

Supporting Information

Open-Air Alkylation Reactions in Photoredox Catalyzed DNA-Encoded Library Synthesis

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Key to Abbreviated Terms:

AOP: 15-amino-4,7,10,13-tetraoxapentadecanoic acid
DHP: 4-alkyl-1,4-dihydropyridine
EDTA: ethylenediaminetetraacetic acid
HFIP: hexafluoroisopropanol
MOPS: 3-(*N*-morpholino)propanesulfonic acid
TEA: triethylamine
TMHD: 2,2,6,6-Tetramethyl-3,5-heptanedione
TMG: 1,1,3,3-tetramethylguanidine
4CzIPN: 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile

General Considerations:

General: All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 4- or 5-port dual-bank manifold. Argon or nitrogen was used to provide such an atmosphere. LED irradiation was accomplished using a Kessil H150-Blue LED lamp (30 W High Luminous DEX 2100 LED) placed 1.5 inches away from the reaction vessel. (**Safety note:** Looking directly into the LEDs can cause retinal damage. Reactions were viewed through orange-tinted safety glasses.) NMR spectra (^1H , ^{13}C , ^{19}F) were obtained at 298° K. ^1H NMR spectra were referenced to residual, non-deuterated chloroform (δ 7.26) in CDCl_3 , ^{13}C NMR spectra were referenced to CDCl_3 (δ 77.3), and ^{19}F NMR spectra were referenced to hexafluorobenzene (δ -164.9)¹ as an internal standard and were run with C-F/C-H decoupling. Reactions were monitored by HPLC, GC/MS, ^1H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using permanganate stain, Seebach's stain,² ninhydrin stain, and/or UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32-63 μm). Flash chromatography was accomplished using an automated system (monitoring at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 μm). Solvents were purified with drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected.

Chemicals: Deuterated NMR solvents were stored over 4Å molecular sieves and/or K_2CO_3 (CDCl_3). Na_2SO_4 , MgSO_4 , DMA, DMSO, CH_2Cl_2 , CHCl_3 , EtOAc, pentane, hexanes, MeOH, Et_2O , and toluene were used as purchased. Et_3N was purchased from commercial suppliers and distilled from CaH_2 prior to use. THF was purchased and dried *via* a solvent delivery system. DMSO and DMF (99.8%, extra dry) were stored over 4 Å molecular sieves. The transition metal photocatalyst $[\text{Ir}\{\text{dFCF}_3\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6$ ³ and 4CzIPN⁴ were prepared in-house by the

procedures outlined in our previous publications. Borylated arenes were purchased from commercial suppliers. The organotrifluoroborate reagent potassium trifluoro(3,3,3-trifluoroprop-1-en-2-yl)borate was prepared via our previously published protocol.⁵ Methyl 4-(3,3,3-Trifluoroprop-1-en-2-yl)benzoate was prepared as previously reported.⁶ The other trifluoromethyl-substituted alkenes were prepared using the procedures outlined here. All other CF₃-substituted olefins were prepared in-house using the procedures outlined here. Organobis(catecholato)silicates were prepared as previously described (**1a**).⁷ Carboxylic acids were purchased from commercial suppliers. 1,4-Dihydropyridines were prepared according to the procedures outlined here or according to literature procedures.⁸

Analysis of “on-DNA” reactions: Analysis of on-DNA reactions was performed by LC/MS: After reaction, an aliquot of the reaction mixture was diluted with water to approximately 0.05 mM. 5 μ L of the LC/MS samples was injected onto a reverse-phase chromatography column (Halo ES-C18, 3.4 μ m particle size, 2.1x30 mm) and eluted (10-90% B over 4 min at 0.5 mL/min flow rate; Solvent A: 0.75% v/v HFIP / 0.038% TEA / 5 μ M EDTA in H₂O; Solvent B: 0.75% HFIP, 0.038% TEA, 5 μ M EDTA in 90/10 MeOH/deionized H₂O) with monitoring at UV 260 nm. Effluent was analyzed on a Bruker microTOF in negative ion mode. % conversion was determined based on reported peak intensities following deconvolution (between 3,000 and 10,000 Da) of the DNA charge states using the Bruker Compass DataAnalysis software version 4.2 (build 383.1). An intensity of 5% of the maximum peak intensity observed for a given spectra was set as the reporting threshold. The maximum intensity peak for each distribution of peaks was manually selected as the representative peak for reporting. % conversion was then calculated by dividing the peak intensity of the product peak by the sum of the reported peaks for that spectra.

Materials for “on-DNA” synthesis: DNA headpiece HP-NH₂(5'-/5Phos/GAGTCA/iSp9/iUniAmM/iSp9/TGACTCCC-3') was obtained from Biosearch Technologies, Novato, CA. The spacer-elongated AOP-Headpiece (Figure S1) was prepared via HATU coupling following the general procedure described later in this document with 5 equivalents each of Fmoc-15-amino-4,7,10,13-tetraoxapentadecanoic acid (Fmoc-AOP), *i*-Pr₂EtN and HATU. The lyophilized product of this reaction was then deprotected by exposure to a 10% piperidine in H₂O soln. After the reaction was deemed complete by LC/MS analysis, the reaction was precipitated following the EtOH protocol and is typically pure enough to be used without further purification.

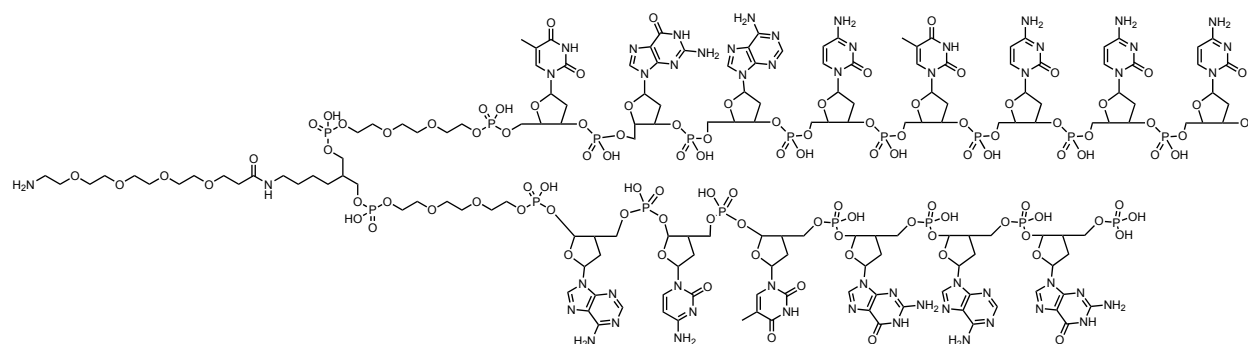
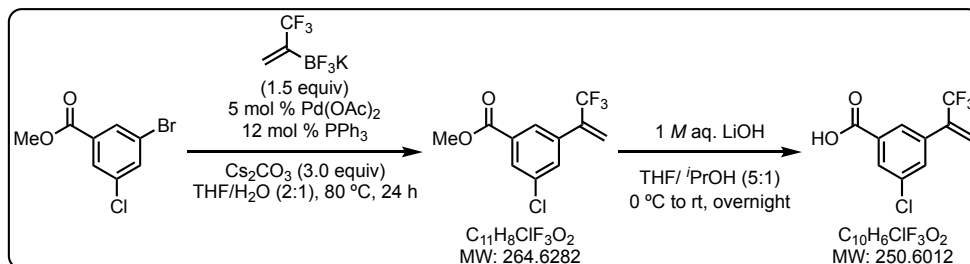


Figure S1. Sequence and structure of the AOP-Headpiece. MW = 5184.5220

On-DNA aryl halides and trifluoromethyl-substituted alkenes were prepared according to procedures outlined here. Photoredox-catalyzed reactions were performed using snap-cap microcentrifuge tubes (Fisher catalog number 05-402-18). DMSO was used as received and H₂O was ultrapurified to 18.2 MΩcm and passed through a 0.2 μm filter cartridge. All reactions were set up on the benchtop, open to air, and under ambient conditions.

Synthesis of Trifluoromethyl Alkene-Substituted Benzoic Acids

Synthesis of 3-chloro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid



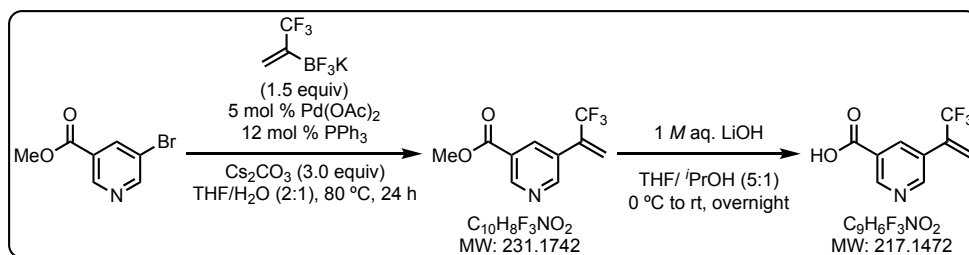
Cross-Coupling

Methyl 3-chloro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoate, S1. To a 50 mL microwave tube was added methyl 3-bromo-5-chlorobenzoate (237 mg, 0.95 mmol, 1.0 equiv), Cs₂CO₃ (929 mg, 2.85 mmol, 3.0 equiv), potassium trifluoro(3,3,3-trifluoroprop-1-en-2-yl)borate (288 mg, 1.43 mmol, 1.5 equiv), Pd(OAc)₂ (11 mg, 0.05 mmol, 0.05 equiv), and PPh₃ (32 mg, 0.12 mmol, 0.12 equiv). The tube was sealed with a crimp-top cap containing a TFE-lined silicone septum and placed under an argon atmosphere *via* an inlet needle. The tube was evacuated three times *via* an inlet needle, then purged with argon. A mixture of degassed THF (6 mL) and degassed, and deionized H₂O (3 mL) was added *via* syringe. The reaction mixture was stirred at 80 °C overnight. Reaction progress was monitored by GC/MS. Once complete, the reaction was cooled to rt and diluted in EtOAc (25 mL). The reaction mixture was transferred to a separatory funnel and washed with saturated aq NaHCO₃ (2 x 25 mL) and brine (25 mL). The layers were separated, and the combined aq layer was extracted with EtOAc (2 × 25 mL). The combined organic layers were dried (Na₂SO₄), and the solvent was removed *in vacuo* by rotary evaporation. Further purification by SiO₂ column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the title compound (138.3 mg, 55%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (s, 1H), 8.01 (s, 1H), 7.62 (s, 1H), 6.07 (s, 1H), 5.86 (s, 1H), 3.95 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.4, 137.41 (d, J_{C-C-F} = 31 Hz, C), 135.6, 135.1, 132.4, 131.8, 130.2, 127.0, 123.0 (q, J_{C-C-F} = 6.4 Hz, CH₂), 122.6 (q, J_{C-F} = 274.0 Hz, CF₃), 52.7. ¹⁹F NMR (471 MHz, CDCl₃) δ -68.08 (s, 3F). FT-IR (cm⁻¹, neat, ATR) 3073 (w), 3003 (w), 2956 (w), 1729 (s), 1278 (vs), 1170 (vs), 1123 (vs), 989 (m), 769 (m), 650 (m). HRMS (ES⁺) calcd for C₁₁H₉ClF₃O₂ [M+H]⁺: 265.0238, found: 265.0246.

Hydrolysis

3-Chloro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid, S2. To a round bottom flask equipped with a stir bar was added methyl 3-chloro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (138 mg, 0.52 mmol, 1.0 equiv) followed by THF (0.36 M, 1.4 mL). The reaction mixture was cooled to 0 °C in an ice-water bath. After stirring for approximately 10 min, an aq 1 M solution of LiOH (0.78 mL, 0.78 mmol, 1.5 equiv) was added, followed by *i*-PrOH (1.8 M, 0.29 mL). After stirring for 10 min, the ice-bath was removed, and the solution was stirred overnight at rt, at which time it was judged to be complete by HPLC. The crude reaction was concentrated *in vacuo* by rotary evaporation, and the resulting residue was dissolved in H₂O (5 mL). This aq solution was transferred to a separatory funnel and washed with Et₂O (2 × 5 mL). The aq layer was then acidified with 1 M aq HCl to a pH of ~1 and extracted with EtOAc (4 × 5 mL). The combined EtOAc layers were then dried (MgSO₄) and filtered. The solvent was removed *in vacuo* by rotary evaporation to give the title compound as a white solid (88.7 mg, 68%) (mp = 99-101 °C). ¹H NMR (500 MHz, CDCl₃) δ 12.11 (s, 1H, CO₂H) 8.12 (s, 1H), 8.09 (s, 1H), 7.69 (s, 1H), 6.10 (s, 1H), 5.89 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 170.8, 137.3 (q, *J*_{C-C-F} = 31.0 Hz, C), 135.8, 135.3, 132.8, 131.5, 130.8, 127.6, 122.9 (q, *J*_{C-C-F} = 273.9 Hz, CH₂), 122.8 (q, *J*_{C-F} = 5.7 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -68.09 (s, 3F). FT-IR (cm⁻¹, neat, ATR) 3100 (w), 3014 (w), 2961 (w), 2872 (w, br), 2552 (w), 1694 (s), 1290 (s), 1096 (vs), 890 (s), 713 (s), 646 (s). HRMS (ES⁻) calcd for C₁₀H₅ClF₃O₂ [M-H]⁻: 248.9930, found: 248.9902.

Synthesis of 5-(3,3,3-trifluoroprop-1-en-2-yl)nicotinic acid



Cross-Coupling

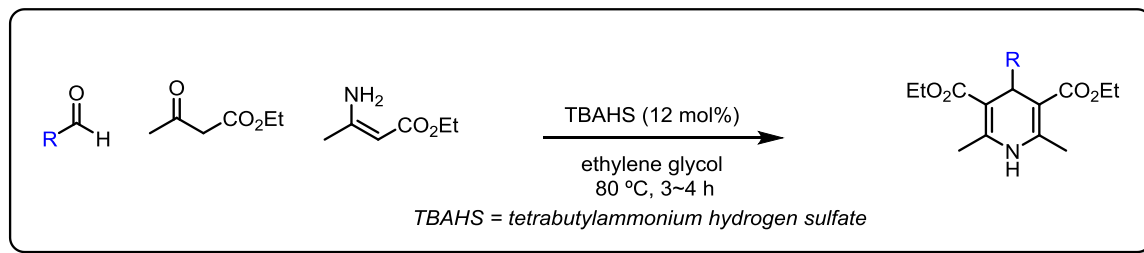
Methyl 5-(3,3,3-trifluoroprop-1-en-2-yl)nicotinate, S3 (74.1 mg, 32%) was prepared following the procedure for the preparation of methyl 3-chloro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoate

with the following modification: The reaction was conducted using methyl 5-bromonicotinate (215 mg, 1.0 mmol, 1.0 equiv). The pure carboxylic acid was obtained as a yellow oil. **¹H NMR** (500 MHz, CDCl₃) δ 9.23 (s, 1H), 8.85 (s, 1H), 8.36 (s, 1H), 6.14 (s, 1H), 5.91 (s, 1H), 3.98 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.30, 151.95, 151.17, 135.82, 135.61 (d, *J*_{C-C-F} = 31.5 Hz, C), 129.58, 125.96, 123.21 (q, *J*_{C-C-C-F} = 6.4 Hz, CH₂), 122.82 (q, *J*_{C-F} = 274.0 Hz, CF₃), 52.75. **¹⁹F NMR** (471 MHz, CDCl₃) δ -68.33 (s, 3F). **FT-IR** (cm⁻¹, neat, ATR) 3063 (w), 3013 (w), 2958 (w), 1730 (vs), 1285 (vs), 1173 (vs), 1126 (vs), 957 (m), 770 (m). **HRMS** (ES+) calcd for C₁₀H₉F₃NO₂ [M+H]⁺: 232.0580, found: 232.0605.

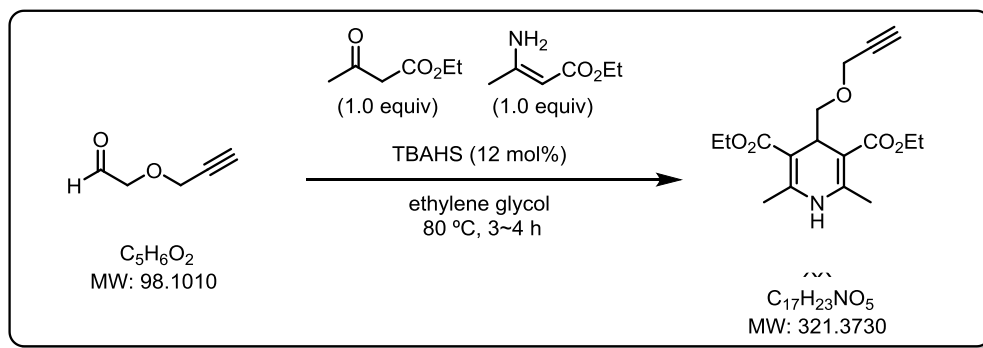
Hydrolysis

5-(3,3,3-Trifluoroprop-1-en-2-yl)nicotinic Acid, S4 (52.1 mg, 75%) was prepared following the procedure for the preparation of 3-chloro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid with the following modification: The reaction was conducted methyl 5-(3,3,3-trifluoroprop-1-en-2-yl)nicotinate (74 mg, 0.32 mmol, 1.0 equiv). The pure carboxylic acid was obtained as a powdery white solid (mp: 153-155 °C). **¹H NMR** (500 MHz, CD₃OD) δ 9.16 (s, 1H), 8.85 (s, 1H), 8.44 (s, 1H), 6.23 (s, 1H), 6.15 (s, 1H). [No CO₂H proton was observed due to H/D exchange with solvent.] **¹³C NMR** (125 MHz, CD₃OD) δ 167.1, 152.2, 151.7, 137.3, 136.2 (q, *J*_{C-C-F} = 31.4 Hz, C), 131.2, 128.3, 125.0 (q, *J*_{C-C-C-F} = 5.6 Hz) 124.4 (q, *J*_{C-F} = 273.0 Hz). **¹⁹F NMR** (471 MHz, CD₃OD) δ -66.13 (s, 3F). **FT-IR** (cm⁻¹, neat, ATR) 3075 (w), 3012 (w), 2924 (w), 2433 (br, w), 1717 (m), 1289 (m), 1174 (s), 1116 (vs), 819 (m), 753 (s), 647 (s). **HRMS** (ES+) calcd for C₉H₇F₃NO₂ [M+H]⁺: 218.0429, found: 218.0437.

Synthesis of 1,4-Dihydropyridines



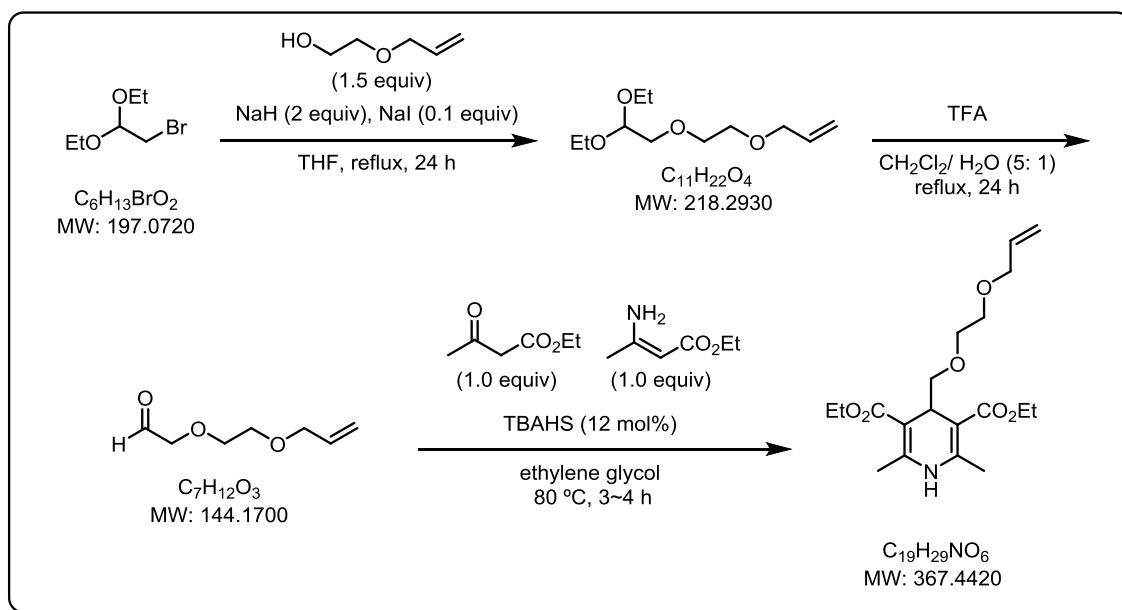
General procedure for preparation of 1,4-dihydropyridines: 1,4-Dihydropyridines were prepared according to literature procedures.^{8,9} To a stirred solution of ethyl 3-aminocrotonate (1.0 equiv) and ethyl acetoacetate (1.0 equiv) in ethylene glycol (2.5 M) were added the aldehyde (1.0 equiv) and Bu₄NHSO₄ (12 mol %). The flask was warmed to 80 °C and stirred for 3-4 h. The reaction was cooled to rt and diluted in EtOAc. The mixture was washed with brine and extracted with EtOAc three times. The combined organic layers were dried (MgSO₄) and concentrated *in vacuo*. The residue was purified by column chromatography on SiO₂ (gradient hexane to 50:50 hexane/EtOAc) to give the 1,4-dihydropyridines.



Diethyl 2,6-dimethyl-4-((prop-2-yn-1-yloxy)methyl)-1,4-dihydropyridine-3,5-dicarboxylate, **S5**

Following general procedure for preparation of 1,4-dihydropyridines using 2-(prop-2-yn-1-yloxy)acetaldehyde (3.0 g, 30.6 mmol). The product **S5** was isolated as a yellowish solid (5.0 g, 15.6 mmol, 51%) (mp = 96-97 °C). ¹H NMR (500 MHz, CDCl₃) δ 5.83 (s, 1H), 4.17 (m, 5H), 4.09 (d, *J* = 2.4 Hz, 2H), 3.37 (d, *J* = 5.5 Hz, 2H), 2.32 (t, *J* = 2.4 Hz, 1H), 2.27 (s, 6H), 1.28 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 168.0, 146.1, 100.4, 80.6, 73.9, 73.3, 60.0, 58.1, 33.9, 19.7, 14.7. FT-IR (cm⁻¹, neat, ATR) 3352 (m), 3242 (m), 2977 (w), 1688 (s), 1645 (s), 1487

(s), 1321 (m), 1259 (m), 1092 (s), 658 (m). **HRMS** (ESI+) calcd for C₁₇H₂₄NO₅ [M+H]⁺: 322.1654, found: 322.1643.



Alkylation

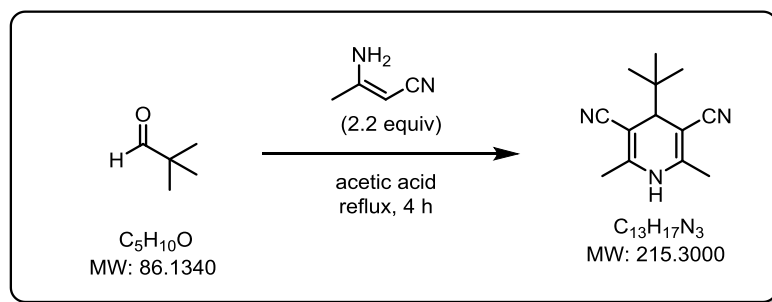
3-(2-(2,2-Diethoxyethoxy)ethoxy)prop-1-ene, S6. To a solution of NaH (1.2 g, 30 mmol, 2.0 equiv) in THF (10 mL) was slowly added 2-(allyloxy)ethan-1-ol (2.4 mL, 2.3 mmol, 1.5 equiv) in THF (2 mL) at 0 °C. After stirring for 30 min at rt, a solution of 2-bromo-1,1-diethoxyethane (3.0 g, 2.3 mL, 15 mmol, 1.0 equiv) and NaI (220 mg, 1.5 mmol, 0.1 equiv) in THF (5 mL) was added to the reaction mixture. The reaction was heated at reflux for 24 h and cooled to rt. The mixture was washed with brine (15 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (MgSO₄) and concentrated *in vacuo*. The residue was quickly purified by column chromatography on SiO₂ (60:40 hexane/EtOAc) to give the 3-(2-(2,2-diethoxyethoxy)ethoxy)prop-1-ene, which was used without further purification (2.3 g, 10.5 mmol, 70%). **¹H NMR** (500 MHz, CDCl₃) δ 5.90 (m, 1H), 5.26 (ddq, *J* = 17.2, 8.5, 1.7 Hz, 1H), 5.17 (ddq, *J* = 14.7, 10.4, 1.4 Hz, 1H), 4.62 (t, *J* = 5.2 Hz, 1H), 4.01 (ddt, *J* = 7.2, 5.6, 1.4, 2H), 3.68 (m, 4H), 3.56 (m, 6H), 1.20 (t, *J* = 7.0 Hz, 6H)

Oxidation

To a solution of 3-(2-(2,2-diethoxyethoxy)ethoxy)prop-1-ene (2.2 g, 10.0 mmol) in H₂O (10 mL) and CH₂Cl₂ (50 mL) was added TFA (10 mL). The reaction mixture was heated at reflux for 24 h and cooled to rt. The mixture was washed with saturated aq NaHCO₃ (25 mL) and extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layers were dried (MgSO₄) and concentrated *in vacuo* to afford 2-(2-(allyloxy)ethoxy)acetaldehyde.

1,4-Dihydropyridine Synthesis

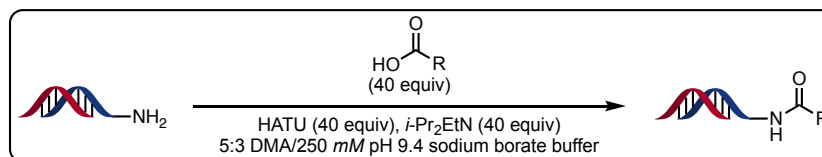
Diethyl 4-((2-(allyloxy)ethoxy)methyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate, S7. Following the general procedure for preparation of 1,4-dihydropyridines using crude 2-(2-(allyloxy)ethoxy)acetaldehyde, product **S7** was isolated as a colorless oil (1.5 g, 4.1 mmol, 41%). **¹H NMR** (500 MHz, CDCl₃) δ 6.28 (s, 1H), 5.83 (ddd, J = 17.6, 10.5, 5.8 Hz, 1H), 5.19 (dd, J = 17.3, 1.7 Hz, 1H), 5.09 (dd, J = 10.4, 1.5 Hz, 1H), 4.13 (m, 5H), 3.92 (d, J = 5.7 Hz, 2H), 3.54 (dd, J = 5.9, 3.9 Hz, 2H), 3.46 (dd, J = 5.9, 3.9 Hz, 2H), 3.24 (d, 6.0 Hz, 2H), 2.21 (s, 6H), 1.24 (t, J = 7.1 Hz, 6H). **¹³C NMR** (126 MHz, CDCl₃) δ 168.1, 146.1, 135.0, 117.0, 100.3, 74.3, 72.3, 70.2, 69.8, 59.8, 33.7, 19.3, 14.6. **FT-IR** (cm⁻¹, neat, ATR) 3325 (w), 3075 (w), 2932 (w), 1732 (m), 1446 (s), 1169 (s), 925 (m), 774 (m). **HRMS** (ESI+) calcd for C₁₉H₃₀NO₆ [M+H]⁺: 368.2068, found: 368.2080.



4-(tert-Butyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile, S8. To a stirred solution of 3-aminocrotononitrile (7.5 g, 92 mmol, 2.0 equiv) in AcOH (30 mL) was added pivalaldehyde (4.0 g, 5.0 mL, 46 mmol, 1.0 equiv). The reaction mixture was heated at reflux for 4 h. The reaction was diluted in EtOAc (30 mL) and quenched with saturated aq NaHCO₃ (30 mL). The mixture was washed with brine (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was dried (MgSO₄) and concentrated *in vacuo*. The residue was purified by column

chromatography on SiO₂ (gradient hexane to 30:70 hexane/EtOAc) to give the 4-(tert-butyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile **S8** as a white solid (3.8 g, 17.5 mmol, 38%) (mp = 195–196 °C). **¹H NMR** (500 MHz, CDCl₃) δ 6.60 (s, 1H), 2.87 (s, 1H), 2.18 (s, 6H), 0.95 (s, 9H). **¹³C NMR** (126 MHz, CDCl₃) δ 148.4, 120.6, 81.8, 46.6, 41.0, 26.3, 18.7. **FT-IR** (cm⁻¹, neat, ATR) 3329 (m), 2969 (m), 2188 (s), 1494 (s), 1367 (s), 521 (m). **HRMS** (ESI+) calcd for C₁₃H₁₈N₃ [M+H]⁺: 216.1501, found: 216.1530.

Preparation of on-DNA Substrates



General Procedure

HATU Premix Protocol for Acylation of DNA Headpiece. Cool the individual HATU (200 mM in DMA, 40 equiv), *i*-Pr₂NEt (200 mM in DMA, 40 equiv), and carboxylic acid (200 mM in DMA, 40 equiv) solutions in a 4 °C for 5 min. Once chilled, the acid, *i*-Pr₂NEt, and HATU solutions were added sequentially to a centrifuge tube, vortexed briefly, and allowed to react at 4 °C for 20 min. The oligomer solution (1 mM in 250 mM pH 9.4 sodium borate buffer) was then added, and the mixture was vortexed. The reaction was allowed to proceed at rt and monitored by LC/MS. Upon completion, the reaction was worked up following the “EtOH Precipitation Protocol.”

EtOH Precipitation Protocol. Transfer the reaction mixture to a centrifuge tube where it fills at most 1/4 of the total volume. A volume of aq 5 M NaCl equal to 1/10 of the reaction volume was then added followed by cold (–20 °C) EtOH equal to 2.5 reaction volumes. The resulting mixture was then left to stand in a –20 °C freezer for at least 1 h. The chilled mixture was then centrifuged for 15 min at 4 °C in a microcentrifuge at 13,000 rpm. The supernatant was then removed, and the sample was re-centrifuged under the same conditions, and the supernatant was again removed. The remaining precipitate was then frozen in liquid N₂ and placed on a lyophilizer for at least 10 min to remove any residual EtOH, providing the desired on-DNA substrate as a white solid.

Reaction Workflow

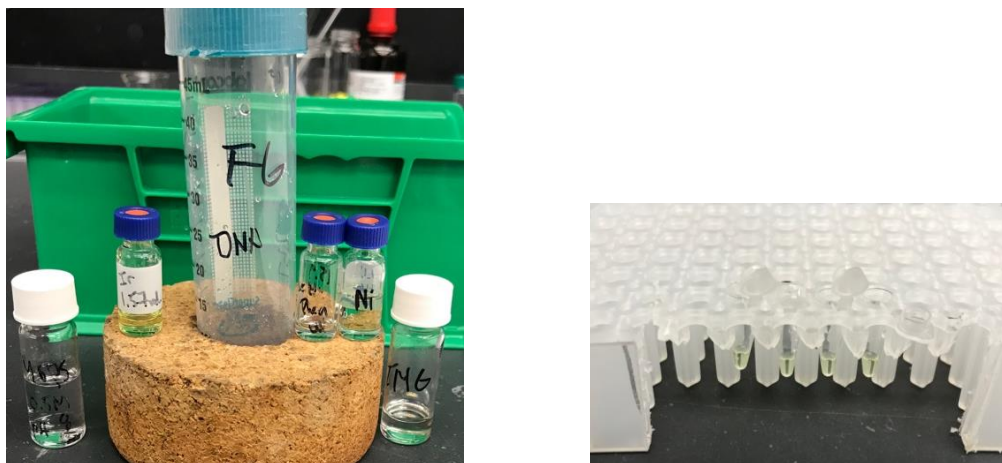


Figure S2. Reaction components were added to Eppendorf tubes as stock solutions on the benchtop, open to air.



Figure S3. The vials were vortexed and placed 1.5 inches away from a Kessil H150-Blue LED Lamp (30 W High Luminous DEX 2100 LED) and irradiated for 10-45 min.

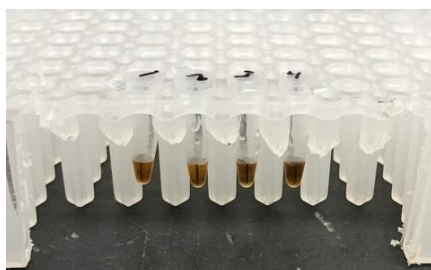
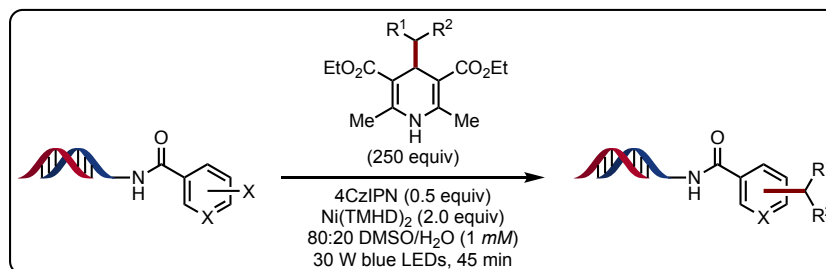


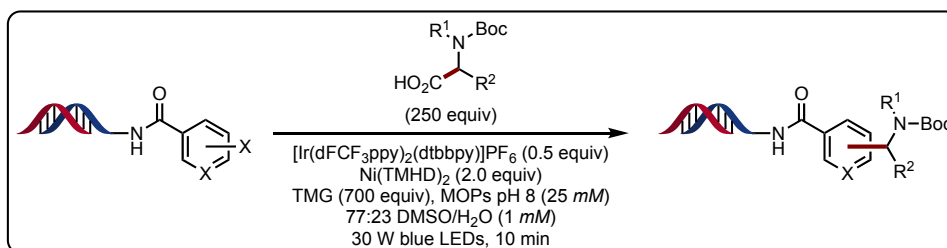
Figure S4. Upon completion, the reactions were removed from the light and analyzed.

C(sp³)-C(sp²) Cross-Coupling of on-DNA Aryl Halides

Cross-Coupling Employing 4-Alkyl-1,4-dihydropyridines



General Procedure. To a PCR Eppendorf tube was added 4-alkyl-1,4-dihydropyridine (10 μ L of a 625 nmol/ μ L solution in DMSO, 6.25 μ mol, 250 equiv), 4CzIPN (5 μ L of a 2.5 nmol/ μ L solution in DMSO, 12.5 nmol, 0.50 equiv), Ni(TMHD)₂ (5 μ L of a 10 nmol/ μ L solution in DMSO, 50 nmol, 2.0 equiv), and aryl halide (5 μ L of a 5 nmol/ μ L solution in deionized H₂O, 25 nmol, 1.0 equiv). The tube was then capped and vortexed to give a homogeneous solution and placed 1.5 inches away from a 40 W tuna blue LED lamp and irradiated for 45 min. Upon completion, the reaction was removed from the light and analyzed by LC/MS.



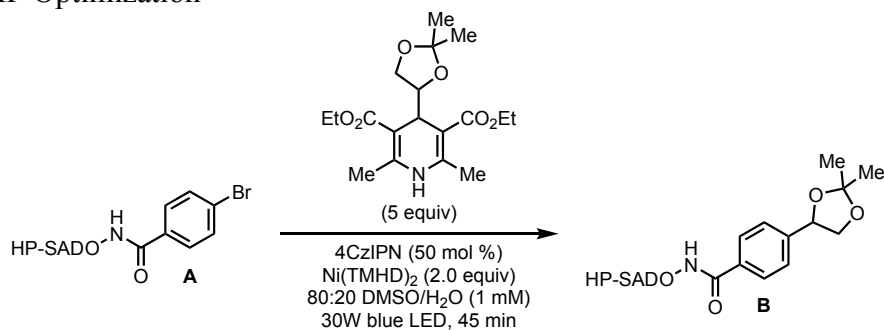
Cross-Coupling Employing Amino Acids

General Procedure. To a PCR Eppendorf tube was added amino acid (10 μ L of a 625 nmol/ μ L solution in DMSO, 6.25 μ mol, 250 equiv), [Ir(dFCF₃ppy)₂(dtbbpy)]PF₆ (5 μ L of a 2.5 nmol/ μ L solution in DMSO, 12.5 nmol, 0.50 equiv), Ni(TMHD)₂ (5 μ L of a 10 nmol/ μ L solution in DMSO, 50 nmol, 2.0 equiv), aryl halide (5 μ L of a 5 nmol/ μ L solution in deionized H₂O, 25 nmol, 1.0 equiv), MOPs pH 8 buffer (1 μ L of a 500 mM solution), and TMG (2.35 μ L, 175 nmol, 700 equiv). The tube was then capped and vortexed to give a homogeneous solution and placed 1.5 inches

away from a 40 W tuna blue LED lamp and irradiated for 10 mins. Upon completion, the reaction was removed from the light and analyzed by LC/MS.

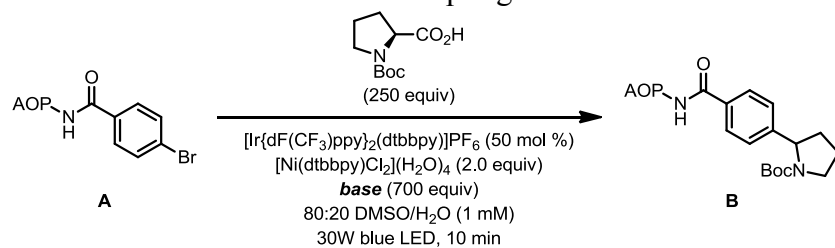
C(sp³)-C(sp²) Cross-Coupling Optimization

Table S1. DHP Optimization

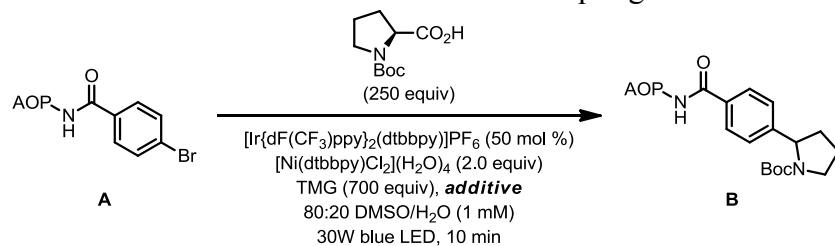


Entry	Deviation from Standard Conditions	TIC Conversion to B ^a
1	none	63%
2	[Ir{dF(CF ₃)ppy} ₂ (dtbbpy)]PF ₆	0%
3	[Ni(Phen)Cl ₂](H ₂ O) ₄	10%
4	[Ni(BPhen)Cl ₂](H ₂ O) ₄	5%
5	[Ni(dtbbpy)Cl ₂](H ₂ O) ₄	0%
6	[Ni(dMeObpy)Cl ₂](H ₂ O) ₄	0%
7	[Ni(bpy)Cl ₂](H ₂ O) ₄	0%
8	100 mM pH 8 TRIS buffer	6%
9	100 mM pH 8 MOPS buffer	4%
10	100 mM pH 8.5 MOPS buffer	13%
11	100 mM pH 8 HEPES buffer	23%
12	No Ni(TMHD) ₂	0%
13	No 4CzIPN	0%
14	No light	0%

^aDetermined by comparing intensity of all DNA-containing components in the TIC trace

Table S2. Impact of base on amino acid cross-coupling

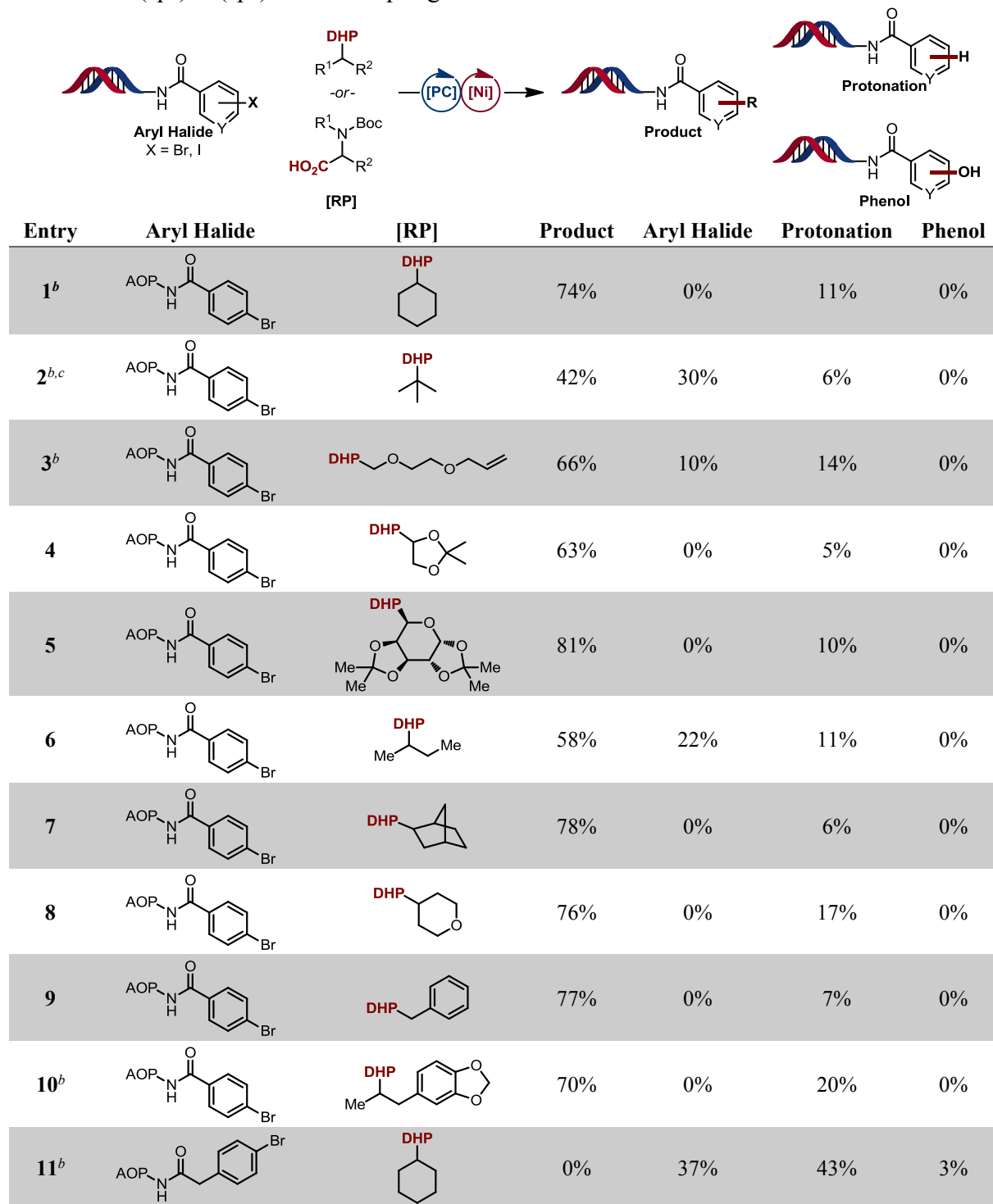
Entry	Base	Relative Conversion to B
1	Cs ₂ CO ₃	0.73
2	TMG	1.0
3	2,6-Lutidine	0.58
4	ⁱ Pr ₂ NH	0.65
5	Hunig's Base	0
6	DBU	0.23

Table S3. Impact of buffer additive on amino acid cross-coupling

Entry	Base	Relative Conversion to B
1	CAPSO, pH 9.4	0.93
2	TRIS, pH 8	0.60
3	TRIS, pH 8.4	0.47
4	TRIS, pH 8.8	0.63
5	TRIS, pH 9	0
6	TES, pH 8	0.90
7	MOPS, pH 8	1.0
8	MOPS, pH 8.5	0.80
9	HEPES, pH 7.5	0.70
10	HEPES, pH 9	0.57
11	Na Borate, pH 9	0.87
12	Na Phosphate, pH 7	0.63
13	Maleate, pH 6	0.77
14	MgCl ₂	0
15	MgBr ₂	0

Cross-Coupling Scope

Table S4. C(sp³)–C(sp²) Cross-Coupling Products^a



12^{b,c}			0%	89%	5%	0%
13^b			6%	86%	8%	0%
14^b			9%	73%	5%	0%
15^b			16%	53%	27%	0%
16^b			67%	0%	28%	0%
17^{b,c}			24%	13%	57%	3%
18^b			58%	0%	35%	0%
19^b			69%	0%	10%	0%
20^b			46%	0%	54%	0%
21^b			79%	0%	13%	0%
22^{b,c}			46%	0%	30%	10%
23^b			62%	0%	14%	5%
24^b			66%	0%	90%	0%
25^b			71%	0%	17%	12%
26^b			55%	0%	35%	0%
27^{b,c}			21%	18%	46%	0%

44 ^b			75%	0%	21%	0%
45 ^b			20%	0%	60%	0%
46 ^b			43%	0%	46%	5%
47 ^b			5%	0%	62%	7%
48 ^b			5%	0%	54%	5%
49 ^b			5%	13%	82%	5%
50 ^b			65%	9%	18%	0%
51 ^b			51%	4%	30%	0%
52 ^b			72%	4%	19%	0%
53 ^b			15%	69%	16%	0%
54 ^b			0%	0%	94%	6%
55 ^b			8%	12%	73%	7%
56 ^b			0%	0%	54%	3%
57 ^b			0%	0%	57%	0%

58 ^b			26%	11%	45%	5%
59 ^d			45%	2%	0%	31%
60 ^d			37%	46%	7%	0%
61 ^d			5%	90%	0%	0%
62 ^d			12%	63%	0%	0%
63 ^d			29%	47%	3%	0%
64 ^d			17%	78%	5%	0%
65 ^d			5%	88%	7%	0%
66 ^d			6%	88%	6%	0%
67 ^d			0%	100%	0%	0%
68 ^d			8%	81%	6%	0%
69 ^d			51%	0%	18%	7%
70 ^d			18%	0%	53%	6%
71 ^d			17%	0%	20%	4%
72 ^d			33%	5%	30%	4%
73 ^d			19%	0%	22%	9%

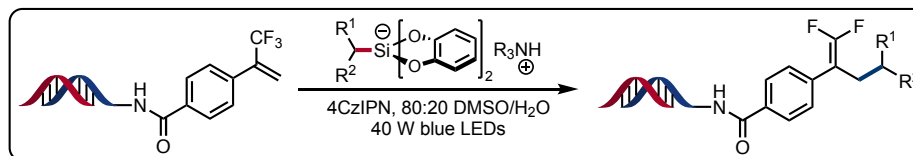
74 ^d			17%	0%	48%	12%
75 ^d			6%	0%	58%	14%
76 ^d			16%	0%	45%	19%
77 ^d			46%	0%	17%	9%
78 ^d			8%	0%	44%	11%
79 ^d			67%	6%	23%	0%
80 ^d			42%	5%	26%	5%
81 ^d			35%	15%	35%	2%
82 ^d			40%	17%	32%	2%
83 ^d			20%	21%	24%	6%
84 ^d			42%	0%	48%	0%
85 ^d			56%	0%	17%	4%
86 ^d			65%	0%	20%	4%
87 ^d			51%	3%	17%	4%
88 ^d			38%	0%	29%	4%
89 ^d			51%	0%	16%	3%
90 ^d			53%	0%	17%	0%

91^d			0%	0%	0%	0%
92^d			0%	0%	62%	4%
93^d			0%	59%	5%	5%
94^d			0%	0%	67%	5%
95^d			0%	3%	53%	0%
96^d			0%	0%	0%	0%

^aAll values indicate conversion to the indicated product as determined by LC/MS. ^bReaction conditions: DHP (250 equiv, 6.25 μ mol), **4CzIPN** (50 mol %, 12.5 nmol), Ni(TMHD)₂ (2.0 equiv, 50 nmol), aryl halide (25 nmol, 1.0 equiv), 80:20 DMSO/H₂O (1 mM), 45 min, irradiating with blue LED (30 W). ^cUsing 4-(*tert*-butyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile. ^dReaction conditions: amino acid (250 equiv, 6.25 μ mol), **Ir-1** (50 mol %, 12.5 nmol), Ni(TMHD)₂ (2.0 equiv, 50 nmol), aryl halide (25 nmol, 1.0 equiv), TMG (700 equiv, 17.5 μ mol), MOPS pH 8 buffer (25 mM), 77:23 DMSO/H₂O (1 mM), 10 min, irradiating with blue LED (30 W). TMG = 1,1,3,3-tetramethylguanidine. MOPS = 3-(*N*-morpholino)propanesulfonic acid. See Supporting Information for additional details.

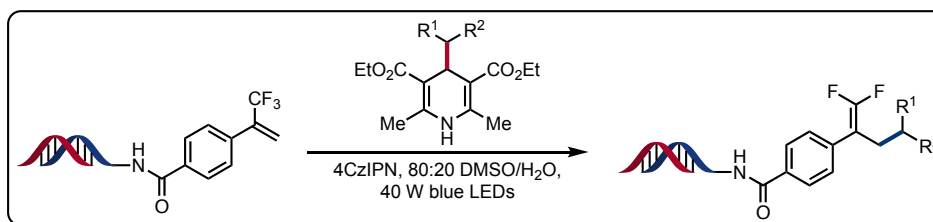
Defluorinative Alkylation of on-DNA Trifluoromethyl Alkenes

Alkylation Employing Alkyl Bis(catecholato)silicates



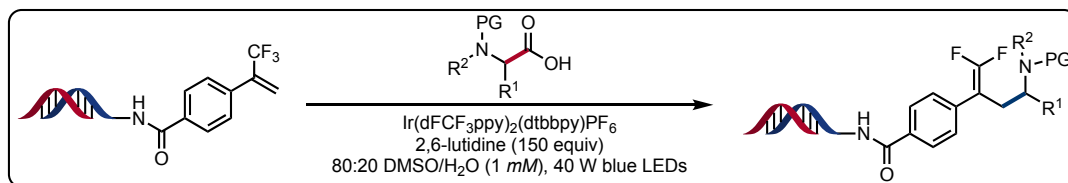
General Procedure. To a PCR Eppendorf tube was added alkyl bis(catecholato)silicate (15 μL of a 83.3 nmol/ μL solution in DMSO, 1.25 μmol , 50 equiv), 4CzIPN (5 μL of a 2.5 nmol/ μL solution in DMSO, 12.5 nmol, 0.50 equiv), and trifluoromethyl alkene (5 μL of a 5 nmol/ μL solution in deionized H_2O , 25 nmol, 1.0 equiv). The tube was then capped and vortexed to give a homogeneous solution and placed 1.5 inches away from a 40 W tuna blue LED lamp and irradiated for 10 min. Upon completion, the reaction was removed from the light and analyzed by LC/MS.

Alkylation Employing 1,4-Dihydropyridines



General Procedure. To a PCR Eppendorf tube was added 4-alkyl-1,4-dihydropyridine (15 μL of a 20.8 nmol/ μL solution in DMSO, 312.5 nmol, 12.5 equiv), 4CzIPN (5 μL of a 2.5 nmol/ μL solution in DMSO, 12.5 nmol, 0.50 equiv), and trifluoromethyl alkene (5 μL of a 5 nmol/ μL solution in deionized H_2O , 25 nmol, 1.0 equiv). The tube was then capped and vortexed to give a homogeneous solution and placed 1.5 inches away from a 40 W tuna blue LED lamp and irradiated for 10 min. Upon completion, the reaction was removed from the light and analyzed by LC/MS.

Alkylation Employing Amino Acids



General Procedure (5 mol % [Ir], 5 equiv acid). To a PCR Eppendorf tube was added DMSO (9 μL), amino acid (1 μL of a 125 nmol/ μL solution in DMSO, 125 μmol , 5 equiv), $[\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (5 μL of a 0.25 nmol/ μL solution in DMSO, 1.25 nmol, 5 mol %), trifluoromethyl alkene (5 μL of a 5 nmol/ μL solution in deionized H₂O, 25 nmol, 1.0 equiv), and 2,6-lutidine (5 μL of a 750 nmol/ μL solution in DMSO, 3.75 μmol , 150 equiv). The tube was then capped and vortexed to give a homogeneous solution and placed 1.5 inches away from a 40 W tuna blue LED lamp and irradiated for 10 min. Upon completion, the reaction was removed from the light and analyzed by LC/MS.

General Procedure (10 mol % [Ir], 25 equiv acid). To a PCR Eppendorf tube was added DMSO (5 μL), amino acid (5 μL of a 125 nmol/ μL solution in DMSO, 625 μmol , 25 equiv), $[\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (5 μL of a 0.5 nmol/ μL solution in DMSO, 2.5 nmol, 10 mol %), trifluoromethyl alkene (5 μL of a 5 nmol/ μL solution in deionized H₂O, 25 nmol, 1.0 equiv), and 2,6-lutidine (5 μL of a 750 nmol/ μL solution in DMSO, 3.75 μmol , 150 equiv). The tube was then capped and vortexed to give a homogeneous solution and placed 1.5 inches away from a 40 W tuna blue LED lamp and irradiated for 10 min. Upon completion, the reaction was removed from the light and analyzed by LC/MS.

General Procedure (25 mol % [Ir], 50 equiv acid). To a PCR Eppendorf tube was added amino acid (5 μL of a 250 nmol/ μL solution in DMSO, 1250 μmol , 50 equiv), $[\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (5 μL of a 1.25 nmol/ μL solution in DMSO, 6.25 nmol, 25 mol %), trifluoromethyl alkene (5 μL of a 5 nmol/ μL solution in deionized H₂O, 25 nmol, 1.0 equiv), and 2,6-lutidine (5 μL of a 750 nmol/ μL solution in DMSO, 3.75 μmol , 150 equiv). The tube was then capped and vortexed to give a homogeneous solution and placed 1.5 inches away from a 40 W tuna blue LED lamp and irradiated for 10 min. Upon completion, the reaction was removed from the light and analyzed by LC/MS.

Table S5. Impact of *tert*-butyl-radical precursor loading on reaction outcome.

Entry	Ar	Equiv C	TIC Conversion to B ^a
1	D	12.5	48%
2	D	10	58%
3	D	5	72%
4	E	12.5	38%
5	E	10	49%
6	E	5	58%
7	F	12.5	44%
8	F	10	53%
9	F	5	61%

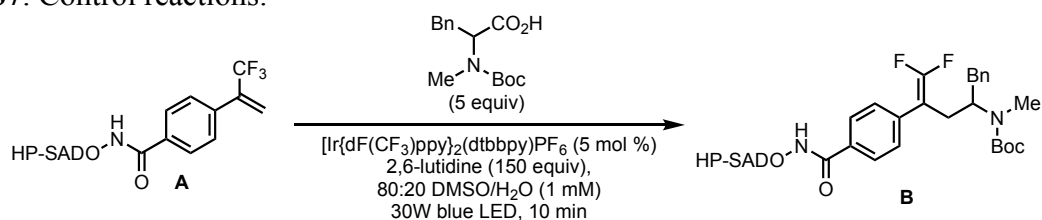
^aDetermined by comparing intensity of all DNA-containing components in the TIC trace

Ar:

Table S6. Impact of base on amino acid alkylation.

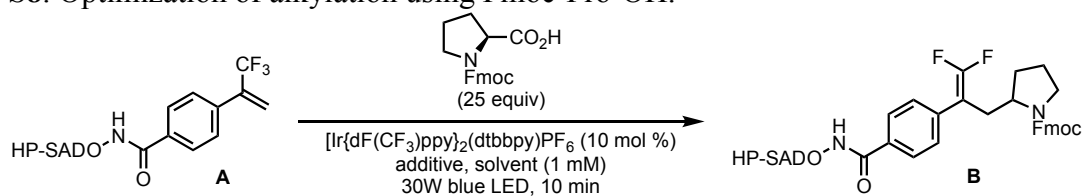
Entry	Base	Result ^a
1	TMG (150 equiv)	decomposition
2	2,6-lutidine (150 equiv)	full conversion to B, <10% C
3	150 mM pH 7 Na Phosphate buffer	full conversion to B, >10% C

^aDetermined by comparing intensity of all DNA-containing components in the TIC trace

Table S7. Control reactions.

Entry	Deviation from Standard Conditions	TIC Conversion to B ^a
1	none	82%
2	Minus Photocatalyst	0%
3	Minus Base	26%
4	Minus Light	0%

^aDetermined by comparing intensity of all DNA-containing components in the TIC trace

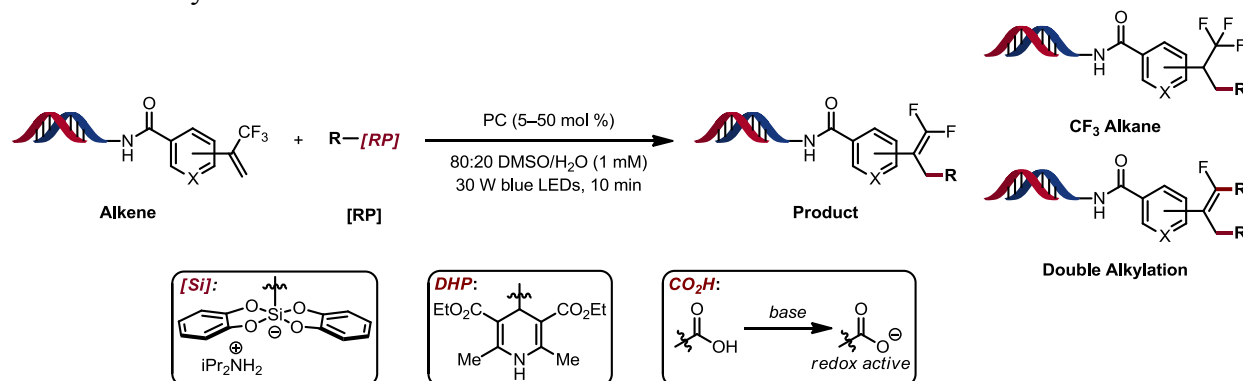
Table S8. Optimization of alkylation using Fmoc-Pro-OH.

Entry	Additive	Solvent	ratio A : B ^a	TIC conversion ^b
1	2,6-lutidine (150 equiv)	80:20 DMSO/H ₂ O	0 : 100	32%
2	100 mM TRIS pH 8	60:40 DMSO/H ₂ O	0 : 100	67%
3	100 mM TRIS pH 9	60:40 DMSO/H ₂ O	0 : 100	—
4	100 mM Na borate pH 9	60:40 DMSO/H ₂ O	0 : 100	—
5	100 mM Maleate pH 6	60:40 DMSO/H ₂ O	70 : 30	—
6	100 mM HEPES pH 9	60:40 DMSO/H ₂ O	80 : 20	—

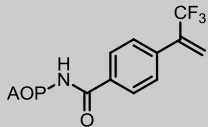
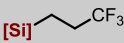
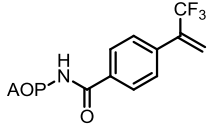
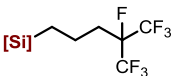
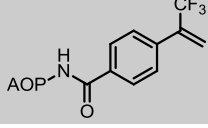
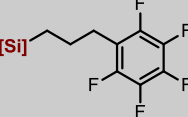
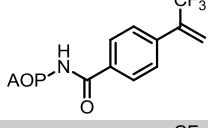
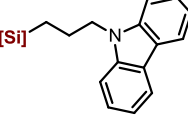
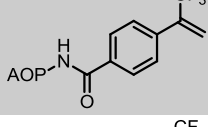
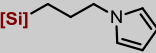
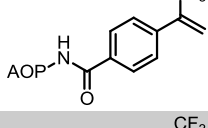
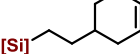
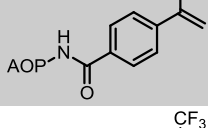
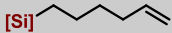
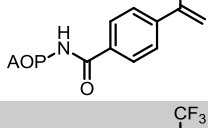
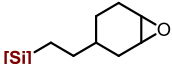
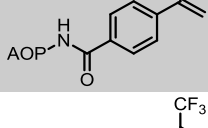
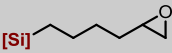
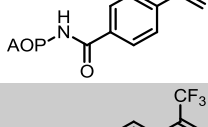
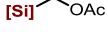
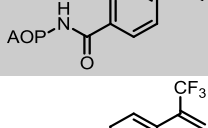
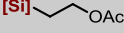
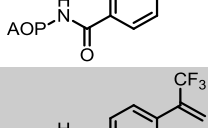
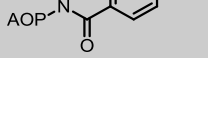
^aDetermined by comparing relative ratio of starting material **A** to product **B**. ^bDetermined by comparing intensity of all DNA-containing components in the TIC trace

Defluorinative Alkylation Substrate Scope

Table S9. Alkylation Products^a



Entry	ELT_DNA	[RP]	Product	Alkene	Double Alkylation	CF ₃ Alkane
1 ^b			68%	13%	0%	8%
2 ^b			58%	24%	0%	6%
3 ^b			64%	16%	0%	7%
4 ^b			81%	8%	0%	6%
5 ^b			76%	4%	0%	7%
6 ^b			73%	6%	7%	5%
7 ^b			43%	0%	0%	13%
8 ^b			75%	4%	0%	5%

9^b			60%	18%	0%	6%
10^b			80%	0%	0%	8%
11^b			73%	0%	0%	8%
12^b			61%	11%	0%	10%
13^b			64%	19%	1%	1%
14^b			82%	6%	0%	8%
15^b			79%	0%	0%	10%
16^b			71%	0%	5%	9%
17^b			56%	8%	5%	7%
18^b			32%	0%	0%	11%
19^b			61%	21%	11%	8%
20^b			74%	5%	0%	9%
21^b			65%	15%	0%	5%

22^b			45%	42%	0%	10%
23^b			59%	23%	2%	3%
24^b			65%	13%	10%	11%
25^b			72%	4%	9%	14%
26^b			64%	19%	1%	2%
27^b			51%	24%	5%	5%
28^b			48%	14%	0%	5%
29^b			70%	4%	0%	9%
30^b			70%	5%	0%	6%
31^b			42%	23%	3%	7%
32^b			72%	4%	0%	8%
33^b			77%	7%	0%	6%
34^b			37%	35%	2%	6%

35 ^c			77%	0%	0%	0%
36 ^c			63%	0%	9%	0%
37 ^c			51%	7%	10%	0%
38 ^c			44%	9%	0%	0%
39 ^{c,e}			72%	0%	7%	0%
40 ^{c,d}			64%	0%	0%	0%
41 ^c			62%	0%	10%	0%
42 ^c			68%	0%	7%	0%
43 ^c			74%	0%	0%	0%
44 ^c			62%	0%	0%	0%
45 ^c			61%	0%	9%	0%
46 ^c			33%	0%	0%	0%
47 ^{c,e}			58%	0%	6%	5%

48 ^{c,d}			44%	0%	0%	0%
49 ^c			42%	0%	7%	0%
50 ^c			41%	0%	6%	0%
51 ^c			86%	0%	0%	0%
52 ^c			77%	0%	0%	0%
53 ^c			61%	0%	10%	0%
54 ^c			58%	0%	0%	0%
55 ^{c,e}			61%	0%	7%	0%
56 ^{c,d}			76%	0%	0%	0%
57 ^c			44%	0%	6%	0%
58 ^c			35%	12%	4%	0%
59 ^{f,g}			75%	4%	0%	0%
60 ^{f,i}			70%	0%	0%	0%
61 ^f			46%	0%	0%	0%

62 ⁱ			62%	0%	13%	0%
63 ⁱ			59%	0%	6%	4%
64 ^f			82%	0%	0%	0%
65 ^f			65%	0%	0%	0%
66 ^j			74%	0%	0%	0%
67 ^j			66%	0%	17%	0%
68 ^j			67%	0%	20%	0%
69 ^f			84%	0%	0%	0%
70 ^f			65%	0%	11%	0%
71 ^j			84%	0%	0%	0%
72 ^k			45%	0%	0%	0%
73 ^l			64%	0%	12%	0%
74 ^m			47%	9%	0%	0%

75 ^l			66%	0%	5%	0%
76 ^k			50%	0%	6%	0%
77 ^h			67%	0%	0%	7%
78 ^h			50%	0%	6%	0%
79 ^h			65%	0%	8%	0%
80 ^h			65%	0%	8%	0%
81 ^h			50%	0%	6%	0%
82 ^h			69%	0%	13%	0%
83 ^h			70%	0%	13%	0%
84 ^j			48%	16%	13%	0%
85 ^j			64%	0%	6%	5%
86 ^j			57%	0%	13%	0%
87 ^j			61%	4%	5%	0%

88 ^j			45%	0%	30%	0%
89 ^j			38%	0%	31%	0%
90 ^j			61%	0%	7%	6%
91 ^j			69%	12%	5%	6%
92 ^j			48%	24%	9%	0%
93 ^j			55%	0%	29%	0%
94 ^j			84%	0%	0%	0%

^aAll values represent conversion to the indicated product as determined by LC/MS. All reactions were run using alkene (1.0 equiv, 25 nmol), 80:20 DMSO/H₂O (1 mM), 10 min, irradiating with blue LED (30 W). See Supporting Information for additional details. ^bSilicate (50 equiv, 1.25 μmol), 4CzIPN (50 mol %, 12.5 nmol). ^cDHP (12.5 equiv, 312.5 nmol), 4CzIPN (50 mol %, 12.5 nmol). ^dUsing 25 equiv of DHP. ^eUsing 4-(*tert*-butyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile. ^fAcid (5 equiv, 125 nmol), [Ir(dFCF₃ppy)₂dtbbpy]PF₆ (5 mol %, 1.25 nmol), 2,6-[Ir(dFCF₃ppy)₂dtbbpy]PF₆/lutidine (150 equiv, 3.75 μmol). ^gUsing 2.5 mol % [Ir(dFCF₃ppy)₂dtbbpy]PF₆. ^hAcid (25 equiv, 625 nmol), I (10 mol %, 12.5 nmol), pH 9 TRIS buffer (100 mM), 60:40 DMSO/H₂O (1 mM). ⁱUsing 10 equiv of acid. ^jAcid (25 equiv, 625 nmol), [Ir(dFCF₃ppy)₂dtbbpy]PF₆ (10 mol %, 12.5 nmol), 2,6-lutidine (150 equiv, 3.75 μmol). ^kAcid (50 equiv, 1.25 μmol), [Ir(dFCF₃ppy)₂dtbbpy]PF₆ (25 mol %, 6.25 nmol), 2,6-lutidine (150 equiv, 3.75 μmol). ^lUsing 25 equiv of acid, 10 mol % [Ir(dFCF₃ppy)₂dtbbpy]PF₆. ^mUsing 50 equiv of acid, 50 mol % [Ir(dFCF₃ppy)₂dtbbpy]PF₆.

qPCR, PCR, and Sequencing

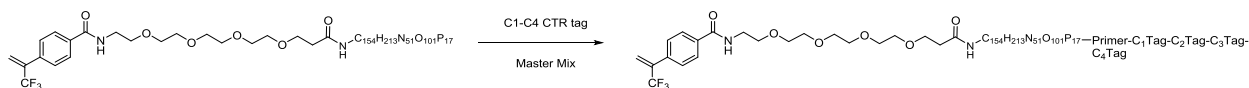


Figure S5: C1-C4 Tag Elongation

Top Strand: 5'-/5Phos/A AAT CGA TGT GTT CCG CAA GAA GCC TGG TAA GCG GAG AAA GGT CGT T -3'

Bottom Strand: 5'-/5Phos/C GAC CTT TCT CCG CTT ACC AGG CTT CTT GCG GAA CAC ATC GAT TTG G -3'

The top and bottom strands (purchased from IDT as lyophilized powders) of a control 4-cycle tag were annealed by combining 330 nmol of each strand (2 mM in H₂O), heating to 95 °C for 5 min, then cooling to rt. The annealed tag solution (1.1 equiv) was then added to the CF₃-alkene headpiece (1 equiv, 300 nmol, 600 µL H₂O, 0.5 mM), followed by a master mix solution (1.95 mL H₂O, 60 µL 10x T4 ligation buffer, and 6 µL T4 DNA ligase purchased from Syngene). The ligation solution was vortexed and let sit for 15 min, at which point a primer tag was added to the solution (1.05 equiv, 315 nmol, 414 µL, 0.76 mM). The reaction was again capped, vortexed, and left at rt overnight. Following addition of 300 µL of 5 M NaCl (aq) and 10 mL of cold EtOH, the reaction was precipitated at -80 °C over 4 d. The precipitated solution was then centrifuged at 3400 rpm at 4 °C for 45 min, and the solvent was decanted to afford the DNA pellet. The crude pellet was resuspended in 0.6 mL of H₂O and purified by HPLC (Column: Gemini C18, 5 µm particle size, 21.2 x 100 mm; Gradient: 5 to 90% B in 30 min, 20 mL/min; UV at 260 nm; Solvent A: 50 mM TEAA, pH 7.5; Solvent B: 1% H₂O in MeCN) to afford the desired product. The lyophilized product was analyzed by optical density using a composite extinction coefficient of 1023700 L/(mol-cm) to determine isolated yield (97.7 nmol, 32.6%). **LCMS** calcd: 34455, found: 34453.8.

Compound Spectrum Report

Analysis Info

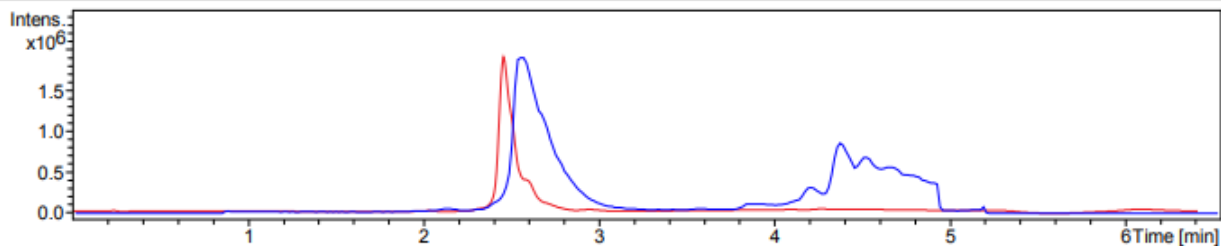
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Comment

Acquisition Date 6/13/2018 2:46:11 PM

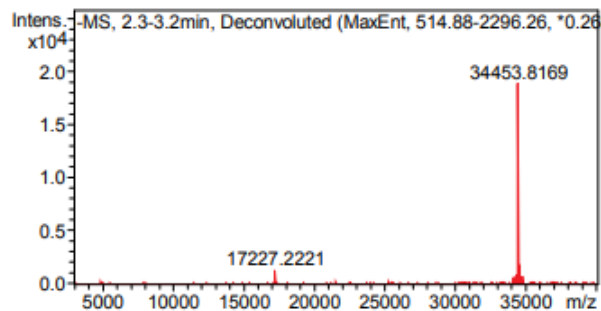
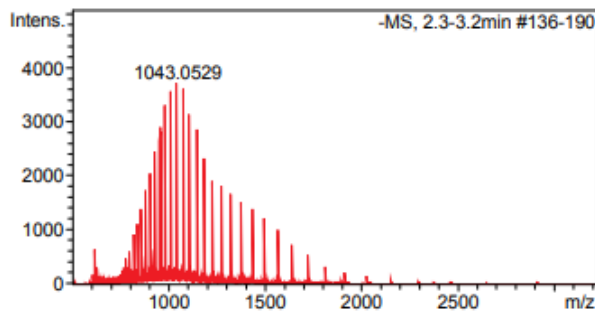
Operator gsk
Instrument micrOTOF 213750.00199

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.7 Bar
Focus	Not active			Set Dry Heater	225 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.3-3.2min #136-190



Reactions on Elongated CF₃-alkene HP:

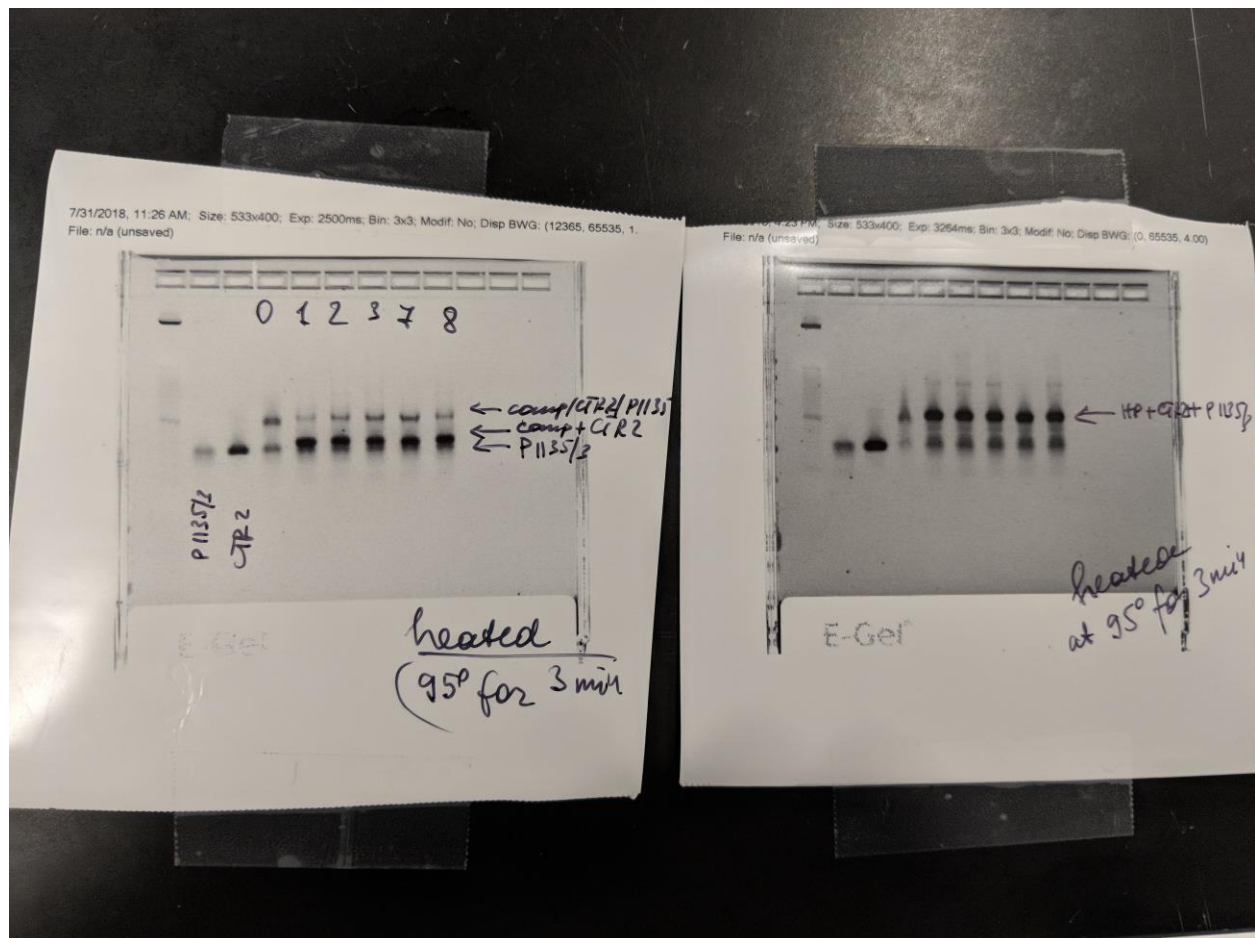
General Protocol - Closing Primer Ligation on Reacted Material:

Top Strand: 5'-/5Phos/ACG ATG CCC GGT CTA CNN NNN NNN NNN NCT GAT GGC
GCG AGG GAG GC-3'

Bottom Strand: 5'-GTA GAC CGG GCA TCG TAA-3'

The lyophilized product from the exemplary reaction on elongated CF₃-alkene headpiece was diluted with 200 μ L milliQ H₂O. The concentration of the stock solution was measured using optical density as determined on a Thermo NanoDrop 2000. Three measurements were obtained, and the average A₂₆₀ used to determine concentration. The samples were lyophilized and then

redissolved to ~ 0.5 mM in H_2O . To this solution was then added annealed closing primer (1.05 equiv, 1 mM in H_2O , purchased as dry powders from IDT then annealed), followed by enough mastermix to dilute reactions to 0.1 mM relative to starting DNA. The reaction was capped, vortexed, centrifuged and left to react overnight at rt for 2 d. 2 equiv of additional closing primer, buffer, and ligase were added, the reaction left at rt overnight, and then transferred to $4^\circ C$ for 4 d. At this point, it was determined that the ligase was not behaving as expected (in comparison to a no-chemistry, no-headpiece CTR tag), so fresh ligase from a separate tube was added (6 equiv), followed by additional ligation buffer (6 equiv), and enough H_2O to achieve a final concentration of ~ 0.05 mM. Ligations were allowed to run overnight. Samples were analyzed by gel electrophoresis and determined to have gone to sufficient completion.



General Protocol – qPCR:

5' 565 Cla Primer: 5'-TGA CTC CCA AAT CGA TGT G -3'

3' 454 Short Primer: 5'-GCC TCC CTC GCG CCA -3'

Quantitative PCR was performed on a Roche LightCycler 480 II PCR system with SYBR Green I as the detection dye. A bulk master mix solution was prepared by combining 1 mL SYBR green, 60 µL of 10 µM PCR primer 565 Cla, 60 µL of 10 µM PCR primer 454 short, and 680 uL of H₂O. To 2 µL of sample was then added 18 µL of master mix. Samples were subjected to qPCR:

Stage	Temperature/Time	Number of Cycles
UNG	50 °C / 2 min	1
HotStart	95 °C / 5 min	1
Amplification	95 °C / 15 sec 55 °C / 30 sec 72 °C / 30 sec	40
Melt	95 °C / 1 sec 70 °C / 1 sec	1
Cool	45 °C / 30 sec	

Samples were then analyzed using the 2nd derivative maximum standard protocol on the instrument.

General Protocol – PCR Amplification:

Samples were subjected to 14 cycles of PCR amplification using the Roche FastStart Taq Polymerase dNTPack and Illumina P5 and P7 primer. The standard Taq-PCRamp program is as follows:

1. 95 °C for 10min
2. 95 °C for 30sec
3. 59 °C for 30sec
4. 72 °C for 30sec
5. Repeat STEP 2-4, 13 times
6. 72 °C for 7 min
7. 4 °C hold
8. End

After PCR, samples were purified using Beckman Coulter AMPure beads, then quantified on an Agilent Bioanalyzer following the standard manufacturer's protocol.

Chemistry ID	Amp cycles	[bioanalyzer] (nM)
--------------	------------	--------------------

Sample A	14	29.5
Sample B	14	14.6
Sample C	14	15.8
Sample E	14	17.7
Sample D	14	43.8

General Protocol – Illumina Sequencing:

Approximately 1E8 molecules were prepared for sequencing following the manufacturer's standard protocol with an Illumina MiSeq v3 kit, then submitted for sequencing on an Illumina MiSeq. Samples were subjected to 111 cycles for Read 1 and 9 cycles for index runs. % sequences without mutations was determined based on a comparison of the desired sequence against the top 19 other sequences identified.

Table S10.

%	Chemistry ID	Rank	Count	Sequence
92.6%	Sample A	1	3943911	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAACACATC GATTGTTGGGAGT
1.5%	Sample A	2	65783	TAGACCGGGCATCGTAACGACCTTTCTCC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.8%	Sample A	3	34529	GTAGACCGGGCATCGTAACGACCTTTCTC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.6%	Sample A	4	26282	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.6%	Sample A	5	24875	GTAGACCGGGCATCGTAACGACCTTTCCC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.6%	Sample A	6	23570	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.4%	Sample A	7	16491	GTAGACCGGGCATCGTAACGACCTTTCTC CGTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.4%	Sample A	8	15736	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGCTTCTTGCGGAACACATCG ATTTGGGAGT

0.4%	Sample A	9	15280	GTAGACCGGGCATCGTAACGACCTTTCTC CCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.3%	Sample A	10	12030	GTAGACCGGGCATCGTAACGACCTTCTCC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.2%	Sample A	11	10091	GTAGACCGGGCATCGTAAGACCTTTCTCC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.2%	Sample A	12	9576	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTCCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.2%	Sample A	13	8700	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.2%	Sample A	14	8568	GTAGACCGGCATCGTAACGACCTTTCTCC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.2%	Sample A	15	8497	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAACAAATC GATTTGGGAG
0.2%	Sample A	16	8348	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAGCACATC GATTTGGGAG
0.2%	Sample A	17	7268	GTAGACCGGGCATCGTAACGACCCTTCTC CGCTTACCAGGCTTCTTGCGGAACACATC GATTTGGGAG
0.2%	Sample A	18	7140	GTAGGCCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAACACATC GATTTGGGAG
0.2%	Sample A	19	6961	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAACACATC GATTTGGGAG
0.2%	Sample A	20	6793	GTAGACCGGGCATCGTAACGACCTTTCTC CACTTACCAGGCTTCTTGCGGAACACATC GATTTGGGAG
92.3%	Sample B	1	3049417	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAACACATC GATTTGGGAG
1.5%	Sample B	2	49828	TAGACCGGGCATCGTAACGACCTTTCTCC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.8%	Sample B	3	26676	GTAGACCGGGCATCGTAACGACCTTTCTC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT

0.6%	Sample B	4	21002	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.6%	Sample B	5	19168	GTAGACCGGGCATCGTAACGACCTTTCCC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.6%	Sample B	6	18329	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.4%	Sample B	7	13049	GTAGACCGGGCATCGTAACGACCTTTCTC CGTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.4%	Sample B	8	12569	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.4%	Sample B	9	12261	GTAGACCGGGCATCGTAACGACCTTTCTC CCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.3%	Sample B	10	9738	GTAGACCGGGCATCGTAACGACCTTCTCC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.3%	Sample B	11	9639	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAACAAATC GATTTGGGAG
0.3%	Sample B	12	8623	GTAGACCGGGCATCGTAAGACCTTTCTCC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.2%	Sample B	13	7364	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTCCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
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0.2%	Sample B	15	6985	GTAGACCGGGCATCGTAACGACCTTTCTC CACTTACCAGGCTTCTTGCGGAACACATC GATTTGGGAG
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0.2%	Sample B	17	6778	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCGGCTTCTTGCGGAACACATCG ATTTGGGAGT
0.2%	Sample B	18	6352	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAGCACATC GATTTGGGAG

0.2%	Sample B	19	6177	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGAACACATC GATTGGGAG
0.2%	Sample B	20	6173	GTAGACCGGGCATCGTAACAACCTTTCTC CGCTTACCAGGCTTCTTGCGAACACATC GATTGGGAG
92.4%	Sample C	1	3605332	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGAACACATC GATTGGGAG
1.5%	Sample C	2	59419	TAGACCGGGCATCGTAACGACCTTTCTCC GCTTACCAGGCTTCTTGCGAACACATCG ATTTGGGAGT
0.8%	Sample C	3	31764	GTAGACCGGGCATCGTAACGACCTTTCTC GCTTACCAGGCTTCTTGCGAACACATCG ATTTGGGAGT
0.6%	Sample C	4	25003	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACAGGCTTCTTGCGAACACATCG ATTTGGGAGT
0.6%	Sample C	5	22514	GTAGACCGGGCATCGTAACGACCTTTCCC GCTTACCAGGCTTCTTGCGAACACATCG ATTTGGGAGT
0.6%	Sample C	6	22212	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTACCAGGCTTCTTGCGAACACATCG ATTTGGGAGT
0.4%	Sample C	7	15311	GTAGACCGGGCATCGTAACGACCTTTCTC CGTTACCAGGCTTCTTGCGAACACATCG ATTTGGGAGT
0.4%	Sample C	8	15047	GTAGACCGGGCATCGTAACGACCTTTCTC CCTTACCAGGCTTCTTGCGAACACATCG ATTTGGGAGT
0.4%	Sample C	9	14740	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGCTTCTTGCGAACACATCG ATTTGGGAGT
0.3%	Sample C	10	11231	GTAGACCGGGCATCGTAACGACCTTCTCC GCTTACCAGGCTTCTTGCGAACACATCG ATTTGGGAGT
0.3%	Sample C	11	10614	GTAGACCGGGCATCGTAAGACCTTTCTCC GCTTACCAGGCTTCTTGCGAACACATCG ATTTGGGAGT
0.3%	Sample C	12	10537	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGAACAAATC GATTGGGAG
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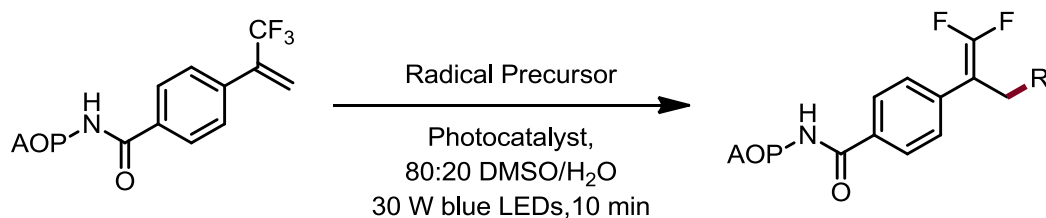
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0.1%	Sample C	19	5785	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTCCTTGCGGAACACATC GATTTGGGAG
0.1%	Sample C	20	5576	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCCTCTTGCGGAACACATC GATTTGGGAG
92.5%	Sample E	1	3657840	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAACACATC GATTTGGGAG
1.5%	Sample E	2	59666	TAGACCGGGCATCGTAACGACCTTTCTCC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
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92.4%	Sample D	1	4627752	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAACACATC GATTTGGGAG
1.5%	Sample D	2	76078	TAGACCGGGCATCGTAACGACCTTTCTCC GCTTACCAGGCTTCTTGCGGAACACATCG ATTTGGGAGT
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0.2%	Sample D	17	10084	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGAAACACATC GATTTGGGAG
0.2%	Sample D	18	9741	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGGCTTCTTGCGGAGCACATC GATTTGGGAG

0.2%	Sample D	19	9715	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAGACTTCTTGCGGAACACATC GATTTGGGAG
0.2%	Sample D	20	9586	GTAGACCGGGCATCGTAACGACCTTTCTC CGCTTACCAAGCTTCTTGCGGAACACATC GATTTGGGAG

Table S11. qPCR Results



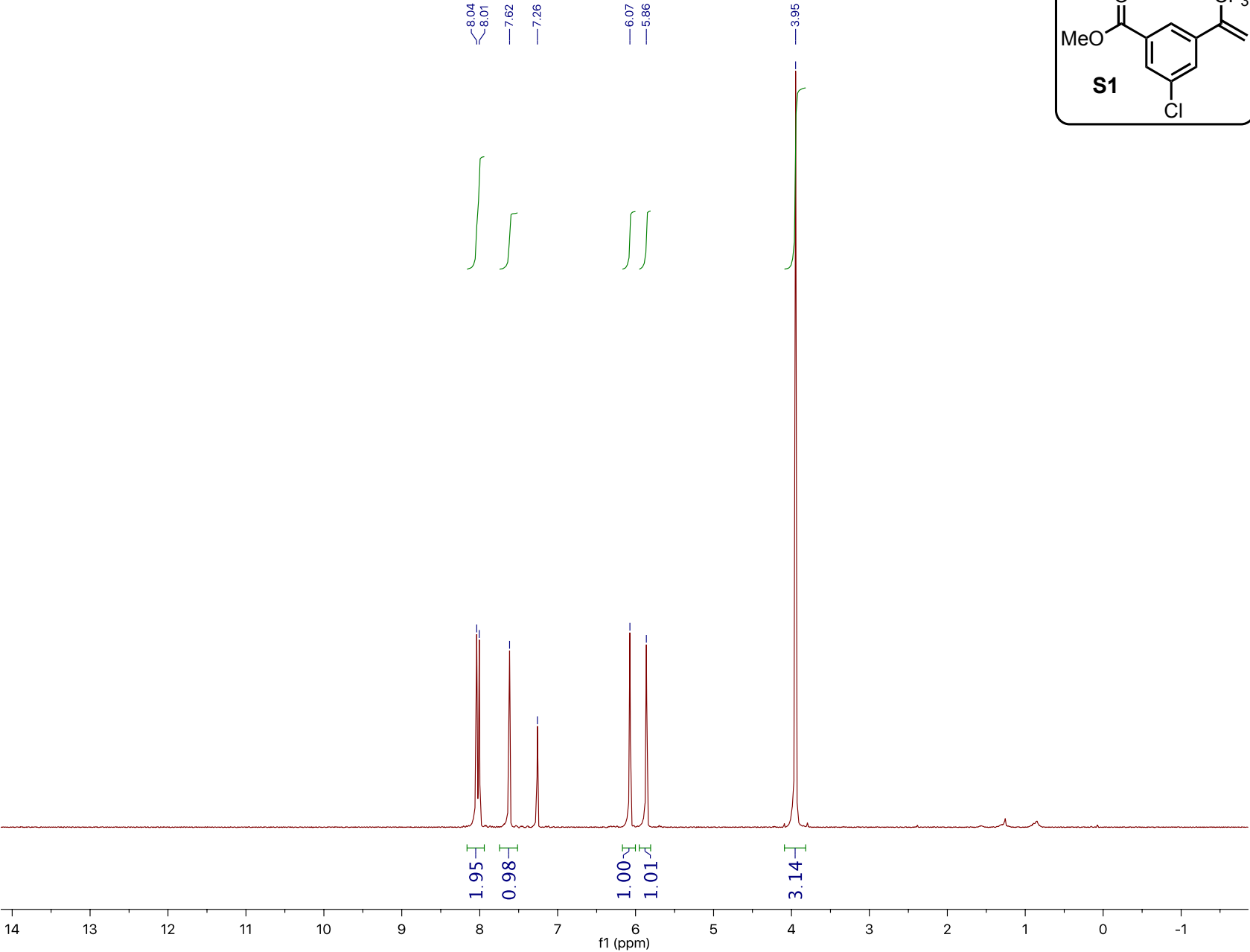
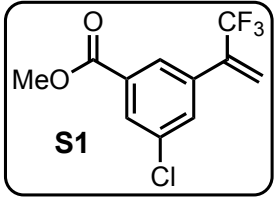
Sample	Radical Precursor	Photocatalyst	Mutated Sequences	Molecules per 1 μ l qPCR
A	 <i>[Si]</i>	4CzIPN	7.43%	6.10E+13
B	 <i>DHP</i>	4CzIPN	7.10%	4.42E+13
C	 <i>HO₂C</i>	[Ir{dF(CF ₃)ppy} ₂ dtbbpy]PF ₆	7.58%	5.23E+13
D	<i>none</i>	4CzIPN	7.61%	1.48E+14
E	<i>none</i>	<i>none</i>	7.47%	6.60E+13

References

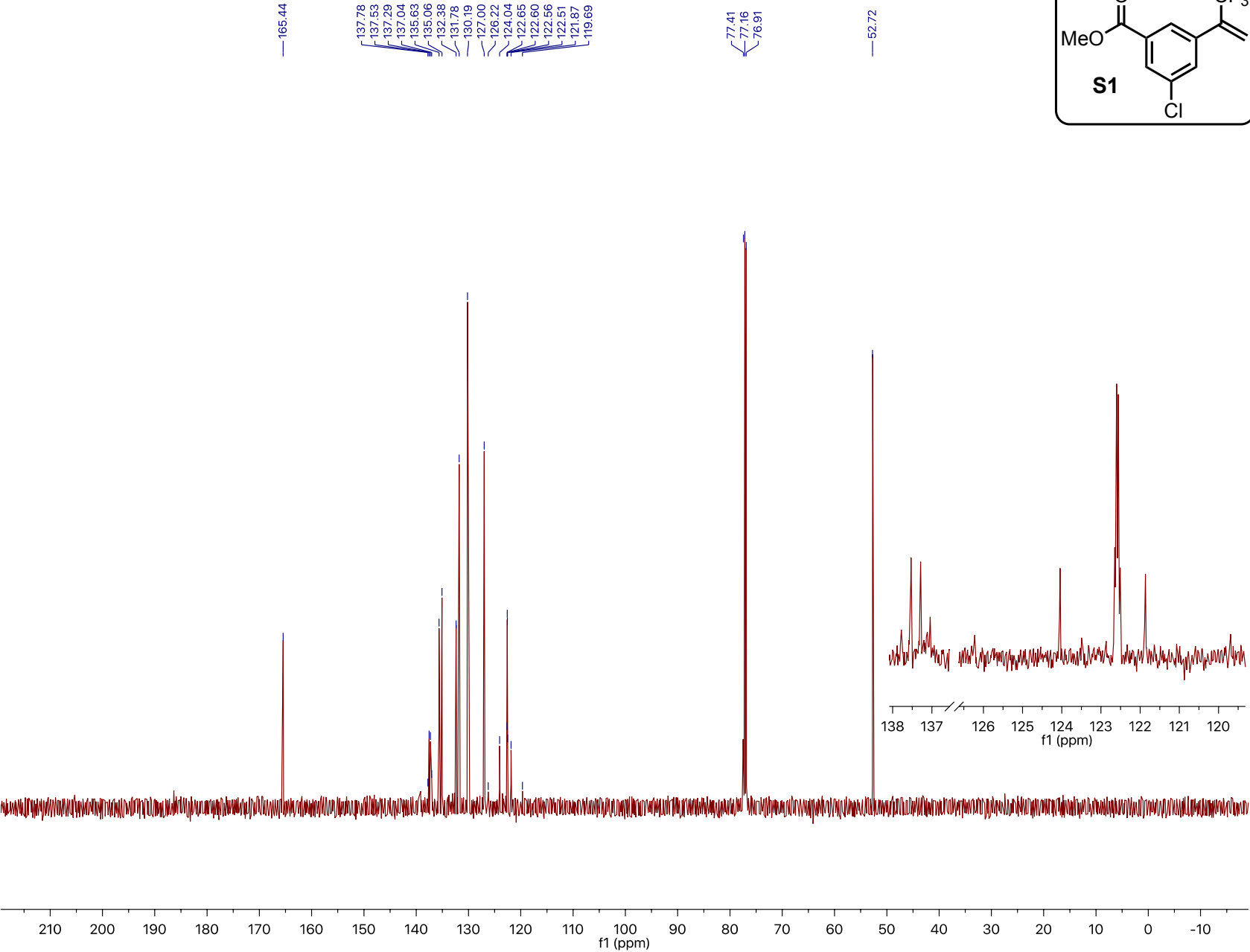
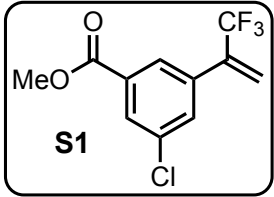
1. Ravikumar, I.; Saha, S.; Ghosh, P. *Chem. Commun.* **2011**, 47, 4721.
2. Seebach, D.; Imwinkelried, R.; Stucky, G. *Helv. Chim. Acta* **1987**, 70, 448.
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4. Patel, N. P.; Kelly, C. B.; Siegenfeld, A. P.; Molander, G. A. *ACS Catal.* **2017**, 7, 1766.
5. Lang, S. B.; Wiles, R. J.; Kelly, C. B.; Molander, G. A. *Angew. Chem., Int. Ed.* **2017**, 56, 15073.
6. Phelan, J. P.; Lang, S. B.; Compton, J. S.; Kelly, C. B.; Dykstra, R.; Gutierrez, O.; Molander, G. A. *J. Am. Chem. Soc.* **2018**, 140, 8037.
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8. (a) Dumoulin, A.; Matsui, J. K.; Gutiérrez-Bonet, Á.; Molander, G. A. *Angew. Chem., Int. Ed.* **2018**, 57, 6614; (b) Gutiérrez-Bonet, Á.; Tellis, J. C.; Matsui, J. K.; Vara, B. A.; Molander, G. A. *ACS Catal.* **2016**, 6, 8004.
9. (a) Verrieer, C.; Alandin, N.; Pezzetta, C.; Moliterno, M.; Buzzetti, L.; Hepburn, H. B.; Vega-Peñaloza, A.; Silvi, M.; Melchiorre, P. *ACS Catal.* **2018**, 8, 1062; (b) Tewari, N.; Dwivedi, N.; Tripathi, R. P. *Tetrahedron Lett.* **2004**, 45, 9011.

NMR Spectra of Synthesized Compounds

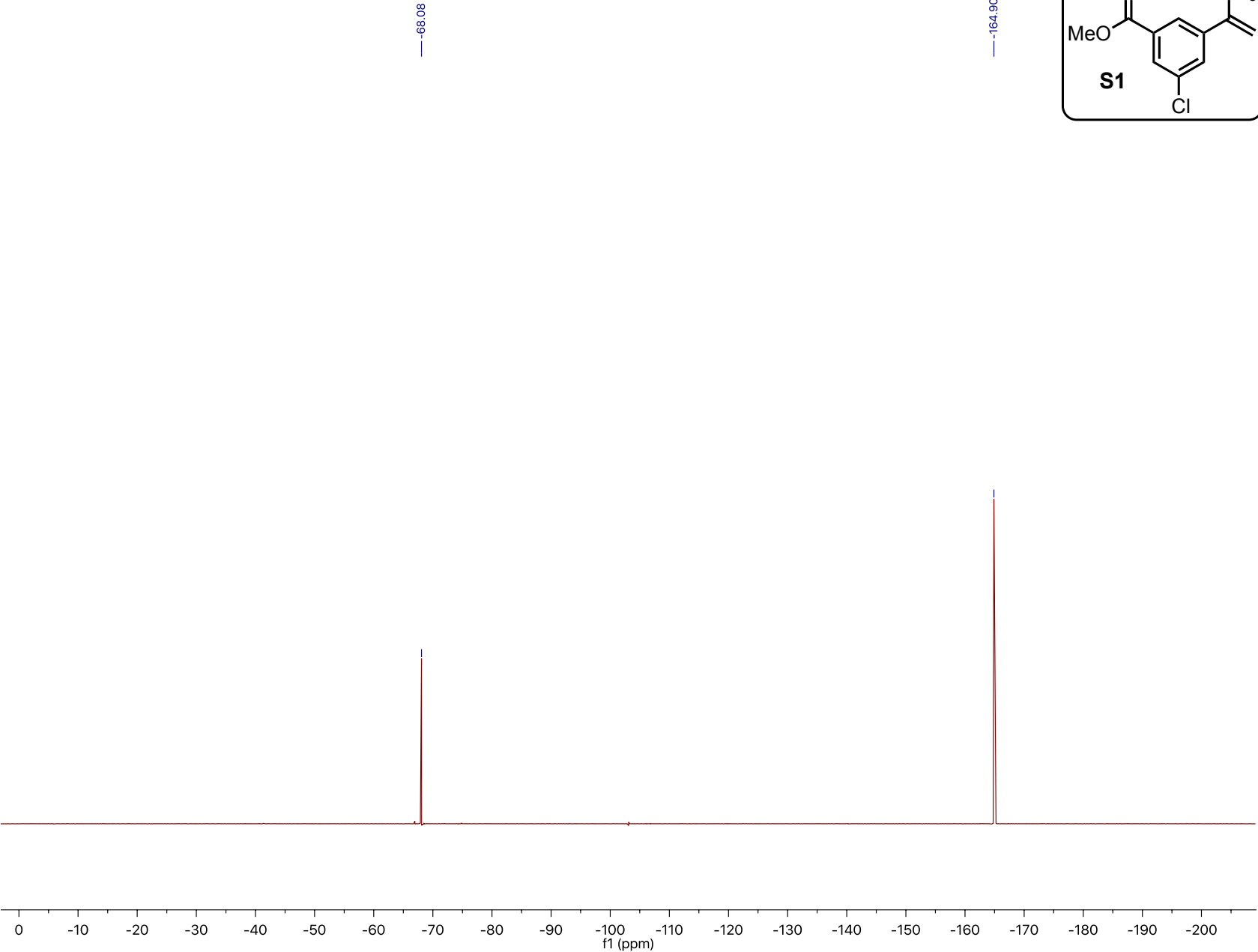
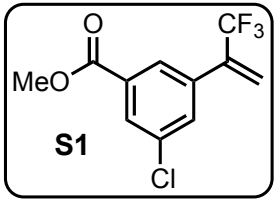
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¹H, 500 MHz, CDCl₃



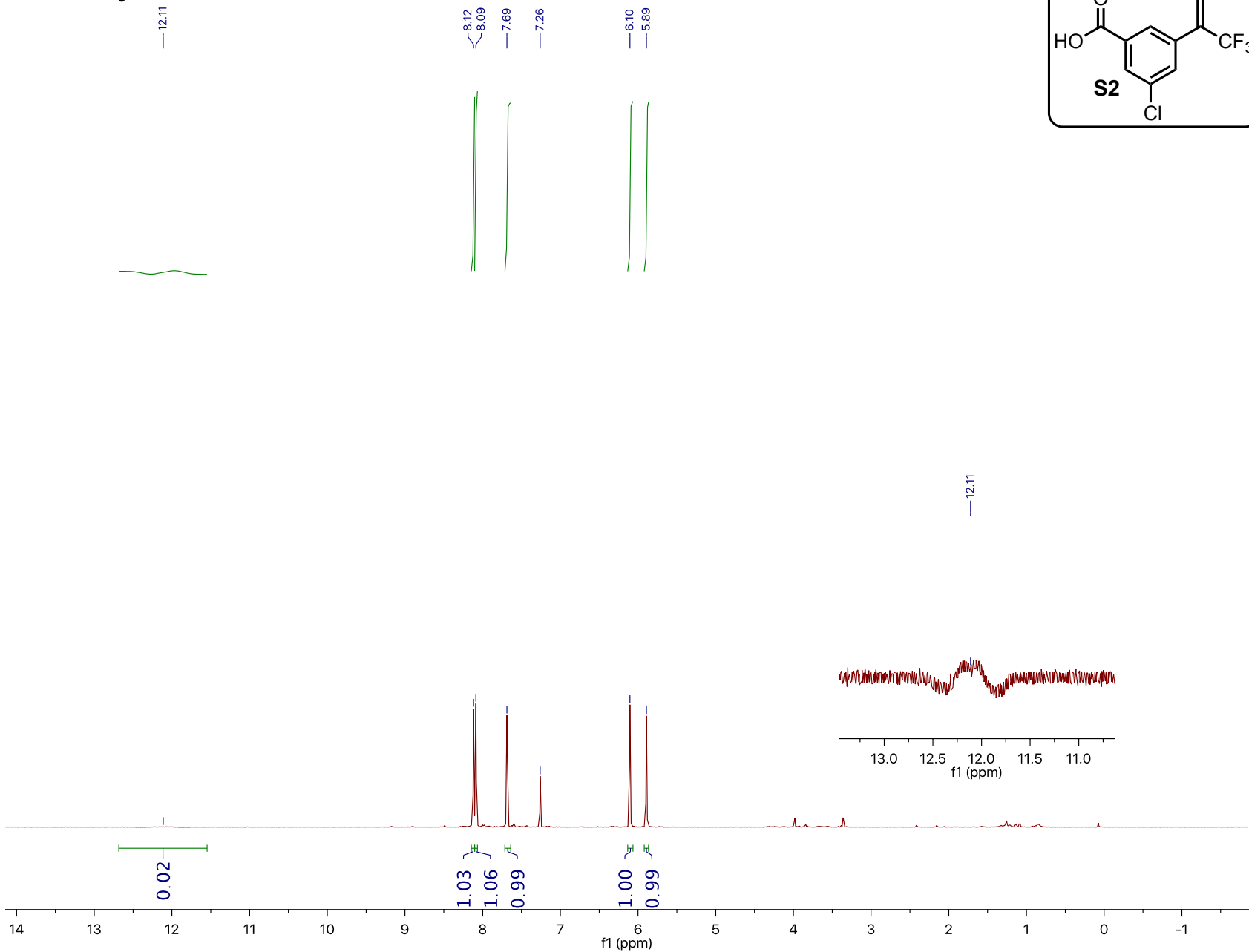
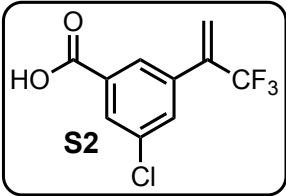
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¹³C, 126 MHz, CDCl₃



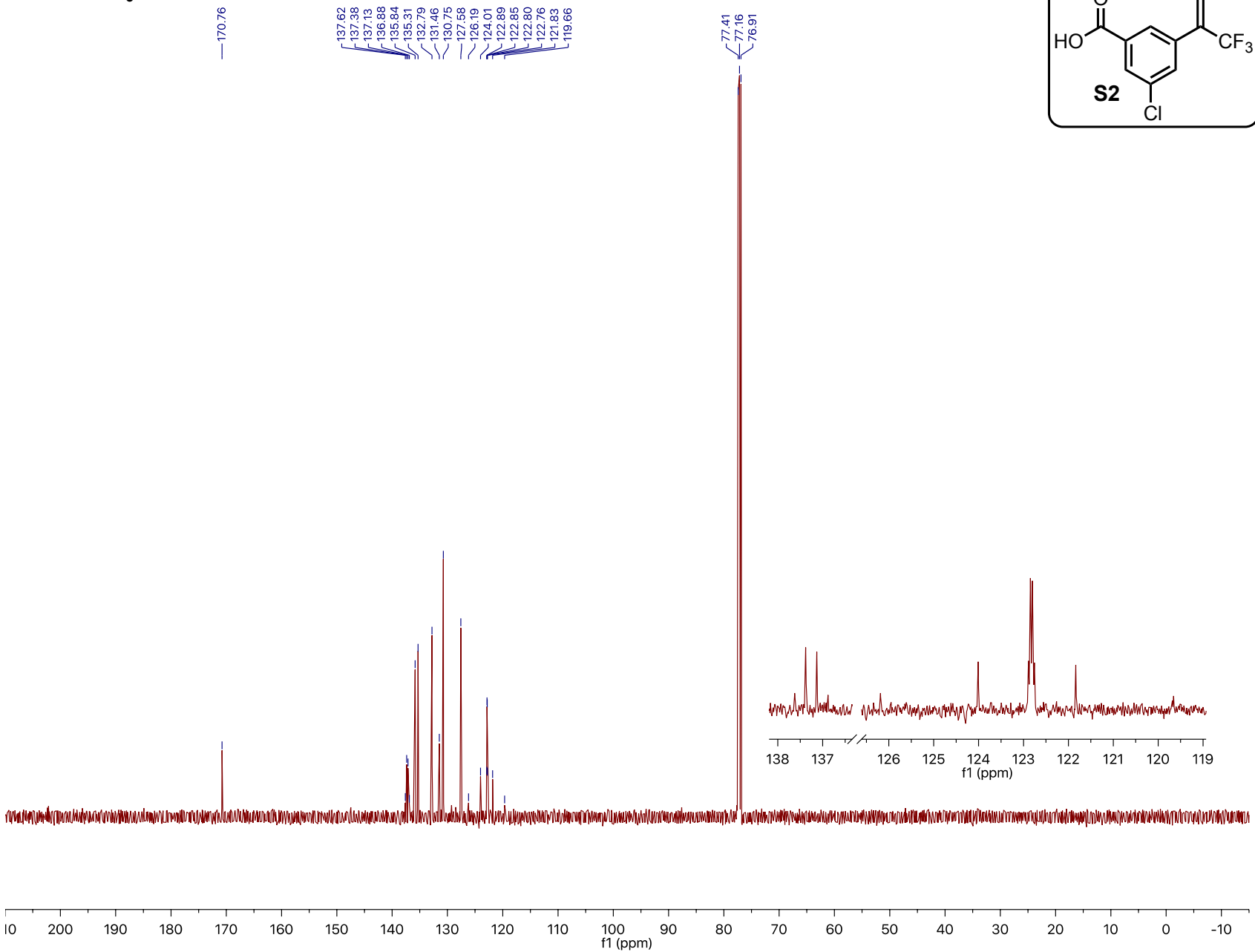
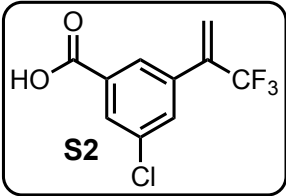
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¹⁹F, 471 MHz, CDCl₃



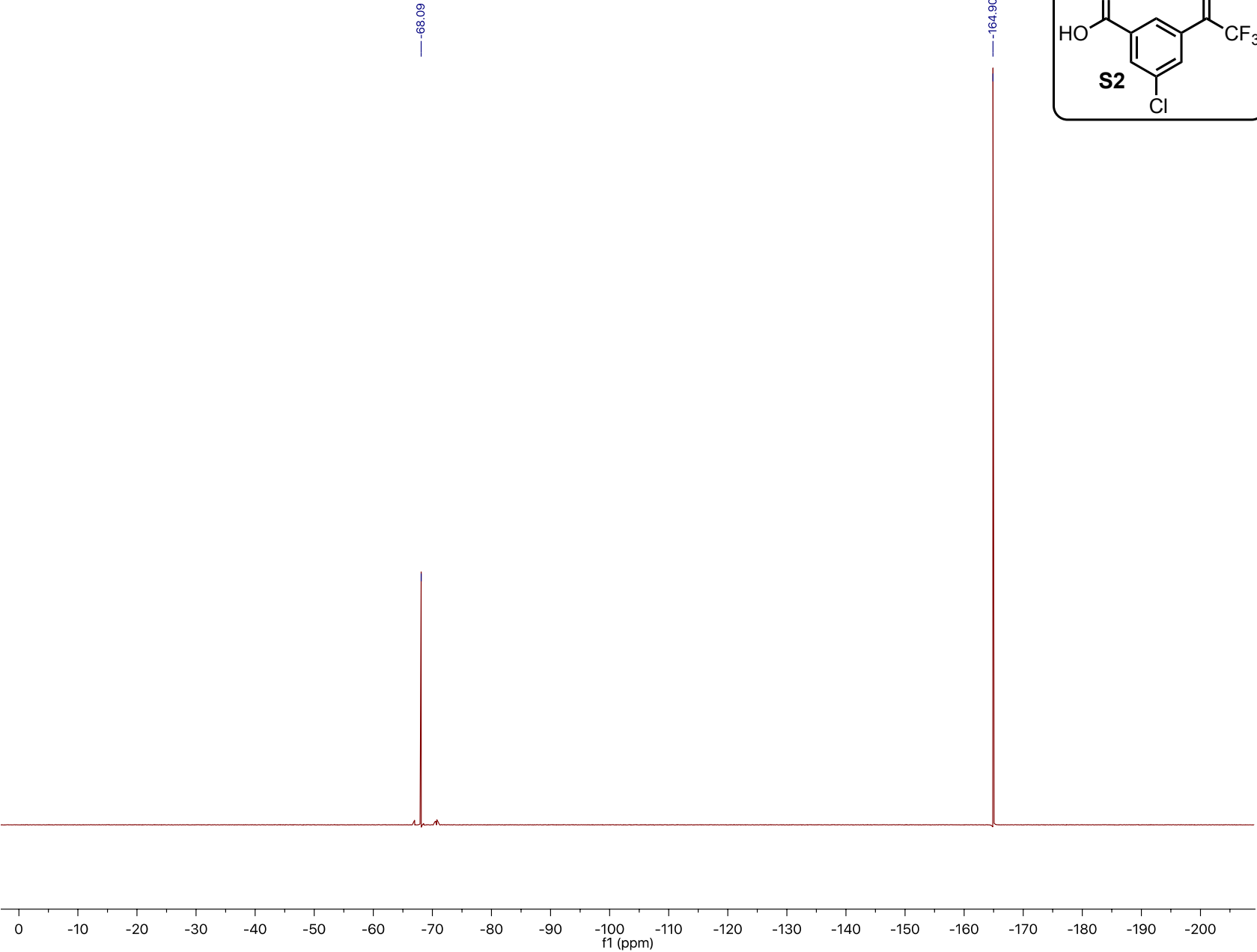
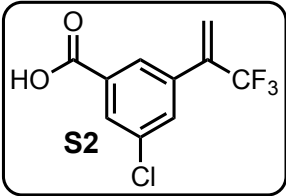
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¹H, 500 MHz, CDCl₃



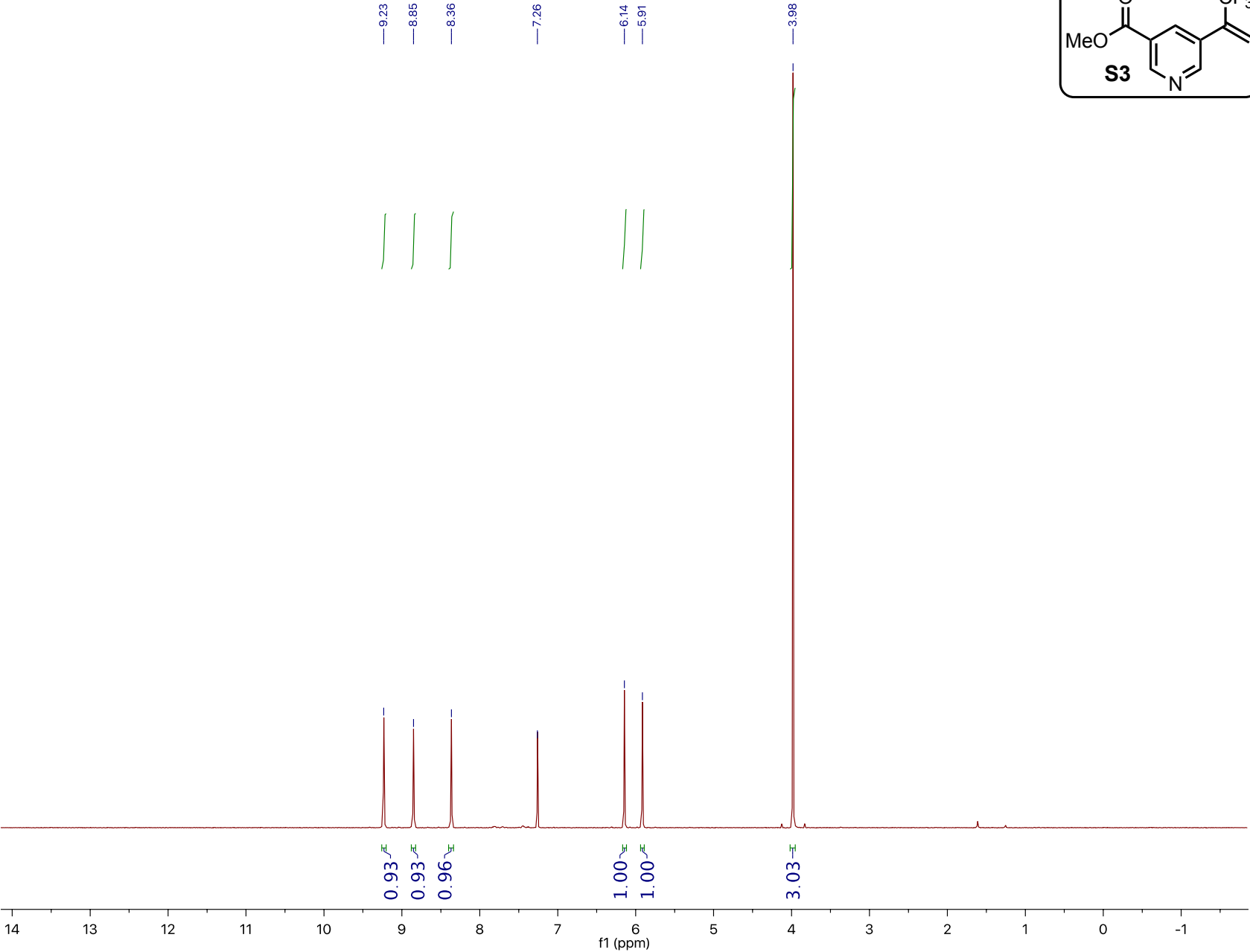
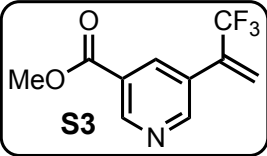
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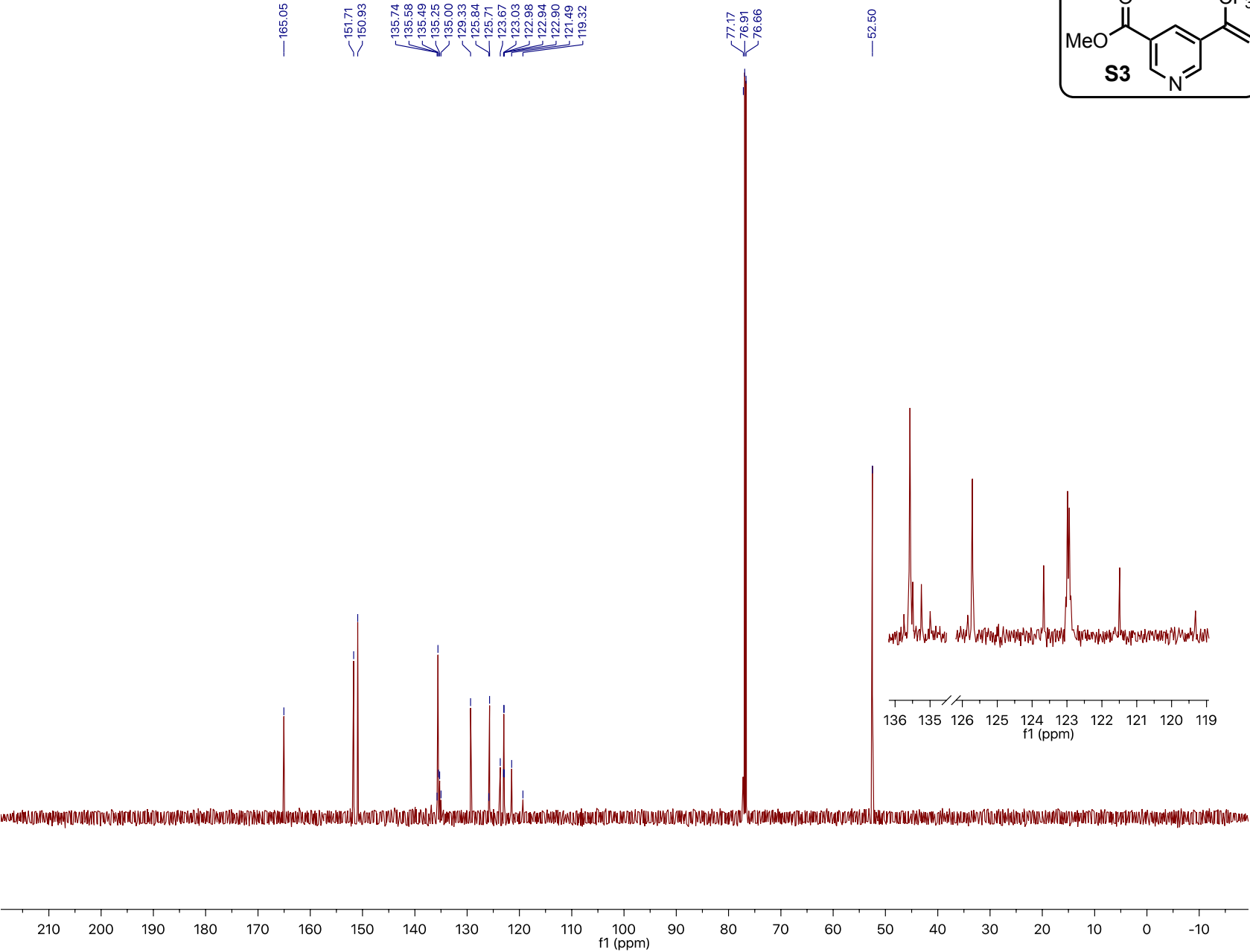
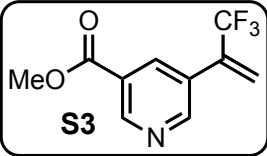
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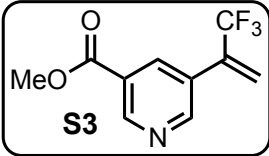
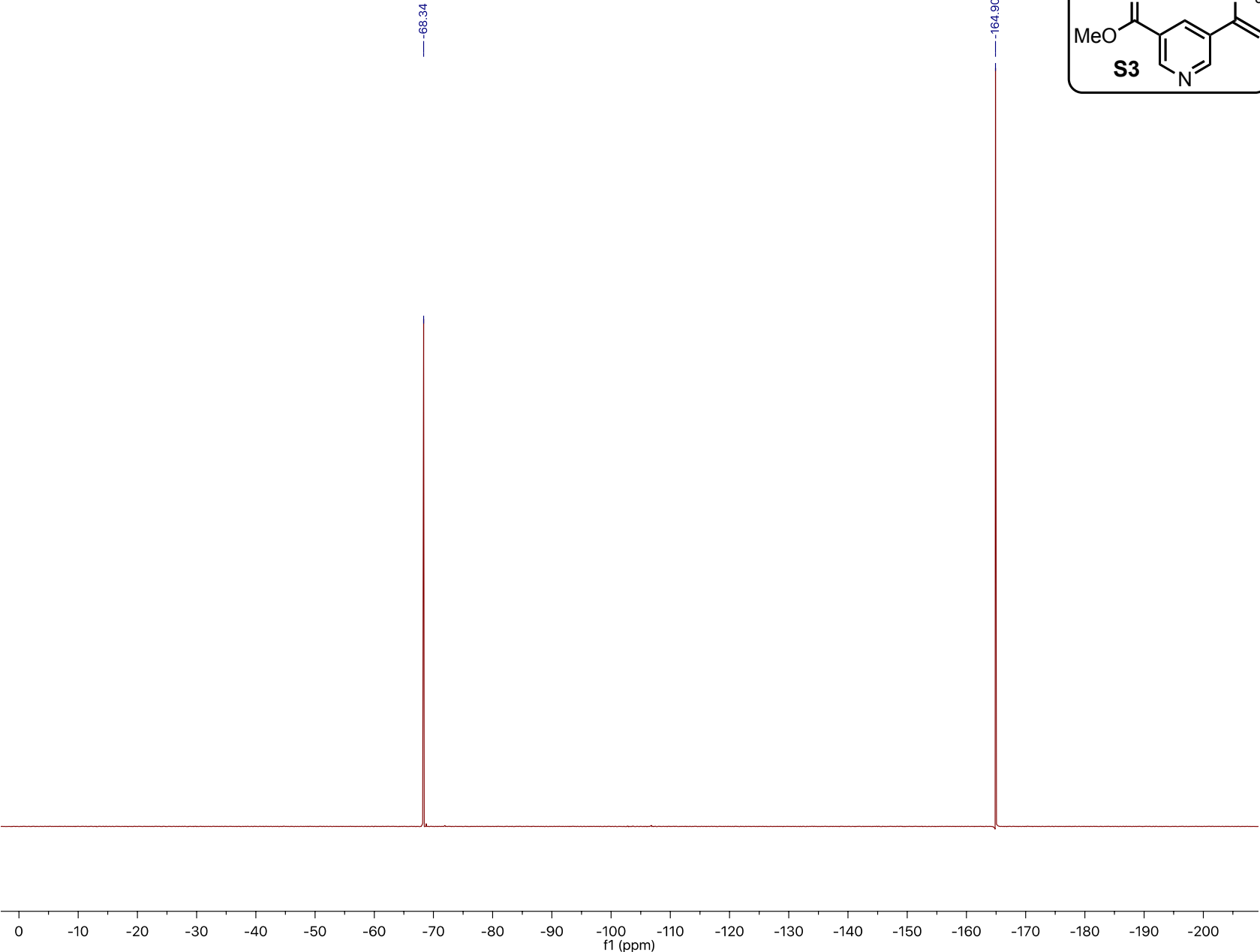
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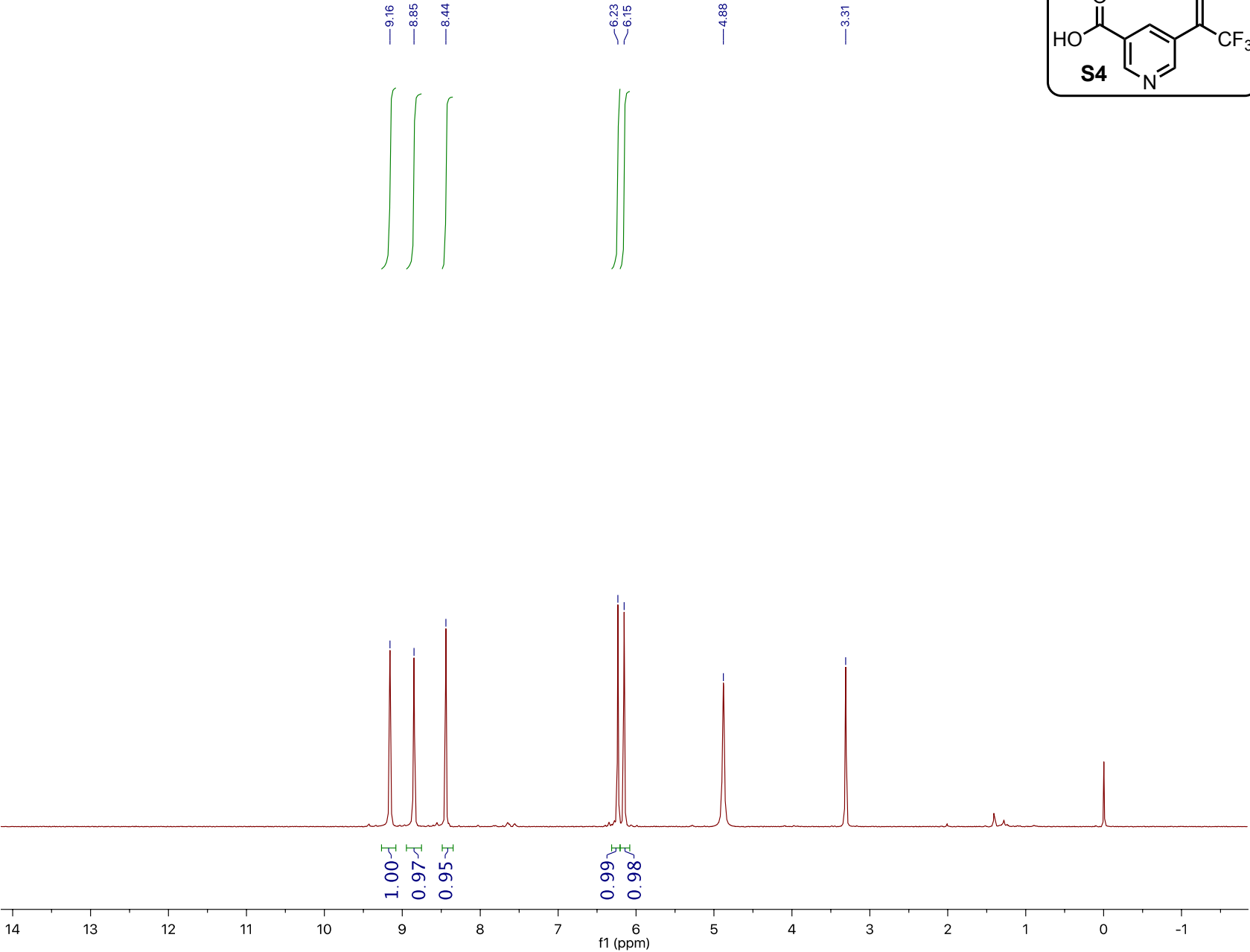
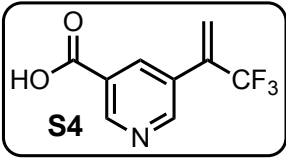
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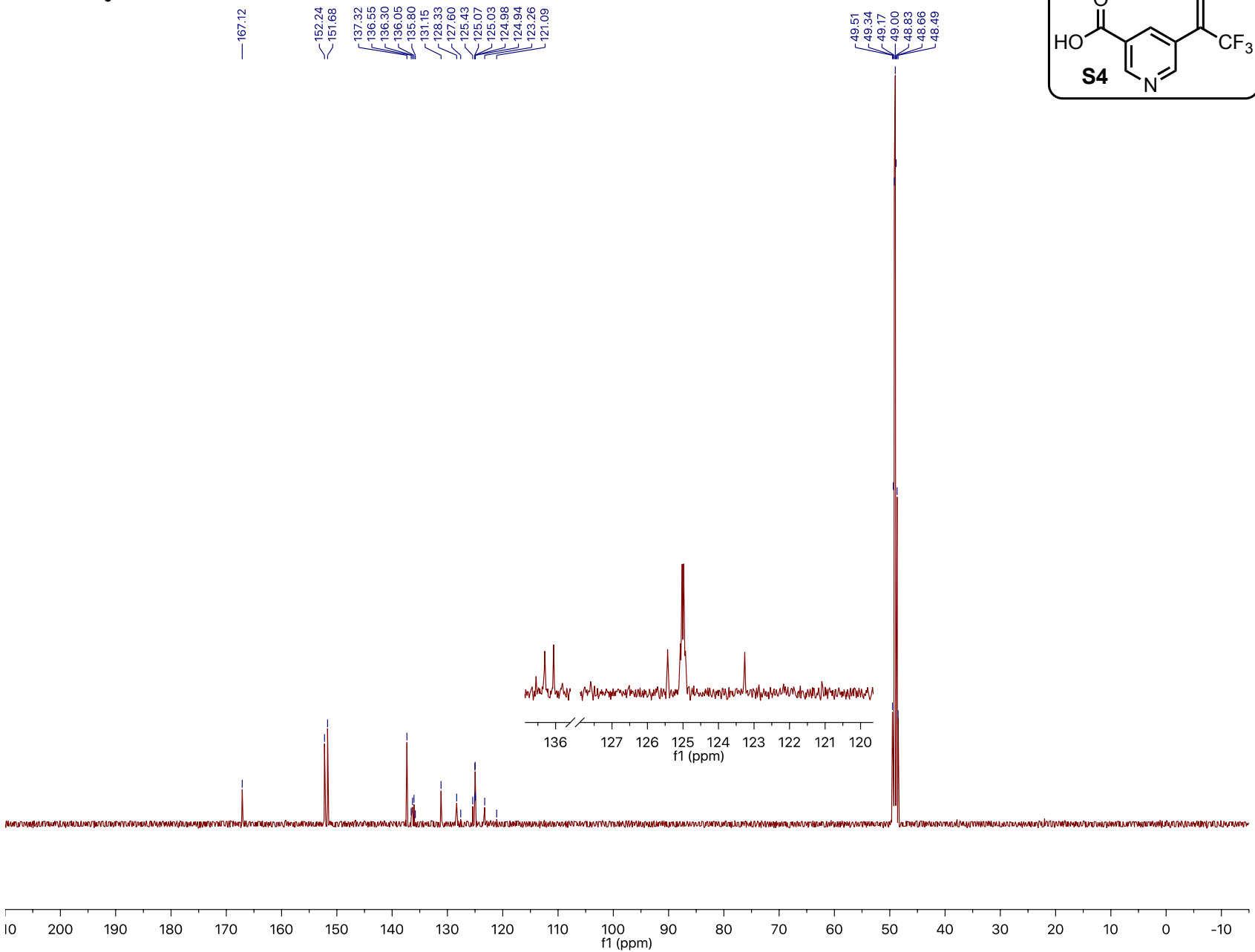
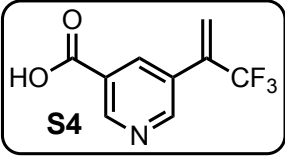
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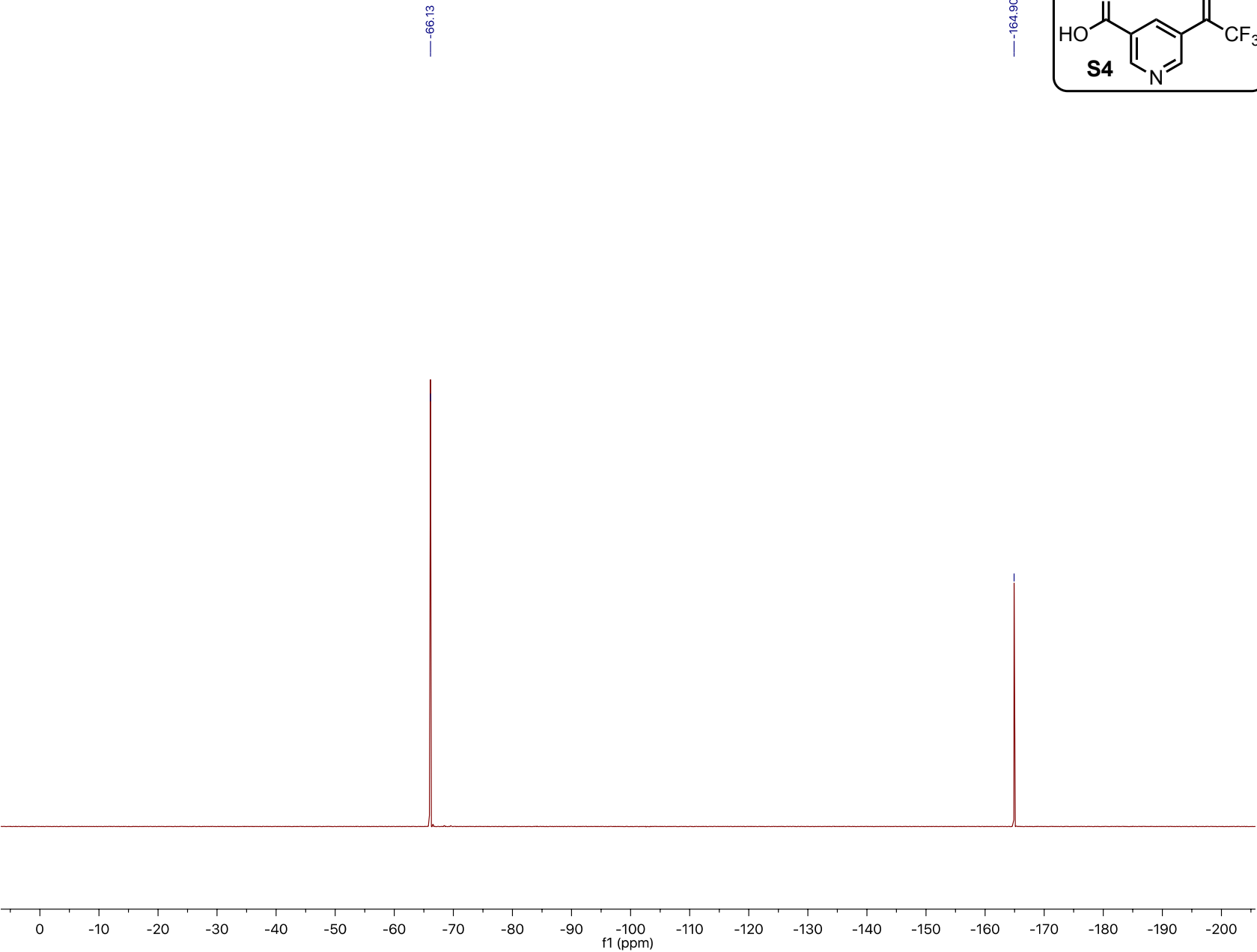
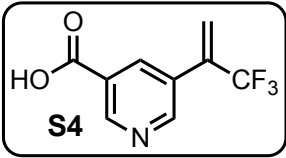
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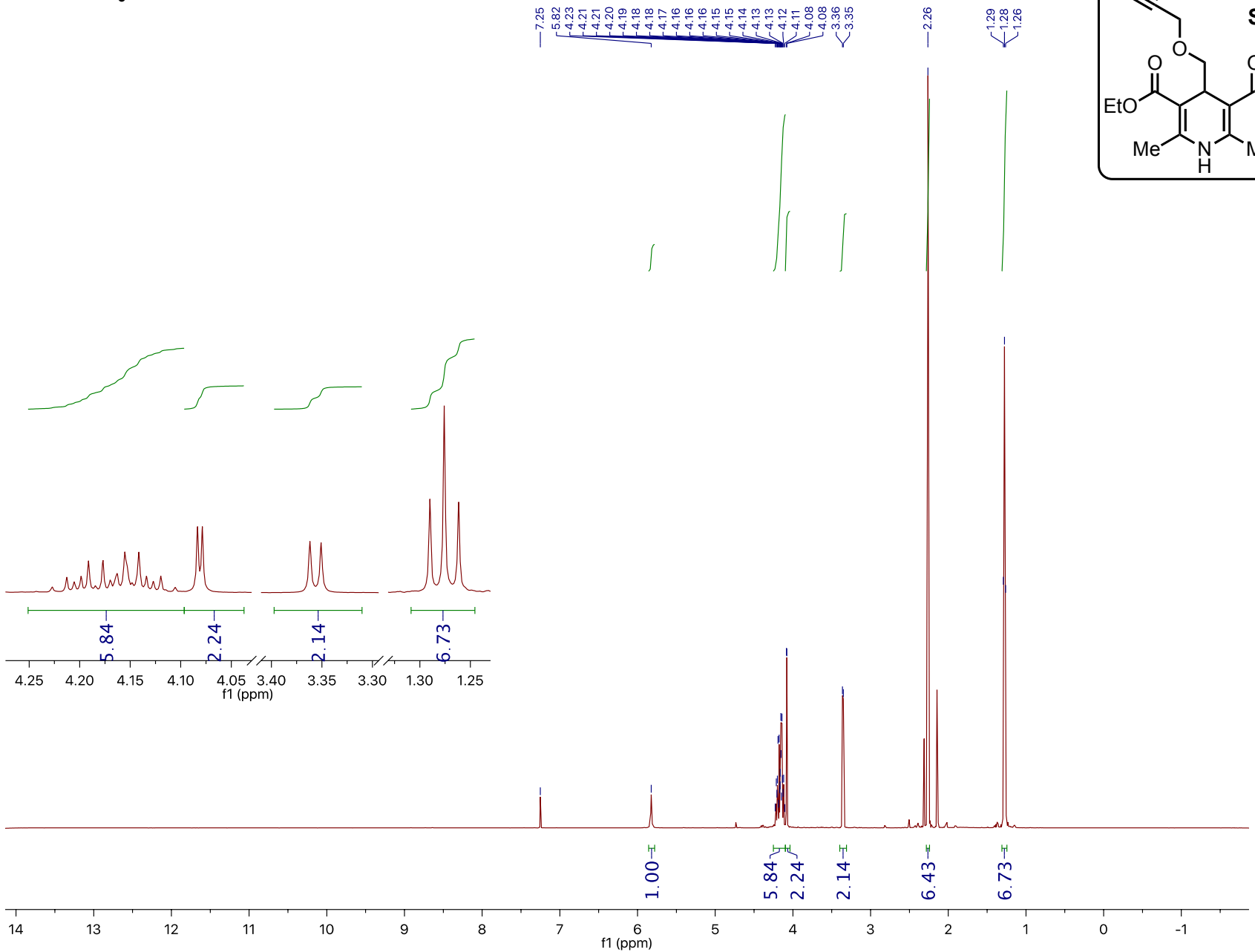
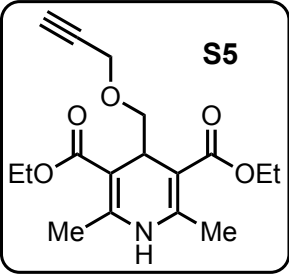
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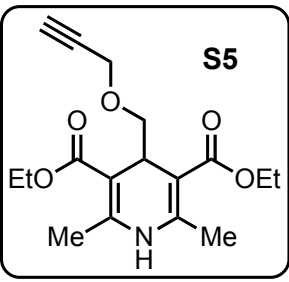
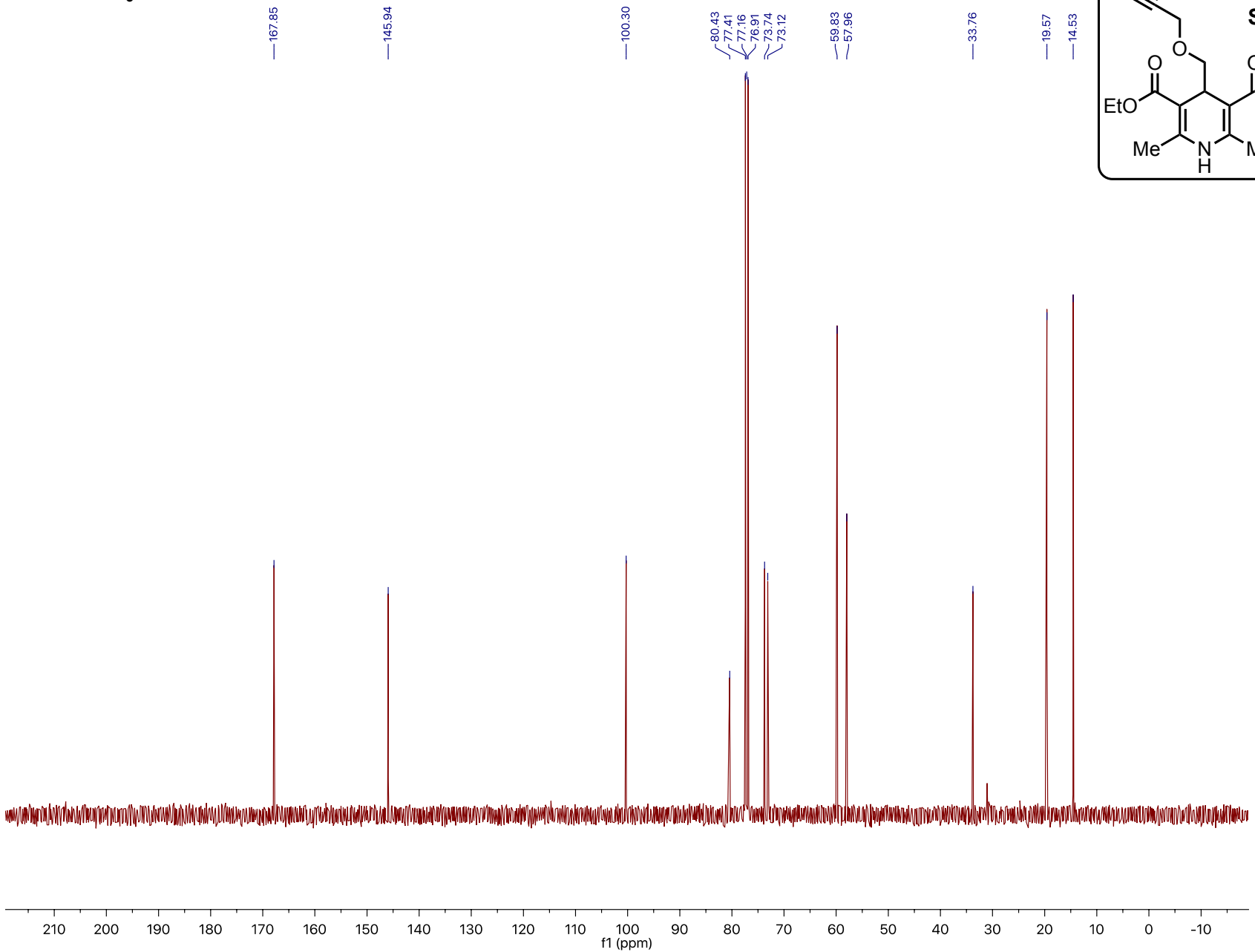
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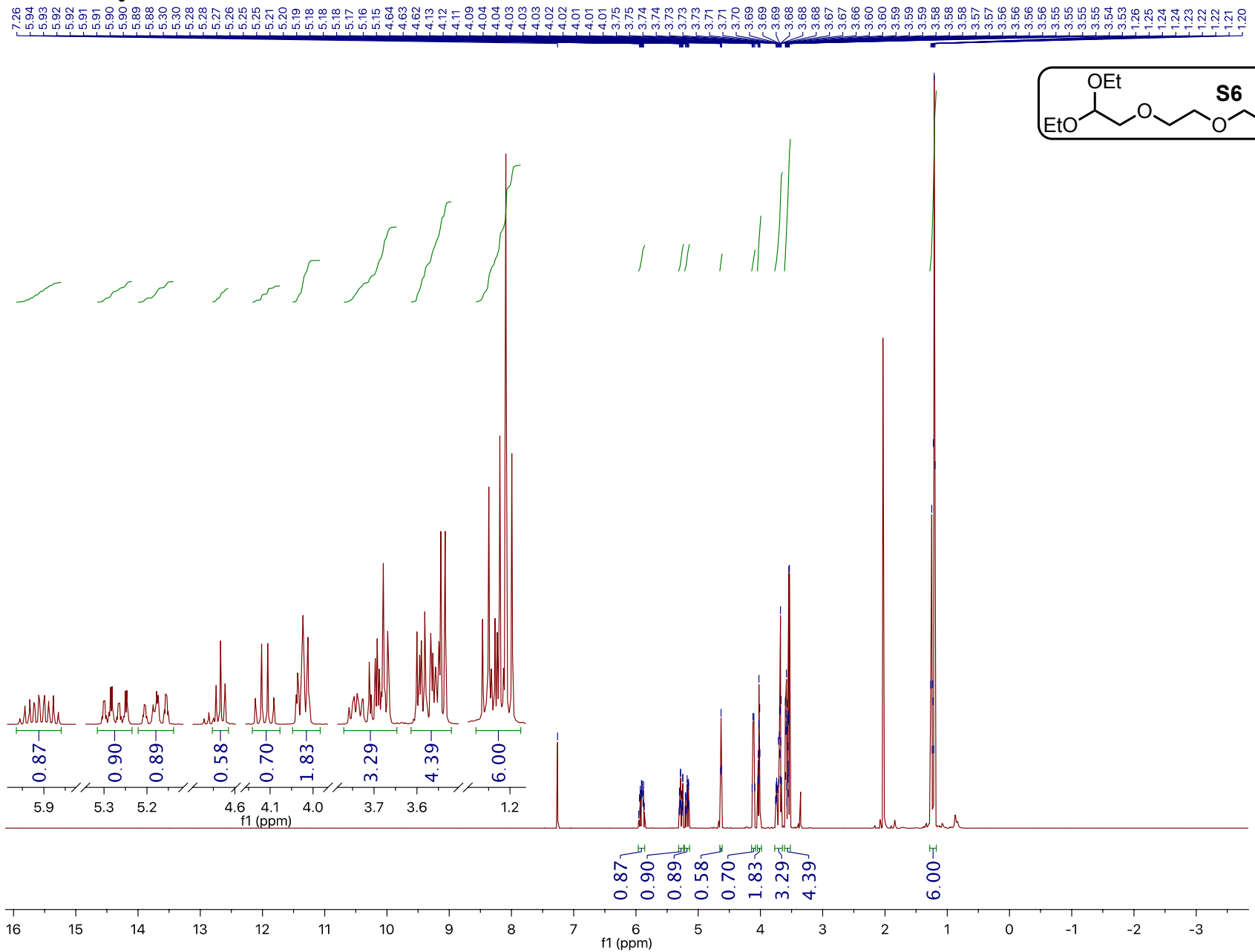
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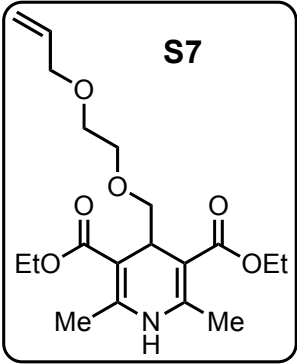


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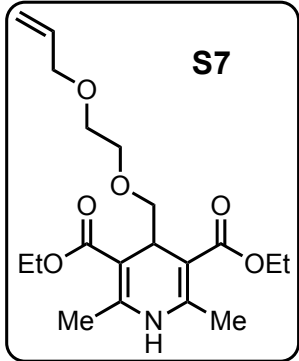
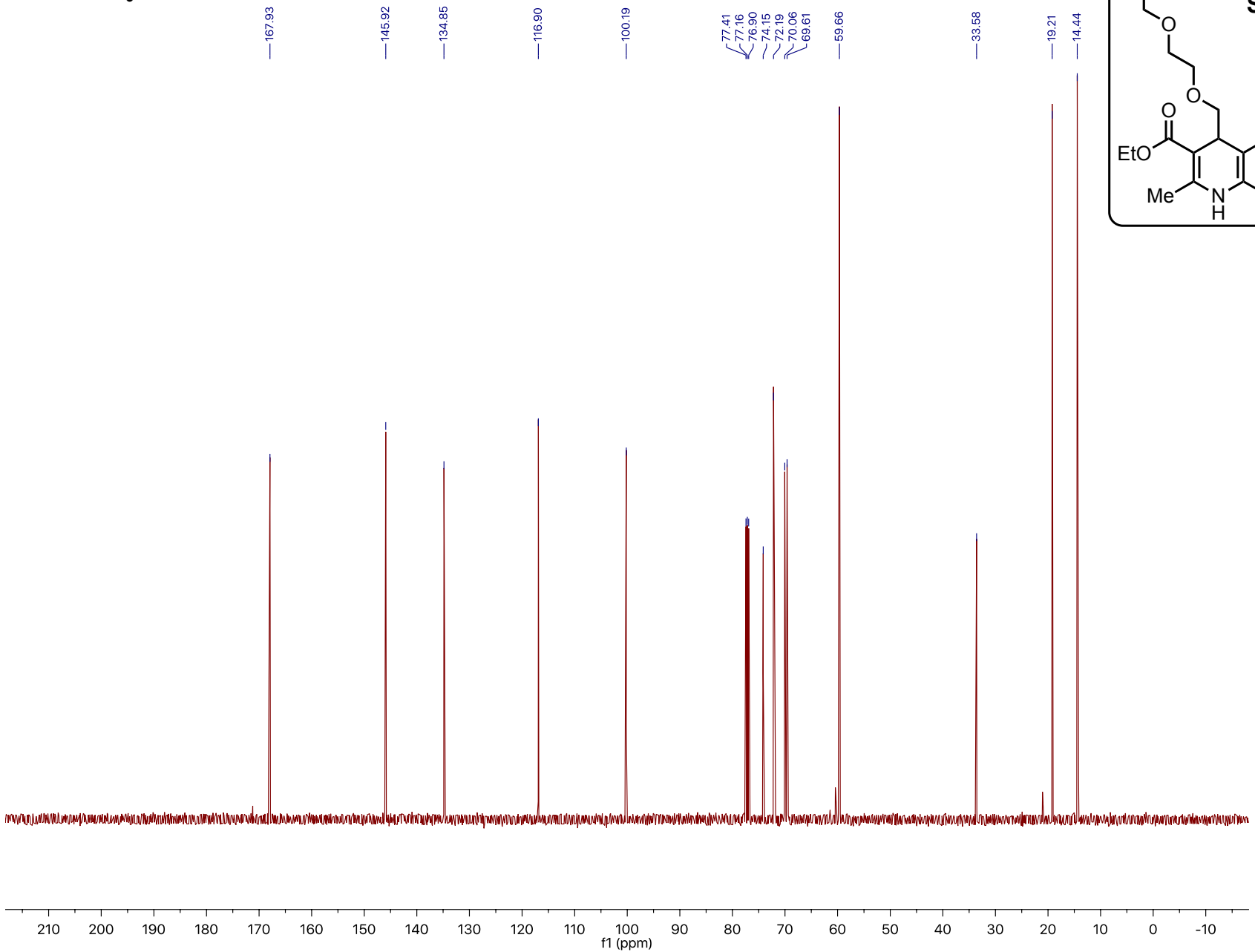


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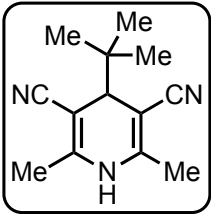


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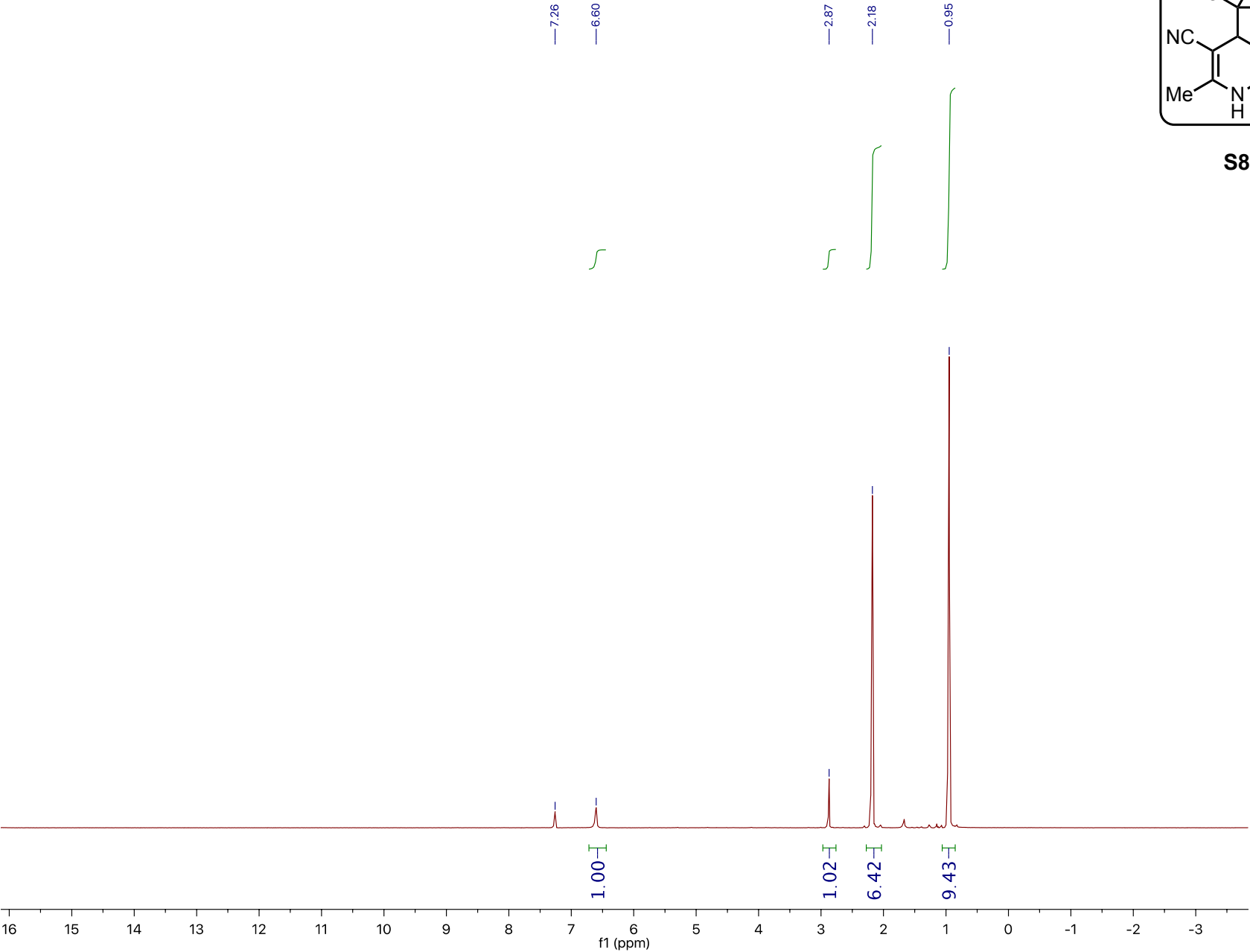
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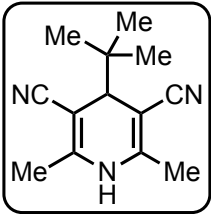
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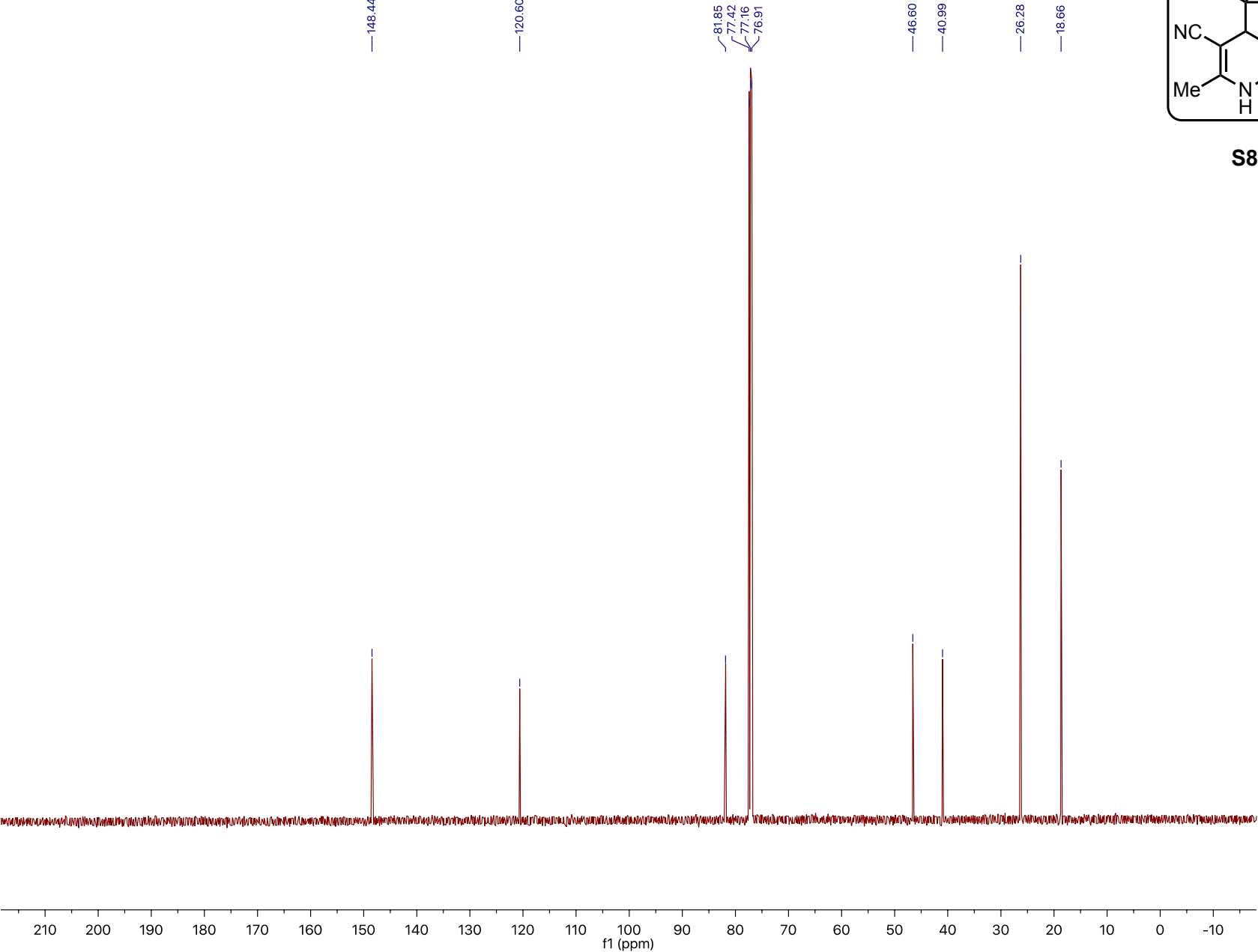
S8



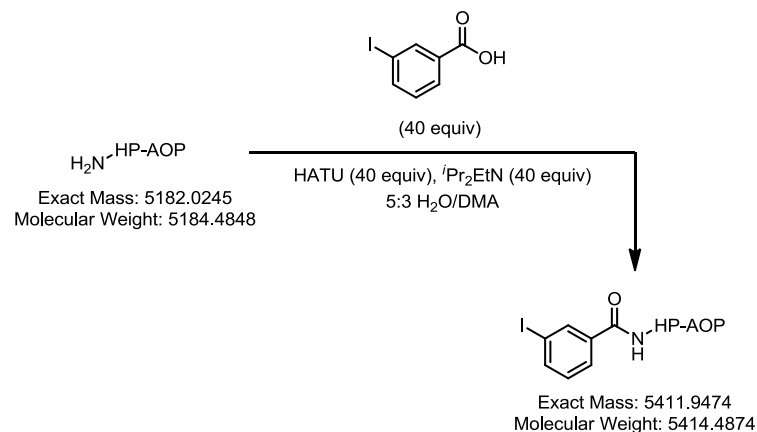
4-(tert-butyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile
¹³C, 126 MHz, CDCl₃



S8



Aryl Iodide Synthesis



Product: 100%

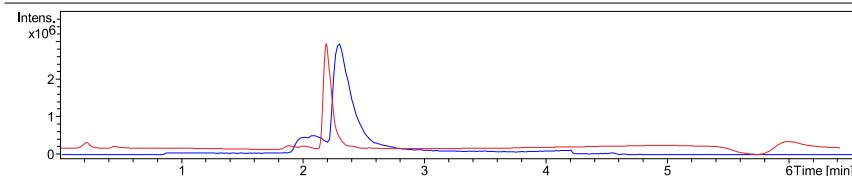
Compound Spectrum List Report

Analysis Info

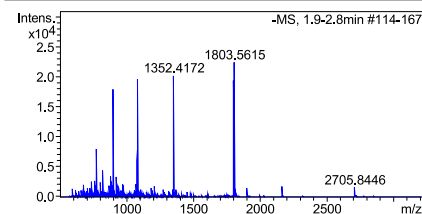
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Sample Name	KJB-N68389-11-3	Instrument	micrOTOF
Comment			213750.00199

Acquisition Parameter

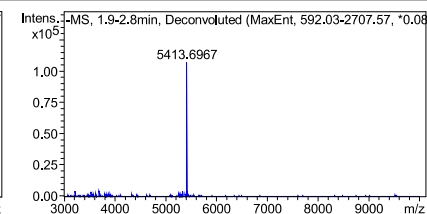
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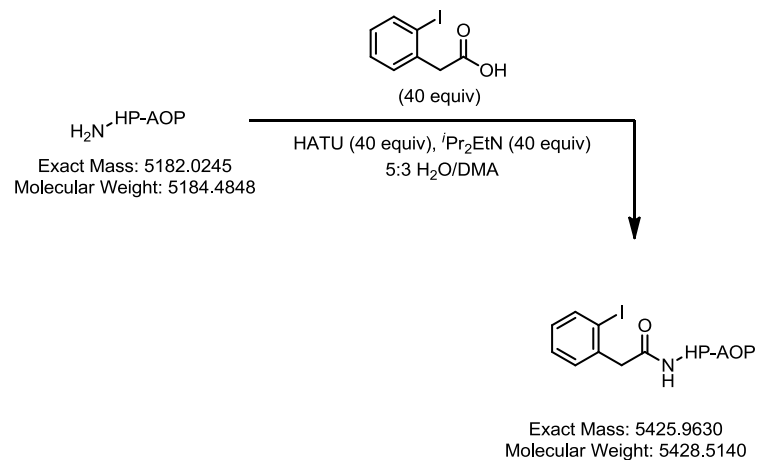
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7	1352.6592	17261
8	1803.2286	19347
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Product: 95%

Compound Spectrum List Report

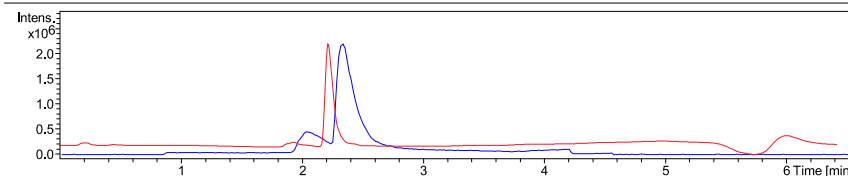
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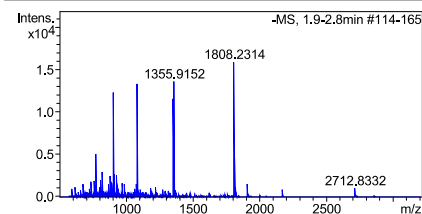
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 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

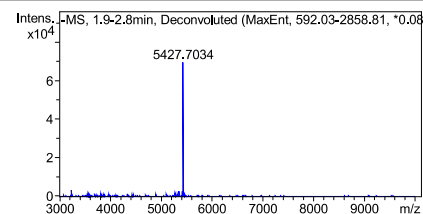
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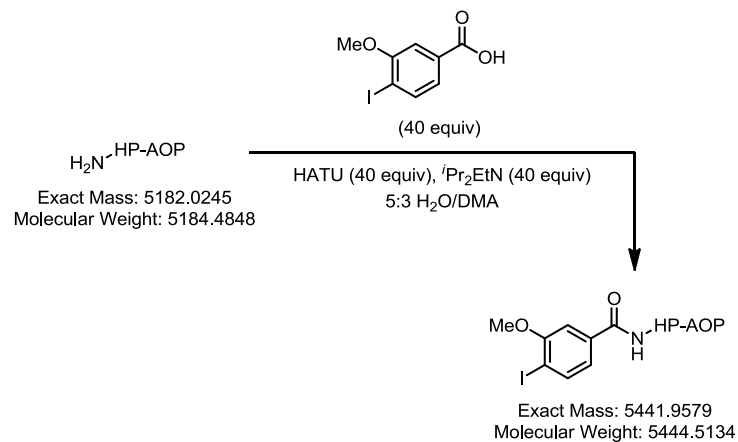
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6	1355.9152	13566
7	1356.1625	12273
8	1807.8969	13374
9	1808.2314	15862
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2	5427.7034	69520



Product: 95%

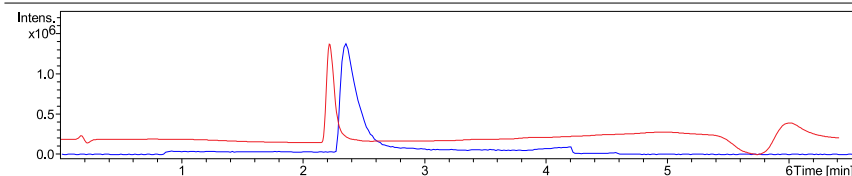
Compound Spectrum List Report

Analysis Info

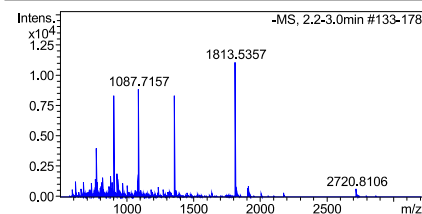
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Comment					213750.00199

Acquisition Parameter

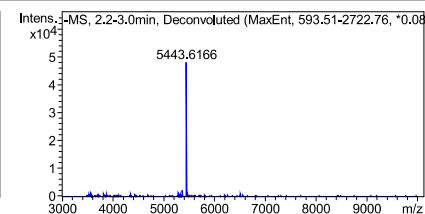
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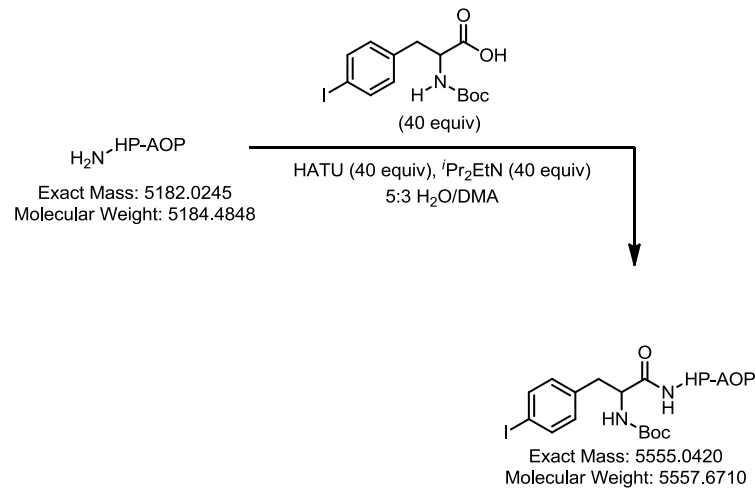
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7	1360.1391	7274
8	1813.2041	8858
9	1813.5357	11055
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#	m/z	I
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2	5443.6166	48001



Product: 100%

Compound Spectrum List Report

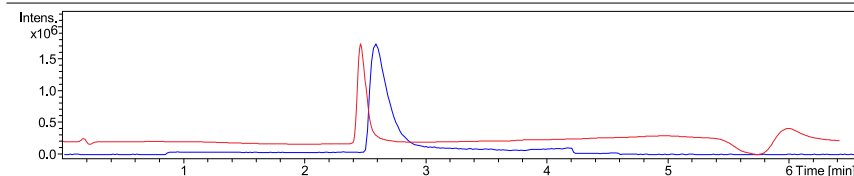
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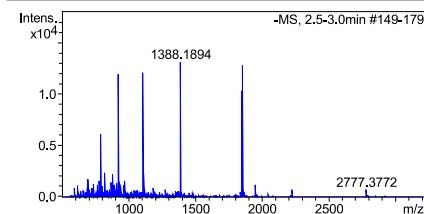
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 Operator: gsk
 Instrument: micrOTOF
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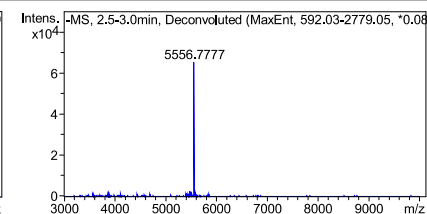
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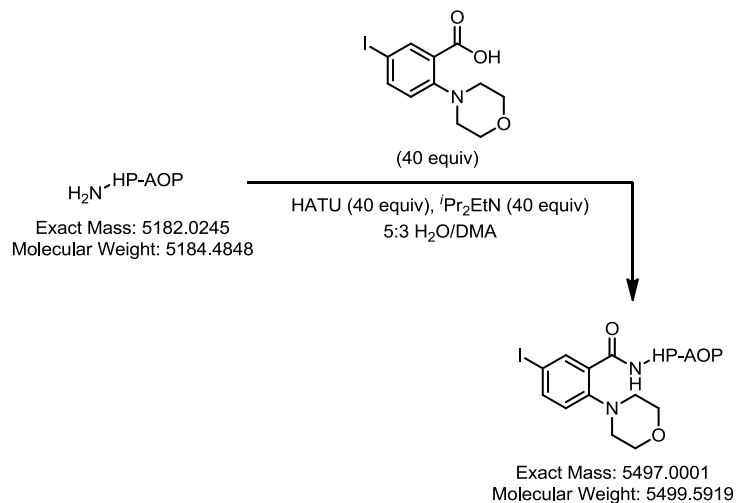
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8	1388.4334	12411
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#	m/z	I
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Product: 94%

Compound Spectrum List Report

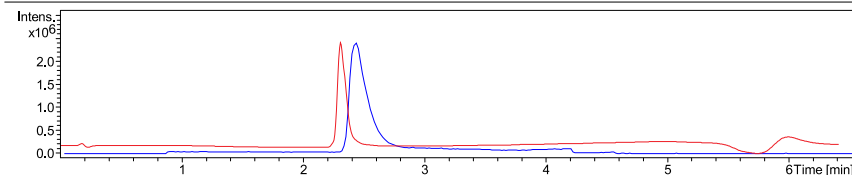
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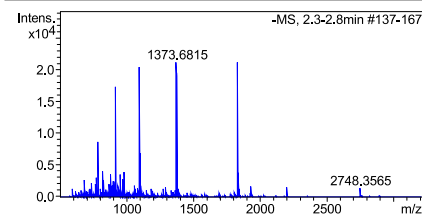
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 213750.00199

Acquisition Parameter

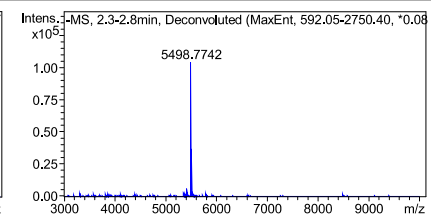
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



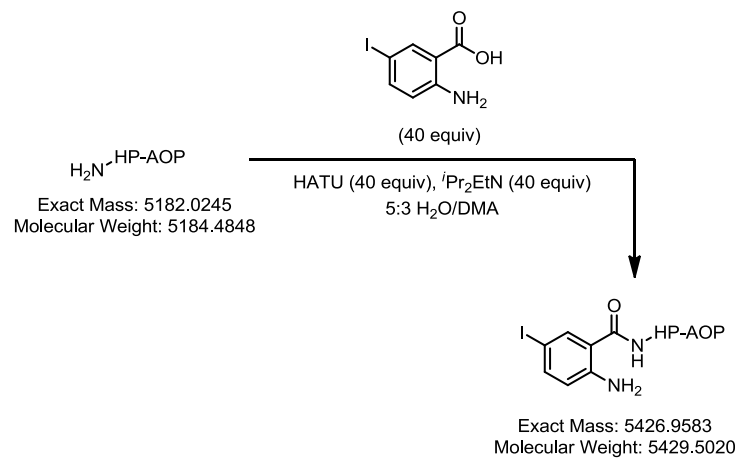
-MS, 2.3-2.8min #137-167



#	m/z	I
1	915.4544	17281
2	1098.5551	16679
3	1098.7511	20338
4	1098.9498	16645
5	1373.4382	16657
6	1373.6815	21123
7	1373.9286	19508
8	1831.5857	18402
9	1831.9180	21158
10	1832.2484	18453



#	m/z	I
1	5420.8039	6113
2	5498.7742	103886



Product: 100%

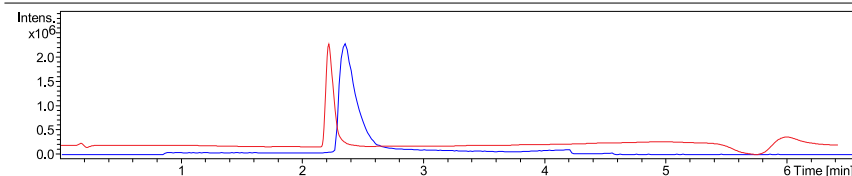
Compound Spectrum List Report

Analysis Info

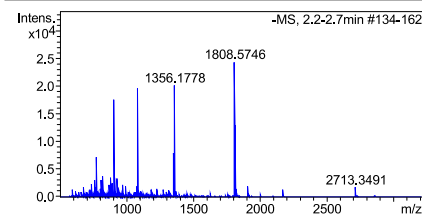
Analysis Name	X:\Chem MS Data\utof\Data_2018\Nov 2018\utof-110918\KJB-N68389-11-11_92_01_10070.d			Acquisition Date	11/9/2018 7:09:26 PM
Method	1200ccl2_10to90in4.m			Operator	gsk
Sample Name	KJB-N68389-11-11			Instrument	micrOTOF
Comment					213750.00199

Acquisition Parameter

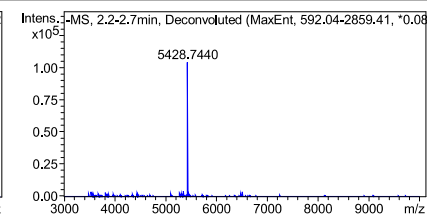
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.2-2.7min #134-162



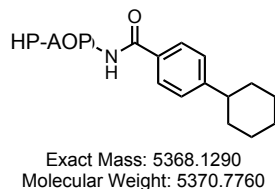
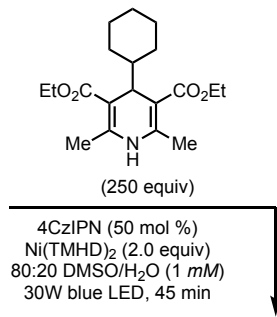
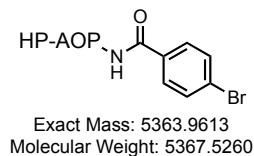
#	m/z	I
1	903.7817	17535
2	1084.5465	15741
3	1084.7431	19480
4	1084.9419	16365
5	1355.9310	16543
6	1356.1778	20047
7	1356.4210	17337
8	1808.2450	21050
9	1808.5746	24321
10	1808.9036	21242



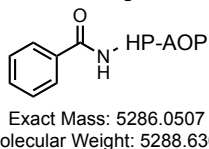
#	m/z	I
1	5428.7440	104142

Nickel/Photoredox Dual Catalytic Cross-Coupling using DHP's

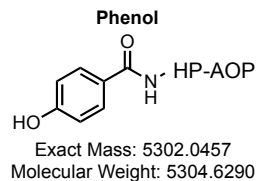
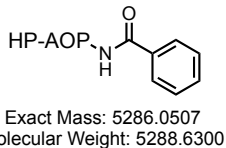
Cross-Coupling Product-3b



Protodehalogenation



Protodebromination



Product: 74%
Starting material: 0%
Protodebromination: 11%

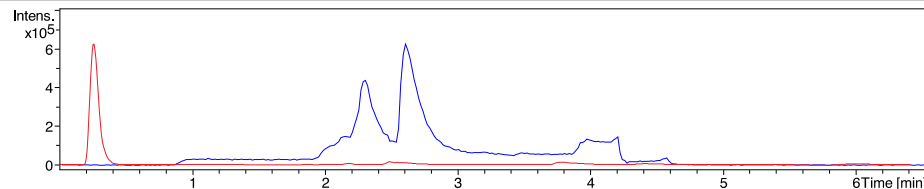
Compound Spectrum List Report

Analysis Info

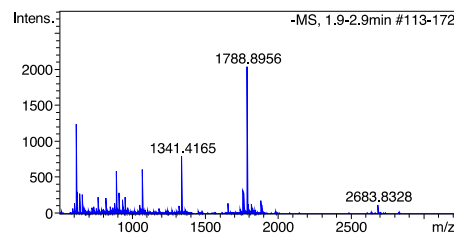
Analysis Name: D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-2-2_12_01_8172.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20180430-2-2
 Comment:
 Acquisition Date: 5/8/2018 5:58:58 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

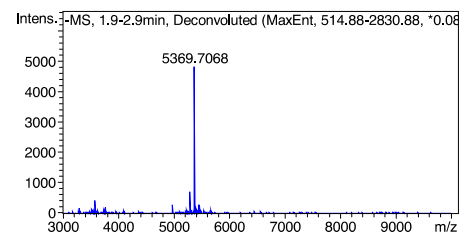
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #113-172



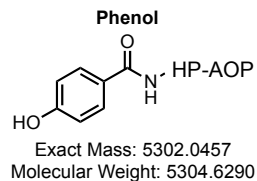
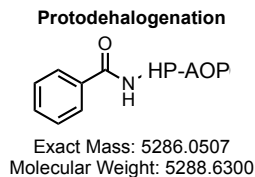
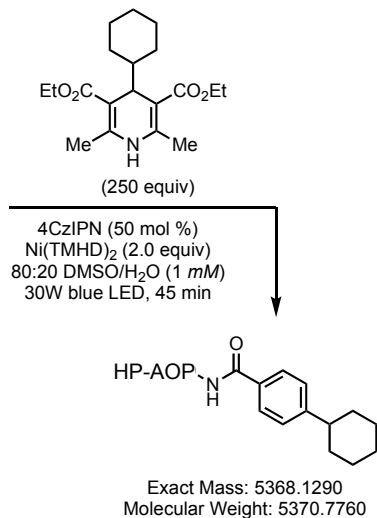
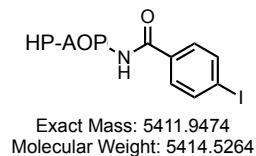
#	m/z	I
1	621.0664	1246
2	1341.1686	652
3	1341.4165	792
4	1787.8470	697
5	1788.2151	1165
6	1788.5582	1867
7	1788.8956	2034
8	1789.2307	1779
9	1789.5643	1171
10	1789.8967	650



#	m/z	I
1	3579.8246	420
2	4978.5118	281
3	5287.6642	727
4	5369.7068	4817
5	5453.8048	298

protodebromination
 product

Cross-Coupling Product-3b



Product: 66%
Starting material: 0%
Protodebromination: 16%

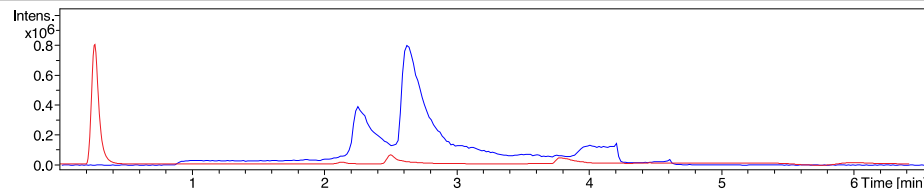
Compound Spectrum List Report

Analysis Info

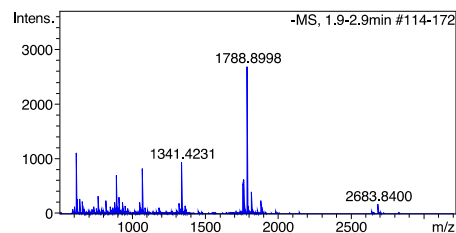
Analysis Name: D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-7-1_71_01_8199.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20180430-7-1
 Comment:
 Acquisition Date: 5/8/2018 9:18:23 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

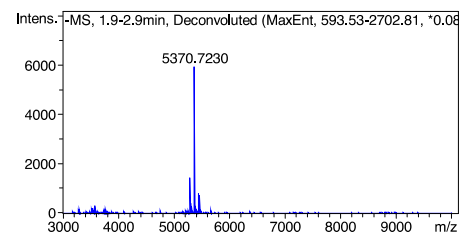
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #114-172

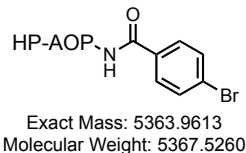


#	m/z	I
1	621.0637	1111
2	1341.1774	866
3	1341.4231	940
4	1341.6641	864
5	1788.2332	1048
6	1788.5669	2192
7	1788.8998	2684
8	1789.2314	2419
9	1789.5643	1654
10	1789.8975	1035

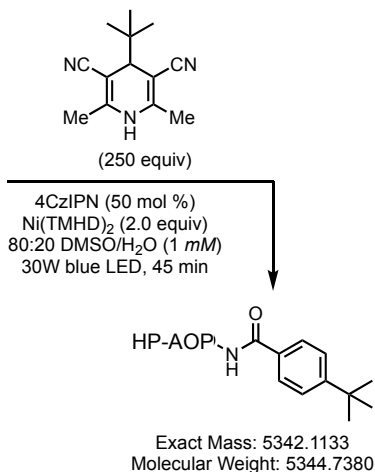
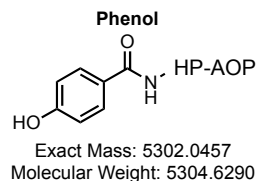
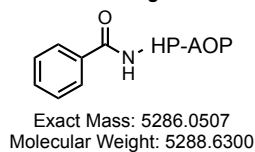


#	m/z	I	
1	3579.8164	312	
2	5287.6580	1448	protodebromination
3	5312.6286	433	
4	5370.7230	5933	
5	5453.7985	800	product

Cross-Coupling Product-3c



Protodehalogenation



Product: 42%
Starting material: 30%
Protodebromination: 6%

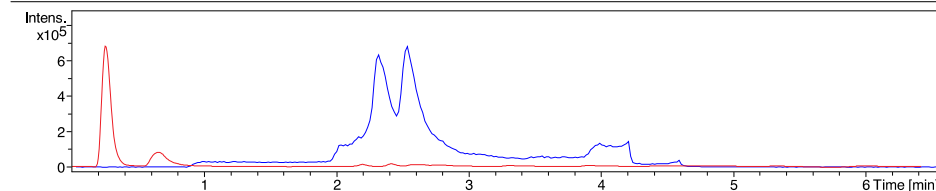
Compound Spectrum List Report

Analysis Info

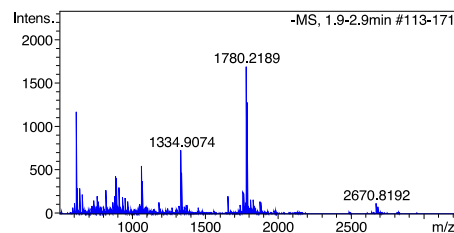
Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-2-5_15_01_8175.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180430-2-5
 Comment
 Acquisition Date 5/8/2018 6:21:13 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

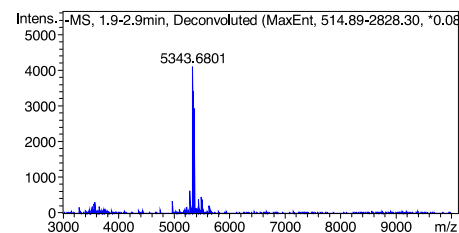
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #113-171



#	m/z	I
1	621.0626	1164
2	1779.8859	1490
3	1780.2189	1686
4	1780.5535	1474
5	1780.8818	1044
6	1787.1742	757
7	1787.5056	1124
8	1787.8342	1276
9	1788.1692	1165
10	1788.5003	927



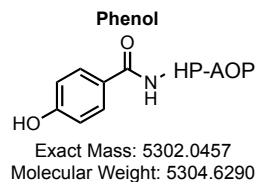
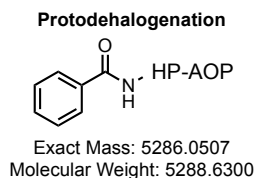
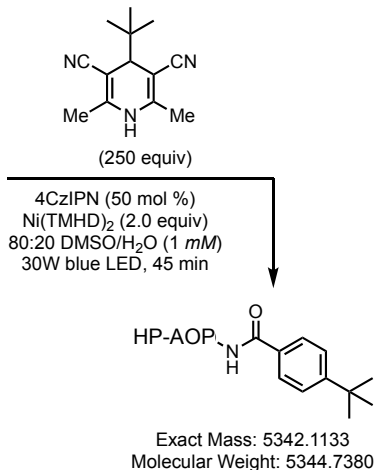
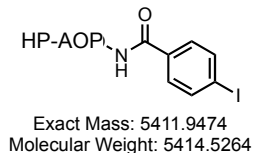
#	m/z	I
1	3564.4931	265
2	3577.6994	322
3	4978.4951	350
4	5287.6271	622
5	5343.6801	4094
6	5366.5271	2920
7	5442.6513	382
8	5500.7465	462
9	5635.7506	226

protodebromination

product

starting material

Cross-Coupling Product-3c



Product: 42%
Starting material: 0%
Protodebromination: 29%

Compound Spectrum List Report

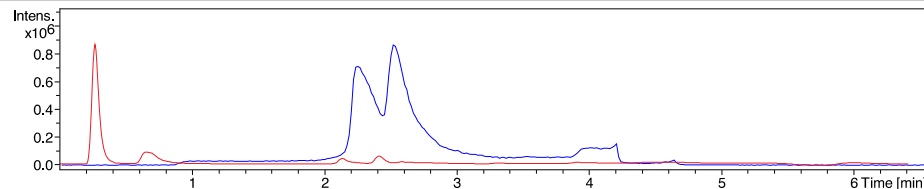
Analysis Info

Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-7-2_01_8200.d
Method 1200col2_10to90in4.m
Sample Name JPP-20180430-7-2
Comment

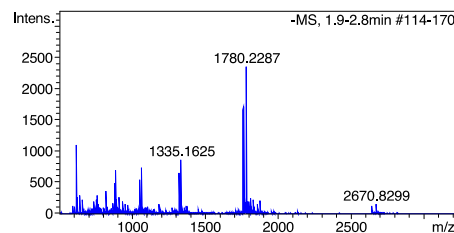
Acquisition Date 5/8/2018 9:25:45 PM
Operator gsk
Instrument micrOTOF 213750.00199

Acquisition Parameter

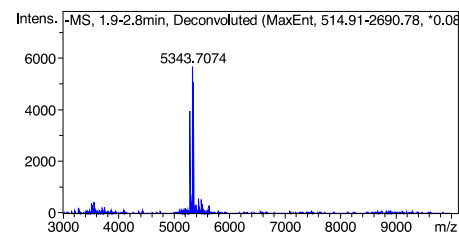
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.8min #114-170



#	m/z	I
1	621.0628	1103
2	1761.2096	1537
3	1761.5404	1715
4	1761.8743	1483
5	1762.2089	1128
6	1779.5603	984
7	1779.8944	2026
8	1780.2287	2348
9	1780.5618	2155
10	1780.8937	1488

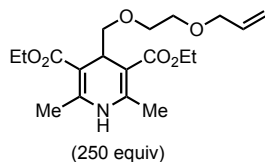
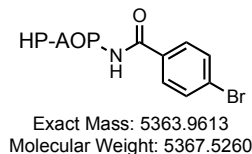


#	m/z	I
1	3524.4449	412
2	3562.4852	452
3	5287.6490	3969
4	5301.6622	735
5	5312.6358	581
6	5343.7074	5671
7	5365.6647	291
8	5399.7548	346
9	5442.6970	589
10	5500.7201	552

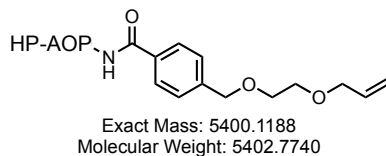
protodebromination

product

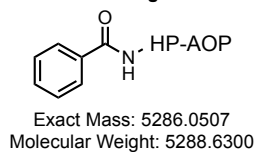
Cross-Coupling Product-3d



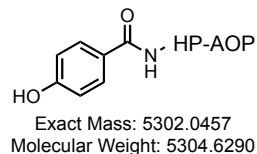
4CzIPN (50 mol %)
 Ni(TMHD)₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 45 min



Protodehalogenation



Phenol



Product: 66%
Starting material: 10%
Protodebromination: 14%

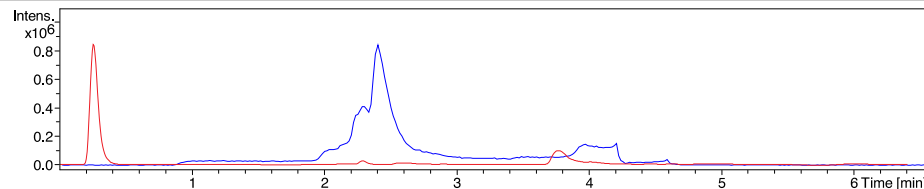
Compound Spectrum List Report

Analysis Info

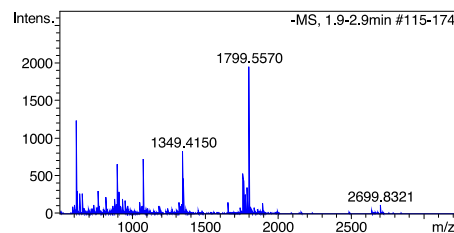
Analysis Name	D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-2-4_14_01_8174.d	Acquisition Date	5/8/2018 6:13:44 PM
Method	1200col2_10to90in4.m	Operator	gsk
Sample Name	JPP-20180430-2-4	Instrument	micrOTOF
Comment			213750.00199

Acquisition Parameter

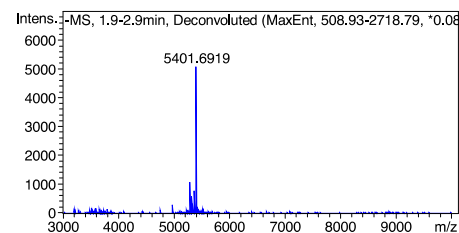
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #115-174

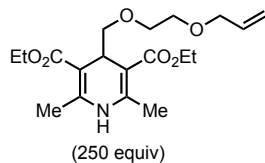
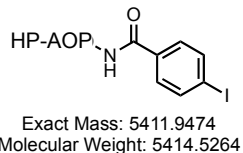


#	m/z	I
1	621.0622	1228
2	1079.3308	727
3	1349.4150	833
4	1349.6595	666
5	1798.8931	726
6	1799.2270	1633
7	1799.5570	1952
8	1799.8895	1672
9	1800.2203	1253
10	1800.5525	742

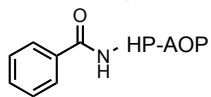


#	m/z	I	
1	4977.5186	277	
2	5287.6480	1080	protodebromination
3	5327.6681	619	
4	5366.5290	788	starting material
5	5401.6919	5075	product

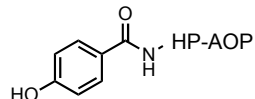
Cross-Coupling Product-3d



Protodehalogenation



Phenol



Product: 72%
Starting material: 0%
Protodebromination: 24%

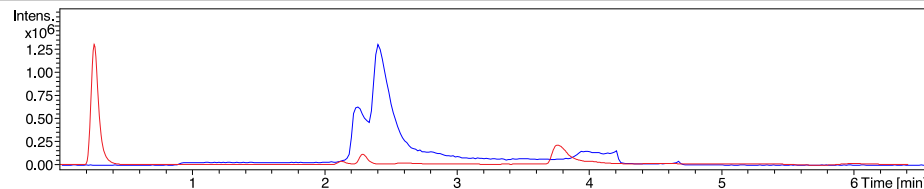
Compound Spectrum List Report

Analysis Info

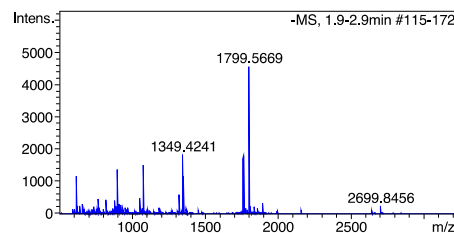
Analysis Name: D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-7-4_74_01_8202.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20180430-7-4
 Comment:
 Acquisition Date: 5/8/2018 9:40:32 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

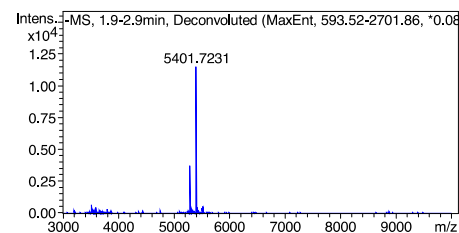
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #115-172

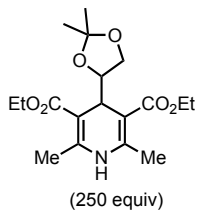
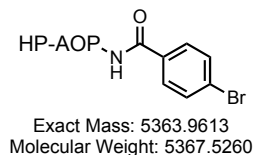


#	m/z	I
1	1349.4241	1832
2	1349.6668	1654
3	1761.2118	1539
4	1761.5461	1804
5	1798.9051	1615
6	1799.2351	3571
7	1799.5669	4558
8	1799.8997	4027
9	1800.2307	2795
10	1800.5607	1556

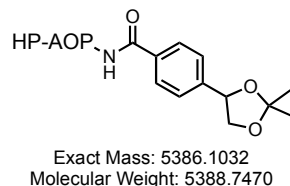


#	m/z	I	
1	3524.4637	679	protodebromination
2	5267.6652	3761	
3	5401.7231	11502	product

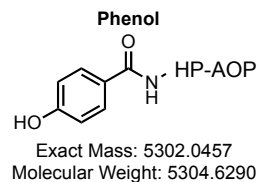
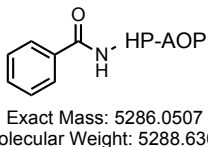
Cross-Coupling Product-3a



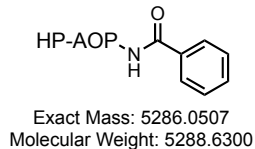
4CzIPN (50 mol %)
Ni(TMHD)₂ (2.0 equiv)
80:20 DMSO/H₂O (1 mM)
30W blue LED, 45 min



Protodehalogenation



Protodebromination



Product: 63%
Starting material: 0%
Protodebromination: 5%

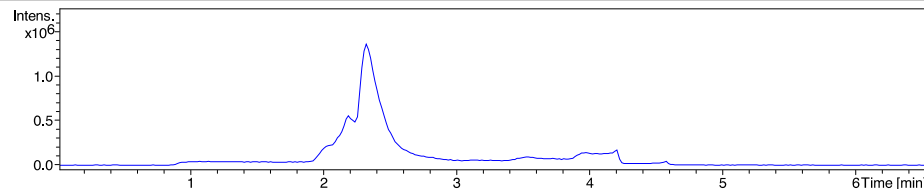
Compound Spectrum List Report

Analysis Info

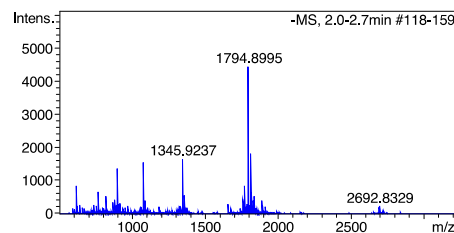
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-050118\JPP-20180425-8-1J_76_01_8153.d
Method 1200col2_10to90in4.m
Sample Name JPP-20180425-8-1J
Comment
Acquisition Date 5/1/2018 5:48:17 PM
Operator gsk
Instrument micrOTOF 213750.00199

Acquisition Parameter

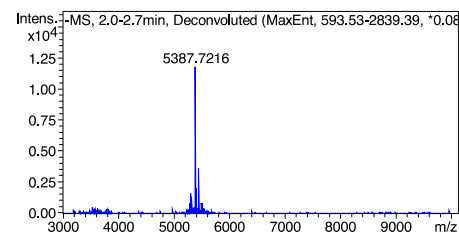
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-2.7min #118-159



#	m/z	I
1	1076.5378	1559
2	1345.9237	1659
3	1794.2320	1780
4	1794.5649	3870
5	1794.8995	4438
6	1795.2279	4344
7	1795.5641	2924
8	1795.8929	1644
9	1814.2309	1825
10	1814.5661	1706

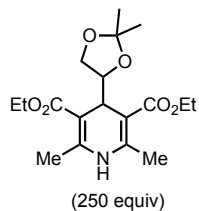
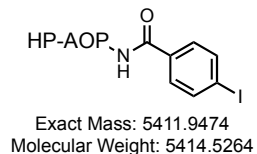


#	m/z	I
1	5285.6617	871
2	5312.6590	1622
3	5387.7216	11797
4	5445.7161	3615
5	5502.7507	846

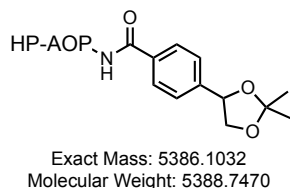
protodebromination

product

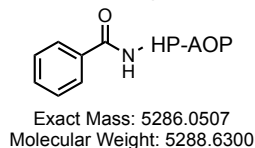
Cross-Coupling Product-3a



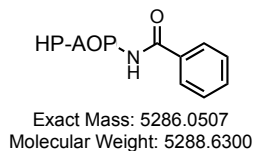
4CzIPN (50 mol %)
 Ni(TMHD)₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 45 min



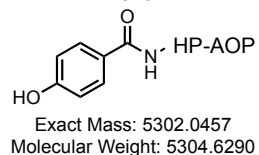
Protodehalogenation



Protodeiodination



Phenol



Product: 45%
Starting Material: 3%
Protodehalogenation: 6%

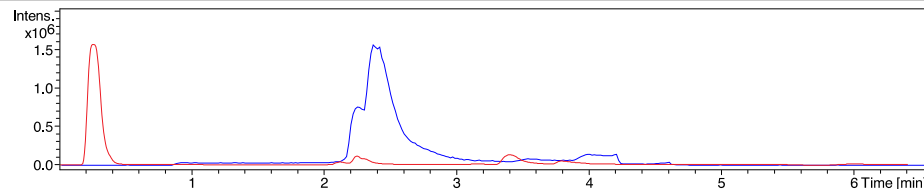
Compound Spectrum List Report

Analysis Info

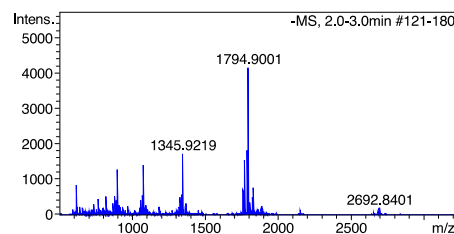
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-051718\DNA-20180514-1-6_16_01_8296.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180514-1-6
 Comment
 Acquisition Date 5/17/2018 3:18:49 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

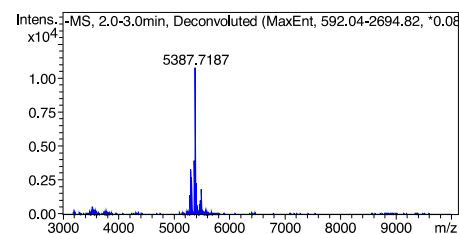
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.0min #121-180



#	m/z	I
1	1345.9219	1724
2	1346.1670	1579
3	1769.8814	1538
4	1788.8971	1822
5	1794.2348	1773
6	1794.5651	3752
7	1794.9001	4145
8	1795.2312	3858
9	1795.5633	2739
10	1795.8978	1744



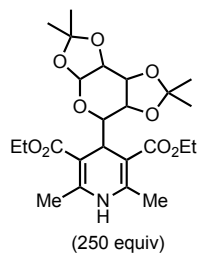
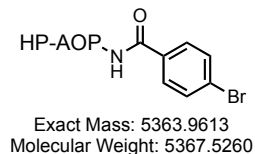
#	m/z	I
1	3540.4264	599
2	5287.6688	1403
3	5312.6513	3318
4	5369.7115	3938
5	5387.7187	10740
6	5413.7211	736
7	5471.7553	1063
8	5489.7705	1842

Protodehalogenation

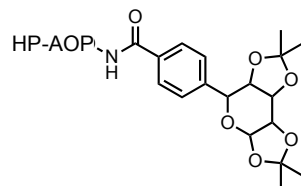
product

Starting material

Cross-Coupling Product-3e

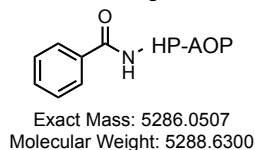


4CzIPN (50 mol %)
Ni(TMHD)₂ (2.0 equiv)
80:20 DMSO/H₂O (1 mM)
30W blue LED, 45 min

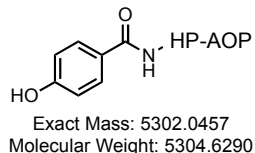


Exact Mass: 5514.1505
Molecular Weight: 5516.8740

Protodehalogenation



Phenol



Product: 81%
Starting material: 0%
Protodebromination: 10%

Compound Spectrum List Report

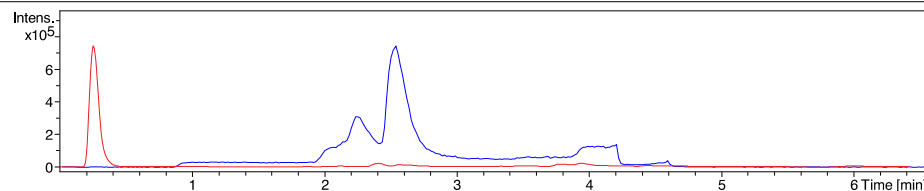
Analysis Info

Analysis Name: D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-2-12_22_01_8182.d
Method: 1200col2_10to90in4.m
Sample Name: JPP-20180430-2-12
Comment:

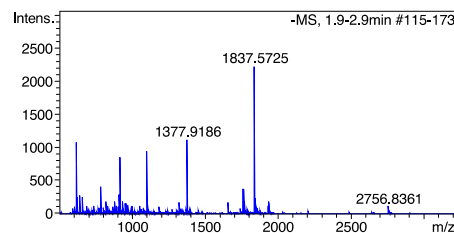
Acquisition Date: 5/8/2018 7:12:54 PM
Operator: gsk
Instrument: micrOTOF
213750.00199

Acquisition Parameter

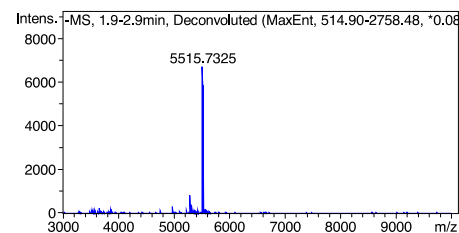
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #115-173

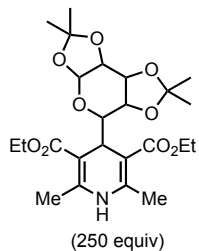


#	m/z	I
1	621.0636	1076
2	1102.1399	947
3	1377.6741	962
4	1377.9186	1112
5	1378.1652	1024
6	1837.2366	1765
7	1837.5725	2218
8	1837.9015	2036
9	1838.2323	1361
10	1838.5661	869

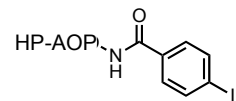


#	m/z	I	
1	4977.5292	336	protodebromination
2	5287.6540	826	
3	5313.6458	395	product
4	5515.7325	6707	

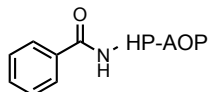
Cross-Coupling Product-3e



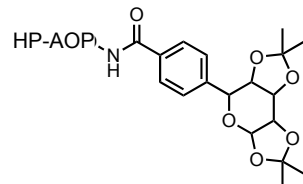
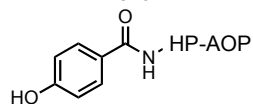
4CzIPN (50 mol %)
 Ni(TMHD)₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 45 min



Protodehalogenation



Phenol



Product: 71%
Starting material: 0%
Protodebromination: 24%

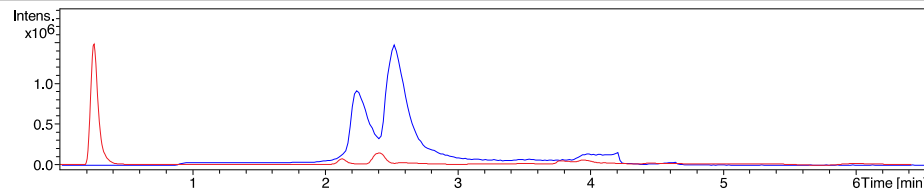
Compound Spectrum List Report

Analysis Info

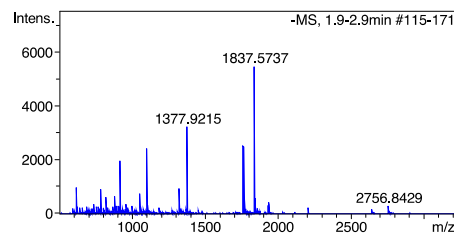
Analysis Name	D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-7-3_73_01_8201.d	Acquisition Date	5/8/2018 9:33:09 PM	
Method	1200col2_10to90in4.m	Operator	gsk	
Sample Name	JPP-20180430-7-3	Instrument	micrOTOF	213750.00199
Comment				

Acquisition Parameter

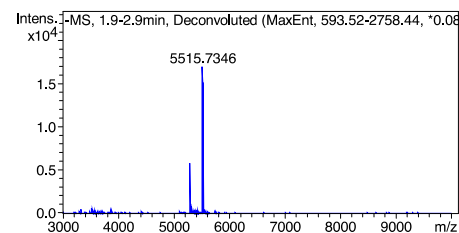
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #115-171

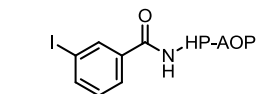


#	m/z	I
1	1102.1414	2419
2	1377.6752	2423
3	1377.9215	3219
4	1378.1689	2822
5	1761.5422	2497
6	1761.8748	2321
7	1837.2399	4853
8	1837.5737	5457
9	1837.9053	4889
10	1838.2373	3668



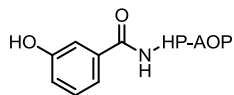
#	m/z	I	
1	5287.6521	5812	← protodebromination
2	5312.6400	1084	
3	5515.7346	16952	← product

Cross-Coupling Product-3f



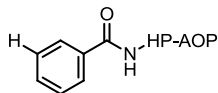
Exact Mass: 5411.9474
Molecular Weight: 5414.4874

Phenol

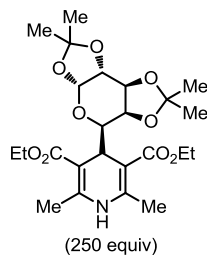


Exact Mass: 5302.0457
Molecular Weight: 5304.5903

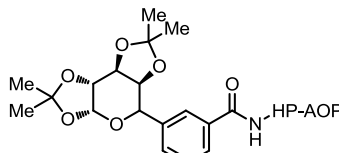
Protodehalogenation



Exact Mass: 5286.0507
Molecular Weight: 5288.5909



4CzIPN (50 mol %)
Ni(TMHD)₂ (2 equiv)
80:20 DMSO/H₂O
30 W blue LED, 45 min



Exact Mass: 5514.1505
Molecular Weight: 5516.8326

Product: 55%
Aryl Halide: 0%
Protodehalogenation: 13%
Phenol: 5%

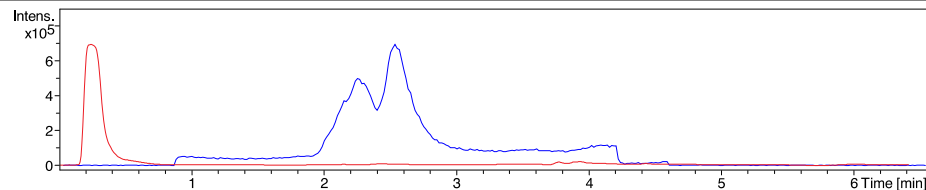
Compound Spectrum List Report

Analysis Info

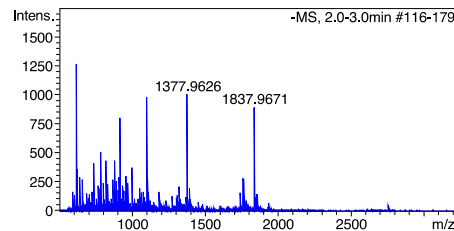
Analysis Name X:\Chem MS Data\TOF\Data_2018\Nov 2018\utof-111618\JHS-181105-4_14_01_10238.d
Method 1200col2_10to90in4.m
Sample Name JHS-181105-4
Comment
Acquisition Date 11/16/2018 6:02:37 PM
Operator gsk
Instrument micrOTOF 213750.00199

Acquisition Parameter

Source Type ESI Ion Polarity Negative Set Nebulizer 3.5 Bar
Focus Active Set Dry Heater 220 °C
Scan Begin 510 m/z Set Capillary 2500 V Set Dry Gas 11.0 l/min
Scan End 3200 m/z Set End Plate Offset -400 V Set Divert Valve Waste

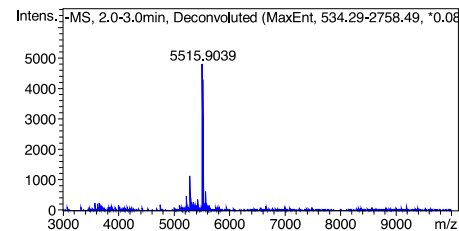


-MS, 2.0-3.0min #116-179



#	m/z	I
1	621.0814	1266
2	918.3091	803
3	1101.9833	950
4	1102.1775	980
5	1102.3760	830
6	1377.7242	799
7	1377.9626	1000
8	1378.2144	843
9	1837.6330	878
10	1837.9671	892

#	m/z	I
1	621.0814	1266
2	918.3091	803
3	1101.9833	950
4	1102.1775	980
5	1102.3760	830
6	1377.7242	799
7	1377.9626	1000
8	1378.2144	843
9	1837.6330	878
10	1837.9671	892



#	m/z	I
1	3582.4397	265
2	3656.7145	251
3	5225.8091	485
4	5287.8301	1129
5	5302.8638	432
6	5312.8265	411
7	5345.8170	295
8	5436.8953	376
9	5515.9039	4805
10	5537.8081	255

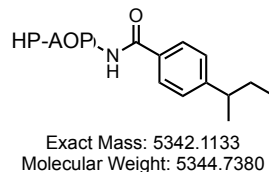
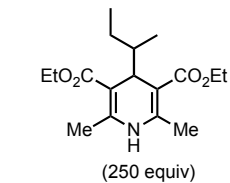
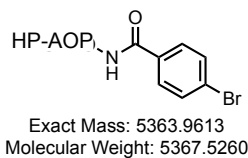
#	m/z	I
1	5573.9171	630

protodehalogenation

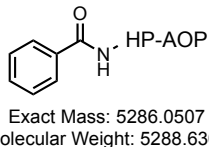
Phenol

Product

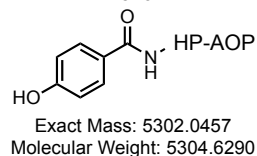
Cross-Coupling Product-3g



Protodehalogenation



Phenol



Product: 77%
Starting material: 0%
Protodebromination: 7%

Compound Spectrum List Report

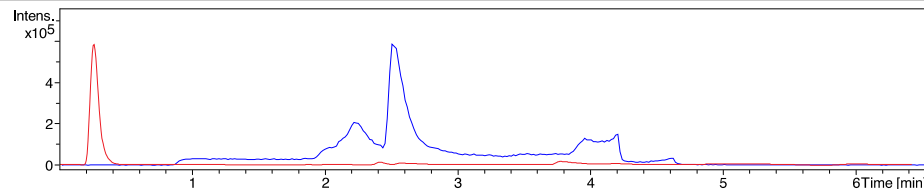
Analysis Info

Analysis Name: D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-2-10_20_01_8180.d
Method: 1200col2_10to90in4.m
Sample Name: JPP-20180430-2-10
Comment:

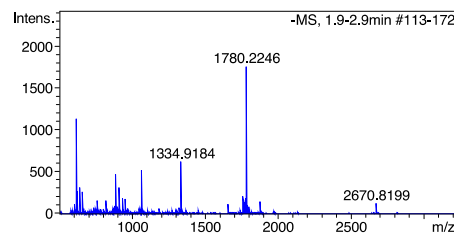
Acquisition Date: 5/8/2018 6:58:12 PM
Operator: gsk
Instrument: micrOTOF
213750.00199

Acquisition Parameter

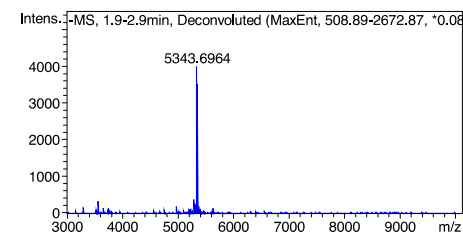
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #113-172



#	m/z	I
1	621.0620	1125
2	1067.7272	521
3	1334.6690	522
4	1334.9184	621
5	1779.5559	672
6	1779.8917	1357
7	1780.2246	1754
8	1780.5573	1554
9	1780.8878	1073
10	1781.2173	613

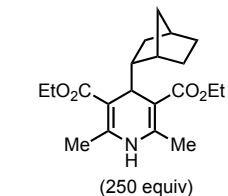
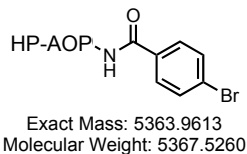


#	m/z	I
1	3561.8002	324
2	4978.4784	206
3	5286.6625	383
4	5311.6285	269
5	5343.6964	3991

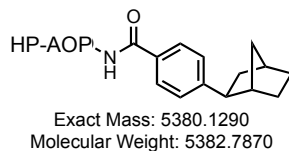
protodebromination

product

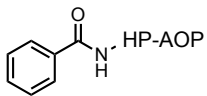
Cross-Coupling Product-3h



4CzIPN (50 mol %)
 Ni(TMHD)₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 45 min

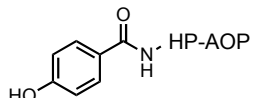


Protodehalogenation



Exact Mass: 5286.0507
 Molecular Weight: 5288.6300

Phenol



Exact Mass: 5302.0457
 Molecular Weight: 5304.6290

Product: 76%
Starting material: 0%
Protodebromination: 17%

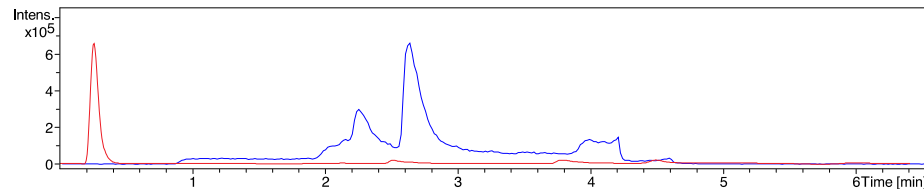
Compound Spectrum List Report

Analysis Info

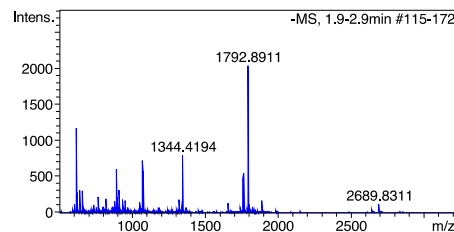
Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-2-6_16_01_8176.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180430-2-6
 Comment
 Acquisition Date 5/8/2018 6:28:32 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

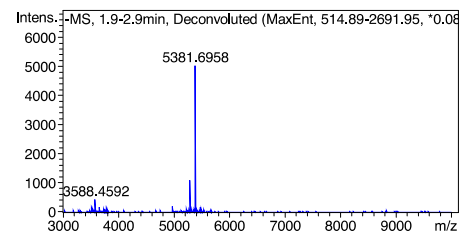
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #115-172

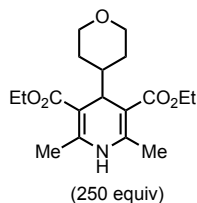
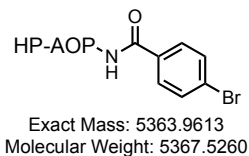


#	m/z	I
1	621.0620	1172
2	1075.3313	720
3	1344.4194	799
4	1344.6616	722
5	1792.2288	785
6	1792.5596	1736
7	1792.8911	2039
8	1793.2224	1795
9	1793.5555	1221
10	1793.8860	740

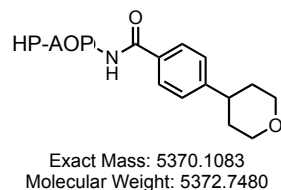


#	m/z	I	
1	3588.4592	449	protodebromination
2	5287.6254	1097	
3	5381.6958	5022	product

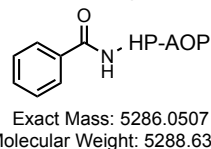
Cross-Coupling Product-3i



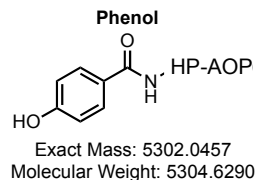
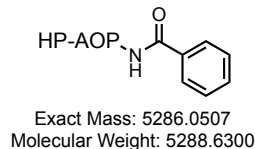
4CzIPN (50 mol %)
 Ni(TMHD)₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 45 min



Protodehalogenation



Protodebromination



Product: 58%
Starting material: 22%
Protodebromination: 11%

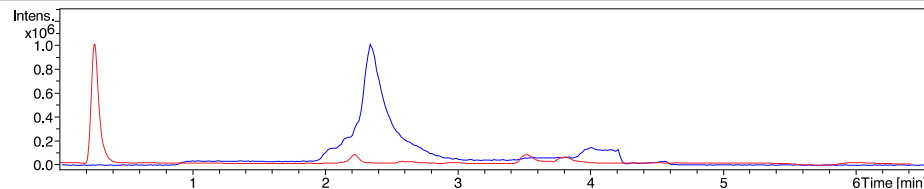
Compound Spectrum List Report

Analysis Info

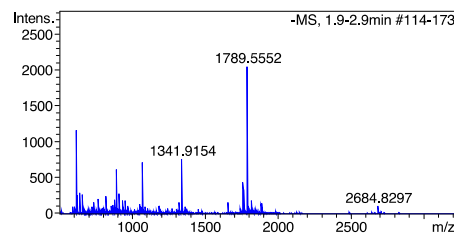
Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-2-1_11_01_8171.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180430-2-1
 Comment
 Acquisition Date 5/8/2018 5:51:34 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

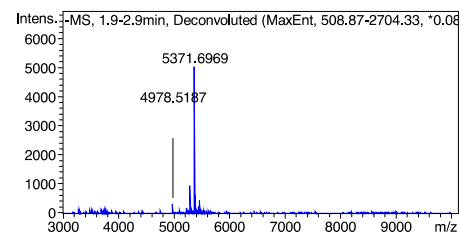
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #114-173

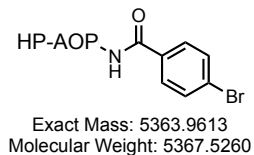


#	m/z	I
1	621.0663	1155
2	1073.3336	719
3	1341.9154	761
4	1787.8427	714
5	1788.1754	753
6	1788.8829	1001
7	1789.2239	1660
8	1789.5552	2044
9	1789.8879	1659
10	1790.2194	1147

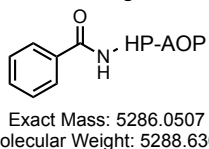


#	m/z	I	
1	4978.4968	326	protodebromination
2	5287.6573	955	
3	5366.5494	1959	starting material
4	5371.6969	5029	
5	5457.7443	465	product

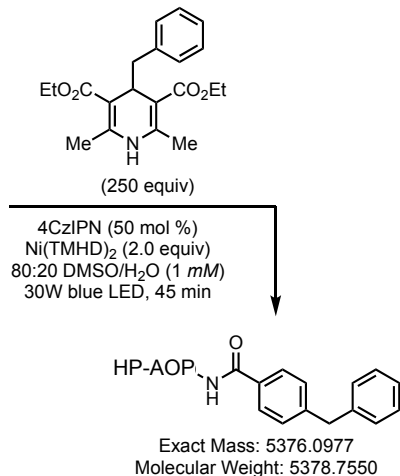
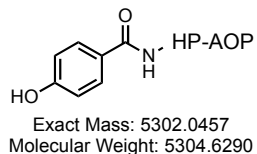
Cross-Coupling Product-3j



Protodehalogenation



Phenol



Product: 78%
Starting material: 0%
Protodebromination: 6%

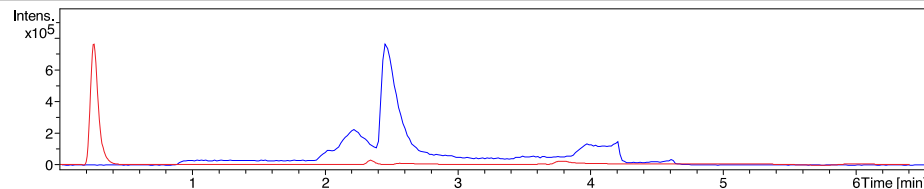
Compound Spectrum List Report

Analysis Info

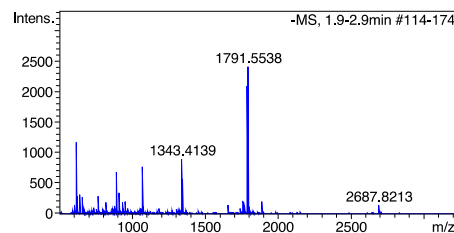
Analysis Name: D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-2-3_13_01_8173.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20180430-2-3
 Comment:
 Acquisition Date: 5/8/2018 6:06:20 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

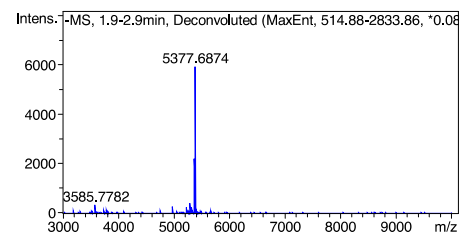
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #114-174

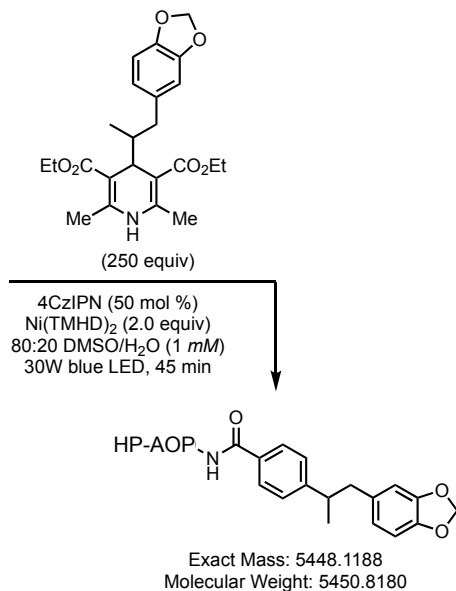
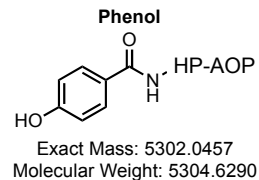
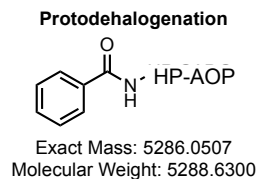
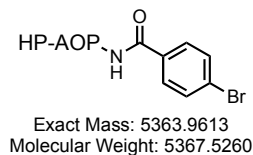


#	m/z	I
1	621.0655	1163
2	1074.5327	774
3	1343.4139	903
4	1343.6638	806
5	1790.8911	857
6	1791.2218	2085
7	1791.5538	2409
8	1791.8847	2048
9	1792.2192	1438
10	1792.5498	892



#	m/z	I	
1	3585.7782	345	
2	4978.5219	283	
3	5286.6425	430	protodebromination
4	5312.6456	266	
5	5313.6525	241	
6	5377.6874	5923	product

Cross-Coupling Product-3k



Product: 70%
Starting material: 0%
Protodebromination: 20%

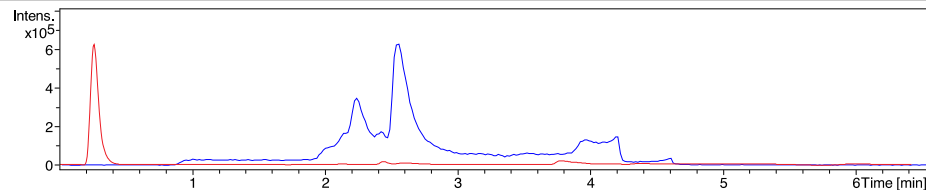
Compound Spectrum List Report

Analysis Info

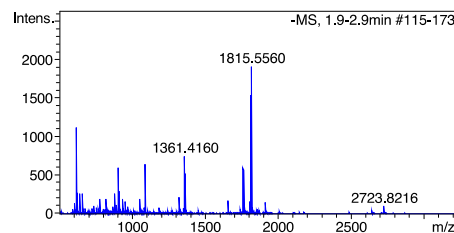
Analysis Name	D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-2-11_21_01_8181.d	Acquisition Date	5/8/2018 7:05:33 PM
Method	1200col2_10to90in4.m	Operator	gsk
Sample Name	JPP-20180430-2-11	Instrument	micrOTOF
Comment			213750.00199

Acquisition Parameter

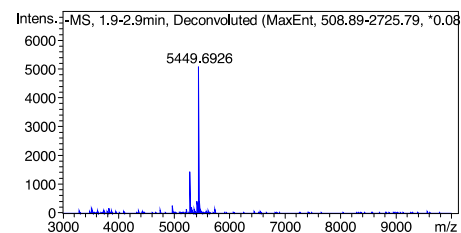
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #115-173



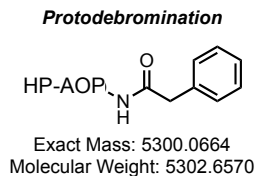
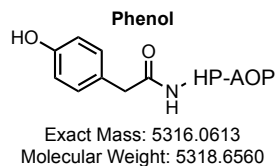
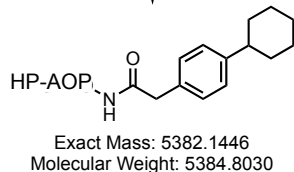
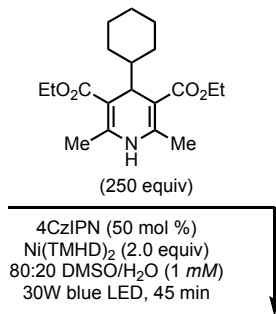
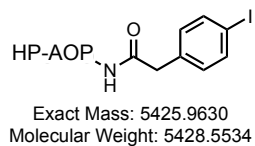
#	m/z	I
1	621.0638	1113
2	1089.1323	639
3	1361.4160	750
4	1361.6624	665
5	1814.8960	675
6	1815.2236	1536
7	1815.5560	1906
8	1815.8897	1547
9	1816.2196	1111
10	1816.5548	659



#	m/z	I	
1	4978.5130	276	
2	5267.6409	1433	
3	5421.6638	424	
4	5449.6926	5078	

protodebromination
 product

Cross-Coupling Product-3I



Product: 55%
Starting material: 0%
Protodebromination: 35%

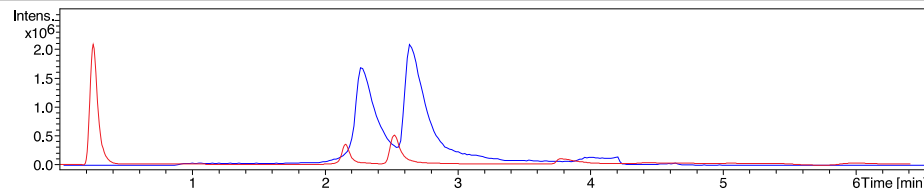
Compound Spectrum List Report

Analysis Info

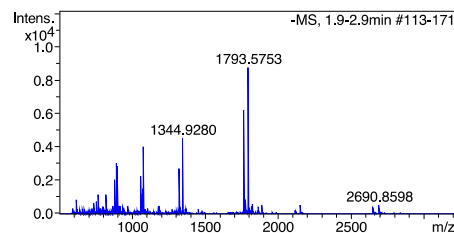
Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-6-1_61_01_8195.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180430-6-1
 Comment
 Acquisition Date 5/8/2018 8:48:56 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

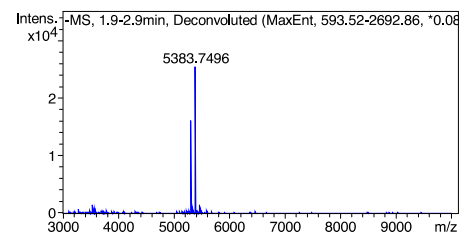
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #113-171

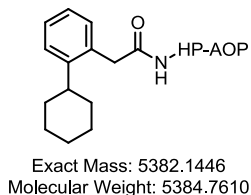
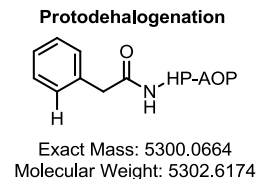
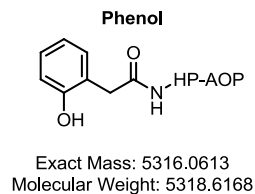
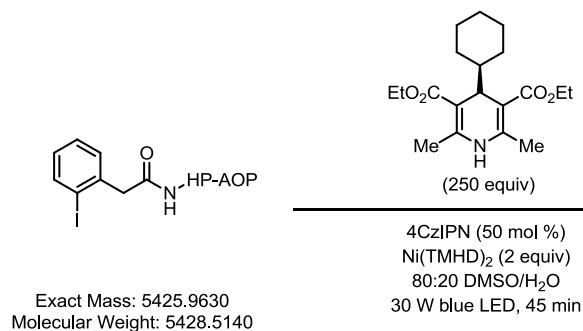


#	m/z	I
1	1075.7427	4032
2	1344.9280	4520
3	1345.1759	4040
4	1765.8859	5487
5	1766.2202	6219
6	1766.5513	5360
7	1793.2431	7206
8	1793.5753	8751
9	1793.9088	7826
10	1794.2397	5877



#	m/z	I	
1	3535.1542	1545	
2	5301.6823	16113	protodebromination
3	5326.6916	1974	
4	5383.7496	25453	
5	5467.8305	1487	product

Cross-Coupling Product-3m



Product: 75%
Aryl Halide: 0%
Protodehalogenation: 21%
Phenol: 0%

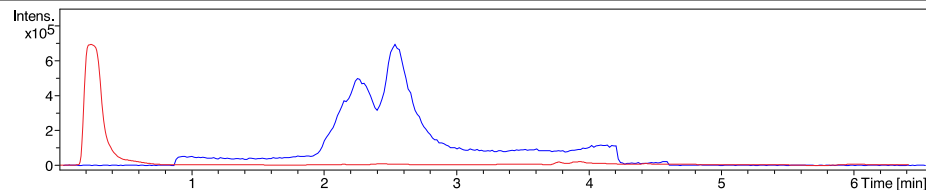
Compound Spectrum List Report

Analysis Info

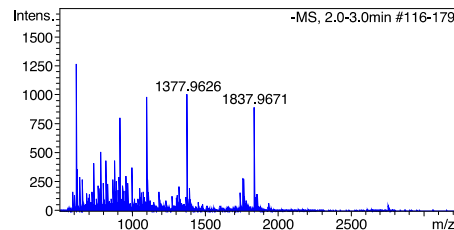
Analysis Name: X:\Chem MS Data\TOF\Data_2018\Nov 2018\utof-111618\JHS-181105-4_14_01_10238.d
 Method: 1200col2_10to90in4.m
 Sample Name: JHS-181105-4
 Comment:
 Acquisition Date: 11/16/2018 6:02:37 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste

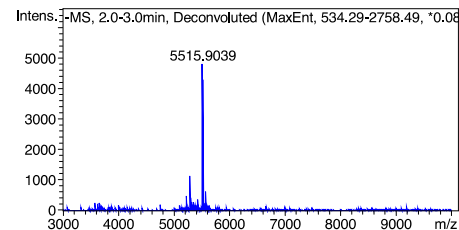


-MS, 2.0-3.0min #116-179



#	m/z	I
1	621.0814	1266
2	918.3091	803
3	1101.9833	950
4	1102.1775	980
5	1102.3760	830
6	1377.7242	799
7	1377.9626	1000
8	1378.2144	843
9	1837.6330	878
10	1837.9671	892

#	m/z	I
1	621.0814	1266
2	918.3091	803
3	1101.9833	950
4	1102.1775	980
5	1102.3760	830
6	1377.7242	799
7	1377.9626	1000
8	1378.2144	843
9	1837.6330	878
10	1837.9671	892



#	m/z	I
1	3582.4397	265
2	3656.7145	251
3	5225.8091	485
4	5287.8301	1129
5	5302.8638	432
6	5312.8265	411
7	5345.8170	295
8	5436.8953	376
9	5515.9039	4805
10	5537.8081	255

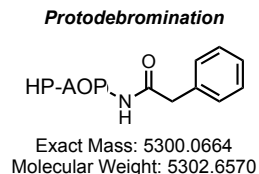
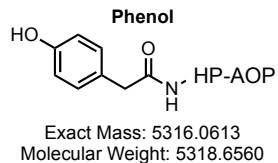
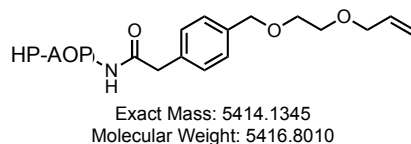
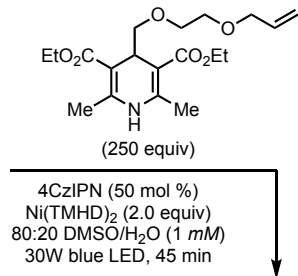
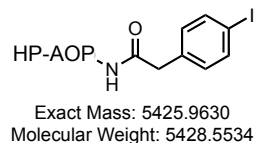
#	m/z	I
1	5573.9171	630

protodehalogenation

Phenol

Product

Cross-Coupling Product-3n



Product: 40%
Starting material: 2%
Protodebromination: 46%

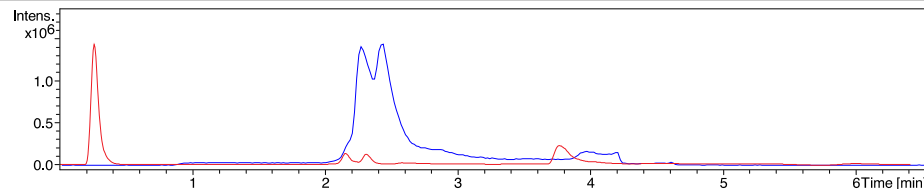
Compound Spectrum List Report

Analysis Info

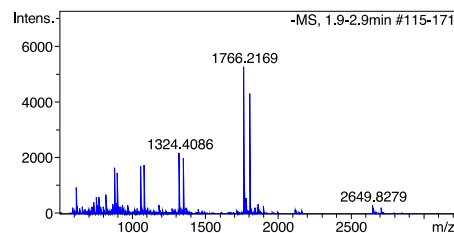
Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-6-4_64_01_8198.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180430-6-4
 Comment
 Acquisition Date 5/8/2018 9:11:02 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

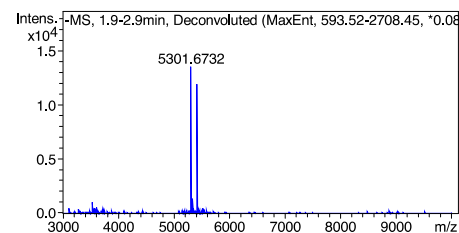
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #115-171

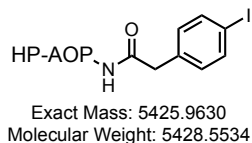


#	m/z	I
1	1324.4086	2194
2	1765.5519	2452
3	1765.8830	4726
4	1766.2169	5271
5	1766.5513	4498
6	1766.8835	3030
7	1803.9059	3710
8	1804.2400	4308
9	1804.5696	3929
10	1804.9029	2760

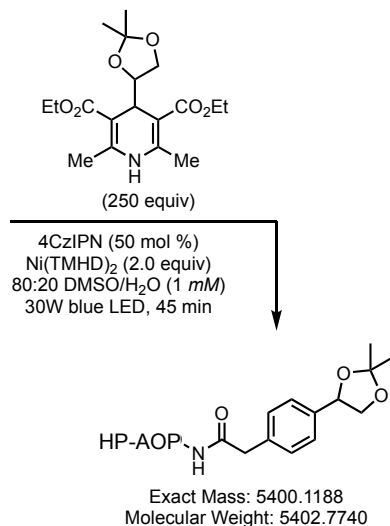
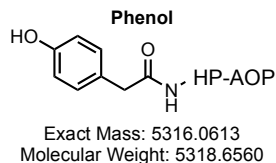
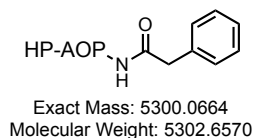


#	m/z	I	
1	3535.1482	1077	
2	5301.6732	13489	← protodebromination
3	5326.6919	977	
4	5341.6841	1342	
5	5415.7398	11945	← product
6	5427.5768	679	← starting material

Cross-Coupling Product-3o



Protodebromination



Product: 55%
Starting material: 5%
Protodebromination: 18%

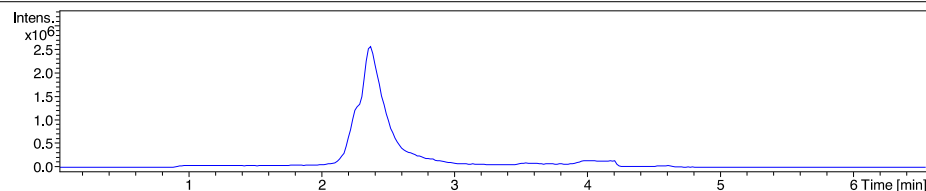
Compound Spectrum List Report

Analysis Info

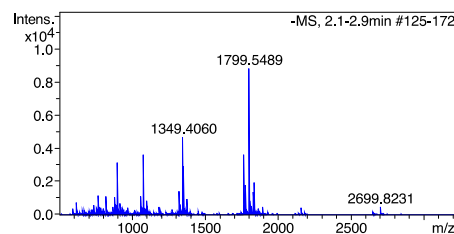
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-050118\JPP-20180425-8-6J_79_01_8156.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180425-8-6J
 Comment
 Acquisition Date 5/1/2018 6:10:36 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

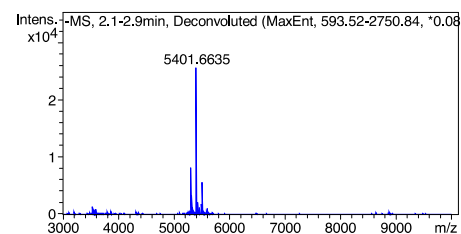
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.1-2.9min #125-172

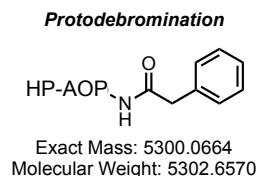
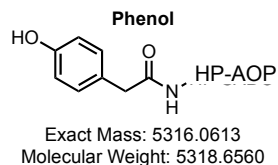
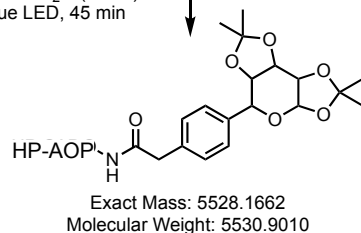
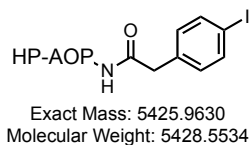


#	m/z	I
1	1079.3238	3647
2	1349.1598	3784
3	1349.4060	4683
4	1349.6543	4345
5	1766.2013	3651
6	1799.2169	7213
7	1799.5489	8834
8	1799.8800	8298
9	1800.2110	6199
10	1800.5455	3581



#	m/z	I	
1	3535.0998	1342	
2	5301.6204	8184	
3	5325.6164	3368	
4	5401.6635	25593	product
5	5427.5702	2141	
6	5503.7362	5560	starting material

Cross-Coupling Product-3p



Product: 48%
Starting material: 0%
Protodebromination: 42%

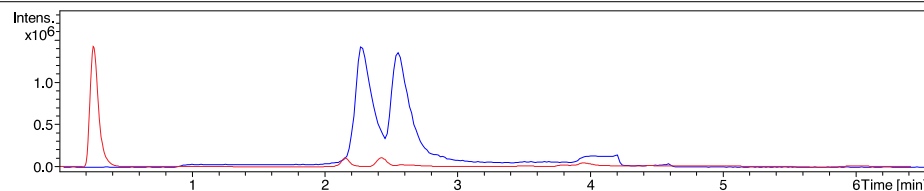
Compound Spectrum List Report

Analysis Info

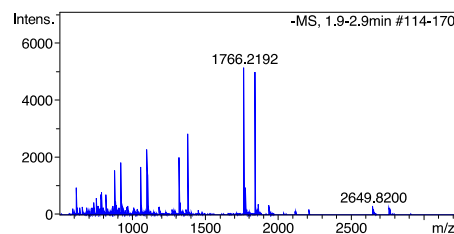
Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-6-3_63_01_8197.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180430-6-3
 Comment
 Acquisition Date 5/8/2018 9:03:40 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

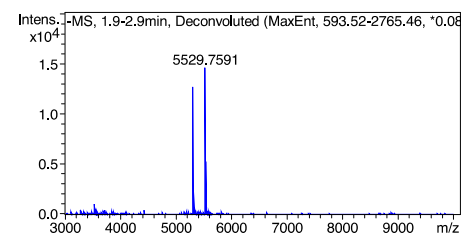
Source Type ESI
 Focus Active
 Scan Begin 510 m/z
 Scan End 3200 m/z
 Ion Polarity Negative
 Set Capillary 2500 V
 Set End Plate Offset -400 V
 Set Nebulizer 3.5 Bar
 Set Dry Heater 220 °C
 Set Dry Gas 11.0 l/min
 Set Divert Valve Waste



-MS, 1.9-2.9min #114-170



#	m/z	I
1	1381.4304	2814
2	1381.6763	2507
3	1765.8862	4529
4	1766.2192	5138
5	1766.5520	4199
6	1766.8826	2918
7	1841.9159	3998
8	1842.2464	4991
9	1842.5809	4588
10	1842.9124	3294

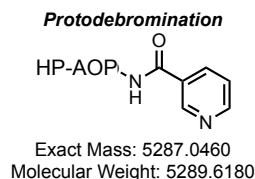
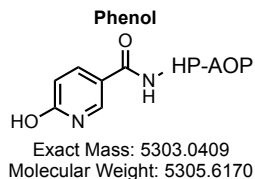
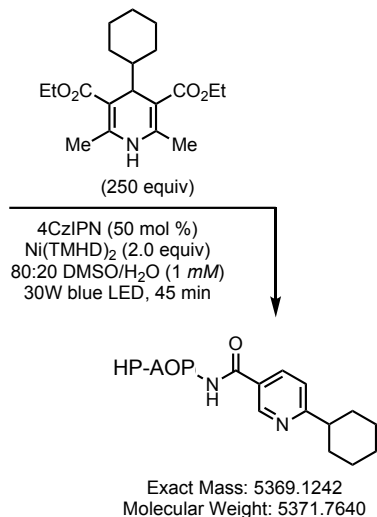
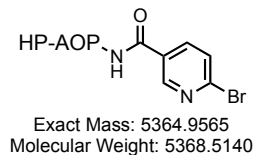


#	m/z	I
1	3533.7743	1086
2	5301.6831	12724
3	5326.6878	2228
4	5529.7591	14584

protodebromination

product

Cross-Coupling Product-3q



Product: 79%
Starting material: 0%
Protodebromination: 13%

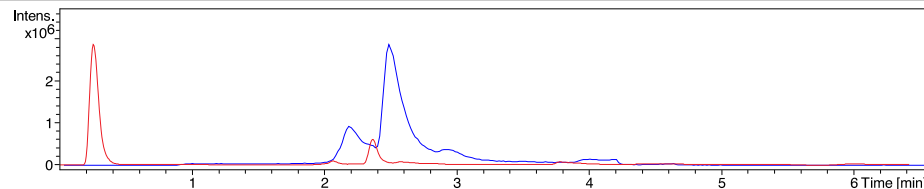
Compound Spectrum List Report

Analysis Info

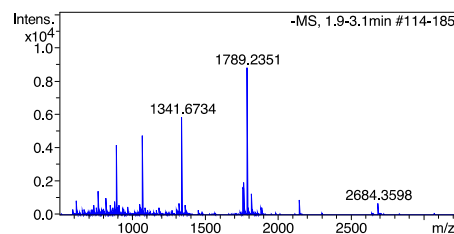
Analysis Name: D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-5-1_51_01_8191.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20180430-5-1
 Comment:
 Acquisition Date: 5/8/2018 8:19:25 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

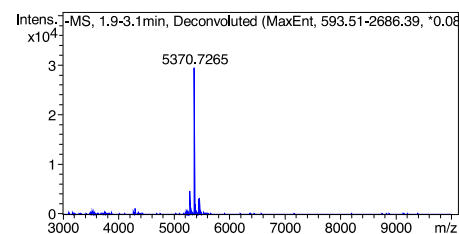
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.1min #114-185

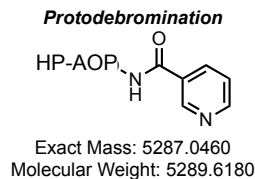
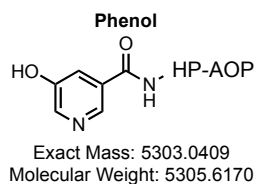
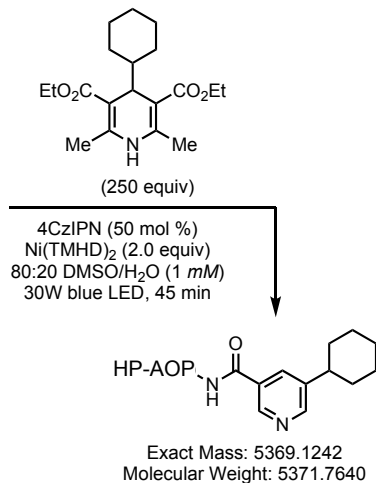
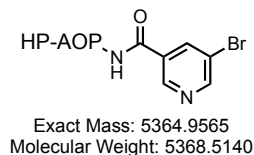


#	m/z	I
1	894.1118	4158
2	1073.1389	4746
3	1073.3384	4127
4	1341.4252	4753
5	1341.6734	5845
6	1341.9210	5021
7	1788.9022	7653
8	1789.2351	8787
9	1789.5664	8097
10	1789.8967	5606



#	m/z	I	
1	5288.6603	4714	protodebromination
2	5370.7265	29434	
3	5454.8048	3337	product

Cross-Coupling Product-3r



Product: 67%

Starting material: 0%

Protodebromination: 28%

Compound Spectrum List Report

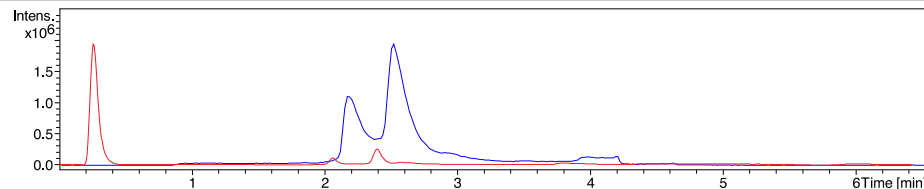
Analysis Info

Analysis Name: D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-4-1_41_01_8187.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20180430-4-1
 Comment:

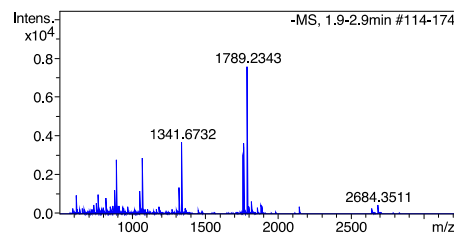
Acquisition Date: 5/8/2018 7:49:46 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

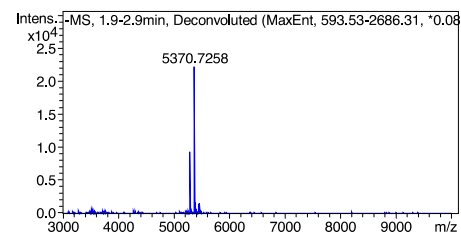
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #114-174



#	m/z	I
1	1341.4264	3058
2	1341.6732	3663
3	1341.9205	3315
4	1761.5442	3205
5	1761.8764	3605
6	1762.2089	3224
7	1788.9020	6425
8	1789.2343	7559
9	1789.5662	6591
10	1789.8975	4770

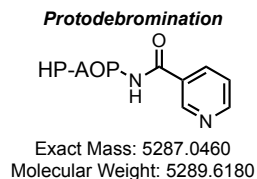
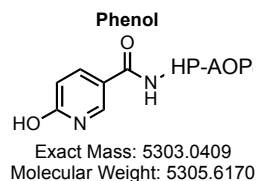
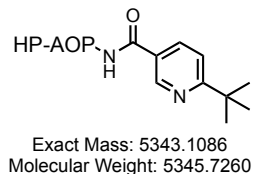
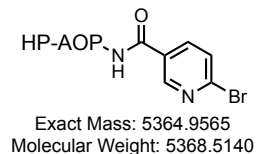


#	m/z	I
1	5288.6576	9311
2	5370.7258	22187
3	5454.8100	1579

protodebromination

product

Cross-Coupling Product-3s



Product: 46%
Starting material: 0%
Protodebromination: 30%
Phenol: 10%

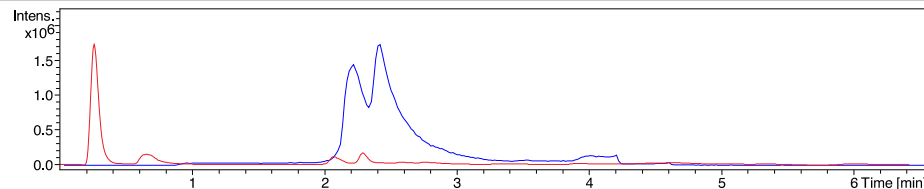
Compound Spectrum List Report

Analysis Info

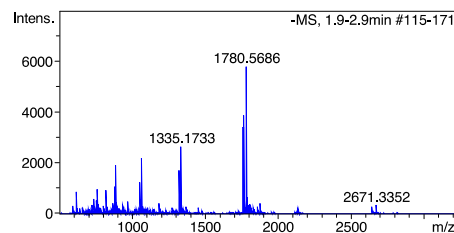
Analysis Name: D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-5-2_52_01_8192.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20180430-5-2
 Comment:
 Acquisition Date: 5/8/2018 8:26:50 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

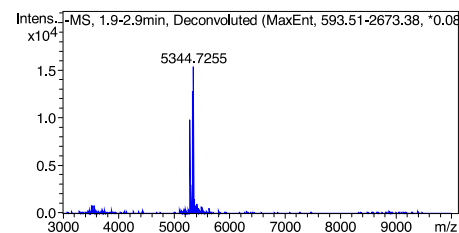
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #115-171

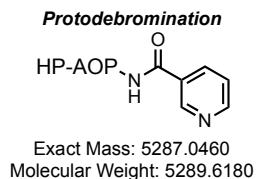
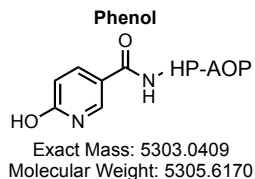
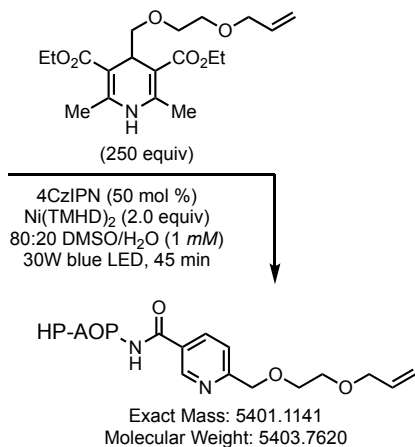
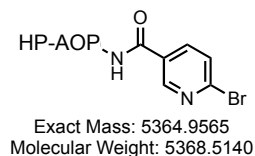


#	m/z	I
1	1335.1733	2642
2	1335.4204	2400
3	1761.5455	3385
4	1761.8773	3881
5	1762.2108	3245
6	1762.5428	2321
7	1780.2348	4792
8	1780.5686	5789
9	1780.9002	4822
10	1781.2308	3413



#	m/z	I	
1	3535.1737	796	
2	3565.1274	797	
3	5288.6544	9789	protodebromination
4	5302.6752	3016	phenol
5	5344.7255	15361	
6	5363.7013	1510	
7	5400.7630	800	product
8	5418.7893	1042	

Cross-Coupling Product-3t



Product: 62%
Starting material: 0%
Protodebromination: 14%
Phenol: 5%

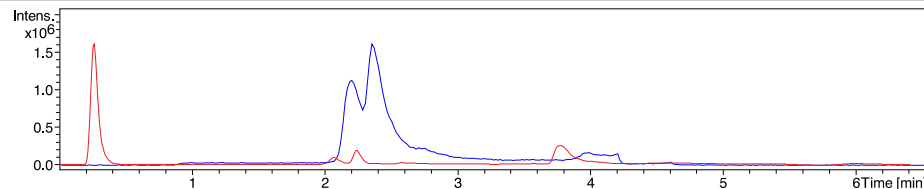
Compound Spectrum List Report

Analysis Info

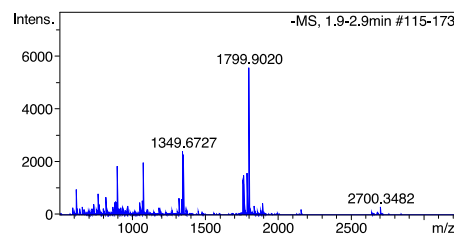
Analysis Name: D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-5-4_54_01_8194.d
 Acquisition Date: 5/8/2018 8:41:36 PM
 Method: 1200col2_10to90in4.m
 Operator: gsk
 Sample Name: JPP-20180430-5-4
 Instrument: micrOTOF
 Comment: 213750.00199

Acquisition Parameter

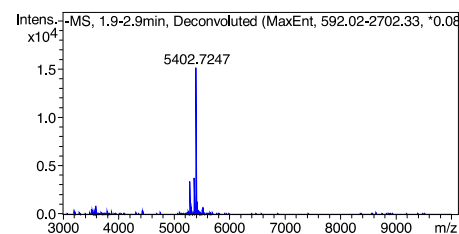
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #115-173

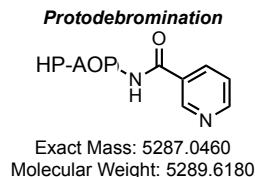
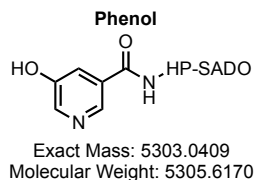
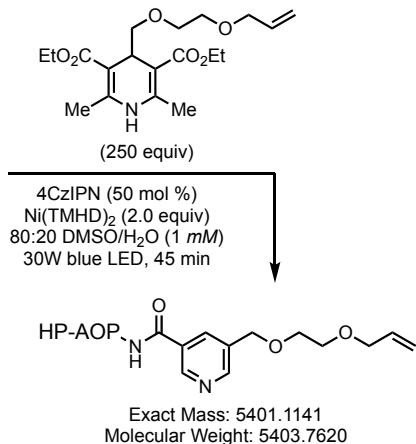
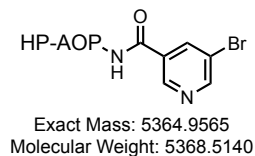


#	m/z	I
1	1079.5379	1973
2	1349.4255	1978
3	1349.6727	2406
4	1349.9153	2286
5	1799.2362	2178
6	1799.5685	4369
7	1799.9020	5559
8	1800.2335	4944
9	1800.5636	3400
10	1800.8949	2122



#	m/z	I	
1	5288.6647	3448	protodebromination
2	5303.6614	1146	phenol
3	5362.6921	3816	
4	5402.7247	15126	product
5	5518.7926	779	

Cross-Coupling Product-3u



Product: 58%
Starting material: 0%
Protodebromination: 35%

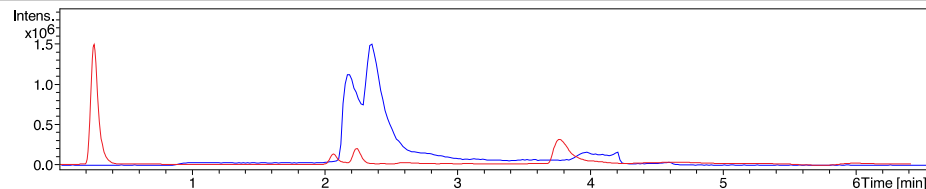
Compound Spectrum List Report

Analysis Info

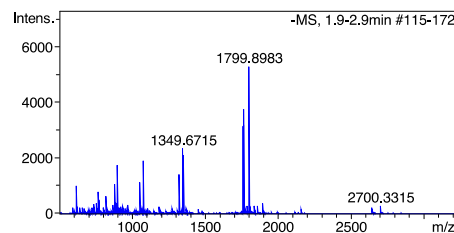
Analysis Name: D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-4-4_44_01_8190.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20180430-4-4
 Comment:
 Acquisition Date: 5/8/2018 8:12:02 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

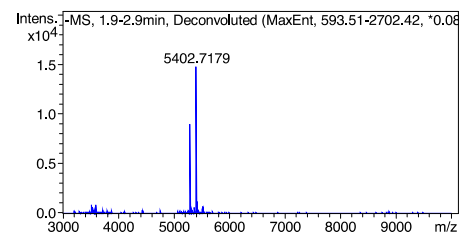
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #115-172

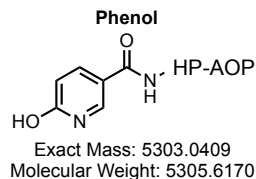
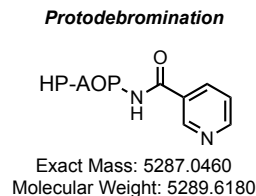
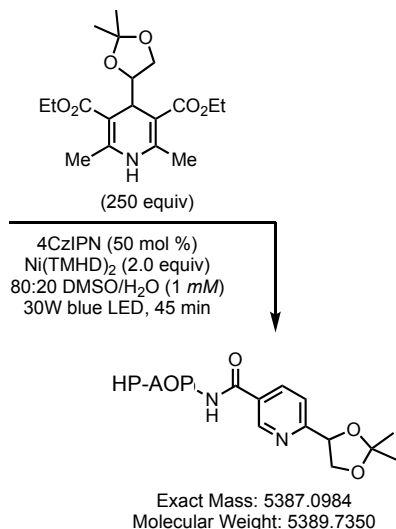
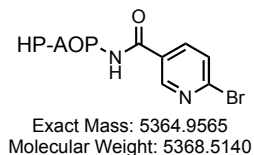


#	m/z	I
1	1349.6715	2334
2	1349.9162	2104
3	1761.5447	3149
4	1761.8763	3733
5	1762.2118	3173
6	1762.5428	2152
7	1799.5645	4494
8	1799.8983	5283
9	1800.2297	4648
10	1800.5621	3382



#	m/z	I	
1	3525.7641	919	
2	5288.6545	8971	protodebromination
3	5402.7179	14751	
4	5517.7955	737	product

Cross-Coupling Product-3v



Product: 66%
Starting material: 0%
Protodebromination: 9%

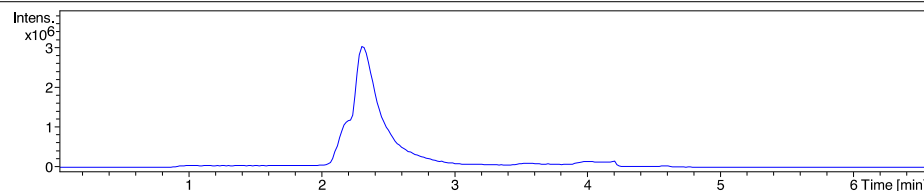
Compound Spectrum List Report

Analysis Info

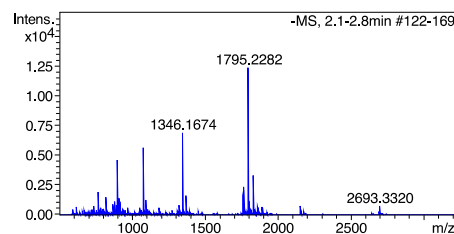
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-050118\JPP-20180425-8-5J_78_01_8155.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180425-8-5J
 Comment
 Acquisition Date 5/1/2018 6:03:12 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

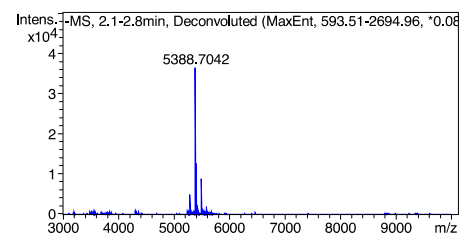
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.1-2.8min #122-169



#	m/z	I
1	897.1077	4630
2	1076.7330	5654
3	1345.9206	5812
4	1346.1674	6909
5	1346.4163	6310
6	1794.5614	4670
7	1794.8948	9877
8	1795.2282	12335
9	1795.5602	10553
10	1795.8899	7395

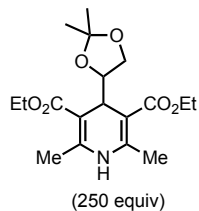
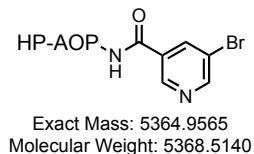


#	m/z	I
1	5288.6526	4916
2	5388.7042	36427
3	5406.7089	2790
4	5490.7539	8853
5	5592.7828	1902

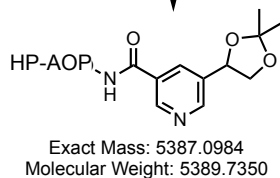
protodebromination

product

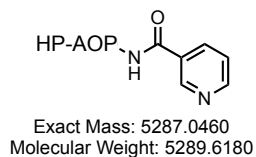
Cross-Coupling Product-3w



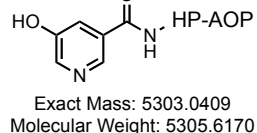
4CzIPN (50 mol %)
Ni(TMHD)₂ (2.0 equiv)
80:20 DMSO/H₂O (1 mM)
30W blue LED, 45 min



Protodebromination



Phenol



Product: 69%
Starting material: 0%
Protodebromination: 10%

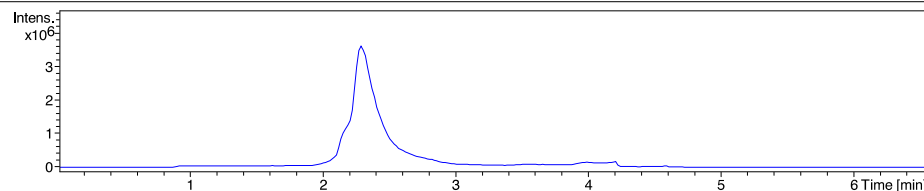
Compound Spectrum List Report

Analysis Info

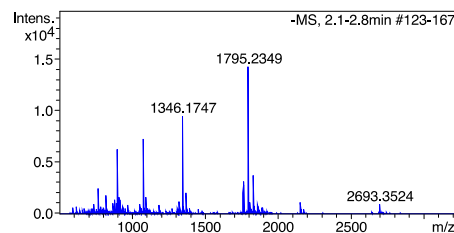
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-050118\JPP-20180425-8-4J_77_01_8154.d
Method 1200col2_10to90in4.m
Sample Name JPP-20180425-8-4J
Comment
Acquisition Date 5/1/2018 5:55:41 PM
Operator gsk
Instrument micrOTOF 213750.00199

Acquisition Parameter

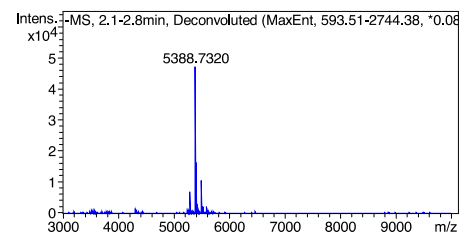
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.1-2.8min #123-167

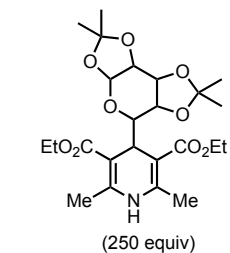
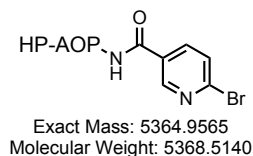


#	m/z	I
1	1076.5415	6274
2	1076.7411	7227
3	1076.9387	6662
4	1345.9269	7924
5	1346.1747	9449
6	1346.4213	8268
7	1794.9036	12068
8	1795.2349	14227
9	1795.5668	12380
10	1795.8976	8526

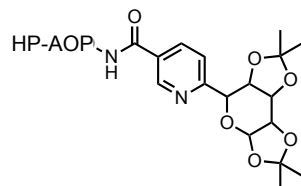


#	m/z	I	
1	5288.6759	7049	protodebromination
2	5388.7320	47139	
3	5415.7341	3102	
4	5489.7778	10719	product

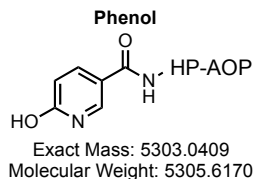
Cross-Coupling Product-3x



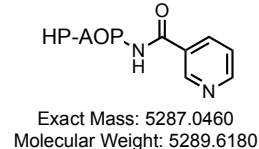
4CzIPN (50 mol %)
 Ni(TMHD)₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 45 min



Exact Mass: 5515.1458
 Molecular Weight: 5517.8620



Protodebromination



Product: 71%
Starting material: 0%
Protodebromination: 17%
Phenol: 12%

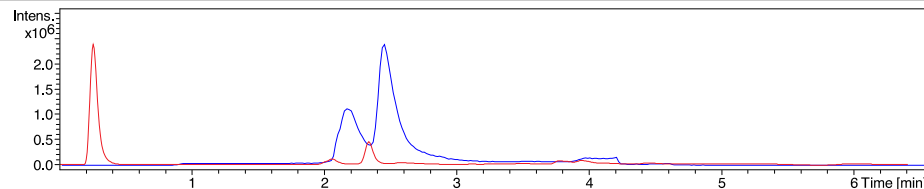
Compound Spectrum List Report

Analysis Info

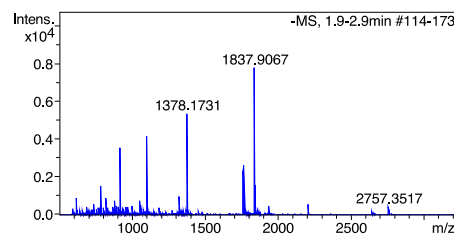
Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-5-3_53_01_8193.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180430-5-3
 Comment
 Acquisition Date 5/8/2018 8:34:13 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

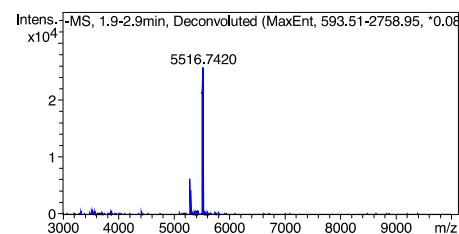
Source Type ESI Ion Polarity Negative Set Nebulizer 3.5 Bar
 Focus Active Set Dry Heater 220 °C
 Scan Begin 510 m/z Set Capillary 2500 V Set Dry Gas 11.0 l/min
 Scan End 3200 m/z Set End Plate Offset -400 V Set Divert Valve Waste



-MS, 1.9-2.9min #114-173



#	m/z	I
1	918.4498	3568
2	1102.3425	4130
3	1102.5406	3837
4	1377.9254	4180
5	1378.1731	5357
6	1378.4209	4713
7	1837.5750	5897
8	1837.9067	7758
9	1838.2406	6958
10	1838.5709	5043



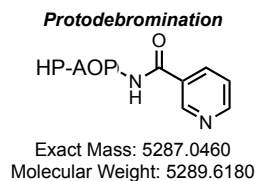
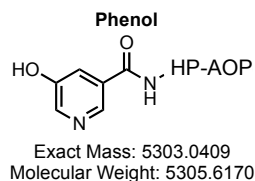
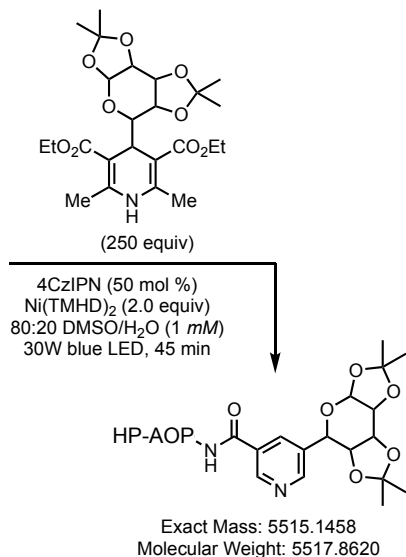
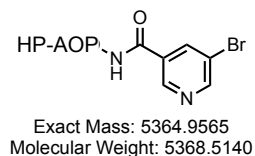
#	m/z	I
1	5288.6448	6183
2	5304.6517	4210
3	5516.7420	25692

protodebromination

phenol

product

Cross-Coupling Product-3y



Product: 46%
Starting material: 0%
Protodebromination: 54%

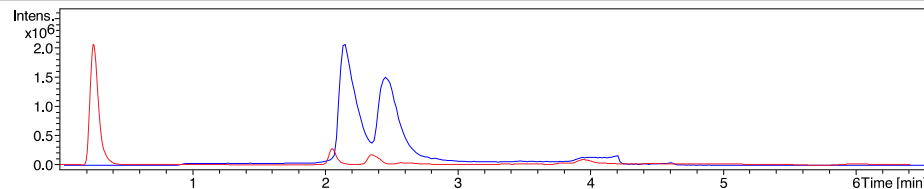
Compound Spectrum List Report

Analysis Info

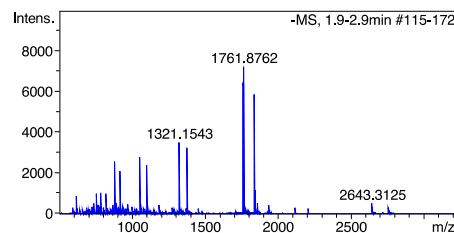
Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180430-4-3_43_01_8189.d Acquisition Date 5/8/2018 8:04:39 PM
Method 1200col2_10to90in4.m Operator gsk
Sample Name JPP-20180430-4-3 Instrument micrOTOF 213750.00199
Comment

Acquisition Parameter

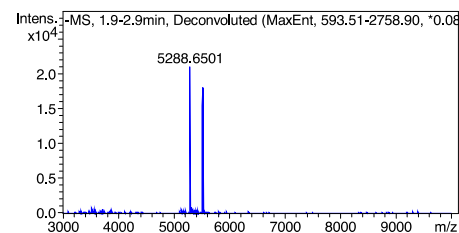
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #115-172



#	m/z	I
1	1321.1543	3500
2	1378.1704	3245
3	1761.5430	6380
4	1761.8762	7207
5	1762.2078	6473
6	1762.5383	4551
7	1837.5711	4726
8	1837.9010	5834
9	1838.2340	5415
10	1838.5659	3823

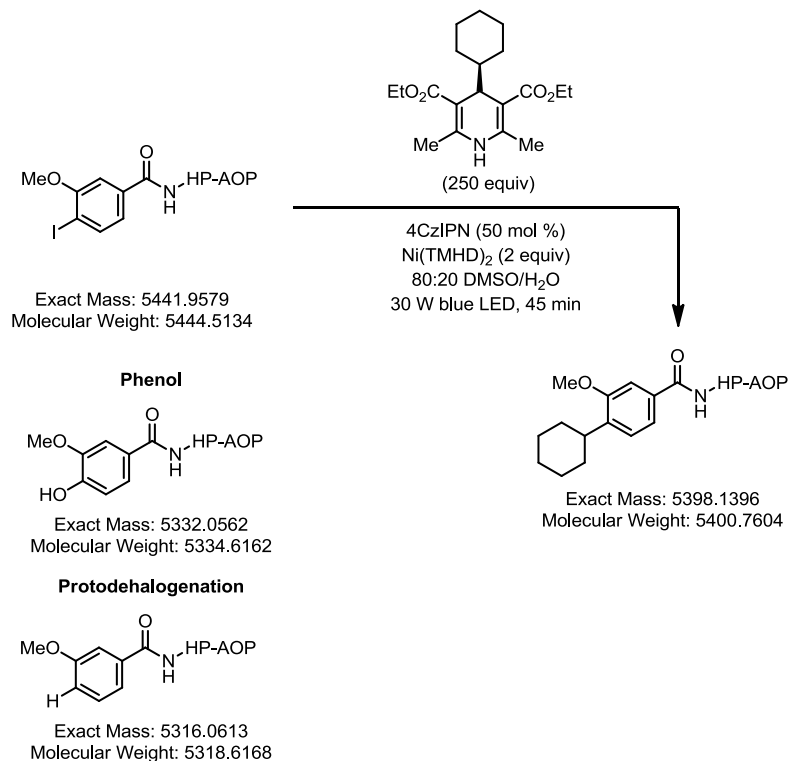


#	m/z	I
1	5288.6501	21002
2	5516.7249	17983

protodebromination

product

Cross-Coupling Product-3z



Product: 43%
Aryl Halide: 0%
Protodehalogenation: 46%
Phenol: 5%

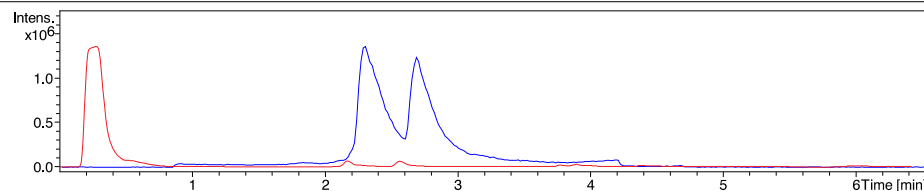
Compound Spectrum List Report

Analysis Info

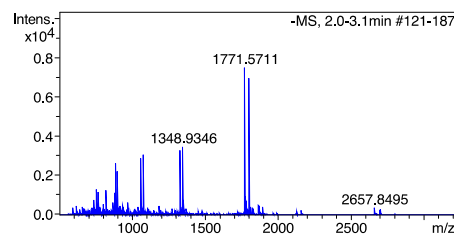
Analysis Name: X:\Chem MS Data\TOF\Data_2018\Dec 2018\JPP-20181201-P1-A5_74_01_10459.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20181201-P1-A5
 Comment:
 Acquisition Date: 12/7/2018 1:32:04 PM
 Operator: gsk
 Instrument: micrOTOF 213750.00199

Acquisition Parameter

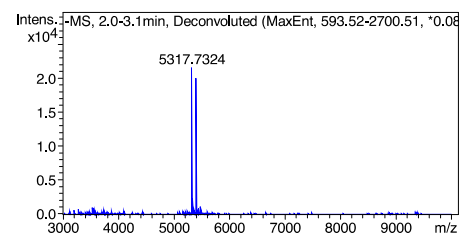
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.1min #121-187

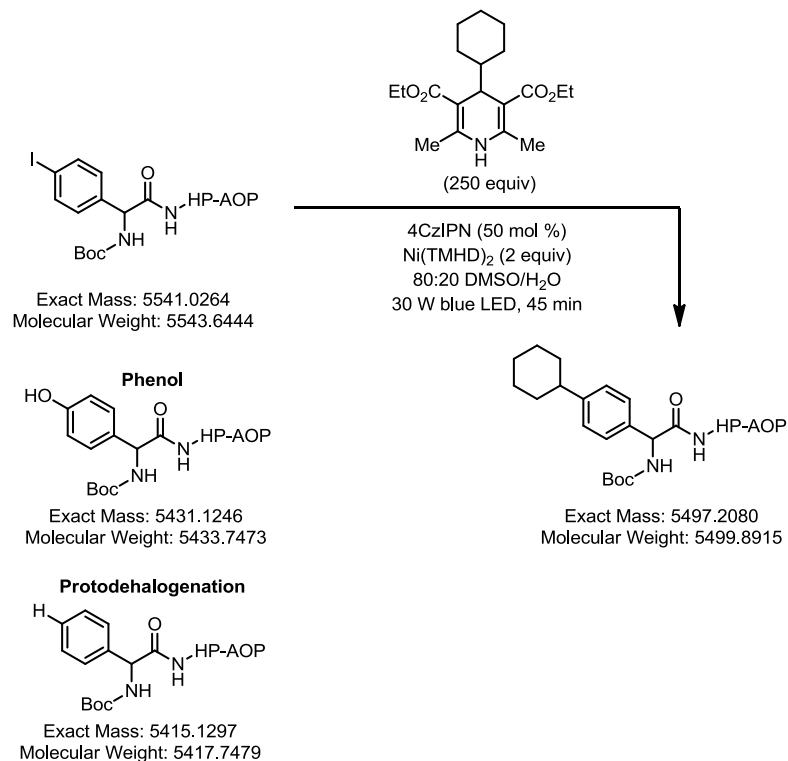


#	m/z	I
1	1328.4259	3289
2	1348.9346	3460
3	1771.2379	6431
4	1771.5711	7498
5	1771.9034	6597
6	1772.2361	4655
7	1798.5908	5382
8	1798.9254	6944
9	1799.2559	6493
10	1799.5871	4596



#	m/z	I	
1	5317.7324	21521	protodehalogenation
2	5332.7268	2339	phenol
3	5341.7129	1485	
4	5399.7872	19968	
5	5484.8924	1139	product

Cross-Coupling Product-3aa



Product: 65%
Aryl Halide: 9%
Protodehalogenation: 18%
Phenol: 0%

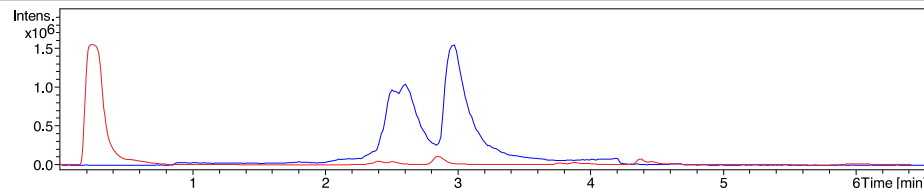
Compound Spectrum List Report

Analysis Info

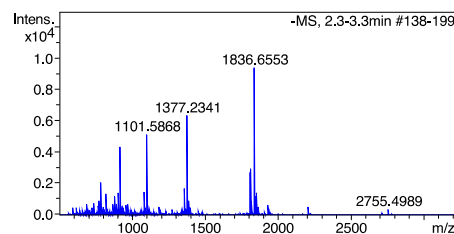
Analysis Name: X:\Chem MS Data\TOF\Data_2018\Dec 2018\utof-12072018\JPP-20181201-P1-A9_78_01_10463.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20181201-P1-A9
 Comment:
 Acquisition Date: 12/7/2018 2:01:45 PM
 Operator: gsk
 Instrument: micrOTOF 213750.00199

Acquisition Parameter

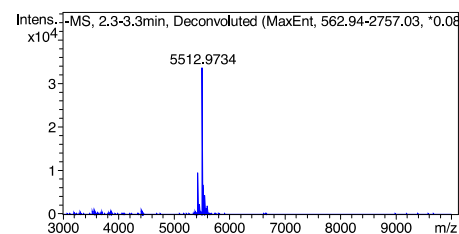
Source Type: ESI
 Focus: Active
 Scan Begin: 510 m/z
 Scan End: 3200 m/z
 Ion Polarity: Negative
 Set Capillary: 2500 V
 Set End Plate Offset: -400 V
 Set Nebulizer: 3.5 Bar
 Set Dry Heater: 220 °C
 Set Dry Gas: 11.0 l/min
 Set Divert Valve: Waste



-MS, 2.3-3.3min #138-199

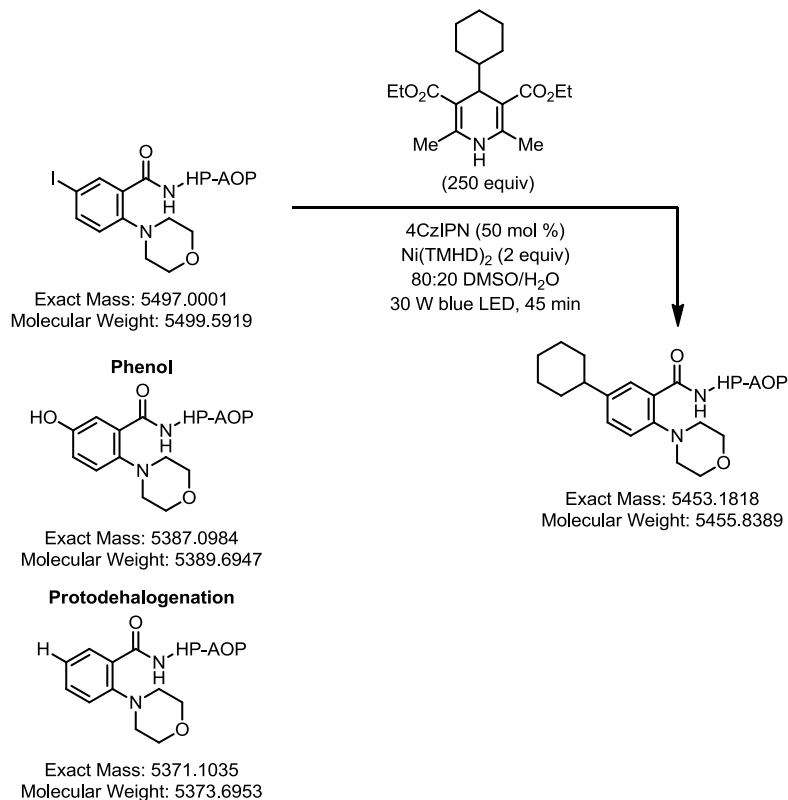


#	m/z	I
1	1101.5868	5108
2	1101.7865	4583
3	1376.9840	5004
4	1377.2341	6312
5	1377.4790	6117
6	1377.7240	4735
7	1836.3192	7399
8	1836.6553	9359
9	1836.9885	8380
10	1837.3187	6361



#	m/z	I	Label
1	5430.9025	9527	protodehalogenation
2	5455.9022	2388	
3	5512.9734	33599	product
4	5556.7905	4466	
5	5597.0609	2019	Aryl Halide

Cross-Coupling Product-3ab



Product: 51%
Aryl Halide: 4%
Protodehalogenation: 30%
Phenol: 0%

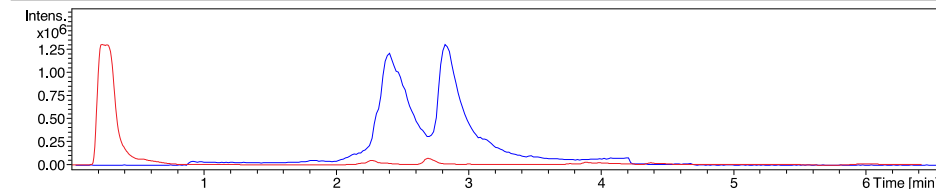
Compound Spectrum List Report

Analysis Info

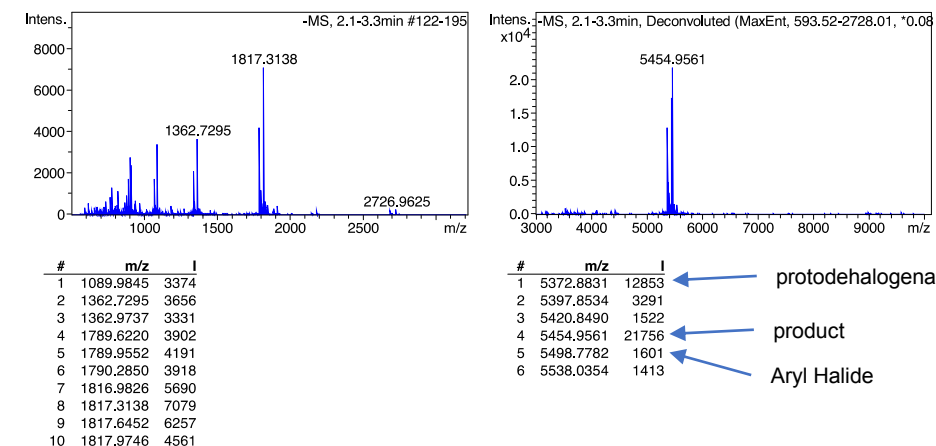
Analysis Name: X:\Chem MS Data\TOF\Data_2018\Dec 2018\JPP-20181201-P1-A10_79_01_10464.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20181201-P1-A10
 Comment:
 Acquisition Date: 12/7/2018 2:09:08 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

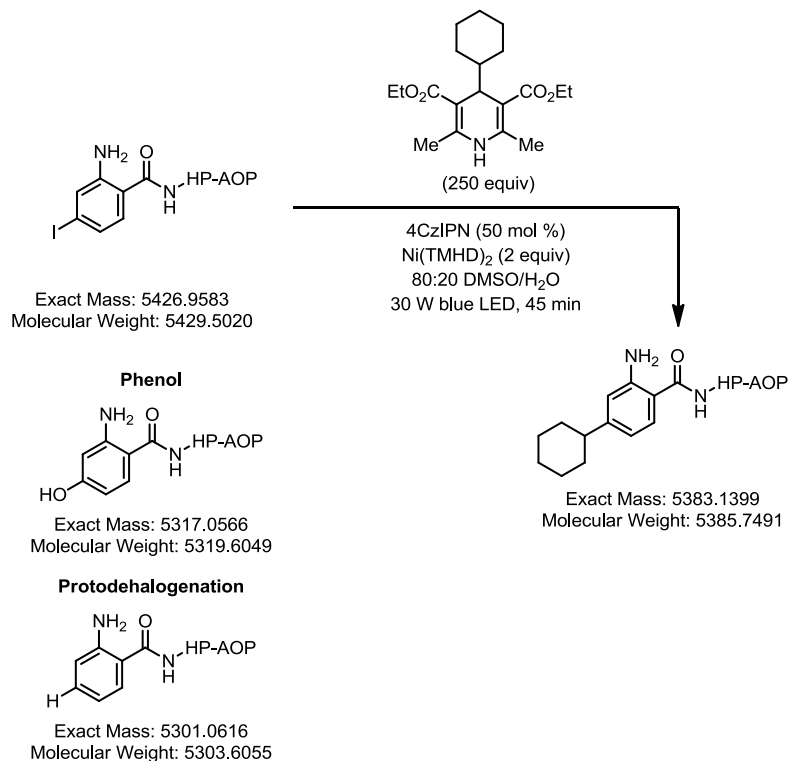
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.1-3.3min #122-195



Cross-Coupling Product-3ac



Product: 72%
Aryl Halide: 4%
Protodehalogenation: 19%
Phenol: 0%

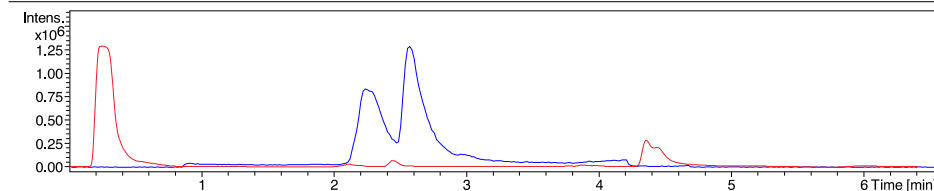
Compound Spectrum List Report

Analysis Info

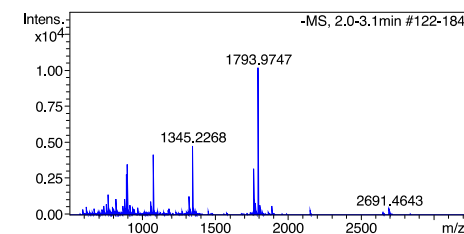
Analysis Name: X:\Chem MS Data\TOF\Data_2018\Dec 2018\JPP-20181201-P1-A11_80_01_10465.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20181201-P1-A11
 Comment:
 Acquisition Date: 12/7/2018 2:16:31 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

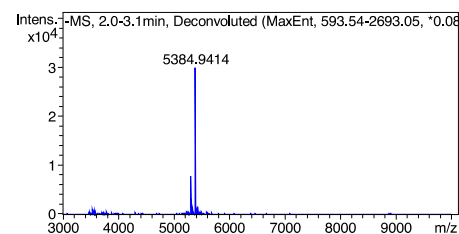
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.1min #122-184

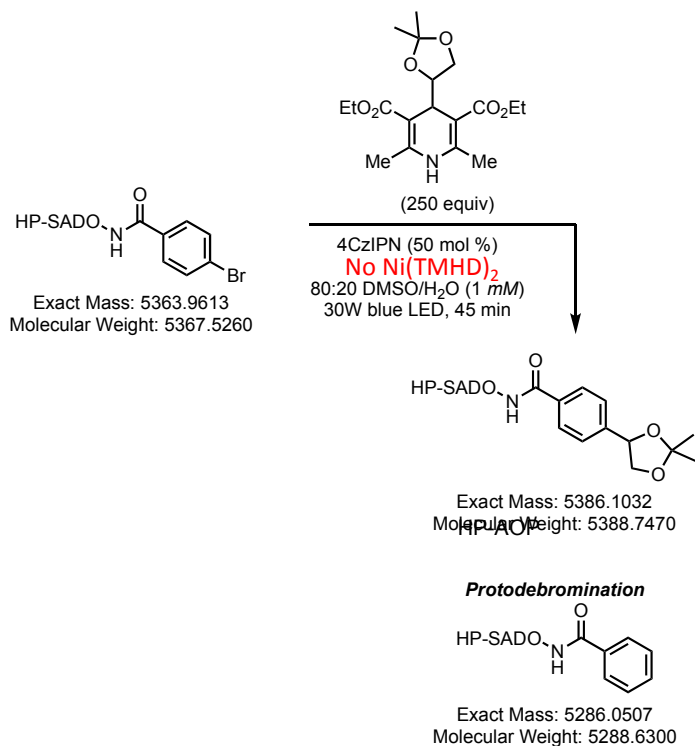


#	m/z	I
1	1075.9812	4165
2	1344.9845	3996
3	1345.2268	4765
4	1345.4733	4630
5	1793.3128	4057
6	1793.6437	8537
7	1793.9747	10160
8	1794.3093	8731
9	1794.6440	6130
10	1794.9742	3755



#	m/z	I	
1	5302.8653	7748	← protodehalogenation
2	5327.8554	2297	
3	5384.9414	29918	← product
4	5428.7732	1670	← Aryl Halide

Nickel/Photoredox Dual Catalytic Cross-Coupling using DHP's Control Reactions

Control Reaction

Product: 0%
Starting material: 100%
Protodebromination: 0%

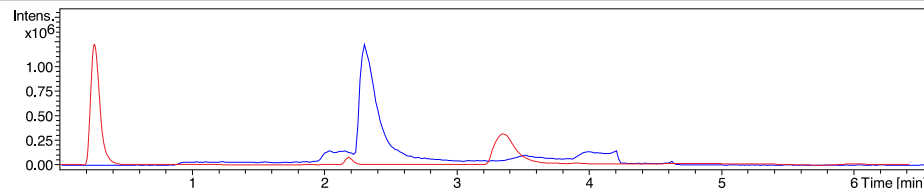
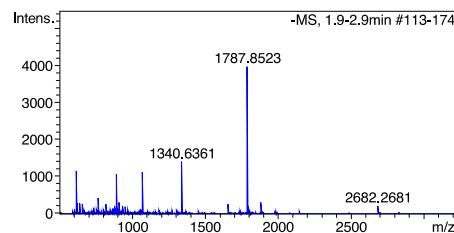
Compound Spectrum List Report**Analysis Info**

Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180501-1-1_81_01_8203.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180501-1-1
 Comment

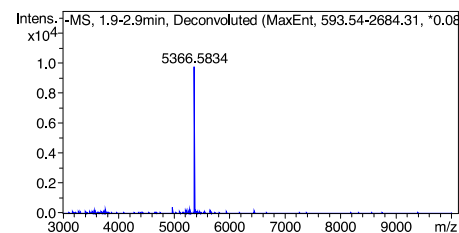
Acquisition Date 5/8/2018 9:47:55 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste

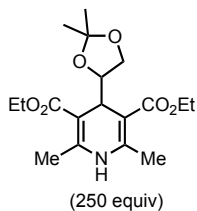
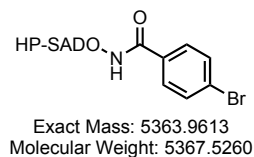
**-MS, 1.9-2.9min #113-174**

#	m/z	I
1	621.0676	1156
2	1340.3885	1276
3	1340.6361	1408
4	1340.8841	1359
5	1787.1869	2048
6	1787.5214	3291
7	1787.8523	3965
8	1788.1841	3369
9	1788.5167	2825
10	1788.8504	1628

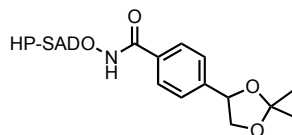


#	m/z	I
1	5366.5834	9754

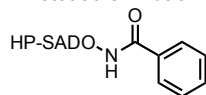
← starting material

Control Reaction

No 4CzIPN
 Ni(TMHD)₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 45 min



Exact Mass: 5386.1032
 Molecular Weight: 5388.7470
 HP-AOP

Protodebromination

Exact Mass: 5286.0507
 Molecular Weight: 5288.6300

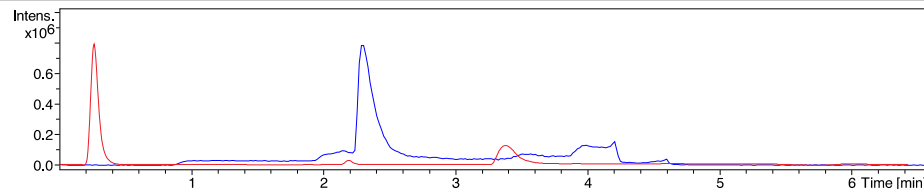
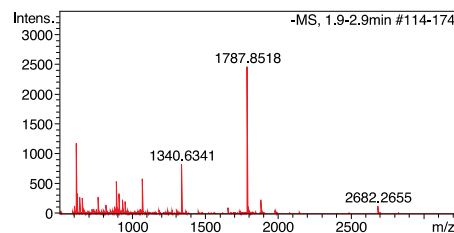
Product: 0%
Starting material: 100%
Protodebromination: 0%

Compound Spectrum List Report**Analysis Info**

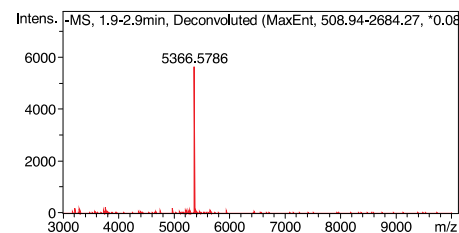
Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180501-1-2_82_01_8204.d Acquisition Date 5/8/2018 9:55:18 PM
 Method 1200col2_10to90in4.m Operator gsk
 Sample Name JPP-20180501-1-2 Instrument micrOTOF 213750.00199
 Comment

Acquisition Parameter

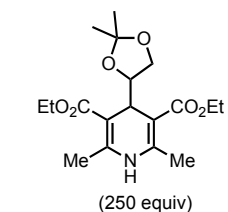
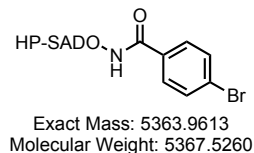
Source Type ESI Ion Polarity Negative Set Nebulizer 3.5 Bar
 Focus Active Set Dry Heater 220 °C
 Scan Begin 510 m/z Set Capillary 2500 V Set Dry Gas 11.0 l/min
 Scan End 3200 m/z Set End Plate Offset -400 V Set Divert Valve Waste

**-MS, 1.9-2.9min #114-174**

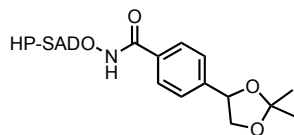
#	m/z	I
1	621.0671	1183
2	1340.3914	667
3	1340.6341	835
4	1340.8789	761
5	1787.1876	1231
6	1787.5188	1989
7	1787.8518	2459
8	1788.1829	2153
9	1788.5168	1563
10	1788.8504	947



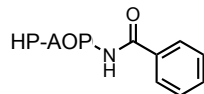
#	m/z	I
1	5366.5786	5636

Control Reaction

4CzIPN (50 mol %)
 Ni(TMHD)₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
No light



Exact Mass: 5386.1032
 Molecular Weight: 5388.7470

Protodebromination

Exact Mass: 5286.0507
 Molecular Weight: 5288.6300

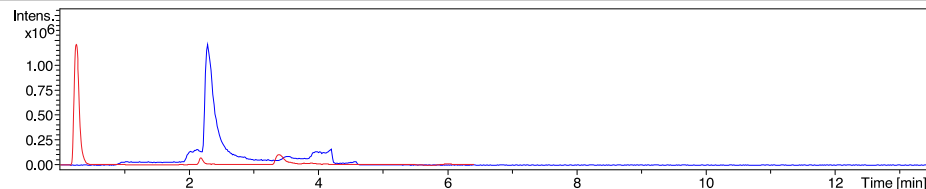
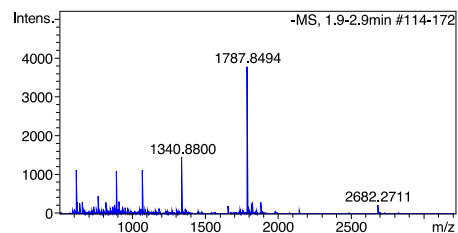
Product: 0%
Starting material: 93%
Protodebromination: 0%

Compound Spectrum List Report**Analysis Info**

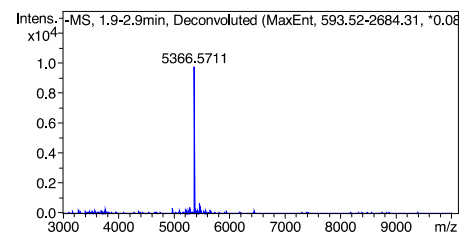
Analysis Name D:\Data\Data 2018\May 2018\utof-050818\JPP-20180501-1-3_83_01_8205.d Acquisition Date 5/8/2018 10:02:52 PM
 Method 1200col2_10to90in4.m Operator gsk
 Sample Name JPP-20180501-1-3 Instrument micrOTOF 213750.00199
 Comment

Acquisition Parameter

Source Type ESI Ion Polarity Negative Set Nebulizer 3.5 Bar
 Focus Active Set Dry Heater 220 °C
 Scan Begin 510 m/z Set Capillary 2500 V Set Dry Gas 11.0 l/min
 Scan End 3200 m/z Set End Plate Offset -400 V Set Divert Valve Waste

**-MS, 1.9-2.9min #114-172**

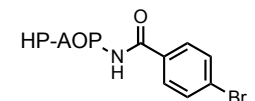
#	m/z	I
1	1072.3088	1119
2	1340.3844	1318
3	1340.6324	1443
4	1340.8800	1443
5	1787.1854	2048
6	1787.5182	3211
7	1787.8494	3779
8	1788.1795	3552
9	1788.5131	2619
10	1788.8444	1518



#	m/z	I
1	5366.5711	9755
2	5468.6279	724

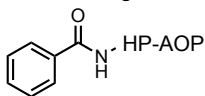
starting material

Cross-Coupling Product-3a



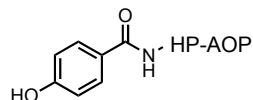
Exact Mass: 5363.9613
 Molecular Weight: 5367.5260

Protodehalogenation

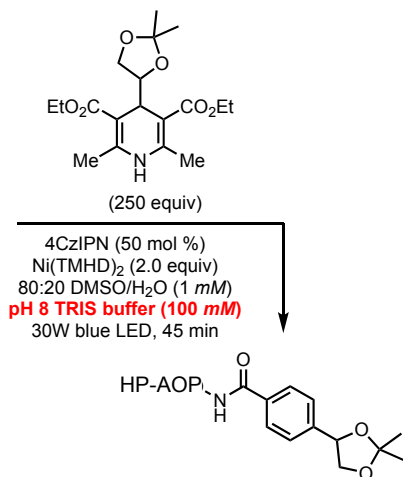


Exact Mass: 5286.0507
 Molecular Weight: 5288.6300

Phenol



Exact Mass: 5302.0457
 Molecular Weight: 5304.6290



Exact Mass: 5386.1032
 Molecular Weight: 5388.7470

Product: 6%
Starting Material: 63%
Protodehalogenation: 0%

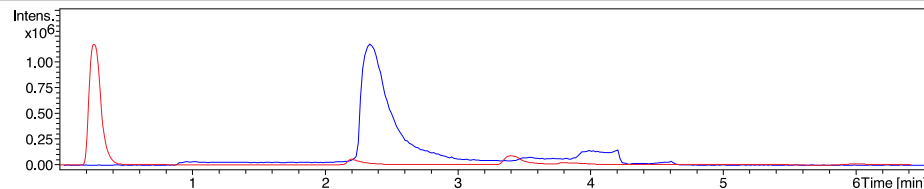
Compound Spectrum List Report

Analysis Info

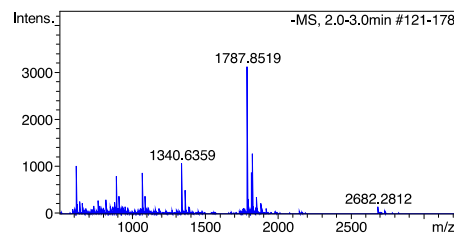
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-051718\DNA-20180514-2-1_21_01_8297.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180514-2-1
 Comment
 Acquisition Date 5/17/2018 3:26:13 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

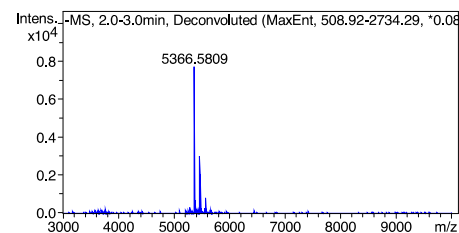
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.0min #121-178



#	m/z	I
1	1340.6359	1067
2	1787.1906	1489
3	1787.5188	2571
4	1787.8519	3123
5	1788.1842	2922
6	1788.5181	2228
7	1788.8477	1399
8	1821.5370	1181
9	1821.8702	1281
10	1822.2069	1200

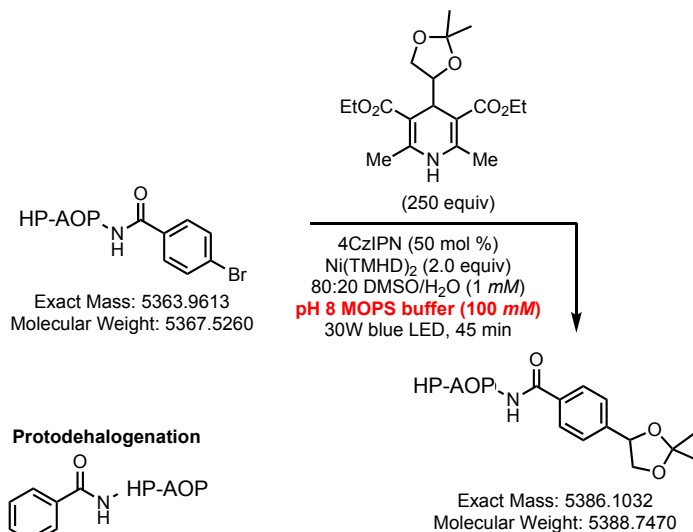


#	m/z	I
1	5366.5809	7687
2	5368.6578	679
3	5468.6349	3013
4	5569.6949	846

Starting material

Product

Cross-Coupling Product-3a



Product: 4%
Starting Material: 71%
Protodehalogenation: 0%

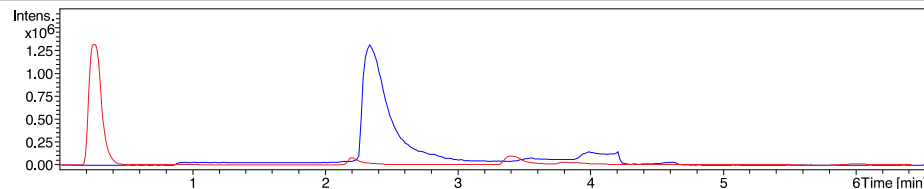
Compound Spectrum List Report

Analysis Info

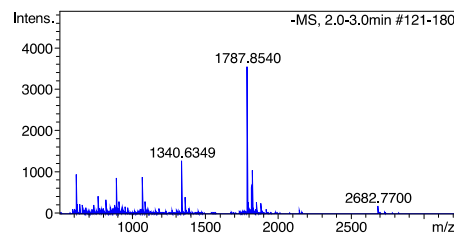
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-051718\DNA-20180514-2-2_22_01_8298.d
 Acquisition Date 5/17/2018 3:33:33 PM
 Method 1200col2_10to90in4.m
 Operator gsk
 Sample Name DNA-20180514-2-2
 Instrument micrOTOF 213750.00199
 Comment

Acquisition Parameter

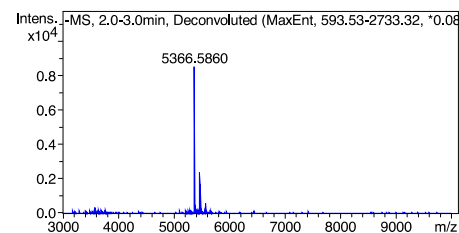
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.0min #121-180



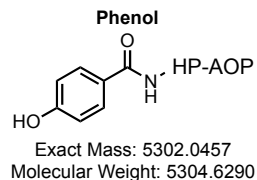
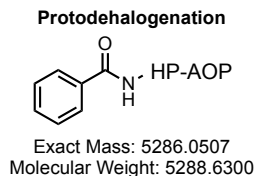
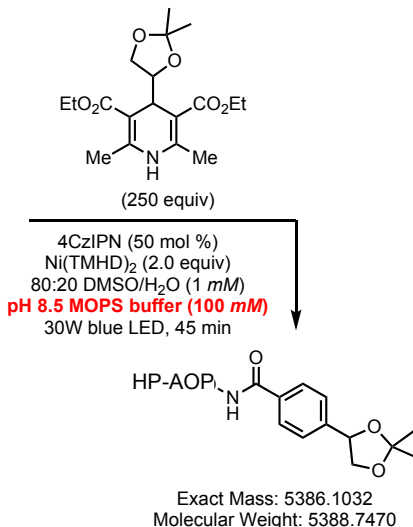
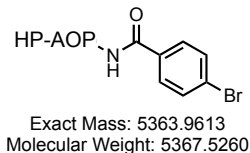
#	m/z	I
1	1340.3855	1102
2	1340.6349	1274
3	1340.8813	1270
4	1787.1860	1816
5	1787.5212	2915
6	1787.8540	3540
7	1788.1862	3296
8	1788.5181	2422
9	1788.8482	1561
10	1821.8694	1046



#	m/z	I
1	5366.5860	8514
2	5387.6464	499
3	5468.6610	2391
4	5568.6745	609

Starting material
 Product

Cross-Coupling Product-3a



Product: 13%
Starting Material: 58%
Protodehalogenation: 0%

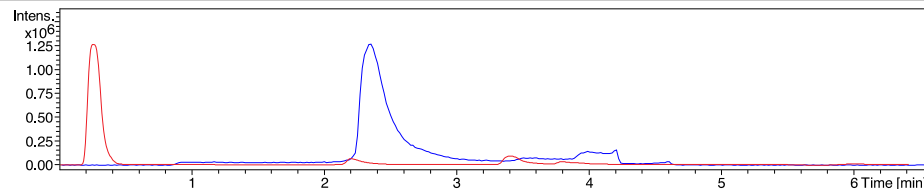
Compound Spectrum List Report

Analysis Info

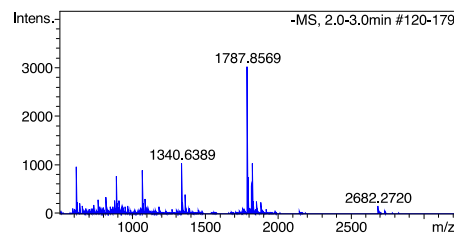
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-051718\DNA-20180514-2-3_23_01_8299.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180514-2-3
 Comment
 Acquisition Date 5/17/2018 3:40:55 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

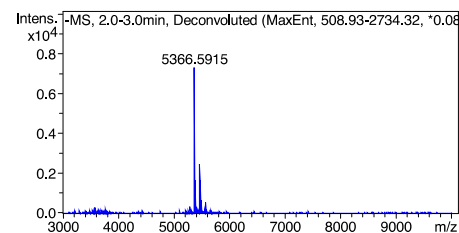
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.0min #120-179



#	m/z	I
1	621.0678	964
2	1340.6389	1038
3	1340.8820	970
4	1787.1926	1497
5	1787.5241	2406
6	1787.8569	3022
7	1788.1892	2701
8	1788.5215	2099
9	1788.8540	1312
10	1821.8744	1030

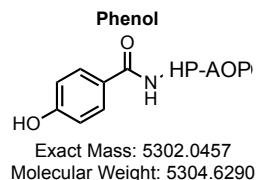
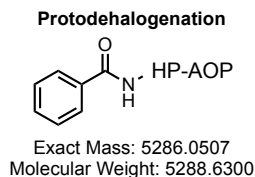
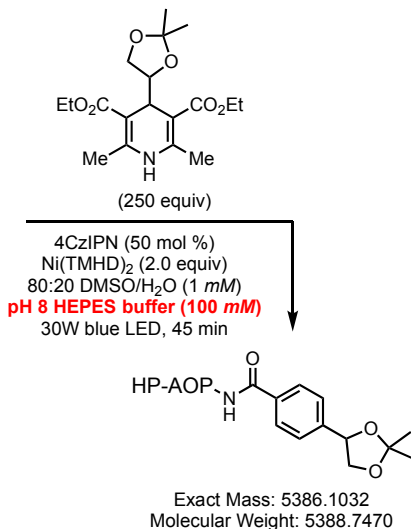
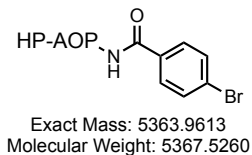


#	m/z	I
1	5366.5915	7299
2	5387.7191	1648
3	5468.6470	2466
4	5489.7578	643
5	5568.7063	575

Starting material

Product

Cross-Coupling Product-3a



Product: 23%
Starting Material: 47%
Protodehalogenation: 4%

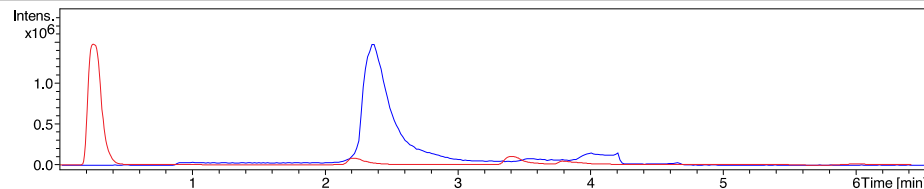
Compound Spectrum List Report

Analysis Info

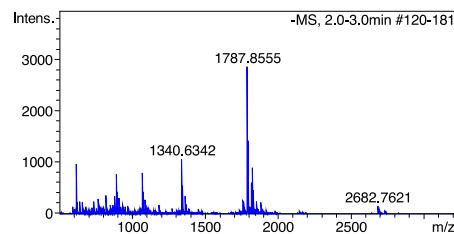
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-051718\DNA-20180514-2-4_24_01_8300.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180514-2-4
 Comment
 Acquisition Date 5/17/2018 3:48:18 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

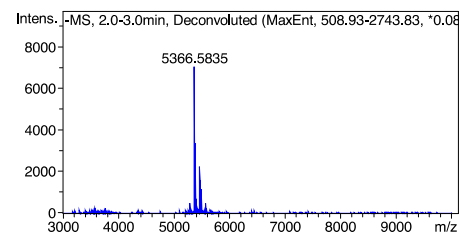
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.0min #120-181



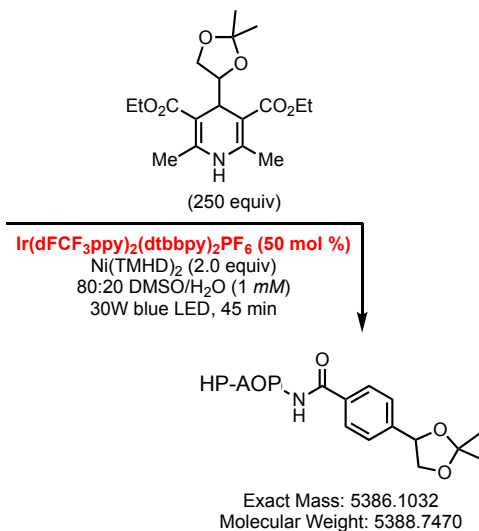
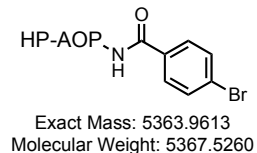
#	m/z	I
1	1340.6342	1070
2	1787.1906	1478
3	1787.5227	2338
4	1787.8555	2856
5	1788.1868	2709
6	1788.5197	2119
7	1788.8543	1370
8	1794.5645	1173
9	1794.8951	1427
10	1795.2266	1286



#	m/z	I
1	5287.6617	521
2	5366.5835	7037
3	5387.7148	3360
4	5468.6401	2243
5	5489.7970	1155
6	5570.7086	505

Protodehalogenation
 Starting material
 Product

Cross-Coupling Product-3a



DNA Decomposition

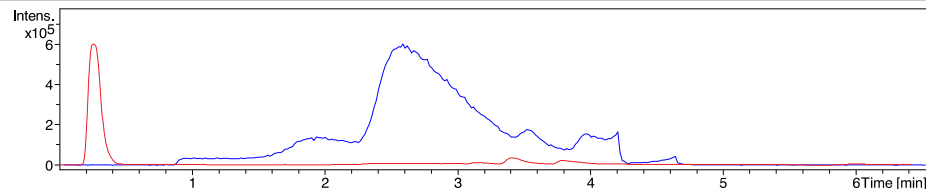
Compound Spectrum List Report

Analysis Info

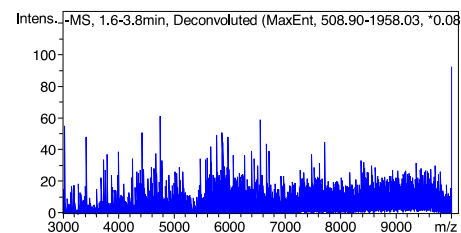
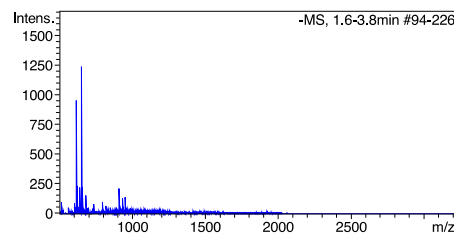
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-051718\DNA-20180514-2-5_25_01_8301.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180514-2-5
 Comment
 Acquisition Date 5/17/2018 3:55:43 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste

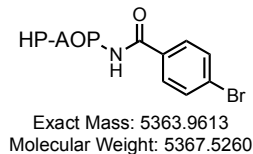


-MS, 1.6-3.8min #94-226

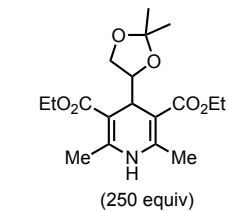
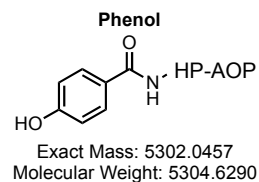
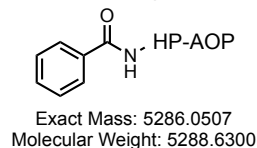


#	m/z	I
1	621.0668	950
2	622.0698	232
3	643.0463	223
4	656.9102	1238
5	657.9159	178
6	659.0133	219
7	682.9041	158
8	913.1454	212
9	935.1284	135
10	951.0955	140

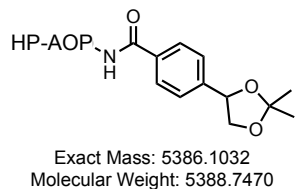
Cross-Coupling Product-3a



Protodehalogenation



4CzIPN (50 mol %)
Ni(Phen)Cl₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 45 min



Product: 10%
Starting Material: 48%
Protodehalogenation: 17%

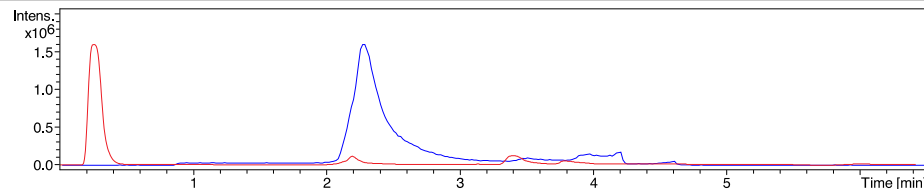
Compound Spectrum List Report

Analysis Info

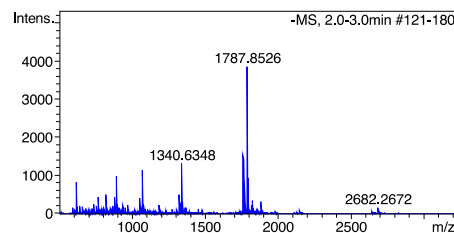
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\tof-051718\DNA-20180514-2-6_01_8302.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180514-2-6
 Comment
 Acquisition Date 5/17/2018 4:03:10 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

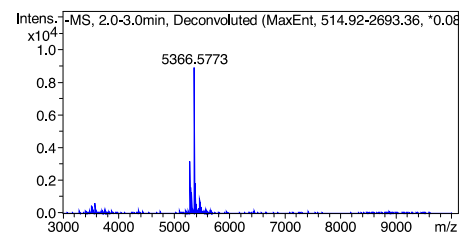
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.0min #121-180



#	m/z	I
1	1340.6348	1321
2	1340.8798	1314
3	1761.2181	1331
4	1761.5466	1544
5	1787.1869	1926
6	1787.5204	3134
7	1787.8526	3850
8	1788.1832	3474
9	1788.5154	2571
10	1788.8489	1633



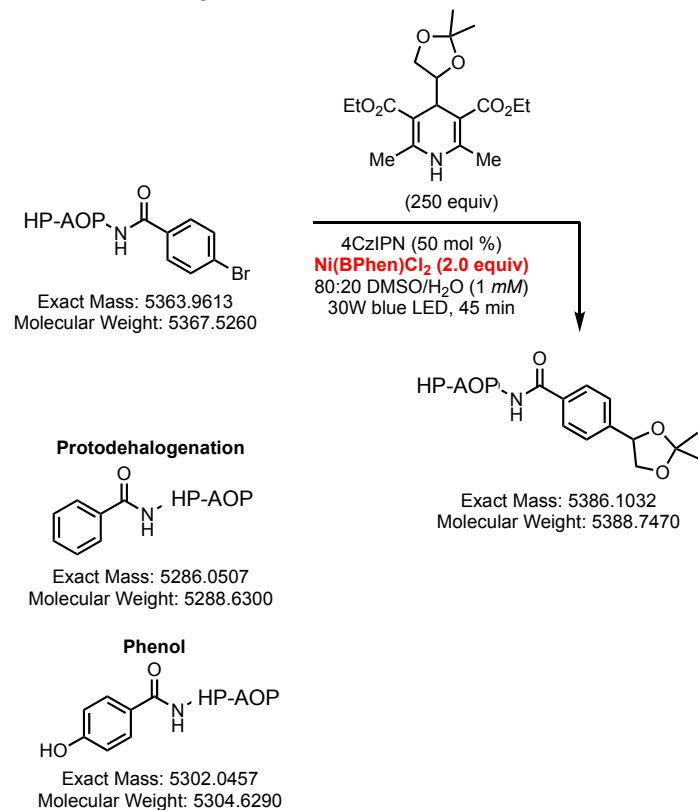
#	m/z	I
1	3525.1163	489
2	3577.7223	629
3	5287.6631	3204
4	5302.6856	557
5	5312.6593	1571
6	5322.6204	591
7	5366.5773	8904
8	5387.7124	1878
9	5468.6375	891

Protodehalogenation

Starting material

Product

Cross-Coupling Product-3a



Product: 5%
Starting Material: 20%
Protodehalogenation: 3%

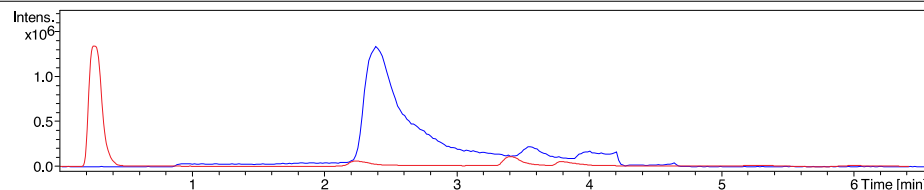
Compound Spectrum List Report

Analysis Info

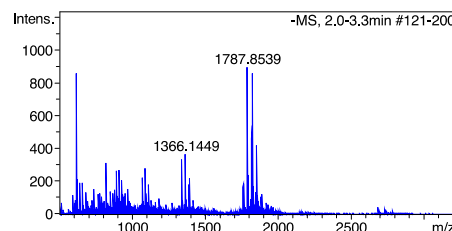
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-051718\DNA-20180514-2-7_27_01_8303.d
 Acquisition Date 5/17/2018 4:10:31 PM
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180514-2-7
 Operator gsk
 Instrument micrOTOF 213750.00199
 Comment

Acquisition Parameter

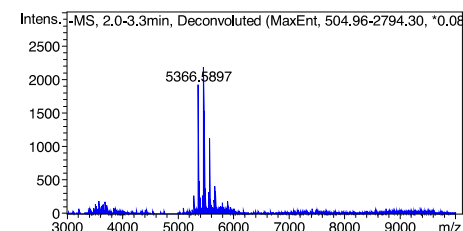
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.3min #121-200

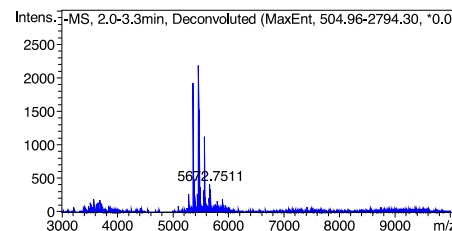


#	m/z	I
1	621.0669	854
2	1787.5216	728
3	1787.8539	893
4	1788.1851	871
5	1788.5165	607
6	1821.2069	539
7	1821.5381	764
8	1821.8709	856
9	1822.2073	782
10	1822.5419	615

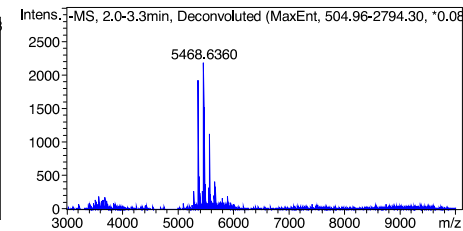


#	m/z	I
1	3524.4561	144
2	3540.3923	117
3	3576.3840	196
4	3636.5097	124
5	3645.1531	132
6	3660.5128	138
7	3700.4127	178
8	3720.5288	136
9	5287.6705	275
10	5366.5897	1921

Protodehalogenation
 Starting material



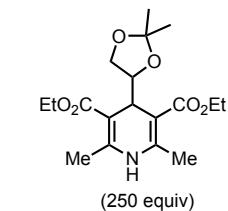
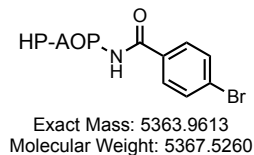
#	m/z	I
1	5672.7511	418
2	5682.7157	115
3	5771.8149	122
4	5802.7980	170
5	5820.8306	112
6	5904.8266	191



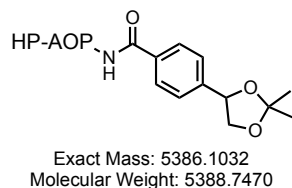
#	m/z	I
1	5389.7055	492
2	5451.6117	271
3	5468.6360	2185
4	5490.7631	373
5	5552.6746	325
6	5570.6961	1126
7	5592.8037	221
8	5616.7304	112
9	5652.7302	210

Product

Cross-Coupling Product-3a



4CzIPN (50 mol %)
Ni(dtbppy)Cl₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 45 min



DNA Decomposition

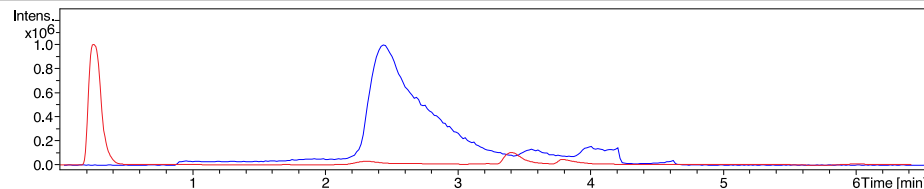
Compound Spectrum List Report

Analysis Info

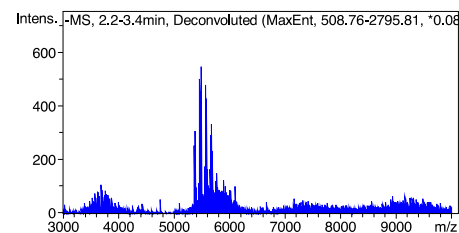
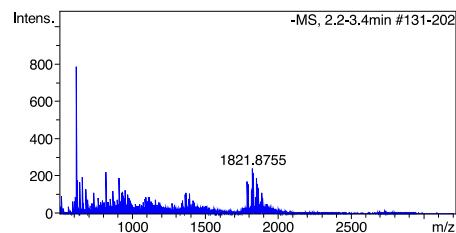
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-051718\DNA-20180514-2-8_28_01_8304.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180514-2-8
 Comment
 Acquisition Date 5/17/2018 4:17:58 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste

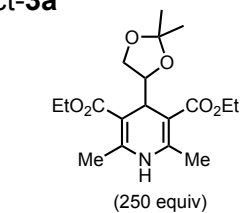
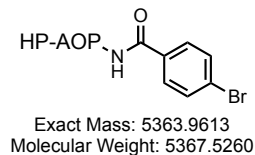


-MS, 2.2-3.4min #131-202

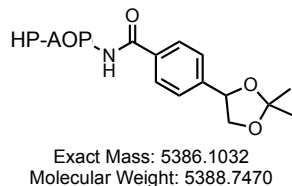


#	m/z	I
1	621.0646	785
2	659.0155	195
3	819.0446	222
4	913.1421	191
5	1821.8755	243
6	1822.2193	213
7	1822.5585	207
8	1822.8979	208
9	1828.9273	221
10	1855.8944	193

Cross-Coupling Product-3a



4CzIPN (50 mol %)
Ni(dMeObpy)Cl₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 45 min



DNA Decomposition

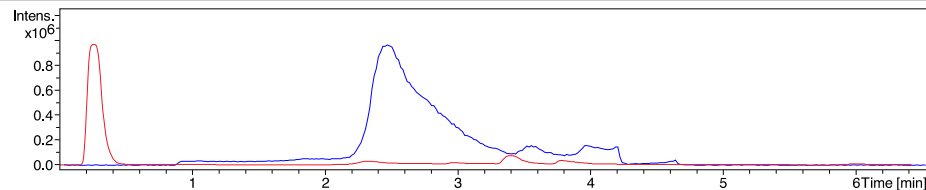
Compound Spectrum List Report

Analysis Info

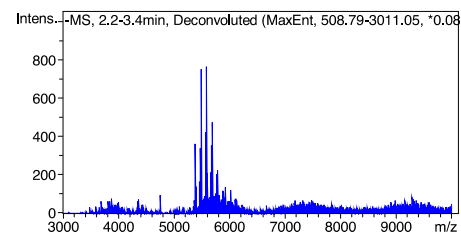
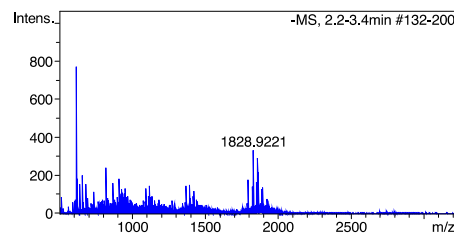
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-051718\DNA-20180514-2-9_29_01_8305.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180514-2-9
 Comment
 Acquisition Date 5/17/2018 4:25:22 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste

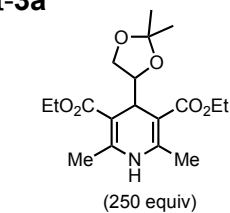
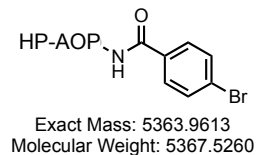


-MS, 2.2-3.4min #132-200

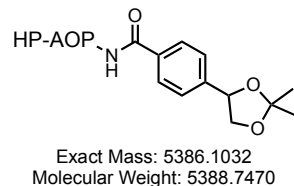


#	m/z	I
1	621.0652	768
2	659.0167	203
3	819.0457	243
4	1828.5837	279
5	1828.9221	335
6	1829.2504	275
7	1829.5824	215
8	1862.6037	276
9	1862.9338	291
10	1863.2621	220

Cross-Coupling Product-3a



4CzIPN (50 mol %)
Ni(bpy)Cl₂ (2.0 equiv)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 45 min



DNA Decomposition

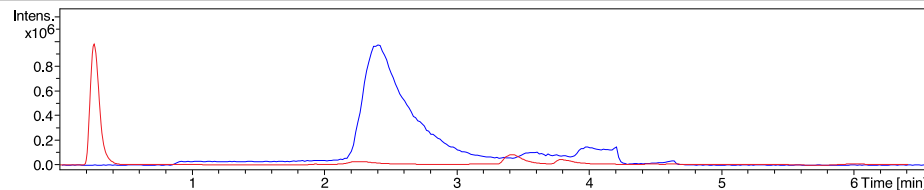
Compound Spectrum List Report

Analysis Info

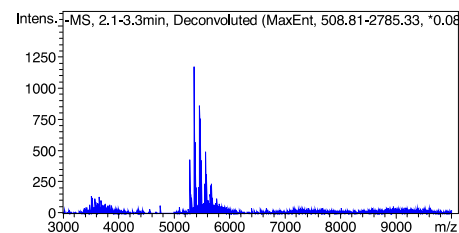
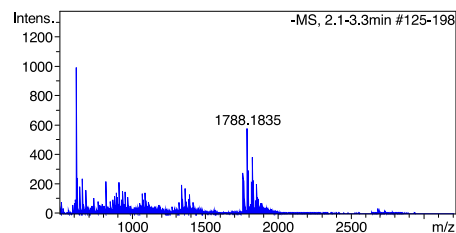
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-051718\DNA-20180514-2-10_30_01_8306.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180514-2-10
 Comment
 Acquisition Date 5/17/2018 4:32:43 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



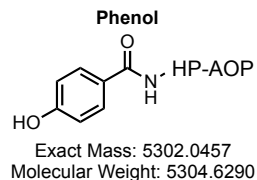
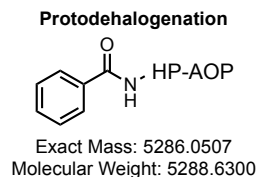
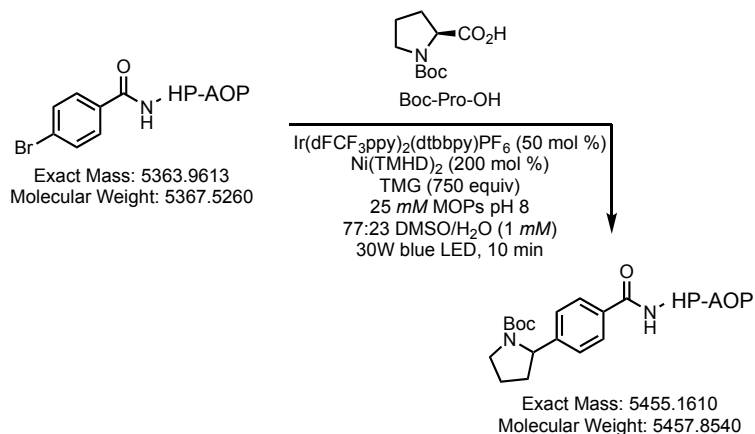
-MS, 2.1-3.3min #125-198



#	m/z	I
1	621.0667	992
2	1787.5177	484
3	1787.8496	556
4	1788.1835	578
5	1788.5145	422
6	1788.8541	297
7	1795.2253	296
8	1821.5397	308
9	1821.8697	382
10	1822.2108	338

Nickel/Photoredox Dual Catalytic Cross-Coupling using Amino Acids

Cross-Coupling Product-3ad



Product: 45%
Aryl Halide: 2%
Protodehalogenation: 0%
Phenol: 31%

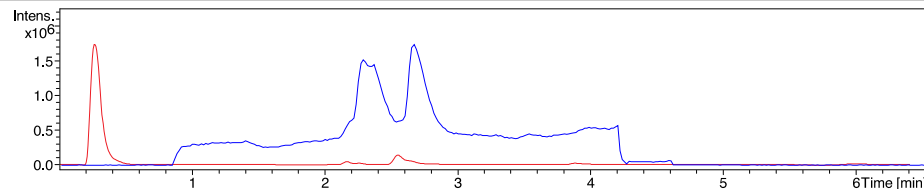
Compound Spectrum List Report

Analysis Info

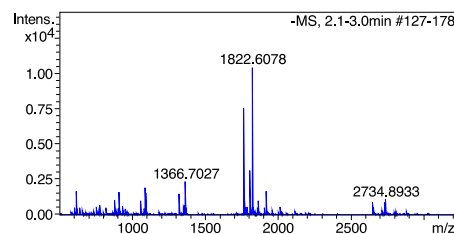
Analysis Name X:\Chem MS Data\TOF\Data_2018\July 2018\utof-071218\DNA-20180616-3-8_62_01_8842.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180616-3-8
 Comment
 Acquisition Date 7/12/2018 6:28:54 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

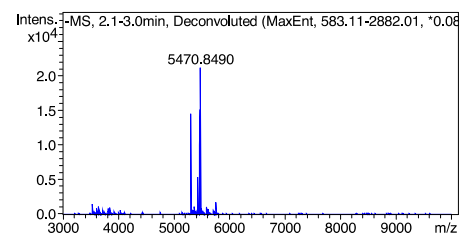
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.1-3.0min #127-178



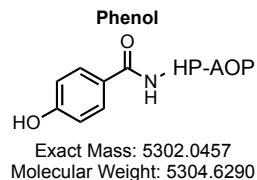
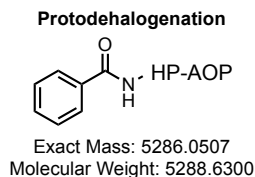
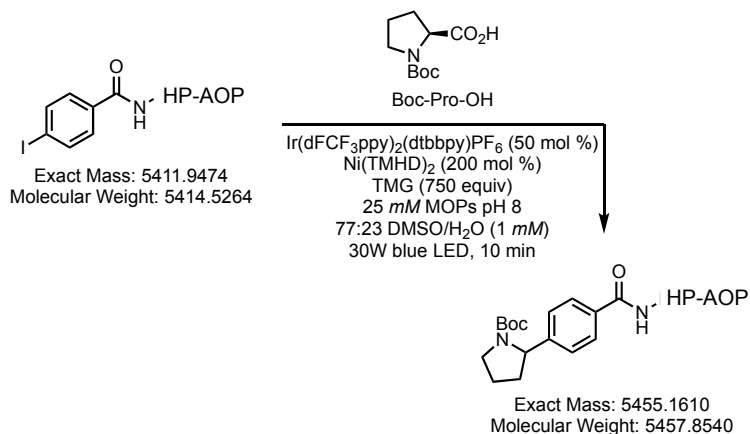
#	m/z	I
1	1765.9068	6489
2	1766.2389	7507
3	1766.5714	6304
4	1766.9031	4411
5	1821.9425	3920
6	1822.2744	8417
7	1822.6078	10396
8	1822.9423	9534
9	1823.2759	6474
10	1823.6036	4193



#	m/z	I
1	3533.8153	1243
2	3647.2280	1173
3	5301.7406	14498
4	5371.7754	1111
5	5427.6354	5386
6	5470.8490	21160
7	5593.8330	1083
8	5762.9264	1764

Phenol
 Aryl Halide
 Product

Cross-Coupling Product-3ad



Product: 42%
Aryl Halide: 0%
Protodehalogenation: 48%
Phenol: 0%

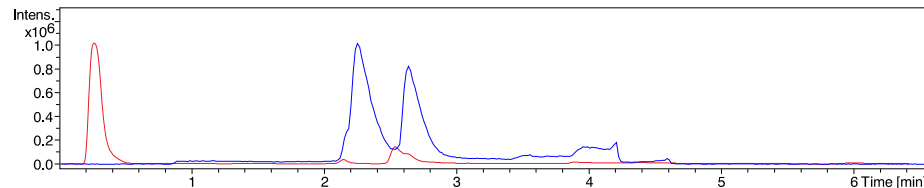
Compound Spectrum List Report

Analysis Info

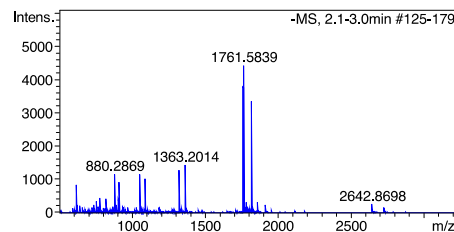
Analysis Name: X:\Chem MS Data\TOF\Data_2018\July 2018\utof-071218\DNA-20180508-A6_16_01_8814.d
 Method: 1200col2_10to90in4.m
 Sample Name: DNA-20180508-A6
 Comment:
 Acquisition Date: 7/12/2018 3:03:13 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

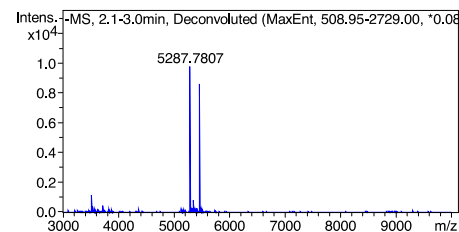
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.1-3.0min #125-179



#	m/z	I
1	1363.2014	1437
2	1760.9164	1912
3	1761.2488	3792
4	1761.5839	4417
5	1761.9187	3839
6	1762.2477	2501
7	1817.6140	2706
8	1817.9463	3351
9	1818.2794	3003
10	1818.6140	2159

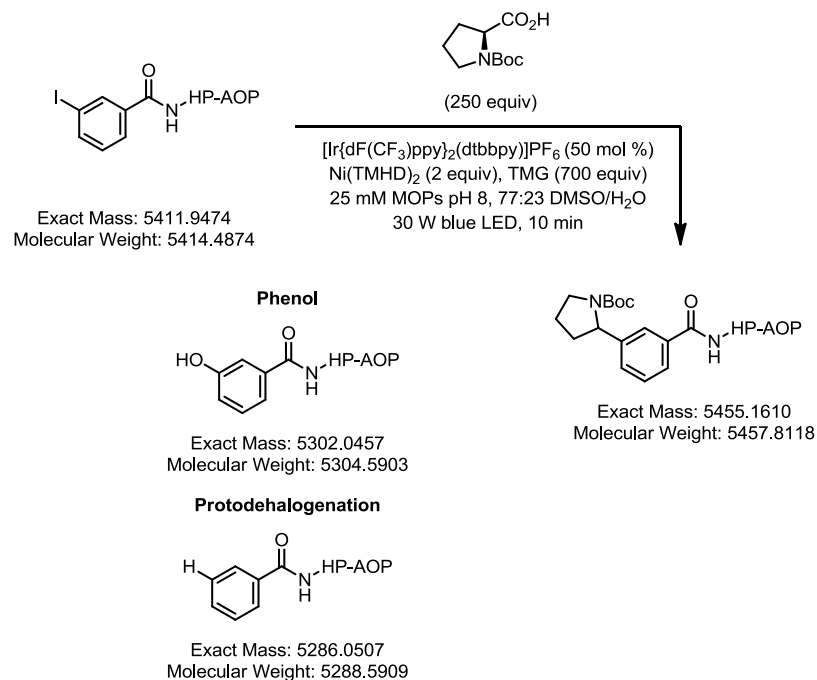


#	m/z	I
1	3525.1846	1189
2	5287.7807	9773
3	5357.8134	805
4	5456.8583	8614

Proto

Product

Cross-Coupling Product-3ae



Product: 51%
Aryl Halide: 0%
Protodehalogenation: 16%
Phenol: 3%

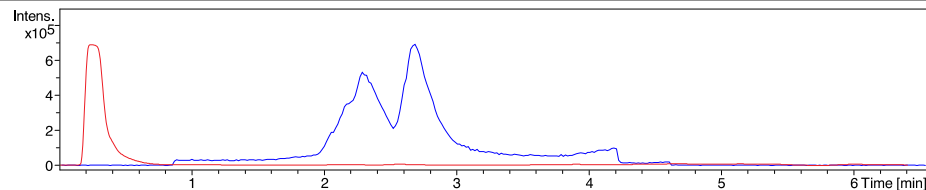
Compound Spectrum List Report

Analysis Info

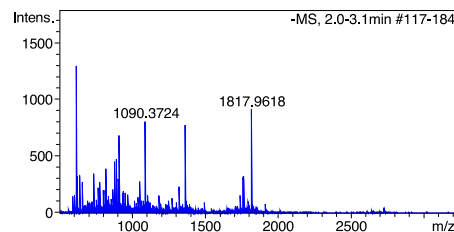
Analysis Name: X:\Chem MS Data\TOF\Data_2018\Nov 2018\tof-111618\JHS-181105-5_15_01_10239.d
 Method: 1200col2_10to90in4.m
 Sample Name: JHS-181105-5
 Comment:
 Acquisition Date: 11/16/2018 6:10:02 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

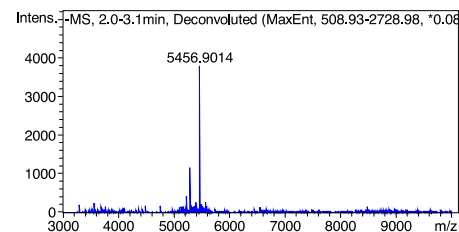
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.1min #117-184



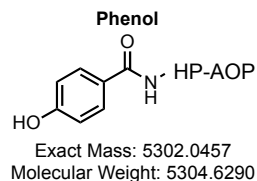
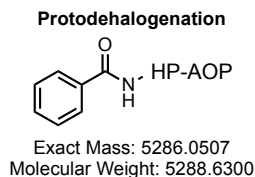
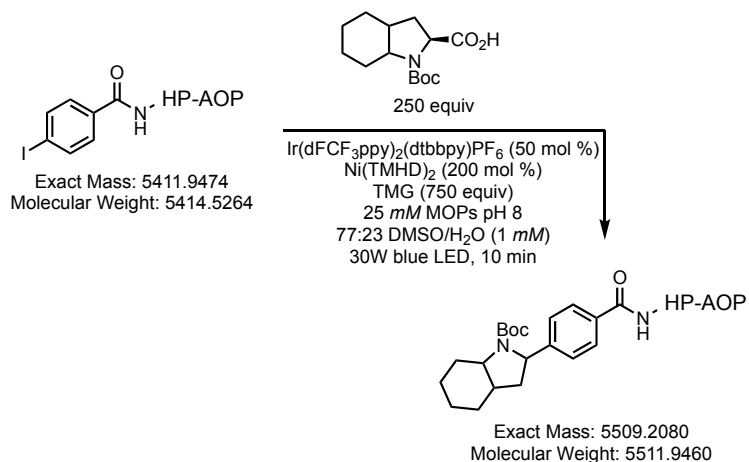
#	m/z	I
1	621.0803	1289
2	908.4723	682
3	1090.1807	648
4	1090.3724	804
5	1090.5752	711
6	1363.2187	770
7	1363.4618	707
8	1817.6294	780
9	1817.9618	908
10	1818.2964	777



#	m/z	I
1	3300.2187	206
2	3567.4460	241
3	4760.5811	189
4	5225.7983	434
5	5287.8011	1166
6	5305.7971	197
7	5376.9208	195
8	5394.8895	281
9	5456.9014	3793
10	5485.9013	205

protodehalogenation
 Phenol
 product

Cross-Coupling Product-3af



Product: 56%
Aryl Halide: 0%
Protodehalogenation: 17%
Phenol: 4%

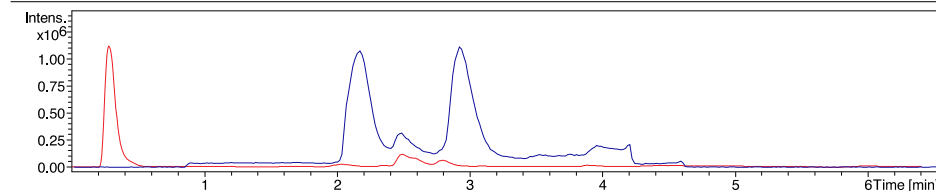
Compound Spectrum List Report

Analysis Info

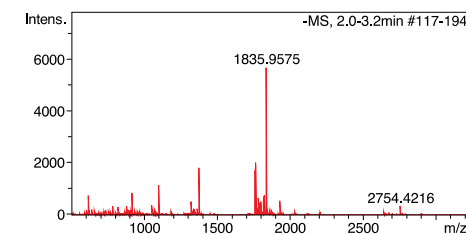
Analysis Name: X:\Chem MS Data\TOF\Data_2018\July 2018\utof-071218\DNA-20180508-B6_26_01_8820.d
 Method: 1200col2_10to90in4.m
 Sample Name: DNA-20180508-B6
 Comment:
 Acquisition Date: 7/12/2018 3:47:31 PM
 Operator: gsk
 Instrument: micrOTOF 213750.00199

Acquisition Parameter

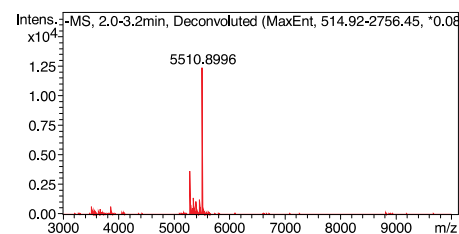
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.2min #117-194



#	m/z	I
1	1376.7159	1809
2	1376.9629	1706
3	1761.2445	1679
4	1761.5768	2029
5	1835.2934	2067
6	1835.6249	4636
7	1835.9575	5673
8	1836.2903	5078
9	1836.6257	3561
10	1836.9578	2098



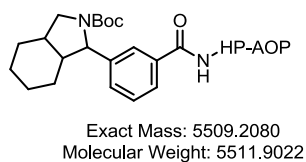
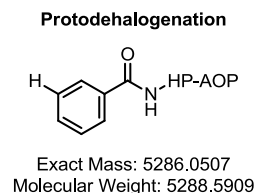
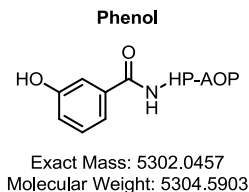
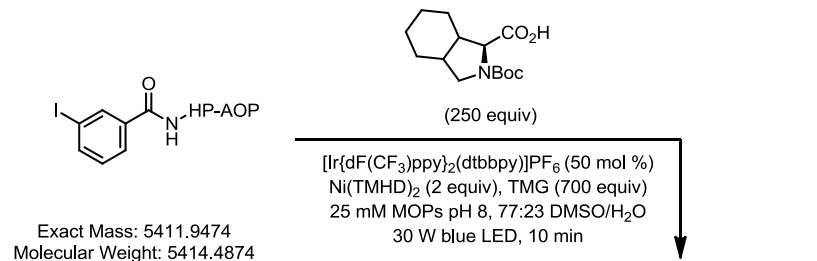
#	m/z	I
1	3525.1745	674
2	3669.3188	673
3	5302.7730	846
4	5302.7730	846
5	5357.8000	1426
6	5400.8341	1127
7	5466.7263	1227
8	5510.8996	12373

Proto

Phenol

Product

Cross-Coupling Product-3ag



Product: 53%
Aryl Halide: 0%
Protodehalogenation: 17%
Phenol: 0%

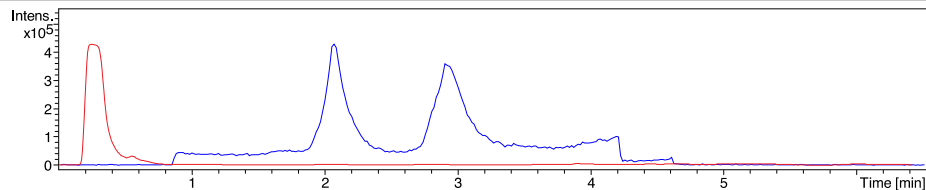
Compound Spectrum List Report

Analysis Info

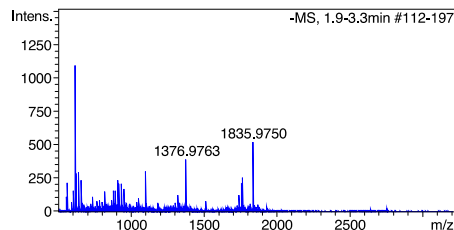
Analysis Name: X:\Chem MS Data\utof\Data_2018\Nov 2018\utof-111618\JHS-181105-6_16_01_10240.d
 Method: 1200col2_10to90in4.m
 Sample Name: JHS-181105-6
 Comment:
 Acquisition Date: 11/16/2018 6:17:29 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

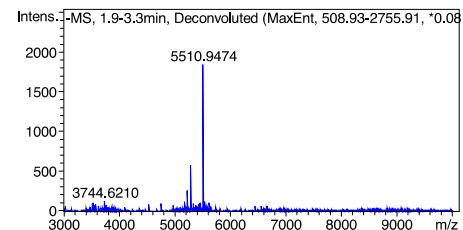
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.3min #112-197



#	m/z	I
1	621.0811	1093
2	643.0617	296
3	1101.1851	297
4	1376.4764	378
5	1376.7250	390
6	1376.9763	392
7	1835.6457	360
8	1835.9750	521
9	1836.3069	494
10	1836.6376	355

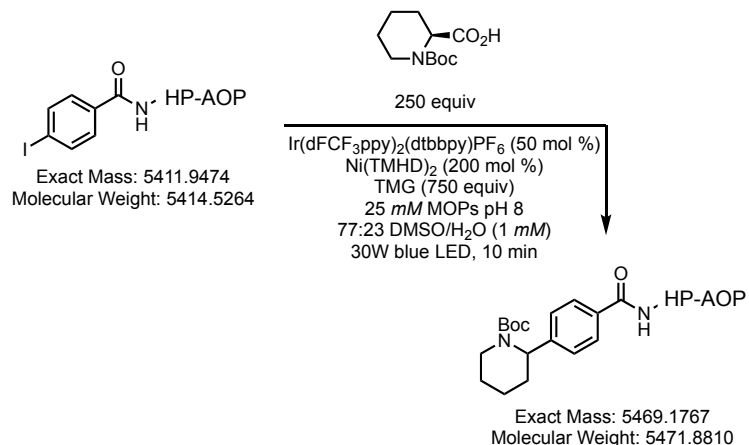


#	m/z	I
1	3540.4763	113
2	3744.6210	131
3	4760.6102	106
4	5180.9003	126
5	5225.7687	267
6	5287.7850	581
7	5332.7988	103
8	5455.9178	108
9	5510.9474	1838
10	5537.8851	124

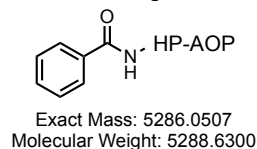
protodehalogenation

product

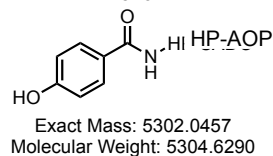
Cross-Coupling Product-3ah



Protodehalogenation



Phenol



Product: 65%
Aryl Halide: 0%
Protodehalogenation: 20%
Phenol: 4%

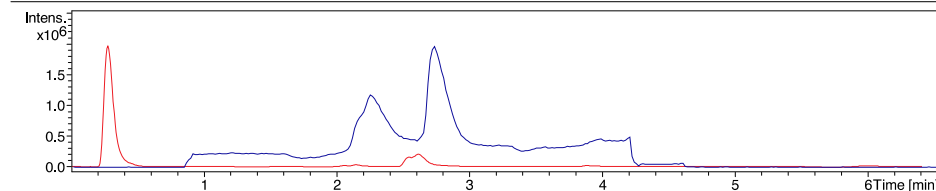
Compound Spectrum List Report

Analysis Info

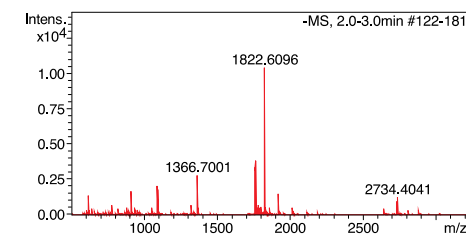
Analysis Name X:\Chem MS Data\TOF\Data_2018\July 2018\utof-071218\DNA-20180508-C6_36_01_8827.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180508-C6
 Comment
 Acquisition Date 7/12/2018 4:38:55 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

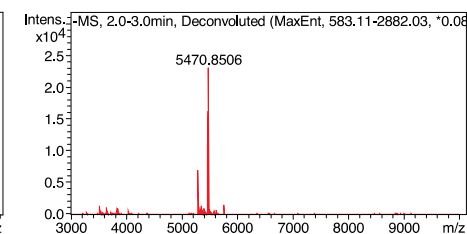
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.0min #122-181

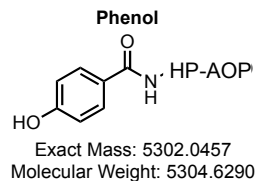
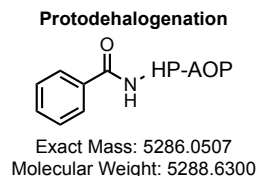
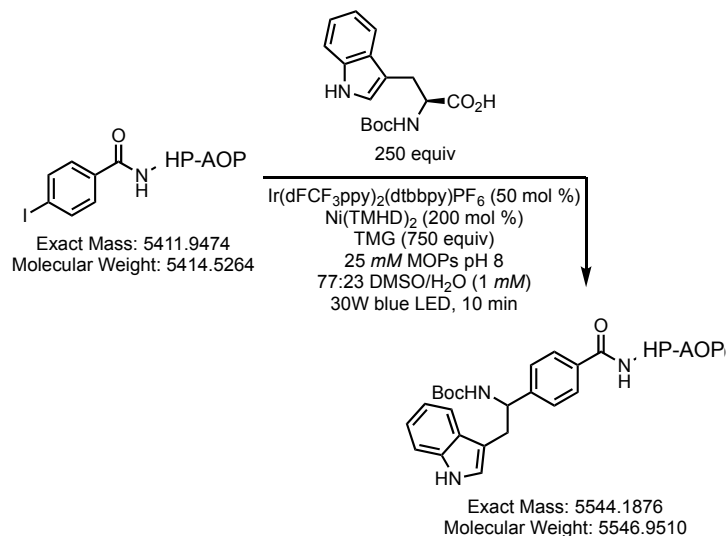


#	m/z	I
1	1366.7001	2785
2	1761.2363	3347
3	1761.5704	3846
4	1761.9042	3198
5	1821.9425	4055
6	1822.2743	8953
7	1822.6096	10364
8	1822.9426	9620
9	1823.2764	7033
10	1823.6068	4338



#	m/z	I	
1	3524.4934	1396	
2	5287.7381	7000	Proto
3	5301.7246	1280	Phenol
4	5357.7727	1349	
5	5470.8506	23023	Product
6	5762.9175	1489	

Cross-Coupling Product-3ai



Product: 51%
Aryl Halide: 3%
Protodehalogenation: 17%
Phenol: 4%

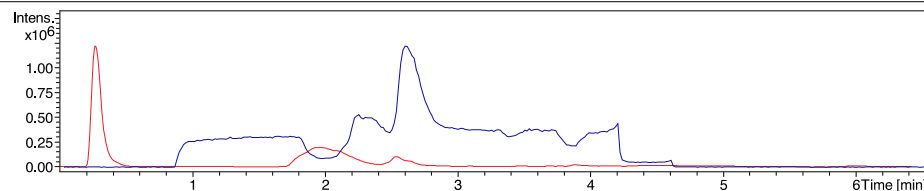
Compound Spectrum List Report

Analysis Info

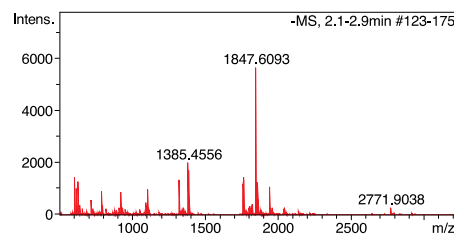
Analysis Name X:\Chem MS Data\TOF\Data_2018\July 2018\utof-071218\DNA-20180508-E6_46_01_8833.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180508-E6
 Comment
 Acquisition Date 7/12/2018 5:22:56 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

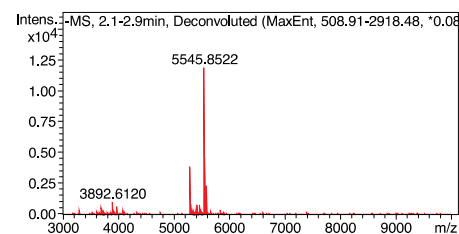
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.1-2.9min #123-175



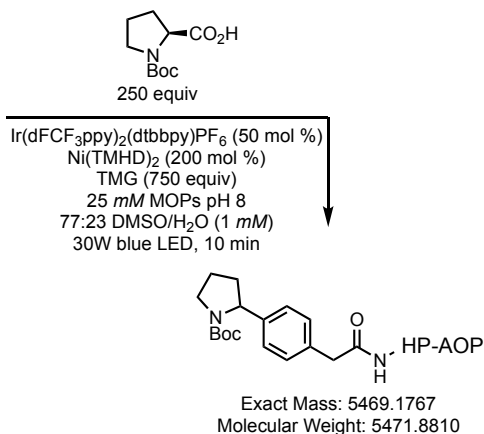
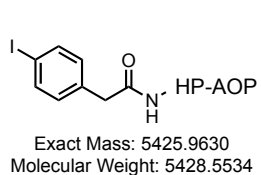
#	m/z	I
1	607.2312	1455
2	1385.2057	1435
3	1385.4556	1995
4	1385.7041	1721
5	1846.9477	2015
6	1847.2769	4659
7	1847.6093	5640
8	1847.9411	5141
9	1848.2746	3698
10	1848.6083	2259



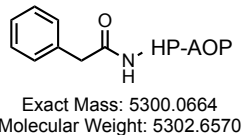
#	m/z	I
1	3697.9000	597
2	3892.6120	1014
3	3976.3850	662
4	5287.7368	3890
5	5302.7453	837
6	5414.6532	769
7	5466.7376	794
8	5545.8522	11847
9	5566.8937	661
10	5589.8348	2354

Proto
 Phenol
 Aryl Halide
 Product

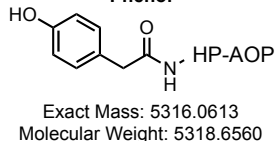
Cross-Coupling Product-3aj



Protodehalogenation



Phenol



Product: 67%
Aryl Halide: 6%
Protodehalogenation: 23%
Phenol: 0%

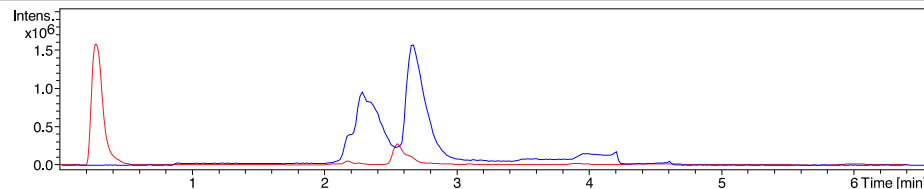
Compound Spectrum List Report

Analysis Info

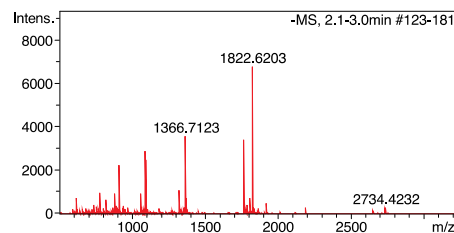
Analysis Name: X:\Chem MS Data\ToF\Data_2018\July 2018\utof-071218\DNA-20180508-A5_15_01_8813.d
 Method: 1200col2_10to90in4.m
 Sample Name: DNA-20180508-A5
 Comment:
 Acquisition Date: 7/12/2018 2:55:47 PM
 Operator: gsk
 Instrument: micrOTOF 213750.00199

Acquisition Parameter

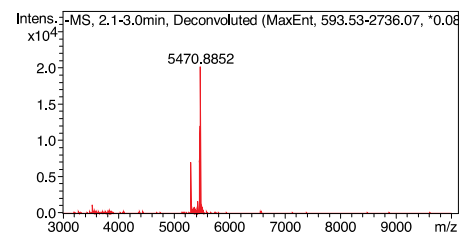
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.1-3.0min #123-181



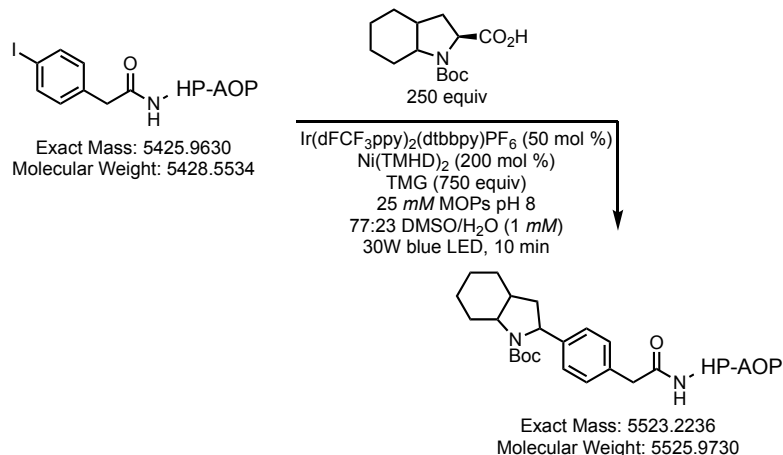
#	m/z	I
1	1093.1744	2870
2	1366.7123	3578
3	1366.9574	3257
4	1765.9196	2811
5	1766.2519	3388
6	1766.5829	2781
7	1822.2868	5418
8	1822.6203	6772
9	1822.9562	5942
10	1823.2864	4288



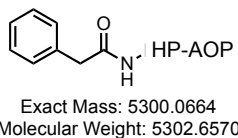
#	m/z	I
1	3535.2106	1251
2	5301.7810	6997
3	5427.6831	1681
4	5470.8852	20118

Proto
 Aryl Halide
 Product

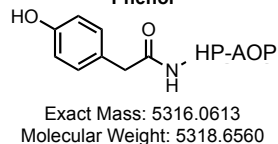
Cross-Coupling Product-3ak



Protodehalogenation



Phenol



Product: 42%
Aryl Halide: 5%
Protodehalogenation: 26%
Phenol: 5%

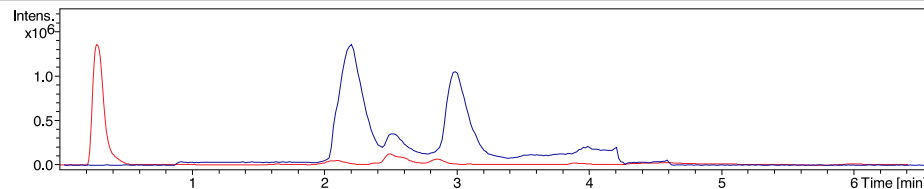
Compound Spectrum List Report

Analysis Info

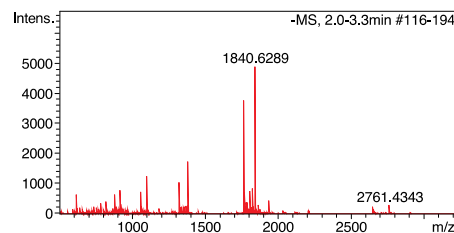
Analysis Name: X:\Chem MS Data\TOF\Data_2018\July 2018\utof-071218\DNA-20180508-B5_25_01_8819.d
 Method: 1200col2_10to90in4.m
 Sample Name: DNA-20180508-B5
 Comment:
 Acquisition Date: 7/12/2018 3:40:11 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

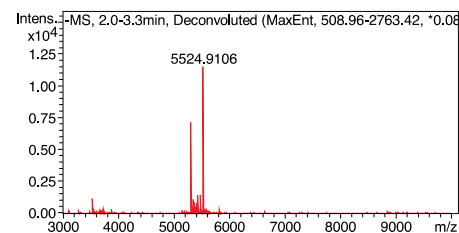
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.3min #116-194



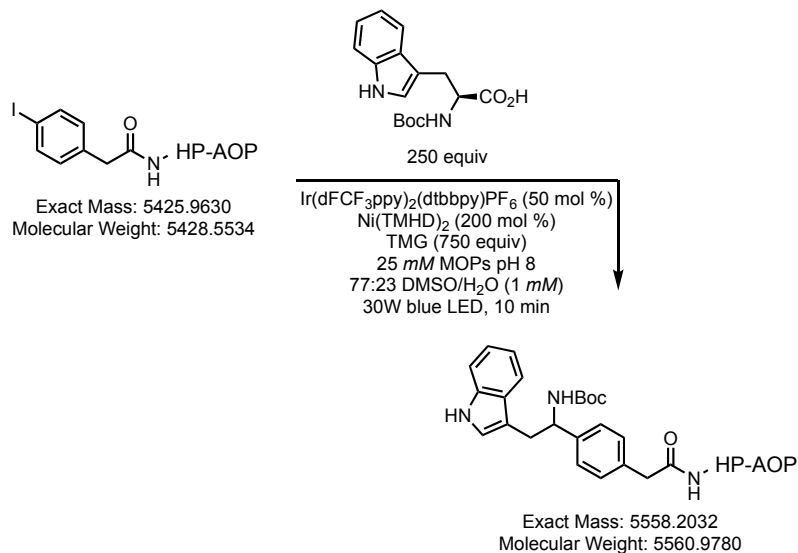
#	m/z	I
1	1765.9174	2988
2	1766.2495	3741
3	1766.5802	3211
4	1766.9150	2026
5	1839.9626	1961
6	1840.2962	4016
7	1840.6289	4884
8	1840.9618	4394
9	1841.2951	3186
10	1841.6286	1986



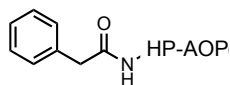
#	m/z	I
1	3535.2015	1138
2	5301.7736	7139
3	5316.7680	1237
4	5345.7541	1080
5	5365.7265	635
6	5372.8124	900
7	5414.8451	824
8	5427.6650	1432
9	5480.7499	1420
10	5524.9106	11451

Proto
 Phenol
 Aryl Halide
 Product

Cross-Coupling Product-3aI

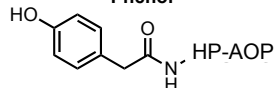


Protodehalogenation



Exact Mass: 5300.0664
 Molecular Weight: 5302.6570

Phenol



Exact Mass: 5316.0613
 Molecular Weight: 5318.6560

Product: 40%
Aryl Halide: 17%
Protodehalogenation: 32%
Phenol: 2%

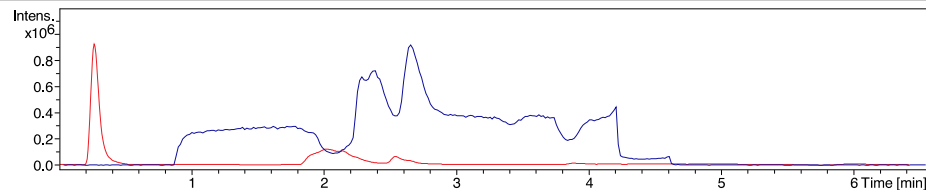
Compound Spectrum List Report

Analysis Info

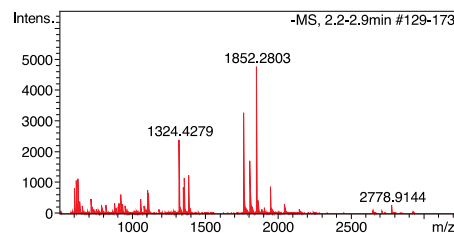
Analysis Name: X:\Chem MS Data\TOF\Data_2018\July 2018\utof-071218\DNA-20180508-E5_45_01_8832.d
 Method: 1200col2_10to90in4.m
 Sample Name: DNA-20180508-E5
 Comment:
 Acquisition Date: 7/12/2018 5:15:36 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

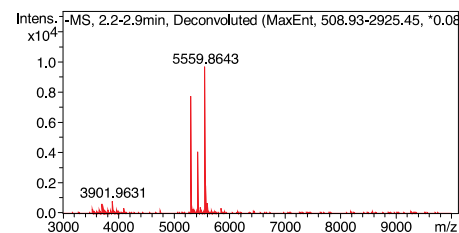
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.2-2.9min #129-173



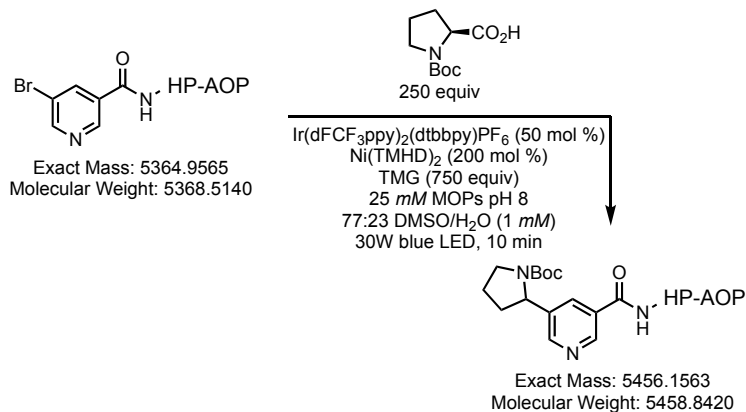
#	m/z	I
1	1324.1814	1853
2	1324.4279	2404
3	1324.6745	1882
4	1765.9068	2508
5	1766.2374	3268
6	1766.5705	2634
7	1851.9479	3643
8	1852.2803	4760
9	1852.6109	4247
10	1852.9460	2784



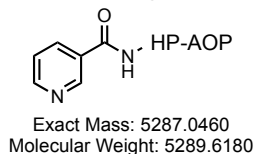
#	m/z	I
1	3705.8705	621
2	3901.9631	840
3	5301.7389	7746
4	5315.7526	565
5	5427.6176	4044
6	5559.8643	9649
7	5604.8482	710

Proto
 Phenol
 Aryl Halide
 Product

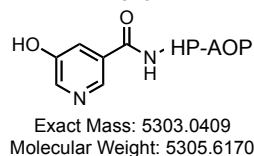
Cross-Coupling Product-3am



Protodehalogenation



Phenol



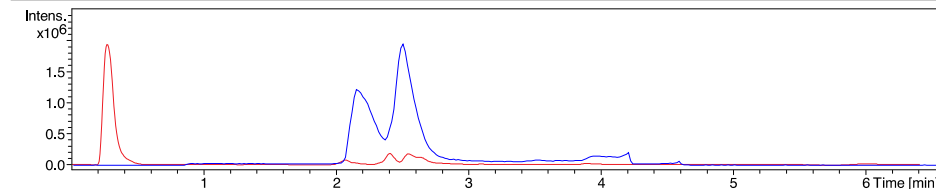
Compound Spectrum List Report

Analysis Info

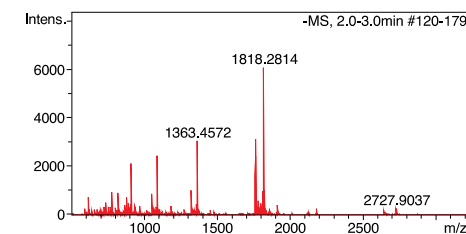
Analysis Name	X:\Chem MS Data\TOF\Data_2018\July 2018\utof-071218\DNA-20180508-A3_13_01_8811.d	Acquisition Date	7/12/2018 2:40:48 PM
Method	1200col2_10to90in4.m	Operator	gsk
Sample Name	DNA-20180508-A3	Instrument	micrOTOF 213750.00199
Comment			

Acquisition Parameter

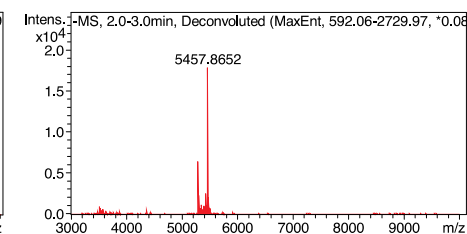
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.0min #120-179



#	m/z	I
1	1090.5677	2446
2	1363.4572	3035
3	1363.7050	2859
4	1761.5834	2900
5	1761.9181	3139
6	1762.2474	2670
7	1817.9480	5060
8	1818.2814	6068
9	1818.6147	5344
10	1818.9462	3775

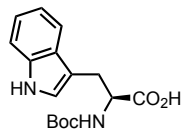
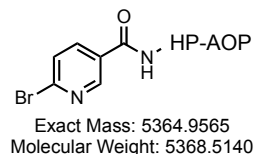


#	m/z	I	
1	3525.8685	984	
2	5288.7716	6484	
3	5303.7719	2375	
4	5352.7255	1206	
5	5401.8370	1028	
6	5435.7819	2554	
7	5457.8652	17811	
8	5467.7389	2816	

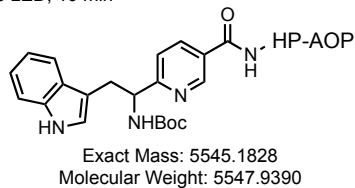
Proto
 Phenol
 Product

Product: 51%
Aryl Halide: 0%
Protodehalogenation: 18%
Phenol: 7%

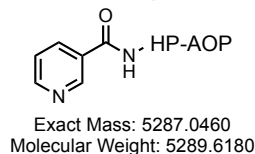
Cross-Coupling Product-3an



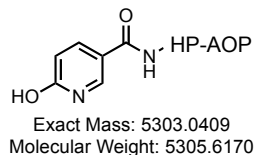
Ir(dFCF₃ppy)₂(dtbbpy)PF₆ (50 mol %)
 Ni(TMHD)₂ (200 mol %)
 TMG (750 equiv)
 25 mM MOPs pH 8
 77:23 DMSO/H₂O (1 mM)
 30W blue LED, 10 min



Protodehalogenation



Phenol



Product: 46%
Aryl Halide: 0%
Protodehalogenation: 17%
Phenol: 9%

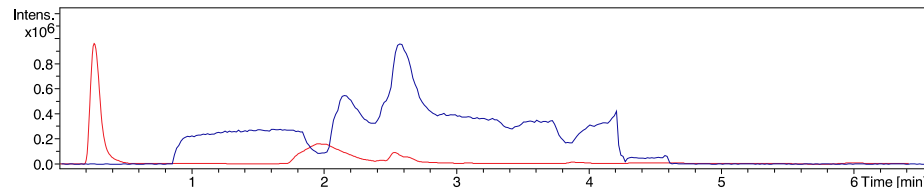
Compound Spectrum List Report

Analysis Info

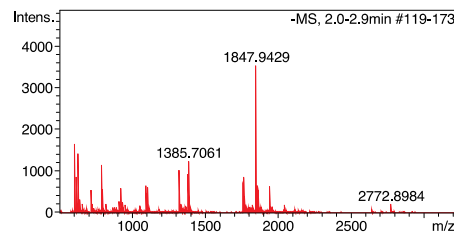
Analysis Name X:\Chem MS Data\TOF\Data_2018\July 2018\utof-071218\DNA-20180508-E4_44_01_8831.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180508-E4
 Comment
 Acquisition Date 7/12/2018 5:08:16 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

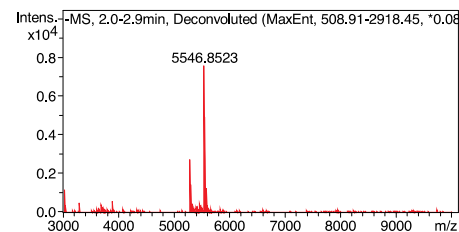
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-2.9min #119-173



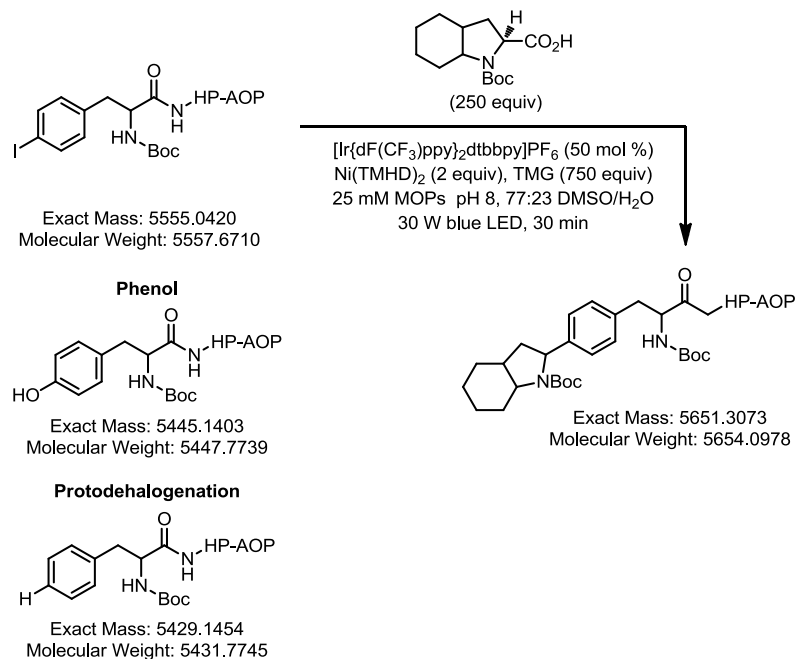
#	m/z	I
1	607.2311	1655
2	629.2124	1430
3	794.2740	1141
4	1385.7061	1239
5	1847.2784	1310
6	1847.6112	2842
7	1847.9429	3532
8	1848.2760	3267
9	1848.6083	2284
10	1848.9358	1524



#	m/z	I
1	3041.1904	1154
2	3298.2546	497
3	3697.8975	409
4	3893.2680	607
5	5288.7259	2730
6	5303.7327	1436
7	5333.7105	473
8	5467.7481	448
9	5546.8523	7539
10	5591.8505	1249

Proto
 Phenol
 Product

Cross-Coupling Product-3ao



Product: 55%
Aryl Halide: 7%
Protodehalogenation: 25%
Phenol: 7%

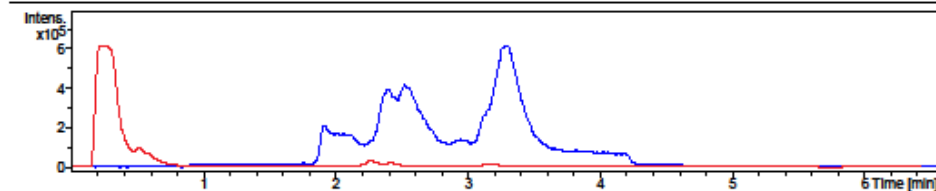
Compound Spectrum List Report

Analysis Info

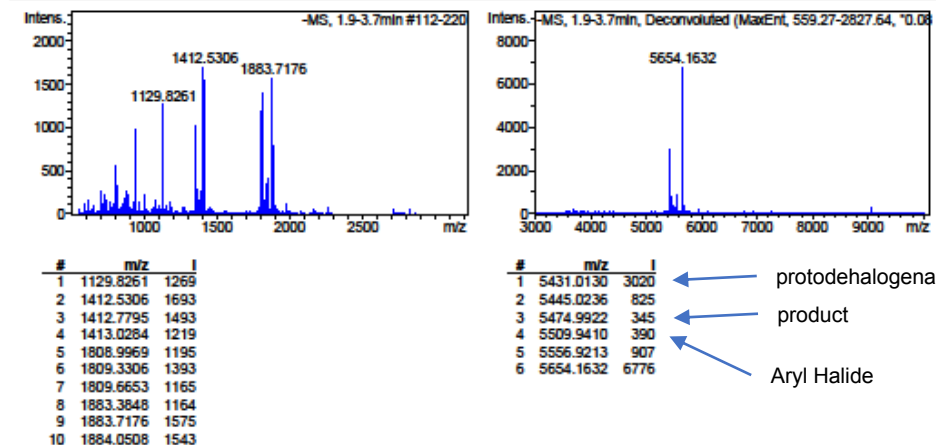
Analysis Name: X:\Chem MS Data\TOF\Data_2019\January\SB-N3-0220-C5_14_01_10591.d
 Method: 1200col2_10to90in4.m
 Sample Name: SB-N3-0220-C5
 Acquisition Date: 1/7/2019 2:58:48 PM
 Operator: gsk
 Instrument: micrOTOF
 Comment: 213750.00199

Acquisition Parameter

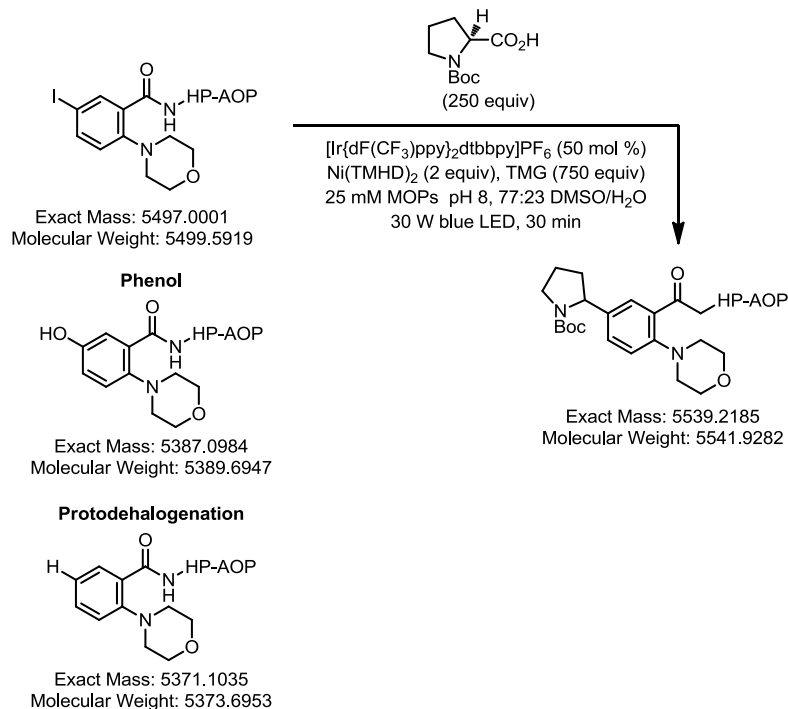
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.7min #112-220



Cross-Coupling Product-3ap



Product: 41%
Aryl Halide: 0%
Protodehalogenation: 26%
Phenol: 4%

Compound Spectrum List Report

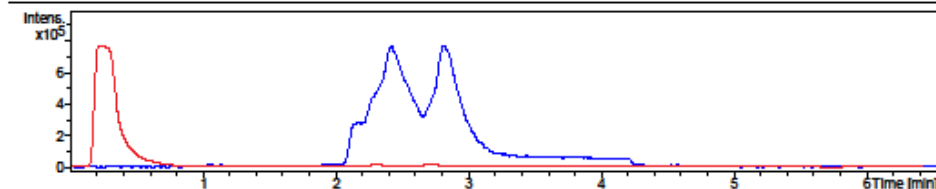
Analysis Info

Analysis Name: X:\Chem MS Data\TOF\Data_2019\January\SB-N3-0220-D2_18_01_10595.d
 Method: 1200col2_10to90in4.m
 Sample Name: SB-N3-0220-D2
 Comment:

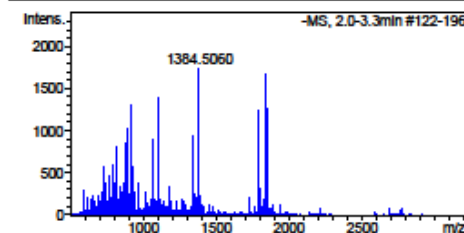
Acquisition Date: 1/7/2019 3:28:39 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste

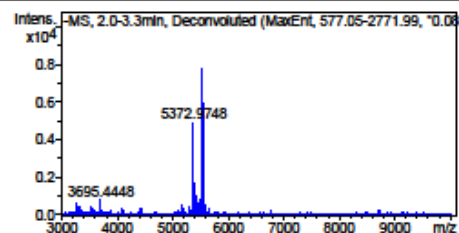


-MS, 2.0-3.3min #122-196



#	m/z	I
1	922.6703	1299
2	1107.4079	1395
3	1107.6072	1238
4	1384.2584	1336
5	1384.5060	1739
6	1384.7563	1531
7	1789.9827	1248
8	1846.0181	1410
9	1846.3525	1676
10	1846.6830	1514

#	m/z	I
1	922.6703	1299
2	1107.4079	1395
3	1107.6072	1238
4	1384.2584	1336
5	1384.5060	1739
6	1384.7563	1531
7	1789.9827	1248
8	1846.0181	1410
9	1846.3525	1676
10	1846.6830	1514

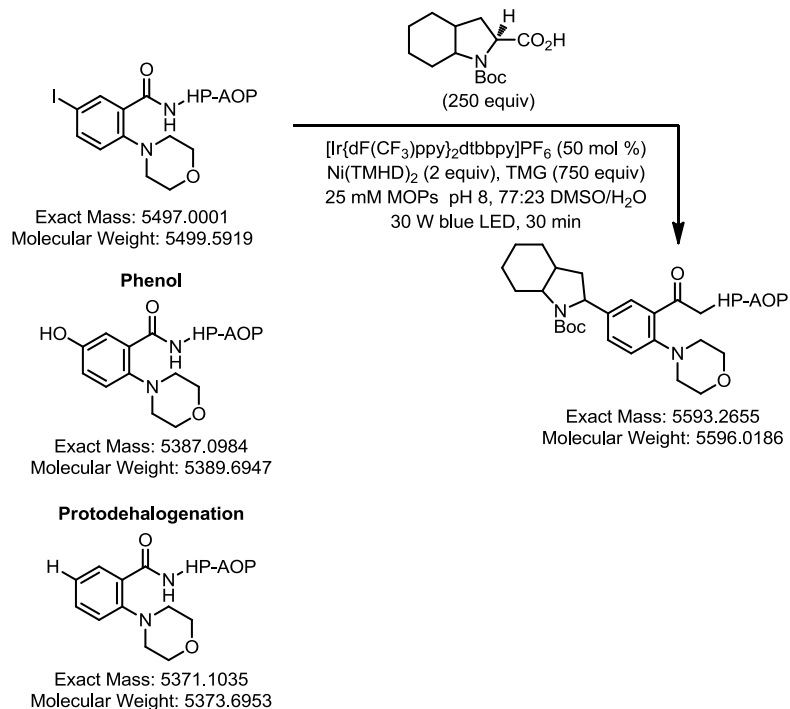


#	m/z	I
1	3280.3558	607
2	3353.7969	438
3	3540.5251	452
4	3695.4448	791
5	5183.8975	574
6	5310.9490	415
7	5372.9748	4892
8	5386.9790	707
9	5415.9777	1071
10	5486.0621	793

#	m/z	I
1	5542.0752	7732
2	5586.0623	554

← protodehalogenation
 ← product
 ← Aryl Halide

Cross-Coupling Product-3aq



Product: 86%
Aryl Halide: 0%
Protodehalogenation: 8%
Phenol: 0%

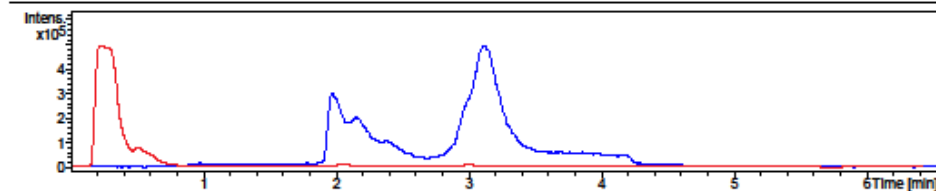
Compound Spectrum List Report

Analysis Info

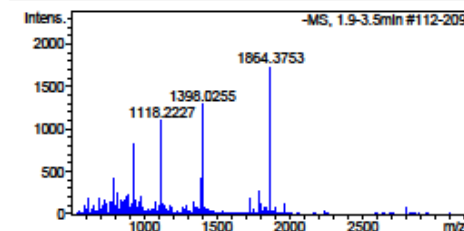
Analysis Name: X:\Chem MS Data\TOF\Data_2019\January\SB-N3-0220-C3_13_01_10590.d
 Method: 1200col2_10to90in4.m
 Sample Name: SB-N3-0220-C3
 Acquisition Date: 1/7/2019 2:51:18 PM
 Operator: gsk
 Instrument: micrOTOF
 Comment: 213750.00199

Acquisition Parameter

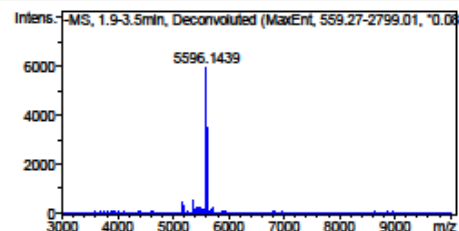
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.5min #112-209

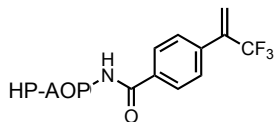
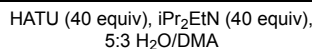


#	m/z	I
1	1118.2227	1090
2	1118.4188	899
3	1397.7747	1003
4	1398.0255	1284
5	1398.2716	1269
6	1398.5222	912
7	1864.0419	1267
8	1864.3753	1721
9	1864.7039	1487
10	1865.0396	1075

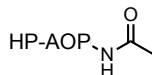


#	m/z	I	
1	5183.9343	454	← protodehalogenation
2	5372.9966	553	← product
3	5596.1439	5948	← Aryl Halide

Trifluoromethylalkene Synthesis

CC(F)(F)F=C1C=CC(=C1)C(=O)O
(40 equiv)

Exact Mass: 5380.0538
Molecular Weight: 5382.6662



Exact Mass: 5224.0351
Molecular Weight: 5226.5590

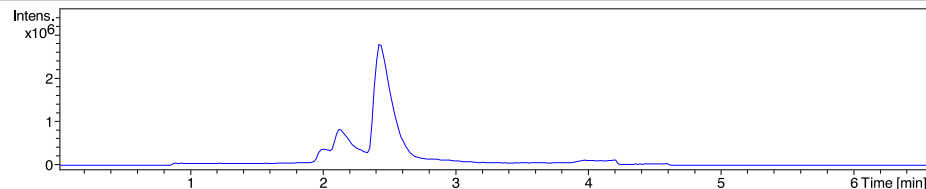
Analysis Info

Analysis Name	I:\People\Katelyn\UPer
Method	1200col2_10to90in4.m
Sample Name	JPP-5096
Comment	

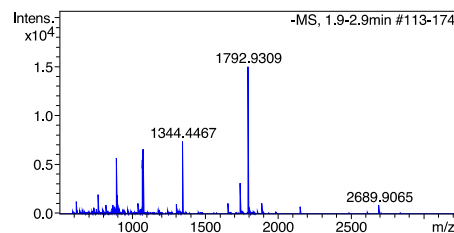
Acquisition Date 4/17/2018 11:57:01 AM
_8026.d
Operator gsk
Instrument micrOTOF 213750.00199

Acquisition Parameter

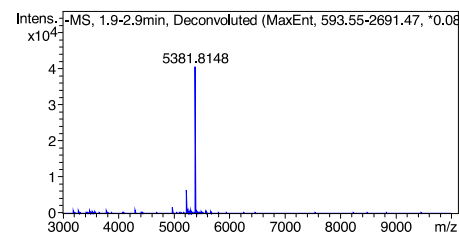
Required Parameters					
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #113-174



#	m/z	I
1	895.9576	5720
2	1075.3561	6543
3	1344.1995	5950
4	1344.4467	7391
5	1344.6974	5902
6	1792.2652	5847
7	1792.5971	11938
8	1792.9309	14995
9	1793.2635	12439
10	1793.5954	8640

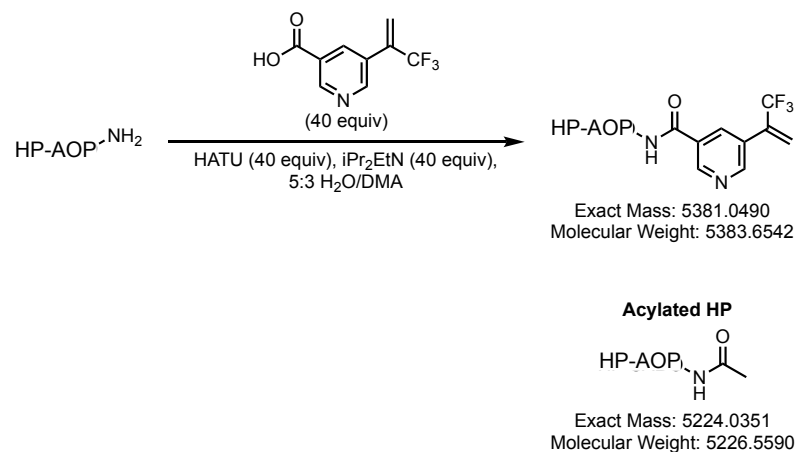


#	m/z	I
1	5225.8027	6481
2	5381.8148	40564

Acylated HP

product

Product: 86%
Starting Material: 0%



Product: 94%
Starting Material: 0%

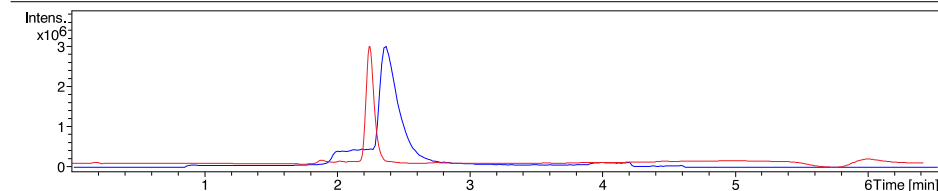
Compound Spectrum List Report

Analysis Info

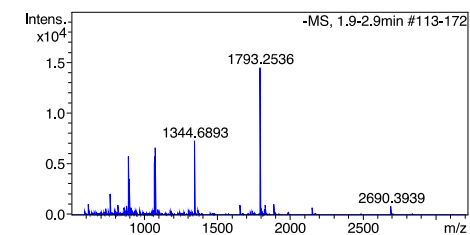
Analysis Name I:\People\Katelyn\UPenn\Data for Analysis\JPP-5170_93_01_8028.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-5170
 Comment
 Acquisition Date 4/17/2018 12:11:47 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

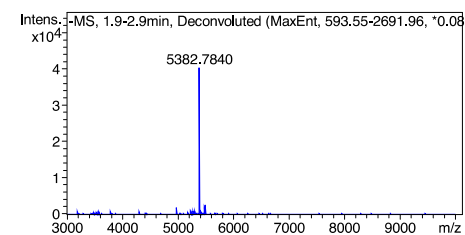
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #113-172



#	m/z	I
1	1075.3500	5781
2	1075.5481	6640
3	1075.7483	5916
4	1344.4412	6030
5	1344.6893	7277
6	1792.5875	5873
7	1792.9210	12182
8	1793.2536	14456
9	1793.5867	11963
10	1793.9184	8362

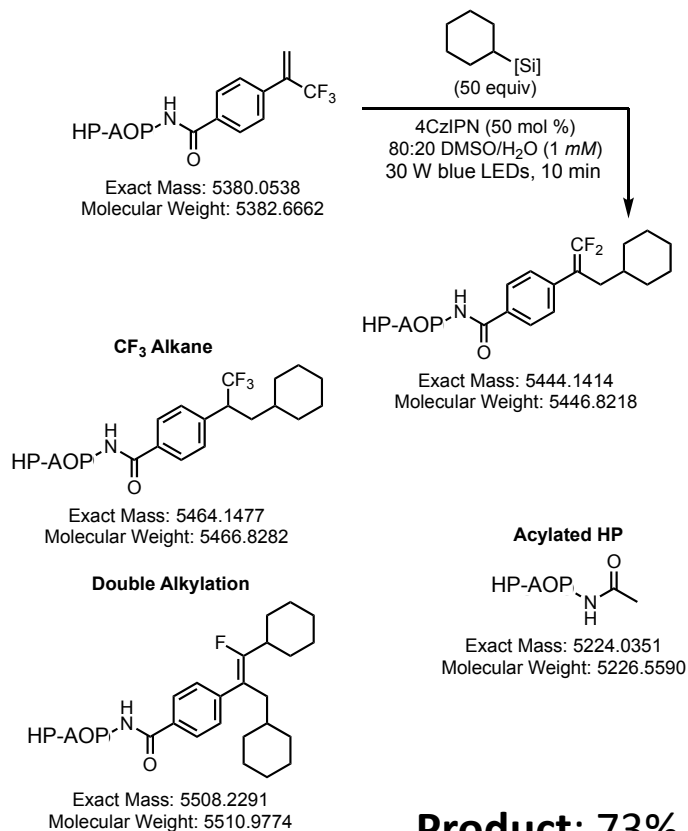


#	m/z	I
1	5382.7840	40314
2	5486.6663	2637

product

Defluorinative Alkylation using Silicates

CF₂-Alkene-7a



Product: 73%
Starting Material: 6%
Double alkylation: 7%
CF₃ alkane: 5%

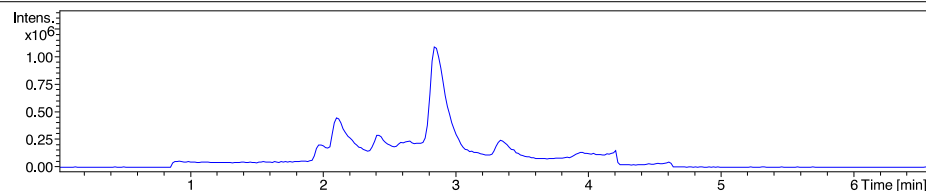
Compound Spectrum List Report

Analysis Info

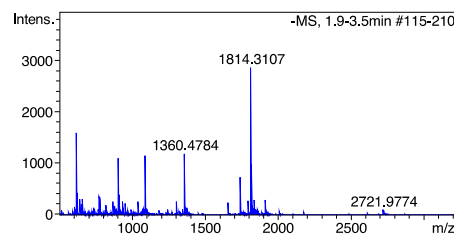
Analysis Name D:\Data\Data 2018\April 2018\utof-041318\JPP-180307-2-8_16_01_7961.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-180307-2-8
 Comment
 Acquisition Date 4/13/2018 2:50:10 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

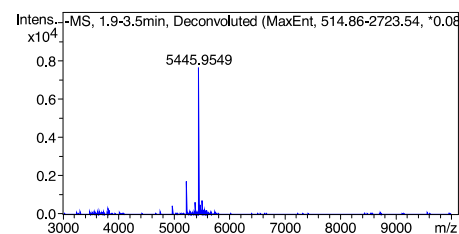
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.5min #115-210

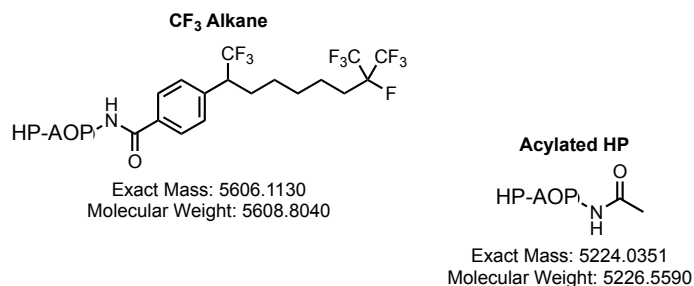
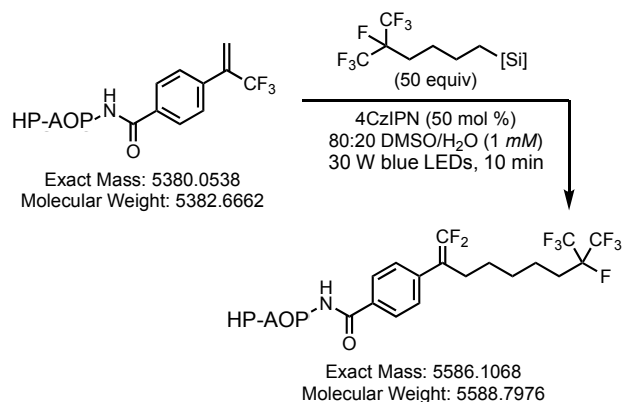


#	m/z	I
1	621.0959	1587
2	906.6495	1100
3	1088.1843	1145
4	1360.4784	1187
5	1813.6415	1059
6	1813.9773	2285
7	1814.3107	2859
8	1814.6429	2456
9	1814.9748	1680
10	1815.3103	984



#	m/z	I
1	4978.7261	464
2	5225.8576	1712
3	5381.8640	633
4	5445.9549	7609
5	5465.9540	476
6	5481.9367	490
7	5510.0296	735

Acylated HP
 Starting material
 product
 CF₃ alkane
 Double alkylation



Product: 80%
Starting Material: 0%
Double alkylation: 0%
CF₃ alkane: 8%

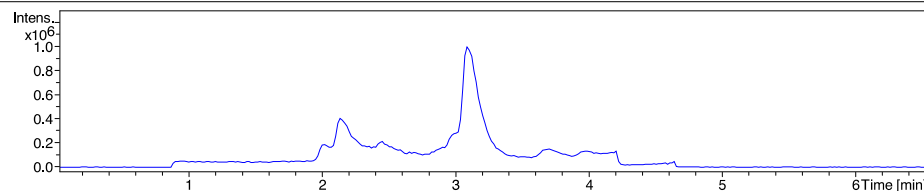
Compound Spectrum List Report

Analysis Info

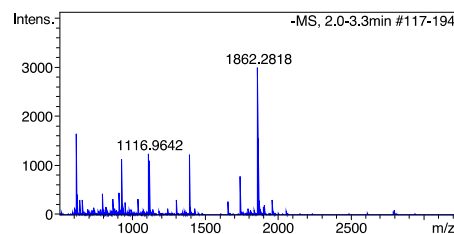
Analysis Name D:\Data\Data 2018\April 2018\utof-041318\JPP-180307-2-16_23_01_7968.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-180307-2-16
 Comment
 Acquisition Date 4/13/2018 3:41:42 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

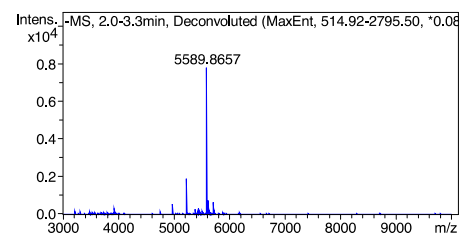
Source Type ESI Ion Polarity Negative Set Nebulizer 3.5 Bar
 Focus Active Set Dry Heater 220 °C
 Scan Begin 510 m/z Set Capillary 2500 V Set Dry Gas 11.0 l/min
 Scan End 3200 m/z Set End Plate Offset -400 V Set Divert Valve Waste



-MS, 2.0-3.3min #117-194

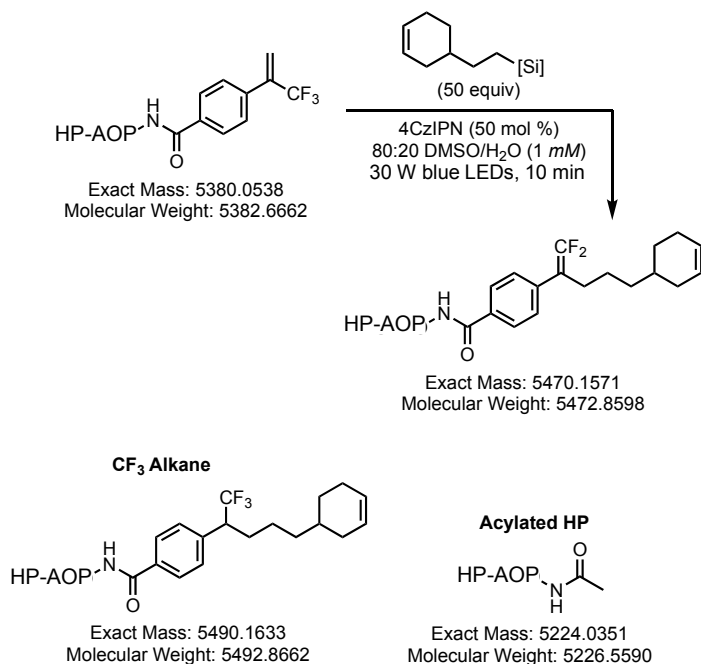


#	m/z	I
1	621.0926	1637
2	930.6338	1125
3	1116.7666	1109
4	1116.9642	1243
5	1117.1661	1100
6	1396.4601	1214
7	1861.9492	2408
8	1862.2818	2992
9	1862.6164	2593
10	1862.9486	1708



#	m/z	I
1	4978.7070	552
2	5225.8385	1890
3	5589.8657	7783
4	5609.8715	760
5	5717.8971	632

Acylated HP
 product
 CF₃ alkane



Product: 82%
Starting Material: 6%
Double alkylation: 0%
CF₃ alkane: 8%

Compound Spectrum List Report

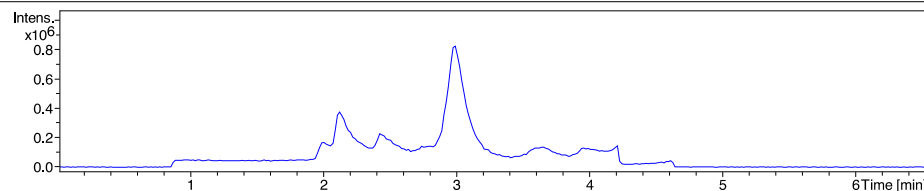
Analysis Info

Analysis Name D:\Data\Data 2018\April 2018\utof-041318\JPP-180307-2-10_18_01_7963.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-180307-2-10
 Comment

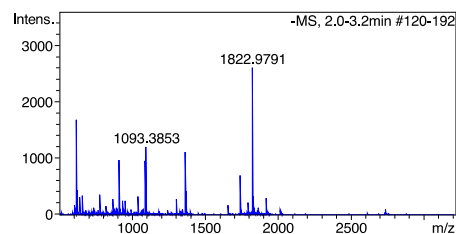
Acquisition Date 4/13/2018 3:04:56 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

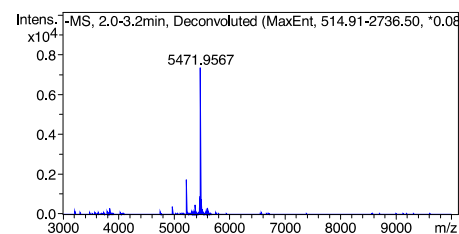
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.2min #120-192

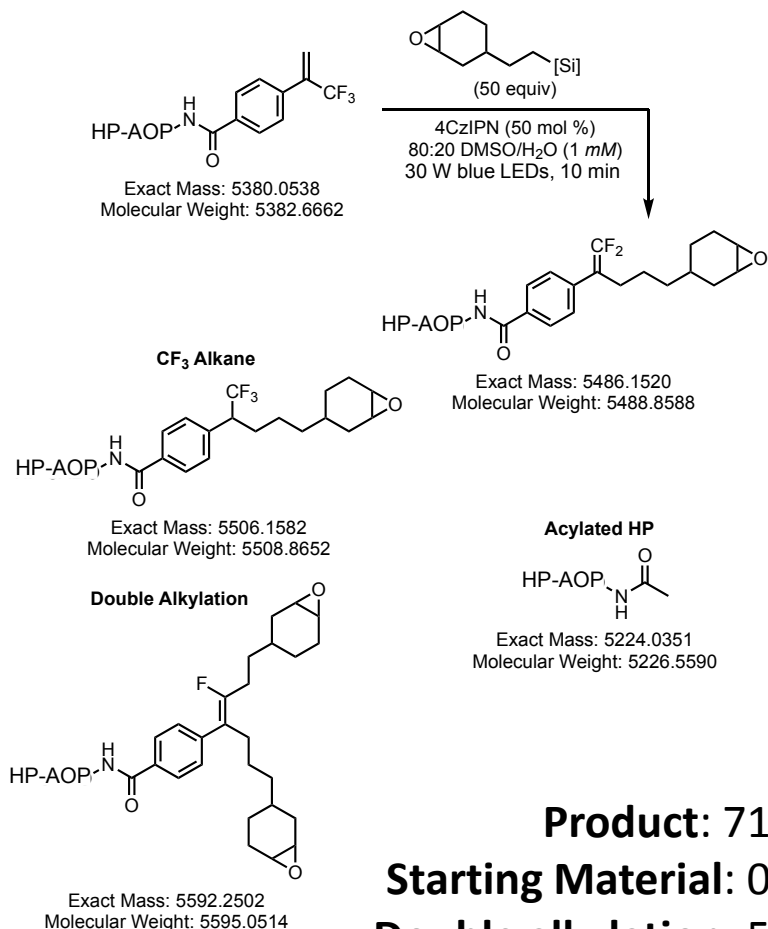


#	m/z	I
1	621.0938	1684
2	1093.3853	1208
3	1093.5834	988
4	1366.9784	1105
5	1367.2287	979
6	1822.6451	2145
7	1822.9791	2602
8	1823.3149	2381
9	1823.6472	1762
10	1823.9778	1022



#	m/z	I
1	4978.6984	394
2	5225.8448	1746
3	5381.8501	499
4	5471.9567	7322
5	5492.9517	735

Acylated HP
 Starting material
 product
 CF₃ alkane



Product: 71%
Starting Material: 0%
Double alkylation: 5%
CF₃ alkane: 9%

Compound Spectrum List Report

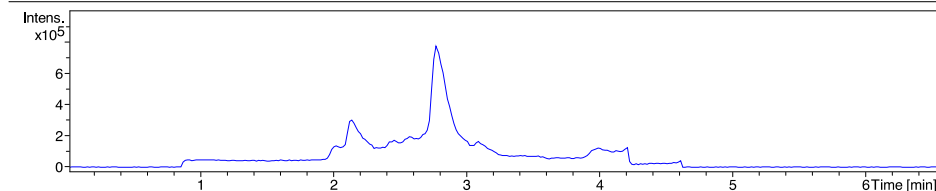
Analysis Info

Analysis Name D:\Data\Data 2018\April 2018\utof-041318\JPP-180307-2-14_21_01_7966.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-180307-2-14
 Comment

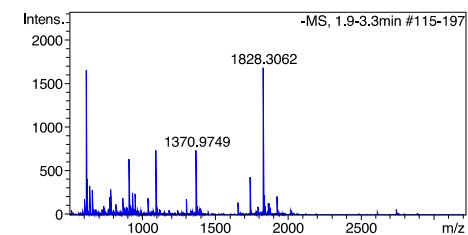
Acquisition Date 4/13/2018 3:27:01 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

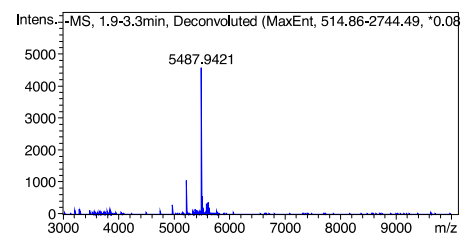
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.3min #115-197

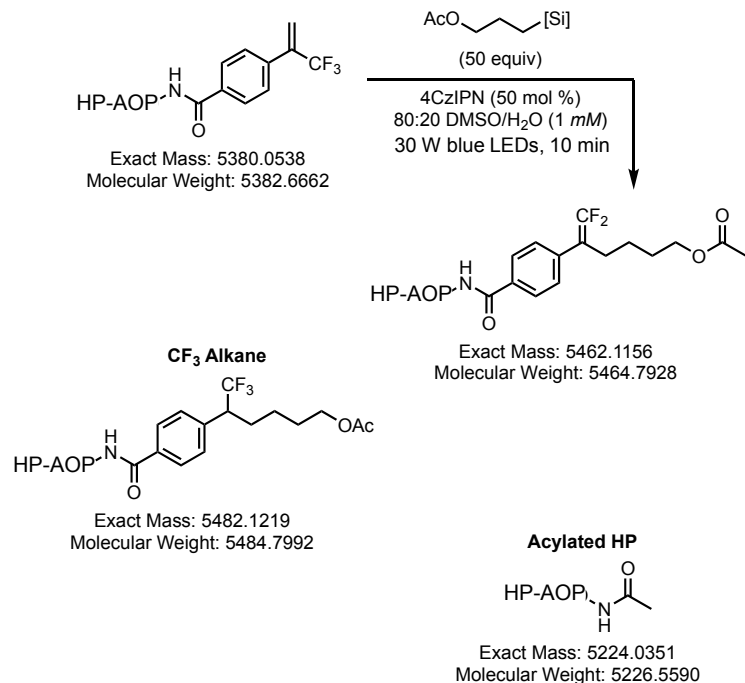


#	m/z	I
1	621.0928	1650
2	913.6471	633
3	1096.5794	735
4	1096.7799	673
5	1370.9749	737
6	1371.2237	633
7	1827.9741	1307
8	1828.3062	1681
9	1828.6374	1437
10	1828.9718	1009



#	m/z	I
1	4978.6986	290
2	5225.8315	1070
3	5487.9421	4572
4	5507.9492	585
5	5523.9301	230
6	5595.0155	335
7	5616.9749	390

Acylated HP
 product
 CF₃ alkane
 Double alkylation



Product: 74%
Starting Material: 5%
Double alkylation: 0%
CF₃ alkane: 9%

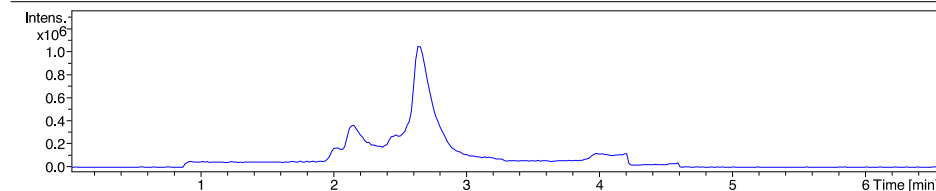
Compound Spectrum List Report

Analysis Info

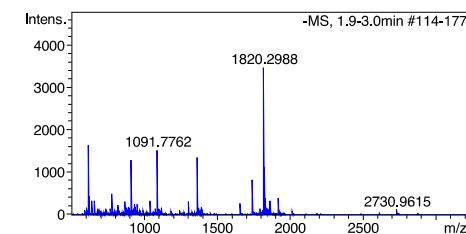
Analysis Name D:\Data\Data 2018\April 2018\utof-041318\JPP-180307-2-26_30_01_7975.d
 Acquisition Date 4/13/2018 4:33:17 PM
 Method 1200col2_10to90in4.m
 Operator gsk
 Sample Name JPP-180307-2-26
 Instrument micrOTOF 213750.00199
 Comment

Acquisition Parameter

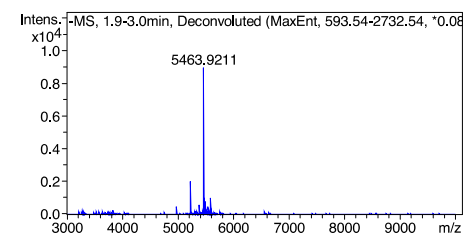
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.0min #114-177

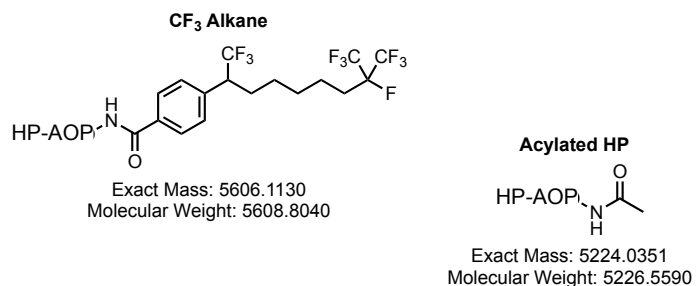
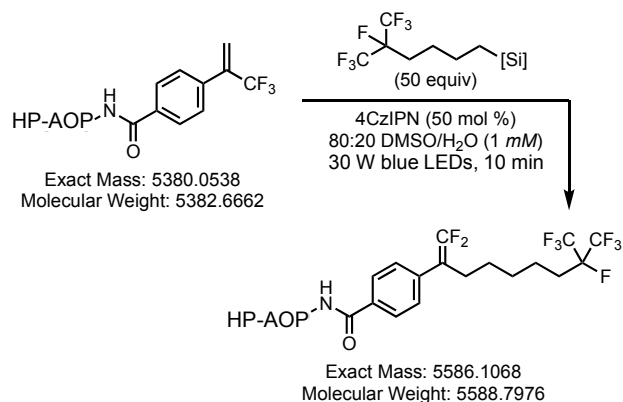


#	m/z	I
1	621.0955	1635
2	909.6429	1289
3	1091.5767	1360
4	1091.7762	1521
5	1364.9711	1352
6	1819.6365	1300
7	1819.9658	2807
8	1820.2988	3464
9	1820.6336	2795
10	1820.9662	1961



#	m/z	I	
1	4978.7220	512	
2	5225.8547	2004	
3	5382.8851	572	
4	5463.9211	8926	
5	5483.9219	997	
6	5591.9432	991	

Acylated HP
 Starting material
 product
 CF₃ alkane



Product: 80%
Starting Material: 0%
Double alkylation: 0%
CF₃ alkane: 8%

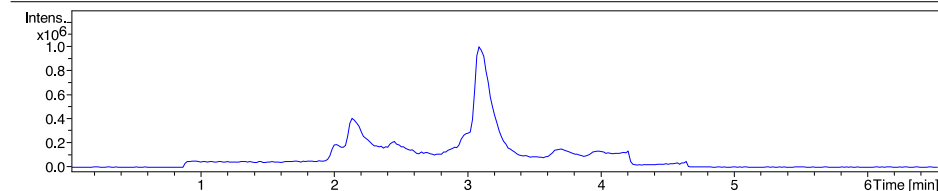
Compound Spectrum List Report

Analysis Info

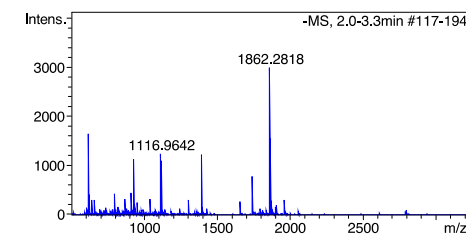
Analysis Name D:\Data\Data 2018\April 2018\utof-041318\JPP-180307-2-16_23_01_7968.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-180307-2-16
 Comment
 Acquisition Date 4/13/2018 3:41:42 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

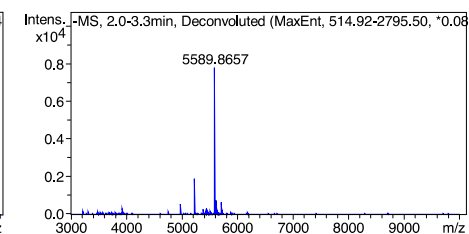
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.3min #117-194

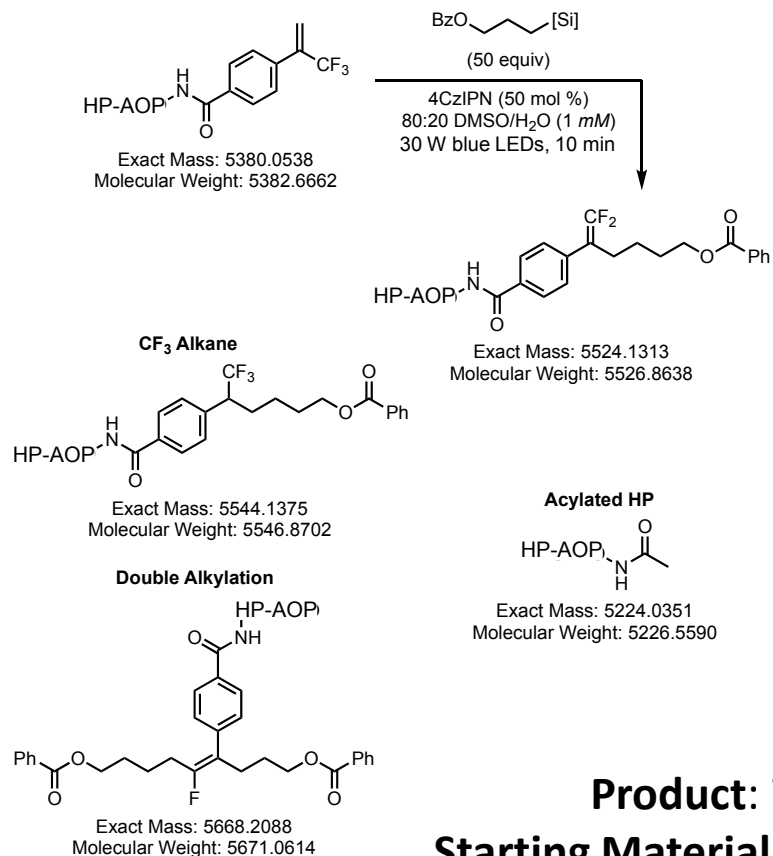


#	m/z	I
1	621.0926	1637
2	930.6338	1125
3	1116.7666	1109
4	1116.9642	1243
5	1117.1661	1100
6	1396.4601	1214
7	1861.9492	2408
8	1862.2818	2992
9	1862.6164	2593
10	1862.9486	1708



#	m/z	I
1	4978.7070	552
2	5225.8385	1890
3	5589.8657	7783
4	5609.8715	760
5	5717.8971	632

Acylated HP
 product
 CF₃ alkane



Product: 72%
Starting Material: 4%
Double alkylation: 9%
CF₃ alkane: 14%

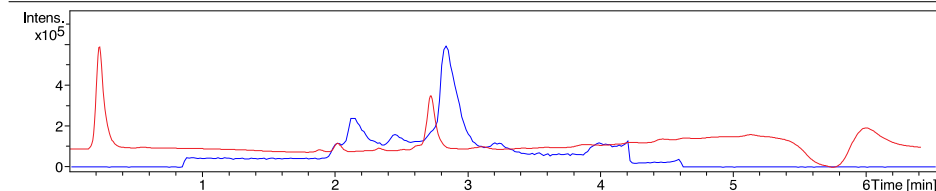
Compound Spectrum List Report

Analysis Info

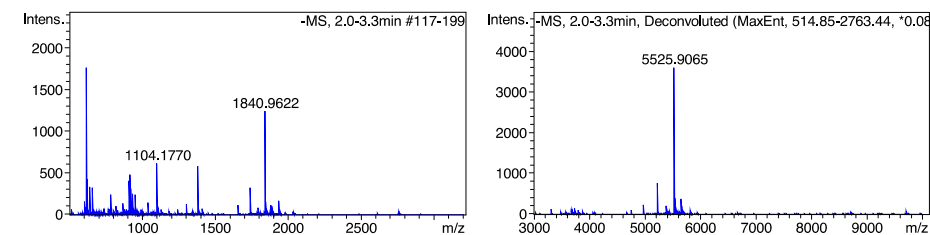
Analysis Name D:\Data\Data 2018\April 2018\utof-041318\JPP-180307-2-32_35_01_7980.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-180307-2-32
 Comment
 Acquisition Date 4/13/2018 5:10:09 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.3min #117-199



#	m/z	I
1	621.0918	1761
2	1104.1770	614
3	1104.3732	511
4	1380.4665	586
5	1380.7210	500
6	1840.6305	1076
7	1840.9622	1237
8	1841.2964	1222
9	1841.6310	814
10	1841.9607	501

#	m/z	I
1	4978.6963	228
2	5225.8259	764
3	5381.8245	216
4	5525.9065	3595
5	5545.9095	398
6	5653.9254	387
7	5669.9827	217

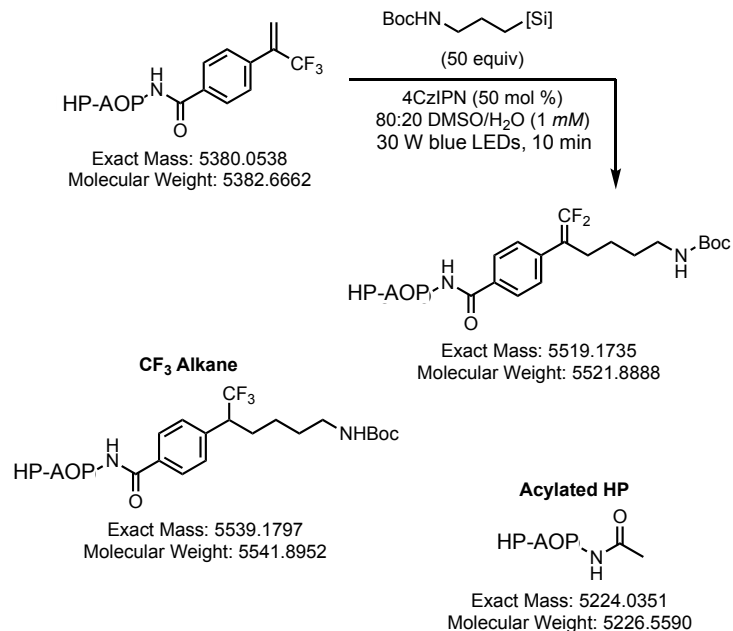
CF₃ alkene

Acylated HP

Starting material

product

Double alkylation



Product: 64%
Starting Material: 19%
Double alkylation: 1%
CF₃ alkane: 2%

Compound Spectrum List Report

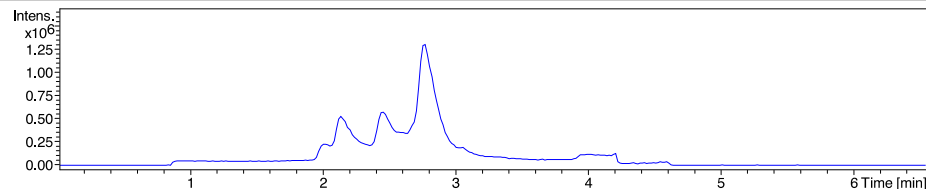
Analysis Info

Analysis Name D:\Data\Data 2018\April 2018\utof-041318\JPP-180307-2-34_37_01_7982.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-180307-2-34
 Comment

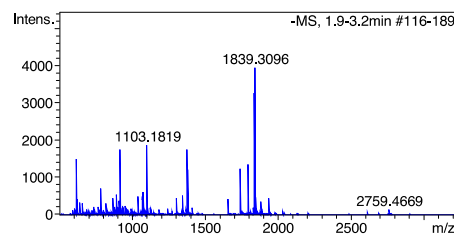
Acquisition Date 4/13/2018 5:24:54 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

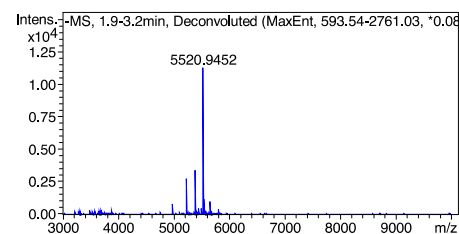
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.2min #116-189



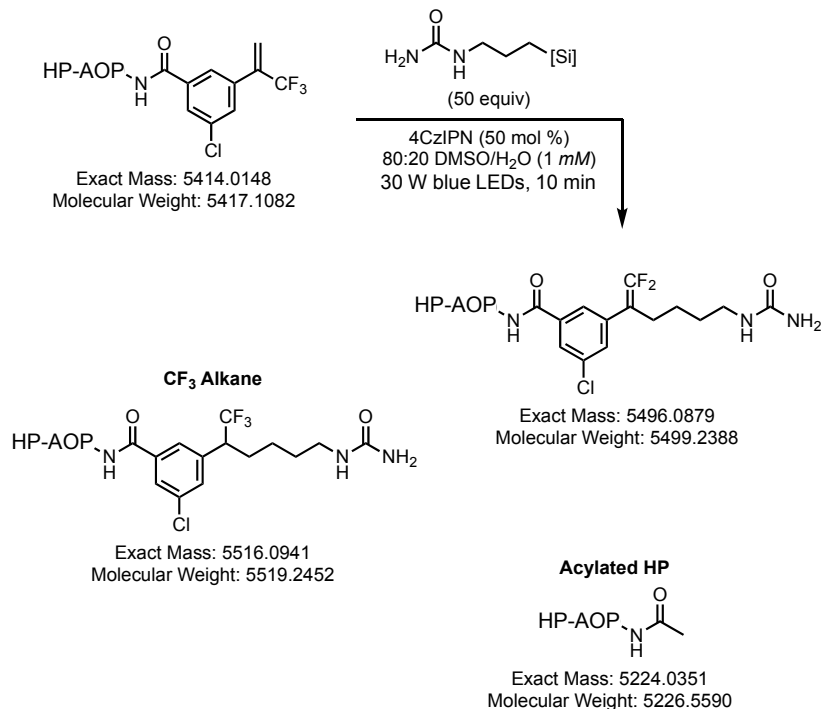
#	m/z	I
1	919.1480	1754
2	1102.9822	1671
3	1103.1819	1869
4	1379.2271	1742
5	1379.4771	1687
6	1838.6408	1525
7	1838.9743	3268
8	1839.3096	3941
9	1839.6424	3404
10	1839.9746	2423



#	m/z	I
1	4978.6963	822
2	5225.8161	2768
3	5381.8315	3397
4	5520.9452	11228
5	5540.9495	1214
6	5648.9652	1027

CF₃ alkane →
 Acylated HP →
 Starting material →
 product →

CF₂-Alkene-7ac



Product: 70%
Starting Material: 4%
Double alkylation: 0%
CF₃ alkane: 9%

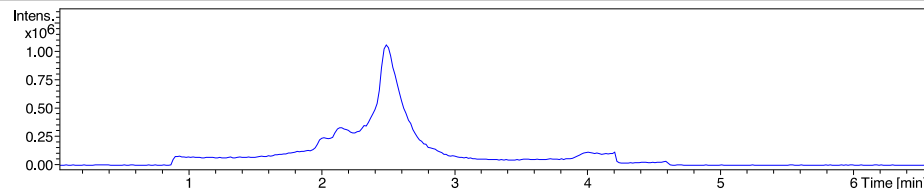
Compound Spectrum List Report

Analysis Info

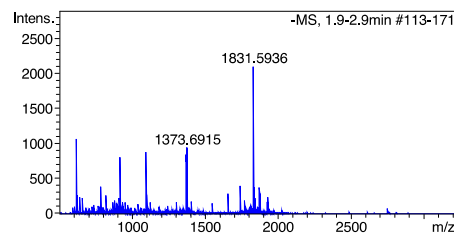
Analysis Name: X:\Chem MS Data\TOF\Data_2018\April 2018\utof-041718\JPP-180328-1-1_81_01_8016.d
 Acquisition Date: 4/17/2018 10:43:05 AM
 Method: 1200col2_10to90in4.m
 Operator: gsk
 Sample Name: JPP-180328-1-1
 Instrument: micrOTOF
 Comment: 213750.00199

Acquisition Parameter

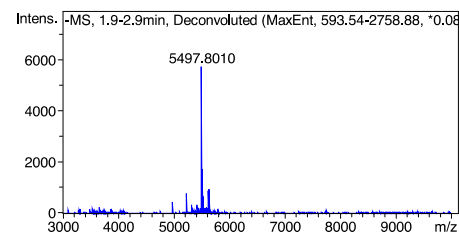
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-2.9min #113-171



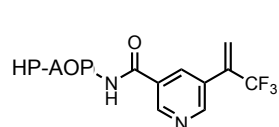
#	m/z	I
1	621.0851	1067
2	1098.5527	885
3	1098.7535	829
4	1373.4425	842
5	1373.6915	941
6	1831.2615	1498
7	1831.5936	2092
8	1831.9258	2011
9	1832.2623	1706
10	1832.5916	1240



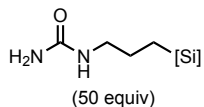
#	m/z	I
1	4978.6492	450
2	5225.7682	795
3	5417.7857	357
4	5497.8010	5731
5	5518.8117	700
6	5626.8197	960

Acylated HP
 Starting material
 product
 CF₃ alkane

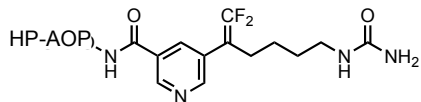
CF₂-Alkene-7ah



Exact Mass: 5381.0490
Molecular Weight: 5383.6542

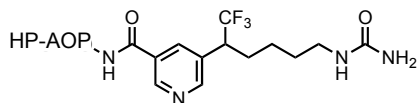


4CzIPN (50 mol %)
80:20 DMSO/H₂O (1 mM)
30 W blue LEDs, 10 min



Exact Mass: 5463.1221
Molecular Weight: 5465.7848

CF₃ Alkane



Exact Mass: 5483.1283
Molecular Weight: 5485.7912

Product: 72%
Starting Material: 4%
Double alkylation: 0%
CF₃ alkane: 8%

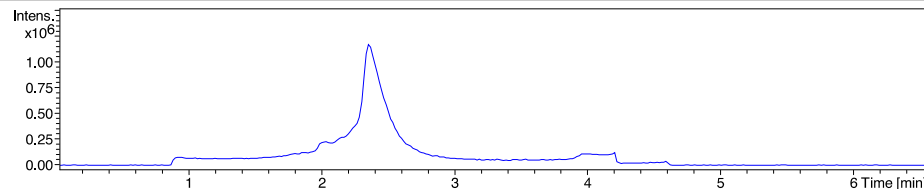
Compound Spectrum List Report

Analysis Info

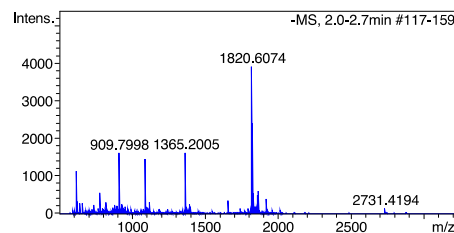
Analysis Name X:\Chem MS Data\TOF\Data_2018\April 2018\utof-041718\JPP-180328-1-5_85_01_8020.d
Acquisition Date 4/17/2018 11:12:31 AM
Method 1200col2_10to90in4.m
Sample Name JPP-180328-1-5
Operator gsk
Instrument micrOTOF 213750.00199
Comment

Acquisition Parameter

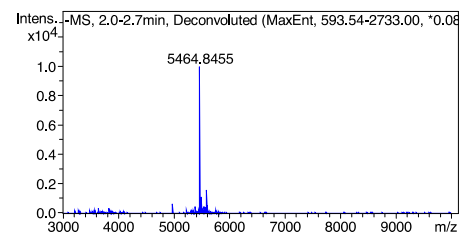
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-2.7min #117-159



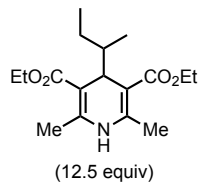
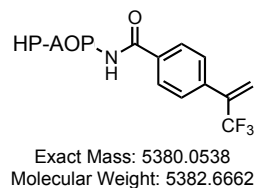
#	m/z	I
1	909.7998	1609
2	909.9628	1278
3	1091.9620	1461
4	1365.2005	1619
5	1819.9420	1469
6	1820.2739	3241
7	1820.6074	3905
8	1820.9417	3198
9	1821.2743	2393
10	1821.6045	1434



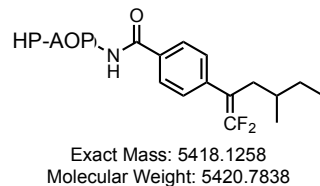
#	m/z	I
1	4978.6559	637
2	5384.8451	510
3	5464.8455	9950
4	5485.8489	1139
5	5592.8715	1615

Starting material
product
CF₃ alkane

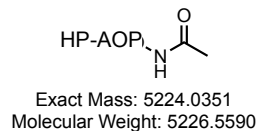
Defluorinative Alkylation using DHP's



4CzIPN (50 mol %)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 10 min



Acylated HP



Product: 77%
Starting Material: 0%

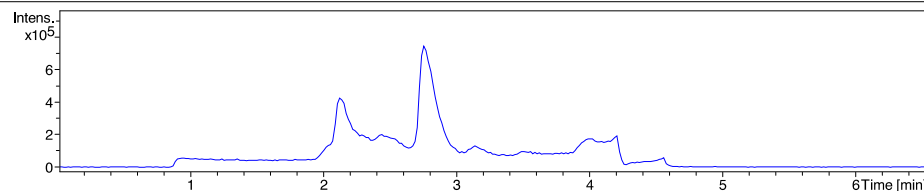
Compound Spectrum List Report

Analysis Info

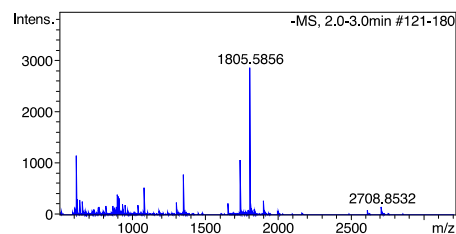
Analysis Name X:\Chem MS Data\wTOF\Data_2018\May 2018\wtof-050118\JPP-20180425-3-4_34_01_8120.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180425-3-4
 Comment
 Acquisition Date 5/1/2018 1:33:12 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

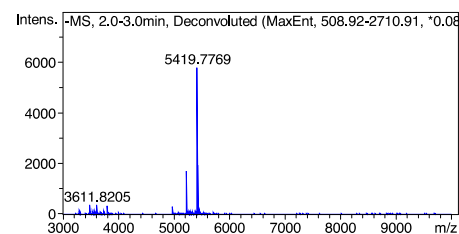
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.0min #121-180

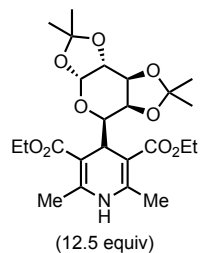
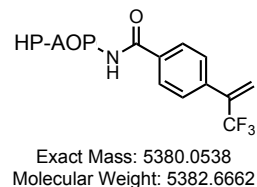


#	m/z	I
1	621.0729	1147
2	1740.5583	845
3	1740.8877	1075
4	1741.2201	867
5	1804.9189	1107
6	1805.2505	2339
7	1805.5856	2859
8	1805.9187	2546
9	1806.2510	1828
10	1806.5832	1031

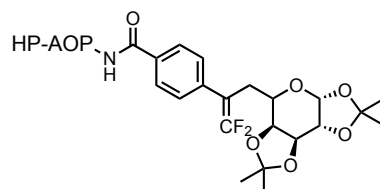


#	m/z	I
1	3483.7933	379
2	3611.8205	381
3	3808.5146	365
4	4978.5811	320
5	5225.6894	1704
6	5419.7769	5785
7	5440.7681	302

Acylated HP
 Product

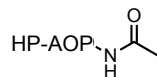


4CzIPN (50 mol %)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 10 min



Exact Mass: 5590.1630
 Molecular Weight: 5592.9198

Acylated HP



Exact Mass: 5224.0351
 Molecular Weight: 5226.5590

Product: 64%
Starting Material: 0%
Double Addition: 0%

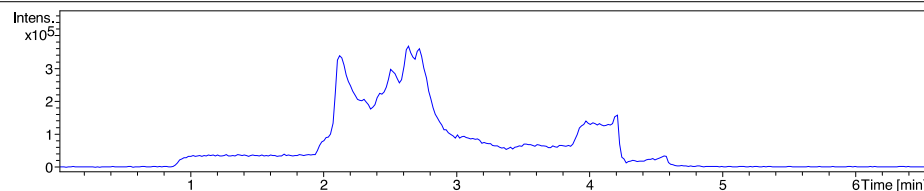
Compound Spectrum List Report

Analysis Info

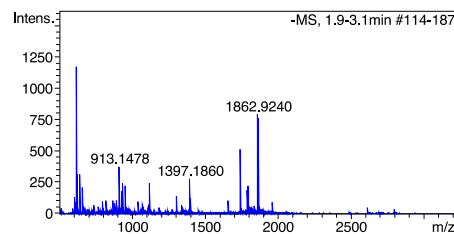
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-050118\JPP-20180425-6-1_61_01_8144.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180425-6-1
 Comment
 Acquisition Date 5/1/2018 4:41:42 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

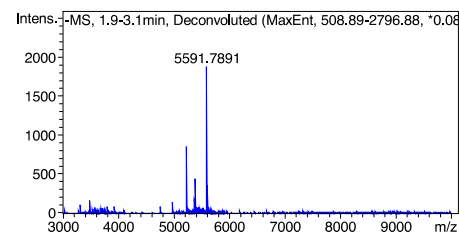
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.1min #114-187



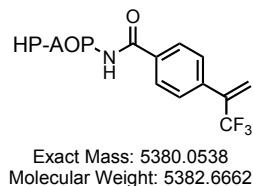
#	m/z	I
1	621.0729	1166
2	913.1478	372
3	1740.5583	420
4	1740.8851	512
5	1741.2176	399
6	1862.5886	623
7	1862.9240	786
8	1863.2539	760
9	1863.5895	533
10	1863.9201	332



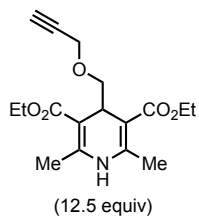
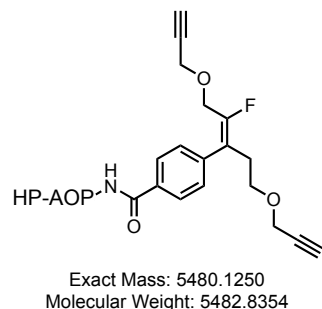
#	m/z	I
1	3319.7247	109
2	3484.4447	168
3	3808.4120	97
4	4760.5052	96
5	4977.5603	142
6	5225.6834	860
7	5377.7092	442
8	5591.7891	1878

← Acylation HP
 ← Product

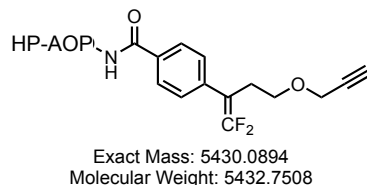
CF₂-Alkene-7k



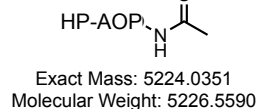
Double Alkylation



4CzIPN (50 mol %)
80:20 DMSO/H₂O (1 mM)
30W blue LED, 10 min



Acylated HP



Product: 62%
Starting Material: 0%
Double Alkylation: 10%

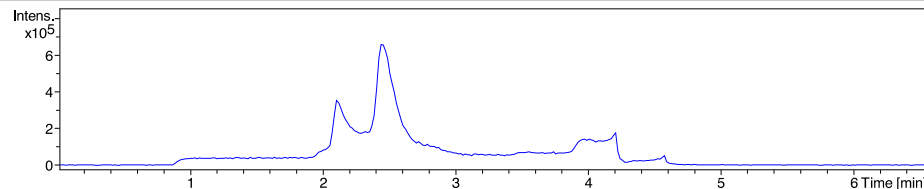
Compound Spectrum List Report

Analysis Info

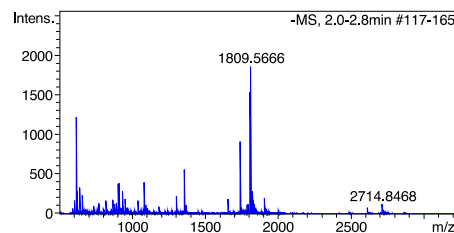
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-050118\JPP-20180425-3-7_37_01_8126.d
Method 1200col2_10to90in4.m
Sample Name JPP-20180425-3-7
Comment
Acquisition Date 5/1/2018 2:17:59 PM
Operator gsk
Instrument micrOTOF 213750.00199

Acquisition Parameter

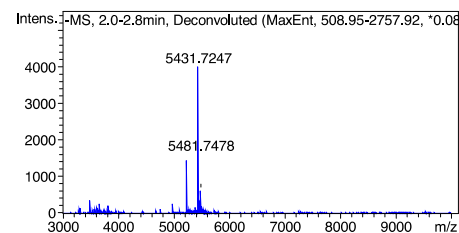
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-2.8min #117-165



#	m/z	I
1	621.0718	1222
2	1740.5541	773
3	1740.8831	916
4	1741.2136	691
5	1808.9031	759
6	1809.2333	1531
7	1809.5666	1857
8	1809.8983	1642
9	1810.2301	1174
10	1810.5637	676



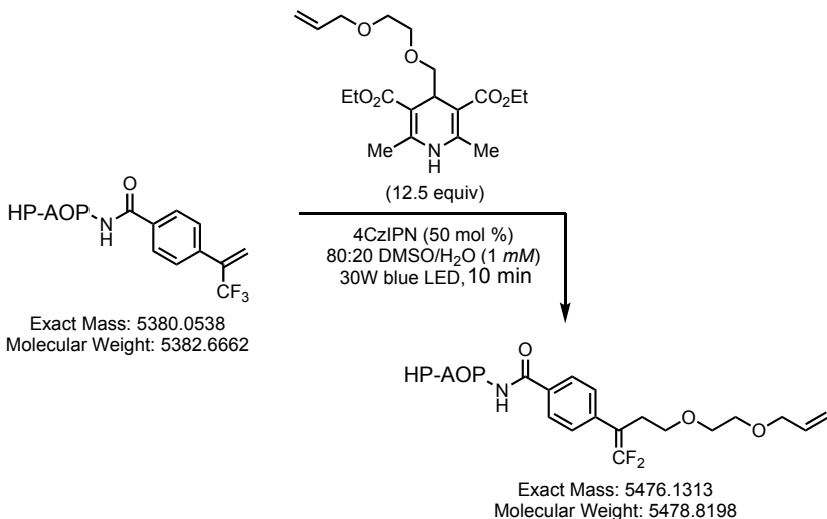
#	m/z	I
1	3483.7926	349
2	3656.5511	259
3	3816.5215	216
4	4977.5452	257
5	5225.6768	1438
6	5431.7247	4000
7	5451.7011	426
8	5468.6970	340
9	5481.7478	624

← Acylated HP

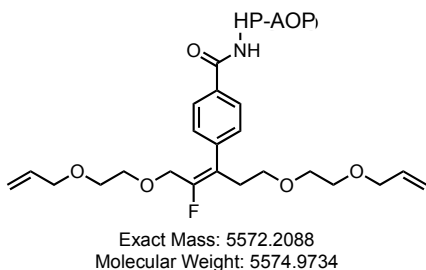
← Product

← Double Alkylation

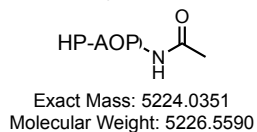
CF₂-Alkene-7I



Double Alkylation



Acylated HP



Product: 68%
Starting Material: 0%
Double Alkylation: 7%

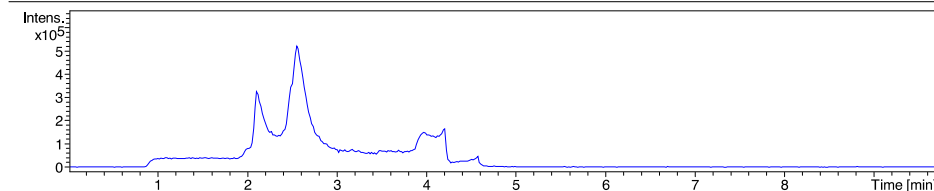
Compound Spectrum List Report

Analysis Info

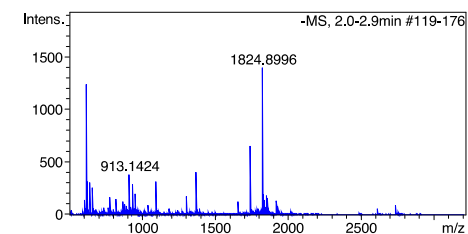
Analysis Name: X:\Chem MS Data\TOF\Data_2018\May 2018\utof-050118\JPP-20180425-3-8_38_01_8127.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20180425-3-8
 Comment:
 Acquisition Date: 5/1/2018 2:25:35 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

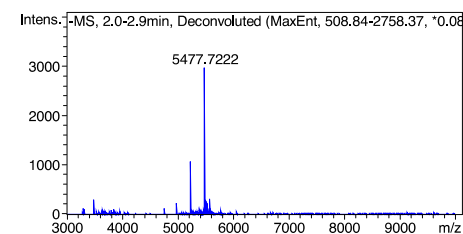
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-2.9min #119-176

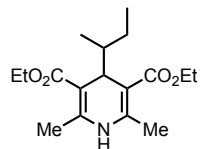
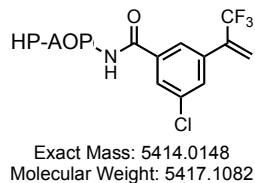


#	m/z	I
1	621.0677	1236
2	1740.5423	566
3	1740.8729	653
4	1741.2100	520
5	1824.2374	491
6	1824.5674	1076
7	1824.8996	1393
8	1825.2306	1183
9	1825.5677	819
10	1825.9007	470

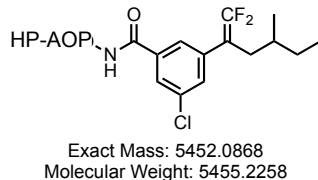


#	m/z	I	Assignment
1	3484.4159	294	
2	4978.5147	239	Acylated HP
3	5225.6430	1079	
4	5477.7222	2967	Product
5	5497.7203	259	
6	5515.7076	269	
7	5573.7968	317	Double Alkylation

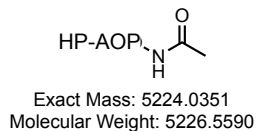
CF₂-Alkene-7ad



4CziPN (50 mol %)
 80:20 DMSO/H₂O (1 mM)
 30W blue LED, 10 min



Acylated HP



Product: 74%
Starting Material: 0%

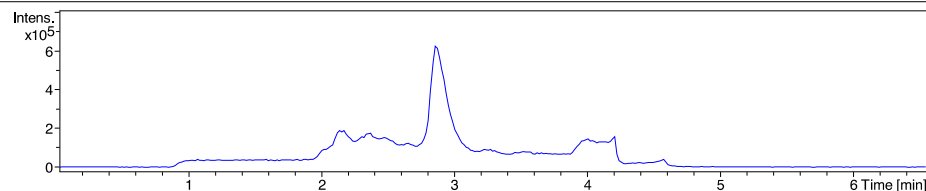
Compound Spectrum List Report

Analysis Info

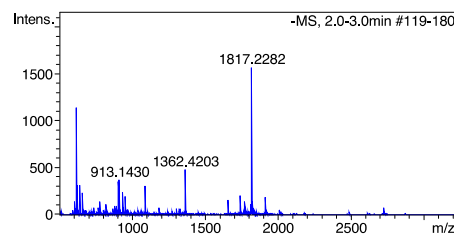
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-050118\JPP-20180425-4-4_44_01_8131.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180425-4-4
 Comment
 Acquisition Date 5/1/2018 3:01:42 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

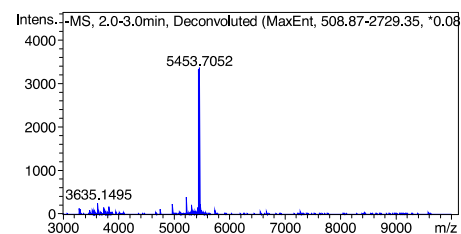
Source Type ESI Ion Polarity Negative Set Nebulizer 3.5 Bar
 Focus Active Set Dry Heater 220 °C
 Scan Begin 510 m/z Set Capillary 2500 V Set Dry Gas 11.0 l/min
 Scan End 3200 m/z Set End Plate Offset -400 V Set Divert Valve Waste



-MS, 2.0-3.0min #119-180



#	m/z	I
1	621.0693	1139
2	1362.4203	481
3	1362.6672	480
4	1816.2263	572
5	1816.5618	1145
6	1816.8919	1553
7	1817.2282	1562
8	1817.5602	1362
9	1817.8895	916
10	1818.2272	568

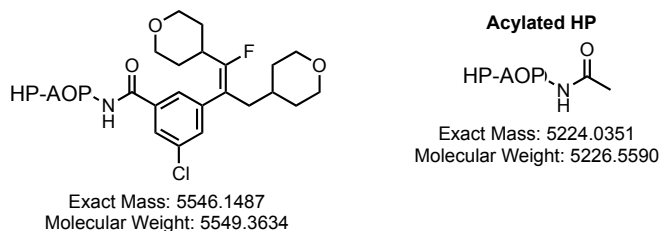
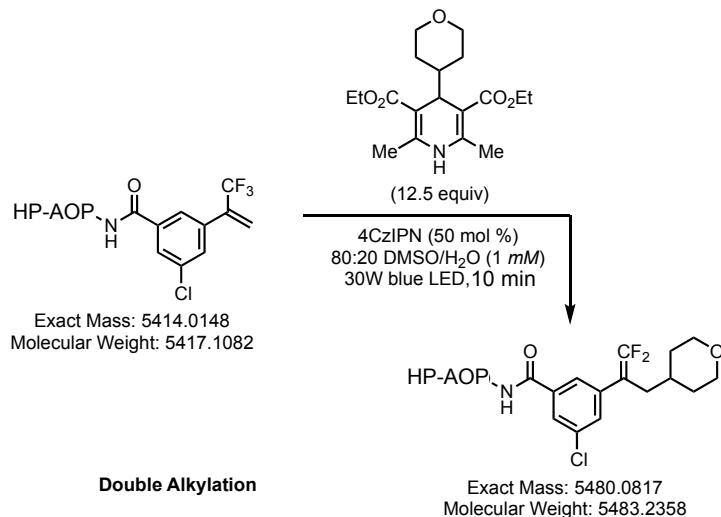


#	m/z	I
1	3635.1495	269
2	3831.1822	181
3	4978.5461	252
4	5225.6785	401
5	5321.6296	233
6	5453.7052	3325
7	5474.7112	244

Acylated HP

Product

CF₂-Alkene-7ae



Product: 61%
Starting Material: 0%
Double Alkylation: 9%

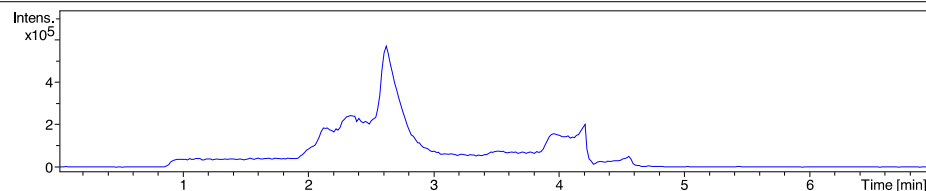
Compound Spectrum List Report

Analysis Info

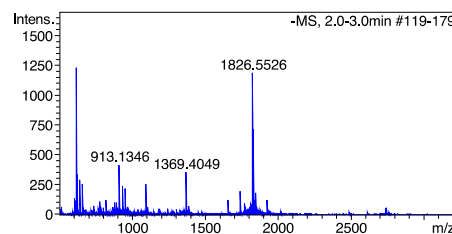
Analysis Name: X:\Chem MS Data\TOF\Data_2018\May 2018\utof-050118\JPP-20180425-4-2_42_01_8129.d
 Method: 1200col2_10to90in4.m
 Sample Name: JPP-20180425-4-2
 Acquisition Date: 5/1/2018 2:46:07 PM
 Operator: gsk
 Instrument: micrOTOF
 Comment: 213750.00199

Acquisition Parameter

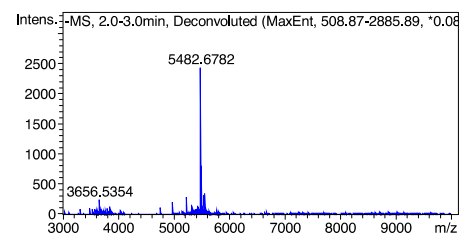
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.0min #119-179



#	m/z	I
1	621.0680	1230
2	913.1346	418
3	1369.4049	356
4	1825.5537	385
5	1825.8873	840
6	1826.2197	1146
7	1826.5526	1181
8	1826.8895	1005
9	1827.2175	716
10	1827.5496	413

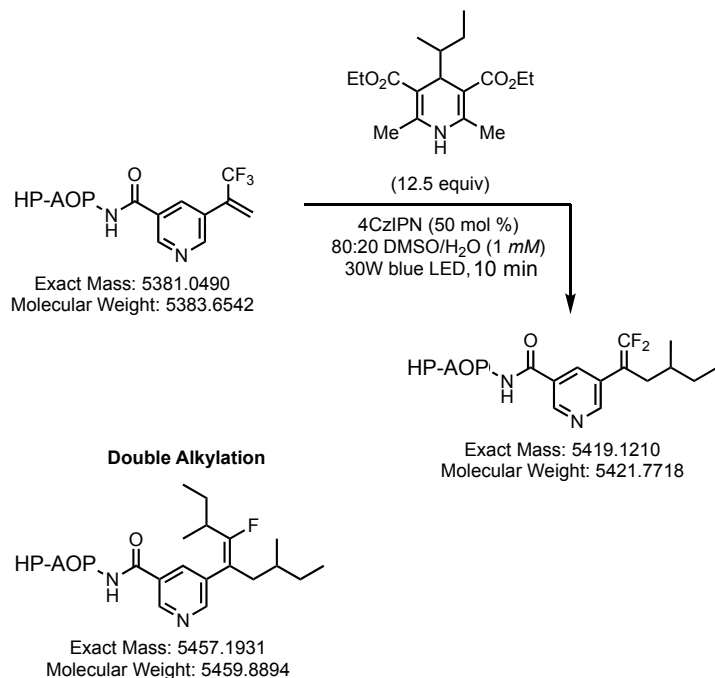


#	m/z	I
1	3656.5354	243
2	3849.1607	130
3	4977.5223	201
4	5225.6520	288
5	5322.6455	159
6	5433.6362	144
7	5482.6782	2428
8	5492.6213	151
9	5503.6718	149
10	5548.7397	345

Acylated HP

Product

Double Alkylation



Product: 86%
Starting Material: 0%

Compound Spectrum List Report

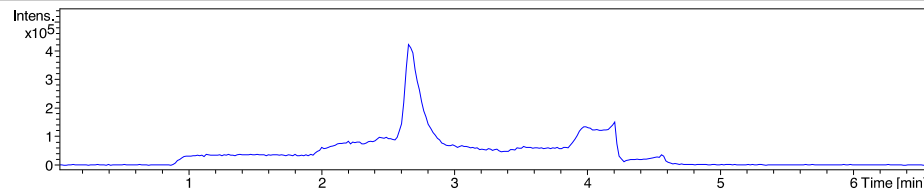
Analysis Info

Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-050118\JPP-20180425-5-4_54_01_8139.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180425-5-4
 Comment

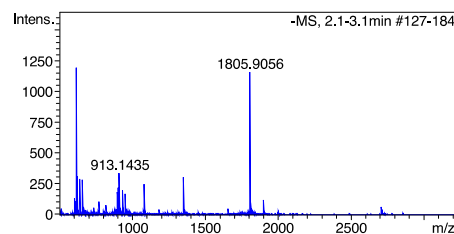
Acquisition Date 5/1/2018 4:04:34 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

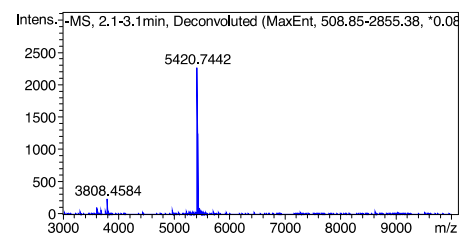
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.1-3.1min #127-184

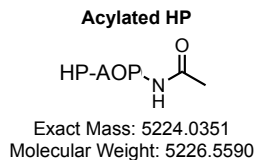
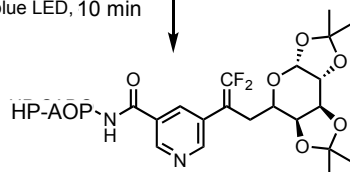
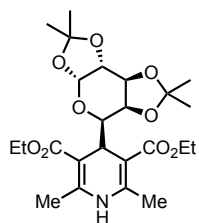
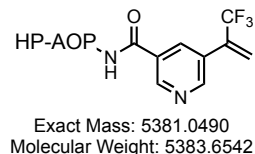


#	m/z	I
1	621.0701	1188
2	622.0735	311
3	913.1435	339
4	1354.1762	304
5	1805.2406	411
6	1805.5706	862
7	1805.9056	1154
8	1806.2423	957
9	1806.5711	640
10	1806.9037	389



#	m/z	I
1	3808.4584	243
2	5420.7442	2265
3	5442.6996	121

← Product



Product: 76%
Starting Material: 0%

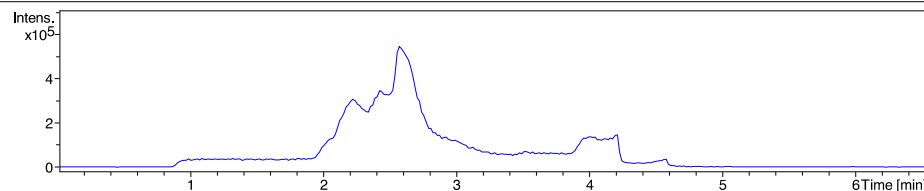
Compound Spectrum List Report

Analysis Info

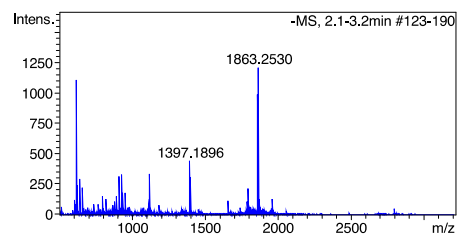
Analysis Name X:\Chem MS Data\TOF\Data_2018\May 2018\utof-050118\JPP-20180425-6-4_64_01_8147.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-20180425-6-4
 Comment
 Acquisition Date 5/1/2018 5:03:52 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

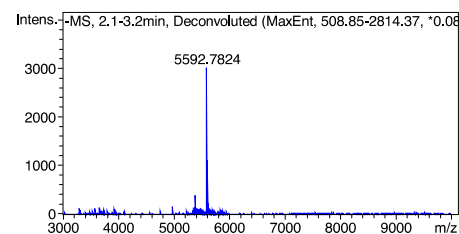
Source Type ESI Ion Polarity Negative Set Nebulizer 3.5 Bar
 Focus Active Set Dry Heater 220 °C
 Scan Begin 510 m/z Set Capillary 2500 V Set Dry Gas 11.0 l/min
 Scan End 3200 m/z Set End Plate Offset -400 V Set Divert Valve Waste



-MS, 2.1-3.2min #123-190



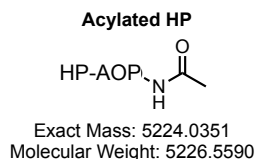
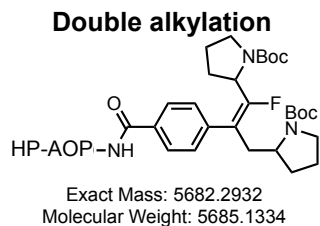
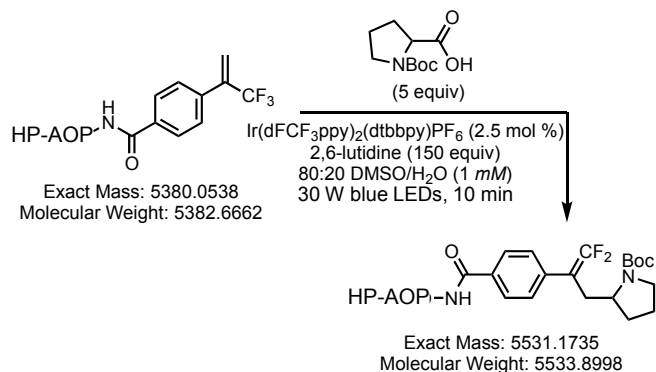
#	m/z	I
1	621.0726	1104
2	1396.9337	375
3	1397.1896	443
4	1397.4269	441
5	1862.5868	454
6	1862.9175	982
7	1863.2530	1207
8	1863.5841	1102
9	1863.9165	789
10	1864.2511	473



#	m/z	I
1	4978.5546	168
2	5363.6673	153
3	5378.7261	394
4	5592.7824	3010
5	5612.7820	244

← Product

Defluorinative Alkylation using Carboxylates



Product: 75%
Starting Material: 4%
Double Alkylation: 0%

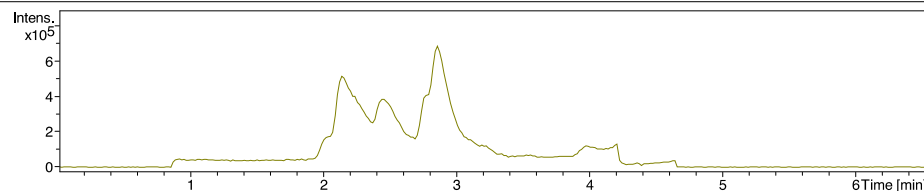
Compound Spectrum List Report

Analysis Info

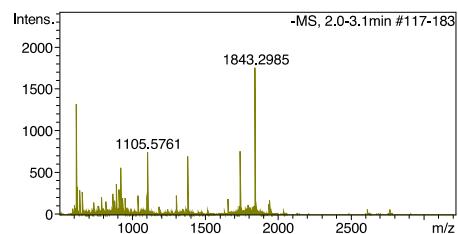
Analysis Info		Acquisition Date		4/17/2018 3:08:20 PM
Analysis Name	X:\Chem MS Data\utof\Data_2018\April 2018\utof-041318\JPP-180314-7-26_26_01_8046.d			
Method	1200col2_10to90in4.m	Operator	gsk	
Sample Name	JPP-180314-7-26	Instrument	micrOTOF	213750.00199
Comment				

Acquisition Parameter

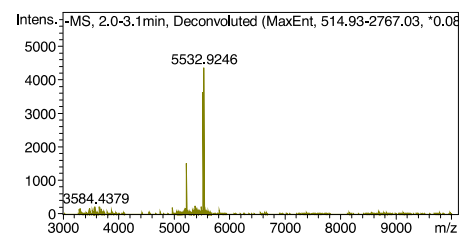
Acquisition Parameters					
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.1min #117-183



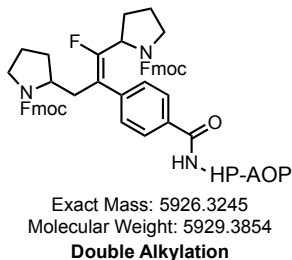
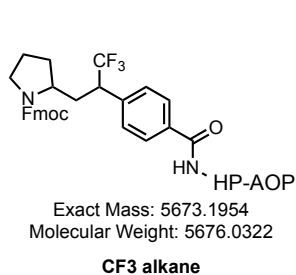
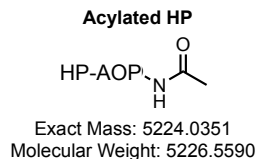
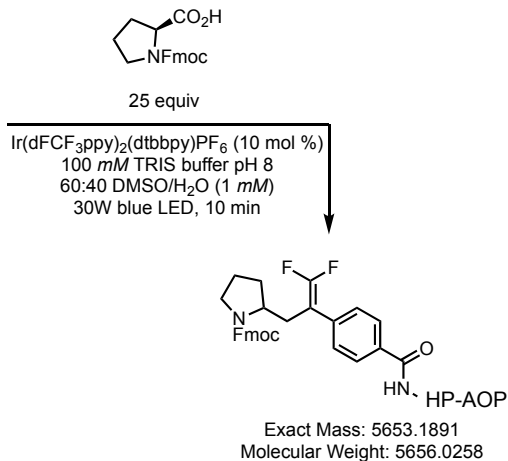
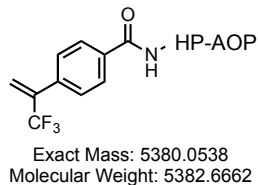
#	m/z	I
1	621.0897	1316
2	1105.5761	743
3	1382.2219	695
4	1740.9272	755
5	1842.6343	689
6	1842.9683	1481
7	1843.2985	1748
8	1843.6341	1585
9	1843.9668	1090
10	1844.2980	676



#	m/z	I
1	3584.4379	235
2	3656.7280	230
3	4977.6677	223
4	5225.8034	1520
5	5381.8294	259
6	5492.8811	229
7	5532.9246	4356
8	5552.8964	244

3 ← Acylated HP
 9 ← Starting Material
 6
 4 ← product

CF₂-Alkene-7n



Product: 67%
Starting Material: 0%
Double Alkylation: 0%
CF₃ Alkane: 7%

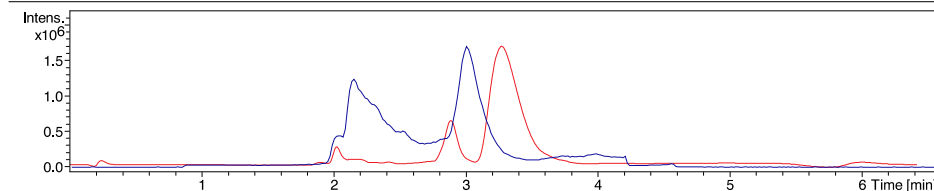
Compound Spectrum List Report

Analysis Info

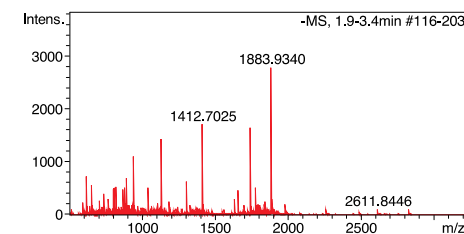
Analysis Name	X:\Chem MS Data\TOF\Data_2018\July 2018\utof-070518\DNA-20180521-1-8_17_01_8716.d	Acquisition Date	7/5/2018 5:41:38 PM
Method	1200col2_10to90in4.m	Operator	gsk
Sample Name	DNA-20180521-1-8	Instrument	micrOTOF 213750.00199
Comment			

Acquisition Parameter

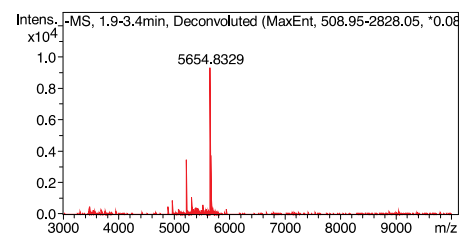
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.4min #116-203



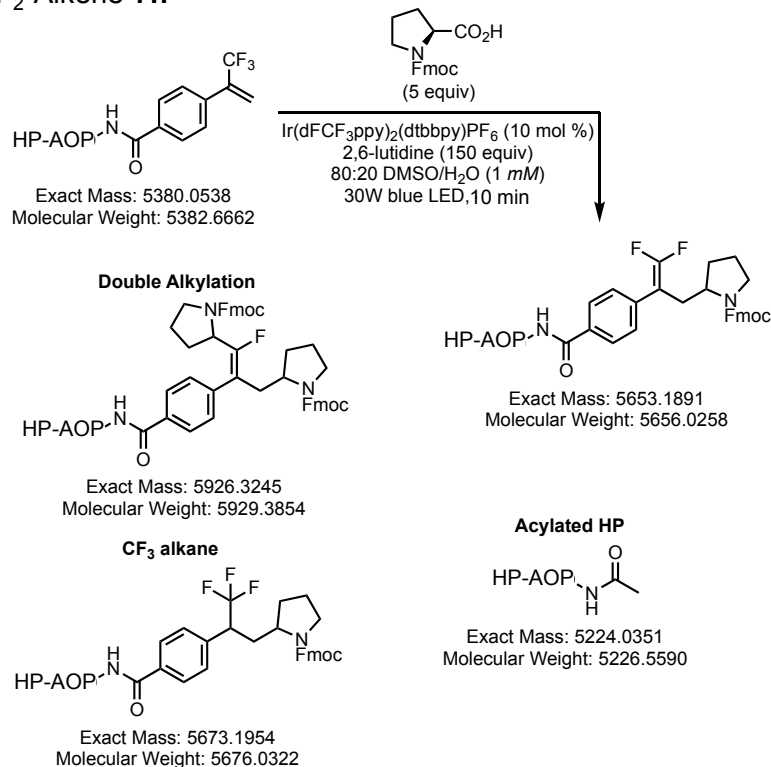
#	m/z	I
1	1129.9598	1424
2	1412.7025	1708
3	1412.9501	1654
4	1740.5596	1454
5	1740.8942	1645
6	1741.2247	1455
7	1883.6022	2166
8	1883.9340	2777
9	1884.2684	2631
10	1884.5993	2004



#	m/z	I
1	3483.8136	532
2	4896.6792	489
3	4978.5808	891
4	5225.7292	3495
5	5325.7973	1130
6	5521.7957	642
7	5654.8329	9308
8	5674.8473	975

← Acylated HP
 ← product
 ← CF₃ alkane

CF₂-Alkene-7n



Product: 32%
Starting Material: 6%
Double Alkylation: 0%
CF₃ Alkane: 4%

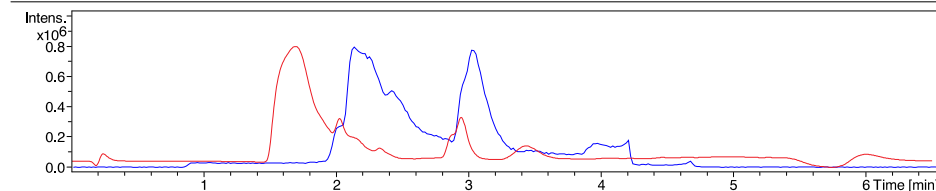
Compound Spectrum List Report

Analysis Info

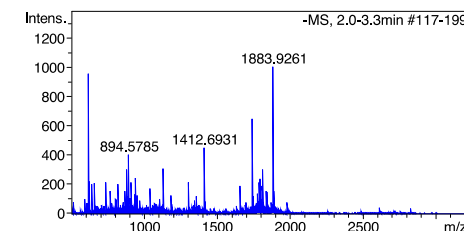
Analysis Name: X:\Chem MS Data\utof\Data_2018\May 2018\utof-051718\DNA-20180515-3-1_71_01_8332.d
 Method: 1200col2_10to90in4.m
 Sample Name: DNA-20180515-3-1
 Comment: Acquisition Date: 5/17/2018 7:46:30 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

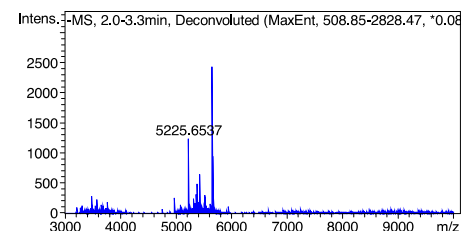
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



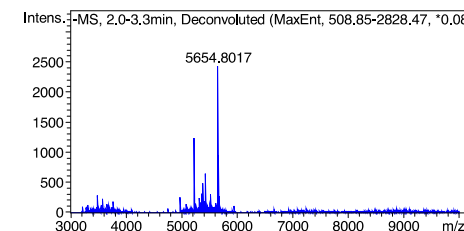
-MS, 2.0-3.3min #117-199



#	m/z	I
1	621.0654	952
2	1412.6931	451
3	1412.9414	425
4	1740.5526	647
5	1740.8874	631
6	1741.2242	559
7	1883.5923	824
8	1883.9261	1000
9	1884.2548	860
10	1884.5888	627



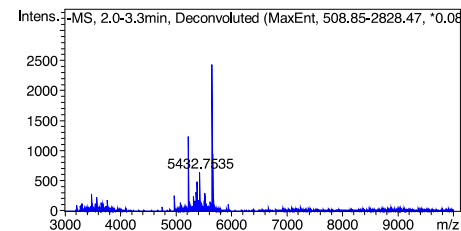
#	m/z	I
1	3319.7040	128
2	3483.8184	291
3	3567.3456	131
4	3584.3683	228
5	3656.6152	147
6	3695.3529	138
7	3768.5313	194
8	4978.5566	256
9	5092.6701	148
10	5225.6537	1237



#	m/z	I
1	5545.7488	126
2	5614.8072	166
3	5635.7783	134
4	5654.8017	2430
5	5672.7889	324

product

CF₃ alkane

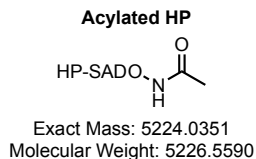
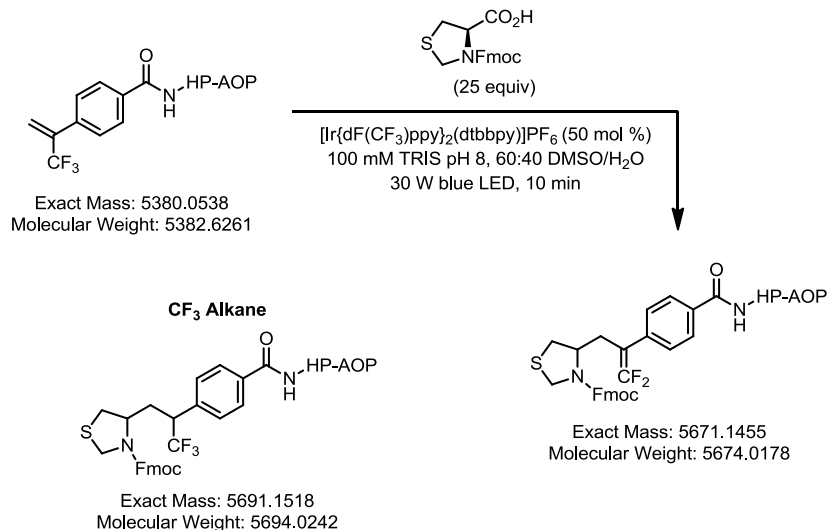


#	m/z	I
1	5241.6885	154
2	5325.7326	248
3	5340.7211	164
4	5361.6807	326
5	5376.6202	168
6	5381.6722	488
7	5390.7185	165
8	5411.7176	196
9	5432.7535	650
10	5520.7815	302

Acylated HP

Starting material

S168



Product: 65%
Starting material: 0%
CF₃ Alkane: 8%
Double Alkylation: 0%

Compound Spectrum List Report

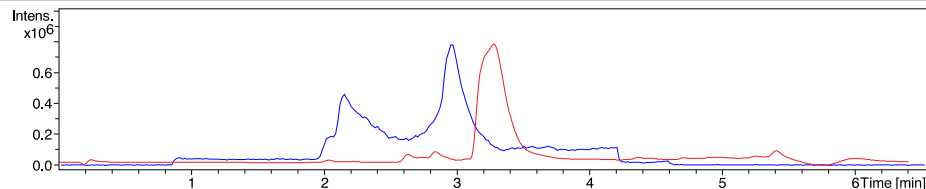
Analysis Info

Analysis Name: X:\Chem MS Data\wTOF\Data_2018\Nov 2018\wtof-111618\JHS-181030-A7_7_01_10230.d
 Method: 1200col2_10to90in4.m
 Sample Name: JHS-181030-A7
 Comment:

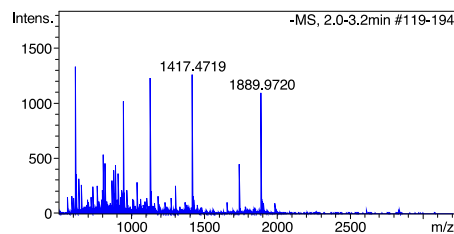
Acquisition Date: 11/16/2018 4:59:32 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

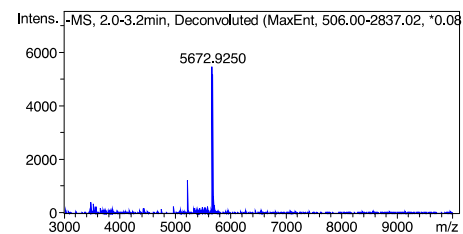
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.2min #119-194

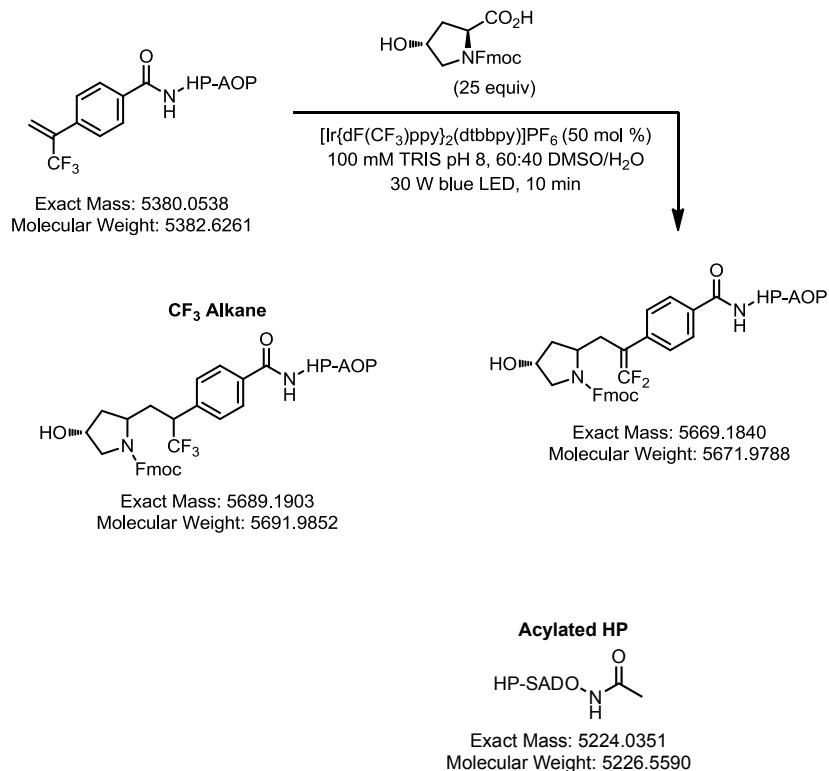


#	m/z	I
1	621.0839	1328
2	944.4785	1012
3	1133.3830	877
4	1133.5798	1230
5	1133.7782	1066
6	1417.2245	1122
7	1417.4719	1257
8	1417.7166	972
9	1889.9720	1091
10	1890.2980	959



#	m/z	I
1	3484.6075	423
2	3540.4492	364
3	5225.8236	1239
4	5672.9250	5464
5	5692.9125	639
6	5716.8863	293

product (pointing to peak 4)
 CF₃ alkane (pointing to peak 6)



Product: 50%
Starting material: 0%
CF₃ Alkane: 6%
Double Alkylation: 0%

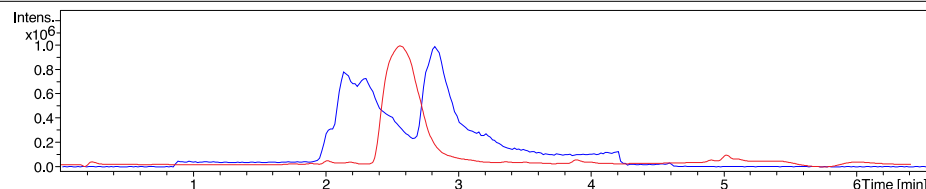
Analysis Info

Analysis Name X:\Chem MS Data\wTOF\Data_2018\Nov 2018\utof-111618\JHS-181030-A9_8_01_10231.d
 Method 1200col2_10to90in4.m
 Sample Name JHS-181030-A9
 Comment

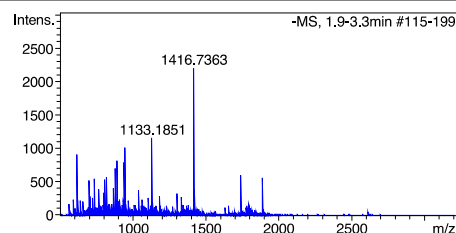
Acquisition Date 11/16/2018 5:06:53 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste

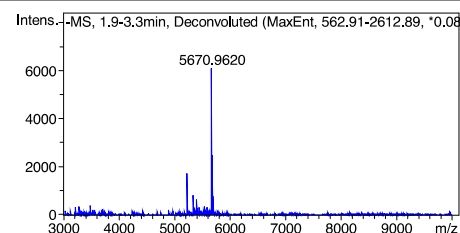


-MS, 1.9-3.3min #115-199



#	m/z	I
1	621.0842	908
2	944.1554	1010
3	1132.9895	959
4	1133.1851	1156
5	1133.3862	1074
6	1416.4863	1668
7	1416.7363	2195
8	1416.9817	2096
9	1417.2334	1631
10	1417.4757	994

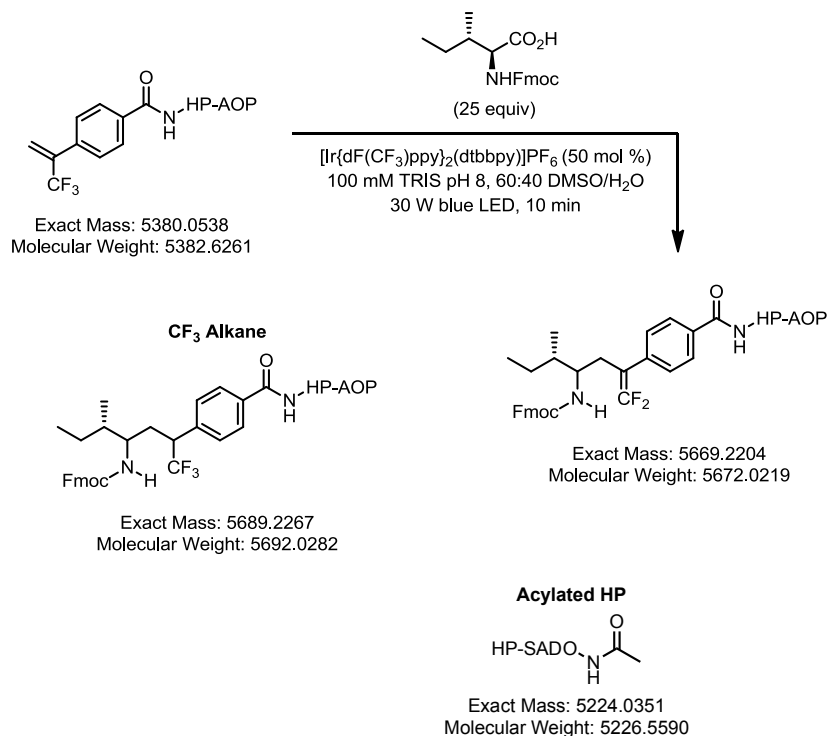
#	m/z	I
1	621.0842	908
2	944.1554	1010
3	1132.9895	959
4	1133.1851	1156
5	1133.3862	1074
6	1416.4863	1668
7	1416.7363	2195
8	1416.9817	2096
9	1417.2334	1631
10	1417.4757	994



#	m/z	I
1	3220.5451	325
2	3280.2928	370
3	3483.8168	408
4	5225.8251	1737
5	5341.9223	827
6	5393.8539	650
7	5448.8495	320
8	5537.9140	385
9	5592.9000	346
10	5670.9620	6093

#	m/z	I
1	5690.9602	791

product
 CF₃ alkane



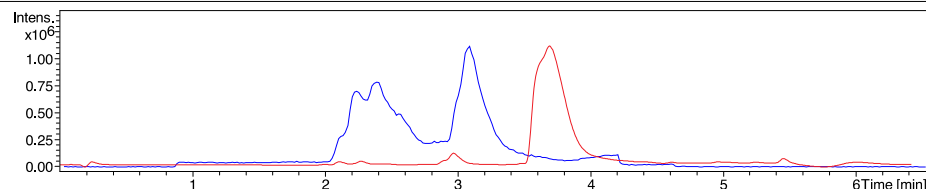
Product: 50%
Starting material: 0%
CF₃ Alkane: 6%
Double Alkylation: 0%

Analysis Info

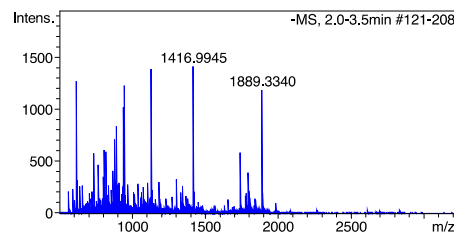
Analysis Name	X:\Chem MS Data\utof\Data_2018\Nov 2018\utof-111618\JHS-181030-A5_5_01_10228.d	Acquisition Date	11/16/2018 4:44:45 PM
Method	1200col2_10to90in4.m	Operator	gsk
Sample Name	JHS-181030-A5	Instrument	micrOTOF
Comment			213750.00199

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste

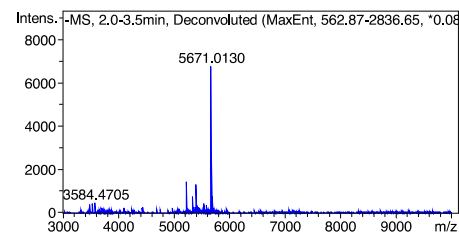


-MS, 2.0-3.5min #121-208



#	m/z	I
1	621.0843	1265
2	944.1602	1222
3	1133.1942	1387
4	1133.3917	1315
5	1416.4973	1145
6	1416.7506	1362
7	1416.9945	1411
8	1417.2397	1161
9	1889.3340	1187
10	1889.6596	1128

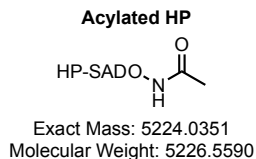
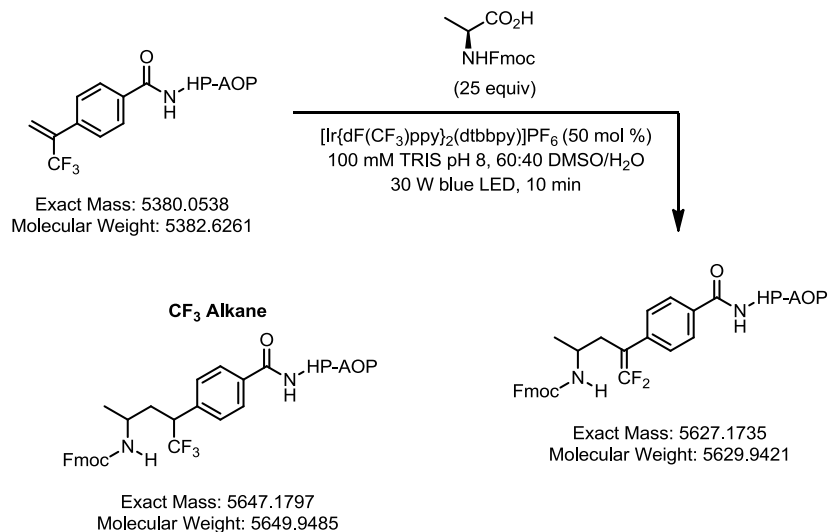
#	m/z	I
1	621.0843	1265
2	944.1602	1222
3	1133.1942	1387
4	1133.3917	1315
5	1416.4973	1145
6	1416.7506	1362
7	1416.9945	1411
8	1417.2397	1161
9	1889.3340	1187
10	1889.6596	1128



#	m/z	I
1	3483.8598	389
2	3540.4383	462
3	3584.4705	474
4	5225.8238	1450
5	5341.9494	774
6	5393.8603	1313
7	5413.8670	372
8	5537.9442	455
9	5592.9702	362
10	5671.0130	6762

product
 CF₃ alkane

CF₂-Alkene-7s



Product: 65%
Starting material: 0%
CF₃ Alkane: 8%
Double Alkylation: 0%

Compound Spectrum List Report

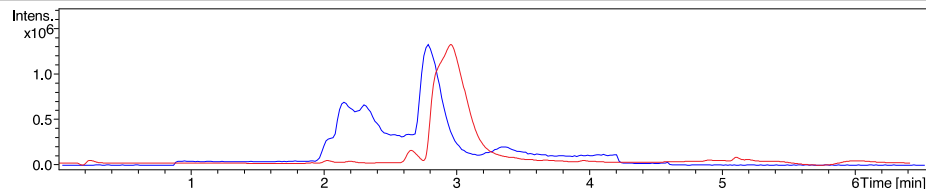
Analysis Info

Analysis Name X:\Chem MS Data\wTOF\Data_2018\Nov 2018\wtof-111618\JHS-181030-A6_6_01_10229.d
 Method 1200col2_10to90in4.m
 Sample Name JHS-181030-A6
 Comment

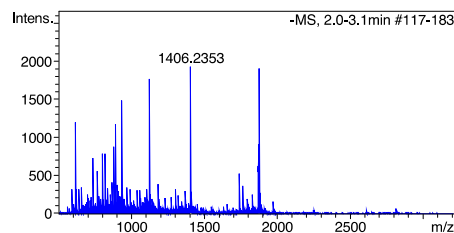
Acquisition Date 11/16/2018 4:52:07 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

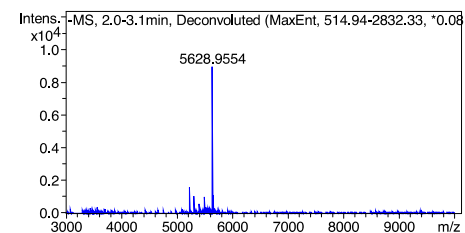
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.1min #117-183

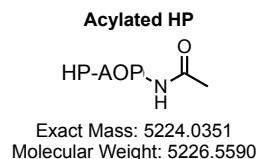
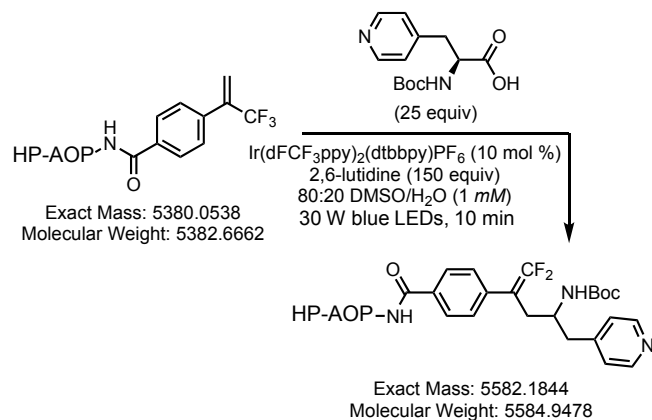


#	m/z	I
1	937.1510	1480
2	1124.7857	1760
3	1124.9853	1621
4	1405.9813	1574
5	1406.2353	1926
6	1406.4779	1860
7	1406.7294	1538
8	1874.9829	1524
9	1875.3095	1902
10	1875.6436	1631



#	m/z	I
1	5225.8297	1575
2	5299.9312	1094
3	5496.9059	1012
4	5628.9554	8911
5	5649.9582	1131

product
 CF₃ alkane



Product: 74%
Starting Material: 0%

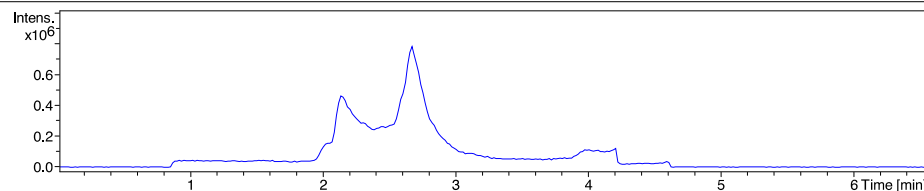
Compound Spectrum List Report

Analysis Info

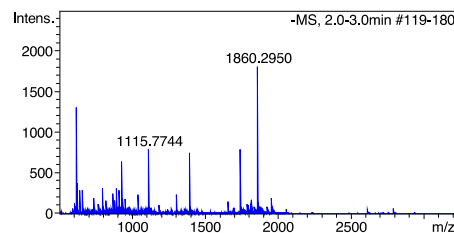
Analysis Info		Acquisition Date		4/17/2018 1:10:46 PM
Analysis Name	X:\Chem MS Data\wTOF\Data_2018\April 2018\wtof-041318\JPP-180314-4-13_17_01_8036.d			
Method	1200col2_10to90in4.m	Operator	gsk	
Sample Name	JPP-180314-4-13	Instrument	micrOTOF	213750.00199
Comment				

Acquisition Parameter

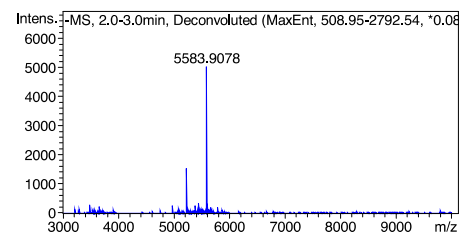
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.0min #119-180



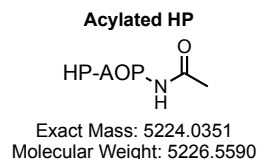
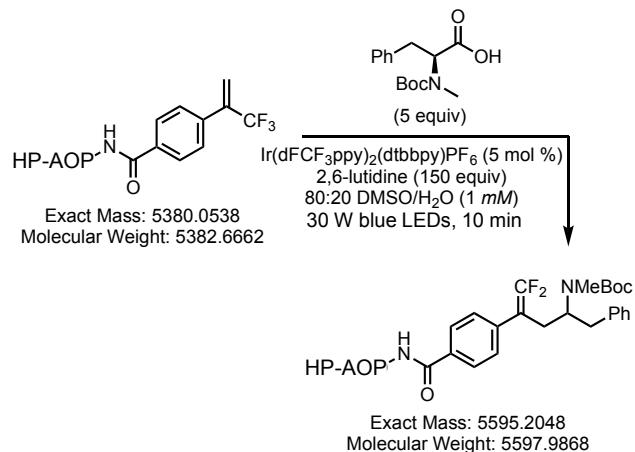
#	m/z	I
1	621.0857	1305
2	1115.7744	790
3	1394.9687	746
4	1740.5811	696
5	1740.9139	789
6	1859.9601	1448
7	1860.2950	1806
8	1860.6280	1576
9	1860.9593	1109
10	1861.2928	697



#	m/z	I
1	3484.4830	292
2	3656.6688	252
3	4978.6400	289
4	5225.7755	1546
5	5376.7401	276
6	5450.8633	362
7	5583.9078	5020
8	5604.9060	321

- Acylated HP

- product



Product: 82%
Starting Material: 0%

Compound Spectrum List Report

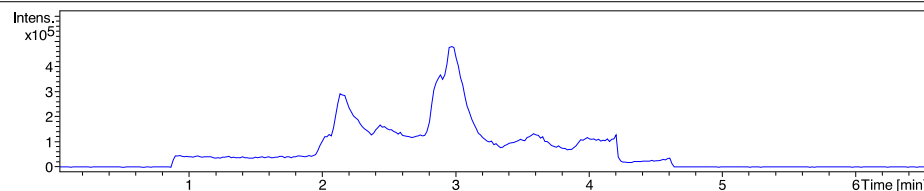
Analysis Info

Analysis Name X:\Chem MS Data\TOF\Data_2018\April 2018\utof-041318\JPP-180314-2-4_12_01_8031.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-180314-2-4
 Comment

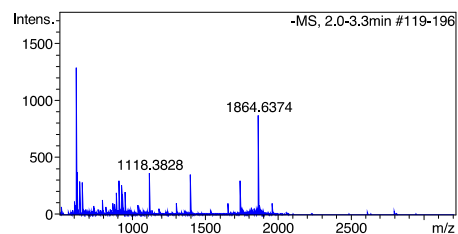
Acquisition Date 4/17/2018 12:33:57 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

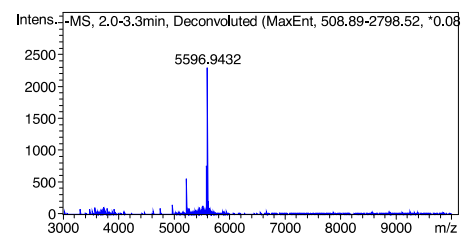
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.3min #119-196



#	m/z	I
1	621.0883	1286
2	622.0895	371
3	1118.3828	366
4	1398.2255	350
5	1863.9707	338
6	1864.3062	721
7	1864.6374	871
8	1864.9734	829
9	1865.3051	589
10	1865.6372	343

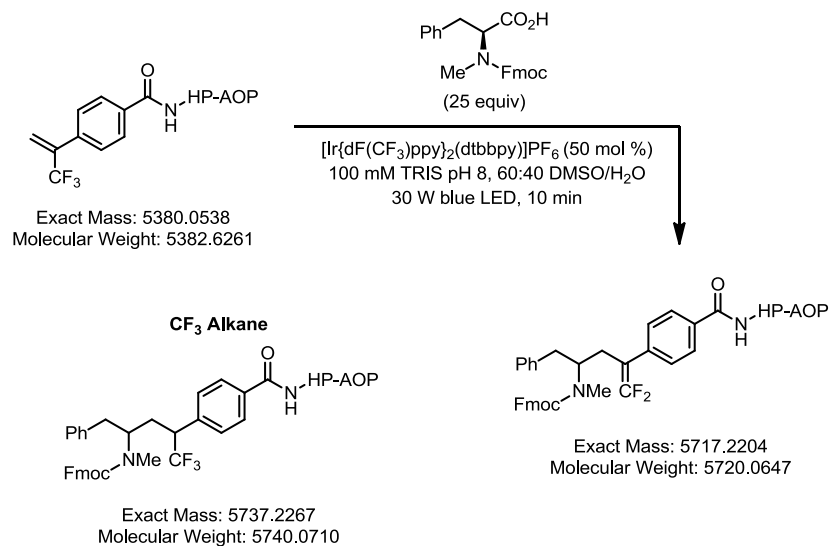


#	m/z	I
1	4978.6685	158
2	5225.7899	557
3	5516.9459	136
4	5596.9432	2290
5	5616.9448	203

Acylated HP

product

CF₃-Alkene-7v



Product: 69%
Starting material: 0%
CF₃ Alkene: 13%
Double Alkylation: 0%

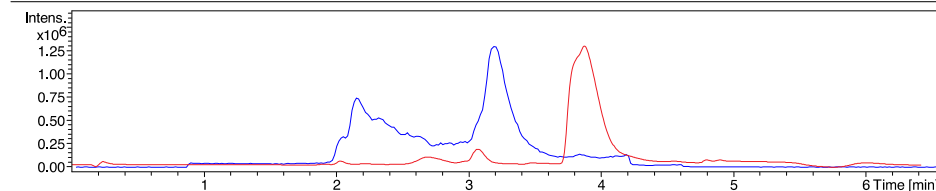
Compound Spectrum List Report

Analysis Info

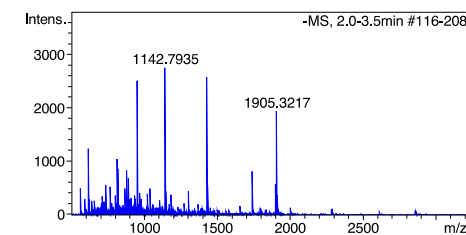
Analysis Name: X:\Chem MS Data\TOF\Data_2018\Nov 2018\utof-111618\JHS-181030-A10_9_01_10232.d
 Method: 1200col2_10to90in4.m
 Sample Name: JHS-181030-A10
 Comment:
 Acquisition Date: 11/16/2018 5:14:17 PM
 Operator: gsk
 Instrument: micrOTOF
 213750.00199

Acquisition Parameter

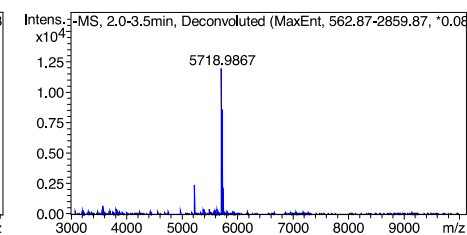
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.5min #116-208



#	m/z	I
1	952.1575	2500
2	952.3170	2093
3	1142.5952	2010
4	1142.7935	2747
5	1142.9911	2461
6	1143.1875	1891
7	1428.7410	2559
8	1428.9879	2502
9	1429.2314	2036
10	1905.3217	1942

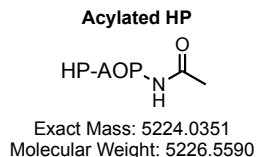
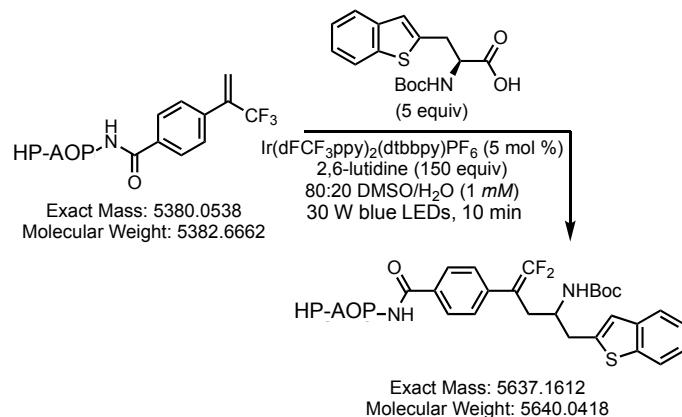


#	m/z	I
1	3582.4433	707
2	5225.8195	2428
3	5718.9867	11946
4	5739.0064	2181

product

CF₃ alkane

Compound Spectrum List Report



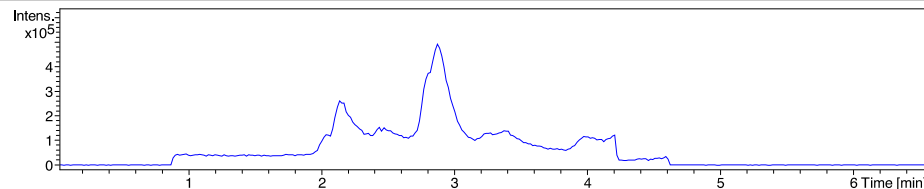
Product: 84%
Starting Material: 0%

Analysis Info

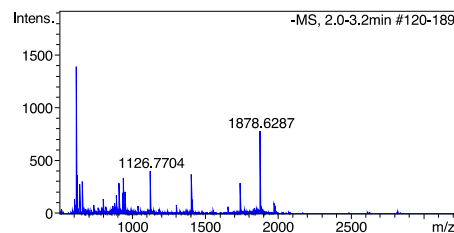
Analysis Info		Acquisition Date		4/17/2018 12:41:16 PM	
Analysis Name	X:\Chem MS Data\wTOF\Data_2018\April 2018\wtof-041318\JPP-180314-2-5_13_01_8032.d				
Method	1200col2_10to90in4.m	Operator	gsk		
Sample Name	JPP-180314-2-5	Instrument	microTOF 213750.00199		
Comment					

Acquisition Parameter

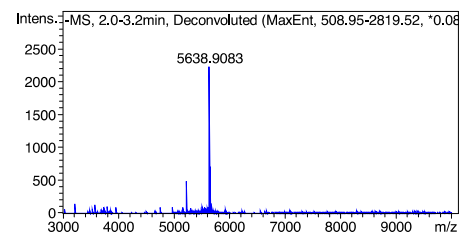
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.2min #120-189

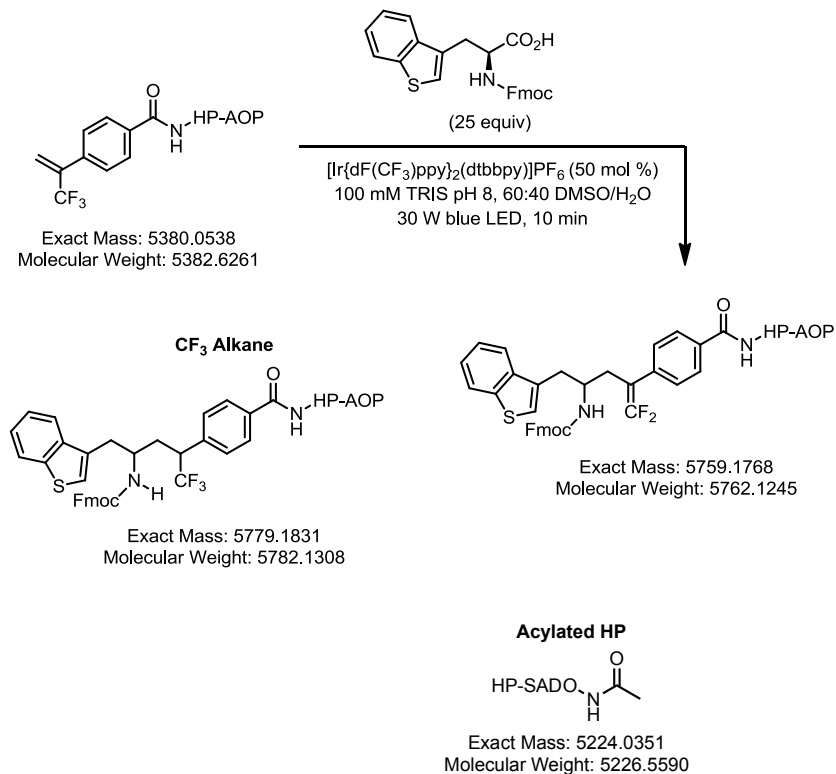


#	m/z	I
1	621.0885	1385
2	622.0890	361
3	1126.7704	401
4	1408.7201	372
5	1408.9728	373
6	1878.2937	639
7	1878.6287	778
8	1878.9650	751
9	1879.2931	585
10	1879.6234	355



#	m/z	I
1	3220.4064	145
2	3582.4353	138
3	5225.7891	483
4	5638.9083	2225
5	5658.9160	155

Acylated HP
product



Product: 70%
Starting material: 0%
CF₃ Alkane: 13%
Double Alkylation: 0%

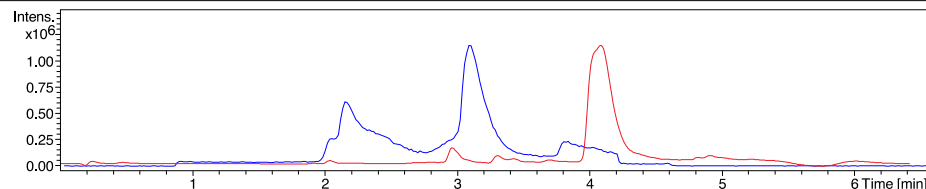
Compound Spectrum List Report

Analysis Info

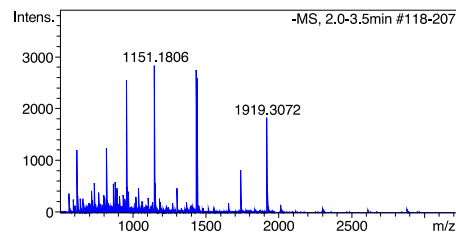
Acquisition Date 11/16/2018 5:21:40 PM
 Analysis Name X:\Chem MS Data\wTOF\Data_2018\Nov 2018\utof-111618\JHS-181030-A12_10_01_10233.d
 Method 1200col2_10to90in4.m
 Sample Name JHS-181030-A12
 Comment
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

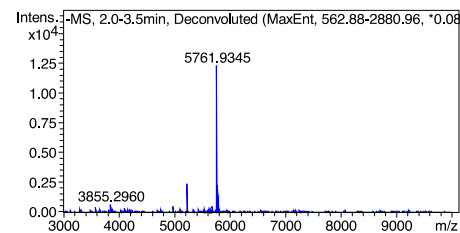
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.5min #118-207

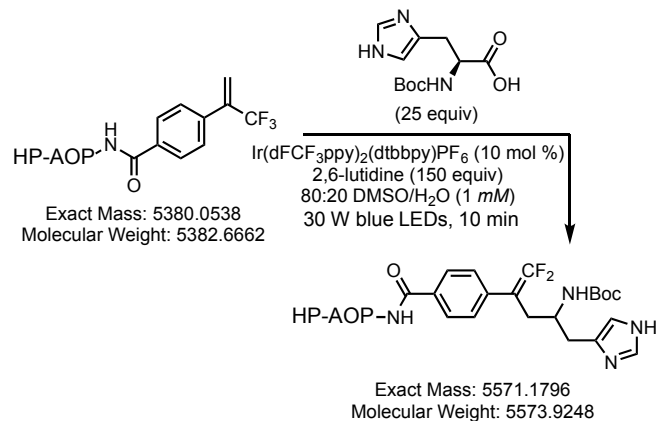


#	m/z	I
1	959.1481	2546
2	959.3127	2195
3	1150.9850	1891
4	1151.1806	2828
5	1151.3791	2735
6	1151.5739	2065
7	1438.9791	2032
8	1439.2284	2735
9	1439.4772	2593
10	1439.7196	2066

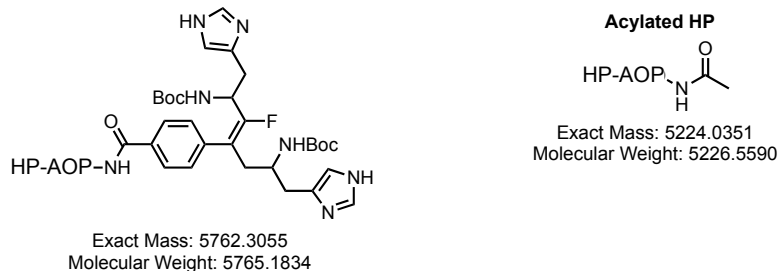


#	m/z	I
1	3855.2960	645
2	5225.8119	2442
3	5761.9345	12242
4	5780.9287	2269

product (pointing to peak 3)
 CF₃ alkene (pointing to peak 4)



Double alkylation



Product: 67%
Starting Material: 0%
Double Alkylation: 20%

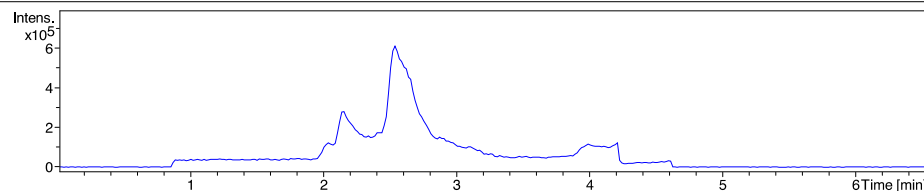
Compound Spectrum List Report

Analysis Info

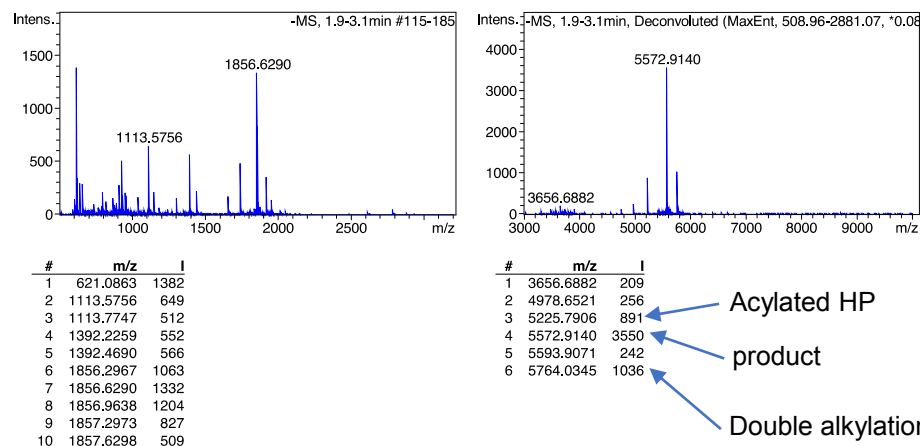
Analysis Info		Acquisition Date		4/17/2018 1:03:23 PM
Analysis Name	X:\Chem MS Data\utof\Data_2018\April 2018\utof-041318\JPP-180314-3-11_16_01_8035.d			
Method	1200col2_10to90in4.m	Operator	gsk	
Sample Name	JPP-180314-3-11	Instrument	micrOTOF	213750.00199
Comment				

Acquisition Parameter

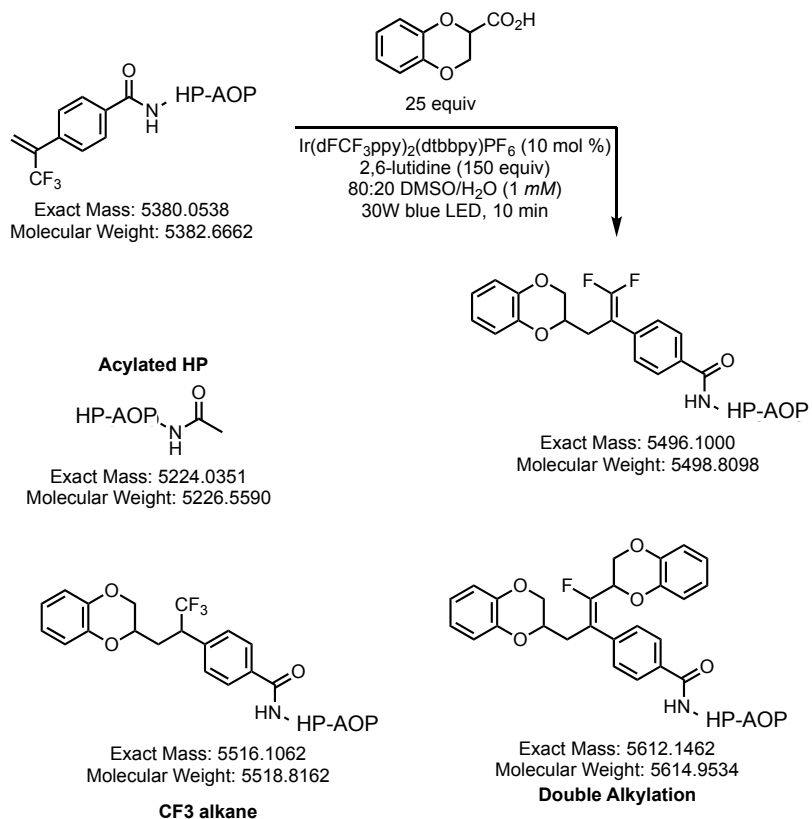
Acquisition Parameters					
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.1min #115-185



CF₂-Alkene-7z



Product: 64%
Starting Material: 0%
Double Alkylation: 12%
CF₃ Alkane: 0%

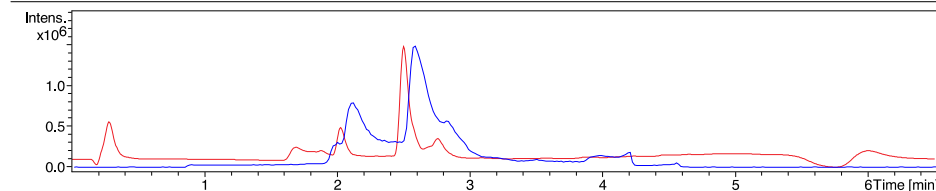
Compound Spectrum List Report

Analysis Info

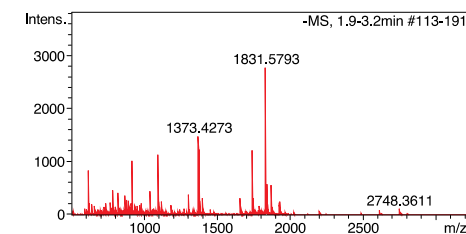
Analysis Name X:\Chem MS Data\TOF\Data_2018\July 2018\utof-070518\DNA-20180516-2-1_11_01_8710.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180516-2-1
 Comment
 Acquisition Date 7/5/2018 4:57:24 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

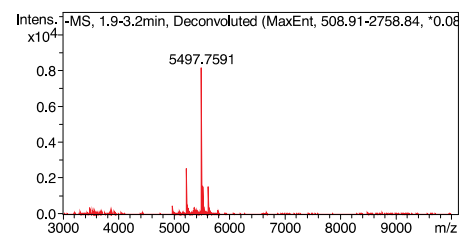
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.2min #113-191



#	m/z	I
1	1098.5466	1127
2	1373.1803	1174
3	1373.4273	1479
4	1373.6765	1409
5	1740.8958	1216
6	1831.2482	2259
7	1831.5793	2775
8	1831.9113	2447
9	1832.2424	1794
10	1832.5766	1107

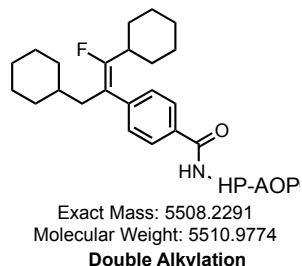
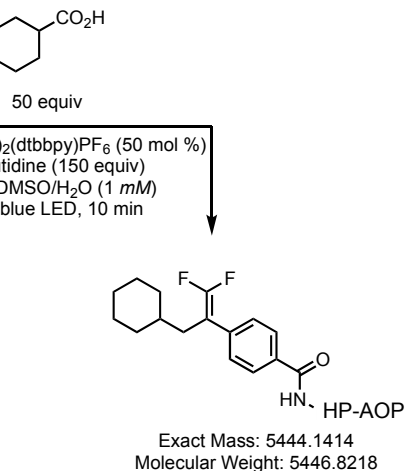
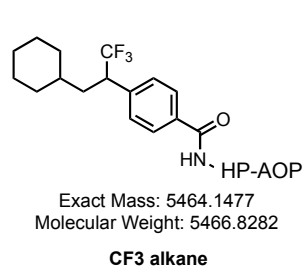
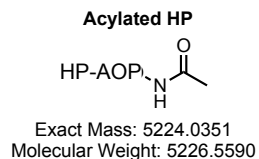
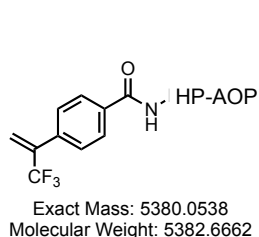


#	m/z	I
1	4978.5947	511
2	5225.7122	2559
3	5249.7050	483
4	5497.7591	8149
5	5521.7579	1529
6	5539.7575	444
7	5613.8038	1533

Acylated HP
 Product

Double alkylation

CF₂-Alkene-7aa



Product: 47%
Starting Material: 9%
Double Alkylation: 0%
CF₃ Alkane: 0%

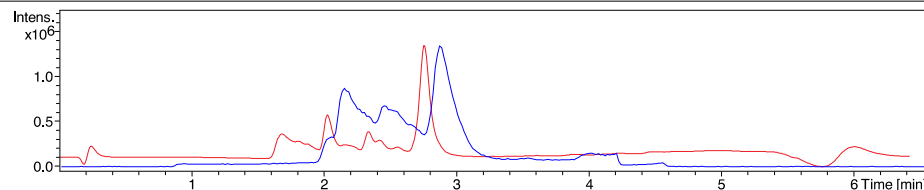
Compound Spectrum List Report

Analysis Info

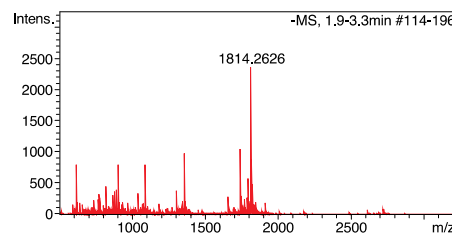
Acquisition Date 7/5/2018 5:04:46 PM
 Analysis Name X:\Chem MS Data\TOF\Data_2018\July 2018\utof-070518\DNA-20180516-2-2_12_01_8711.d
 Method 1200col2_10to90in4.m
 Sample Name DNA-20180516-2-2
 Comment
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

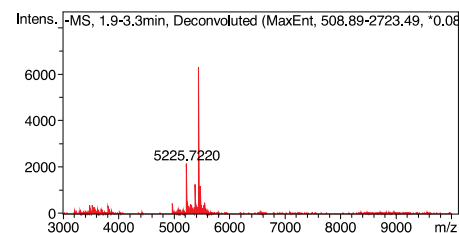
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.3min #114-196



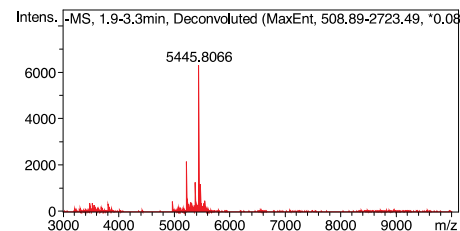
#	m/z	I
1	1360.4415	959
2	1360.6845	977
3	1740.5628	921
4	1740.8993	1045
5	1741.2297	948
6	1813.5961	895
7	1813.9283	1919
8	1814.2626	2357
9	1814.5961	2018
10	1814.9283	1471



#	m/z	I
1	3484.4540	399
2	3540.4453	366
3	3825.3205	330
4	4977.5829	466
5	5225.7220	2151
6	5248.7260	500
7	5312.7754	420
8	5376.7171	565
9	5381.7402	1259
10	5405.7552	350

← Acyated HP

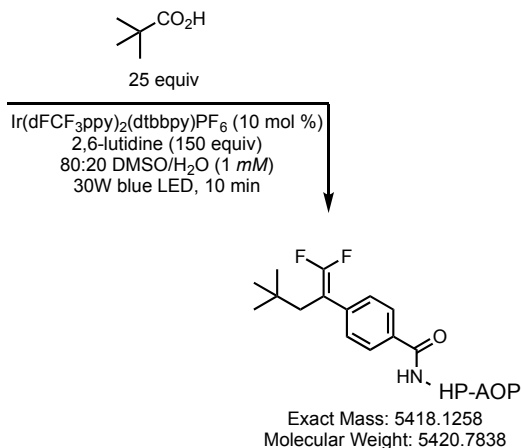
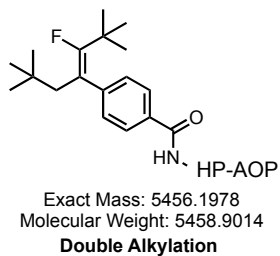
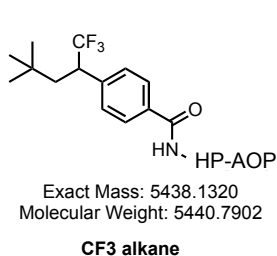
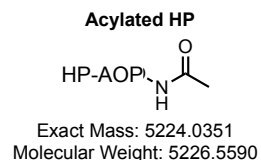
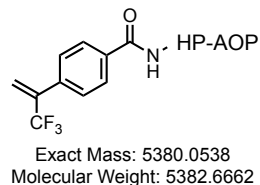
← CF₃ alkene



#	m/z	I
1	5445.8066	6297
2	5460.7877	474
3	5469.8101	1183
4	5488.8115	370
5	5548.8305	502

← Product

CF₂-Alkene-7ab



Product: 66%
Starting Material: 0%
Double Alkylation: 5%
CF₃ Alkane: 0%

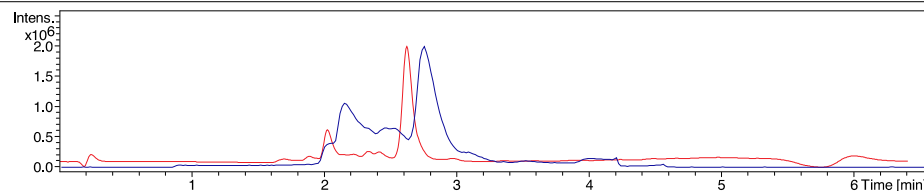
Compound Spectrum List Report

Analysis Info

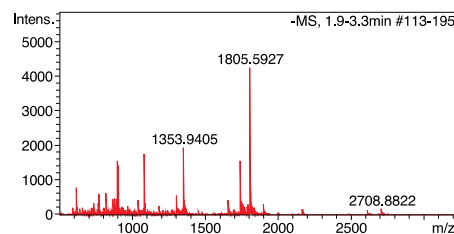
Analysis Name	X:\Chem MS Data\TOF\Data_2018\July 2018\utof-070518\DNA-20180516-2-3_13_01_8712.d	Acquisition Date	7/5/2018 5:12:09 PM
Method	1200col2_10to90in4.m	Operator	gsk
Sample Name	DNA-20180516-2-3	Instrument	micrOTOF
Comment			213750.00199

Acquisition Parameter

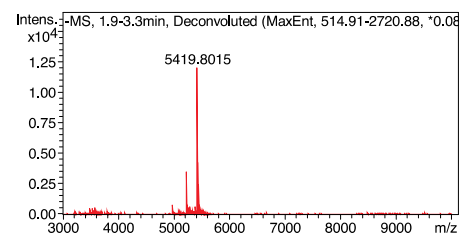
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.3min #113-195



#	m/z	I
1	1082.9564	1765
2	1353.6928	1667
3	1353.9405	1936
4	1354.1861	1793
5	1804.9264	1676
6	1805.2591	3507
7	1805.5927	4246
8	1805.9258	3534
9	1806.2565	2507
10	1806.5871	1597

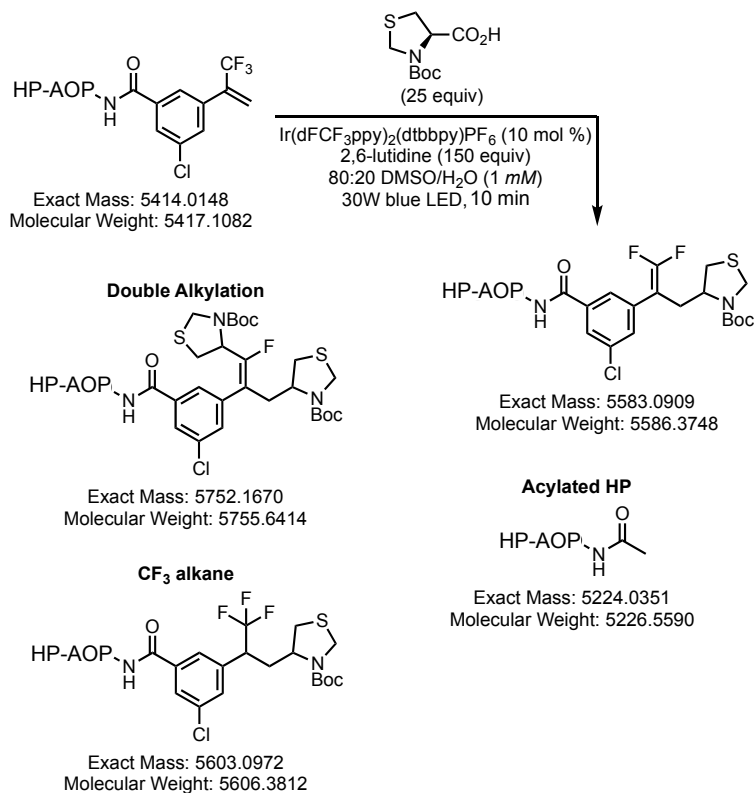


#	m/z	I
1	4978.5819	768
2	5225.7203	3478
3	5249.7351	710
4	5285.7684	622
5	5380.7280	680
6	5419.8015	11992
7	5443.8113	2504
8	5460.7757	823

← Acyated HP

← product

← Double alkylation

CF₂-Alkene-7af

Product: 64%
Starting Material: 0%
Double Alkylation: 6%
CF₃ Alkane: 5%

Compound Spectrum List Report

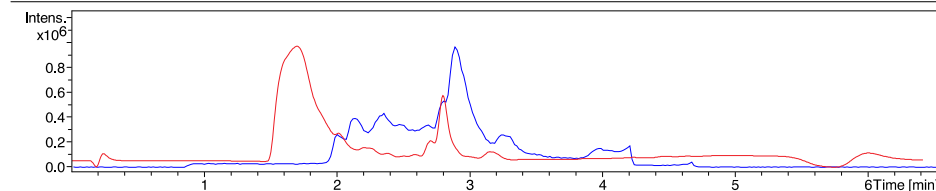
Analysis Info

Analysis Name	X:\Chem MS Data\wTO
Method	1200col2_10to90in4.m
Sample Name	DNA-20180515-1-5
Comment	

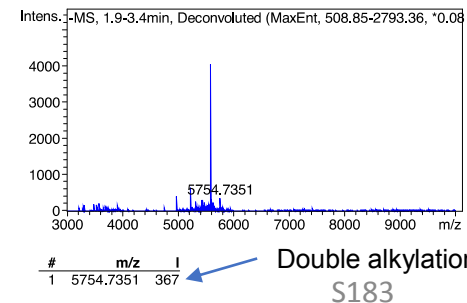
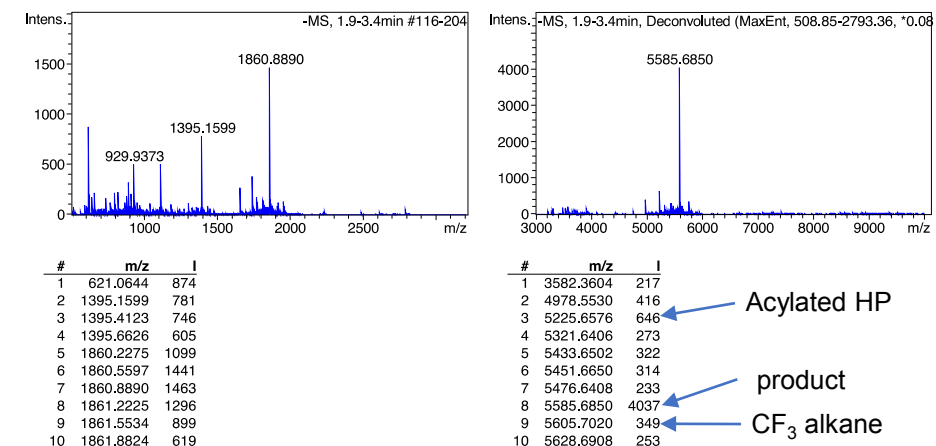
Acquisition Date 5/17/2018 7:23:57 PM
DNA-20180515-1-5_63_01_8329.d
Operator gsk
Instrument micrOTOF 213750.00199

Acquisition Parameter

Required Parameters					
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.4min #116-204

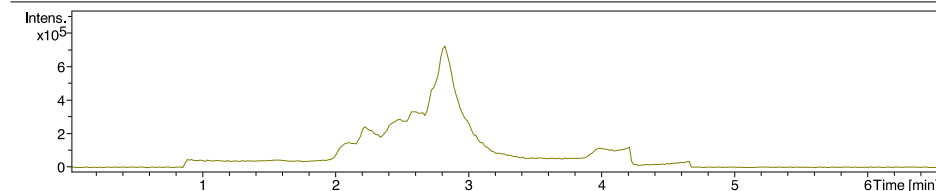


Analysis Info

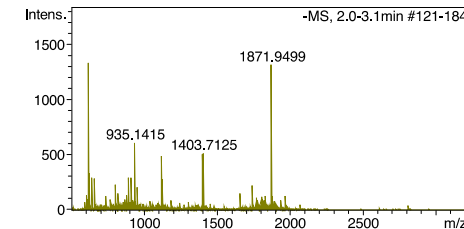
Analysis Name	X:\Chem MS Data\TOF\Data_2018\April 2018\utof-041318\JPP-180328-3-11_35_01_8055.d	Acquisition Date	4/17/2018 4:14:26 PM
Method	1200col2_10to90in4.m	Operator	gsk
Sample Name	JPP-180328-3-11	Instrument	micrOTOF 213750.00199
Comment			

Acquisition Parameter

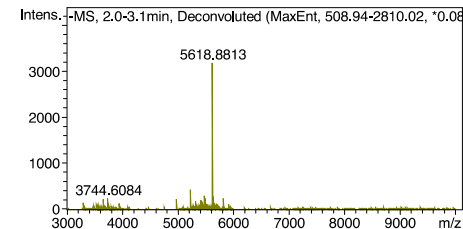
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.1min #121-184



#	m/z	I
1	621.0866	1327
2	935.1415	608
3	935.4680	499
4	1403.4630	502
5	1403.7125	515
6	1871.2865	921
7	1871.6180	1237
8	1871.9499	1312
9	1872.2830	1007
10	1872.6160	676

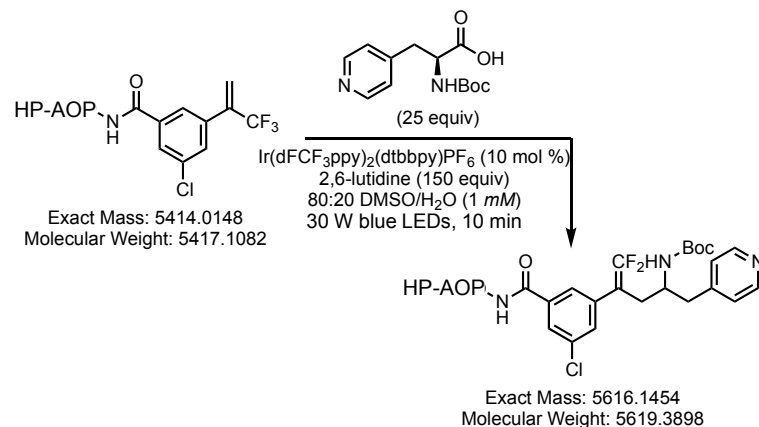


#	m/z	I
1	3656.6800	229
2	3744.6084	243
3	4978.6591	238
4	5225.7772	433
5	5321.7627	184
6	5414.7619	204
7	5434.7560	177
8	5447.7638	164
9	5484.8975	302
10	5618.8813	3176

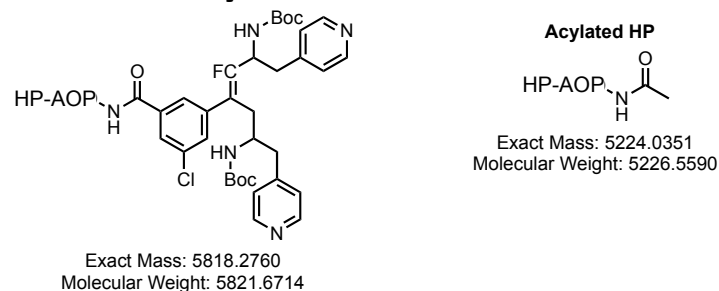
Acylated HP

Starting material

Product



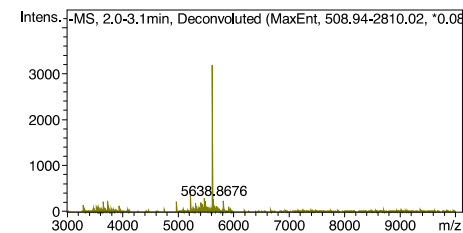
Double Alkylation



Product: 61%

Starting Material: 4%

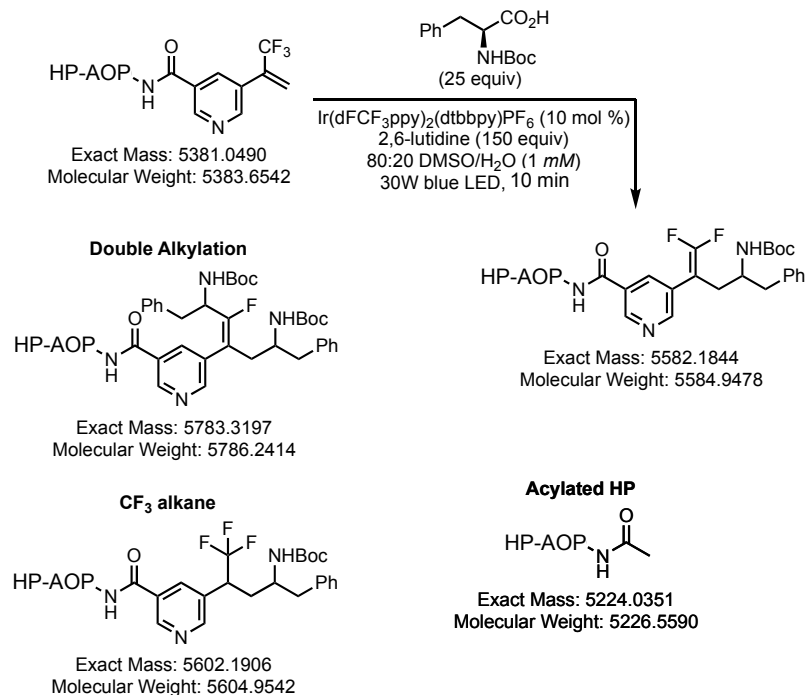
Double Alkylation: 5%



#	m/z	I
1	5638.8676	282
2	5821.0043	252

Double Alkylation

CF₂-Alkene-7ak



Product: 69%
Starting Material: 12%
Double Alkylation: 5%
CF₃ Alkane: 6%

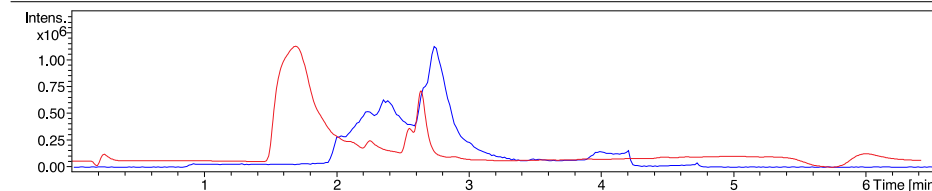
Compound Spectrum List Report

Analysis Info

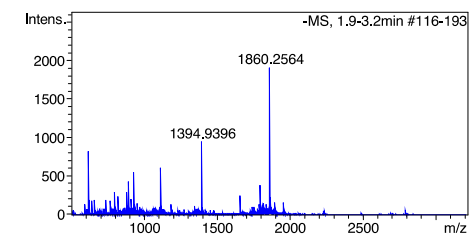
Analysis Name	X:\Chem MS Data\utof\Data_2018\May 2018\utof-051718\DNA-20180515-1-8_65_01_8331.d	Acquisition Date	5/17/2018 7:38:55 PM
Method	1200col2_10to90in4.m	Operator	gsk
Sample Name	DNA-20180515-1-8	Instrument	micrOTOF 213750.00199
Comment			

Acquisition Parameter

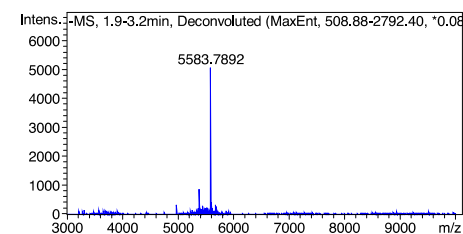
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



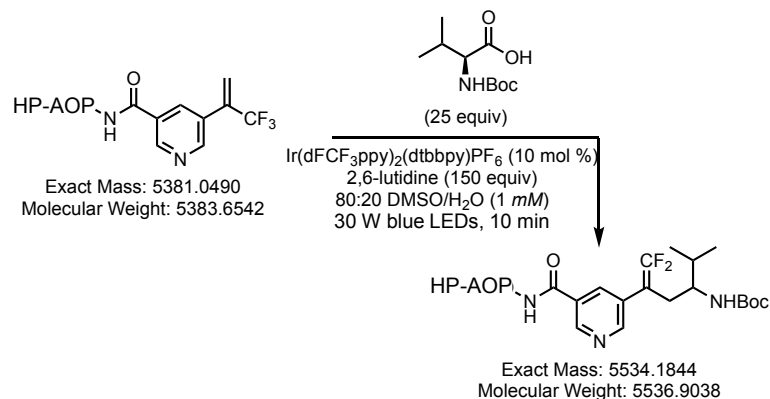
-MS, 1.9-3.2min #116-193



#	m/z	I
1	621.0656	823
2	1394.6912	682
3	1394.9396	942
4	1395.1859	868
5	1859.5943	734
6	1859.9254	1598
7	1860.2564	1905
8	1860.5918	1688
9	1860.9210	1202
10	1861.2481	789



#	m/z	I	Assignment
1	4977.4998	342	Starting material
2	5382.6650	861	product
3	5450.7490	305	
4	5583.7892	5056	CF ₃ alkane
5	5604.7780	427	
6	5687.6870	331	Double alkylation



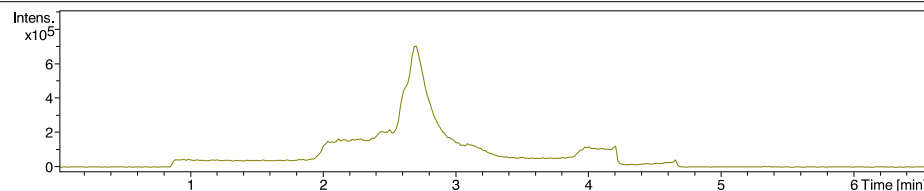
Compound Spectrum List Report

Analysis Info

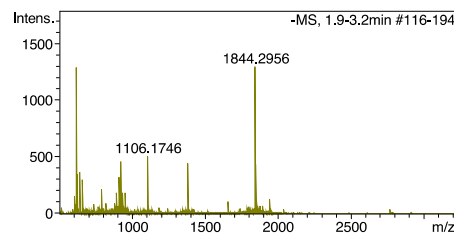
Analysis Name X:\Chem MS Data\TOF\Data_2018\April 2018\utof-041318\JPP-180328-3-21_45_01_8065.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-180328-3-21
 Comment
 Acquisition Date 4/17/2018 5:27:52 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

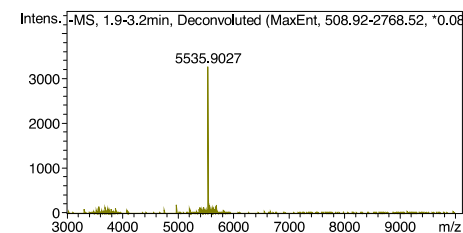
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 1.9-3.2min #116-194



#	m/z	I
1	621.0850	1282
2	921.8076	462
3	1106.1746	504
4	1106.3733	498
5	1383.2181	447
6	1843.6258	523
7	1843.9637	979
8	1844.2956	1292
9	1844.6298	1105
10	1844.9579	846

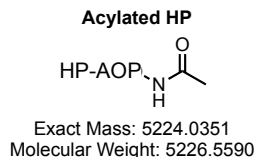
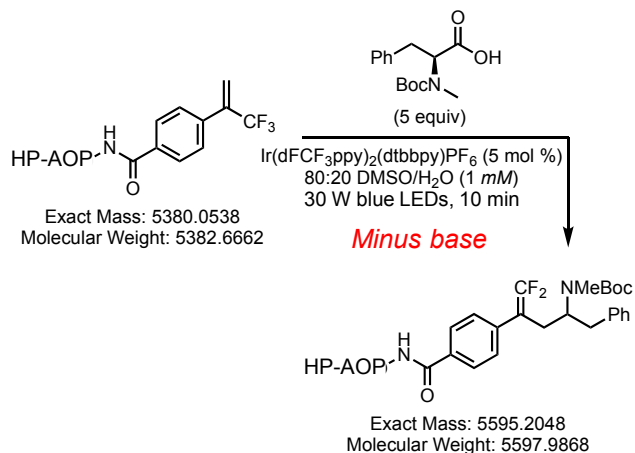


#	m/z	I
1	4977.6532	188
2	5535.9027	3261
3	5556.9063	241
4	5689.0284	178

← Product

Product: 84%
Starting Material: 0%

Defluorinative Alkylation Control Reactions



Product: 26%
Starting Material: 58%

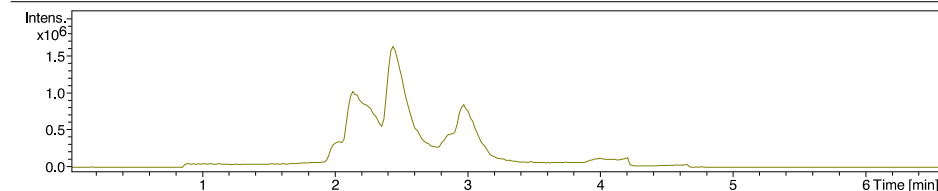
Compound Spectrum List Report

Analysis Info

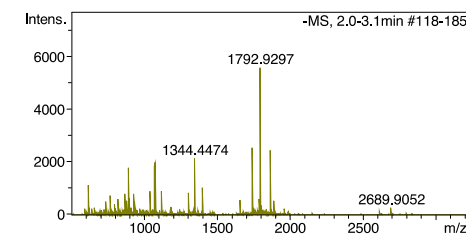
Analysis Name X:\Chem MS Data\TOF\Data_2018\April 2018\utof-041318\JPP-180314-9-2_33_01_8053.d
 Method 1200col2_10to90in4.m
 Sample Name JPP-180314-9-2
 Comment
 Acquisition Date 4/17/2018 3:59:45 PM
 Operator gsk
 Instrument micrOTOF 213750.00199

Acquisition Parameter

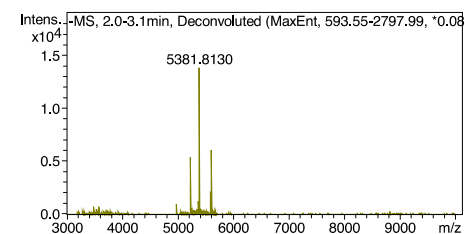
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	3.5 Bar
Focus	Active			Set Dry Heater	220 °C
Scan Begin	510 m/z	Set Capillary	2500 V	Set Dry Gas	11.0 l/min
Scan End	3200 m/z	Set End Plate Offset	-400 V	Set Divert Valve	Waste



-MS, 2.0-3.1min #118-185



#	m/z	I
1	1740.5925	2233
2	1740.9225	2556
3	1741.2561	2194
4	1792.2628	2432
5	1792.5962	4939
6	1792.9297	5577
7	1793.2635	4808
8	1793.5958	3289
9	1864.6384	2451
10	1864.9738	2157



#	m/z	I
1	3484.5019	779
2	3582.4428	710
3	4978.6666	972
4	5225.7951	5372
5	5361.8019	1253
6	5381.8130	13811
7	5596.9424	6066

Acylated HP

Starting material

Product

