Supporting Information

Photoredox-Mediated Hydroalkylation and Hydroarylation of Functionalized Olefins for DNA-Encoded Library Synthesis

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1. General Considerations

1.1. General

All chemical transformations requiring inert atmospheric conditions were carried out using Schlenk line techniques with a 4- or 5-port dual-bank manifold. For blue light irradiation, two Kessil PR160-456nm lamps (19VDC 40W Max) were placed 1.5 inches away from PCR tubes. Reactions conducted in 24-well screening plates were irradiated using blue LED lights and performed at the Penn/Merck Center for High Throughput Experimentation at the University of Pennsylvania (plate reactors contained glass reaction vials). NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 ºK using 400 or 500 MHz spectrometers. ^{1}H NMR spectra were referenced to residual $CHCl_3$ (δ 7.26 ppm) in $CDCl_3$. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.3 ppm). Reactions were monitored by LC/MS, GC/MS, ^{1}H 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 ninhydrin, *p*-anisaldehyde stain, and/or UV light. Flash chromatography was accomplished using an automated system (CombiFlash®, UV detector, λ = 254 nm and 280 nm) with RediSep® R_f silica gel disposable flash columns (60 Å porosity, 40–60 μm) or RediSep R_f Gold® silica gel disposable flash columns (60 Å porosity, 20–40 μm). Accurate mass measurement analyses were conducted using electron ionization (EI) or electrospray ionization (ESI). The signals were mass measured against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GCMS, and leucine enkephalin for ESI-LC/MS. IR spectra were recorded on an FT-IR using either neat oil or solid products. Solvents were purified with drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected.

1.2. Chemicals

Deuterated NMR solvents were purchased and stored over 4Å molecular sieves. CH_2Cl_2, $CHCl_3$, EtOAc, pentane, hexanes, MeOH, Et_2O, and toluene were used as purchased. THF was purchased and dried *via* a solvent delivery system. HITU was prepared in-house according to the literature.[1] DIPEA was purchased from commercial suppliers and used without further purification. Trifluoromethyl alkene-substituted benzoic acids, used in the preparation of select on-DNA substrates, were prepared according to the literature.[2,3] Synthesis of all new benzoic acids and new on-DNA substrates is outlined here. Carboxylic acids and alkenes were purchased from commercial suppliers. Redox-active esters were prepared according to the literature.[4-16] The synthesis of all new redox-active esters is reported here. Umemoto's reagent [5-(trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate], Hantzsch ester, and $Ir(ppy)_3$ were purchased from commercial suppliers and used without further manipulation. All other reagents were purchased commercially and used as received. Photoredox-catalyzed reactions were performed using PCR 8-strip tubes (Ref. Fisher 781320) with PCR strips of 8 caps (Ref. Fisher 781340). DMSO was purchased and used as received. HyPure™ Molecular Biology Grade Water was purchased and used as received without further manipulation.

1.3. Analysis of "on-DNA" reactions

Analysis of on-DNA reactions was performed by LC/MS: After reaction completion, an aliquot of the reaction mixture was diluted with H_2O to approximately 0.05–0.13 mM. At this point, 5 or 8 µL aliquots of the LC/MS sample was injected onto reverse-phase chromatography columns (for analysis performed at GSK: Clarity 2.6um Oligo-MS 100A 2.1X50mm; for analysis performed at UPenn: Cortecs T3 2.7 µm, 2.1x30 mm, Waters) 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 µM EDTA in H_2O; Solvent B: 0.75% HFIP, 0.038% TEA, 5 µM EDTA in 90/10 MeOH/deionized H_2O) with monitoring at UV 254 nm (UPenn) and no UV monitoring (GSK). Effluent was analyzed on a Waters SQ Detector 2 ACQUITY UPLC System in negative ion mode (UPenn) or a Thermo Exactive Plus LC-esiMS with a Vanquish uHPLC (GSK). For the functionalized headpiece samples (the on-DNA aryl halides/alkenes), % conversion was determined based on reported peak intensities following deconvolution (between 3,000-10,000 Da) of the DNA charge states using Intact Mass™ by Protein Metrics Inc. (version 3.7-32x64). For the photoredox scope reactions, % conversion was determined using Intact Mass™ by Protein Metrics Inc. (version 3.7-32x64) (GSK) or using MassLynx at UPenn. Data was scanned between 0.3-2.2 min and deconvoluted between 4,000-6,000 Da, with a mass tolerance window of 2 Da, with 5% of base peak threshold was set for reporting (GSK). For conversion calculations for each example, the peaks annotated with colored dots were used for the calculations. Alternativly, data was scanned between 1.0-3.0 min and deconvoluted between 3,000-8,000 Da, with a mass tolerance window of 1 Da, with 10% of base peak threshold was set for reporting (UPenn). Na, K, NH_4, and HFIP adducts were included in the product percentage. Detailed parameters can be found later in the Supporting Information.

1.4. Materials for "on-DNA" synthesis

DNA headpiece HP-NH_2(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 equiv each of Fmoc-15-amino-4,7,10,13-tetraoxapentadecanoic acid (Fmoc-AOP), *i*-Pr_2NEt, and HATU. The lyophilized product of this reaction was then deprotected by exposure to a 10% piperidine in H_2O solution. 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.

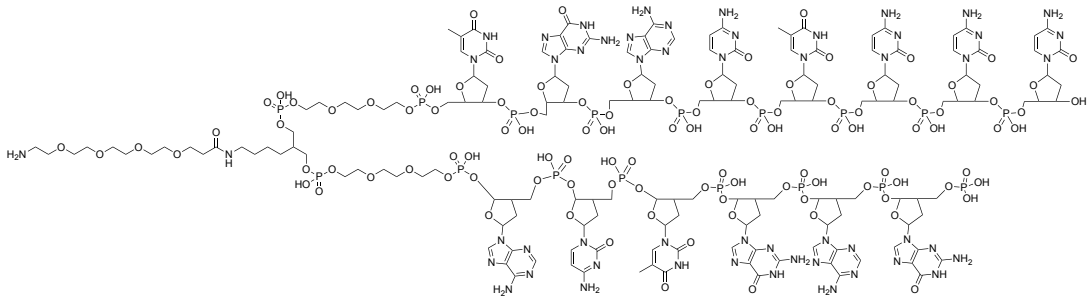
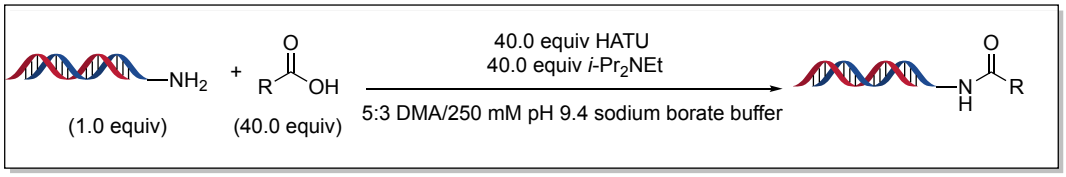


Figure S1. Sequence and structure of the AOP-headpiece (molecular weight = 5184.5220).

2. Preparation of on-DNA Substrates



2.1. HATU premix protocol for acylation of DNA headpieces

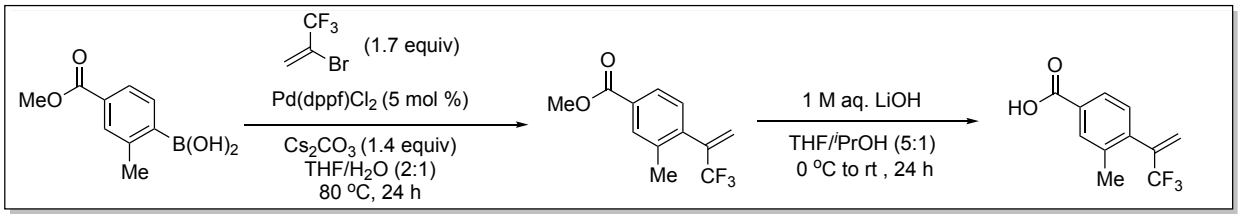
The HATU (200 mM in DMA, 40.0 equiv), *i*-Pr_2NEt (200 mM in DMA, 40.0 equiv), and the corresponding carboxylic acid (200 mM in DMA, 40.0 equiv) solutions were individually cooled at 4 °C for 5 min. Once chilled, the acid, *i*-Pr_2NEt, and HATU solutions were added sequentially to a centrifuge tube, 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 below.

2.2. EtOH precipitation protocol

The reaction mixture was transferred to a centrifuge tube where it filled at most 1/4 of the total volume. A volume of 5 M aq 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 –80 °C freezer for at least 1 h or overnight. The chilled mixture was then centrifuged for 30 min at 4 °C at 3,300 rpm. The supernatant was then decanted and allowed to dry under reduced pressure. The resulting pellet was re-dissolved in H_2O to give a theoretical concentration of 2 or 5 mM. Purity was assessed by LC/MS, and optical density was obtained via NanoDrop. For long term storage, solutions were frozen in liquid nitrogen and lyophilized to dryness to give a white solid. If purity was less than 90% by LC/MS, HPLC purification was performed: gradient of 95% A (50 mM TEAA, pH = 7.5)/5% B (1% H_2O in CH_3CN) to 60% A/40% B, through a Gemini C18 (5 µm, 110 Å, 30x100 mm), with UV visualization at 260 nm.

3. Synthesis of Benzoic Acid Derivatives

*2-Methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (**23B**)*

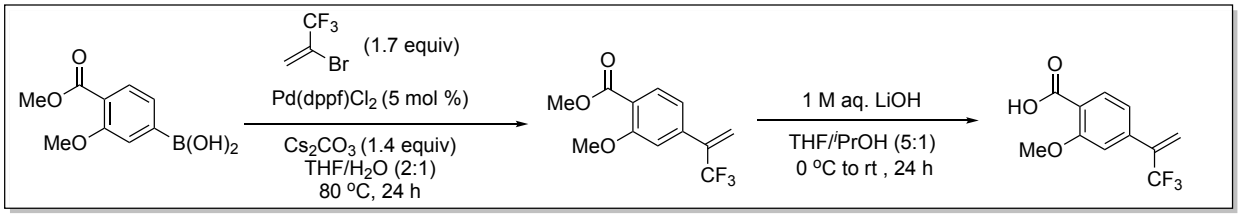


Step 1 (cross-coupling): Methyl 3-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (22B). To a 20 mL microwave vial was added boronic acid (582 mg, 3.0 mmol, 1.0 equiv), Cs_2CO_3 (1.37 g, 4.2 mmol, 1.4 equiv), and $Pd(dppf)Cl_2$ (0.11 g, 0.15 mmol, 0.05 equiv). The vial was sealed with a crimp-top cap containing a TFE-lined silicone septum. The tube was then evacuated three times *via* an inlet needle, then purged with argon. A degassed mixture of THF (10 mL) and deionized H_2O (5 mL) was added, followed by 2-bromo-3,3,3-trifluoroprop-1-ene (0.892 g, 0.55 mL, 5.1 mmol, 1.7 equiv). The mixture was heated to 80 °C overnight. Upon completion, the reaction was diluted with Et_2O (25 mL) and transferred to a separatory funnel. After extraction with Et_2O (3 × 25 mL), the combined organic layers were washed with brine (25 mL) and then dried (Na_2SO_4). The solvent was removed under reduced pressure, and the crude product was purified using flash chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the title compound (521 mg, 2.13 mmol, 71%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.26 (s, 1H), 7.18 (d, J = 8.0 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 5.48 (s, 1H), 4.84 (s, 1H), 3.24 (s, 3H), 1.67 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 166.8, 138.2, 137.9 (q, J = 31.9 Hz), 137.5, 131.5, 130.6, 130.0, 126.8, 123.2 (q, J = 5.4 Hz), 122.9 (q, J = 274.0 Hz, CF_3), 52.3, 19.9. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = –64.86 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1725, 1438, 1401, 1344, 1299, 1257, 1068, 1007, 958, 898, 832. **HRMS** (EI) calcd for $C_{12}H_{11}F_3O_2$ [M]+: 244.0711, found: 247.0709.

Step 2 (hydrolysis): 3-Methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (23B). To a 40 mL vial equipped with a stir bar was added the ester (521 mg, 2.13 mmol, 1.0 equiv) and THF (5 mL). The reaction mixture was cooled to 0 °C for 10 min. An aq soln of LiOH (1 M, 6.60 mL) was then added, followed by *i*-PrOH (2.56 mL). The reaction was allowed to slowly warm to rt and then stirred overnight. Upon completion, the crude reaction was concentrated under reduced pressure and then dissolved in H_2O (5 mL). This residue was transferred to a separatory funnel and washed with Et_2O (2 × 10 mL). The aq layer was then acidified with 1 M HCl to achieve a pH of ~1 and subsequently extracted with EtOAc (4 × 10 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure to afford the desired benzoic acid as a colorless solid (353 mg, 1.55 mmol, 73%). **Mp** = 117.0–118.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 11.45 (s, 1H), 8.02 (d, J = 1.8 Hz, 1H), 7.94 (dd, J = 8.0, 1.8 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 6.18 (d, J = 1.4 Hz, 1H), 5.54 (d, J = 1.4 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 172.0, 139.2, 137.8 (q, J = 31.4 Hz), 137.7, 132.2, 130.2, 129.7, 127.5, 123.3 (q, J = 5.2 Hz), 122.8 (q, J = 274.4 Hz, CF_3), 19.9. **^{19}F NMR** (376 MHz, $CDCl_3$), δ

(ppm) = –66.93 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2980, 1612, 1347, 1267, 1206, 1067, 959, 905, 776, 759. **HRMS** (ESI, *m*/*z*) calcd for $C_{11}H_{10}F_3O_2$ $[M+H]^+$: 231.0633, found: 231.0647.

*2-Methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (**23C**)*

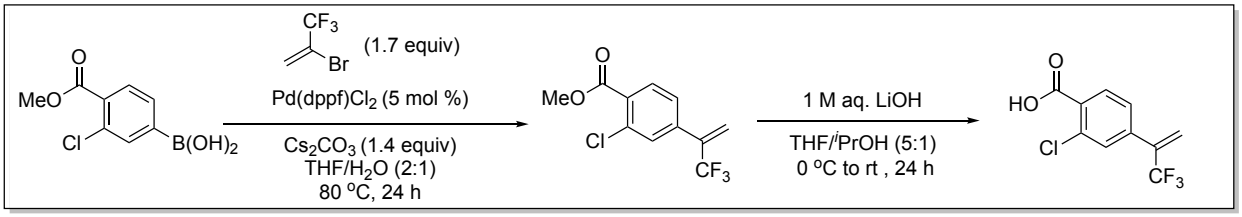


Step 1 (cross-coupling): Methyl 2-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (22C). To a 20 mL microwave vial was added boronic acid (630 mg, 3.0 mmol, 1.0 equiv), Cs_2CO_3 (1.37 g, 4.2 mmol, 1.4 equiv), and $Pd(dppf)Cl_2$ (0.11 g, 0.15 mmol, 0.05 equiv). The vial was sealed with a crimp-top cap containing a TFE-lined silicone septum. The tube was then evacuated three times via an inlet needle, then purged with argon. A degassed mixture of THF (10 mL) and deionized H_2O (5 mL) was added, followed by 2-bromo-3,3,3-trifluoroprop-1-ene (0.892 g, 0.55 mL, 5.1 mmol, 1.7 equiv). The mixture was heated to 80 ºC overnight. Upon completion, the reaction was diluted with Et_2O (25 mL) and transferred to a separatory funnel. After extraction with Et_2O (3 × 25 mL), the combined organic layers were washed with brine (25 mL) and then dried (Na_2SO_4). The solvent was removed under reduced pressure, and the crude product was purified using flash chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the title compound (434 mg, 1.67 mmol, 56%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.26 (d, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.49 (s, 1H), 5.49 (s, 1H), 5.30 (s, 1H), 3.38 (s, 3H), 3.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 166.2, 159.1, 138.7, 138.4 (q, J = 30.6 Hz), 132.0, 123.1 (q, *J* = 174.2 Hz, CF_3), 122.0 (q, *J* = 5.7 Hz), 120.6, 119.4, 111.2, 56.1, 52.2. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = –62.52 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1610, 1566, 1505, 1465, 1409, 1347, 1296, 1033, 862. **HRMS** (EI) calcd for $C_{12}H_{11}F_3O_3$ [M]+: 260.2122, found: 260.2126.

Step 2 (hydrolysis): 2-Methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (23C). To a 40 mL vial equipped with a stir bar was added the ester (434, 1.67 mmol, 1.0 equiv) and THF (5 mL). The reaction mixture was cooled to 0 ºC for 10 min. An aq soln LiOH (1 M, 2.59 mL) was then added, followed by *i*-PrOH (1.0 mL). The reaction was allowed to slowly warm to rt and then stirred overnight. Upon completion, the crude reaction was concentrated under reduced pressure and then dissolved in H_2O (5 mL). This residue was transferred to a separatory funnel and washed with Et_2O (2 × 10 mL). The aq layer was then acidified with 1 M HCl to achieve a pH of ~1 and subsequently extracted with EtOAc (4 × 10 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure to afford the desired benzoic acid as a colorless solid (300 mg, 1.22 mmol, 73%). **Mp** = 76.0–77.0 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 10.28 (s, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.20 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.10 (d, *J* = 1.6 Hz, 1H), 6.10–6.07 (m, 1H), 5.91–5.89 (m, 1H), 4.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 165.6, 158.2, 140.3, 137.9 (q, *J* = 30.7 Hz), 134.1, 123.0 (d, *J* = 273.4 Hz, CF_3),

122.9 (q, J = 5.6 Hz), 121.2, 118.2, 110.9, 56.9. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = –64.66 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2950, 1610, 1465, 1439, 1395, 1356, 1274, 1070, 951, 934. **HRMS** (ESI, *m*/*z*) calcd for $C_{11}H_{10}F_3O_3$ $[M+H]^+$: 247.0582, found: 247.0572.

*Synthesis of 2-chloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (**23D**)*

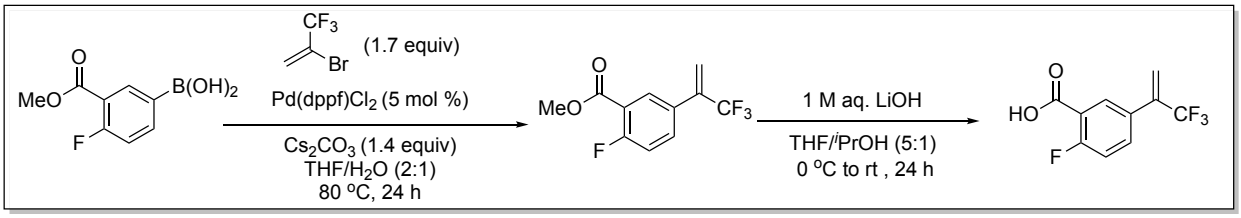


Step 1 (cross-coupling): Methyl 2-chloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (22D). To a 20 mL microwave vial was added boronic acid (643.0 mg, 3.0 mmol, 1.0 equiv), Cs_2CO_3 (1.37 g, 4.2 mmol, 1.4 equiv), and $Pd(dppf)Cl_2$ (0.11 g, 0.15 mmol, 0.05 equiv). The vial was sealed with a crimp-top cap containing a TFE-lined silicone septum. The tube was then evacuated three times *via* an inlet needle, then purged with argon. A degassed mixture of THF (10 mL) and deionized H_2O (5 mL) was added, followed by 2-bromo-3,3,3-trifluoroprop-1-ene (0.892 g, 0.55 mL, 5.1 mmol, 1.7 equiv). The mixture was heated to 80 °C overnight. Upon completion, the reaction was diluted with Et_2O (25 mL) and transferred to a separatory funnel. After extraction with Et_2O (3 × 25 mL), the combined organic layers were washed with brine (25 mL) and then dried (Na_2SO_4). The solvent was removed under reduced pressure, and the crude product was purified using flash chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the title compound (530 mg, 2.0 mmol, 67%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.84 (dd, J = 8.1, 1.3 Hz, 1H), 7.54 (s, 1H), 7.41–7.37 (m, 1H), 6.06 (s, 1H), 5.87 (s, 1H), 3.93 (d, J = 1.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 165.6, 137.9, 137.3 (q, J = 30.8 Hz), 134.2, 131.8, 130.4, 130.1, 125.6, 122.9 (q, J = 273.9 Hz, CF_3), 122.8 (q, J = 5.6 Hz), 52.7. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = –64.79 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1733, 1605, 1548, 1436, 1416, 1384, 1348, 1254, 956, 847. **HRMS** (EI) calcd for $C_{10}H_5ClF_3O$ $[M–OMe]^+$: 232.9981, found: 232.9984.

Step 2 (hydrolysis): 2-Chloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (23D). To a 40 mL vial equipped with a stir bar was added the ester (530.0 mg, 2.0 mmol, 1.0 equiv) and THF (5.6 mL). The reaction mixture was cooled to 0 °C for 10 min. An aq soln LiOH (1 M, 3.1 mL) was then added, followed by *i*-PrOH (1.2 mL). The reaction was allowed to slowly warm to rt and then stirred overnight. Upon completion, the crude reaction was concentrated under reduced pressure and then dissolved in H_2O (5 mL). This residue was transferred to a separatory funnel and washed with Et_2O (2 × 10 mL). The aq layer was then acidified with 1 M HCl to achieve a pH of ~1 and subsequently extracted with EtOAc (4 × 10 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure to afford the desired benzoic acid as a colorless solid (383.0 mg, 1.53 mmol, 77%). **Mp** = 84.0–85.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 11.88 (s, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 1.7 Hz, 1H), 7.45 (dd, J = 8.1, 1.7 Hz, 1H), 6.11 (d, J = 1.6 Hz, 1H), 5.92 (d, J = 1.7 Hz, 1H). **^{13}C**

NMR (101 MHz, $CDCl_3$), δ (ppm) = 170.7, 139.0, 137.2 (q, J = 30.9 Hz), 135.4, 132.9, 130.5, 128.7, 125.7, 123.2 (q, J = 5.7 Hz), 122.9 (q, J = 274.0 Hz, CF_3). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = –64.70 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2985, 1605, 1547, 1409, 1259, 1194, 1050, 955, 892, 848. **HRMS** (EI) calcd for $C_{10}H_6ClF_3O_2$ $[M]^+$: 250.0008, found: 250.0020.

*Synthesis of 2-fluoro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (**23E**)*

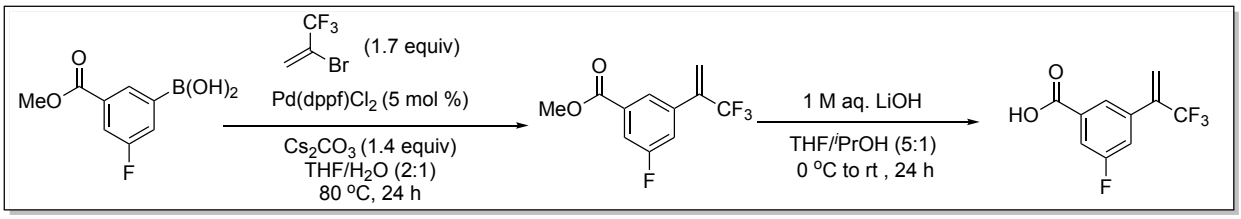


Step 1 (cross-coupling): Methyl 2-fluoro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (22E). To a 20 mL microwave vial was added boronic acid (594 mg, 3.0 mmol, 1.0 equiv), Cs_2CO_3 (1.37 g, 4.2 mmol, 1.4 equiv), and $Pd(dppf)Cl_2$ (0.11 g, 0.15 mmol, 0.05 equiv). The vial was sealed with a crimp-top cap containing a TFE-lined silicone septum. The tube was then evacuated three times *via* an inlet needle, then purged with argon. A degassed mixture of THF (10 mL) and deionized H_2O (5 mL) was added, followed by 2-bromo-3,3,3-trifluoroprop-1-ene (0.892 g, 0.55 mL, 5.1 mmol, 1.7 equiv). The mixture was heated to 80 °C overnight. Upon completion, the reaction was diluted with Et_2O (25 mL) and transferred to a separatory funnel. After extraction with Et_2O (3 × 25 mL), the combined organic layers were washed with brine (25 mL) and then dried (Na_2SO_4). The solvent was removed under reduced pressure, and the crude product was purified using flash chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the title compound (510 mg, 2.05 mmol, 68%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 8.02 (dd, J = 6.8, 2.5 Hz, 1H), 7.63–7.55 (m, 1H), 7.16 (dd, J = 10.2, 8.7 Hz, 1H), 6.01 (s, 1H), 5.79 (s, 1H), 3.94 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 164.5 (d, J = 3.9 Hz), 162.2 (d, J = 262.8 Hz), 137.4 (q, J = 30.7 Hz), 133.5 (d, J = 9.2 Hz), 131.6, 129.9 (d, J = 4.1 Hz), 123.1 (q, J = 273.6 Hz, CF_3), 121.7 (q, J = 5.4 Hz), 119.1 (d, J = 10.5 Hz), 117.5 (d, J = 23.1 Hz), 52.7. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = –65.18 (s, 3F), –108.81 (s, 1F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1722, 1614, 1504, 1416, 1281, 1095, 979, 954, 905, 804. **HRMS** (EI) calcd for $C_{11}H_8F_4O_2$ $[M]^+$: 248.0460, found: 248.0458.

Step 2 (hydrolysis): 2-Fluoro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (23E). To a 40 mL vial equipped with a stir bar was added the ester (510 mg, 2.05 mmol, 1.0 equiv) and THF (5.6 mL). The reaction mixture was cooled to 0 °C for 10 min. An aq soln of LiOH (1 M, 3.1 mL) was then added, followed by *i*-PrOH (1.2 mL). The reaction was allowed to slowly warm to rt and then stirred overnight. Upon completion, the crude reaction was concentrated under reduced pressure and then dissolved in H_2O (5 mL). This residue was transferred to a separatory funnel and washed with Et_2O (2 × 10 mL). The aq layer was then acidified with 1 M HCl to achieve a pH of ~1 and subsequently extracted with EtOAc (4 × 10 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure to afford the desired benzoic acid as a colorless solid (365 mg, 1.56

mmol, 76%). **Mp** = 96.0–97.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 11.99 (s, 1H), 8.14 (dd, J = 6.8, 2.5 Hz, 1H), 7.68 (ddd, J = 8.7, 4.4, 2.5 Hz, 1H), 7.21 (dd, J = 10.3, 8.7 Hz, 1H), 6.05 (d, J = 1.4 Hz, 1H), 5.83 (d, J = 1.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 169.6 (d, J = 3.5 Hz), 163.0 (d, J = 265.3 Hz), 137.2 (q, J = 30.7 Hz), 134.7 (d, J = 9.6 Hz), 132.2, 130.1 (d, J = 4.2 Hz), 123.1 (q, J = 273.3 Hz, CF_3), 121.9 (q, J = 5.6 Hz), 118.0 (d, J = 9.5 Hz), 117.8 (d, J = 22.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = –65.17 (s, 3F), –107.18 (s, 1F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3000, 1698, 1614, 1504, 1416, 1351, 1281, 1095, 979, 954, 905, 804. **HRMS** (EI) calcd for $C_{10}H_6F_4O_2$ $[M]^+$: 234.0304, found: 234.0306.

*Synthesis of 3-fluoro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (**23F**)*

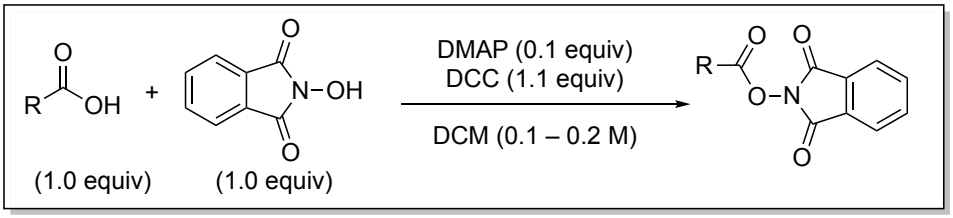


Step 1 (cross-coupling): Methyl 3-fluoro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (22F). To a 20 mL microwave vial was added boronic acid (594 mg, 3.0 mmol, 1.0 equiv), Cs_2CO_3 (1.37 g, 4.2 mmol, 1.4 equiv), and $Pd(dppf)Cl_2$ (0.11 g, 0.15 mmol, 0.05 equiv). The vial was sealed with a crimp-top cap containing a TFE-lined silicone septum. The tube was then evacuated three times *via* an inlet needle, then purged with argon. A degassed mixture of THF (10 mL) and deionized H_2O (5 mL) was added, followed by 2-bromo-3,3,3-trifluoroprop-1-ene (0.892 g, 0.55 mL, 5.1 mmol, 1.7 equiv). The mixture was heated to 80 °C overnight. Upon completion, the reaction was diluted with Et_2O (25 mL) and transferred to a separatory funnel. After extraction with Et_2O (3 × 25 mL), the combined organic layers were washed with brine (25 mL) and then dried (Na_2SO_4). The solvent was removed under reduced pressure, and the crude product was purified using flash chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the title compound (461 mg, 1.86 mmol, 62%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.92 (s, 1H), 7.75–7.69 (m, 1H), 7.34 (d, J = 9.5 Hz, 1H), 6.05 (s, 1H), 5.87 (s, 1H), 3.93 (dd, J = 2.5, 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 165.5 (t, J = 2.8 Hz), 162.5 (d, J = 247.9 Hz), 137.4 (qd, J = 30.9, 2.2 Hz), 135.9 (d, J = 7.9 Hz), 132.8 (d, J = 7.9 Hz), 124.6, 123.0 (q, J = 174.0 Hz, CF_3), 122.4 (q, J = 5.7 Hz), 119.0 (d, J = 23.4 Hz), 117.1 (dd, J = 23.2, 2.1 Hz), 52.6. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = –65.06 (s, 3F), –111.60 (s, 1F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1594, 1437, 1412, 1363, 1173, 1000, 952, 807, 755, 702. **HRMS** (EI) calcd for $C_{11}H_8F_4O_2$ $[M]^+$: 248.0460, found: 248.0467.

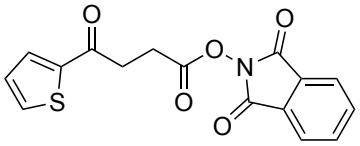
Step 2 (hydrolysis): 3-Fluoro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (23F). To a 40 mL vial equipped with a stir bar was added the ester (461 mg, 1.86 mmol, 1.0 equiv) and THF (5 mL). The reaction mixture was cooled to 0 °C for 10 min. An aq soln of LiOH (1 M, 2.78 mL) was then added, followed by *i*-PrOH (1.0 mL). The reaction was allowed to slowly warm to rt and then stirred overnight. Upon completion, the crude reaction was concentrated under reduced pressure and then dissolved in H_2O (5 mL). This residue was transferred to a separatory

funnel and washed with Et_2O (2 × 10 mL). The aq layer was then acidified with 1 M HCl to achieve a pH of ~1 and subsequently extracted with EtOAc (4 × 10 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure to afford the desired benzoic acid as a colorless solid (324 mg, 1.38 mmol, 74%). **Mp** = 87.0–85.5 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 12.01 (s, 1H), 8.02 (s, 1H), 7.82 (dt, J = 8.5, 2.0 Hz, 1H), 7.43 (d, J = 9.2 Hz, 1H), 6.11 (s, 1H), 5.91 (d, J = 1.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 170.9 (d, J = 3.0 Hz), 162.6 (d, J = 248.6 Hz), 137.2 (qd, J = 30.9, 2.7 Hz), 136.2 (d, J = 7.9 Hz), 131.9 (d, J = 8.0 Hz), 125.2 (d, J = 3.0 Hz), 123.0 (q, J = 273.8 Hz, CF_3), 122.7 (q, J = 5.6 Hz), 120.1 (d, J = 23.3 Hz), 117.7 (d, J = 23.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = –64.99 (s, 3F), –110.93 (s, 1F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2950, 1699, 1611, 1596, 1453, 1361, 1247, 967, 924. **HRMS** (ESI, m/z) calcd for $C_{10}H_5F_4O_2$ $[M–H]^-$: 233.0226, found: 233.0220.

4. Synthesis of Redox-Active Esters

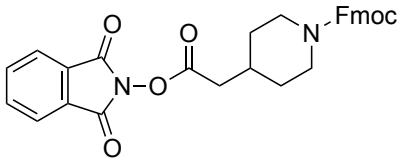


To a round-bottom flask equipped with a stir bar was added the corresponding carboxylic acid (if solid) (1.0 equiv), *N*-hydroxyphthalimide (1.0 equiv), and DMAP (0.1 equiv). The flask was then charged with CH_2Cl_2 (0.1 – 0.2 M). At this point, carboxylic acid (1.0 equiv) was added via syringe (if liquid). DCC (1.1 equiv) was added, and the reaction was allowed to stir at rt until full consumption of the starting material as determined by TLC. The mixture was then filtered over Celite and rinsed with additional CH_2Cl_2. The solvent was removed under reduced pressure, and the crude material was purified via flash chromatography. *Note:* some redox-active esters are prone to hydrolysis on silica gel during column chromatography and therefore should be purified as quickly as possible.

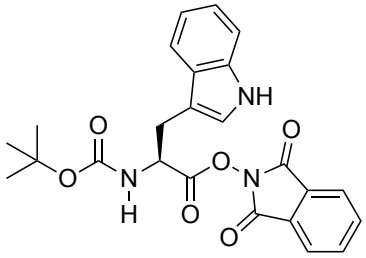


1,3-Dioxoisoindolin-2-yl 4-oxo-4-(thiophen-2-yl)butanoate, (**2a**, 20 mmol scale, 4.61 g, 70%) was prepared following the general procedure. The product was obtained as a brown solid. **Mp** = 115 – 117 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.90 – 7.81 (m, 2H), 7.81 – 7.73 (m, 3H), 7.64 (d, J = 4.9 Hz, 1H), 7.12 (t, J = 4.4 Hz, 1H), 3.39 (t, J = 7.0 Hz, 2H), 3.12 (t, J = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 189.4, 169.2, 161.8 (2C), 143.1, 134.9 (2C), 134.2, 132.4, 128.9 (2C), 128.3, 124.0 (2C), 33.6, 25.4. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1816, 1787, 1741, 1666, 1518, 1467, 1415, 1356, 1250, 1219, 1186. **HRMS** (ESI, m/z) calcd for $C_{16}H_{12}NO_5S$

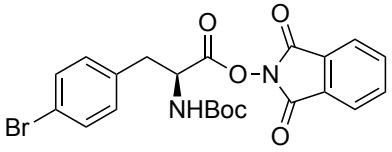
$[M+H]^+$: 330.0436, found: 330.0452.



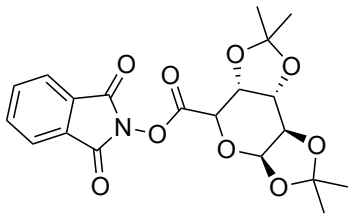
(9*H*-Fluoren-9-yl)methyl 4-(2-((1,3-dioxoisoindolin-2-yl)oxy)-2-oxoethyl)piperidine-1-carboxylate, (**2g**, 2.7 mmol scale, 896 mg, 65%) was prepared following the general procedure. The product was obtained as a white solid. **Mp** = 57 – 59 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.93 – 7.86 (m, 2H), 7.83 – 7.79 (m, 2H), 7.77 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 7.5 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.33 (td, J = 7.4, 1.3 Hz, 2H), 4.45 (bs, 2H), 4.25 (t, J = 6.6 Hz, 1H), 4.12 (q, J = 7.1 Hz, 1H), 2.83 (bs, 2H), 2.59 (bs, 2H), 2.15 – 2.04 (m, 1H), 2.04 (s, 1H), 1.86 (d, J = 13.4 Hz, 2H), 1.57 (d, J = 11.5 Hz, 1H), 1.26 (t, J = 7.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 168.4, 162.1, 155.3, 144.2, 141.5, 135.0 (3C), 129.0, 127.8 (3C), 127.2 (3C), 125.1, 124.2 (3C), 120.1 (3C), 67.3, 47.6, 44.0 (2C), 37.9, 33.4, 31.6 (2C). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2939, 1814, 1787, 1743, 1697, 1450, 1365, 1281, 1244, 1215, 1186, 1133, 1065. **HRMS** (ESI, *m*/*z*) calcd for $C_{30}H_{26}BrN_2O_6Na$ $[M+Na]^+$: 533.1689, found: 533.1682.



1,3-Dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)-*L*-tryptophanate, (**2x**, 20 mmol scale, 4.5 g, 50%) was prepared following the general procedure. The product was obtained as a yellow solid. **Mp** = 176 – 178 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 10.92 (s, 1H), 8.00 – 7.89 (m, 4H), 7.67 (d, J = 7.9 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 7.4 Hz, 1H), 4.66 – 4.41 (m, 1H), 3.30 – 3.08 (m, 2H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, DMSO), δ (ppm) = 169.4, 161.7, 155.3, 136.2, 135.6 (2C), 128.2 (2C), 126.9, 124.3, 124.1 (2C), 121.1, 118.6, 118.0, 111.6, 108.8, 78.9, 53.2, 28.1 (3C), 27.6, 26.9. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3400, 2950, 1732, 1702, 1506, 1366, 1329, 1239, 1152, 1102, 1051, 976, 942, 880. **HRMS** (ESI, *m*/*z*) calcd for $C_{24}H_{23}N_3NaO_6$ $[M+Na]^+$: 472.1485, found: 472.1480.



1,3-Dioxoisoindolin-2-yl (*S*)-3-(4-bromophenyl)-2-((*tert*-butoxycarbonyl)amino)propanoate, (**2y**, 2.9 mmol scale, 922 mg, 65%) was prepared following the general procedure. The product was obtained as a white solid. **Mp** = 142 – 144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.94 – 7.87 (m, 2H), 7.84 – 7.78 (m, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 5.07 – 4.90 (m, 1H), 3.37 – 3.11 (m, 2H), 4.80 (br s, 1 H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 168.6, 161.6 (2C), 154.7, 135.1 (4C), 132.0, 131.7, 128.9 (2C), 124.3 (4C), 80.9, 52.6, 37.9, 28.4 (3C). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3400, 2950, 1817, 1789, 1743, 1715, 1490, 1468, 1392, 1367, 1251, 1185, 1162. **HRMS** (ESI, *m*/*z*) calcd for $C_{22}H_{22}BrN_2O_6$ $[M+H]^+$: 511.0481, found: 511.0474.



1,3-Dioxoisoindolin-2-yl (3a*R*,5a*R*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-5-carboxylate, (**2z**, 20 mmol scale, 6.0 g, 72%) was prepared following the general procedure. The product was obtained as a white solid. **Mp** = 176 – 178 °C. **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = 7.92 – 7.87 (m, 2H), 7.82 – 7.76 (m, 2H), 5.70 (d, J = 5.0 Hz, 1H), 4.83 (d, J = 2.3 Hz, 1H), 4.73 (qd, J = 7.5, 2.5 Hz, 2H), 4.45 (dd, J = 5.1, 2.7 Hz, 1H), 1.57 (d, J = 32.9 Hz, 6H), 1.39 (d, J = 22.3 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 164.9 (2C), 161.4, 134.9 (2C), 129.0, 128.9, 124.1 (2C), 111.0, 109.6, 96.6, 72.0, 70.9, 70.3, 68.4, 26.2, 26.0, 25.1, 24.9. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2989, 2933, 1833, 1792, 1624, 1374, 1256, 1213, 1186, 1071. **HRMS** (ESI, *m*/*z*) calcd for $C_{20}H_{21}NO_9Na$ $[M+Na]^+$: 442.1114, found: 442.1118.

5. Reaction Workflow

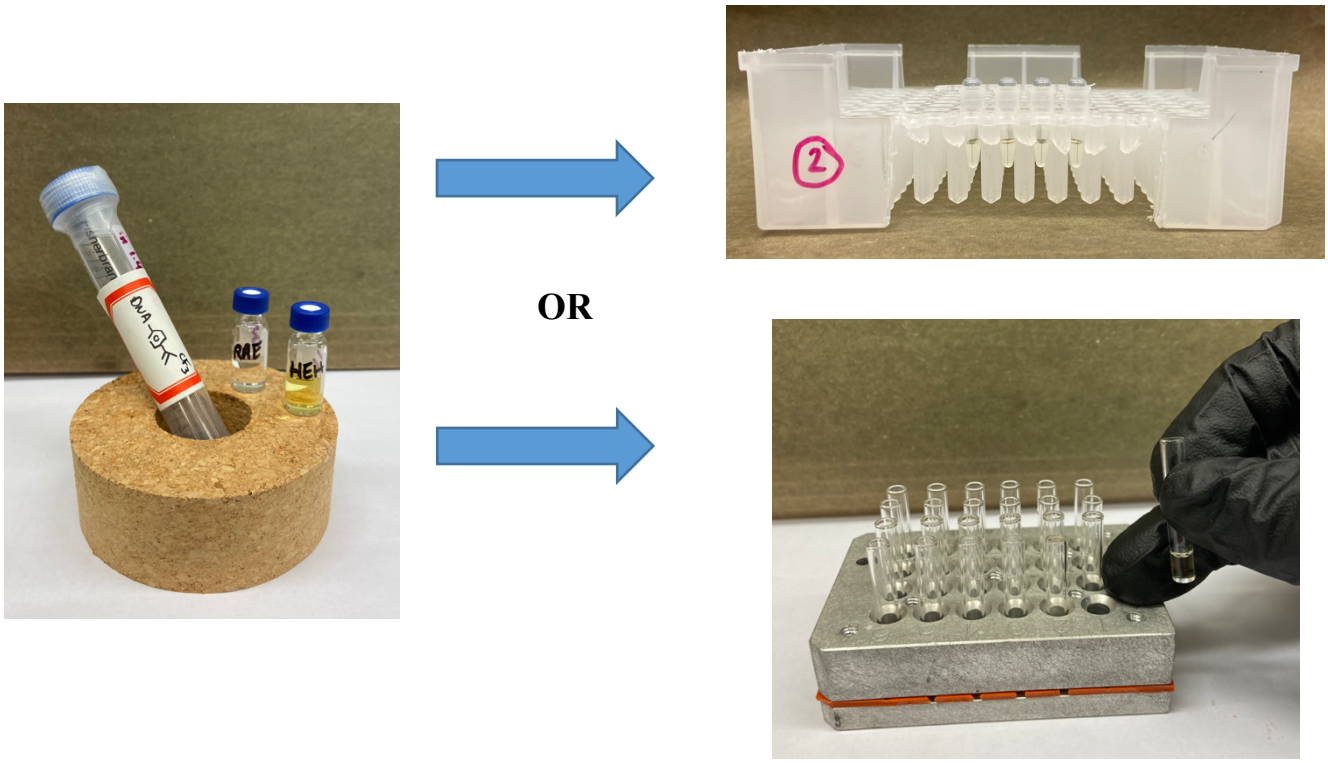


Figure S2. Reactions were set up under air in PCR tubes or screening plates containing glass vials equipped with Teflon-coated magnetic stir bars. Each reagent was added as a stock solution.

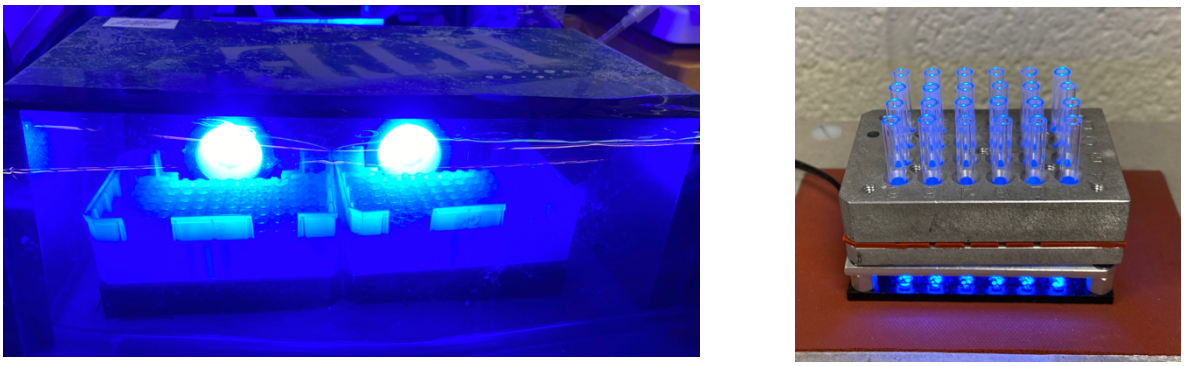


Figure S3. Reaction vessels were vortexed then placed 1.5 inches away from Kessil PR160 lamps ($\lambda = 456$ nm, 19VDC 40W Max) for the time designated for each experiment. Alternatively, reactions were irradiated using blue LEDs in 24-well screening plates at the Penn/Merck Center for High Throughput Experimentation at the University of Pennsylvania.

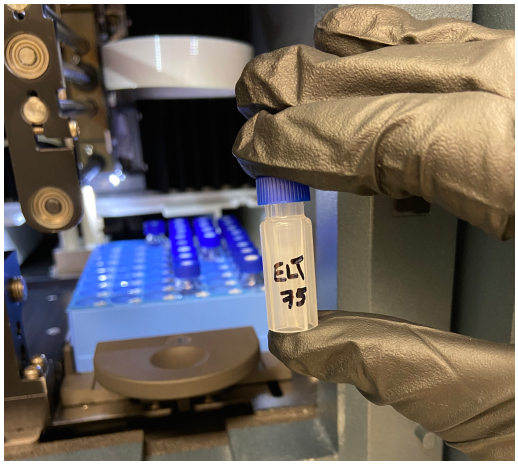
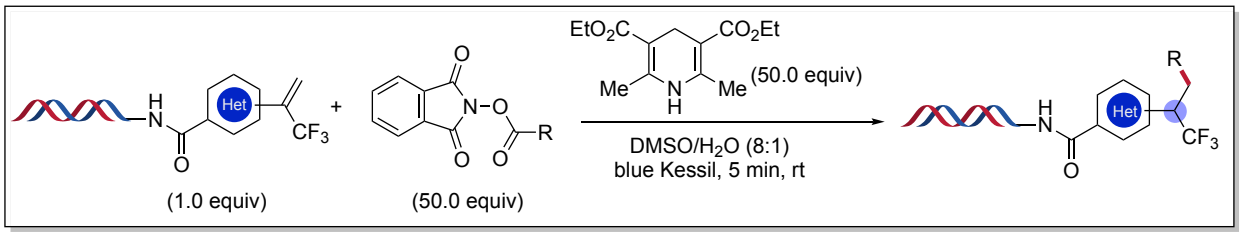


Figure S4. Reactions were diluted with water and % conversion was determined using LC/MS analysis. If necessary, a small amount of DMSO (~ 20 μL) was added during the workup to facilitate solubility.

6. Procedures for Photoinduced Transformations

6.1. General Procedure I

On-DNA photoinduced decarboxylative alkylation using isolated redox-active esters



To a PCR Eppendorf tube was added Hantzsch ester (10 µL of a 125 nmol/µL soln in DMSO, 1250 nmol, 50 equiv), redox-active ester (30 µL of a 41.67 nmol/µL soln in DMSO, 1250 nmol, 50 equiv), and DNA-tethered alkene (5 µL of a 5 nmol/µL soln in H_2O, 25 nmol, 1.0 equiv). The PCR tube was then capped, vortexed, and irradiated for 5 min with Kessil PR160 lamps at a distance of 1.5 inches. An aliquot of the reaction (20 µL) was then diluted with H_2O (150 µL) and analyzed by LC/MS. If necessary, a small amount of DMSO (~ 20 µL) was added during the workup to facilitate solubility.

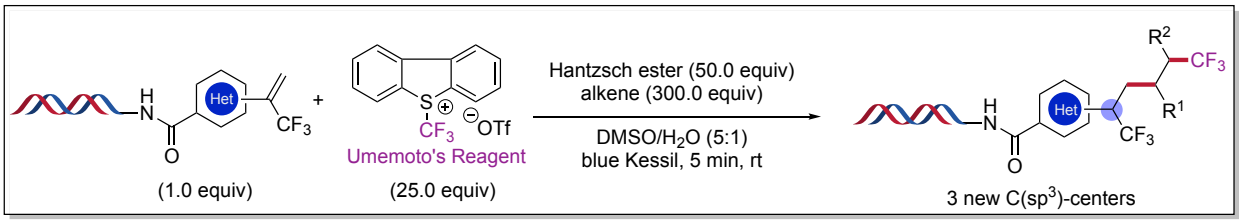
On-DNA photoinduced decarboxylative alkylation using redox-active esters synthesized in situ from carboxylic acids

Step 1: To a 24-well plate containing glass reaction vials equipped with Teflon-coated magnetic stir bars was added carboxylic acid (60 µL of a 125 nmol/µL soln in DMSO, 7.5 µmol, 1 equiv), DIPEA (60 µL of a 187.5 nmol/µL soln in DMSO, 11.3 µmol, 1.5 equiv), and HITU (60 µL of a 187.5 nmol/µL solution in DMSO, 11.3 µmol, 75 equiv) in this order. The plate was sealed and the mixture was stirred for 3 h.

Step 2: To a 24-well plate containing glass reaction vials was added Hantzsch ester (30 µL of a 41.7 nmol/µL soln in DMSO, 1250 nmol, 50 equiv), redox-active ester soln from a premix plate (see step 1) (30 µL of a 41.7 nmol/µL soln in DMSO, 1250 nmol, 50 equiv), and DNA-tethered alkene (5 µL of a 5 nmol/µL soln in H_2O, 25 nmol, 1.0 equiv). The plate was then irradiated for 10 min with blue LEDs as shown in the "Reaction Workflow" section. An aliquot of the reaction (20 µL) was then diluted with H_2O (150 µL) and analyzed by LC/MS. If necessary, a small amount of DMSO (~ 20 µL) was added during the workup to facilitate solubility.

6.2. General Procedure II

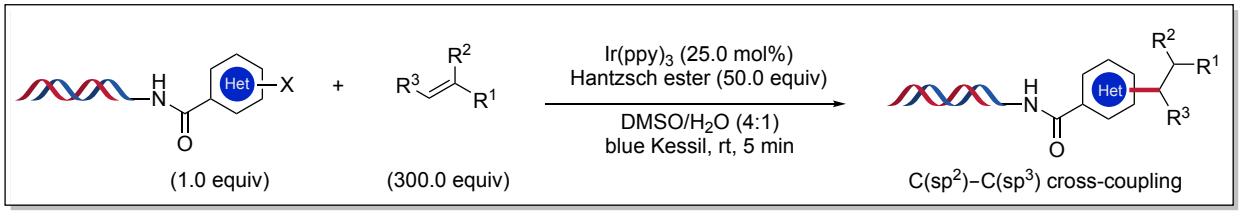
On-DNA photoinduced trifluoromethylation of alkenes



To a PCR Eppendorf tube was added Hantzsch ester (10 µL of a 125 nmol/µL soln in DMSO, 1250 nmol, 50 equiv), Umemoto's reagent (5 µL of a 125 nmol/µL soln in DMSO, 625 nmol, 25 equiv), alkene (10 µL of a 750 nmol/µL soln in DMSO, 7500 nmol, 300 equiv), and DNA-tethered alkene (5 µL of a 5 nmol/µL solution in H_2O, 25 nmol, 1.0 equiv). The PCR tube was then capped, vortexed, and irradiated for 5 min with Kessil PR160 lamps at a distance of 1.5 inches. An aliquot of the reaction (20 µL) was then diluted with H_2O (100 µL) and analyzed by LC/MS. If necessary, a small amount of DMSO (~ 20 µL) was added during the workup to facilitate solubility.

6.3. General Procedure III

On-DNA photoinduced arylation of alkene feedstocks



To a PCR Eppendorf tube was added Hantzsch ester (10 µL of a 125 nmol/µL soln in DMSO, 1250 nmol, 50 equiv), $Ir(ppy)_3$ (5 µL of a 1.25 nmol/µL soln in DMSO, 6.25 nmol, 0.25 equiv), alkene (5 µL of a 1500 nmol/µL soln in DMSO, 7500 nmol, 300 equiv), and DNA-tethered halide (5 µL of a 5 nmol/µL soln in H_2O, 25 nmol, 1.0 equiv). The PCR tube was then capped, vortexed, and irradiated for 5 min with Kessil PR160 lamps at a distance of 1.5 inches. An aliquot of the reaction (20 µL) was then diluted with H_2O (150 µL) and analyzed by LC/MS. If necessary, a small amount of DMSO (~ 20 µL) was added during the workup to facilitate solubility.

7. UV/vis Studies

UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a Genesys 150 UV/vis spectrophotometer from Thermo Scientific. Absorption spectra of individual reaction components and a mixture thereof were recorded. A bathochromic shift was observed for a mixture of RAE and HE in DMSO/H_2O (ratio 8:1, 0.028 M,

reflecting the actual loading of these reagents). This indicates the formation of an electron donor-acceptor (EDA) complex (**A** & **B**, blue bands)

To underline the formation of EDA complexes of RAEs with He, we further recorded the corresponding UV/vis absorption spectra using the more electron deficient tetrachloro *N*-hydroxyphthalimide ester derivative (**C** & **D**). As expected, this species functions as a potent electron acceptor, and a more significant bathochromic shift was detected in this case (see **C** & **D**).

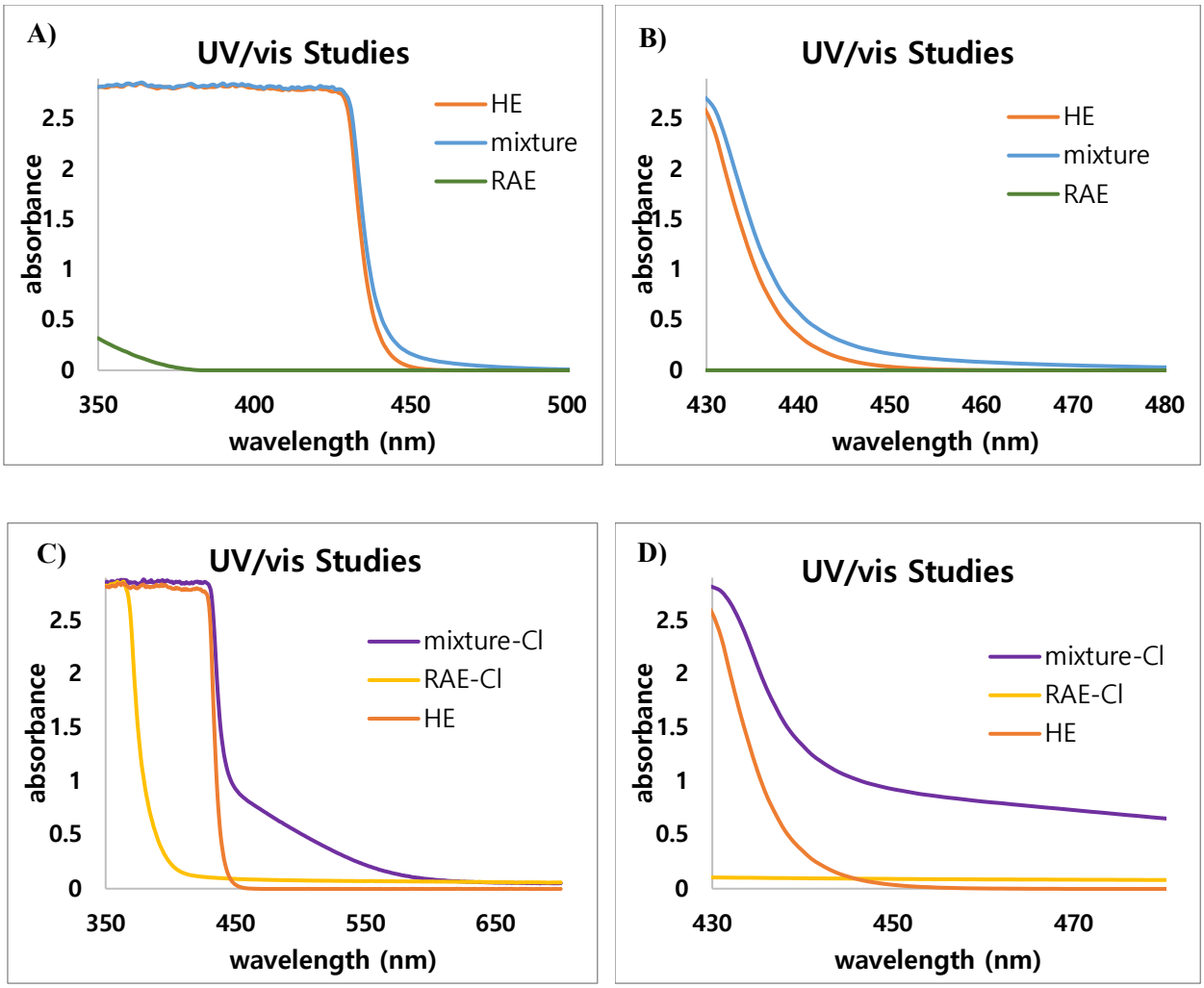
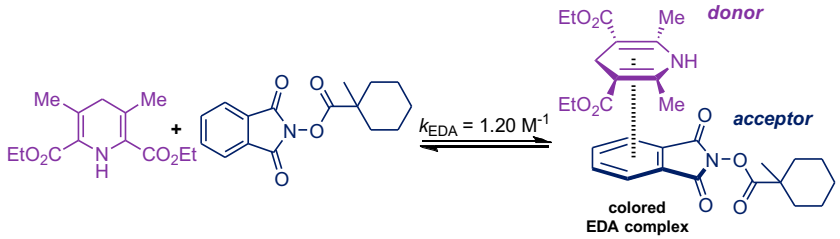


Figure S5. UV/vis spectra of individual reaction components and a combination thereof (A–D). All spectra were measured in DMSO/H_2O (8:1) and with a concentration of: 0.028 M HE, and 0.028 M RAE/RAE-Cl. The stoichiometry and concentration of sample "mixture" reflects the reaction conditions. The stoichiometry and concentration of sample "mixture-Cl" reflects the reaction conditions, and instead of RAE, RAE-Cl was used. RAE = cyclohexylmethyl-*N*-hydroxyphthalimide-ester, RAE-Cl = cyclohexylmethyl-*N*-hydroxy-3,4,5,6-tetra-chlorophthalimide-ester.

7.1. Job's method

The stoichiometry of the EDA complex was determined using Job's method with varying ratios of cyclohexylmethyl-*N*-hydroxyphthalimide-ester and HE in DMSO/H_2O (ratio 8:1, 0.056 mM) at 456 nm. The absorbance was plotted against the molar fraction of HE. Maximum absorbance was detected at 50% molar fraction of HE, indicating a 1:1 stoichiometry of the EDA complex.



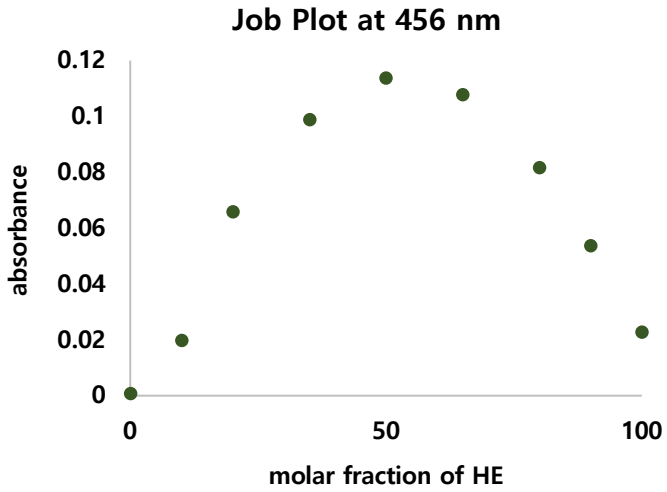


Figure S6. Job plot of the EDA complex (0.056 mM total concentration in DMSO/H_2O (8:1)) between Hantzsch ester HE and cyclohexylmethyl-*N*-hydroxyphthalimide-ester recorded at 456 nm.

7.2. Determination of association constant (k_{EDA})

The association constant for the EDA complex formed between cyclohexylmethyl-*N*-hydroxyphthalimide-ester and HE was determined by UV/vis measurements in DMSO/H_2O (8:1) employing the Benesi-Hildebrand method. The absorption of a constant concentration of RAE (0.02 M) and an increasing concentration of HE (0.02-0.07 M) was recorded at 450 nm. The absorption spectra shown in Figure S7 were recorded in 1 cm path quartz cuvette. To determine the k_{EDA}, the reciprocal concentration of HE was plotted against the reciprocal absorbance (A) of the EDA complex at 450 nm (Table S1 and Figure S8). A straight line was obtained, and by dividing the intercept through the slope: k_{EDA} = 1.20 M^{-1} for RAE/HE.

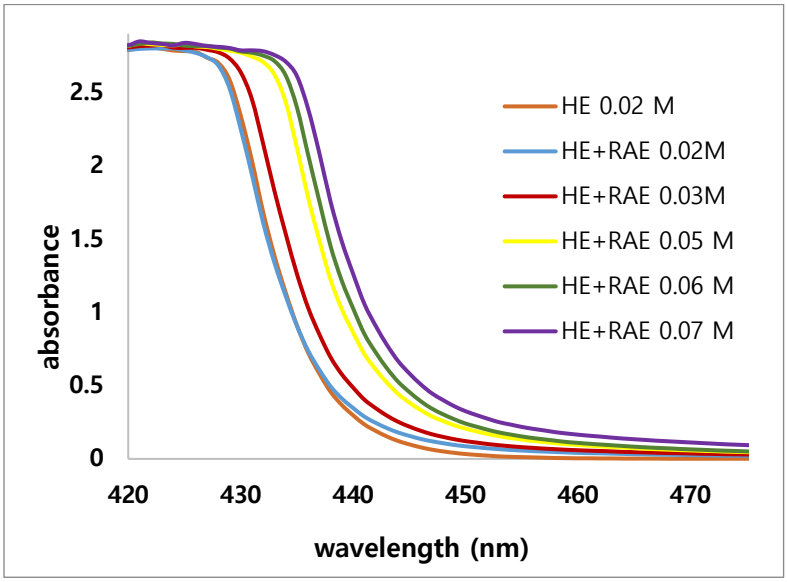


Figure S7. UV/vis spectra of cyclohexylmethyl-*N*-hydroxyphthalimide-ester ester (0.02 M in DMSO/H_2O (8:1)) in combination with increasing concentrations of HE (0.02 M up to 0.07 M in DMSO/H_2O).

Table S1. Data obtained from the UV/vis absorption spectra of the EDA complex between RAE and HE in DMSO/H_2O (8:1). The concentration of RAE was kept at 0.02 M in DMSO/H_2O.

HE (M)	1/HE [M^{-1}]	Abs_{EDA}	$1/[Abs_{EDA}-A_0]$
0.02	50	0.086	11.6
0.03	33.3	0.121	8.3
0.05	20	0.187	5.3
0.06	16.7	0.241	4.1
0.07	14.3	0.325	3.1

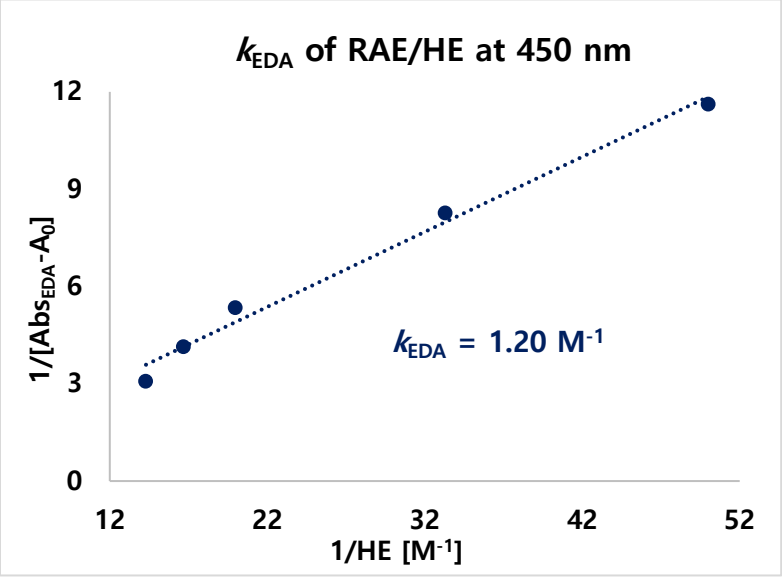


Figure S8. Hildebrand-Benesi plot for the EDA complex generated in DMSO/H_2O (8:1) upon association of cyclohexylmethyl-*N*-hydroxyphthalimide-ester with HE.

8. qPCR, PCR, and Sequencing

8.1. 4-Cycle tag mimic sequence

SAdo---------- 4-cycle----------

5' T G A C T C C C A A A T C G A T G T G T T C C G C A A G A A G C C T G G T A A G C G G A G A A A G G T C G T T 3'
3' A C T G A G G G T T T A G C T A C A C A A G G C G T T C T T C G G A C C A T T C G C C T C T T T C C A G C 5'

SAdo---------- 4-cycle----------

8.2. 4-Cycle tag synthesis (CF_3 styrene)

The top and bottom strands (purchased from IDT as lyophilized powders) of a control 4-cycle tag were annealed by combining 300 nmol of each strand (2 mM in H_2O), heating to 95 °C for 5 min, then cooling to rt. The annealed tag solution (1.2 equiv) was then added to the trifluorostyrene headpiece (250 µL, 2 mM in H_2O), followed by 100 µL 10x T4 ligation buffer, 2 mL of H_2O, and 10 µL T4 DNA ligase purchased from Syngene. The ligation solution was vortexed and let sit at rt overnight then in a cold room for ~3 days. The ligation was pushed with additional annealed rc tag only (150 nmol, 2 mM in H_2O), followed by 10x T4 ligation buffer (25 µL), and ligase (2.5 µL). The reaction was again capped, vortexed, and left to react at rt overnight. The ligation was precipitated for 30 minutes at -80 °C following addition of 300 µL of 5 M NaCl (aq) and 12 mL of cold EtOH. The precipitated solution was then centrifuged at 3,300 rpm at 4 °C for 30 minutes, and the solvent was decanted to afford the DNA pellet, which was dried on a lyophilizer overnight. The crude pellet was resuspended in 260 µL of H_2O and purified by HPLC (Column: Gemini C18, 5µm, 21.2x100 mm; Gradient: 5 to 90%B in 25 min, 22 mL/min; UV at 260 nm; Solvent A: 50 mM TEAA, pH 7.5; Solvent B: 1% H_2O 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 (45 nmol, 18%). LCMS calcd: 34,455, found: 34,454.

8.3. 4-Cycle tag synthesis (aryl iodide)

The top and bottom strands (purchased from IDT as lyophilized powders) of a control 4-cycle tag were annealed by combining 1.2 µmol of each strand (2 mM in H_2O), heating to 95 °C for 5 min, then cooling to rt. The annealed tag solution (1.2 equiv) was then added to the 4-chloro-3-iodobenzoic acid headpiece (500 µL, 2 mM in H2O), followed by 400 µL 10x T4 ligation buffer, 8 mL of H_2O, and 40 µL T4 DNA ligase purchased from Syngene. The ligation solution was vortexed and let sit at rt overnight. The ligation was precipitated for 30 minutes at -80 °C following addition of 0.8 mL of 5 M NaCl (aq) and 20 mL of cold EtOH. The precipitated solution was then centrifuged at 3,300 rpm at 4 °C for 30 minutes, and the solvent was decanted to afford the DNA pellet, which was dried on a lyophilizer for 30 minutes. The crude pellet was resuspended in 8 mL of H_2O and spit into two 30,000 molecular weight cut off spin filters. The spin filters were put on the centrifuge for 15 minutes (20 °C, 3500 rpm) and the filtrate was collected. The original reaction flask was washed with 4 mL of water and again split into the two spin filter and put on the centrifuge for 15 minutes (20 °C, 3500 rpm). The filtrate was then collected and the wash process was repeated 2 more times. Once complete, the product was collected and lyophilized overnight. The resulting white pellet was dissolved in 500 uL of water and a QC was taken showing 36% starting material and 47% desired product (this was not seen on the µTOF QC that was taken before). The ligation was pushed with additional annealed control tag (300 nmol, 1 mM in H2O) followed by 200 µL 10x T4 ligation buffer, 4 mL of H_2O, and 20 µL T4 DNA ligase purchased from Syngene. The reaction was again capped, vortexed, and left to react at rt overnight. The ligation was precipitated for 30 minutes at -80 °C following addition of 0.8 mL of 5 M NaCl (aq) and 20 mL of cold EtOH. The precipitated solution was then centrifuged at 3,300 rpm at 4 °C for 30 minutes, and the solvent was decanted to afford the DNA pellet, which was dried on a lyophilizer for 30 minutes. The crude pellet was resuspended in 8 mL of H_2O and spit into two 30,000 molecular weight cut off spin filters. The spin filters were put on the centrifuge for 15 minutes (20 °C, 3500 rpm) and the filtrate was collected. The original reaction flask was washed with 4 mL of water and again split into the two spin filter and put on the centrifuge for 15 minutes (20 °C, 3500 rpm). The filtrate was then collected and the wash process was repeated 2 more times. Once complete, the product was collected and lyophilized overnight. The lyophilized product was analyzed by optical density using a composite extinction coefficient of 1023700 L/(mol-cm) to determine isolated yield (715 nmol, 71.5%). LCMS calcd: 34,521, found: 34,521

8.4. 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’

To each of the six exemplar reaction samples (2 nmol aliquot, 0.04 mM in H_2O) was added the closing primer (5

nmol, 1 mM in H_2O), 10X ligation buffer (10 µL), T4 DNA ligase (2 µL, 10 mg/mL), and H_2O (33 µL) for a final reaction volume of 100 µL. Ligations were allowed to proceed overnight at rt. Samples were analyzed by gel electrophoresis and all were determined to have gone to sufficient completion.

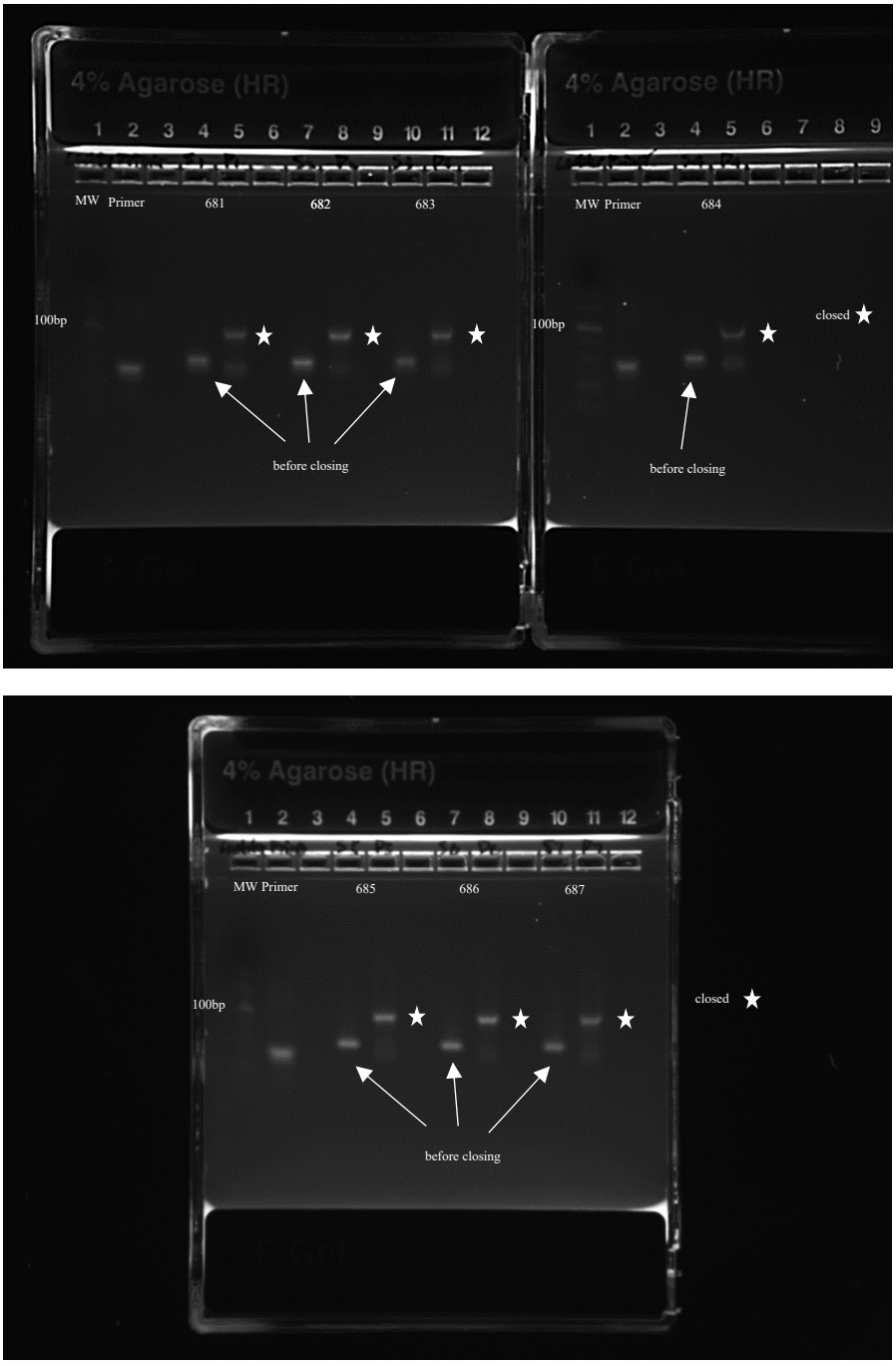


Figure S9. Gel electrophoresis of closing primer ligation on reacted material.

qPCR

qFor: 5'-GCT ACC TCT GAC TCC CAA ATC GAT GT -3'

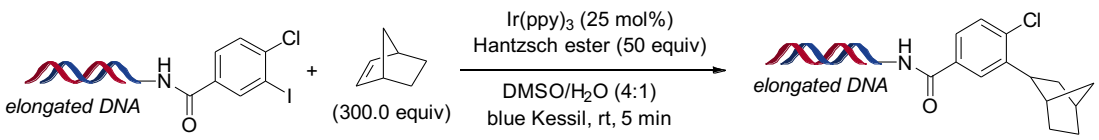
qRev: 5'-*ATA TTA GCC TCC CTC GCG CCA* TCA -3'

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 of SYBR green, 60 µL of 10 µM PCR primer 565 Cla, 60 µL of 10 µM PCR primer 454 short, and 680 µL of H_2O. To 2 µL of sample was then added 18 µL of master mix. Samples were subjected to qPCR:

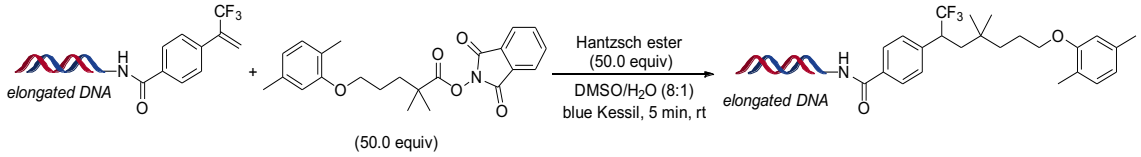
Table S2. Quantitative PCR analysis.

Stage	Temperature/Time	Number of Cycles
HotStart	95°C / 5 min	1
Amplification	95°C / 10 sec 55°C / 15 sec 72°C / 15 sec	40
Melt	95°C / 1 sec 70°C / 1 sec 95°C	1
Cool	45°C / 30 sec	0

Samples were then analyzed using the 2nd derivative maximum standard protocol on the instrument to determine how many molecules were present per µL sample. Samples achieved acceptable consistency across conditions in comparison to the no-light control sample ELT_684 and ELT_686, suggesting that the conditions developed are not impacting the amount of amplifiable DNA present in a significant way.



Sample Name	Deviations	Molecules / µL sample
ELT_681	No deviation from standard conditions	1.04×10^{13}
ELT_682	No Hantzsch ester	1.01×10^{13}
ELT_683	No PC	8.48×10^{12}
ELT_684	No light	1.21×10^{13}



ELT_685	No Hantzsch ester	1.80×10^{13}
ELT_686	No light	1.51×10^{13}
ELT_687	No deviation from standard conditions	1.35×10^{13}

Based on the Agilent TapeStation results following the PCR amplification and purification described above, an aliquot of each sample, representing approximately 1E8 molecules, were prepared for sequencing following the manufacturer's standard protocol with an Illumina MiSeq v3 kit, and sequenced on an Illumina MiSeq. Samples were subjected to 101 cycles for Read 1 and 9 cycles for Index 1. The resulting sequences were aligned to the 71 base reference sequence (below). The number of single base differences were counted and reported as a percentage of the total sequence count.

71 base sequence

5' – GTA GAC CGG GCA TCG TAA CGA CCT TTC TCC GCT TAC CAG GCT TCT TGC GGA ACA CAT CGA TTT GGG AGT CA – 3'

alkene arylation: standard conditions (ELT 681)

# of matched bases (out of 71)	% of total sequences (n = 2992625)
71	**81.96**
70	14.70
69	2.10
68	0.51
67	0.21
66	0.13
65	0.11
64	0.08
63	0.06
62	0.04
61	0.02
56	0.02
60	0.01
57	0.01
59	0.01
58	0.01
55	0.01
54	0.01
53	< 0.01
52	< 0.01
51	< 0.01
50	< 0.01
47	< 0.01
48	< 0.01
46	< 0.01
49	< 0.01
45	< 0.01
41	< 0.01
44	< 0.01
43	< 0.01
42	< 0.01
24	< 0.01

71 base sequence

5’ – GTA GAC CGG GCA TCG TAA CGA CCT TTC TCC GCT TAC CAG GCT TCT TGC GGA ACA CAT CGA TTT GGG AGT CA – 3’

alkene arylation: no HE (ELT 682)

# of matched bases (out of 71)	% of total sequences (n = 3433979)
71	**85.01**
70	12.21
69	1.69
68	0.46
67	0.20
66	0.11
65	0.09
64	0.06
63	0.05
62	0.03
61	0.02
60	0.01
57	0.01
56	0.01
58	0.01
59	0.01
55	0.01
54	< 0.01
53	< 0.01
52	< 0.01
51	< 0.01
50	< 0.01
49	< 0.01
48	< 0.01
47	< 0.01
46	< 0.01
45	< 0.01
44	< 0.01
43	< 0.01
42	< 0.01
40	< 0.01
41	< 0.01
39	< 0.01
32	< 0.01

71 base sequence

5’ – GTA GAC CGG GCA TCG TAA CGA CCT TTC TCC GCT TAC CAG GCT TCT TGC GGA ACA CAT CGA TTT GGG AGT CA – 3’

alkene arylation: no photo catalyst control (ELT 683)

# of matched bases (out of 71)	% of total sequences (n = 2769948)
71	**85.67**
70	11.81
69	1.55
68	0.41
67	0.18
66	0.13
65	0.08
64	0.05
63	0.04
62	0.02
61	0.01
57	0.01
56	0.01
58	0.01
60	0.01
55	0.01
59	0.01
54	0.01
53	< 0.01
52	< 0.01
51	< 0.01
49	< 0.01
48	< 0.01
50	< 0.01
47	< 0.01
45	< 0.01
43	< 0.01
44	< 0.01
42	< 0.01

71 base sequence

5’ – GTA GAC CGG GCA TCG TAA CGA CCT TTC TCC GCT TAC CAG GCT TCT TGC GGA ACA CAT CGA TTT GGG AGT CA – 3’

alkene arylation: no light control (ELT 684)

# of matched bases (out of 71)	% of total sequences (n = 2637791)
71	**84.40**
70	12.69
69	1.75
68	0.45
67	0.20
66	0.12
65	0.09
64	0.07
63	0.05
62	0.04
56	0.02
61	0.02
55	0.02
60	0.01
57	0.01
58	0.01
54	0.01
59	0.01
53	0.01
52	< 0.01
51	< 0.01
50	< 0.01
41	< 0.01
42	< 0.01
46	< 0.01
49	< 0.01
43	< 0.01
47	< 0.01
45	< 0.01
44	< 0.01
40	< 0.01
48	< 0.01
39	< 0.01
22	< 0.01

71 base sequence

5’ – GTA GAC CGG GCA TCG TAA CGA CCT TTC TCC GCT TAC CAG GCT TCT TGC GGA ACA CAT CGA TTT GGG AGT CA – 3’

CF_3-styrene alkylation: standard conditions (ELT 687)

# of matched bases (out of 71)	% of total sequences (n = 3205062)
71	**83.07**
70	13.28
69	2.06
68	0.60
67	0.29
66	0.22
65	0.14
64	0.11
63	0.08
62	0.04
61	0.03
60	0.01
56	0.01
55	0.01
57	0.01
58	0.01
59	0.01
54	0.01
53	< 0.01
52	< 0.01
51	< 0.01
47	< 0.01
49	< 0.01
48	< 0.01
43	< 0.01
44	< 0.01
50	< 0.01
45	< 0.01
46	< 0.01
42	< 0.01

71 base sequence

5’ – GTA GAC CGG GCA TCG TAA CGA CCT TTC TCC GCT TAC CAG GCT TCT TGC GGA ACA CAT CGA TTT GGG AGT CA – 3’

CF_3-styrene alkylation: no light control (ELT 686)

# of matched bases (out of 71)	% of total sequences (n = 4166261)
71	**84.99**
70	11.75
69	1.82
68	0.56
67	0.26
66	0.19
65	0.13
64	0.09
63	0.08
62	0.04
61	0.02
60	0.01
56	0.01
55	0.01
57	0.01
58	0.01
59	0.01
54	< 0.01
53	< 0.01
52	< 0.01
51	< 0.01
50	< 0.01
48	< 0.01
45	< 0.01
47	< 0.01
43	< 0.01
49	< 0.01
46	< 0.01
44	< 0.01
42	< 0.01
36	< 0.01
23	< 0.01

71 base sequence

5’ – GTA GAC CGG GCA TCG TAA CGA CCT TTC TCC GCT TAC CAG GCT TCT TGC GGA ACA CAT CGA TTT GGG AGT CA – 3’

CF_3-styrene alkylation: no Hantzsch ester (ELT 685)

# of matched bases (out of 71)	% of total sequences (n = 3677546)
71	**83.18**
70	13.19
69	2.04
68	0.59
67	0.29
66	0.22
65	0.14
64	0.12
63	0.08
62	0.05
61	0.03
60	0.02
55	0.01
56	0.01
59	0.01
57	0.01
54	0.01
58	0.01
53	0.01
52	< 0.01
51	< 0.01
49	< 0.01
48	< 0.01
47	< 0.01
45	< 0.01
50	< 0.01
46	< 0.01
44	< 0.01
43	< 0.01
41	< 0.01
40	< 0.01
34	< 0.01
22	< 0.01

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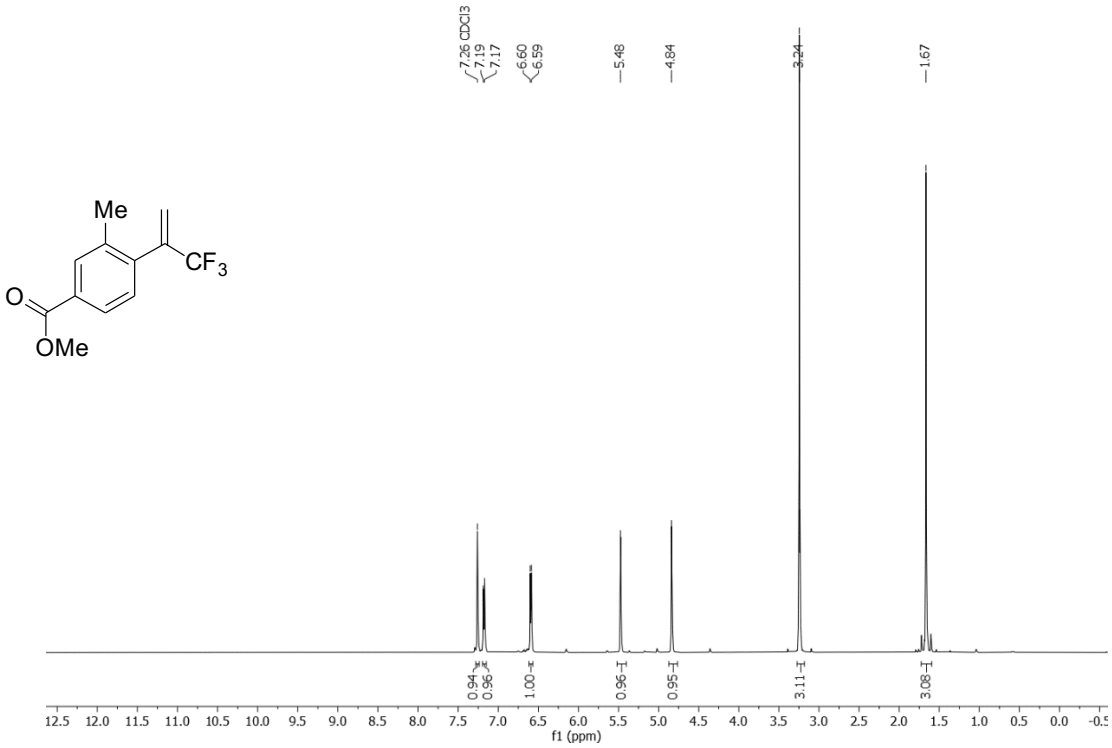
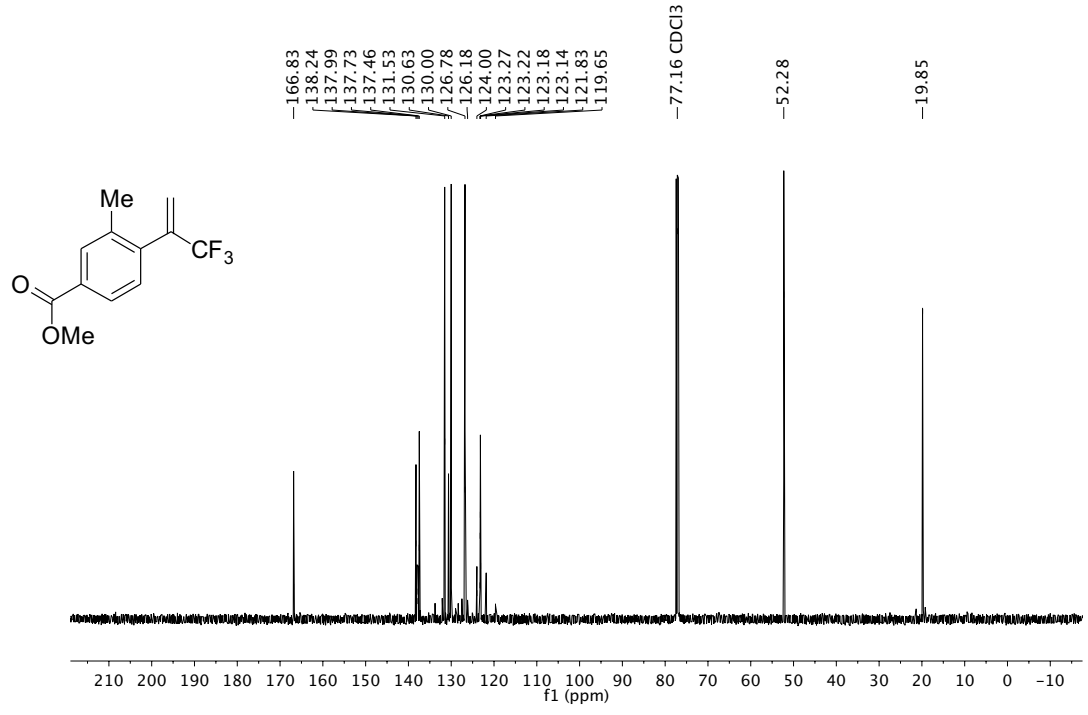
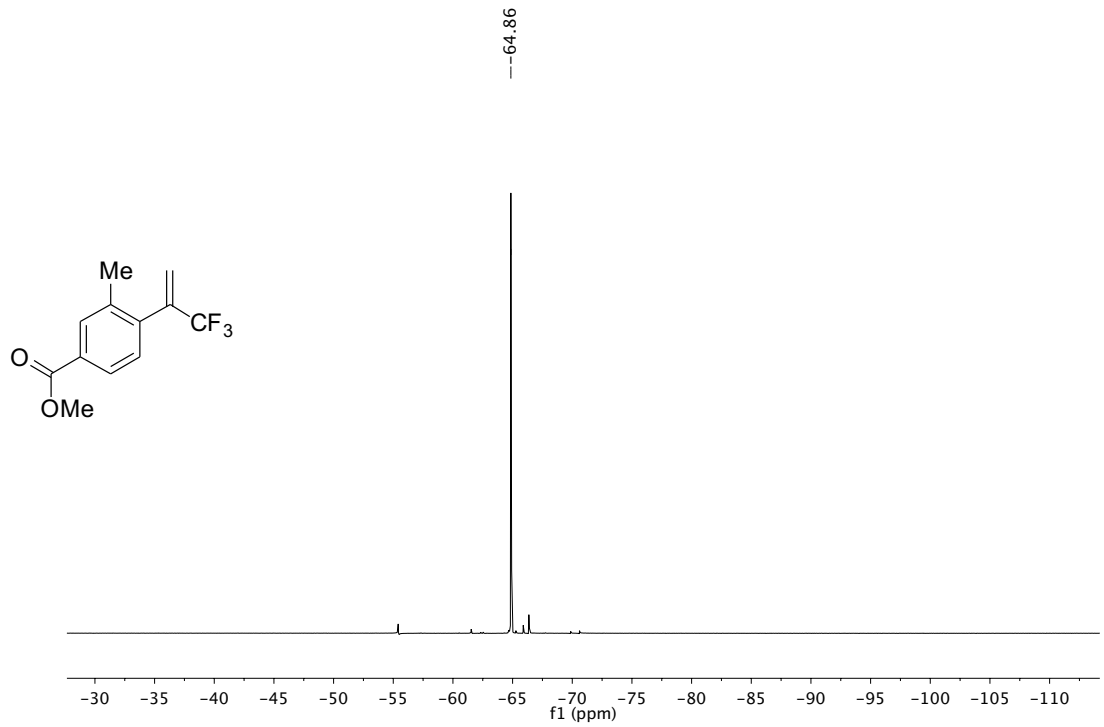
10. NMR Spectra



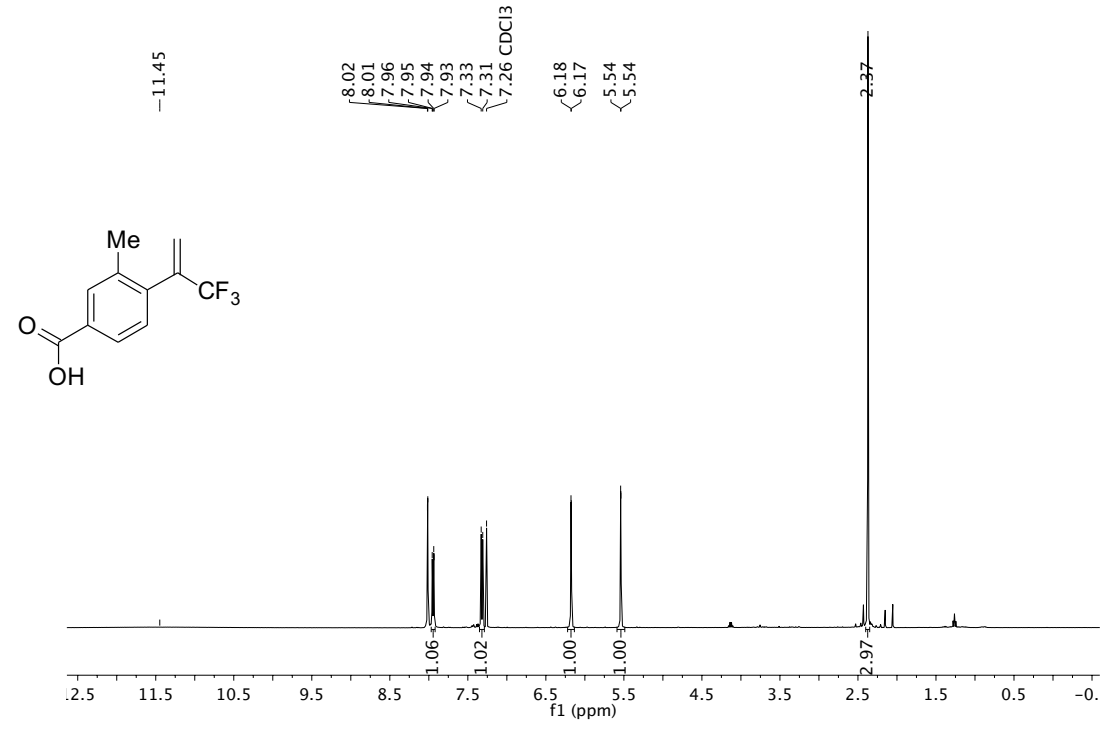
^{1}H NMR (400 MHz, $CDCl_3$) of compound **22B**.



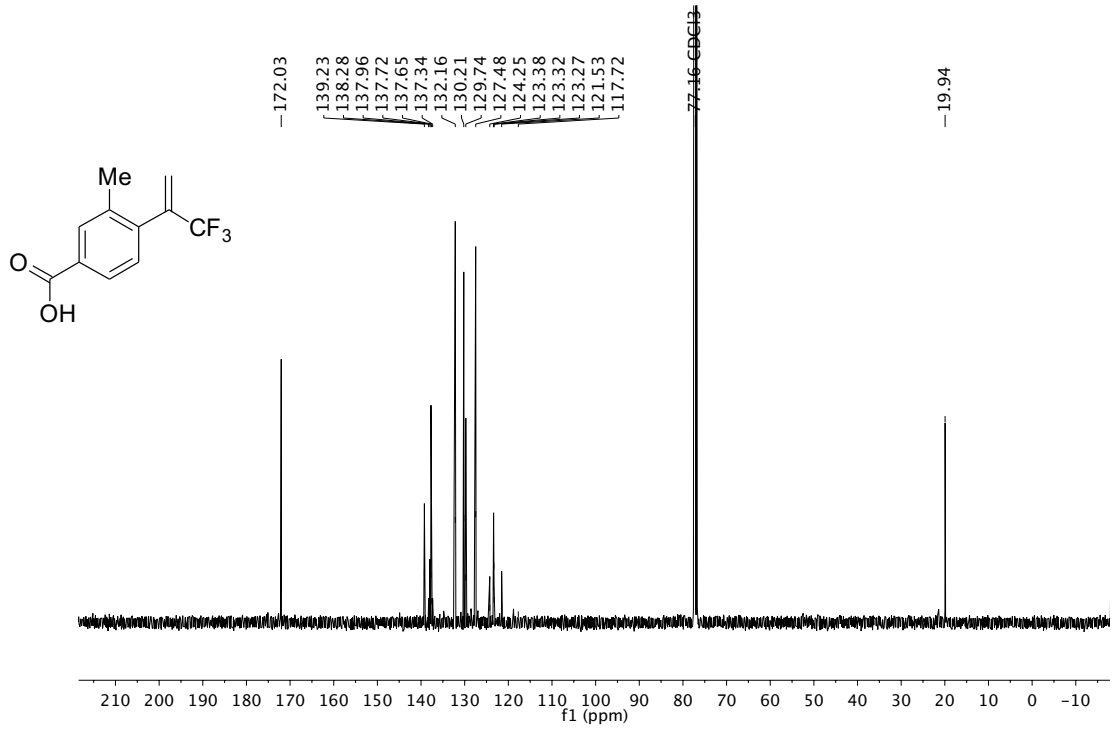
^{13}C NMR (101 MHz, $CDCl_3$) of compound **22B**.



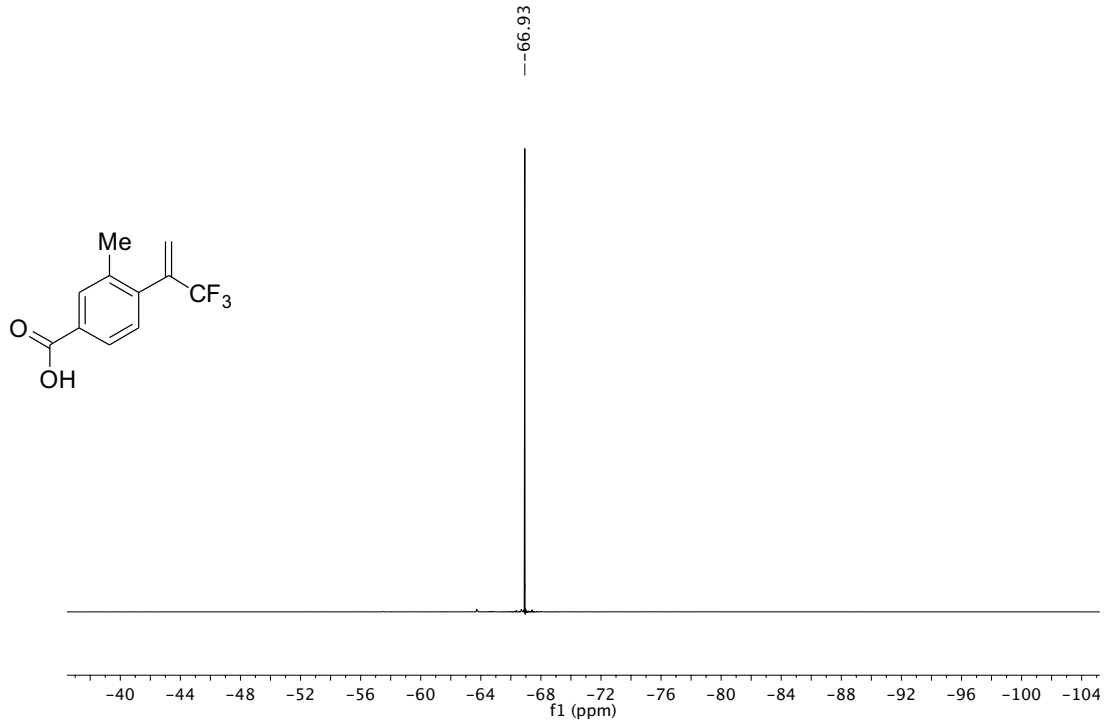
^{19}F NMR (376 MHz, $CDCl_3$) of compound **22B**.



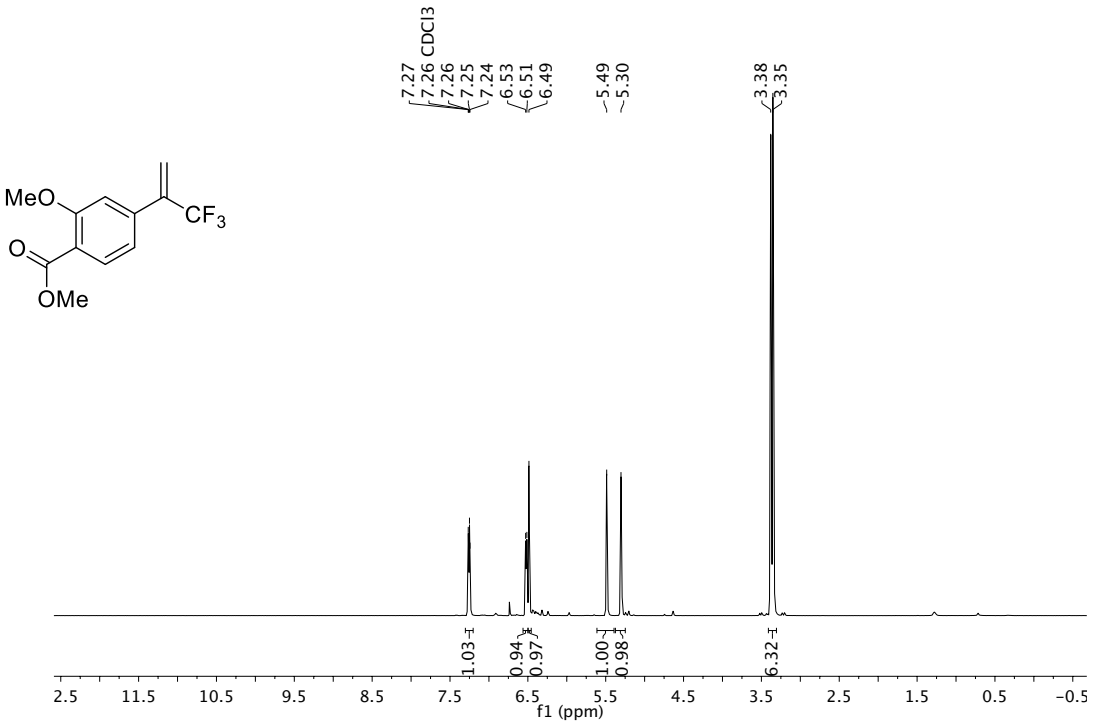
^{1}H NMR (400 MHz, $CDCl_3$) of compound **23B**.



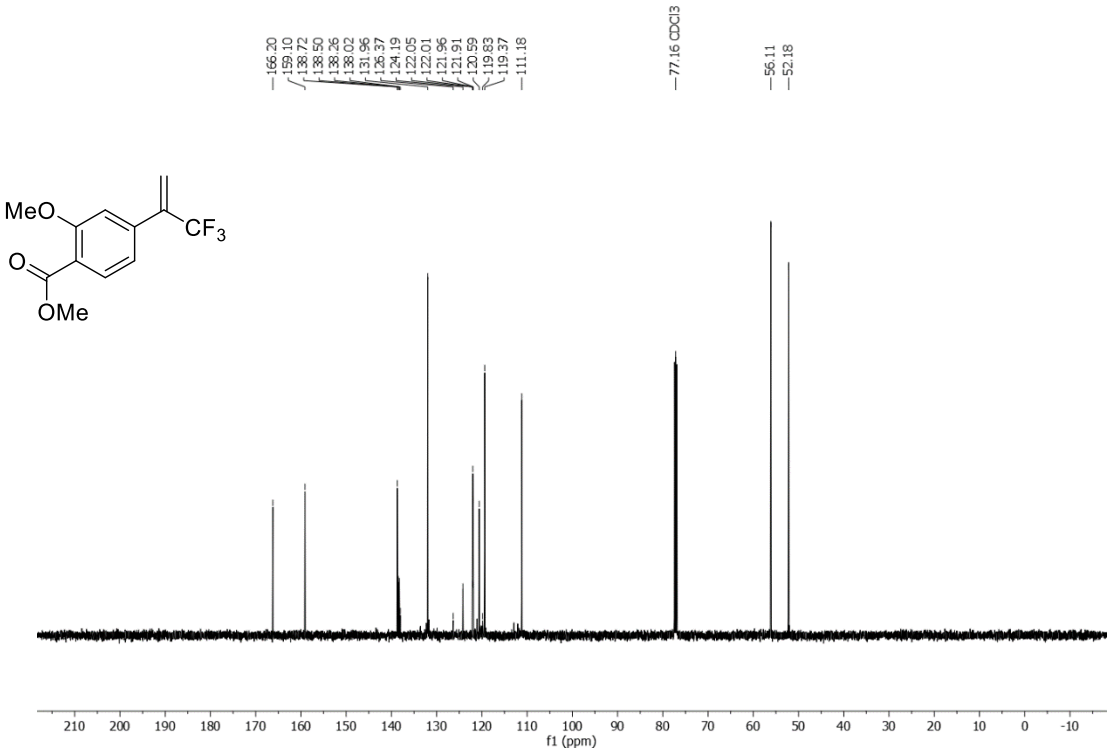
^{13}C NMR (101 MHz, $CDCl_3$) of compound **23B**.



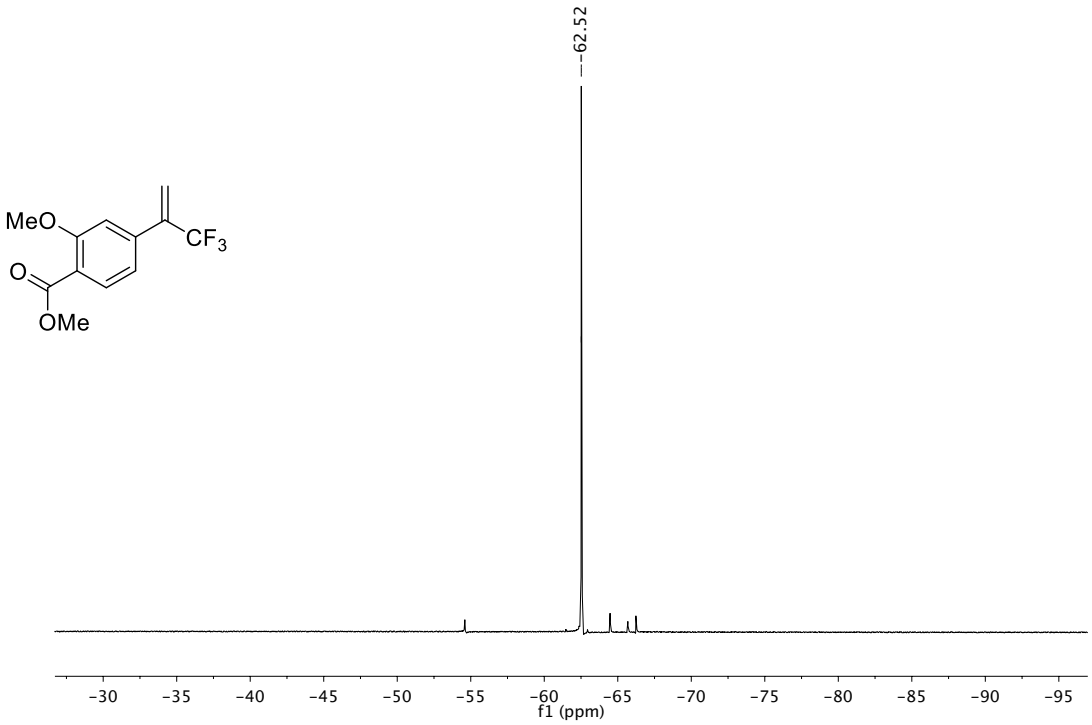
^{19}F NMR (376 MHz, $CDCl_3$) of compound **23B**.



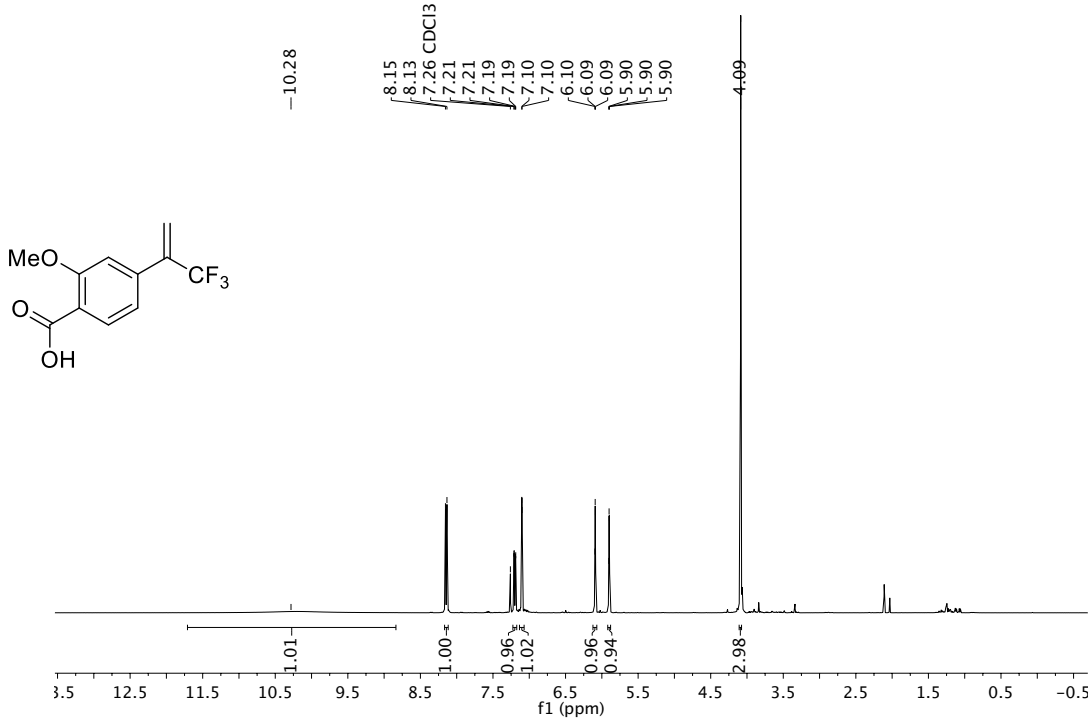
^{1}H NMR (400 MHz, $CDCl_3$) of compound **22C**.



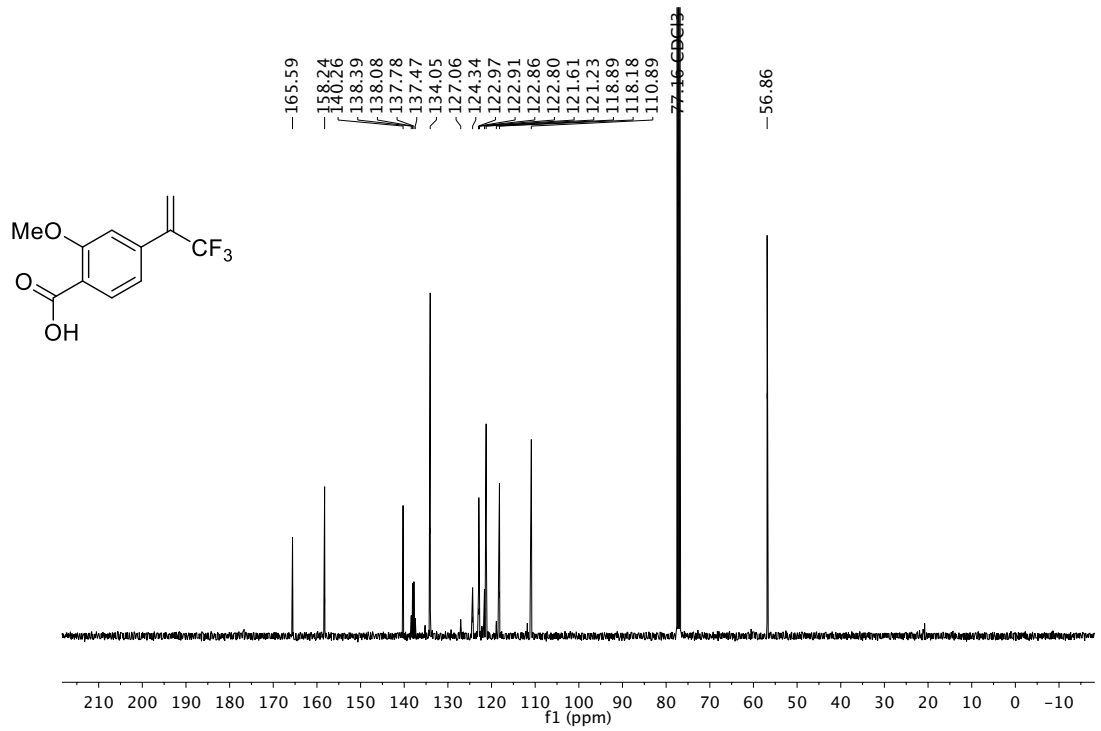
^{13}C NMR (101 MHz, $CDCl_3$) of compound **22C**.



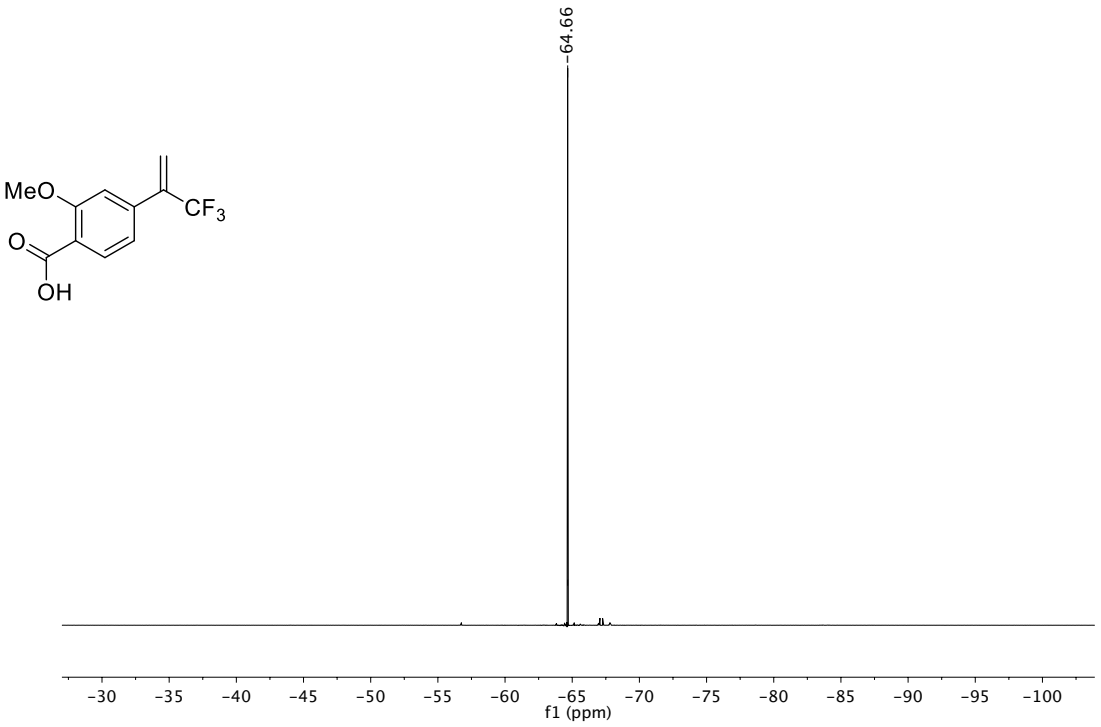
^{19}F NMR (376 MHz, $CDCl_3$) of compound **22C**.



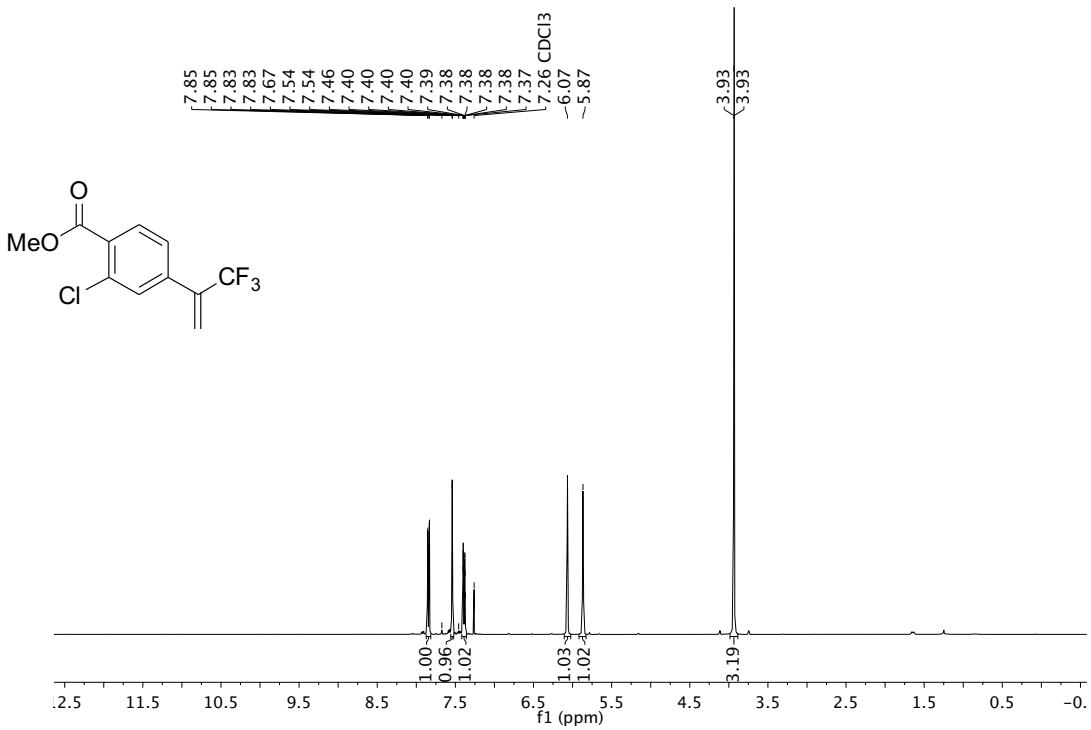
^{1}H NMR (400 MHz, $CDCl_3$) of compound **23C**.



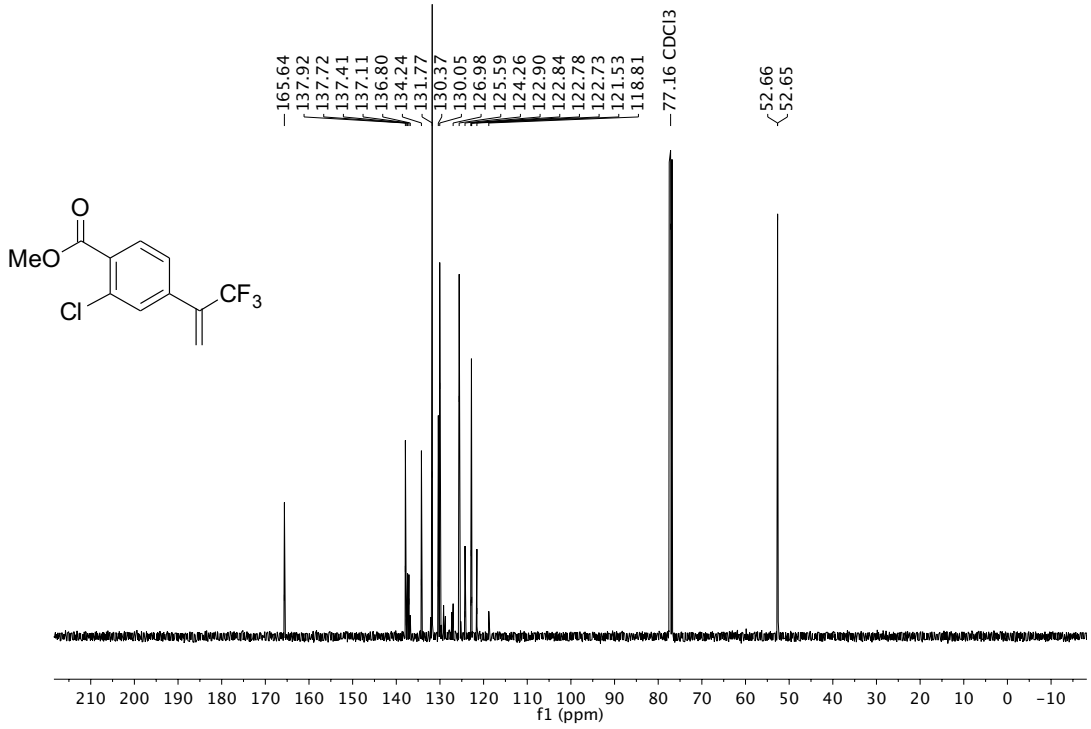
^{13}C NMR (101 MHz, $CDCl_3$) of compound **23C**.



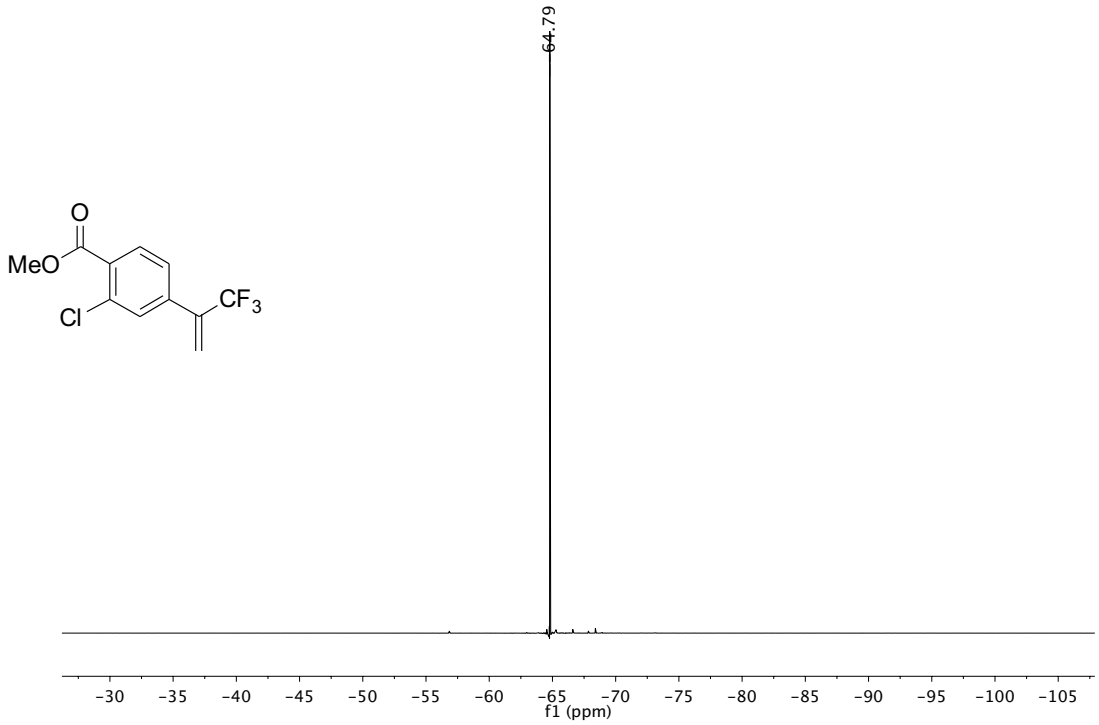
^{19}F NMR (376 MHz, $CDCl_3$) of compound **23C**.



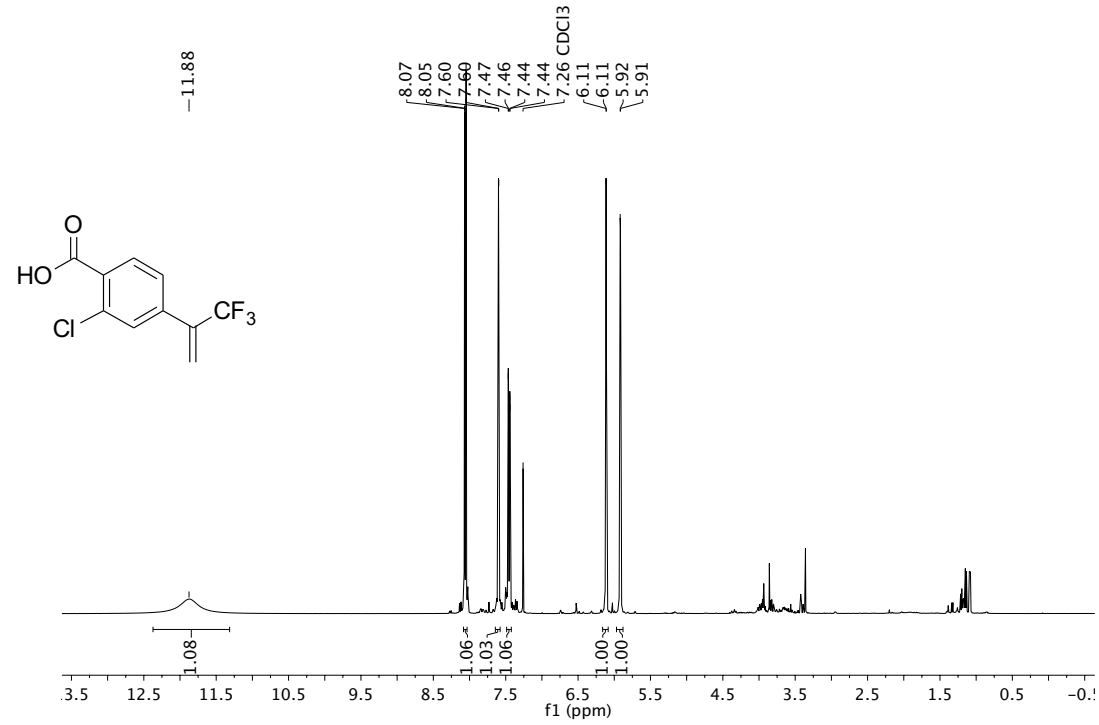
^{1}H NMR (400 MHz, $CDCl_3$) of compound **22D**.



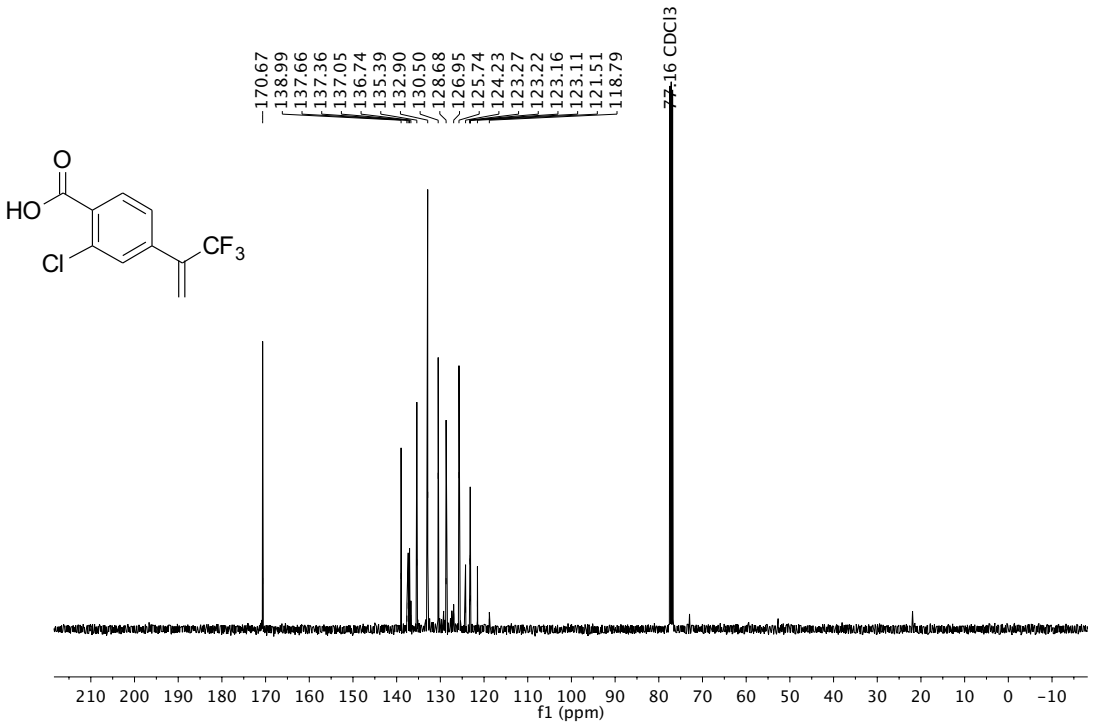
^{13}C NMR (101 MHz, CDCl3) of compound **22D**.



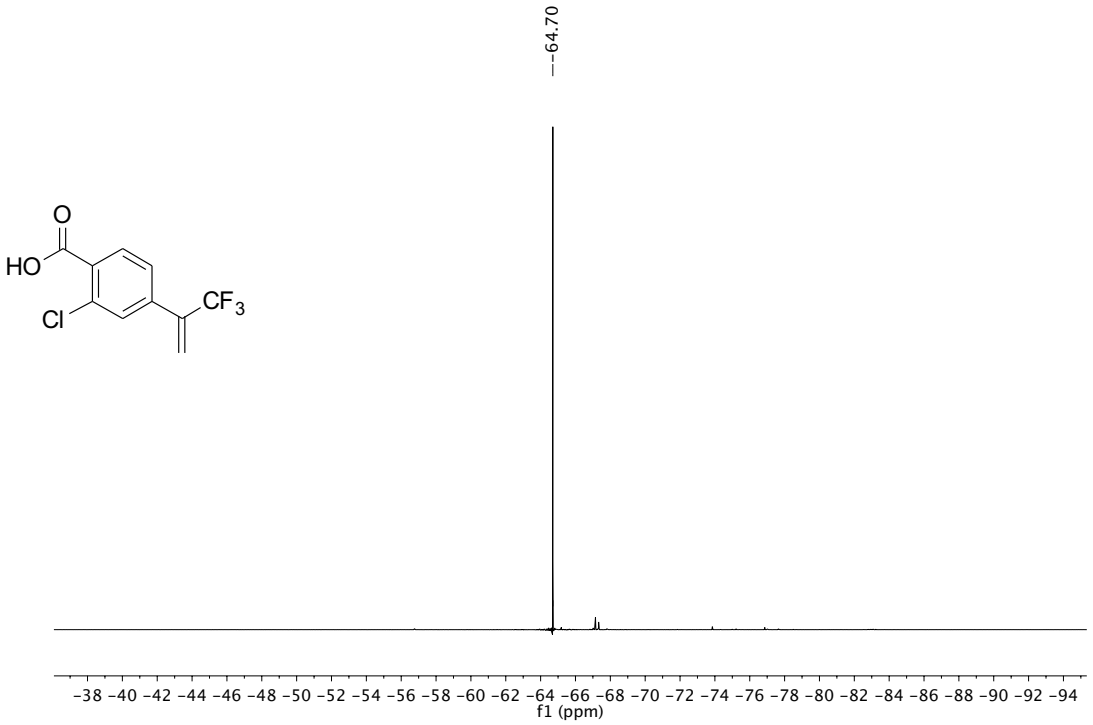
^{19}F NMR (376 MHz, CDCl3) of compound **22D**.



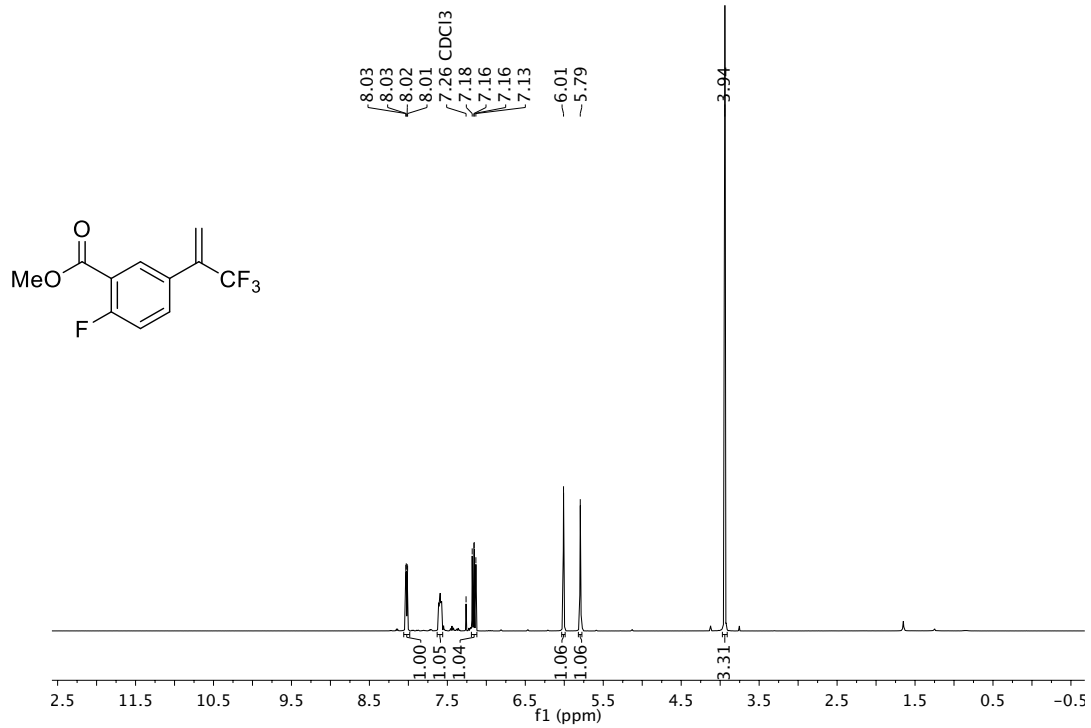
^{1}H NMR (400 MHz, $CDCl_3$) of compound **23D**.



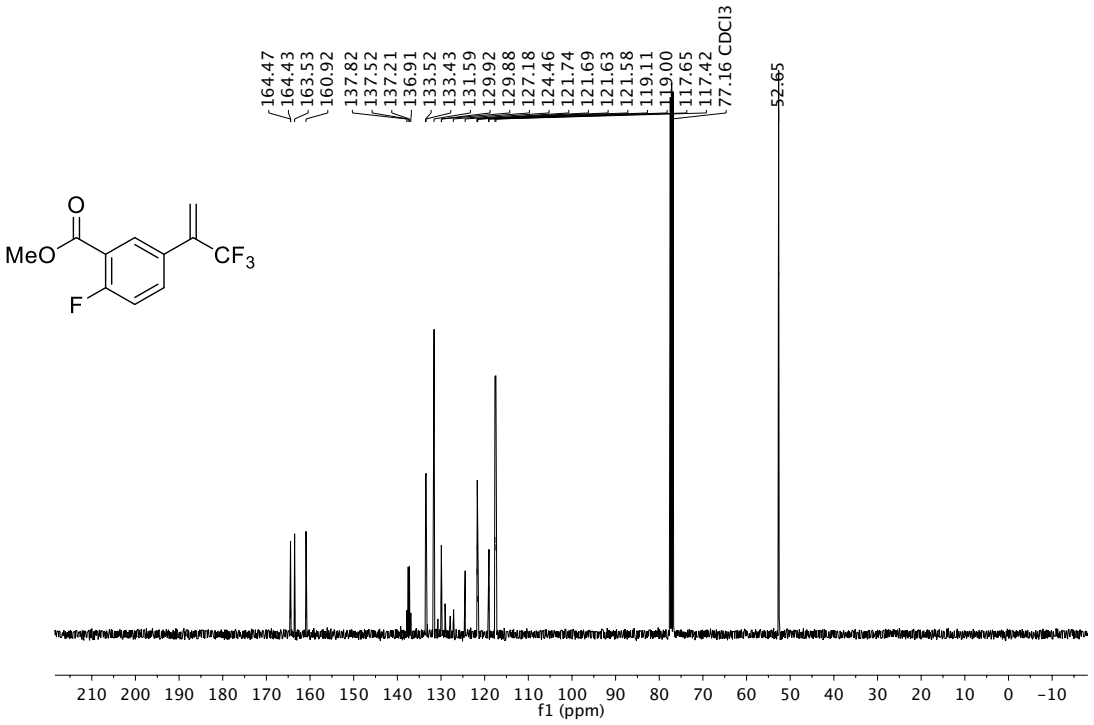
^{13}C NMR (101 MHz, CDCl3) of compound **23D**.



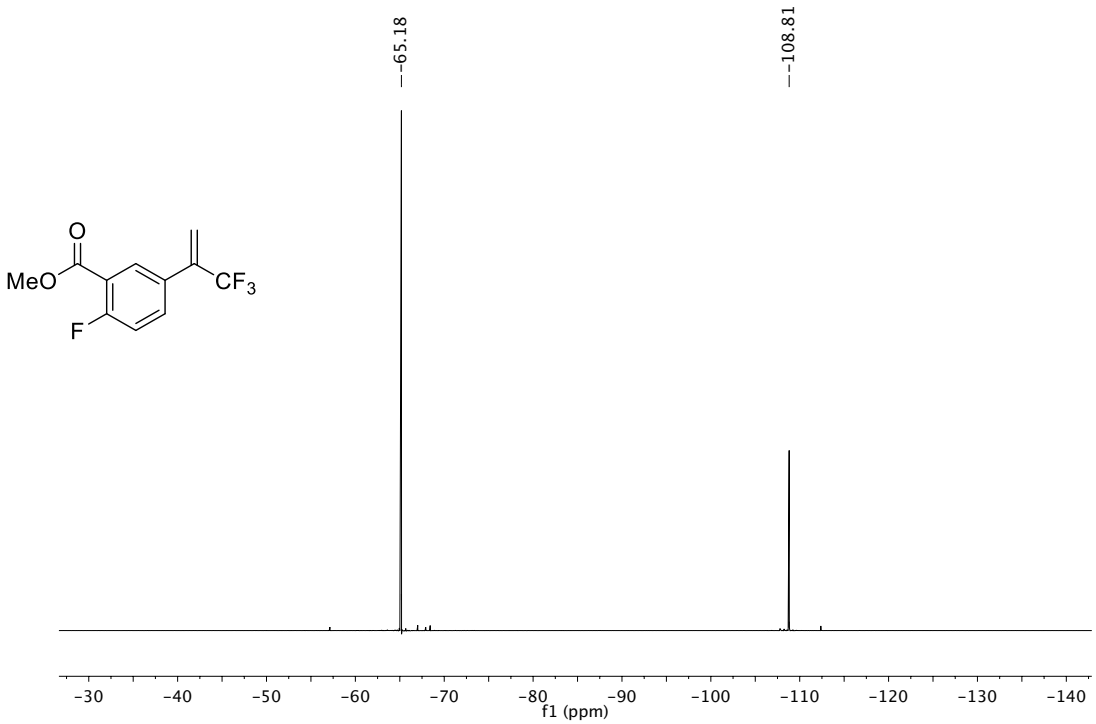
^{19}F NMR (376 MHz, CDCl3) of compound **23D**.



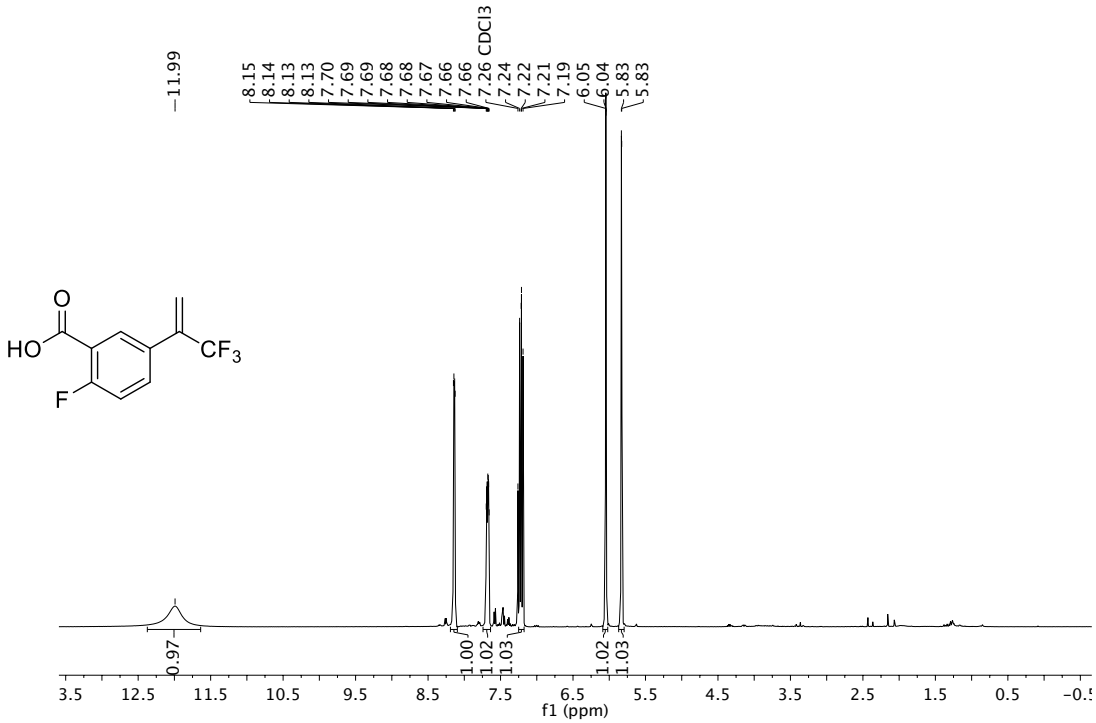
^{1}H NMR (400 MHz, $CDCl_3$) of compound **22E**.



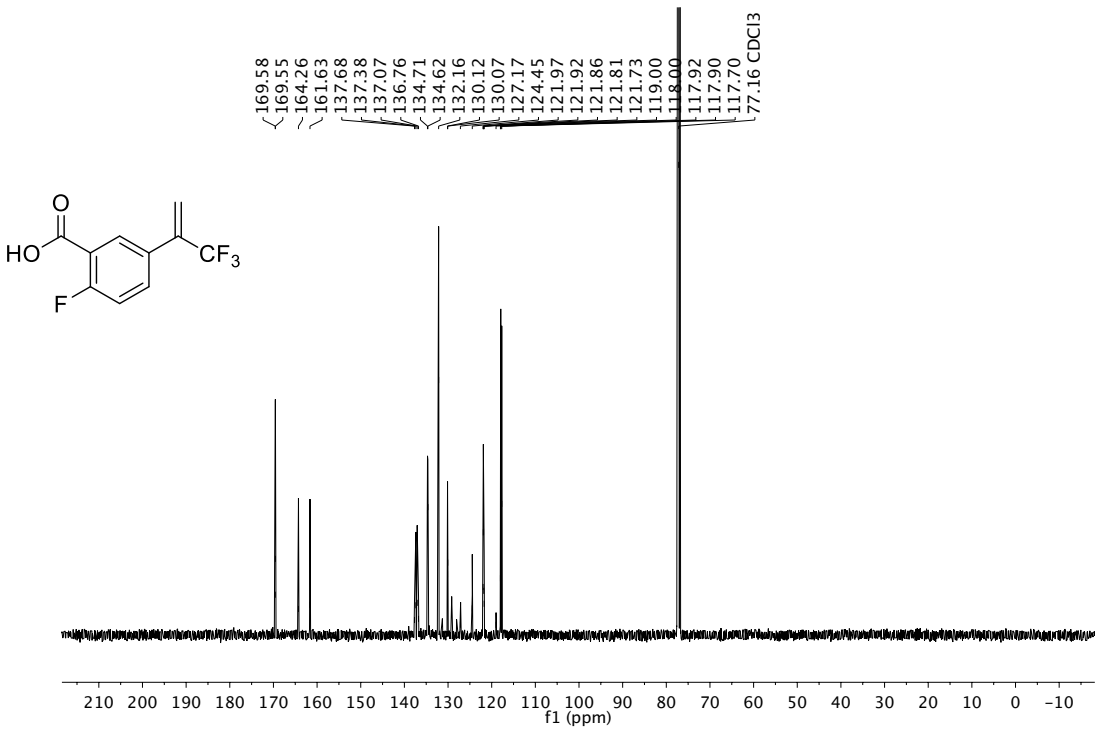
^{13}C NMR (101 MHz, $CDCl_3$) of compound **22E**.



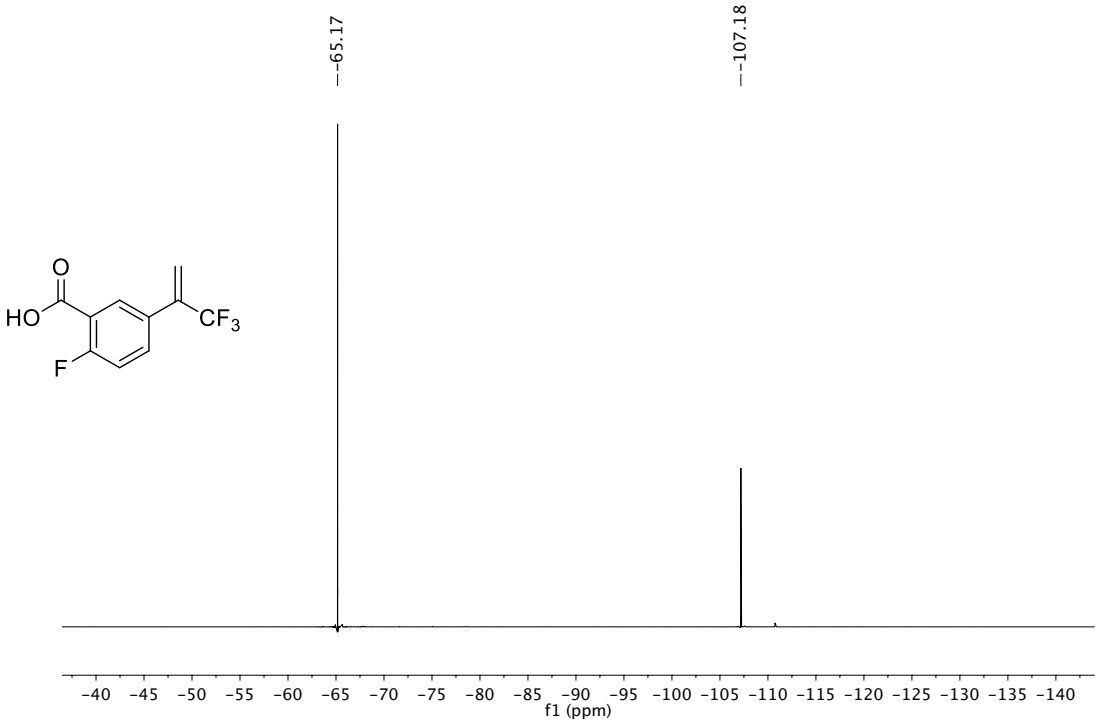
^{19}F NMR (376 MHz, $CDCl_3$) of compound **22E**.



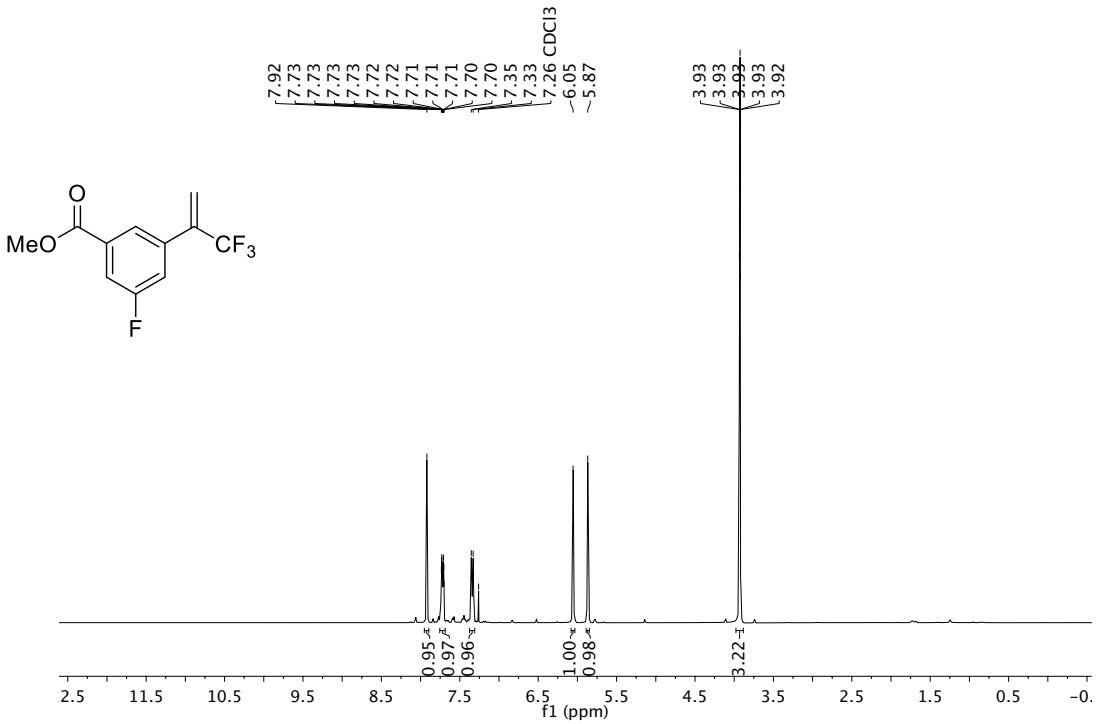
^{1}H NMR (400 MHz, $CDCl_3$) of compound **23E**.



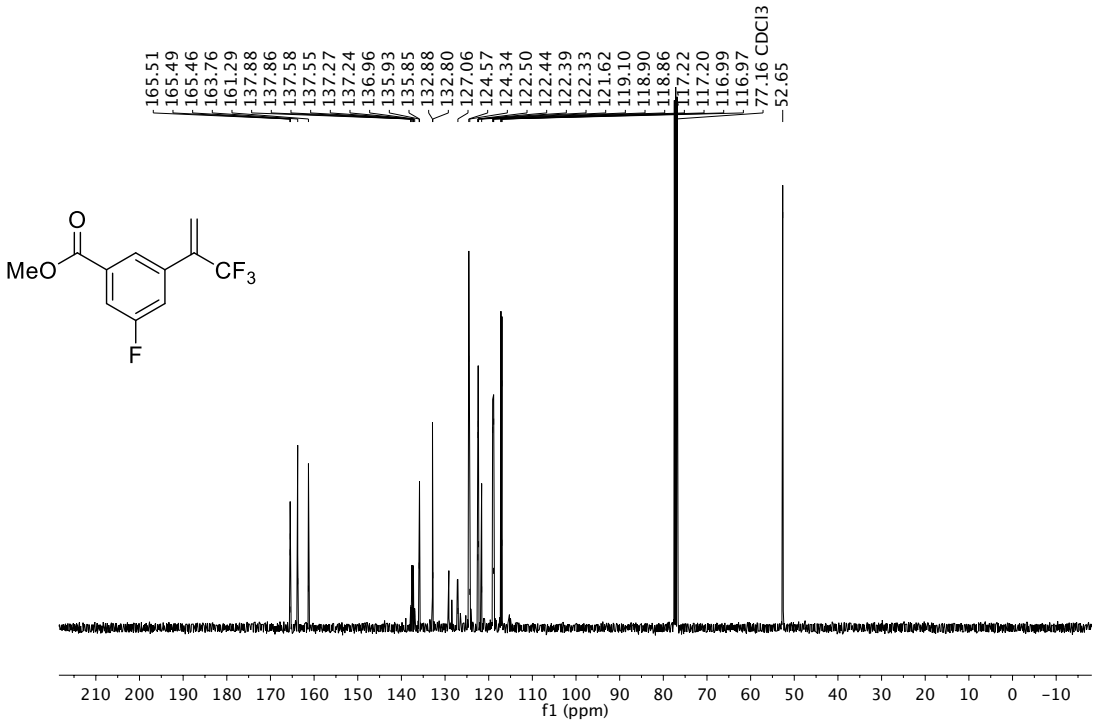
^{13}C NMR (101 MHz, $CDCl_3$) of compound **23E**.



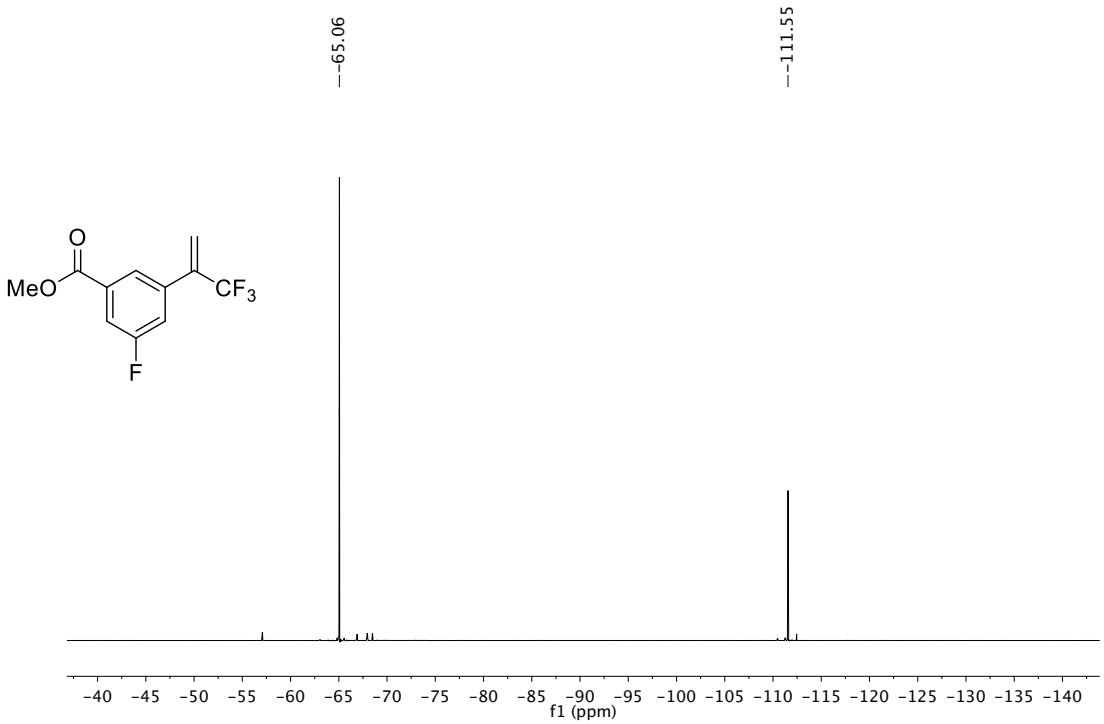
^{19}F NMR (376 MHz, $CDCl_3$) of compound **23E**.



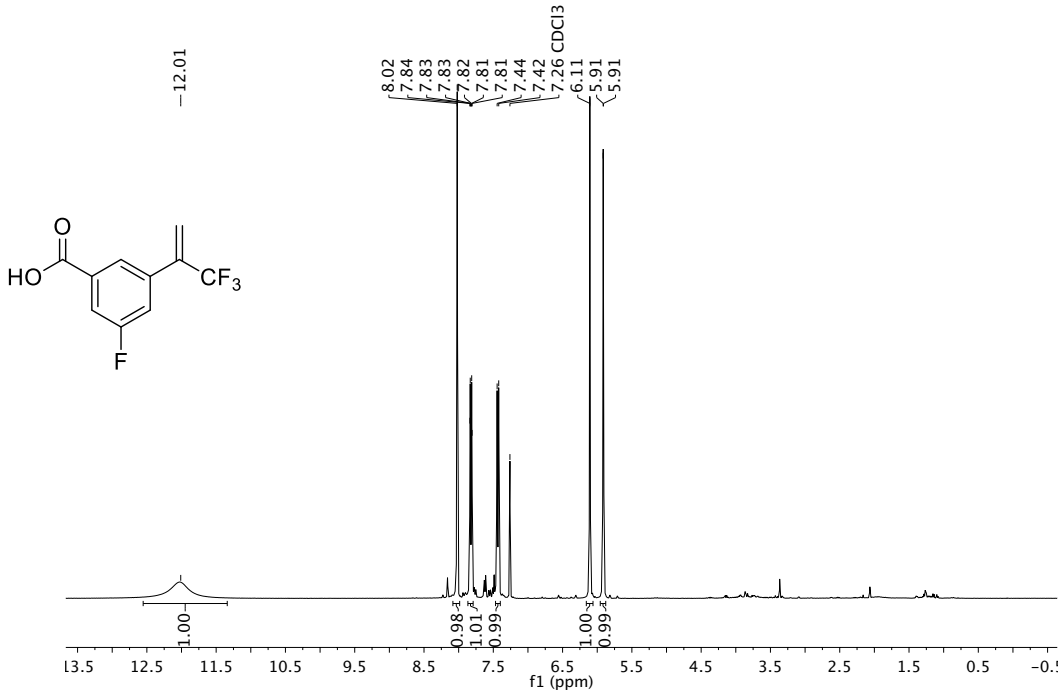
^{1}H NMR (400 MHz, $CDCl_3$) of compound **22F**.



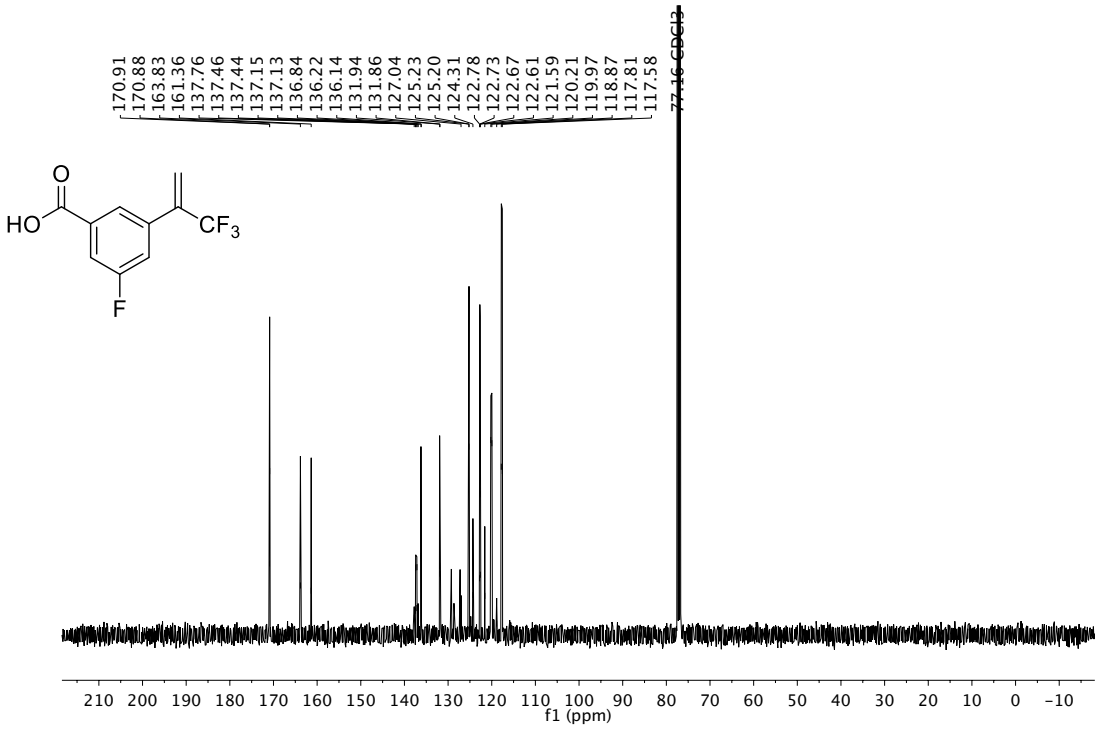
^{13}C NMR (101 MHz, $CDCl_3$) of compound **22F**.



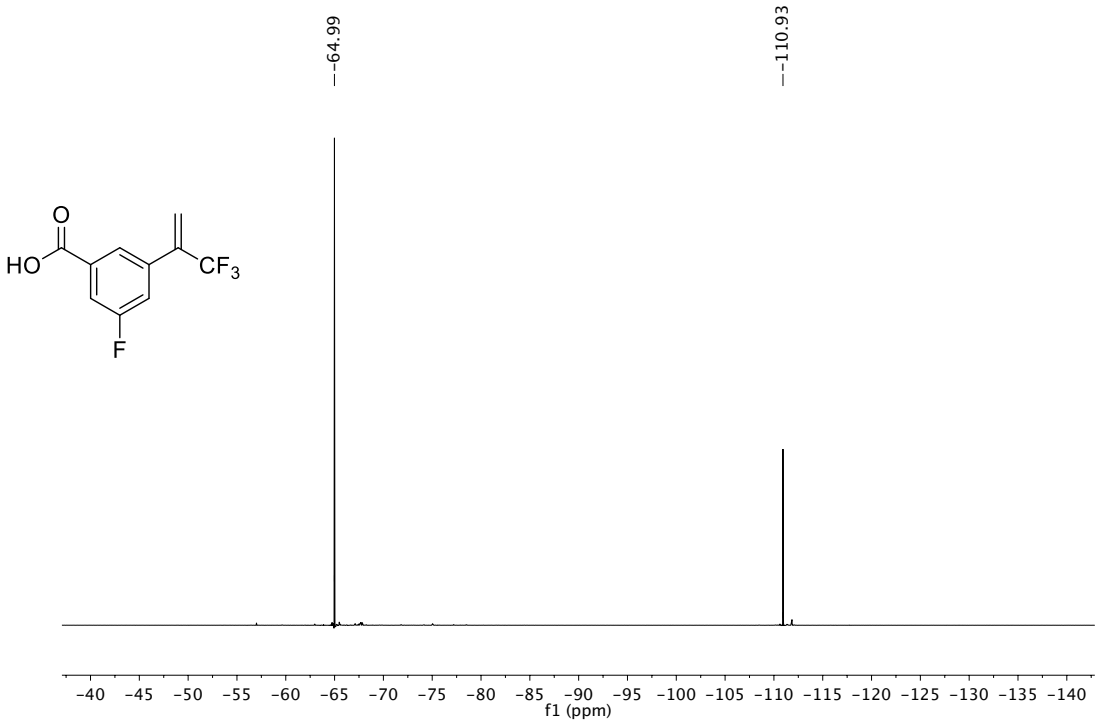
^{19}F NMR (376 MHz, $CDCl_3$) of compound **22F**.



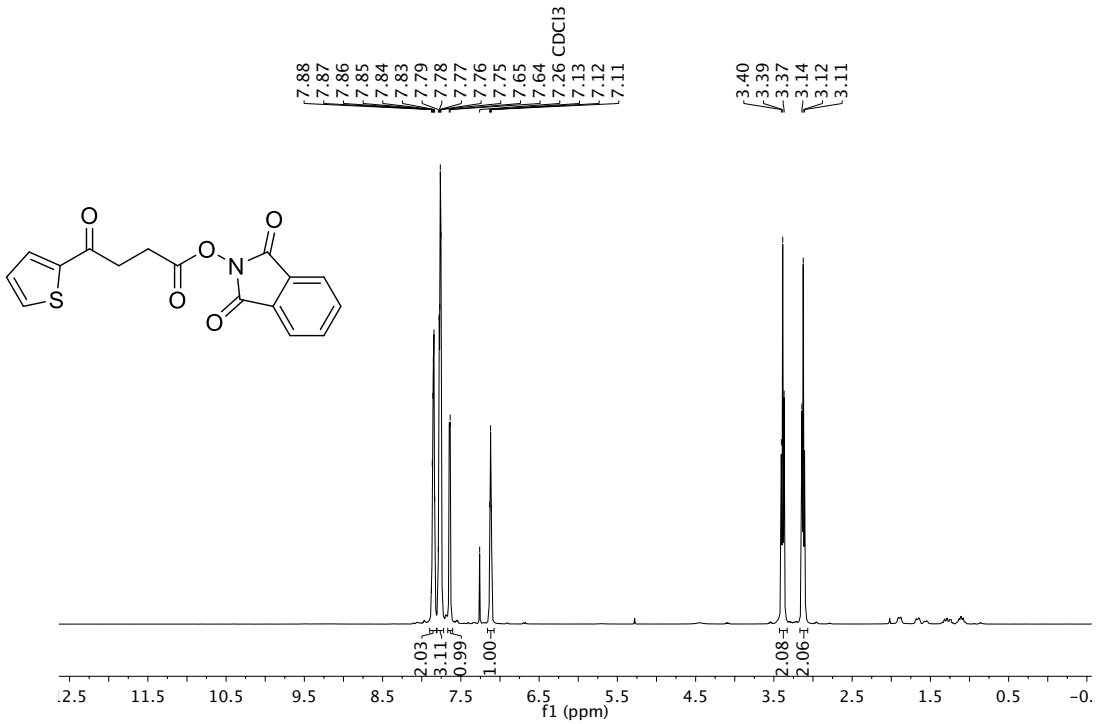
^{1}H NMR (400 MHz, $CDCl_3$) of compound **23F**.



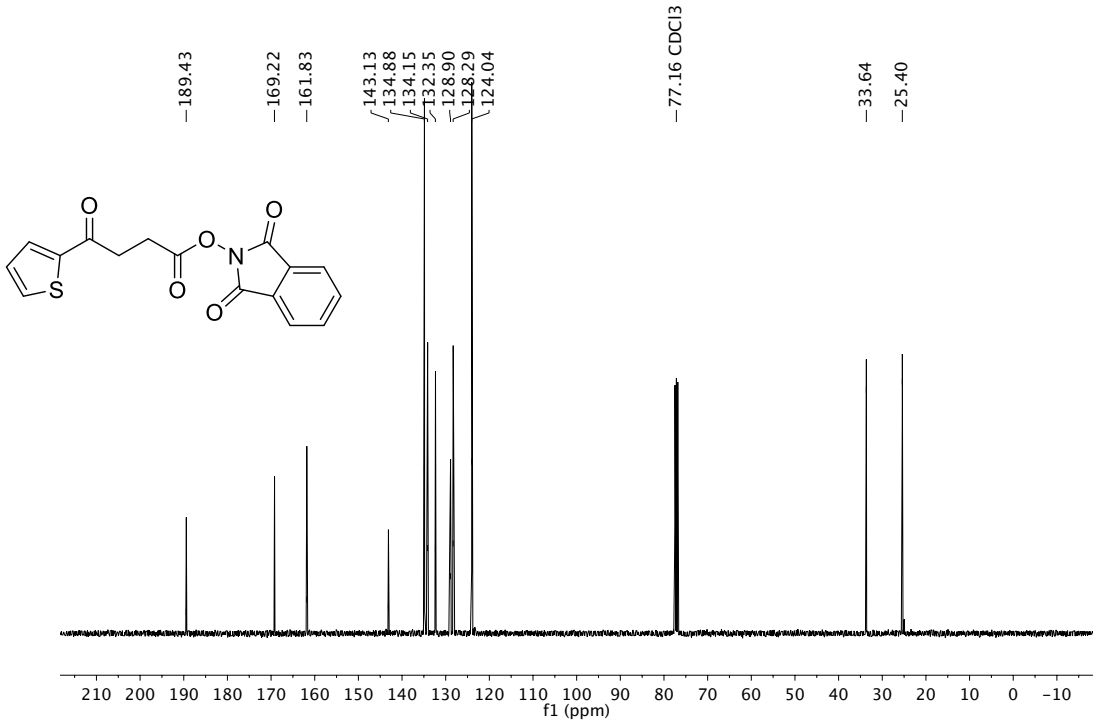
^{13}C NMR (101 MHz, $CDCl_3$) of compound **23F**.



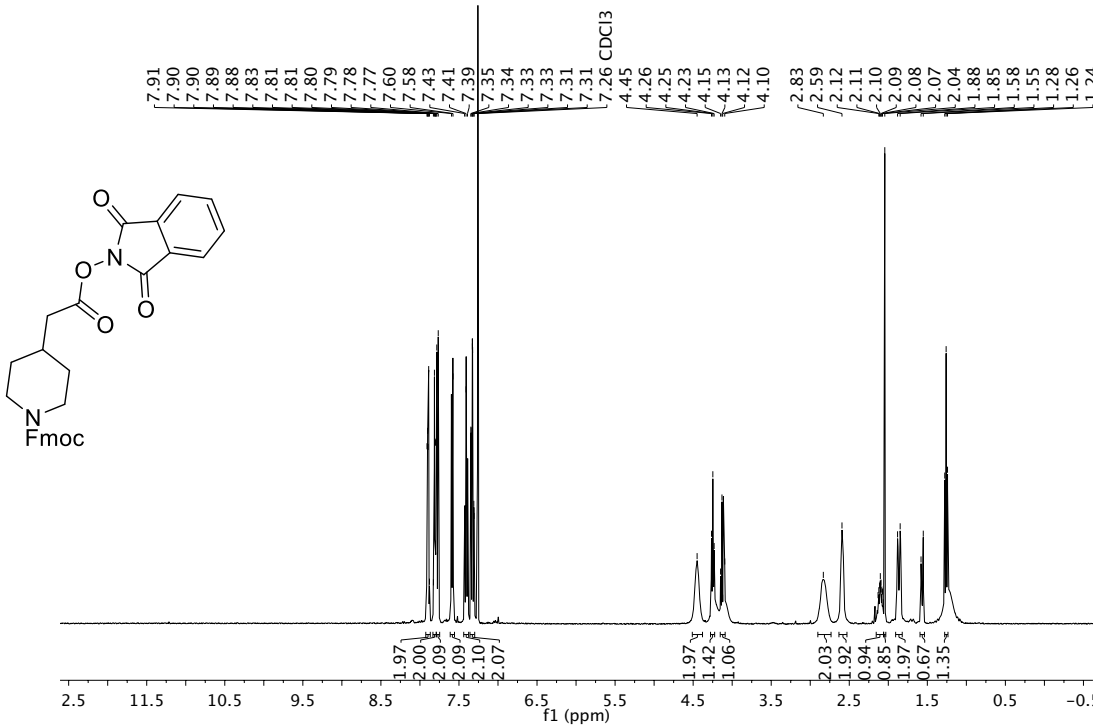
^{19}F NMR (376 MHz, $CDCl_3$) of compound **23F**.



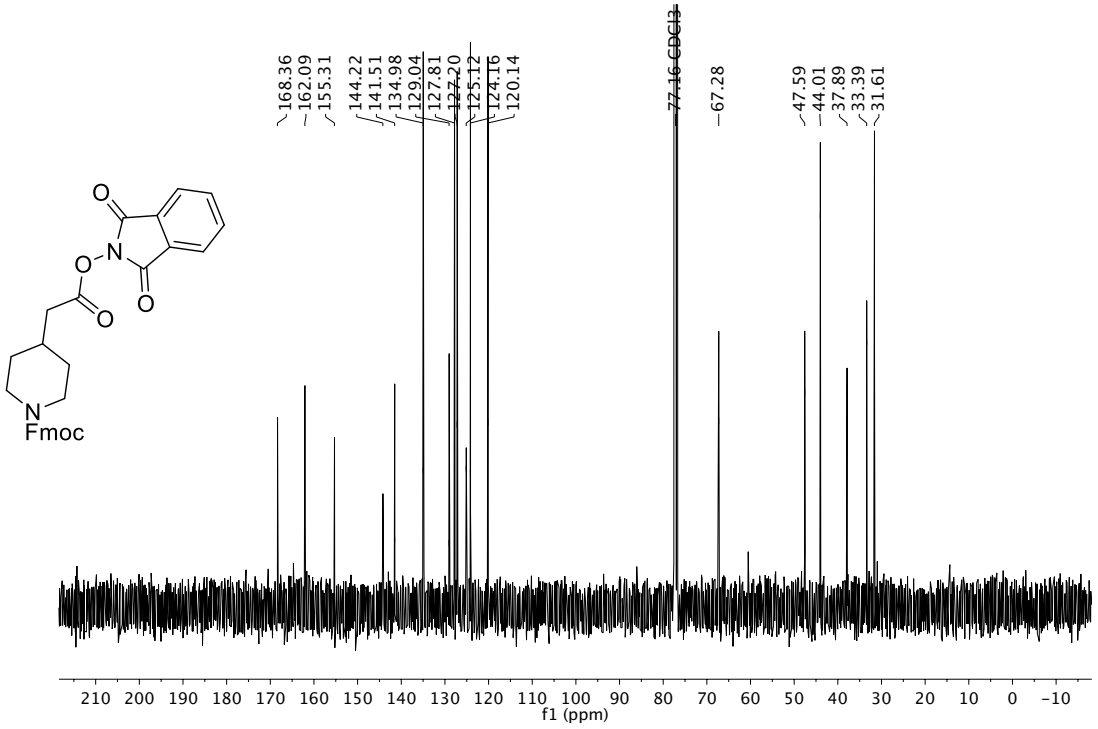
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.



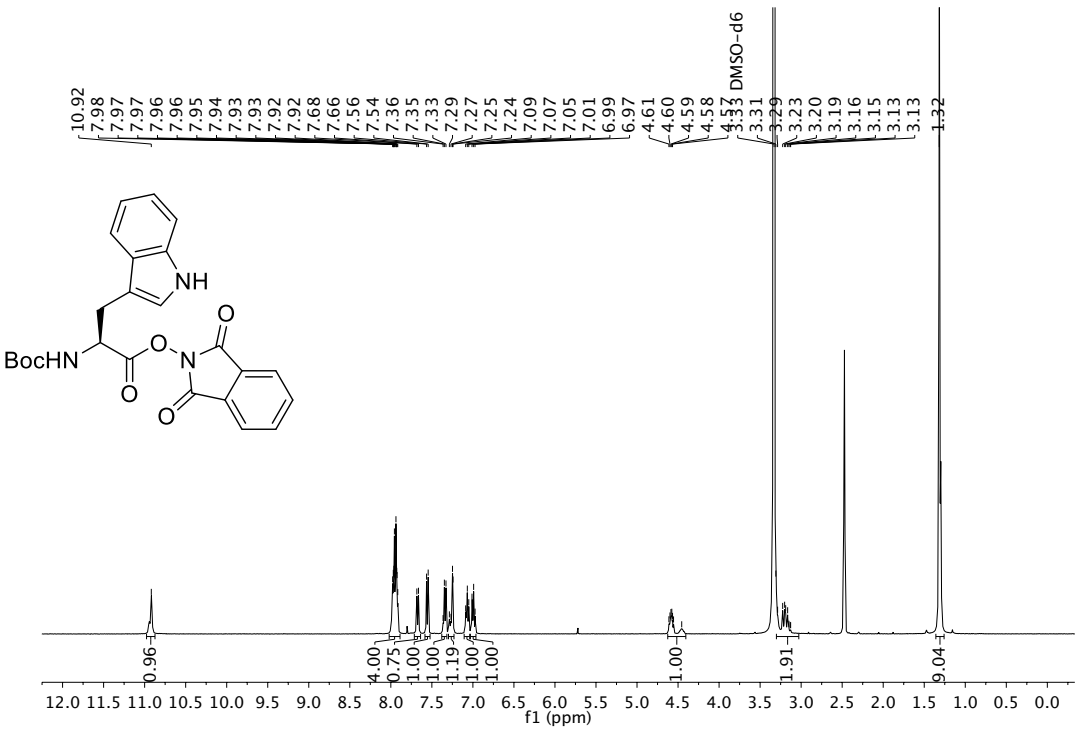
^{13}C NMR (101 MHz, $CDCl_3$) of compound **2a**.



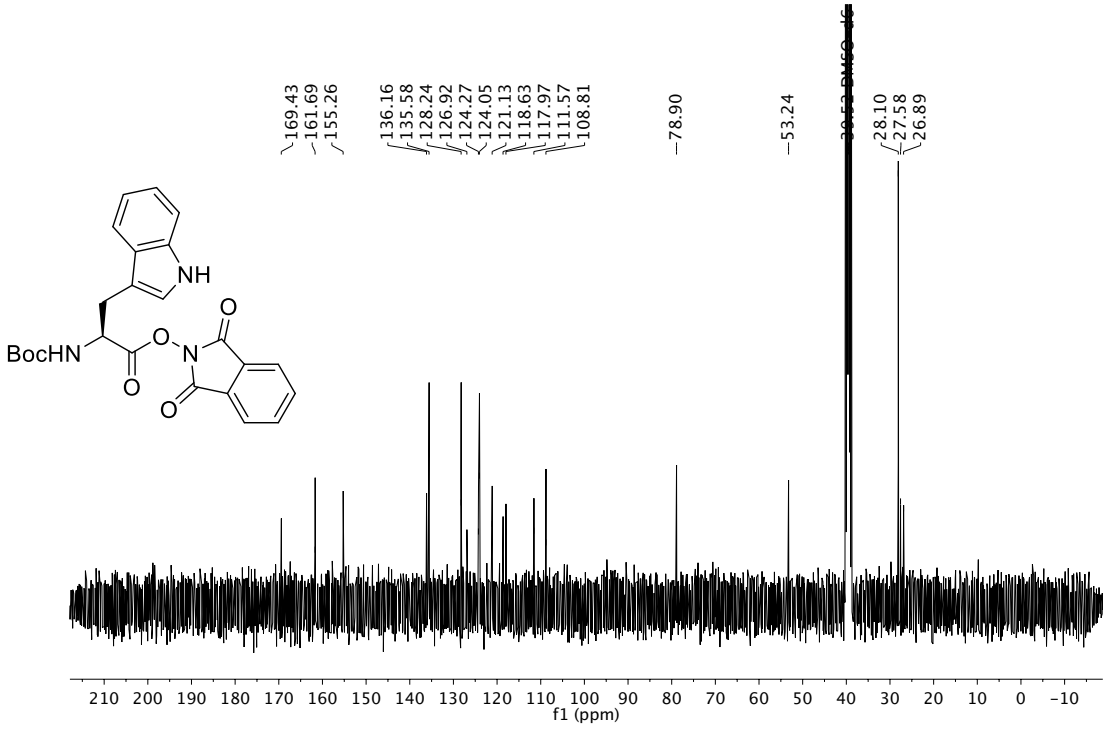
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2g**.



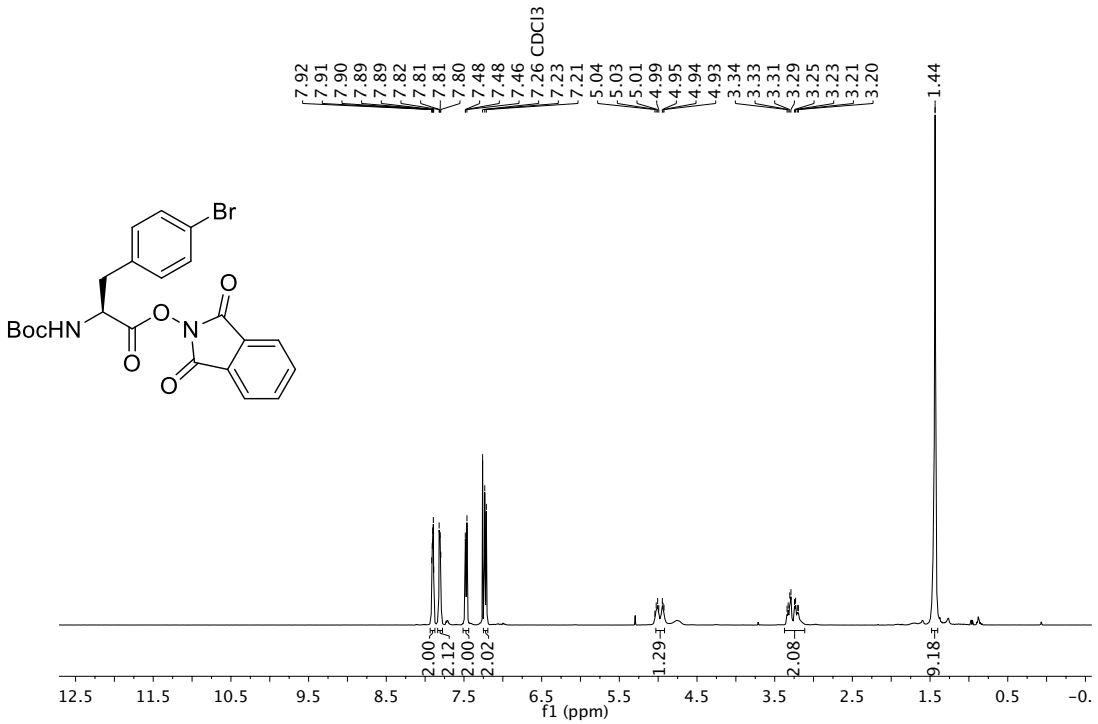
^{13}C NMR (101 MHz, $CDCl_3$) of compound **2g**.



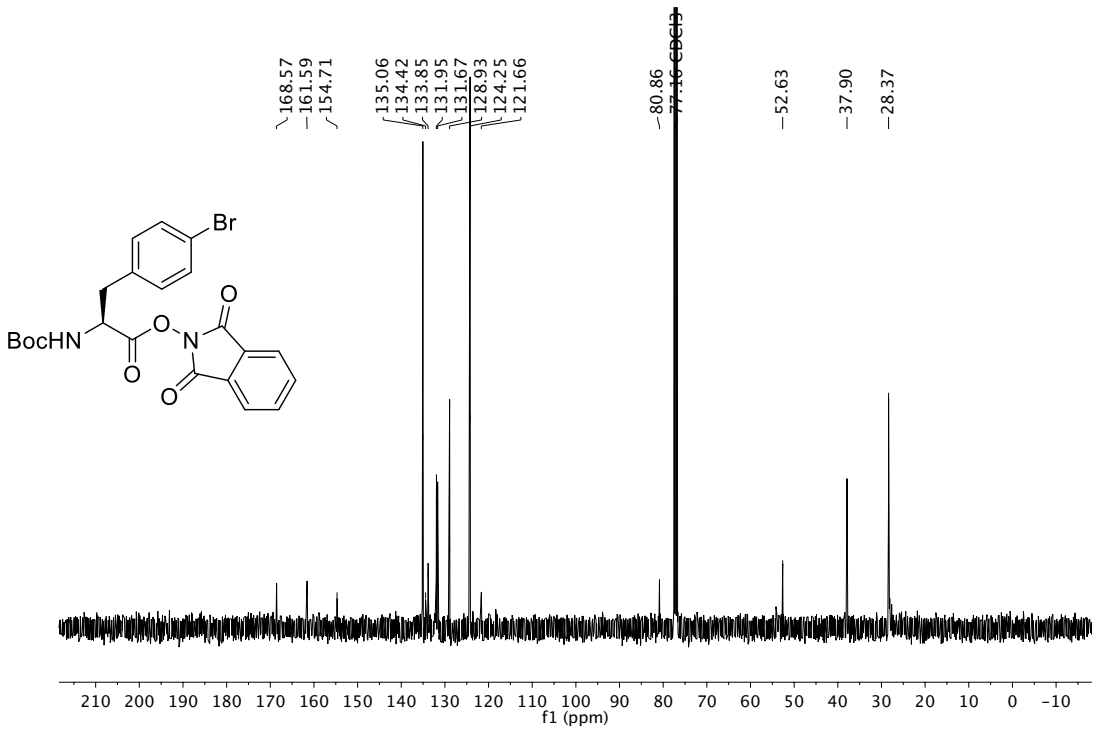
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2x**.



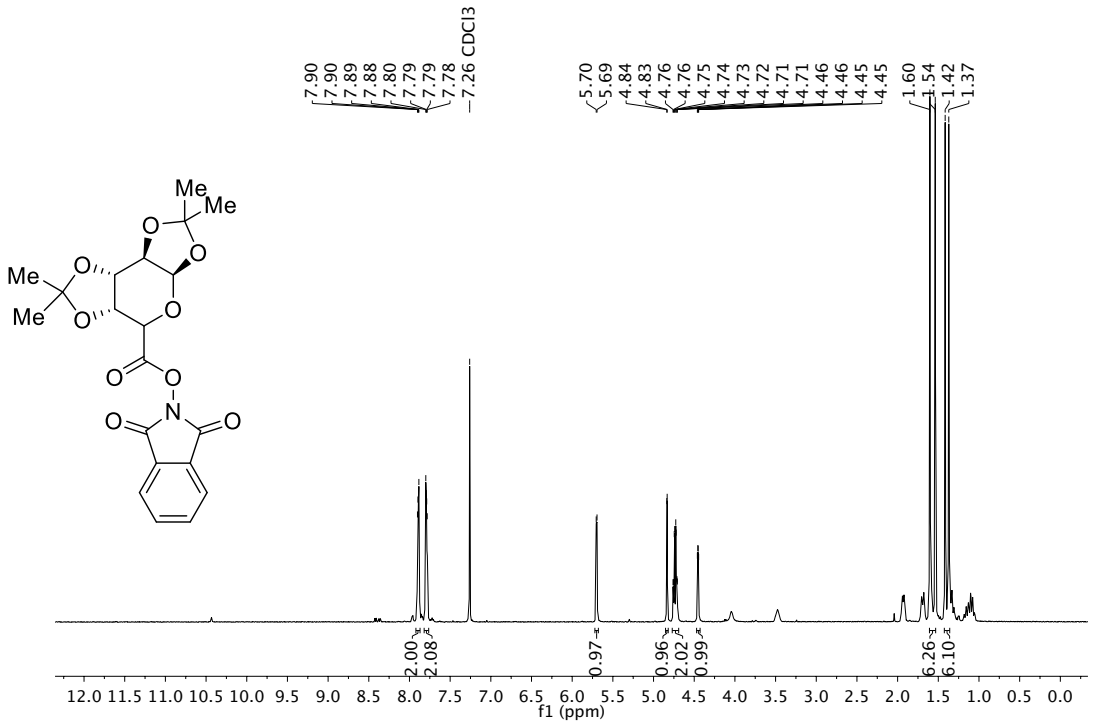
^{13}C NMR (101 MHz, $CDCl_3$) of compound **2x**.



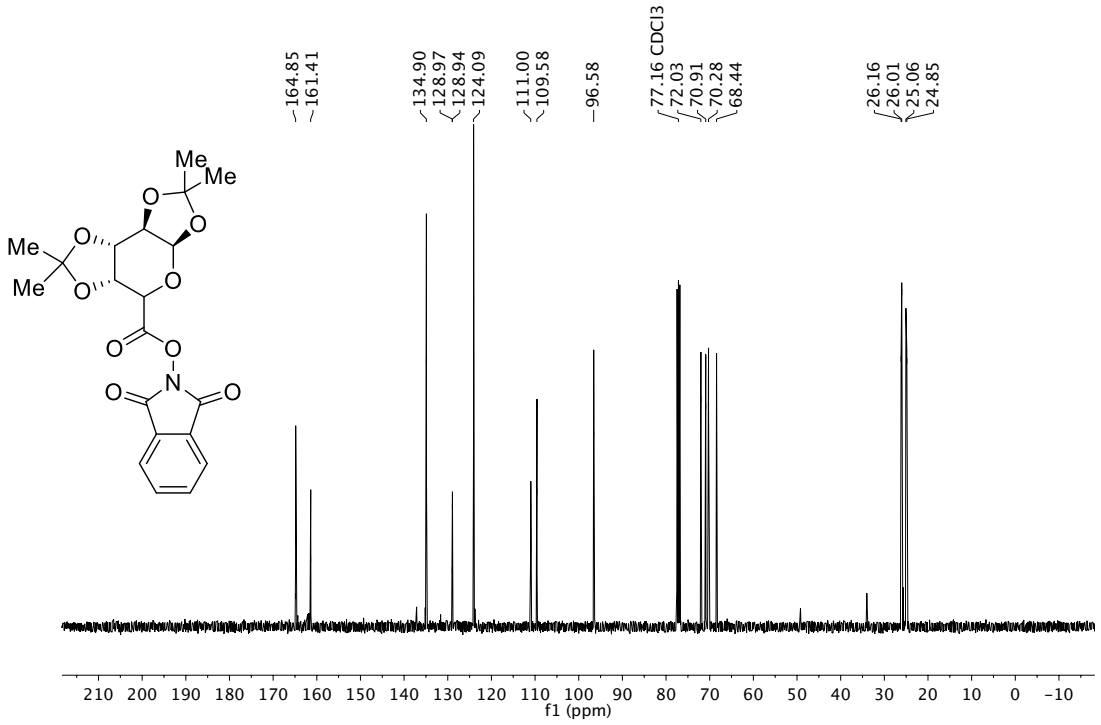
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2y**.



^{13}C NMR (101 MHz, $CDCl_3$) of compound **2y**.



^{1}H NMR (400 MHz, $CDCl_3$) of compound **2z**.



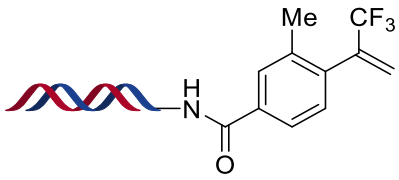
^{13}C NMR (101 MHz, $CDCl_3$) of compound **2z**.

11. UPLC/MS Spectra

11.1 Functionalized DNA Headpieces

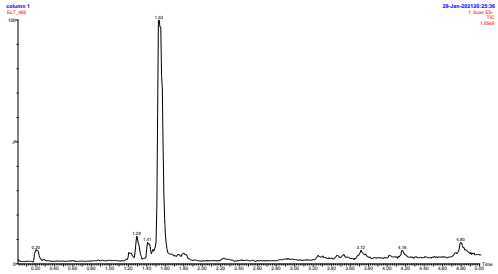
The synthesis of on-DNA aryl trifluoromethyl alkene **1A** and on-DNA aryl halide **13A-G** starting materi als was previously reported in *J. Am. Chem. Soc.* **2019**, *141*, 8, 3723-3732 and *Org. Lett.* **2020**, *22*, 3, 1046–105.

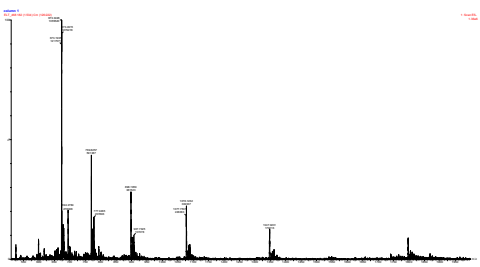
Headpiece 1B

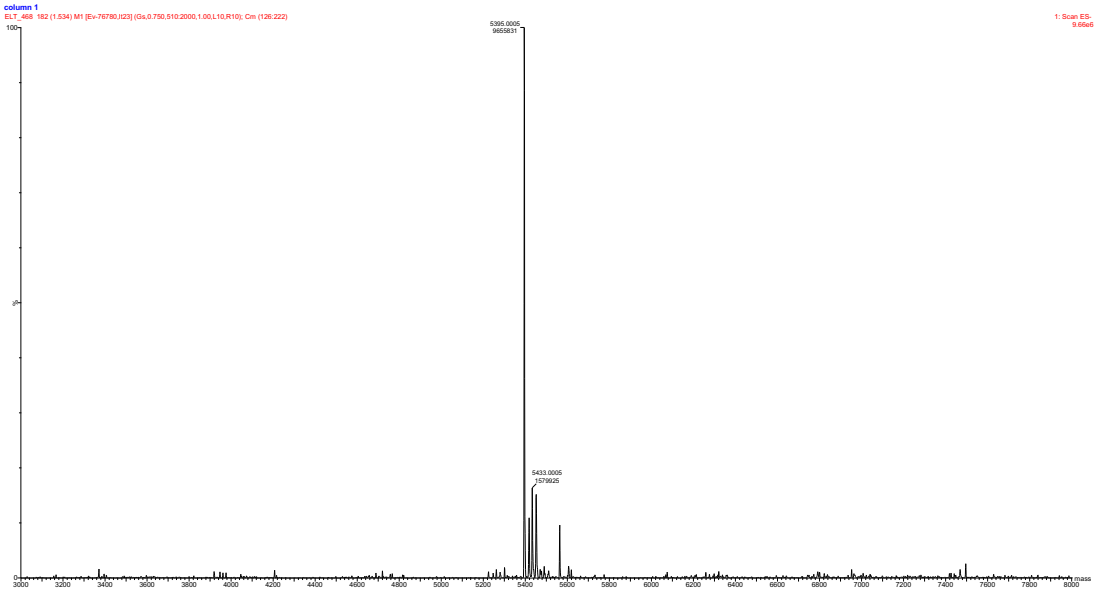


Molecular Weight: 5396.69

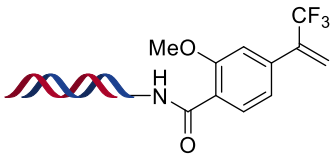
ELT_468 - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)





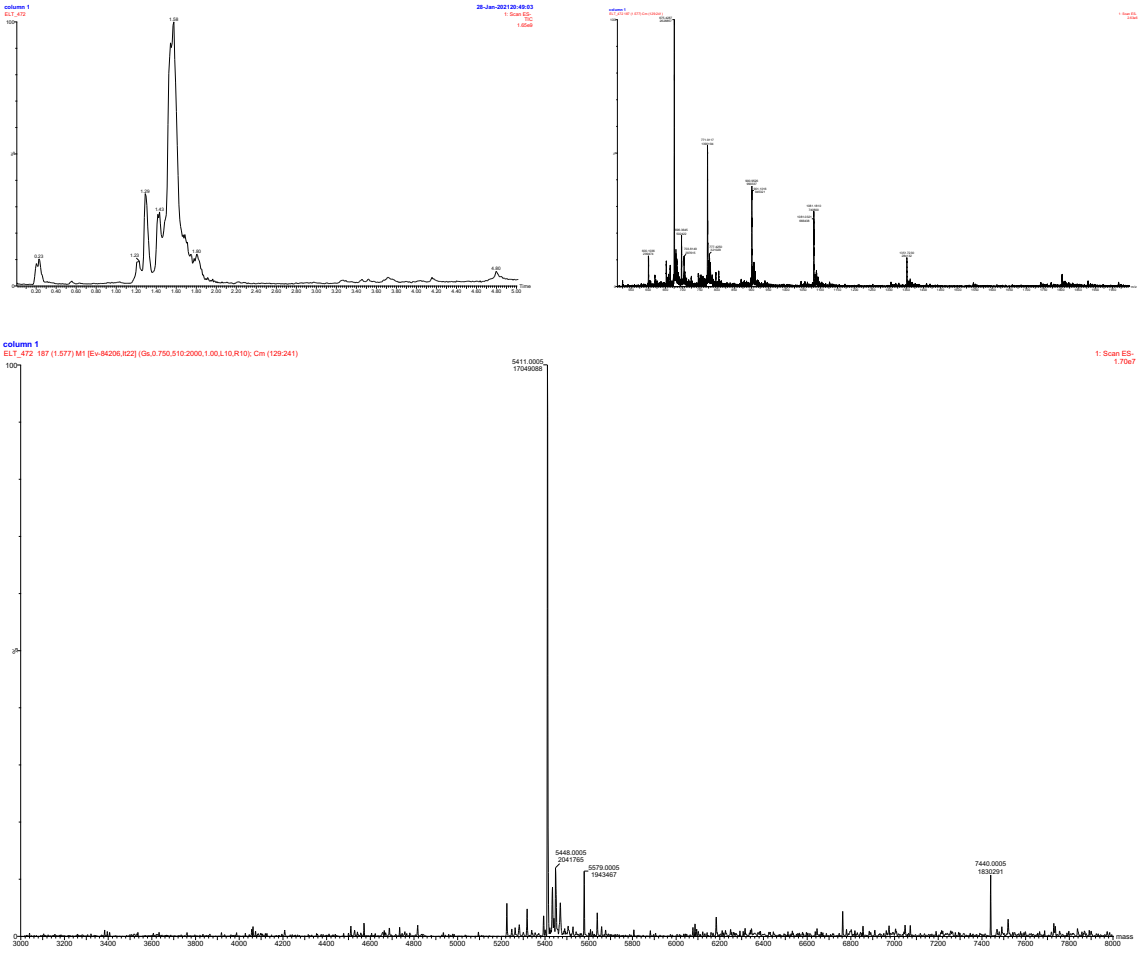


Headpiece 1C

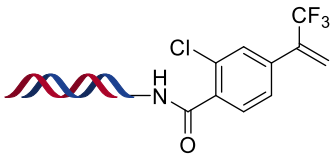


Molecular Weight: 5412.69

ELT_472 - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

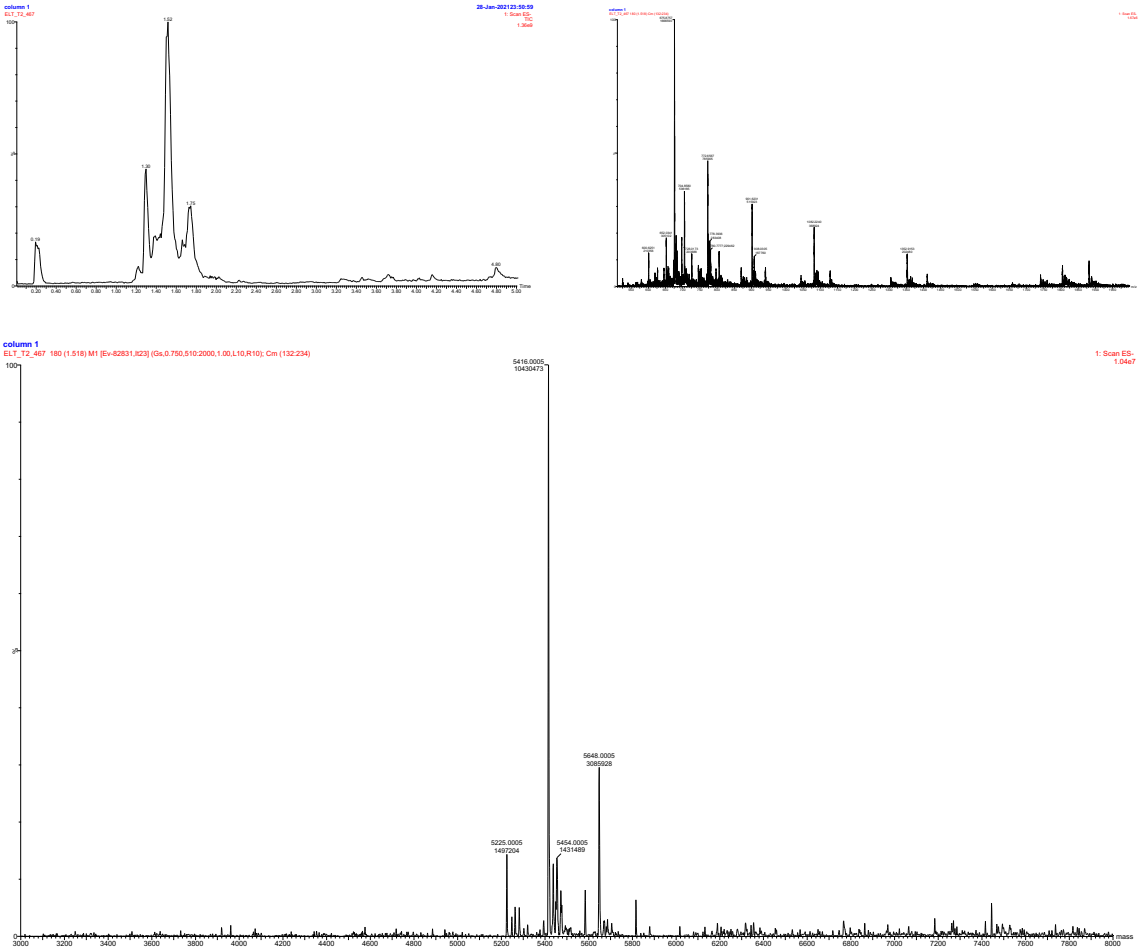


Headpiece 1D

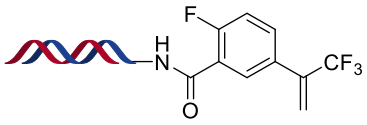


Molecular Weight: 5417.11

ELT_467 - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

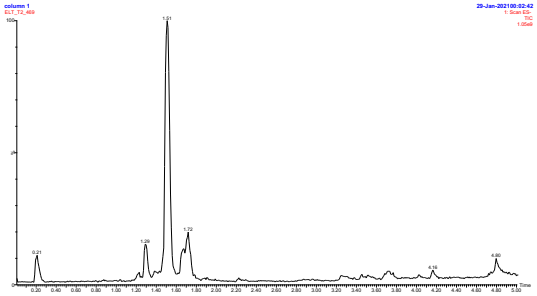


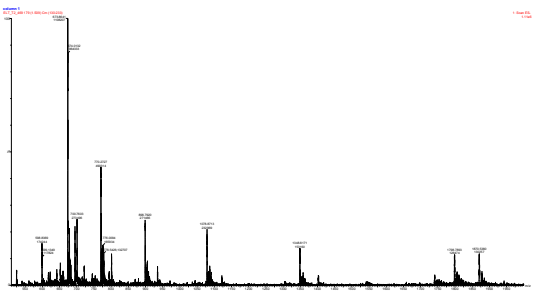
Headpiece 1E

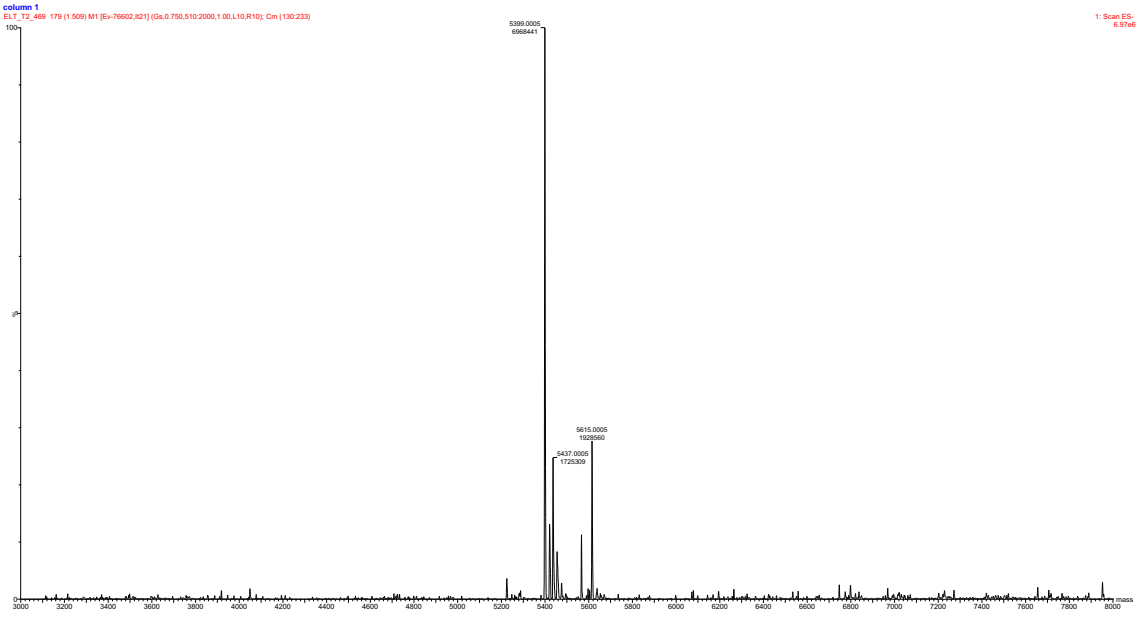


Molecular Weight: 5400.66

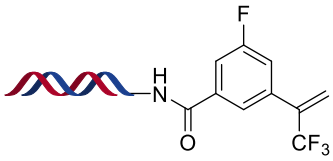
ELT_469 - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)





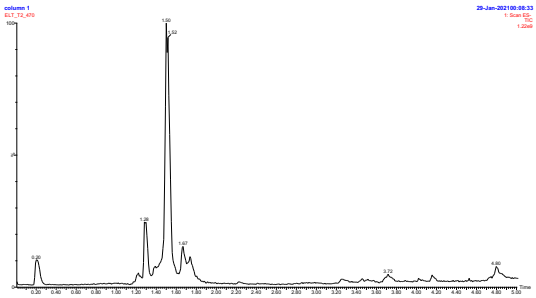


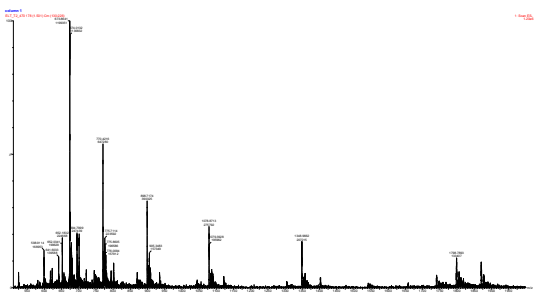
Headpiece 1F

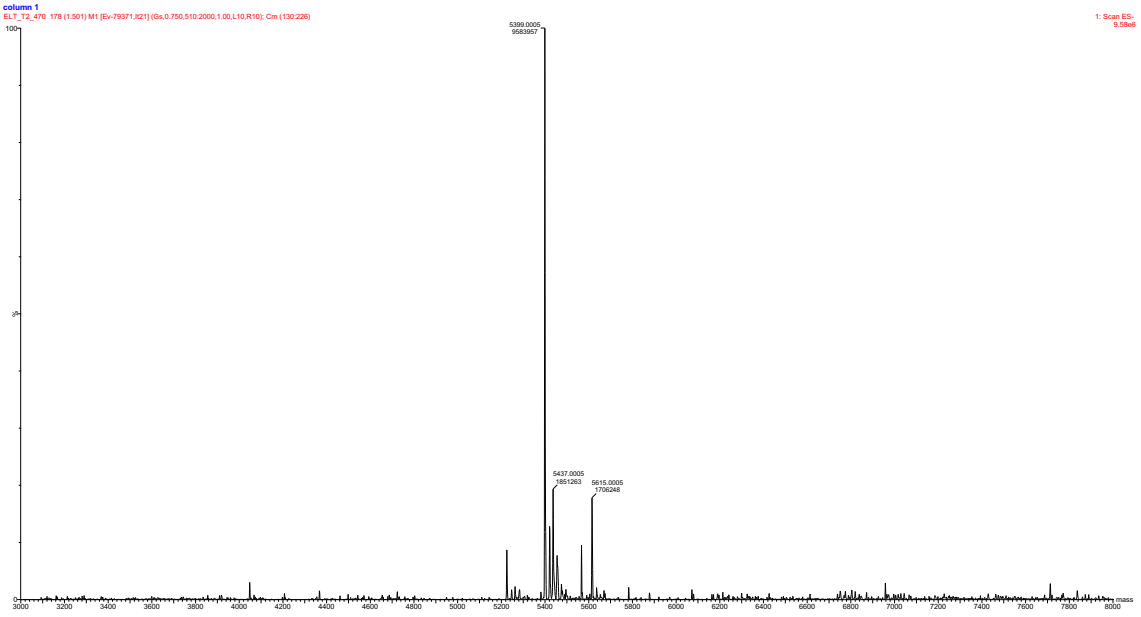


Molecular Weight: 5400.66

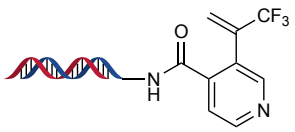
ELT_470 - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)





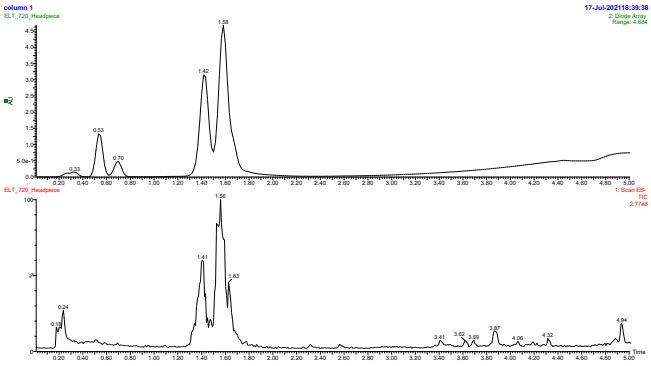


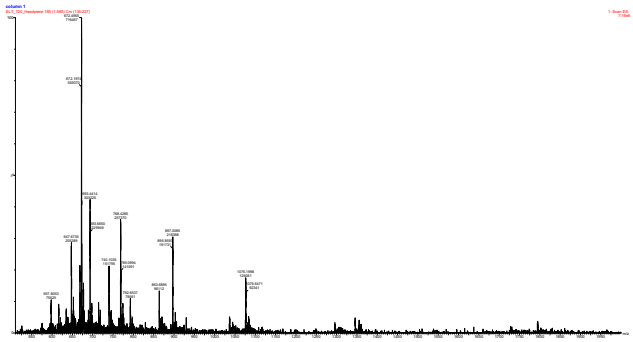
Headpiece 1G

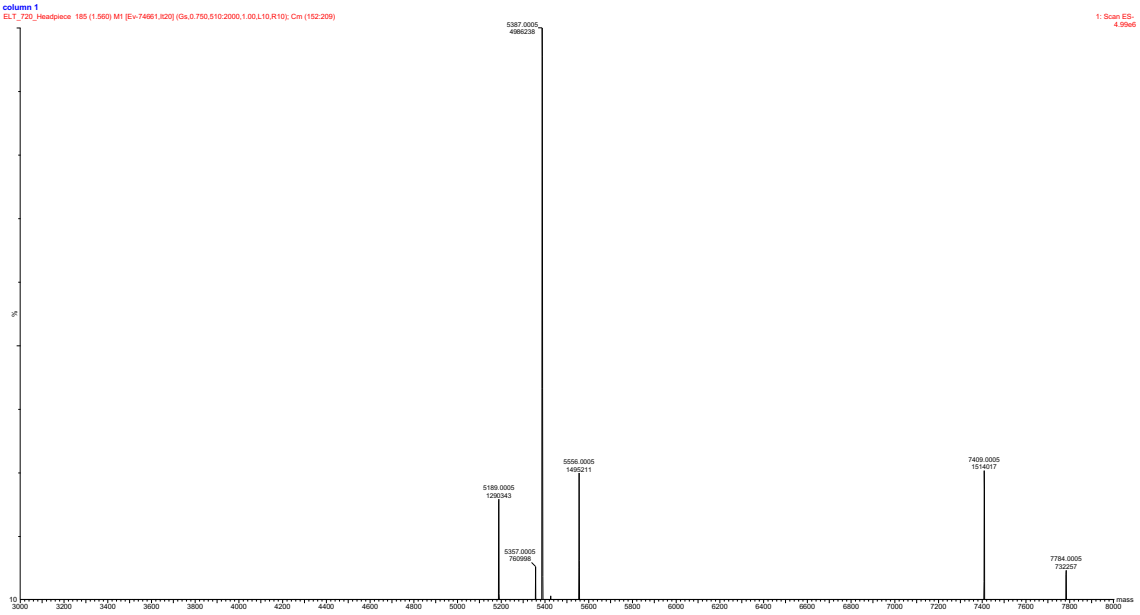


Molecular Weight: 5383.6542

ELT_720_Headpiece - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



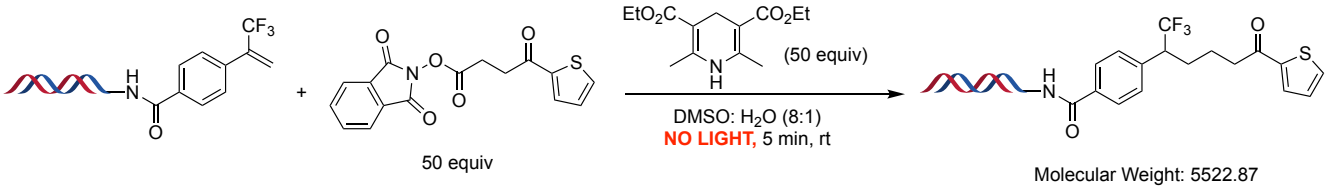




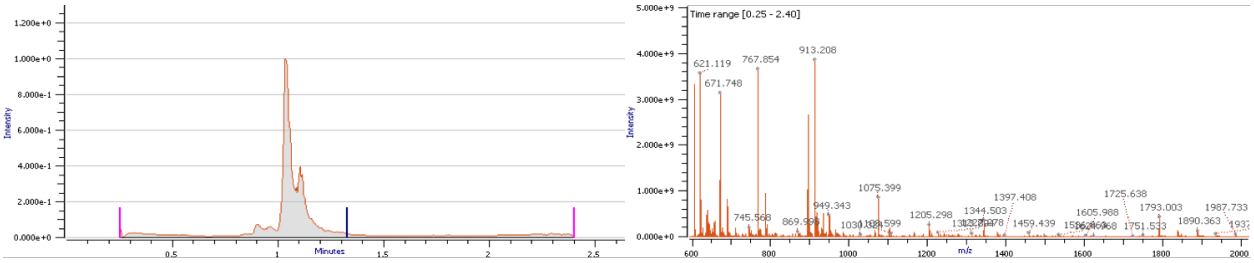
11.1. Control Experiments for On-DNA Reactions

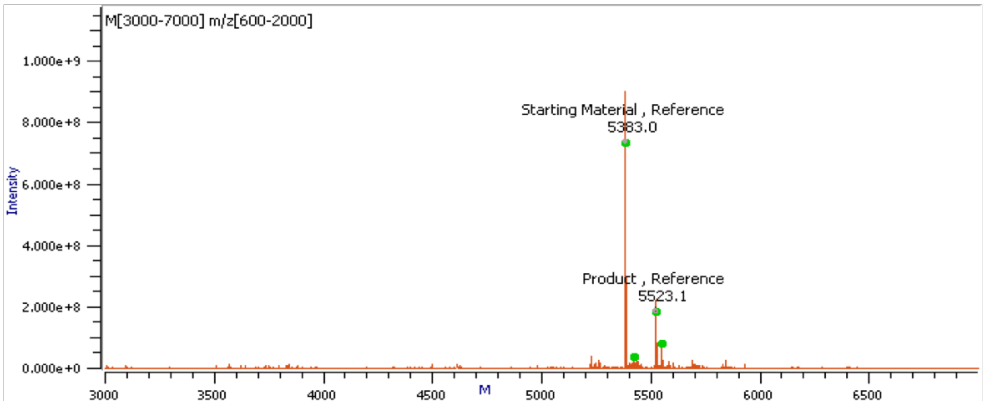
On-DNA photoinduced decarboxylative alkylation of CF_3-alkenes

No light: Product **3a**, minimal product obtained



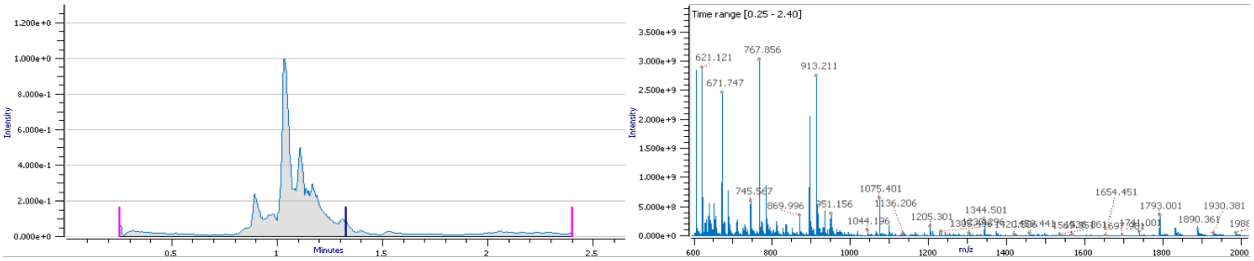
AJC-UPenn-41.raw - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

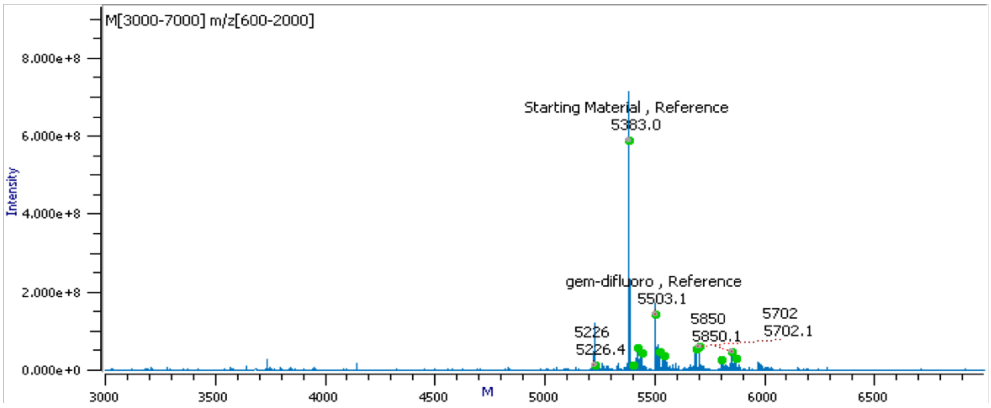




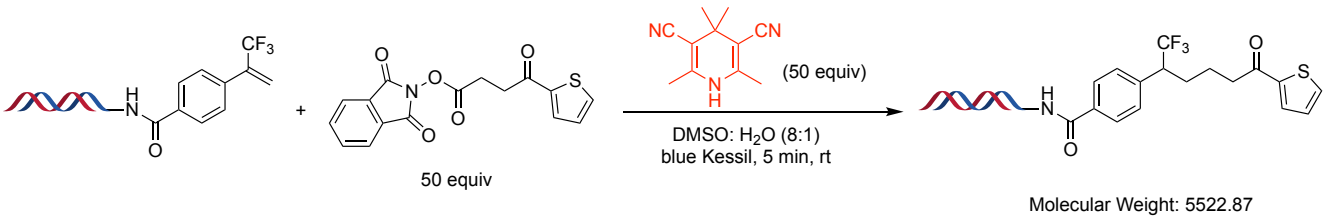
No Hantzsch ester: Product **3a**, traces of product obtained

AJC-UPenn-40.raw - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



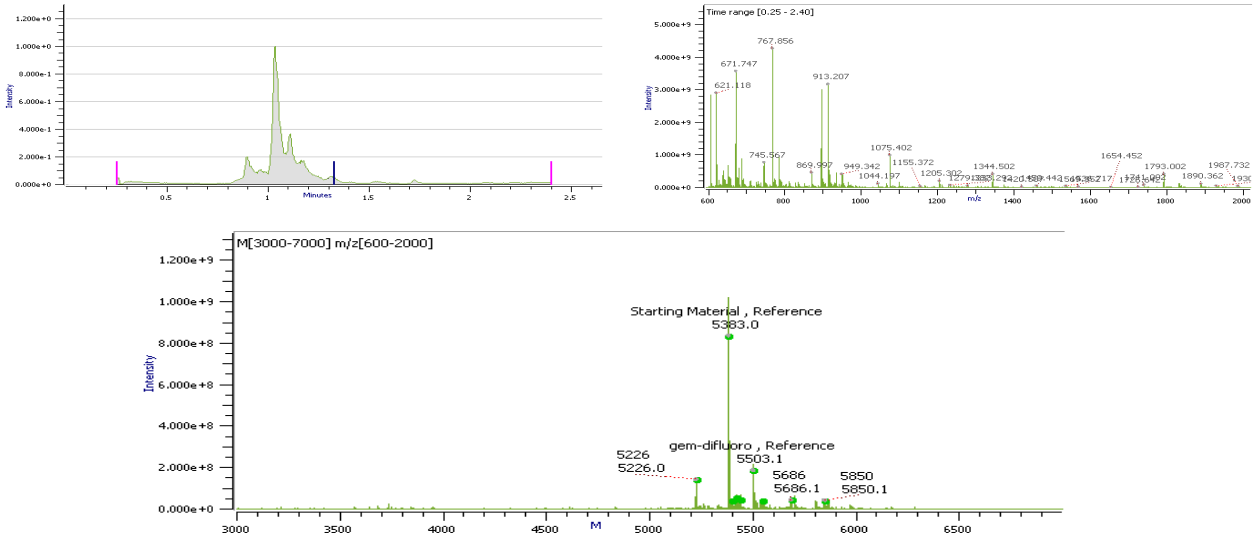


CN-substituted Hantzsch ester: Product **3a**, no product formed



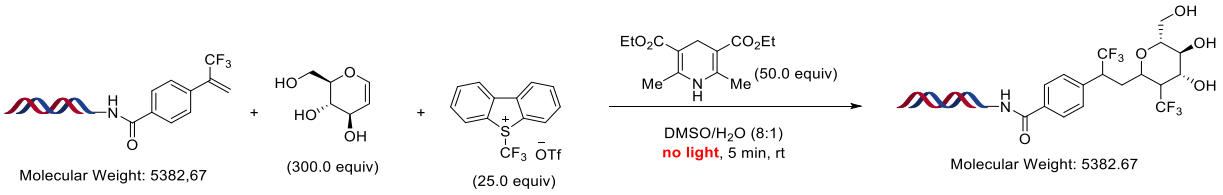
Molecular Weight: 5522.87

AJC-UPenn-44.raw - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

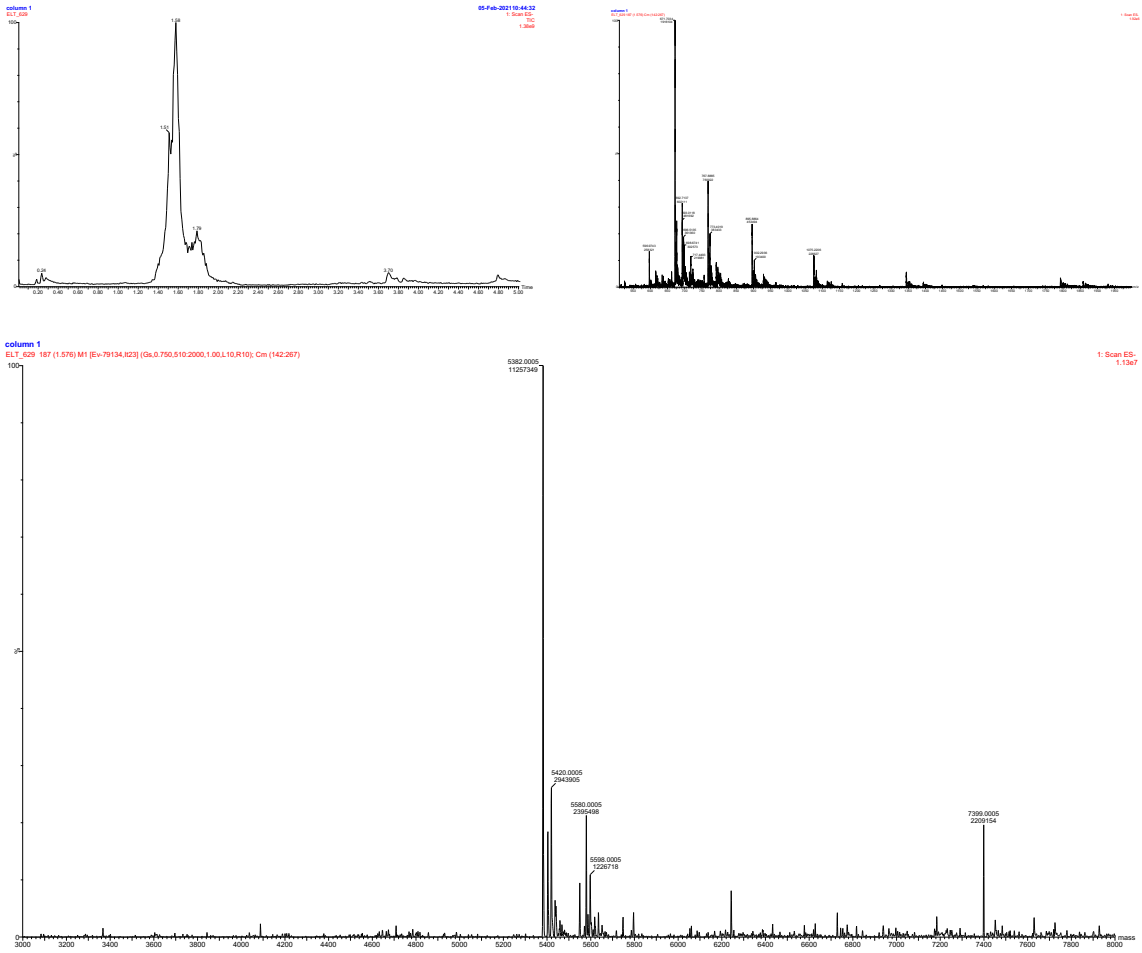


On-DNA photoinduced trifluoromethylation of alkenes

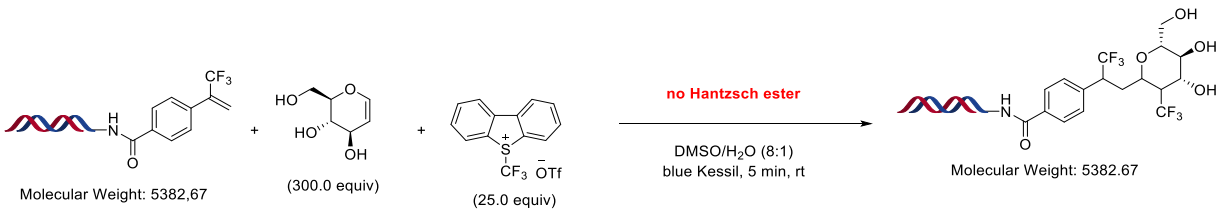
No light: Product **12e**, 5% yield



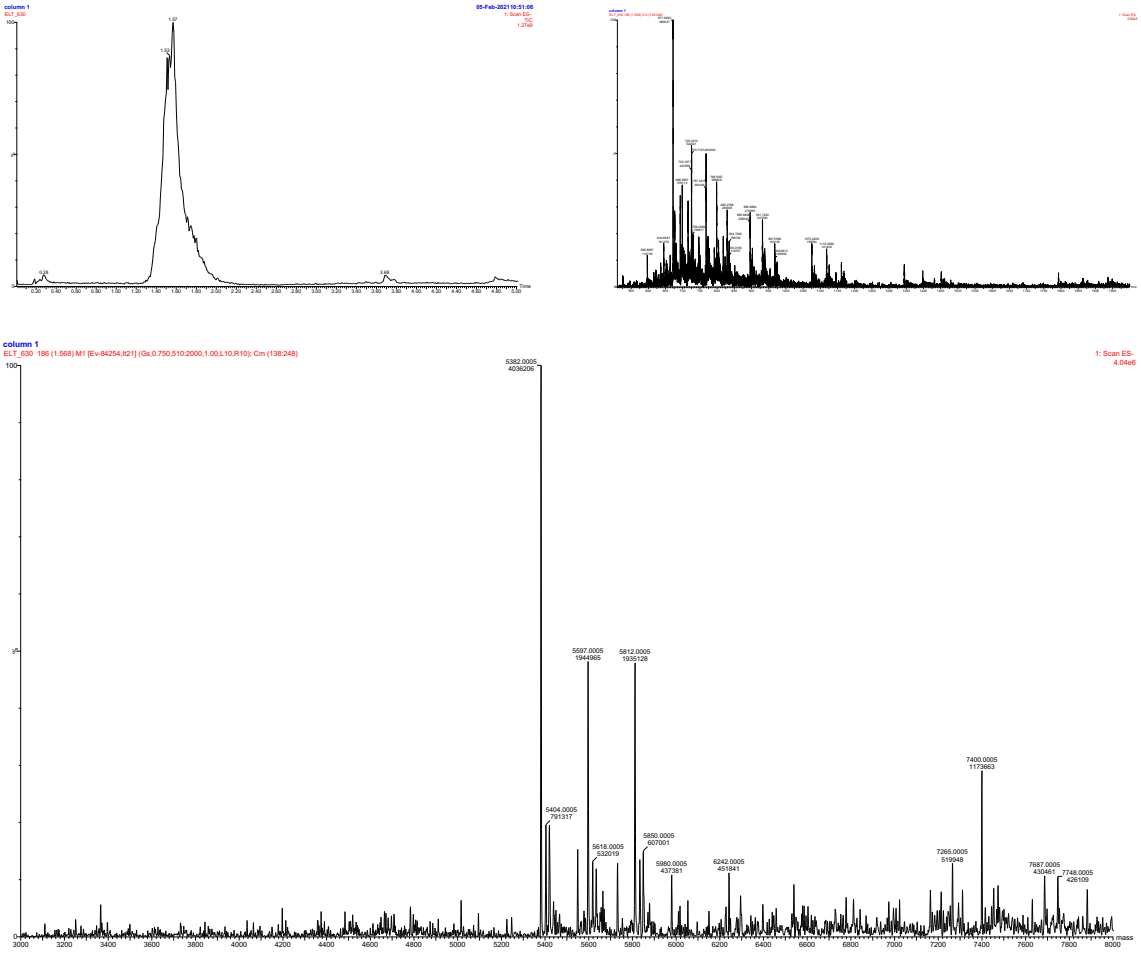
ELT_629 - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



No Hantzsch ester: Product **12e**, 17% yield

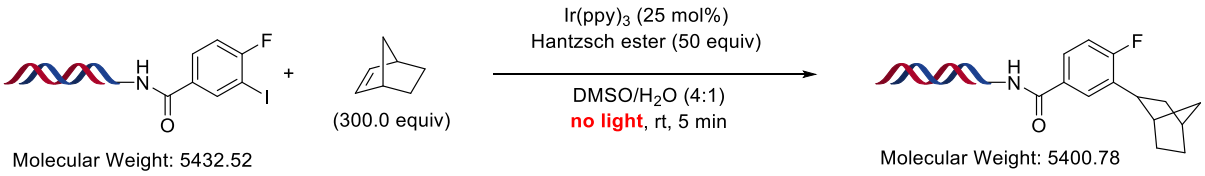


ELT_630 - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



On-DNA photoinduced arylation of alkene feedstocks

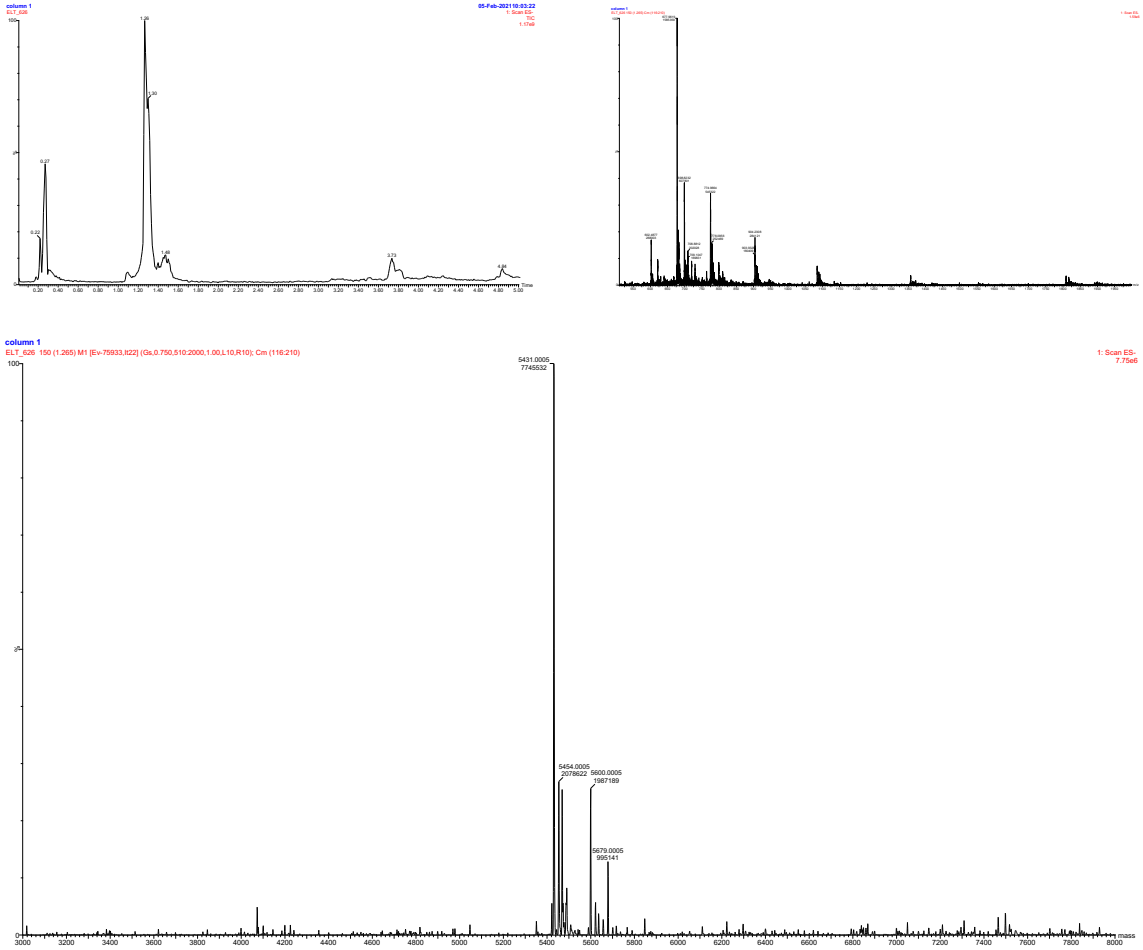
No light: Product **21a**, 0% yield



Molecular Weight: 5432.52

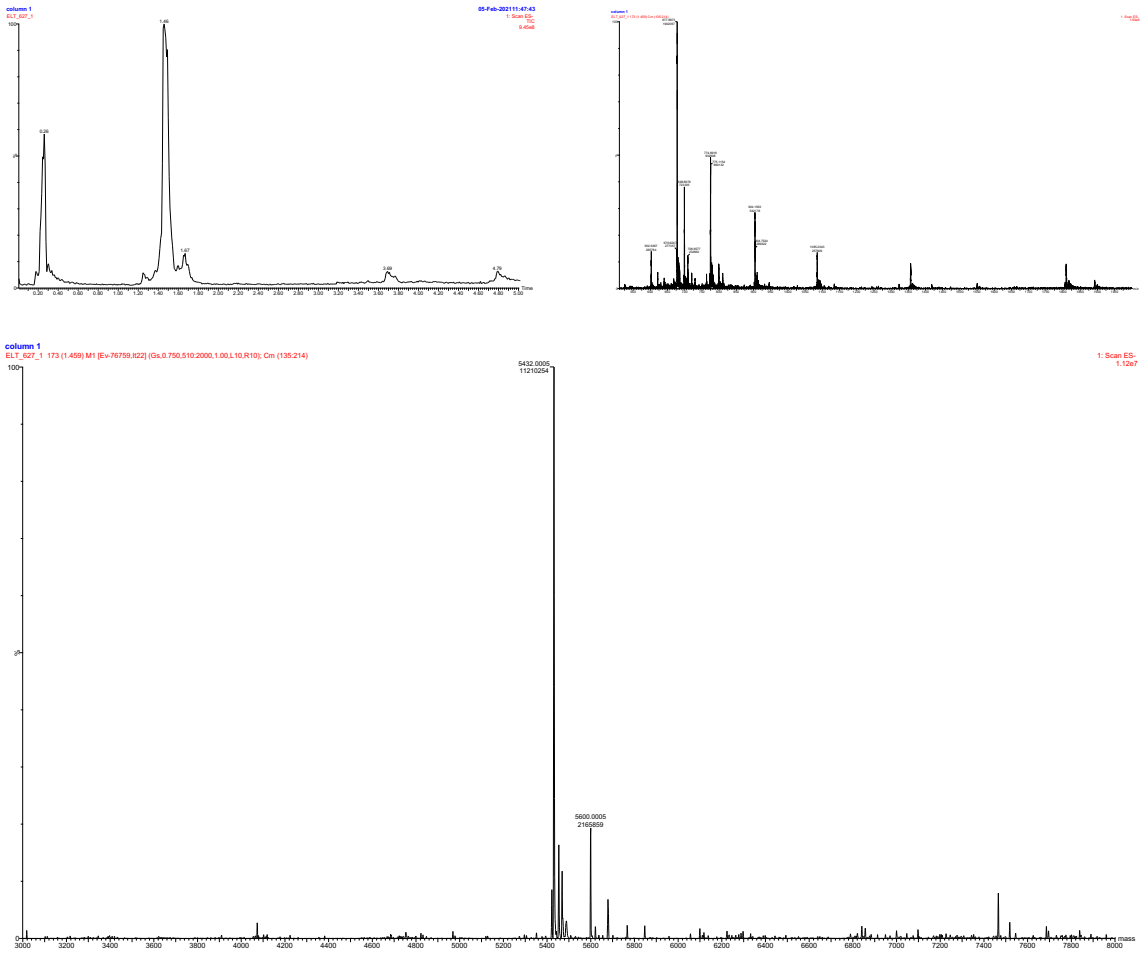
Molecular Weight: 5400.78

ELT_626 - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



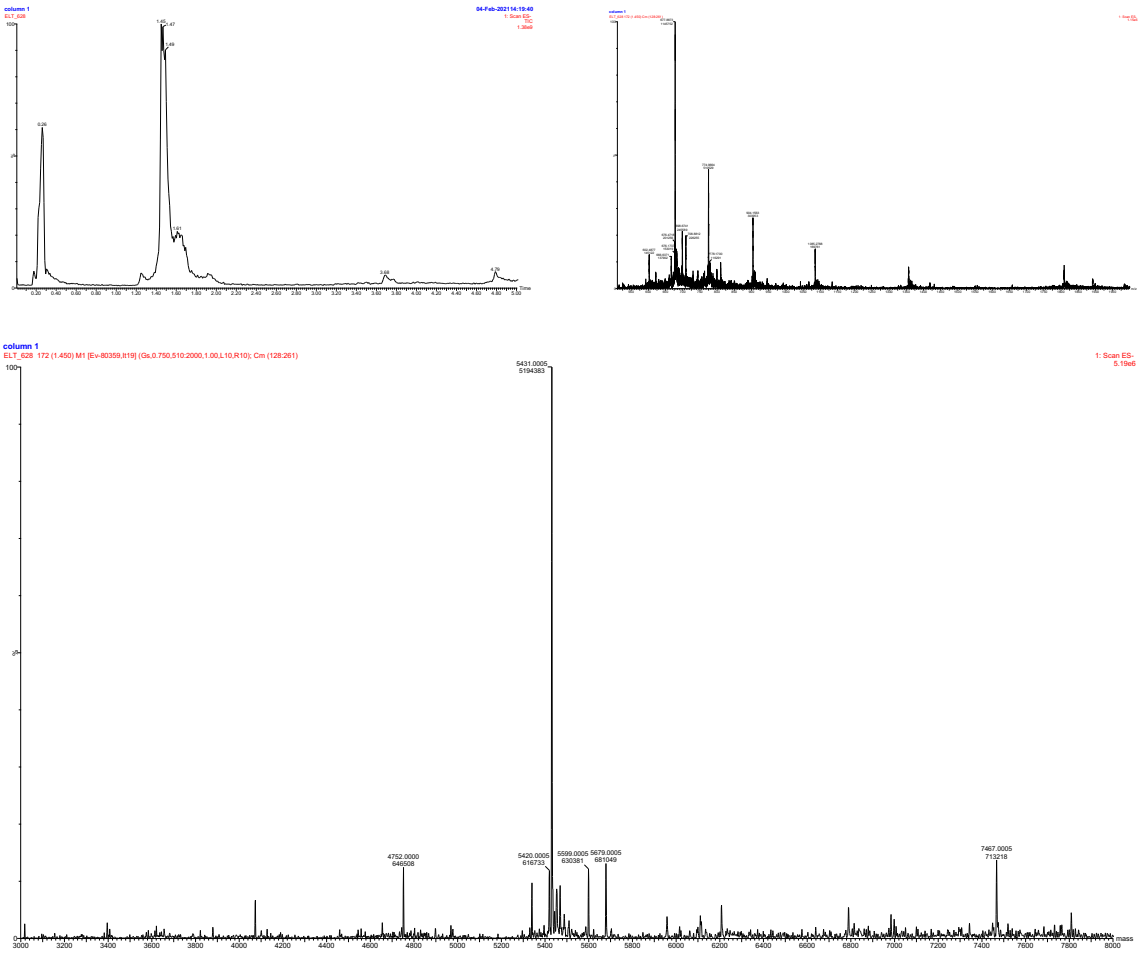
No photocatalyst: Product **21a**, 0% yield

ELT_627 - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



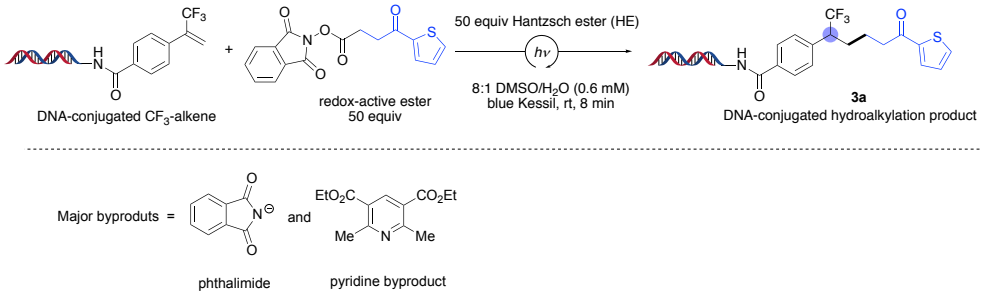
No Hantzsch ester: Product **21a**, 0% yield

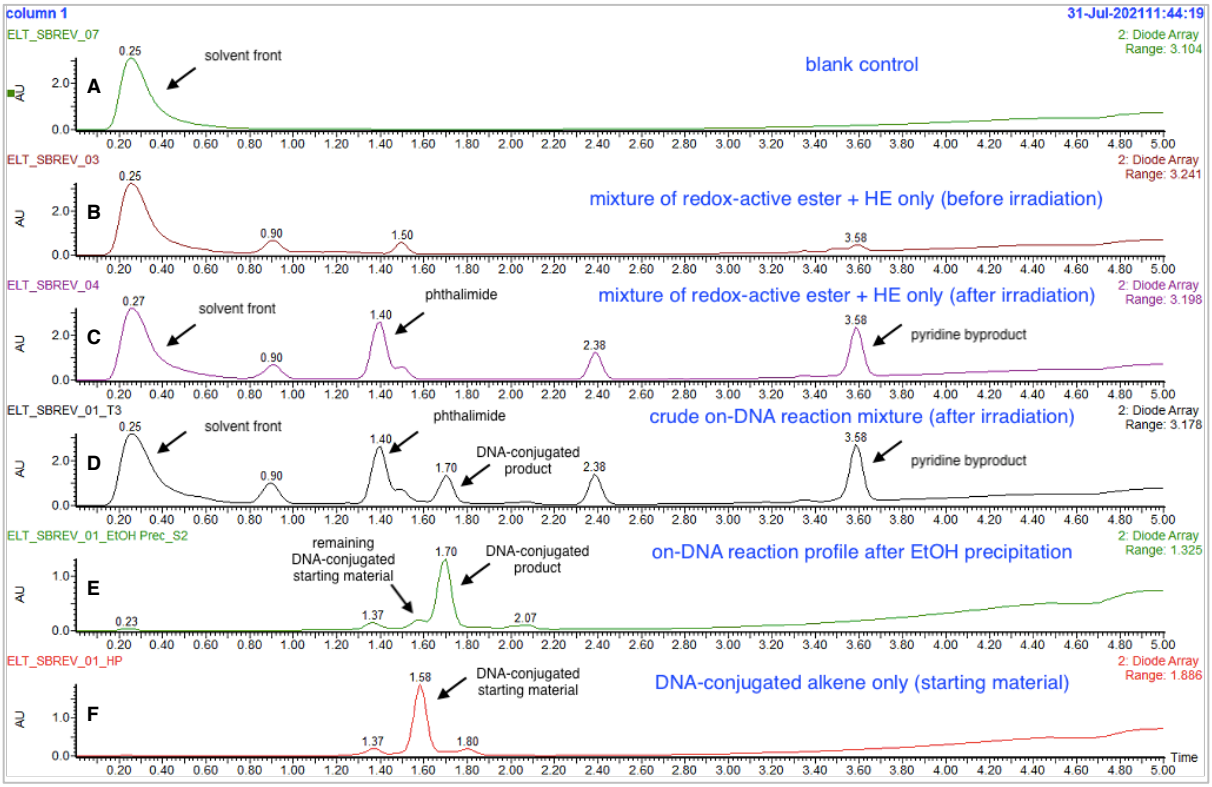
ELT_628 - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



11.2. Determination of Yields for On-DNA Reactions

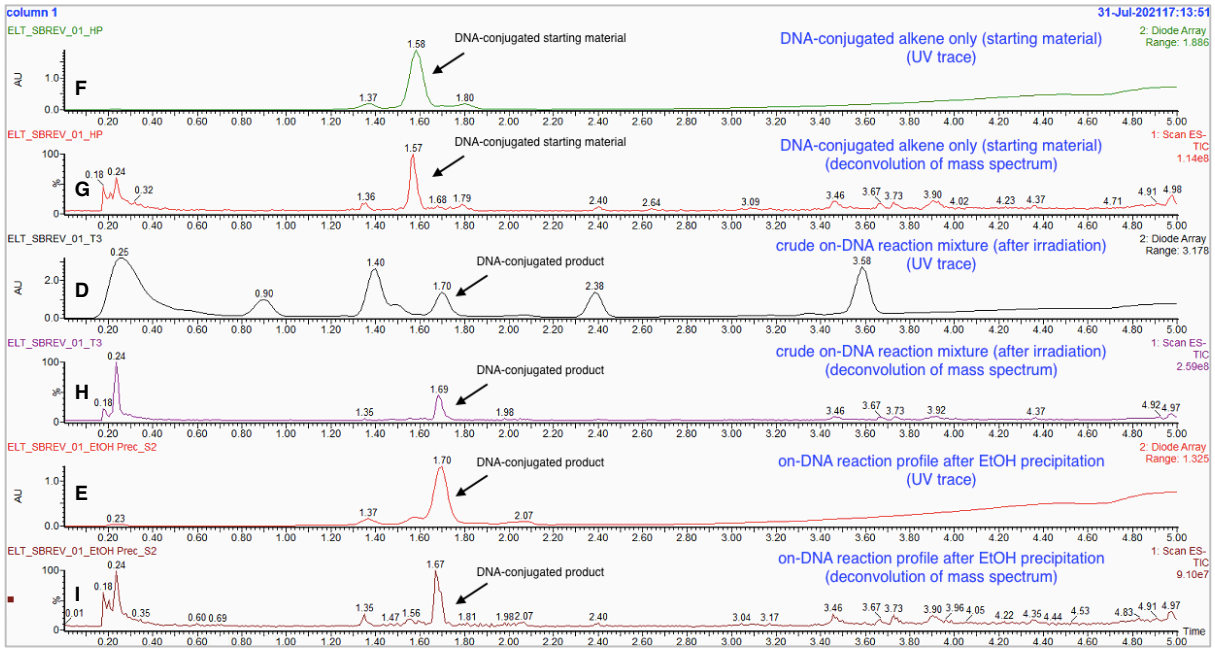
*LCMS analysis of exemplary example **3a**: Analysis of reaction components as well as the on-DNA reaction mixtures before and after ethanol precipitation:*





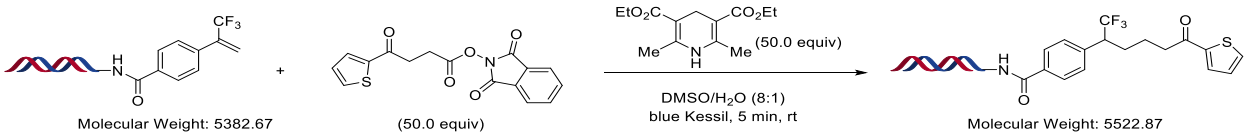
As demonstrated from UV traces **D** & **E** for exemplary substrate **3a**, the organic byproducts can be removed by standard DEL purification procedures (following the EtOH precipitation protocol described in section 2.2). These UV traces correlate with MS chromatograms **H** & **I** (see below). Because the MS chromatograms are similar, and the UV trace post purification resemble the MS trace, the conversions herein were judged from the deconvoluted MS spectra on unpurified reaction samples for practical reasons.

Correlation of UV traces of DNA-adducts with MS chromatograms for substrate **3a**:

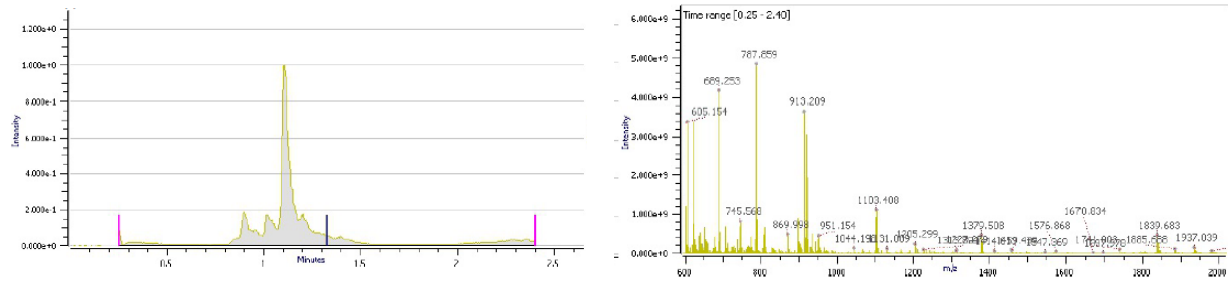


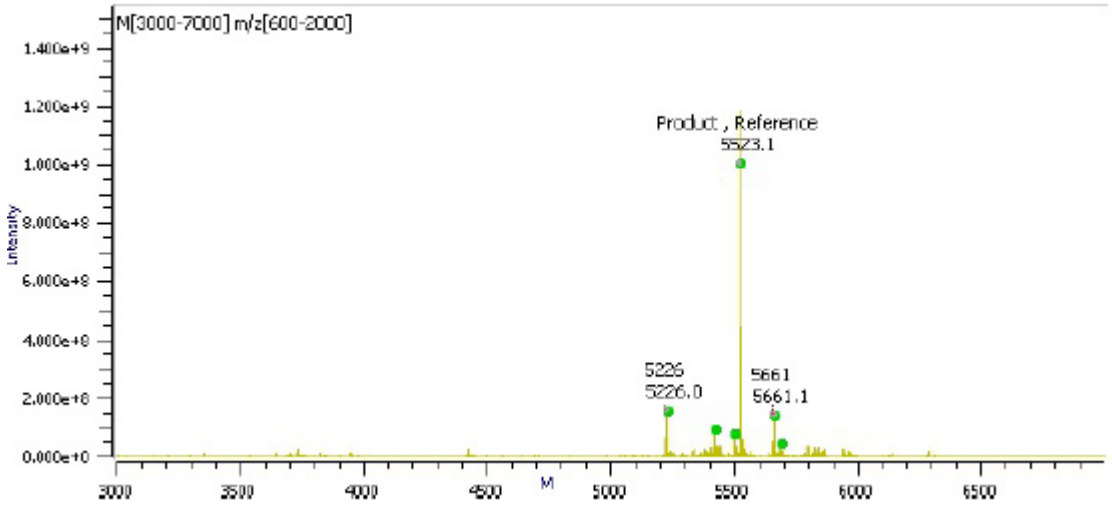
Conversion of on-DNA photoinduced decarboxylative alkylation of CF_3-alkenes (Scheme 3 and 4):

Product **3a**, 84% yield

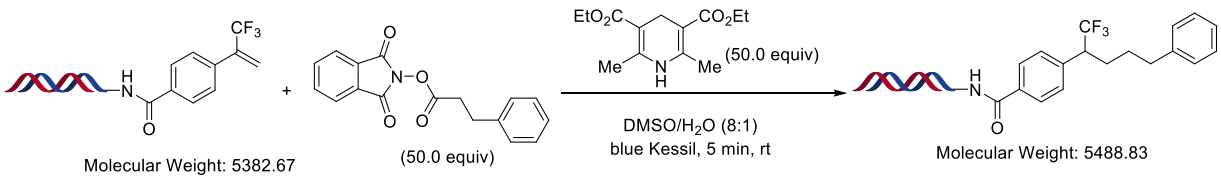


ELT_038, AJC-UPenn-035.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

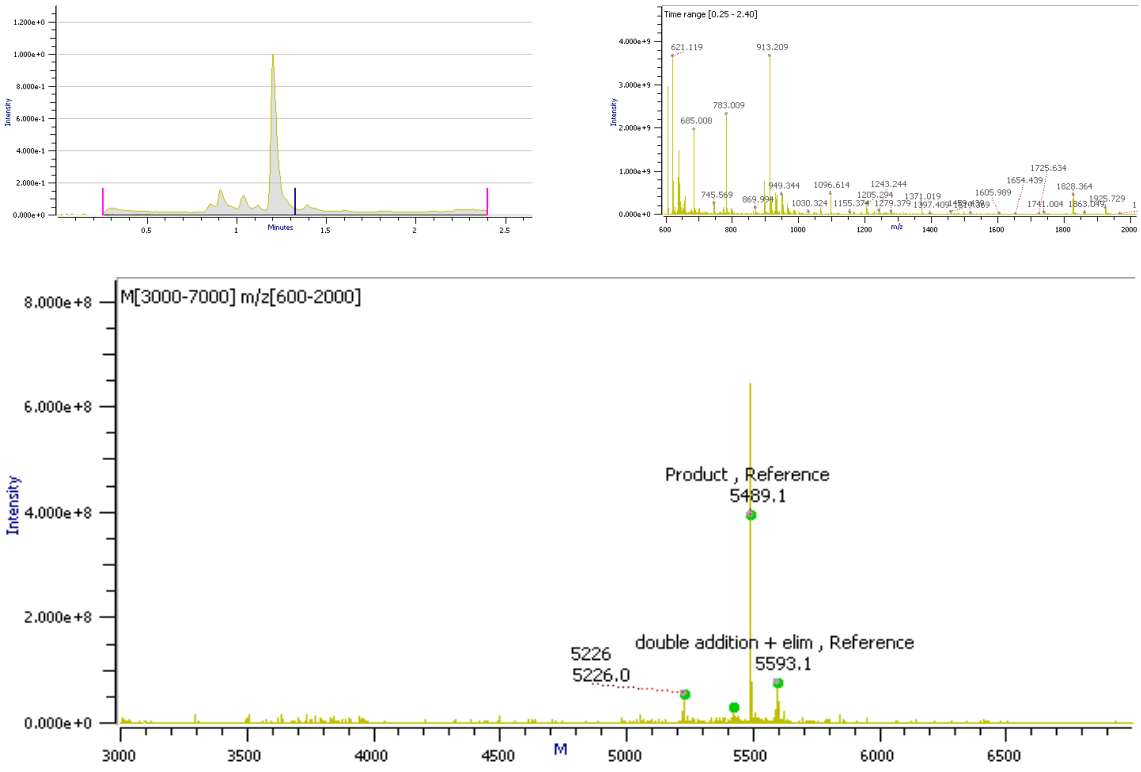




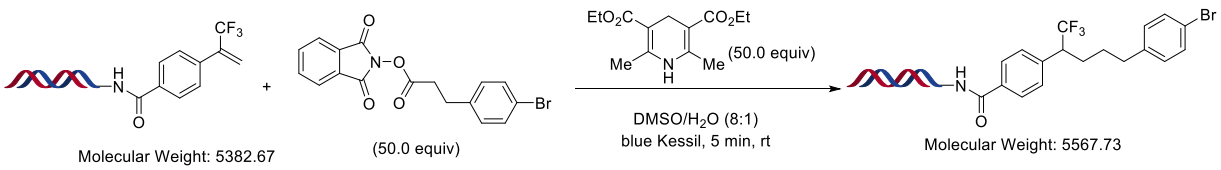
Product **3b**, 89% yield



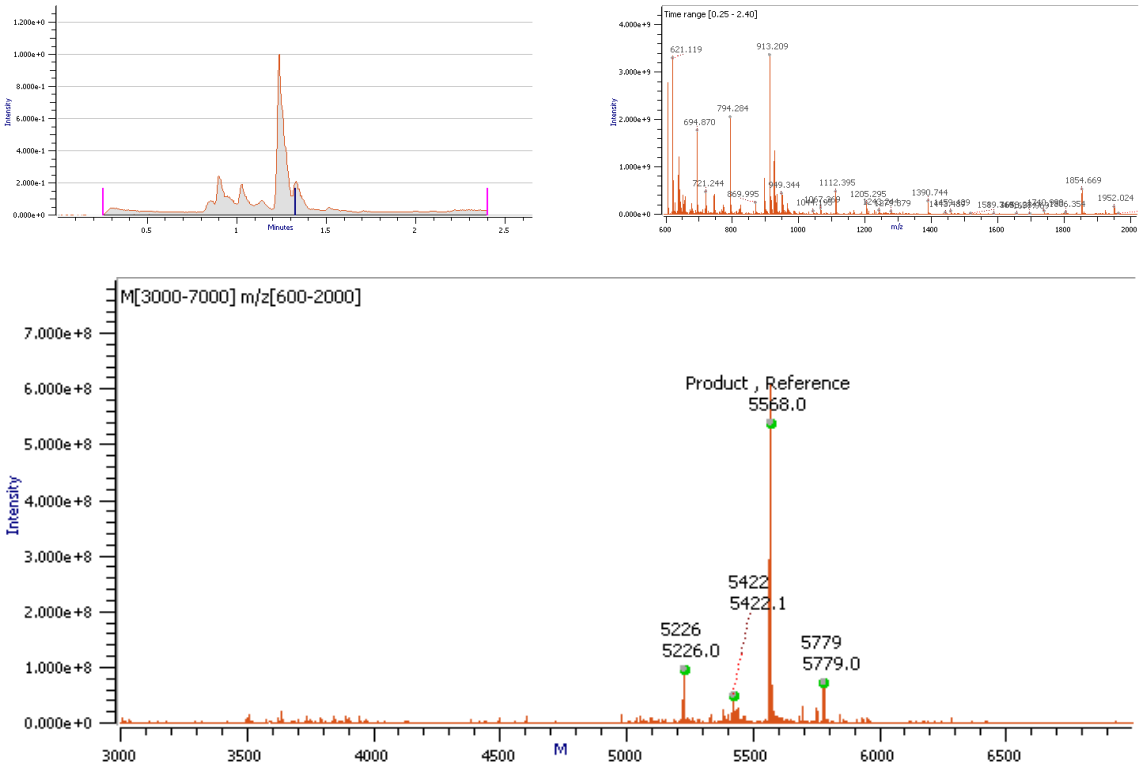
ELT_76, AJC-UPenn-76.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



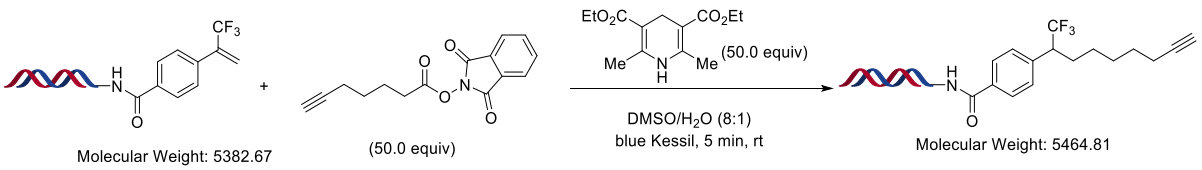
Product **3c**, 90% yield



ELT_69, AJC-UPenn-69.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



Product **3d**, 59% yield

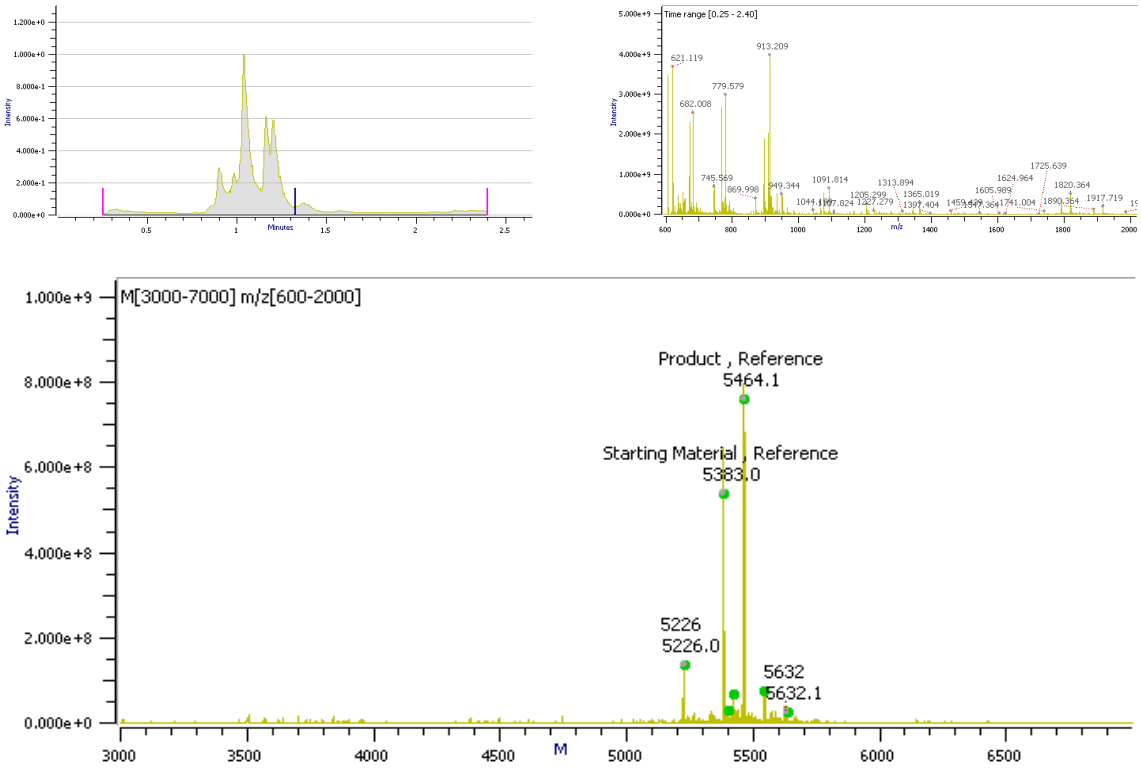


Molecular Weight: 5382.67

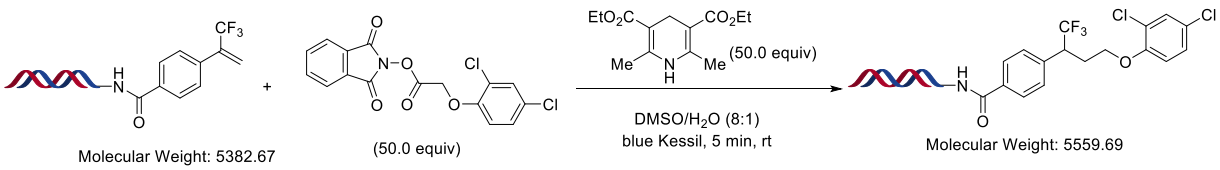
(50.0 equiv)

Molecular Weight: 5464.81

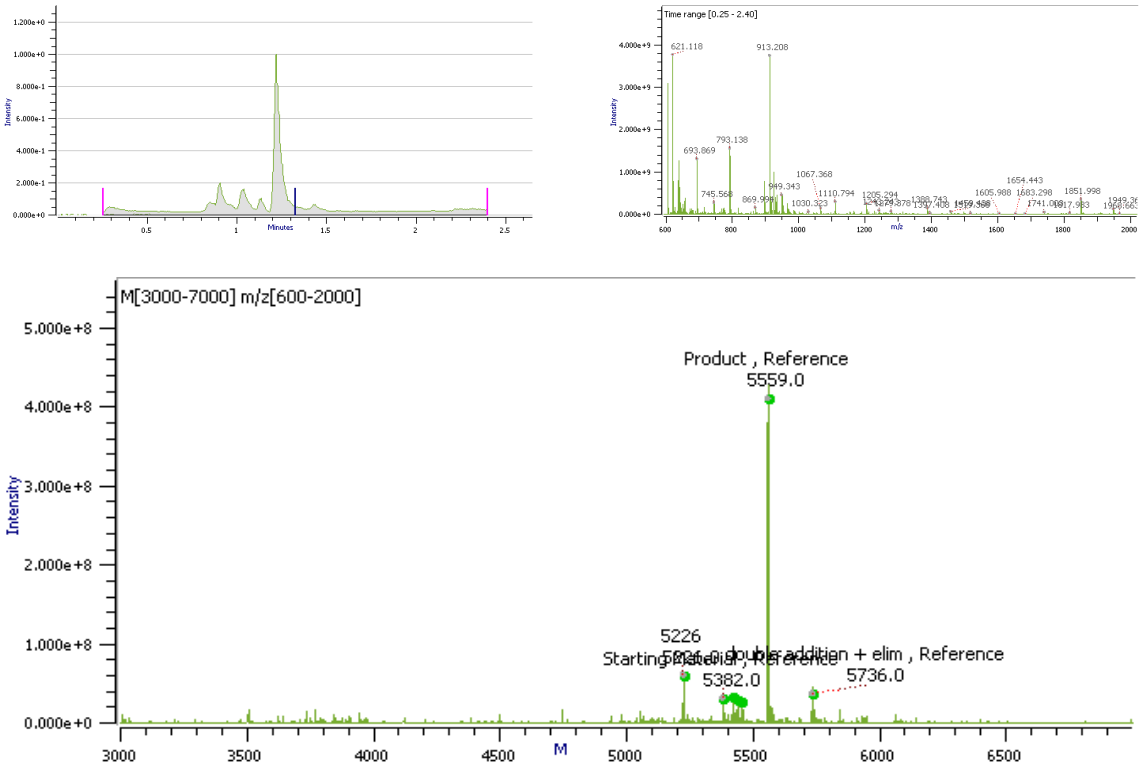
ELT_63, AJC-UPenn-63.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



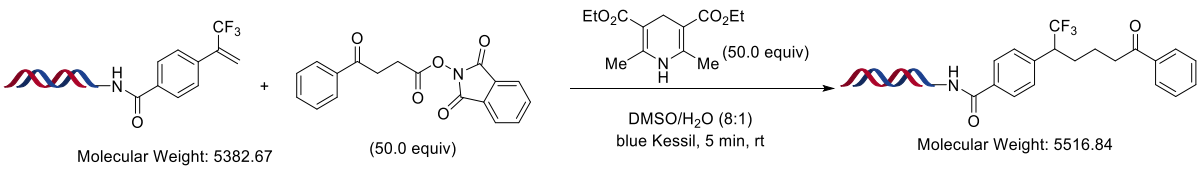
Product **3e**, 83% yield



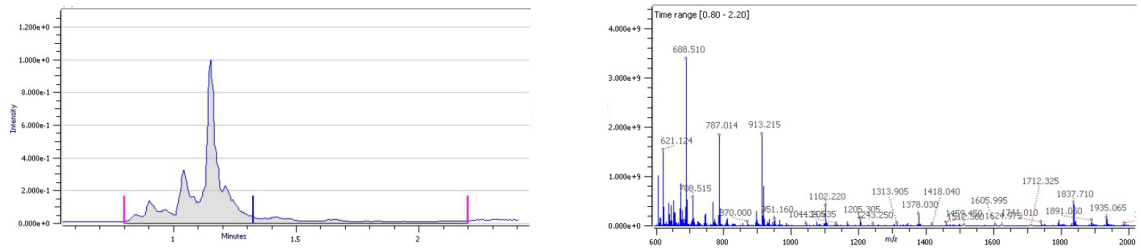
ELT_85, AJC-UPenn-85.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

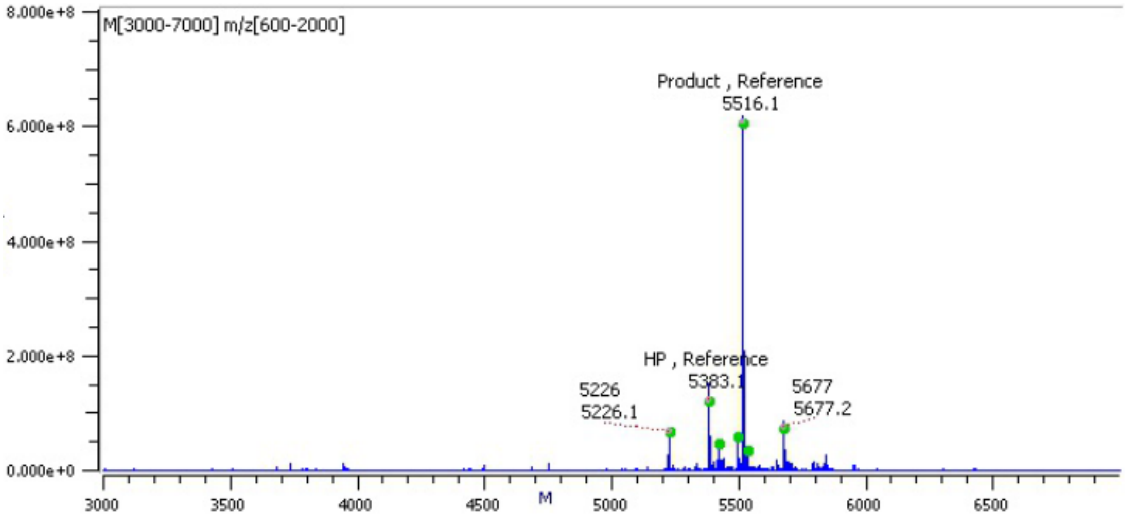


Product **3f**, 76% yield

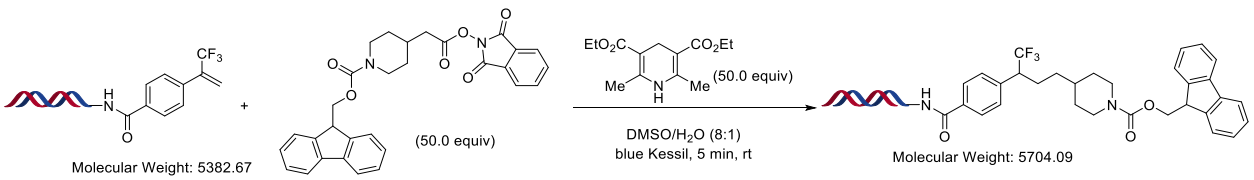


ELT_113, AJC-UPenn-8-19-113.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

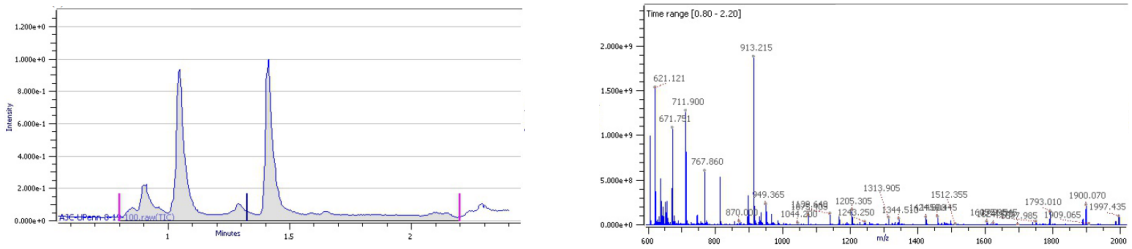


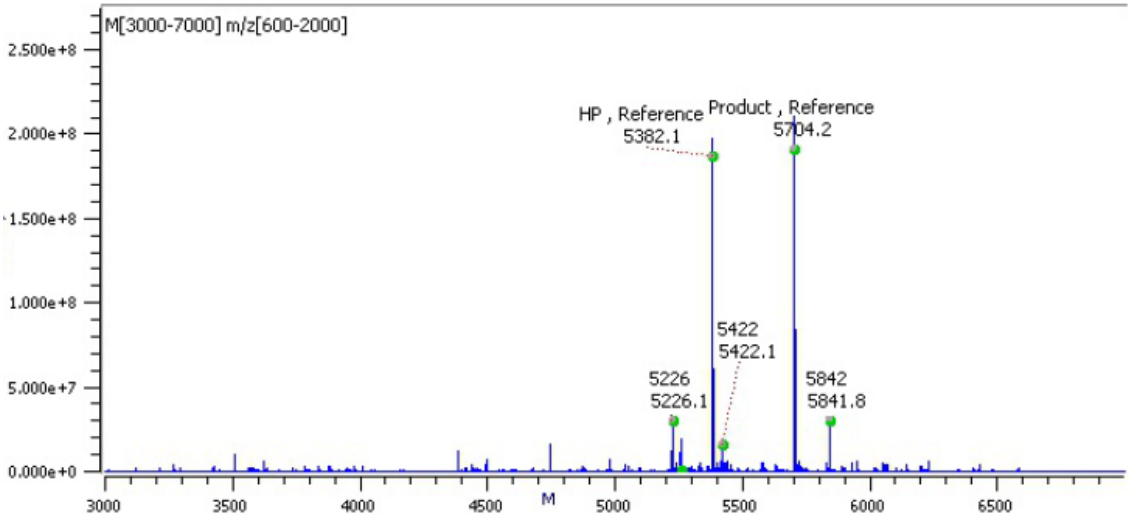


Product **3g**, 53% yield

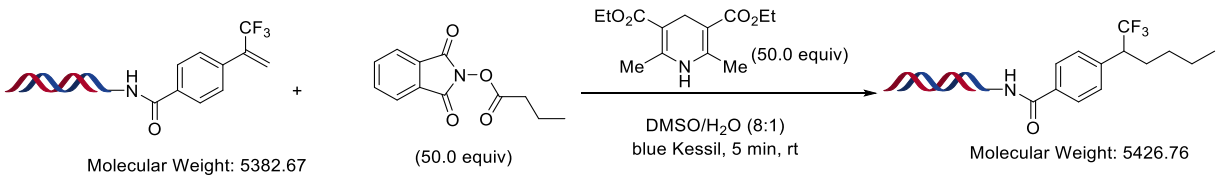


ELT_100, AJC-UPenn-8-19-100.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)





Product **3h**, 80% yield

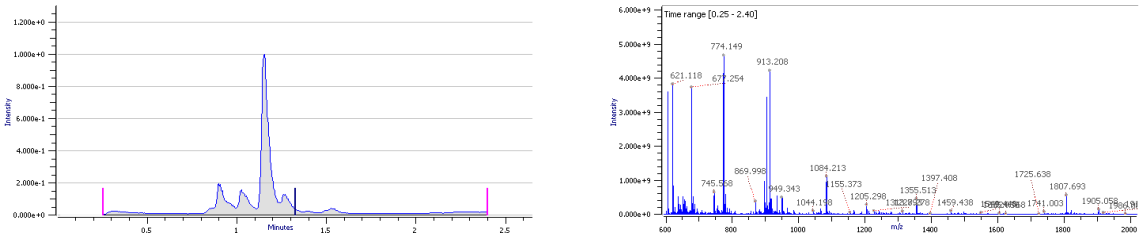


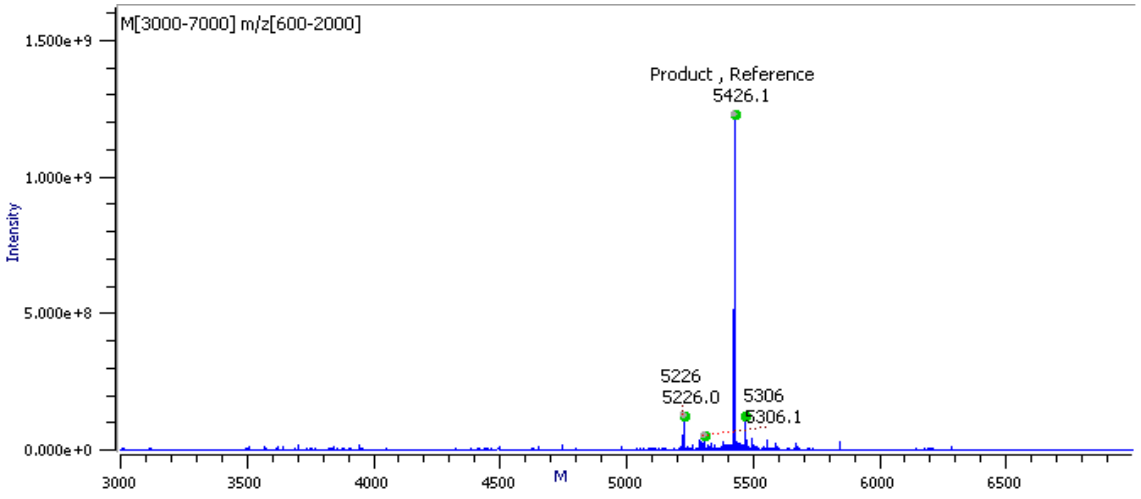
Molecular Weight: 5382.67

(50.0 equiv)

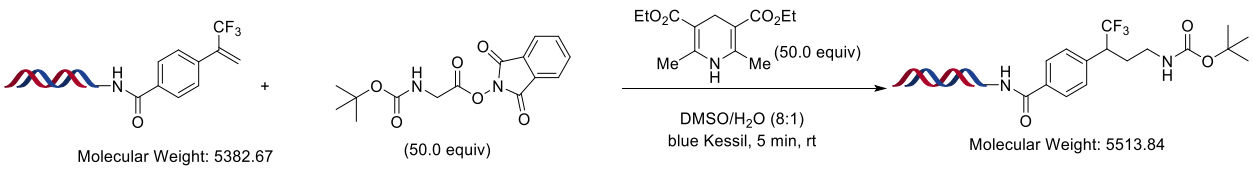
Molecular Weight: 5426.76

ELT_61, AJC-UPenn-61.raw - (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

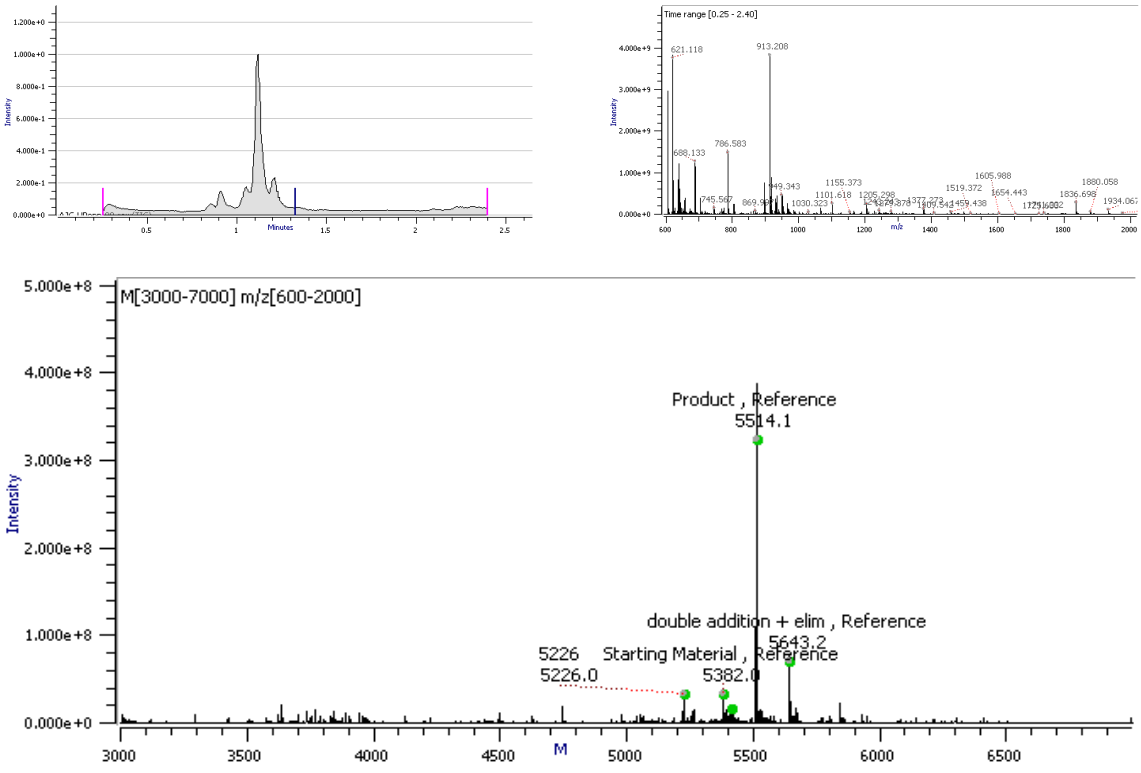




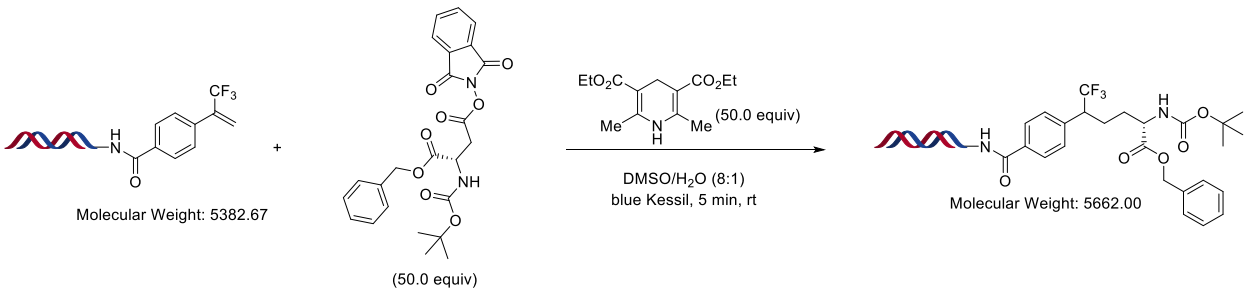
Product **3i**, 86% yield



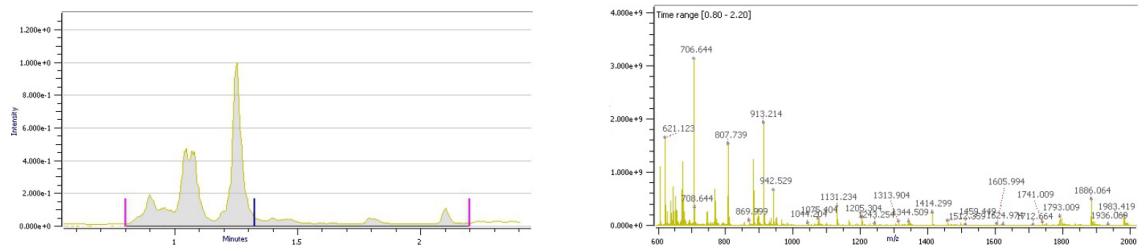
ELT_80, AJC-UPenn-80.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

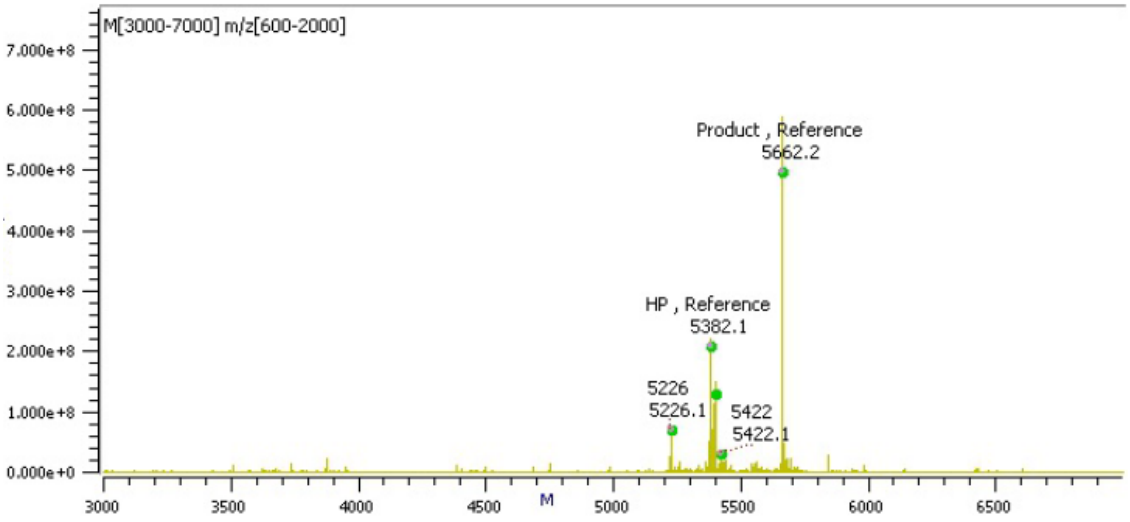


Product **3j**, 67% yield

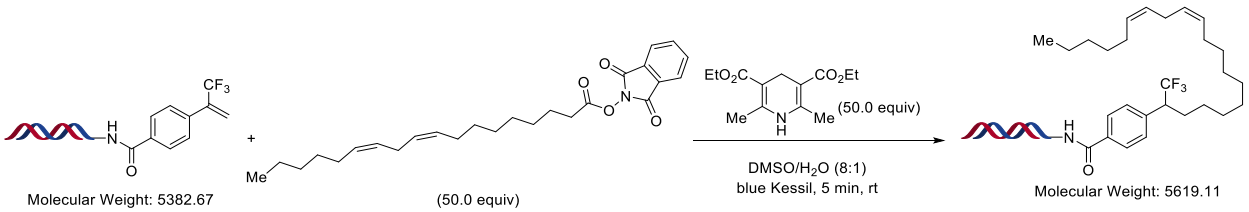


ELT_115, AJC-UPenn-8-19-115.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

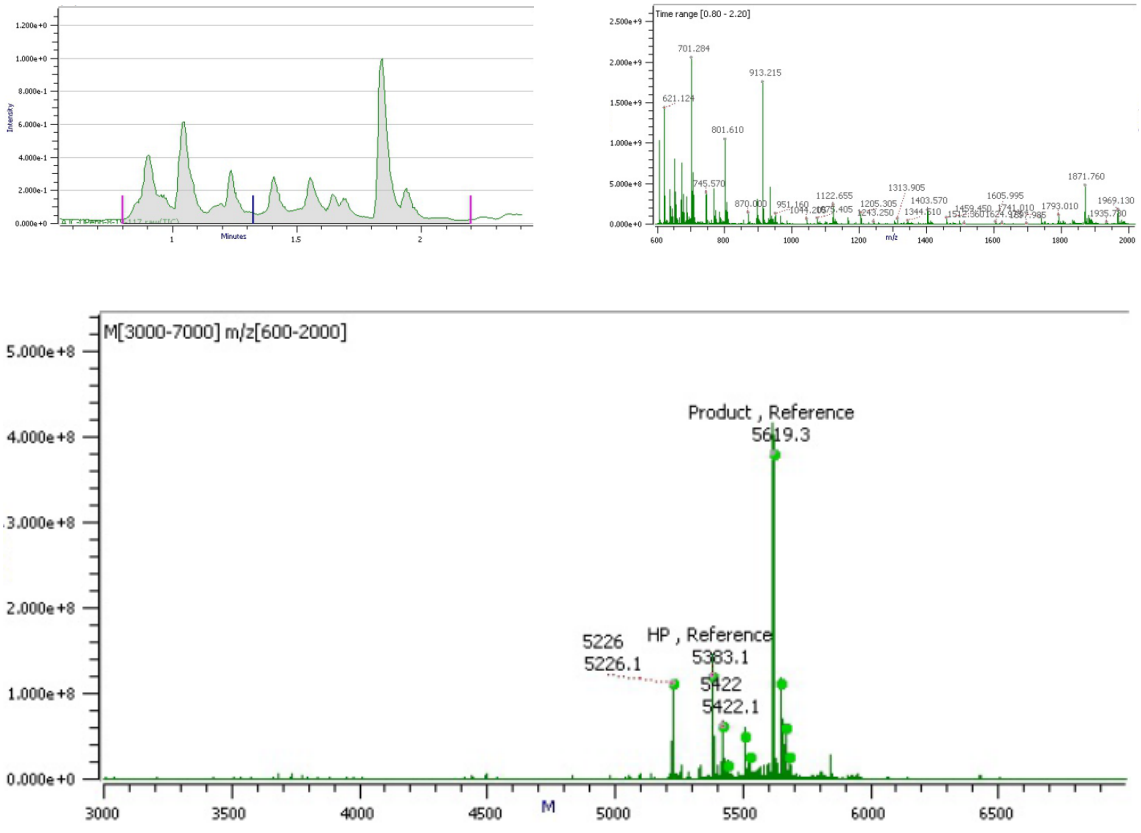




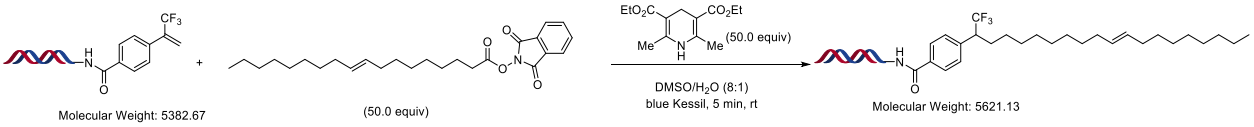
Product **3k**, 50% yield



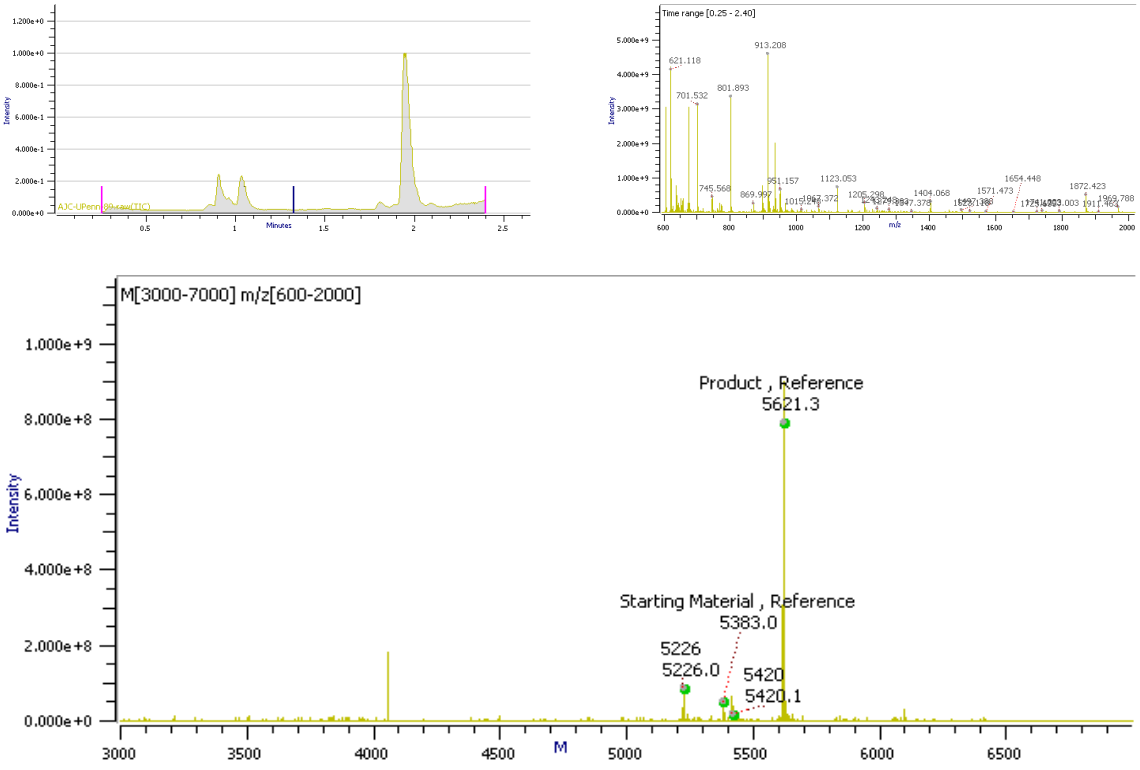
ELT_117, AJC-UPenn-8-19-117.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



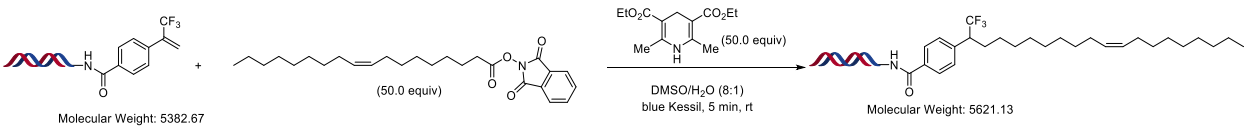
Product **3l**, 83% yield



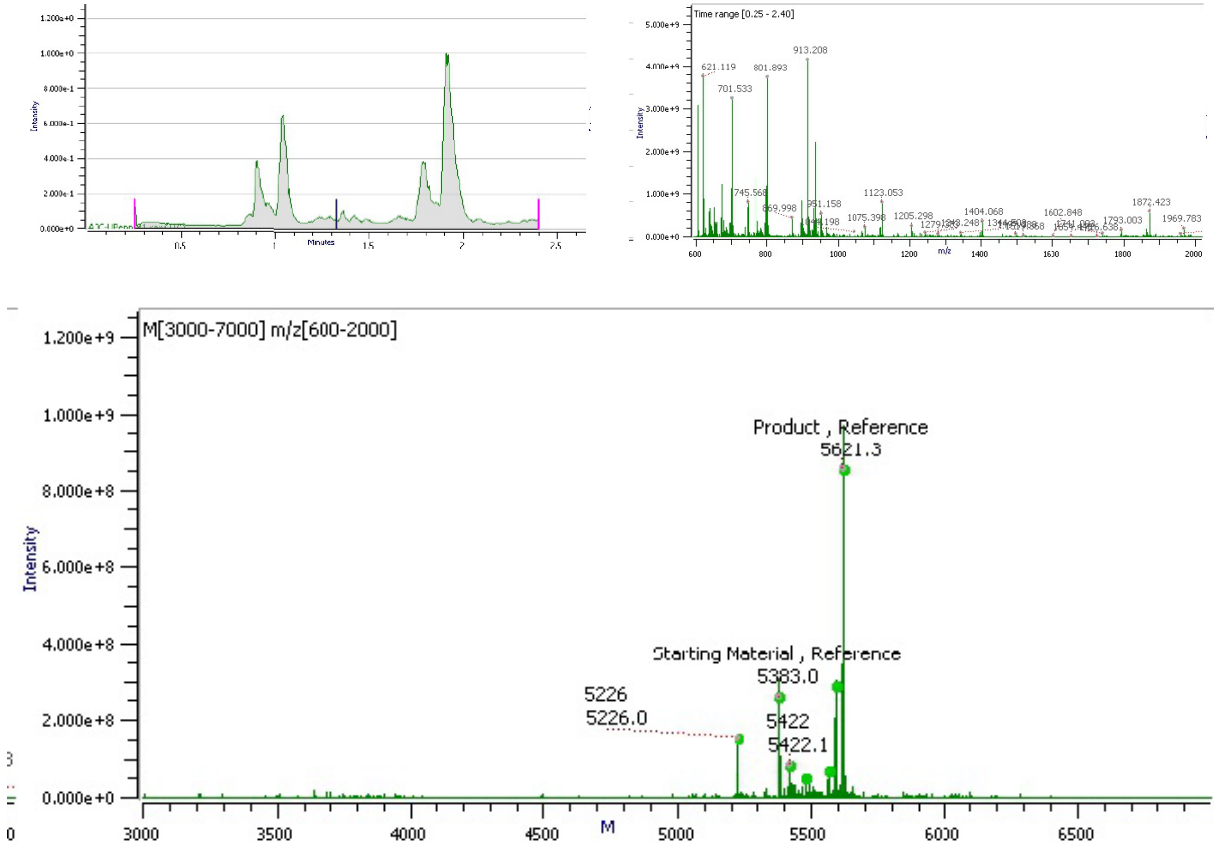
ELT_89, AJC-UPenn-89.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



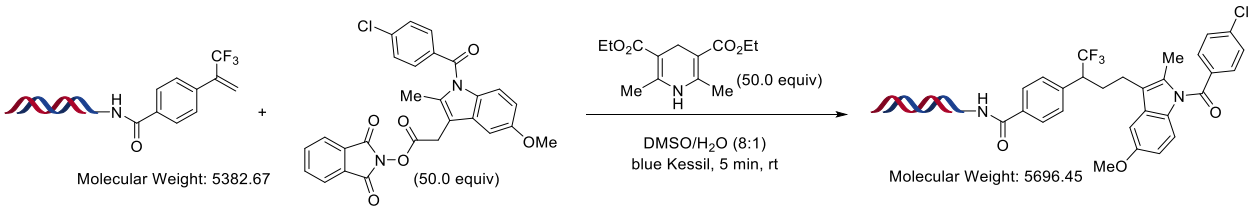
Product **3m**, 61% yield



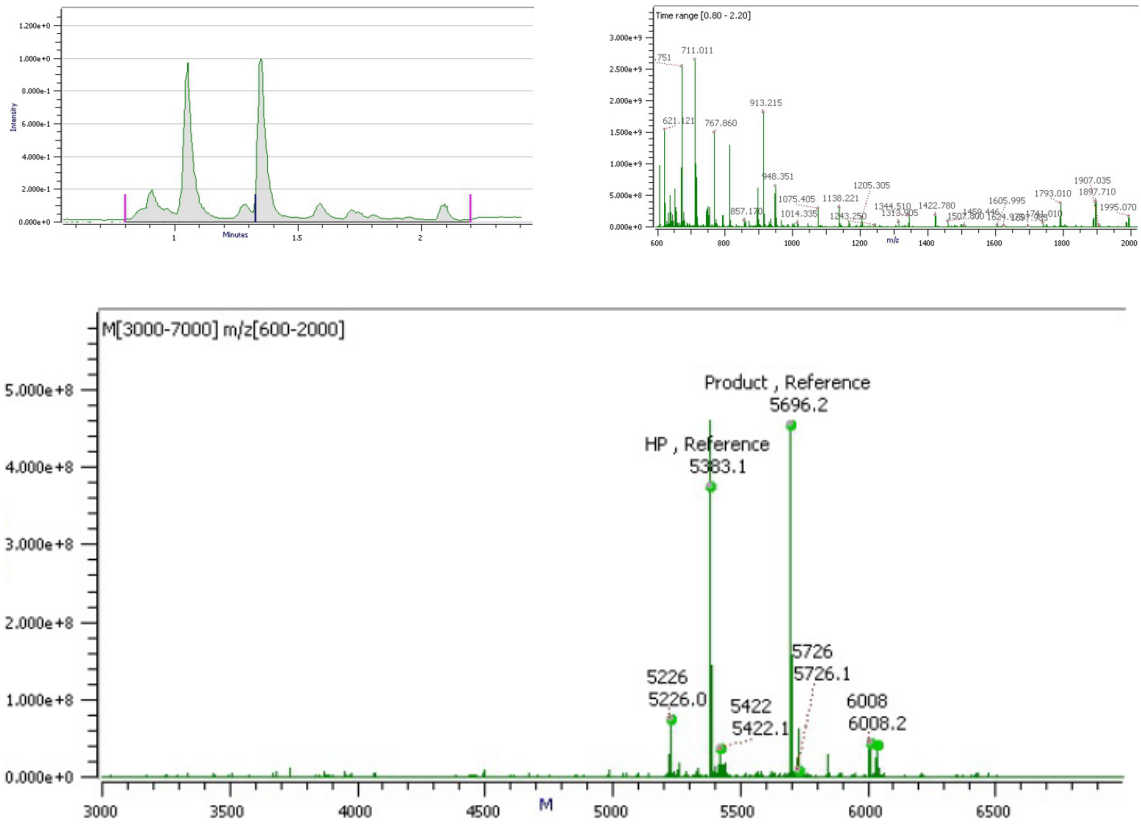
ELT_118, AJC-UPenn-91.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



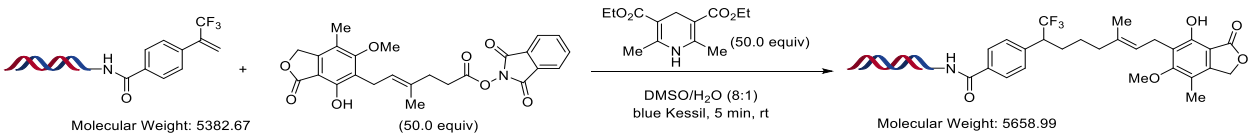
Product **3n**, 56% yield



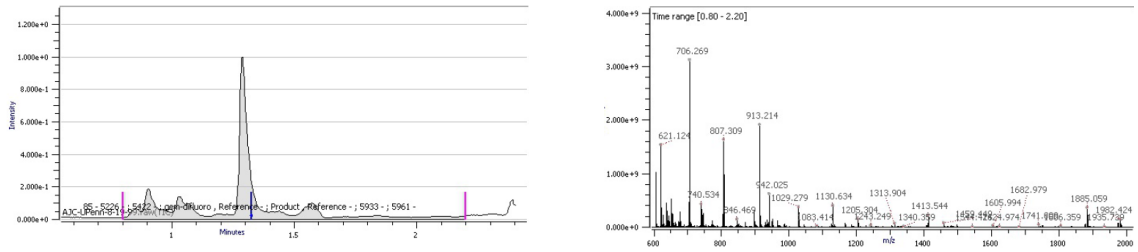
ELT_104, AJC-UPenn-8-19-104.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

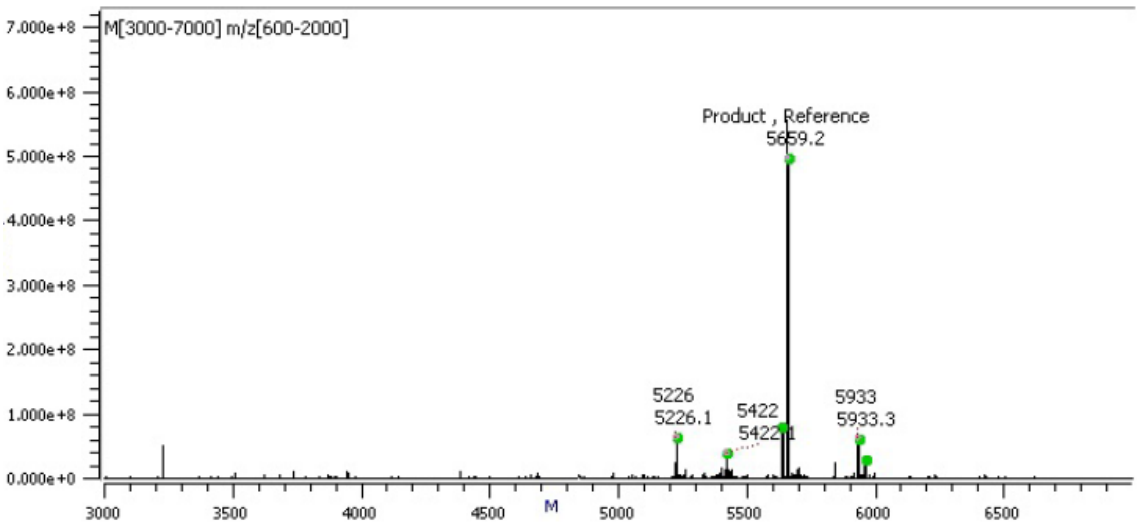


Product **3o**, 82% yield

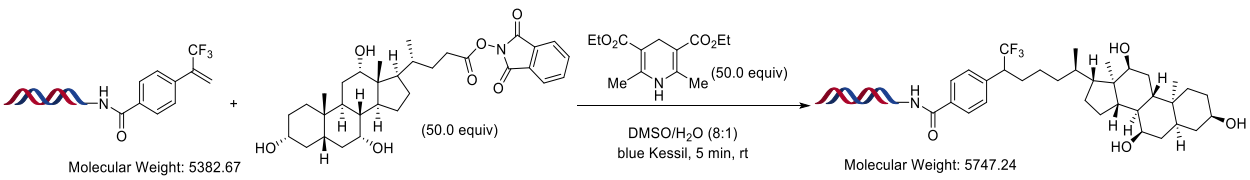


ELT_99, AJC-UPenn-99.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

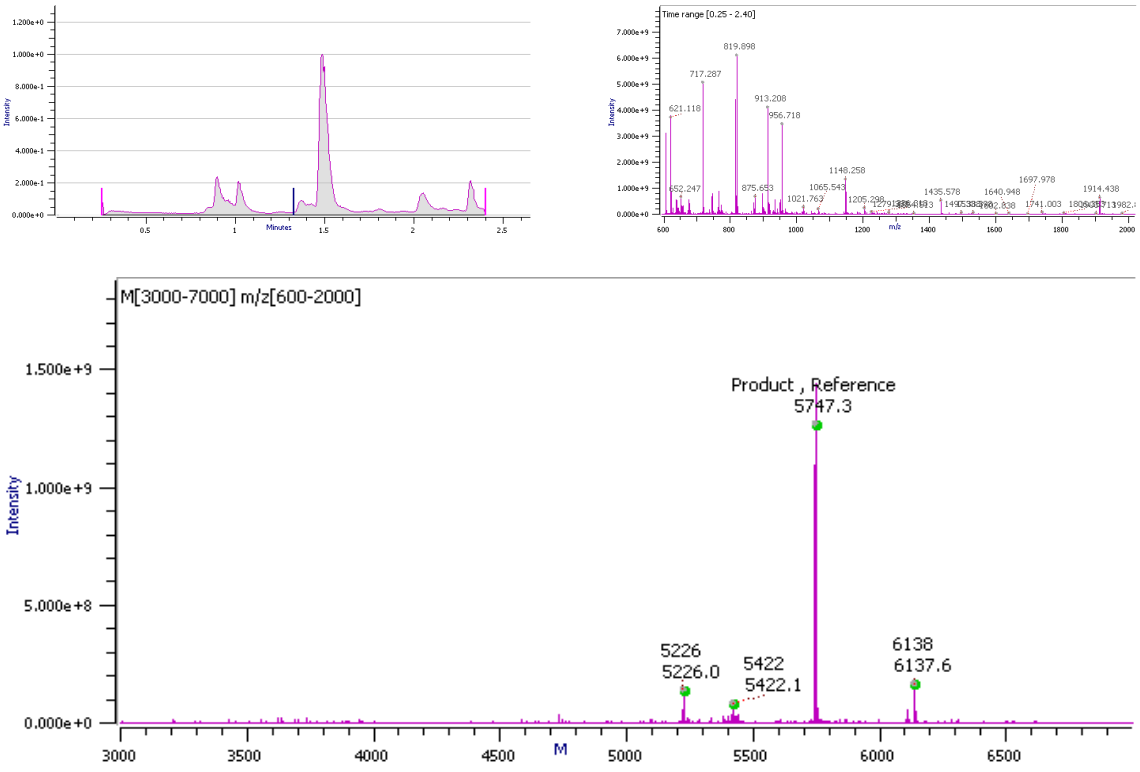




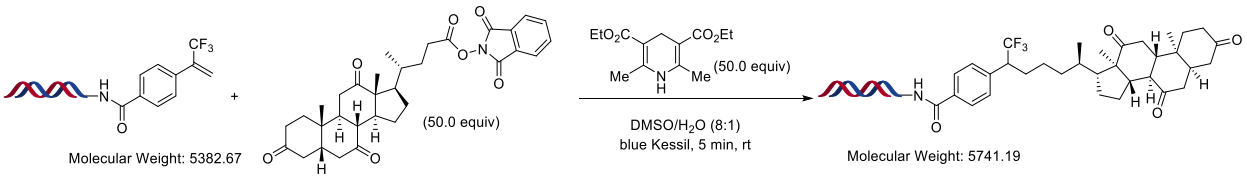
Product **3p**, 97% yield



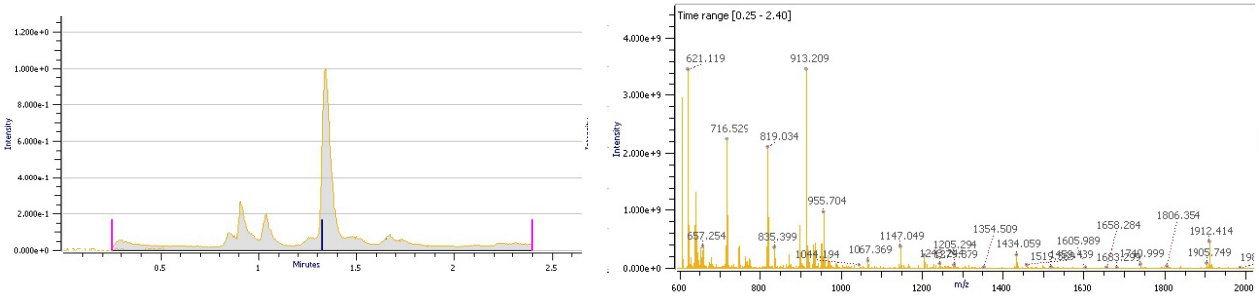
ELT_90, AJC-UPenn-90.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

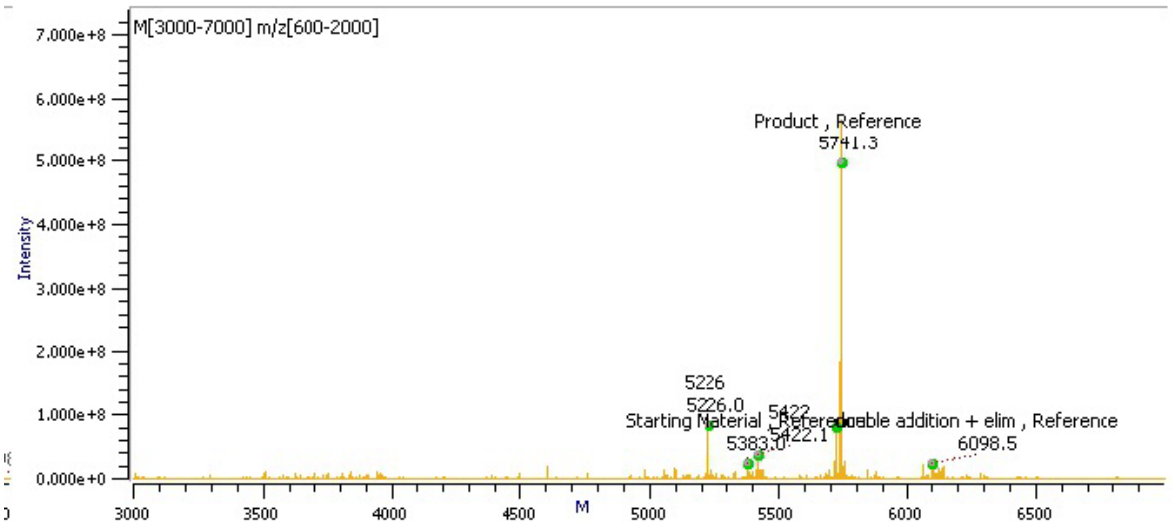


Product **3q**, 84% yield

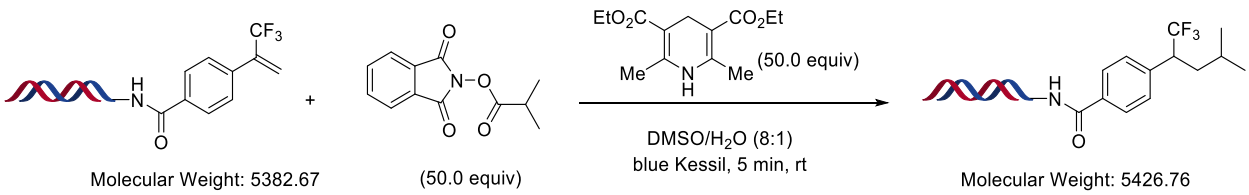


ELT_92, AJC-UPenn-83.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



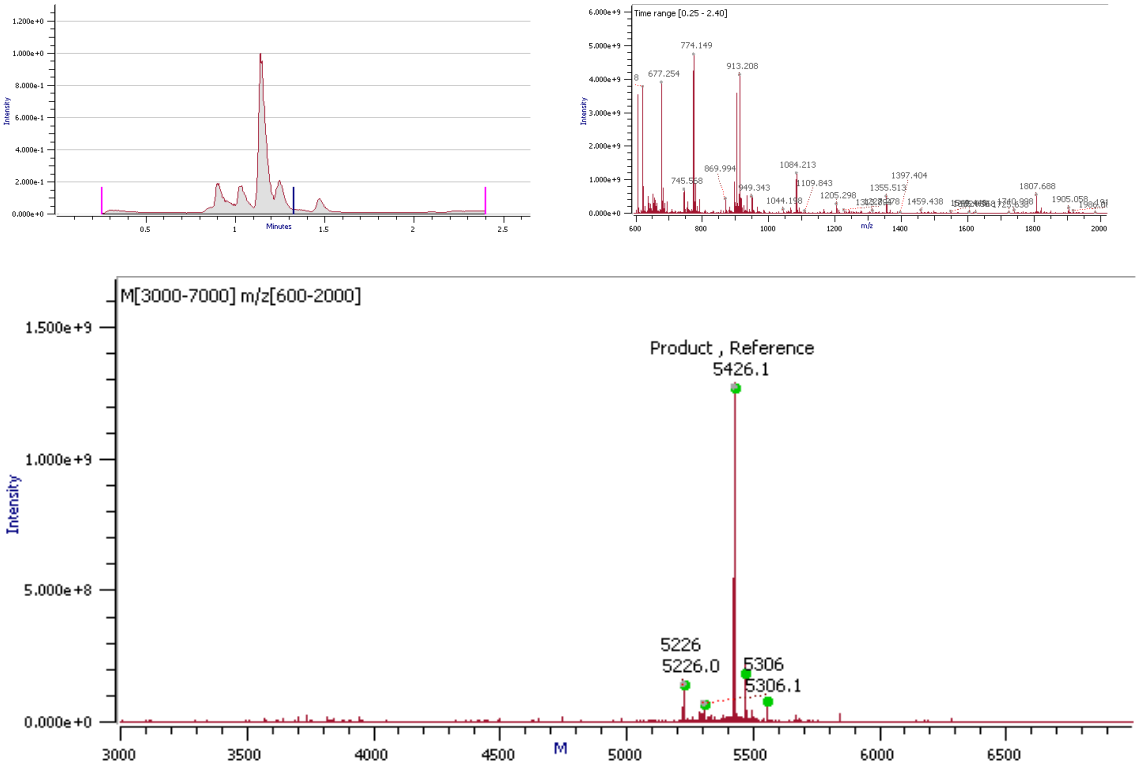


Product **3r**, 92% yield

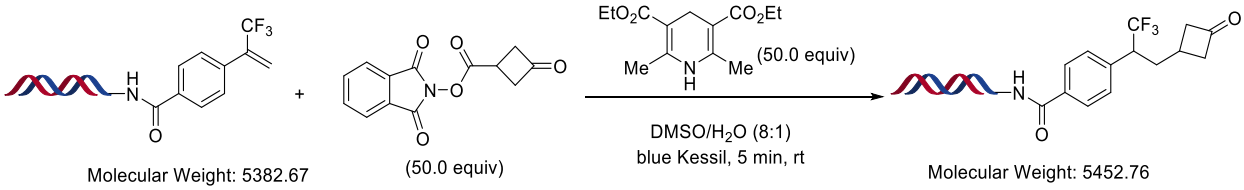


Molecular Weight: 5382.67 (50.0 equiv) Molecular Weight: 5426.76

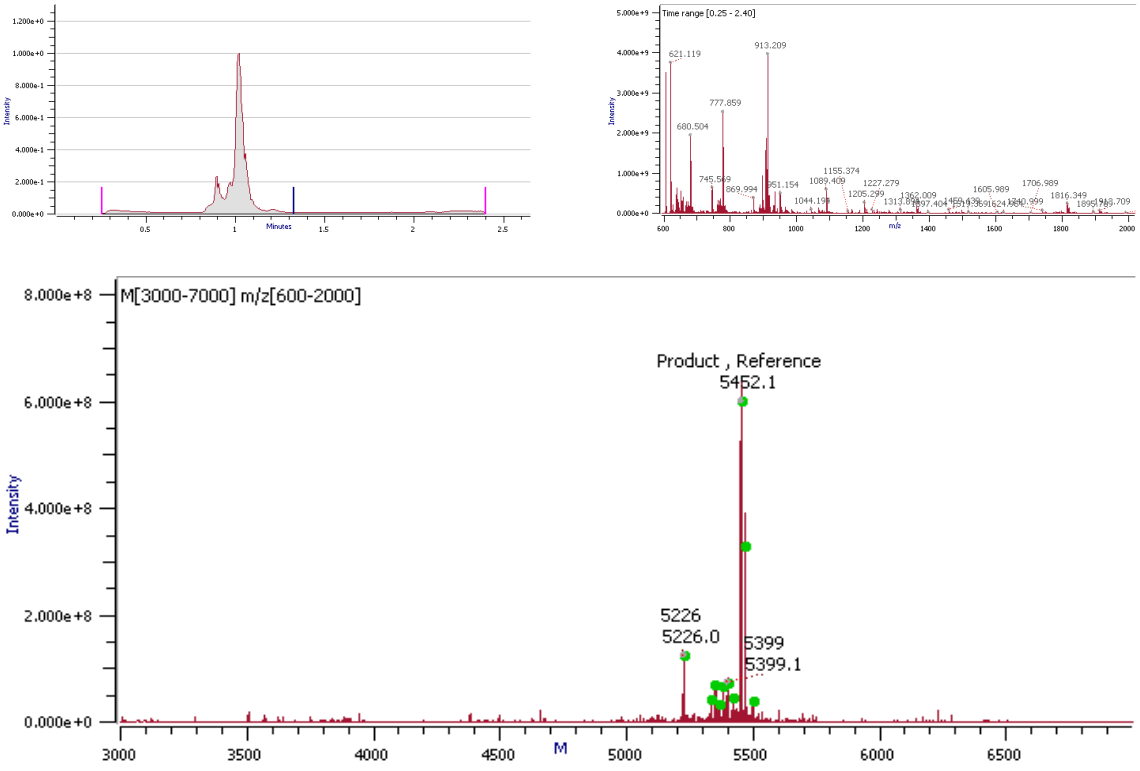
ELT_62, AJC-UPenn-62.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



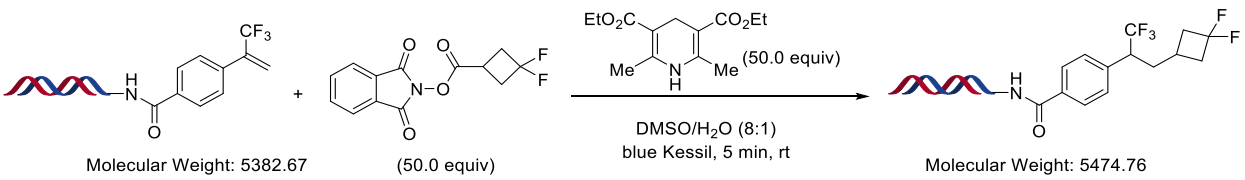
Product **3s**, 53% yield



ELT_49, AJC-UPenn-49.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

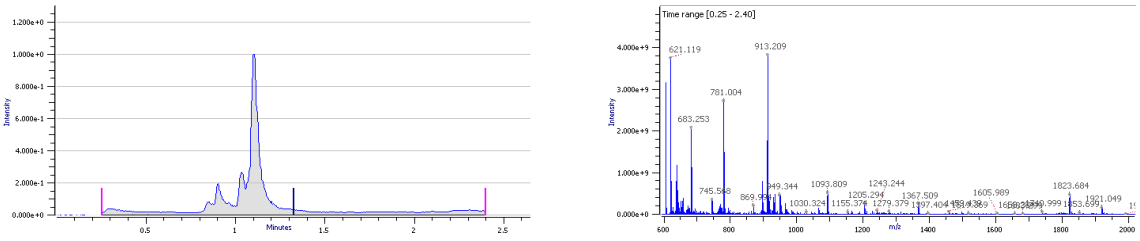


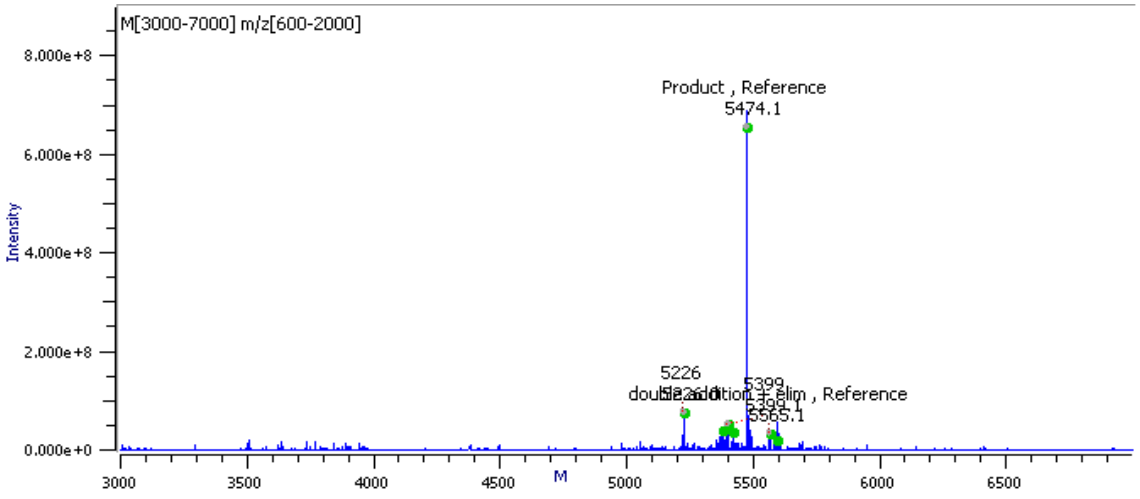
Product **3t**, 91% yield



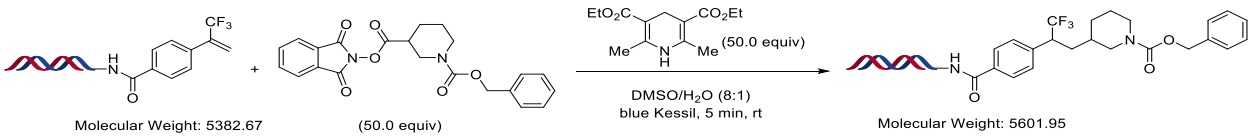
Molecular Weight: 5382.67 (50.0 equiv) Molecular Weight: 5474.76

ELT_87, AJC-UPenn-87.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

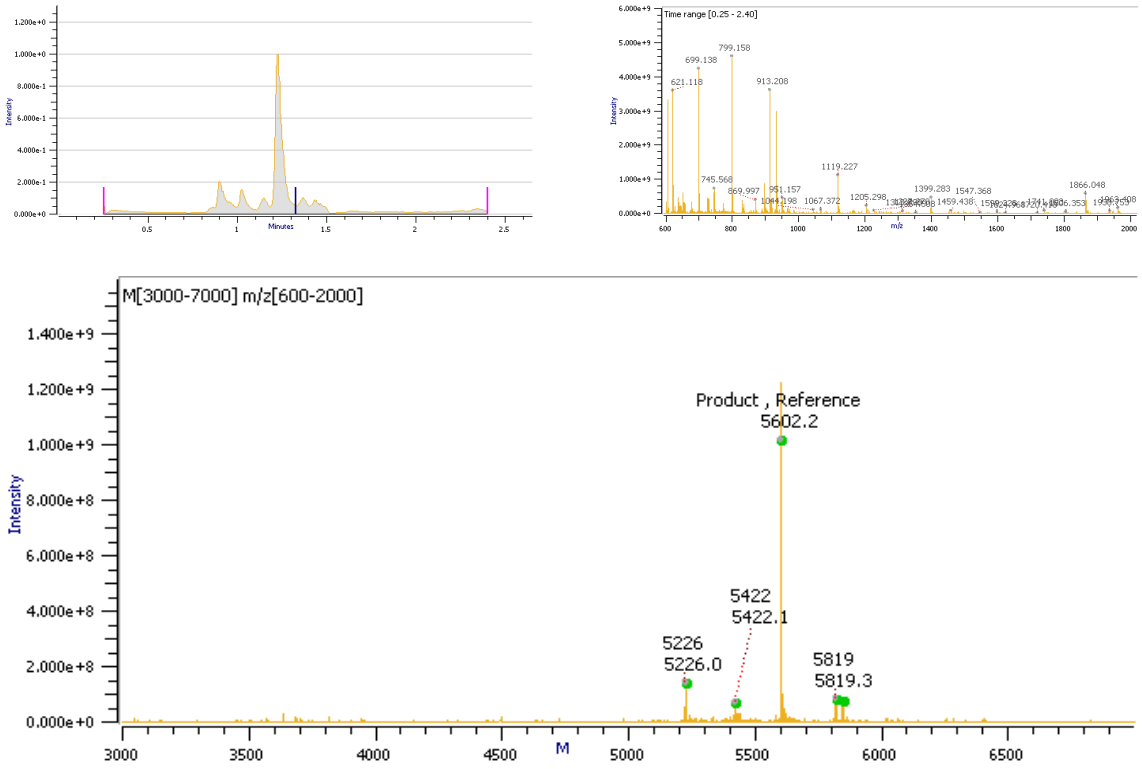




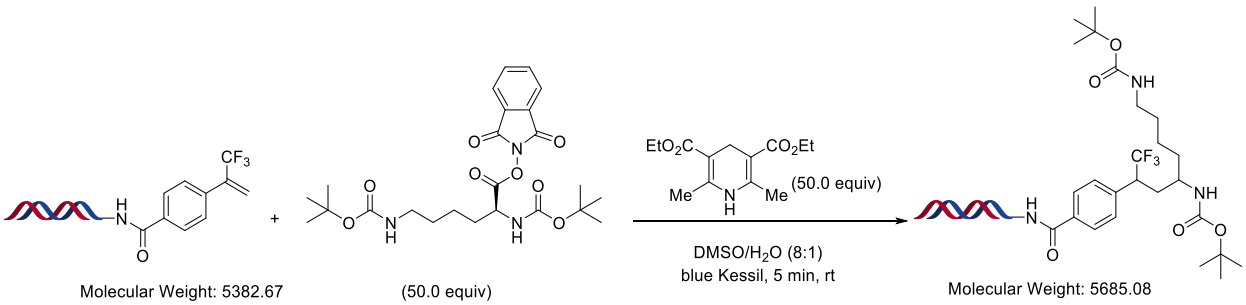
Product **3u**, 93%



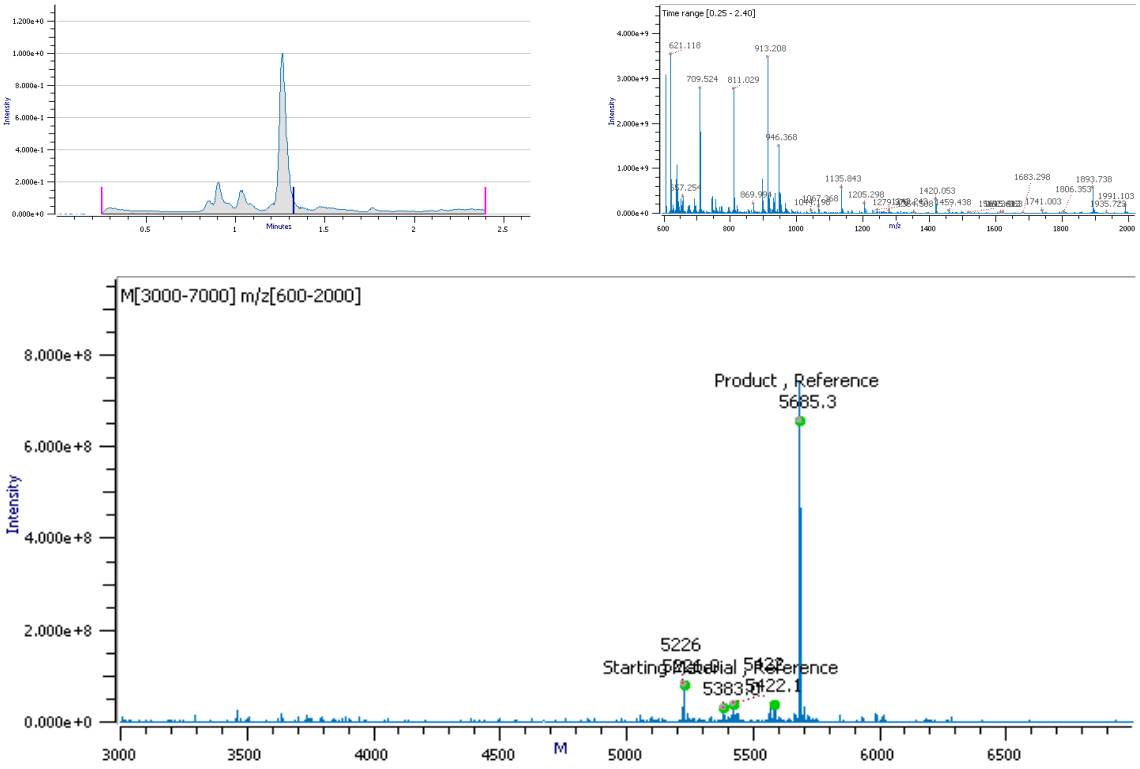
ELT_57, AJC-UPenn-57.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



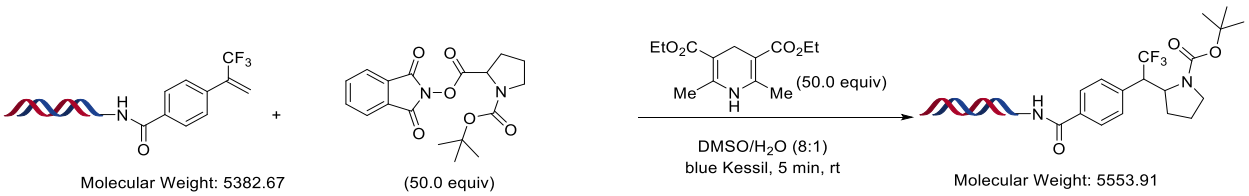
Product **3v**, 98% yield



ELT_81, AJC-UPenn-81.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

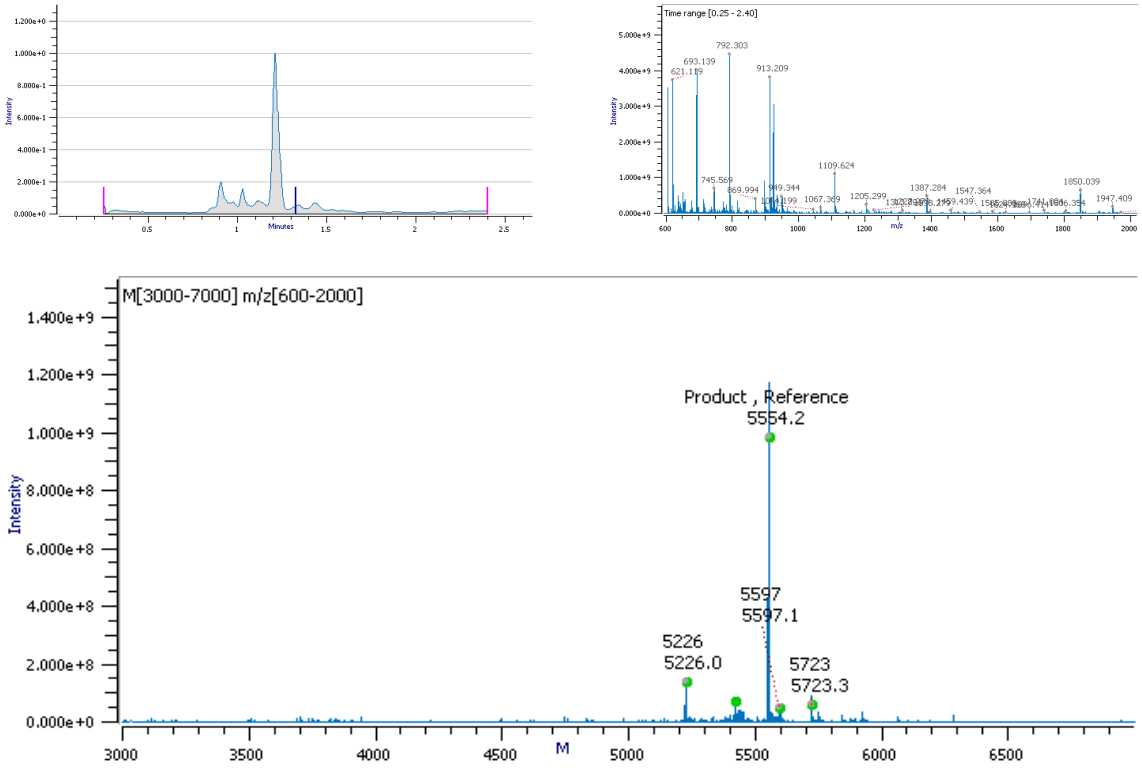


Product **3w**, 95% yield

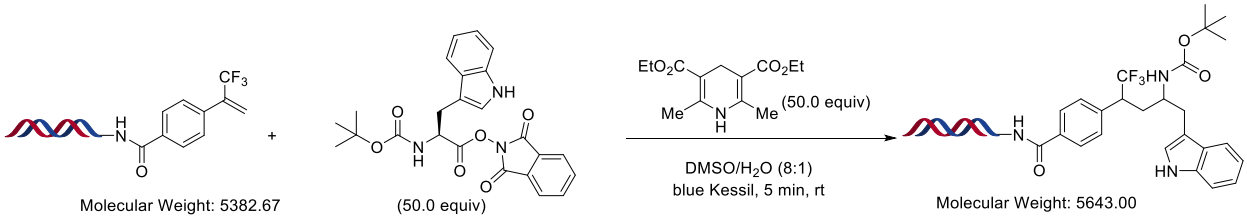


Molecular Weight: 5382.67 (50.0 equiv) Molecular Weight: 5553.91

ELT_55, AJC-UPenn-55.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

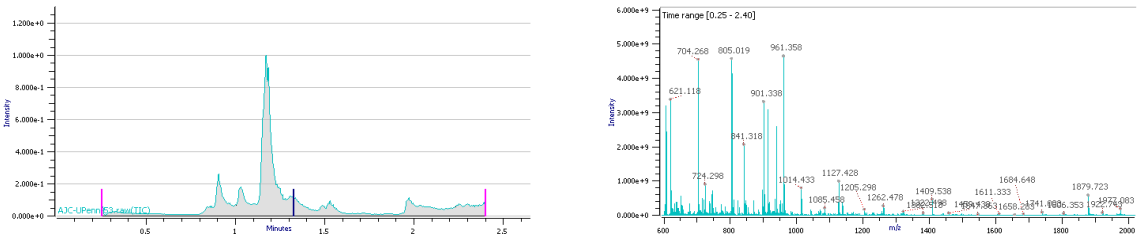


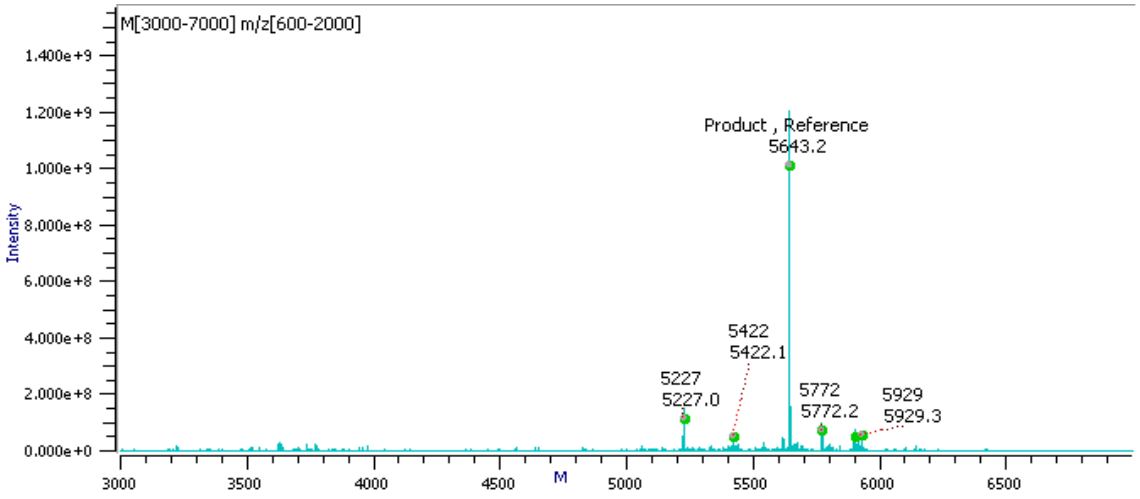
Product **3x**, 94% yield



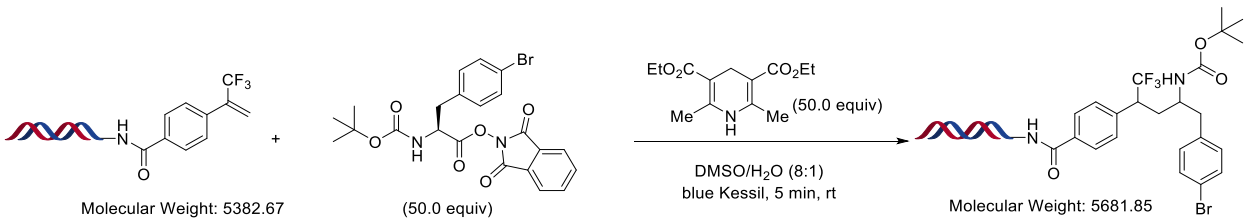
Molecular Weight: 5382.67 (50.0 equiv) Molecular Weight: 5643.00

ELT_53, AJC-UPenn-53.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

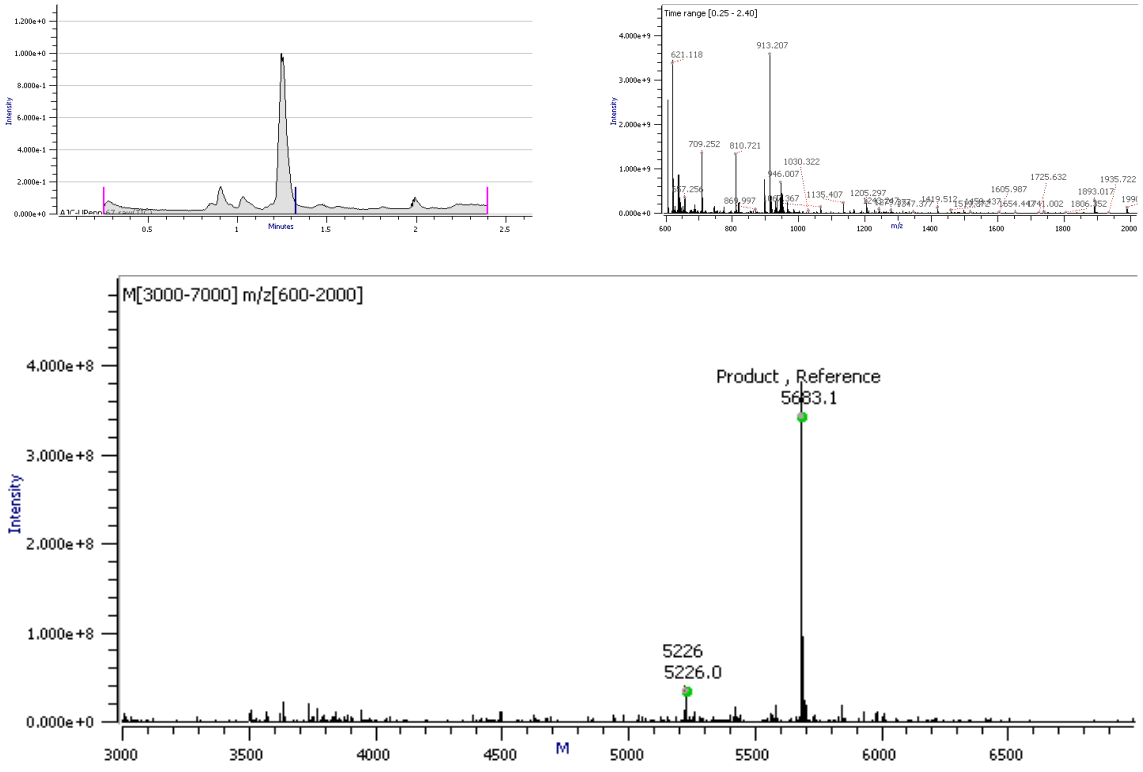




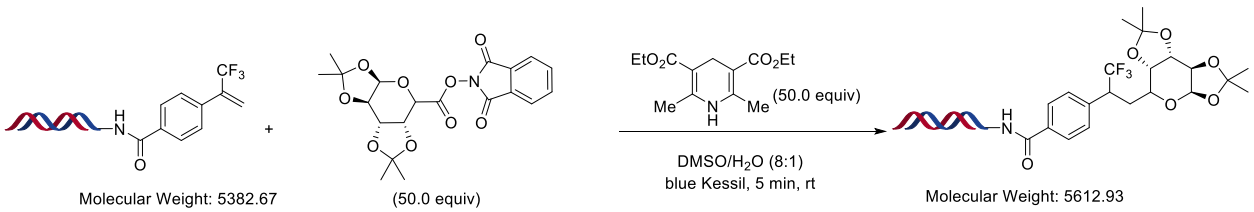
Product **3y**, 91% yield



ELT_67, AJC-UPenn-67.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

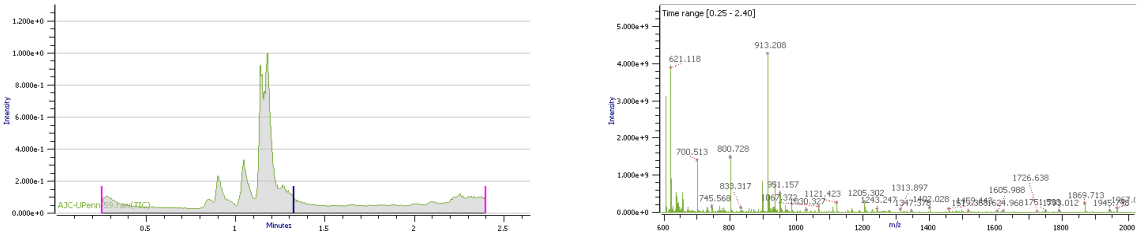


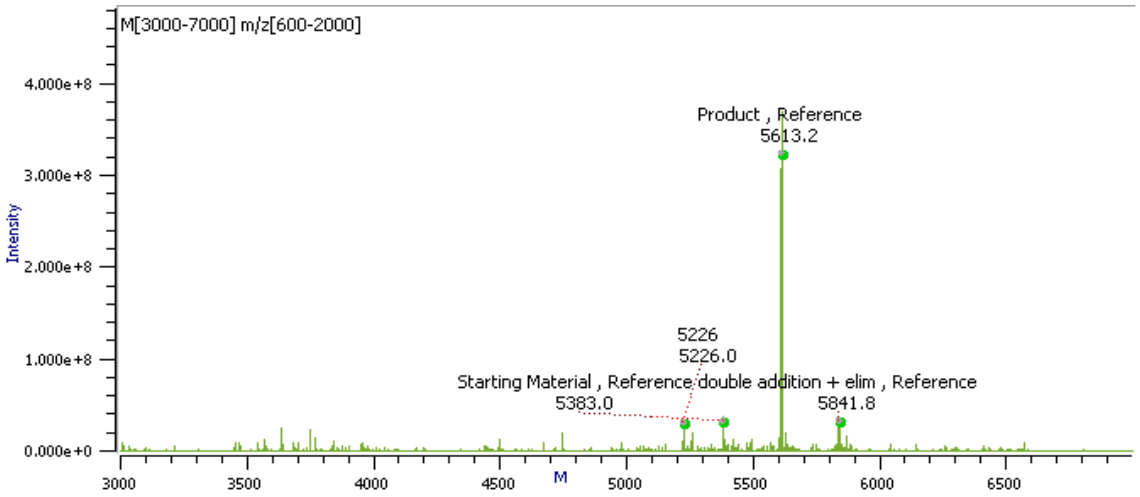
Product **3z**, 98% yield



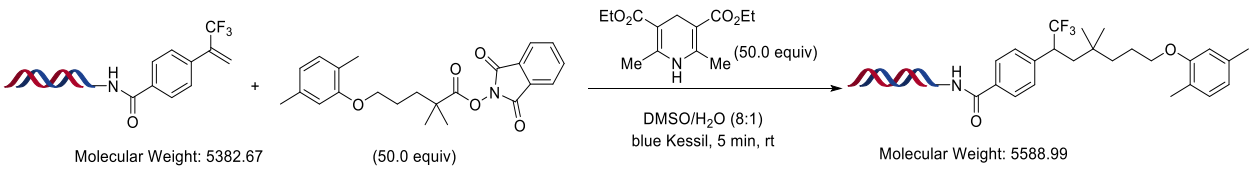
Molecular Weight: 5382.67 (50.0 equiv) Molecular Weight: 5612.93

ELT_59. AJC-UPenn-59.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

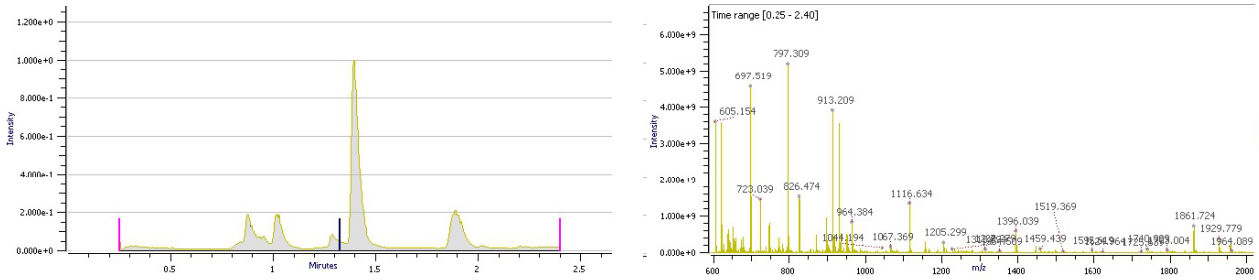


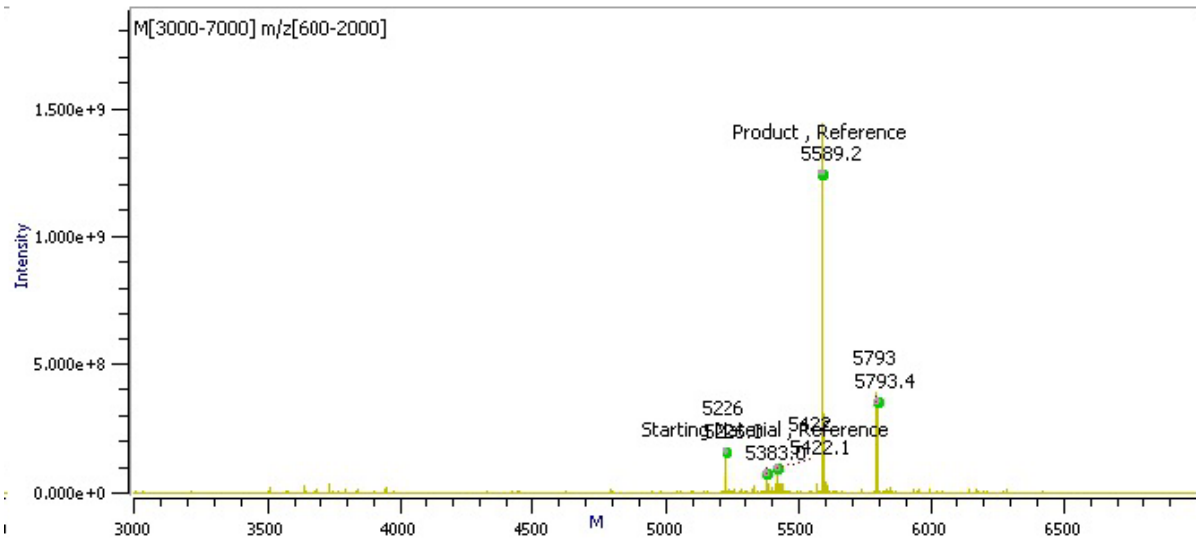


Product **3za**, 82% yield

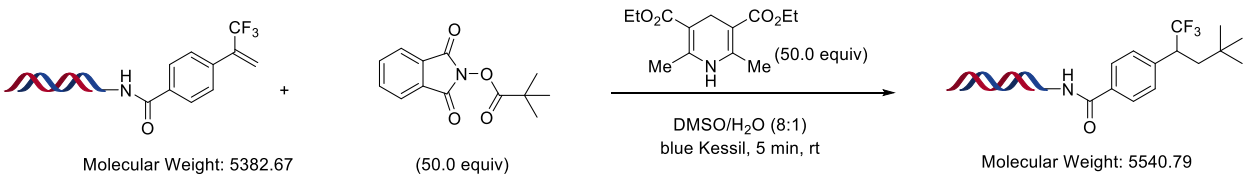


ELT_446. AJC-UPenn-50.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



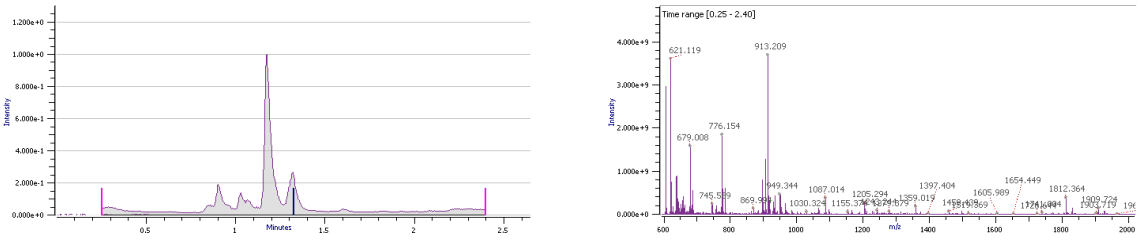


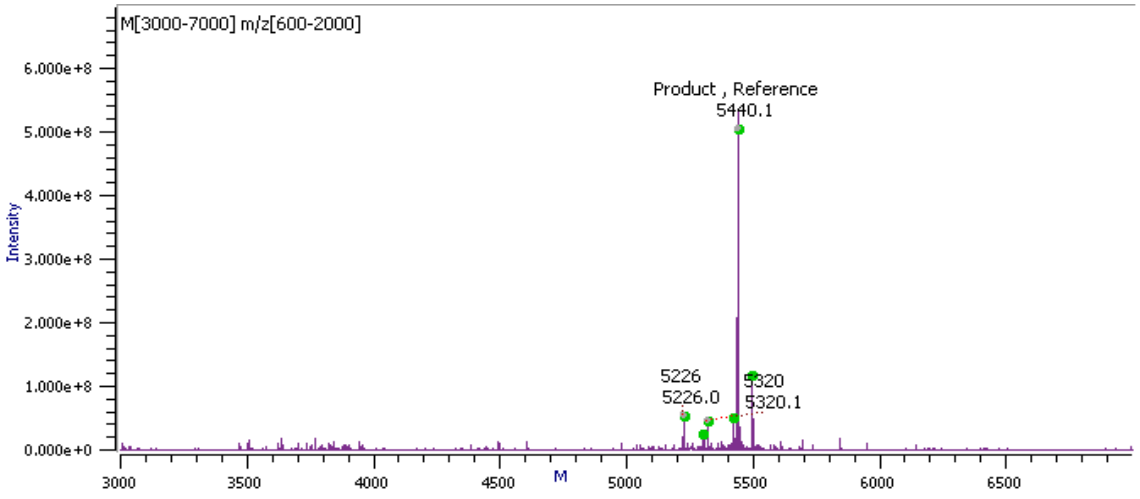
Product **3zb**, 80% yield



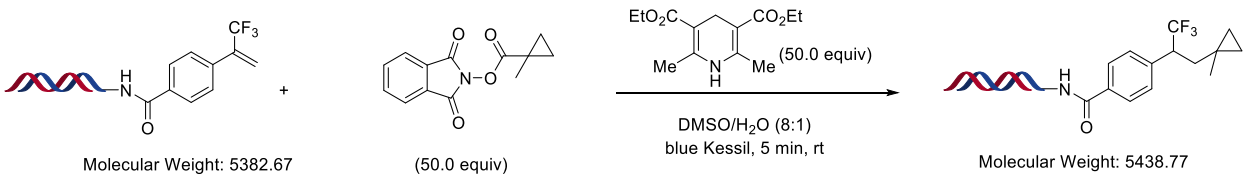
Molecular Weight: 5382.67 (50.0 equiv) Molecular Weight: 5540.79

ELT_71, AJC-UPenn-71.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



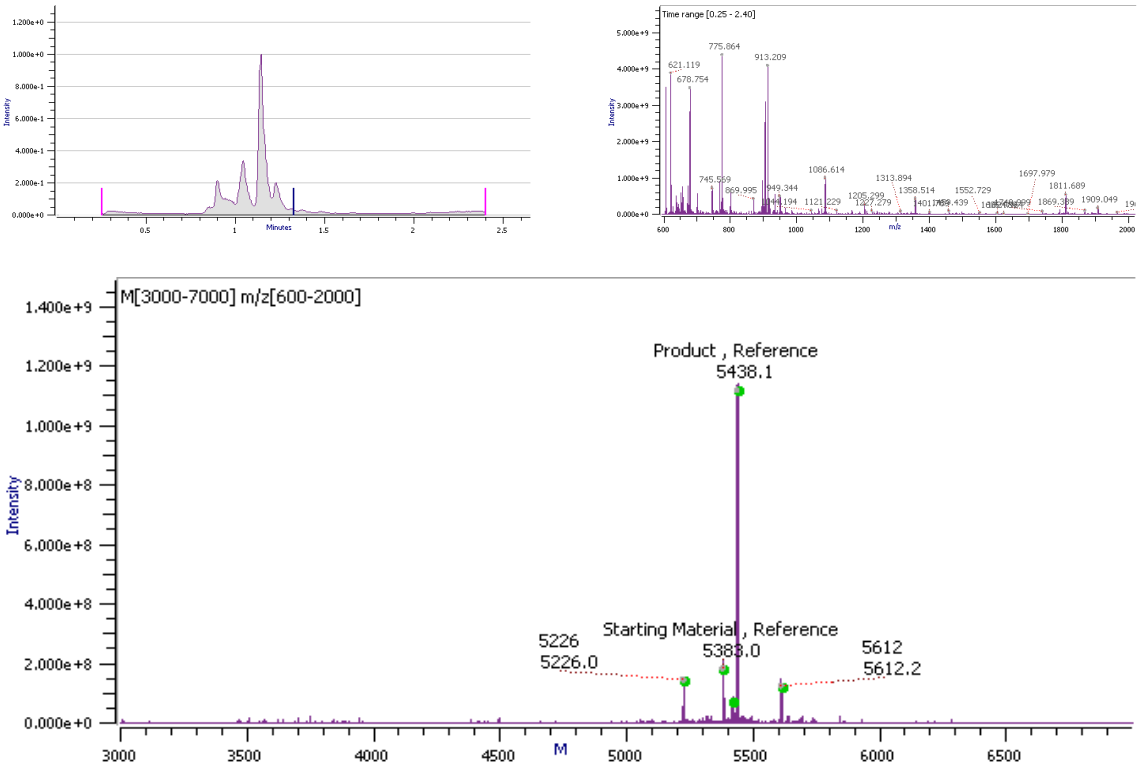


Product **3zc**, 87% yield

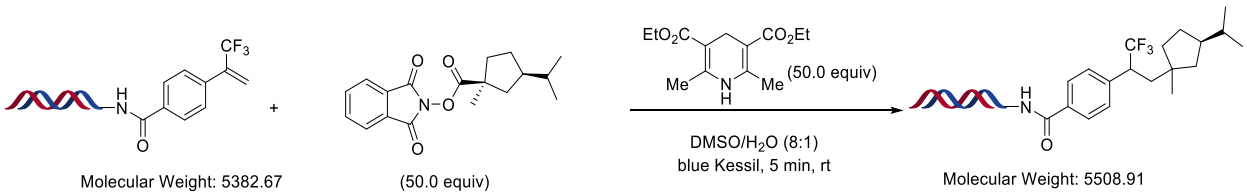


Molecular Weight: 5382.67 (50.0 equiv) Molecular Weight: 5438.77

ELT_58, AJC-UPenn-58.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

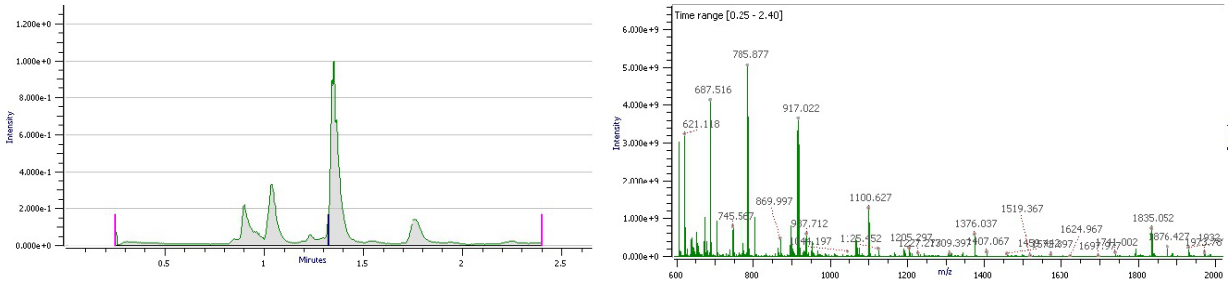


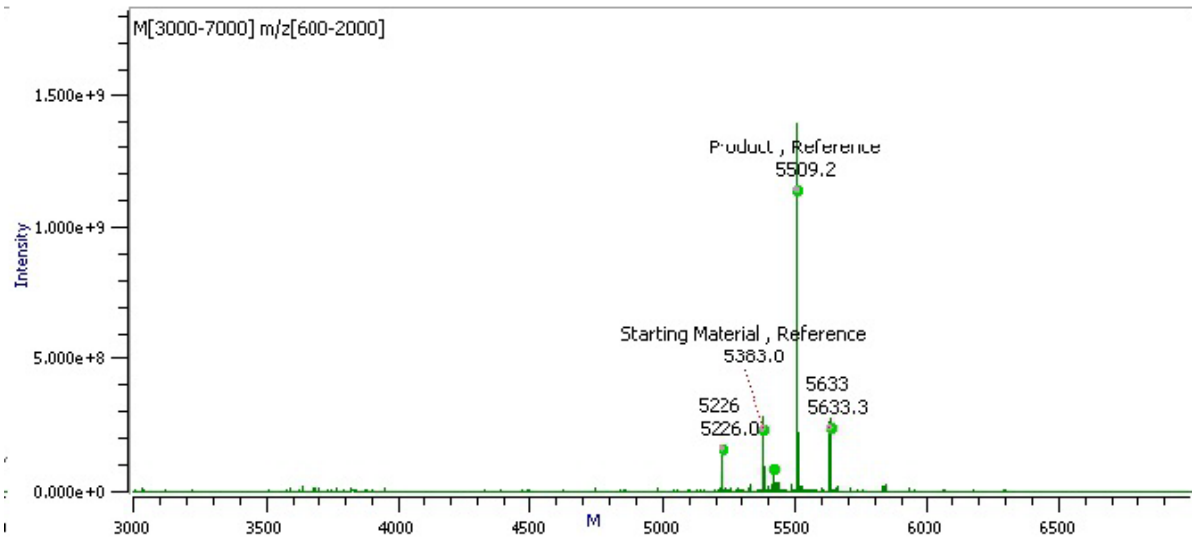
Product **3zd**, 77% yield



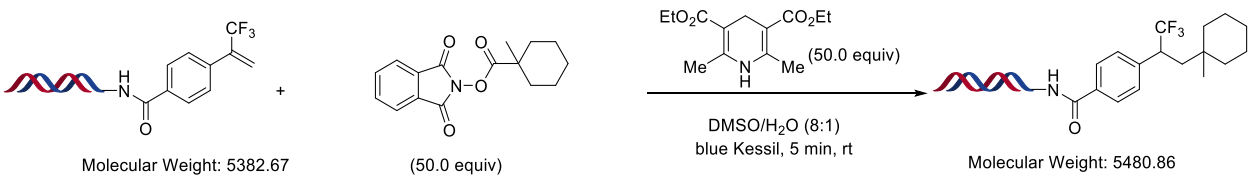
Molecular Weight: 5382.67 (50.0 equiv) Molecular Weight: 5508.91

ELT_105, AJC-UPenn-52.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



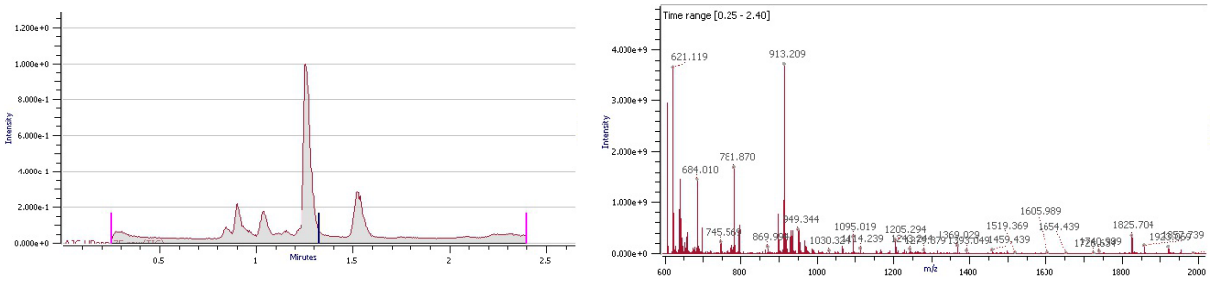


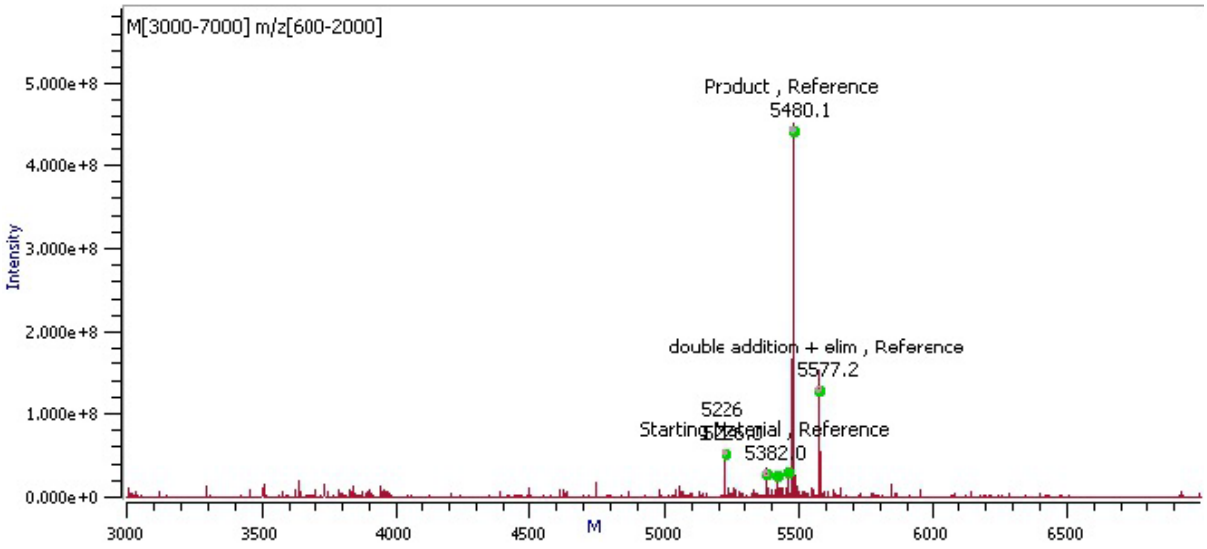
Product **3ze**, 79% yield



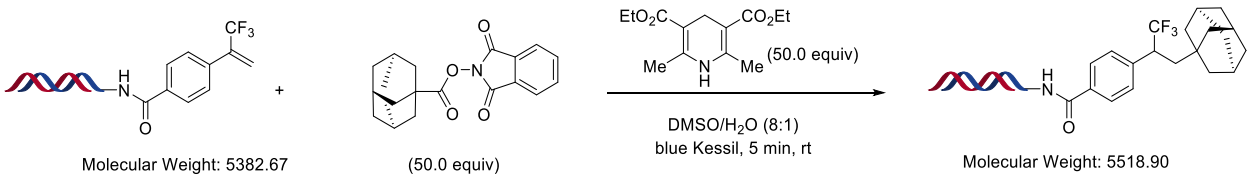
Molecular Weight: 5382.67 (50.0 equiv) Molecular Weight: 5480.86

ELT_114, AJC-UPenn-75.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



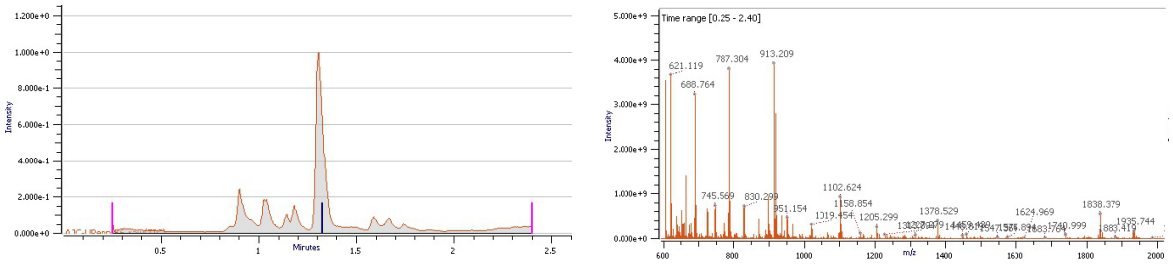


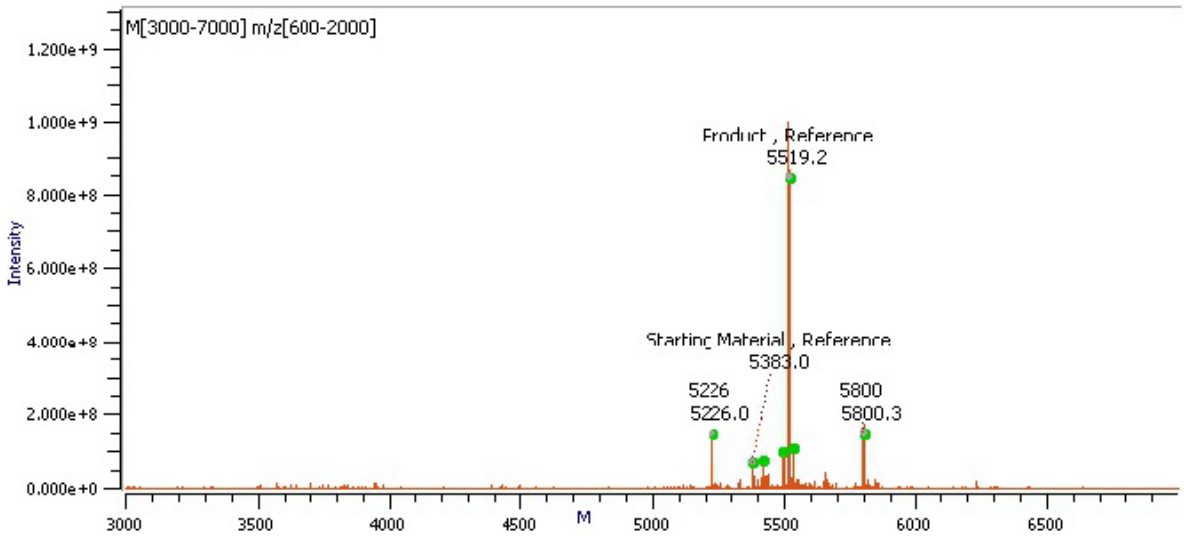
Product **3zf**, 71% yield



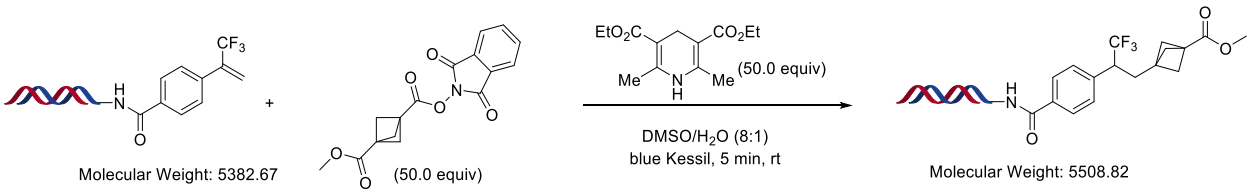
Molecular Weight: 5382.67 (50.0 equiv) Molecular Weight: 5518.90

ELT_107, AJC-UPenn-56.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)





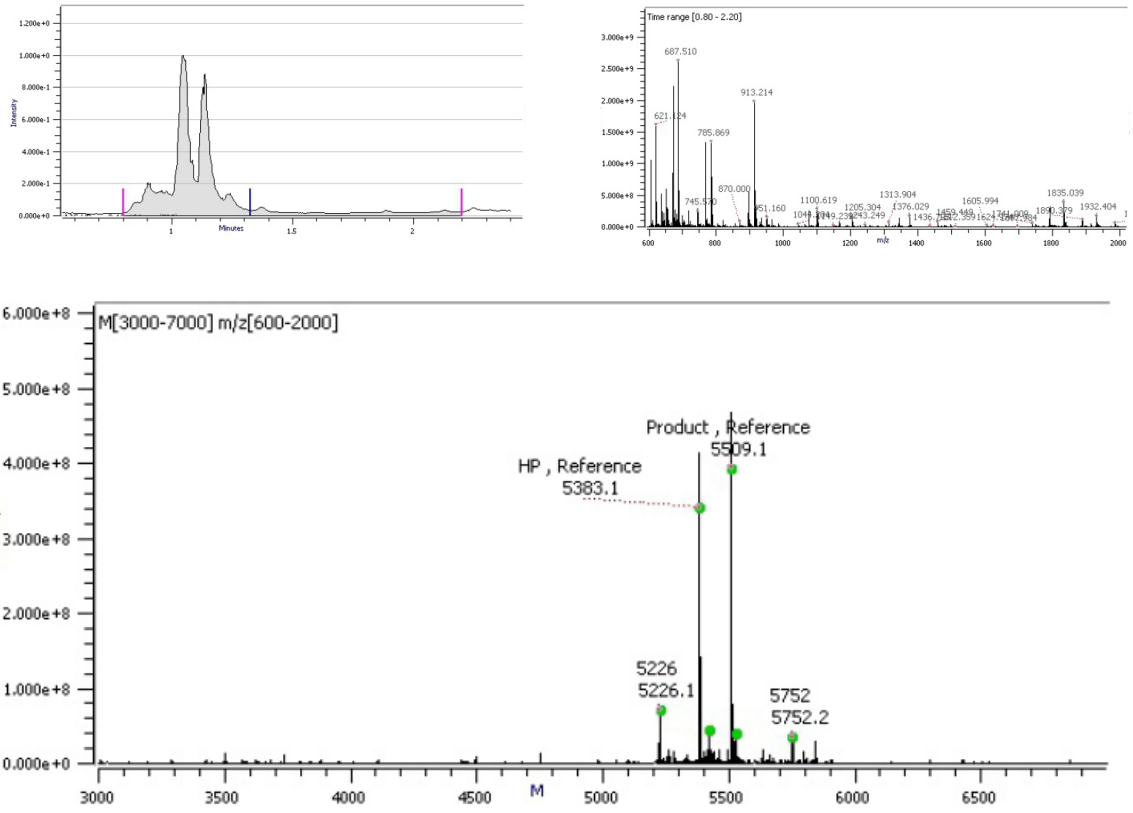
Product **3zg**, 54% yield



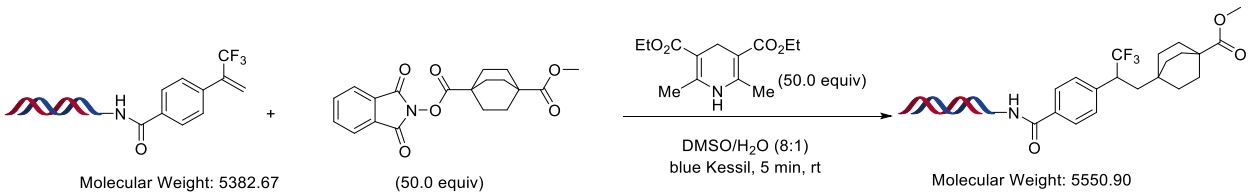
Molecular Weight: 5382.67

Molecular Weight: 5508.82

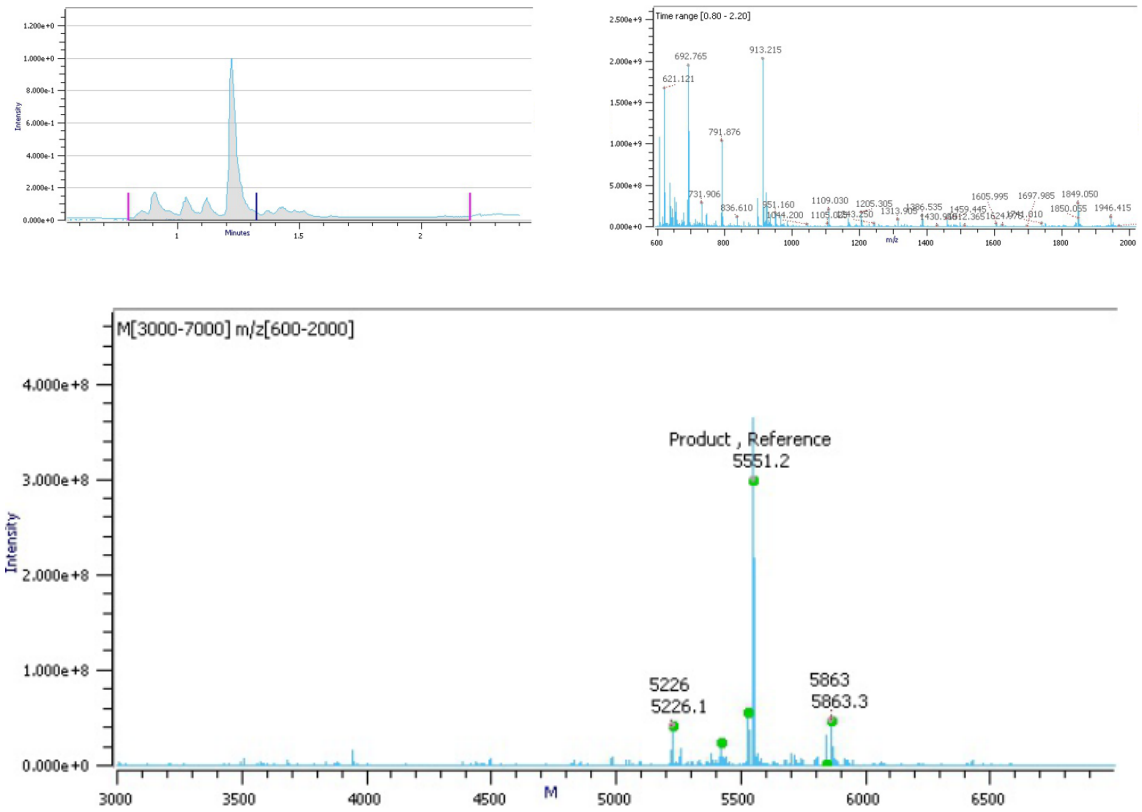
ELT_106, AJC-UPenn-8-19-106.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



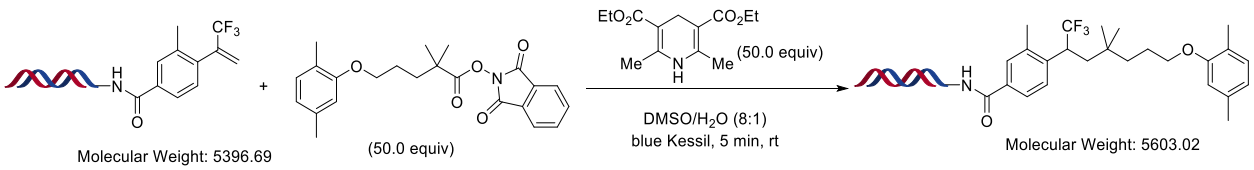
Product **3zh**, 81% yield



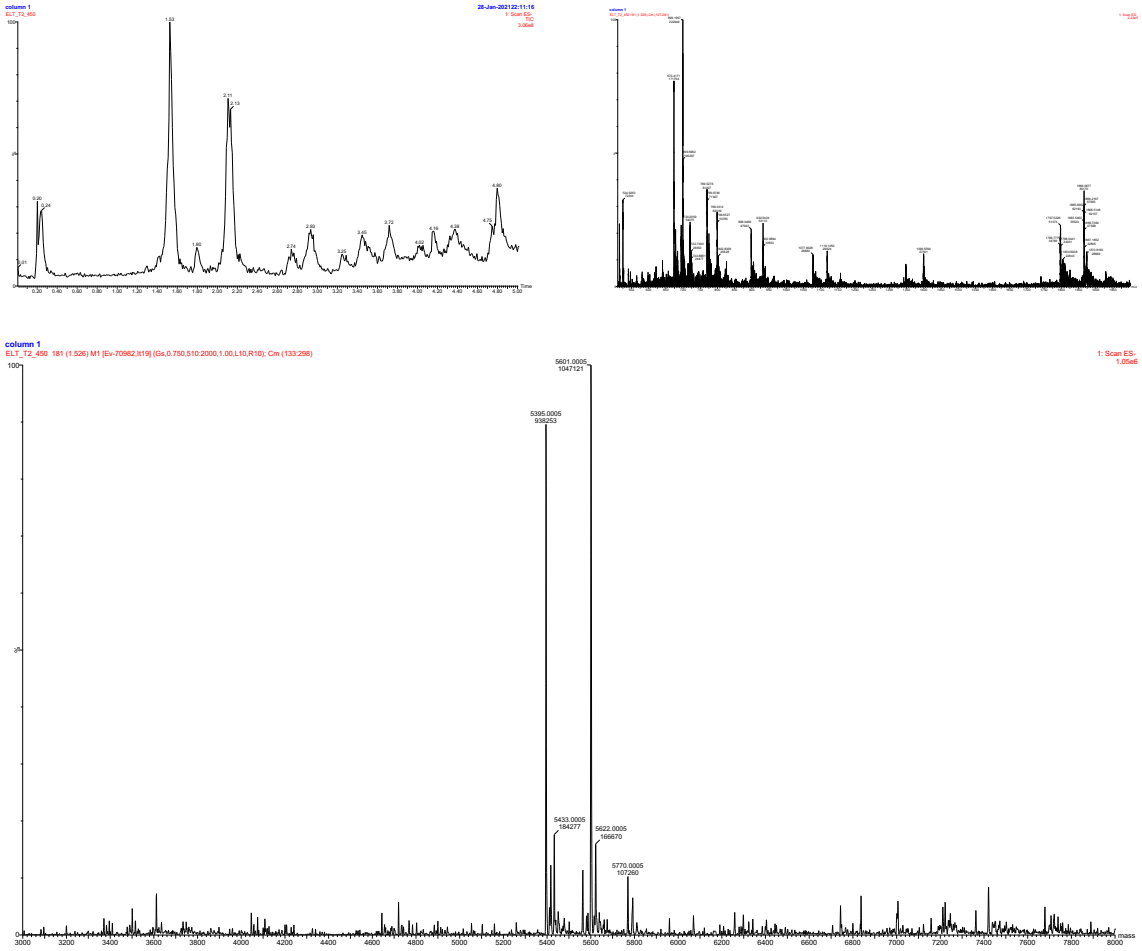
ELT_112, AJC-UPenn-8-19-112.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



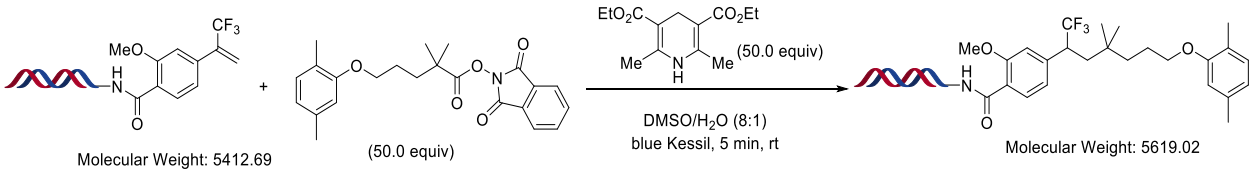
Product **4za**, 47% yield



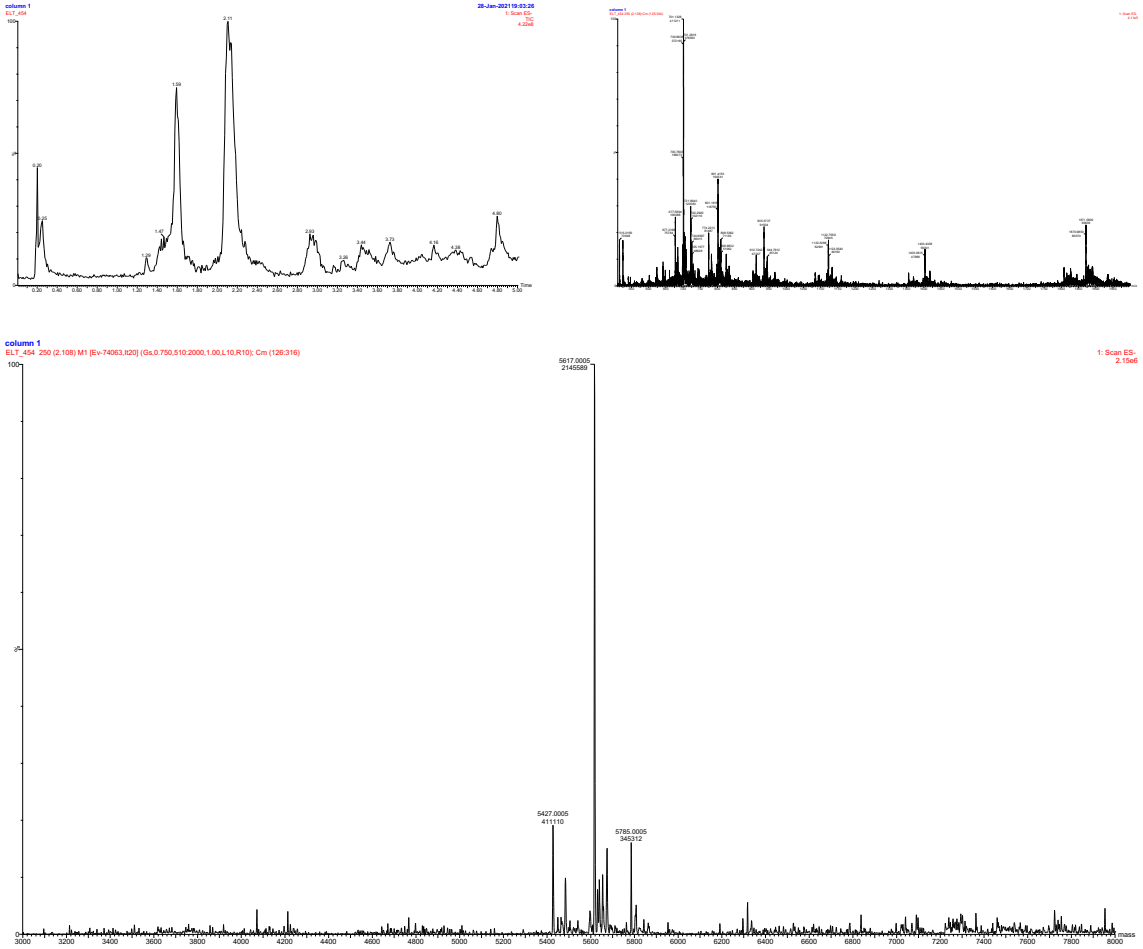
ELT_450 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



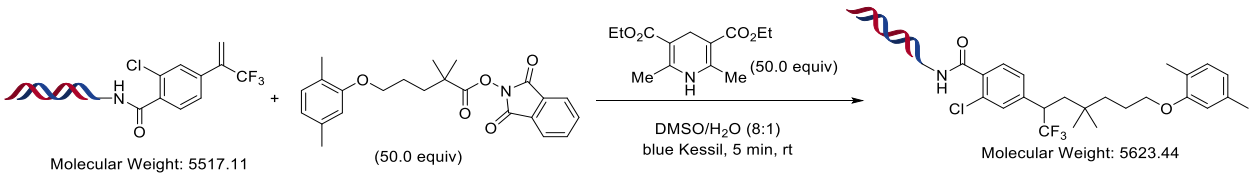
Product **5za**, 72% yield



ELT_454 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



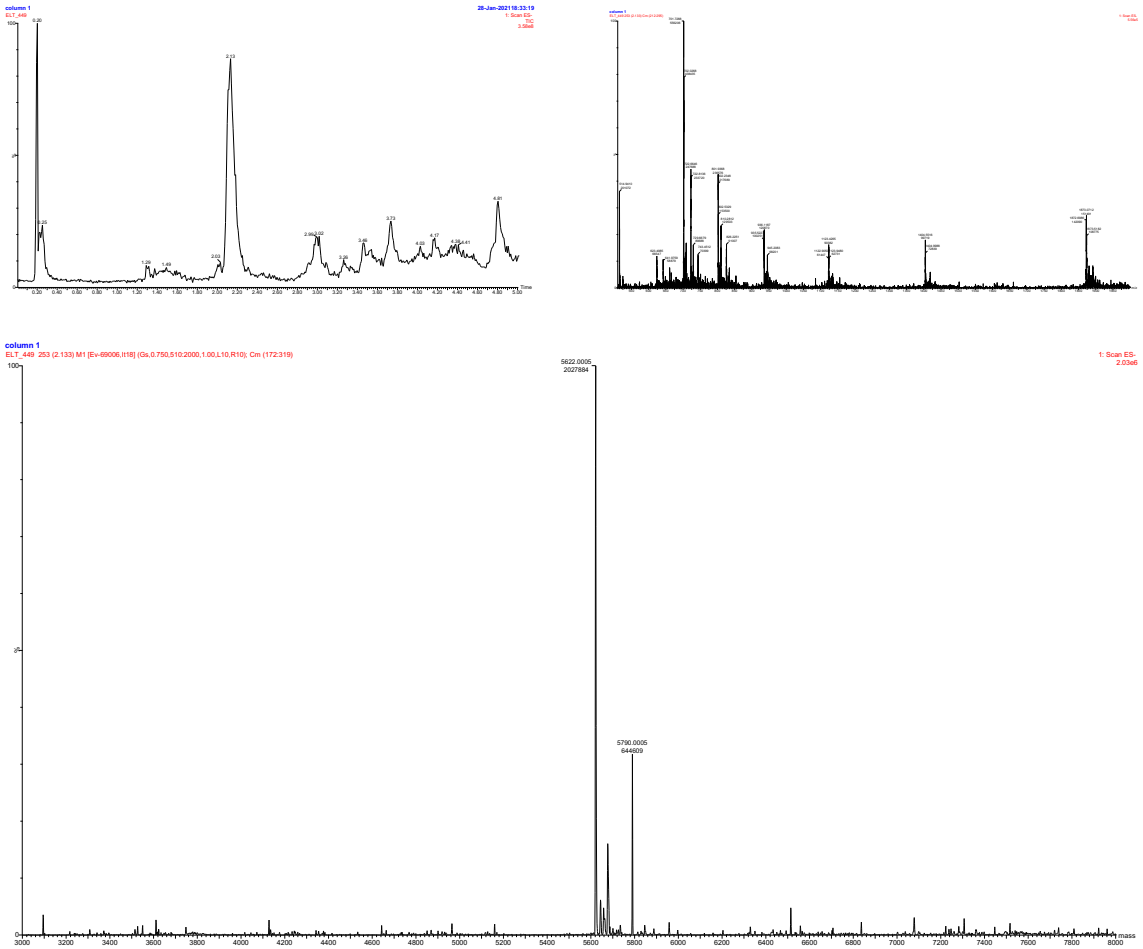
Product **6za**, 90% yield



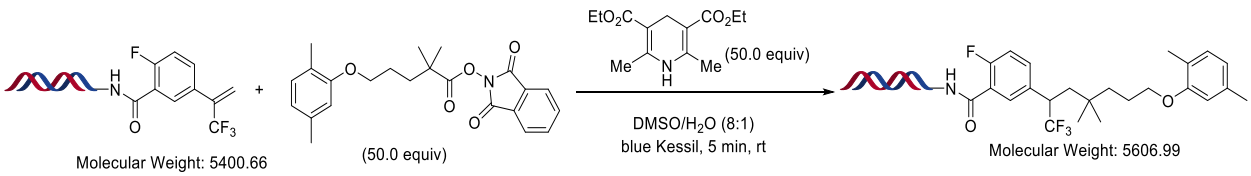
Molecular Weight: 5517.11

Molecular Weight: 5623.44

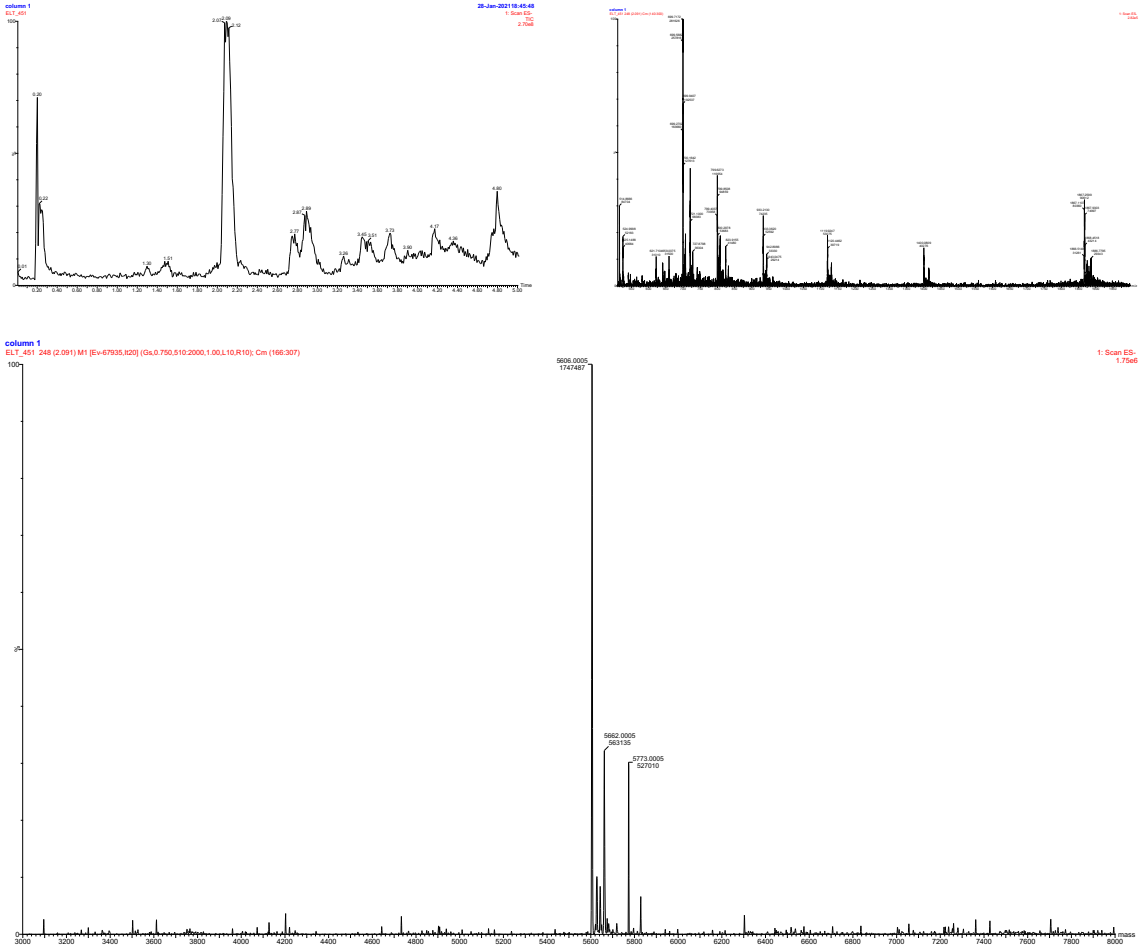
ELT_449 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



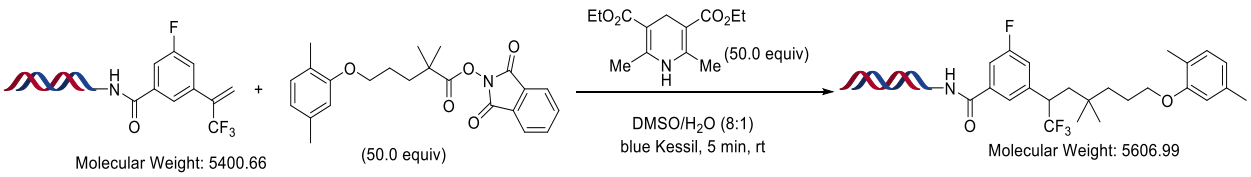
Product **7za**, 82% yield



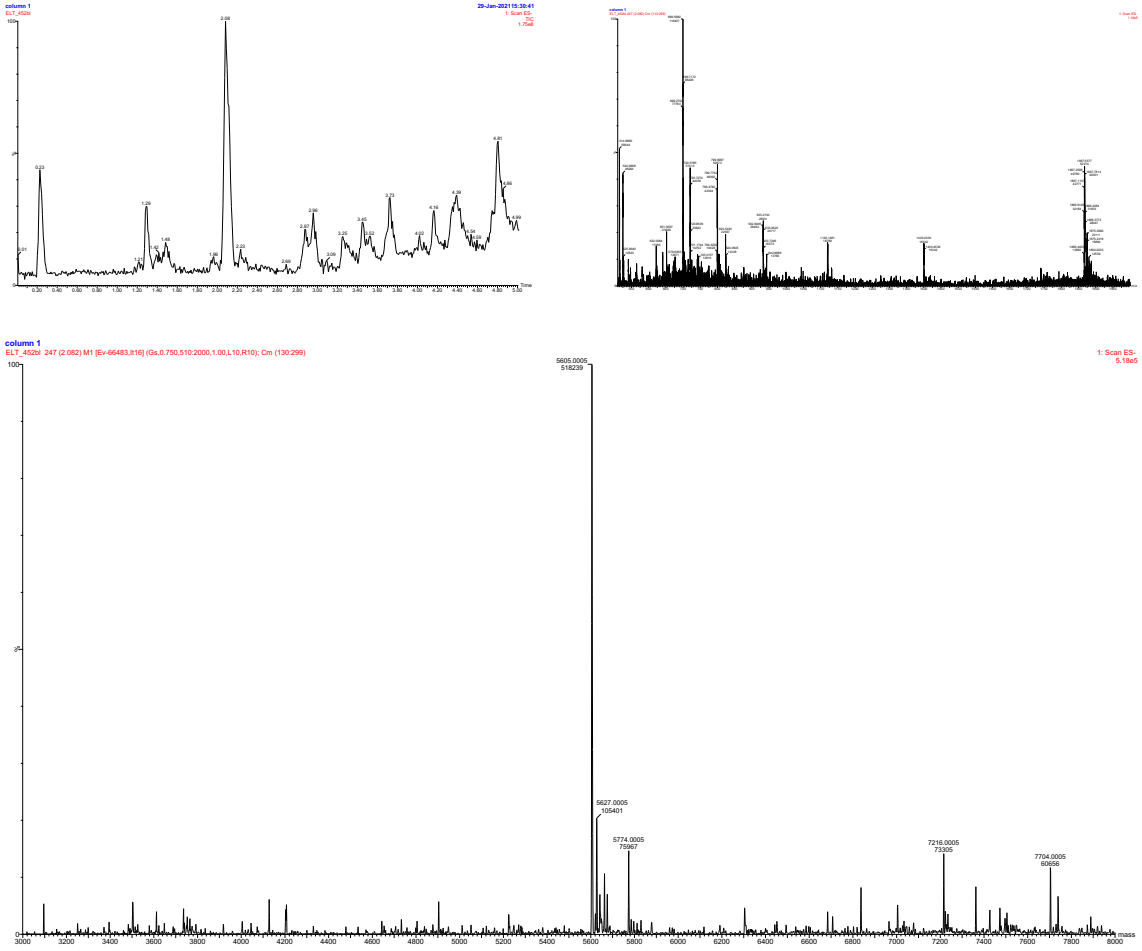
ELT_451 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



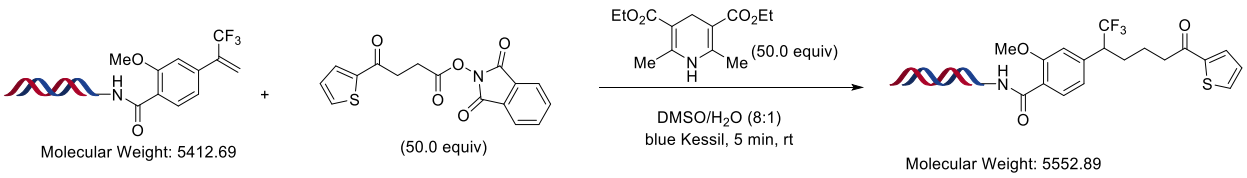
Product **8za**, 79% yield



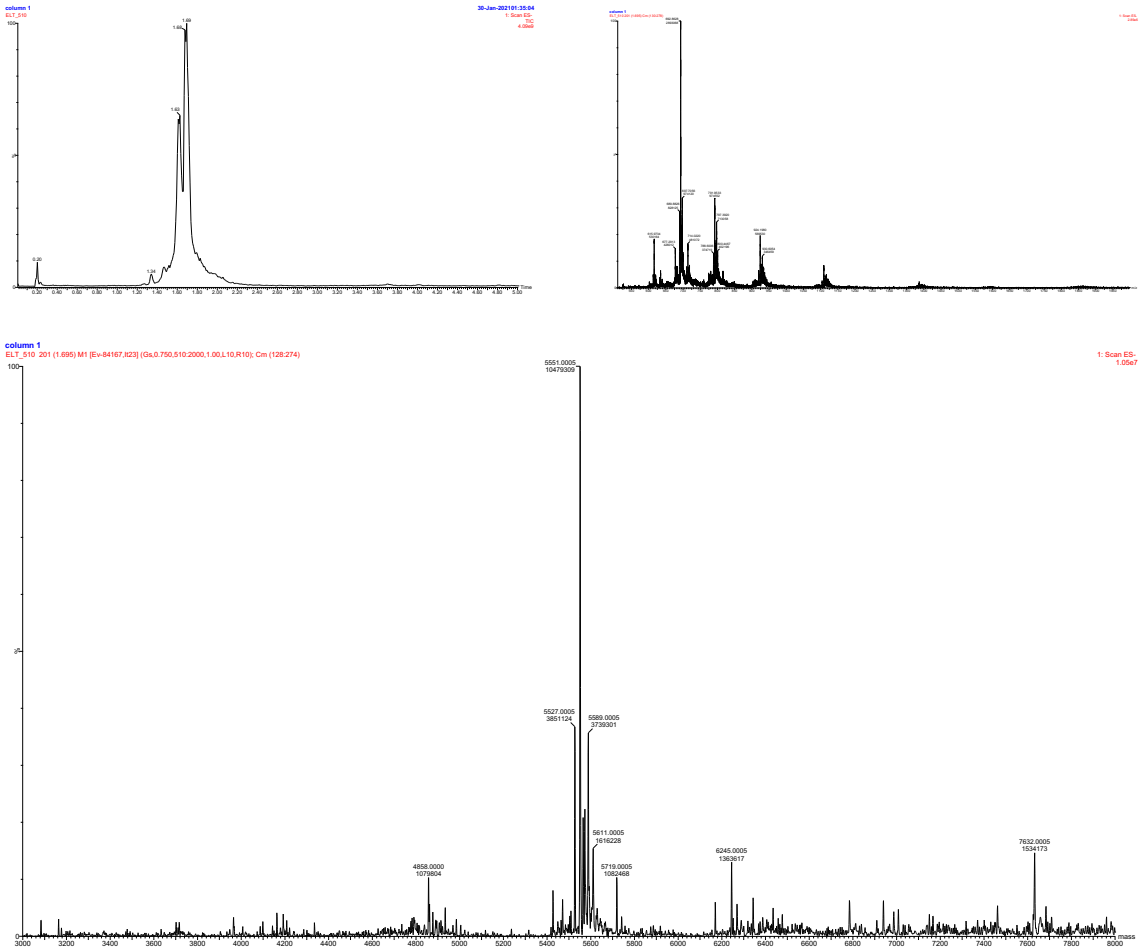
ELT_452 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



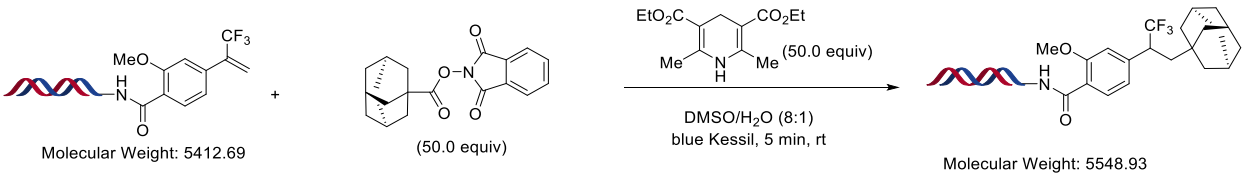
Product **5a**, 66% yield



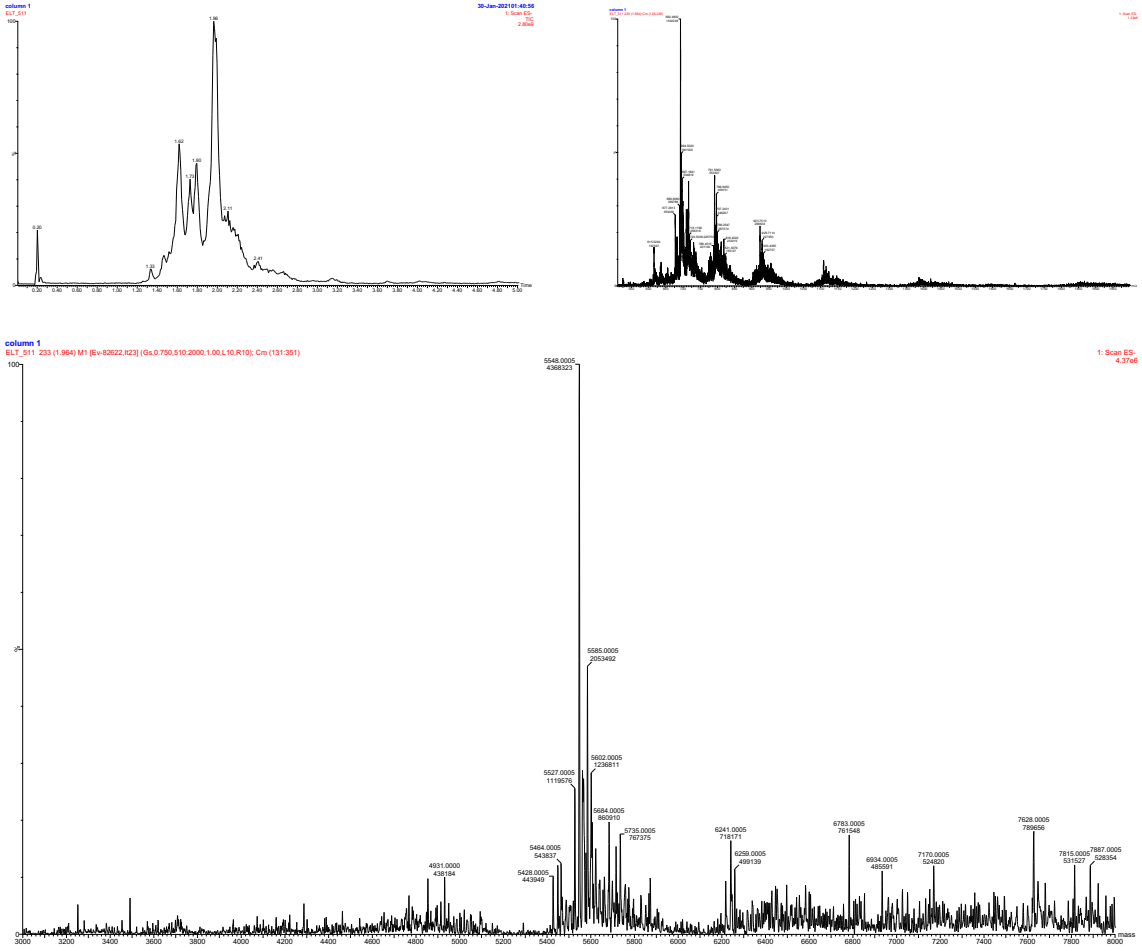
ELT_510 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



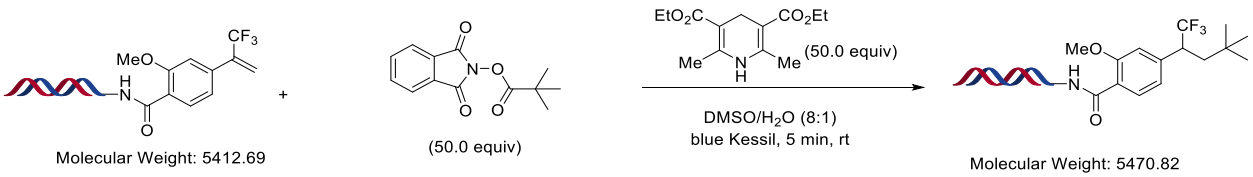
Product **5zf**, 63% yield



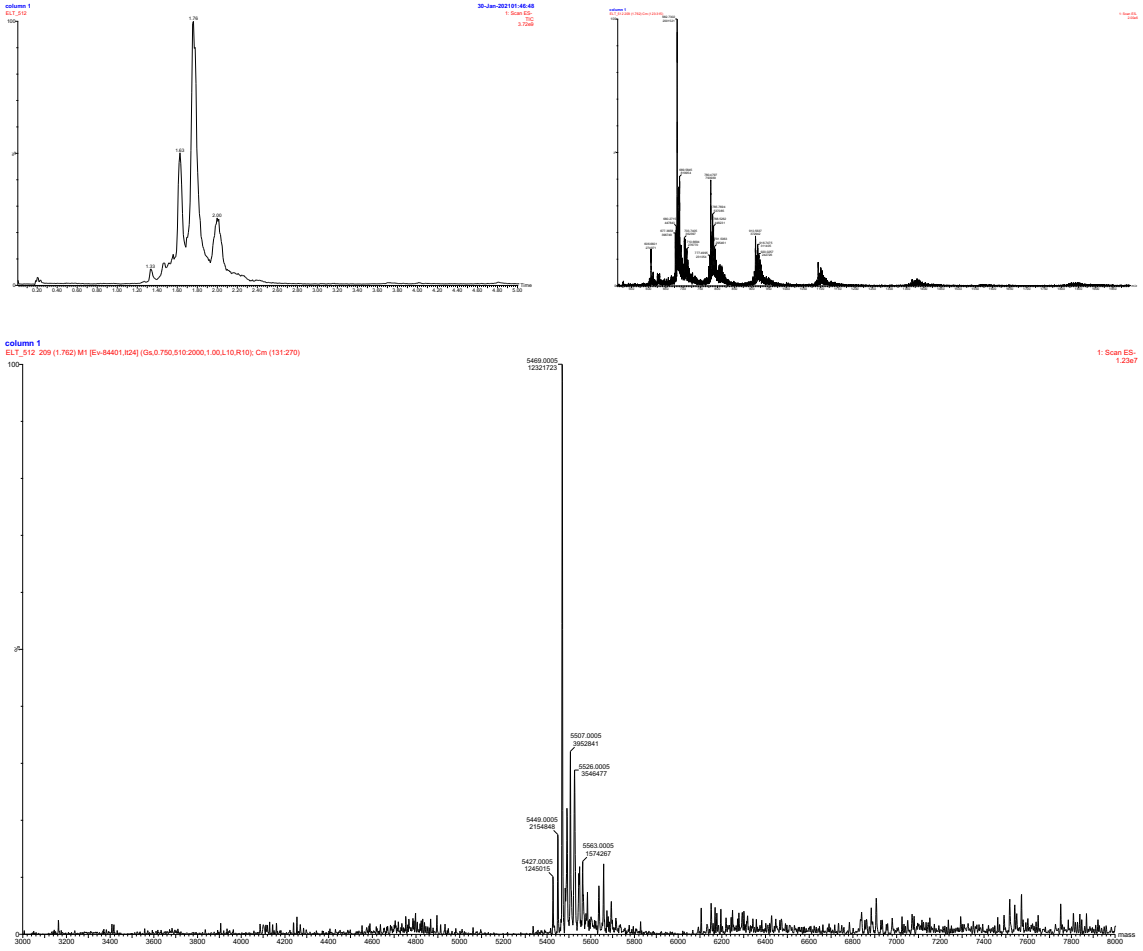
ELT_511 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



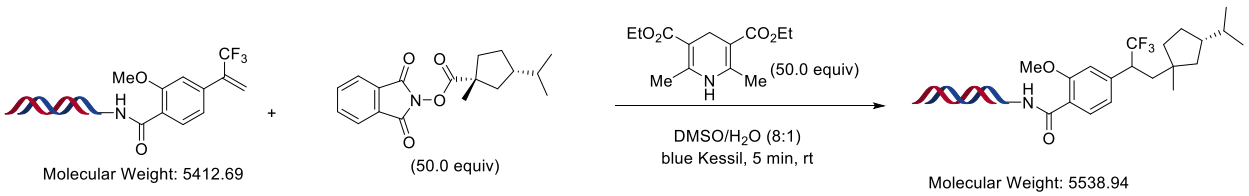
Product **5zb**, 65% yield



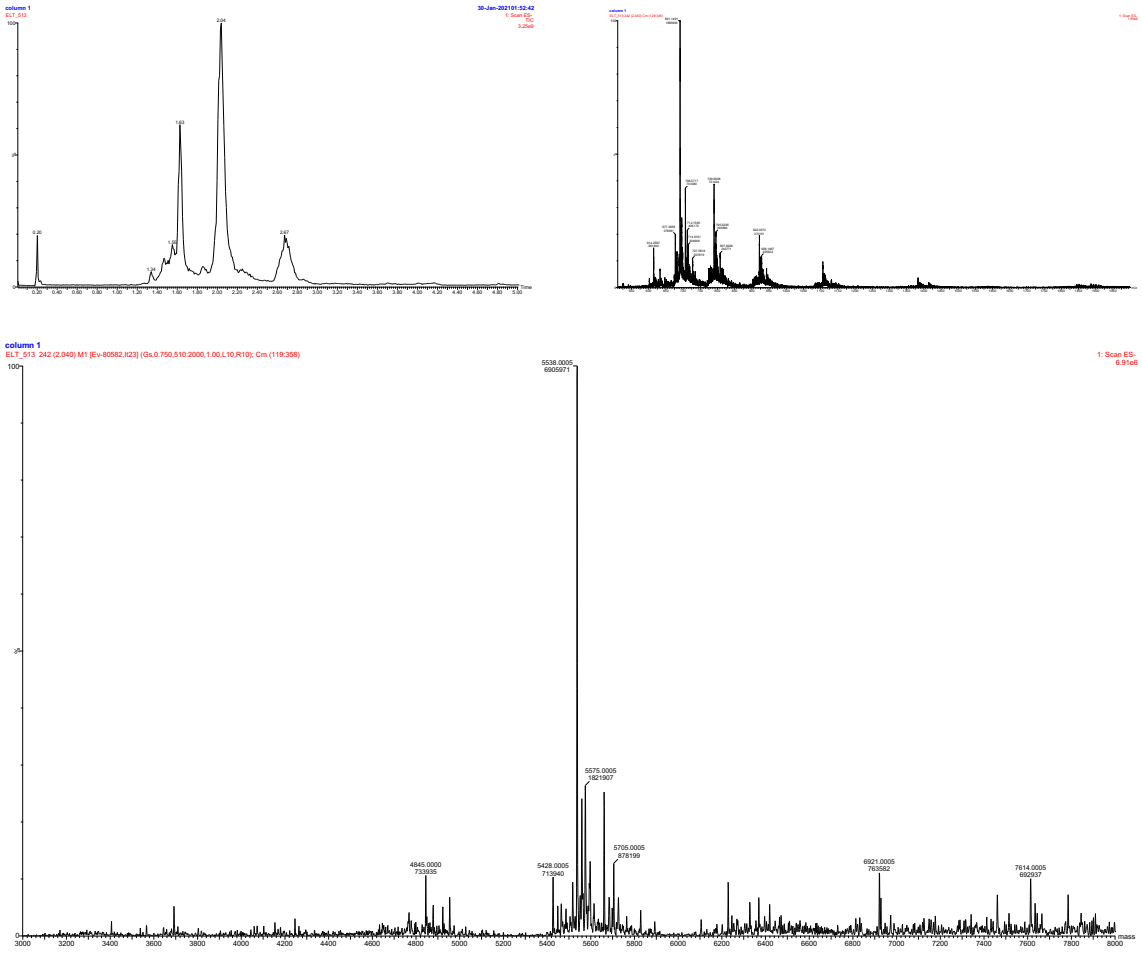
ELT_512 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



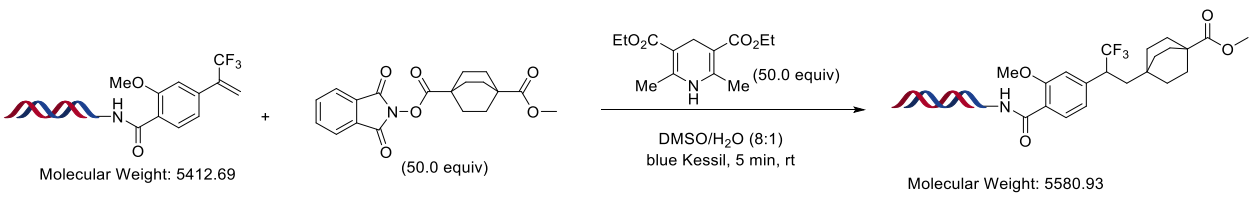
Product **5zd**, 73% yield



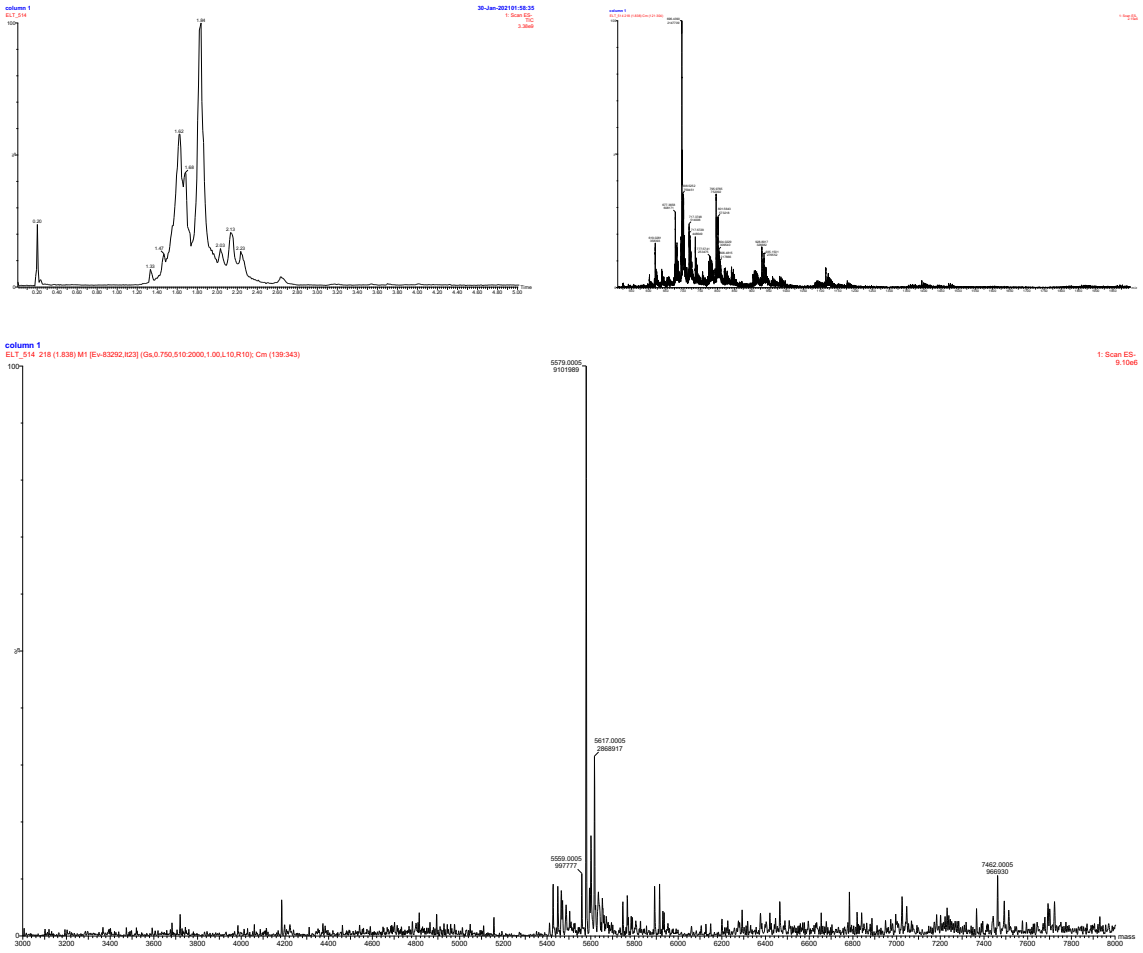
ELT_513 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



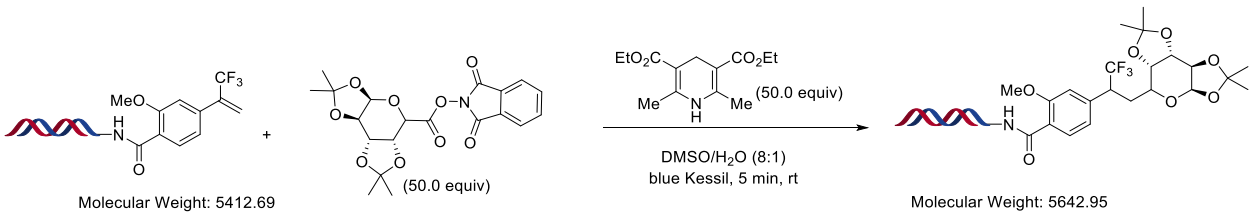
Product **5zh**, 87% yield



ELT_514 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



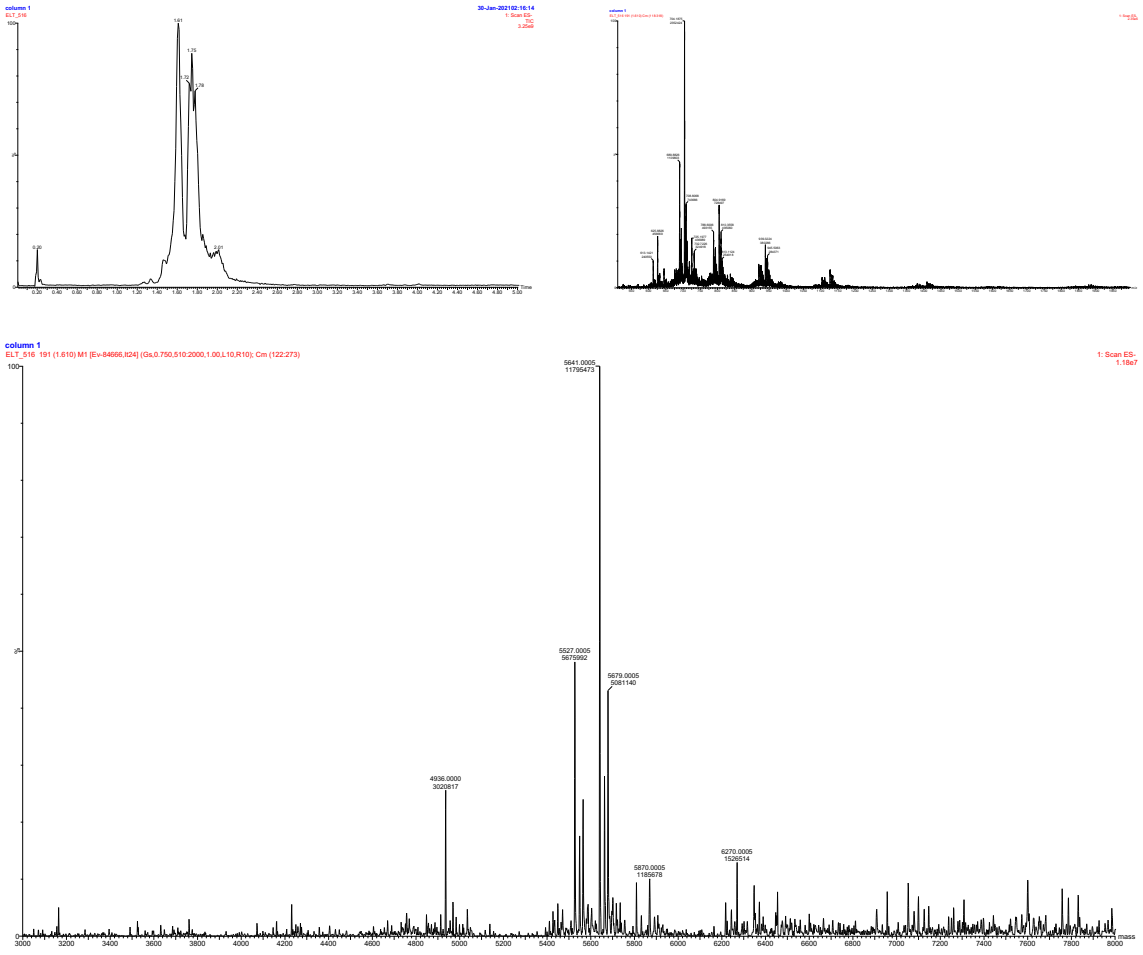
Product **5z**, 57% yield



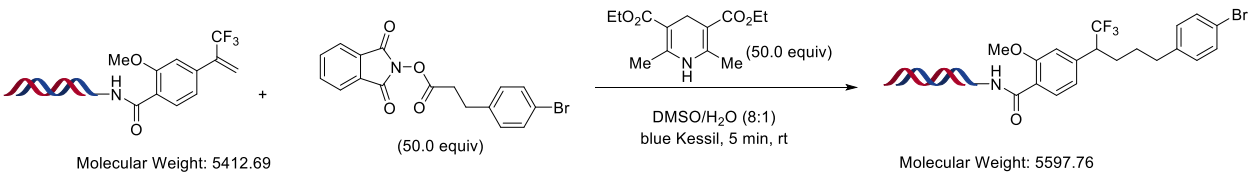
Molecular Weight: 5412.69

Molecular Weight: 5642.95

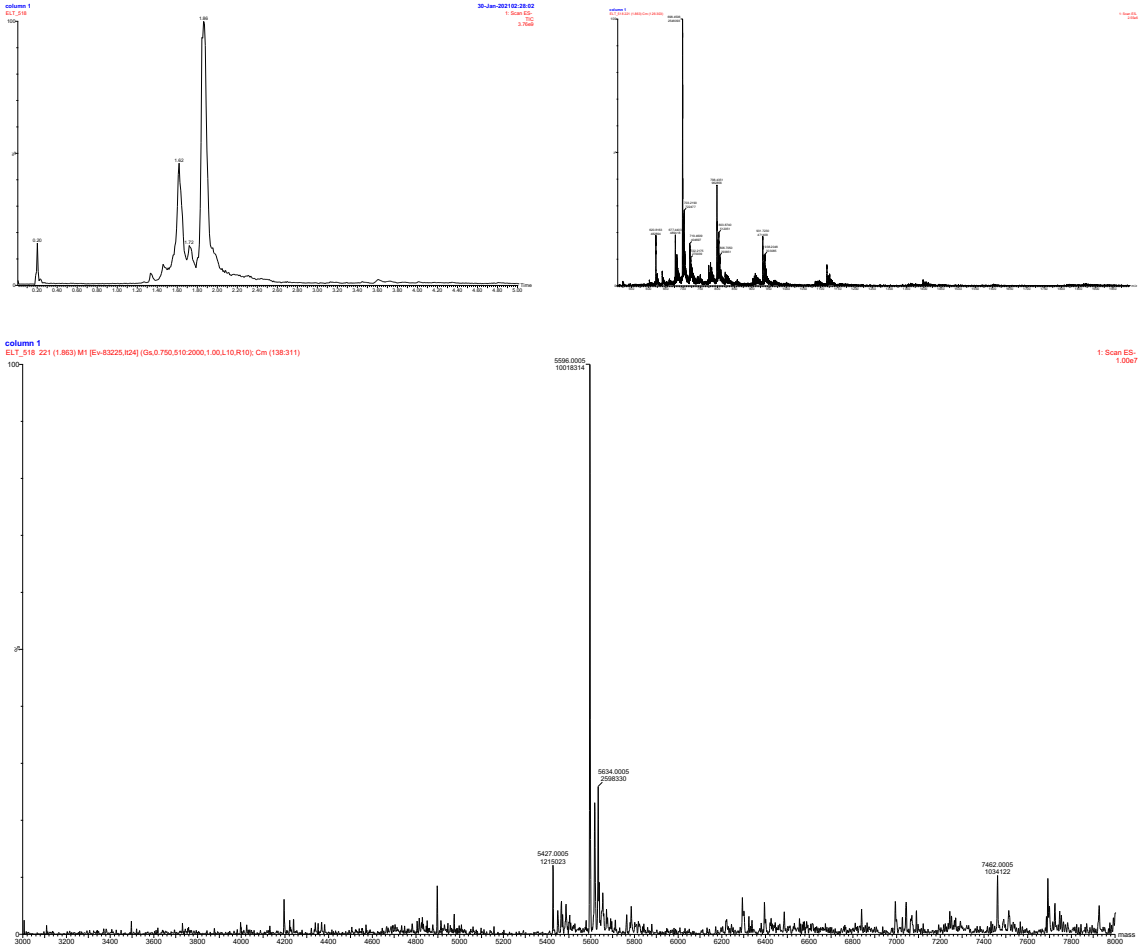
ELT_516 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



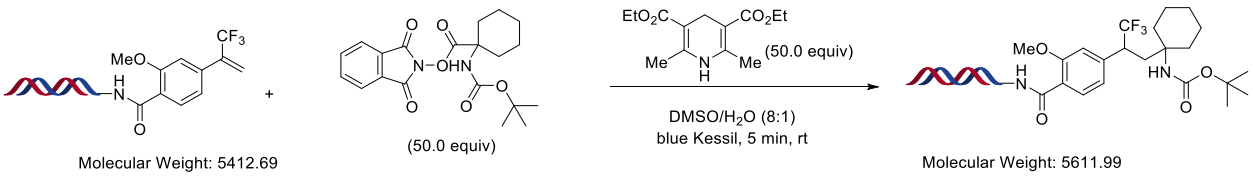
Product **5c**, 87% yield



ELT_518 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



Product **5zi**, 82% yield

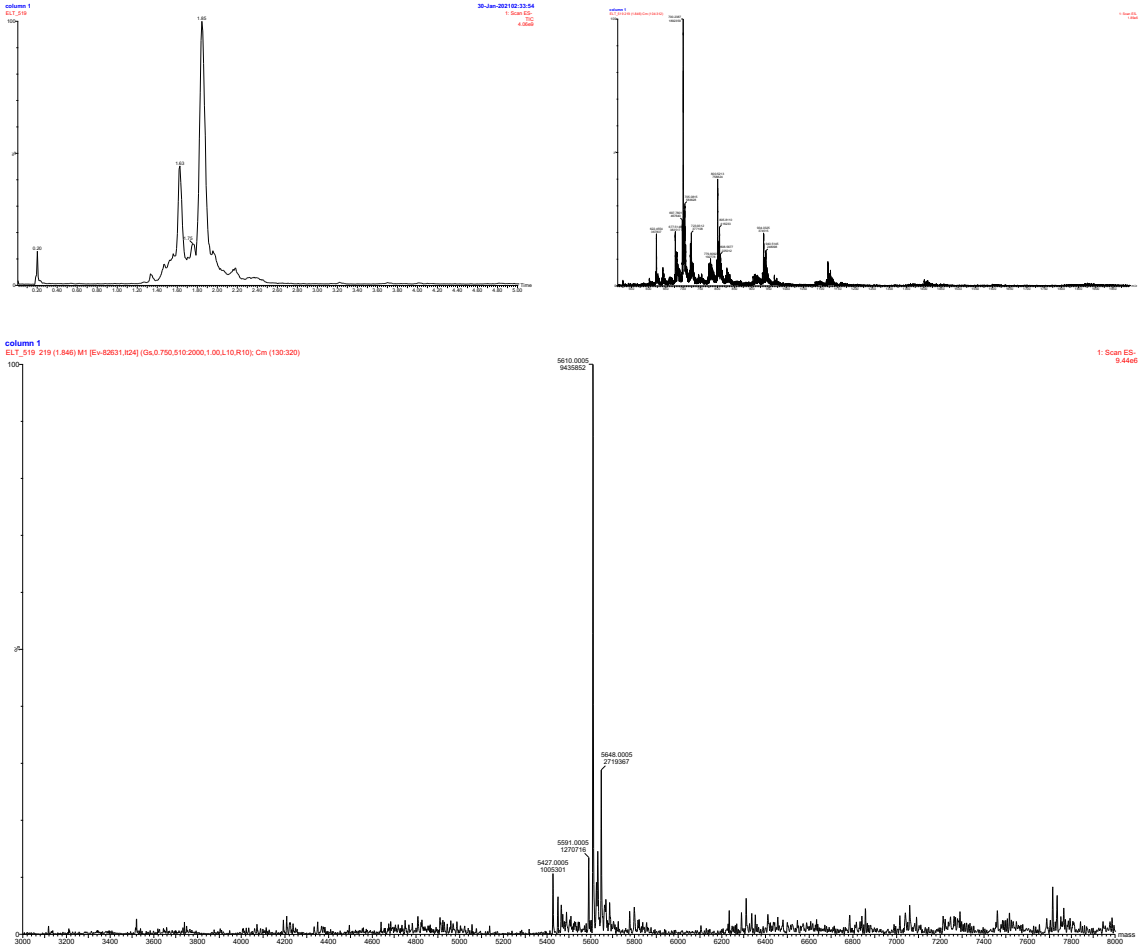


Molecular Weight: 5412.69

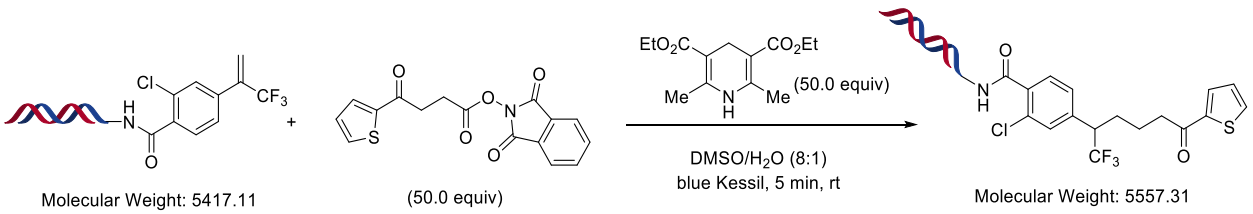
(50.0 equiv)

Molecular Weight: 5611.99

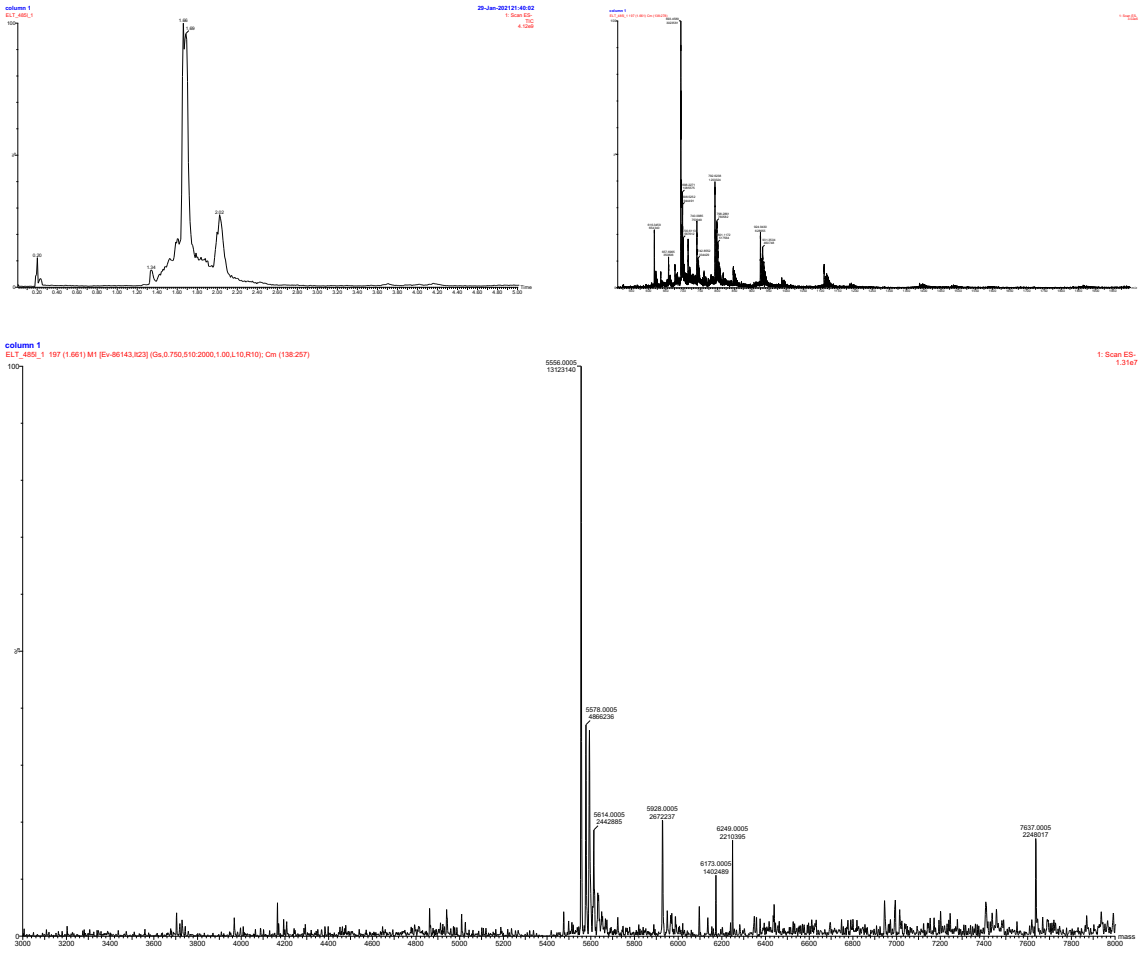
ELT_519 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



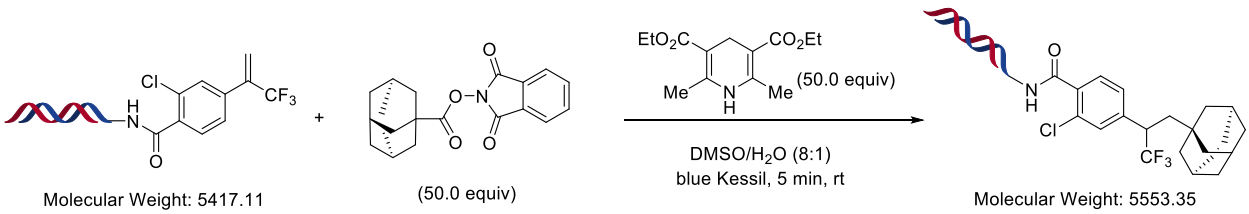
Product **6a**, 62% yield



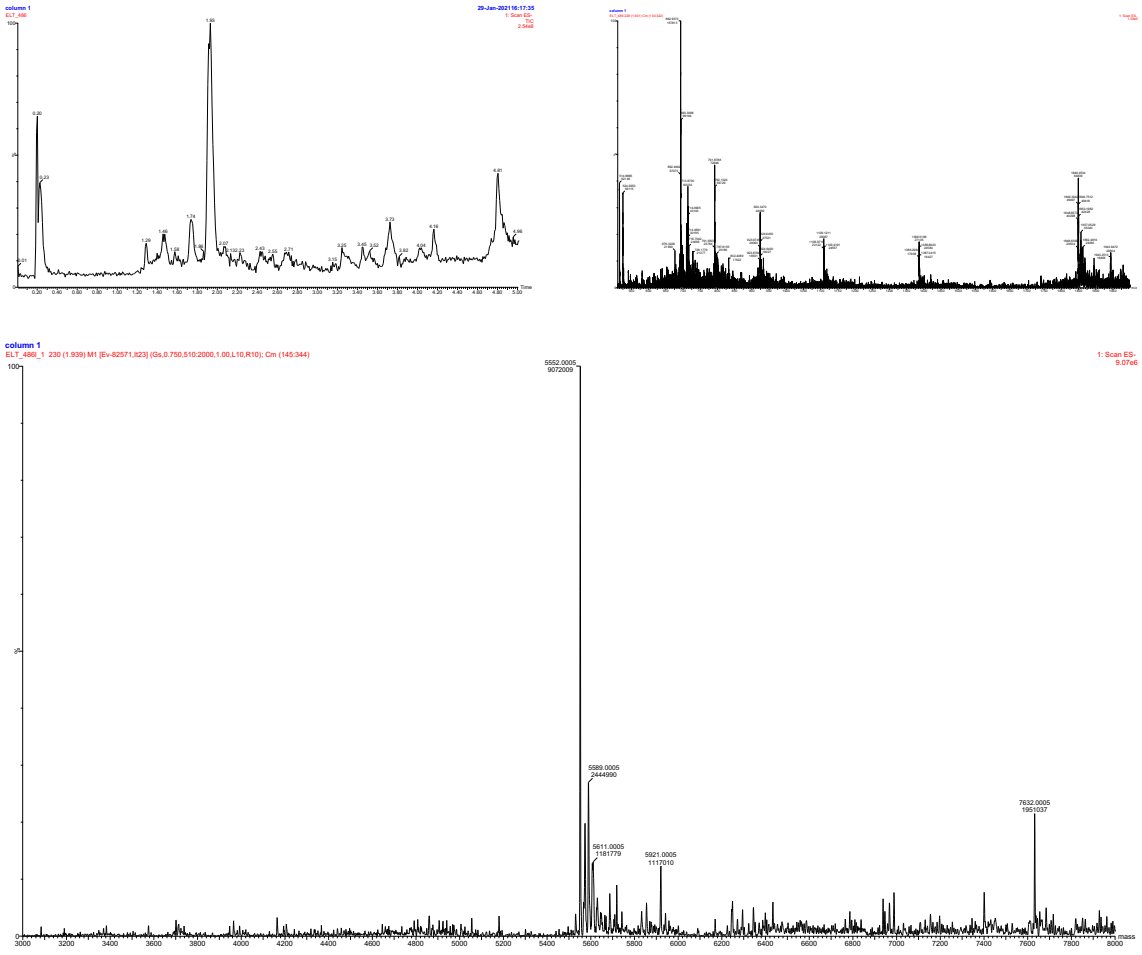
ELT_485 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



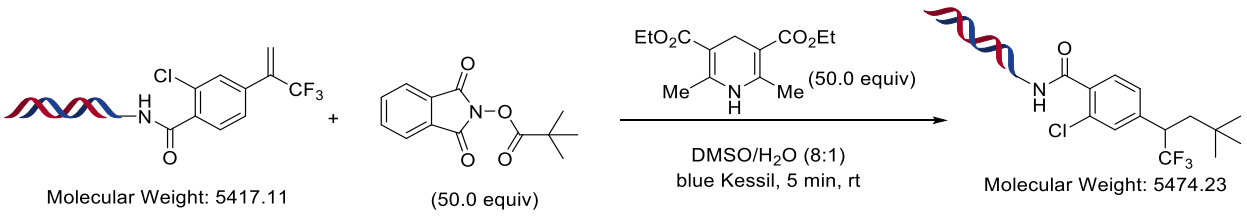
Product **6zf**, 78% yield



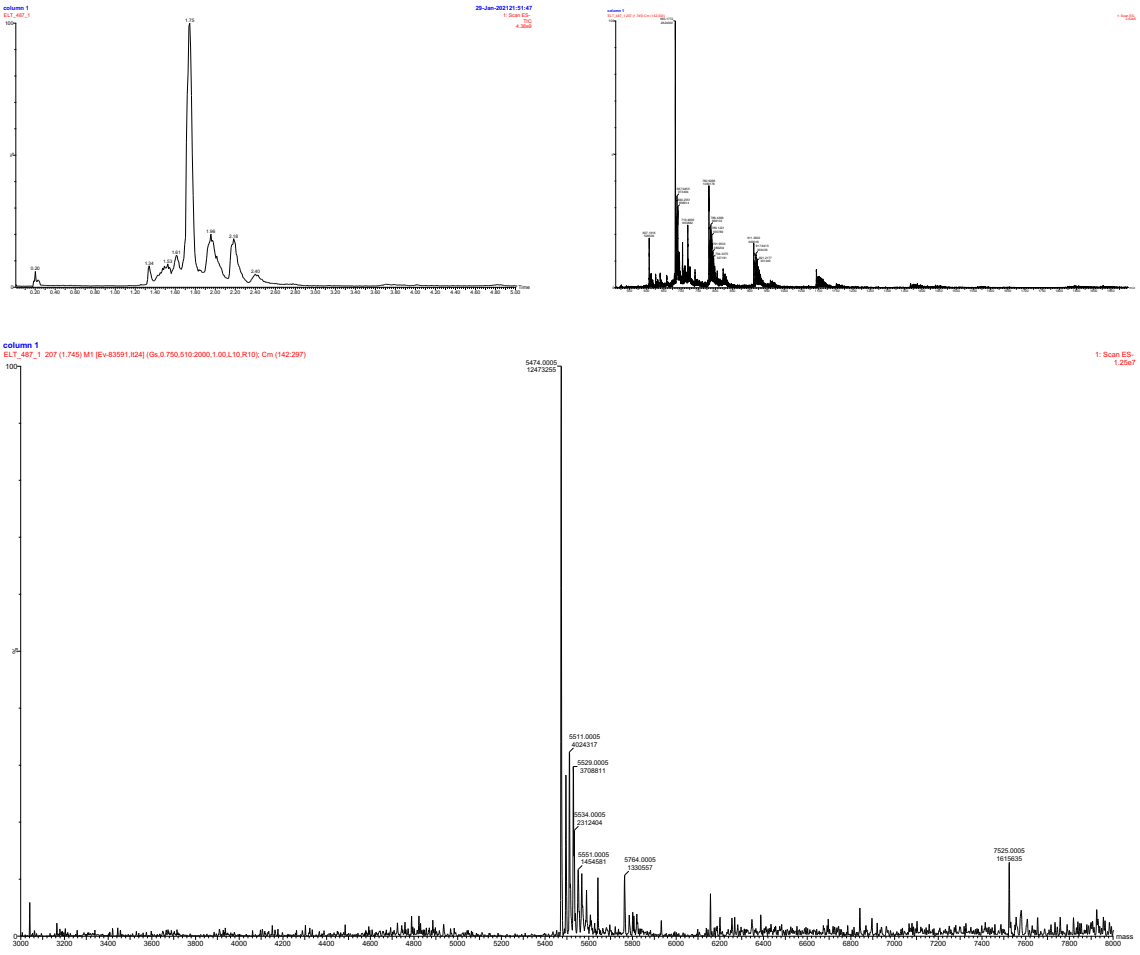
ELT_486 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



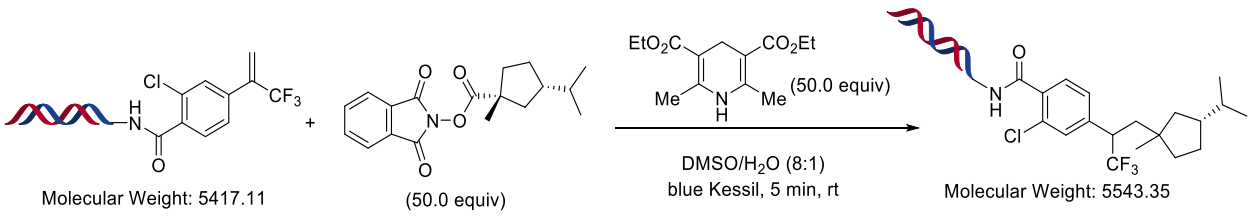
Product **6zb**, 72% yield



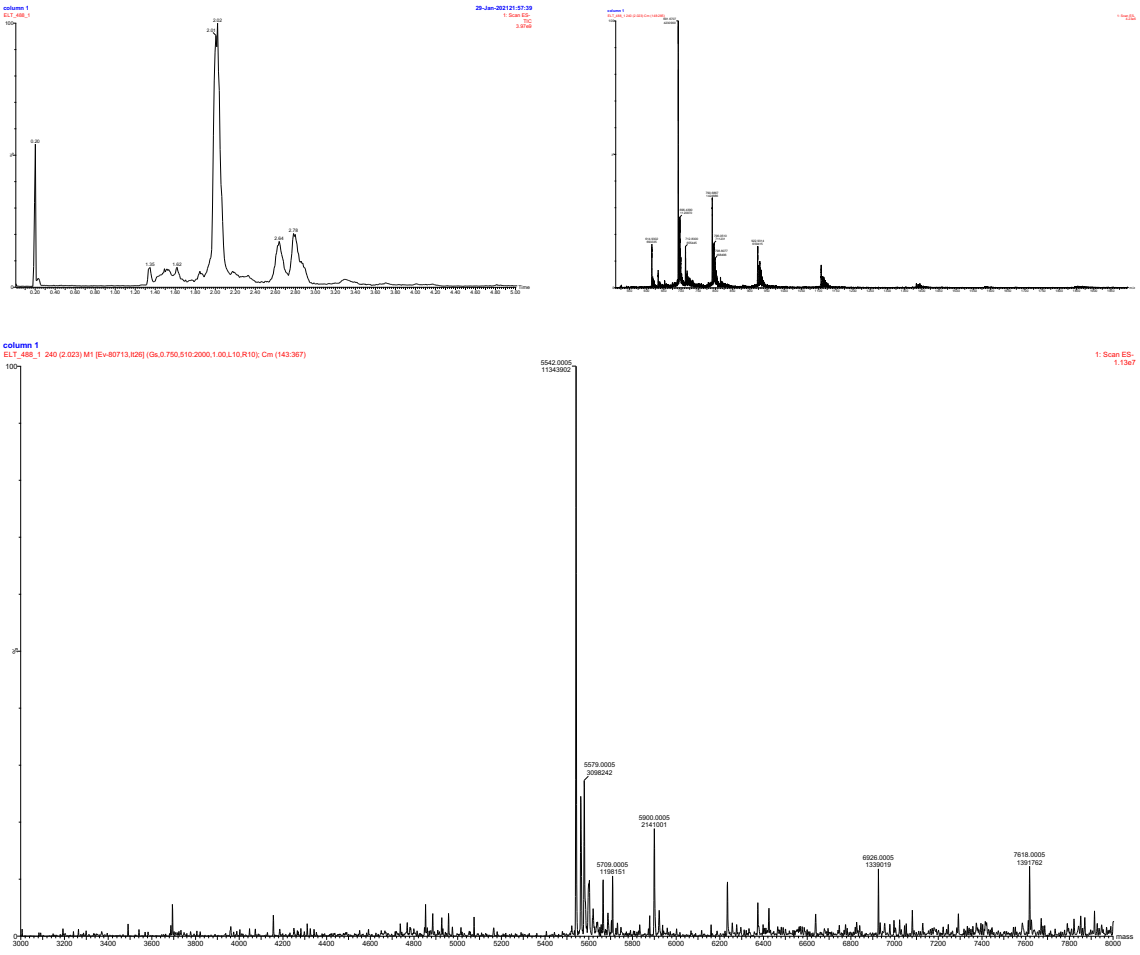
ELT_487 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



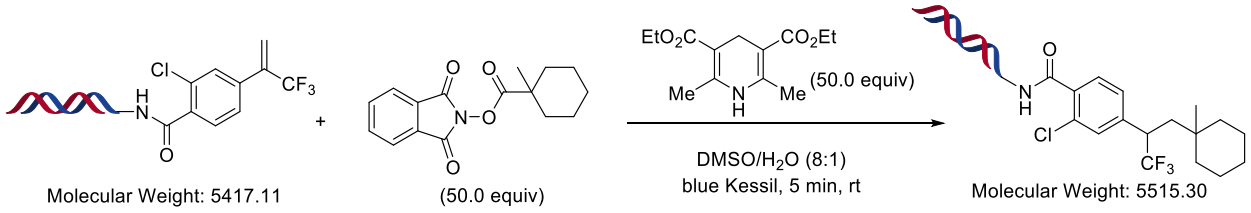
Product **6zd**, 73% yield



ELT_488 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

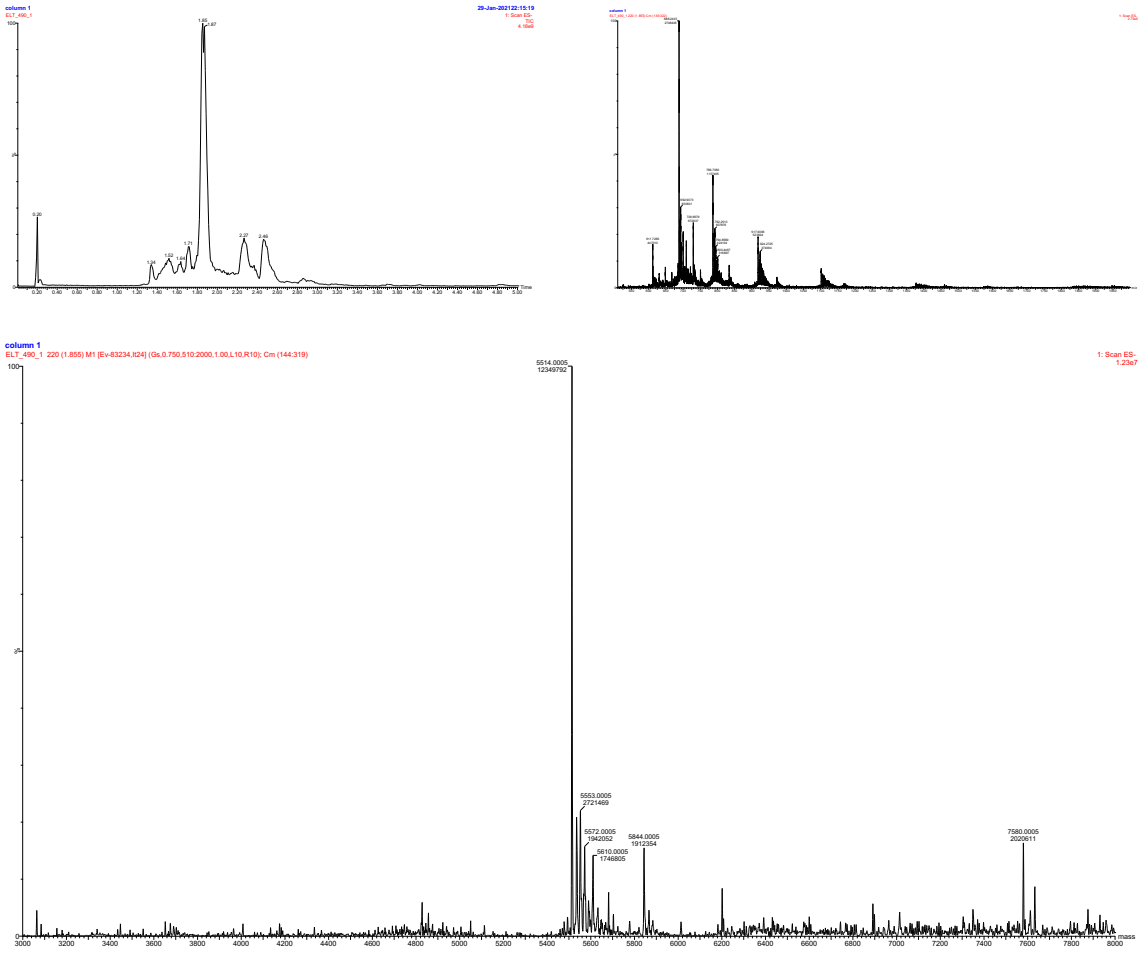


Product **6ze**, 72% yield

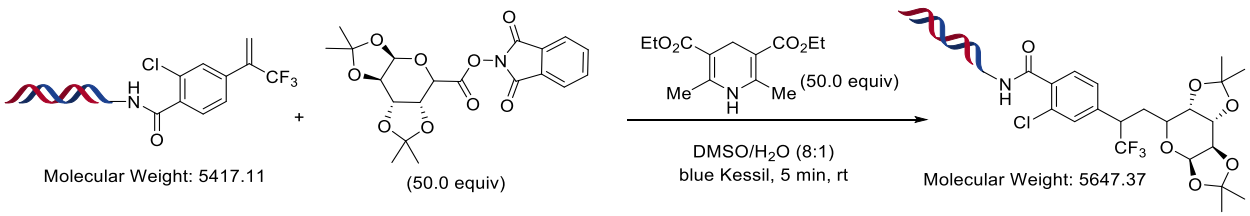


Molecular Weight: 5417.11 (50.0 equiv) Molecular Weight: 5515.30

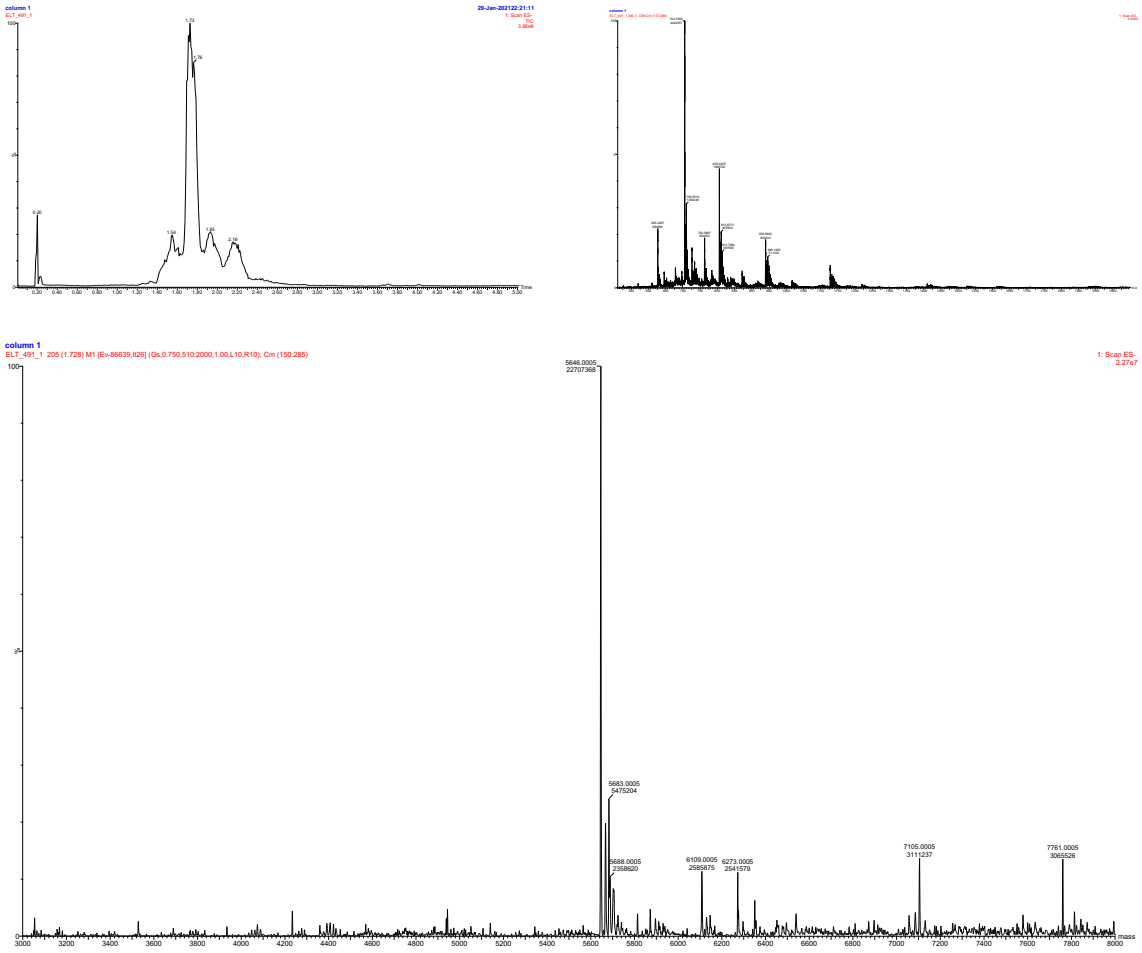
ELT_490 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



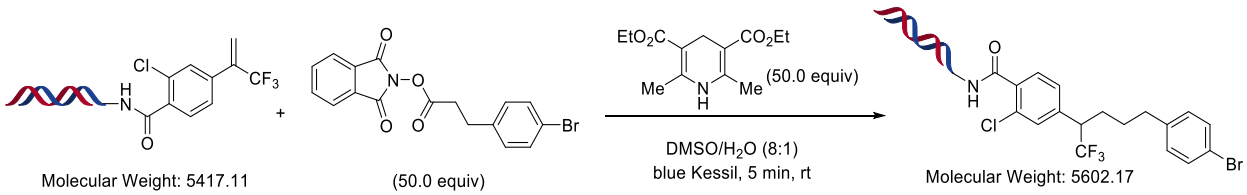
Product **6z**, 61% yield



ELT_491 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

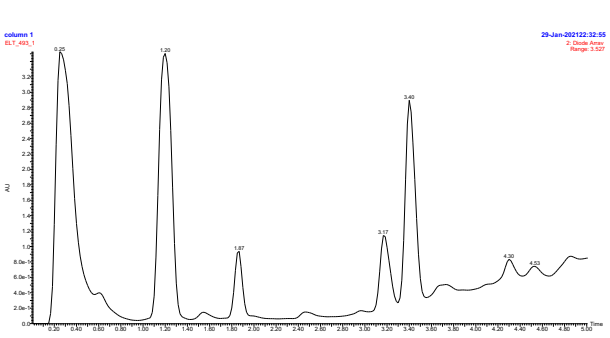


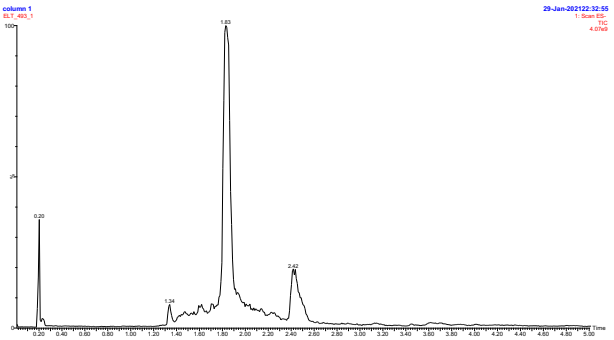
Product **6c**, 78% yield

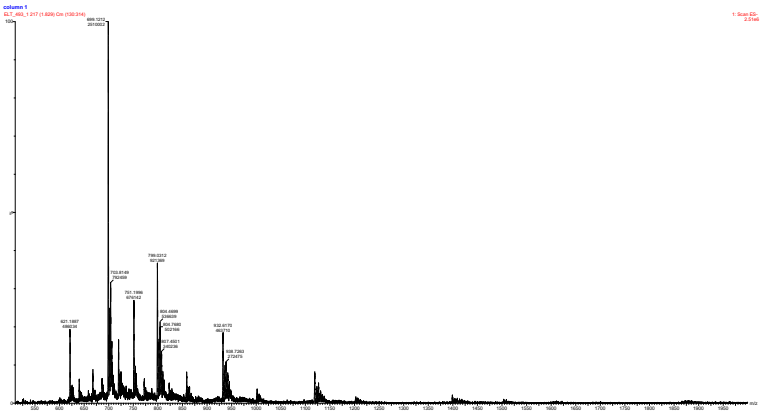


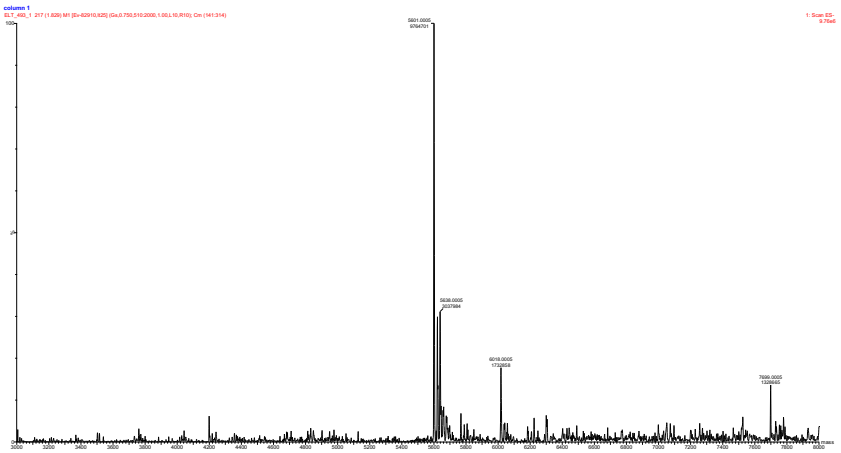
Molecular Weight: 5417.11 (50.0 equiv) Molecular Weight: 5602.17

ELT_493 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

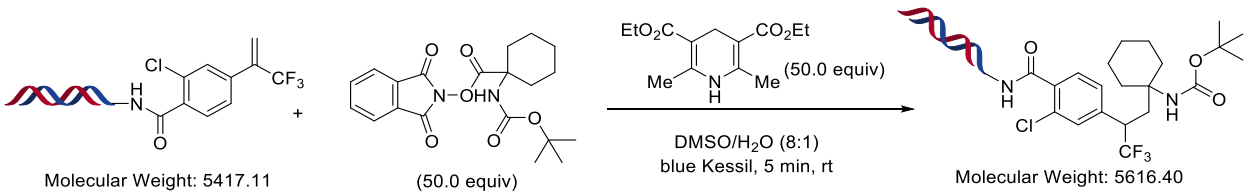




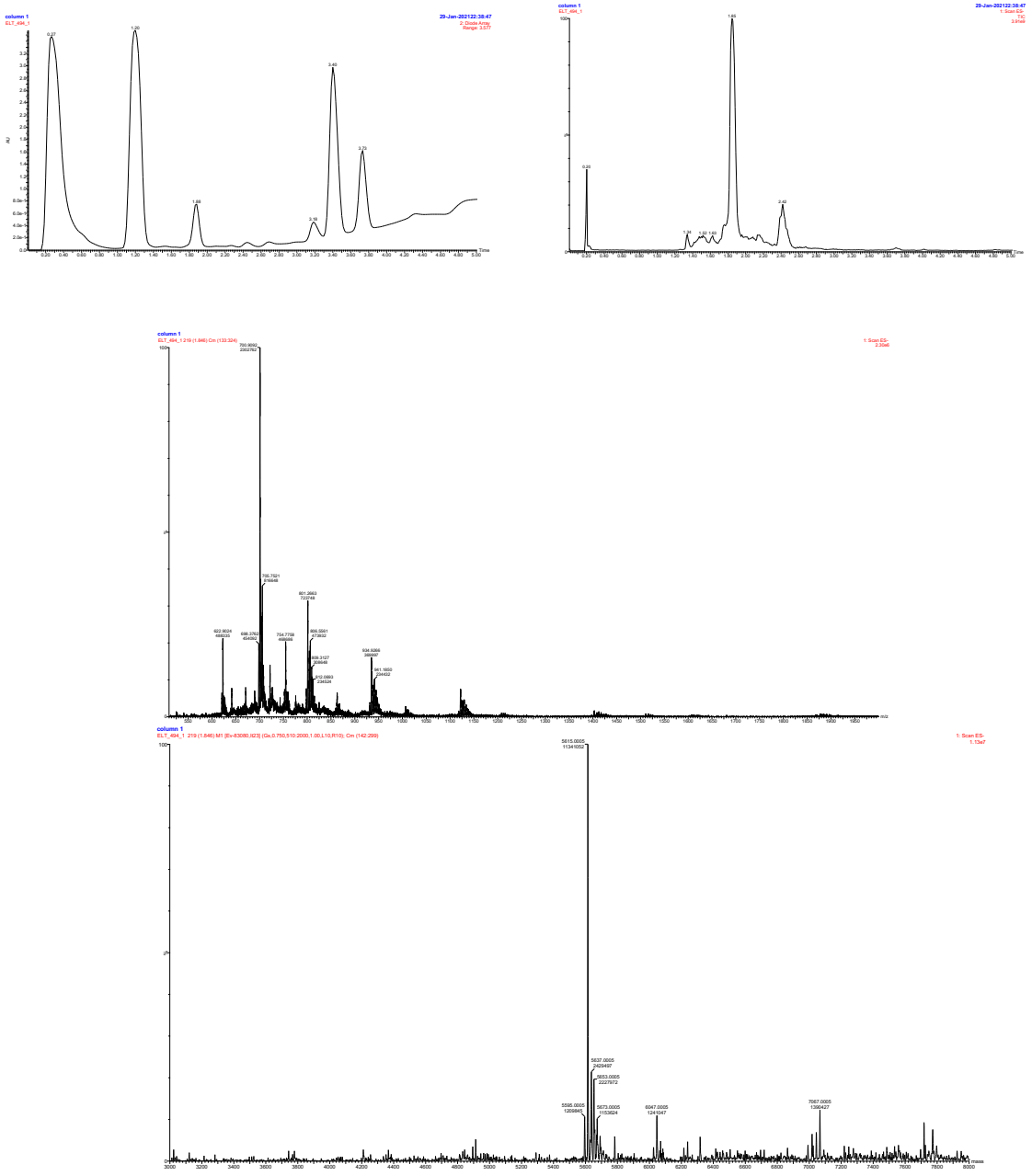




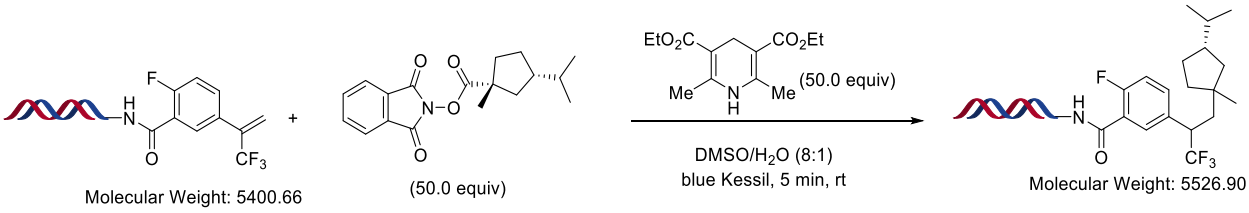
Product **6zi**, 77% yield



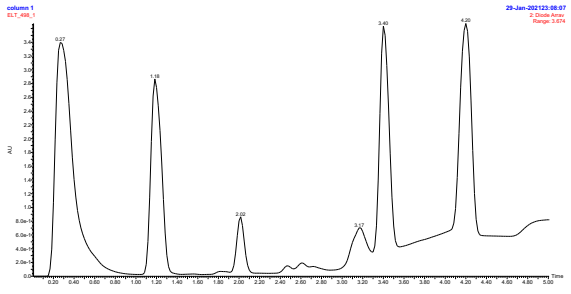
ELT_494 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

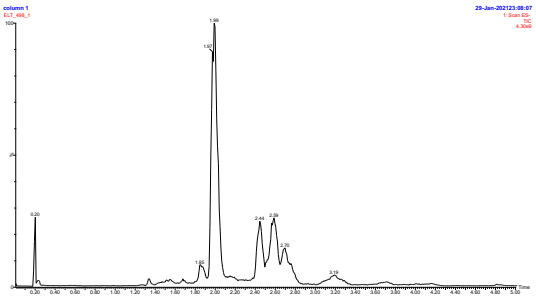


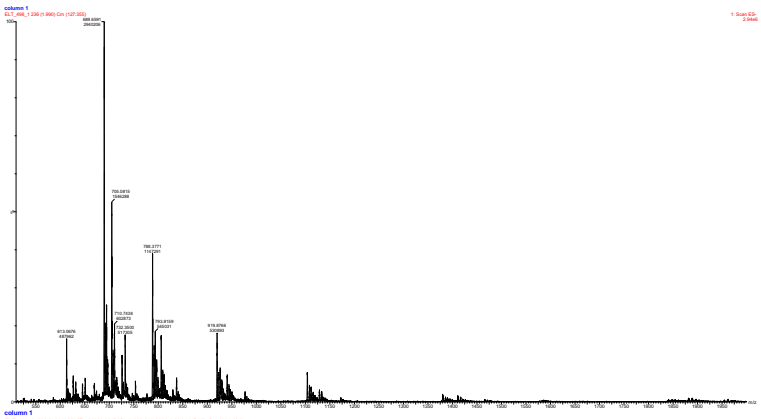
Product **7zd**, 70% yield

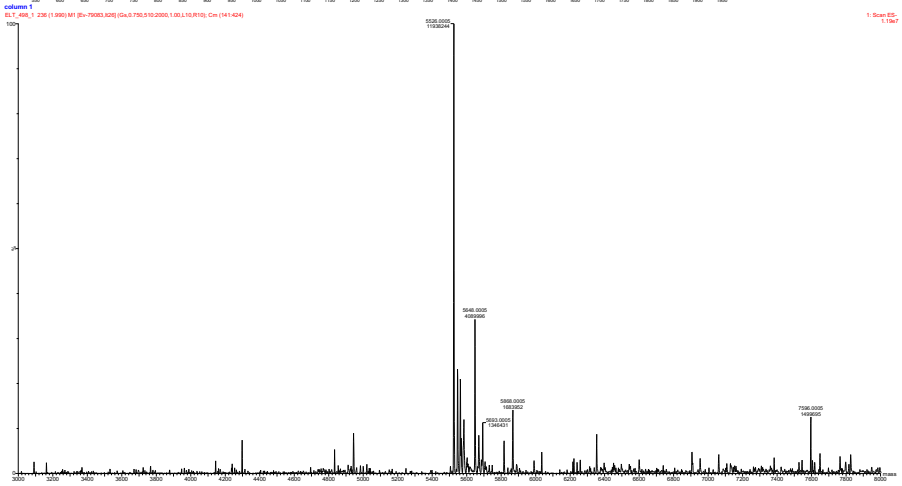


ELT_498 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

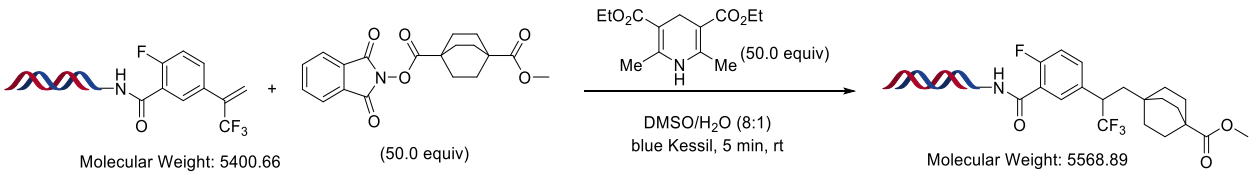




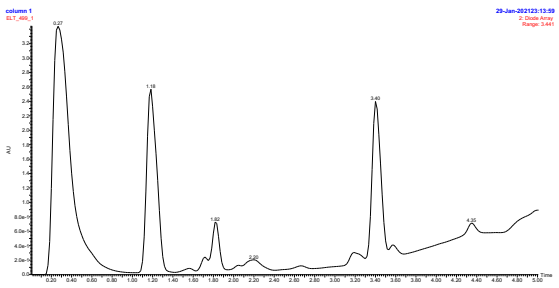


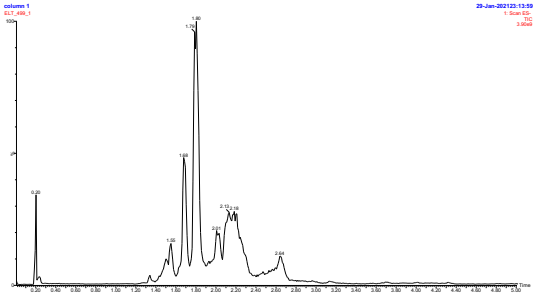


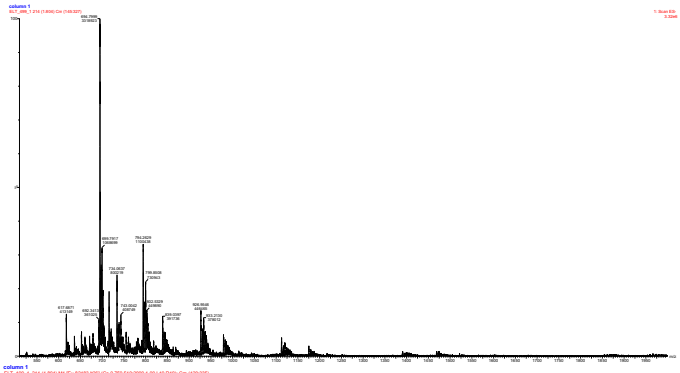
Product **7zh**, 75% yield



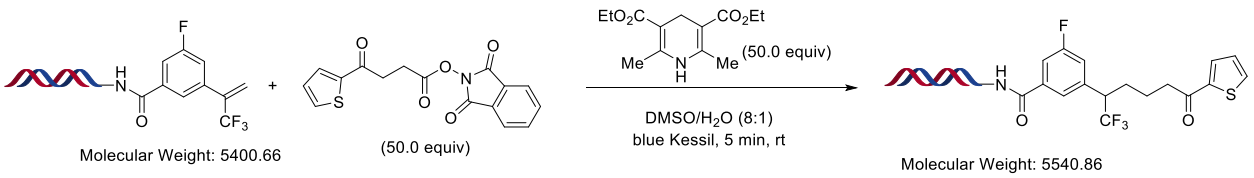
ELT_499 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



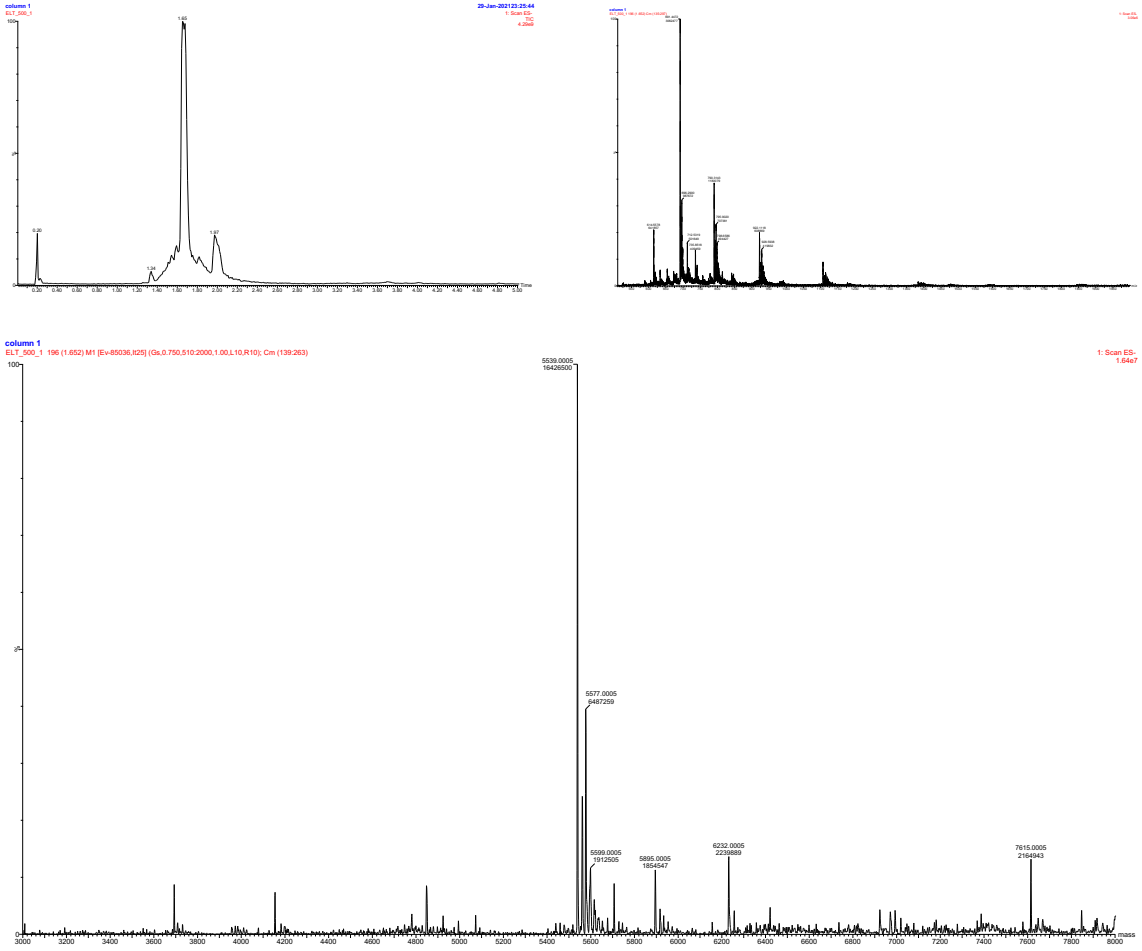




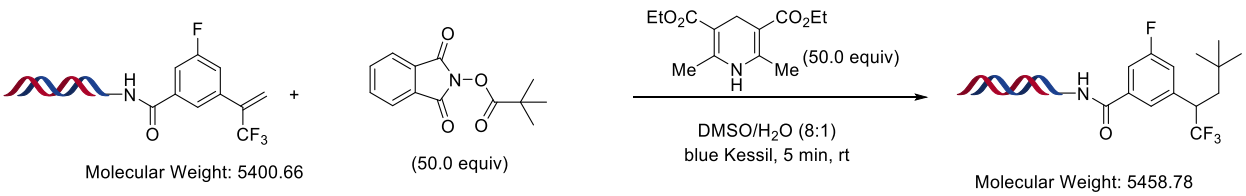
Product **8a**, 83% yield



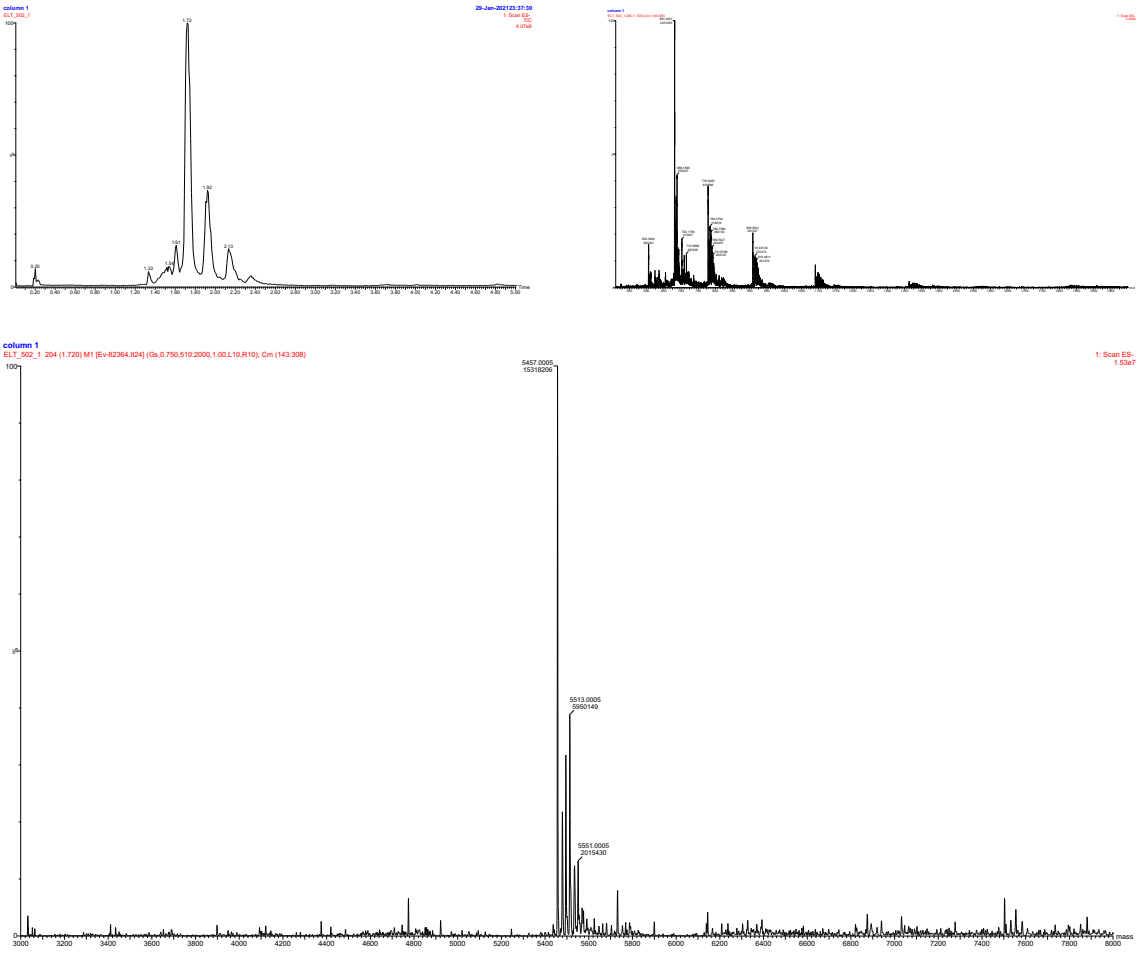
ELT_500 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



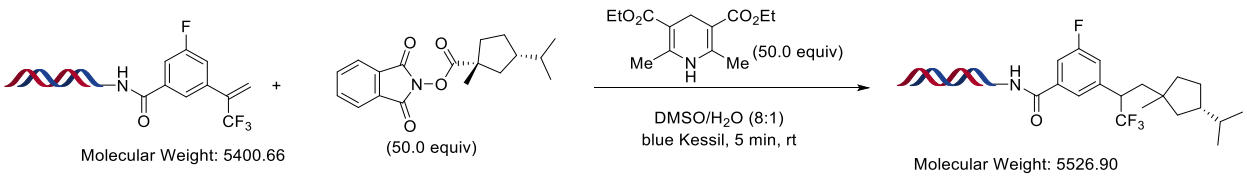
Product **8zb**, 70%



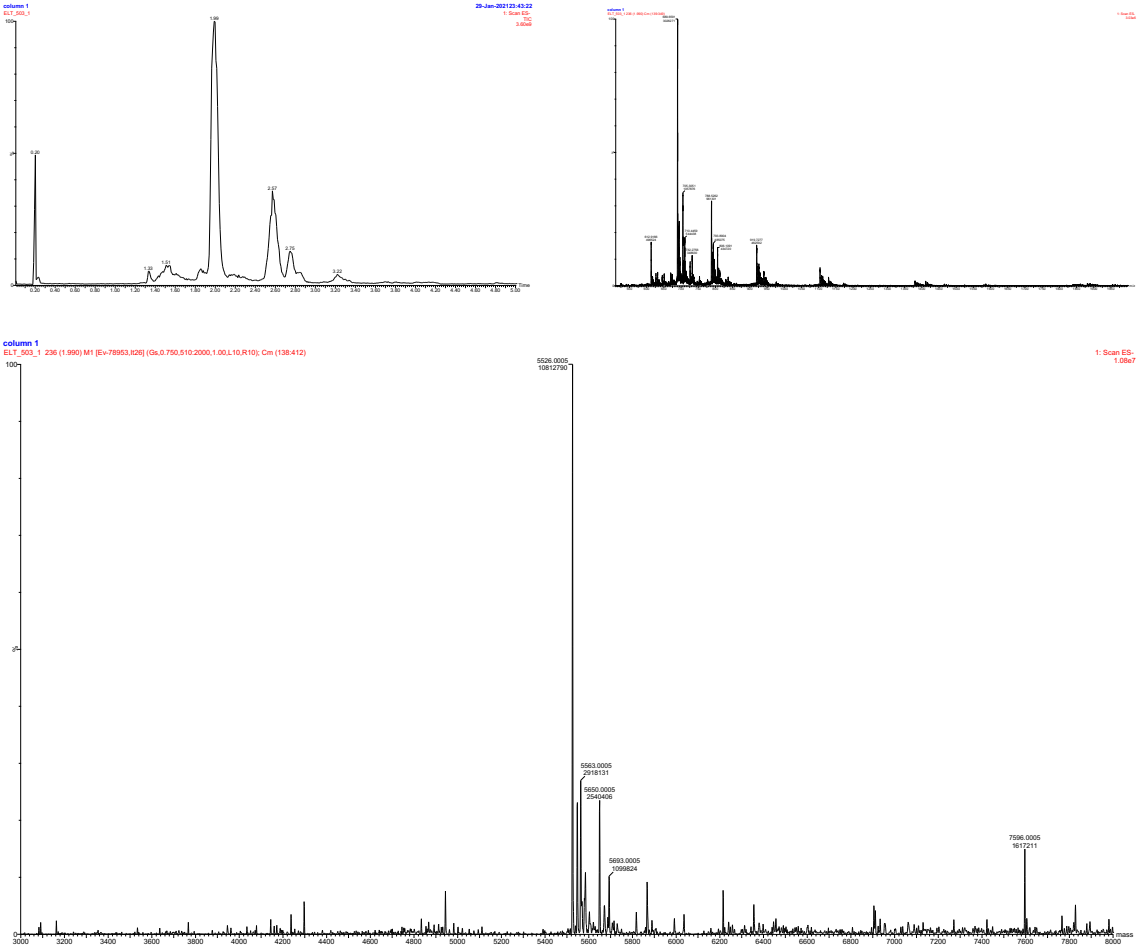
ELT_502 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



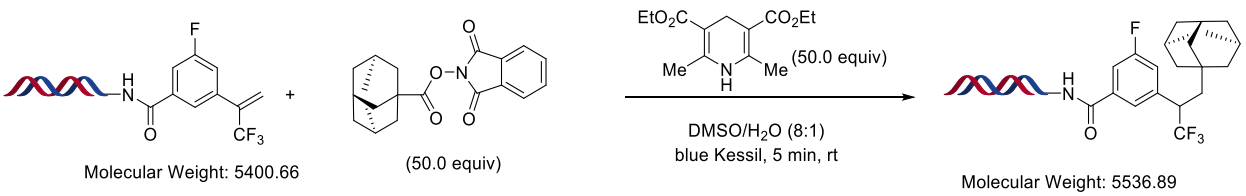
Product **8zd**, 77% yield



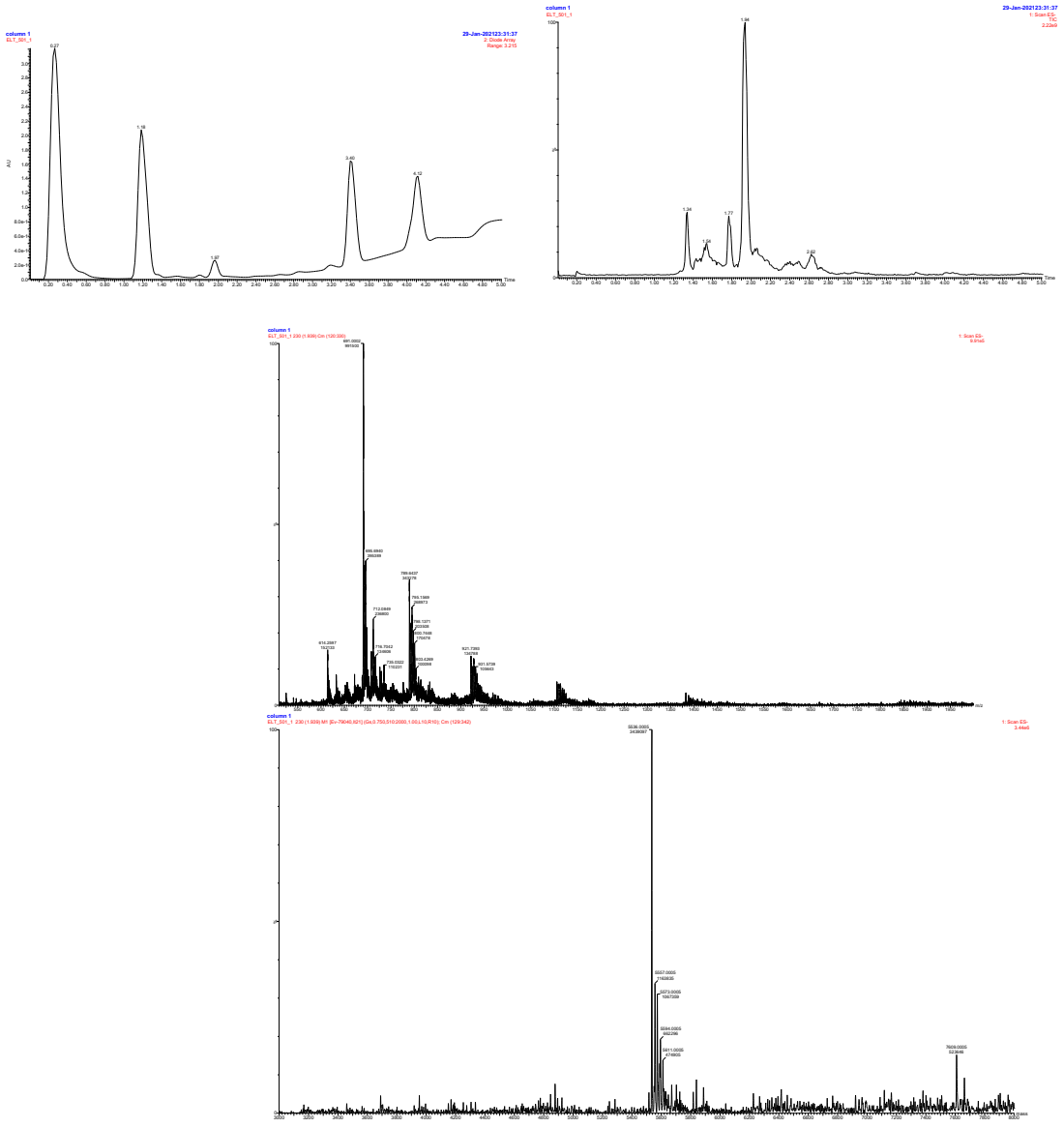
ELT_503 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



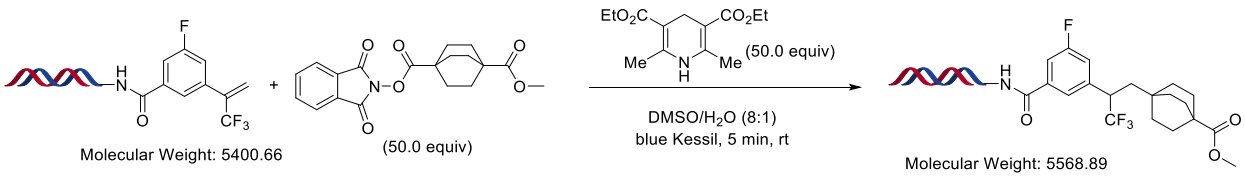
Product **8zf**, 81% yield



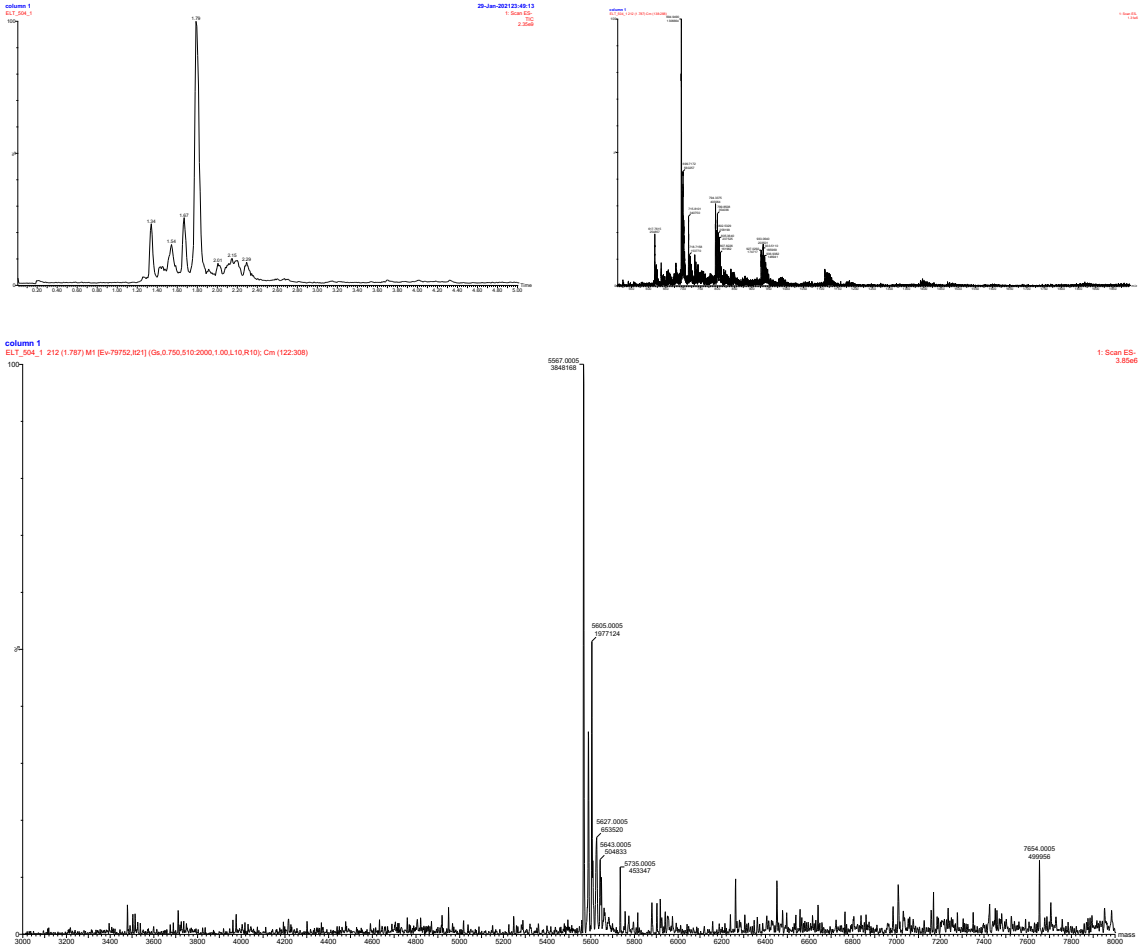
ELT_501 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



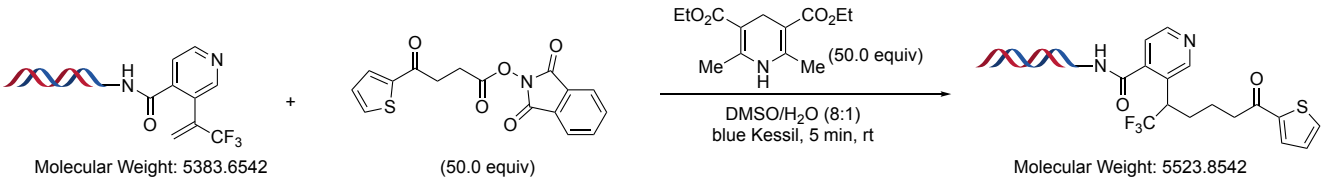
Product **8zh**, 81% yield



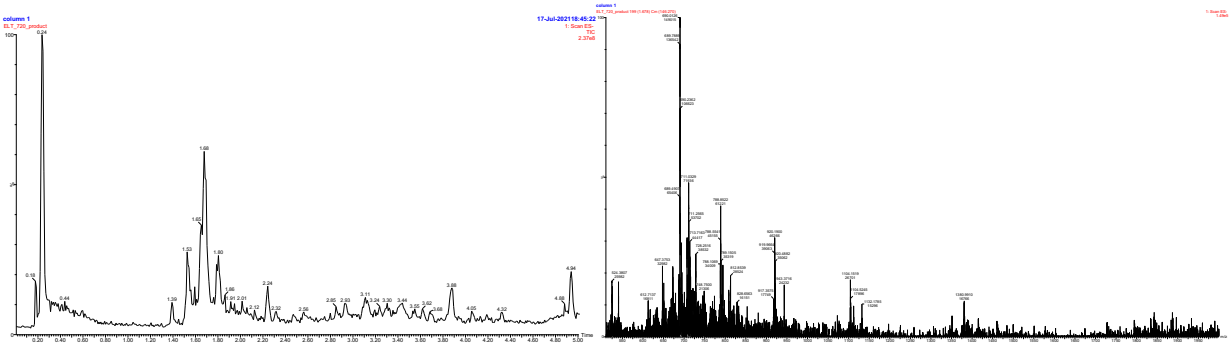
ELT_504 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

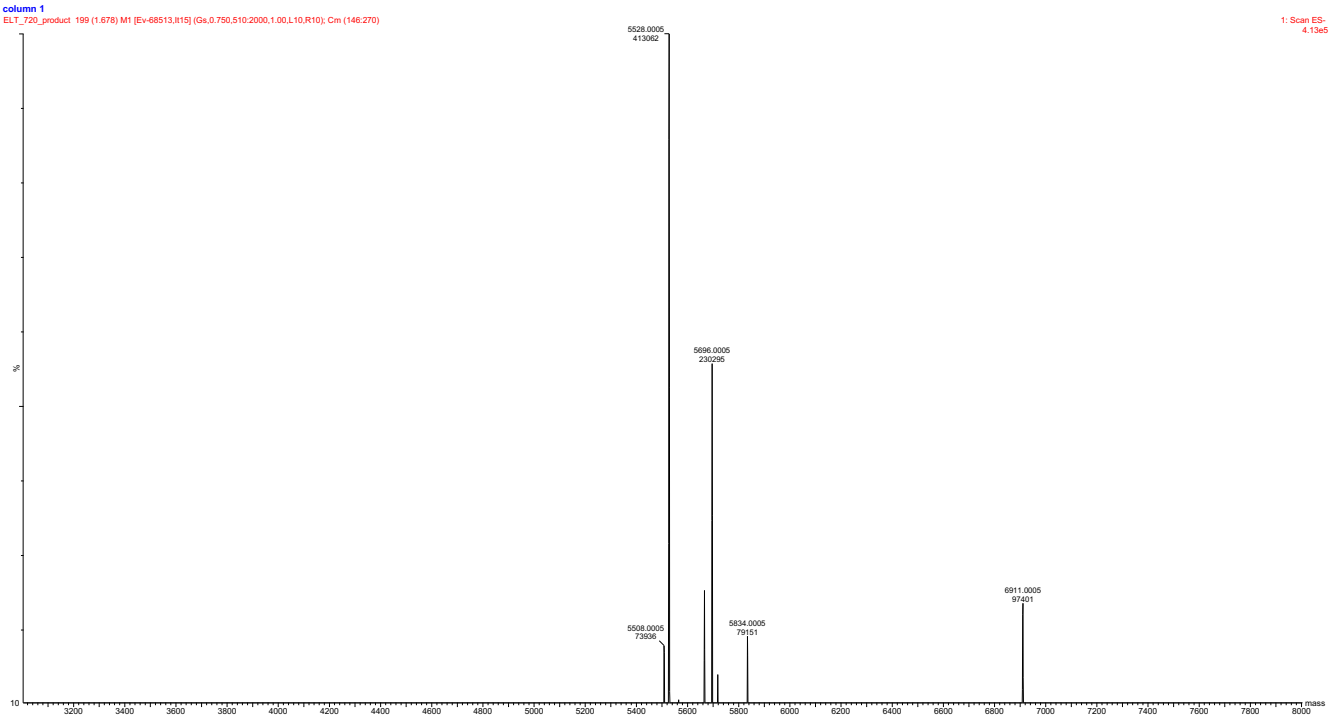


Product **9a**, 73% yield



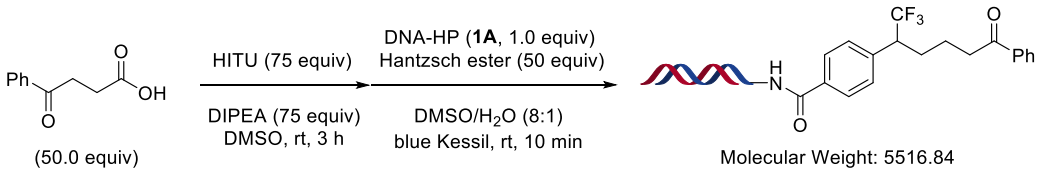
ELT_504 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



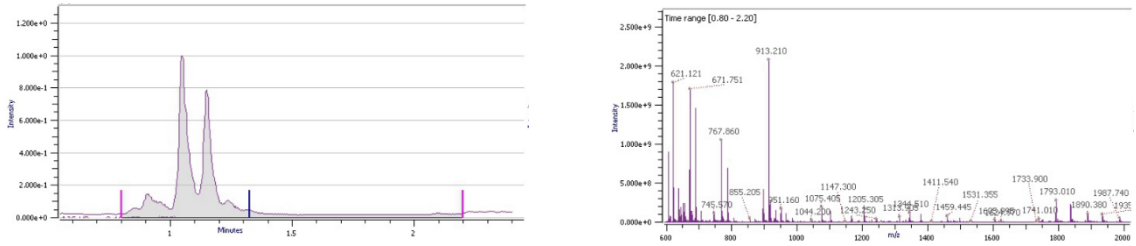


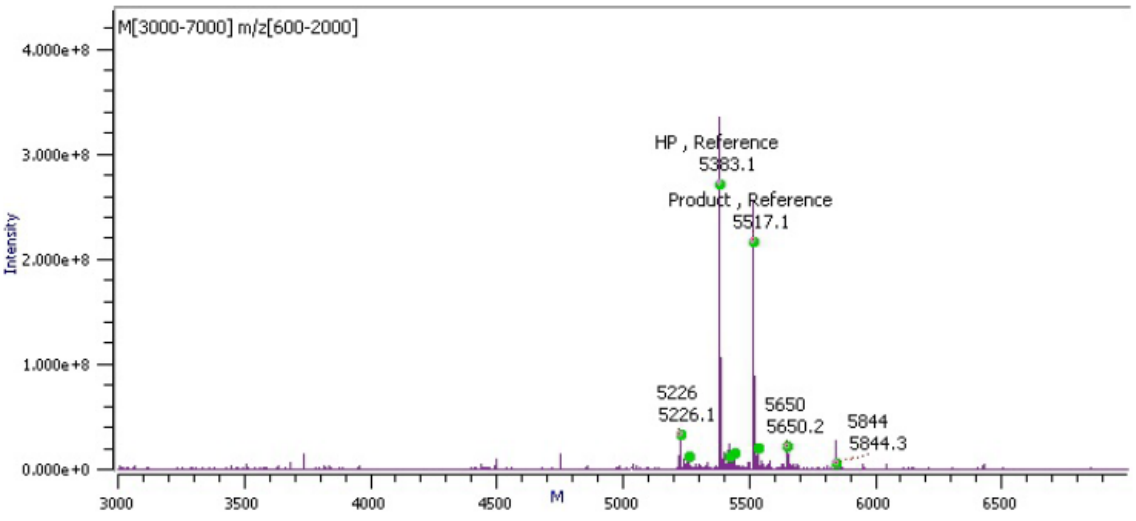
On-DNA photoinduced decarboxylative alkylation of CF_3-alkenes with in situ generated redox-active esters (Scheme 5)

Product **3f**, 45% yield

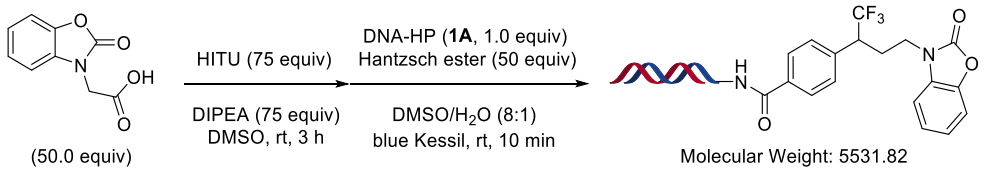


ELT_175, AJC-UPenn-8-19-175.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

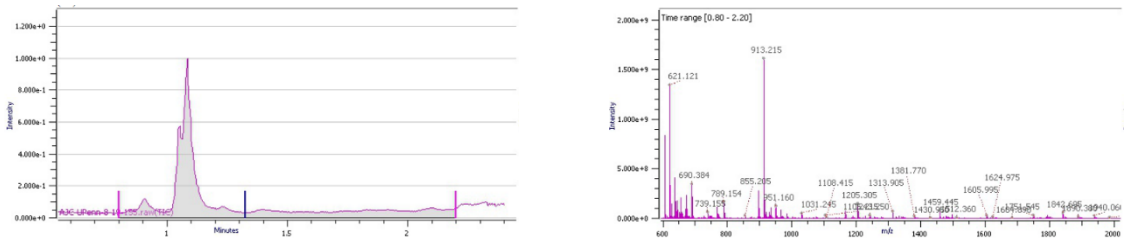


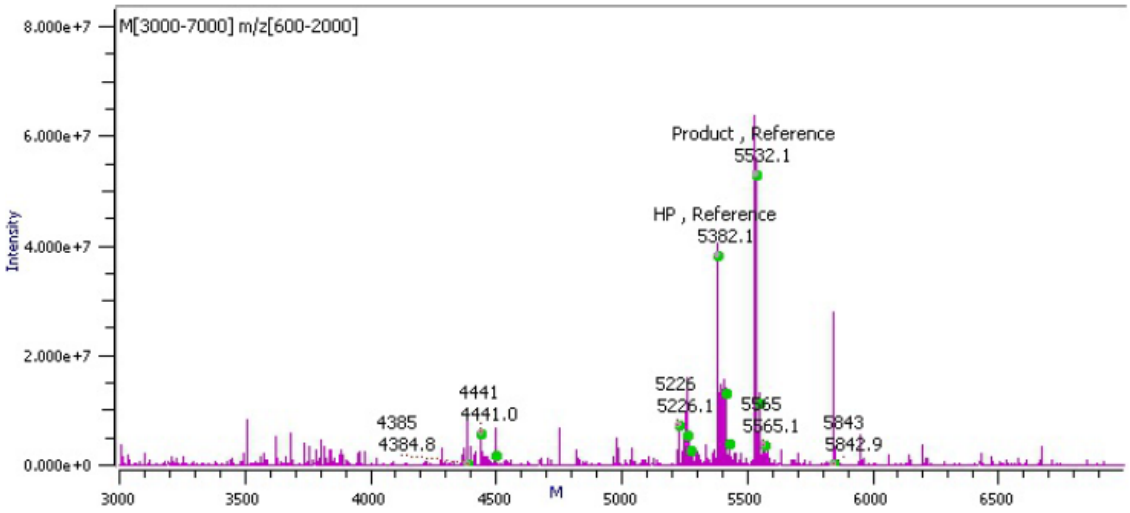


Product **3zi**, 46% yield

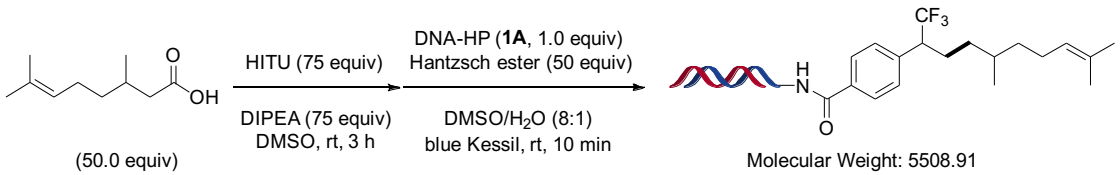


ELT_155, AJC-UPenn-8-19-155.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

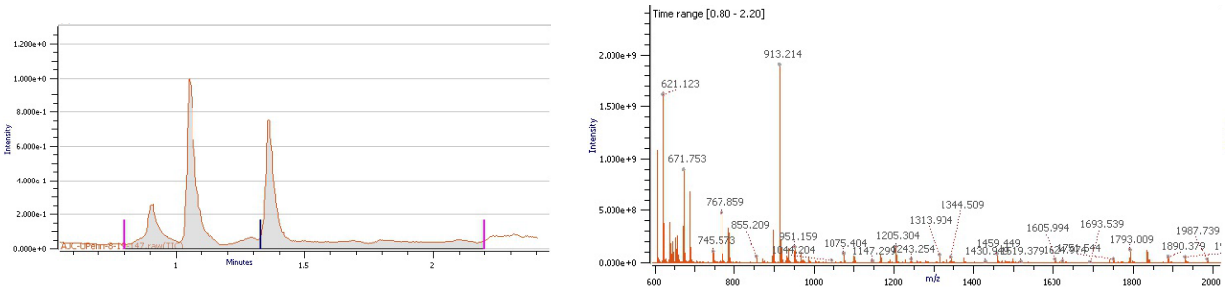


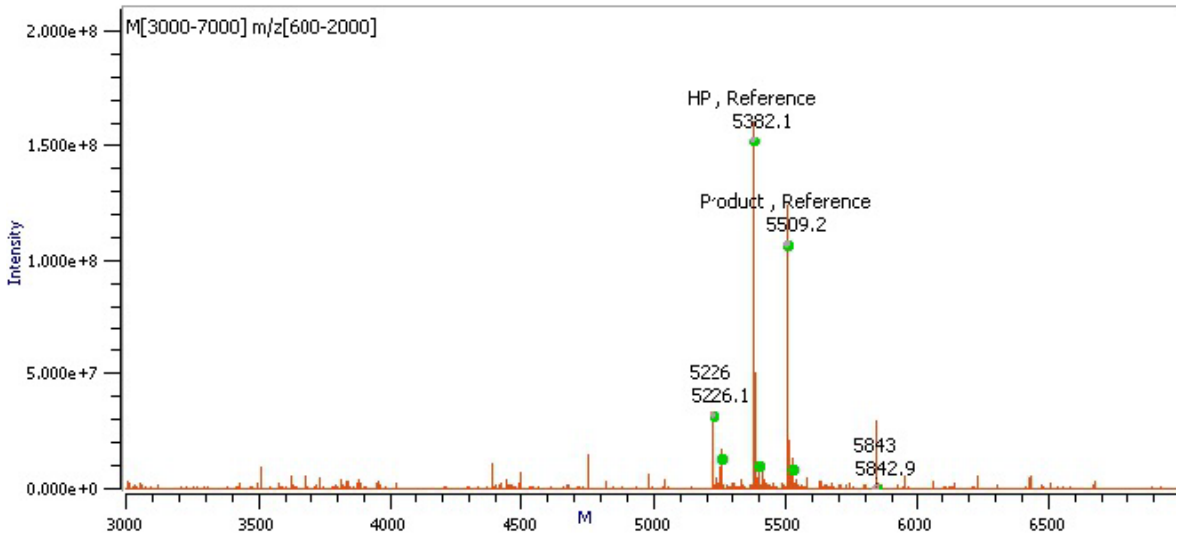


Product **3zj**, 42% yield

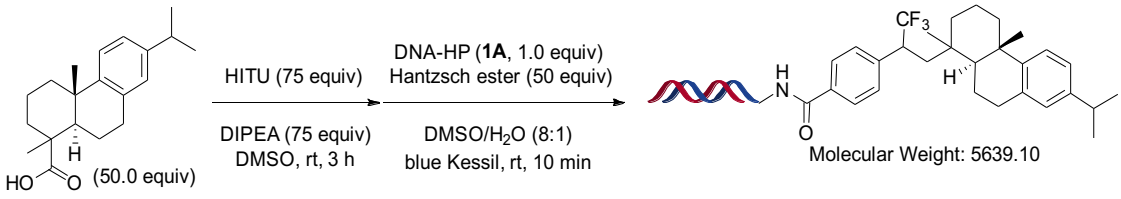


ELT_147, AJC-UPenn-8-19-147.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

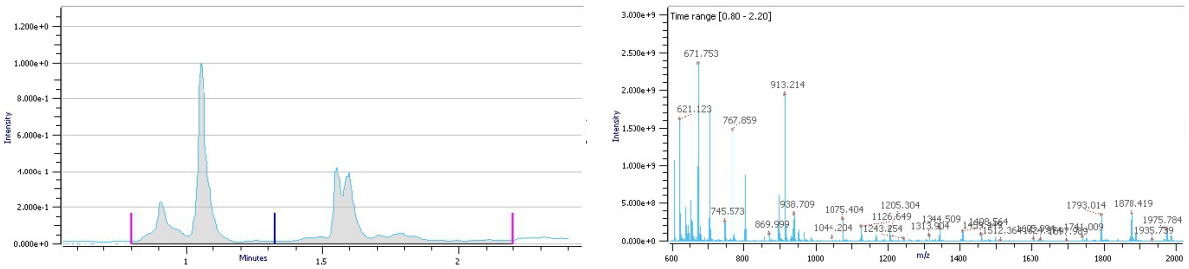


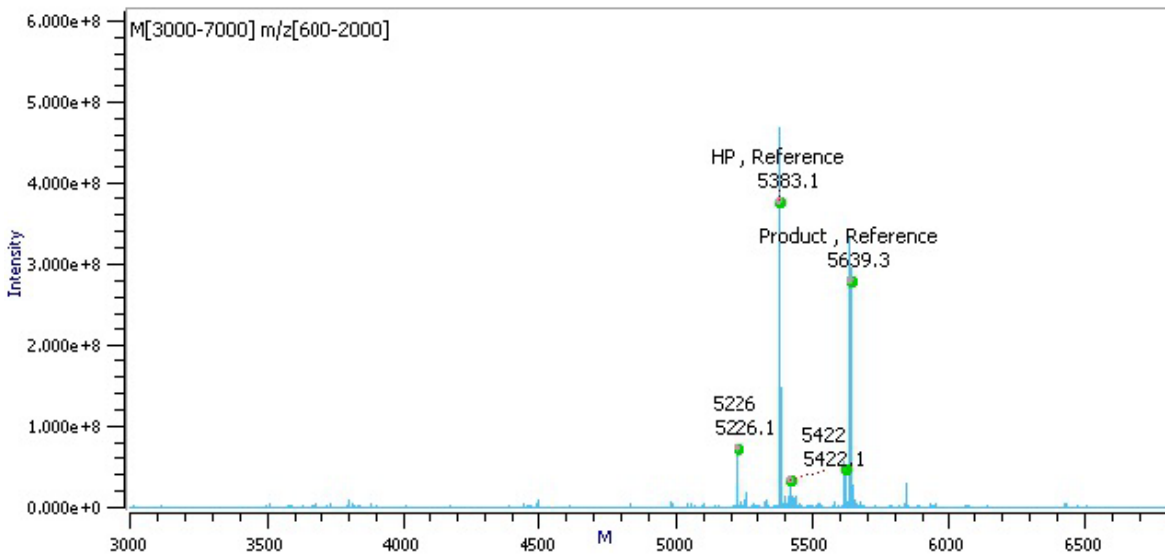


Product **3zk**, 44% yield



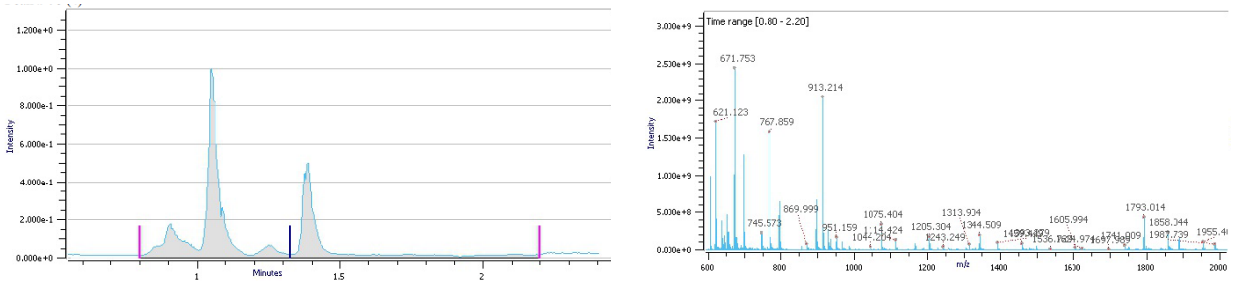
ELT_125, AJC-UPenn-8-19-125.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

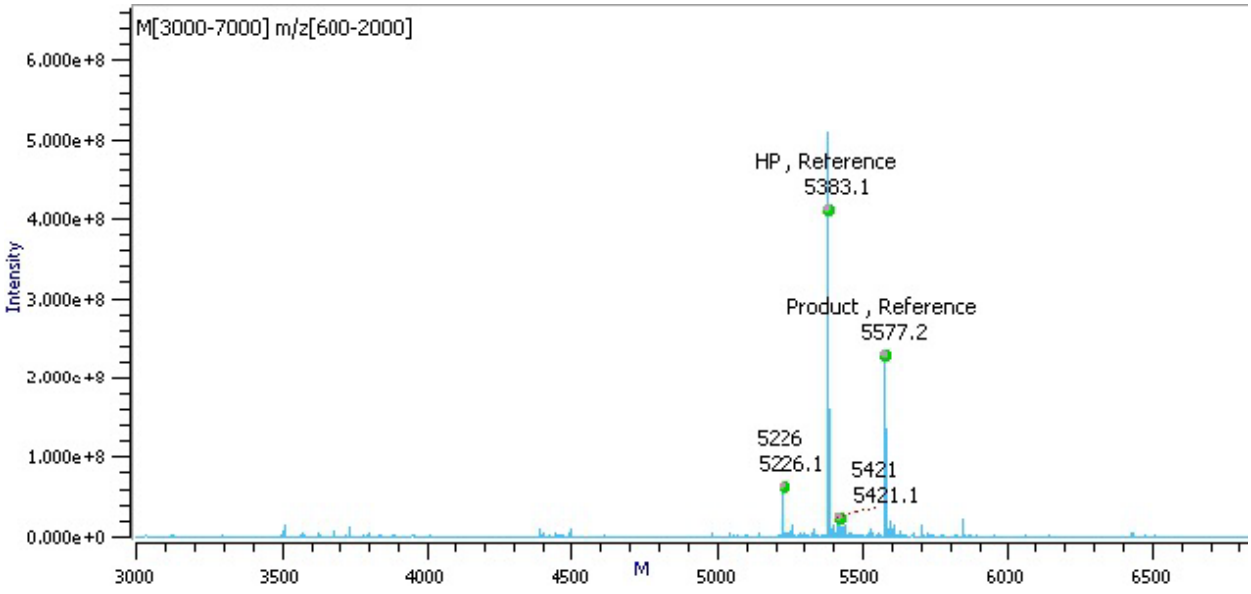




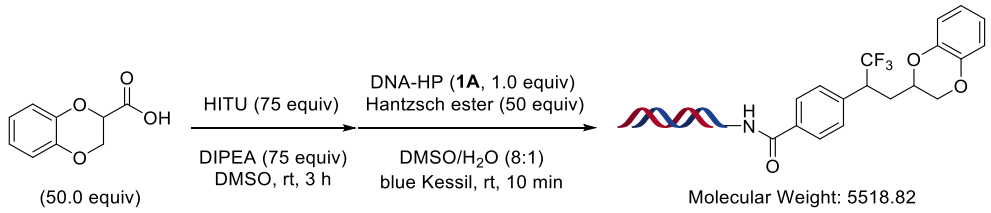
Product **3zl**, 40% yield

ELT_177, AJC-UPenn-8-19-177.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

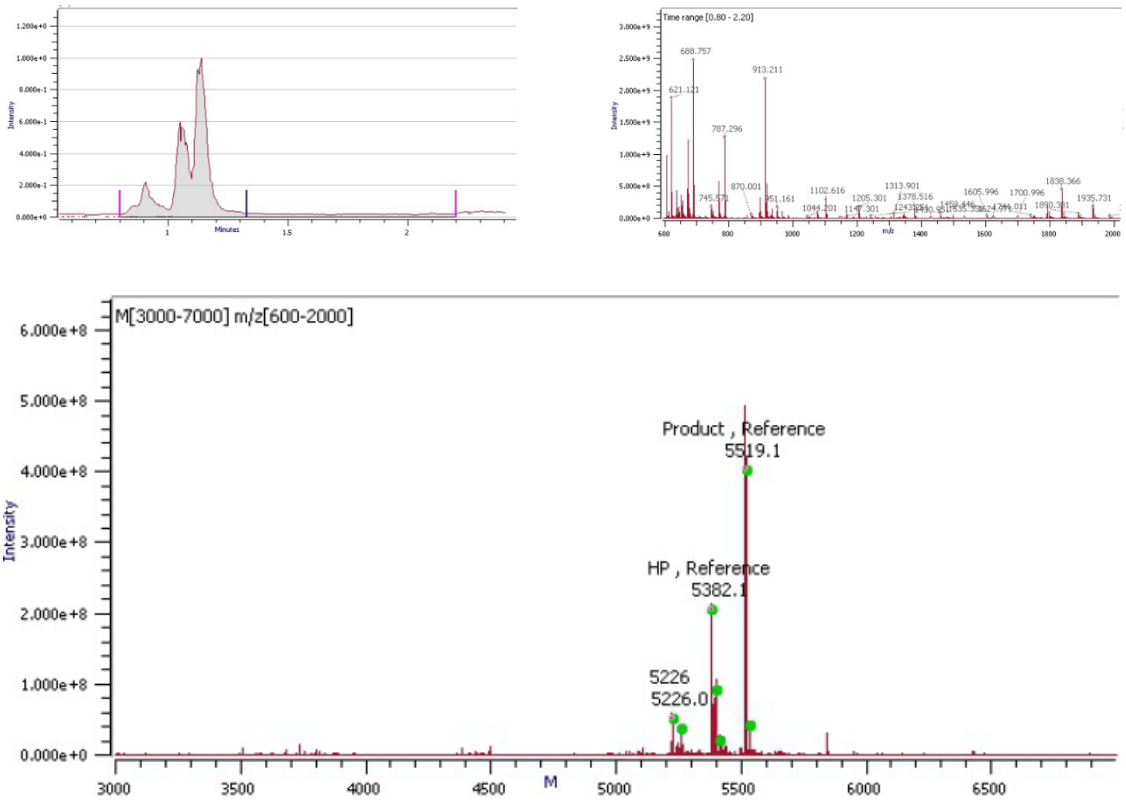




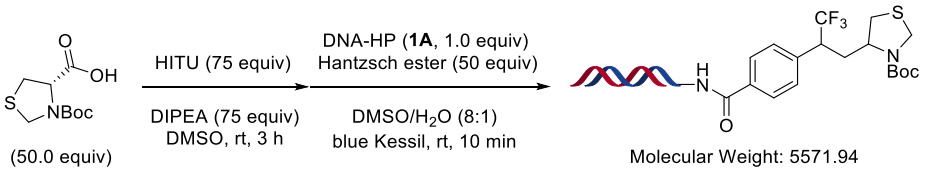
Product **3zm**, 60% yield



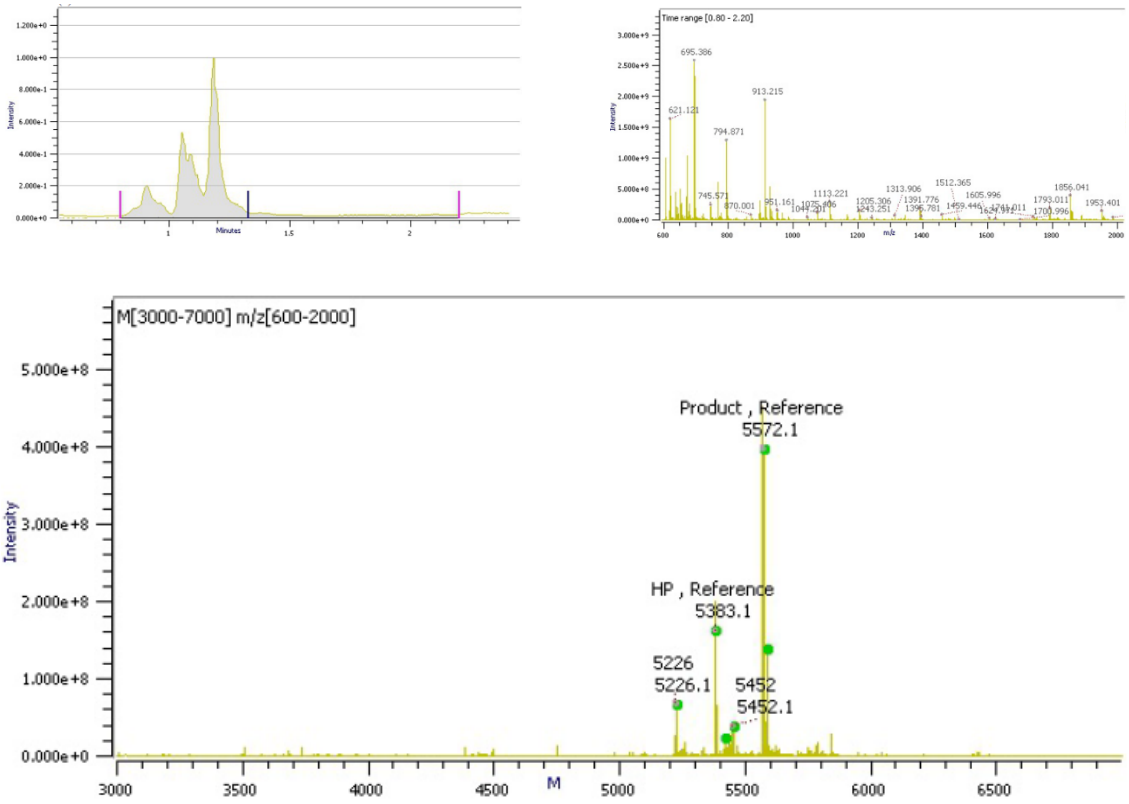
ELT_179, AJC-UPenn-8-19-179.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



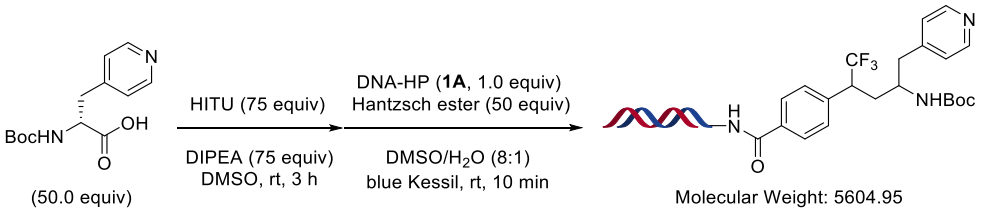
Product **3zn**, 61% yield



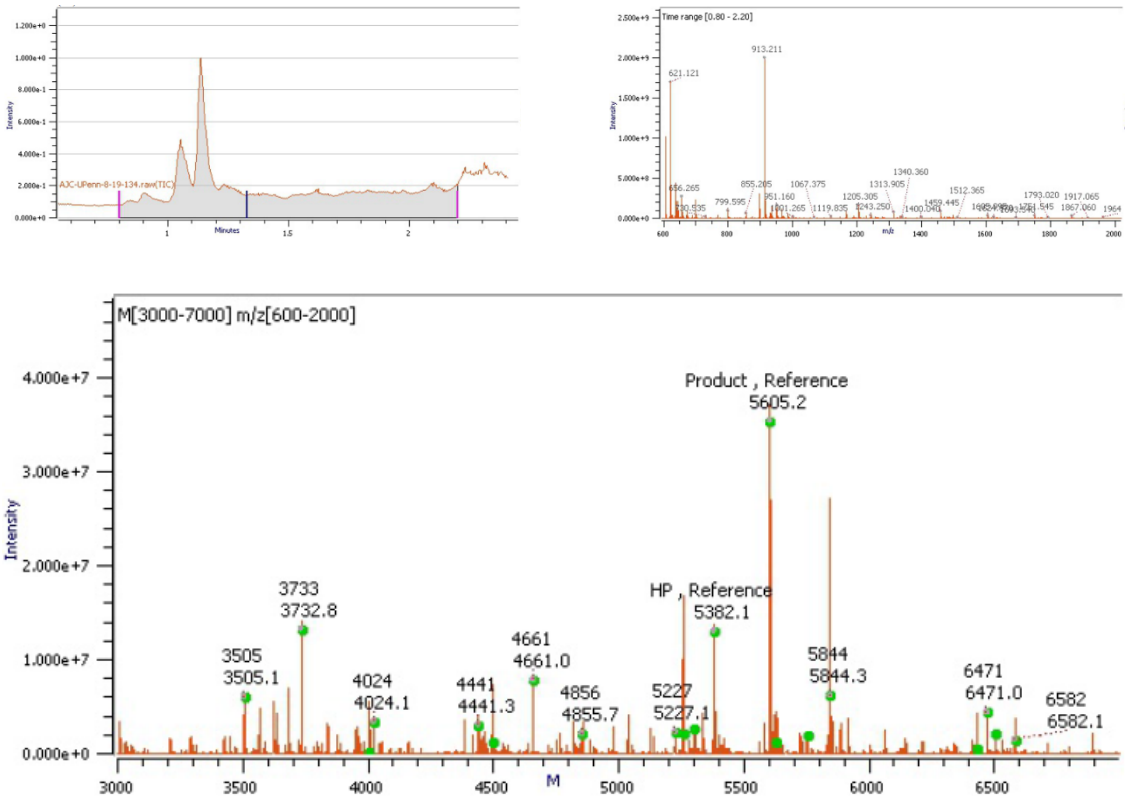
ELT_128, AJC-UPenn-8-19-128.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



Product **3zo**, 40% yield

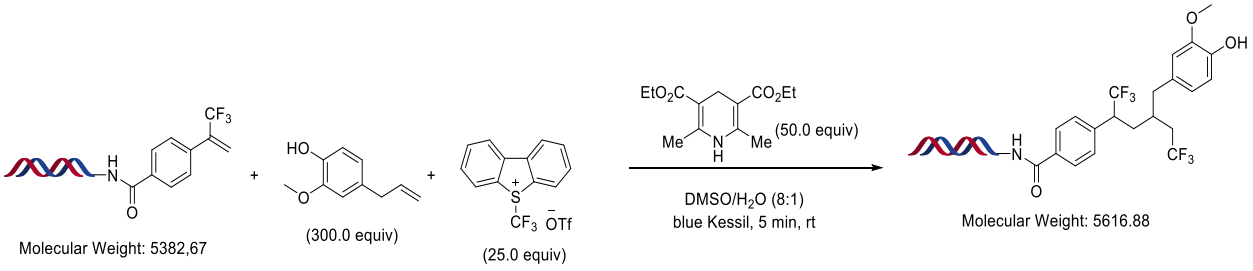


ELT_134, AJC-UPenn-8-19-134.raw (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

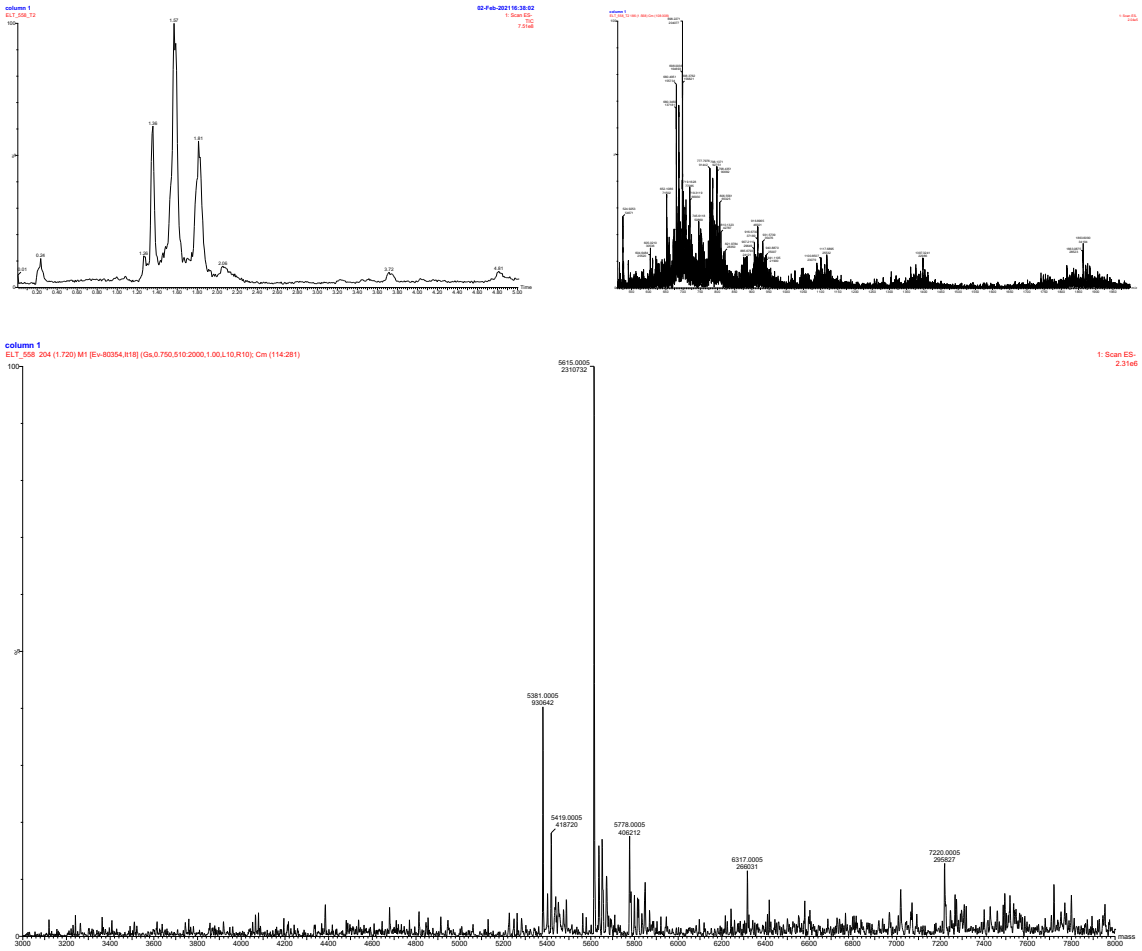


On-DNA photoinduced trifluoromethylation of alkenes (Scheme 6)

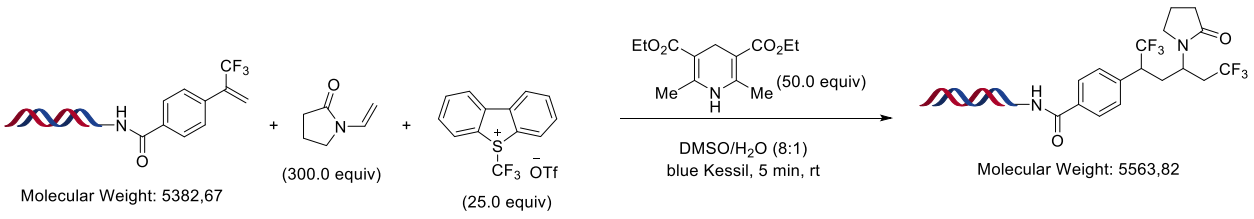
Product **12a**, 55% yield



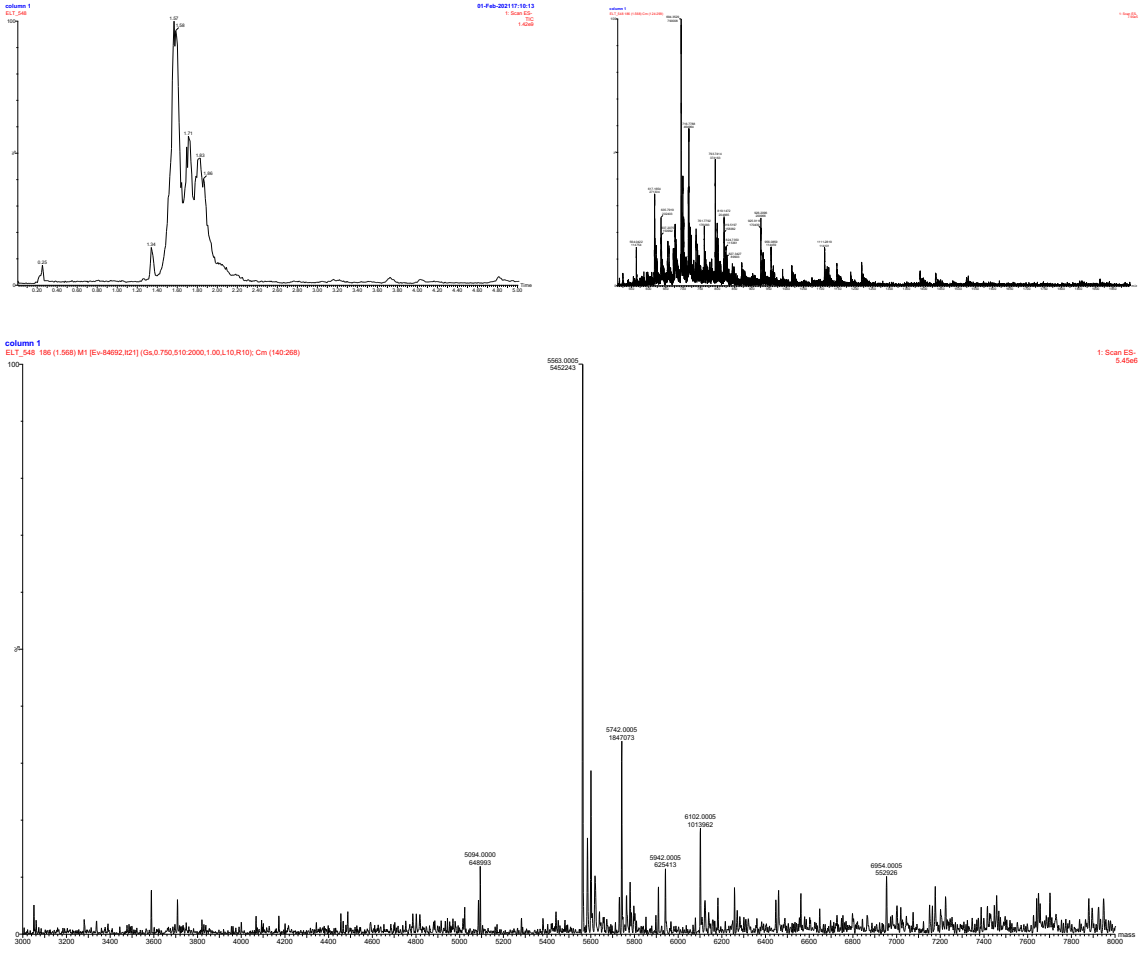
ELT_558 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



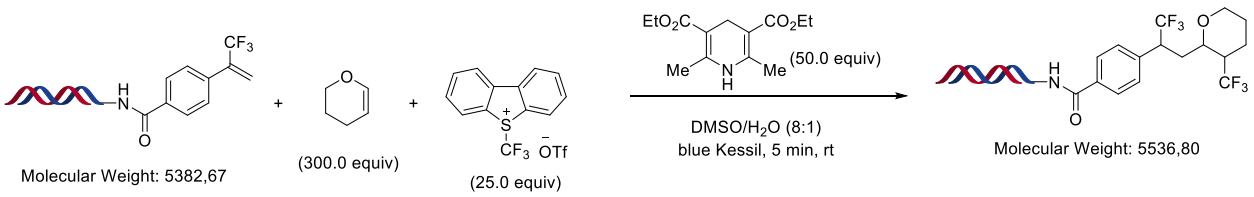
Product **12b**, 60% yield



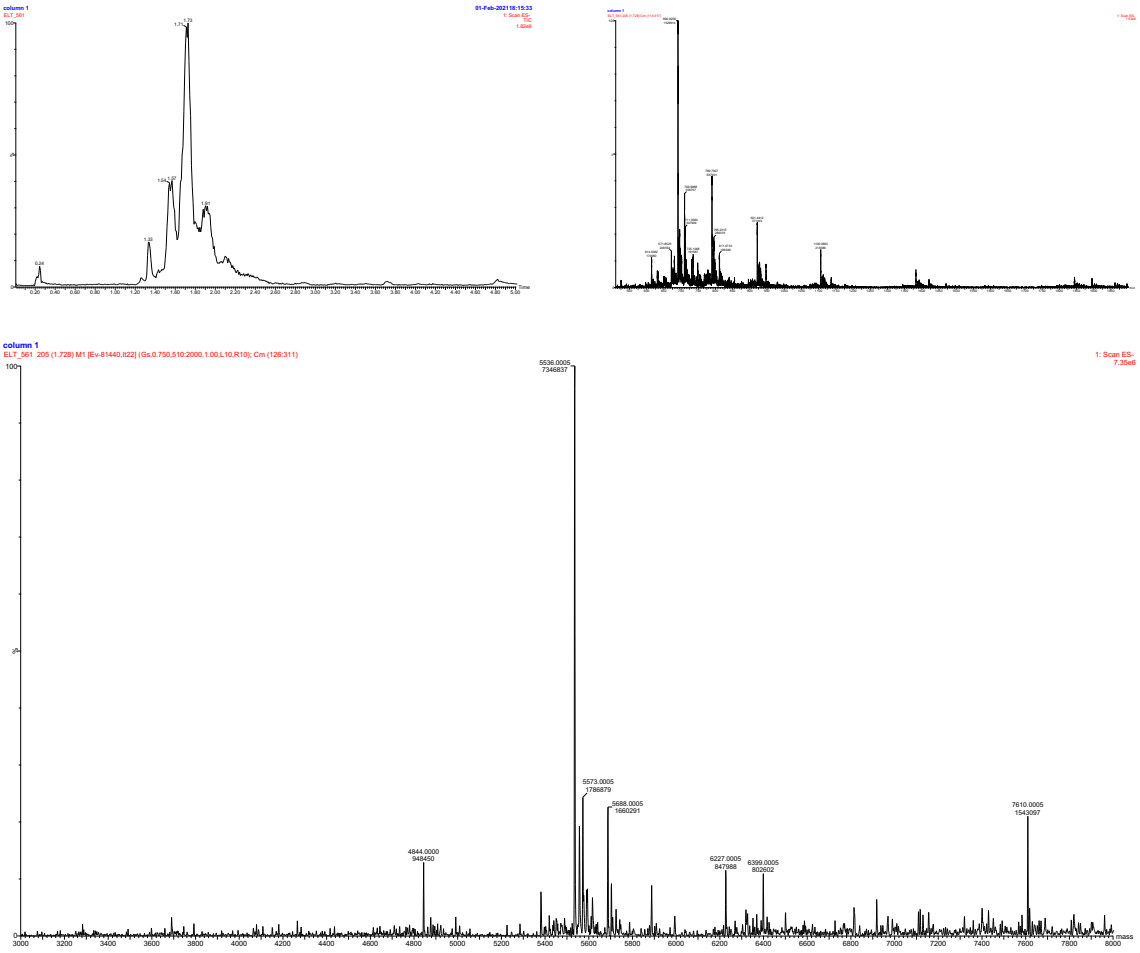
ELT_ 548 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



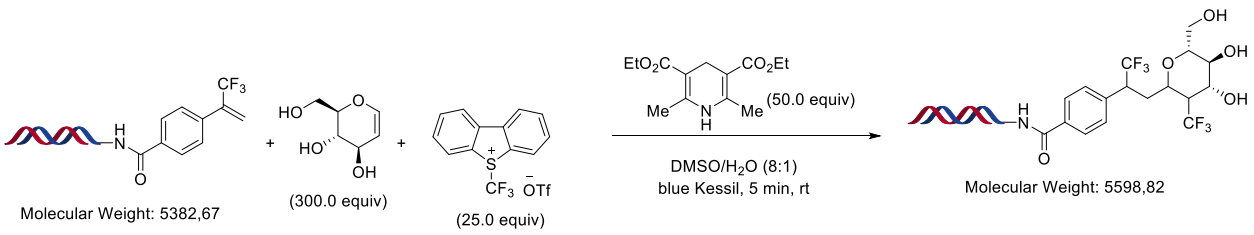
Alkylated Product **12c**, 65% yield



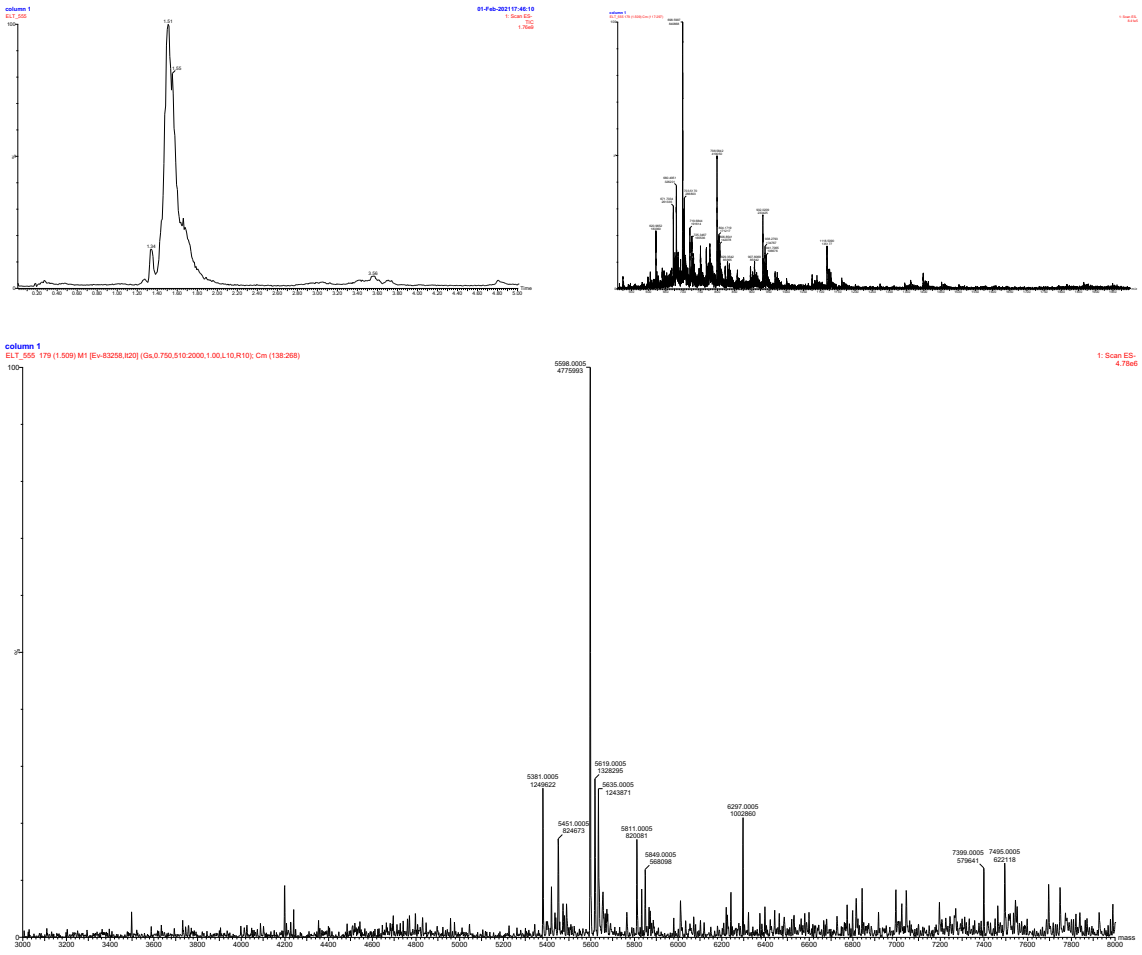
ELT_561 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



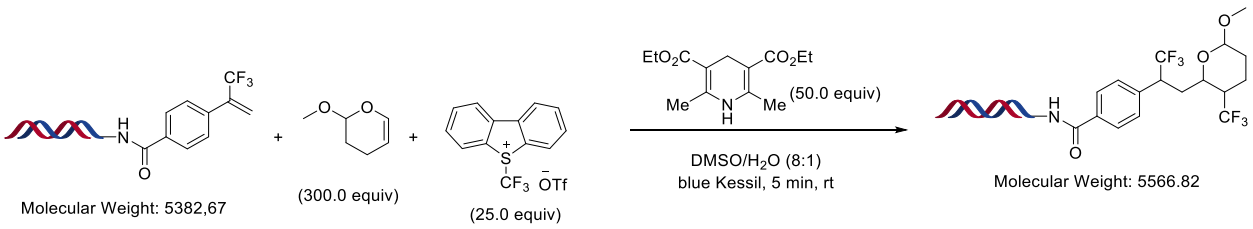
Alkylated Product **12d**, 56% yield



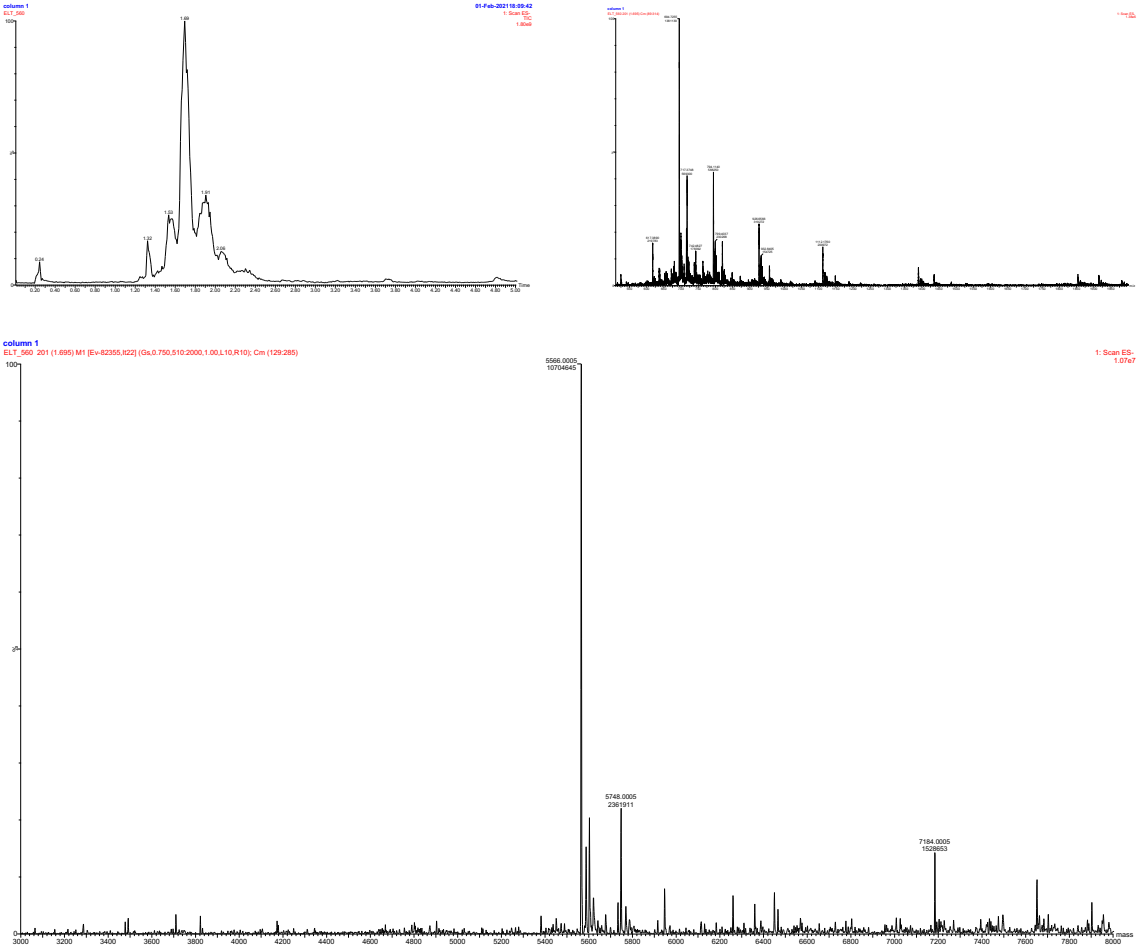
ELT_555 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



Product **12e**, 78% yield

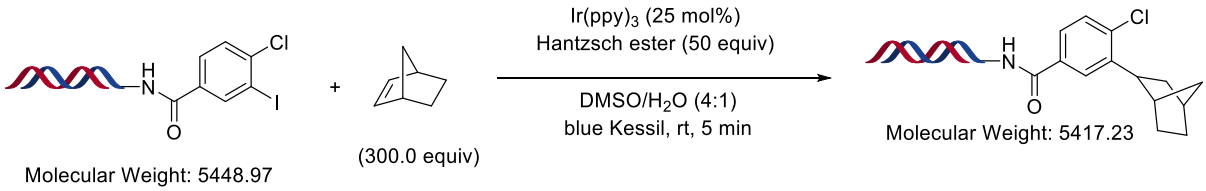


ELT_560 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

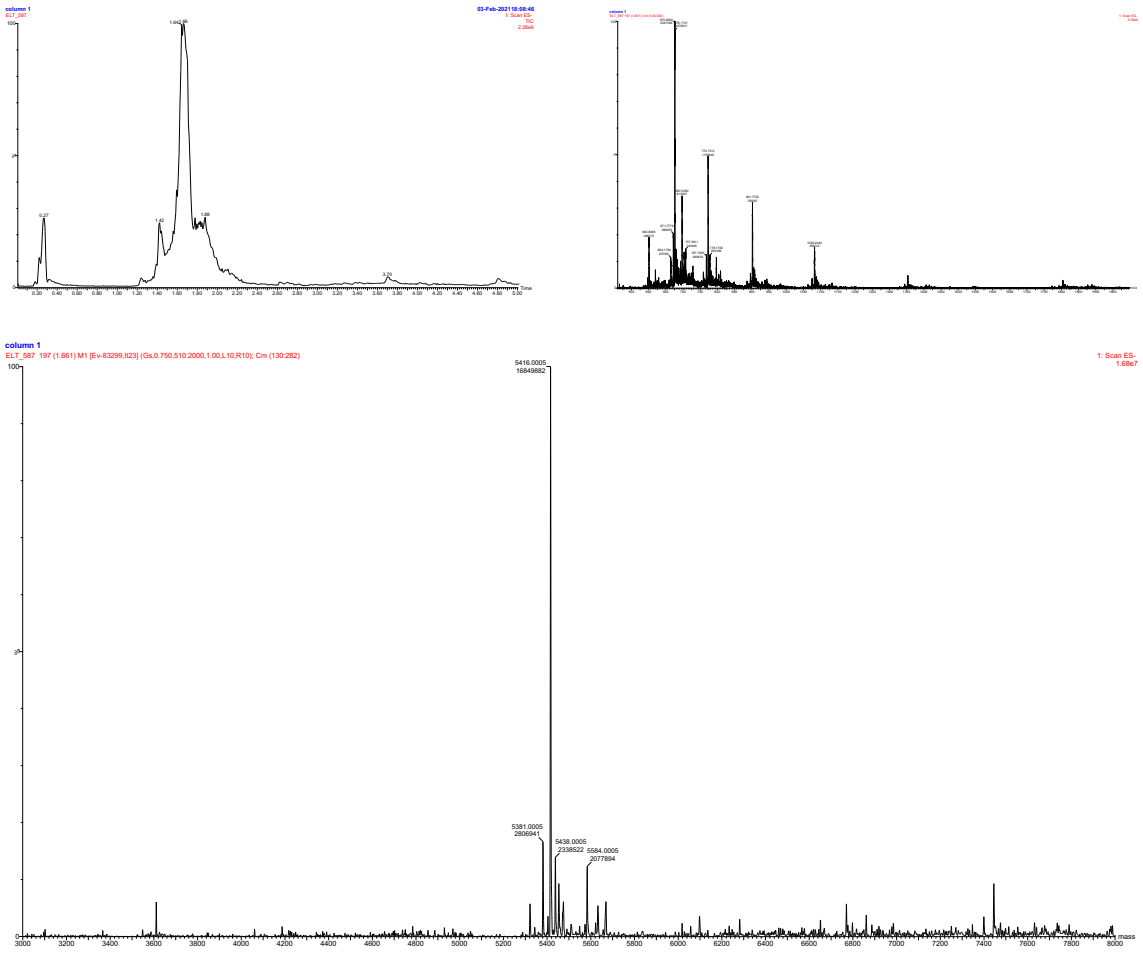


On-DNA photoinduced arylation of alkene feedstocks (Scheme 7)

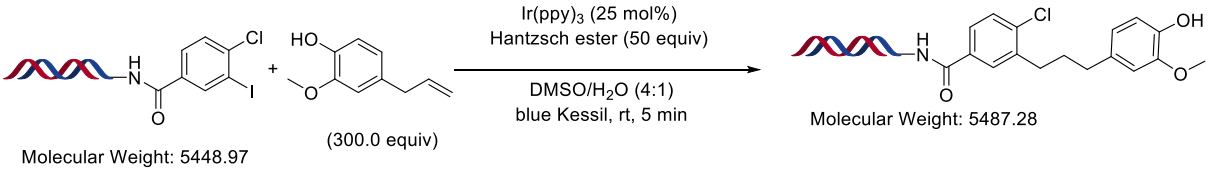
Product **15a**, 88% yield



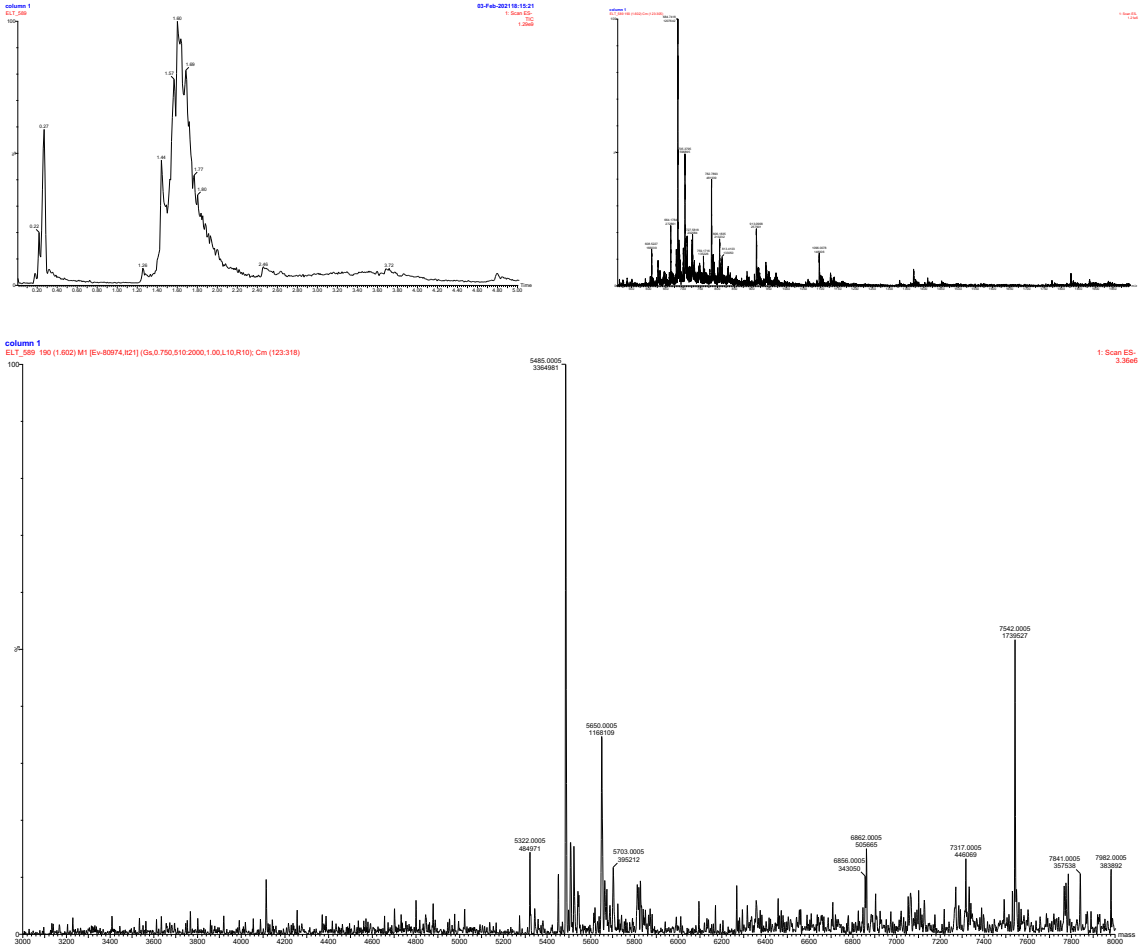
ELT_587 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



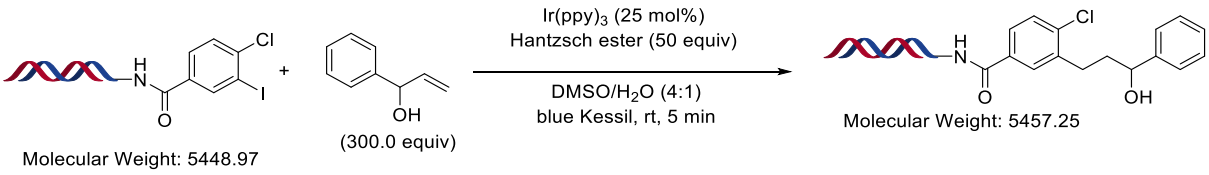
Product **15b**, 54% yield



ELT_589 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



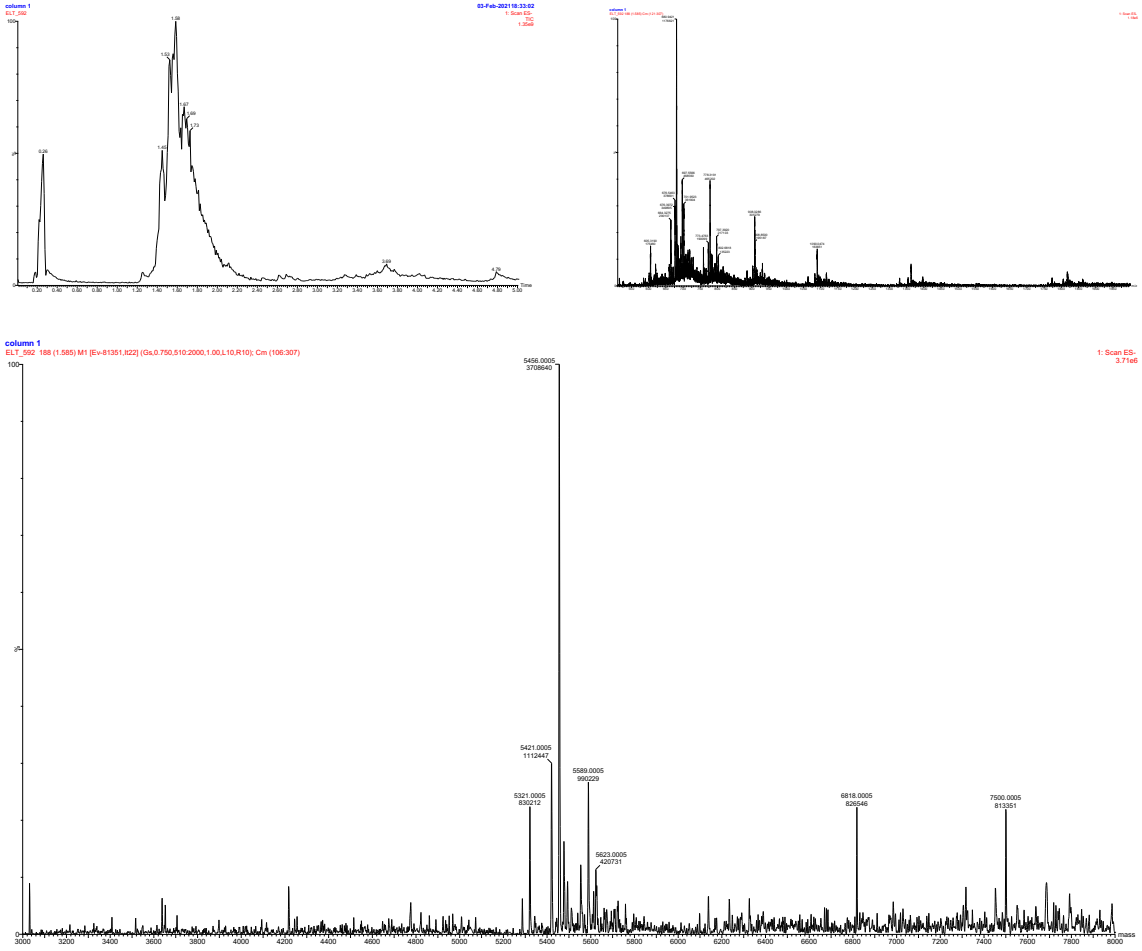
Product **15c**, 49% yield



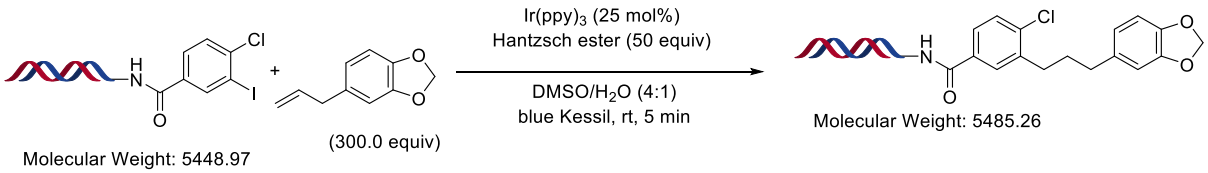
Molecular Weight: 5448.97

Molecular Weight: 5457.25

ELT_592 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



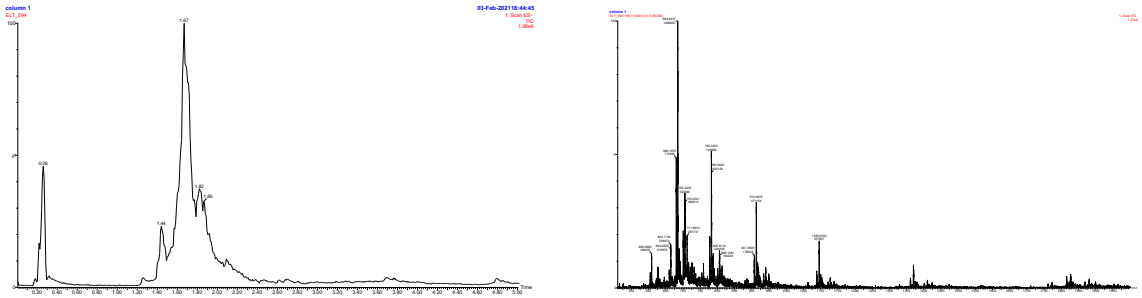
Product **15d**, 59% yield

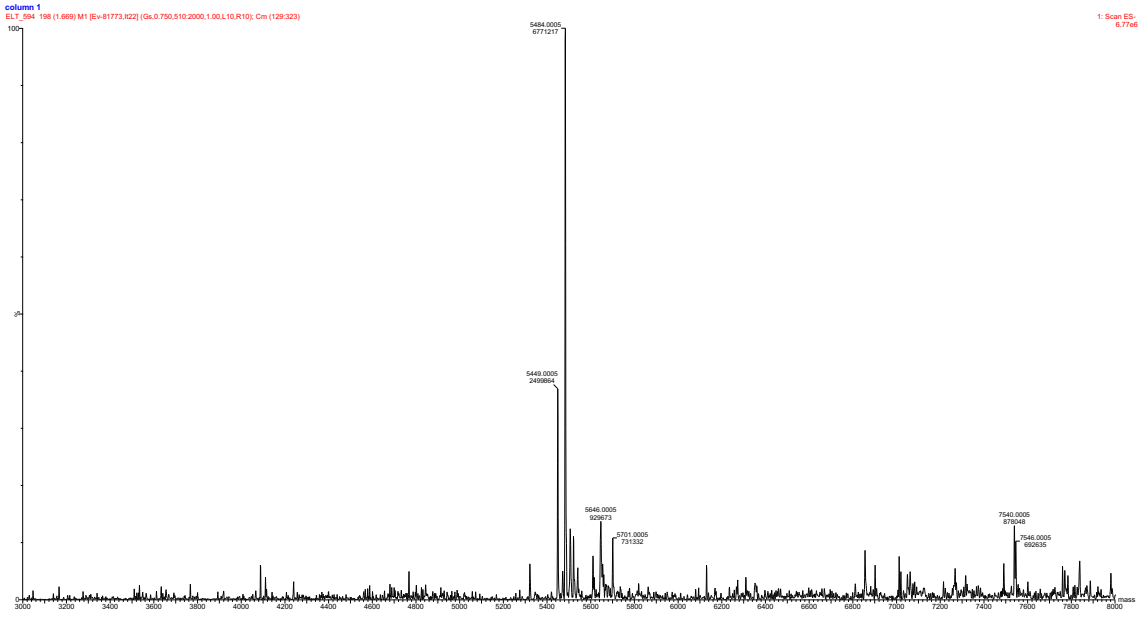


Molecular Weight: 5448.97

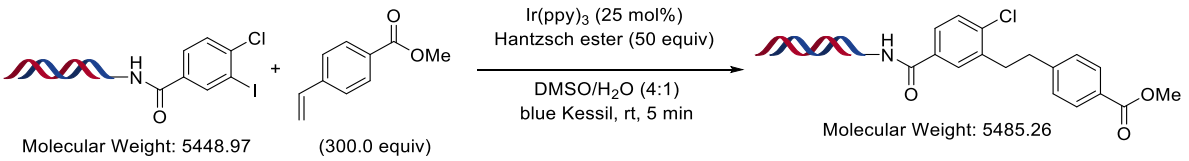
Molecular Weight: 5485.26

ELT_594 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



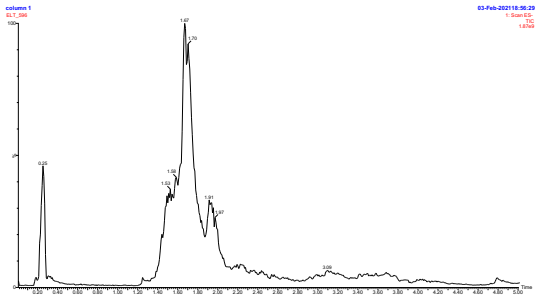


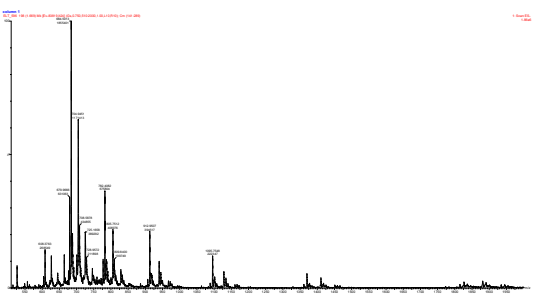
Product **15e**, 36% yield

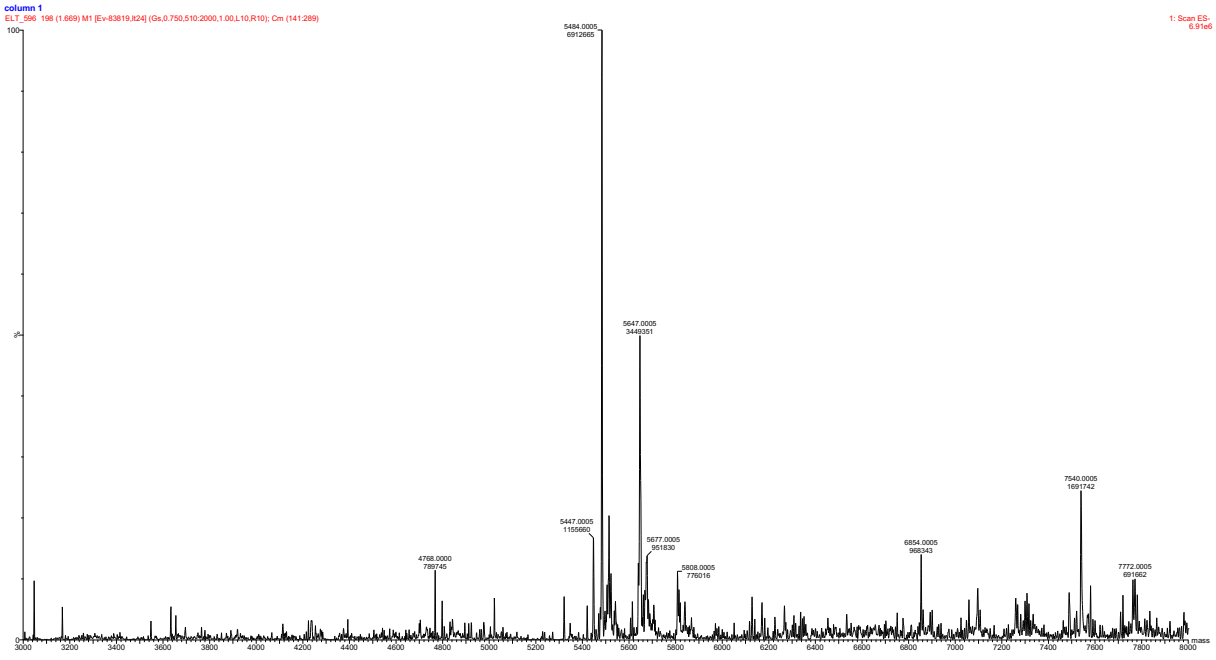


Molecular Weight: 5448.97 (300.0 equiv) Molecular Weight: 5485.26

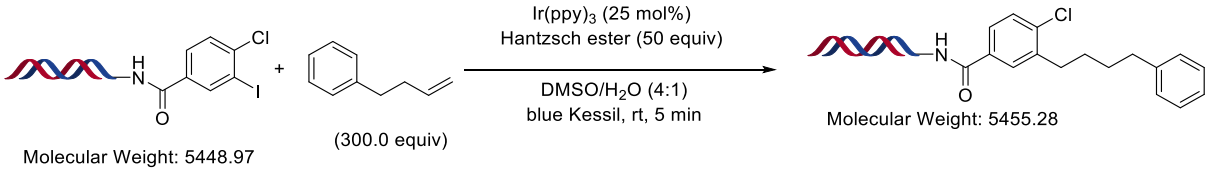
ELT_596 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)







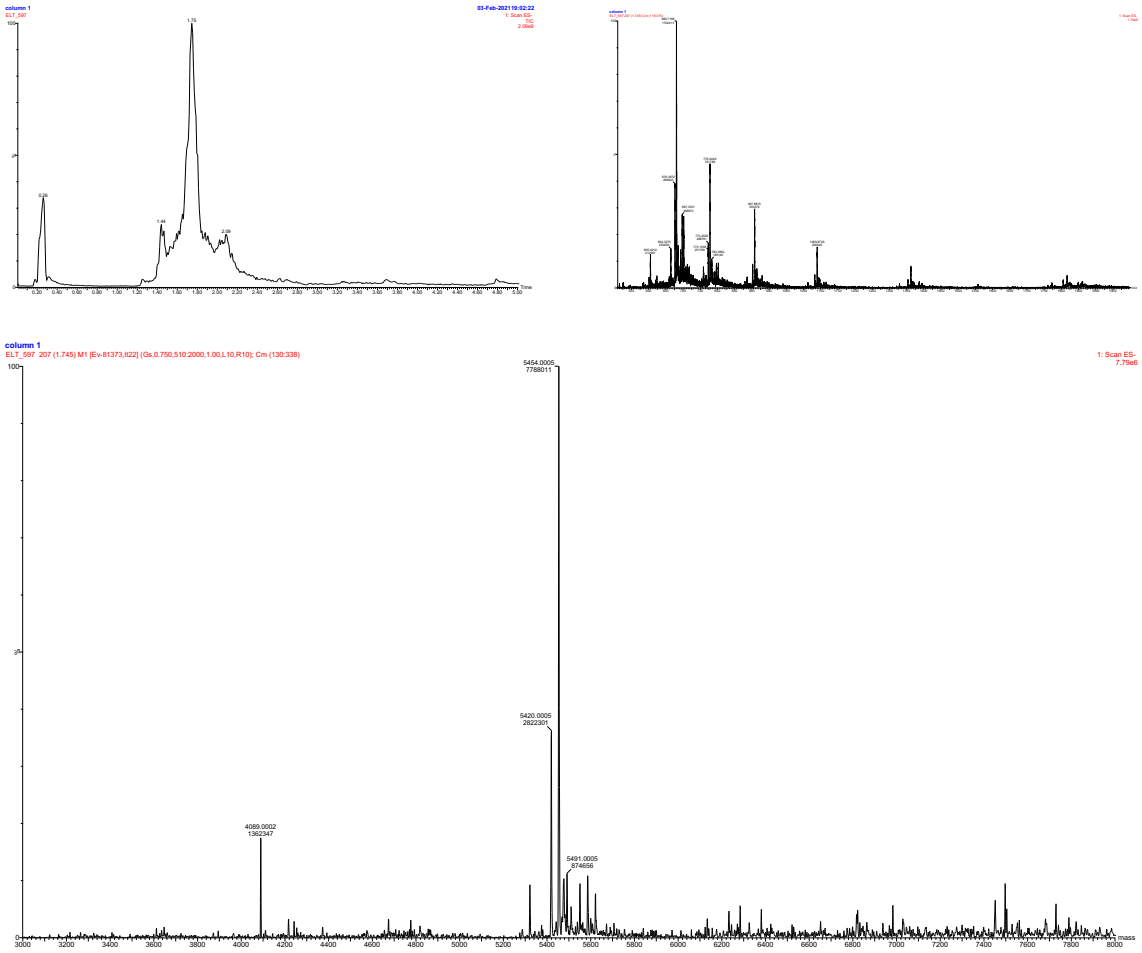
Product **15f**, 63% yield



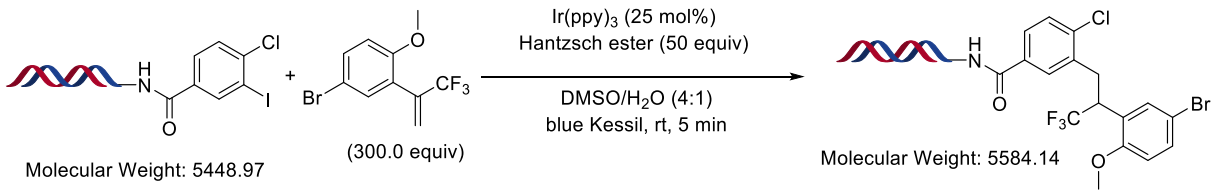
Molecular Weight: 5448.97

Molecular Weight: 5455.28

ELT_597 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



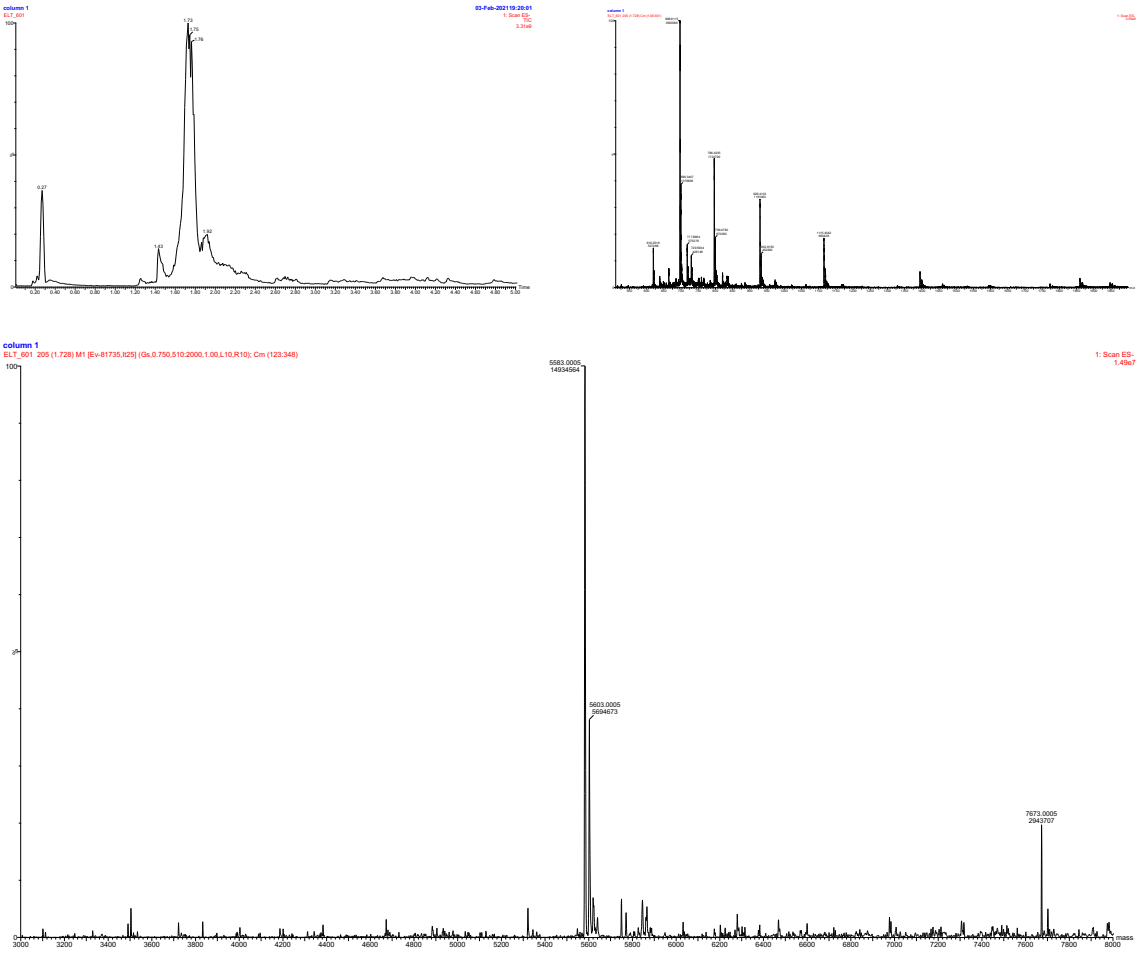
Product **15g**, 63% yield



Molecular Weight: 5448.97

Molecular Weight: 5584.14

ELT_ 601(Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

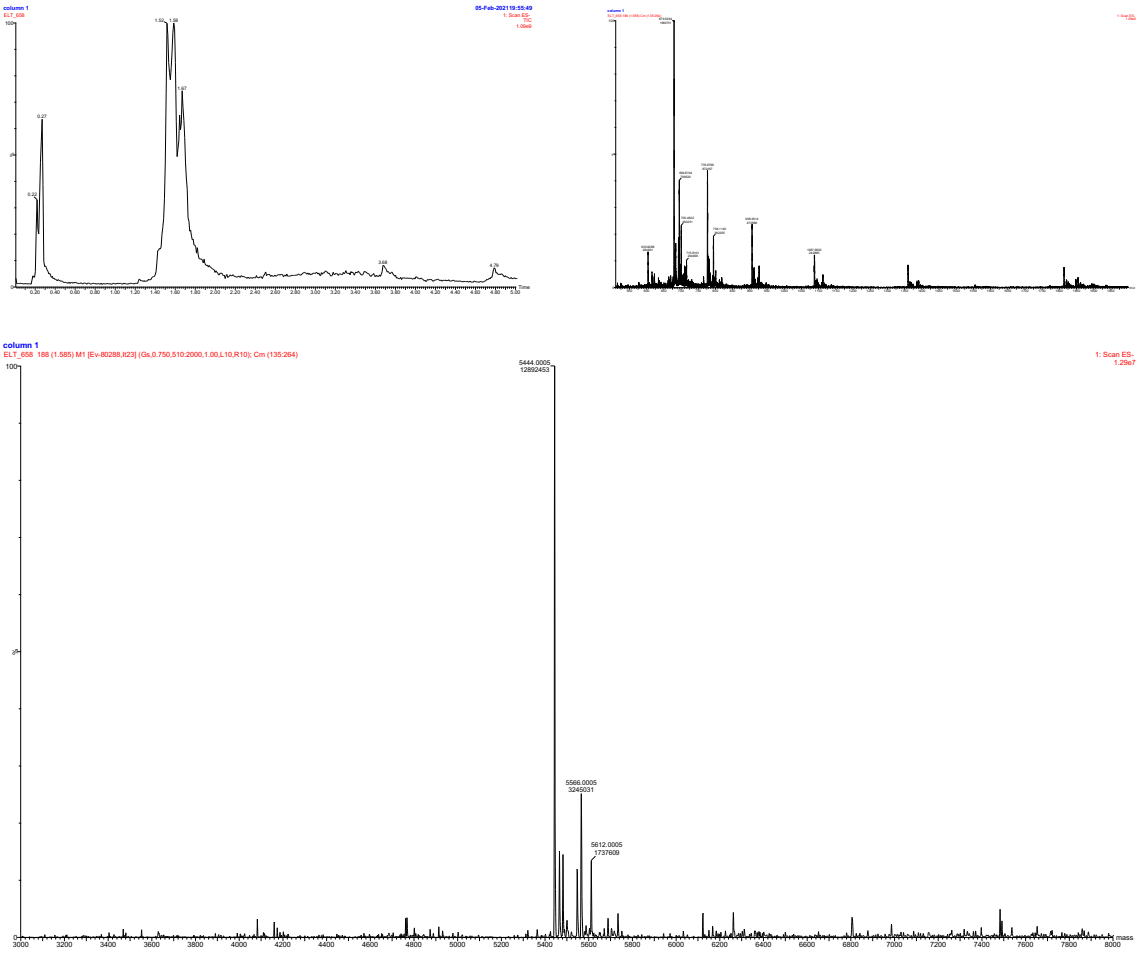


Product **15h**, 79% yield

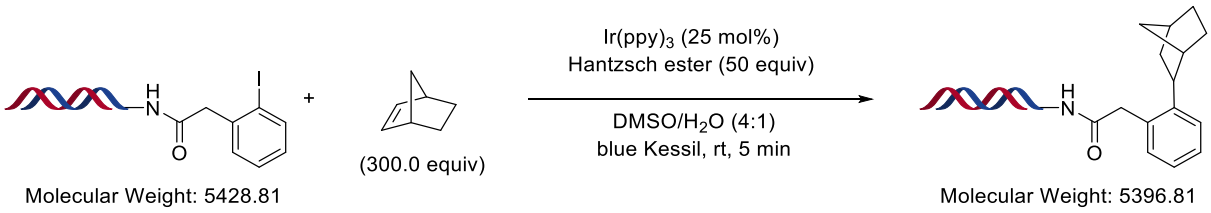
Molecular Weight: 5448.97

Molecular Weight: 5445.25

ELT_658 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



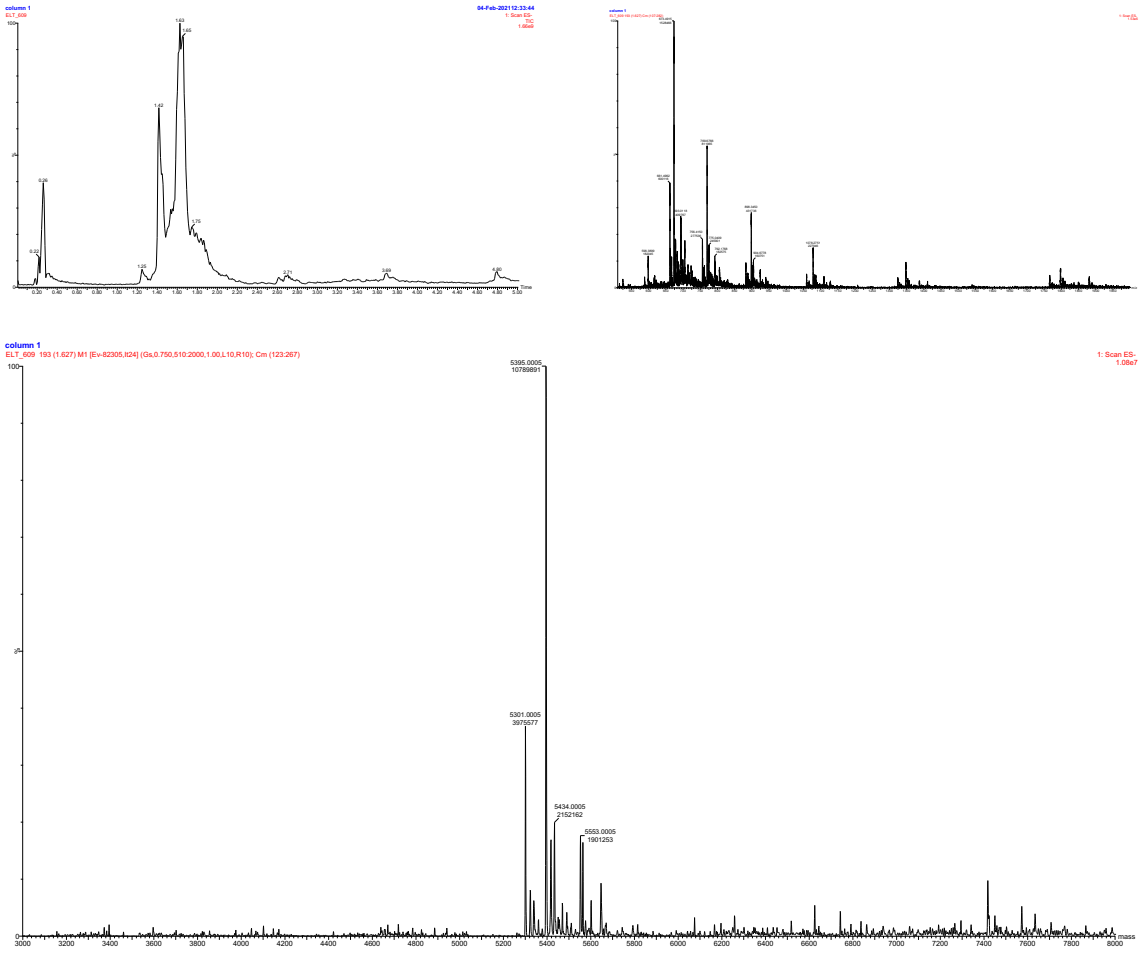
Product **16a**, 71% yield



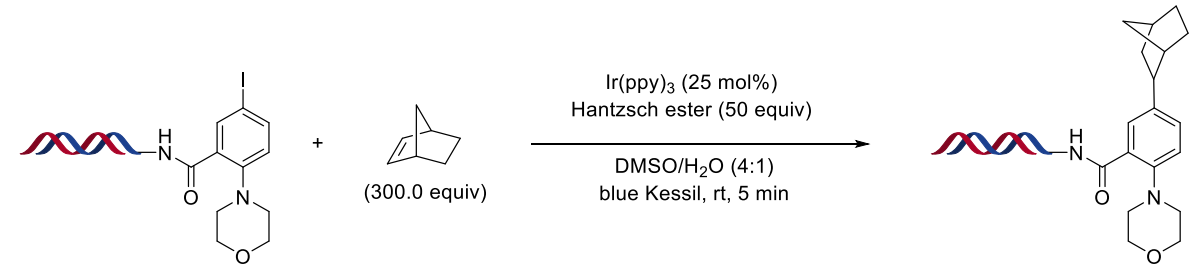
Molecular Weight: 5428.81

Molecular Weight: 5396.81

ELT_609 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



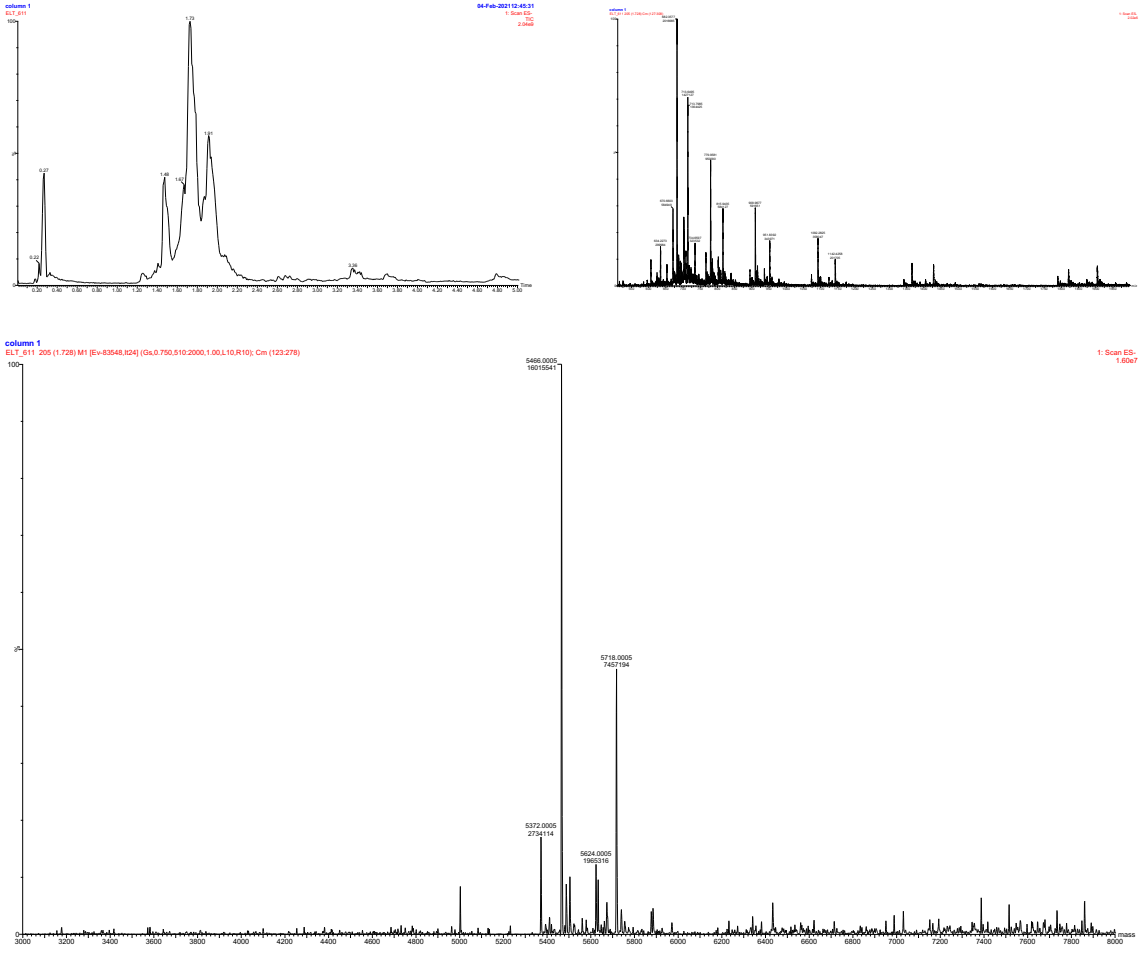
Product **17a**, 61% yield



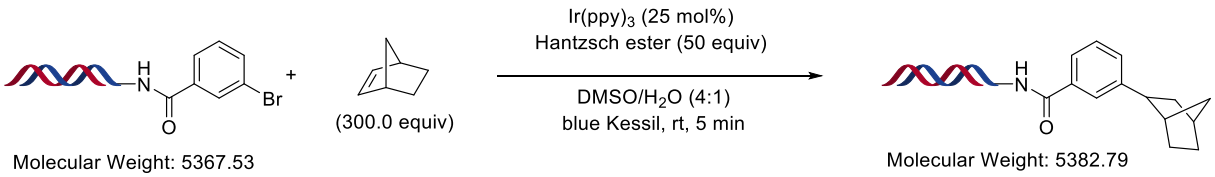
Molecular Weight: 5499.63

Molecular Weight: 5467.89

ELT_611 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



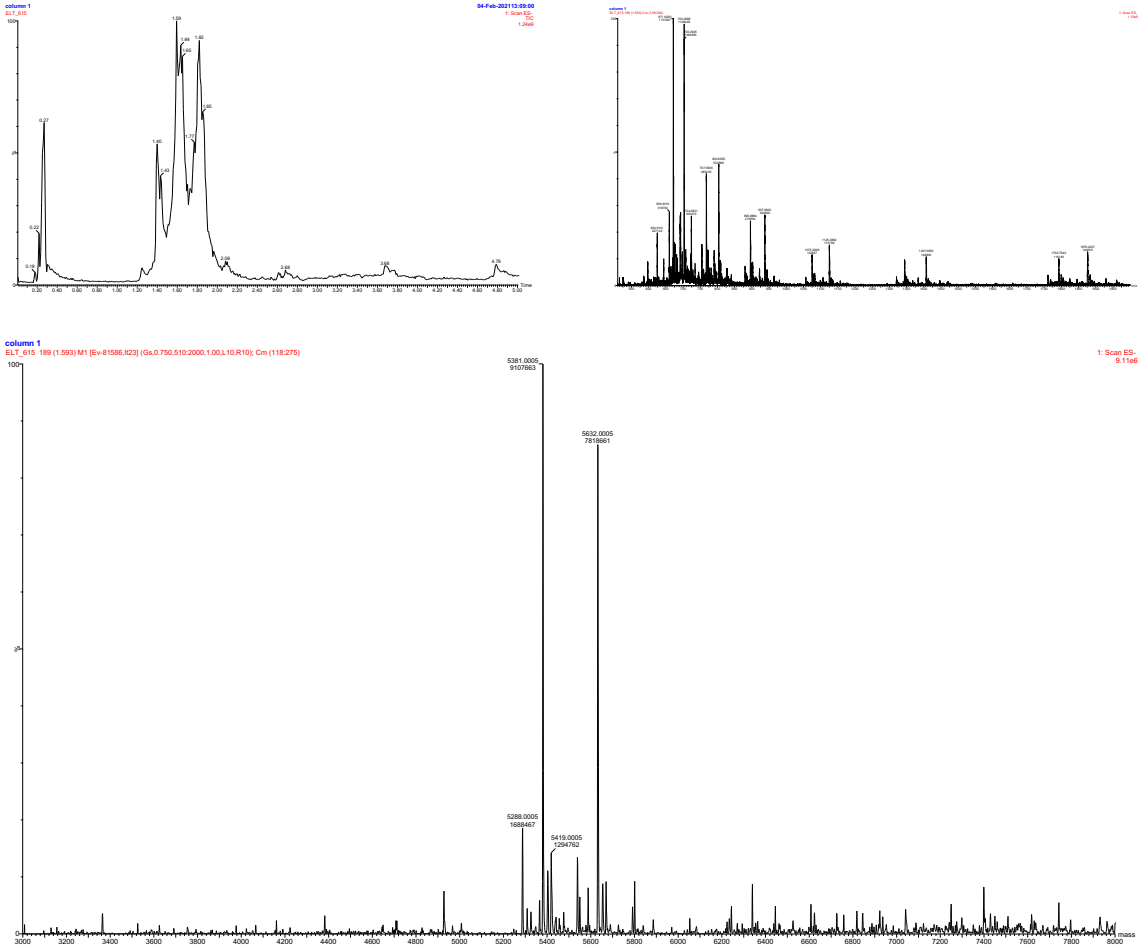
Product **18a**, 51% yield



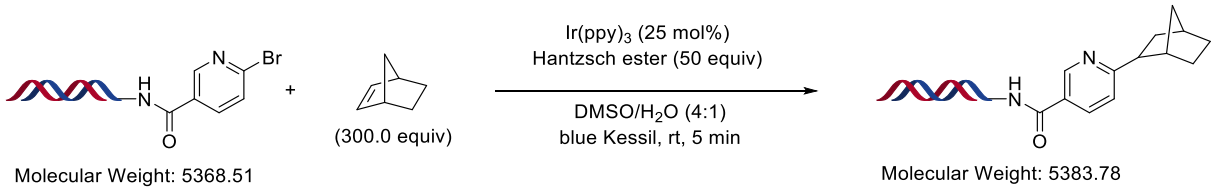
Molecular Weight: 5367.53

Molecular Weight: 5382.79

ELT_615 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



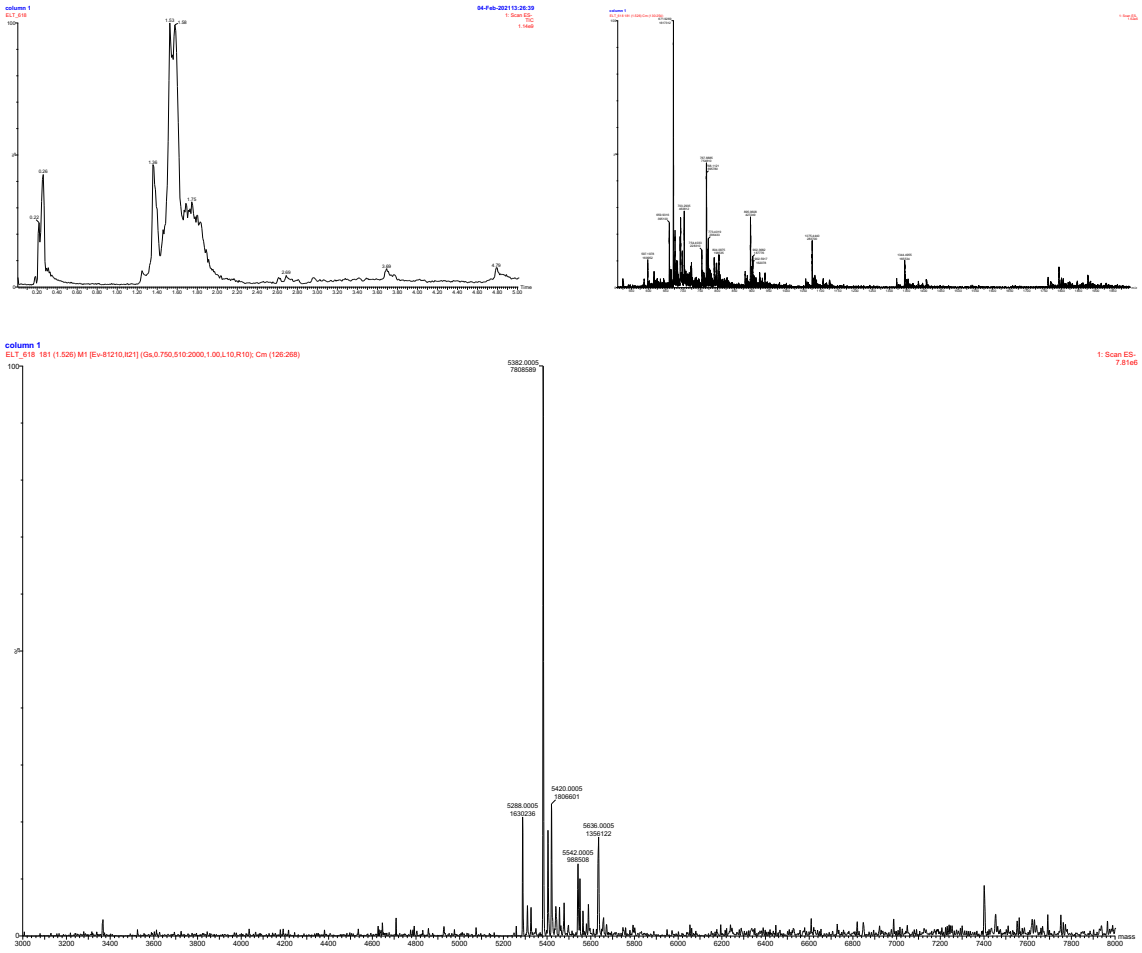
Product **19a**, 75% yield



Molecular Weight: 5368.51

Molecular Weight: 5383.78

ELT_618 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)

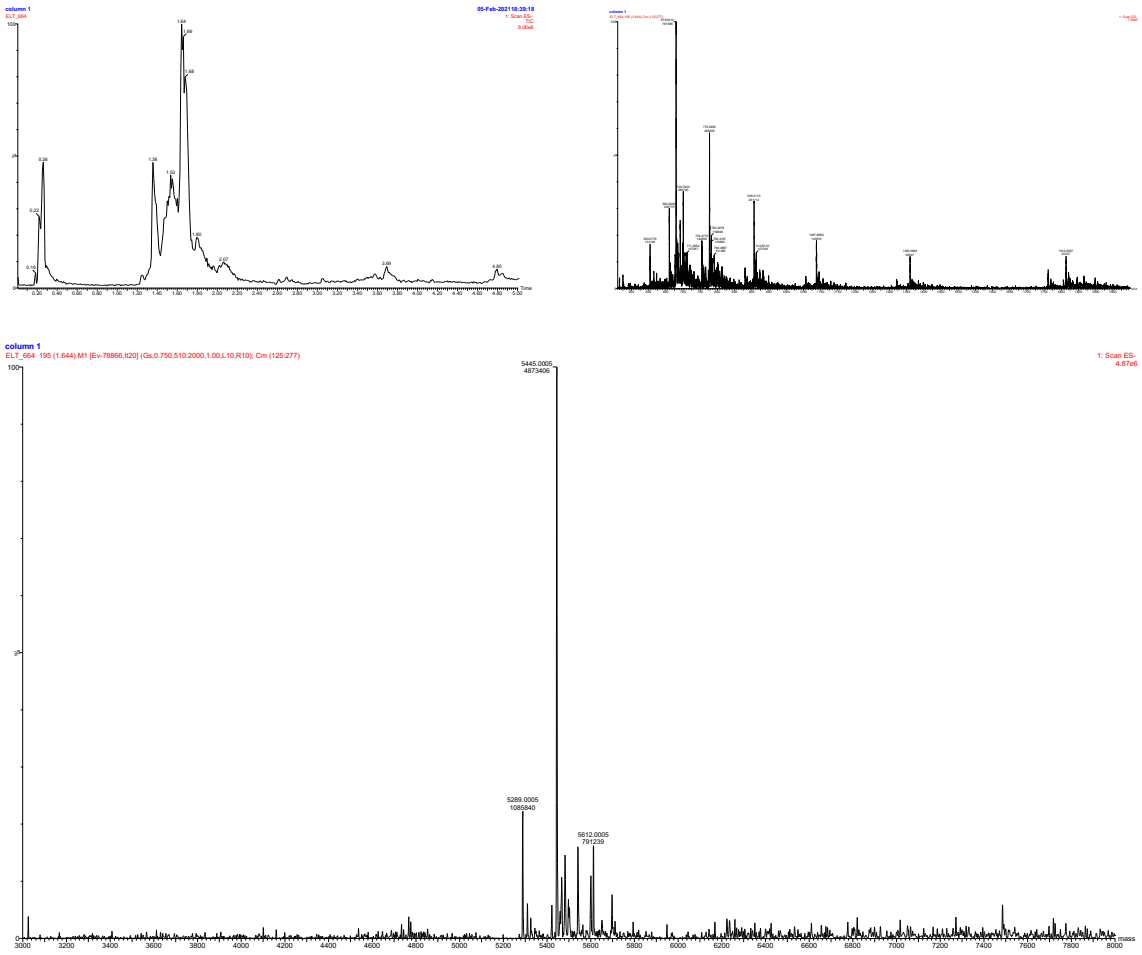


Product **19j**, 74% yield

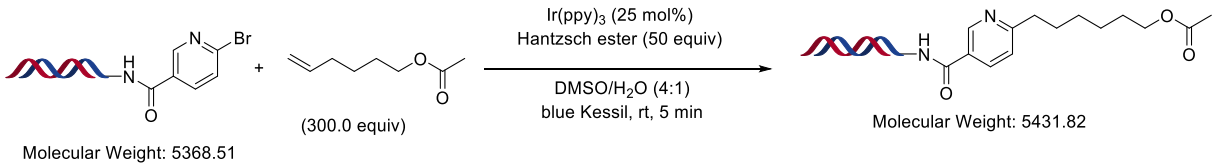
Molecular Weight: 5368.51

Molecular Weight: 5445.89

ELT_664 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



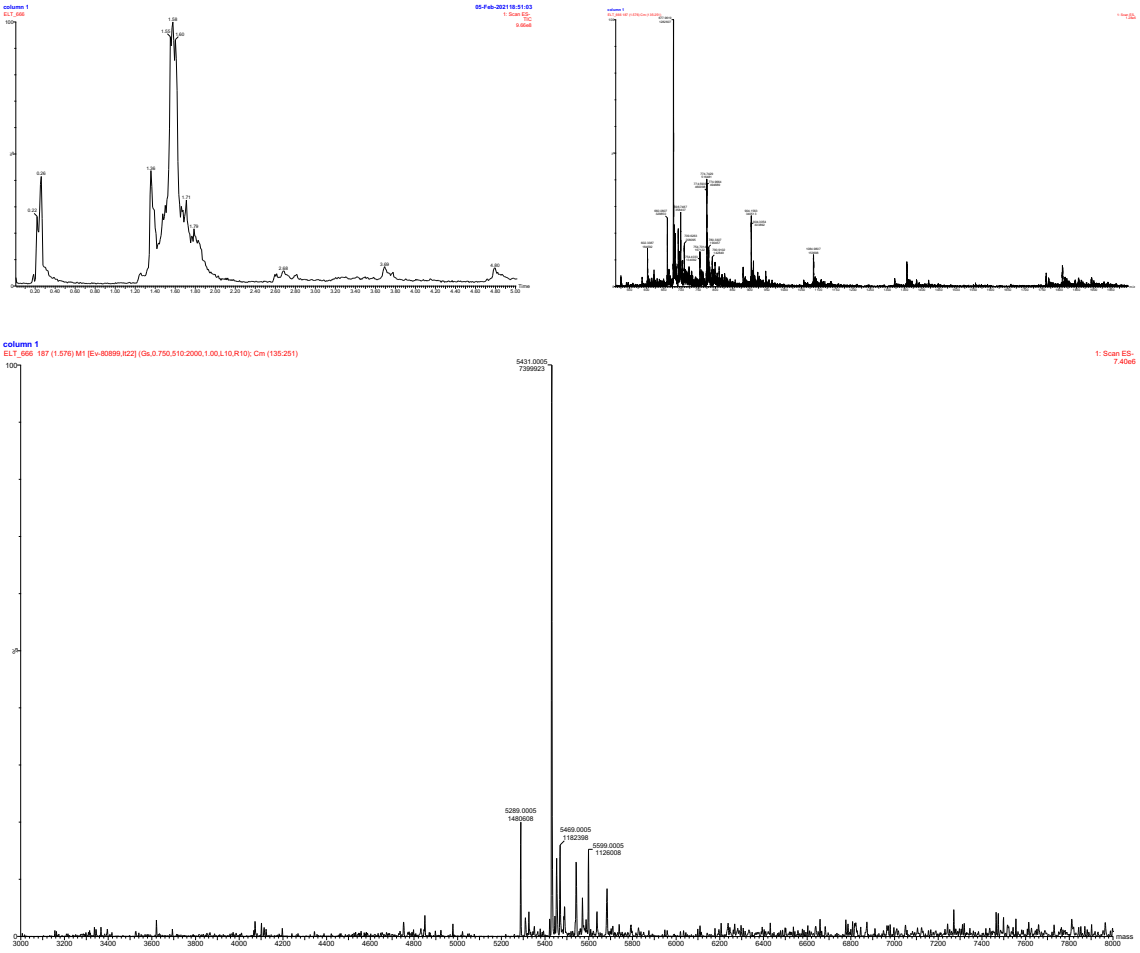
Product **19k**, 80% yield



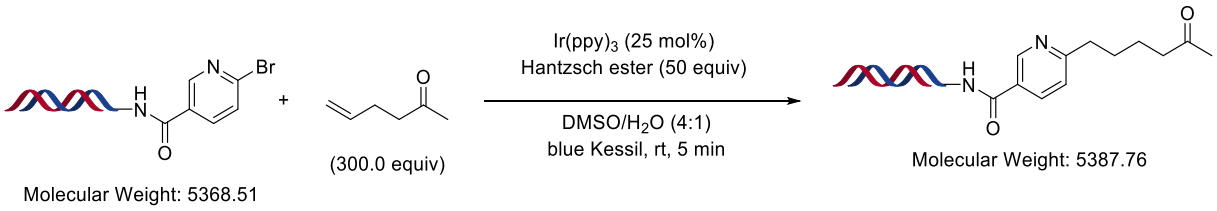
Molecular Weight: 5368.51

Molecular Weight: 5431.82

ELT_666 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



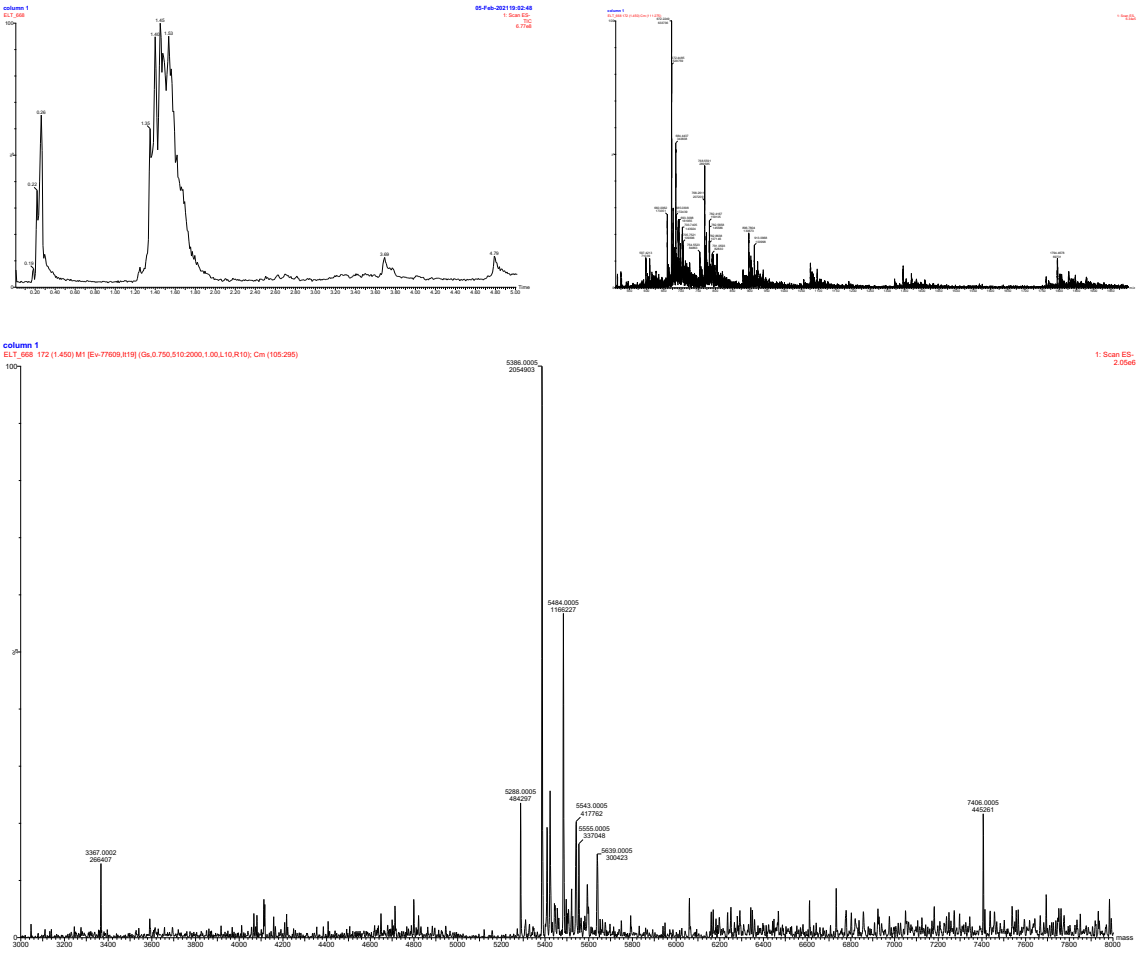
Product **19l**, 51% yield



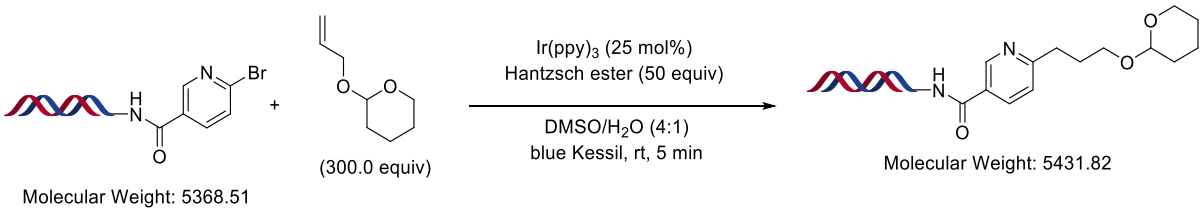
Molecular Weight: 5368.51

Molecular Weight: 5387.76

ELT_668 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



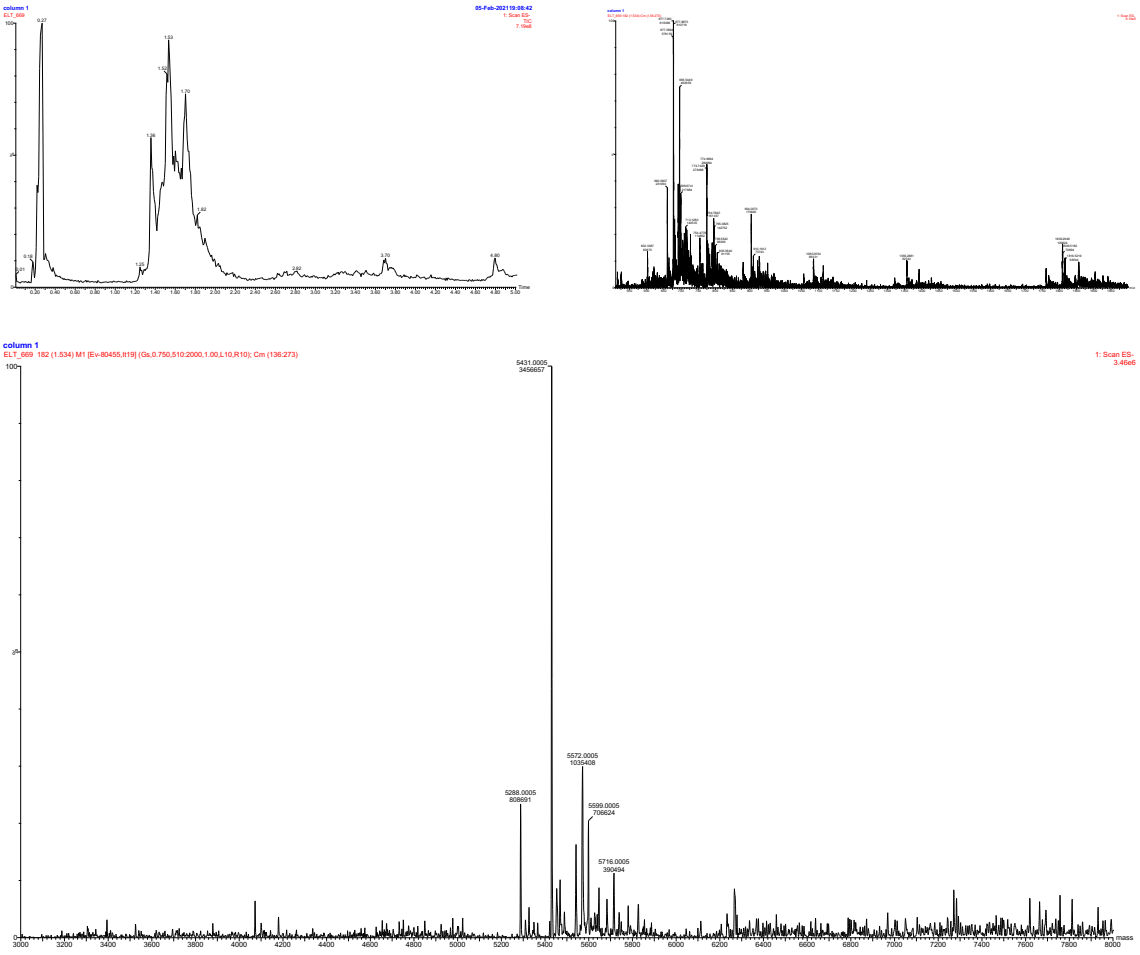
Product **19m**, 62% yield



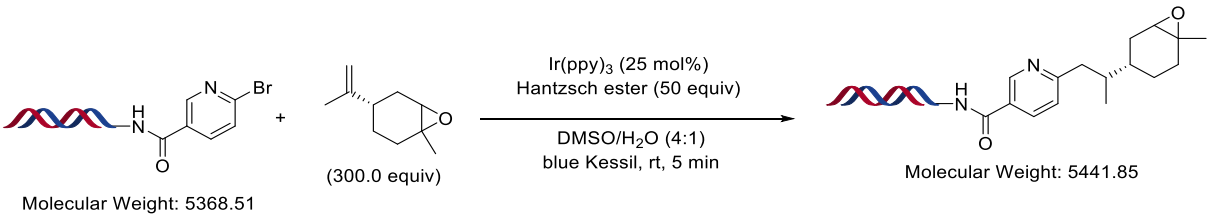
Molecular Weight: 5368.51

Molecular Weight: 5431.82

ELT_669 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



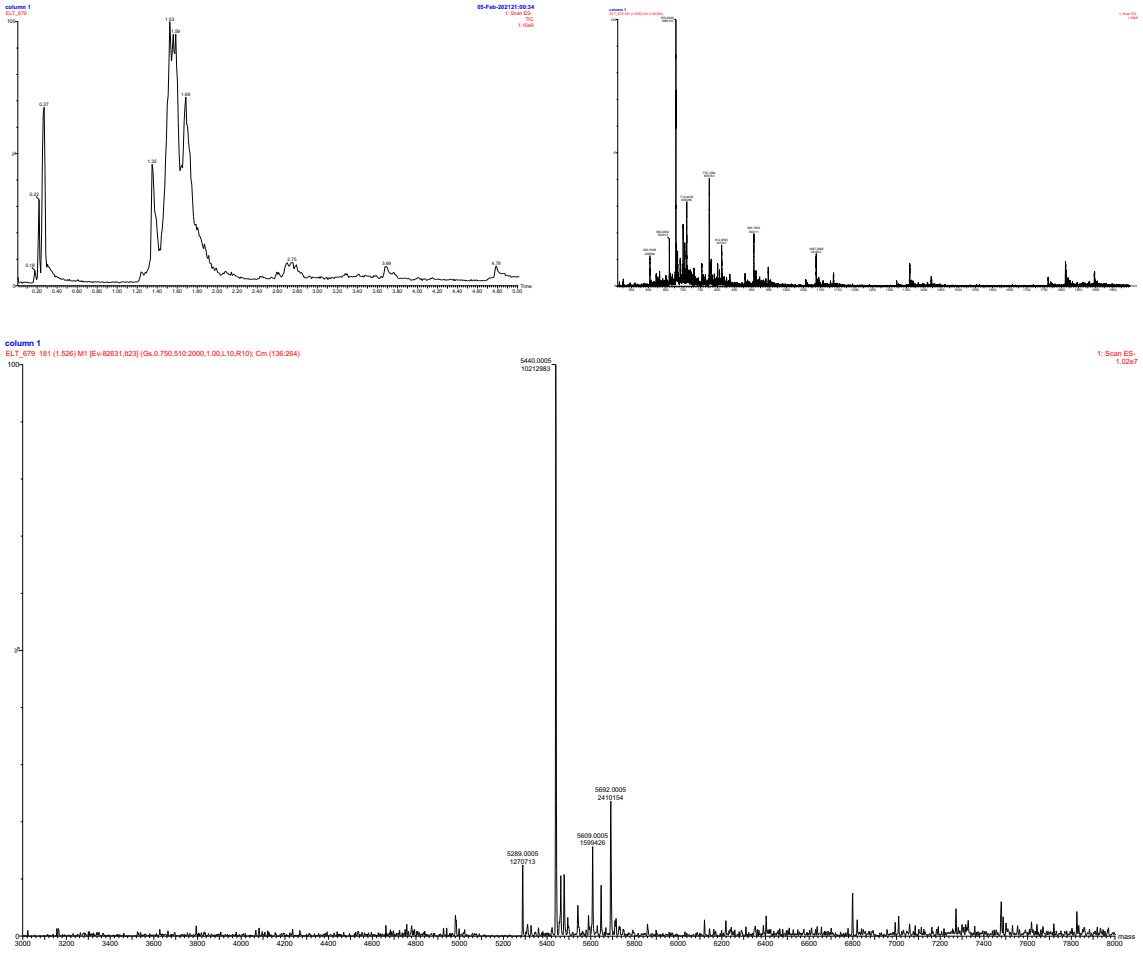
Product **19n**, 79% yield



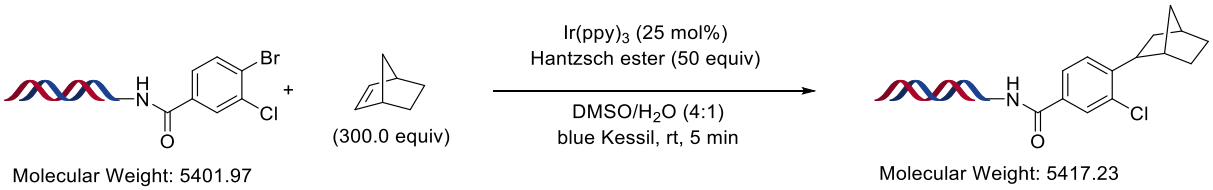
Molecular Weight: 5368.51

Molecular Weight: 5441.85

ELT_679 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



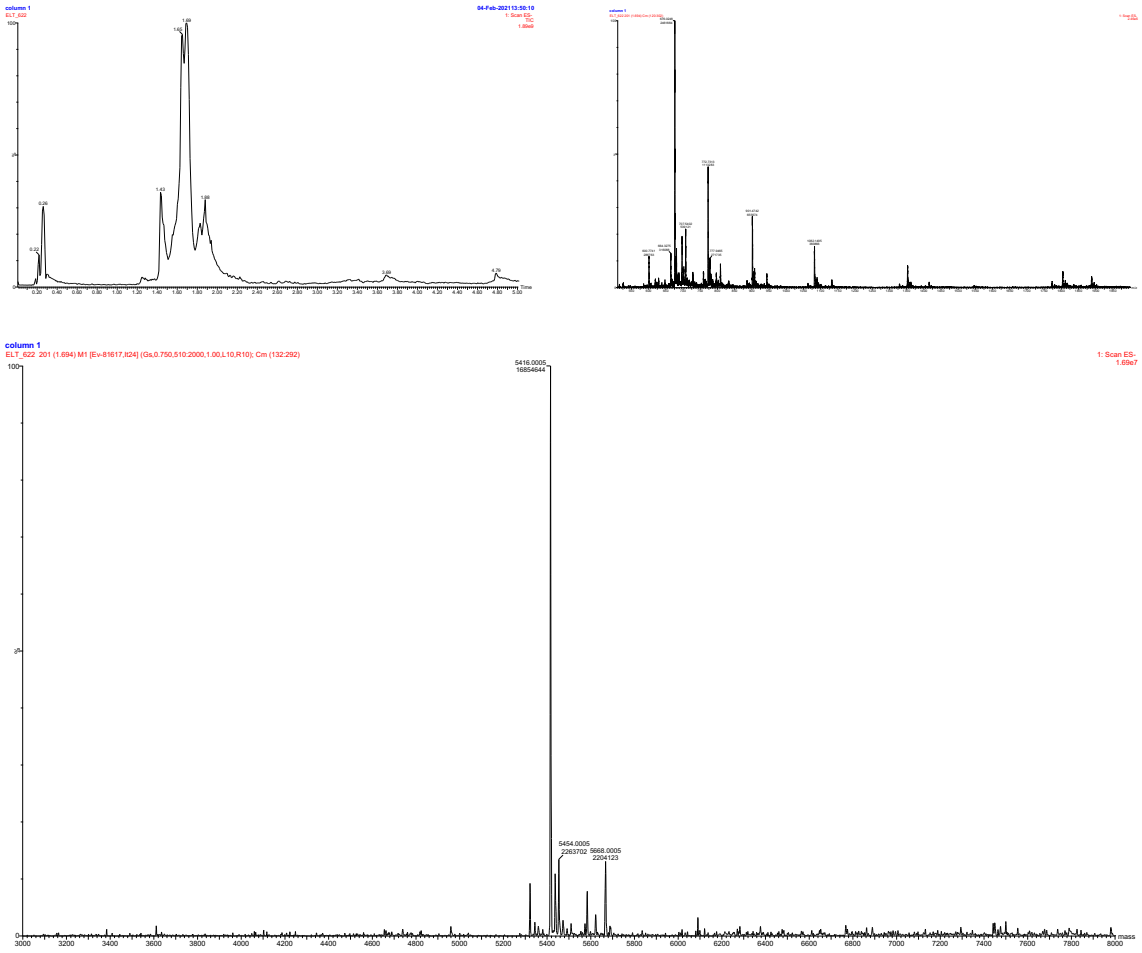
Product **20a**, 90% yield



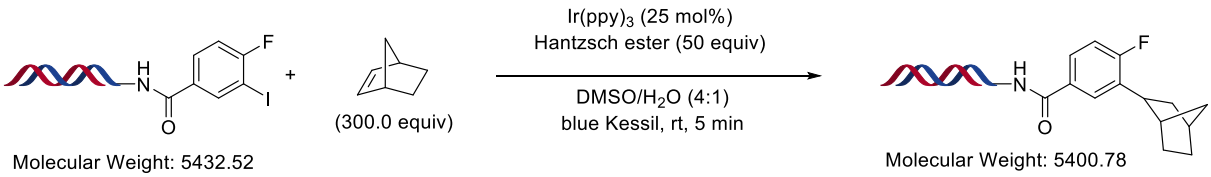
Molecular Weight: 5401.97

Molecular Weight: 5417.23

ELT_622 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)



Product **21a**, 81% yield



ELT_650 (Plot Elution Peak - Plot MS1 - Plot Deconvoluted Mass spectrum)