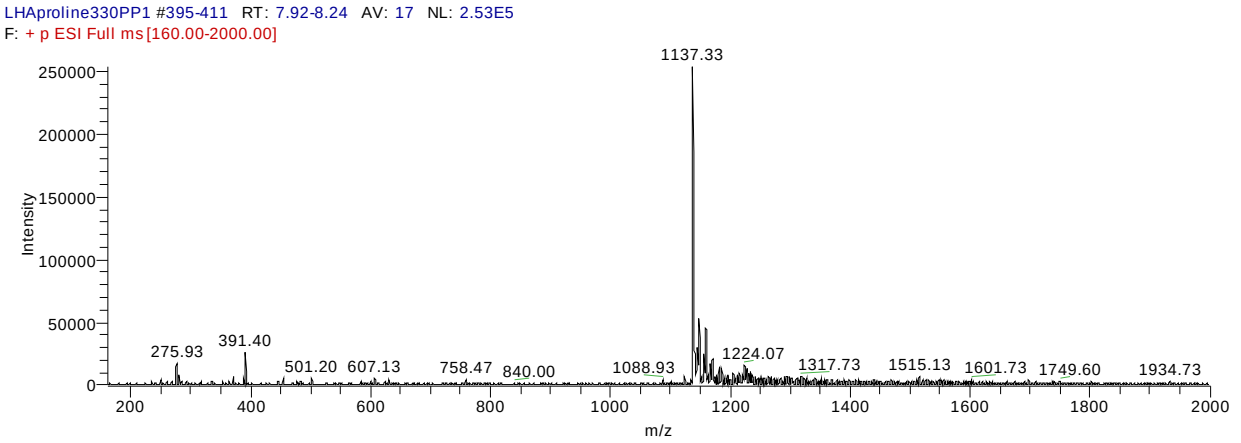

RT: 0.00 - 14.60 SM: 7B
3S-LHA
uAU
Time (min)
14.31 NL: 7.10E5 Spectrum Maximum nm=200.0-600.0 PDA LHAprolineNewPP13
0.62
0.93
1.56
3.26
3.62
4.78
5.13
5.59
5.91
6.39
6.82
8.19
8.94
12.11
13.90

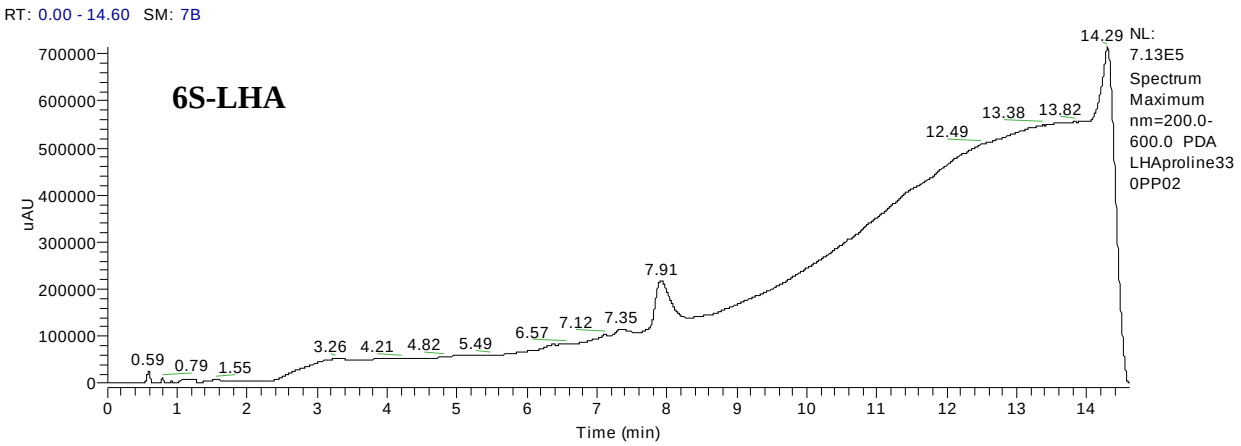

LHAprolineNewPP13 #310-331 RT: 6.28-6.68 AV: 22 NL: 7.90E5
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
1748.67
875.00
1770.67
279.00
391.27
583.80
727.00
826.73
883.13
1010.67
1166.13
1414.53
1650.53
1844.40
1960.07

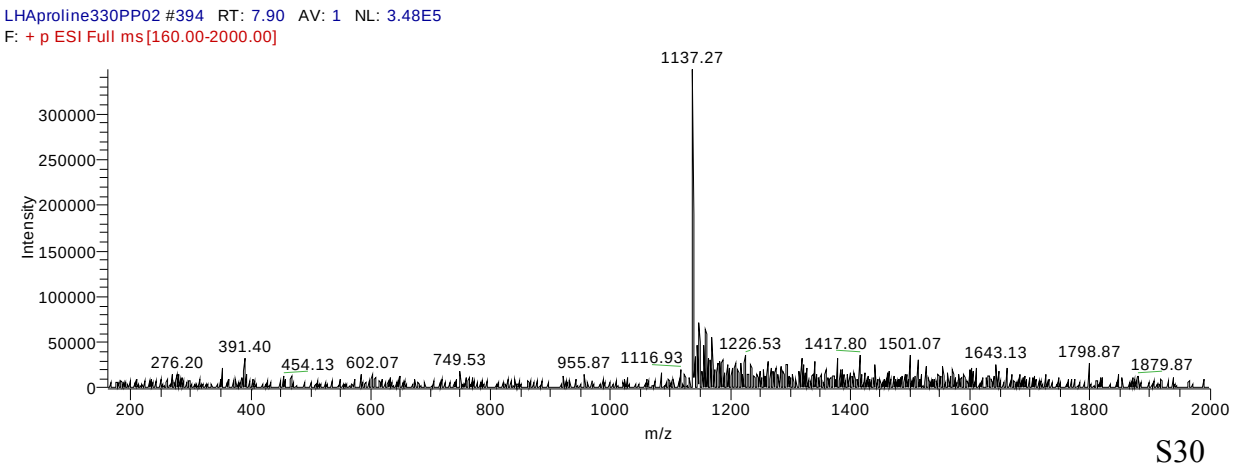

RT: 0.00 - 14.60 SM: 7B
4S-LHA
uAU
Time (min)
NL: 8.13E5 Spectrum Maximum nm=200.0-600.0 PDA LHAprolineNewPP14
0.62
1.56
2.21
3.50
4.67
5.11
5.39
6.48
8.52
11.19
11.91
12.29
12.98
13.15
14.31

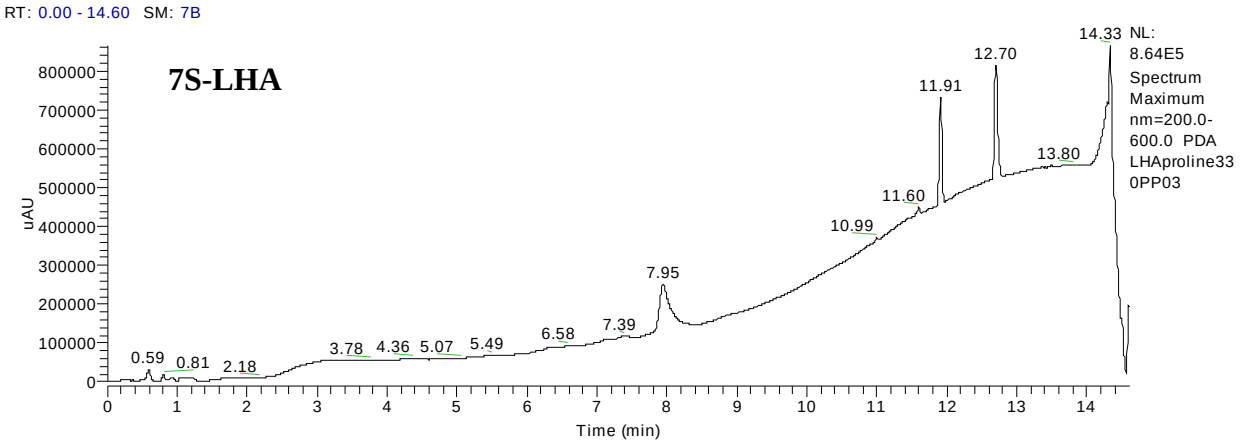

LHAprolineNewPP14 #322 RT: 6.50 AV: 1 NL: 2.92E6
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
874.53
1747.67
338.00
406.33
584.73
695.07
827.67
883.13
991.93
1149.07
1338.67
1440.40
1652.47
1764.40
1901.13

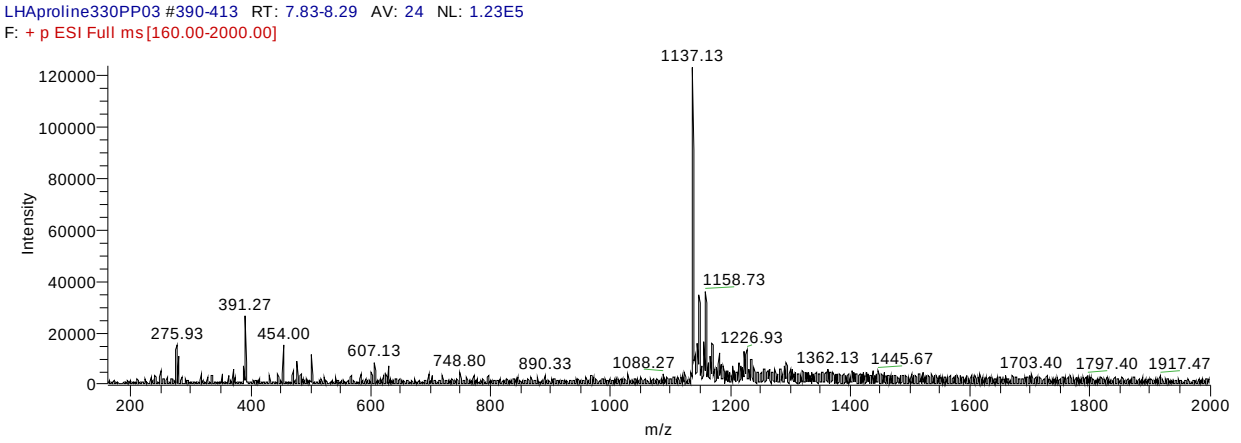

RT: 0.00 - 14.60 SM: 7B
5S-LHA
14.31 NL:
7.24E5
Spectrum
Maximum
nm=200.0-
600.0 PDA
LHAproline33
0PP1
12.67
8.00
7.43
7.21
6.57
5.47
4.19
3.59
1.63
1.08
0.59
uAU
Time (min)

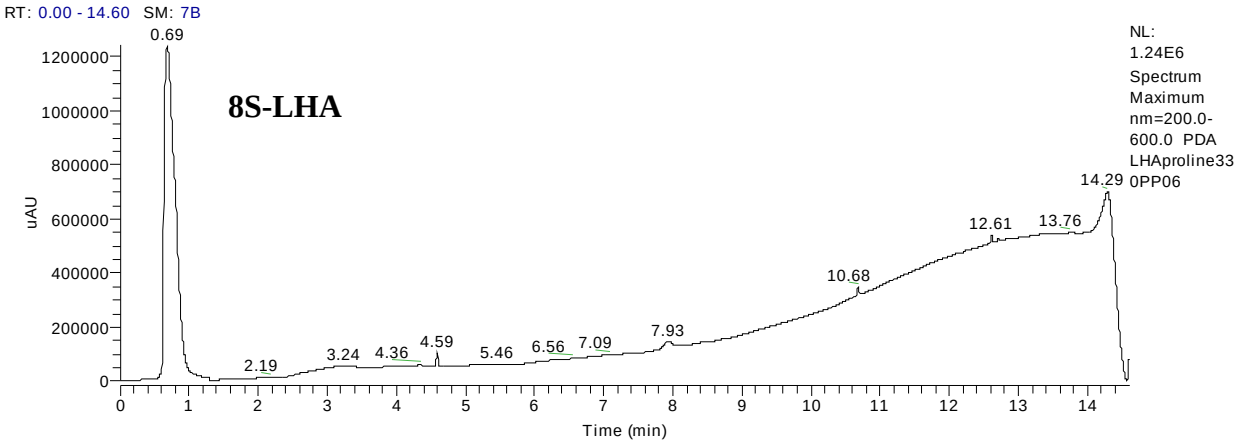

LHAproline330PP1 #395-411 RT: 7.92-8.24 AV: 17 NL: 2.53E5
F: + p ESI Full ms [160.00-2000.00]
1137.33
1224.07
391.40
275.93
501.20
607.13
758.47
840.00
1088.93
1317.73
1515.13
1601.73
1749.60
1934.73
Intensity
m/z

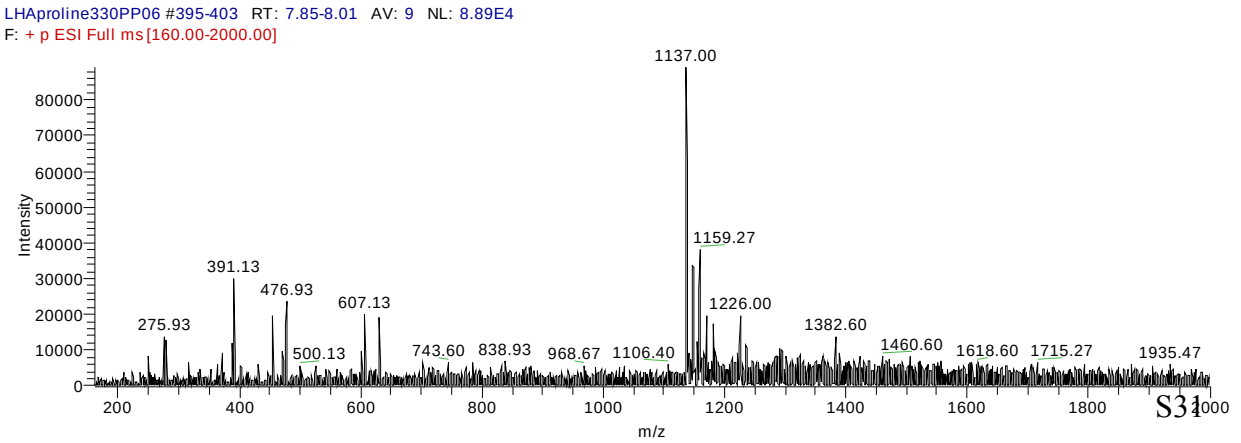

RT: 0.00 - 14.60 SM: 7B
6S-LHA
14.29 NL:
7.13E5
Spectrum
Maximum
nm=200.0-
600.0 PDA
LHAproline33
0PP02
13.38
13.82
12.49
7.91
7.35
7.12
6.57
5.49
4.82
4.21
3.26
1.55
0.79
0.59
uAU
Time (min)

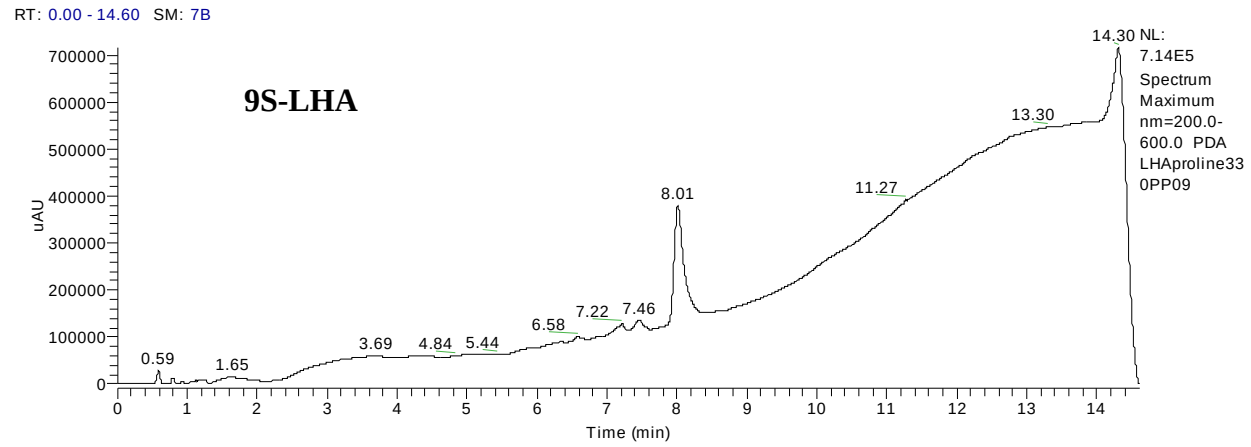

LHAproline330PP02 #394 RT: 7.90 AV: 1 NL: 3.48E5
F: + p ESI Full ms [160.00-2000.00]
1137.27
1226.53
391.40
276.20
454.13
602.07
749.53
955.87
1116.93
1417.80
1501.07
1643.13
1798.87
1879.87
Intensity
m/z

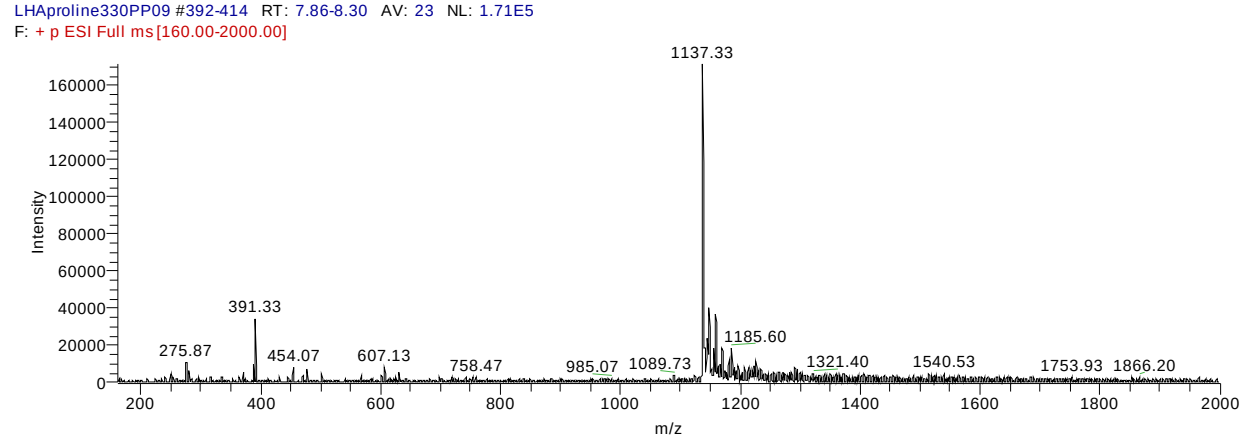

RT: 0.00 - 14.60 SM: 7B
7S-LHA
uAU
Time (min)
NL: 8.64E5 Spectrum Maximum nm=200.0-600.0 PDA LHAproline330PP03
14.33
12.70
11.91
13.80
11.60
10.99
7.95
0.59
0.81
2.18
3.78
4.36
5.07
5.49
6.58
7.39

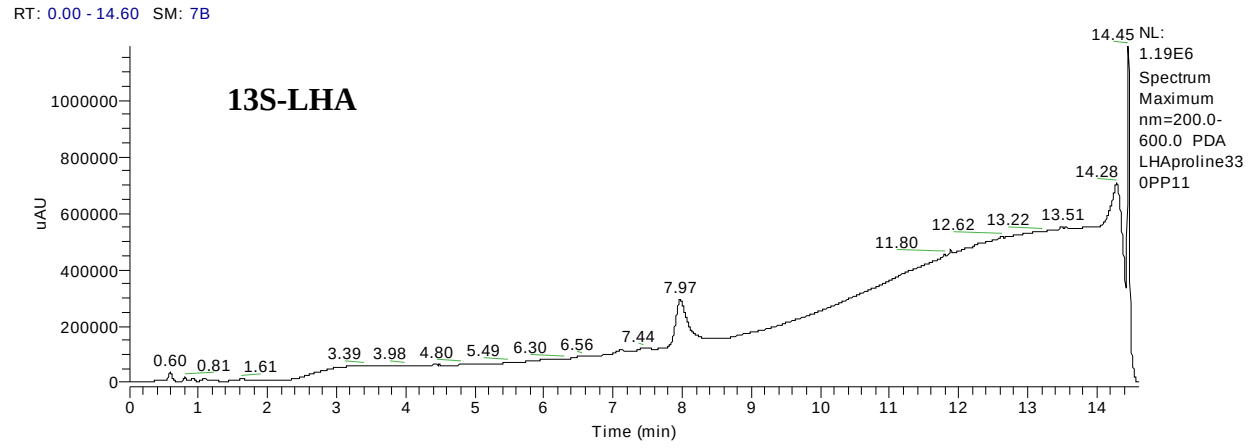

LHAproline330PP03 #390-413 RT: 7.83-8.29 AV: 24 NL: 1.23E5
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
1137.13
1158.73
391.27
275.93
454.00
607.13
748.80
890.33
1088.27
1226.93
1362.13
1445.67
1703.40
1797.40
1917.47

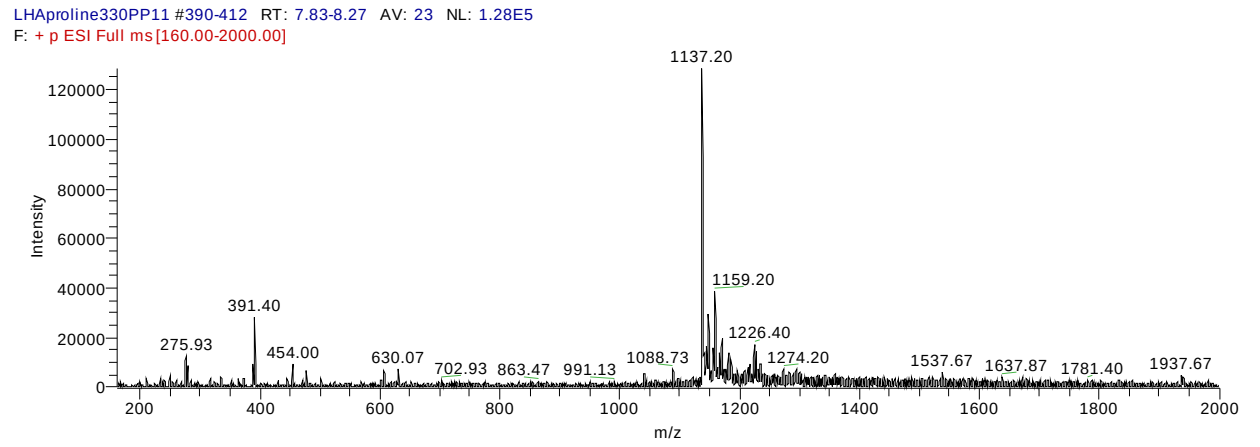

RT: 0.00 - 14.60 SM: 7B
8S-LHA
uAU
Time (min)
NL: 1.24E6 Spectrum Maximum nm=200.0-600.0 PDA LHAproline330PP06
0.69
14.29
12.61
13.76
10.68
7.93
2.19
3.24
4.36
4.59
5.46
6.56
7.09

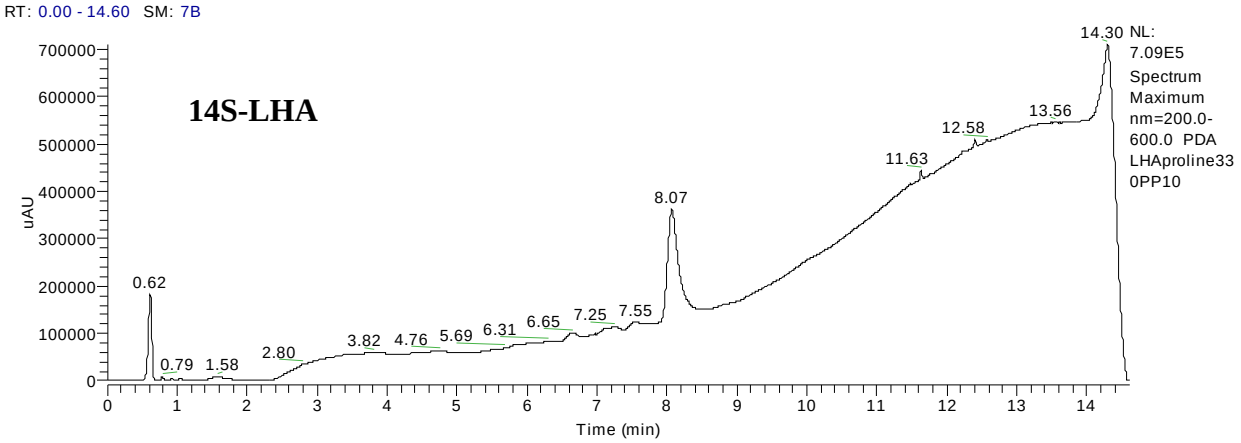

LHAproline330PP06 #395-403 RT: 7.85-8.01 AV: 9 NL: 8.89E4
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
1137.00
1159.27
391.13
476.93
607.13
275.93
500.13
743.60
838.93
968.67
1106.40
1226.00
1382.60
1460.60
1618.60
1715.27
1935.47

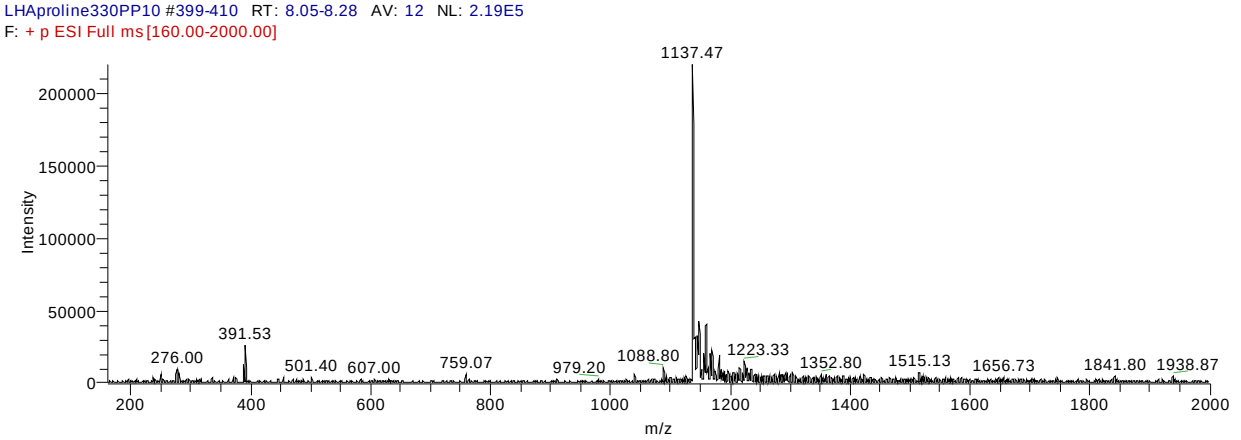

RT: 0.00 - 14.60 SM: 7B
9S-LHA
14.30 NL: 7.14E5 Spectrum Maximum nm=200.0-600.0 PDA LHAproline330PP09
13.30
11.27
8.01
7.22
7.46
6.58
3.69
4.84
5.44
0.59
1.65
uAU
Time (min)

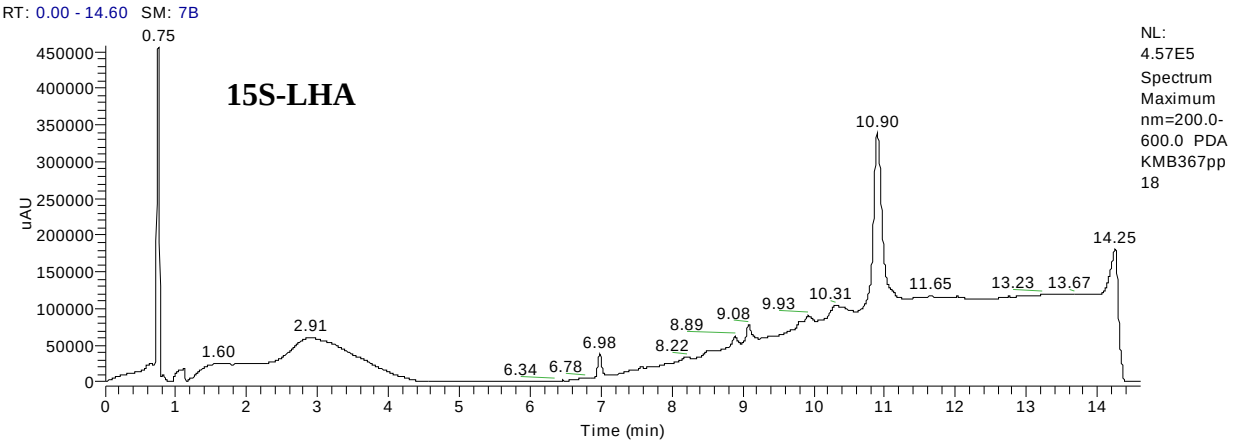

LHAproline330PP09 #392-414 RT: 7.86-8.30 AV: 23 NL: 1.71E5
F: + p ESI Full ms [160.00-2000.00]
1137.33
391.33
275.87
454.07
607.13
758.47
985.07
1089.73
1185.60
1321.40
1540.53
1753.93
1866.20
Intensity
m/z

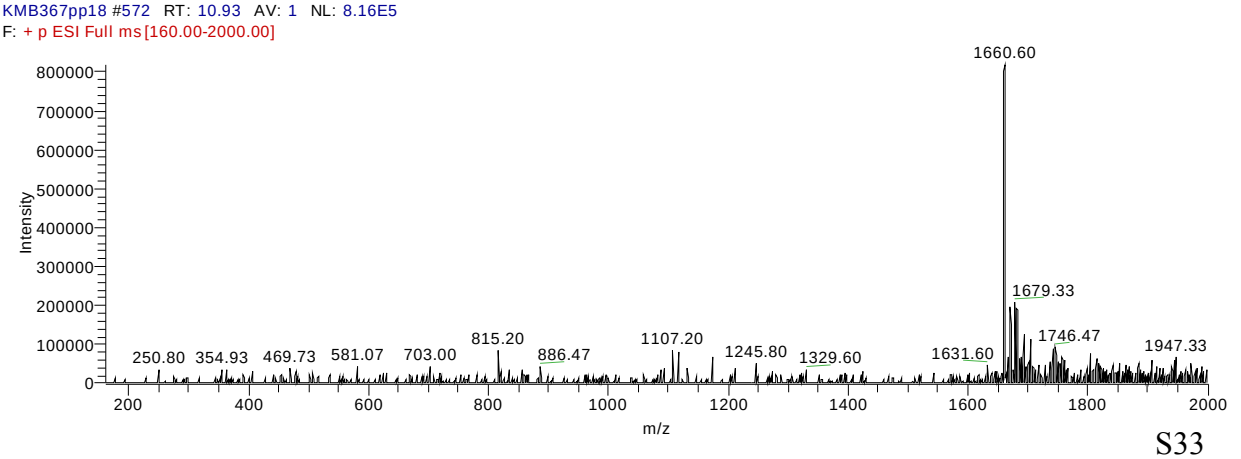

RT: 0.00 - 14.60 SM: 7B
13S-LHA
14.45 NL: 1.19E6 Spectrum Maximum nm=200.0-600.0 PDA LHAproline330PP11
14.28
12.62
13.22
13.51
11.80
7.97
7.44
3.39
3.98
4.80
5.49
6.30
6.56
0.60
0.81
1.61
uAU
Time (min)


LHAproline330PP11 #390-412 RT: 7.83-8.27 AV: 23 NL: 1.28E5
F: + p ESI Full ms [160.00-2000.00]
1137.20
1159.20
391.40
275.93
454.00
630.07
702.93
863.47
991.13
1088.73
1226.40
1274.20
1537.67
1637.87
1781.40
1937.67
Intensity
m/z


RT: 0.00 - 14.60 SM: 7B
14S-LHA
uAU
Time (min)
14.30 NL: 7.09E5 Spectrum Maximum nm=200.0-600.0 PDA LHAproline330PP10
0.62
0.79
1.58
2.80
3.82
4.76
5.69
6.31
6.65
7.25
7.55
8.07
11.63
12.58
13.56


LHAproline330PP10 #399-410 RT: 8.05-8.28 AV: 12 NL: 2.19E5
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
1137.47
391.53
276.00
501.40
607.00
759.07
979.20
1088.80
1223.33
1352.80
1515.13
1656.73
1841.80
1938.87


RT: 0.00 - 14.60 SM: 7B
15S-LHA
uAU
Time (min)
NL: 4.57E5 Spectrum Maximum nm=200.0-600.0 PDA KMB367pp18
0.75
1.60
2.91
6.34
6.78
6.98
8.22
8.89
9.08
9.93
10.31
10.90
11.65
13.23
13.67
14.25


KMB367pp18 #572 RT: 10.93 AV: 1 NL: 8.16E5
F: + p ESI Full ms [160.00-2000.00]
Intensity
m/z
1660.60
1679.33
1746.47
1947.33
250.80
354.93
469.73
581.07
703.00
815.20
886.47
1107.20
1245.80
1329.60
1631.60

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