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Supporting Information

Light-induced β-Hydroxy Sulfone synthesis in DNA-Encoded Libraries

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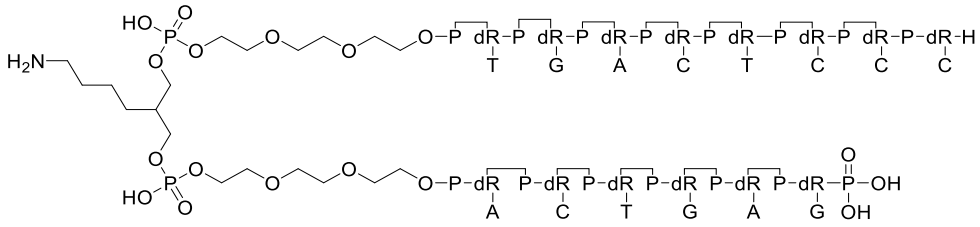
1. General Information

All reagents were obtained from commercial sources unless otherwise noted. The central dsDNA oligonucleotide with chemically modified phosphates that end in an amine terminus (**HP**, Figure S1) and encoding 5'-phosphorylated oligonucleotides were purchased from Genscript Biotech Corp. All other DNA oligonucleotides were obtained from General Biological System (Anhui) Co., Ltd. and assessed through the general analytical procedure for purity. DNA working solutions were prepared using DNAse/RNAse-free ultrapure water (Invitrogen), DMSO (Fisher). LC-MS running solvents were made from Optima LC-MS grade water (Fisher), Optima LC-MS grade methanol (Fisher), hexafluoroisopropanol (99+% purity, Sigma-Aldrich) and HPLC-grade triethylamine (Fisher). T4 DNA Ligase was obtained from ThermoFisher Scientific Coorporation (#EL0012). The 10X ligation buffer stock used in ligation reactions was composed as follows: 400 mM Tris-HCl, 100 mM $MgCl_2$, 100 mM DTT, 5 mM ATP (pH 7.8 at 25 °C). Eosin Y (90+% dye content) was purchased from Sigma Aldrich. All ionic solutions, including aq. NaCl (5.0 M) and basic borate buffer (250.0 mM sodium borate/boric acid, pH 9.5), were prepared in-house. The **HP** used for experiments has the following chemical structure**.**



HP

Figure S1. The structure of DNA **HP**.

Chemical building blocks and reagents were purchased from various vendor sources and used without further purification. Building blocks were generally used from aliquots dissolved in water (H_2O), dimethyl sulfoxide (DMSO), and stored in 2D barcoded tubes with septa-caps at -80 °C. Solutions were transferred by

Eppendorf pipettes. Reactions and large volume DNA precipitations were generally performed in centrifuge tubes (Axygen). All reactions were agitated in a custom-made thermo mixer at 1,000.0 to 2,000.0 RPM (thermomixer was made by a local vendor; https://www.made-in-china.com /products-search/hot-china-products/Thermo_Mixer.html). The reaction containers are Eppendorf tubes or 96-well plates. Eppendorf tubes can be well fitted into a thermomixer to allow the on-DNA chemistry performed in combinatorial fashion. For irradiation with green light Zhongzhan Illumination (green, λmax = 535 nm, Imax = 1000 mA, 3.0 W) was used.

Solutions were centrifuged in high-speed freezing centrifuge (Eppendorf). A Vanquish UHPLC system was integrated with LTQ XL ion trap mass spectrometer (ThermoFisher Scientific) for LC-MS analysis of oligonucleotides. DNA was visualized with Molecular Imager Gel Doc XR system (BIO-RAD) after staining in an ethidium bromide solution.

2. Analytical Conditions

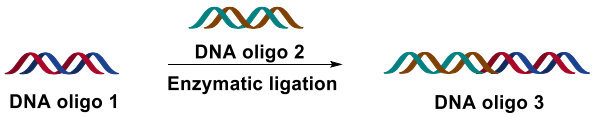
On-DNA reactions conducted during validation, library synthesis, or single compound synthesis was analyzed by LC-MS (ESI-MS). Samples (ca. 100.0 pmol diluted with 40.0 µL of water) were injected onto a reverse-phase chromatography column (DNA Pac^{TM}RP 4.0 µm, 2.1 x 50.0 mm) and eluted (30-60% solvent B over 1.5 minutes, 0.60 mL/min flow rate; Solvent A: 0.75% V/V hexafluoroisopropanol (HFIP)/0.038% V/V triethylammonium acetate (TEAA)/5.0 µM EDTA in deionized water; Solvent B: 0.75% V/V HFIP/0.038% TEAA/5 µM EDTA in 90/10 methanol/ deionized water) with monitoring at UV 260.0 nm wavelength and TIC. Percent of conversion (% PDT = (purity of PDT/purity of SM) x 100) for on-DNA reactions were determined by LC-MS analysis. Chromatographic purification was likewise achieved using reverse-phase liquid chromatography (XBridge® BEH C18 3.5 µm, 4.6 x 100.0 mm), Solvent A: 0.75% v/v hexafluoroisopropanol (HFIP)/0.18% v/v N, N-Diisopropylethylamine (DIEA) in deionized water; Solvent B: MeOH. The data analysis was performed by exporting the raw instrument data (.RAW) to an

automated biomolecule deconvolution and reporting software (ProMass) which uses a novel algorithm (ZNova) to produce artifact-free mass spectra.

3. DNA Precipitation Protocol

To a DNA reaction mixture was added 5% (v/v) 5.0 M NaCl solution and 2.5 times the reaction volume of absolute ethanol. The mixture was mixed thoroughly before stored at −80 °C overnight for DNA precipitation. The slurry was then centrifuged at 4000.0 rpm for 1 hour, followed by decanting the supernatant. The DNA pellets were dried in air after supernatant was decanted. Invitrogen UltraPure distilled water was added to reconstitute the DNA solids to the needed concentration. Generally, ethanol precipitation was performed after each chemical reaction and ligation.

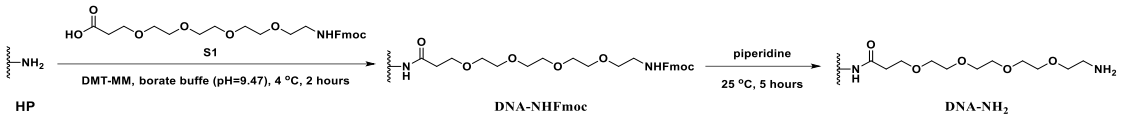
4. General DNA Ligation Procedure



The **DNA oligo 1** (1.0 mM, 10.0 nmol, 1.0 equiv.) was dissolved in 10.0 μL of distilled water, to which were added **DNA oligo 2** (11.0 μL of a 1.0 mM solution in distilled water, 1.1 equiv.), followed by the addition of 4.0 μL of 10 X ligation buffer and 12.0 U T4 DNA ligase, add H_2O to a final volume of 40.0 μl. The solution was agitated at 25 °C for 1 hour. The reaction mixture was quenched thermally by incubation for 20 minutes at 65 °C completely inactivates T4 DNA Ligase and the reaction mixture was analyzed by LC-MS. The DNA product **DNA oligo 3** was precipitated with 5.0 M NaCl and ethanol. Then, it was directly used for the next step. The OD measurement was performed to quantify the reaction yield, and the product quality was assessed by LC-MS.

5. Experimental Procedures

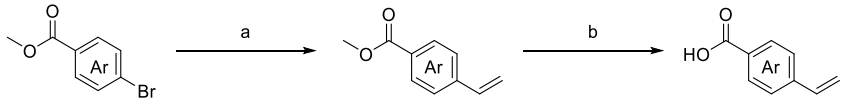
5.1. Synthesis of DNA-NH_2



Preparation of **DNA-NHFmoc**: In a tube, was placed 1-(9H-fluoren-9-yl)-3-oxo-2,7,10,13,16 -pentaoxa-4- azanonadecan-19-oic acid **S1** (200.0 mM in DMSO, 600.0 μL, 40.0 equiv.) in borate buffer (250.0 mM in H_2O, pH = 9.47, 3.0 mL, 250.0 equiv.), to which were added DMT-MM (200.0 mM in H_2O, 600.0 μL, 40.0 equiv.) and **HP** (1.0 mM in H_2O, 3.0 mL, 1.0 equiv.). The mixture was agitated at 4 °C for 2 hours. After ethanol precipitation, the reaction conversion rate (100%) was monitored by LC-MS, and the product **DNA-NHFmoc** (2,400.0 nmol) was collected for the next step use.

Preparation of **DNA-NH_2**: Into a tube was loaded with **DNA-NHFmoc** (1.0 mM in H_2O, 2,400.0 μL), to which was added with 1,200.0 μL of 10% (v/v) piperidine in water. The mixture was agitated at 25 °C for 5 hours. Afterwards, the product **DNA-NH_2** was obtained by ethanol precipitation and then used for the next step without further purification. The reaction conversion rate was 96% determined by LC-MS analysis.

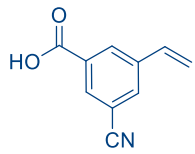
5.2. General Procedure for Synthesis of Vinylbenzoic Acid



Reagents and conditions: (a) Potassium vinyltrifluoroborate, $Pd(dppf)Cl_2$, K_2CO_3, 1,4-dioxane/H_2O (2:1), 80 °C; (b) $LiOH·H_2O$, CH_3CN/H_2O (1:1)

General Procedure A. To a solution of brominated aromatic hydrocarbons (1.0 equiv) and potassium vinyltrifluoroborate (1.5 equiv) in 1,4-dioxane and H_2O were added K_2CO_3 (3.0 equiv) and $Pd(dppf)Cl_2$ (0.05 equiv). After stirring for 4 hours at 80 °C under a nitrogen atmosphere, the resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography, eluted with hexane/ethyl acetate to afford the corresponding ester-based olefin.

To a stirred solution of ester-based olefin (1.0 equiv) in CH_3CN/H_2O (1:1) was added $LiOH·H_2O$ (2.0 equiv) at 25 °C and stirred for 2 hours. After completion, the mixture was acidified to pH = 2.0 with 1.00 N HCl aqueous solution. The residue was purified by silica gel column chromatography to afford the corresponding carboxyl olefin.

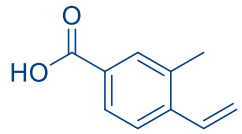


M. W. = 173.2

S2m

3-Cyano-5-vinylbenzoic acid (S2m)

Prepared according to general procedure A: Using methyl 3-bromo-5-cyanobenzoate (590 mg, 2.47 mmol) to afford carboxyl olefin **S2m** (325 mg, 76%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d6) δ 13.56 (s, 1H), 8.26 (dt, J = 4.5, 1.7 Hz, 2H), 8.16 (t, J = 1.6 Hz, 1H), 6.86 (dd, J = 17.7, 11.1 Hz, 1H), 6.11 (d, J = 17.7 Hz, 1H), 5.48 (d, J = 11.1 Hz, 1H). MS (ESI-MS) m/z: 174 $[M + H]^+$.

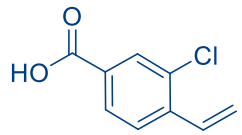


M. W. = 162.2

S2p

3-Methyl-4-vinylbenzoic acid (S2p)

Prepared according to general procedure A: Using methyl 4-bromo-3-methylbenzoate (2.00 g, 8.77 mmol) to afford carboxyl olefin **S2p** (803 mg, 57%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d6) δ 12.84 (s, 1H), 7.79 – 7.71 (m, 2H), 7.62 (d, J = 7.9 Hz, 1H), 6.99 (dd, J = 17.5, 11.0 Hz, 1H), 5.83 (dd, J = 17.4, 1.3 Hz, 1H), 5.44 (dd, J = 11.1, 1.3 Hz, 1H), 2.36 (s, 3H). MS (ESI-MS) m/z: 163 $[M + H]^+$.

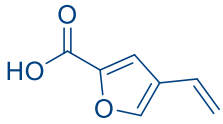


M. W. = 182.6

S2r

3-Chloro-4-vinylbenzoic acid (S2r)

Prepared according to general procedure A: Using methyl 4-bromo-3-chlorobenzoate (3.00 g, 12.10 mmol) to afford carboxyl olefin **S2r** (1.49 g, 68%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d6) δ 13.30 (s, 1H), 7.97 – 7.81 (m, 2H), 7.05 (dd, J = 17.5, 11.1 Hz, 1H), 6.03 (dd, J = 17.5, 0.9 Hz, 1H), 5.59 (dd, J = 11.1, 0.9 Hz, 1H). MS (ESI-MS) m/z: 183 $[M + H]^+$.

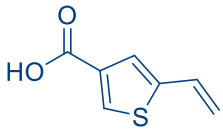


M. W. = 138.1

S2w

4-Vinylfuran-2-carboxylic acid (S2w)

Prepared according to general procedure A: Using methyl 4-bromofuran-2-carboxylate (2.50 g, 12.30 mmol) to afford carboxyl olefin **S2w** (1.39 g, 82%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d6) δ 13.22 (s, 1H), 8.20 – 7.93 (m, 1H), 7.54 – 7.37 (m, 1H), 6.57 (dd, J = 17.6, 10.9 Hz, 1H), 5.70 (dd, J = 17.6, 1.4 Hz, 1H), 5.22 (dd, J = 10.9, 1.4 Hz, 1H). MS (ESI-MS) m/z: 139 $[M + H]^+$.

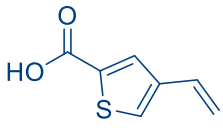


M. W. = 154.2

S2x

5-Vinylthiophene-3-carboxylic acid (S2x)

Prepared according to general procedure A: Using methyl 5-bromothiophene-3-carboxylate (2.00 g, 9.09 mmol) to afford carboxyl olefin **S2x** (930 mg g, 66%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d6) δ 12.74 (s, 1H), 8.20 – 8.05 (m, 1H), 7.40 (d, J = 1.4 Hz, 1H), 6.89 (dd, J = 17.5, 10.9 Hz, 1H), 5.60 (d, J = 17.5 Hz, 1H), 5.23 (d, J = 10.9 Hz, 1H). MS (ESI-MS) m/z: 155 $[M + H]^+$.



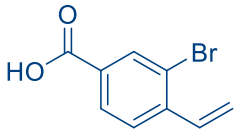
M. W. = 154.2

S2y

4-Vinylthiophene-2-carboxylic acid (S2y)

Prepared according to general procedure A: Using methyl 4-bromothiophene-2-carboxylate (2.00 g, 9.09 mmol) to afford carboxyl olefin **S2y** (1.04 g g, 74%) as

a white solid. ^{1}H NMR (400 MHz, DMSO-d6) δ 13.14 (s, 1H), 7.93 (d, J = 1.5 Hz, 1H), 7.80 (d, J = 1.4 Hz, 1H), 6.70 (dd, J = 17.7, 11.0 Hz, 1H), 5.76 (dd, J = 17.7, 1.2 Hz, 1H), 5.24 (dd, J = 10.9, 1.2 Hz, 1H). MS (ESI-MS) m/z: 155 [M + H]$^+$.



M. W. = 227.1

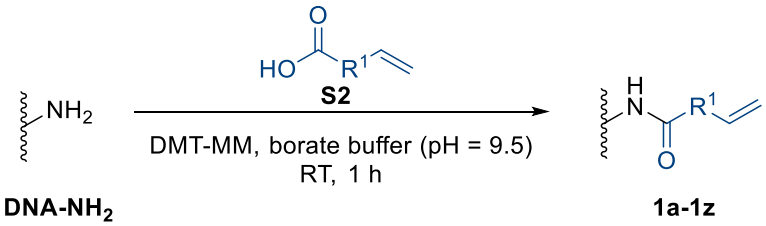
S2s

3-Bromo-4-vinylbenzoic acid (S2s)

A solution of methyltriphenylphosphanium bromide (3.56 g, 9.97 mmol, 1.2 equiv) in 1, 4-dioxane (40 mL) was treated with K_2CO_3 (1.72 g, 12.47 mmol, 1.5 equiv) for 30 minutes under nitrogen atmosphere followed by the addition of methyl 3-bromo-4-formylbenzoate (2.00 g, 8.31 mmol, 1.0 equiv) at room temperature for overnight. After completion, the resulting mixture was concentrated under reduced pressure. The residue was purified by reversed-phase flash chromatography to afford methyl 3-bromo-4-vinylbenzoate (1.53 g, 76%) as a white solid.

To a stirred solution of methyl 3-bromo-4-vinylbenzoate (1.50 g, 6.25 mmol, 1.0 equiv) in CH_3CN/H_2O (1:1) was added $LiOH·H_2O$ (525 mg, 12.5 mmol, 2.0 equiv) at 25 °C and stirred for 2 hours. After completion, the mixture was acidified to pH=2 with 1 N HCl. The residue was purified by silica gel column chromatography to afford 3-bromo-4-vinylbenzoic acid (**S2s**, 1.24 g, 88%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d6) δ 13.28 (s, 1H), 8.09 (d, J = 1.6 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.87 – 7.80 (m, 1H), 7.01 (dd, J = 17.4, 11.0 Hz, 1H), 6.00 (dd, J = 17.4, 0.9 Hz, 1H), 5.58 (dd, J = 11.0, 0.9 Hz, 1H). MS (ESI-MS) m/z: 227 [M + H]$^+$.

5.3. General Acylation Procedure of DNA-Conjugated Olefins

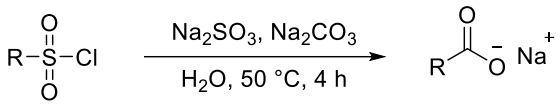


DNA-NH$_2$ **1a-1z**

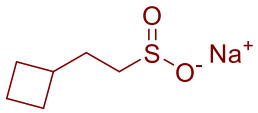
The modified carboxyl olefin (200.0 mM in DMSO, 10.0 μL, 40.0 equiv.) and DMT-MM (200.0 mM in H_2O, 10.0 μL, 40.0 equiv.) were mixed, which followed by

the addition of **DNA-NH$_2$** (1 mM in H_2O, 50.0 μL, 50.0 nmol, 1.0 equiv.) and borate buffer (250 mM, pH = 9.5, 50.0 μL). The reaction was quenched in 1 hour and precipitated with cold ethanol. The reaction conversion rates were in the range of 92% to >99%, determined by LC-MS analysis.

5.4. General Procedure for Synthesis of Sodium Sulfinates



General Procedure B. A solution of Na_2SO_3 (1.5 equiv) in H_2O was treated with Na_2CO_3 (2.0 equiv) for 20 minutes at 50 °C under nitrogen atmosphere followed by the addition of the corresponding sulfonyl chloride (1.0 equiv) dropwise and the resulting mixture was stirred for 2 hours at 50 °C. After completion of the reaction, the solvents were removed in vacuo, and the white residue was re-dissolve in hot EtOH. The resulting mixture was filtered, the filtrate was concentrated under reduced pressure to provide the corresponding sulfonate.

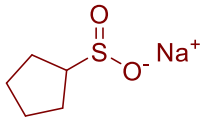


M. W. = 170.2

4c

Sodium 2-cyclobutylethane-1-sulfinate (4c)

Prepared according to general procedure B: Using 2-cyclobutylethane-1-sulfonyl chloride (1.00 g, 5.93 mmol) to afford sodium 2-cyclobutylethane-1-sulfinate (460 mg) as a crude product without further purification. Crude ^{1}H NMR (400 MHz, Deuterium Oxide) δ 2.39 – 2.25 (m, 3H), 2.11 – 1.98 (m, 2H), 1.93 – 1.75 (m, 2H), 1.70 – 1.57 (m, 4H).



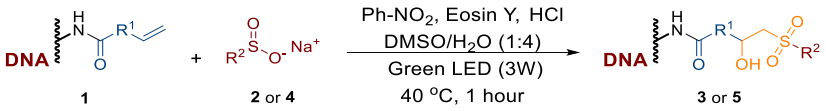
M. W. = 156.2

4h

Sodium cyclopentanecarboxylate (4h)

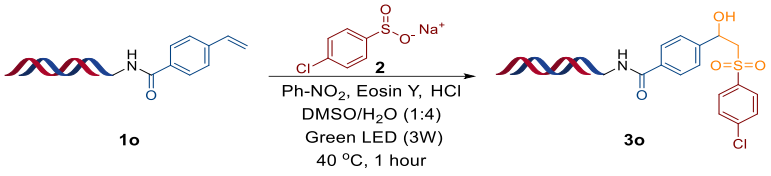
Prepared according to general procedure B: Using cyclopentanesulfonyl chloride (1.00 g, 5.49 mmol) to afford sodium cyclopentanecarboxylate (576 mg) as a crude product without further purification. Crude ^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.45 – 2.55 (m, 1H), 2.08 – 1.68 (m, 5H), 1.66 – 1.55 (m, 3H).

5.5. General Reaction Conditions for the Photocatalytic Sulfone Synthesis



General reaction conditions: A 0.6-mL centrifuge tube was charged with the DNA starting materials **1** (10.0 nmol, 1.0 equiv., 2.0 mM in H_2O, 5.0 μL, 0.8 mM final concentration), **2** or **4** (600.0 mM in H_2O, 5.0 μL, 240.0 mM final concentration), nitrobenzene (Ph-NO_2, 2,000.0 mM in DMSO, 0.5 μL, 80.0 mM final concentration) and photocatalyst (Eosin Y/HCl, 1:2, premixed, 250.0 mM in DMSO, 2.0 μL, Eosin Y with 40.0 mM final concentration). The reaction mixture was agitated and irradiated using green LEDs (535 nm) for 1 h at 40 °C. Afterwards, the sample was analyzed by LC-MS after EtOH precipitation. The reaction conversion rates were in the range of 36% to >99%, determined by LC-MS analysis.

5.6. Scale-up Procedure of On-DNA Sulfone

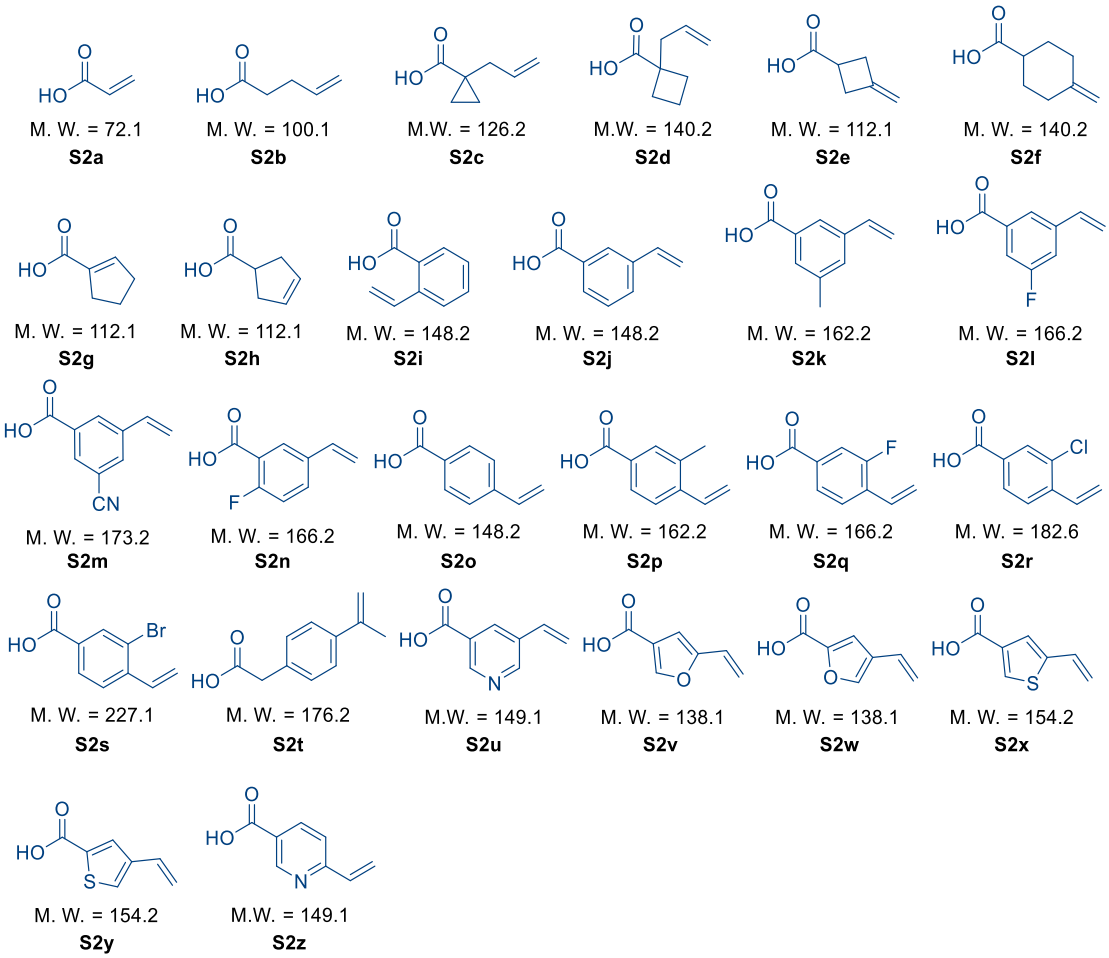


A 0.6-mL centrifuge tube was charged with the DNA starting materials **1o** (100.0 nmol, 1.0 equiv., 2.0 mM in H_2O, 50.0 μL, 0.8 mM final concentration), **2** (600.0 mM in H_2O, 50.0 μL, 240.0 mM final concentration), nitrobenzene (Ph-NO_2, 2,000.0 mM in DMSO, 5.0 μL, 80.0 mM final concentration) and photocatalyst (Eosin Y/HCl, 1:2, premixed, 250.0 mM in DMSO, 20.0 μL, Eosin Y with 40.0 mM final concentration). The reaction mixture was agitated and irradiated using green LEDs (535 nm) for 1 h at 40 °C. Afterwards, the sample was analyzed by LC-MS

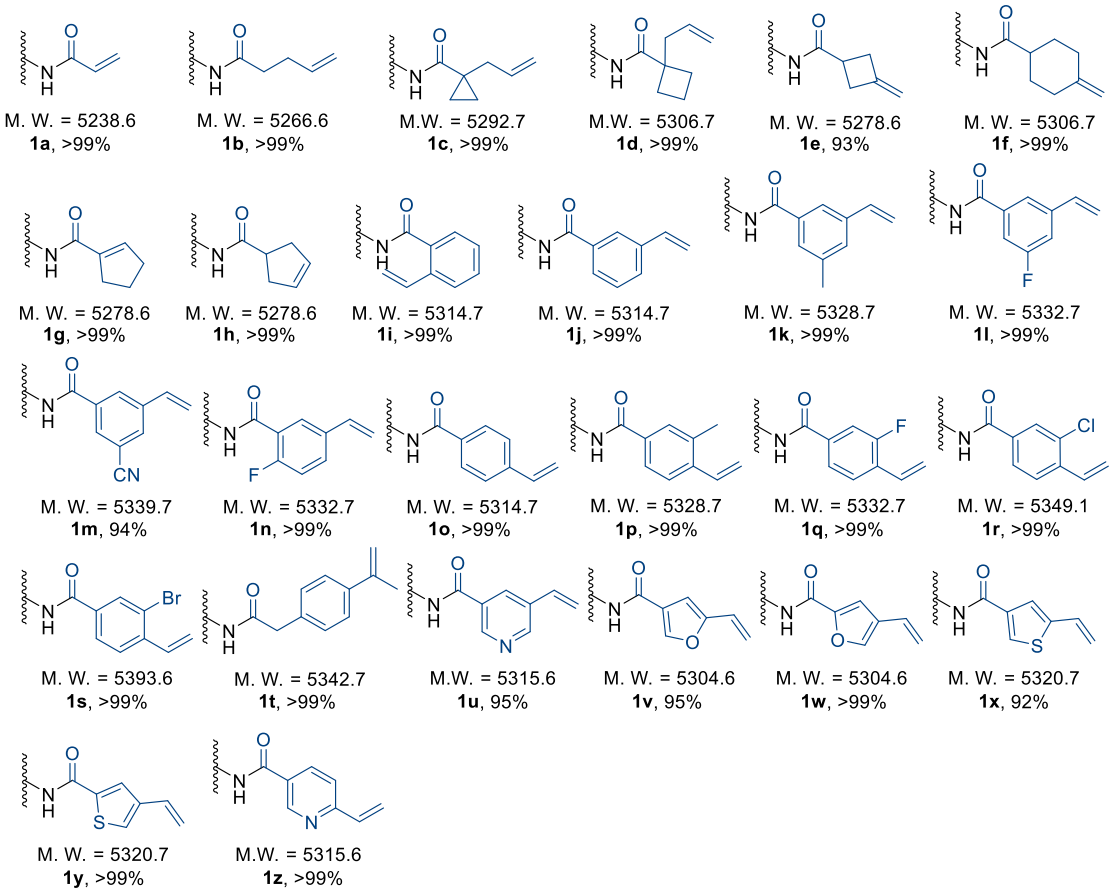
after EtOH precipitation. The reaction conversion rate was 84% determined by LC-MS analysis.

6. Structure, Purity, and Conversion

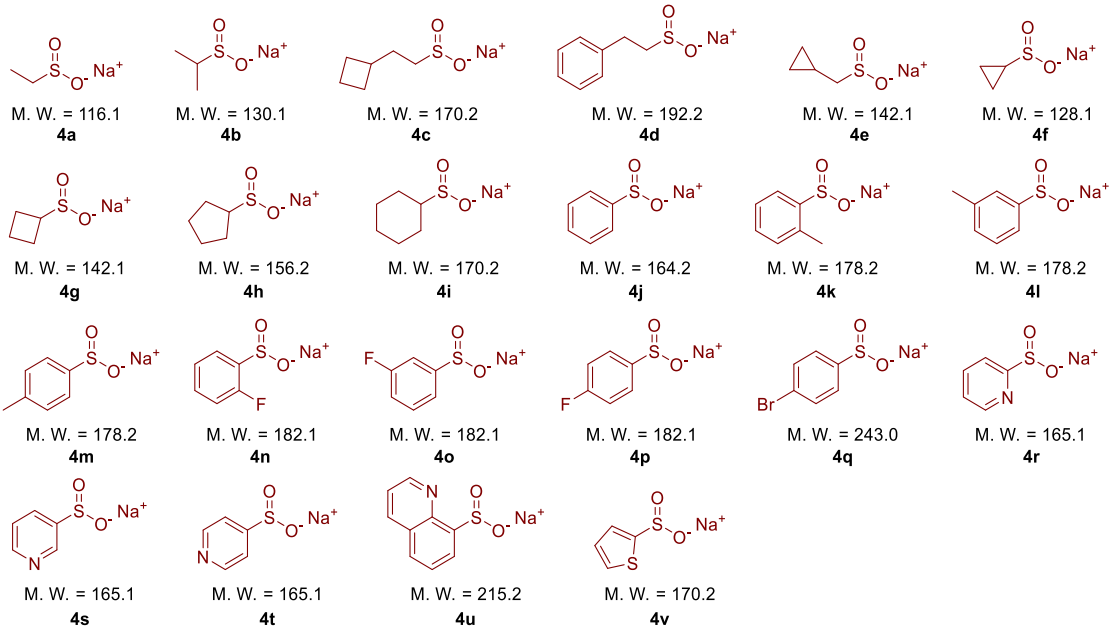
6.1. The Structure of Carboxyl Olefins



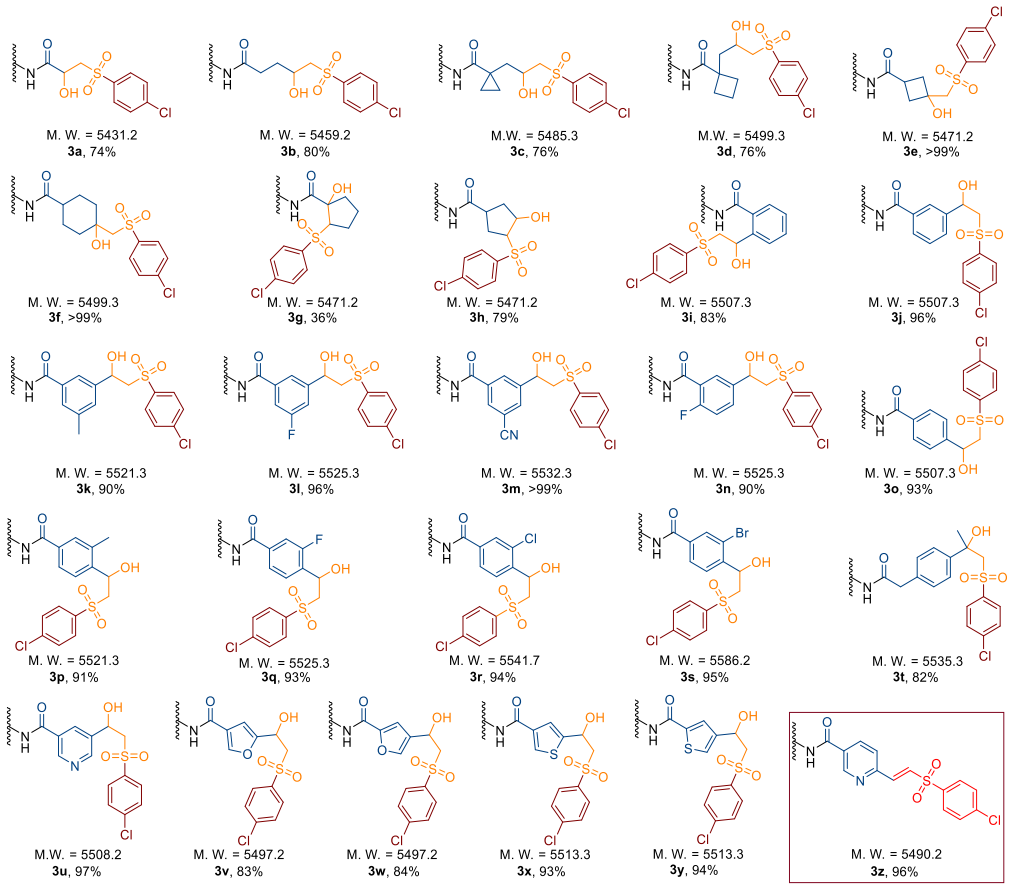
6.2. The Structure and Purity of DNA-Conjugated Compounds 1a-1z



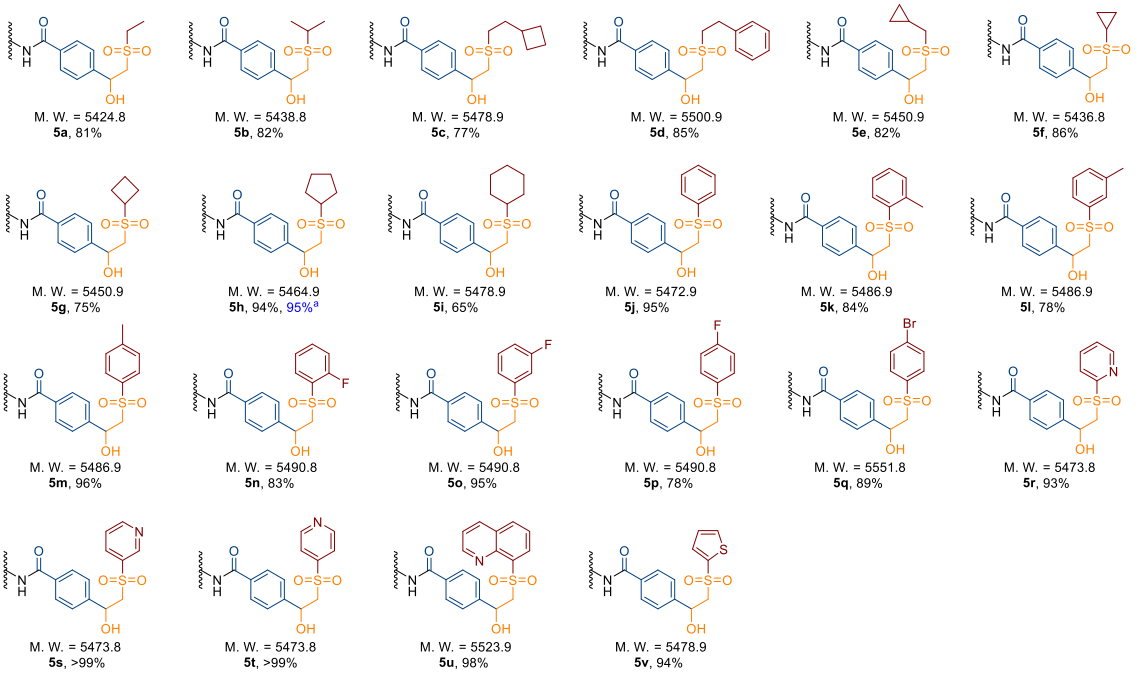
6.3. The Structure of Sodium Sulfinates



6.4. The Structure and Conversion Rate of DNA-Conjugated 3a-3z



6.5. The Structure and Conversion Rate of DNA-Conjugated 5a-5v



[a]When the sodium sulfinate (**4h**) used was a crude product synthesized in the

laboratory, the conversion rate of **5h** was 94%. When the sodium sulfinate (**4h**) used was obtained from commercial source (99% purity), the conversion rate of **5h** was 95%.

7. Synthesis of A Prototype DEL

Primer & Tags. The DNA Tags all 5 -ends were phosphorylated.

Primer Ligation: The **DNA-NH$_2$** (M.W. = 5184, 1.0 mM, 100.0 nmol, 1.0 equiv.) was dissolved in 100.0 µL water. Primer duplexes were added (M.W. = 9949, 110.0 µL of a 1.0 mM solution in water, 110.0 nmol, 1.1 equiv.), followed by 40.0 µL 10X ligation buffer and 120.0 U T4 DNA ligase, and H_2O to a final volume of 400.0 µl. The reaction mixture was incubated at 25 °C for 1 hour. The DNA product was precipitated with NaCl and ethanol and taken on to the first cycle of library synthesis without further purification. The product was 96 nmol determined by O.D. measurement.

DEL Cycle 1: A 1.0 mM solution of the primer-elongated AOP headpiece (**P-DNA-NH$_2$**, 96.0 nmol, 96.0 µL) was split into 6 wells (16.0 nmol/well). To each well was then added 6.4 µL of 10X ligation buffer, 19.2 U T4 DNA ligase, 1 of 6 Tag A solutions (M.W. = 8404, 17.6 µL of 1.0 mM stock solutions in water), and H_2O to a final volume of 64.0 µl. The ligation was agitated at 25 °C for 1 hour. The DNA was precipitated to afford the pellet (**A-P-DNA-NH$_2$**), which was then dissolved in 16.0 µL of distilled H_2O.

To a solution of 1 of 6 carboxyl olefins (200.0 mM in DMSO, 3.2 µL, 40.0 eq) and DMT-MM (200.0 mM in H_2O, 3.2 µL, 40.0 equiv.), which followed by the addition of **A-P-DNA-NH$_2$** (1.0 mM in H_2O, 16.0 µL, 16.0 nmol/well, 1.0 equiv.) and borate buffer (pH = 9.5, 16.0 µL). The acylation mixture was agitated at 25 °C for 1 hour. All reactions were monitored by LC-MS. After completion, the reactions

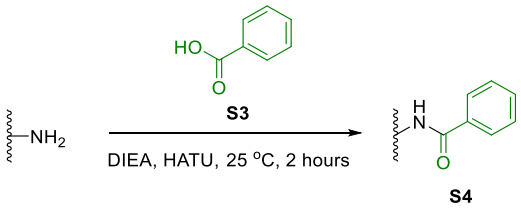
were pooled and then precipitated with ethanol to yield 72.0 nmol of crude cycle 1 products, the cycle 1 products were dissolved in 72.0 μL of distilled H_2O. The OD measurement was used to quantify the reaction yields.

DEL Cycle 2: The cycle 1 products (72.0 nmol, 72.0 μL) were split into 6 wells (12.0 nmol/well, 12.0 μL/well). To each well was then added 4.8 μL of 10X ligation buffer, 14.4 U T4 DNA ligase, 1 of 6 Tag B solutions (M.W. = 8103.0, 13.2 μL of 1.0 mM stocks in water), and H_2O to a final volume of 48.0 μl. The reaction mixture was agitated at 25 °C for 1 hour. The DNA was precipitated to afford the pellet.

Then, to each well (**B-A-P-DNA-NH_2-BB1**, 12.0 nmol, 1.0 equiv., 2.0 mM in H_2O, 6.0 μL, 0.8 mM final concentration) was added 1 of 6 sodium sulfinates (600.0 mM in H_2O, 6.0 μL, 240.0 mM final concentration), nitrobenzene (Ph-NO_2, 2,000.0 mM in DMSO, 0.6 μL, 80.0 mM final concentration) and photocatalyst (Eosin Y/HCl, 1:2, premixed, 250.0 mM in DMSO, 2.4 μL, Eosin Y with 40.0 mM final concentration). The reaction mixture was agitated and irradiated using green LEDs (535 nm) for 1 h at 40 °C. All reactions were monitored by LC-MS. After completion, the reactions were pooled, precipitated with ethanol, and purified by reverse-phase HPLC, yielded 45.0 nmol of products.

8. Control Experiment

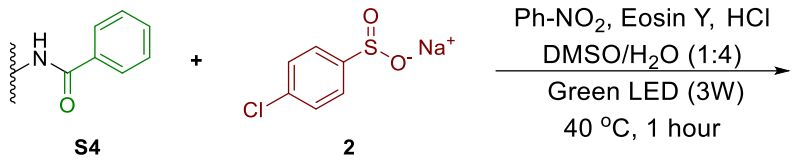
8.1. General Procedure for the Synthesis of S4



Into a tube was loaded with **S3** (20.0 μL, 200.0 mM in DMSO, 80.0 equiv.), HATU (12.5 μL, 200.0 mM in DMSO, 50.0 equiv.), DIEA (125.0 μL, 200.0 mM in DMSO, 500.0 equiv.) and **DNA-NH_2** (50.0 μL, 1.0 mM in H_2O, 1.0 equiv.). The reaction mixture was agitated at 25.0 °C for 2 hours and monitored by LC-MS. After

ethanol precipitation, the obtained solid was dissolved in distilled water and then directly used for the next step without further purification.

8.2. General Procedure for Photoreaction of S4



S4 **2**

A 0.6-mL centrifuge tube was charged with the DNA starting materials **S4** (10.0 nmol, 1.0 equiv., 2.0 mM in H_2O, 5.0 μL, 0.8 mM final concentration), **2** (600.0 mM in H_2O, 5.0 μL, 240.0 mM final concentration), nitrobenzene (Ph-NO_2, 2,000.0 mM in DMSO, 0.5 μL, 80.0 mM final concentration) and photocatalyst (Eosin Y/HCl, 1:2, premixed, 250.0 mM in DMSO, 2.0 μL, Eosin Y with 40.0 mM final concentration). The reaction mixture was agitated and irradiated using green LEDs (535 nm) for 1 h at 40 °C. Afterwards, the sample was analyzed by LC-MS after EtOH precipitation. The reaction was determined by LC-MS analysis.

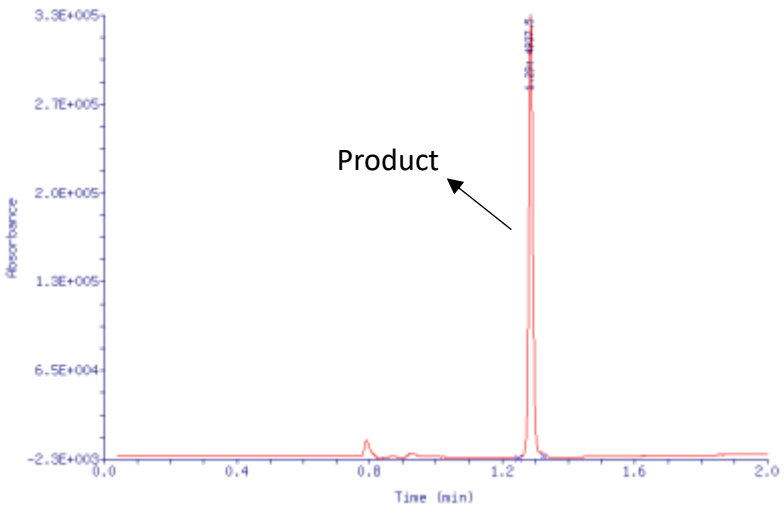
9. Characterization Data

9.1. Mass Spectrum of Starting Material (HP)

HP

Conversion rate: 100%
Expected mass: 4937.2
Observed mass: 4937.5

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.29	4937.5	3.76E+005	ok	2.80E+005	100.00

Deconvoluted mass spectrum of product:

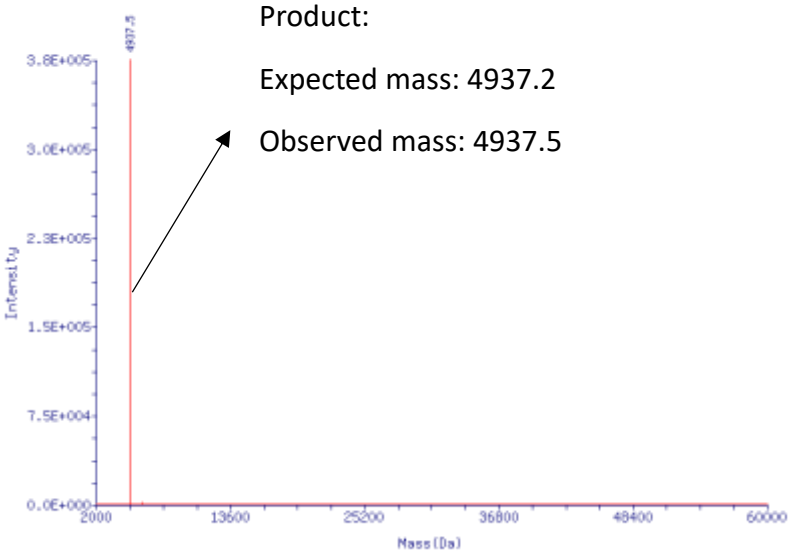
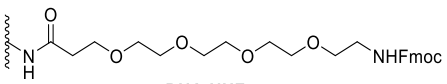


Figure S2. LC-MS Spectrum of compound **HP**.

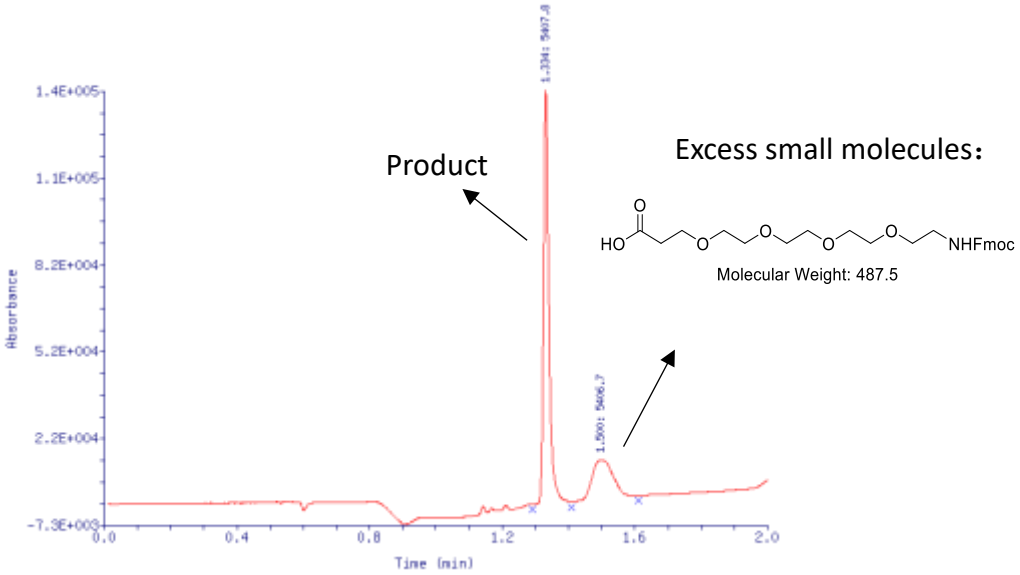
9.2. Mass Spectrum of DNA-NHFmoc



DNA-NHFmoc

Conversion rate: 100%
Expected mass: 5406.7
Observed mass: 5407.8

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.334	5407.8	1.08E+005	ok	1.69E+005	69.04
1.500	5406.7	2.02E+003	ok	7.57E+004	30.96

Deconvoluted mass spectrum of product:

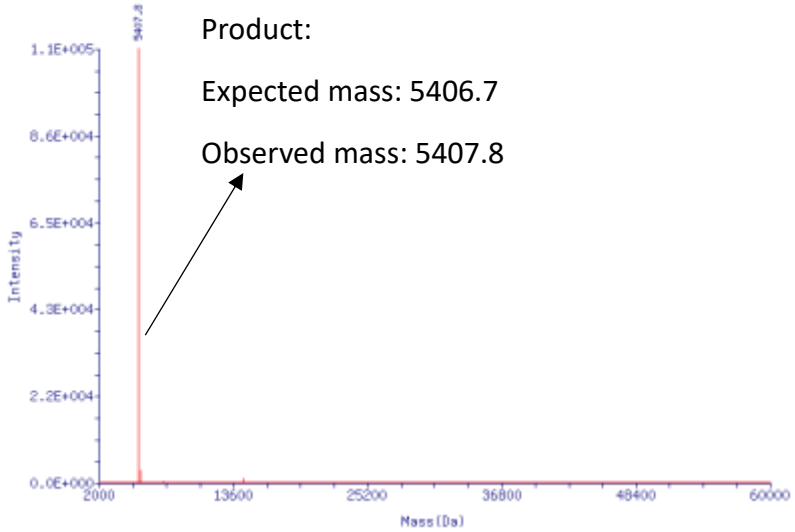
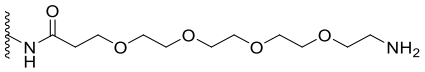


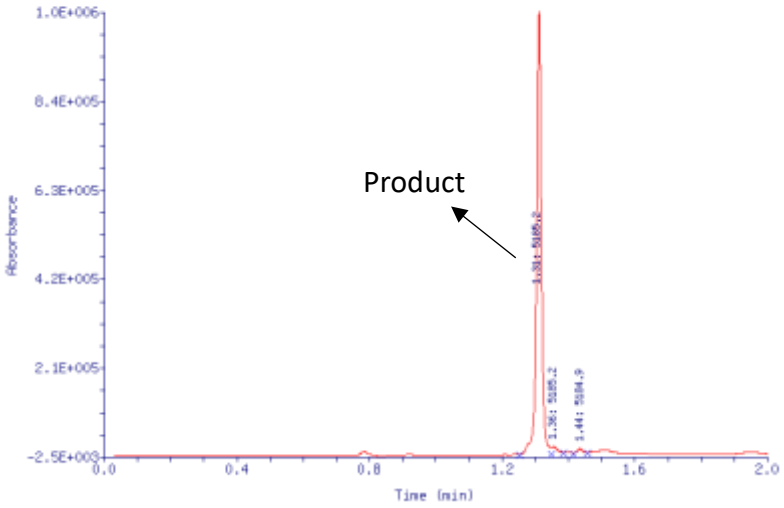
Figure S3. LC-MS Spectrum of **DNA-NHFmoc**.

9.3. Mass Spectrum of DNA-NH_2



DNA-NH_2
Conversion rate: 96%
Expected mass: 5184.5
Observed mass: 5185.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.31	5185.2	5.43E+005	ok	1.04E+006	97.61
1.36	5185.2	2.82E+005	ok	1.63E+004	1.53
1.44	5184.9	4.26E+004	ok	9.16E+003	0.86

Deconvoluted mass spectrum of product:

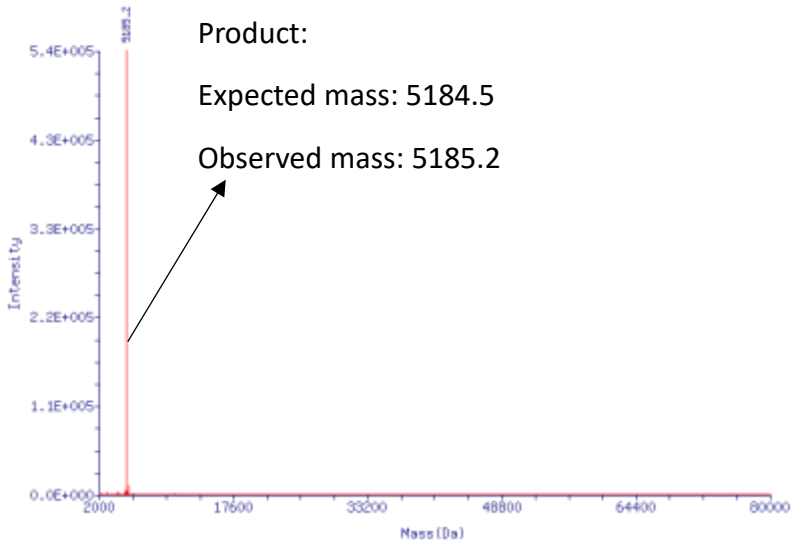


Figure S4. LC-MS Spectrum of **DNA-NH$_2$**.

9.4. ^{1}H NMR Study of Off-DNA Carboxyl Olefins

^{1}H NMR spectrum for 3-cyano-5-vinylbenzoic acid (**S2m**), DMSO-d6, 400 MHz:

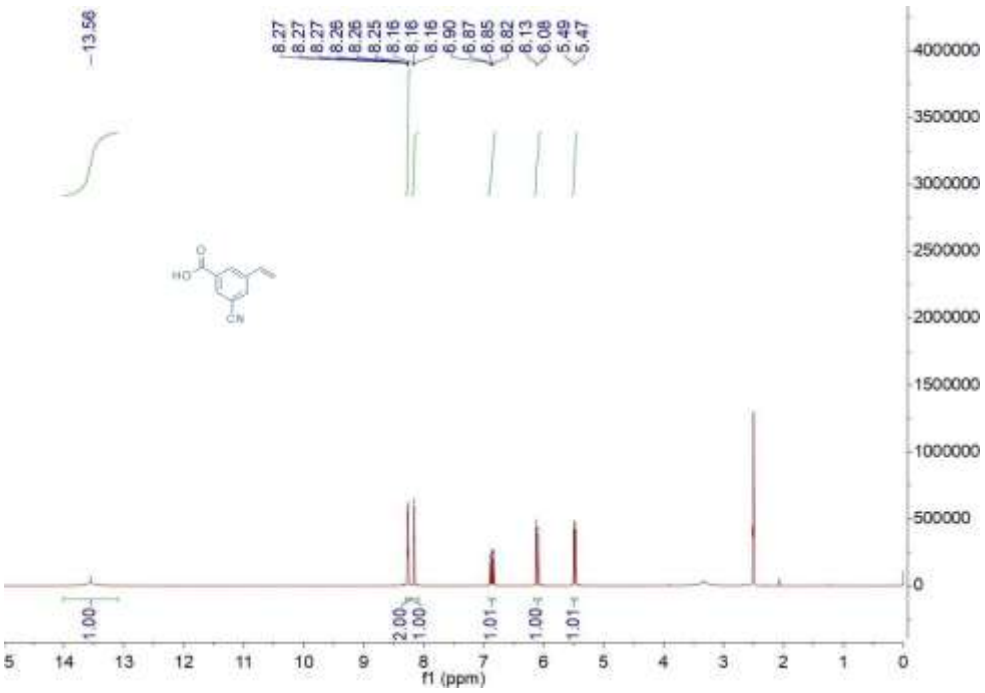


Figure S5. [1]H NMR spectrum of **S2m**.

1H NMR spectrum for 3-methyl-4-vinylbenzoic acid (**S2p**), DMSO-d6, 400 MHz:

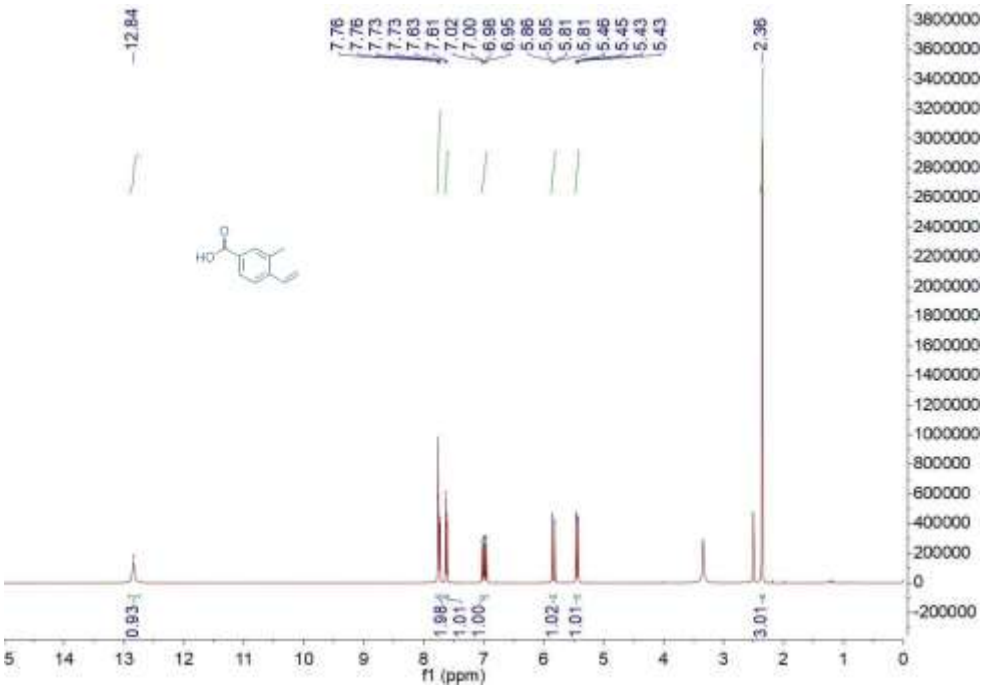


Figure S6. [1]H NMR spectrum of **S2p**.

[1]H NMR spectrum for 3-chloro-4-vinylbenzoic acid (**S2r**), DMSO-d6, 400 MHz:

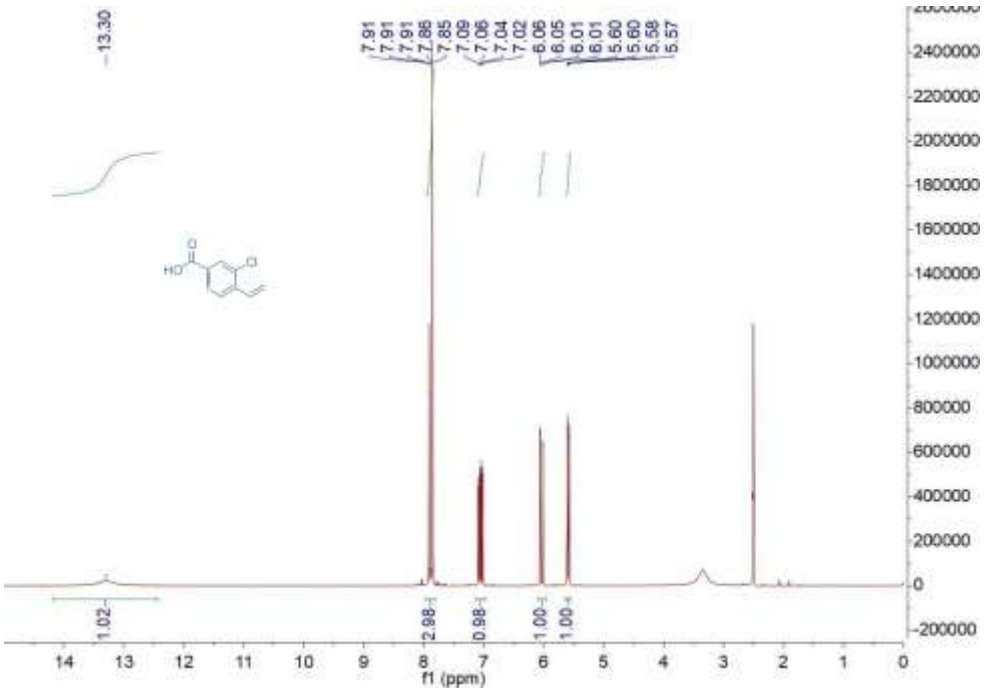


Figure S7. ^{1}H NMR spectrum of **S2r**.

^{1}H NMR spectrum for 4-vinylfuran-2-carboxylic acid (**S2w**), DMSO-d6, 400 MHz:

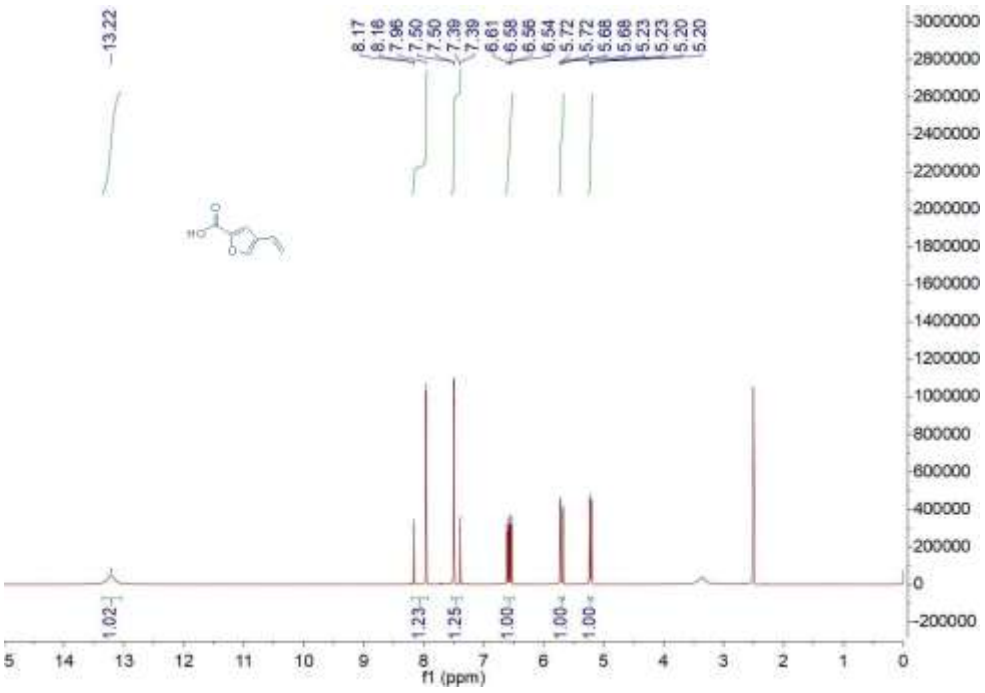


Figure S8. ^{1}H NMR spectrum of **S2w**.

^{1}H NMR spectrum for 5-vinylthiophene-3-carboxylic acid (**S2x**), DMSO-d6, 400 MHz:

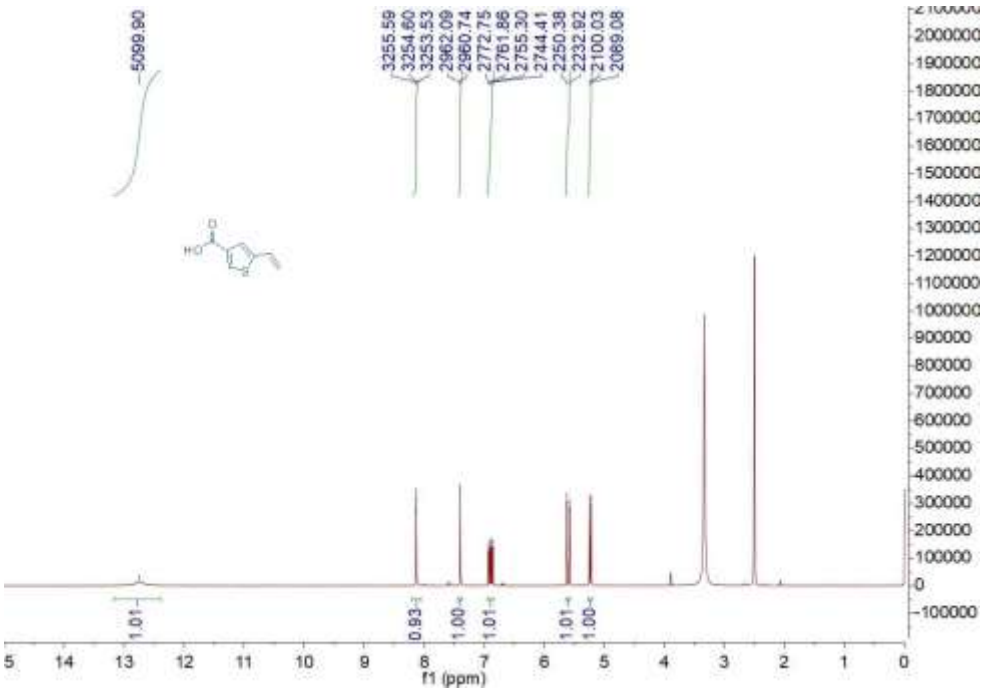


Figure S9. ^{1}H NMR spectrum of **S2x**.

^{1}H NMR spectrum for 4-vinylthiophene-2-carboxylic acid (**S2y**), DMSO-d6, 400 MHz:

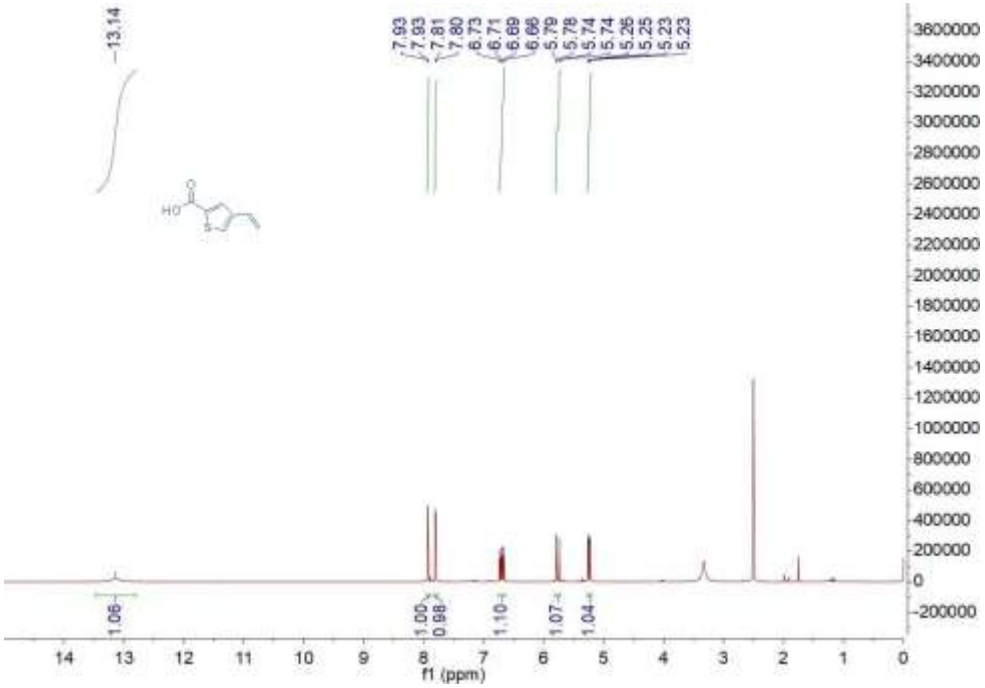


Figure S10. ^{1}H NMR spectrum of **S2y**.

^{1}H NMR spectrum for 3-bromo-4-vinylbenzoic acid (**S2s**), DMSO-d6, 400 MHz:

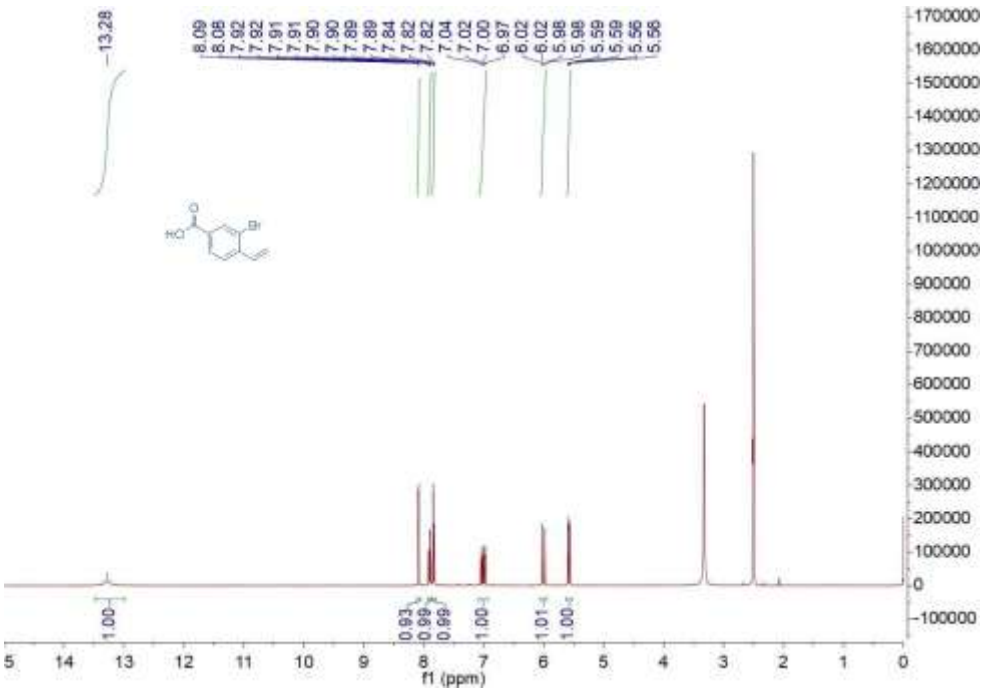
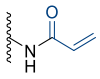


Figure S11. ^{1}H NMR spectrum of **S2s**.

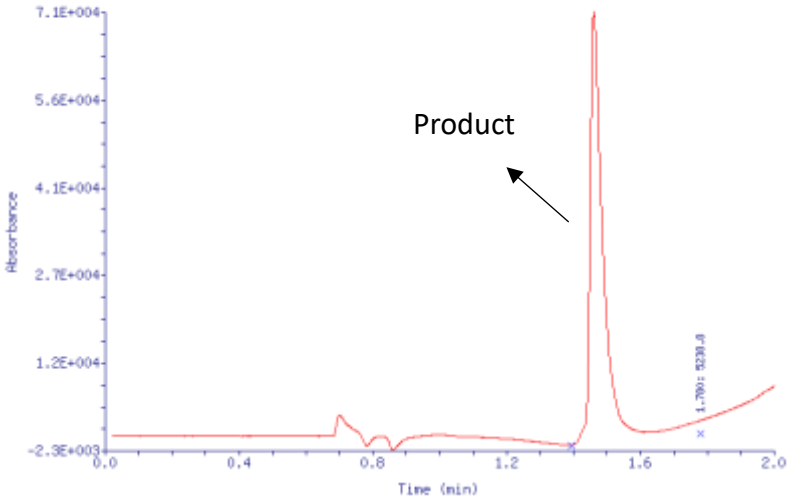
9.5. Mass Spectrum of DNA-Conjugated Olefins



1a

Purity: >99%
Expected mass: 5238.6
Observed mass: 5238.8

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.780	5238.8	9.94E+003	ok	2.00E+005	100.00

Deconvoluted mass spectrum of product:

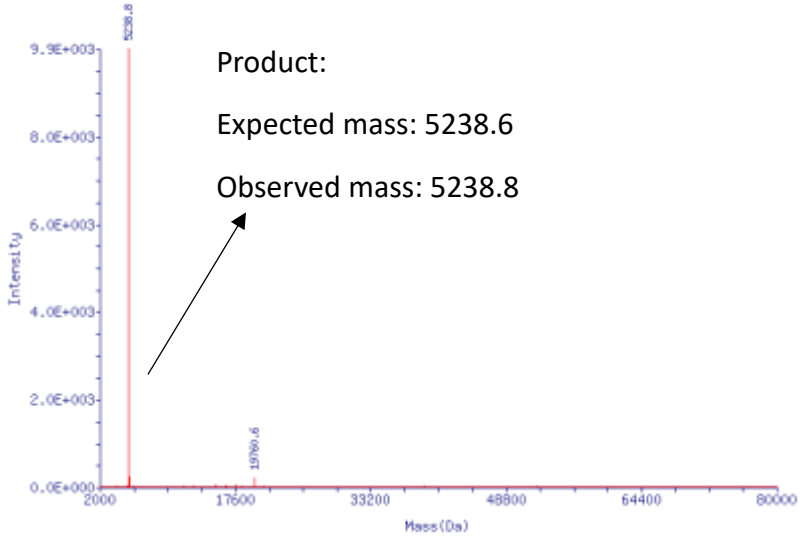
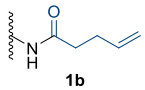


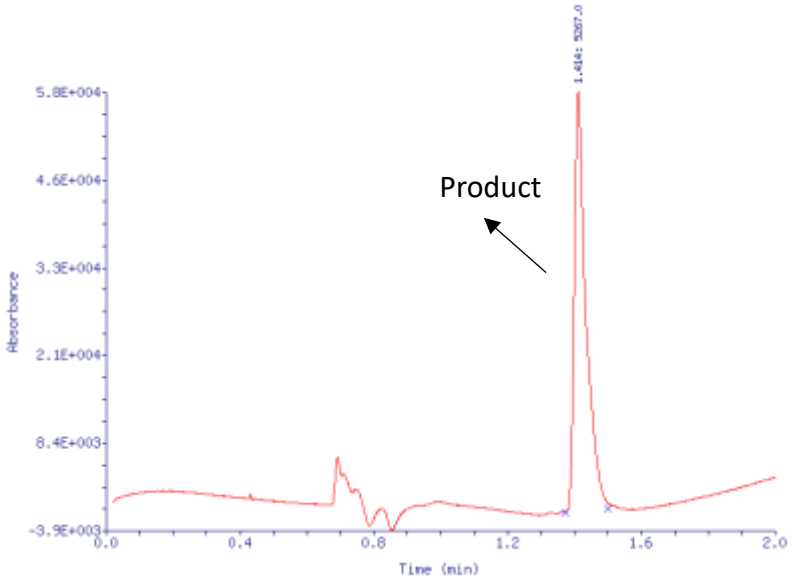
Figure S12. LC-MS Spectrum of Compound **1a**.



1b

Purity: >99%
Expected mass: 5266.6
Observed mass: 5267.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.414	5267.0	1.00E+005	ok	1.43E+005	100.00

Deconvoluted mass spectrum of product:

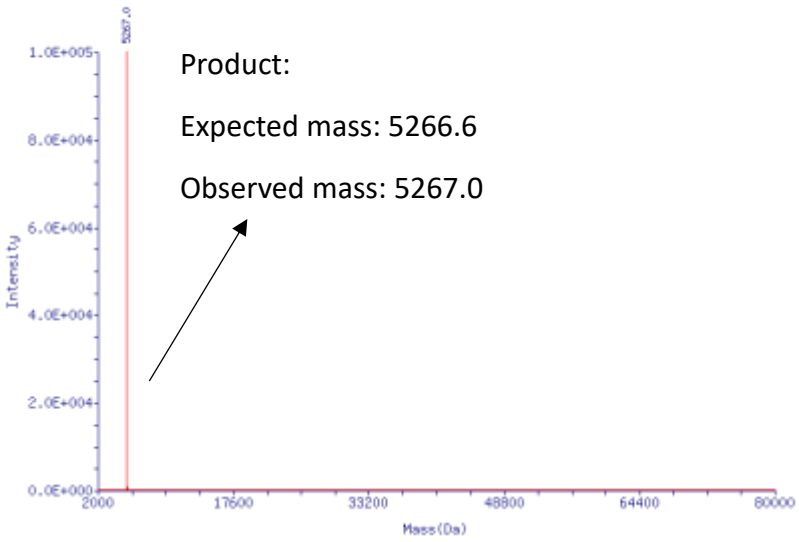
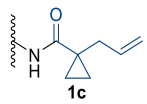


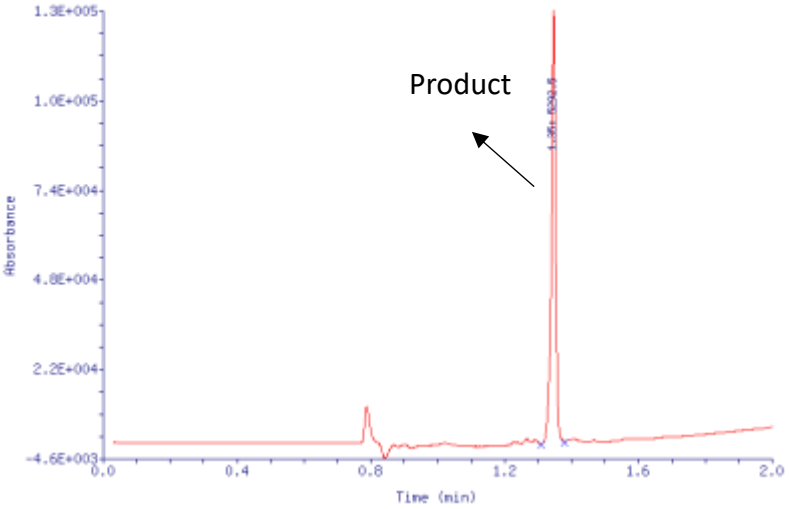
Figure S13. LC-MS Spectrum of Compound **1b**.



1c

Purity: >99%
Expected mass: 5292.7
Observed mass: 5292.5

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.35	5292.5	5.98E+005	ok	1.10E+005	100.00

Deconvoluted mass spectrum of product:

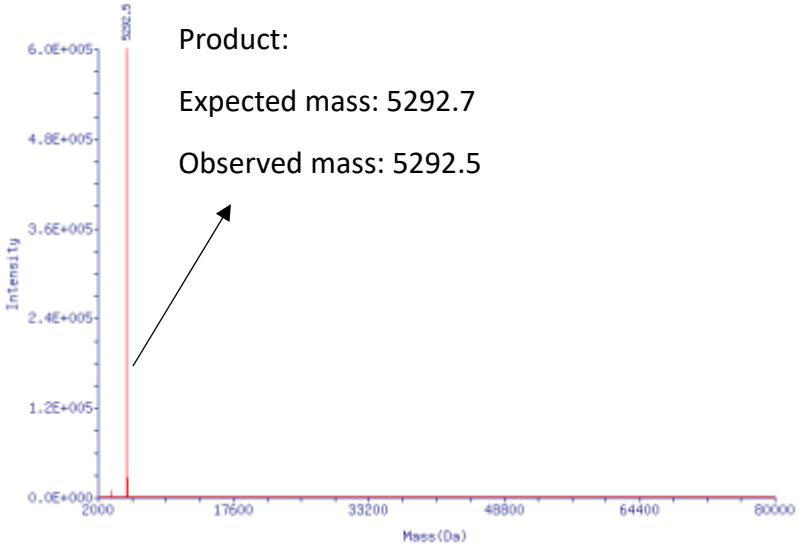
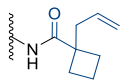


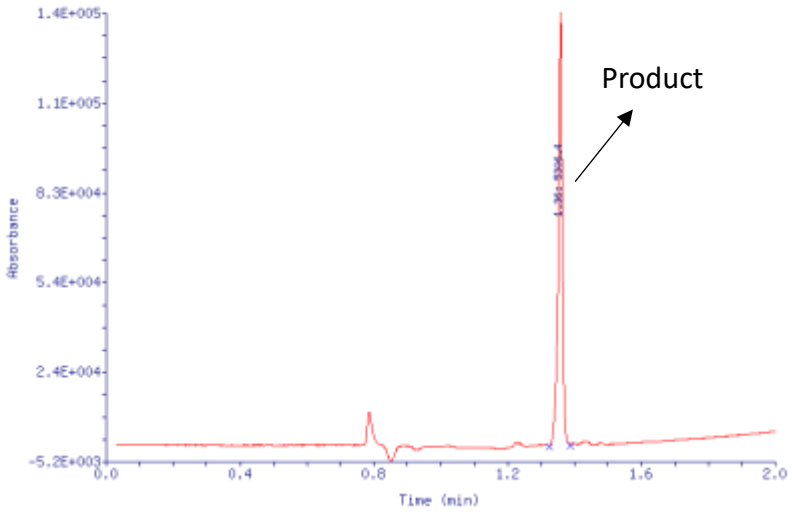
Figure S14. LC-MS Spectrum of Compound **1c**.



1d

Purity: >99%
Expected mass: 5306.7
Observed mass: 5306.4

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.36	5306.4	7.01E+005	ok	1.21E+005	100.00

Deconvoluted mass spectrum of product:

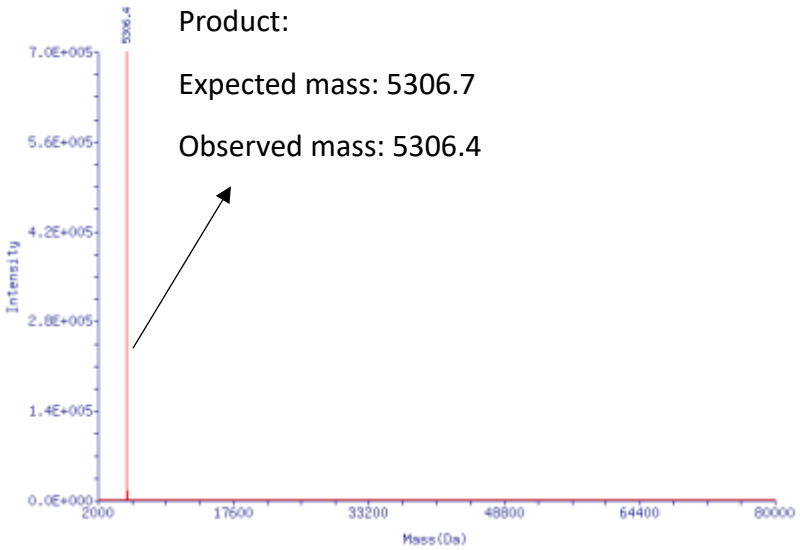
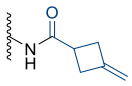
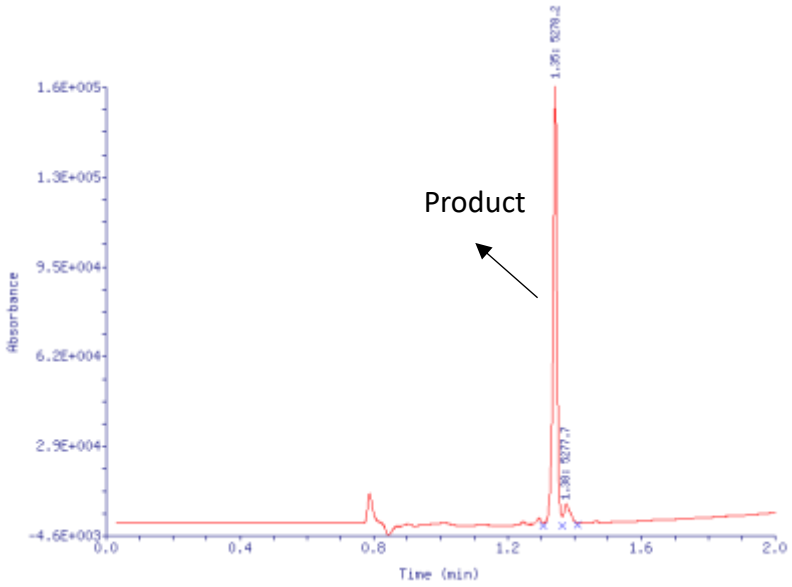


Figure S15. LC-MS Spectrum of Compound **1d**.



1e
Purity: 93%
Expected mass: 5278.6
Observed mass: 5278.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.35	5278.2	2.80E+005	ok	1.30E+005	92.97
1.38	5277.7	6.80E+004	ok	9.87E+003	7.03

Deconvoluted mass spectrum of product:

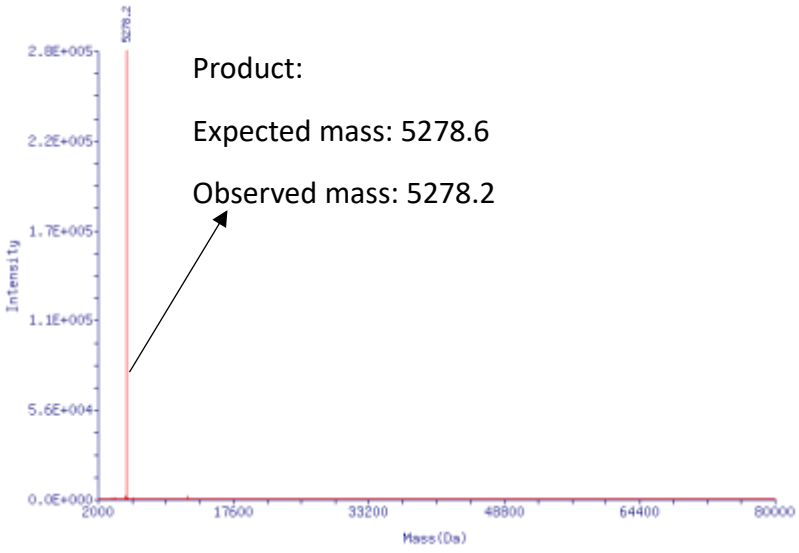
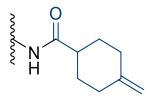


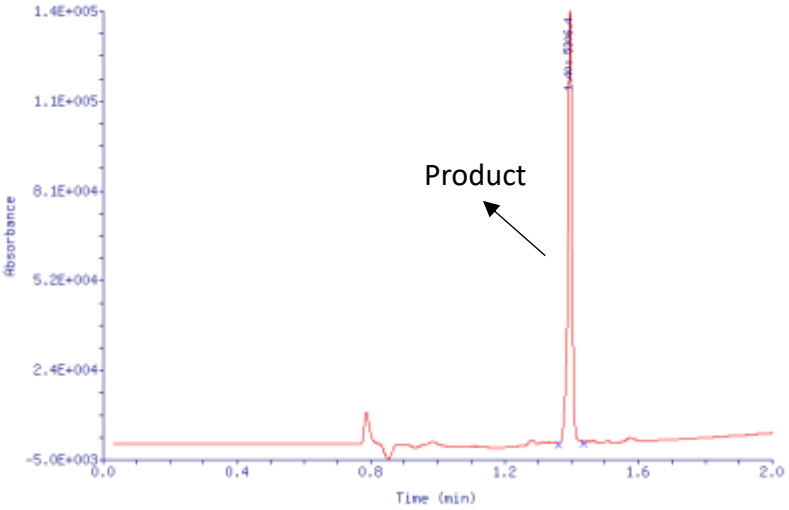
Figure S16. LC-MS Spectrum of Compound **1e**.



1f

Purity: >99%
Expected mass: 5306.7
Observed mass: 5306.4

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.40	5306.4	4.84E+005	ok	1.18E+005	100.00

Deconvoluted mass spectrum of product:

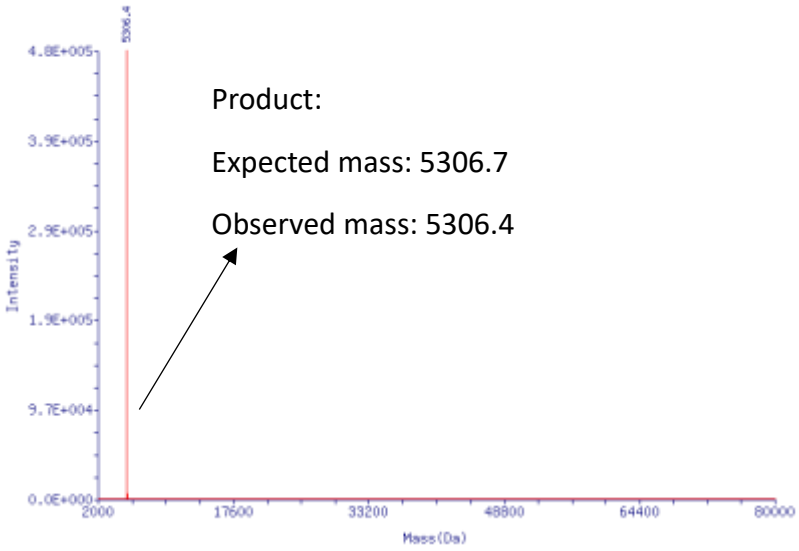
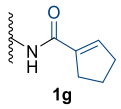


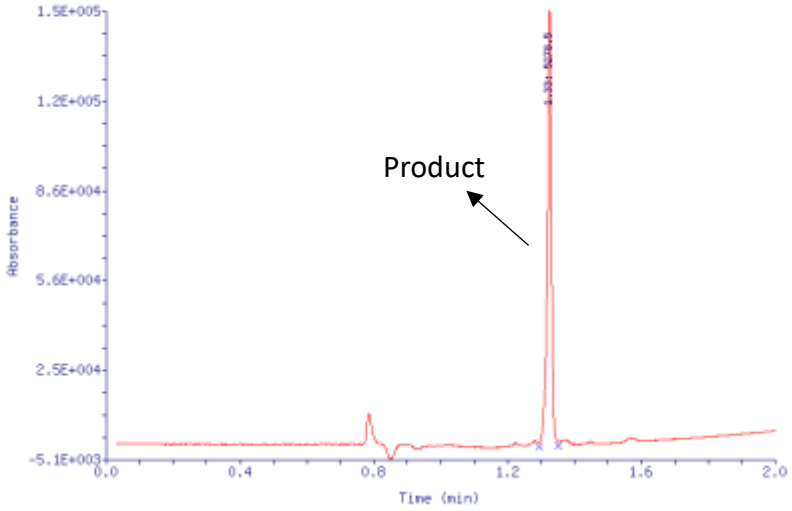
Figure S17. LC-MS Spectrum of Compound **1f**.



1g

Purity: >99%
Expected mass: 5278.6
Observed mass: 5278.5

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.33	5278.5	7.46E+005	ok	1.25E+005	100.00

Deconvoluted mass spectrum of product:

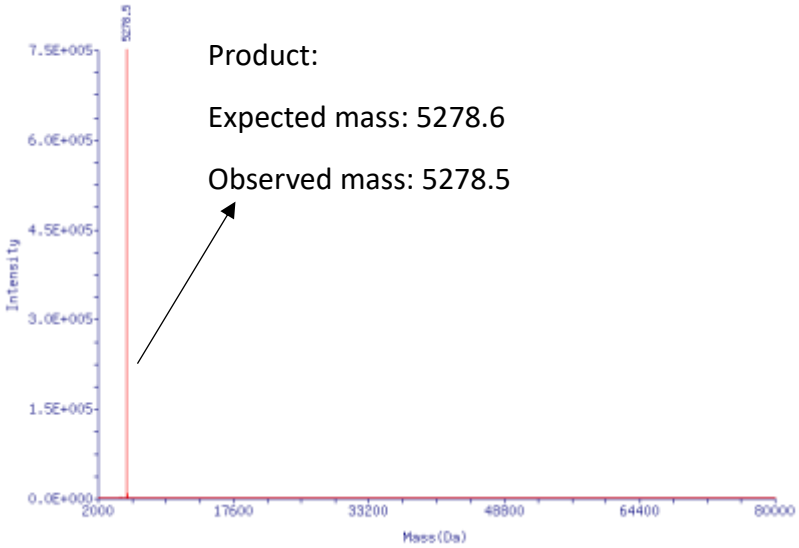
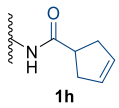


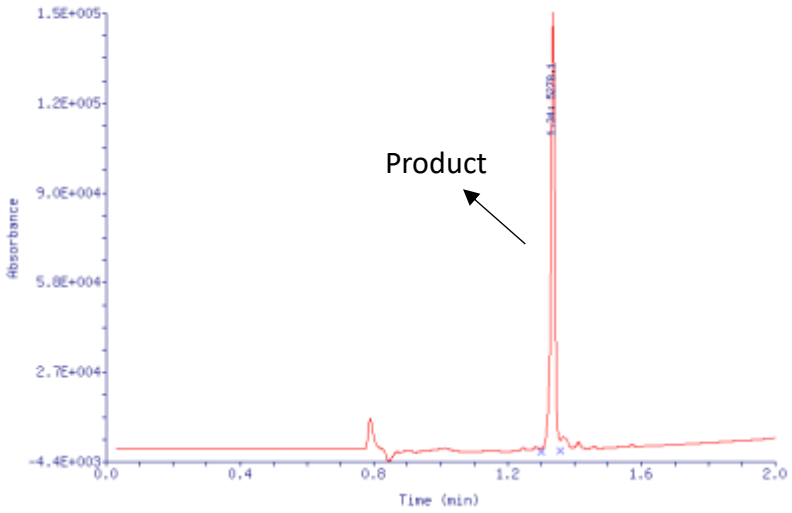
Figure S18. LC-MS Spectrum of Compound **1g.**



1h

Purity: >99%
Expected mass: 5278.6
Observed mass: 5278.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.34	5278.1	2.39E+005	ok	1.25E+005	100.00

Deconvoluted mass spectrum of product:

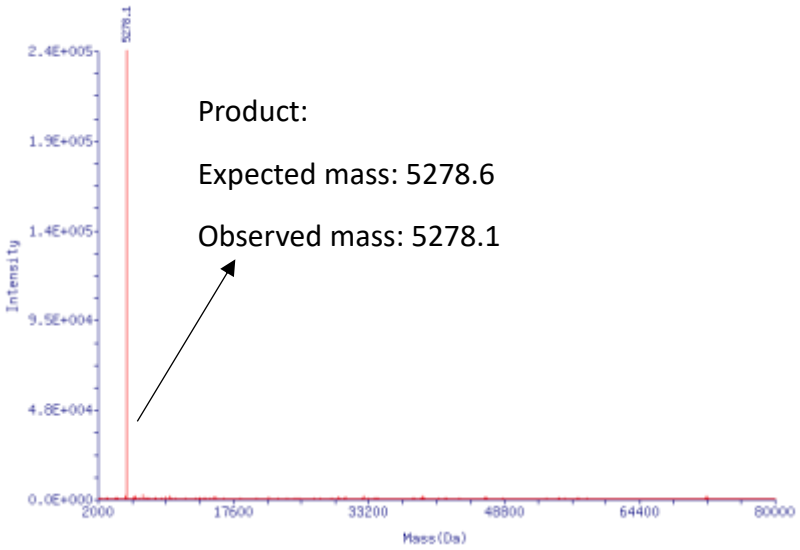
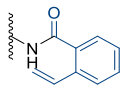


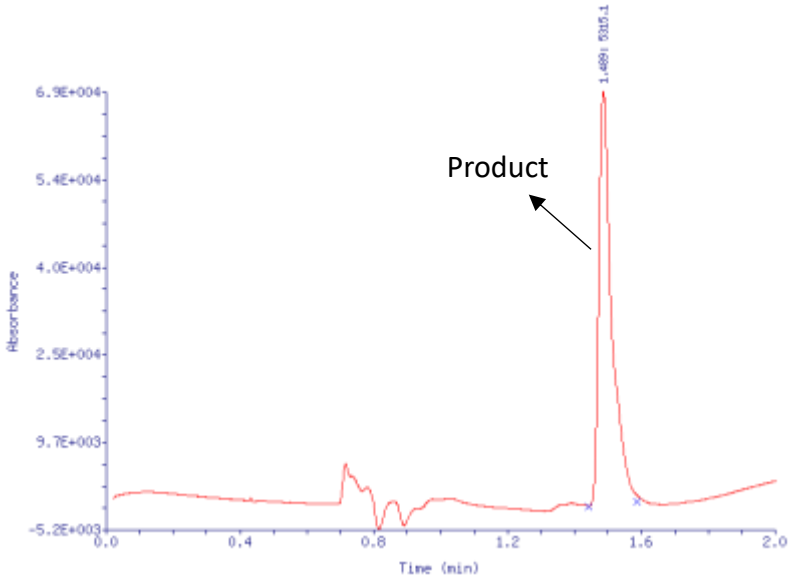
Figure S19. LC-MS Spectrum of Compound **1h**.



1i

Purity: >99%
Expected mass: 5314.7
Observed mass: 5315.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.489	5315.1	1.26E+005	ok	1.88E+005	100.00

Deconvoluted mass spectrum of product:

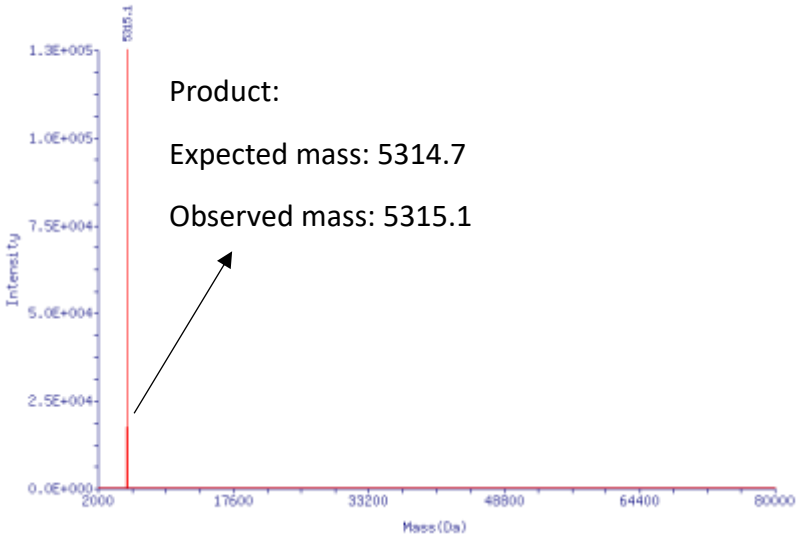
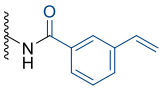


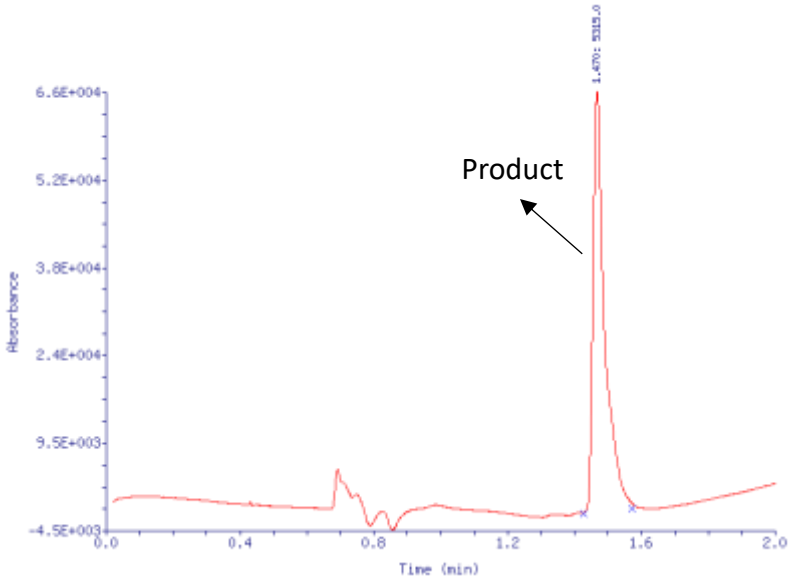
Figure S20. LC-MS Spectrum of Compound **1i**.



1j

Purity: >99%
Expected mass: 5314.7
Observed mass: 5315.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.470	5315.0	9.75E+004	ok	1.62E+005	100.00

Deconvoluted mass spectrum of product:

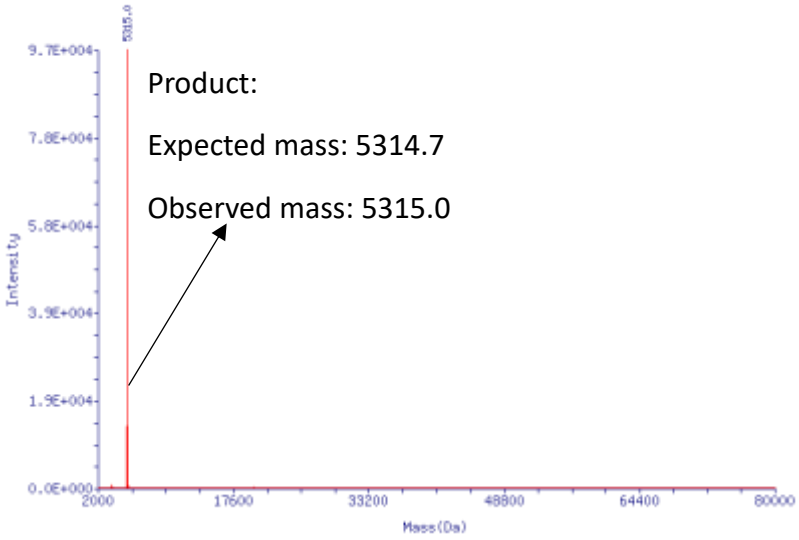
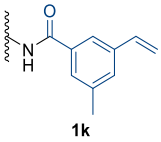


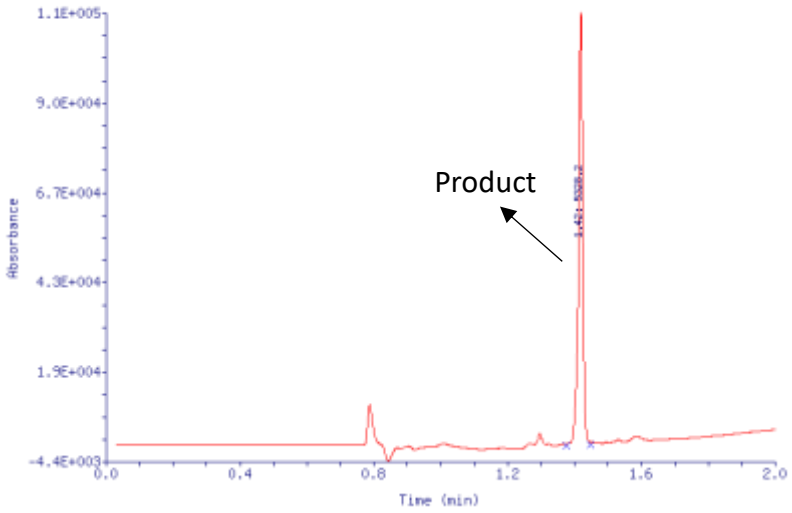
Figure S21. LC-MS Spectrum of Compound **1j**.



1k

Purity: >99%
Expected mass: 5328.7
Observed mass: 5328.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.42	5328.2	3.30E+005	ok	9.92E+004	100.00

Deconvoluted mass spectrum of product:

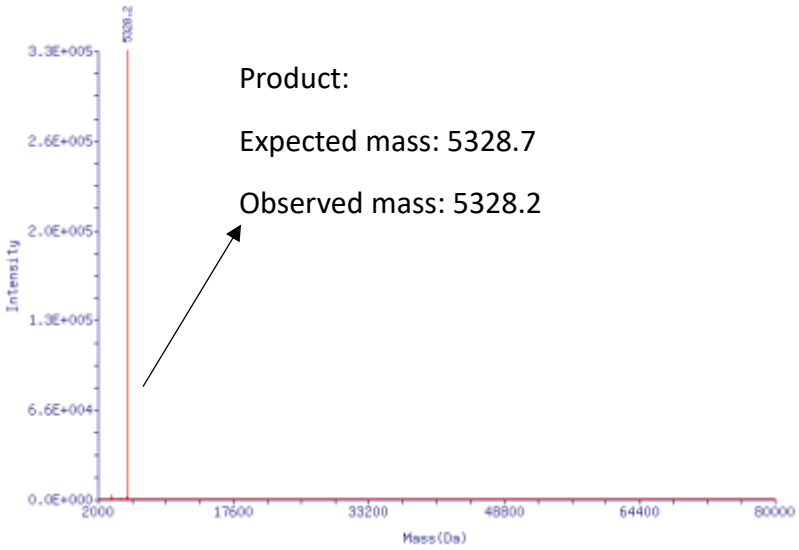
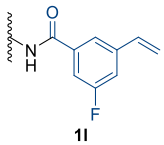


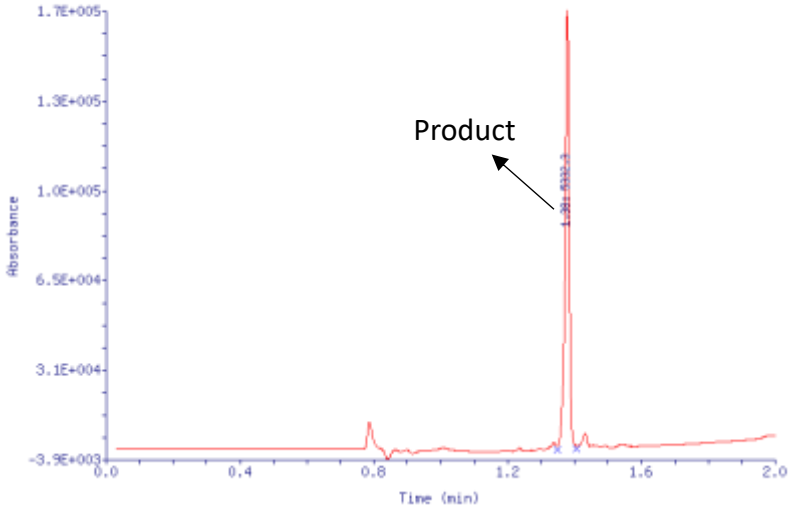
Figure S22. LC-MS Spectrum of Compound **1k**.



1l

Purity: >99%
Expected mass: 5332.7
Observed mass: 5332.3

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.38	5332.3	7.13E+005	ok	1.42E+005	100.00

Deconvoluted mass spectrum of product:

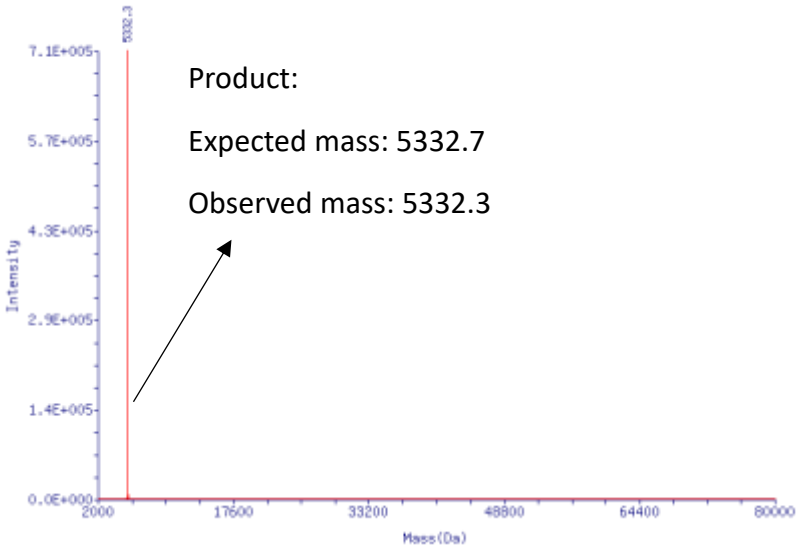
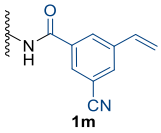


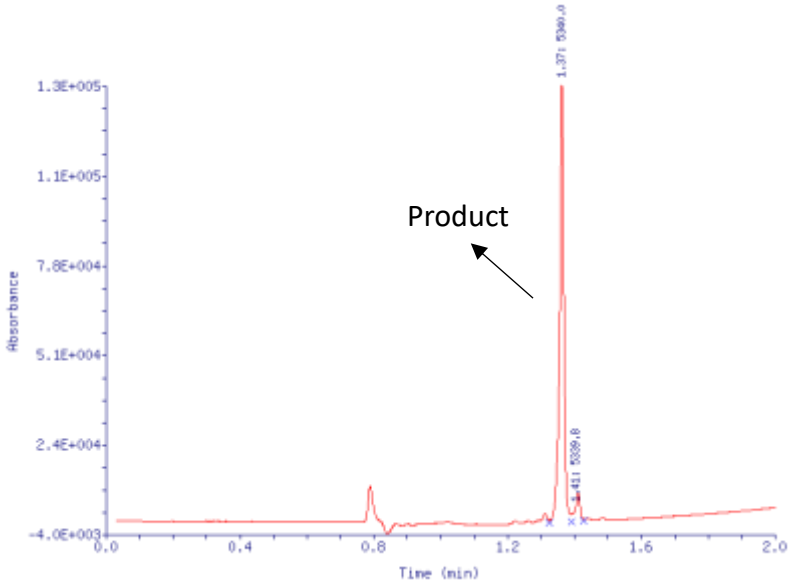
Figure S23. LC-MS Spectrum of Compound **1l**.



1m

Purity: 94%
Expected mass: 5339.7
Observed mass: 5340.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.37	5340.0	5.95E+005	ok	1.21E+005	93.72
1.41	5339.8	6.37E+004	ok	8.12E+003	6.28

Deconvoluted mass spectrum of product:

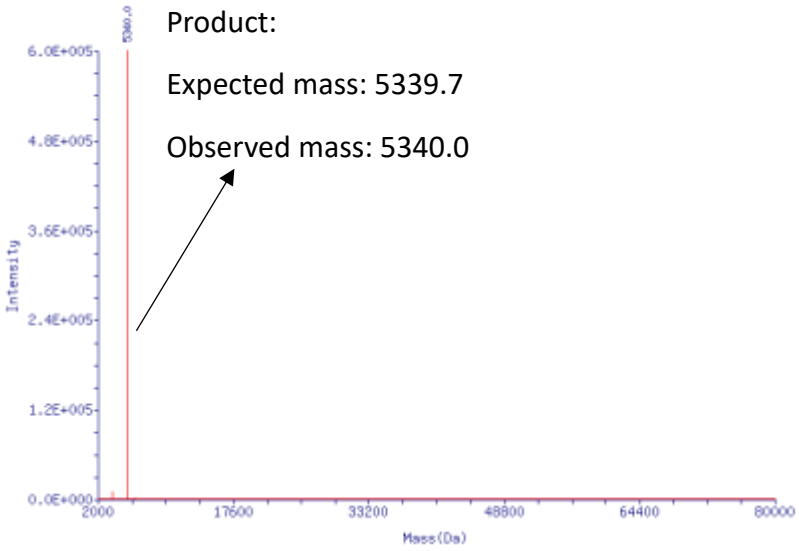
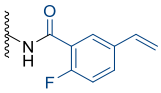


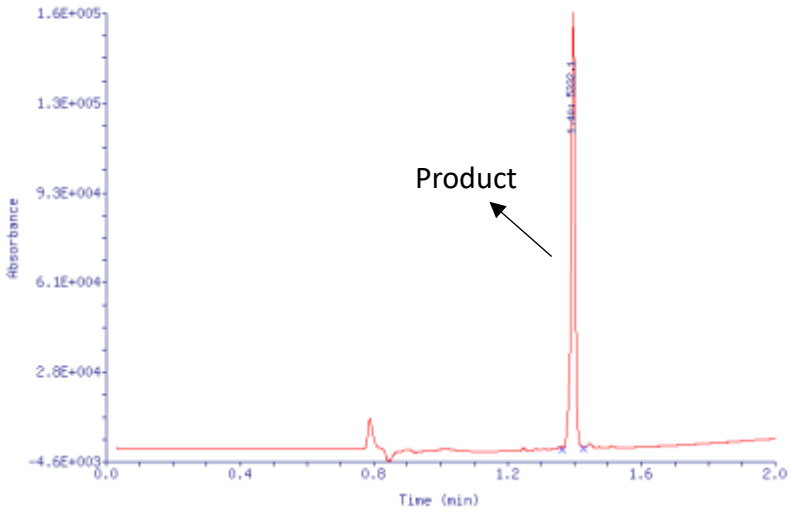
Figure S24. LC-MS Spectrum of Compound **1m**.



1n

Purity: >99%
Expected mass: 5332.7
Observed mass: 5332.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.40	5332.1	2.61E+005	ok	1.31E+005	100.00

Deconvoluted mass spectrum of product:

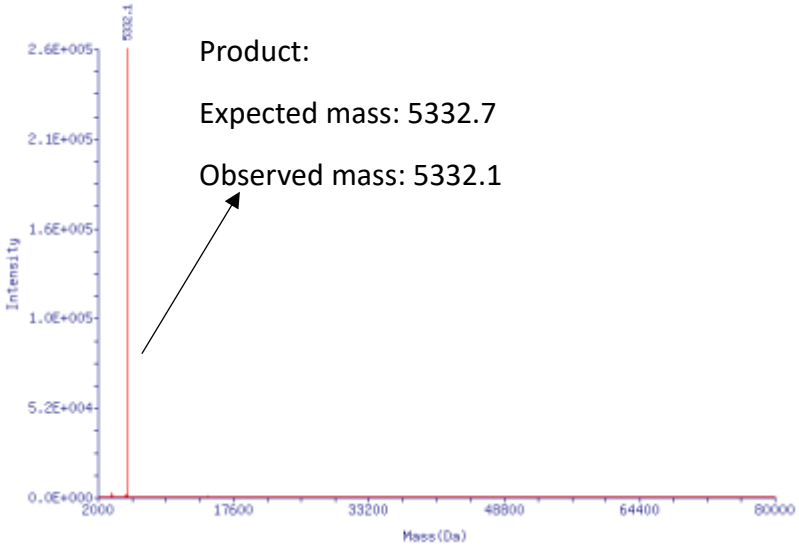
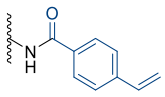


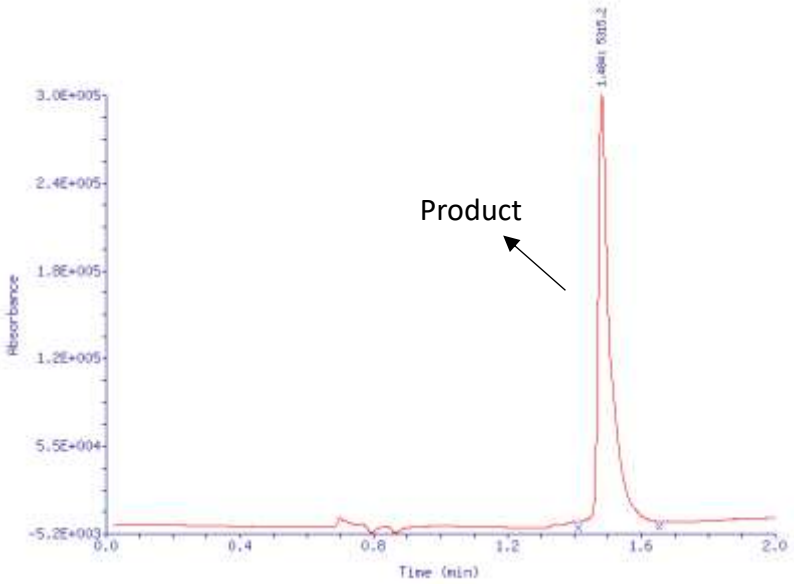
Figure S25. LC-MS Spectrum of Compound **1n**.



1o

Purity: >99%
Expected mass: 5314.7
Observed mass: 5315.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.484	5315.2	1.04E+005	ok	7.62E+005	100.00

Deconvoluted mass spectrum of product:

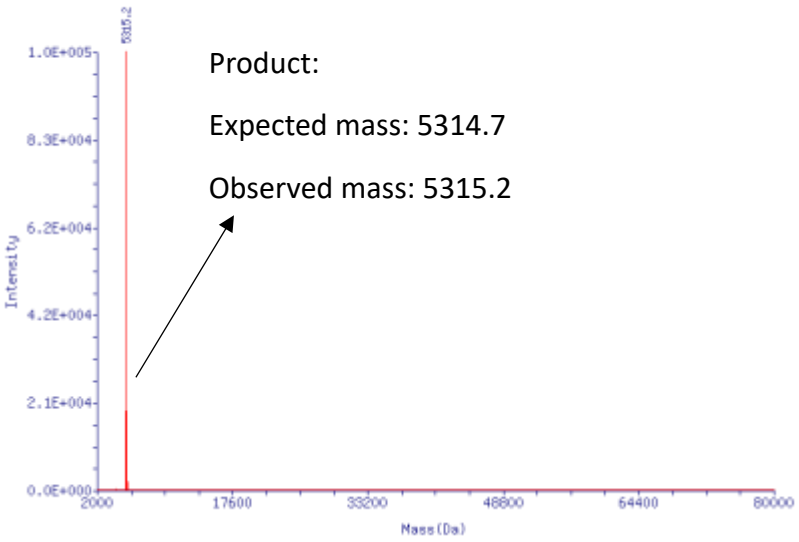
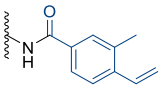


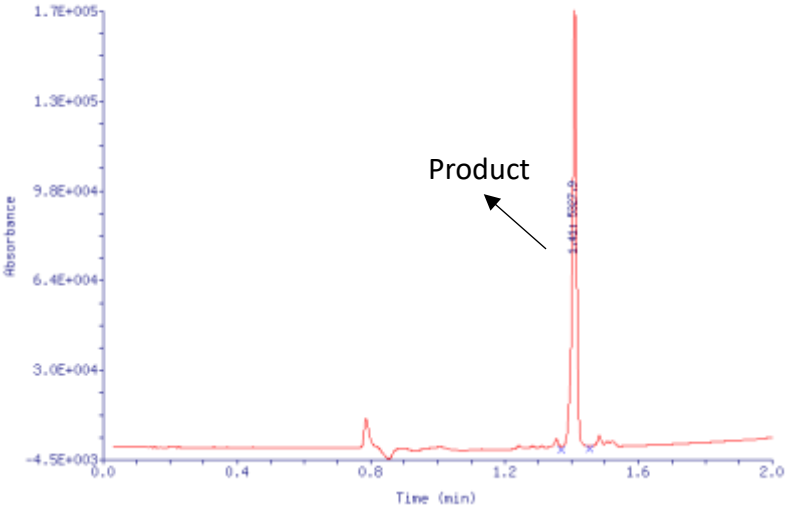
Figure S26. LC-MS Spectrum of Compound **1o**.



1p

Purity: >99%
Expected mass: 5328.7
Observed mass: 5327.9

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.41	5327.9	2.24E+005	ok	1.49E+005	100.00

Deconvoluted mass spectrum of product:

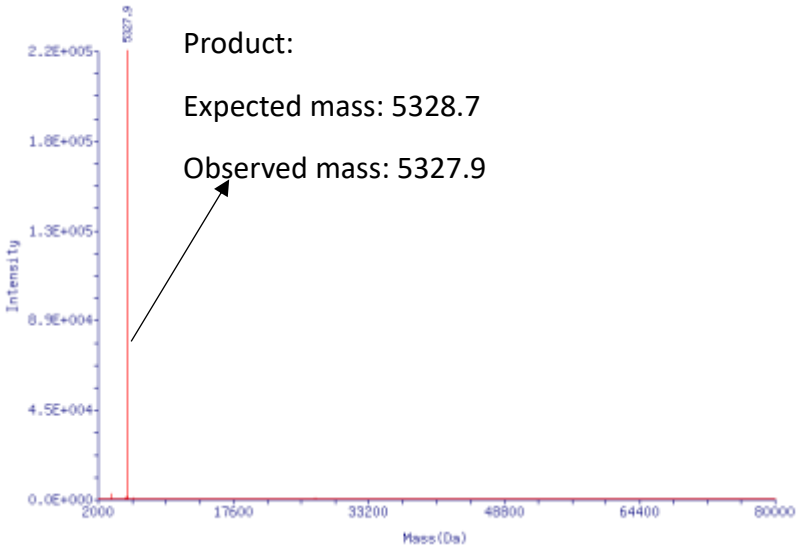
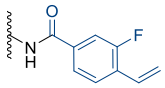


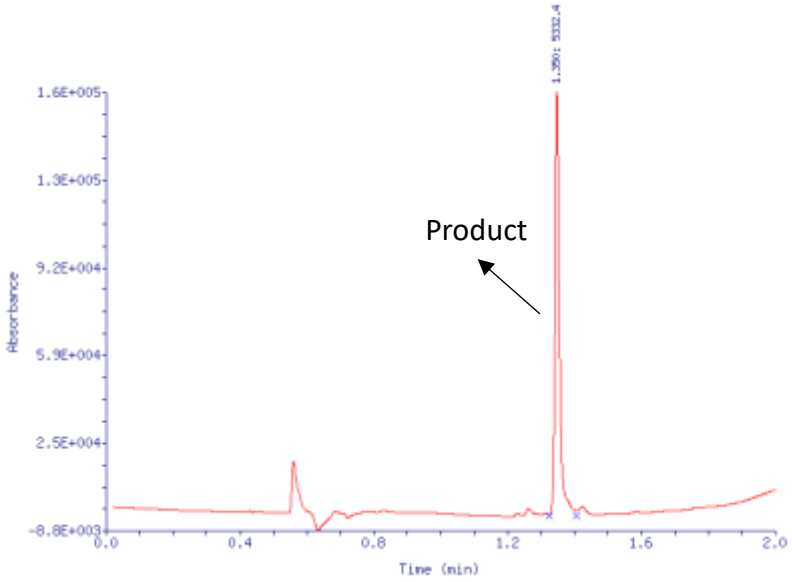
Figure S27. LC-MS Spectrum of Compound **1p**.



1q

Purity: >99%
Expected mass: 5332.7
Observed mass: 5332.4

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.350	5332.4	5.89E+005	ok	1.49E+005	100.00

Deconvoluted mass spectrum of product:

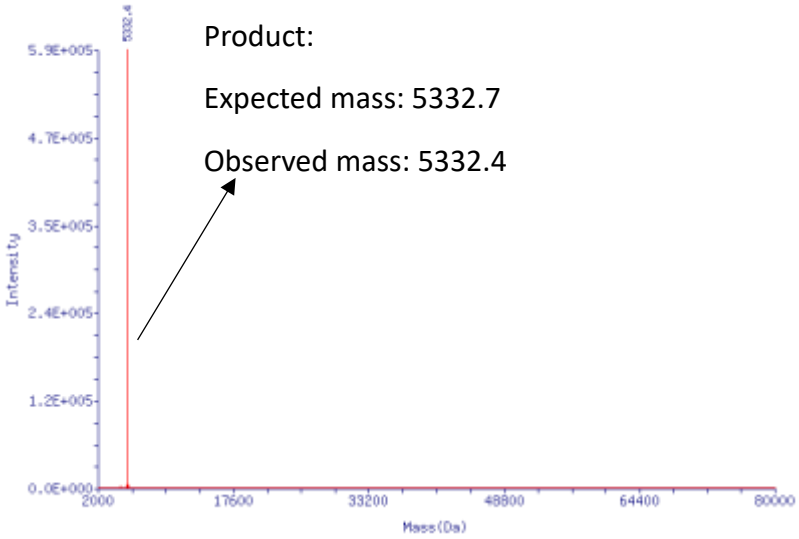
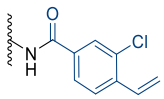


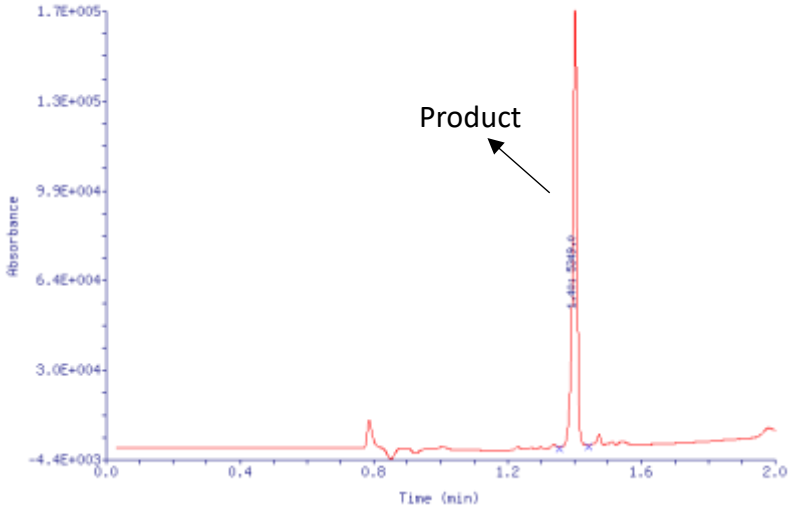
Figure S28. LC-MS Spectrum of Compound **1q**.



1r

Purity: >99%
Expected mass: 5349.1
Observed mass: 5349.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.40	5349.0	5.23E+005	ok	1.50E+005	100.00

Deconvoluted mass spectrum of product:

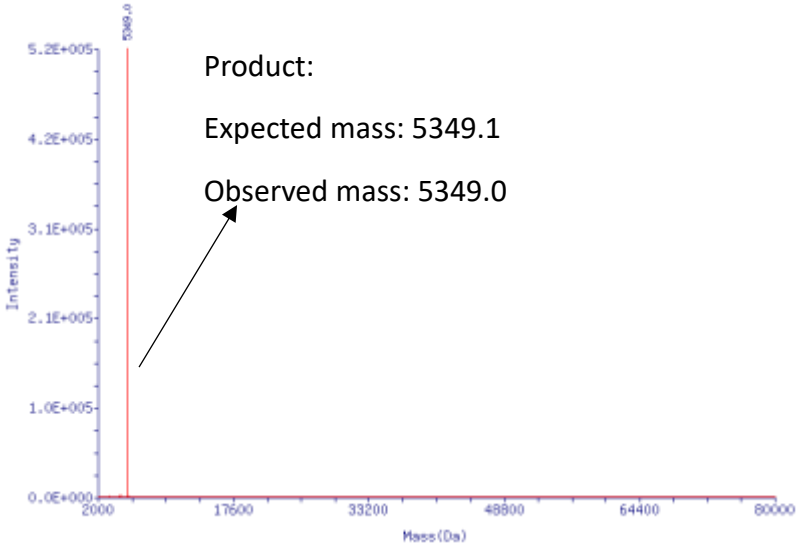
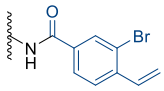


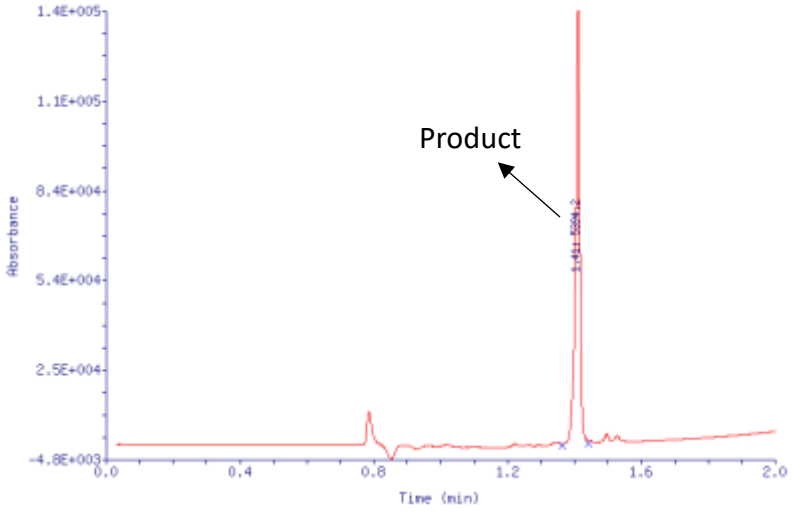
Figure S29. LC-MS Spectrum of Compound **1r**.



1s

Purity: >99%
Expected mass: 5393.6
Observed mass: 5394.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.41	5394.2	4.09E+005	ok	1.29E+005	100.00

Deconvoluted mass spectrum of product:

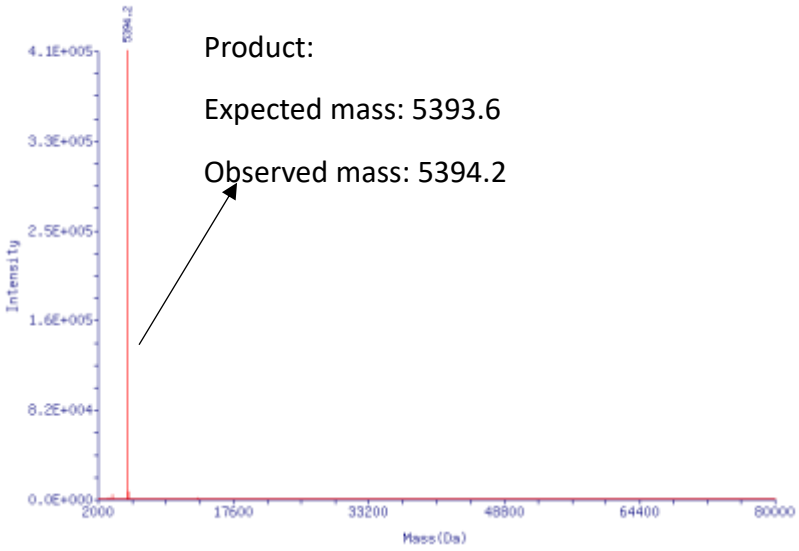
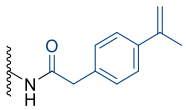
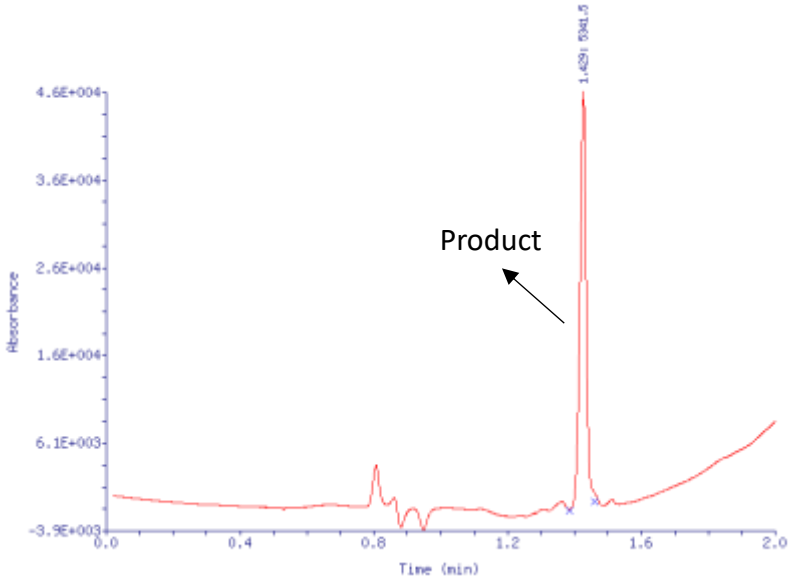


Figure S30. LC-MS Spectrum of Compound **1s**.



1t
Purity: >99%
Expected mass: 5342.7
Observed mass: 5341.5

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.429	5341.5	3.63E+004	ok	5.93E+004	100.00

Deconvoluted mass spectrum of product:

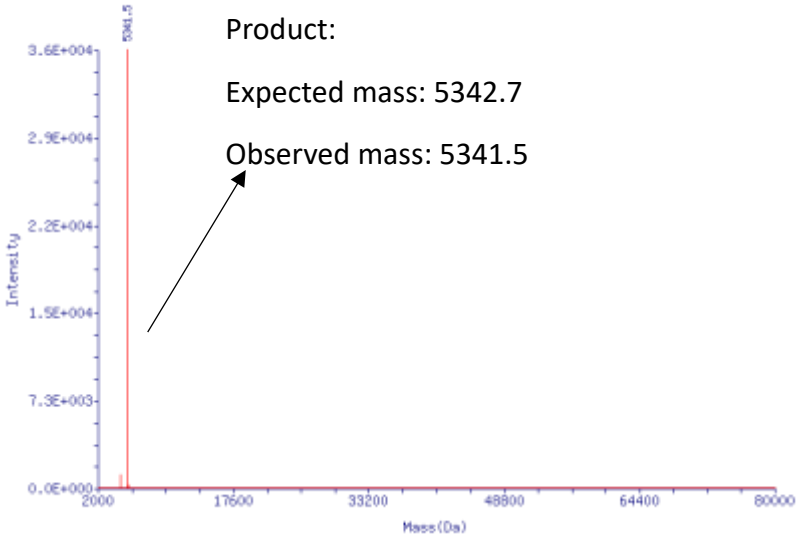
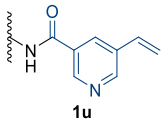


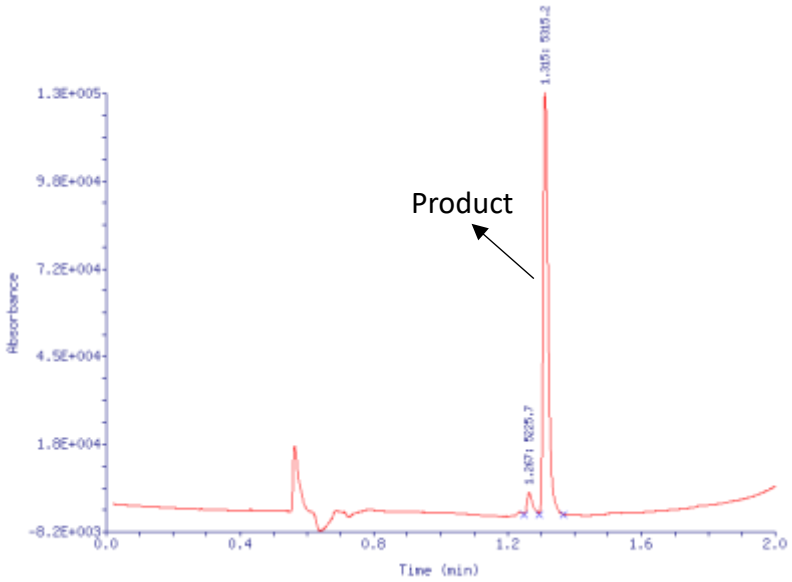
Figure S31. LC-MS Spectrum of Compound **1t**.



1u

Purity: 95%
Expected mass: 5315.6
Observed mass: 5315.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.267	5225.7	4.48E+004	ok	7.34E+003	5.32
1.315	5315.2	6.27E+005	ok	1.31E+005	94.68

Deconvoluted mass spectrum of product:

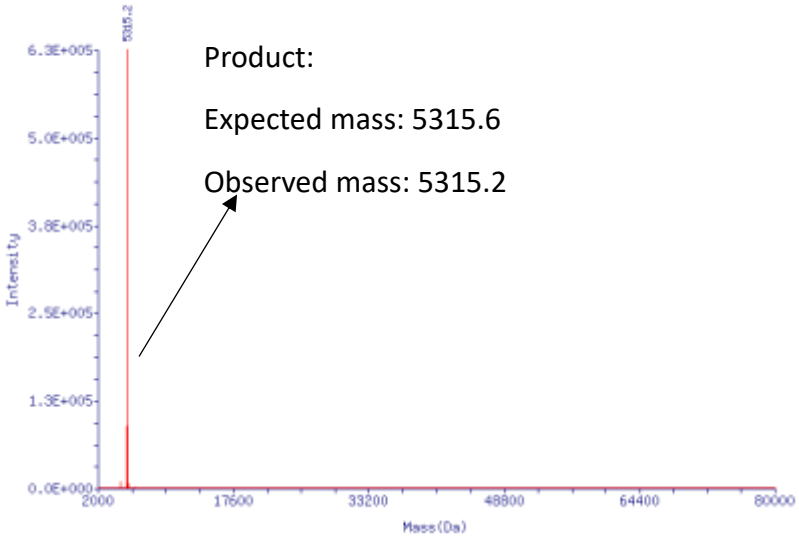
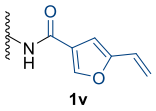


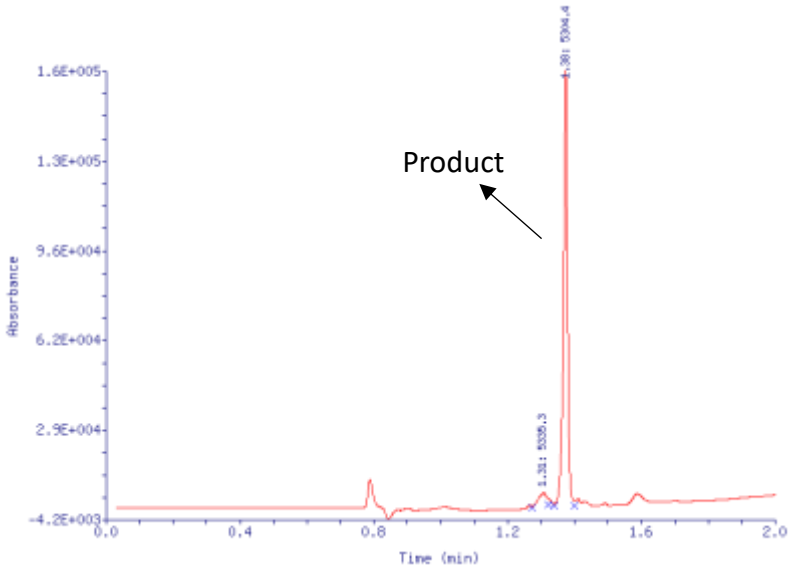
Figure S32. LC-MS Spectrum of Compound **1u**.



1v

Purity: 95%
Expected mass: 5304.6
Observed mass: 5304.4

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.31	5335.3	8.49E+003	ok	7.05E+003	5.01
1.38	5304.4	5.05E+005	ok	1.34E+005	94.99

Deconvoluted mass spectrum of product:

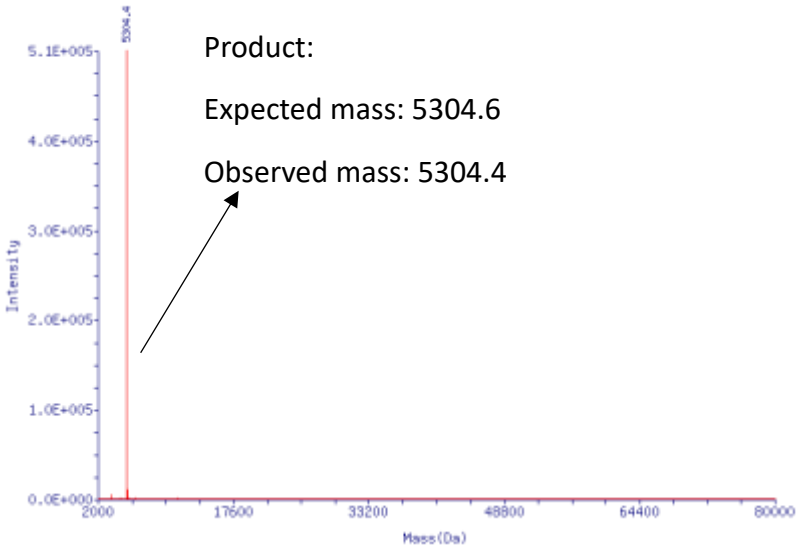
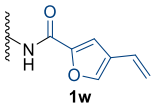


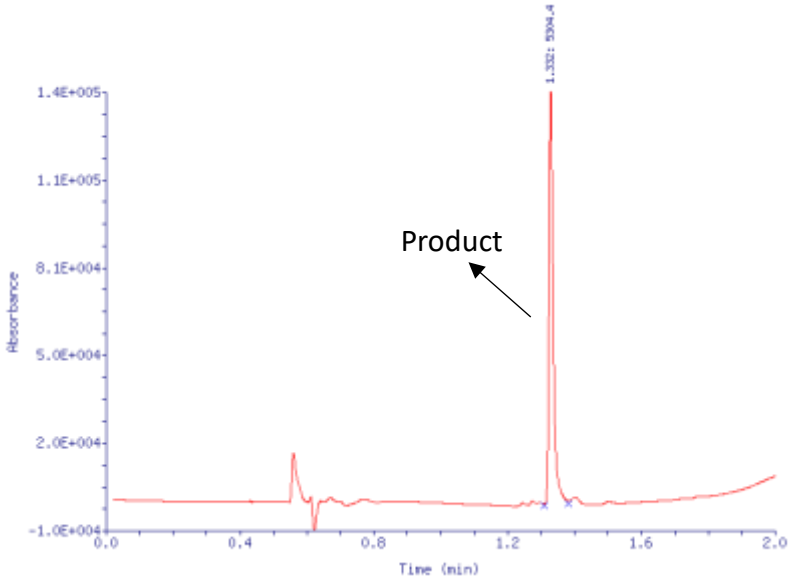
Figure S33. LC-MS Spectrum of Compound **1v**.



1w

Purity: >99%
Expected mass: 5304.6
Observed mass: 5304.4

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.332	5304.4	5.50E+005	ok	1.25E+005	100.00

Deconvoluted mass spectrum of product:

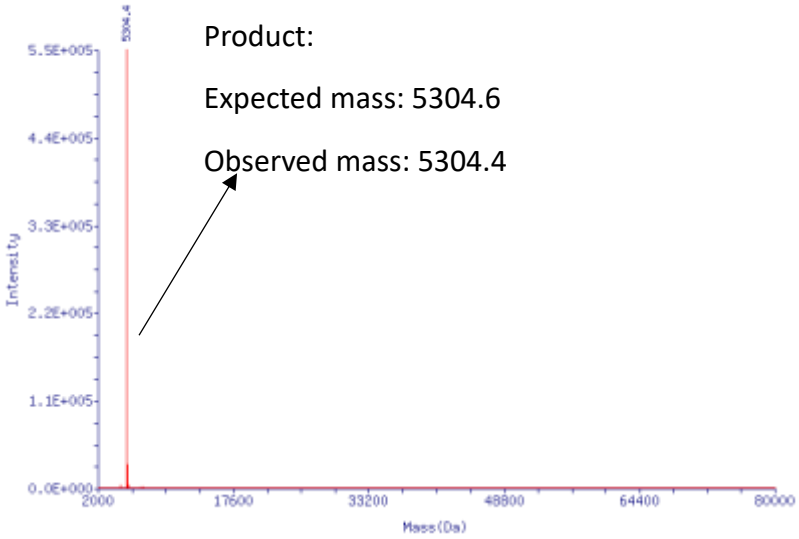
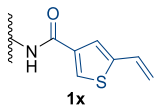


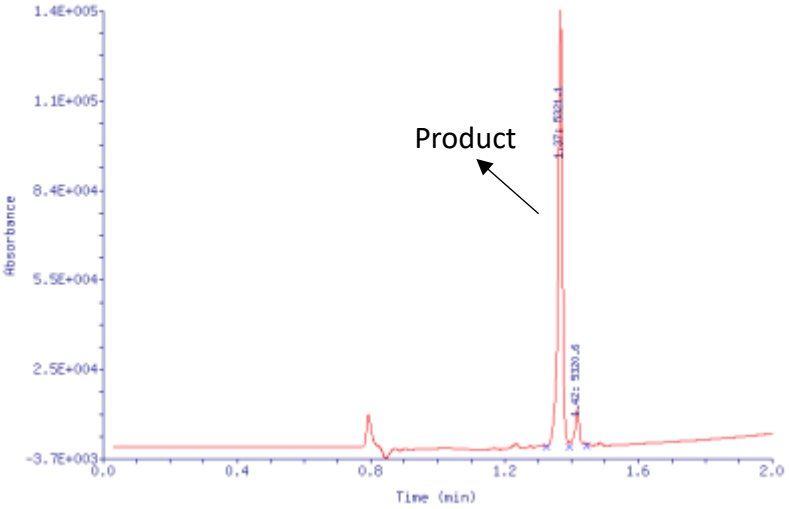
Figure S34. LC-MS Spectrum of Compound **1w**.



1x

Purity: 92%
Expected mass: 5320.7
Observed mass: 5321.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.37	5321.1	5.05E+005	ok	1.25E+005	92.07
1.42	5320.6	8.92E+004	ok	1.07E+004	7.93

Deconvoluted mass spectrum of product:

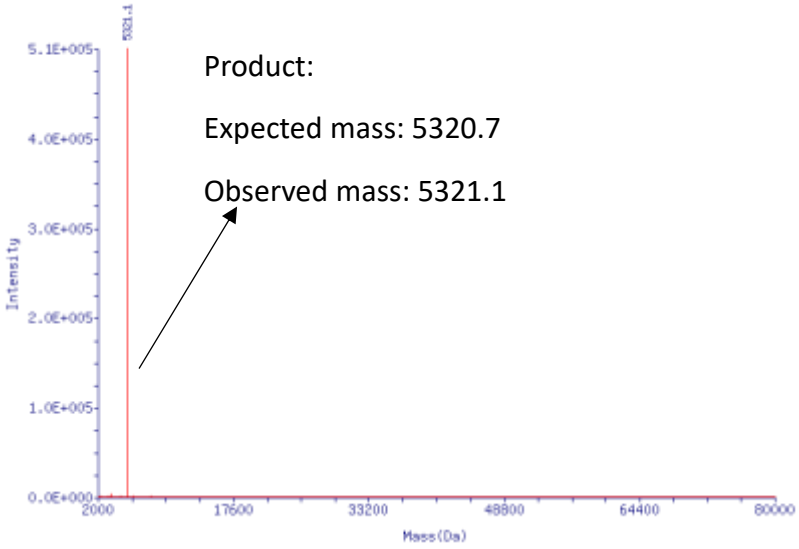
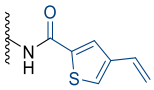


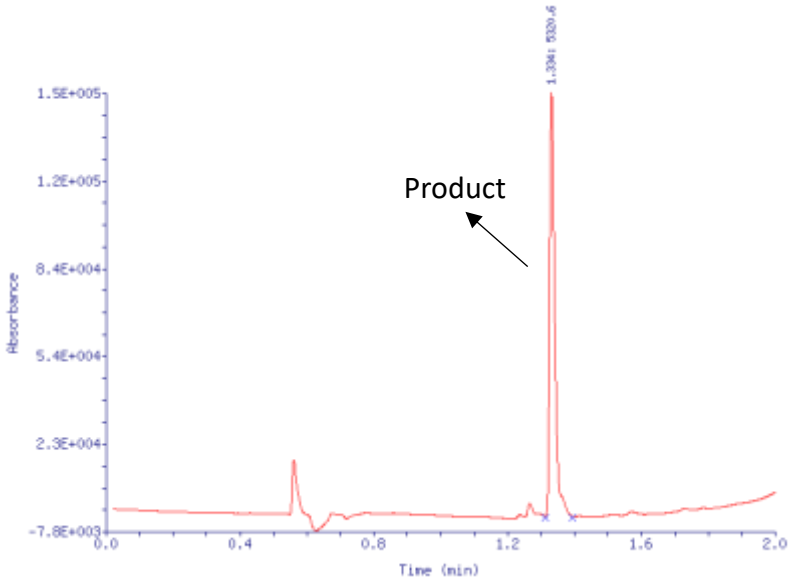
Figure S35. LC-MS Spectrum of Compound **1x**.



1y

Purity: >99%
Expected mass: 5320.7
Observed mass: 5320.6

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.334	5320.6	6.70E+005	ok	1.57E+005	100.00

Deconvoluted mass spectrum of product:

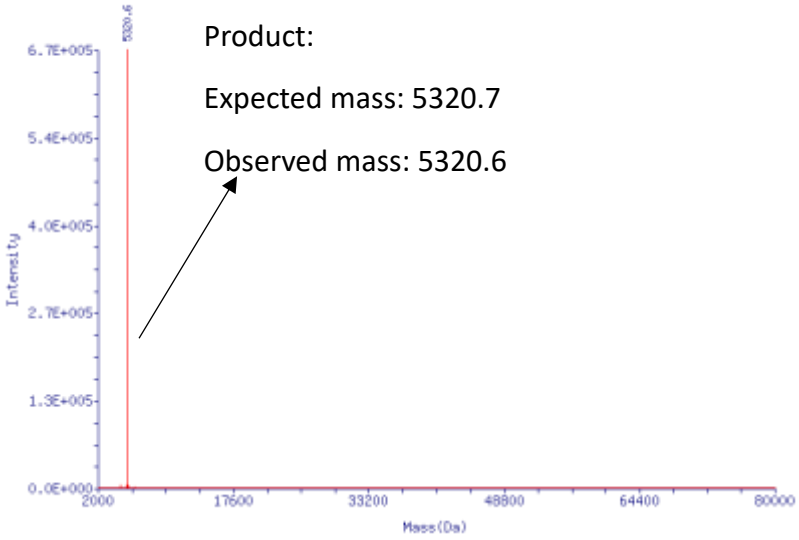
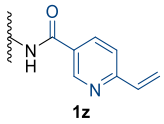


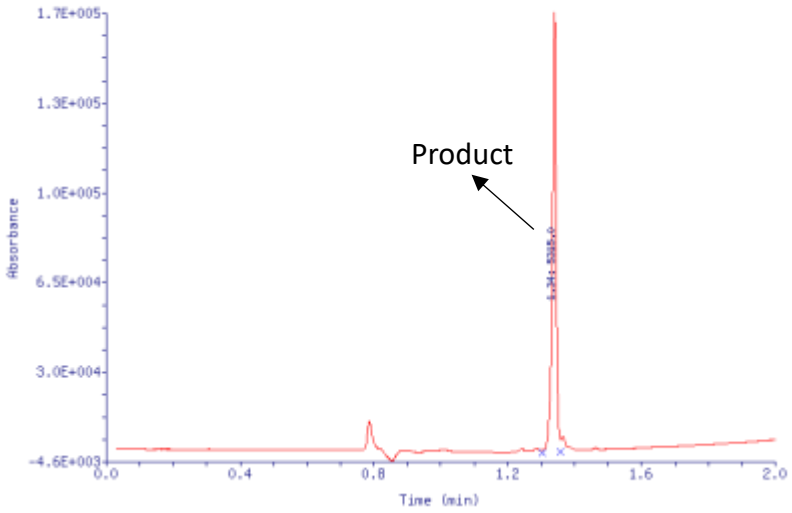
Figure S36. LC-MS Spectrum of Compound **1y**.



1z

Purity: >99%
Expected mass: 5315.6
Observed mass: 5315.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.34	5315.0	3.22E+005	ok	1.37E+005	100.00

Deconvoluted mass spectrum of product:

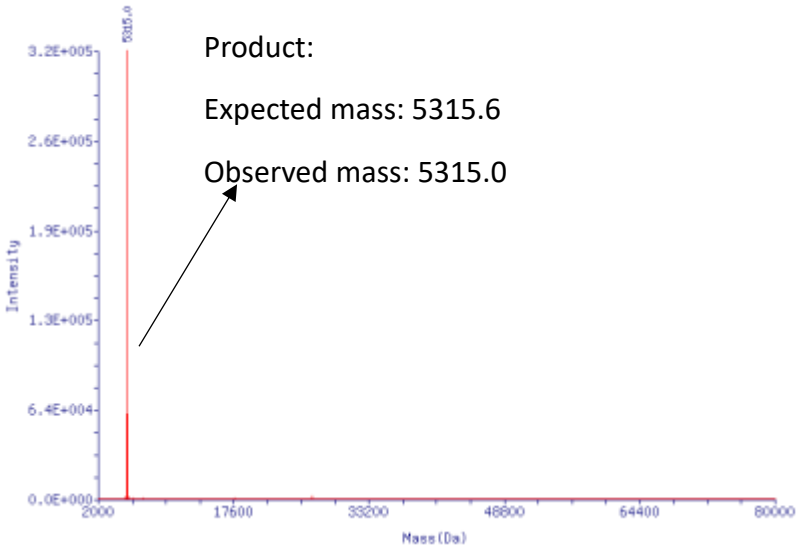


Figure S37. LC-MS Spectrum of Compound **1z**.

9.6. ^{1}H NMR Study of Sodium Sulfinates

^{1}H NMR spectrum for sodium 2-cyclobutylethane-1-sulfinate (**4c**), Deuterium Oxide, 400 MHz:

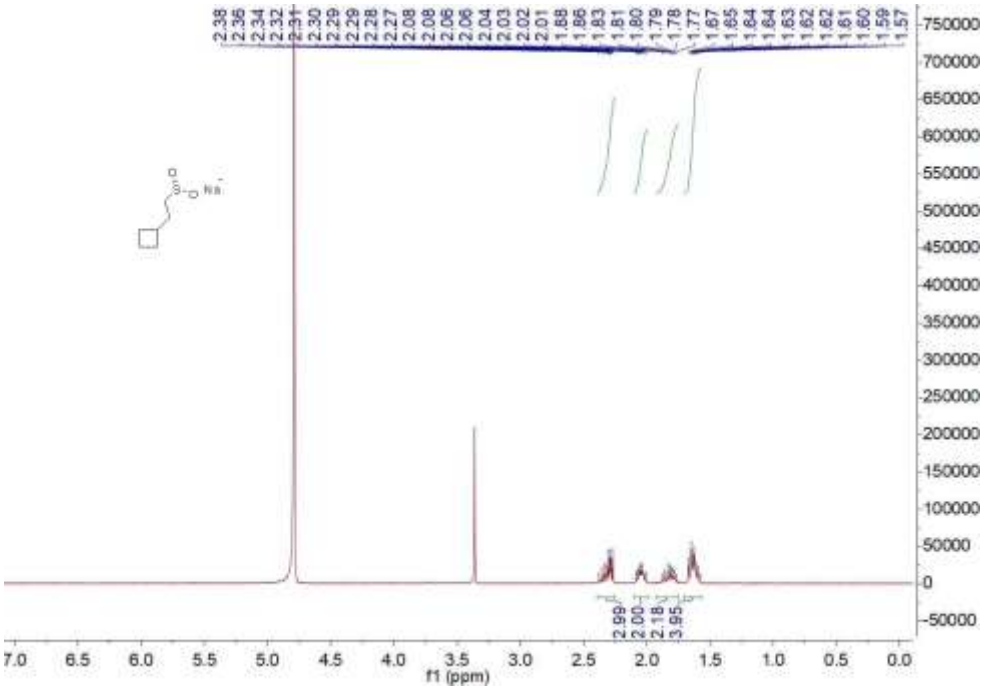


Figure S38. ^{1}H NMR spectrum of **4c**.

^{1}H NMR spectrum for sodium cyclopentanecarboxylate (**4h**), Deuterium Oxide, 400 MHz:

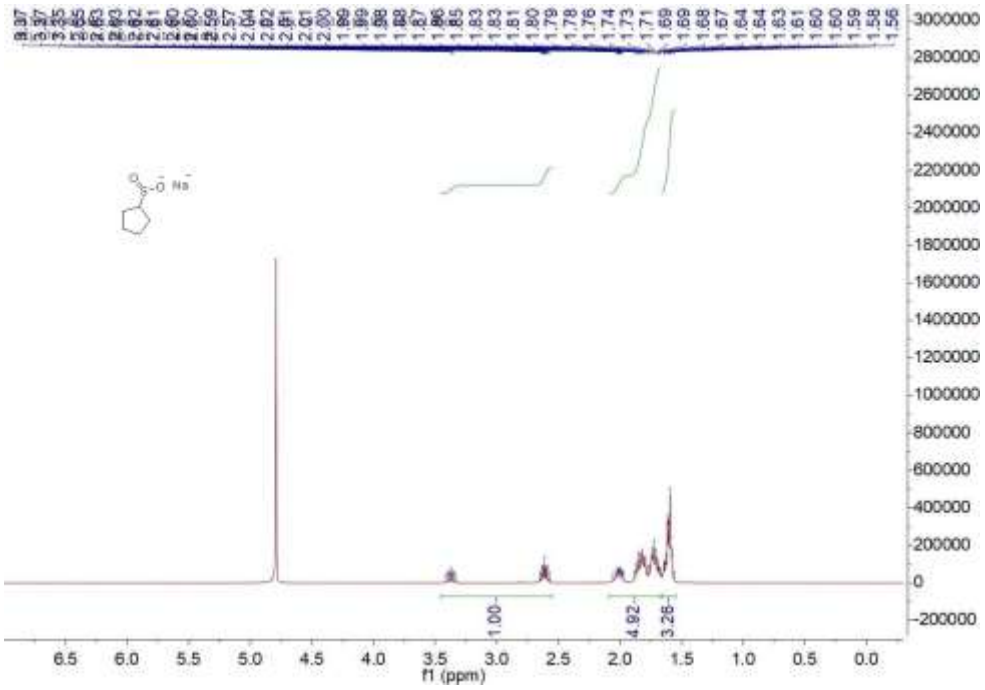
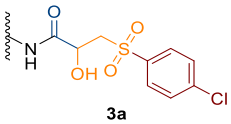


Figure S39. ^{1}H NMR spectrum of **4h**.

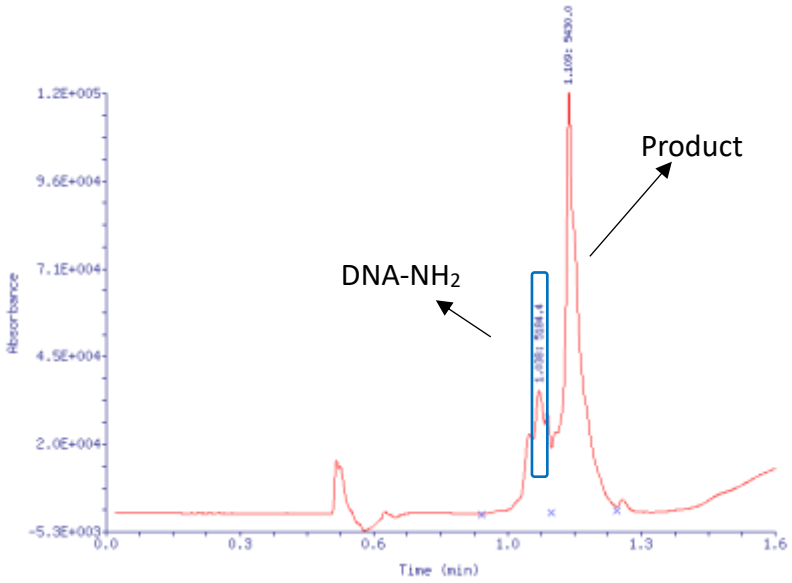
9.7. Mass Spectrum of 3a-3z



3a

Purity: 74%
Conversion rate: 74%
Expected mass: 5431.2
Observed mass: 5430.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.038	5184.4	3.68E+004	ok	1.07E+005	26.29
1.109	5430.0	1.26E+005	ok	2.99E+005	73.71

Deconvoluted mass spectrum of product:

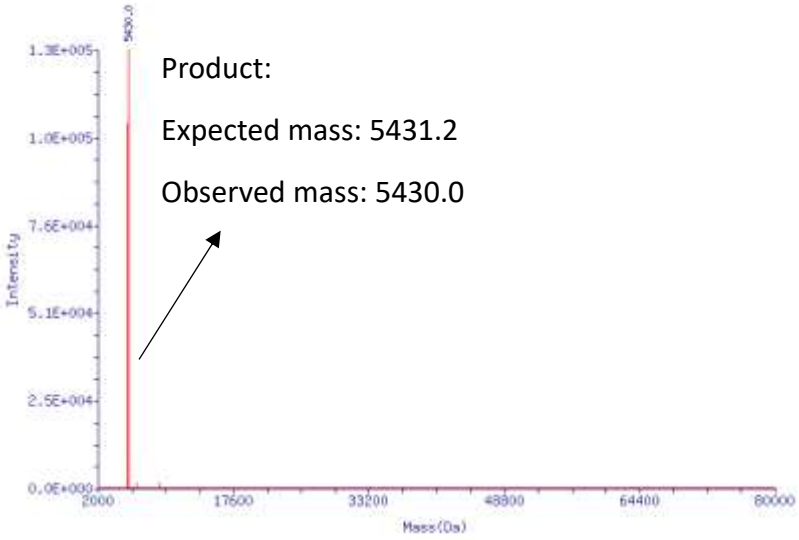
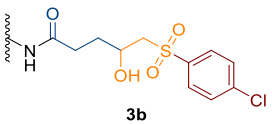


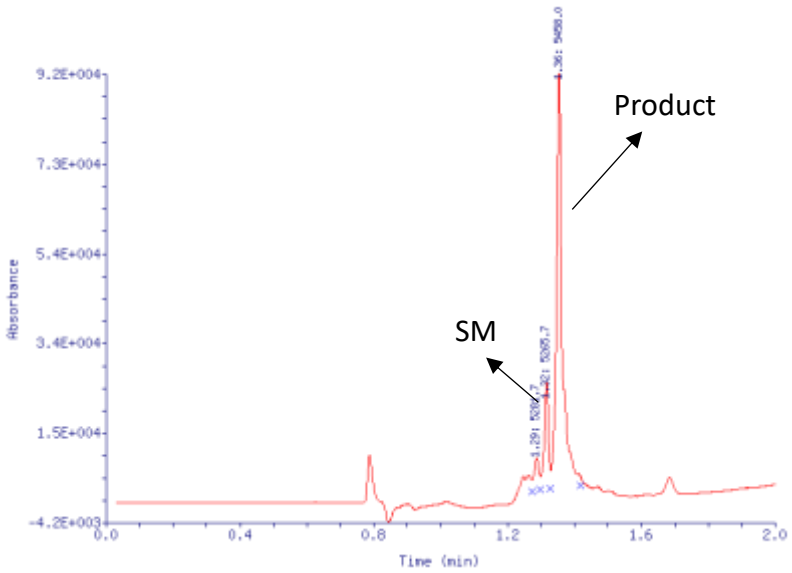
Figure S40. LC-MS Spectrum of DEL Compound **3a**.



3b

Purity: 80%
Conversion rate: 80%
Expected mass: 5459.2
Observed mass: 5458.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.29	5281.7	1.91E+004	ok	6.51E+003	4.93
1.32	5265.7	6.93E+004	ok	1.93E+004	14.60
1.36	5458.0	9.90E+004	ok	1.06E+005	80.48

Deconvoluted mass spectrum of product:

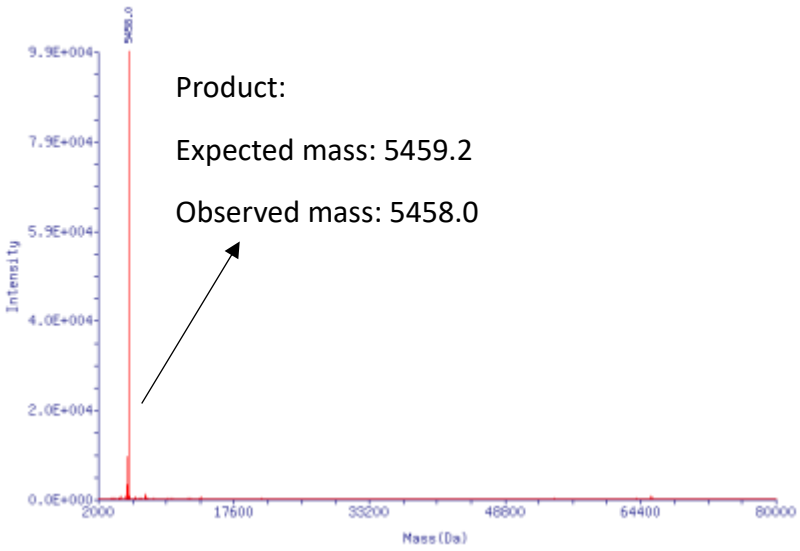
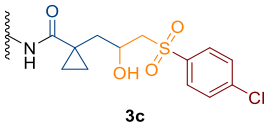


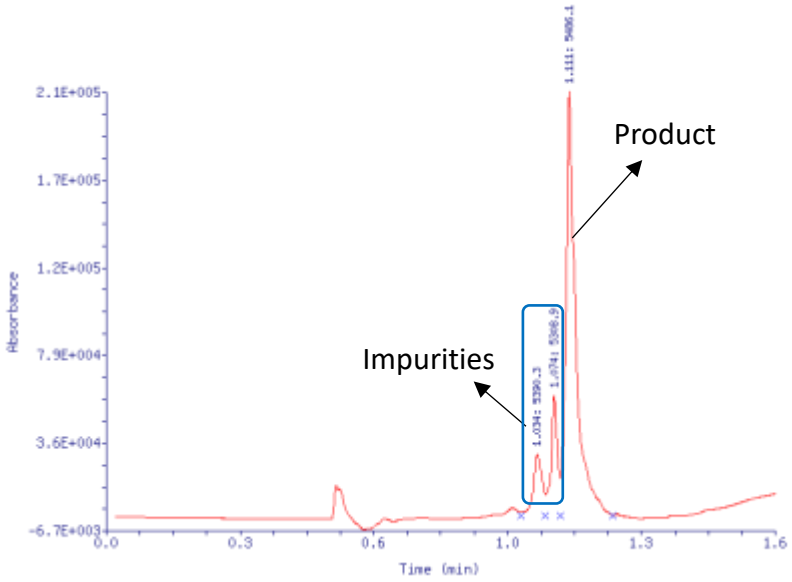
Figure S41. LC-MS Spectrum of DEL Compound **3b**.



3c

Purity: 76%
Conversion rate: 76%
Expected mass: 5485.3
Observed mass: 5486.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.034	5390.3	4.28E+004	ok	4.28E+004	9.64
1.074	5308.9	2.62E+005	ok	6.16E+004	13.88
1.111	5486.1	2.77E+005	ok	3.39E+005	76.47

Deconvoluted mass spectrum of product:

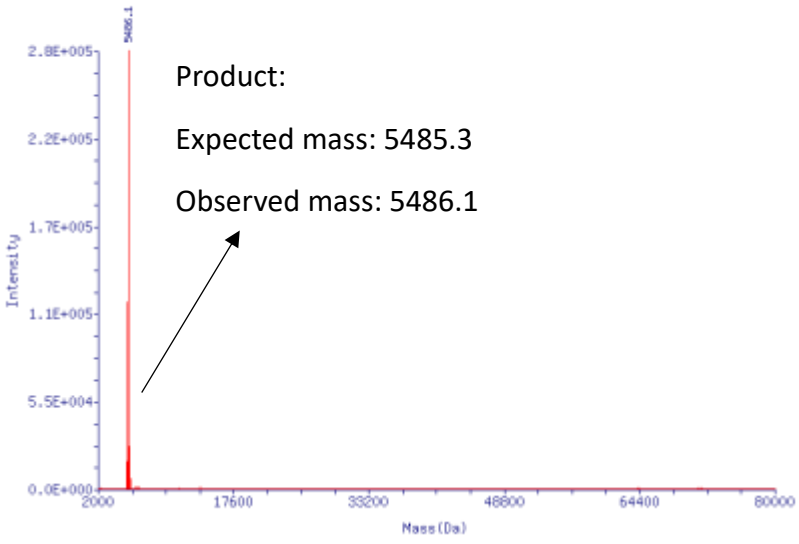
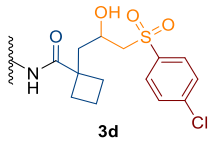


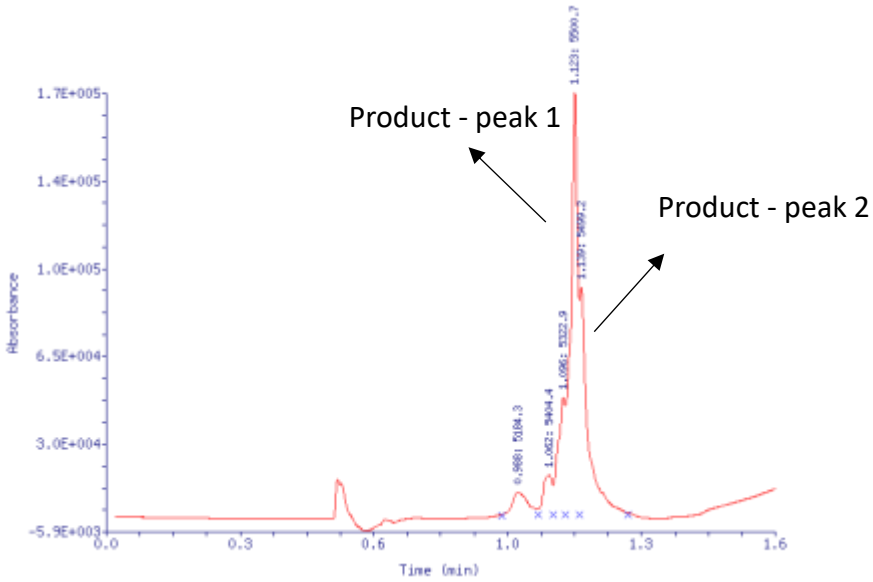
Figure S42. LC-MS Spectrum of DEL Compound **3c**.



3d

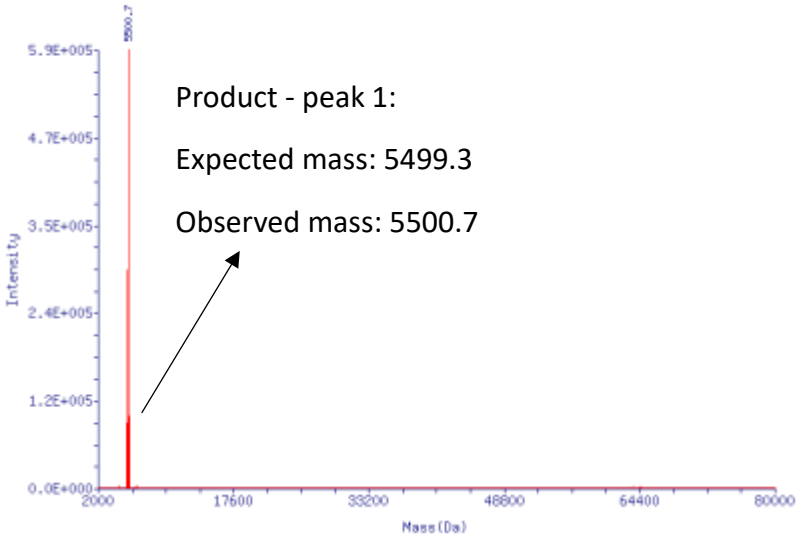
Purity: 76%
Conversion rate: 76%
Expected mass: 5499.3
Observed mass: 5500.7 and 5499.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
0.988	5184.3	5.45E+004	ok	2.19E+004	5.23
1.062	5404.4	5.11E+004	ok	2.31E+004	5.52
1.096	5322.9	3.08E+005	ok	5.56E+004	13.28
1.123	5500.7	5.90E+005	ok	1.96E+005	46.90
1.139	5499.2	1.86E+005	ok	1.22E+005	29.07

Deconvoluted mass spectrum of product:



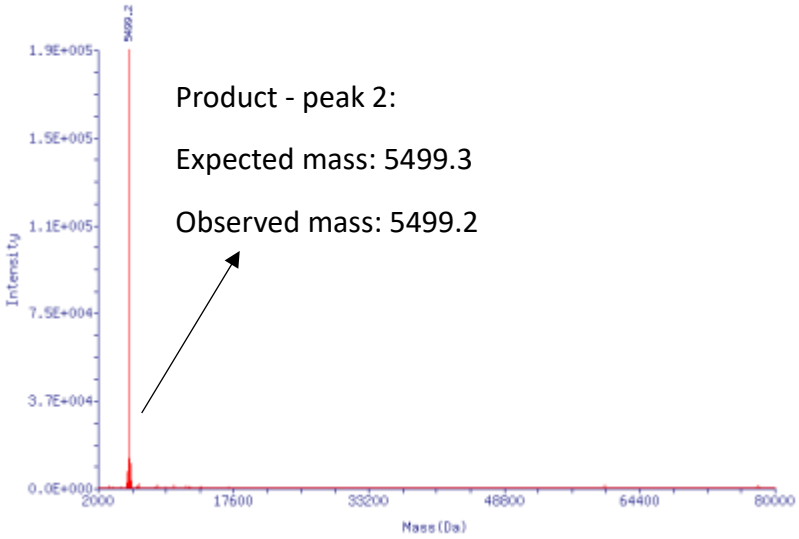
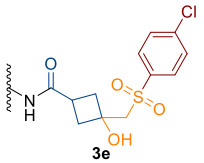


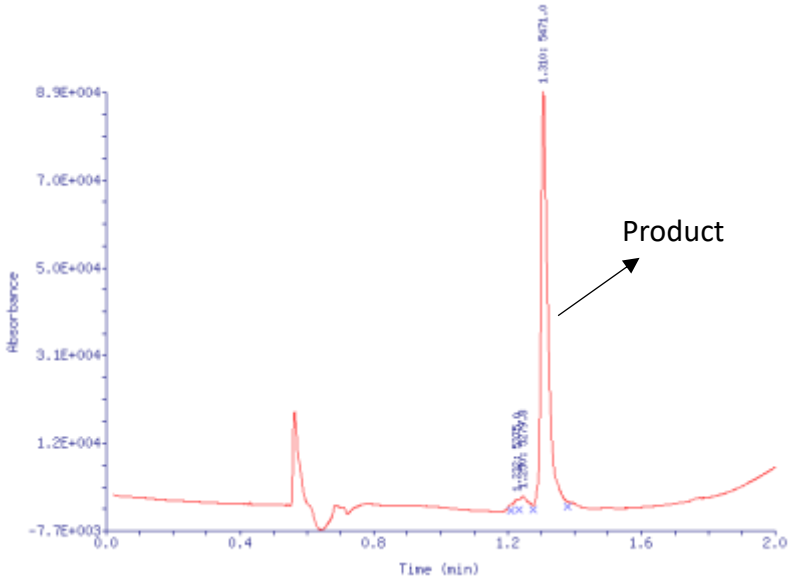
Figure S43. LC-MS Spectrum of DEL Compound **3d**.



3e

Purity: 95%
Conversion rate: >99%
Expected mass: 5471.2
Observed mass: 5471.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.232	5375.0	5.47E+003	ok	2.59E+003	1.85
1.250	5279.8	1.52E+004	ok	4.46E+003	3.20
1.310	5471.0	2.81E+005	ok	1.32E+005	94.95

Deconvoluted mass spectrum of SM:

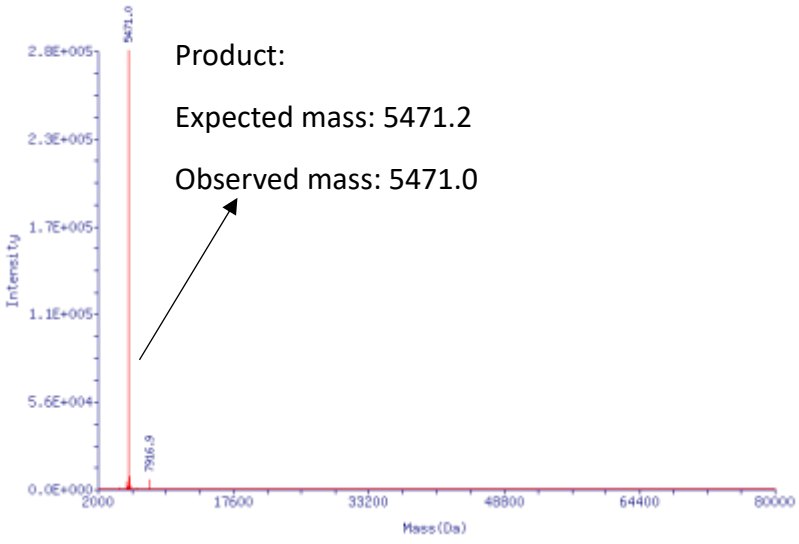
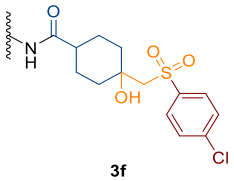


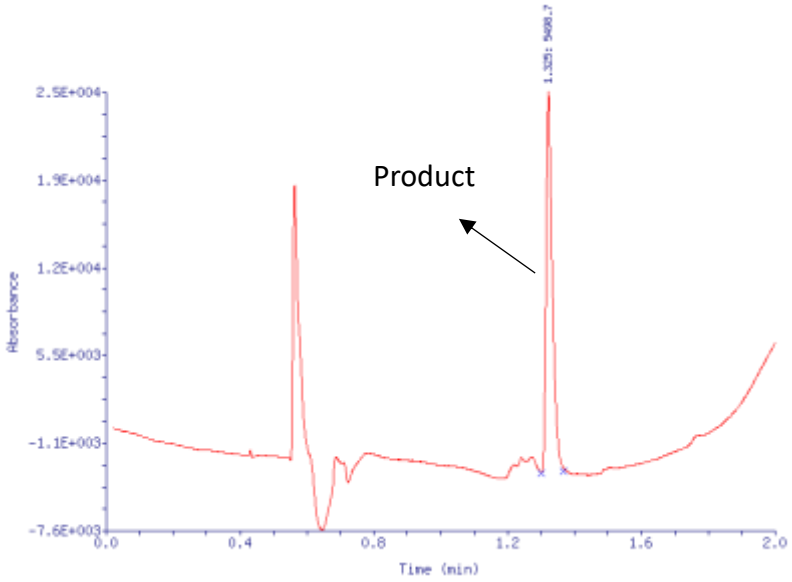
Figure S44. LC-MS Spectrum of DEL Compound **3e**.



3f

Purity: >99%
Conversion rate: >99%
Expected mass: 5499.3
Observed mass: 5498.7

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.325	5498.7	1.17E+005	ok	3.62E+004	100.00

Deconvoluted mass spectrum of product:

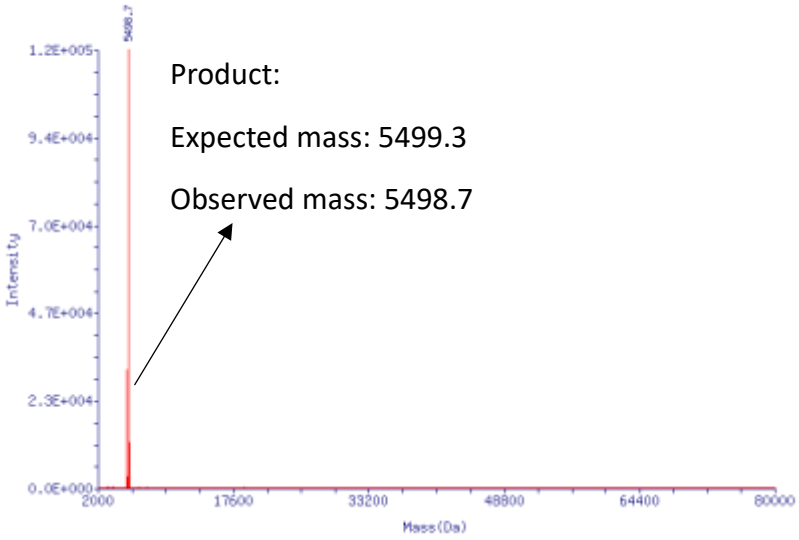
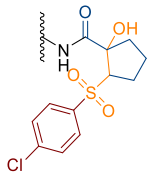


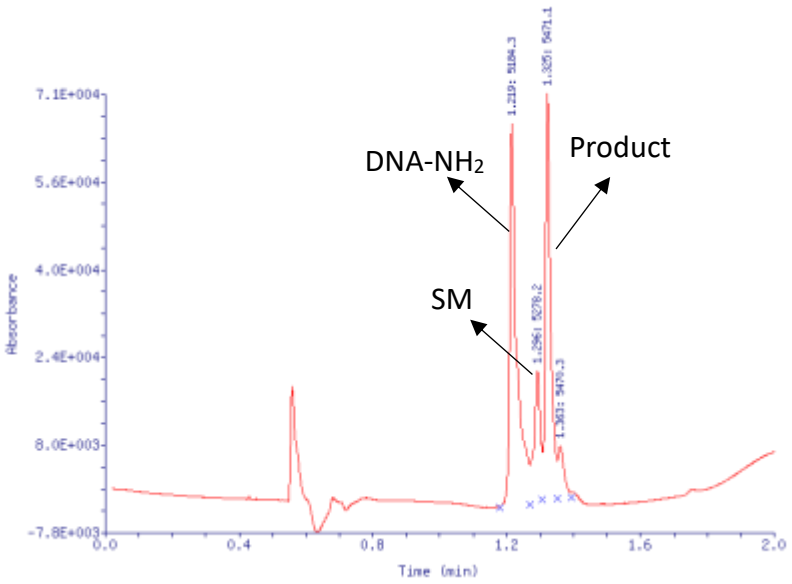
Figure S45. LC-MS Spectrum of DEL Compound **3f**.



3g

Purity: 36%
Conversion rate: 36%
Expected mass: 5471.2
Observed mass: 5471.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.219	5184.3	1.94E+005	ok	1.00E+005	45.33
1.296	5278.2	7.71E+004	ok	3.04E+004	13.76
1.325	5471.1	4.32E+005	ok	7.86E+004	35.59
1.363	5470.3	3.82E+004	ok	1.17E+004	5.32

Deconvoluted mass spectrum of product:

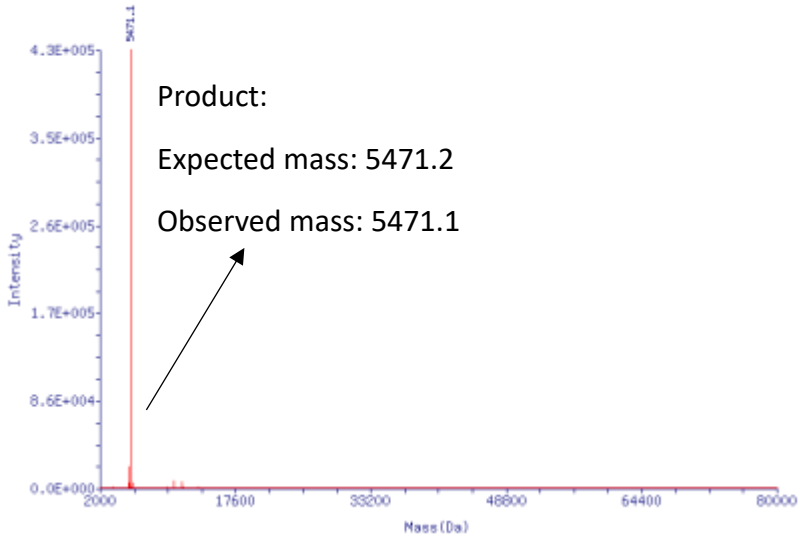
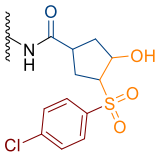


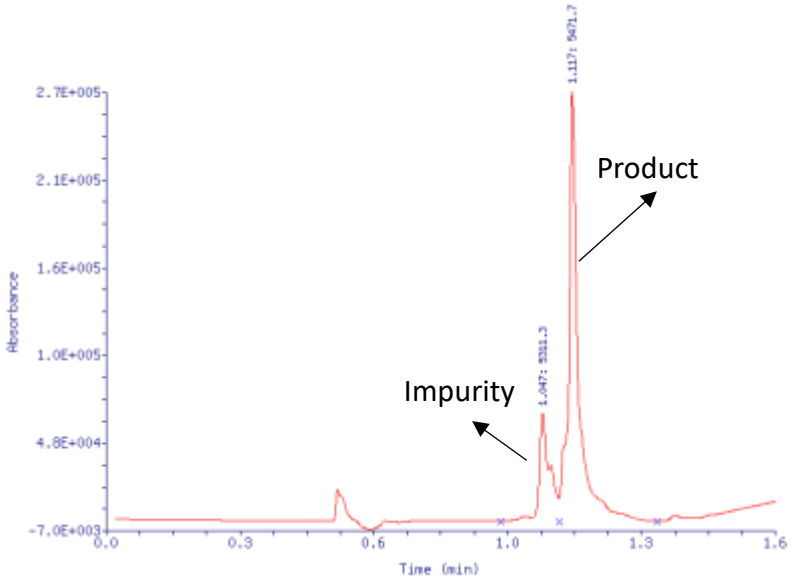
Figure S46. LC-MS Spectrum of DEL Compound **3g**.



3h

Purity: 79%
Conversion rate: 79%
Expected mass: 5471.2
Observed mass: 5471.7

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.047	5311.3	1.09E+005	ok	1.15E+005	21.03
1.117	5471.7	3.97E+005	ok	4.30E+005	78.97

Deconvoluted mass spectrum of product:

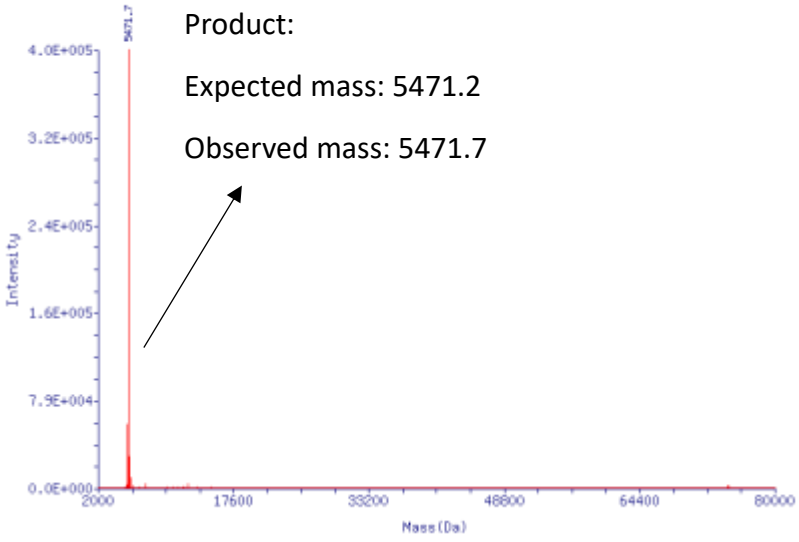
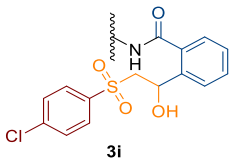


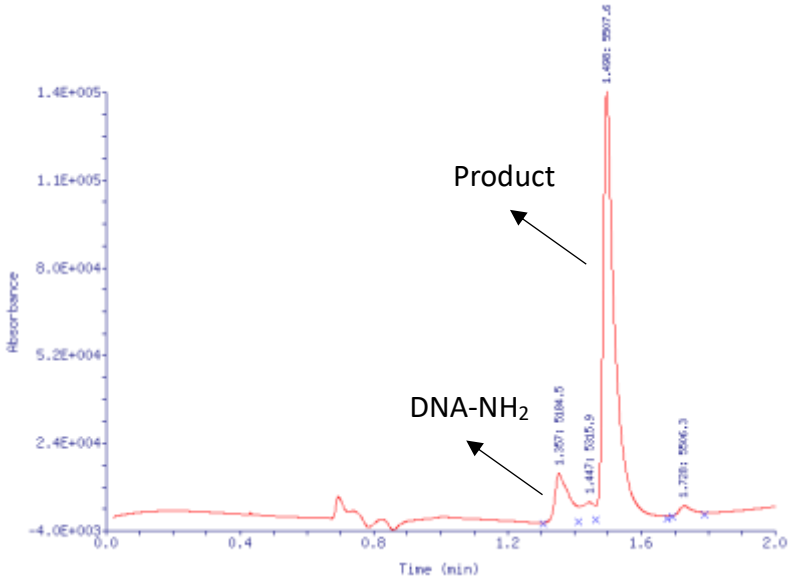
Figure S47. LC-MS Spectrum of DEL Compound **3h**.



3i

Purity: 83%
Conversion rate: 83%
Expected mass: 5507.3
Observed mass: 5507.6

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.357	5184.5	2.25E+004	ok	4.50E+004	11.22
1.447	5315.9	4.86E+003	ok	1.50E+004	3.74
1.498	5507.6	9.37E+004	ok	3.33E+005	83.04
1.728	5506.3	2.93E+002	ok	8.00E+003	1.99

Deconvoluted mass spectrum of product:

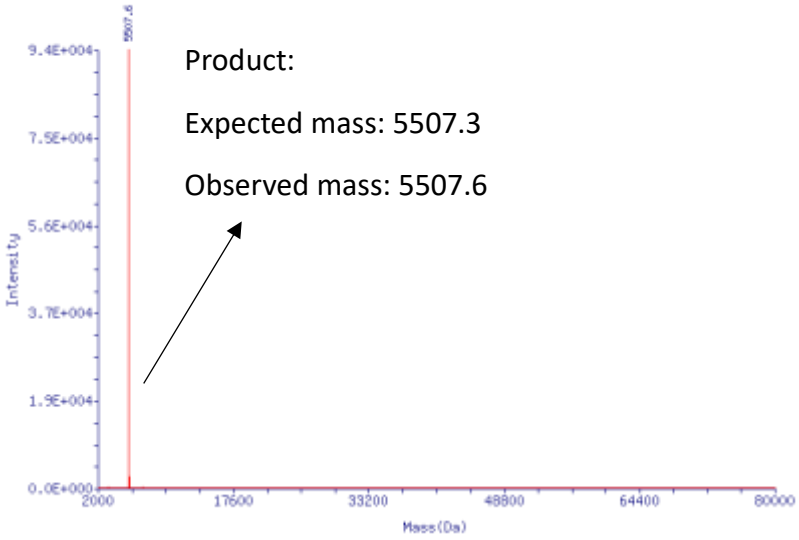
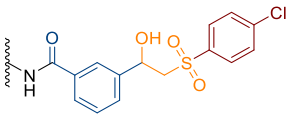
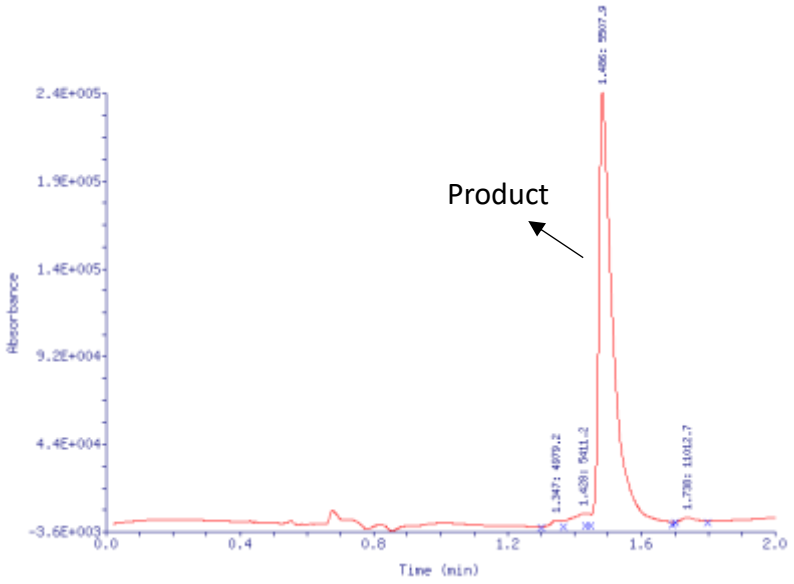


Figure S48. LC-MS Spectrum of DEL Compound **3i**.



3j
Purity: 96%
Conversion rate: 96%
Expected mass: 5507.3
Observed mass: 5507.9

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.347	4979.2	2.99E+003	ok	6.42E+003	0.90
1.428	5411.2	2.47E+003	ok	1.72E+004	2.41
1.486	5507.9	1.61E+005	ok	6.84E+005	95.84
1.738	11012.7	9.23E+002	ok	6.06E+003	0.85

Deconvoluted mass spectrum of product:

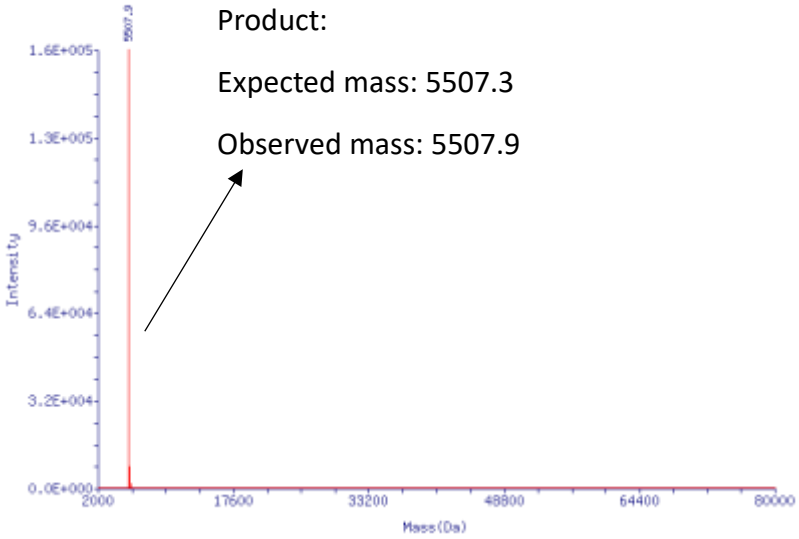
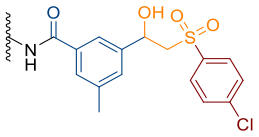
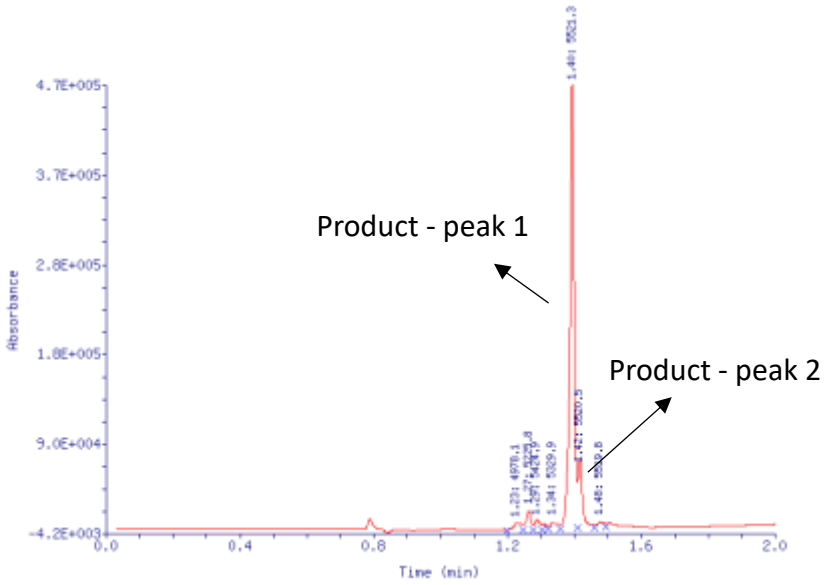


Figure S49. LC-MS Spectrum of DEL Compound **3j**.



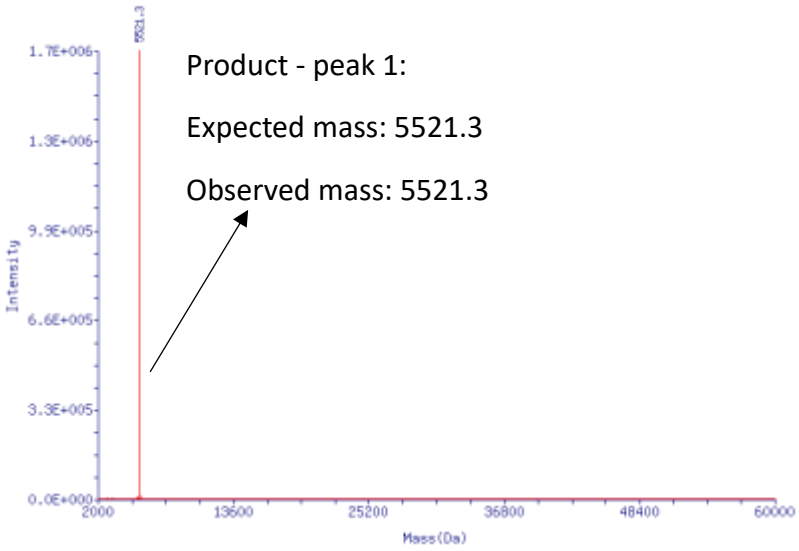
3k
Purity: 90%
Conversion rate: 90%
Expected mass: 5521.3
Observed mass: 5521.3 and 5520.5

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.23	4978.1	2.66E+004	ok	1.01E+004	1.89
1.27	5225.8	1.12E+005	ok	1.72E+004	3.21
1.29	5424.9	3.41E+004	ok	9.82E+003	1.83
1.34	5329.9	1.78E+004	ok	8.99E+003	1.68
1.40	5521.3	1.66E+006	ok	4.18E+005	78.06
1.42	5520.5	5.90E+005	ok	6.50E+004	12.13
1.48	5519.8	3.53E+004	ok	6.42E+003	1.20

Deconvoluted mass spectrum of product:



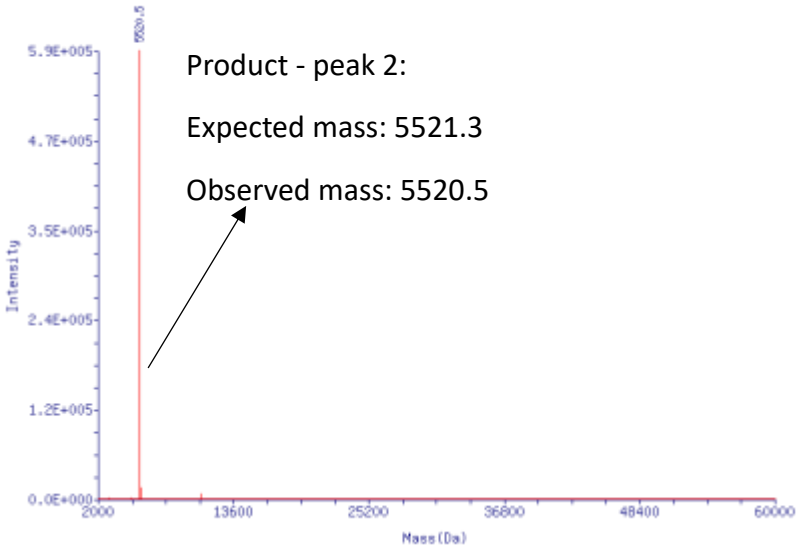
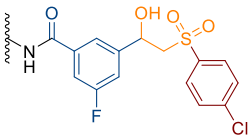


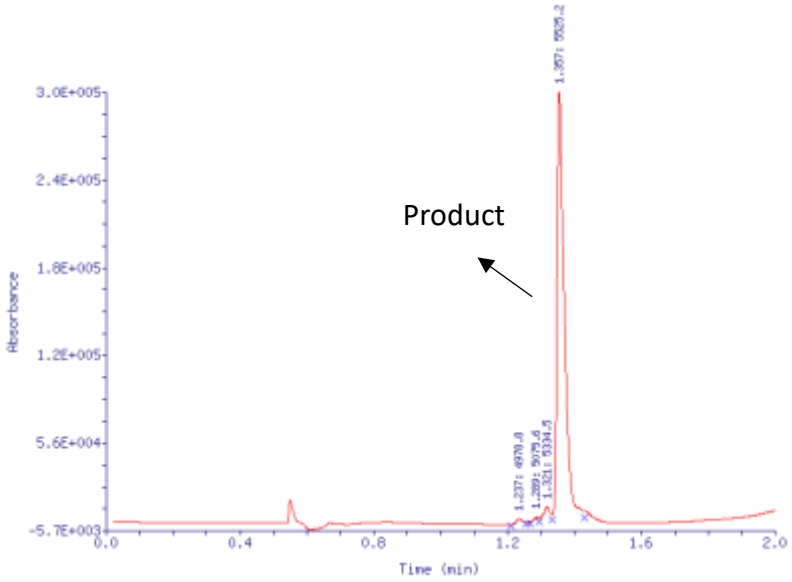
Figure S50. LC-MS Spectrum of DEL Compound **3k**.



3l

Purity: 96%
Conversion rate: 96%
Expected mass: 5525.3
Observed mass: 5525.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.237	4978.8	2.55E+004	ok	3.76E+003	0.81
1.289	5075.6	1.28E+004	ok	2.30E+003	0.49
1.321	5334.5	4.16E+004	ok	1.08E+004	2.32
1.357	5525.2	1.47E+006	ok	4.48E+005	96.38

Deconvoluted mass spectrum of product:

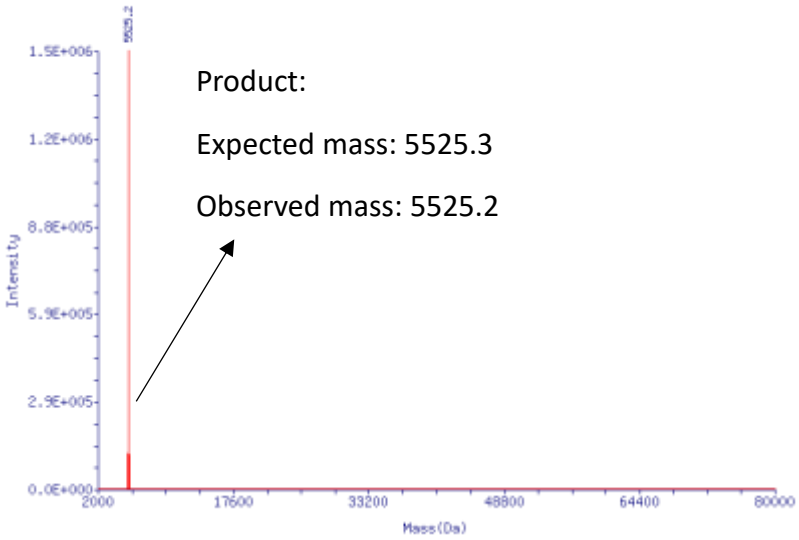
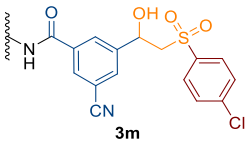


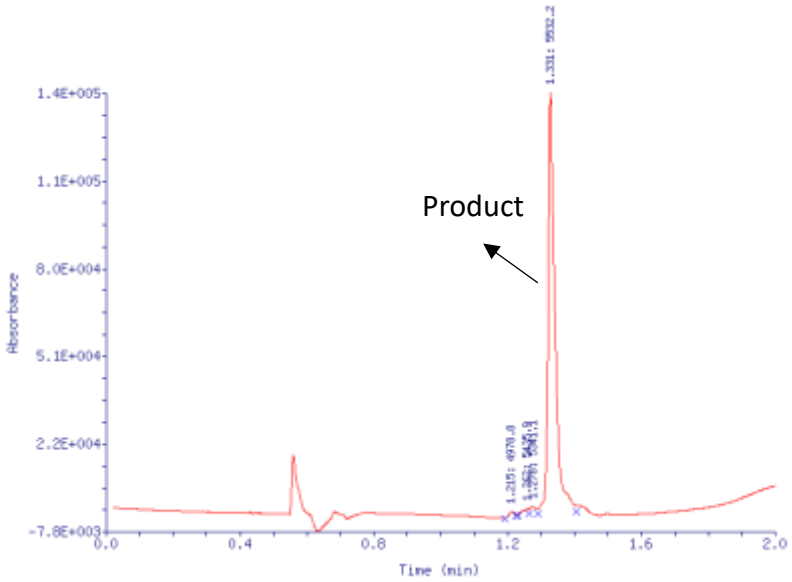
Figure S51. LC-MS Spectrum of DEL Compound **3l**.



3m

Purity: 97%
Conversion rate: >99%
Expected mass: 5532.3
Observed mass: 5532.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.215	4978.8	1.44E+004	ok	1.22E+003	0.60
1.262	5435.9	7.10E+003	ok	1.77E+003	0.88
1.278	5341.1	1.01E+004	ok	2.69E+003	1.33
1.331	5532.2	4.36E+005	ok	1.97E+005	97.20

Deconvoluted mass spectrum of product:

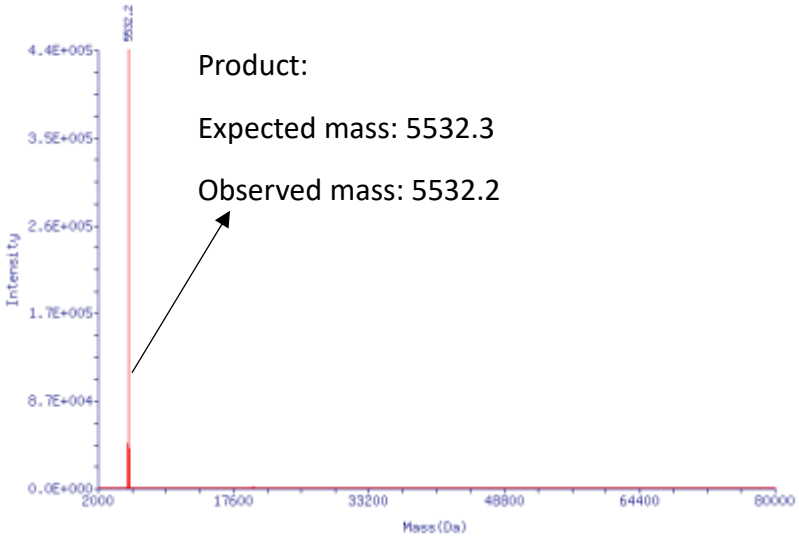
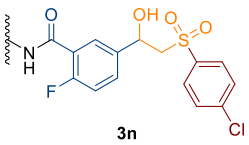


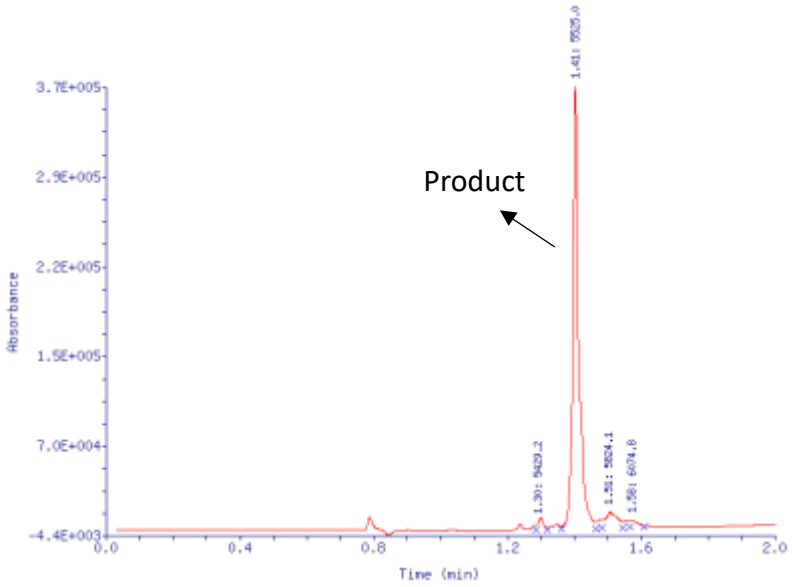
Figure S52. LC-MS Spectrum of DEL Compound **3m**.



3n

Purity: 90%
Conversion rate: 90%
Expected mass: 5525.3
Observed mass: 5525.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.30	5429.2	4.36E+004	ok	9.32E+003	1.92
1.41	5525.0	7.78E+005	ok	4.39E+005	90.37
1.51	5824.1	1.27E+004	ok	3.02E+004	6.22
1.58	6074.8	1.59E+004	ok	7.25E+003	1.49

Deconvoluted mass spectrum of product:

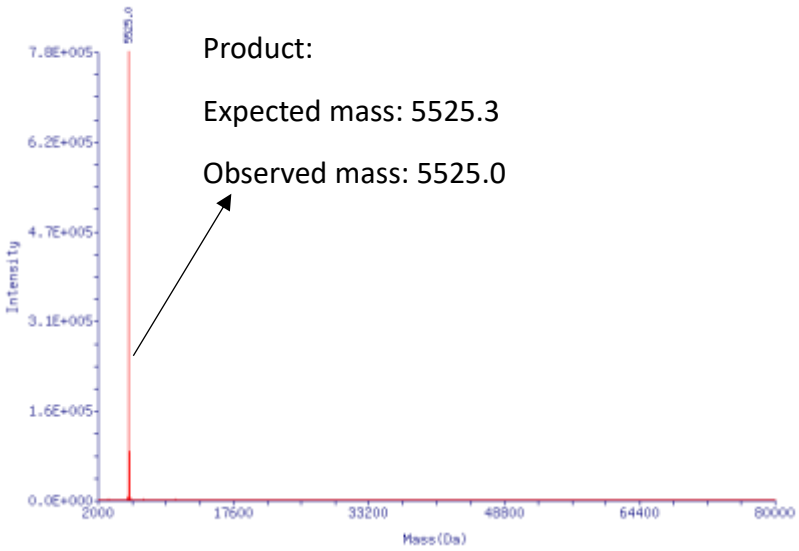
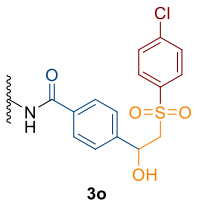
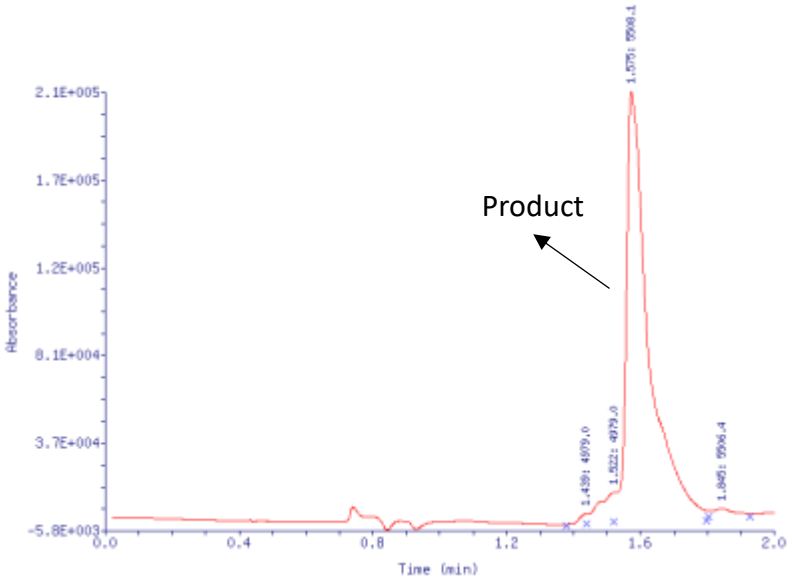


Figure S53. LC-MS Spectrum of DEL Compound **3n**.



3o
Purity: 93%
Conversion rate: 93%
Expected mass: 5507.3
Observed mass: 5508.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.439	4979.0	2.95E+003	ok	6.39E+003	0.60
1.522	4979.0	4.15E+003	ok	4.53E+004	4.29
1.575	5508.1	1.58E+005	ok	9.88E+005	93.46
1.845	5506.4	1.98E+003	ok	1.74E+004	1.65

Deconvoluted mass spectrum of product:

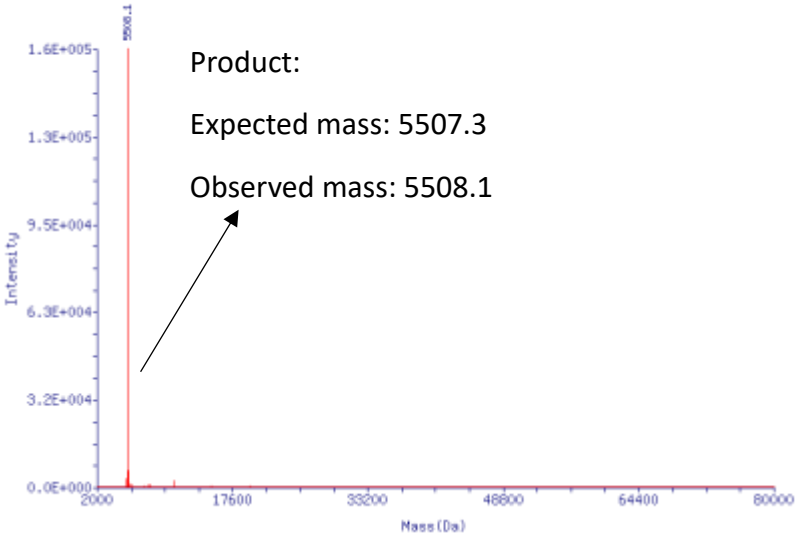
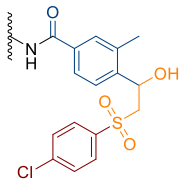


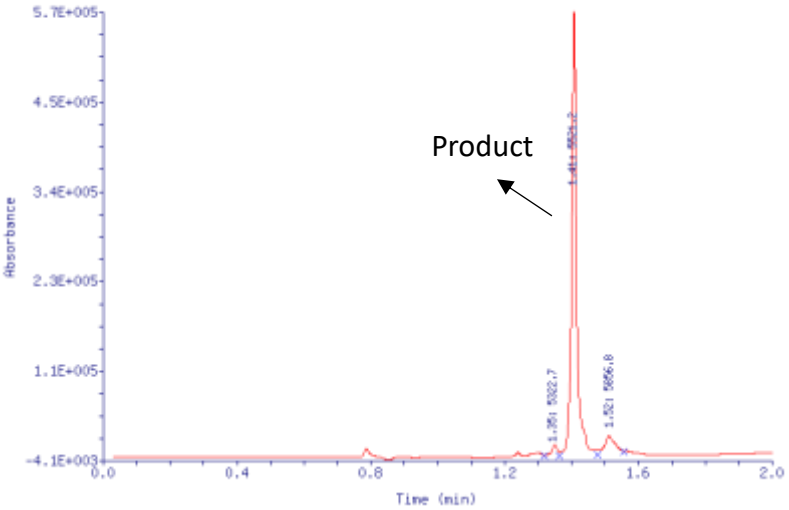
Figure S54. LC-MS Spectrum of DEL Compound **3o**.



3p

Purity: 91%
Conversion rate: 91%
Expected mass: 5521.3
Observed mass: 5521.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.35	5322.7	4.21E+004	ok	1.29E+004	2.05
1.41	5521.2	1.02E+006	ok	5.73E+005	91.14
1.52	5856.8	4.38E+004	ok	4.28E+004	6.82

Deconvoluted mass spectrum of product:

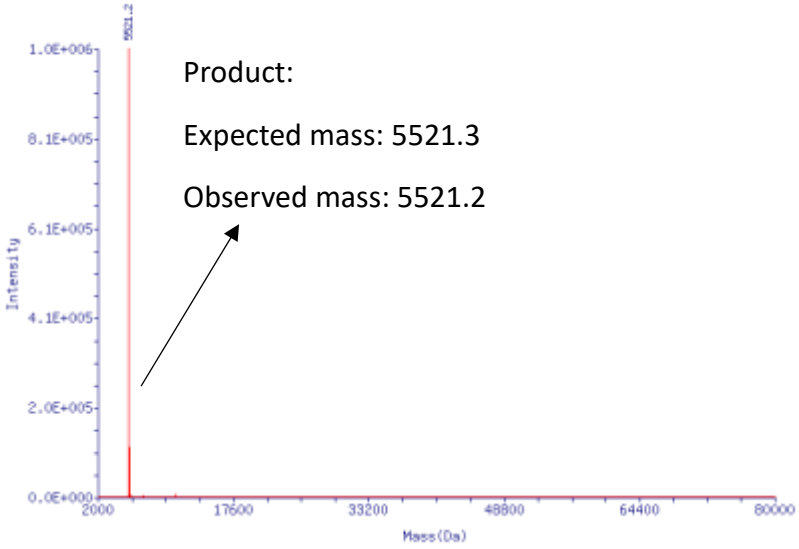
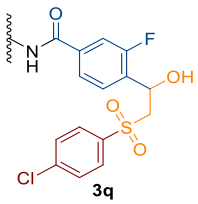


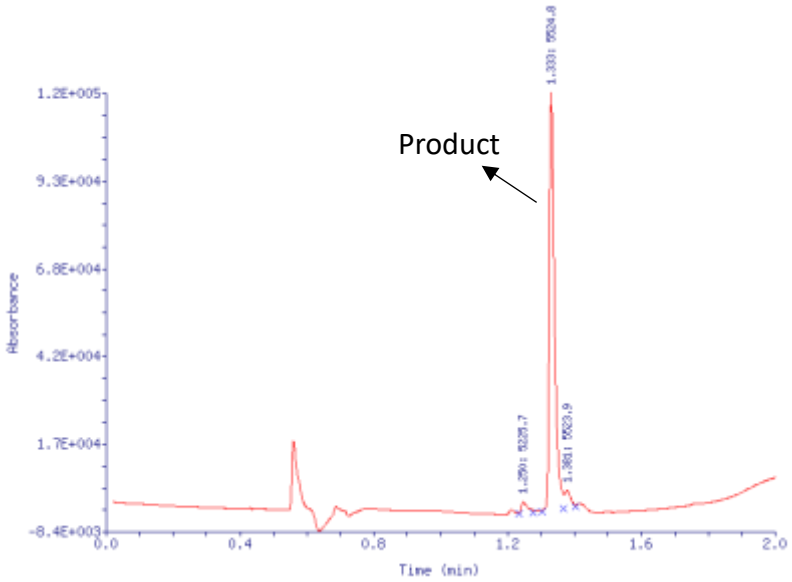
Figure S55. LC-MS Spectrum of DEL Compound **3p**.



3q

Purity: 93%
Conversion rate: 93%
Expected mass: 5525.3
Observed mass: 5524.8

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.250	5225.7	2.36E+004	ok	3.88E+003	2.81
1.333	5524.8	6.47E+005	ok	1.28E+005	92.87
1.381	5523.9	5.79E+004	ok	5.97E+003	4.32

Deconvoluted mass spectrum of product:

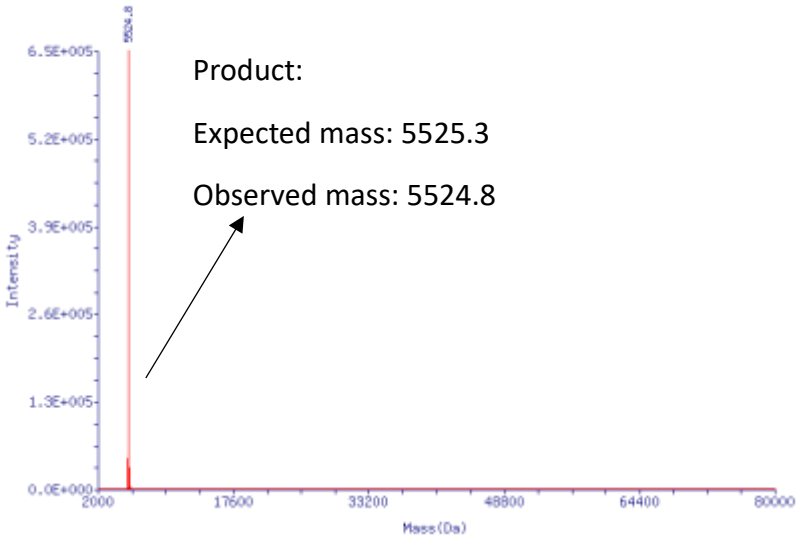
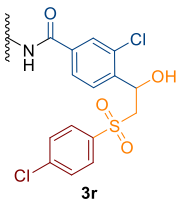


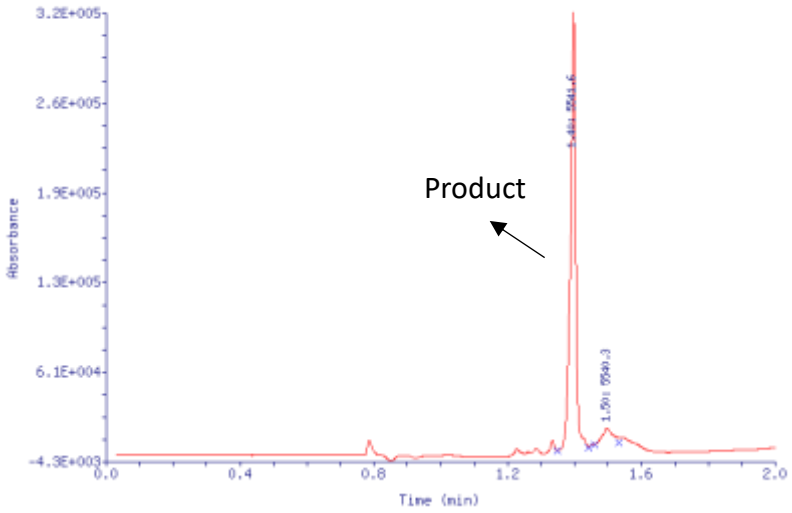
Figure S56. LC-MS Spectrum of DEL Compound **3q**.



3r

Purity: 94%
Conversion rate: 94%
Expected mass: 5541.7
Observed mass: 5541.6

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.40	5541.6	7.50E+005	ok	3.38E+005	94.03
1.50	5540.3	1.43E+004	ok	2.15E+004	5.97

Deconvoluted mass spectrum of product:

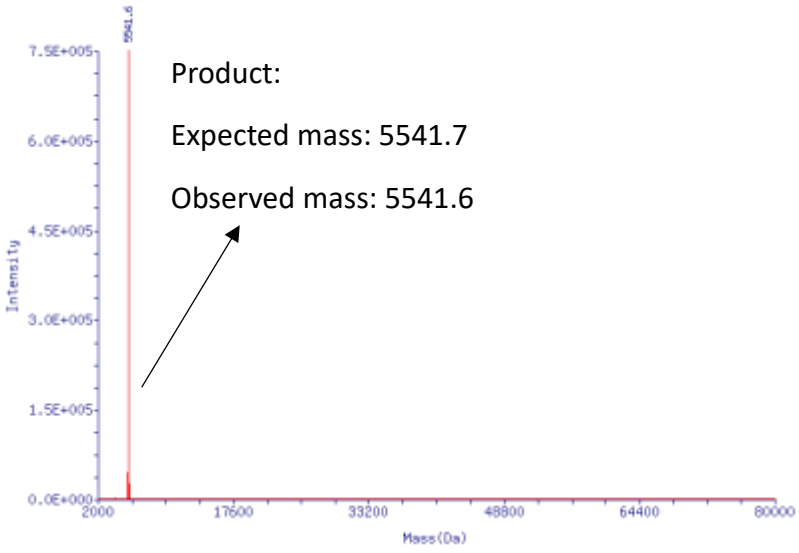
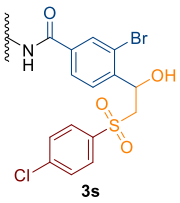


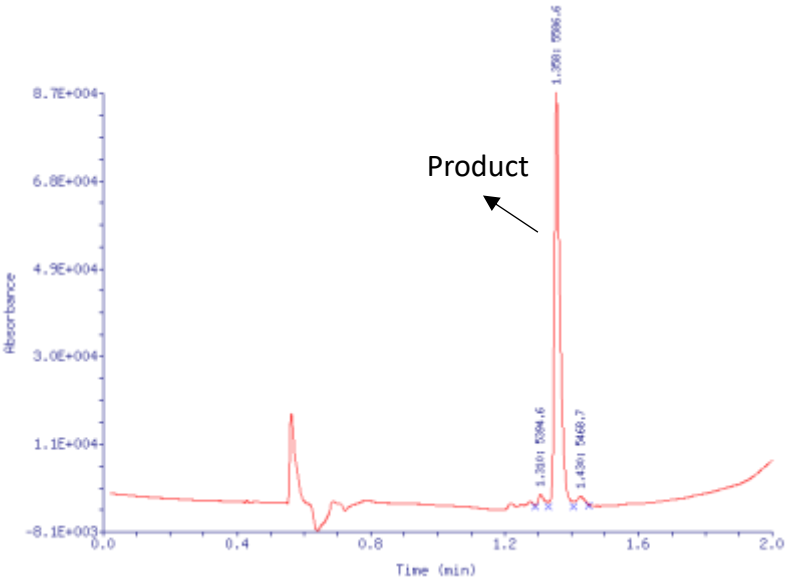
Figure S57. LC-MS Spectrum of DEL Compound **3r**.



3s

Purity: 95%
Conversion rate: 95%
Expected mass: 5586.2
Observed mass: 5586.6

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.310	5394.6	1.47E+004	ok	2.91E+003	2.67
1.358	5586.6	3.97E+005	ok	1.03E+005	94.59
1.430	5468.7	8.13E+003	ok	2.99E+003	2.74

Deconvoluted mass spectrum of product:

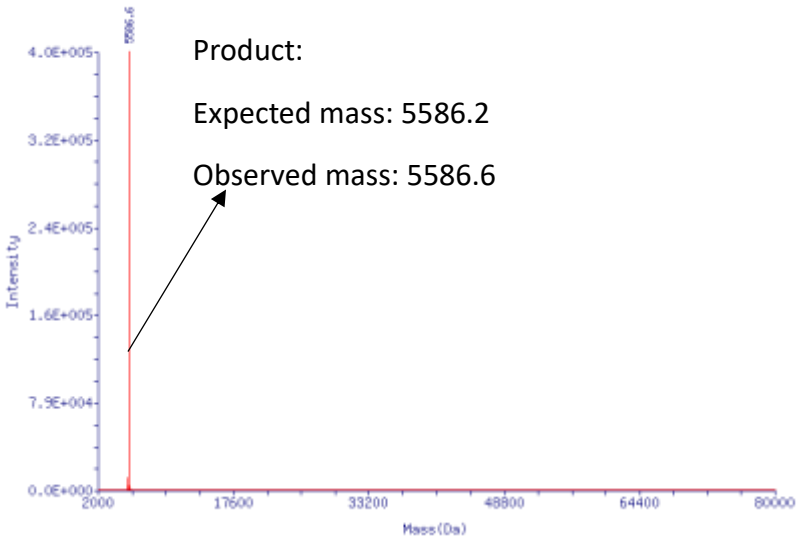
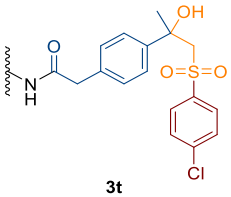


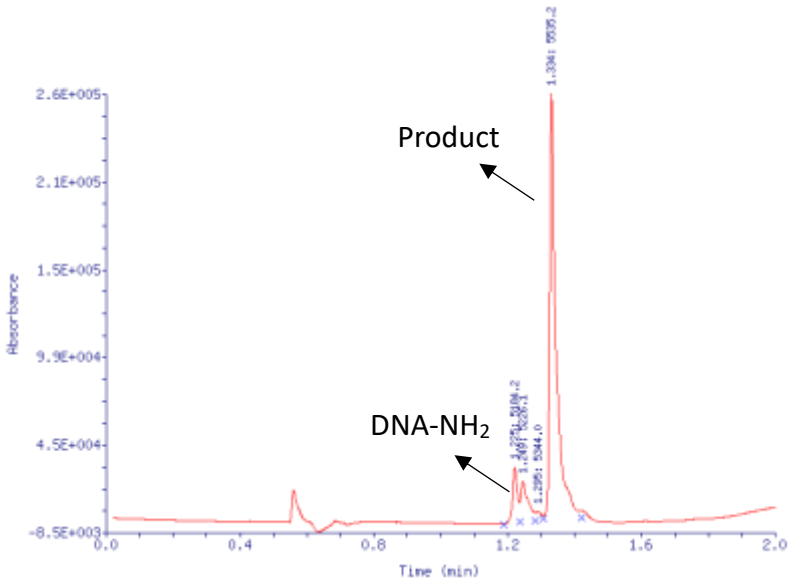
Figure S58. LC-MS Spectrum of DEL Compound **3s**.



3t

Purity: 82%
Conversion rate: 82%
Expected mass: 5535.3
Observed mass: 5535.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.225	5184.2	1.70E+005	ok	3.23E+004	7.74
1.249	5226.1	1.26E+005	ok	3.60E+004	8.63
1.295	5344.0	9.90E+003	ok	4.93E+003	1.18
1.334	5535.2	7.91E+005	ok	3.44E+005	82.45

Deconvoluted mass spectrum of product:

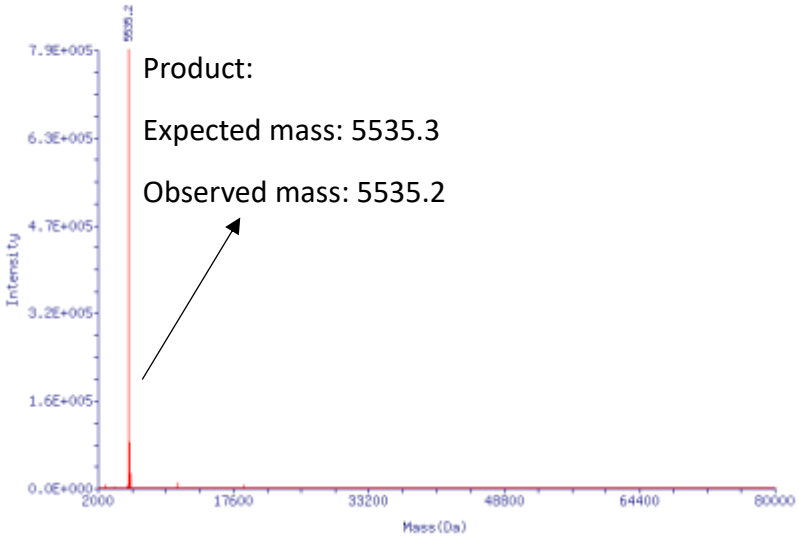
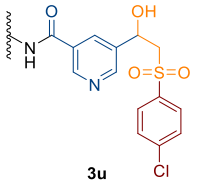


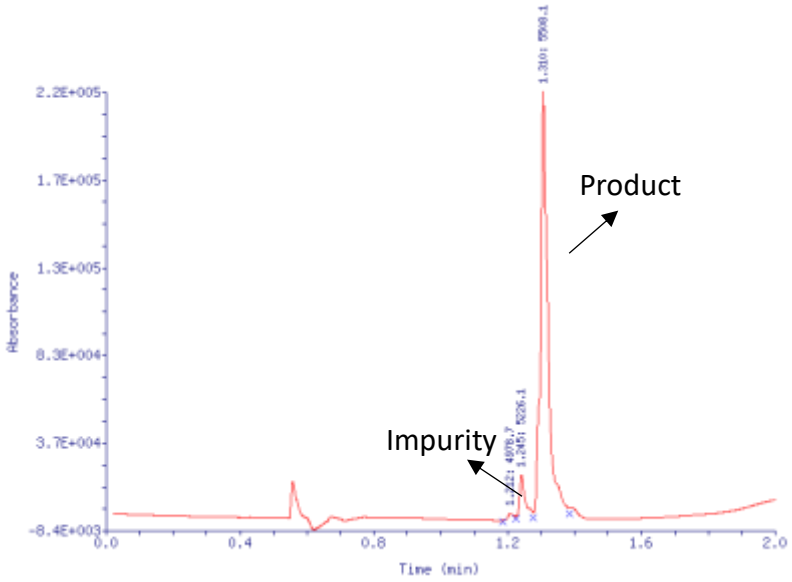
Figure S59. LC-MS Spectrum of DEL Compound **3t**.



3u

Purity: 92%
Conversion rate: 97%
Expected mass: 5508.2
Observed mass: 5508.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.212	4978.7	2.19E+004	ok	2.95E+003	0.82
1.245	5226.1	1.18E+005	ok	2.50E+004	6.93
1.310	5508.1	8.29E+005	ok	3.32E+005	92.25

Deconvoluted mass spectrum of product:

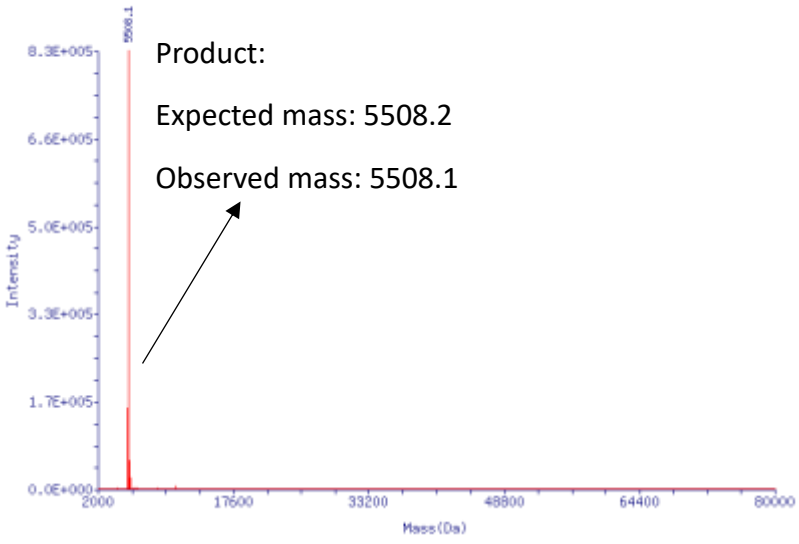
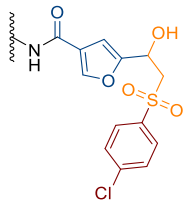


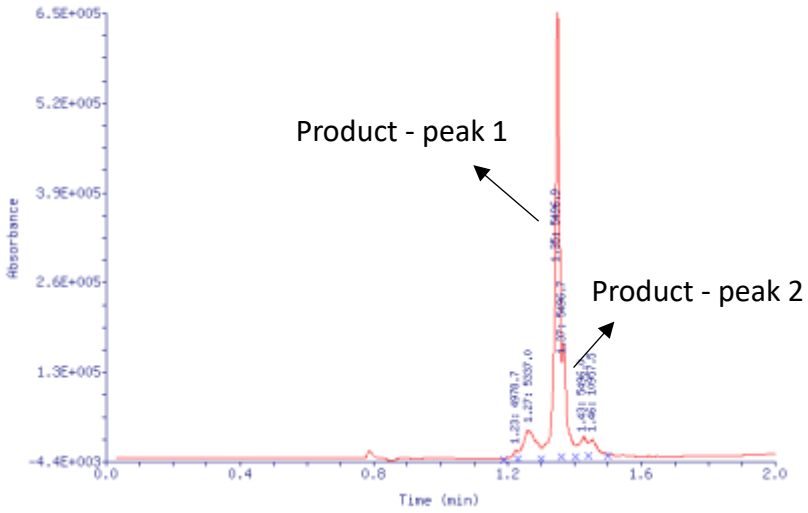
Figure S60. LC-MS Spectrum of DEL Compound **3u**.



3v

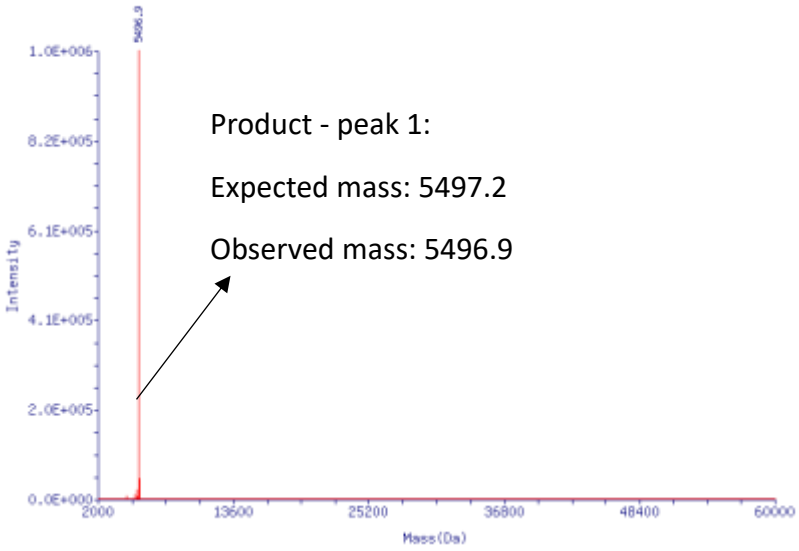
Purity: 79%
Conversion rate: 83%
Expected mass: 5497.2
Observed mass: 5496.9 and 5496.7

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.23	4978.7	1.56E+004	ok	1.06E+004	1.09
1.27	5337.0	4.78E+004	ok	1.05E+005	10.76
1.35	5496.9	1.02E+006	ok	6.10E+005	62.77
1.37	5496.7	2.06E+006	ok	1.62E+005	16.71
1.43	5496.0	2.37E+005	ok	4.59E+004	4.73
1.46	10957.5	2.46E+004	ok	3.84E+004	3.95

Deconvoluted mass spectrum of product:



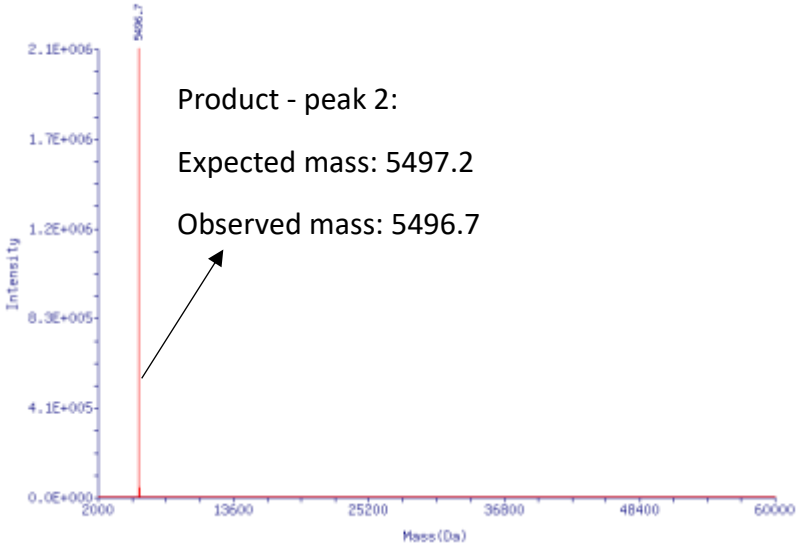
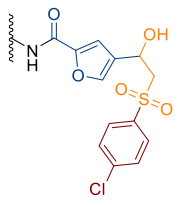


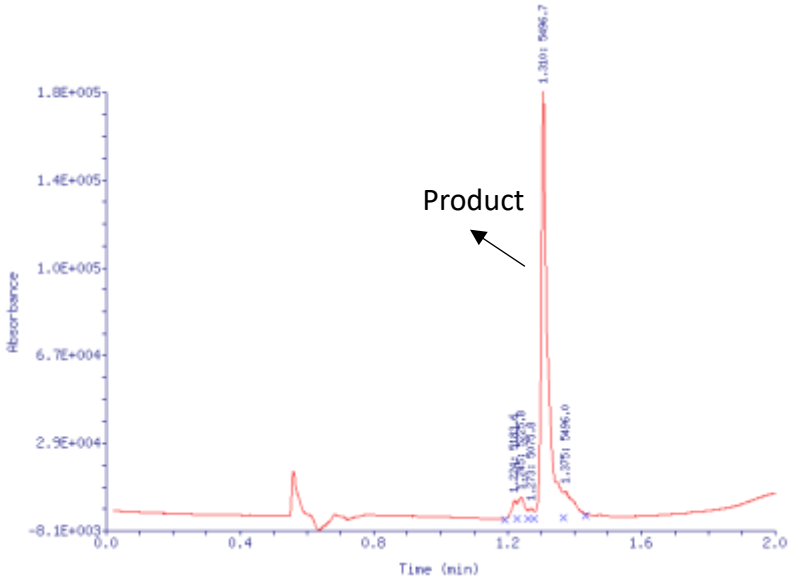
Figure S61. LC-MS Spectrum of DEL Compound **3v**.



3w

Purity: 84%
Conversion rate: 84%
Expected mass: 5497.2
Observed mass: 5496.7

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.224	5183.6	3.36E+004	ok	7.29E+003	2.59
1.245	5225.8	2.61E+004	ok	1.28E+004	4.57
1.273	5075.8	1.44E+004	ok	3.70E+003	1.32
1.310	5496.7	6.99E+005	ok	2.35E+005	83.66
1.375	5496.0	3.86E+004	ok	2.21E+004	7.86

Deconvoluted mass spectrum of product:

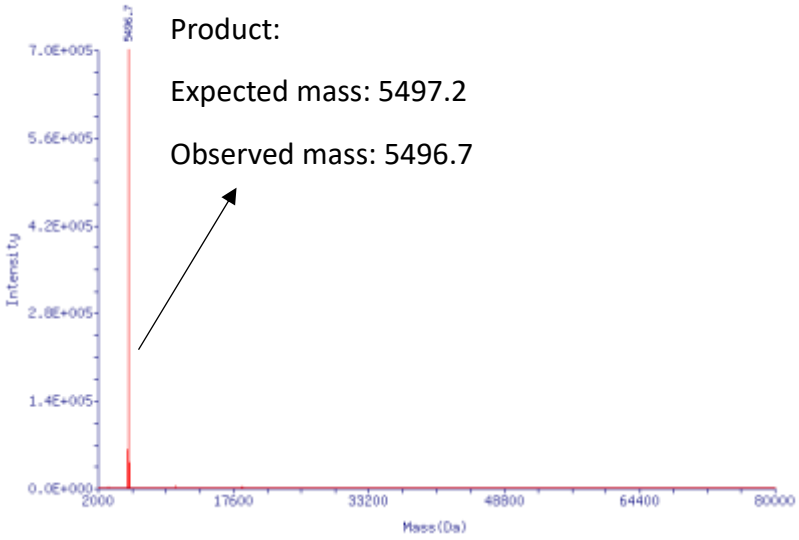
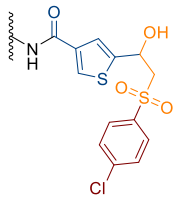


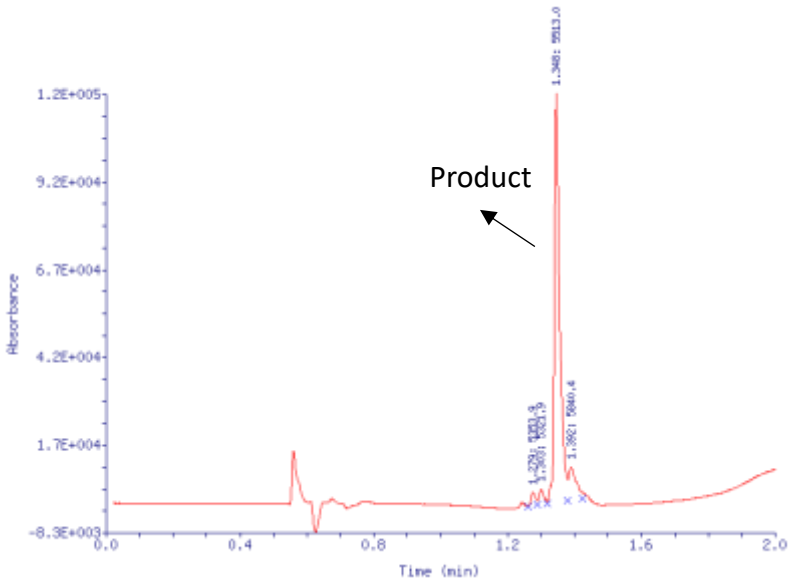
Figure S62. LC-MS Spectrum of DEL Compound **3w**.



3x

Purity: 86%
Conversion rate: 93%
Expected mass: 5513.3
Observed mass: 5513.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.279	5353.9	2.05E+004	ok	3.03E+003	2.06
1.303	5321.9	2.75E+004	ok	3.62E+003	2.46
1.348	5513.0	5.94E+005	ok	1.27E+005	86.07
1.392	5840.4	4.56E+004	ok	1.39E+004	9.42

Deconvoluted mass spectrum of product:

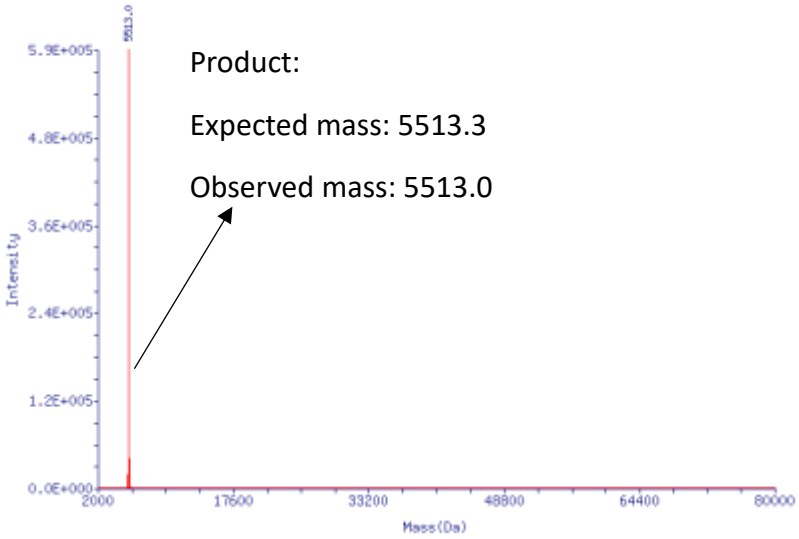
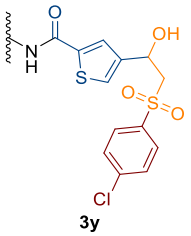


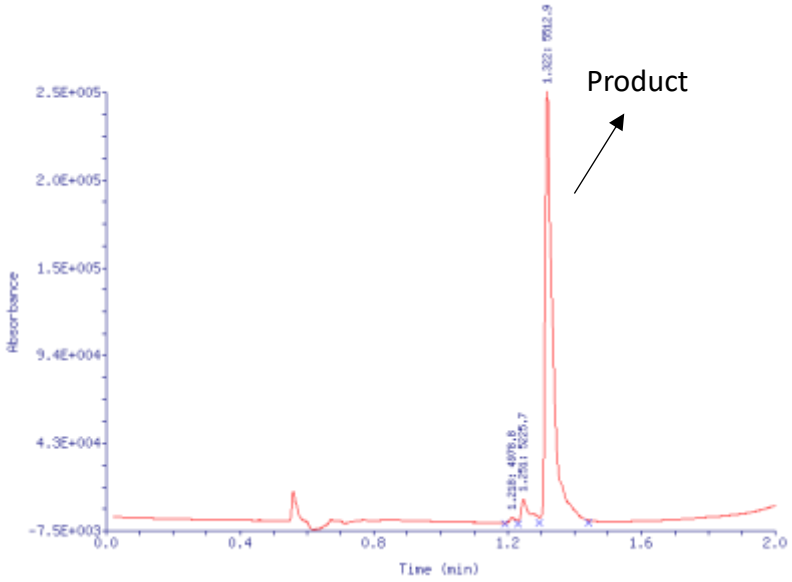
Figure S63. LC-MS Spectrum of DEL Compound **3x**.



3y

Purity: 94%
Conversion rate: 94%
Expected mass: 5513.3
Observed mass: 5512.9

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.218	4978.8	1.89E+004	ok	3.34E+003	0.80
1.251	5225.7	6.54E+004	ok	2.28E+004	5.43
1.322	5512.9	7.88E+005	ok	3.94E+005	93.77

Deconvoluted mass spectrum of product:

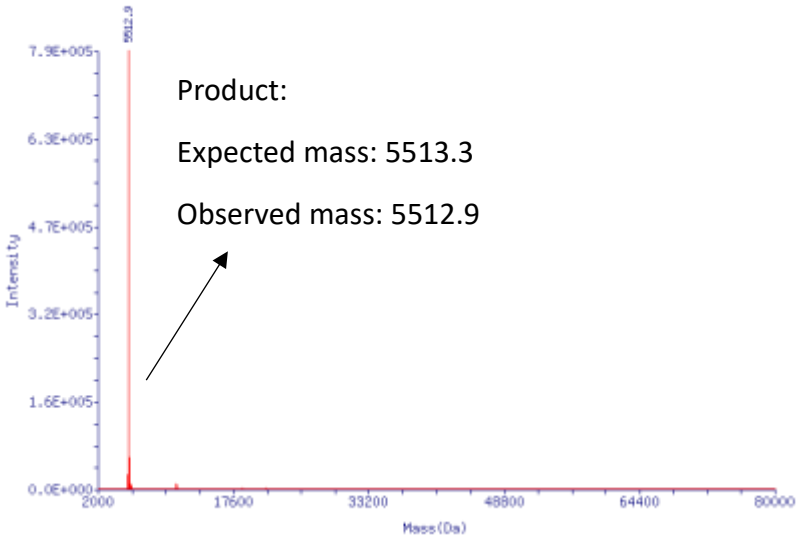
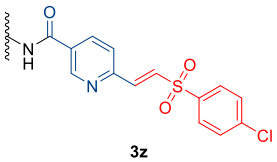


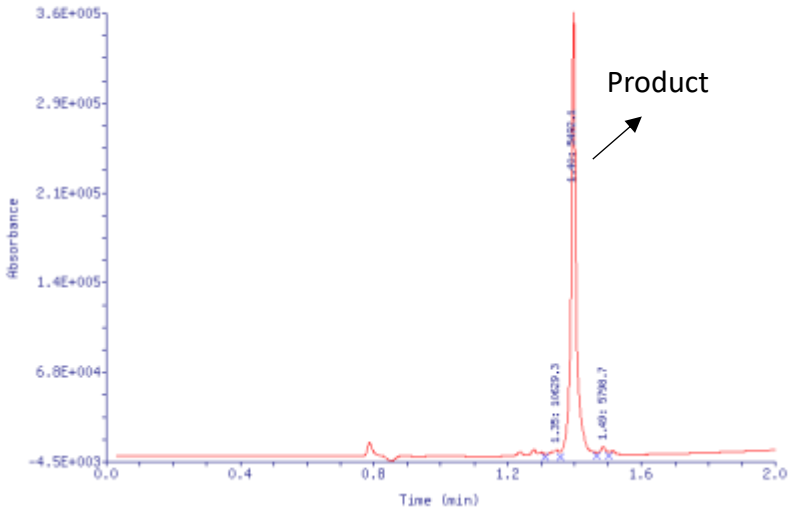
Figure S64. LC-MS Spectrum of DEL Compound **3y**.



3z

Purity: 96%
Conversion rate: 96%
Expected mass: 5490.2
Observed mass: 5492.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.35	10629.3	1.55E+004	ok	6.99E+003	1.79
1.40	5492.1	7.09E+005	ok	3.75E+005	96.17
1.49	5798.7	2.84E+004	ok	7.93E+003	2.03

Deconvoluted mass spectrum of product:

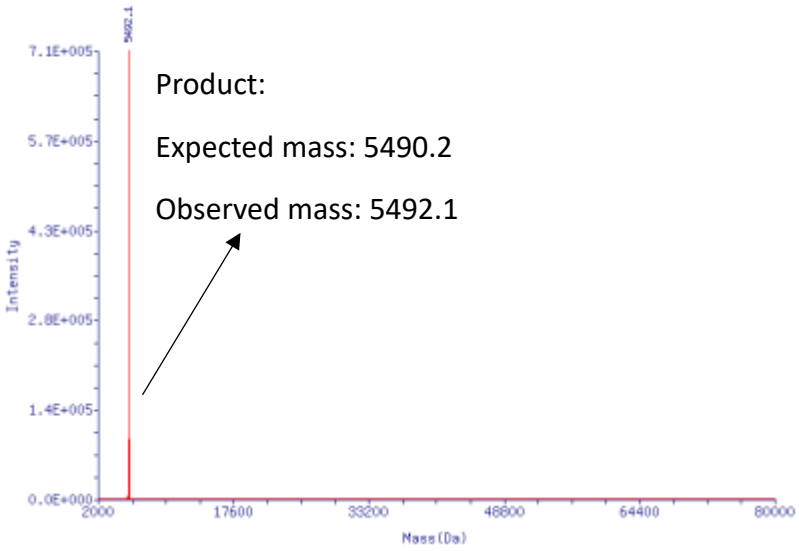
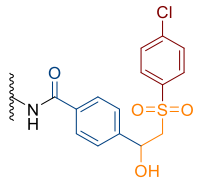


Figure S65. LC-MS Spectrum of DEL Compound **3z**.

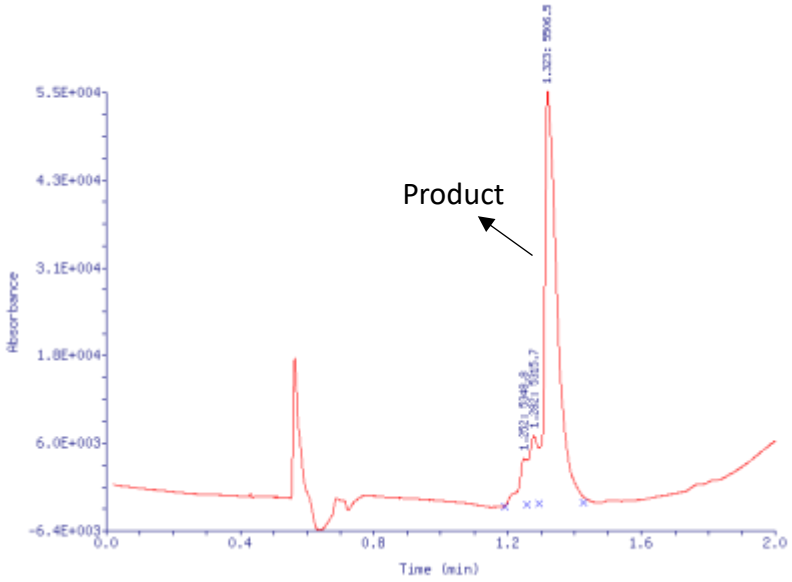
9.8. Mass Spectrum of 3o at A Scale of 100 nmol



3o

Purity: 84%
Conversion rate: 84%
Expected mass: 5507.3
Observed mass: 5506.5

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.252	5348.8	3.73E+003	ok	1.08E+004	6.13
1.282	5315.7	1.63E+004	ok	1.68E+004	9.50
1.323	5506.5	1.12E+005	ok	1.49E+005	84.37

Deconvoluted mass spectrum of product:

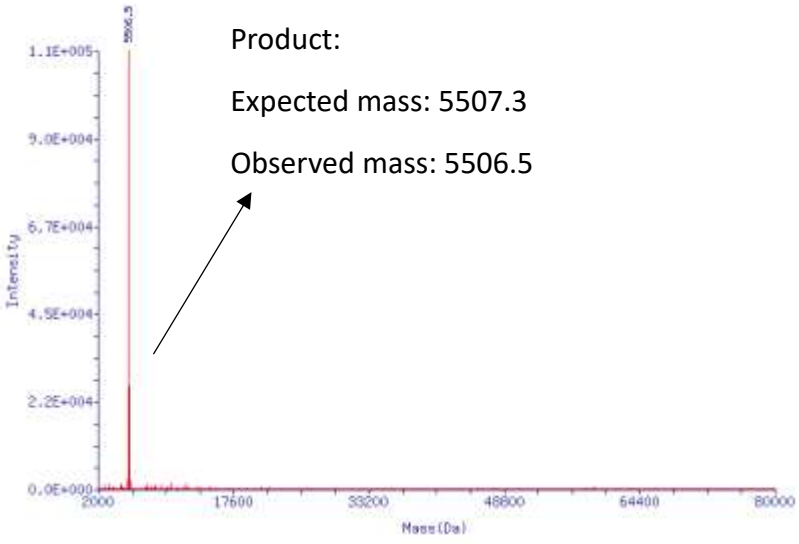
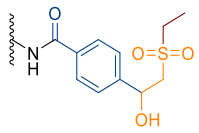


Figure S66. LC-MS Spectrum of **3o** at a scale of 100 nmol.

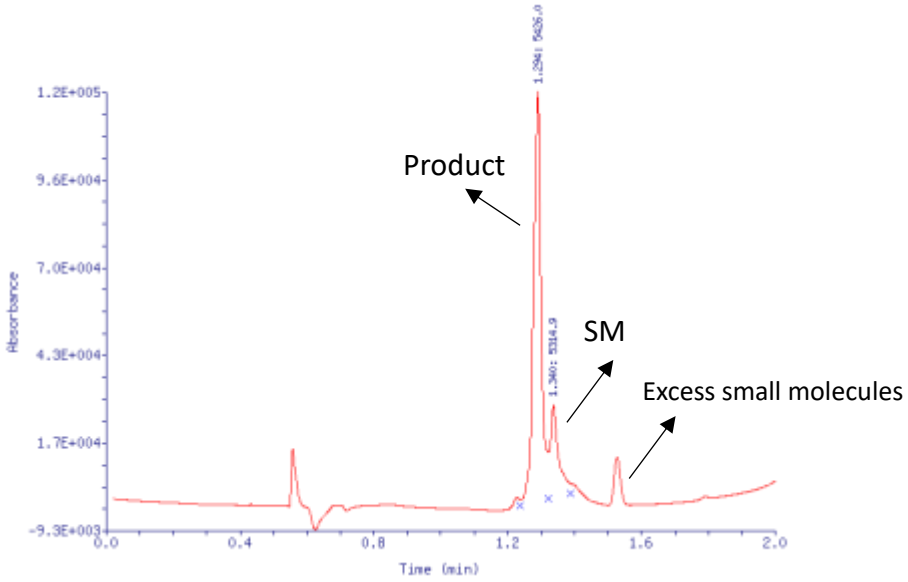
9.9. Mass Spectrum of 5a-5v



5a

Purity: 81%
Conversion rate: 81%
Expected mass: 5424.8
Observed mass: 5426.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.294	5426.0	4.37E+004	ok	1.94E+005	80.54
1.340	5314.9	7.30E+003	ok	4.68E+004	19.46

Deconvoluted mass spectrum of product:

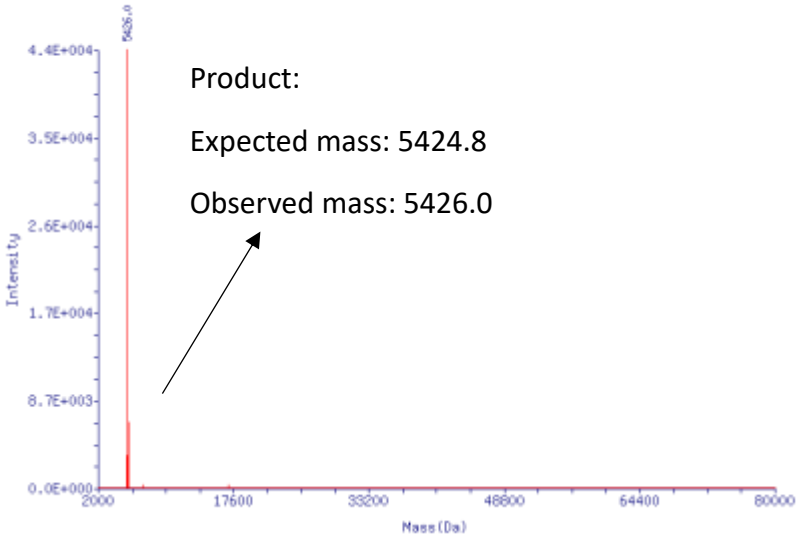
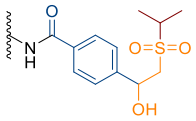


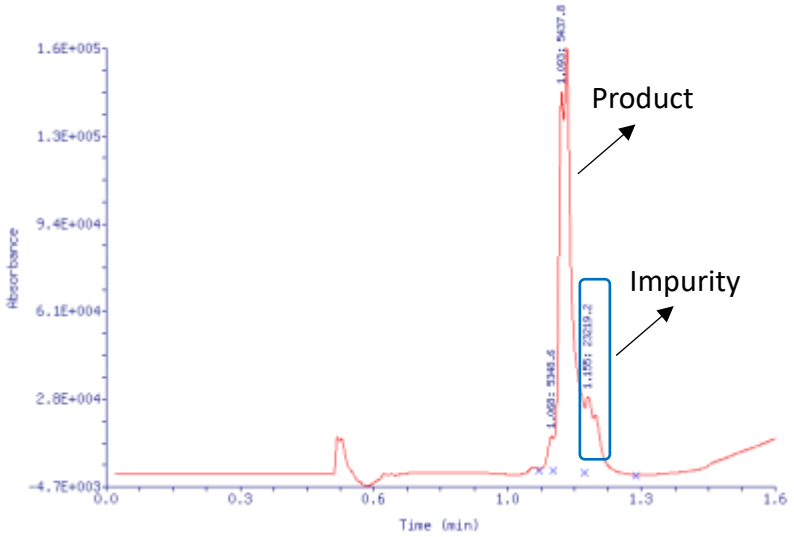
Figure S67. LC-MS Spectrum of DEL Compound **5a**.



5b

Purity: 82%
Conversion rate: 82%
Expected mass: 5438.8
Observed mass: 5437.8

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.068	5348.6	8.24E+003	ok	1.15E+004	2.93
1.093	5437.8	2.69E+005	ok	3.23E+005	82.25
1.155	23219.2	2.68E+004	ok	5.81E+004	14.81

Deconvoluted mass spectrum of product:

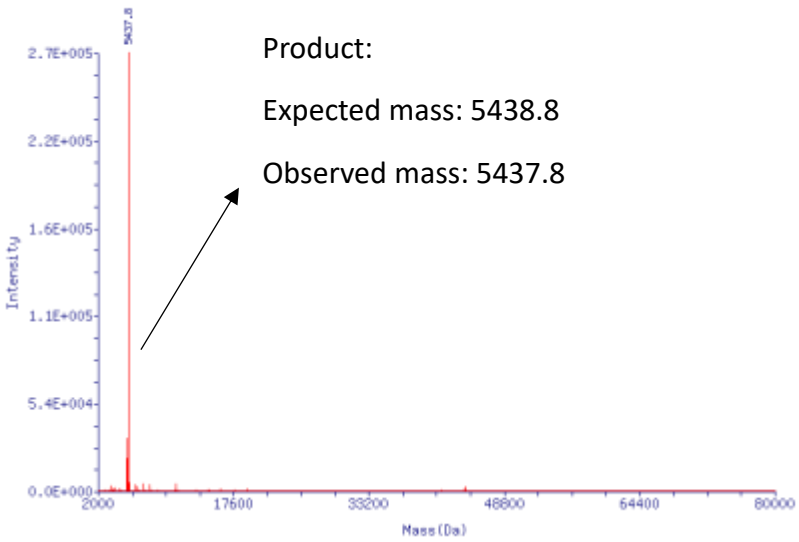
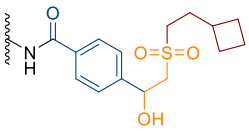


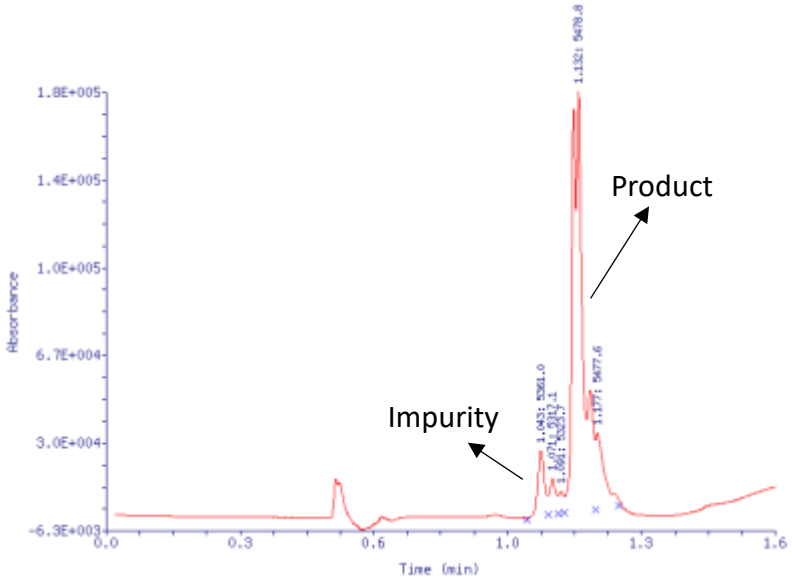
Figure S68. LC-MS Spectrum of DEL Compound **5b**.



5c

Purity: 77%
Conversion rate: 77%
Expected mass: 5478.9
Observed mass: 5478.8

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.043	5361.0	7.93E+004	ok	2.90E+004	7.15
1.071	5317.1	1.06E+005	ok	1.43E+004	3.54
1.091	5323.7	7.17E+004	ok	7.06E+003	1.74
1.132	5478.8	1.21E+006	ok	3.10E+005	76.52
1.177	5477.6	4.62E+004	ok	4.47E+004	11.04

Deconvoluted mass spectrum of product:

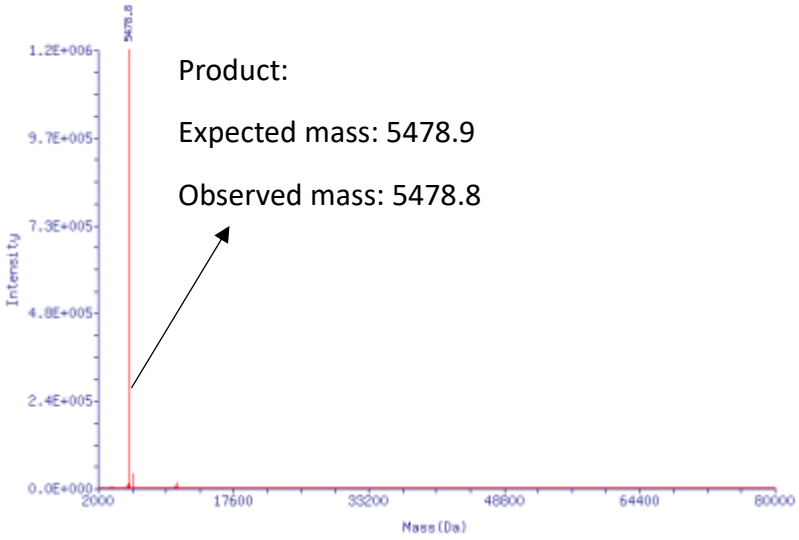
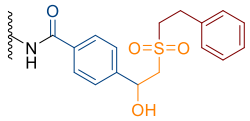


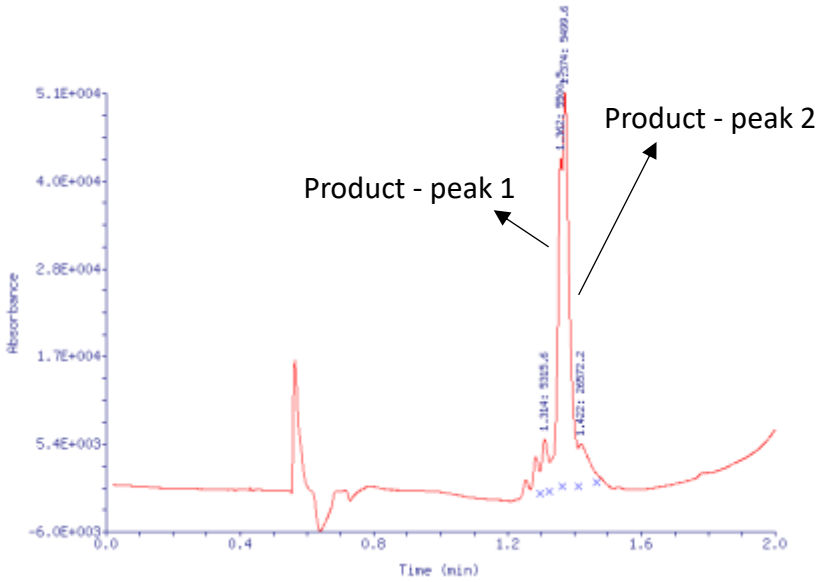
Figure S69. LC-MS Spectrum of DEL Compound **5c**.



5d

Purity: 85%
Conversion rate: 85%
Expected mass: 5500.9
Observed mass: 5500.5 and 5499.6

LC Spectrum:



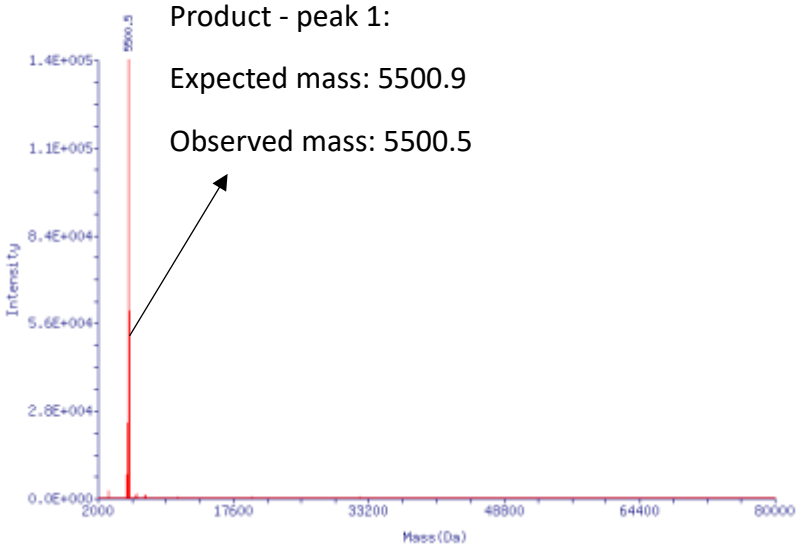
RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.314	5315.6	2.65E+004	ok	8.59E+003	6.63
1.362	5500.5	1.40E+005	ok	3.83E+004	29.57
1.374	5499.6	3.66E+005	ok	7.15E+004	55.15
1.422	26572.2	5.66E+003	ok	1.12E+004	8.65

Deconvoluted mass spectrum of product:

Product - peak 1:

Expected mass: 5500.9

Observed mass: 5500.5



Product - peak 2:

Expected mass: 5500.9

Observed mass: 5499.6

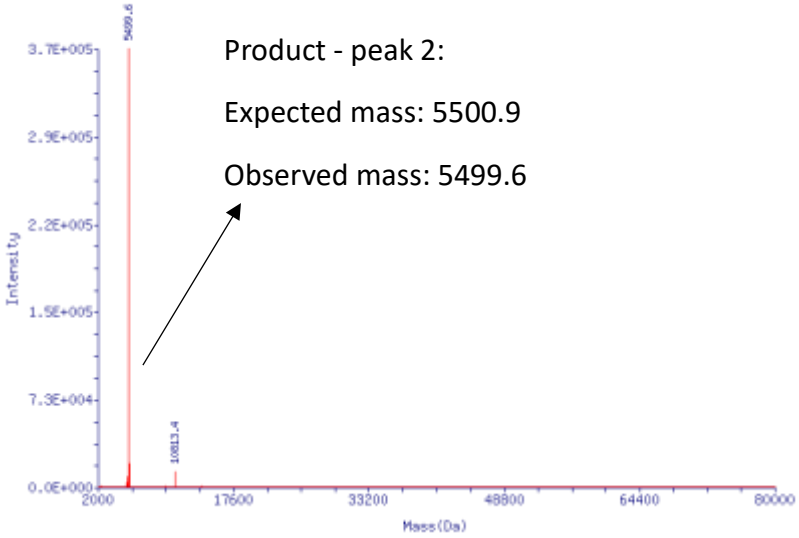
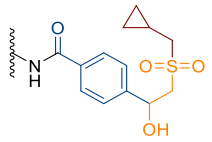


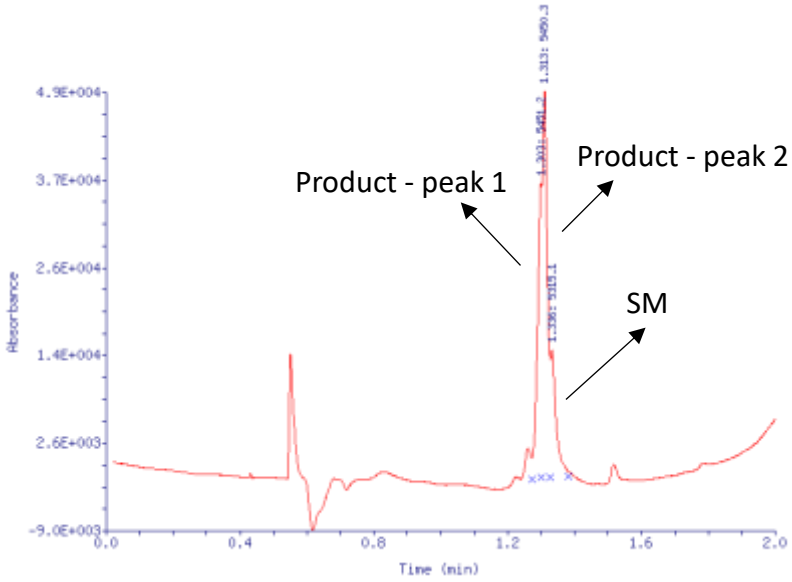
Figure S70. LC-MS Spectrum of DEL Compound **5d**.



5e

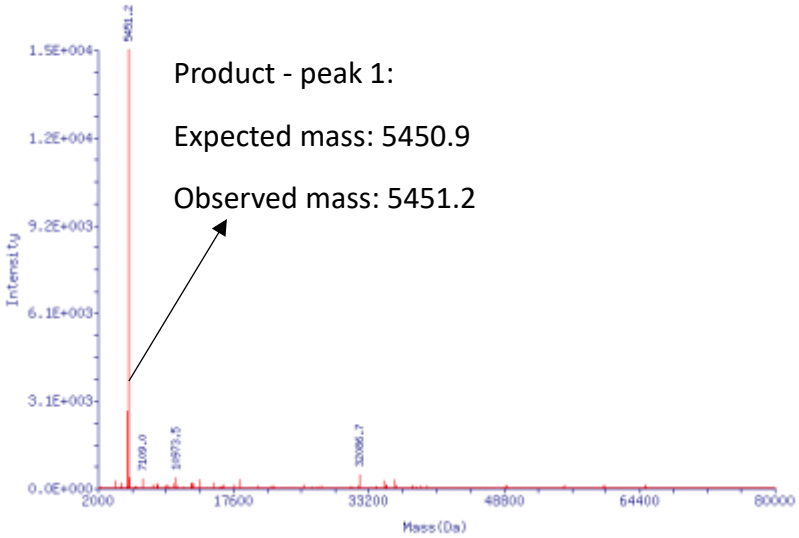
Purity: 82%
Conversion rate: 82%
Expected mass: 5450.9
Observed mass: 5451.2 and 5450.3

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.303	5451.2	1.53E+004	ok	3.21E+004	30.57
1.313	5450.3	5.31E+004	ok	5.37E+004	51.24
1.336	5315.1	6.11E+003	ok	1.91E+004	18.18

Deconvoluted mass spectrum of product:



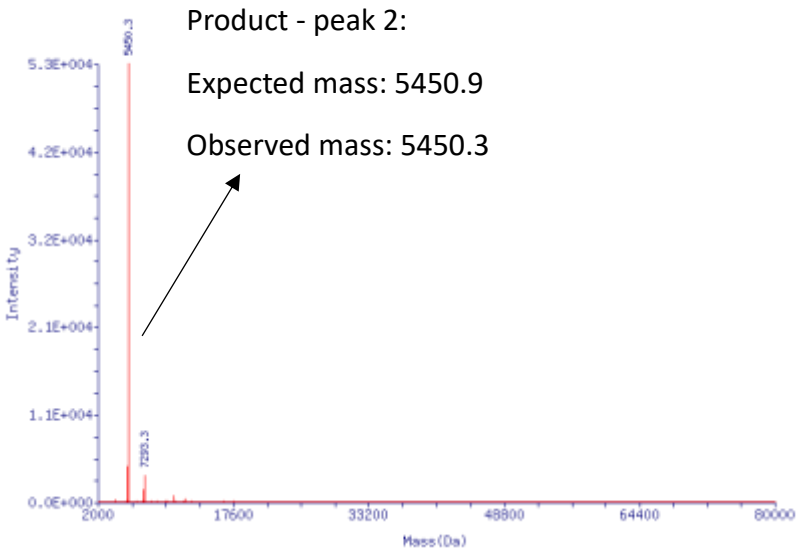
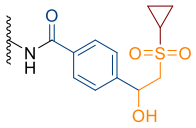


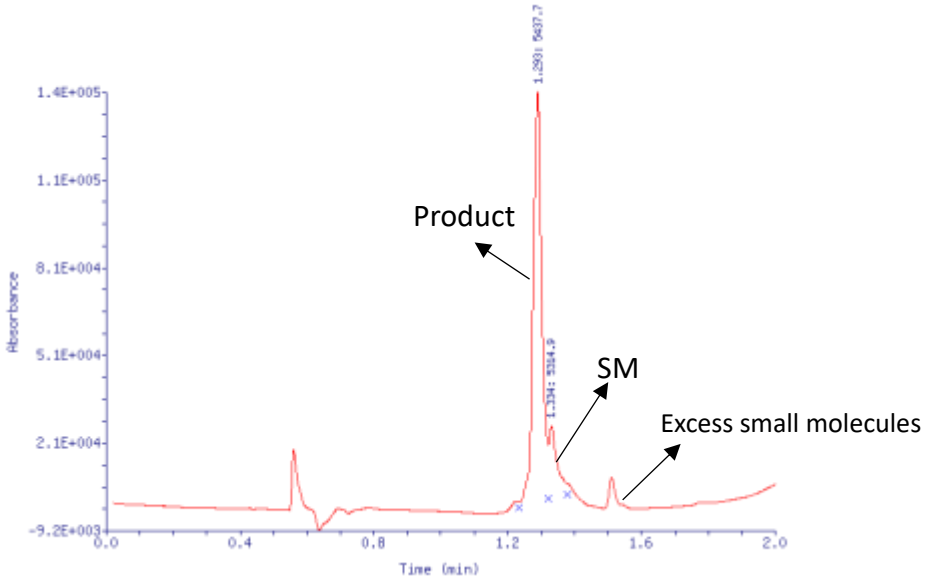
Figure S71. LC-MS Spectrum of DEL Compound **5e**.



5f

Purity: 86%
Conversion rate: 86%
Expected mass: 5436.8
Observed mass: 5437.7

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.293	5437.7	2.75E+004	ok	2.49E+005	85.99
1.334	5314.9	4.64E+003	ok	4.06E+004	14.01

Deconvoluted mass spectrum of product:

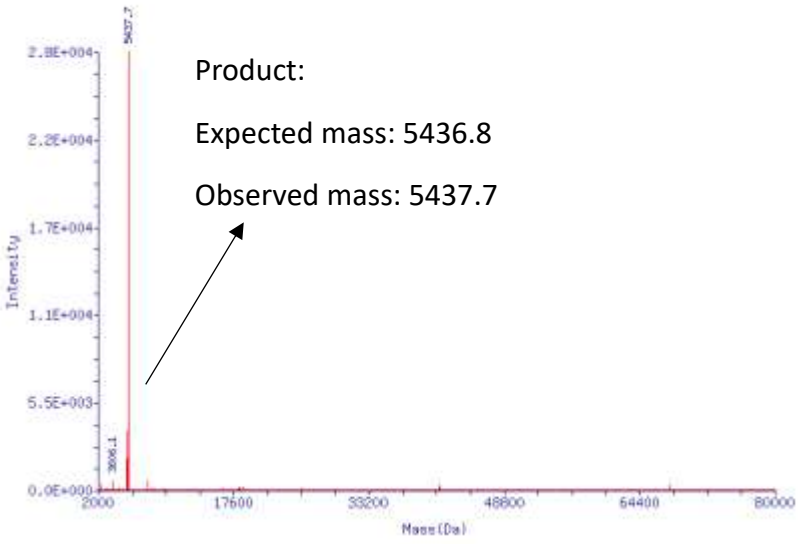
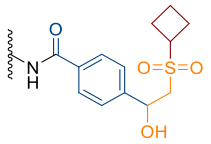


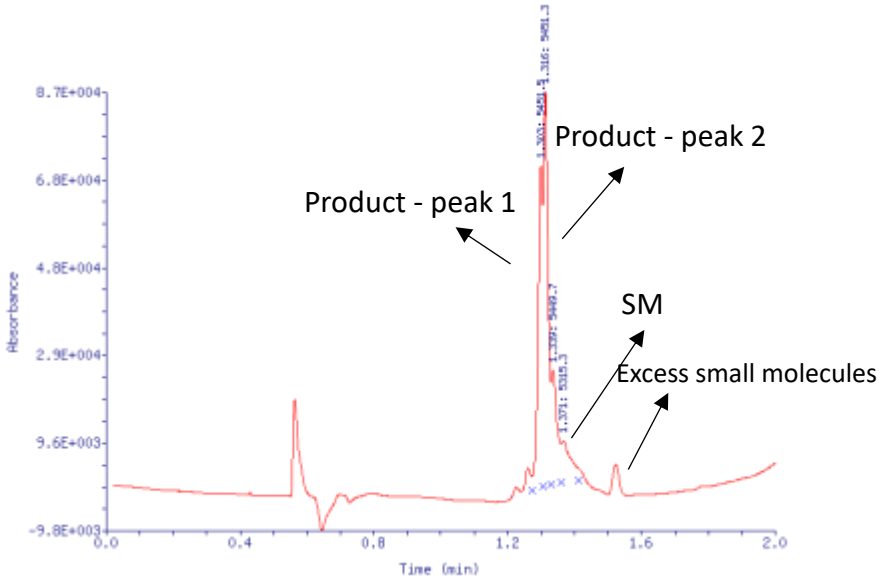
Figure S72. LC-MS Spectrum of DEL Compound **5f**.



5g

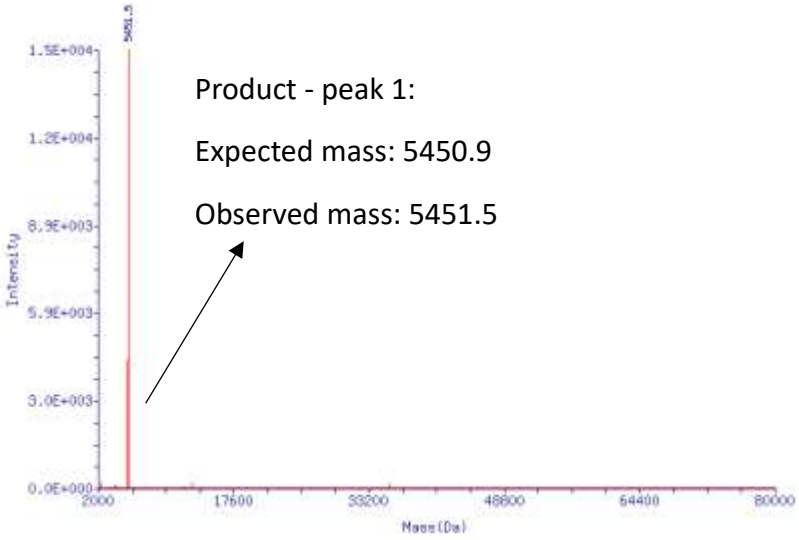
Purity: 75%
Conversion rate: 75%
Expected mass: 5450.9
Observed mass: 5451.5 and 5451.3

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.303	5451.5	1.48E+004	ok	6.26E+004	32.09
1.316	5451.3	1.15E+005	ok	8.45E+004	43.32
1.339	5449.7	4.49E+004	ok	3.06E+004	15.68
1.371	5315.3	1.83E+003	ok	1.74E+004	8.92

Deconvoluted mass spectrum of product:



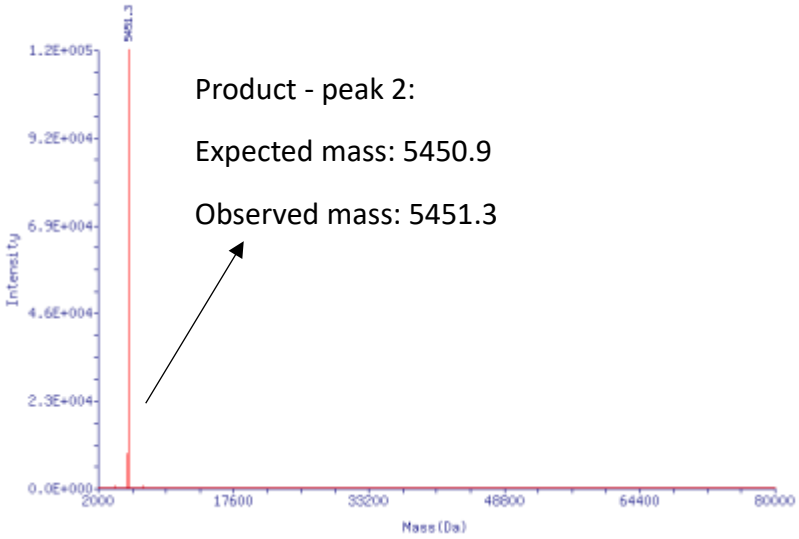
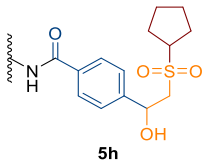


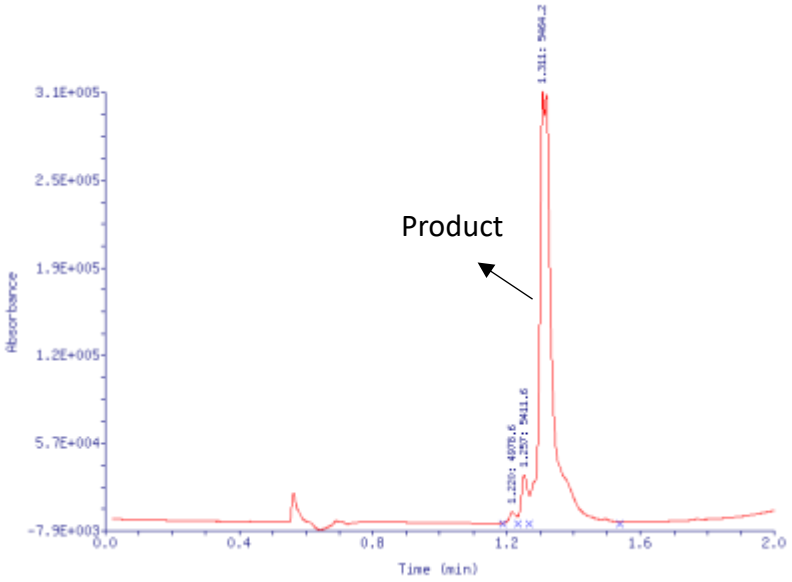
Figure S73. LC-MS Spectrum of DEL Compound **5g**.



5h

Purity: 94%
Conversion rate: 94%
Expected mass: 5464.9
Observed mass: 5464.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.220	4978.6	2.67E+004	ok	1.02E+004	1.14
1.257	5411.6	1.45E+005	ok	4.68E+004	5.25
1.311	5464.2	4.63E+005	ok	8.34E+005	93.60

Deconvoluted mass spectrum of product:

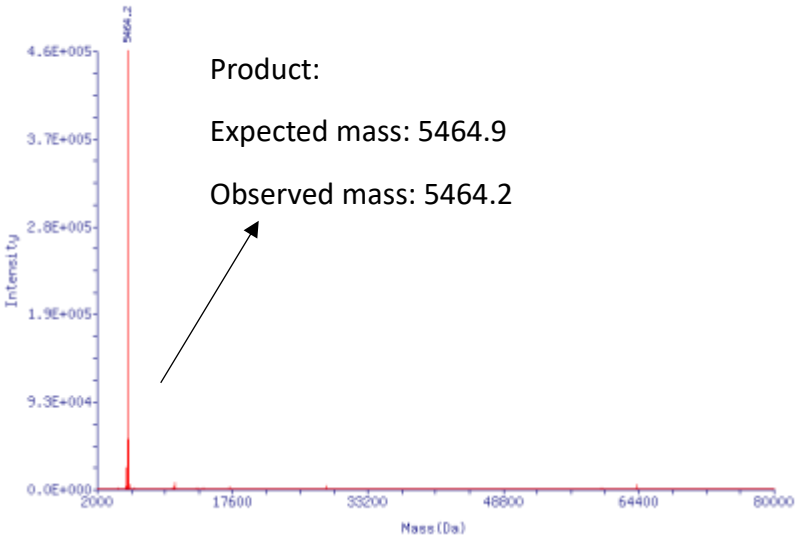
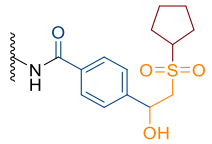


Figure S74. LC-MS Spectrum of DEL Compound **5h**. The sodium sulfinate (**4h**)

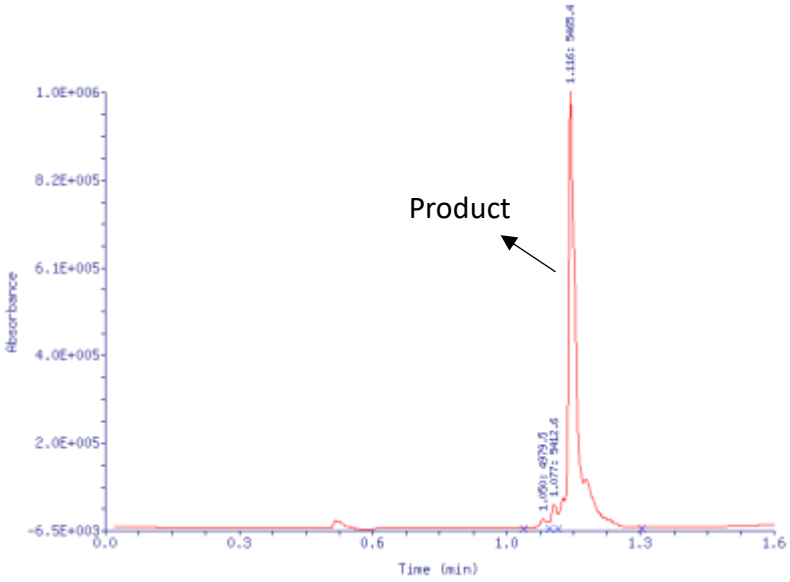
used was a crude product synthesized in the laboratory.



5h

Purity: 95%
Conversion rate: 95%
Expected mass: 5464.9
Observed mass: 5465.4

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.050	4979.5	5.98E+004	ok	2.38E+004	1.66
1.077	5412.6	1.94E+005	ok	4.92E+004	3.44
1.116	5465.4	1.22E+006	ok	1.36E+006	94.90

Deconvoluted mass spectrum of product:

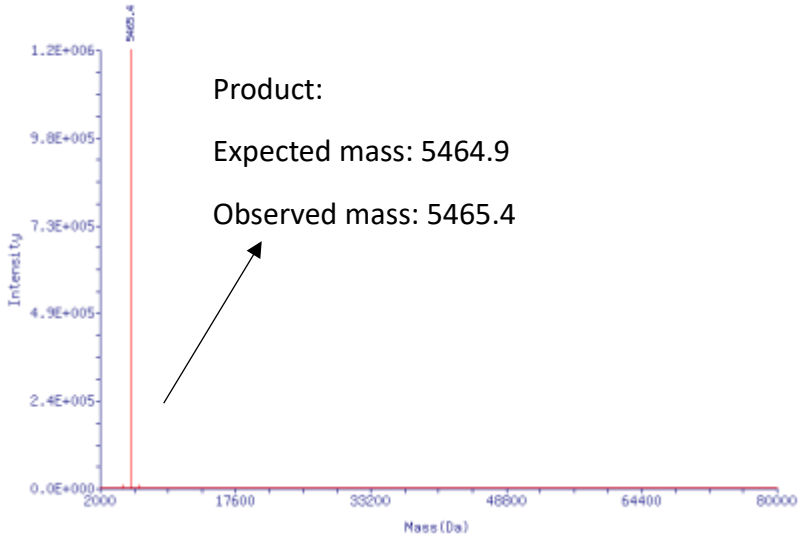
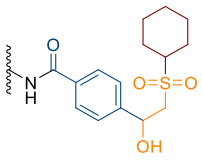


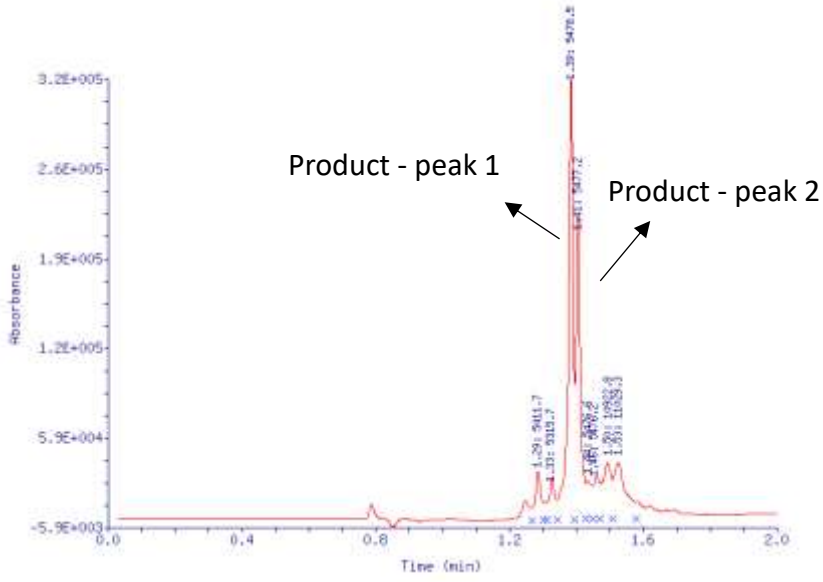
Figure S75. LC-MS Spectrum of DEL Compound **5h**. The sodium sulfinate (**4h**) used was obtained from commercial sources.



5i

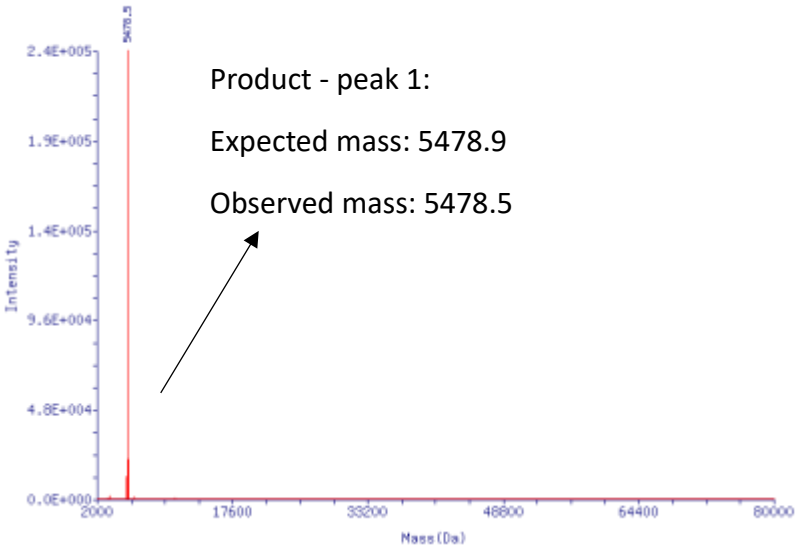
Purity: 65%
Conversion rate: 65%
Expected mass: 5478.9
Observed mass: 5478.5 and 5477.2

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.29	5411.7	3.39E+004	ok	3.79E+004	4.38
1.33	5315.7	3.19E+004	ok	3.38E+004	3.90
1.39	5478.5	2.40E+005	ok	3.11E+005	38.80
1.41	5477.2	5.02E+005	ok	2.06E+005	25.83
1.44	5476.6	1.21E+005	ok	3.16E+004	3.65
1.46	5476.2	3.19E+004	ok	3.23E+004	3.73
1.50	10922.8	9.33E+003	ok	7.27E+004	8.40
1.53	11029.3	2.19E+004	ok	9.81E+004	11.33

Deconvoluted mass spectrum of product:



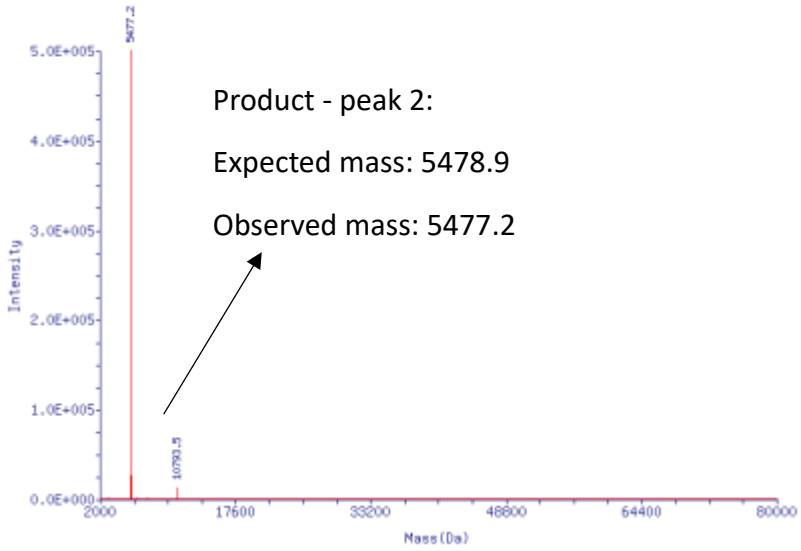
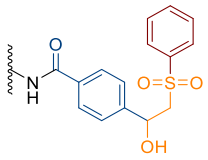


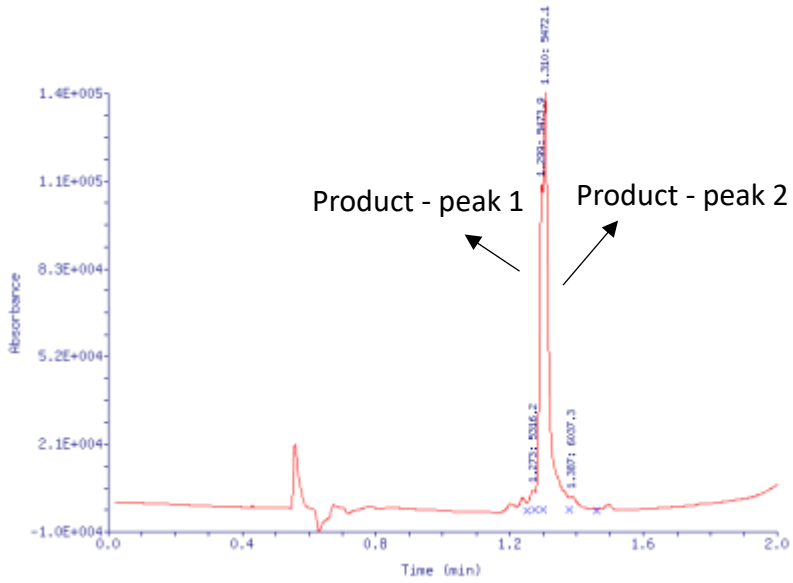
Figure S76. LC-MS Spectrum of DEL Compound **5i**.



5j

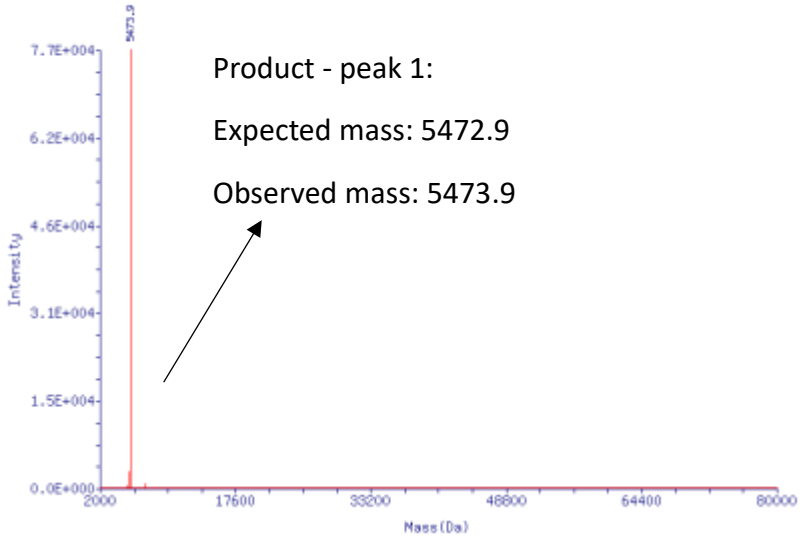
Purity: 95%
Conversion rate: 95%
Expected mass: 5472.9
Observed mass: 5473.9 and 5472.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.273	5316.2	1.68E+003	ok	6.93E+003	2.68
1.299	5473.9	7.74E+004	ok	7.34E+004	28.42
1.310	5472.1	5.66E+004	ok	1.71E+005	66.18
1.387	6037.3	1.10E+002	ok	7.03E+003	2.72

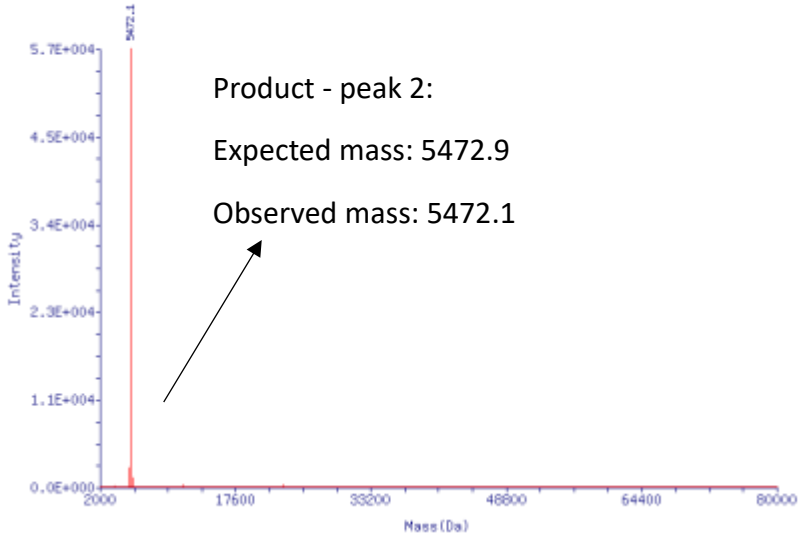
Deconvoluted mass spectrum of product:



Product - peak 1:

Expected mass: 5472.9

Observed mass: 5473.9

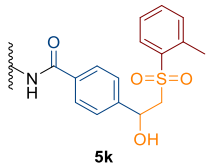


Product - peak 2:

Expected mass: 5472.9

Observed mass: 5472.1

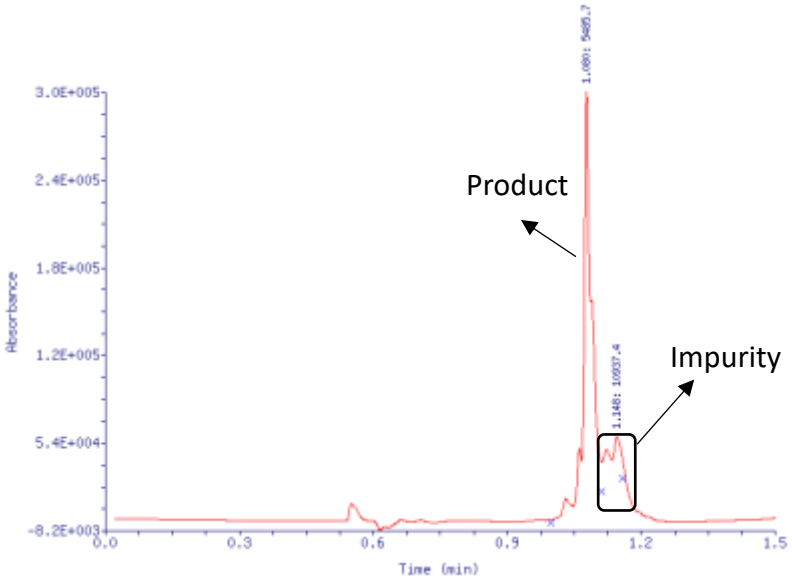
Figure S77. LC-MS Spectrum of DEL Compound **5j**.



5k

Purity: 84%
Conversion rate: 84%
Expected mass: 5486.9
Observed mass: 5485.7

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.080	5485.7	7.58E+004	ok	3.41E+005	83.88
1.148	10937.4	5.68E+003	ok	6.56E+004	16.12

Deconvoluted mass spectrum of product:

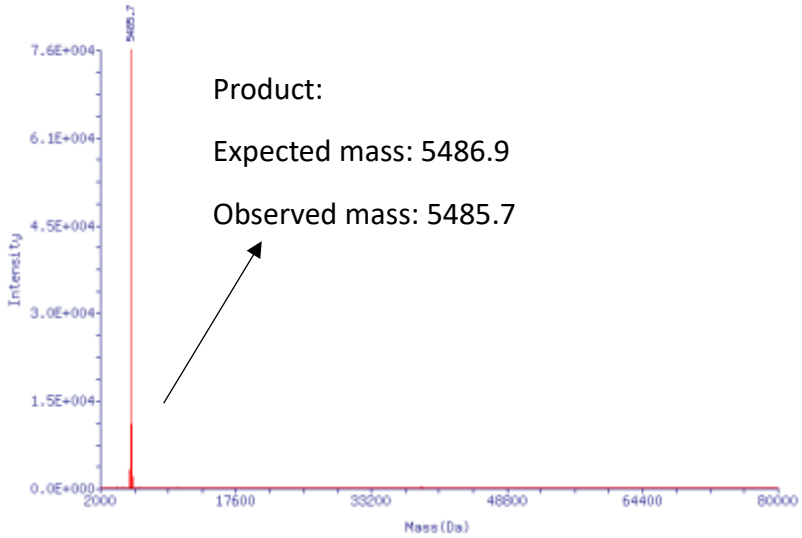
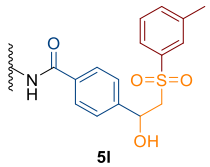


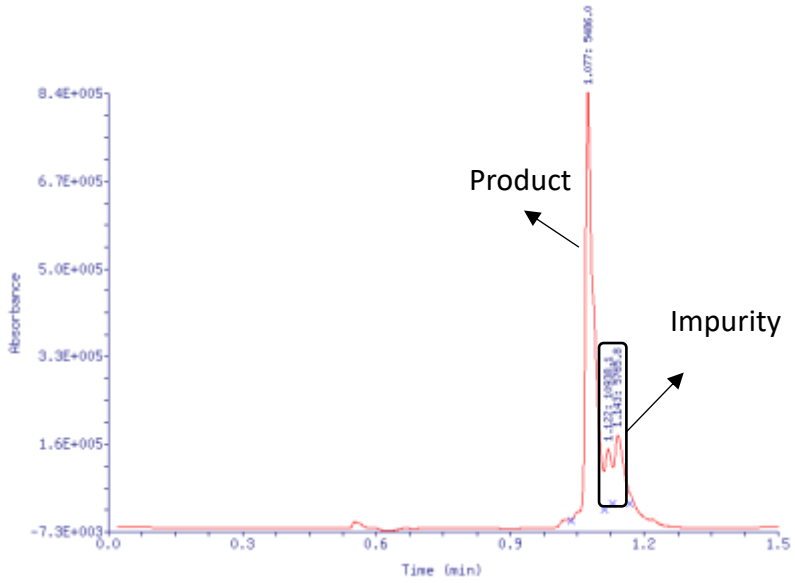
Figure S78. LC-MS Spectrum of DEL Compound **5k**.



5l

Purity: 78%
Conversion rate: 78%
Expected mass: 5486.9
Observed mass: 5486.0

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.077	5486.0	3.72E+005	ok	1.01E+006	78.21
1.122	10938.1	4.75E+004	ok	1.07E+005	8.31
1.143	5765.8	2.31E+004	ok	1.74E+005	13.48

Deconvoluted mass spectrum of product:

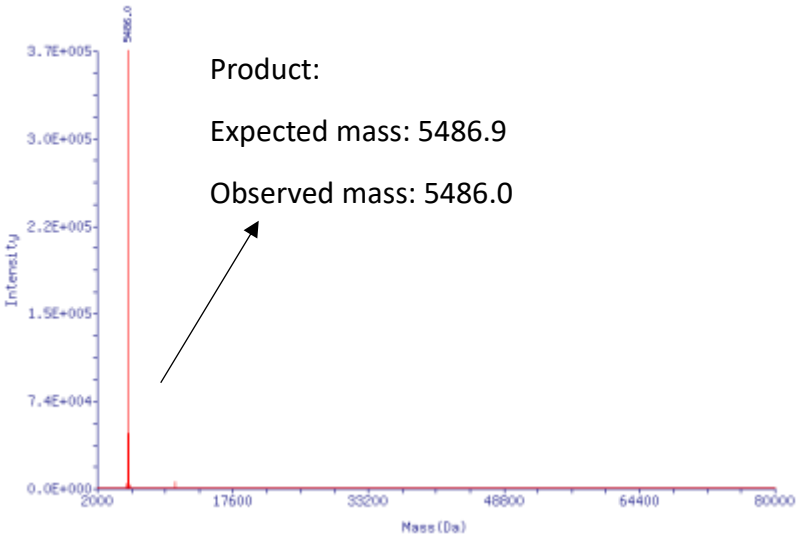
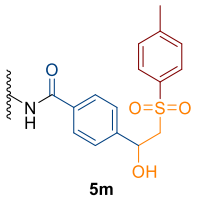


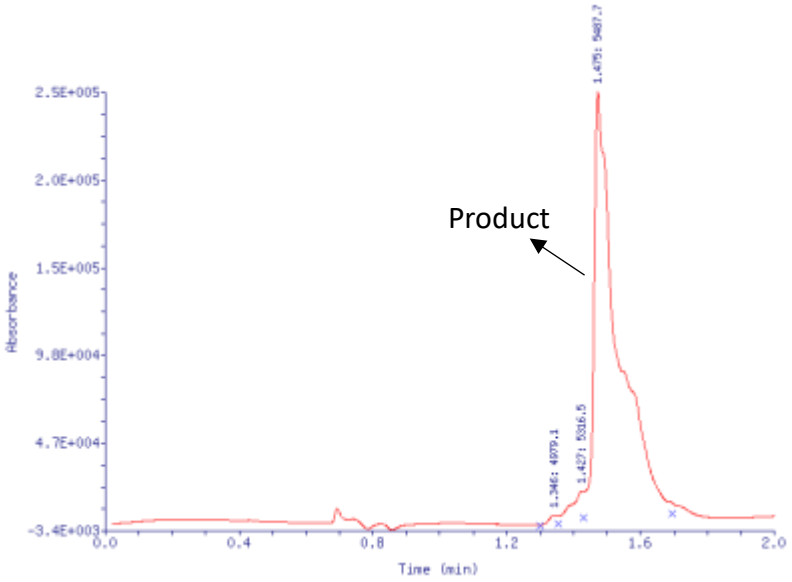
Figure S79. LC-MS Spectrum of DEL Compound **5l**.



5m

Purity: 96%
Conversion rate: 96%
Expected mass: 5486.9
Observed mass: 5487.7

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.346	4979.1	5.44E+003	ok	8.51E+003	0.69
1.427	5316.5	3.57E+003	ok	3.81E+004	3.07
1.475	5487.7	1.30E+005	ok	1.19E+006	96.24

Deconvoluted mass spectrum of product:

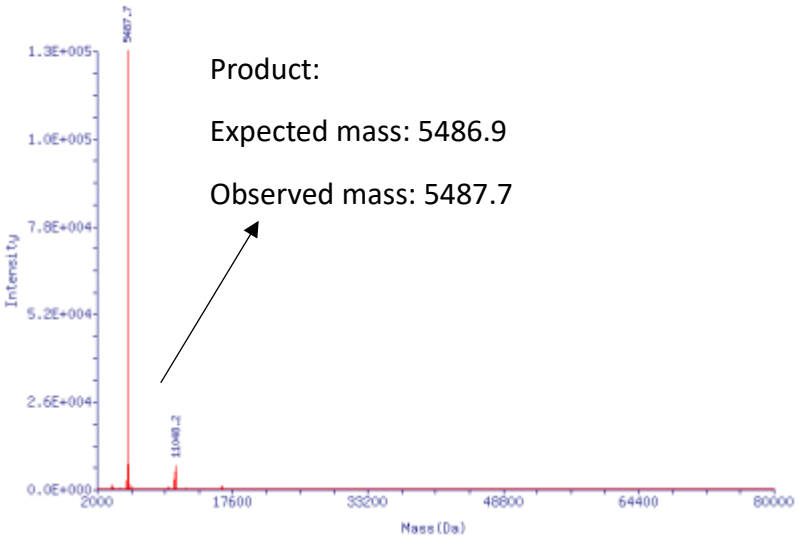
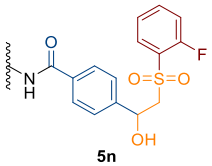


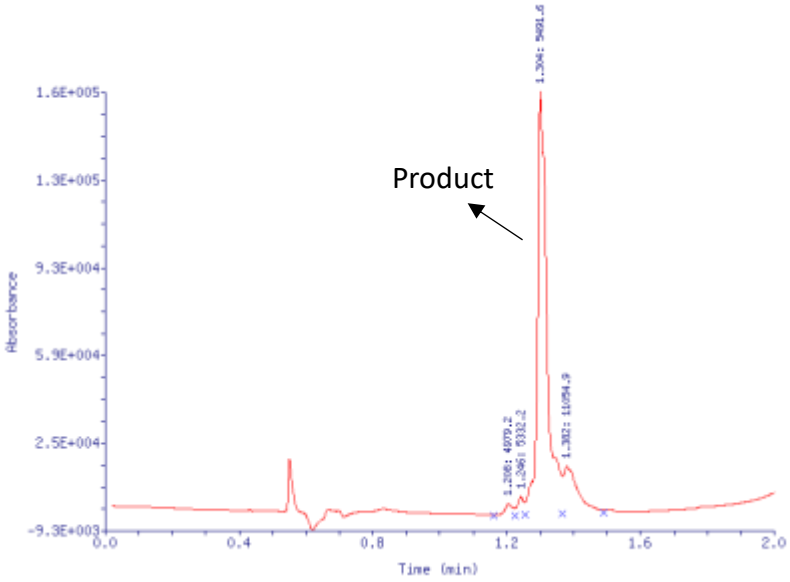
Figure S80. LC-MS Spectrum of DEL Compound **5m**.



5n

Purity: 83%
Conversion rate: 83%
Expected mass: 5490.8
Observed mass: 5491.6

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.208	4979.2	1.09E+003	ok	6.35E+003	1.62
1.246	5332.2	1.60E+003	ok	8.65E+003	2.20
1.304	5491.6	5.02E+004	ok	3.24E+005	82.52
1.382	11054.9	8.43E+002	ok	5.36E+004	13.66

Deconvoluted mass spectrum of product:

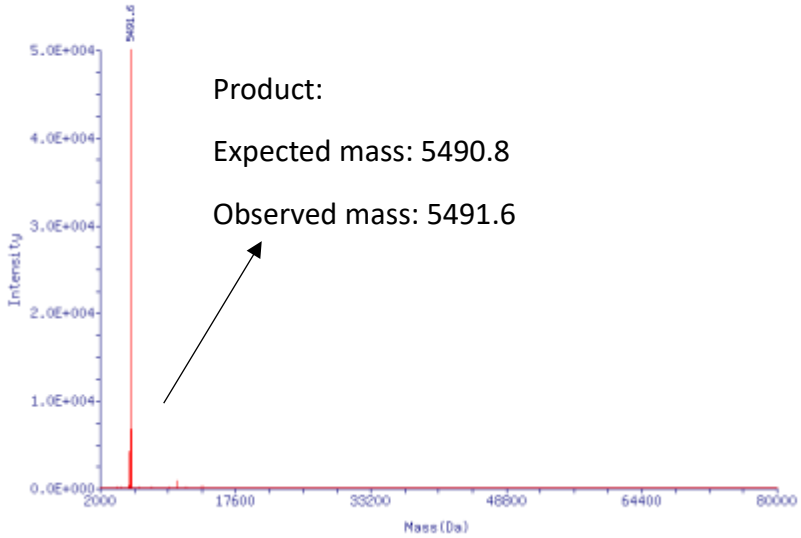
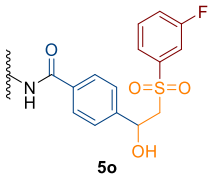


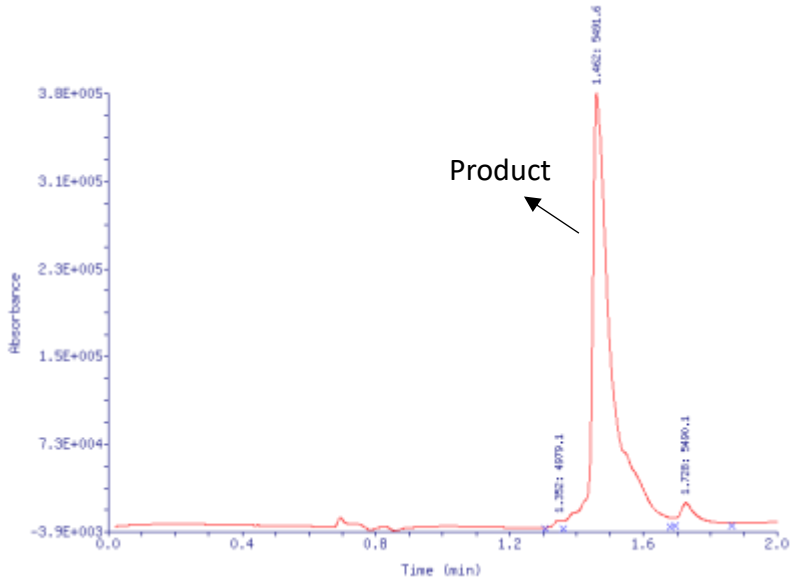
Figure S81. LC-MS Spectrum of DEL Compound **5n**.



5o

Purity: 95%
Conversion rate: 95%
Expected mass: 5490.8
Observed mass: 5491.6

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.352	4979.1	6.14E+003	ok	1.02E+004	0.64
1.462	5491.6	1.32E+005	ok	1.51E+006	95.26
1.728	5490.1	1.36E+003	ok	6.50E+004	4.10

Deconvoluted mass spectrum of product:

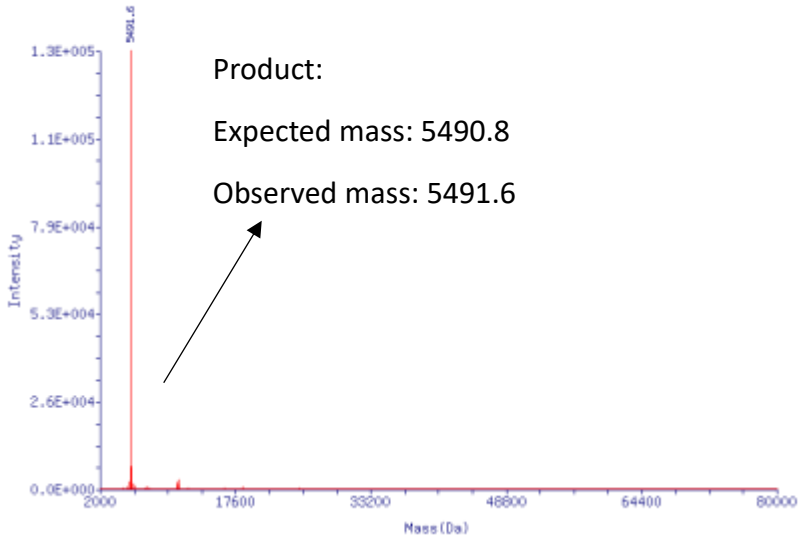
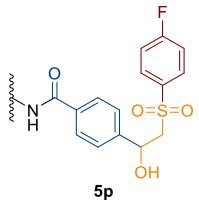


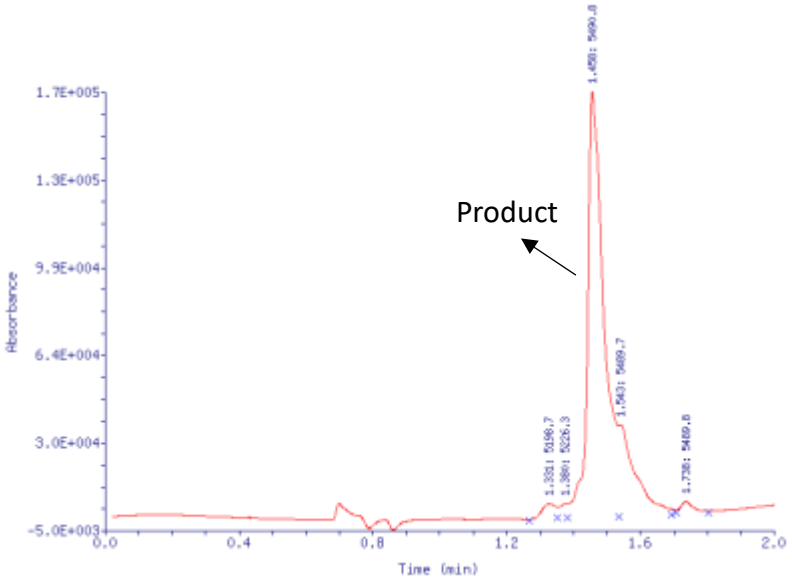
Figure S82. LC-MS Spectrum of DEL Compound **5o**.



5p

Purity: 78%
Conversion rate: 78%
Expected mass: 5490.8
Observed mass: 5490.8

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.331	5198.7	1.81E+003	ok	1.53E+004	2.13
1.380	5226.3	1.74E+003	ok	8.13E+003	1.13
1.458	5490.8	9.32E+004	ok	5.65E+005	78.29
1.543	5489.7	2.87E+003	ok	1.23E+005	17.07
1.738	5489.8	2.07E+002	ok	1.00E+004	1.39

Deconvoluted mass spectrum of product:

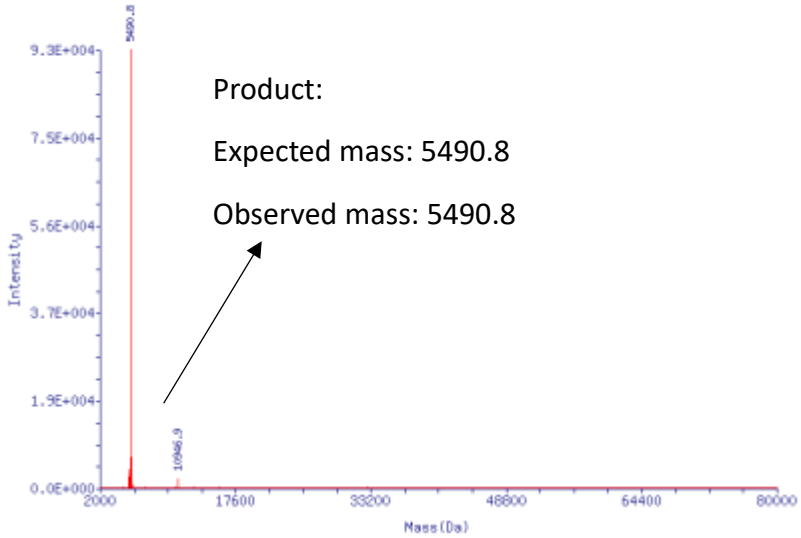
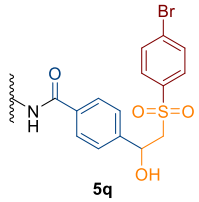


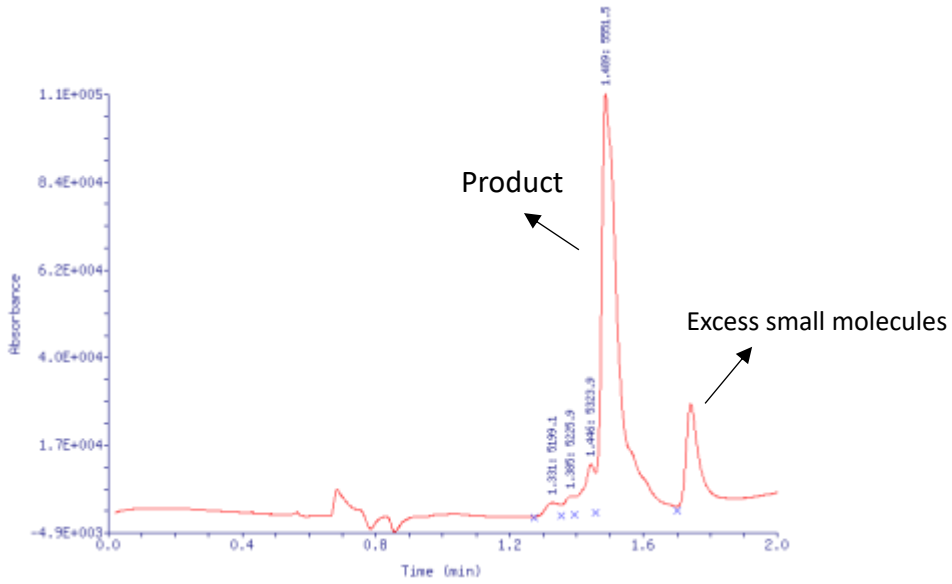
Figure S83. LC-MS Spectrum of DEL Compound **5p**.



5q

Purity: 89%
Conversion rate: 89%
Expected mass: 5551.8
Observed mass: 5551.5

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.331	5199.1	8.96E+002	ok	9.60E+003	2.33
1.385	5225.9	9.66E+002	ok	8.62E+003	2.09
1.446	5323.9	3.38E+003	ok	2.89E+004	7.00
1.489	5551.5	3.69E+004	ok	3.66E+005	88.58

Deconvoluted mass spectrum of product:

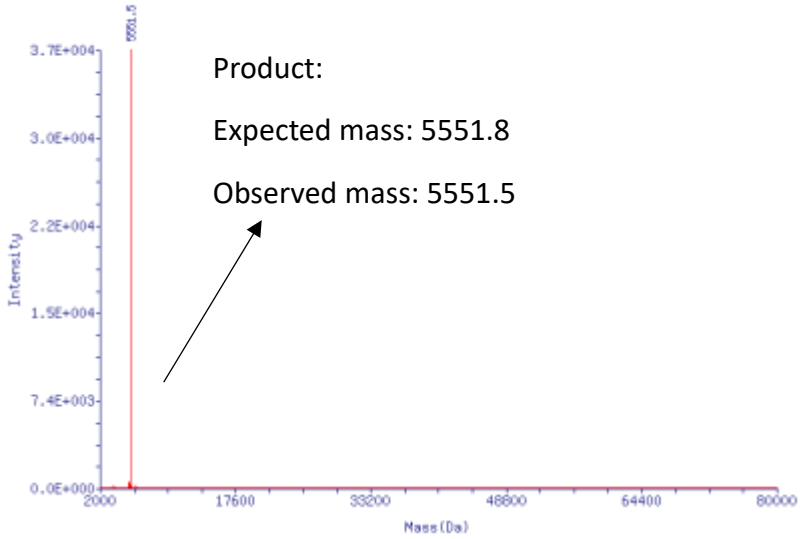
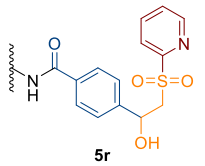


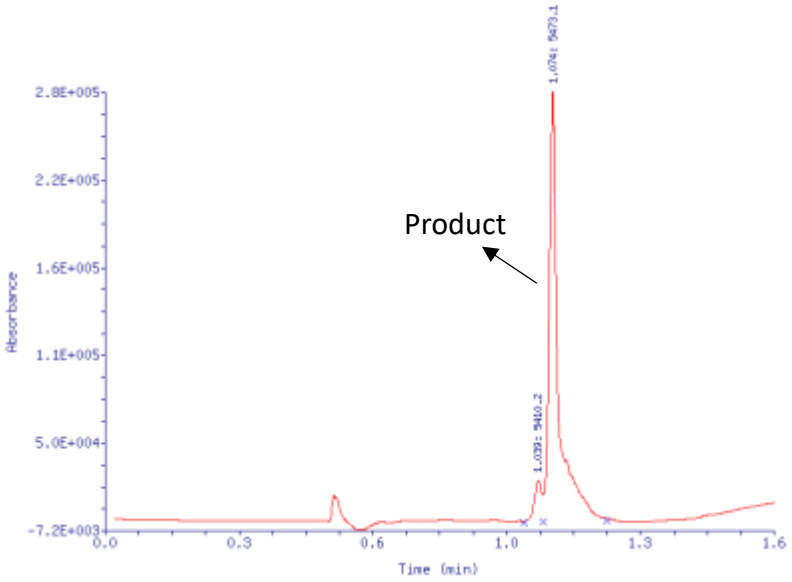
Figure S84. LC-MS Spectrum of DEL Compound **5q**.



5r

Purity: 93%
Conversion rate: 93%
Expected mass: 5473.8
Observed mass: 5473.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.039	5410.2	9.42E+004	ok	3.00E+004	6.56
1.074	5473.1	7.09E+005	ok	4.28E+005	93.44

Deconvoluted mass spectrum of product:

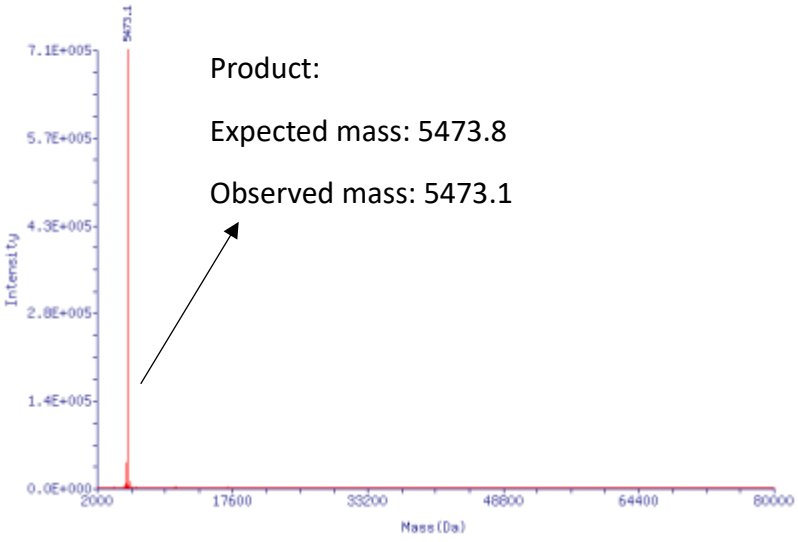
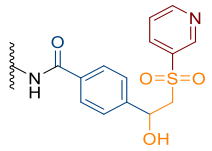


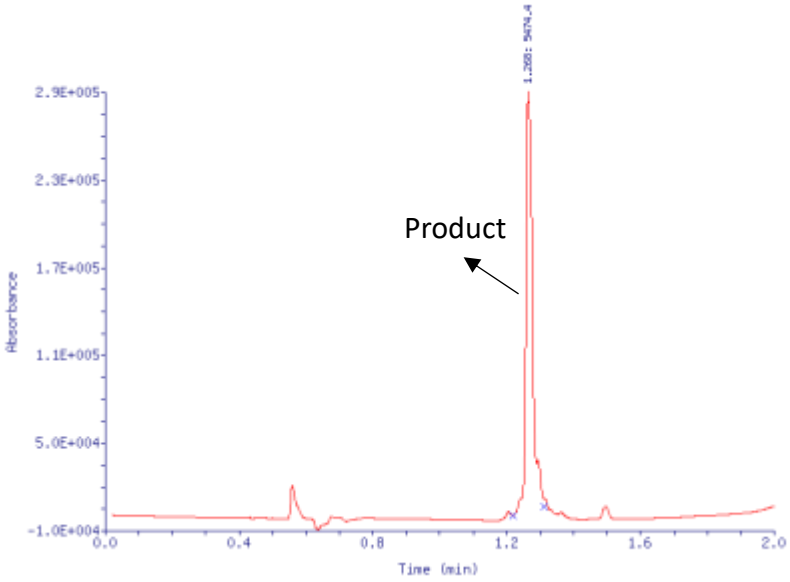
Figure S85. LC-MS Spectrum of DEL Compound **5r**.



5s

Purity: >99%
Conversion rate: >99%
Expected mass: 5473.8
Observed mass: 5474.4

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.268	5474.4	1.94E+005	ok	3.88E+005	100.00

Deconvoluted mass spectrum of product:

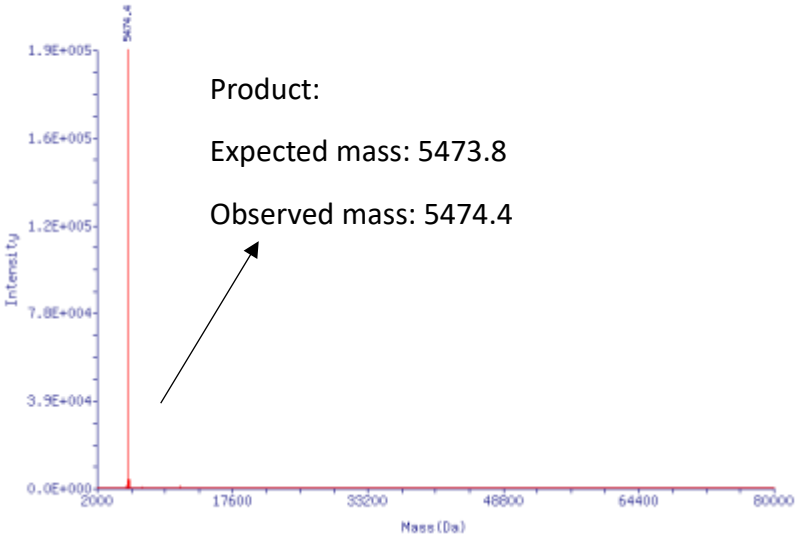
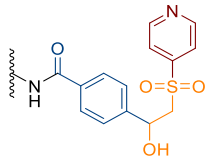


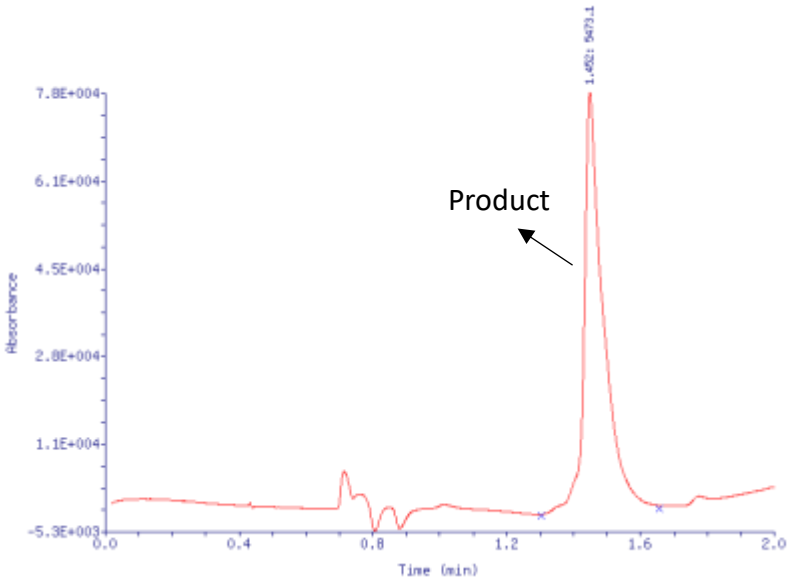
Figure S86. LC-MS Spectrum of DEL Compound **5s**.



5t

Purity: >99%
Conversion rate: >99%
Expected mass: 5473.8
Observed mass: 5473.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.452	5473.1	3.65E+004	ok	3.16E+005	100.00

Deconvoluted mass spectrum of product:

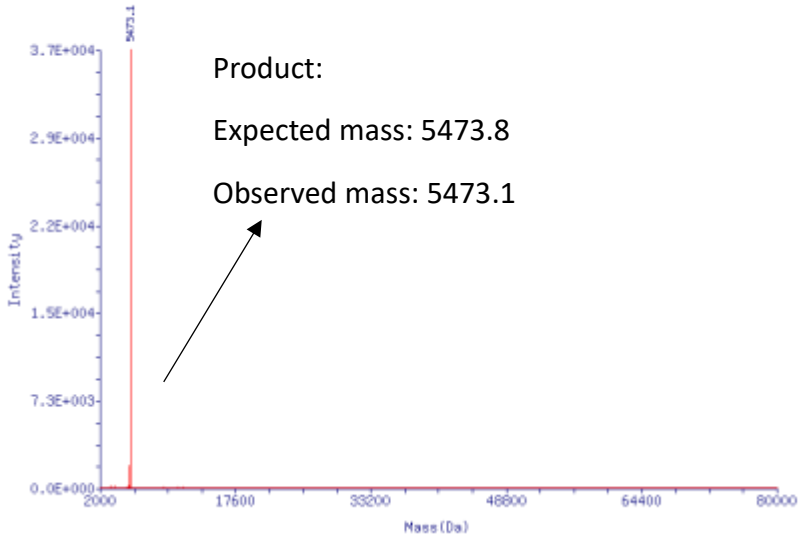
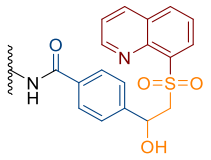


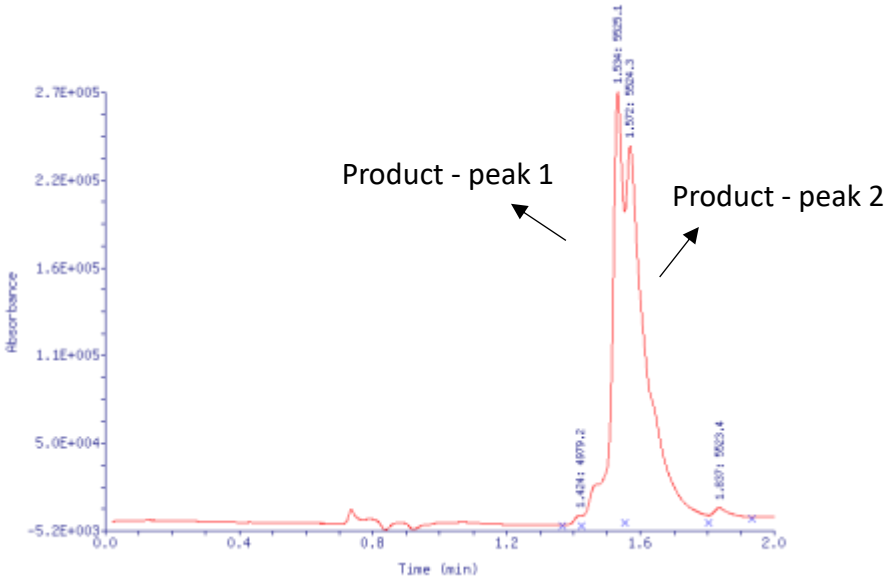
Figure S87. LC-MS Spectrum of DEL Compound **5t**.



5u

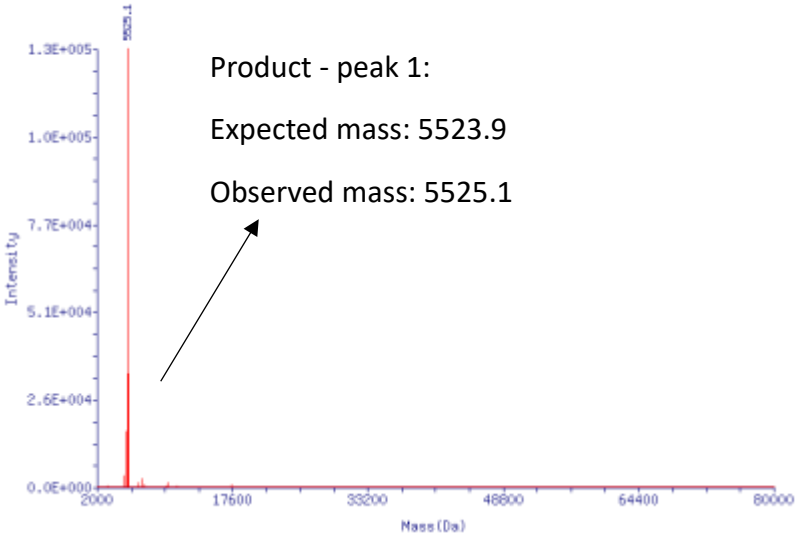
Purity: 98%
Conversion rate: 98%
Expected mass: 5523.9
Observed mass: 5525.1 and 5524.3

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.424	4979.2	5.52E+003	ok	7.94E+003	0.47
1.534	5525.1	1.28E+005	ok	6.43E+005	37.76
1.572	5524.3	1.23E+005	ok	1.02E+006	59.92
1.837	5523.4	1.07E+003	ok	3.16E+004	1.85

Deconvoluted mass spectrum of product:



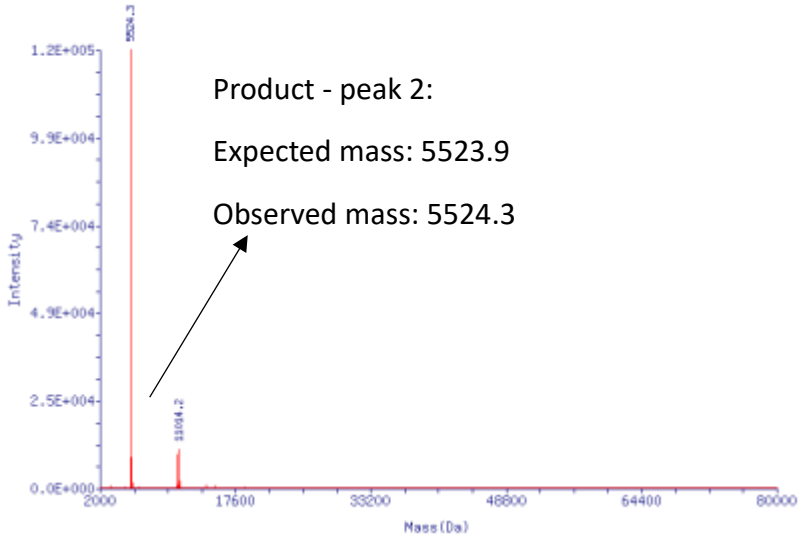
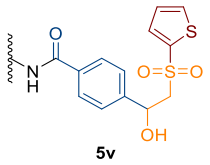


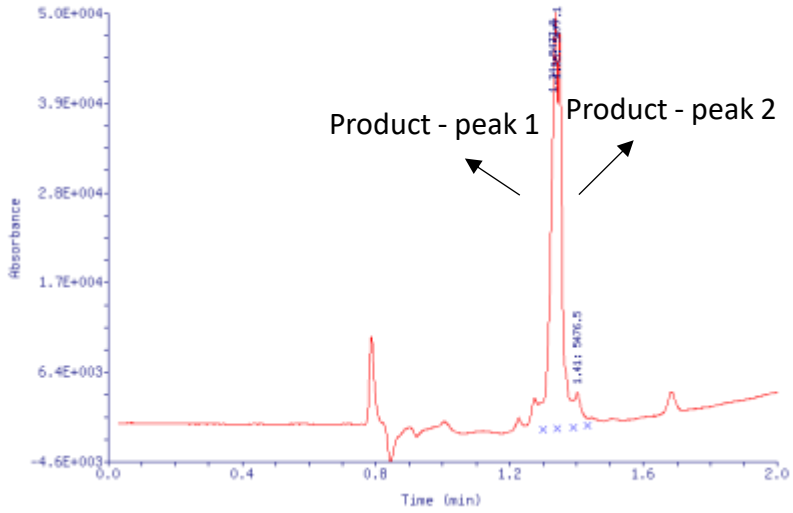
Figure S88. LC-MS Spectrum of DEL Compound **5u**.



5v

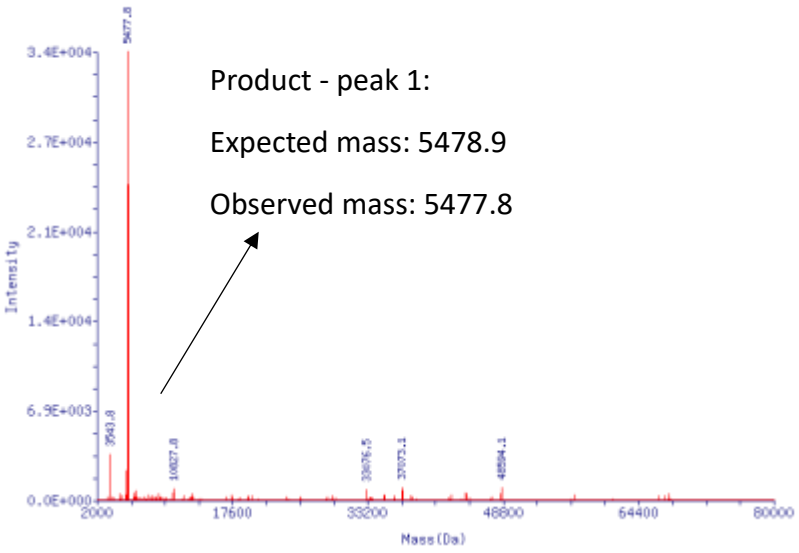
Purity: 94%
Conversion rate: 94%
Expected mass: 5478.9
Observed mass: 5477.8 and 5477.1

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.34	5477.8	3.43E+004	ok	6.24E+004	55.10
1.35	5477.1	5.56E+004	ok	4.45E+004	39.29
1.41	5476.5	2.82E+003	ok	6.36E+003	5.62

Deconvoluted mass spectrum of product:



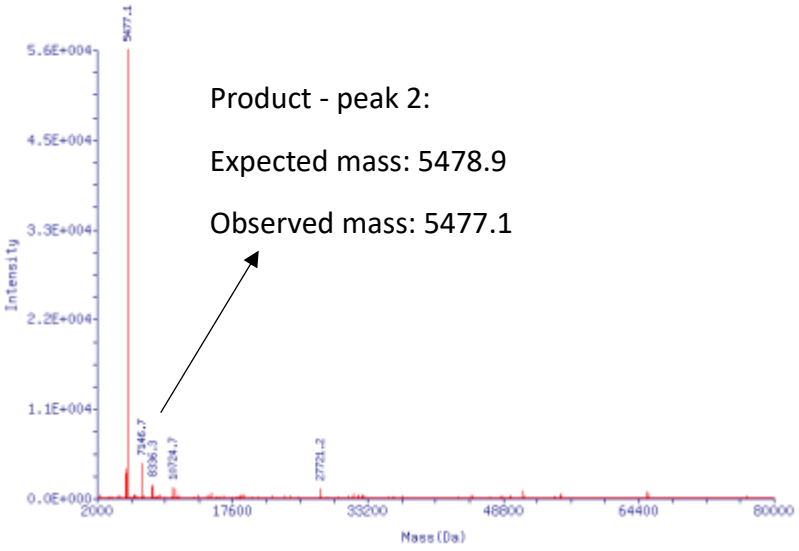


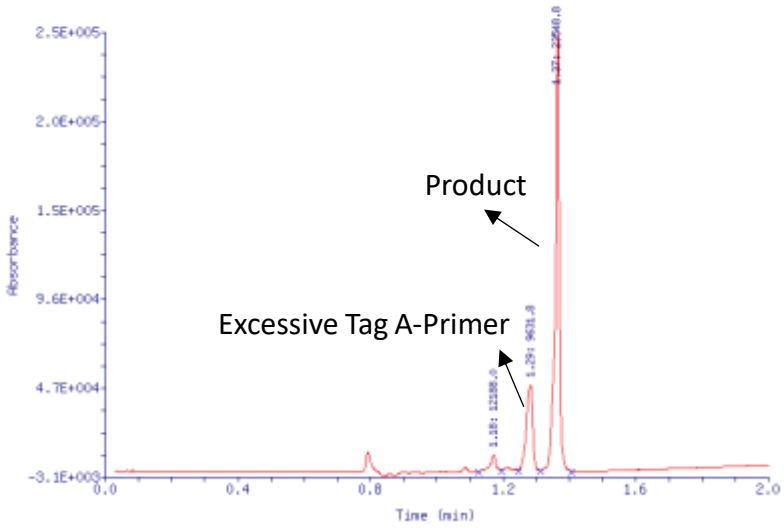
Figure S89. LC-MS Spectrum of DEL Compound **5v**.

9.10. Mass Spectra of DEL

Cycle 1 Analysis, well **A1**

Expected mass: 23546.7
Observed mass: 23548.8

LC/UV Spectrum:



Deconvoluted mass spectrum of Product:

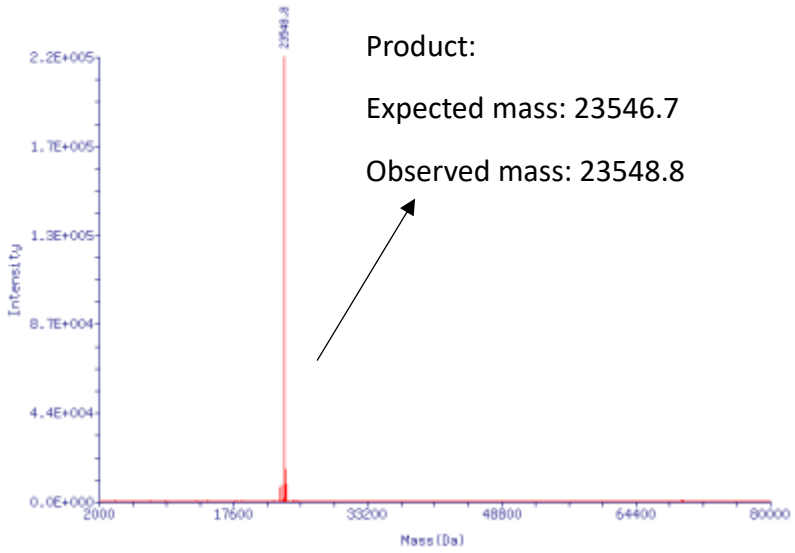
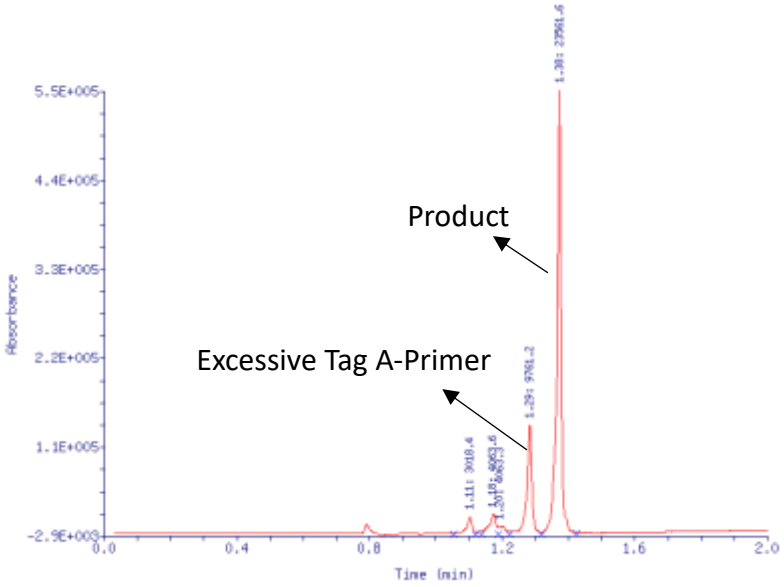


Figure S90. LC/UV Spectrum and deconvoluted mass spectrum of cycle 1 well **A1**.

Cycle 1 Analysis, well **A2**

Expected mass: 23558.7
Observed mass: 23561.6

LC/UV Spectrum:



Deconvoluted mass spectrum of Product:

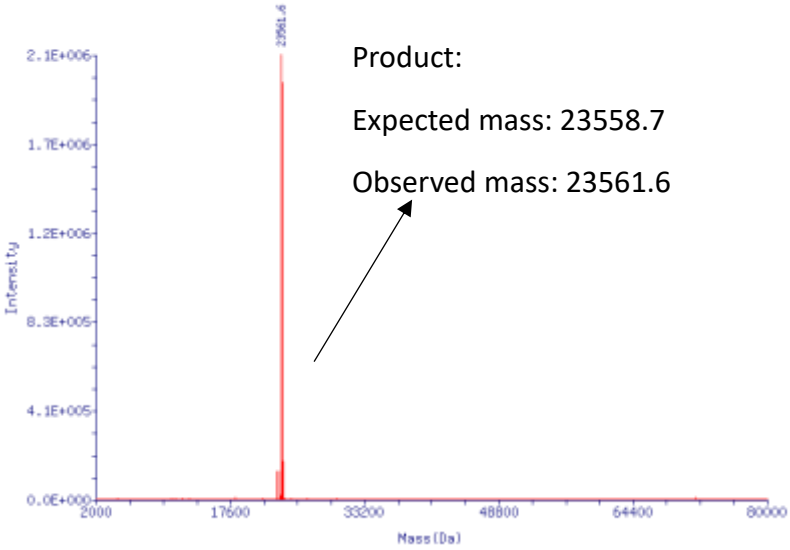
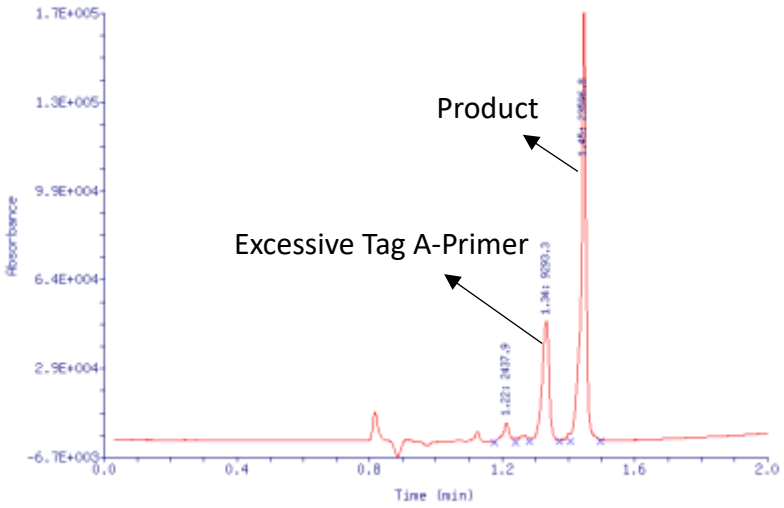


Figure S91. LC/UV Spectrum and deconvoluted mass spectrum of cycle 1 well **A2**.

Cycle 1 Analysis, well **A3**

Expected mass: 23594.8
Observed mass: 23596.8

LC/UV Spectrum:



Deconvoluted mass spectrum of Product:

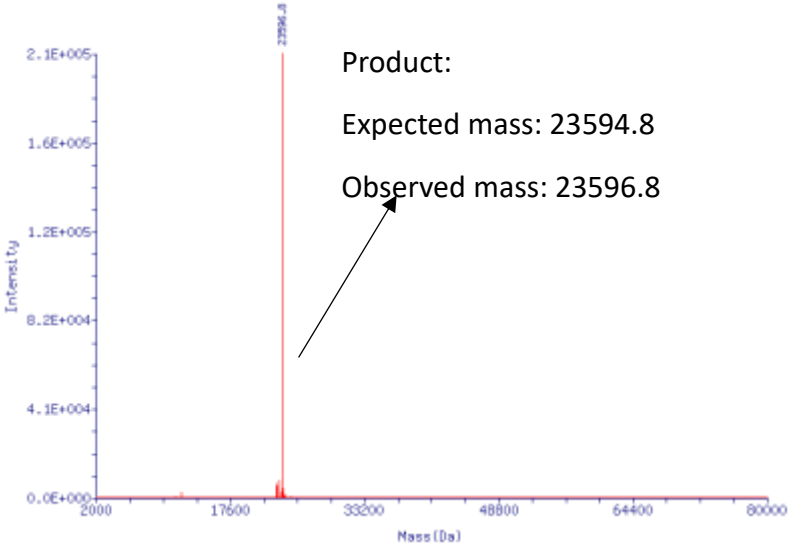
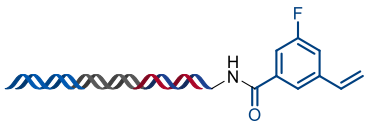


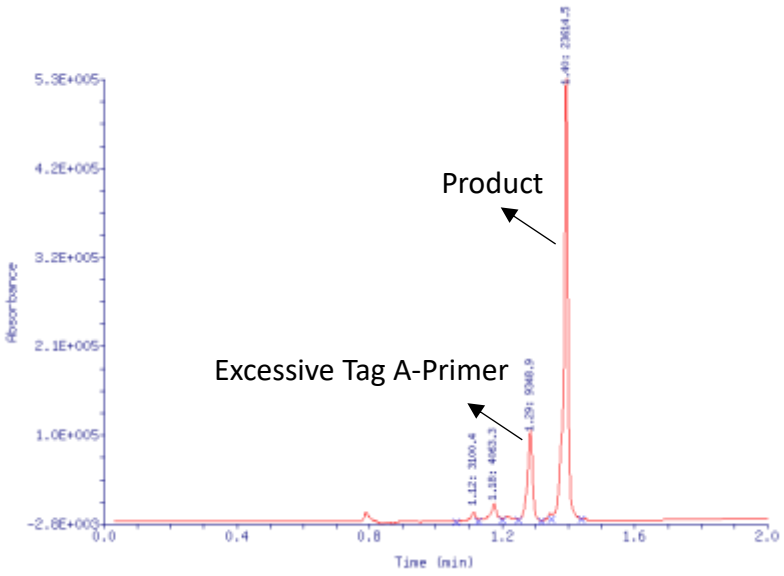
Figure S92. LC/UV Spectrum and deconvoluted mass spectrum of cycle 1 well **A3**.

Cycle 1 Analysis, well **A4**



Expected mass: 23612.8
Observed mass: 23614.5

LC/UV Spectrum:



Deconvoluted mass spectrum of Product:

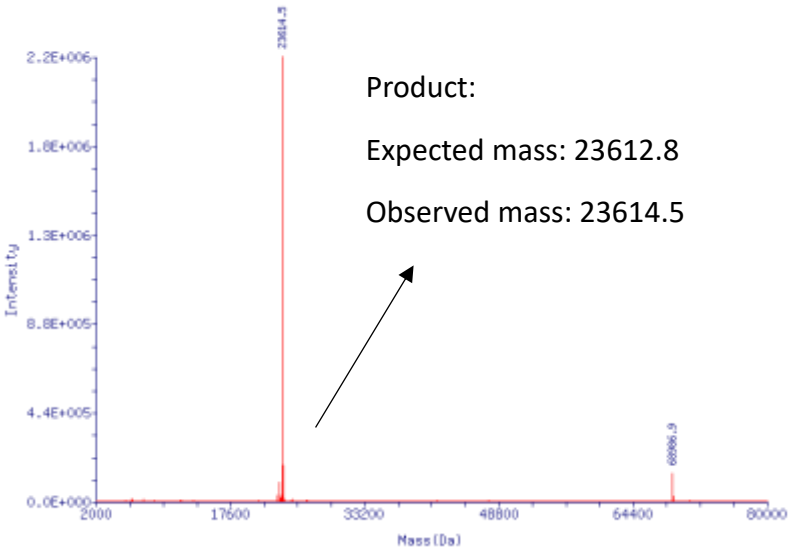
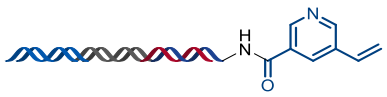


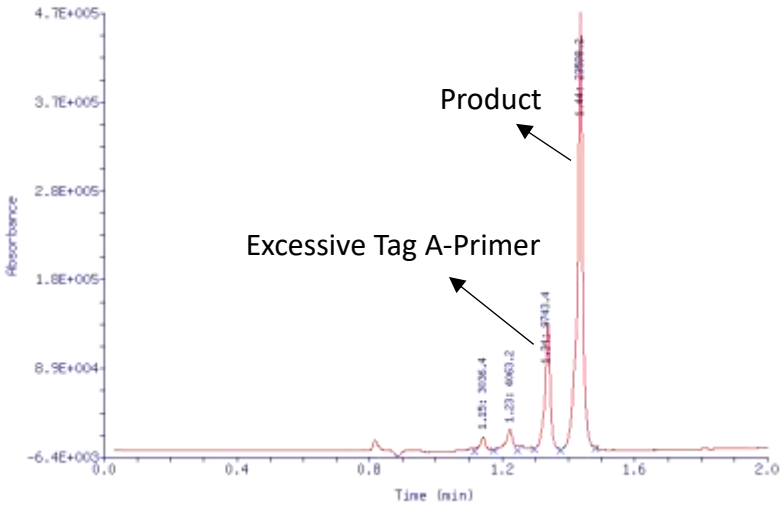
Figure S93. LC/UV Spectrum and deconvoluted mass spectrum of cycle 1 well **A4**.

Cycle 1 Analysis, well **A5**



Expected mass: 23595.7
Observed mass: 23598.2

LC/UV Spectrum:



Deconvoluted mass spectrum of Product:

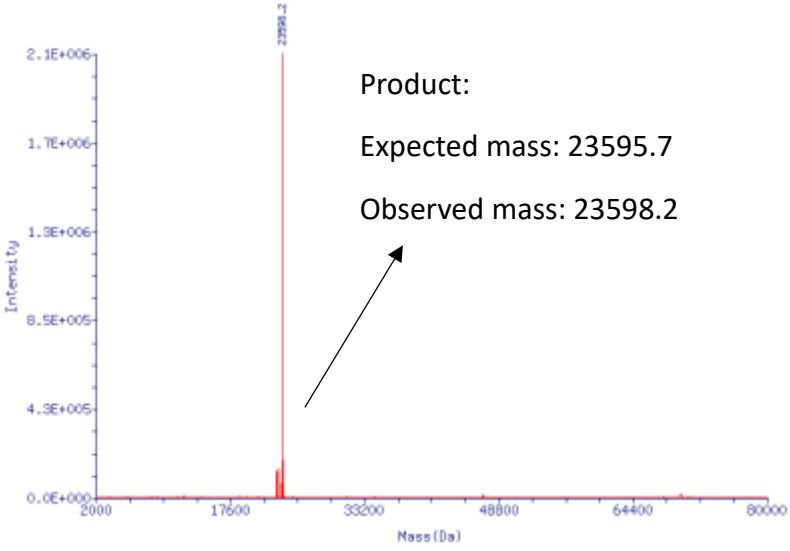
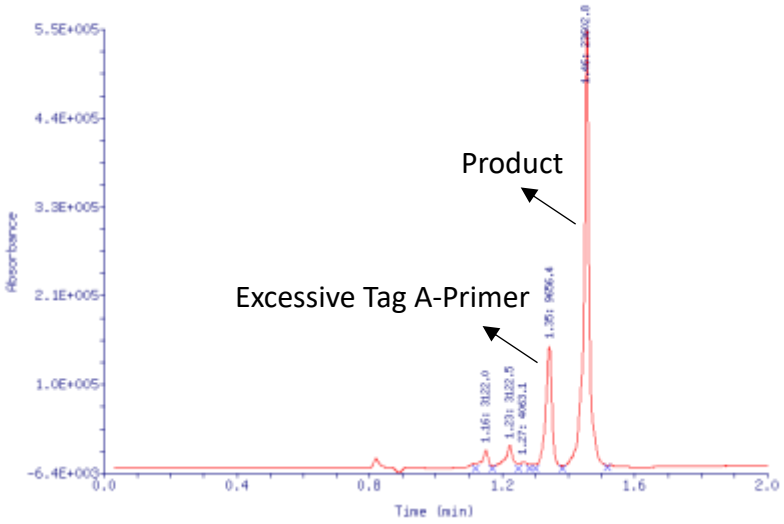


Figure S94. LC/UV Spectrum and deconvoluted mass spectrum of cycle 1 well **A5**.

Cycle 1 Analysis, well **A6**

Expected mass: 23600.8
Observed mass: 23602.8

LC/UV Spectrum:



Deconvoluted mass spectrum of Product:

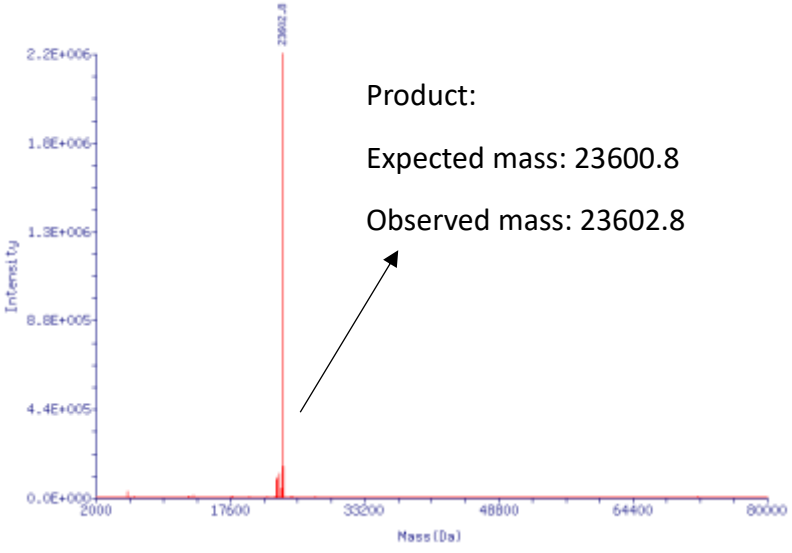
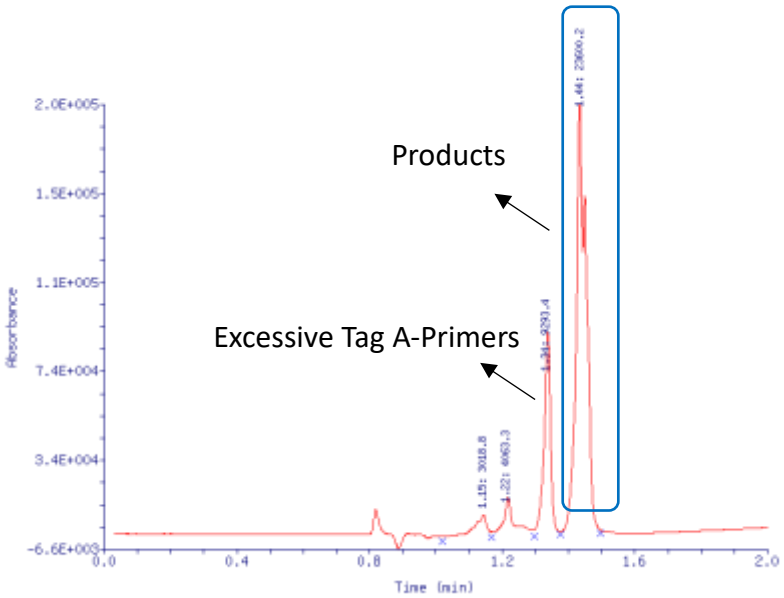


Figure S95. LC/UV Spectrum and deconvoluted mass spectrum of cycle 1 well **A6**. Crude cycle 1 products, pooled and precipitated.

Expected mass: 23546.7-23612.8

LC/UV Spectrum:



Deconvoluted mass spectrum of Products:

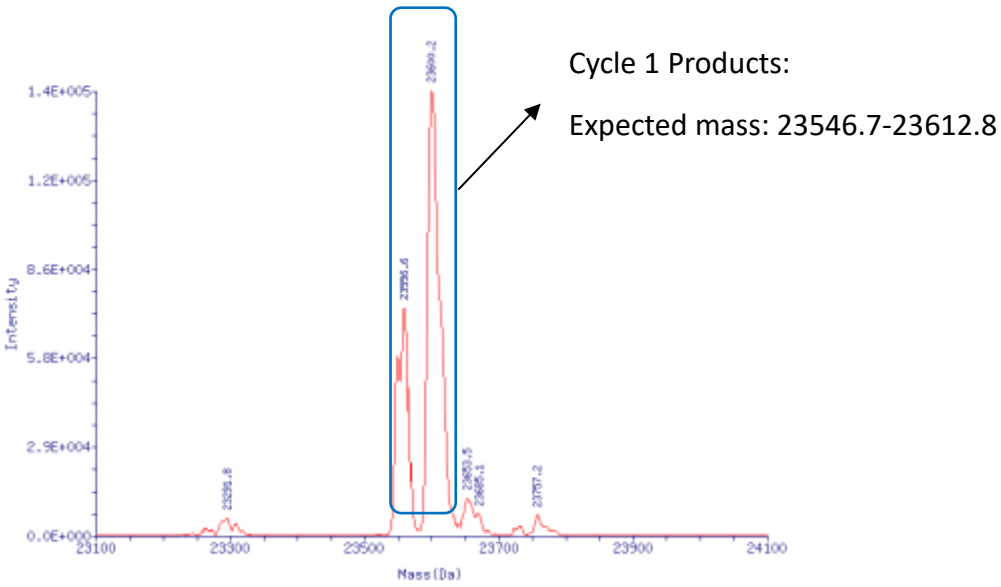
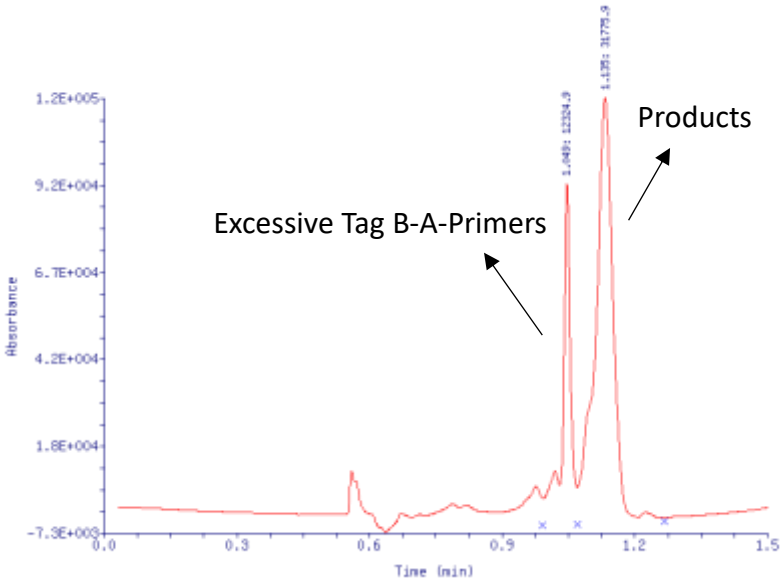


Figure S96. LC/UV Spectrum and deconvoluted mass spectrum of crude pooled cycle 1 products.

Cycle 2 Analysis, well **A1**

Expected mass: 31722.3-31788.4

LC/UV Spectrum:



Deconvoluted mass spectrum of Products:

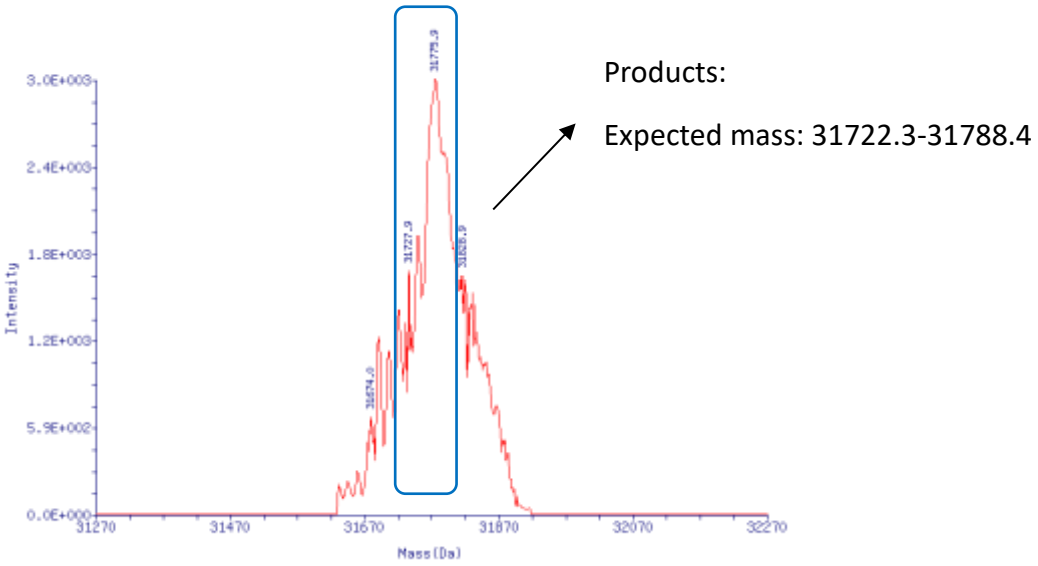
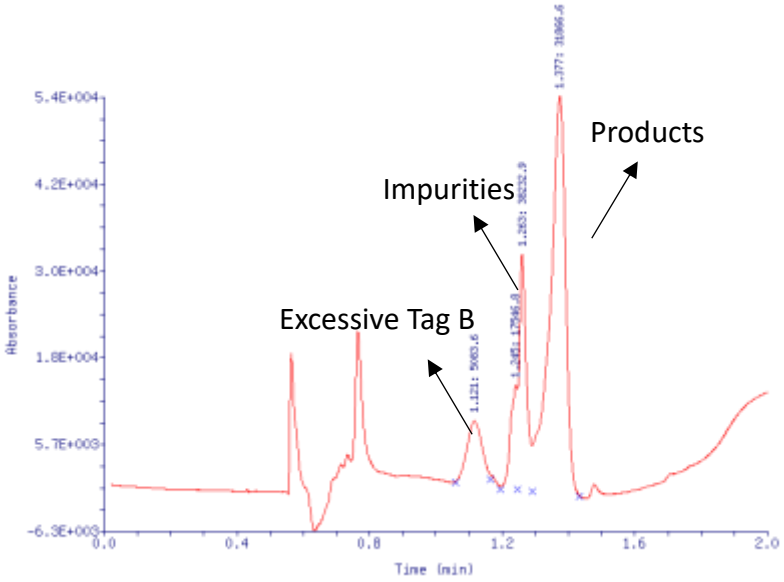


Figure S97. LC/UV Spectrum and deconvoluted mass spectrum of well **A1**.

Cycle 2 Analysis, well **A2**

Expected mass: 31748.3-31814.4

LC/UV Spectrum:



Deconvoluted mass spectrum of Products:

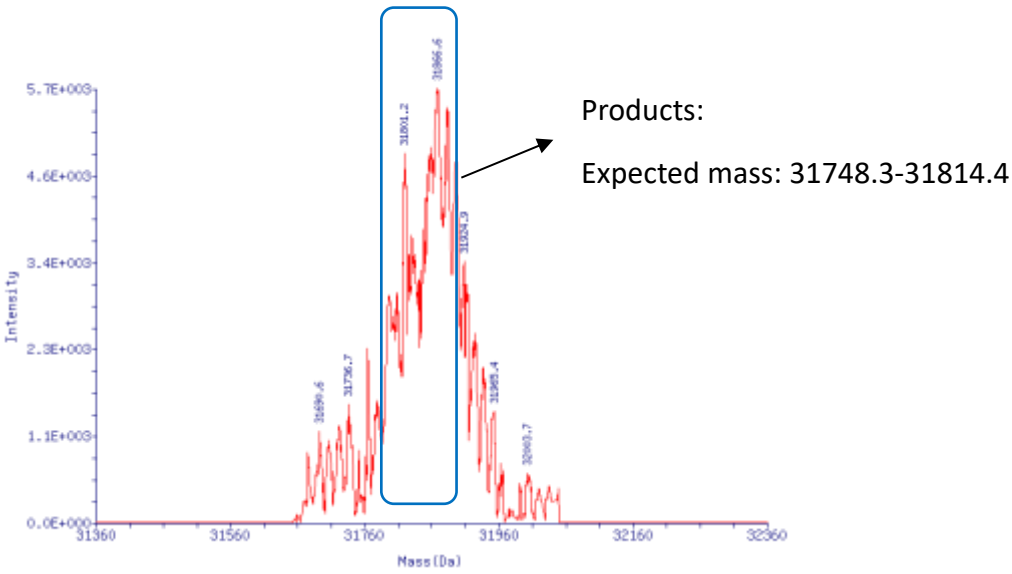
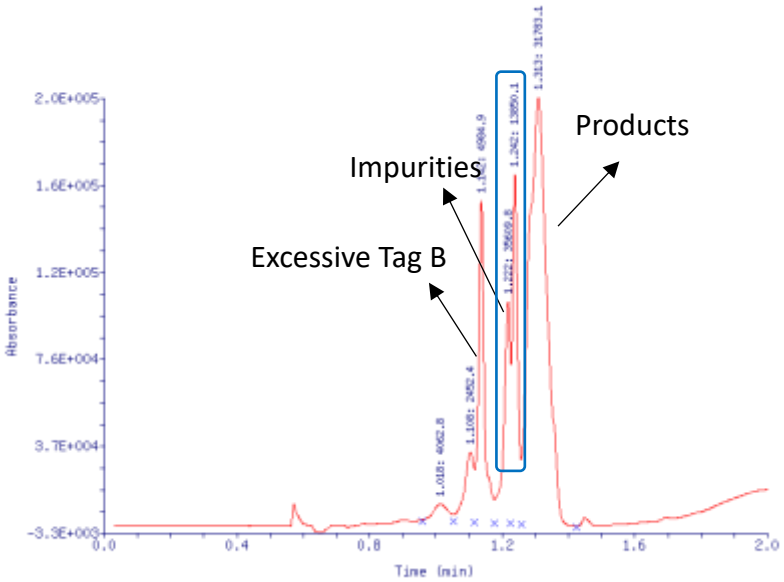


Figure S98. LC/UV Spectrum and deconvoluted mass spectrum of well **A2**.

Cycle 2 Analysis, well **A3**

Expected mass: 31734.3-31800.4

LC/UV Spectrum:



Deconvoluted mass spectrum of Products:

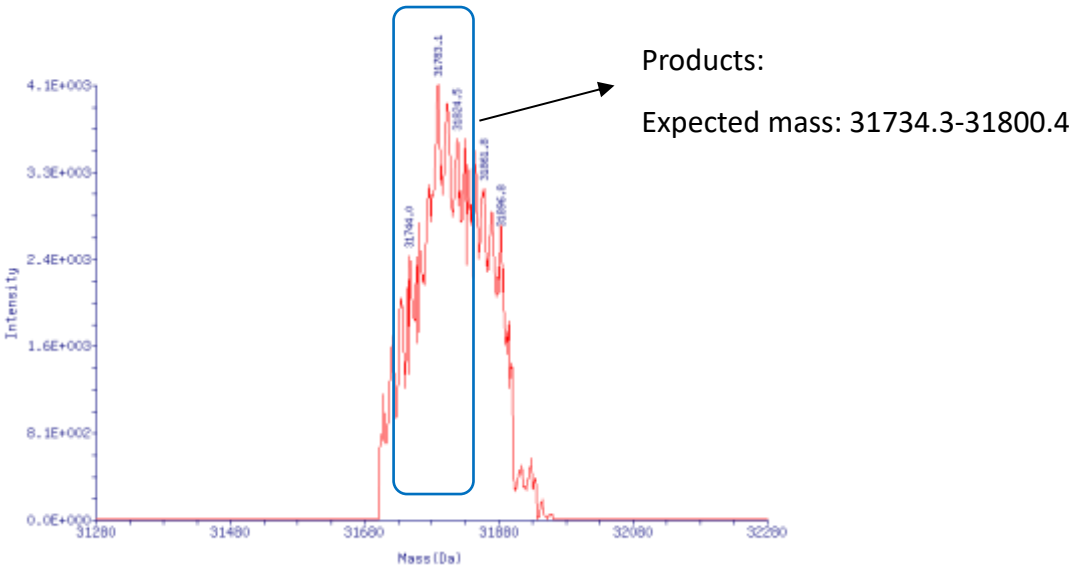
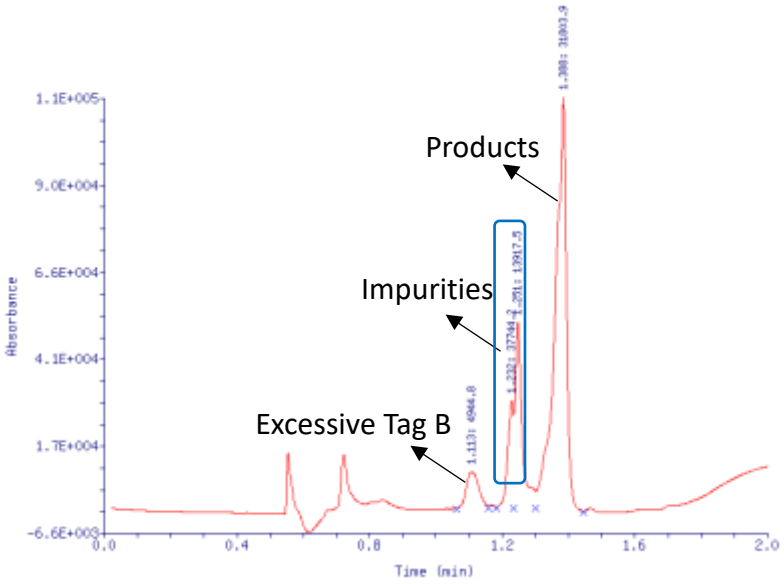


Figure S99. LC/UV Spectrum and deconvoluted mass spectrum of well **A3**.

Cycle 2 Analysis, well **A4**

Expected mass: 31748.3-31814.4

LC/UV Spectrum:



Deconvoluted mass spectrum of Products:

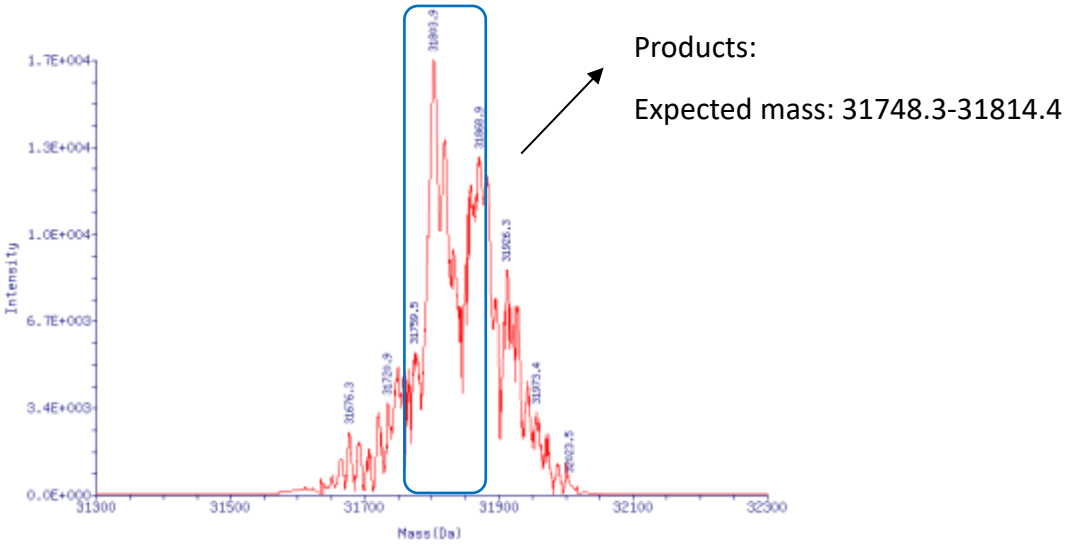
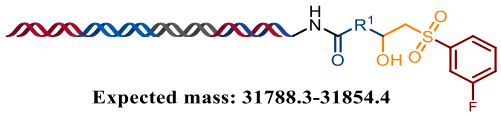


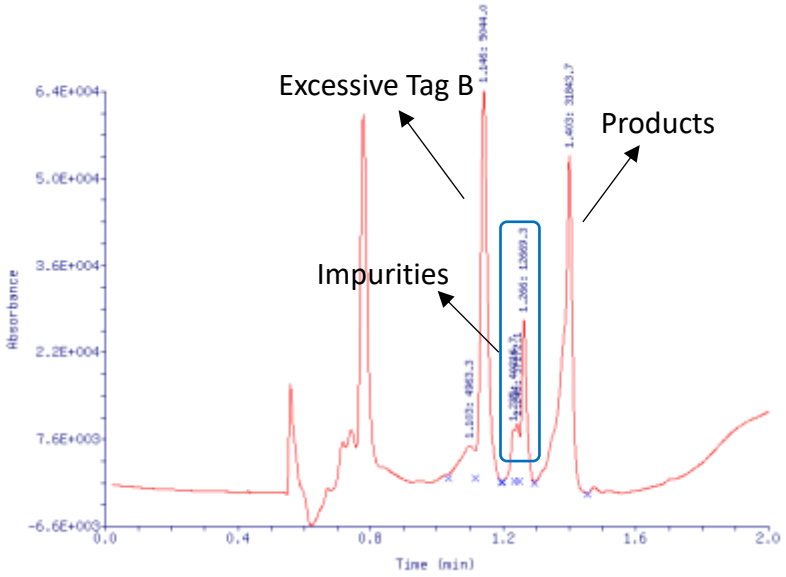
Figure S100. LC/UV Spectrum and deconvoluted mass spectrum of well **A4**.

Cycle 2 Analysis, well **A5**



Expected mass: 31788.3-31854.4

LC/UV Spectrum:



Deconvoluted mass spectrum of Products:

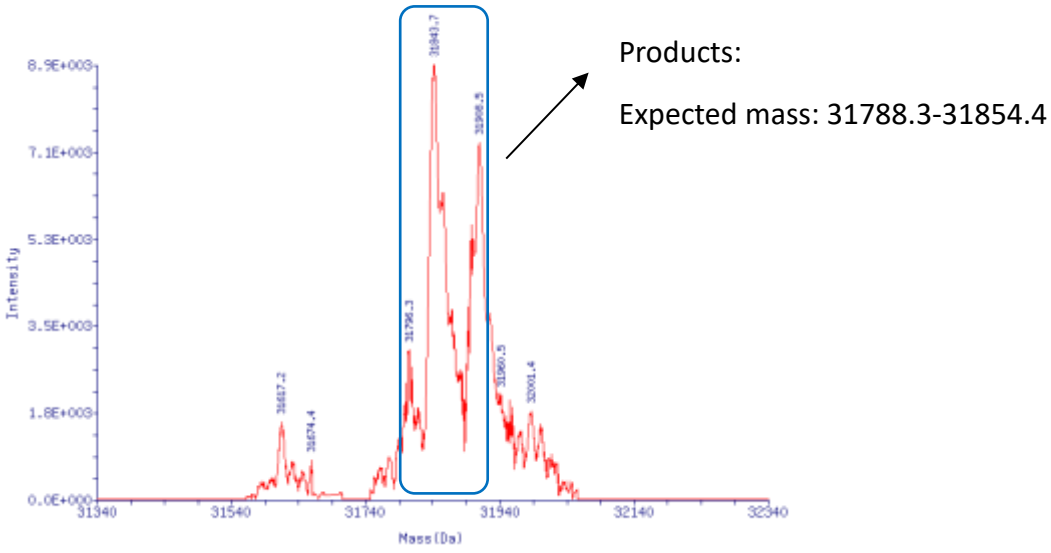
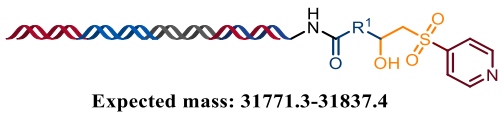


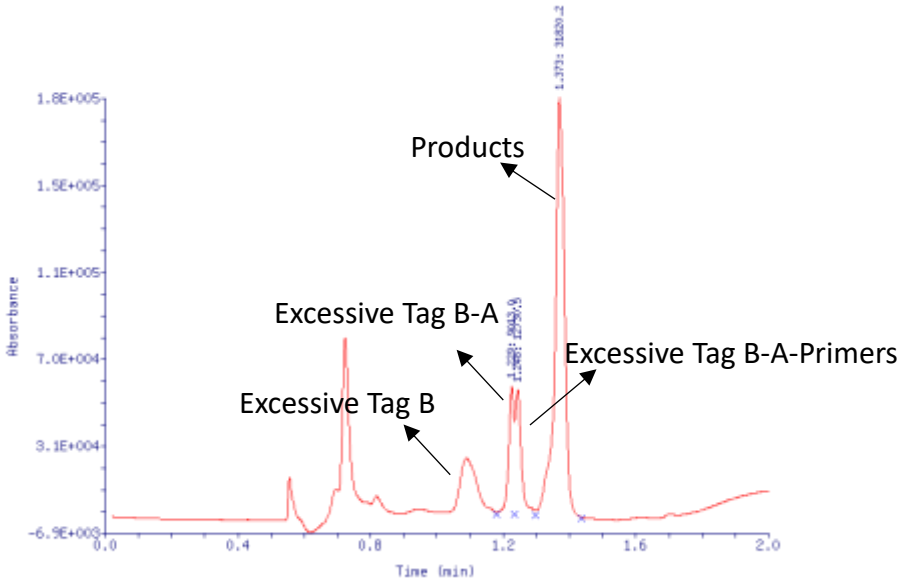
Figure S101. LC/UV Spectrum and deconvoluted mass spectrum of well **A5**.

Cycle 2 Analysis, well **A6**



Expected mass: 31771.3-31837.4

LC/UV Spectrum:



Deconvoluted mass spectrum of Products:

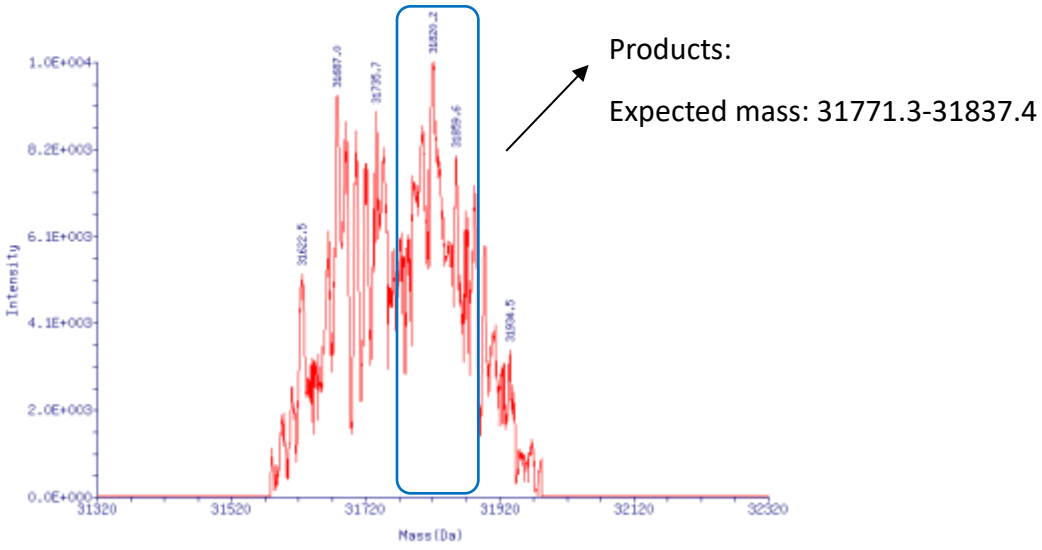
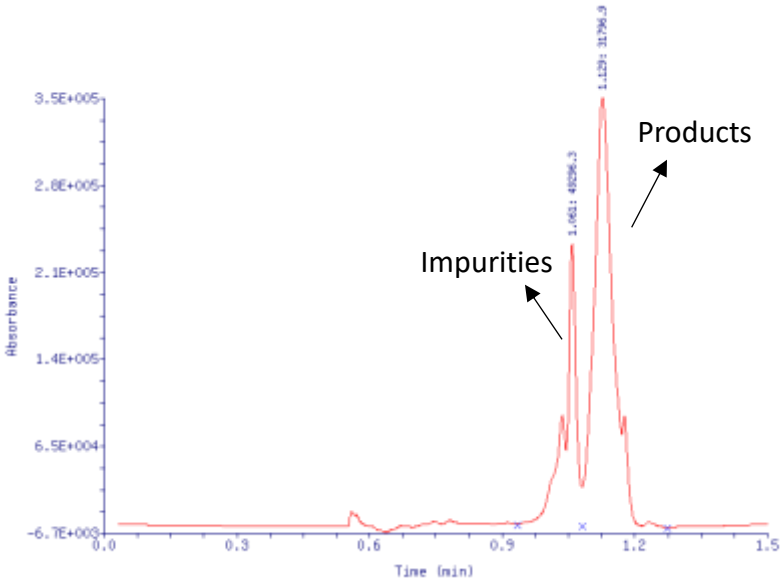


Figure S102. LC/UV Spectrum and deconvoluted mass spectrum of well **A6**. Crude cycle 2 products, pooled and precipitated.

Expected mass: 31722.3-31854.4

LC/UV Spectrum:



Deconvoluted mass spectrum of Products:

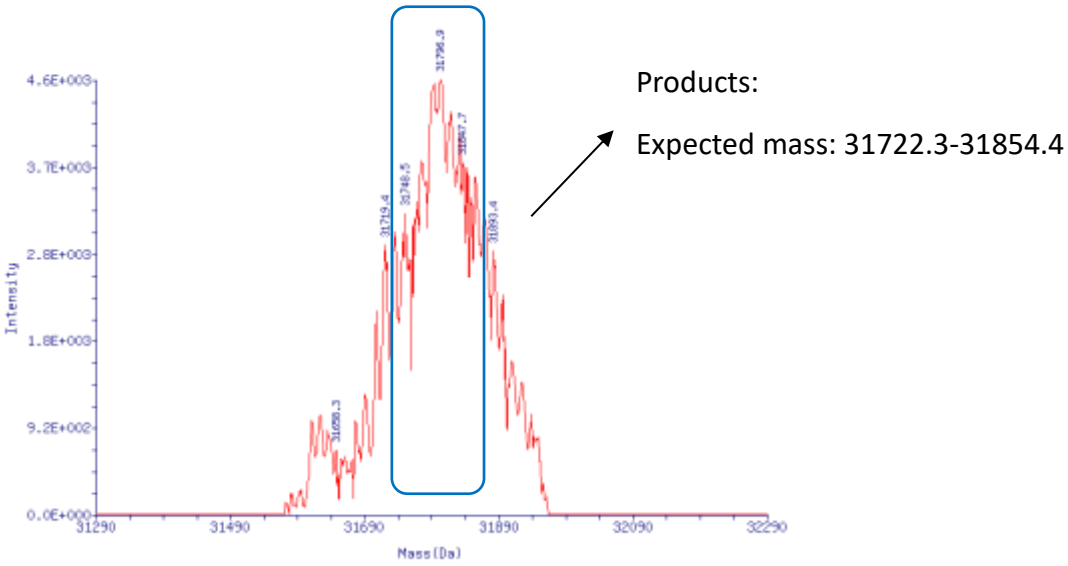
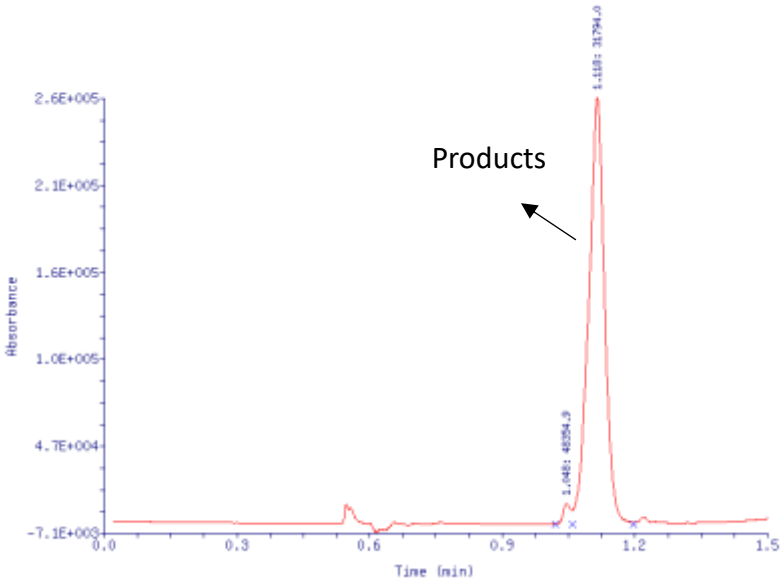


Figure S103. LC/UV Spectrum and deconvoluted mass spectrum of crude pooled cycle 2 products.

Purified cycle 2 products, pooled and precipitated.

Expected mass: 31722.3-31854.4

LC/UV Spectrum:



Deconvoluted mass spectrum of Products:

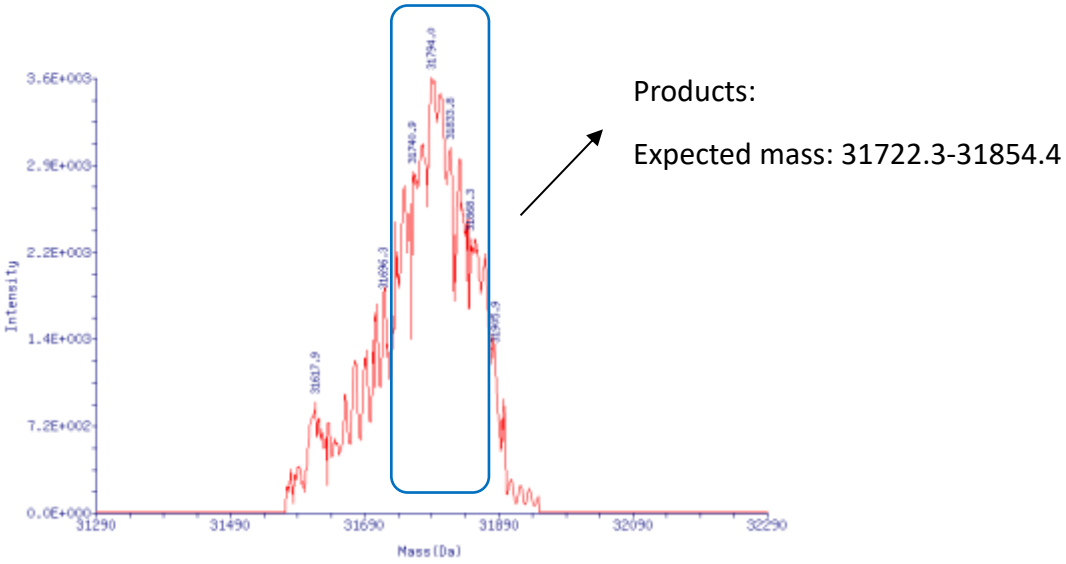
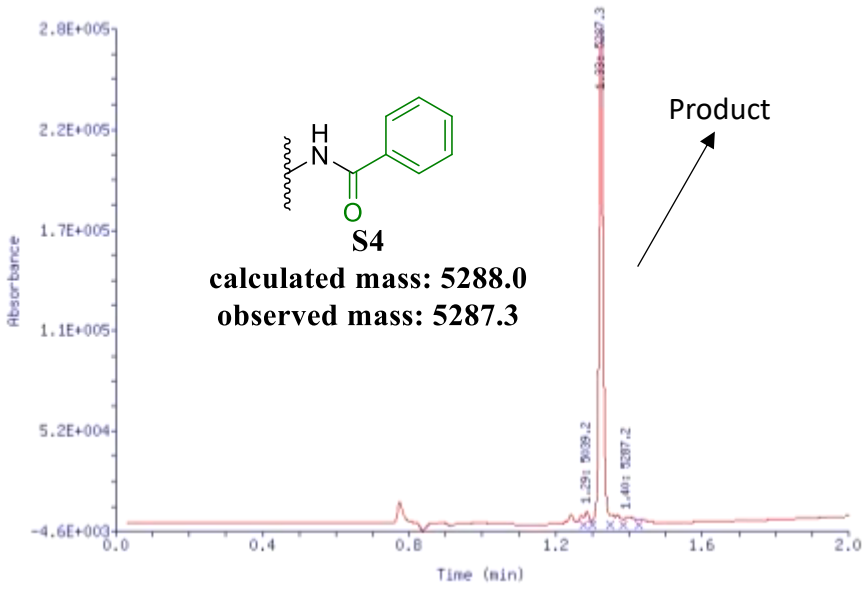


Figure S104. LC/UV Spectrum and deconvoluted mass spectrum of purified pooled cycle 2 products.

9.11. Mass Spectra of S4 from Control Experiment

LC/UV Spectrum:



Deconvoluted mass spectrum of Product:

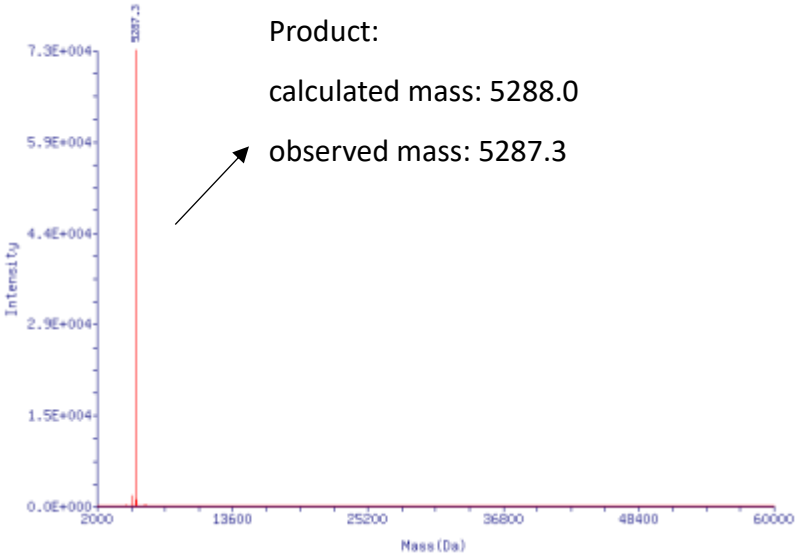
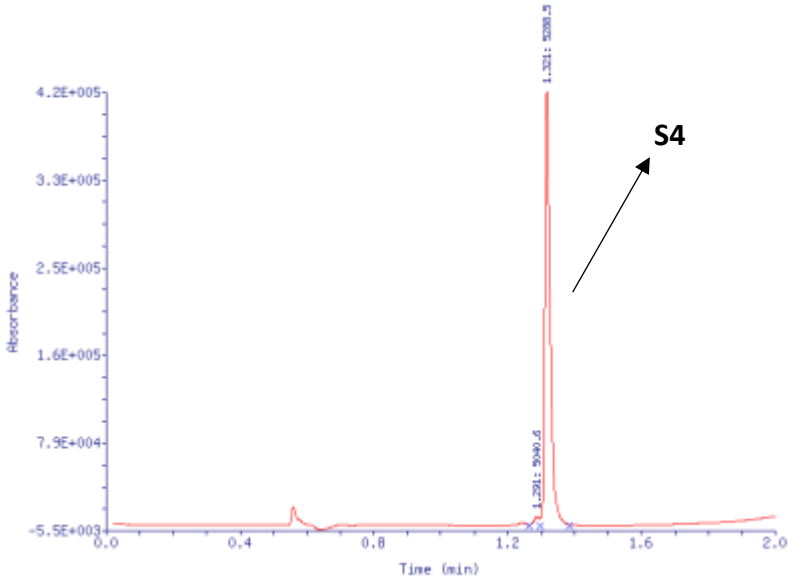


Figure S105. LC/UV Spectrum and deconvoluted mass spectrum of **S4**.

LC/UV Spectrum:



Deconvoluted mass spectrum of Product:

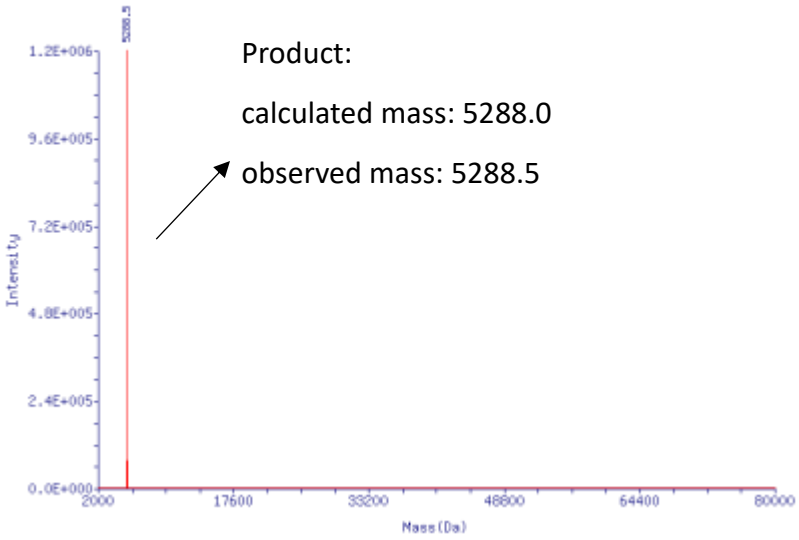


Figure S106. LC/UV Spectrum and deconvoluted mass spectrum of photoreaction of **S4**.

10. DNA Damage Evaluation

10.1. Ligation Procedure for the Product 6

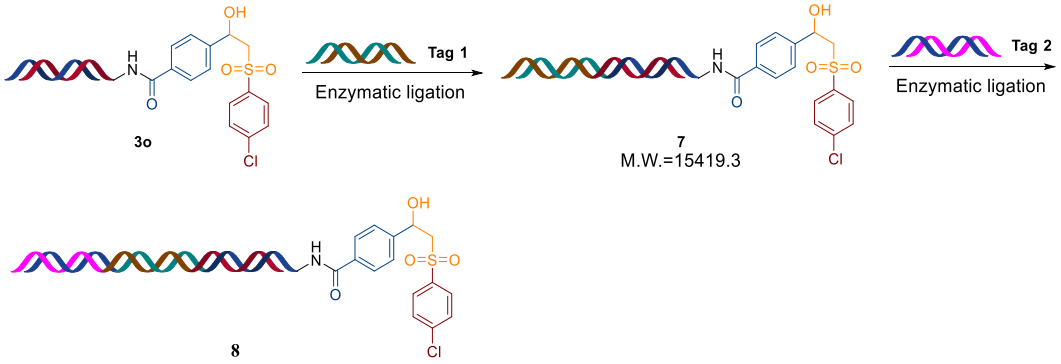
HP 6

Tag 1: The sequences of 5 '-phosphorylated Tag 1-F chain are 5'-ACTXXXXXXXXAG -3', and the sequences of their complementary 5'-phosphorylated Tag 1-R are 5'- GCACCTXXXXXXXXAGTGG -3'.

Tag 2: The sequences of 5 '-phosphorylated Tag 2 -F chain are 5'-GTGCCXXXXXXXXXXXXXXXXXXXTTGCCTCTACTGT -3', and the sequences of their complementary 5'-phosphorylated Tag 2 -R are 5'-CTCGXXXXXXXXXXXXXXXXXTACCNNNNNNACAGXXXXXXXXXXXXXXXXXXXXXCGAATAGTGG -3'.

To DNA sample **HP** (5.0 nmol, 5.0 μL, 1.0 equiv.) was added DNA **Tag 1** (5.5 nmol, 1.1 equiv.), **Tag 2** (6.1 nmol, 1.2 equiv.), followed by the addition of 10X ligation buffer (4.0 μL) and T4 DNA ligase (12.0 U), and H_2O to a final volume of 40.0 μl. The reaction mixture was incubated at 25 °C for 2 hours. The ligation was assessed for completion by LC-MS analysis. The reaction mixture was quenched thermally by incubation for 20 minutes at 65 °C. The crude material **6** was purified by ethanol precipitation. Product **6** (149 nt, 4.0 nmol, 80% recovery rate) was obtained as white solids.

10.2. Synthesis of Product 8



3o 7 M.W.=15419.3 8

Tag 1: The sequences of 5 '-phosphorylated Tag 1-F chain are 5'-ACTXXXXXXXXAG -3', and the sequences of their complementary 5'-

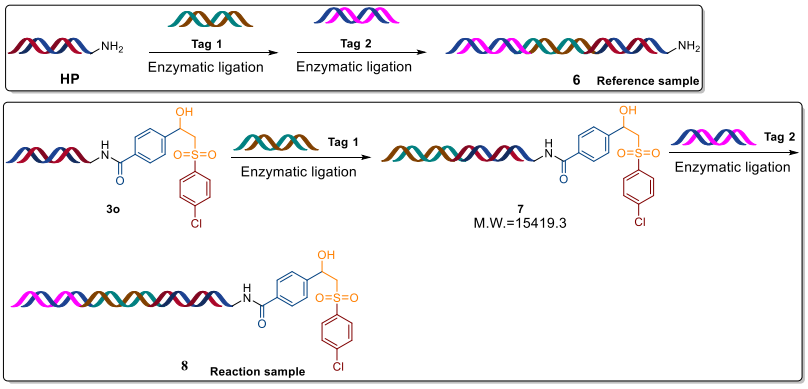
phosphorylated Tag 1-R are 5'- GCACCTXXXXXXXXAGTGG -3'.

Tag 2: The sequences of 5 '-phosphorylated Tag 2-F chain are 5'-GTGCCXXXXXXXXXXXXXXXXXXXTTGCCTCTACTGT -3', and the sequences of their complementary 5'-phosphorylated Tag 2-R are 5'-CTCGXXXXXXXXXXXXXXXXXTACCNNNNNNACAGXXXXXXXXXXXXXXXXXXXXCGAATAGTGG -3'.

Preparation of **7**: To DNA sample **3o** (5.0 nmol, 5.0 μL, 1.0 equiv.) was added DNA **Tag 1** (5.5 nmol, 1.1 equiv.), followed by the addition of 10X ligation buffer (2.0 μL) and T4 DNA ligase (6.0 U), and H_2O to a final volume of 20.0 μl. The reaction mixture was incubated at 25 °C for 1 hour. The reaction mixture was quenched thermally by incubation for 20 minutes at 65 °C. The crude material **7** was purified by ethanol precipitation. Product **7** (4.3 nmol, 86% recovery rate) was obtained as white solids.

Preparation of **8**: To **7** (4.3 nmol, 4.3 μL, 1.0 equiv.) was added DNA **Tag 2** (4.7 nmol, 1.1 equiv.), followed by the addition of 10X ligation buffer (1.72 μL) and T4 DNA ligase (5.16 U), and H_2O to a final volume of 17.2 μl. The reaction mixture was incubated at 25 °C for 1 hour. The ligation was assessed for completion by LC-MS analysis. The reaction mixture was quenched thermally by incubation for 20 minutes at 65 °C. The crude material **8** was purified by ethanol precipitation. Product **8** (3.44 nmol, 80% recovery rate) was obtained as white solids.

10.3. qPCR Test



The photoreaction for the synthesis of DNA-conjugated β-hydroxy sulfone was performed with a DNA conjugated compound containing a double stranded DNA coding region to mimic the library component. The product DNA-conjugated **3o** was ligated with a full-length of oligonucleotide to furnish **8**. Ligation of **HP** to form DNA **6** was used as a control experiment as described in previous experimental sections. Then the amplification efficiency was analyzed by qPCR (Quant Standio 3, Thermo Fisher).

The product **6** and **8** were subjected to a stepwise dilution with 10 folds each time until it reached a final 10^8 folds dilution. The last seven 10-folds serial dilutions were used as templates for qPCR tests using a SYBR Green Master Mix kit (Thermo) on a Real-Time PCR System (Quant studio 3). All samples were run in triplicates and subjected to PCR cycles as follows: 50 °C heat activation for 2 mins, then 95 °C heat for 10 mins followed by 30 cycles of 95 °C denaturation for 15 seconds, 60 °C annealing for 60 seconds. Melt curve stage: 95 °C denaturation for 15 seconds, 60 °C annealing for 60 seconds, and 95 °C dissociation for 15 seconds.

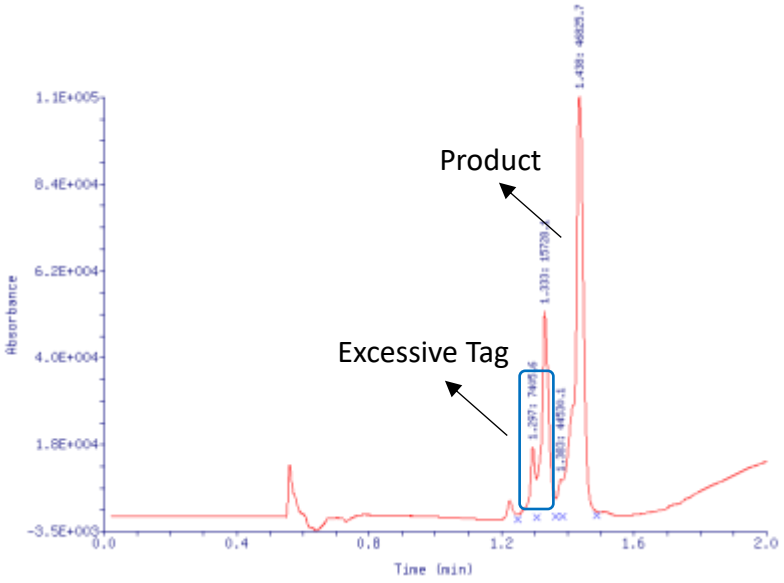
To further assess the amplification efficiency, the quantity of the full-length DNA templates was first normalized based on the Bioanalyzer results and qPCR with serial dilution was performed. Linear fitting was then calculated respectively based on the CT values. According to the slope, the amplification efficacy was calculated. Compared between the experimental groups, the amplification efficiency of DNA **8** (102%) was close to control experiment DNA **6** (102%) indicated no obvious impact on PCR efficiency by the reaction. Thus, in summary, the DNA remained in good integrity after the photoreaction.

10.4. Mass Spectra of the Product 6-8

6

Expected mass: 46797.1
Observed mass: 46825.7

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.297	7405.6	4.37E+003	ok	2.08E+004	7.04
1.333	15728.1	5.94E+003	ok	7.63E+004	25.84
1.383	44530.1	1.54E+003	ok	8.71E+003	2.95
1.438	46825.7	3.65E+004	ok	1.89E+005	64.18

Deconvoluted mass spectrum of product:

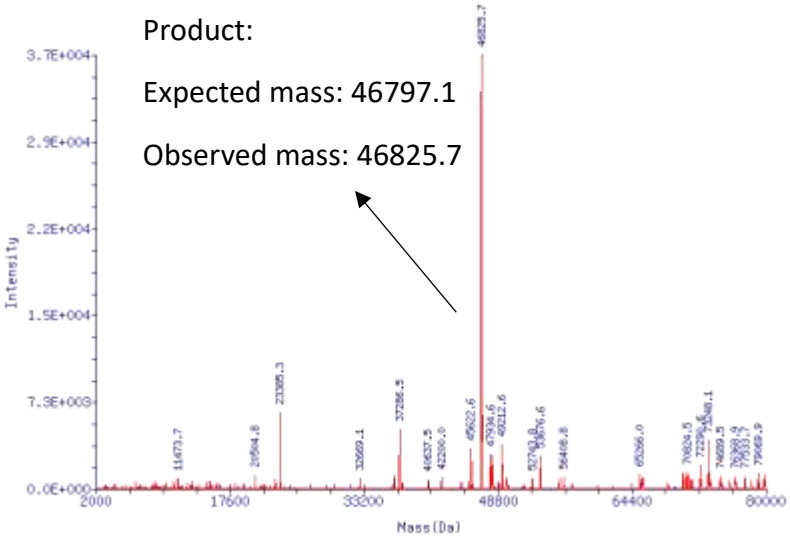
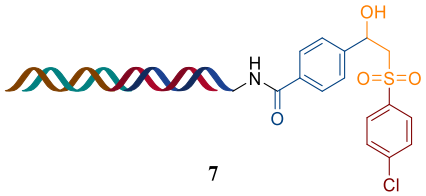


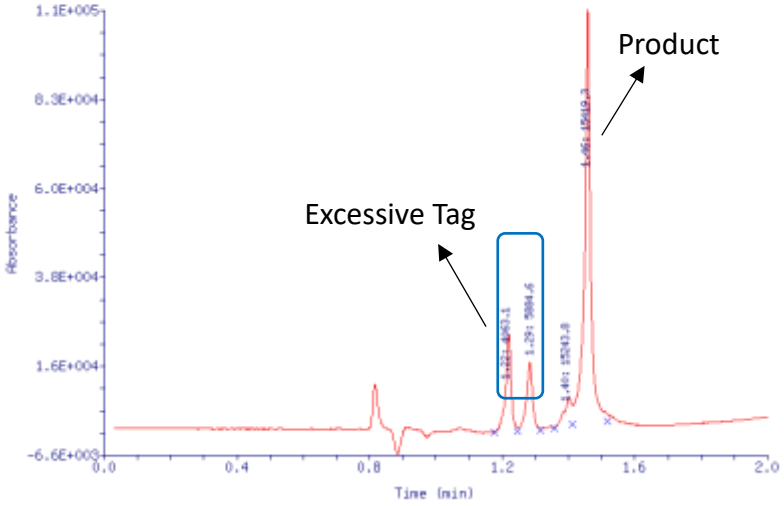
Figure S107. LC-MS Spectrum of **6**.



7

Expected mass: 15419.3
Observed mass: 15419.3

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.22	4063.1	4.20E+004	ok	2.77E+004	14.44
1.29	5884.6	1.22E+004	ok	2.17E+004	11.32
1.40	15243.8	1.12E+004	ok	1.05E+004	5.50
1.46	15419.3	3.12E+005	ok	1.32E+005	68.74

Deconvoluted mass spectrum of product:

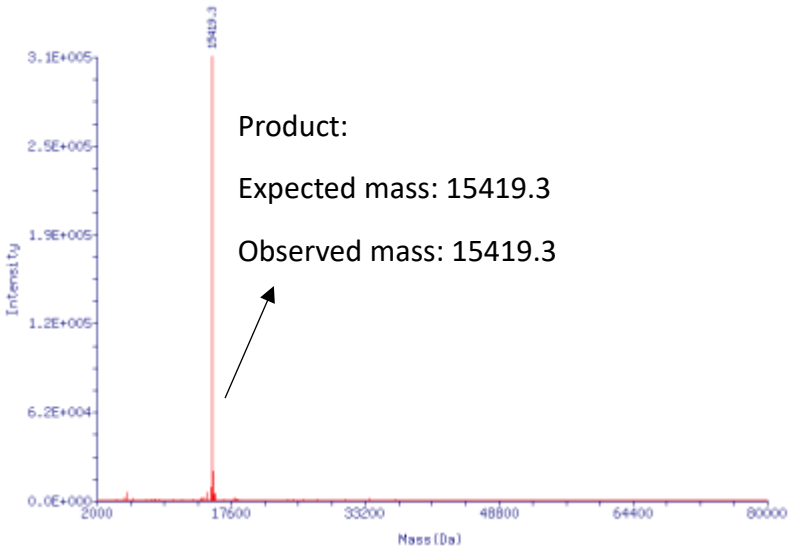
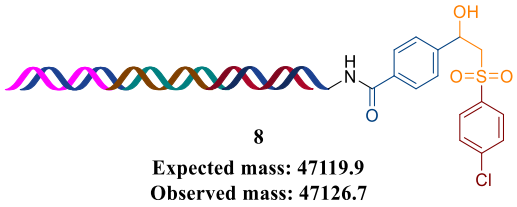


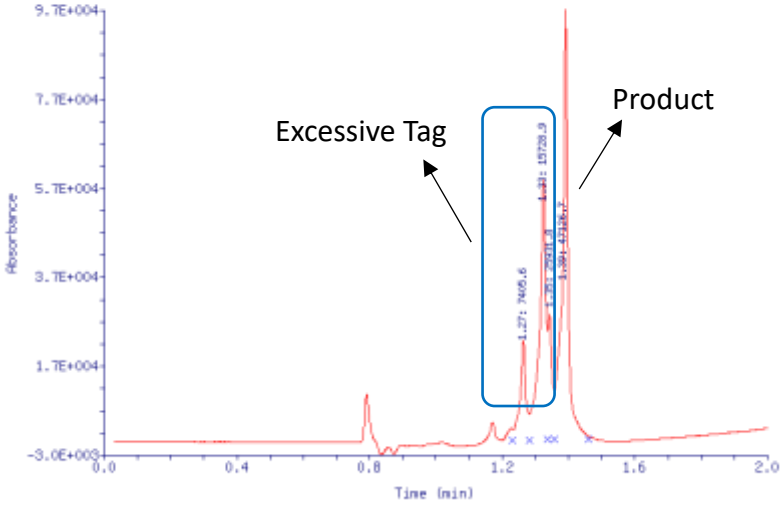
Figure S108. LC-MS Spectrum of **7**.



8

Expected mass: 47119.9
Observed mass: 47126.7

LC Spectrum:



RT (min)	Base Peak Mass (Da)	Intensity	Spectral Quality	LC/UV Peak Area	LC/UV Area Percent
1.27	7405.6	6.36E+003	ok	2.68E+004	10.91
1.33	15728.9	8.81E+003	ok	7.70E+004	31.34
1.35	25931.8	4.18E+003	ok	2.40E+004	9.76
1.39	47126.7	1.68E+004	ok	1.18E+005	48.00

Deconvoluted mass spectrum of product:

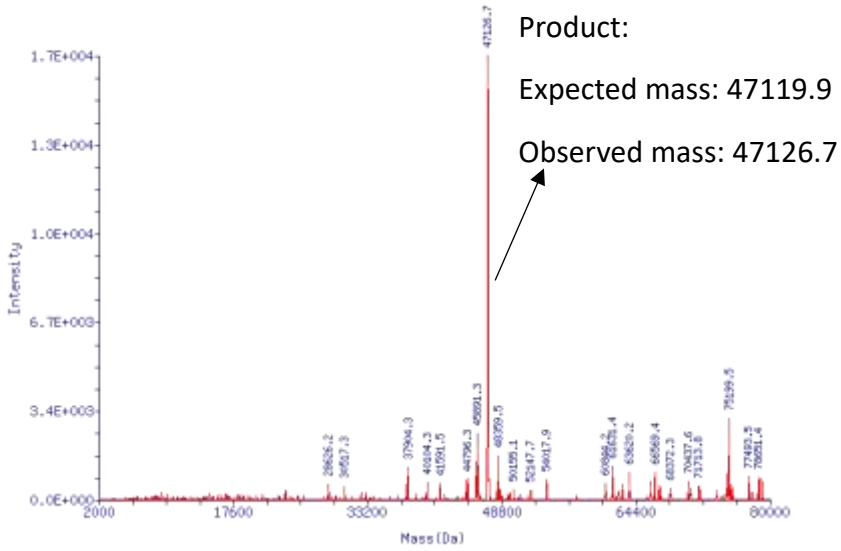


Figure S109. LC-MS Spectrum of **8**.

10.5. Gel Electrophoresis

Gel electrophoresis was performed with a 12-well 3% TBE agarose gel (Invitrogen) in 1X TBE buffer which was prepared in-house. The ligation mixture was diluted to the concentration of 50.0 ng/μL. The DNA loading sample was prepared by adding 10.0 μL of the diluted DNA sample and 2.0 μL of 6X DNA loading dye. The first lane of the gel was loaded with a DNA molecular weight ladder, and 5.0 μL of DNA-dye mixed samples was loaded into each lane. Gels were run at 120 V for 35 minutes and stained with 3X GelStain ethidium bromide

in 0.1M NaCl for 40 min. DNA fragments were visualized under a UV light device and assessed for completed ligation. For smaller scale of ligation experiment, master-mix can be prepared by pre-mixing water, 10X ligation buffer and DNA ligase before adding into the designated DNA starting material. The crude oligo was cleaned up by ethanol precipitation.

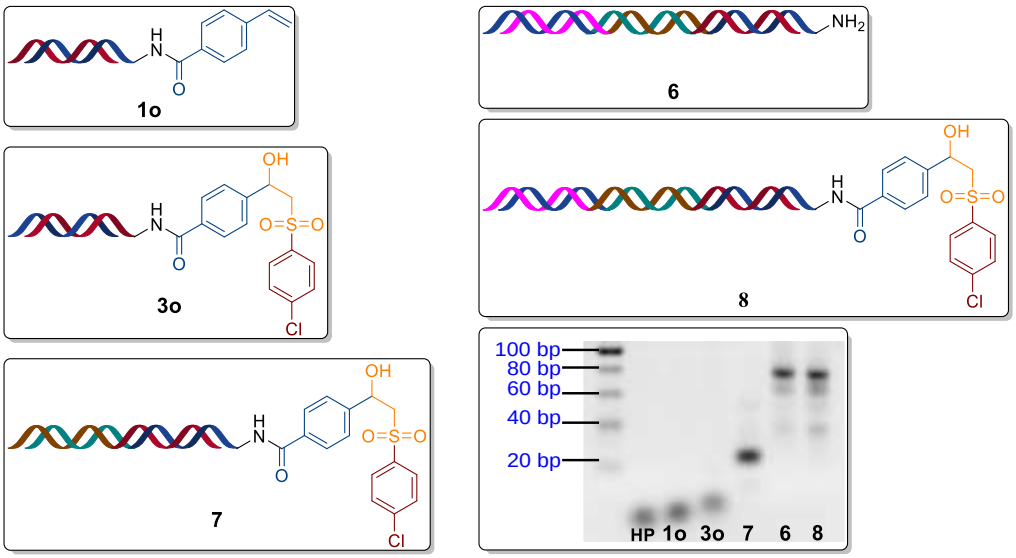


Figure S110. Gel electrophoresis image of oligo products: the DNA headpiece (**HP**), DNA-conjugated olefin (**1o**), product **3o**, the subsequent ligation crude products **7**, **6** and **8**.

10.6. qPCR

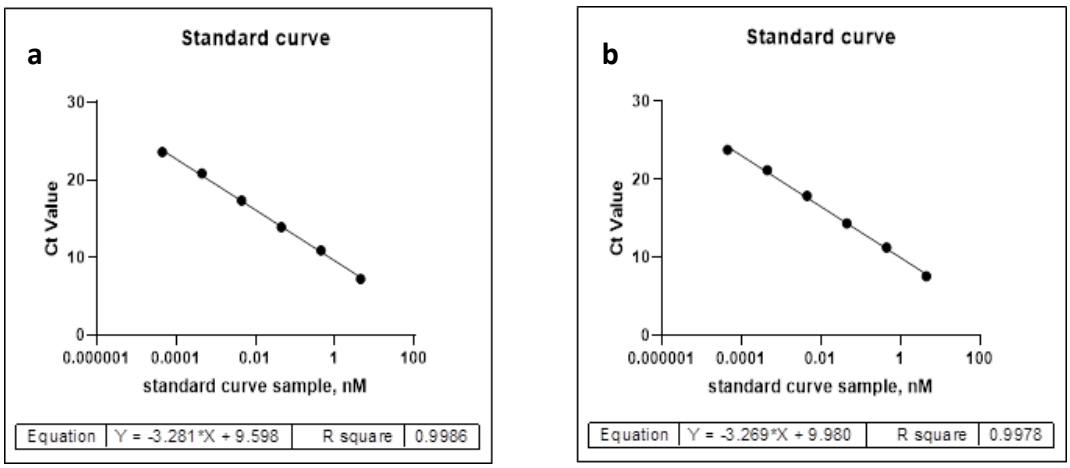


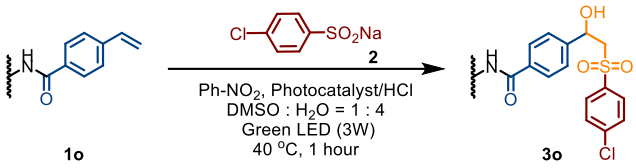
Figure S111. Standard curve of the qPCR products (a) DNA **6**; (b) DNA **8**.

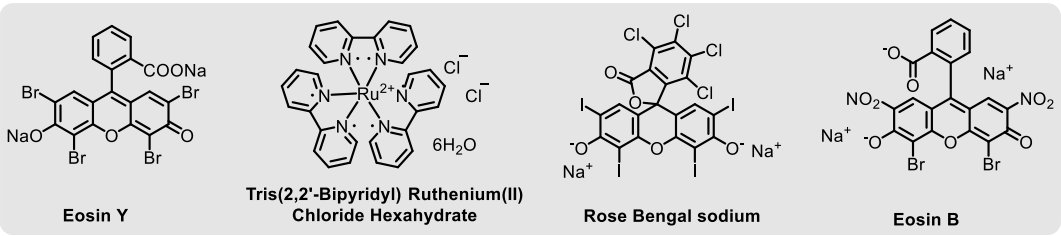
Standard (nM)	Target (DNA 8)		Relative Amount of Target (%)	Average Relative Amount of Target (%)
	CT1	Sample (nM)		
0.045	14.38	0.035	77.4	**78**
0.0045	17.65	0.0035	78.0	
0.00045	20.92	0.00035	78.7	

Table S1. Calculation of DNA Damage.

In conclusions: The amplifiable DNA in the photoreaction product (DNA 8) is 78.0%. Thus, the DNA damage is 22% after 2 steps of chemical conversion including acylation and photoreaction, in addition to AOP installation.

11. Optimization of the photocatalyst





Entry	Photocatalyst	HCl (mM)[a]	3o (%)[b]
1	Eosin Y	80	93
2	Tris(2,2'-Bipyridyl) Ruthenium(II) Chloride Hexahydrate	/	72
3	Rose Bengal sodium	/	46
4	Eosin B	/	62
5	Rose Bengal sodium	80	41
6	Eosin B	80	59

[a]Final concentration. [b]Conversions were determined by LC-MS. [c]General reaction conditions: **1o** (10.0 nmol, 1.0 equiv., 0.8 mM final concentration), **2** (240.0 mM final concentration), Ph-NO_2 (80.0 mM final concentration) and photocatalyst/HCl (1:2, premixed, photocatalyst with 40.0 mM final concentration) in DMSO/H_2O (1:4 by volume) was irradiated with green light for 1 h at 40 °C.