Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Photochemical organocatalytic enantioselective radical γ-functionalization of α-branched enals

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A. General Information

The NMR spectra were recorded at 400 MHz and 500 MHz for ^{1}H and 100 or 125 MHz for ^{13}C. The chemical shift (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm ^{1}H NMR and 77.16 ppm ^{13}C NMR, and tetramethylsilane @ 0 ppm). Coupling constants are given in Hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; m, multiplet; bs, broad signal; app, apparent.
High resolution mass spectra (HRMS) were obtained from the ICIQ HRMS unit on MicroTOF Focus and Maxis Impact (Bruker Daltonics) with electrospray ionization (ESI). Yields of isolated products refer to materials of >95% purity as determined by ^{1}H NMR analysis.
The authors are indebted to the team of the Research Support Area at ICIQ, particularly to the NMR and the High-Resolution Mass Spectrometry Units. Grace Fox is thanked for proofreading the manuscript.

General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware. Synthesis grade solvents were used as purchased, anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using forced-flow chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were employed, using UV light as the visualizing agent and an acidic mixture of vanillin or basic aqueous potassium permanganate ($KMnO_4$) stain solutions, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator.

Determination of Enantiomeric Purity. UPC^2 analysis on chiral stationary phase was performed on a Waters Acquity instrument using ID3, IG, IA3, IC, IB and OJ chiral columns. The exact conditions for the analyses are specified within the characterization section.

Materials. The starting materials used in this study are commercial and were purchased in the highest purity available from Sigma-Aldrich, Fluka, Alfa Aesar, Fluorochem, and used as received, without further purifications. Phenacyl chlorides that are not commercially available were synthetized using known literature procedures[1] and their characterization matched with the literature reported data. The synthesis of the enal substrates and the *celistolide* bromide is described in section **B**.

Experimental Setup. Experiments were performed using a 3D printed photoreactor consisting of a 9 cm diameter crystallizing dish with a 3D printed support of 6 positions, and a hole of 22 mm in the middle to allow ventilation (Figure S1). A commercial 1-meter LED strip was wrapped around the crystallizing dish. A fan was used to cool down the reactor and control the reaction temperature. The reaction temperature, measured within the reaction vessel using a thermometer, was between 35-40 ºC. Each of the positions could be used to fit a standard 16 mm diameter vial with a Teflon screw cap.

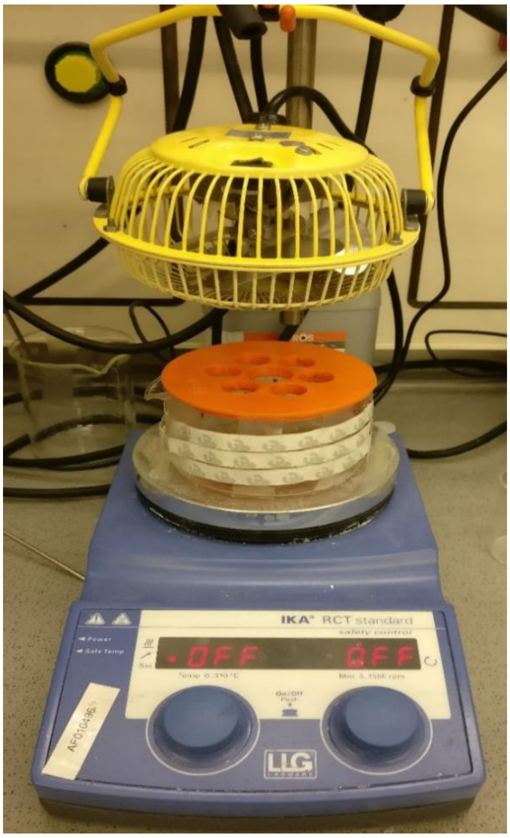


Figure S1: Photoreactor used for the photochemical catalytic reactions.

Experiments with illumination at 465 nm were conducted using a 1m blue LED strip, 14.4W "LEDXON MODULAR 9009083 LED, SINGLE 5050" purchased from Farnell, catalog number 9009083. The emission spectrum of the LED strip was recorded (Figure S2).

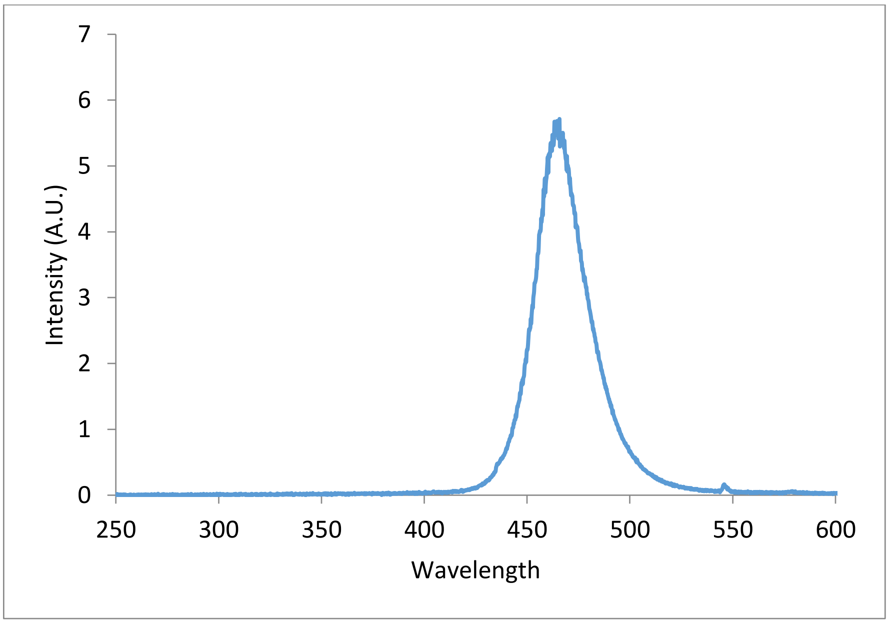


Figure S2: Emission spectrum of the 465 nm blue LED strip used in this study.

The emission maximum was determined as 465 nm with a spectral width of 30 nm (450-480 nm) at half peak intensity and a total spectral width of 120 nm (420-540 nm).

B. Substrate Synthesis

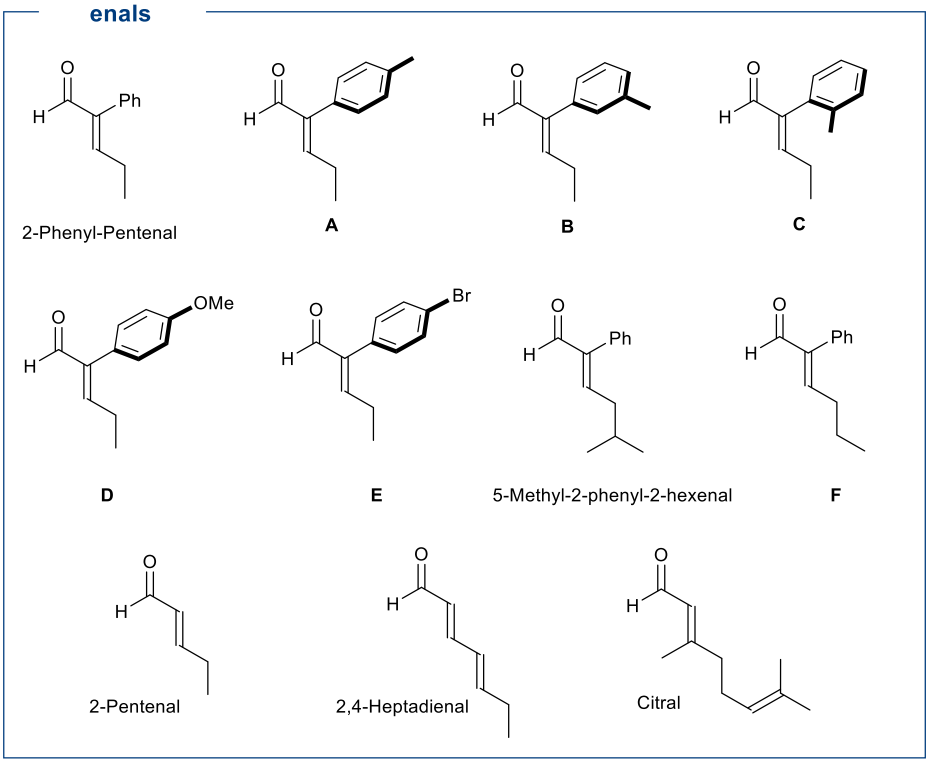
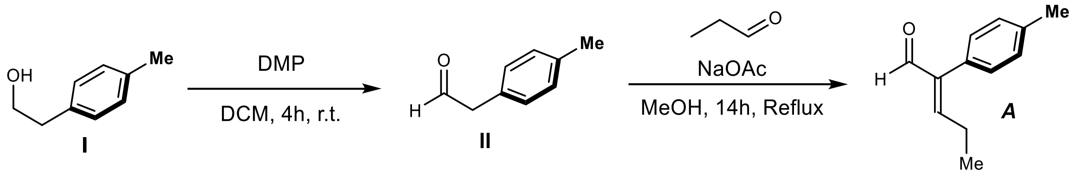


Figure S3: Enal substrates used in this study.

2-Phenyl-2-pentenal, 2-pentenal, 2,4-heptadienal, 5-methyl-2-phenyl-2-hexenal and *citral* were commercially available and used as received, without further purifications. Enals **A**, **B**, **C**, **D**, **E** and **G** were synthetized through a two-step procedure using reported and slightly modified protocols.[2,3]

Synthesis of *(E)*-2-(p-tolyl)pent-2-enal (A):



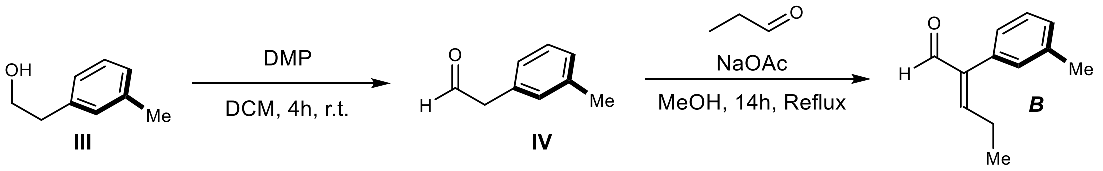
To a stirred solution of alcohol **I** (1.36 g, 10.0 mmol) in CH_2Cl_2 dry (60 mL), Dess-Martin periodinane (15 mmol, 6.4 g) was added under argon. After 3h stirring, the reaction was quenched with saturated aqueous solutions of $NaHCO_3$ and $Na_2S_2O_3$ (20 mL). After 30 min, the resulting mixture was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure, and purified by column chromatography (eluent: hexane/EtOAc 10:1) to give 631 mg of the corresponding aldehyde **II** (4.7 mmol, 47% yield) as a colorless oil.

To a stirred solution of **II** (631 mg, 4.7 mmol) in MeOH (9.5 mL), 1.0 mL of propionaldehyde (14.1 mmol) and 385 mg of NaOAc (4.7 mmol) were sequentially added. The resulting mixture was heated to reflux for 14h. Subsequently, the solvent was evaporated under vacuum and the resulting material was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure. The excess of propionaldehyde was removed by column chromatography (eluent: hexane/EtOAc 99:1) and then the residue (mixture of desired product and self-condensed by-product) purified by Kugelrohr distillation (2.1×10^{-1} bar, 90 °C) to afford 296 mg the corresponding enal **A** (1.7 mmol, 36% yield) as a colorless oil.

^{1}<u>H NMR</u> (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.71 (t, *J* = 7.5 Hz, 1H), 2.49 – 2.33 (m, 5H), 1.14 (t, *J* = 7.5 Hz 3H).

^{13}<u>C NMR</u> (126 MHz, $CDCl_3$) δ 194.1, 157.7, 143.3, 137.7, 129.6, 129.3 (2C), 129.0 V, 23.3, 21.3, 13.3.

Synthesis of *(E)*-2-(m-tolyl)pent-2-enal (B):



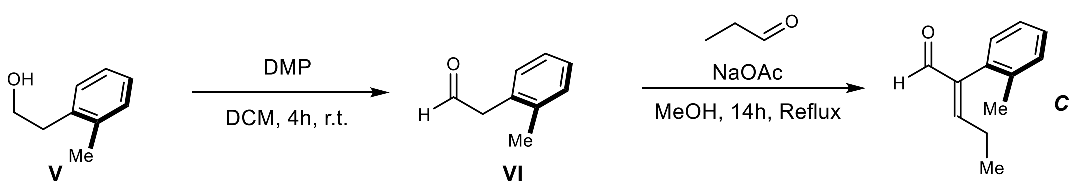
To a stirred solution of alcohol **III** (1.36 g, 10.0 mmol) in dry CH_2Cl_2 (60 mL), Dess-Martin periodinane (15 mmol, 6.4 g) was added under argon. After 3h the reaction was quenched with saturated aqueous solutions of $NaHCO_3$ and $Na_2S_2O_3$ (20 mL). After 30 min, the resulting mixture was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure, and purified by column chromatography (eluent: hexane/EtOAc 10:1) to give 872 mg of the corresponding aldehyde **IV** (6.5 mmol, 65% yield) as a colorless oil.

To a stirred solution of **IV** (872 mg, 6.5 mmol) in MeOH (13 mL), 1.39 mL of propionaldehyde (19.5 mmol) and 540 mg of NaOAc (6.5 mmol) were sequentially added. The resulting mixture was heated to reflux for 14h. Subsequently, the solvent was evaporated under vacuum and the resulting material was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure. The excess of propionaldehyde was removed by column chromatography (eluent: hexane/EtOAc 99:1) and then the residue (mixture of desired product and self-condensed by-product) purified by Kugelrohr distillation (2.1×10^{-1} bar, 90 °C) to afford 362 mg the corresponding enal **B** (2.1 mmol, 32% yield) as a colorless oil.

^{1}<u>H NMR</u> (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.03 – 6.94 (m, 2H), 6.71 (t, *J* = 7.5 Hz, 1H), 2.47 – 2.33 (m, 5H), 1.13 (t, *J* = 7.5 Hz, 3H).

^{13}<u>C NMR</u> (126 MHz, $CDCl_3$) δ 193.9, 157.7, 143.6, 137.8, 132.5, 130.0, 128.7, 128.1, 126.4, 23.2, 21.5, 13.3.

Synthesis of *(E)*-2-(o-tolyl)pent-2-enal (C):



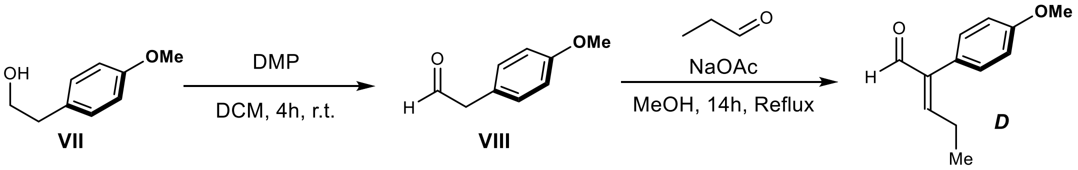
To a stirred solution of alcohol **V** (1.36 g, 10.0 mmol) in dry CH_2Cl_2 (60 mL), Dess-Martin periodinane (15 mmol, 6.4 g) was added under argon. After 3h the reaction was quenched with saturated aqueous solutions of $NaHCO_3$ and $Na_2S_2O_3$ (20 mL). After 30 min, the resulting mixture was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure, and purified by column chromatography (eluent: hexane/EtOAc 10:1) to give 791 mg of the corresponding aldehyde **VI** (5.9 mmol, 59% yield) as a colorless oil.

To a stirred solution of **VI** (591 mg, 5.9 mmol) in MeOH (12 mL), 1.26 mL of propionaldehyde (17.7 mmol) and 484 mg of NaOAc (5.9 mmol) were sequentially added. The resulting mixture was heated to reflux for 14h. Subsequently, the solvent was evaporated under vacuum and the resulting material was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure, and purified by column chromatography (eluent: pentane/Et_2O 9:1) to afford 452 mg the corresponding enal **C** (2.6 mmol, 44% yield) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.64 (d, *J* = 0.6 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.25 – 7.16 (m, 2H), 6.96 (d, *J* = 7.1 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 2.24 – 2.14 (m, 2H), 2.12 (s, 3H), 1.09 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.10, 157.65, 143.33, 137.71, 129.30, 128.96, 23.25, 21.28, 13.31.

Synthesis of *(E)*-2-(4-methoxyphenyl)pent-2-enal (D):



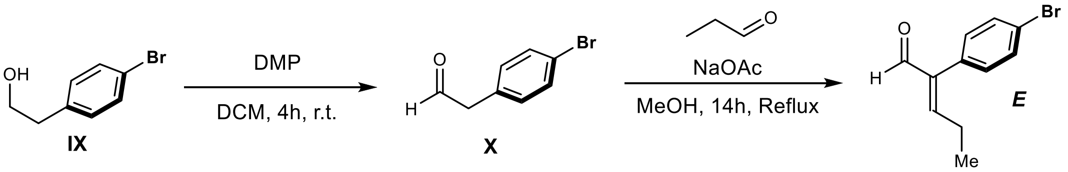
To a stirred solution of alcohol **VII** (1.5 g, 10.0 mmol) in dry CH_2Cl_2 (60 mL), Dess-Martin periodinane (15 mmol, 6.4 g) was added under argon. After 3h the reaction was quenched with saturated aqueous solutions of $NaHCO_3$ and $Na_2S_2O_3$ (20 mL). After 30 min, the resulting mixture was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure, and purified by column chromatography (eluent: hexane/EtOAc 4:1) to give 795 mg of the corresponding aldehyde **VIII** (5.3 mmol, 53% yield) as a colorless oil.

To a stirred solution of **VIII** (795 mg, 5.3 mmol) in MeOH (10 mL), 1.13 mL of propionaldehyde (15.9 mmol) and 434 mg of NaOAc (5.3 mmol) were sequentially added. The resulting mixture was heated to reflux for 14h. Subsequently, the solvent was evaporated under vacuum and the resulting material was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure, and purified by column chromatography (eluent: hexane/EtOAc 9:1) to afford 413 mg the corresponding enal **D** (2.2 mmol, 41% yield) as a pale-yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.68 (t, *J* = 7.5 Hz, 1H), 3.85 (s, 3H), 2.42 (p, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.2, 159.3, 157.5, 142.9, 130.6 (2C), 124.7, 113.7 (2C), 55.3, 23.2.

Synthesis of *(E)*-2-(4-bromophenyl)pent-2-enal (E):



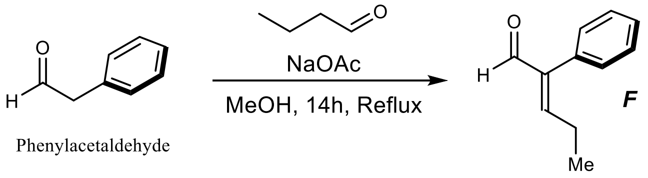
To a stirred solution of alcohol **IX** (2.0 g, 10.0 mmol) in dry CH_2Cl_2 (60 mL), Dess-Martin periodinane (15 mmol, 6.4 g) was added under argon. After 3h the reaction was quenched with saturated aqueous solutions of $NaHCO_3$ and $Na_2S_2O_3$ (20 mL). After 30 min, the resulting mixture was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure, and purified by column chromatography (eluent: hexane/EtOAc 3:1) to give 1.4 g the corresponding aldehyde **X** (7.1 mmol, 72% yield) as a pale-yellow oil.

To a stirred solution of **X** (1.4 g, 7.1 mmol) in MeOH (14 mL), 1.52 mL of propionaldehyde (21.3 mmol) and 582 mg of NaOAc (7.1 mmol) were sequentially added. The resulting mixture was heated to reflux for 14h. Subsequently, the solvent was evaporated under vacuum and the resulting material was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure, and purified by column chromatography (eluent: hexane/EtOAc 9:1) to afford 899 mg the corresponding enal **E** (3.7 mmol, 53% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 9.59 (s, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 2.37 (p, *J* = 7.5 Hz 2H), 1.12 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 158.2, 142.4, 131.5 (2C), 131.4, 131.1 (2C), 23.2, 13.2.

Synthesis of *(E)*-2-phenylhex-2-enal (F):

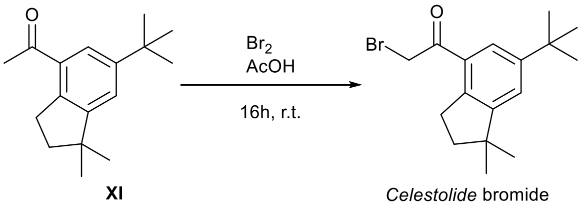


To a stirred solution of phenylacetaldehyde (1.0 g, 8.3 mmol) in MeOH (16 mL), 2.24 mL of butyraldehyde (24.9 mmol) and 680 mg of NaOAc (8.3 mmol) were sequentially added. The resulting mixture was heated to reflux for 14h. Subsequently, the solvent was evaporated under vacuum and the resulting material was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure, and purified by column chromatography (eluent: hexane/Et_2O 97:3) to afford 709 mg the corresponding enal **F** (4.1 mmol, 49% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.45 – 7.34 (m, 3H), 7.20 – 7.16 (m, 2H), 6.75 (t, *J* = 7.5 Hz, 1H), 2.37 (q, *J* = 7.5 Hz, 2H), 1.56 (q, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 156.4, 144.1, 132.7, 129.4 (2C), 128.2 (2C), 127.9, 31.7, 22.1, 13.8.

Synthesis of 2-bromo-1-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-one:

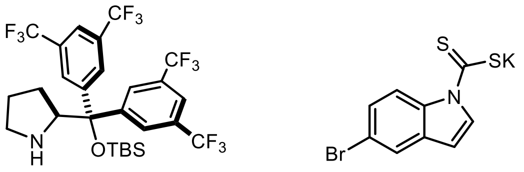


Ketone **XI** (1.95 g, 8.0 mmol) was dissolved in glacial AcOH (0.2M) and treated dropwise with Br_2 (0.411 mL, 17.7 mmol) in AcOH (1.3 M) at ambient temperature. The mixture was stirred for 16h and then the solvent was removed by rotary evaporation. The crude mixture was evaporated under reduced pressure, and purified by column chromatography (eluent: pentane/Et_2O 8:2) to afford 1.50 g of the desired product (4.64 mmol, 58% yield) as a colorless oil.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.71 (s, 1H), 7.38 (s, 1H), 4.48 (s, 1H), 3.18 (td, J = 7.3, 1.2 Hz, 2H), 1.95 (td, J = 7.3, 1.3 Hz, 2H), 1.36 (s, 9H), 1.27 (s, 6H).

13C NMR (101 MHz, CDC13) δ 192.88, 154.99, 150.24, 142.52, 130.41, 124.89, 124.40, 43.65, 41.47, 34.91, 33.13, 31.60, 30.93, 28.88.

C. Catalyst Synthesis



B **G**

Figure S4: Catalysts used in this study.

The indole-based dithiocarbamate catalyst **G** was synthetized from 5-bromoindole following a previously reported one-step process.[4]

The chiral dienamine catalyst **B** was synthetized starting from *L*-proline following a 5-step procedure described below. All the intermediates and products matched the spectroscopic characterization reported in literature.[5]

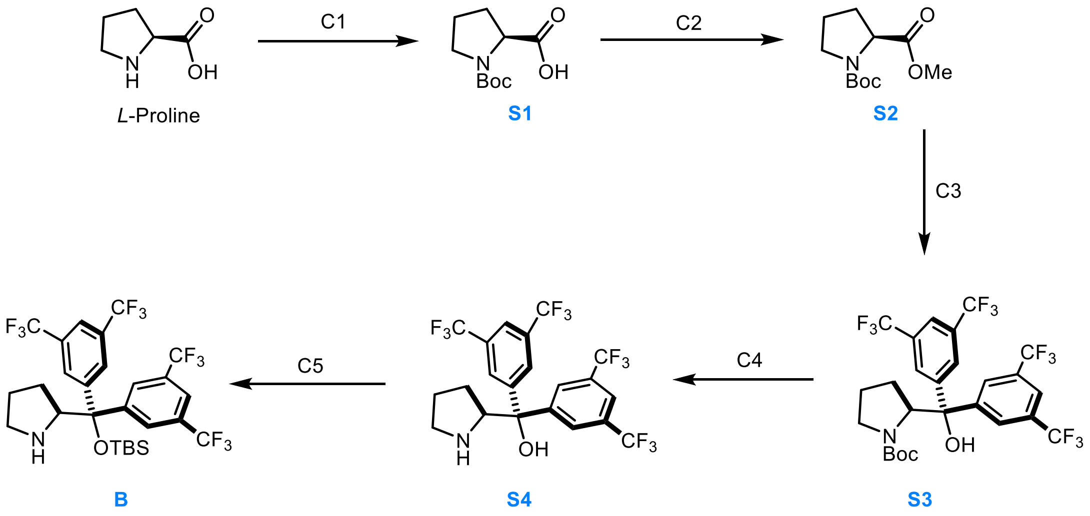
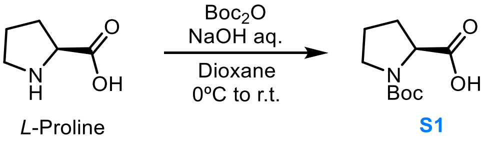


Figure S5: Route for preparation of catalyst **B**.

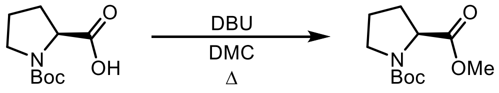
C1. Synthesis of (tert-butoxycarbonyl)-L-proline



To a solution of (S)-proline (8.0 g, 69 mmol) in aq. NaOH (1M, 130 mL) and dioxane (33 mL) at 0 °C was added Boc$_2$O (18 g, 82 mmol) portionwise over 20 min. The resulting mixture was stirred at 0 °C for 30 min, then allowed to warm to 23 °C and stirred overnight. The organic solvent was removed under reduced pressure. The remaining aqueous solution was acidified to pH ~2 with aq. KHSO$_4$ (1 M). The aqueous solution was extracted with $CHCl_3$ (3 x 150 mL). The combined organic layers were washed with brine (200 mL), dried over Na_2SO_4, and concentrated by rotary evaporation to afford the target carbamate **S1** (14.2 g, 95% yield) as a white solid, which was sufficiently pure to be taken on to the next step.

^{1}<u>H NMR</u> (400 MHz, $CDCl_3$) <u>mixture of rotamers</u> δ 4.42 – 4.21 (m, 1H *rot1*+ *rot2*), 3.65 – 3.28 (m, 2H, *rot1*+ *rot2*), 2.53 – 2.18 (m, 1H, *rot1*+ *rot2*), 2.16 – 1.79 (m, 3H, *rot1*+ *rot2*), 1.57– 1.32 (bs, 3H, *rot1*+ *rot2*).

C2. Synthesis of 1-(tert-butyl) 2-methyl (S)-pyrrolidine-1,2-dicarboxylate

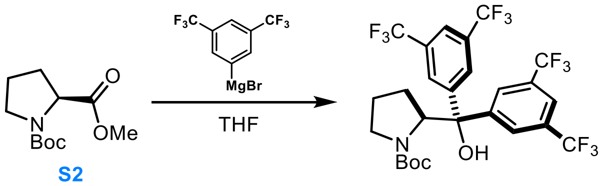


S1 **S2**

DBU (9.9 g, 9.8 mL equiv) was added to a solution of N-Boc proline **S1** (14 g, 65 mmol) in dimethyl carbonate (DMC) (250 mL 0.25M), and the resulting mixture was heated to reflux. Upon completion, the reaction mixture was cooled to room temperature and diluted with either EtOAc and H_2O. The aqueous layer was removed, and the organic layer was washed with H_2O, twice with 2 M HCl or 10% aqueous citric acid, twice with saturated aqueous $NaHCO_3$, and twice with H_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum to afford the target ester **S2** (14,6 g, 98% yield) as a pale-yellow oil which was sufficiently pure to be taken on to the next step.

^{1}<u>H NMR</u> (400 MHz, $CDCl_3$) <u>mixture of rotamers</u> δ 4.31 (dd, *J* = 8.7, 3.2 Hz, *rot1*) + 4.21 (dd, *J* = 8.5, 4.2 Hz, *rot2* 1H), 3.71 (s, 3H, *rot1*+ *rot2*), 3.58 – 3.31 (m, 2H, *rot1*+ *rot2*), 2.28 – 2.10 (m, 1H), 2.02 – 1.79 (m, 3H), 1.45 + 1.19 (two singlets 9H, *rot1*+ *rot2*).

C3. Synthesis of (S)-bis(3,5-bis(trifluoromethyl)phenyl)(pyrrolidin-2-yl)methanol



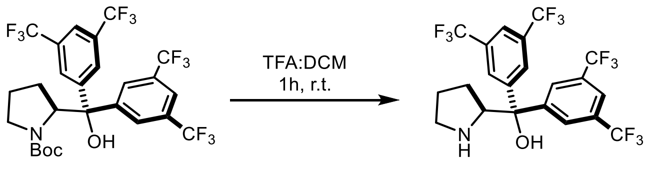
S2 **S3**

In a two-necked round bottom flask equipped with septum and condenser containing a stirring bar were added the Mg turnings (1.59 g, 65.4 mmol). The air was removed through vacuum air flaming for 30 minutes. To the Mg was added anhydrous THF (30 mL) and the reaction was stirred for 2 minutes after which a crystal of I_2 was added (the solution turns brownish). At this stage the aryl bromide (11.98 mL, 65.4 mmol) was added portion wise to the suspension of Mg. During the addition the solution turns gradually to grey (note: exothermic reaction). Once the addition of the aryl bromide was complete, the solution was refluxed for 1 hour at 65ºC. After the indicated time the solution was cooled to 0ºC and the Proline ester **S2** (as 1M solution in dry THF, 5 g, 21.8 mmol) was added via syringe. The reaction was stirred overnight and then slowly quenched with H_2O. The reaction crude was then filtered on cotton before being extracted 2 times with AcOEt (or DCM). The collected organic phase were then collected and anhydrified over $MgSO_4$, filtered and concentrated under vacuum to obtain a dark brown oil which contains the product. The oil was then purified by Flash Chromatography o silica gel (100%hexane to

95:5 hexane:AcOEt) to afford the prolinol **S3** (10.1 g, 73% yield) as an orange and dense oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 4H), 7.81 (s, 2H), 4.85 – 4.78 (m, 1H), 3.46 (ddd, J = 11.2, 8.2, 5.9 Hz, 1H), 2.84 (dt, J = 11.3, 7.2 Hz, 1H), 2.15 – 2.01 (m, 1H), 1.77 (dq, J = 13.4, 6.7 Hz, 1H), 1.62 (dt, J = 14.6, 7.5 Hz, 1H), 1.40 (s, 9H), 1.06 – 0.98 (m, 1H).

C4. Synthesis of *tert*-butyl (S)-2-(bis(3,5bis(trifluoromethyl)phenyl)(hydroxy)methyl) pyrrolidine-1-carboxylate

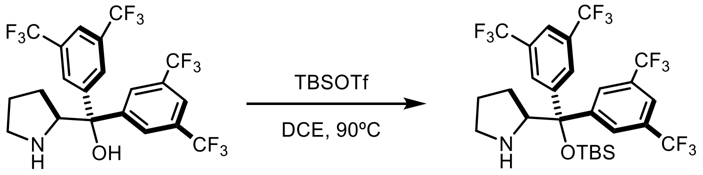


S3 **S4**

Prolinol **S3** (9.4 g, 15.95 mmol) was dissolved in a 1:1 mixture of DCM:TFA and stirred for 1 hour at room temperature. The solution was then basified to pH 7 using a solution of $NaHCO_3$. The organic phase was then extracted with DCM 3 times. After anhydrification with $NaSO_4$ and removal of the solvent the free amine **S4** (7.3 g, 92% yield) was obtained as an orange oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.95 (s, 2H), 7.76 (d, J = 5.5 Hz, 2H), 4.35 (t, J = 7.7 Hz, 1H), 3.13 – 2.98 (m, 2H), 1.85 – 1.73 (m, 2H), 1.64 – 1.47 (m, 2H).

C5. Synthesis of Catalyst B



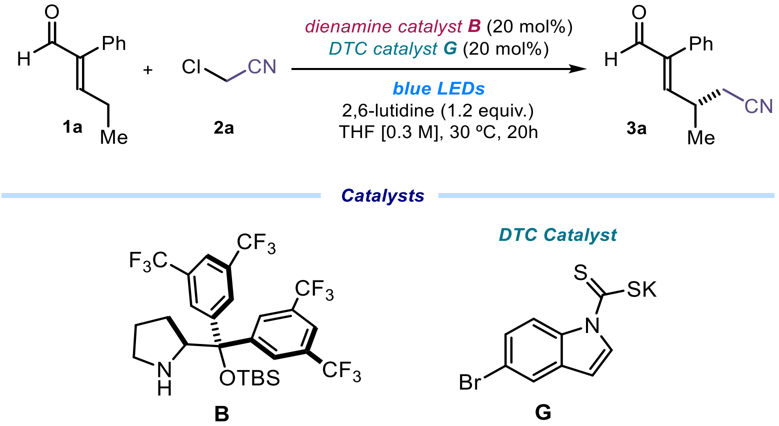
S4 **B**

In a two-necked round bottom flask equipped with condenser and a magnetic stirring bar was made a 0.4M solution of substrate **S4** (5.00 g, 9.5 mmol) in DCE. Triethylamine (5.97 mL, 42.8 mmol) and TBSOTf (4.38 mL, 19.04 mmol) were added sequentially while stirring. The reaction was then stirred under reflux overnight. After cooling the reaction mixture was quenched with brine. The organic phase was extracted with Et_2O 3 times and after anhydrification over $MgSO_4$ the crude was purified by Flash Chromatography on silica gel (2% Et_2O in Pentane) to afford the catalyst **B** (3.2 g, 50% yield) as a pale-yellow oil which solidifies at low temperature.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 2H), 7.85 (s, 2H), 7.74 (s, 2H), 4.24 (dd, J = 8.0, 6.0 Hz, 1H), 2.90 (dt, J = 10.2, 7.0 Hz, 1H), 2.59 – 2.46 (m, 1H), 1.77 (dt, J = 12.7, 7.6 Hz, 1H), 1.53 – 1.37 (m, 2H), 0.94 (s, 9H), 0.92 – 0.86 (m, 1H), -0.21 (s, 3H), -0.47 (s, 3H).

D. Optimization of the reaction conditions

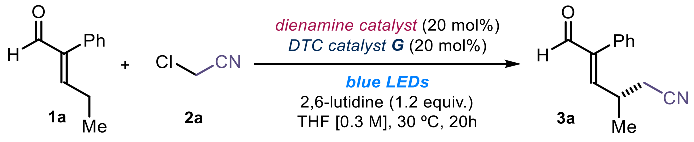
Table S1. Optimisation studies

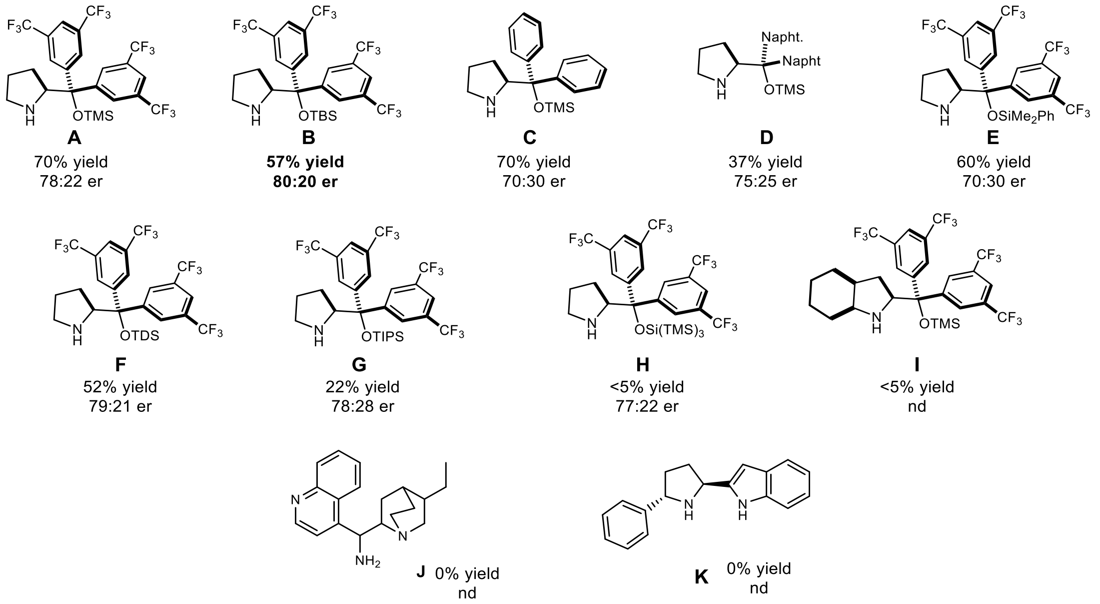


entry	**B** (x mol%)	**G** (y mol%)	solvent	T (°C)	yield (%)[a]	e.r.[b]
1	20	20	toluene	35	40	77:23
2	20	20	CH_2Cl_2	35	65	77:23
3	20	20	CH_3CN	35	18	79:21
4	20	20	$CHCl_3$	35	66	78:22
5	20	20	THF	35	70	78:22
6	20	20	TFT	35	42	78:22
7	**10**	20	THF	35	20	77:23
8	20	**10**	THF	35	25	n.d.
9	20	20	THF	**10**	7	n.d.

Reactions performed under argon using **1a** (0.6 mmol), **2a** (0.2 mmol), catalysts **B** (20 mol%) and **G** (20 mol%) and 2,6-lutidine (1.2 equiv.) in the surveyed solvent (0.03 M) under blue LEDs irradiation for 20 hours. [a] Yields determined by ^{1}H NMR analysis on the crude of the reaction using trimethyl orthoformate as the internal standard. [b] Determined by UPC^2 analysis; n.d. = not determined. TFT = trifluorotoluene

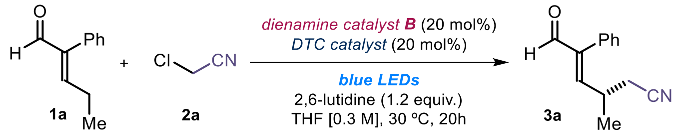
Table S2. Screening of chiral dienamine catalysts

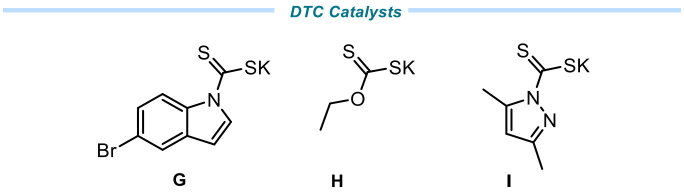




Reactions performed under argon using **1a** (0.6 mmol), **2a** (0.2 mmol), the dienamine catalysts (20 mol%), **G** (20 mol%) and 2,6-lutidine (1.2 equiv.) in THF (0.03 M) under blue LEDs irradiation at 35-40 °C for 20 hours.

Table S3. Screening of other parameters

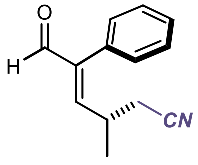




Entry[a]	Deviation	yield [%]	e.r.
1	-	57	80:20
3	**B** (40 mol%)	59	80:20
5	**H** instead of **G**	<5	nd
6	**I** instead of **G**	<5	nd
7	**G** (30 mol%)	67 (60)	80:20
8	concentration [0.7 M]	75 (70)	80:20
10	**G** (30 mol%) and [0.7 M]	69 (61)	80:20
11	**G** (30 mol%) and 4 equiv. of **1a**	70 (65)	80:20

E. Experimental Procedures

E1. General Procedure. The general procedure is detailed for the model reaction leading to product **3a**. It was then applied to perform all other catalytic photochemical processes.



3a

In an oven dried 5 mL vial equipped with a Teflon septum screw cap and a magnetic stirring bar, *(E)*-2-phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.) and aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.) were dissolved in 250 µL of degassed THF. After 5 minutes, 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.), α-chloroacetonitrile **2a** (0.2 mmol, 12.6 µL) and dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) were sequentially added. The reaction mixture was degassed through Ar sparging for 20 seconds before closing the cap. The vial was then sealed with parafilm and placed in the 3D printed support photoreactor (Figure S1) and irradiated under stirring. After 20 hours, the solvent was evaporated under reduced pressure and the residue purified by column chromatography (eluent: hexane/EtOAc 8:2) to afford 27.9 mg of the corresponding product (0.14 mmol, 70%, 80:20 *er*) as a pale-orange oil. The enantiomeric ratio was determined to be 80:20 by UPC^2 analysis on a Daicel Chiralpak IA-3 column (eluent: CO_2/IPA = 90:10; flow rate 1 mL/min, λ = 300 nm. τ_{Major} = 3.5 min, τ_{Minor} = 3.7 min.

$[\alpha]_D^{20}$ = +86.2 (c = 0.5 g/100 mL, $CHCl_3$)

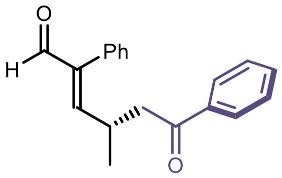
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.49 – 7.37 (m, 3H), 7.20 – 7.11 (m, 2H), 6.54 (d, *J* = 10.3 Hz, 1H), 3.11 – 2.99 (m, 1H), 2.44 (d, *J* = 6.3 Hz, 2H), 1.28 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 153.9, 144.7, 131.9, 129.0 (2C), 128.6 (2C), 128.5, 117.3, 30.7, 24.1, 19.7.

HRMS (ESI): m/z calculated for $[C_{18}H_{25}NO_4Na]^+$ $[M+ Na]^+$: 222.0895; found: 222.0889.

E2. Scope of the Radical Precursors

Synthesis of *(S,E)*-4-methyl-6-oxo-2,6-diphenylhex-2-enal [(-)-3b]



3b

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-chloro-1-phenylethan-1-one (30.9 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **3b** (31.2 mg, 56% yield) as a yellow oil. The enantiomeric ratio was determined to be 84:16 by UPC^2 analysis on a Daicel Chiralpak IG column (eluent: CO_2/IPA = 90:10; flow rate 1 mL/min, λ = 320 nm. τ_{Major} = 3.2 min, τ_{Minor} = 3.9 min.

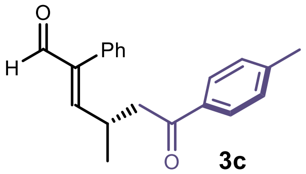
$[\alpha]_D^{20}$ = -76.4 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.93 – 7.81 (m, 2H), 7.57 (ddt, *J* = 7.9, 6.9, 1.3 Hz, 1H), 7.48 – 7.34 (m, 5H), 7.21 – 7.15 (m, 2H), 3.39 – 3.37 (m, 1H), 3.10 – 3.07 (m, 2H), 1.19 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9, 193.8, 159.2, 143.2, 136.6, 133.3, 132.6, 129.2 (2C), 128.7 (2C), 128.4 (2C), 128.1 (2C), 128.0, 45.0, 30.4, 20.1.

HRMS (ESI): m/z calculated for $[C_{19}H_{18}O_2Na]^+$ $[M+Na]^+$: 301.1204; found: 301.1199.

Synthesis of *(S,E)*-4-methyl-6-oxo-2-phenyl-6-(p-tolyl)hex-2-enal [(-)-3c]



3c

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-chloro-1-(p-tolyl)ethan-1-one (42.6 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **3c** (28.1 mg, 48% yield) as a pale yellow oil. The enantiomeric ratio was determined to be 85:15 by UPC^2 analysis on a Daicel Chiralpak IG column (eluent: CO_2/IPA = 90:10; flow rate 1 mL/min, λ = 320 nm. τ_{Major} = 3.80 min, τ_{Minor} = 4.10 min.

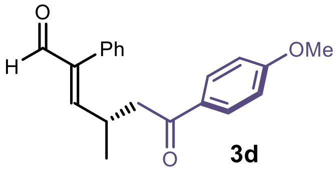
$[\alpha]_D^{20}$ = -15.6 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) 9.61 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.32 (m, 3H), 7.25 – 7.21 (m, 2H), 7.20 – 7.15 (m, 2H), 6.61 (d, *J* = 10.2 Hz, 1H), 3.38 – 3.27 (m, 1H), 3.06 (dd, *J* = 6.8, 1.5 Hz, 2H), 2.42 (s, 3H), 1.17 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 193.8, 159.4, 144.1, 143.1, 134.2, 132.6, 129.4 (2C), 129.2 (2C), 128.4 (2C), 128.2 (2C), 128.0, 44.9, 30.5, 21.7, 20.0.

HRMS (ESI): m/z calculated for $[C_{20}H_{20}O_2Na]^+$ $[M+Na]^+$: 315.1361; found: 315.1356.

Synthesis of *(S,E)*-6-(4-methoxyphenyl)-4-methyl-6-oxo-2-phenylhex-2-enal [(-)-3d]



3d

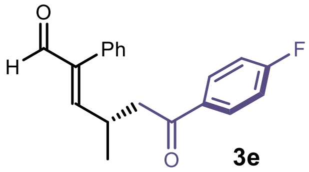
Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-chloro-1-(4-methoxy)ethan-1-one (45.8 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), DTC catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 7:3) to afford product **3d** (32.0 mg, 53% yield) as a colorless oil. The enantiomeric ratio was determined to be 83:17 by UPC^2 analysis on a Daicel Chiralpak IG column (eluent: CO_2/IPA=20:80; flow rate 1 mL/min, λ = 320 nm. τ_{Major} = 4.15 min, τ_{Minor} = 4.4 min. $[\alpha]_D^{20}$ = -51.1 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.84 (d, *J* = 8.9 Hz, 2H), 7.43 – 7.32 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J*= 10.1 Hz, 1H), 3.88 (s, 3H), 3.39 – 3.23 (m, 1H), 3.03 (d, *J* = 6.8 Hz, 2H), 1.17 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 193.8, 163.6, 159.4, 143.1, 132.6, 130.4 (2C), 129.7, 129.2 (2C), 128.4 (2C), 128.0, 113.8 (2C), 55.5, 44.7, 30.6, 20.1.

HRMS (ESI): m/z calculated for $[C_{20}H_{20}O_3Na]^+$ $[M+Na]^+$: 331.1310; found: 331.1305.

Synthesis of *(S,E)*-6-(4-fluorophenyl)-4-methyl-6-oxo-2-phenylhex-2-enal [(+)-3e]



3e

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-chloro-1-(4-fluorophenyl)ethan-1-one (43.4 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **3e** (31.4 mg, 53% yield) as a colorless oil. The enantiomeric ratio was determined to be 83:17 by UPC^2 analysis on a Daicel Chiralpak IG column (eluent: CO_2/IPA = 90:10; flow rate 1 mL/min, λ = 320 nm. τ_{Major} = 3.30 min, τ_{Minor} = 3.5 min.

$[\alpha]_D^{20}$ = +63.4 (c = 0.5 g/100 mL, $CHCl_3$)

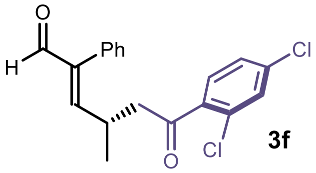
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.87 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.48 – 7.32 (m, 3H), 7.22 – 7.14 (m, 2H), 7.14 – 7.04 (m, 2H), 6.60 (d, *J* = 10.2 Hz, 1H), 3.39 – 3.24 (m, 1H), 3.04 (d, *J* = 6.8 Hz, 2H), 1.19 (d, *J* = 6.7 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -104.87.

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 193.7, 165.8 (d, $^1J_{C.F}$ = 255 Hz), 158.9, 143.2, 133.0 (d, $^4J_{C.F}$ = 3 Hz), 132.6, 130.7 (d, $^3J_{C.F}$ = 9 Hz, 2C), 129.2 (2C), 128.4 (2C), 128.1, 115.8 (d, $^2J_{C.F}$ = 22 Hz, 2C), 44.9, 30.4, 20.0.

HRMS (ESI): m/z calculated for $[C_{19}H_{17}FO_2Na]^+$ $[M+Na]^+$: 319.1110; found: 319.1105.

Synthesis of *(S,E)*-6-(2,4-dichlorophenyl)-4-methyl-6-oxo-2-phenylhex-2-enal [(+)-3f]



3f

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-chloro-1-(2,4-dichlorophenyl)ethan-1-one (53.6 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 75:25) to afford product **3f** (34.7 mg, 50% yield) as a yellowish oil. The enantiomeric ratio was determined to be 76:24 by UPC^2 analysis on a Daicel Chiralpak IG column (eluent: 85:15 CO_2/MeOH; flow rate 1.00 mL/min, λ = 240 nm. τ_{Major} = 3.5 min, τ_{Minor} = 3.8 min.

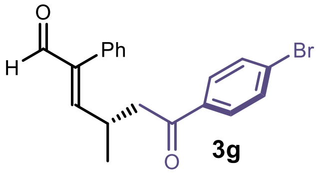
$[\alpha]_D^{20}$ = +87.0 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.44 – 7.35 (m, 4H), 7.33 – 7.28 (m, 1H), 7.18 – 7.14 (m, 2H), 6.56 (d, *J* = 10.2 Hz, 1H), 3.35 – 3.23 (m, 1H), 3.07 (dd, *J* = 6.8, 1.7 Hz, 2H), 1.19 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.6, 193.6, 158.2, 143.2, 137.7, 137.0, 132.4, 132.1, 130.5, 130.2, 129.1 (2C), 128.4 (2C), 128.1, 127.5, 49.1, 30.4, 20.1.

HRMS (ESI): m/z calculated for $[C_{19}H_{16}Cl_2O_2Na]^+$ $[M+Na]^+$: 369.0425; found: 369.0420.

Synthesis of *(S,E)*-6-(4-bromophenyl)-4-methyl-6-oxo-2-phenylhex-2-enal [(+)-3g]



3g

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-chloro-1-(4-bromophenyl)ethan-1-one (55.6 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 7:3) to afford product **3g** (42 mg, 58% yield) as a colorless oil. The enantiomeric ratio was determined to be 82:18 by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 85:15; flow rate 1 mL/min, λ = 320 nm. τ_{Major} = 3.5 min, τ_{Minor} = 3.7 min.

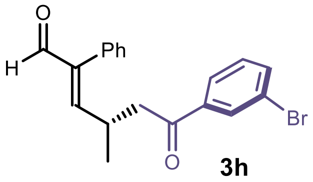
$[\alpha]_D^{20}$ = +19.2 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.70 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.19 – 7.14 (m, 2H), 6.59 (d, J = 10.2 Hz, 1H), 3.32 (dq, J = 10.2, 6.8 Hz, 1H), 3.04 (d, J = 6.8 Hz, 2H), 1.19 (d, J = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.76, 193.58, 158.59, 143.26, 135.21, 132.53, 131.98, 129.55, 129.14, 128.50, 128.40, 128.07, 44.97, 30.39, 20.04.

HRMS (ESI): m/z calculated for $[C_{19}H_{17}BrO_2Na]^+$ $[M+Na]^+$: 379.0310; found: 379.0291.

Synthesis of *(S,E)*-6-(3-bromophenyl)-4-methyl-6-oxo-2-phenylhex-2-enal [(-)-3h]



3h

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-bromo-1-(3-bromophenyl)ethan-1-one (55.6 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **3h** (39.3 mg, 52% yield) as a yellowish oil. The enantiomeric ratio was determined to be 82:18 by UPC^2 analysis on a Daicel Chiralpak IG column (eluent: 80:20 CO_2/MeCN; flow rate 1.00 mL/min, λ = 250 nm. τ_{Major} = 3.9 min, τ_{Minor} = 4.2 min.

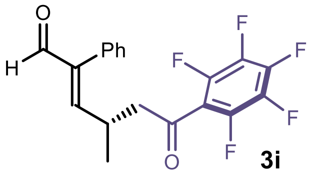
$[\alpha]_D^{20}$ = -30.7 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.01 (t, *J* = 1.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.45 – 7.34 (m, 3H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.20 – 7.15 (m, 2H), 6.59 (d, *J* = 10.2 Hz, 1H), 3.38 – 3.25 (m, 1H), 3.06 (d, *J* = 6.7 Hz, 2H), 1.19 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 193.6, 158.6, 143.3, 138.3, 136.1, 132.5, 131.1, 130.3, 129.2 (2C), 128.4 (2C), 128.1, 126.5, 123.1, 45.0, 30.3, 20.1.

HRMS (ESI): m/z calculated for $[C_{19}H_{17}BrO_2Na]^+$ $[M+Na]^+$: 379.0310; found: 379.0304.

Synthesis of *(S,E)*-4-methyl-6-oxo-6-(perfluorophenyl)-2-phenylhex-2-enal [(-)-3i]



3i

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-bromo-1-(perfluorophenyl)ethan-1-one (57.8 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: 85:15) to afford product **3i** (60.8 mg, 80% yield) as a yellowish oil. The enantiomeric ratio was determined to be 82:18 by UPC^2 analysis on a Daicel Chiralpak IA-3 column (eluent: 91:9 CO_2/MeCN; flow rate 1.00 mL/min, λ = 255 nm. τ_{Minor} = 2.2 min, τ_{Major} = 2.3 min. $[\alpha]_D^{20}$ = -57.3 (c = 0.5 g/100 mL, $CHCl_3$)

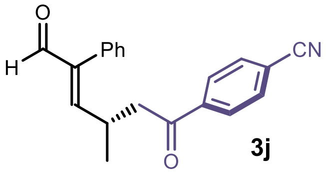
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.45 – 7.33 (m, 3H), 7.19 – 7.13 (m, 2H), 6.53 (d, J=10.2, 1H), 3.34 – 3.22 (m, 1H), 2.98 (dt, J=7.0, 1.4, 1.4, 2H), 1.22 (d, J=6.7, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -140.63 – -141.10 (m), -148.61 (t, *J* = 20.7 Hz), -159.26 – -159.84 (m).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.4, 191.8, 157.0, 144.2 (d, $^1J_{C.F}$ = 255 Hz), 143.4, 142.8 (d, $^1J_{C.F}$ = 260 Hz), 137.5 (d, $^1J_{C.F}$ = 255 Hz), 132.2, 129.0 (2C), 128.4 (2C), 128.2, 114.3 (t, $^2J_{C.F}$ =18 Hz), 51.2 (t, $^4J_{C.F}$ = 2 Hz), 30.1, 20.0.

HRMS (ESI): m/z calculated for $[C_{19}H_{13}F_5O_2Na]^+$ $[M+Na]^+$: 391.0733; found: 391.0728.

Synthesis of *(S,E)*-4-(3-methyl-6-oxo-5-phenylhex-4-enoyl)benzonitrile [(-)-3j]



3j

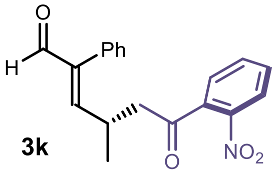
Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 4-(2-chloroacetyl)benzonitrile (44.8 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 7:3) to afford product **3j** (26.0 mg, 42% yield) as a colorless oil. The enantiomeric ratio was determined to be 82:18 by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: 85:15 CO_2/MeCN; flow rate 1.00 mL/min, λ = 220 nm. τ_{Major} = 3.5 min, τ_{Minor} = 3.7 min. $[\alpha]_D^{20}$ = -46.2 (c = 0.5 g/100 mL, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.94 – 7.83 (m, 2H), 7.77 – 7.63 (m, 2H), 7.43 – 7.31 (m, 3H), 7.19 – 7.10 (m, 2H), 6.56 (d, *J* = 10.1 Hz, 1H), 3.30 (dq, *J* = 10.1, 6.7 Hz, 1H), 3.12 – 3.01 (m, 2H), 1.19 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.34, 193.44, 158.00, 143.35, 139.26, 132.50, 132.44, 129.09, 128.40, 128.12, 117.76, 116.51, 45.21, 30.17, 19.98.

HRMS (ESI): m/z calculated for $[C_{20}H_{17}NO_2Na]^+$ $[M+Na]^+$: 326.1157; found: 326.1151.

Synthesis of *(S,E)*-4-methyl-6-(2-nitrophenyl)-6-oxo-2-phenylhex-2-enal [(+)-3k]



3k

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-chloro-1-(2-nitrophenyl)ethan-1-one (48.8 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), DTC catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **3k** (27.8 mg, 43% yield) as a brownish oil. The enantiomeric ratio was determined to be 82:18 by UPC^2 analysis on a Daicel Chiralpak IC column (eluent: 90:10 CO_2/IPA; flow rate 1.00 mL/min, λ = 250 nm. τ_{Major} = 4.2 min, τ_{Minor} = 4.3 min.

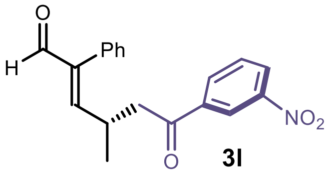
$[\alpha]_D^{20}$ = +15.3 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.15 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.65 – 7.59 (m, 1H), 7.47 – 7.42 (m, 2H), 7.41 – 7.38 (m, 1H), 7.26 – 7.23 (m, 3H), 6.64 (d, *J* = 10.2 Hz, 1H), 3.40 – 3.29 (m, 1H), 2.99 – 2.85 (m, 2H), 1.23 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 193.8, 158.4, 143.3, 137.6, 134.4, 132.6, 130.6, 129.3, 129.2 (2C), 128.4 (2C), 128.1, 127.4, 124.5, 49.0, 29.8, 19.9.

HRMS (ESI): m/z calculated for $[C_{19}H_{17}NO_4Na]^+$ $[M+Na]^+$: 346.1055; found: 346.1050.

Synthesis of *(S,E)*-4-methyl-6-(3-nitrophenyl)-6-oxo-2-phenylhex-2-enal [(+)-3l]



3l

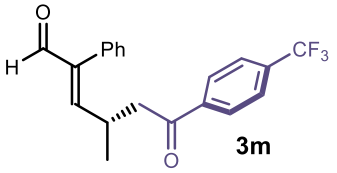
Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-bromo-1-(3-nitrophenyl)ethan-1-one (48.8 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 7:3) to afford product **3l** (33.6 mg, 52% yield) as a colorless oil. The enantiomeric ratio was determined to be 78:22 by UPC^2 analysis on a Daicel Chiralpak IG column (eluent: 85:15 CO_2/MeCN; flow rate 1.00 mL/min, λ = 220 nm. τMajor = 4.00 min, τMinor = 4.12 min. $[\alpha]_D^{20}$ = +21.0 (c = 0.5 g/100 mL, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.68 (t, *J* = 1.9 Hz, 1H), 8.42 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 8.18 (ddd, *J* = 7.7, 1.7, 1.1 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.19 – 7.15 (m, 2H), 6.60 (d, *J* = 10.2 Hz, 1H), 3.43 – 3.30 (m, 1H), 3.15 (d, *J* = 6.7 Hz, 2H), 1.24 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.5, 193.5, 158.0, 143.4, 137.7, 133.5, 132.4, 130.0, 129.7, 129.1 (2C), 128.4 (2C), 128.2, 127.6, 122.9, 45.2, 30.2, 20.1.

HRMS (ESI): m/z calculated for $[C_{19}H_{17}NO_4Na]^+$ $[M+Na]^+$: 346.1055; found: 346.1050.

Synthesis of (S,E)-4-methyl-6-oxo-2-phenyl-6-(4-(trifluoromethyl)phenyl)hex-2-enal [3m]


3m

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-chloro-1-(4-trifluoromethyl)ethan-1-one (44.2 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **3m** (27.8 mg, 59% yield) as a brownish oil. The enantiomeric ratio was determined to be 81:19 by UPC^2 analysis on a Daicel Chiralpak OJ column (eluent: 90:10 CO_2/EtOH; flow rate 1.00 mL/min, λ = 250 nm. τ_{Major} = 2.3 min, τ_{Minor} = 2.8 min. $[\alpha]_D^{20}$ = +58.7 (c = 0.5 g/100 mL, $CHCl_3$).

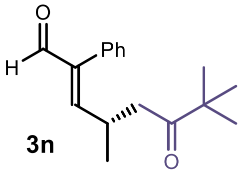
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.94 – 7.88 (m, 2H), 7.74 – 7.65 (m, 2H), 7.40 – 7.31 (m, 3H), 7.11 – 7.17 (m, 2H), 6.57 (d, *J* = 10.1 Hz, 1H), 3.25 – 3.38 (m, 1H), 3.08 (d, *J* = 6.8 Hz, 2H), 1.19 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.80, 193.52, 158.25, 143.36, 139.09, 134.56 (q, J = 32.7 Hz), 132.50, 129.12, 128.39, 128.37, 128.11, 125.73 (q, J = 3.8 Hz), 123.50 (q, J = 272.8 Hz), 45.29, 30.30, 20.04.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.27

HRMS (ESI): m/z calculated for $[C_{19}H_{17}NO_4Na]^+$ $[M+Na]^+$: 346.1055; found: 346.1050.

Synthesis of *(S,E)*-4,7,7-trimethyl-6-oxo-2-phenyloct-2-enal [(-)-3n]


3n

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 1-chloro-3,3-dimethylbutan-2-one (35.8 mg, 0.2 mmol), aminocatalyst **C** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **E** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 9:1) to afford product **3n** (13.0 mg, 25% yield) as a colorless oil. The enantiomeric ratio was determined to be 87:13 by UPC^2 analysis on a Daicel Chiralpak IC column (eluent: 93:7 CO_2/MeCN; flow rate 1.00 mL/min, λ = 250 nm. τ_{Minor} = 2.7 min, τ_{Major} = 2.85 min.

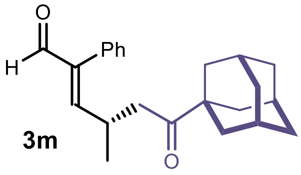
$[\alpha]_D^{20}$ = -11.2 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.46 – 7.39 (m, 2H), 7.38 – 7.33 (m, 1H), 7.23 – 7.19 (m, 2H), 6.53 (d, *J* = 10.2 Hz, 1H), 3.25 – 3.12 (m, 1H), 2.61 (ABq, *J* = 17.3, 6.5 Hz, 2H), 1.12 (s, 9H), 1.07 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.3, 193.9, 159.7, 142.9, 132.6, 129.2 (2C), 128.4 (2C), 128.0, 42.8, 31.6, 29.7, 26.2, 19.9.

HRMS (ESI): m/z calculated for $[C_{17}H_{22}O_2Na]^+$ $[M+Na]^+$: 281.1518; found: 281.1512.

Synthesis of *(S,E)*-6-*((3R,5R,7R)*-adamantan-1-yl)-4-methyl-6-oxo-2-phenylhex-2-enal [(+)-3m]


3m

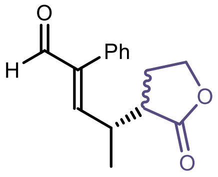
Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 1-((*3r*,*5r*,*7r*)-adamantan-1-yl)-2-bromoethan-1-one (51.4 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 9:1) to afford product **3m** (17 mg, 41% yield) as a colorless oil. The enantiomeric ratio was determined to be 89:11 by UPC^2 analysis on a Daicel Chiralpak OJ column (eluent: 90:10 CO_2/MeCN; flow rate 1.00 mL/min, λ = 220 nm. τ_{Minor} = 2.4 min, τ_{Major} = 2.9 min. $[\alpha]_D^{20}$ = +23.1 (c = 0.5 g/100 mL, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.45 – 7.40 (m, 2H), 7.38 – 7.33 (m, 1H), 7.24 – 7.19 (m, 2H), 6.52 (d, *J* = 10.2 Hz, 1H), 3.23 – 3.11 (m, 1H), 2.57 (ABq, *J* = 17.2, 6.5 Hz, 2H), 2.09 – 2.01 (m, 2H), 1.79 – 1.74 (m, 8H), 1.71 – 1.65 (m, 3H), 1.58 (s, 2H), 1.06 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.1, 193.9, 160.0, 142.8, 132.7, 129.2 (2C), 128.3 (2C), 128.0, 42.4, 38.1, 36.5, 29.6, 27.9, 20.0.

HRMS (ESI): m/z calculated for $[C_{23}H_{28}O_2Na]^+$ $[M+Na]^+$: 359.1987; found: 359.1982.

Synthesis of *(E)*-4-(2-oxotetrahydrofuran-3-yl)-2-phenylpent-2-enal [(-)-3p]



3p

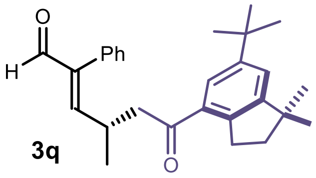
Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 3-bromodihydrofuran-2(3*H*)-one (33.0 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **3p** as a mixture 1.2:1 of the two diastereoisomers (20.0 mg, 41% yield) as a colorless oil. The enantiomeric ratio of the diastereoisomeric products was determined to be 91:9 for diastereoisomer 1 and 86:14 for diastereoisomer 2 by UPC^2 analysis on a Daicel Chiralpak IC column (eluent: 87:13 CO_2/IPA; flow rate 1.00 mL/min, λ = 250 nm. $\tau Major_{dias1}$ = 4.91 min, $\tau Minor_{dias1}$ = 5.04 min; $\tau Minor_{dias2}$ = 5.39 min, $\tau Major_{dias2}$ = 5.83 min. $[\alpha]_D^{20}$ = -8.2 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.66 (s, 1H_{dias1} + 1H_{dias2}), 7.46 – 7.35 (m, 3H_{dias1} + 3H_{dias2}), 7.18 – 7.13 (m, 2H_{dias1} + 2H_{dias2}), 6.75 (d, *J* = 10.6 Hz, 1H_{dias1}), 6.64 (d, *J* = 10.5 Hz, 1H_{dias2}), 4.33 (td, *J* = 8.9, 8.8, 2.8 Hz, 1H_{dias1}), 4.28 – 4.22 (m, 1H_{dias2}), 4.22 – 4.16 (m, 1H_{dias1} + 1H_{dias2}), 3.10 – 2.97 (m, 1H_{dias1} + 1H_{dias2}), 2.70 – 2.58 (m, 1H_{dias1} + 1H_{dias2}), 2.38 – 2.27 (m, 1H_{dias1} + 1H_{dias2}), 2.11 – 1.95 (m, 1H_{dias1} + 1H_{dias2}), 1.29 (d, *J* = 6.7 Hz, 1H_{dias1}), 1.21 (d, *J* = 6.9 Hz, 1H_{dias2}).

^{13}C NMR (126 MHz, $CDCl_3$) [signals of both diastereoisomers] δ 193.5, 193.4, 176.9, 176.8, 155.8, 155.2, 144.3, 144.0, 132.4, 132.3, 129.1 (4C), 128.6 (4C), 128.3, 128.2, 66.3 (2C), 43.9, 43.4, 34.0, 33.9, 26.5, 26.0, 17.6, 17.0.

HRMS (ESI): m/z calculated for $[C_{15}H_{16}O_3Na]^+$ $[M+Na]^+$: 267.0997; found: 267.0992.

Synthesis of *(S,E)*-6-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1*H*-inden-4-yl)-4-methyl-6-oxo-2-phenylhex-2-enal [(+)-3q]



3q

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 2-bromo-1-(6-(*tert*-butyl)-1,1-dimethyl-2,3-dihydro-1*H*-inden-4-yl)ethan-1-one (64.6 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 9:1) to afford product **3q** (40.0 mg, 50% yield) as a pale-yellow oil. The enantiomeric ratio was determined to be 79:21 by UPC^2 analysis on a Daicel Chiralpak IA-3 column (eluent: 92:8 CO2/IPA; flow rate 1.00 mL/min, λ = 250 nm. τ_{Major} = 3.8 min, τ_{Minor} = 3.7 min.

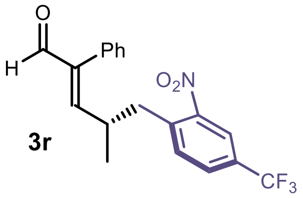
$[\alpha]_D^{20}$ = +51.4 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.56 (d, *J* = 1.8 Hz, 1H), 7.38 – 7.27 (m, 4H), 7.14 – 7.07 (m, 2H), 6.61 (d, *J* = 10.3 Hz, 1H), 3.31 (dq, *J* = 10.3, 6.7 Hz, 1H), 3.11 (m, 2H), 3.05 (m, 2H), 1.91 (t, *J* = 7.2 Hz, 2H), 1.32 (s, 9H), 1.25 (d, *J* = 3.3 Hz, 6H), 1.17 (d, *J* = 6.7 Hz, 3H).

<u>^{13}C NMR</u> (126 MHz, $CDCl_3$) δ 199.97, 193.82, 159.45, 154.58, 149.97, 142.85, 141.17, 133.16, 132.50, 129.14, 128.29, 127.96, 123.80, 123.42, 46.55, 43.40, 41.39, 34.70, 31.48, 30.78, 30.58, 28.74, 28.72, 20.16.

<u>HRMS (ESI)</u>: m/z calculated for $[C_{28}H_{34}O_2Na]^+$ $[M+Na]^+$: 425.2456; found: 425.2451.

Synthesis of *(S,E)*-4-methyl-5-(2-nitro-4-(trifluoromethyl)phenyl)-2-phenylpent-2-enal [(+)-3r]



3r

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 1-(bromomethyl)-2-nitro-4-(trifluoromethyl)benzene (56.8 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **3r** (29.1 mg, 41% yield) as a pale orange oil. The enantiomeric ratio was determined after reduction to the corresponding alcohol by adding 2 eq. of $NaBH_4$ to a 1:1=MeOH:DCM solution of the product (cooled at 0ºC through ice bath). The enantiomeric ratio of the corresponging alchol was measured to be 76:24 by UPC^2 analysis on a Daicel Chiralpak IA-3 column (eluent: 90:10 CO_2/IPA; flow rate 1.00 mL/min, λ = 250 nm. τ_{Major} = 2.90 min, τ_{Minor} = 3.12 min.

$[\alpha]_D^{20}$ = +69.8 (c = 0.5 g/100 mL, $CHCl_3$)

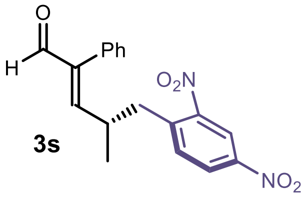
<u>^{1}H NMR</u> (500 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.11 – 8.08 (m, 1H), 7.70 – 7.63 (m, 1H), 7.34 – 7.21 (m, 4H), 6.67 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.50 (d, *J* = 10.4 Hz, 1H), 3.19 (dd, *J* = 12.8, 4.6 Hz, 1H), 3.14 – 3.06 (m, 1H), 3.02 (dd, *J* = 12.8, 9.3 Hz, 1H), 1.27 (d, *J* = 6.4 Hz, 3H).

<u>^{19}F NMR</u> (471 MHz, $CDCl_3$) δ -62.89.

<u>^{13}C NMR</u> (126 MHz, $CDCl_3$) δ 193.2, 157.2, 144.2, 138.3, 133.4, 131.9, 130.4 (q, $^4J_{C.F}$ = 34 Hz), 129.1 (q, $^3J_{C.F}$ = 4 Hz), 128.8 (d, $^2J_{C.F}$ = 80 Hz) 128.7 (2C), 128.2 (2C), 128.1, 122.7 (q, $^1J_{C.F}$ = 273 Hz), 122.2 (d, $^3J_{C.F}$ = 4 Hz), 39.4, 35.2, 20.4.

<u>HRMS (ESI)</u>: m/z calculated for $[C_{19}H_{16}F_3NO_3Na]^+$ $[M+Na]^+$: 386.0979; found: 386.0974.

Synthesis of *(S,E)*-5-(2,4-dinitrophenyl)-4-methyl-2-phenylpent-2-enal [(-)-3s]



3s

Synthesized according to the general procedure using phenylpent-2-enal **1a** (0.6 mmol, 96 mg, 3 equiv.), 1-(chloromethyl)-2,4-dinitrobenzene (52.2 mg, 0.2 mmol), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **3s** (34.7 mg, 51% yield) as an orange oil. The enantiomeric ratio was determined to be 76:24 by UPC^2 analysis on a Daicel Chiralpak IC column (eluent: 90:10 CO_2/IPA; flow rate 1.00 mL/min, λ = 255 nm. τ_{Major} = 5.35 min, τ_{Minor} = 5.4 min. $[\alpha]_D^{20}$ = -91.1 (c = 0.5 g/100 mL, $CHCl_3$).

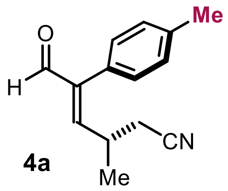
<u>^{1}H NMR</u> (500 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.67 (d, *J* = 2.3 Hz, 1H), 8.25 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.38 – 7.22 (m, 5H), 6.77 – 6.71 (m, 2H), 6.50 (d, *J* = 10.2 Hz, 1H), 3.22 (1/2 ABq, *J* = 12.7, 4.7 Hz, 1H), 3.18 – 3.10 (m, 1H), 3.07 (1/2 ABq, *J* = 12.7, 9.0 Hz, 1H), 1.29 (d, *J* = 6.4 Hz, 3H).

<u>^{13}C NMR</u> (126 MHz, $CDCl_3$) δ 193.0, 156.6, 149.2, 146.6, 144.2, 141.2, 133.7, 131.9, 128.7 (2C), 128.3 (2C), 128.2, 126.6, 120.3, 39.4, 35.1, 20.5.

<u>HRMS (ESI)</u>: m/z calculated for $[C_{18}H_{16}N_2O_5Na]^+$ $[M+Na]^+$: 363.0957; found: 363.0961.

E3. Scope of Enals

Synthesis of *(S,E)*-3-methyl-6-oxo-5-(p-tolyl)hex-4-enenitrile [(+)-4a]



4a

Synthesized according to the general procedure using *(E)*-2-(p-tolyl)pent-2-enal **A** (0.6 mmol, 104 mg, 3 equiv.), α-chloroacetonitrile **2a** (0.2 mmol, 12.6 µL), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 9:1) to afford product **4a** (17.1 mg, 40% yield) as a colorless oil. The enantiomeric ratio was determined to be 80:20 by UPC^2 analysis on a Daicel Chiralpak IC column (eluent: 90:10 CO_2/IPA; flow rate 1.00 mL/min, $\lambda = 250$ nm. $\tau_{Minor} = 4.0$ min, $\tau_{Major} = 4.2$ min.

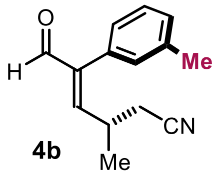
$[\alpha]_D^{20} = +45.0$ (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.25 (d, J = 7.7 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 6.51 (d, J = 10.3 Hz, 1H), 3.14 – 3.01 (m, 1H), 2.44 (d, J = 6.3 Hz, 2H), 2.40 (s, 3H), 1.28 (d, J = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.3, 153.8, 144.6, 138.4, 129.4 (2C), 128.9 (3C), 117.4, 30.6, 24.1, 21.3, 19.7.

HRMS (ESI): m/z calculated for $[C_{14}H_{15}NONa]^+$ $[M+Na]^+$: 236.1051; found: 236.1046.

Synthesis of *(R,E)*-3-methyl-6-oxo-5-(m-tolyl)hex-4-enenitrile [(-)-4b]



4b

Synthesized according to the general procedure using *(E)*-2-(m-tolyl)pent-2-enal **B** (0.6 mmol, 104 mg, 3 equiv.), α-chloroacetonitrile **2a** (0.2 mmol, 12.6 µL), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 9:1) to afford product **4b** (13.6 mg, 40% yield) as a colorless oil. The enantiomeric ratio was determined to be 80:20 by UPC^2 analysis on a Daicel Chiralpak IC column (eluent: 90:10 CO_2/MeCN; flow rate 1.00 mL/min, $\lambda = 225$ nm. $\tau_{Minor} = 3.1$ min, $\tau_{Major} = 3.2$ min.

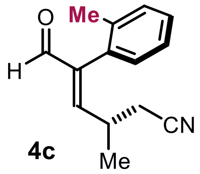
$[\alpha]_D^{20} = -19.7$ (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.37 – 7.31 (m, 1H), 7.24 – 7.20 (m, 1H), 6.98 – 6.92 (m, 2H), 6.52 (d, J = 10.3 Hz, 1H), 3.11 – 2.99 (m, 1H), 2.45 (d, J = 6.3 Hz, 2H), 2.42 – 2.36 (m, 3H), 1.29 (d, J = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 153.8, 144.9, 138.4, 131.9, 129.6, 129.3, 128.5, 126.7, 126.0, 117.4, 30.6, 24.1, 19.7.

HRMS (ESI): m/z calculated for $[C_{14}H_{15}NONa]^+$ $[M+Na]^+$: 236.1051; found: 236.1041.

Synthesis of *(R,E)*- 3-methyl-6-oxo-5-(o-tolyl)hex-4-enenitrile [(+ o -)-5fa]



4c

Synthesized according to the general procedure using *(E)*-2-(o-tolyl)pent-2-enal **C** (0.6 mmol, 104 mg, 3 equiv.), α-chloroacetonitrile **2a** (0.2 mmol, 12.6 µL), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 9:1) to afford product **4c** as a mixture 1:1 of the *two rotamers* (21.3 mg, 50% yield) as a colorless oil. The enantiomeric ratio of the product was determined to be 80:20 for both rotamers by UPC^2 analysis on a Daicel

Chiralpak IC column (eluent: 90:10 CO_2/MeCN; flow rate 1.00 mL/min, λ = 225 nm. $\tau Minor_{rot1}$ = 3.2 min, $\tau Major_{rot1}$ = 3.4 min; $\tau Minor_{rot2}$ = 3.7 min, $\tau Major_{rot2}$ = 3.9 min.

$[\alpha]_D^{20}$ = -44.1 (c = 0.5 g/100 mL, $CHCl_3$)

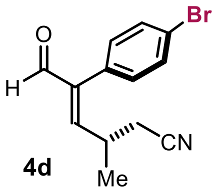
<u>^{1}H NMR</u> (500 MHz, $CDCl_3$, 25 °C) δ 9.70 – 9.66 (m, $1H_{rot1} + 1H_{rot2}$), 7.35 – 7.17 (m, $3H_{rot1} + 3H_{rot2}$), 7.02 (d, J = 7.4 Hz, $1H_{rot1}$), 6.94 (d, J = 7.5 Hz, $1H_{rot2}$), 6.69 – 6.63 (m, $1H_{rot1} + 1H_{rot2}$), 2.85 – 2.74 (m, $1H_{rot1} + 1H_{rot2}$), 2.45 (d, J = 6.3 Hz, $2H_{rot1}$), 2.39 (d, J = 6.3 Hz, $2H_{rot2}$), 2.16 (s, $3H_{rot1}$), 2.12 (s, $3H_{rot2}$), 1.28 (d, J = 6.8 Hz, $3H_{rot1}$), 1.20 (d, J = 6.7 Hz, $3H_{rot2}$).

<u>^{1}H NMR</u> (500 MHz, $CDCl_3$, 60 °C) δ 9.67 (s, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.18 (m, 1H), 7.03 – 6.93 (m, 1H), 6.63 (d, J = 9.9 Hz, 1H), 2.86 – 2.74 (m, 1H), 2.44 – 2.36 (m, 2H), 2.15 (s, 3H), 1.29 – 1.19 (m, 3H).

<u>^{13}C NMR</u> (101 MHz, $CDCl_3$) [signals of both rotamers] δ 192.7, 192.6, 154.3, 154.2, 145.5 (2C), 136.4, 136.1, 132.0 (2C), 130.5, 130.3, 129.2, 129.0, 128.8 (2C) 126.1, 126.0, 117.4 (2C), 31.0, 30.9, 24.1, 23.7, 19.9, 19.8, 19.7, 19.6.

<u>HRMS (ESI)</u>: m/z calculated for $[C_{14}H_{15}NOH]^+$ $[M+H]^+$: 214.1231; found: 214.1224.

Synthesis of *(R,E)*-5-(4-methoxyphenyl)-3-methyl-6-oxohex-4-enenitrile [(-)-4d]



4d

Synthesized according to the general procedure using *(E)*-2-(4-methoxyphenyl)pent-2-enal **D** (0.6 mmol, 114 mg, 3 equiv.), α-chloroacetonitrile **2a** (0.2 mmol, 12.6 µL), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 7:3) to afford product **4d** (28.4 mg, 62% yield) as a colorless oil. The enantiomeric ratio was determined to be 80:20 by UPC^2 analysis on a Daicel Chiralpak IC column (eluent: 85:15 CO_2/IPA; flow rate 1.00 mL/min, λ = 250 nm. τ_{Minor} = 4.3 min, τ_{Major} = 4.5 min.

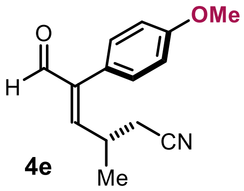
$[\alpha]_D^{20}$ = -96.1 (c = 0.5 g/100 mL, $CHCl_3$)

<u>^{1}H NMR</u> (500 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.10 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 6.49 (d, J = 10.3 Hz, 1H), 3.85 (s, 3H), 3.15 – 3.05 (m, 1H), 2.45 (d, J = 6.3 Hz, 2H), 1.29 (d, J = 6.8 Hz, 3H).

<u>^{13}C NMR</u> (126 MHz, $CDCl_3$) δ 193.4, 159.7, 153.8, 144.2, 130.3 (2C), 123.9, 117.4, 114.2 (2C), 55.3, 30.7, 24.1, 19.7.

<u>HRMS (ESI)</u>: m/z calculated for $[C_{14}H_{15}NO_2Na]^+$ $[M+Na]^+$: 252.1000; found: 252.0995.

Synthesis of *(S,E)*-5-(4-bromophenyl)-3-methyl-6-oxohex-4-enenitrile [(-)-4e]



4e

Synthesized according to the general procedure using *(E)*-2-(4-bromophenyl)pent-2-enal **E** (0.6 mmol, 143 mg, 3 equiv.), α-chloroacetonitrile **2a** (0.2 mmol, 12.6 µL), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **4e** (20.0 mg, 36% yield) as a colorless oil. The enantiomeric ratio was determined to be 82:18 by UPC^2 analysis on a Daicel Chiralpak IC column (eluent: 80:20 CO_2/IPA; flow rate 1.00 mL/min, λ = 250 nm. τ_{Minor} = 4.1 min, τ_{Major} = 4.3 min.

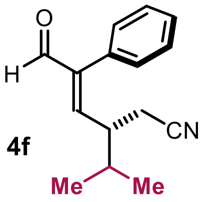
$[\alpha]_D^{20}$ = -33.9 (c = 0.5 g/100 mL, $CHCl_3$)

<u>^{1}H NMR</u> (500 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 6.56 (d, J = 10.4 Hz, 1H), 3.13 – 2.93 (m, 1H), 2.46 (d, J = 6.0 Hz, 2H), 1.28 (d, J = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.5, 154.4, 143.8, 131.9 (2C), 130.8 (2C), 130.7, 123.0, 117.2, 30.8, 24.1, 19.7.

HRMS (ESI): m/z calculated for $[C_{13}H_{12}BrNONa]^+$ $[M+Na]^+$: 299.9999; found: 299.9987.

Synthesis of *(S,E)*-3-isopropyl-6-oxo-5-phenylhex-4-enenitrile [(+)-4f]



4f

Synthesized according to the general procedure using *(E)*-5-methyl-2-phenylhex-2-enal (0.6 mmol, 113 mg, 3 equiv.), α-chloroacetonitrile **2a** (0.2 mmol, 12.6 μL), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 μL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **4f** (19.1 mg, 42% yield) as a colorless oil. The enantiomeric ratio was determined to be 79:21 by UPC^2 analysis on a Daicel Chiralpak IB column (eluent: 90:10 CO_2/MeCN; flow rate 1 mL/min, $\lambda = 320$ nm. $\tau_{Minor} = 2.6$ min, $\tau_{Major} = 2.7$ min.

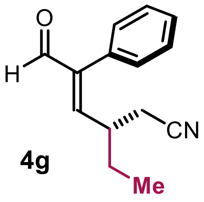
$[\alpha]_D^{20} = +35.3$ (c = 1 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.55 – 7.31 (m, 3H), 7.20 – 7.13 (m, 2H), 6.59 (d, *J* = 10.8 Hz, 1H), 2.75 – 2.62 (m, 1H), 2.52 – 2.49 (m, 2H), 1.96 – 1.83 (m, 1H), 0.95 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 152.3, 146.8, 132.1, 129.2 (2C), 128.6 (2C), 128.4, 117.6, 41.7, 31.4, 20.7, 20.1, 19.6.

HRMS (ESI): m/z calculated for $[C_{15}H_{17}NONa]^+$ $[M+Na]^+$: 250.1208; found: 250.1202.

Synthesis of *(S,E)*-3-ethyl-6-oxo-5-phenylhex-4-enenitrile [(+)-4g]



4g

Synthesized according to the general procedure using *(E)*- 2-phenylhex-2-enal **F** (0.6 mmol, 104 mg, 3 equiv.), α-chloroacetonitrile **2a** (0.2 mmol, 12.6 μL), aminocatalyst **B** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 μL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford product **4g** (12.8 mg, 30% yield) as a colorless oil. The enantiomeric ratio of the product was determined to be 79:21 by UPC^2 analysis on a Daicel Chiralpak IB column (eluent: 90:10 CO_2/MeCN; flow rate 1.00 mL/min, $\lambda = 250$ nm. $\tau_{Minor} = 2.5$ min, $\tau_{Major} = 2.6$ min.

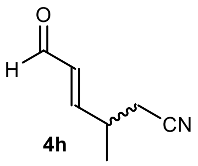
$[\alpha]_D^{20} = +12.1$ (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.48 – 7.38 (m, 3H), 7.20 – 7.13 (m, 2H), 6.51 (d, *J* = 10.6 Hz, 1H), 2.89 – 2.77 (m, 1H), 2.47 (d, *J* = 6.2 Hz, 2H), 1.75 – 1.59 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.89, 153.20, 146.22, 132.00, 129.08, 128.55, 128.38, 117.38, 37.03, 27.08, 22.29, 11.39.

HRMS (ESI): m/z calculated for $[C_{14}H_{15}NOH]^+$ $[M+H]^+$: 214.1226; found: 214.1226.

Synthesis of Rac-(E)-6-methyl-3-(4-oxobut-2-en-2-yl)hept-5-enenitrile [4h]



4h

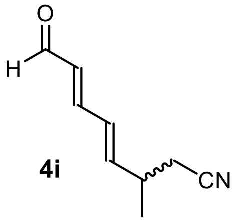
Synthesized according to the general procedure using *trans*-2-pentenal (0.6 mmol, 50.5 mg, 3 equiv.), α-chloroacetonitrile **2a** (0.2 mmol, 12.6 μL), aminocatalyst **D** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 μL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 7:3) to afford product **4h** (14.5 mg, 59% yield) as a colorless oil. After derivatization with 2,4-dinitrophenylhydrazine, the enantiomeric ratio of the product was determined to be 55:45 by UPC^2 analysis on a Daicel Chiralpak ID column (eluent: 88:12 CO_2/MeOH; flow rate 1.00 mL/min, λ = 250 nm. τ_{Minor} = 5.98 min, τ_{Major} = 6.14 min.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (d, *J* = 7.6 Hz, 1H), 6.76 (dd, *J* = 15.8, 6.9 Hz, 1H), 6.18 (ddd, *J* = 15.8, 7.6, 1.3 Hz, 1H), 2.89 (m, 1H), 2.51 (dd, *J* = 6.5, 1.4 Hz, 2H), 1.31 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.15, 156.78, 132.66, 117.27, 33.44, 23.64, 18.63.

HRMS (ESI): m/z calculated for $[C_7H_{10}NO]^+$ $[M+H]^+$: 124.0762; found: 124.0757.

Synthesis of Rac-(4E,6E)-3-methyl-8-oxoocta-4,6-dienenitrile



4i

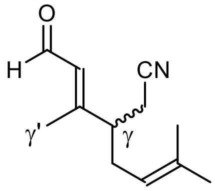
Synthesized according to the general procedure using *2,4-Heptadienal* (0.6 mmol, 66 mg, 3 equiv.), α-chloroacetonitrile **2a** (0.2 mmol, 12.6 µL), aminocatalyst **D** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 85:15) to afford product **4i** (13 mg, 43% yield) as a colorless oil. After derivatization with 2,4-dinitrophenylhydrazine, the enantiomeric ratio of the product was determined to be 56:44 by UPC^2 analysis on a Daicel Chiralpak IA column (eluent: 95:5 CO_2/MeOH; flow rate 1.00 mL/min, λ = 250 nm. τ_{Minor} = 7.09 min, τ_{Major} = 7.64 min.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57 (d, *J* = 7.9 Hz, 1H), 7.13 – 7.02 (m, 1H), 6.47 – 6.34 (m, 1H), 6.17 (dt, *J* = 15.2, 7.5 Hz, 2H), 2.77 (m, 1H), 2.45 (d, *J* = 6.5 Hz, 2H), 1.27 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.52, 150.82, 145.63, 132.03, 129.00, 117.67, 33.97, 24.28, 19.15.

HRMS (ESI): m/z calculated for $[C_9H_{10}NO]^+$ $[M]^+$: 148.0762; found: 148.0757.

Synthesis of Rac-(E)-6-methyl-3-(4-oxobut-2-en-2-yl)hept-5-enenitrile [4j]



4j

Synthesized according to the general procedure using *citral* (0.6 mmol, 91 mg, 3 equiv.), α-chloroacetonitrile **2a** (0.2 mmol, 12.6 µL), aminocatalyst **D** (0.04 mmol, 25.6 mg, 0.2 equiv.), dithiocarbamate catalyst **G** (0.04 mmol, 12.4 mg, 0.2 equiv.) and 2,6-lutidine (0.24 mmol, 25.5 µL, 1.2 equiv.). The reaction produced a γ to γ' regioisomeric mixture in a 83:17 ratio. The crude mixture was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford exclusively the regioisomeric product **4j** (21 mg, 55% yield) as a yellowish oil. After derivatization with 2,4-dinitrophenylhydrazine, the enantiomeric ratio of the product was determined to be 52:48 by UPC^2 analysis on a Daicel Chiralpak IG column (eluent: 85:15 CO_2/IPA; flow rate 1.00 mL/min, λ = 250 nm. τ_{Minor} = 5.54 min, τ_{Major} = 5.77 min.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (d, J = 7.5 Hz, 1H), 5.92 (d, J = 7.5 Hz, 1H), 5.00 – 4.94 (m, 1H), 2.62 – 2.41 (m, 3H), 2.29 (t, J = 6.9 Hz, 2H), 2.19 (d, J = 1.2 Hz, 3H), 1.70 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.79, 160.77, 136.13, 128.59, 119.21, 117.92, 45.90, 31.09, 25.90, 20.78, 18.11, 15.57.

HRMS (ESI): m/z calculated for $[C_{15}H_{17}NONa]^+$ $[M+Na]^+$: 146.0581; found: 146.0585.

E4. Scale-up Reaction

E4.1 Experimental Setup

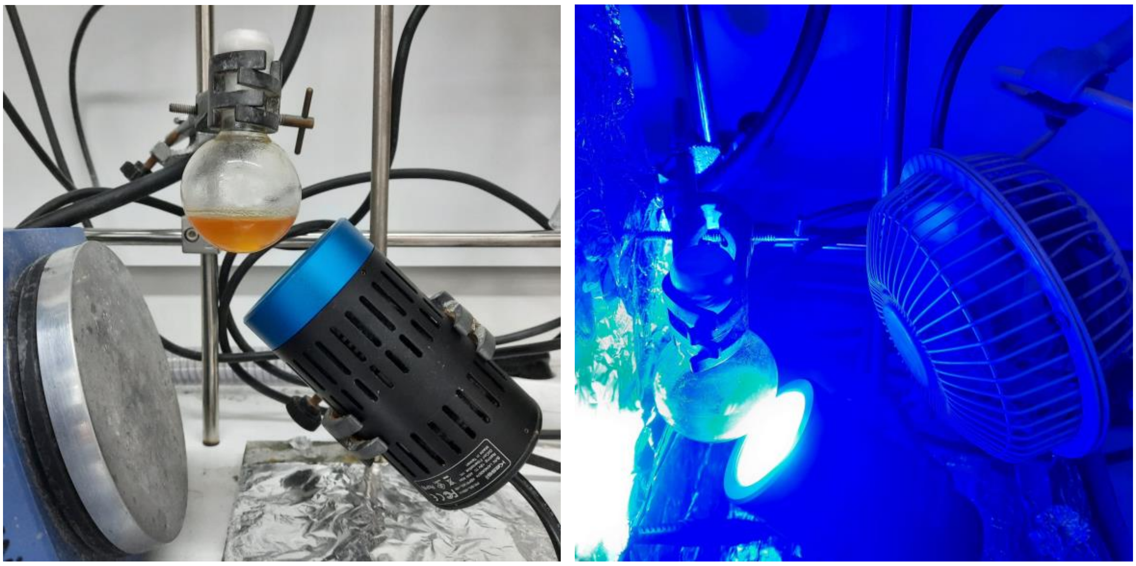


Figure S6: Setup used for the scaled-up reaction

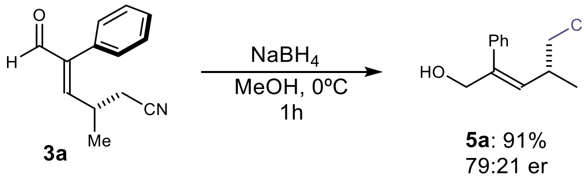
The experimental setup for the large-scale reaction consisted of a 50 mL round-bottom flask placed on a stirring plate. The light source was a 456 nm Kessil lamp placed under the reactor; to avoid over heating, the reactor was cooled using a cooling fan placed on the side of the reactor as illustrated in Figure S6.

E4.2 General Procedure for the large scale reaction

In a 50 mL round-bottom flask charged with a stirring bar, the aminocatalyst **B** (1 mmol, 640 mg, 0.2 eq.), THF (3.5 mL) and phenylpent-2-enal **1a** (15 mmol, 2.40 mL, 3 equiv.) were added sequentially. The reaction was stirred for 5 minutes before the addition of 2,6-lutidine (6 mmol, 395 μL, 1.2 equiv.) and chloroacetonitrile **2a** (5 mmol, 317 μL, 1 equiv.). Finally, dithiocarbamate catalyst **G** (1 mmol, 310 mg, 0.2 eq.) was added and the reactor was closed with a rubber septum. The solution was degassed through argon bubbling for 5 minutes while stirring and then the reactor capped with a septum and sealed with parafilm. A 456nm Kessil lamp was placed approximatively 3 cm away from the reactor and switched on at 100% intensity. The solution was irradiated under vigorous stirring overnight. After 20 hours, the lamp was turned off and the solvent was removed through rotary evaporation. The product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) to afford the product **5a** as a pale-orange oil in a 67% yield (average yield on 2 different runs). The enantiomeric ratio of the product was determined to be 80:20 by UPC^2 analysis on a Daicel Chiralpak IA-3 column (eluent: CO_2/IPA = 90:10; flow rate 1 mL/min, λ = 300 nm. τMajor = 3.54 min, τMinor = 3.66 min.

E5. Derivatization of Products

E5.1 Aldehyde Reduction



3a

5a: 91%
79:21 er

In a 10 mL round bottom flask charged with a magnetic stirring bar, substrate **3a** (60.0 mg, 0.3 mmol, 1 equiv) was dissolved in MeOH (0.5M). The solution was placed in an ice bath and cooled to 0°C before the addition of $NaBH_4$ (34.0 mg, 0.9 mmol, 3 equiv). The reaction was stirred at 0°C for 1 hour and then removed from the ice bath. Distilled water (2 mL) was then slowly added to the solution while stirring. The organic phase was extracted two times with EtOAc and dried over anhydrous magnesium sulfate. After filtration, the solution was concentrated under vacuum to afford the title compound **5a** in 91% yield as pale-yellow oil. The enantiomeric ratio of the product was determined to be 79:21 by UPC^2 analysis on a Daicel Chiralpak IA-3 column (eluent: 80:20 CO_2/IPA; flow rate 1.00 mL/min, λ = 220 nm. τ_{Major} = 3.5 min, τ_{Mjnor} = 3.6 min.

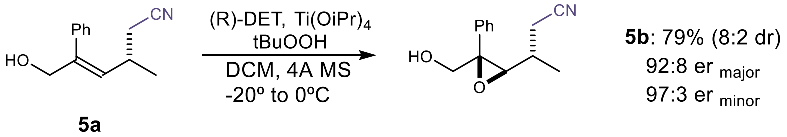
$[\alpha]_D^{20}$ = -17.2 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.33 (m, 1H), 7.19 (m, 2H), 5.58 (d, *J* = 10.1 Hz, 1H), 4.31 (d, *J* = 1.4 Hz, 2H), 2.65 (m, 1H), 2.27 (d, *J* = 6.6 Hz, 2H), 1.13 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.79, 137.92, 129.19, 128.87, 128.53, 127.90, 118.60, 67.60, 30.15, 25.17, 20.80

HRMS (ESI): m/z calculated for $[C_{14}H_{16}NO]^+$ $[M+H]^+$: 202.1232; found: 202.1226.

E5.2 Sharpless Epoxidation



5a

5b: 79% (8:2 dr)
92:8 er major
97:3 er minor

Diethyl *L*-(+)-tartrate (7.9 μL, 0.046 mmol) and titanium tetraisopropoxide (12 μL, 0.04 mmol) were added sequentially to a mixture of powdered activated 4 Å molecular sieves and dichloromethane (200 mL) at 0 °C with stirring. The reaction mixture was cooled to -20 °C, *tert*-butyl hydroperoxide (6 M in hexane, 87 μL, 0.520 mmol) was added dropwise over 0.2 h, and the resulting mixture was stirred at -20 °C for 1 h. A 1.1M solution of **5a** (40.25 mg, 0.200 mmol) in dry DCM was then added dropwise over 0.2 h. After stirring for 15 h at -20 °C, the reaction mixture was poured into 7 mL of a freshly prepared ferrous sulfate solution (66 g of $FeSO_4$, $7H_2O$ and 22 g of citric acid in 200 mL of H_2O) at -20 °C and stirred for 1 h. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layer was dried, filtered, and concentrated in vacuo. To the residue in Et_2O (300 mL) was added 30% NaOH (3 mL), and the resultant mixture was stirred at 0 °C for 1 h. The two phases were separated, and the aqueous phase was extracted twice with Et_2O. The combined organic phases were washed with brine, dried, filtered, and then concentrated in vacuo. The product was purified by Flash Chromatography on silica gel (7:3 Hex:EtOAc) to afford the title compound **5b** as a colorless oil in 79% yield (8:2 mixture of both diastereoisomers). The enantiomeric ratio of the two diastereoisomers of the product was determined to be 97:3 and 92:8 by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: 80:20 CO_2/IPA; flow rate 1.00 mL/min, λ = 250 nm $\tau Major_{dias1}$ = 4.13 min, $\tau Minor_{dias1}$ = 4.06 min; $\tau Minor_{dias2}$ = 4.32 min, $\tau Major_{dias2}$ = 4.40 min.

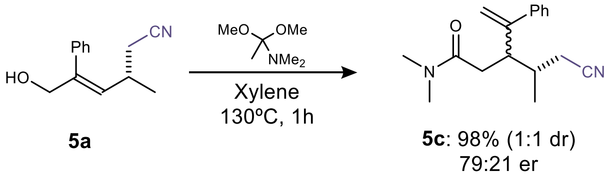
$[\alpha]_D^{20}$ = +40.9 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 – 7.32 (m, 10H *diast1* + *diast2*), 4.00 (d, J = 1.7 Hz, 1H *diast1*), 3.97 (d, J = 1.3 Hz, 1H *diast2*), 3.26 (m, 4H *diast1* + *diast2*) 1.43 – 1.24 (m, 2H *diast1* + *diast2*) 1.21 (d, J = 6.7 Hz, 3H *diast1*), 1.00 (d, J = 6.9 Hz, 3H *diast2*).

^{13}C NMR (126 MHz, CDCl$_3$) δ 134.78, 134.75, 128.92, 128.59, 128.56, 128.34, 126.66, 126.55, 117.90, 117.50, 67.55, 66.88, 66.63, 64.13, 63.65, 63.13, 29.97, 29.02, 22.12, 20.75, 17.05, 15.00.

HRMS (ESI): m/z calculated for [$C_{20}H_{23}N_2$] [M+H]$^+$: 291.1861; found: 291.1856

E5.3 Eshenmoser-Claisen Rearrangement



In an oven dried Schlenk tube charged with a magnetic stirring bar, alchol **5a** (40 mg, 0.2 mmol, 1 eq.) was dissolved in xylene (0.3M). *N,N*-dimethylacetamide dimethyl acetal (88 μL, 0.6 mmol, 3 equiv.) was added and the solution was then stirred for 1 hour at 130 °C. The starting material was totally consumed (checked by TLC) and the reaction was removed from the oil bath. After the reaction cooled down, the solution was concentrated through rotary evaporation and the product purified by flash chromatography on silica gel (1:1 Hex:EtOAc) to afford the title compound **5c** as a brownish oil in quantitative yield (53 mg). The enantiomeric ratio was determined to be 79:21 by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: 90:10 CO$_2$/EtOH; flow rate 1.00 mL/min, λ = 250 nm. τMajor$_{\text{dias1}}$ = 6.85 min, τMinor$_{\text{dias1}}$ = 7.12 min; τMinor$_{\text{dias2}}$ = 7.84 min, τMajor$_{\text{dias2}}$ = 8.35 min.

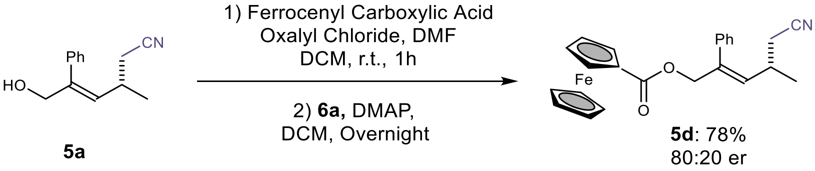
$[\alpha]_D^{20}$ = -88.3 (c = 0.5 g/100 mL, CHCl$_3$)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.48 (m, 4H *diast1* + *diast2*), 7.34 (m, 6H *diast1* + *diast2*), 5.38 (s, 1H, *diast1*), 5.34 (s, 1H, *diast2*), 5.06 (s, 1H, *diast1*), 4.99 (s, 1H, *diast2*), 3.47 (m, 1H, *diast2*), 3.37 (m, 1H, *diast1*), 3.07 (s, 3H, *diast2*), 3.03 (s, 3H, *diast1*), 2.97 (s, 3H, *diast2*), 2.94 (s, 3H, *diast1*),2.80-2.65 (m, 2H *diast1* + *diast2*), 2.60-2.00 (m, 8H *diast1* + *diast2*), 1.13 (d, *J* = 6.7 Hz, 3H, *diast2*), 1.09 (d, *J* = 6.8 Hz, 3H, *diast1*).

^{13}C NMR (126 MHz, CDCl$_3$) δ 171.09, 170.99, 150.88, 150.19, 142.76, 142.39, 128.56, 128.53, 127.80, 126.89, 126.88, 119.26, 119.16, 113.72, 113.65, 44.48, 44.13, 37.39, 37.35, 35.69, 34.45, 34.26, 33.90, 33.37, 22.97, 22.00, 17.17, 16.98.

HRMS (ESI): m/z calculated for [$C_{17}H_{23}N_2O$] [M+H]$^+$: 271.1810; found: 271.1805

E5.4 Esterification



To a suspension of ferrocenecarboxylic acid (104 mg, 0.450 mmol, 1.4 equiv.) in DCM (1 mL) were added oxalyl chloride (0.036 mL, 0.420 mmol, 1.3 equiv.) and three drops of dry DMF at 0 C. After the gas evolution ceased and the reaction mixture turned into a clear solution, it was stirred for 0.5 h at ambient temperature. Next, a solution of **5a** (65 mg, 0.32 mmol, 1.0 equiv.) and DMAP (106 mg, 0.870 mmol, 2.7 equiv.) in DCM (1 mL) was added and the reaction mixture was stirred for 16 h at ambient temperature. The reaction mixture was quenched by adding a small amount of silica gel and concentrating to dryness. The crude product was purified by flash chromatography on silica gel (70:30 Hexane:EtOAc) to afford the title product **5d** as an orange oil in 78% yield. The enantiomeric ratio was determined to be 79:21 by UPC^2 analysis on a Daicel Chiralpak IB column (eluent: 85:15 CO_2/MeCN; flow rate 1.00 mL/min, λ = 250 nm. τ_{Minor} = 3.5 min, τ_{Major} = 3.7 min.

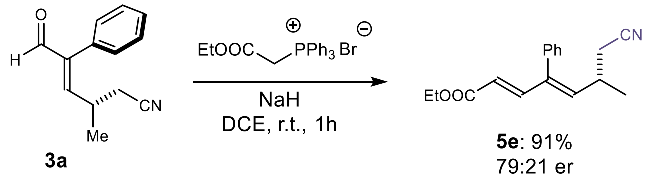
$[\alpha]_D^{20}$ = -54.7 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (m, 2H), 7.34 (m, 1H), 7.28 (m, 2H), 5.69 (d, *J* = 10.2 Hz, 1H), 4.89 (qd, *J* = 13.0, 1.1 Hz, 2H), 4.74 (bs, 2H), 4.28 (bs, 2H), 2.72 (m, 1H), 2.31 (d, *J* = 6.5 Hz, 2H), 1.16 (d, *J* = 6.7 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.40, 138.57, 137.60, 132.30, 128.75, 128.45, 127.95, 118.29, 71.62, 70.35, 69.98, 68.12, 30.18, 24.97, 20.55

HRMS (ESI): m/z calculated for $[C_{24}H_{23}NNaO_2Fe]^+$ $[M+Na]^+$: 436.0975; found: 436.0970

E5.5 Wittig Olefination



In an oven dried Schlenk tube, the Wittig reagent (86 mg, 0.2 mmol, 2 equiv.) was dissolved in DCE (0.1M respect to the substrate). Sodium hydride (60% in mineral oil) (5 mg, 0.12 mmol, 1.2 equiv.) was subsequently added to the solution which was stirred for additional 10 minutes. The substrate (20 mg, 0.1 mmol, 1 equiv.) was added and the reaction was stirred 1h. After total consumption of the starting material (checked by TLC), the reaction was quenched with water and the organic phase was extracted twice with EtOAc, dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation. The product was purified by flash chromatography on silica gel (85:15 Hex:EtOAc) to afford the title compound **5e** as a brownish oil in 93% yield. The enantiomeric ratio was determined to be 79:21 by UPC^2 analysis on a Daicel Chiralpak IG column (eluent: 90:10 CO_2/IPA; flow rate 1.00 mL/min, λ = 250 nm. $\tau Minor_{rot1}$ = 5.3 min, $\tau Major_{rot1}$ = 4.0 min.

$[\alpha]_D^{20}$ = +65.9 (c = 0.5 g/100 mL, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 15.6 Hz 1H), 7.41 (m, 2H), 7.36 (m, 1H), 7.11 (m, 2H), 5.92 (d, *J* = 10.2 Hz, 2H), 5.40 (d, *J* = 15.6 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.59 (m, 1H), 2.29 (d, *J* = 6.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.03, 147.49, 141.78, 141.40, 135.82, 128.96, 128.88, 128.02, 121.47, 117.97, 60.48, 30.99, 24.56, 20.16, 14.35.

HRMS (ESI): m/z calculated for $[C_{17}H_{19}NO_2Na]^+$ $[M+Na]^+$: 292.1313; found: 292.1883

E6. Unsuccessful Substrates

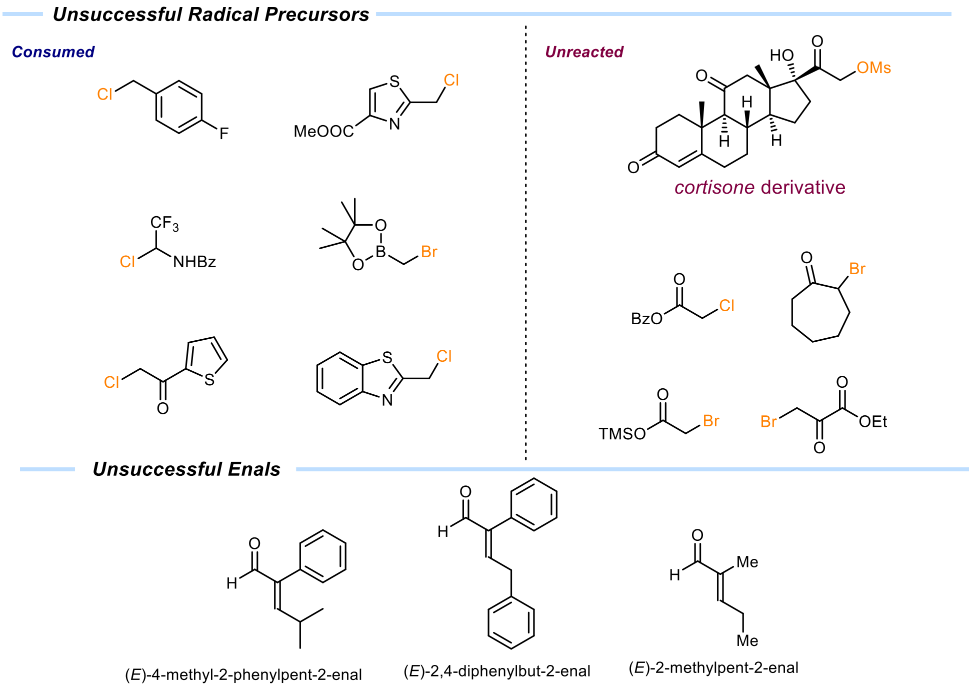


Figure S7: Survey of substrates which failed to afford the expected products under optimal conditions.

Figure S7 highlights a survey of radical precursors which failed to give the expected products. Radical precursors that were consumed under standard conditions but were not trapped by the dienamine intermediate (probably due to the less electrophilic character of the generated radicals) are shown on the left panel. The right panel displays substrates that remained unreacted and were not consumed under standard conditions.

As for the enals (lower panel), (*E*)-4-methyl-2-phenylpent-2-enal did not react probably because of a difficult dienamine formation. (*E*)-2,4-diphenylbut-2-enal and (*E*)-2-methylpent-2-enal also did not afford the expected products. Despite our efforts to rationalise their poor performance, we could not find a satisfactory answer to their failure as substrates.

E7. Determination of the Absolute Configuration

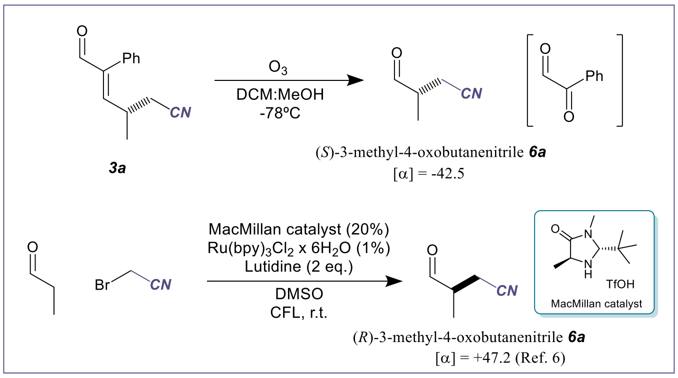
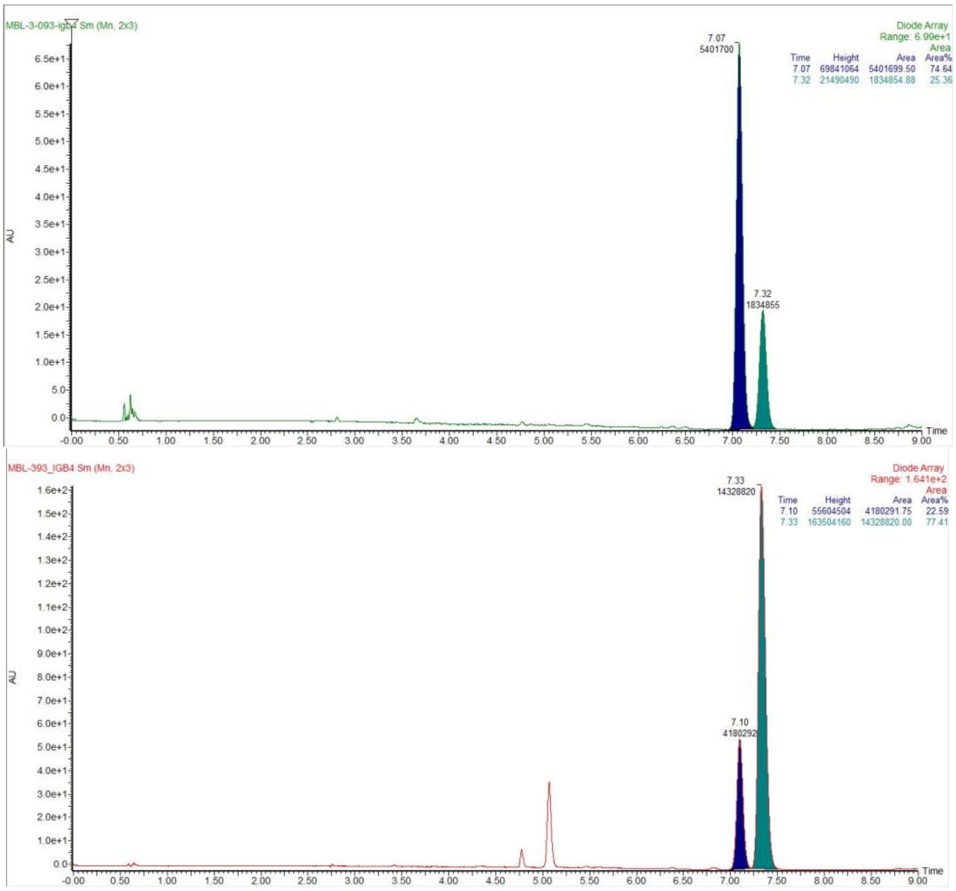


Figure S8: Determination of the absolute configuration by correlation.

The absolute configuration was obtained by correlation with a known compound. The model product **3a** was subjected to ozonolysis to achieve the corresponding α-branched aldehyde **6a** which optical rotation was measured to be $[\alpha]_D^{20}$ = -42.5 (c = 1 g/100 mL, $CHCl_3$). The same compound was obtained subjecting propanal to conditions reported by MacMillan et al. for the asymmetric α-cyanomethylation of aldehydes.[6] Although this very compound (**6a**) was not synthetized by MacMillan, the same reaction using octanal afforded the corresponding product with a (*R*) absolute configuration. Assuming a consistent stereochemical outcome for the alkylation of propanal, we prepared an authentic sample of **6a** applying the MacMillan conditions; the optical rotation was measured to be $[\alpha]_D^{20}$ = +47.2 (c = 1 g/100 mL, $CHCl_3$).

Because of the opposite optical rotation values, we therefore assigned an (*S*) absolute configuration to the stereocenter produced with our protocol. That the opposite enantiomers of **6a** were obtained using the two procedures was also corroborated by UPC^2 analysis, as shown by the chromatograms reported below:



Time	Height	Area	Area%
7.07	69841064	5401699.50	74.64
7.32	21490490	1834854.88	25.36

Time	Height	Area	Area%
7.10	55604504	4180291.75	22.59
7.33	163504160	14328820.00	77.41

Figure S9: *Upper chromatogram*: **6a** synthetized through ozonolysis of **3a**, prepared according to the presented γ-alkylation protocol of enals. *Lower chromatogram*: **6a** synthetized t according to the MacMillan protocol (Ref. 5).

E8. Quantum Yield Measurement

A ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in the Handbook of Photochemistry[7]. The ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed.

The following solutions were prepared and stored in a dark laboratory (red light):

1. Potassium ferrioxalate solution: 294.8 mg of potassium ferrioxalate (commercially available from Alfa Aesar) and 139 µL of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water (HPLC grade).

2. Phenanthroline solution: 0.2% by weight of 1,10-phenanthroline in water (100 mg in 50 mL volumetric flask).
3. Buffer solution: 2.47 g of NaOAc and 0.5 mL of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water (HPLC grade).

The actinometry measurements were done as follows:

1. 1 mL of the actinometer solution was added to a vial. The vial was placed in the reactor.
2. The solution was irradiated at 460 nm (irradiance 238 mW/cm^2). This procedure was repeated 4 times, quenching the solutions after different time intervals: 1 sec, 2 sec, 4 sec, and 6 sec. Then a model reaction was set following the general procedure (See paragraph E2.1), placed in the irradiation set up and it has been irradiated for 25 minutes. This procedure has been performed other two times with different irradiation times (30 min and 35 min).
3. After irradiation, the actinometer solutions were removed and placed in a 10 mL volumetric flask containing 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution. These flasks were filled to the mark with water (HPLC grade).
4. The UV-Vis spectra of the complexed actinometer samples were recorded for each time interval. The absorbance of the complexed actinometer solution was monitored at 510 nm.

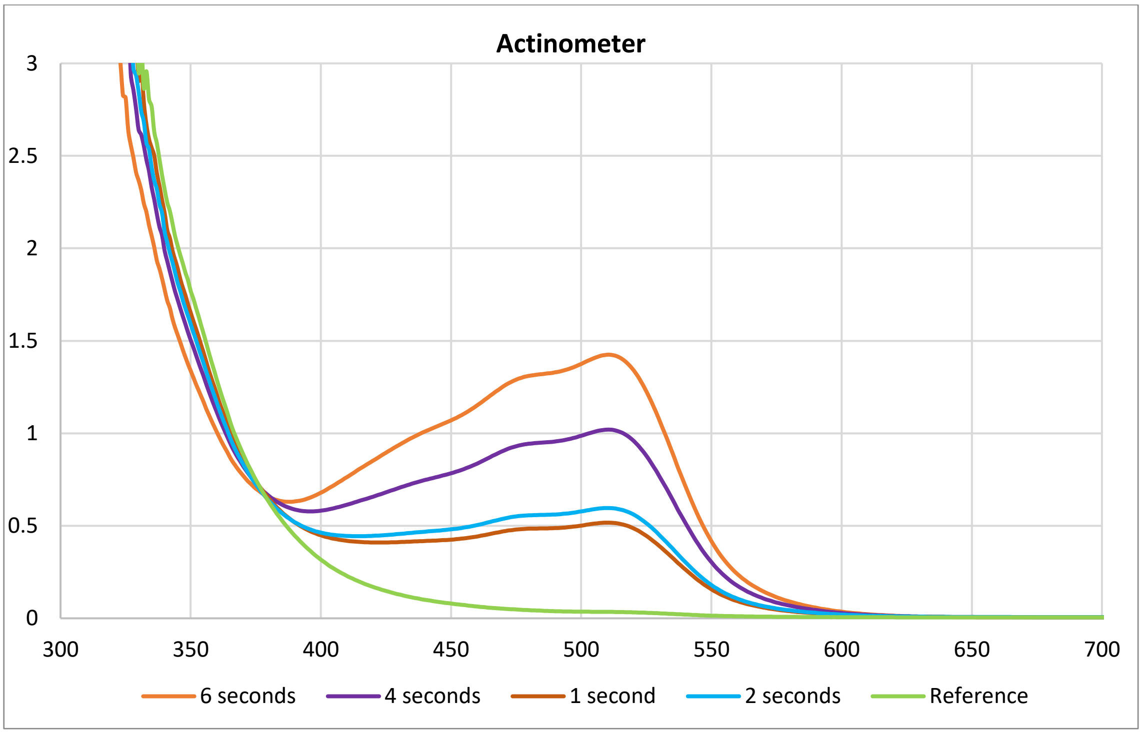


Figure S10: Actinometry

The moles of Fe^{2+} formed for each sample is determined using Beers' Law (Eq. 1) :

$$\text{Mols of Fe(II)} = V1 \times V3 \times \Delta A(510\ \text{nm})/10^3 \times V2 \times l \times \varepsilon(510\ nm)\ \text{(Eq. 1)}$$

where V1 is the irradiated volume (1 mL), V2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V3 is the final volume after complexation with phenanthroline (10 mL), l is the optical path-length of the irradiation cell (1 cm), ΔA(510 nm) is the optical difference in absorbance between the irradiated solution and the one stored in the dark, ε(510 nm) is the extinction coefficient the complex $Fe(phen)_3^{2+}$ at 510 nm (11100 L mol-1 cm1). The moles of Fe2+ formed (x) are plotted as a function of time (t). The slope of this line was correlated to the moles of incident photons by unit of time (q0 n,p) by the use of the following Equation 2:

$$\Phi(\lambda) = dx/dt\ qn,p\ 0\ [1-10-A(\lambda)\ ]\ \text{(Eq. 2)}$$

where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe2+ at 458 nm is 1.1,[8] [1-$10^{-A(\lambda)}$] is the ratio of absorbed photons by the solution, and A(λ) is the absorbance of the actinometer at the wavelength used to carry out the experiments (460 nm). The absorbance at 460 nm A(460) was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in a 10 mm path quartz cuvette, obtaining an absorbance of 0.14. $q^0_{n,p}$, the photon flux was determined to be 1.12x10^{-6}.

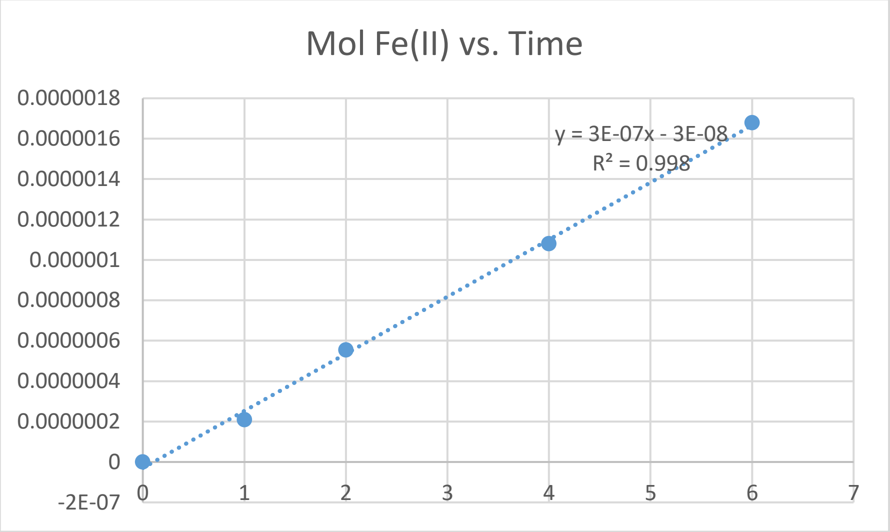


Figure S11: Plot of mols of Fe2+ formed vs irradiation time. Slope of the line correlates to the moles of incident photons by unit of time.

The moles of product 3a formed for the model reaction were determined by GC measurement (FID detector) using 1,3,5-trimethoxybenzene as internal standard. The moles of product per unit of time are related to the number of photons absorbed. The photons absorbed are correlated to the number of incident photons by the use of Equation 1. According to this, if we plot the moles of product (x) versus the moles of incident photons (q0 n,p·dt), the slope is equal to: Φ·(1-10-A(460 nm)), where Φ is the quantum yield to be determined and A(460 nm) is the absorption of the reaction under study. A (460 nm) was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in 10 mm path quartz. An absorbance of 1.12 was determined for the model reaction mixture.

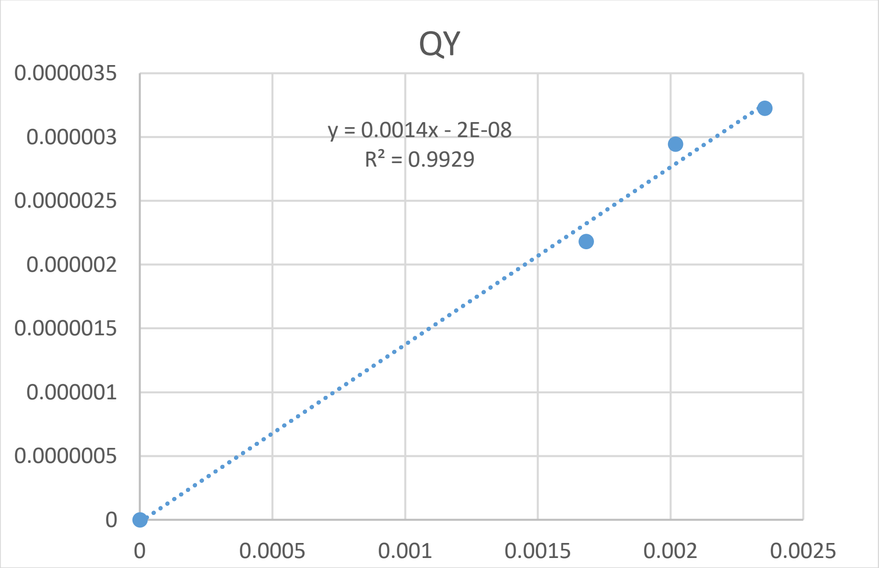


Figure S12: Plot of mols of incident photons vs mols of product formed. Slope of the line correlates to quantum yield of the photochemical transformation.

The quantum yield $(\Phi)_{cat.}$ of the photochemical transformation was measured to be **0.0014**, which hints to a closed catalytic cycle being operational.

F. References

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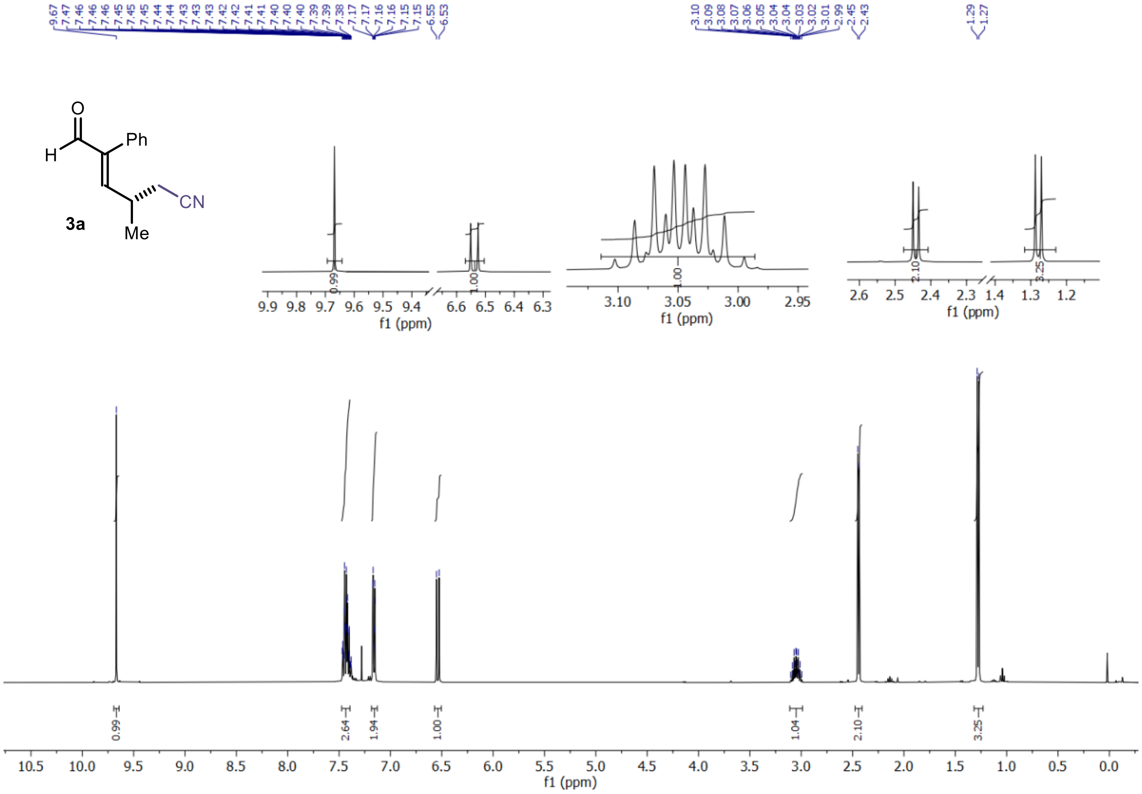
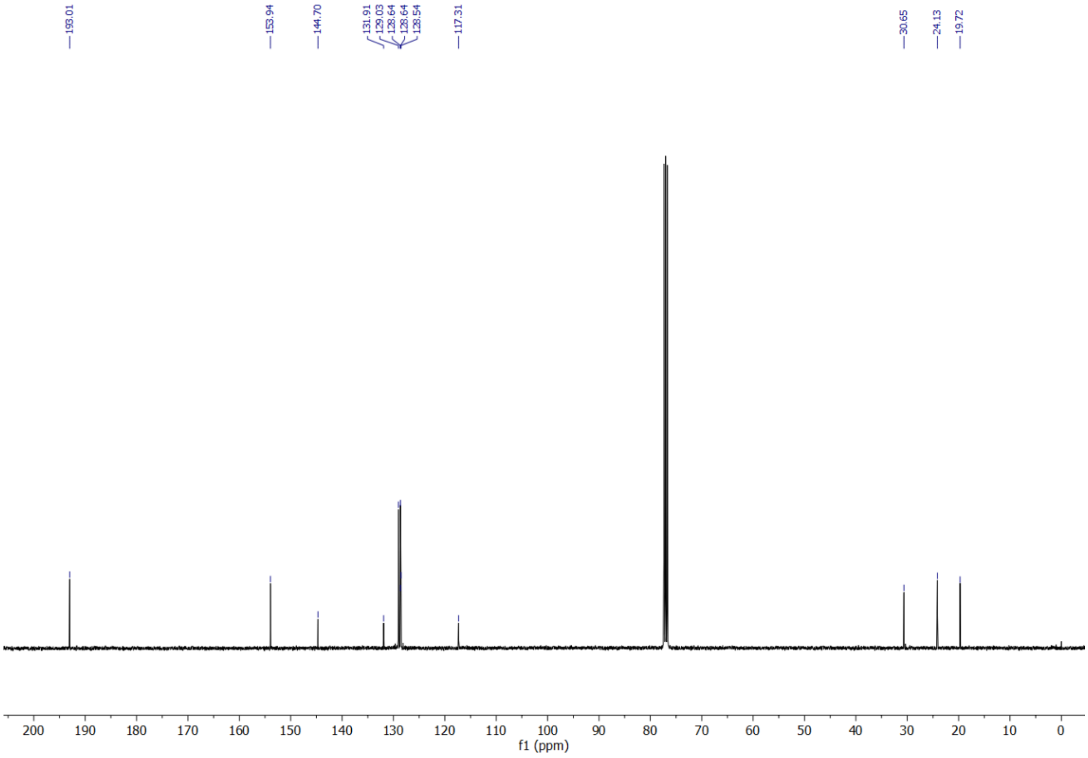
G. NMR Spectra

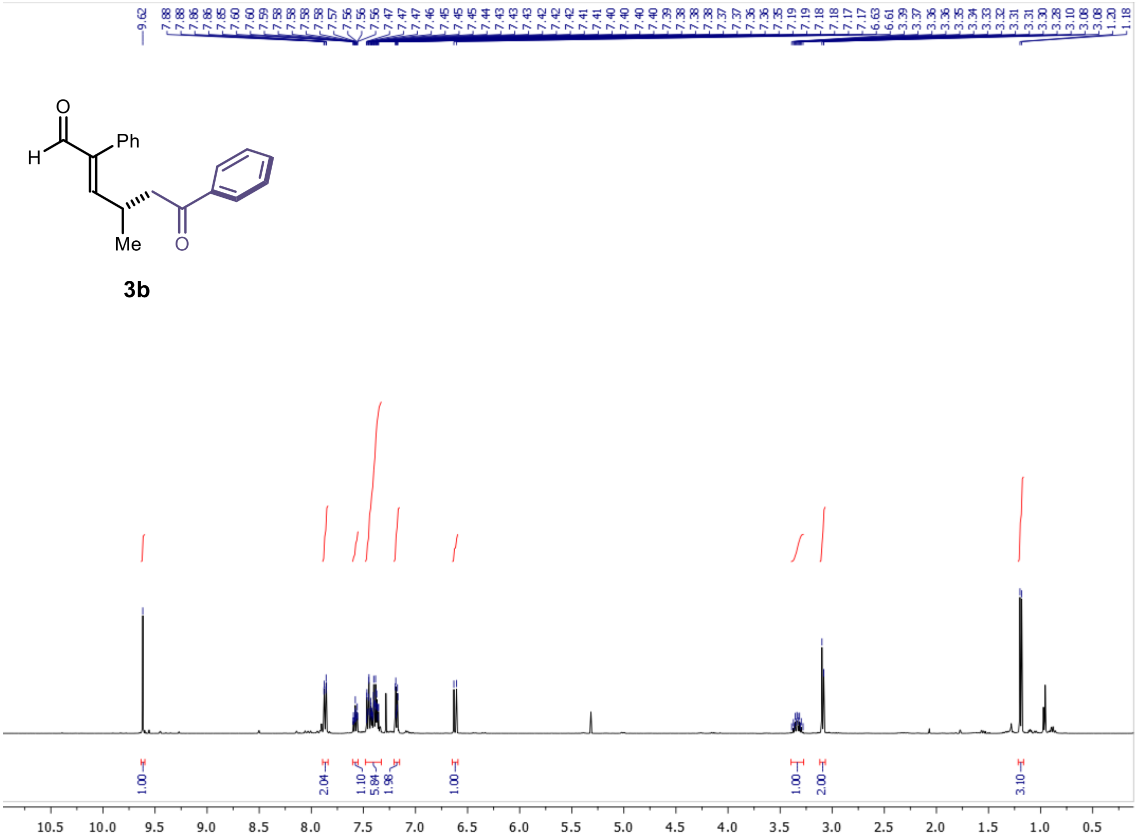
^{1}H NMR (500 MHz, $CDCl_3$)



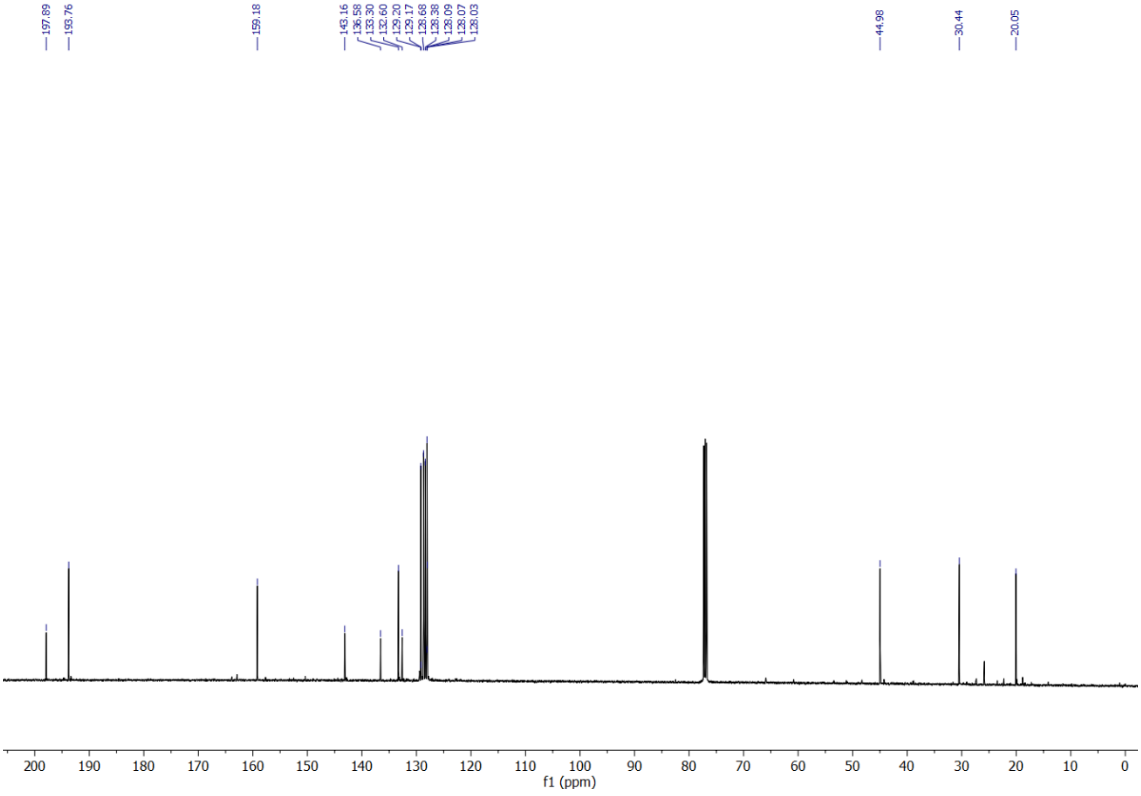
^{13}C NMR (126 MHz, $CDCl_3$)



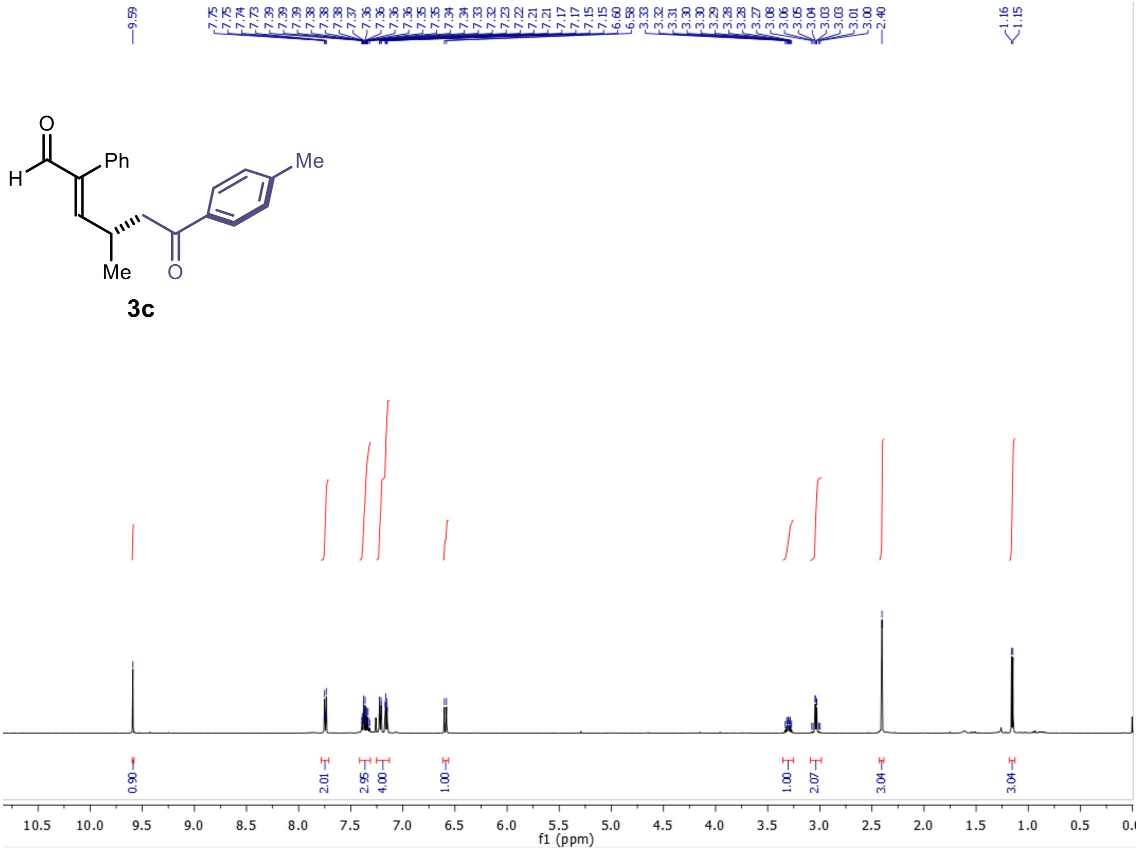
^{1}H NMR (500 MHz, CDCl$_3$)



^{13}C NMR (126 MHz, CDCl$_3$)

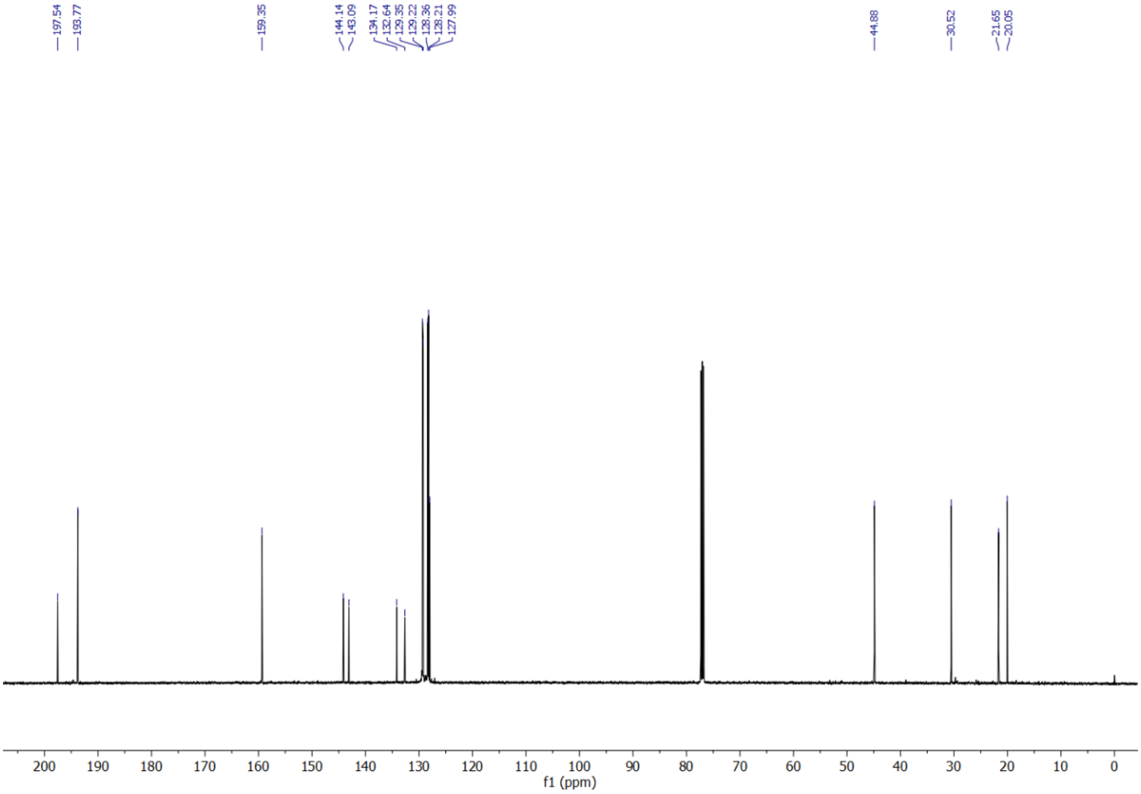


^{1}H NMR (500 MHz, CDCl$_3$)

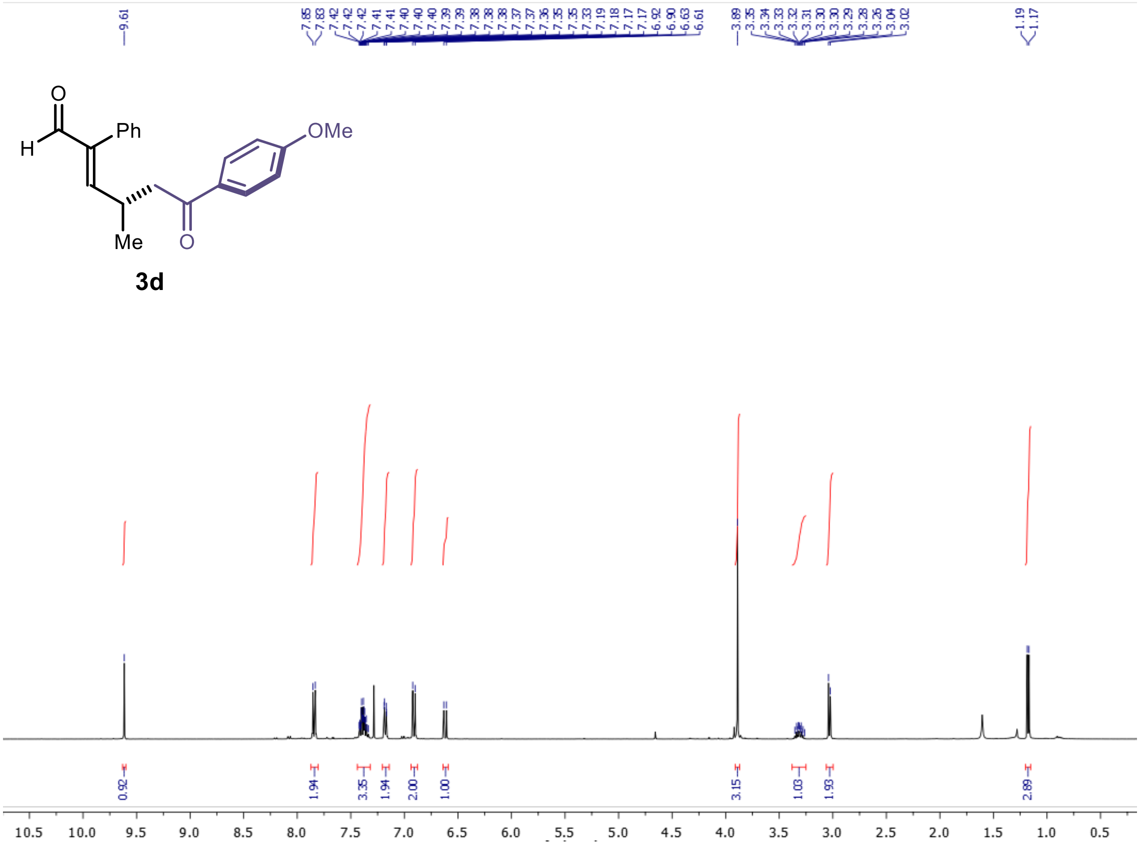


3c

^{13}C NMR (126 MHz, CDCl$_3$)

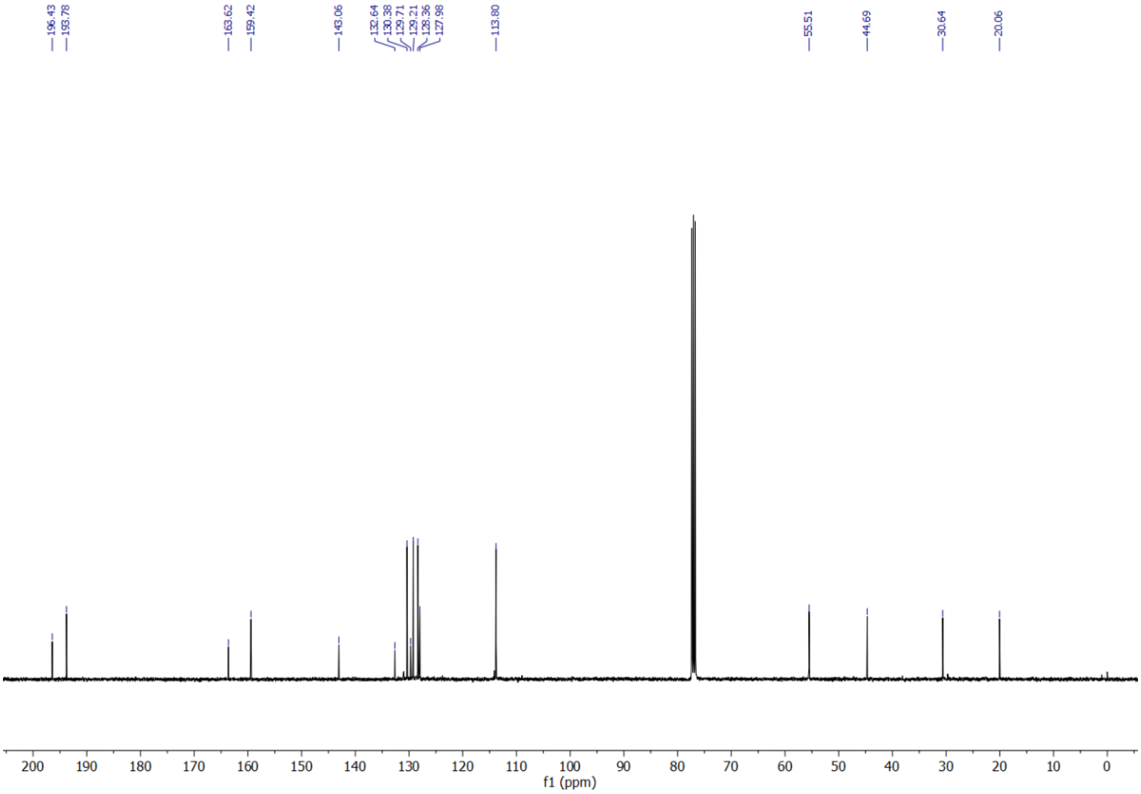


^{1}H NMR (500 MHz, $CDCl_3$)

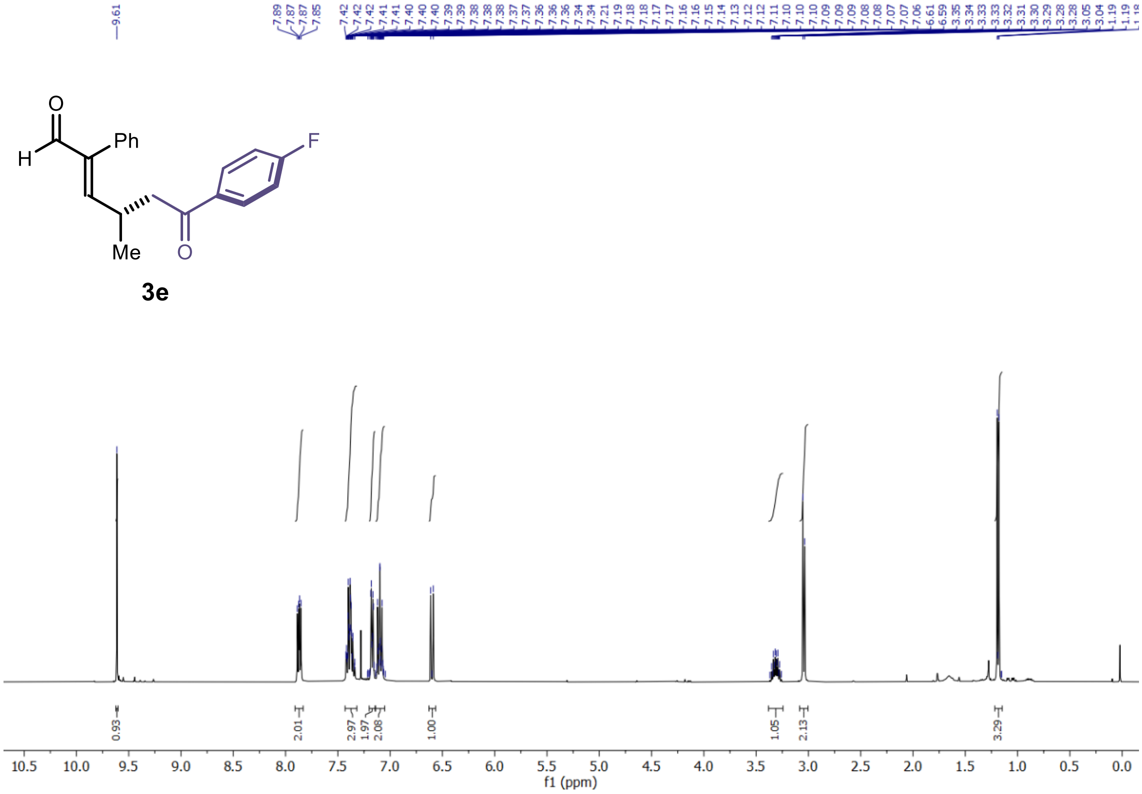


3d

^{13}C NMR (126 MHz, $CDCl_3$)

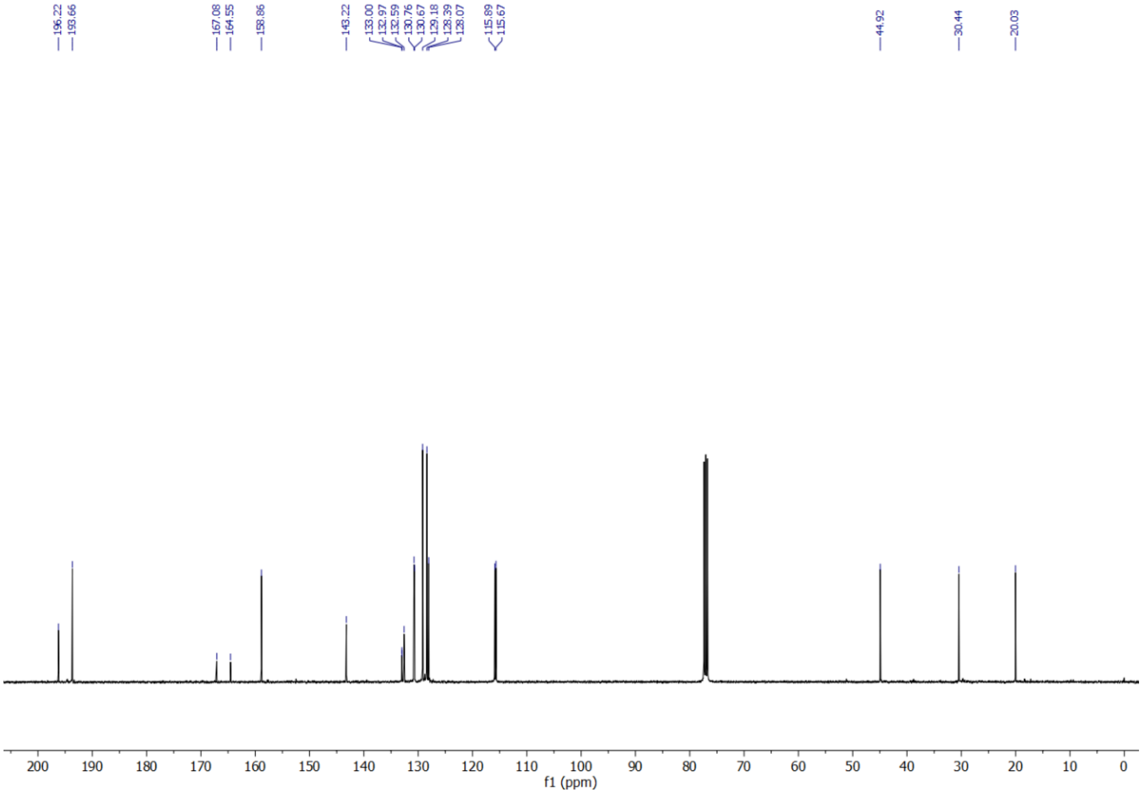


^{1}H NMR (500 MHz, $CDCl_3$)

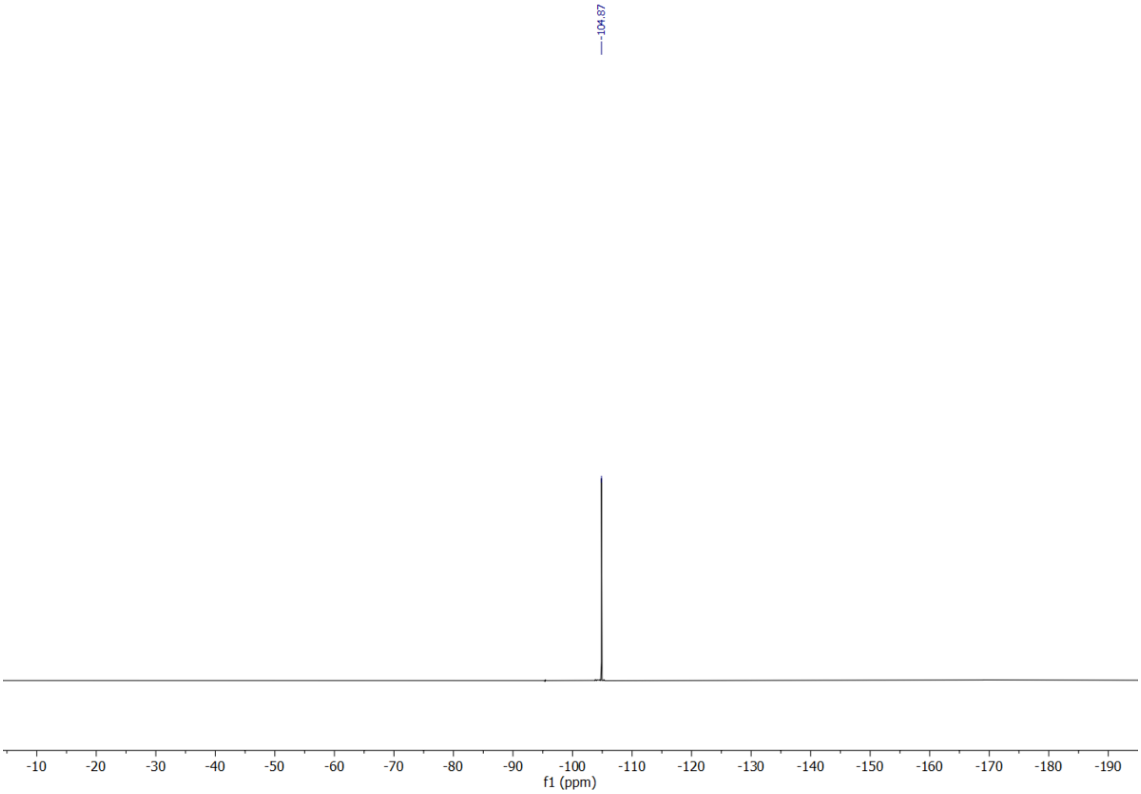


3e

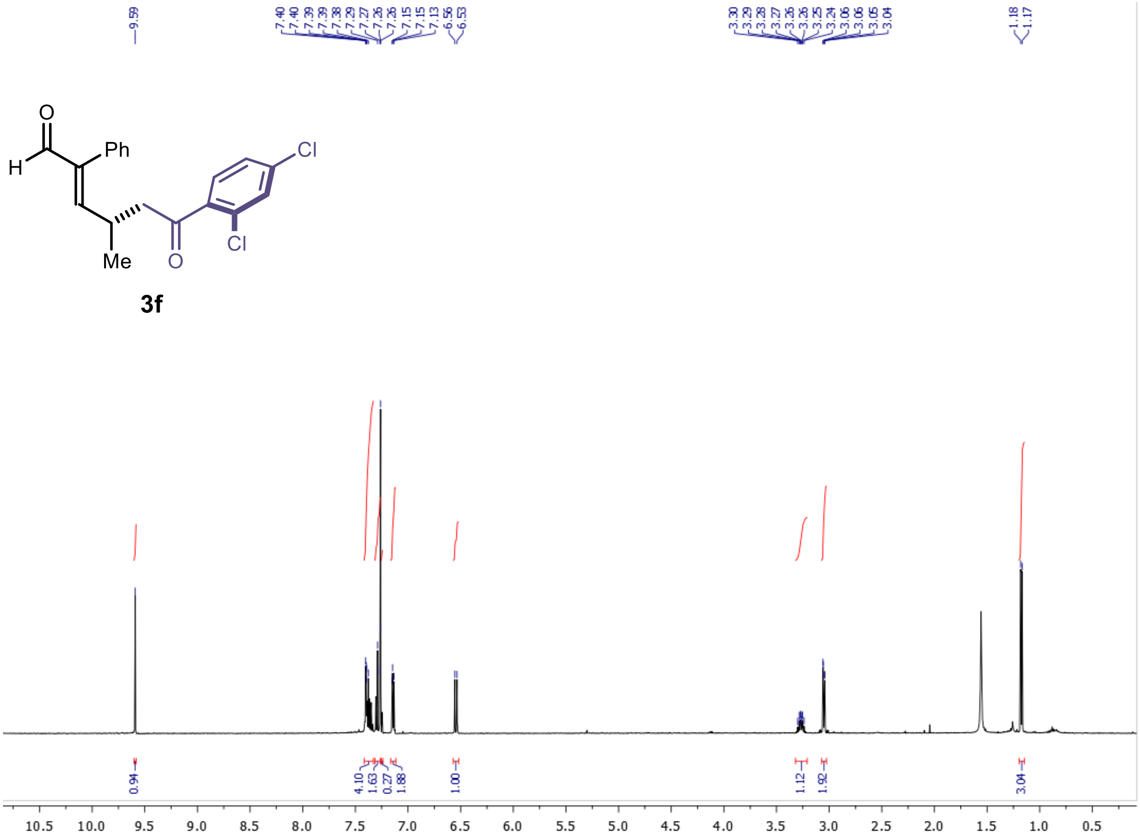
^{13}C NMR (126 MHz, $CDCl_3$)



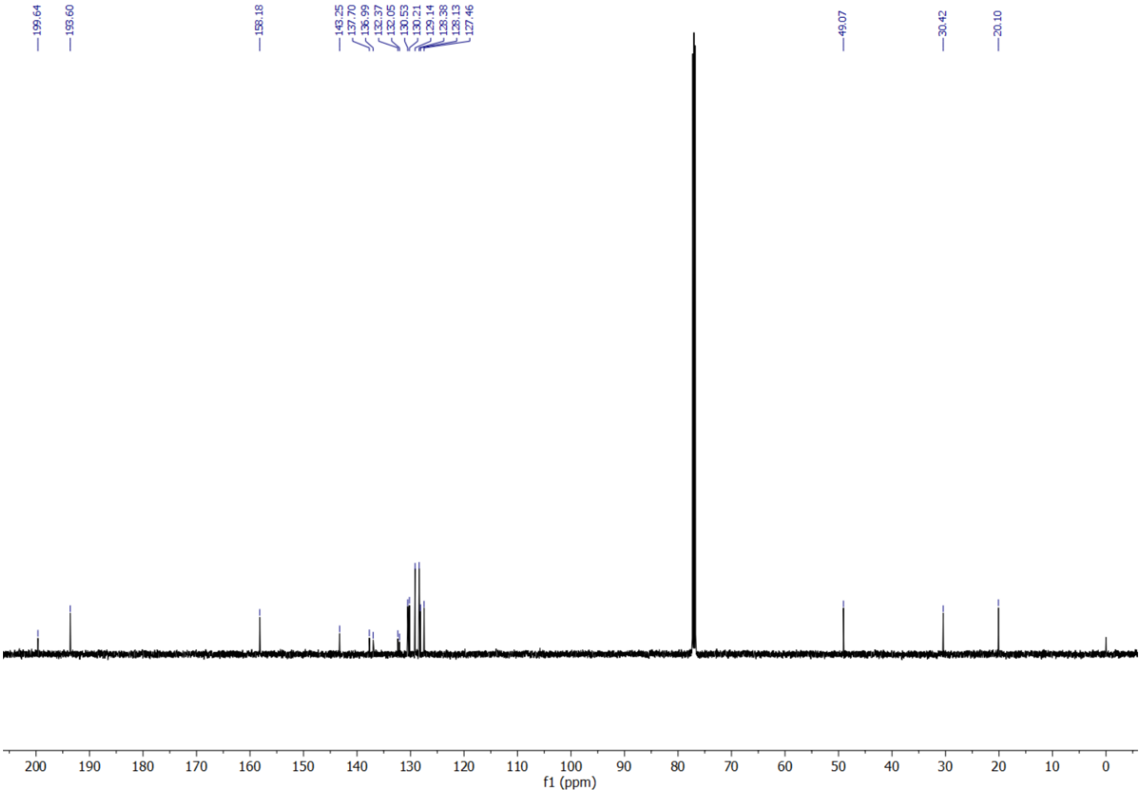
^{19}F NMR (471 MHz, $CDCl_3$)



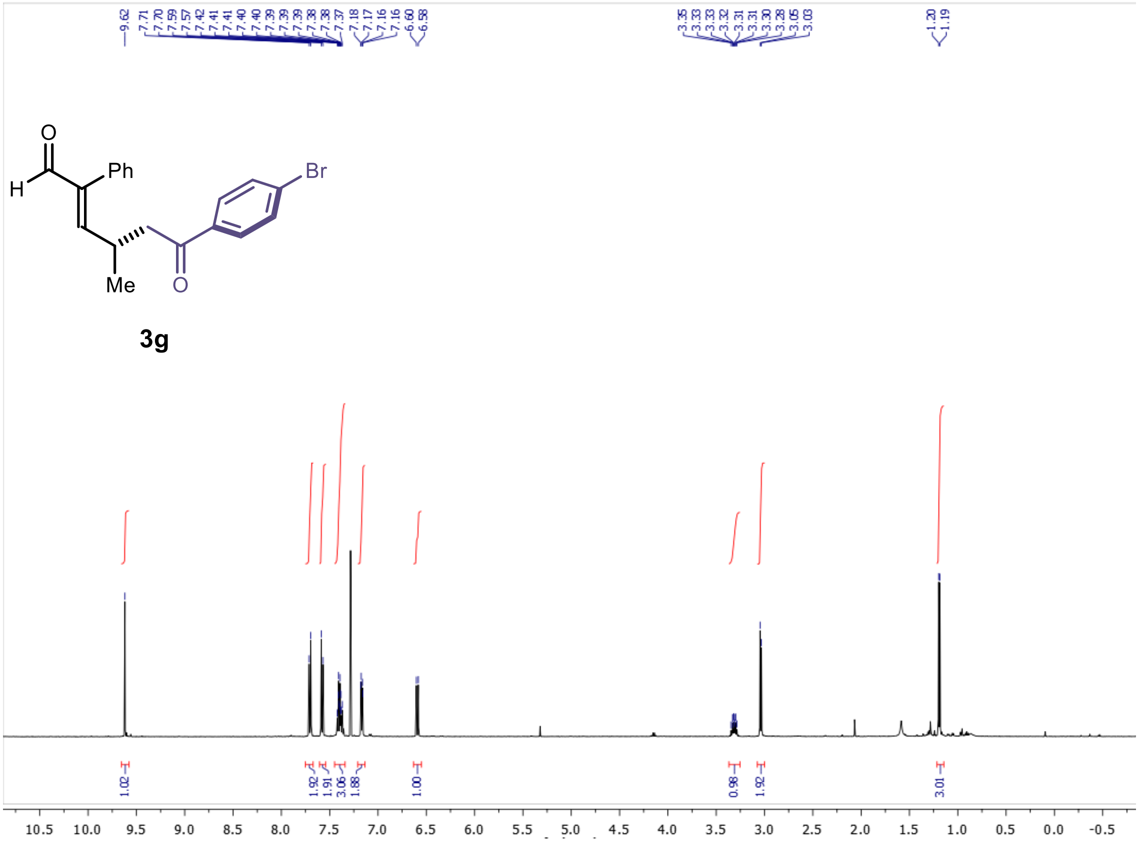
^{1}**H NMR** (500 MHz, CDCl$_3$)



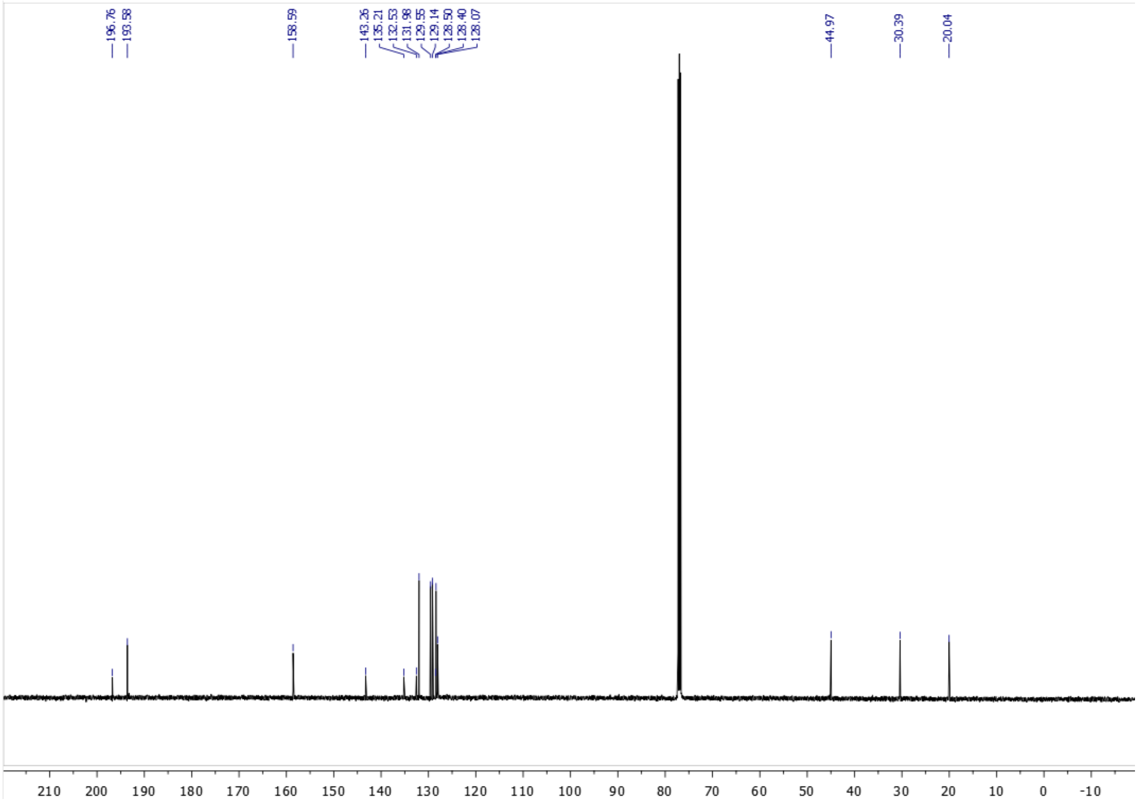
^{13}**C NMR** (126 MHz, CDCl$_3$)



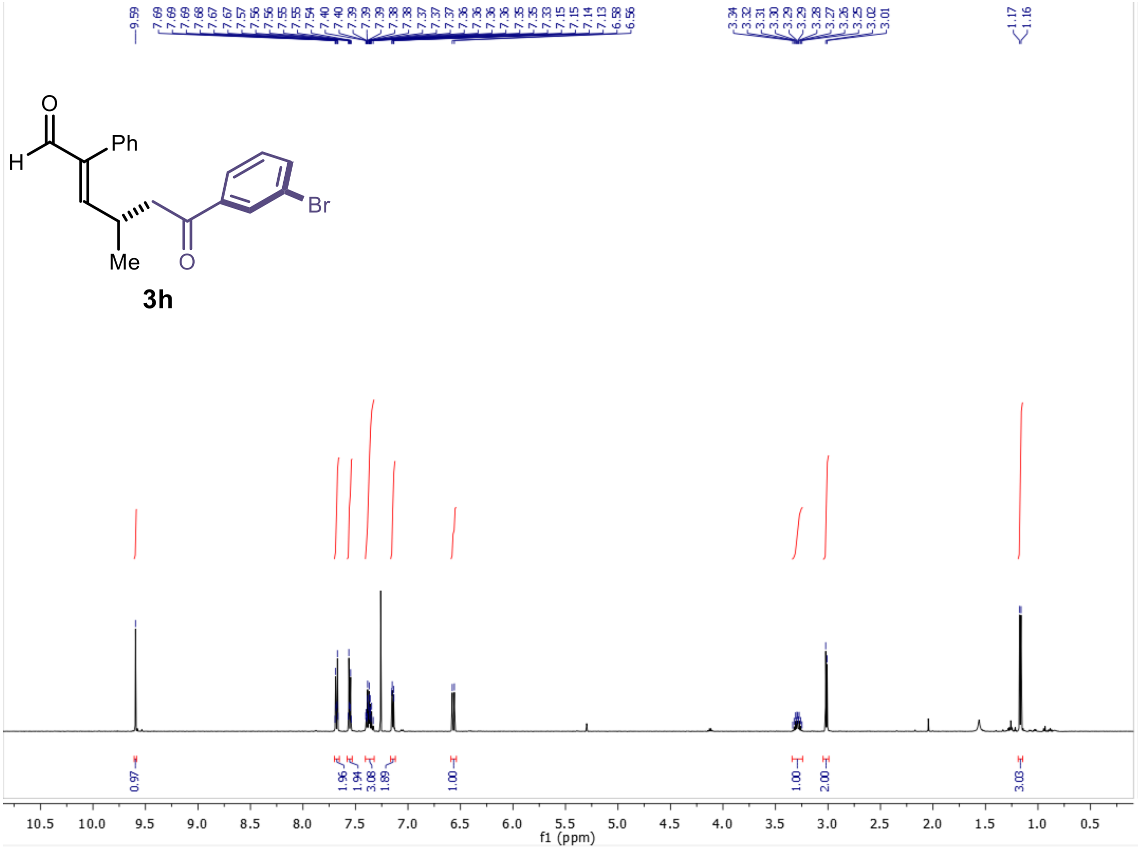
^{1}H NMR (500 MHz, CDCl$_3$)



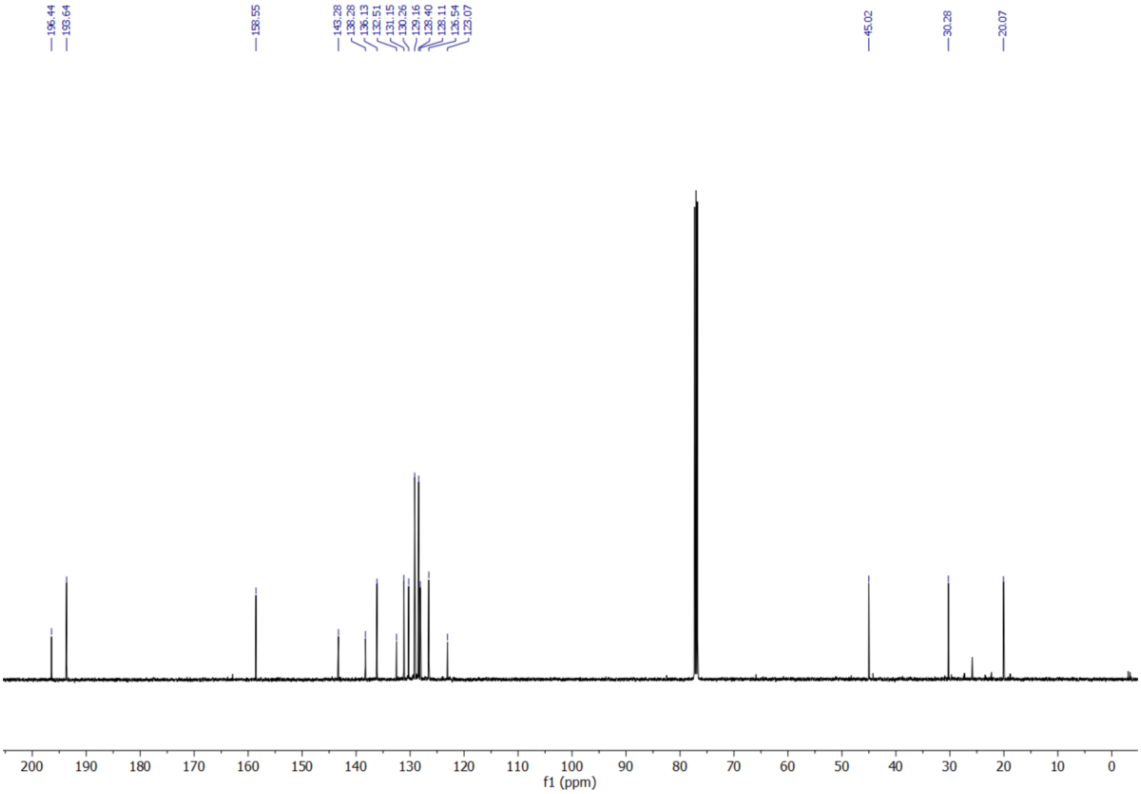
^{13}C NMR (126 MHz, CDCl$_3$)



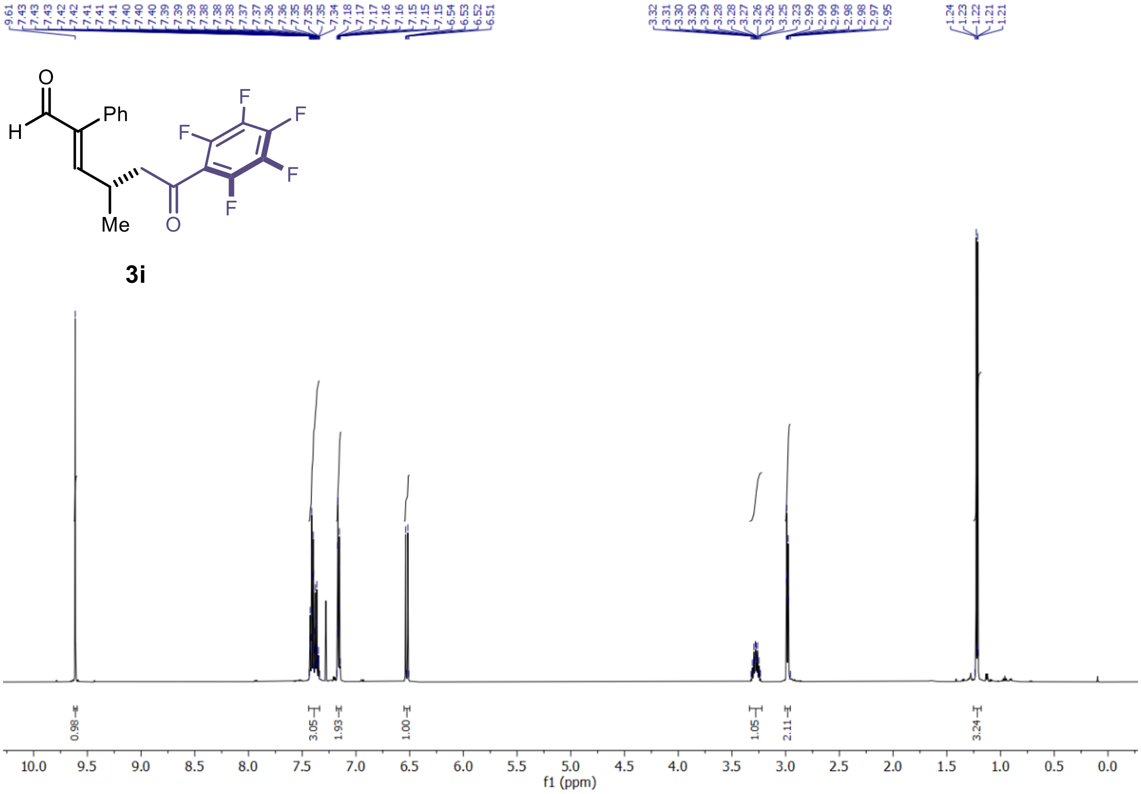
^{1}H NMR (500 MHz, CDCl$_3$)



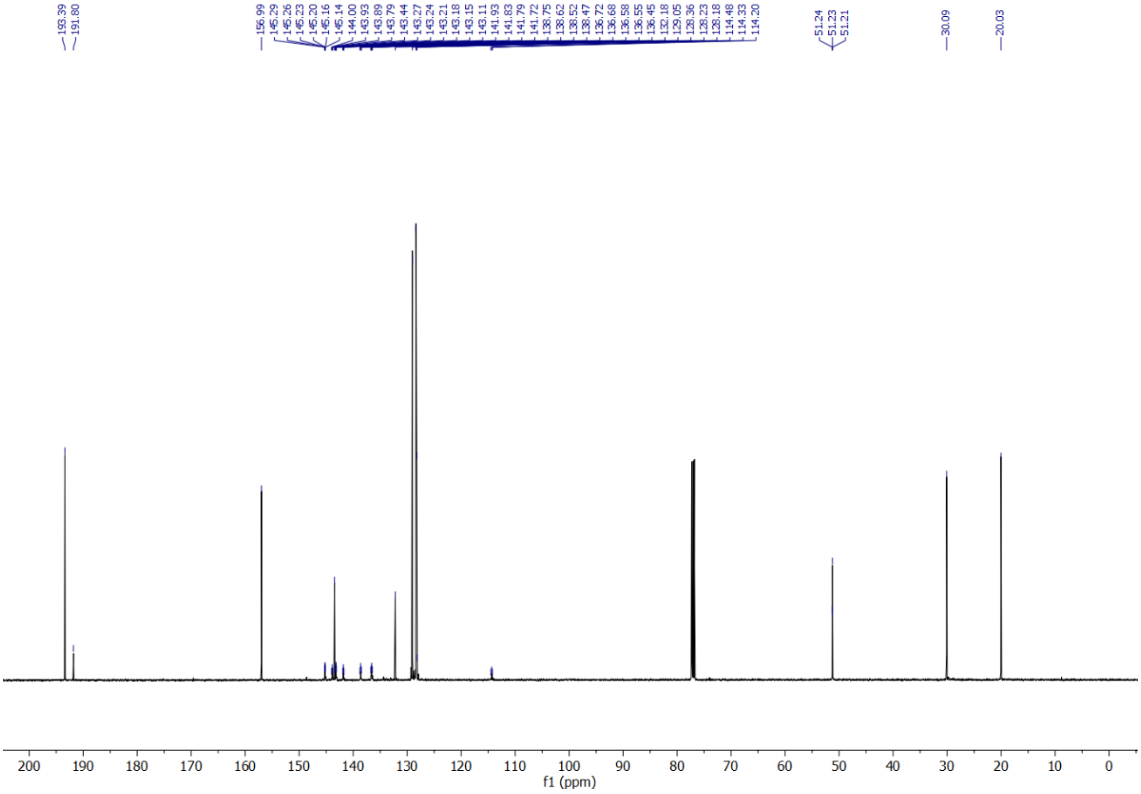
^{13}C NMR (126 MHz, CDCl$_3$)



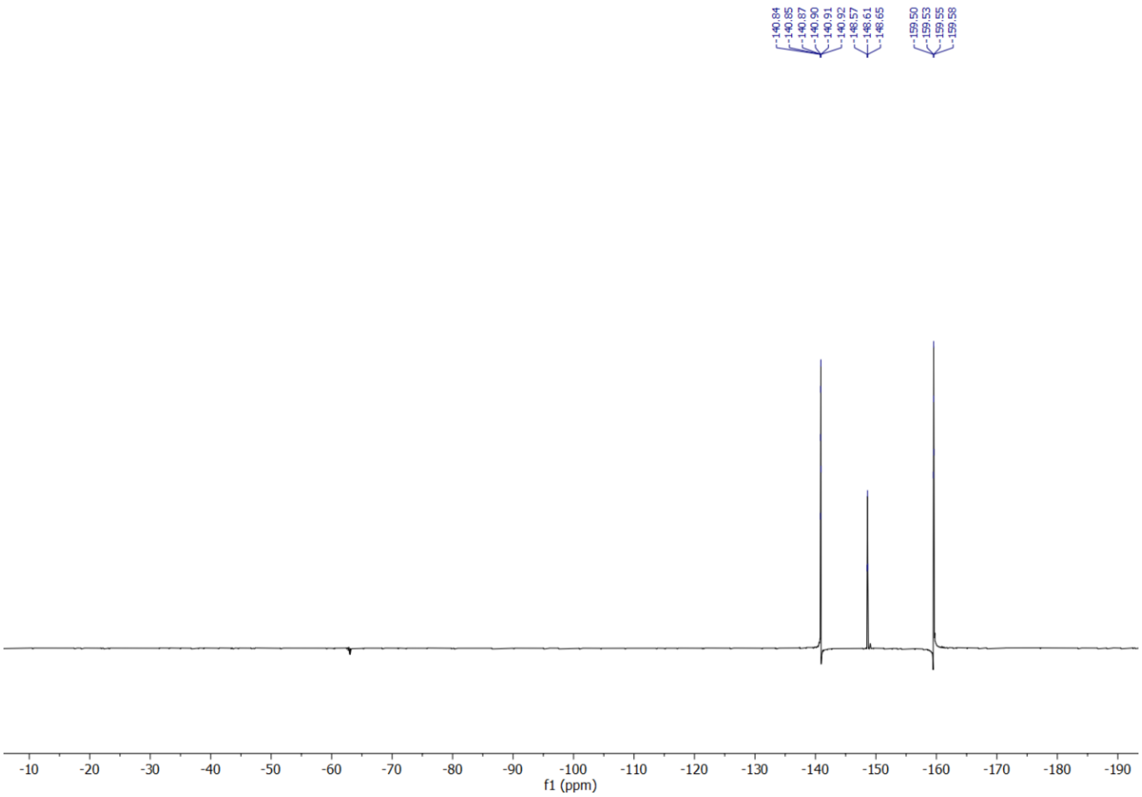
^{1}H NMR (500 MHz, $CDCl_3$)



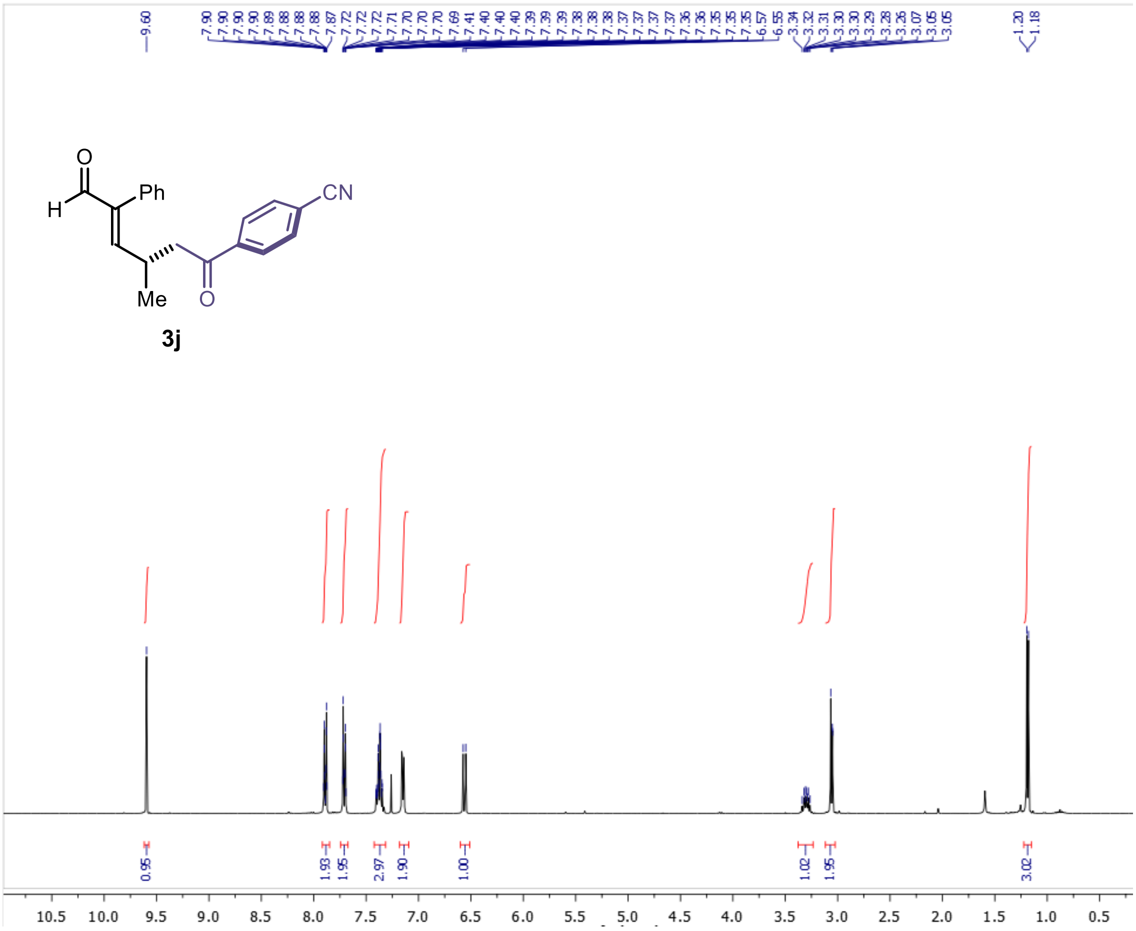
^{13}C NMR (126 MHz, $CDCl_3$)



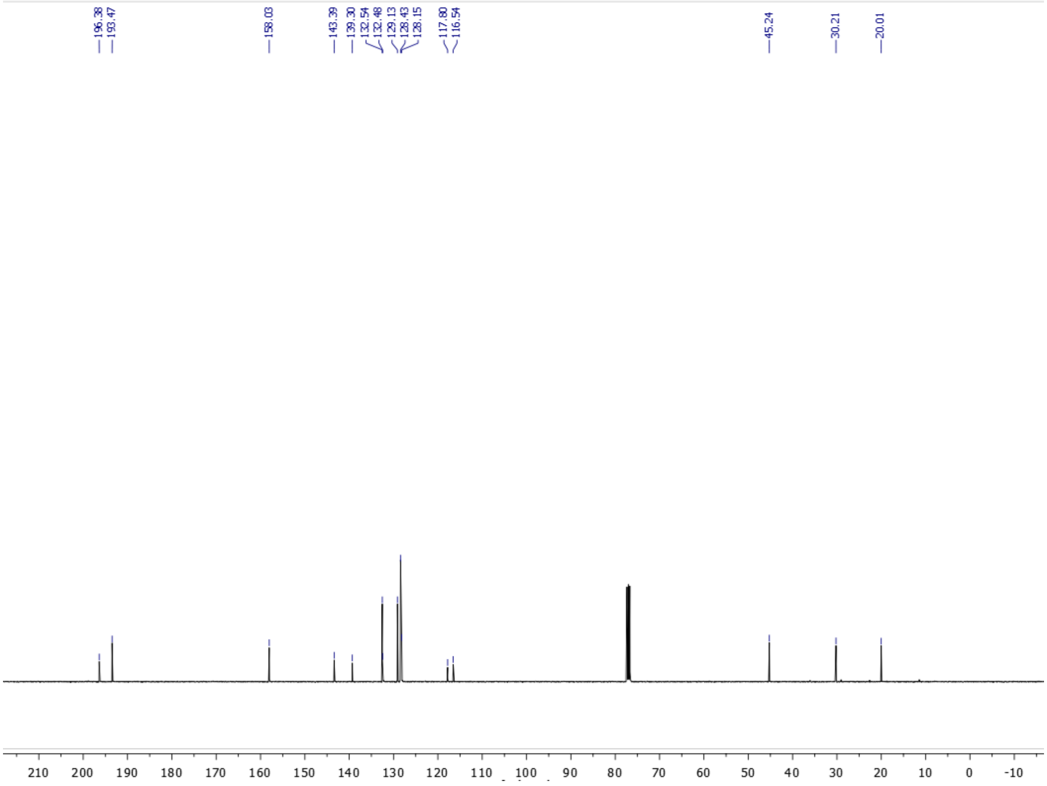
^{19}F NMR (471 MHz, CDCl$_3$)



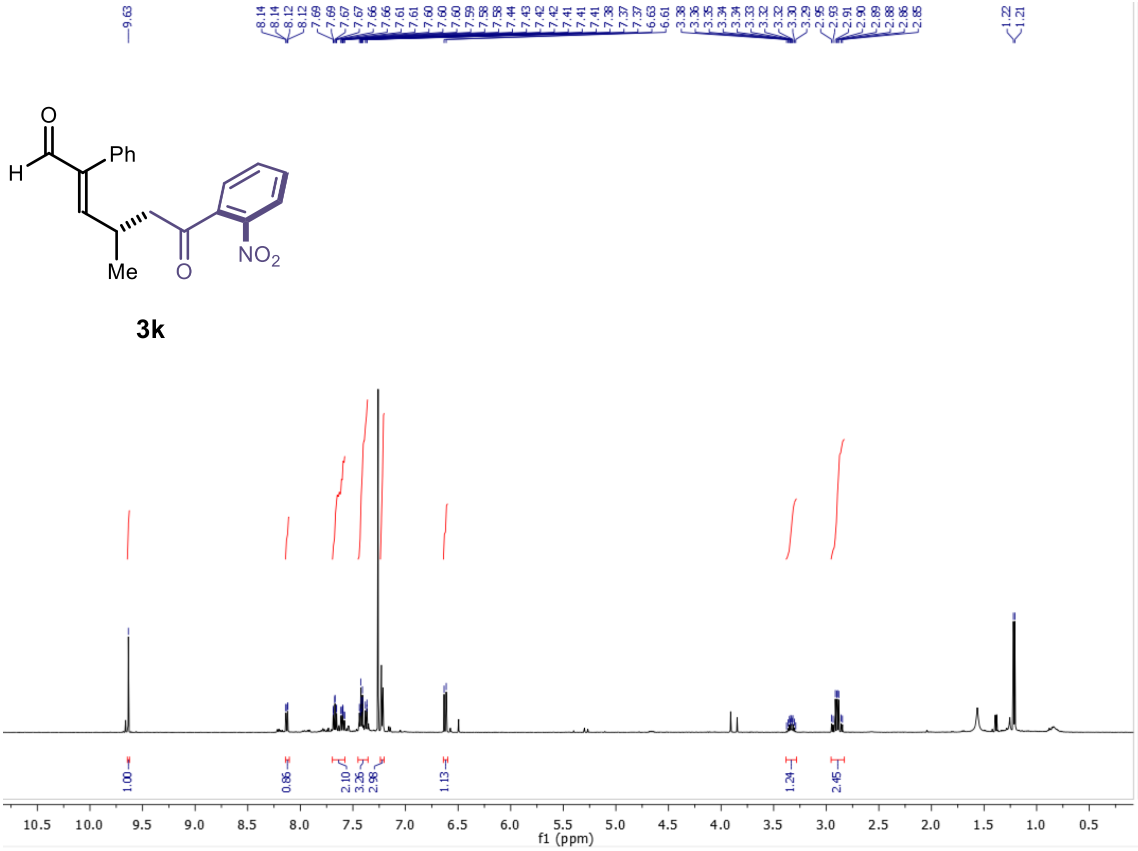
^{1}H NMR (500 MHz, CDCl$_3$)



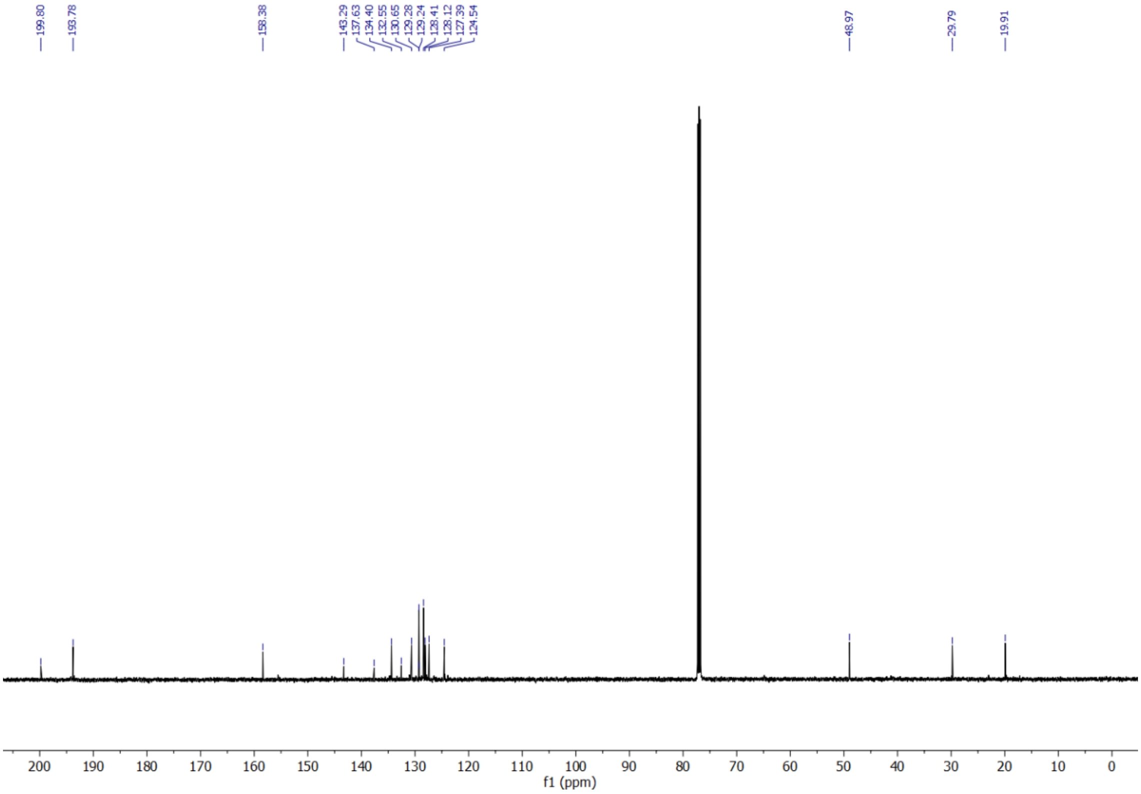
^{13}C NMR (126 MHz, CDCl$_3$)



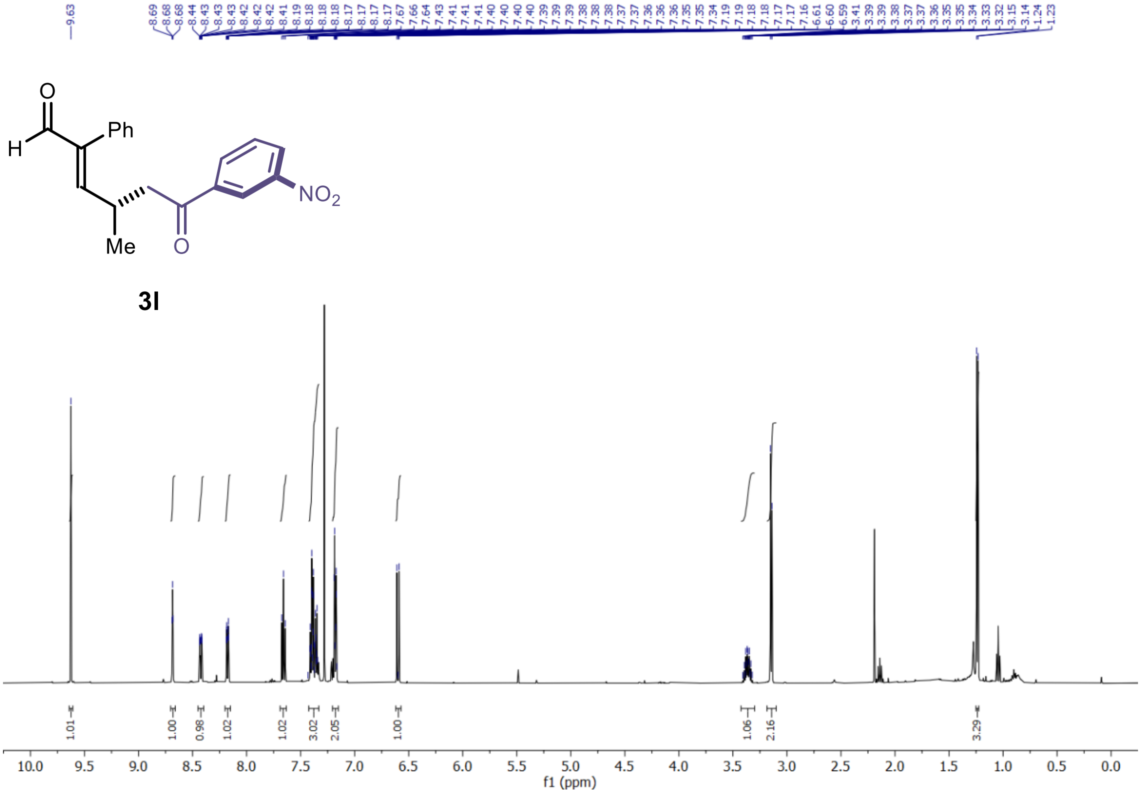
^{1}H NMR (500 MHz, $CDCl_3$)



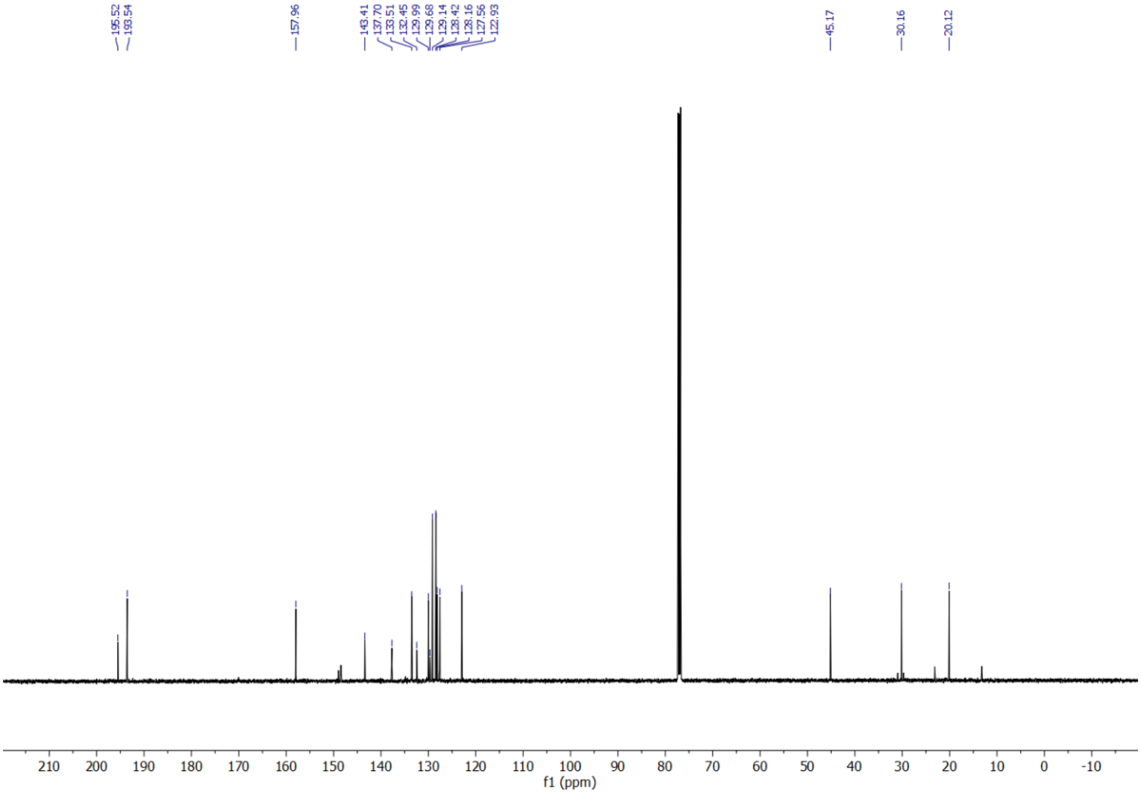
^{13}C NMR (126 MHz, $CDCl_3$)



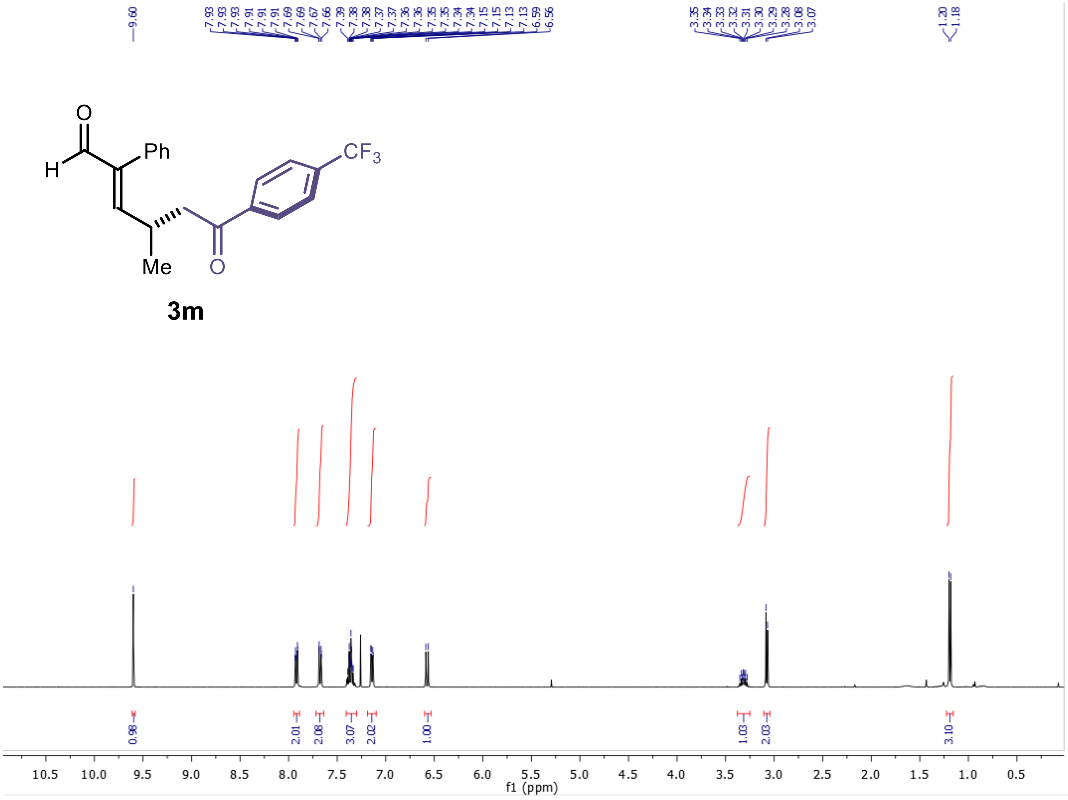
^{1}H NMR (500 MHz, $CDCl_3$)



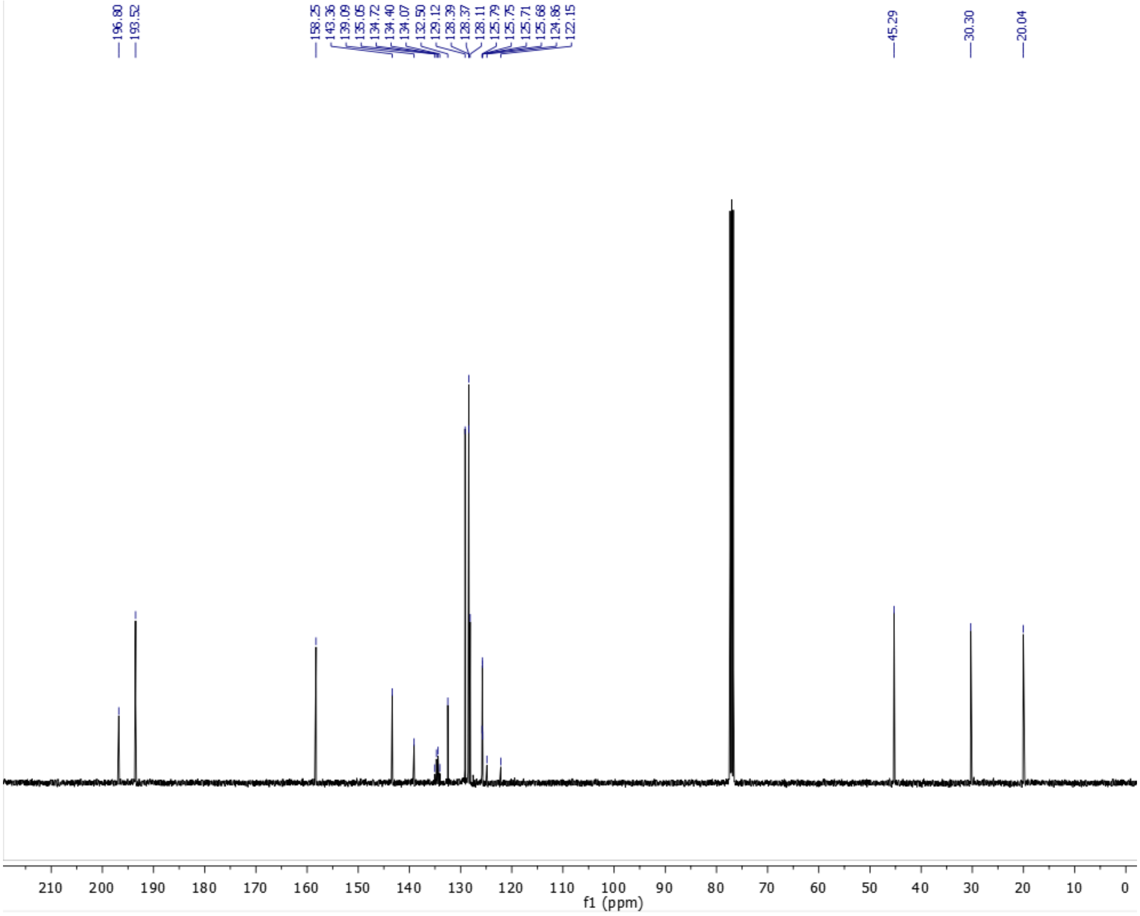
^{13}C NMR (126 MHz, $CDCl_3$)



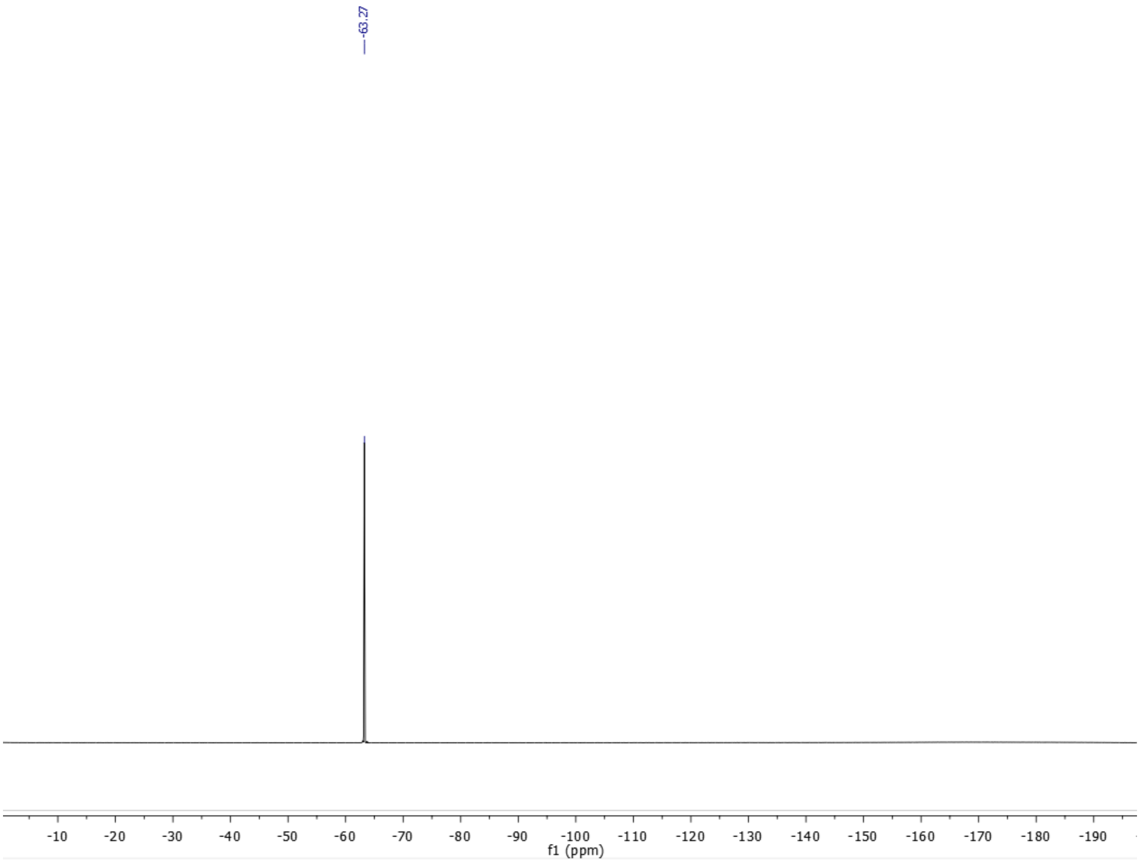
^{1}**H NMR** (400 MHz, $CDCl_3$)



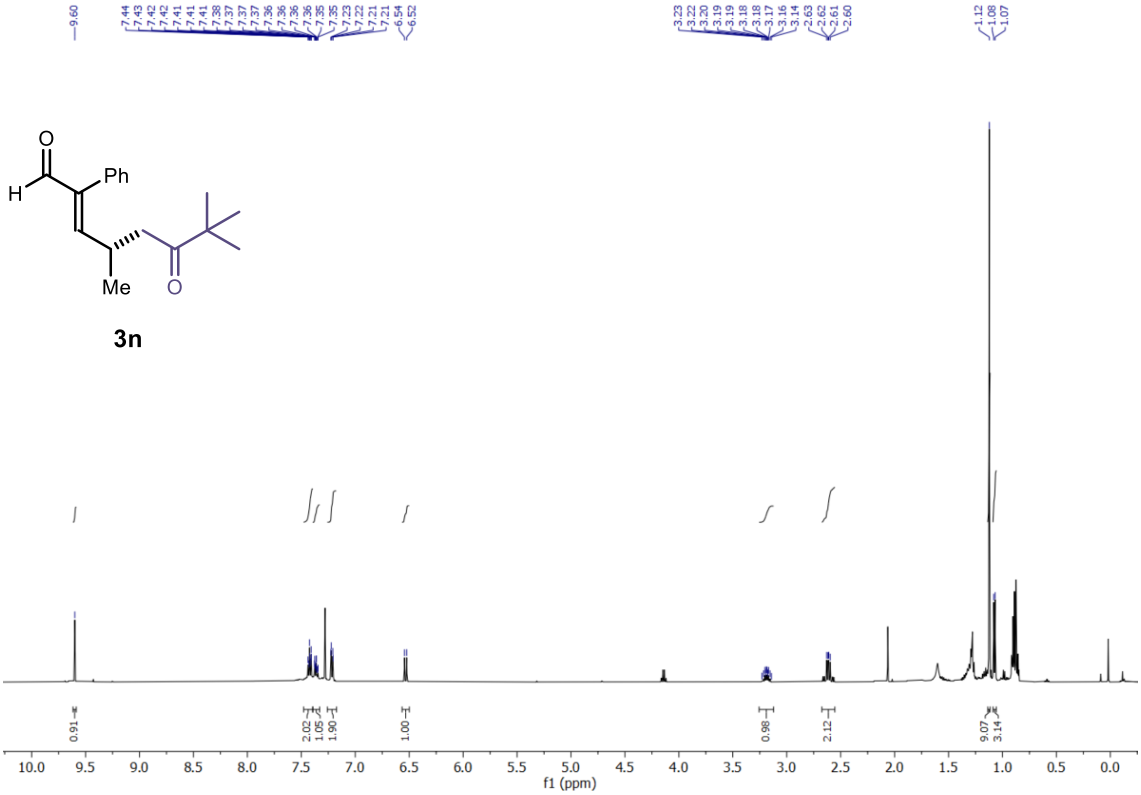
^{13}**C NMR** (126 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)

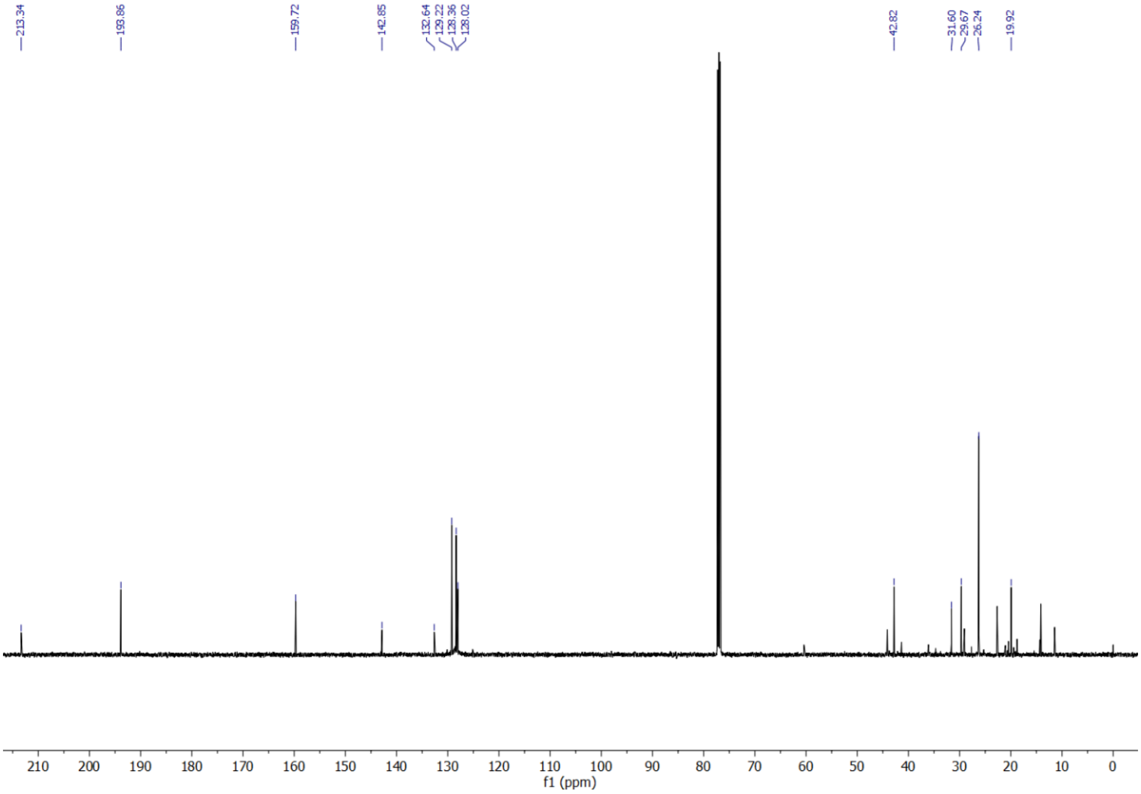


^{1}H NMR (500 MHz, CDCl$_3$)

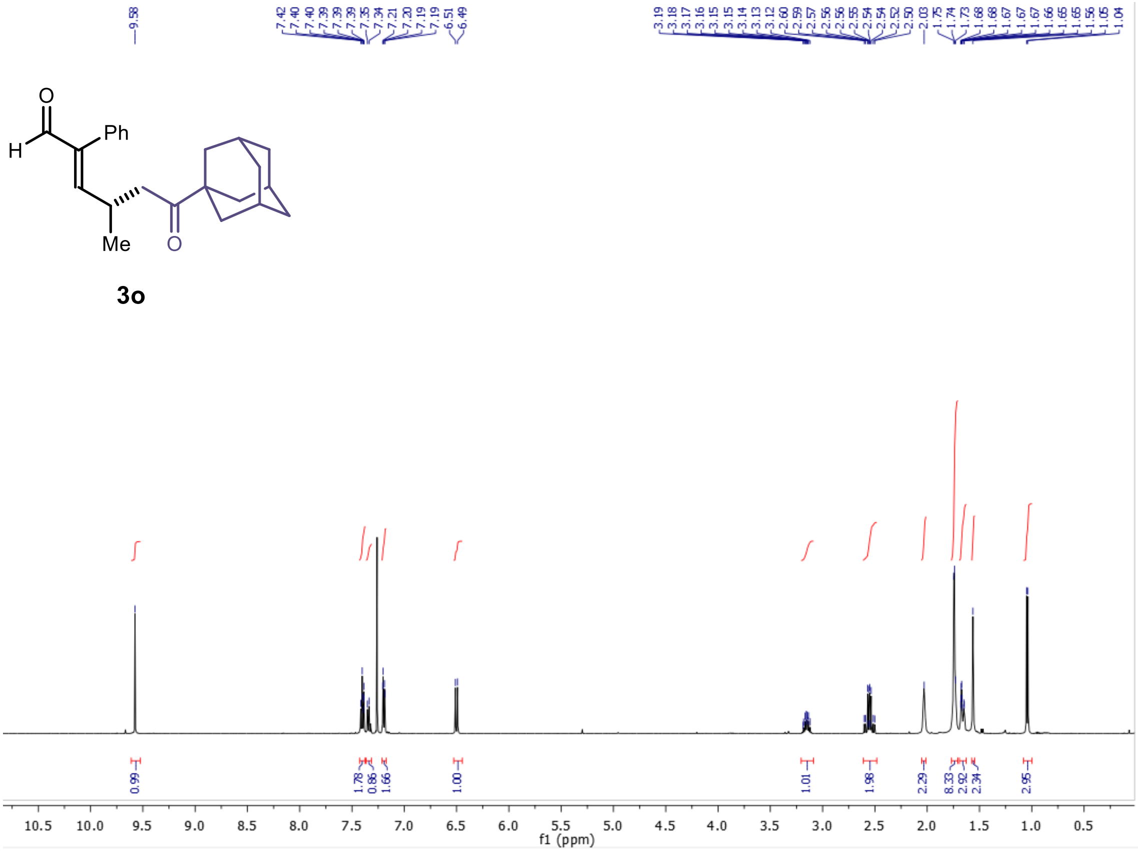


3n

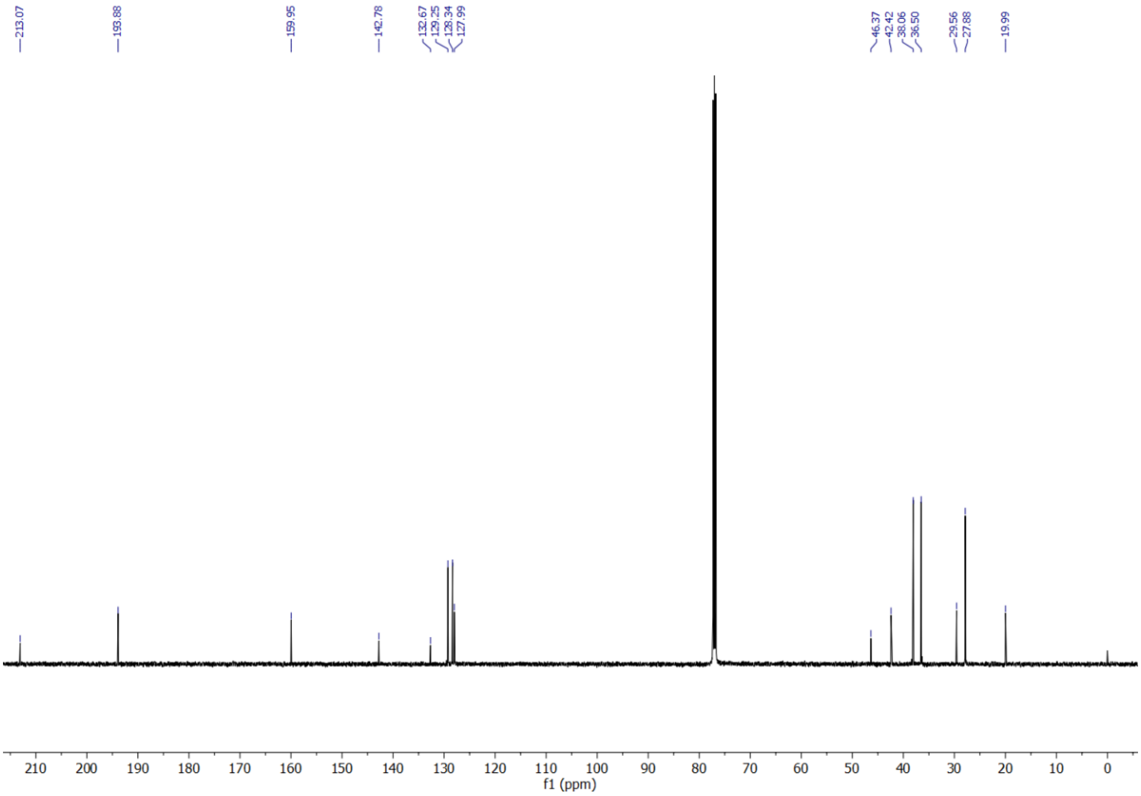
^{13}C NMR (126 MHz, CDCl$_3$)



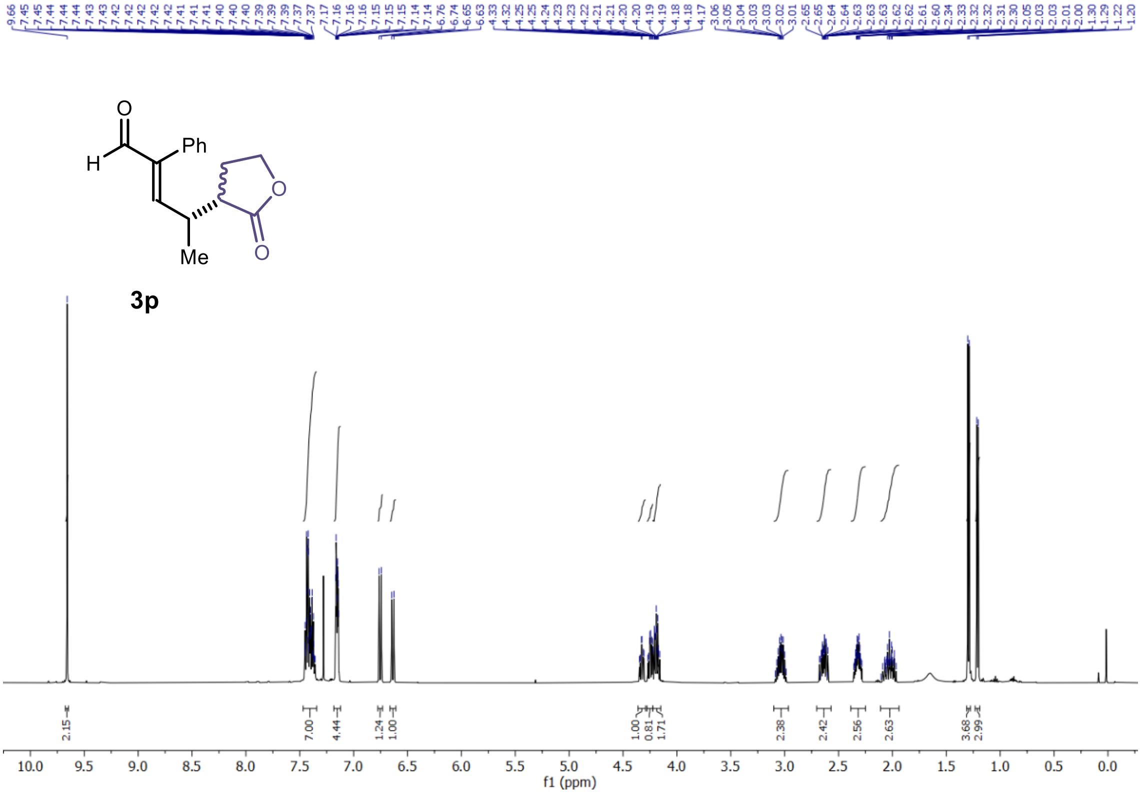
^{1}**H NMR** (500 MHz, CDCl$_3$)



^{13}**C NMR** (126 MHz, CDCl$_3$)

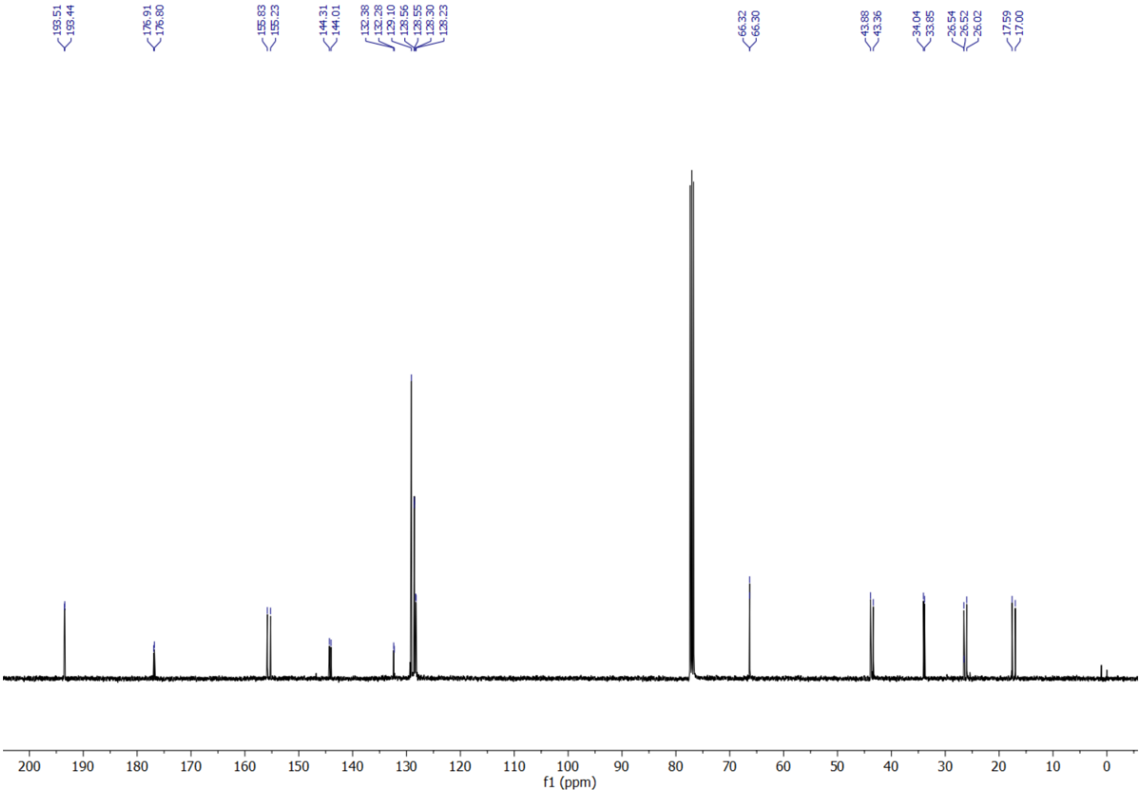


^{1}H NMR (500 MHz, CDCl$_3$)

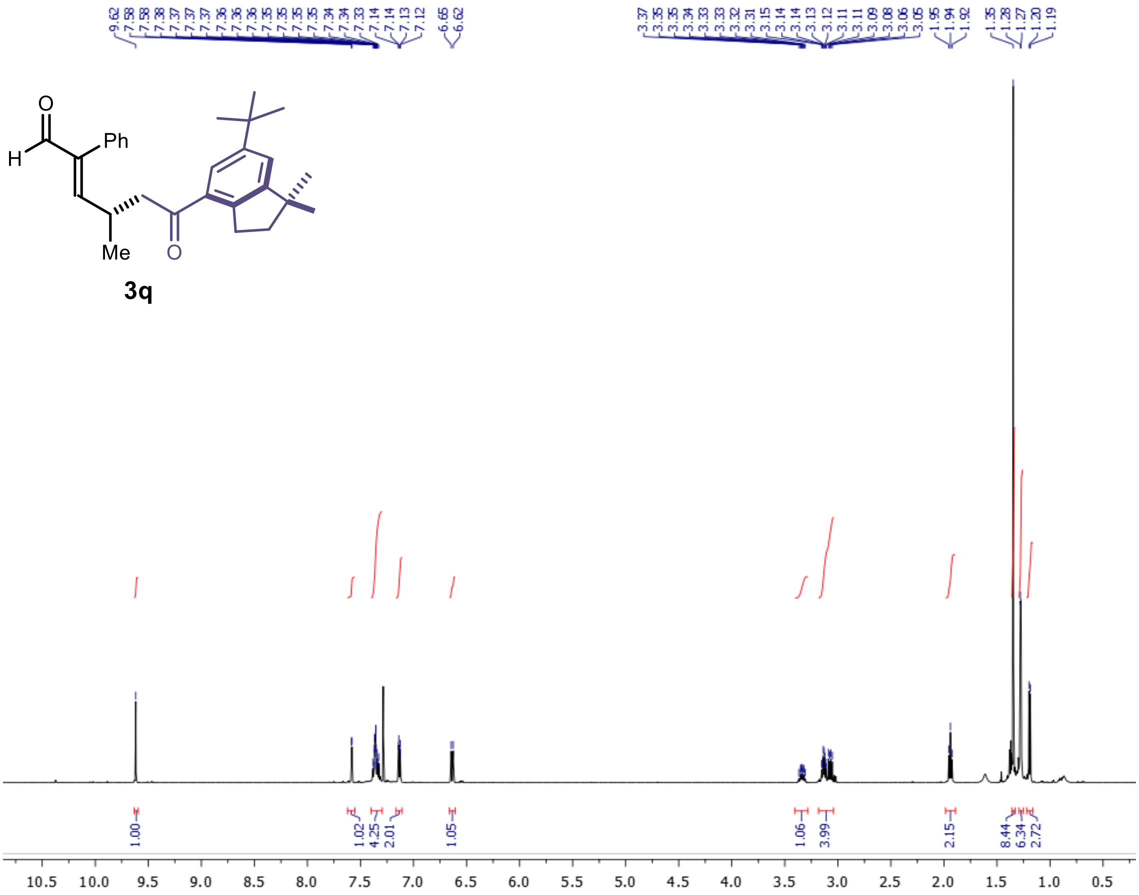


3p

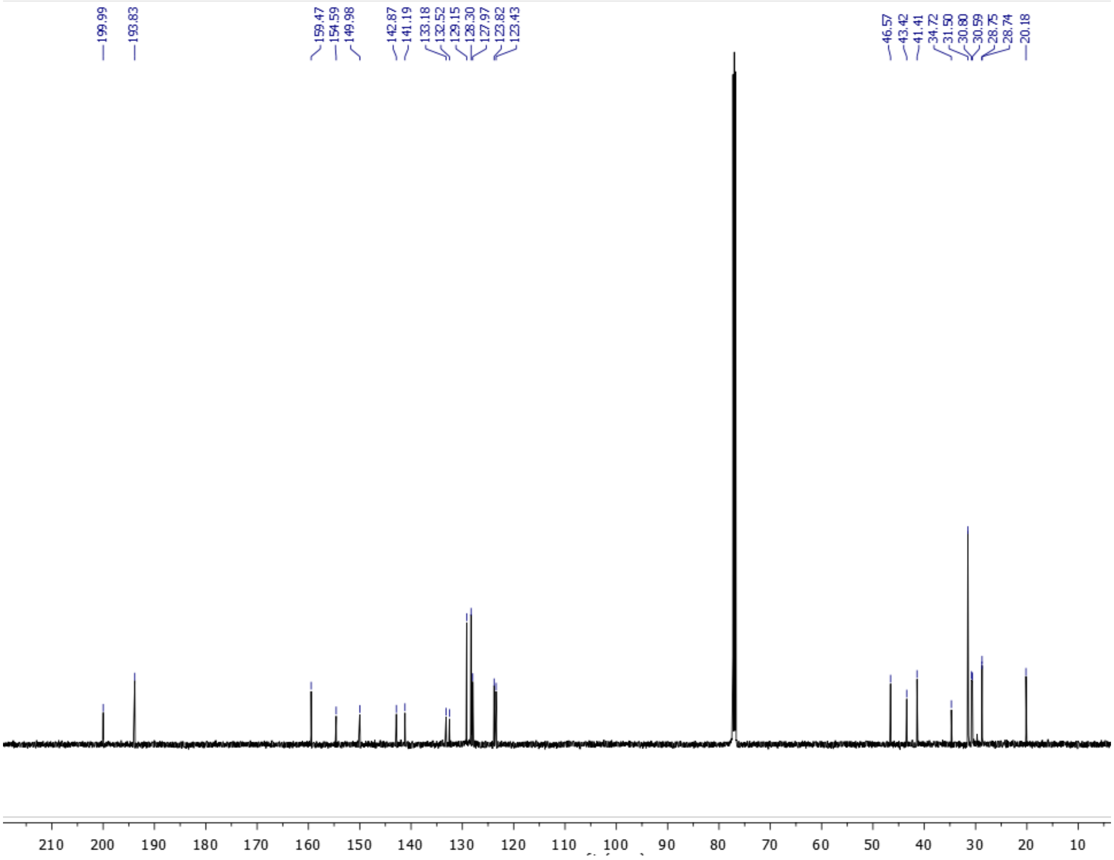
^{13}C NMR (126 MHz, CDCl$_3$)



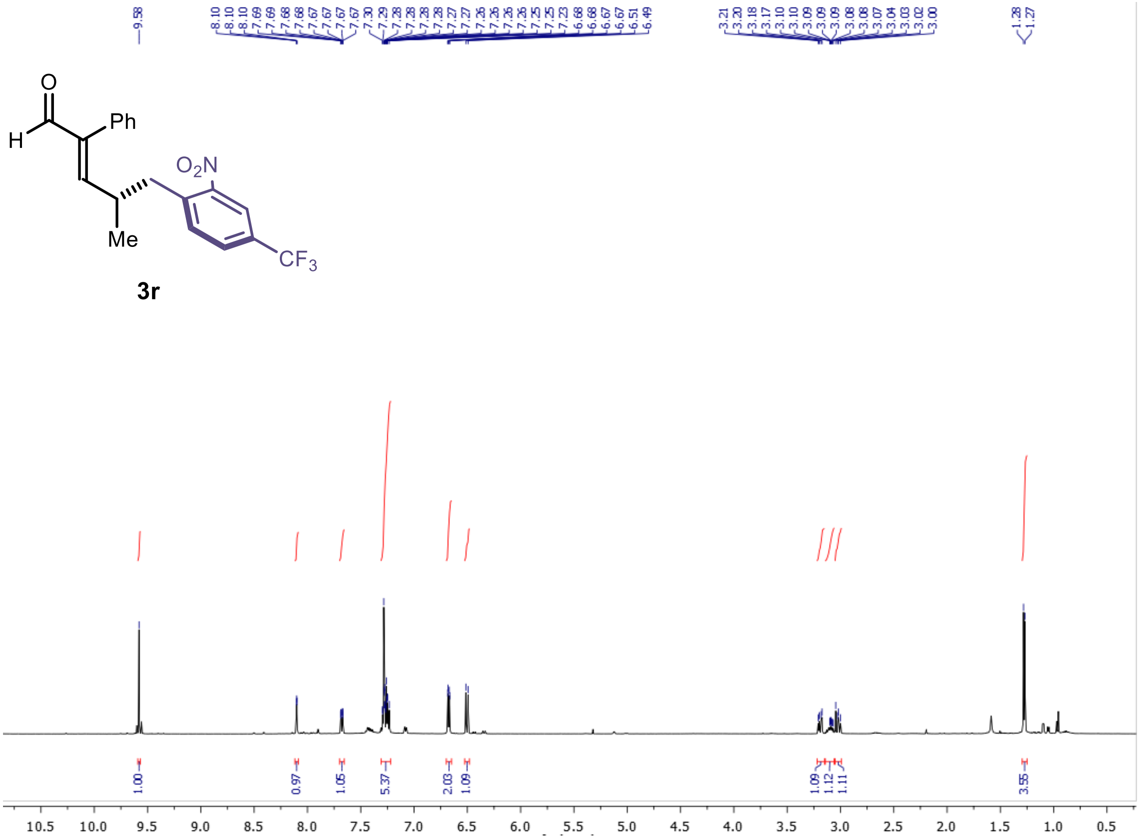
^{1}H NMR (500 MHz, CDCl$_3$)



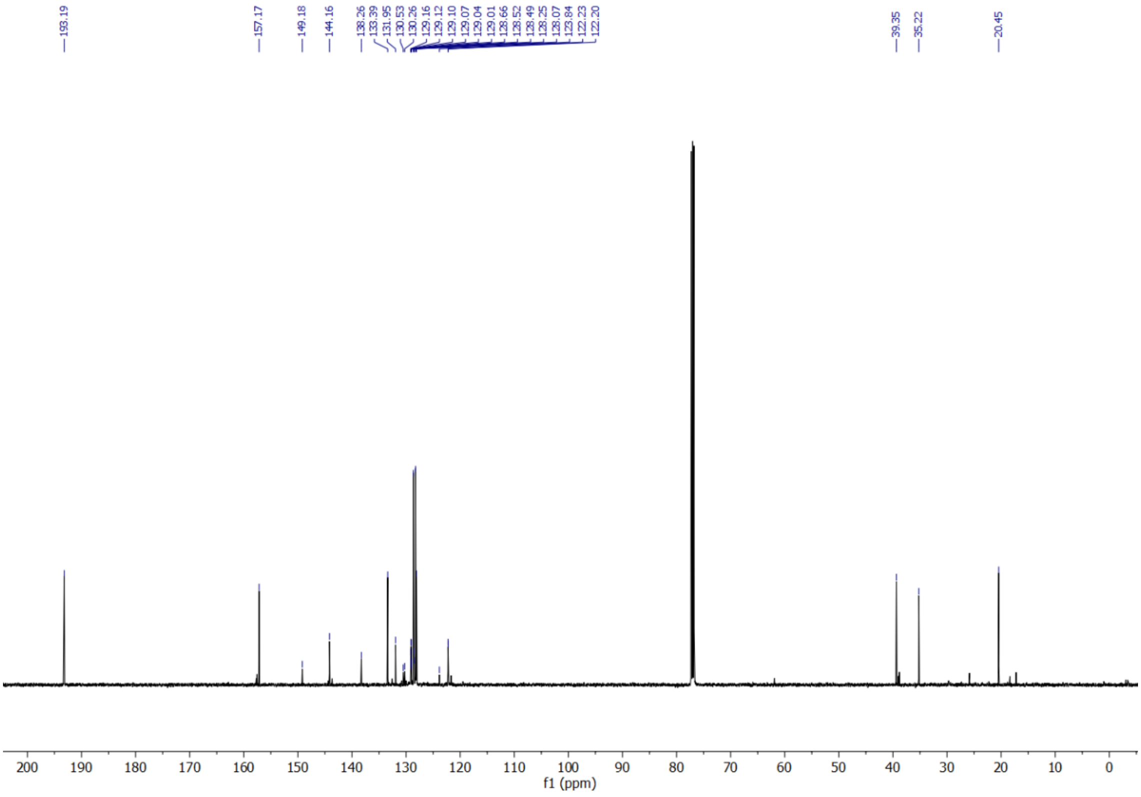
^{13}C NMR (126 MHz, CDCl$_3$)



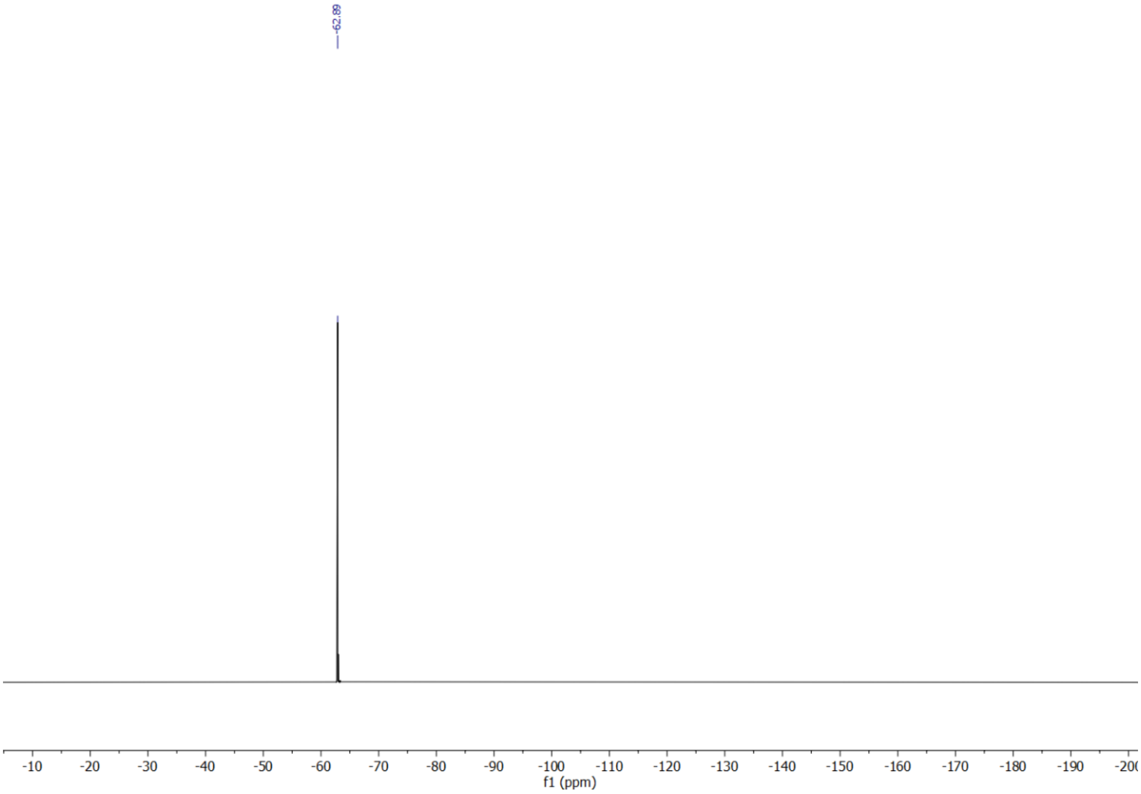
^{1}H NMR (500 MHz, CDCl$_3$)



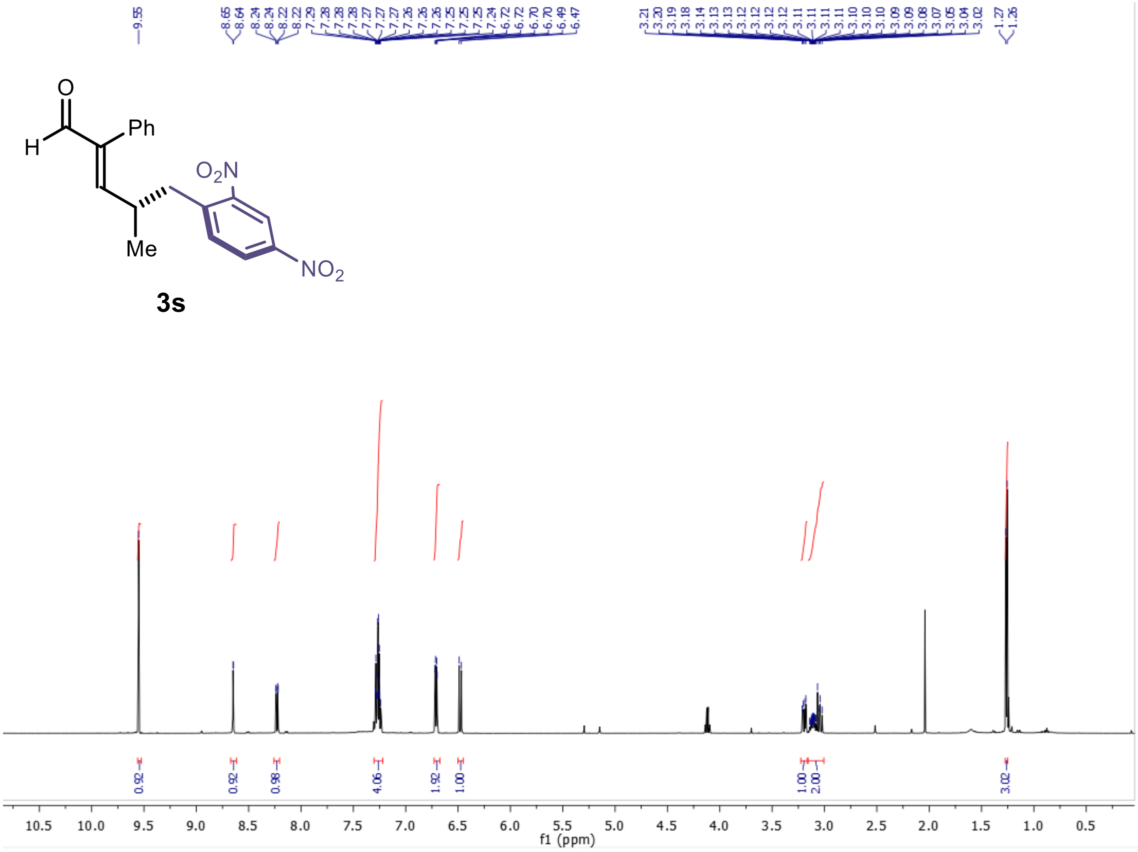
^{13}C NMR (126 MHz, CDCl$_3$)



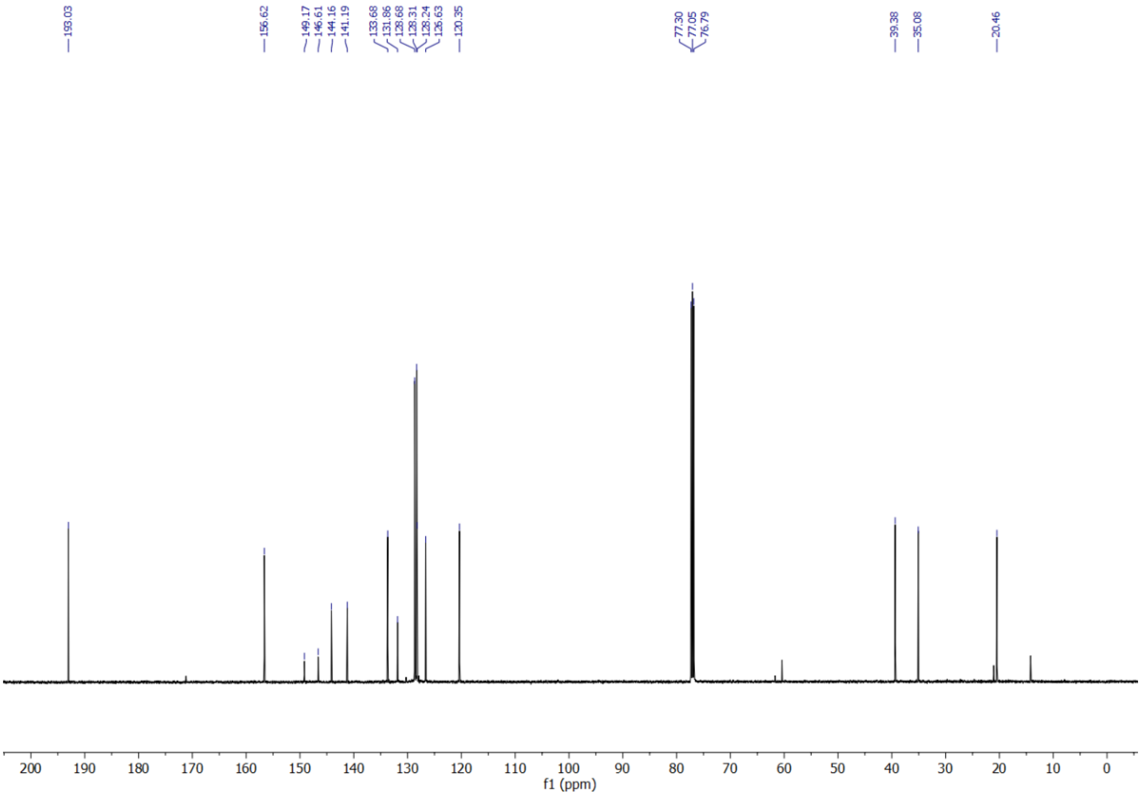
^{19}**F NMR** (471 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

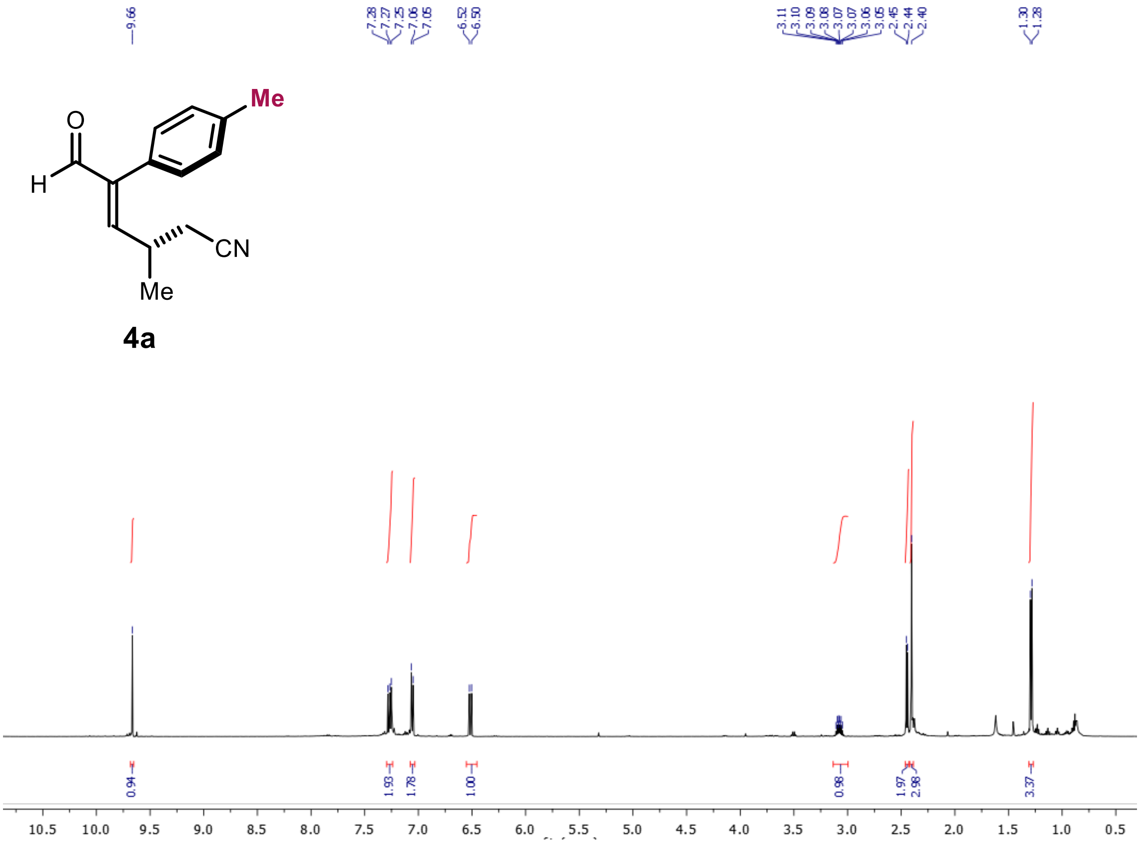


^{13}C NMR (126 MHz, $CDCl_3$)

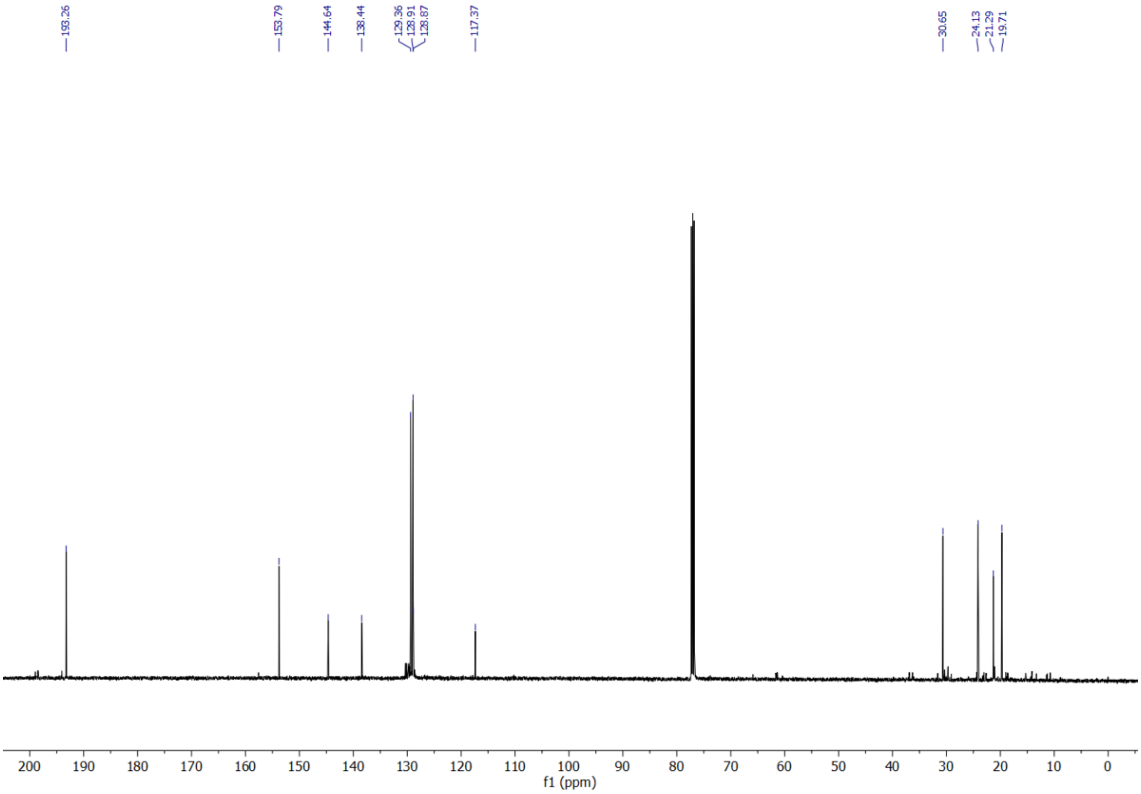


^{1}H NMR (500 MHz, $CDCl_3$)

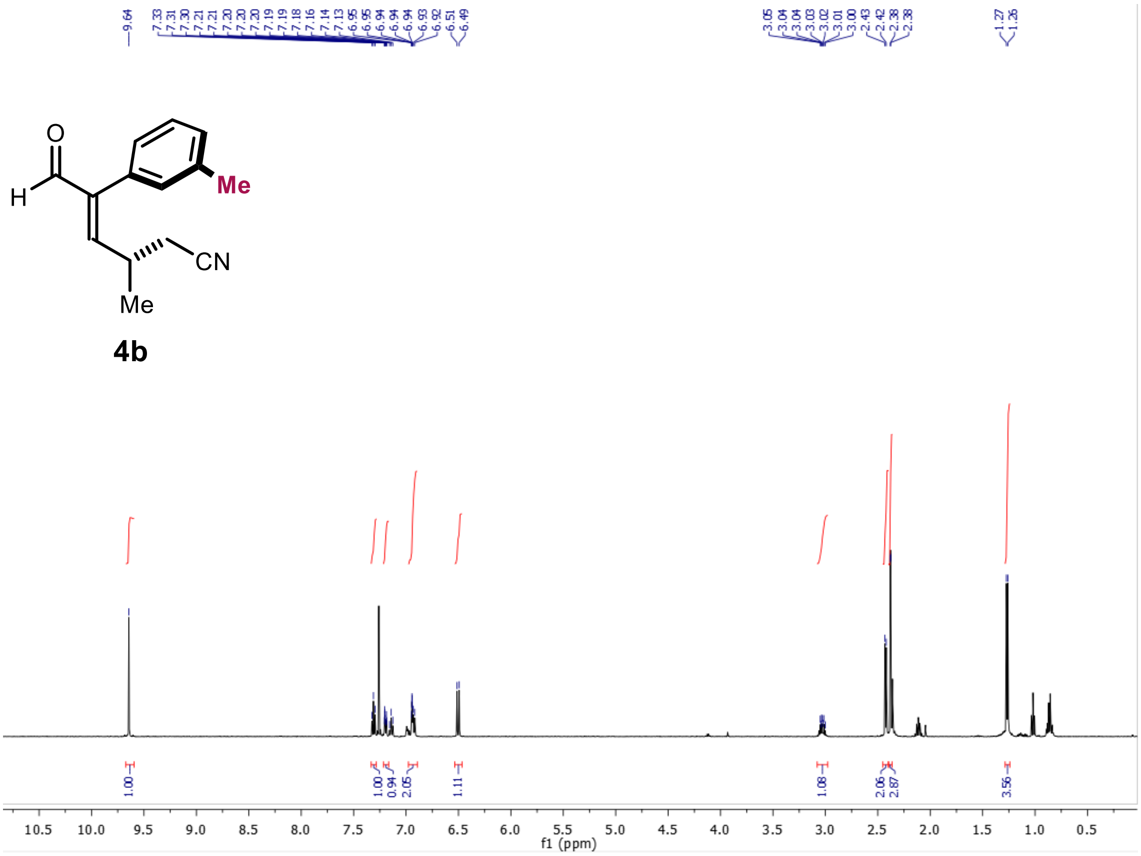
4a



^{13}C NMR (126 MHz, $CDCl_3$)

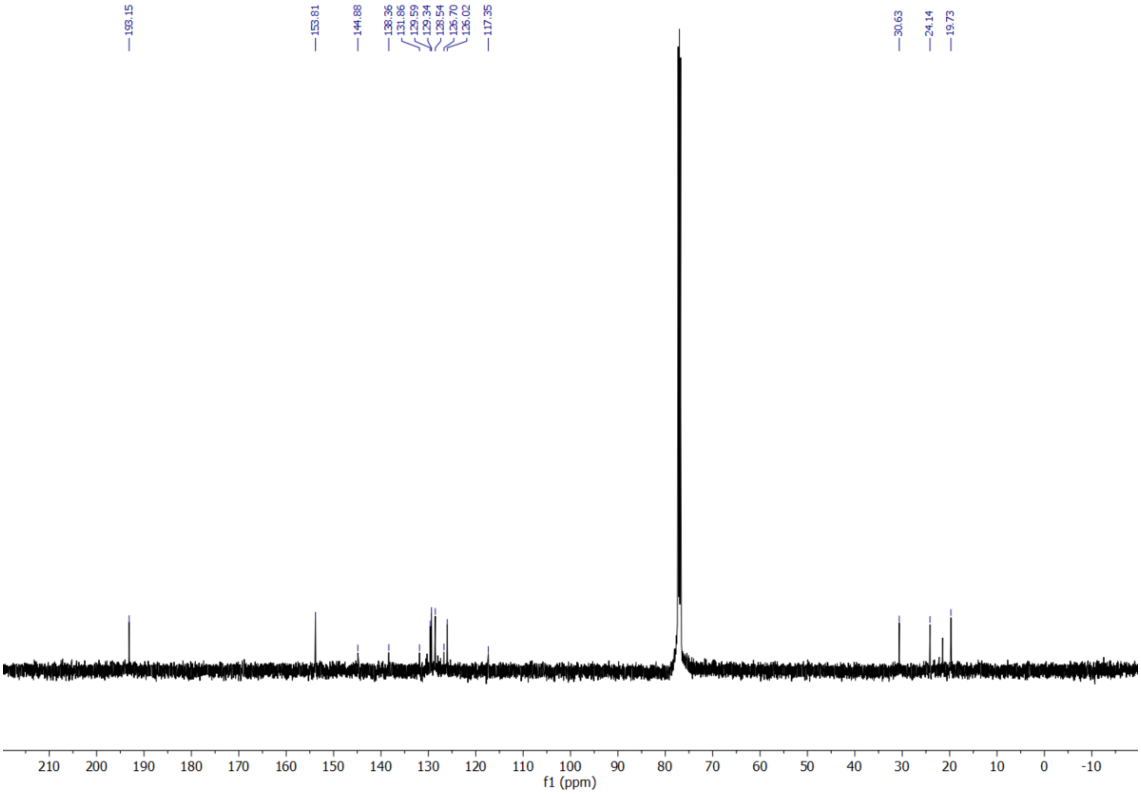


^{1}**H NMR** (500 MHz, CDCl$_3$)

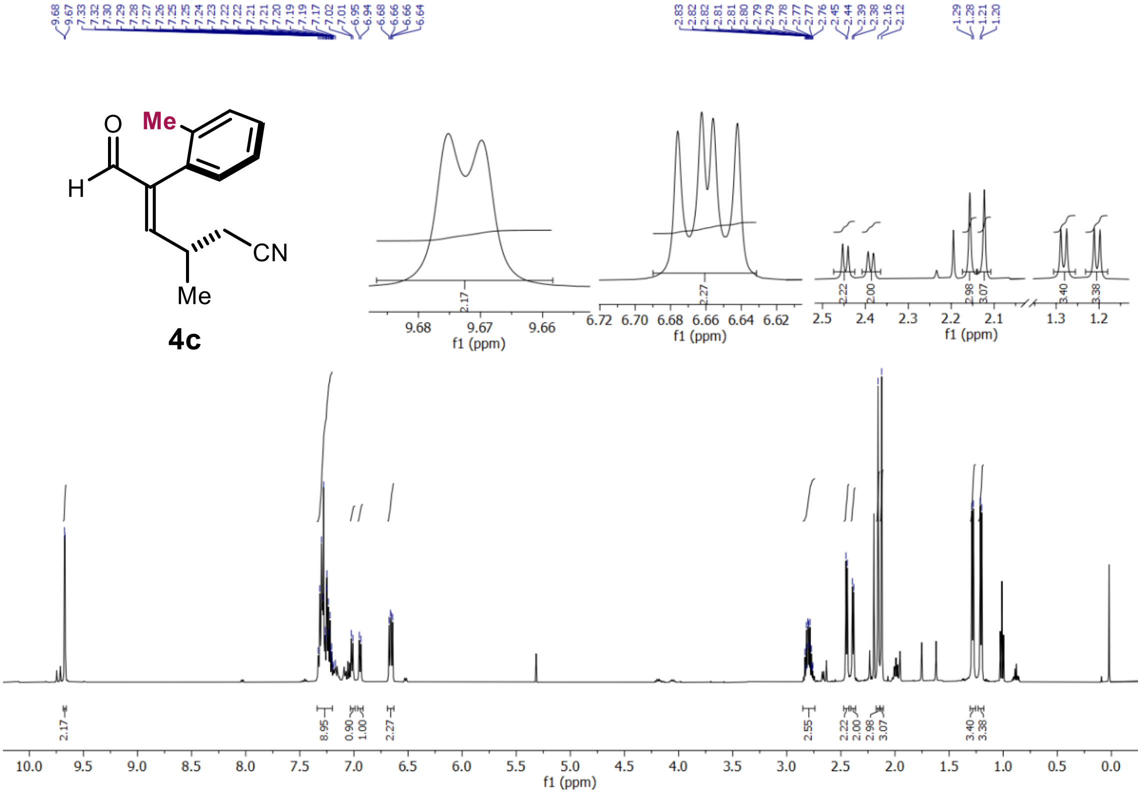


4b

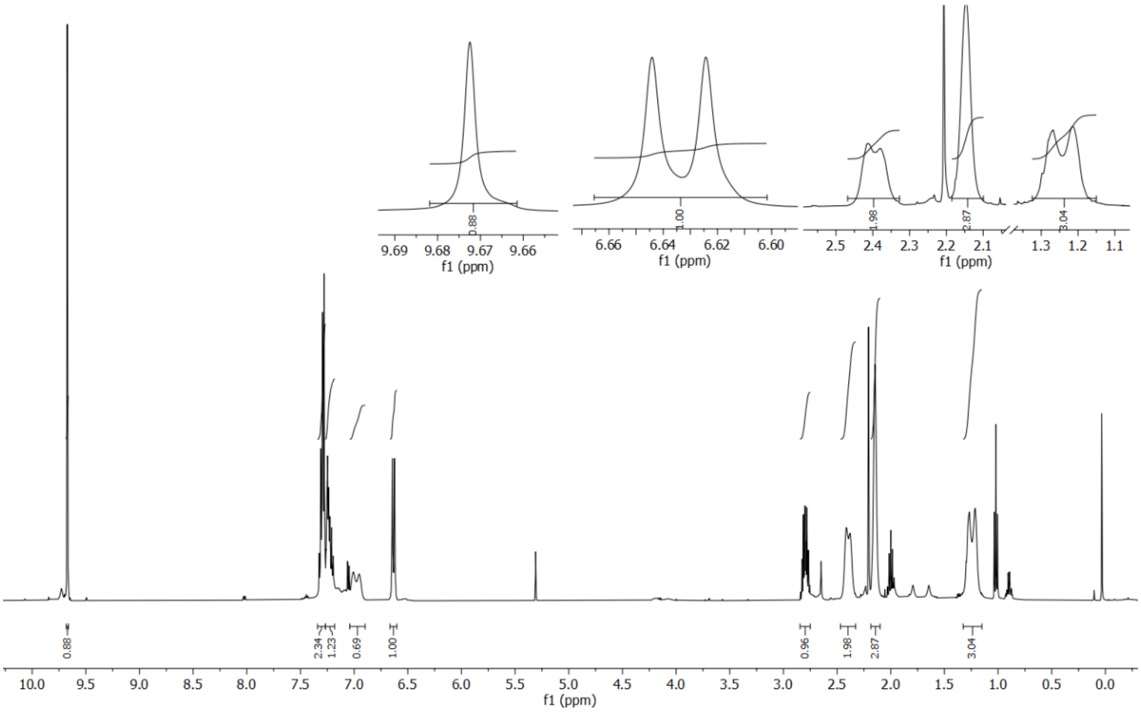
^{13}**C NMR** (126 MHz, CDCl$_3$)



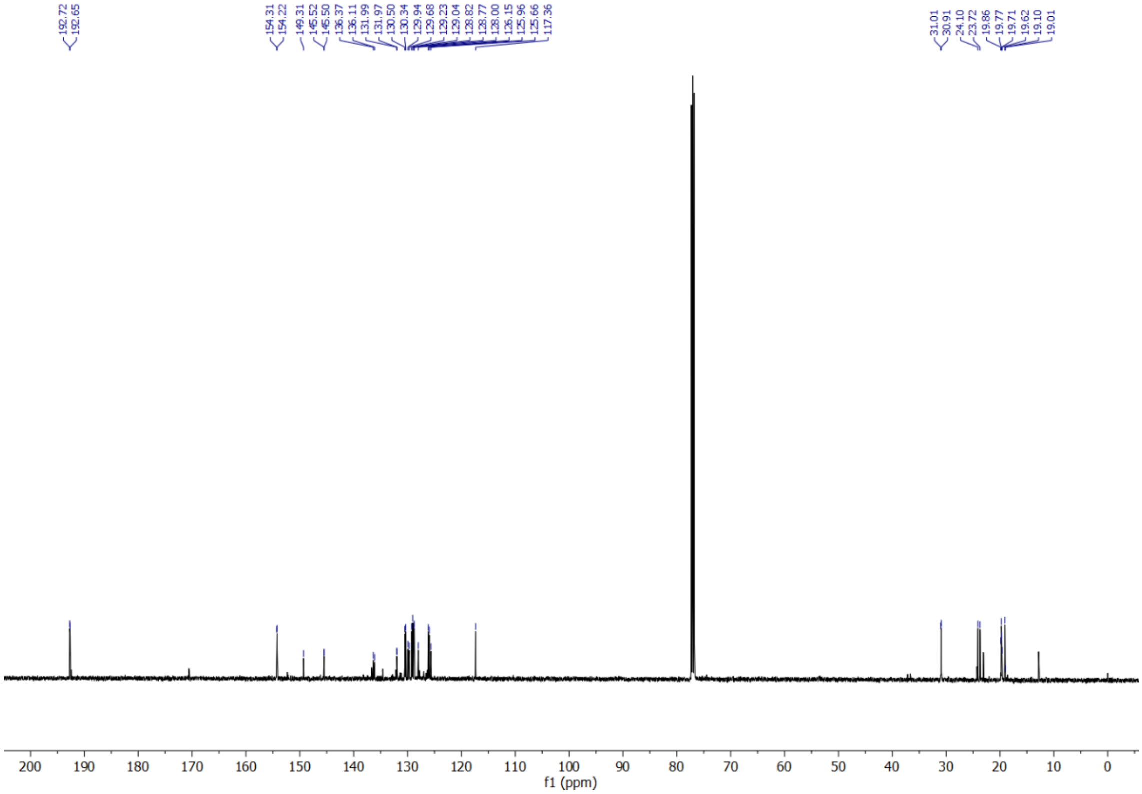
^{1}H NMR (500 MHz, CDCl$_3$, 25 °C)



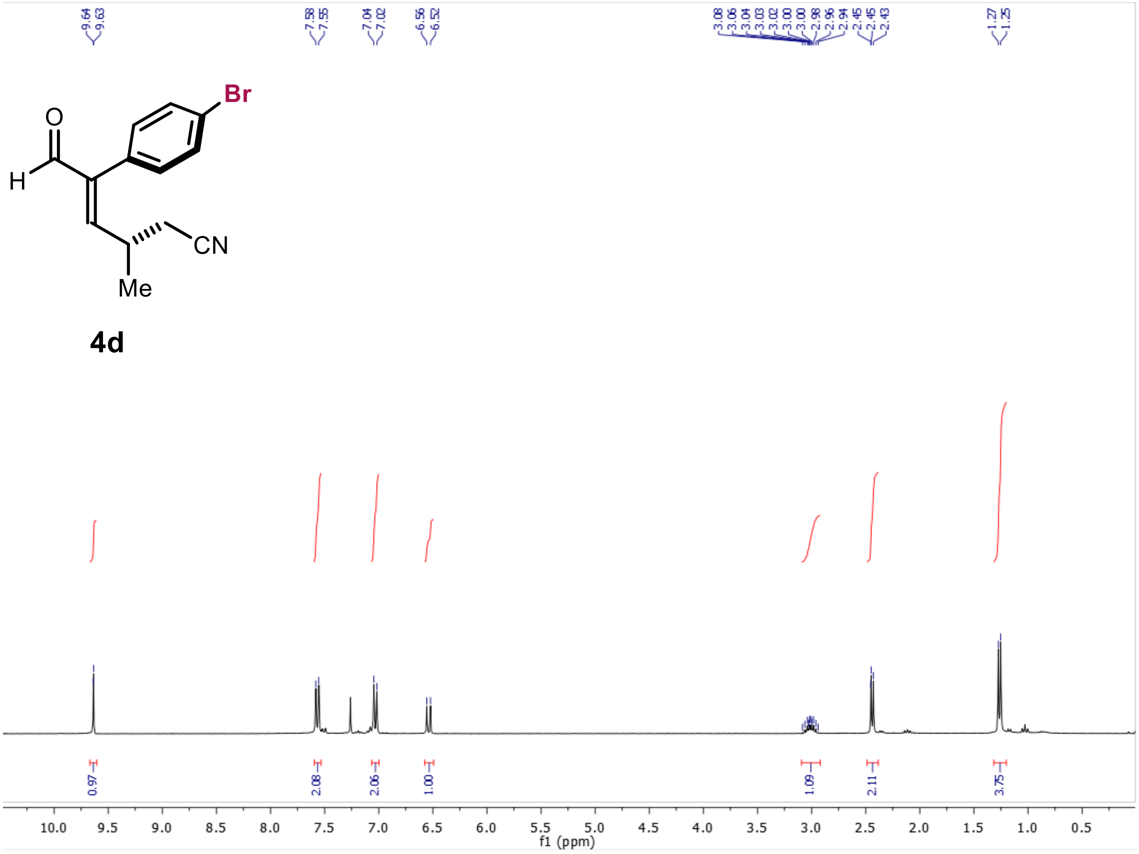
^{1}H NMR (500 MHz, CDCl$_3$, 60 °C)



^{13}C NMR (126 MHz, $CDCl_3$)

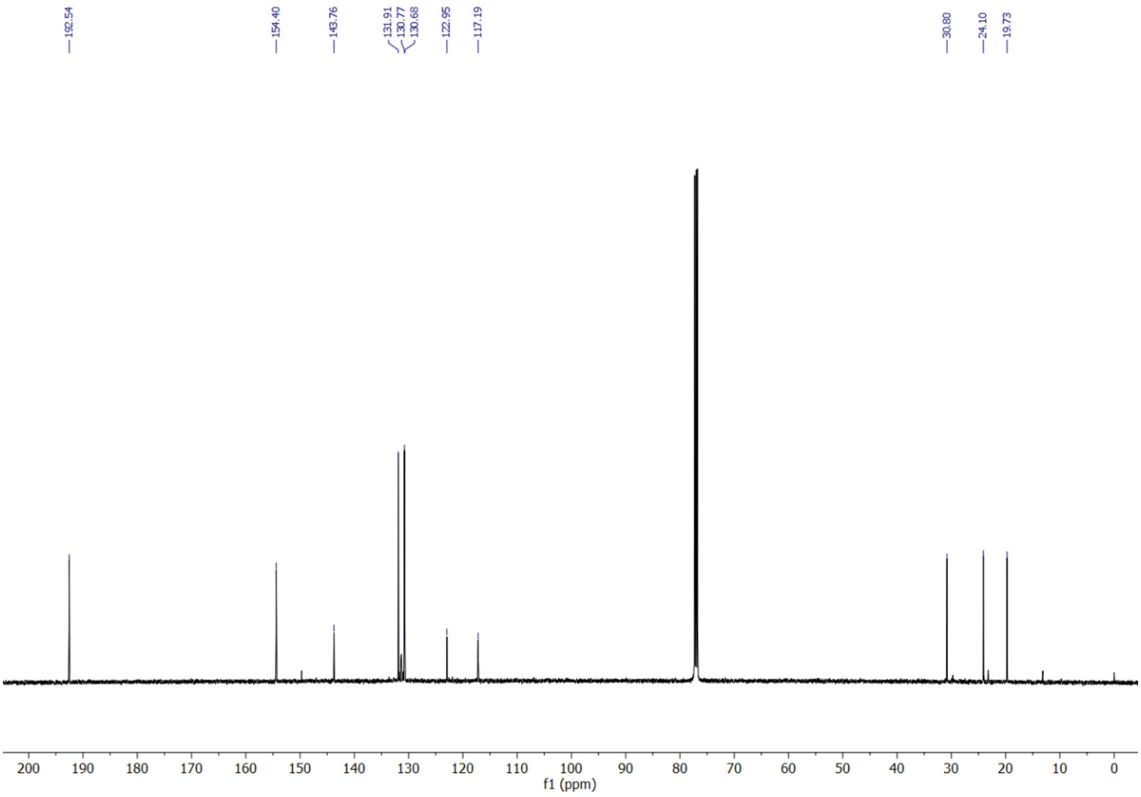


^{1}H NMR (500 MHz, $CDCl_3$)

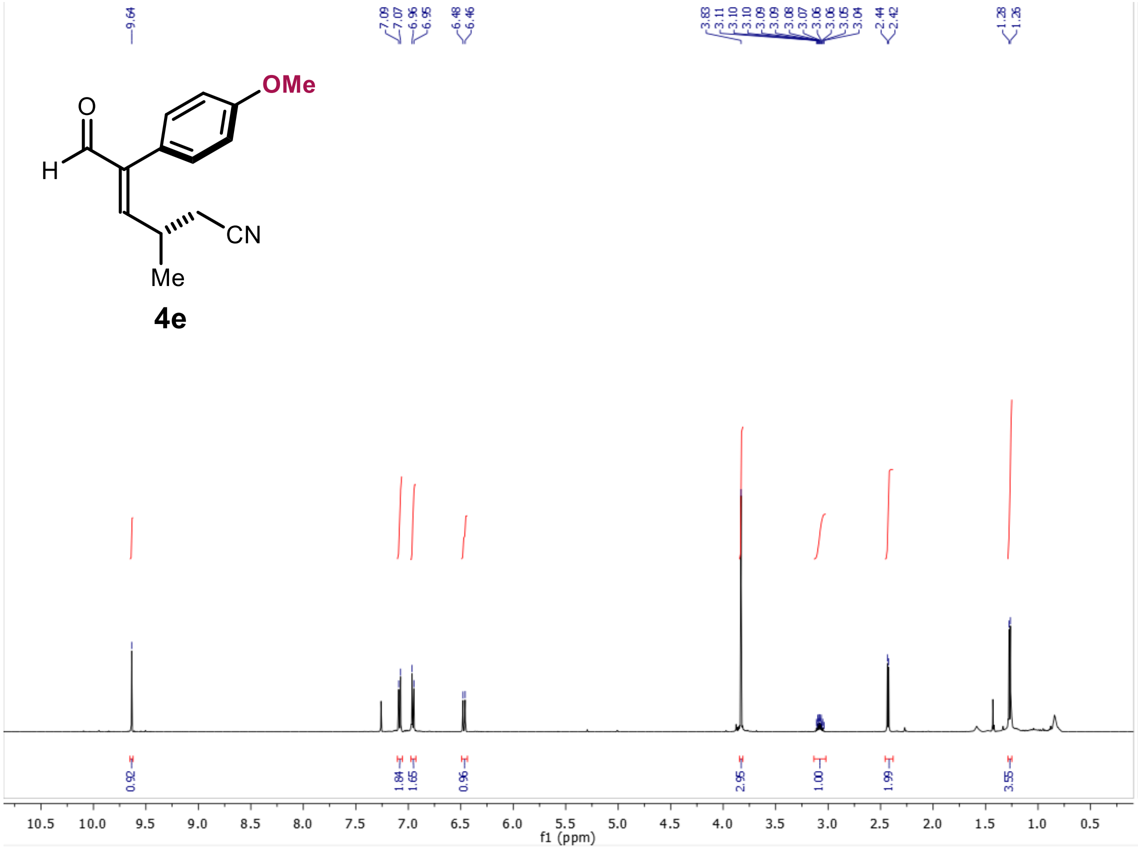


4d

^{13}C NMR (126 MHz, $CDCl_3$)

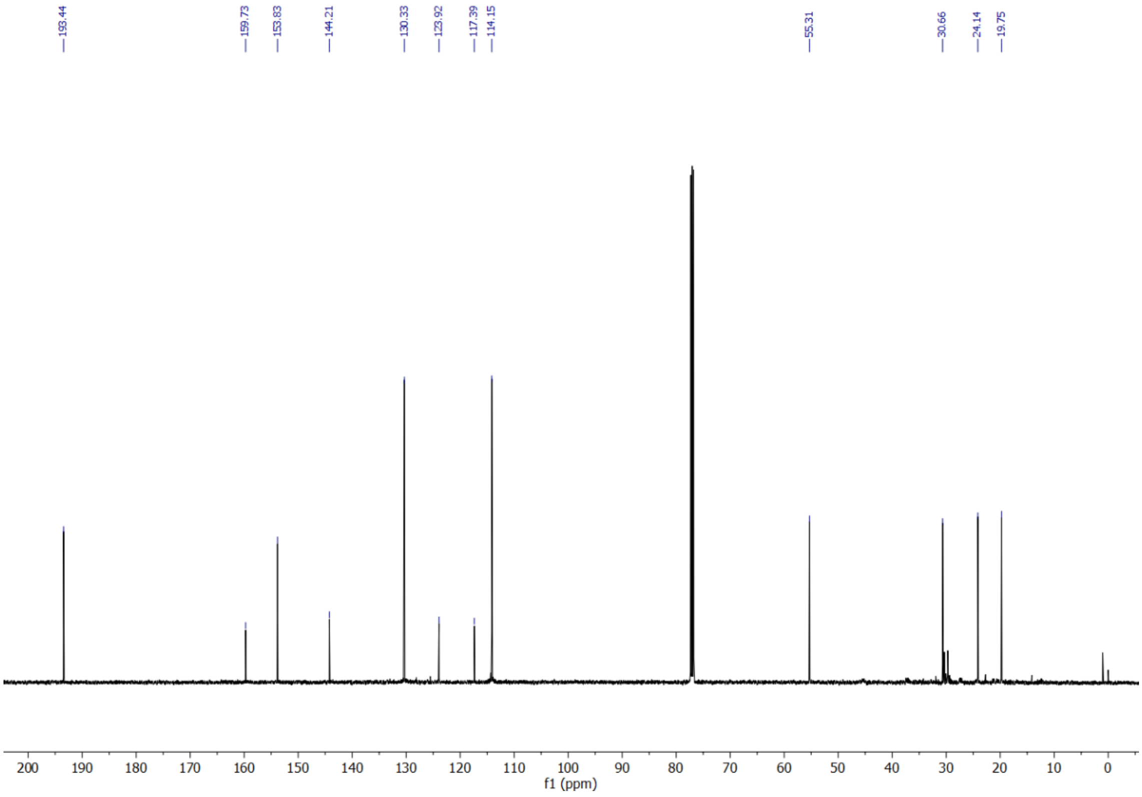


^{1}H NMR (500 MHz, $CDCl_3$)

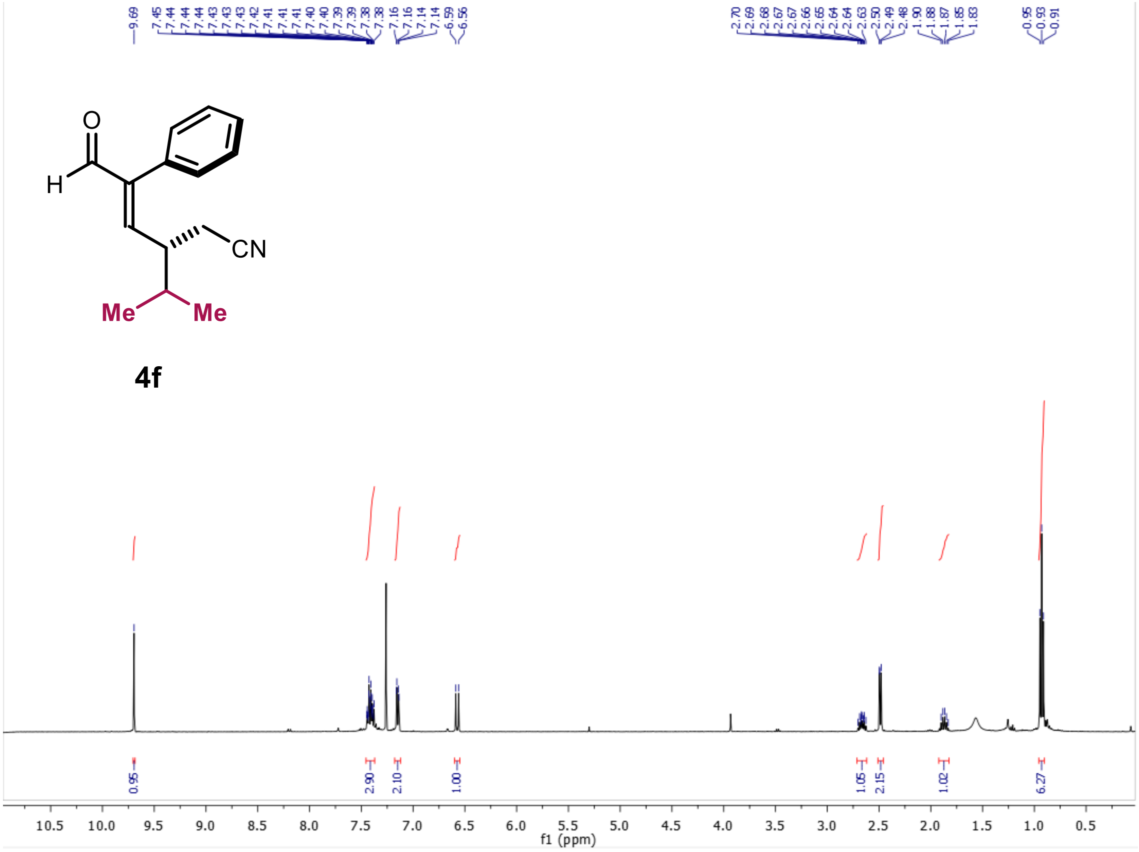


4e

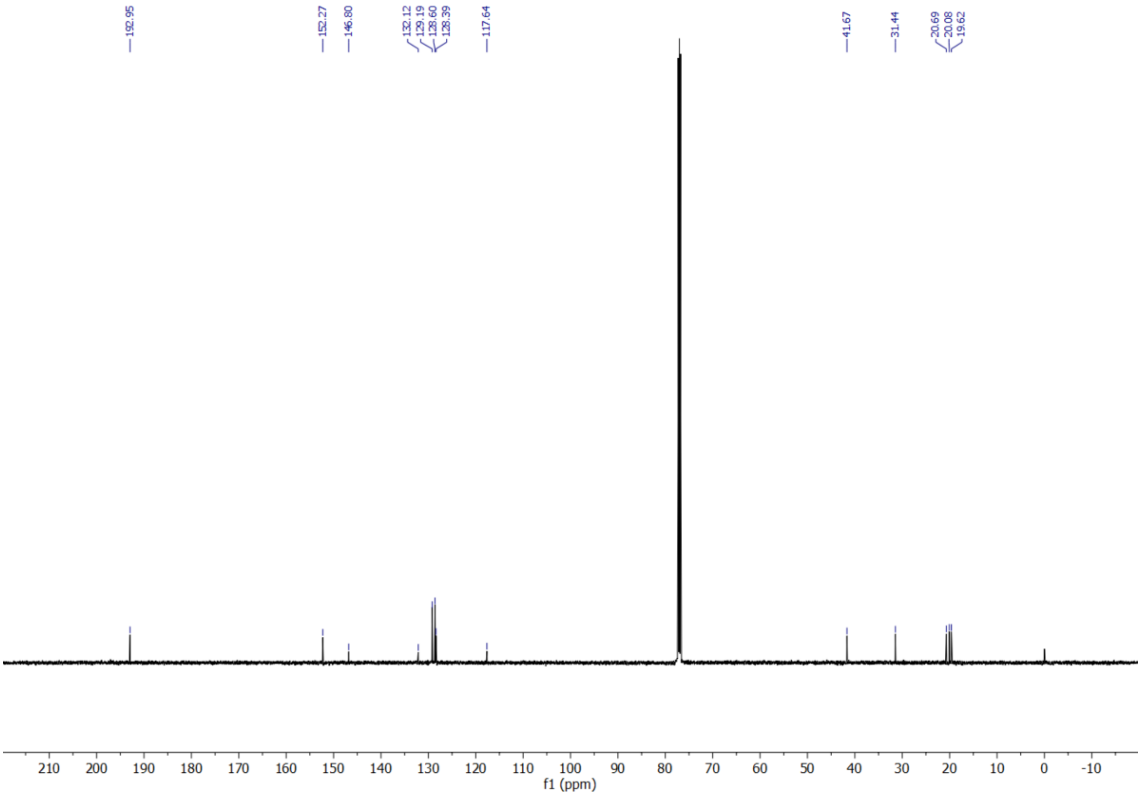
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}**H NMR** (500 MHz, CDCl$_3$)

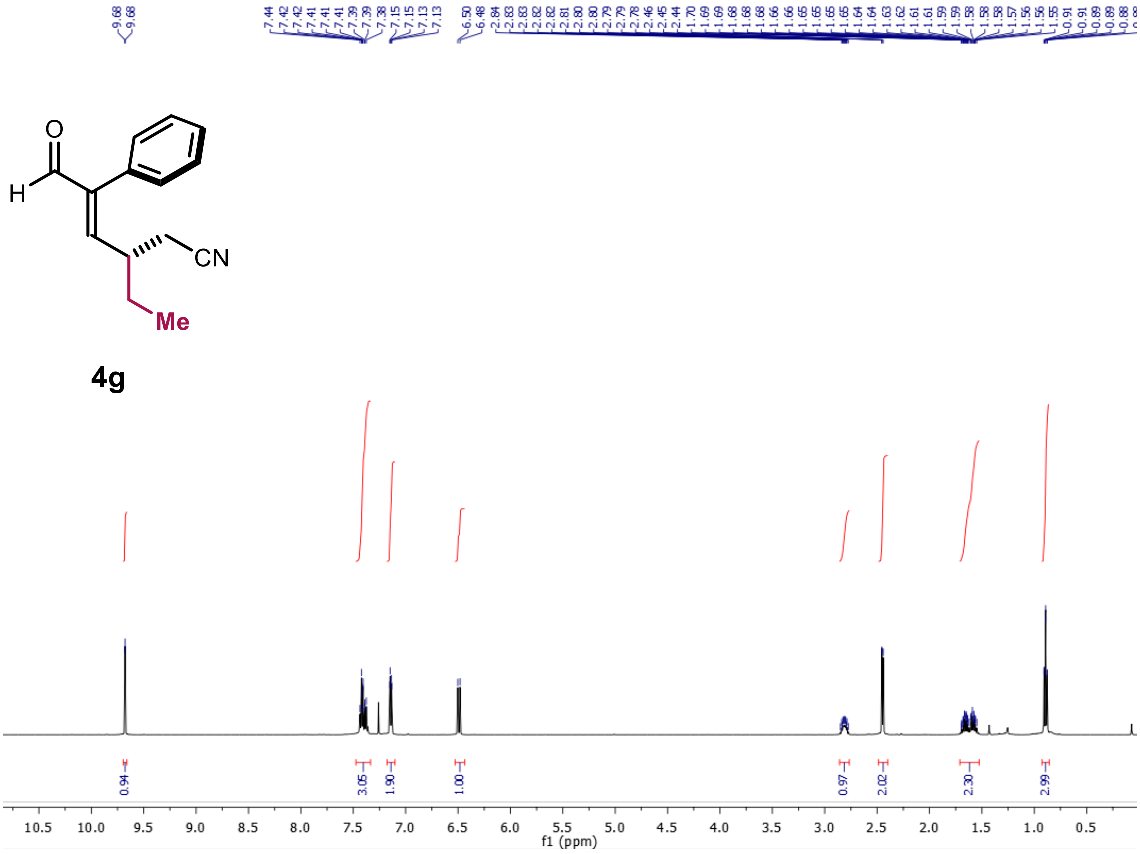


^{13}**C NMR** (126 MHz, CDCl$_3$)

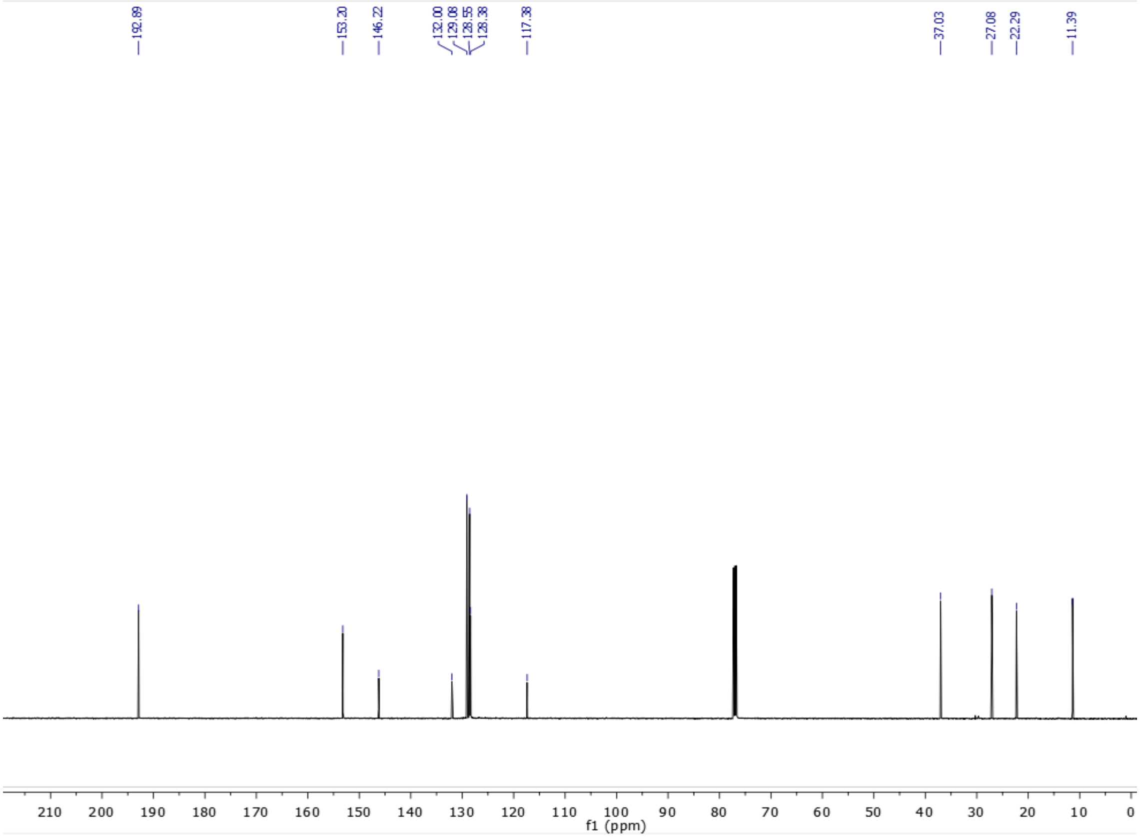


^{1}H NMR (500 MHz, CDCl$_3$)

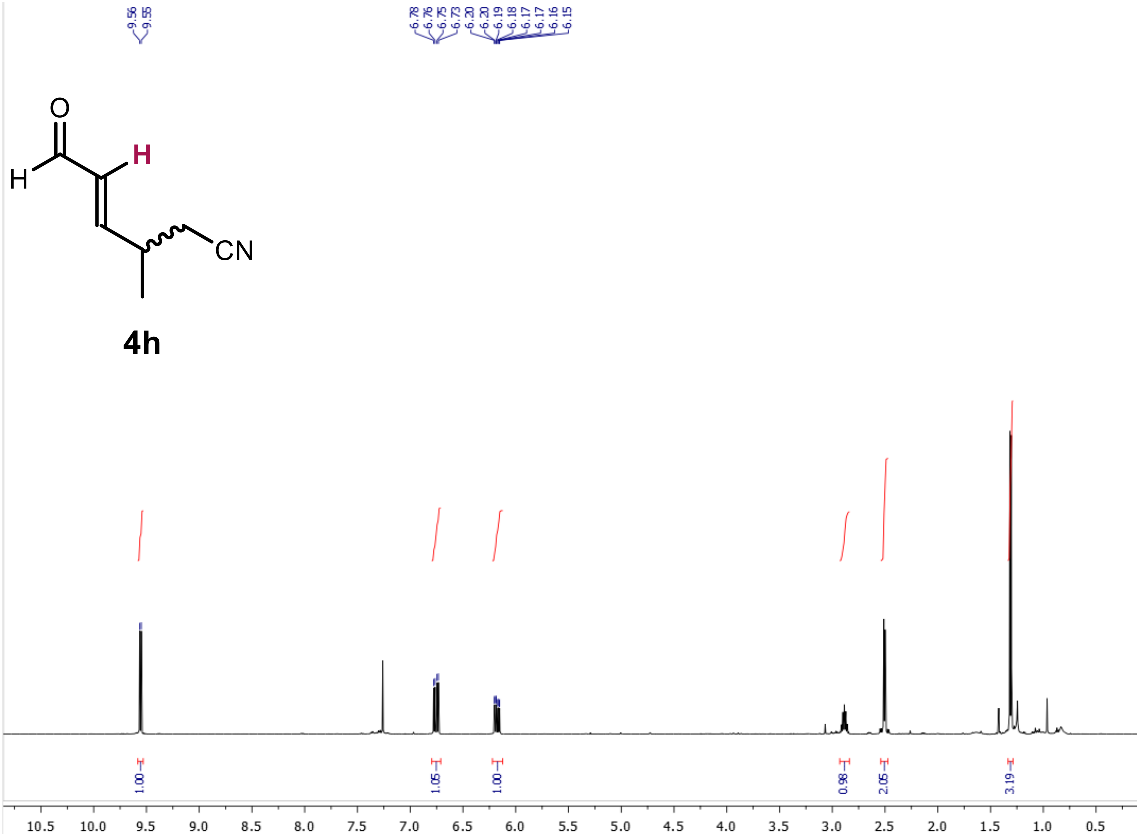
4g



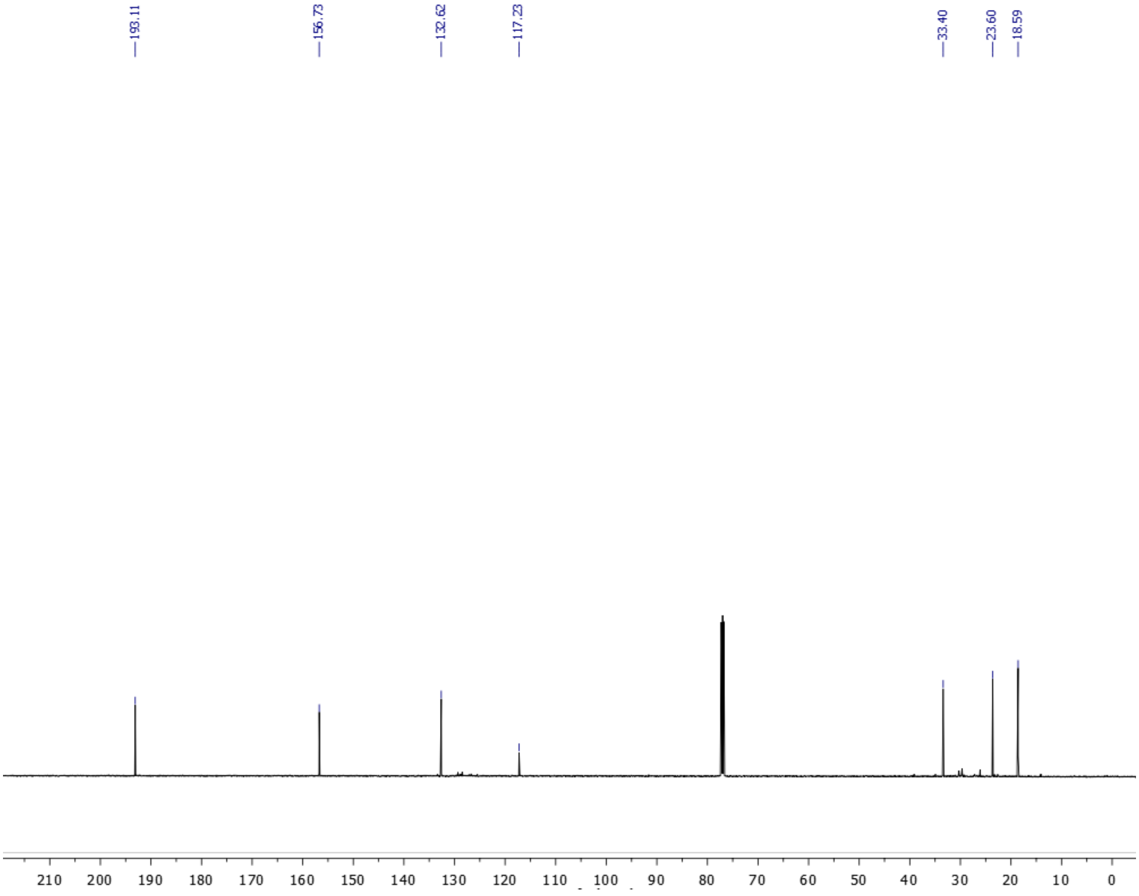
^{13}C NMR (126 MHz, CDCl$_3$)



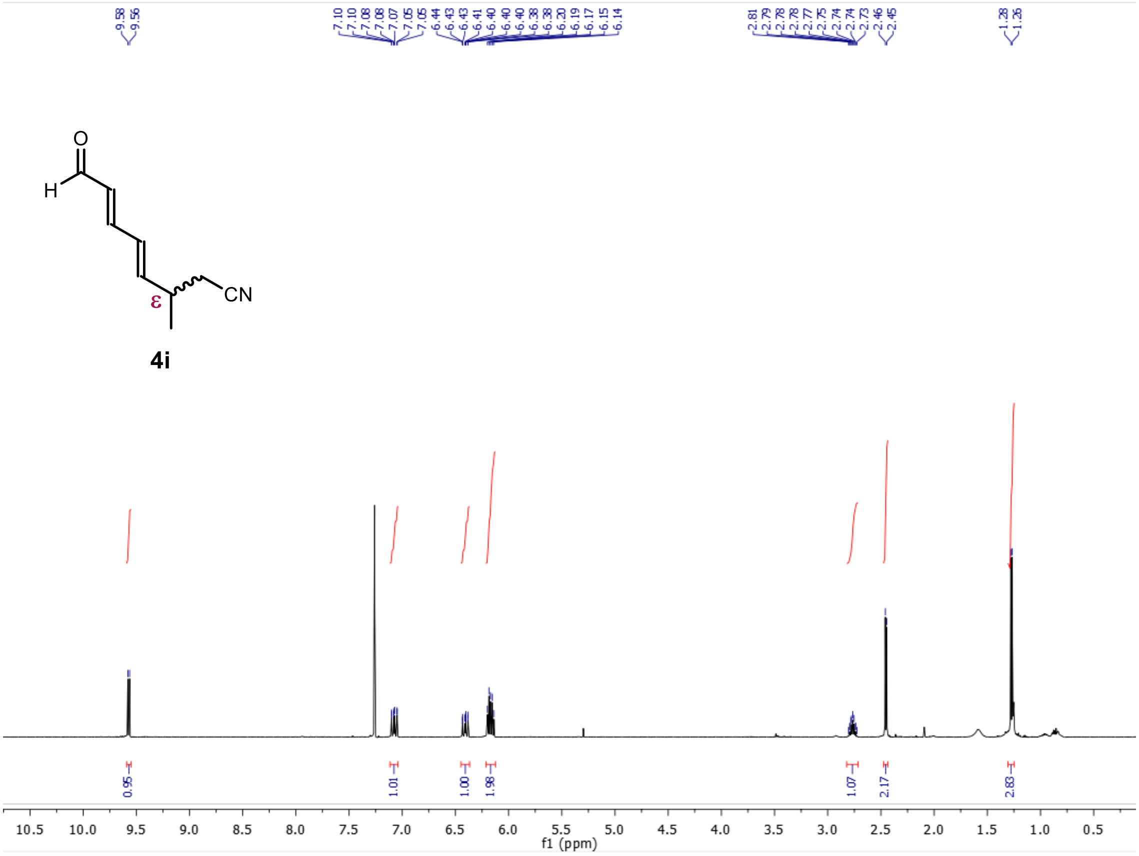
^{1}H NMR (500 MHz, CDCl$_3$)



^{13}C NMR (126 MHz, CDCl$_3$)

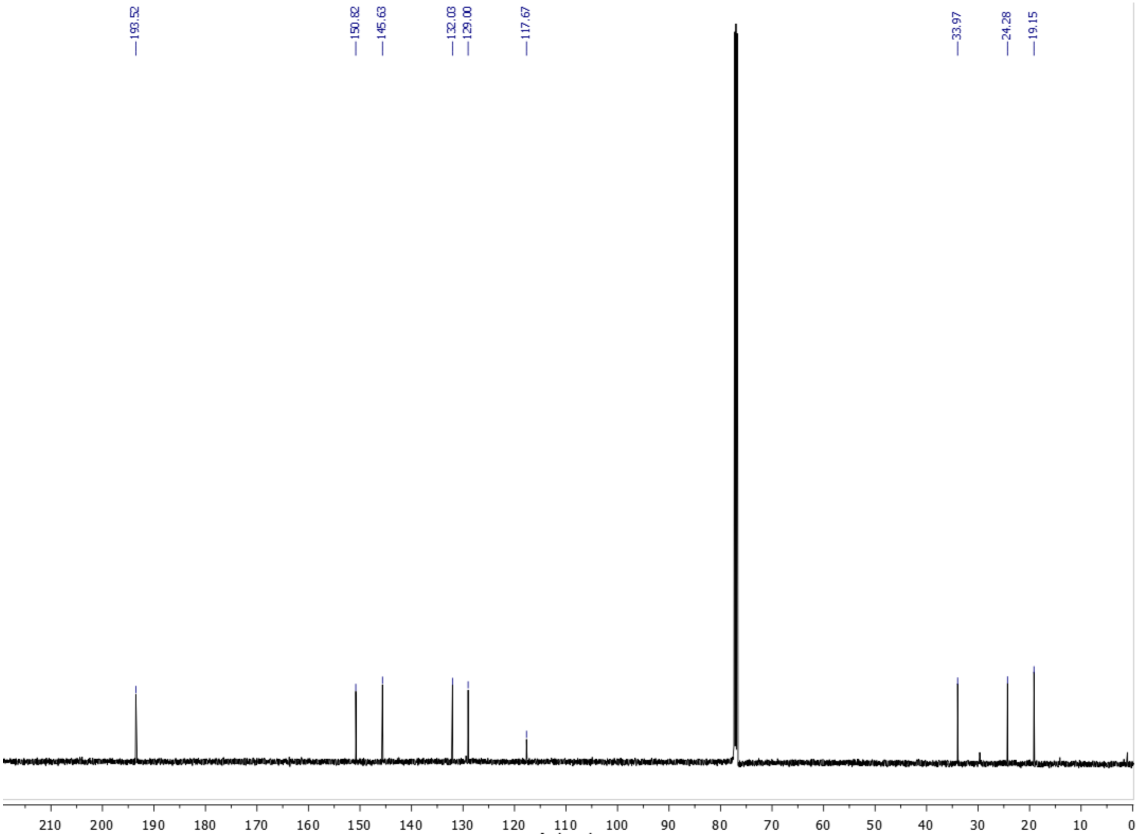


^{1}**H NMR** (500 MHz, CDCl$_3$)

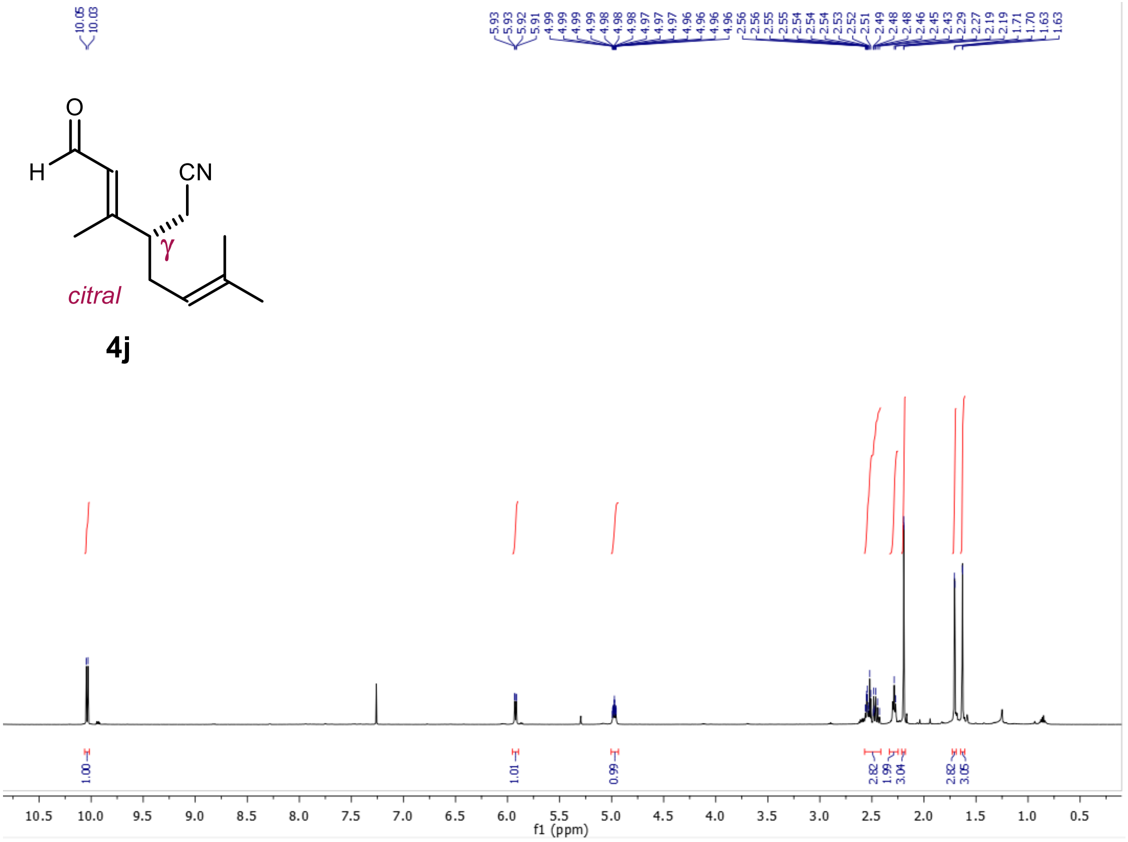


4i

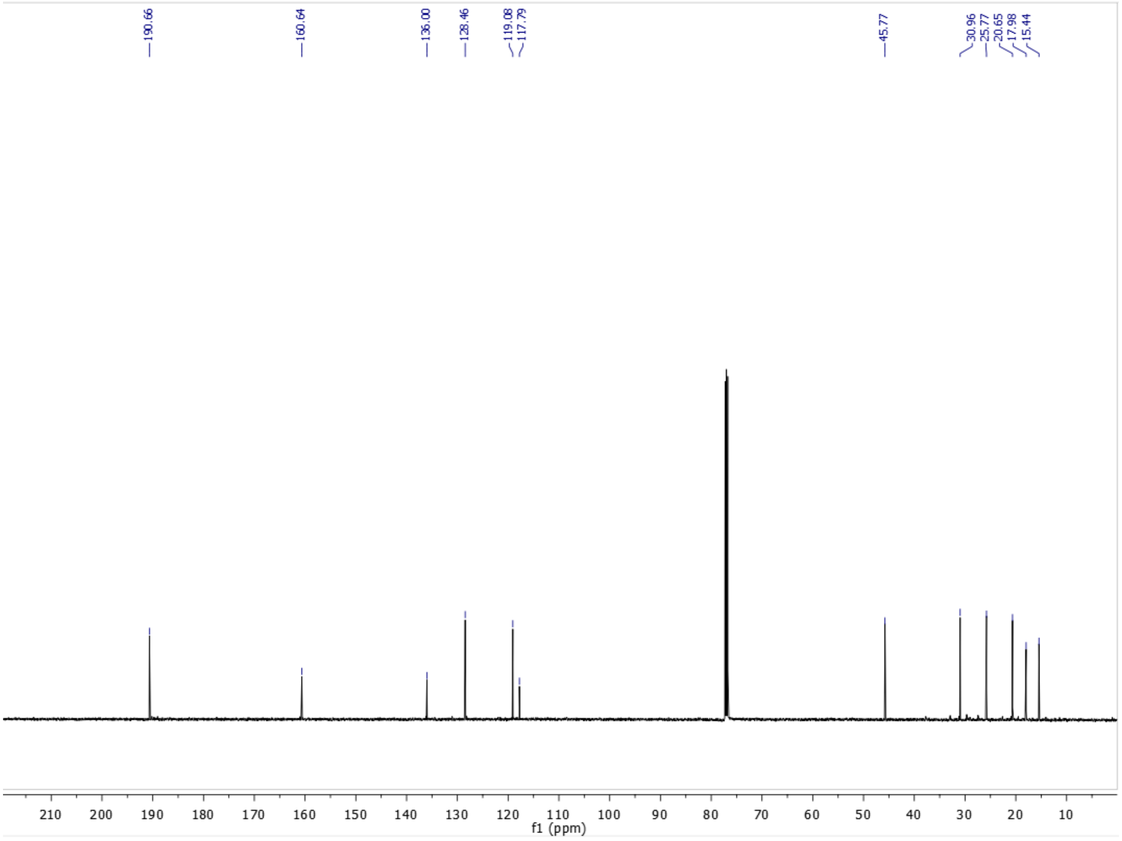
^{13}**C NMR** (126 MHz, CDCl$_3$)



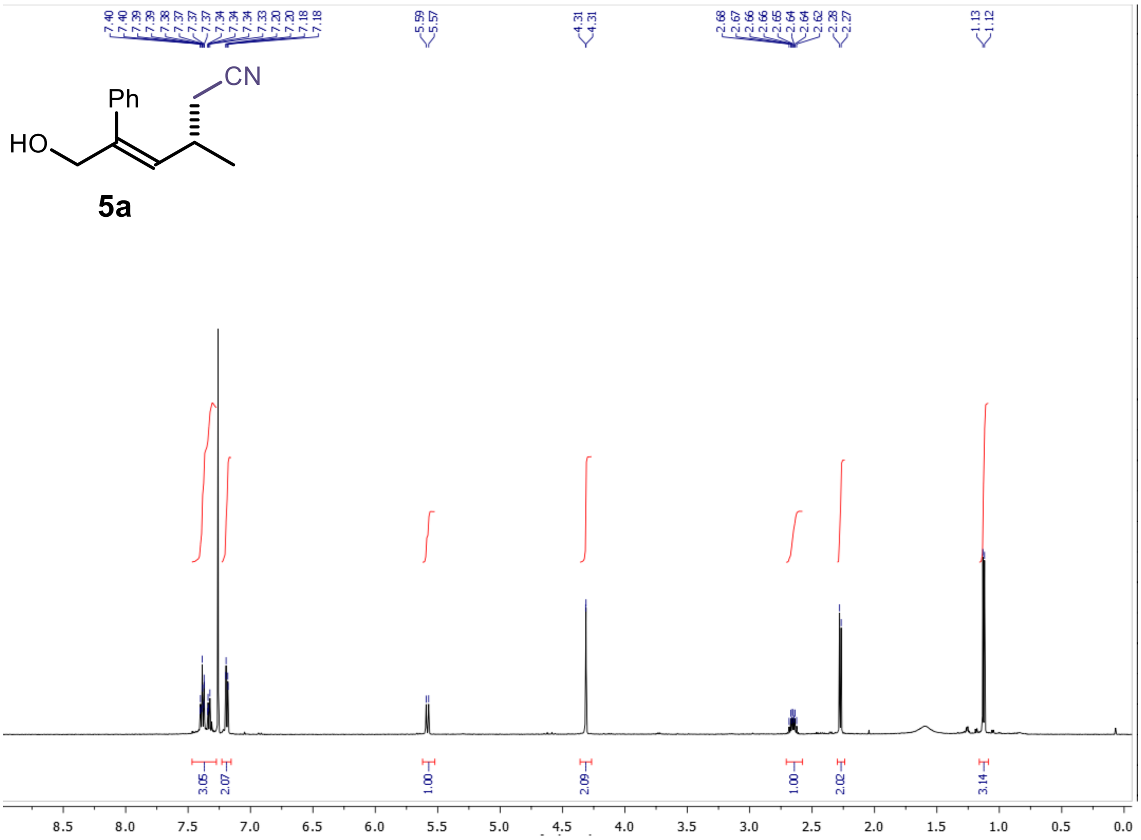
^{1}H NMR (500 MHz, CDCl$_3$)



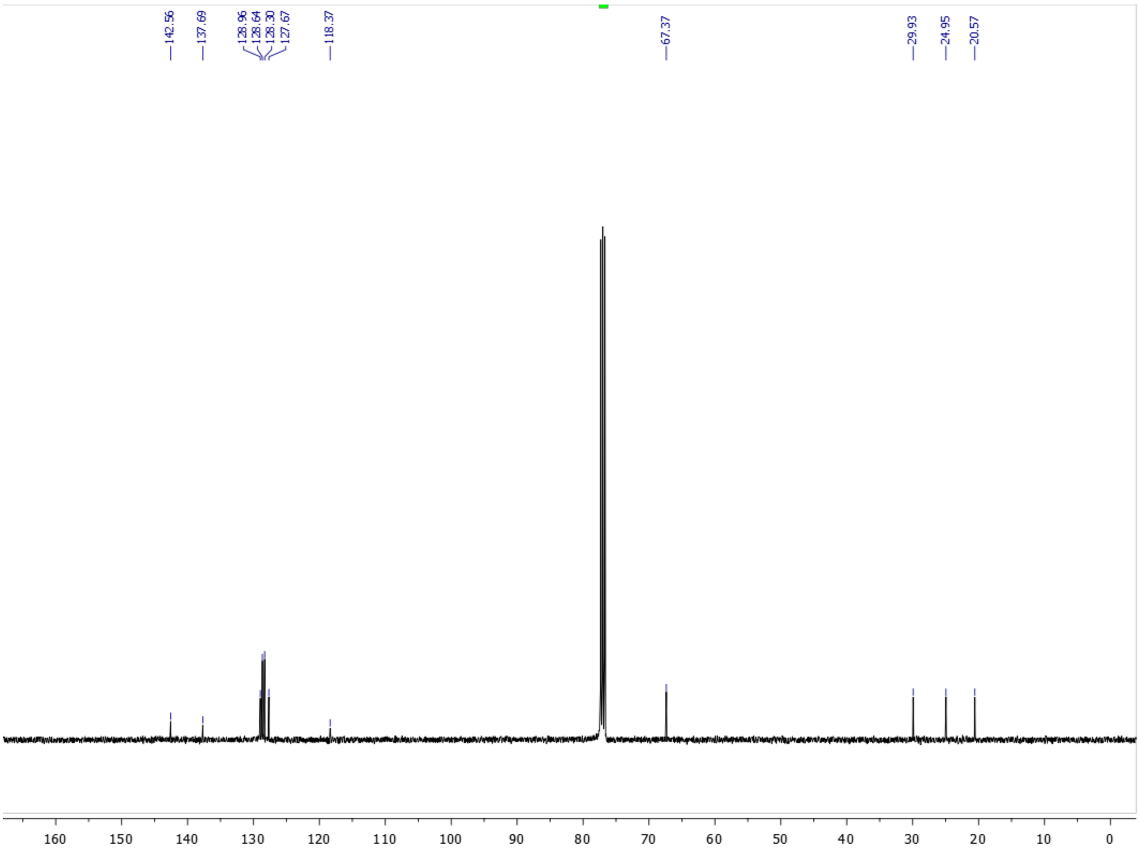
^{13}C NMR (126 MHz, CDCl$_3$)



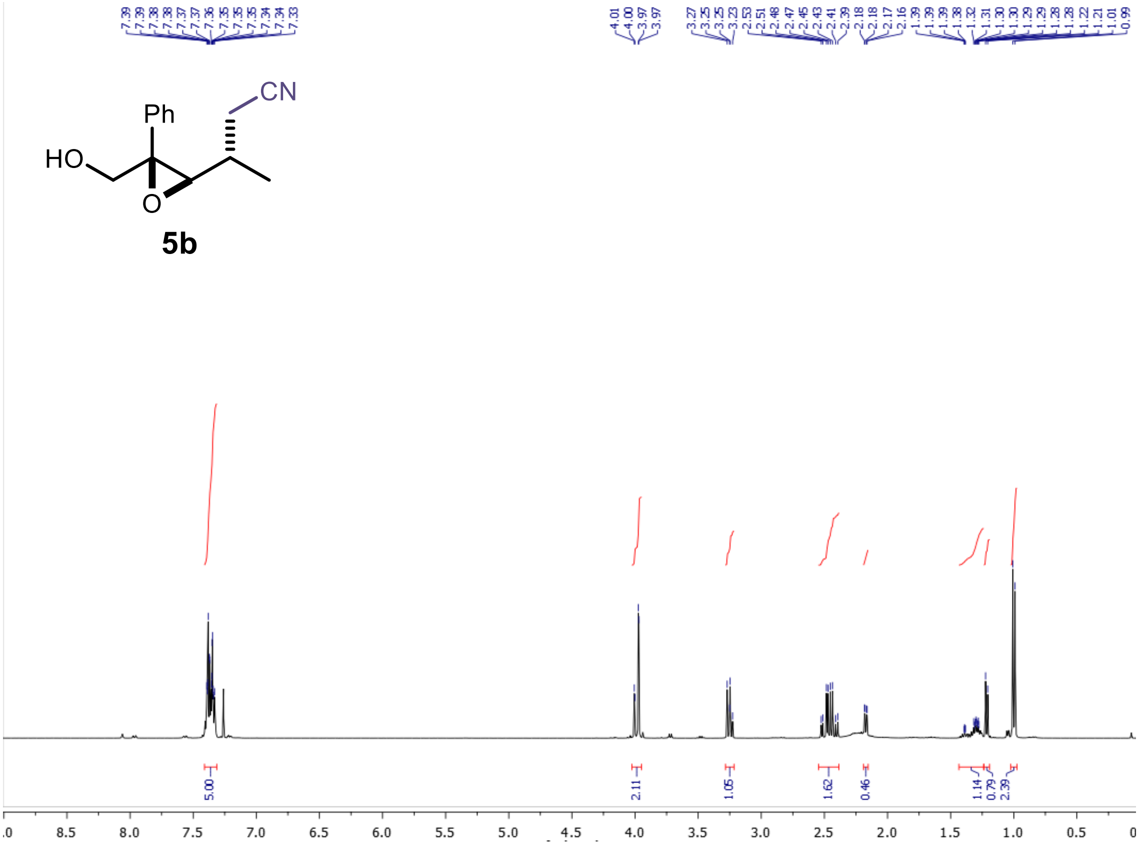
^{1}**H NMR** (500 MHz, $CDCl_3$)



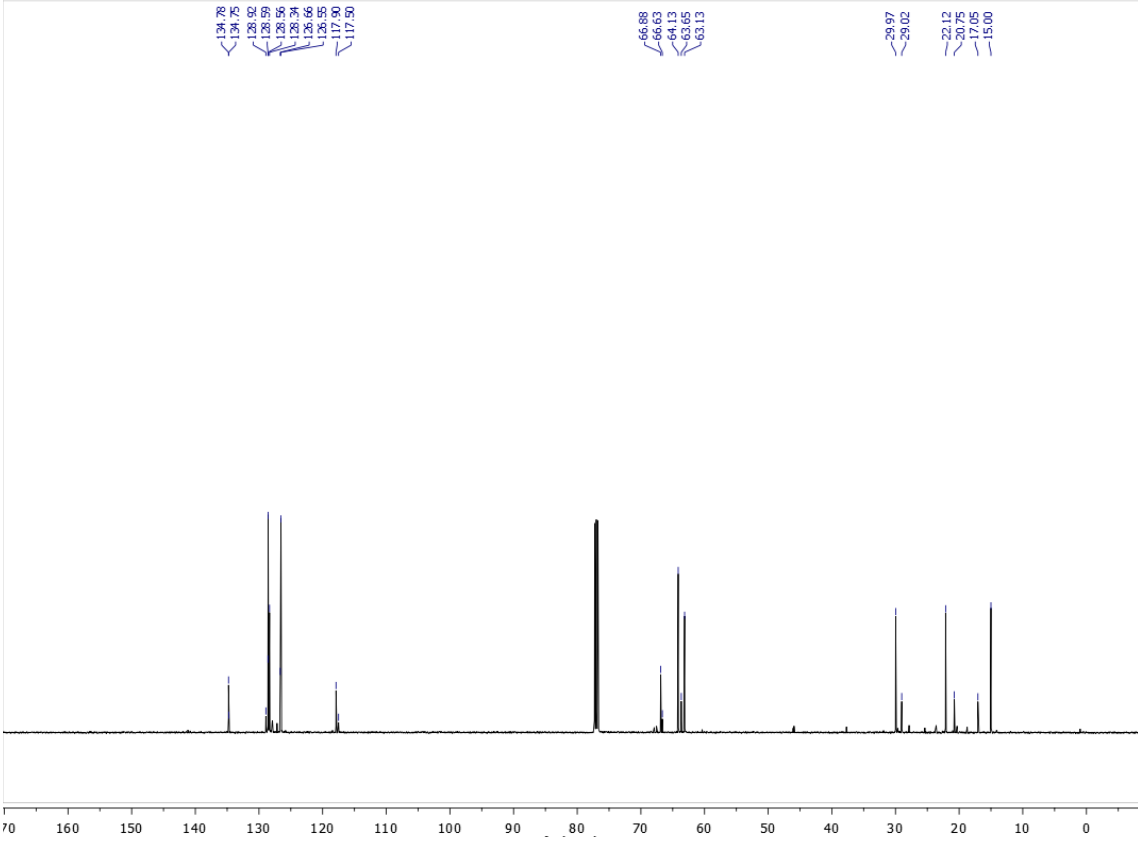
^{13}**C NMR** (126 MHz, $CDCl_3$)



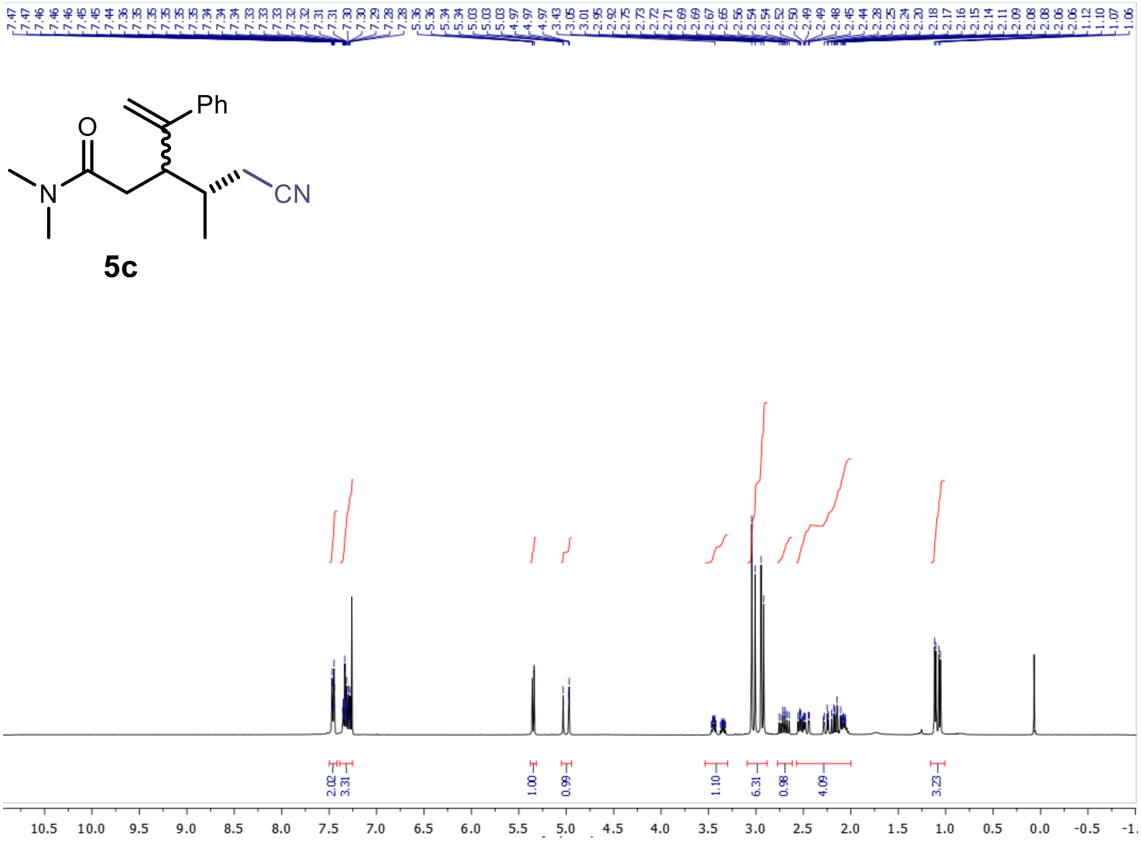
^{1}**H NMR** (500 MHz, CDCl$_3$)



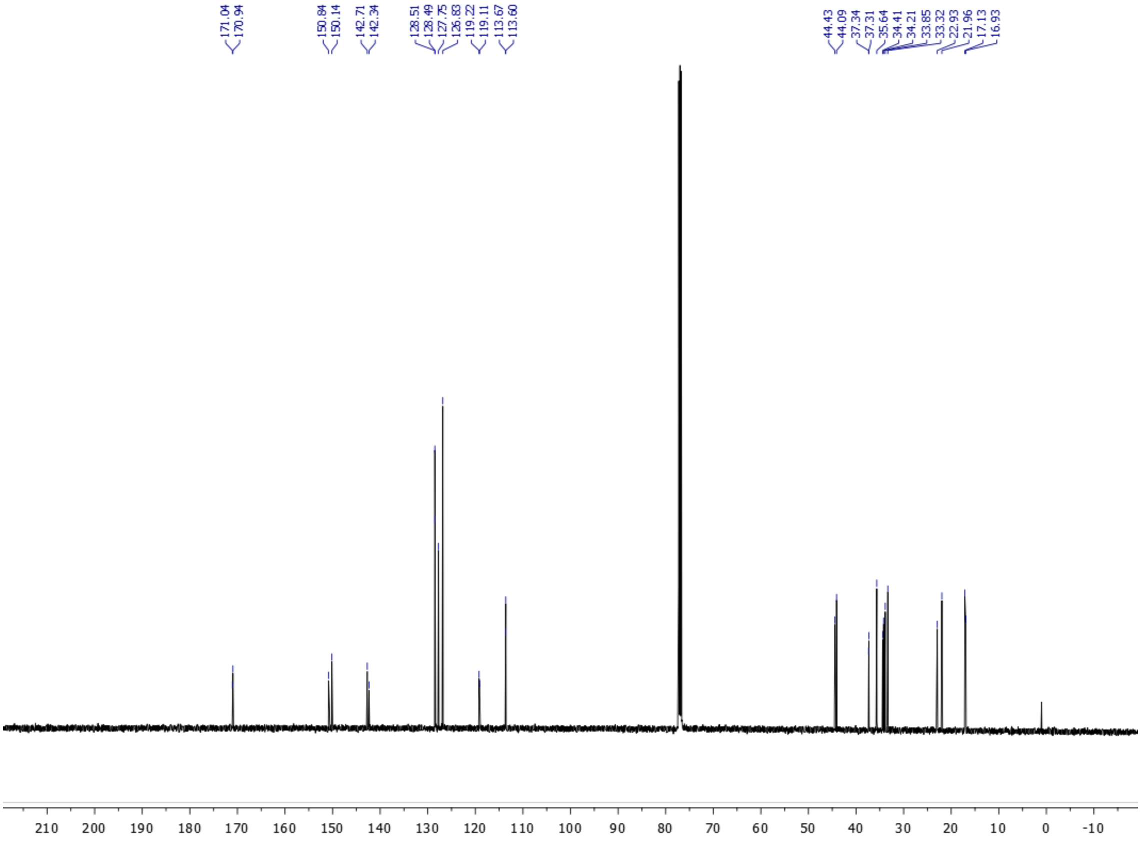
^{13}**C NMR** (126 MHz, CDCl$_3$)



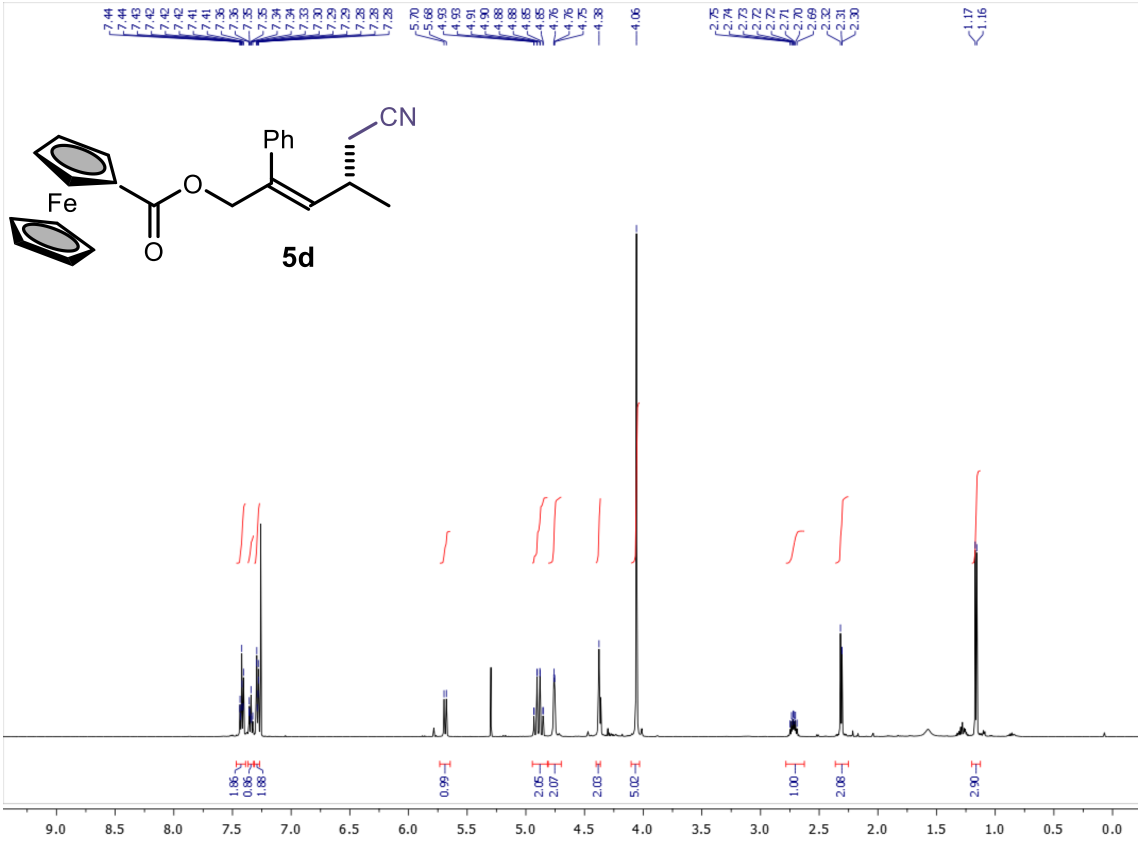
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

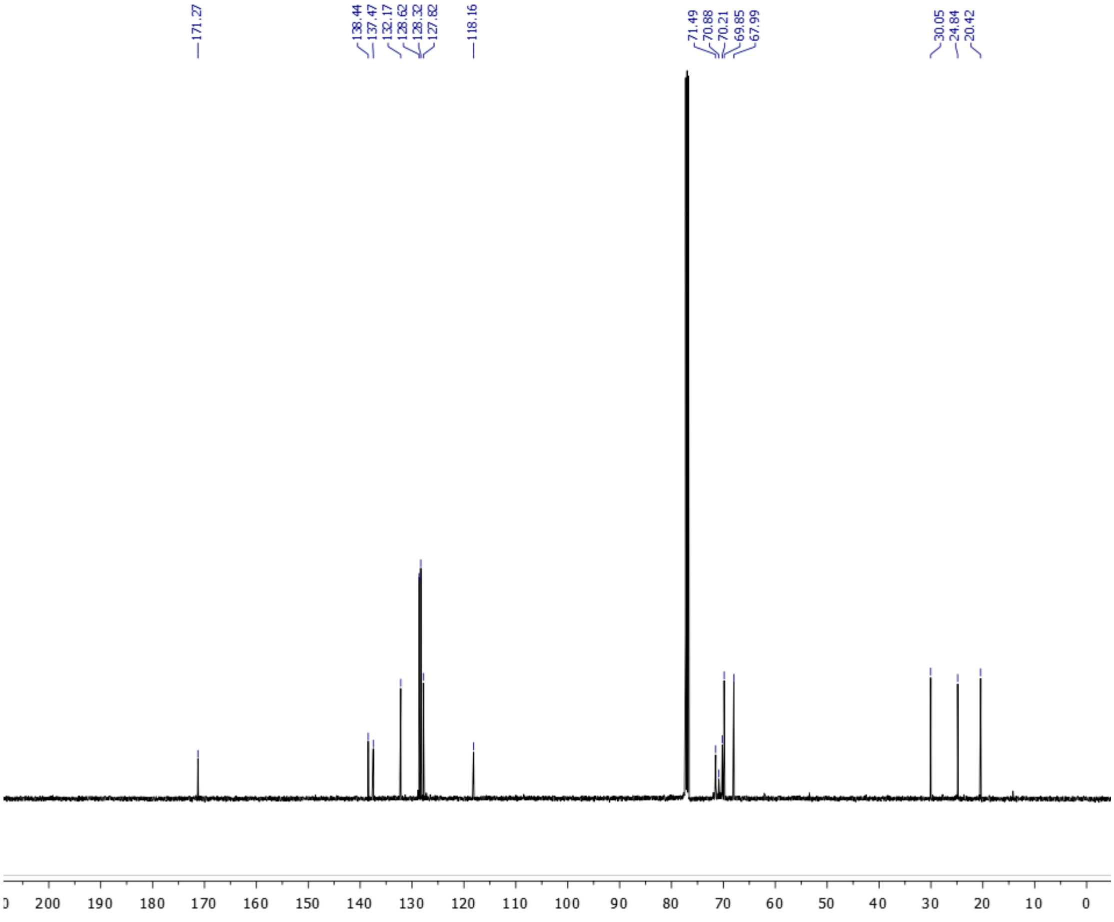


^{1}H NMR (500 MHz, CDCl$_3$)

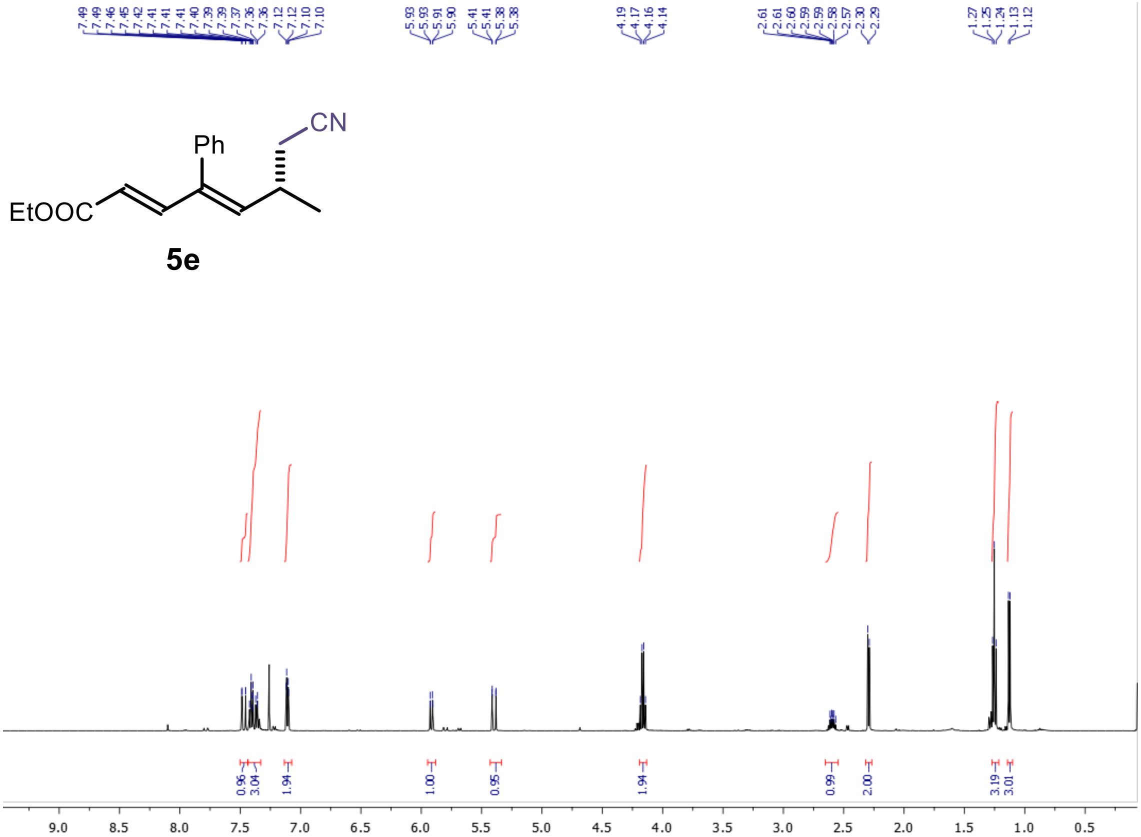


5d

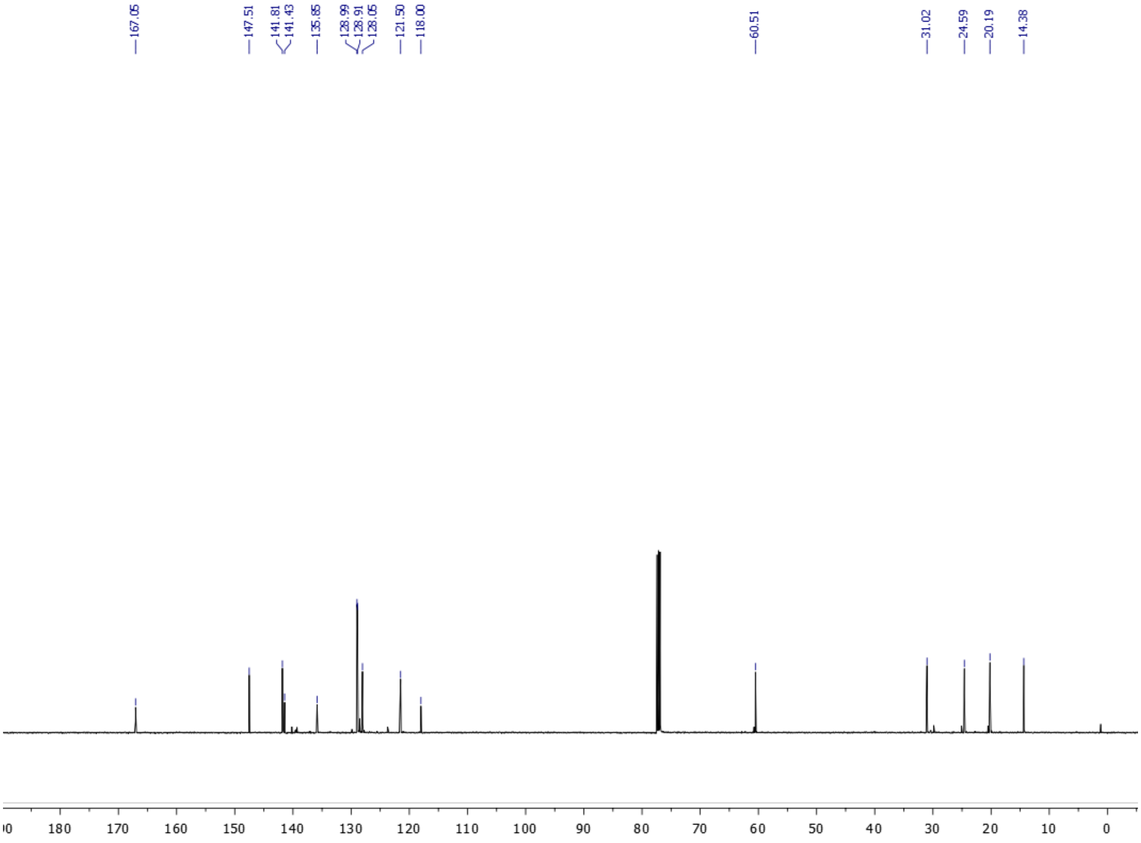
^{13}C NMR (126 MHz, CDCl$_3$)



^{1}H NMR (500 MHz, CDCl$_3$)

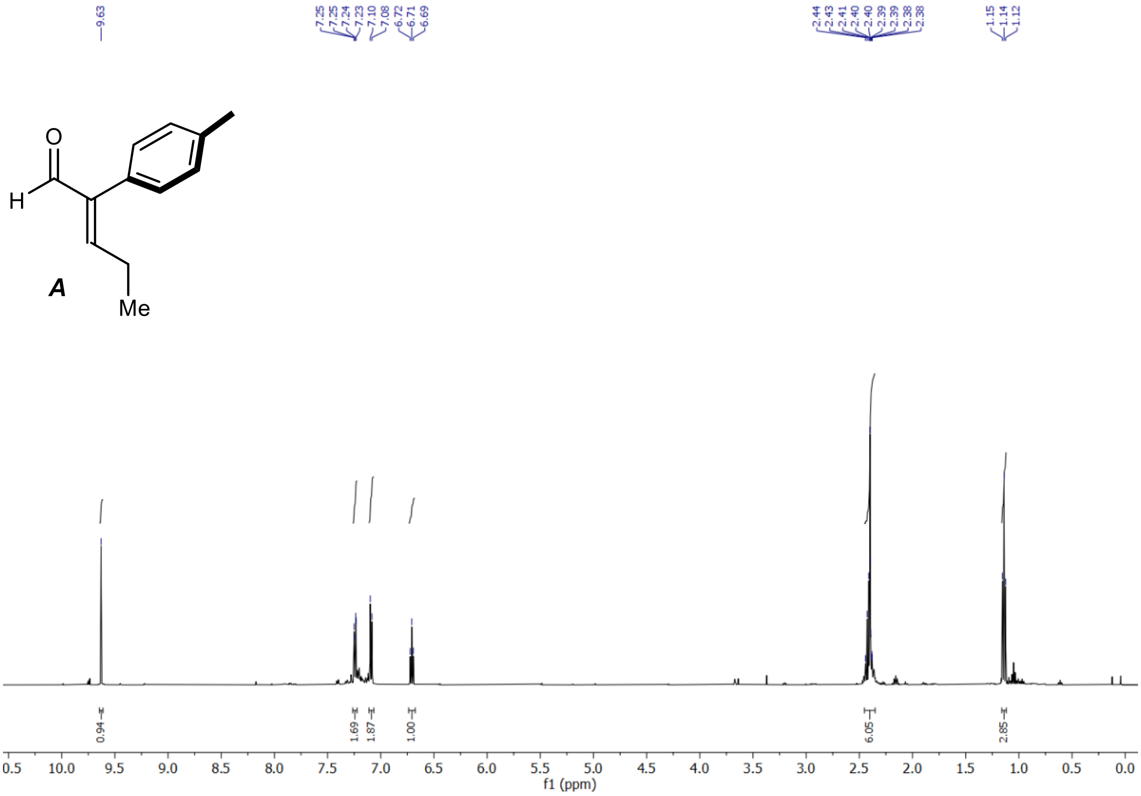


^{13}C NMR (126 MHz, CDCl$_3$)

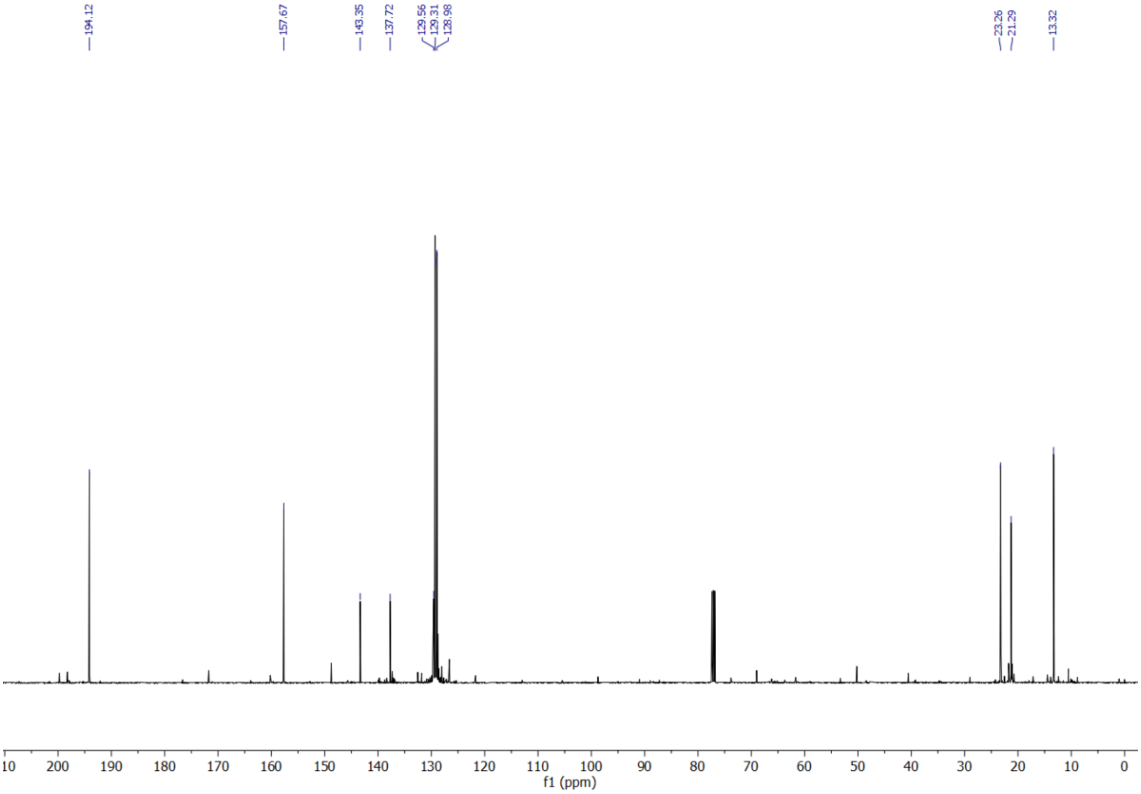


Starting material precursor

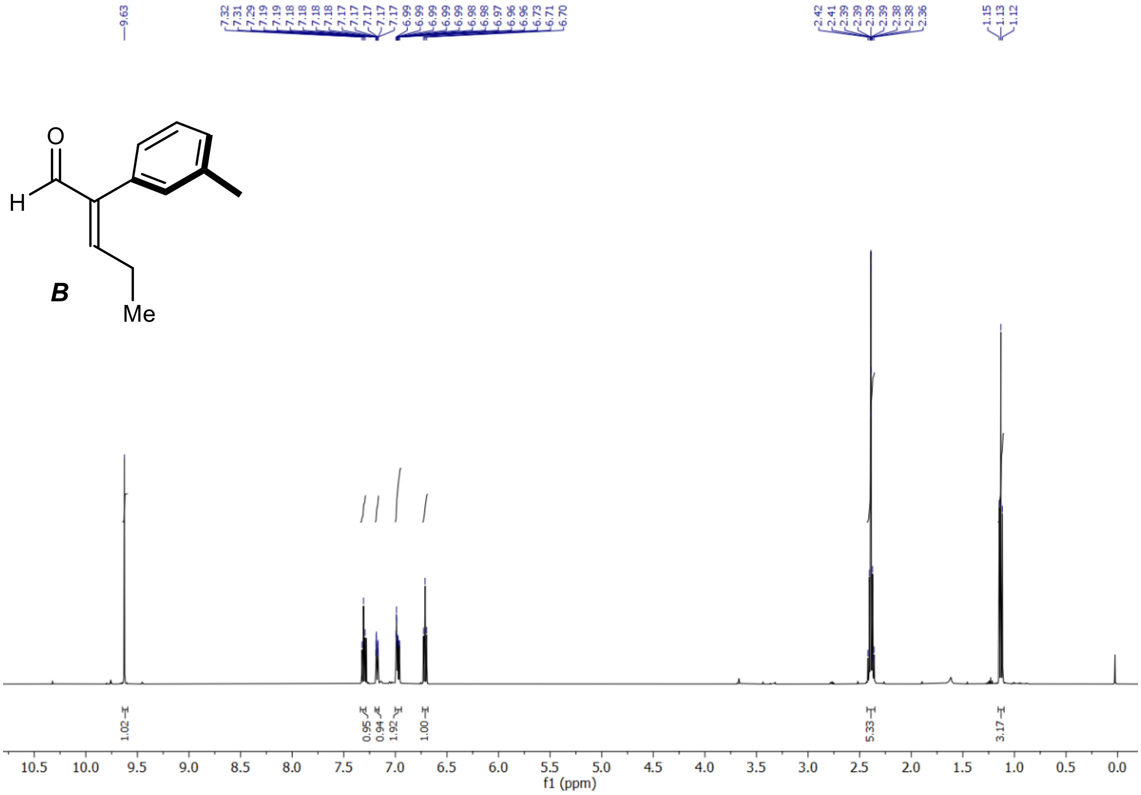
^{1}H NMR (500 MHz, $CDCl_3$)



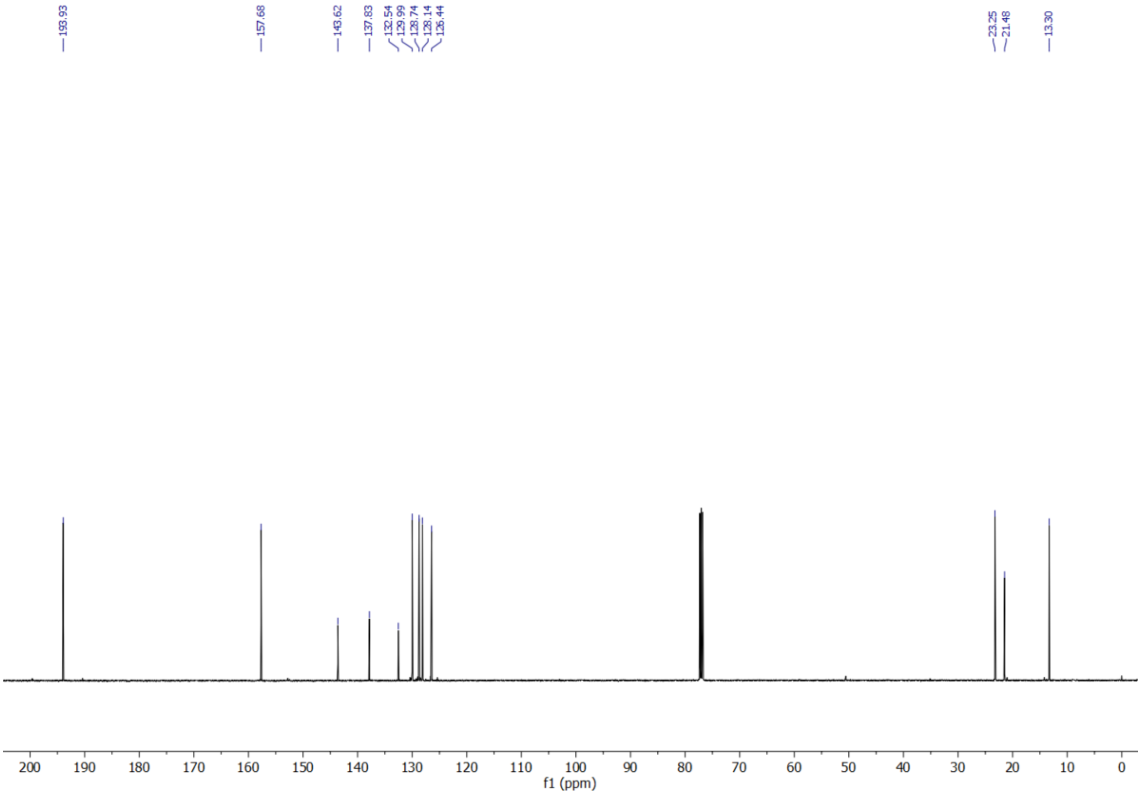
^{13}C NMR (126 MHz, $CDCl_3$)



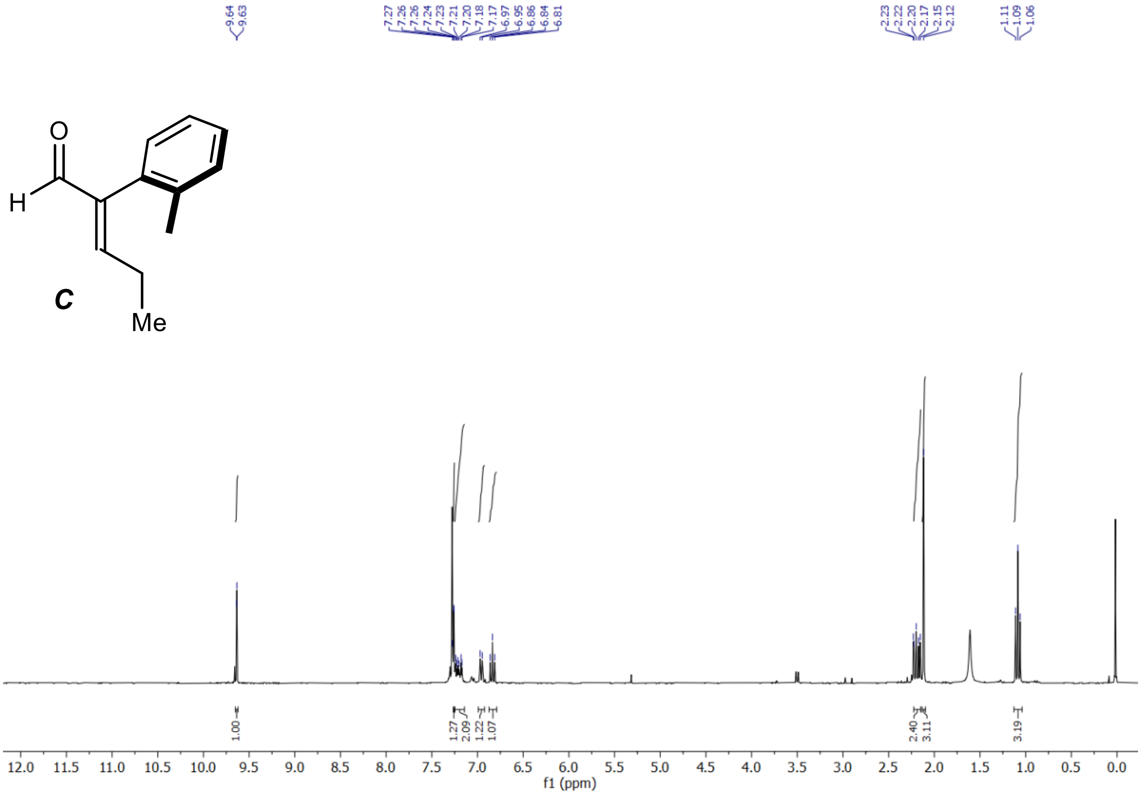
^{1}H NMR (500 MHz, CDCl$_3$)



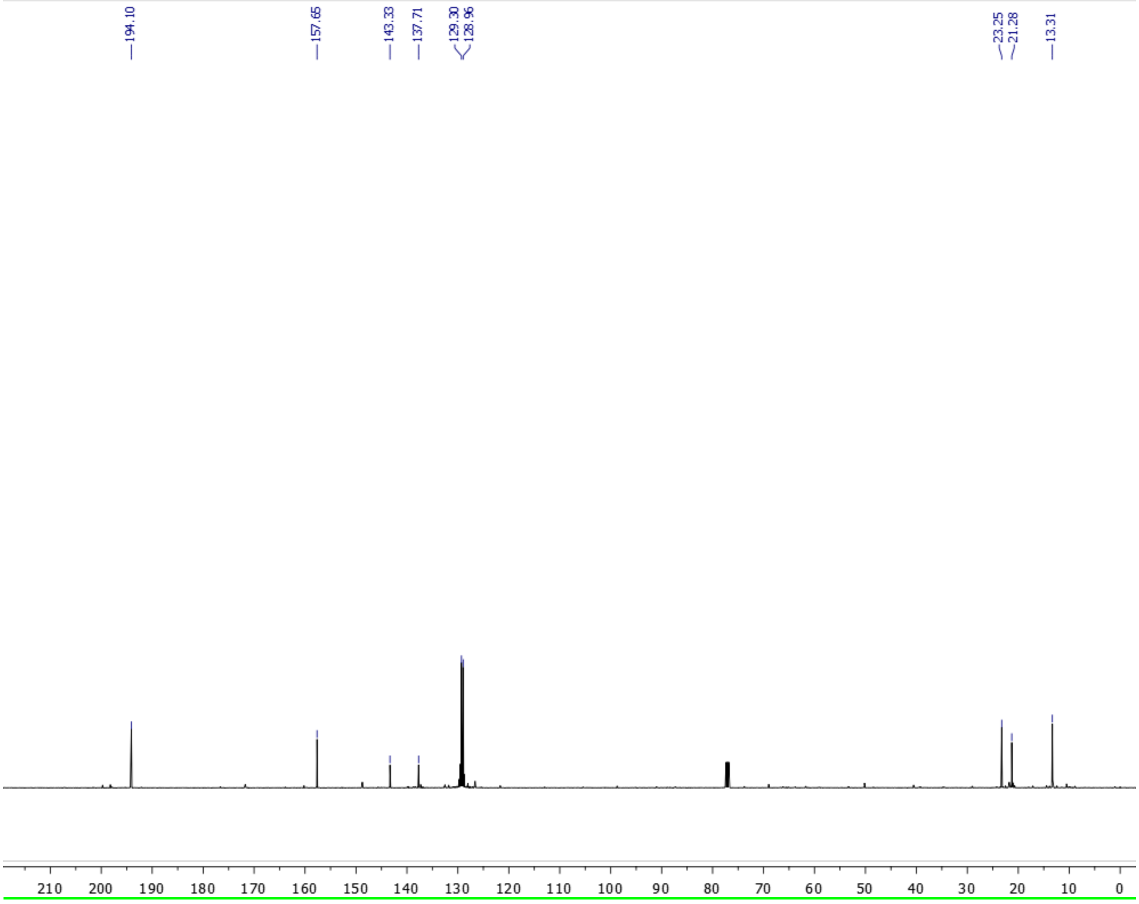
^{13}C NMR (126 MHz, CDCl$_3$)



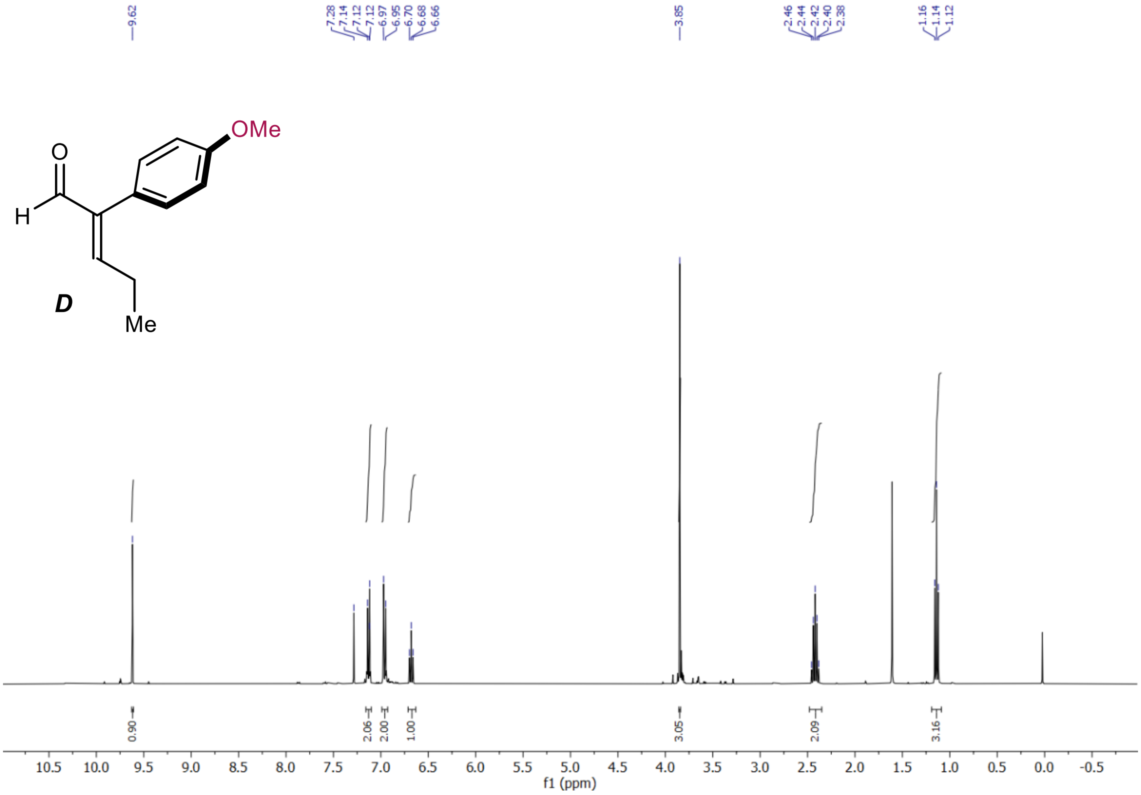
^{1}H NMR (500 MHz, $CDCl_3$)


C

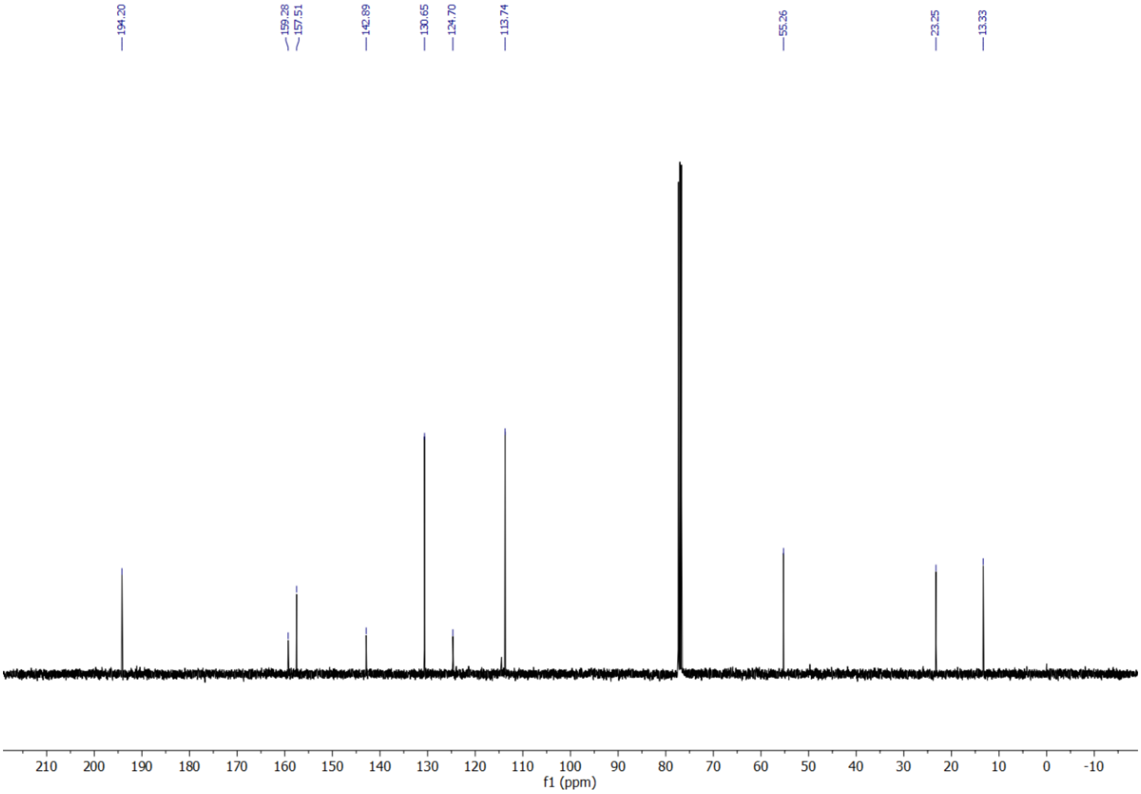
^{13}C NMR (126 MHz, $CDCl_3$)



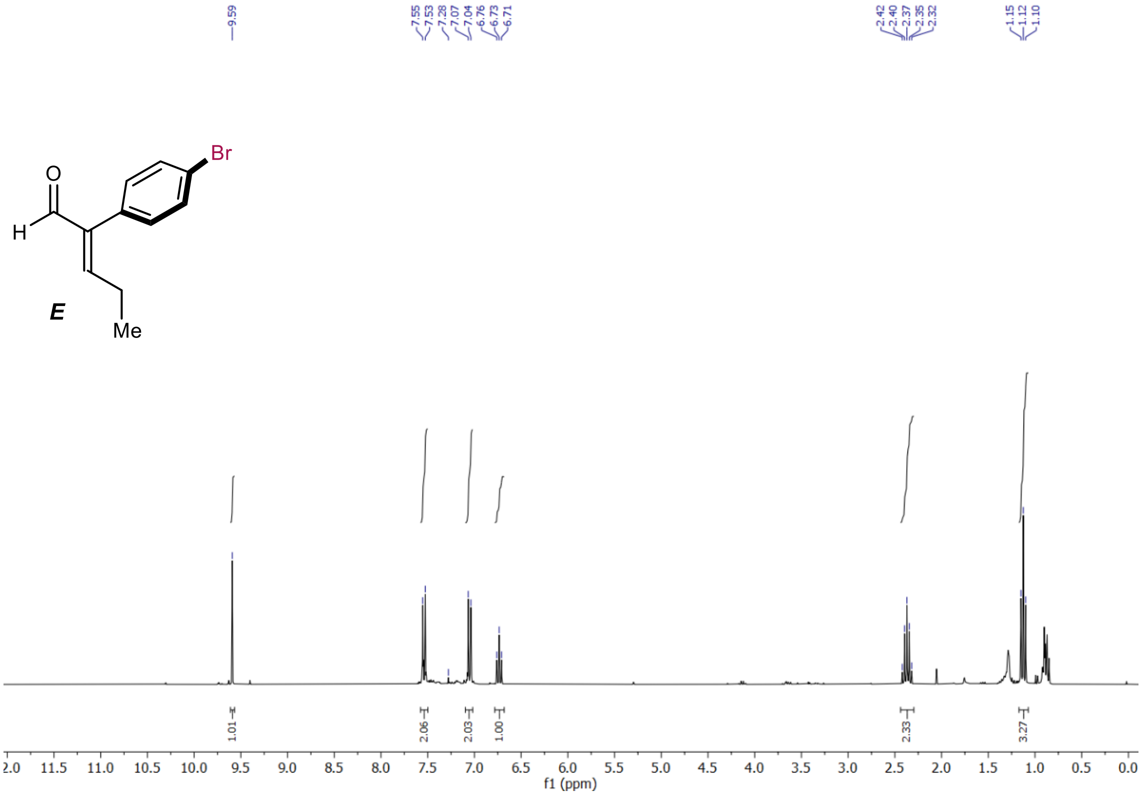
^{1}H NMR (500 MHz, $CDCl_3$)



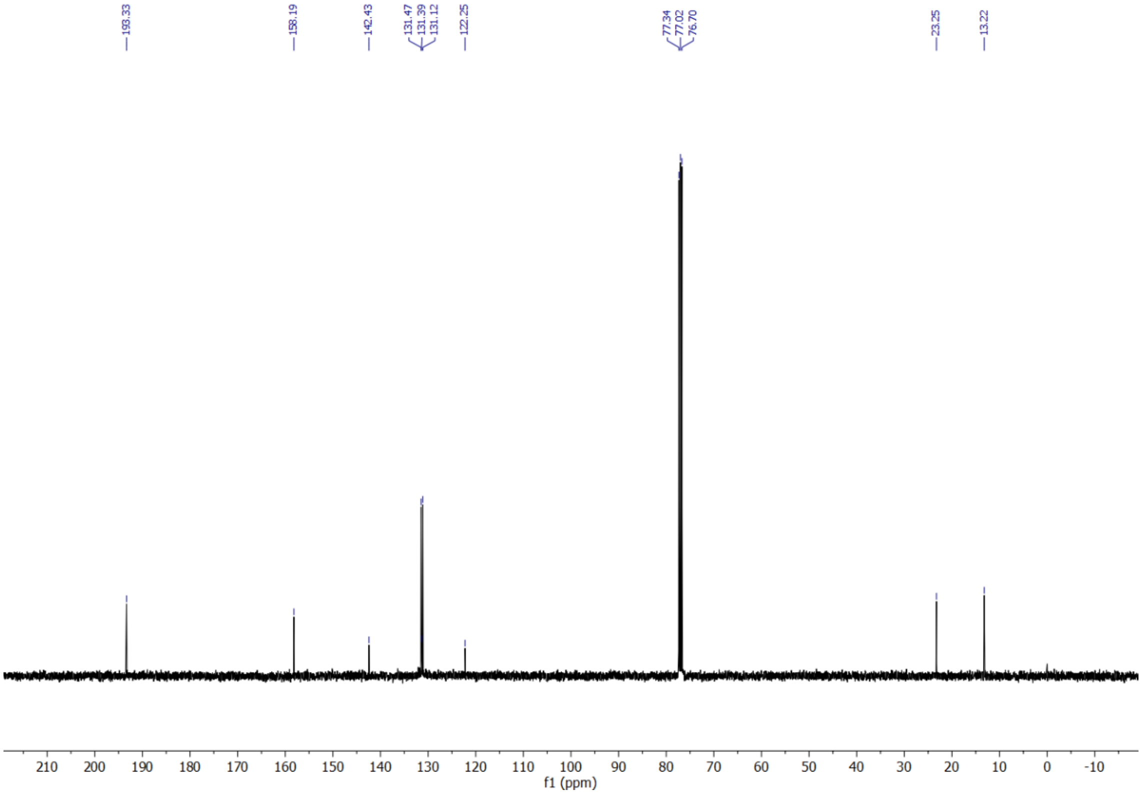
^{13}C NMR (126 MHz, $CDCl_3$)



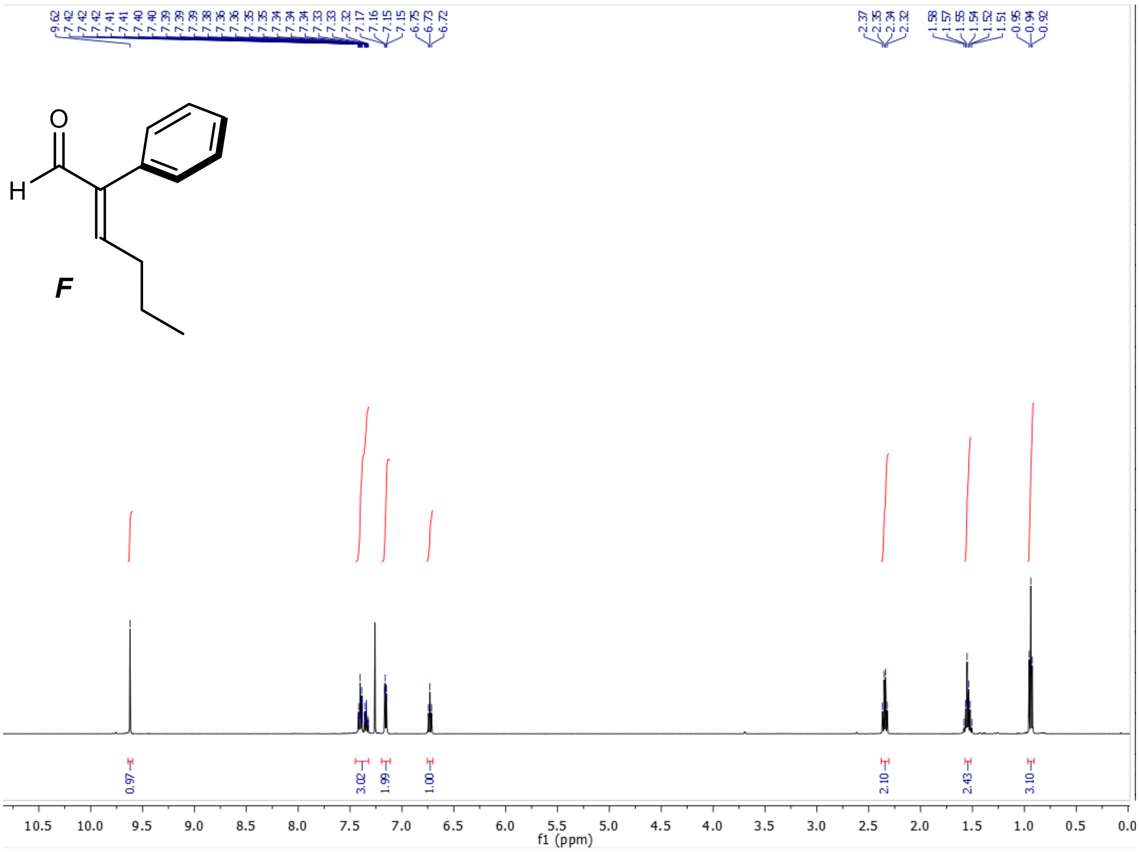
^{1}H NMR (400 MHz, $CDCl_3$)



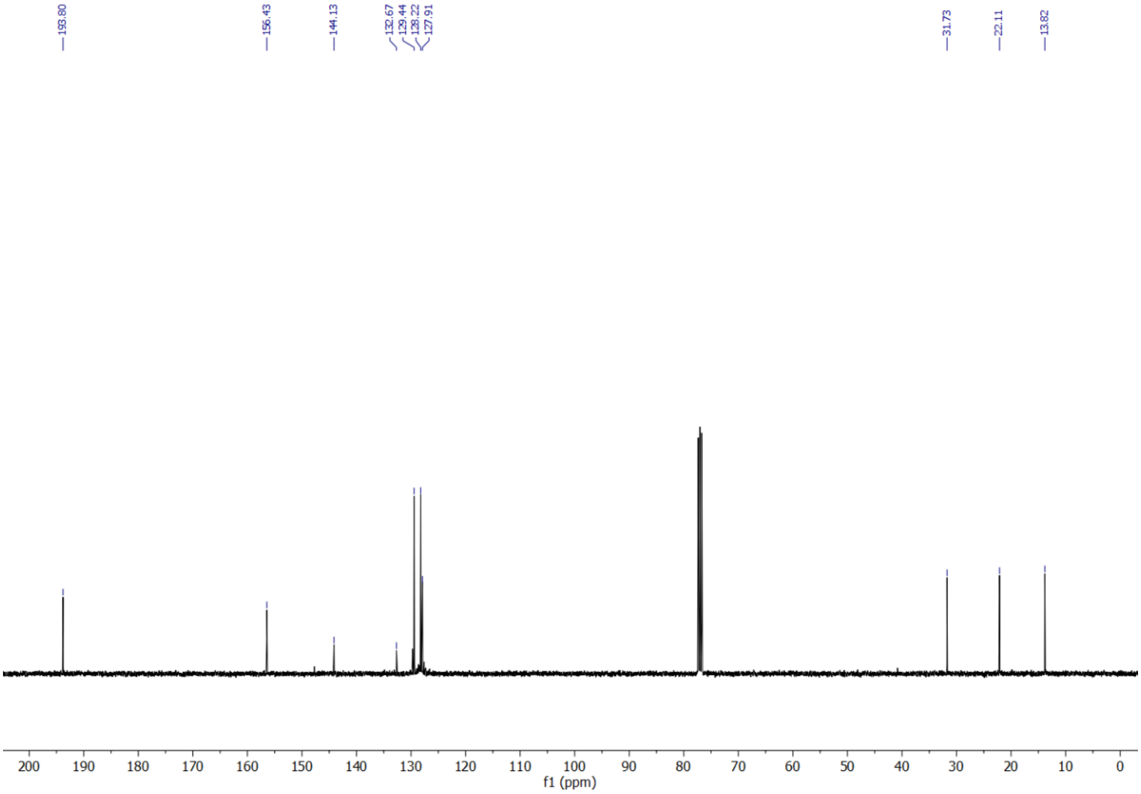
^{13}C NMR (101 MHz, $CDCl_3$)



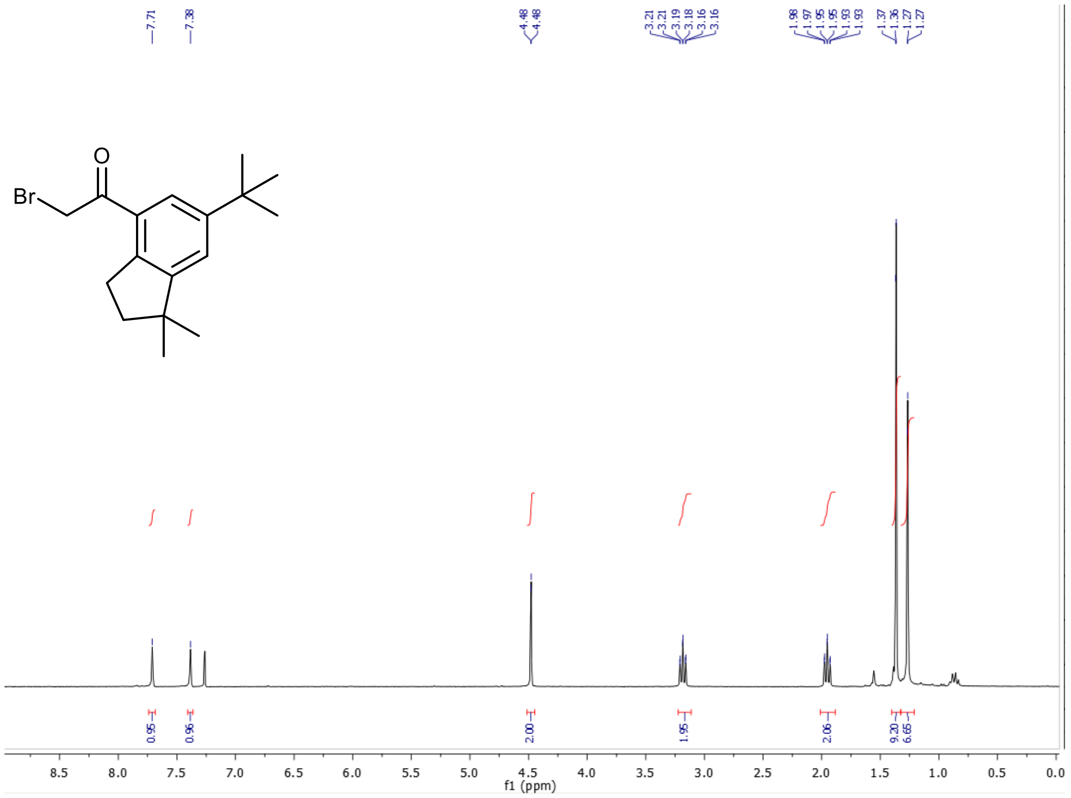
^{1}H NMR (400 MHz, CDCl$_3$)



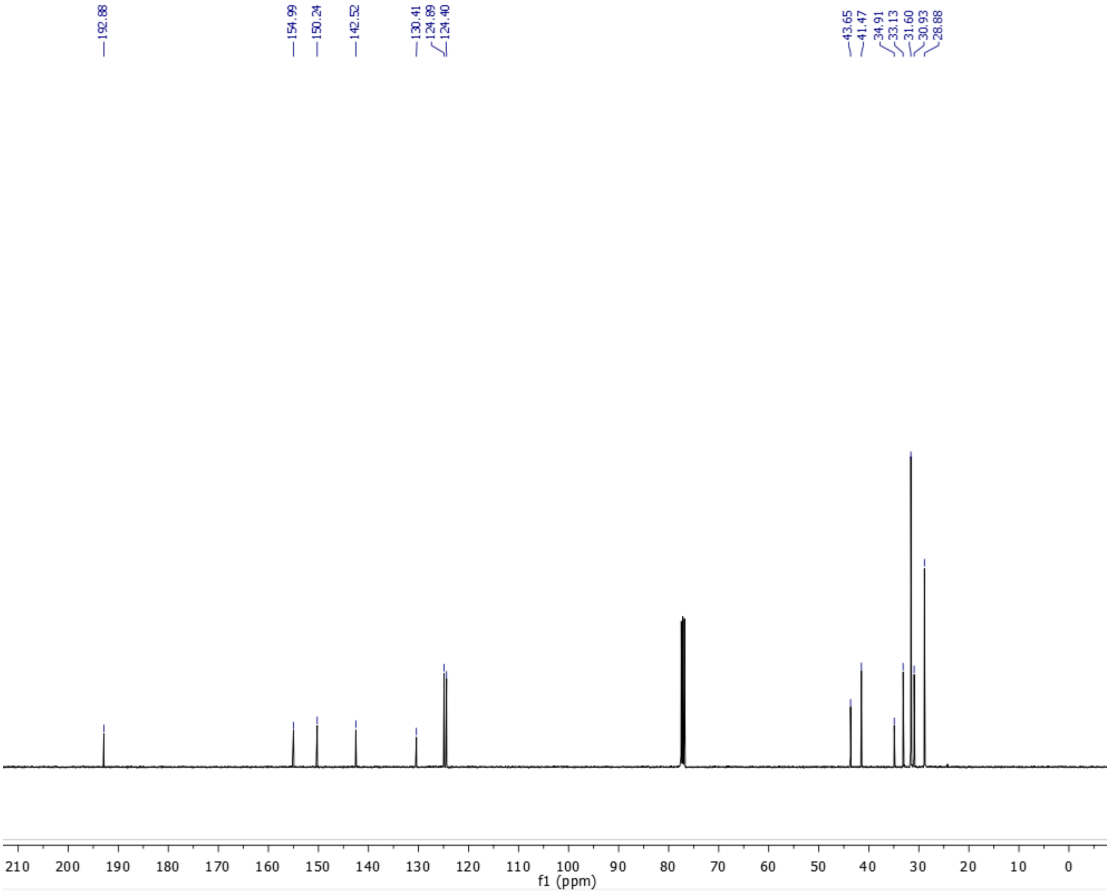
^{13}C NMR (101 MHz, CDCl$_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

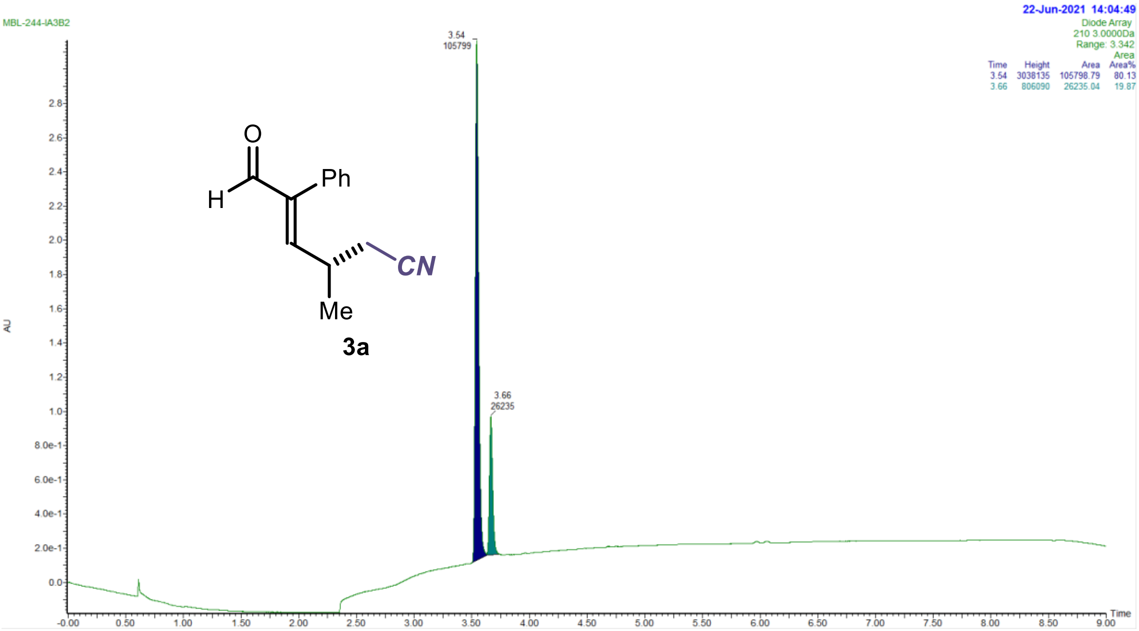


^{13}C NMR (101 MHz, $CDCl_3$)



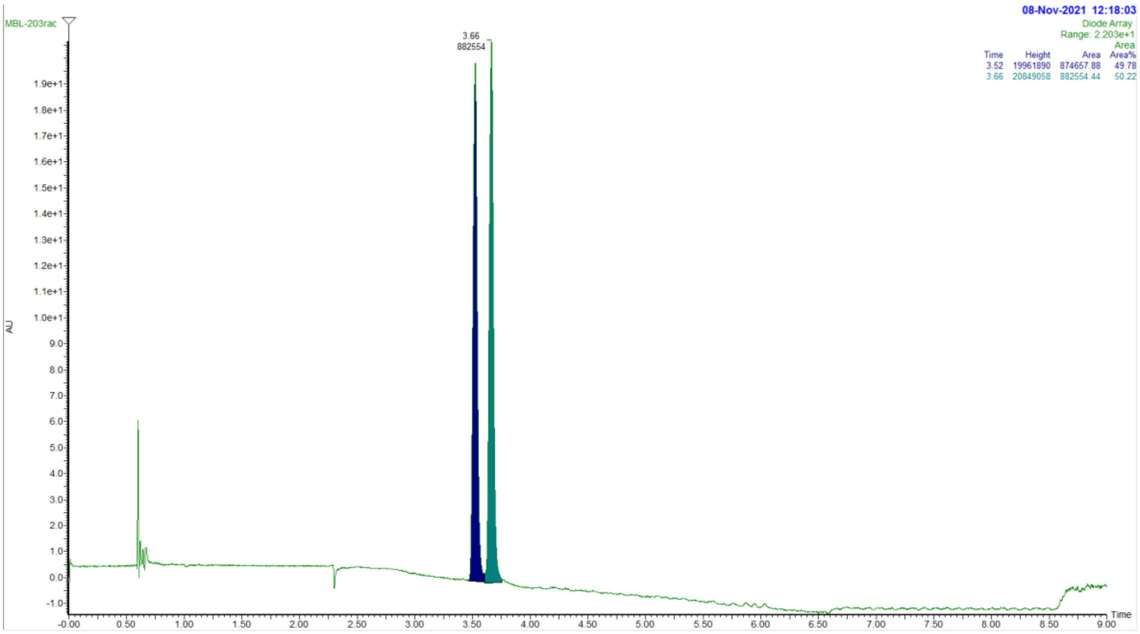
H. UPC^2 traces

Full trace for **3a** enantioenriched:



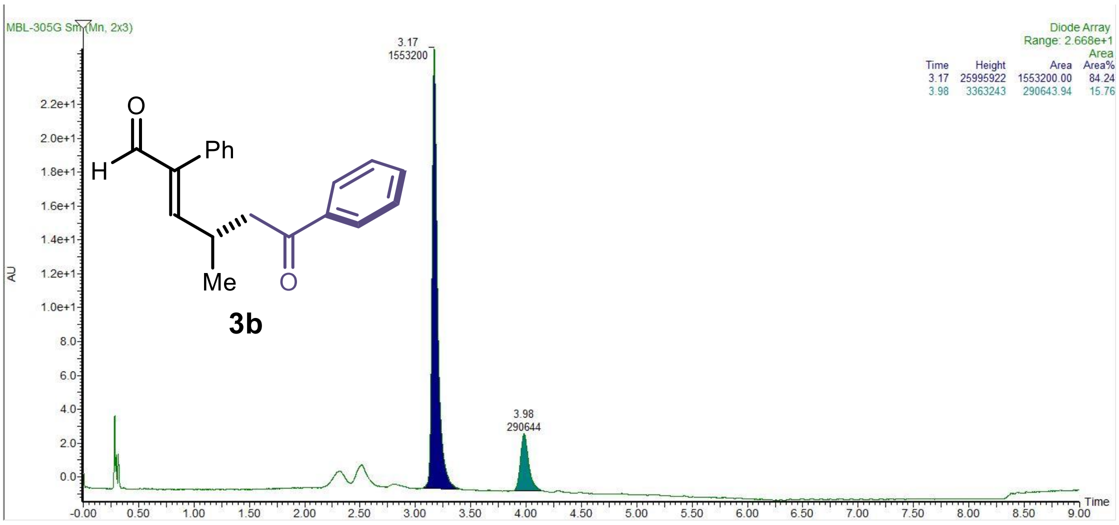
Time	Height	Area	Area%
3.54	3038135	105798.79	80.13
3.66	806090	26235.04	19.87

Full trace for **3a** *racemic*:



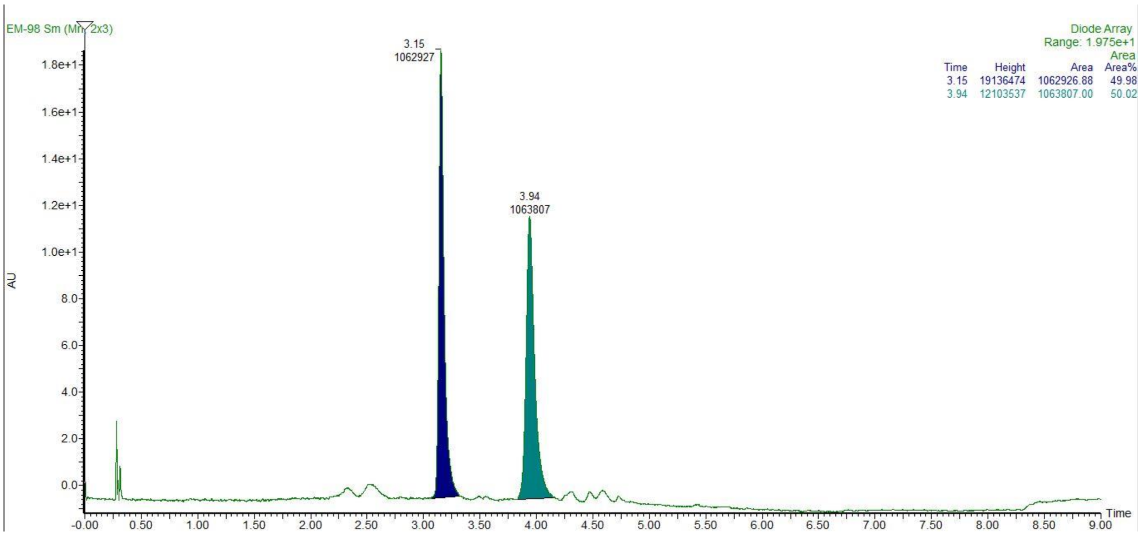
Time	Height	Area	Area%
3.52	19961890	874657.88	49.78
3.66	20849058	882554.44	50.22

Full trace for **3b** enantioenriched:



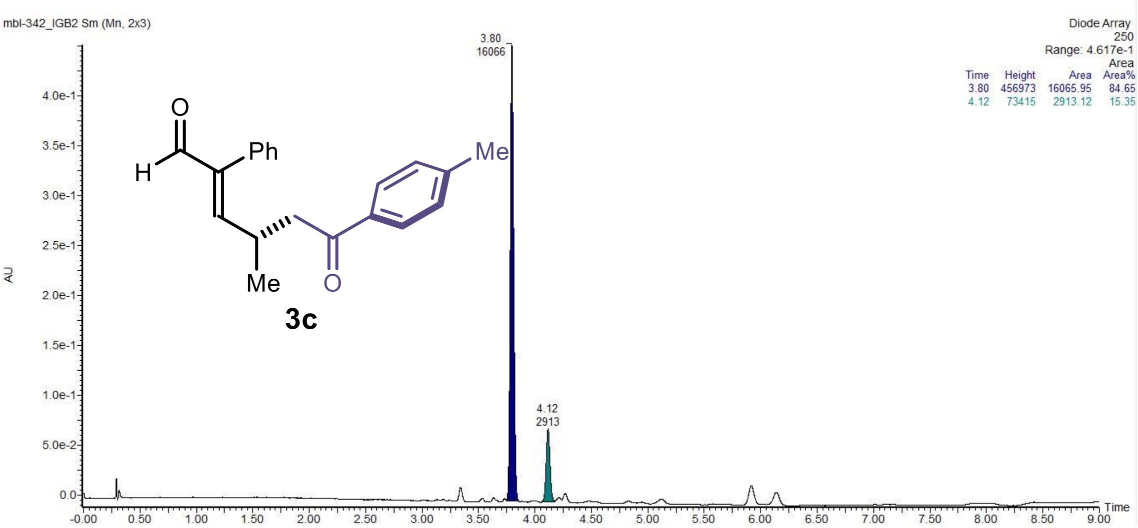
Time	Height	Area	Area%
3.17	25995922	1553200.00	84.24
3.98	3363243	290643.94	15.76

Full trace for **3b** *racemic*:

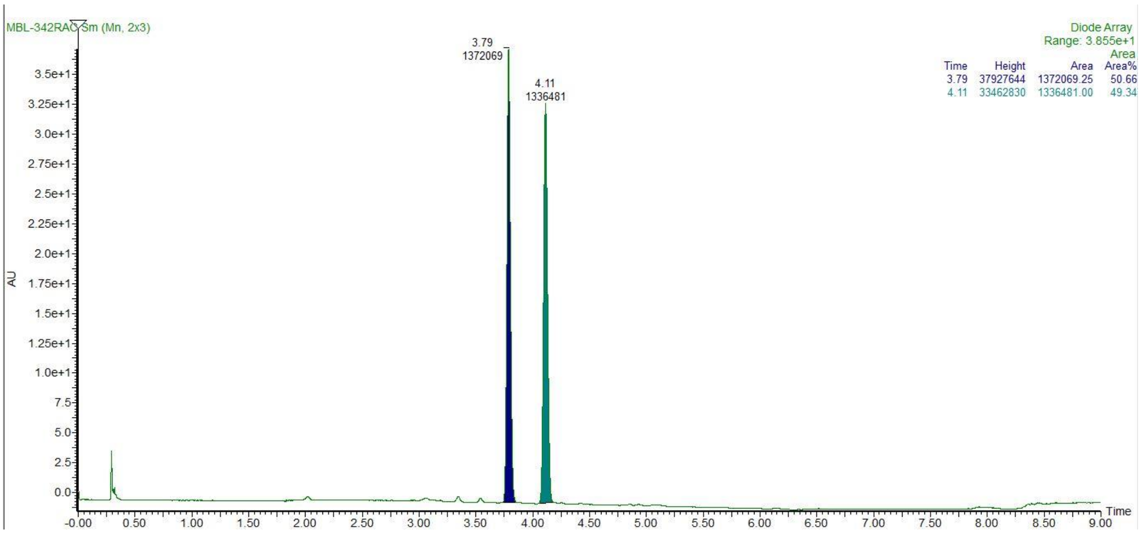


Time	Height	Area	Area%
3.15	19136474	1062926.88	49.98
3.94	12103537	1063807.00	50.02

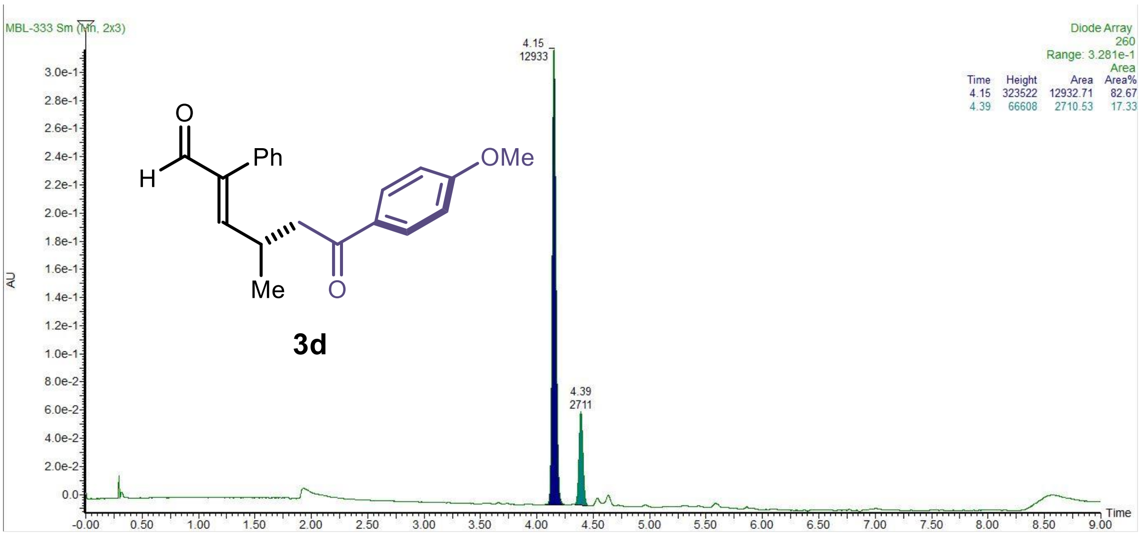
Full trace for **3c** enantioenriched:



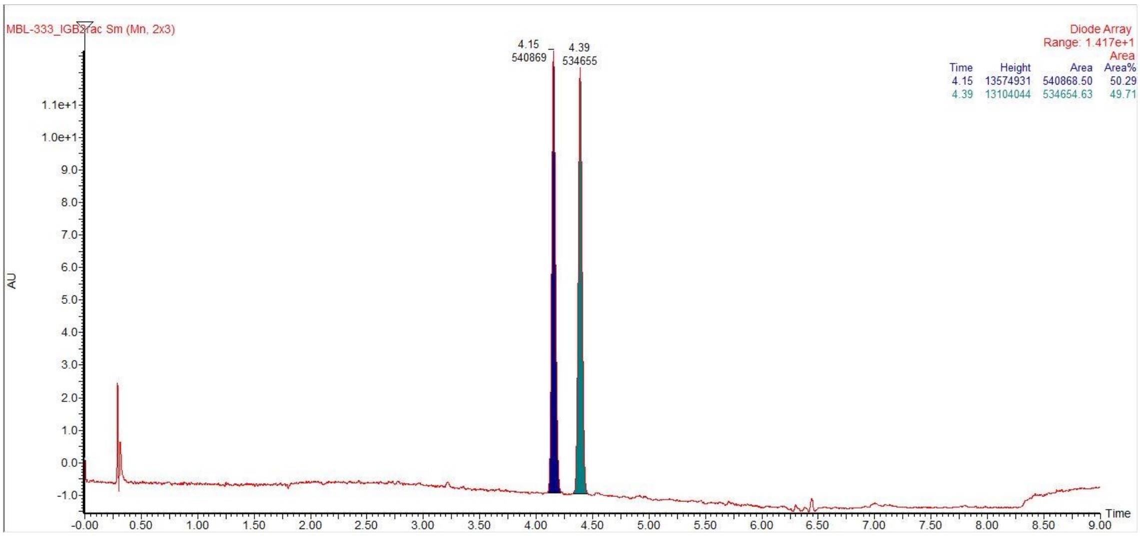
Full trace for **3c** *racemic*:



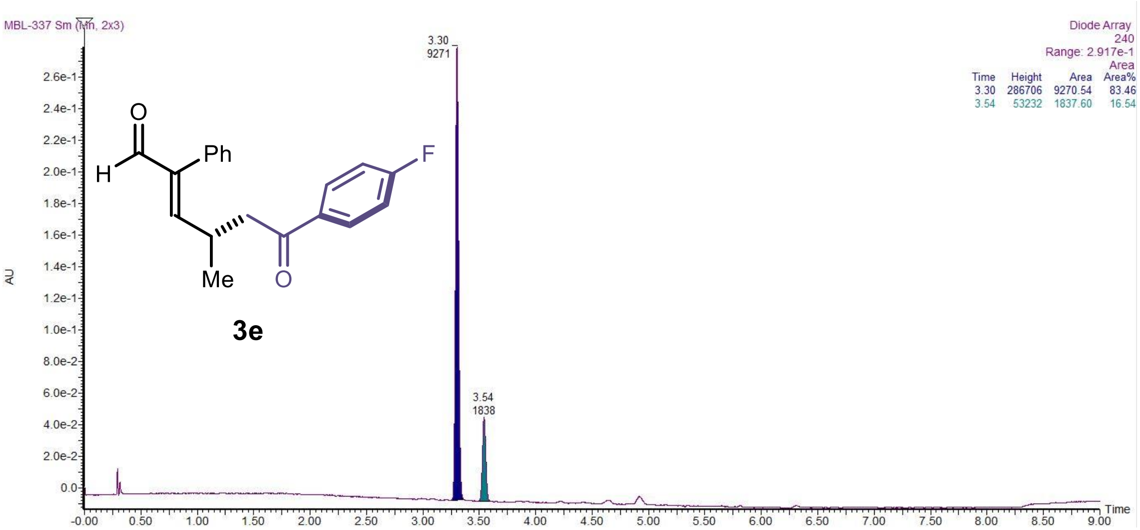
Full trace for **3d** enantioenriched:



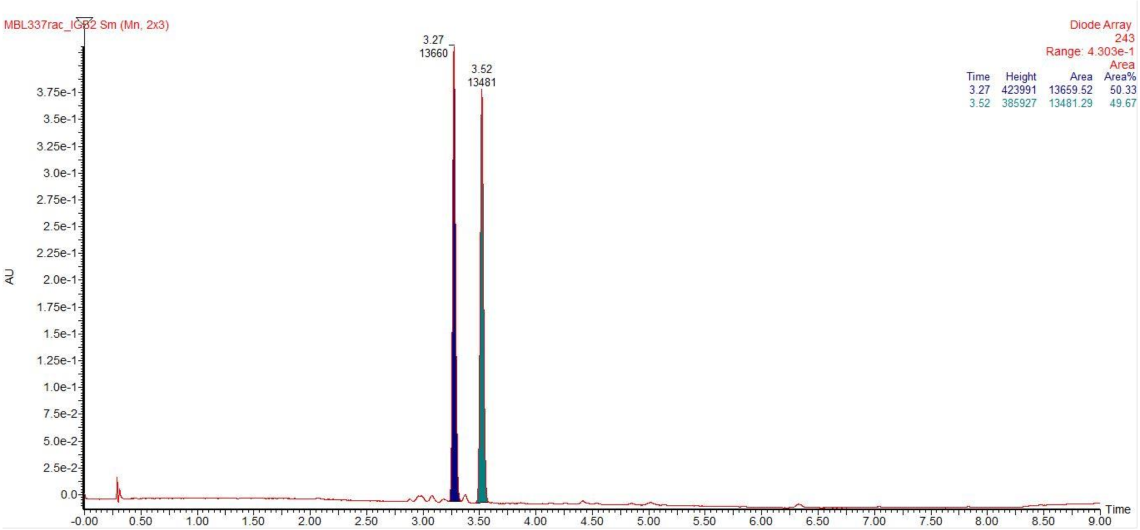
Full trace for **3d** *racemic*:



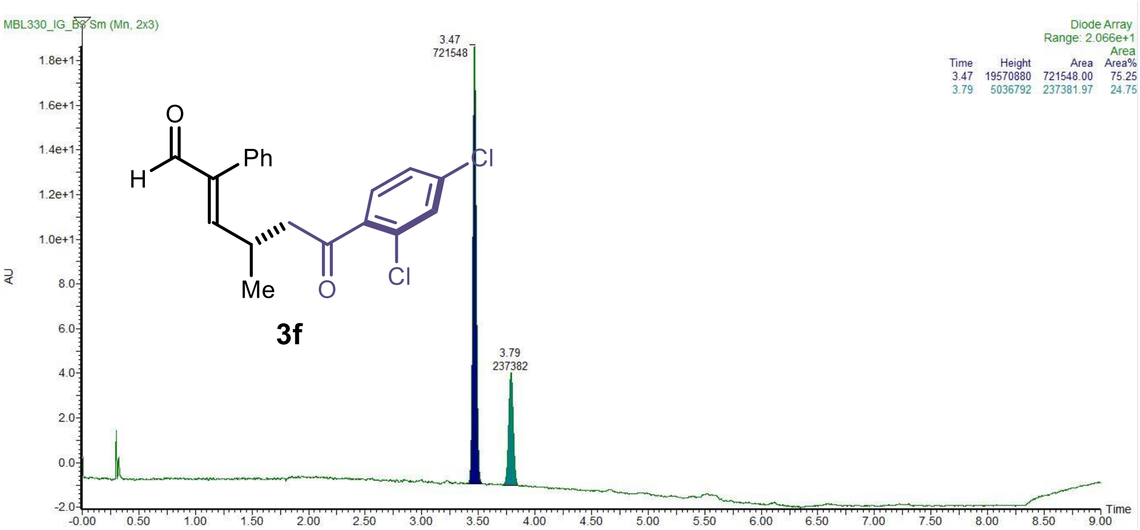
Full trace for **3e** enantioenriched:



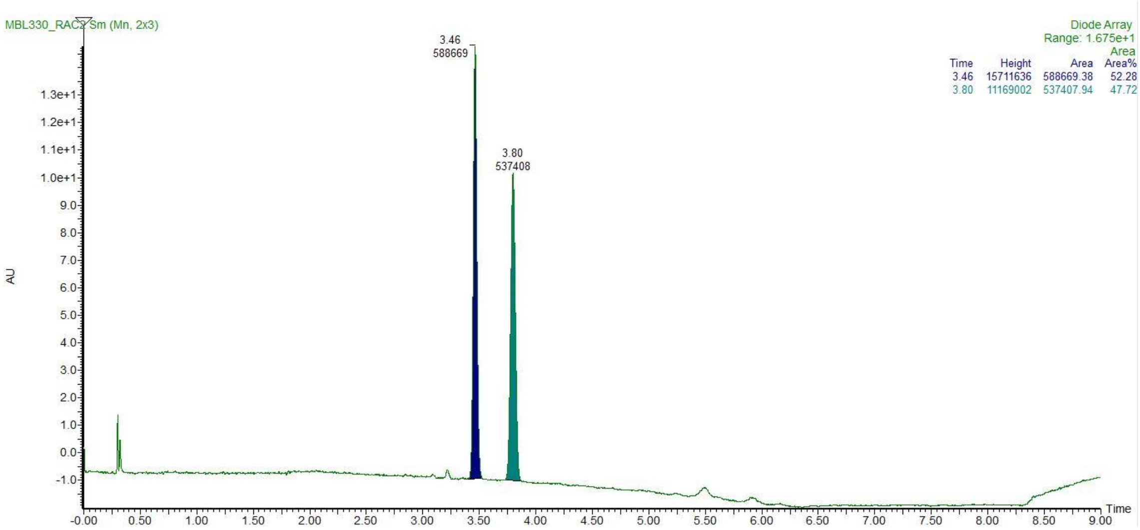
Full trace for **3e** *racemic*:



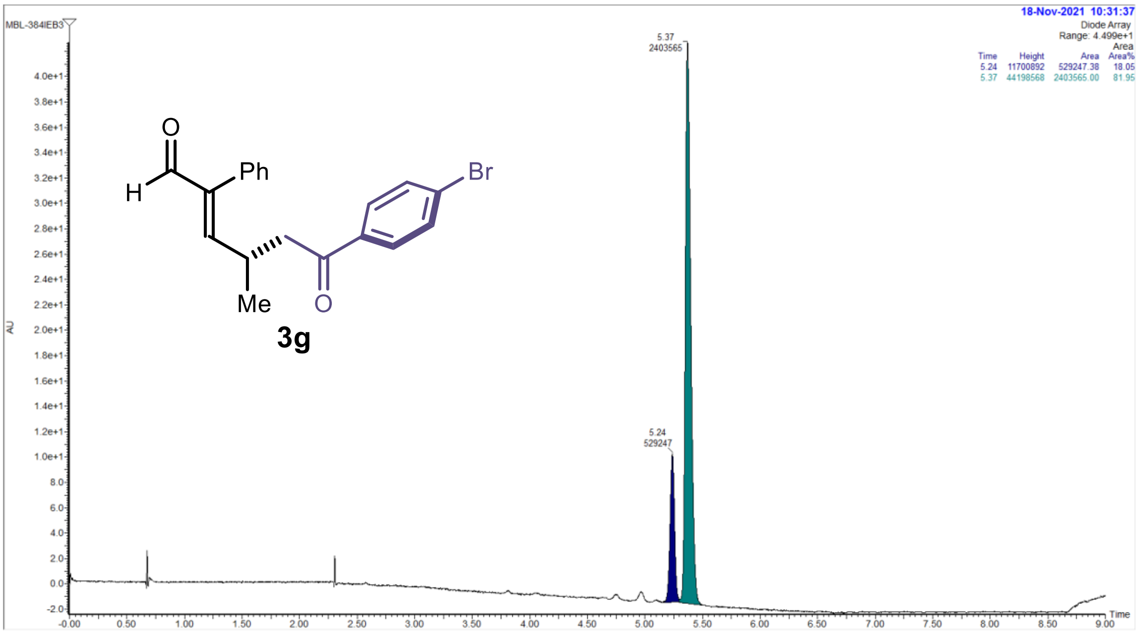
Full trace for **3f** enantioenriched:



Full trace for **3f** *racemic*:

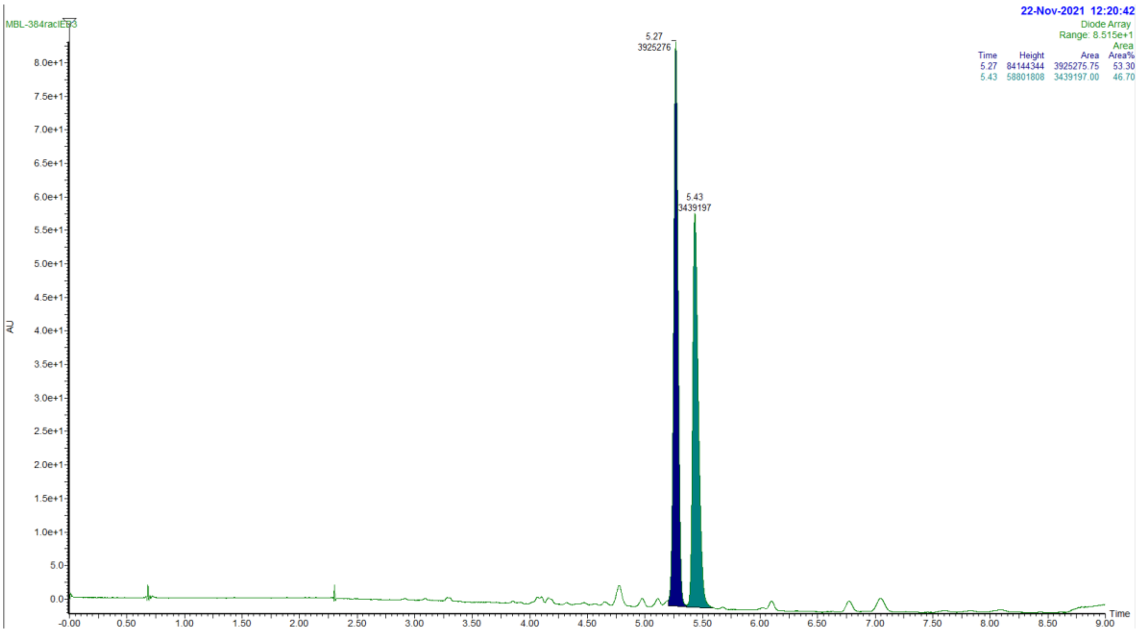


Full trace for **3g** enantioenriched:



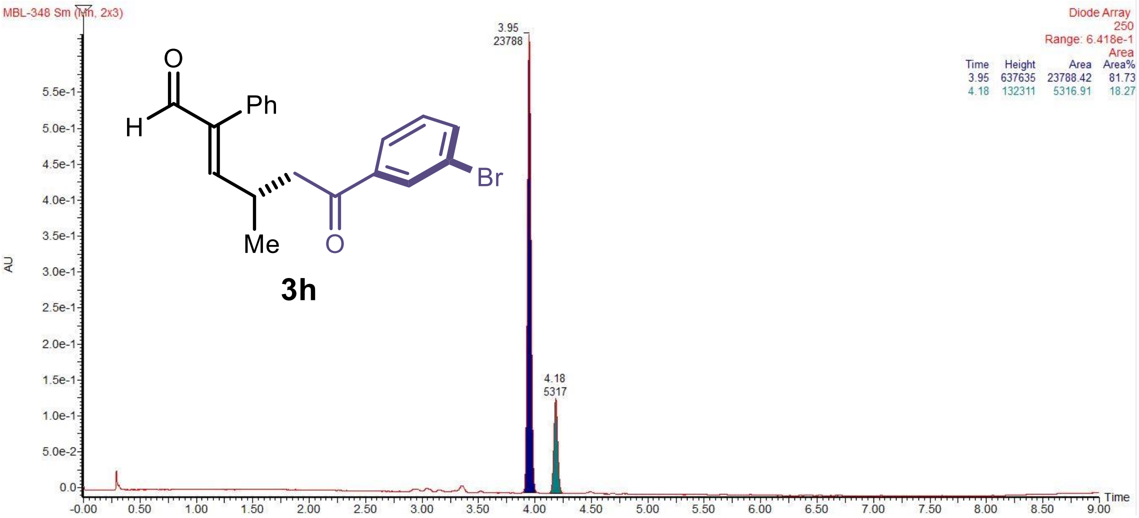
Time	Height	Area	Area Area%
5.24	11700892	529247.38	18.05
5.37	44198568	2403565.00	81.95

Full trace for **3g** *racemic*:

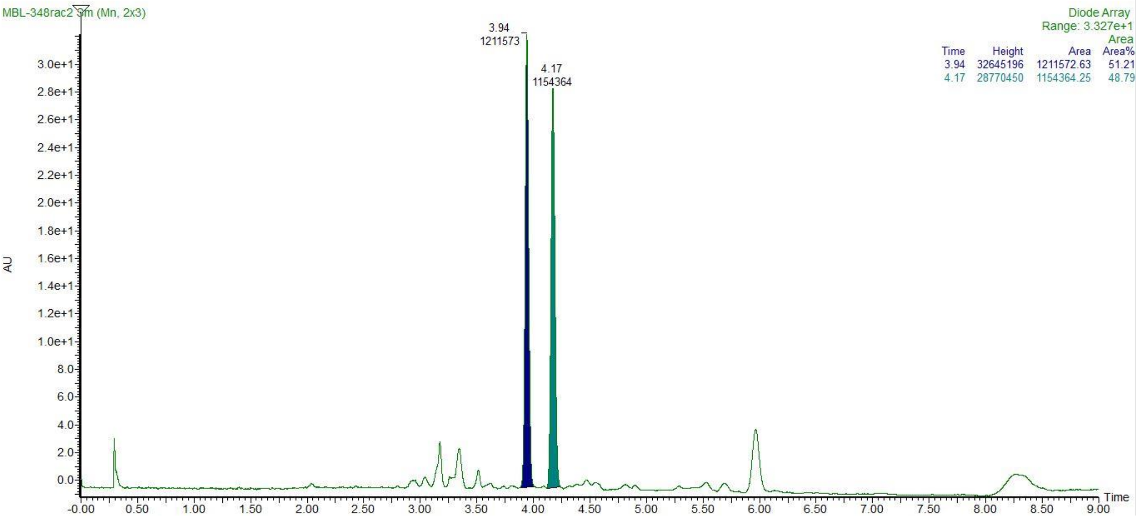


Time	Height	Area	Area Area%
5.27	84144344	3925275.75	53.30
5.43	58801808	3439197.00	46.70

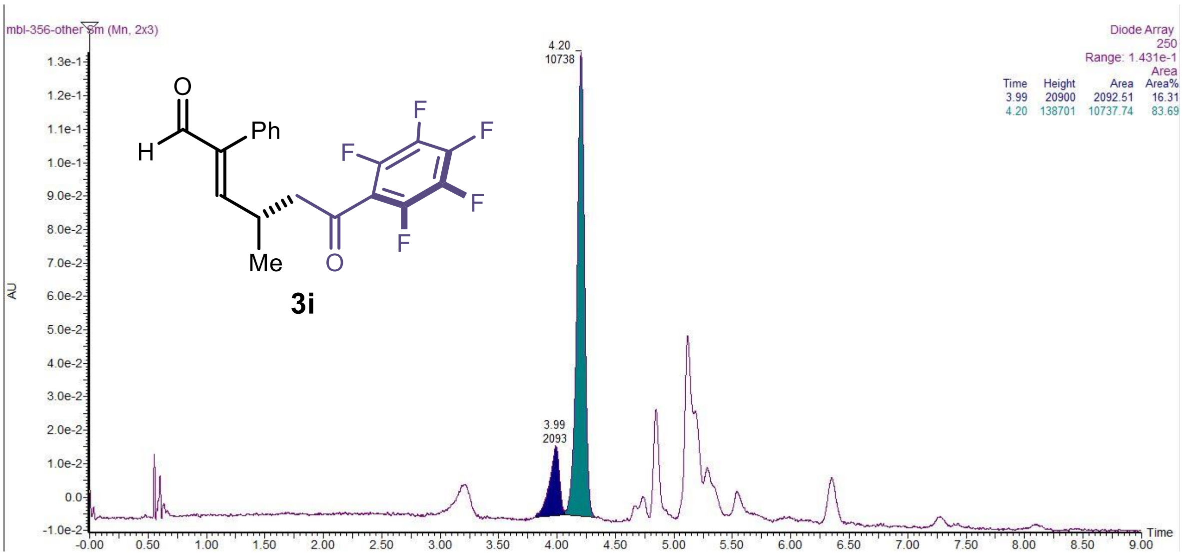
Full trace for **3h** enantioenriched:



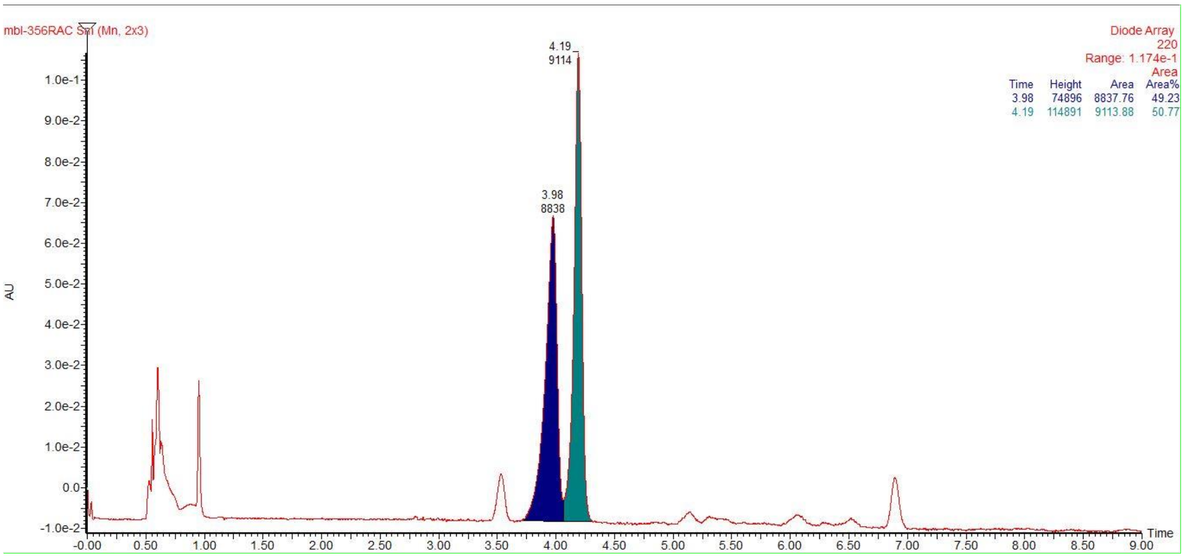
Full trace for **3h** *racemic*:



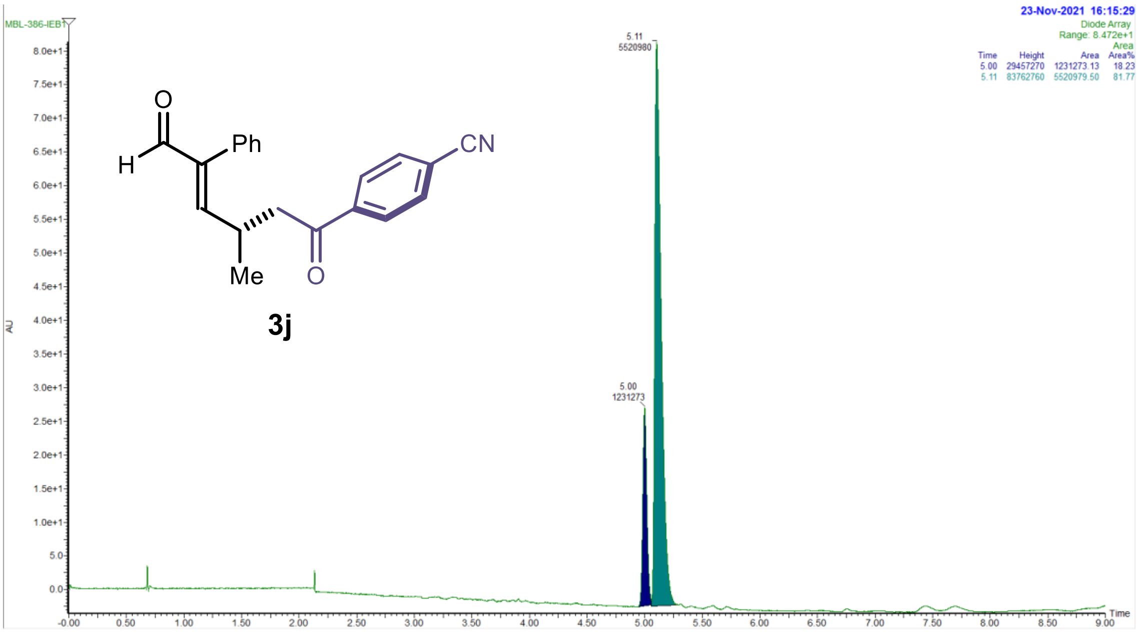
Full trace for **3i** enantioenriched:



Full trace for **3i** *racemic*:

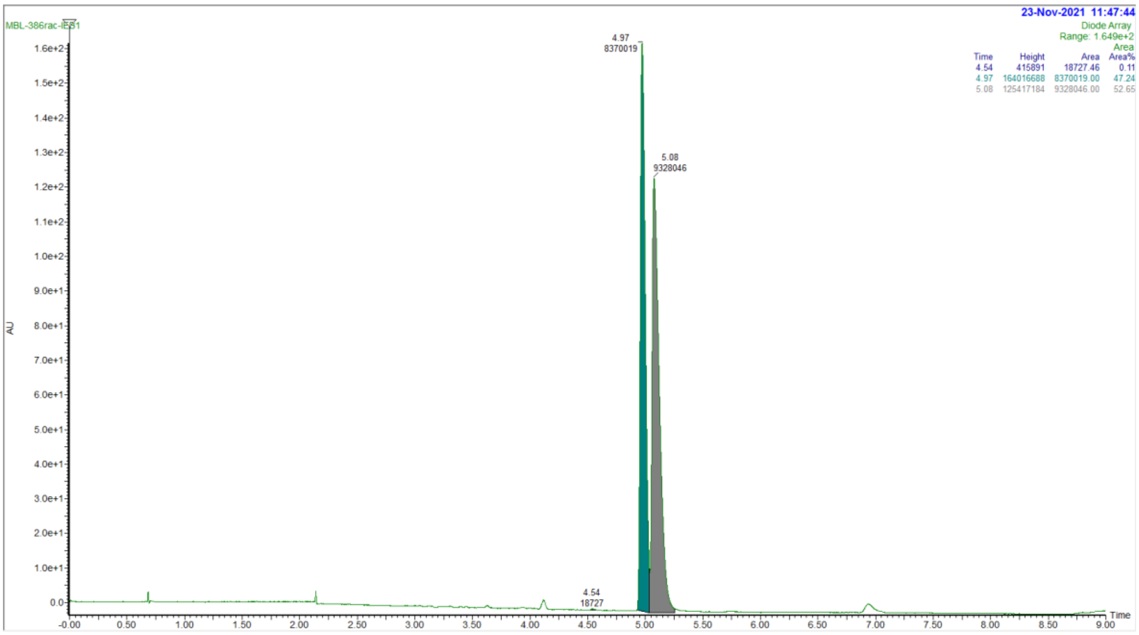


Full trace for **3j** enantioenriched:



```
                    23-Nov-2021  16:15:29
                              Diode Array
                         Range: 8.472e+1
                                     Area
Time     Height          Area       Area%
5.00   29457270    1231273.13       18.23
5.11   83762760    5520979.50       81.77
```

Full trace for **3j** *racemic*:



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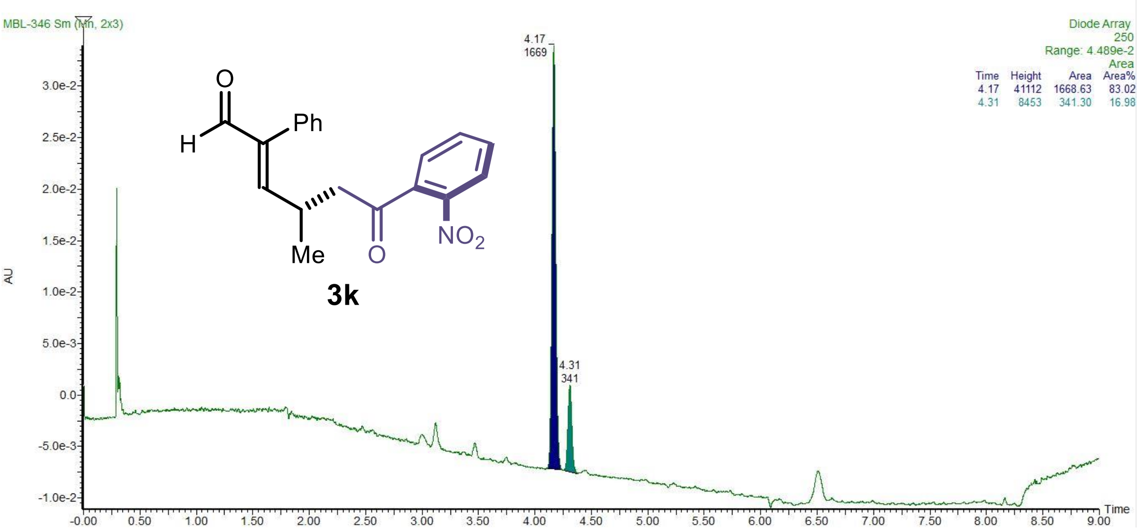
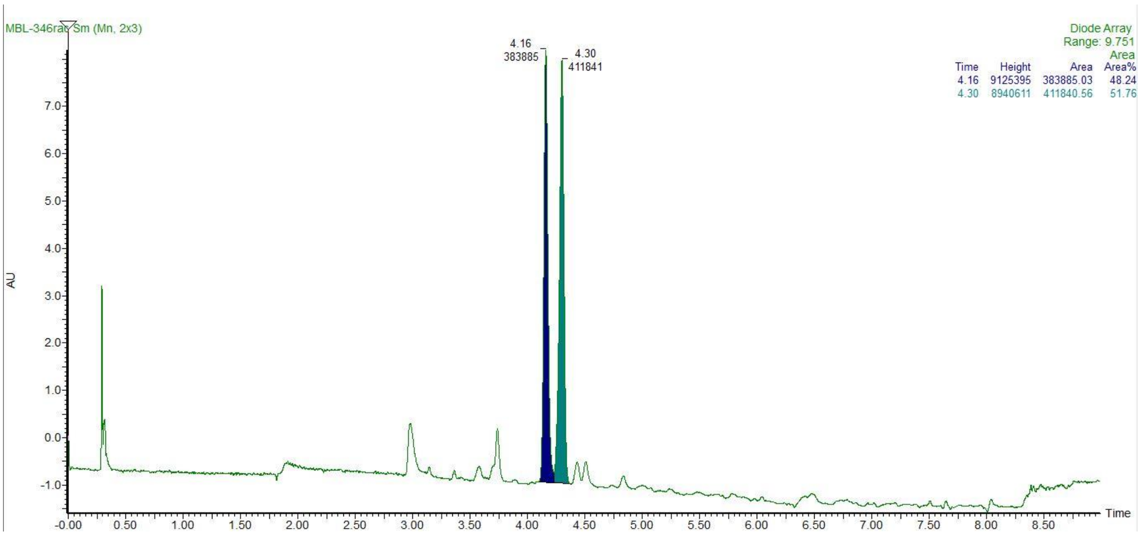
                     23-Nov-2021  11:47:44
                               Diode Array
                          Range: 1.649e+2
                                      Area
Time      Height          Area       Area%
4.54      415891      18727.46        0.11
4.97   164016688    8370019.00       47.24
5.08   125417184    9328046.00       52.65
```

Full trace for **3k** enantioenriched:



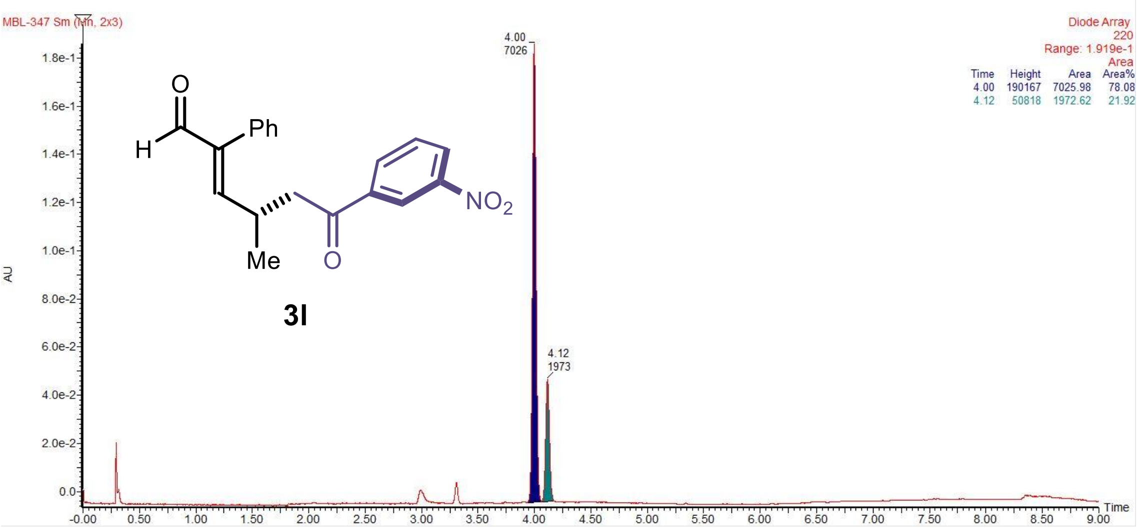
Time	Height	Area	Area%
4.17	41112	1668.63	83.02
4.31	8453	341.30	16.98

Full trace for **3k** *racemic*:

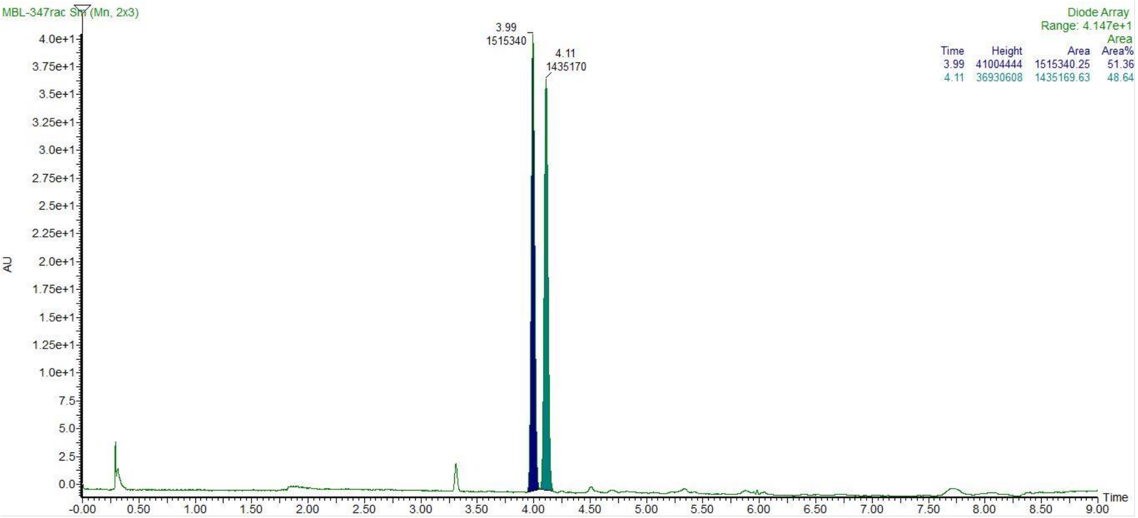


Time	Height	Area	Area%
4.16	9125395	383885.03	48.24
4.30	8940611	411840.56	51.76

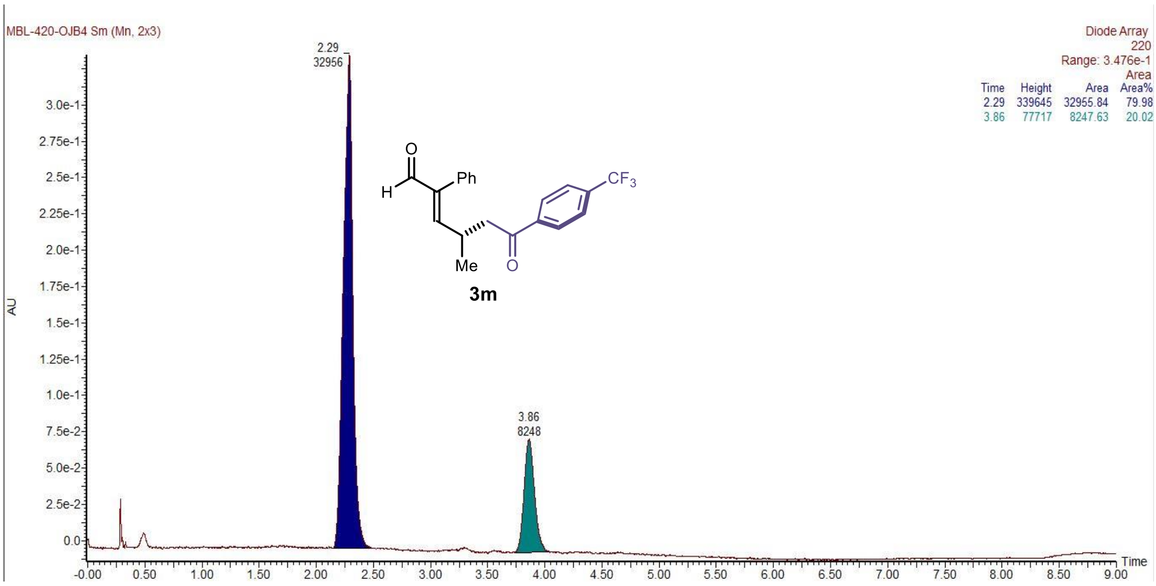
Full trace for **3l** enantioenriched:



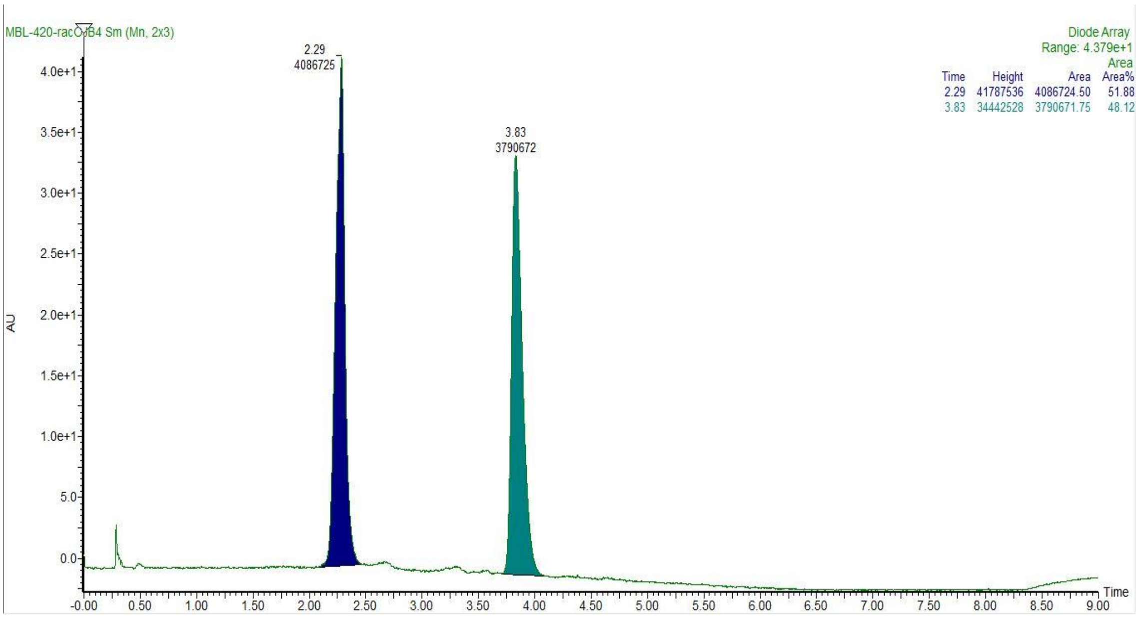
Full trace for **3l** *racemic*:



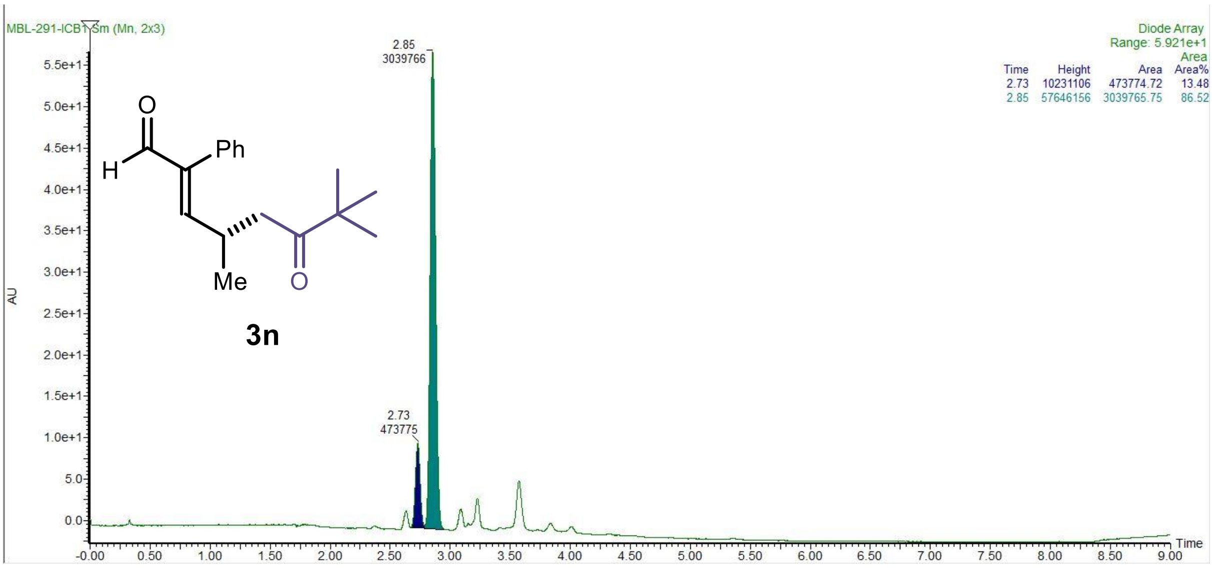
Full trace for **3m** enantioenriched:



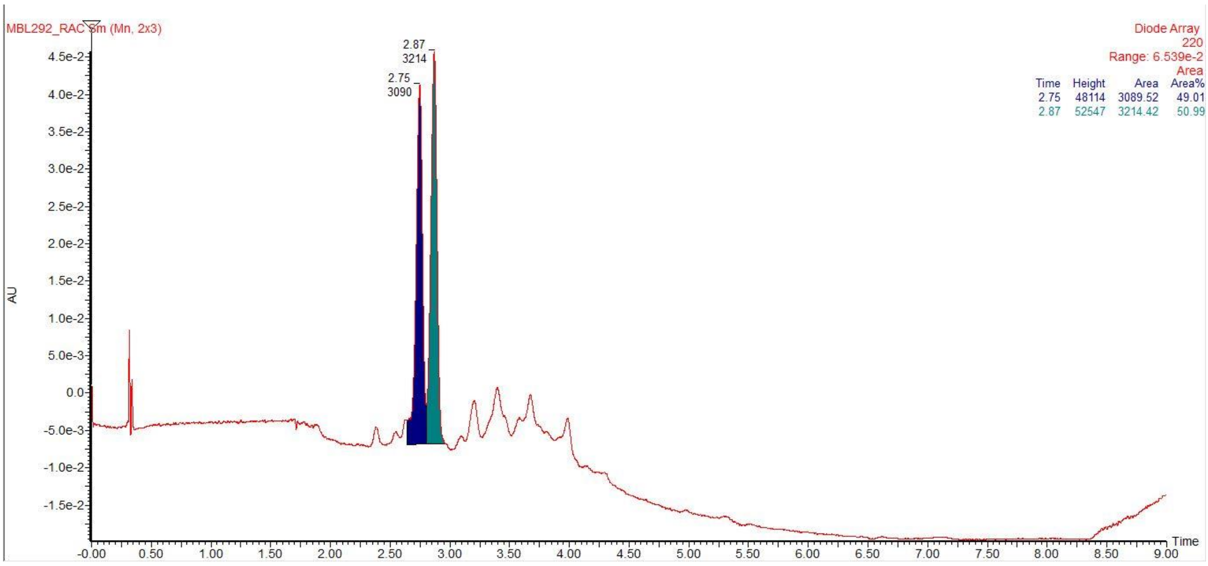
Full trace for **3m** *racemic*:



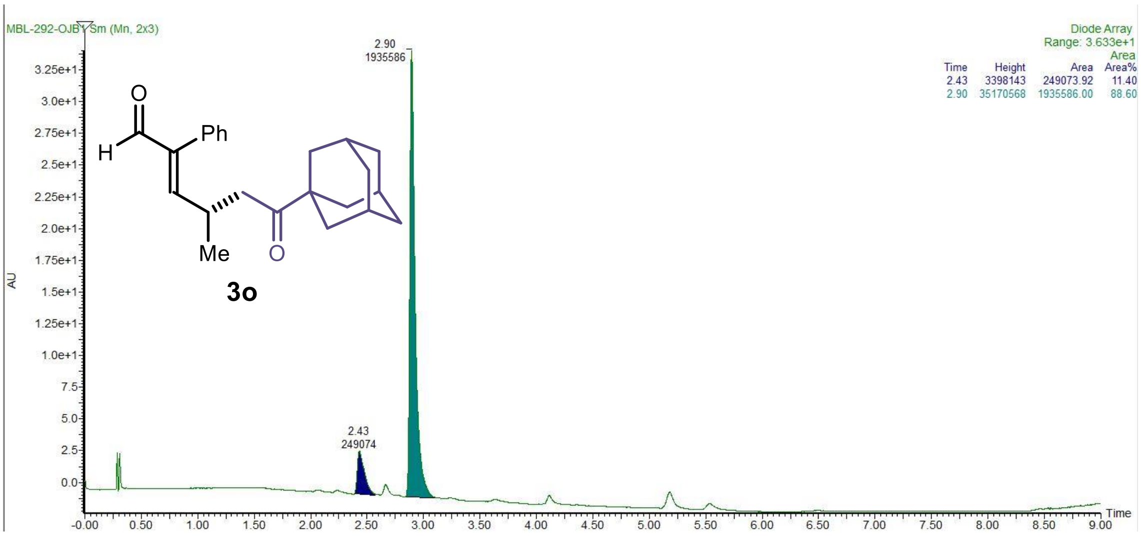
Full trace for **3n** enantioenriched:



Full trace for **3n** *racemic*:

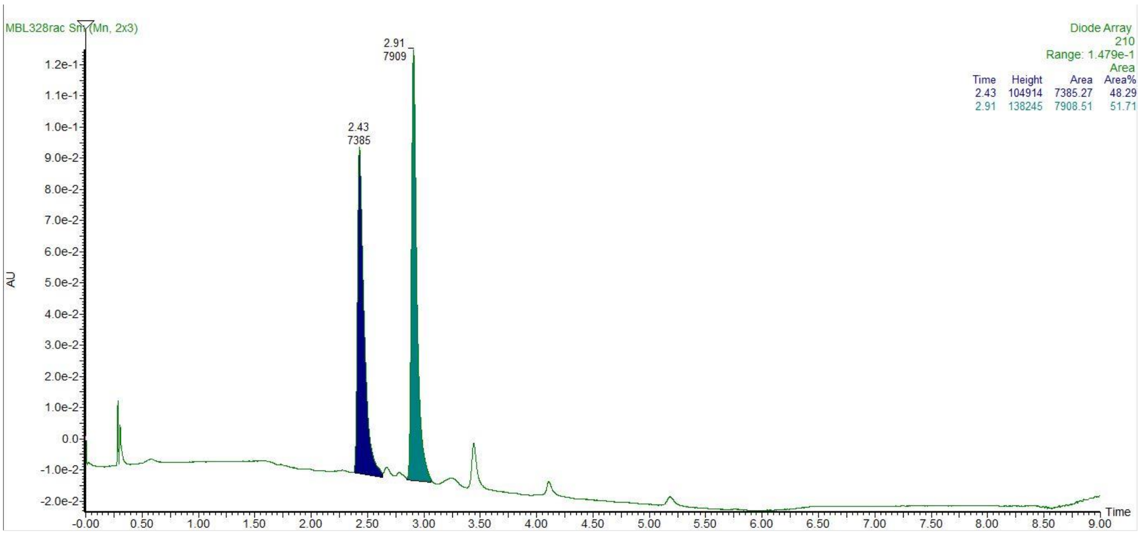


Full trace for **3o** enantioenriched:



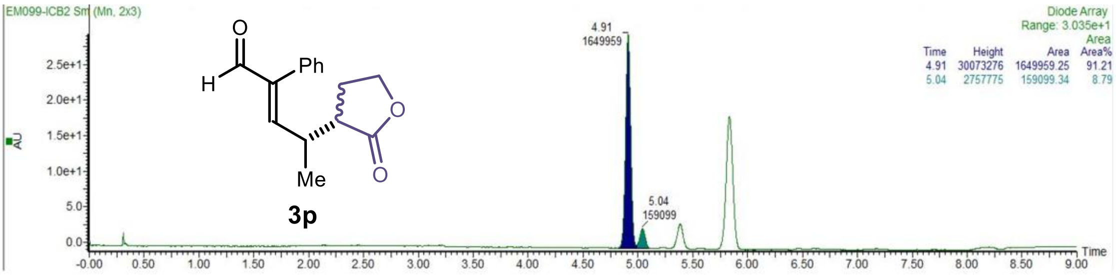
Time	Height	Area	Area Area%
2.43	3398143	249073.92	11.40
2.90	35170568	1935586.00	88.60

Full trace for **3o** *racemic*:



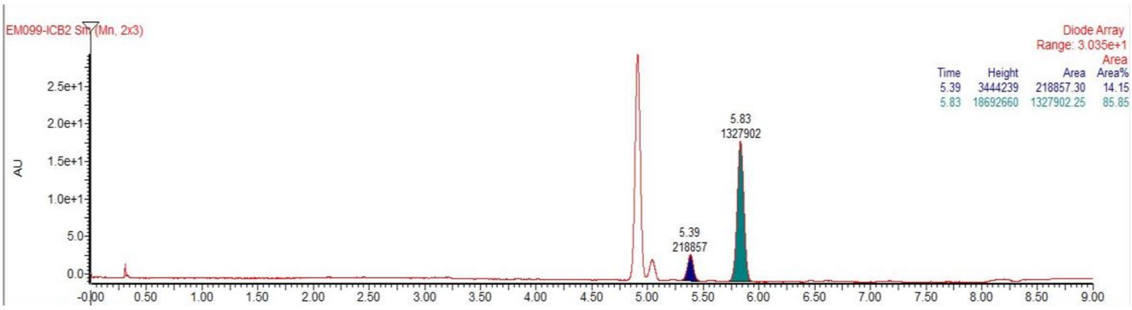
Time	Height	Area	Area Area%
2.43	104914	7385.27	48.29
2.91	138245	7908.51	51.71

Full trace for **3p** (diastereoisomer 1) enantioenriched:



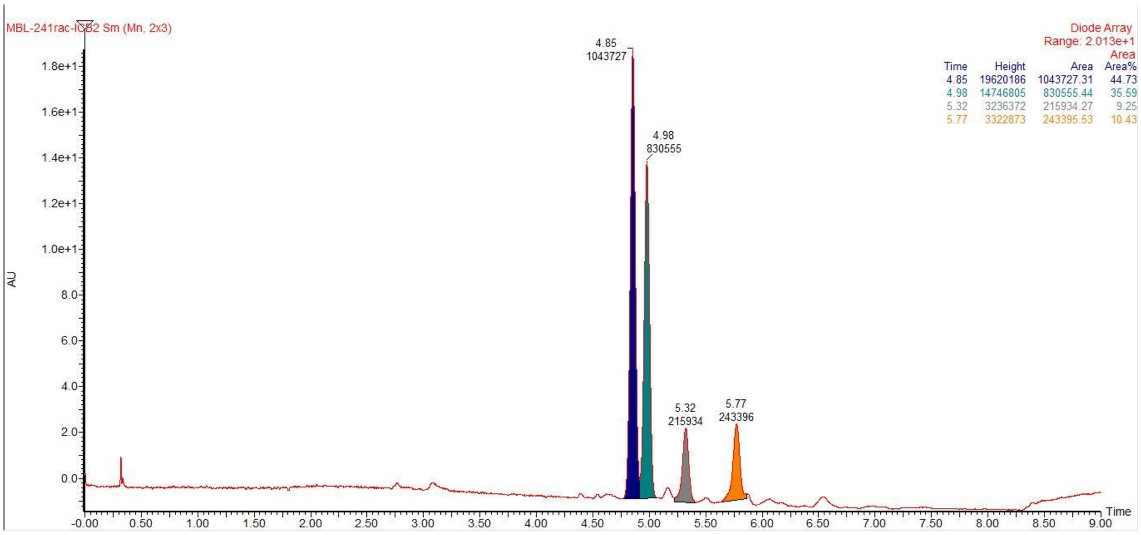
Time	Height	Area	Area Area%
4.91	30073276	1649959.25	91.21
5.04	2757775	159099.34	8.79

Full trace for **3p** (diastereoisomer 2) enantioenriched:



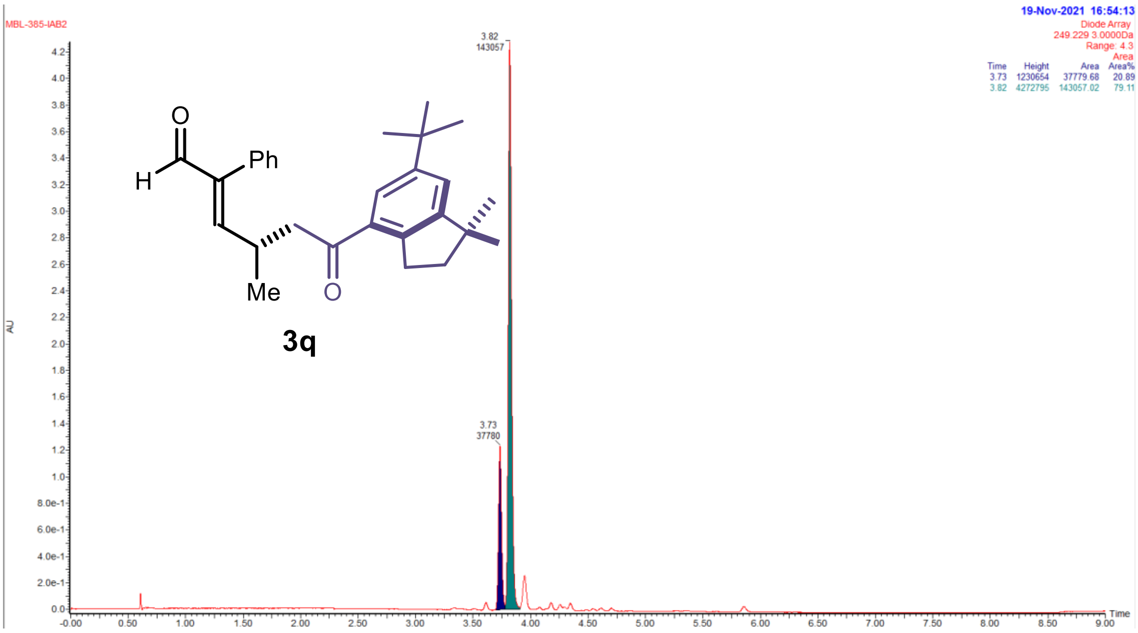
Time	Height	Area	Area Area%
5.39	3444239	218857.30	14.15
5.83	18692660	1327902.25	85.85

Full trace for **3p** (Both diastereoisomers) *racemic*:



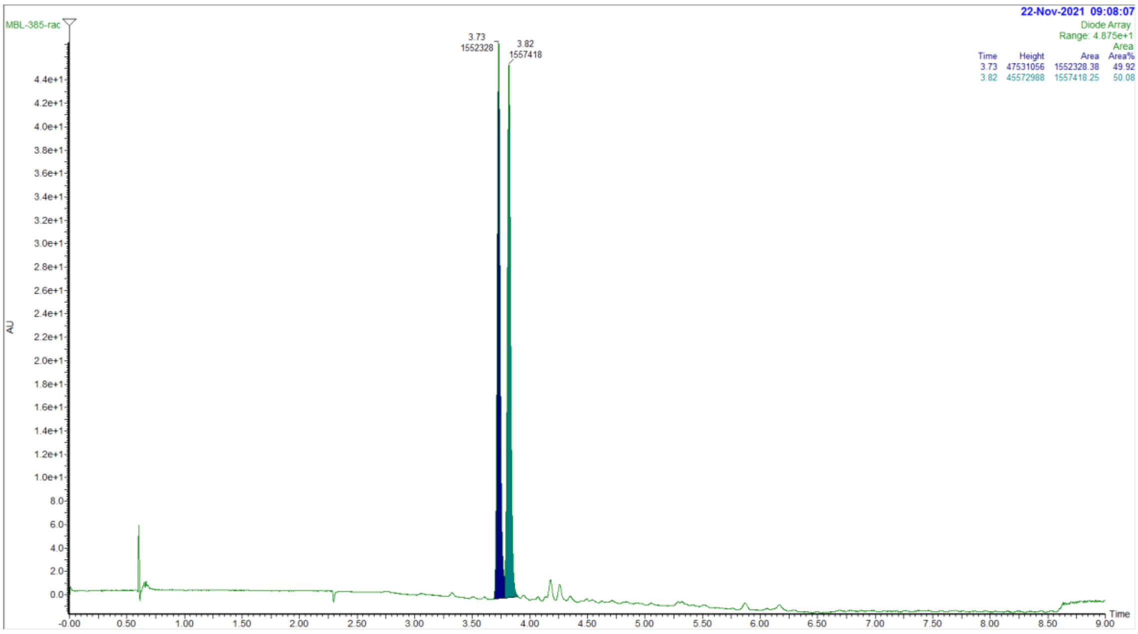
Time	Height	Area	Area Area%
4.85	19620186	1043727.31	44.73
4.98	14746805	830555.44	35.59
5.32	3236372	215934.27	9.25
5.77	3322873	243395.53	10.43

Full trace for **3q** enantioenriched:



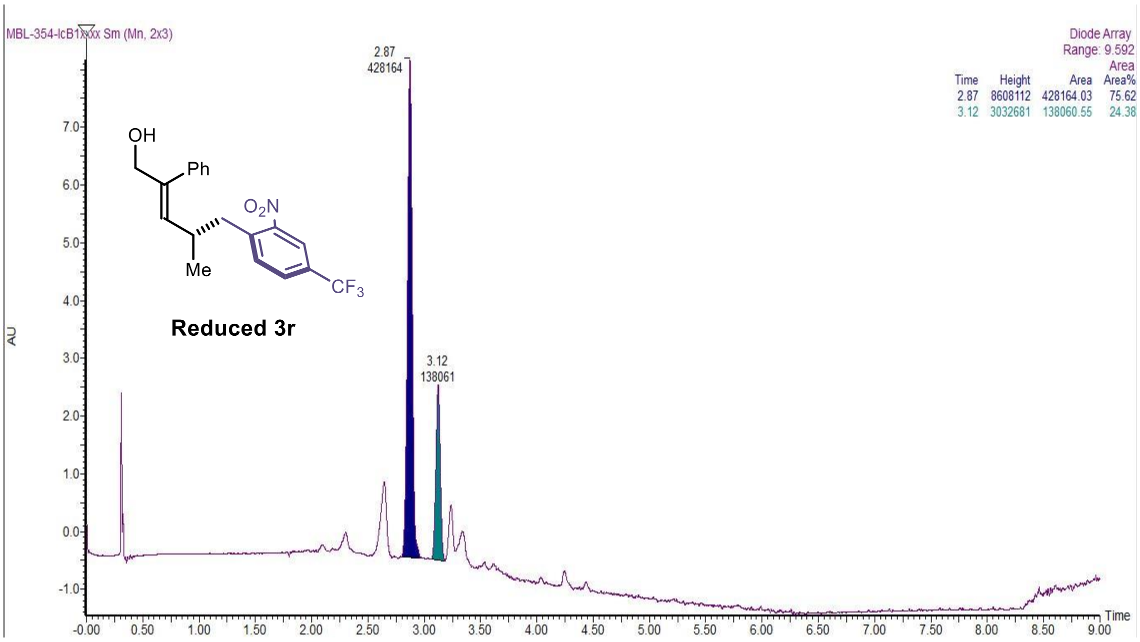
Time	Height	Area	Area Area%
3.73	1230654	37779.68	20.89
3.82	4272795	143057.02	79.11

Full trace for **3q** *racemic*:

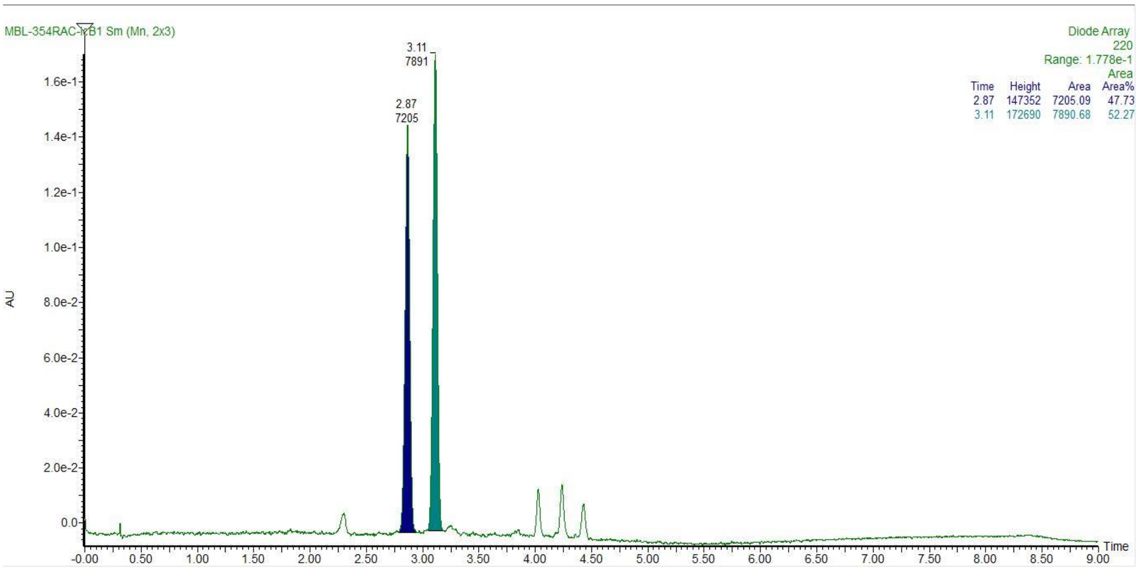


Time	Height	Area	Area Area%
3.73	47531056	1552328.38	49.92
3.82	45572988	1557418.25	50.08

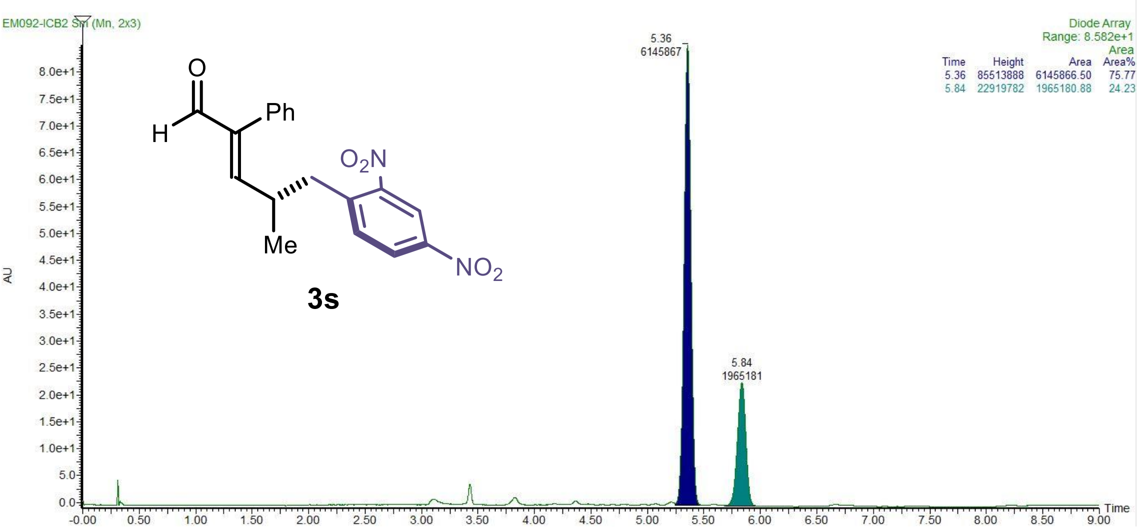
Full trace for **3r** enantioenriched:



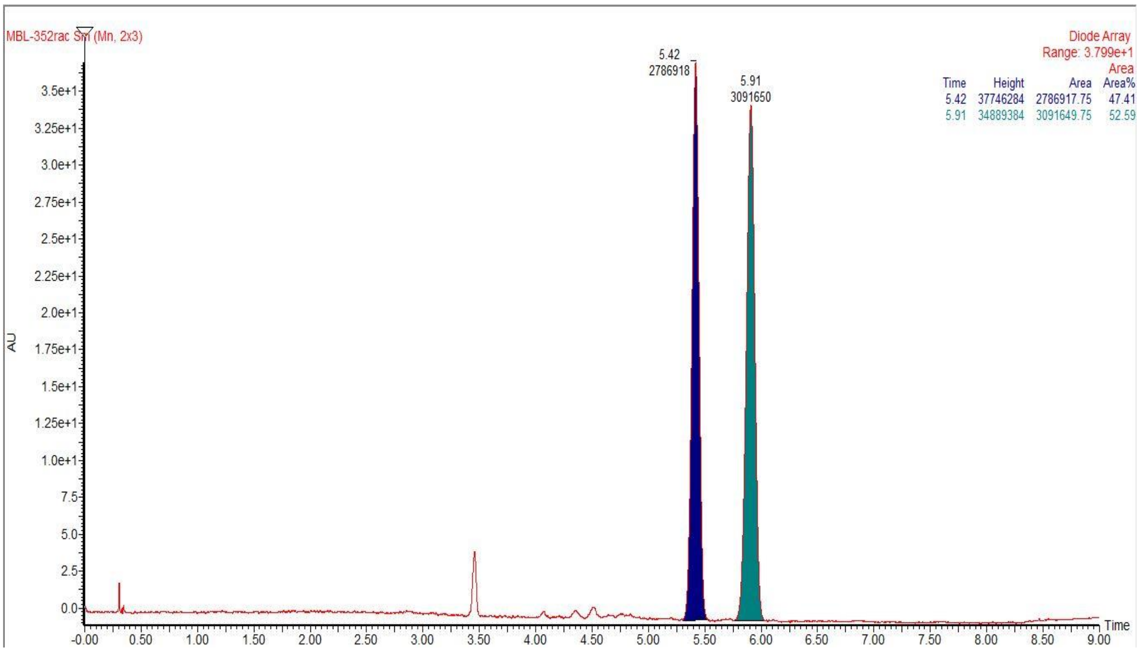
Full trace for **3r** *racemic*:



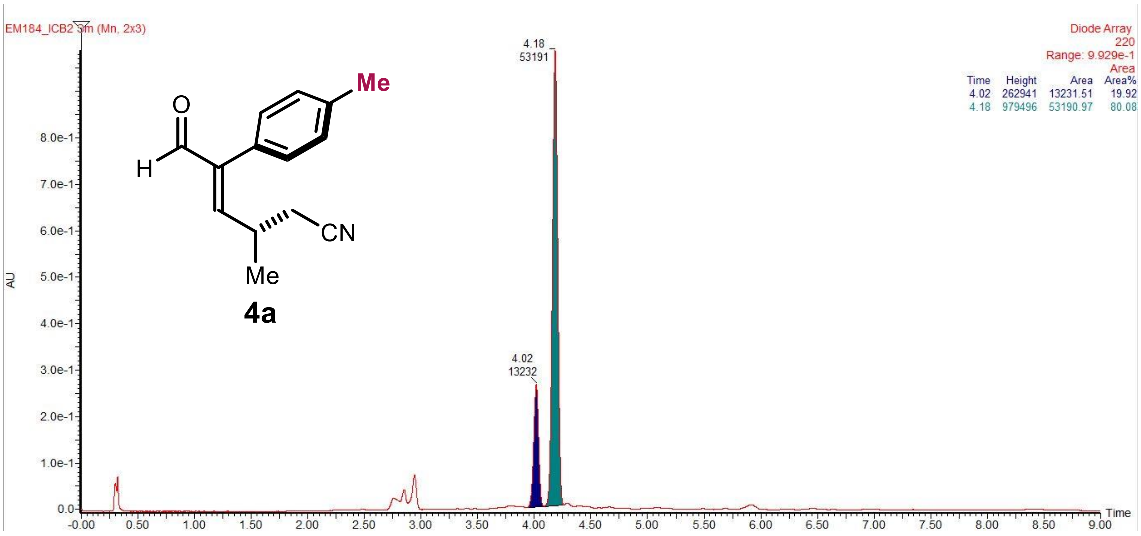
Full trace for **3s** enantioenriched:



Full trace for **3s** *racemic:*



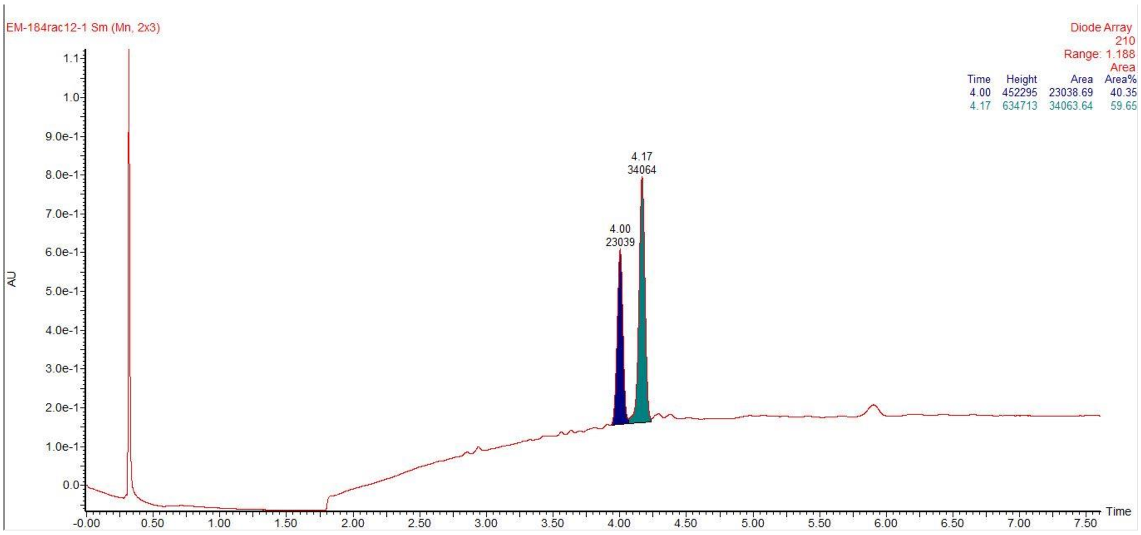
Full trace for **3s** enantioenriched:



Area

Time	Height	Area	Area%
4.02	262941	13231.51	19.92
4.18	979496	53190.97	80.08

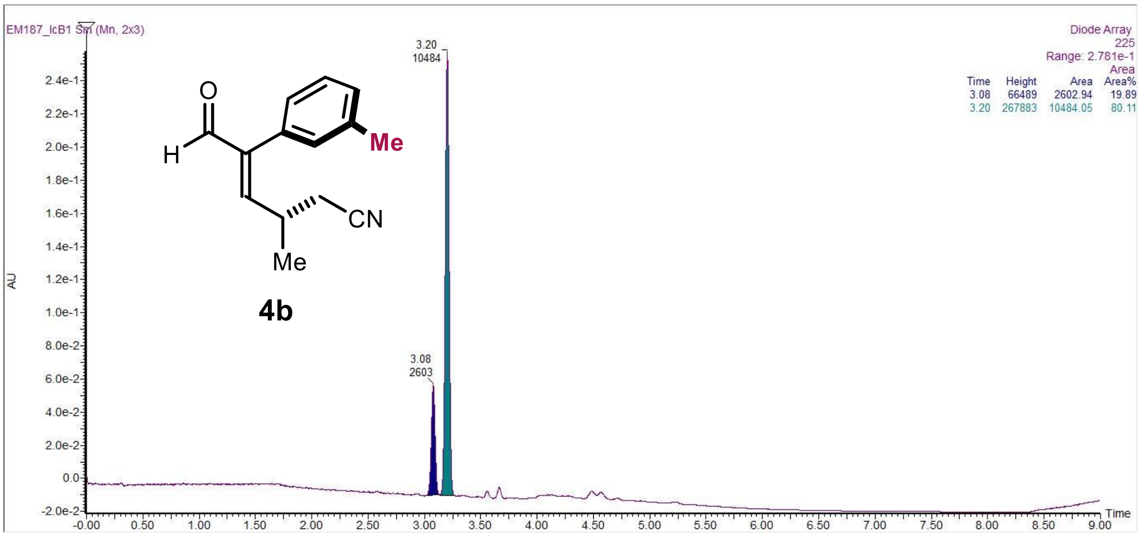
Zoom trace for **3s** *racemic*:



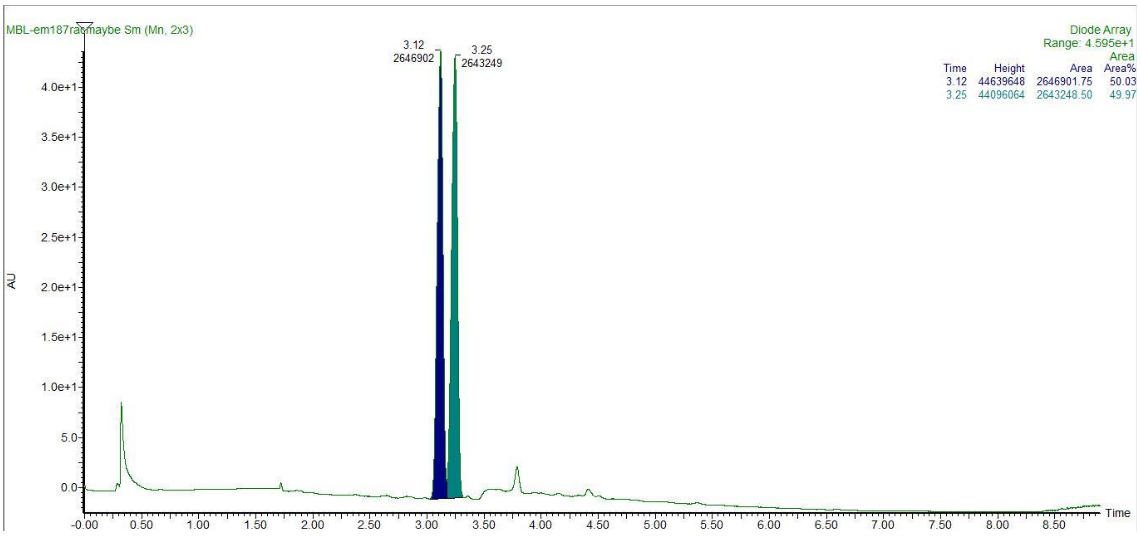
Area

Time	Height	Area	Area%
4.00	452295	23038.69	40.35
4.17	634713	34063.64	59.65

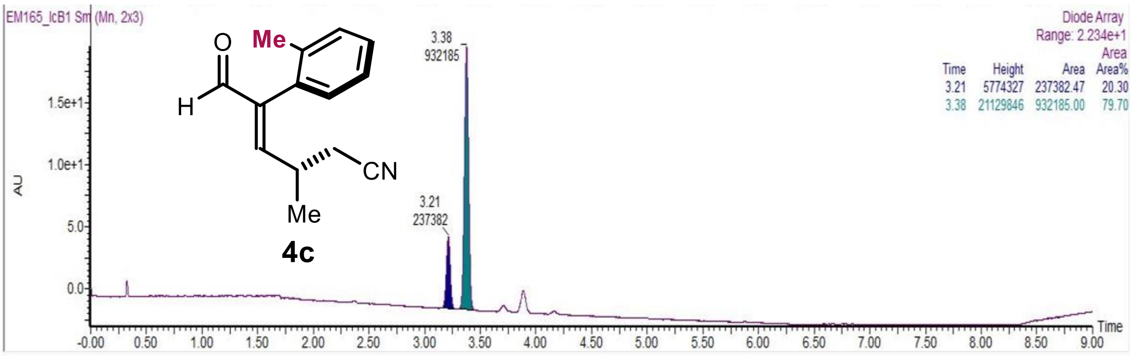
Full trace for **4b** enantioenriched:



Zoom trace for **4b** *racemic*:

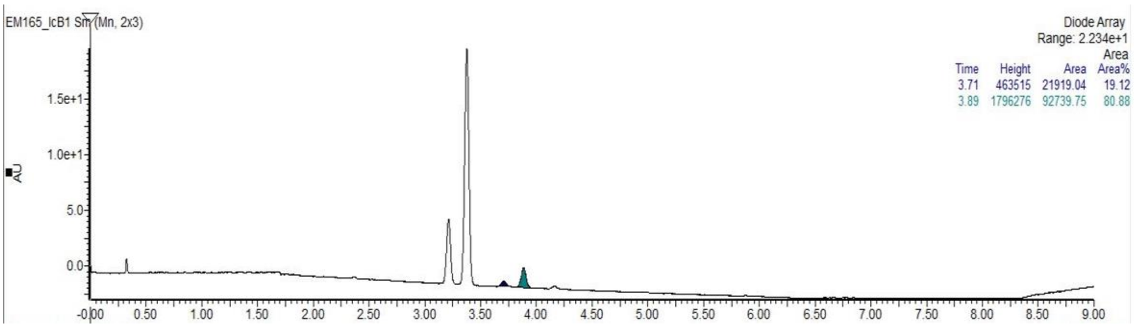


Full trace for **4c** (rotamer 1) enantioenriched:



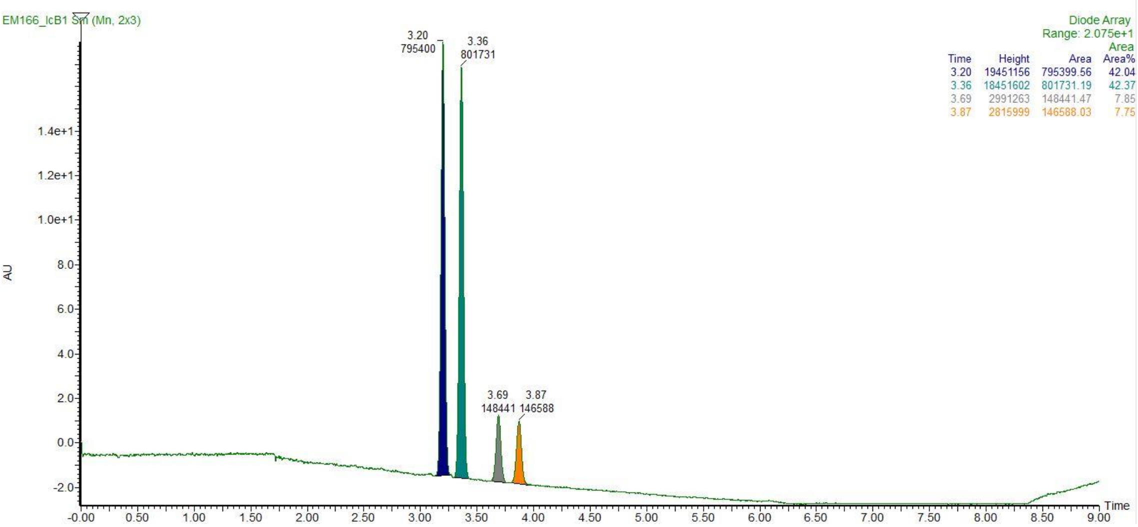
Time	Height	Area	Area Area%
3.21	5774327	237382.47	20.30
3.38	21129846	932185.00	79.70

Full trace for **4c** (rotamer 2) enantioenriched:



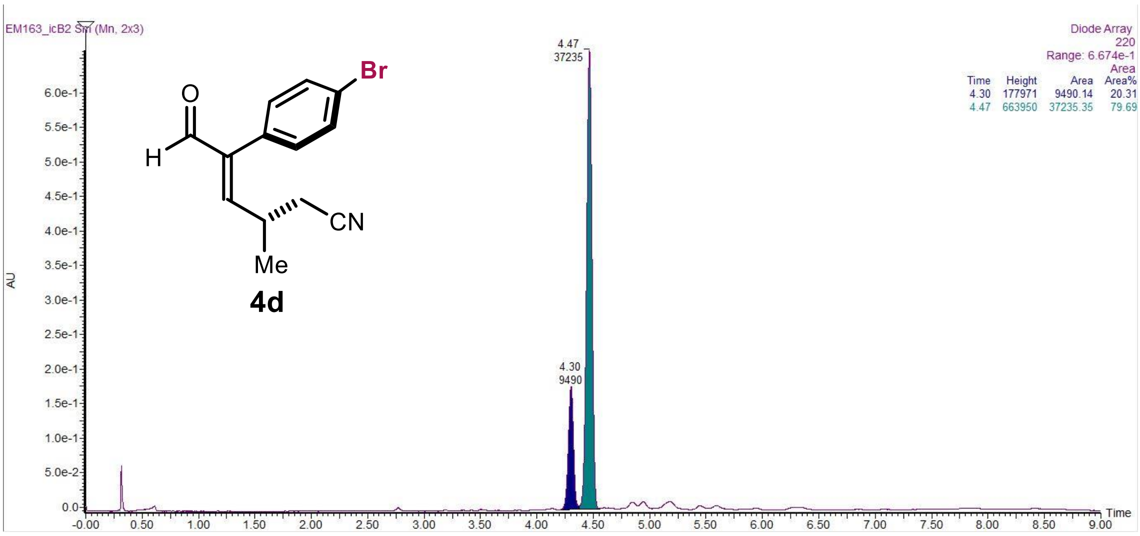
Time	Height	Area	Area Area%
3.71	463515	21919.04	19.12
3.89	1796276	92739.75	80.88

Full trace for **4c** (rotamer 1 + rotamer 2) *racemic*:



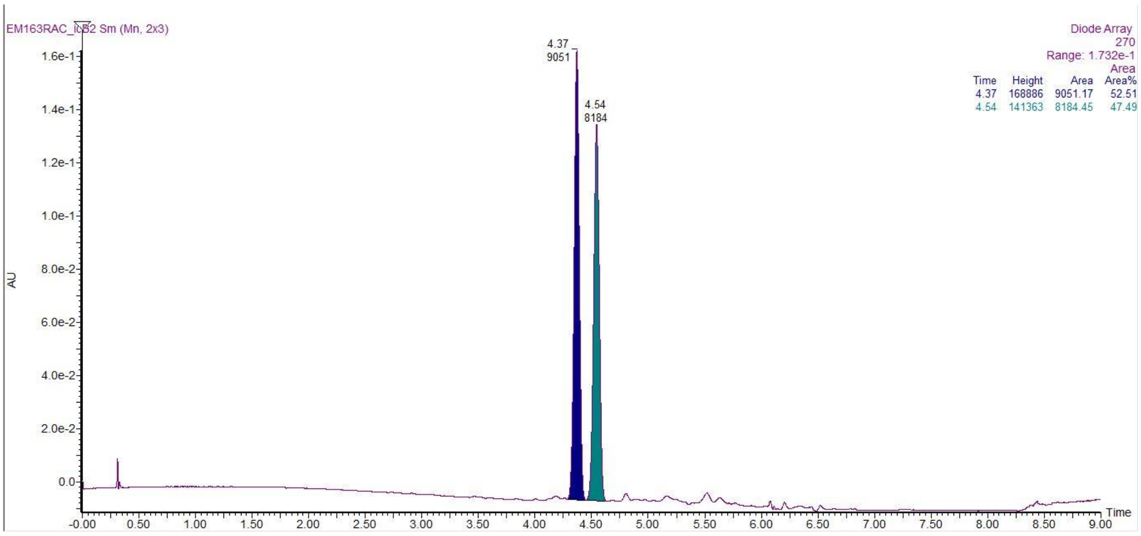
Time	Height	Area	Area Area%
3.20	19451156	795399.56	42.04
3.36	18451602	801731.19	42.37
3.69	2991263	148441.47	7.85
3.87	2815999	146588.03	7.75

Full trace for **4d** enantioenriched:



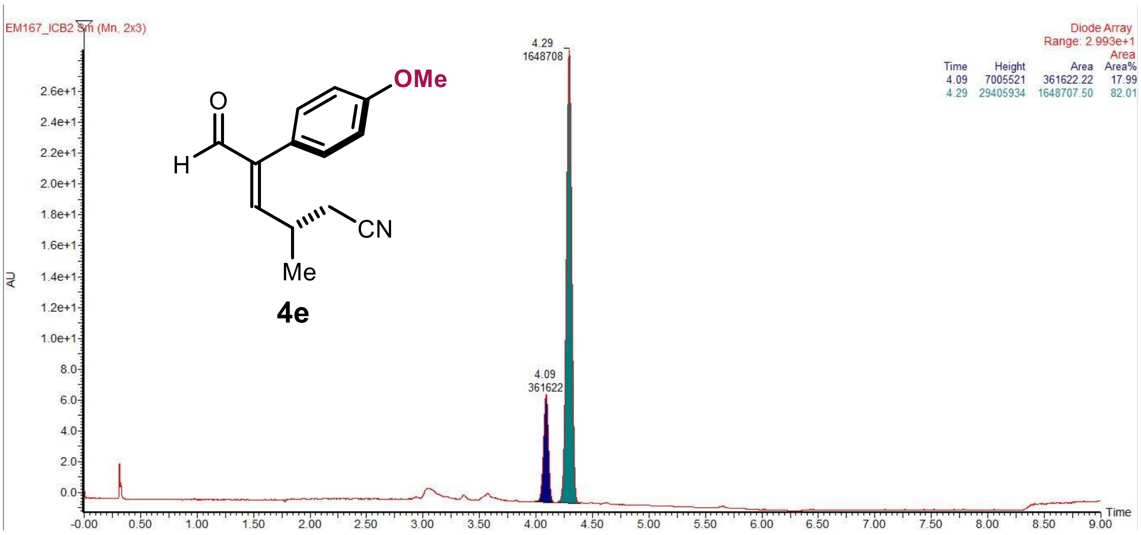
Time	Height	Area	Area%
4.30	177971	9490.14	20.31
4.47	663950	37235.35	79.69

Full trace for **4d** *racemic*:



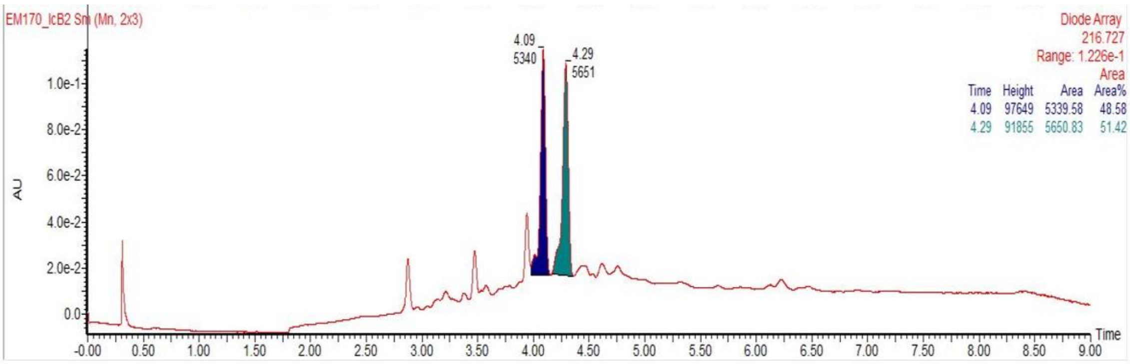
Time	Height	Area	Area%
4.37	168886	9051.17	52.51
4.54	141363	8184.45	47.49

Full trace for **4e** enantioenriched:



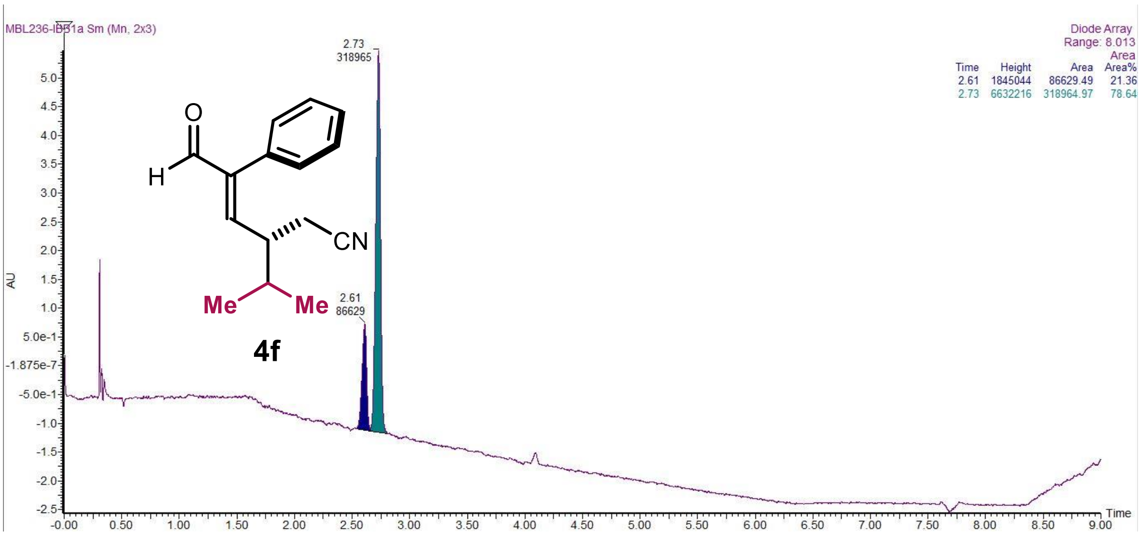
Time	Height	Area	Area%
4.09	7005521	361622.22	17.99
4.29	29405934	1648707.50	82.01

Full trace for **4e** *racemic*:

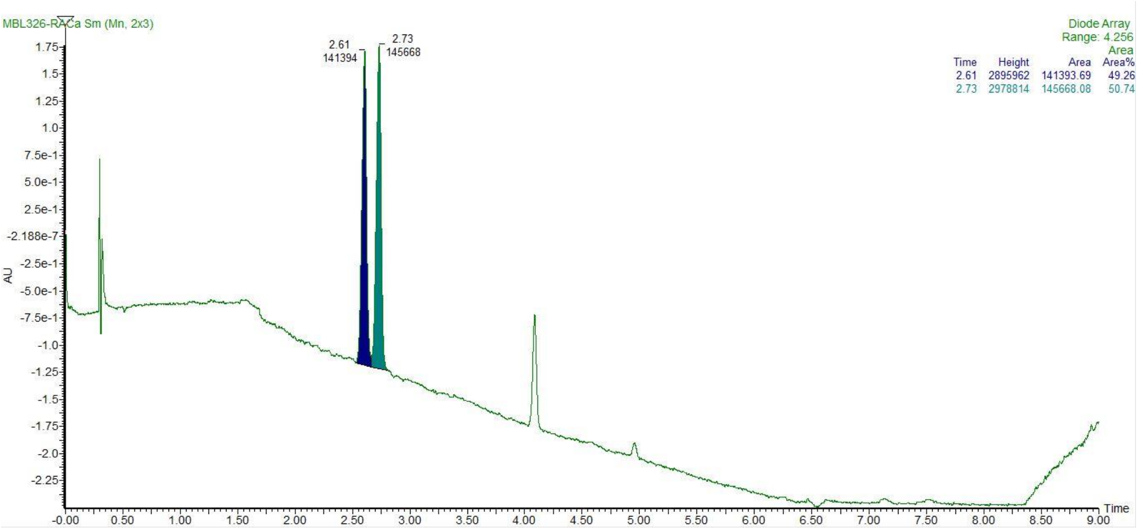


Time	Height	Area	Area%
4.09	97649	5339.58	48.58
4.29	91855	5650.83	51.42

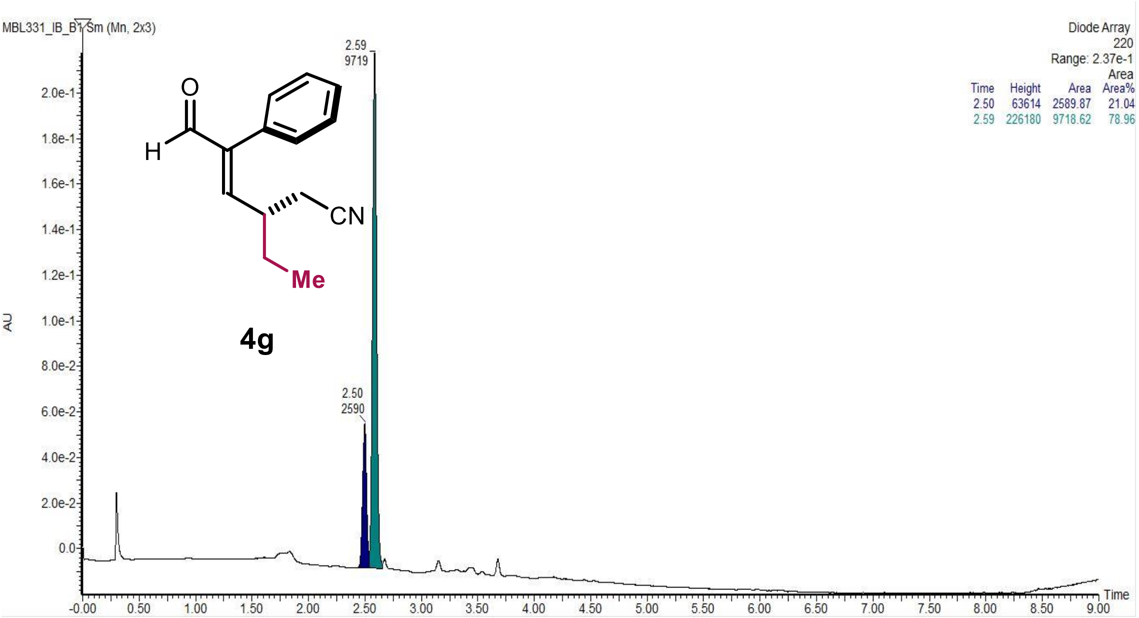
Full trace for **4f** enantioenriched:



Full trace for **4f** *racemic*:

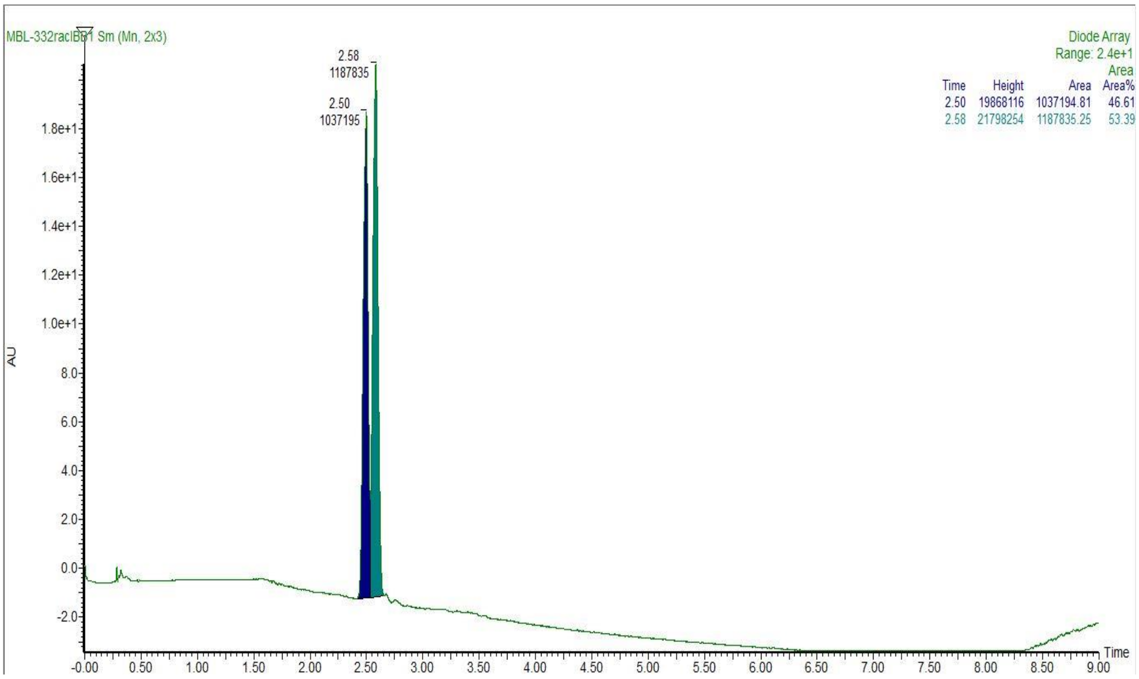


Full trace for **4g** enantioenriched:



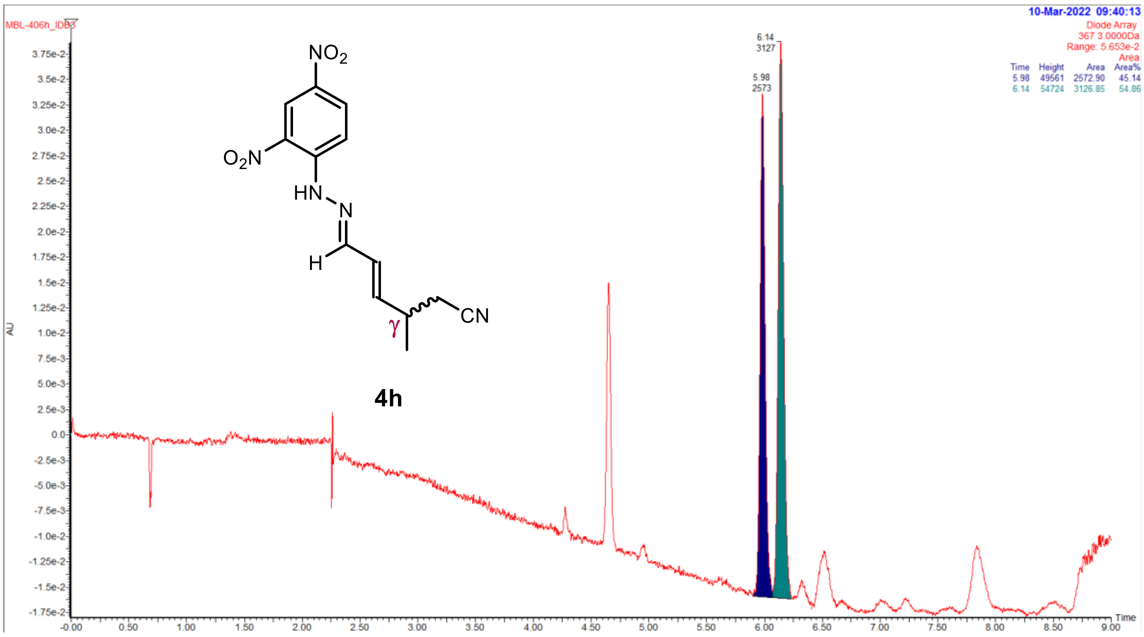
Time	Height	Area	Area%
2.50	63614	2589.87	21.04
2.59	226180	9718.62	78.96

Full trace for **4g** *racemic*:

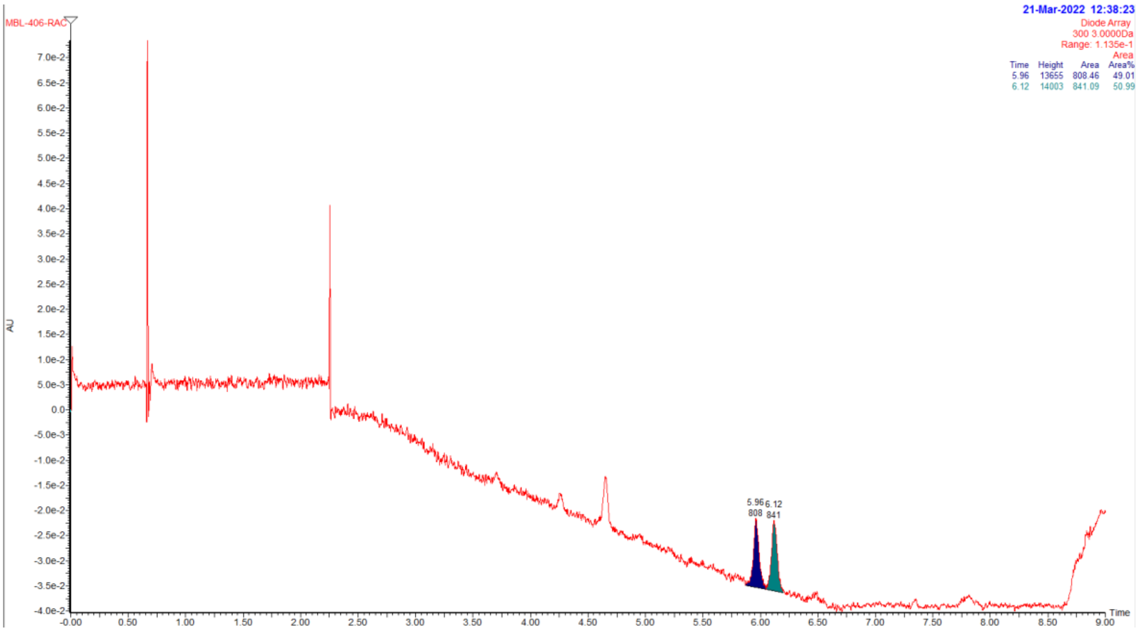


Time	Height	Area	Area%
2.50	19868116	1037194.81	46.61
2.58	21798254	1187835.25	53.39

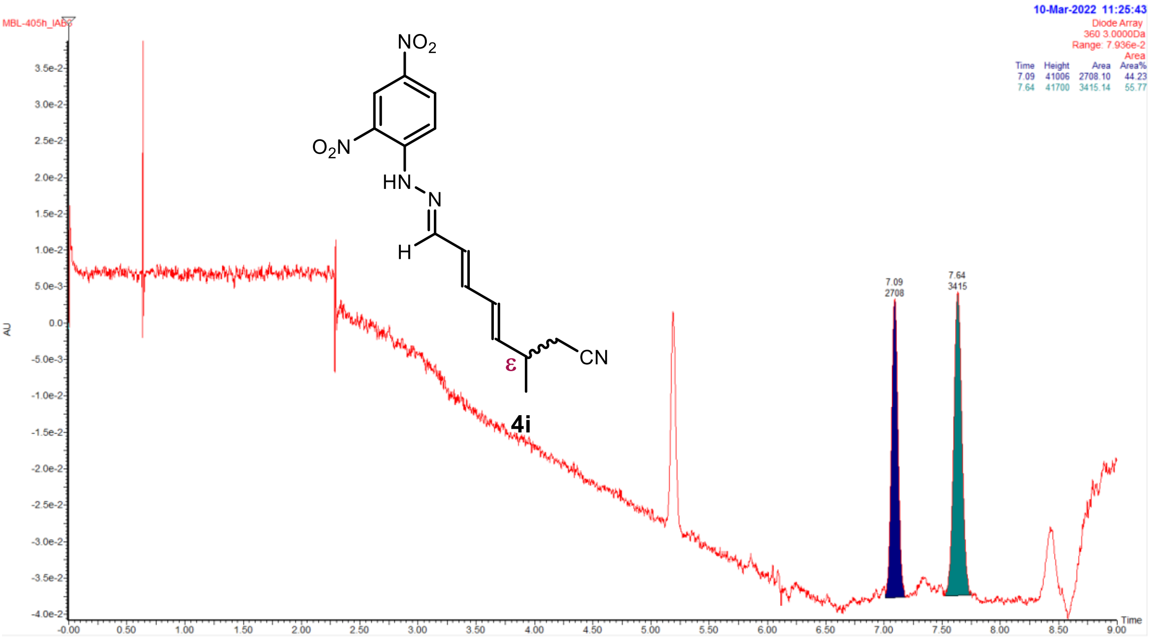
Full trace for **4h** (2,4-dinitrophenylhydrazone derivatized) enantioenriched:



Full trace for **4h** (2,4-dinitrophenylhydrazone derivatized) *racemic*:



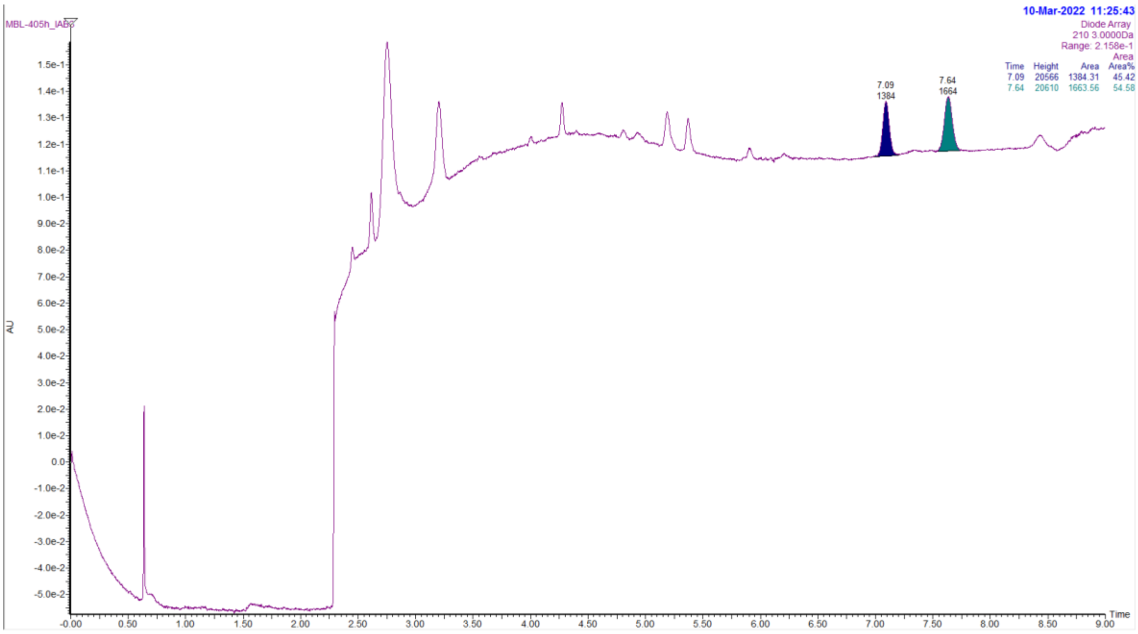
Full trace for **4i** (2,4-dinitrophenylhydrazone derivatized) enantioenriched:



4i

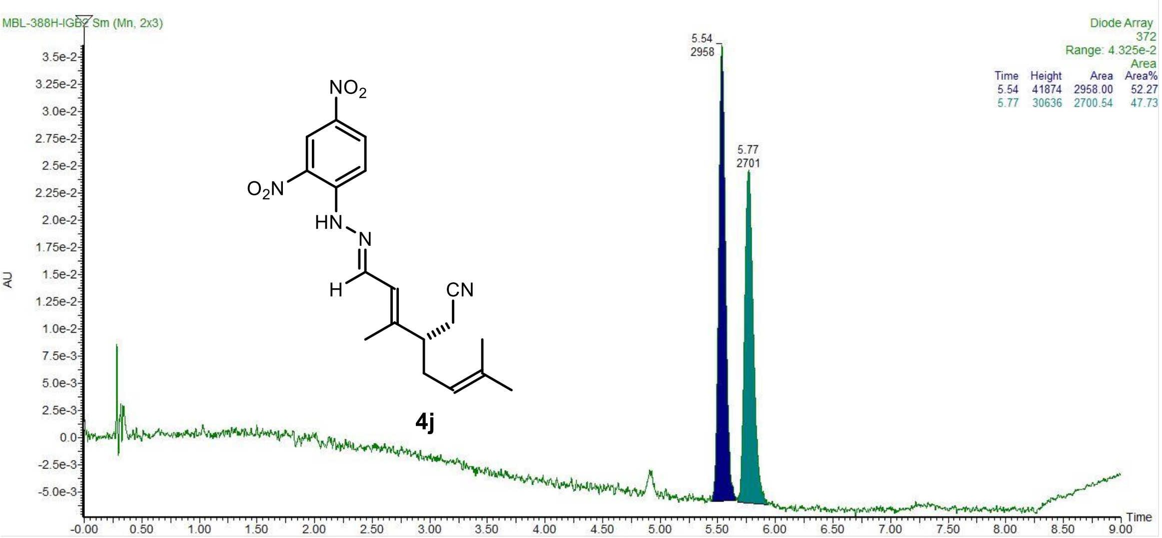
Time	Height	Area	Area Area%
7.09	41006	2708.10	44.23
7.64	41700	3415.14	55.77

Full trace for **4i** (2,4-dinitrophenylhydrazone derivatized) *racemic*:



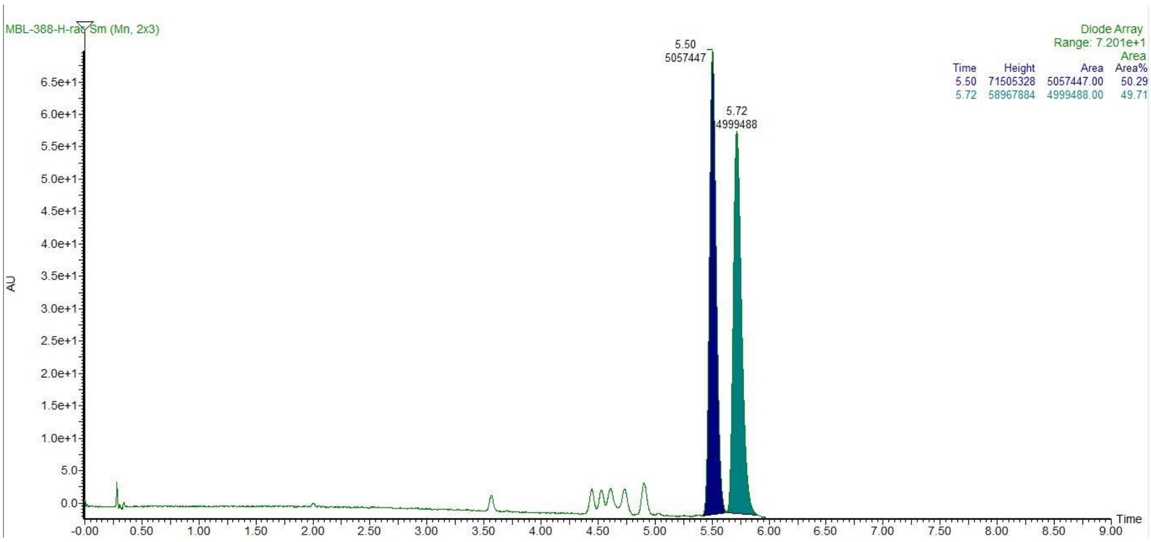
Time	Height	Area	Area Area%
7.09	20566	1384.31	45.42
7.64	20610	1663.56	54.58

Full trace for **4j** (2,4-dinitrophenylhydrazone derivatized) enantioenriched:



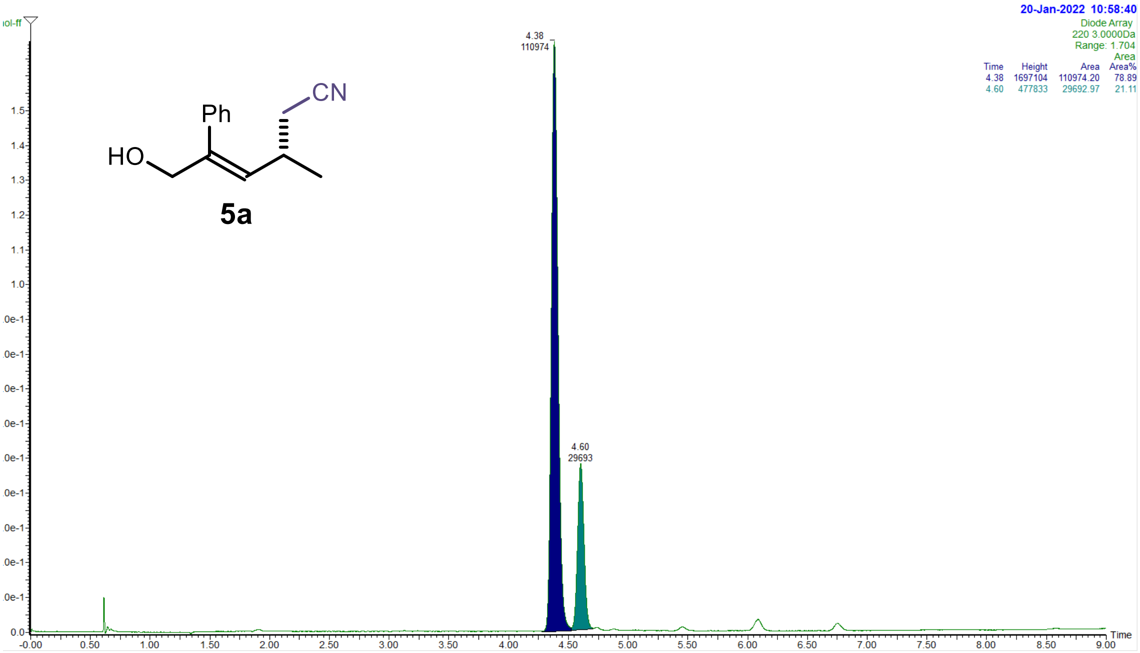
Time	Height	Area	Area%
5.54	41874	2958.00	52.27
5.77	30636	2700.54	47.73

Full trace for **4j** *racemic*:



Time	Height	Area	Area%
5.50	71505328	5057447.00	50.29
5.72	58967884	4999488.00	49.71

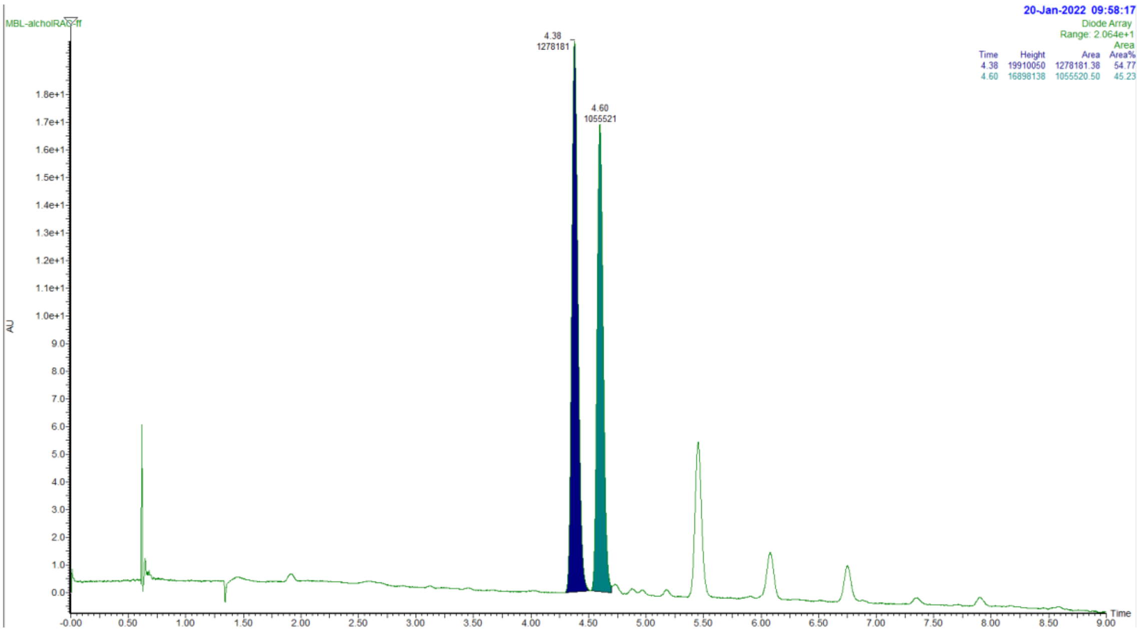
Full trace for **5a** enantioenriched:



20-Jan-2022 10:58:40
Diode Array
220 3.0000Da
Range: 1.704

Time	Height	Area	Area Area%
4.38	1697104	110974.20	78.89
4.60	477833	29692.97	21.11

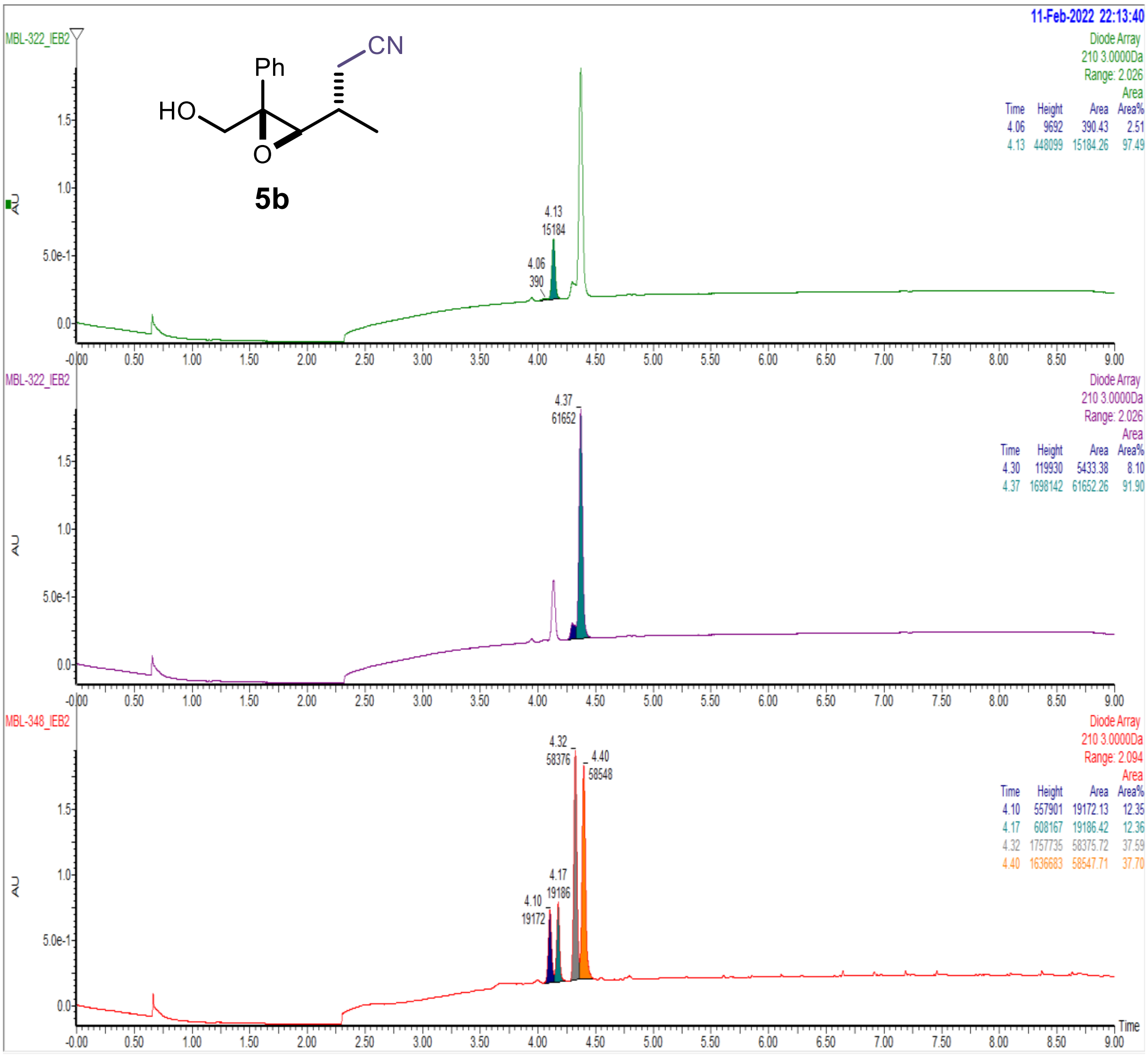
Full trace for **5a** *racemic*:



20-Jan-2022 09:58:17
Diode Array
Range: 2.064e+1

Time	Height	Area	Area Area%
4.38	19910050	1278181.38	54.77
4.60	16898138	1055520.50	45.23

Full traces for **5b** enantioenriched (both enantiomers), and Full traces for **5b** Racemic (Bottom):

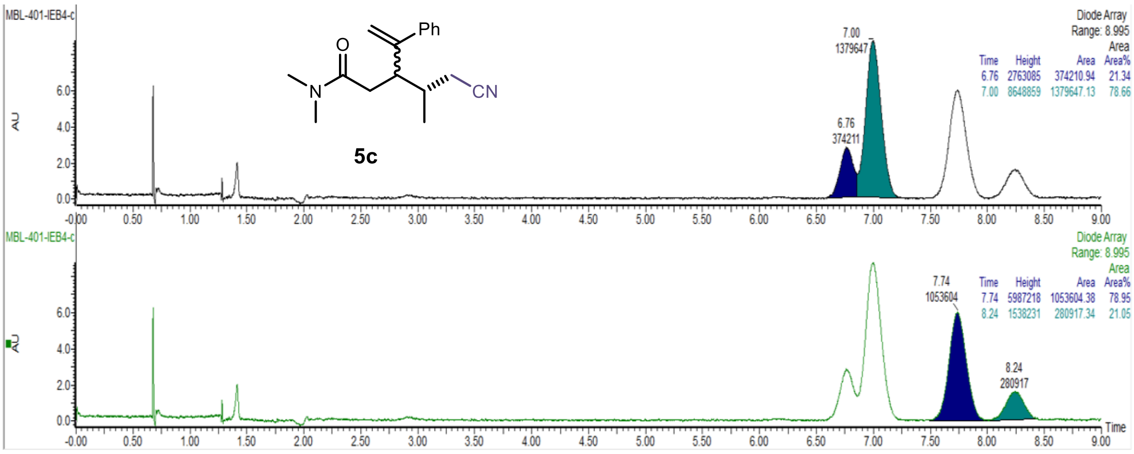


Time	Height	Area	Area Area%
4.06	9692	390.43	2.51
4.13	448099	15184.26	97.49

Time	Height	Area	Area Area%
4.30	119930	5433.38	8.10
4.37	1698142	61652.26	91.90

Time	Height	Area	Area Area%
4.10	557901	19172.13	12.35
4.17	608167	19186.42	12.36
4.32	1757735	58375.72	37.59
4.40	1636683	58547.71	37.70

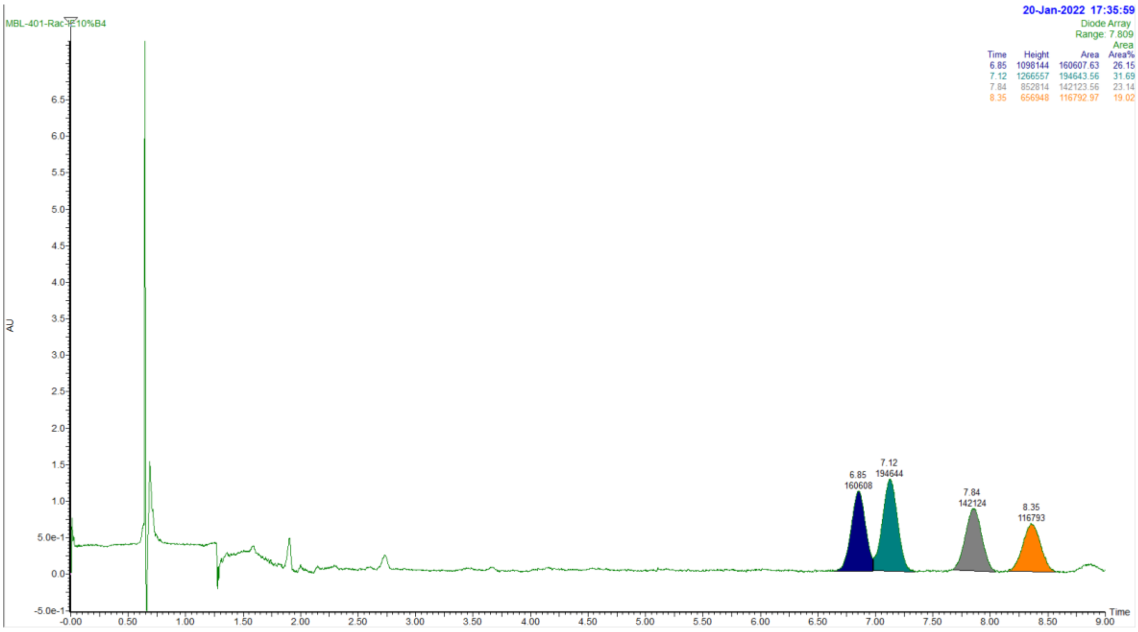
Full trace for **5c** enantioenriched:



Time	Height	Area	Area Area%
6.76	2763085	374210.94	21.34
7.00	8648859	1379647.13	78.66

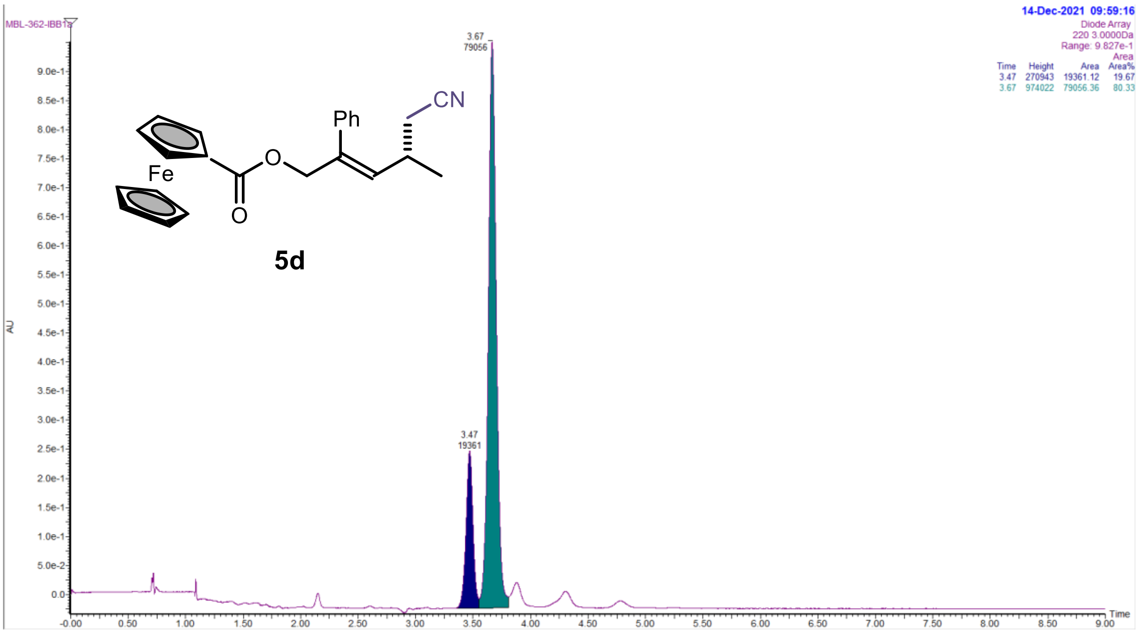
Time	Height	Area	Area Area%
7.74	5987218	1053604.38	78.95
8.24	1538231	280917.34	21.05

Full trace for **5c** *racemic*:



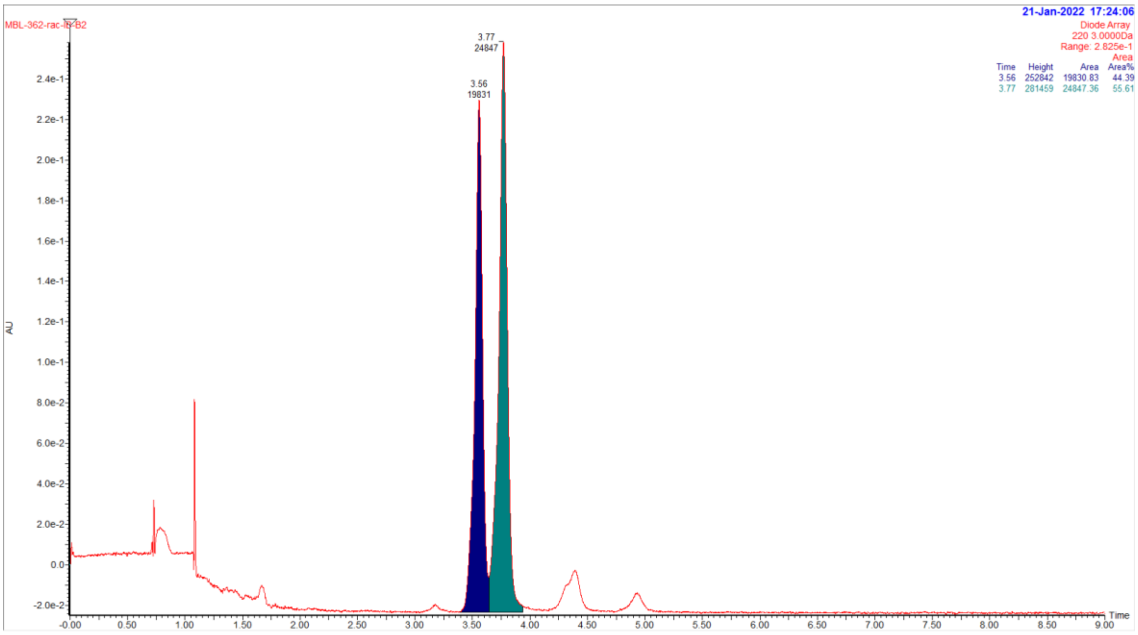
Time	Height	Area	Area Area%
6.85	1098144	160607.63	26.15
7.12	1266557	194643.56	31.69
7.84	852814	142123.56	23.14
8.35	656948	116792.97	19.02

Full trace for **5d** enantioenriched:



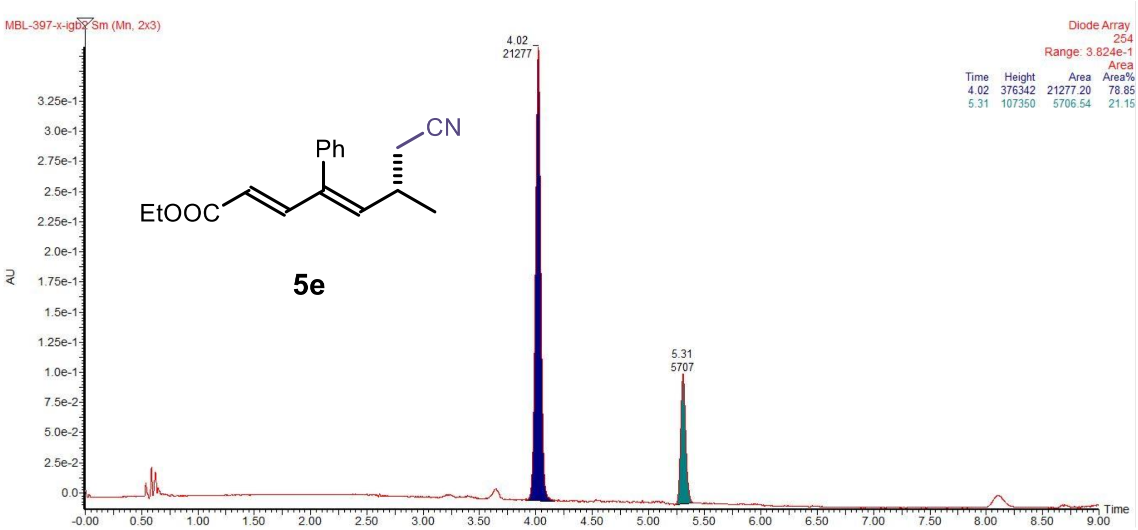
Time	Height	Area	Area Area%
3.47	270943	19361.12	19.67
3.67	974022	79056.36	80.33

Full trace for **5d** *racemic*:



Time	Height	Area	Area Area%
3.56	252842	19830.83	44.39
3.77	281459	24847.36	55.61

Full trace for **5e** enantioenriched:



Full trace for **5e** *racemic*: