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Supporting Information

Enantioselective Formal α-Methylation and α-Benzylation of Aldehydes by Means of Photo-Organocatalysis

*Giacomo Filippini, Mattia Silvi, and Paolo Melchiorre**

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Author Contributions

G.F. Formal analysis: Equal; Investigation: Lead; Methodology: Lead; Writing—original draft: Supporting
M.S. Conceptualization: Equal; Formal analysis: Supporting; Investigation: Supporting; Methodology: Supporting; Writing—review & editing: Supporting
P.M. Conceptualization: Equal; Formal analysis: Supporting; Funding acquisition: Lead; Investigation: Equal; Methodology: Supporting; Project administration: Lead; Supervision: Lead; Writing—original draft: Lead; Writing—review & editing: Lead.

Supplementary Information for

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A. General Information

The NMR spectra were recorded at 400 MHz for ^{1}H, 101 MHz for ^{13}C and 376 MHz for ^{1}H decoupled ^{19}F. The chemical shift (δ) for ^{1}H, ^{13}C and ^{1}H decoupled ^{19}F 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.
High resolution mass spectra (HRMS) were obtained from the ICIQ HRMS unit on Waters GCT gas chromatograph coupled time-of-flight mass spectrometer (GC/MS-TOF) with electrospray ionization (ESI).
Optical rotations Optical rotations were measured on a Polarimeter Jasco P-1030 and are reported as follows: $[\alpha]_D$ r.T. (c in g per 100 mL, solvent).
Cyclic voltammetry studies were carried out on a Princeton Applied Research PARSTAT 2273 potentiostat offering compliance voltage up to ± 100 V (available at the counter electrode), ± 10 V scan range and ± 2 A current range.
UV-vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with photomultiplier detector, double beam optics and D_2 and W light sources.
Cut-off and band-pass photochemical experiments have been performed using a 300 W xenon lamp (*Asashi* Spectra Co., Ltd.) to irradiate the reaction mixture.

The authors are indebted to the team of the Research Support Area at ICIQ. Grace Fox is thanked for proofreading the manuscript.

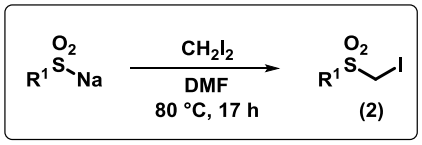
General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques, unless otherwise stated. Synthesis grade solvents were used as purchased. Anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using force-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 *para*-anisaldehyde or basic aqueous potassium permangante ($KMnO_4$) stain solutions, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator.

Determination of Enantiomeric Purity: HPLC analysis on chiral stationary phase was performed on an Agilent 1200-series instrument, employing Daicel Chiralpak IA, IB, ID, IC, and IC-3 chiral columns, or a Waters ACQUITY® UPC^2 instrument, using Trefoil IC, AMY1, CEL1, and CEL2 chiral columns. The exact conditions for the analyses are specified within the characterisation section. HPLC and UPC^2 traces were compared to racemic samples prepared performing the reactions in the presence of a racemic mixture of the amine catalyst **A**.

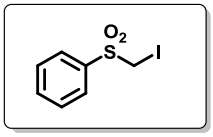
Materials. Commercial reagents and solvents were purchased at the highest commercial quality from Sigma-Aldrich, Fluka, Alfa Aesar, Fluorochem, SynQuest and used as received, without further purification, unless otherwise stated. The chiral secondary amine catalysts *(S)*-**A** is commercially available, but was purified by flash column chromatography prior to use and stored at 4 ºC under argon to avoid undesired desilylation that would affect the catalytic potential of the amine. Sodium thiosulfate anhydrous (extra pure, 98.5%) was purchased from Acros Organic and used as received. Butyraldehyde **2a**, hexanal **2b,** octanal **2c**, dodecanal **2d**, hydrocinnamaldehyde **2e**, isovaleraldehyde **2f**, 3,3-dimethylbutyraldehyde **2g**, 10-undecenal **2h**, 2-(1-methyl-4-piperidinyl)acetaldehyde **2i** and methional **2j** are all commercially available. The preparation of the α-iodo sulfones is detailed in Section B of the Supplementary Information (SI).

B. Synthesis of α-Iodo Sulfones

General Procedure 1: Synthesis of α-Iodo Sulfones (2a), (2k) and (2l)

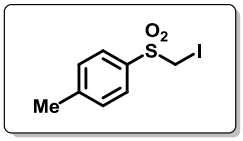


The reaction was conducted in an oven dried, argon purged, two neck flask fitted with a condenser/argon inlet and septum and following a modified literature procedure (*1*). A solution of sodium sulfinate (1.0 equiv) in dimethylformamide (0.25 M) was stirred at room temperature for 15 minutes. Diiodomethane (1.2 equiv) was added dropwise and the solution was heated up to 80 ºC and stirring was continued over 17 hours. The reaction was quenched by the addition of water (100 mL). The solution was then transferred to a separatory funnel and extracted with ethyl acetate (3 x 50 mL). The organic phases were combined and washed with brine (50 mL), saturated solution of sodium thiosulfate (50 mL) and then dried over magnesium sulfate before concentration *in vacuo*. The residue was purified by flash column chromatography to afford the desired α-iodo-sulfone (**2**).



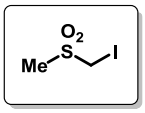
(Iodomethyl)sulfonyl)benzene (2a) was prepared according to general Procedure **1** using sodium benzenesulfinate (10.0 g, 60.9 mmol, 1.0 equiv) The residue was purified by flash column chromatography (*n*-hexane:ethyl acetate = 3:1) affording the desired iodo-sulfone **2a** as a white solid (12.0 g, 70% yield).

^{1}H NMR:(400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.72 (tt, *J* = 6.9, 1.2 Hz, 1H), 7.66 – 7.58 (m, 2H), 4.48 (s, 2H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 135.9, 134.6, 129.4, 129.0, 16.9.



1-((Iodomethyl)sulfonyl)-4-methylbenzene (2k) was prepared according to general Procedure **1** using sodium 4-methylbenzenesulfinate (10.80 g, 60.0 mmol, 1.0 equiv) The residue was purified by flash column chromatography (*n*-hexane:ethyl acetate = 3:1) affording the desired iodo-sulfone **2k** as a white solid (11.6 g, 65% yield).

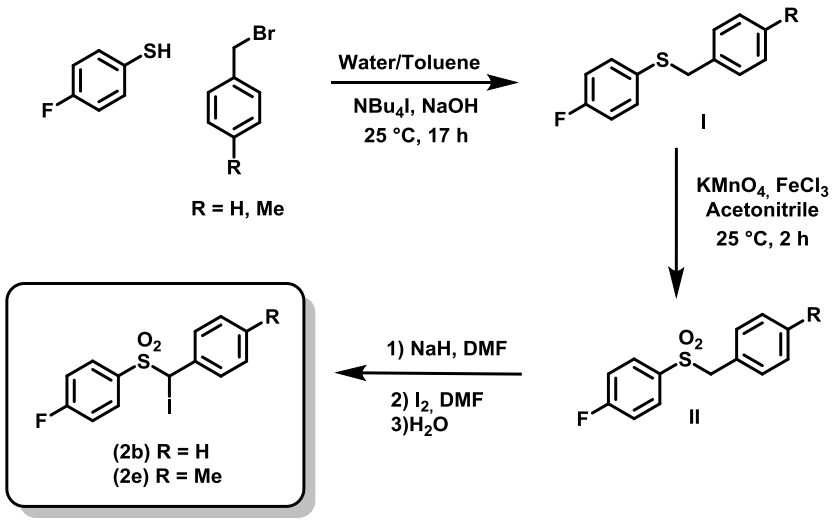
^{1}H NMR:(400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.44 (s, 2H), 2.48 (s, 3H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 145.89 , 133.18 , 130.12 , 129.20 , 21.89 , 17.07.



1-((Iodomethyl)sulfonyl)-4-methylbenzene (2l) was prepared according to general Procedure **1** using sodium methanesulfinate (6.0 g, 60.0 mmol, 1.0 equiv) The residue was purified by flash column chromatography (*n*-hexane:ethyl acetate = 3:1) affording the desired iodo-sulfone (**2l**) as a white solid (6.6 g, 50% yield).

^{1}H NMR:(400 MHz, $CDCl_3$) δ 4.38 (q, *J* = 0.8 Hz, 2H), 3.18 (d, *J* = 0.9 Hz, 3H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 38.54 , 13.59.

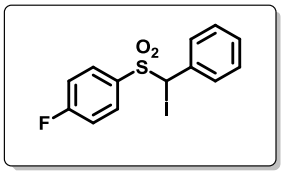
General Procedure 2: Synthesis of α-Iodo Sulfones (2b) and (2e)



STEP 1: A solution of 4-fluorobenzenethiol (45 mmol, 5.8 g) and the appropriate benzyl bromide (48 mmol, 1.06 equiv) in toluene (20 mL) was added to a solution containing NaOH (75 mmol, 3 g) and Bu_4NI (1.4 mmol, 0.5 g) in H_2O (20 mL). The biphasic system was stirred vigorously during 16 hours at room temperature. The aqueous phase was extracted with Et_2O (3 x 20 mL), the combined organic phases were washed with NaOH (20 mL, 1M) and brine (50 mL) and then dried over magnesium sulfate before concentration *in vacuo*. The residue (**I**) was used without any further purification (R = H: 95% yield; R = Me: 97% yield).

STEP 2, according to a modified literature procedure (*2*): A solution of **I** (25 mmol), $FeCl_3$ (0.9 mmol, 0.15 g), and $KMnO_4$ (95 mmol, 15 g) in acetonitrile (100 mL, 0.25 M) was stirred at room temperature for 2 hours. The crude reaction mixture was filtered over celite before concentration *in vacuo*. The residue was purified by flash column chromatography (*n*-hexane:ethyl acetate = 6:4) affording the desired product (**II**) as a white solid (R = H: 82% yield, R = Me: 80% yield).

STEP 3, according to a modified literature procedure (*3*): Compound **II** (17 mmol) was placed in a two-necked round-bottom flask and dissolved with 85 mL of dry DMF at room temperature under argon. To this solution was added 1.6 g of sodium hydride (60% dispersion in mineral oil). A temperature of 25 ºC was maintained constant while stirring the solution. In the meanwhile, the color changed from colorless to yellow. After 10 minutes, the solution was transferred via cannula to a solution of 4.2 g of iodine in 25 mL of dry DMF under argon. The resulting mixture was poured into 500 mL of water and the precipitate was collected and recrystallized from acetone to give the final compound (R = H: 40% yield, R= Me: 13% yield).

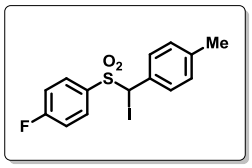


1-fluoro-4-((iodo(phenyl)methyl)sulfonyl)benzene (2b) was prepared according to the General Procedure **2** using benzyl bromide (8.2 g, 48 mmol, 1.06 equiv).

^{1}H NMR: (400 MHz, Chloroform-*d*) δ 7.62 – 7.53 (m, 2H), 7.37 – 7.27 (m, 3H), 7.25 – 7.18 (m, 2H), 7.11 – 6.99 (m, 2H), 5.90 (s, 1H).

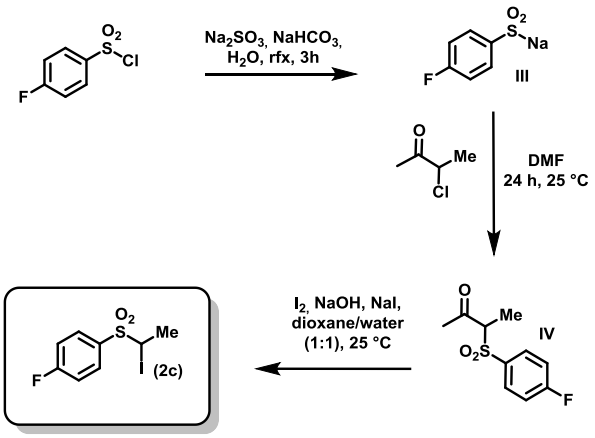
^{13}C NMR: (101 MHz, Chloroform-*d*) δ 166.20 (d, *J* = 257.8 Hz), 133.33, 132.70 (d, *J* = 9.8 Hz), 130.60, 130.22, 129.97 (d, *J* = 3.2 Hz), 128.88, 116.33 (d, *J* = 22.7 Hz), 43.35. **^{1}H decoupled ^{19}F NMR:** (376 MHz, Chloroform-*d*) δ -102.28 (s, 1F).

HRMS: Calculated for $C_{13}H_{10}FINaO_2S$ 398.9322, found 398.9328.



1-fluoro-4-((iodo(p-tolyl)methyl)sulfonyl)benzene (2e) was prepared according to general Procedure **II** using 4-methylbenzyl bromide (8.9 g, 48 mmol, 1.06 equiv).
^{1}H NMR: (400 MHz, Chloroform-*d*) δ 7.71 – 7.50 (m, 2H), 7.25 – 7.15 (m, 2H), 7.12 – 6.94 (m, 4H), 5.88 (s, 1H), 2.32 (s, 3H).
^{13}C NMR: δ 166.18 (d, *J* = 257.5 Hz), 140.55, 132.74 (d, *J* = 9.7 Hz), 130.44, 130.28, 129.57, 116.30 (d, *J* = 22.7 Hz), 43.36, 21.44. **^{1}H decoupled ^{19}F NMR:** (376 MHz, Chloroform-*d*) δ -102.45 (1F). **HRMS**: Calculated for $C_{14}H_{12}FINaO_2S$ 412.9479, found 412.9485.

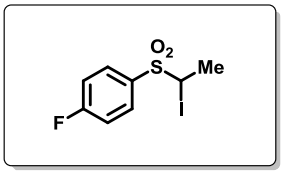
Synthesis of α-Iodo Sulfone 2c



STEP 1, according to (*4*): Commercially available 4-fluorobenzenesulfonyl chloride (1 equiv, 5 mmol, 0.98 g) was dissolved in 15 mL of water. Sodium sulfite (8 mmol, 1.0 g) and sodium bicarbonate (8 mmol, 0.7 g) were added and the reaction mixture was refluxed for 3 hours. Water was evaporated and ethanol was added to the residue. The suspension was heated for 10 minutes, cooled and filtered. This procedure was repeated twice using the residue of the filtration. The ethanol fractions were combined and the solvent was evaporated *in vacuo*. Adduct **III** was used without any further purification (95% yield).

STEP 2, according to a modified literature procedure (*5*): To a solution of commercially available 3-chloro butanone (1 equiv, 5 mmol, 0.5 g) in DMF (10 mL, 0.5 M) was added **III** (1 equiv, 5 mmol) in one portion. The reaction mixture was stirred at room temperature for 24 hours. The reaction was quenched by the addition of water (50 mL), the mixture was extracted with DCM (3 x 35 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure. Product **IV** was used without any further purification (92% yield).

STEP 3, according to (*6*): To a dioxane-water (1:1, 0.5 M) solution of **IV** (4.7 mmol, 1.0 g) and iodine (18.8 mmol, 4.8 g) in the presence of potassium iodide (37.6 mmol, 6.2 g), 1 M solution of NaOH is added under stirring at room temperature until decoloration of the excess of iodine occurred. After 20 minutes stirring, the reaction mixture was diluted with water and extracted with DCM (3 x 20 mL). The final α-iodo sulfone **2c** was used without any further purification (45% yield).



1-fluoro-4-((1-iodoethyl)sulfonyl)benzene (2c)
^{1}H NMR: (400 MHz, Chloroform-*d*) δ 8.04 – 7.95 (m, 2H), 7.34 – 7.22 (m, 2H), 5.00 (q, *J* = 7.1 Hz, 1H), 2.11 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR: (101 MHz, Chloroform-*d*) δ 166.47 (d, *J* = 257.8 Hz), 133.09 (d, *J* = 9.8 Hz), 130.38 (d, *J* = 3.3 Hz), 116.69 (d, *J* = 22.7 Hz), 34.78, 22.41.
^{1}H decoupled ^{19}F NMR: (376 MHz, Chloroform-*d*) δ -102.04 (s, 1F).

HRMS: Calculated for $C_8H_8FINaO_2S$ 336.9166, found 336.9168.

C. General Procedures for the Photo-Organocatalytic Enantioselective Formal α-Methylation and α-Benzylation of Aldehydes

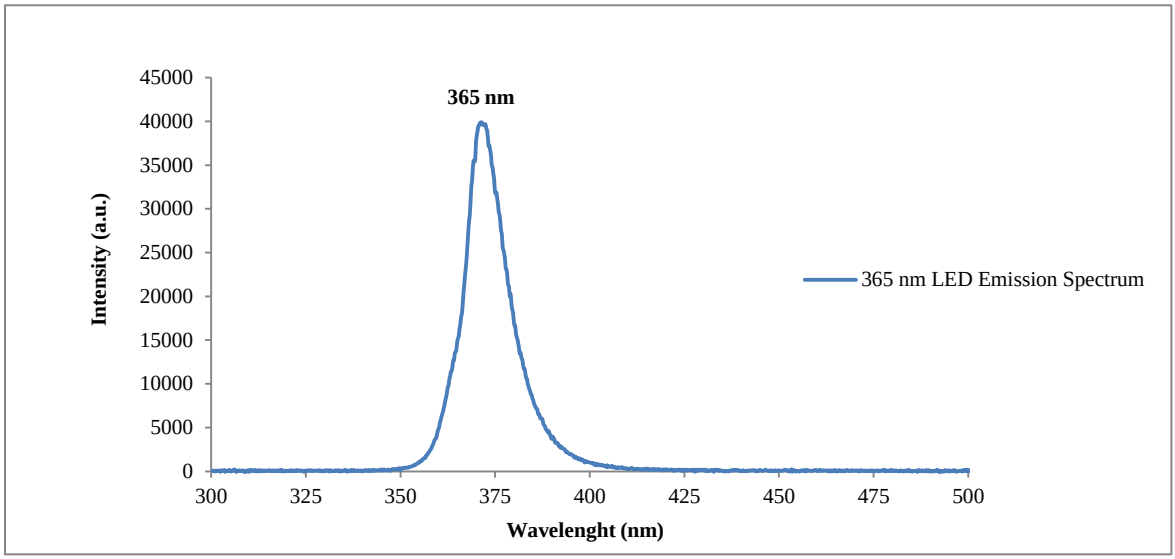
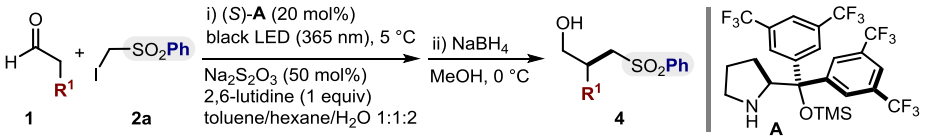


Figure S1. Emission spectrum of the single black-light-emitting diode (black LED, λ_{max} = 365 nm) used in our experiments.

C.1 General Procedure for the Enantioselective Photo-organocatalytic (Phenylsulfonyl)methylation of Aldehydes with α-Iodo-Sulfone 2a



A 10 mL Schlenk tube was charged with the α-iodomethyl phenyl sulfone **2a** (0.1 mmol, 28.2 mg), the chiral secondary amine catalyst (*S*)-**A** (0.02 mmol, 20 mol%), sodium thiosulfate (0.05 mmol, 50 mol%), 2,6-lutidine (0.1 mmol, 1 equiv) and the appropriate aldehyde **1** (0.3 mmol, 3 equiv). To this mixture was then added hexane, toluene, and water in a 1:1:2 ratio (100μL, 100μL, 200μL, respectively; $[\mathbf{2a}]_0$= 0.25 M). The reaction mixture was thoroughly degassed via 3 cycles of freeze-pump-thaw, and the vessel was refilled with argon, sealed with parafilm, and placed into a single black LED plate (λ = 365 nm, intensity of emission = 100 μA, as controlled by an external power supply). The temperature was kept at 5 ºC with a chiller connected to the irradiation plate (the set-up is detailed in Figure S2). In order to avoid condensation of moisture on the plate, a flux of nitrogen was blown over the plate for the entire duration of the experiments by means of a bell-shaped glass. Stirring was maintained for the indicated time (generally 20 hours), and then the irradiation was stopped. The reaction mixture was then diluted with methanol (2 mL) and the aldehyde product was reduced with sodium borohydride (5 equiv) at 0 ºC. The reaction was quenched after 15 minutes by addition of a saturated solution of ammonium chloride (5 mL). The crude mixture was extracted with dichloromethane (3 x 5 mL). The volatiles were removed *in vacuo* and the residue was purified by column chromatography to give the alcohols products **4** in the stated yield and optical purity.

The light source used for illuminating the reaction vessel consisted of a single black LED (3.6 W, EOLD-365-525 LED, UV, 5 mm, 365 nm) produced by OSA OPTO Light and purchased from Farnell (more information [here]).

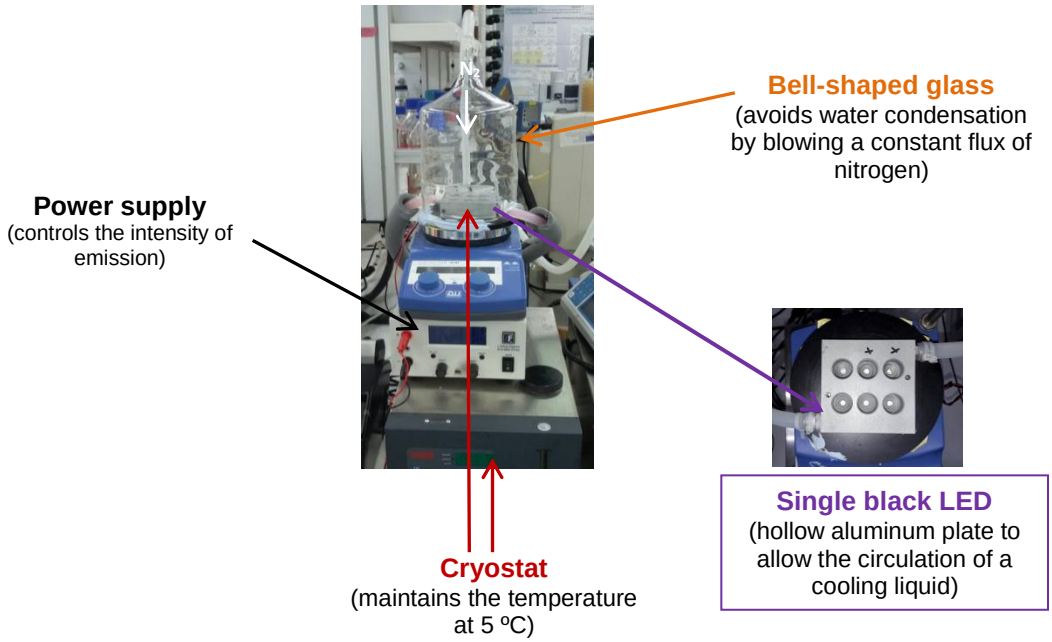
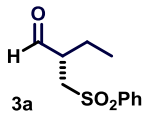


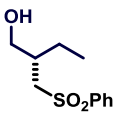
Figure S2. The reaction set-up of the photochemical organocatalytic (phenylsulfonyl)methylation of aldehydes.

Characterization Data



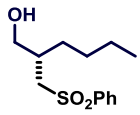
3a

(*S*)-2-((phenylsulfonyl)methyl)butanal (3a). Time of irradiation: 16 hours; using butyraldehyde (0.3 mmol, 27 µL). Prepared using a slightly modified procedure, since the crude aldehyde product **3a** was not in situ reduced. Instead, **3a** was directly purified by rapid flash column chromatography (total elution time < 2 minutes) using a hexane/ethyl acetate (6:4) solvent mixture pre-cooled at 5 ºC. (Phenylsulfonyl)methylated aldehyde **3a** was isolated as a colourless oil (17 mg, 76% yield). The enantiomeric excess was determined to be 80% by UPC[2] analysis on a Acquity Trefoil IC column with a gradient 100% CO_2 to 60:40 CO_2/Isopropanol over 4 minutes, 20 ºC, flow rate 3 mL/min, λ = 215 nm: τ_{Major} = 3.72 min, τ_{Minor} = 3.94 min. $[\alpha]_D^{26}$ = +22.2 (c = 0.20, $CHCl_3$, 80% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 1.1 Hz, 1H), 7.91 (dt, *J* = 8.2, 1.1 Hz, 2H), 7.74 – 7.63 (m, 1H), 7.61 – 7.44 (m, 2H), 3.70 (dd, *J* = 14.2, 6.8 Hz, 1H), 3.06 (dd, *J* = 14.2, 5.1 Hz, 1H), 2.99 (ddd, *J* = 6.5, 5.3, 1.2 Hz, 1H), 1.94 – 1.68 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H)..
^{13}C NMR:(101 MHz, $CDCl_3$) δ 200.12, 139.41, 134.13, 129.58, 128.15, 53.87, 47.10, 22.11, 10.60.
HRMS: Calculated for $C_{11}H_{14}NaO_3S$: 249.0556, found: 249.0557.

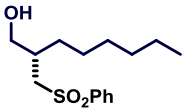


(*S*)-2-((phenylsulfonyl)methyl)butan-1-ol (4a). Prepared according to the general procedure using butyraldehyde (0.3 mmol, 27 µL). Time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 6:4) to afford the product as colourless oil (22 mg, 94% yield). The enantiomeric excess was determined to be 82% by HPLC analysis on a Daicel Chiralpak IC-3 column: 60:40 hexane/IPA, flow rate 0.8 mL/min, λ = 254 nm: τ_{Major} = 22.6 min, τ_{Minor} = 18.4 min. $[\alpha]_D^{26}$ = -7.4 (c = 0.90, $CHCl_3$, 82% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 8.02 – 7.87 (m, 2H), 7.72 – 7.63 (m, 1H), 7.58 (dd, *J* = 8.3, 6.9 Hz, 2H), 3.86 (dt, *J* = 10.5, 5.1 Hz, 1H), 3.63 (dt, *J* = 11.3, 5.7 Hz, 1H), 3.31 (dd, *J* = 14.2, 7.6 Hz, 1H), 3.05 (dd, *J* = 14.2,

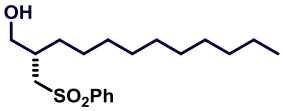
4.7 Hz, 1H), 2.19 – 2.01 (m, 1H), 1.93 (t, *J* = 5.9 Hz, 1H), 1.67 – 1.37 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 140.0, 133.9, 129.5, 127.9, 63.7, 57.6, 37.9, 24.4, 11.2.
HRMS: Calculated for $C_{11}H_{16}NaO_3S$: 251.0712, found: 251.0718.



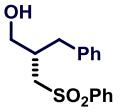
(*S*)-2-((phenylsulfonyl)methyl)hexan-1-ol (4b). Prepared according to the general procedure using hexanal (0.3 mmol, 38 µL). Time of irradiation: 20 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 6:4) to afford the product as a colourless oil (24 mg, 92% yield). The enantiomeric excess was determined to be 86% by HPLC analysis on a Daicel Chiralpak IC-3 column: 60:40 hexane/IPA, flow rate 0.8 mL/min, λ = 254 nm: τ_{Major} = 21.3 min, τ_{Minor} = 18.0 min. $[\alpha]_D^{26}$= -5.2 (c = 1.2, $CHCl_3$, 86% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 8.02 – 7.85 (m, 2H), 7.76 – 7.62 (m, 1H), 7.62 – 7.49 (m, 2H), 3.94 – 3.73 (m, 1H), 3.60 (dt, *J* = 11.1, 5.4 Hz, 1H), 3.32 (dd, *J* = 14.2, 7.6 Hz, 1H), 3.04 (dd, *J* = 14.3, 4.6 Hz, 1H), 2.30 – 2.08 (m, 1H), 2.04 (t, *J* = 6.0 Hz, 1H), 1.58 – 1.32 (m, 2H), 1.38-1.20 (m, 4H), 0.97 – 0.70 (m, 3H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 140.0, 133.9, 129.5, 127.9, 64.1, 57.9, 36.3, 31.2, 28.9, 22.7, 14.0.
HRMS: Calculated for $C_{13}H_{20}NaO_3S$: 279.1025; found: 279.1031.



(*S*)-2-((phenylsulfonyl)methyl)octan-1-ol (4c). Prepared according to the general procedure using octanal (0.3 mmol, 48 µL). Time of irradiation: 20 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 7:3) to afford the product as a colourless oil (27 mg, 93% yield). The enantiomeric excess was determined to be 85% by HPLC analysis on a Daicel Chiralpak IC-3 column: 60:40 hexane/IPA, flow rate 0.8 mL/min, λ = 254 nm: τ_{Major} = 19.2 min, τ_{Minor} = 16.7 min. $[\alpha]_D^{26}$= -7.0 (c = 1.0, $CHCl_3$, 85% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 8.00 – 7.87 (m, 2H), 7.72 – 7.63 (m, 1H), 7.62-7.54 (m, 2H), 3.86 (dd, *J* = 11.3, 4.3 Hz, 1H), 3.61 (dd, *J* = 11.3, 5.7 Hz, 1H), 3.32 (dd, *J* = 14.2, 7.7 Hz, 1H), 3.04 (dd, *J* = 14.2, 4.5 Hz, 1H), 2.16 (t, *J* = 6.3 Hz, 1H), 1.96 (t, *J* = 6.0 Hz, 1H), 1.41 (dt, *J* = 14.3, 7.1 Hz, 2H), 1.34 – 1.12 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 140.0, 133.9, 129.5, 128.0, 64.1, 57.9, 36.3, 31.8, 31.6, 29.3, 26.7, 22.7, 14.2. **HRMS**: Calculated for $C_{15}H_{24}NaO_3S$: 307.1338, found: 307.1349.

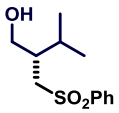


(*S*)-2-((phenylsulfonyl)methyl)dodecan-1-ol (4d). Prepared according to the general procedure using dodecanal (0.3 mmol, 67 µL). Time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 7:3) to afford the product as colourless oil (31 mg, 90% yield). The enantiomeric excess was determined to be 82% by UPC^2 analysis on a Acquity Trefoil IC column with a gradient (100% CO_2 to 60:40 CO_2/CH_3CN over 4 minutes, curve 6), flow rate 3 mL/min, λ = 270 nm: τ_{Major} = 4.61 min, τ_{Minor} = 4.36 min. $[\alpha]_D^{26}$= -5.0 (c = 0.68, $CHCl_3$, 82% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.72 – 7.65 (m, 1H), 7.60 (dd, *J* = 8.4, 7.1 Hz, 2H), 3.87 (dt, *J* = 10.2, 4.7 Hz, 1H), 3.63 (dt, *J* = 10.9, 5.2 Hz, 1H), 3.34 (dd, *J* = 14.2, 7.6 Hz, 1H), 3.06 (dd, *J* = 14.2, 4.5 Hz, 1H), 2.23 – 2.13 (m, 1H), 2.07 (t, *J* = 5.9 Hz, 1H), 1.48-1.40 (m, 2H), 1.34-1.16 (m, 16H), 0.90 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 140.0, 133.8, 129.5, 128.0, 64.1, 57.9, 36.4, 32.0, 31.6, 29.7, 29.7, 29.6, 29.6, 29.4, 26.7, 22.8, 14.2. **HRMS**: Calculated for $C_{19}H_{32}NaO_3S$: 363.1964, found: 363.1969.

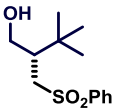


(*S*)-2-benzyl-3-(phenylsulfonyl)propan-1-ol (4e). Prepared according to general procedure using hydrocinnamaldehyde (0.3 mmol, 40 µL). Time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 6:4) to afford the product as a colourless oil (22 mg, 74% yield). The enantiomeric excess was determined to be 76% by HPLC analysis on a Daicel Chiralpak IC-3 column: 60:40 hexane/IPA, flow rate 0.8 mL/min, λ = 254 nm: τ_{Major} = 25.7 min, τ_{Minor} = 20.3 min. $[\alpha]_D^{26}$= -13.4 (c = 0.60, $CHCl_3$, 76% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 7.93 – 7.81 (m, 2H), 7.73 – 7.63 (m, 1H), 7.62 – 7.51 (m, 2H), 7.32 – 7.18 (m, 3H), 7.15 – 7.06 (m, 2H), 3.89 (ddd, *J* = 11.3, 5.9, 4.3 Hz, 1H), 3.66 (dt, *J* = 11.0, 5.4 Hz, 1H), 3.33 (dd, *J* = 14.3, 7.6 Hz, 1H), 3.09 (dd, *J* = 14.3, 4.7 Hz, 1H), 2.88 – 2.73 (m, 2H), 2.54 – 2.37 (m, 1H), 2.01 (t, *J* = 5.9

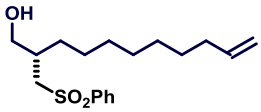
Hz, 1H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 139.7, 138.5, 133.8, 129.5, 129.2, 128.7, 127.9, 126.7, 63.4, 56.6, 38.2, 37.5. **HRMS**: Calculated for $C_{16}H_{18}NaO_3S$: 313.0869, found: 313.0873.



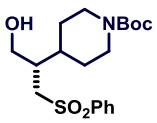
(*S*)-3-methyl-2-((phenylsulfonyl)methyl)butan-1-ol (4f). Prepared according to the general procedure using isovaleraldehyde (0.3 mmol, 32 µL). Time of irradiation: 20 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 6:4) to afford the product as a colourless oil (23 mg, 95% yield). The enantiomeric excess was determined to be 87% by HPLC analysis on a Daicel Chiralpak IC-3 column: 60:40 hexane/IPA, flow rate 0.8 mL/min, λ = 254 nm: τ_{Major} = 27.4 min, τ_{Minor} = 17.7 min. $[\alpha]_D^{26}$= -13.0 (c = 0.68, $CHCl_3$, 87% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 8.01 – 7.88 (m, 2H), 7.71 – 7.64 (m, 1H), 7.63 – 7.54 (m, 2H), 3.85 (ddd, *J* = 11.0, 5.9, 4.9 Hz, 1H), 3.70 (dt, *J* = 11.5, 5.8 Hz, 1H), 3.25 (dd, *J* = 14.3, 8.5 Hz, 1H), 3.08 (dd, *J* = 14.3, 3.3 Hz, 1H), 2.21 (t, *J* = 6.0 Hz, 1H), 2.10 – 1.97 (m, 1H), 1.92-1.84 (m, 1H), 0.84 (dd, *J* = 6.8, 4.1 Hz, 6H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 139.7, 133.9, 129.5, 128.1, 63.0, 55.9, 41.9, 29.4, 19.7, 19.2.
HRMS: Calculated for $C_{12}H_{18}NaO_3S$: 265.0869, found: 265.0868.



(*S*)-3,3-dimethyl-2-((phenylsulfonyl)methyl)butan-1-ol (4g). Prepared according to the general procedure using 3,3-dimethylbutyraldehyde (0.3 mmol, 38 µL). Time of irradiation: 20 hours. The crude mixture was purified by flash column chromatography (dichloromethane/ethyl acetate 85:15) to afford the product as a colourless oil (13 mg, 50% yield). The enantiomeric excess was determined to be 96% by UPC^2 analysis on a Acquity Trefoil IC column with a gradient (100% CO_2 to 60:40 CO_2/CH_3CN over 4 minutes, curve 6), flow rate 3 mL/min, λ = 216 nm: τ_{Major} = 4.37 min, τ_{Minor} = 4.03 min. $[\alpha]_D^{26}$= -15.2 (c = 0.31, $CHCl_3$, 96% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.72 – 7.64 (m, 1H), 7.62 – 7.55 (m, 2H), 4.01 (ddd, *J* = 11.6, 5.5, 4.6 Hz, 1H), 3.66 (dt, *J* = 11.5, 6.6 Hz, 1H), 3.34 (dd, *J* = 14.3, 8.8 Hz, 1H), 3.18 (dd, *J* = 14.2, 2.2 Hz, 1H), 2.50 (dd, *J* = 6.9, 5.5 Hz, 1H), 2.00 (ddt, *J* = 6.4, 4.2, 2.2 Hz, 1H), 0.87 (s, 9H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 139.7, 133.9, 129.5, 128.2, 62.2, 55.6, 45.2, 33.2, 27.9.
HRMS: Calculated for $C_{13}H_{20}NaO_3S$: 279.1025, found: 279.1024.

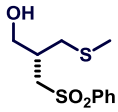


(*S*)-2-((phenylsulfonyl)methyl)undec-10-en-1-ol (4h). Prepared according to the general procedure using 10-undecenal (0.3 mmol, 61 µL). Time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 6:4) to afford the product as a colourless oil (30 mg, 92% yield). The enantiomeric excess was determined to be 82% by HPLC analysis on a Daicel Chiralpak IC-3 column: 60:40 hexane/IPA, flow rate 0.8 mL/min, λ = 254 nm: τ_{Major} = 19.0 min, τ_{Minor} = 16.8 min. $[\alpha]_D^{26}$= -4.30 (c = 1.9, $CHCl_3$, 82% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 8.01 – 7.86 (m, 2H), 7.74 – 7.62 (m, 1H), 7.62 – 7.52 (m, 2H), 5.91 – 5.66 (m, 1H), 5.09 – 4.79 (m, 2H), 3.85 (dd, *J* = 10.7, 5.2 Hz, 1H), 3.61 (dt, *J* = 10.8, 5.6 Hz, 1H), 3.31 (dd, *J* = 14.2, 7.6 Hz, 1H), 3.04 (dd, *J* = 14.2, 4.5 Hz, 1H), 2.25 – 2.09 (m, 1H), 2.08 – 1.91 (m, 2H), 1.57 – 1.02 (m, 12H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 140.0, 139.3, 133.9, 129.5, 128.0, 114.3, 64.1, 57.9, 36.4, 33.9, 31.6, 29.6, 29.4, 29.1, 28.9, 26.7. **HRMS**: Calculated for $C_{18}H_{28}NaO_3S$: 347.1651, found: 347.1651.

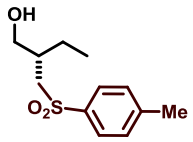


***tert*-butyl (*S*)-4-(1-hydroxy-3-(phenylsulfonyl)propan-2-yl)piperidine-1-carboxylate (4i)**. Prepared according to the general procedure using *tert*-butyl 4-(2-oxoethyl)piperidine-1-carboxylate (0.3 mmol, 23 µL). Time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 6:4) to afford the product as a colourless oil (27 mg, 70% yield). The enantiomeric excess was determined to be 80% by UPC^2 analysis on a Acquity Trefoil IC-3 column with a gradient (100% CO_2 to 60:40 CO_2/EtOH over 4 minutes, curve 6), flow rate 3 mL/min, λ = 264 nm: τ_{Major} = 5.0 min, τ_{Minor} = 4.9 min. $[\alpha]_D^{26}$= -5.8 (c = 1.0, $CHCl_3$, 80% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 7.99 – 7.88 (m, 2H), 7.72 – 7.64 (m, 1H), 7.59 (dd, *J* = 8.3, 6.9 Hz, 2H), 4.11 (s, 1H), 3.91 (dt, *J* = 10.8, 5.1 Hz, 1H), 3.74 (dt, *J* = 11.2, 5.6 Hz, 1H), 3.29 (dd, *J* = 14.2, 8.3 Hz, 1H), 3.08 (dd, *J* = 14.2, 3.6 Hz, 1H), 2.62-2.50 (m, 2H), 2.17 – 1.98 (m, 2H), 1.80 – 1.62 (m, 1H), 1.65-1.53 (m, 1H),

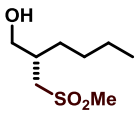
1.44 (s, 9H), 1.18-1.10 (m, 2H), 0.93-0.85 (m, 1H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 155.0, 140.0, 134.3, 129.8, 128.3, 79.9, 62.4, 55.7, 40.9, 38.0, 29.4, 28.8.
HRMS: Calculated for $C_{19}H_{29}NNaO_5S$: 406.1659, found: 406.1660.



(*R*)-3-(methylthio)-2-((phenylsulfonyl)methyl)propan-1-ol (4j). Prepared according to the general procedure using methional (0.3 mmol, 30 µL). Time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 6:4) to afford the product as colourless oil (11 mg, 40% yield). The enantiomeric excess was determined to be 75% by UPC^2 analysis on a Acquity Trefoil AMY-1 column with a gradient (100% CO_2 to 60:40 CO_2/CH_3CN over 4 minutes, curve 6), flow rate 2 mL/min, λ = 220 nm: τ_{Major} = 4.68 min, τ_{Minor} = 4.82 min. $[\alpha]_D^{26}$= -26.9 (c = 0.4, $CHCl_3$, 75% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 8.08 – 7.87 (m, 2H), 7.78 – 7.67 (m, 1H), 7.65 – 7.55 (m, 2H), 3.95 (d, *J* = 11.4 Hz, 1H), 3.88 – 3.71 (m, 1H), 3.40 (dd, *J* = 14.2, 5.0 Hz, 1H), 3.32 (dd, *J* = 14.2, 7.3 Hz, 1H), 2.72 (dd, *J* = 13.5, 6.7 Hz, 1H), 2.64 (dd, *J* = 13.5, 7.3 Hz, 1H), 2.48-2.40 (m, 1H), 2.10-2.00 (m, 4H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 139.6, 133.9, 129.4, 127.9, 63.5, 56.1, 36.0, 35.5, 15.6.
HRMS: Calculated for $C_{11}H_{16}NaO_3S_2$: 283.0433, found: 283.0435.

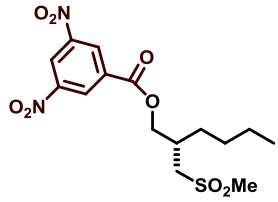


(S)-2-(tosylmethyl)butan-1-ol (4k). Prepared according to the general procedure using butyraldehyde (0.3 mmol, 27 µL) and 1-((iodomethyl)sulfonyl)-4-methylbenzene **2k** (0.1 mmol, 30 mg). Time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 6:4) to afford the product as colourless oil (23 mg, 95% yield). The enantiomeric excess was determined to be 80% by HPLC analysis on a Daicel Chiralpak IC-3 column: 60:40 hexane/IPA, flow rate 0.8 mL/min, λ = 254 nm: τ_{Major} = 27.3 min, τ_{Minor} = 22.9 min. $[\alpha]_D^{26}$= -8.0 (c = 1.3, $CHCl_3$, 80% *ee*).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.83 (ddd, *J* = 10.6, 6.0, 4.3 Hz, 1H), 3.61 (dt, *J* = 11.4, 5.7 Hz, 1H), 3.28 (dd, *J* = 14.2, 7.6 Hz, 1H), 3.02 (dd, *J* = 14.2, 4.7 Hz, 1H), 2.45 (s, 3H), 2.17-1.98 (m, 1H), 1.59 – 1.30 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ 144.7, 137.0, 130.1, 127.9, 63.7, 57.7, 37.9, 24.4, 21.8, 11.2.
HRMS: Calculated for $C_{12}H_{18}NaO_3S$: 265.0869, found: 265.0865.



(*S*)-2-((methylsulfonyl)methyl)hexan-1-ol (4l). Prepared according to the general procedure using hexanal (0.3 mmol, 38 µL) and 1-((iodomethyl)sulfonyl)-4-methylbenzene **2l** (0.1mmol, 22 mg). Time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 1:1) to afford the product as colourless oil (10 mg, 50% yield). The enantiomeric excess was determined upon esterification of the alcohol moiety with 3,5-dinitrobenzoyl chloride (see procedure detailed below).
^{1}H NMR:(400 MHz, $CDCl_3$) δ 3.87 (dt, *J* = 9.5, 4.2 Hz, 1H), 3.69 – 3.52 (m, 1H), 3.26 (dd, *J* = 14.0, 7.7 Hz, 1H), 3.09 – 2.90 (m, 4H), 2.33 – 2.15 (m, 1H), 2.10 (s, 1H), 1.55-1.45 (m, 2H), 1.35-1.26 (m, 4H), 1.01 – 0.80 (m, 3H). **^{13}C NMR**:(101 MHz, $CDCl_3$) δ 64.0, 56.4, 41.2, 36.2, 31.4, 29.0, 22.8, 14.1.
HRMS: Calculated for $C_8H_{18}NaO_3S$: 217.0869, found: 217.0870.

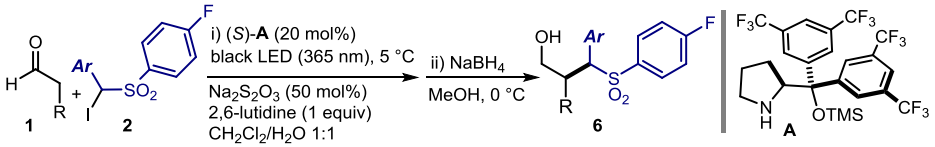
*Derivatization to evaluate the enantiomeric excess of compound **4l**.*



(*S*)-2-((methylsulfonyl)methyl)hexyl 3,5-dinitrobenzoate (8a) was prepared from (*S*)-2-((methylsulfonyl)methyl)hexan-1-ol (**4l**) (0.1 mmol, 19.4 mg) adding 3,5-dinitrobenzoyl chloride (0.15 mmol, 36 mg), 4-(dimethylamino)pyridine (0.02 mmol, 3mg) and trimethylamine (0.15 mmol, 20 µL) to a dry dichloromethane solution of **4l**. Reaction Time: 7 hours. The crude product was purified by flash column chromatography (hexane/ethyl acetate 3:7) to afford **8a** as yellow oil (35 mg, 90% yield). The enantiomeric excess was determined to be 83% by UPC^2 analysis on a

Acquity Trefoil AMY-1 column with a gradient (100% CO_2 to 60:40 CO_2/MeOH over 4 minutes, curve 6), flow rate 2 mL/min, λ = 208 nm: τ_{Major} = 5.7 min, τ_{Minor} = 6.0 min. $[\alpha]_D^{26}$= -5.9 (c = 1.0, $CHCl_3$, 83% *ee*).
^{1}H NMR: (400 MHz, Chloroform-*d*) δ 9.24 (t, *J* = 2.1 Hz, 1H), 9.16 (d, *J* = 2.2 Hz, 2H), 4.63 (dd, *J* = 11.3, 4.8 Hz, 1H), 4.54 (dd, *J* = 11.3, 5.9 Hz, 1H), 3.22 (dd, *J* = 14.0, 7.5 Hz, 1H), 3.12 (dd, *J* = 14.0, 4.5 Hz, 1H), 2.98 (s, 3H), 2.75-2.62 (m, 1H), 1.70 – 1.58 (m, 2H), 1.50 – 1.31 (m, 4H), 0.94 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR:** (101 MHz, Chloroform-*d*) δ 162.6, 148.9, 133.7, 129.6, 122.7, 67.9, 56.2, 42.3, 32.9, 31.6, 28.7, 22.7, 14.0.
HRMS: Calculated for $C_{15}H_{20}N_2NaO_8S$: 411.0833, found: 411.0828.

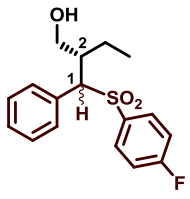
C.2 General Procedure for the Enantioselective Photo-Organocatalytic (Arylsulfonyl)Benzylation of Aldehydes



A 10 mL Schlenk tube was charged with the α-iodo sulfone (0.1 mmol, 1 equiv), the chiral secondary amine catalyst (*S*)-**A** (0.02 mmol, 20 mol%), sodium thiosulfate (0.05 mmol, 50 mol%), 2,6-lutidine (0.1 mmol, 1 equiv) and the appropriate aldehyde **1** (0.3 mmol, 3 equiv). To this mixture was then added dichloromethane and water in a 1:1ratio (200 μL each, for a total of 400μL; $[\mathbf{2}]_0$= 0.25 M). The reaction mixture was thoroughly degassed via 3 cycles of freeze pump thaw, and the vessel was refilled with argon, sealed with parafilm and placed into a single black LED plate (λ = 365 nm, intensity of emission = 100 μA, as controlled by an external power supply). The temperature was kept at 5 ºC with a chiller connected to the irradiation plate (the reaction set-up is detailed in Figure S2). In order to avoid condensation of moisture on the plate, a flux of nitrogen was blown over the plate for the entire duration of the experiments by means of a bell-shaped glass. Stirring was maintained for the indicated time, and then the irradiation was stopped. The reaction was then diluted with methanol (2 mL) and the aldehyde product was reduced with sodium borohydride (5 equiv) at 0 ºC. The reaction was quenched after 15 minutes by addition of a sutured solution of ammonium chloride (5 mL). The crude mixture was extracted with dichloromethane (3 x 5 mL). The volatiles were removed *in vacuo* and the residue was purified by column chromatography to give the alcohols products **6** in the stated yield and optical purity.

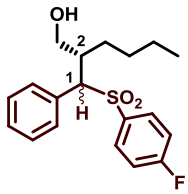
The light source used for illuminating the reaction vessel consisted of a single black LED (3.6 W, EOLD-365-525 LED, UV, 5 mm, 365 nm).

Characterization Data

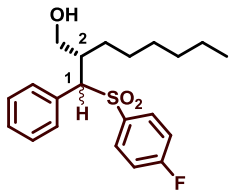


(2*S*)-2-(((4-fluorophenyl)sulfonyl)(phenyl)methyl)butan-1-ol (6a). Prepared according to the general procedure using butyraldehyde (0.3 mmol, 27 μL), 1-fluoro-4-((iodo(phenyl)methyl)sulfonyl)benzene **2b** (0.1 mmol, 37.6 mg) and a mixture of dichloromethane:water 1:1 as solvent. Time of irradiation: 70 hours. The crude mixture was purified by flash column chromatography (dichloromethane/ethyl acetate 20:1) to afford the product as colourless oil (20 mg, 62% yield, 3.3:1.0 d.r., 96% ee_{major}, 80% $ee_{\mathbf{minor}}$). The enantiomeric excesses were determined by UPC[2] analysis on a Acquity Trefoil CEL-1 column with a gradient (100% CO_2 to 60:40 CO_2/EtOH over 4 minutes, curve 6), flow rate 2 mL/min, λ = 212 nm: Major diastereoisomer (96% ee): τ_{Major} = 3.53 min, τ_{Minor} = 3.64 min; Minor diastereoisomer (80% ee): τ_{Major} = 3.29 min, τ_{Minor} = 3.35 min. $[\alpha]_D^{26}$= +33.7 (c = 0.47, $CHCl_3$, 3.2:1 dr, 96% $ee_{\mathbf{Major}}$, 80% $ee_{\mathbf{minor}}$).
^{1}H NMR: (400 MHz, Chloroform-*d*) δ 7.56 – 7.47 (m, 2H *major*), 7.47 – 7.41 (m, 2H *minor*), 7.27 – 7.06 (m, 5H *major* +5H *minor*), 7.02 – 6.91 (m, 2H *major* +2H *minor*), 4.52 – 4.38 (m, 1H *minor*), 4.35 – 4.23 (m, 1H *major* +1H *minor*), 3.89 (dt, *J* = 11.5, 4.5 Hz, 1H *major*), 3.86 – 3.79 (m, 1H *minor*), 3.43 (ddd, *J* = 11.4, 6.9,

4.3 Hz, 1H *major*), 2.76 – 2.59 (m, 1H *major* +1H *minor*), 2.53 (ddd, *J* = 9.7, 6.4, 3.2 Hz, 1H *minor*), 1.97 (dtd, *J* = 14.8, 7.4, 5.2 Hz, 1H *major*), 1.80 (ddt, *J* = 14.2, 8.4, 7.3 Hz, 1H *major*), 1.72 (dd, *J* = 7.0, 4.5 Hz, 1H *major*), 1.48 – 1.34 (m, 1H *minor*), 1.07 (t, *J* = 7.4 Hz, 3H *major*), 0.90 (t, *J* = 7.4 Hz, 3H *minor*).
^{13}C NMR: (101 MHz, Chloroform-*d*) δ 165.5 (d, *J* = 256.0 Hz, *minor*), 165.9 (d, *J* = 256.0 Hz, *major*), 135.0 (d, *J* = 3.2 Hz, *major*), 134.6 (d, *J* = 2.9 Hz, *minor*), 133.1 (*minor*), 132.4 (*major*), 131.5 (d, *J* = 9.5 Hz, *minor*), 131.4 (d, *J* = 9.6 Hz, *major*), 130.4 (*major*), 130.2 (*major*), 128.9 (*major*), 128.8 (*major*), 115.9 (d, *J* = 22.6 Hz, *major*), 73.4 (*major*), 72.7 (*minor*), 61.6 (*major*), 60.7 (*minor*), 43.5 (*minor*), 43.1 (*major*), 22.6 (*minor*), 22.3 (*major*), 11.7 (*major*), 11.6 (*minor*).
^{1}H decoupled ^{19}F NMR: (376 MHz, Chloroform-*d*) δ -104.03 (s, 1F*minor*), -104.27 (s, 1F*major*).
HRMS: Calculated for $C_{17}H_{19}FNaO_3S$:345.0931, found: 345.0944.

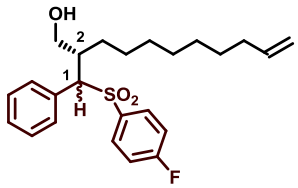


(2*S*)-2-(((4-fluorophenyl)sulfonyl)(phenyl)methyl)hexan-1-ol (6b) Prepared according to the general procedure using hexanal (0.3 mmol, 38 µL) and 1-fluoro-4-((iodo(phenyl)methyl)sulfonyl)benzene **2b** (0.1 mmol, 37.6 mg). Time of irradiation: 70 hours. The reaction mixture was purified by flash column chromatography (hexane/ethyl acetate 7:3) to afford the product as colourless oil (19 mg, 57% yield, 3.1:1.0 d.r., 97% $ee_{\mathbf{major}}$, 88% $ee_{\mathbf{minor}}$). The enantiomeric excesses were determined by UPC^2 analysis on a Acquity Trefoil CEL-1 column with a gradient (100% CO_2 to 60/40 CO_2/Isopropanol over 4 minutes, curve 6), flow rate 2 mL/min, λ = 220 nm: Major diastereoisomer (97% ee): $\tau_{\boldsymbol{Major}}$ = 3.82 min, $\tau_{\boldsymbol{Minor}}$ = 3.90 min; minor diastereoisomer (88% ee): $\tau_{\boldsymbol{Major}}$ = 3.53 min, $\tau_{\boldsymbol{Minor}}$ = 3.64 min. $[\alpha]_D^{26}$= +43.0 (c = 0.80, $CHCl_3$, 3:1 dr, 97% $ee_{\mathbf{Major}}$, 88% $ee_{\mathbf{minor}}$).
^{1}H NMR: (400 MHz, Chloroform-*d*) δ 7.55 – 7.46 (m, 2H *major*), 7.45 – 7.37 (m, 2H *minor*), 7.25 – 7.12 (m, 5H *major* +5H *minor*), 7.02 – 6.87 (m, 2H *major* +2H *minor*), 4.40 (d, *J* = 12.3 Hz, 1H *minor*), 4.32 – 4.14 (m, 1H *major* +1H *minor*), 3.87 (dd, *J* = 11.5, 4.8 Hz, 1H *major*), 3.77 (d, *J* = 12.9 Hz, 1H *minor*), 3.40 (dd, *J* = 11.5, 4.3 Hz, 1H *major*), 2.79 – 2.64 (m, 1H *major* +1H *minor*), 2.58 (d, *J* = 2.9 Hz, 1H *minor*), 1.83 (ddt, *J* = 15.2, 10.9, 5.2 Hz, 2H *major*), 1.72 – 1.60 (m, 1H *major* +1H *minor*), 1.49 – 1.27 (m, 4H *major* +4H *minor*), 0.92 (t, *J* = 7.0 Hz, 3H *major*), 0.76 (t, *J* = 7.1 Hz, 3H *minor*).
^{13}C NMR: (101 MHz, Chloroform-*d*) δ 165.4 (d, *J* = 256.3 Hz, *minor*), 165.3 (d, *J* = 256.0 Hz, *major*), 134.9 (d, *J* = 3.2 Hz, *major*), 134.5 (d, *J* = 3.2 Hz, *minor*), 132.9 (*minor*), 132.1 (*major*), 131.3 (d, *J* = 9.6 Hz, *major*), 130.3 (*major*), 130.0 (*minor*), 128.7 (*major*), 128.65 (*major*), 128.62 (*major*), 115.8 (d, *J* = 22.6 Hz, *major*), 115.7 (d, *J* = 22.6 Hz, *minor*), 73.5 (*major*), 72.6 (*minor*), 61.9 (*major*), 61.0 (*minor*), 41.7 (*minor*), 41.4 (*major*), 29.3 (*major*), 29.0 (*minor*), 29.0 (*major*), 28.9 (*minor*), 22.7 (*major*), 22.4 (*minor*), 14.0 (*major*), 13.8 (*minor*). **^{1}H decoupled ^{19}F NMR:** (376 MHz, Chloroform-*d*) δ -104.05 (s, 1F*minor*), -104.25 (s, 1F*major*).
HRMS: Calculated for $C_{19}H_{23}FNaO_3S$: 373.1244, found: 373.1227.

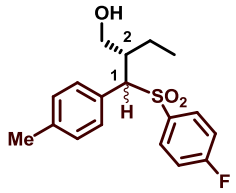


(2*S*)-2-(((4-fluorophenyl)sulfonyl)(phenyl)methyl)octan-1-ol (6c) Prepared according to the general procedure using octanal (0.3 mmol, 48 µL) and 1-fluoro-4-((iodo(phenyl)methyl)sulfonyl)benzene **2b** (0.1 mmol, 37.6 mg). Time of irradiation: 70 hours. The crude mixture was purified by flash column chromatography (dichloromethane/ethyl acetate 20:1) to afford the product as colourless oil (16 mg, 43% yield, 3.3:1.0 d.r., 95% $ee_{\mathbf{major}}$, 86% $ee_{\mathbf{minor}}$). The enantiomeric excesses were determined by UPC^2 analysis on a Acquity Trefoil AMY-1 column with a gradient (100% CO_2 to 60/40 CO_2/ethanol over 4 minutes, curve 6), flow rate 2 mL/min, λ = 220 nm: Major diastereoisomer (95% ee): $\tau_{\boldsymbol{Major}}$ = 4.52min, $\tau_{\boldsymbol{Minor}}$ = 4.83 min; minor diastereoisomer (86% ee): $\tau_{\boldsymbol{Major}}$ = 3.87 min, $\tau_{\boldsymbol{Minor}}$ = 3.95 min. $[\alpha]_D^{26}$= +38.7 (c = 0.57, $CHCl_3$, 3.2:1 dr, 95% $ee_{\mathbf{major}}$, 86% $ee_{\mathbf{minor}}$).
^{1}H NMR: (400 MHz, Chloroform-*d*) δ 7.58 – 7.49 (m, 2H *major*), 7.47 – 7.40 (m, 2H *minor*), 7.29 – 7.08 (m, 5H *major* +5H *minor*), 7.05 – 6.87 (m, 2H *major* +2H *minor*), 4.49 – 4.36 (m, 1H *minor*), 4.34 – 4.20 (m, 1H *major* +1H *minor*), 3.93 – 3.84 (m, 1H *major*), 3.79 (ddd, *J* = 11.9, 8.1, 3.3 Hz, 1H *minor*), 3.43 (dt, *J* = 10.9, 5.4 Hz, 1H *major*), 2.81 – 2.65 (m, 1H *major* +1H *minor*), 2.65 – 2.53 (m, 1H *minor*), 1.92 – 1.78 (m, 2H *major*), 1.71 (ddt, *J* = 14.1, 9.9, 6.7 Hz, 1H *major*), 1.55 – 1.01 (m, 8H *major* + 8H *minor*), 0.95 – 0.87 (t, *J* = 7.0 Hz, 3H *major*), 0.83 (t, *J* = 7.1 Hz, 3H *minor*).

^{13}C NMR: (101 MHz, Chloroform-*d*) δ 165.6 (d, *J* = 256.3 Hz, *minor*), 165.5 (d, *J* = 256.0 Hz, *major*), 135.1 (d, *J* = 3.1 Hz, *major*), 134.6 (d, *J* = 3.3 Hz, *minor*), 133.0 (*minor*), 132.3 (*major)*, 131.5 (d, *J* = 9.6 Hz, *major*), 130.5 (*major*), 130.2 (*minor*), 128.9 (*major*), 128.8 (*major*), 128.7 (*major*), 115.9 (d, *J* = 22.6 Hz, *major*), 115.8 (d, *J* = 22.6 Hz, *minor*), 73.6 (*major*), 72.8 (*minor*), 62.1 (*major*), 61.1 (*minor*), 41.8 (*minor*), 41.6 (*major*), 31.9 (*major*), 31.7 (*minor*), 29.4 (*major*), 29.2 (*minor*), 27.3 (*major*), 26.9 (*minor*), 22.8 (*major*), 22.6 (*minor*), 14.2 (*major*), 14.1 (*minor*).
^{1}H decoupled ^{19}F NMR: (376 MHz, Chloroform-*d*) δ -104.06 (s, 1F*minor*), -104.25 (s, 1F*major*).
HRMS: Calculated for $C_{21}H_{27}FNaO_3S$: 401.1557, found: 401.1556.



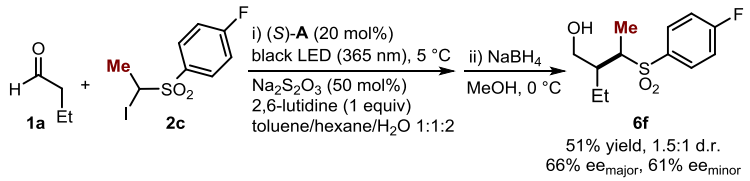
(2*S*)-2-(((4-fluorophenyl)sulfonyl)(phenyl)methyl)undec-10-en-1-ol (6d) Prepared according to the general procedure using 10-undecenal (0.3 mmol, 61 µL) and 1-fluoro-4-((iodo(phenyl)methyl)sulfonyl)benzene **2b** (0.1 mmol, 37.6 mg). Time of irradiation: 20 hours. The crude mixture was purified by preparative TLC (hexane/ethyl acetate 9:1) to afford the product as colourless oil (22 mg, 52% yield, 3.4:1.0 d.r., 97% $ee_{\mathbf{major}}$, 83% $ee_{\mathbf{minor}}$). The enantiomeric excesses were determined by UPC[2] analysis on a Acquity Trefoil CEL-2 column with a gradient (100% CO_2 to 60/40 CO_2/MeOH over 4 minutes, curve 6), flow rate 2 mL/min, λ = 212 nm: major diastereoisomer (97% ee): τ_{Major} = 4.27 min, τ_{Minor} = 4.08 min; ninor diastereoisomer (83% ee): τ_{Major} = 3.96 min, τ_{Minor} = 4.45 min. $[\alpha]_D^{26}$= +29.3 (c = 0.33, $CHCl_3$, 3.4:1 dr, 97% $ee_{\mathbf{Major}}$, 83% $ee_{\mathbf{minor}}$).
^{1}H NMR: (400 MHz, Chloroform-*d*) δ 7.54 – 7.46 (m, 2H *major*), 7.47 – 7.41 (m, 2H *minor*), 7.26 – 7.03 (m, 5H *major* +5H *minor*), 7.02 – 6.88 (m, 2H *major* +2H *minor*), 5.90-5.70 (m, 1H *major* +1H *minor*), 5.07 – 4.86 (m, 2H *major* +2H *minor*), 4.46 – 4.35 (m, 1H *minor*), 4.30 – 4.18 (m, 1H *major* +1H *minor*), 3.87 (dd, *J* = 11.6, 4.7 Hz, 1H *major*), 3.81 – 3.72 (m, 1H *minor*), 3.48 – 3.35 (m, 1H *major*), 2.77 – 2.63 (m, 1H *major* +1H *minor*), 2.62 – 2.51 (m, 1H *minor*), 2.12 – 1.91 (m, 2H *major* +2H *minor*), 1.92 – 1.61 (m, 3H *major* +1H *minor*), 1.53 – 1.19 (m, 10H *major* +10H *minor*).
^{13}C NMR: (101 MHz, Chloroform-*d*) δ 165.5 (d, *J* = 256.1 Hz, *major*), 139.3 (*major*), 139.3 (*minor*), 135.0 (d, *J* = 3.2 Hz, *major*), 134.6 (d, *J* = 3.1 Hz, *minor*), 133.1 (*minor*), 132.3 (*minor*), 131.5 (d, *J* = 9.6 Hz, *major*), 130.4 (*major*), 128.9 (*major*), 128.81 (*major*), 128.78 (*major*), 115.80 (d, *J* = 22.7 Hz, *major*), 115.76 (d, *J* = 22.5 Hz, *minor*) 114.31 (*major*), 114.27 (*minor*), 73.6 (*major*), 72.9 (*minor*), 62.1 (*major*), 61.1 (*minor*), 41.8 (*minor*), 41.5 (*major*), 33.9 (*major*), 33.8 (*minor*), 29.8 (*minor*), 29.7 (*major*), 29.5 (*major*), 29.4 (*major*), 29.34 (*minor*), 29.32 (*minor*), 29.2 (*major*), 29.1 (*minor*), 29.0 (*major*), 28.9 (*minor*), 27.3 (*major*), 26.9 (*minor*). **^{1}H decoupled ^{19}F NMR:** (376 MHz, Chloroform-*d*) δ -104.04 (s, 1F*minor*), -104.23 (s, 1F*major*).
HRMS: Calculated for $C_{24}H_{31}FNaO_3S$: 441.1870, found: 441.1870.

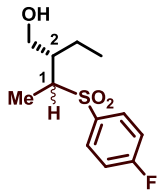


(2*S*)-2-(((4-fluorophenyl)sulfonyl)(p-tolyl)methyl)butan-1-ol (6e) Prepared according to the general procedure using butyraldehyde (0.3 mmol, 27 µL) and 1-fluoro-4-((iodo(p-tolyl)methyl)sulfonyl)benzene **2e** (0.1 mmol, 39.0 mg). Time of irradiation: 70 hours. The reaction mixture was purified by flash column chromatography (hexane/ethyl acetate 6:4) to afford the product as colourless oil (11 mg, 35% yield, 3.4:1.0 d.r., 94% $ee_{\mathbf{major}}$, 74% $ee_{\mathbf{minor}}$). The enantiomeric excesses were determined by UPC[2] analysis on a Acquity Trefoil CEL-1 column with a gradient (100% CO_2 to 60/40 CO_2/EtOH over 4 minutes, curve 6), flow rate 2 mL/min, λ = 212 nm: Major diastereoisomer (94% ee): τ_{Major} = 3.47 min, τ_{Minor} = 3.52 min; minor diastereoisomer (74% ee): τ_{Major} = 3.25 min, τ_{Minor} = 3.35 min. $[\alpha]_D^{26}$= +77.4 (c = 0.25, $CHCl_3$, 3.2:1 dr, 94% $ee_{\mathbf{Major}}$, 74% $ee_{\mathbf{minor}}$).
^{1}H NMR: (400 MHz, Chloroform-*d*) δ 7.55 – 7.47 (m, 2H *major*), 7.46 – 7.39 (m, 2H *minor*), 7.11 – 6.85 (m, 6H *major* + 6H *minor*), 4.45 – 4.28 (m, 1H *minor*), 4.31 – 4.10 (m, 1H *major* + 1H *minor*), 3.86 (dt, *J* = 11.6, 4.0 Hz, 1H *major*), 3.79 (ddd, *J* = 11.9, 8.0, 3.3 Hz, *minor*), 3.42 (dt, *J* = 11.2, 5.1 Hz, 1H *major*), 2.76 – 2.54 (m, 1H *major* + 1H *minor*), 2.47 (ddt, *J* = 13.0, 9.6, 3.6 Hz, 1H *minor*), 2.28 (s, 3H *major*), 2.27 (s, 3H *minor*), 1.98 – 1.67 (m, 3H *major*), 1.46 – 1.18 (m, 3H *minor*), 1.02 (t, *J* = 7.4 Hz, 3H *major*), 0.86 (t, *J* = 7.4 Hz, 3H *minor*).

^{13}C NMR: (101 MHz, Chloroform-*d*) δ 165.53 (d, *J* = 256.1 Hz, *minor*), 165.48 (d, *J* = 255.8 Hz, *major*), 138.86 (*major*), 138.78 (*minor*), 135.1 (d, *J* = 3.0 Hz, *major*), 134.7 (d, *J* = 3.3 Hz, *minor*), 131.5 (d, *J* = 9.5 Hz, *minor*), 131.4 (d, *J* = 9.5 Hz, *major*), 130.3 (*major*), 130.1 (*minor*), 129.8 (*minor*), 129.5 (*major*), 129.4 (*minor*), 129.0 (*major*), 115.74 (d, *J* = 22.6 Hz, *major*), 115.70 (d, *J* = 22.6 Hz, *minor*), 73.1 (*major*), 72.4 (*minor*), 61.7 (*major*), 60.7 (*minor*), 43.5 (*minor*), 43.1 (*major*), 22.5 (*minor*), 22.4 (*major*), 21.2 (*major*), 11.7 (*major*), 11.6 (*minor*).
^{1}H decoupled ^{19}F NMR: (376 MHz, Chloroform-*d*) δ -104.20 (s, 1F*minor*), -104.38 (s, 1F*major*).
HRMS: Calculated for $C_{18}H_{21}FNaO_3S$:359.1088, found: 359.1090.

C.3 Procedure for the Enantioselective Photo-Organocatalytic Formal α-Ethylation of Butanal.





(2S)-2-ethyl-3-((4-fluorophenyl)sulfonyl)butan-1-ol (6f) Prepared according to the general procedure using butyraldehyde (0.3 mmol, 27 µL), 1-fluoro-4-((1-iodoethyl)sulfonyl)benzene (0.1 mmol, 31.4 mg) and a hexane/toluene/water mixture (1:1:2). Time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 7:3) to afford the product as colourless oil (13 mg, 51% yield, 1.5:1.0 d.r., 66% $ee_{\mathbf{major}}$, 61% $ee_{\mathbf{minor}}$). The enantiomeric excesses were determined by UPC[2] analysis on a Acquity Trefoil IC-3 column with a gradient (100% CO_2 to 60/40 CO_2/CH_3CN over 4 minutes, curve 6), flow rate 3 mL/min, λ = 219 nm; major diastereoisomer (66% ee): τ_{Major} = 3.62 min, τ_{Minor} = 3.50 min; minor diastereoisomer (61% ee): τ_{Major} = 3.94 min, τ_{Minor} = +3.85 min. $[\alpha]_D^{26}$= +8.6 (c = 0.34, $CHCl_3$, 1.5:1 dr, 66% $ee_{\mathbf{Minor}}$, 61% $ee_{\mathbf{major}}$).
^{1}H NMR: (400 MHz, Chloroform-*d*) δ 7.99 – 7.86 (m, 2H *major* + 2H *minor*), 7.33 – 7.18 (m, 2H *major* + 2H *minor*), 3.90-3.85 (m, 1H *major* + 1H *minor*), 3.64 (dd, *J* = 11.6, 4.8 Hz, 1H *minor*), 3.54 – 3.34 (m, 2H *major*), 3.21 (qd, *J* = 7.2, 2.3 Hz, 1H *minor*), 2.53 (s, 1H *minor*), 2.25-2.15 (m, 1H *major* + 1H *minor*), 1.76 (dtd, *J* = 15.2, 7.6, 3.1 Hz, 2H *minor*), 1.72 – 1.49 (m, 3H *major*), 1.28 (d, *J* = 7.2 Hz, 3H *minor*), 1.22 (d, *J* = 7.1 Hz, 3H *major*), 0.95 (t, *J* = 7.4 Hz, 3H *major*), 0.89 (t, *J* = 7.4 Hz, 3H *minor*).
^{13}C NMR: (101 MHz, Chloroform-*d*) δ 166.0 (d, *J* = 256.6 Hz, *minor*), 165.9 (d, *J* = 256.2 Hz, *major*), 134.7 (d, *J* = 3.2 Hz, *major*), 134.2 (d, *J* = 3.2 Hz, *minor*), 131.7 (d, *J* = 9.6 Hz, *minor*), 131.6 (d, *J* = 9.5 Hz, *major*), 116.7 (d, *J* = 22.6 Hz, *minor*), 116.6 (d, *J* = 22.6 Hz, *major*), 62.3 (*major*) , 62.1 (*minor*), 62.0 (*minor*), 60.1 (*major*), 41.9 (*minor*), 41.6 (*major*), 23.1 (*minor*), 19.4 (*major*), 12.4 (*major*), 12.1 (*minor*), 9.6 (*major*), 9.5 (*minor*). **^{1}H decoupled ^{19}F NMR:** (376 MHz, Chloroform-*d*) δ -104.40 (s, 1F*minor*), -103.95 (s, 1F*major*).
HRMS: Calculated for $C_{12}H_{17}FNaO_3S$: 283.0775, found: 283.0777.

D. Strategies for the Removal of the Sulfonyl Group

The main goal of our studies was to provide an efficient method for stereoselectively installing a methyl or a benzyl group. Desulfonylation of compounds **4** and **6** can be easily achieved under reducing conditions to unveil the methyl and benzyl group, respectively, while affording the desired adducts **5** and **7** without eroding the enantiomeric purity.
Two different reduction conditions have been used:
Method A - activated Mg in dry MeOH at 50 ºC
Method B - SmI_2 in H_2O/THF at ambient temperature.

As detailed in the following Sections D1-2, the feasibility of the reductive desulfonylation has been demonstrated for 9 structurally different substrates. In addition, four different adducts (**4c**, **4e**, **4f**, and **6a**) have been subjected to both reduction conditions. These allowed us to delineate the generality and the limitations of both desulfonylation methods, indicating which substrates cannot be reduced efficiently by Mg or Sm.

D.1 Revealing the Methyl Group

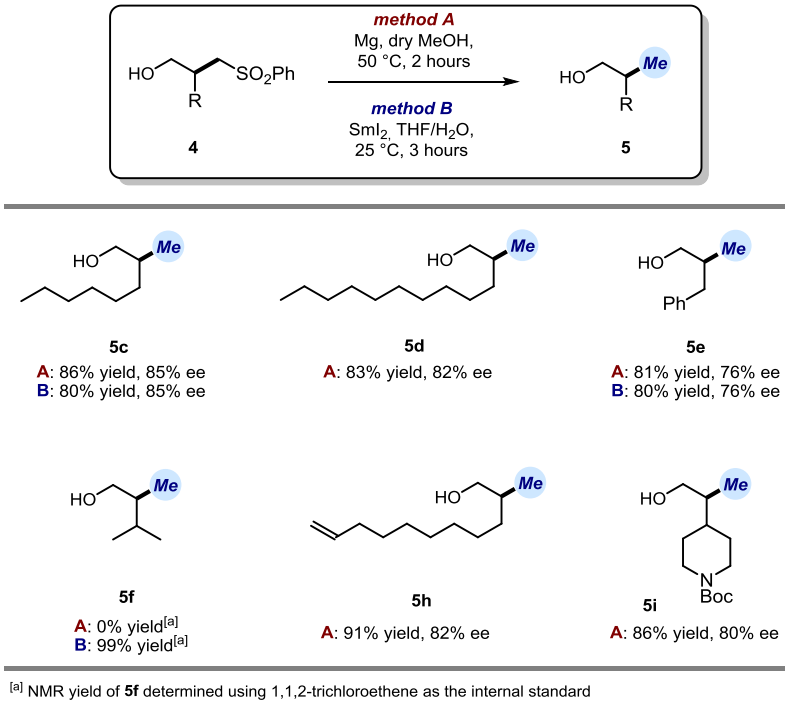


Figure S3. Desulfonylation to reveal the methyl group – direct comparison between Method A and Method B

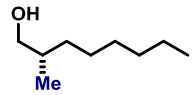
Method **A** (activated Mg in dry MeOH at 50 ºC) was found to be compatible with substrates bearing a variety of aliphatic groups, since long alkyl chains (adducts **5c**, **5d**), containing aromatic (adduct **5e**), or alkene functionalities (adduct **5h**), as well as a heteroatom group, are all well tolerated. However, method **A** is not suitable for revealing the methyl group for substrates bearing short alkyl chains, such as compound **4f**. This is because the volatility of product **5f** is not compatible with the reaction temperature (50 ºC) of method A. Indeed, while full conversion of the starting material **4f** was observed by ^{1}H NMR analysis of the crude reaction mixture, the desired product **5f** was not observed.
On the contrary, the milder conditions of method **B** (SmI_2 in H_2O/THF at 25 ºC) allowed the desired compound **5f** to be achieved in high yield, as determined by ^{1}H NMR analysis of the crude reaction mixture. Importantly, method **B** is suitable for the desulfonylation of compounds **4c** and **4e** too, since it affords the

corresponding methylated products **5** without any erosion of the enantiomeric excesses and with comparable efficiency with respect to Method A.

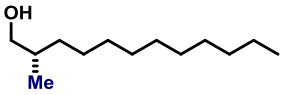
General Guidelines for the Desulfonylation of Adducts **4** (revealing the Methyl group):
Method **A** (activated Mg in dry MeOH at 50 ºC): Suitable for adducts **4** bearing long alkyl chains, terminal olefin, aromatic moiety and heteroatoms. Not suitable for adducts bearing short alkyl chains.

Method **B** (SmI_2 in H_2O/THF at 25 ºC): General applicability because of the mild reaction conditions.

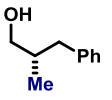
Characterization of adducts 5



(*S*)-2-methyloctan-1-ol (5c). Prepared according to a reported procedure (*7*). To a solution of (*S*)-2-((methylsulfonyl)methyl)hexan-1-ol (**4c**, 0.1 mmol, 28 mg, 85% *ee*) in dry methanol (2 mL) was added freshly activated magnesium (40 equiv) at 50 ºC. After 1.5 hours stirring, the reaction was quenched by adding an aqueous solution of HCl (0.1 M, 5 mL). The crude mixture was then transferred to a separatory funnel and extracted with dichloromethane (3 x 10 mL). The organic phases were combined and dried over magnesium sulfate before concentration *in vacuo*. The mixture was purified by flash column chromatography (hexane/ethyl acetate 8:2) to afford the product **5c** as colourless oil (13 mg, 86% yield). The enantiomeric excess was determined to be 85% by GC analysis on an Beta DEX column 120 (30m x 0.25mm, 0.25µm, isotherm 70 ºC, FID detector, carrier gas: He): τ_{Major} = 230.1 min, τ_{Minor} = 221.7 min. $[\alpha]_D^{25}$= -3.6 (c = 0.35, EtOH, 85% *ee*). An (*S*) absolute configuration was inferred by comparison of the optical rotation with the value reported in the literature ($[\alpha]_D^{25}$ = -9.8, c = 1.00, EtOH, 96% ee for (*S*)-**5c**, *8*). The characterization of the compound matches with the data reported in the literature (*8*).

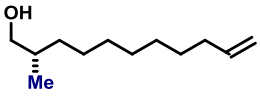


(*S*)-2-methyldodecan-1-ol (5d) Prepared according to a reported procedure (*7*). To a solution of (*S*)-2-((phenylsulfonyl)methyl)dodecan-1-ol (**4d**) (0.05 mmol, 17 mg, 82% *ee*) in dry methanol (3 mL) was added freshly activated magnesium (40 equiv). After 2 hours stirring at 50 ºC, the reaction was quenched by adding an aqueous solution of HCl (0.1 M, 5 mL). The crude mixture was then transferred to a separatory funnel and extracted with dichloromethane (3 x 10 mL). The organic phases were combined and dried over magnesium sulfate before concentration *in vacuo*. The mixture was purified by flash column chromatography (hexane/ethyl acetate 8:2) to afford the product **5d** as colourless oil (8.3 mg, 83% yield, 82% *ee*).
$[\alpha]_D^{25}$= -8.3 (c = 0.25, EtOH). An (*S*) absolute configuration was inferred by comparison of the optical rotation with the value reported in the literature ($[\alpha]_D^{25}$ = -10.0, c = 0.50, EtOH, 99% ee for (*S*)-**5d**, *9*).
The NMR characterization of the compound matches with the data reported in the literature (*9*).

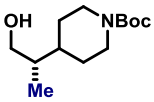


(*S*)-2-methyl-3-phenylpropan-1-ol (5e). Prepared according to a reported procedure (*7*). To a solution of (*S*)-2-benzyl-3-(phenylsulfonyl)propan-1-ol (**4e**, 0.2 mmol, 58 mg, 76% *ee*) in dry methanol (4 mL) was added freshly activated magnesium (40 equiv) at 50 ºC. After 1.5 hours stirring, the reaction was quenched by adding an aqueous solution of HCl (0.1 M, 5 mL). The crude mixture was then transferred to a separatory funnel and extracted with dichloromethane (3 x 15 mL). The organic phases were combined and dried over magnesium sulfate before concentration *in vacuo*. The mixture was purified by flash column chromatography (hexane/ethyl acetate 8:2) to afford the product **5e** as a colourless oil (24 mg, 81% yield). The enantiomeric excess was determined to be 76% by UPC[2] analysis on a Acquity Trefoil CEL-1 column with a gradient (100% CO_2 to 60:40 CO_2/Methanol over 4 minutes, curve 6), flow rate 2 mL/min, λ = 208 nm: τ_{Major} = 2.53 min, τ_{Minor} = 2.59 min. $[\alpha]_D^{25}$= -2.8 (c = 0.5, $CHCl_3$, 76% *ee*). An (*S*) absolute configuration was inferred by comparison of the optical rotation with the value reported in the literature ($[\alpha]_D^{25}$ = -3.0, c = 0.67, $CHCl_3$, 99% ee for (*S*)-**5e**, *10*). The characterization of the compound matches with the data reported in the literature (*10*).

(*S*)-2,3-dimethylbutan-1-ol (5f). Prepared according to a reported procedure (*7*). (*S*)-3-methyl-2-((phenylsulfonyl)methyl)butan-1-ol (**4f**, 0.15 mmol, 36 mg, 87% *ee*) was dissolved in a 10:1 solution of THF/H_2O (2.6 mL). The solution was thoroughly degassed via 3 cycles of freeze pump thaw, and the vessel was refilled with argon. Then, a solution of SmI_2 (0.1 M in THF, 8 mL, 6 equiv) was added at 25 ºC. After stirring for 3 hours, the reaction was quenched with saturated $NaHCO_3$ solution (10 mL) and extracted with cold diethyl ether (3 x 10 mL). The combined organic phase was washed with brine (15 mL) and dried over magnesium sulfate before concentration *in vacuo* at low temperature (5ºC). The yield of **5f** was determined by ^{1}H NMR spectroscopy to be 99%, in reference to 1,1,2-trichloroethylene (0.15 mmol, δ 6.5 (s, 1H)). The characterization of the compound matches with the data reported in the literature (*11*). The compound was not isolated upon flash chromatography due to its volatility.



(*S*)-2-methylundec-10-en-1-ol (5h) Prepared according to a reported procedure (*7*). To a solution of (*S*)-2-((phenylsulfonyl)methyl)undec-10-en-1-ol (**4h**) (0.2 mmol, 65 mg, 82% *ee*) in dry methanol (4 mL) was added freshly activated magnesium (40 equiv) at 50 ºC. After 1.5 hours stirring, the reaction was quenched by adding an aqueous solution of HCl (0.1 M, 5 mL). The crude mixture was then transferred to a separatory funnel and extracted with dichloromethane (3 x 15 mL). The organic phases were combined and dried over magnesium sulfate before concentration *in vacuo*. The mixture was purified by flash column chromatography (hexane/ethyl acetate 8:2) to afford the product **5h** as a colourless oil (33 mg, 91% yield, 82% *ee*). Although it was not possible to measure the *ee* of compound **5h**, the experiments conducted demonstrated that the reductive desulfonylation generally proceeds without eroding the enantiomeric purity of the alcohol precursor **4**.
$[\alpha]_D^{25}$= -5.1 (c = 0.85, $CHCl_3$). An (*S*) absolute configuration was inferred by comparison of the optical rotation with the value reported in the literature ($[\alpha]_D^{25}$ = +8.4, c = 0.85, $CHCl_3$, 99% ee for (*R*)-**5h**, *12*). The NMR characterization of the compound matches with the data reported in the literature (*12*).



***tert*-butyl (*S*)-4-(1-hydroxypropan-2-yl)piperidine-1-carboxylate (5i)** Prepared according to a reported procedure (*7*). To a solution of *tert*-butyl (*S*)-4-(1-hydroxy-3-(phenylsulfonyl)propan-2-yl)piperidine-1-carboxylate (**4i**) (0.12 mmol, 46 mg, 80% *ee*) in dry methanol (3 mL) was added freshly activated magnesium (40 equiv) at 50 ºC. After 2 hours stirring, the reaction was quenched by adding water (10 mL). The crude mixture was then transferred to a separatory funnel and extracted with dichloromethane (3 x 15 mL). The organic phases were combined and dried over magnesium sulfate before concentration *in vacuo*. The mixture was purified by flash column chromatography (hexane/ethyl acetate 8:2) to afford the product **5i** as a colourless oil (25 mg, 86% yield, 80% *ee*). The enantiomeric excess was determined to be 80% by UPC^2 analysis on a AMY-1 column with a gradient (100% CO_2 to 60:40 CO_2/Isopropanol over 4 minutes, curve 6), flow rate 2 mL/min, λ = 215 nm: τ_{Major} = 3.71 min, τ_{Minor} = 3.65 min. $[\alpha]_D^{25}$= +1.50 (c = 0.25, $CHCl_3$, 80% *ee*). The characterization of the compound matches with the data reported in the literature (*13*).

D.2 Revealing the Benzyl Group

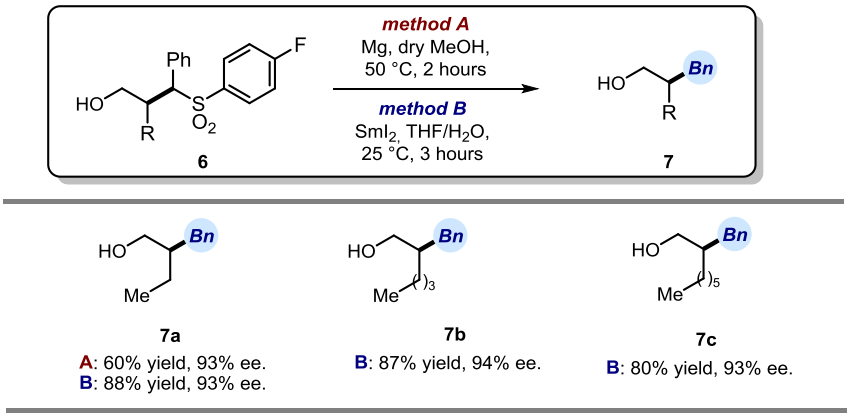
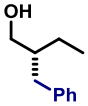


Figure S4. Desulfonylation to reveal the benzyl group – direct comparison between Method A and Method B

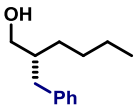
General Guidelines for the Desulfonylation of Adducts **6** (revealing the benzyl group):
Method **A** (activated Mg in dry MeOH at 50 ºC): although the target benzylated adduct **7a** could be obtained without erosion of the enantiomeric purity, it could be isolated with a moderate chemical yield (60%).

Method **B** (SmI_2 in H_2O/THF at 25 ºC): General applicability, which makes it the preferred method to synthesize adducts **7**. Compounds **7a**, **7b**, and **7c**, were isolated after desulfonylation with chemical yields ranging from 80 to 88% and without erosion of the enantiomeric purity.

Characterization of adducts 7

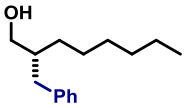


(*R*)-2-benzylbutan-1-ol (7a). Prepared according to a reported procedure (*7*). ((2*S*)-2-(((4-fluorophenyl)sulfonyl)(phenyl)methyl)butan-1-ol (**6a**, 0.13 mmol, 41.2 mg, d.r.=3.2:1.0, 96% ee_M, 80% ee_m) was dissolved in a 10:1 solution of THF/H_2O (2.6 mL). The solution was thoroughly degassed via 3 cycles of freeze pump thaw, and the vessel was refilled with argon. Then, a solution of SmI_2 (0.1 M in THF, 8 mL, 6 equiv) was added at 25 ºC. After stirring for 3 hours, the reaction was quenched with saturated $NaHCO_3$ solution (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (15 mL) and dried over magnesium sulfate before concentration *in vacuo*. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 8:2) to afford the benzylated product **7a** as colourless oil (20 mg, 88% yield). The enantiomeric excess was determined to be 93% by by UPC^2 analysis on a Acquity Trefoil CEL-1 column with a gradient (100% CO_2 to 60:40 CO_2/Isopropanol over 4 minutes, curve 6), flow rate 2 mL/min, λ = 220 nm: τ_{Major} = 3.14 min, τ_{Minor} = 3.03 min. $[\alpha]_D^{25}$= -6.02 (c = 0.50, $CHCl_3$, 93% *ee*). An (*R*) absolute configuration was inferred by comparison of the optical rotation with the value reported in the literature (Lit. $[\alpha]^{25}_D$ = +6.2 (c = 24, $CHCl_3$, 95% *ee* for (*S*)-compound, *14*). The characterization of the compound matches with the data reported in the literature (*14*).



(*R*)-2-benzylhexan-1-ol (7b). Prepared according to a reported procedure (*7*). (2*S*)-2-(((4-fluorophenyl)sulfonyl)(phenyl)methyl)hexan-1-ol (**6b**, 0.05 mmol, 17 mg, d.r.= 3.1:1.0, 97% ee_M, 88% ee_m) was dissolved in a 10:1 solution of THF/H_2O (1.5 mL). The solution was thoroughly degassed via 3 cycles of freeze pump thaw, and the vessel was refilled with argon. Then, a solution of SmI_2 (0.1 M in THF, 4 mL, 6 equiv) was added at 25 ºC. After stirring for 3 hours, the reaction was quenched with saturated $NaHCO_3$ solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (5 mL) and dried over magnesium sulfate before concentration *in vacuo*. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 8:2) to afford the benzylated product **7b** as colourless oil (8.5 mg, 87% yield). The enantiomeric excess was determined to be 94% by by UPC^2 analysis on a Acquity Trefoil CEL-1 column with a gradient (100% CO_2 to

60:40 CO_2/Ethanol over 4 minutes, curve 6), flow rate 2 mL/min, λ = 213 nm: τ_{Major} = 2.87 min, τ_{Minor} = 2.73 min. $[\alpha]_D^{25}$= +3.5 (c = 0.25, CH_2Cl_2, 94% *ee*). An (*R*) absolute configuration was inferred by comparison of the optical rotation with the value reported in the literature (Lit. $[\alpha]^{25}_D$ = -4.0 (c = 0.5, CH_2Cl_2, 90% *ee* for (*S*)-compound, *15*). The characterization of the compound matches with the data reported in the literature (*15*).



(*R*)-2-benzyloctan-1-ol (7c). Prepared according to a reported procedure (*7*). (2*S*)-2-(((4-fluorophenyl)sulfonyl)(phenyl)methyl)octan-1-ol (**6c**, 0.050 mmol, 19 mg, d.r.= 3.2:1.0, 95% ee_M, 86% ee_m) was dissolved in a 10:1 solution of THF/H_2O (1.5 mL). The solution was thoroughly degassed via 3 cycles of freeze pump thaw, and the vessel was refilled with argon. Then, a solution of SmI_2 (0.1 M in THF, 4 mL, 6 equiv) was added at 25 ºC. After stirring for 3 hours, the reaction was quenched with saturated $NaHCO_3$ solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (5 mL) and dried over magnesium sulfate before concentration *in vacuo*. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate 8:2) to afford the benzylated product **7c** as colourless oil (9.2 mg, 80% yield). The enantiomeric excess was determined to be 93% by by UPC^2 analysis on a Acquity Trefoil CEL-1 column with a gradient (100% CO_2 to 60:40 CO_2/Isopropanol over 4 minutes, curve 6), flow rate 2 mL/min, λ = 215 nm: τ_{Major} = 3.45 min, τ_{Minor} = 3.23 min. $[\alpha]_D^{25}$= +1.5 (c = 0.25, $CHCl_3$, 93% *ee*). An (*R*) absolute configuration was inferred by comparison of the optical rotation with the value reported in the literature (Lit. $[\alpha]^{25}_D$ = -0.076 (c = 0.15, $CHCl_3$, 95% *ee* for (*S*)-compound, *16*). The characterization of the compound matches with the data reported in the literature (*16*).

D.3 Determination of the Absolute Configuration

The stereochemical outcome of the photochemical alkylation of aldehydes (**1**) with α-iodo-sulfone derivatives (**2**) has been established by cleaving the sulfone moiety of compounds **4c, 4e, 4h**, **6a** and **6b** under reductive conditions (see Sections D1 and D2), and by comparison of the optical rotations for products **5**/**7** with the values reported in the literature (Figure S5, note that the (*S*)-enantiomer of the aminocatalyst **A** was used in the photochemical alkylations).

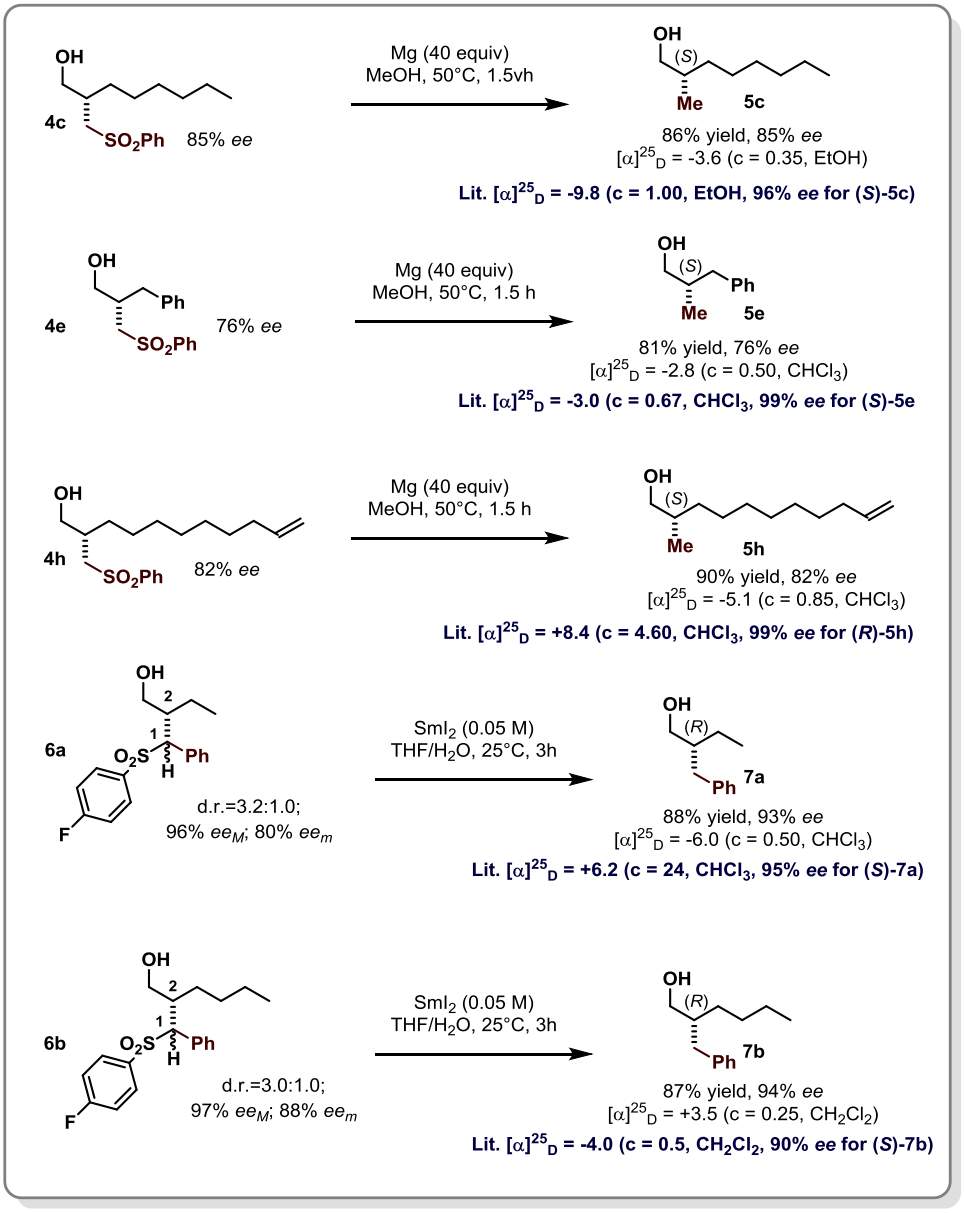


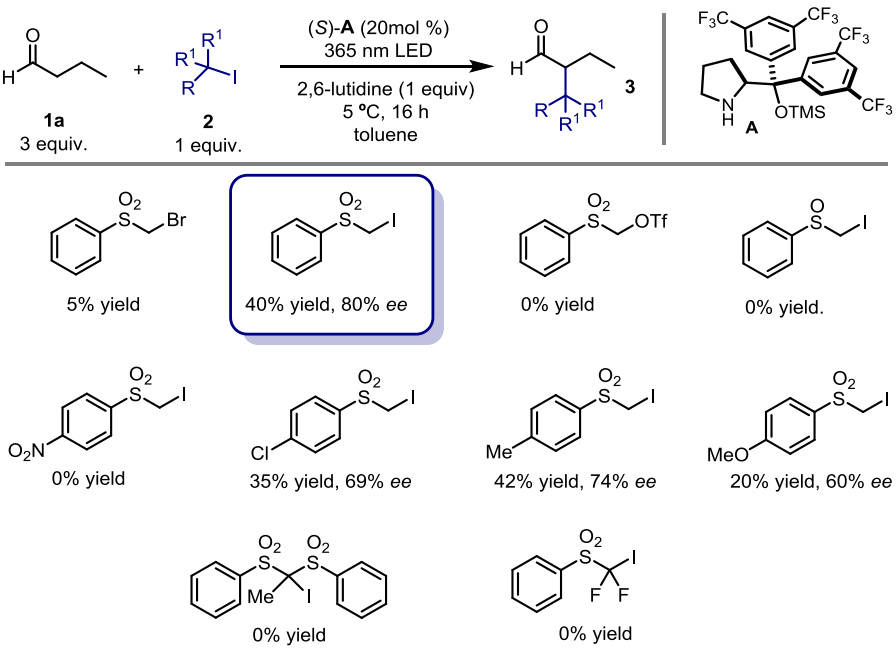
Figure S5. Establishing the stereochemical outcome of the photochemical asymmetric catalytic alkylation of aldehydes with α-iodo sulfones.

The (*S*) absolute configuration for compounds **5c**, **5e**, and **5h** was assigned by comparison of the optical rotations with the values reported in the literature (*8*, *10* and *12*, respectively). For all the other products **5**, the absolute configuration has been established by analogy and assuming a similar mechanistic pathway being

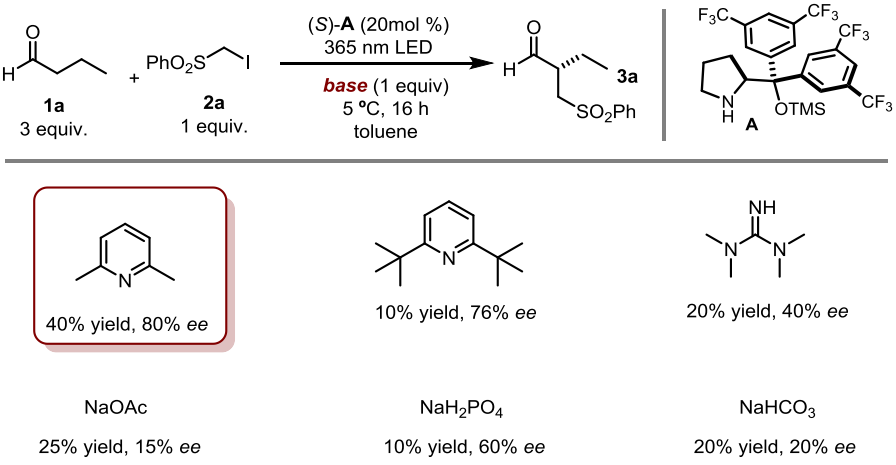
operative. The (*R*) absolute configuration for compounds **7a** and **7b** were assigned by comparison of the optical rotation with the value reported in the literature (*14* and *15* respectively).

E. Optimization of the Reaction Conditions

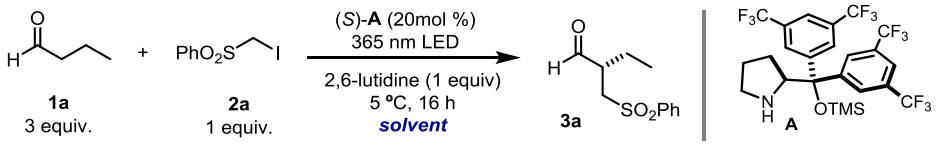
E.1 Preliminary screening of the radical precursors



E.2 Screening of the bases



E.3 Screening of the solvents



Entry	**Solvent**	% Yield[a]	% *ee*[b]
1	toluene	40	80
2	DCM	40	72
3	MTBE	35	80
4	THF	0	-
5	Et_2O	0	-
6	DCE	20	68
7	$CHCl_3$	42	73
8	$PhCF_3$	20	70
9	PhCl	43	69
10	DMF	25	69
11	MeOH	0	-
12	EtOAc	15	80

Reaction performed on a 0.1 mmol scale. [a] Determined by ^{1}H NMR analysis of the crude mixture using 1,1,2-trichloroethene as the internal standard. [b] Enantiomeric excess determined by HPLC analysis on the corresponding alcohol after in situ $NaBH_4$ reduction of **3a**.

F. Cyclic Voltammetry

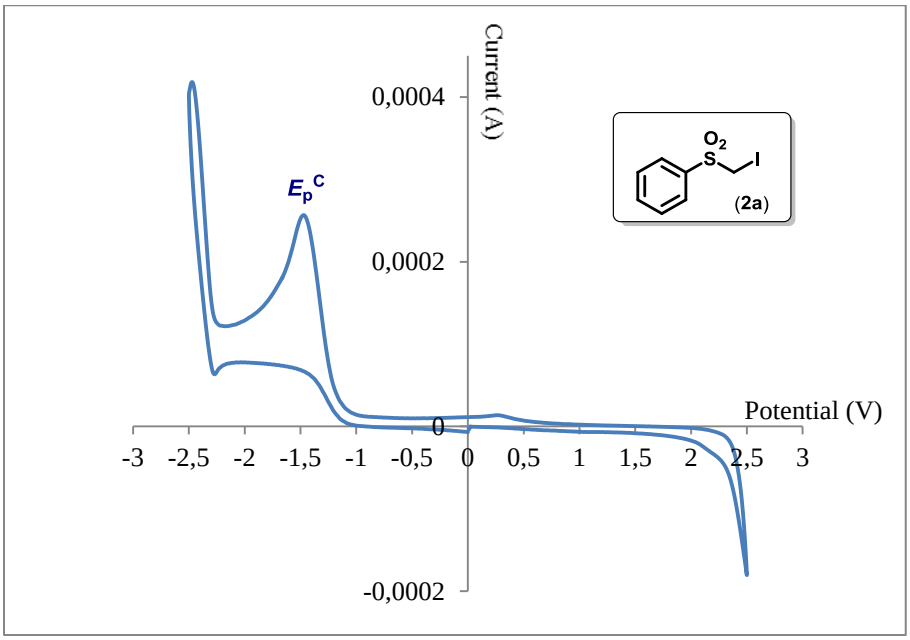


Figure S6. Cyclic voltammogram of **2a** [0.01 M] in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Graphite electrode working electrode, Ag/AgCl (KCl saturated) reference electrode, Pt wire auxiliary electrode. Irreversible reduction. $E_p^C = E_{red}$ (**2a**/**2a**$^{\bullet-}$) = -1.49 V; E_p^C is the cathodic peak potential, while E_{red} value describes the electrochemical properties of **2a**.

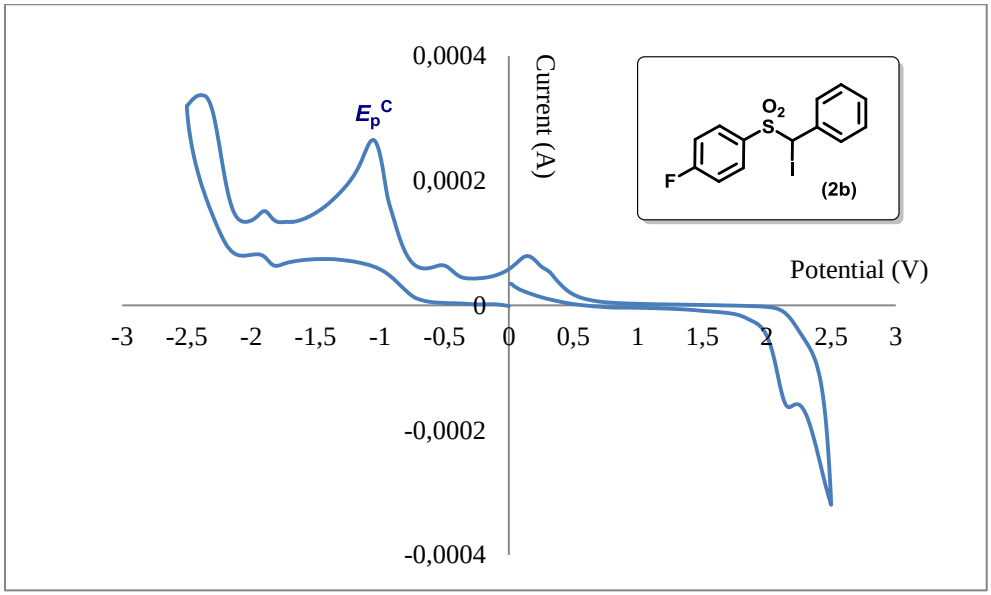


Figure S7. Cyclic voltammogram of **2b** [0.01 M] in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Graphite electrode working electrode, Ag/AgCl (KCl saturated) reference electrode, Pt wire auxiliary electrode. Irreversible reduction. $E_p^C = E_{red}$ (**2b**/**2b**$^{\bullet-}$) = -1.02 V; E_p^C is the cathodic peak potential, while E_{red} value describes the electrochemical properties of **2b**.

F.2 Estimating the Redox Properties of the α-Amino Radical Intermediates

We prepared and isolated the iminium ion **VI** (Figure S6), derived from the condensation of pyrrolidine and isobutyraldehyde, which mimics the actual iminium ion intermediate **V** involved in the catalytic cycle depicted in Figure 3 of the main manuscript and reproduced in Figure S6 below. **V** could not be synthesized because of the steric hindrance of catalyst **A** hampering a facile condensation with the aldehydic product **3a**.

Evaluating the redox properties of **VI** is pertinent since its electrochemical reduction provides access to α-aminoalkyl radical of type **III**, the key intermediate of the chain propagation. We measured by cyclic voltammetry a reduction potential (E_p^{red} of **VI**) of -0.95 V *vs* Ag/Ag^+ in CH_3CN (irreversible reduction to give the α-aminoalkyl radical **VII**, see Figure S7). This value means that the α-amino radical of type **III** is incapable of reducing **2a** (E_p^{red} of **2a** = -1.49 V *vs* Ag/Ag^+ in CH_3CN, see Figure S4) by a direct SET mechanism, which would be a highly endergonic step, indicating that an iodine-transfer mechanism is likely operative instead.

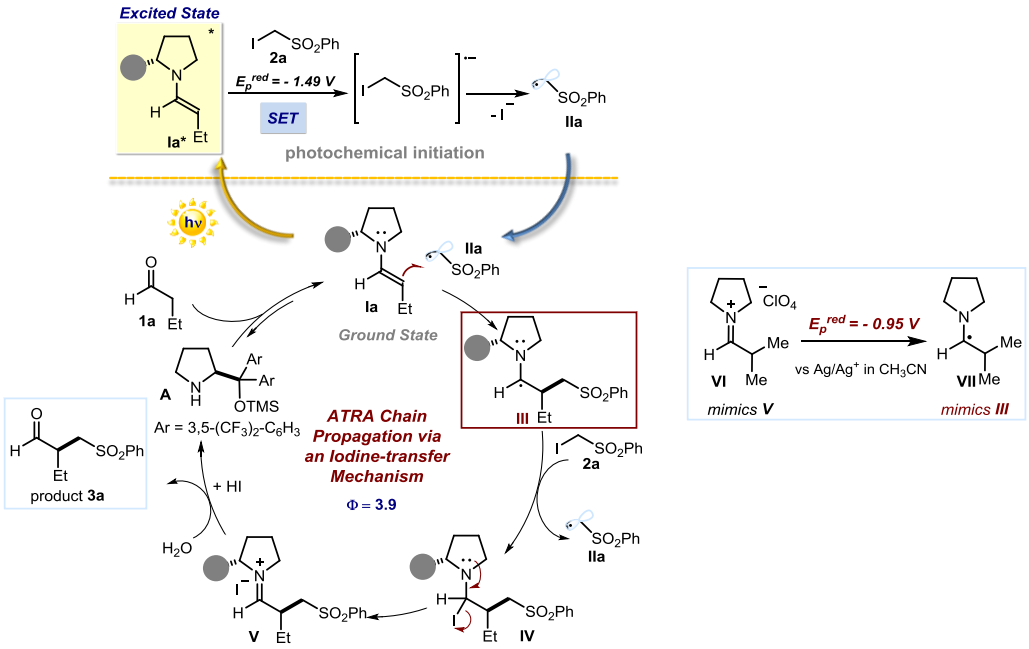


Figure S8. The chain propagation manifold underlying the mechanism of the photochemical enamine-mediated enantioselective α-(phenylsulfonyl)methylation of butanal and the evaluation of the redox potential of the crucial α-aminoalkyl radical of type **III**.

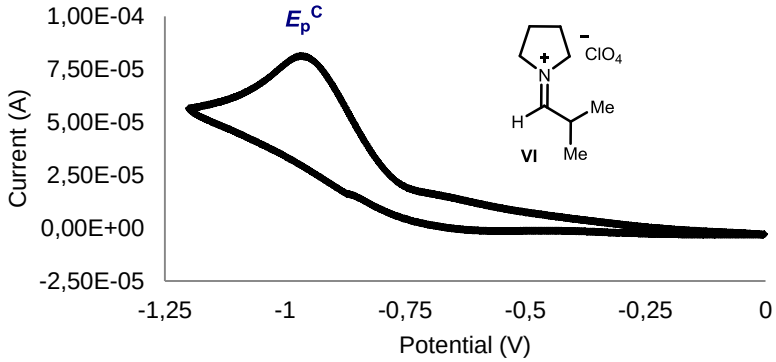


Figure S9. Cyclic voltammogram of the iminium ion **VI** [0.02 M] in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 10 mV/s. Pt electrode working electrode, Ag/AgCl (NaCl saturated) reference electrode, Pt wire auxiliary electrode. Irreversible reduction. $E_p^C = E_{red}$ (**VI**/**VII**) = -0.95 V; E_p^C is the cathodic peak potential, while E_{red} value describes the electrochemical properties of **VI**.

Compound **VI** was synthesized from pyrrolidine, perchloric acid and isobutyraldehyde according to (*17*). The pyrrolidine perchlorate salt was prepared by adding 3 mmol of pyrrolidine (0.025 mL) to a solution of 3 mmol of perchloric acid (0.026 mL of a 70% solution) in 1 mL of ether. A slightly yellow precipitate formed, which was filtered and washed with dry ether. The pyrrolidinium perchlorate salt was used for the following step without further purification. Pyrrolidinium perchlorate (0.23 mmol, 40 mg) was suspended in 2 mL of dry ether and freshly distilled *iso*butryladehyde (1 mmol, 0.91 mL) was added. After the addition, the precipitate dissolved while the slow precipitation of a white solid was observed. The reaction was stirred overnight at room temperature. The precipitate was washed with dry hexane (10 mL) under argon and then dried using high vacuum pump. The iminium ion **VI** was obtained in a 23% yield (12 mg) as a white solid.
^{1}H NMR (400 MHz, CD_3CN): δ 8.16 (d, *J* = 9.2 Hz, 1H), 4.07 (t, *J* = 7.0 Hz, 2H), 3.94 (t, *J* = 7.0 Hz, 2H), 2.93 (dh, *J* = 9.2, 6.6 Hz, 1H), 2.13 (m, 4H), 1.24 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, CD_3CN) δ 180.90, 58.62, 52.25, 32.33, 23.98, 23.63, 17.10.

G. Quantum Yield Measurement

The quantum yield measurement of the model reaction, depicted in Table 1 of the main manuscript, was performed in acetonitrile, where the reaction mixture is completely soluble. This choice was motivated by the need to avoid the presence of biphasic solvent systems with water, in order to elude any scattering of the irradiating light which would preclude a reliable measurement.
A ferrioxalate actinometer solution was prepared following the Hammond variation of the Hatchard and Parker procedure outlined in the *Handbook of Photochemistry (18)*. 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.

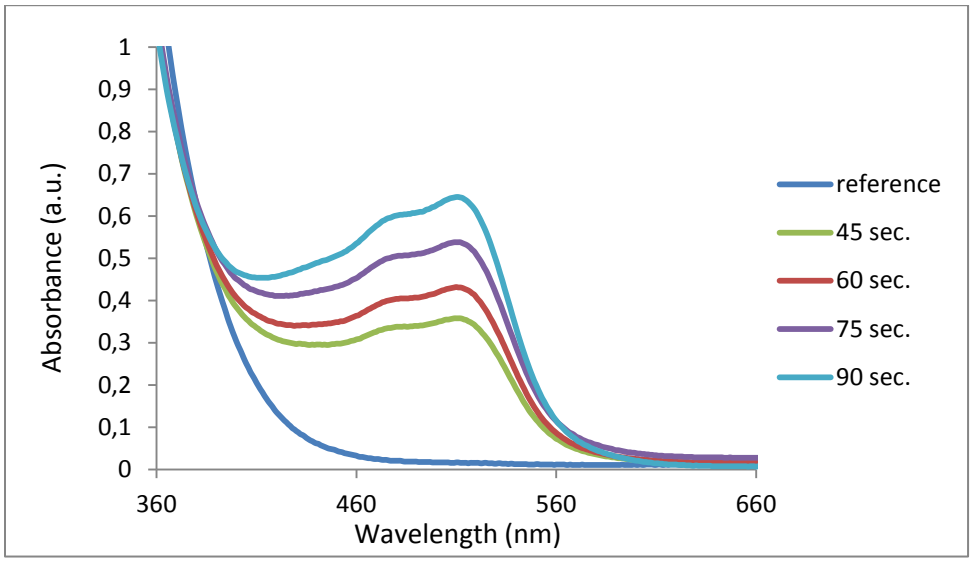
The following solutions were prepared and stored in a dark laboratory (red light):

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).
4. Model reaction solution: α-iodo sulfone **2a** (0.4 mmol), butanal **1a** (1.2 mmol), amine catalyst **A** (0.08 mmol) and 2,6-lutidine (0.4 mmol) were dissolved in acetonitrile (1 mL).

The actinometry and the model reaction solution measurements were done as follows:

1. 1 mL of the actinometer solution was added to a Schlenk tubes (*diameter* = 12 mm). The Schlenk tube was placed 10 cm away from the light source. It was irradiated with a 300 W Xenon Lamp operating at 100% of light intensity with a high transmittance bandpass filter of 400 ± 5 nm without stirring. This procedure was repeated 4 times, quenching the reaction after different time intervals: 45 sec, 60 sec, 75 sec and 90 sec.
2. After irradiation, the actinometer solution was removed and placed in a 10 mL volumetric flask containing 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution. This flask was filled to the mark with water (HPLC grade).
3. 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.
4. 1 mL of the model reaction (α -alkylation of **1a** with **2a** catalyzed by amine **A**) was added to a Schlenk tubes (diameter = 12 mm). The Schlenk tube was placed 10 cm away from the light source. It was irradiated with a 300 W Xenon Lamp operating at 100% of light intensity with a high transmittance

bandpass filter of 400 ± 5 nm without stirring. This procedure was repeated 4 times, quenching the reaction after different time intervals: 7.5 min, 15 min, 30 min and 60 min.



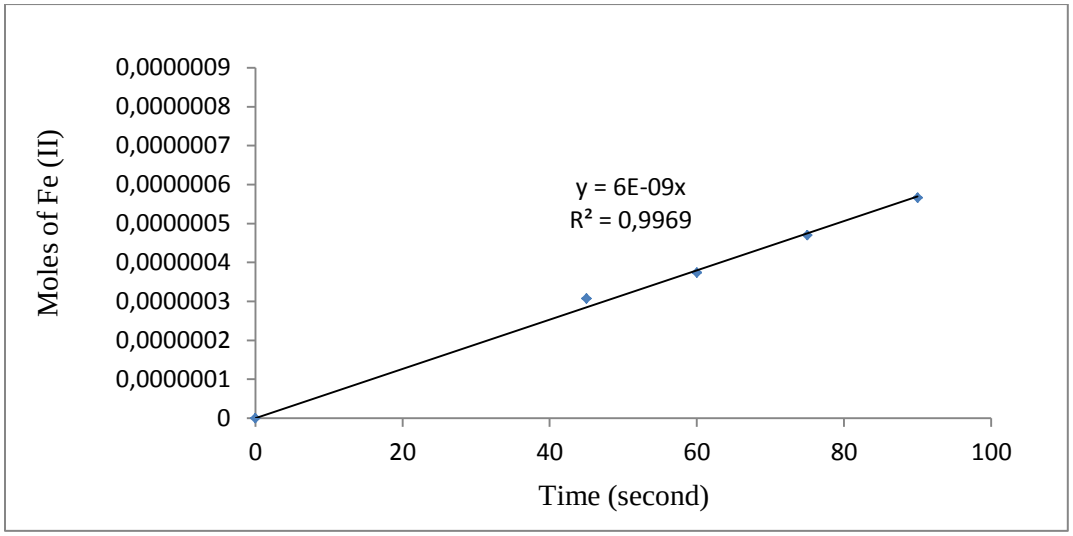
The moles of Fe^{2+} formed for each sample is determined using Beers' Law (Eq. S1):

$$\text{Mols of Fe(II)} = \frac{V_1 \times V_3 \times \Delta A(510\text{ nm})}{10^3 \times V_2 \times l \times \varepsilon(510\ nm)} \text{ (Eq. S1)}$$

where V_1 is the irradiated volume (1 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V_3 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} cm^{1}).
The moles of Fe^{2+} 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 ($q^0_{n,p}$) by the use of the following Equation S2:

$$\Phi(\lambda) = \frac{dx/dt}{q^0_{n,p}[1-10^{-A(\lambda)}]} \quad \text{(Eq. S2)}$$

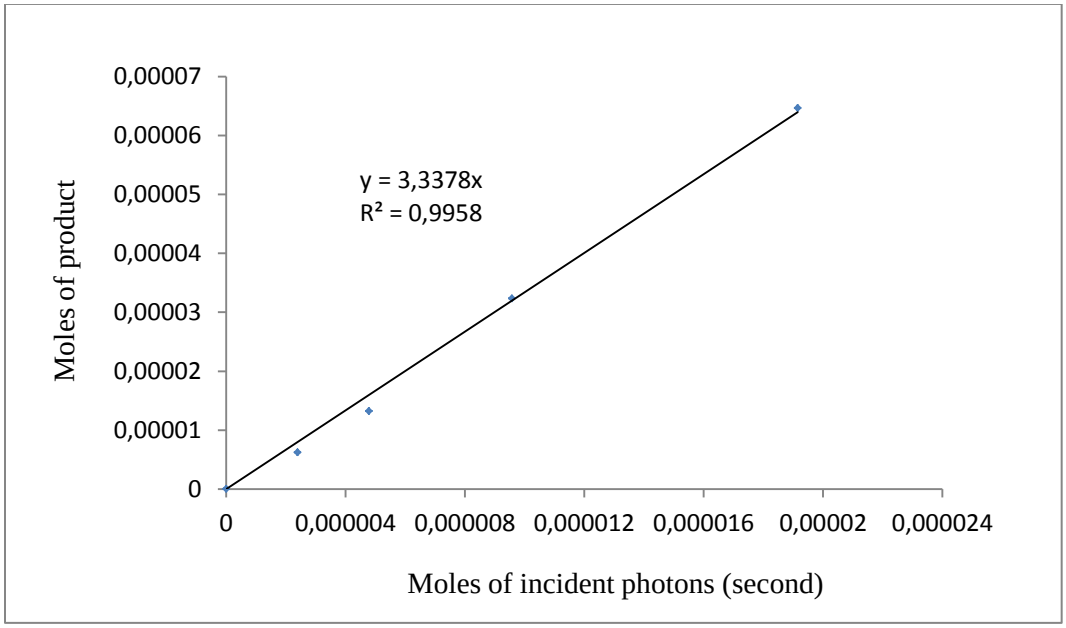
where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe^{2+} at 400 nm is 1.13 (*53*), $[1\text{-}10^{-A(\lambda)}]$ is the ratio of absorbed photons by the solution, and $A(\lambda)$ is the absorbance of the actinometer at the wavelength used to carry out the experiments (400 nm). The absorbance at 400 nm $A(400)$ was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in a 10 mm path quartz cuvette, obtaining an absorbance of 2.819.
$q^0_{n,p}$, which is the photon flux, was determined to be 5.32×10^{-9} einstein s^{-1}.



The moles of product **3a** formed for the model reaction were determined by GC measurement using trichloroethylene 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 S2. According to this, when plotting the moles of product (x) versus the moles of incident photons ($q^0_{n,p}$·dt), the slope is equal to: $\mathbf{\Phi \cdot (1-10^{-A(400\ nm)})}$, where Φ is the quantum yield to be determined and *A*(400 nm) is the absorption of the reaction under study.

A(400 nm) was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in 10 mm path quartz. An absorbance of 0.86 was determined for the model reaction mixture.



The quantum yield (Φ) of the photochemical alkylation of butanal **1a** with α-iodo sulfone **2a** catalyzed by **A** was calculated to be **3.9**.

H. References

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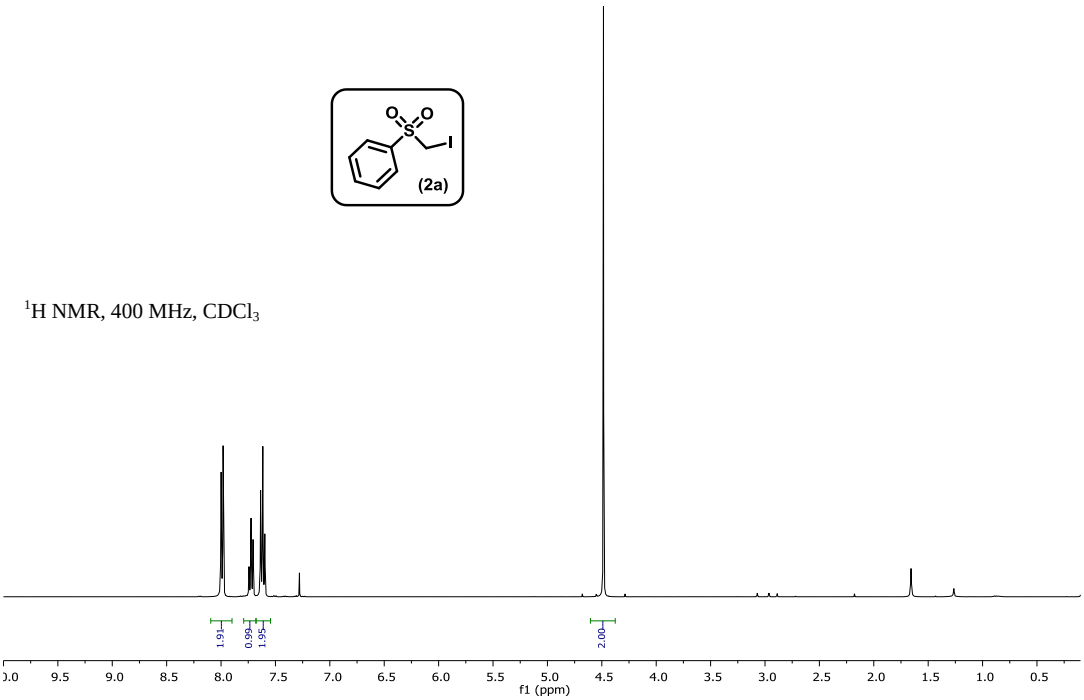
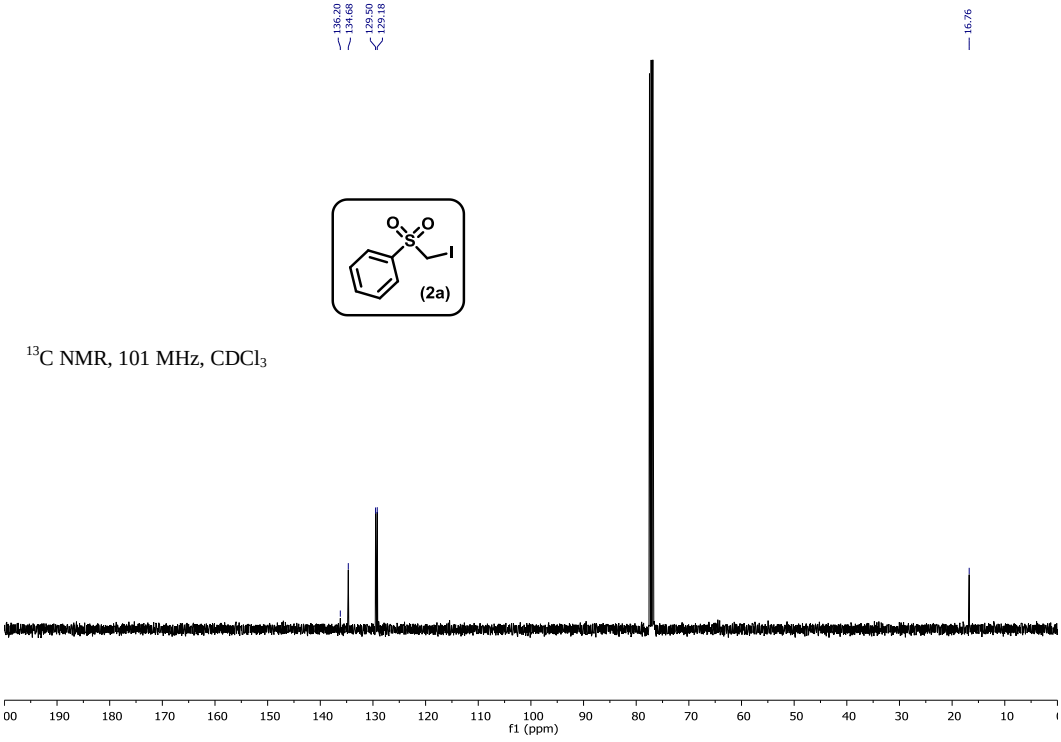
I. NMR Spectra

I.1 Starting Materials

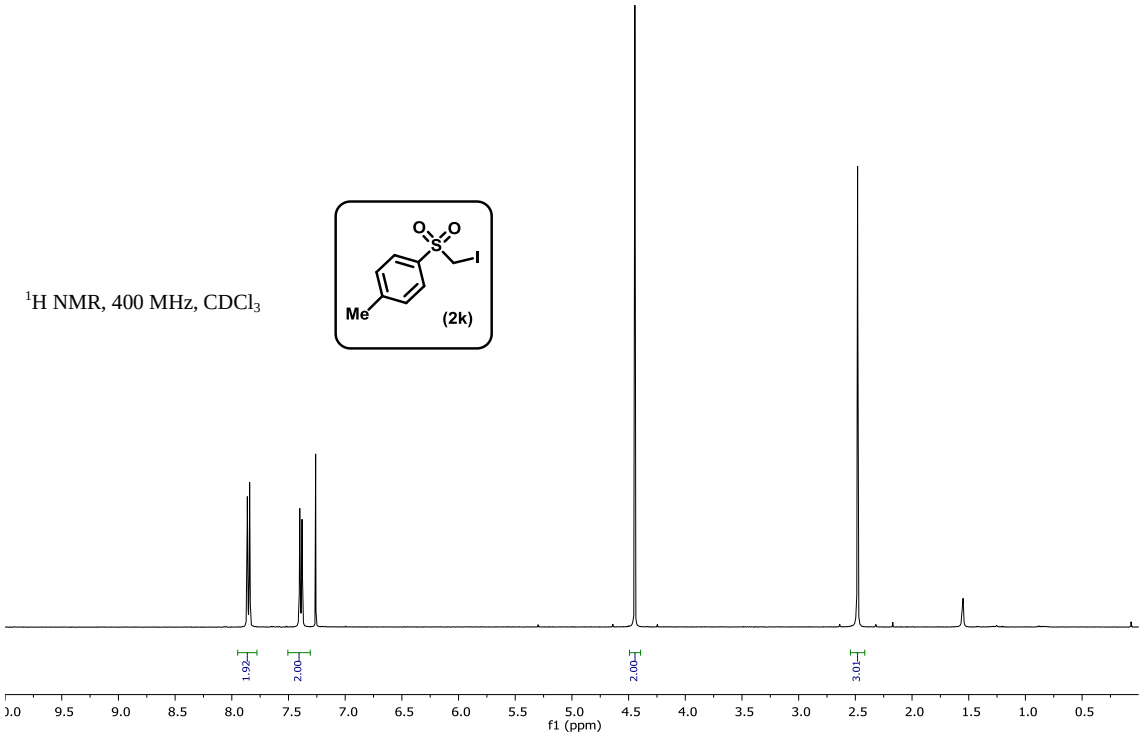


^{1}H NMR, 400 MHz, $CDCl_3$

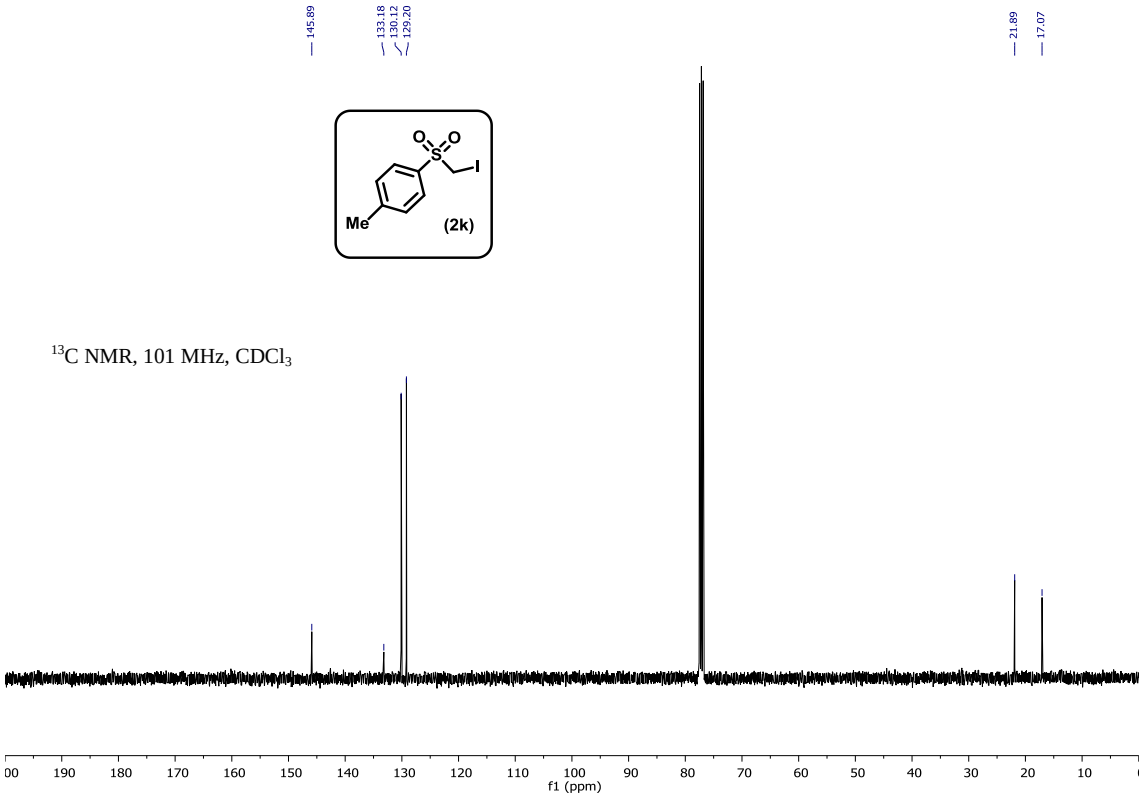


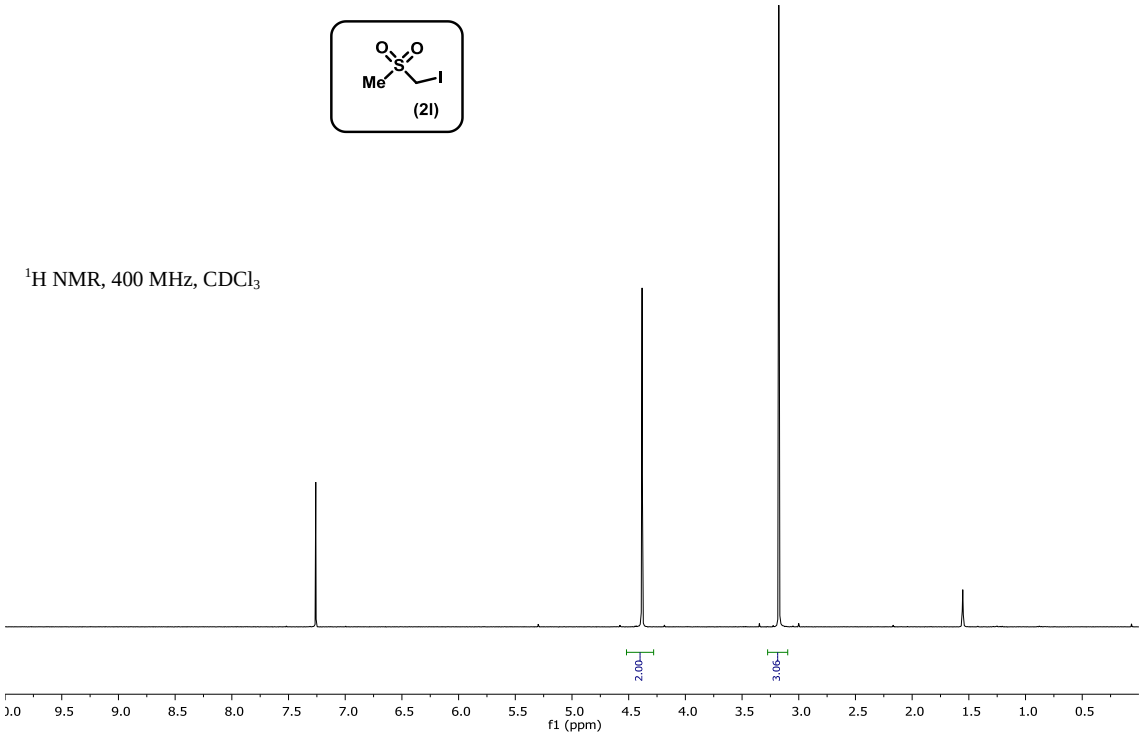
^{13}C NMR, 101 MHz, $CDCl_3$

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

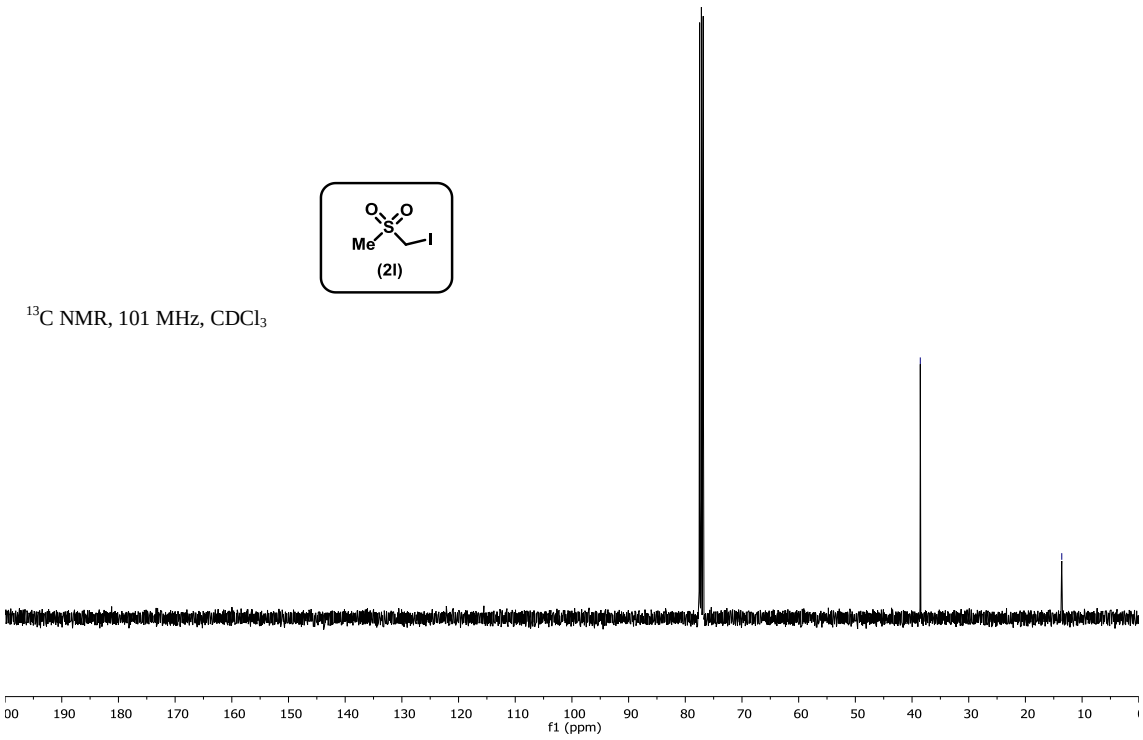


^{13}C NMR, 101 MHz, $CDCl_3$



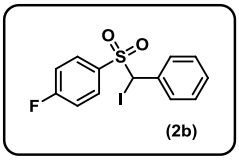


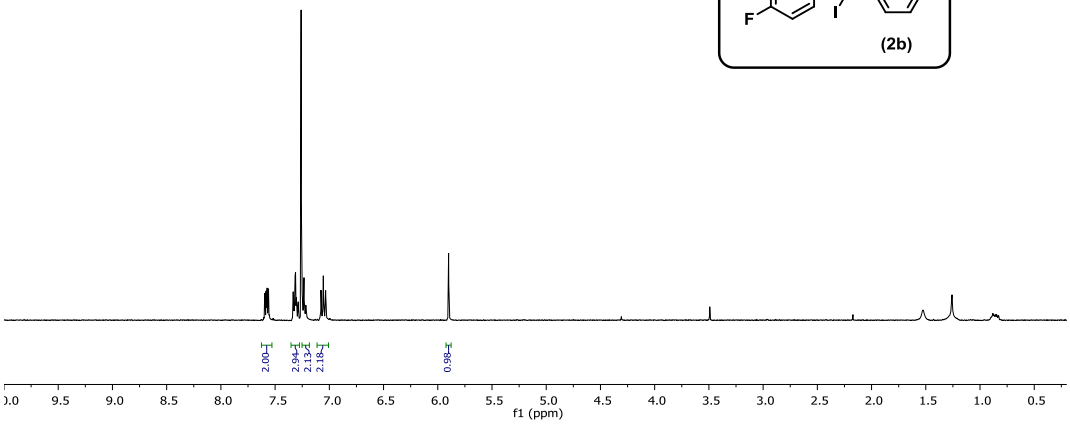
^{1}H NMR, 400 MHz, $CDCl_3$



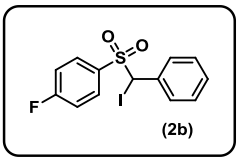
^{13}C NMR, 101 MHz, $CDCl_3$

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

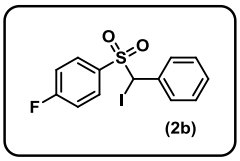




^{13}C NMR, 101 MHz, $CDCl_3$

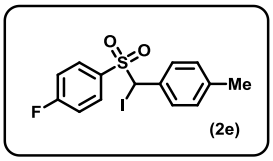


^{1}H decoupled ^{19}F NMR, 376 MHz, $CDCl_3$

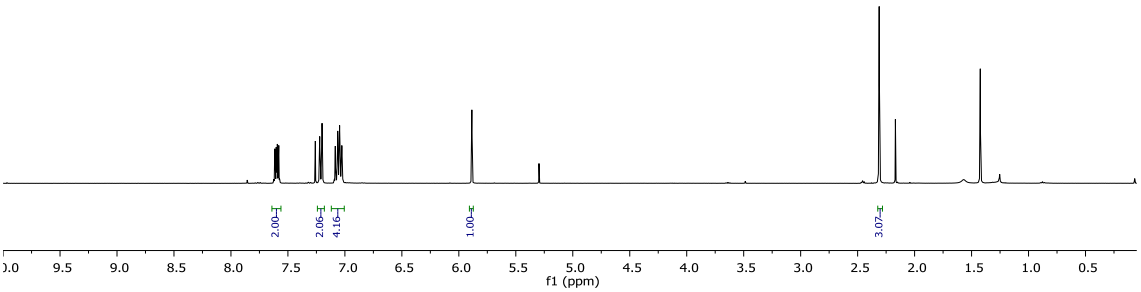


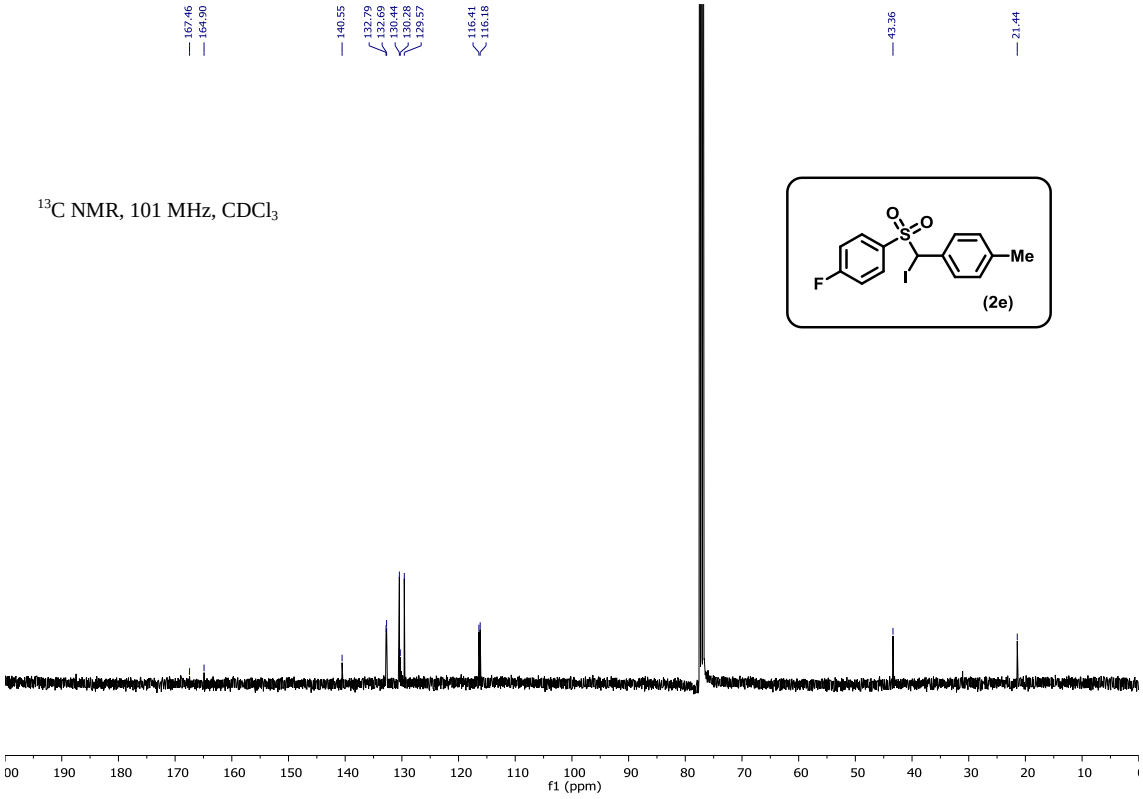
(2b)

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

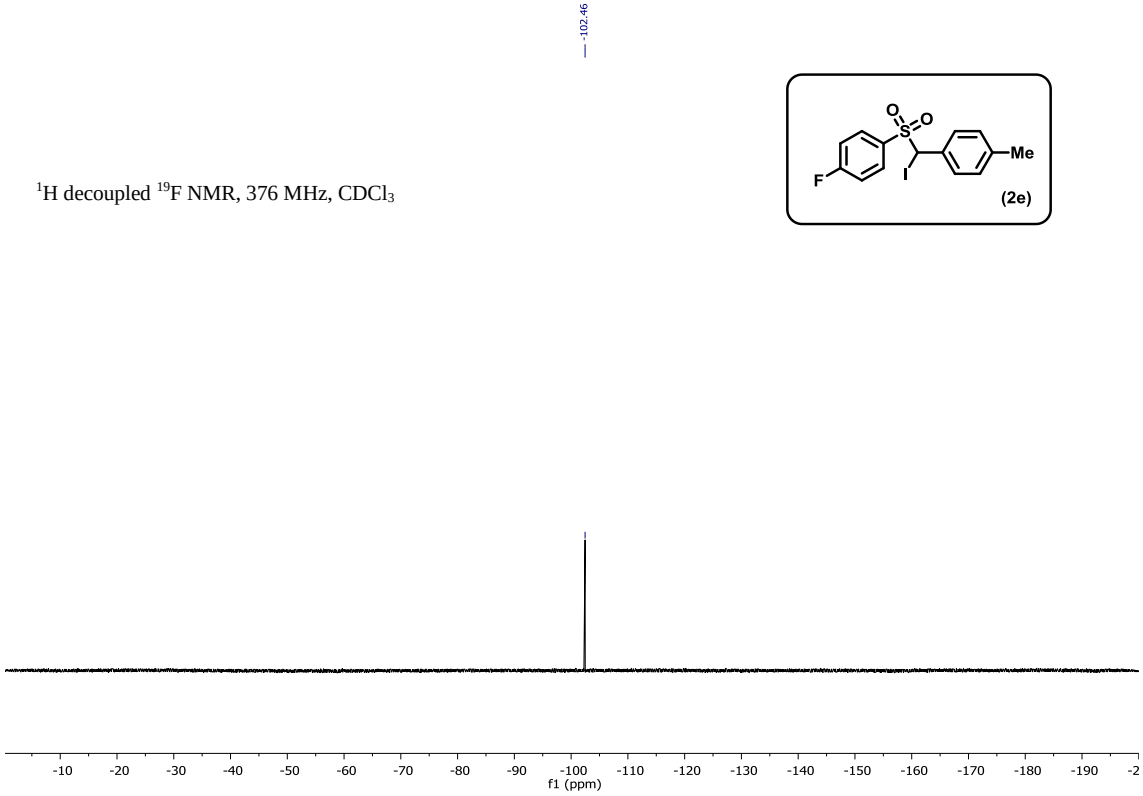


(2e)

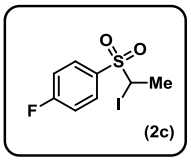




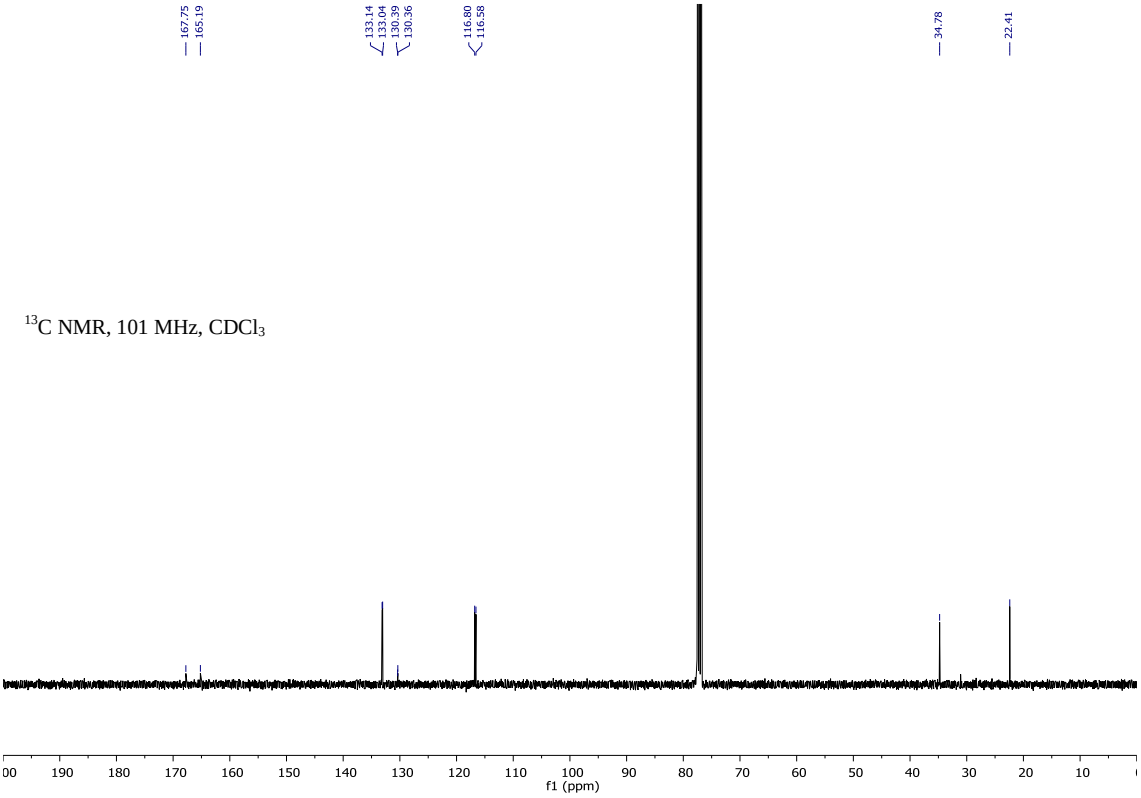
^{13}C NMR, 101 MHz, $CDCl_3$



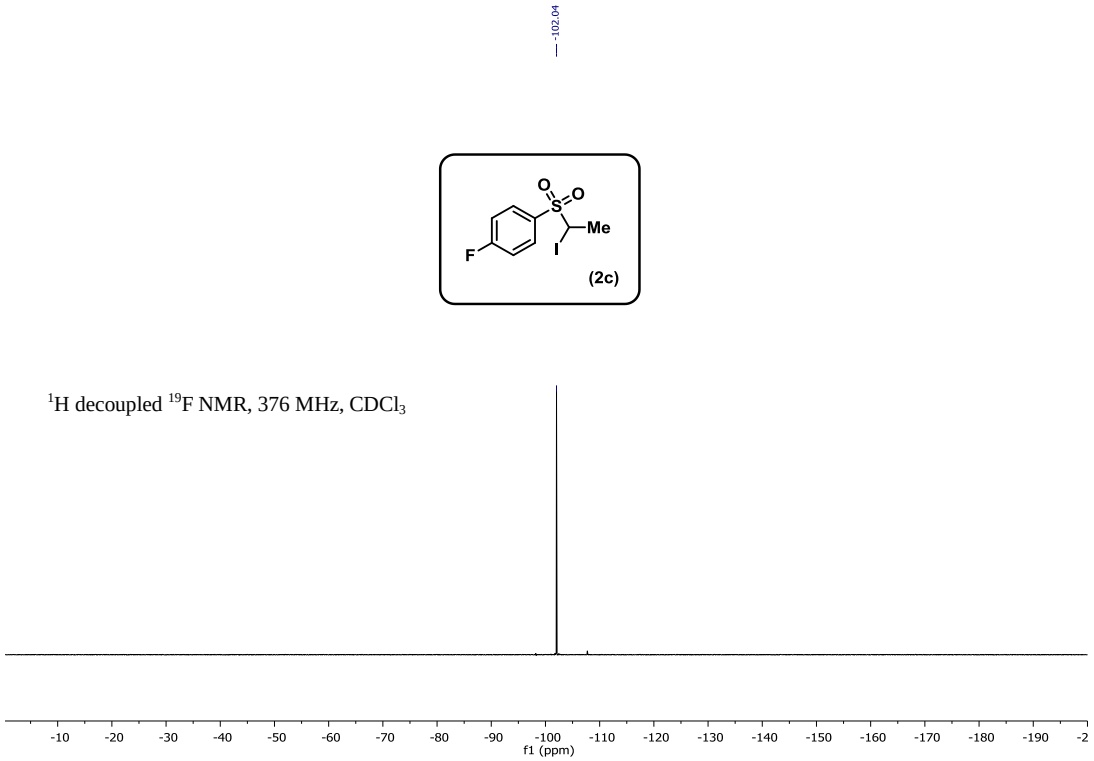
^{1}H decoupled ^{19}F NMR, 376 MHz, $CDCl_3$



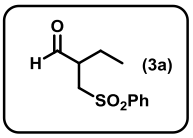
^{1}H NMR, 400 MHz, $CDCl_3$



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


-102.04
O
S
O
Me
I
F
(2c)
^{1}H decoupled ^{19}F NMR, 376 MHz, $CDCl_3$
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

I.2 Products



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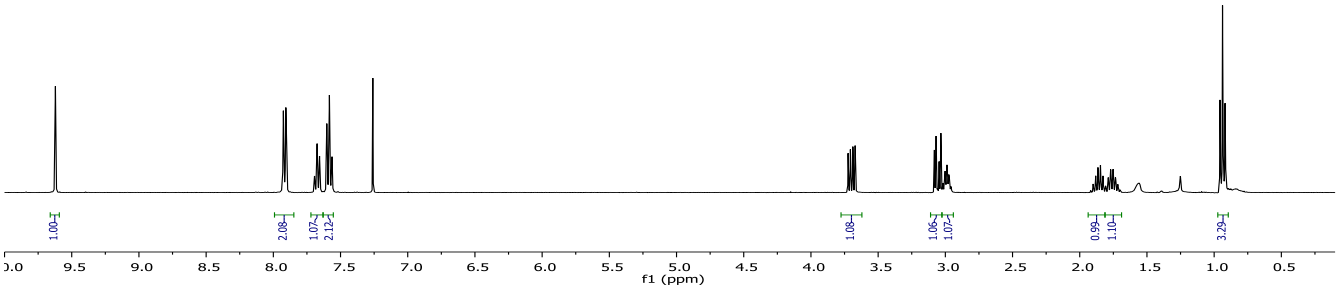
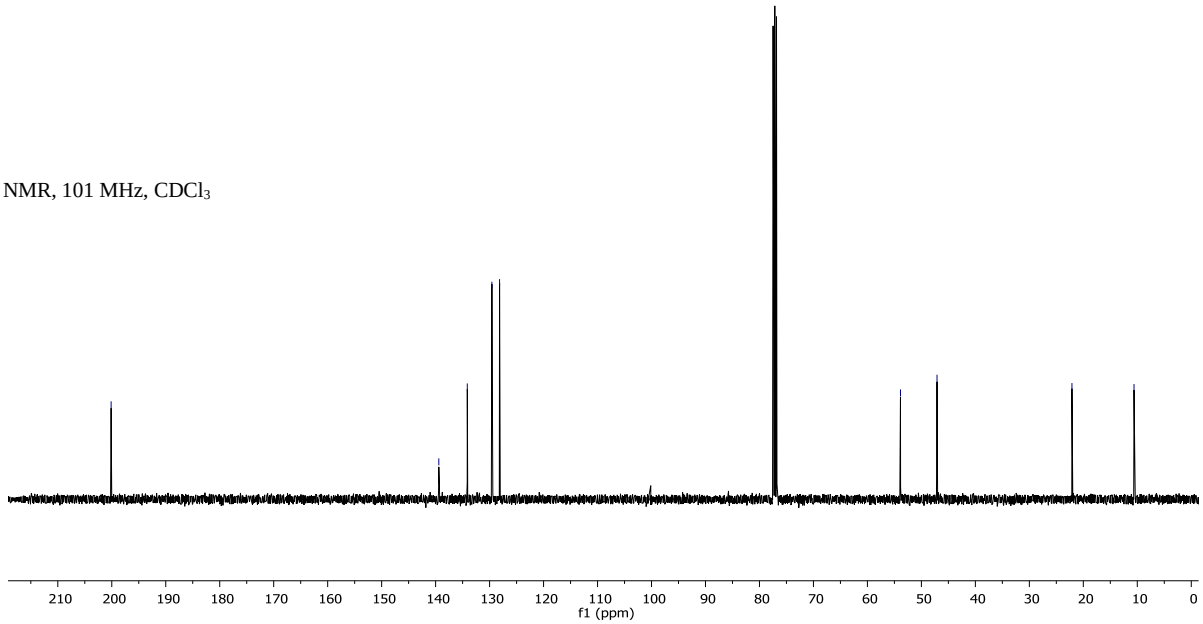
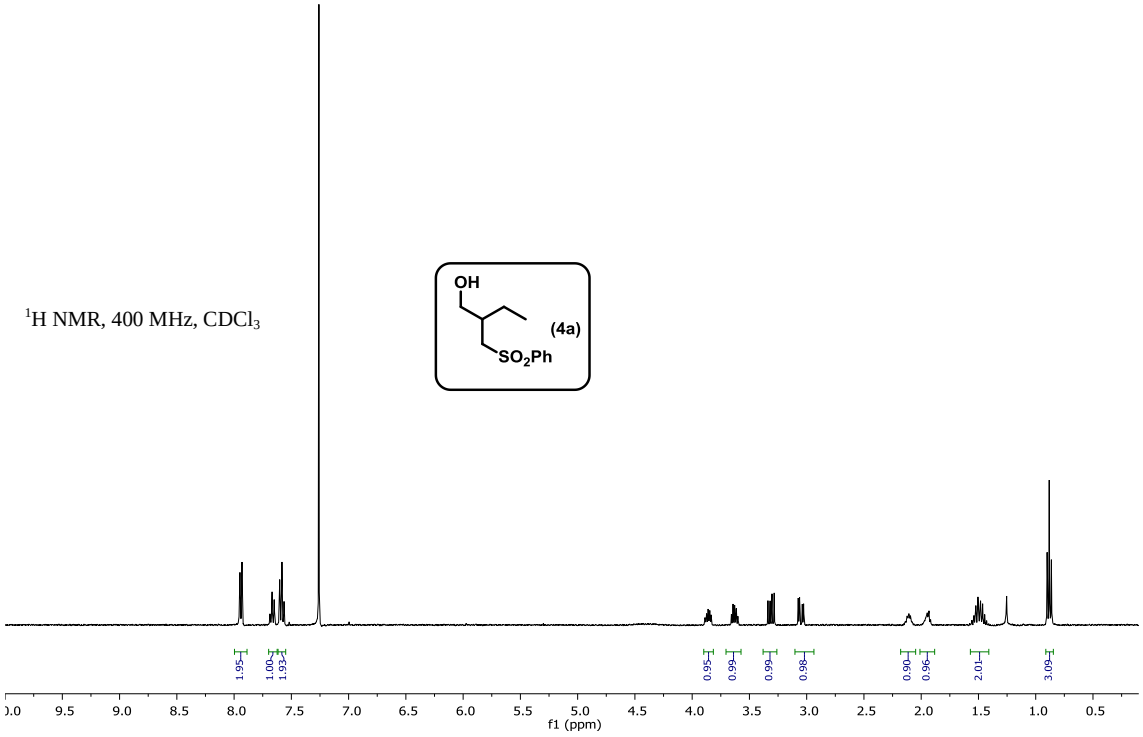


^{13}C NMR, 101 MHz, $CDCl_3$



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



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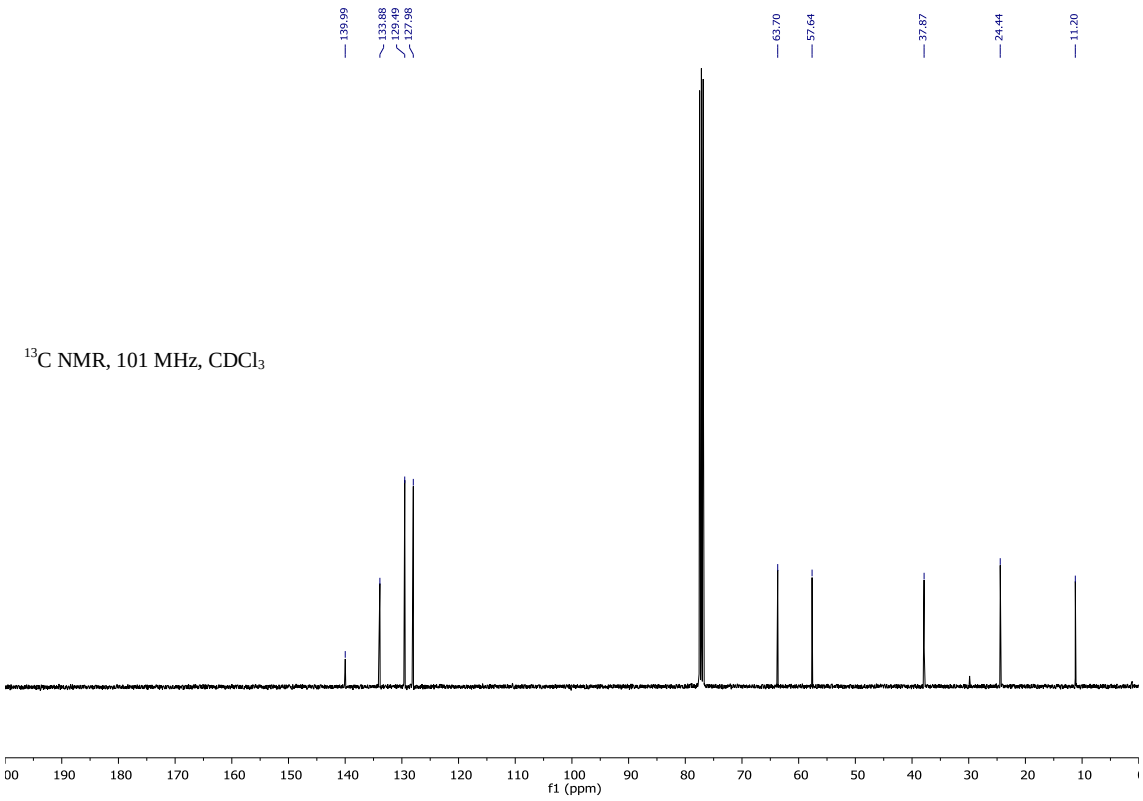

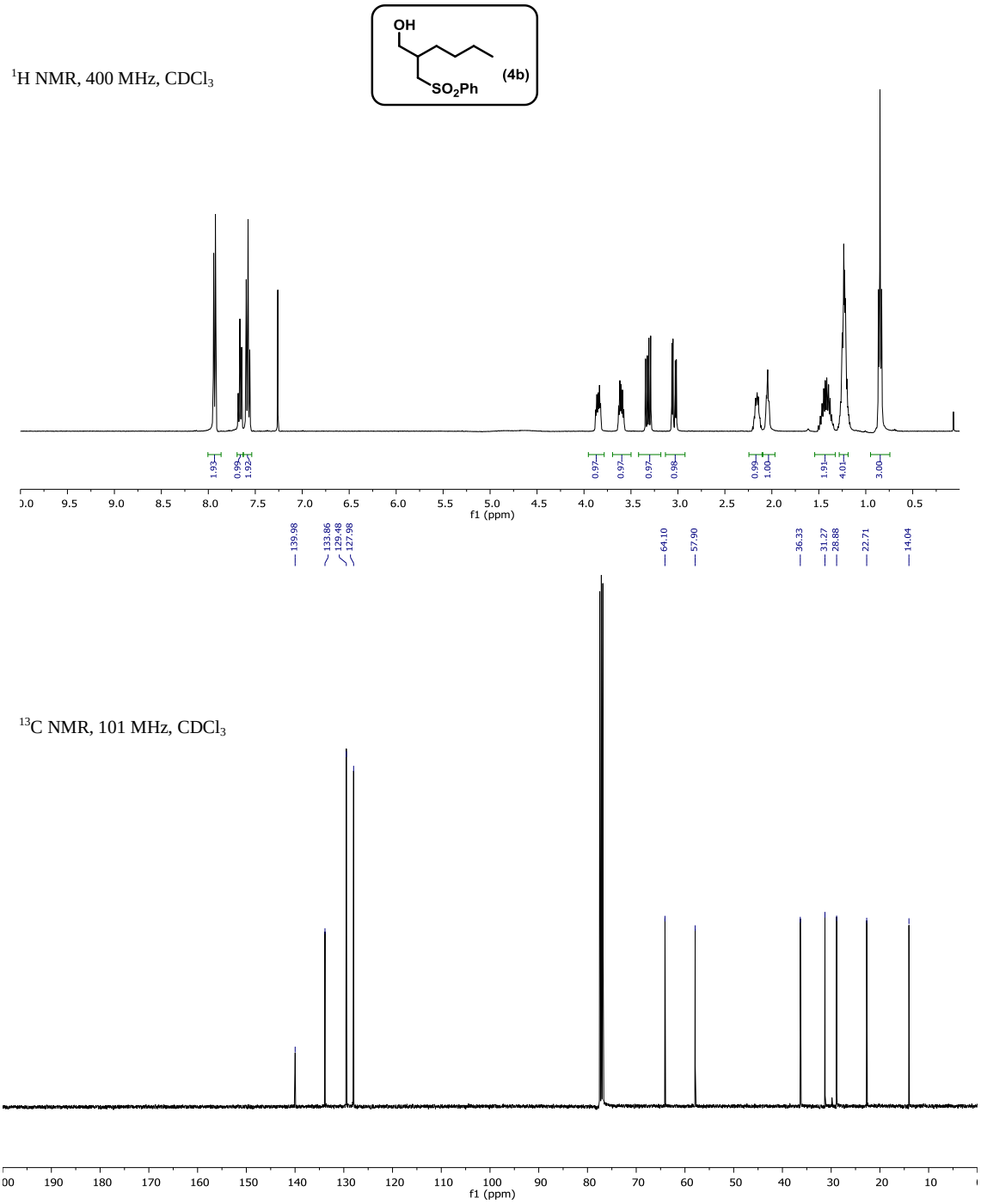
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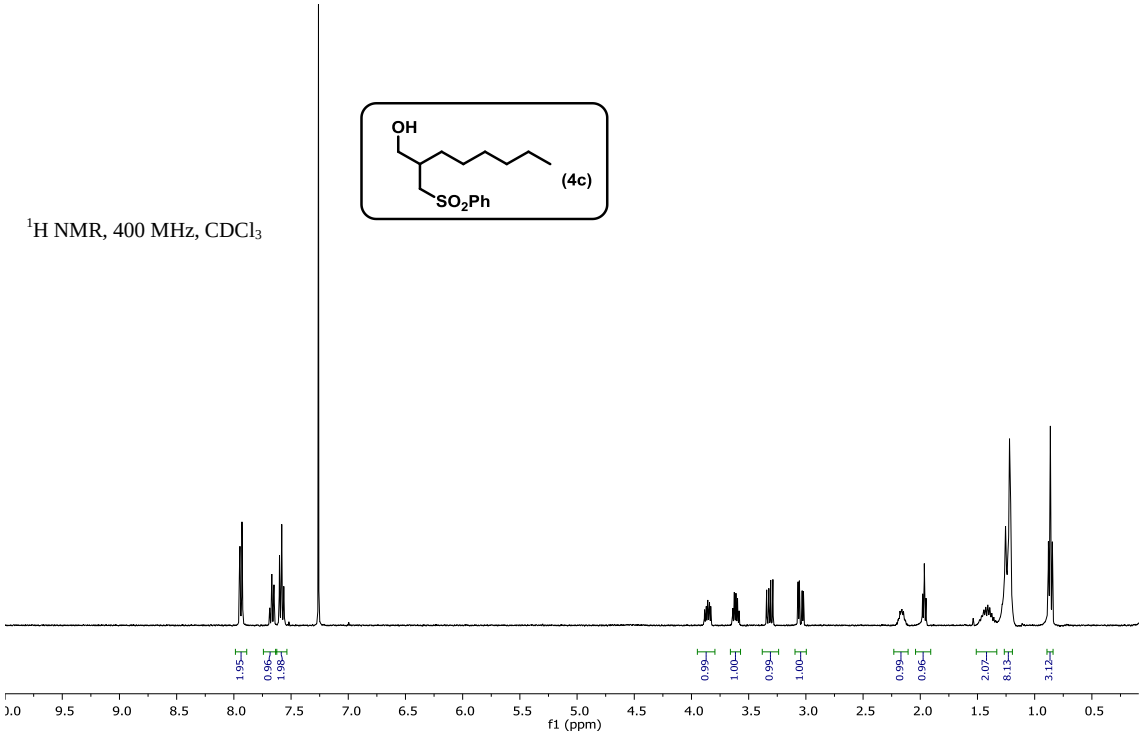
SO2Ph
(4b)
1H NMR, 400 MHz, CDCl3
1.93
0.99
1.92
0.97
0.97
0.97
0.98
0.99
1.00
1.91
4.01
3.00
f1 (ppm)
139.98
133.86
129.48
127.98
64.10
57.90
36.33
31.27
29.88
22.71
14.04
13C NMR, 101 MHz, CDCl3
f1 (ppm)


OH
SO2Ph
(4c)
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1.98
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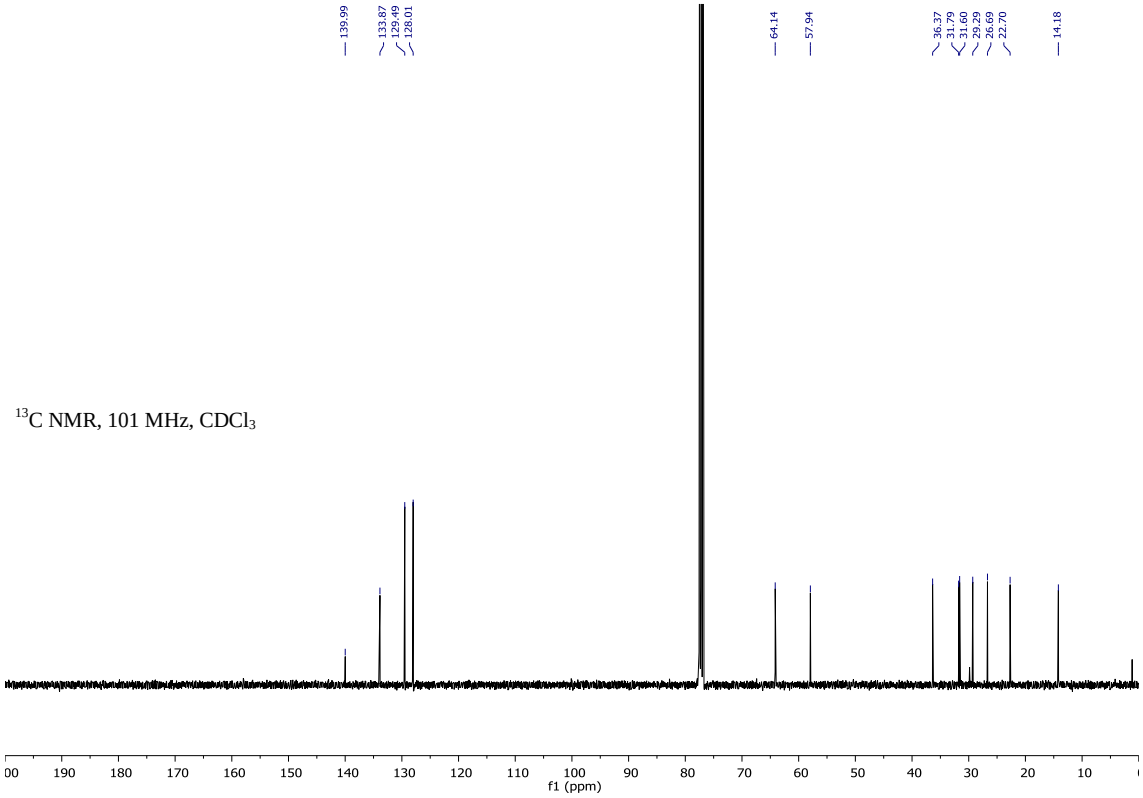
1.00
0.99
1.00
0.99
0.96
2.07
8.13
3.12
f1 (ppm)


139.99
133.87
129.49
128.01
64.14
57.94
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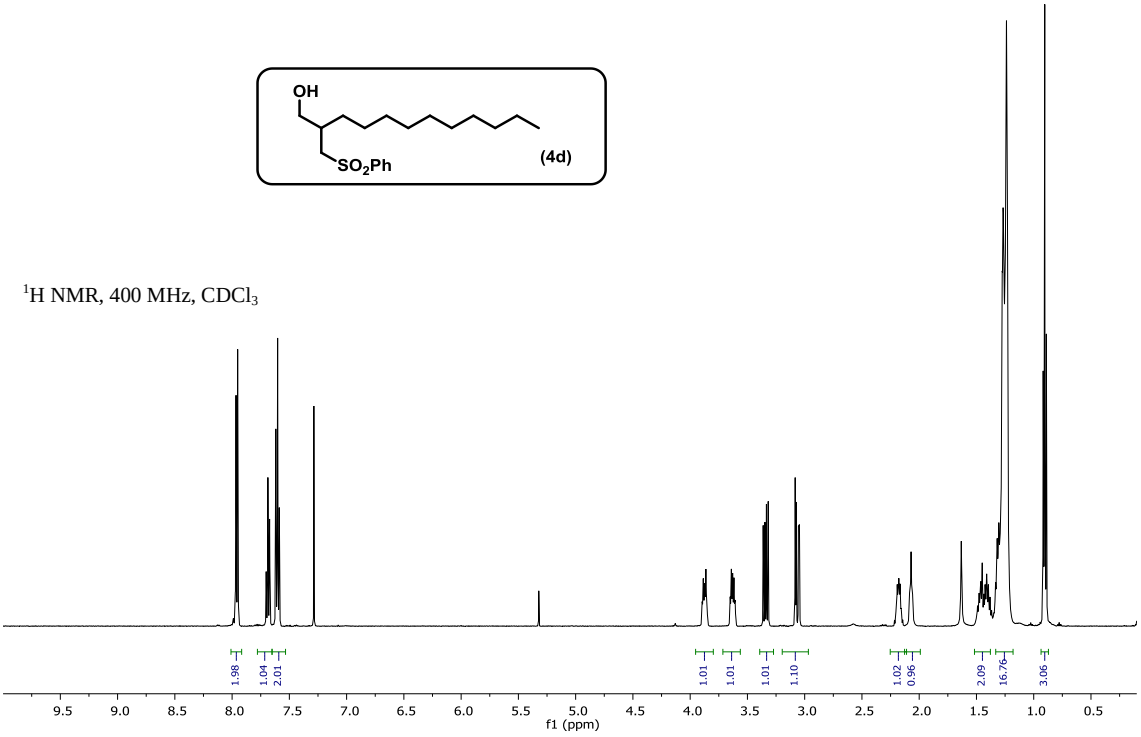
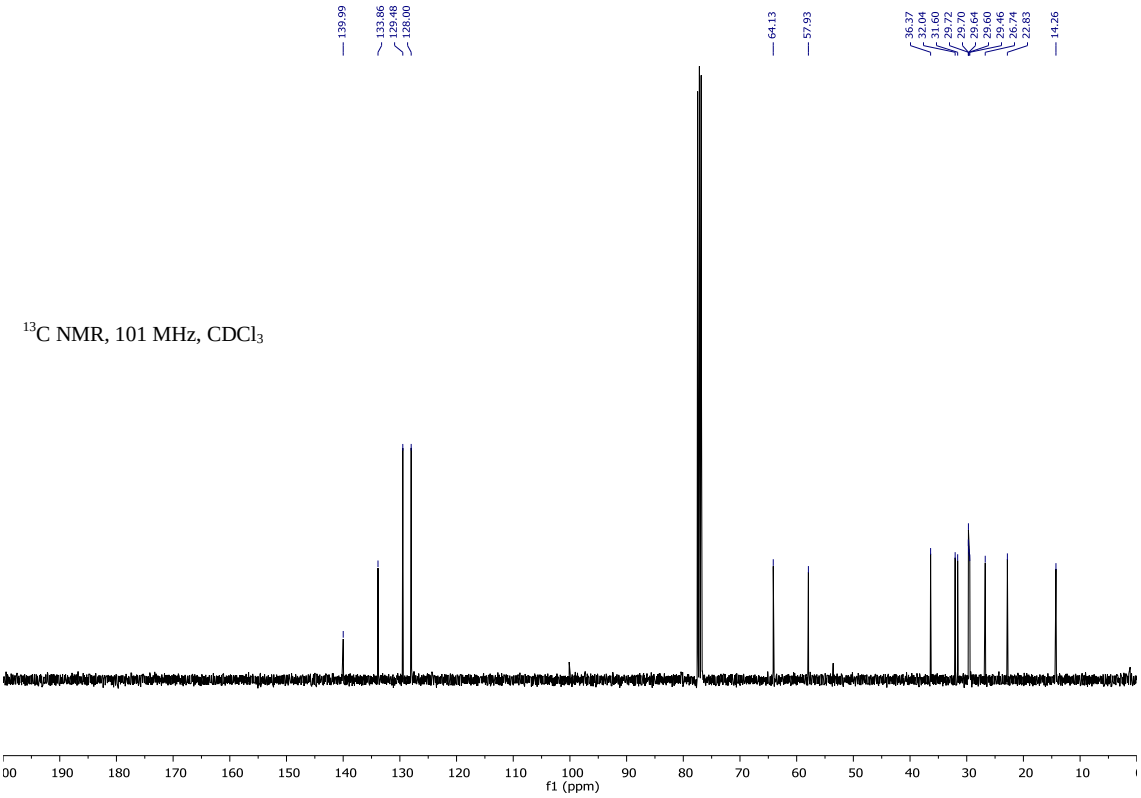
31.79
31.60
29.29
26.69
22.70
14.18
13C NMR, 101 MHz, CDCl3
f1 (ppm)


OH
SO2Ph
(4d)
1H NMR, 400 MHz, CDCl3
1.98
1.04
2.01
1.01
1.01
1.01
1.10
1.02
0.96
2.09
16.76
3.06
f1 (ppm)


139.99
133.86
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128.00
64.13
57.93
36.37
32.04
31.60
29.72
29.70
29.64
29.60
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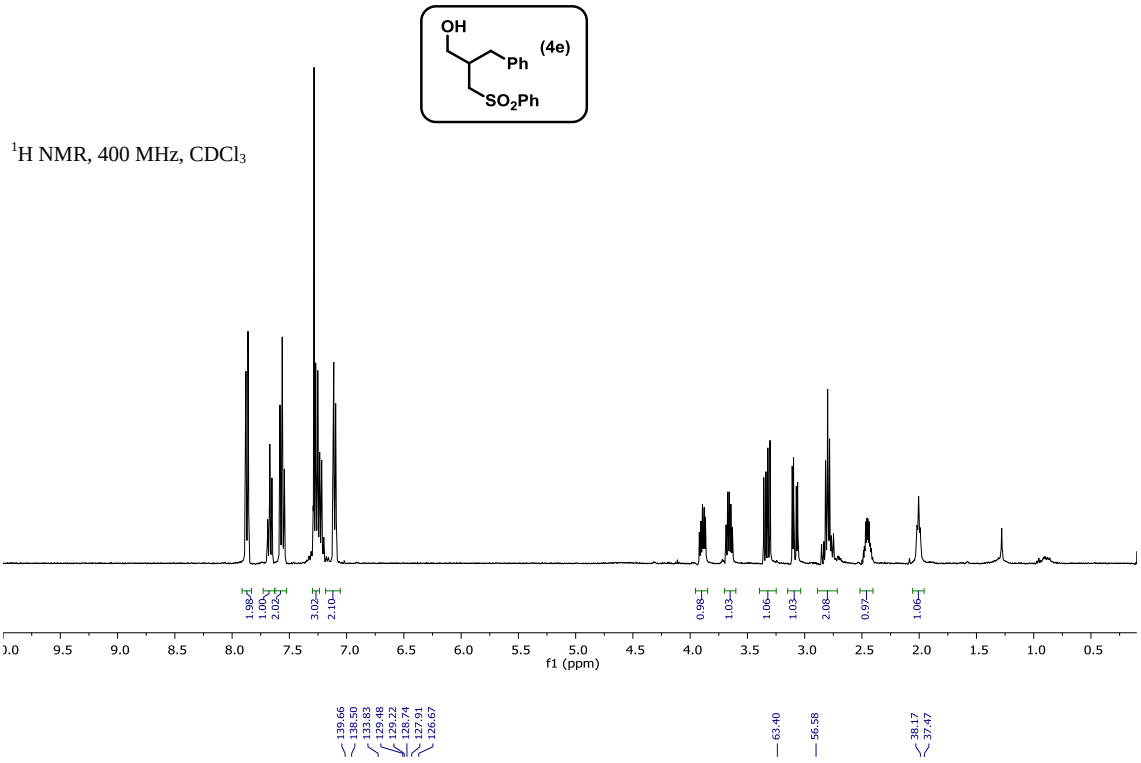
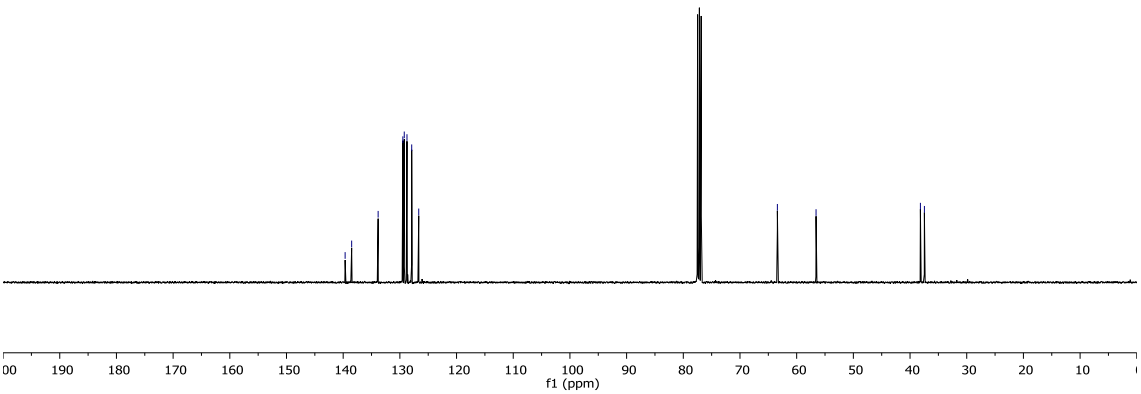
22.83
14.26
13C NMR, 101 MHz, CDCl3
f1 (ppm)


OH
Ph
(4e)
SO2Ph
1H NMR, 400 MHz, CDCl3
1.98
1.00
2.02
3.02
2.10
0.98
1.03
1.06
1.03
2.08
0.97
1.06
f1 (ppm)
139.66
138.50
133.83
129.48
129.22
128.74
127.91
126.67
63.40
56.58
38.17
37.47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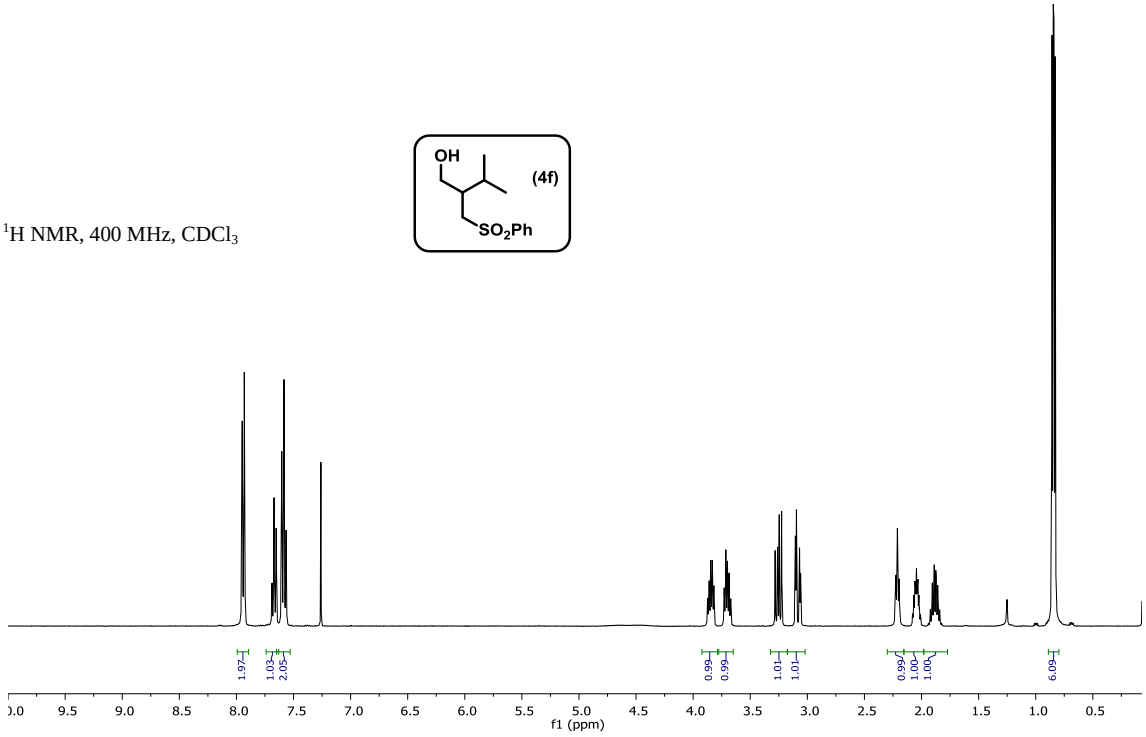
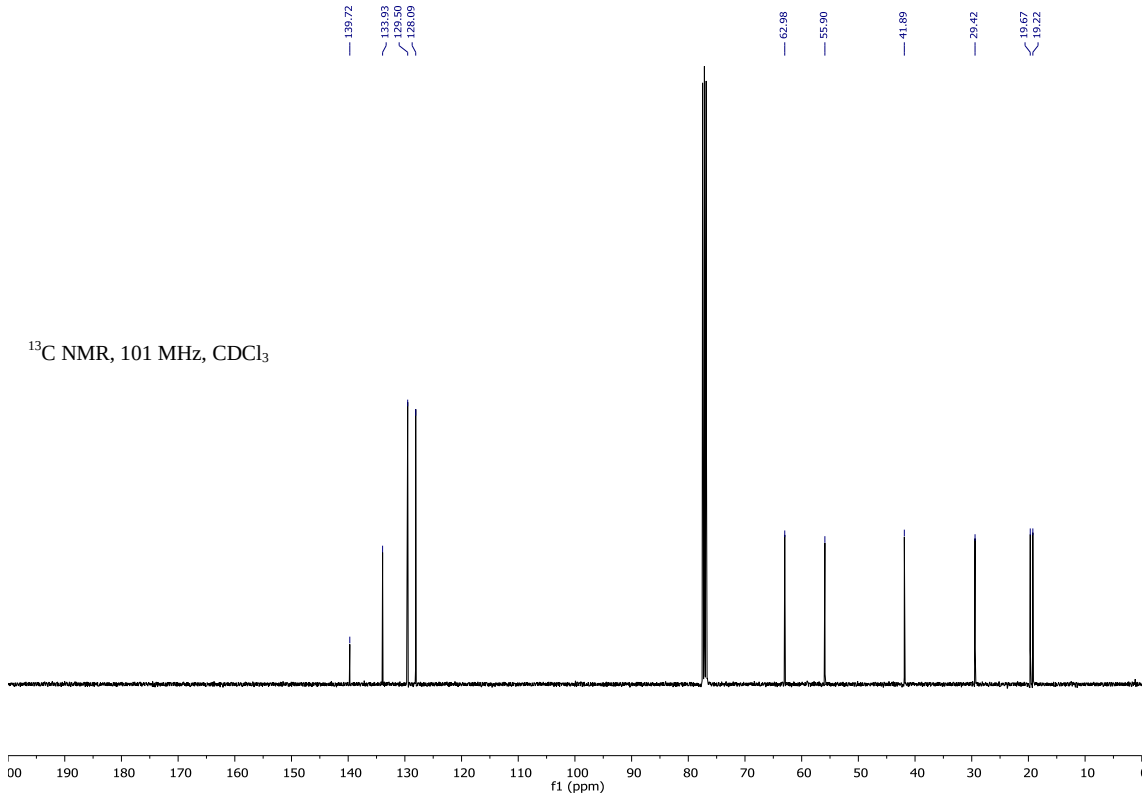
f1 (ppm)



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



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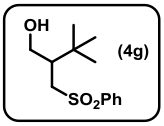
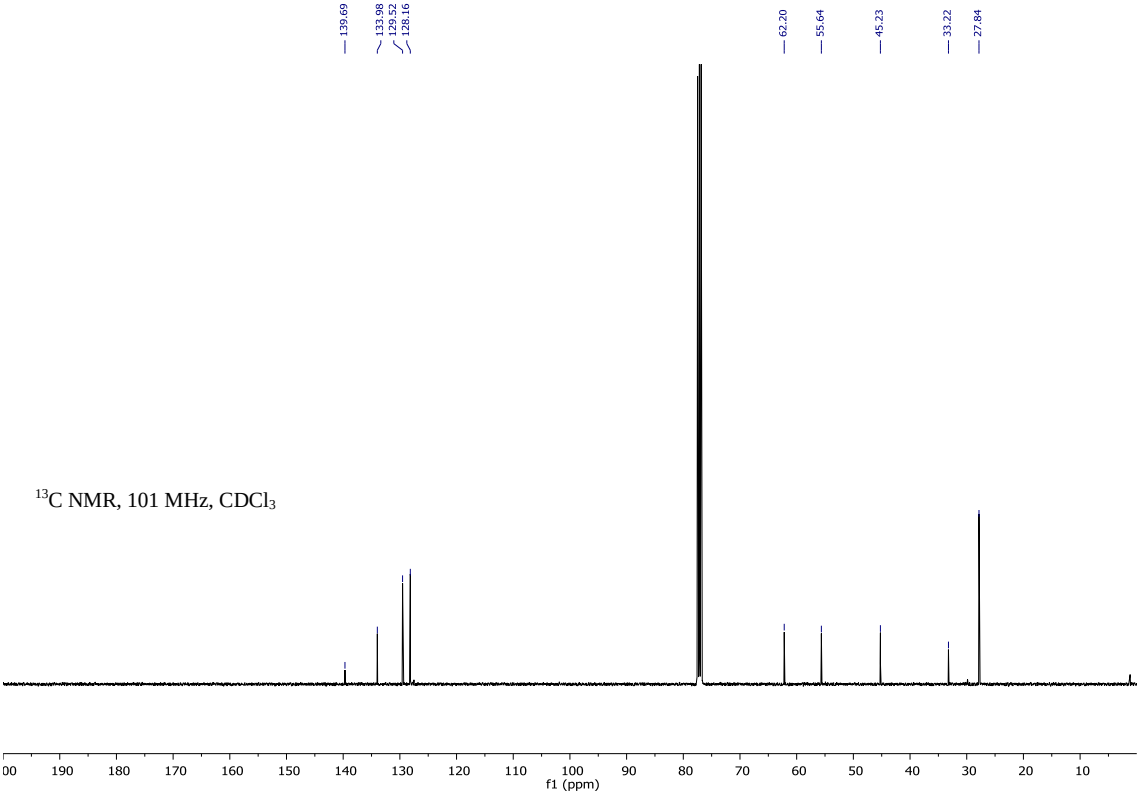
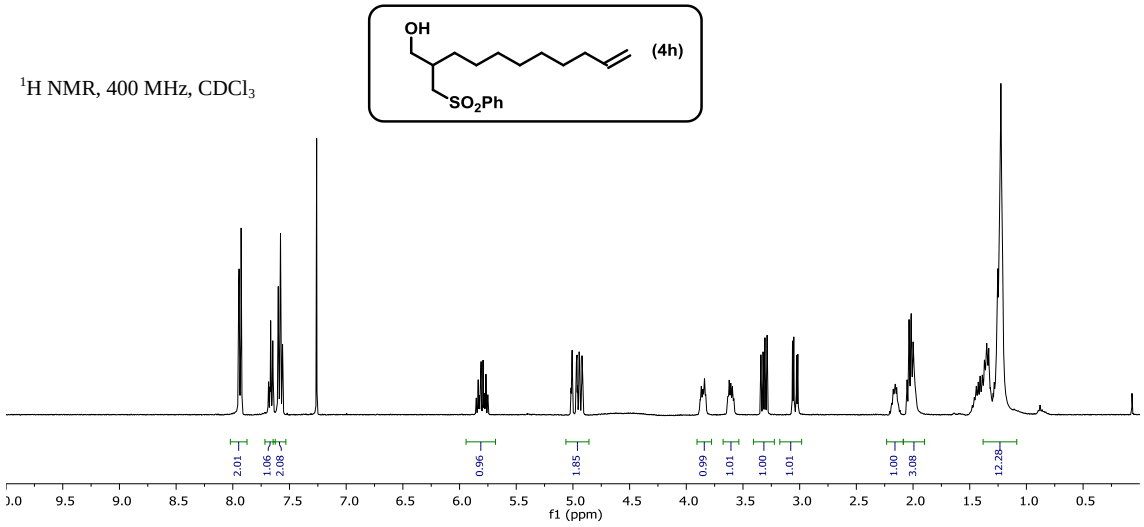


^{1}H NMR, 400 MHz, $CDCl_3$

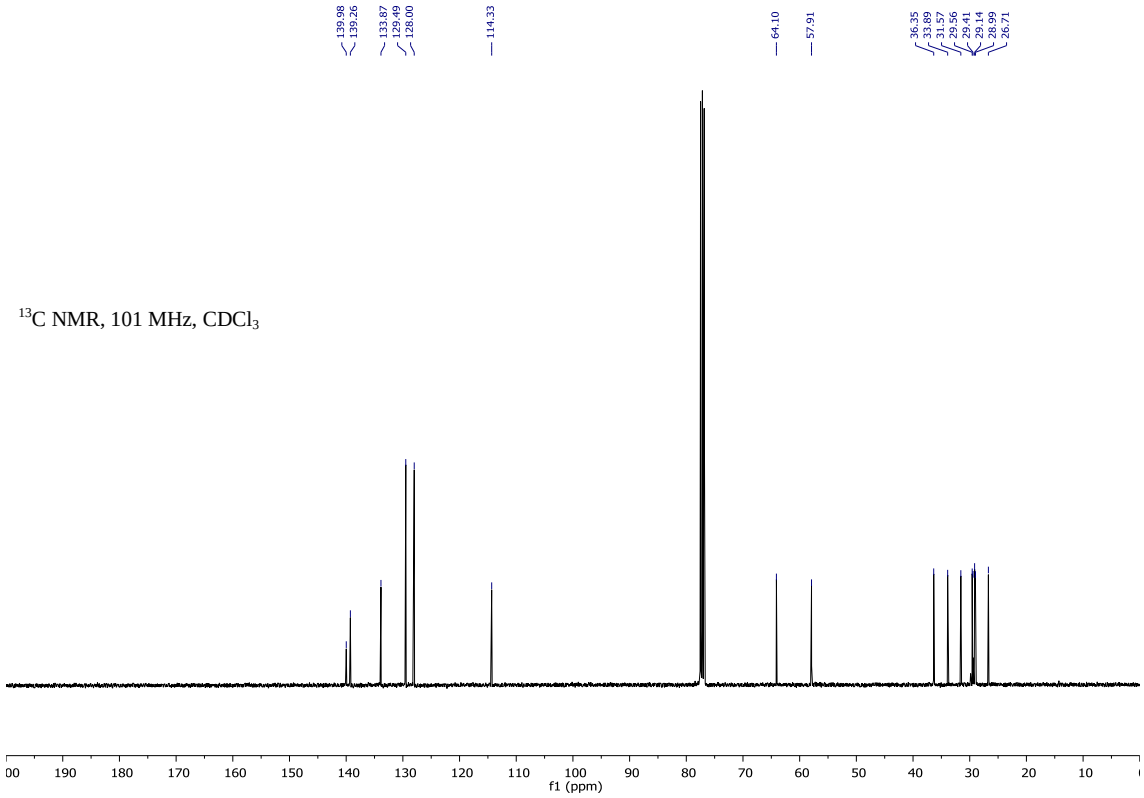
^{13}C NMR, 101 MHz, $CDCl_3$



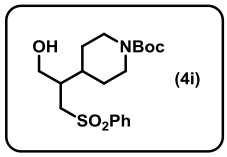
^{1}H NMR, 400 MHz, $CDCl_3$



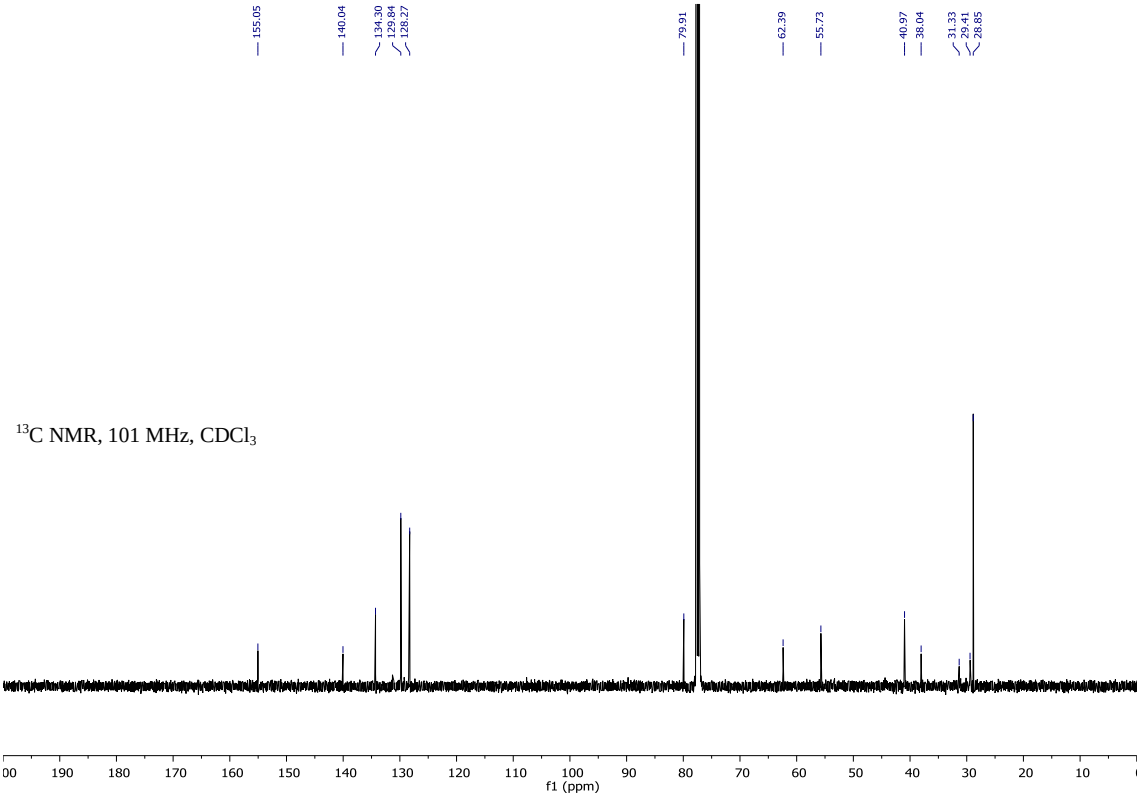
^{13}C NMR, 101 MHz, $CDCl_3$

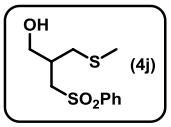


^{1}H NMR, 400 MHz, $CDCl_3$



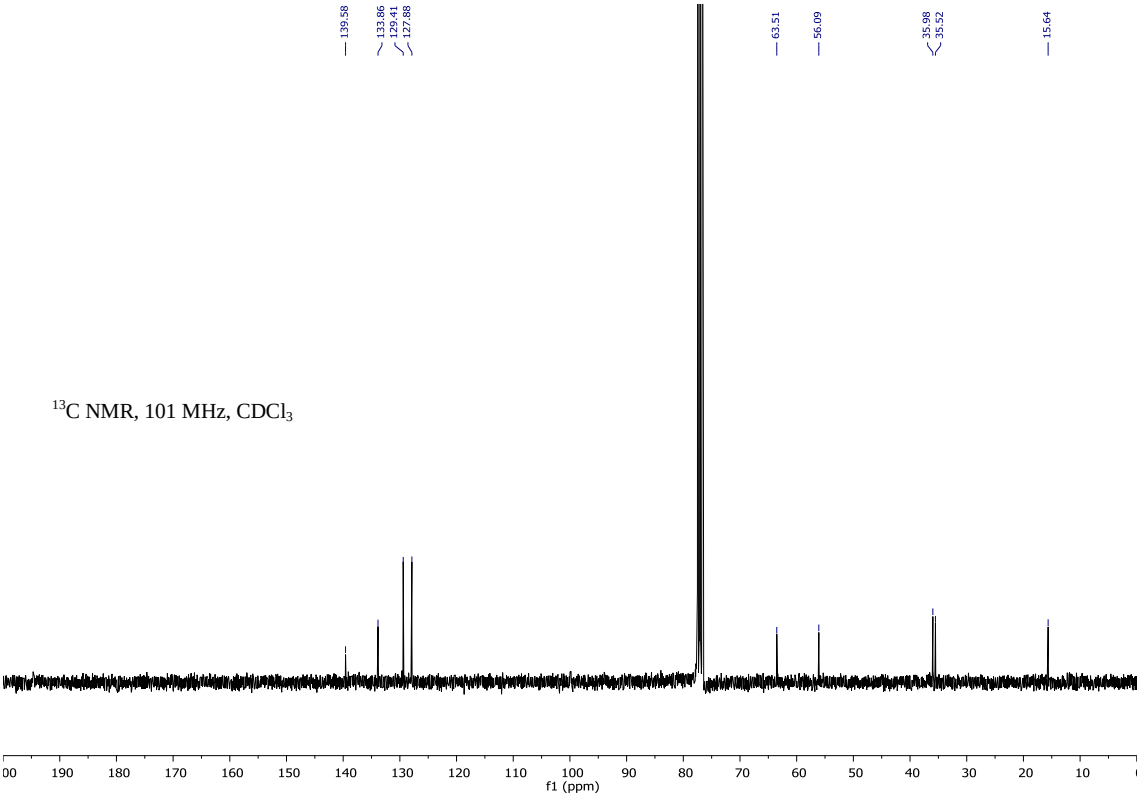
^{13}C NMR, 101 MHz, $CDCl_3$

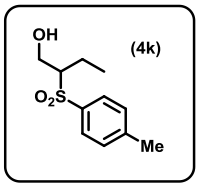




^{1}H NMR, 400 MHz, $CDCl_3$

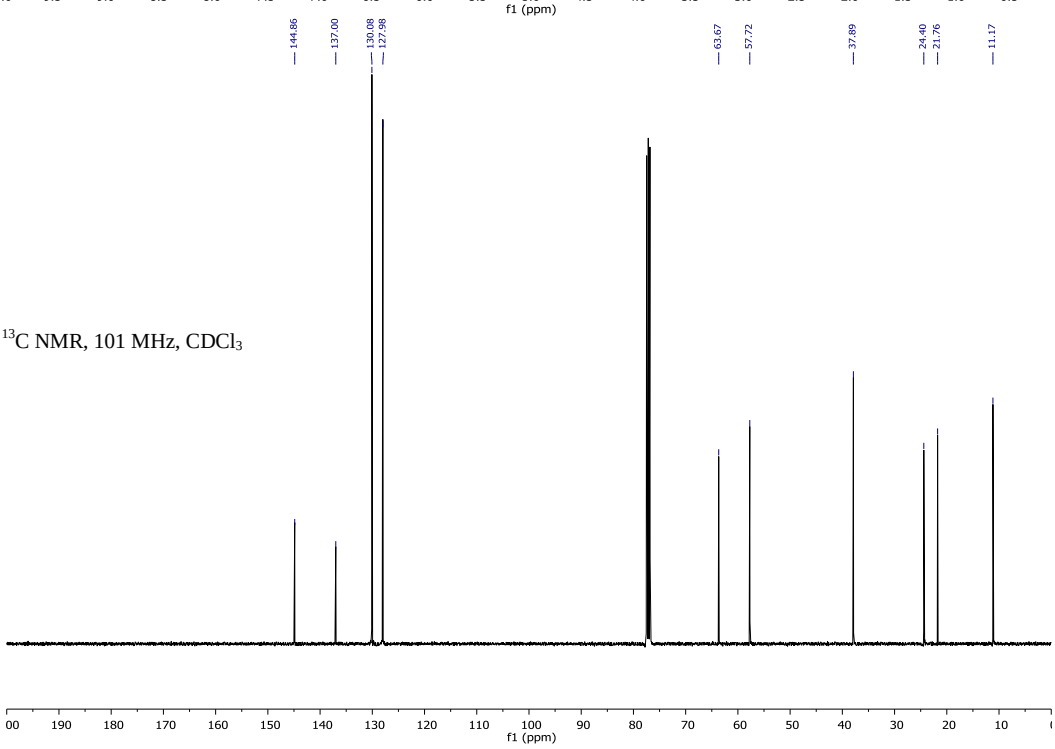
^{13}C NMR, 101 MHz, $CDCl_3$

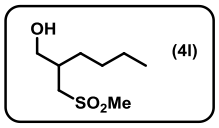




^{1}H NMR, 400 MHz, $CDCl_3$

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

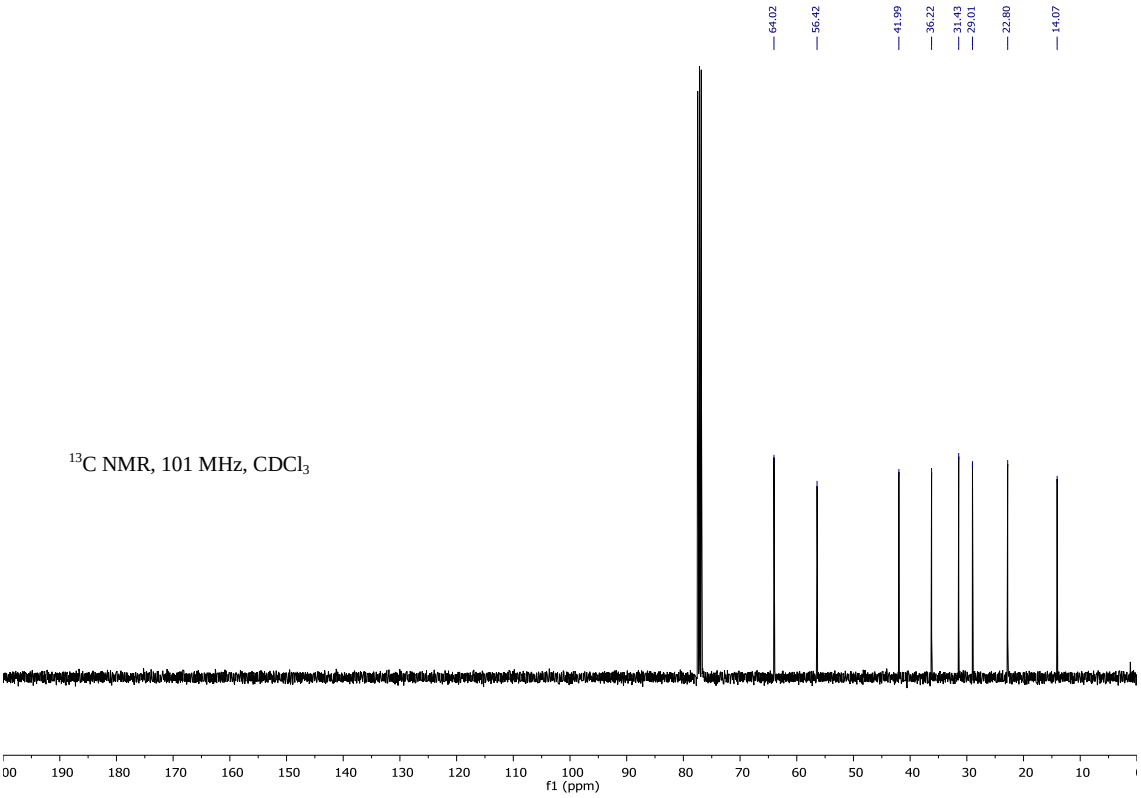


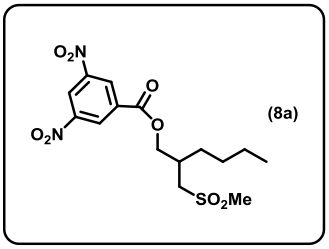


(4l)

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

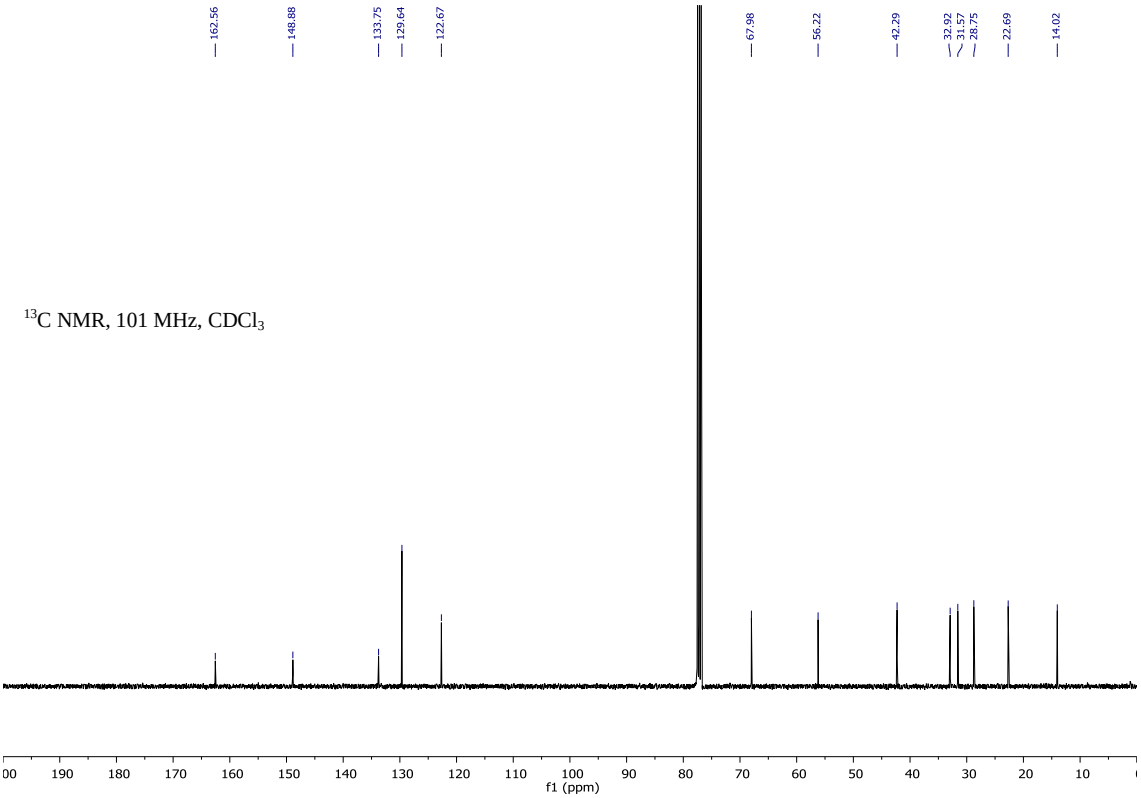
^{13}C NMR, 101 MHz, $CDCl_3$

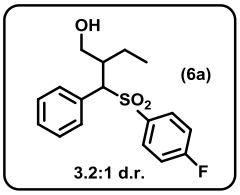




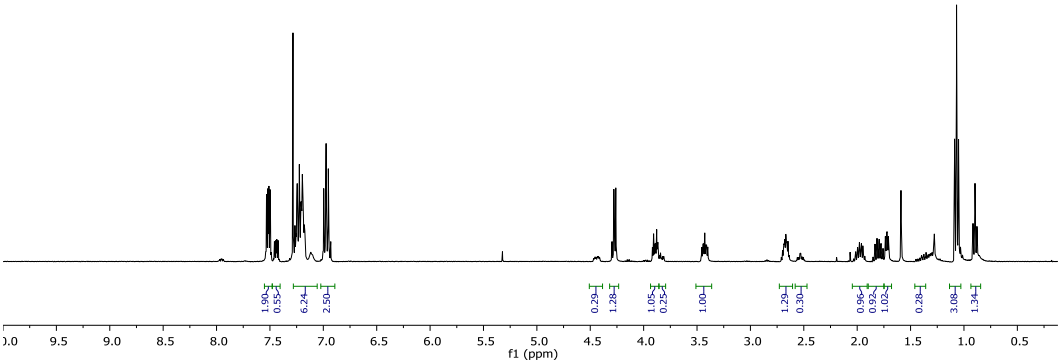
^{1}H NMR, 400 MHz, $CDCl_3$

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

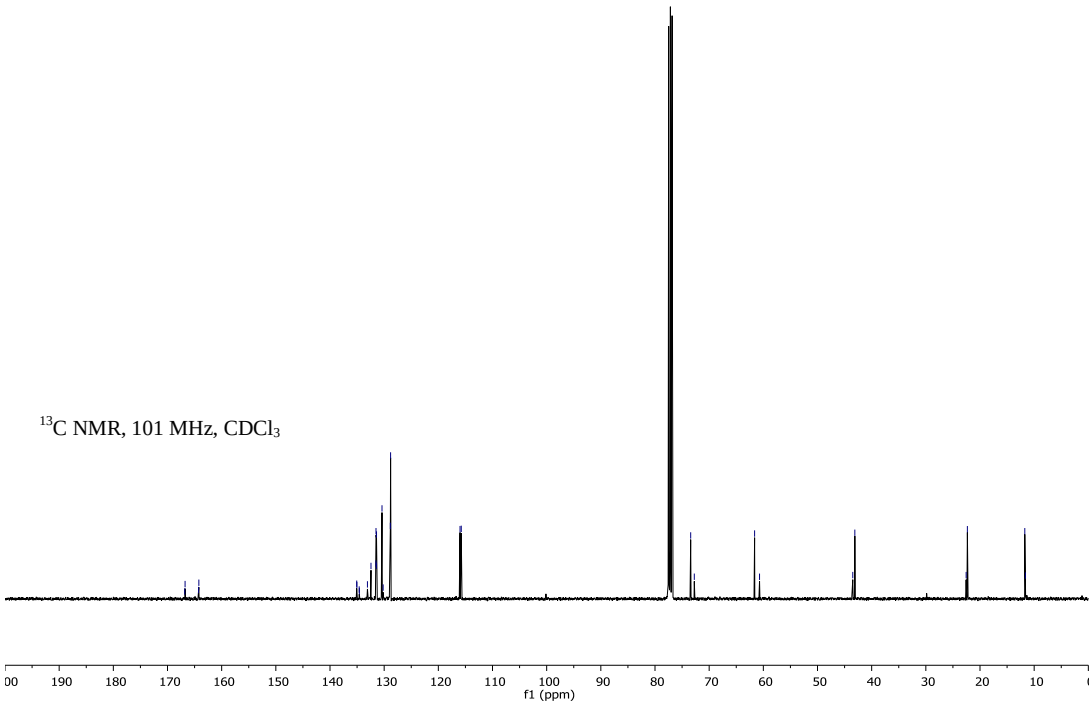


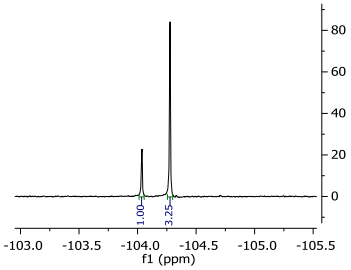


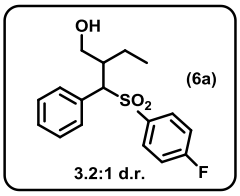
^{1}H NMR, 400 MHz, $CDCl_3$



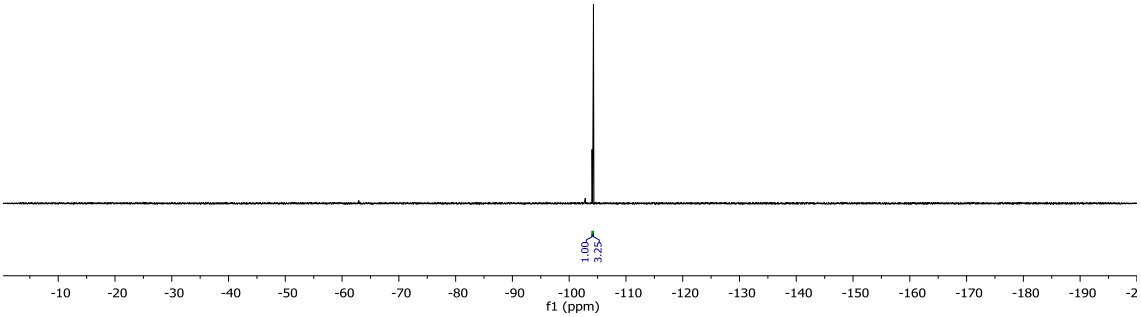
^{13}C NMR, 101 MHz, $CDCl_3$

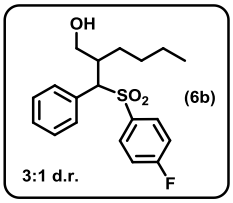




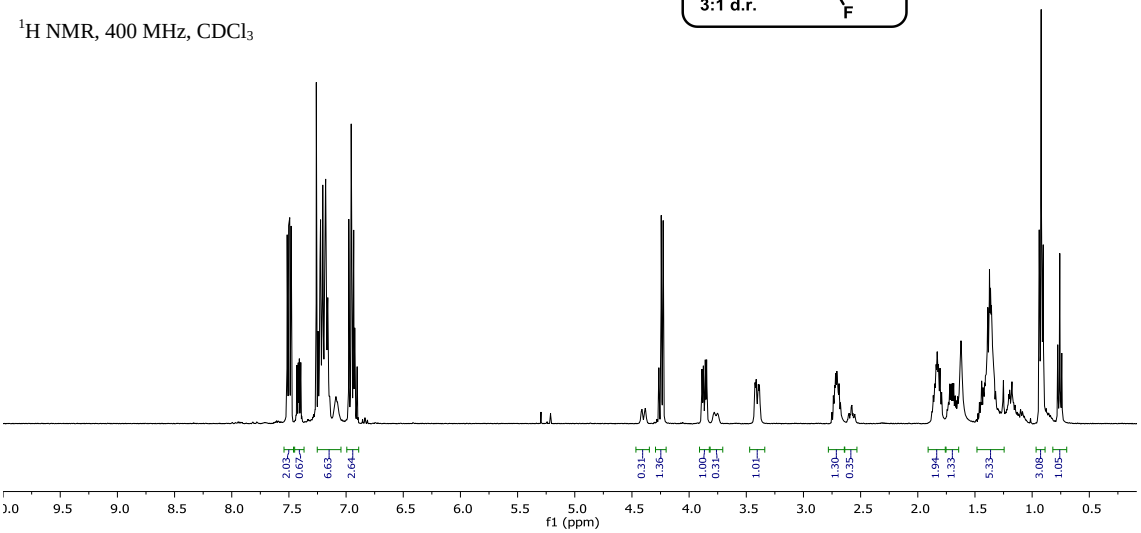


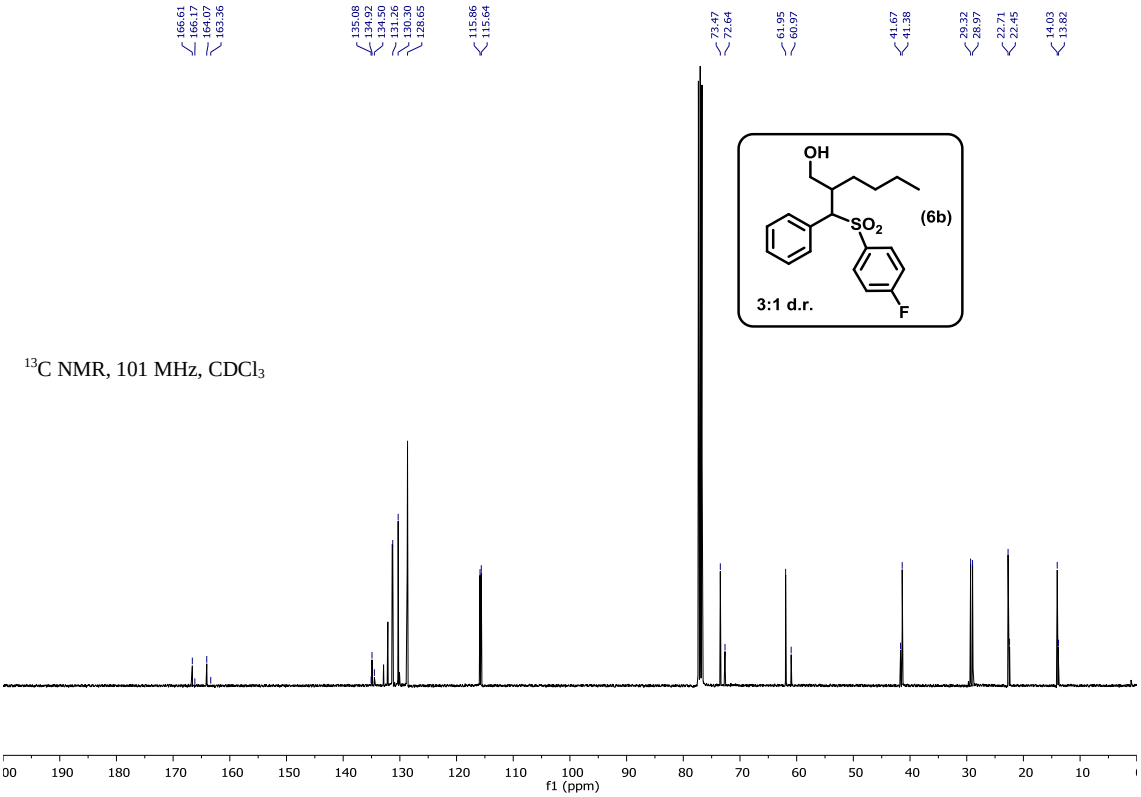
^{1}H decoupled ^{19}F NMR, 376 MHz, $CDCl_3$



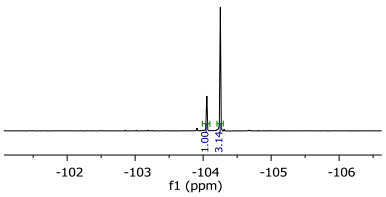


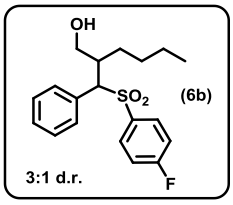
^{1}H NMR, 400 MHz, $CDCl_3$



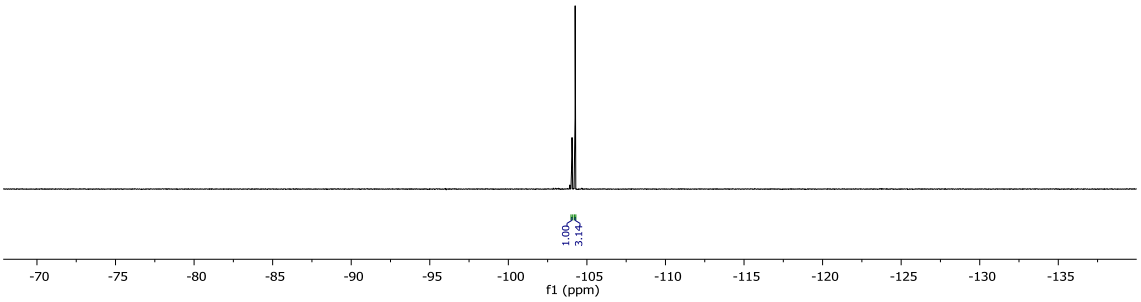


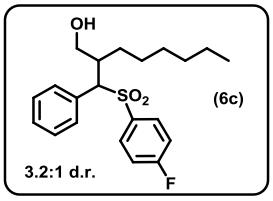
^{13}C NMR, 101 MHz, $CDCl_3$



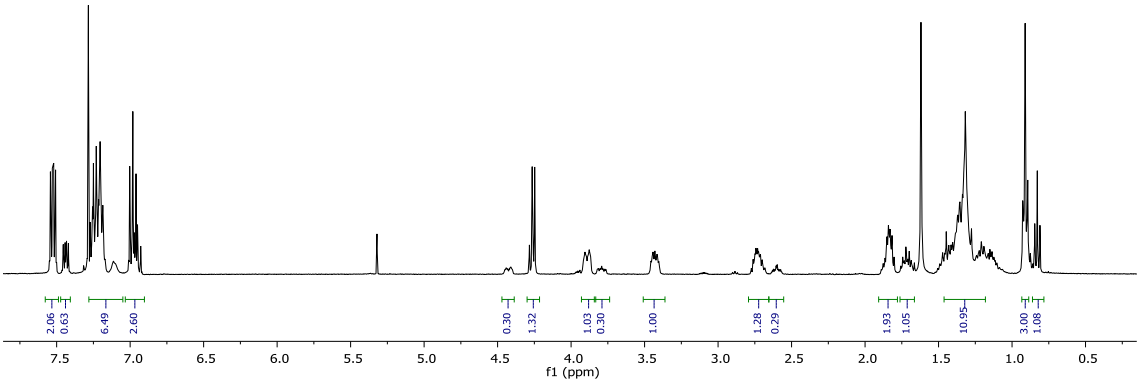


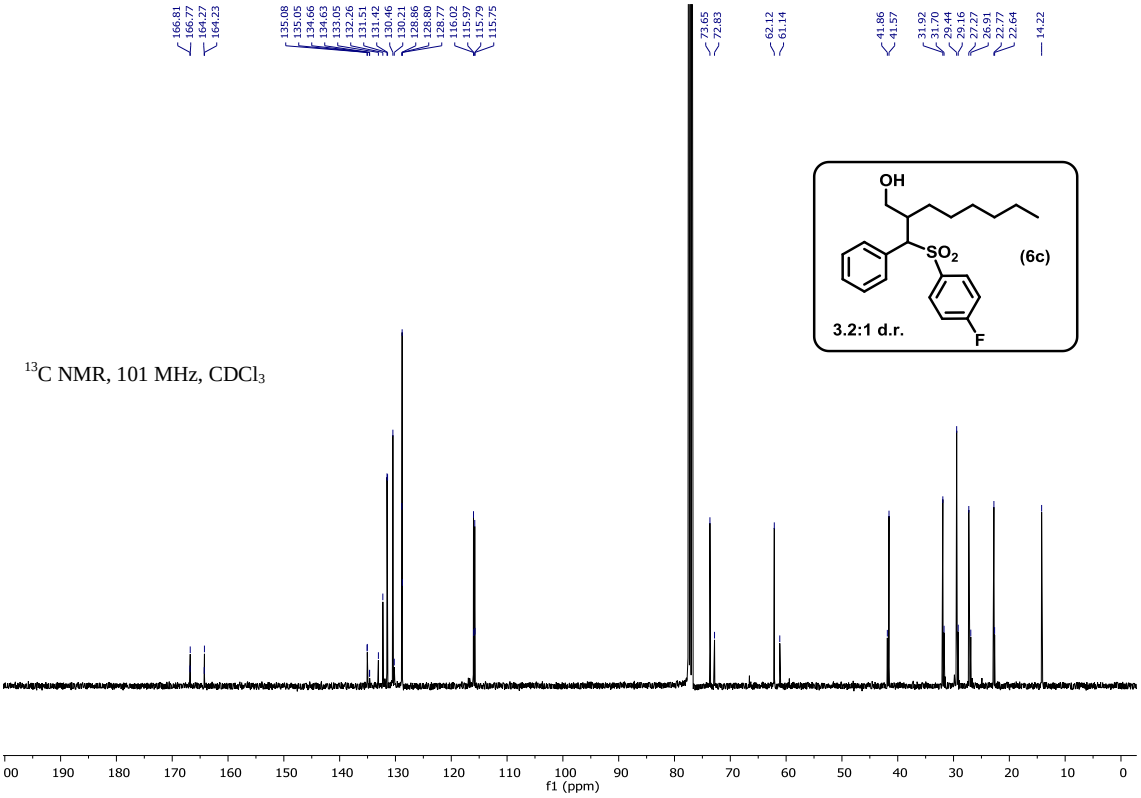
^{1}H decoupled ^{19}F NMR, 376 MHz, $CDCl_3$



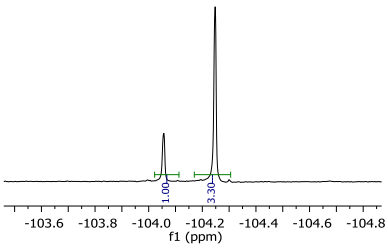


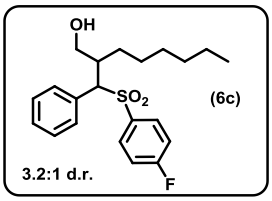
^{1}H NMR, 400 MHz, $CDCl_3$



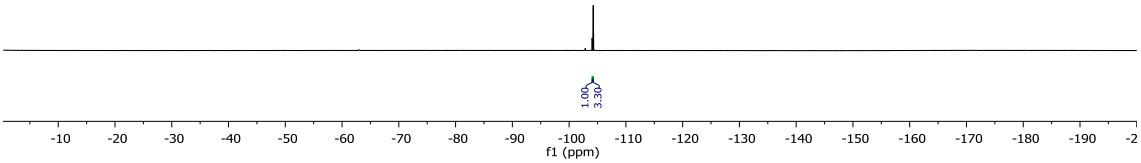


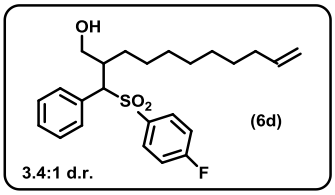
^{13}C NMR, 101 MHz, $CDCl_3$



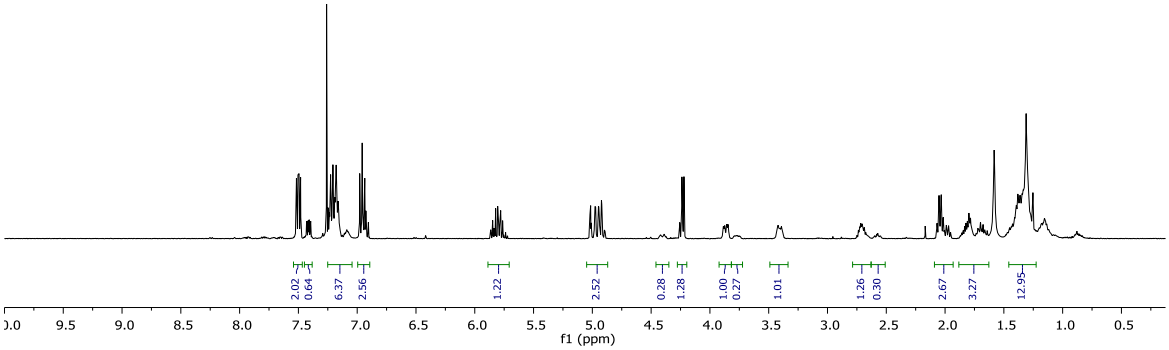


^{1}H decoupled ^{19}F NMR, 376 MHz, $CDCl_3$

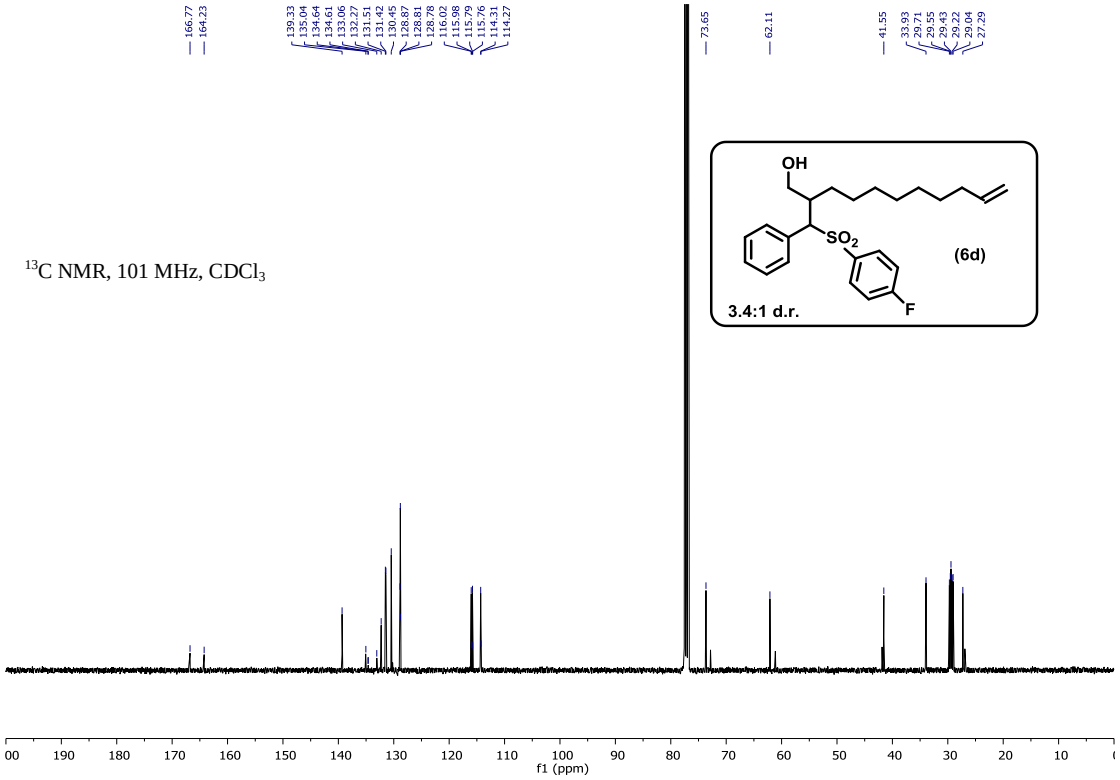


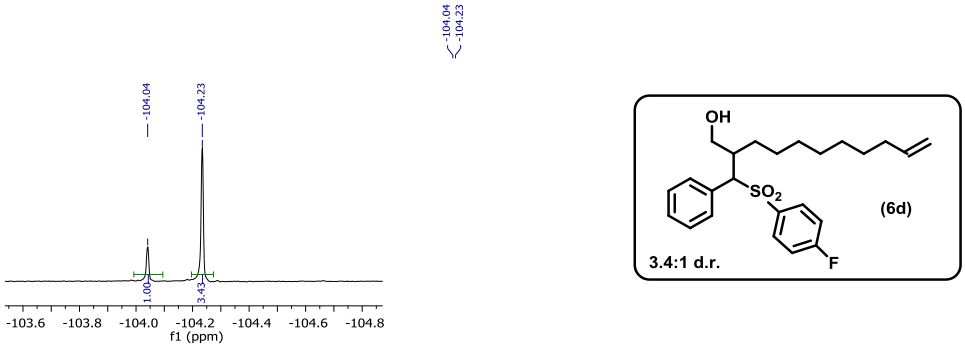


^{1}H NMR, 400 MHz, $CDCl_3$

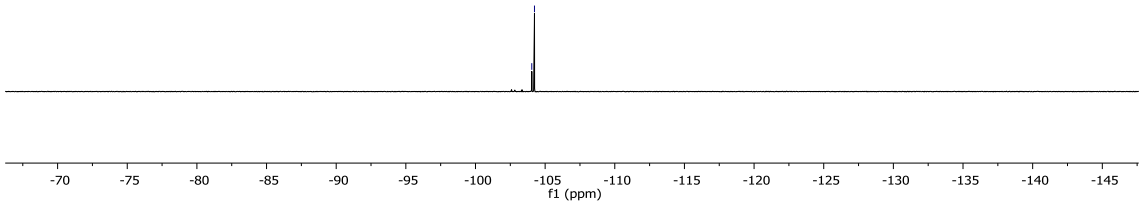


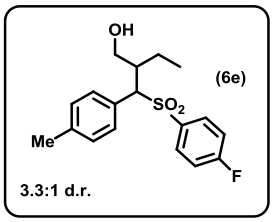
^{13}C NMR, 101 MHz, $CDCl_3$



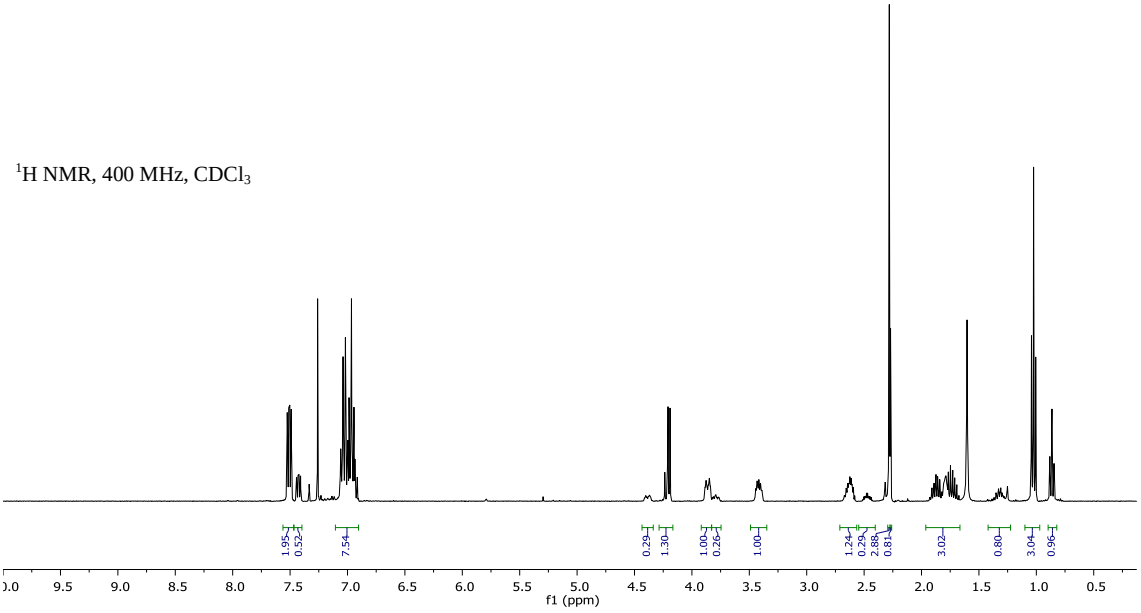


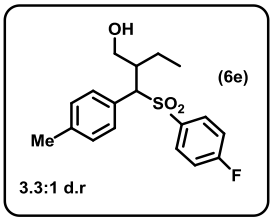
^{1}H decoupled ^{19}F NMR, 376 MHz, $CDCl_3$



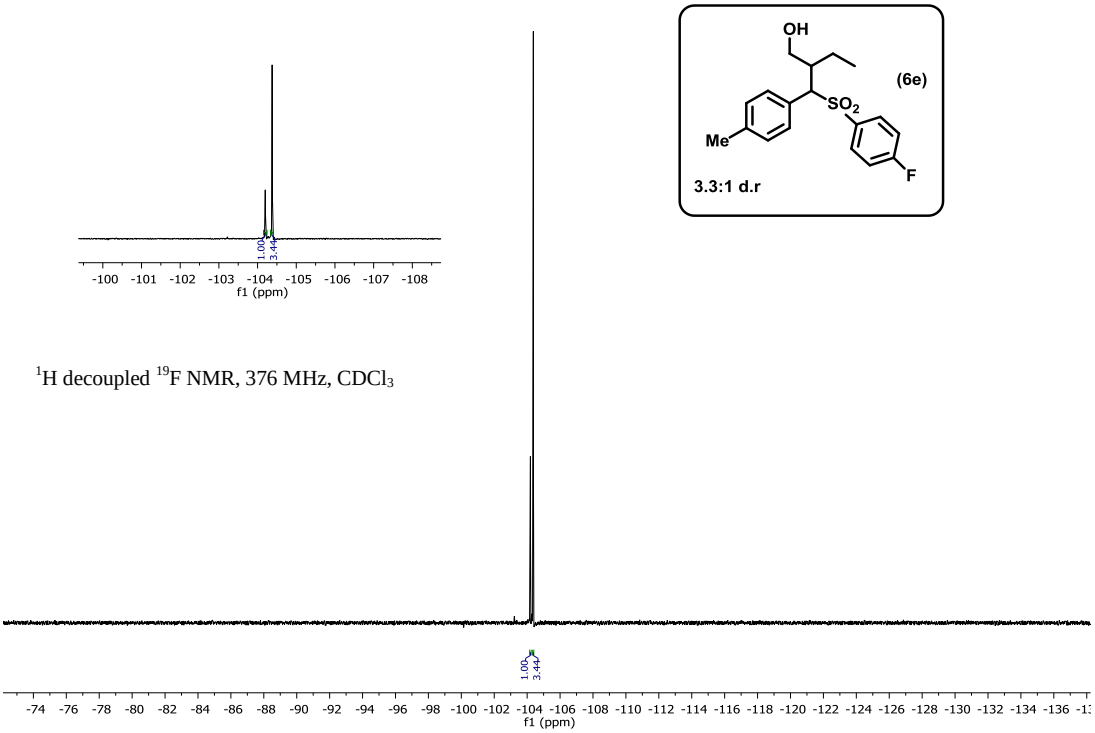


^{1}H NMR, 400 MHz, $CDCl_3$

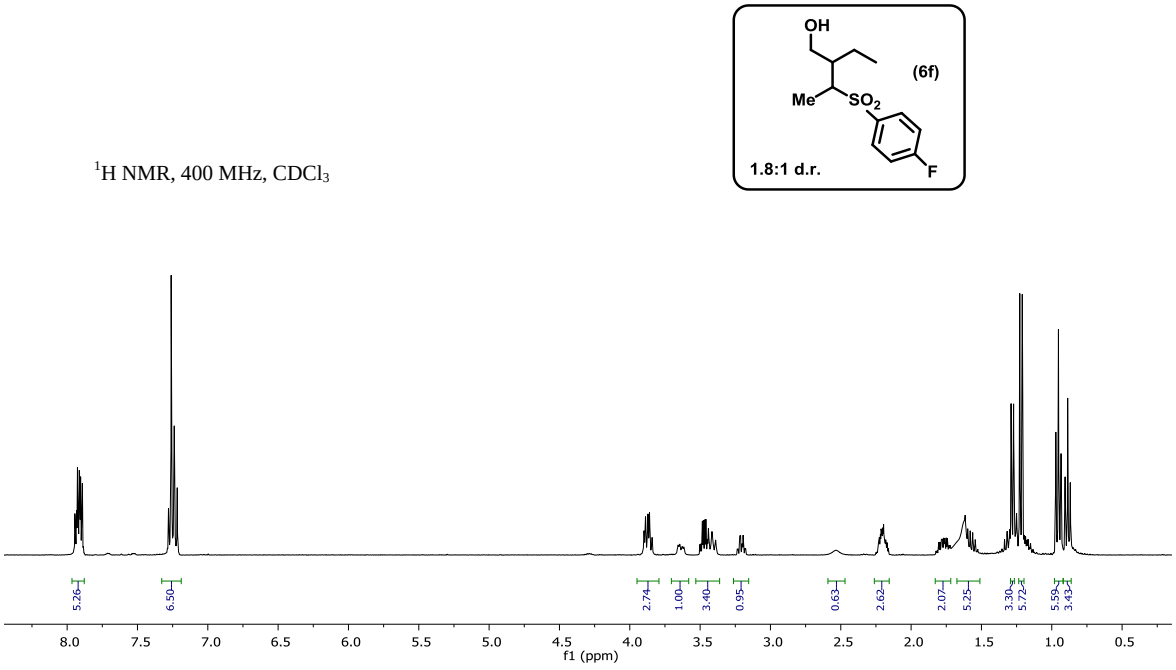




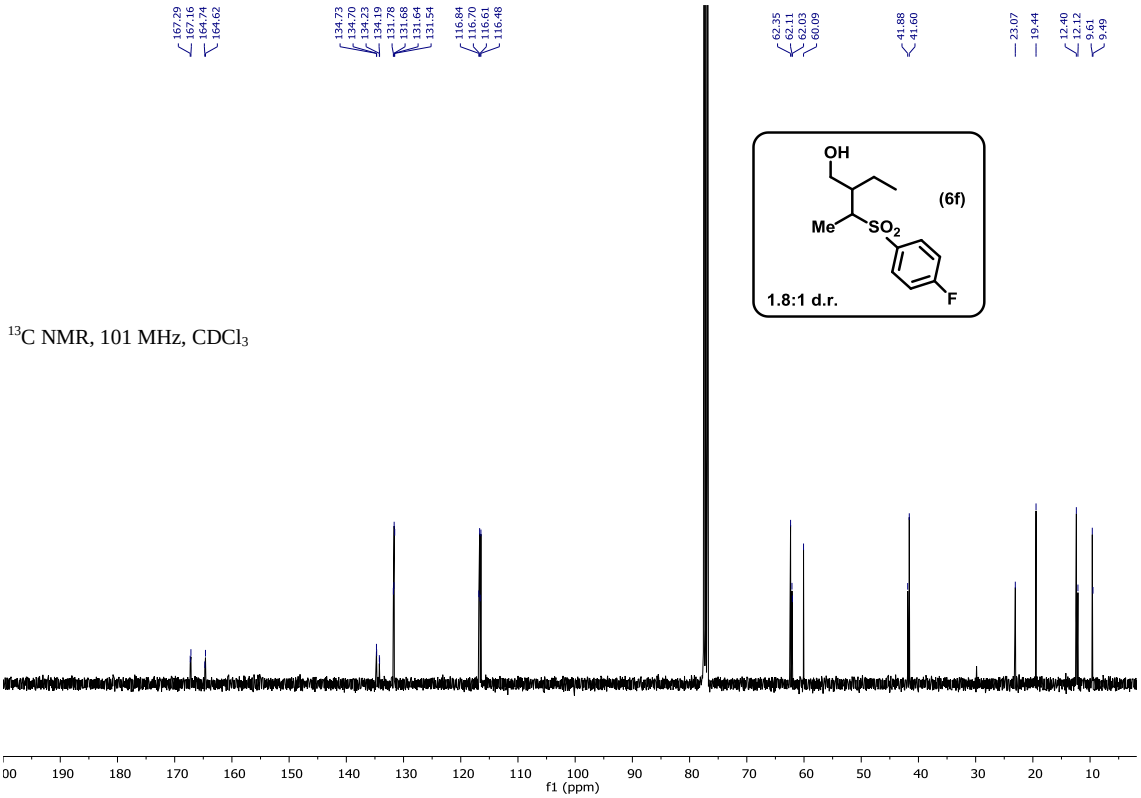
^{13}C NMR, 101 MHz, $CDCl_3$



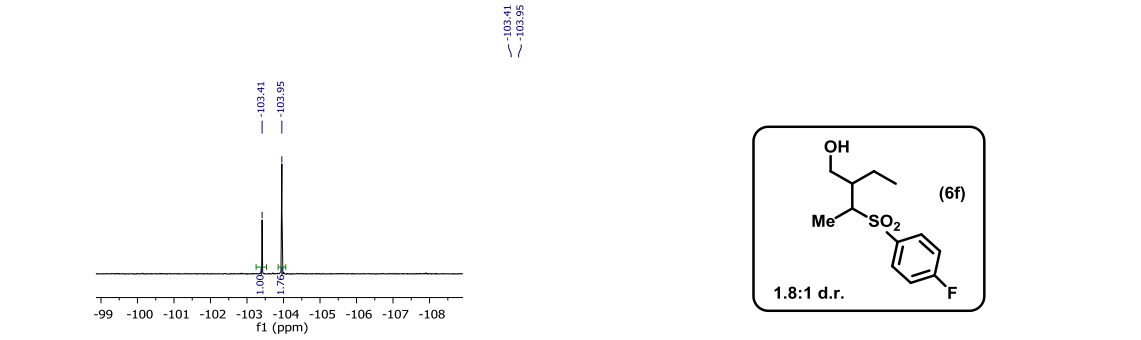
^{1}H decoupled ^{19}F NMR, 376 MHz, $CDCl_3$



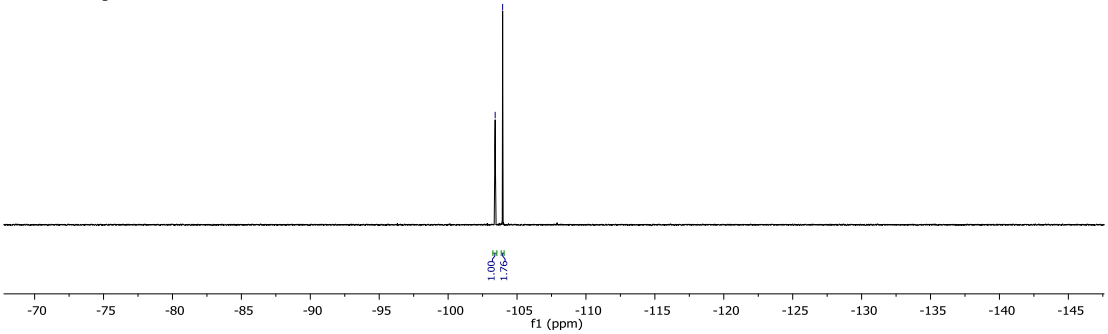
^{1}H NMR, 400 MHz, $CDCl_3$



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

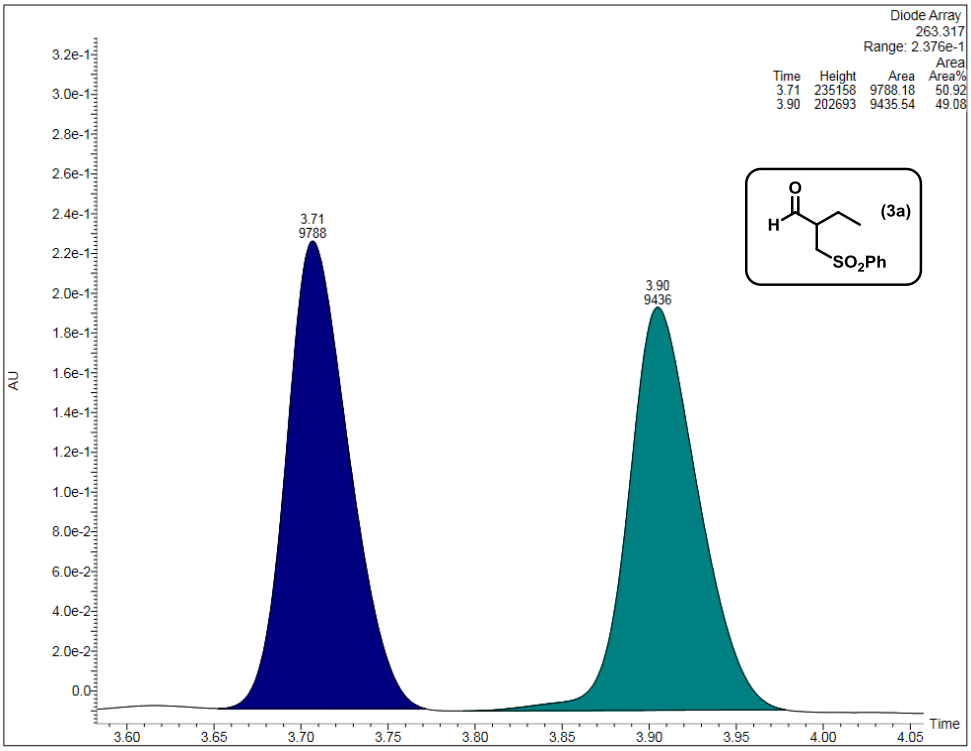


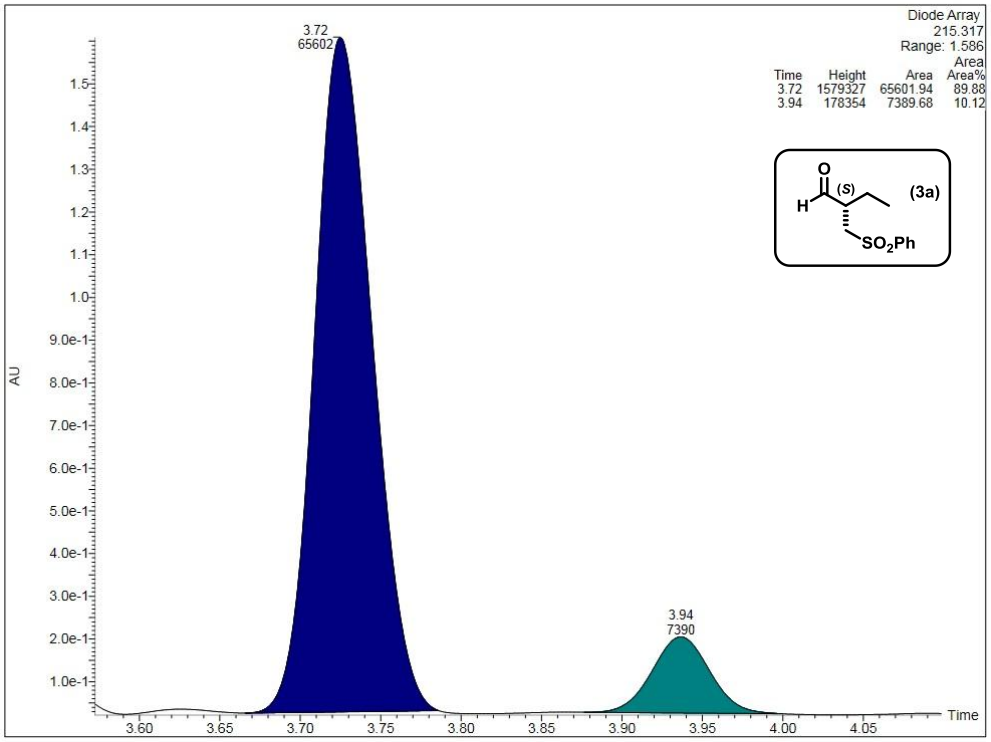
^{1}H decoupled ^{19}F NMR, 376 MHz, $CDCl_3$



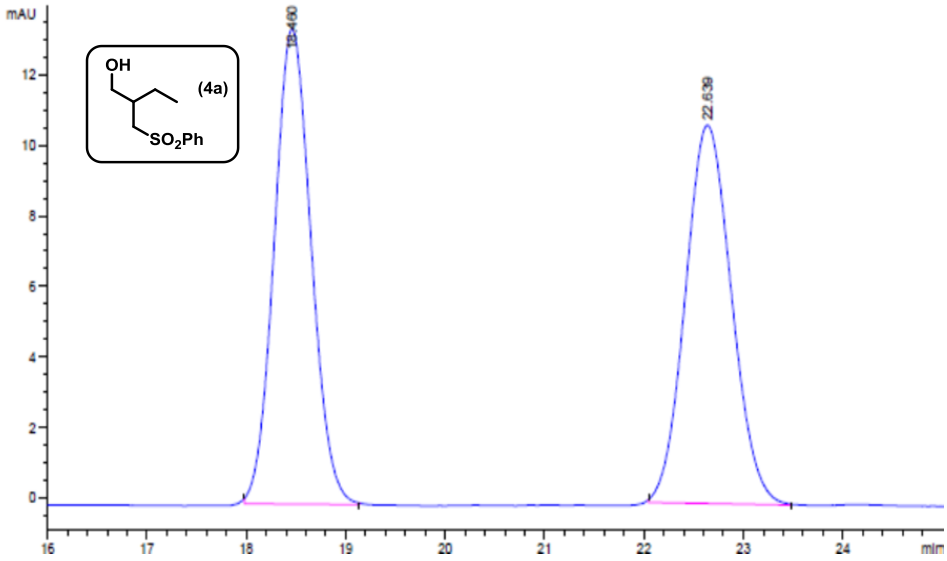
J. HPLC/UPC^2 Traces

Conditions: UPC^2 (IC column with a gradient 100% CO_2 to 60:40 CO_2/Isopropanol over 4 minutes, 20 ºC, flow rate 3 mL/min, λ = 215 nm)

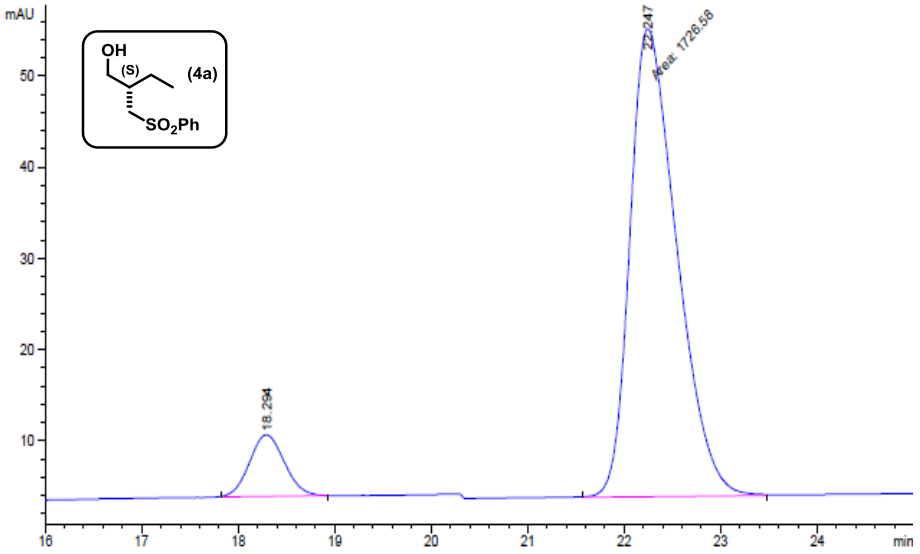




Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 ºC, 60:40 hexane/*i*PrOH, flow rate 0.8 mL/min, λ = 254 nm)

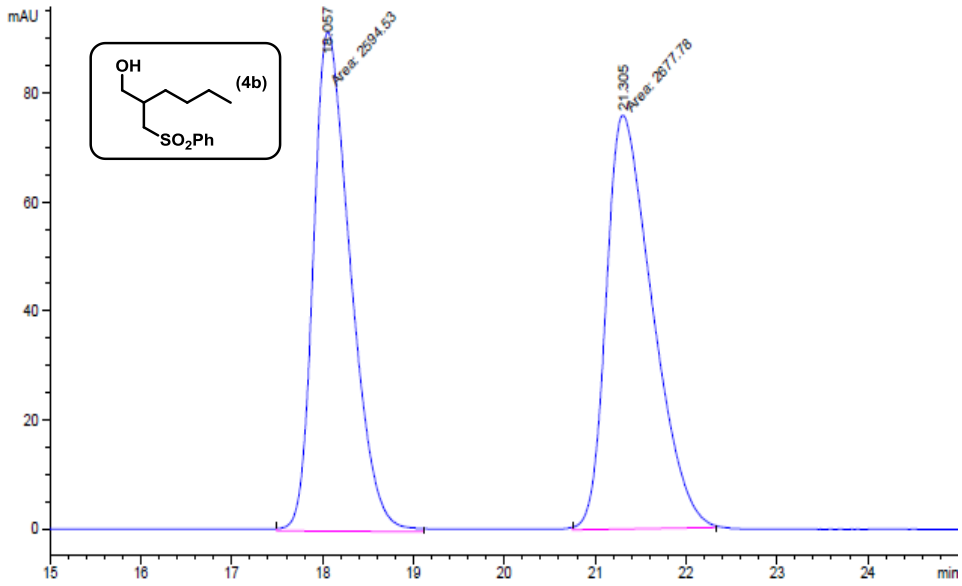


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.460	BB	0.4010	348.15021	13.49625	50.1268
2	22.639	BB	0.5022	346.38904	10.74359	49.8732

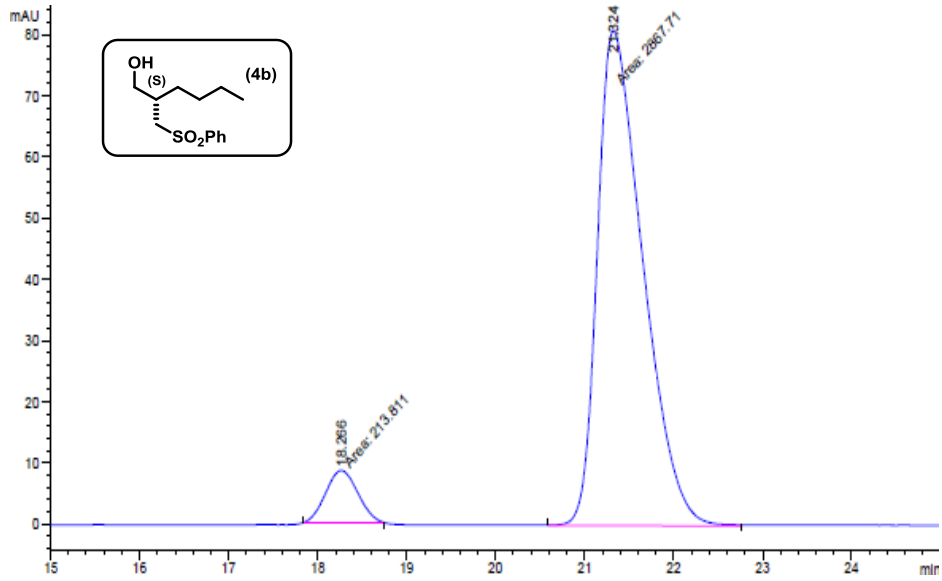


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.294	BB	0.3895	169.61604	6.74185	8.9451
2	22.247	MM	0.5610	1726.57751	51.29112	91.0549

Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 ºC, 60:40 hexane/*i*PrOH, flow rate 0.8 mL/min, λ = 254 nm)

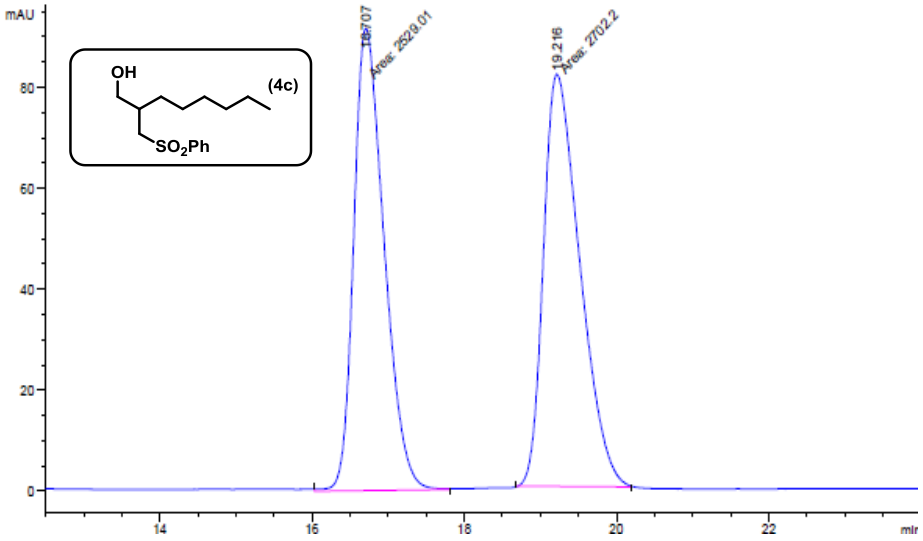


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.057	MM	0.4716	2594.53174	91.69650	49.2105
2	21.305	MM	0.5875	2677.78296	75.96684	50.7895

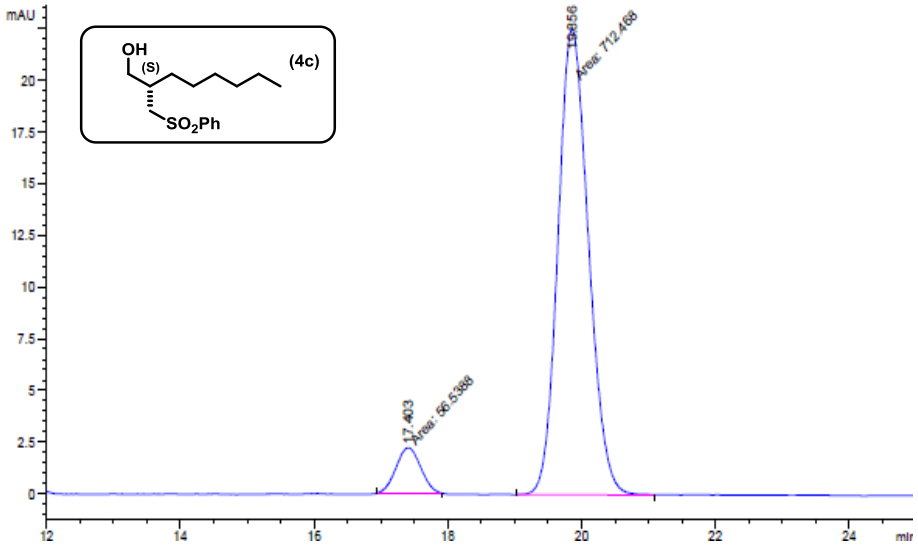


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.266	MM	0.4191	213.81050	8.50177	6.9385
2	21.324	MM	0.5913	2867.70703	80.83408	93.0615

Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 ºC, 60:40 hexane/*i*PrOH, flow rate 0.8 mL/min, λ = 254 nm)

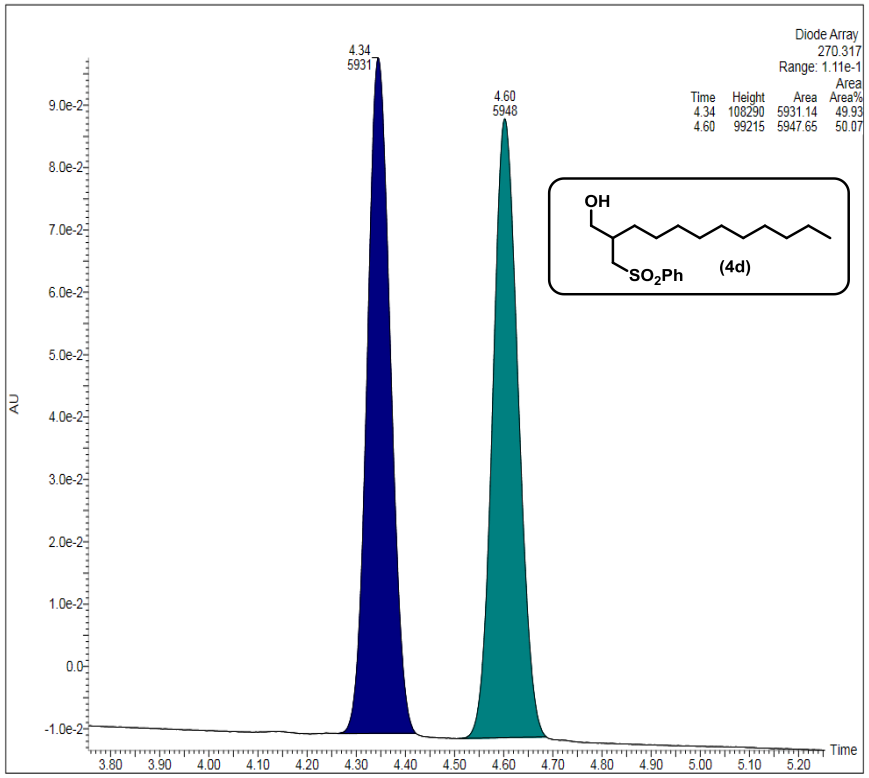


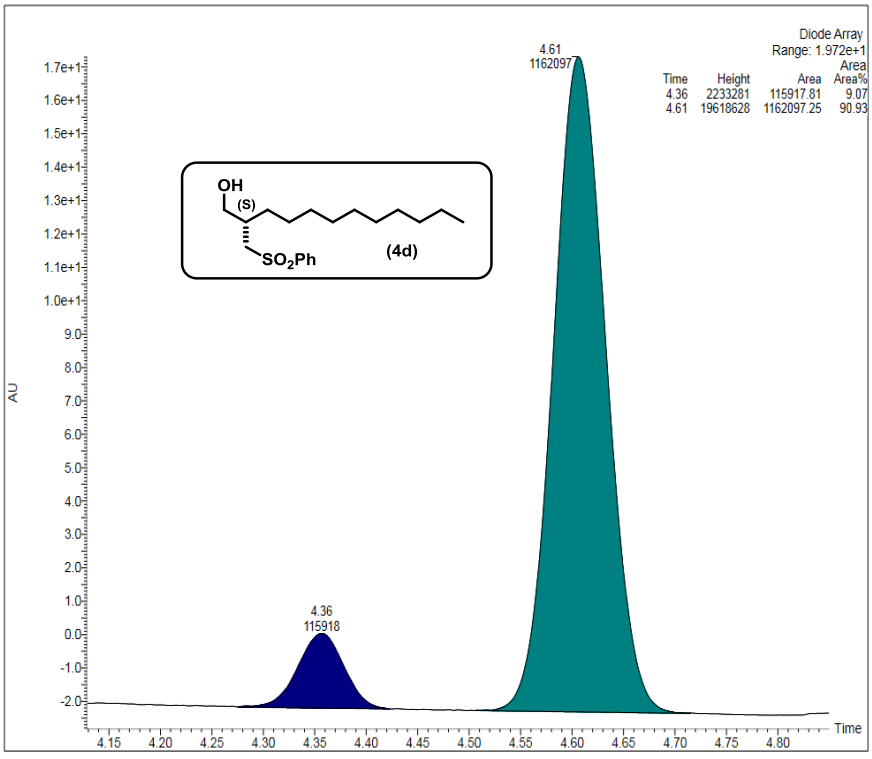
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.707	MM	0.4609	2529.01465	91.45702	48.3447
2	19.216	MM	0.5525	2702.20435	81.51830	51.6553



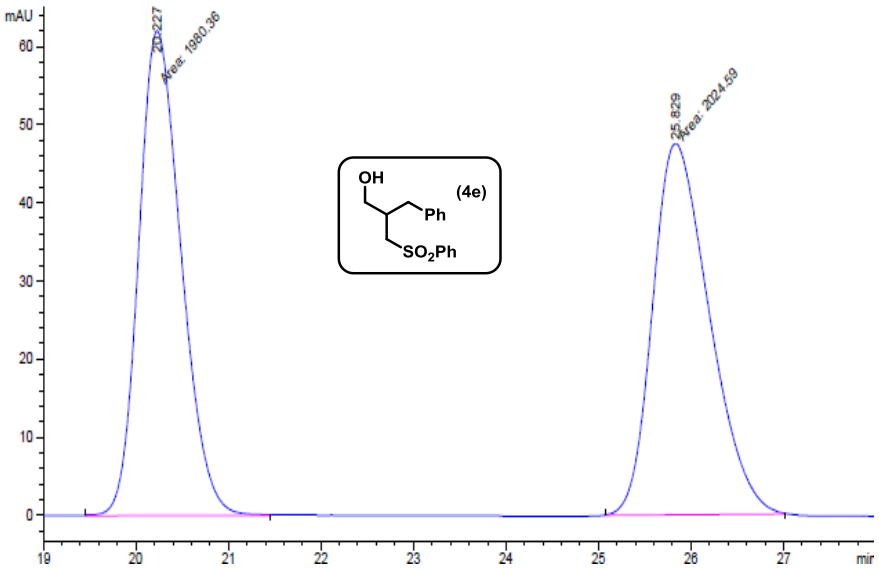
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.403	MM	0.4270	56.53884	2.20669	7.3522
2	19.856	MM	0.5268	712.46771	22.53863	92.6478

Conditions: UPC^2 (IC column with a gradient 100% CO_2 to 60:40 CO_2/CH_3CN over 4 minutes, 20 ºC, flow rate 3 mL/min, λ = 270 nm)

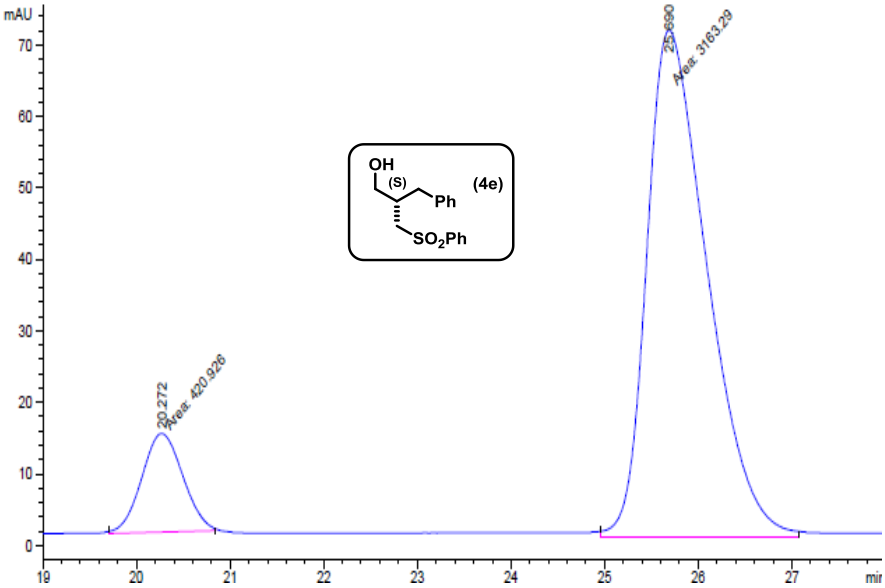




Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 ºC, 60:40 hexane/*i*PrOH, flow rate 0.8 mL/min, λ = 254 nm)

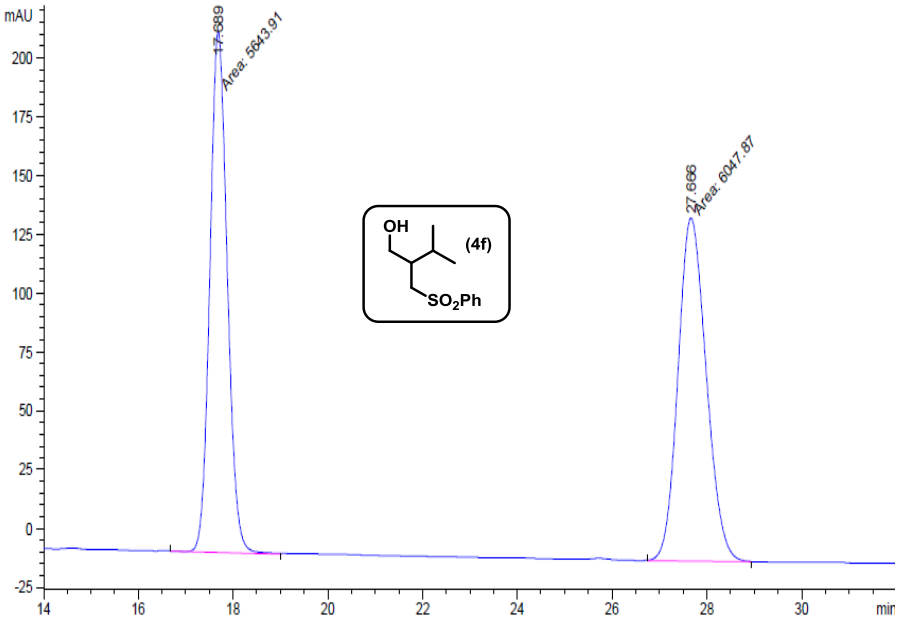


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.227	MM	0.5318	1980.36035	62.06652	49.4479
2	25.829	MM	0.7094	2024.58508	47.56415	50.5521

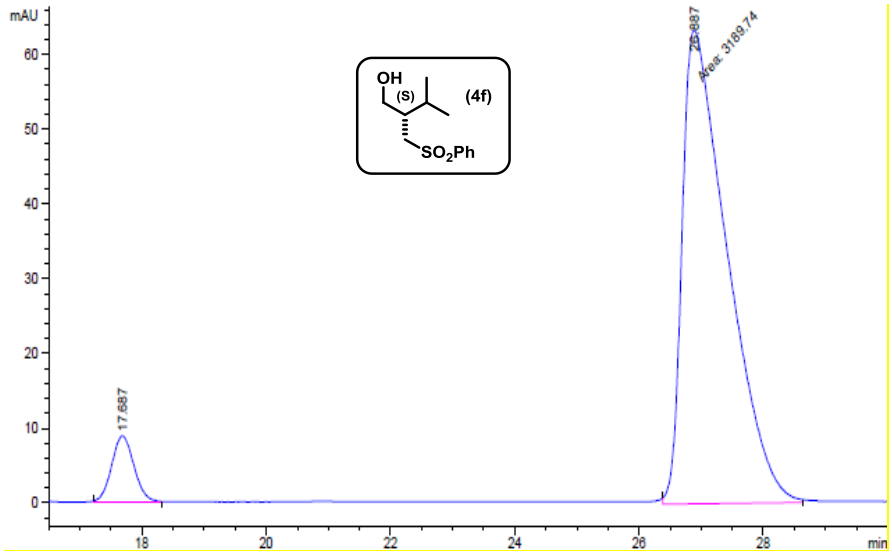


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.272	MM	0.5091	420.92590	13.77976	11.7439
2	25.690	MM	0.7445	3163.28735	70.81880	88.2561

Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 ºC, 60:40 hexane/*i*PrOH, flow rate 0.8 mL/min, λ = 254 nm)

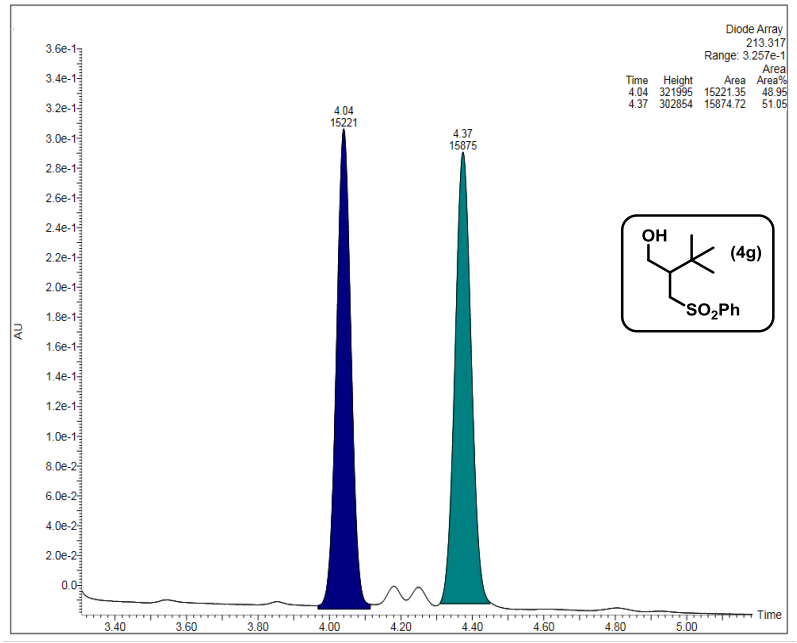


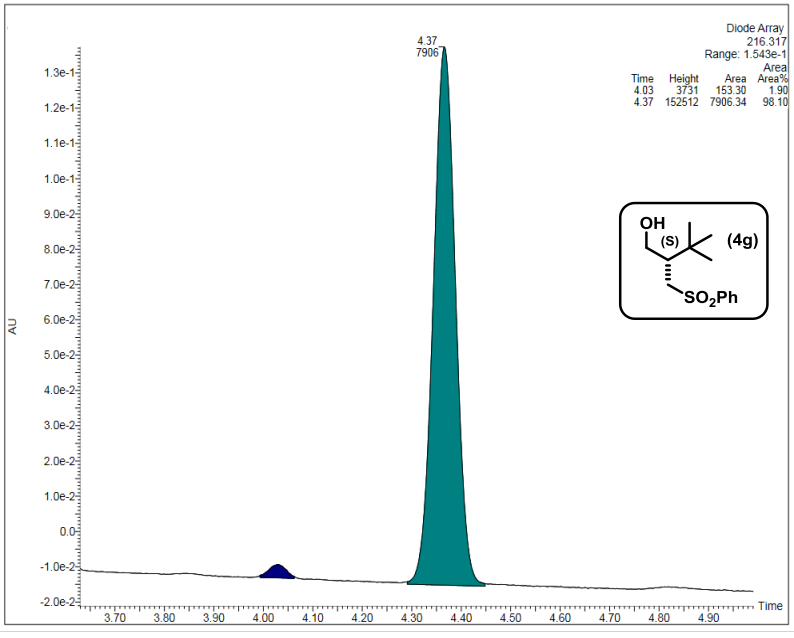
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.689	MM	0.4254	5643.91309	221.13087	48.2725
2	27.666	MM	0.6915	6047.86768	145.76768	51.7275



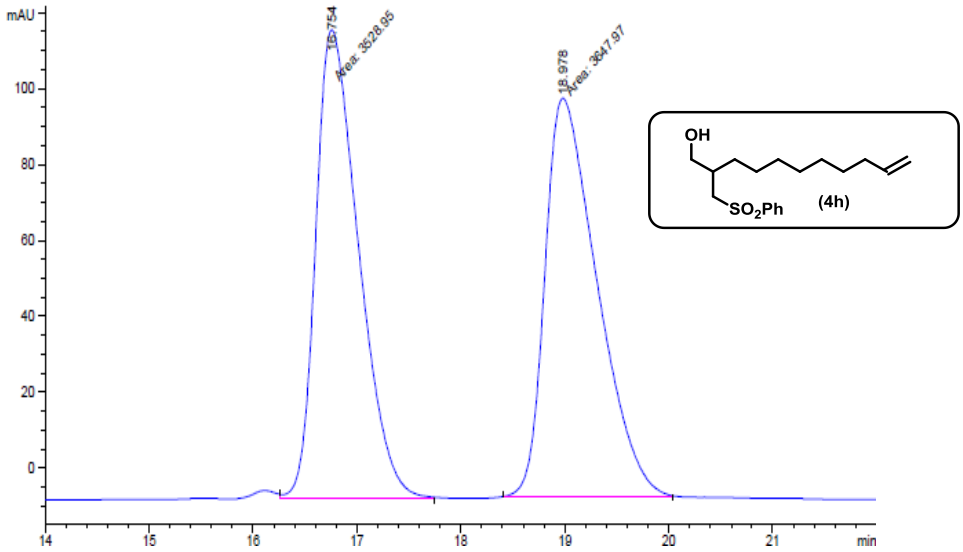
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.687	BB	0.3853	216.94608	8.74986	6.3682
2	26.887	MM	0.8393	3189.73901	63.34037	93.6318

Conditions: UPC^2 (IC column with a gradient 100% CO_2 to 60:40 CO_2/CH_3CN over 4 minutes, 20 ºC, flow rate: 3 mL/min, λ = 213 nm)

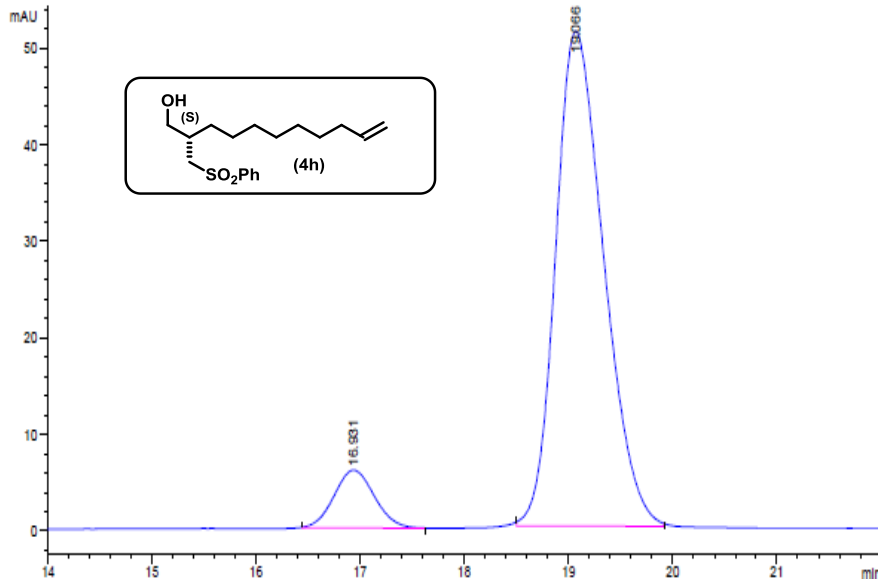




Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 ºC, 60:40 hexane/*i*PrOH, flow rate 0.8 mL/min, λ = 254 nm)

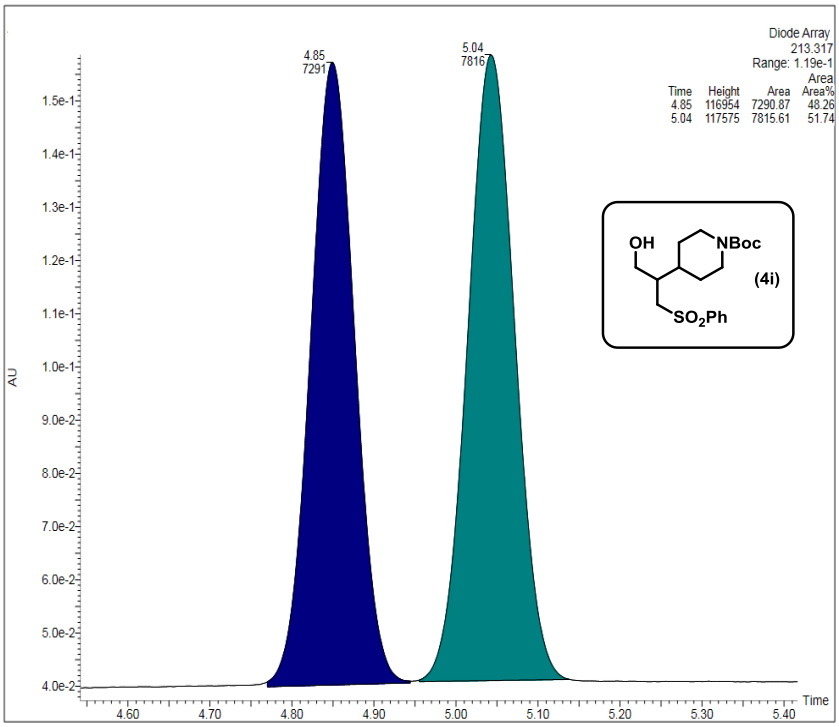


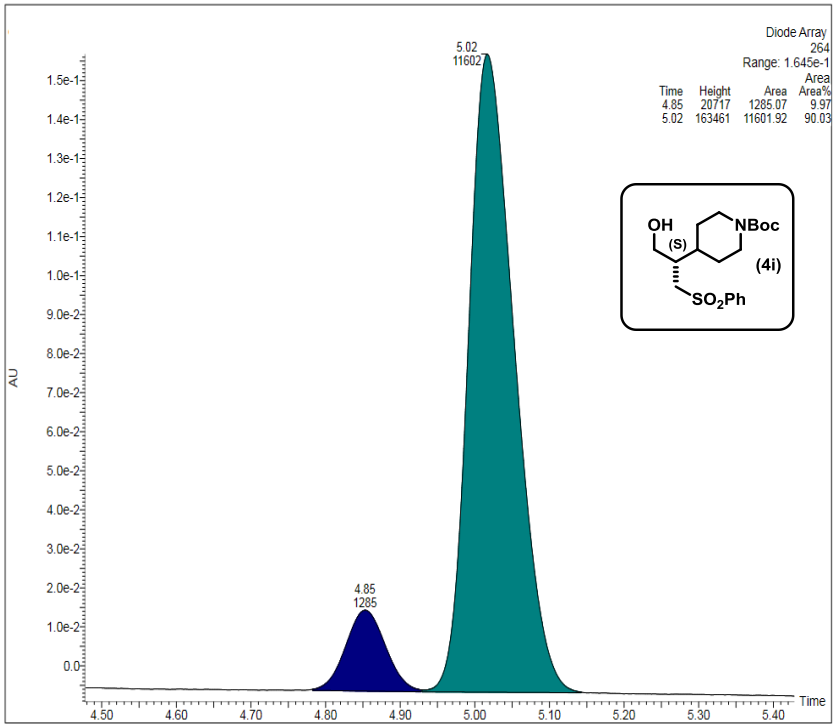
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.754	MM	0.4764	3528.94775	123.45523	49.1708
2	18.978	MM	0.5794	3647.96729	104.92992	50.8292



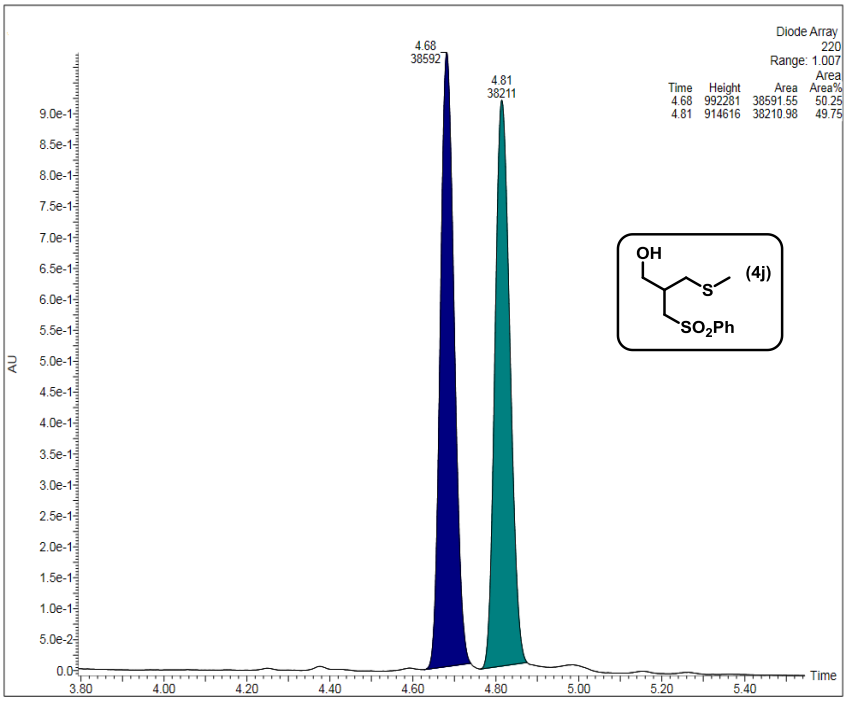
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.931	BB	0.4146	160.17126	5.97857	8.8770
2	19.066	BB	0.4942	1644.17334	51.26318	91.1230

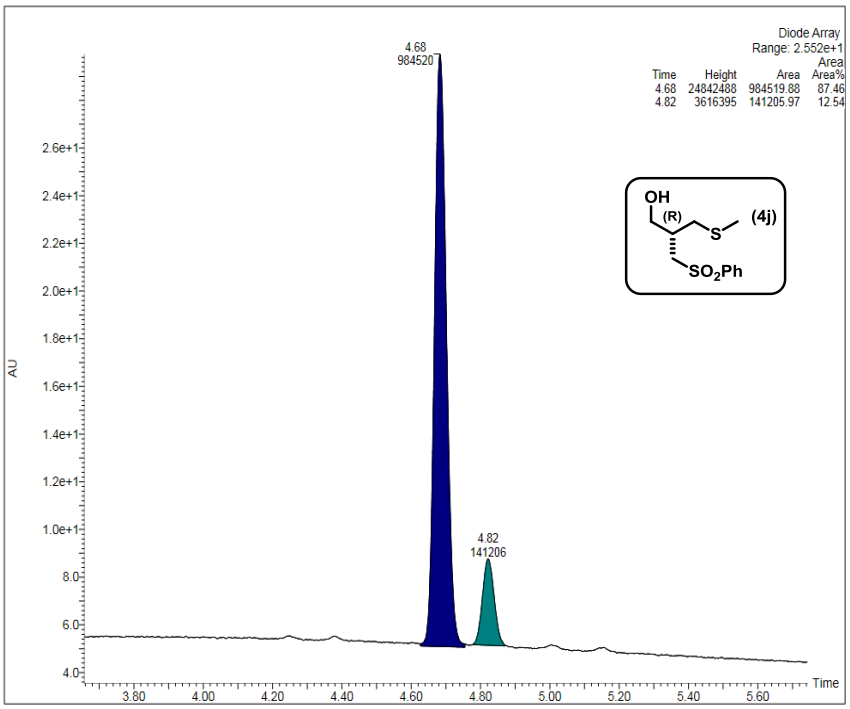
Conditions: UPC^2 (IC-3 column with a gradient 100% CO_2 to 60:40 CO_2/EtOH over 4 minutes, 20 ºC, flow rate: 3 mL/min, λ = 213 nm)



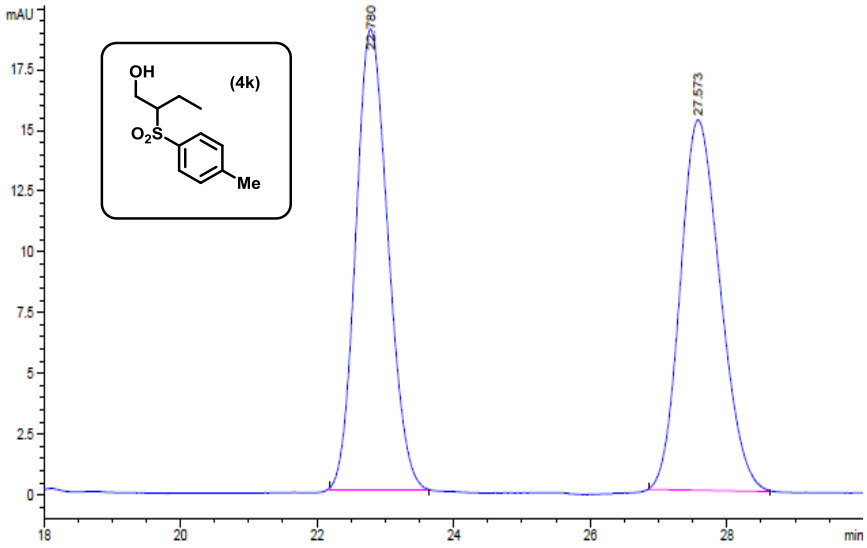


Conditions: UPC^2 (column with a gradient 100% CO_2 to 60:40 CO_2/CH_3CN over 4 minutes, 20 ºC, flow rate: 2 mL/min, λ = 220 nm)

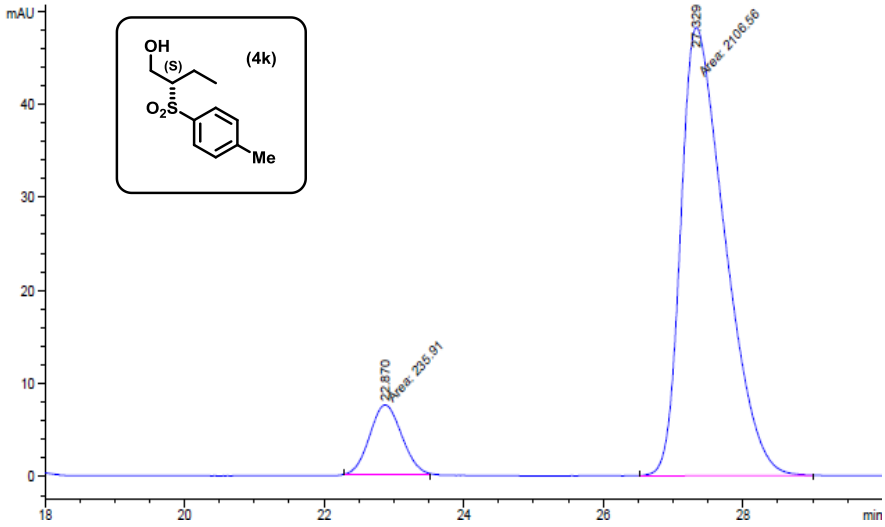




Conditions: HPLC (Daicel Chiralpak IC-3 column, 20 ºC, 60:40 hexane/*i*PrOH, flow rate 0.8 mL/min, λ = 254 nm)

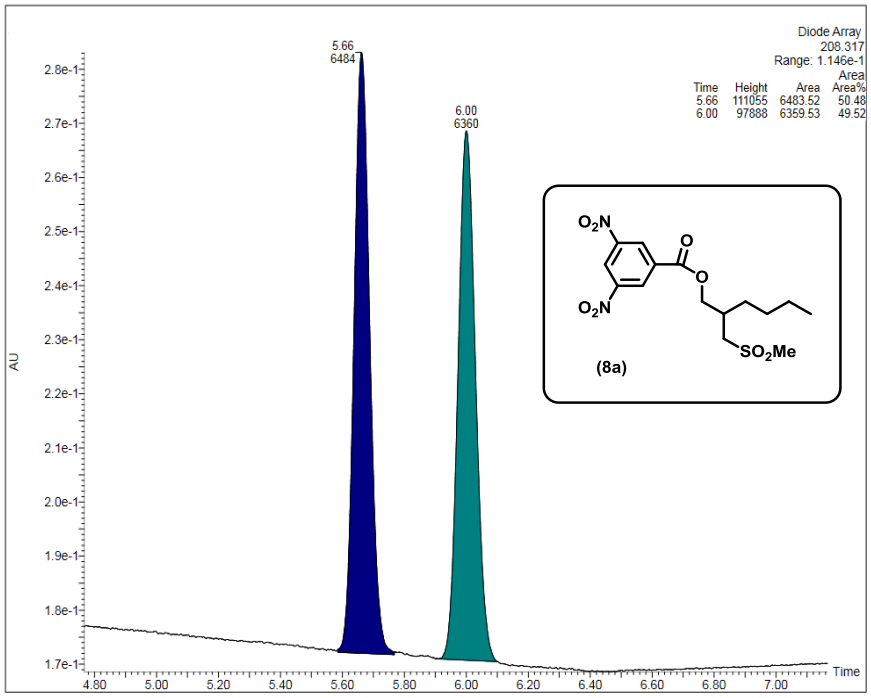


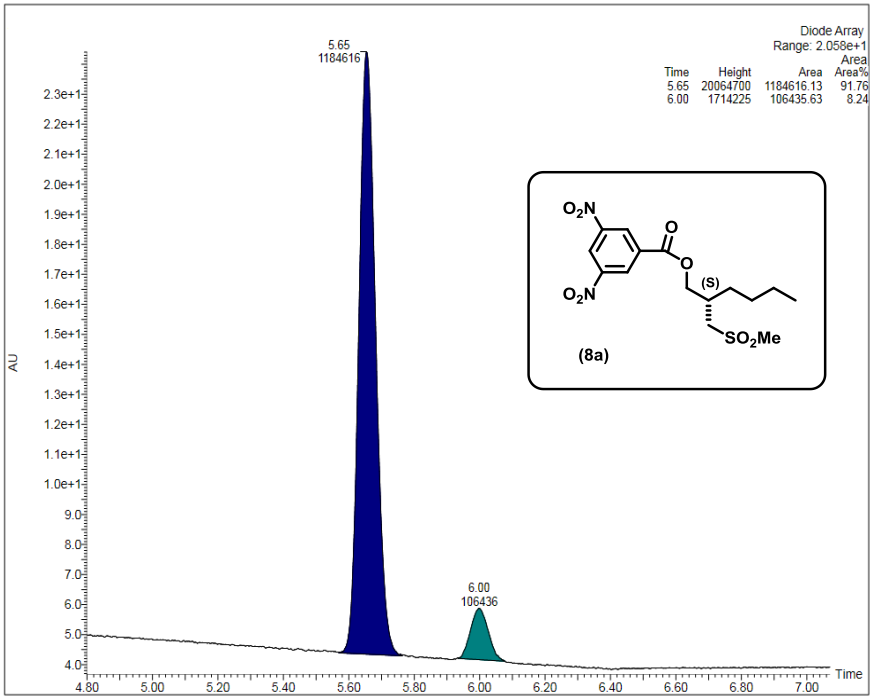
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.780	BB	0.5086	622.70380	18.98913	50.1230
2	27.573	BB	0.6304	619.64764	15.23756	49.8770



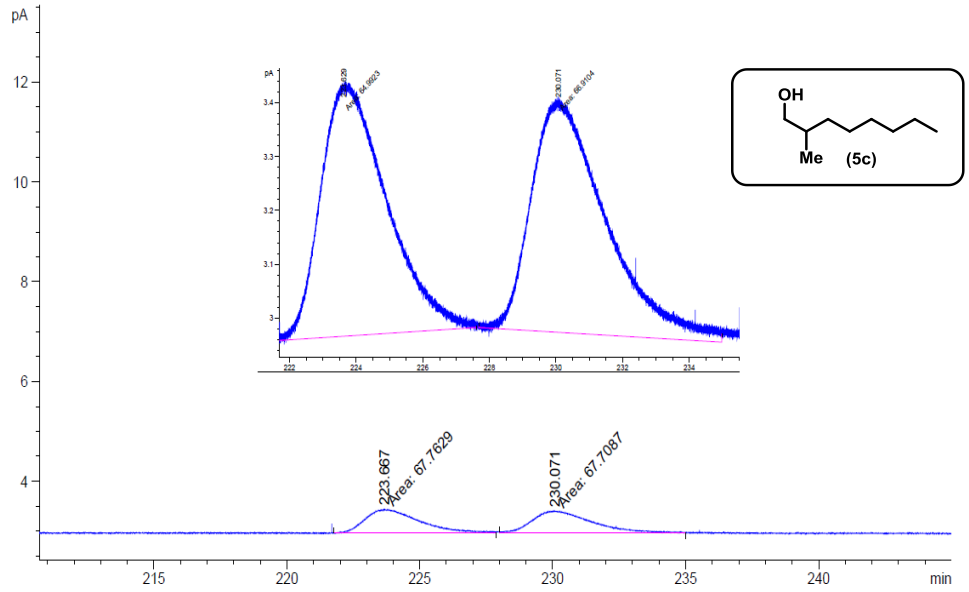
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.870	MM	0.5284	235.91039	7.44084	10.0710
2	27.329	MM	0.7301	2106.55981	48.08664	89.9290

Conditions: UPC^2 (AMY-1 column with a gradient 100% CO_2 to 60:40 CO_2/MeOH over 4 minutes, 20 ºC, flow rate: 2 mL/min, λ = 208 nm)

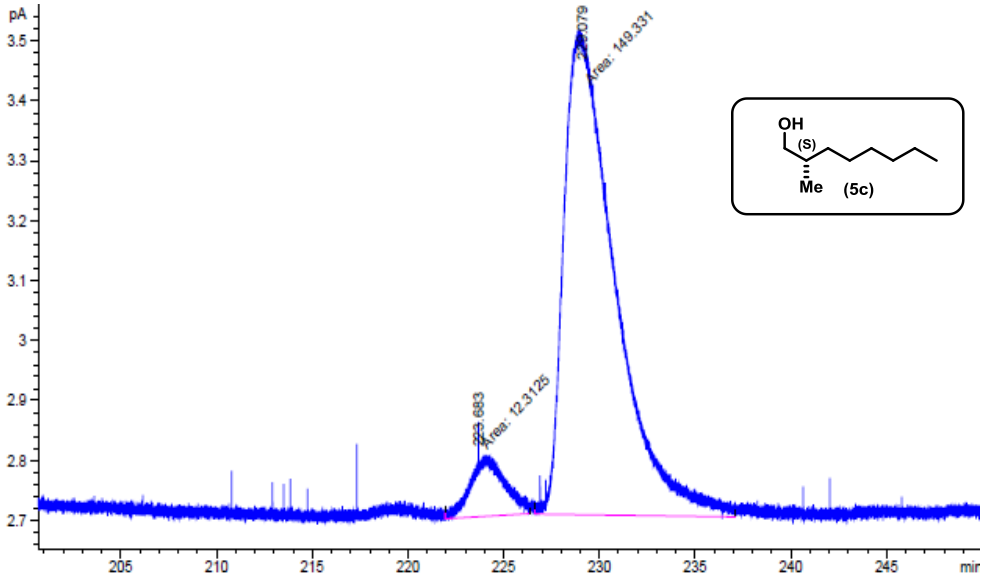




Conditions: GC (Beta-DEX column 120, 30m x 0.25mm, 0.25µm, isotherm 70 ºC, FID detector, carrier gas: He)

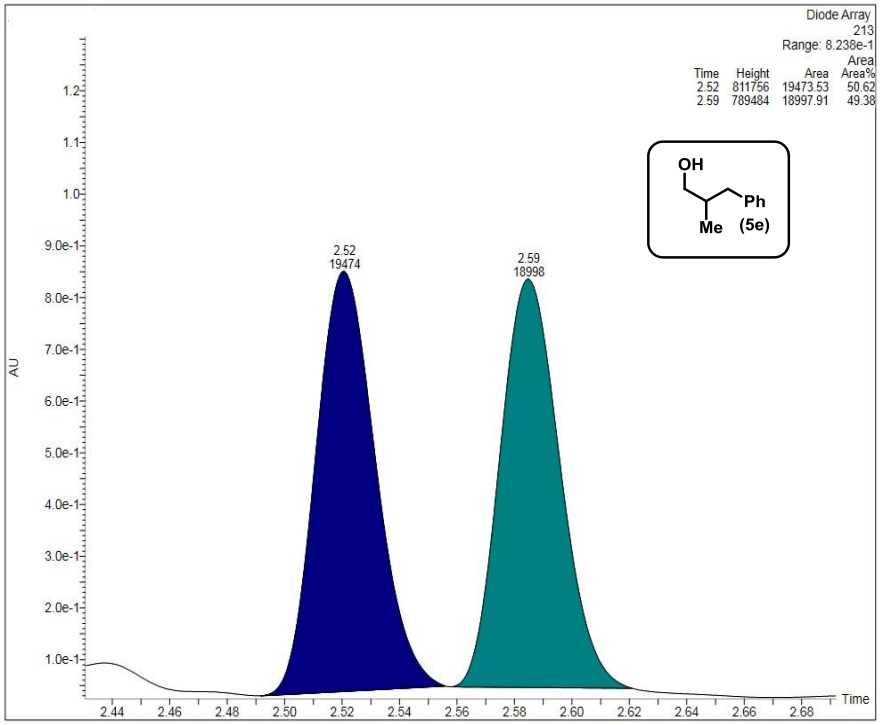


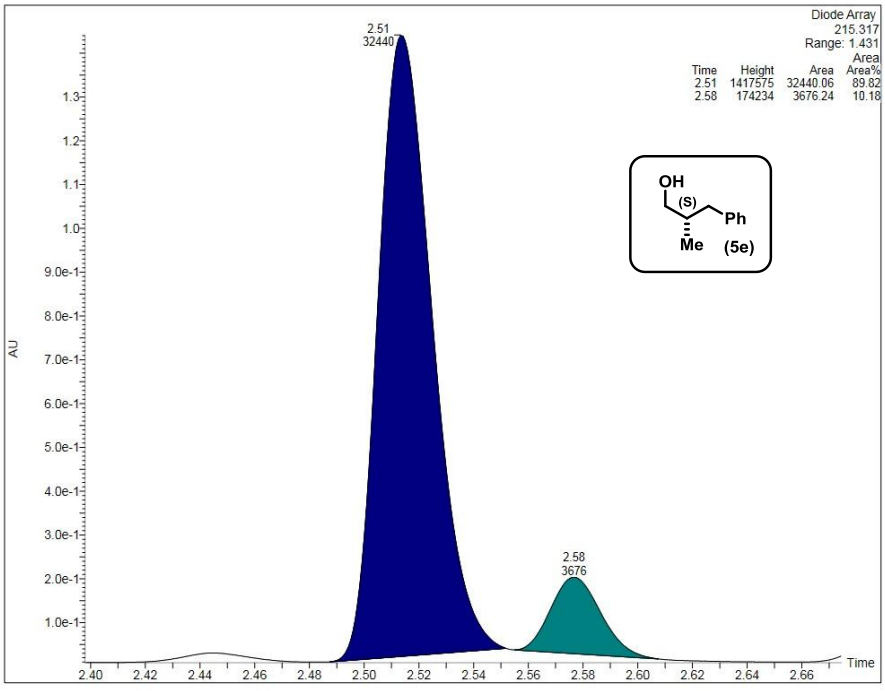
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	223.629	MM	2.2942	64.99231	4.72144e-1	49.27293
2	230.071	MM	2.5598	66.91036	4.35646e-1	50.72707



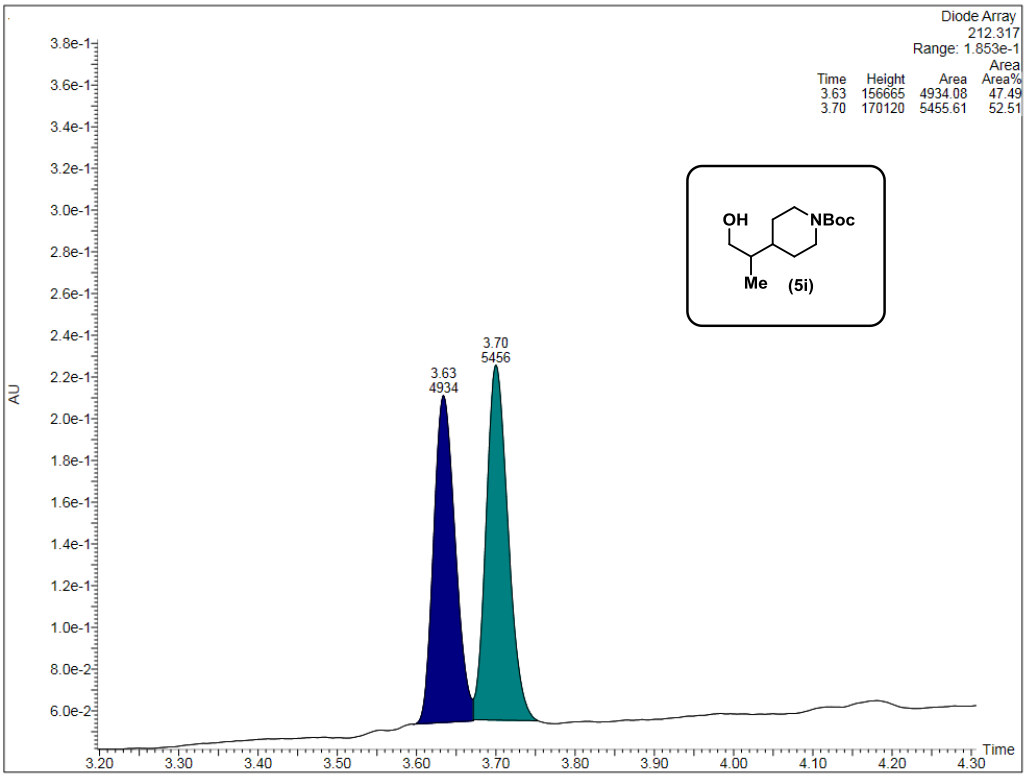
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	223.683	MM	1.8861	12.31249	1.08798e-1	7.61706
2	229.079	MM	3.0912	149.33113	8.05140e-1	92.38294

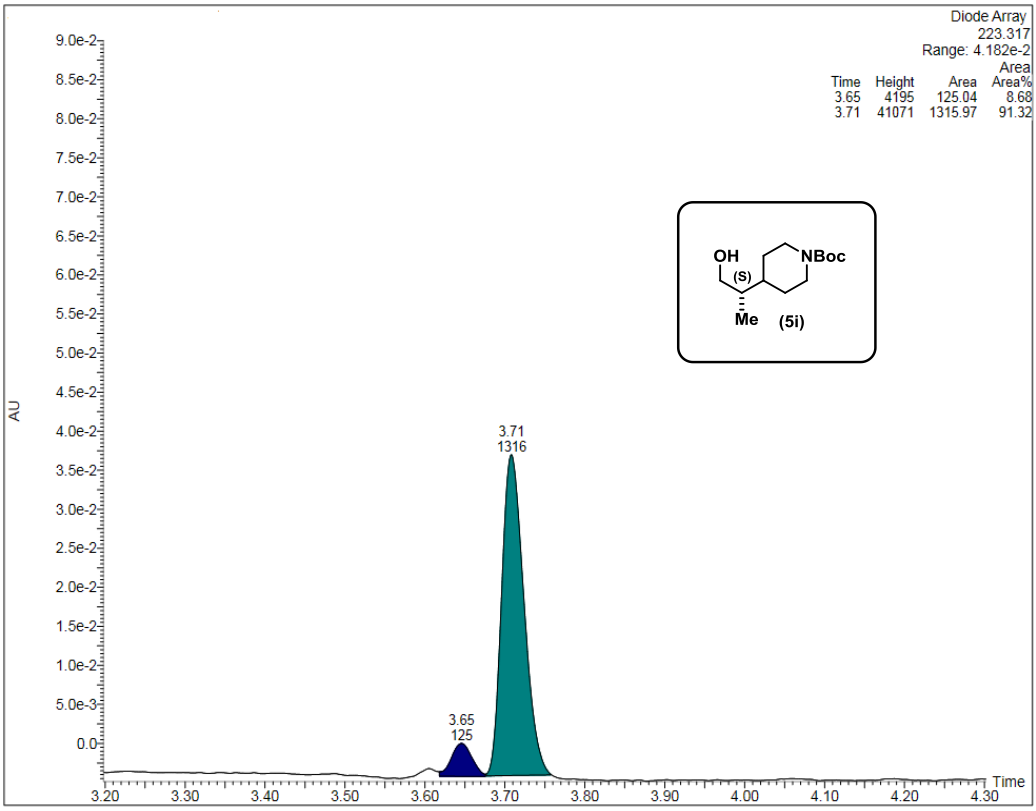
Conditions: UPC^2 (CEL-1 column with a gradient 100% CO_2 to 60:40 CO_2/Methanol over 4 minutes, 20ºC, flow rate: 2 mL/min, λ = 208 nm)



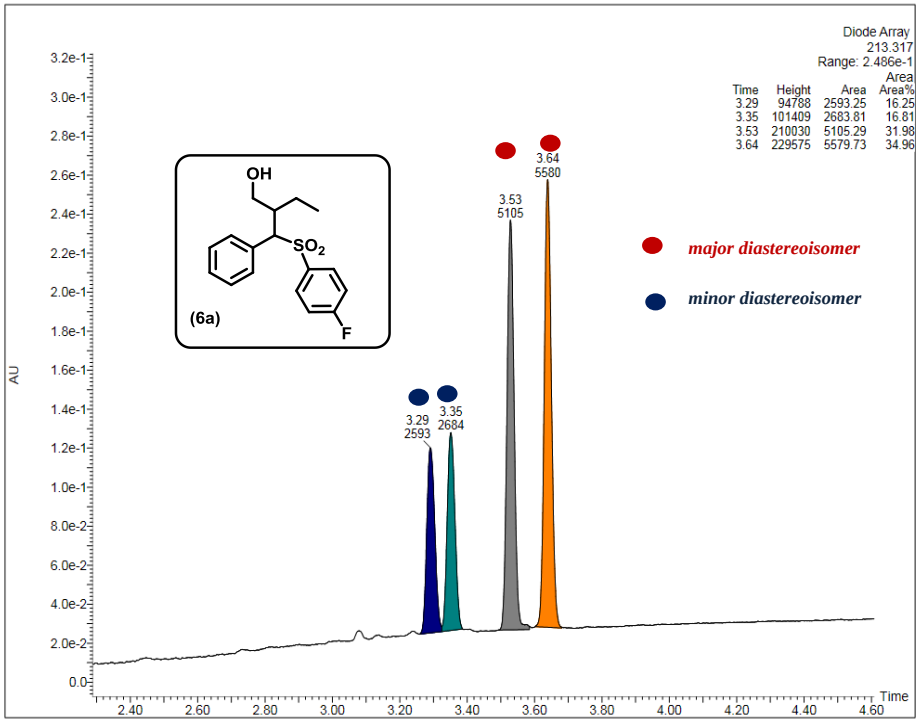


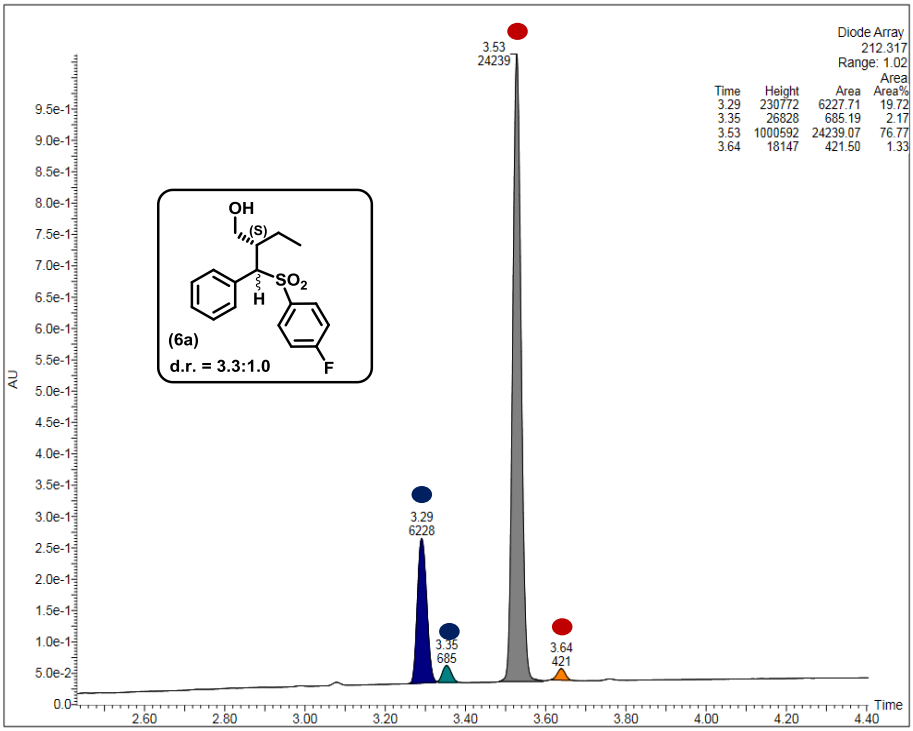
Conditions: UPC^2 (AMY-1 column with a gradient 100% CO_2 to 60:40 CO_2/Isopropanol over 4 minutes, 20 ºC, flow rate: 2 mL/min, λ = 215 nm)



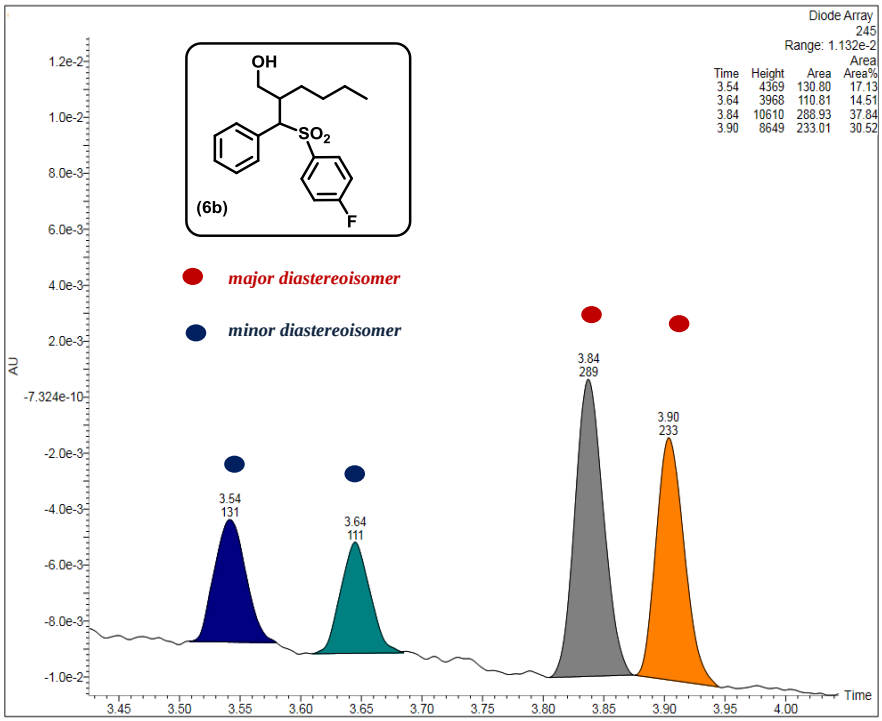


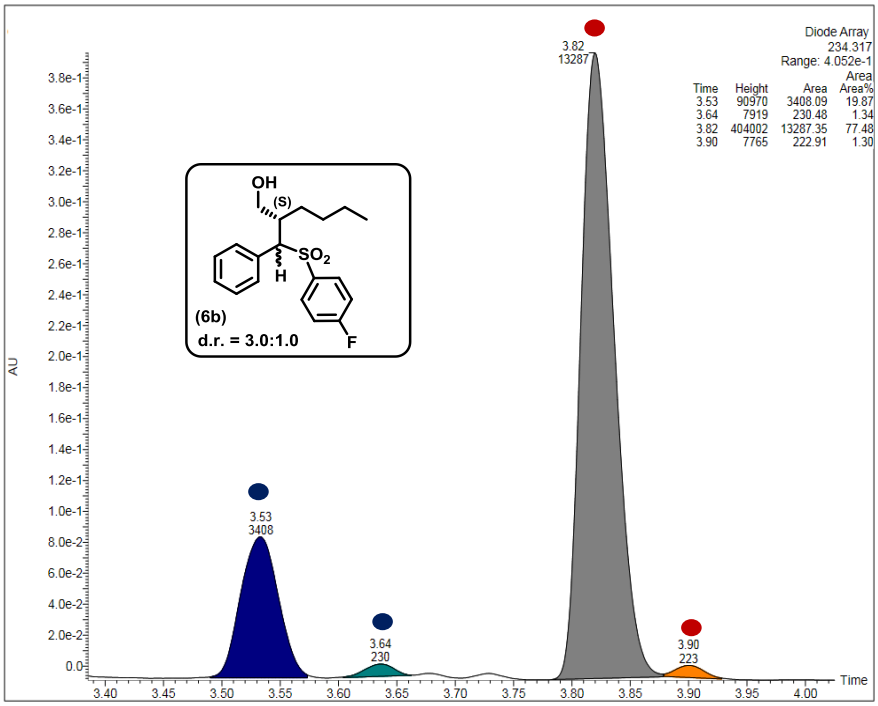
Conditions: UPC^2 (CEL-1 column with a gradient 100% CO_2 to 60:40 CO_2/EtOH over 4 minutes, 20 ºC, flow rate: 2 mL/min, λ = 213 nm)



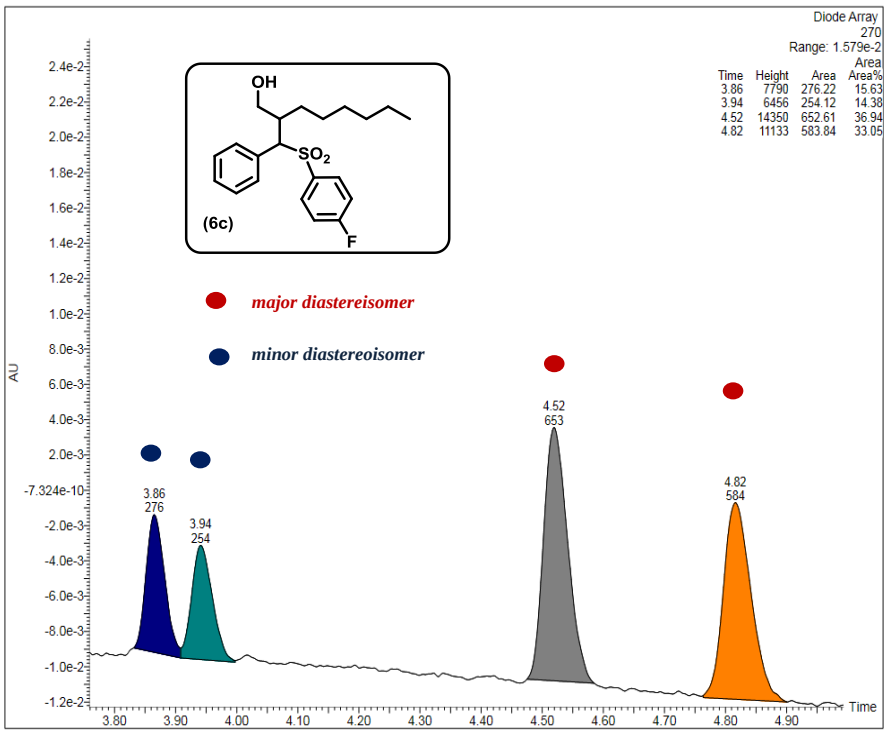


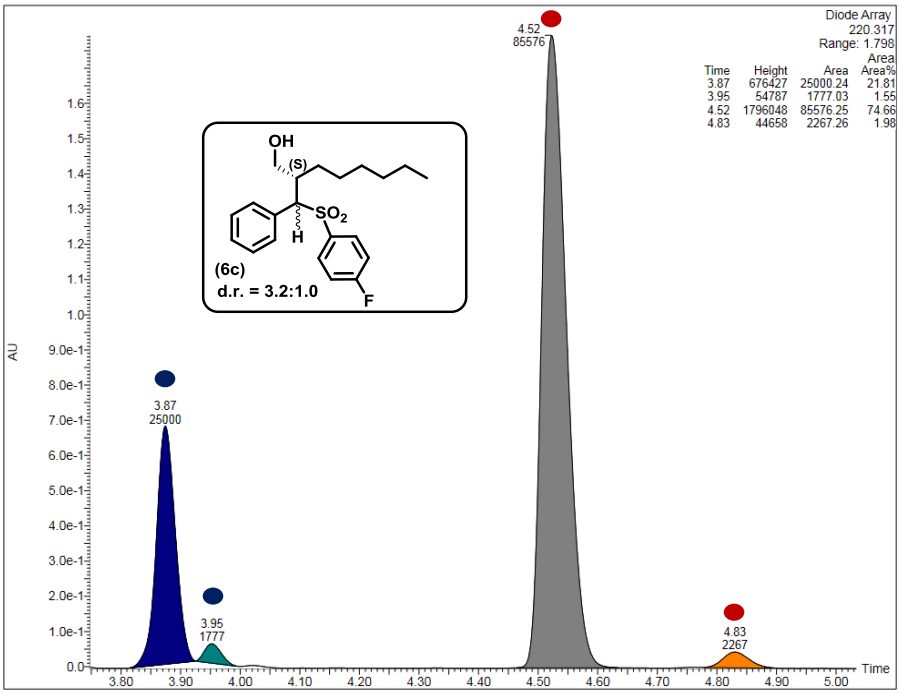
Conditions: UPC^2 (CEL-1 column with a gradient 100% CO_2 to 60/40 CO_2/Isopropanol over 4 minutes, 20 ºC, flow rate: 2 mL/min, λ = 245 nm)



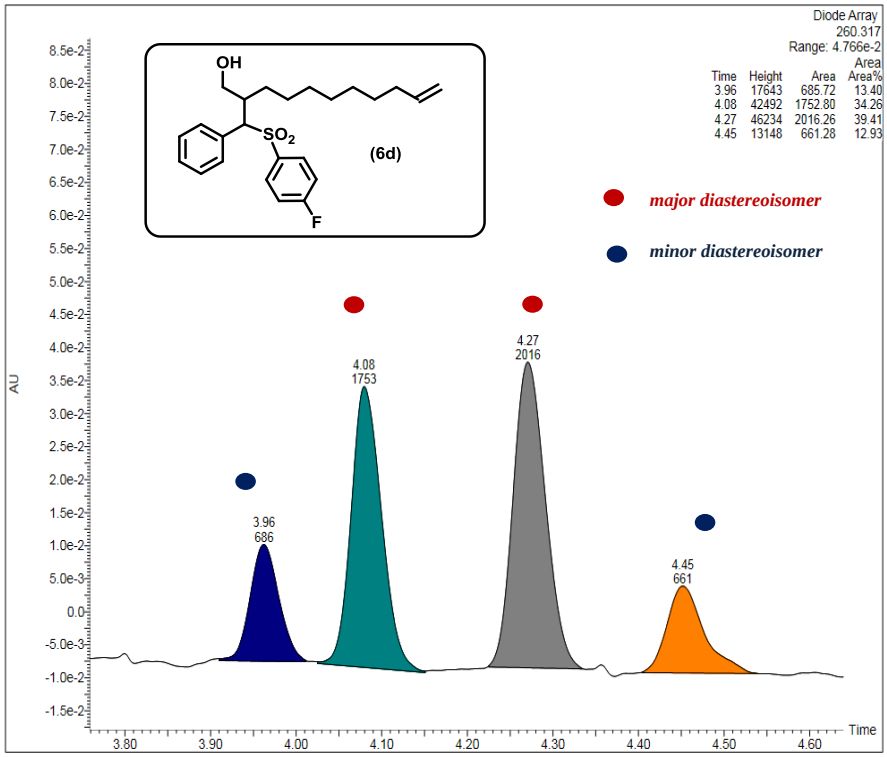


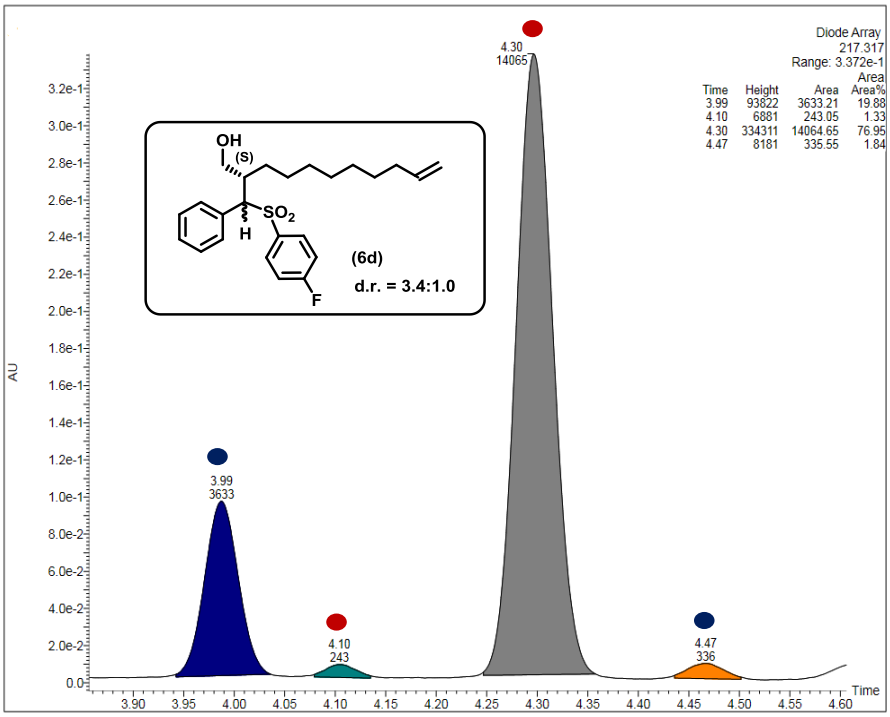
Conditions: UPC^2 (AMY-1 column with a gradient 100% CO_2 to 60/40 CO_2/ethanol over 4 minutes, 20ºC, flow rate: 2 mL/min, λ = 270 nm)



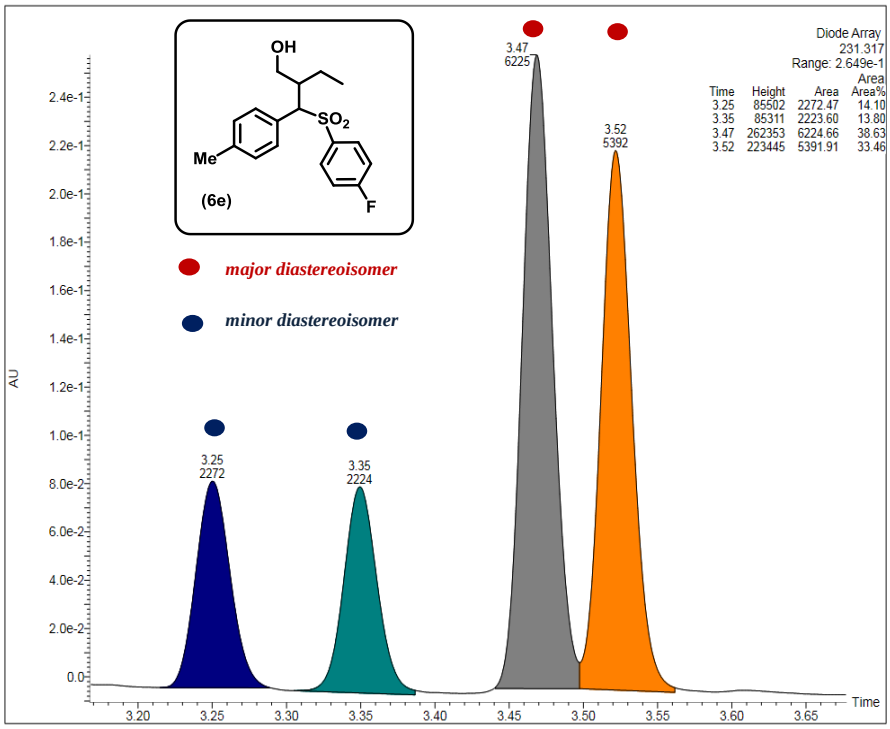


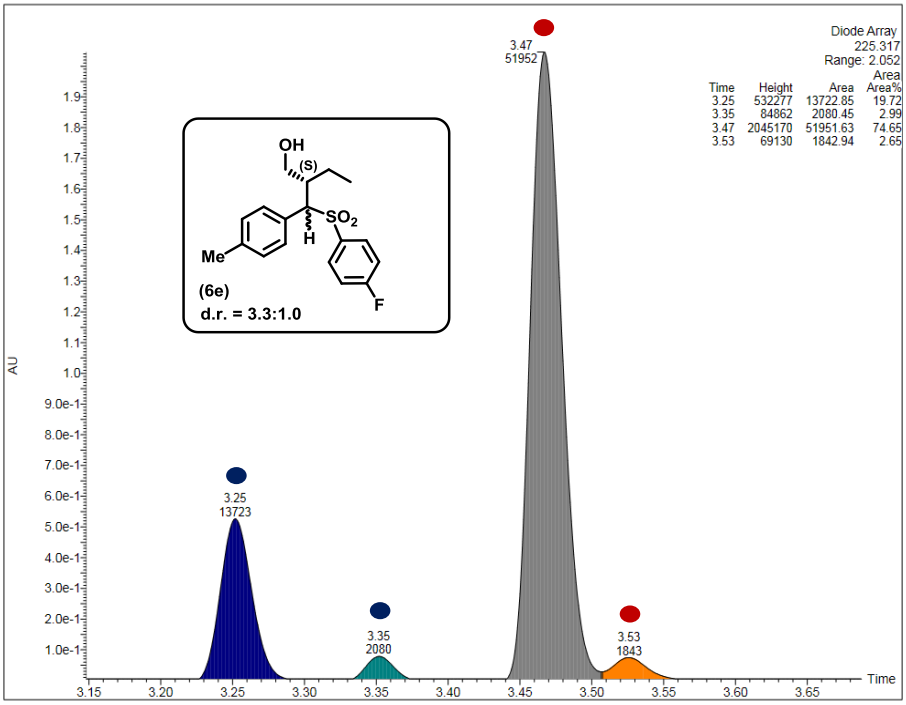
Conditions: UPC^2 (CEL-2 column with a gradient 100% CO_2 to 60/40 CO_2/MeOH over 4 minutes, 20ºC, flow rate: 2 mL/min, λ = 260 nm)



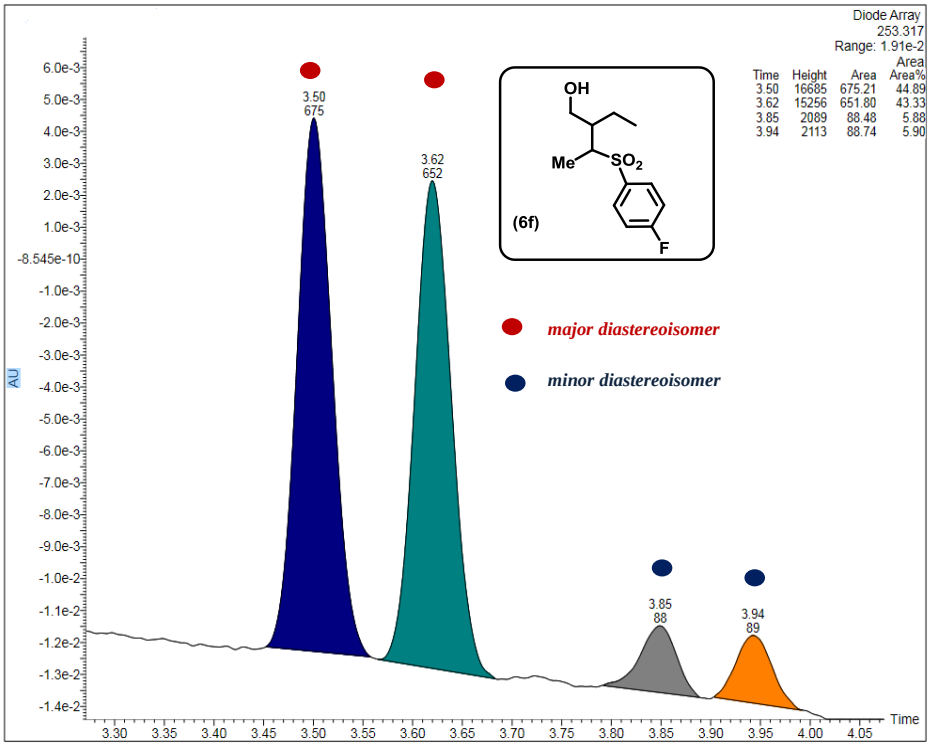


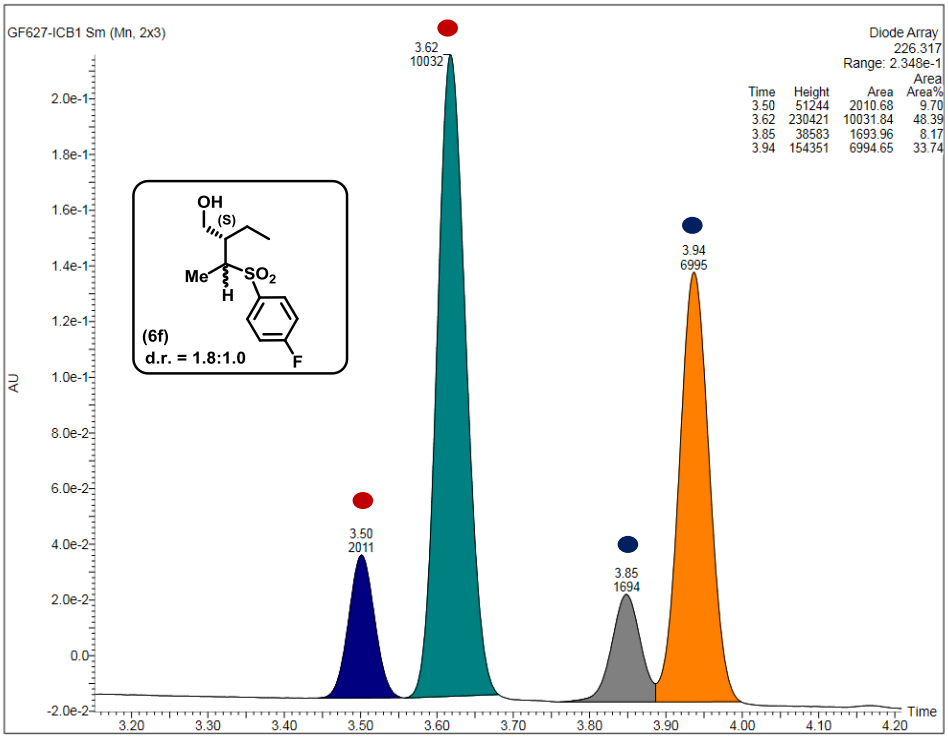
Conditions: UPC[2] (CEL-1 column with a gradient 100% CO_2 to 60/40 CO_2/EtOH over 4 minutes, 20 ºC, flow rate: 2 mL/min, λ = 231 nm)



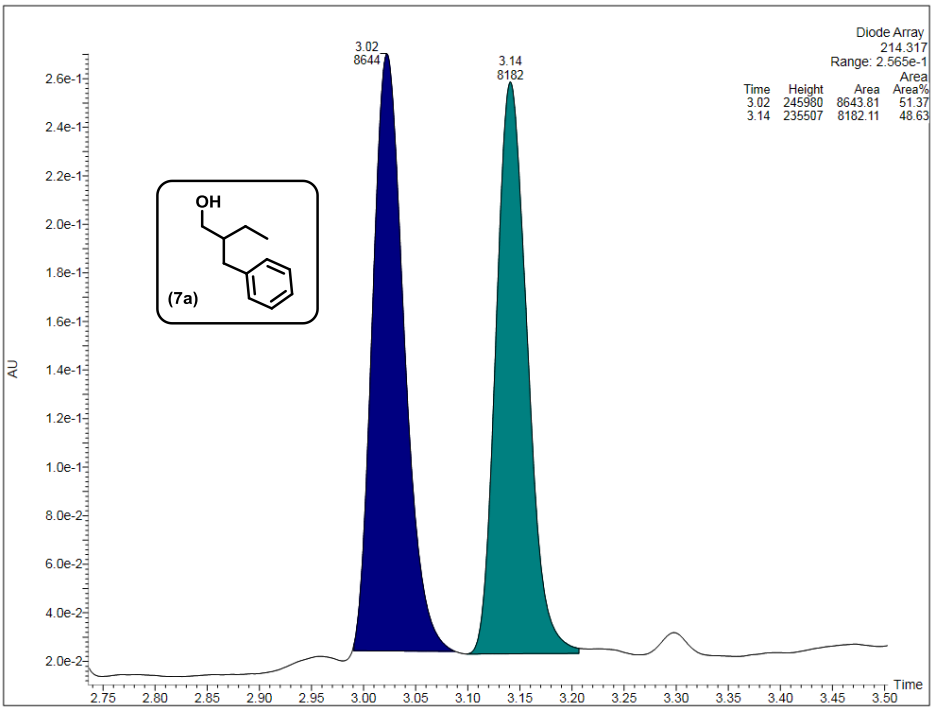


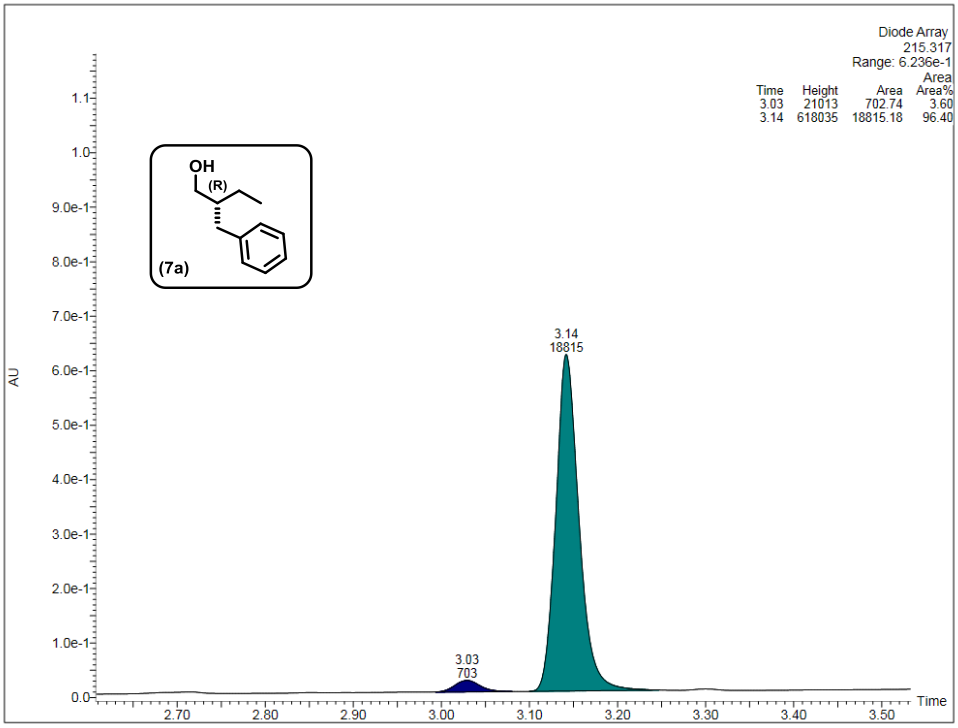
Conditions: UPC^2 (IC-3 column with a gradient 100% CO_2 to 60/40 CO_2/CH_3CN over 4 minutes, 20ºC, flow rate: 3 mL/min, λ = 253 nm)



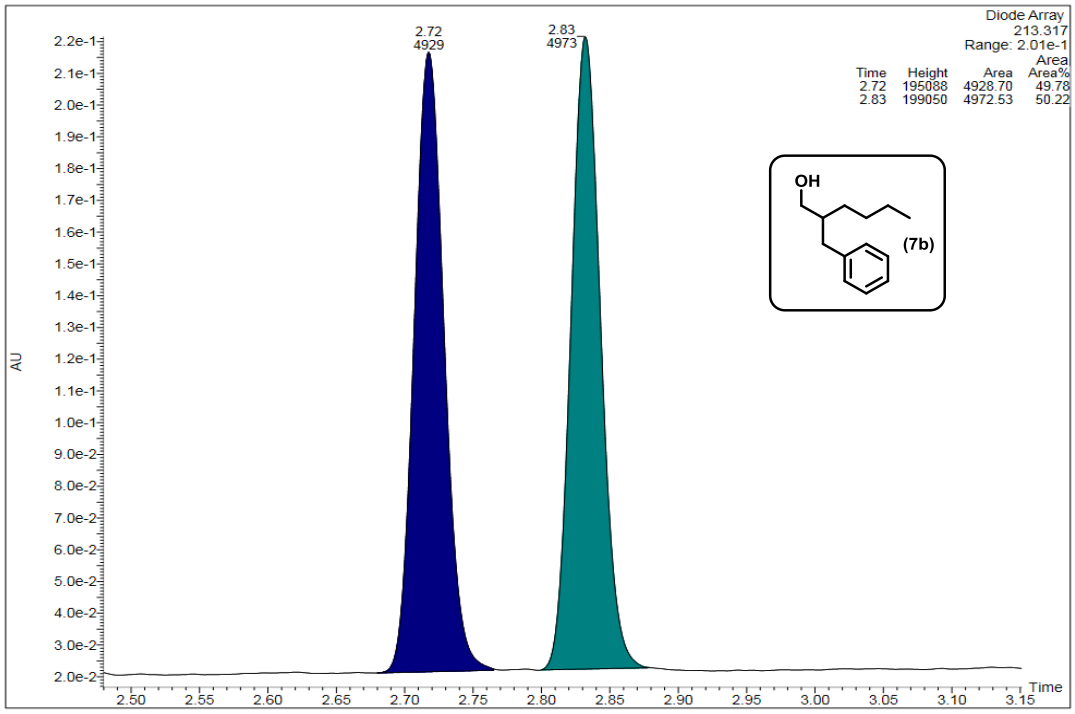


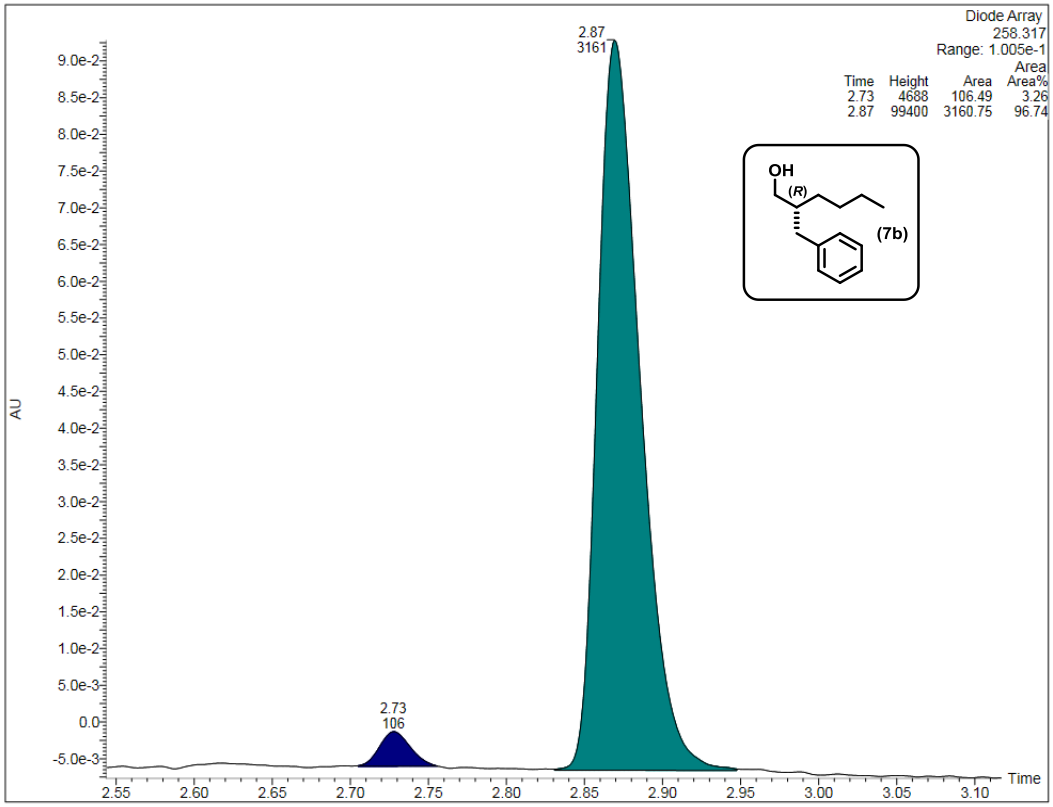
Conditions: UPC^2 (CEL-1 column with a gradient 100% CO_2 to 60:40 CO_2/Isopropanol over 4 minutes, 20ºC, flow rate: 2 mL/min, λ = 214 nm)





Conditions: UPC^2 (CEL-1 column with a gradient 100% CO_2 to 60:40 CO_2/Ethanol over 4 minutes, 20ºC, flow rate: 2 mL/min, λ = 213 nm)





Conditions: UPC^2 (CEL-1 column with a gradient 100% CO_2 to 60:40 CO_2/Isopropanol over 4 minutes, 20ºC, flow rate: 2 mL/min, λ = 215nm)