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Title, authors, and address

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A. General Methods

General. All boronic acid coupling reactions were performed in oven-dried microwave vials (catalog # 50-978-405)_sealed with microwave caps (catalog # 50-872-811) and stirred using Teflon-coated magnetic stir bars, using the lowest possible stir speed (50 rpm) to prevent resin beads from getting crushed. All oxidation studies were performed in 4 mL scintillation vials with screw caps containing inserted septa. Polystyrene Rink Amide resin (0.61 mmol/g or 0.69 mmol/g) was purchased from Protein Technology, Inc., and the manufacturer's reported loading of the resin was used in the calculation of the yields. Solid phase peptide synthesis (SPPS) was performed using an automated Biotage Syro Wave™ peptide synthesizer in 10 mL parallel reactors with PTFE frits. Incorporation of the *N*-aryl glycine residue was performed manually in disposable filter columns with 20 μM PE frit filters and caps purchased from Applied Separations (catalog # 2413 for 3 mL filter columns) with gentle agitation on a Thermo Fisher vortex mixer equipped with a microplate tray. Solution draining and washing of the resin was done by connecting the filter columns to a water aspirator vacuum *via* a waste trap. Analytical LCMS analyses were performed using an Agilent Technologies 1260 Infinity II series LCMS Single Quad instrument with ESI ion-source and positive mode ionization, equipped with a 5 μM, 150 mm x 4.6 mm C18 Luna column purchased from Phenomenex (catalog # 00F-4252-E0). A flow rate of 0.5 mL/min and gradients of CH₃CN [0.1% trifluoroacetic acid (TFA)] in water (0.1% TFA) over 12 min (total run time = 22 min) were used for LCMS analyses. Peptides were purified on a preparative HPLC (Agilent 218 purification system) using a preparative column (10-20 μM, 250 x 22 mm, C18 Vydac column, catalog # 00G-4253-P0-AX) at a flow rate of 10 mL/min with gradients of CH₃CN (0.1% TFA) in water (0.1% TFA) over 30 min (total run time = 60 min). Nuclear magnetic resonance (NMR) spectra (¹H) were recorded on a 700 MHz Bruker spectrometer (ppm, δ scale) and are referenced to residual protium in the NMR solvent (DMSO-d₆, δ 2.50 ppm).

Reagents. Fmoc-L-Gly-OH, Fmoc-L-Ala-OH, Fmoc-L-Phe-OH, Fmoc-L-Pro-OH, Fmoc-L-Leu-OH, Fmoc-L-Gln(Trt)-OH, Fmoc-L-Glu(^tBu)-OH, Fmoc-L-Trp(Boc)-OH, Fmoc-L-Lys(Boc)-OH, Fmoc-L-Thr(^tBu)-OH, Fmoc-L-Tyr(^tBu)-OH, Fmoc-L-Arg(Pbf)-OH, Fmoc-L-Cys(Trt)-OH, Fmoc-L-His(Trt)-OH, Fmoc-L-Asp(^tBu)-OH, Fmoc-L-Val-OH, Fmoc-L-Ile-OH, *N,N*-diisopropylethylamine (DIEA), triisopropylsilane (TIPS), bromoacetic acid, and diisopropylcarbodiimide (DIC) were purchased from Chem Impex Int'l, Inc. Reagents such as piperidine, *p*-anisidine, *tert*-butyl hydrogen peroxide (5-6 M in decane), copper (I) bromide, and *N,N*-dimethyl-*p*-phenylenediamine were purchased from Sigma Aldrich. Trifluoroacetic acid (TFA) and solvents were purchased from Fisher Chemical. *N,N,N',N'*-Tetramethyl-O-(1H-benzotriazol-1-yl)uronium hexafluorophosphate (HBTU) was purchased from Oakwood Chemicals. DL- α -bromophenylacetic acid, *N,N*-diethyl-*p*-phenylenediamine, phenylboronic acid, 4-methoxyphenyl boronic acid, 4-tolylboronic acid, and furan-2-boronic acid were purchased from Acros Organics. 4-Bromobenzeneboronic acid, 4-(trifluoromethyl)benzene boronic acid, biphenyl-4-boronic acid, and 4-*n*-heptyloxybenzene boronic acid were purchased from Alfa Aesar. All chemicals were used as received without further purification.

B. Experimental Procedures and Characterization Data

Fmoc-Based SPPS: Fmoc Deprotection and HBTU Couplings. Peptide synthesis was performed on Polystyrene Rink Amide resin (0.61 mmol/g or 0.69 mmol/g) using standard manual solid phase peptide synthesis (SPPS) procedures on an automated shaker or using a Biotage Syro Wave™ peptide synthesizer. Fmoc-amino acids (3 equiv) were activated with HBTU (3 equiv) and DIEA (6 equiv) in DMF. Fmoc deprotections were performed using 20% piperidine in

DMF (v/v) for 20 minutes. The resin was rinsed with DMF three times after each coupling and deprotection step. Prior to cleavage from the resin or storage, the resin was rinsed with DMF, MeOH, and CH₂Cl₂ (x 3).

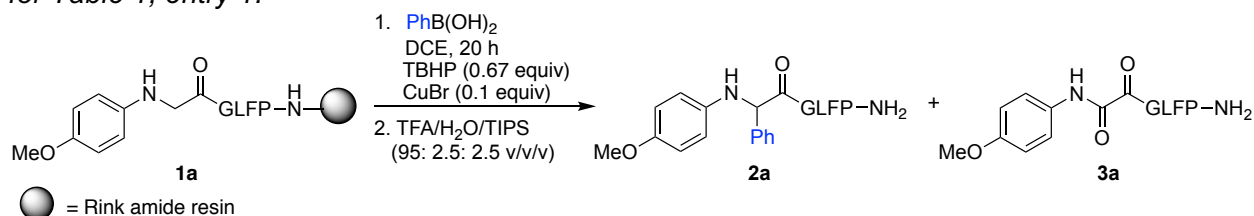
Incorporation of *N*-terminal *N*-aryl Amino Acid Residues. *N*-Arylglycyl peptides (e.g. **1a-c**, **6a-j**, **9-12**) were synthesized following previously published procedures,^{1,2} using solid phase submonomer peptoid synthesis methods for the incorporation of the *N*-aryl amino acid. Briefly, resin-bound peptides (200 mg, 0.12 or 0.14 mmol) swollen in DMF were treated with bromoacetic acid (0.6 M in DMF, 2 mL, 1.2 mmol) or DL- α -bromophenylacetic acid (0.6 M in DMF, 2 mL, 1.2 mmol) and DIC (172 μ L, 1.12 mmol) for 25 minutes. The solution was drained and a 2 M solution of 4-methoxyaniline, 4-amino-*N,N*-dimethylaniline, or 4-amino-*N,N*-diethylaniline in DMF was added (2 mL, 4 mmol). The resin was left shaking for 2 hours before the solution was drained and the resin was washed with DMF (3 x 1 mL).

Test Cleavage of Resin-Bound Peptides. A small aliquot of resin (~1-5 mg) was transferred to a 1 mL disposable filter column with a 20 μ M PE frit filter. A freshly made solution of TFA/TIPS/H₂O (95:2.5:2.5 v/v/v, 0.2 mL) was added to the cartridge and allowed to shake at room temperature for at least 30 minutes. The resin was filtered through the PE frit, and the filtrate was collected in a 20 mL scintillation vial and evaporated to dryness on a Biotage V10 evaporator (volatile setting). For peptides **21-23**, cold diethyl ether (1 mL) was added to the crude oil and the precipitate was redissolved in 1:1 CH₃CN/H₂O v/v (1 mg/mL) prior to LCMS analysis.

Full Cleavage of Resin-Bound Peptides. The dry resin-bound peptide (50 mg, 0.031 or 0.035 mmol) was transferred to a 20 mL scintillation vial and treated with a freshly made solution of TFA/TIPS/H₂O (95:2.5:2.5 v/v/v, 4.0 mL). The vial was capped and allowed to shake at room temperature for 2 h. For peptides **21-23**, the cleavage mixture was filtered through a 3 mL disposable filter column with a 20 μ M PE frit filter into a 50 mL falcon tube containing cold diethyl ether (20-30 mL). The falcon tube was centrifuged for 5 min at 7000 rpm, the diethyl ether was decanted, and the precipitate was redissolved in 1:1 CH₃CN/H₂O v/v before freeze drying. For peptides **2a-c**, **5a-h**, **7a-j**, and **17-20**, the cleavage mixture was filtered through a 3 mL disposable filter column with a 20 μ M PE frit filter into a 20 mL scintillation vial and evaporated to dryness on a Biotage V10 evaporator (volatile setting), without precipitation with diethyl ether. The crude oil was dissolved in CH₂Cl₂ and subjected to evaporation on a Biotage V10 again to help eliminate residual TFA. The crude oil was then redissolved in 1:1 CH₃CN/H₂O v/v before freeze drying.

General Procedures for the Boronic Acid Coupling Reactions.

Procedure using TBHP and CuBr with *N*-(*p*-MeO-Ph)glycine-GLFP. This procedure was used for Table 1, entry 1.



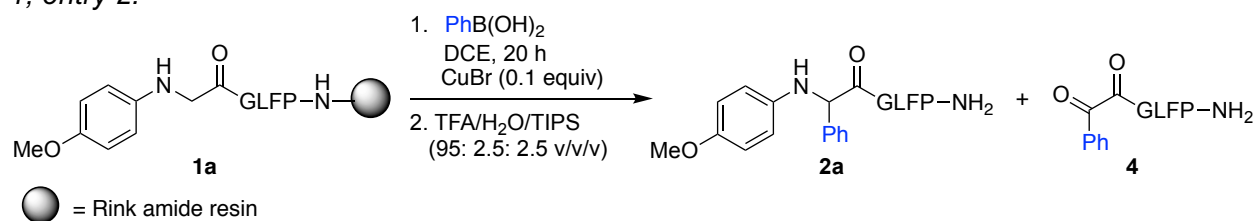
The resin-bound peptide (20 mg, 0.014 mmol) was transferred to an oven-dried 5 mL microwave vial. DCE (200 μ L) was added to the microwave vial containing the dry resin, followed by *tert*-butyl hydrogen peroxide (0.0092 mmol, 0.67 equiv, 100 μ L of a 90-108 mM stock solution in DCE), and CuBr (0.0014 mmol, 0.1 equiv, 100 μ L of a 14 mM stock solution in DCE). The resin was

allowed to stir for ten minutes at room temperature prior to the addition of phenylboronic acid (0.0092 mmol, 0.67 equiv, 100 μ L of a 90 mM stock solution in DCE). The microwave vial was capped, placed in a pre-heated oil bath (100 $^{\circ}$ C), and stirred for 20 hours at a stir speed of 50 rpm. The resin was transferred to a 1 mL disposable filter column with 20 μ M frit, the solution was drained, and the resin was washed with DMF, MeOH, and CH_2Cl_2 (3 x 1 mL).

Notes:

1. The reaction was performed under air, without special precautions.
2. The phenyl boronic acid stock solution was prepared by dissolving 11 mg of $\text{PhB}(\text{OH})_2$ in 1 mL of DCE.
3. The TBHP stock solution was prepared by diluting 18 μ L of TBHP (5-6 M in decane) with 982 μ L of DCE.
4. The CuBr stock solution was prepared by dissolving 2 mg of CuBr in 1 mL of DCE and placing the solution in a heated sonicator for \sim 30 minutes to help dissolve the CuBr.

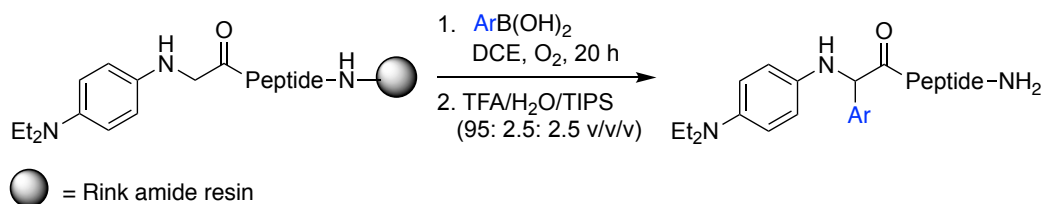
Procedure using CuBr with *N*-(*p*-MeO-Ph)glycine-GLFP. This procedure was used for Table 1, entry 2.



The resin-bound peptide (20 mg, 0.014 mmol, 1 equiv) was transferred to an oven-dried 5 mL microwave vial. DCE (300 μ L) was added to the microwave vial containing the dry resin, followed by phenylboronic acid (0.0092 mmol, 0.67 equiv, 100 μ L of a 90 mM stock solution in DCE) and CuBr (0.0014 mmol, 0.1 equiv, 100 μ L of a 14 mM stock solution in DCE) with no time in between additions. The microwave vial was capped, oxygen gas was bubbled through the solution for 30 seconds, and the exit needle and oxygen balloon were removed. The microwave vial was stirred for 20 hours at a stir speed of 50 rpm. The resin was transferred to a 1 mL disposable filter column with 20 μ M frit, the solution was drained, and the resin was washed with DMF, MeOH, and CH_2Cl_2 (3 x 1 mL).

Note: the phenyl boronic acid and CuBr stock solutions were prepared as described above (see procedure for Table 1, entry 1).

Optimized general procedure for *N*-(*p*- Et_2N -Ph)glycine-peptides under O_2 atmosphere. This procedure was used for the optimization Table 1, entries 5, 8, and 11, and for all subsequent oxidative coupling reactions reported in the paper.



The desired aryl boronic acid (0.018 mmol, 1.5 equiv) was dissolved in dichloroethane (DCE, 500 μ L) in a 4 mL scintillation vial and sonicated if it did not readily dissolve. The boronic acid solution was then transferred to an oven-dried 5 mL microwave vial equipped with a stir bar that contained

the dry resin-bound peptide (20 mg, 0.012 or 0.014 mmol). The microwave vial was capped and oxygen gas was bubbled through the solution for 30 seconds, the exit needle was removed, and the oxygen balloon was kept in place. The microwave vial was placed in a pre-heated oil bath (70 °C) and stirred for 20 hours at a stir speed of 50 rpm. The resin was transferred to a 1 mL disposable filter column with 20 µM frit, the solution was drained, and the resin was washed with DMF, MeOH, and CH₂Cl₂ (3 x 1 mL).

Notes:

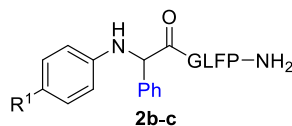
1. To prevent reagent and resin from sticking to the wall of the microwave vial, it was imperative to 1) pre-dissolve the phenylboronic acid in DCE before transferring it to the microwave vial, and 2) use small gauge (20 gauge) needles to better control the flow of oxygen.
2. Oxidative coupling with *N*-(*p*-MeO-Ph)glycine-GLFP appear to be done between 2-4 h.

Analysis, Purification and Characterization of Peptides 2b-c, 5a-h,7a-i, and 17-23.

Crude peptides were analyzed and characterized by LCMS as described in the General Methods. Following gradient optimization, the peptides were purified by preparative HPLC as described in the General Methods. HPLC fractions containing the desired peptides were collected, frozen immediately, and lyophilized. Characterization data for all peptides can be found in Tables S1-S4.

Peptides **2b**, **17-19**, and **23** were purified using a gradient of 40-95% CH₃CN (0.1% TFA) in water (0.1% TFA). Peptides **2c**, **5g**, **7a** were purified using a gradient of 30-70% CH₃CN (0.1% TFA) in water (0.1% TFA). Peptide **5b** was purified using a gradient of 50-95% CH₃CN (0.1% TFA) in water (0.1% TFA). Peptides **5a**, **c-f**, **7d**, **7g-7h** were purified using a gradient of 30-90% CH₃CN (0.1% TFA) in water (0.1% TFA). Peptides **5h**, **7b-c**, **f**, **i**, **20-21** were purified using a gradient of 20-80% CH₃CN (0.1% TFA) in water (0.1% TFA). Peptide **7e** was purified using a gradient of 20-60% CH₃CN (0.1% TFA) in water (0.1% TFA). Peptide **22** was purified using a gradient of 10-70% CH₃CN (0.1% TFA) in water (0.1% TFA).

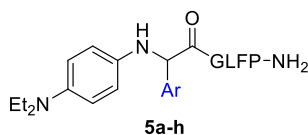
Table S1. Characterization data for peptides **2b-c**.



	R ¹	crude purity (%) ^a	purity (%) ^b	yield (%) ^c	<i>m/z</i> [M+H] ⁺ (calc)	<i>m/z</i> [M+H] ⁺ (obs)	retention time (min)
2b	NMe ₂	56	97	12	684.3868	684.3846	11.12, 11.30
2c	NEt ₂	67	>99	17	712.4181	712.4183	10.88, 10.95

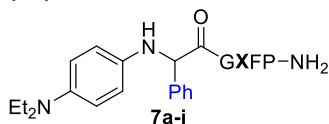
^aUnless otherwise noted, analytical LCMS analyses were performed on a 5 µM, 150 x 4.6 mm C18 Luna column purchased from Phenomenex (catalog # 00F-4252-E0) with a flow rate of 0.5 mL/min using a 12 min 5-95% linear gradient of MeCN (0.1% TFA) in water (0.1% TFA). The purity at 214 nm wavelength is reported in all cases.

^bRP-HPLC purity at 214 nm after purification. ^cYields after purification by RP-HPLC are based on resin loading.

Table S2. Characterization data for peptides **5a-h**.

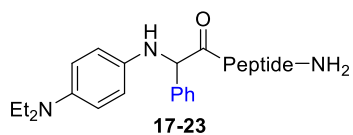
	Ar	crude purity (%) ^a	purity (%) ^b	yield (%) ^c	<i>m/z</i> [M+H] ⁺ (calc)	<i>m/z</i> [M+H] ⁺ (obs)	retention time (min)
5a	4-MeO-C ₆ H ₄	91	>99	32	742.4287	742.4262	11.00, 11.03
5b	4-C ₇ H ₁₅ O-C ₆ H ₄	88	>99	34	826.5226	826.5198	13.51, 13.61
5c	4-Me-C ₆ H ₄	70	92	15	726.4337	726.4319	11.27, 11.34
5d	2-Me-C ₆ H ₄	84	>99	32	726.4337	726.4313	11.18, 11.25
5e	4-Ph-C ₆ H ₄	84	96	41	788.4494	788.4471	11.97, 12.08
5f	4-Br-C ₆ H ₄	59	81	15	790.3286	790.3273	11.49, 11.60
5g	4-CF ₃ -C ₆ H ₄	19	99	3	780.4055	780.4047	11.70, 11.85
5h	4-C ₄ H ₃ O	29	93	8	702.3974	702.3975	10.61

^aUnless otherwise noted, analytical LCMS analyses were performed on a 5 μM, 150 x 4.6 mm C18 Luna column purchased from Phenomenex (catalog # 00F-4252-E0) with a flow rate of 0.5 mL/min using a 12 min 5-95% linear gradient of MeCN (0.1% TFA) in water (0.1% TFA). The purity at 214 nm wavelength is reported in all cases. ^bRP-HPLC purity at 214 nm after purification. ^cYields after purification by RP-HPLC are based on resin loading.

Table S3. Characterization data for peptides **7a-i**.

	X	crude purity (%) ^a	purity (%) ^b	yield (%) ^c	<i>m/z</i> [M+H] ⁺ (calc)	<i>m/z</i> [M+H] ⁺ (obs)	retention time (min)
7a	Ala	56	>99	19	670.3711	670.3718	10.06, 10.09
7b	Gln	45	90	13	727.3926	727.3935	9.70
7c	Glu	40	86	25	728.3766	728.3774	9.87
7d	Trp	54	>99	15	785.4133	785.4130	11.00, 11.07
7e	Lys	53	>99	18	727.4290	727.4286	9.31
7f	Thr	56	>99	9	700.3817	700.3823	9.99
7g	Tyr	66	>99	16	762.3974	762.3951	10.77, 10.96
7h	Arg	54	97	22	755.4351	755.4323	9.61, 9.78
7i	Cys	50	85	9	702.3432	702.3416	10.88, 11.20

^aUnless otherwise noted, analytical LCMS analyses were performed on a 5 μM, 150 x 4.6 mm C18 Luna column purchased from Phenomenex (catalog # 00F-4252-E0) with a flow rate of 0.5 mL/min using a 12 min 5-95% linear gradient of MeCN (0.1% TFA) in water (0.1% TFA). The purity at 214 nm wavelength is reported in all cases. ^bRP-HPLC purity at 214 nm after purification. ^cYields after purification by RP-HPLC are based on resin loading.

Table S4. Characterization data for peptides **17-23**.

	peptide	crude purity (%) ^a	purity (%) ^b	yield (%) ^c	<i>m/z</i> [M+H] ⁺ (calc)	<i>m/z</i> [M+H] ⁺ (obs)	retention time (min)
17	LGFP	39	>99	3	712.4181	712.4165	11.37, 11.46
18	LFGP	17	>99	19	712.4181	712.4163	11.35, 11.48
19	LFPG	18	86	4	712.4181	712.4157	11.31
20	KGFP	33	99	17	727.4290	727.4264	9.50, 9.59
21	SEDQA	63	>99	6	828.3886	828.3862	8.94, 9.03
22	GSEDQA	77	99	15	885.4101	885.4084	8.59, 8.83
23	GDRVYIHPFHL	17	>99	4	817.5 ^d	817.7 ^d	8.48

^aUnless otherwise noted, analytical LCMS analyses were performed on a 5 μ M, 150 x 4.6 mm C18 Luna column purchased from Phenomenex (catalog # 00F-4252-E0) with a flow rate of 0.5 mL/min using a 12 min 5-95% linear gradient of MeCN (0.1% TFA) in water (0.1% TFA). The purity at 214 nm wavelength is reported in all cases. ^bRP-HPLC purity at 214 nm after purification. ^cYields after purification by RP-HPLC are based on resin loading. ^d*m/z* [M + 2H]²⁺

Additional Supporting Data

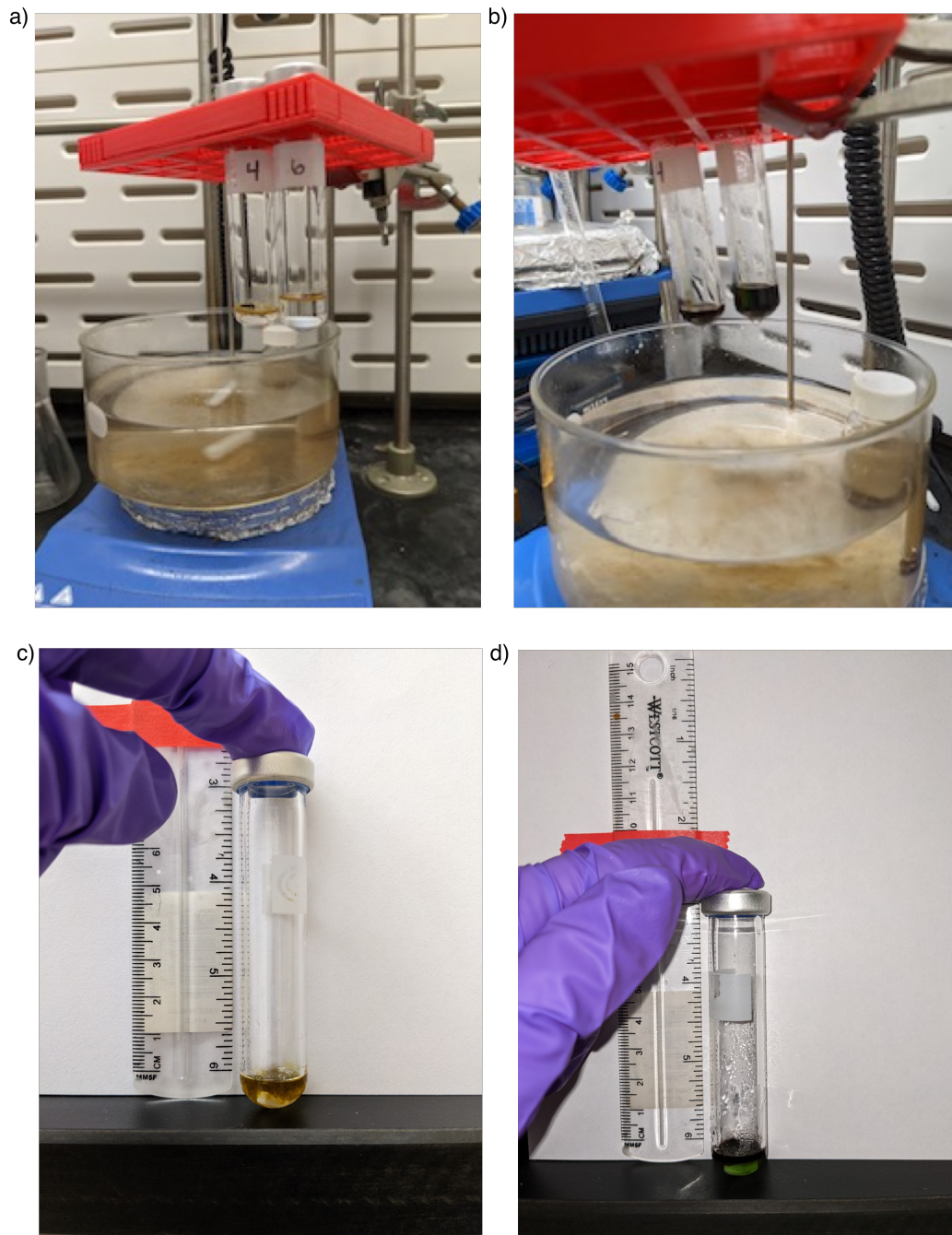


Figure S1. Microwave vial containing resin a) prior to exposure to heat, b) after stirring for 20 hours at 70 °C, c) prior to exposure to heat, and d) after stirring for 20 hours at 100 °C. Two different reaction scales are shown in a)-b): 20 mg of resin and 50 mg of resin.

To confirm the site-selective installment of the phenyl group during the on-resin α C–H functionalization reaction, **2c** was synthesized using two different procedures: a Petasis-type reaction (*this work*, see p. S4) and the submonomer method (see p. S3, incorporation of *N*-terminal *N*-aryl amino acid residues using racemic α -bromophenylacetic acid). The two products have identical retention times (Figure S2) and ¹H NMR spectra (Figure S3).

Note: the α C–H functionalization reaction likely has modest diastereoselectivity given that the ratios of **2c** are not 1:1 in Figure S2a.

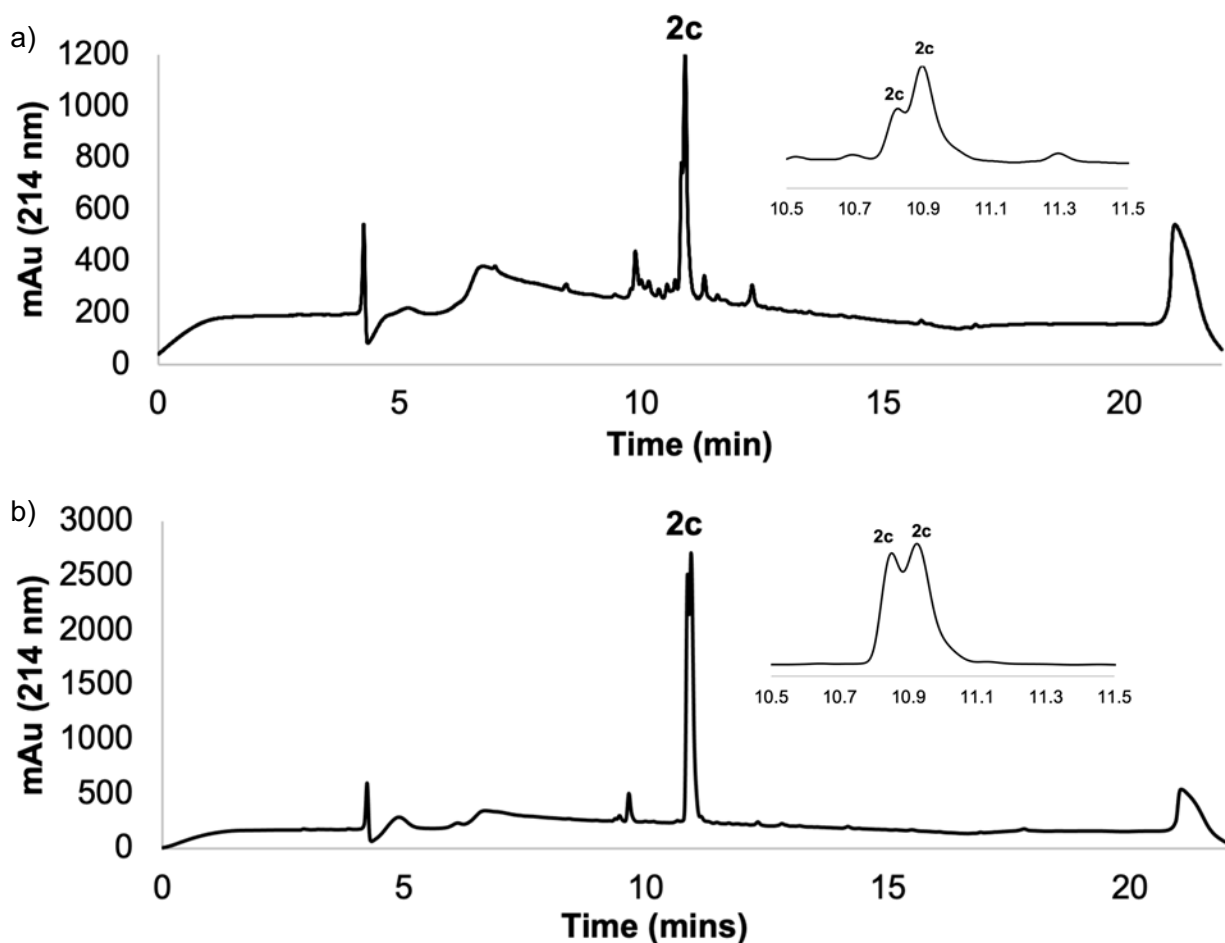


Figure S2. LC chromatograms corresponding to *N*-aryl peptide **2c**, made via a) the Petasis-type reaction (*this work*) and b) submonomer method.

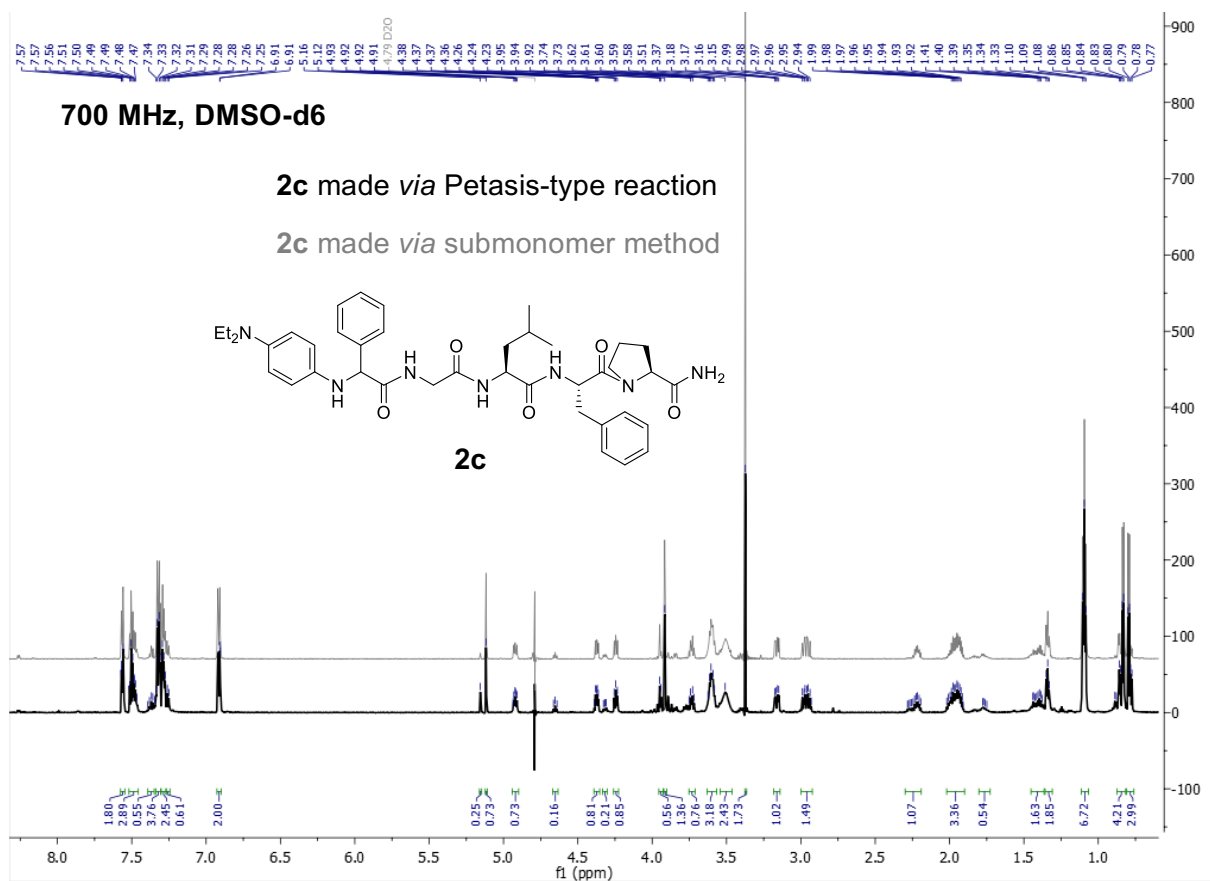


Figure S3. Overlay of ¹H NMR spectra corresponding to *N*-aryl peptide **2c**, made *via* the Petasis-type reaction (*this work*, in black) and submonomer method (in grey).

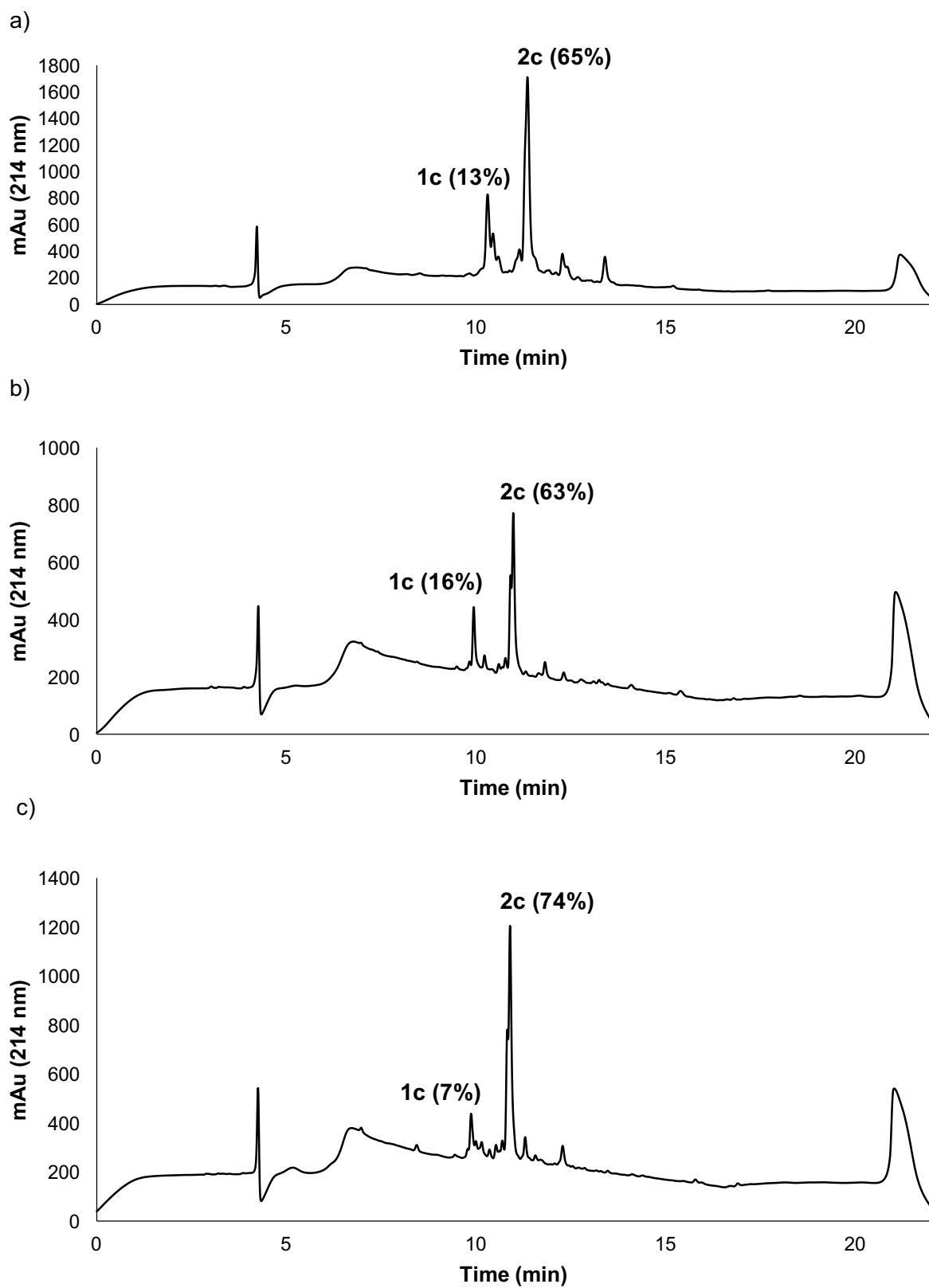
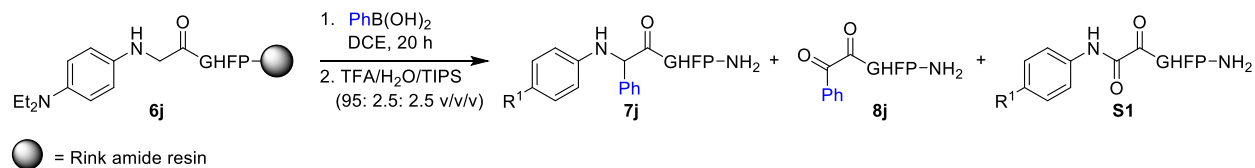


Figure S4. LC chromatograms corresponding to crude reaction traces of *N*-aryl peptide **2c** when a) 20 mg, b) 50 mg, and c) 100 mg of resin were used.

Table S5. Effect of increasing boronic acid equivalents on coupling with resin-bound *N*-(*p*-Et₂N-Ph)G-GHFP, where His is protected with a trityl group.



entry	PhB(OH) ₂ (equiv)	6j (%)	7j (%)	8j (%)	S1 (%)
1	1.5	14	5	8	16
2	3.0	0	8	57	0

Oxidation of *N*-aryl peptides 2a-c and 5a-g.

The ability of C α -arylated *N*-aryl peptide products to oxidize was studied under various conditions to gain a deeper understanding of the stability and reactivity of our reaction products.

Note: unpurified crude material of **2a-c** was used for these studies. *N*-aryl peptide **5g** was excluded from this study since very little material could be isolated from this low converting reaction.

Procedure in DCE

The *N*-aryl peptide (0.001 mmol) was transferred to an oven-dried 3 mL microwave vial and dissolved in DCE (1 mL) to give a final concentration of 1 mM for the *N*-aryl peptide. The microwave vial was capped and placed in a preheated oil bath (70 °C) or stirred at room temperature for 20 h. An aliquot was transferred into a 20 mL vial, evaporated using the Biotage V10 (volatile setting), and redissolved in 1:1 MeCN/H₂O for LCMS analysis.

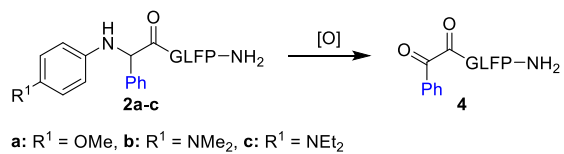
Procedure in buffer

The *N*-aryl peptide (0.001 mmol) was transferred to a 4 mL scintillation vial and dissolved in the desired buffer (1 mL, 0.1 M pH 4.5 ammonium acetate buffer or 0.1 M pH 7 potassium phosphate buffer) to give a final concentration of 1 mM for the *N*-aryl peptide. Oxygen gas was bubbled through the solution for 30 seconds, the exit needle was removed, and the oxygen balloon was kept in place. An aliquot was directly transferred to a LCMS vial for analysis.

Procedure in TFA/H₂O

The *N*-aryl peptide (0.001 mmol) was transferred to a 4 mL scintillation vial and dissolved in 950 μ L TFA and 50 μ L of H₂O to give a final concentration of 1 mM for the *N*-aryl peptide. The solution was stirred at room temperature for 1 hour. The solution was evaporated to dryness on the Biotage V10 prior to redissolving it in 1:1 MeCN/H₂O for LCMS analysis.

Table S6. Oxidation of *N*-aryl peptides **2a-c**.



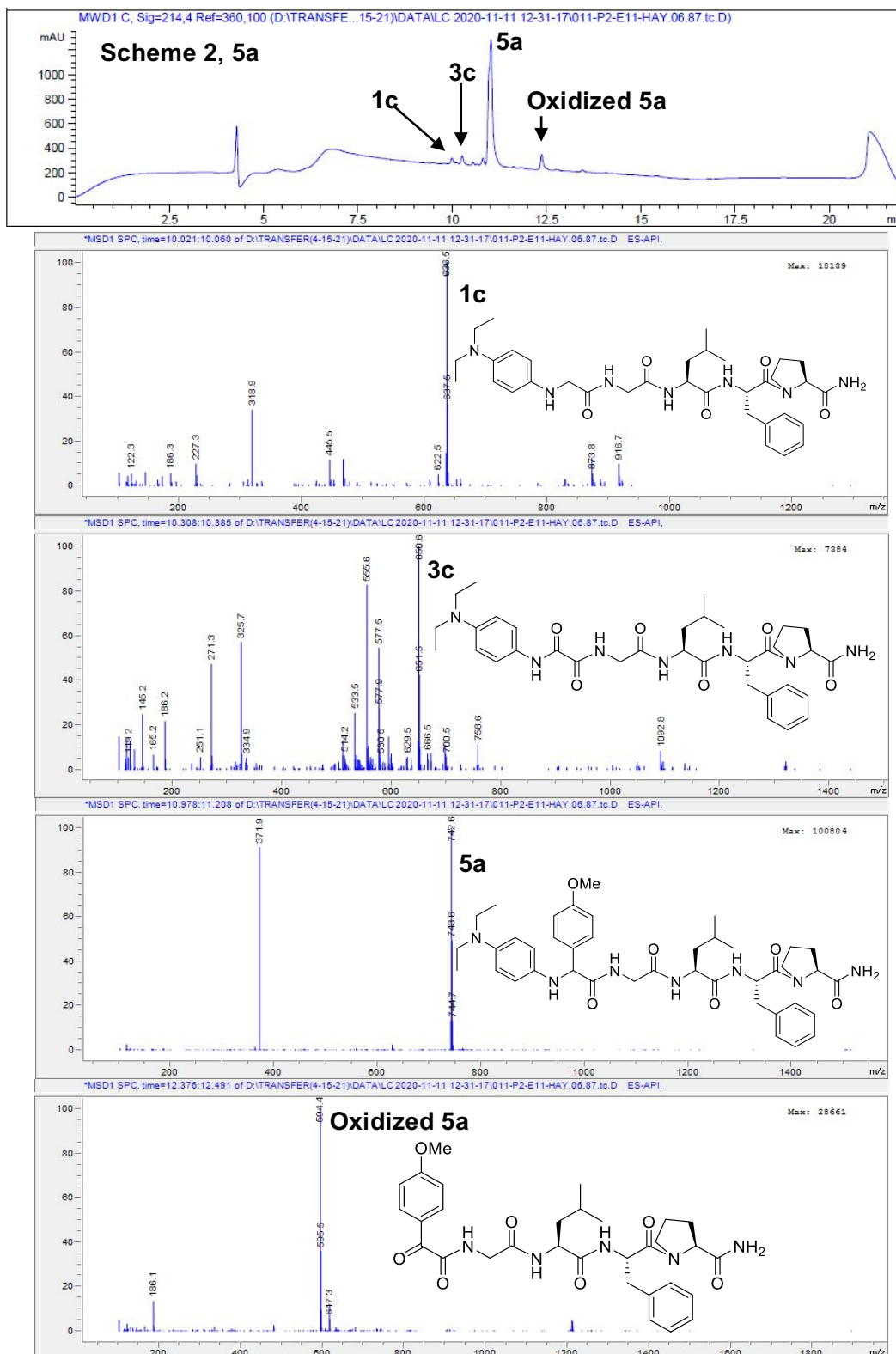
conditions	R ¹ = OMe (2a)	R ¹ = NMe ₂ (2b)	R ¹ = NEt ₂ (2c)
DCE, 70 °C	Yes	Yes	Yes
DCE, rt	Yes	Some	Minimal
pH 4.5, O ₂	Minimal	Some	Minimal
pH 7, O ₂	No	Yes	Minimal
TFA/H ₂ O	Minimal	No	No

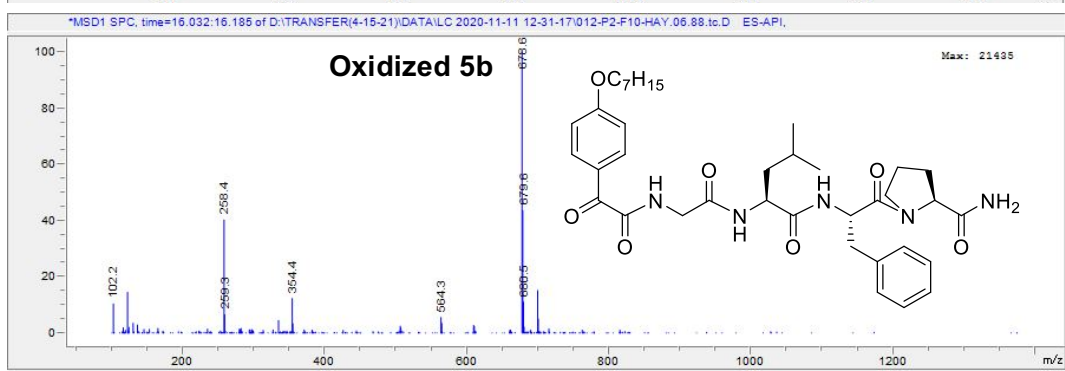
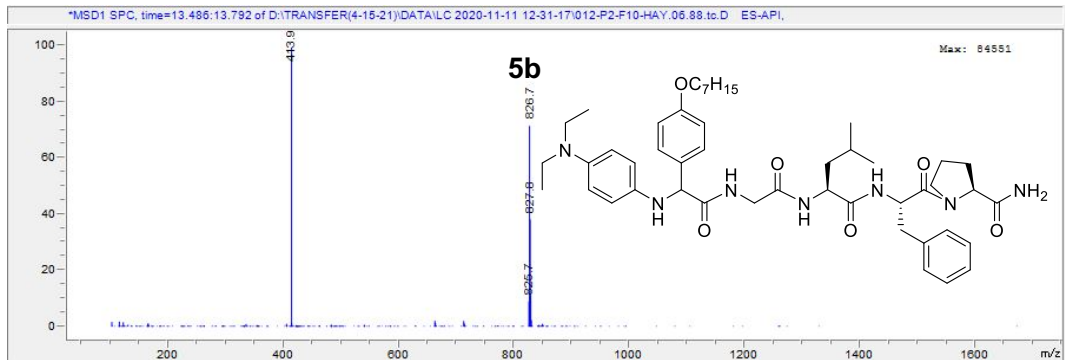
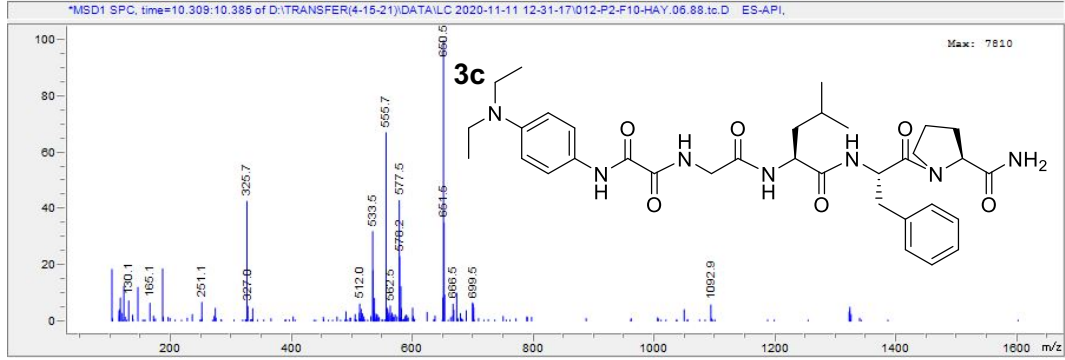
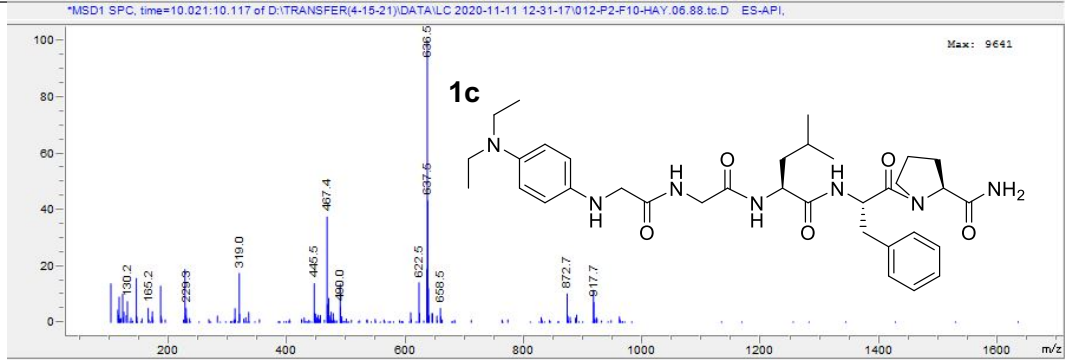
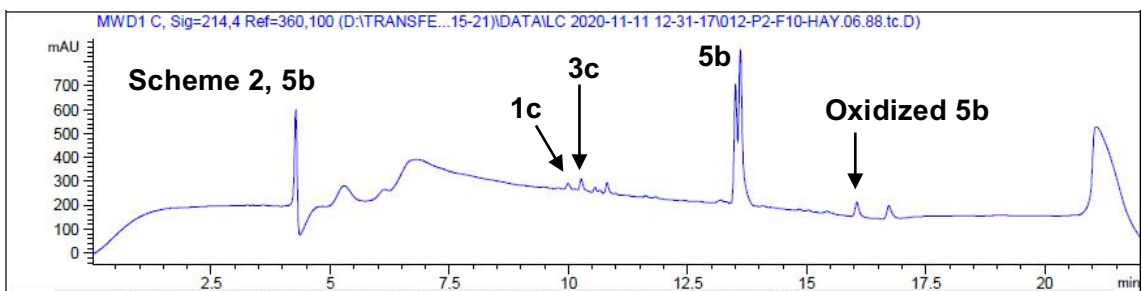
Yes = % crude purity of **4** > 50%, some = % crude purity of **4** is 20-50%, minimal = % crude purity of **4** < 20%

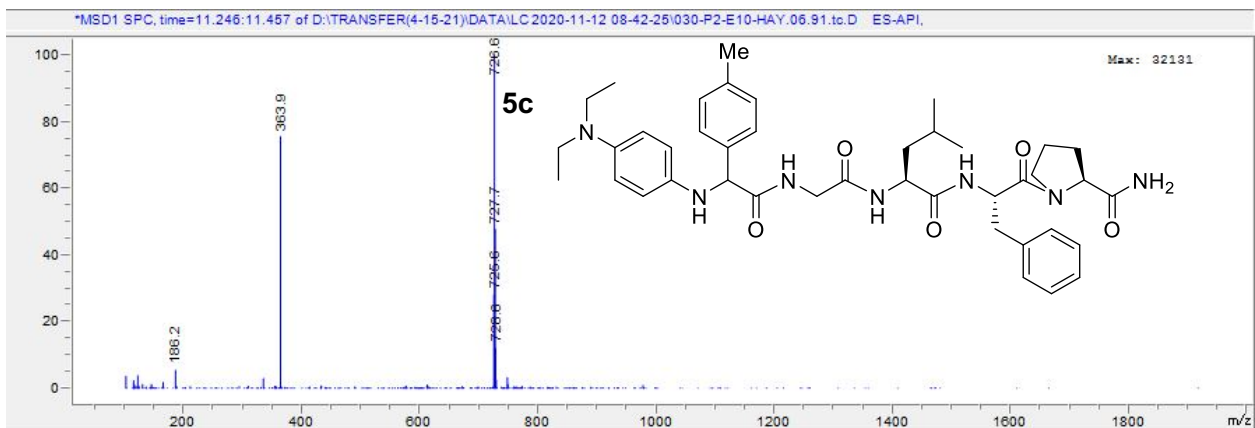
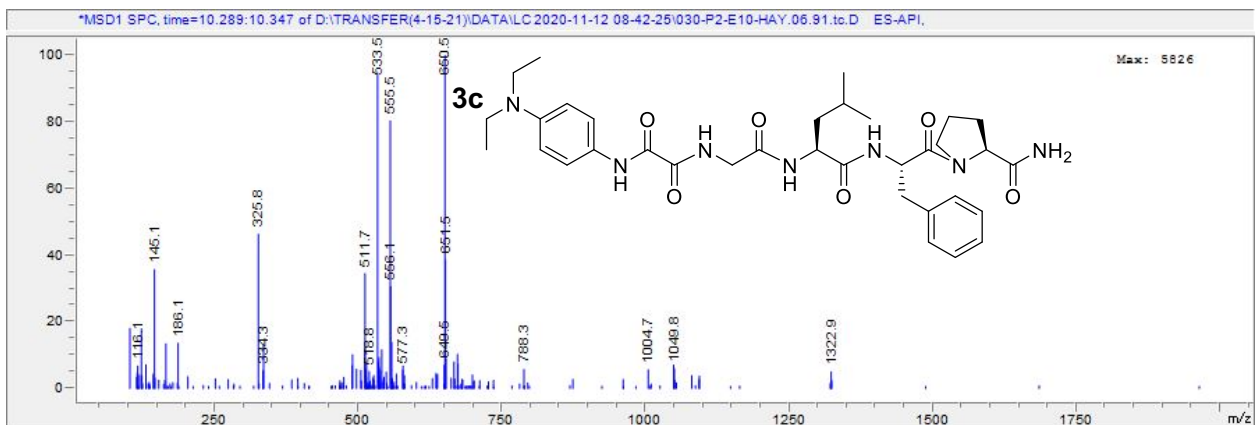
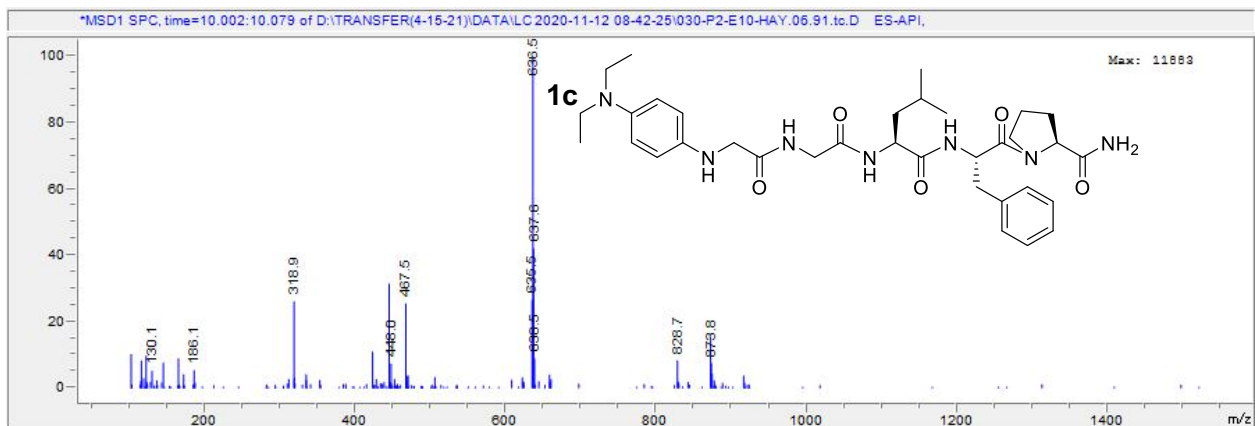
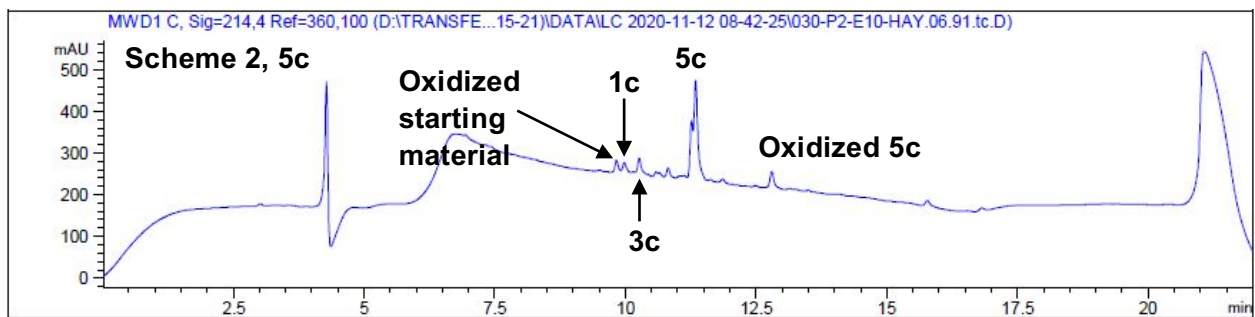
D. LCMS Chromatograms

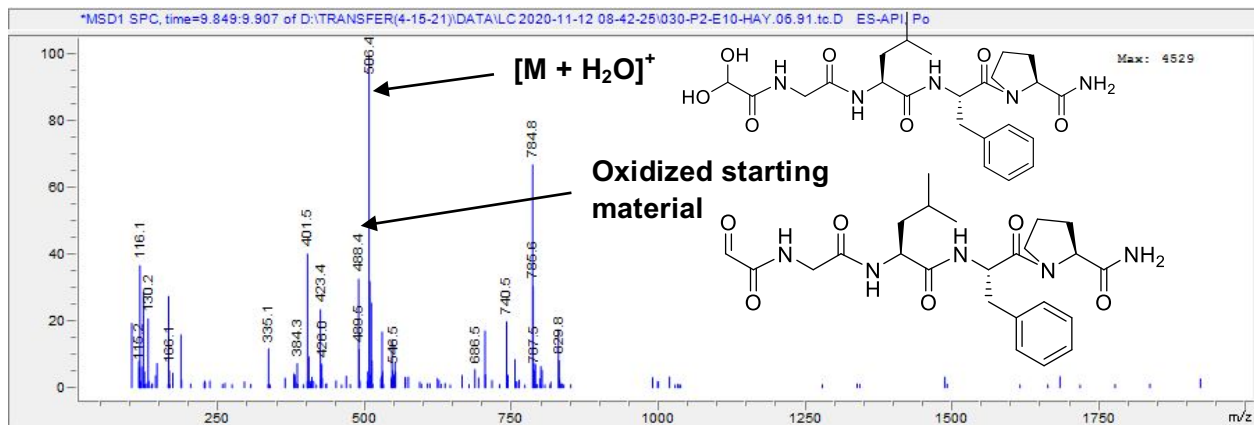
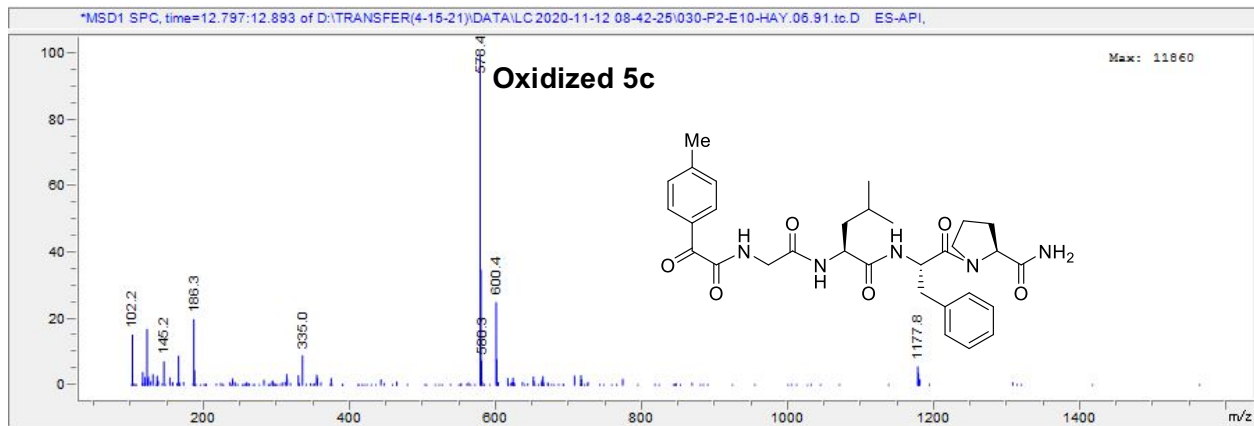
Crude Reaction Data

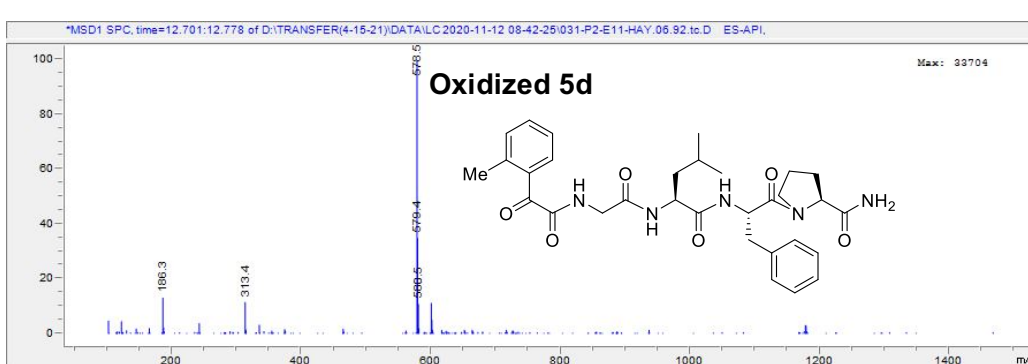
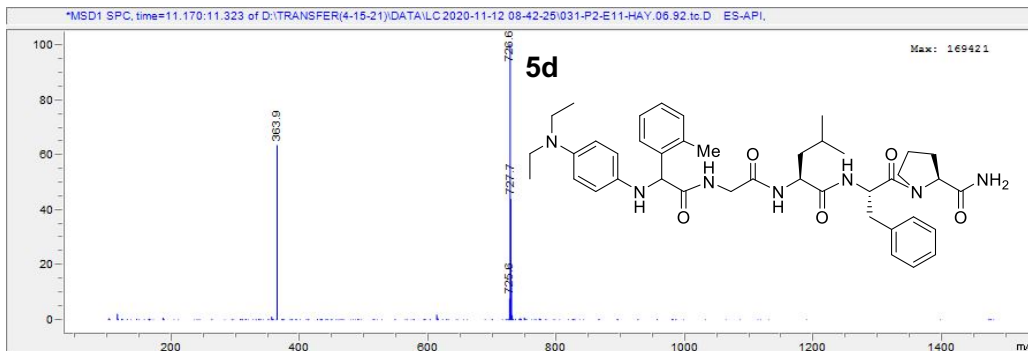
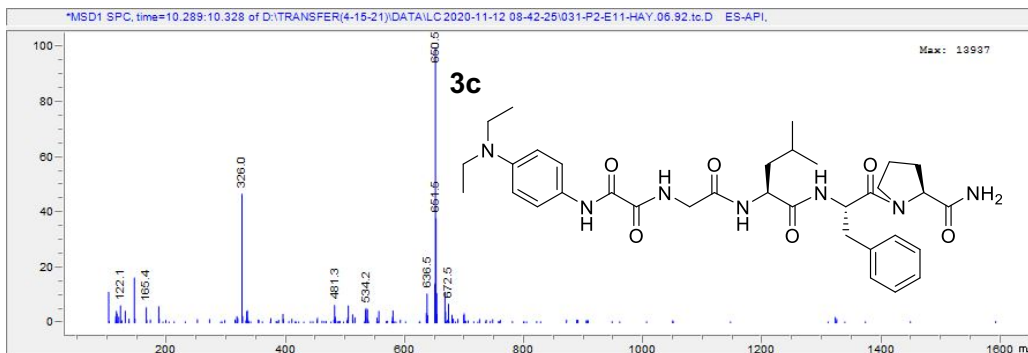
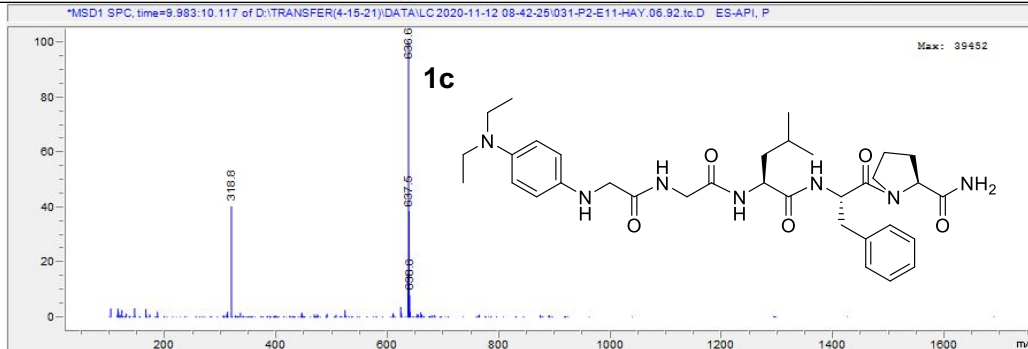
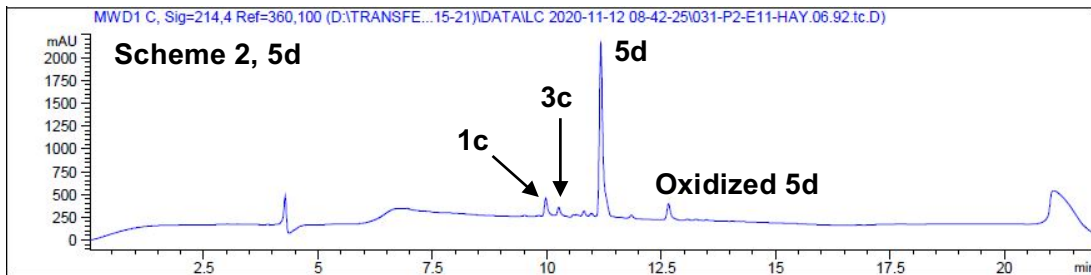
Crude reaction data from Scheme 2

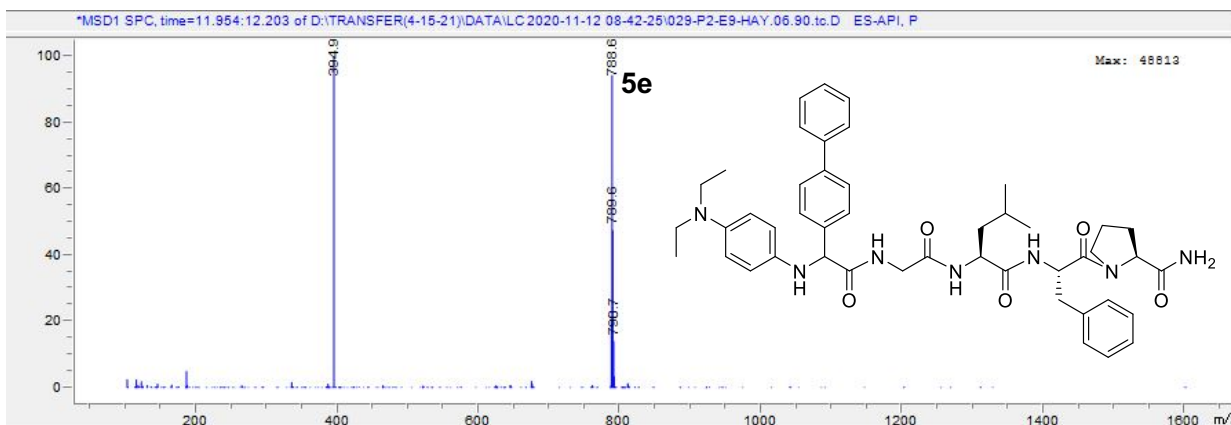
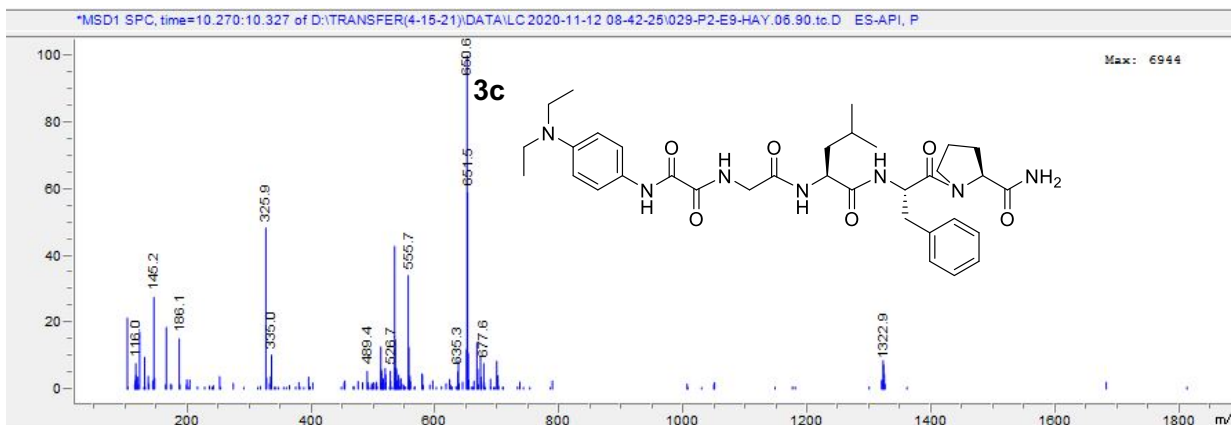
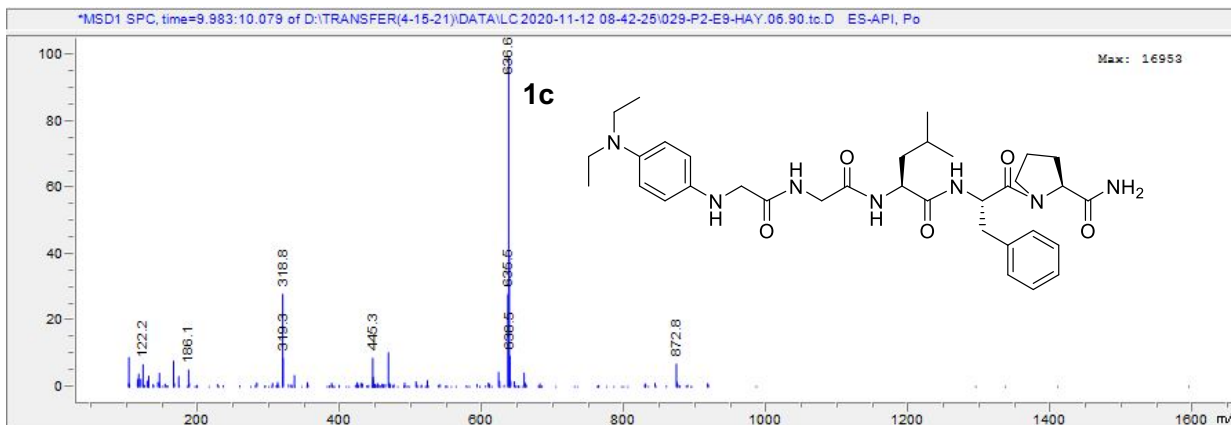
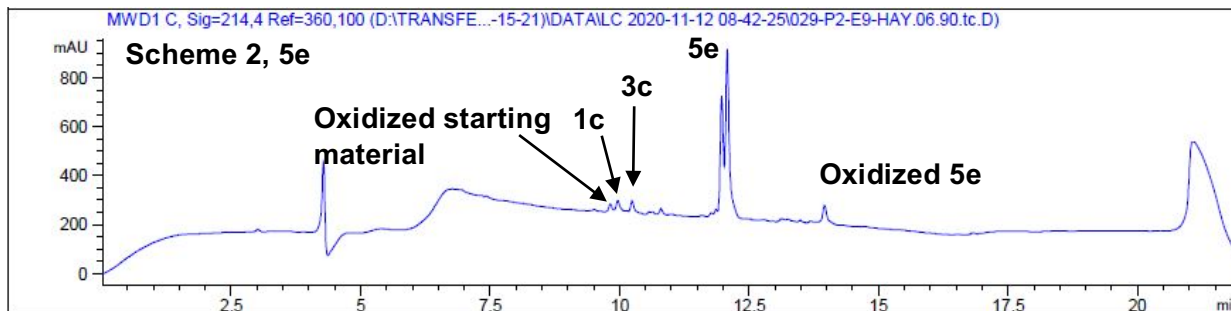


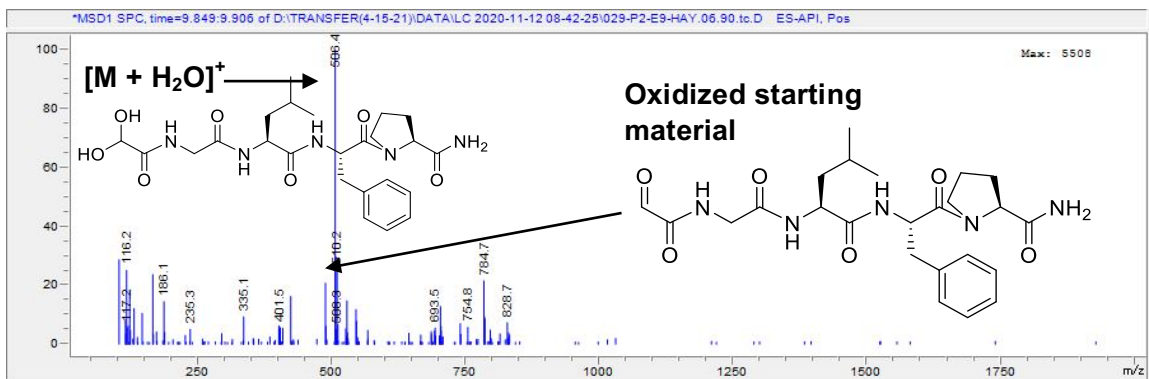
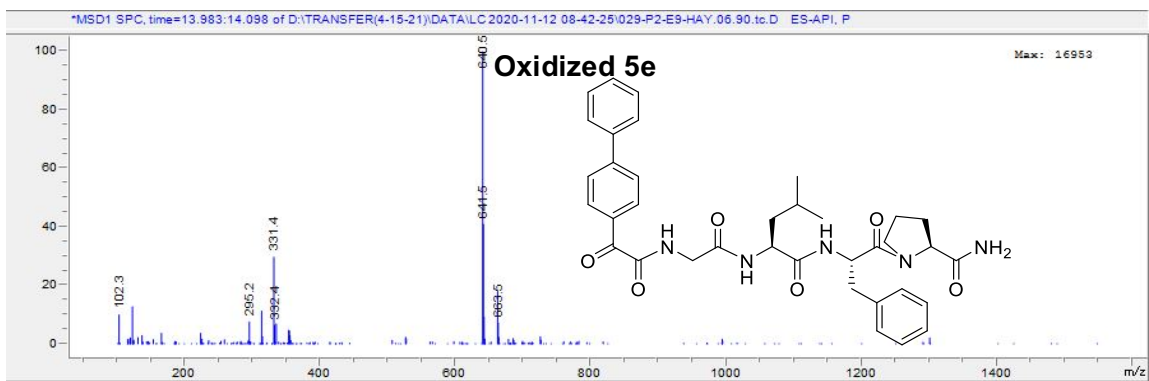


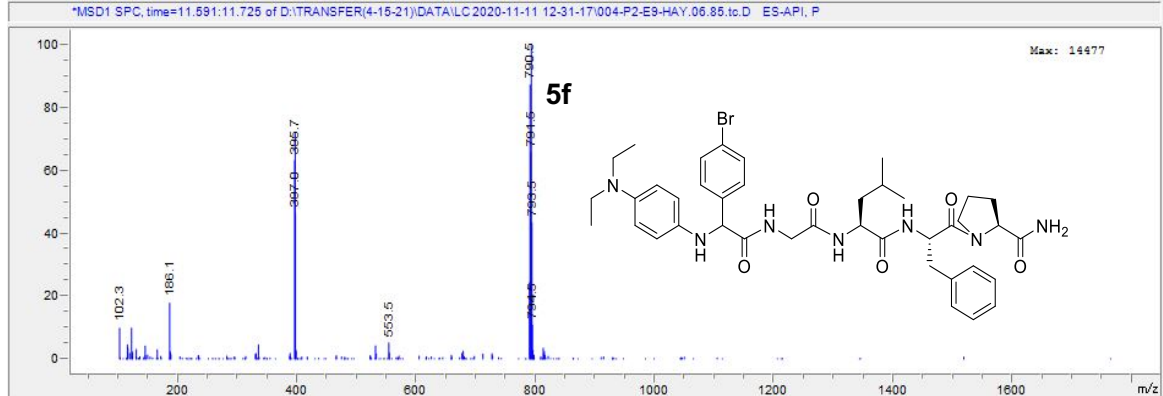
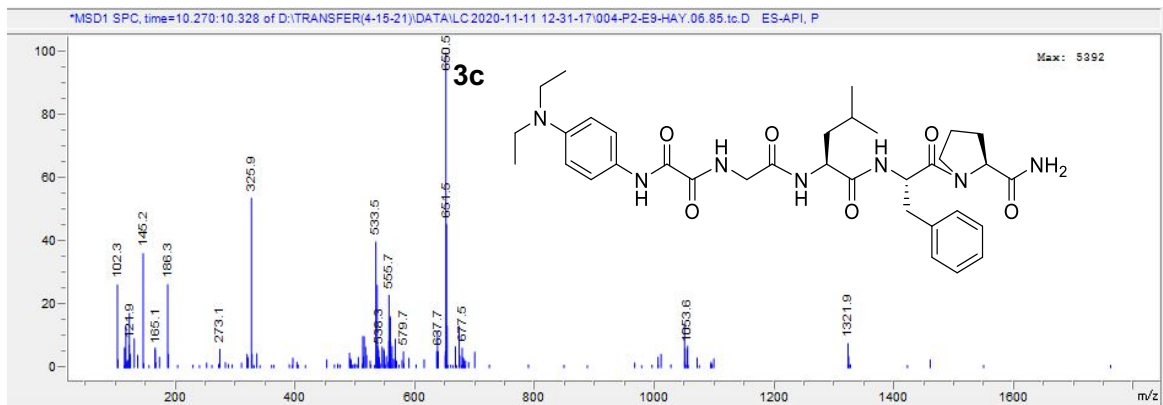
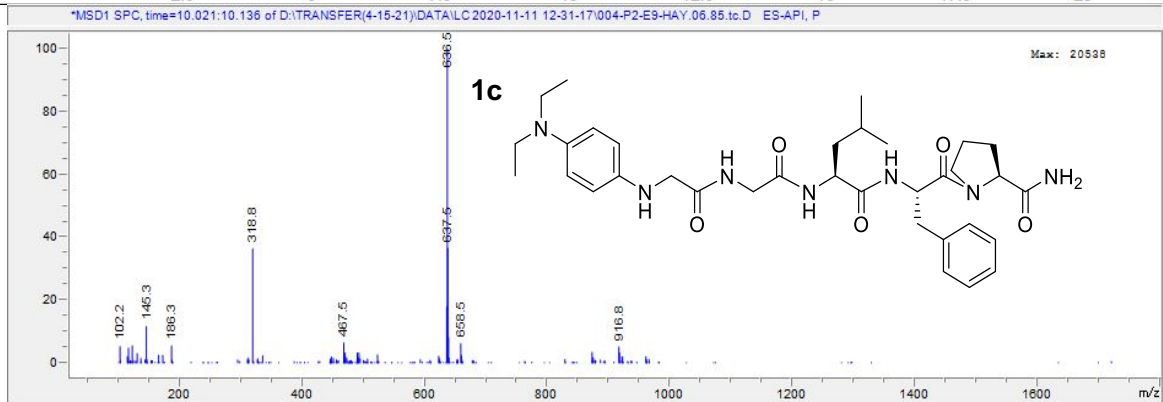
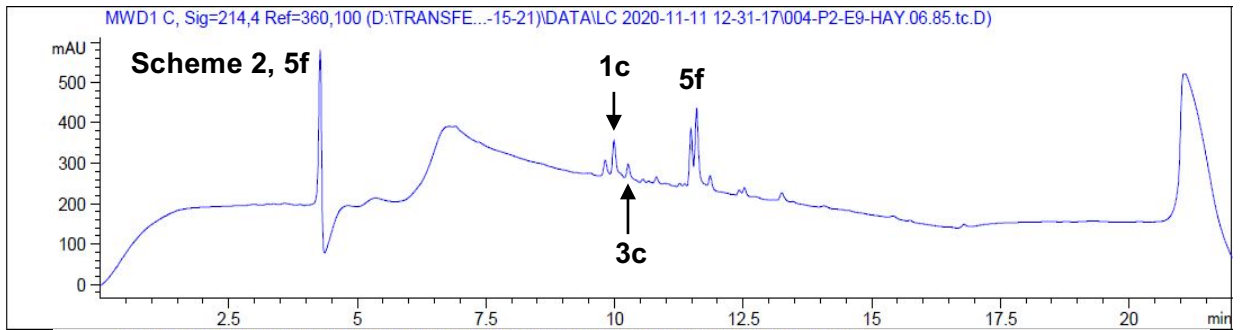


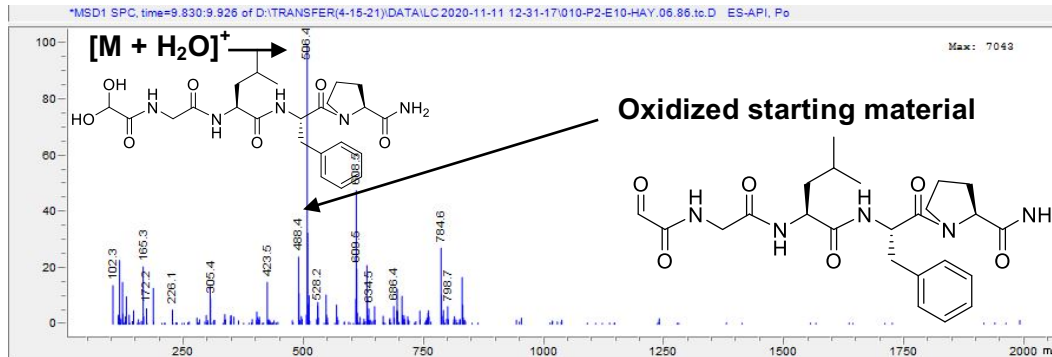
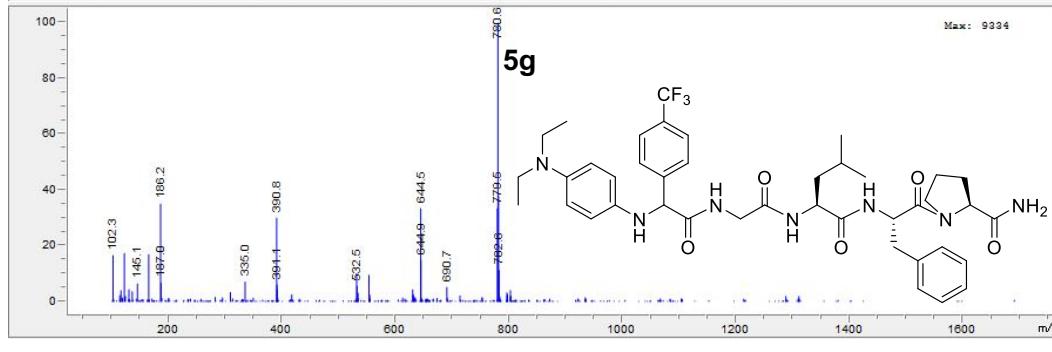
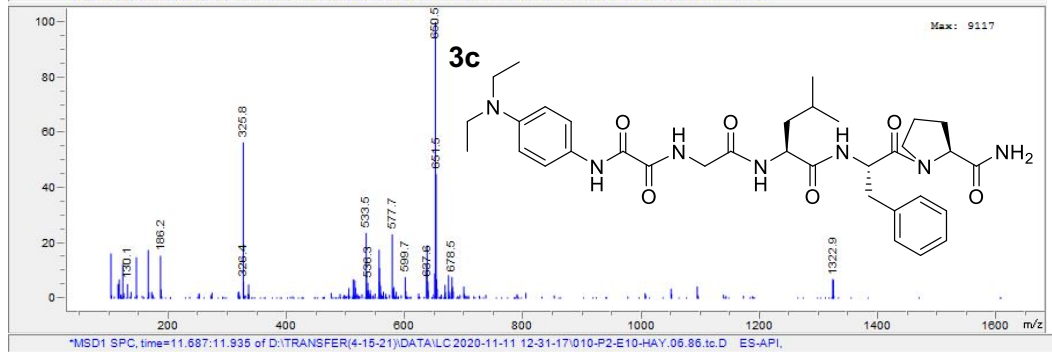
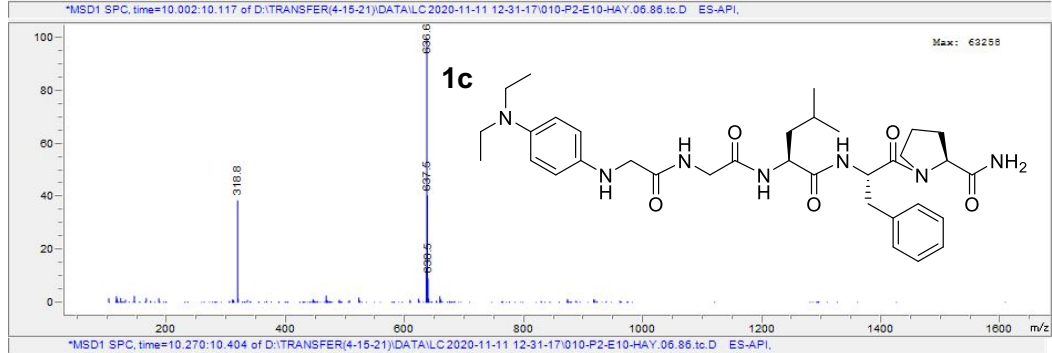
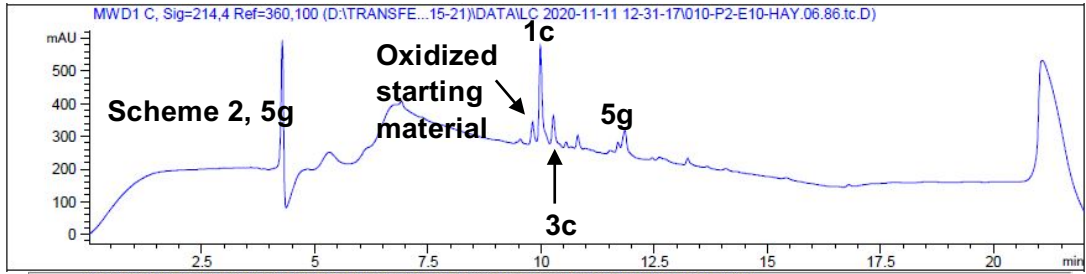


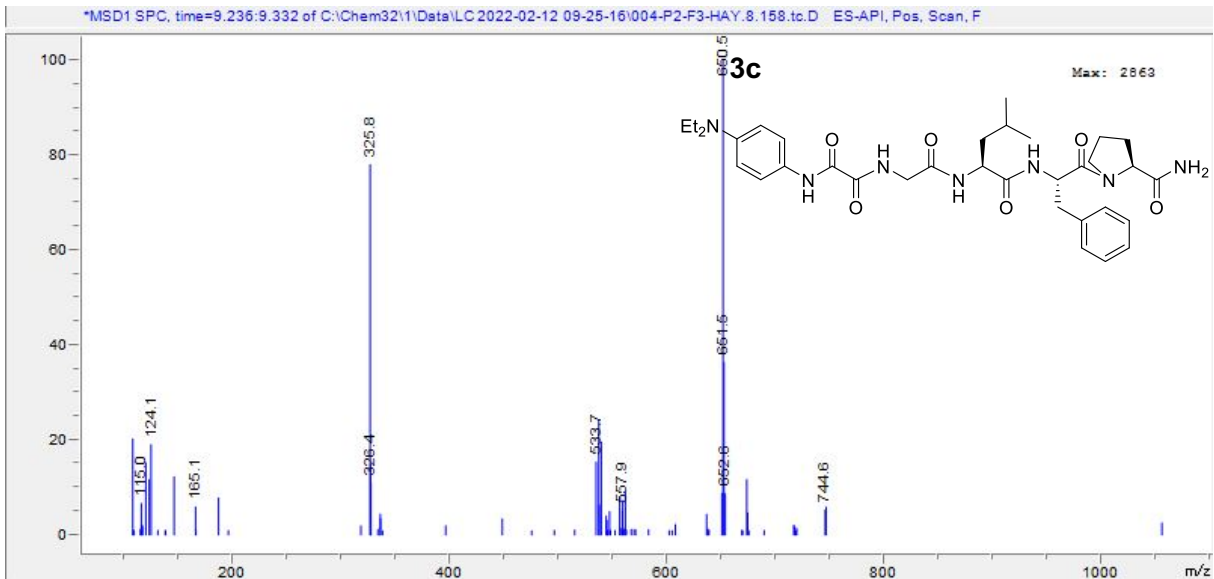
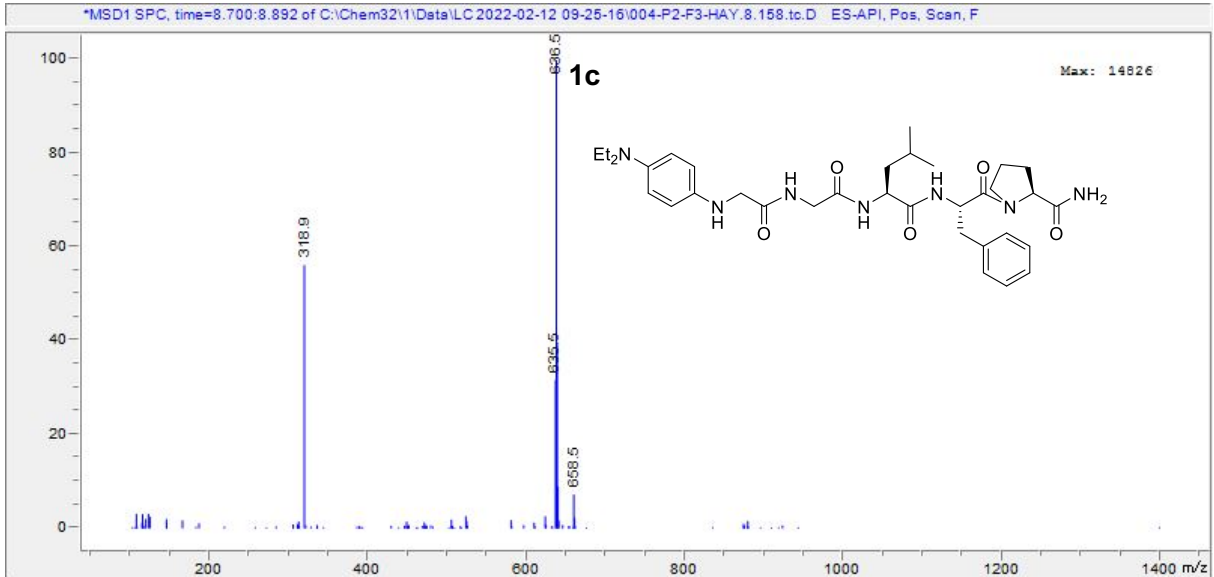
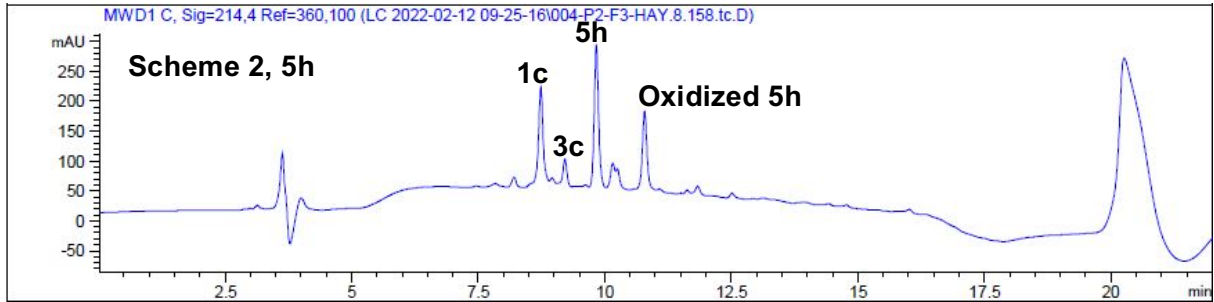


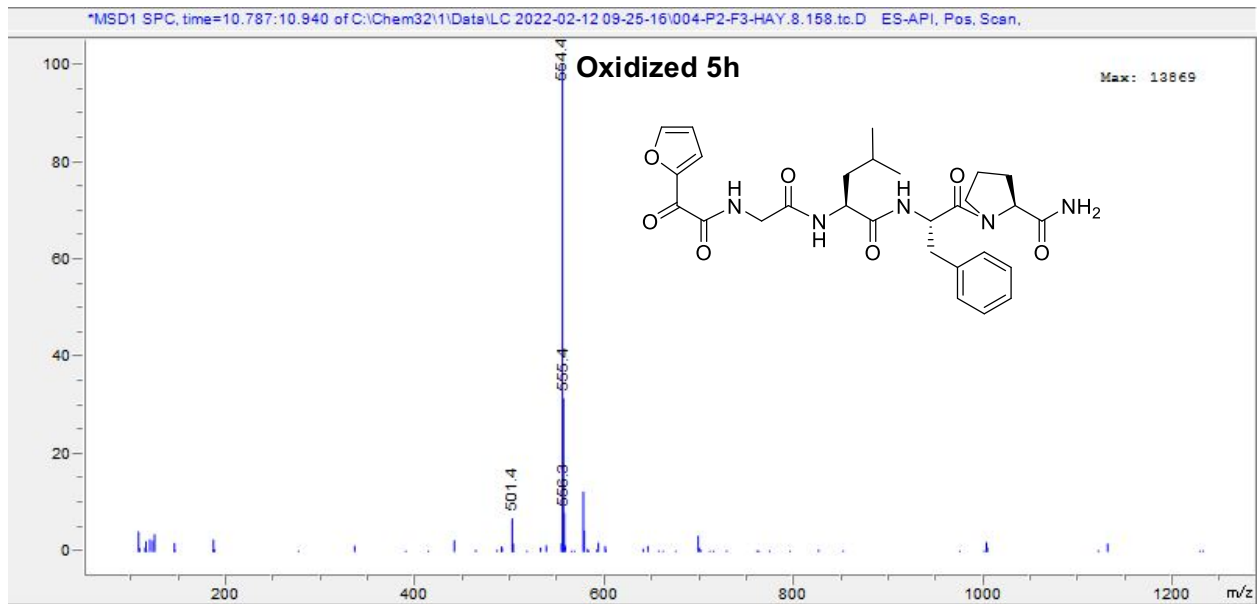
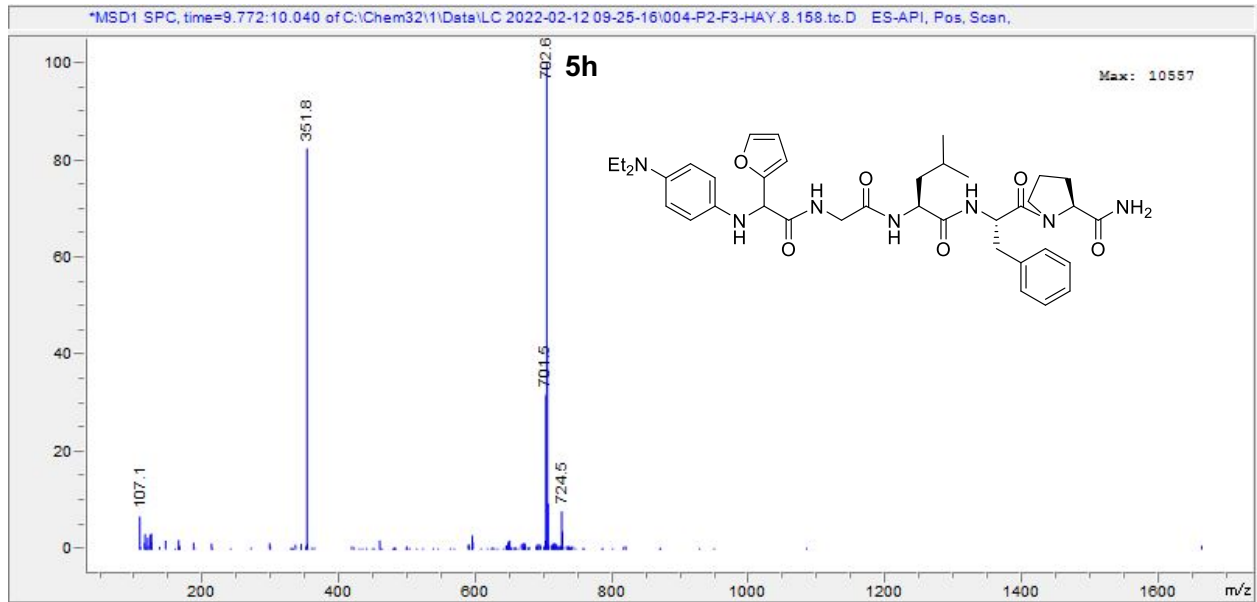




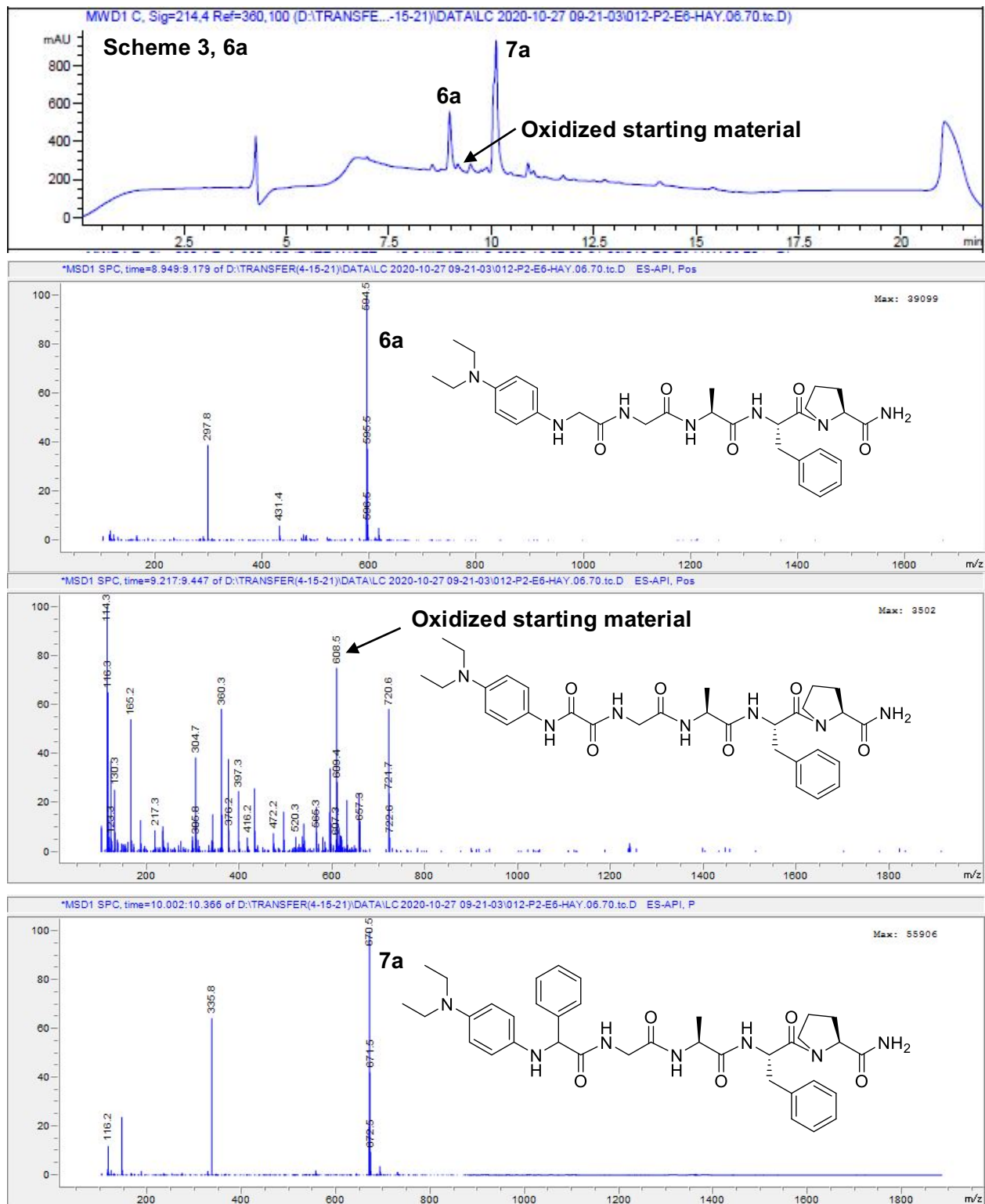


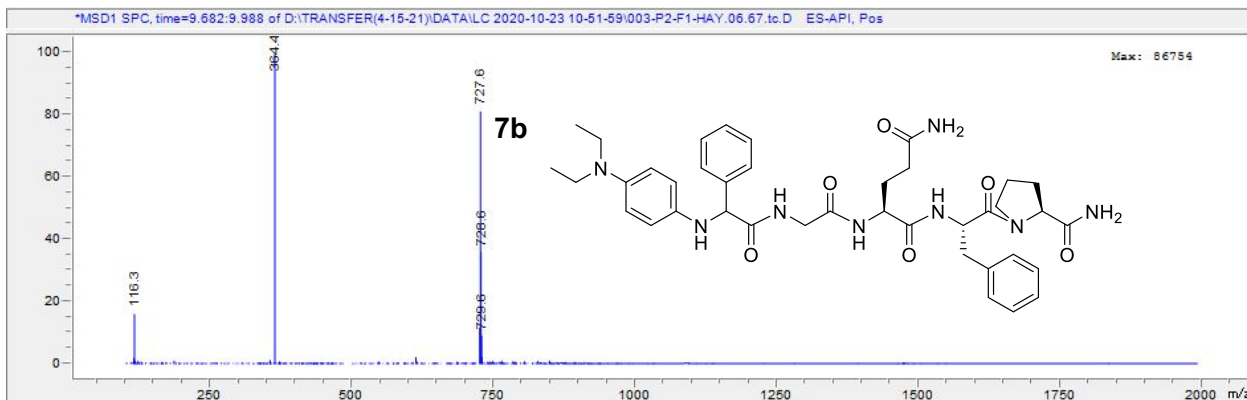
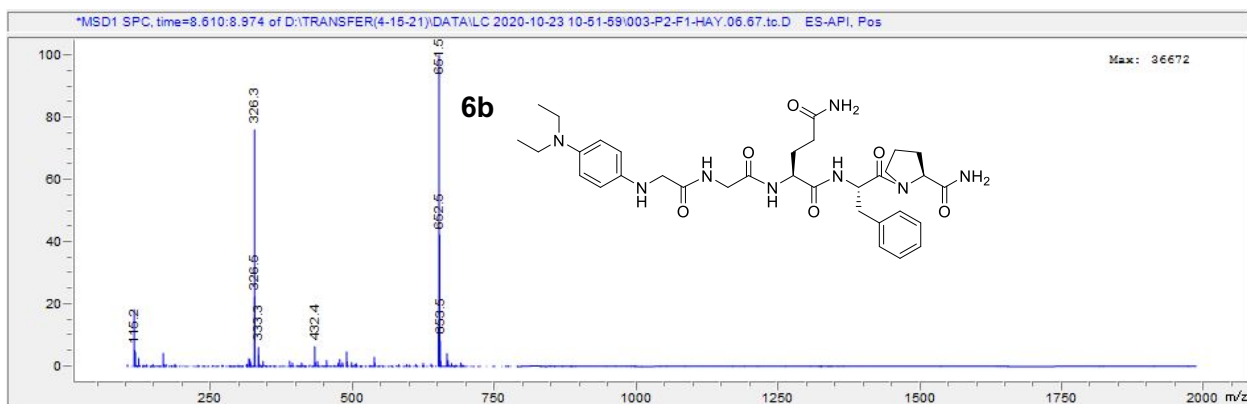
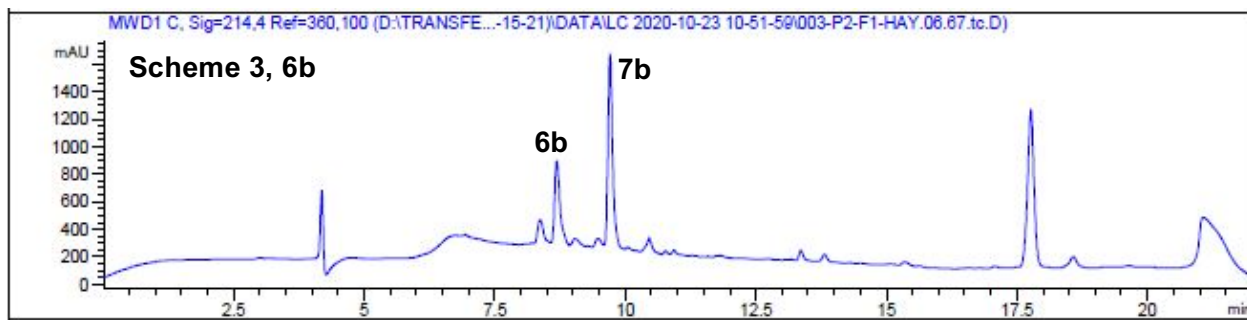


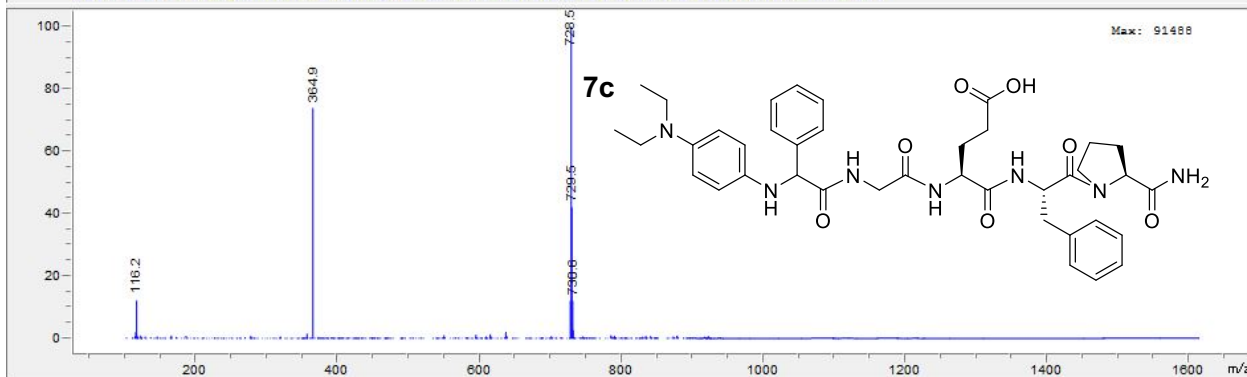
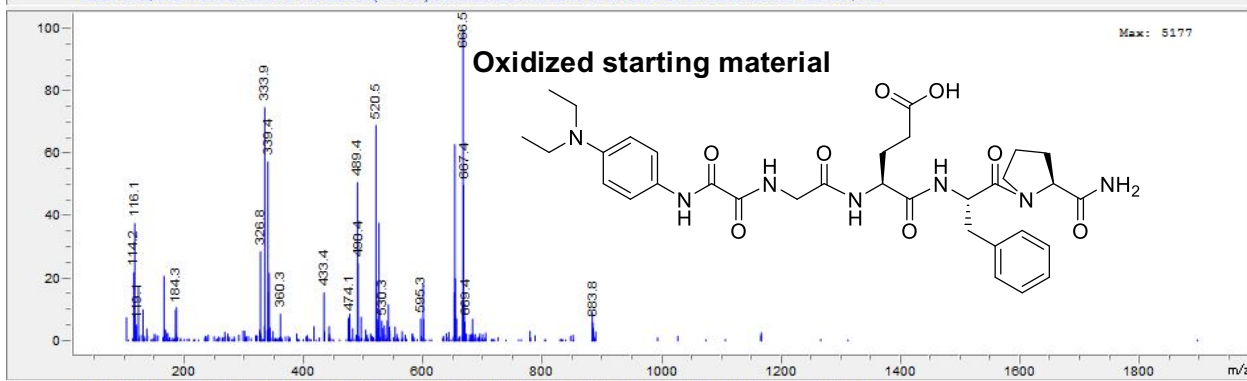
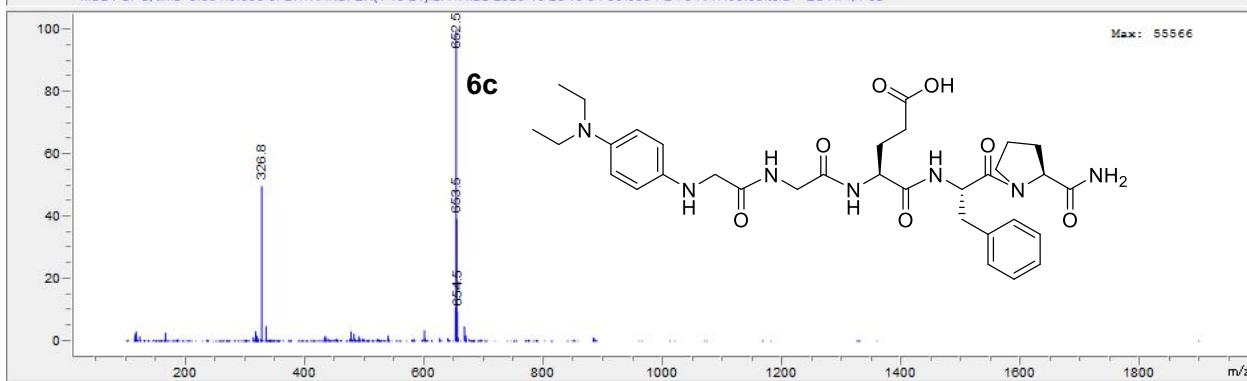
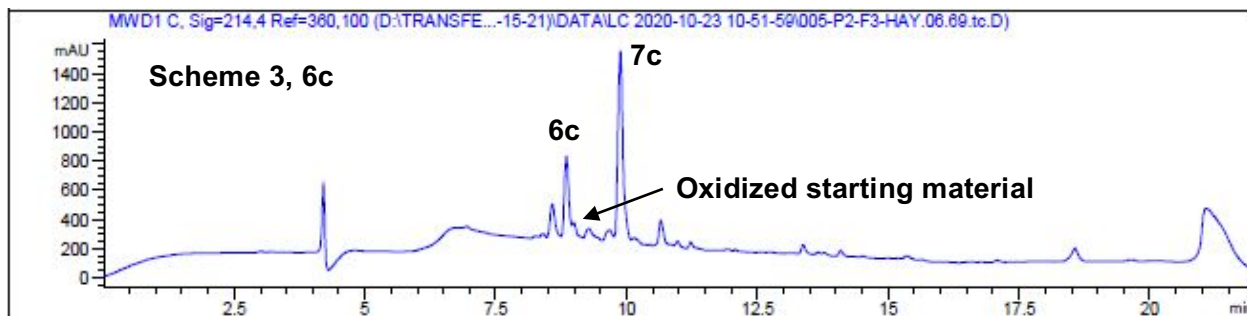


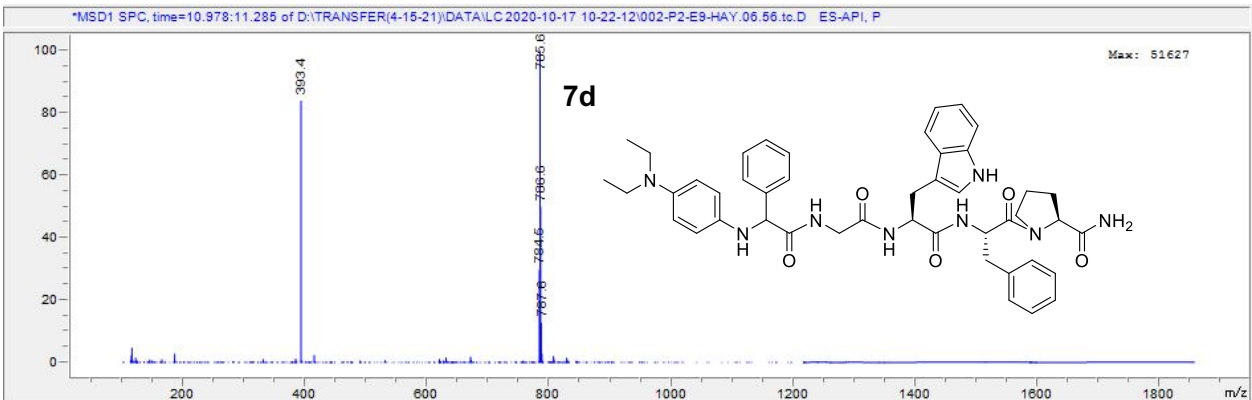
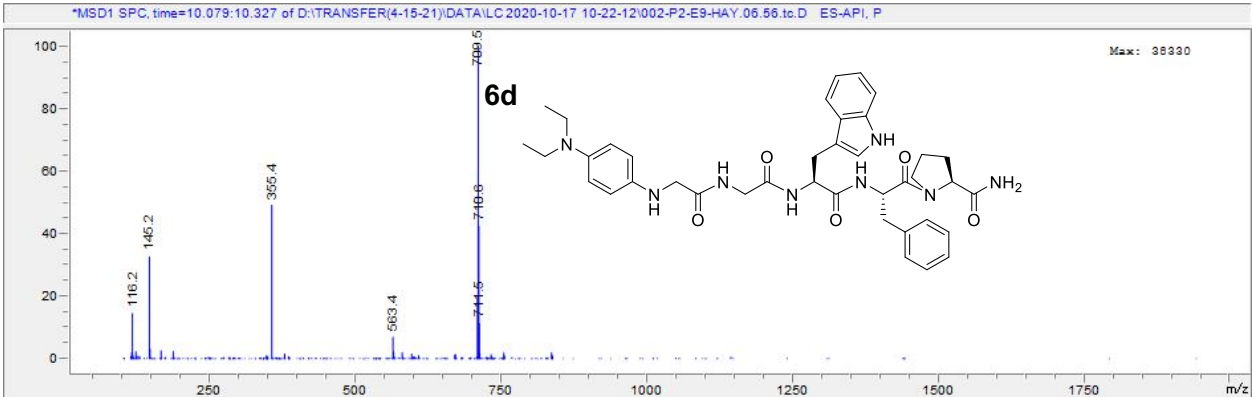
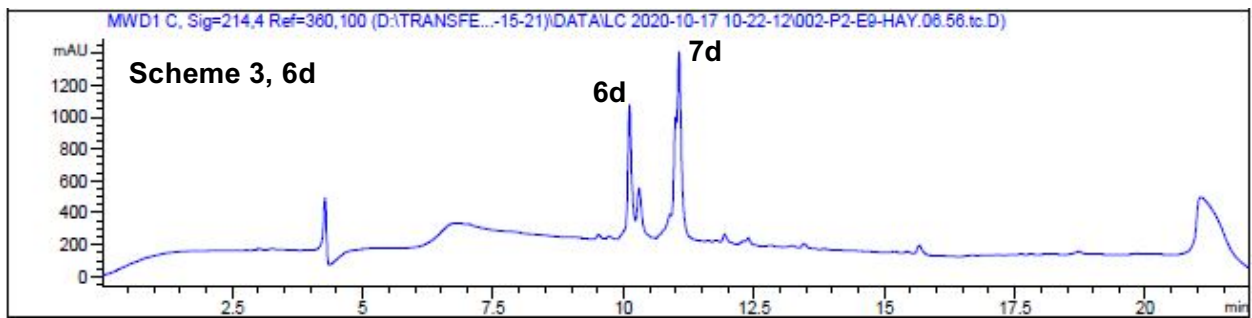


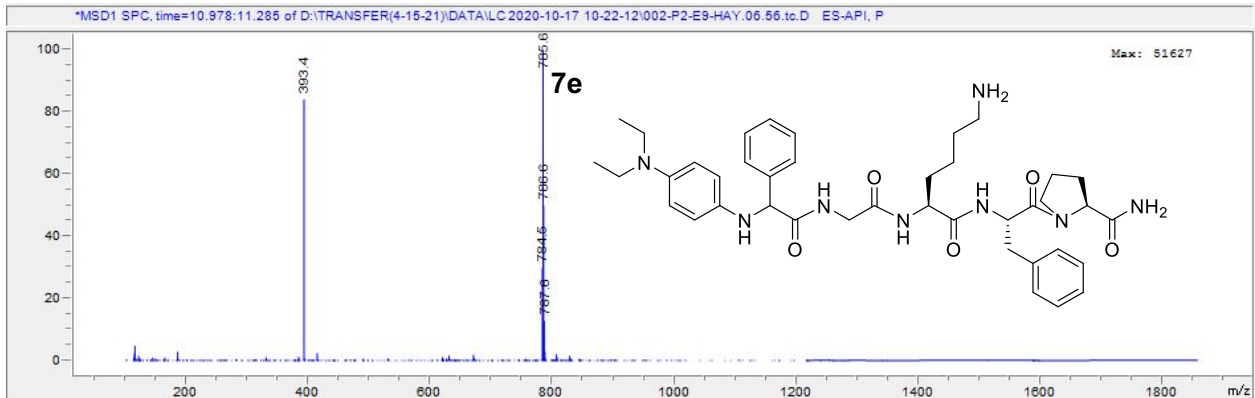
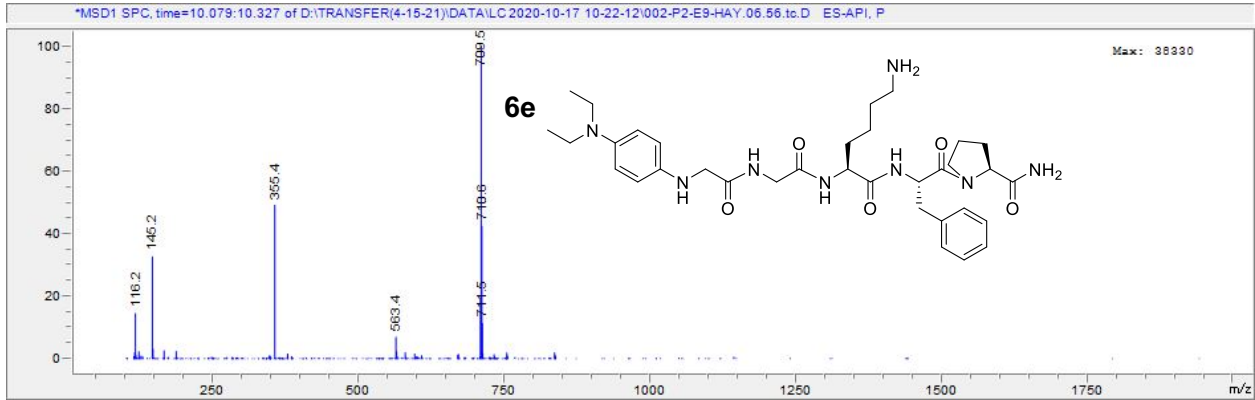
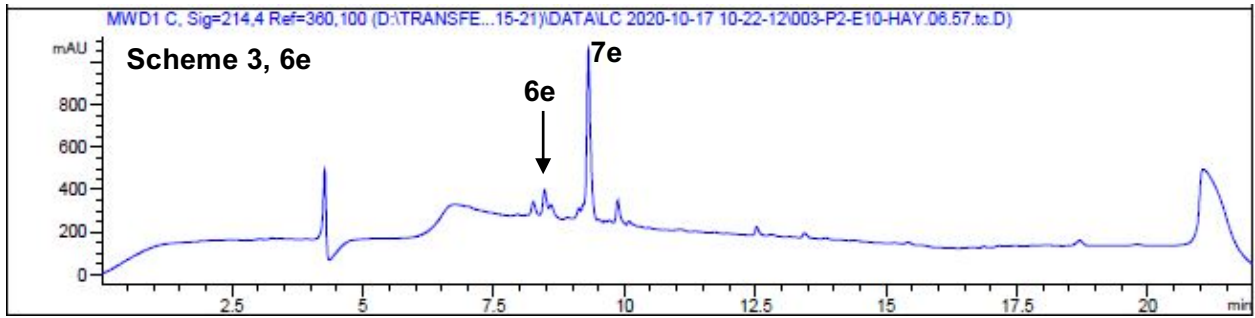
Crude reaction data from Scheme 3

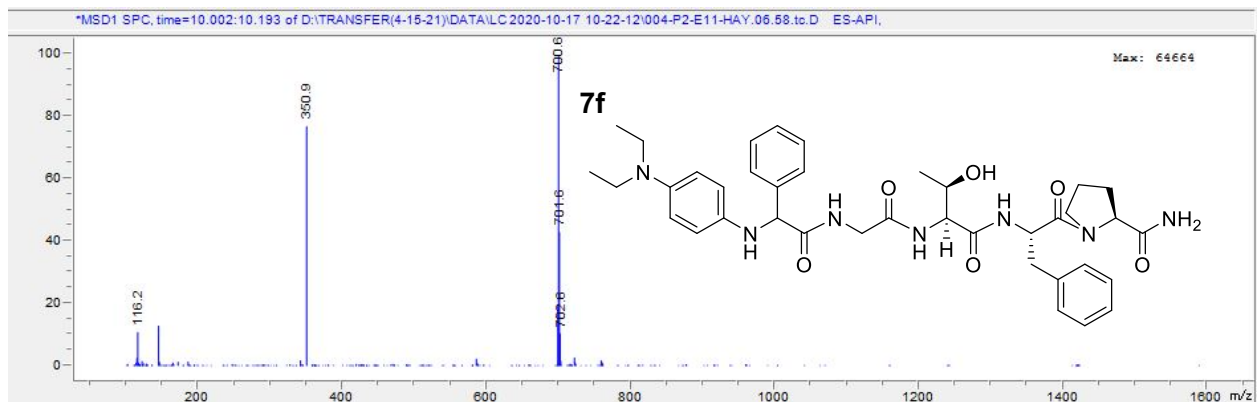
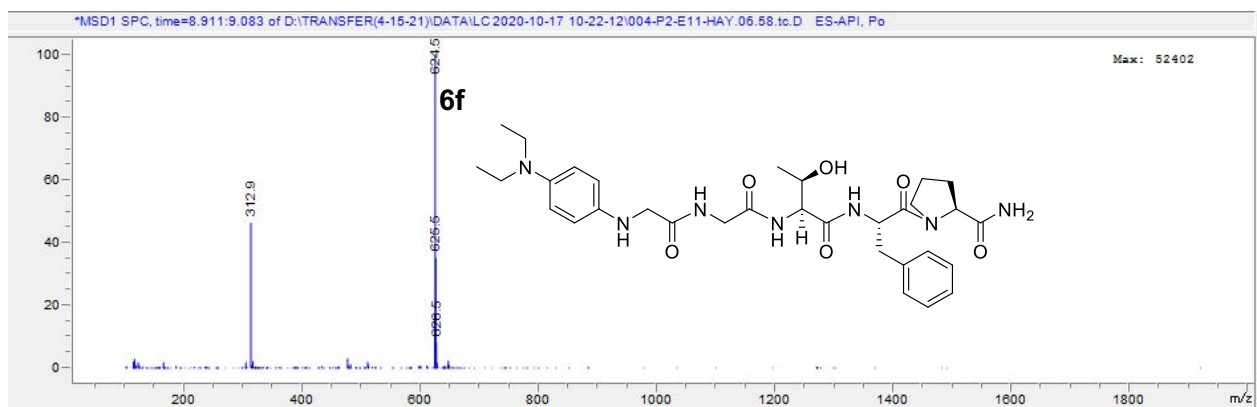
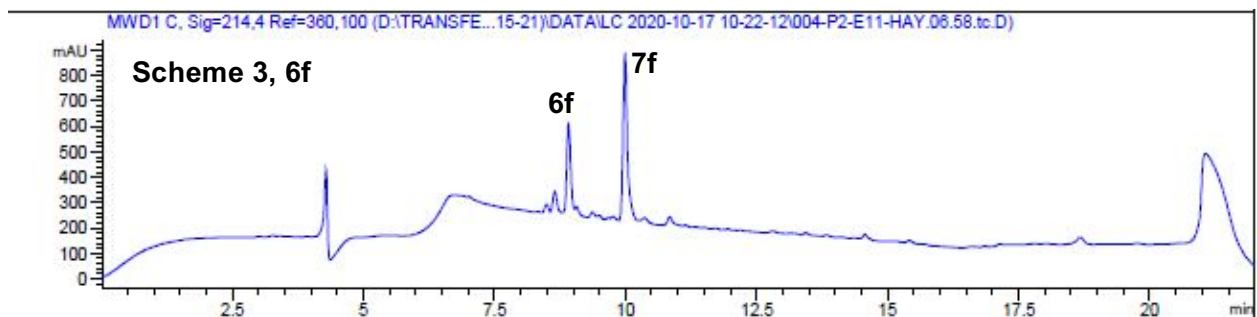


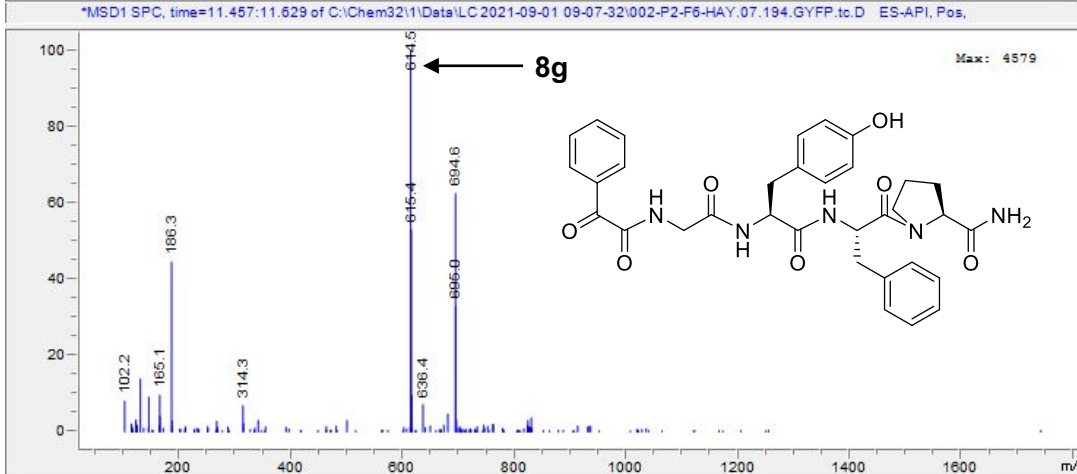
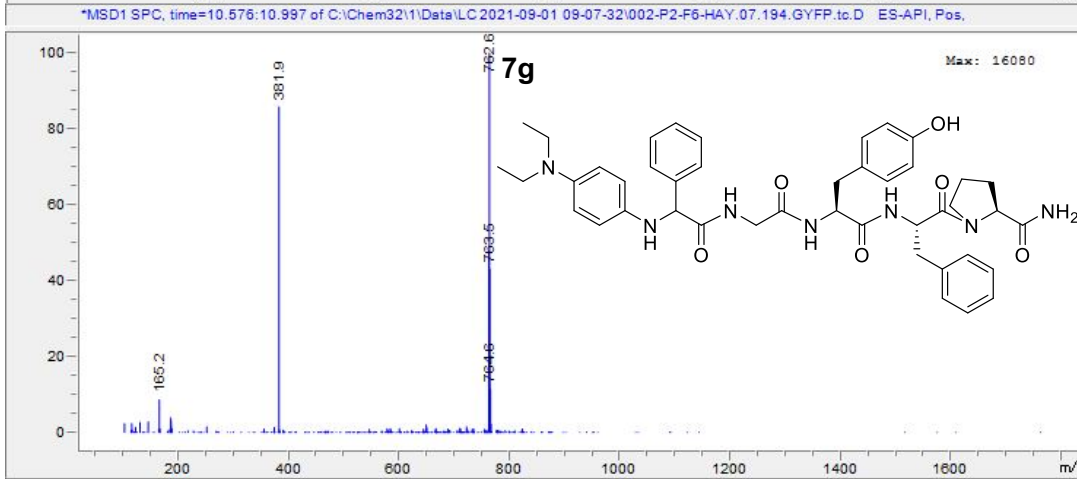
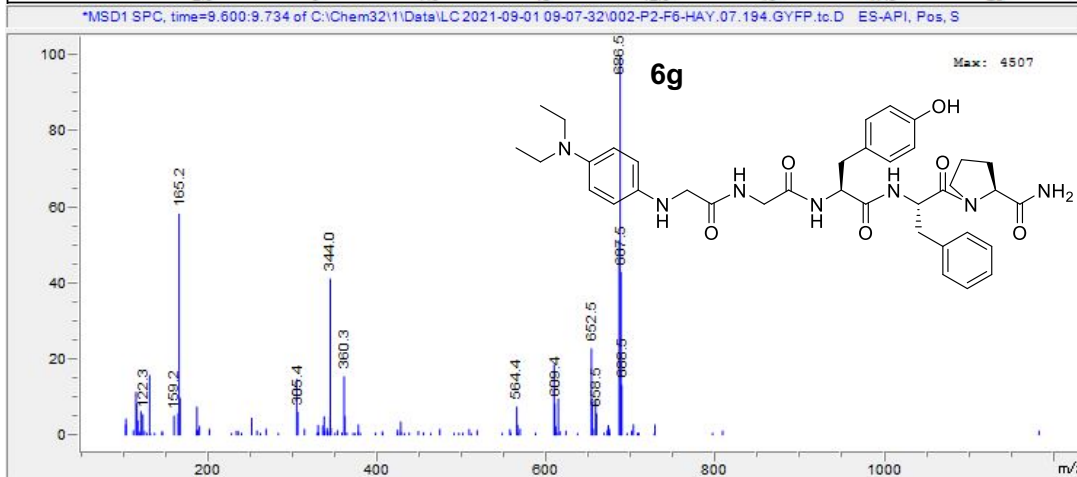
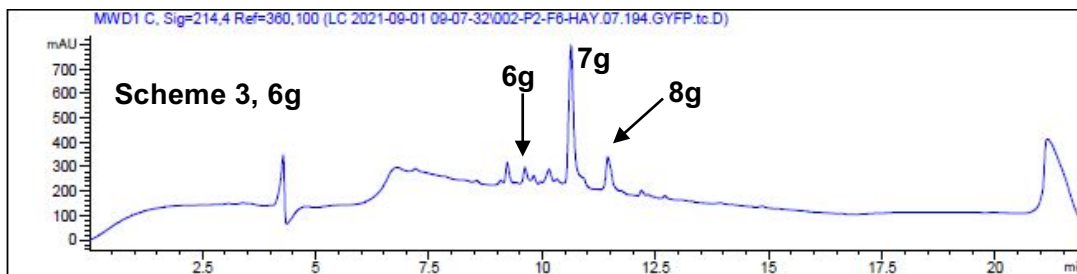


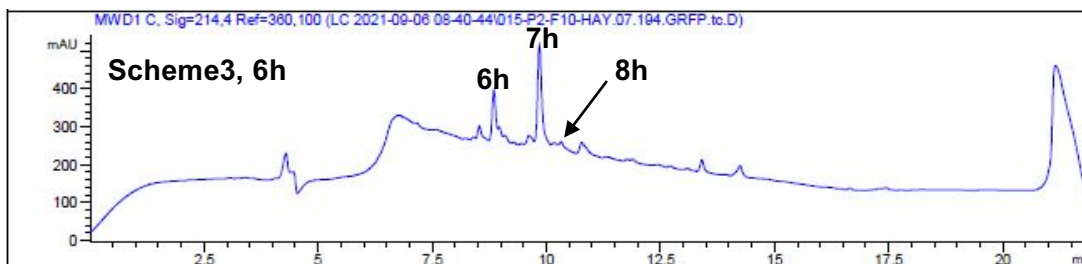




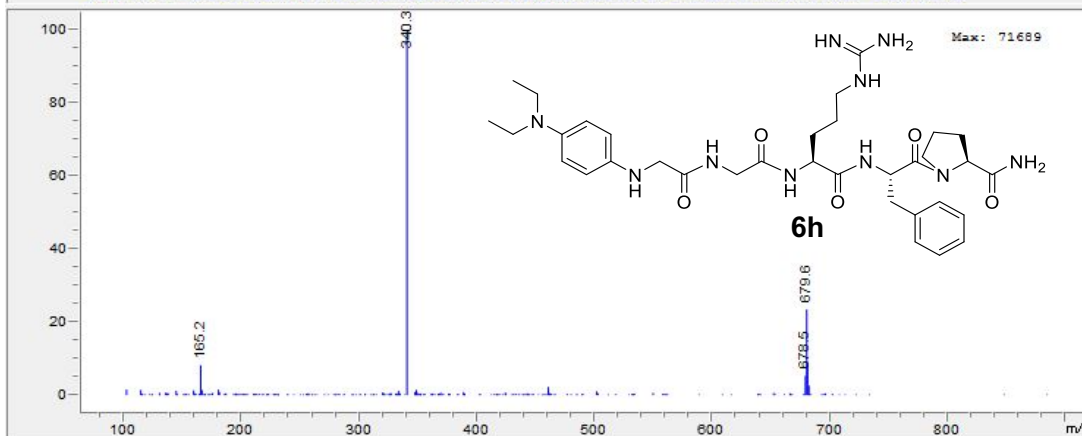




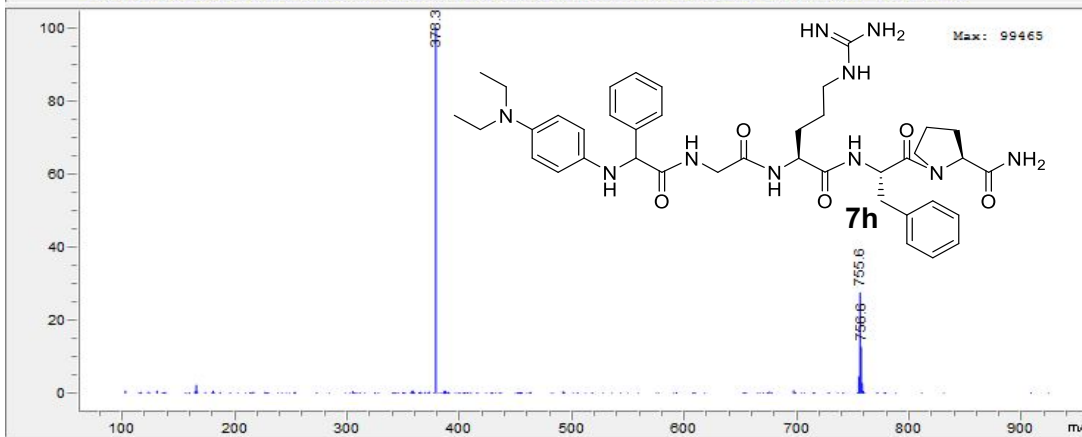




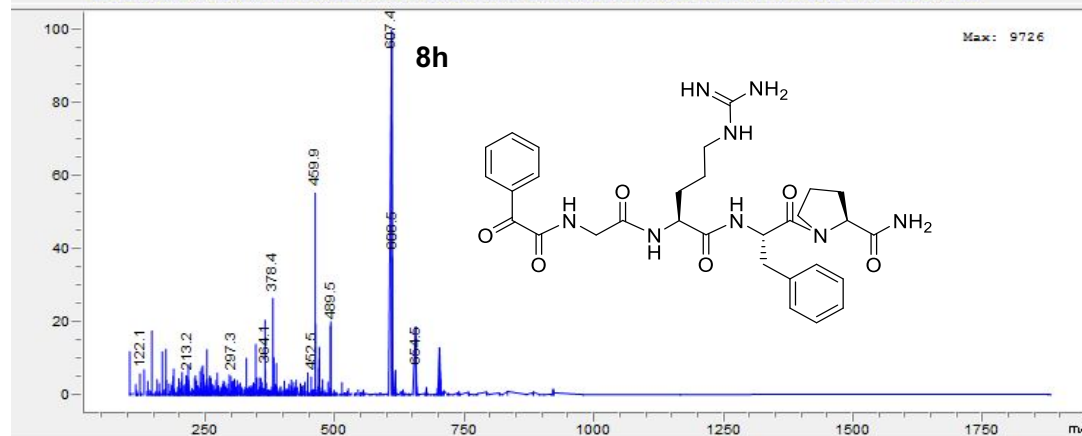
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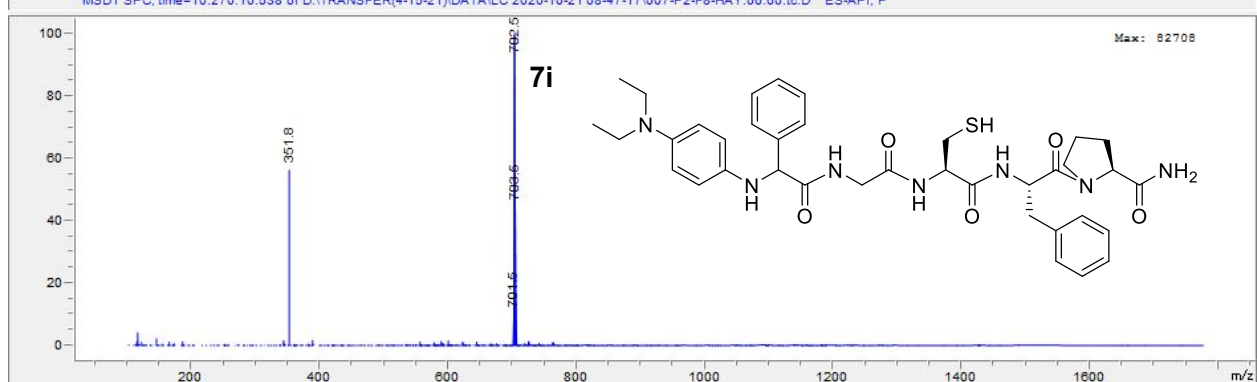
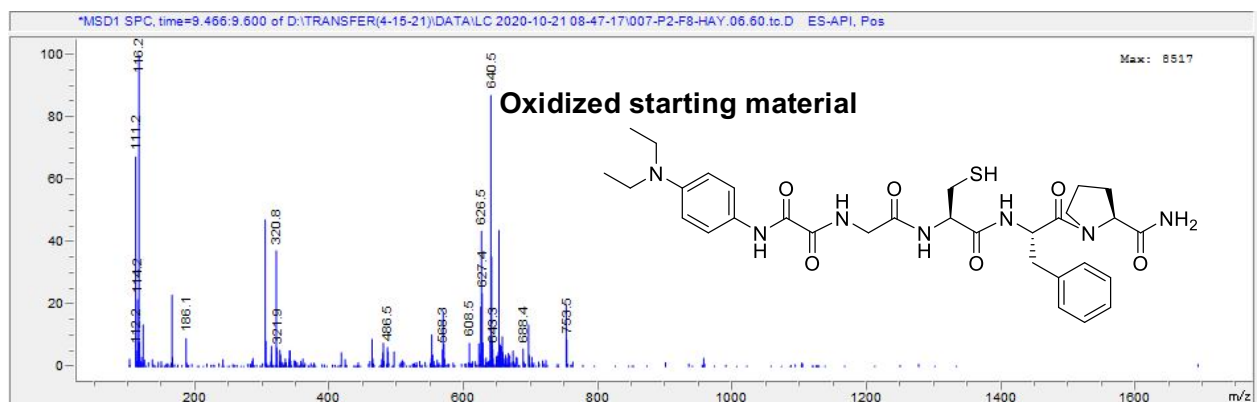
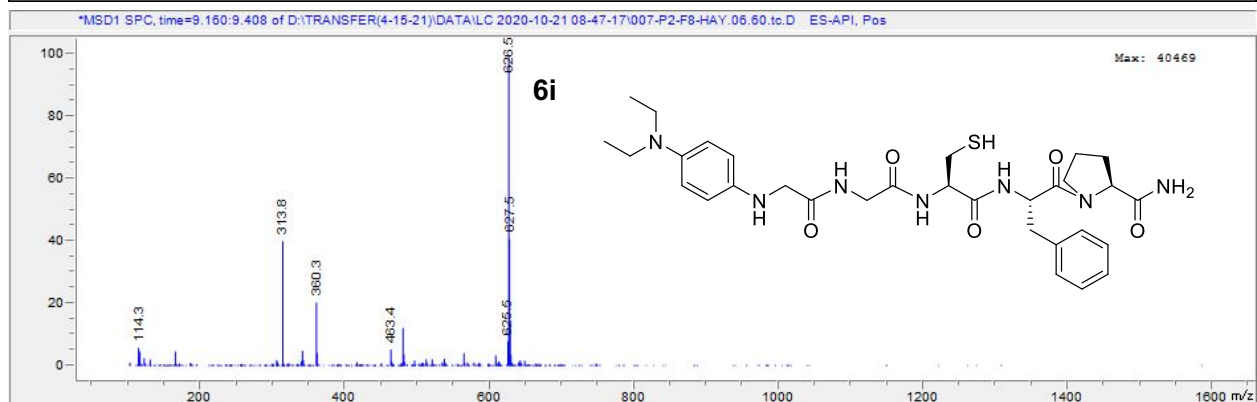
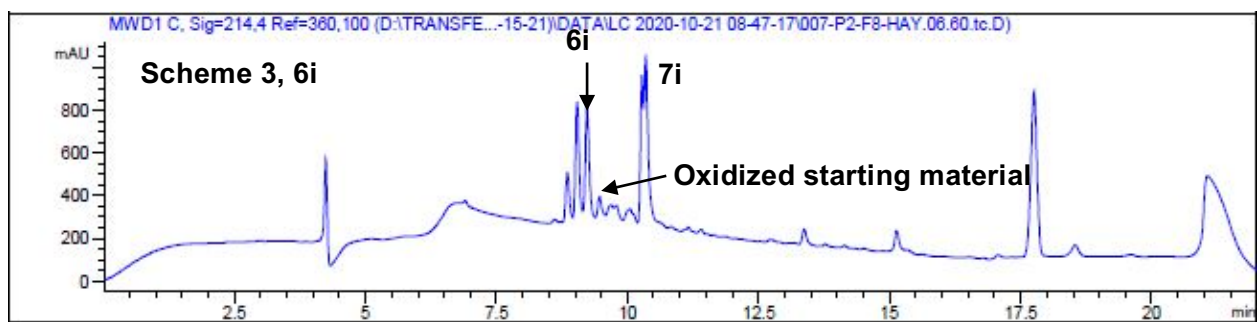


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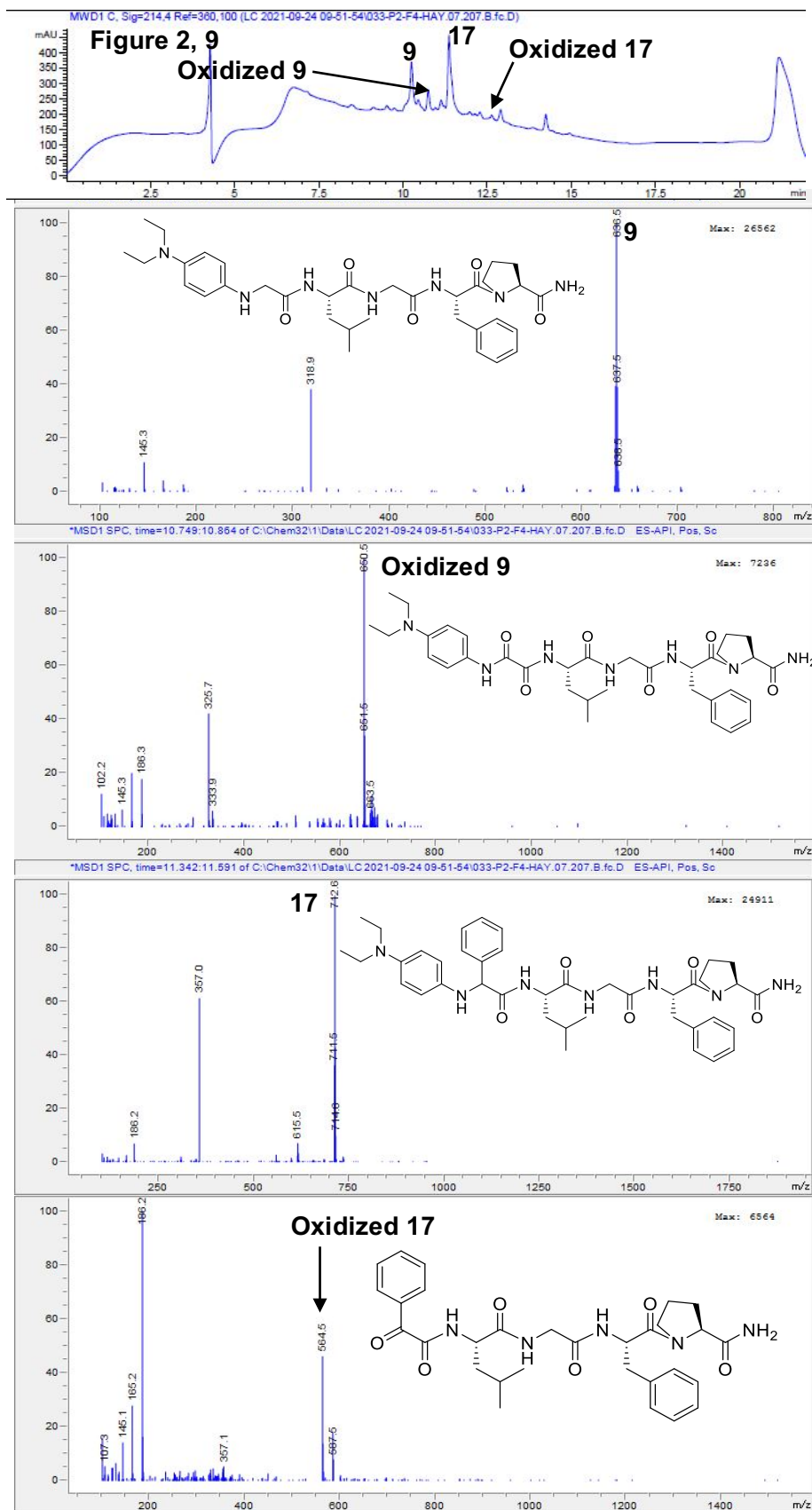


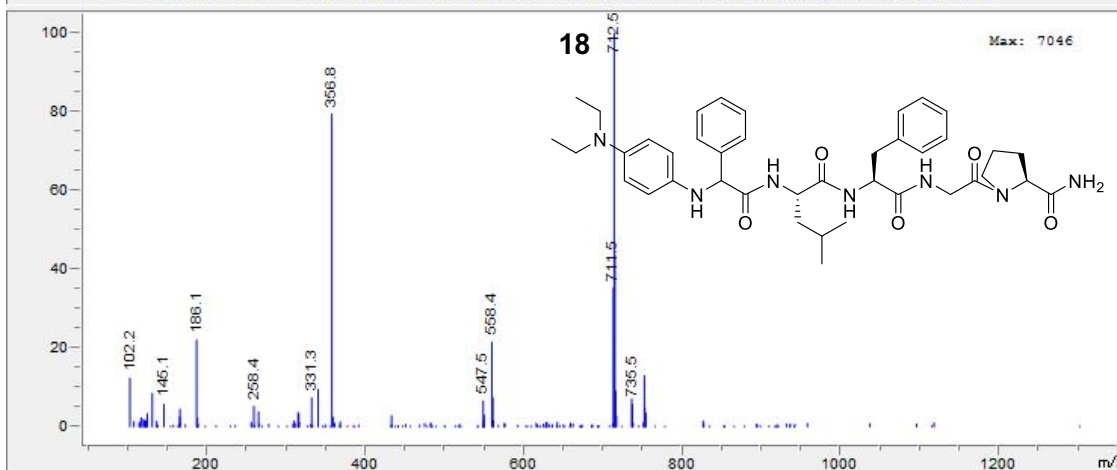
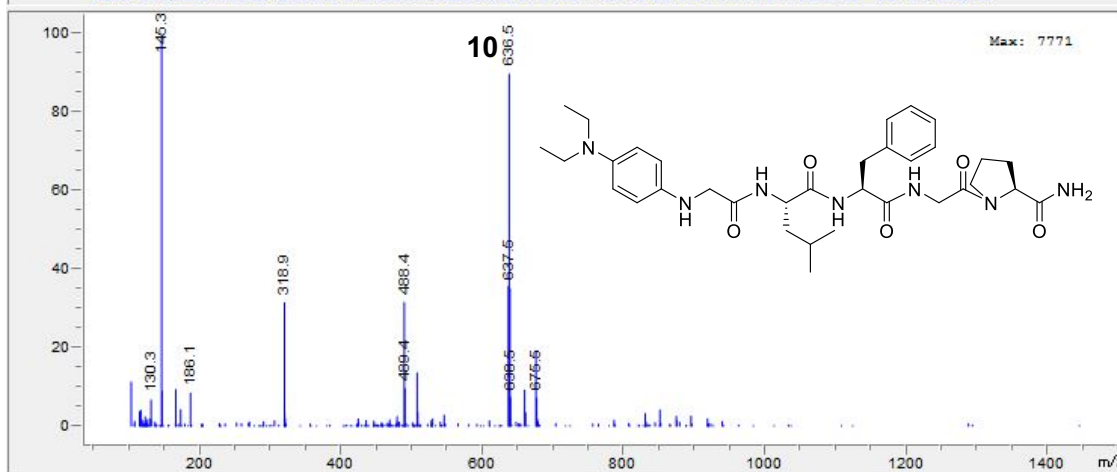
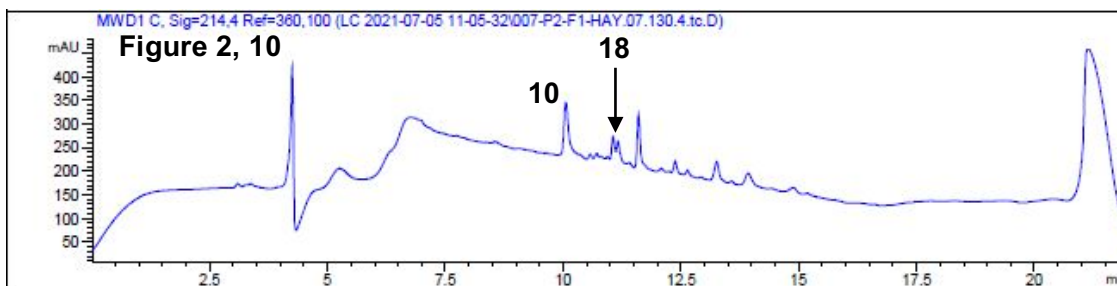
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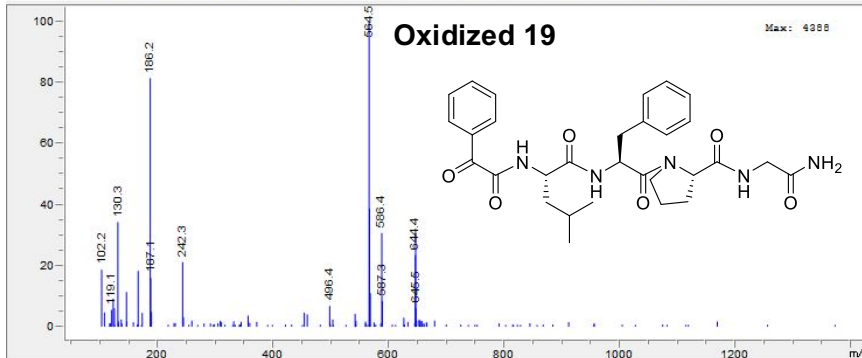
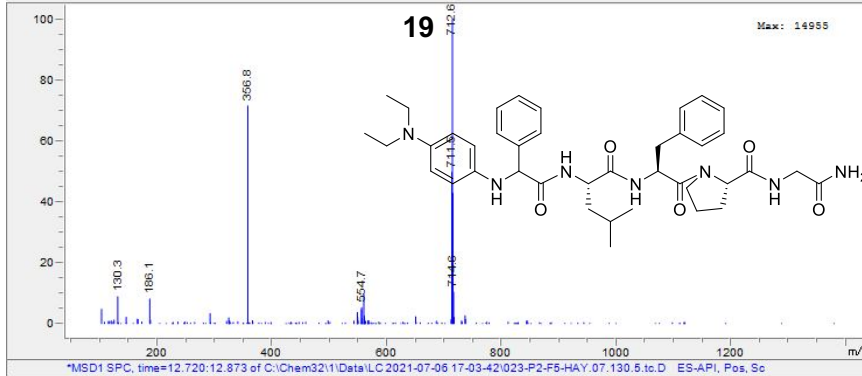
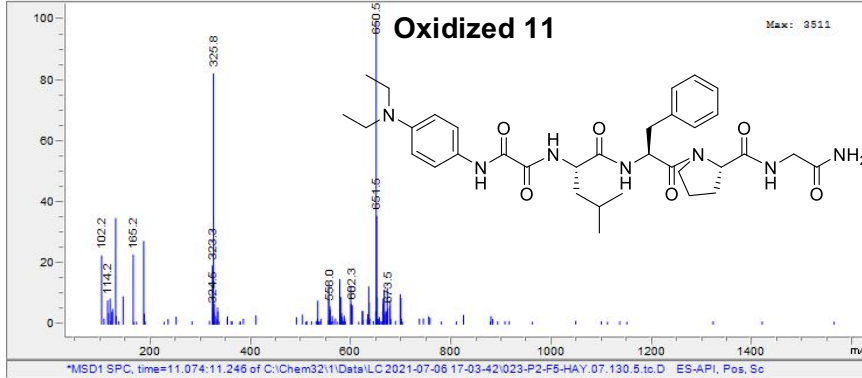
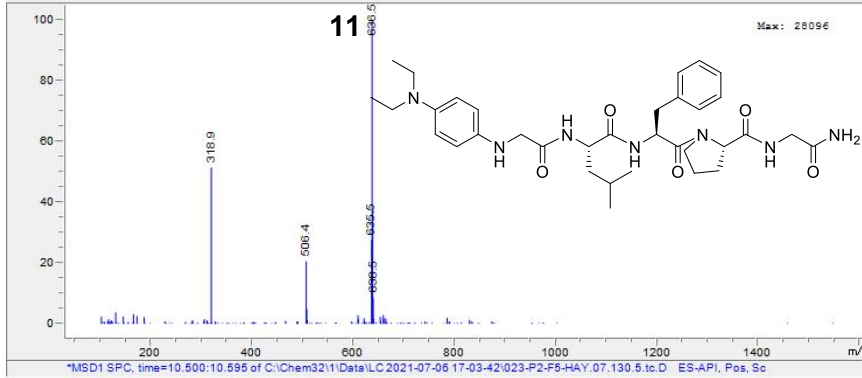
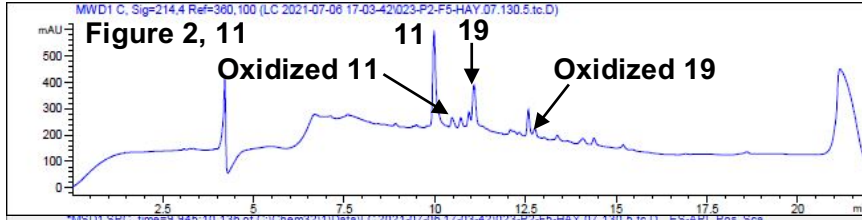


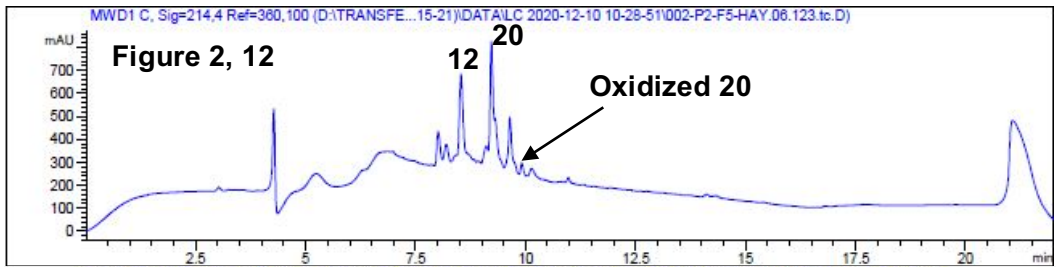


Crude reaction data from Figure 2

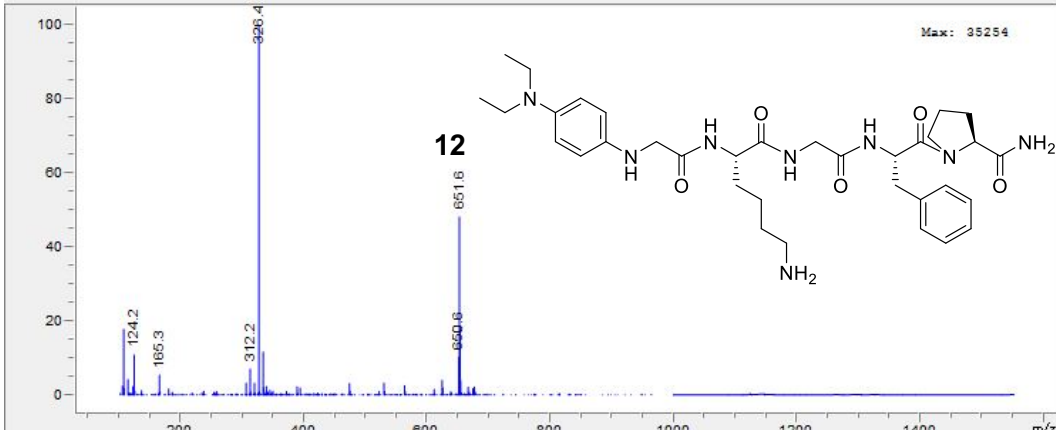




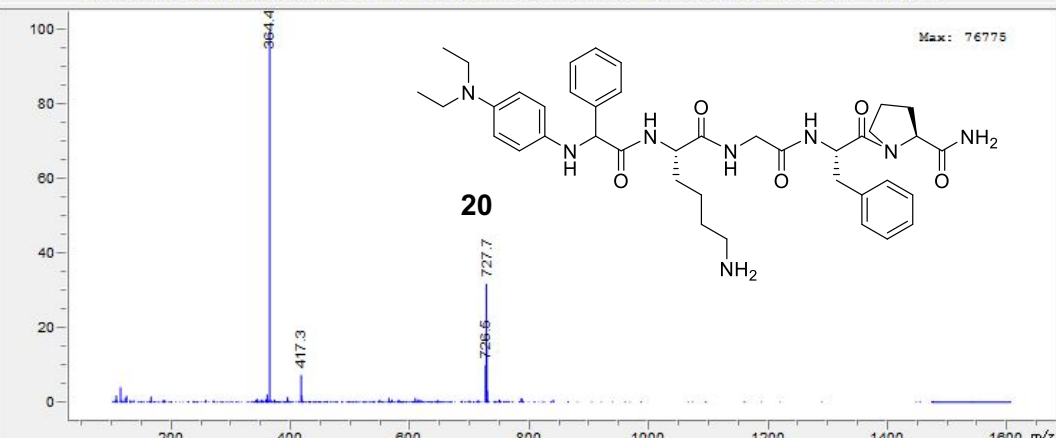




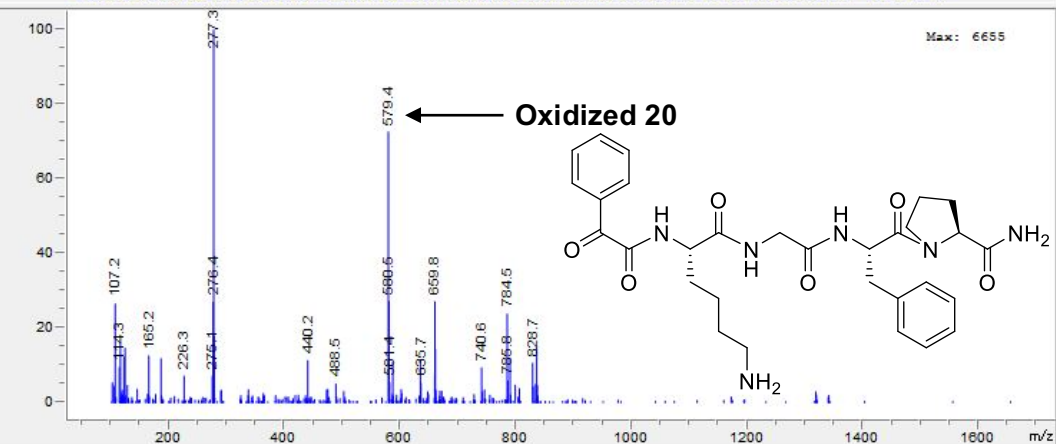
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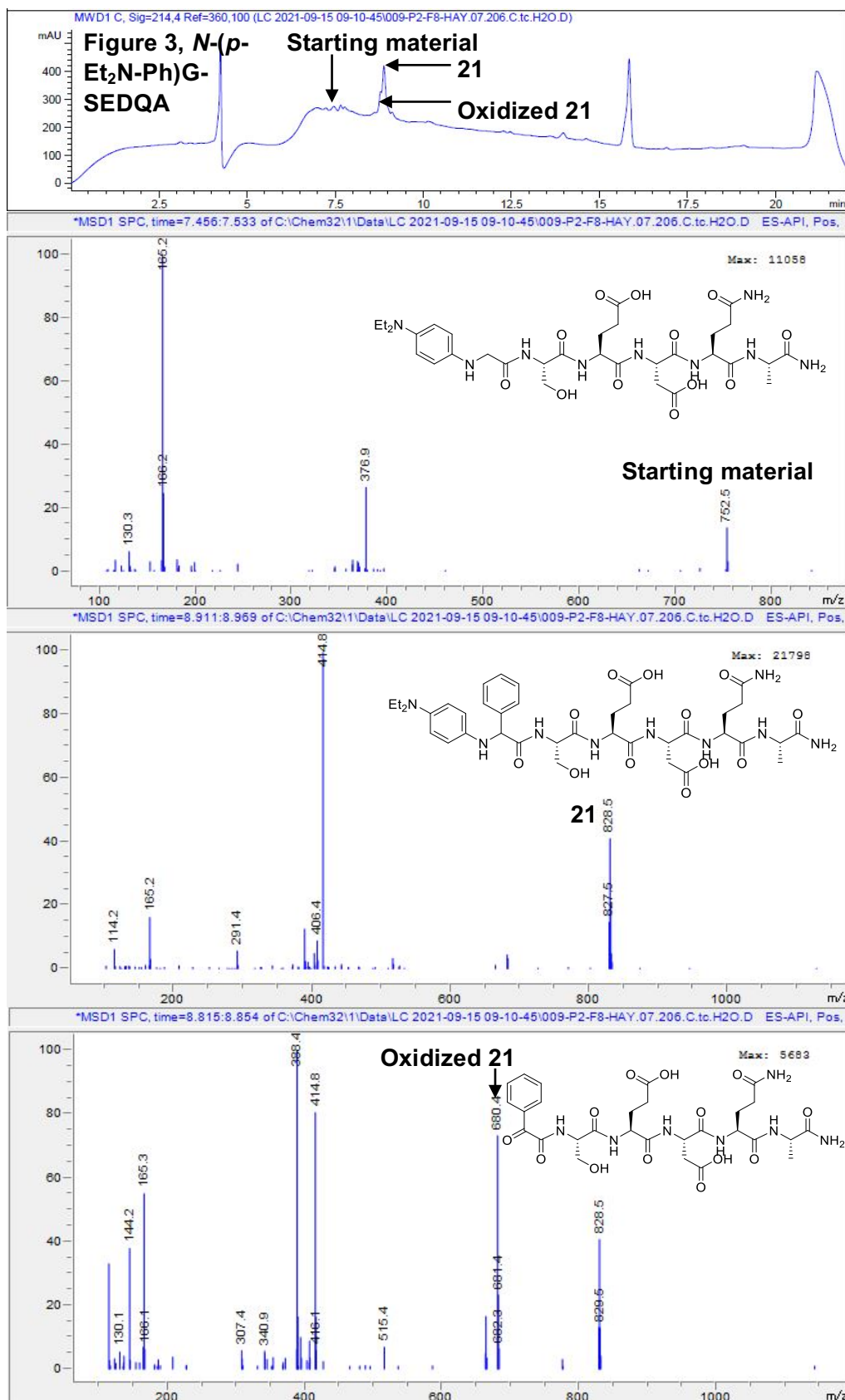
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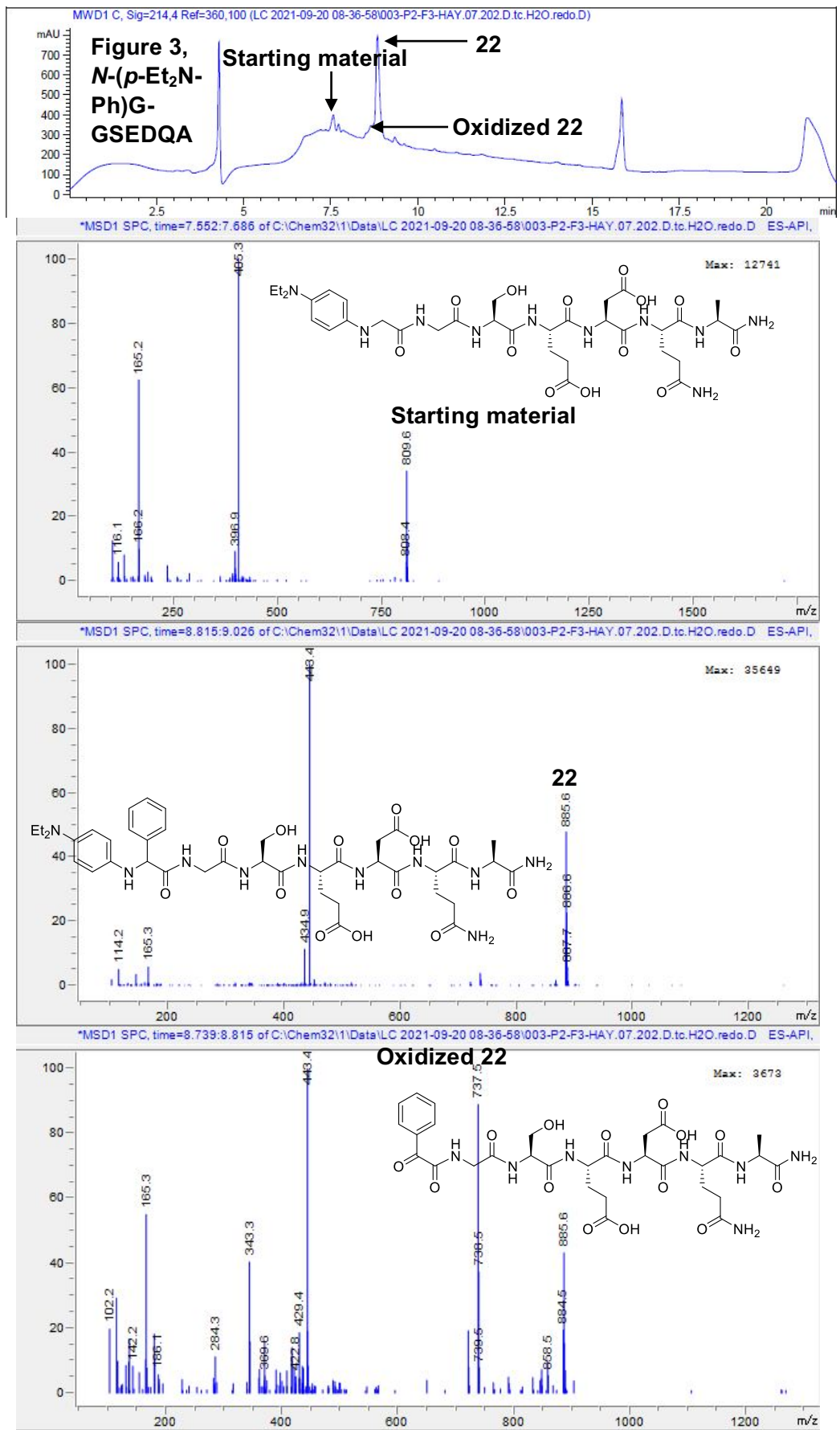


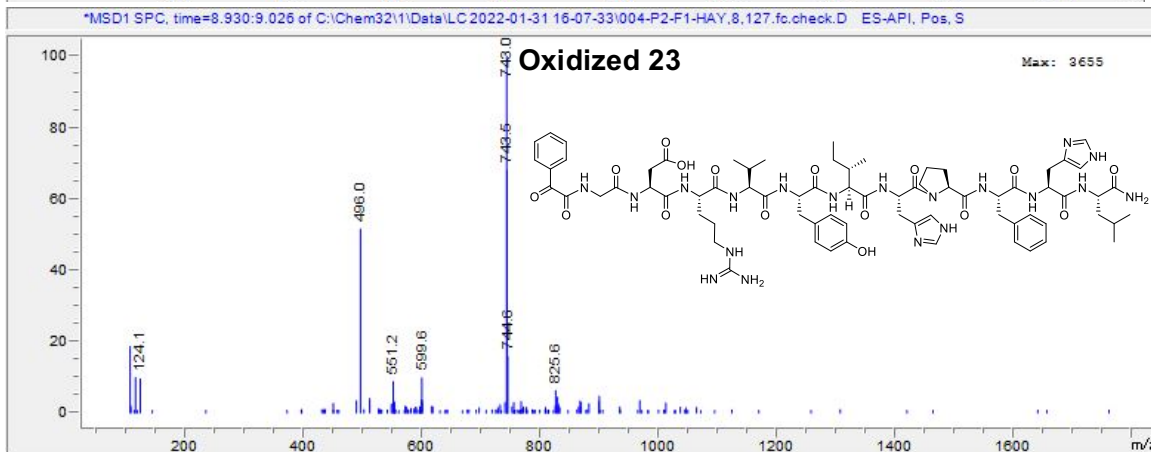
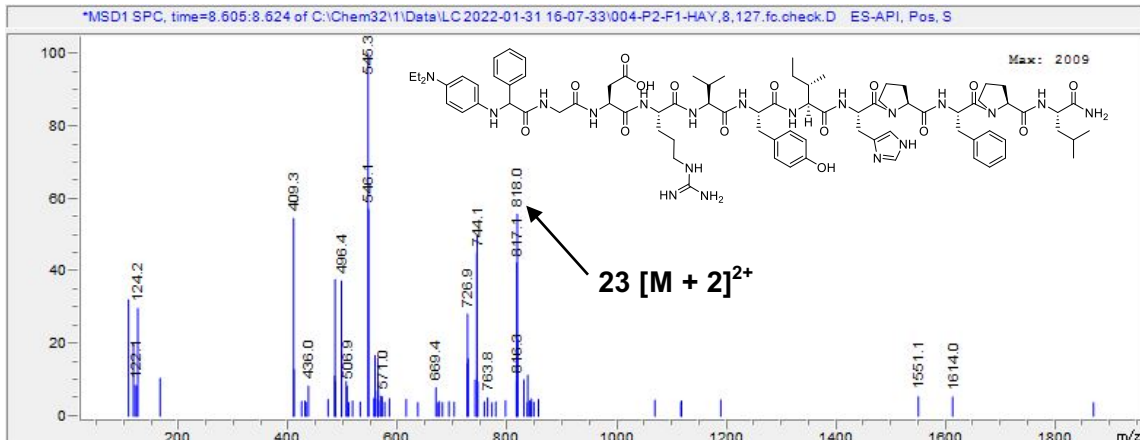
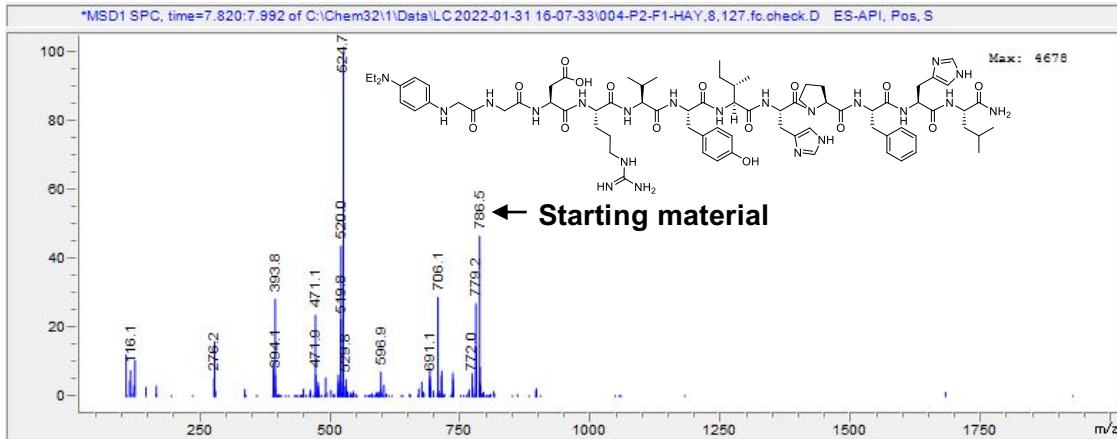
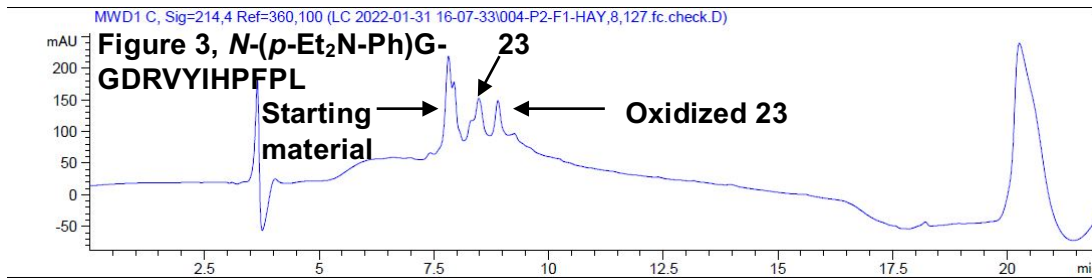
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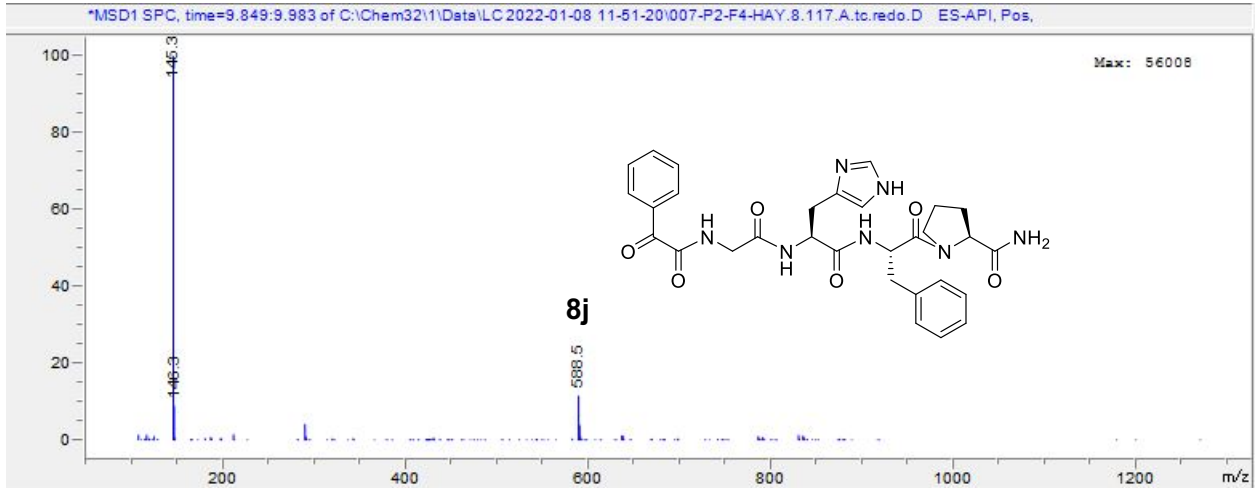
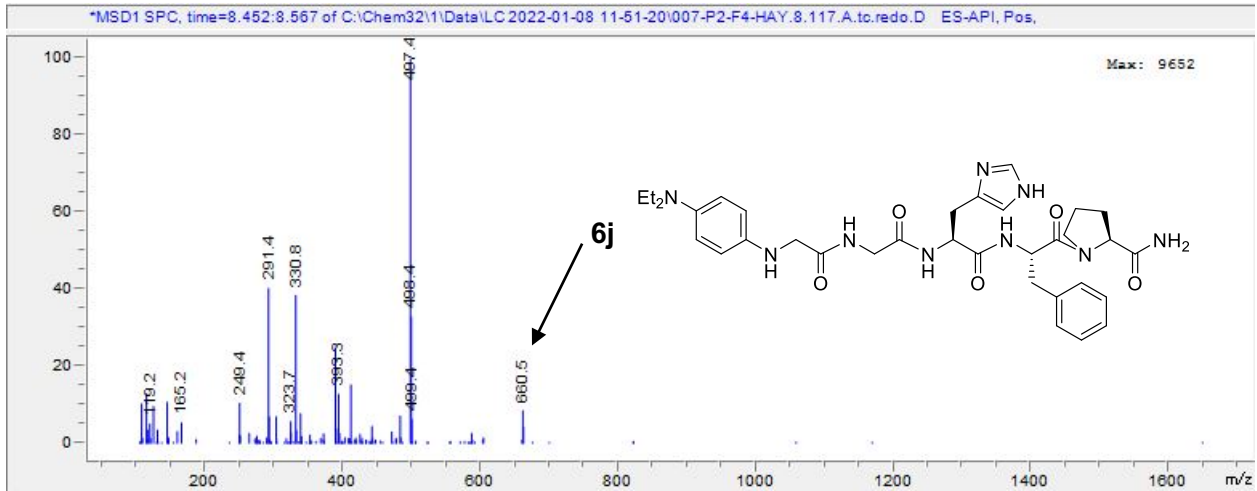
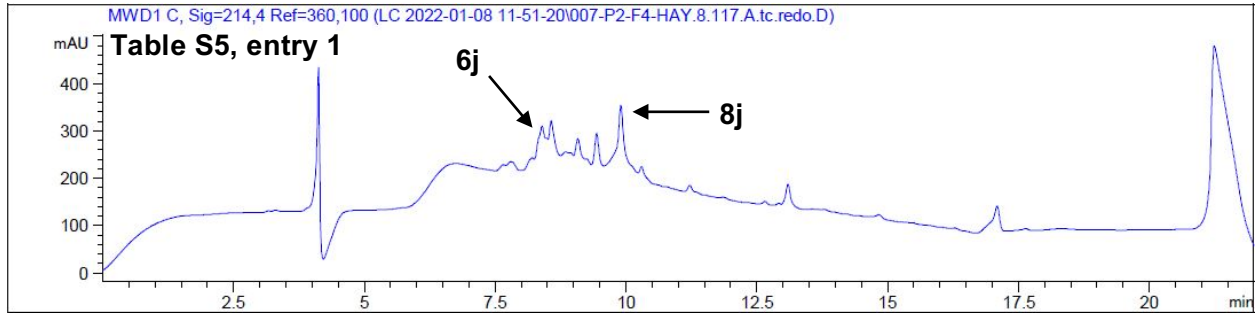
Crude reaction data from Figure 3

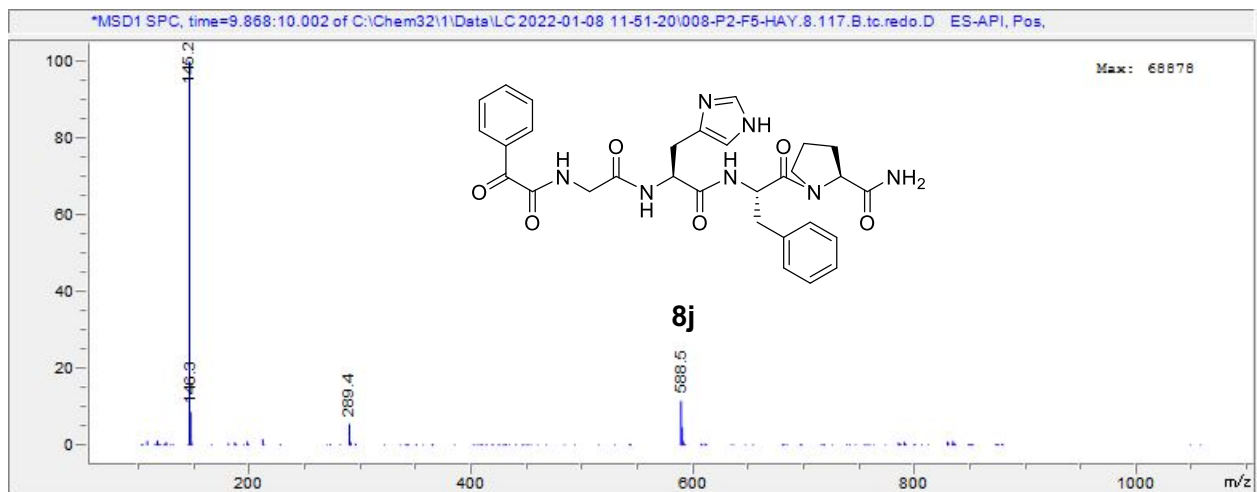
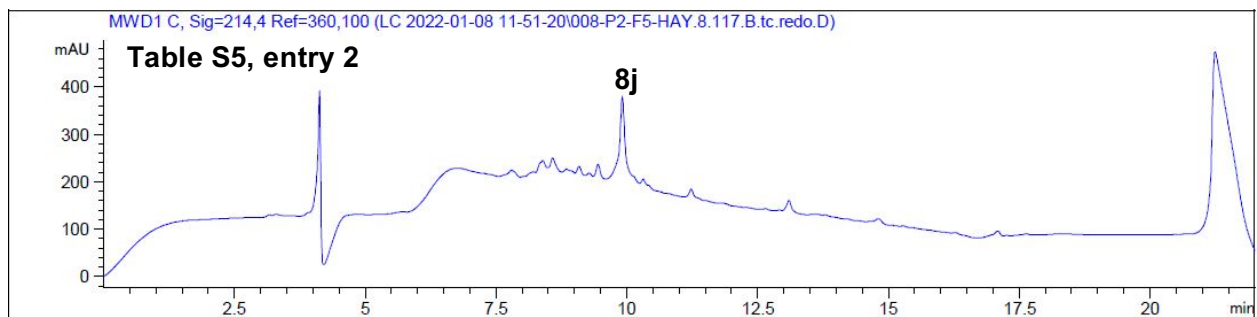






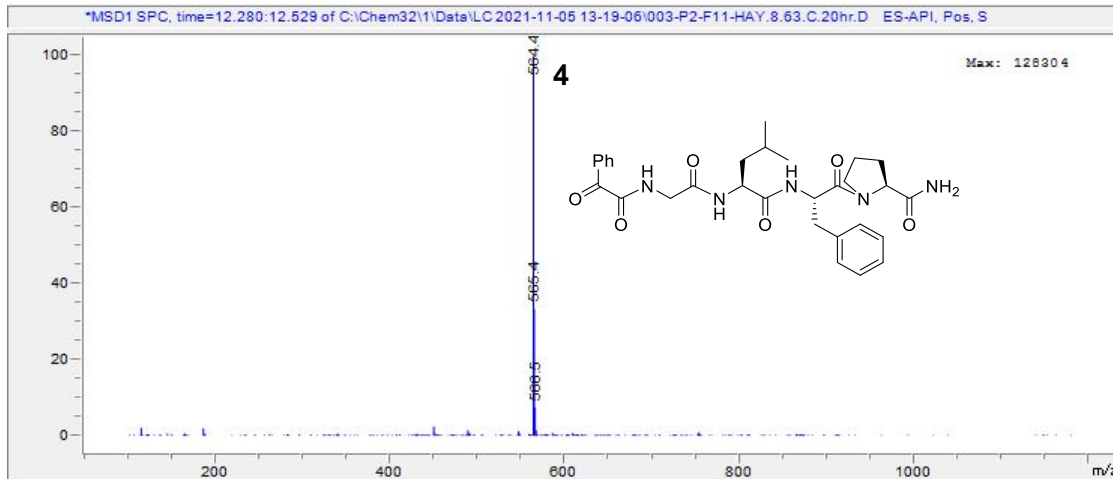
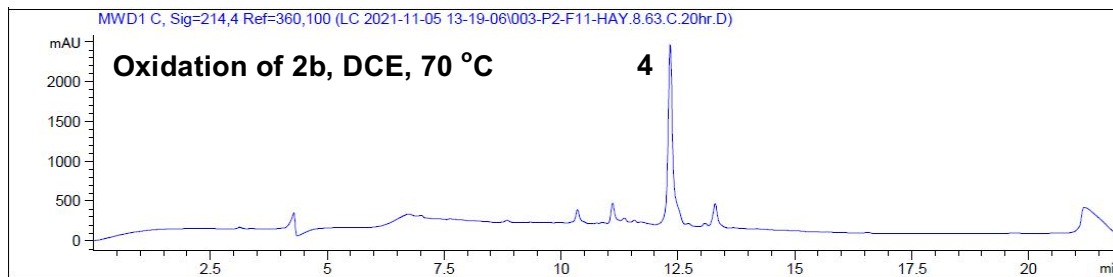
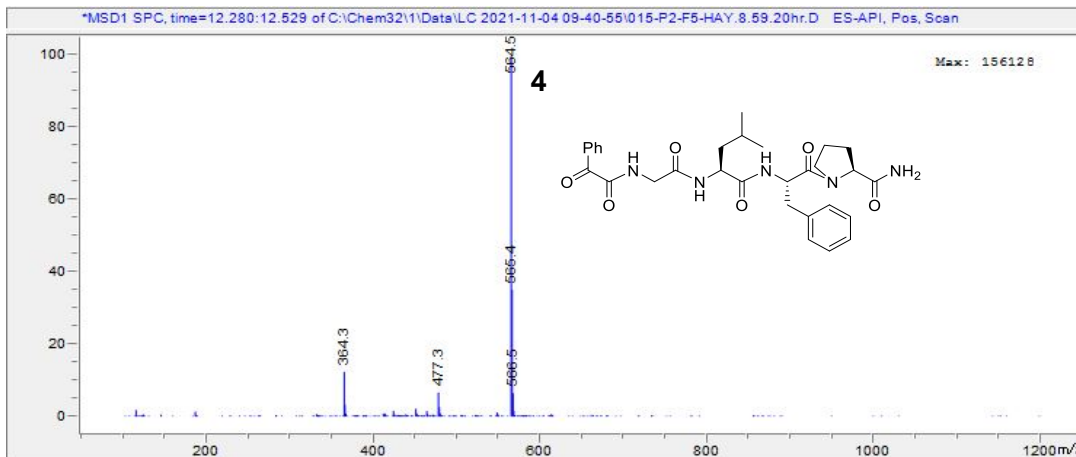
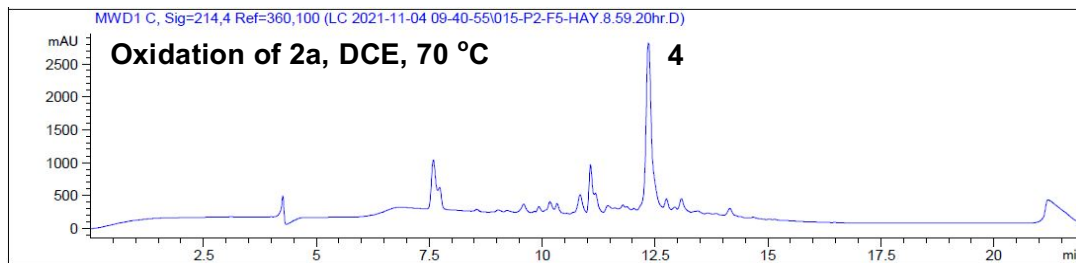
Crude reaction data from Table S5

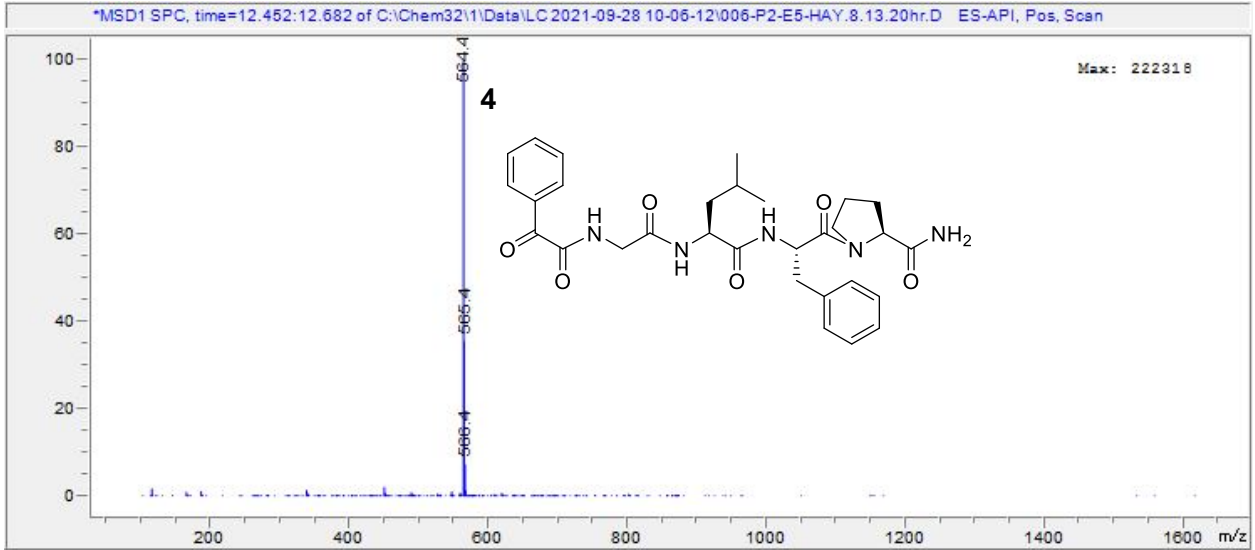
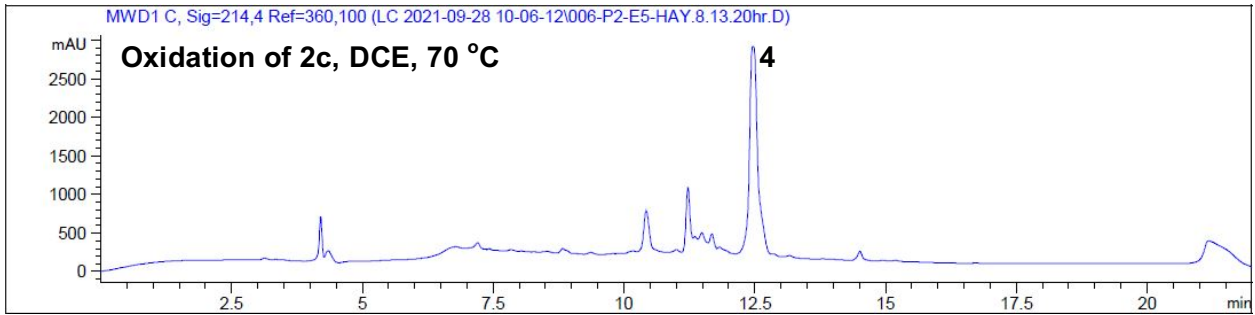




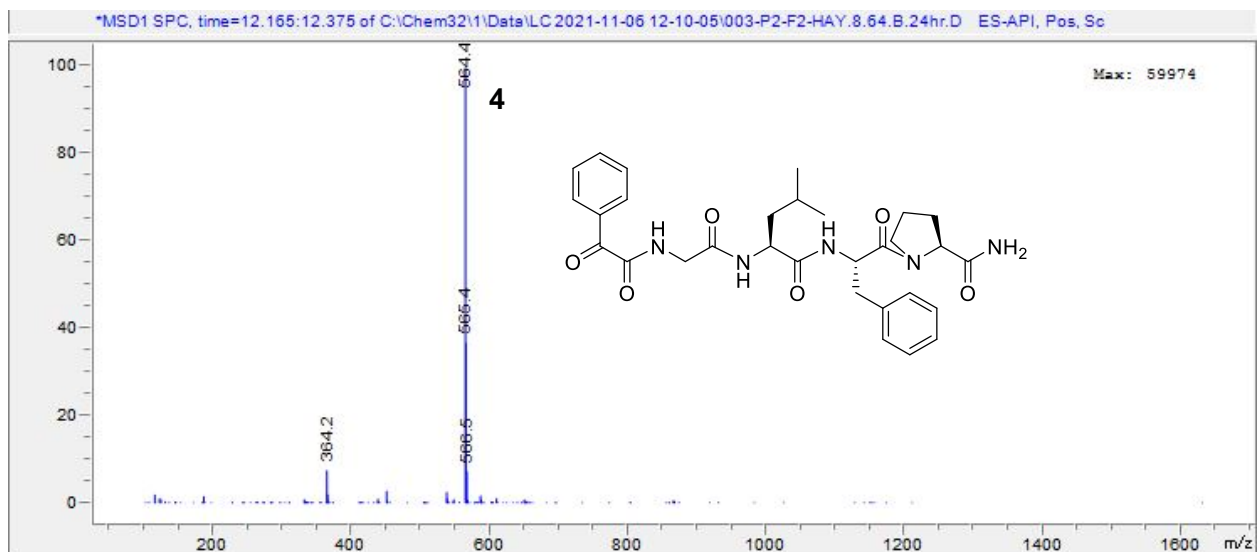
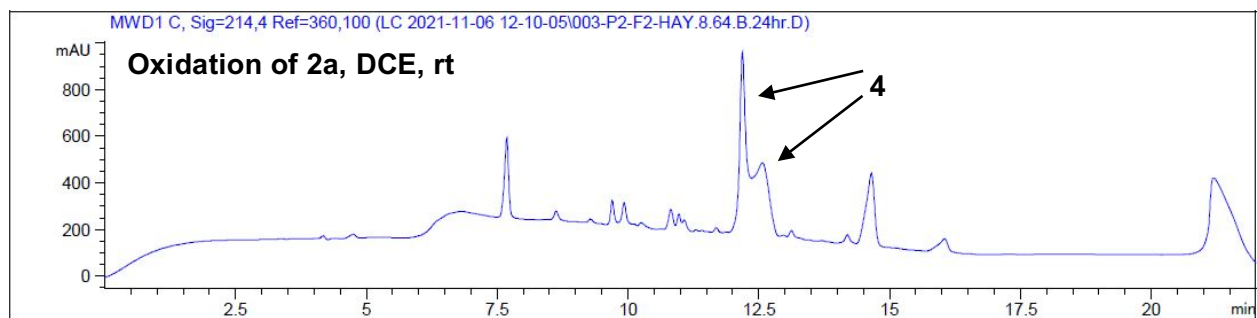
Crude reaction data from Table S6

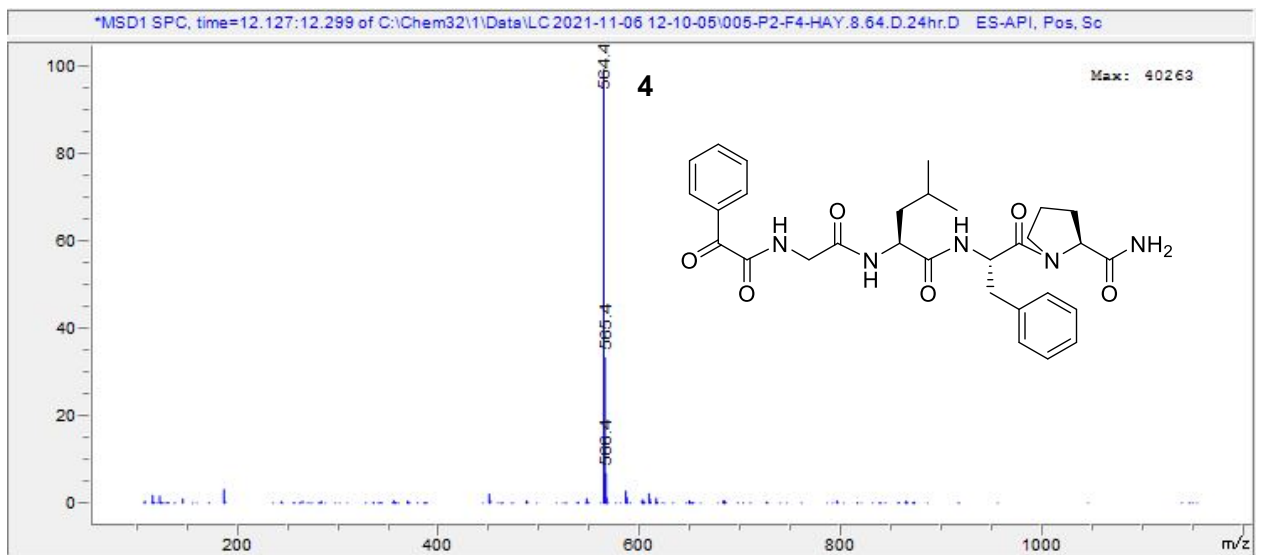
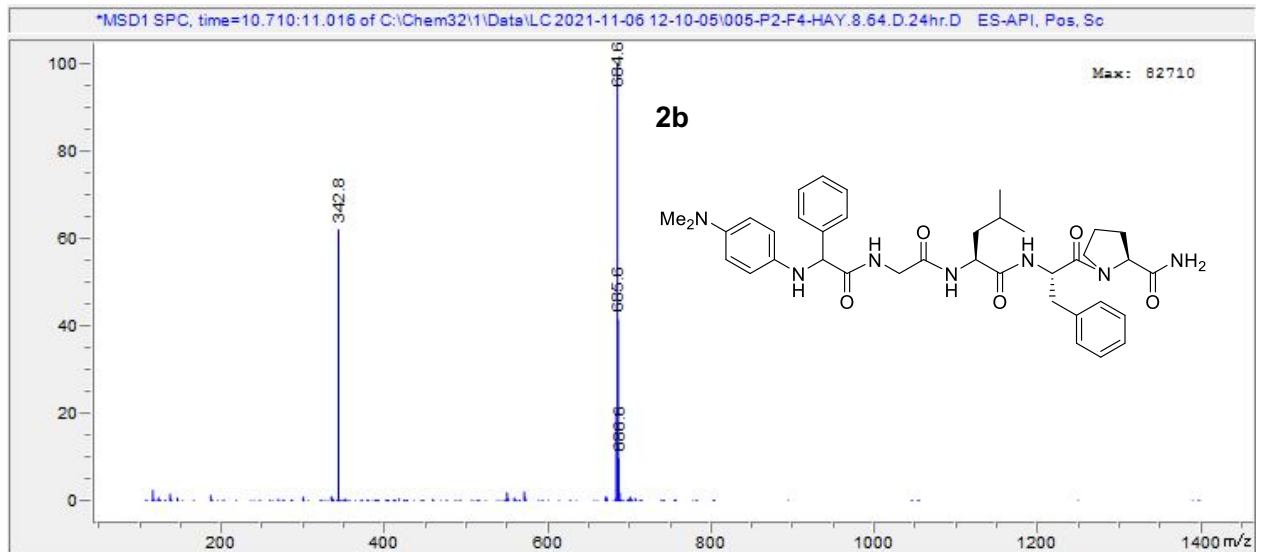
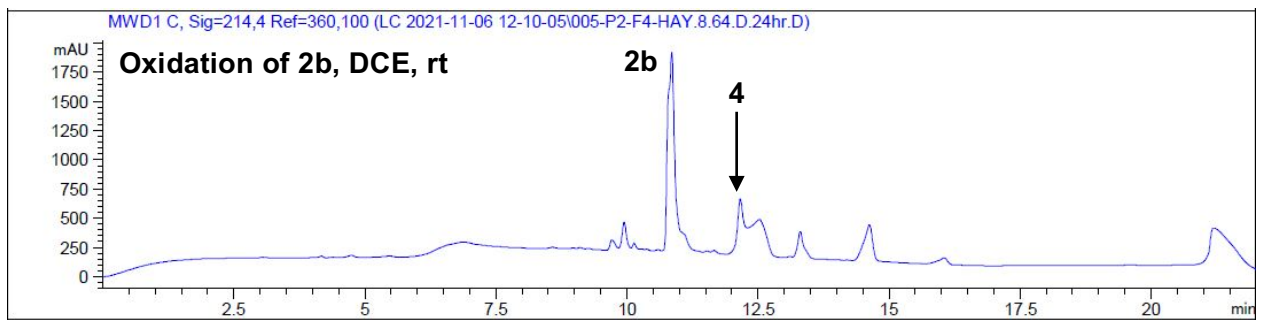
DCE, 70 °C

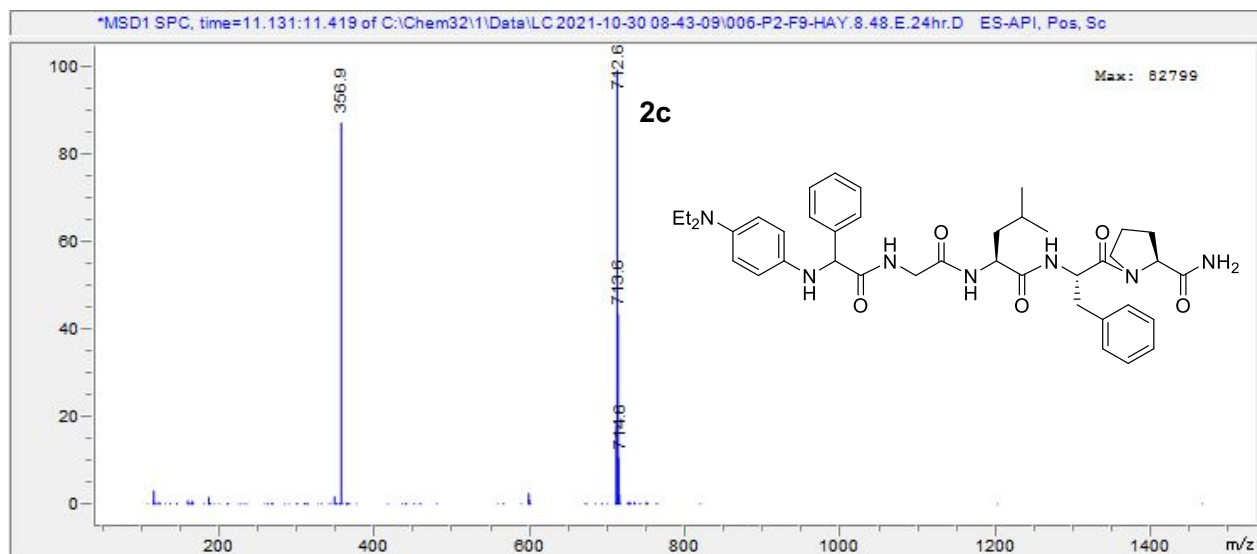
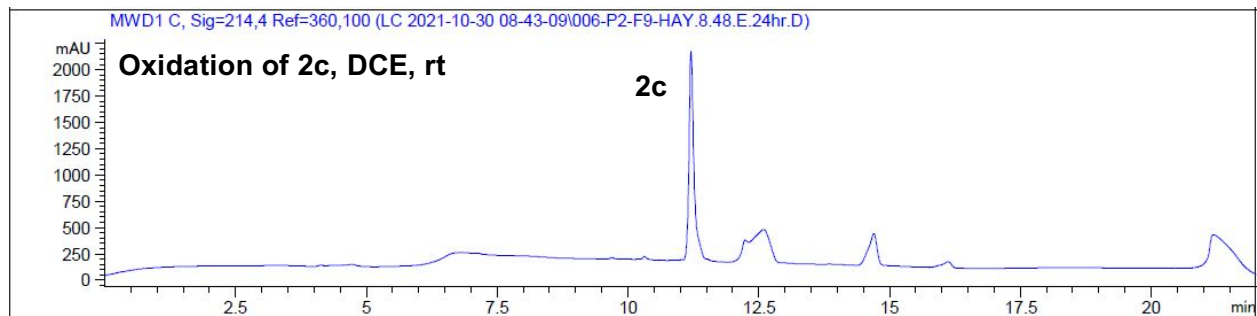




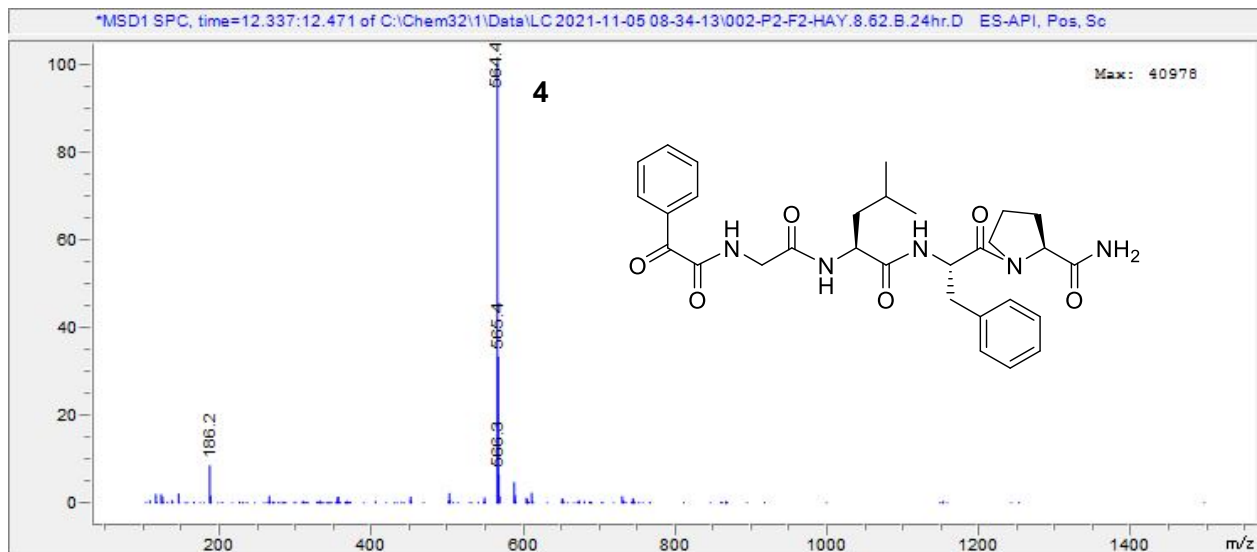
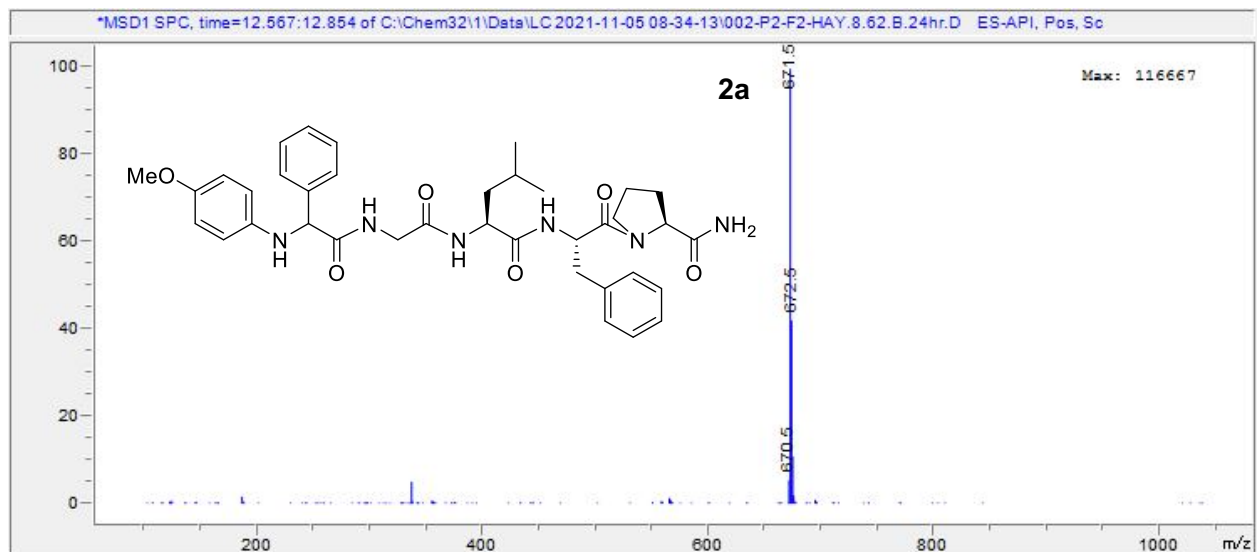
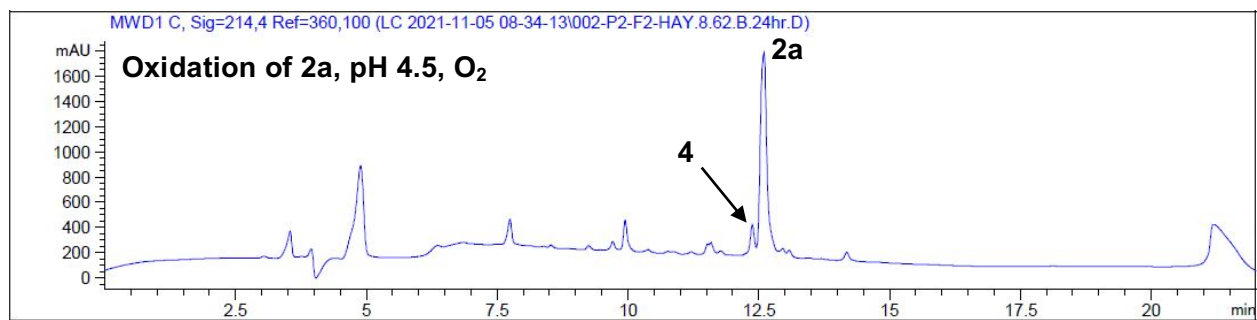
DCE, room temperature

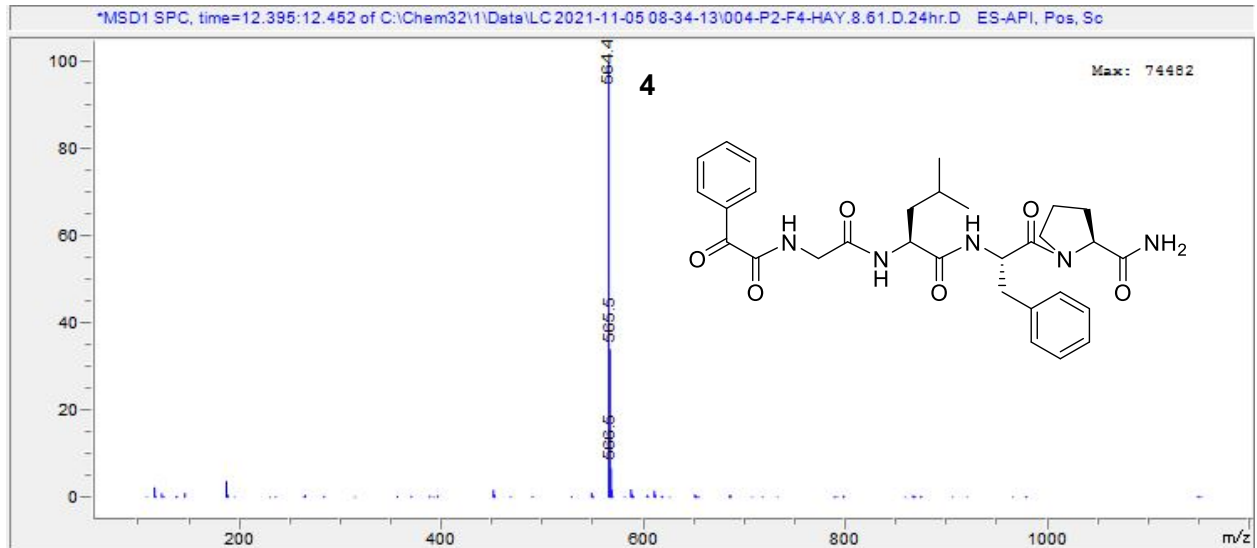
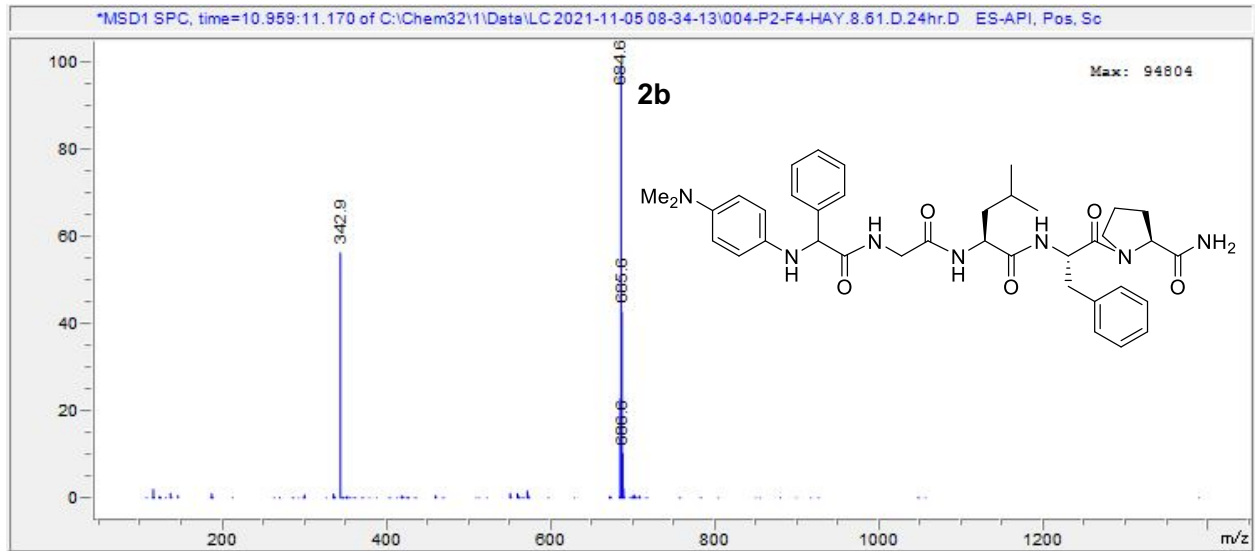
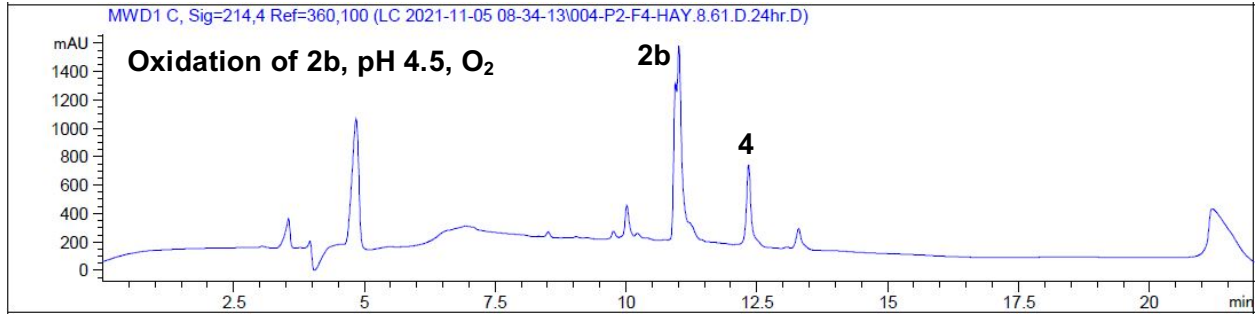


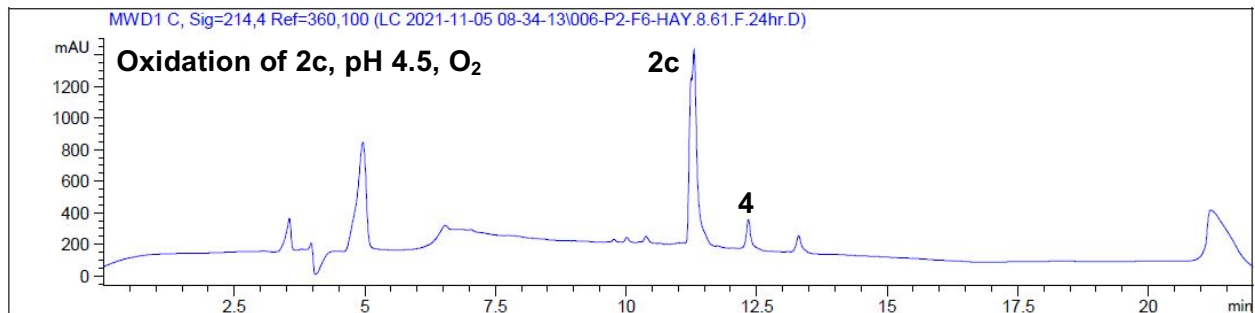




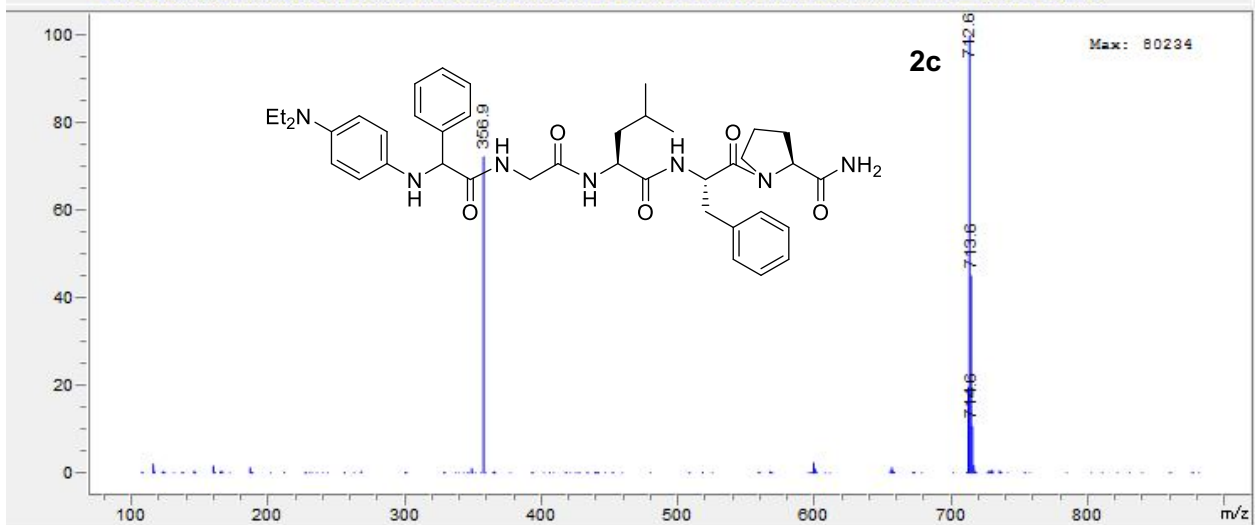
pH 4.5, O₂



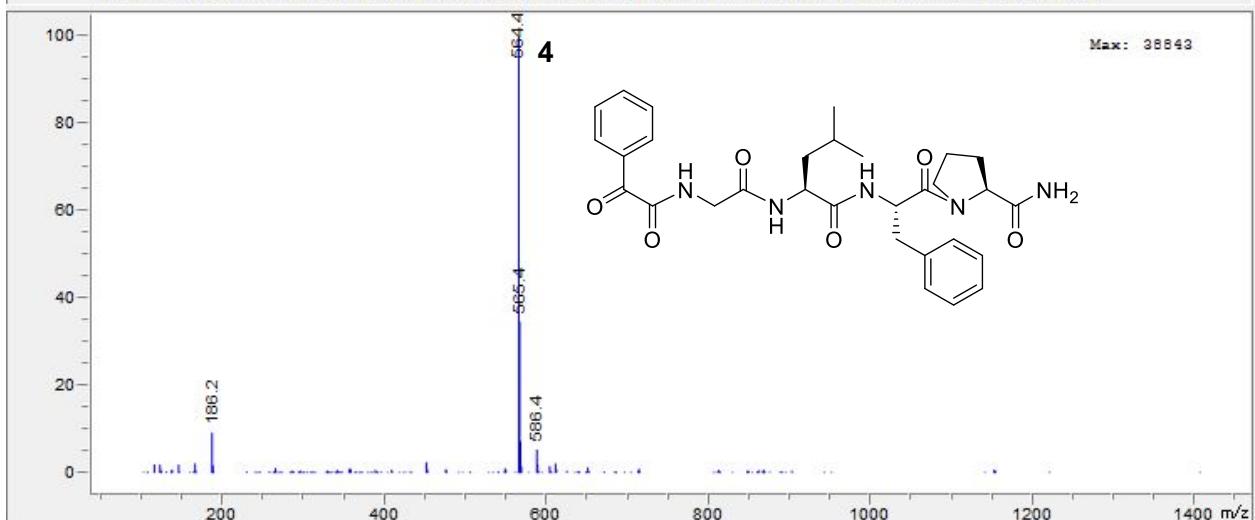




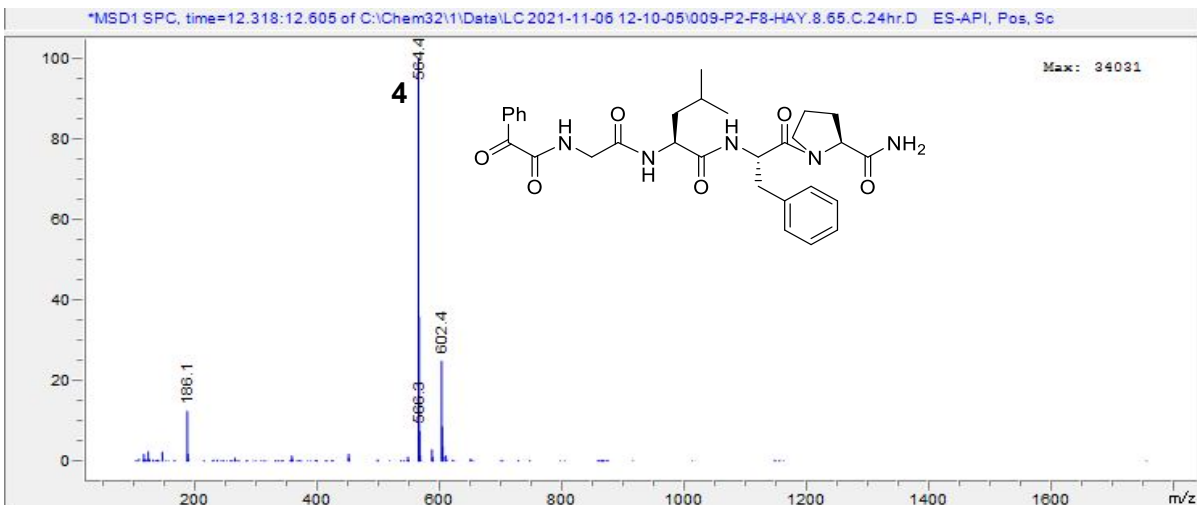
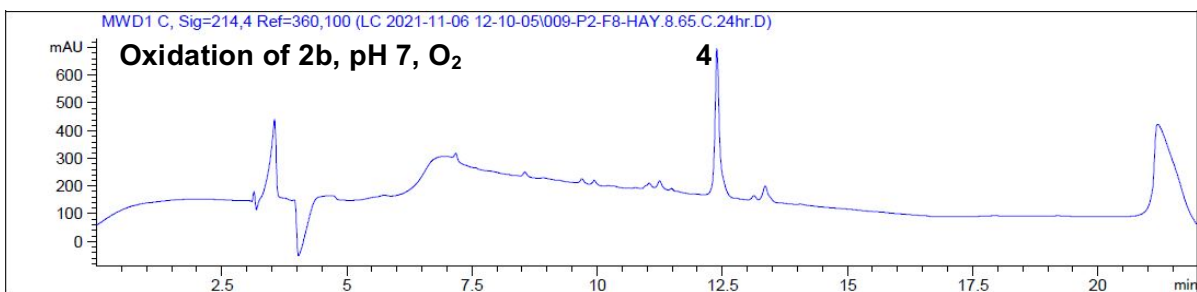
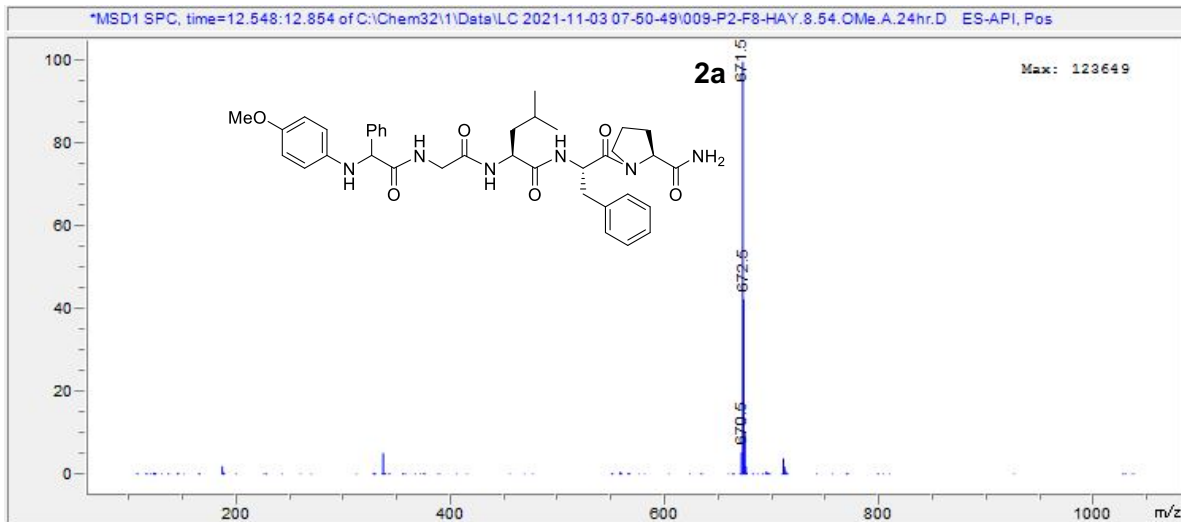
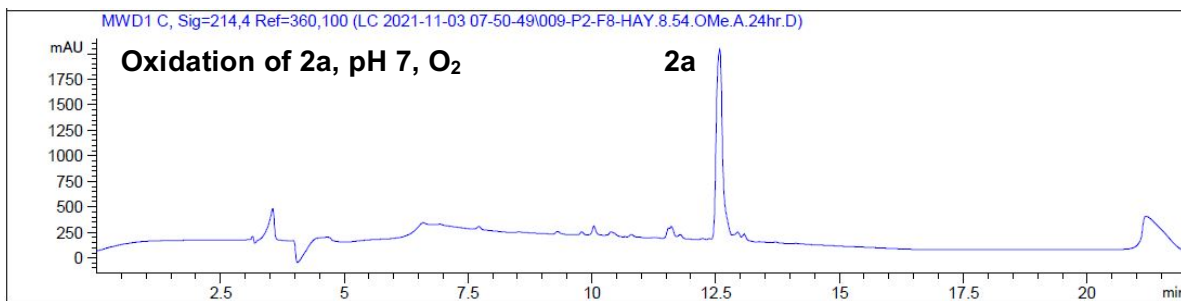
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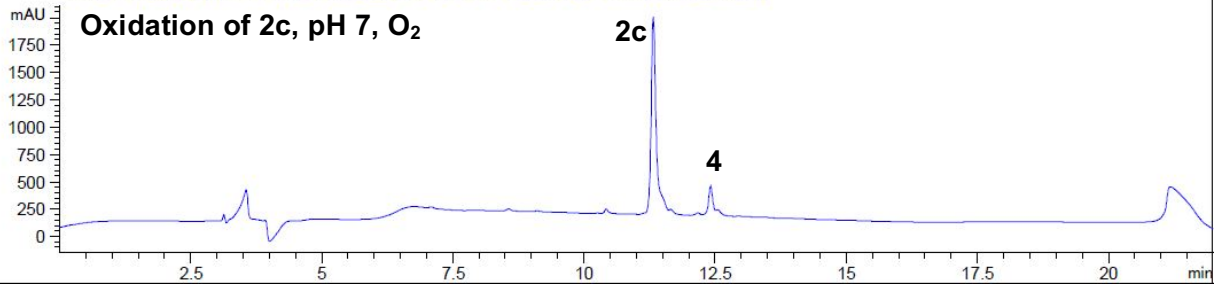
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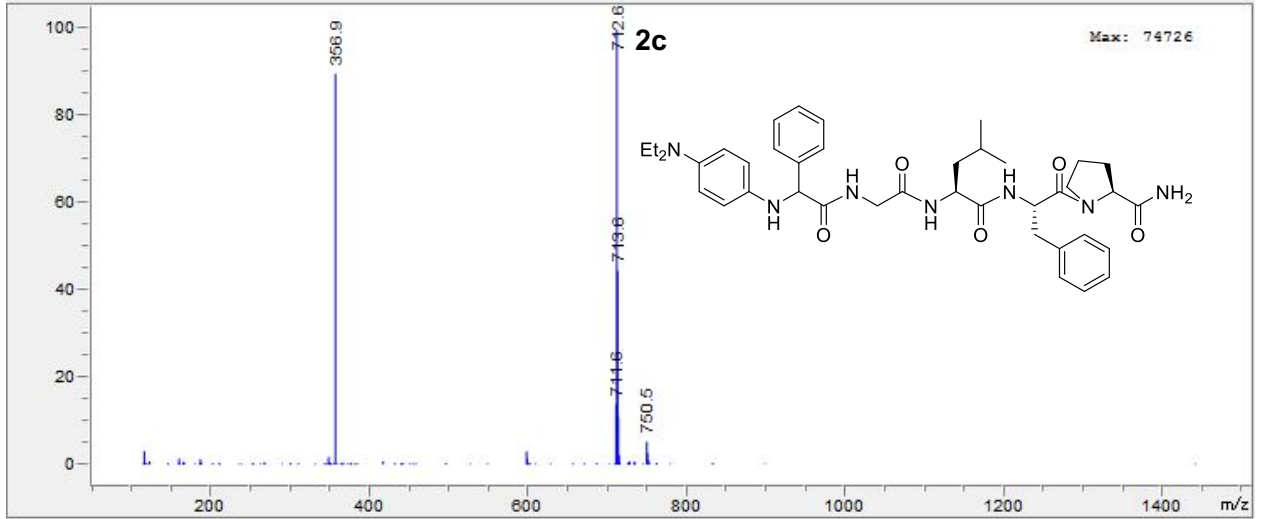
pH 7, O₂



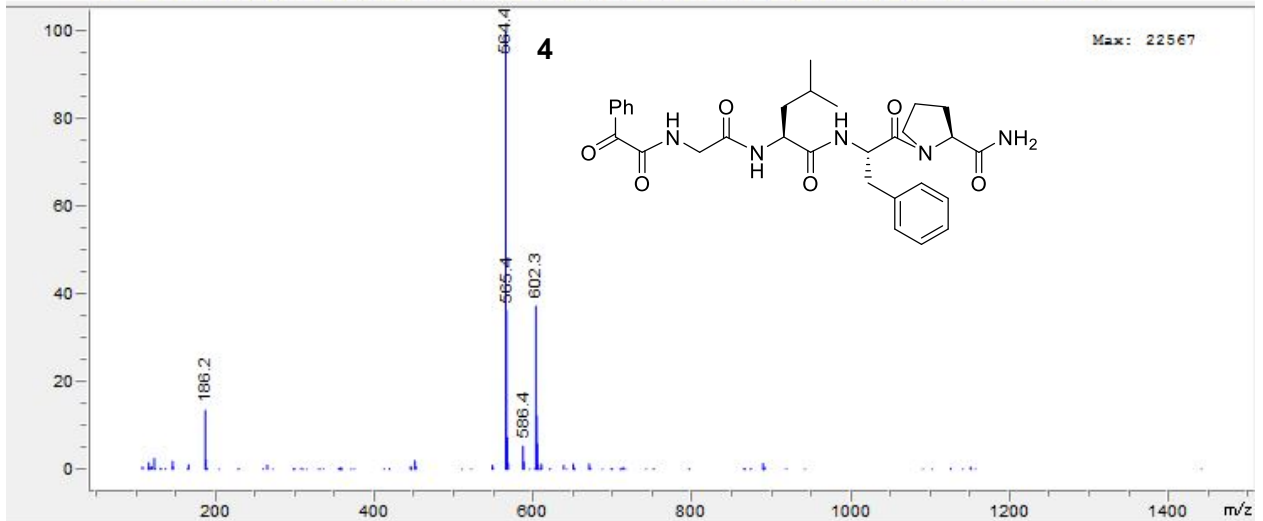
MWD1 C, Sig=214,4 Ref=360,100 (LC 2021-10-30 08-43-09\002-P2-F5-HAY.8.48.A.24hr.D)



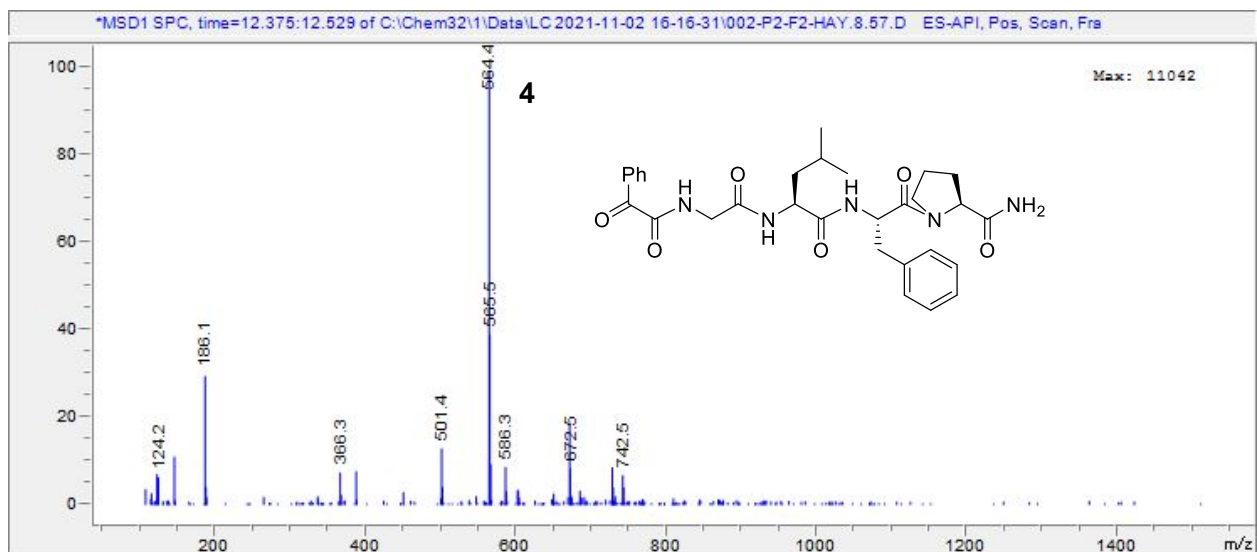
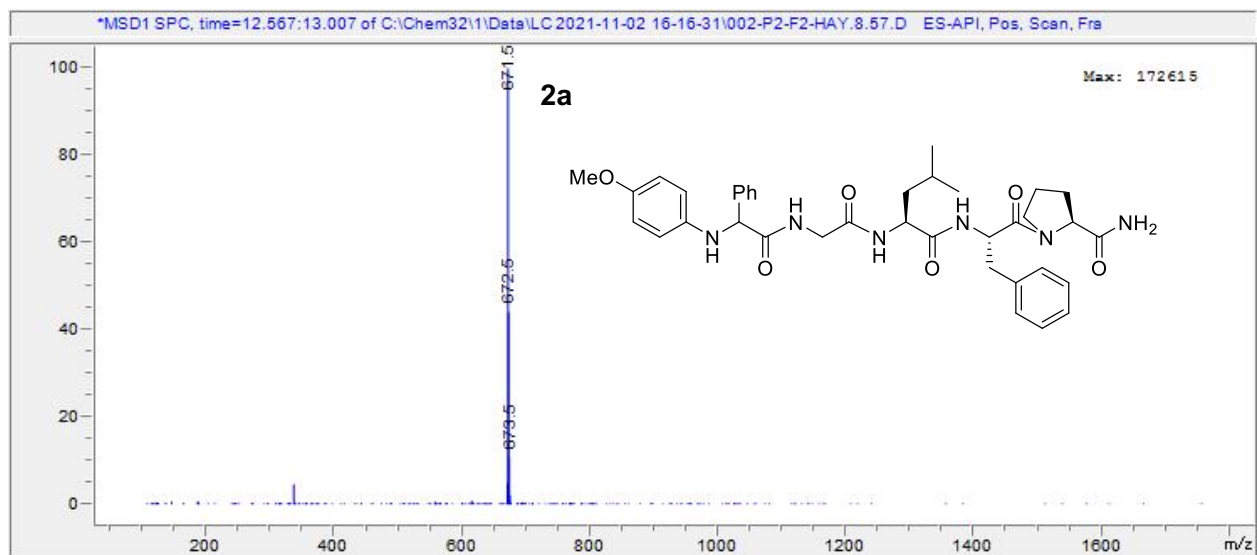
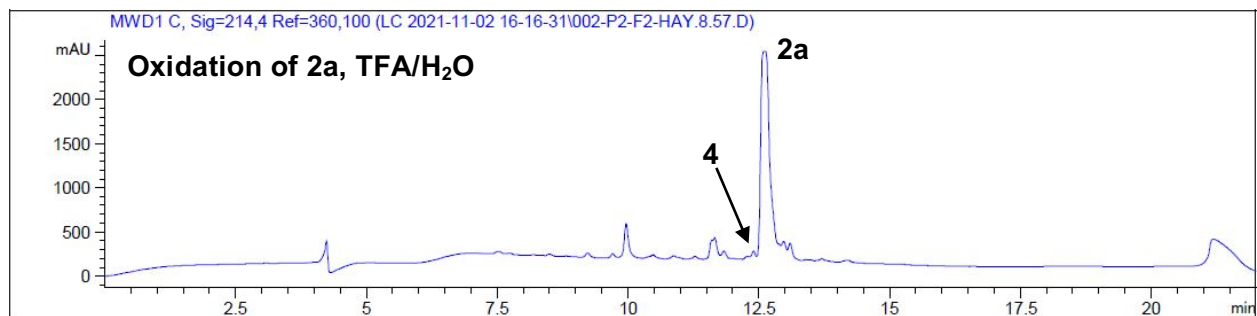
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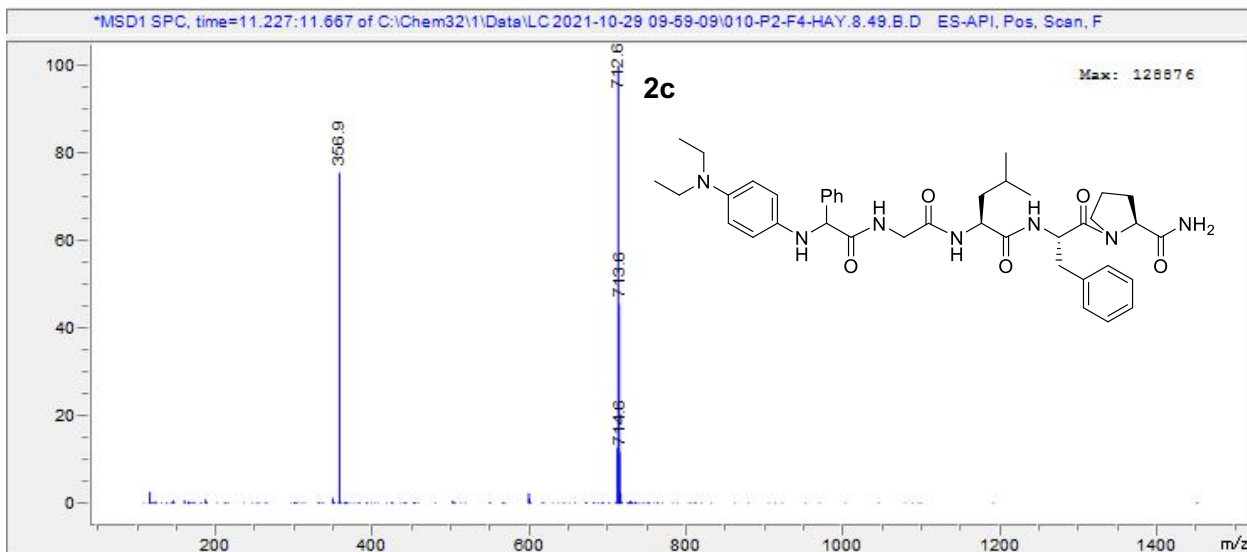
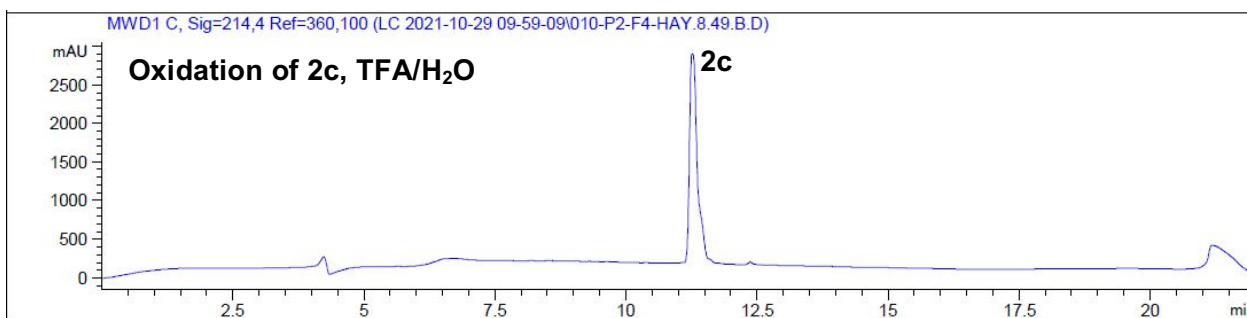
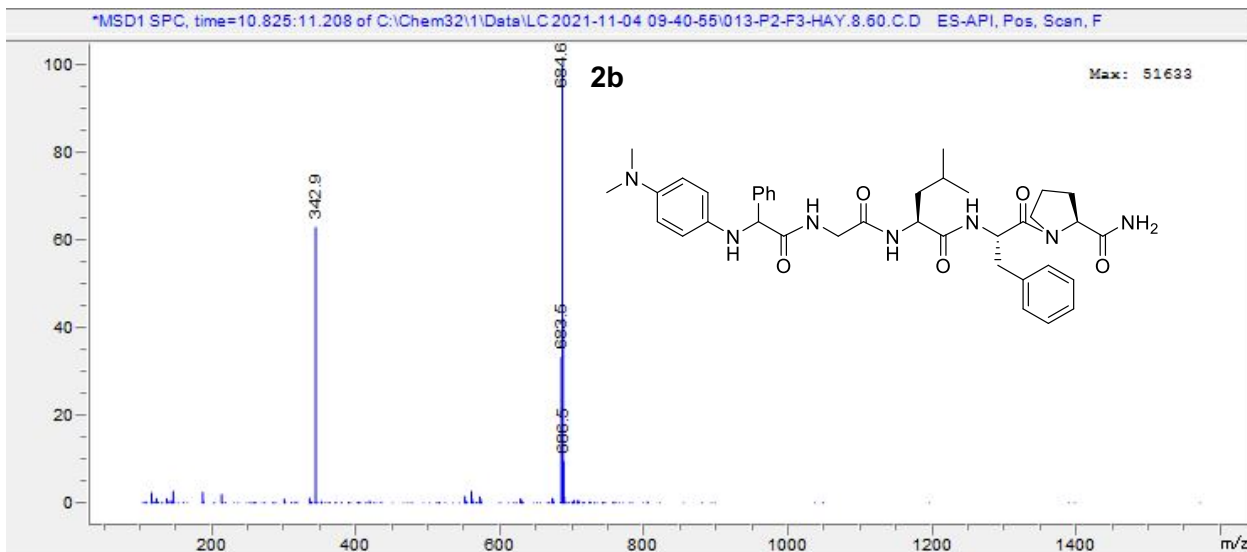
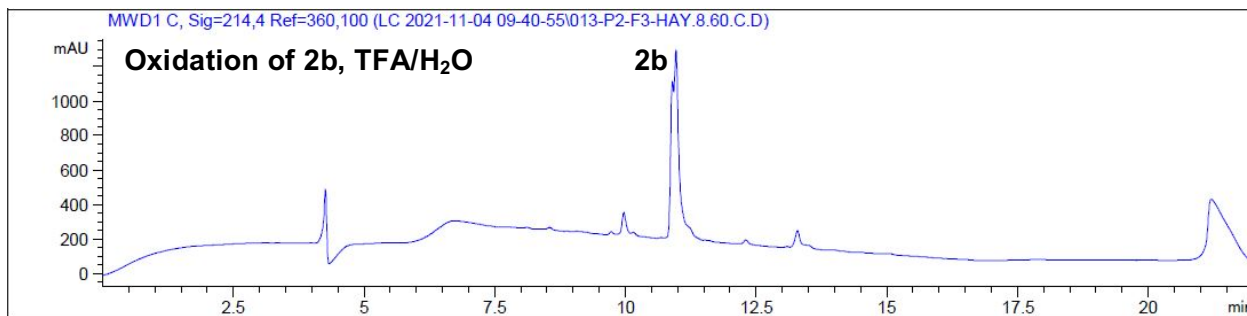


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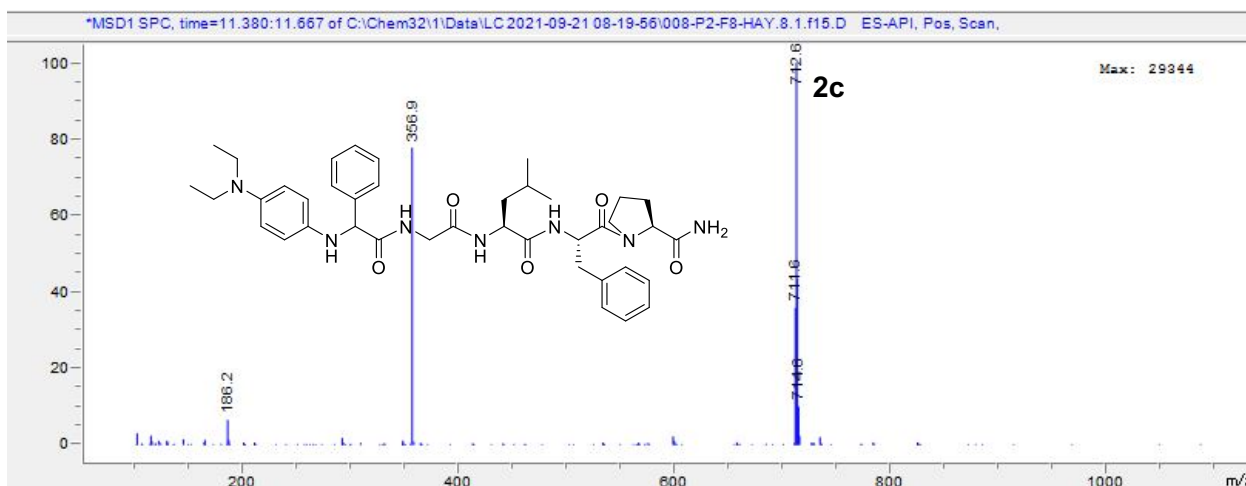
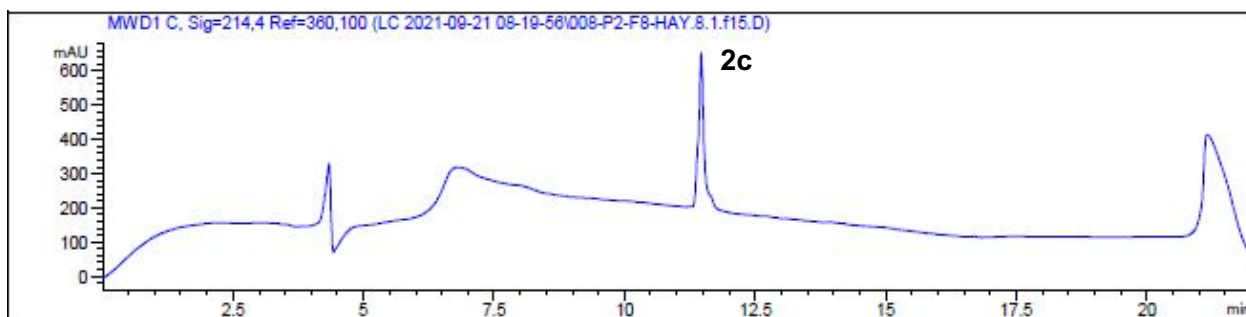
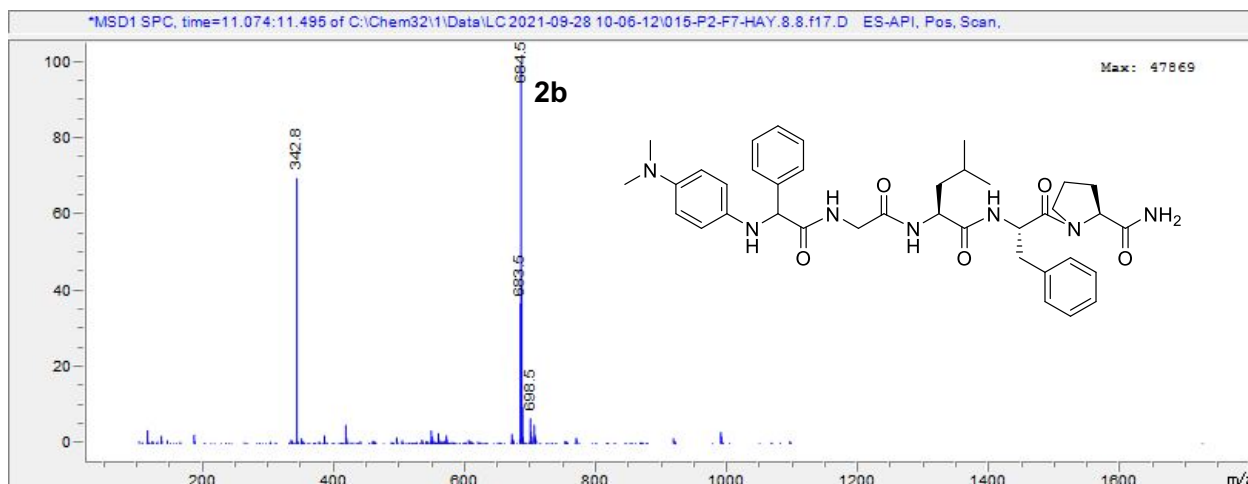
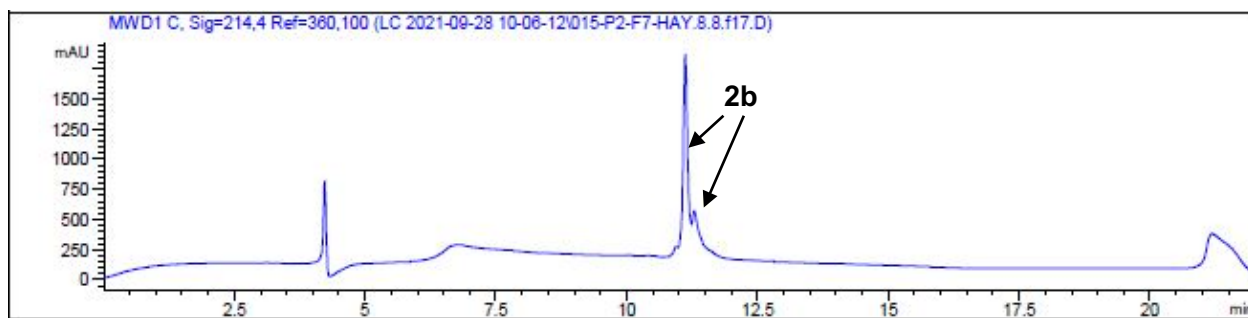


TFA/H₂O

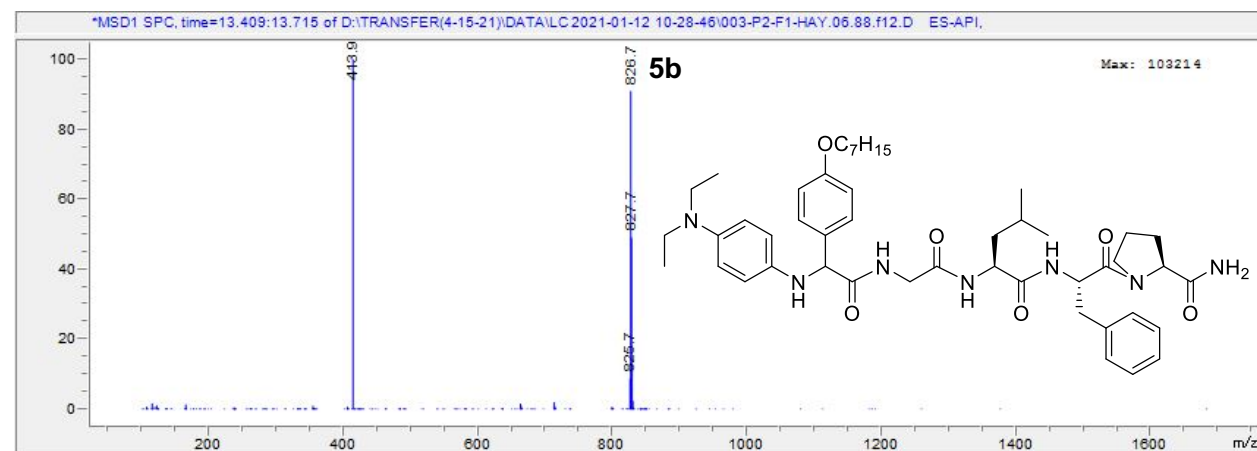
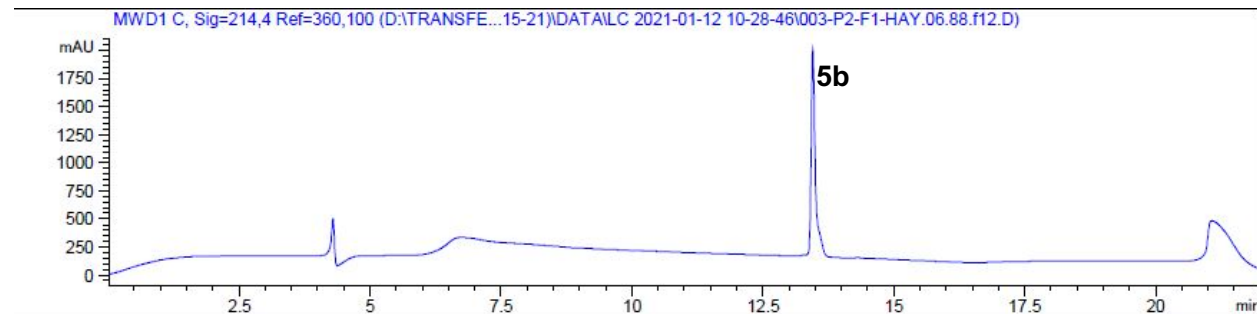
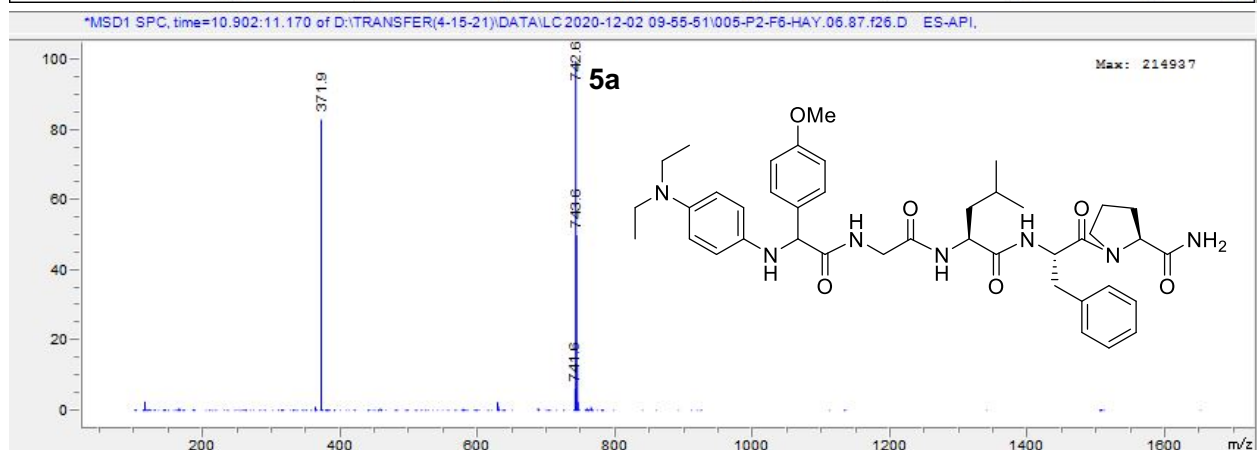
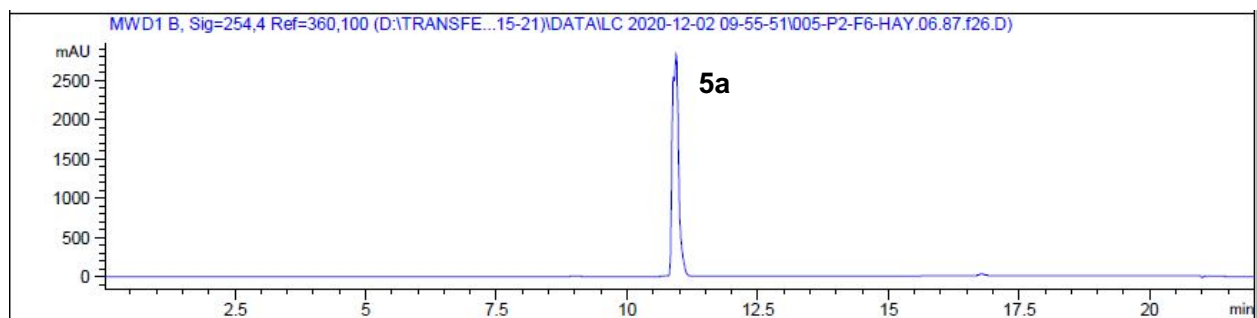


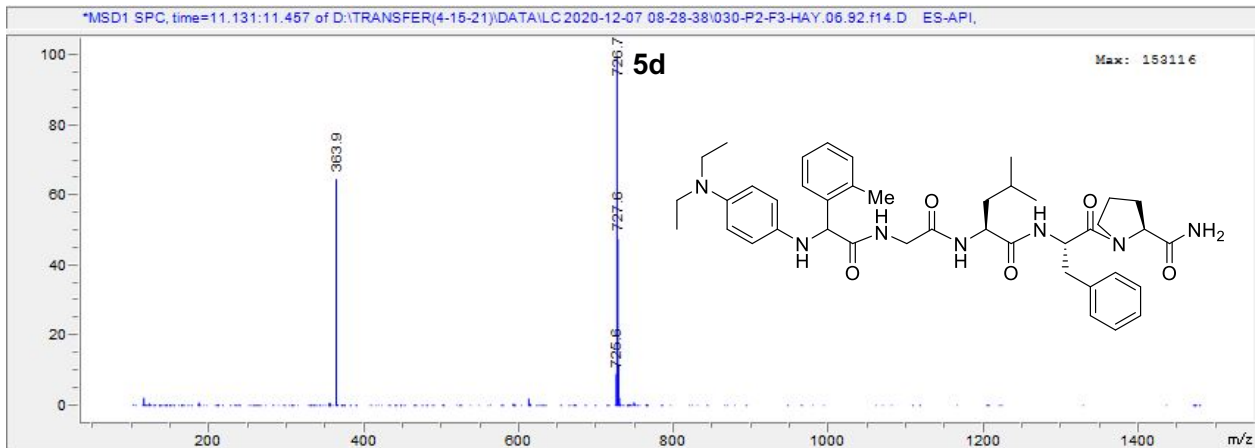
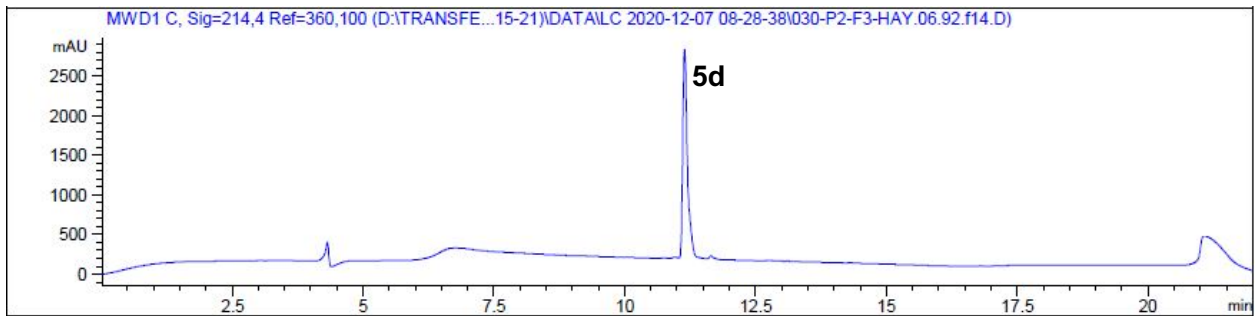
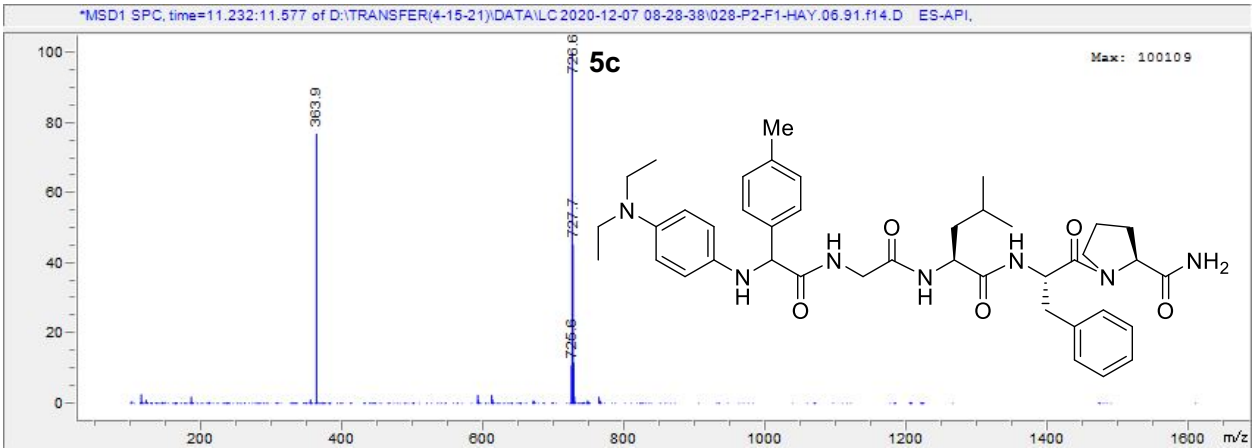
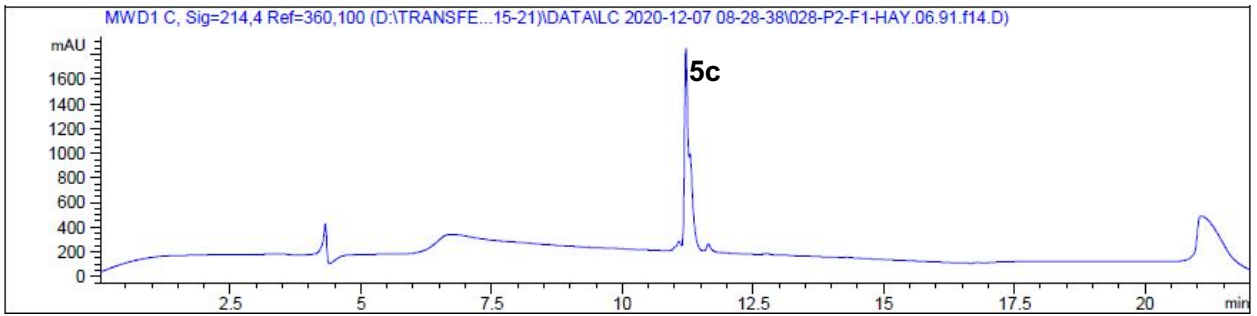


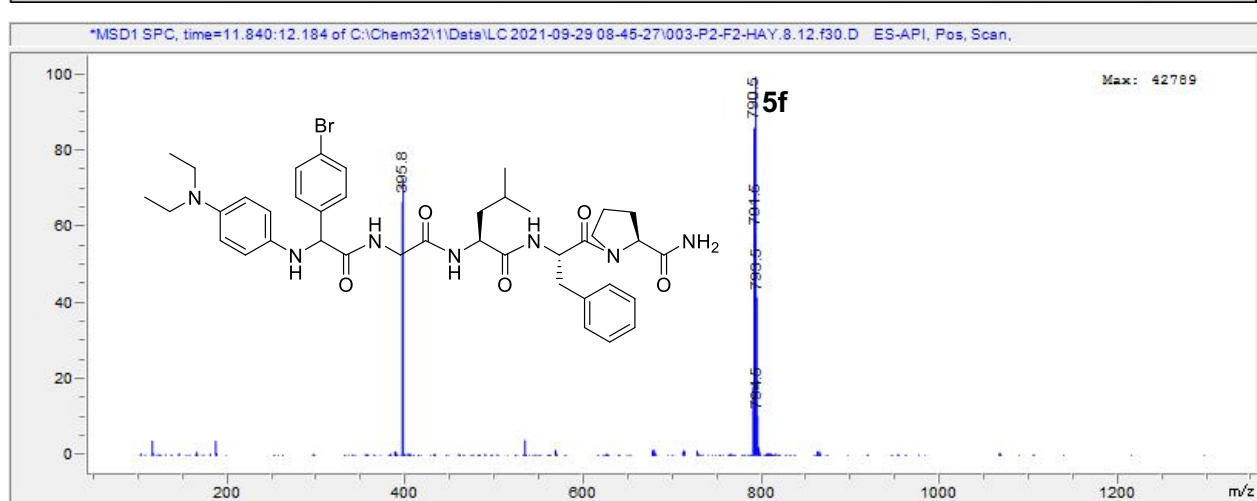
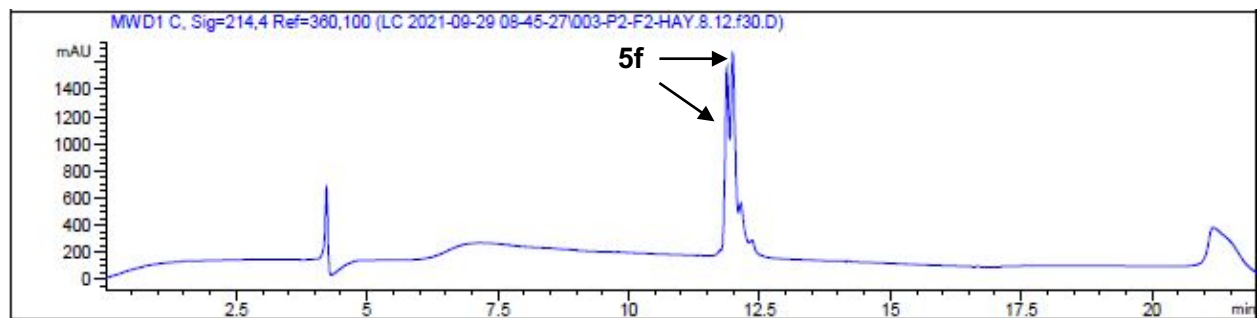
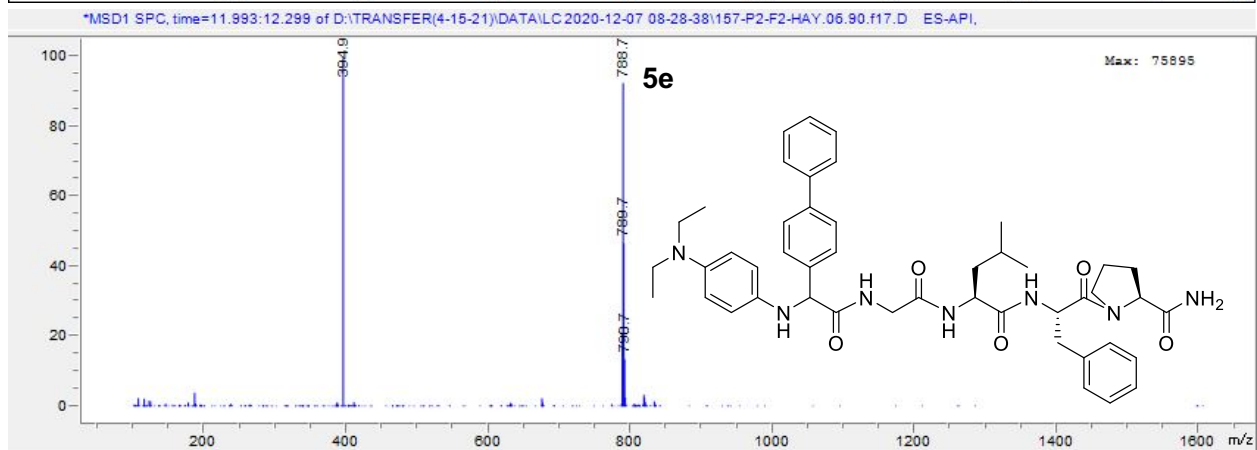
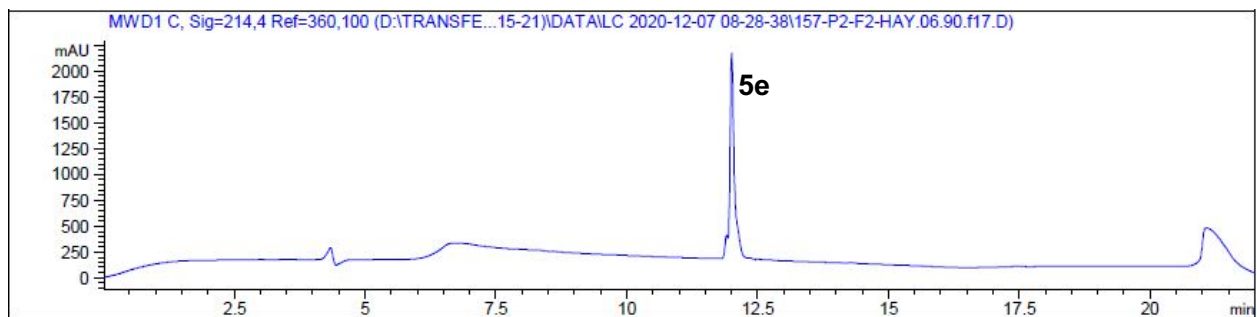
Characterization of 2b-c after purification

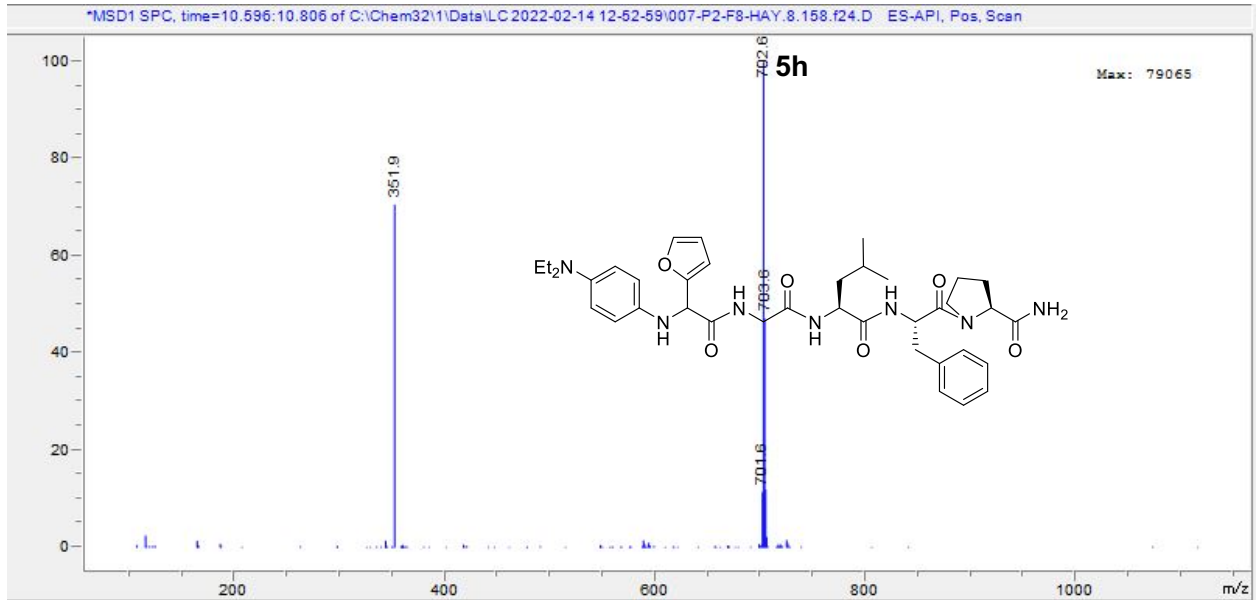
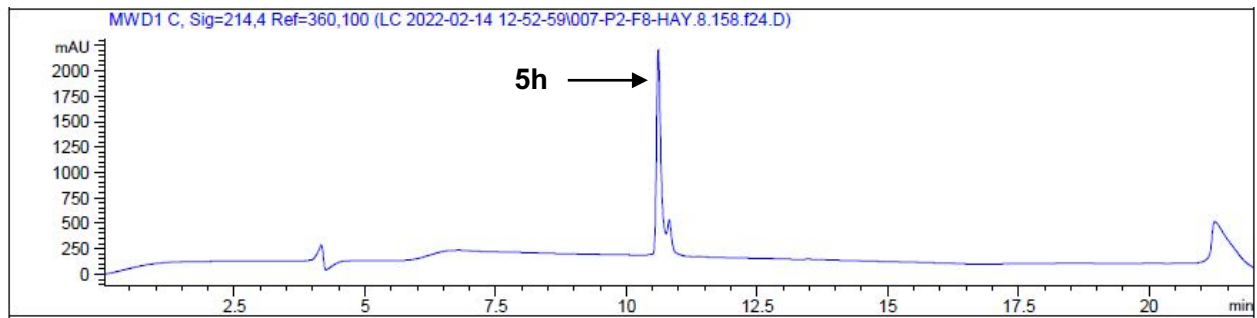
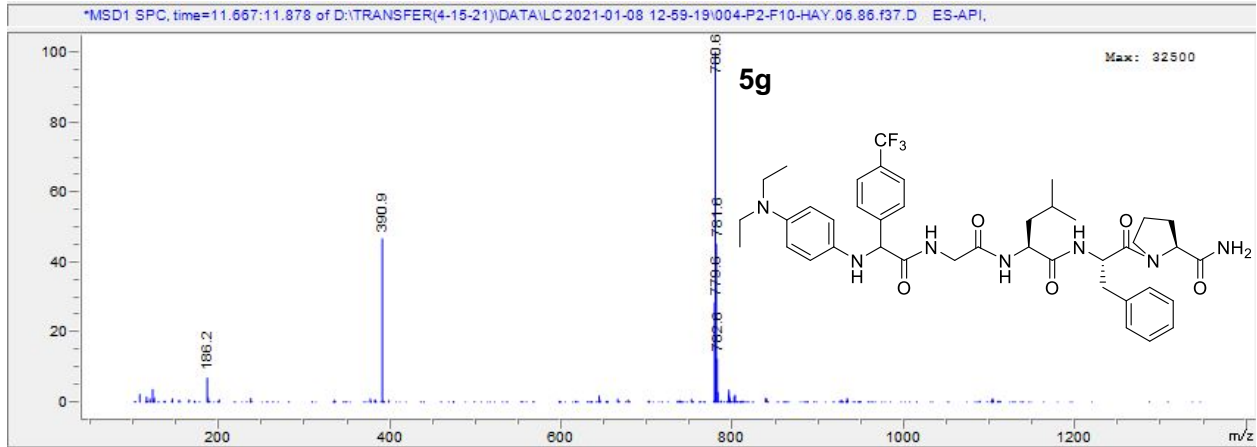
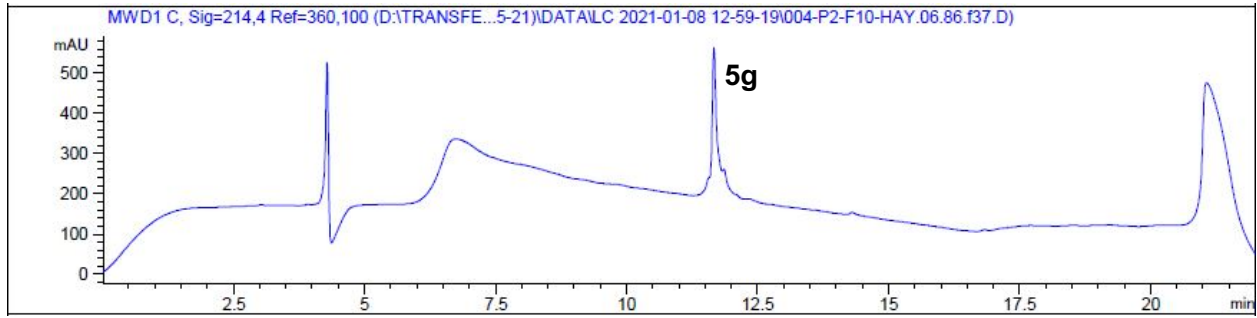


Characterization of 5a-h after purification

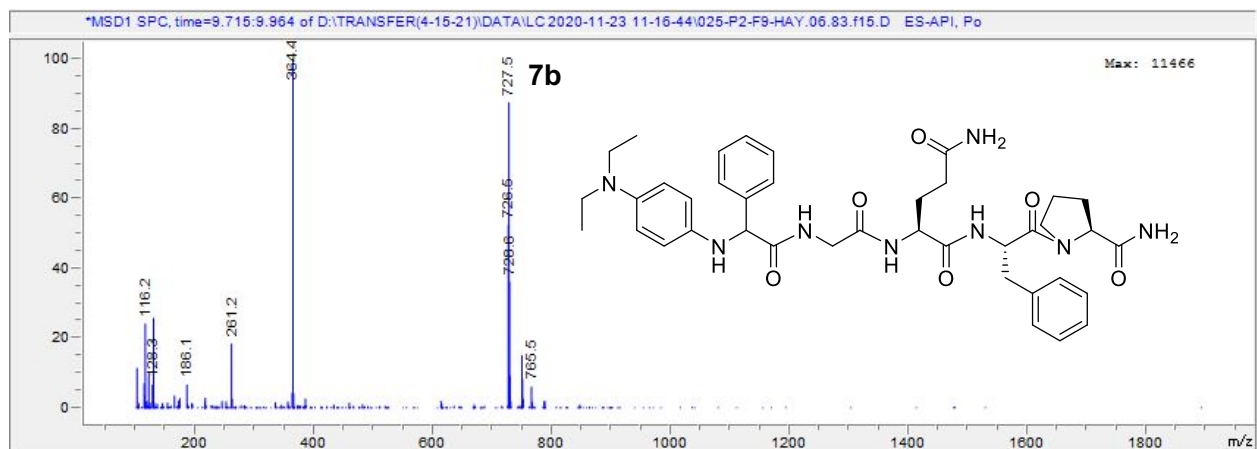
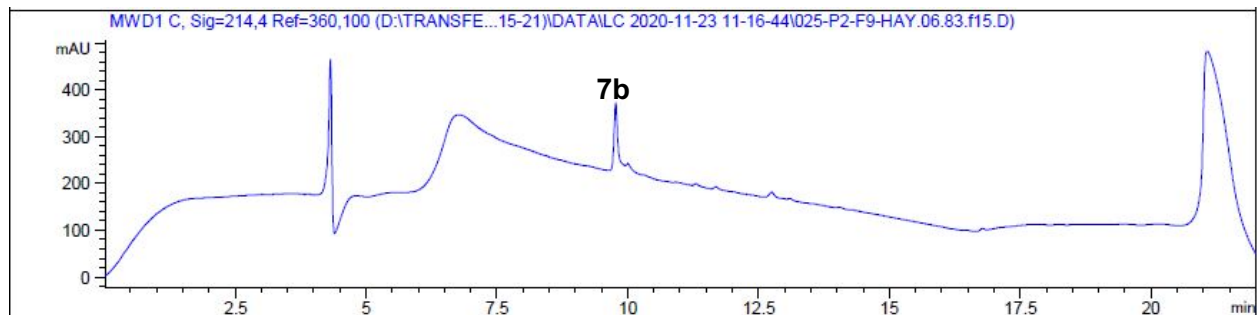
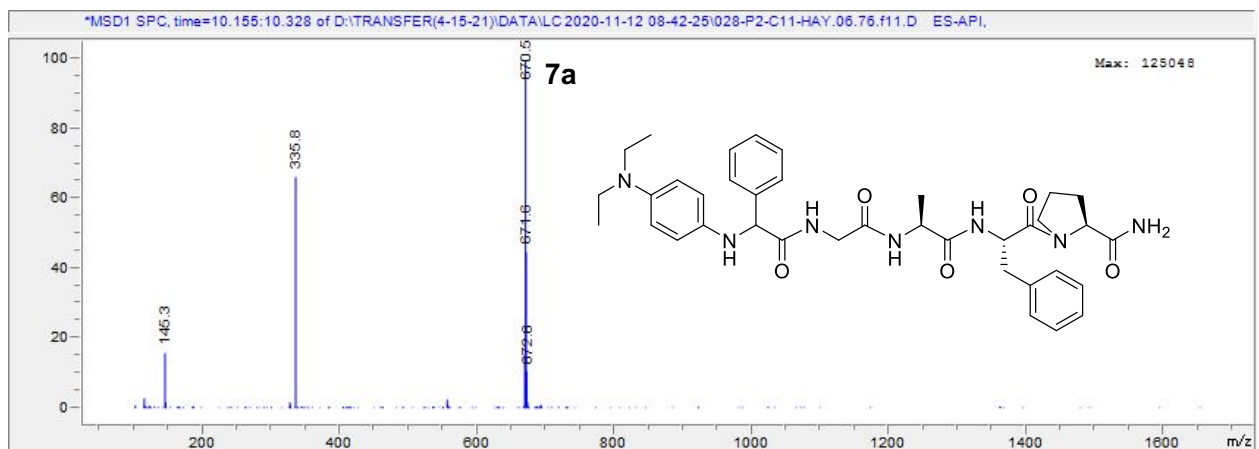
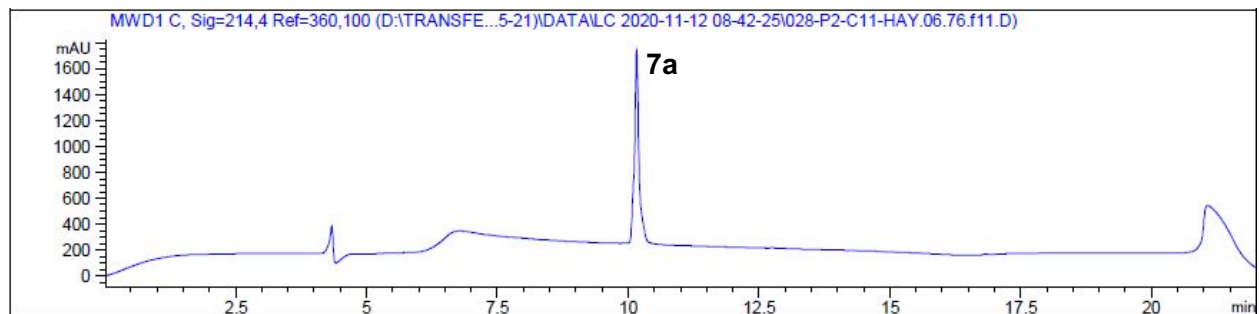


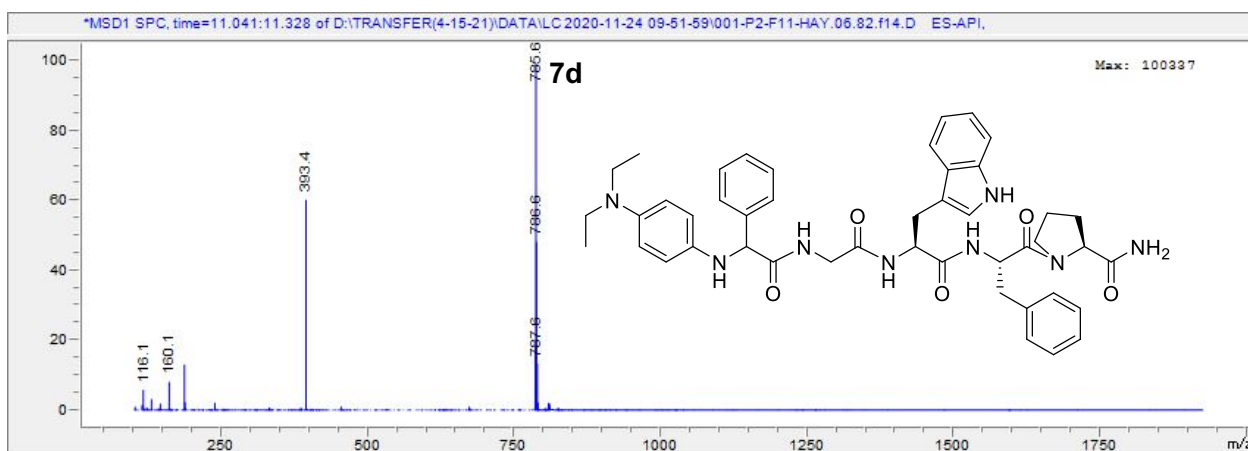
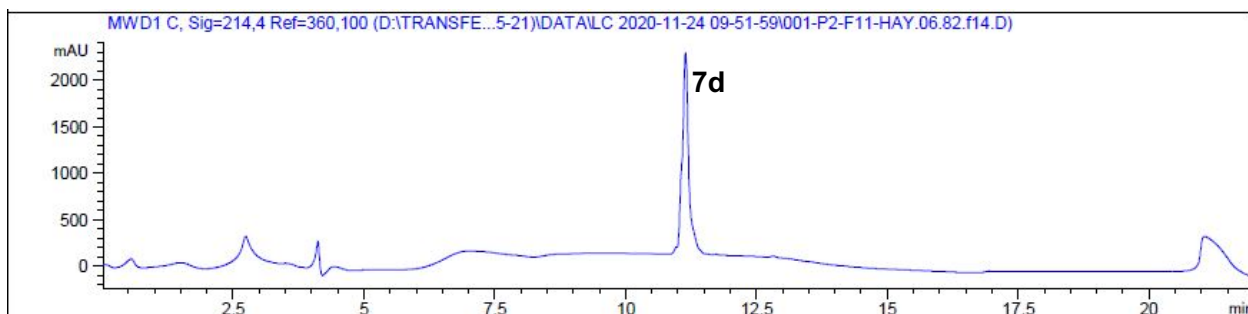
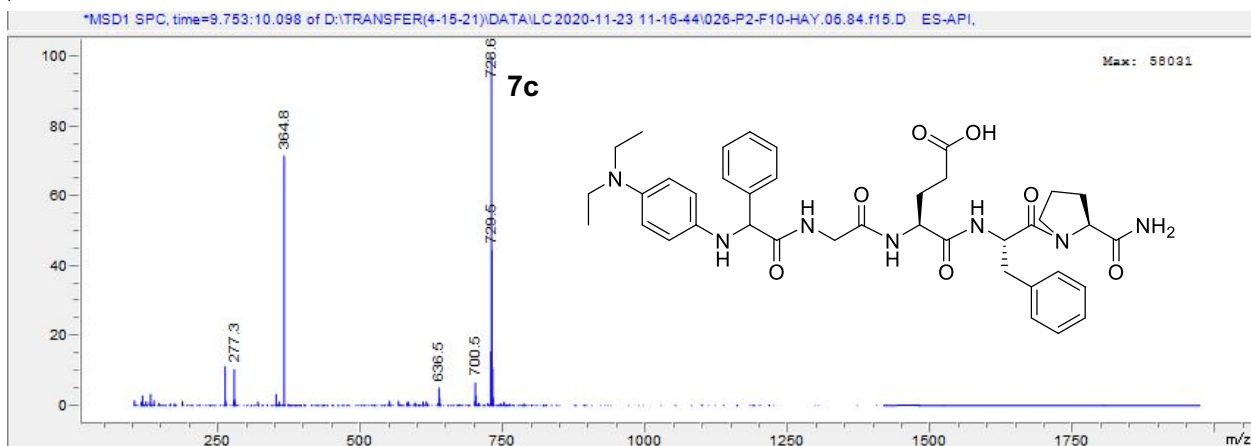
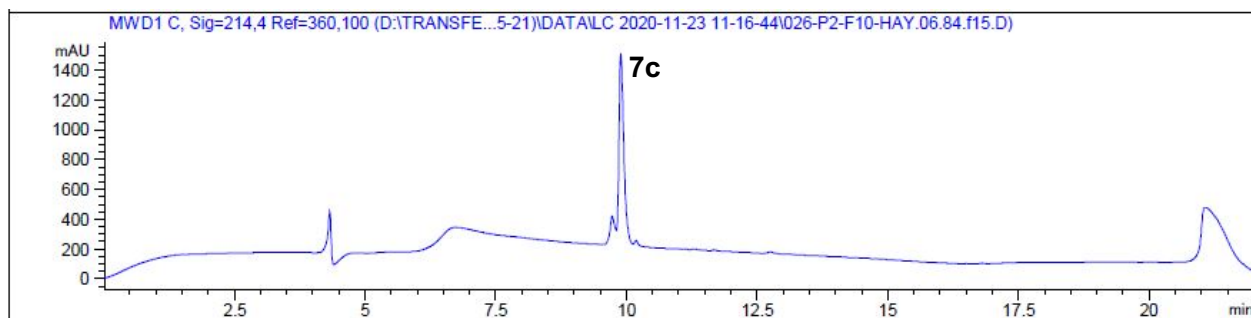


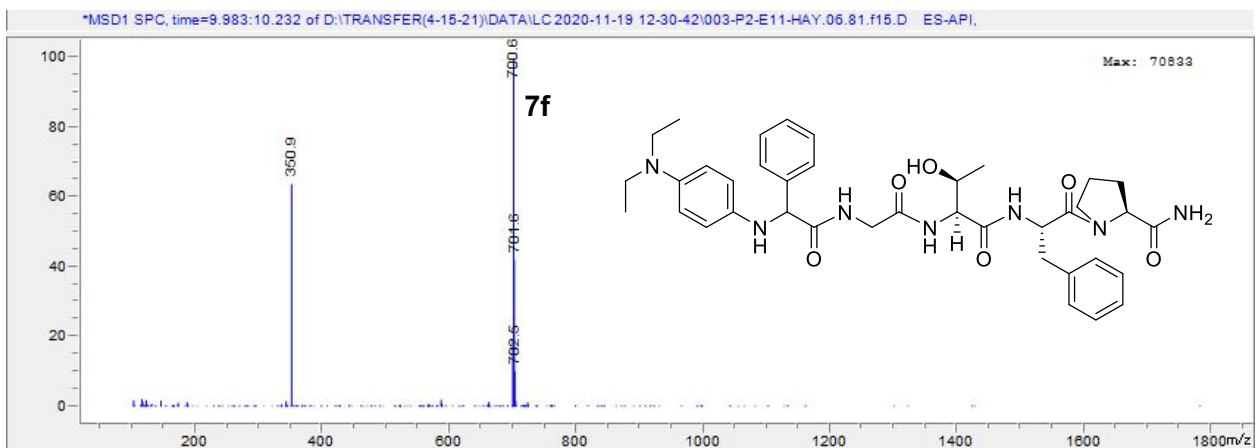
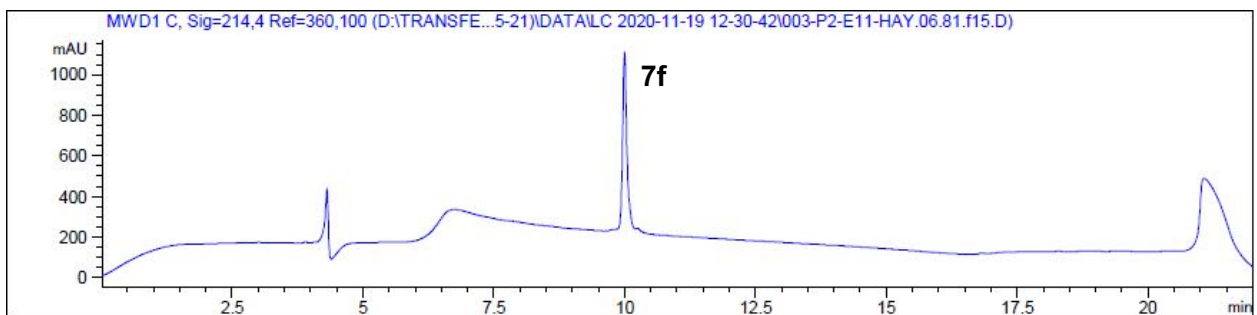
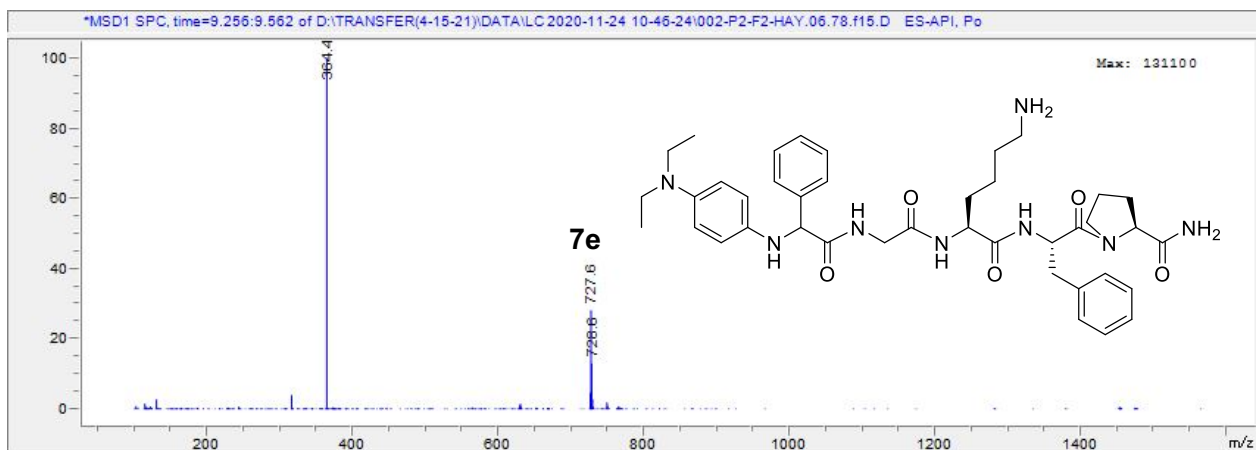
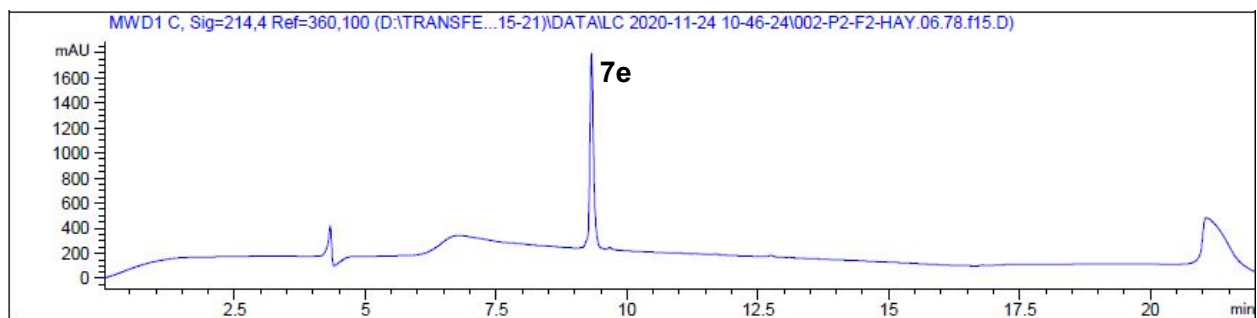


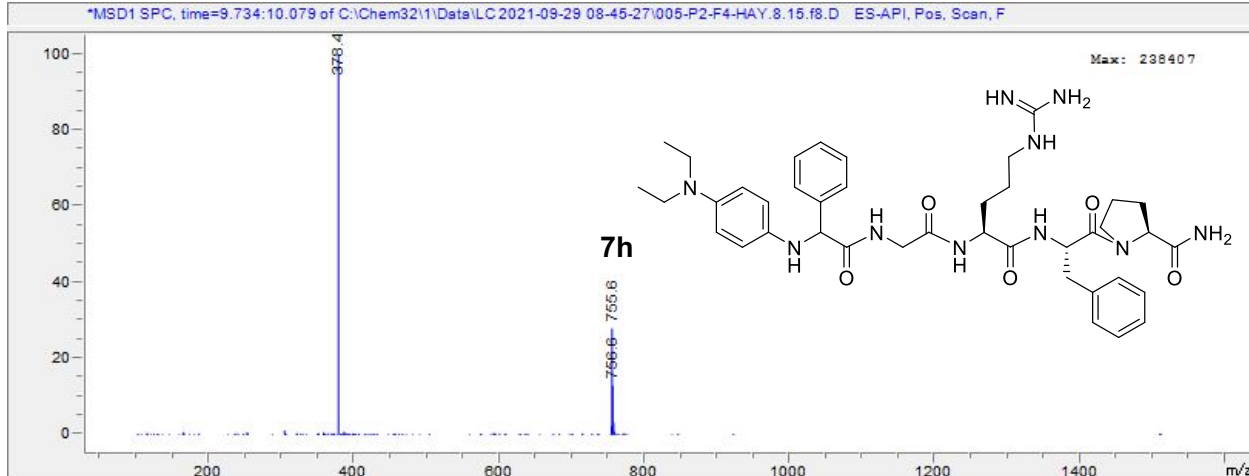
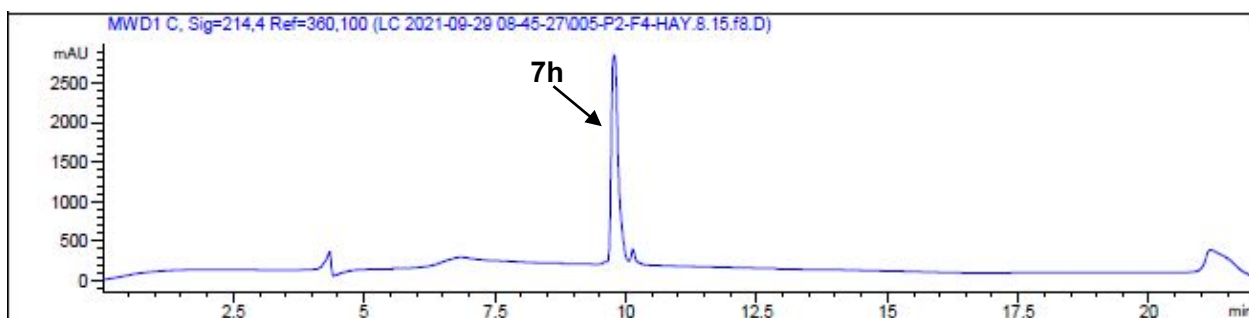
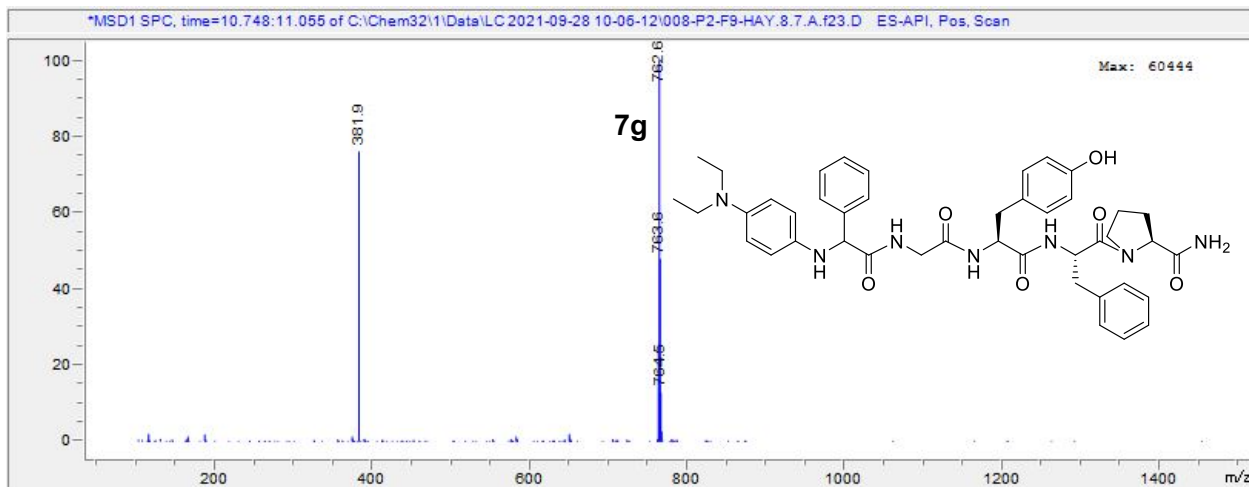
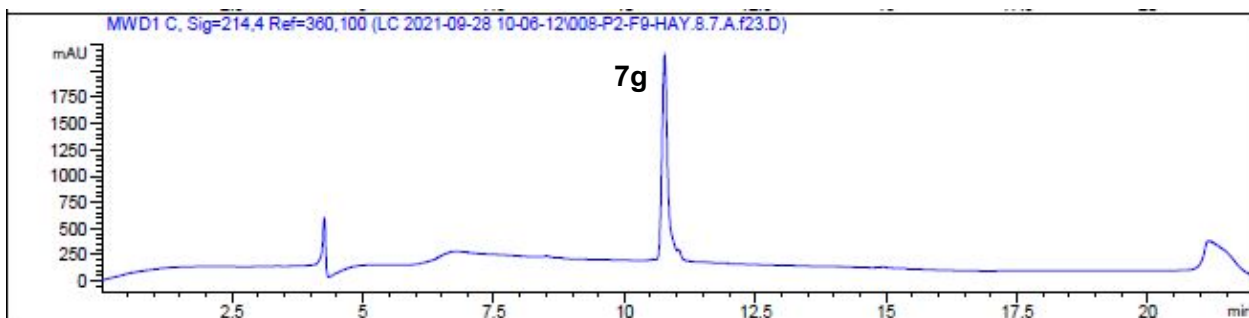


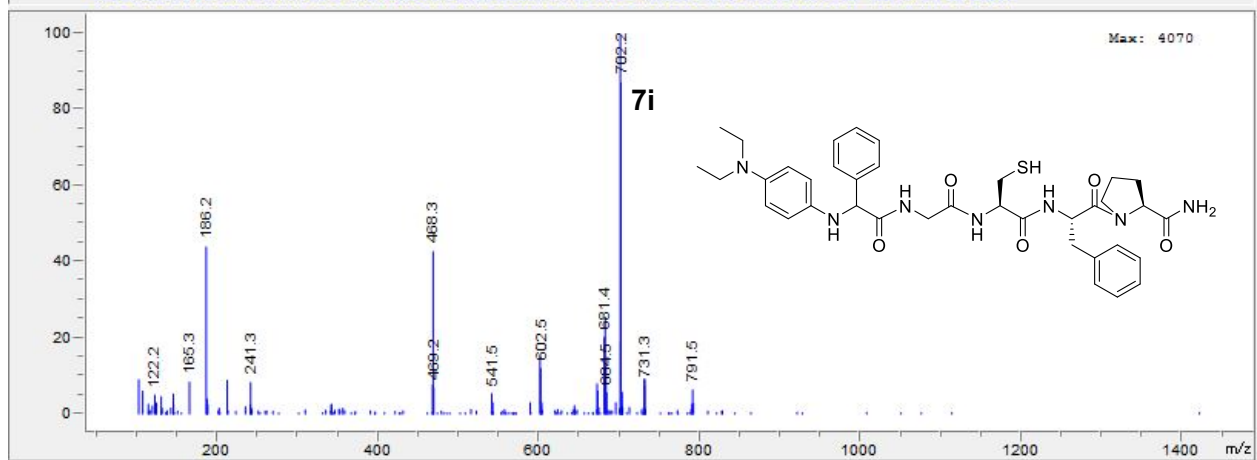
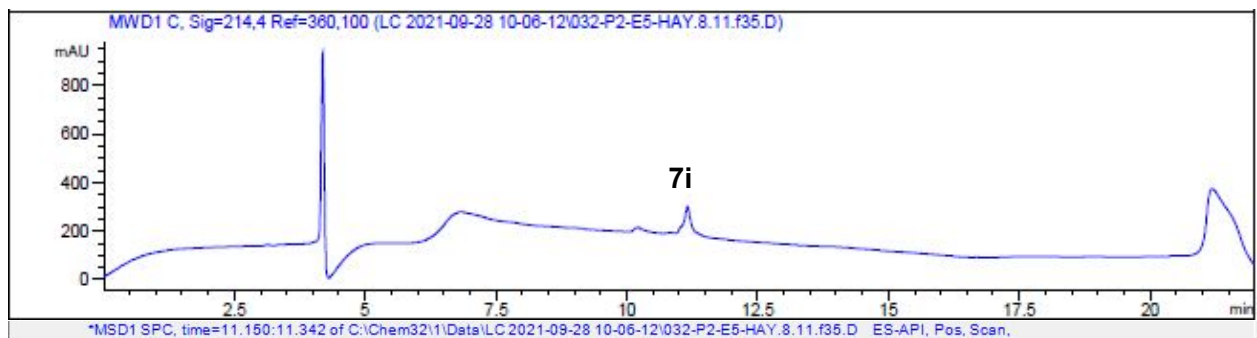
Characterization of 7a-7i after purification



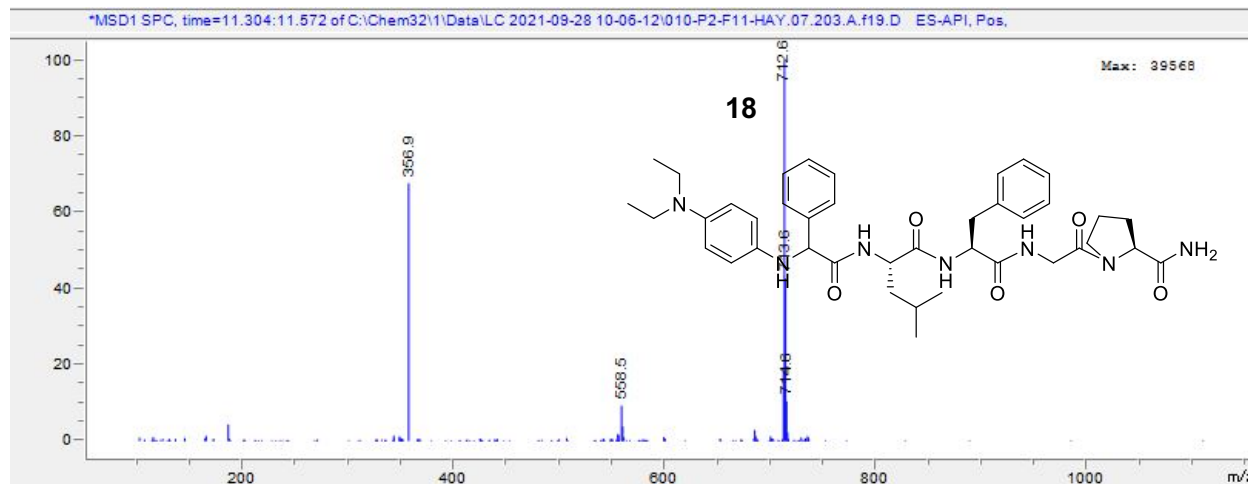
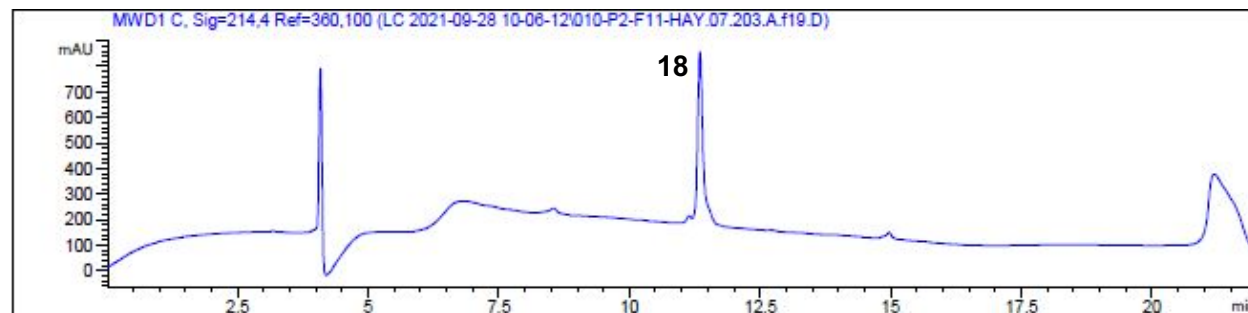
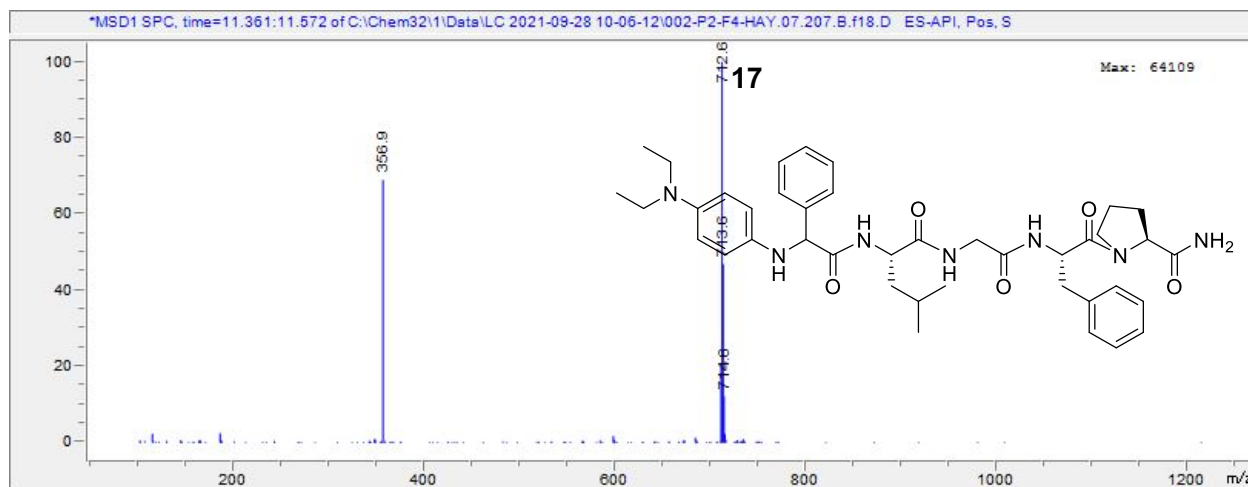
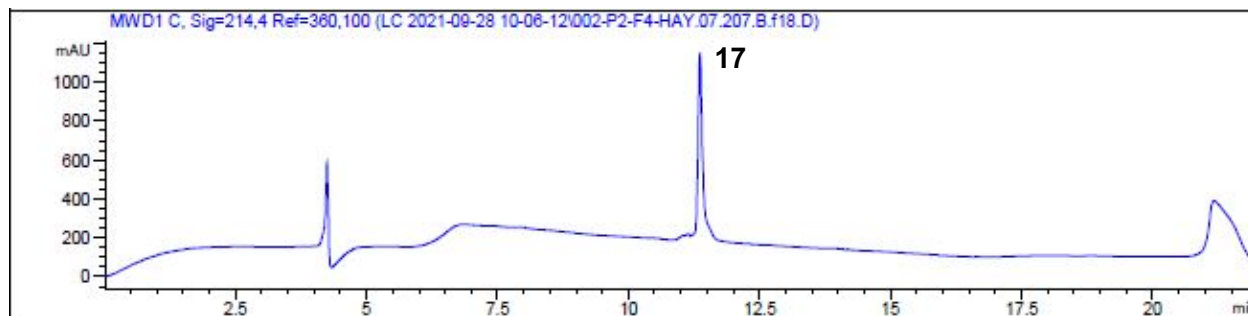


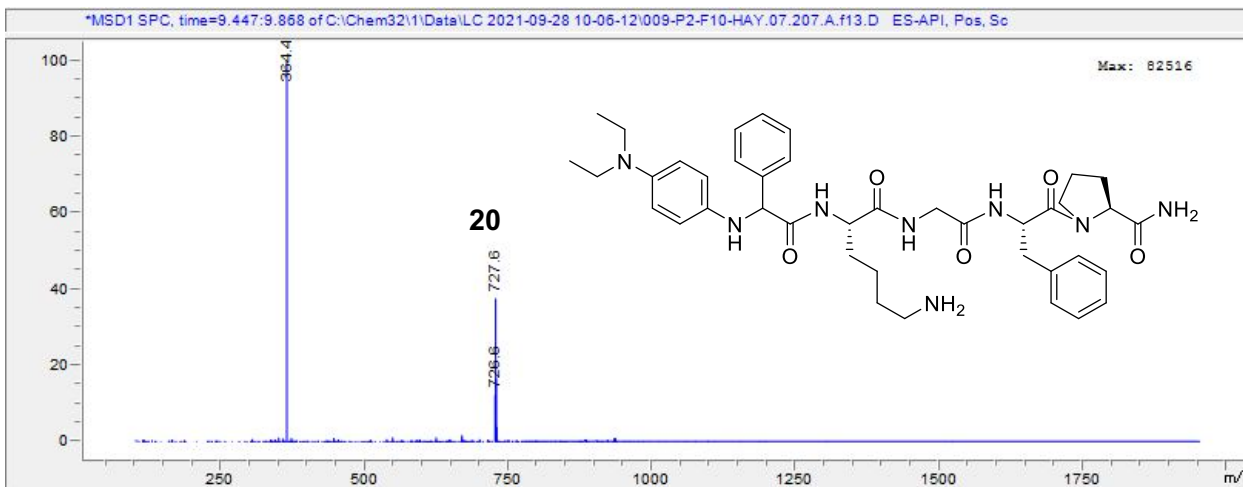
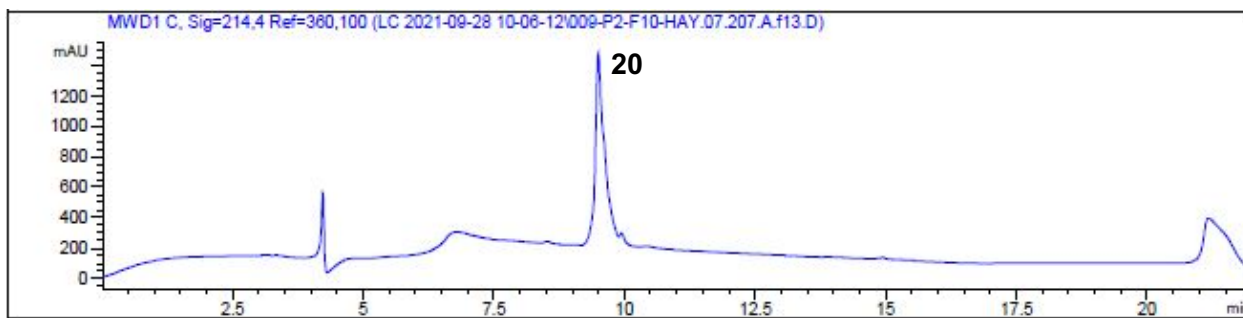
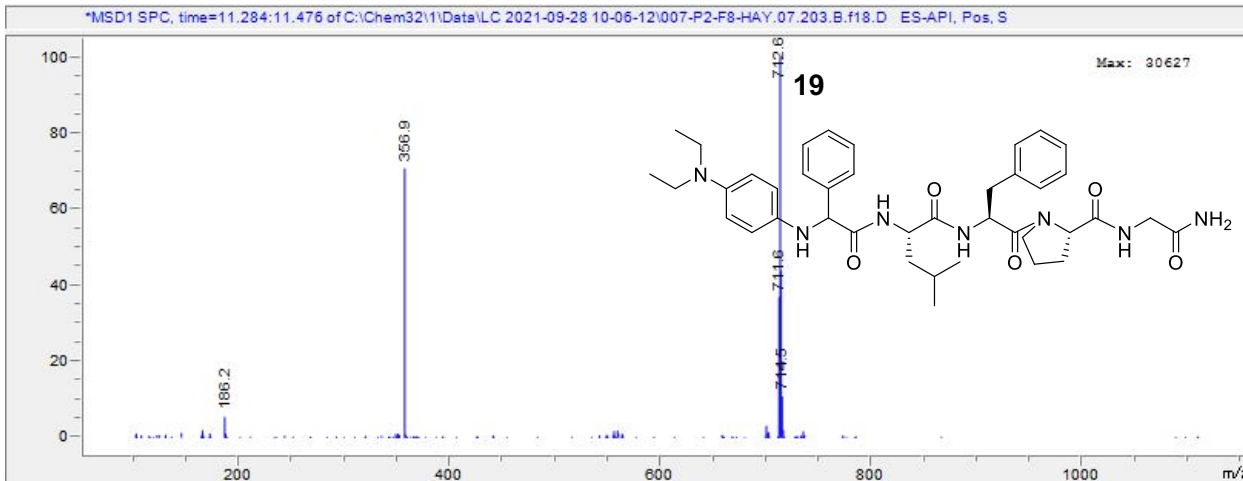
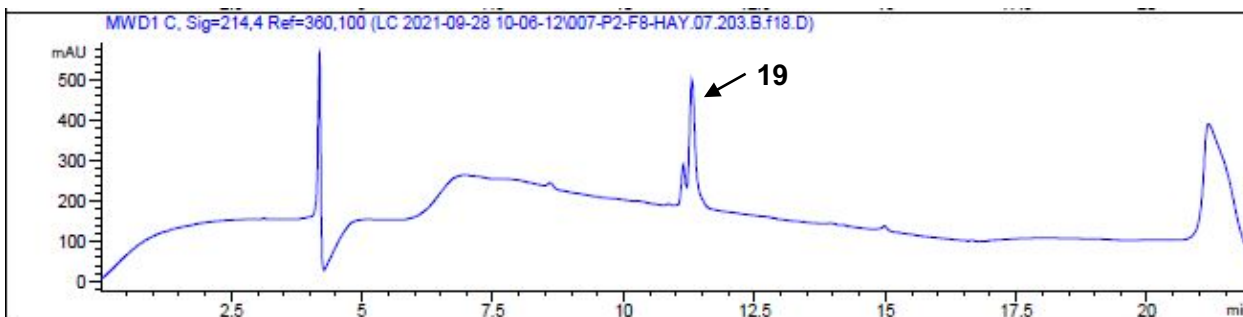


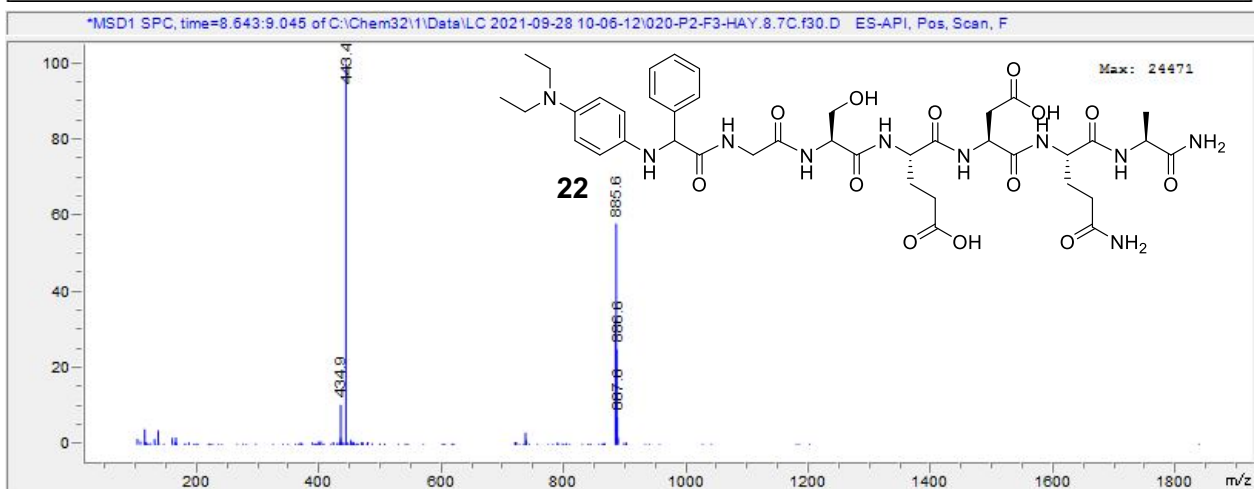
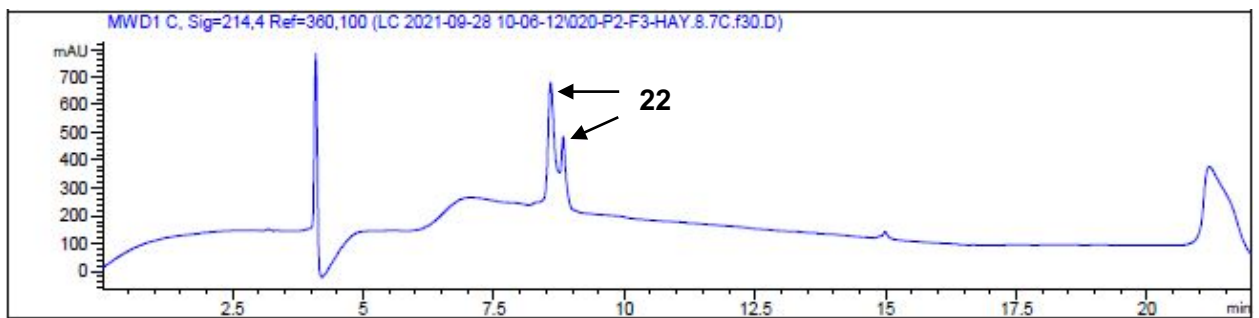
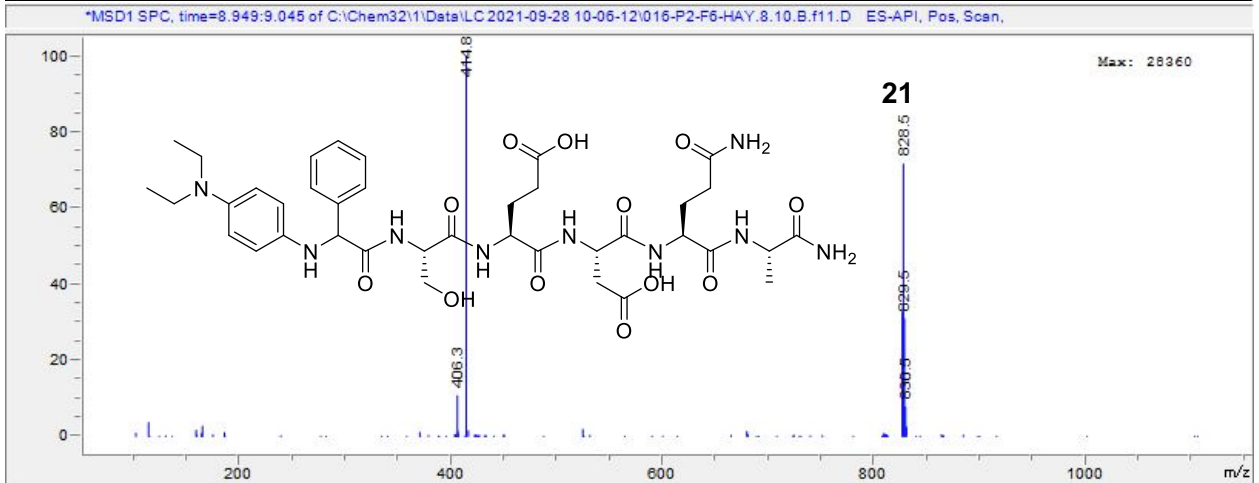
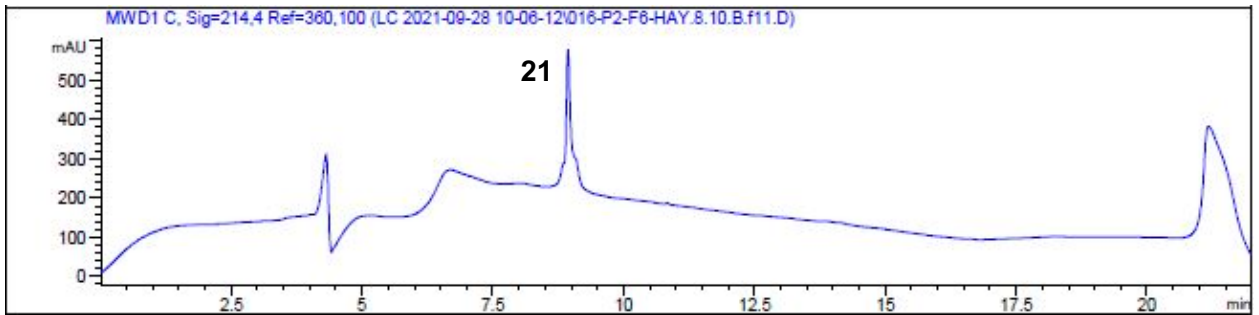


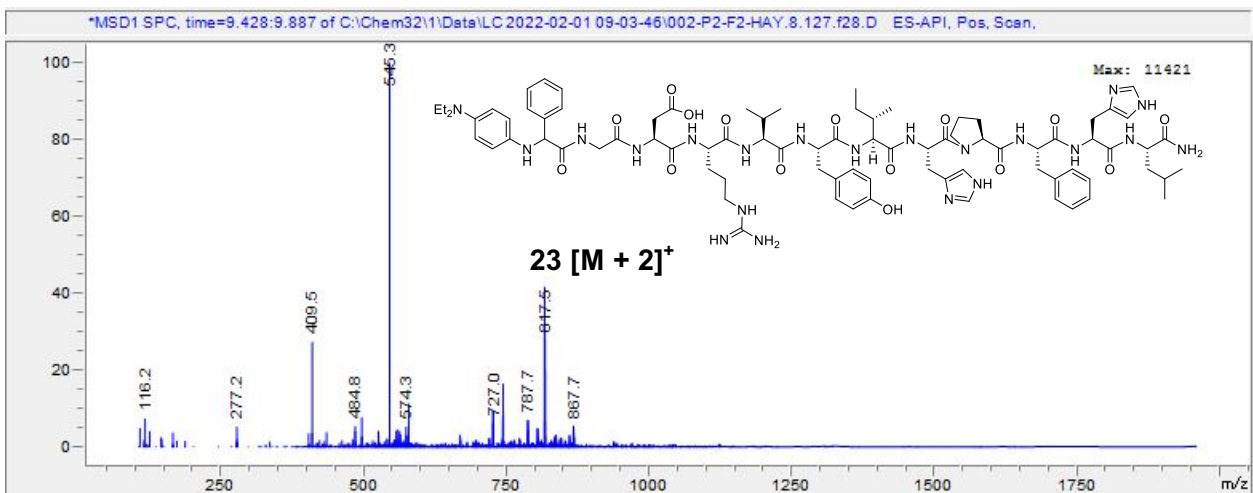
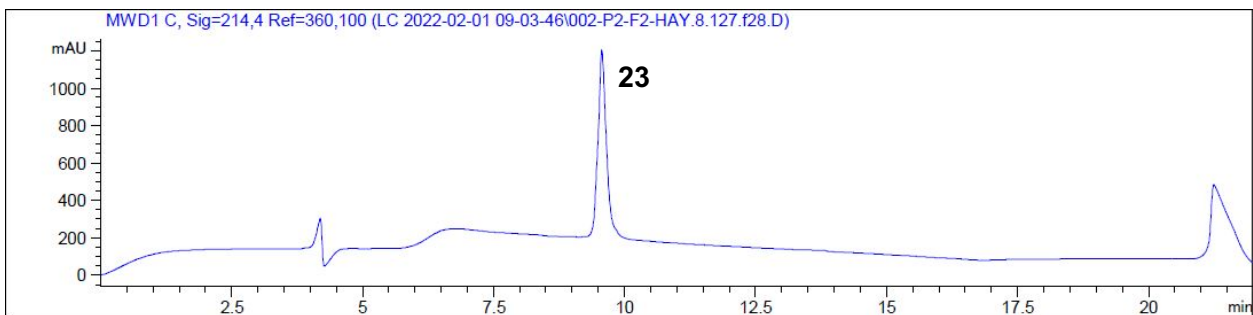


Characterization of 17-23 after purification









F. References

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